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Development of Organic Synthesis Concepts with Earth-Abundant Catalysts

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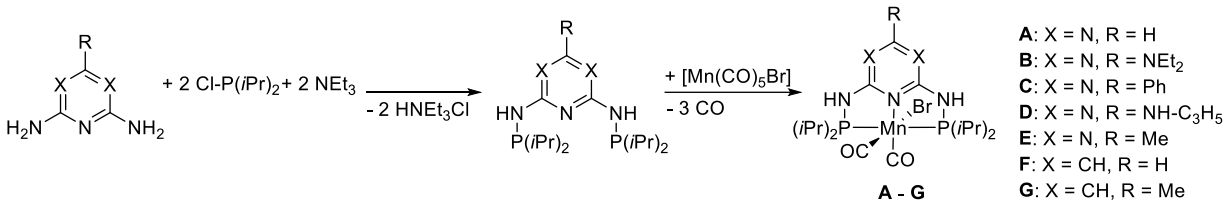
2 Summary / Zusammenfassung

2.1 Summary

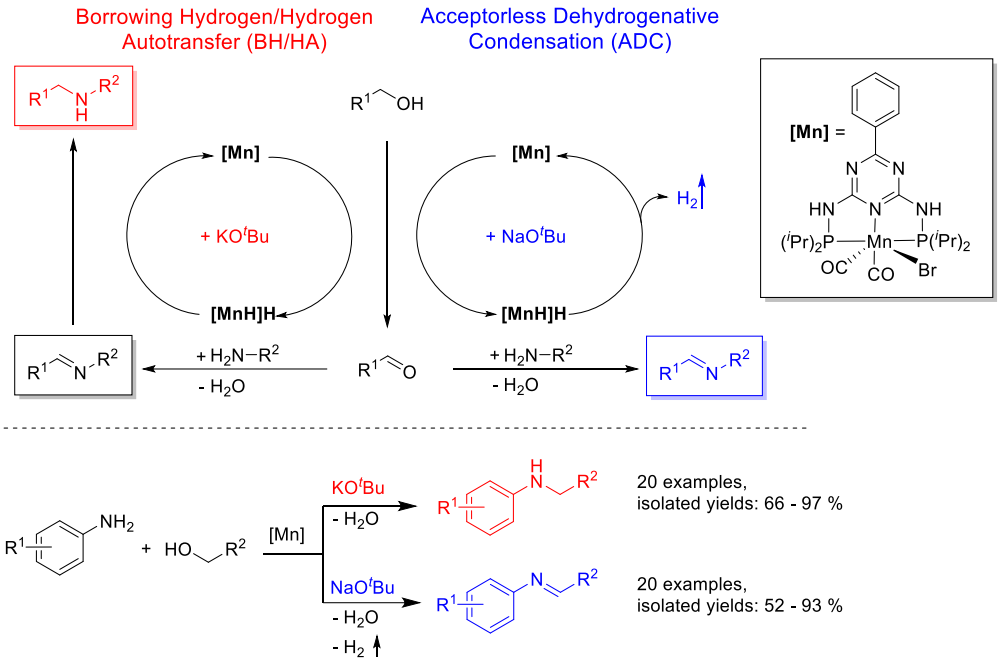
In the present work, the development of sustainable catalytic synthesis methods using manganese catalysts and alcohols as starting materials is presented. The catalysts are based on functionalizable $PN_{3\text{-}5}P$ pincer ligands. New organic syntheses following borrowing hydrogen/hydrogen autotransfer and acceptorless dehydrogenation condensation were developed using a library of manganese precatalysts (Scheme 2.1).



Scheme 2.1: Synthesis of Mn precatalysts used for the development of new reactions.

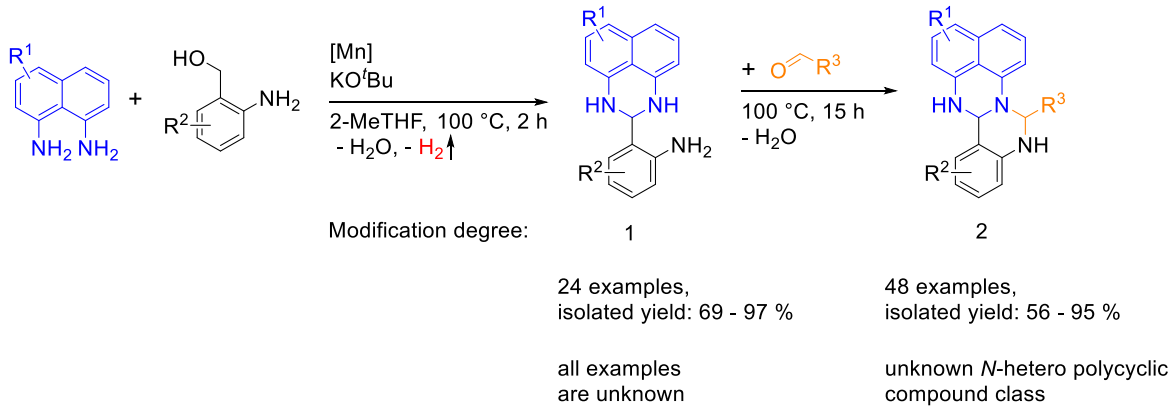
In 2016, the group of Kempe reported on the use of these Mn precatalysts for the hydrogenation of carbonyls and, in 2017, on the synthesis of substituted pyrimidines using the concept of Acceptorless Dehydrogenation Condensation (ADC). In this work, a catalytic system was developed that can switch between the concept of Borrowing Hydrogen / Hydrogen Autotransfer (BH/HA) and the concept of Acceptorless Dehydrogenation Condensation (ADC) (Scheme 2.2). By using KO^{t}Bu as metal base to activate the precatalyst, the reaction follows the concept of BH/HA, while the reaction with NaO^{t}Bu as metal base follows the concept of ADC. Secondary amines are obtained for *N*-alkylation according to the concept of BH/HA, while imines are obtained according to the concept of ADC. After screening all reaction parameters, the optimal parameters for amine synthesis are 3 mol% precatalyst **C**, 1 eq. KO^{t}Bu, alcohol/amine ratio (1.4/1), 80 °C (oil bath temperature), THF, and for imine synthesis 1 mol% precatalyst **C**, 1.5 eq. NaO^{t}Bu, alcohol/amine ratio (1.6/1), 110 °C (oil bath temperature), 2-MeTHF.

A total of 20 imines and 20 amines were isolated in yields ranging from 52 - 97 %. The imine-amine selectivity was always higher than 98 %. A wide variety of functional groups were tolerated, such as halogen substituents, C-C double bonds or thiophene groups. Mechanistic studies showed a spatially different coordination of the potassium or sodium cation at the deprotonated amino functions of the ligand, leading to a significant difference in the hydride transfer rate to the imine. This difference in the rate of transfer is responsible for the observed imine/amine selectivity.



Scheme 2.2: Concept for the base-switchable synthesis of imines and amines.

While the first topic of this thesis has focused on the development of a new synthesis concept starting from alcohols and primary amines, the second topic is based on a new synthesis concept using amino alcohols and diamines. Consecutive addition of an aldehyde after a certain time to this reaction leads to a previously undescribed *N*-hetero polycyclic compound class (Scheme 2.3).



Scheme 2.3: Consecutive one-pot reaction for the synthesis of an unknown class of N-heterocyclic compounds.

The reaction pathway presented here allows the synthesis of 2,3-dihydro-1H-perimidines bearing an NH_2-functionality (modification degree 1). All 24 of these "amino-dihydro-perimidines" are presented for the first time in this work. Consecutive addition of an aldehyde to the reaction leads to a class of compounds consisting of two six-membered *N*-heterocycles (modification degree 2). This polycyclic ring system is a class of compounds that has not been described before. The name fertigine is proposed for this compound class. The ideal parameters for this consecutive multicomponent reaction were found

to be 1 mol% precatalyst **C**, 30 mol% KO^{t}Bu, 1:1:1 ratio amino alcohol:diamine:aldehyde, 2-MeTHF, 100 °C (oil bath temperature). After 2 h, the aldehyde was added, and after about 15 h, the desired fertigine was obtained. In total, 48 fertigines were isolated in yields of 56 – 95 %. This reaction showed excellent functional group tolerance, e.g. halogens, *N*-,*O*-,*S*-heterocycles, or ferrocene derivatives could be introduced (Figure 2.1).

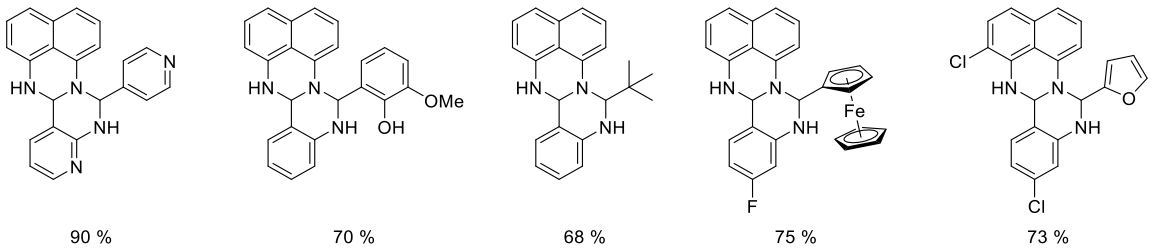


Figure 2.1 Selected examples of fertigines. Yields of isolated products are shown.

All fertigines can be easily crystallized. Since no structural data exist for this class of compounds, the molecular structure of several fertigines was investigated by means of single crystal structure analysis. Nine fertigines were crystallized and the influence of the substitution on the core region around the nitrogen atoms was investigated. The aminal bond lengths of **1** are with C11-N1: 1.438(2) Å and C11-N2: 1.490(2) Å in the same ranges as for reported, structurally similar 2,3-dihydro-1*H*-perimidines (Figure 2.2). The C-N bond lengths of C18-N2: 1.463(2) Å and C18-N3: 1.452(2) Å are in line with typical values for a C_{sp^3}-N_{sp^3}-bond. The Fertigines crystallized in different conformations, six of nine structures showed a similar conformation in which all three aromatic planes of the fertigine are nearly perpendicular to each other. In Figure 2.2 is for example the naphthalene plane (red) oriented with 85.65 ° to the plane of the fused phenyl ring (blue) and with 89.69 ° to the plane of the phenyl substituent (green). At the same time, the plane of the phenyl substituent (green) has an angle of 84.68 ° to the plane of the fused phenyl ring (blue).

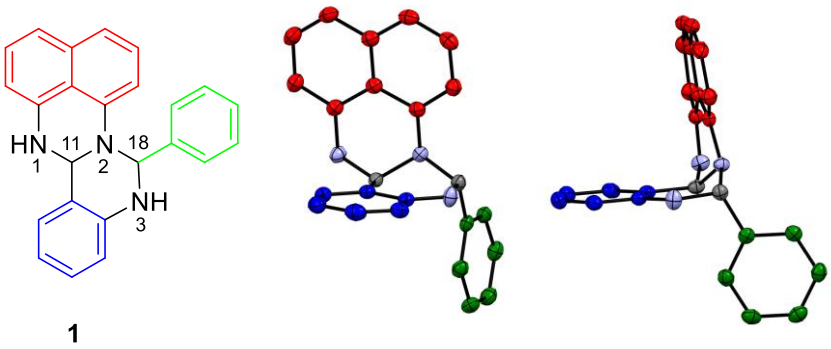
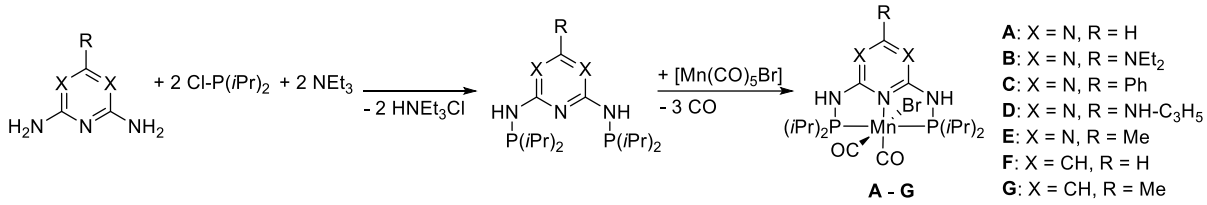


Figure 2.2: Molecular structure of a fertigine. Single crystal structure analysis shows the orientation of the aromatic regions (red, blue, green) of one conformation.

2.2 Zusammenfassung

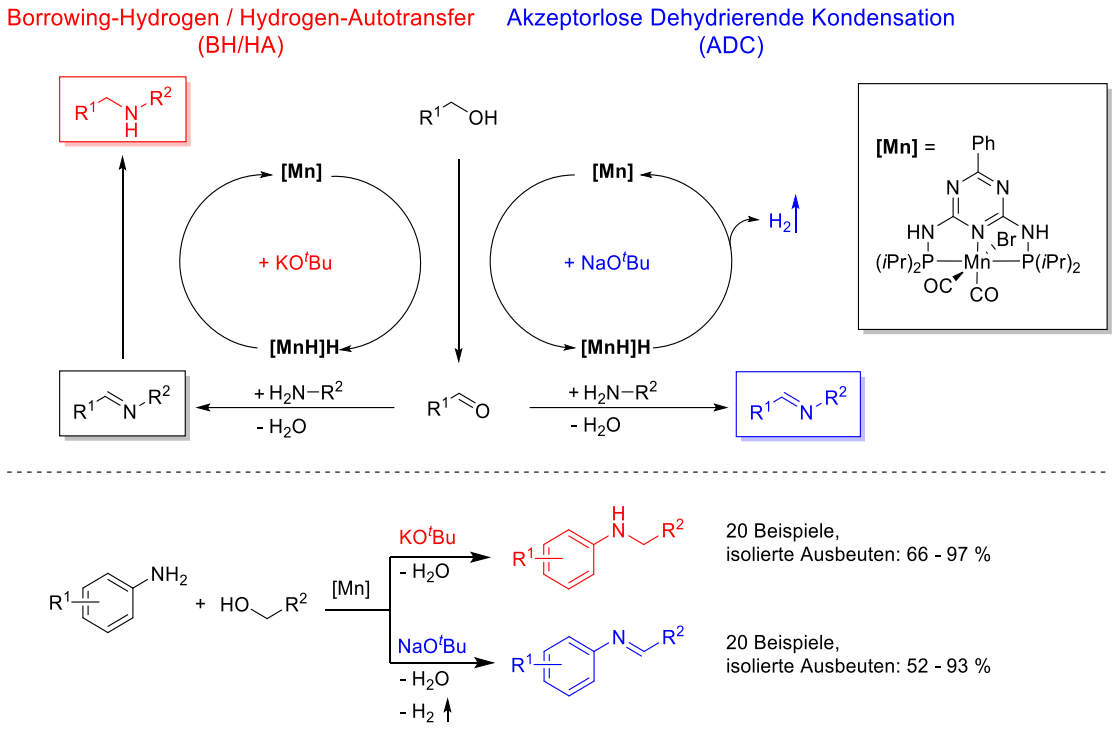
In der vorliegenden Arbeit wird die Entwicklung von nachhaltigen katalytischen Synthesemethoden unter Verwendung von Mangan-Katalysatoren und Alkoholen als Ausgangsmaterialien vorgestellt. Die Katalysatoren basieren auf leicht funktionalisierbaren $PN_{3\text{-}5}P$-Pinzetten-Liganden. Mithilfe der in Schema 2.1 dargestellten Bibliothek von Mangan-Präkatalysatoren konnten in dieser Arbeit neue organische Synthesen nach Borrowing-Hydrogen / Hydrogen-Autotransfer und der Akzeptorlosen Dehydrierenden Kondensation entwickelt werden.



Schema 2.1: Synthese der Mn-Präkatalysatoren, welche für die Entwicklung neuer Reaktionen verwendet wurden.

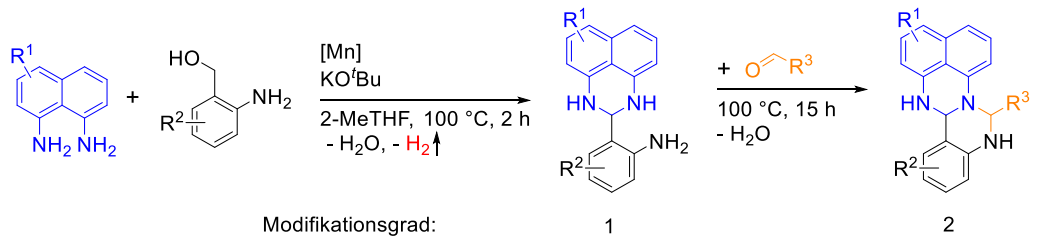
Im Jahr 2016 berichtete die Arbeitsgruppe um Kempe über die Verwendung eines dieser Mn-Präkatalysatoren für die Hydrierung von Carbonylen und 2017 über die Synthese von substituierten Pyrimidinen nach dem Konzept der Akzeptorlosen Dehydrierenden Kondensation (ADC). Im Rahmen dieser Arbeit wurde ein katalytisches System entwickelt, das zwischen dem Konzept des Borrowing-Hydrogen / Hydrogen-Autotransfer (BH/HA) und dem Konzept der Akzeptorlosen Dehydrierenden Kondensation (ADC) umschalten kann (Schema 2.2). Durch Verwendung von KO^{t}Bu als Metallbase zur Aktivierung des Präkatalysators folgt die Reaktion dem Konzept des BH/HA, während die Reaktion mit NaO^{t}Bu als Metallbase dem Konzept der ADC folgt. Bei der *N*-Alkylierung nach dem Konzept des BH/HA erhält man sekundäre Amine, während man nach dem Konzept der ADC Imine erhält. Die optimalen Reaktionsparameter für die Amin-Synthese sind 3 mol% Präkatalysator **C**, 1 eq. KO^{t}Bu, Alkohol/Amin-Verhältnis (1,4/1), 80 °C (Ölbadtemperatur), THF, und für die Imin-Synthese sind es 1 mol% Präkatalysator **C**, 1,5 eq. NaO^{t}Bu, Alkohol/Amin-Verhältnis (1,6/1), 110 °C (Ölbadtemperatur), 2-MeTHF.

Insgesamt wurden 20 Imine und 20 Amine auf Basis der gleichen Edukte in Ausbeuten von 52 – 97 % isoliert. Die Imin-Amin-Selektivität war immer höher als 98 %. Es wurden verschiedenste funktionellen Gruppen während der Katalyse toleriert, wie z.B. Halogensubstituenten, C-C-Doppelbindungen oder Thiophengruppen. Mechanistische Untersuchungen zeigten eine räumlich verschiedene Koordination des Kalium- bzw. Natriumkations an den deprotonierten Aminofunktionen des Liganden, was zu einem signifikanten Unterschied in der Hydridtransferrate zum Imin führt. Dieser Unterschied in der Geschwindigkeit des Transfers ist für die beobachtete Imin-/Amin-Selektivität verantwortlich.



Schema 2.2: Konzept für die katalytische Synthese von Iminen und Aminen.

Während das erste Thema dieser Arbeit sich auf die Entwicklung eines neuen Synthesekonzeptes ausgehend von Alkoholen und primären Aminen konzentriert hat, basiert das zweite Thema auf einem neuen Synthesekonzept, welches Aminoalkohole und Diamine als Edukte verwendet. Die konsekutive Zugabe eines Aldehyds nach einer bestimmten Zeit zu dieser Reaktion führt zu einer bisher noch nicht beschriebenen *N*-hetero-polyzyklischen Verbindungsklasse (Schema 2.3).



Schema 2.3: Konsekutive Eintopfreaktion für die Synthese einer unbekannten Klasse von *N*-hetero-polyzyklischen Verbindungen.

Der hier vorgestellte Reaktionsweg ermöglicht die Synthese von 2,3-Dihydro-1*H*-perimidinen, welche eine NH_2-Funtionalität tragen (Modifikationsgrad 1). Alle 24 dieser isolierten „Amino-dihydroperimidine“ werden in dieser Arbeit zum ersten Mal vorgestellt. Die konsekutive Zugabe eines Aldehyds zu der Reaktion führt zu einer Klasse von Verbindungen, die unteranderem aus

zwei sechsgliedrigen *N*-Heterocyclen besteht (Modifikationsgrad 2). Bei diesem polycyclischen Ringsystem handelt es sich um eine neue, bisher nicht beschriebene Verbindungsklasse. Der Name Fertigine wird für diese *N*-hetero-polyzyklische Verbindungsklasse vorgeschlagen. Nach der Optimierung aller Reaktionsparameter ergaben sich als ideale Paramater für diese konsekutive Multikomponentenreaktion 1 mol% Präkatalysator **C**, 30 mol% KO^{t}Bu, 1:1:1-Verhältnis Aminoalkohol:Diamin:Aldehyd, 2-MeTHF, 100 °C (Ölbadtemperatur). Nach 2 h wurde der Aldehyd zu der Reaktion gegeben, nach ca. 15 h konnte das gewünschte Fertigin erhalten werden. Insgesamt wurden in diesem Projekt 48 Fertigine in Ausbeuten von 56 – 95 % isoliert. Dabei zeigte diese Reaktion eine exzellente funktionelle Gruppentoleranz, so konnten zum Beispiel verschiedenste Halogene, *N*-,*O*-,*S*-Heterozyklen, C-C-Doppelbindungen oder Ferrocen-Derivate eingeführt werden (Abb. 2.1).

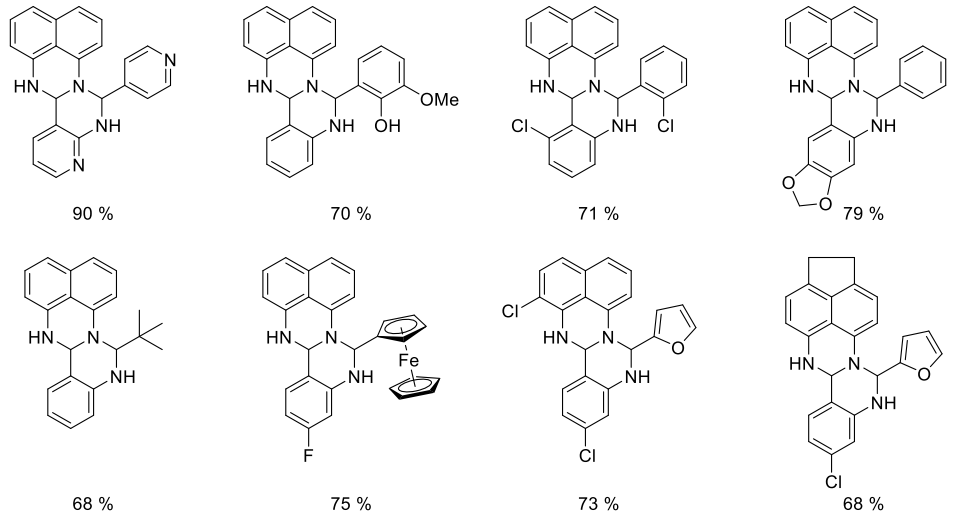


Abb. 2.1 Ausgewählte Beispiele der synthetisierten Fertigine. Die Ausbeuten der isolierten Produkte sind angegeben.

Bei allen Fertiginen handelt es sich um Feststoffe, welche sich leicht kristallisieren lassen. Da zu dieser unbekannten Verbindungsklasse bisher noch keine Strukturdaten existieren, war es von Interesse mittels Einkristallstrukturanalyse die molekulare Struktur mehrerer Fertigine zu untersuchen. Neun Fertigine wurden kristallisiert und der Einfluss der Substitution auf den Kernbereich um die Stickstoffatome untersucht. Die Aminal Bindungslängen von **1** liegen mit einer Länge von C11-N1: 1,438(2) Å und C11-N2: 1,490(2) Å in den gleichen Bereichen wie für bereits berichtete, strukturähnliche 2,3-Dihydro-1*H*-perimidine (Abb. 2.2). Die C-N Bindungslängen von C18-N2: 1,463(2) Å und C18-N3: 1,452(2) Å entsprechen den typischen Werten für eine C_{sp^3}-N_{sp^3}-Bindung. Die Fertigine kristallisierten in unterschiedlichen Konformationen, dabei zeigten sechs der neun untersuchten Strukturen eine ähnliche Konformation, bei der alle drei aromatischen Ebenen des Fertigins nahezu senkrecht zueinander stehen. So ist z.B. bei dem Fertigin in Abb. 2.2 die planare Naphthalinebene (rot) mit 85,65 ° zu der Ebene des anellierten Phenylrings (blau) und mit 89,69 ° zu der Ebene des Phenylsubstituenten (grün) orientiert. Gleichzeitig besitzt die Ebene des Phenylsubstituenten (grün) einen Winkel von 84,68 ° zu der Ebene des anellierten Phenylrings (blau).

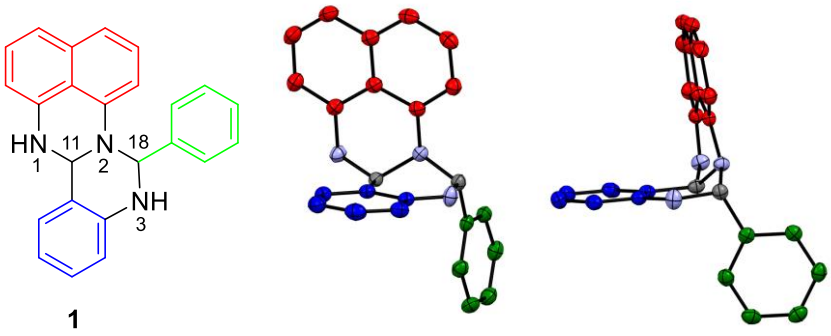


Abb. 2.2: Molekulare Struktur eines Fertigins. Einkristallstrukturanalyse zeigt von einer Konformation die Orientierung der aromatischen Bereiche (rot, blau, grün) zueinander.

3 Introduction

3.1 Motivation

In the early part of the 19th century, Henry Ford proposed as a logical and unavoidable option for a wealth and growing civilization the implementation of a bio-based economy.[1] Due to the uncompetitive cheap price of fossil fuels compared to any other alternatives, the bio-based approach was postponed a long time. But this price advantage will shrink in future.[2,3] Furthermore, serious threats for humanity caused by increasing environmental problems, can be traced back to the mass consumption of fossil fuels. These growing concerns of the society are, besides the economic considerations, one of the driving forces to find more sustainable and "greener" approaches. The 12 principles of "green chemistry" as proposed by Anastas and Warner in 1998, represents a famous approach to a more sustainable chemical industry (Table 3.1).[4] In general the principles are about the substitution of hazardous/toxic chemicals with benign, renewable chemicals and the avoidance of waste in any form.

Table 3.1: The twelve principles of Green Chemistry as proposed by Anastas and Warner.

12 Principles of Green Chemistry		
1 Prevent Waste	**2** Atom Economy	**3** Less Hazardous Synthesis
4 Design Benign Chemicals	**5** Benign Solvents & Auxiliaries	**6** Design for Energy Efficiency
7 Use of Renewable Feedstock	**8** Reduce Derivatives	**9** Catalysis
10 Design for Degradation	**11** Real-Time Analysis for Pollution Prevention	**12** Inherently Benign Chemistry for Accident Prevention

Fossil fuels are not only used to generate energy, but also as the starting materials for a tremendous amount of platform chemicals used in the chemical industry.[5] To push chemical processes more to the approaches of a "green chemistry", it is mandatory to substitute the finite fossil fuels with renewable resources. (7th principle). One sustainable, abundantly available feedstock, that had come into focus of research is lignocellulosic biomass.[6–9] It fulfills several promising criteria, as such as it is generated from available atmospheric carbon dioxide, water and sunlight through photosynthesis and is the only sustainable source of organic carbon in earth with net zero carbon emission.[10] Furthermore, it is

indigestible (no competition with food production), has no significant application in industrial processes and it is a worldwide available renewable feedstock with high abundance.[11,12]

With respect to petroleum resources, lignocellulosic biomass has higher amount of oxygen and lower fractions of carbon and hydrogen. Due to this variety, more classes of products can be obtained from lignocellulosic biomass compared with fossil sources.[1] The treatment of the biomass requires a large range of complex processing technologies, but the (cost-) effectiveness will increase, since the technologies will overcome the pre-commercial stage.[13–15] Owing to the downstream products from the petroleum industry, common synthesis methods are based on functionalization chemistry to obtain products for the chemical industry. Since lignocellulosic biomass provides a mixture of various alcohols,[16] a different approach for the synthesis of chemical products is necessitated. Compared to the established functionalization-chemistry for olefins, there is a demand for re-functionalization-methods using alcohols as renewable starting materials (Figure 3.1).

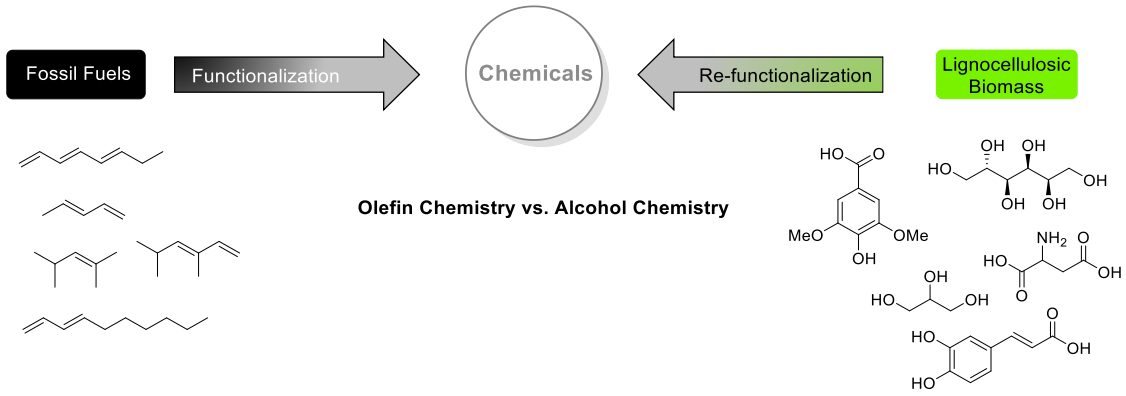


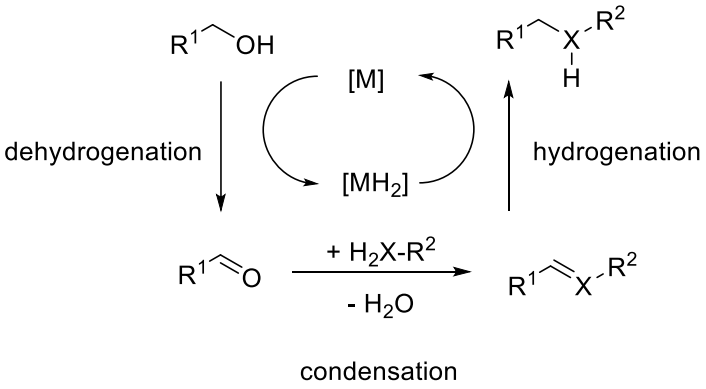
Figure 3.1: Resource-depending conversion methods for producing chemical for the industry.

However, alcohols must be activated first to use them efficiently in organic reactions. According to the 12 principles of "green chemistry" (Table 3.1), it is desirable to apply syntheses proceeding in only one step while producing as less as possible non-toxic by-products. The concept of Borrowing Hydrogen / Hydrogen Autotransfer (BH/HA) is a popular concept to accomplish alcohol activation in a sustainable manner.

3.2 Borrowing Hydrogen / Hydrogen Autotransfer

The Borrowing Hydrogen / Hydrogen Autotransfer concept was first presented by Watanabe[17] and Grigg[18] in 1981. In this concept, an alcohol is first dehydrogenated by a transition-metal catalyst to the corresponding carbonyl species, while the hydrogen from the alcohol is transferred to the metal complex. The reactive carbonyl can undergo a condensation reaction with a nucleophile (e.g., an amine or the anion of a CH-acidic compound) obtaining an unsaturated compound under elimination of water. In a final step, this unsaturated compound is hydrogenated from the catalyst, using the "borrowed" hydrogen

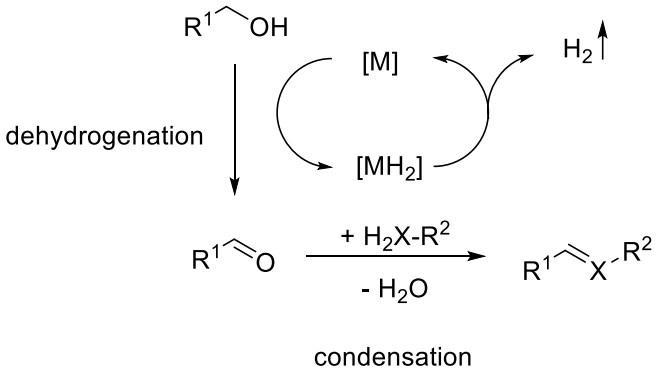
from the initial dehydrogenation step. This reaction concept proceeds within one single step liberating water as the only by-product (Scheme 3.1). Due to its atom economy and broad applicability for organic reactions, this synthesis concept has received a lot of attention. The groups around Beller[19–25], Fujita[26–30], Williams[31–40], Grigg[41–43], Yus[44–48] and Kempe[49–54] contributed to this topic with several elegant synthesis routes.



Scheme 3.1: Concept of the Borrowing Hydrogen / Hydrogen Autotransfer. X = CH, N; [M] = transition-metal catalyst.

3.3 Acceptorless Dehydrogenative Condensation

Like the concept of Borrowing Hydrogen / Hydrogen Autotransfer is the Acceptorless Dehydrogenative Condensation a "green" and sustainable synthesis route for the conversion of alcohols. In analogy to the BH/HA-concept, the alcohol is dehydrogenated with a transition-metal catalyst and the active carbonyl compound reacts with a nucleophile to an unsaturated product releasing one equivalent water as by-product. But instead of transferring back the "borrowed" hydrogen from the metal complex to the unsaturated compound, it is released as molecular hydrogen (Scheme 3.2). Since the hydrogenation of the imine or olefine is suppressed, this concept provides unsaturated compounds like olefins or imines, which can be used for subsequent cyclisation reactions allowing the synthesis of aromatic compounds.



Scheme 3.2: Concept of the Acceptorless Dehydrogenative Condensation. X = CH, N; [M] = transition-metal catalyst.

N-Heterocyclic compounds are widely spread in many pharmaceuticals, natural products, and functional materials.[55] About 59 % of the FDA approved small-molecule drugs contain at least one nitrogen heterocycle, thus it is one of the most frequent motifs in pharmaceuticals.[56] The concept of ADC is especially attractive for the synthesis of *N*-heterocycles, since alcohols and amino alcohols from renewable resources can be used as starting materials.[55] The group of Watanabe first synthesized benzoxazoles and benzimidazoles with a Ru-catalyst using the concept of ADC.[57] The groups of Crabtree, Beller, Milstein, Saito and Kempe contributed to the development of synthesis concepts of aromatic *N*-heterocycles (Figure 3.2). Several groups introduced the catalytic synthesis of pyrroles following the ADC concept, whereas each group differs in the possibilities of substitution around the pyrrole: In 2011 Crabtree started using 1,4-diols and primary amines, providing symmetrical pyrroles with $R^2 = R^5$ and R^3, R^4 = H. The groups of Kempe, Milstein and Saito synthesized pyrroles with R^1 = H, and the group of Beller obtained fully substituted pyrroles using the ADC concept. Subsequently, further syntheses of aromatic *N*-heterocycles were reported on, including the synthesis of pyridines[58,59], quinolines[59,60], 3-aminopyridines[61], benzimidazoles[57,62], 2-arylquinazolines[63], quinoxalines[62] and pyrimidines[64] (Figure 3.2).

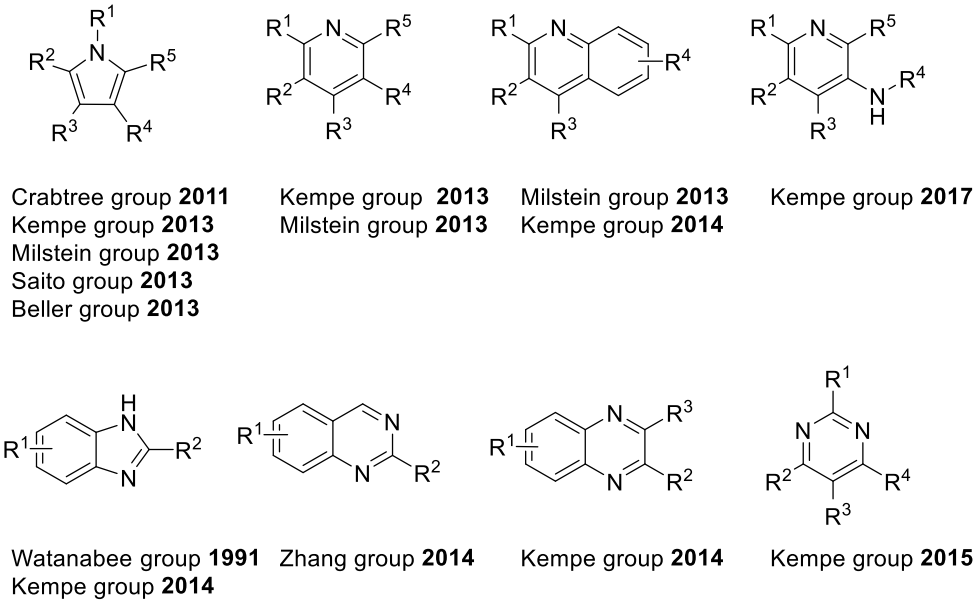


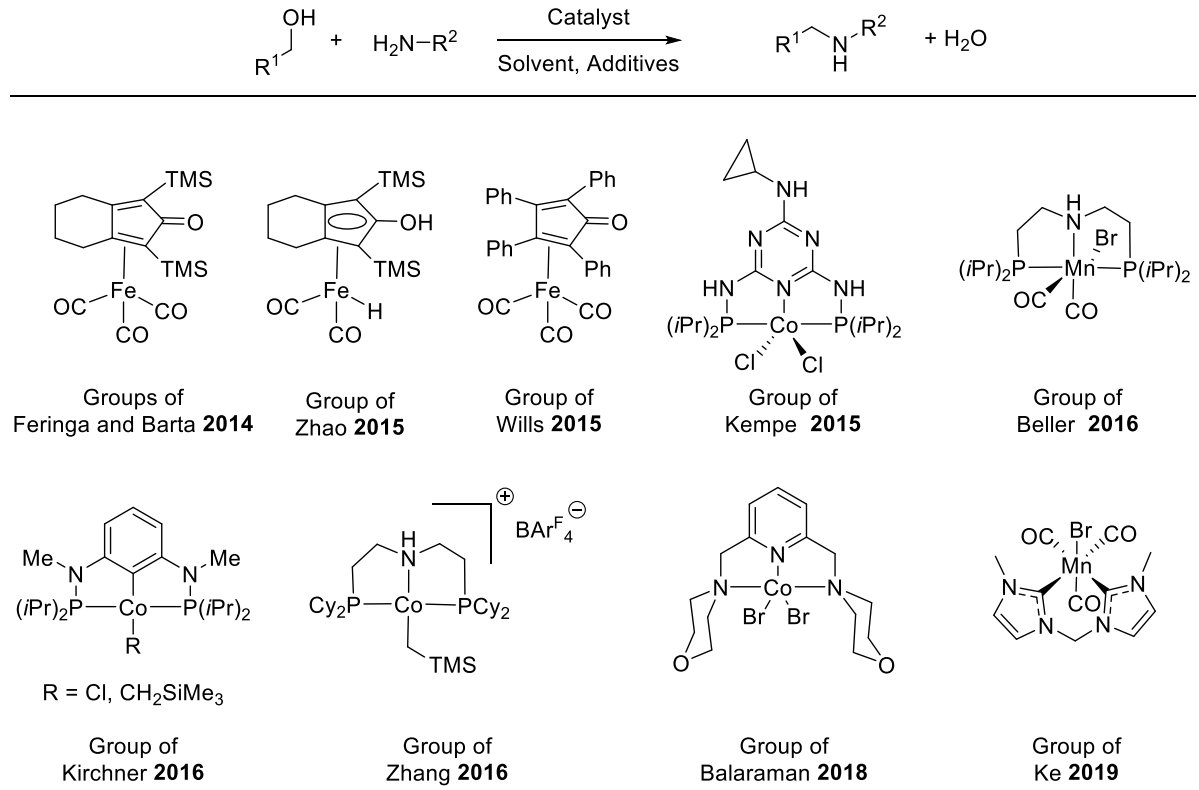
Figure 3.2: Aromatic *N*-heterocycles synthesized from alcohols as starting materials using the concept of ADC.

All of those presented aromatic *N*-heterocyclic compound classes were synthesized using alcohols and / or amino alcohols as renewable starting materials indicating the future viability of the ADC concept.

3.4 Base-Metal-Catalyzed Amine Alkylation using BH/HA and ADC

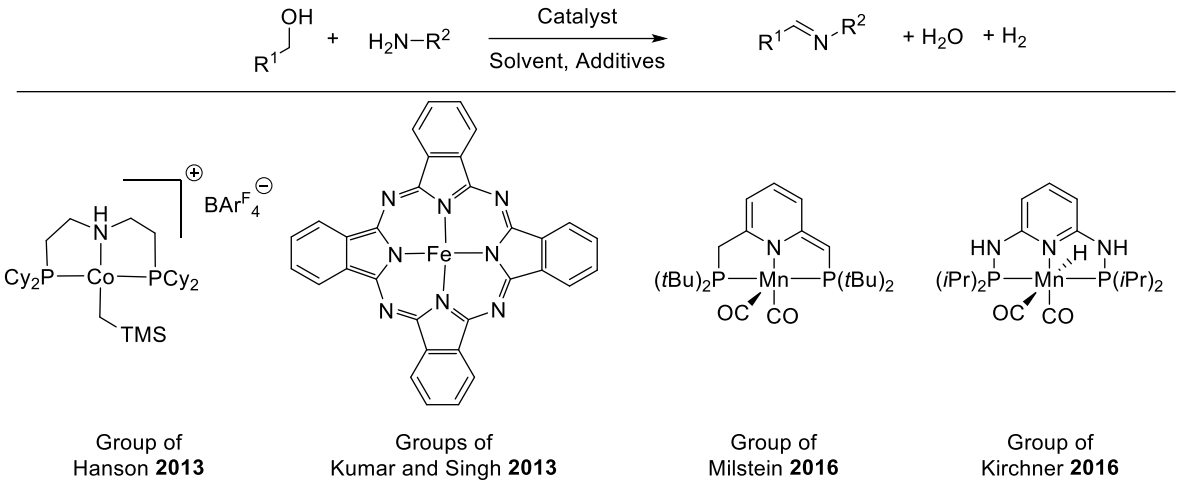
There are several advantages regarding BH/HA and ADC reactions, like high atom-economy, low formation of by-products, and the use of alcohols as sustainable resources. Nevertheless, the use of catalysts based on rarely occurring precious metals like Ir and Ru diminishes this advantage, due to their high costs, toxicity and big impact on the global warming caused by their high energy consumption during processing and purification.[65–67] Owing to this, there has recently started the development of catalysts based on earth-abundant metals improving the overall sustainability of BH/HA and ADC reactions.

The first explored base-metal for homogeneous catalysis was iron based on a Knoelker-type complex reported by the group of Feringa and Barta in 2014 (Scheme 3.3).[68] Considerable work on the use of this iron complexes has been contributed by the groups of Zhao[69] and Wills[70]. The first cobalt complex that can selectively alkylate primary amines with alcohols was published by the group of Kempe[71], subsequently followed by the groups of Kirchner[72], Zhang[73] and Balaraman[74]. In 2016, the group of Beller reported on a well-defined PNP manganese pincer complex based on a MACHO ligand for the selective *N*-alkylation of amines with alcohols. As a special highlight the chemoselective monomethylation of primary amines with methanol under mild conditions was presented.[75] The group of Ke described the first example of a phosphine-free manganese catalyst based on a *N*-heterocyclic carbene ligand catalyzing the *N*-alkylation at room temperature.[76]



Scheme 3.3: Selected examples of base-metal catalysts for amine alkylation using the BH/HA concept.

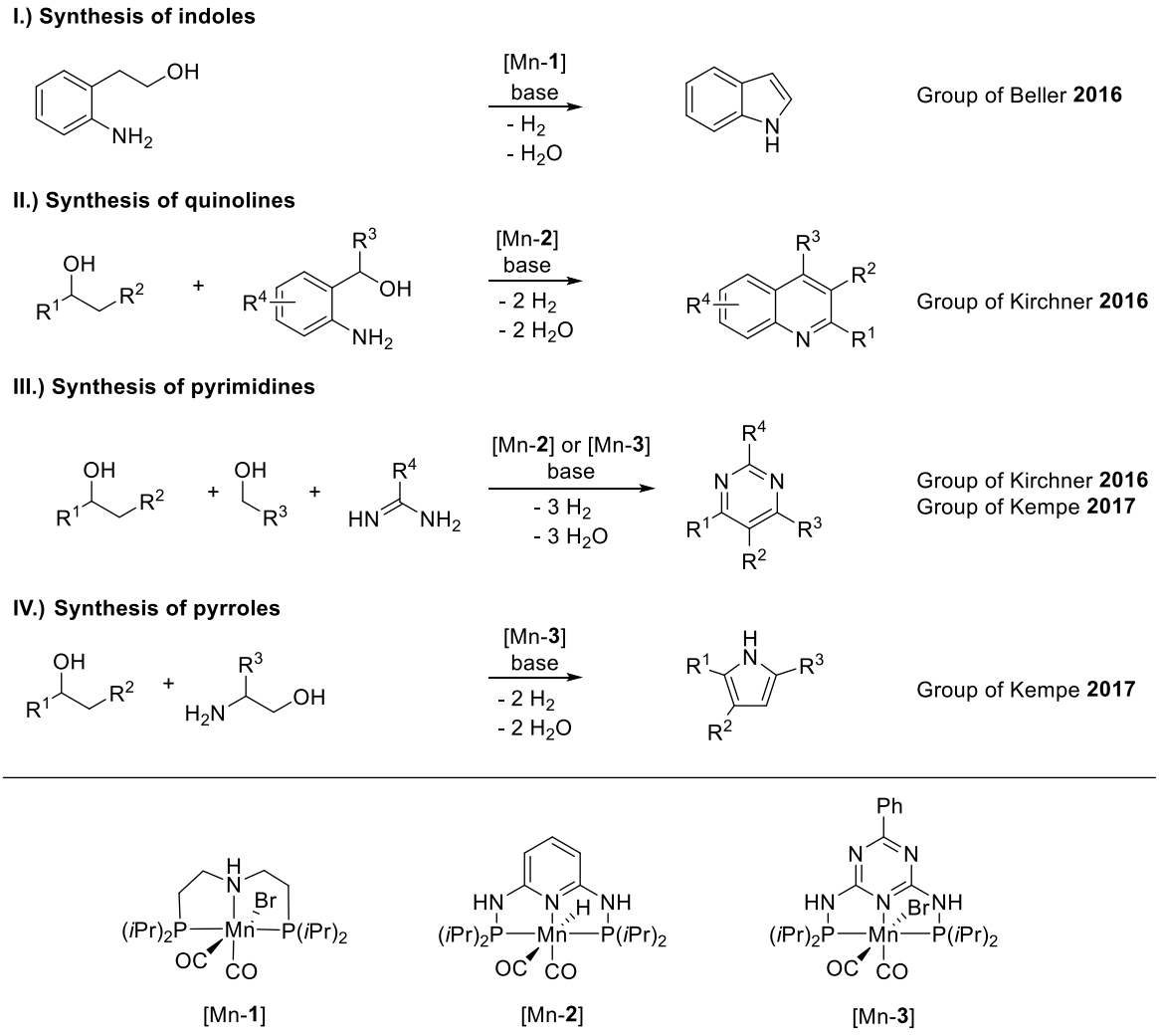
Reports on ADC reactions for imine synthesis catalyzed by base-metals are rare (Scheme 3.4). In 2013, the group of Hanson reported on the first homogeneous cobalt catalyst for the synthesis of imines from alcohols and amines based on a cationic cobalt(II) alkyl complex.[77] Kumar and Singh introduced a Fe-phthalocyanine complex for imine synthesis using the ADC concept.[78] The first manganese catalyst was published by the group of Milstein allowing the selective synthesis of imines.[79] The group of Kirchner reported on a related PNP ligand-stabilized Mn-complex, catalyzing imines from alcohols and amines under similar reaction conditions but with shorter reaction time.[80]



Scheme 3.4: Selected examples of base-metal catalysts for amine alkylation using the ADC concept.

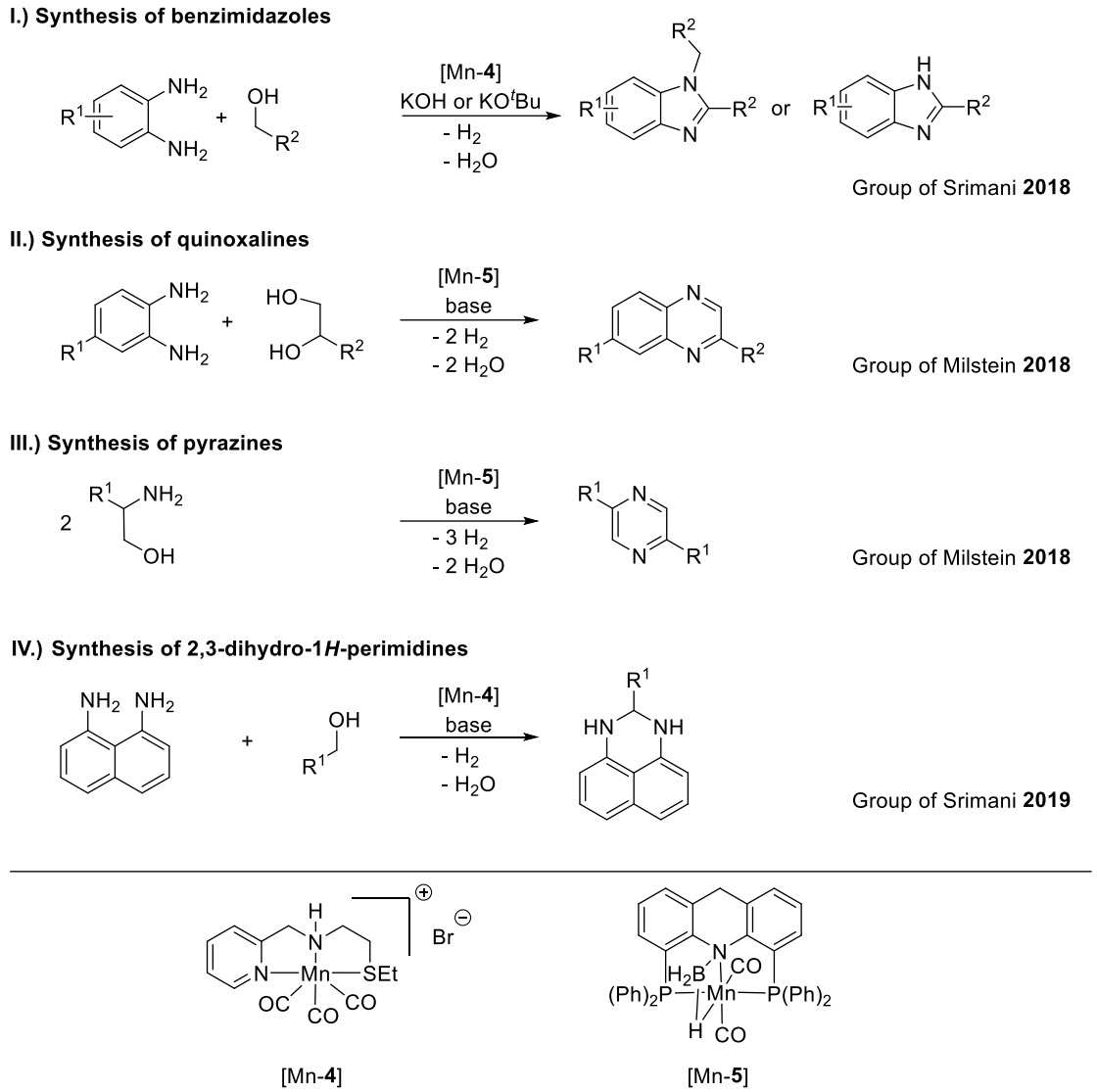
3.5 Manganese-Catalyzed Synthesis of *N*-Heterocycles using the ADC

Several manganese catalysts have been developed for the sustainable synthesis of *N*-heterocycles using the Acceptorless Dehydrogenative Condensation. The group of Beller used the manganese precatalyst [Mn-**1**] synthesizing indole via an intramolecular dehydrogenative coupling of 2-aminophenethyl alcohol under mild reaction conditions (Scheme 3.5, **I.)**).[81] The base-metal complex [Mn-**2**] was developed by the group of Kirchner. They introduced the environmentally benign synthesis of quinolines using 2-aminobenzyl alcohols and alcohols as starting materials (Scheme 3.5, **II.)**).[82] The same catalyst also allows the synthesis of pyrimidines via a 3-component synthesis consisting of benzamidine, a secondary alcohol and a primary one (Scheme 3.5, **III.)**).[82] The variability in the substitution pattern of pyrimidines is increased through the use of the precatalyst [Mn-**3**] introduced by the group of Kempe.[83] It is achieved by a consecutive 4-component reaction, whereas a β-alkylation between a primary and a secondary alcohol proceeds in the first part. [Mn-**3**] was also used for the first base-metal catalyzed synthesis of pyrroles using alcohols and amino alcohols as renewable resources (Scheme 3.5, **IV.)**).[84] In 2018, Srimani and co-workers presented a phosphine-free tridentate NNS ligand-derived manganese(I) complex ([Mn-**4**]) for the selective synthesis of 2-substituted and 1,2-disubstituted benzimidazoles by Acceptorless Dehydrogenative Condensation of aromatic diamines with primary alcohols.[85] The observed selectivity is achieved by changing the necessitated base, if KO^{t}Bu is used, 1,2-disubstituted benzimidazoles were obtained, while 2-substitued ones were isolated using KOH as base (Scheme 3.6, **I.)**).



Scheme 3.5: Advancements in the synthesis of *N*-heterocycles using Mn-catalysts.

The group of Milstein developed an acridine-based pincer complex of manganese, [Mn-**5**], for the synthesis of substituted quinoxaline derivatives by dehydrogenative coupling of 1,2-diaminobenzene and 1,2-diols (Scheme 3.6, **II.)**).[86] Furthermore, Milstein and co-workers used [Mn-**5**] to catalyze the synthesis of 2,5-dialkyl substituted symmetrical pyrazine derivatives by the self-coupling of 2-aminoalcohols (Scheme 3.6, **III.)**), the only by-products are water and hydrogen.[86] In 2019, the group of Srimani synthesized selectively important 2,3-dihydro-1*H*-perimidines catalyzed by [Mn-**4**] (Scheme 3.6, **IV.)**). They showed that through the nature and stoichiometry of the applied base the selectivity of the amino alkylation is controlled.[87]



Scheme 3.6: Manganese-catalyzed synthesis of *N*-heterocycles via ADC.

The discussed syntheses of *N*-heterocycles in this section show the high potential for manganese catalysts for ADC reactions. The use of new manganese catalysts with sustainable starting materials like alcohols enables new synthesis routes due to different reactivity compared to precious-metal catalysts. In section 5 one manganese catalyst system is presented, which can selectively switch between the concept of BH/HA and ADC. In section 6 this catalyst system is used for a consecutive multicomponent reaction to synthesize an *N*-hetero polycyclic compound class, that has not been reported yet.

4 Overview of Thesis Results

This thesis consists of three different projects, which are presented in section 4-6.

4.1 Synopsis

$PN_{3-5}P$ ligand stabilized complexes have shown a high activity for BH/HA and ADC reactions in previous works of the Kempe group. First reactions were conducted with catalysts based on Ir, but soon base-metal catalysts were established deriving from the PN_5P ligand type. The modular design of this ligand class allows to customize the steric and electronic properties of the catalyst system in a unique way. The Kempe group showed that PN_5P cobalt complexes are highly active in the homogeneous hydrogenation of C=O bonds as well as in the amino alkylation using alcohols as starting materials. Subsequently, a library of PN_5P ligand-derived Mn(I) complexes was synthesized and their activity in the hydrogenation of carbonyl bonds was presented (Figure 4.1). During the investigation of those Mn-precatalyst in the alkylation of primary amines using the BH/HA concept, a unique, base-dependent reactivity was observed.

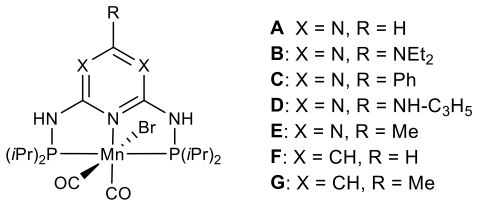


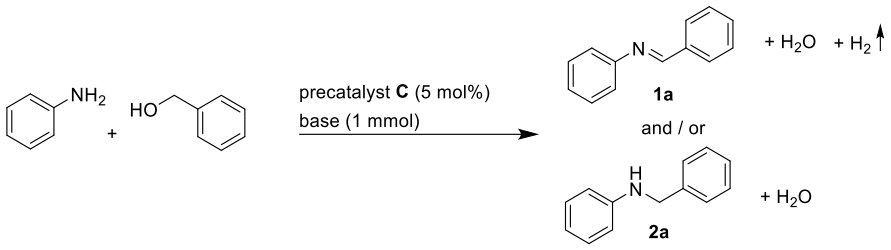
Figure 4.1: General structure of the investigated PNP ligand-stabilized Mn pincer complexes.

4.1.1 Manganese-Catalyzed and Base-Switchable Synthesis of Amines or Imines via Borrowing Hydrogen or Dehydrogenative Condensation

The development of catalysts based on Mn is of high interest since manganese is the third most abundant transition metal in earth's upper crust. The *N*-alkylation of primary amines by alcohols is an elegant, broadly applicable and sustainable method for the synthesis of alkyl and aryl amines. A library of Mn-precatalysts was investigated for the reaction between aniline and benzyl alcohol. The active species of the catalyst is generated by deprotonation of the amines via addition of a base. Interestingly, an alkali metal base-dependant product formation was observed (Table 4.1). If LiO^{t}Bu or NaO^{t}Bu were used for the activation of the catalyst system, the imine **1a** was obtained, while the corresponding amine **2a** was

received preferentially using KO^{t}Bu or CsO^{t}Bu. The use of related bases led to a similar selectivity (Table 4.1).

Table 4.1: Base screening for the Mn-catalyzed alkylation of aniline with benzyl alcohol.[a]



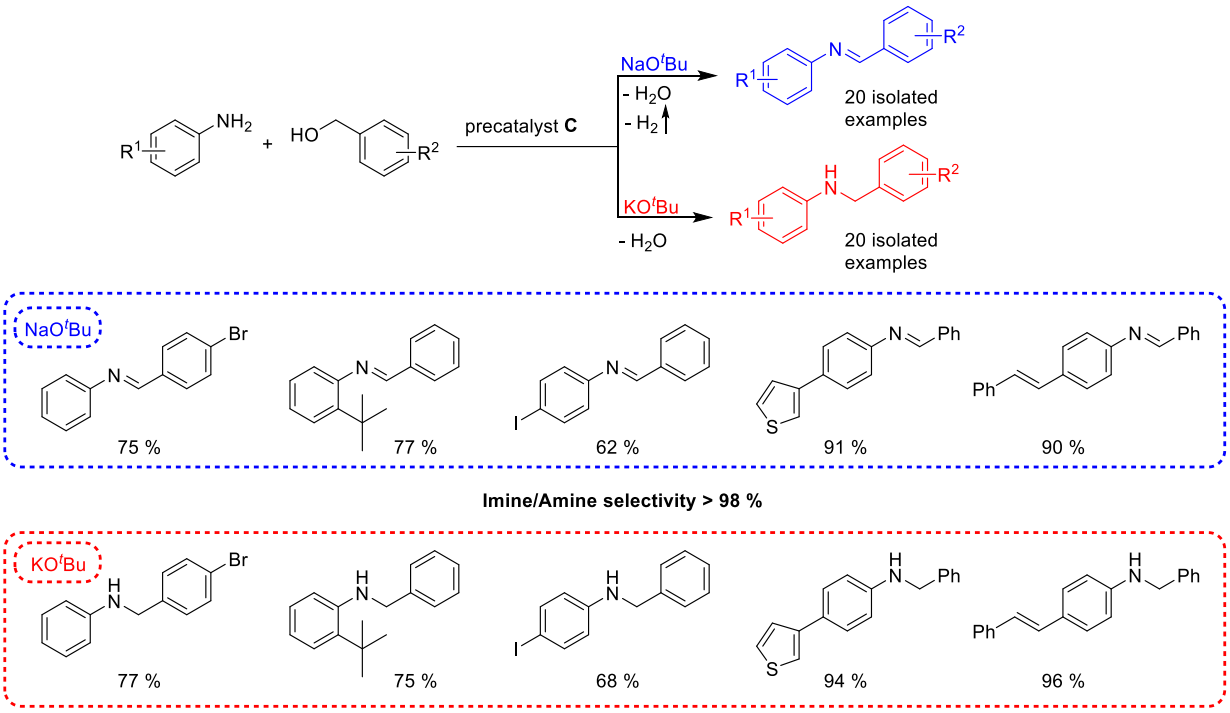
Entry	Base	Imine **1a** [%][b]	Amine **2a** [%][b]
1	LiO^{t}Bu	5	0
2	NaO^{t}Bu	26	6
3	KO^{t}Bu	0	60
4	CsO^{t}Bu	0	62
5	LiHMDS	4	1
6	NaHMDS	24	19
7	KHMDS	0	95

[a] Reaction conditions: 1 mmol aniline, 1 mmol benzyl alcohol, 5 mol% precatalyst **C**, 1 mmol base, 5 mL THF, 80 °C (oil bath), 18 h, pressure tube. [b] Yield determined via GC with decane as an internal standard.

We compared the Mn-precatalyst **C** with six different manganese precatalysts and observed a decrease in the activity if the ligand backbone is based on a pyridine moiety. The Ir- and Co-precatalyst for amino alkylation previously described by the Kempe group were selected and tested for comparison. Both catalysts showed a high activity and selectivity in the amine formation if KO^{t}Bu is used, but the activation with NaO^{t}Bu led to the imine only in low yields. Next, all reaction parameters for the imine and the amine synthesis were separately optimized to improve the yield of both reactions. A yield of >99 % with a selectivity of >99 % was achieved for the amine synthesis using an alcohol/amine ratio of 1.4/1, 3 mol% of precatalyst **C**, 1 equiv. KO^{t}Bu, 80 °C (oil bath), closed flask in THF. A yield of >99 % with a selectivity of >99 % was obtained for the imine synthesis using an alcohol/amine ratio of 1.6/1, 1 mol% of precatalyst **C** and 1.5 equiv. NaO^{t}Bu at 110 °C (oil bath). An open flask with a bubble counter was used for imine synthesis to release the generated molecular hydrogen. Conducted scale-up experiments for imine and amine synthesis (50 times of the normal scale) showed similar selectivity and yields.

With these conditions at hand, the addressable product scope was explored by investigating a variety of alcohols and primary amines for the *N*-alkylation catalyzed by the PN_5P pincer complex. For this, the same alcohol/amine educt combination was used for imine and amine synthesis. Substrates bearing both electron-withdrawing and electron-donating substituents on the alcohol as well as on the primary amine were converted smoothly. The imines were isolated in yields from 52 to 93 % (average yield of 77 %)

and the corresponding amines were isolated in yields ranging from 66 to 97 % (average yield of 86 %). Some selected examples are shown in Scheme 4.1, indicating the good functional group tolerance for the conversion into the respective *N*-alkyl amine or imine. The observed imine/amine selectivity was always higher than 98%.



Scheme 4.1: Selected imines and amines for the base-switchable amino alkylation using the Mn-precatalyst **C**. Yields of isolated products are shown.

Finally, mechanistic experiments were conducted to understand the observed selectivity. Time-conversion plots showed that amine formation can be suppressed if K^+ is masked with 18-crown-6. If KO^{t}Bu was added to the manganese hydride [**MnH**], a change in ^{31}P NMR spectra from 160.25 ppm to 157.54 ppm was observed (Figure 4.2). Since the acidic NH protons of the ligand backbone disappeared after the addition of the respective base, a coordination of the potassium or sodium cation at the deprotonated amino functions of the ligand is assumed, additionally stabilized via the nitrogen atoms of the triazine backbone.

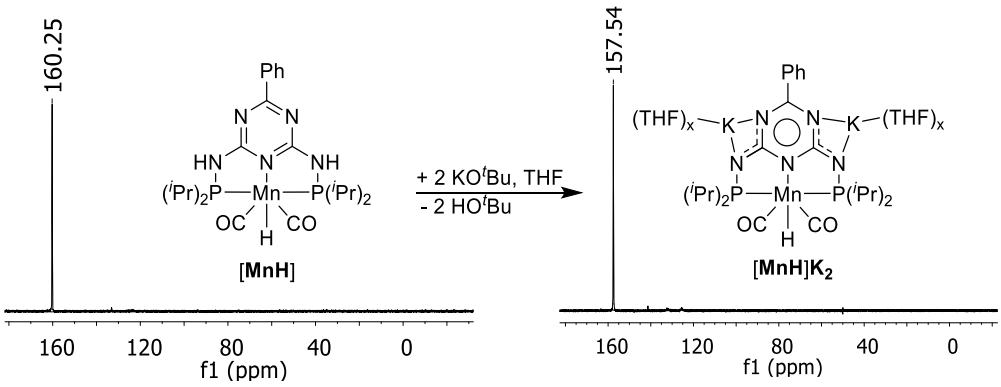
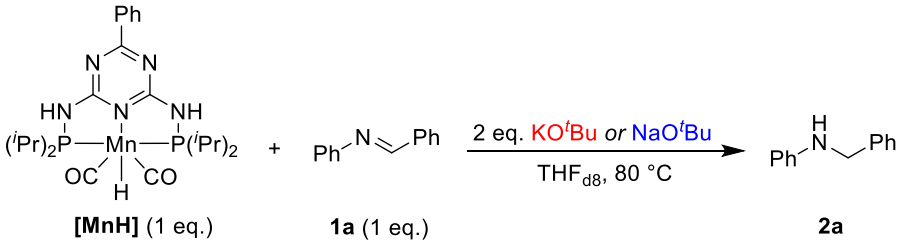


Figure 4.2: ^{31}P NMR-signal of the manganese hydride [**MnH**] and after activation with KO^{t}Bu.

The potassium manganate hydride [**MnH**]**K**$_2$ and the corresponding sodium salt revealed significant differences in their reactivity. A remarkable different hydride transfer rate to the imine **1a** generating the amine **2a** was observed via ^{1}H NMR-based time-conversion studies. A fast reaction to the amine **2a** for the *in situ* generated [**MnH**]**K**$_2$ was observed, while under the same reaction conditions the amine **2a** was only formed in low amounts and slowly, if [**MnH**]**Na**$_2$ was reacted with **1a** (Figure 4.3). This hydride transfer rate takes place about 40 times faster for [**MnH**]**K**$_2$ compared to [**MnH**]**Na**$_2$. This key step is responsible for the selective *N*-alkyl amine or imine formation.



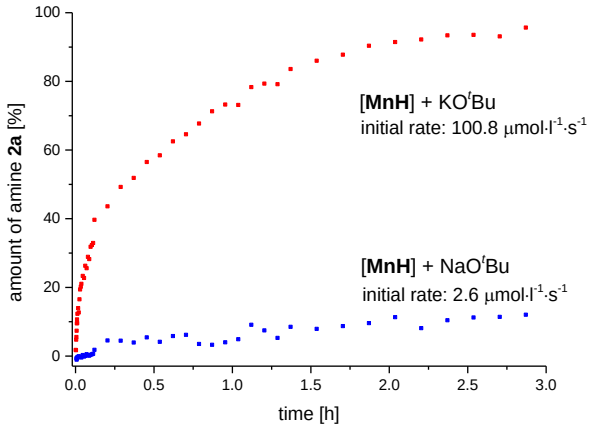
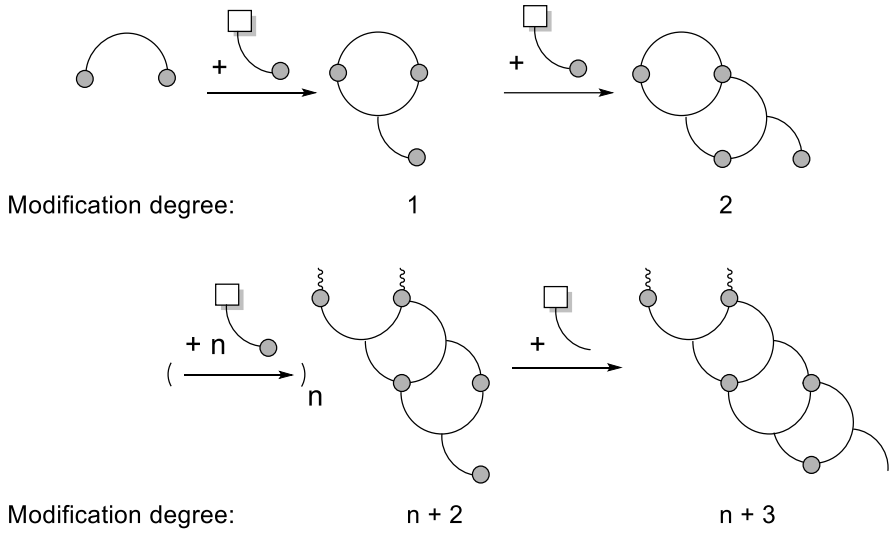


Figure 4.3: Reaction of the imine **1a** with the manganese hydride [**MnH**] after deprotonation with two equivalents of KO^{t}Bu or NaO^{t}Bu. Reaction conditions: 60 µmol of [**MnH**], 60 µmol of **1a**, 120 µmol of base, 800 µmol of THF$_{d8}$, 80 °C.

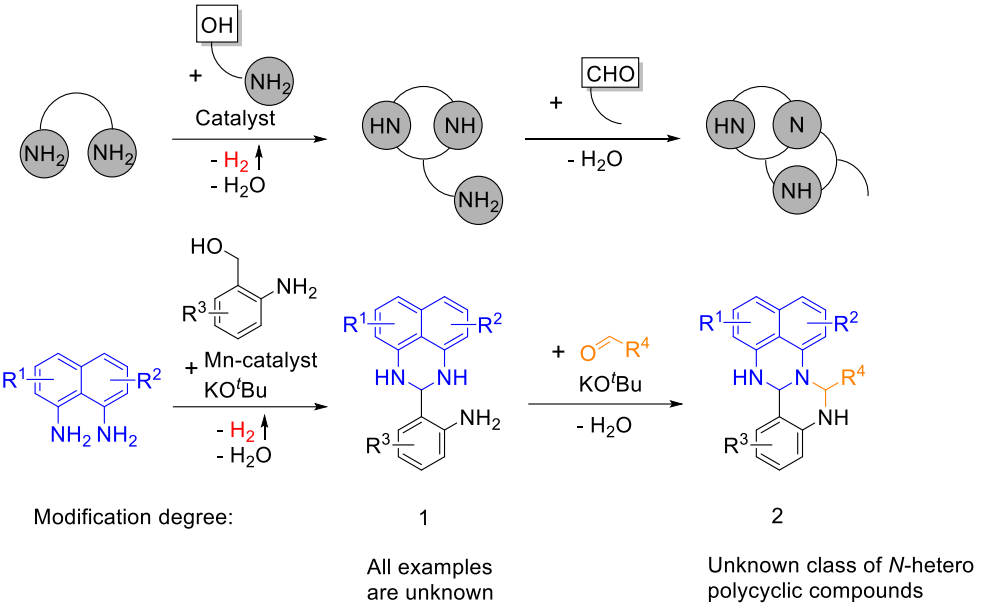
4.1.2 Rational Design of N-Heterocyclic Compound Classes via Regenerative Cyclization of Diamines

The discovery of reactions is a central topic in chemistry. It is of high interest if the discovered reaction can be used to reach inaccessible substitution patterns of an existing class of compounds or even permit the synthesis of an unknown class of compounds. Especially the access to unknown *N*-heterocyclic compounds is desirable due to their numerous applications in life and material sciences, for instance as pharmaceuticals, agro chemicals, dyes and conductive materials. We report here on a concept that could permit access to various cyclic compound classes. For this, the pair of functional groups required for ring closure must be formed again after ring closure. Repetition of the ring closure results in an unknown (hetero-) polycycle after a distinct time (Scheme 4.2).



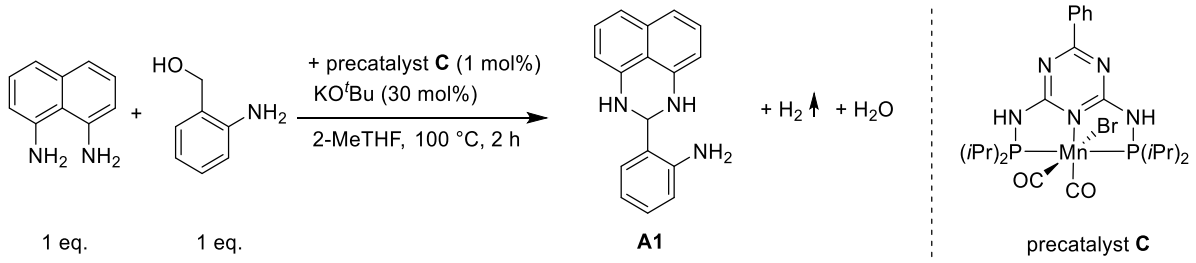
Scheme 4.2: General concept to design classes of polycyclic compounds via ring closure.

This concept is introduced by synthesizing a class of *N*-hetero polycycles via a catalytic consecutive multicomponent reaction. If naphthalene-1,8-diamine reacts selectively with an amino alcohol via dehydrogenation and condensation, a new pair of diamines is generated that can undergo ring closure again, for example with an aldehyde, to form an unknown class of *N*-hetero polycyclic compounds after the second ring closure (Scheme 4.3).



Scheme 4.3: Synthesis of an unreported class of *N*-hetero polycycles via a catalytic consecutive multicomponent reaction.

Interestingly, there is no one-pot reaction for the synthesis of 2,3-dihydro-1*H*-perimidines bearing a NH_2-functionality (modification degree 1, "aminoperimidine") reported since now. All these synthesized aminoperimidines have not been described yet. We started our investigation with an optimisation of the reaction conditions for the first ring closure leading to 2-(2,3-dihydro-1*H*-perimidin-2yl)aniline **A1**. The optimal reaction parameters for the synthesis of aminoperimidine **A1** were 1 mol% precatalyst **C**, 30 mol% KO^{t}Bu, 2 mmol 1,8-diamino naphthalene and 2-aminobenzyl alcohol, 3 mL 2-MeTHF at 100 °C with a reaction time of 2 h (Scheme 4.4). The reaction proceeded in a tube with a bubble counter to facilitate the release of hydrogen during the dehydrogenation of the amino alcohol.



Scheme 4.4: Optimized reaction conditions for the synthesis of **A1**.

Under optimized reaction conditions 24 unreported aminoperimidines were synthesized with yields ranging from 69 – 97 % (average isolated yield of 84 %). A high functional group tolerance was observed during catalysis including substituents like halogens, methoxy-groups and acetals. By means of a fluoro- and a methyl-substituent, as exemplary electron-withdrawing and electron-donating groups, the tolerance of a substitution on every position at the phenyl ring was demonstrated for catalysis (Figure 4.4).

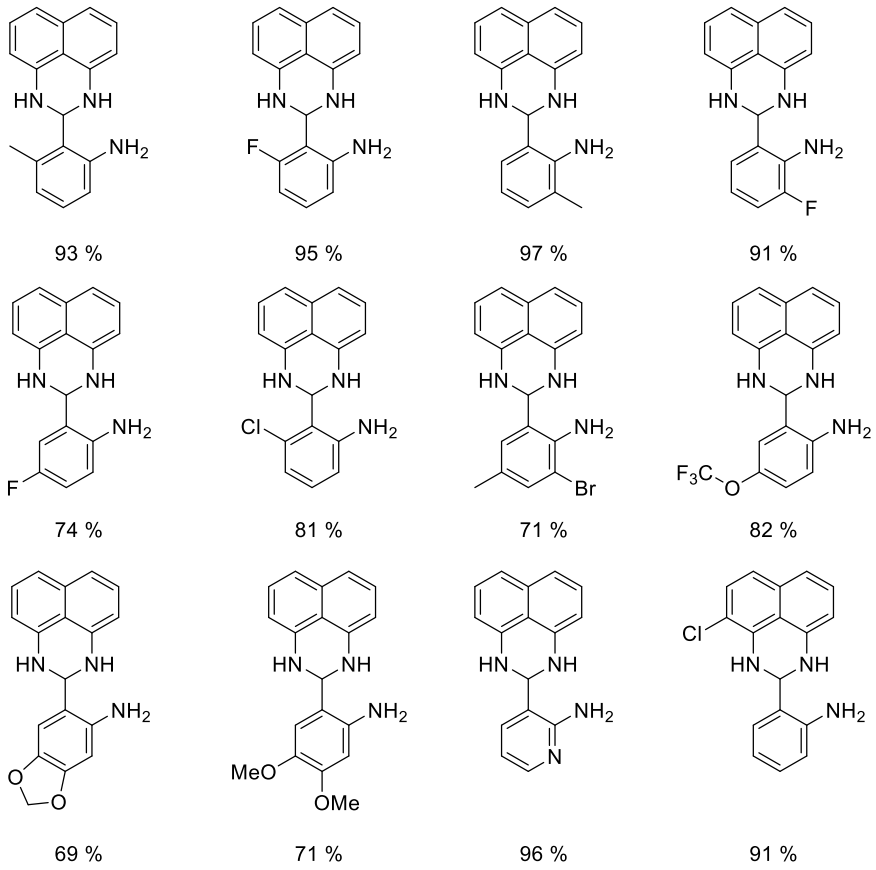
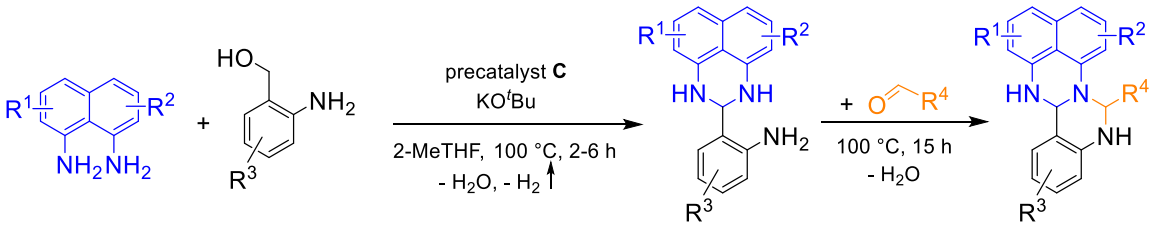


Figure 4.4: Selected examples of isolated aminoperimidines. Isolated yields are shown.

The spatial distance of the primary amine functionality to the NH-groups of the aminoperimidine enables the access to a second ring closure (modification degree 2). Due to price, easy-handling, sustainability aspects and broad availability, aldehydes represent the ideal building blocks for condensation reactions with amines. The second ring closure leads to compounds consisting of two annulated six-membered *N*-heterocyclic ring systems with an aminal in each ring. One of these six-membered rings has an annulated naphthene ring, one an annulated benzene ring. Every compound with this build-up is novel. The name fertigine is proposed for this class of *N*-hetero polycyclic compounds. Keeping the synthesis procedure of the fertigines as simple as possible, they were synthesized via a consecutive multicomponent one-pot reaction using the conditions optimized for the synthesis of the amino perimidines followed by the addition of an aldehyde (Scheme 4.5).



Scheme 4.5: Consecutive multicomponent one-pot synthesis of fertigines.

The substrate scope of this reaction was investigated by synthesizing fertigines with several derivatives of each starting material of this three-component reaction. Halogenated as well as alkylated substrates were used and reacted smoothly to the respective fertigines. In Figure 4.5 some selected examples of isolated fertigines are shown. Fertigines were isolated containing a stilbene moiety, *N*-, *S*-, or *O*-heterocyclic moieties, ferrocene moieties, phenolic or acetalic moieties. This synthesis concept permits access to multiple substituted fertigines. At all, a total amount of 48 fertigines with various substitutions was isolated in yields from 56 – 95 % (average yield of 79 %), demonstrating the high applicability of this synthesis concept.

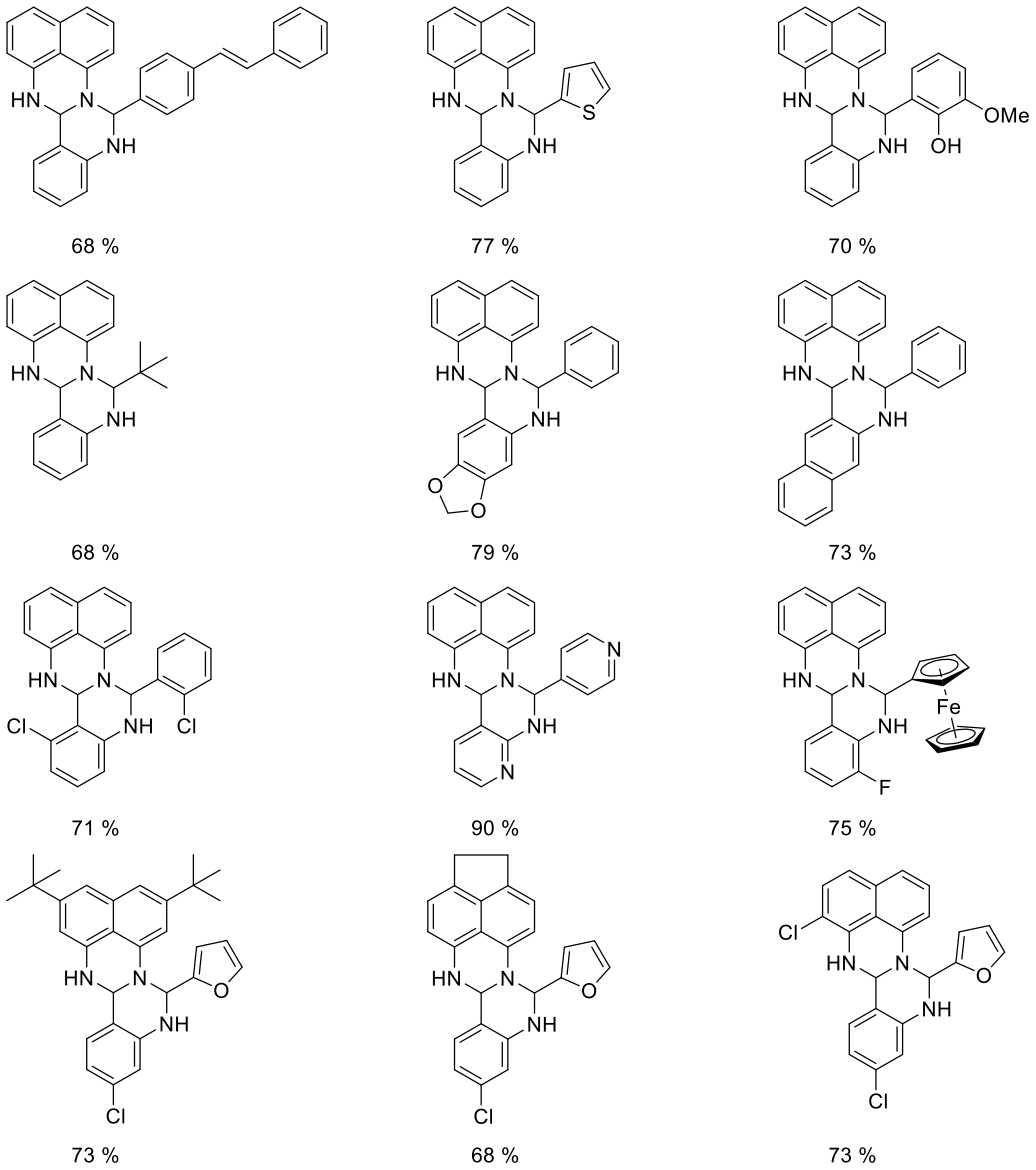


Figure 4.5: Selected examples of substituted fertigines. Isolated yields are shown.

4.1.3 Investigation of the Molecular Structure of Fertigines via X-Ray Crystallography

Recently, we have submitted a work about a synthesis concept that enables the synthesis of an unknown class of *N*-hetero polycyclic compounds, named fertigines. *N*-Heterocyclic compounds are of high importance as their motifs are found in many pharmaceuticals, natural products, and functional materials. Since chapter 4.1.2 has described the synthesis and high functionalizability of fertigines, this work is focused on the description of their molecular structures via X-ray crystallography. Nine different fertigines were compared with each other and the influence of the substitution on the molecular structure of the fertigines was investigated. Although the fertigines contain two stereo centers, we did not observe all diastereomers via ^{1}H NMR analysis, indicating a diastereoselectivity for the synthesis of this *N*-hetero polycyclic compounds. We started with the determination of the absolute configuration of each fertigine via X-ray analysis (Figure 4.6).

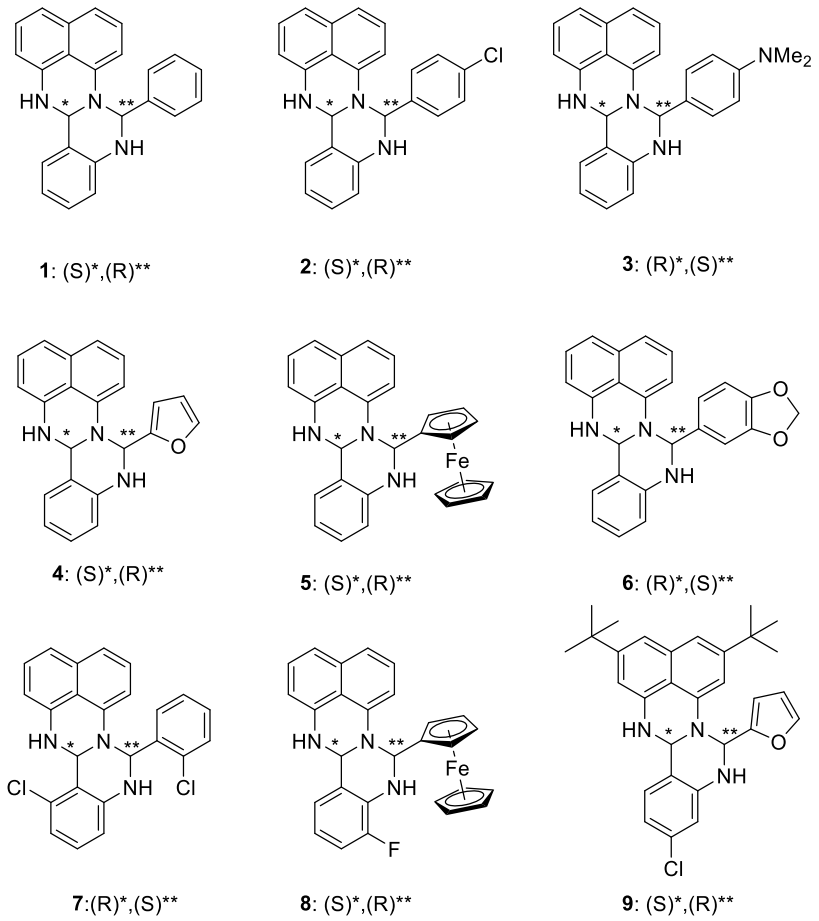


Figure 4.6: Absolute configuration of the fertigines found in the crystal analyzed via X-ray crystallography.

The bond lengths and angles of all nine fertigines were determined. In Figure 4.7 the molecular structure of **1**, obtained via X-ray crystallography, is presented. The angles C1-N1-C11: 117.4(1) ° and C11-N2-C18: 110.3(1) ° indicate a distorted trigonal pyramidal geometry for N1 and N2. According to the trigonal planar molecular geometry of N3 (C17-N3-C18: 120.9(1) °) and to the bond length of

N3-C17 (1.377(2) Å), N3 shows more the character of a sp^2-hybridization than of a sp^3-hybridization (lit.: $C_{arom.}-N_{sp^2}$: 1.353 ± 0.007 Å vs. $C_{arom.}-N_{sp^3}$: 1.419 ± 0.017). The influence of the substitution at C18 was investigated by comparing the core region (i.e., the two six-membered *N*-heterocyclic ring systems) of **1** with the structures of **2** – **5**. The investigated substituents do not have a significant impact on bond lengths and angles in the core region.

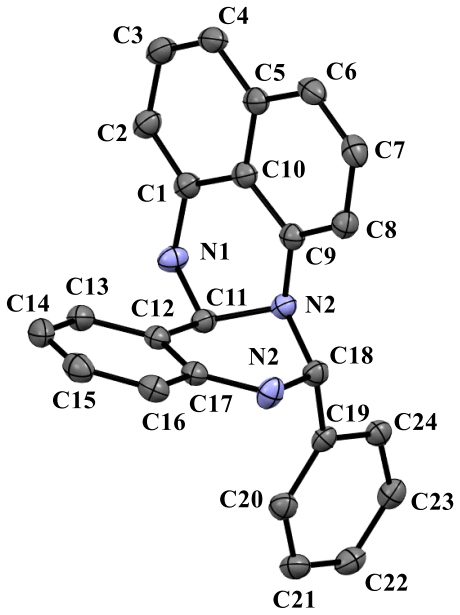


Figure 4.7: Molecular structure of **1** in the crystal (ORTEP drawing and atom labelling scheme with 50 % probability level). Selected bond lengths/Å and angles/°: N1-C11, 1.438(2); N2-C11, 1.490(2); N2-C18, 1.463(3); N3-C17, 1.377(2); N3-C18, 1.452(2); C11-C12, 1.52.

Next, the molecular structure of substituted fertigines (**6** – **9**) was analyzed. The bond lengths and angles of **6 - 9** are of comparable values like the fertigines **1** – **5**. The fertigines **1**, **2**, **3**, **5**, **6** and **8** showed a similar conformation in the crystal, where all three aromatic regions of the molecule are nearly perpendicular to each other. Regarding fertigine **1** (Figure 4.8), the naphthalene plane (red) is oriented with 85.65 ° to the plane of the fused phenyl ring (blue) and with 89.69 ° to the plane of the phenyl substituent (green). The plane of the phenyl substituent (green) has an angle of 84.68 ° to the plane of the fused phenyl ring (blue).

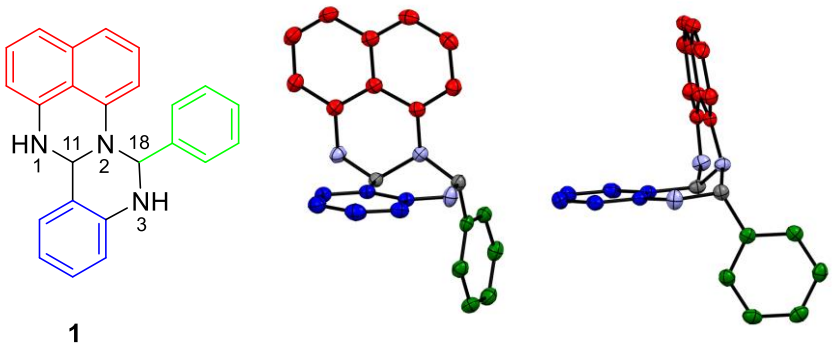


Figure 4.8: Orientation of the three aromatic regions (red, blue, green) of fertigine **1** in the crystal (ORTEP drawing and atom labelling scheme with 50 % probability level).

Fertigine **4**, **7** and **9** crystallized in a more flatten conformation, whereby especially the angle between the naphthene and the fused phenyl plane shrinks to values between 37.71 and 58.81 °.

In Table 2 some crystallographic details about the investigated crystals of the fertigines are presented. Five of the nine investigated single crystals are based on a monoclinic crystal system with 4 independent fertigines in the unit cell.

Table 2: Crystallographic details of the investigated fertigines.

Fertigine	Crystal system	Space group	Z	R_{int}	R_1	CCDC No.
1	monoclinic	P 21/c	4	0.0246	0.0433	2083140
2	orthorhombic	P 21 21 21	4	0.0798	0.0561	2083142
3	monoclinic	P 21/n	4	0.0468	0.0544	2083143
4	orthorhombic	P b c a	8	0.1330	0.0948	2083141
5	monoclinic	Cc	4	0.0256	0.0358	2083149
6	triclinic	P -1	2	0.0311	0.0520	2083146
7	orthorhombic	P n a 21	4	0.0376	0.0417	2083153
8	monoclinic	Cc	4	0.0266	0.0337	2083151
9	monoclinic	P21/n	4	0.0611	0.0858	2083155

4.2 Individual Contributions to Joint Publications

The results presented in this thesis were obtained in collaboration with others and were published as indicated below. In the following, the contributions of all co-authors and contributors to the publications are specified. The asterisk denotes the corresponding author.

Chapter 5

This work was published in ACS Catalysis (*ACS Catal*. **2018**, *8*, 8525–8530) with the title **"Manganese-Catalyzed and Base-Switchable Synthesis of Amines or Imines via Borrowing Hydrogen or Dehydrogenative Condensation"**.
Authors: Robin Fertig, Torsten Irrgang, Frederik Freitag, Judith Zander, and Rhett Kempe*

I conducted the experiments and characterized all compounds as presented in the final publication. Judith Zander was involved in this project during her B.Sc. thesis and helped with the synthesis and isolation of the imine derivatives. The help of Fabian Kallmeier in the initial reaction development is greatly acknowledged. Frederik Freitag was involved in mechanistic discussions and helped performing the mechanistic NMR studies. Torsten Irrgang and Rhett Kempe supervised the work, were involved in scientific discussions and co-wrote the manuscript with me.

Chapter 6

This work is submitted to Nature Communications (**2022**) with the title **"Rational Design of N-Heterocyclic Compound Classes via Regenerative Cyclization of Diamines"**.
Authors: Robin Fertig, Torsten Irrgang and Rhett Kempe*

I conceived the concept, performed the synthesis of starting materials, and conducted the experiments as presented in the final publication. The help of Felix Schreiner in the synthesis of the amino alcohols is greatly acknowledged. Torsten Irrgang and Rhett Kempe supervised the work, were involved in scientific discussions and co-wrote the manuscript with me.

Chapter 7

This work is to be submitted with the title **"Structure Investigations of Fertigines via X-Ray Crystallography"**.
Authors: Robin Fertig, Torsten Irrgang and Rhett Kempe*

I performed the synthesis of the crystals, conducted the experiments and measurements as presented in this work. Torsten Irrgang and Rhett Kempe supervised the work, were involved in scientific discussions and co-wrote the manuscript with me.

5 Manganese-Catalyzed and Base-Switchable Synthesis of Amines or Imines via Borrowing Hydrogen or Dehydrogenative Condensation

Robin Fertig, Torsten Irrgang, Frederik Freitag, Judith Zander, and Rhett Kempe*

Manganese-Catalyzed and Base-Switchable Synthesis of Amines or Imines via Borrowing Hydrogen or Dehydrogenative Condensation.

*Inorganic Chemistry II - Catalyst Design, University of Bayreuth, 95440 Bayreuth, Germany

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Manganese-Catalyzed and Base-Switchable Synthesis of Amines or Imines via Borrowing Hydrogen or Dehydrogenative Condensation

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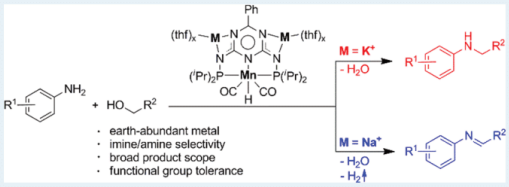
Supporting Information

ABSTRACT: The use of earth-abundant transition metals as a noble metal replacement in catalysis is especially interesting if different catalytic reactivity is observed. We report, here, on the selective manganese-catalyzed base-switchable synthesis of *N*-alkylated amines or imines. In both reactions, borrowing hydrogen/hydrogen autotransfer (*N*-alkyl amine formation) or dehydrogenative condensation (imine formation), we start from the same amines and alcohols and use the same Mn precatalyst. The key is the presence of a potassium base to prefer *N*-alkylation and a sodium base to permit imine formation. Both bases react with the manganese hydride via deprotonation. The potassium manganate hydride reacts about 40 times faster with an imine to give the corresponding amine than the sodium manganate hydride. The selectivity seems unique for manganese complexes. We observe a broad scope with a complete product overlap, all amine alcohol combinations can be converted into an *N*-alkyl amine or an imine, and a good functional group tolerance.

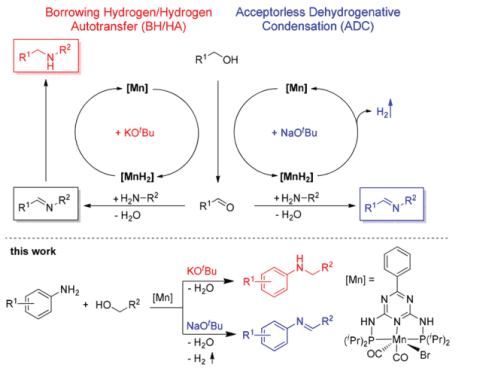


KEYWORDS: *amines, base-switchable, borrowing hydrogen, dehydrogenative condensation, imines, manganese, N-alkylation*

The "replacement" of noble metals in key technologies, such as catalysis by earth-abundant metals, is a possible rare element conservation strategy. It is especially attractive if it goes beyond a simple replacement and, additionally, different catalytic reactivity is observed. Manganese catalysts have been used successfully in hydrogenation and dehydrogenation reactions since 2016[1] and an impressive similarity to Ir and Ru catalysts in the (transfer) hydrogenation of ketones,[2] esters,[2e,3] amides,[4] and CO_2,[5] and dehydrogenative coupling,[6] dehydrogenative condensation,[7] and borrowing hydrogen/hydrogen autotransfer[8] has been observed. Unfortunately, examples of catalytic transformations, not yet observed with noble metals, are rare.[9] The *N*-alkylation of amines by alcohols[10,11] is an elegant, broadly applicable and sustainable method for the synthesis of alkyl amines (Scheme 1, top left). It follows the borrowing hydrogen[12] or hydrogen autotransfer[13] (BH/HA) concept. The dehydrogenative imine synthesis starting from amines and alcohols introduced by Milstein and co-workers is of similar conceptional importance.[14] This reaction proceeds via H_2 liberation. Both reactions can be catalyzed by Mn,[7,8] Co,[15,16] and Fe[17,18] complexes.

We report, herein, the manganese-catalyzed selective synthesis of *N*-alkyl amines or imines from the same alcohol amine couples. The presence of the metal base determines the product with potassium bases giving selectively *N*-alkyl amines and sodium bases giving selectively imines. The base-switchable reaction has a broad scope and an attractive functional group tolerance. Related Co, Fe, and Ir complexes are significantly less switchable. Mechanistic investigations revealed that both bases react with the PN_5P ligand-stabilized manganese hydride [**MnH**] via deprotonation. The potassium manganate hydride reacts about 40 times faster with an imine via amine formation than the sodium manganate hydride.

Scheme 1. Borrowing Hydrogen/Hydrogen Autotransfer (BH/HA, Red) and Acceptorless Dehydrogenative Condensation (ADC, Blue) Concept and the Product Selectivity Observed for the Mn-Catalyzed Base-Switchable Amine or Imine Synthesis



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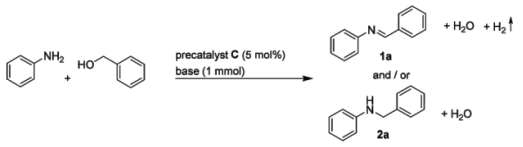
We investigated the reaction between aniline and benzyl alcohol in the presence of a PN_5P ligand-stabilized manganese catalyst and observed an alkali metal base-dependent product formation (Table 1). If LiO^{t}Bu or NaO^{t}Bu were used for the

Table 1. Base Screening for the Mn-Catalyzed Alkylation of Aniline with Benzyl Alcohol[a]



entry	base	imine **1a** [%][b]	amine **2a** [%][b]
1	LiO^{t}Bu	5	0
2	NaO^{t}Bu	26	6
3	KO^{t}Bu	0	60
4	CsO^{t}Bu	0	62
5	LiHMDS	4	1
6	NaHMDS	24	19
7	KHMDS	0	95

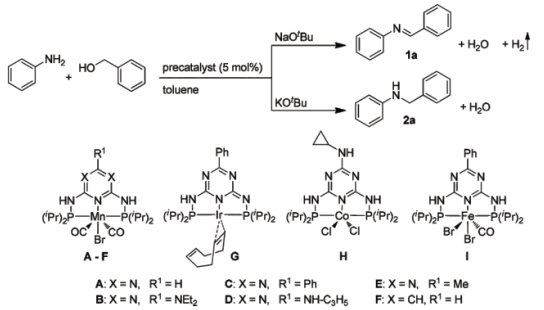
[a]Reaction conditions: 1 mmol aniline, 1 mmol benzyl alcohol, 5 mol % precatalyst **C**, 1 mmol base, 5 mL THF, 80 °C (oil bath), 18 h, pressure tube. [b]Yield determined via GC with decane as an internal standard.

activation of the catalyst system, the imine **1a** was obtained, while the corresponding amine **2a** was received preferentially using KO^{t}Bu or CsO^{t}Bu. A similar selectivity was observed using related bases. A library of Mn complexes (**A**–**F**) was tested next to find the best catalyst for these divergent reaction pathways (Table 2).

Regarding the most selective and highly active catalyst (**C**), activation with KO^{t}Bu led to the amine **2a** with about a 50% yield and a selectivity higher than 90%. Using NaO^{t}Bu as the base, the imine **1a** was received with about a 30% yield and 98% selectivity under same reaction conditions. If the ligand backbone is a pyridine moiety (precatalyst **F**), a significantly lower activity was observed. Our group described previously the alkylation of amines with alcohols using Ir and Co catalysts.[19,15a] Efficient Ir (**G**) and Co (**H**) catalysts reported in these publications were selected and tested for comparison. The use of **G** and KO^{t}Bu as the base led to the amine **2a** in a 66% yield and 99% selectivity, while the amine was obtained in a 58% yield and 97% selectivity using the Co precatalyst **H**. A very low formation of the imine **1a** was observed with the same precatalysts (**G**, **H**) and NaO^{t}Bu. The amine **2a** was obtained with KO^{t}Bu in a 30% yield and about 90% selectivity using the Fe precatalyst **I**,[17d] but negligible conversion was observed if NaO^{t}Bu instead of KO^{t}Bu was used as a base.

All reaction parameters for the imine and the amine synthesis were separately optimized to improve the yield in both reactions (see SI). A yield of >99% with a selectivity of >99% was achieved for the amine synthesis using an alcohol/amine ratio of 1.4/1, 3 mol % of precatalyst **C**, 1 equiv KO^{t}Bu, 80 °C (oil bath), closed flask in THF. A yield of >99% with a selectivity of >99% was obtained for the imine synthesis using an alcohol/amine ratio of 1.6/1, 1 mol % of precatalyst **C** and 1.5 equiv NaO^{t}Bu at 110 °C (oil bath). Because of its higher boiling point 2-MeTHF was used as solvent for imine synthesis. To increase the yield, it is important that the generated hydrogen can be released, thus we changed to an

Table 2. Precatalyst Screening of the Model Reaction[a]



	KO^{t}Bu		NaO^{t}Bu	
precatalyst	imine **1a**[b] [%][b]	amine **2a**[b] [%][b]	imine **1a**[b] [%][b]	amine **2a**[b] [%][b]
A	5	23	28	1
B	2	52	24	0
C	1	53	27	0
D	4	51	27	2
E	4	35	1	5
F	1	8	3	0
G	0	66	7	0
H	2	58	2	2
I	5	30	0	0

[a]Reaction conditions: 1 mmol aniline, 1 mmol benzyl alcohol, 1 mmol base, 5 mol % precatalyst, 5 mL toluene, 80 °C (oil bath), 20 h, pressure tube. [b]Yield determined via GC with decane as an internal standard.

open flask with bubble counter for imine synthesis. The liberation of one equivalent H_2 during imine synthesis was confirmed via GC-analysis (see SI). In the absence of amine, the formation of benzaldehyde from benzyl alcohol was observed with precatalyst **C** and NaO^{t}Bu (see SI). We investigated scale up experiments for imine and amine synthesis (50 times of the normal scale) and observed similar selectivity and comparable yields (see SI).

We next explored the substrate scope. Aniline was alkylated with various benzyl alcohol derivatives (Table 3). Substrates bearing both electron-withdrawing (Table 3, entries 2, 3) and electron-donating (Table 3, entries 4, 5) substituents were converted smoothly. The heteroaromatic 2-thiophenemethanol led to the imine (**1i**) and amine (**2i**) desired with a selectively higher than 98% in a 91 and 72% isolated yield, respectively. All imines and amines could be isolated in good to nearly quantitative yields (75–96%) with an imine/amine selectivity higher than 98%. We observed the selective formation of amines under BH/HA and ADC conditions when purely aliphatic alcohols were used (Table 3, entries 10 and 11).

A representative variety of substituted anilines was investigated next (Table 4). Halogenated imines (**3a**–**c**) and amines (**4a**–**c**) could be isolated in yields up to 97%. When using 4-iodoaniline, the imine **3c** and the corresponding amine **4c** could still be isolated with a 62% and 68% yield, respectively. The formation of all products took place with a selectivity higher than 98%. Sterically demanding groups, such as *tert*-butyl (**3e**, **4e**) or phenyl (**3f**, **4f**), were tolerated for imine and amine synthesis and the products could be isolated in yields from 66 to 82%. 3,5-Dimethylaniline provided the corresponding imine **3g** and amine **4g** with a high selectivity and nearly quantitative isolated yield. Using substrates, such as

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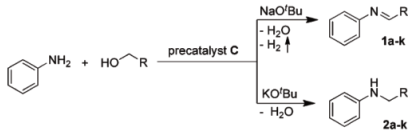
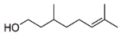
Table 3. Synthesis of Imines 1a−k[a] and Amines 2a−k[b] Using Aniline and Various Alcohol Derivatives



entry	alcohol	imine[c]	amine[c]
1	R = C_6H_5	**1a** (84%)	**2a** (91%)
2	R = 4-Cl(C_6H_4)	**1b** (90%)	**2b** (96%)
3	R = 4-Br(C_6H_4)	**1c** (75%)	**2c** (77%)
4	R = 4-*tert*-Butyl(C_6H_4)	**1d** (86%)	**2d** (81%)
5	R = 4-OMe(C_6H_4)	**1e** (80%)	**2e** (94%)
6	R = 3-Me(C_6H_4)	**1f** (87%)	**2f** (88%)
7	R = 2-Me(C_6H_4)	**1g** (88%)	**2g** (81%)
8		**1h** (78%)	**2h** (93%)
9		**1i** (91%)	**2i** (72%)
10			**2j** (94%)
11	R = $(CH_2)_6CH_3$		**2k** (96%)

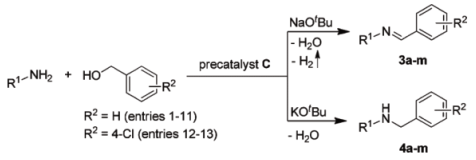
[a]Reaction conditions: 1 mmol aniline, 1.6 mmol benzyl alcohol, 1 mol % precatalyst **C**, 1.5 mmol NaO^{t}Bu, 3 mL 2-MeTHF, 110 °C (oil bath), 6 h, open system. [b]Reaction conditions: 1 mmol aniline, 1.4 mmol benzyl alcohol, 3 mol % precatalyst **C**, 1 mmol KO^{t}Bu, 2 mL THF, 80 °C (oil bath), 18 h, pressure tube. [c]Yield of isolated product in parentheses.

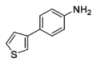
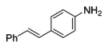
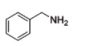
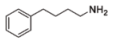
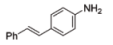
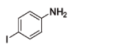
4-(thiophen-3-yl) aniline (formation of imine **3h** and the amine **4h**), indicated the tolerance of heterocyclic moieties. Both imine **3i** and amine **4i** could be isolated in a yield of 90 and 96%, respectively, indicating the tolerance of C−C double bonds. The use of aliphatic amines led selectively to the corresponding imines under ADC and BH/HA conditions (Table 4, entries 10, 11).

We finally conducted mechanistic studies to understand the selectivity observed. Time−conversion plots were obtained for both reactions (see SI) and indicate that imine formation is not kinetically controlled and that amine formation can be suppressed if K^+ is masked with 18-crown-6. We concluded that a coordinative interaction of the K^+ ions with the catalyst could play a key role. When KO^{t}Bu or NaO^{t}Bu was added to the manganese hydride [**MnH**], a change in ^{31}P NMR spectra from 160 to 157 ppm was observed (Figure 1). ^{1}H NMR spectroscopy revealed that the acidic NH protons at 8.14 ppm disappeared after the addition of the bases (see SI). The characteristic triplet of the hydride signal was still observed after activation with each base but shifted from −5.89 to −5.66 ppm. We assume a coordination of the potassium or sodium cation at the deprotonated amino functions of the ligand, additionally stabilized via the nitrogen atoms of the triazine backbone (Figure 1).

Exploration of the reactivity of the potassium manganate hydride [**MnH**]$\mathbf{K_2}$ and the corresponding sodium salt revealed remarkable differences. ^{1}H NMR-based time−conversion plots of the reaction of manganate hydrides [**MnH**]$\mathbf{K_2}$ or [**MnH**]$\mathbf{Na_2}$ generated in situ with imine **1a** showed a drastically different rate regarding the formation of the amine **2a** (Figure 2). A fast reaction was observed for [**MnH**]$\mathbf{K_2}$, delivering an initial rate of 100.8 μmol·L^{-1}·s^{-1} under the conditions given.

Table 4. Synthesis of Imines 3a−m[a] and Amines 4a−m[b] Using Primary Amines and Various Benzyl Alcohols



entry	amine	imine[c]	amine[c]
1	R^1 = 4-Cl(C_6H_4)	**3a** (64%)	**4a** (97%)
2	R^1 = 4-Br(C_6H_4)	**3b** (73%)	**4b** (86%)
3	R^1 = 4-I(C_6H_4)	**3c** (62%)	**4c** (68%)
4	R^1 = 4-Et(C_6H_4)	**3d** (83%)[d]	**4d** (85%)
5	R^1 = 2-*tert*-Butyl(C_6H_4)	**3e** (77%)[d]	**4e** (75%)
6	R^1 = 2-Phenyl(C_6H_4)	**3f** (66%)	**4f** (82%)
7	R^1 = 3,5-Dimethyl(C_6H_3)	**3g** (93%)	**4g** (94%)
8		**3h** (91%)	**4h** (94%)
9		**3i** (90%)	**4i** (96%)
10		**3j** (79%)	
11		**3k** (55%)	
12		**3l** (58%)	**4l** (77%)
13		**3m** (52%)	**4m** (66%)

[a]Reaction conditions: 1 mmol aniline, 1.6 mmol benzyl alcohol, 1 mol % precatalyst **C**, 1.5 mmol NaO^{t}Bu, 3 mL 2-MeTHF, 110 °C (oil bath), 18 h, open system. [b]Reaction conditions: 1 mmol aniline, 1.4 mmol benzyl alcohol, 3 mol % precatalyst **C**, 1 mmol KO^{t}Bu, 2 mL THF, 80 °C (oil bath), 18 h, pressure tube. [c]Yield of isolated product in parentheses. [d]Reaction time: 6 h.

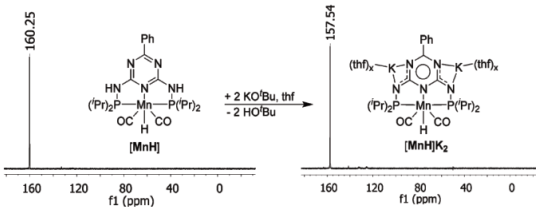


Figure 1. ^{31}P NMR-signal of the manganese hydride [**MnH**] and after activation with KO^{t}Bu.

The amine **2a** was formed only in a low amount and very slowly, with an initial rate of 2.6 μmol·L^{-1}·s^{-1} under the same reaction conditions if [**MnH**]$\mathbf{Na_2}$ (generated in situ) was reacted with **1a**. This key step seems to take a pace about 40 times faster for [**MnH**]$\mathbf{K_2}$ in comparison to [**MnH**]$\mathbf{Na_2}$.

In summary, we report on the manganese-catalyzed base-switchable synthesis of *N*-alkylated amines or imines from the

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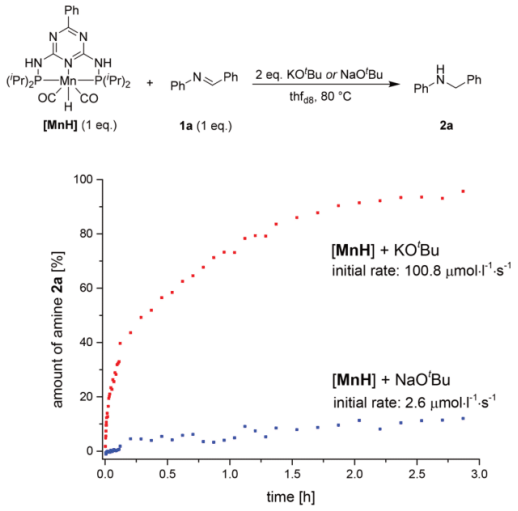

Figure 2. Reaction of the imine **1a** with the manganese hydride [**MnH**] after deprotonation with two equivalents of KO^{t}Bu or NaO^{t}Bu. Reaction conditions: 60 μmol of [**MnH**], 60 μmol of **1a**, 120 μmol of base, 240 μmol of benzyl alcohol, 800 μmol of thf$_{d8}$, 80 °C.

same alcohol and amine combinations. Both reactions are sustainable and very important, since the products are used diversely. We observed a broad scope, meaning a large variety of amine/alcohol combinations can be converted selectively into one or the other product. Furthermore, a very good functional group tolerance has been observed. Mechanistic investigations revealed that the manganese hydride is a precatalyst and reacts with KO^{t}Bu or NaO^{t}Bu via double deprotonation to form the corresponding potassium or sodium manganate hydride. The potassium manganate hydride reacts, under identical conditions, about 40 times faster with the imine *N*-benzylideneaniline via amine formation than the corresponding sodium salt. This difference in rate seems responsible for the selective *N*-alkyl amine or imine formation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b02530.

General information, screening reactions for the synthesis of amines, screening reactions for the synthesis of imines, additional screening reactions, synthesis of ligands and complexes, synthesis of amines, synthesis of imines, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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Supporting Information

Manganese-Catalyzed and Base-Switchable Synthesis of Amines or Imines via Borrowing Hydrogen or Dehydrogenative Condensation

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General

All reactions and manipulations with air sensitive compounds being present were performed under dry argon (Ar 5.0) or nitrogen (N_2 5.0), using Schlenk and glove box techniques. Nonhalogenated solvents were dried over sodium benzophenone, 2-methyltetrahydrofuran (2-MeTHF) was dried over calcium hydride, and halogenated solvents were dried over P_2O_5. Deuterated solvents were bought from Cambridge Isotope Laboratories, distilled accordingly, and stored over molecular sieves (3 Å). Other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were collected on a Varian INOVA 300 MHz spectrometer or on a Bruker Avance III HD 500 MHz. Chemical shifts (δ) are reported in ppm relative to residual solvent signal. Coupling constants (J) are given in Hz (coupling patterns: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet). GC analyses were carried out using an Agilent Technologies 6890N system equipped with a Macherey-Nagel (MN) Optima 5 HT column (30 m, 320 µm, 0.25 µm) or an Agilent Technologies 6850 system equipped with a MN Optima 17 column (30 m, 320 µm, 0.25 µm). GC/MS analyses were carried out on an Agilent 7890A/MSD 5975C system equipped with a HP-5MS column (30 m, 320 µm, 0.25 µm). MN silica gel 60 (0.040 – 0.063 mm particle size) was used for flash column chromatography. FTIR measurements were carried out under a nitrogen atmosphere on an Agilent Cary 630 FTIR equipped with a Diamond ATR unit. UV-Vis analyses were carried out using an Agilent Cary 60 spectrometer.

General procedure for the synthesis of amines

In a nitrogen filled glovebox, a pressure tube was filled with 1 eq. KO^{t}Bu (1 mmol, 112 mg) and 3 mol% precatalyst (0.03 mmol, with respect to the amine). The solution was stirred 5 minutes in 1 mL thf, then 1 eq. amine (1 mmol), 1.4 eq. alcohol (1.4 mmol) and 1 mL thf were added. The reaction mixture was stirred for 18 h at 80 °C (oil bath). The reaction was stopped by addition of 1 mL water. 100 µL of decane was added as internal standard. The aqueous layer was extracted using diethyl ether, the organic layers were combined, dried using Na_2SO_4 and the solvents were removed in vacuo. The crude product was purified by column chromatography.

General procedure for the synthesis of imines

In a nitrogen filled glovebox, a Schlenk tube was filled with 1.5 eq. NaO^tBu (1.5 mmol, 144 mg) and 1 mol% precatalyst (0.01 mmol, with respect to the amine). The solution was stirred 5 minutes in 1 mL 2-MeTHF, then 1 eq. amine (1 mmol), 1.6 eq. alcohol (1.6 mmol) and 2 mL 2-MeTHF were added. The reaction mixture was stirred for 18 h at 110 °C (oil bath). The reaction was stopped by addition of 1 mL water. 100 µL of decane was added as internal standard. The aqueous layer was extracted using diethyl ether, the organic layers were combined, dried using Na_2SO_4 and the solvents were removed in vacuo. The crude product was purified by column chromatography.

Screening reactions for the synthesis of amines

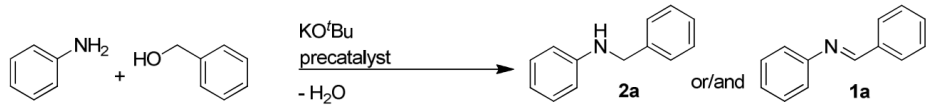
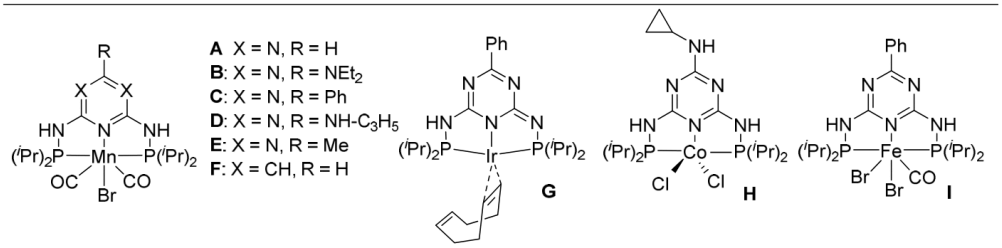


Figure S1: General reaction for the synthesis of *N*-benzylaniline (**2a**)

Table S1: Precatalyst screening[a]



Entry	Precatalyst	Amine **2a** [%][b]	Imine **1a** [%][b]
1	**A**	23	5
2	**B**	52	2
3	**C**	53	1
4	**D**	51	4
5	**E**	35	4
6	**F**	8	1
7	**G**	66	0
8	**H**	58	2
9	**I**	30	5
10	$[MnBr(CO)_5]$	0	0

[a] Reaction conditions: 1 mmol benzyl alcohol, 1 mmol aniline, 1 mmol KO^{t}Bu, 5 mol% precatalyst, 5 mL toluene, 80 °C (oil bath), 20 h, pressure tube. [b] Determined by GC with decane as an internal standard.

Table S2: Solvent screening[a]

Entry	Solvent	Amine **2a** [%][b]	Imine **1a** [%][b]
1	1,4-dioxane	19	0
2	1-methoxy-2-(2-methoxyethoxy)ethane (diglyme)	52	0
3	toluene	53	0
4	thf	59	0
5	2-MeTHF	53	0
6	2-methylene-2-butanol	5	7

[a] Reaction conditions: 1 mmol benzyl alcohol, 1 mmol aniline, 1 mmol KO^{t}Bu, 5 mol% precatalyst **C**, 5 mL solvent, 80 °C (oil bath), 18 h. [b] Determined by GC with decane as an internal standard.

Table S3: Base screening[a]

Entry	Base	Amine **2a** [%][b]	Imine **1a** [%][b]
1	LiO^{t}Bu	0	5
2	NaO^{t}Bu	0	26
3	KO^{t}Bu	60	0
4	CsO^{t}Bu	77	0
5	LiHMDS	1	4
6	NaHMDS	19	24
7	KHMDS	95	0
8	LiOH	0	0
9	NaOH	0	11
10	KOH	0	8
11	Cs_2CO_3	0	2

[a] Reaction conditions: 1 mmol benzyl alcohol, 1 mmol aniline, 1 mmol base, 5 mol% precatalyst **C**, 5 mL thf, 80 °C (oil bath), 18 h. [b] Determined by GC with decane as an internal standard.

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Table S4: Base amount screening[a]

Entry	Amount of KO^{t}Bu (equivalents with respect to the aniline)	Amine **2a** [%][b]	Imine **1a** [%][b]
1	0	0	0
2	0.05	0	1
3	0.6	7	2
4	0.8	43	2
5	1	56	3
6	1.5	21	0
7	2	15	1

[a] Reaction conditions: 1 mmol benzyl alcohol, 1 mmol aniline, 5 mol% precatalyst **C**, 5 mL thf, 80 °C (oil bath), 18 h. [b] Determined by GC with decane as an internal standard.

Table S5: Solvent amount screening[a]

Entry	Amount of thf [mL]	Amine **2a** [%][b]	Imine **1a** [%][b]
1	1	86	0
2	2	84	0
3	3	76	6
4	4	59	5
5	5	56	4

[a] Reaction conditions: 1 mmol benzyl alcohol, 1 mmol aniline, 1 mmol KO^{t}Bu, 5 mol% precatalyst **C**, thf, 80 °C (oil bath), 18 h. [b] Determined by GC with decane as an internal standard.

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Table S6: Substrate ratio screening[a]

Entry	Aniline [mmol]	Benzyl alcohol [mmol]	Amine **2a** [%][b]	Imine **1a** [%][b]
1	1	1	84	0
2	1	1.2	88	0
3	1	1.4	99	0
4	1	1.6	99	0
5	1.2	1	71	0
6	1.4	1	66	0

[a] Reaction conditions: 1 mmol KO^{t}Bu, 5 mol% precatalyst **C**, 2 mL thf, 80 °C (oil bath), 18 h. [b] Determined by GC with decane as an internal standard.

Table S7: Temperature screening[a]

Entry	Temperature [°C]	Amine **2a** [%][b]	Imine **1a** [%][b]
1	50	76	5
2	60	92	0
3	80	99	0
4	100	99	0
5	120	93	0

[a] Reaction conditions: 1.4 mmol benzyl alcohol, 1 mmol aniline, 1 mmol KO^{t}Bu, 5 mol% precatalyst **C**, 2 mL thf, 18 h, oil bath temperature. [b] Determined by GC with decane as an internal standard.

Table S8: Precatalyst C loading screening[a]

Entry	Precatalyst **C** [mol%][b]	Amine **2a** [%][c]	Imine **1a** [%][c]
1	5	99	0
2	3	99	0
3	2	82	0
4	1	56	1
5	0.5	23	1
6	0.1	6	1
7	0	0	0

[a] Reaction conditions: 1.4 mmol benzyl alcohol, 1 mmol aniline, 1 mmol KO^{t}Bu, 2 mL thf, 80 °C (oil bath), 18 h. [b] With respect to the aniline. [c] Determined by GC with decane as an internal standard.

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Screening reactions for the synthesis of imines

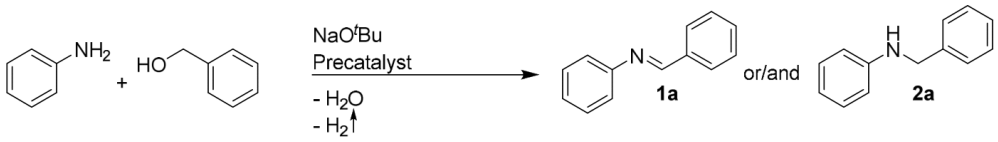
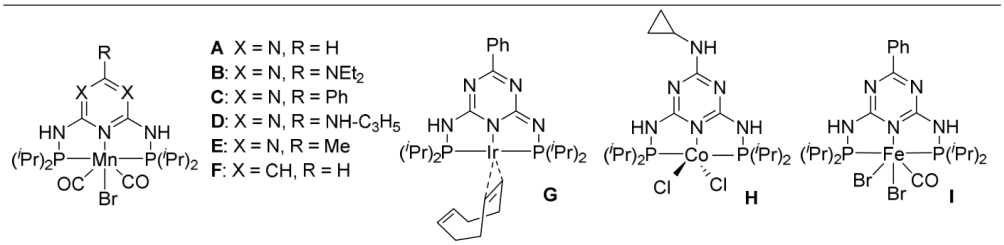


Figure S2: General reaction for the synthesis of *N*-benzylideneaniline (**1a**)

Table S9: Precatalyst screening[a]



Entry	Precatalyst	Imine **1a** [%][b]	Amine **2a** [%][b]
1	**A**	28	1
2	**B**	24	0
3	**C**	27	0
4	**D**	27	2
5	**E**	1	5
6	**F**	3	0
7	**G**	7	0
8	**H**	2	2
9	**I**	0	0
10	[$MnBr(CO)_5$]	0	0

[a] Reaction conditions: 1 mmol benzyl alcohol, 1 mmol aniline, 1 mmol NaO^{t}Bu, 5 mol% precatalyst, 5 mL toluene, 80 °C (oil bath), 20 h, pressure tube. [b] Determined by GC with decane as an internal standard.

Table S10: Solvent screening[a]

Entry	Solvent	Imine **1a** [%][b]	Amine **2a** [%][b]
1	1,4-dioxane	22	0
2	1-methoxy-2-(2-methoxyethoxy)ethane (diglyme)	7	45
3	toluene	24	0
4	thf	27	2
5	2-MeTHF	22	0
6	2-methyl-2-butanol	8	0

[a] Reaction conditions: 1 mmol benzyl alcohol, 1 mmol aniline, 1 mmol NaO^{t}Bu, 5 mol% precatalyst **C**, 5 mL solvent, 80 °C (oil bath), 18 h, pressure tube. [b] Determined by GC with decane as an internal standard.

Table S11: Base screening[a]

Entry	Base	Imine **1a**[%][b]	Amine **2a** [%][b]
1	LiO^{t}Bu	5	0
2	NaO^{t}Bu	26	0
3	KO^{t}Bu	0	60
4	CsO^{t}Bu	0	77
5	LiHMDS	4	1
6	NaHMDS	24	19
7	KHMDS	0	95
8	LiOH	0	0
9	NaOH	11	0
10	KOH	8	0
11	Cs_2CO_3	2	0

[a] Reaction conditions: 1 mmol benzyl alcohol, 1 mmol aniline, 1 mmol base, 5 mol% precatalyst **C**, 5 mL thf, 80 °C (oil bath), 18 h, pressure tube. [b] Determined by GC with decane as an internal standard.

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Table S12: Solvent amount screening[a]

Entry	Amount of thf [mL]	Imine **1a** [%][b]	Amine **2a** [%][b]
1	2	53	4
2	3	57	7
3	4	52	9
4	5	49	4

[a] Reaction conditions: 1 mmol benzyl alcohol, 1 mmol aniline, 1 mmol NaO^{t}Bu, 5 mol% precatalyst **C**, 80 °C (oil bath), 18 h. [b] Determined by GC with decane as an internal standard.

Table S13: Substrate ratio screening[a]

Entry	Aniline [mmol]	Benzyl alcohol [mmol]	Imine **1a** [%][b]	Amine **2a** [%][b]
1	1	1	52	1
2	1	1.4	61	2
3	1	1.6	68	4
4	1.4	1	50	2

[a] Reaction conditions: 1 mmol NaO^{t}Bu, 5 mol% precatalyst **C**, 3 mL thf, 80 °C (oil bath), 18 h. [b] Determined by GC with decane as an internal standard.

Table S14: Temperature screening[a]

Entry	Temperature [°C]	Imine **1a** [%][b]	Amine **2a** [%][b]
1	80	48	7
2	100	52	2
3	110	58	3
4	120	58	5
5	130	61	0

[a] Reaction conditions: 1 mmol benzyl alcohol, 1 mmol aniline, 1 mmol NaO^{t}Bu, 5 mol% precatalyst **C**, 3 mL thf, 18 h, oil bath temperature. [b] Determined by GC with decane as an internal standard.

Entry	Amount of NaO^{t}Bu (equivalents with respect to aniline)	Imine **1a** [%][b]	Amine **2a** [%][b]
1	0	0	0
2	0.05	0	0
3	0.5	17	0
4	1	55	0
5	1.5	73	7
6	2	60	28

[a] Reaction conditions: 1.6 mmol benzyl alcohol, 1 mmol aniline, 5 mol% precatalyst **C**, 3 mL thf, 18 h, 110 °C (oil bath). [b] Determined by GC with decane as an internal standard.

Table S15: Base amount screening[a]

Entry	Precatalyst **C** [mol%][b]	Imine **1a** [%][c]	Amine **2a** [%][c]
1	0	2	0
2	0.5	69	1
3	1	84	3
4	2	77	3
5	3	64	5
6	5	73	10

[a] Reaction conditions: 1.6 mmol benzyl alcohol, 1 mmol aniline, 1.5 mmol NaO^{t}Bu, precatalyst **C**, 3 mL thf, 18 h, 110 °C (oil bath). [b] With respect to aniline. [c] Determined by GC with decane as an internal standard.

Table S16: Precatalyst C loading screening[a]

Table S17: Final solvent screening[a]

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Entry	Solvent	Imine **1a** [%][b]	Amine **2a** [%][b]
1	thf	81	10
2	1,4-dioxane	69	5
3	2-MeTHF	95	0
4	toluene	65	0
5	*tert*-amyl alcohol	34	0
6	1-methoxy-2-(2-methoxyethoxy)ethane (diglyme)	48	6

[a] Reaction conditions: 1.6 mmol benzyl alcohol, 1 mmol aniline, 1.5 mmol NaO^{t}Bu, 1 mol% precatalyst **C**, 3 mL solvent, 18 h, 110 °C (oil bath). [b] Determined by GC with decane as an internal standard.

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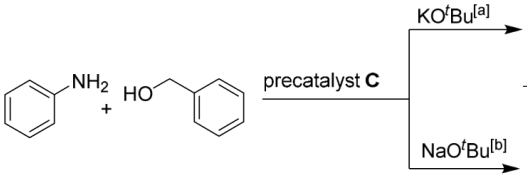
Additional screening reactions

For imine synthesis, the release of one equivalent hydrogen was proofed by analysing the gas mixture with methane as an internal standard in the Schlenk tube after reaction. The gas mixture was analyzed using an Agilent Technologies 6890N equipped with a TCD and an Agilent special plot and molsieve capillary column (30 m, 320 µm, 0.25 µm). Reaction conditions: 0.2 mmol aniline, 0.32 mmol benzyl alcohol, 1 mol% precatalyst **C**, 0.3 mmol NaO^{t}Bu and 800 µL 2-MeTHF were added to a closed Schlenk tube (150 mL) and heated at 110 °C (oil bath) for 13 h.

In the absence of aniline, the formation of benzaldehyde from benzyl alcohol was observed using precatalyst **C** and NaO^{t}Bu. Reaction conditions: 1 mmol benzyl alcohol, 1.5 mmol NaO^{t}Bu, 1 mol% precatalyst **C** and 3 mL 2-MeTHF were added to a Schlenk tube and heated at 110 °C (oil bath) in an open system (bubble counter) for 13 h. The reaction mixture was analyzed with GC giving benzaldehyde in yield of 78 %.

Control experiments using aniline and benzaldehyde instead of benzyl alcohol in the presence of precatalyst **C** and KO^{t}Bu showed a formation of the imine **1a**. To obtain the amine **2a** a source to generate the hydrogen for the reduction step is needed.

Table S18: Comparison of imine and amine synthesis using closed and opened systems.



Entry	System	Imine **1a** [%][c]	Amine **2a** [%][c]
1	closed	0 %	99 %
2	open	3 %	2 %
3	closed	41 %	5 %
4	open	99 %	1 %

[a] Reaction conditions: 1 mmol aniline, 1.4 mmol benzyl alcohol, 3 mol% precatalyst **C**, 1 mmol KO^{t}Bu, 2 mL thf, 80 °C (oil bath), 18 h. [b] Reaction conditions: 1 mmol aniline, 1.6 mmol benzyl alcohol, 1 mol% precatalyst **C**, 1.5 mmol

NaO^{t}Bu, 3 mL 2-MeTHF, 110 °C (oil bath),18 h. [c] Yield determined via GC with decane as an internal standard.

Scale up experiments

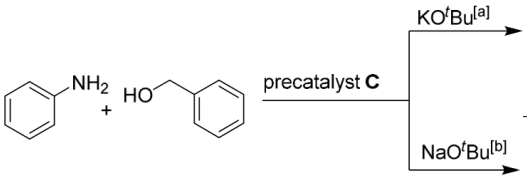
Reaction conditions for upscaling the amine synthesis:

Aniline (50 mmol, 4.57 mL), benzyl alcohol (70 mmol, 7.3 mL), KO^{t}Bu (50 mmol, 5.6 g) and precatalyst C (2 mol%, 600 mg) were added in THF (120 mL) and heated at 80 °C for 18 h. The reaction was stopped by adding 30 mL H_2O, extracted with Et_2O and analysed via GC with decane as internal standard, obtaining the amine **2a** in 96 % GC-yield.

Reaction conditions for upscaling the imine synthesis:

Aniline (50 mmol, 4.57 mL), benzyl alcohol (80 mmol, 8.3 mL), NaO^{t}Bu (75 mmol, 7.2 g) and precatalyst **C** (1 mol%, 300 mg) were added in 2-MeTHF (180 mL) and heated at 110 °C in an open system (bubble counter). After 18 h the reaction was stopped by adding 30 mL H_2O, extracted with Et_2O and analysed via GC with decane as internal standard, obtaining the imine **1a** in 85 % GC-yield.

Table S19: Effects on the reaction in the presence of 18-crown-6



Entry	18-crown-6	Imine **1a** [%][c]	Amine **2a** [%][c]
1	-	0 %	70 %
2	+	4 %	27 %
3	-	92 %	0 %
4	+	84 %	12 %

[a] Reaction conditions: 1 mmol aniline, 1.4 mmol benzyl alcohol, 3 mol% precatalyst **C**, 1 mmol KO^{t}Bu, 1.1 mmol 18-crown-6, 2 mL thf, 80 °C (oil bath), 4 h, pressure tube. [b] Reaction conditions: 1 mmol aniline, 1.6 mmol benzyl alcohol, 1 mol% precatalyst **C**, 1.5 mmol NaO^{t}Bu, 1.7 mmol 18-crown-6, 3 mL 2-MeTHF, 110 °C (oil bath), 4 h, open

system. [c] Yield determined via GC with decane as an internal standard.

Time-conversion plots for imine and amine synthesis

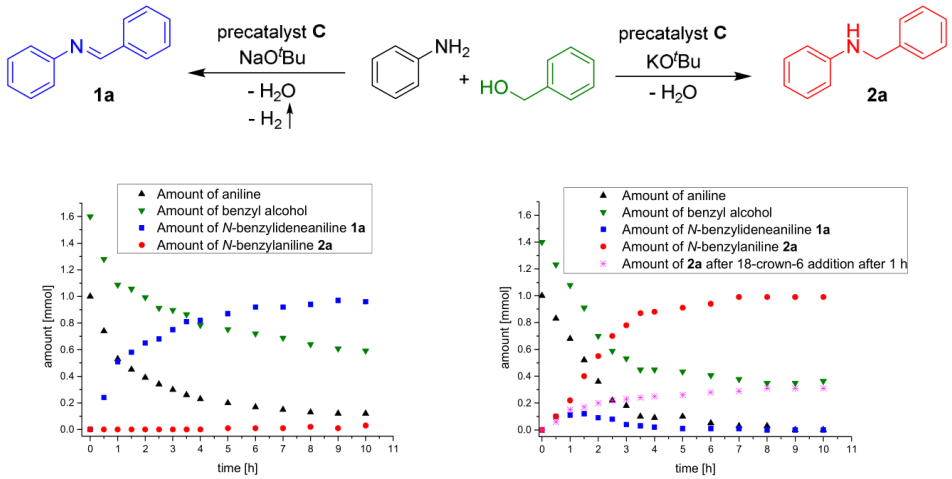
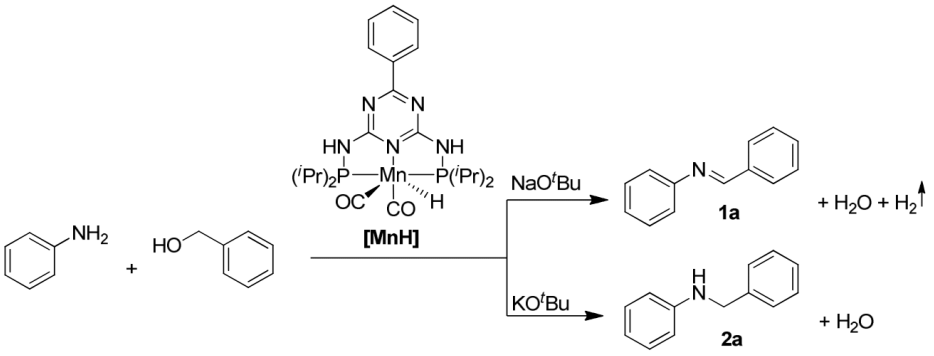


Figure S3: Time-conversion plots for imine (left) and amine (right) synthesis. Reaction conditions for imine **1a** synthesis (left): 1 mmol aniline (black), 1.6 mmol benzyl alcohol (green), 1.5 mmol NaO^{t}Bu, 1 mol% precatalyst **C**, 3 mL 2-MeTHF, 110 °C (oil bath), open system. Reaction conditions for amine **2a** synthesis (right): 1 mmol aniline (black), 1.4 mmol benzyl alcohol (green), 1 mmol KO^{t}Bu, 3 mol% precatalyst **C**, 2 mL thf, 80 °C (oil bath). Amount determined via GC with decane as an internal standard.

Table S20: **Amino alkylation with the hydride complex of precatalyst C in dependence of the base**



Entry	Base	Amount of base [mmol]	Imine **1a** [%][c]	Amine **2a** [%][c]
1[a]	KO^{t}Bu	0	0	0
2[a]	KO^{t}Bu	0.05	0	0
3[a]	KO^{t}Bu	0.25	0	18
4[a]	KO^{t}Bu	1	0	41
5[b]	NaO^{t}Bu	0	0	0
6[b]	NaO^{t}Bu	0.05	0	0
7[b]	NaO^{t}Bu	0.25	0	0
8[b]	NaO^{t}Bu	1.5	71	0

[a] Reaction conditions: 1 mmol aniline, 1.4 mmol benzyl alcohol, KO^{t}Bu, 3 mol% **[MnH]**, 2 mL thf, 80 °C (oil bath), 3.5 h. [b] Reaction conditions: 1 mmol aniline, 1.6 mmol benzyl alcohol, NaO^{t}Bu, 1 mol% **[MnH]**, 3 mL 2-MeTHF, 110 °C (oil bath), 3.5 h. [c] Determined via GC with decane as an internal standard.

Activation of the manganese hydride [MnH] with KO^{t}Bu

To a solution of manganese hydride [**MnH**] (1 eq., 60 µmol, 31.88 mg) in thf$_{d8}$, a solution of KO^{t}Bu (2 eq., 120 µmol, 13.44 mg) in thf$_{d8}$ was added. The resulting solution was stirred for 10 minutes and analyzed via ^{1}H and ^{31}P NMR spectroscopy. The ^{1}H NMR-spectra of [**MnH**] showed the characteristic signal of both NH-protons at 8.16 ppm (Figure S4) while in ^{31}P NMR-spectra one signal at 160.25 ppm (Figure S5) was observed. After addition of KO^{t}Bu the NH-

signal disappeared in ^{1}H NMR-spectra (Figure S6) and the ^{31}P signal shifted to 157.25 ppm (Figure S7).

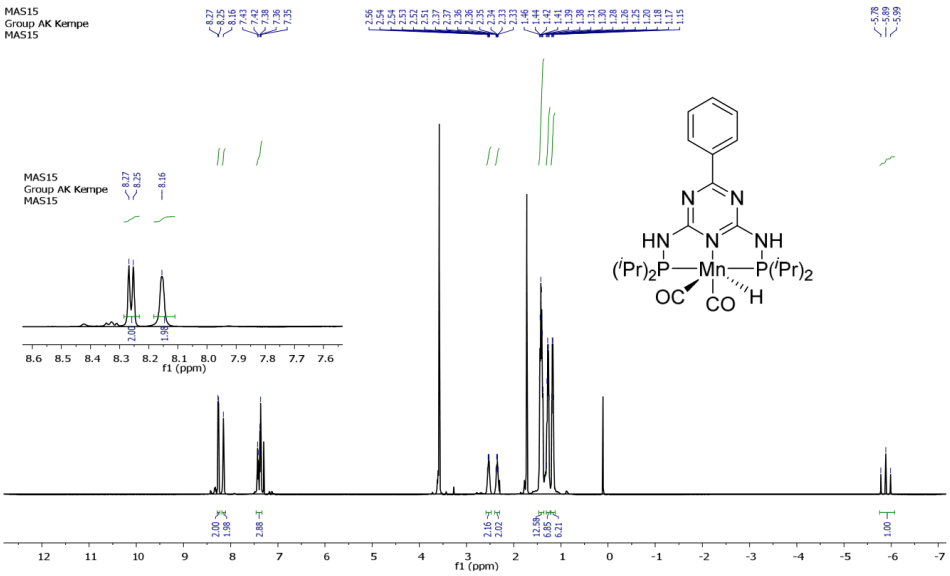


Figure S4: ^{1}H NMR of the manganese hydride [**MnH**]. ^{1}H NMR (500 MHz, 296.15 K, thf_{d8}): 8.27-8.25 (d, J = 7.5 Hz, 2 H, $CH_{arom.}$), 8.16 (s, 2 H, NH), 7.43-7.35 (m, 3 H, $CH_{arom.}$), 2.56-2.51 (m, 2 H, CH), 2.37-2.33 (m, 2 H, CH), 1.45-1.38 (m, 12 H, CH_3), 1.31-1.25 (m, 6 H, CH_3), 1.20-1.15 (m, 6 H, CH_3), -5.78 - -5.99 (t, J = 50.9 Hz, 1 H, $H_{hydride}$) ppm.

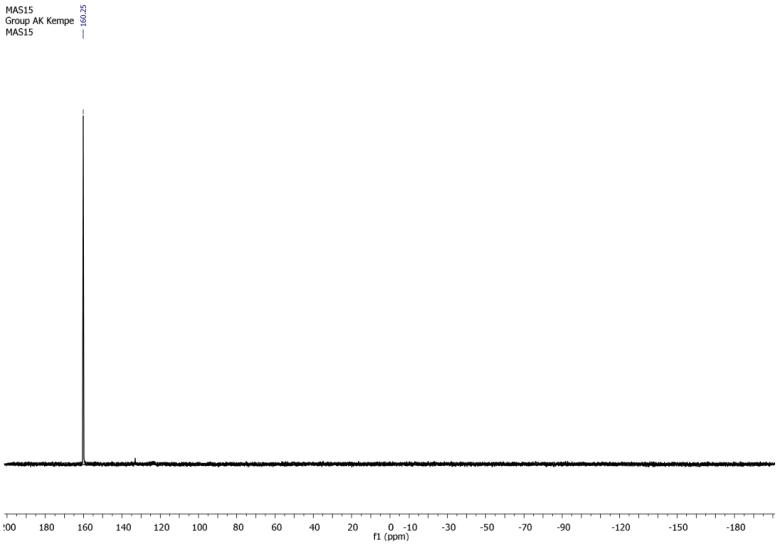


Figure S5: ^{31}P NMR of the manganese hydride [**MnH**]. ^{31}P NMR (202 MHz, 296.15 K, thf_{d8}): 160.25 ppm.

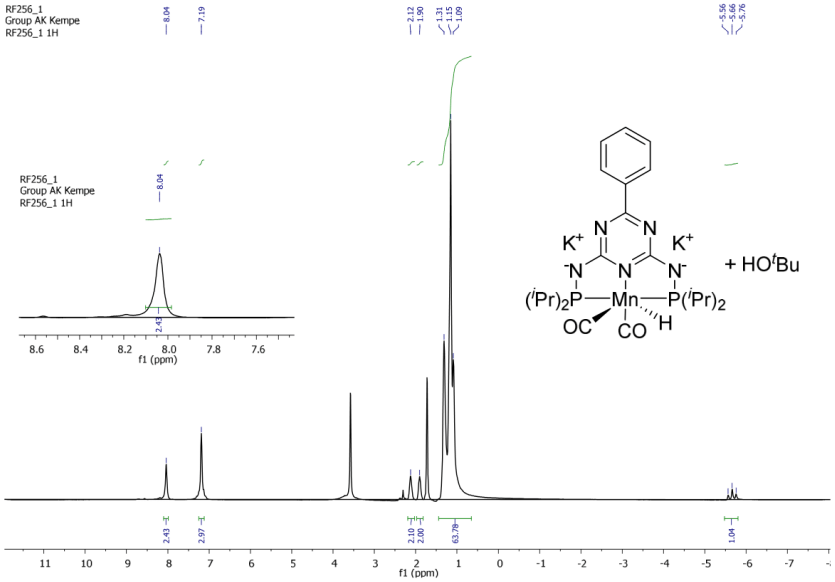


Figure S6: ^{1}H NMR of [**MnH**] activated with KO^{t}Bu. ^{1}H NMR (500 MHz, 296.15 K, thf_{d8}): 8.04 (s, 2 H, $CH_{arom.}$), 7.19 (s, 3 H, $CH_{arom.}$), 2.12 (s, 2 H, CH), 1.90 (s, 2 H, CH), 1.31-1.09 (m, 63 H, CH_3), -5.56 - -5.76 (t, J = 48.0 Hz, 1 H, $H_{hydride}$) ppm.

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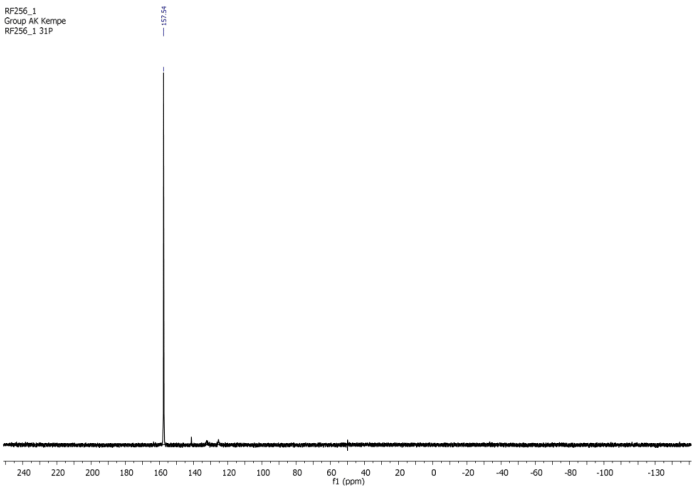

Figure S7: ^{31}P NMR of the manganese hydride [**MnH**] activated with KO^{t}Bu. ^{31}P NMR (202 MHz, 296.15 K, thf_{d8}): 157.54 ppm.

Activation of the manganese hydride [MnH] with NaO^{t}Bu

To a solution of manganese hydride [**MnH**] (1 eq., 60 µmol, 31.88 mg) in thf_{d8}, a solution of NaO^{t}Bu (2 eq., 120 µmol, 11.5 mg) in thf_{d8} was added. The resulting solution was stirred for 10 minutes and analyzed via ^{1}H and ^{31}P NMR spectroscopy. Analog to the activation with KO^{t}Bu the NH-signals disappeared in ^{1}H NMR-spectra (Figure S8), when the [**MnH**] was activated with NaO^{t}Bu and the ^{31}P NMR-signal shifted from 160.25 ppm to 157.46 ppm (Figure S9).

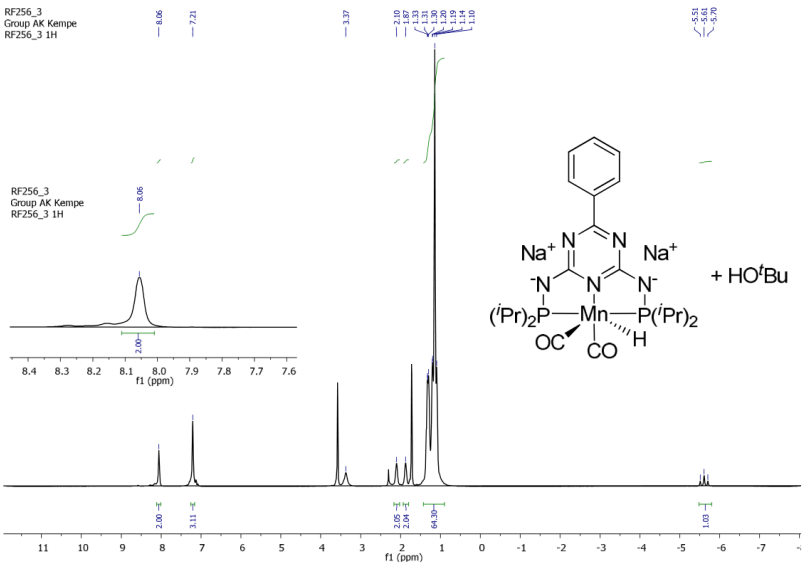

Figure S8: ^{1}H NMR of [**MnH**] activated with NaO^{t}Bu. ^{1}H NMR (500 MHz, 296.15 K, thf$_{d8}$): 8.06 (s, 2 H, CH$_{arom.}$), 7.21 (s, 3 H, CH$_{arom.}$), 3.37 (s, 2 H, OH), 2.10 (s, 2 H, CH), 1.87 (s, 2 H, CH), 1.33-1.10 (m, 64 H, CH$_3$), -5.51 - -5.70 (t, J = 48.4 Hz, 1 H, H$_{hydride}$) ppm.

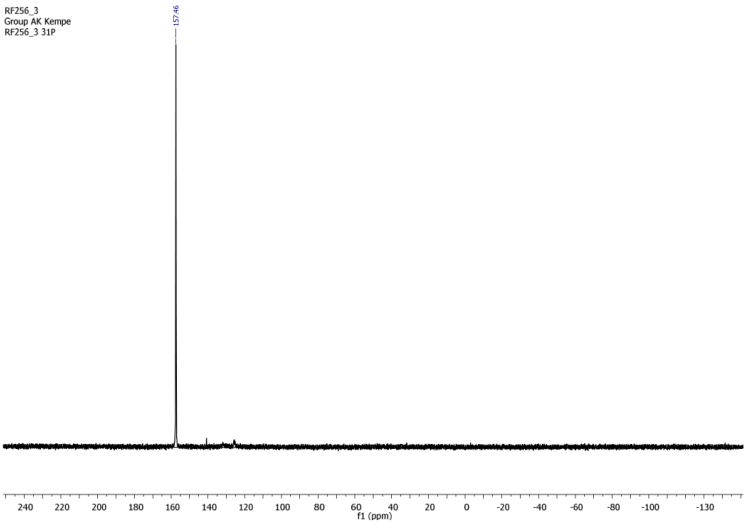

Figure S9: ^{31}P NMR of the manganese hydride [**MnH**] activated with NaO^{t}Bu. ^{31}P NMR (202 MHz, 296.15 K, thf$_{d8}$): 157.46 ppm.

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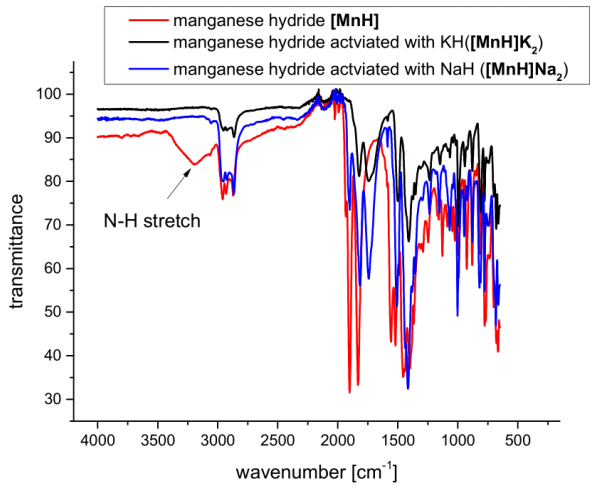


Figure S10: IR-spectra of the manganese hydride **[MnH]** (red) and of the manganese hydride **[MnH]** activated with KH (black) and NaH (blue), respectively.

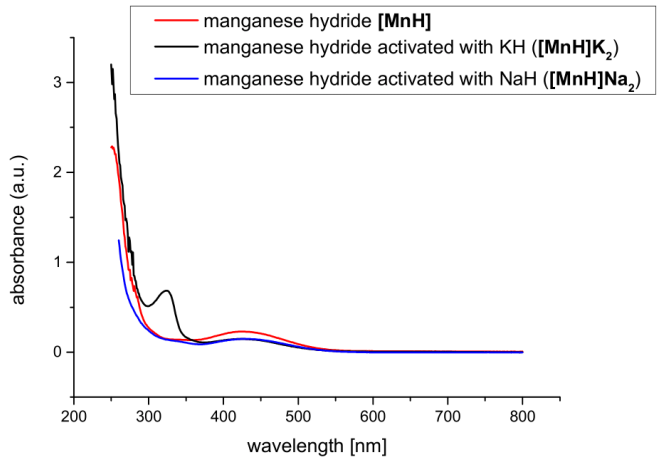


Figure S11: UV-VIS-spectra of the manganese hydride **[MnH]** (red) and of the manganese hydride **[MnH]** activated with KH (black) and NaH (blue), respectively.

Base-dependant hydrogenation of the imine 1a using the manganese hydride [MnH] analyzed via NMR-studies

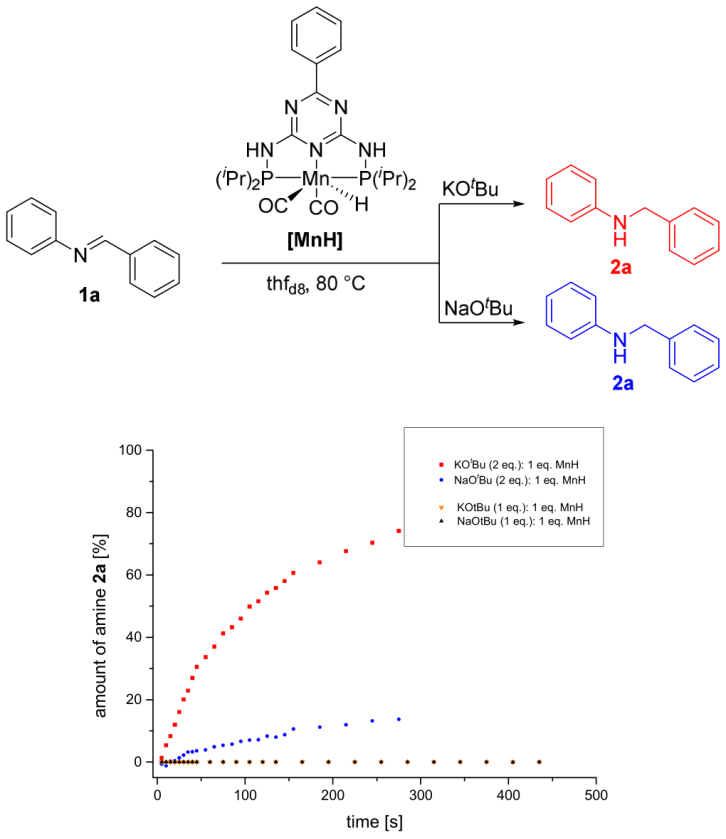


Figure S12: Reaction conditions: 60 µmol imine **1a**, 60 µmol [**MnH**], 120 µmol/60 µmol base, 800 µL thf$_{d8}$, 80 °C. NMR-studies were carried out on a Varian INOVA 300 MHz spectrometer. The reaction is cooled first in liquid nitrogen to prevent an immediate start of the reaction, before the base is added. Regions chosen for the integration are the CH_2-group of the amine **2a** (4.3 ppm) and the characteristic C-H of the imine **1a** (8.4 ppm). The formation of the amine **2a** is calculated via the change of the relative integrals and referenced on the imine integral.

Base-dependant hydrogenation of the imine 1a in the presence of benzyl alcohol using the manganese hydride [MnH] analyzed via NMR-studies

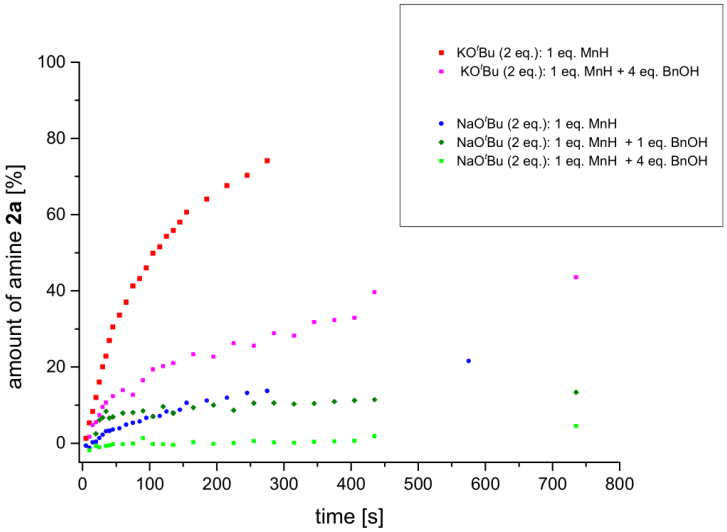


Figure S13: Reaction conditions: 60 µmol imine **1a**, 60 µmol [**MnH**], 120 µmol base, 800 µL thf_{d8}, 80 °C. NMR-studies were carried out on a Varian INOVA 300 MHz spectrometer. The reaction is cooled first in liquid nitrogen to prevent an immediate start of the reaction, before the base is added. Regions chosen for the integration are the CH_2-group of the amine **2a** (4.3 ppm) and the characteristic C-H of the imine **1a** (8.4 ppm). The formation of the amine **2a** is calculated via the change of the relative integrals and referenced on the imine integral.

Initial rates for the base-dependant transfer hydrogenation of the imine 1a to the amine 2a with the manganese hydride [MnH]

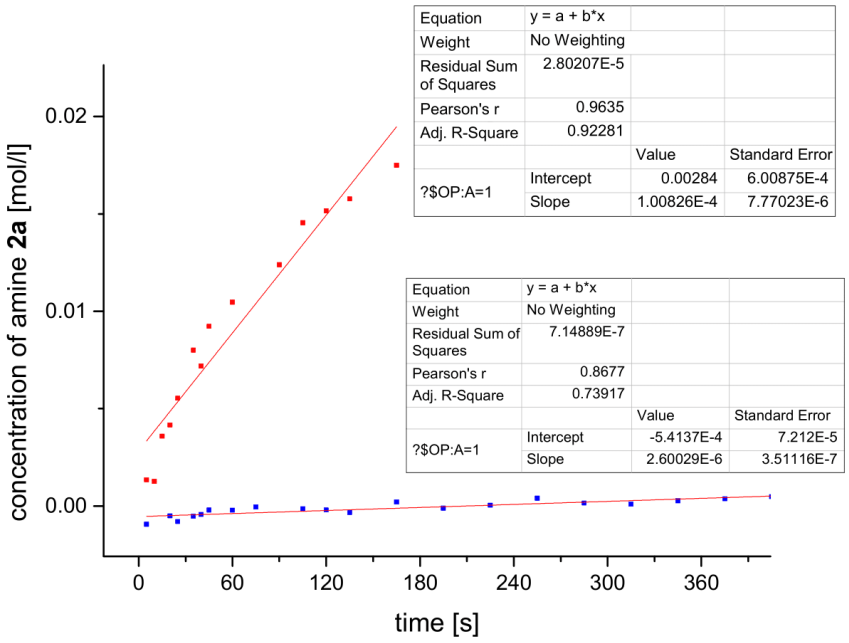
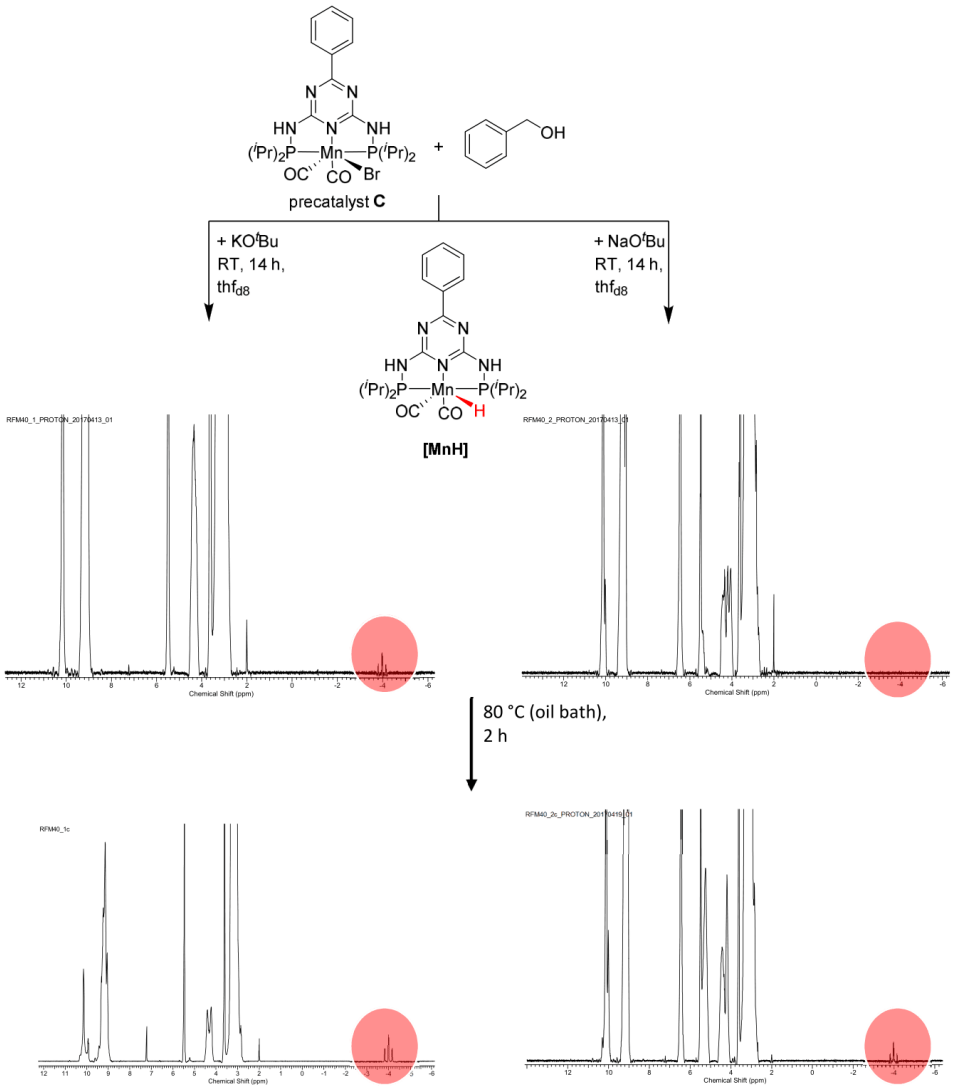


Figure S14: Reaction conditions: 60 µmol imine **1a**, 60 µmol [**MnH**], 120 µmol base, 240 µmol benzyl alcohol, 800 µL thf_{d8}, 80 °C. NMR-studies were carried out on a Varian INOVA 300 MHz spectrometer. The reaction is cooled first in liquid nitrogen to prevent an immediate start of the reaction, before the base is added. Regions chosen for the integration are the CH_2-group of the amine **2a** (4.3 ppm) and the characteristic C-H of the imine **1a** (8.4 ppm). The formation of the amine **2a** is calculated via the change of the relative integrals and referenced on the imine integral.

Base-dependant formation of the manganese hydride [MnH] using precatalyst C and benzyl alcohol



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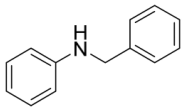
Synthesis of ligands and complexes

The ligands and precatalysts **A**-**E**[1,2], **F**,**G**[3,4], **H**[5,6], **I**[7], and **J**[8] were synthesized according to published procedures.

The synthesis of **[MnH]** follows published procedures.[2] To prevent base contamination of the precatalyst, the hydride complex was made once with KO^{t}Bu (Table S20, entries 1-4) and once with NaO^{t}Bu (Table S20, entries 5-8).

Synthesis of amines

Synthesis of *N*-benzylaniline (2a)



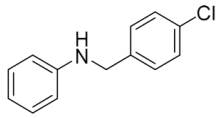
Chemical Formula: $C_{13}H_{13}N$
Molecular Weight: 183.25

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and benzyl alcohol (1.4 mmol, 146 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as a white solid (167 mg, 0.913 mmol, 91 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.42-7.32 (m, 5 H, $CH_{arom.}$), 7.25-7.20 (t, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 6.80-6.75 (t, *J* = 7.03 Hz, 1 H, $CH_{arom.}$), 6.70-6.67 (d, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 4.37 (s, 2 H, CH_2), 4.08 (s, 1 H, NH) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 148.17, 139.46, 129.31, 128.67, 127.56, 127.27, 117.61, 112.88, 48.35 ppm.

Synthesis of *N*-(4-chlorobenzyl) aniline (2b)



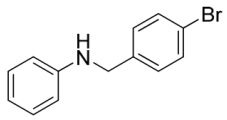
Chemical Formula: $C_{13}H_{12}ClN$
Molecular Weight: 217.70

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and 4-chlorobenzyl alcohol (1.4 mmol, 200 mg) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as a light yellow oil (208 mg, 0.958 mmol, 96 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.35 (s, 3 H, $CH_{arom.}$), 7.26-7.21 (t, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 6.82-6.77 (t, *J* = 7.61 Hz, 1 H, $CH_{arom.}$), 6.67-6.65 (d, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 4.35 (s, 2 H, CH_2), 4.09 (s, 1 H, NH) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 147.88, 138.07, 132.88, 129.37, 128.79, 128.75, 117.84, 112.94, 47.62 ppm.

Synthesis of *N*-(4-bromobenzyl) aniline (2c)



Chemical Formula: $C_{13}H_{12}BrN$
Molecular Weight: 262.15

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and 4-bromobenzyl alcohol (1.4 mmol, 262 mg) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.5) as a yellow oil (201 mg, 0.767 mmol, 77 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.52-7.49 (m, 2 H, $CH_{arom.}$), 7.30-7.20 (m, 4 H, $CH_{arom.}$), 6.81-6.76 (t, *J* = 7.61 Hz, 1 H, $CH_{arom.}$), 6.67-6.65 (d, *J* = 7.03 Hz, 2 H, $CH_{arom.}$), 4.34 (s, 2 H, CH_2), 3.97 (s, 1 H, NH) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 147.84, 138.60, 131.74, 129.34, 129.08, 120.97, 117.87, 112.94, 47.68 ppm.

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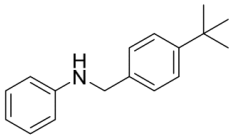
Synthesis of *N*-(4-*tert*-butylbenzyl) aniline (2d)



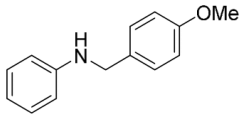
Chemical Formula: $C_{17}H_{21}N$
Molecular Weight: 239.36

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and 4-*tert*-butylbenzyl alcohol (1.4 mmol, 248 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.4) as a white solid (193 mg, 0.807 mmol, 81 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.41-7.32 (m, 4 H, $CH_{arom.}$), 7.20-7.18 (m, 2 H, $CH_{arom.}$), 6.76-6.65 (m, 3 H, $CH_{arom.}$), 4.31 (s, 2 H, CH_2), 4.01 (s, 1 H, NH), 1.35 (s, 9 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 129.27, 127.39, 125.56, 117.49, 112.80, 48.02, 31.39 ppm.

Synthesis of *N*-(4-methoxybenzyl) aniline (2e)



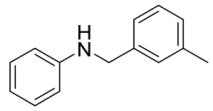
Chemical Formula: $C_{14}H_{15}NO$
Molecular Weight: 213.28

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and 4-methoxybenzyl alcohol (1.4 mmol, 174 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as a white solid (200 mg, 0.94 mmol, 94 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.33-7.31 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.23-7.18 (t, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 6.92-6.89 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 6.77-6.72 (t, *J* = 7.61 Hz, 1 H, $CH_{arom.}$), 6.68-6.65 (d, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 4.28 (s, 2 H, CH_2), 3.97 (s, 1 H, NH), 3.83 (s, 3 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 158.87, 148.22, 131.42, 129.27, 128.84, 117.50, 114.02, 112.83, 110.00, 55.33, 47.80 ppm.

Synthesis of *N*-(3-methylbenzyl) aniline (2f)



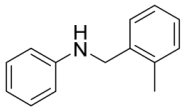
Chemical Formula: $C_{14}H_{15}N$
Molecular Weight: 197.28

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and 3-ethylbenzyl alcohol (1.4 mmol, 165 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.5) as a yellow oil (174 mg, 0.881 mmol, 88 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.39-7.31 (m, 5 H, $CH_{arom.}$), 7.26-7.24 (d, *J* = 7.03 Hz, 1 H, $CH_{arom.}$), 6.91-6.86 (t, *J* = 7.03 Hz, 1 H, $CH_{arom.}$), 6.79-6.76 (d, *J* = 7.61 Hz 2 H, $CH_{arom.}$), 4.41 (s, 2 H, CH_2), 4.09 (s, 1 H, NH), 2.51 (s, 3 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 148.38, 139.53, 138.41, 129.40, 128.43, 128.14, 124.73, 117.62, 112.97, 48.44, 21.59 ppm.

Synthesis of *N*-(2-methylbenzyl) aniline (2g)



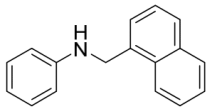
Chemical Formula: $C_{14}H_{15}N$
Molecular Weight: 197.28

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and 2-methylbenzyl alcohol (1.4 mmol, 171 mg) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 12/1) as a colorless oil (159 mg, 0.807 mmol, 81 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.44-7.42 (d, *J* = 6.44 Hz, 1 H, $CH_{arom.}$), 7.30-7.26 (m, 5 H, $CH_{arom.}$), 6.85-6.80 (t, *J* = 6.44 Hz, 1 H, $CH_{arom.}$), 6.74-6.71 (d, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 4.35 (s, 2 H, CH_2), 3.99 (s, 1 H, NH), 2.47 (s, 3 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 148.37, 137.09, 136.42, 130.50, 129.37, 128.34, 127.51, 126.26, 117.53, 112.77, 46.45, 19.04 ppm.

Synthesis of *N*-phenyl-1-naphtalenemethanamine (2h)



Chemical Formula: $C_{17}H_{15}N$
Molecular Weight: 233.31

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and 1-naphthalenemethanol (1.4 mmol, 221 mg) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 10/0.5) as a colorless solid (217 mg, 0.930 mmol, 93 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.23-8.09 (m, 1 H, $CH_{arom.}$), 8.08-8.07 (m, 1 H, $CH_{arom.}$), 8.01-7.99 (d, *J* = 8.2 Hz, 1 H, $CH_{arom.}$), 7.72-7.67 (m, 3 H, $CH_{arom.}$), 7.63-7.58 (t, *J* = 7.61 Hz, 1 H, $CH_{arom.}$), 7.44-7.39 (m, 2 H, $CH_{arom.}$), 7.00-6.95 (m, 1 H, $CH_{arom.}$), 6.84-6.82 (d, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 4.85 (s, 2 H, CH_2), 4.08 (s, 1 H, NH) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 148.29, 134.39, 133.94, 131.60, 129.39, 128.84, 128.24, 126.40, 126.11, 125.91, 125.62, 123.65, 117.64, 112.79, 46.49 ppm.

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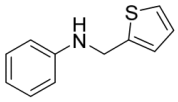
Synthesis of *N*-phenyl-2-thiophenemethanamine (2i)



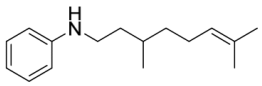
Chemical Formula: $C_{11}H_{11}NS$
Molecular Weight: 189.28

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and 2-thiophenemethanol (1.4 mmol, 133 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 10/0.5) as a yellow oil (137 mg, 0.724 mmol, 72 %).

^{1}H NMR (CD_2Cl_2, 299.86 MHz, 296.15 K): δ = 7.32-7.22 (m, 3 H, $CH_{arom.}$), 7.10-7.04 (m, 2 H, $CH_{arom.}$), 6.83-6.72 (m, 3 H, $CH_{arom.}$), 7.72-7.67 (m, 3 H, $CH_{arom.}$), 4.58 (s, 2 H, CH_2), 4.23 (s, 1 H, NH) ppm.

^{13}C NMR (CD_2Cl_2, 75.41 MHz, 296.15 K): δ = 147.79, 143-46, 129.21, 126.86, 124.98, 124.48, 117.88, 113.09, 43.33 ppm.

Synthesis of *N*-(3,7-dimethyl-6-octen-1yl)-benzenamine (2j)



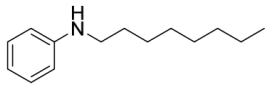
Chemical Formula: $C_{16}H_{25}N$
Molecular Weight: 231,38

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and citronellol (1.4 mmol, 254 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.8) as a light orange oil (218 mg, 0.944 mmol, 94 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.28-7.23 (t, *J* = 7.23 Hz, 2 H, $CH_{arom.}$), 6.80-6.78 (t, *J* = 7.23 Hz, 1 H, $CH_{arom.}$), 6.70-6.67 (d, *J* = 8.25 Hz, 2 H, $CH_{arom.}$), 5.22-5.17 (t, *J* = 7.23 Hz, 1 H, $CH_{vinyl.}$), 3.61 (s, 1 H, NH), 3.24-3.17 (m, 2 H, CH_2), 2.12-2.07 (m, 2 H, CH_2), 1,79 (s, 1 H, CH_3), 1.75-1.63 (m, 5 H, $CH_{aliph.}$), 1.58-1.43 (m, 2 H, $CH_{aliph.}$), 1.36-1.29 (m, 1 H, $CH_{aliph.}$), 1.05-1.03 (d, *J* = 7.23 Hz, 3 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 149.07, 131.84, 129.74, 125.20, 117.61, 113.21, 42.46, 37.64, 37.24, 30.96, 26.29, 26.02, 20.15, 18.23 ppm.

Synthesis of *N*-octylaniline (2k)



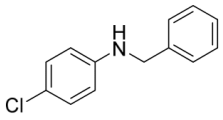
Chemical Formula: $C_{14}H_{23}N$
Molecular Weight: 205,35

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, aniline (1 mmol, 91.3 µL) and 1-octanol (1.4 mmol, 223 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as a light orange oil (197 mg, 0.961 mmol, 96 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.31-7.23 (m, 2 H, $CH_{arom.}$), 6.83-6.64 (m, 3 H, $CH_{arom.}$), 3.58 (s, 1 H, NH), 3.25-3.13 (m, 2 H, CH_2), 1.75-1.67 (m, 2 H, CH_2), 1.44-1.39 (m, 10 H, CH_2), 1.04-0.97 (m, 3 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 148.19, 128.85, 116.68, 112.19, 43.65, 31.53, 29.25, 29.12, 28.97, 25.83, 22.36, 13.80 ppm.

Synthesis of *N*-benzyl-4-chloroaniline (4a)



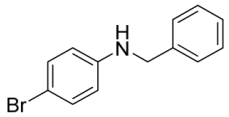
Chemical Formula: $C_{13}H_{12}ClN$
Molecular Weight: 217.70

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 4-chloroaniline (1 mmol, 128 mg) and benzyl alcohol (1.4 mmol, 146 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as a light yellow oil (210 mg, 0.968 mmol, 97 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.43-7.36 (m, 5 H, $CH_{arom.}$), 7.20-7.16 (m, 2 H, $CH_{arom.}$), 6.61-6.57 (m, 2 H, $CH_{arom.}$), 4.35 (s, 2 H, CH_2), 4.11 (s, 1 H, NH) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 146.74, 139.03, 129.14, 128.79, 127.50, 122.11, 114.01, 48.37 ppm.

Synthesis of *N*-benzyl-4-bromoaniline (4b)



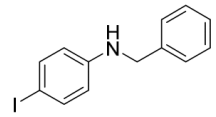
Chemical Formula: $C_{13}H_{12}BrN$
Molecular Weight: 262.15

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 4-bromoaniline (1 mmol, 172 mg) and benzyl alcohol (1.4 mmol, 146 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as a yellow oil (225 mg, 0.862 mmol, 86 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.39-7.27 (m, 7 H, $CH_{arom.}$), 6.55-6.52 (d, *J* = 8.97 Hz, 2 H, $CH_{arom.}$), 4.33 (s, 2 H, CH_2), 4.11 (s, 1 H, NH) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 147.10, 138.92, 131.98, 128.76, 127.45, 114.48, 109.14, 48.25 ppm.

Synthesis of *N*-benzyl-4-iodoaniline (4c)



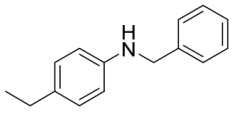
Chemical Formula: $C_{13}H_{12}IN$
Molecular Weight: 309.15

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 4-iodoaniline (1 mmol, 219 mg) and benzyl alcohol (1.4 mmol, 146 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.8) as a yellow solid (209 mg, 0.676 mmol, 68 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.47-7.43 (d, *J* = 7.03 Hz, 2 H, $CH_{arom.}$), 7.40-7.33 (m, 5 H, $CH_{arom.}$), 6.46-6.43(d, *J* = 7.03 Hz, 2 H, $CH_{arom.}$), 4.34-4.32 (d, *J* = 4.34 Hz, 2 H, CH_2), 4.13 (s, 1 H, NH) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 147.68, 138.88, 137.84, 128.78, 127.44, 115.14, 48.08 ppm.

Synthesis of *N*-benzyl-4-ethylaniline (4d)



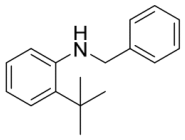
Chemical Formula: $C_{15}H_{17}N$
Molecular Weight: 211.31

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 4-ethylaniline (1 mmol, 125 µL) and benzyl alcohol (1.4 mmol, 146 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.4) as a yellow oil (179 mg, 0.849 mmol, 85 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.43-7.34 (m, 5 H, $CH_{arom.}$), 7.10-7.08 (d, 2 H, $CH_{arom.}$), 6.67-6.64 (d, 2 H, $CH_{arom.}$), 4.37 (s, 2 H, CH_2), 3.97 (s, 1 H, NH), 2.65-2.58 (q, *J* = 7.61 Hz, 2 H, CH_2), 1.29-1.23 (t, *J* = 7.61 Hz, 3 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 146.19, 139.72, 133.46, 128.66, 127.59, 127.22, 113.03, 48.70, 28.01, 16.07 ppm.

Synthesis of *N*-benzyl-2-*tert*-butylaniline (4e)



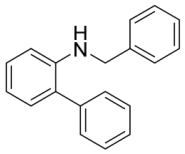
Chemical Formula: $C_{17}H_{21}N$
Molecular Weight: 239.36

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 2-*tert*-butylaniline (1 mmol, 156 µL) and benzyl alcohol (1.4 mmol, 146 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.1) as a yellow oil (179 mg, 0.749 mmol, 75 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.59-7.42 (m, 6 H, $CH_{arom.}$), 7.29-7.26 (m, 1 H, $CH_{arom.}$), 6.90-6.84 (m, 2 H, $CH_{arom.}$), 4.58-5.56 (d, *J* = 6.44 Hz, 2 H, CH_2), 4.45 (s, 1 H, NH), 1.62 (s, 9 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 146.16, 139.66, 133.25, 128.75, 127.53, 127.24, 126.24, 117.26, 111.95, 48.87, 34.24, 29.98 ppm.

Synthesis of *N*-benzyl-2-phenylaniline (4f)



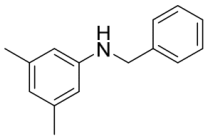
Chemical Formula: $C_{19}H_{17}N$
Molecular Weight: 259.35

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 2-phenylaniline (1 mmol, 169 µL) and benzyl alcohol (1.4 mmol, 146 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 10/0.08) as a white solid (211 mg, 0.815 mmol, 82 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.78-7.76 (d, *J* = 7.03 Hz, 2 H, $CH_{arom.}$), 7.72-7.67 (t, *J* = 7.03 Hz, 2 H, $CH_{arom.}$), 7.61-7.40 (m, 7 H, $CH_{arom.}$), 7.09-7.04 (t, *J* = 7.03 Hz, 1 H, $CH_{arom.}$), 6.95-6.93 (d, *J* = 8.20 Hz, 1 H, $CH_{arom.}$), 4.69 (s, 1 H, NH), 4.55 (s, 2 H, CH_2) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 145.18, 139.79, 130.55, 129.69, 129.27, 129.05, 128.88, 127.94, 127.57, 127.31, 117.52, 111.09, 48.35 ppm.

Synthesis of *N*-benzyl-3,5-dimethylaniline (4g)



Chemical Formula: $C_{15}H_{17}N$
Molecular Weight: 211.31

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 3,5-dimethylaniline (1 mmol, 125 µL) and benzyl alcohol (1.4 mmol, 146 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 10/0.4) as a yellow oil (199 mg, 0.943 mmol, 94 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.63-7.54 (m, 5 H, $CH_{arom.}$), 6.67-6.66 (d, *J* = 3.50 Hz, 1 H, $CH_{arom.}$), 6.55-6.53 (d, *J* = 4.10 Hz, 2 H, $CH_{arom.}$), 4.55-4.54 (d, *J* = 4.10 Hz, 2 H, CH_2), 4.12 (s, 1 H, NH), 2.51-2.49 (d, *J* = 4.10 Hz, 6 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 148.45, 139.81, 139.02, 128.72, 127.66, 127.27, 119.71, 110.90, 48.47, 21.65 ppm.

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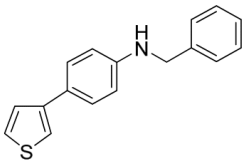
Synthesis of *N*-benzyl-4-(thiophen-3-yl) aniline (4h)



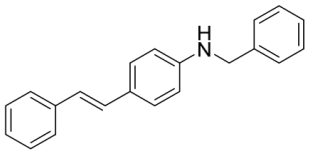
Chemical Formula: $C_{17}H_{15}NS$
Molecular Weight: 265.37

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 4-(thiophen-3-yl) aniline (1 mmol, 175 mg) and benzyl alcohol (1.4 mmol, 146 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as a white solid (252 mg, 0.951 mmol, 94 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.46-7.28 (m, 11 H, $CH_{arom.}$), 6.70-6.68 (d, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 4.39 (s, 2 H, CH_2), 4.21 (s, 1 H, NH) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 147.35, 142.54, 139.31, 128.70, 127.51, 127.45, 127.33, 126.14, 125.80, 125.67, 117.75, 113.08, 48.32 ppm.

Synthesis of *N*-benzyl-4-aminostilbene (4i)



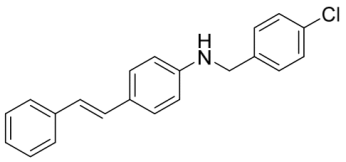
Chemical Formula: $C_{21}H_{19}N$
Molecular Weight: 285.39

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 4-aminostilbene (1 mmol, 195 mg) and benzyl alcohol (1.4 mmol, 146 µL) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/3) as a light yellow solid (277 mg, 0.971 mmol, 96 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.52-7.49 (d, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 7.41-7.34 (m, 9 H, $CH_{arom.}$), 7.27-7.21 (m, 1 H, $CH_{arom.}$), 7.09-7.04 (d, *J* = 15.82 Hz, 1 H, CH_1), 6.96-6.91 (d, *J* = 15.82 Hz, 1 H, CH_1), 6.67-6.65 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 4.39 (s, 2 H, CH_2), 4.24 (s, 1 H, NH) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 147.77, 139.15, 138.10, 128.81, 128.72, 128.61, 127.80, 127.50, 127.34, 127.07, 126.08, 124.63, 112.99, 48.23 ppm.

Synthesis of 4-chloro-N-[4-[2-phenylethenyl]phenyl] benzenemethanamine (4l)



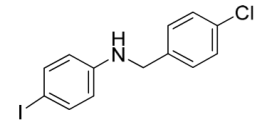
Chemical Formula: $C_{21}H_{18}ClN$
Molecular Weight: 319.83

Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 4-aminostilbene (1 mmol, 195 mg) and 4-chlorobenzyl alcohol (1.4 mmol, 200 mg) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 9/1) as a light yellow solid (245 mg, 0.773 mmol, 77 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 7.44-7.41 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.32-7.27 (m, 8 H, $CH_{arom.}$), 7.22-7.16 (m, 1 H, $CH_{arom.}$), 7.01-6.96 (d, *J* = 16.4 Hz, 1 H, CH_1), 6.89-6.83 (d, *J* = 16.40 Hz, 1 H, CH_1), 6.57-6.55 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 4.30 (s, 2 H, CH_2), 4.22 (s, 1 H, NH) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 147.42, 137.97, 137.68, 132.92, 128.76, 128.62, 128.56, 127.75, 126.79, 126.03, 124.76, 122.95, 47.44 ppm.

Synthesis of 4-chloro-*N*-(4-iodophenyl) benzenemethanamine (4m)



Chemical Formula: $C_{13}H_{11}ClIN$
Molecular Weight: 343.59

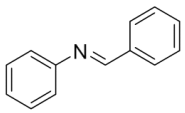
Precatalyst **C** (0.03 mmol, 3 mol%, 18 mg), KO^{t}Bu (1 mmol, 112 mg), 2 mL thf, 4-iodoaniline (1 mmol, 219 mg) and 4-chlorobenzyl alcohol (1.4 mmol, 200 mg) are added consecutively to a pressure tube. After heating at 80 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 10/0.8) as a white solid (227 mg, 0.664 mmol, 66 %).

^{1}H NMR (CD_2Cl_2, 299.86 MHz, 296.15 K): δ = 7.41-7.39 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.34-7.28 (t, *J* = 9.96 Hz, 4 H, $CH_{arom.}$), 6.42-6.39 (d, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 4.29 (s, 2 H, CH_2), 4.29 (s, 1 H, NH) ppm.

^{13}C NMR (CD_2Cl_2, 75.41 MHz, 296.15 K): δ = 148.05, 138.30, 138.24, 133.27, 129.18, 115.63, 78.44, 47.65 ppm.

Synthesis of imines

Synthesis of *N*-benzylideneaniline (1a)



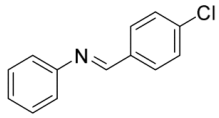
Chemical Formula: $C_{13}H_{11}N$
Molecular Weight: 181.24

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^tBu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, aniline (1 mmol, 91.3 µL) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as a white solid (152 mg, 0.839 mmol, 84 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.48 (s, 1 H, CH_1), 7.95-7.92 (m, 2 H, $CH_{arom.}$), 7.53-7.50 (m, 3 H, $CH_{arom.}$), 7.43-7.41 (m, 2 H, $CH_{arom.}$), 7.26-7.24 (m, 3 H, $CH_{arom.}$) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 160.42, 152.11, 136.24, 131.40, 129.17, 128.84, 128.79, 125.95, 120.89 ppm.

Synthesis of *N*-(4-chlorobenzylidene) aniline (1b)



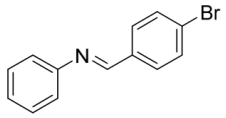
Chemical Formula: $C_{13}H_{10}ClN$
Molecular Weight: 215.68

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^tBu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, aniline (1 mmol, 91.3 µL) and 4-chlorobenzyl alcohol (1.6 mmol, 308 mg) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.8) as a yellow solid (194 mg, 0.903 mmol, 90 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.44 (s, 1 H, CH_1), 7.88-7.85 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.48-7.46 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.42-7.40 (d, *J* = 7.03 Hz, 2 H, $CH_{arom.}$), 7.29-7.22 (m, 3 H, $CH_{arom.}$) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 158.82, 151.66, 137.38, 134.71, 129.97, 129.22, 129.08, 126.21, 129.86 ppm.

Synthesis of *N*-(4-bromobenzylidene) aniline (1c)



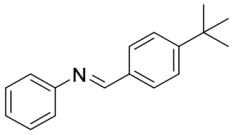
Chemical Formula: $C_{13}H_{10}BrN$
Molecular Weight: 260.13

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^tBu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, aniline (1 mmol, 91.3 µL) and 4-bromobenzyl alcohol (1.6 mmol, 299 mg) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.8) as a light yellow solid (194 mg, 0.746 mmol, 75 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.42 (s, 1 H, CH_1), 7.81-7.78 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.64-7.61 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.45-7.40 (t, *J* = 7.61 Hz, 2 H, $CH_{arom.}$), 7.27-7.22 (t, *J* = 7.61 Hz, 3 H, $CH_{arom.}$) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 158.91, 151.66, 135.13, 132.06, 130.17, 129.24, 126.26, 125.91, 120.87 ppm.

Synthesis of *N*-(4-*tert*-butylbenzylidene) aniline (1d)



Chemical Formula: $C_{17}H_{19}N$
Molecular Weight: 237.35

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^tBu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, aniline (1 mmol, 91.3 µL) and 4-*tert*-butylbenzyl alcohol (1.6 mmol, 283 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.4) as an orange oil (203 mg, 0.857 mmol, 86 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.48 (s, 1 H, CH_1), 7.92-7.89 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.57-7.54 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.44-7.42 (t, *J* = 7.03 Hz, 2 H, $CH_{arom.}$), 7.27-7.25 (t, *J* = 8.20 Hz, 3 H, $CH_{arom.}$), 1.41 (s, 9 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 160.33, 154.99, 152.40, 133.68, 129.17, 128.72, 125.80, 120.94, 35.08, 31.28 ppm.

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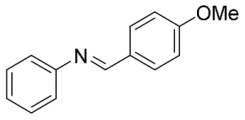
Synthesis of *N*-(4-methoxybenzylidene) aniline (1e)



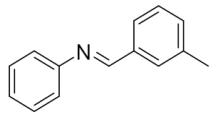
Chemical Formula: $C_{14}H_{13}NO$
Molecular Weight: 211.26

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^tBu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, aniline (1 mmol, 91.3 µL) and 4-methoxybenzyl alcohol (1.6 mmol, 199 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/4) as a yellow solid (168 mg, 0.796 mmol, 80 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.41 (s, 1 H, CH_1), 7.90-7.88 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.45-7.40 (t, *J* = 8.79 Hz, 2 H, $CH_{arom.}$), 7.27-7.23 (t, *J* = 8.20 Hz, 3 H, $CH_{arom.}$), 7.03-7.00 (d, *J* = 8.20 Hz, 2 H, CH_3), 3.88 (s, 3 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 162.27, 159.72, 152.40, 130.56, 129.30, 129.17, 125.62, 120.95, 114.22, 55.45 ppm.

Synthesis of *N*-(3-methylbenzylidene) aniline (1f)



Chemical Formula: $C_{14}H_{13}N$
Molecular Weight: 195.27

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, aniline (1 mmol, 91.3 µL) and 3-methylbenzyl alcohol (1.6 mmol, 189 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as an orange oil (170 mg, 0.872 mmol, 87 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.47 (s, 1 H, CH_1), 7.83 (s, 1 H, $CH_{arom.}$), 7.74-7.71 (d, *J* = 7.61 Hz, 1 H, $CH_{arom.}$), 7.45-7.26 (m, 7 H, $CH_{arom.}$), 2.48 (s, 3 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 160.71, 152.21, 138.59, 136.22, 132.32, 129.20, 129.02, 128.72, 126.50, 125.94, 120.95, 21.38 ppm.

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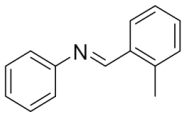
Synthesis of *N*-(2-methylbenzylidene) aniline (1g)



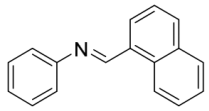
Chemical Formula: $C_{14}H_{13}N$
Molecular Weight: 195.27

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^tBu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, aniline (1 mmol, 91.3 µL) and 2-methylbenzyl alcohol (1.6 mmol, 195 mg) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as an orange oil (172 mg, 0.882 mmol, 88 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.81 (s, 1 H, CH_1), 8.18-8.15 (d, *J* = 7.03 Hz, 1 H, $CH_{arom.}$), 7.50- 7.27 (m, 8 H, $CH_{arom.}$), 2.65 (s, 3 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 159.14, 152.78, 138.66, 134.18, 131.08, 129.22, 127.91, 126.44, 125.88, 120.98, 19.50 ppm.

Synthesis of *N*-(1-naphthylmethylene) aniline (1h)



Chemical Formula: $C_{17}H_{13}N$
Molecular Weight: 231.30

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, aniline (1 mmol, 91.3 µL) and 1-naphthalenemethanol (1.6 mmol, 253 mg) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.6) as a yellow solid (181 mg, 0.782 mmol, 78 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 9.13 (s, 1 H, CH_1), 9.09-9.06 (d, *J* = 8.20 Hz, 1 H, $CH_{arom.}$), 8.15-8.12 (d, *J* = 7.03 Hz, 1 H, $CH_{arom.}$), 8.02-7.94 (dd, *J* = 16.99 Hz, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.68-7.56- 7.27 (m, 3 H, $CH_{arom.}$), 7.50-7.47 (d, *J* = 8.20 Hz, 1 H, $CH_{arom.}$), 7.44 (s, 1 H, $CH_{arom.}$), 7.34-7.27 (dd, *J* = 13.47 Hz, *J* = 8.20 Hz, 3 H, $CH_{arom.}$) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 160.13, 152.67, 133.95, 132.00, 131.54, 131.48, 129.89, 129.27, 128.81, 127.53, 126.28, 125.99, 125.36, 124.26, 120.98 ppm.

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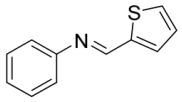
Synthesis of *N*-(2-thienylmethylene) aniline (1i)



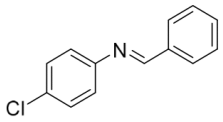
Chemical Formula: $C_{11}H_9NS$
Molecular Weight: 187.26

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^tBu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, aniline (1 mmol, 91.3 µL) and 2-thiophenemethanol (1.6 mmol, 152 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 10/0.7) as a yellow oil (171 mg, 0.914 mmol, 91 %).

^{1}H NMR (CD_2Cl_2, 299.86 MHz, 296.15 K): δ = 8.60 (s, 1 H, CH_1), 7.56-7.52 (m, 2 H, $CH_{arom.}$), 7.46-7.41 (t, J = 7.64 Hz, 2 H, $CH_{arom.}$), 7.30-7.24 (m, 3 H, $CH_{arom.}$), 7.18-7.16 (m, 1 H, $CH_{arom.}$) ppm.

^{13}C NMR (CD_2Cl_2, 75.41 MHz, 296.15 K): δ = 153.01, 151.42, 143.06, 132.46, 130.32, 129.27, 127.91, 126.11, 121.01, 113.12 ppm.

Synthesis of *N*-benzyliden-4-chloroaniline (3a)



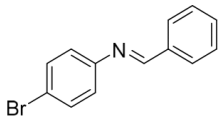
Chemical Formula: $C_{13}H_{10}ClN$
Molecular Weight: 215.68

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 4-chloroaniline (1 mmol, 128 mg) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.1) as a light yellow solid (138 mg, 0.642 mmol, 64 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.45 (s, 1 H, CH_1), 7.93-7.91 (d, *J* = 4.96 Hz, 2 H, $CH_{arom.}$), 7.51-7.50 (m, 3 H, $CH_{arom.}$), 7.39-7.36 (d, *J* = 8.79 Hz, 2 H, $CH_{arom.}$), 7.19-7.16 (d, *J* = 8.79 Hz, 2 H, $CH_{arom.}$) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 160.73, 150.52, 135.95, 131.65, 131.48, 129.25, 128.90, 128.84, 122.23 ppm.

Synthesis of *N*-benzyliden-4-bromoaniline (3b)



Chemical Formula: $C_{13}H_{10}BrN$
Molecular Weight: 260.13

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 4-bromoaniline (1 mmol, 172 mg) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.2) as an orange solid (189 mg, 0.727 mmol, 73 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.44 (s, 1 H, CH_1), 7.93-7.91 (d, *J* = 5.70 Hz, 2 H, $CH_{arom.}$), 7.54-7.51 (m, 5 H, $CH_{arom.}$), 7.13-7.10 (d, *J* = 8.79 Hz, 2 H, $CH_{arom.}$) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 160.79, 150.98, 135.92, 132.21, 131.69, 128.92, 128.85, 122.61, 119.33 ppm.

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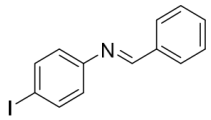
Synthesis of *N*-benzyliden-4-iodoaniline (3c)



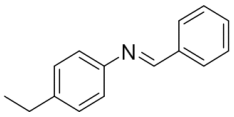
Chemical Formula: $C_{13}H_{10}IN$
Molecular Weight: 307.13

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 4-iodoaniline (1 mmol, 219 mg) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.6) as a white solid (189 mg, 0.616 mmol, 62 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.43 (s, 1 H, CH_1), 7.93-7.91 (m, 2 H, $CH_{arom.}$), 7.74-7.71 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.52-7.50 (m, 3 H, $CH_{arom.}$), 7.01-6.98 (d, *J* = 8.79 Hz, 2 H, $CH_{arom.}$) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 160.79, 151.68, 138.22, 135.96, 131.74, 128.99, 128.90, 123.09, 90.50 ppm.

Synthesis of *N*-benzyliden-4-ethylaniline (3d)



Chemical Formula: $C_{15}H_{15}N$
Molecular Weight: 209.29

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 4-ethylaniline (1 mmol, 124 mg) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.8) as an orange oil (173 mg, 0.828 mmol, 83 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.52 (s, 1 H, CH_1), 7.96-7.93 (m, 2 H, $CH_{arom.}$), 7.52-7.50 (m, 3 H, $CH_{arom.}$), 7.29-7.26 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.23-7.21 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$) 2.76-2.68 (q, *J* = 7.61 Hz, 2 H, $CH_{2.}$), 1.33-1.29 (t, *J* = 7.61 Hz, 3 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 159.63, 149.71, 142.25, 136.42, 131.23, 128.78, 128.63, 120.95, 28.49, 15.73 ppm.

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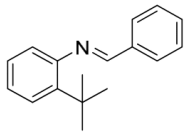
Synthesis of *N*-benzyliden-2-*tert*-butylaniline (3e)



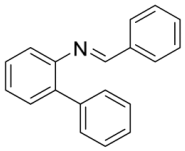
Chemical Formula: $C_{17}H_{19}N$
Molecular Weight: 237.35

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 2-*tert*-butylaniline (1 mmol, 156 µL) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 6 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.1) as an orange oil (183 mg, 0.772 mmol, 77 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.63 (s, 1 H, CH_1), 8.23-8.20 (m, 2 H, $CH_{arom.}$), 7.79-7.77 (m, 3 H, $CH_{arom.}$), 7.72-7.69 (m, 1 H, $CH_{arom.}$), 7.53-7.47 (m, 2 H, $CH_{arom.}$), 7.17-7.14 (m, 1 H, $CH_{arom.}$), 1.77 (s, 9 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 158.06, 151.54, 143.09, 136.82, 131.14, 128.85, 127.10, 126.09, 125.70, 119.26, 35.72, 30.55 ppm.

Synthesis of *N*-benzyliden-2-phenylaniline (3f)



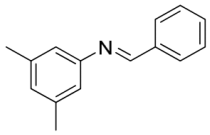
Chemical Formula: $C_{19}H_{15}N$
Molecular Weight: 257.34

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 2-phenylaniline (1 mmol, 169 mg) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.2) as a yellow oil (169 mg, 0.658 mmol, 66 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.51 (s, 1 H, CH_1), 7.86-7.84 (d, *J* = 7.03 Hz, 2 H, $CH_{arom.}$), 7.58-7.36 (m, 11 H, $CH_{arom.}$), 7.15-7.13 (d, *J* = 7.61 Hz, 1 H, $CH_{arom.}$) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 160.36, 149.74, 139.53, 136.48, 135.38, 131.25, 130.40, 130.29, 128.90, 128.75, 128.43, 127.74, 126.81, 126.06, 118.95 ppm.

Synthesis of *N*-benzyliden-3,5-dimethylaniline (3g)



Chemical Formula: $C_{15}H_{15}N$
Molecular Weight: 209.29

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 3,5-dimethylaniline (1 mmol, 125 µL) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.5) as a yellow oil (194 mg, 0.928 mmol, 93 %).

^{1}H NMR ($CDCl_3$, 299.86 MHz, 296.15 K): δ = 8.53 (s, 1 H, CH_1), 8.00-7.97 (m, 2 H, $CH_{arom.}$), 7.57-7.55 (m, 3 H, $CH_{arom.}$), 6.98 (s, 1 H, $CH_{arom.}$), 6.94 (s, 2 H, $CH_{arom.}$), 2.44 (s, 6 H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 75.41 MHz, 296.15 K): δ = 159.97, 152.14, 138.79, 136.38, 131.25, 128.76, 127.65, 118.66, 21.35 ppm.

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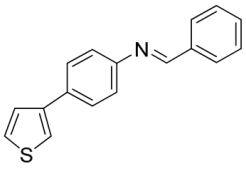
Synthesis of *N*-benzyliden-4-(thiophen-3-yl) aniline (3h)



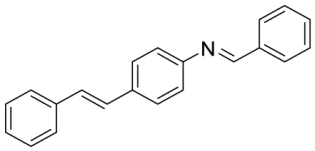
Chemical Formula: $C_{17}H_{13}NS$
Molecular Weight: 263.36

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 4-(thiophen-3-yl) aniline (1 mmol, 175 mg) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/1) as a light yellow solid (238 mg, 0.905 mmol, 91 %).

^{1}H NMR (CD_2Cl_2, 299.86 MHz, 296.15 K): δ = 8.57 (s, 1 H, CH_1), 7.97-7.96 (m, 2 H, $CH_{arom.}$), 7.71-7.69 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.54 (m, 4 H, $CH_{arom.}$), 7.47 (m, 2 H, $CH_{arom.}$), 7.33-7.30 (d, *J* = 8.20 Hz 2 H, $CH_{arom.}$) ppm.

^{13}C NMR (CD_2Cl_2, 75.41 MHz, 296.15 K): δ = 159.87, 150.86, 141.73, 136.38, 133.60, 131.34, 128.76, 127.10, 126.35, 126.12, 121.42, 119.99 ppm.

Synthesis of *N*-benzyliden-4-aminostilbene (3i)



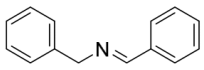
Chemical Formula: $C_{21}H_{17}N$
Molecular Weight: 283.37

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 4-aminostilbene (1 mmol, 195 mg) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/3) as a yellow solid (254 mg, 0.898 mmol, 90 %).

^{1}H NMR (CD_2Cl_2, 299.86 MHz, 296.15 K): δ = 8.56 (s, 1 H, CH_1), 7.97-7.95 (m, 2 H, $CH_{arom.}$), 7.63-7.54 (m, 7 H, $CH_{arom.}$), 7.43-7.33 (m, 2 H, $CH_{arom.}$), 7.33-7.27 (m, 3 H, $CH_{arom.}$), 7.19 (s, 2 H, $CH_{arom.}$) ppm.

^{13}C NMR (CD_2Cl_2, 75.41 MHz, 296.15 K): δ = 159.77, 151.25, 137.37, 136.36, 135.29, 131.34, 128.73, 128.69, 128.12, 127.98, 127.57, 127.31, 126.61, 125.91, 121.36 ppm.

Synthesis of *N*-(phenylmethylene)-benzenmethanamine (3j)



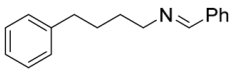
Chemical Formula: $C_{14}H_{13}N$
Molecular Weight: 195,27

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^tBu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, benzyl amine (1 mmol, 109 µL) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 10/0.2) as a light orange oil (154 mg, 0.791 mmol, 79 %).

^{1}H NMR (CD_2Cl_2, 299.86 MHz, 296.15 K): δ = 8.44 (s, 1 H, CH), 7.85-7.82 (m, 2 H, $CH_{arom.}$), 7.49-7.30 (m, 8 H, $CH_{arom.}$), 4.83 (s, 2 H, CH_2 ppm.

^{13}C NMR (CD_2Cl_2, 75.41 MHz, 296.15 K): δ = 162.54, 140.60, 137.30, 131.58, 129.49, 129.33, 129.07, 128.89, 127.81, 65.95 ppm.

Synthesis of *N*-(phenylmethylene)-benzenebutanamine (3k)



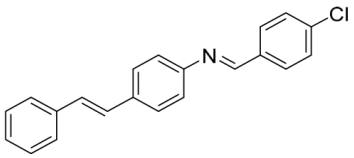
Chemical Formula: $C_{17}H_{19}N$
Molecular Weight: 237,35

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, benzenebutanamine (1 mmol, 158 µL) and benzyl alcohol (1.6 mmol, 166 µL) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 20/0.03) as a light orange oil (131 mg, 0.553 mmol, 55 %).

^{1}H NMR (CD_2Cl_2, 299.86 MHz, 296.15 K): δ = 8.36 (s, 1 H, CH), 7.84-7.81 (m, 2 H, $CH_{arom.}$), 7.52-2.27 (m, 8 H, $CH_{arom.}$), 3.73-3.70 (t, *J* = 6.87 Hz, 2 H, CH_2), 2.78-2.75 (t, *J* = 6.87 Hz, 2 H, $CH_{arom.}$), 1.83-1.80 (m, 4 H, CH_2) ppm.

^{13}C NMR (CD_2Cl_2, 75.41 MHz, 296.15 K): δ = 160.98, 143.29, 137.17, 130.90, 129.08, 128.99, 128.79, 128.50, 126.18, 62.02, 36.30, 31.18, 29.91 ppm.

Synthesis of *N*-[(4-chlorophenyl)methylene]-4-[2-phenylethenyl] benzenamine (3l)



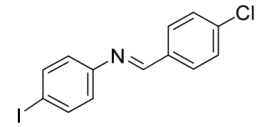
Chemical Formula: $C_{21}H_{16}ClN$
Molecular Weight: 317.82

Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 4-aminostilbene (1 mmol, 195 mg) and 4-chlorobenzyl alcohol (1.6 mmol, 228 mg) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 10/0.8) as a yellow solid (184 mg, 0.583 mmol, 58 %).

^{1}H NMR (CD_2Cl_2, 299.86 MHz, 296.15 K): δ = 8.49 (s, 1 H, CH_1), 7.89-7.86 (d, *J* = 7.03 Hz, 2 H, $CH_{arom.}$), 7.59-7.53 (t, *J* = 8.20 Hz, 4 H, $CH_{arom.}$), 7.49-7.47 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.40-7.35 (m, 2 H, $CH_{arom.}$), 7.29-7.23 (m, 3 H, $CH_{arom.}$), 7.15 (s, 2 H, $CH_{arom.}$) ppm.

^{13}C NMR (CD_2Cl_2, 125.76 MHz, 296.15 K): δ = 158.77, 151.37, 137.87, 137.71, 136.10, 135.50, 130.50, 129.58, 129.25, 128.83, 128.45, 128.15, 127.89, 126.97, 121.95 ppm.

Synthesis of *N*-[(4-chlorophenyl)methylene]-4-iodobenzenamine (3m)



Chemical Formula: $C_{13}H_9ClIN$
Molecular Weight: 341.58

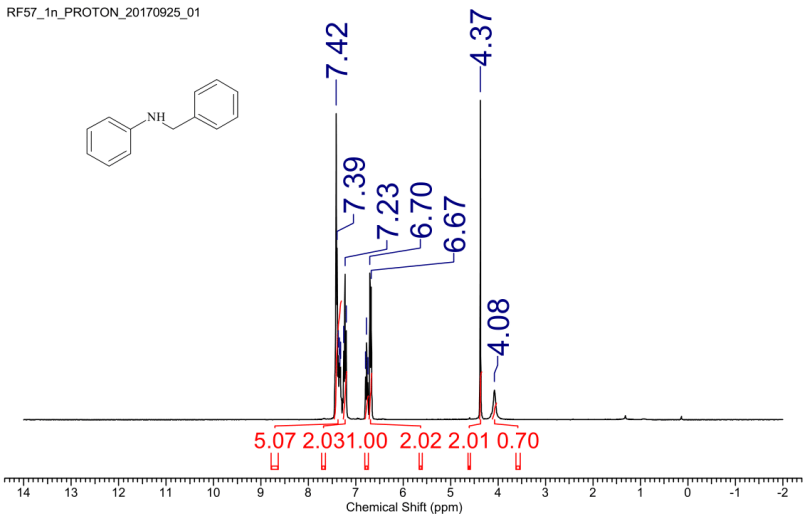
Precatalyst **C** (0.01 mmol, 1 mol%, 6 mg), NaO^{t}Bu (1.5 mmol, 144 mg), 3 mL 2-MeTHF, 4-iodoaniline (1 mmol, 175 mg) and 4-chlorobenzyl alcohol (1.6 mmol, 228 mg) are added consecutively to a Schlenk tube. After heating at 110 °C for 18 hours, the reaction was stopped by adding 1 mL water. The product was isolated via column chromatography over SiO_2 (pentane/diethyl ether: 10/0.3) as a white solid (177 mg, 0.524 mmol, 52 %).

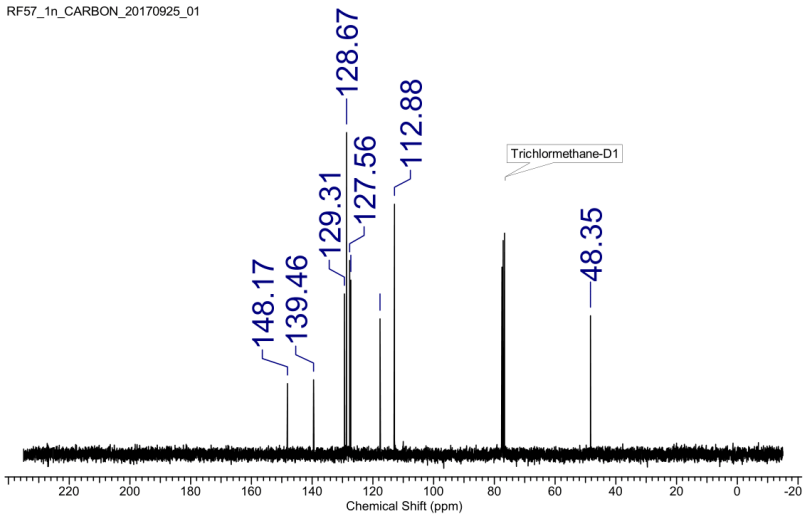
^{1}H NMR (CD_2Cl_2, 299.86 MHz, 296.15 K): δ = 8.41 (s, 1 H, CH_1), 7.87-7.84 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.73-7.70 (d, *J* = 8.79 Hz, 2 H, $CH_{arom.}$), 7.49-7.45 (d, *J* = 8.20 Hz, 2 H, $CH_{arom.}$), 7.00-6.96 (d, *J* = 8.79 Hz, 2 H, $CH_{arom.}$) ppm.

^{13}C NMR (CD_2Cl_2, 125.76 MHz, 296.15 K): δ = 159.81, 151.89, 138.78, 138.00, 135.17, 130.59, 129.62, 123.49, 90.93 ppm.

NMR-Spectra

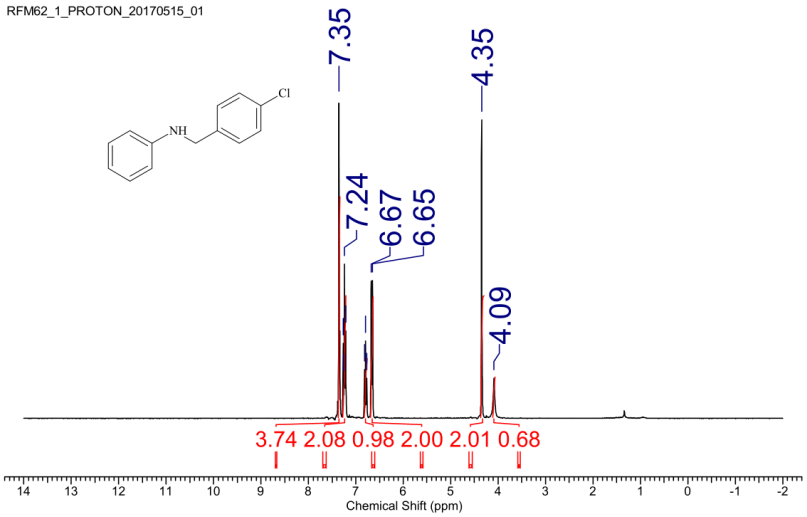
NMR-Spectra of *N*-benzylaniline (2a)

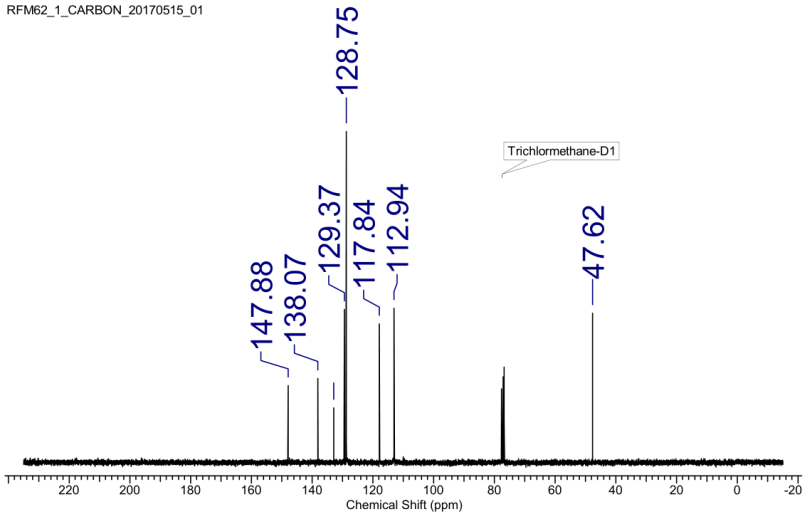




72

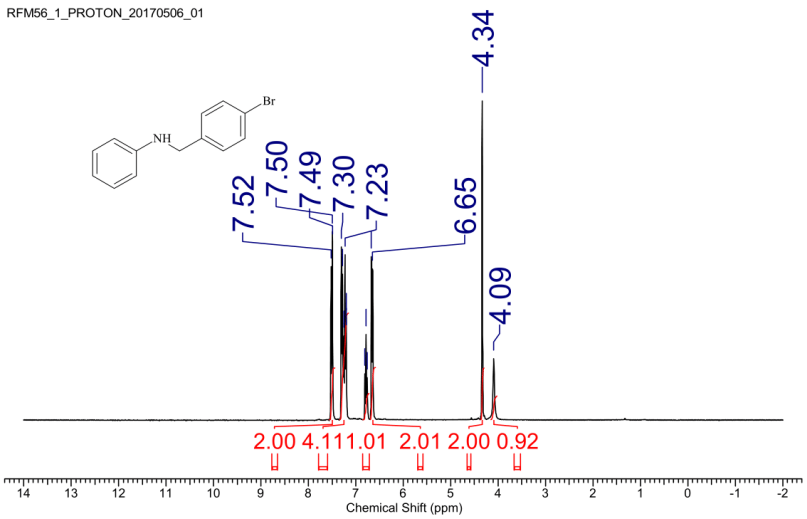
NMR-Spectra of *N*-(4-chlorobenzyl) aniline (2b)

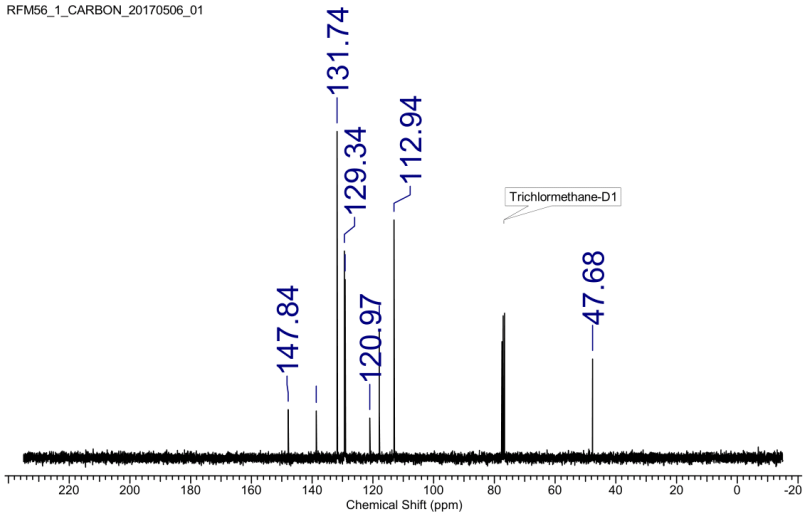




73

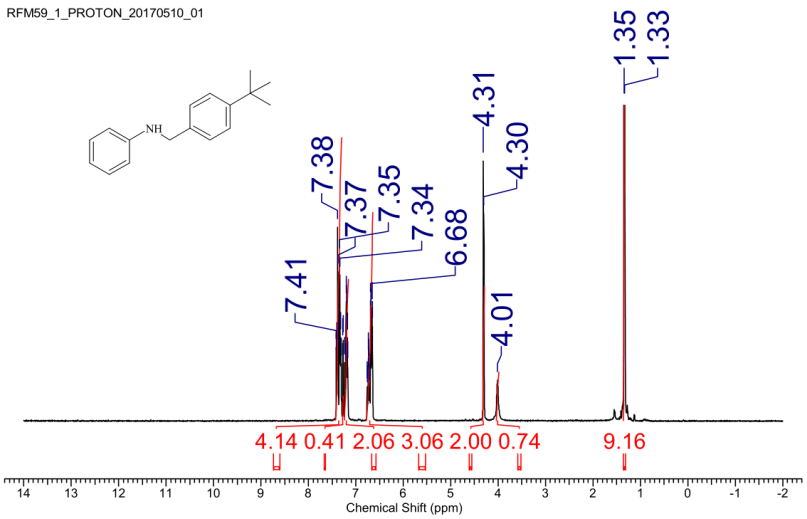
NMR-Spectra of *N*-(4-bromobenzyl) aniline (2c)

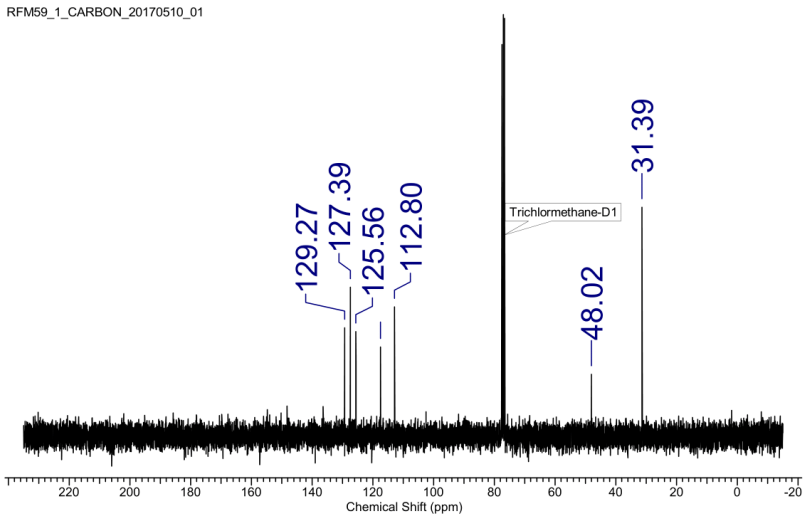




74

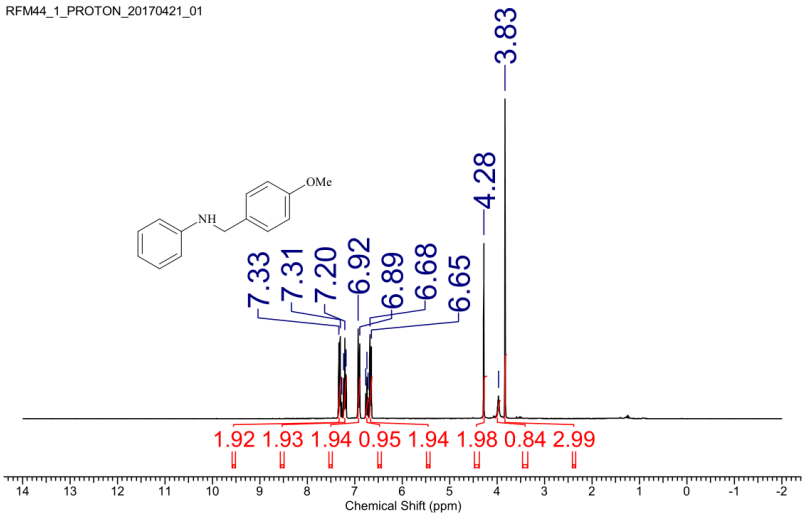
NMR-Spectra of *N*-(4-*tert*-butylbenzyl) aniline (2d)

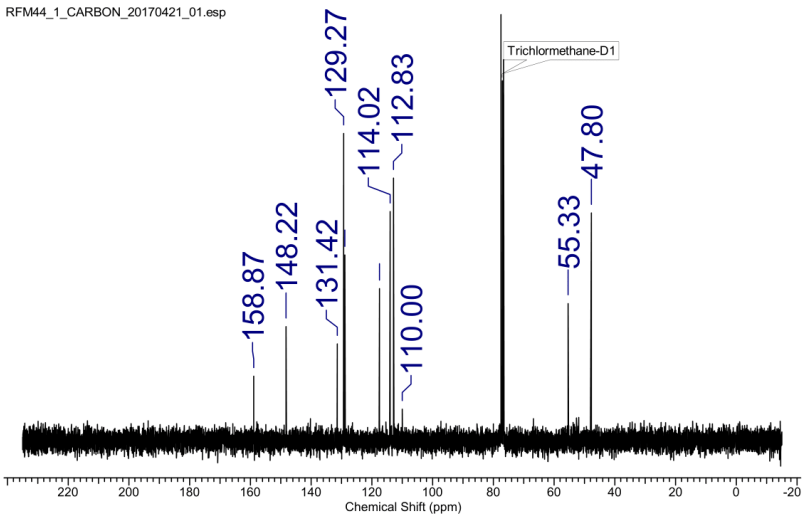




75

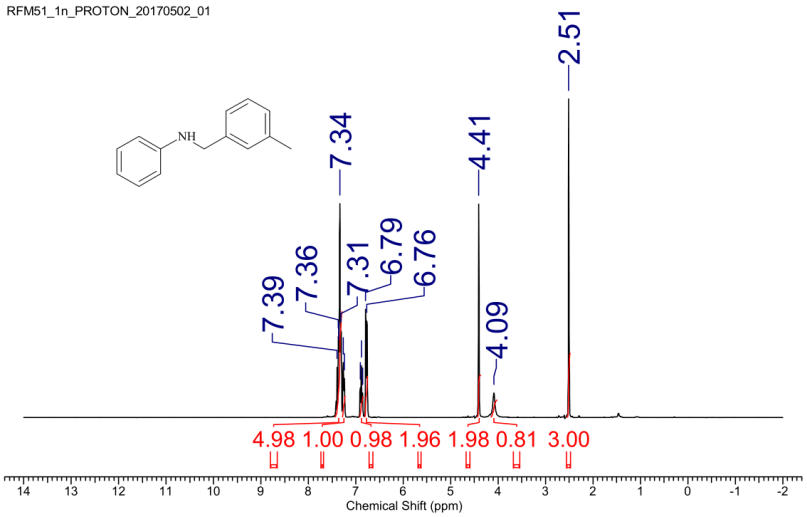
NMR-Spectra of *N*-(4-methoxybenzyl) aniline (2e)

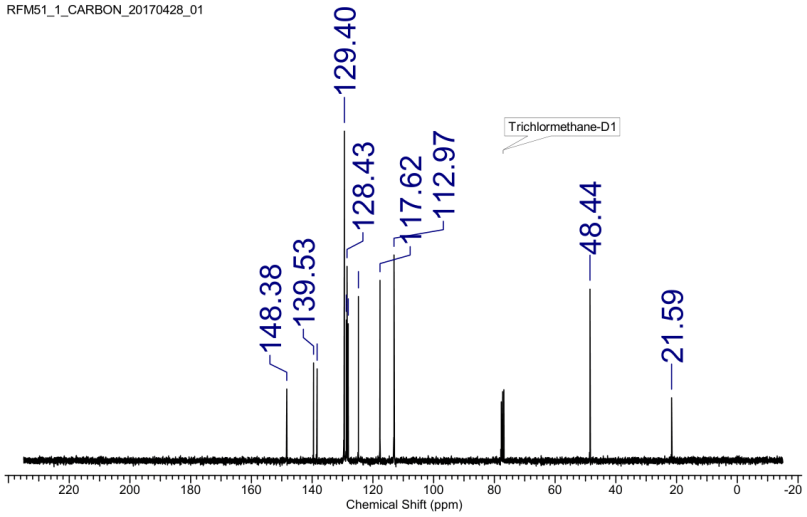




76

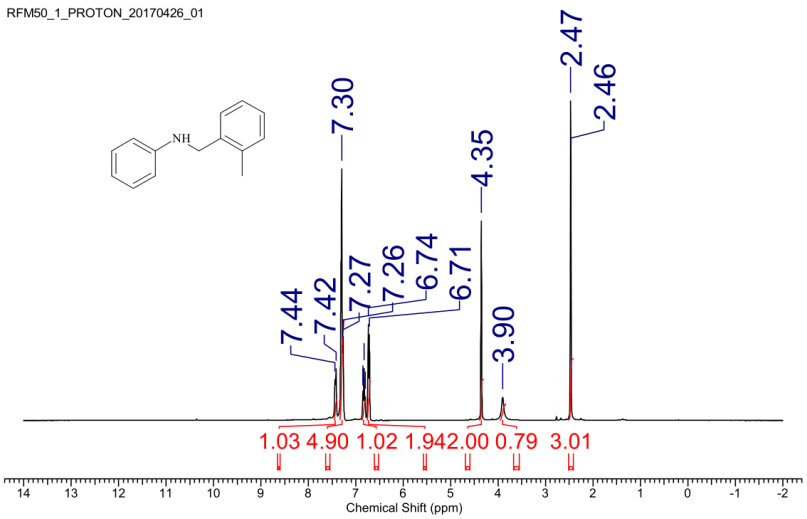
NMR-Spectra of *N*-(3-methylbenzyl) aniline (2f)

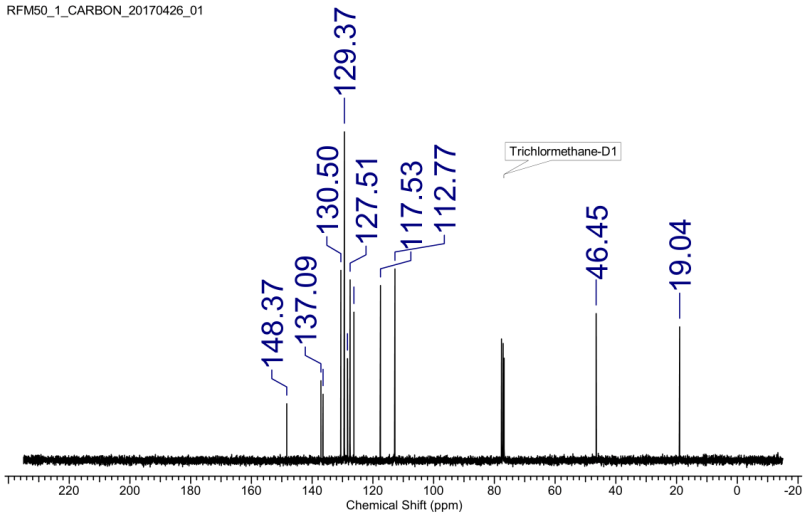




77

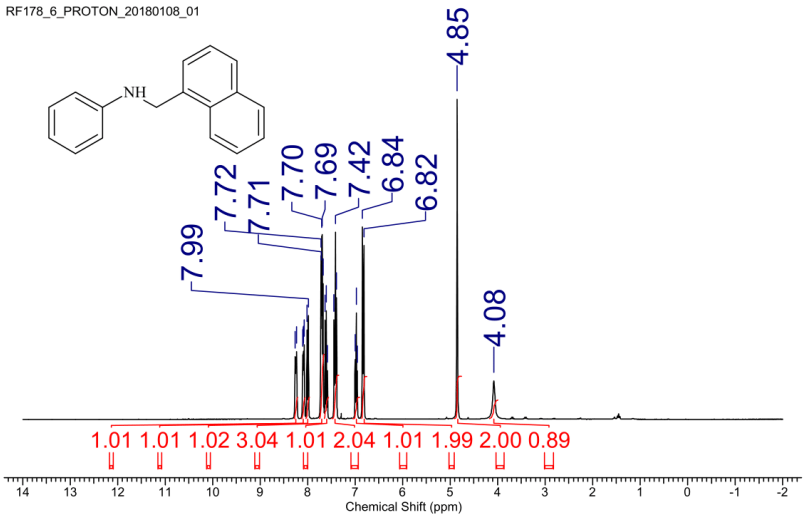
NMR-Spectra of *N*-(2-methylbenzyl) aniline (2g)

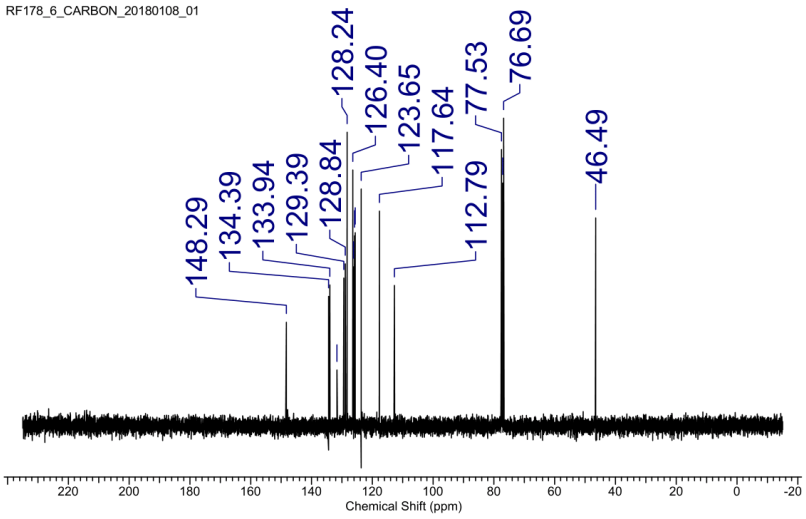




78

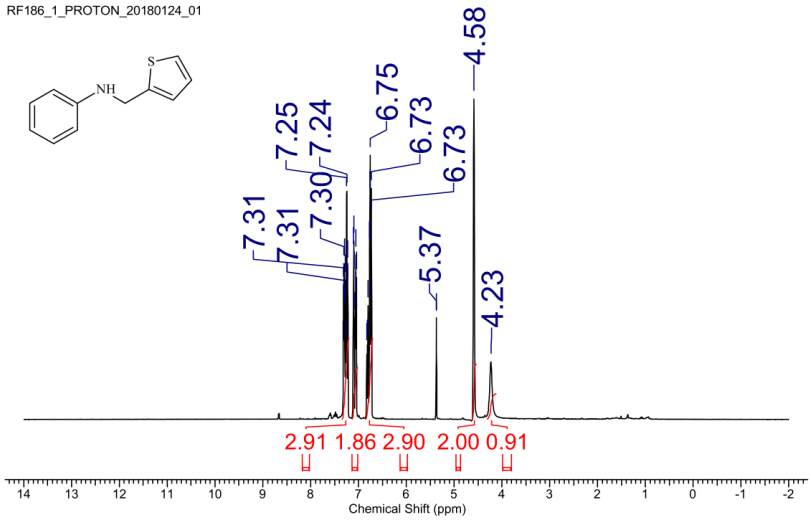
NMR-Spectra of *N*-phenyl-1-naphtalenemethanamine (2h)

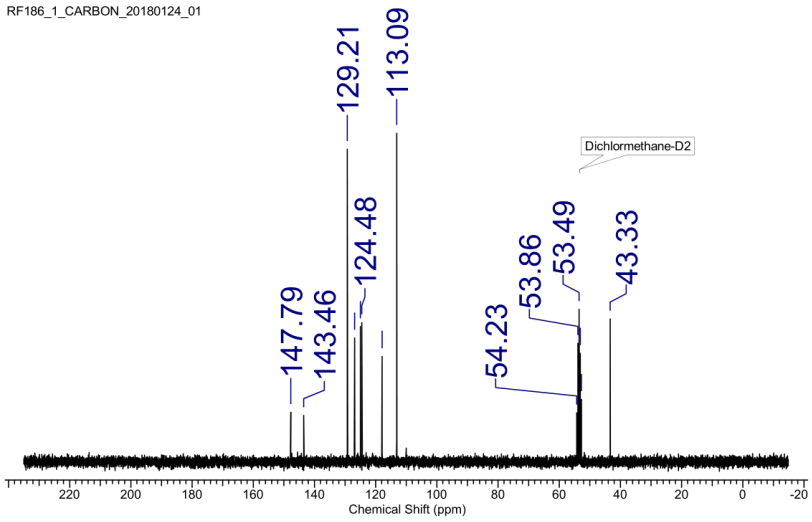




79

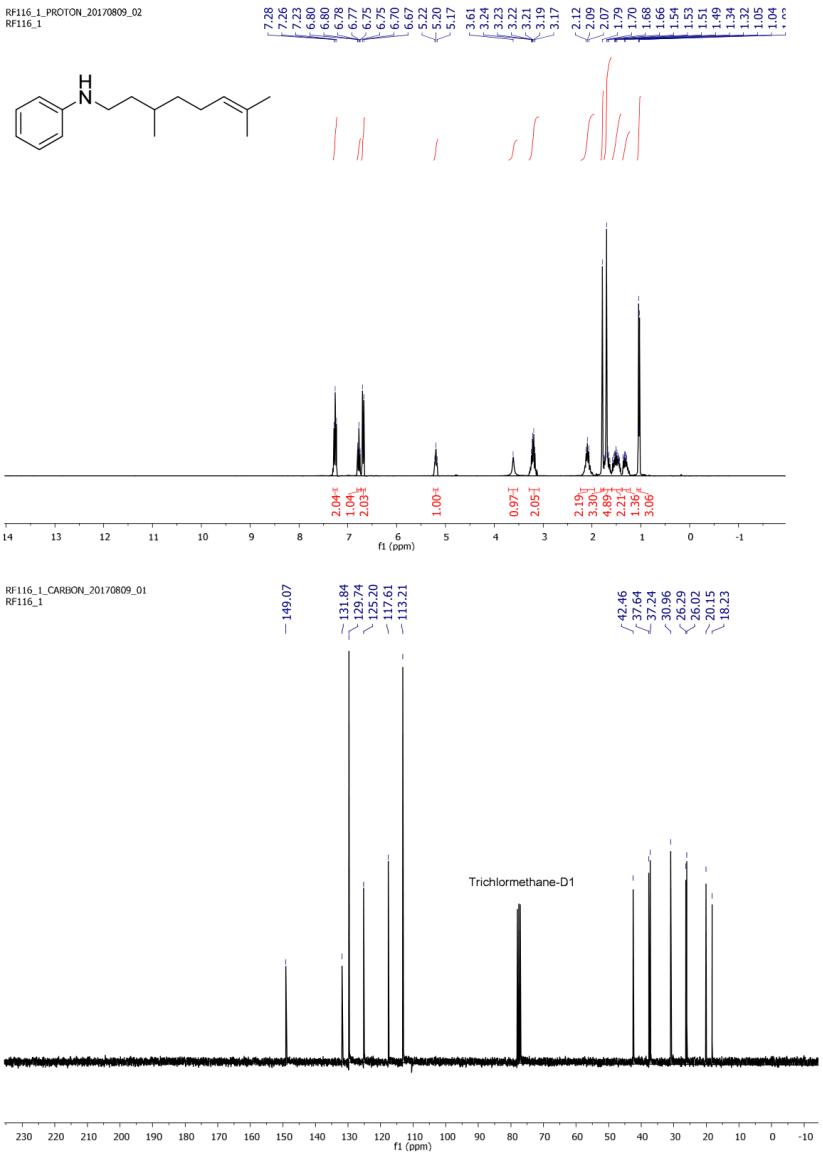
NMR-Spectra of *N*-phenyl-2-thiophenemethanamine (2i)





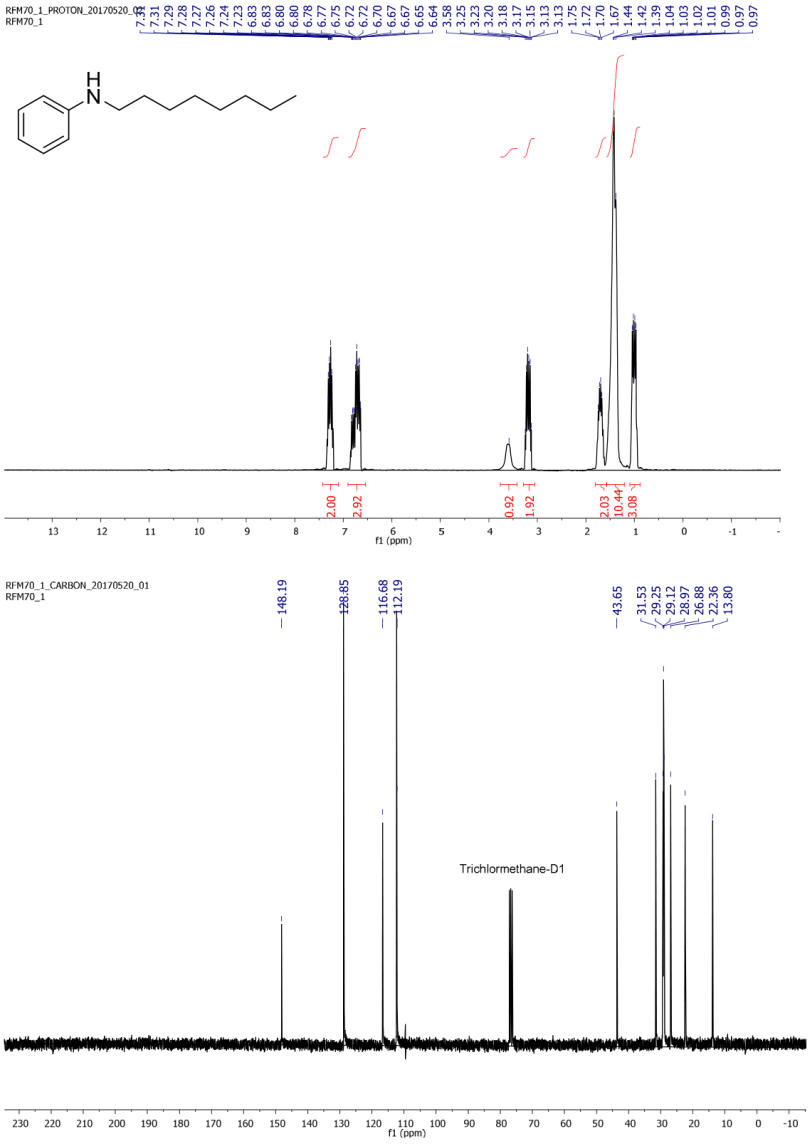
80

NMR-Spectra of N-(3,7-dimethyl-6-octen-1yl)-benzenamine (2j)



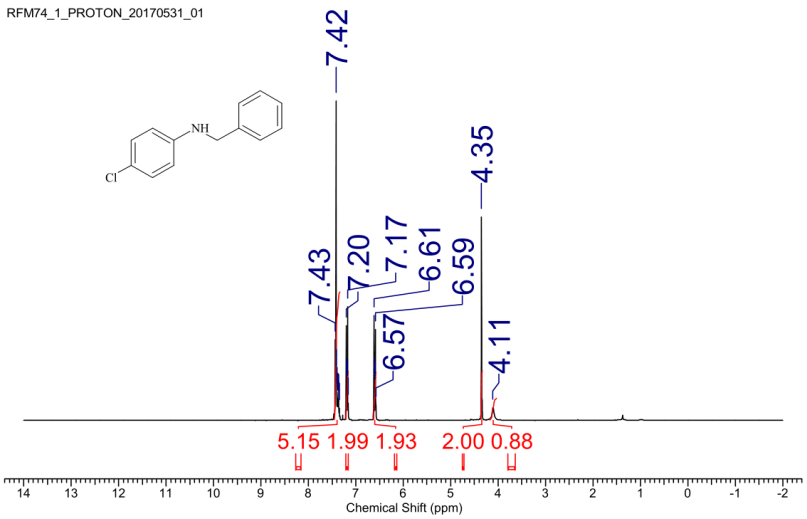
81

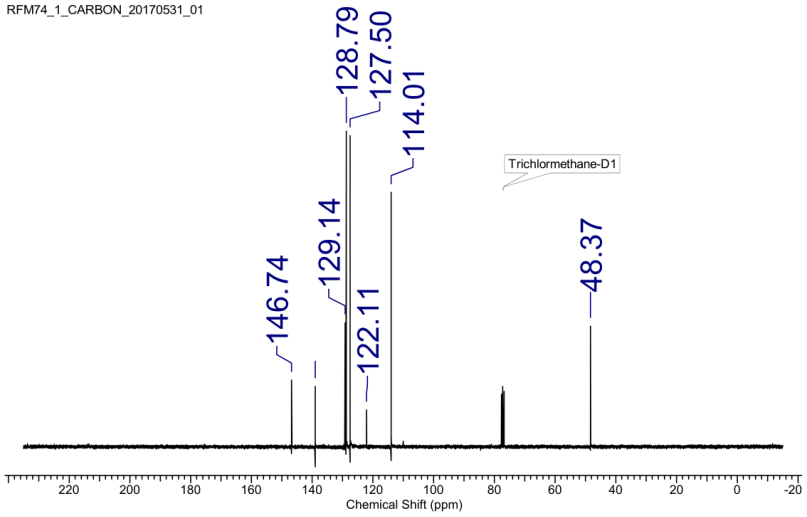
NMR-Spectra of N-octylaniline (2k)



82

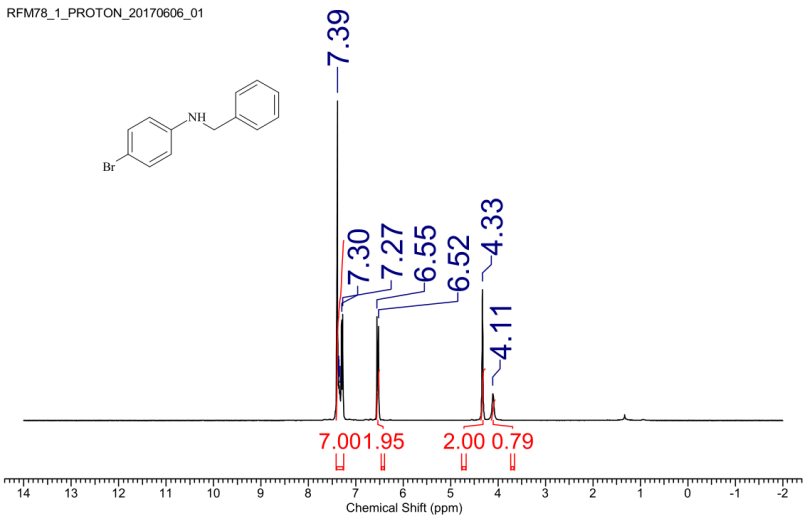
NMR-Spectra of *N*-benzyl-4-chloroaniline (4a)

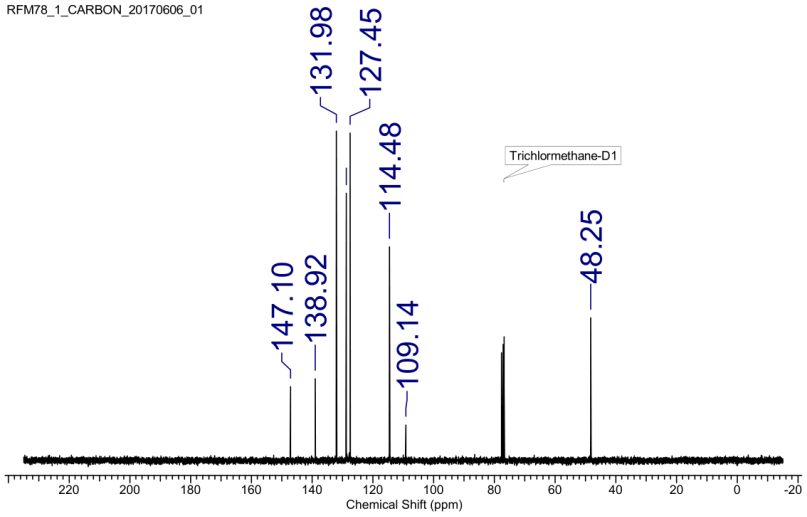




83

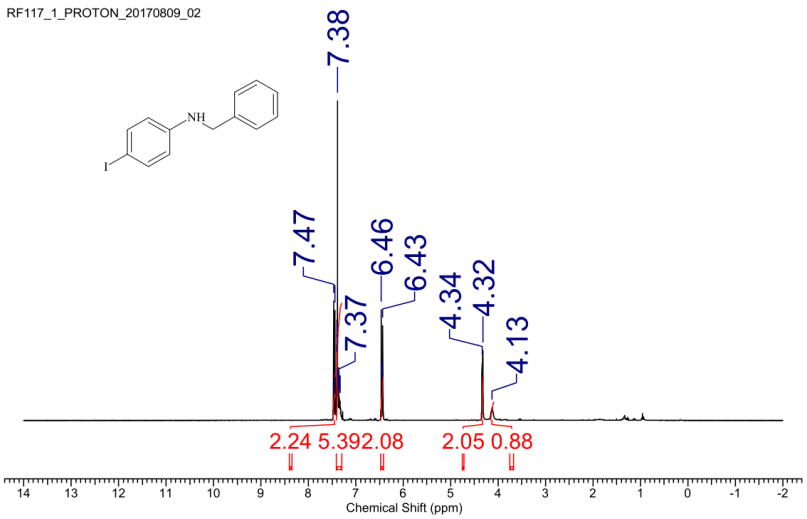
NMR-Spectra of *N*-benzyl-4-bromoaniline (4b)

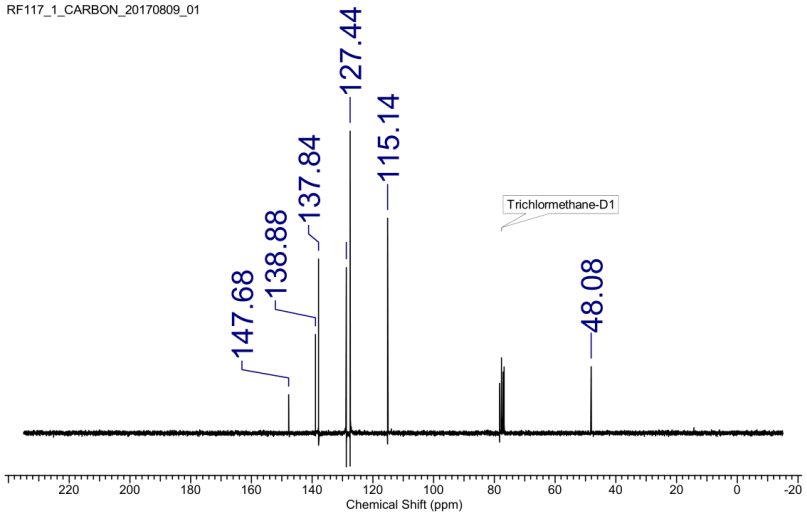




84

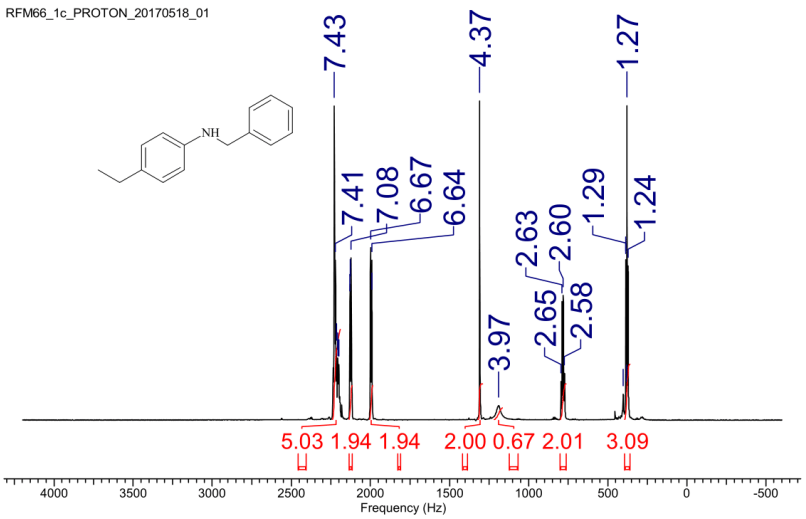
NMR-Spectra of *N*-benzyl-4-iodoaniline (4c)

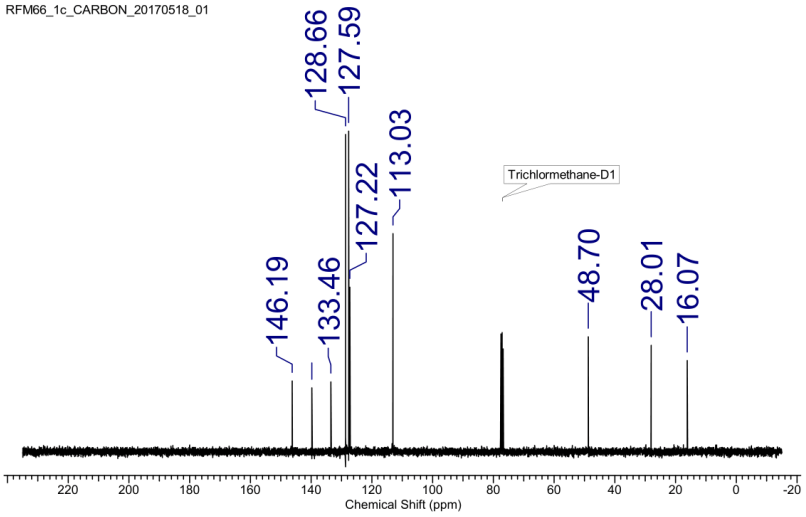




85

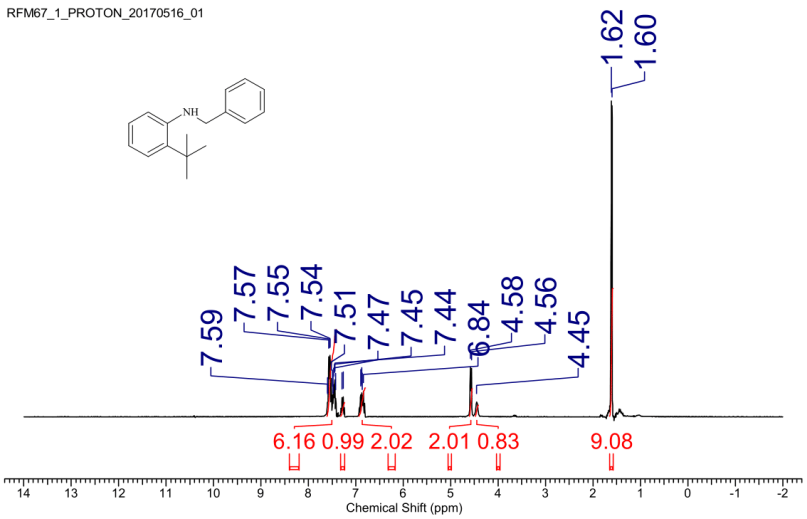
NMR-Spectra of *N*-benzyl-4-ethylaniline (4d)

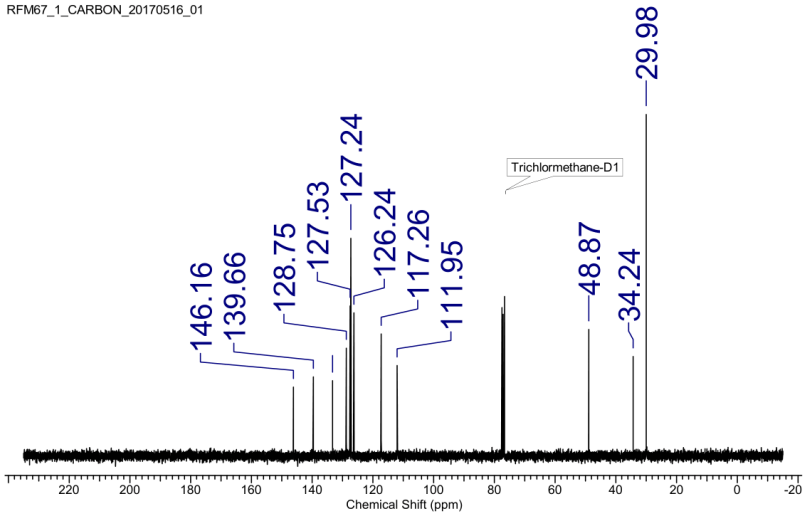




86

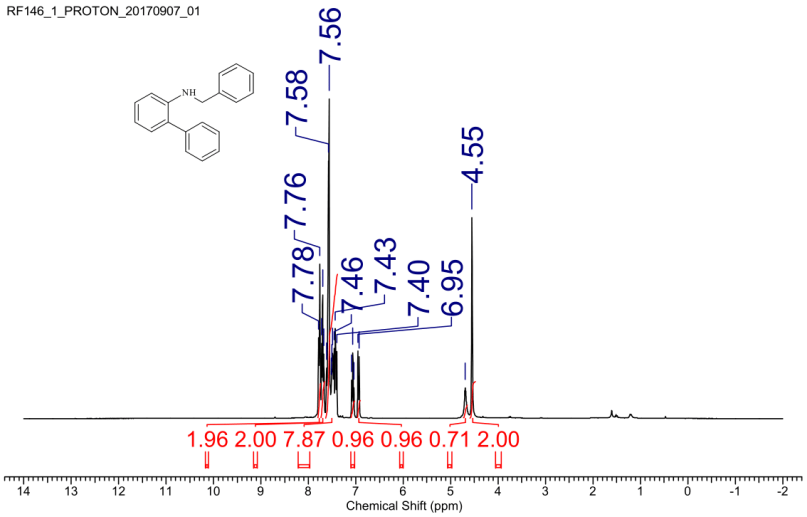
NMR-Spectra of *N*-benzyl-2-*tert*-butylaniline (4e)

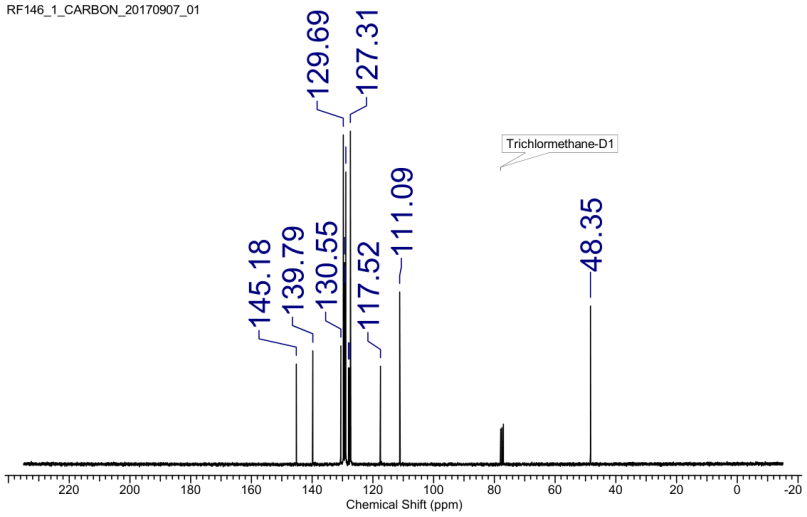




87

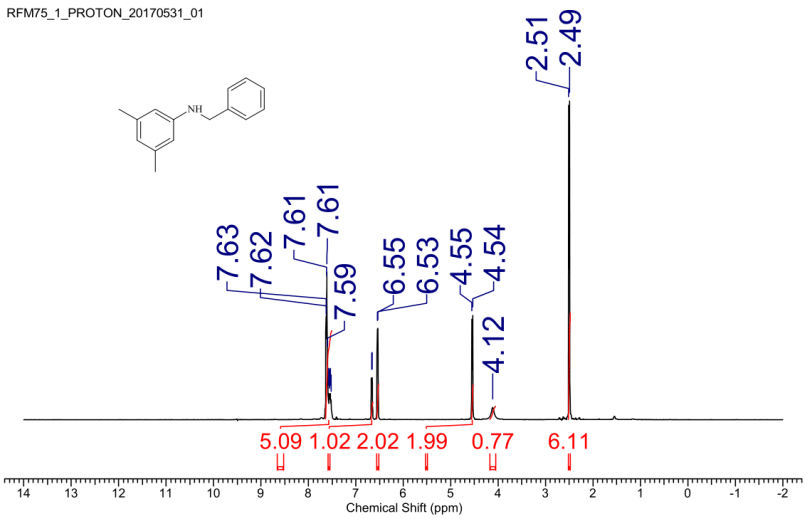
NMR-Spectra of *N*-benzyl-2-phenylaniline (4f)

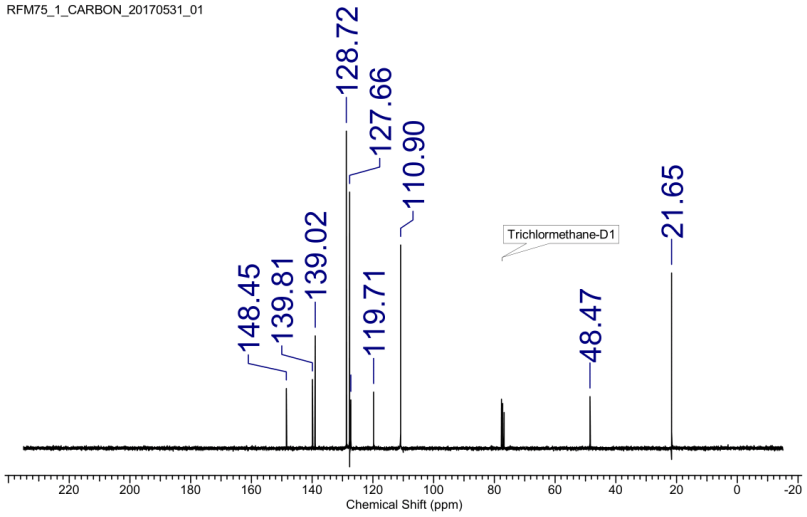




88

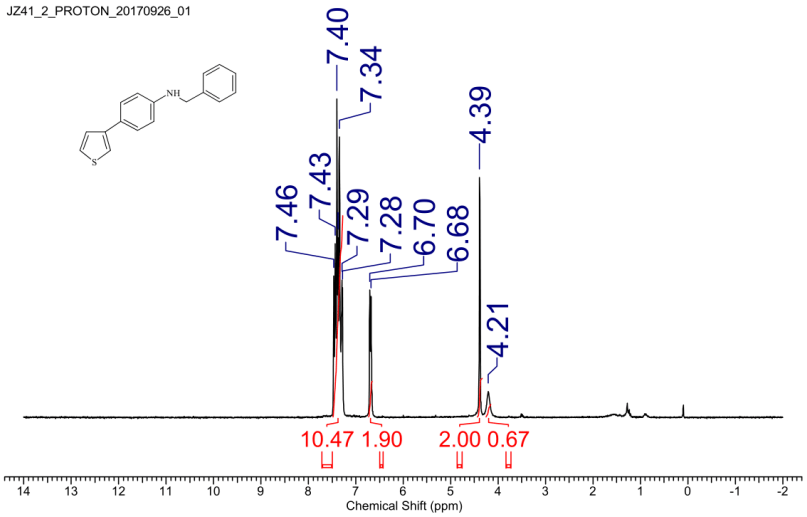
NMR-Spectra of *N*-benzyl-3,5-dimethylaniline (4g)

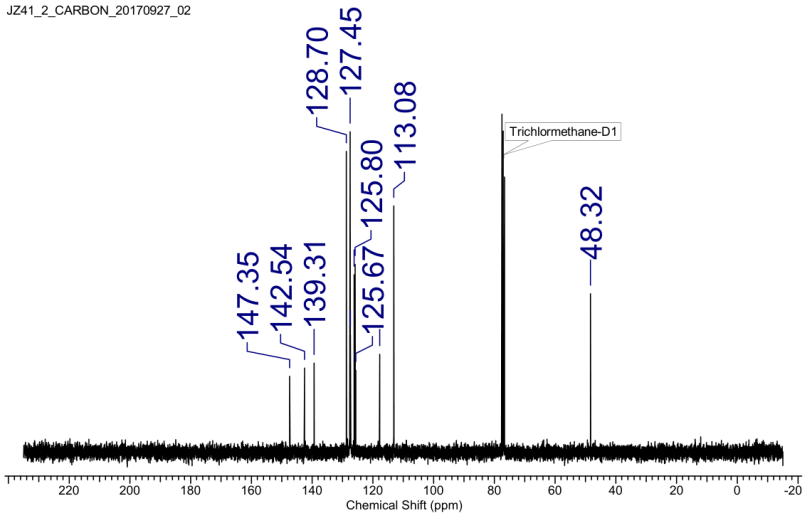




89

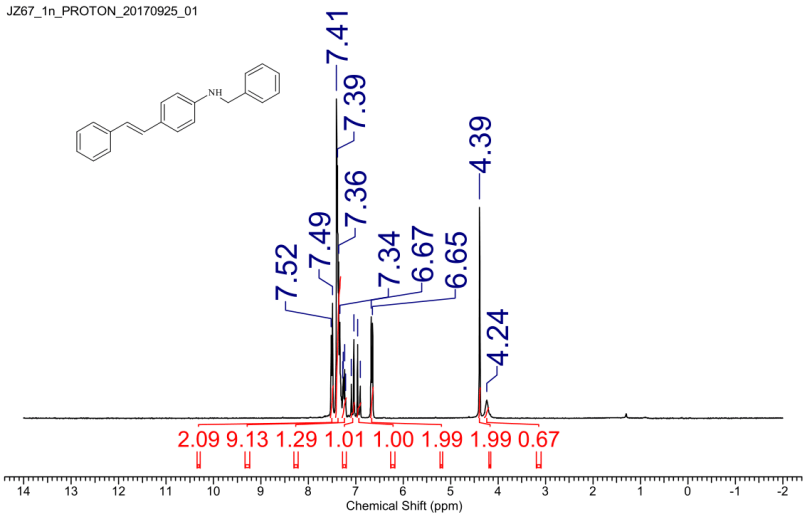
NMR-Spectra of *N*-benzyl-4-(thiophen-3-yl) aniline (4h)

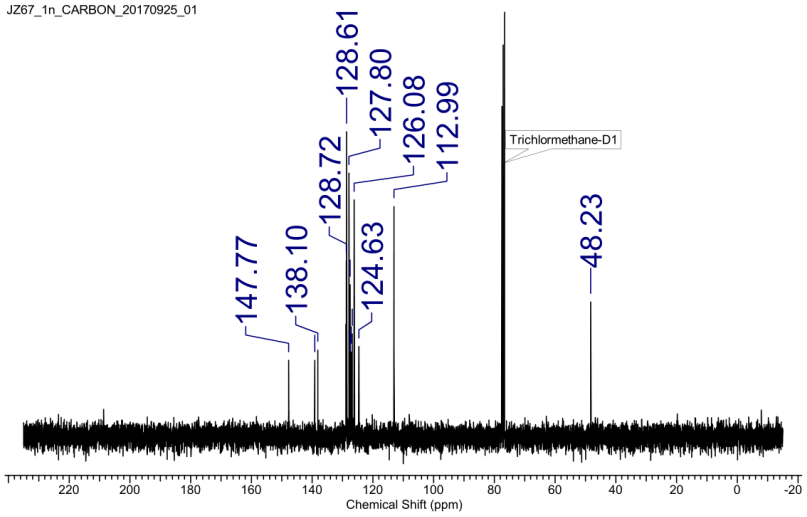




90

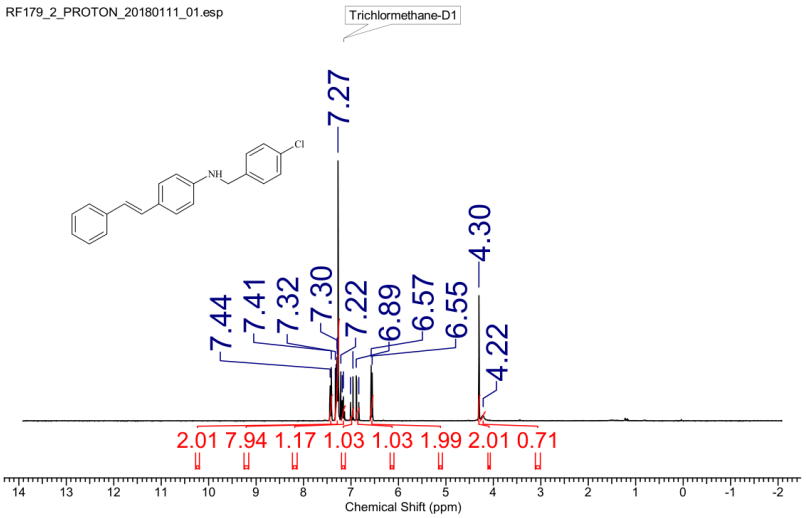
NMR-Spectra of *N*-benzyl-4-aminostilbene (4i)

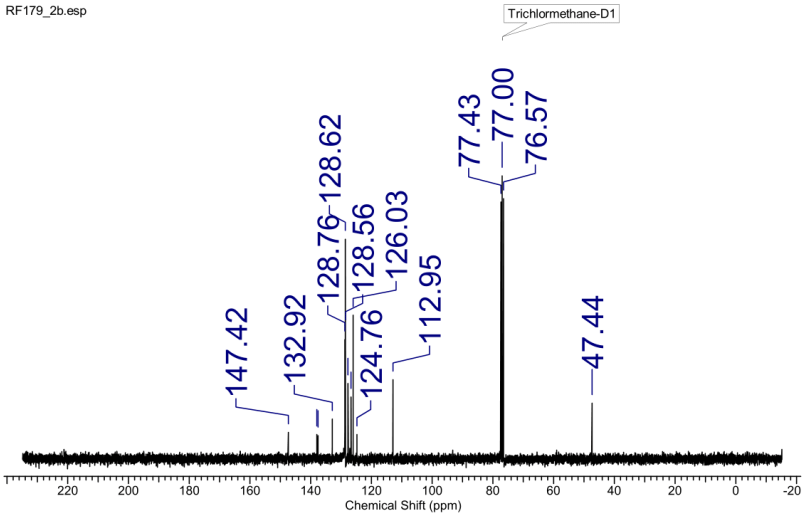




91

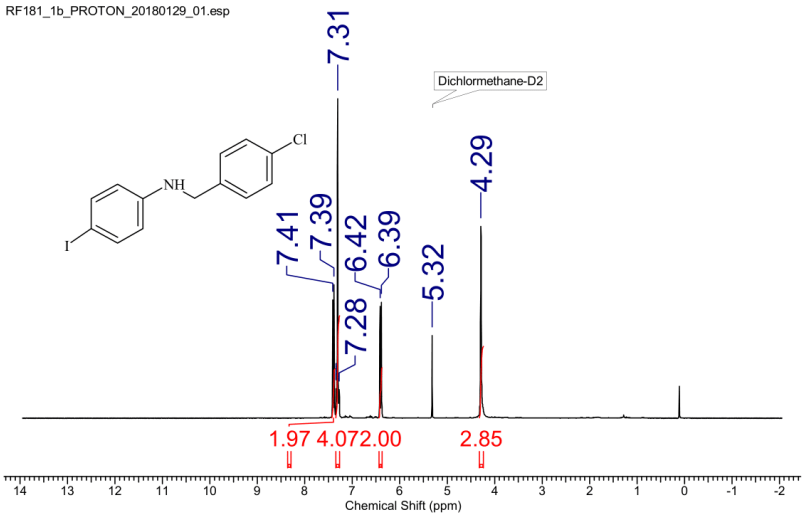
NMR-Spectra of 4-chloro-*N*-[4-[2-phenylethenyl]phenyl] benzenemethanamine (4l)

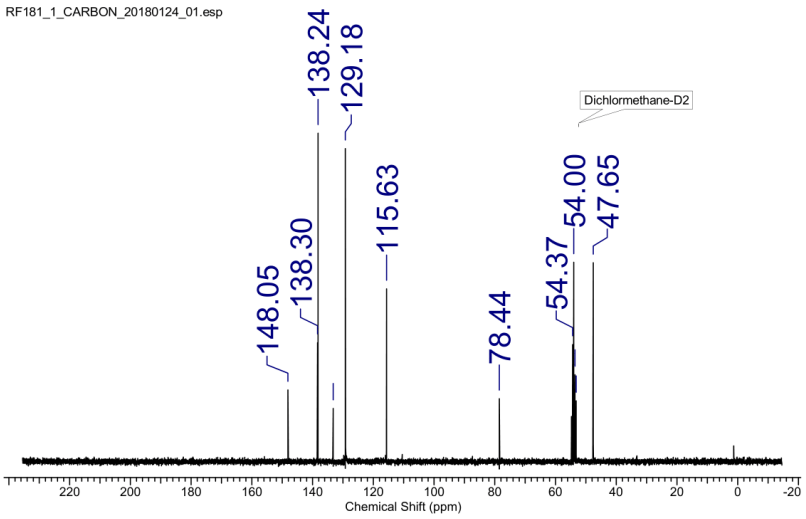




92

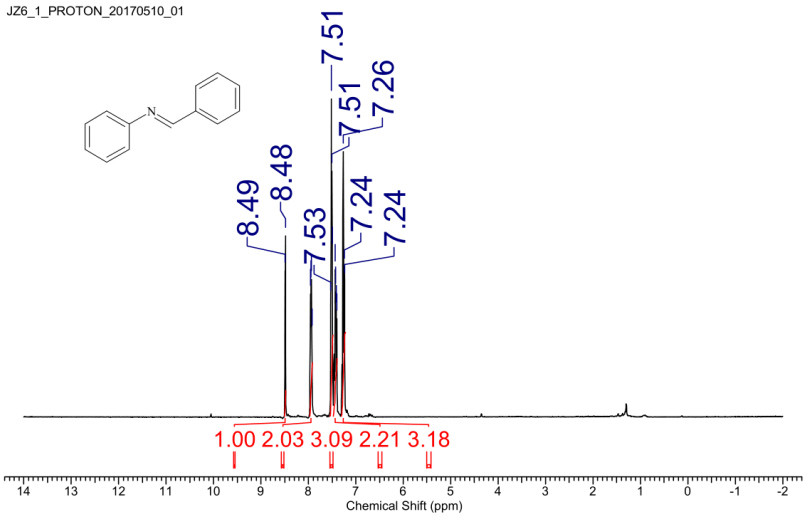
NMR-Spectra of 4-chloro-*N*-(4-iodophenyl) benzenemethanamine (4m)

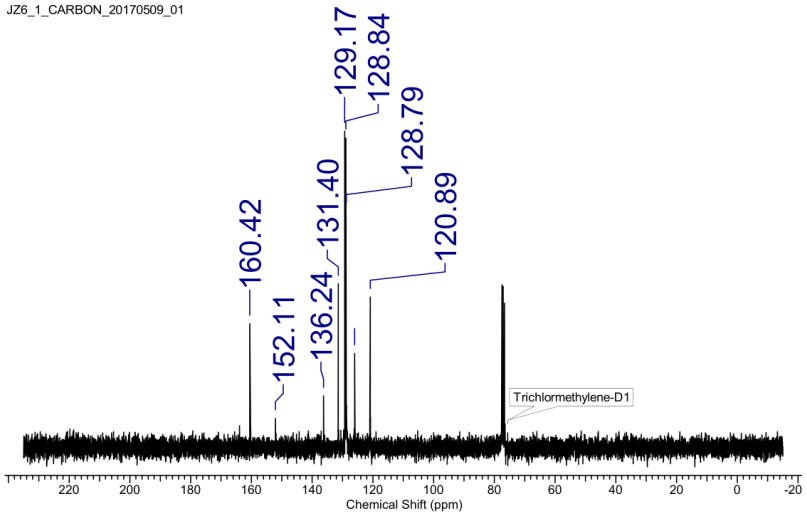




93

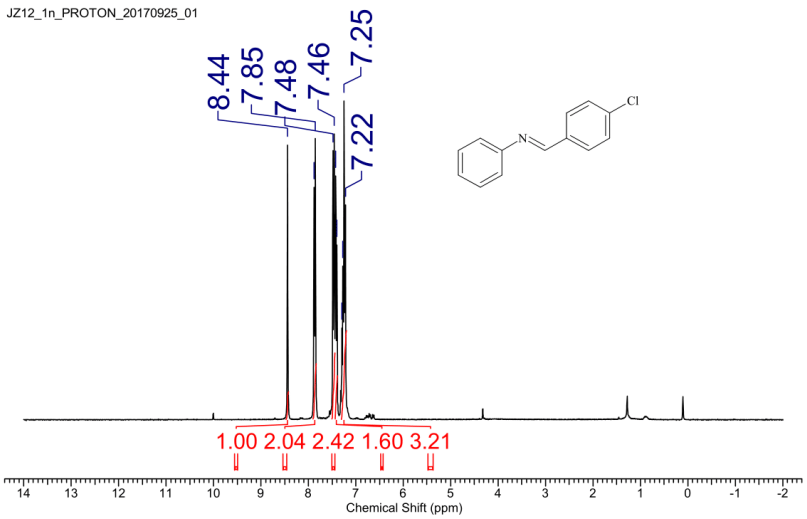
NMR-Spectra of *N*-benzylideneaniline (1a)

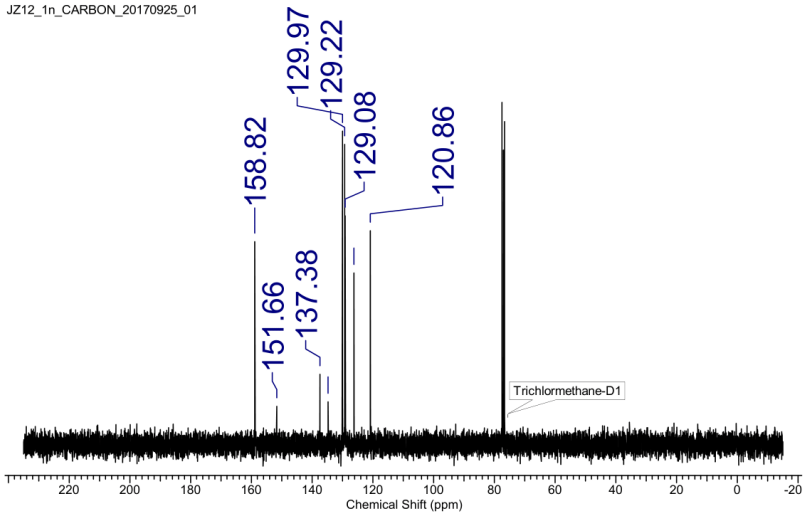




94

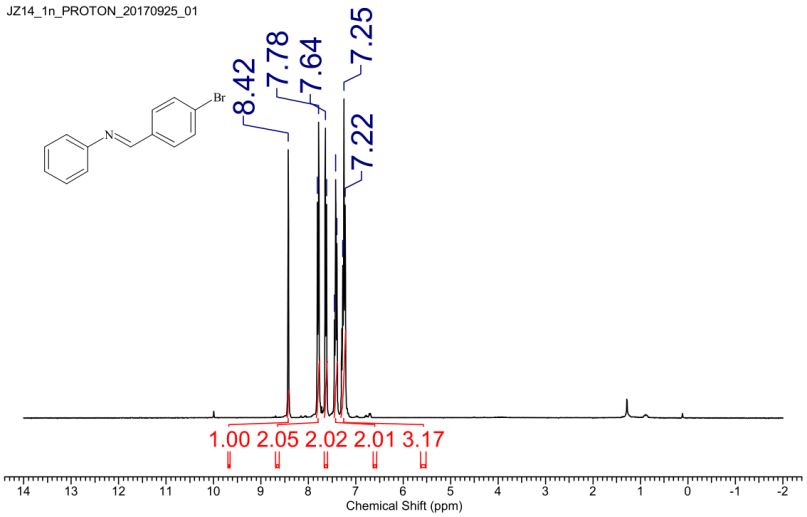
NMR-Spectra of *N*-(4-chlorobenzylidene) aniline (1b)

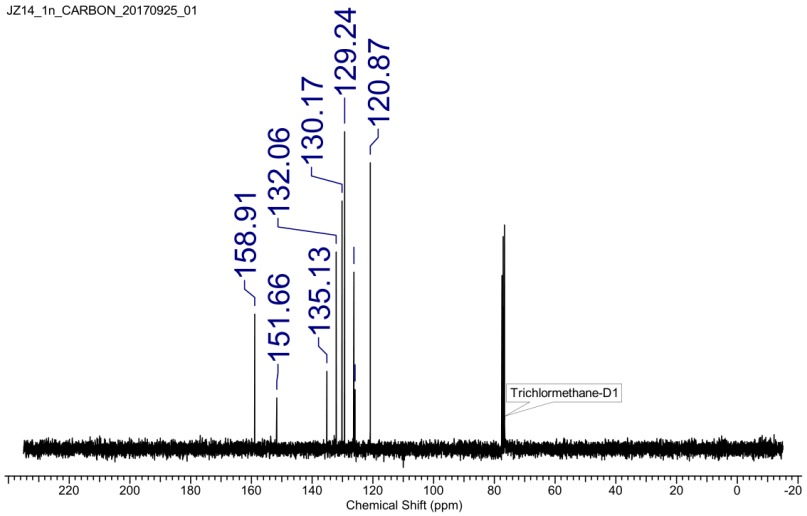




95

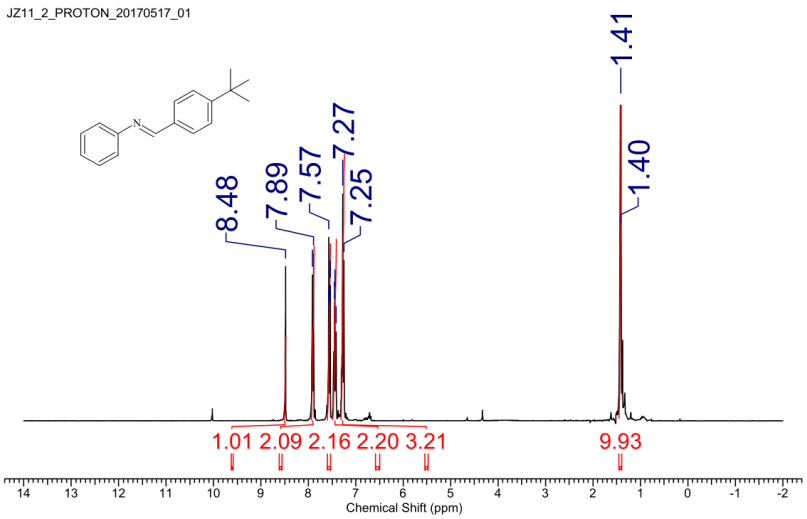
NMR-Spectra of *N*-(4-bromobenzylidene) aniline (1c)

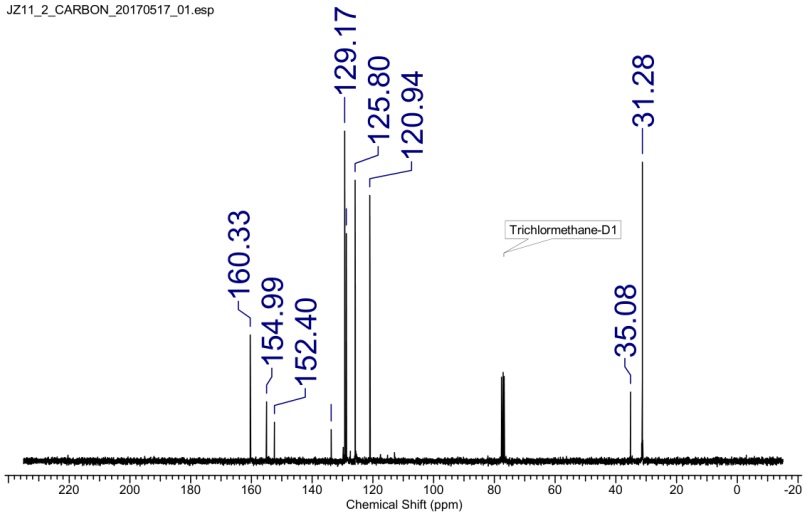




96

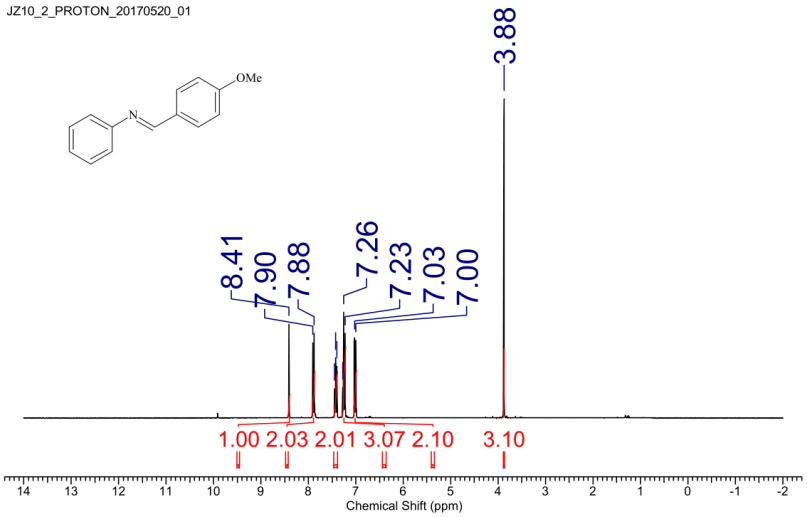
NMR-Spectra of *N*-(4-*tert*-butylbenzylidene) aniline (1d)

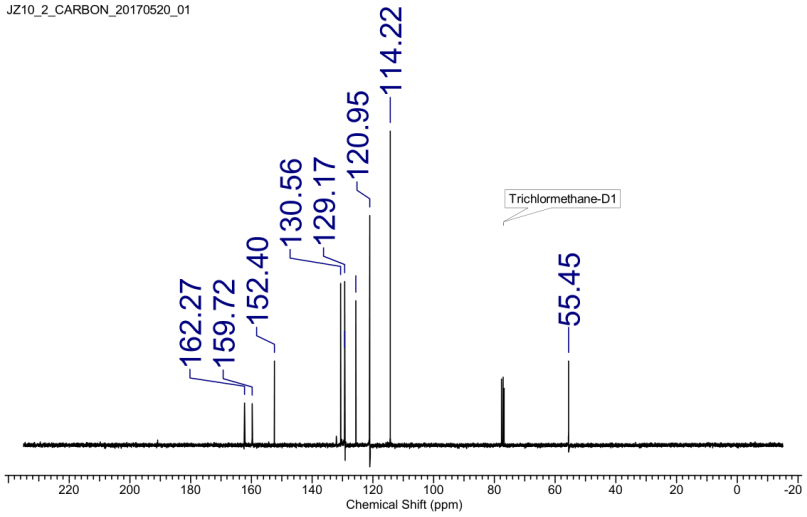




97

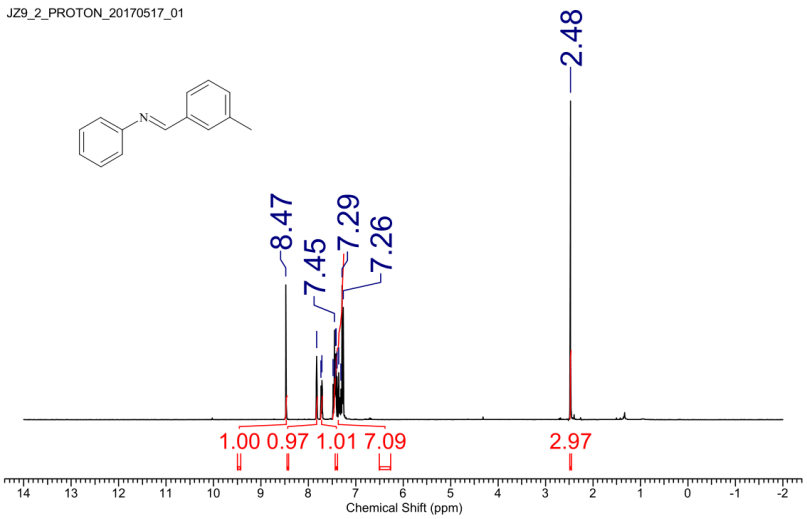
NMR-Spectra of *N*-(4-methoxybenzylidene) aniline (1e)

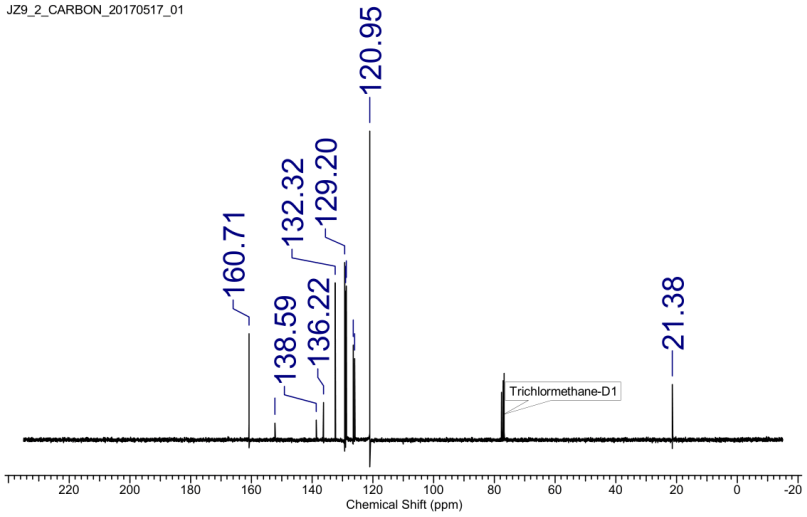




98

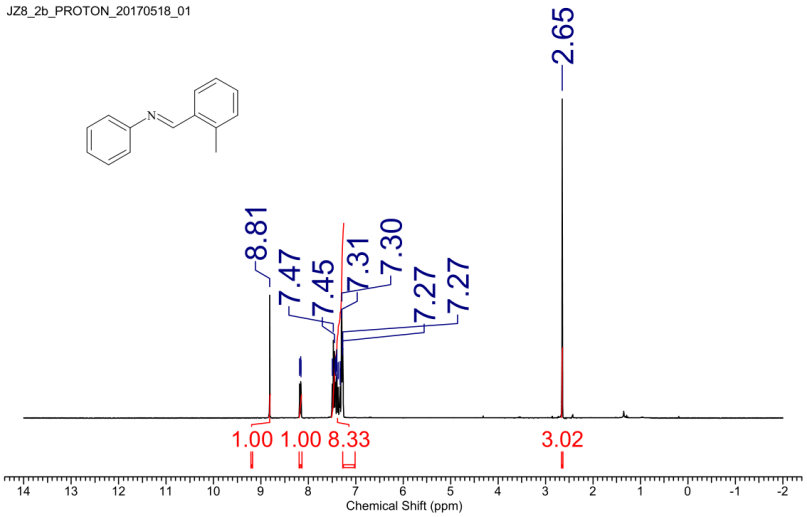
NMR-Spectra of *N*-(3-methylbenzylidene) aniline (1f)

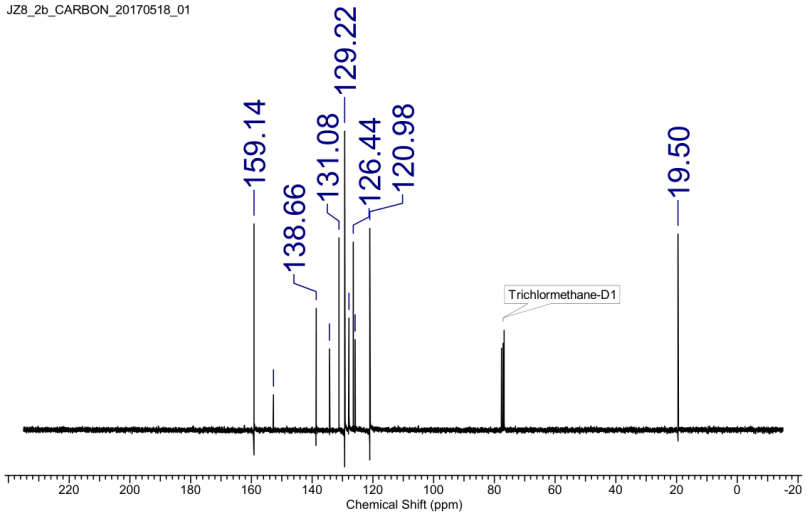




99

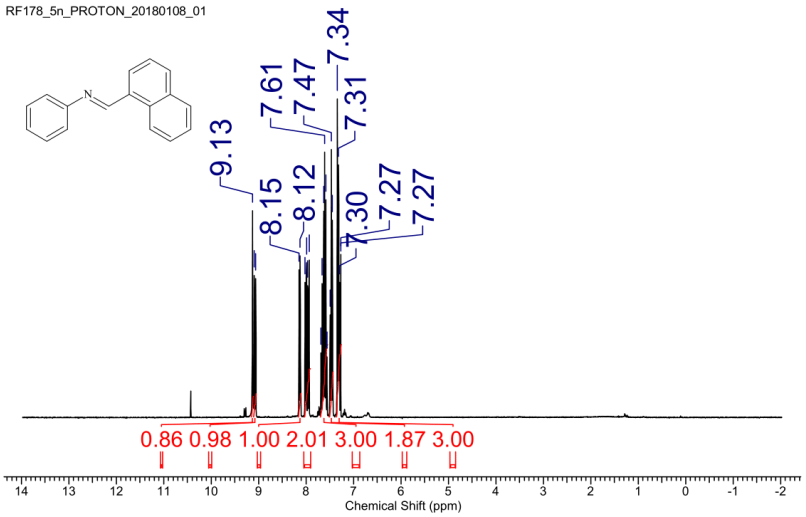
NMR-Spectra of *N*-(2-methylbenzylidene) aniline (1g)

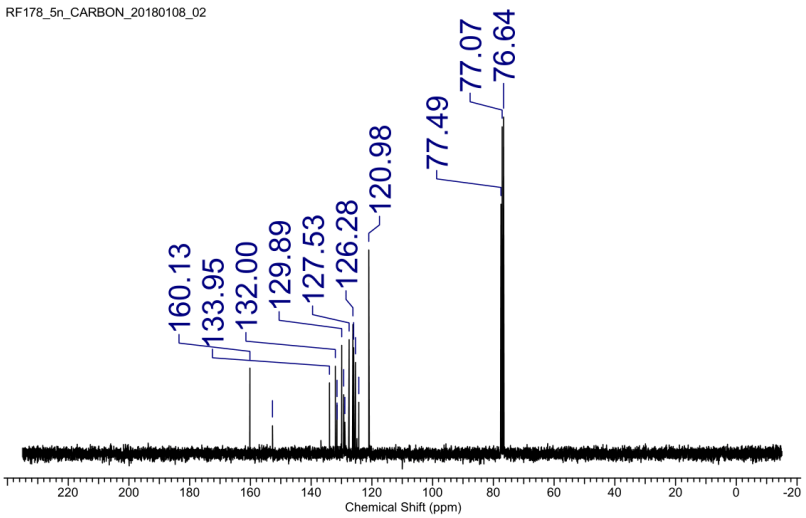




100

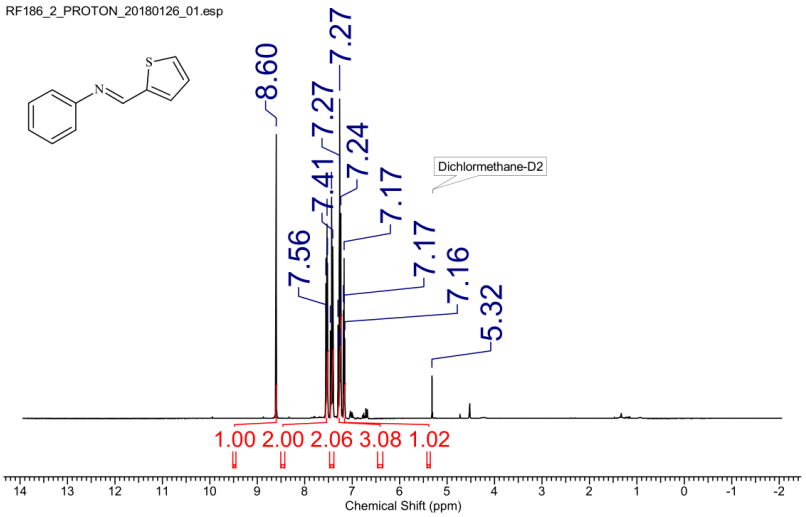
NMR-Spectra of *N*-(1-naphthylmethylene) aniline (1h)

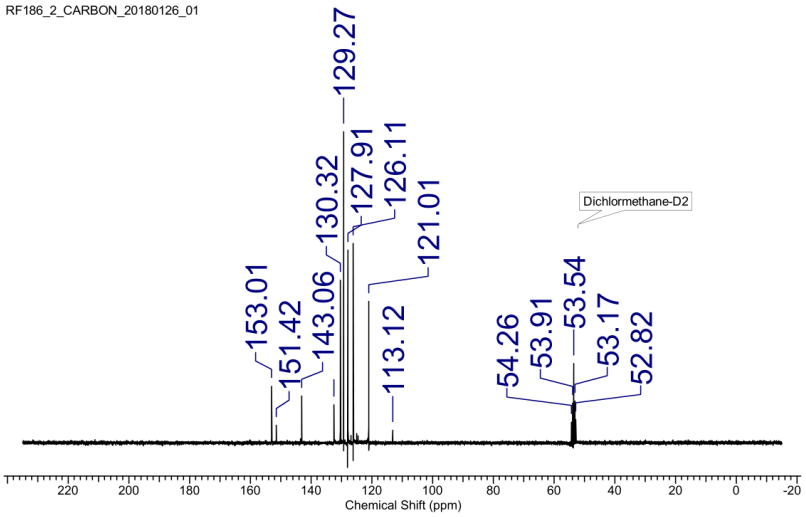




101

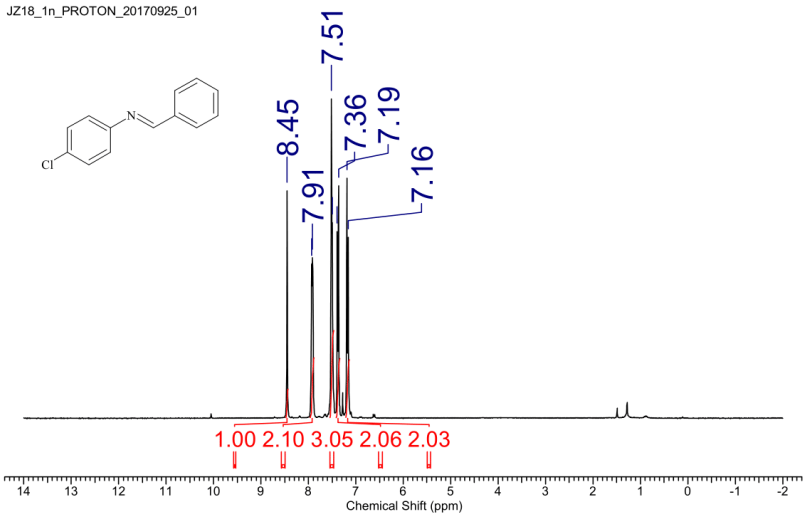
NMR-Spectra of *N*-(2-thienylmethylene) aniline (1i)

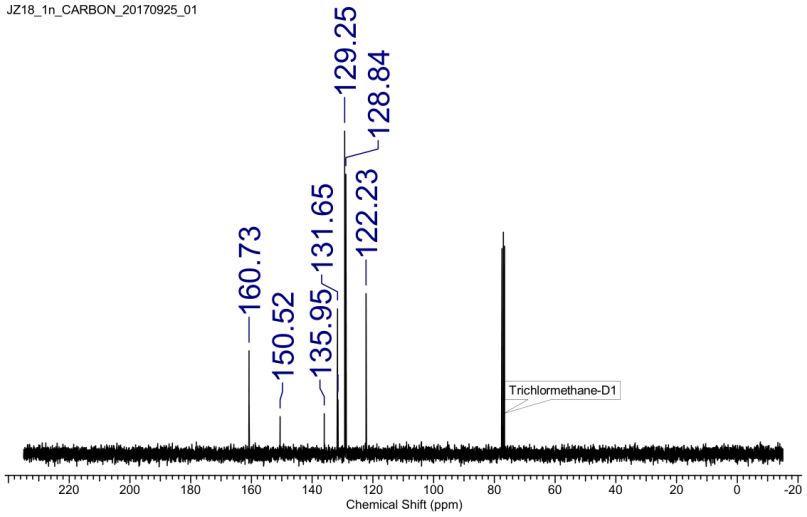




102

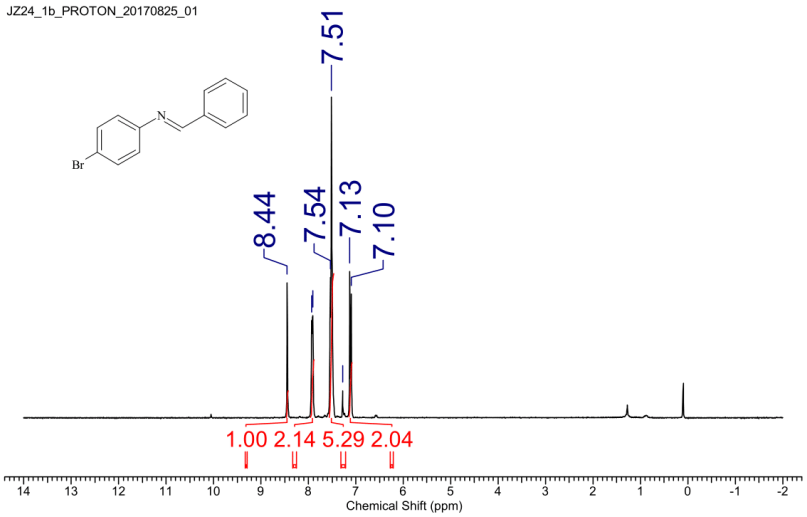
NMR-Spectra of *N*-benzyliden-4-chloroaniline (3a)

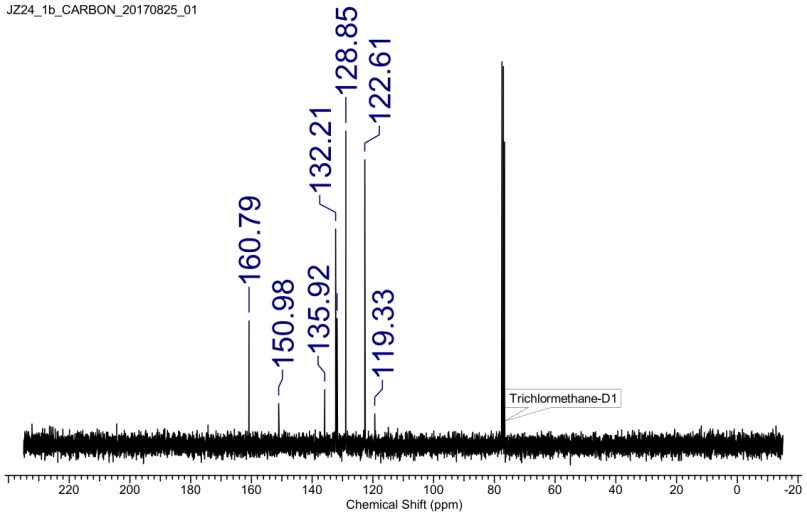




103

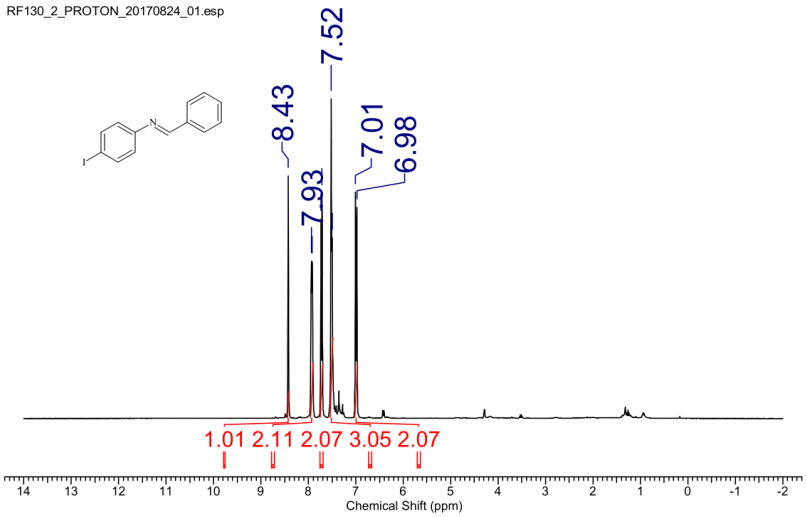
NMR-Spectra of *N*-benzyliden-4-bromoaniline (3b)

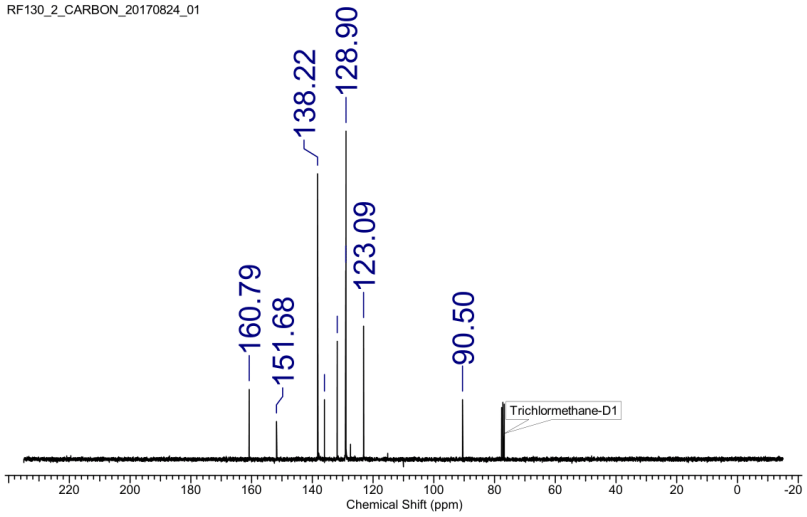




104

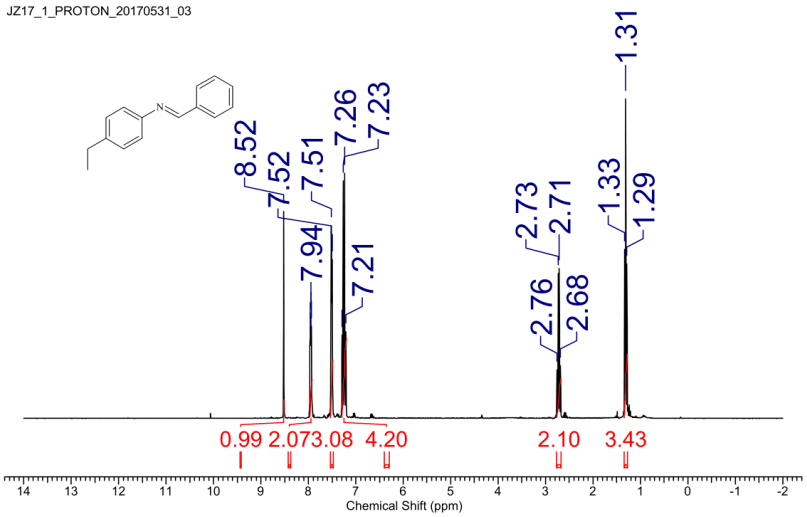
NMR-Spectra of *N*-benzyliden-4-iodoaniline (3c)

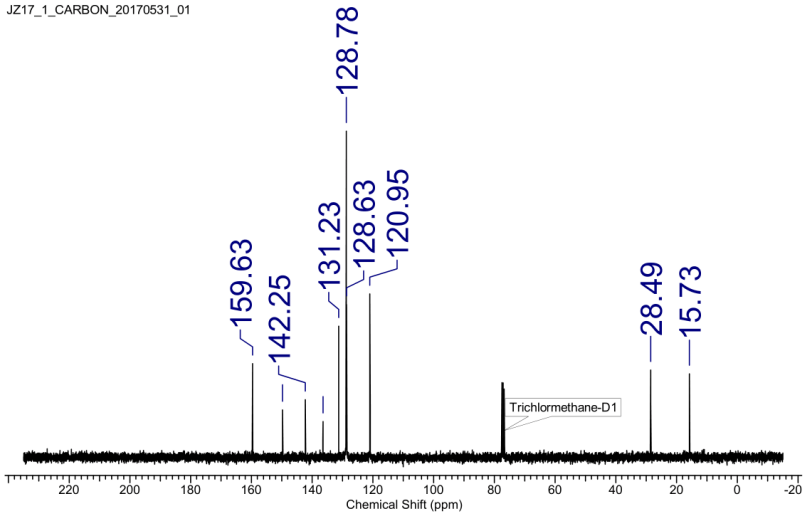




105

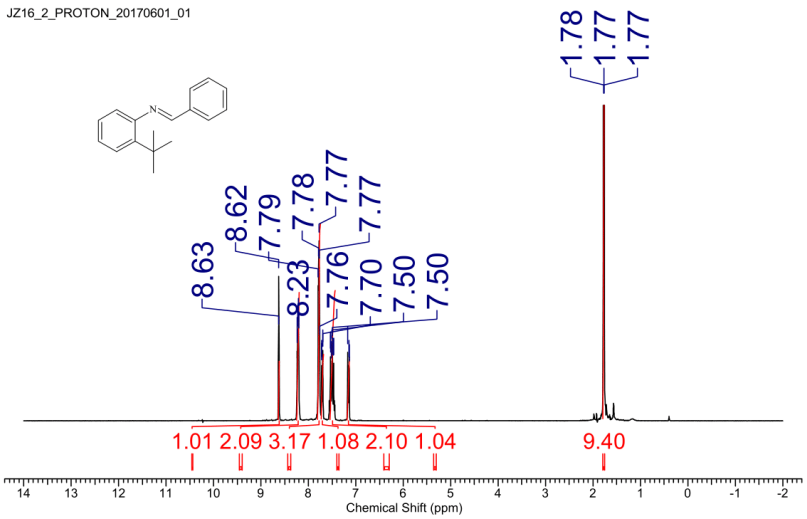
NMR-Spectra of *N*-benzyliden-4-ethylaniline (3d)

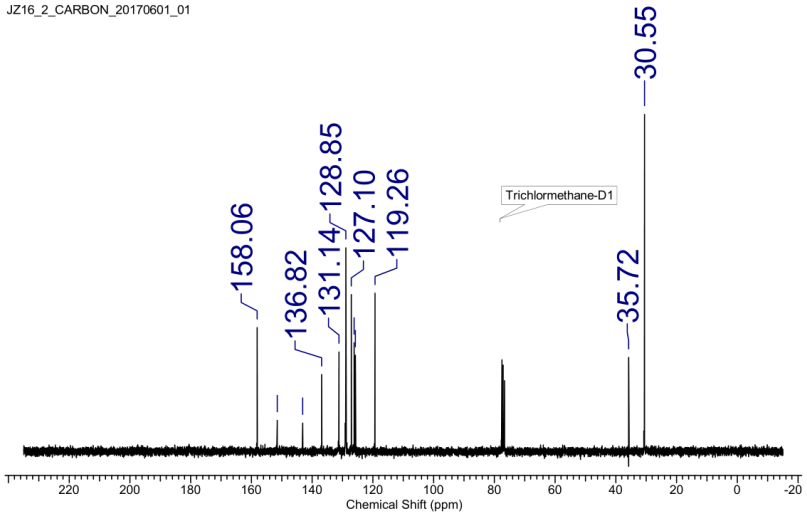




106

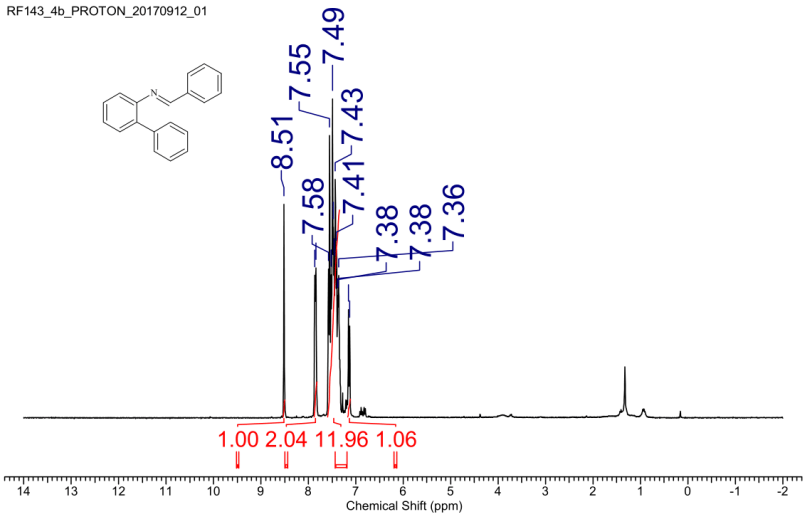
NMR-Spectra of *N*-benzyliden-2-*tert*-butylaniline (3e)

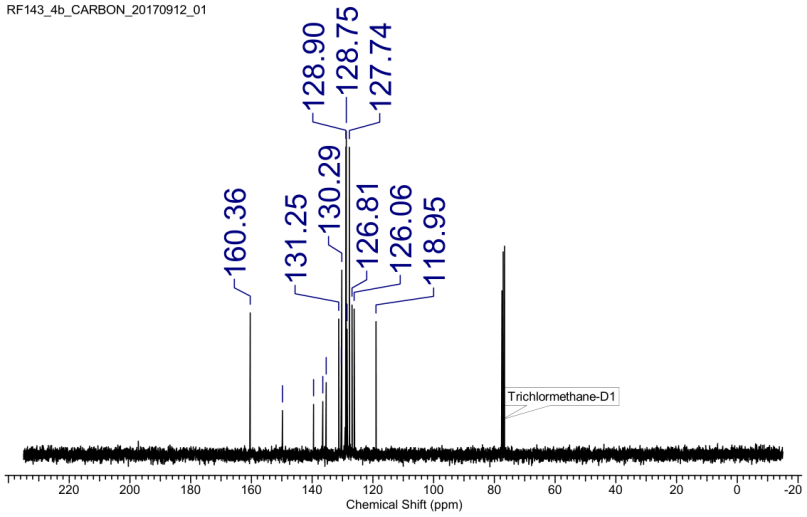




107

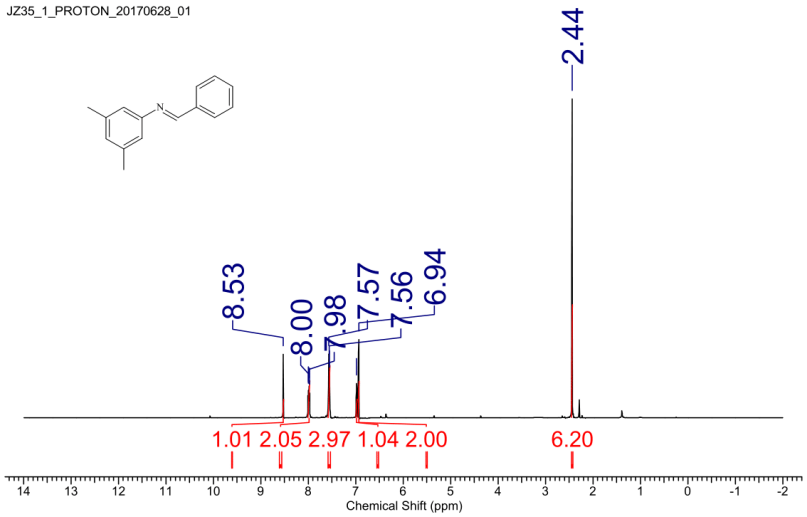
NMR-Spectra of *N*-benzyliden-2-phenylaniline (3f)

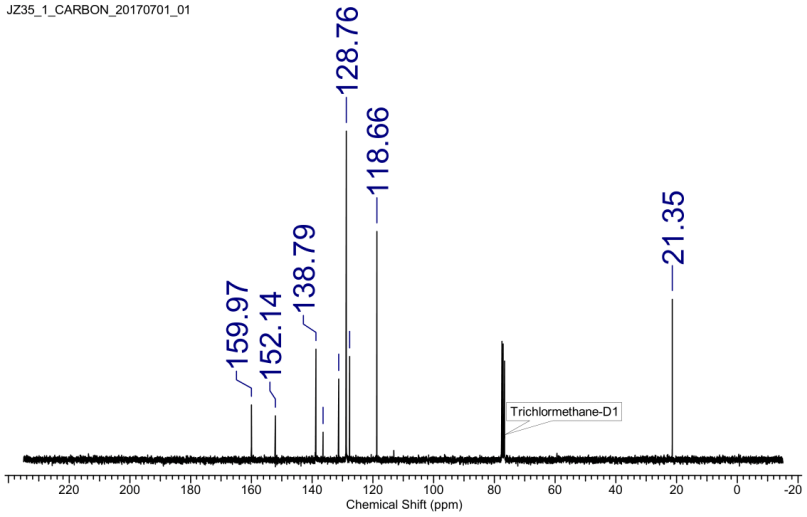




108

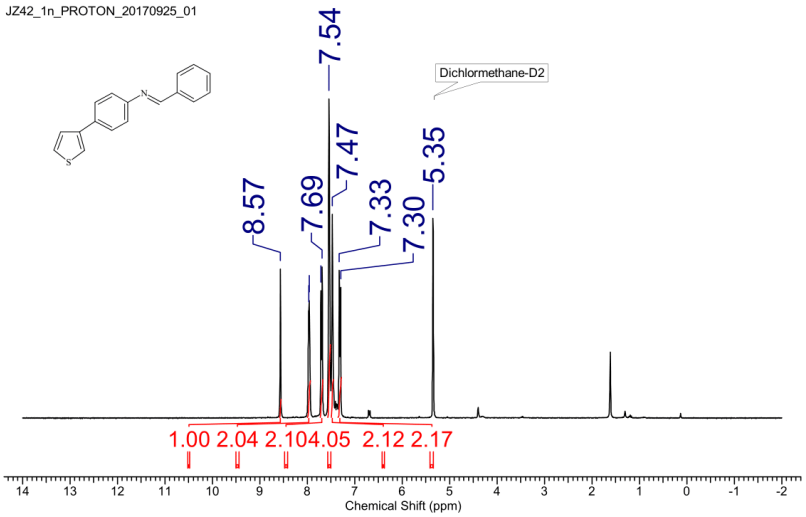
NMR-Spectra of *N*-benzyliden-3,5-dimethylaniline (3g)

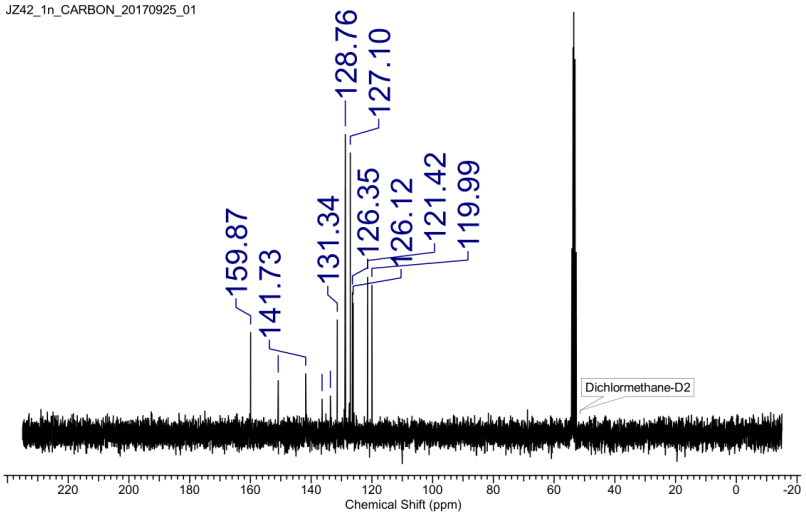




109

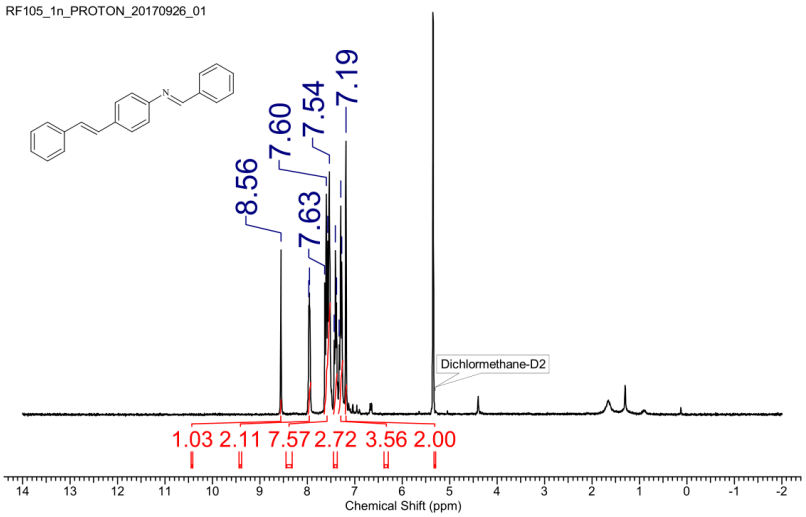
NMR-Spectra of *N*-benzyliden-4-(thiophen-3-yl) aniline (3h)

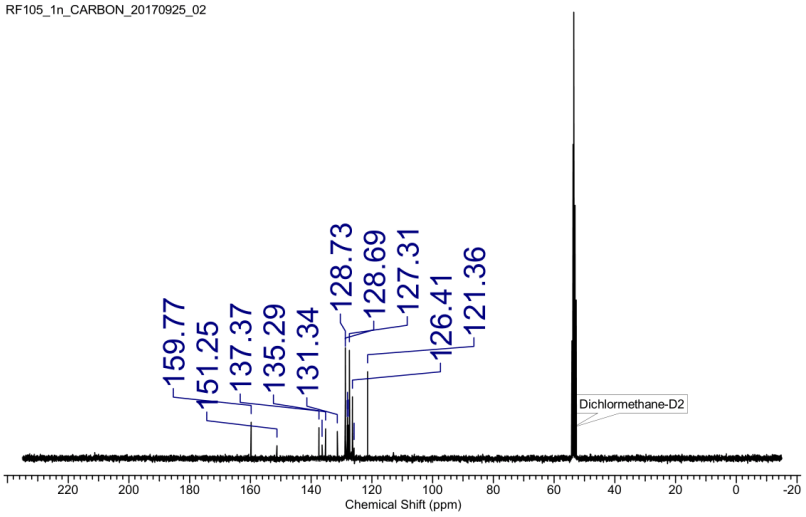




110

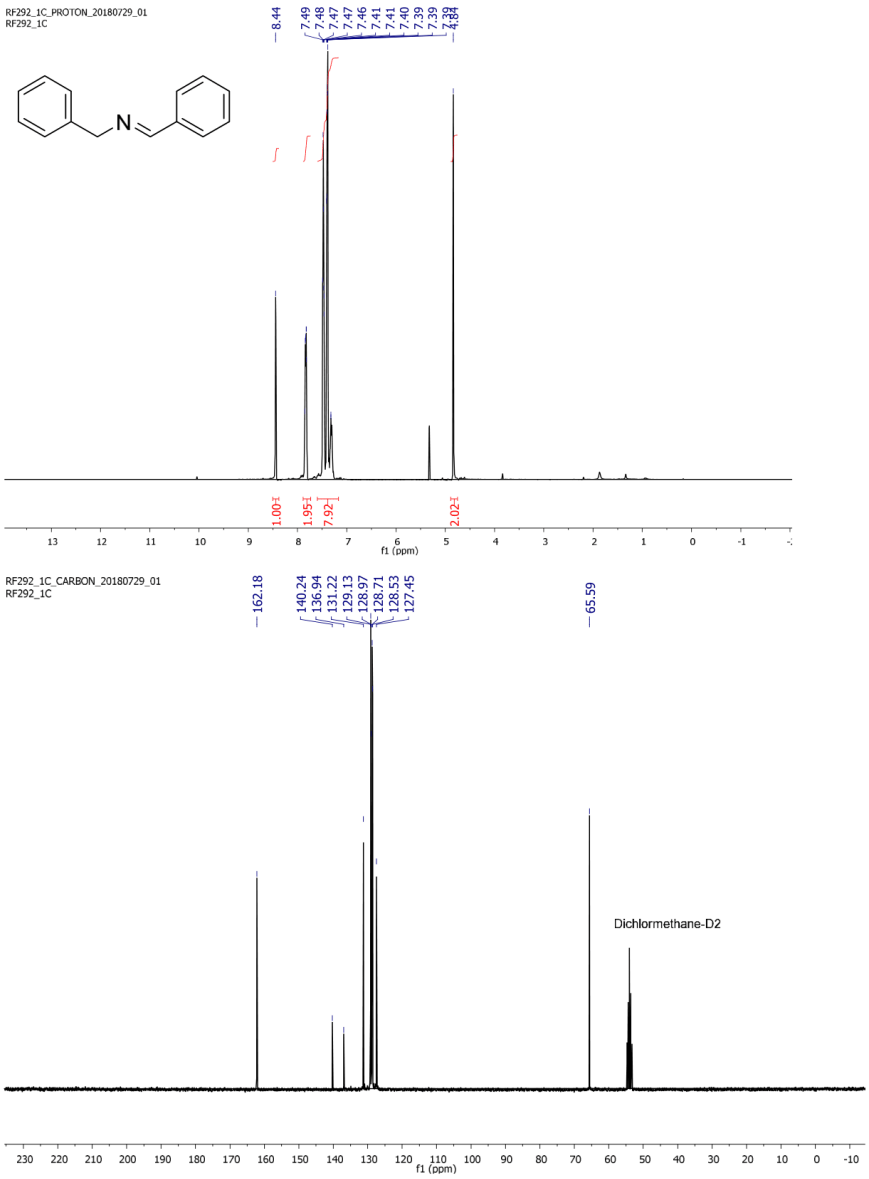
NMR-Spectra of *N*-benzyliden-4-aminostilbene (3i)





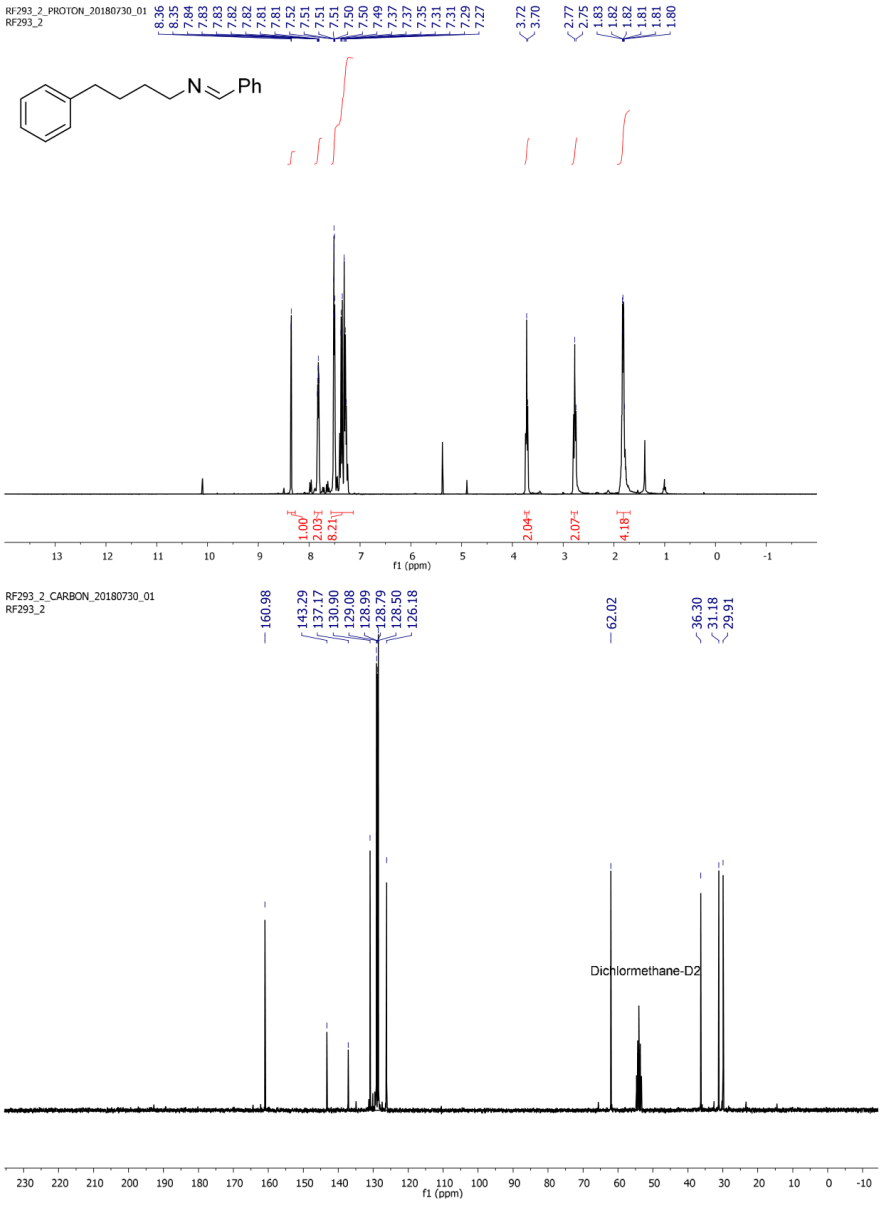
111

NMR-Spectra of *N*-(phenylmethylene)-benzenmethanamine (3j)



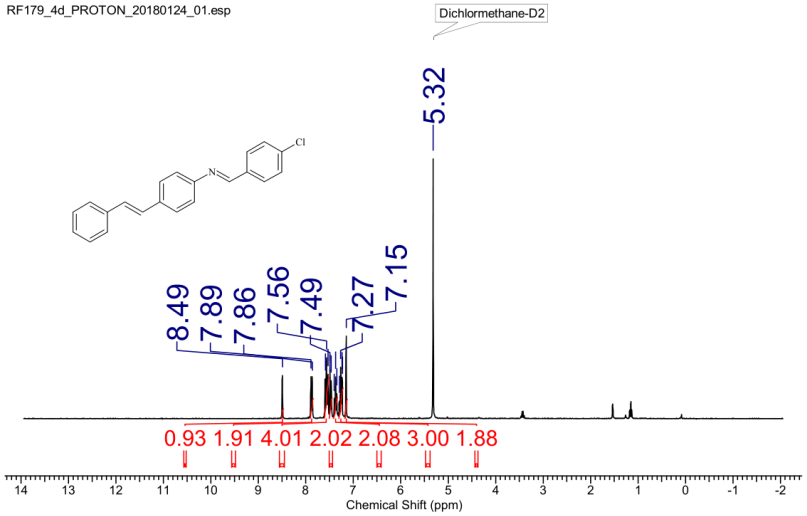
112

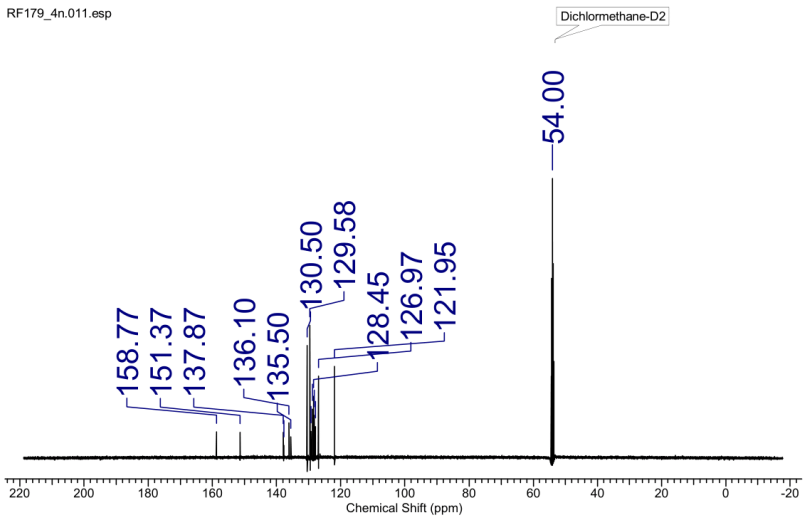
NMR-Spectra of *N*-(phenylmethylene)-benzenebutanamine (3k)



113

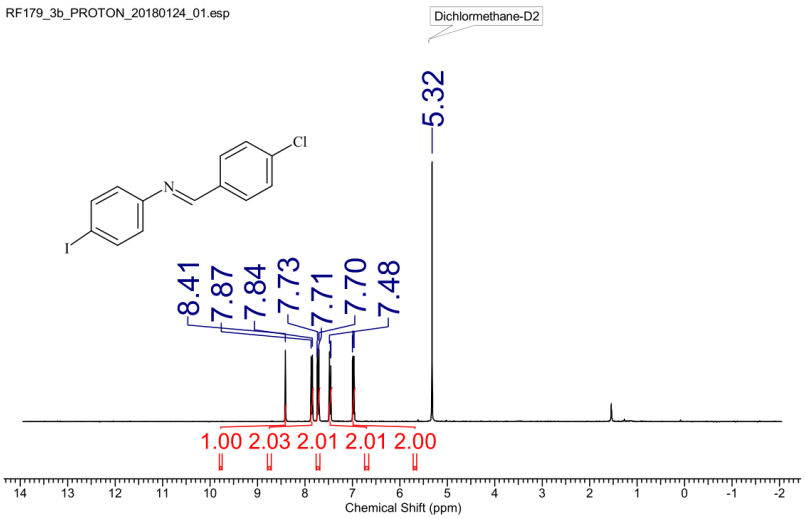
NMR-Spectra of *N*-[(4-chlorophenyl)methylene]-4-[2-phenylethenyl] benzenamine (3l)

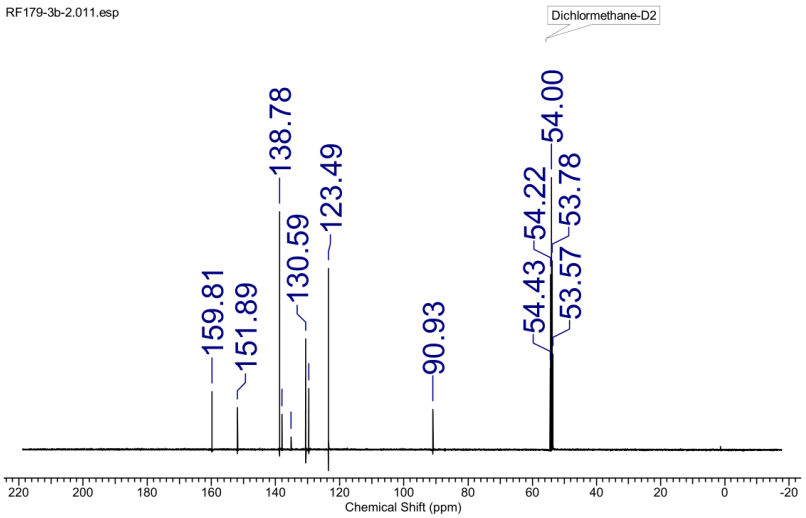




114

NMR-Spectra of *N*-[(4-chlorophenyl)methylene]-4-iodobenzenamine (3m)





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6 Rational Design of N-Heterocyclic Compound Classes via Regenerative Cyclization of Diamines

Robin Fertig, Felix Leowsky-Künstler, Torsten Irrgang, and Rhett Kempe*

Rational design of *N*-heterocyclic compound classes via regenerative cyclization of diamines.

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Rational design of *N*-heterocyclic compound classes via regenerative cyclization of diamines

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The discovery of reactions is a central topic in chemistry and especially interesting if access to compound classes, which have not yet been synthesized, is permitted. *N*-Heterocyclic compounds are very important due to their numerous applications in life and material science. We introduce here a consecutive three-component reaction, classes of *N*-heterocyclic compounds, and the associated synthesis concept (regenerative cyclisation). Our reaction starts with a diamine, which reacts with an amino alcohol via dehydrogenation, condensation, and cyclisation to form a new pair of amines that undergoes ring closure with an aldehyde, carbonyldiimidazole, or a dehydrogenated amino alcohol. Hydrogen is liberated in the first reaction step and the dehydrogenation catalyst used is based on manganese.

Reaction discovery is a central topic in chemistry[1] and especially interesting if access to classes of compounds, which have not yet been synthesized, can be provided. Unfortunately, concepts permitting a rational design of compound classes are rare. Iterative synthesis, the regeneration of the functional group(s) originally modified (Fig. 1A), is a suitable tool to introduce chemical diversity, which might be beneficial to address function or global challenges[2]. Recently, metal catalysed reactions have been in focus[2] and used for automated C-C bond formation[3] and selective olefin syntheses employing ethylene[4]. The ring closure of two functional groups generating a new pair of the same functional groups seems an option for synthesizing cyclic compounds (Fig. 1B)[2,5–7]. *N*-Heterocyclic compounds are very important fine and bulk chemicals due to their numerous applications in life and material sciences, for instance, as pharmaceuticals, agro chemicals, dyes, and conductive materials[8]. Classes of *N*-heterocyclic compounds might be accessible if the pair of functional groups that will be regenerated during cyclization are amines (Fig. 1C). We introduce here a catalytic consecutive three-component reaction and classes of *N*-heterocyclic compounds. Our reaction starts with a diamine, which reacts with an amino alcohol via dehydrogenation, condensation, and cyclisation to form a new pair of amines that undergoes ring closure with an aldehyde (Fig. 1C), carbonyldiimidazole or an amino alcohol. Hydrogen is liberated in the first reaction step[9,10] and the dehydrogenation catalyst used is based on the Earth-abundant metal manganese[11–14]. Our reaction proceeds diastereoselectively, has a large scope, and many functional groups can be tolerated, including hydrogenation-sensitive examples, despite the presence of hydrogen and a hydrogenation catalyst[15]. Upscaling is easily accomplished and a catalytic amount of base is required. All *N*-heterocyclic compounds synthesized here have not yet been reported[16].

Results

Reaction optimization

We started our investigations with an optimisation of the reaction conditions of the reaction of 1,8-diaminonaphthalene with 2-aminobenzyl alcohol to form the 2-(2,3-dihydro-1*H*-perimidin-2yl) aniline **A1** (Fig. 2). The synthesis of 2,3-dihydro-1*H*-perimidines from 1,8-diaminonaphtalene and aldehydes is a classic reaction and has been reported already in 1964[17]. Recently, the catalytic generation of the aldehyde for such a coupling via dehydrogenation catalysis employing a phosphine free manganese complex has been reported[18]. The key to our synthesis is the use of amino alcohols to regenerate the set of two amines and we started our investigation with 2-aminobenzyl alcohol. In case of amino alcohols, the corresponding aldehyde can undergo self-condensation and the catalytic generation via dehydrogenation catalysis seems an elegant way to address this issue. Different Earth-abundant metal (Mn, Fe, Co) complexes stabilized by pincer ligands were tested as precatalysts for the dehydrogenation step. Manganese

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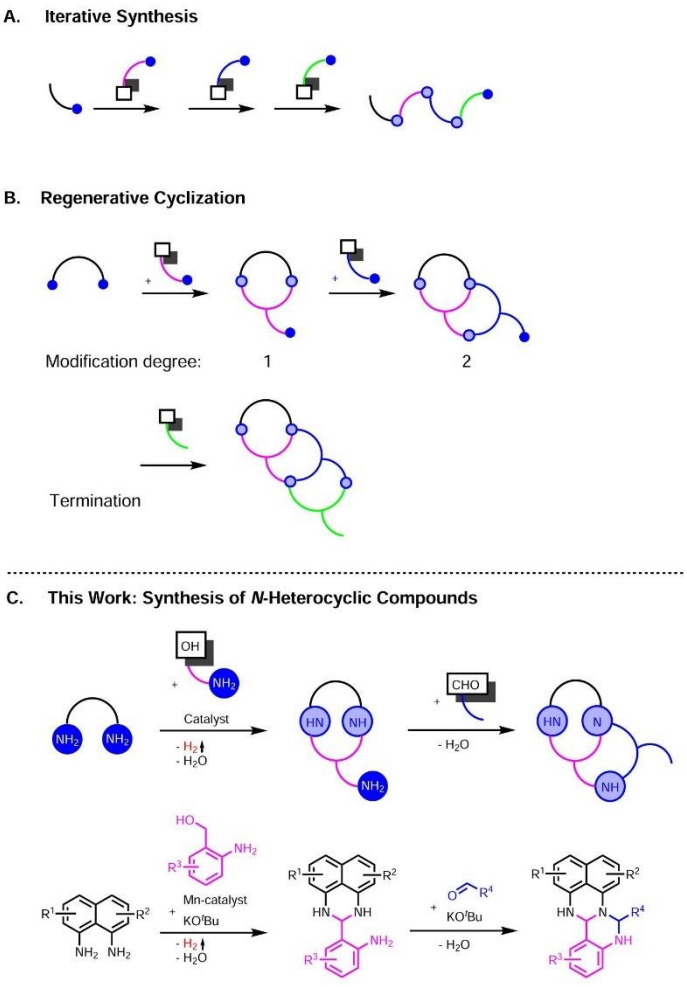

Fig. 1 | Relevant concepts and work introduced here. A Regenerating the functional group again that has been modified originally (iterative synthesis) can lead to chemical diversity if different building blocks are used **B** Classes of (poly)cyclic compounds can be conceived via ring closure chemistry. The set of functional groups originally used has to be formed again during the ring closure reaction (regenerative cyclization). Repeating ring closure steps should lead to classes of (poly)cyclic compounds, which have not yet been synthesized, at some stage or modification degree. **C** *N*-Heterocyclic compounds introduced here with amines being the key functional groups, applying a modification degree of two, and a catalytic amino alcohol dehydrogenation-based ring closure reaction as the first step.

catalysts stabilized by a PN_5P-pincer ligand (Fig. 2. top right) showed the highest activity, determined by the yield of the product obtained under the given conditions. Such ligands are easy to synthesize from 2,6-diaminotriazines and dialkyl- or diarylphosphine chlorides. A significantly lower activity was observed if the ligand backbone of the manganese precatalysts was changed from a triazine (PN_5P) to a pyridine (PN_3P) moiety, (precatalysts Mn-**VI**, Mn-**VII**, Supplementary Table 1)[19–22]. Other reaction parameters, such as temperature, precatalyst loading, type and amount of solvent, and base were optimised—see Supplementary Tables 1–7 for details. The optimal reaction parameters for the synthesis of **A1** (Fig. 2) were 1 mol% precatalyst [Mn-**I**], 30 mol% KO^{t}Bu, 3 mL 2-MeTHF at 100 °C with a reaction time of 2 h. The reaction proceeded in a tube with a bubble counter to facilitate the release of hydrogen during the dehydrogenation of the amino alcohol.

Substrate scope

Regarding the exploration of the functional group tolerance, we used 21 aminobenzyl alcohol derivatives and isolated the corresponding 2,3-dihydro-1*H*-perimidines **A1**-**A21**, referred to here as amino perimidines for simplification (Fig. 2). The model reaction led to the product **A1** in an isolated yield of 90%. Single crystals were obtained via recrystallization from ethyl acetate/pentane (2:1) at −18 °C and analysed by X-ray diffraction confirming the molecular structure of **A1** (Fig. 2; for more details, see Supplementary Data 1).

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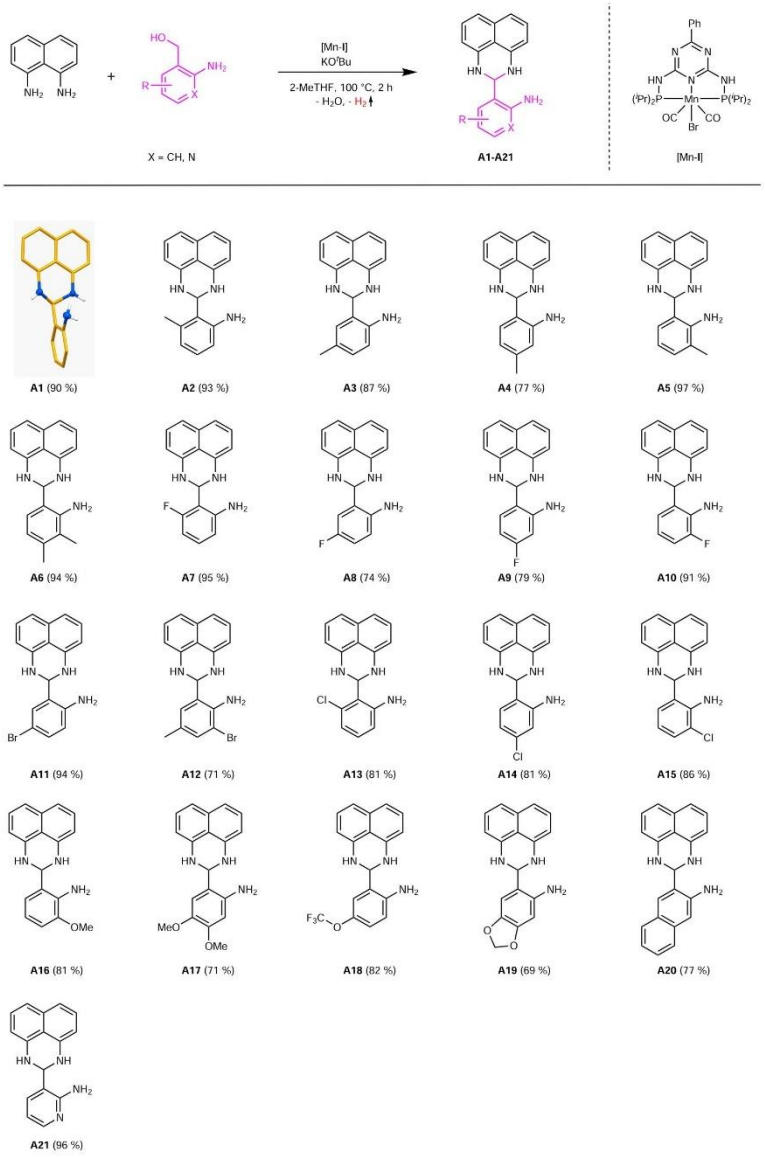

Fig. 2 | Synthesis of 2,3-dihydro-1*H*-perimidines A1-A21 via liberation of H_2. Reaction conditions: 2 mmol 1,8-diaminonaphthalene, 2 mmol amino alcohol, 0.6 mmol KO^{t}Bu, 1 mol% [Mn-**I**] (0.02 mmol), 3 mL 2-MeTHF, 100 °C (oil bath), 2 h, open system (anaerobic conditions). Isolated yields in brackets.

The products **A2**-**A6** were obtained in yields of 77–97%, demonstrating the tolerance of electron-donating groups on every position at the phenyl substituent. The tolerance of electron withdrawing substituents was shown by using fluoro- (**A7**-**A10**), chloro- (**A13**-**A15**), and bromo-aminobenzyl (**A11**, **A12**) alcohols. The corresponding products were isolated in yields ranging from 71–95%. The fluoro substituent was used as an example to show the tolerance at each position of the phenyl substituent. Substrates containing methoxy (**A16**), dimethoxy (**A17**), or trifluormethoxy (**A18**) groups were converted smoothly to the products desired and could be isolated in yields up to 82%. An amino perimidine bearing an acetal (**A19**) could be isolated in a yield of 69%. Using a polycyclic aromatic amino alcohol provided **A20** in a yield of 77%. The use of a *N*-heterocyclic amino alcohol led to **A21** in a nearly quantitative yield. The amino perimidines (**A1**-**A24**) were isolated as solids in colours from white to yellow. Each product was not described at that stage. The

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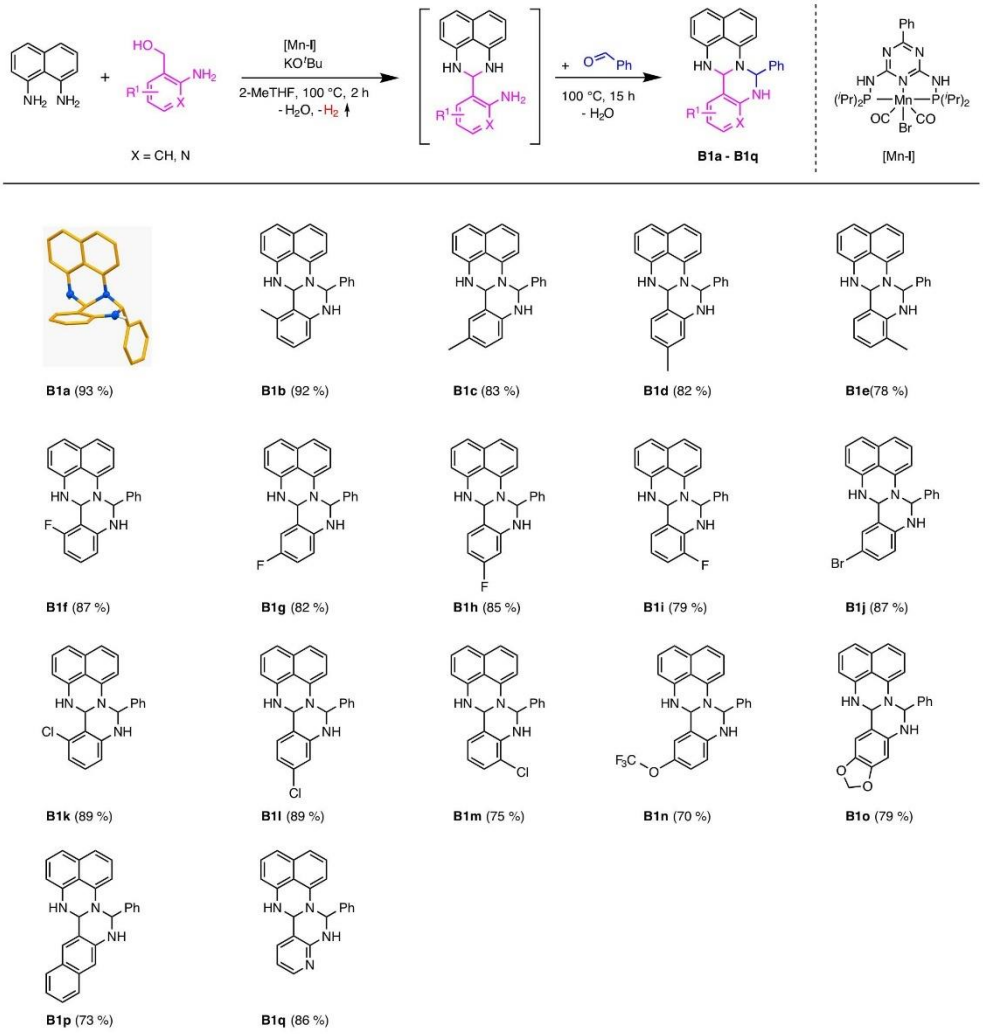

Fig. 3 | Synthesis of fertigines B1a-B1q: 2-aminobenzyl alcohol variations. Reaction conditions: 2 mmol 1,8-diaminonaphthalene, 2 mmol amino alcohol, 0.6 mmol KO^{t}Bu, 1 mol% [Mn-**I**] (0.02 mmol), 3 mL 2-MeTHF, 100 °C (oil bath), 2 h + 15 h, open system (anaerobic conditions). After 2 h: addition of 2 mmol benzaldehyde. Isolated yields in brackets.

amino perimidines generally showed a good solubility in polar solvents, were air-stable, and easy to crystallize (e.g., in ethyl acetate/pentane).

The primary amine functionality of the modification degree 1 and its spatial distance to the NH-groups can be used for a second ring closure (modification degree 2). Aldehydes represent simple, easy-to-handle, inexpensive, diversely available and green or sustainable[23,24] building blocks and can undergo condensation reactions with amines. This modification degree 2 leads to a class of compounds consisting of two six-membered *N*-heterocyclic ring systems (Fig. 3). We propose the name fertigines for this class of *N*-heterocycles. Keeping the synthesis procedure of the fertigines as simple as possible, we synthesized them via a consecutive multicomponent one-pot reaction using the conditions optimised for the synthesis of the amino perimidines followed by the addition of aldehyde (Fig. 3). The addition of benzaldehyde led to the fertigine **B1a** in an isolated yield of 93% after a reaction time of 15 h. **B1a** is a white solid that is soluble in polar solvents. Crystals for single crystal X-ray analysis were obtained by recrystallization of **B1a** (Fig. 3) in ethyl acetate/pentane at −18 °C. The molecular structure of **B1a** is shown in Fig. 3 (for more details, see Supplementary Data 2). The second ring closure proceeded smoothly to the products **B1b-B1e** in yields of 78–92%, indicating no significant influence of the position of electron-donating groups attached to the

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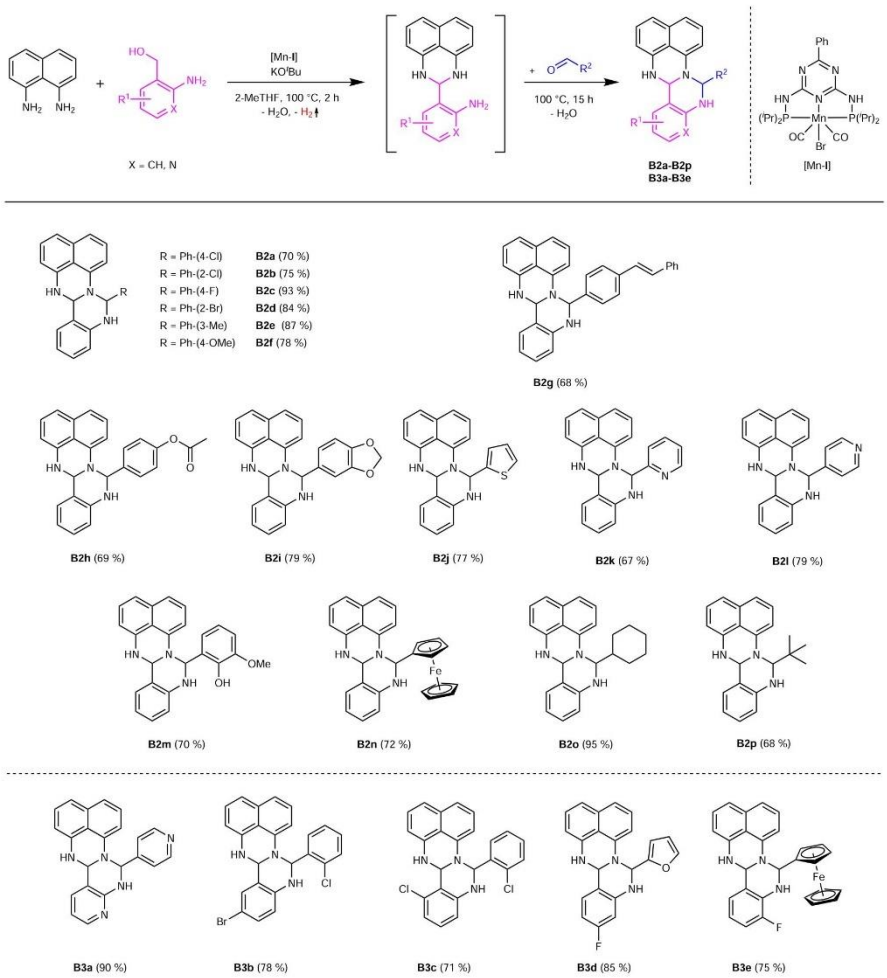

Fig. 4 | Synthesis of fertigines B2a-B2p and B3a-B3e: aldehyde variations. Reaction conditions: 2 mmol 1,8-diaminonaphthalene, 2 mmol 2-aminobenzyl alcohol derivatives, 0.6 mmol KO^{t}Bu, 1 mol% [Mn-**I**] (0.02 mmol), 3 mL 2-MeTHF, 100 °C, 2 h + 15 h, open system (anaerobic conditions). After 2 h: addition of 2 mmol aldehyde. Isolated yields in brackets.

aminobenzyl alcohol moiety. Analogously, we investigated the position-dependent influence of electron-withdrawing groups on the outcome of the reaction. We chose the fluoro substituent and could not observe any significant impact on the second ring closure, obtaining the corresponding fertigines **B1f**-**B1i** in isolated yields of up to 87%. The use of further halogenated substrates, such as 5-bromo- (**B1j**), 6-chloro- (**B1k**), 4-chloro- (**B1l**) or 3-chloro-2-aminobenzyl alcohol (**B1m**), for fertigine synthesis led to the products desired in yields between 75 and 89%. **B1n**, bearing a trifluoromethoxy-group, could be obtained in an isolated yield of 70%. A fertigine with an acetal group (**B1o**) on the former amino alcohol moiety was isolated in a yield of 79%. Applying an amino alcohol with a polycyclic aromatic backbone provided the product **B1p** in an isolated yield of 73%. The use of 2-amino-pyridylmethanol resulted in the corresponding product **B1q** in an isolated yield of 86%.

We next investigated the substrate scope of fertigines by using various aldehydes (Fig. 4). After adding benzaldehydes with chloro-substituents in the *para*- and *ortho*-position, we obtained the corresponding fertigines (**B2a**–**B2b**) in isolated yields of 70 - 75%. Other halogenated benzaldehydes, such as *para*-fluorobenzaldehyde or *ortho*-bromobenzaldehyde, reacted smoothly to the corresponding products (**B2c** and **B2d**) and could be isolated in yields of 93 and 84%, respectively. The addition of 3-methylbenzaldehyde to the model reaction (Fig. 2) led to the product **B2e** in a yield of 87%. Methoxy-substituted benzaldehyde provided the corresponding fertigine **B2f**, respectively, in isolated yield of 78%. According to these results, no coherence between the electronic properties of the substituents on benzaldehyde and the efficiency of the second ring closure was observed. Using benzaldehydes for the synthesis of fertigine with a C–C double bond (**B2g**) or an acetoxy group (**B2h**) in the para-

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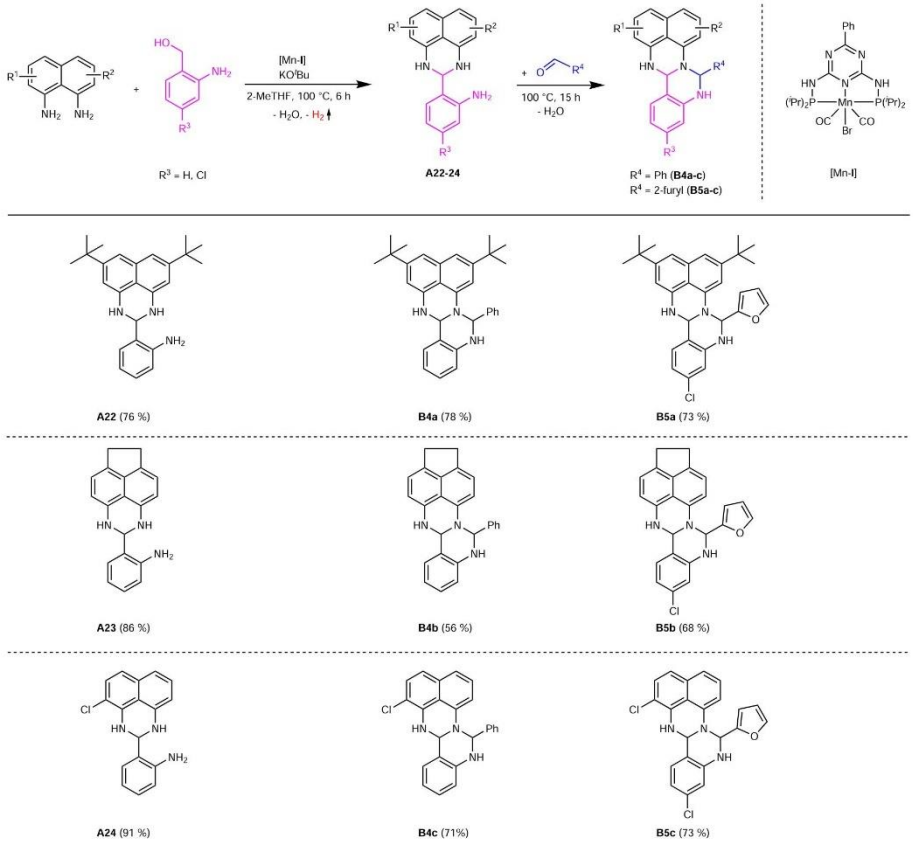

Fig. 5 | Variation of the diamine for the synthesis of amino perimidines and fertigines. Reaction conditions: 1 mmol 1,8-diaminonaphthalene derivative, 1 mmol 2-aminobenzyl alcohol, 0.3 mmol KO^{t}Bu, 1 mol% [Mn-**I**] (0.01 mmol), 3 mL 2-MeTHF, 100 °C, 6 h, open system (anaerobic conditions). In order to synthesize the fertigines, 1 mmol aldehyde is added after 6 h. Isolated yields in brackets.

position, the yields decreased to 68 and 69%, respectively, but no notable side reactions occurred. We next investigated several aldehydes with heterocyclic moieties for the synthesis of the corresponding fertigines such as piperonal (**B2i**), thiophen-2-carbaldehyde (**B2j**), 2-formylpyridine (**B2k**) and 4-formylpyridine (**B2l**) and obtained those products in isolated yields up to 79%. The use of *ortho*-vanillin provided **B2m** in an isolated yield of 70%. We also tested an aldehyde based on a metal organic compound, namely, ferrocenaldehyde, and could isolate the fertigine **B2n** in a yield of 72%. The addition of aliphatic aldehydes to the reaction led to fertigines **B2o** and **B2p** in yields of 95 and 68%, respectively. The solubility properties of the fertigines changed using these aldehydes and a good solubility in pentane was observed. There was almost no limitation on the type of aldehyde that could be used for the second ring closure, indicating a very broad scope of our consecutive 3-component reaction. Using an aldehyde and an amino alcohol with a pyridine-backbone, we obtained the fertigine **B3a** in a yield of 90%. Double halogenated fertigines, such as **B3b** or **B3c**, could be isolated in yields of up to 78% by using the corresponding educts. The synthesis of fluorinated fertigines with an *O*-heterocycle (**B3d**) or a metal organic compound (**B3e**) proceeded in yields of 85 and 75%, respectively.

We next addressed the flexibility of the naphthalene diamine in order to achieve a high degree of functionalisation in the resulting fertigines (Fig. 5). Firstly, we investigated the influence of substituted 1,8-diaminonaphthalenes and isolated the resulting amino perimidines **A22**-**A24** (Fig. 5). The use of 3,6-di-*tert*-butyl-1,8-diaminonaphthalene led to the corresponding product **A22** in an isolated yield of 76%. Applying 5,6-diaminoacenaphthene for the catalytic step, an ethylene-bridged naphthalene moiety was achieved and the amino perimidine **A23** was isolated in a yield of 86%. Using 2-chloro-1,8-naphthalenediamine, no decrease in the catalytic activity was observed and the product **A24** was obtained in a yield of 91%. The second modification degree using this 1,8-diaminonaphthalene derivative (**B4a**-**B4c**; **B5a**-**B5c**) was achieved by adding the respective aldehyde after 6 h reaction time. The addition of benzaldehyde led to the products **B4a**-**B4c** desired in yields of up to 78%, observing no significant impact of the naphthalene substitution on the second ring closure. The yield of **B4b** decreased to 56% due to solvation problems. The products **B5a**-**B5c** were isolated in yields from 68–73%.

Upscaling experiments of the model reaction revealed similar yields for amino perimidine as well as fertigine synthesis, obtaining the

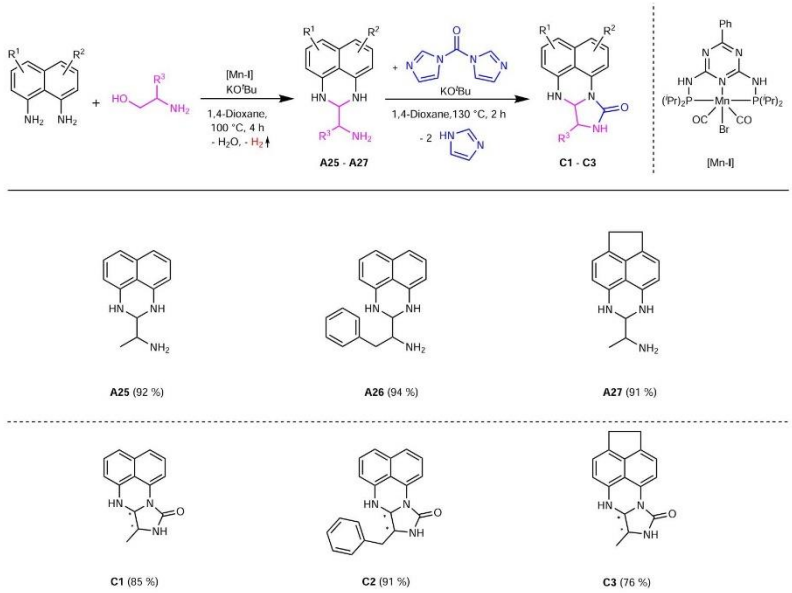

Fig. 6 | Synthesis of amino alkyl perimidines A25-A27[a] and imidazo[1,5-a]perimidin-10-ones (kuenstlerines) C1-C3. Reaction conditions: 2 mmol 1,8-diaminonaphthalene, 2.2 mmol amino alcohol, 0.6 mmol KO^{t}Bu, 1 mol% [Mn-**I**] (0.02 mmol), 12 mL 1,4-Dioxane, 100 °C (oil bath), 4 h, open system (anaerobic conditions). Isolated yields in brackets. [b]Reaction conditions: 2 mmol perimidine **A25-27**, 2.3 mmol CDI, 0.6 mmol KO^{t}Bu, 10 mL 1,4-Dioxane, 130 °C (oil bath), 2 h, pressure tube (anaerobic conditions). Isolated yields in brackets.

products **A1** and **B1a** desired in multigram scale (Supplementary Information Section 4).

We also examined the reaction of the amino perimidines starting from aliphatic amino alcohols to obtain amino alkyl perimidines (Fig. 6). For this, the reactions of L-alaninol or L-phenylalaninol with 1,8-diaminonaphthalene derivatives were carried out under the optimized conditions for the amino perimidines with only changing the solvent from 2-MeTHF to 1,4-dioxane. The resulting amino alkyl perimidines **A25-A27** were obtained in yields of 91–94% as brown viscous oils and showed a good solubility in polar solvents. Compared to the amino perimidines **A1-A21**, the amino alkyl perimidines **A25-A27** are not air stable. Afterwards it was not possible to perform a ring closure reaction between the amino alkyl perimidines **A25-A27** and aldehydes. Therefore we used *N*,*N*'-carbonyldiimidazole (CDI) as coupling agent and C1 building block to achieve a five-membered *N*-heterocyclic ring. By using a base for the reaction of **A25-A27** with CDI we obtained the corresponding kuenstlerines **C1-C3** (Fig. 6). The optimized reaction parameters for the synthesis of **C1-C3** are 30 mol % KO^{t}Bu, 1,4-dioxane as solvent, 1.15 eq. CDI at 130 °C with a reaction time of 2 h in a pressure tube (Supplementary Tables 8–13). We obtained the products desired in yields between 76–91% as light brown to reddish brown solids, which are air sensitive. After the second ring closure, diastereomers were obtained, which can be separated by column chromatography. The diastereomeric ratios varied between 71:29 (**C1**), 88:12 (**C2**), and 61:19 (**C3**). The amino alkyl perimidines **A25-A27** and kuenstlerienes **C1-C3** synthesized here have not yet been reported.

We were also interested in the possibility of synthesizing amino fertigines, from which degree of modification 3 could be achieved. Therefore, we carried out the reactions without further optimization as consecutive one-pot reactions such as for the synthesis of the fertigines **B1-B5**, and used 2-aminobenzyl alcohols instead of aldehydes for the second ring closure step (Fig. 7). The amino fertigines **B6a-B6c** were obtained in yields of 38 – 79% as green solids, are poorly soluble in polar solvents and air-stable.

Mechanistic studies

The mechanism proposed for the catalytic cycle and the ring closure cascade is shown in Fig. 8. The catalyst [Mn-**Ia**] was obtained by adding KO^{t}Bu to the precatalyst complex [Mn-**I**][19,20]. The triazine permits the deprotonation of the ligand backbone by strong metal bases, which has been shown to be beneficial in hydrogenation[19,20] and dehydrogenation catalysis[21,22]. The manganese-catalysed dehydrogenation of 2-aminobenzyl alcohol proceeds via the liberation of one equivalent of hydrogen, as analysed by GC-analysis. In the absence of naphthalene diamine, self-condensation of the 2-aminobenzaldehyde generated in situ took place (Supplementary Fig. 19). We propose the formation of an imine with a subsequent intramolecular ring closure for the amino perimidine synthesis, as revealed by time-dependent ^{1}H NMR studies. Interestingly, no reaction was observed in the absence of KO^{t}Bu, indicating a base-mediated cyclization (Supplementary Figs. 22–24). As the next step, we proposed the in situ deprotonation of one amino functionality of the aminoperimidine obtained by KO^{t}Bu (Fig. 8). A yellow crystalline solid (**A1K**) precipitated if KO^{t}Bu was added to the amino perimidine **A1** in THF (Supplementary Figs. 25–27). If water was added to **A1K**, it was transformed back to the amino perimidine **A1** accompanied by the formation of KOH (Supplementary Fig. 28). Time-dependent ^{1}H NMR studies indicate that **A1K** is an intermediate of the second ring closure step (Fig. 8). **A1K** is able to react to the fertigine with benzaldehyde in the absence of KO^{t}Bu (Supplementary Figs. 29 and 30) and **A1** doesn't (under analogous conditions).

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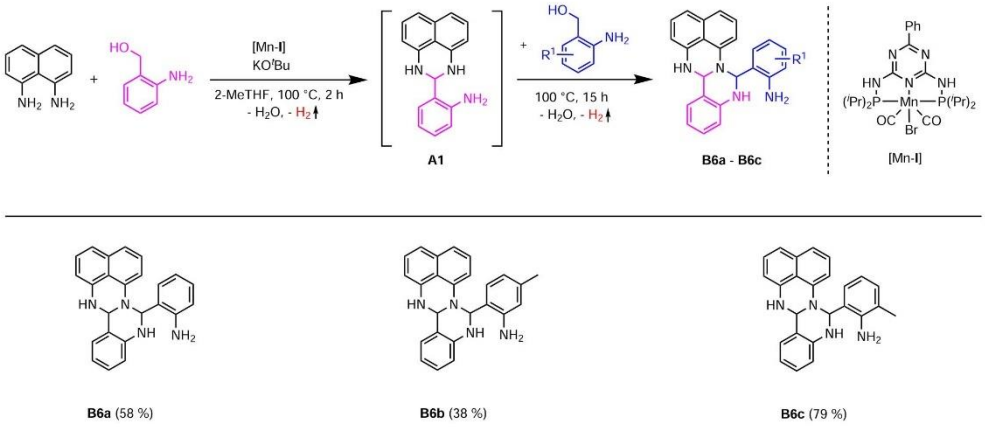

Fig. 7 | Synthesis of amino fertigines B6a-B6c. Reaction conditions: 2 mmol 1,8-diaminonaphthalene, 2 mmol 2-aminobenzyl alcohol, 0.6 mmol KO^{t}Bu, 1 mol% [Mn-**I**] (0.02 mmol), 4 mL 2-MeTHF, 100 °C (oil bath), 2 h + 15 h, open system (anaerobic conditions). After 2 h: addition of 2.0 or 2.2 mmol 2-aminobenzyl alcohol. Isolated yields in brackets.

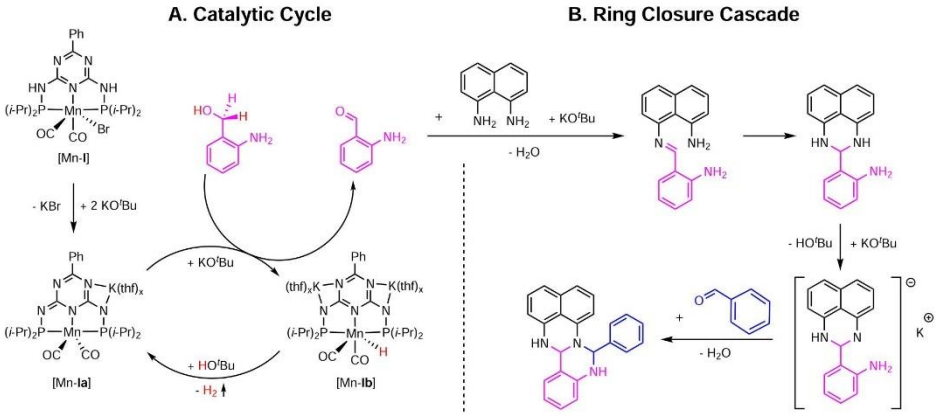

Fig. 8 | Proposed mechanism for the catalytic dehydrogenation and the subsequent ring closure cascade. A Proposed catalytic cycle. **B** Proposed ring closure cascade.

Conclusion

The regeneration of a set of diamines via cyclisation of the original set of diamines (regenerative cyclization) permits rational design and the synthesis of novel classes of *N*-heterocyclic compounds. Catalytic amino alcohol dehydrogenation via liberation of hydrogen seems a suitable protocol to accomplish regenerative cyclization of diamines extending the existing amino alcohol dehydrogenation based *N*-heterocycle syntheses, for instance, the synthesis of pyrroles[25,26] and pyridines[27,28]. Recent work of cyclization of diamines employing methanol[29] holds promises for the generalization of the concept introduced here.

Methods

General procedure for the synthesis 2-aminophenyl-2,3-dihydroperimidines (1) and fertigines (2)

In a glovebox, 2 mmol 1,8-naphthalenediamin and 2 mmol 2-aminobenzyl alcohol derivatives are dissolved in 1 mL 2-MeTHF and added to a Schlenk tube. 0.5 mL of a 0.04 mmol/mL stock solution of the Mn-precatalyst Mn-**I** and 0.5 mL of a 1.2 mmol/mL KO^{t}Bu stock solution are added to the Schlenk tube. 1 mL 2-MeTHF is added, and the reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. **(1):** After 2 h, the reaction is stopped by cooling down to room temperature and the addition of 2 mL H_2O. Depending on the product, two different methods for purification were performed: 1. The mixture is extracted with dichloromethane (3 × 10 mL), the organic layers are dried with Na_2SO_4 and the solvent is removed in vacuo. The crude product is purified by column chromatography using Alox N as stationary phase. 2. H_2O (5 mL) is added, the product is precipitated with pentane, filtrated, and washed with pentane. Finally, it is dried in vacuo. **(2):** After 2 h, 2 mmol of various aldehydes (dissolved in 0.5 mL 2-MeTHF) are added to the reaction. After 15 h, the reaction is stopped by cooling down to room temperature. The work-up depends on the substrates used. Usually, 2 mL H_2O is added, and the reaction mixture

is extracted with dichloromethane (3 × 10 mL). The organic layers were dried with Na_2SO_4 and the solvent is removed in vacuo. The crude product is purified by column chromatography using Alox N as stationary phase.

General procedure for the synthesis of 7,7a,8,9-tetrahydro-10H-imidazo[1,5-a]-perimidin-10-one derivatives

In a glovebox, 2 mmol perimidine derivatives, 30 mol% KO'Bu (0.6 mmol, dissolved in 1.5 mL 1,4-dioxane), and 2.3 mmol carbonyldiimidazol (CDI) are added to a pressure tube, and dissolved in 8.5 mL 1,4-dioxane. The sealed pressure tube is heated at 130 °C for 2 h. After cooling down to room temperature 30 mL water is added and the product is extracted with diethyl ether (4 × 50 mL). The organic layers are dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product is purified via gradient column chromatography using Alox N as stationary phase.

Data availability

Crystallographic data for compounds **A1** and **B1a** are available free of charge from the Cambridge Crystallographic Data Centre under references CCDC 2084882 and CCDC 2083140, respectively. Materials and methods, experimental procedures, mechanistic studies, characterization data, and spectral data are available in the Supplementary Information. Correspondence and requests for materials should be addressed to R.K.

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Author contributions

R.K. conceived the concept. R.F., F.L.-K., T.I., and R.K. jointly devised the experimental program. T.I. supervised the experimental program. R.F. and F.L.-K. carried out the experimental program. All authors jointly wrote the manuscript.

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Supplementary information

Rational design of N-heterocyclic compound classes via regenerative cyclization of diamines

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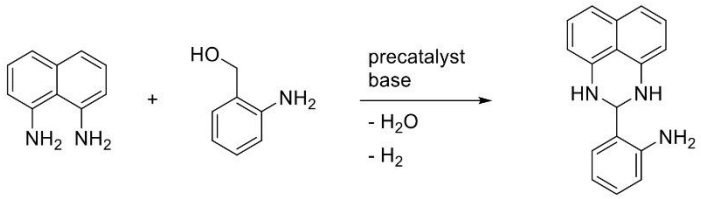
Supplementary Methods

1. Materials and Methods

All reactions and manipulations with air sensitive compounds being present were performed under dry argon (Ar 5.0) or nitrogen (N_2 5.0), using Schlenk and glove box techniques. Nonhalogenated solvents were dried over sodium benzophenone, 2-methyltetrahydrofuran (2-MeTHF) was dried over calcium hydride, and halogenated solvents were dried over P_2O_5. Deuterated solvents were bought from Cambridge Isotope Laboratories, distilled accordingly, and stored over molecular sieves (3 Å). 1,8-Diaminonaphthalene was sublimated before use. Other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were collected on a Varian INOVA 400 MHz spectrometer or on a Bruker Avance III HD 500 MHz. Chemical shifts (δ) are reported in ppm relative to residual solvent signal ($CDCl_3$: 7.26 ppm (^{1}H), 77.16 ppm (^{13}C), DMSO-d_6: 2.50 ppm (^{1}H), 39.51 ppm (^{13}C), C_6D_6: 7.16 ppm (^{1}H), 128.39 ppm (^{13}C), thf-d_8: 1.72 ppm, 3.58 ppm (^{1}H), 67.21 ppm, 25.31 ppm (^{13}C), CD_3CN: 1.94 ppm (^{1}H), 1.32 ppm, 118.26 ppm (^{13}C)). Coupling constants (J) are given in Hz (coupling patterns: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet). GC analyses were carried out using an Agilent Technologies 6890N system equipped with a Macherey-Nagel (MN) Optima 5 HT column (30 m, 320 µm, 0.25 µm) or an Agilent Technologies 6850 system equipped with a MN Optima 17 column (30 m, 320 µm, 0.25 µm). GC/MS analyses were carried out on an Agilent 7890A/MSD 5975C system equipped with a HP-5MS column (30 m, 320 µm, 0.25 µm). For column chromatography, Alox N (90 Å pore withdraw, 50 – 200 µm particle size) from Macherey-Nagel was used. All organic compounds were characterized by ^{1}H and ^{13}C NMR analysis. Unknown compounds or compounds with incomplete spectroscopic literature data were further analysed via elemental analysis (Elementar Unicube or LC-HRMS). Hydrogenations were conducted in PARR Instrument stainless steel autoclaves N-MT5 300 mL equipped with heating mantles and temperature controllers. Liquid chromatography-high resolution mass spectra (LC-HRMS) were obtained from a Thermo Fisher scientific Q-Exactive instrument with a hybrid quadrupole orbitrap analyser in ESI+ mode. For liquid chromatography a Luna Omega PS C18 (100x2.1 mm, 1.6 µm) column was used with a solvent gradient from 30:70 MeCN/water to 90:10 MeCN/water. The samples were dissolved in ethanol or DMSO. The obtained single crystals were mounted on a cryoloop (MiTeGen) with a layer of fomblin YR-1800 (CAS: 69991-67-9). All measurements were performed on a STOE STADIVARI [λ(Mo Kα) = 0.71073 Å] equipped with a dectris (Pilatus 200 K – 20 Hz) detector and an Oxford Cryostream low temperature unit. Structure solution and

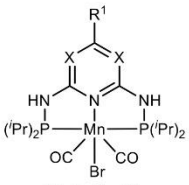
refinement was accomplished with OlexSys2[1], SHELXL-2014[2], and Mercury 2020.1[3]. Non-hydrogen atoms were anisotropically refined, hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms.

2. Screenings for the synthesis of 2-aminophenyl-2,3-dihydro-perimidines (A)

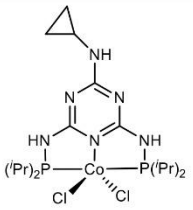


Supplementary Figure 1 Synthesis of **A1** starting from naphthalene-1,8-diamine (**NDA**) and 2-aminobenzyl alcohol (**2-ABA**).

Supplementary Table 1 Precatalyst screening.[a]

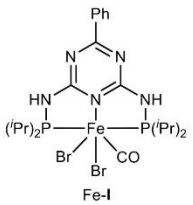


Mn-**I** - Mn-**VII**



Co-**I**

Mn-**I**: X = N, R^1 = Ph
Mn-**II**: X = N, R^1 = H
Mn-**III**: X = N, R^1 = NH-C_3H_5
Mn-**IV**: X = N, R^1 = Ph-(4-CF_3)
Mn-**V**: X = N, R^1 = Me
Mn-**VI**: X = CH, R^1 = Me
Mn-**VII**: X = CH, R^1 = H



Fe-**I**

Entry	Precatalyst	**A1** [%][b]
1	Mn-**I**	75
2	Mn-**II**	41
3	Mn-**III**	68
4	Mn-**IV**	37
5	Mn-**V**	64
6	Mn-**VI**	5
7	Mn-**VII**	7
8	Co-**I**	0
9	Fe-**I**	11
10	[$MnBr(CO)_5$]	6
11	no catalyst	0

[a] Reaction conditions: 1 mmol NDA, 1 mmol 2-ABA, 1 mmol KO^{t}Bu, 1 mol% precatalyst, 4 mL 2-MeTHF, 100 °C (oil bath), 1.5 h. [b] Determined by GC with dodecane as an internal standard.

Supplementary Table 2 Base screening.[a]

Entry	Base	**A1** [%][b]
1	KO^{t}Bu	78
2	NaO^{t}Bu	40
3	KOH	82
4	NaOH	29
5	KH	49
6	NaHMDS	5
7	KHMDS	79
8	Cs_2CO_3	5
9	no base	0

[a] Reaction conditions: 1 mmol NDA, 1 mmol 2-ABA, 1 mmol base, 1 mol% precatalyst Mn-**I**, 4 mL 2-MeTHF, 100 °C (oil bath), 1.5 h. [b] Determined by GC with dodecane as an internal standard.

Supplementary Table 3 Solvent screening.[a]

Entry	Solvent	**A1** [%][b]
1	2-MeTHF	78
2	THF	65
3	Diglyme	0
4	Dioxan	49
5	Toluene	47
6	Pyridine	20
7	*tert*-Amylalcohol	21
8	DME	64

[a] Reaction conditions: 1 mmol NDA, 1 mmol 2-ABA, 1 mmol KO^{t}Bu, 1 mol% precatalyst Mn-**I**, 4 mL solvent, 100 °C (oil bath), 1.5 h. [b] Determined by GC with dodecane as an internal standard.

Supplementary Table 4 Temperature screening.[a]

Entry	Temperature [°C]	**A1** [%][b]
1	50	0
2	60	7
3	80	43
4	100	79
5	120	88
6	140	85

[a] Reaction conditions: 1 mmol NDA, 1 mmol 2-ABA, 1 mmol KO^{t}Bu, 1 mol% precatalyst Mn-**I**, 4 mL 2-MeTHF, 1.5 h. [b] Determined by GC with dodecane as an internal standard.

Supplementary Table 5 Base loading screening.[a]

Entry	Amount of KO^{t}Bu [mmol]	**A1** [%][b]
1	0	0
2	0.1	51
3	0.3	80
4	0.5	88
5	0.7	90
6	1	89
7	1.5	100
8	2	100

[a] Reaction conditions: 1 mmol NDA, 1 mmol 2-ABA, KO^{t}Bu, 1 mol% precatalyst Mn-**I**, 4 mL 2-MeTHF, 100 °C (oil bath), 1.5 h. [b] Determined by GC with dodecane as an internal standard.

Supplementary Table 6 Precatalyst Mn-I loading.[a]

Entry	Amount of precatalyst Mn-**I** [mol%]	**A1** [%][b]
1	0	0
2	0.1	41
3	0.2	65
4	0.5	69
5	1	82
6	1.5	96
7	2	100

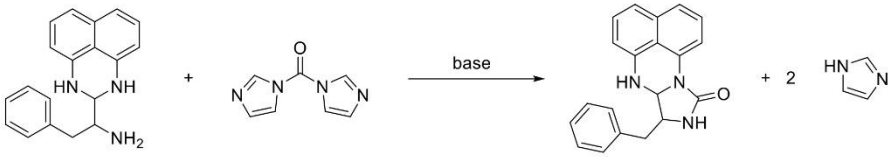
[a] Reaction conditions: 1 mmol NDA, 1 mmol 2-ABA, 0.3 mmol KO^{t}Bu, precatalyst Mn-**I**, 4 mL 2-MeTHF, 100 °C (oil bath), 1.5 h. [b] Determined by GC with dodecane as an internal standard.

Supplementary Table 7 2-MeTHF amount screening.[a]

Entry	2-MeTHF [mL]	**A1** [%][b]
1	2	88
2	3	96
3	4	79
4	5	73

[a] Reaction conditions: 1 mmol NDA, 1 mmol 2-ABA, 0.3 mmol KO^{t}Bu, 1 mol% precatalyst Mn-**I**, 2-MeTHF, 100 °C (oil bath), 1.5 h. [b] Determined by GC with dodecane as an internal standard.

3. Screenings for the synthesis of 7,7a,8,9-tetrahydro-10*H*-imidazo[1,5-*a*]-perimidin-10-ones (C)



A26 **CDI** **C2**

Supplementary Figure 2 Synthesis of **C2** starting from aliphatic aminoperimidin **A26** and carbonyldiimidazol (**CDI**).

Supplementary Table 8 Base screening.[a]

Entry	Base	**C2** [%][b]
1	KO^{t}Bu	91
2	NaO^{t}Bu	86
3	KOH	89
4	NaOH	74
5	DBU	64
6	NaHMDS	83
7	K_2CO_3	59
8	no base	0

[a] Reaction conditions: 0.5 mmol **A26**, 0.6 mmol CDI, 0.15 mmol base, 10 mL 1,4-dioxane, 130 °C (oil bath), 16 h, pressure tube, nitrogen atmosphere. [b] Determined by NMR.

Supplementary Table 9 Solvent screening.[a]

Entry	Solvent	**C2** [%][b]
1	1,4-Dioxane	92
2	THF	82
3	2-MeTHF	84
4	Toluol	86
5	*tert*-Amyl alcohol	72
6	Cyclopentyl methyl ether	89

[a] Reaction conditions: 0.5 mmol **A26**, 0.6 mmol CDI, 0.15 mmol KO^{t}Bu, 10 mL solvent, 130 °C (oil bath), 16 h, pressure tube, nitrogen atmosphere. [b] Determined by NMR.

Supplementary Table 10 Temperature screening.[a]

Entry	Temperature [°C]	**C2** [%][b]
1	80	81
2	90	81
3	100	85
4	110	87
5	120	93
6	130	95
7	140	94

[a] Reaction conditions: 0.5 mmol **A26**, 0.6 mmol CDI, 0.15 mmol KO^{t}Bu, 10 mL 1,4-dioxane, 16 h, pressure tube, nitrogen atmosphere. [b] Determined by NMR.

Supplementary Table 11 Base loading screening.[a]

Entry	Amount of KO^{t}Bu [mmol]	**C2** [%][b]
1	0	0
2	0.05	71
3	0.1	86
4	0.15	92
5	0.2	91
6	0.25	92

[a] Reaction conditions: 0.5 mmol **A26**, 0.6 mmol CDI, x mmol KO^{t}Bu, 10 mL 1,4-dioxane, 130 °C (oil bath), 16 h, pressure tube, nitrogen atmosphere. [b] Determined by NMR.

Supplementary Table 12 Amount of CDI screening.[a]

Entry	Amount of CDI [mmol]	**C2** [%][b]
1	0.5	68
2	0.525	74
3	0.55	73
4	0.575	77
5	0.6	70
6	0.625	66
7	0.65	66

[a] Reaction conditions: 0.5 mmol **A26**, x mmol CDI, 0.15 mmol KO^{t}Bu, 10 mL 1,4-dioxane, 130 °C (oil bath), 30 min, pressure tube, nitrogen atmosphere. [b] Determined by NMR.

Supplementary Table 13 Time screening.[a]

Entry	Time [h]	**C2** [%][b]
1	0.5	76
2	1	85
3	1.5	84
4	2	95
5	3	95
6	4	98
7	5	98
8	6	98

[a] Reaction conditions: 0.5 mmol **A26**, 0.575 mmol CDI, 0.15 mmol base, 10 mL 1,4-dioxane, 130 °C (oil bath), pressure tube, nitrogen atmosphere. [b] Determined by NMR.

4. Scale up experiments

Reaction conditions for upscaling the 2,3-dihydroaminoperimidine synthesis:

In a glovebox, 1,8-naphthalenediamin (15 mmol, 2373 mg) and 2-aminobenzyl alcohol (15 mmol, 1847 mg) are dissolved in 15 mL 2-MeTHF and added to a Schlenk tube. Mn-precatalyst Mn-**I** (0.15 mmol, 90 mg, 1 mol%), KO^{t}Bu (4.5 mmol, 504 mg, 30 mol%) and 30 mL 2-MeTHF are added to the Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 6 h reaction time, it is cooled down to room temperature, 15 mL H_2O is added, and the product is precipitated with pentane. The product **A1** is obtained in 96 % isolated yield (3.752 g) after filtration with pentane and subsequently drying in vacuo.

Reaction conditions for upscaling the fertigine synthesis:

In a glovebox, 1,8-naphthalenediamin (15 mmol, 2373 mg) and 2-aminobenzyl alcohol (15 mmol, 1847 mg) are dissolved in 15 mL 2-MeTHF and added to a Schlenk tube. Mn-precatalyst Mn-**I** (0.15 mmol, 90 mg, 1 mol%), KO^{t}Bu (4.5 mmol, 504 mg, 30 mol%) and 30 mL 2-MeTHF are added to the Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 6 h reaction time, benzaldehyde (15 mmol, 1516 µL) is added to the reaction using a syringe via a septum. The reaction is stirred overnight (15 h) at 100 °C, cooled down to room temperature and 10 mL H_2O is added. For

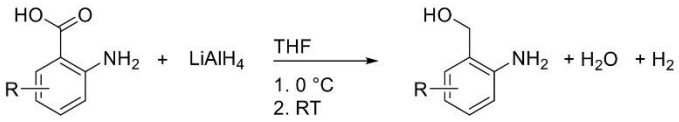
precipitation, pentane is added, the product is filtrated and washed with pentane, obtaining **B1a** in 93 % yield (4.868 g).

5. Synthesis of ligands and complexes

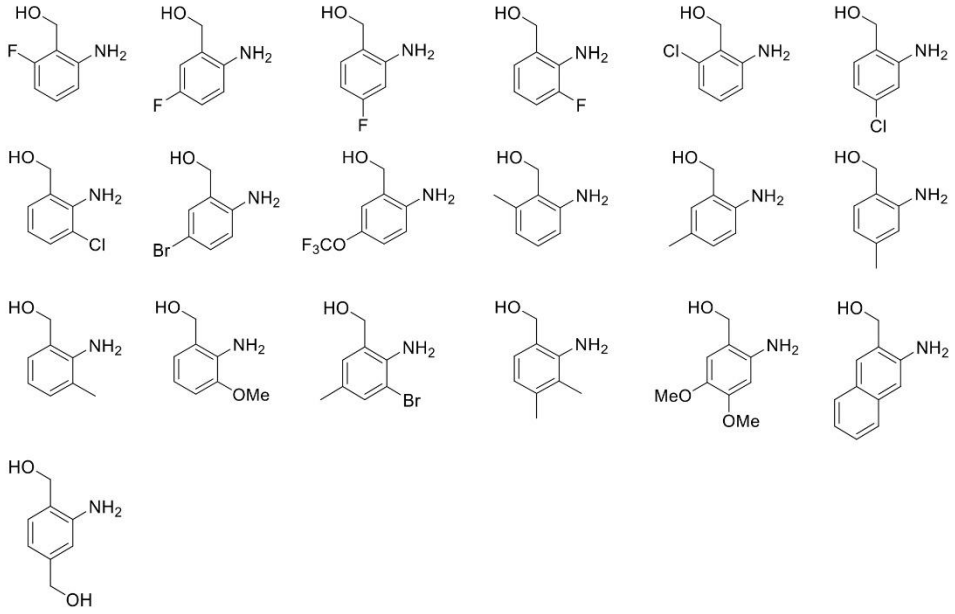
The ligands and precatalysts Mn-**I/II/III/IV/V**[4], Mn-**VI/VII**[5,6], Co-**I**[7,8] and Fe-**I**[9] were synthesized according to published procedures.

6. Synthesis of 2-aminobenzyl alcohol derivatives

15 mmol of anthranilic acid derivatives are dissolved in THF and cooled with an ice bath to 0 °C. 33 mmol $LiAlH_4$ is added in portions under rigorous stirring. After the addition, the reaction is led to warm up to room temperature and stirred overnight (15 h). The reaction is stopped following the Fieser workup: The reaction is cooled to 0 °C, diluted with diethyl ether and 1.25 mL water and 1.25 mL 15% aqueous NaOH solution are added slowly. Water (3.75 mL) is added, and the reaction is stirred for 15 min. Na_2SO_4 is added and the reaction is filtrated to remove the salts. The organic solvent is removed, and the crude product is purified by sublimation (60 – 100 °C). All 2-aminobenzyl alcohol derivatives were checked by ^1H NMR spectroscopy and GC/MS before use.



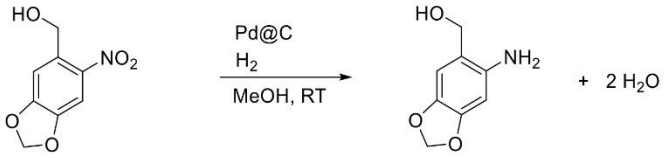
Supplementary Figure 3 General reaction conditions for the synthesis of 2-aminobenzyl alcohols.



Supplementary Figure 4 Overview of the synthesized 2-aminobenzyl alcohols by reduction with $LiAlH_4$.

Synthesis of (6-amino-1,3-benzodioxol-5-yl)methanol

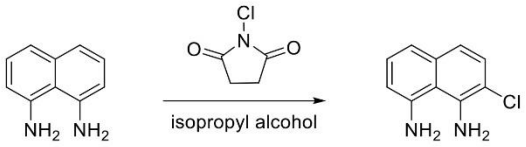
(6-Nitrobenzo[d][1,3]dioxol-5-yl)methanol (30 mmol) is dissolved in 30 mL methanol and a spade point of Pd@C is added. The hydrogen is stored in a rubber balloon, leading to a hydrogen atmosphere (ca. 1 atm) in the reaction flask. The reaction is stirred at room temperature for 24 h, Na_2SO_4 is added, and the reaction is filtrated. After removing the solvent, the crude product is purified by sublimation at 100 °C.



Supplementary Figure 5 Synthesis of (6-amino-1,3-benzodioxol-5-yl)methanol.

7. Synthesis of 1,8-diaminonaphthalene derivatives

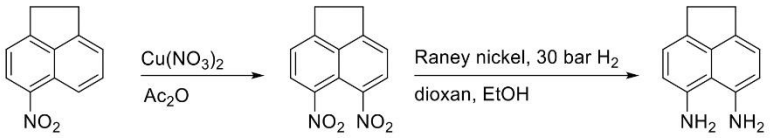
Synthesis of 2-chloronaphthalene-1,8-diamine



Supplementary Figure 6 Synthesis of 2-chloronaphthalene-1,8-diamine.

1,8-Diaminonaphthalene (9.97 g, 63 mmol) is dissolved in 100 mL isopropyl alcohol and *N*-chlorosuccinimide (8.41 g, 63 mmol) is added in small portions. The reaction is stirred at 80 °C with reflux for 2 h. After cooling down to room temperature, the solvent is removed and the reaction mixture is extracted with diethyl ether and water (3 x 30 mL). The organic layer is dried with Na_2SO_4 and the crude product is purified by column chromatography with Alox N (pentane/ethyl acetate: 4:2 → 2:3) obtaining 3.38 g of a white solid (17.5 mmol, 28 %). The purity is proofed via GC/MS and NMR analysis.

Synthesis of 5,6-diaminoacenaphthene

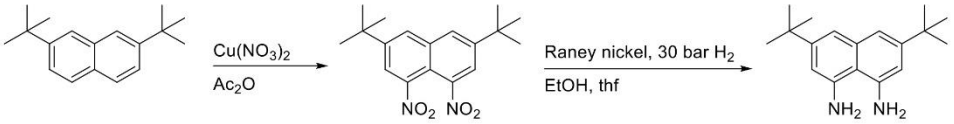


Supplementary Figure 7 Synthesis of 5,6-diaminoacenaphthene.

5-Nitroacenaphthene (6.98 g, 35 mmol) is dissolved in 150 mL Ac_2O and $Cu(NO_3)_2$ (6.56 g, 35 mmol) is added under rigorous stirring in small portions to the solution. The reaction is stirred at room temperature for 15 h, then the Ac_2O is removed in vacuo. 100 mL Water were added, and the mixture is stirred for ca. 30 minutes until the remaining Cu-salts are dissolved. 5,6-Dinitroacenaphthene precipitates, it is filtrated and dried. For further purification, 5,6-dinitroacenaphthene is recrystallized in a 2/1 mixture of dioxane and thf at 70 °C and obtained as white crystals in 38 % yield (3.28 g) after 3 days. The reduction is conducted by dissolving 1 g

of 5,6-dinitroacenaphthene in a 1/1 mixture of dioxan and EtOH and adding 1 mL of a Raney nickel suspension to it. The mixture is stirred at 50 °C and 30 bar H_2 for 15 h. After cooling down to room temperature, the pressure is released, and the mixture is filtrated. Precipitation with HCl in Et_2O, filtration of the HCl-salt and neutralisation with $NaHCO_3$ led to the product in 76 % yield (562 mg, 3.05 mmol). The purity is proofed by GC/MS and NMR analysis.

Synthesis of 3,6-di-*tert*-butylnaphthalene-1,8-diamine

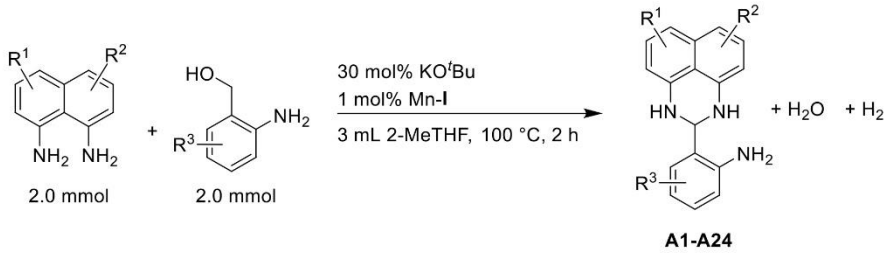


Supplementary Figure 8 Synthesis of 3,6-di-*tert*-butylnaphthalene-1,8-diamine.

2,7-Di-*tert*-butylnaphthalene (5 g, 20.7 mmol) is dissolved in 100 mL Ac_2O and copper(II) nitrate (7.88 g, 42 mmol) is added in small portions at 0 °C within 15 minutes. After stirring the mixture at room temperature for 2 hours, the reaction is stopped by pouring it in 500 mL ice water. The formed precipitate is filtrated, washed with water and dried in vacuo. The obtained yellow solid (5.62 g, 17 mmol) is used without further purification. 3,6-Di-*tert*-butyl-1,8-dinitronaphthalene is dissolved in a 1/1 mixture of EtOH/thf and 1 mL of a Raney nickel suspension is added. The mixture is stirred at 50 °C and 30 bar H_2 for 15 h. After cooling down to room temperature, the pressure is released, and the mixture is filtrated. The crude product is purified via column chromatography over Alox N (pentane/ethyl acetate 5:1 → 3:2) and obtained as a red solid (1244 mg, 4.61 mmol). The purity is proofed by GC/MS and NMR analysis.

8. Synthesis of 2-aminophenyl-2,3-dihydro-perimidines (A)

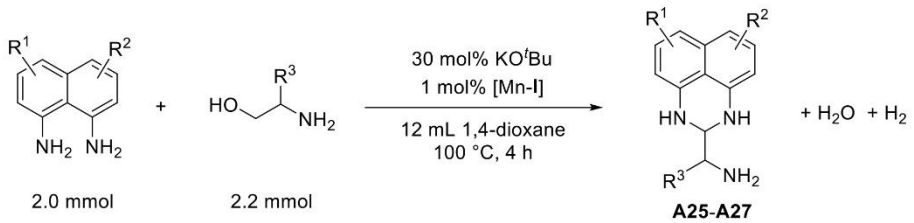
General reaction conditions for the synthesis 2-aminophenyl-2,3-dihydro-perimidines: In a glovebox, 2 mmol 1,8-naphthalenediamin and 2 mmol 2-aminobenzyl alcohol derivatives are dissolved in 1 mL 2-MeTHF and added to a Schlenk tube. 0.5 mL of a 0.04 mmol/mL stock solution of the Mn-precatalyst Mn-**I** and 0.5 mL of a 1.2 mmol/mL KO^{t}Bu stock solution is added to the Schlenk tube. 1 mL 2-MeTHF is added, and the reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 h, the reaction is stopped by cooling down to room temperature and the addition of 2 mL H_2O. Depending on the product, we performed two different methods for purification: 1.) The mixture is extracted with dichloromethane (3 x 10 mL), the organic layers are dried with Na_2SO_4 and the solvent is removed in vacuo. The crude product is purified by column chromatography using Alox N as stationary phase. 2.) 5 mL H_2O is added, the product is precipitated with pentane, filtrated, and washed with pentane. Finally, it is dried in vacuo overnight.



Supplementary Figure 9 Synthesis of 2,3-dihydroaminoperimidines **A1-A24**.

General reaction conditions for the synthesis of 1-(2,3-dihydro-1H-perimidin-2-yl)methanamines: In a glovebox, 1 mol% Mn-precatalyst Mn-**I** (0.02 mmol, dissolved in 1.5 mL 1,4-dioxane), 30 mol% KO^{t}Bu (0.6 mmol, dissolved in 1.5 mL 1,4-dioxane), 2 mmol 1,8-diaminonaphthalene and 2.2 mmol 2-aminopropan-1-ol derivatives are added to a Schlenk tube and dissolved in 9 mL 1,4-dioxane. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. The mixture is stirred for 4 hours, cooled down to room temperature, the 1,4-dioxane is evaporated under vacuo and 6 mL water are added. The reaction mixture is extracted with ethyl acetate (3 x 50 mL), the organic layers are dried with Na_2SO_4 and the solvent is removed in vacuo. The crude product is purified via gradient column

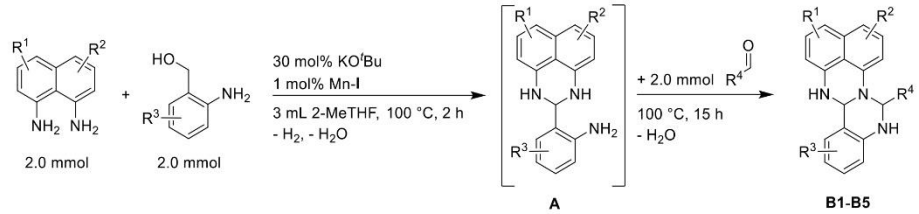
chromatography using Alox N as stationary phase. To the product are 10 mL of an aqueous saturated solution of $NaHCO_3$ added, the product was extracted with ethyl acetate, dried with Na_2SO_4 and the solution was narrowed. At the end the product is purified via column chromatography over Silica C18 ec with ethyl acetate.



Supplementary Figure 10 Synthesis of 1-(2,3-dihydro-1*H*-perimidin-2-yl)methanamines **A25-A27**.

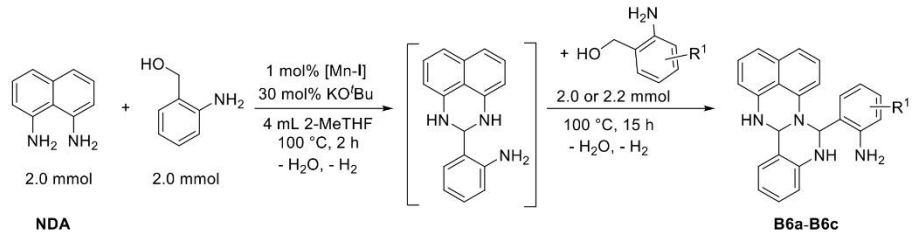
9. Synthesis of fertigines (B)

General reaction conditions for the synthesis of fertigines B1-B5: In a glovebox, 2 mmol 1,8-diaminonaphthalene and 2 mmol 2-aminobenzyl alcohol derivatives are dissolved in 1 mL 2-MeTHF and added to a Schlenk tube. 0.5 mL of a 0.04 mmol/mL stock solution of Mn-**I** and 0.5 mL of a 1.2 mmol/mL KO^{t}Bu stock solution is added to the Schlenk tube. 1 mL 2-MeTHF is added, and the reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2 mmol of various aldehydes are added to the reaction. For this, the aldehyde is dissolved in at least 0.5 mL 2-MeTHF and added to the reaction mixture through a septum with a syringe. After 15 h, the reaction is stopped by cooling down to room temperature. The work-up depends on the substrates used. Usually, 2 mL H_2O is added, and the reaction mixture is extracted with dichloromethane (3 x 10 mL). The organic layers were dried with Na_2SO_4 and the solvent is removed in vacuo. The crude product is purified by column chromatography using Alox N as stationary phase. Using some substrates, the product precipitates during reaction. If this is the case, 5 mL water is added, the reaction mixture is diluted with pentane and filtrated. After washing the residue with H_2O and cold pentane, it is dried in vacuo at 70 °C to obtain the product.



Supplementary Figure 11 Synthesis of fertigines **B1**-**B5**.

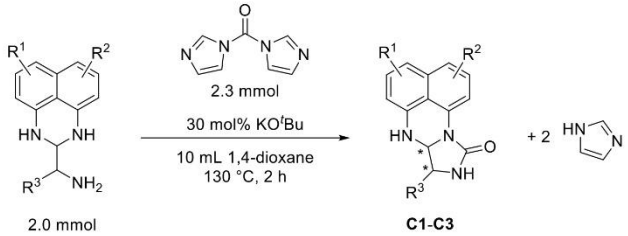
General reaction conditions for the synthesis of amino-fertigine derivatives B6a-B6c: In a glovebox, 1 mol% Mn-precatalyst Mn-**I** (0.02 mmol, dissolved in 0.5 mL 2-MeTHF), 30 mol% KO^{t}Bu (0.6 mmol, dissolved in 0.5 mL 2-MeTHF), 2 mmol 1,8-diaminonaphthalene and 2 mmol 2-aminobenzyl alcohol are added to a Schlenk tube and dissolved in 3 mL 2-MeTHF. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2.0 or 2.2 mmol 2-aminobenzyl alcohol derivatives are dissolved in 1.0 mL 2-MeTHF and added to the reaction mixture through a septum with a syringe. After 15 hours, the reaction is stopped by cooling down to room temperature and 4 mL water are added. The reaction mixture is diluted with pentane, the precipitate is filtrated and washed with water and pentane. The dried solid is slurred with ethanol and stirred for 10 min at 100 °C. After filtration, the product is dried in vacuo.



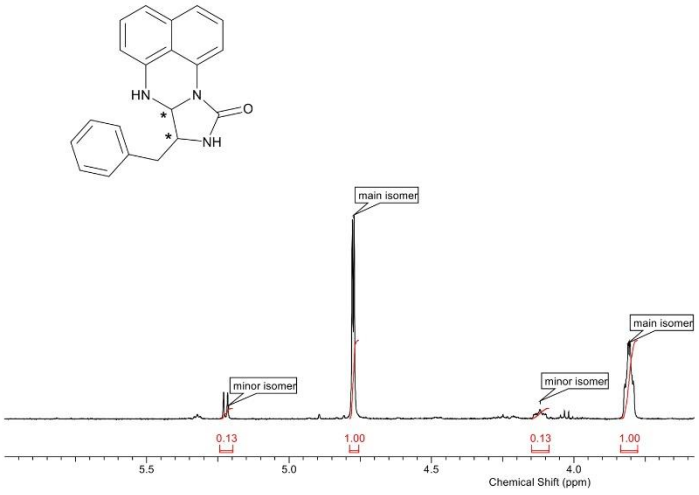
Supplementary Figure 12 Synthesis of amino-fertigines **B6a**-**B6c**.

10. Synthesis of 7,7a,8,9-tetrahydro-10*H*-imidazo[1,5-*a*]-perimidin-10-ones (C)

General reaction conditions for the synthesis of 7,7a,8,9-tetrahydro-10H-imidazo[1,5-a]-perimidin-10-one derivatives C1-C3: In a glovebox, 2 mmol perimidine derivatives, 30 mol% KO^{t}Bu (0.6 mmol, dissolved in 1.5 mL 1,4-dioxane) and 2.3 mmol carbonyldiimidazol (CDI) are added to a pressure tube and dissolved in 8.5 mL 1,4-dioxane. The sealed pressure tube is heated at 130 °C for 2 hours in an oil bath. After cooling down to room temperature 30 mL water are added and the product is extracted with diethyl ether (4 x 50 mL). The organic layers are dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product is purified via gradient column chromatography using Alox N as stationary phase.

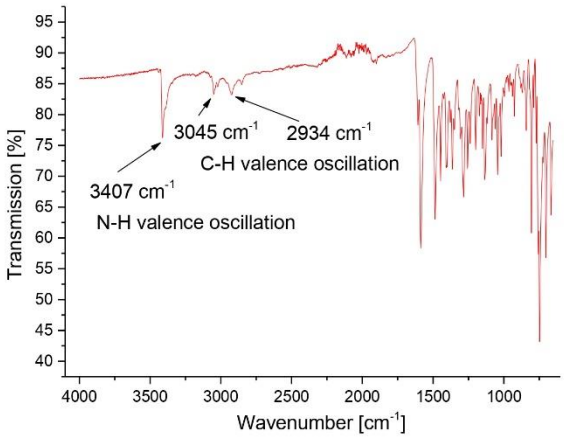


Supplementary Figure 13 Synthesis of 7,7a,8,9-tetrahydro-10*H*-imidazo[1,5-*a*]-perimidin-10-ones **C1-C3**.

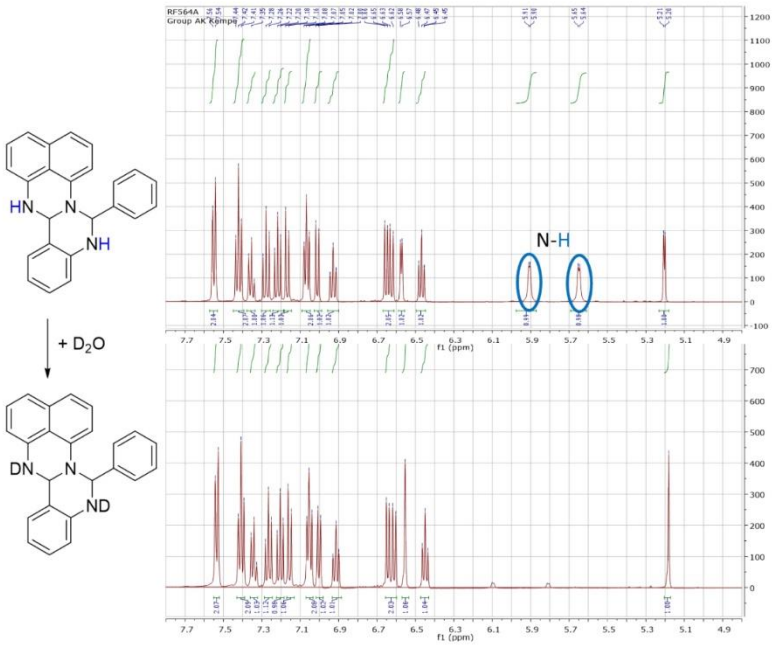


Supplementary Figure 14 Excerpt from ^{1}H NMR-spectrum (500 MHz, 293 K) of the crude **C2** in DMSO-d_6 to determine the diastereomeric ratio based on the integrals of the main and minor isomer.

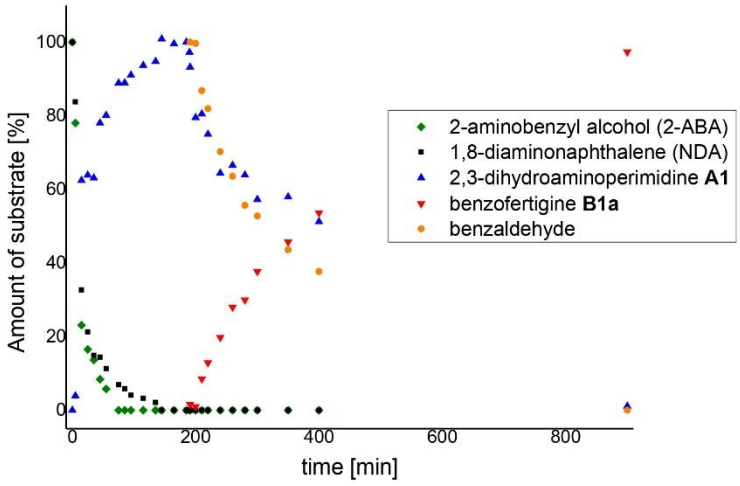
11. Characterization of fertigines (B)



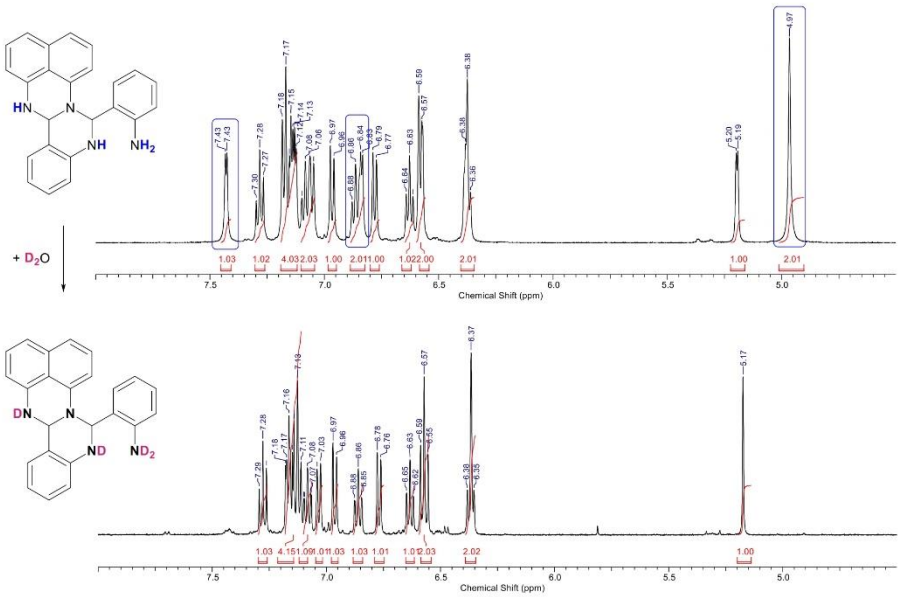
Supplementary Figure 15 IR-spectrum of B1a.



Supplementary Figure 16 ^{1}H NMR (500 MHz, 293 K) of **B1a** in CD_3CN and after the addition of D_2O.



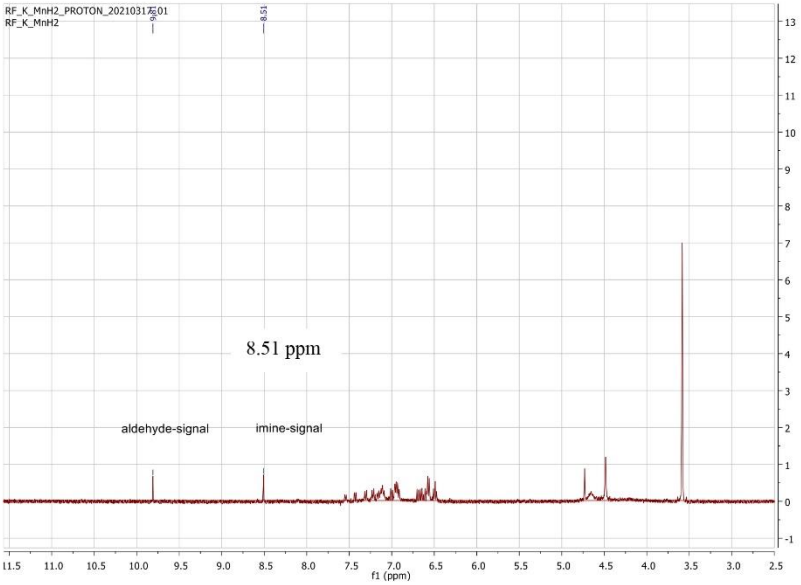
Supplementary Figure 17 Time-conversion plot for the synthesis of fertigine **B1a** (red) over the intermediate product 2,3-dihydroaminoperimidin **A1** (blue)**.** Reaction conditions: 15 mmol NDA (black), 15 mmol 2-aminobenzyl alcohol (green), 4.5 mmol KO^{t}Bu, 0.15 mmol Mn-**I**, 45 mL 2-MeTHF, 100 °C (oil bath). After 190 min. 15 mmol benzaldehyde (orange) is added.



Supplementary Figure 18 ^{1}H NMR (500 MHz, 293 K) of **B6a** in DMSO-d_6 and after the addition of D_2O.

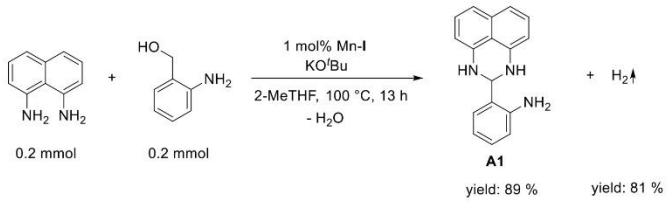
12. Mechanistic investigations

In absence of diaminonaphthalene during catalysis, self-condensation of the aminobenzyl alcohol was observed via ^{1}H NMR analysis. Reaction conditions: 60 µmol 2-aminobenzyl alcohol, 0.6 µmol Mn-**I**, 18 µmol KO^{t}Bu and 700 µL thf-d_8 were heated at 90 °C using an open system for hydrogen release. After 24 h ^{1}H NMR measurement was conducted.



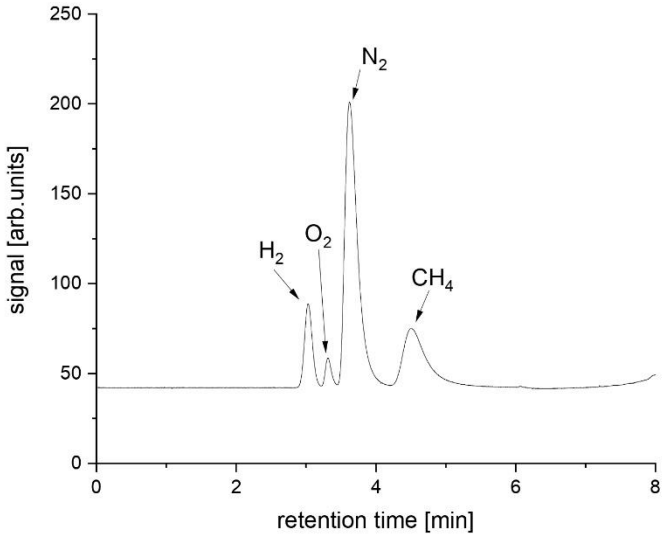
Supplementary Figure 19 ^{1}H NMR spectra showing the self-condensation of the aminobenzyl alcohol in the absence of naphthalene diamine.

Qualitative and quantitative analyses of evolved hydrogen



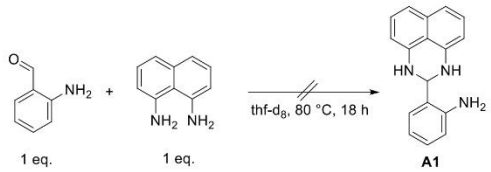
Supplementary Figure 20 Control experiment for the qualitative and quantitative determination of hydrogen.

The release of one equivalent hydrogen was proofed by analyzing the gas mixture with methane as an internal standard in the Schlenk tube after reaction. The gas mixture was analyzed using an Agilent Technologies 6890N equipped with a TCD and an Agilent special plot and molsieve capillary column (30 m, 320 µm, 0.25 µm). Reaction conditions: 0.2 mmol diaminonaphthalene, 0.2 mmol aminobenzyl alcohol, 1 mol% Mn-**I**, 0.06 mmol KO′Bu and 1 ml 2-MeTHF were added to a Schlenk tube (150 mL), closed and heated at 100 °C (oil bath) for 13 h. A yield of 89 % of the perimidine **A1** formed was determined and 81% of hydrogen was detected.



Supplementary Figure 21 Chromatogram of the gas-chromatographic analysis from the upper gas layer over the reaction mixture after 13 h reaction time.

Investigation of the reaction with 2-aminobenzaldehyde via ^{1}H NMR analysis

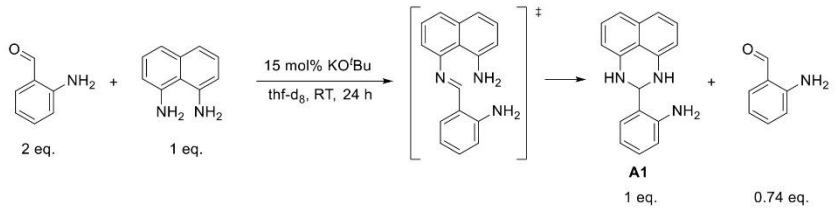


Supplementary Figure 22 Control experiment without KO^{t}Bu.

In absence of KO^{t}Bu no reaction between 2-aminobenzaldehyde and diaminonaphthalene was observed. Reaction conditions: 60 µmol 2-aminobenzaldehyde and 60 µmol diaminonaphthalene were dissolved in 700 µL thf-d_8 and were heated at 80 °C for 18 h. Time-dependant amount of 2-aminobenzaldehyde (referred to the aldehyde signal) and of the diamine (referred to the NH_2-signal) were determined with mesitylene as internal standard.

Control experiment 2: with KO^{t}Bu

Reaction conditions: 120 µmol 2-aminobenzaldehyde, 60 µmol diaminonaphthalene, 9 µmol KO^{t}Bu (15 mol%, stock solution of 30 mg/2 mL thf-d_8), 61 µL stock solution of mesitylene (15 µL / 1 mL thf-d_8), 700 µL thf-d_8 at RT. Time-dependant amount of 2-aminobenzaldehyde (referred to the aldehyde signal) and of the diamine (referred to the NH_2-signal) with mesitylene (2.22 ppm) as internal standard:

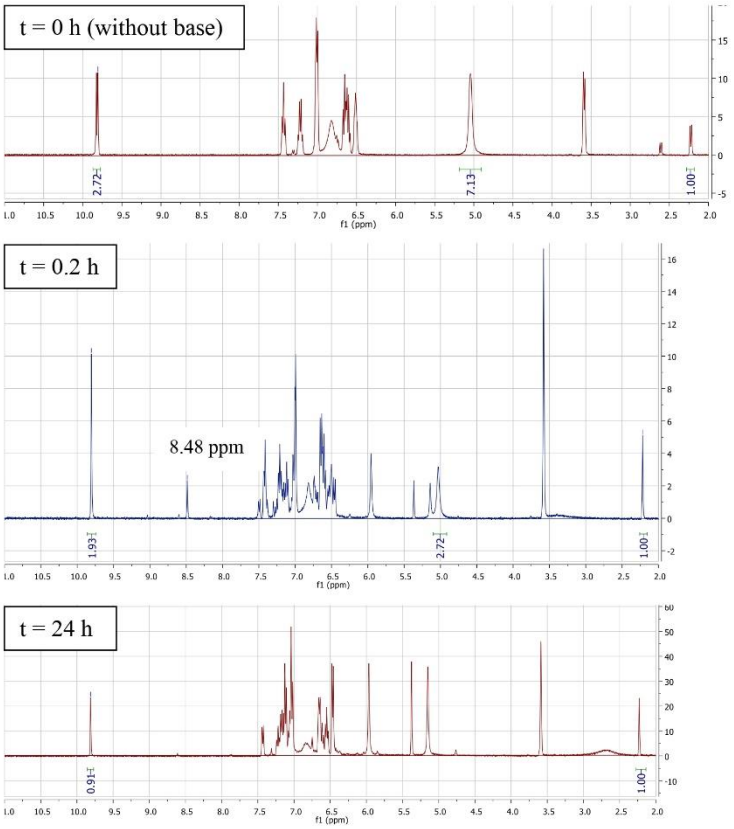


Supplementary Figure 23 Control experiment with KO^{t}Bu.

t = 0 h: 100 % aldehyde (2 eq. compared to 1 eq. diamine), 100 % diamine

t = 0.2 h: 71 % aldehyde (1.4 eq. related to 1 eq. diamine), 38 % diamine

t = 24 h: 37 % aldehyde (0.74 eq. related to 1 eq. diamine), 0 % diamine

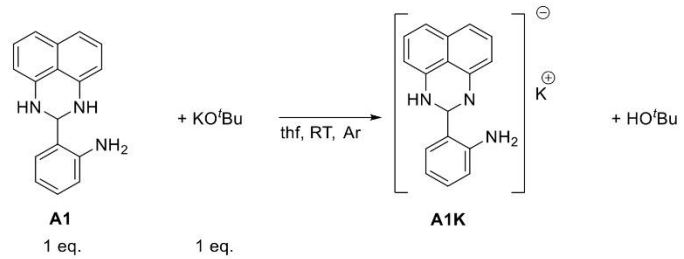


Supplementary Figure 24 Time-dependant ^{1}H NMR studies of the reaction of 2-aminobenzaldehyde with diaminonaphthalene in the presence of KO^{t}Bu (time: before addition of KO^{t}Bu, after 0.2 h and after 24 h).

In addition to the time-dependent consumption of the 2-aminobenzaldehyde, the characteristic imine signal at 8.48 ppm indicates the formation of an imine intermediate, as it differs slightly from the observed imine signal (8.51 ppm) of the self-condensation product of the 2-aminobenzaldehyde in Supplementary Figure 19.

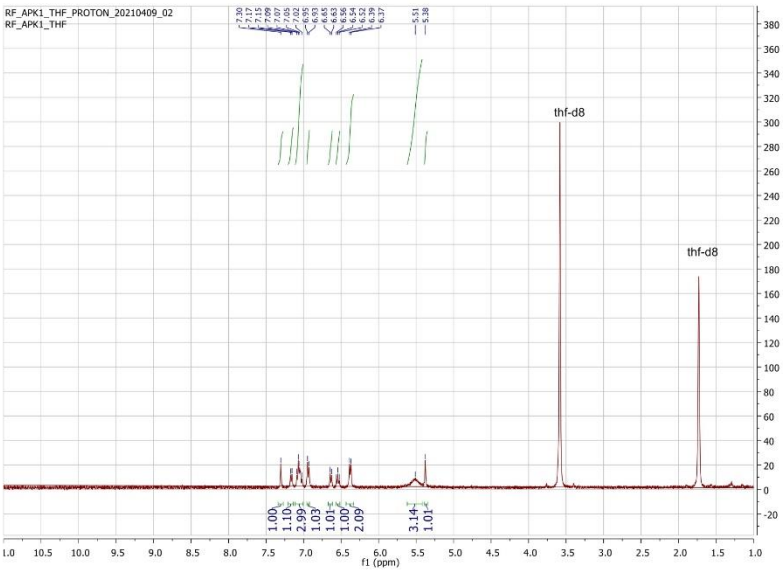
Synthesis and characterisation of A1K

Synthesis of **A1K**: 5 mmol **A1** (1306.7 mg) is dissolved in 30 mL dry thf in a Schlenk tube, 5 mL of a 1 M solution of KO^{t}Bu (5 mmol) in thf is added to the Schlenk tube under argon. A yellow solid precipitate. After 30 min, the thf is filtrated, the yellow solid washed with thf and again filtrated. After drying in vacuo over night the solid is used for further studies.

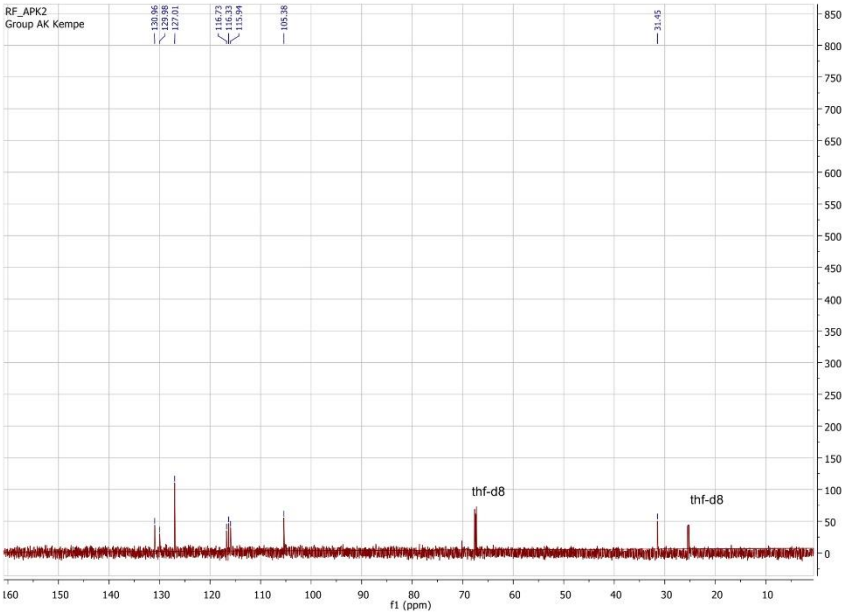


Supplementary Figure 25 Synthesis of **A1K**.

Characterisation of **A1K**:



Supplementary Figure 26 ^{1}H NMR of **A1K** (thf-d$_8$, 400 MHz, 293 K): δ = 7.30 (s, 1H), 7.16 (d, J = 7.0 Hz, 1H), 7.06 (dd, J = 16.8, 9.7 Hz, 3H), 6.94 (d, J = 7.8 Hz, 1H), 6.64 (d, J = 7.3 Hz, 1H), 6.54 (t, J = 8.0 Hz, 1H), 6.38 (d, J = 7.6 Hz, 2H), 5.51 (s, 3H), 5.38 (s, 1H) ppm.



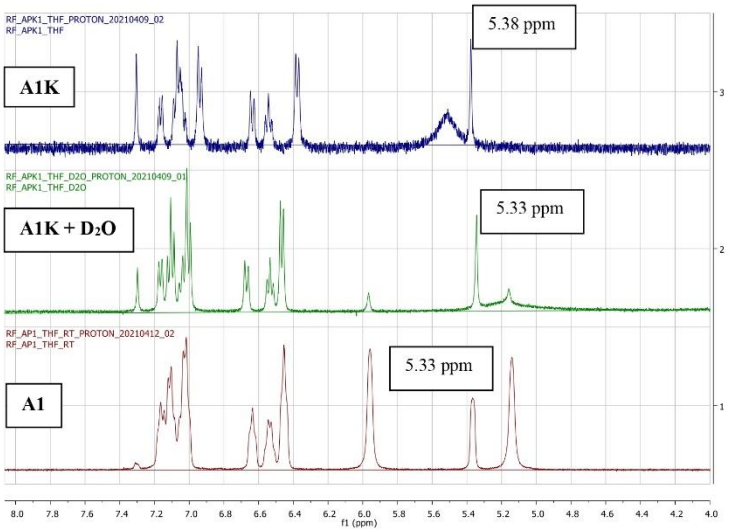
Supplementary Figure 27 ^{13}C NMR of **A1K** (thf-d_8, 125 MHz, 293 K): δ = 130.96, 129.98, 127.01, 116.73, 116.33, 115.94, 105.38, 31.45 ppm.

Elemental analysis calculated (**A1K** + 2 thf): C 68.09, H 7.25, N 9.16

Elemental analysis found: C 68.34, H 6.95, N 9.49

Control experiments with A1K

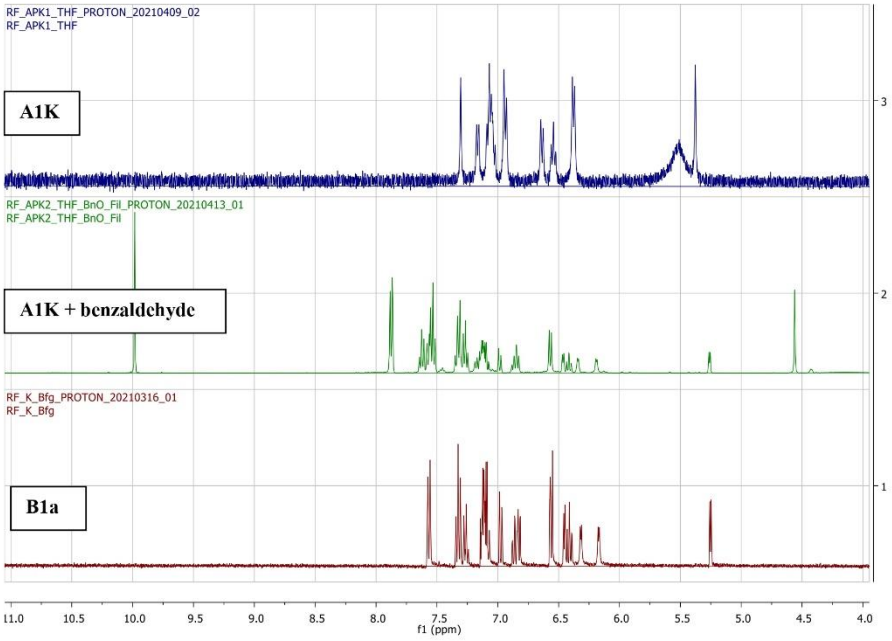
Addition of D_2O to **A1K** in thf-d_8 in the NMR-tube led to the back reaction of **A1K** to **A1**.



Supplementary Figure 28 Addition of D_2O (green) to **A1K** (blue); the bottom spectra show **A1** (red) as reference.

Additionally, the extraction of **A1K** with ethyl acetate/water led to the isolation of **A1** in the organic phase, while a pH-change of the water phase from 7 to 14 is observed. The use of sodium tetraphenylborate for analyzing the potassium amount in the aqueous phase proofed the formation of 1 eq. KOH per 1 eq. **A1K**. Reaction conditions: 0.2 mmol **A1K** (63 mg) is extracted with ethyl acetate/water. To the combined water phases is added an excess of a solution of $NaB(Ph)_4$. After centrifugation, decantation, and drying in vacuo, 81 mg (0.22 mmol) of a white precipitation of $KB(Ph)_4$ was obtained.

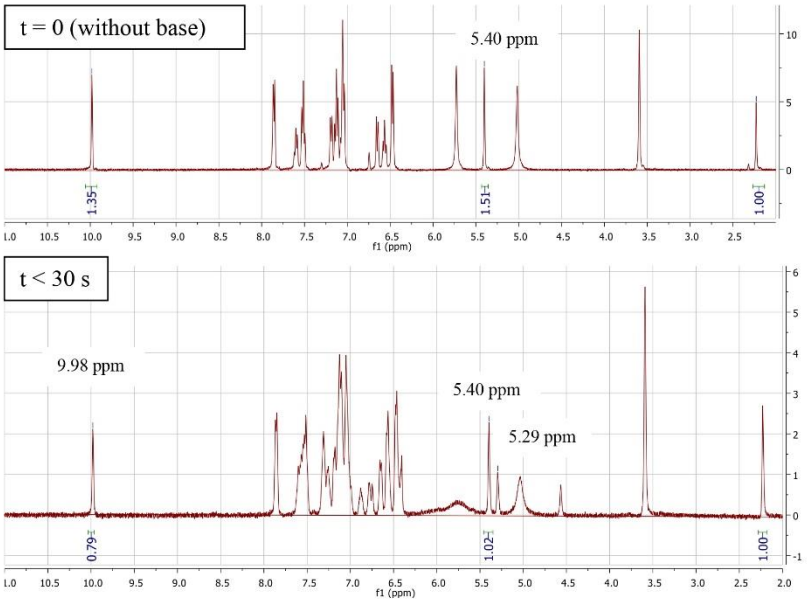
^{1}H NMR control experiments show the reaction of **A1K** to **B1a** after the addition of benzaldehyde:



Supplementary Figure 29 ^{1}H NMR of the formation of **B1a** after the addition of benzaldehyde to **A1K** (green). Reaction conditions: To a suspension of 10 mg **A1K** (ca. 31 µmol) in 700 µL thf-d_8 is added 40 µmol benzaldehyde at room temperature. ^{1}H NMR of **A1K** (blue) and **B1a** (red) for reference.

Investigation of the condensation of A1 with benzaldehyde via ^{1}H NMR analysis

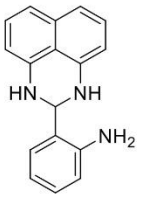
Reaction conditions: 60 µmol **A**1, 60 µmol benzaldehyde, 6 µmol KO^{t}Bu (10 mol%, stock solution 30 mg/3 mL thf-d_8), 61 µL stock solution of mesitylene (15 µL / 1 mL thf-d_8), 700 µL thf-d_8 at RT. Without base no reaction is observed (t = 0 h), after addition of base an instant (< 30 s at RT) consumption of the benzaldehyde to 59 % (9.98 ppm), **A1** to 67 % (5.40 ppm) and formation of **B1a** (5.29 ppm) is observed. Mesitylene (2.22 ppm) is used as internal standard.



Supplementary Figure 30 ^{1}H NMR spectra showing the instant formation of **B1a** after addition of KO^{t}Bu to a solution of **A1** and benzaldehyde.

13. Isolation and characterization of products

Synthesis of **A1**



Chemical Formula: $C_{17}H_{15}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as a white solid (470 mg, 1.8 mmol, 90 %).

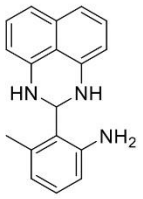
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.27 (d, J = 7.4 Hz, 1H), 7.15 (t, J = 7.7 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 7.0 Hz, 2H), 6.72 (d, J = 6.4 Hz, 1H), 6.64 (s, 2H), 6.58 (t, J = 7.2 Hz, 1H), 6.53 (d, J = 5.5 Hz, 2H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 147.66, 143.93, 134.47, 130.08, 129.19, 126.75, 122.30, 115.75, 115.46, 115.34, 112.70, 104.69, 66.45, 39.52 ppm.

Elemental analysis calculated: C 78.13, H 5.79, N 16.08

Elemental analysis found: C 78.03, H 5.78, N 15.94

Synthesis of **A2**



Chemical Formula: $C_{18}H_{17}N_3$

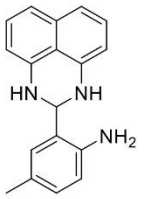
In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-6-methylbenzyl alcohol (2 mmol, 275 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a grey solid (512 mg, 1.86 mmol, 93 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.15 (t, J = 7.8 Hz, 2H), 7.01 (d, J = 8.1 Hz, 2H), 6.95 (t, J = 7.7 Hz, 1H), 6.64 (s, 2H), 6.55 (d, J = 8.0 Hz, 1H), 6.52 (d, J = 7.4 Hz, 2H), 6.40 (d, J = 7.4 Hz, 1H), 5.65 (s, 1H), 5.50 (s, 2H), 2.31 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 148.87, 144.34, 134.54, 128.83, 126.67, 119.17, 118.05, 115.41, 114.44, 112.74, 104.93, 63.48, 20.25 ppm.

Elemental analysis calculated: C 78.52, H 6.22, N 15.26
Elemental analysis found: C 77.84, H 5.96, N 15.93

Synthesis of **A3**



Chemical Formula: $C_{18}H_{17}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-5-methylbenzyl alcohol (2 mmol, 275 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a grey solid (479 mg, 1.74 mmol, 87 %).

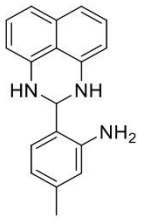
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.14 (t, J = 7.8 Hz, 1H), 7.10 (s, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 6.62 (d, J = 8.1 Hz, 1H), 6.59 (s, 1H), 6.51 (d, J = 7.4 Hz, 1H), 5.34 (s, 1H), 5.14 (s, 1H), 2.18 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ =145.11, 143.97, 134.46, 130.38, 129.63, 126.73, 123.85, 122.39, 116.01, 115.29, 112.67, 104.63, 66.16, 20.10 ppm.

Elemental analysis calculated: C 78.52, H 6.22, N 15.26

Elemental analysis found: C 78.52, H 6.15, N 15.16

Synthesis of **A4**



Chemical Formula: $C_{18}H_{17}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-4-methylbenzyl alcohol (2 mmol, 275 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a grey solid (424 mg, 1.54 mmol, 77 %).

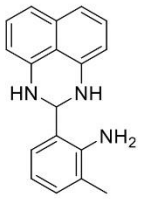
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.14 (t, J = 7.6 Hz, 3H), 6.98 (d, J = 8.1 Hz, 2H), 6.56 (s, 2H), 6.55 – 6.48 (m, 3H), 6.40 (d, J = 7.7 Hz, 1H), 5.33 (s, 1H), 5.27 (s, 2H), 2.19 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 147.46, 144.00, 138.29, 134.47, 130.05, 126.73, 119.71, 116.37, 116.13, 115.27, 112.70, 104.63, 66.27, 21.00 ppm.

Elemental analysis calculated: C 78.52, H 6.22, N 15.26

Elemental analysis found: C 78.12, H 6.05, N 14.88

Synthesis of **A5**



Chemical Formula: $C_{18}H_{17}N_3$

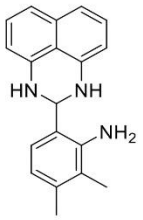
In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-methylbenzyl alcohol (2 mmol, 275 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a grey solid (534 mg, 1.94 mmol, 97 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.14 (dd, J = 15.3, 7.4 Hz, 3H), 7.02 (dd, J = 13.8, 7.8 Hz, 3H), 6.68 (s, 2H), 6.53 (dd, J = 15.2, 7.5 Hz, 3H), 5.37 (s, 1H), 5.19 (s, 2H), 2.12 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 145.65, 143.96, 134.48, 130.33, 128.37, 126.75, 122.51, 121.74, 115.40, 115.33, 112.73, 104.72, 67.79, 17.72 ppm.

Elemental analysis calculated: C 78.52, H 6.22, N 15.26
Elemental analysis found: C 77.94, H 6.07, N 15.08

Synthesis of **A6**



Chemical Formula: $C_{19}H_{19}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3,4-dimethylbenzyl alcohol (2 mmol, 303 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a white solid (544 mg, 1.88 mmol, 94 %).

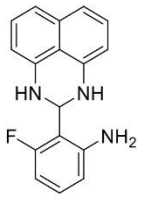
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.15 (t, J = 7.8 Hz, 2H), 7.06 – 6.97 (m, 3H), 6.63 (s, 2H), 6.51 (d, J = 7.4 Hz, 2H), 6.47 (d, J = 7.6 Hz, 1H), 5.32 (s, 1H), 5.15 (s, 2H), 2.22 (s, 3H), 2.02 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 145.54, 144.00, 136.59, 134.49, 127.56, 126.74, 120.70, 119.93, 117.44, 115.37, 112.74, 104.69, 68.12, 20.46, 12.91 ppm.

Elemental analysis calculated: C 78.86, H 6.62, N 14.52

Elemental analysis found: C 78.17, H 6.32, N 14.19

Synthesis of **A7**



Chemical Formula: $C_{17}H_{14}FN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-6-fluorobenzyl alcohol (2 mmol, 282 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a white solid (530 mg, 1.90 mmol, 95 %).

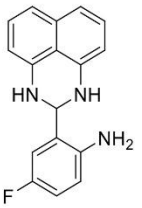
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.17 (t, J = 7.8 Hz, 1H), 7.09 (dd, J = 14.8, 8.1 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 6.73 (s, 1H), 6.57 – 6.49 (m, 2H), 6.35 (dd, J = 10.4, 8.4 Hz, 1H), 5.81 (s, 1H), 5.70 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 162.79, 160.87, 150.53, 150.49, 143.95, 134.48, 130.24, 130.14, 126.73, 115.78, 112.76, 111.58, 108.24, 108.14, 105.10, 101.51, 101.32, 59.66, 59.58, 39.52 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -120.53 (dd, J_1 = 10.6 Hz, J_2 = 6.6 Hz) ppm.

Elemental analysis calculated: C 73.10, H 5.05, N 15.04
Elemental analysis found: C 73.19, H 5.15, N 15.04

Synthesis of **A8**



Chemical Formula: $C_{17}H_{14}FN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-5-fluorobenzyl alcohol (2 mmol, 282 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 7 mL H_2O is added. After adding 10 mL pentane the precipitation is filtered and washed with pentane. The crude product was purified by filtration with dichloromethane over an Alox N plug and obtained as a white solid (469 mg, 1.68 mmol, 84 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.21 – 7.09 (m, 1H), 7.01 (d, J = 7.2 Hz, 1H), 6.95 (s, 1H), 6.71 (s, 1H), 6.65 (s, 1H), 6.52 (d, J = 6.3 Hz, 1H), 5.41 (s, 1H), 5.23 (s, 1H) ppm.

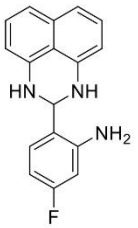
^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 154.91, 153.08, 143.88, 143.53, 134.41, 126.78, 123.96, 123.91, 116.71, 116.65, 115.69, 115.62, 115.49, 112.62, 104.78, 64.56 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -129.58 (m) ppm.

Elemental analysis calculated: C 73.10, H 5.05, N 15.04

Elemental analysis found: C 73.26, H 5.01, N 14.66

Synthesis of **A9**



Chemical Formula: $C_{17}H_{14}FN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-4-fluorobenzyl alcohol (2 mmol, 282 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature 7 mL H_2O is added. After adding 10 mL pentane the precipitation is filtered and washed with pentane. The crude product was purified by filtration with dichloromethane over an Alox N plug and obtained as a white solid (491 mg, 1.76 mmol, 88 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.28 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.8 Hz, 2H), 7.00 (d, J = 8.1 Hz, 2H), 6.62 (s, 2H), 6.52 (d, J = 7.3 Hz, 2H), 6.48 (d, J = 11.8 Hz, 1H), 6.35 (t, J = 8.4 Hz, 1H), 5.70 (s, 2H), 5.38 (s, 1H) ppm.

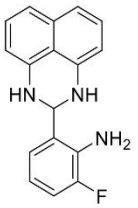
^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 164.27, 162.35, 149.76, 149.66, 143.87, 134.45, 131.93, 131.84, 126.75, 118.63, 115.44, 112.70, 104.75, 101.60, 101.43, 101.30, 101.11, 65.73 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -114.25 (dt, J_1 = 11.9 Hz, J_2 = 7.9 Hz) ppm.

Elemental analysis calculated: C 73.10, H 5.05, N 15.04

Elemental analysis found: C 72.99, H 5.07, N 15.12

Synthesis of **A10**



Chemical Formula: $C_{17}H_{14}FN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-fluorobenzyl alcohol (2 mmol, 282 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a white solid (508 mg, 1.82 mmol, 91 %).

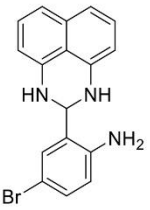
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.15 (dd, J = 14.0, 6.2 Hz, 3H), 7.08 (dd, J = 11.4, 8.1 Hz, 1H), 7.02 (d, J = 8.2 Hz, 2H), 6.71 (s, 2H), 6.64 – 6.55 (m, 1H), 6.52 (d, J = 7.4 Hz, 2H), 5.45 (s, 1H), 5.33 (s, 2H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 152.24, 150.36, 143.59, 135.75, 135.64, 134.42, 126.77, 125.63, 125.13, 125.10, 115.55, 115.00, 114.94, 114.87, 114.72, 112.67, 104.81, 65.92 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -135.02 (dd, J_1 = 11.9 Hz, J_2 = 5.3 Hz) ppm.

Elemental analysis calculated: C 73.10, H 5.05, N 15.04
Elemental analysis found: C 72.97, H 5.09, N 14.55

Synthesis of **A11**



Chemical Formula: $C_{17}H_{14}BrN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-5-bromobenzyl alcohol (2 mmol, 404 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a white solid (640 mg, 1.88 mmol, 94 %).

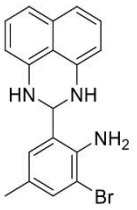
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.42 (d, J = 2.3 Hz, 1H), 7.22 (dd, J = 8.6, 2.4 Hz, 1H), 7.16 (t, J = 7.8 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.71 – 6.63 (m, 3H), 6.52 (d, J = 7.4 Hz, 2H), 5.55 (s, 2H), 5.39 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 146.85, 143.58, 134.40, 132.04, 131.46, 126.77, 124.61, 117.63, 115.52, 112.61, 105.95, 104.79, 64.77 ppm.

Elemental analysis calculated: C 60.02, H 4.15, N 12.35

Elemental analysis found: C 59.79, H 4.03, N 12.09

Synthesis of **A12**



Chemical Formula: $C_{18}H_{16}BrN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-bromo-5-methylbenzyl alcohol (2 mmol, 432 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3x10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a yellow solid (503 mg, 1.42 mmol, 71 %).

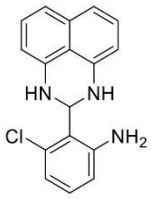
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.32 (s, 1H), 7.22 – 7.12 (m, 3H), 7.04 (d, J = 8.1 Hz, 2H), 6.74 (s, 2H), 6.54 (d, J = 7.4 Hz, 2H), 5.38 (s, 1H), 5.36 (s, 1H), 2.20 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.56, 142.07, 134.43, 132.60, 130.68, 126.79, 125.64, 124.09, 115.67, 112.70, 109.51, 104.91, 67.38, 19.55 ppm.

Elemental analysis calculated: C 61.03, H 4.55, N 11.86

Elemental analysis found: C 61.01, H 4.55, N 11.53

Synthesis of **A13**



Chemical Formula: $C_{17}H_{14}ClN_3$

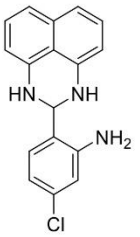
In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-6-chlorobenzyl alcohol (2 mmol, 315 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1→5:3) as a white solid (479 mg, 1.62 mmol, 81 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.17 (t, J = 7.8 Hz, 2H), 7.05 (dd, J = 10.6, 8.2 Hz, 3H), 6.78 (s, 2H), 6.67 (d, J = 8.2 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 6.54 (d, J = 7.3 Hz, 2H), 5.97 – 5.86 (m, 3H) ppm

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 150.60, 143.87, 134.47, 134.27, 130.17, 126.73, 117.16, 115.97, 115.77, 114.91, 112.69, 105.16, 64.29 ppm.

Elemental analysis calculated: C 69.04, H 4.77, N 14.21
Elemental analysis found: C 68.93, H 4.63 N 13.91

Synthesis of **A14**



Chemical Formula: $C_{17}H_{14}ClN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-4-chlorobenzyl alcohol (2 mmol, 315 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature 7 mL H_2O is added. After adding 10 mL pentane the precipitation is filtered and washed with pentane. The crude product was purified by filtration with dichloromethane over an Alox N plug and obtained as a white solid (479 mg, 1.62 mmol, 81 %).

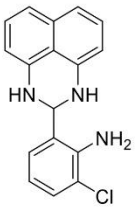
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.27 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 7.6 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.75 (s, 1H), 6.63 (s, 2H), 6.58 (d, J = 7.6 Hz, 1H), 6.52 (d, J = 7.2 Hz, 2H), 5.68 (s, 2H), 5.38 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 149.12, 143.71, 134.43, 133.58, 131.66, 126.76, 121.18, 115.49, 114.75, 114.44, 112.69, 104.79, 65.44 ppm.

Elemental analysis calculated: C 69.04, H 4.77, N 14.21

Elemental analysis found: C 68.73, H 4.45, N 13.79

Synthesis of **A15**



Chemical Formula: $C_{17}H_{14}ClN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-chlorobenzyl alcohol (2 mmol, 315 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a white solid (509 mg, 1.72 mmol, 86 %).

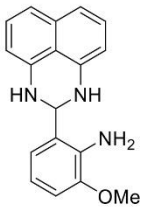
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.29 (dd, J = 16.7, 7.7 Hz, 2H), 7.17 (t, J = 7.8 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 6.75 (s, 2H), 6.63 (t, J = 7.7 Hz, 1H), 6.53 (d, J = 7.3 Hz, 2H), 5.59 (s, 2H), 5.43 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.53, 134.42, 129.34, 129.30, 126.78, 124.07, 118.59, 116.03, 115.66, 112.69, 104.91, 67.10, 39.52 ppm.

Elemental analysis calculated: C 69.04, H 4.77, N 14.21

Elemental analysis found: C 68.93, H 4.63, N 13.91

Synthesis of **A16**



Chemical Formula: $C_{18}H_{17}N_3O$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-methoxybenzyl alcohol (2 mmol, 306 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) as a yellow solid (472 mg, 1.62 mmol, 81 %).

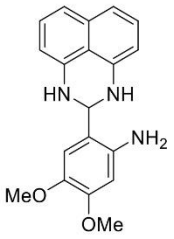
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.14 (t, J = 7.8 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 7.5 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 6.64 (s, 2H), 6.59 (t, J = 7.8 Hz, 1H), 6.51 (d, J = 7.4 Hz, 2H), 5.40 (s, 1H), 4.99 (s, 2H), 3.81 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 147.02, 143.83, 136.82, 134.46, 126.74, 122.49, 122.24, 115.36, 115.21, 112.68, 110.75, 104.68, 66.39, 55.75 ppm.

Elemental analysis calculated: C 74.20, H 5.88, N 14.42

Elemental analysis found: C 73.69, H 5.72, N 14.09

Synthesis of **A17**



Chemical Formula: $C_{19}H_{19}N_3O_2$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-4,5-dimethoxybenzyl alcohol (2 mmol, 367 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1→5:4) as a white solid (463 mg, 1.44 mmol, 72 %).

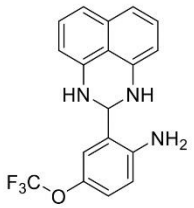
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.14 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.94 (s, 1H), 6.51 (d, J = 9.4 Hz, 1H), 6.40 (s, 1H), 5.34 (s, 1H), 4.98 (s, 1H), 3.71 (s, 1H), 3.64 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 150.17, 144.10, 142.10, 139.79, 134.47, 126.72, 115.42, 115.24, 114.02, 112.69, 104.59, 101.05, 65.06, 56.66, 55.41 ppm.

Elemental analysis calculated: C 71.01, H 5.96, N 13.08

Elemental analysis found: C 70.71, H 5.66, N 12.83

Synthesis of **A18**



Chemical Formula: $C_{18}H_{14}F_3N_3O$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-5-(trifluoromethoxy)benzyl alcohol (2 mmol, 414 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 7 mL H_2O is added. After adding 10 mL pentane the precipitation is filtered and washed with pentane. The crude product was purified by filtration with dichloromethane over an Alox N plug and obtained as a white solid (593 mg, 1.72 mmol, 86 %).

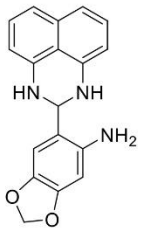
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.28 (d, J = 2.5 Hz, 1H), 7.16 (t, J = 7.8 Hz, 2H), 7.09 (d, J = 8.7 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.8 Hz, 1H), 6.68 (s, 2H), 6.52 (d, J = 7.3 Hz, 2H), 5.59 (s, 2H), 5.42 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 146.94, 143.61, 143.59, 138.07, 134.40, 126.81, 126.76, 123.01, 122.72, 122.31, 121.43, 119.41, 116.15, 115.56, 112.64, 104.84, 64.87 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -57.24 (s) ppm.

Elemental analysis calculated: C 62.61, H 4.09, N 12.17
Elemental analysis found: C 62.23, H 3.75, N 12.48

Synthesis of **A19**



Chemical Formula: $C_{18}H_{15}N_3O_2$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), (6-aminobenzo[d][1,3]dioxol-5-yl)methanol (2 mmol, 335 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 7 mL H_2O is added. After adding 10 mL pentane the precipitation is filtered and washed with pentane. The crude product was purified by filtration with dichloromethane over an Alox N plug and obtained as an orange solid (420 mg, 1.38 mmol, 69 %).

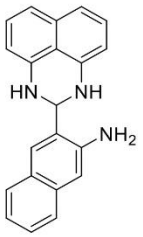
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.14 (t, J = 7.8 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 6.87 (s, 1H), 6.54 – 6.48 (m, 4H), 6.37 (s, 1H), 5.85 (s, 2H), 5.33 (s, 1H), 5.09 (s, 2H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 147.73, 143.96, 142.87, 137.97, 134.45, 126.74, 115.28, 114.69, 112.62, 109.35, 104.62, 100.13, 97.48, 64.85 ppm.

Elemental analysis calculated: C 70.81, H 4.95, N 13.76

Elemental analysis found: C 70.31, H 5.04, N 13.33

Synthesis of **A20**



Chemical Formula: $C_{21}H_{17}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), (3-aminonaphthalen-2-yl)methanol (2 mmol, 346 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 7 mL H_2O is added. After adding 10 mL pentane the precipitation is filtered and washed with pentane. The crude product was purified by filtration with dichloromethane over an Alox N plug and obtained as a grey solid (479 mg, 1.54 mmol, 77 %).

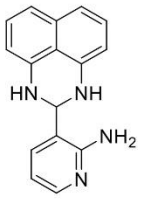
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.87 (s, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.18 (t, J = 7.8 Hz, 2H), 7.13 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 8.1 Hz, 2H), 7.00 (s, 1H), 6.77 (s, 2H), 6.55 (d, J = 7.3 Hz, 2H), 5.63 (s, 2H), 5.58 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 145.76, 143.55, 134.80, 134.46, 129.58, 127.76, 126.81, 126.37, 125.93, 124.68, 121.31, 115.55, 112.73, 108.19, 104.84, 66.72 ppm.

Elemental analysis calculated: C 81.00, H 5.50, N 13.49

Elemental analysis found: C 80.94, H 5.42, N 13.13

Synthesis of **A21**



Chemical Formula: $C_{16}H_{14}N_4$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), (2-aminopyridin-3-yl)methanol (2 mmol, 248 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 2 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1 →5:3) as a white solid (503 mg, 1.92 mmol, 96 %).

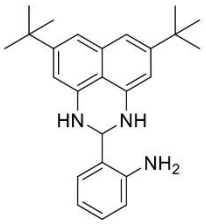
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 8.01 (s, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.18 (t, J = 7.7 Hz, 2H), 7.04 (d, J = 8.1 Hz, 2H), 6.72 (s, 2H), 6.64 – 6.58 (m, 1H), 6.55 (d, J = 7.3 Hz, 2H), 6.11 (s, 2H), 5.38 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 158.08, 148.06, 143.54, 137.79, 134.42, 126.79, 117.43, 115.65, 112.68, 111.93, 104.90, 65.72 ppm.

Elemental analysis calculated: C 73.26, H 5.38, N 21.36

Elemental analysis found: C 73.07, H 5.44, N 21.30

Synthesis of **A22**



Chemical Formula: $C_{25}H_{31}N_3$

In a glovebox, 1,8-diamino-4,6-di-*tert*-butyl-naphthalene (1 mmol, 270.5 mg), 2-aminobenzyl alcohol (1 mmol, 123 mg), KO^{t}Bu (0.3 mmol, 3 mg, 30 mol%), Mn-**I** (0.01 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 6 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with ethyl acetate (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1 →5:3) and obtained as a white solid (283 mg, 0.76 mmol, 76 %).

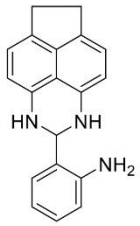
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.24 (d, J = 6.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 1.4 Hz, 1H), 6.70 (d, J = 7.9 Hz, 1H), 6.59 (d, J = 1.4 Hz, 1H), 6.38 (s, 1H), 5.36 (s, 1H), 5.35 (s, 1H), 1.29 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 149.00, 147.71, 143.20, 134.12, 130.09, 129.11, 122.39, 115.72, 115.40, 111.32, 109.94, 102.88, 34.48, 31.23 ppm.

Elemental analysis calculated: C 80.39, H 8.37 N 11.25

Elemental analysis found: C 79.99, H 8.31, N 11.50

Synthesis of **A23**



Chemical Formula: $C_{19}H_{17}N_3$

In a glovebox, 5,6-acenaphthenediamine (1 mmol, 184.3 mg), 2-aminobenzyl alcohol (1 mmol, 123 mg), KO^{t}Bu (0.3 mmol, 3 mg, 30 mol%), Mn-**I** (0.01 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 6 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with ethyl acetate (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:3) and obtained as a yellow solid (247 mg, 0.86 mmol, 86 %).

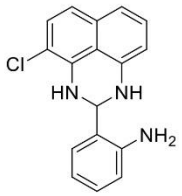
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.24 (d, J = 7.5 Hz, 1H), 7.08 (t, J = 7.7 Hz, 1H), 6.95 (d, J = 7.3 Hz, 1H), 6.70 (d, J = 8.1 Hz, 1H), 6.56 (t, J = 7.4 Hz, 1H), 6.42 (d, J = 7.2 Hz, 1H), 6.38 (s, 1H), 5.34 (s, 1H), 5.30 (s, 1H), 3.20 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 147.64, 140.59, 139.82, 132.13, 130.04, 129.06, 122.59, 119.58, 115.71, 115.43, 111.47, 105.29, 67.77, 29.96 ppm.

Elemental analysis calculated (product + 1 ethyl acetate): C 73.57, H 6.71, N 11.19

Elemental analysis found: C 73.86, H 6.32, N 11.11

Synthesis of **A24**



Chemical Formula: $C_{17}H_{14}ClN_3$

In a glovebox, 2-choro-1,8-diamino-naphthalene (1 mmol, 192.6 mg), 2-aminobenzyl alcohol (1 mmol, 123 mg), KO^{t}Bu (0.3 mmol, 3 mg, 30 mol%), Mn-**I** (0.01 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After stirring for 6 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with ethyl acetate (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:2) and obtained as a grey solid (269 mg, 0.91 mmol, 91%).

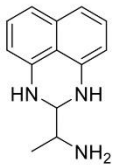
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.24 (dd, J = 17.3, 8.3 Hz, 2H), 7.07 (dd, J = 14.2, 8.5 Hz, 2H), 6.91 (s, 1H), 6.72 (dd, J = 8.0, 0.9 Hz, 1H), 6.67 – 6.62 (m, 1H), 6.56 (td, J = 7.5, 1.0 Hz, 1H), 5.81 (s, 1H), 5.55 (s, 1H), 5.32 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 147.06, 142.82, 138.39, 132.90, 129.07, 128.87, 127.47, 127.01, 122.89, 116.97, 115.92, 115.81, 115.53, 112.85, 107.98, 105.97, 64.31 ppm.

Elemental analysis calculated: C 69.04, H 4.77, N 14.21

Elemental analysis found: C 69.12, H 4.52, N 14.34

Synthesis of **A25**



Chemical Formula: $C_{13}H_{15}N_3$

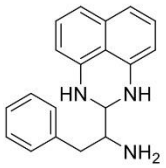
In a glovebox, Mn-precatalyst Mn-**I** (0.02 mmol, 12.3 mg, dissolved in 1.5 mL 1,4-dioxane), KO^{t}Bu (0.6 mmol, 67 mg, dissolved in 1.5 mL 1,4-dioxane), 1,8-diaminonaphthalene (2.0 mmol, 316 mg) and L-alaninol (2.2 mmol, 165 mg, 172 µL) are added to a Schlenk tube and dissolved in 9 mL 1,4-dioxane. The reaction mixture is heated at 100 °C under light argon counter flow using an open system consisting of a reflux condenser and a bubble counter. The mixture is stirred for 4 h, cooled down to room temperature and the 1,4-dioxane is evaporated under vacuo. 6 mL water are added and the organic compounds were extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via gradient column chromatography over Alox N using solvent mixtures beginning with ethyl acetate/pentane 1:1 and switching to ethanol/pentane 1:2. To the product 10 mL of an aqueous saturated solution of $NaHCO_3$ were added, the product was extracted with ethyl acetate and after drying with Na_2SO_4 the solution was narrowed. At the end the product was purified via column chromatography over Silica C18 ec with ethyl acetate and obtained as brown viscous oil (392 mg, 1.84 mmol, 92 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.11 (t, J = 7.6 Hz, 2H), 6.91 (d, J = 8.2 Hz, 2H), 6.47 (dd, J_1 = 7.5 Hz, J_2 = 0.8 Hz, 1H), 6.45 (dd, J_1 = 7.4 Hz, J_2 = 0.7 Hz, 1H), 6.32 (s, 1H), 6.21 (s, 1H), 4.09 (d, J = 4.4 Hz, 1H), 2.94 – 2.89 (m, 1H), 1.79 (s, broad, 2H), 1.09 (d, J = 6.6 Hz, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.02, 142.91, 134.40, 126.89, 114.76, 114.71, 112.46, 104.01, 68.85, 49.64, 17.85 ppm.

LC-HRMS (ESI+) *m/z* calculated for $[C_{13}H_{16}N_3]^+$: 214.13387, found: 214.13420.

Synthesis of **A26**



Chemical Formula: $C_{19}H_{19}N_3$

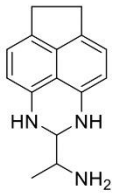
In a glovebox, Mn-precatalyst Mn-**I** (0.02 mmol, 12.3 mg, dissolved in 1.5 mL 1,4-dioxane), KO^{t}Bu (0.6 mmol, 67 mg, dissolved in 1.5 mL 1,4-dioxane), 1,8-diaminonaphthalene (2.0 mmol, 316 mg) and L-phenylalaninol (2.2 mmol, 333 mg) are added to a Schlenk tube and dissolved in 9 mL 1,4-dioxane. The reaction mixture is heated at 100 °C under light argon counter flow using an open system consisting of a reflux condenser and a bubble counter. The mixture is stirred for 4 h, cooled down to room temperature and the 1,4-dioxane is evaporated under vacuo. 6 mL water are added and the organic compounds were extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via gradient column chromatography over Alox N using solvent mixtures beginning with ethyl acetate/pentane 1:1 and switching to ethanol/pentane 1:2. To the product 10 mL of an aqueous saturated solution of $NaHCO_3$ were added, the product was extracted with ethyl acetate and after drying with Na_2SO_4 the solution was narrowed. At the end the product was purified via column chromatography over Silica C18 ec with ethyl acetate and obtained as yellowish brown viscous oil (544 mg, 1.88 mmol, 94 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.31 – 7.27 (m, 4H), 7.21 – 7.17 (m, 1H), 7.14 (td, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2 H), 6.51 (m, 2H), 6,44 (s, 1H), 6.35 (s, 1H), 4.24 (d, J = 3.8 Hz, 1H), 3.11 – 3.02 (m, 2H), 2.56 – 2.51 (m, 1H), 1.53 (s, broad, 2H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.05, 142.98, 140.38, 134.43, 129.25, 128.19, 126.91, 125.80, 114.92, 112.51, 104.24, 104.16, 67.74, 55.90, 37.60 ppm.

LC-HRMS (ESI+) *m/z* calculated for $[C_{19}H_{20}N_3]^+$: 290.16517, found: 290.16551.

Synthesis of **A27**



Chemical Formula: $C_{15}H_{17}N_3$

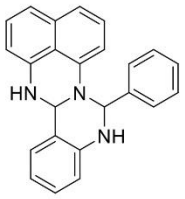
In a glovebox, Mn-precatalyst Mn-**I** (0.02 mmol, 12.3 mg, dissolved in 1.5 mL 1,4-dioxane), KO^{t}Bu (0.6 mmol, 67 mg, dissolved in 1.5 mL 1,4-dioxane), 5,6-diaminoacenaphthene (2.0 mmol, 369 mg) and L-alaninol (2.2 mmol, 165 mg, 172 µL) are added to a Schlenk tube and dissolved in 9 mL 1,4-dioxane. The reaction mixture is heated at 100 °C under light argon counter flow using an open system consisting of a reflux condenser and a bubble counter. The mixture is stirred for 4 h, cooled down to room temperature and the 1,4-dioxane is evaporated under vacuo. 6 mL water are added and the organic compounds were extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N using solvent mixtures beginning with ethyl acetate/pentane 1:1 and switching to ethanol/pentane 1:2. To the product 10 mL of an aqueous saturated solution of $NaHCO_3$ were added, the product was extracted with ethyl acetate and after drying with Na_2SO_4 the solution was narrowed. At the end the product was purified via column chromatography over Silica C18 ec with ethyl acetate and obtained as brown viscous oil (435 mg, 1.82 mmol, 91 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 6.92 (d, J = 7.2 Hz, 2H), 6.39 (d, J = 7.3 Hz, 1H), 6.37 (d, J = 7.2 Hz, 1H), 6.07 (s, 1H), 5.97 (s, 1H), 4.05 (d, J = 4.3 Hz, 1H), 3.16 (s, 4H), 2.93 (m, 1H), 1.68 (s, broad, 2H), 1.10 (d, J = 6.4 Hz, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 139.83, 139.78, 139.72, 131.60, 131.55, 119.69, 111.45, 104.71, 70.20, 49.58, 29.90, 18.09 ppm.

LC-HRMS (ESI+) *m/z* calculated for $[C_{15}H_{18}N_3]^+$: 240.14952, found: 240.14922.

Synthesis of **B1a**



Chemical Formula: $C_{24}H_{19}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µl) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as a white solid (648 mg, 1.86 mmol, 93 %).

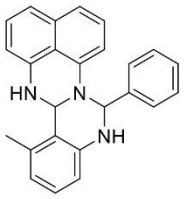
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.50 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.24 (t, J = 7.9 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 7.06 (dd, J = 7.3, 4.0 Hz, 2H), 6.98 – 6.94 (m, 2H), 6.87 (t, J = 7.6 Hz, 1H), 6.64 – 6.55 (m, 3H), 6.38 (t, J = 7.4 Hz, 1H), 5.09 (d, J = 3.4 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.20, 142.38, 141.15, 139.97, 134.28, 128.60, 127.95, 127.74, 126.94, 126.90, 126.62, 125.37, 121.62, 117.87, 115.46, 115.33, 113.78, 113.33, 105.59, 105.30, 65.48, 60.00 ppm.

Elemental analysis calculated: C 82.49, H 5.48, N 12.03

Elemental analysis found: C 82.68, H 5.39, N 11.99

Synthesis of **B1b**



Chemical Formula: $C_{25}H_{21}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-6-methylbenzyl alcohol (2 mmol, 275 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as a yellow solid (669 mg, 1.84 mmol, 92 %).

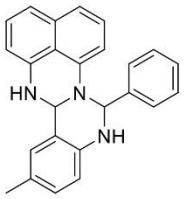
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.31 – 7.19 (m, 7H), 7.08 (d, J = 8.0 Hz, 1H), 7.01 – 6.91 (m, 2H), 6.76 (s, 1H), 6.73 (s, 1H), 6.68 (d, J = 7.4 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 6.46 (d, J = 7.4 Hz, 1H), 6.03 (d, J = 7.4 Hz, 1H), 5.63 (s, 1H), 5.47 (s, 1H), 2.31 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.51, 142.45, 141.59, 141.15, 135.69, 134.41, 128.65, 128.38, 128.26, 128.03, 126.72, 125.51, 120.74, 118.64, 117.44, 117.06, 115.59, 114.64, 112.24, 105.12, 68.11, 64.12, 18.40 ppm.

Elemental analysis calculated: C 82.61, H 5.82, N 11.56

Elemental analysis found: C 82.11, H 5.81, N 11.45

Synthesis of **B1c**



Chemical Formula: $C_{25}H_{21}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-5-methylbenzyl alcohol (2 mmol, 275 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as a yellow solid (603 mg, 1.66 mmol, 83 %).

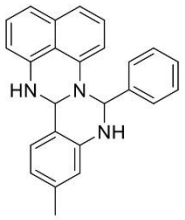
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.49 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 3.6 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.89 (s, 1H), 6.76 (d, J = 4.5 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.57 (d, J = 7.4 Hz, 1H), 6.55 – 6.50 (m, 2H), 5.07 (d, J = 3.6 Hz, 1H), 2.01 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 142.40, 141.22, 140.81, 140.03, 134.29, 128.60, 128.55, 127.67, 126.95, 126.63, 125.67, 123.89, 121.71, 117.74, 115.25, 113.65, 105.52, 105.20, 65.48, 60.03, 20.35 ppm.

Elemental analysis calculated: C 82.61, H 5.82, N 11.56

Elemental analysis found: C 82.83 H 5.83, N 11.47

Synthesis of **B1d**



Chemical Formula: $C_{25}H_{21}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-4-methylbenzyl alcohol (2 mmol, 275 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as a yellow solid (596 mg, 1.64 mmol, 82 %).

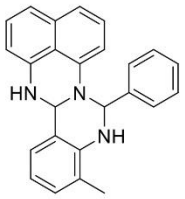
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.50 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.15 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 7.05 (d, J = 7.8 Hz, 1H), 6.95 (t, J = 7.7 Hz, 2H), 6.86 (d, J = 4.3 Hz, 1H), 6.59 – 6.52 (m, 2H), 6.41 (s, 1H), 6.19 (d, J = 7.7 Hz, 1H), 5.06 (d, J = 3.2 Hz, 1H), 2.05 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.00, 142.36, 141.23, 140.02, 137.02, 134.29, 128.58, 127.70, 126.96, 126.87, 126.60, 125.36, 118.95, 117.81, 116.53, 115.28, 113.82, 113.76, 105.60, 105.27, 65.50, 59.95, 20.92 ppm.

Elemental analysis calculated: C 82.61, H 5.82, N 11.56

Elemental analysis found: C 82.96 H 5.82, N 11.70

Synthesis of **B1e**



Chemical Formula: $C_{25}H_{21}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-methylbenzyl alcohol (2 mmol, 275 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as a yellow solid (567 mg, 1.56 mmol, 78 %).

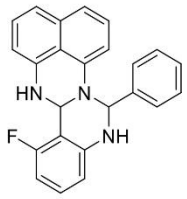
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.51 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 6.1 Hz, 2H), 7.25 (t, J = 7.9 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 7.06 (d, J = 7.7 Hz, 1H), 6.96 (t, J = 8.4 Hz, 2H), 6.78 (d, J = 7.3 Hz, 1H), 6.60 (d, J = 5.0 Hz, 1H), 6.57 (d, J = 7.3 Hz, 1H), 6.34 (dd, J = 14.4, 6.6 Hz, 2H), 5.12 (d, J = 3.7 Hz, 1H), 2.10 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 142.26, 141.16, 141.00, 139.97, 134.28, 128.99, 128.61, 127.73, 126.94, 126.91, 126.68, 123.15, 121.55, 121.03, 117.81, 115.33, 115.23, 113.72, 105.29, 105.23, 65.48, 60.02, 17.22 ppm.

Elemental analysis calculated: C 82.61, H 5.82, N 11.56

Elemental analysis found: C 81.99 H 5.81, N 11.22

Synthesis of **B1f**



Chemical Formula: $C_{24}H_{18}FN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-6-fluorobenzyl alcohol (2 mmol, 282 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as a yellow solid (639 mg, 1.73 mmol, 87 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.41 – 7.29 (m, 6H), 7.20 (t, J = 7.2 Hz, 2H), 7.13 (t, J = 7.8 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 6.97 (dd, J = 14.6, 7.8 Hz, 1H), 6.82 (s, 1H), 6.61 (t, J = 7.7 Hz, 2H), 6.51 (d, J = 8.1 Hz, 1H), 6.30 – 6.21 (m, 1H), 6.20 (d, J = 2.5 Hz, 1H), 5.43 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 161.66, 159.73, 145.53, 145.47, 141.06, 141.00, 140.83, 134.22, 129.36, 129.27, 128.48, 128.15, 127.63, 126.90, 126.15, 119.46, 115.61, 114.92, 109.82, 109.74, 107.48, 107.35, 105.18, 102.61, 102.43, 66.43, 60.08 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -119.89 (s) ppm.

Elemental analysis calculated: C 78.45, H 4.94, N 11.44
Elemental analysis found: C 77.82, H 5.01, N 11.55

Synthesis of **B1g**

Chemical Formula: $C_{24}H_{18}FN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-5-fluorobenzyl alcohol (2 mmol, 282 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as a yellow solid (602 mg, 1.64 mmol, 82 %).

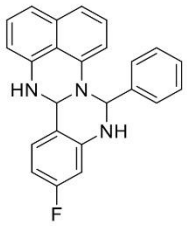
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.50 (d, J = 7.5 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.26 (t, J = 7.9 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 7.13 (d, J = 8.1 Hz, 1H), 7.09 (d, J = 7.7 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.95 (d, J = 4.6 Hz, 1H), 6.91 (dd, J = 9.4, 2.8 Hz, 1H), 6.74 (td, J = 8.7, 2.9 Hz, 1H), 6.62 (dd, J = 9.1, 5.6 Hz, 3H), 5.06 (d, J = 3.7 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 154.85, 153.01, 142.18, 140.84, 139.73, 139.60, 134.25, 128.67, 127.79, 126.94, 126.91, 126.68, 122.99, 122.95, 118.05, 115.64, 114.89, 114.71, 114.46, 114.41, 113.71, 111.94, 111.76, 105.82, 105.49, 65.52, 59.83 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -128.59 (m) ppm.

Elemental analysis calculated: C 78.45, H 4.94, N 11.44
Elemental analysis found: C 78.81, H 4.47, N 11.30

Synthesis of **B1h**



Chemical Formula: $C_{24}H_{18}FN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-4-fluorobenzyl alcohol (2 mmol, 282 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as a yellow solid (625 mg, 1.70 mmol, 85 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.49 (d, J = 7.5 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.39 – 7.30 (m, 2H), 7.26 (t, J = 7.9 Hz, 2H), 7.20 – 7.11 (m, 2H), 7.08 (d, J = 7.7 Hz, 1H), 7.07 – 7.02 (m, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.64 (d, J = 4.0 Hz, 1H), 6.57 (d, J = 7.3 Hz, 1H), 6.39 (dd, J = 11.3, 2.4 Hz, 1H), 6.16 (td, J = 8.7, 2.4 Hz, 1H), 5.05 (d, J = 3.6 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 163.30, 161.39, 144.86, 144.77, 141.97, 140.88, 139.67, 134.27, 128.68, 127.87, 127.14, 127.06, 126.94, 126.88, 126.62, 118.15, 117.71, 115.52, 113.77, 105.79, 105.47, 101.86, 101.68, 99.29, 99.09, 65.49, 59.73 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -114.85 (m) ppm.

Elemental analysis calculated: C 78.45, H 4.94, N 11.44
Elemental analysis found: C 77.88, H 4.99, N 11.28

Synthesis of **B1i**

Chemical Formula: $C_{24}H_{18}FN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-fluorobenzyl alcohol (2 mmol, 282 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as a yellow solid (580 mg, 1.58 mmol, 79 %).

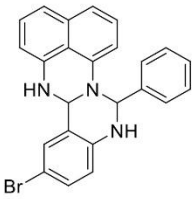
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.51 (d, J = 7.5 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 3.9 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.27 (t, J = 7.9 Hz, 1H), 7.20 – 7.11 (m, 2H), 7.07 (d, J = 7.7 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.92 (d, J = 7.2 Hz, 2H), 6.84 (t, 1H), 6.63 (d, J = 4.7 Hz, 1H), 6.58 (d, J = 7.3 Hz, 1H), 6.37 (dd, J = 12.9, 7.9 Hz, 1H), 5.11 (d, J = 3.8 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 150.57, 148.67, 141.74, 140.71, 139.56, 134.25, 131.33, 131.23, 128.72, 127.90, 126.98, 126.86, 126.65, 124.64, 121.10, 118.23, 115.53, 114.56, 114.51, 113.73, 113.66, 113.59, 105.57, 105.51, 65.10, 59.58 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -136.37 (dd, J_1 = 11.9 Hz, J_2 = 5.3 Hz) ppm.

Elemental analysis calculated: C 78.45, H 4.94, N 11.44
Elemental analysis found: C 77.99, H 5.06, N 11.39

Synthesis of **B1j**



Chemical Formula: $C_{24}H_{18}BrN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-5-bromobenzyl alcohol (2 mmol, 404 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as an orange solid (745 mg, 1.74 mmol, 87 %).

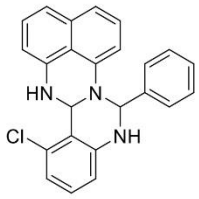
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.48 (d, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.36 (d, J = 4.6 Hz, 2H), 7.27 (t, J = 7.9 Hz, 1H), 7.20 (dd, J = 12.7, 5.2 Hz, 3H), 7.15 (d, J = 8.1 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.64 (d, J = 3.9 Hz, 1H), 6.62 – 6.56 (m, 2H), 5.05 (d, J = 3.6 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 142.55, 141.97, 140.69, 139.42, 134.26, 130.61, 128.71, 127.89, 127.79, 127.02, 126.84, 126.66, 123.82, 118.24, 115.68, 115.35, 113.65, 106.24, 105.84, 105.52, 65.41, 59.62 ppm.

Elemental analysis calculated: C 67.30, H 4.24, N 9.81

Elemental analysis found: C 67.17, H 4.34, N 9.84

Synthesis of **B1k**



Chemical Formula: $C_{24}H_{18}ClN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-6-chlorobenzyl alcohol (2 mmol, 315 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as a yellow solid (683 mg, 1.78 mmol, 89 %).

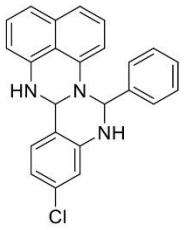
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.35 – 7.26 (m, 4H), 7.24 (dd, J = 9.3, 6.1 Hz, 4H), 7.11 (t, J = 8.5 Hz, 2H), 6.93 (t, J = 7.8 Hz, 1H), 6.78 – 6.70 (m, 3H), 6.68 (d, J = 7.8 Hz, 1H), 6.03 (d, J = 7.4 Hz, 1H), 5.60 (s, 1H), 5.48 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 145.31, 141.98, 140.80, 140.35, 134.26, 132.13, 129.91, 128.96, 128.63, 128.09, 126.75, 125.36, 121.89, 117.38, 116.75, 116.40, 115.99, 115.66, 112.81, 105.63, 68.39, 64.66 ppm.

Elemental analysis calculated: C 75.09, H 4.73, N 10.95

Elemental analysis found: C 75.28, H 4.78, N 11.37

Synthesis of **B1l**



Chemical Formula: $C_{24}H_{18}ClN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-4-chlorobenzyl alcohol (2 mmol, 315 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as a yellow solid (683 mg, 1.78 mmol, 89 %).

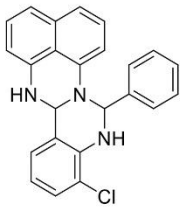
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.49 (d, J = 7.5 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.29 – 7.22 (m, 2H), 7.20 – 7.08 (m, 3H), 7.03 (d, J = 8.1 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.65 (dd, J = 8.1, 3.0 Hz, 2H), 6.57 (d, J = 7.3 Hz, 1H), 6.39 (d, J = 8.1 Hz, 1H), 5.04 (d, J = 3.9 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 144.59, 141.92, 140.78, 139.54, 134.26, 132.35, 128.71, 127.90, 127.14, 126.93, 126.86, 126.62, 120.40, 118.22, 115.60, 114.88, 113.74, 112.20, 105.83, 105.53, 65.47, 59.67 ppm.

Elemental analysis calculated: C 75.09, H 4.73, N 10.95

Elemental analysis found: C 75.19, H 4.95, N 10.99

Synthesis of **B1m**



Chemical Formula: $C_{24}H_{18}ClN_3$

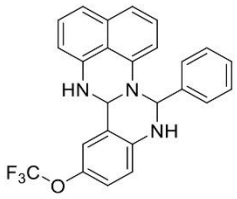
In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-chlorobenzyl alcohol (2 mmol, 315 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product is purified by recrystallization in ethyl acetate/pentane and obtained as orange crystals (575 mg, 1.50 mmol, 75 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.51 – 7.40 (m, 5H), 7.37 (d, J = 6.7 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 7.23 – 7.10 (m, 2H), 7.07 (dd, J = 14.1, 7.4 Hz, 3H), 6.98 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 4.4 Hz, 1H), 6.68 (d, J = 4.0 Hz, 1H), 6.59 (d, J = 7.2 Hz, 1H), 6.42 (t, J = 7.7 Hz, 1H), 5.10 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 141.64, 140.60, 139.41, 139.16, 134.25, 128.77, 128.05, 127.94, 127.02, 126.75, 126.69, 124.29, 123.84, 118.31, 116.71, 115.77, 115.56, 113.65, 105.56, 105.49, 65.30, 59.75 ppm.

Elemental analysis calculated: C 75.09, H 4.73, N 10.95
Elemental analysis found: C 74.86, H 4.79, N 11.20

Synthesis of **B1n**



Chemical Formula: $C_{25}H_{18}F_3N_3O$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-5-(trifluormethoxy)benzyl alcohol (2 mmol, 414 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 7 mL H_2O is added. After adding 10 mL pentane the precipitation is filtered and washed with pentane. The product is obtained as a yellow solid after drying in vacuo overnight (606 mg, 1.40 mmol, 70 %).

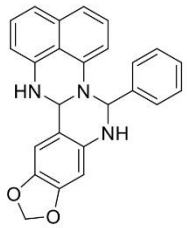
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.50 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.27 (dd, J = 9.6, 6.2 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.13 (dd, J = 11.9, 8.0 Hz, 1H), 7.04 (s, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.87 (dd, J = 8.7, 2.3 Hz, 1H), 6.70 – 6.64 (m, 1H), 6.60 (d, J = 7.3 Hz, 1H), 5.06 (d, J = 3.8 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 142.48, 141.99, 140.67, 139.36, 138.09, 134.24, 128.75, 127.89, 126.97, 126.84, 126.65, 122.45, 121.35, 118.59, 118.25, 115.73, 113.92, 113.70, 105.85, 105.57, 65.46, 59.67 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -57.31 (s) ppm.

Elemental analysis calculated: C 69.28, H 4.19, N 9.69
Elemental analysis found: C 69.62, H 4.23, N 10.02

Synthesis of **B1o**



Chemical Formula: $C_{25}H_{19}N_3O_2$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), (6-aminobenzo[d][1,3]dioxol-5-yl)methanol (2 mmol, 334 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:2) and obtained as a yellow solid (621 mg, 1.58 mmol, 79 %).

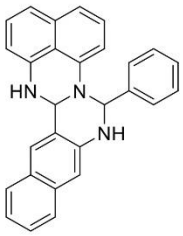
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.48 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.17 (t, J = 7.8 Hz, 1H), 7.12 (d, J = 8.1 Hz, 1H), 7.05 (d, J = 7.8 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.67 (s, 2H), 6.56 (d, J = 7.3 Hz, 1H), 6.52 (d, J = 3.7 Hz, 1H), 6.26 (s, 1H), 5.74 (s, 1H), 5.68 (s, 1H), 4.99 (d, J = 3.4 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 146.91, 142.18, 141.13, 139.86, 138.15, 138.13, 134.26, 128.58, 127.68, 126.95, 126.87, 126.66, 117.80, 115.44, 113.84, 113.74, 105.73, 105.61, 105.28, 99.89, 95.69, 65.61, 60.03 ppm.

Elemental analysis calculated: C 76.32, H 4.87, N 10.68

Elemental analysis found: C 75.96 H 4.87 N 10.39

Synthesis of **B1p**



Chemical Formula: $C_{28}H_{21}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), (3-aminonaphthalen-2-yl)methanol (2 mmol, 347 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature. The product precipitates during reaction. For purification, it was filtrated, washed with H_2O and cold diethyl ether and dried at 70 °C in vacuo. The product is obtained as a colourless solid (583 mg, 1.46 mmol, 73 %).

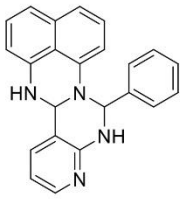
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.60 – 7.54 (m, 3H), 7.53 (d, J = 3.9 Hz, 1H), 7.44 (dd, J = 14.1, 7.2 Hz, 4H), 7.35 (dd, J = 9.7, 5.7 Hz, 2H), 7.27 – 7.15 (m, 3H), 7.11 (dd, J = 13.9, 8.0 Hz, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.91 (s, 1H), 6.70 (d, J = 4.0 Hz, 1H), 6.67 (d, J = 7.4 Hz, 1H), 5.27 (d, J = 3.6 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 142.34, 141.90, 140.83, 139.80, 134.26, 134.14, 128.64, 127.84, 127.34, 126.99, 126.61, 125.89, 125.64, 125.44, 124.76, 124.51, 121.30, 118.08, 115.51, 113.79, 105.78, 105.57, 65.58, 60.19 ppm.

Elemental analysis calculated: C 84.18, H 5.30, N 10.52

Elemental analysis found: C 83.78, H 5.02, N 10.34

Synthesis of **B1q**



Chemical Formula: $C_{23}H_{18}N_4$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-pyridinecarboxaldehyde (2 mmol, 225 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature. The product precipitates during reaction. For purification, it was filtrated, washed with H_2O and cold diethyl ether and dried at 70 °C in vacuo. The product is obtained as a light pink solid (603 mg, 1.72 mmol, 86 %).

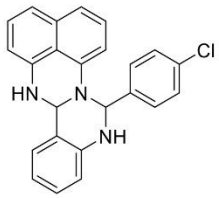
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.76 (d, J = 4.2 Hz, 1H), 7.69 (d, J = 4.4 Hz, 1H), 7.47 (dt, J = 20.0, 7.6 Hz, 5H), 7.36 (dd, J = 16.0, 7.5 Hz, 2H), 7.27 (d, J = 7.9 Hz, 1H), 7.22 – 7.12 (m, 2H), 7.10 (d, J = 7.7 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.66 (d, J = 4.3 Hz, 1H), 6.61 (d, J = 7.3 Hz, 1H), 6.43 – 6.37 (m, 1H), 5.06 (d, J = 3.7 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 154.30, 147.20, 141.73, 140.46, 139.35, 134.25, 132.94, 128.74, 127.95, 126.99, 126.85, 126.66, 118.41, 116.96, 115.68, 113.58, 112.17, 105.74, 64.95, 59.61 ppm.

Elemental analysis calculated: C 78.83, H 5.18, N 15.99

Elemental analysis found: C 78.52, H 5.41, N 16.01

Synthesis of **B2a**



Chemical Formula: $C_{24}H_{18}ClN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 4-chlorobenzaldehyde (2 mmol, 281 mg) is diluted in 0.7 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by recrystallization in ethyl acetate and obtained as yellow crystals (537 mg, 1.40 mmol, 70 %).

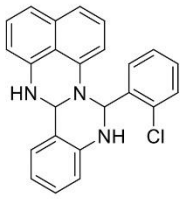
^{1}H NMR (CD_3CN, 500 MHz, 293 K): δ = 7.54 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.27 (t, J = 7.9 Hz, 1H), 7.27 (t, J = 7.9 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.07 (t, J = 6.5 Hz, 2H), 6.99 (d, J = 7.7 Hz, 1H), 6.93 (t, J = 7.7 Hz, 1H), 6.67 (d, J = 7.4 Hz, 1H), 6.67 (d, J = 7.4 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.54 (d, J = 4.8 Hz, 1H), 6.48 (t, J = 7.5 Hz, 1H), 6.48 (t, J = 7.5 Hz, 1H), 5.91 (d, J = 3.2 Hz, 1H), 5.65 (d, J = 4.4 Hz, 1H), 5.19 (d, J = 3.9 Hz, 1H) ppm.

^{13}C NMR (CD_3CN, 125 MHz, 293 K): δ = 143.87, 142.28, 142.08, 140.71, 135.85, 134.29, 130.04, 129.79, 129.54, 128.11, 127.78, 126.59, 123.21, 119.85, 117.89, 117.75, 115.58, 115.11, 107.48, 66.85, 61.77 ppm

Elemental analysis calculated: C 75.09, H 4.73, N 10.95

Elemental analysis found: C 74.82, H 5.04, N 10.80

Synthesis of **B2b**



Chemical Formula: $C_{24}H_{18}ClN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2-chlorobenzaldehyde (2 mmol, 225 µL) is diluted in 0.7 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as an orange solid (575 mg, 1.50 mmol, 75 %).

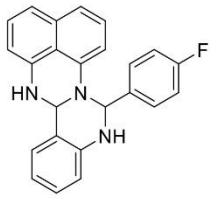
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.58 – 7.49 (m, 2H), 7.46 – 7.39 (m, 2H), 7.36 (d, J = 3.9 Hz, 1H), 7.27 (t, J = 7.9 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 4.6 Hz, 1H), 6.74 (d, J = 4.5 Hz, 1H), 6.59 (dd, J = 10.5, 7.8 Hz, 2H), 6.42 (t, J = 7.4 Hz, 1H), 5.14 (d, J = 3.8 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.32, 140.36, 139.69, 138.73, 134.36, 131.99, 130.14, 129.82, 129.77, 128.15, 126.96, 126.71, 125.31, 121.47, 117.90, 115.69, 115.44, 113.72, 113.06, 105.49, 105.23, 63.94, 59.58 ppm.

Elemental analysis calculated: C 75.09, H 4.73, N 10.95

Elemental analysis found: C 75.58, H 4.51, N 11.02

Synthesis of **B2c**



Chemical Formula: $C_{24}H_{18}FN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 4-fluorobenzaldehyde (2 mmol, 215 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as a yellow solid (683 mg, 1.85 mmol, 92 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.96 (dd, J = 8.5, 5.6 Hz, 2H), 7.77 (d, J = 3.7 Hz, 1H), 7.72 – 7.65 (m, 3H), 7.61 (t, J = 7.8 Hz, 1H), 7.58 – 7.46 (m, 3H), 7.45 – 7.38 (m, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.09 – 7.00 (m, 3H), 6.83 (t, J = 7.4 Hz, 1H), 5.52 (d, J = 3.1 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.47, 141.45, 140.39, 138.97, 134.73, 129.53, 129.46, 128.45, 127.37, 127.05, 125.86, 122.05, 118.46, 116.07, 115.92, 115.84, 115.75, 114.25, 113.88, 106.20, 105.84, 65.47, 60.41 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -115.19 (m) ppm.

Elemental analysis calculated: C 78.45, H 4.94, N 11.44
Elemental analysis found: C 77.87, H 5.15, N 11.41

Synthesis of **B2d**

Chemical Formula: $C_{24}H_{18}BrN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2-bromobenzaldehyde (2 mmol, 234 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via recrystallization in ethyl acetate at -4 °C and obtained as orange crystals (719 mg, 1.67 mmol, 84 %).

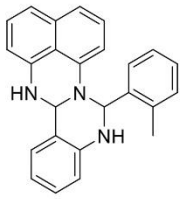
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.70 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.27 (t, J = 8.0 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 4.7 Hz, 1H), 6.63 (d, J = 4.5 Hz, 1H), 6.59 (t, J = 8.1 Hz, 2H), 6.42 (s, 1H), 5.13 (d, J = 3.9 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.31, 140.30, 140.10, 139.67, 134.36, 133.45, 130.10, 129.98, 128.17, 127.51, 126.94, 126.71, 125.33, 122.17, 121.53, 117.92, 115.70, 115.44, 113.76, 113.02, 105.49, 105.37, 66.08, 59.50 ppm.

Elemental analysis calculated: C 67.30, H 4.24, N 9.81

Elemental analysis found: C 67.68, H 3.97, N 9.83

Synthesis of **B2e**



Chemical Formula: $C_{25}H_{21}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2-methylbenzaldehyde (2 mmol, 233 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as a yellow solid (660 mg, 1.82 mmol, 91 %).

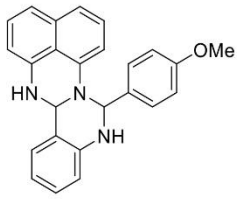
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.39 (d, J = 6.3 Hz, 1H), 7.34 (s, 1H), 7.25 (s, 3H), 7.19 – 7.03 (m, 4H), 6.95 (d, J = 7.6 Hz, 1H), 6.91 – 6.84 (m, 1H), 6.78 (s, 1H), 6.65 (s, 1H), 6.60 (d, J = 7.4 Hz, 1H), 6.56 (d, J = 6.6 Hz, 1H), 6.41 – 6.34 (m, 1H), 5.08 (s, 1H), 2.35 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.71, 140.68, 139.86, 139.51, 135.80, 134.38, 130.92, 128.02, 127.83, 127.60, 126.93, 126.75, 125.50, 125.24, 121.39, 117.72, 115.33, 115.27, 113.79, 112.92, 105.34, 105.14, 63.91, 59.70, 18.30 ppm.

Elemental analysis calculated: C 82.61, H 5.82, N 11.56

Elemental analysis found: C 82.32, H 5.87, N 11.70

Synthesis of **B2f**



Chemical Formula: $C_{25}H_{21}N_3O$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, *p*-anisaldehyde (2 mmol, 244 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via recrystallization in ethyl acetate at -4 °C and obtained as yellow crystals (592 mg, 1.56 mmol, 78 %).

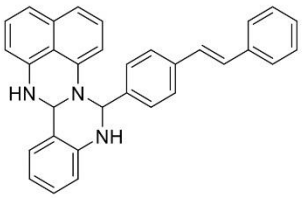
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.40 (d, J = 8.5 Hz, 1H), 7.32 (d, J = 3.4 Hz, 1H), 7.23 (t, J = 7.9 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.08 (dd, J = 14.5, 7.9 Hz, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.97 (dd, J = 13.5, 8.4 Hz, 1H), 6.91 (d, J = 4.0 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.58 (t, J = 8.2 Hz, 1H), 6.52 (d, J = 3.7 Hz, 1H), 6.38 (t, J = 7.3 Hz, 1H), 5.10 (d, J = 3.2 Hz, 1H), 3.76 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 158.83, 143.23, 141.19, 140.05, 134.29, 134.14, 128.13, 127.92, 126.88, 126.62, 125.36, 121.63, 117.80, l115.39, 115.30, 113.94, 113.82, 113.31, 105.63, 105.26, 65.08, 59.89, 55.12 ppm.

Elemental analysis calculated: C 79.13, H 5.58, N 11.07

Elemental analysis found: C 78.70, H 5.58, N 10.89

Synthesis of **B2g**



Chemical Formula: $C_{32}H_{25}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, *trans*-4-stilbenecarboxyaldehyde (2 mmol, 416 mg) is diluted in 2 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature. The product precipitates during reaction. For purification it was filtrated, washed with H_2O and cold diethyl ether and dried at 70 °C in vacuo. The product is obtained as a white solid (614 mg, 1.36 mmol, 68 %).

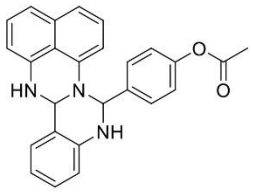
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.67 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.31 – 7.23 (m, 2H), 7.17 (t, J = 7.7 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.97 (t, J = 6.7 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 6.65 – 6.57 (m, 2H), 6.39 (t, J = 7.3 Hz, 1H), 5.14 (d, J = 3.0 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.18, 141.79, 141.11, 140.00, 137.01, 136.58, 134.30, 128.75, 128.60, 128.02, 127.97, 127.71, 127.36, 126.91, 126.73, 126.62, 126.50, 125.40, 121.66, 117.90, 115.51, 115.35, 113.80, 113.38, 105.64, 105.35, 65.40, 60.09 ppm.

Elemental analysis calculated: C 85.11, H 5.58, N 9.31

Elemental analysis found: C 84.77, H 5.37, N 9.03

Synthesis of **B2h**



Chemical Formula: $C_{26}H_{21}N_3O_2$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 4-(acetyloxy)-benzaldehyde (2 mmol, 278 µL) is added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with ethyl acetate (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as an orange-brown solid (562 mg, 1.38 mmol, 69 %).

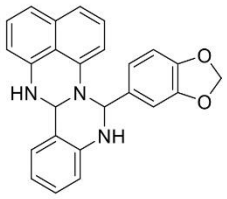
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.52 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 3.5 Hz, 1H), 7.25 (t, J = 7.9 Hz, 1H), 7.21 – 7.14 (m, 1H), 7.11 (d, J = 8.1 Hz, 1H), 7.06 (t, J = 9.0 Hz, 1H), 6.97 (t, J = 6.3 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 6.59 (dd, J = 14.4, 8.1 Hz, 1H), 6.39 (t, J = 7.3 Hz, 1H), 5.10 (d, J = 3.2 Hz, 1H), 2.27 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 169.27, 149.96, 143.05, 141.03, 139.93, 139.82, 134.28, 128.07, 127.98, 126.92, 126.60, 125.41, 121.99, 121.59, 117.96, 115.58, 115.36, 113.78, 113.41, 105.66, 105.34, 65.15, 59.98, 20.87 ppm.

Elemental analysis calculated: C 76.64, H 5.19, N 10.31

Elemental analysis found: C 76.76, H 5.36, N 9.95

Synthesis of **B2i**



Chemical Formula: $C_{25}H_{19}N_3O_2$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, piperonal (2 mmol, 301 mg) is diluted in 0.7 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via recrystallization in ethyl acetate at -4 °C and obtained as yellow crystals (621 mg, 1.58 mmol, 79 %).

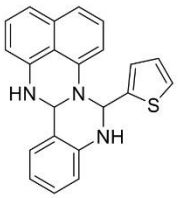
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.32 (d, J = 3.8 Hz, 1H), 7.23 (t, J = 7.9 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.08 (dd, J = 13.7, 7.9 Hz, 2H), 7.01 (d, J = 7.8 Hz, 1H), 6.98 – 6.92 (m, 4H), 6.86 (t, J = 7.5 Hz, 1H), 6.58 (d, J = 7.7 Hz, 2H), 6.47 (d, J = 4.3 Hz, 1H), 6.38 (t, J = 7.4 Hz, 1H), 6.03 (d, J = 5.2 Hz, 2H), 5.13 (d, J = 3.7 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 147.62, 146.82, 143.05, 141.07, 140.00, 136.25, 134.26, 127.94, 126.88, 126.59, 125.37, 121.63, 120.35, 117.86, 115.50, 115.35, 113.81, 113.30, 108.11, 106.95, 105.65, 105.34, 101.15, 65.28, 59.94 ppm.

Elemental analysis calculated: C 76.32, H 4.87, N 10.68

Elemental analysis found: C 76.01, H 4.82, N 10.60

Synthesis of **B2j**



Chemical Formula: $C_{22}H_{17}N_3S$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2-thiophenecarboxaldehyde (2 mmol, 187 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as a yellow solid (547 mg, 1.54 mmol, 77 %).

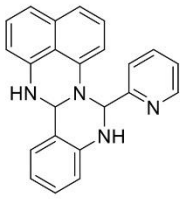
^{1}H NMR (DMSO-d_6, 400 MHz, 293 K): δ = 7.51 (d, J = 4.9 Hz, 1H), 7.37 (d, J = 3.6 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.15 – 7.08 (m, 4H), 7.07 – 6.99 (m, 2H), 6.98 (d, J = 8.1 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 4.4 Hz, 1H), 6.62 (dd, J = 10.0, 7.9 Hz, 2H), 6.44 (t, J = 7.4 Hz, 1H), 5.36 (d, J = 3.5 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 101 MHz, 293 K): δ = 147.26, 142.65, 140.32, 140.17, 134.32, 127.98, 127.19, 126.96, 126.52, 126.34, 125.65, 125.38, 121.42, 118.18, 116.08, 115.46, 113.84, 113.76, 105.73, 105.56, 62.98, 60.58 ppm.

Elemental analysis calculated: C 74.34, H 4.82, N 11.82

Elemental analysis found: C 73.93, H 4.88, N 11.36

Synthesis of **B2k**



Chemical Formula: $C_{23}H_{18}N_4$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2-pyridinecarboxaldehyde (2 mmol, 191 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature. The product precipitates during reaction. For purification it was filtrated, washed with H_2O and cold diethyl ether and dried at 70 °C in vacuo. The product is obtained as a light pink solid (470 mg, 1.34 mmol, 67 %).

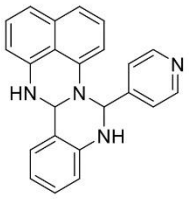
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 8.59 (d, J = 4.1 Hz, 1H), 7.84 (t, J = 7.2 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.34 (dd, J = 7.0, 5.0 Hz, 1H), 7.28 – 7.15 (m, 4H), 7.12 (d, J = 8.1 Hz, 1H), 7.00 (d, J = 8.1 Hz, 1H), 6.98 – 6.88 (m, 3H), 6.64 (d, J = 7.0 Hz, 2H), 6.53 – 6.41 (m, 2H), 5.32 (d, J = 2.7 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 160.39, 149.37, 143.07, 141.23, 140.43, 137.00, 134.34, 128.03, 126.91, 126.59, 125.51, 123.02, 122.09, 121.44, 117.74, 115.77, 115.53, 113.81, 113.61, 105.52, 105.26, 67.17, 60.79 ppm.

Elemental analysis calculated: C 78.83, H 5.18, N 15.99

Elemental analysis found: C 78.35, H 5.11, N 15.70

Synthesis of **B2l**



Chemical Formula: $C_{23}H_{18}N_4$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 4-pyridinecarboxaldehyde (2 mmol, 189 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature. The product precipitates during reaction. For purification it was filtrated, washed with H_2O and cold diethyl ether and dried at 70 °C in vacuo. The product is obtained as a light pink solid (554 mg, 1.58 mmol, 79 %).

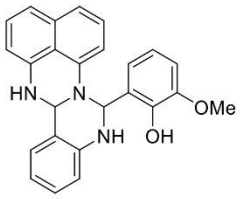
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 8.63 (d, J = 4.1 Hz, 2H), 7.51 (d, J = 4.4 Hz, 2H), 7.34 (d, J = 3.1 Hz, 1H), 7.25 (t, J = 7.9 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.13 (d, J = 8.1 Hz, 1H), 7.07 (t, J = 6.8 Hz, 2H), 7.02 (d, J = 4.2 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.66 – 6.57 (m, 3H), 6.41 (t, J = 7.3 Hz, 1H), 5.04 (d, J = 2.8 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 151.42, 150.12, 142.79, 140.76, 139.83, 134.28, 128.08, 126.97, 126.56, 125.44, 122.18, 121.53, 118.20, 115.94, 115.50, 113.73, 113.64, 105.66, 105.57, 64.88, 60.36 ppm.

Elemental analysis calculated: C 78.83, H 5.18, N 15.99

Elemental analysis found: C 78.79, H 5.10, N 15.53

Synthesis of **B2m**



Chemical Formula: $C_{25}H_{21}N_3O_2$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, *o*-vanilin (2 mmol, 304 mg) is diluted in 1 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product is purified by recrystallization in ethyl acetate at -4 °C. The product is obtained as yellow crystals (554 mg, 1.40 mmol, 70 %).

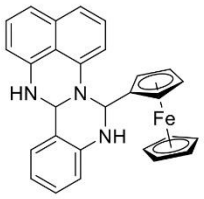
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 8.84 (s, 1H), 7.32 (d, J = 3.8 Hz, 1H), 7.23 (d, J = 7.9 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H), 7.08 (dd, J = 14.3, 7.9 Hz, 2H), 7.01 – 6.91 (m, 3H), 6.86 (d, J = 7.5 Hz, 2H), 6.78 (t, J = 7.9 Hz, 1H), 6.72 (s, 2H), 6.55 (dd, J = 14.2, 7.6 Hz, 2H), 6.39 (s, 1H), 5.32 (d, J = 3.7 Hz, 1H), 3.81 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 147.60, 143.68, 143.37, 140.89, 140.06, 134.33, 128.30, 127.99, 126.85, 126.64, 125.31, 121.34, 120.23, 118.19, 117.48, 115.31, 115.27, 113.77, 112.91, 111.50, 105.41, 105.25, 61.54, 59.90, 55.94 ppm.

Elemental analysis calculated: C 75.93, H 5.35, N 10.63

Elemental analysis found: C 75.79, H 5.05, N 10.55

Synthesis of **B2n**



Chemical Formula: $C_{28}H_{23}FeN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, ferrocenecarboxaldehyde (2 mmol, 428 mg) is diluted in 1.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature. The product precipitates during reaction. For purification it was filtrated, washed with H_2O and cold diethyl ether and dried at 70 °C in vacuo. The product is obtained as a pink solid (659 mg, 1.44 mmol, 72 %).

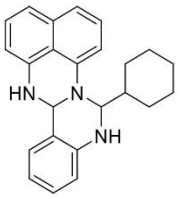
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.30 (d, J = 3.6 Hz, 1H), 7.25 (t, J = 7.9 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.07 (t, J = 7.0 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 4.2 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 7.3 Hz, 1H), 6.44 (d, J = 4.1 Hz, 1H), 6.36 (t, J = 7.4 Hz, 1H), 5.30 (d, J = 3.4 Hz, 1H), 4.35 (s, 3H), 4.21 (s, 1H), 4.13 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.34, 140.53, 140.02, 134.29, 127.86, 126.84, 126.52, 125.25, 121.15, 117.63, 115.22, 115.15, 113.61, 113.10, 105.45, 105.20, 89.74, 68.99, 68.72, 68.14, 66.83, 66.20, 63.43, 59.66 ppm.

Elemental analysis calculated: C 73.53, H 5.07, N 9.19

Elemental analysis found: C 72.85, H 5.07, N 8.99

Synthesis of **B2o**



Chemical Formula: $C_{24}H_{25}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, cyclohexanecarboxaldehyde (2 mmol, 242 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.1) and obtained as a yellow solid (675 mg, 1.90 mmol, 95 %).

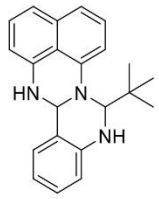
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.45 (d, J = 3.5 Hz, 1H), 7.21 – 7.09 (m, 2H), 7.00 (d, J = 8.1 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 6.78 (dd, J = 16.1, 7.7 Hz, 2H), 6.62 (d, J = 7.3 Hz, 1H), 6.58 (d, J = 4.2 Hz, 1H), 6.42 (d, J = 7.9 Hz, 1H), 6.33 (t, J = 7.3 Hz, 1H), 5.54 (d, J = 3.5 Hz, 1H), 4.86 (dd, J = 9.2, 4.2 Hz, 1H), 2.09 (d, J = 11.7 Hz, 1H), 1.91 (d, J = 12.8 Hz, 1H), 1.83 – 1.60 (m, 4H), 1.30 – 1.06 (m, 4H), 1.02 – 0.92 (m, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.20, 141.54, 139.98, 134.32, 127.65, 126.79, 126.62, 125.17, 121.39, 116.98, 115.22, 114.64, 113.79, 113.02, 105.20, 104.58, 68.05, 59.65, 41.33, 29.29, 27.51, 26.13, 25.38, 25.29 ppm.

Elemental analysis calculated: C 81.09, H 7.09, N 11.82

Elemental analysis found: C 80.49, H 7.16, N 10.99

Synthesis of **B2p**



Chemical Formula: $C_{22}H_{23}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, pivalaldehyde (2 mmol, 125 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product is purified by recrystallization in dichloromethane/pentane at -4 °C. The product is obtained as green crystals (451 mg, 1.37 mmol, 68 %).

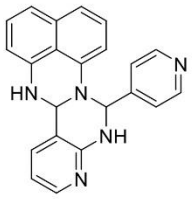
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.41 (d, J = 3.7 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H), 7.01 – 6.91 (m, 3H), 6.87 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 6.70 (d, J = 7.4 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 6.41 (t, J = 7.4 Hz, 1H), 6.10 (d, J = 4.2 Hz, 1H), 5.29 (d, J = 3.6 Hz, 1H), 4.89 (d, J = 4.3 Hz, 1H), 1.11 (s, 9H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 145.35, 142.45, 140.58, 134.52, 127.31, 126.97, 126.83, 126.08, 123.28, 116.46, 115.81, 115.41, 113.95, 113.27, 105.11, 103.85, 73.64, 61.07, 37.95, 26.05 ppm.

Elemental analysis calculated: C 80.21, H 7.04, N 12.76

Elemental analysis found: C 80.09, H 6.79, N 12.57

Synthesis of **B3a**



Chemical Formula: $C_{22}H_{17}N_5$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-pyridinecarboxaldehyde (2 mmol, 225 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 4-pyridinecarboxaldehyde (2 mmol, 189 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature. The product precipitates during reaction. For purification, it was filtrated, washed with H_2O and cold diethyl ether and dried at 70 °C in vacuo. The product is obtained as a light pink solid (632 mg, 1.80 mmol, 90 %).

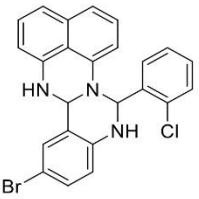
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 8.65 (d, J = 5.1 Hz, 2H), 7.77 (dd, J = 12.8, 4.4 Hz, 2H), 7.52 (d, J = 5.2 Hz, 2H), 7.40 (d, J = 3.9 Hz, 1H), 7.34 (d, J = 7.3 Hz, 1H), 7.28 (t, J = 7.9 Hz, 1H), 7.19 (dd, J = 16.8, 8.3 Hz, 2H), 7.11 (d, J = 7.7 Hz, 1H), 7.02 (d, J = 8.1 Hz, 1H), 6.69 (d, J = 4.3 Hz, 1H), 6.64 (d, J = 7.4 Hz, 1H), 6.43 (dd, J = 7.2, 5.0 Hz, 1H), 5.02 (d, J = 3.8 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 154.05, 150.73, 150.22, 147.33, 140.05, 139.16, 134.23, 133.03, 127.05, 126.59, 122.06, 118.76, 116.82, 115.89, 113.57, 112.57, 106.02, 105.93, 64.39, 60.02 ppm.

Elemental analysis calculated: C 75.19, H 4.88, N 19.93

Elemental analysis found: C 74.66 H 4.85 N 19.27

Synthesis of **B3b**



Chemical Formula: $C_{24}H_{17}BrClN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-5-bromobenzyl alcohol (2 mmol, 404 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2-chlorobenzaldehyde (2 mmol, 225 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:2) and obtained as an orange solid (721 mg, 1.56 mmol, 78 %).

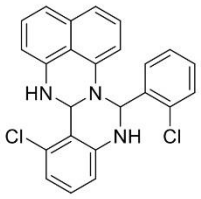
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.56 – 7.52 (m, 1H), 7.50 – 7.46 (m, 1H), 7.44 – 7.41 (m, 2H), 7.38 (d, J = 3.8 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.15 (d, J = 8.2 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 7.05 (d, J = 5.5 Hz, 2H), 7.01 (d, J = 8.1 Hz, 1H), 6.77 (d, J = 4.3 Hz, 1H), 6.61 (t, J = 7.5 Hz, 2H), 5.11 (d, J = 3.7 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 142.67, 139.92, 139.19, 138.27, 134.34, 131.95, 130.80, 130.22, 129.97, 129.69, 127.75, 127.07, 126.77, 123.64, 118.24, 115.80, 115.18, 113.57, 106.54, 105.73, 105.42, 63.88, 59.26 ppm.

Elemental analysis calculated: C 62.29, H 3.70, N 9.08

Elemental analysis found: C 62.30, H 3.67, N 8.94

Synthesis of **B3c**



Chemical Formula: $C_{24}H_{17}Cl_2N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-6-chlorobenzyl alcohol (2 mmol, 315 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2-chlorobenzaldehyde (2 mmol, 225 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:2) and obtained as a yellow solid (594 mg, 1.42 mmol, 71 %).

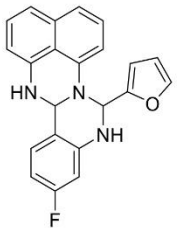
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.85 (d, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.23 (dd, J = 15.5, 7.8 Hz, 2H), 7.13 (dd, J = 13.9, 5.5 Hz, 3H), 6.92 (t, J = 7.8 Hz, 1H), 6.81 (s, 1H), 6.77 – 6.69 (m, 3H), 6.11 (s, 1H), 5.93 (d, J = 7.1 Hz, 1H), 5.45 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 145.25, 141.84, 140.24, 137.25, 134.23, 132.15, 131.46, 130.29, 129.97, 128.98, 127.22, 126.69, 125.12, 122.93, 116.42, 116.03, 115.54, 112.72, 105.71, 65.08, 64.38 ppm.

Elemental analysis calculated: C 68.91, H 4.10, N 10.05

Elemental analysis found: C 68.91, H 4.11, N 10.04

Synthesis of **B3d**



Chemical Formula: $C_{22}H_{16}FN_3O$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-4-fluorobenzyl alcohol (2 mmol, 228 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, furfural (2 mmol, 166 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as an orange solid (607 mg, 1.80 mmol, 85 %).

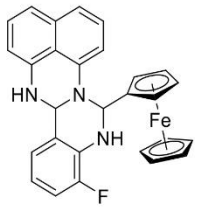
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.71 (s, 1H), 7.32 (d, J = 3.4 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.17 (tt, J = 15.2, 7.5 Hz, 4H), 6.99 (dd, J = 12.0, 8.0 Hz, 2H), 6.63 (d, J = 7.4 Hz, 1H), 6.60 (d, J = 3.8 Hz, 1H), 6.47 (s, 1H), 6.42 (d, J = 3.0 Hz, 1H), 6.37 (d, J = 11.2 Hz, 1H), 6.24 (t, J = 8.7 Hz, 1H), 5.25 (d, J = 3.0 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 163.25, 161.34, 153.54, 144.56, 144.47, 143.29, 140.08, 140.02, 134.30, 127.25, 127.17, 126.95, 126.52, 118.31, 117.23, 115.71, 113.90, 110.55, 109.45, 105.77, 102.37, 102.20, 99.70, 99.50, 61.29, 60.90 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -114.72 (m) ppm.

Elemental analysis calculated: C 73.94, H 4.51, N 11.76
Elemental analysis found: C 73.49 H 4.43 N 11.70

Synthesis of **B3e**



Chemical Formula: $C_{28}H_{22}FFeN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-3-fluorobenzyl alcohol (2 mmol, 228 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-**I** (0.01 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, ferrocenecarboxaldehyde (2 mmol, 428 mg) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1→5:3) and obtained as an orange solid (713 mg, 1.50 mmol, 75 %).

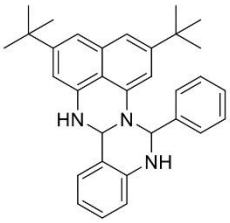
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.39 (d, J = 4.0 Hz, 1H), 7.26 (t, J = 7.9 Hz, 1H), 7.18 – 7.08 (m, 1H), 7.07 (d, J = 24.0 Hz, 1H), 6.99 – 6.91 (m, 1H), 6.88 – 6.80 (m, 1H), 6.78 (d, J = 5.2 Hz, 1H), 6.55 (d, J = 7.4 Hz, 1H), 6.50 (d, J = 5.1 Hz, 1H), 6.36 (dd, J = 12.8, 7.8 Hz, 1H), 5.36 (d, J = 3.8 Hz, 1H), 4.38 (s, 1H), 4.35 (s, 2H), 4.23 (s, 1H), 4.14 (d, J = 11.9 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 150.45, 148.55, 140.09, 139.61, 134.24, 131.50, 131.40, 126.92, 126.54, 124.31, 124.28, 121.10, 118.02, 115.40, 114.31, 114.25, 113.63, 113.50, 105.64, 105.39, 89.45, 69.03, 68.81, 68.02, 66.97, 66.28, 63.13, 59.33, 39.52 ppm.

^{19}F NMR (DMSO-d_6, 376 MHz, 293 K): δ = -136.35 (dd, J_1 = 11.2 Hz, J_2 = 4.6 Hz) ppm.

Elemental analysis calculated: C 70.75, H 4.67, N 8.84
Elemental analysis found: C 70.55, H 4.66, N 8.84

Synthesis of **B4a**



Chemical Formula: $C_{32}H_{35}N_3$

In a glovebox, 1,8-diamino-4,6-di-*tert*-butyl-naphthalene (1 mmol, 270.5 mg), 2-aminobenzyl alcohol (1 mmol, 123 mg), KO^{t}Bu (0.3 mmol, 33 mg, 30 mol%), Mn-**I** (0.01 mmol, 6 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 6 hours reaction time, benzaldehyde (1 mmol, 108 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3x10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as an orange solid (360 mg, 0.78 mmol, 78 %).

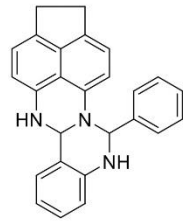
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.48 (d, J = 7.5 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.04 (dd, J = 4.5, 2.3 Hz, 1H), 6.95 – 6.86 (m, 1H), 6.63 (d, J = 10.4 Hz, 1H), 6.49 (d, J = 3.9 Hz, 1H), 6.42 (t, J = 7.4 Hz, 1H), 5.11 (d, J = 3.2 Hz, 1H), 1.30 (s, 1H), 1.28 (s, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 149.10, 148.69, 143.36, 142.45, 140.37, 139.66, 133.97, 128.48, 128.01, 127.75, 127.27, 125.59, 121.48, 115.44, 114.01, 113.36, 111.51, 111.34, 105.40, 103.16, 99.54, 65.70, 61.19, 34.74, 34.39, 31.23, 31.13 ppm.

Elemental analysis calculated: C 83.26, H 7.64, N 9.10

Elemental analysis found: C 83.61, H 7.87, N 9.19

Synthesis of **B4b**



Chemical Formula: $C_{26}H_{21}N_3$

In a glovebox, 5,6-acenaphthenediamine (1 mmol, 184.3 mg), 2-aminobenzyl alcohol (1 mmol, 123 mg), KO^{t}Bu (0.3 mmol, 33 mg, 30 mol%), Mn-**I** (0.01 mmol, 6 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 6 hours reaction time, benzaldehyde (1 mmol, 108 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was isolated by precipitation in pentane and subsequent washing with water and drying in vacuo. A brown solid was obtained (210 mg, 0.56 mmol, 56 %).

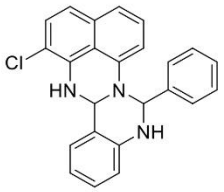
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.50 (d, J = 7.5 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.11 – 7.00 (m, 1H), 6.98 – 6.88 (m, 1H), 6.84 (t, J = 7.2 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 6.49 (t, J = 6.4 Hz, 1H), 6.35 (t, J = 7.1 Hz, 1H), 5.06 (d, J = 3.8 Hz, 1H), 3.15 (dd, J = 35.6, 13.0 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.40, 142.55, 139.55, 138.08, 136.72, 134.58, 132.17, 128.53, 127.79, 127.68, 127.01, 125.64, 121.64, 119.88, 119.47, 115.28, 113.17, 112.55, 106.57, 106.17, 65.72, 60.96, 29.80, 29.73 ppm.

Elemental analysis calculated: C 83.17, H 5.64, N 11.19

Elemental analysis found: C83.15, H 5.81, N 11.25

Synthesis of **B4c**



Chemical Formula: $C_{24}H_{18}ClN_3$

In a glovebox, 2-choro-1,8-diamino-naphthalene (1 mmol, 192.6 mg), 2-aminobenzyl alcohol (1 mmol, 123 mg), KO^{t}Bu (0.3 mmol, 33 mg, 30 mol%), Mn-**I** (0.01 mmol, 6 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 6 hours reaction time, benzaldehyde (1 mmol, 108 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:2) and obtained as a yellow solid (272 mg, 0.71 mmol, 71 %).

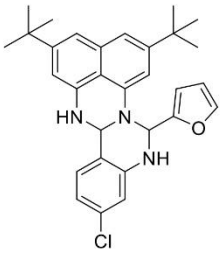
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.53 (d, J = 7.3 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.40 – 7.23 (m, 4H), 7.18 (dd, J = 18.9, 7.9 Hz, 2H), 7.05 – 6.96 (m, 2H), 6.91 (d, J = 7.6 Hz, 1H), 6.87 (dd, J = 11.8, 4.5 Hz, 1H), 6.65 (d, J = 4.4 Hz, 1H), 6.61 (d, J = 7.5 Hz, 1H), 6.37 (dd, J = 10.8, 4.0 Hz, 1H), 5.23 (d, J = 4.5 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.11, 142.25, 140.56, 135.34, 132.80, 128.67, 128.13, 127.81, 127.14, 126.98, 126.92, 125.15, 120.96, 118.12, 116.34, 115.51, 114.23, 113.34, 108.67, 106.83, 65.42, 59.89 ppm.

Elemental analysis calculated: C 75.09, H 4.73, N 10.95

Elemental analysis found: C 75.19, H 4.58, N 11.15

Synthesis of **B5a**



Chemical Formula: $C_{30}H_{32}ClN_3O$

In a glovebox, 1,8-diamino-4,6-di-*tert*-butyl-naphthalene (1 mmol, 270.5 mg), 2-amino-4-chloro-benzyl alcohol (1 mmol, 157 mg), KO^{t}Bu (0.3 mmol, 33 mg, 30 mol%), Mn-**I** (0.01 mmol, 6 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 6 hours reaction time, furfural (1 mmol, 83 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with ethyl acetate (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:2) and obtained as an orange solid (354 mg, 0.73 mmol, 73 %).

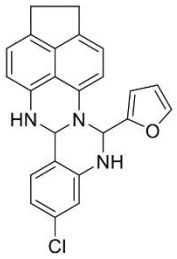
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.68 (d, J = 0.7 Hz, 1H), 7.15 (dd, J = 9.9, 6.0 Hz, 2H), 7.09 (d, J = 0.8 Hz, 1H), 7.03 (d, J = 3.0 Hz, 1H), 6.97 (d, J = 1.5 Hz, 1H), 6.89 (s, 1H), 6.67 (dd, J = 10.2, 1.8 Hz, 2H), 6.56 (d, J = 3.6 Hz, 1H), 6.50 (dd, J = 8.2, 2.0 Hz, 1H), 6.45 (dd, J = 3.1, 1.8 Hz, 1H), 6.40 (d, J = 3.2 Hz, 1H), 5.24 (d, J = 2.9 Hz, 1H), 1.30 (s, 20H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 153.56, 149.17, 148.71, 144.38, 143.14, 139.67, 139.39, 133.99, 132.44, 127.47, 119.69, 115.40, 114.36, 112.60, 111.99, 111.42, 110.51, 109.41, 105.37, 103.78, 61.93, 61.12, 34.80, 34.42, 31.21, 31.11 ppm.

Elemental analysis calculated: C 74.13, H 6.64, N 8.65

Elemental analysis found: C 74.33, H 6.63, N 8.42

Synthesis of **B5b**



Chemical Formula: $C_{24}H_{18}ClN_3O$

In a glovebox, 5,6-acenaphthenediamine (1 mmol, 184.3 mg), 2-amino-4-chloro-benzyl alcohol (1 mmol, 157 mg), KO^{t}Bu (0.3 mmol, 33 mg, 30 mol%), Mn-**I** (0.01 mmol, 6 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 6 hours reaction time, furfural (1 mmol, 83 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The crude product was purified by precipitation in pentane and subsequent washing with water and drying in vacuo. An orange solid was obtained (272 mg, 0.68 mmol, 68 %).

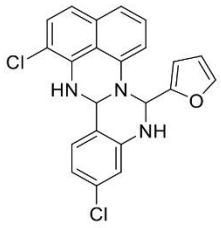
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.71 (s, 1H), 7.14 (d, J = 4.1 Hz, 1H), 7.11 – 7.06 (m, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.98 (d, J = 7.3 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.57 (d, J = 2.0 Hz, 1H), 6.54 (t, J = 5.7 Hz, 1H), 6.47 (dd, J = 3.1, 1.8 Hz, 1H), 6.42 – 6.35 (m, 1H), 5.21 (d, J = 3.7 Hz, 1H), 3.23 – 3.04 (m, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 153.73, 144.45, 143.28, 139.55, 136.83, 136.46, 135.15, 132.71, 132.22, 127.42, 119.99, 119.42, 115.13, 112.35, 110.53, 109.43, 106.82, 106.77, 67.03, 61.71, 61.55, 29.79, 29.72, 25.14 ppm.

Elemental analysis calculated: C 72.09, H 4.54, N 10.51

Elemental analysis found: C 72.26, H 4.52, N 10.73

Synthesis of **B5c**



Chemical Formula: $C_{22}H_{15}Cl_2N_3O$

In a glovebox, 2-choro-1,8-diamino-naphthalene (1 mmol, 192.6 mg), 2-amino-4-chloro-benzyl alcohol (1 mmol, 157 mg), KO^{t}Bu (0.3 mmol, 33 mg, 30 mol%), Mn-**I** (0.01 mmol, 6 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a reflux condenser and a bubble counter. After 6 hours reaction time, furfural (1 mmol, 83 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with DCM (3x10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:3) and obtained as a dark-orange solid (298 mg, 0.73 mmol, 73 %).

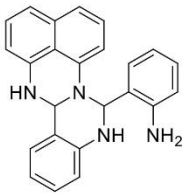
^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.76 (s, 1H), 7.35 (d, J = 4.6 Hz, 1H), 7.30 (dd, J = 16.4, 8.4 Hz, 2H), 7.24 (d, J = 4.3 Hz, 1H), 7.19 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 8.8 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.73 (d, J = 4.2 Hz, 1H), 6.60 (d, J = 2.0 Hz, 1H), 6.51 (dd, J = 3.2, 1.8 Hz, 1H), 6.48 (d, J = 3.2 Hz, 1H), 6.43 (dd, J = 8.2, 2.0 Hz, 1H), 5.36 (d, J = 4.6 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 153.39, 144.21, 143.61, 139.24, 134.98, 132.80, 132.52, 127.09, 127.07, 126.83, 119.47, 118.63, 116.76, 115.35, 114.22, 112.51, 110.64, 109.79, 109.17, 107.02, 61.52, 60.39 ppm.

Elemental analysis calculated (product + 1 ethyl acetate): C 62.91, H 4.67, N 8.47

Elemental analysis found: C 62.81, H 4.54, N, 8.67

Synthesis of **B6a**



Chemical Formula: $C_{24}H_{20}N_4$

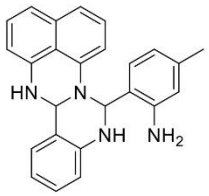
In a glovebox, Mn-**I** (0.02 mmol, 12.3 mg, dissolved in 0.5 mL 2-MeTHF), KO^{t}Bu (0.6 mmol, 67 mg, dissolved in 0.5 mL 2-MeTHF), 1,8-diaminonaphthalene (2.0 mmol, 316 mg) and 2-aminobenzyl alcohol (2.0 mmol, 247 mg) are added to a Schlenk tube and dissolved in 3 mL 2-MeTHF. The reaction mixture is heated at 100 °C under light argon counter flow using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2-aminobenzyl alcohol (2.0 mmol, 247 mg) is dissolved in 1.0 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After 15 hours, the reaction is stopped by cooling to room temperature and 4 mL water are added. The reaction mixture is diluted with 15 mL pentane, the precipitate is filtrated and washed with water and pentane. The dried solid is mortared, slurred with ethanol and stirred for 10 min at 100 °C. After filtration, the product is dried in vacuo and obtained as light green solid (424 mg, 1.16 mmol, 58 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.43 (d, J = 3.7 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H), 7.19 – 7.11 (m, 4H), 7.10 – 7.04 (m, 2H), 6.97 (d, J = 8.1 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.78 (d, J = 7.8 Hz, 1H), 6.63 (t, J = 7.4 Hz, 1H), 6.58 (d, J = 7.0 Hz, 2H), 6.40 – 6.35 (m, 2H), 5.20 (d, J = 3.7 Hz, 1H), 4.97 (s, 2H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 145.53, 143.35, 140.26, 139.82, 134.35, 128.59, 128.20, 128.10, 126.99, 126.63, 125.35, 124.40, 120.96, 118.33, 116.41, 115.94, 115.50, 115.39, 114.13, 113.05, 106.14, 105.49, 63.73, 60.44 ppm.

LC-HRMS (ESI+) *m/z* calculated for $[C_{24}H_{21}N_4]^+$: 365.17607, found: 365.17610.

Synthesis of **B6b**



Chemical Formula: $C_{25}H_{22}N_4$

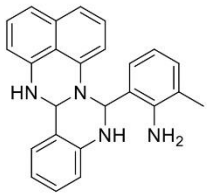
In a glovebox, Mn-**I** (0.02 mmol, 12.3 mg, dissolved in 0.5 mL 2-MeTHF), KO^{t}Bu (0.6 mmol, 67 mg, dissolved in 0.5 mL 2-MeTHF), 1,8-diaminonaphthalene (2.0 mmol, 316 mg) and 2-aminobenzyl alcohol (2.0 mmol, 247 mg) are added to a Schlenk tube and dissolved in 3 mL 2-MeTHF. The reaction mixture is heated at 100 °C under light argon counter flow using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2-amino-4-methylbenzyl alcohol (2.2 mmol, 302 mg) is added to the reaction mixture via a funnel under argon counter flow and diluted with 1.0 mL 2-MeTHF. After 15 hours, the reaction is stopped by cooling to room temperature and 4 mL water are added. The reaction mixture is diluted with 15 mL pentane, the precipitate is filtrated and washed with water and pentane. The dried solid is mortared, slurred with ethanol and stirred for 10 min at 100 °C. After filtration, the product is dried in vacuo and obtained as dark green solid (287 mg, 0.76 mmol, 38 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.42 (d, J = 3.7 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.18 – 7.10 (m, 3H), 7.04 (d, J = 7.6 Hz, 2H), 6.96 (d, J = 8.1 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 4.0, 1H), 6.61 – 6.55 (m, 3H), 6.44 (d, J = 7.5 Hz, 1H), 6.38 – 6.33 (m, 2H), 5.19 (d, J = 3.4 Hz, 1H), 4.88 (s, 2H), 2.19 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 145.33, 143.37, 140.33, 139.86, 137.66, 134.34, 128.22, 128.05, 126.96, 126.63, 125.33, 121.79, 120.98, 118.25, 117.28, 116.51, 115.42, 115.36, 114.13, 113.03, 106.10, 105.44, 63.59, 60.35, 20.93 ppm.

LC-HRMS (ESI+) *m/z* calculated for $[C_{25}H_{23}N_4]^+$: 379.19172, found: 379.19267.

Synthesis of **B6c**



Chemical Formula: $C_{25}H_{22}N_4$

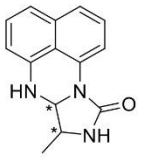
In a glovebox, Mn-**I** (0.02 mmol, 12.3 mg, dissolved in 0.5 mL 2-MeTHF), KO^{t}Bu (0.6 mmol, 67 mg, dissolved in 0.5 mL 2-MeTHF), 1,8-diaminonaphthalene (2.0 mmol, 316 mg) and 2-aminobenzyl alcohol (2.0 mmol, 247 mg) are added to a Schlenk tube and dissolved in 3 mL 2-MeTHF. The reaction mixture is heated at 100 °C under light argon counter flow using an open system consisting of a reflux condenser and a bubble counter. After 2 hours reaction time, 2-amino-3-methylbenzyl alcohol (2.2 mmol, 302 mg) is dissolved in 1.0 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After 15 hours, the reaction is stopped by cooling to room temperature and 4 mL water are added. The reaction mixture is diluted with 15 mL pentane, the precipitate is filtrated and washed with water and pentane. The dried solid is mortared, slurred with ethanol and stirred for 10 min at 100 °C. After filtration, the product is dried in vacuo and obtained as greyish green solid (602 mg, 1.59 mmol, 79 %).

^{1}H NMR (DMSO-d_6, 500 MHz, 293 K): δ = 7.43 (s, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.20 – 7.13 (m, 3H), 7.07 (dd, J_1 = 11.7 Hz, J_2 = 8.0 Hz, 2H), 7.02 (d, J = 6.9 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.59 (d, J = 7.0 Hz, 3H), 6.43 – 6.35 (m, 2H), 5.21 (s, 1H), 4.75 (s, 2H), 2.15 (s, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 143.35, 143.19, 140.21, 139.78, 134.35, 129.85, 128.11, 127.02, 126.62, 126.16, 125.33, 123.89, 122.36, 120.89, 118.42, 116.10, 115.46, 115.39, 114.12, 113.00, 106.09, 105.49, 63.91, 60.47, 17.53 ppm.

LC-HRMS (ESI+) *m/z* calculated for $[C_{25}H_{23}N_4]^+$: 379.19172, found: 379.19234/ 379.19238.

Synthesis of **C1**



Chemical Formula: $C_{14}H_{13}N_3O$

In a glovebox, **A25** (2.0 mmol, 426 mg), KO^{t}Bu (0.6 mmol, 67 mg, dissolved in 1.5 mL 1,4-dioxane) and carbonyldiimidazol (2.3 mmol, 373 mg) are added to a pressure tube and dissolved in 8.5 mL 1,4-dioxane. The sealed pressure tube is heated at 130 °C for 2h in an oil bath. After cooling down to room temperature 30 mL water were added and the product is extracted with diethyl ether (4 x 50 mL). The combined organic phases are dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via gradient column chromatography over Alox N (pentane/ethyl acetate 1:1 → pure ethyl acetate) and obtained as light brown solid (406 mg, 1.7 mmol, 85 %, contains ~ 2 % 1,4-dioxane). Diastereomeric ratio: 71:29.

Main isomer: **^{1}H NMR** (DMSO-d_6, 500 MHz, 293 K): δ = 7.62 (dd, J_1 = 7.3 Hz, J_2 = 1.2 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.29 – 7.25 (m, 1H), 7.19 (dd, J_1 = 8.2 Hz, J_2 = 0.7 Hz, 1H), 6.98 (s, 1H), 6.64 (dd, J_1 = 7.3 Hz, J_2 = 0.9 Hz, 1H), 4.68 (d. J = 4.1 Hz, 1H), 3.63 – 3.57 (m, 1H), 1.31 (d, J = 6.3 Hz, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 156.53, 141.37, 134.06, 132.68, 126.14, 121.25, 116.96, 114.72, 111.70, 106.87, 70.83, 51.41, 19.91 ppm.

Minor isomer: **^{1}H NMR** (DMSO-d_6, 500 MHz, 293 K): δ = 7.71 (dd, J_1 = 7.3 Hz, J_2 = 1.2 Hz, 1H), 7.44 – 7.36 (m, 1H), 7.36 – 7.34 (m, 1H), 7.33 (s, 1H), 7.29 – 7.25 (m, 1H), 7.18 (dd, J_1 = 8.2 Hz, J_2 = 0.7 Hz, 1H), 6.73 (dd, J_1 = 7.5 Hz, J_2 = 0.9 Hz, 1H), 6.63 (s, 1H), 5.07 (d. J = 7.2 Hz, 1H), 3.95 (quin. J = 6.6 Hz, 1H), 1.25 (d, J = 6.6 Hz, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 156.63, 141.79, 133.96, 133.16, 126.92, 120.97, 116.80, 114.03, 110.92, 107.26, 66.20, 47.92, 15.52 ppm.

LC-HRMS (ESI+) *m/z* calculated for $[C_{14}H_{14}N_3O]^+$: 240.11314, found: 240.11347.

Synthesis of **C2**

Chemical Formula: $C_{20}H_{17}N_3O$

In a glovebox, **A26** (2.0 mmol, 578 mg), KO^{t}Bu (0.6 mmol, 67 mg, dissolved in 1.5 mL 1,4-dioxane) and carbonyldiimidazol (2.3 mmol, 373 mg) are added to a pressure tube and dissolved in 8.5 mL 1,4-dioxane. The sealed pressure tube is heated at 130 °C for 2h in an oil bath. After cooling down to room temperature 30 mL water were added and the product is extracted with diethyl ether (4 x 50 mL). The combined organic phases are dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via gradient column chromatography over Alox N (pentane/ethyl acetate 1:1 → pure ethyl acetate) and obtained as reddish brown solid (573 mg, 1.82 mmol, 91 %, contains ~ 5% ethyl acetate). Diastereomeric ratio: 88:12.

Main isomer: **^{1}H NMR** (DMSO-d_6, 500 MHz, 293 K): δ = 7.49 (s, 1H), 7.46 – 7.42 (m, 2H), 7.36 (t, J = 7.8 Hz, 1H), 7.34 – 7.30 (m, 4H), 7.27 – 7.23 (m, 2H), 7.20 – 7.18 (m, 1H), 6.83 (s, 1H), 6.62 (d, J = 7.3 Hz, 1H), 4.78 (d, J = 3.1 Hz, 1H), 3.84 – 3.78 (m, 1H), 3.03 – 2.88 (m, 2H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 156.84, 141.29, 136.92, 134.01, 132.40, 129.62, 128.42, 126.88, 126.53, 126.05, 121.66, 116.98, 115.07, 113.01, 106.95, 68.20, 56.30, 39.64 ppm.

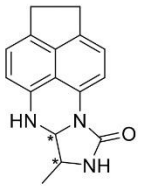
LC-HRMS (ESI+) *m/z* calculated for $[C_{20}H_{18}N_3O]^+$: 316.14444, found: 316.14440.

Minor isomer: **^{1}H NMR** (DMSO-d_6, 500 MHz, 293 K): δ = 7.76 (dd, J_1 = 7.4 Hz, J_2 = 1.1 Hz, 1H), 7.42 (dd, J_1 = 8.2 Hz, J_2 = 1.1 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.34 – 7.31 (m, 4H), 7.29 (d, J = 7.5 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.21 (d, J = 7.6 Hz, 1H), 6.77 (dd, J_1 = 7.4 Hz, J_2 = 0.8 Hz, 1H), 6.76 (s, 1H), 5.22 (d, J = 7.2 Hz, 1H), 4.15 – 4.09 (m, 1H), 3.23 (dd, J_1 = 14.0 Hz, J_2 = 3.4 Hz, 1H), 2.76 (dd, J_1 = 14.0 Hz, J_2 = 10.0 Hz, 1H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 156.56, 141.58, 138.14, 133.97, 133.19, 129.36, 128.45, 126.94, 126.29, 126.20, 120.98, 116.97, 114.03, 110.74, 107.41, 66.50, 53.46, 35.81 ppm.

LC-HRMS (ESI+) *m/z* calculated for $[C_{20}H_{18}N_3O]^+$: 316.14444, found: 316.14431.

Synthesis of **C3**



Chemical Formula: $C_{16}H_{15}N_3O$

In a glovebox, **A27** (2.0 mmol, 478 mg), KO^{t}Bu (0.6 mmol, 67 mg, dissolved in 1.5 mL 1,4-dioxane) and carbonyldiimidazol (2.3 mmol, 373 mg) are added to a pressure tube and dissolved in 8.5 mL 1,4-dioxane. The sealed pressure tube is heated at 130 °C for 2h in an oil bath. After cooling down to room temperature 30 mL water were added and the product is extracted with diethylether (4 x 50 mL). The combined organic phases are dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via gradient column chromatography over Alox N (pentane/ethyl acetate 1:1 → pure ethyl acetate) and obtained as light brown solid (403 mg, 1.52 mmol, 76 %, contains ~ 5% ethyl acetate). Diastereomeric ratio: 81:19.

Main isomer: **^{1}H NMR** (DMSO-d_6, 500 MHz, 293 K): δ = 7.50 (d, J = 7.5 Hz, 1H), 7.28 (s, 1H), 7.15 (d, J = 7.5 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 6.76 (s, 1H), 6.55 (d, J = 7.3 Hz, 1H), 4.64 (dd, J_1 = 5.0 Hz, J_2 = 0.9 Hz, 1H), 3.63 – 3.57 (m, 1H), 3.29 – 3.21 (m, 4H), 1.32 (d, J = 6.4 Hz, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 156.48, 139.34, 138.04, 137.95, 133.88, 129.49, 120.05, 119.27, 113.18, 111.39, 107.68, 72.21, 51.72, 30.13, 29.68, 19.76 ppm.

LC-HRMS (ESI+) *m/z* calculated for $[C_{16}H_{16}N_3O]^+$: 266.12879, found: 266.12865.

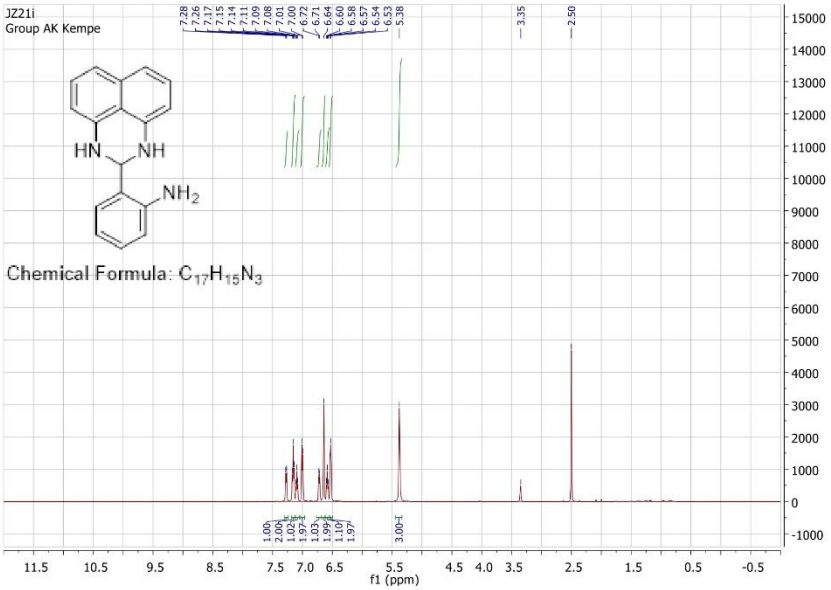
Minor isomer: **^{1}H NMR** (DMSO-d_6, 500 MHz, 293 K): δ = 7.56 (d, J = 7.5 Hz, 1H), 7.23 (s, 1H), 7.14 (d, J = 7.3 Hz, 1H), 7.07 (d, J = 7.3 Hz, 1H), 6.61 (d, J = 7.3 Hz, 1H), 6.47 (s, 1H), 5.03 (d, J = 7.3 Hz, 1H), 3.95 (quin, J = 6.7 Hz, 1H), 3.29 – 3.20 (m, 4H), 1.23 (d, J = 6.4 Hz, 3H) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz, 293 K): δ = 156.56, 139.23, 138.38, 137.76, 133.55, 129.98, 120.05, 119.22, 112.44, 110.79, 107.80, 67.45, 48.20, 30.13, 29.68, 15.69 ppm.

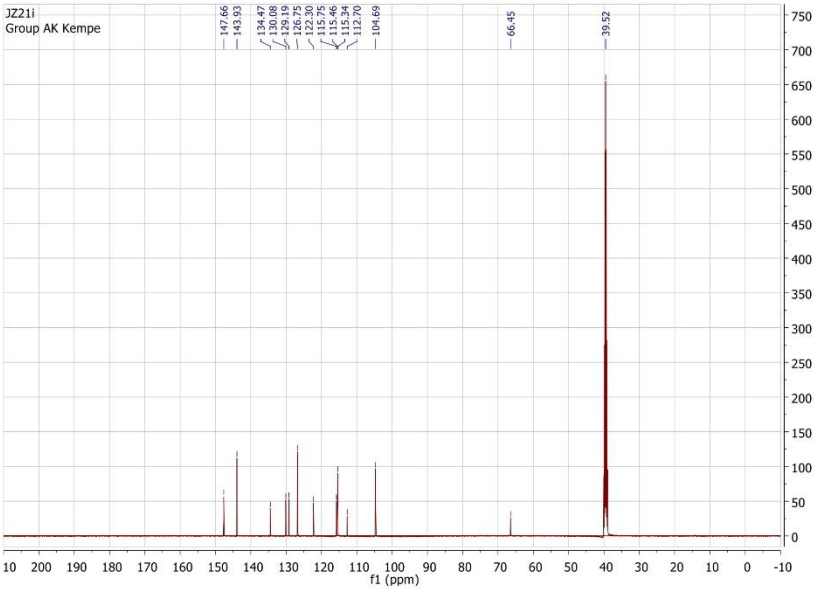
LC-HRMS (ESI+) *m/z* calculated for $[C_{16}H_{16}N_3O]^+$: 266.12879, found: 266.12852.

14. NMR spectra of isolated products

NMR spectra of A1

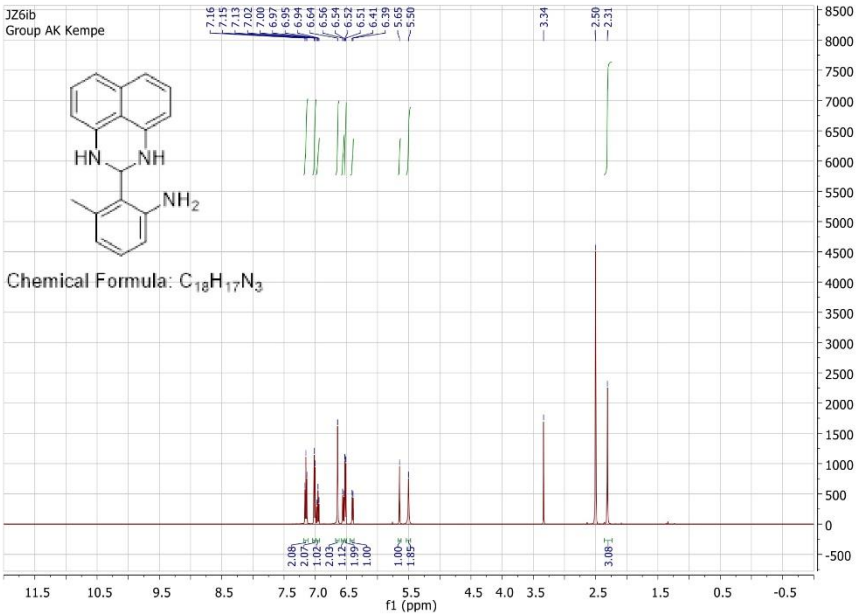


Supplementary Figure 31 ^{1}H NMR spectrum of compound **A1**. (500 MHz, 293 K, DMSO-d_6).

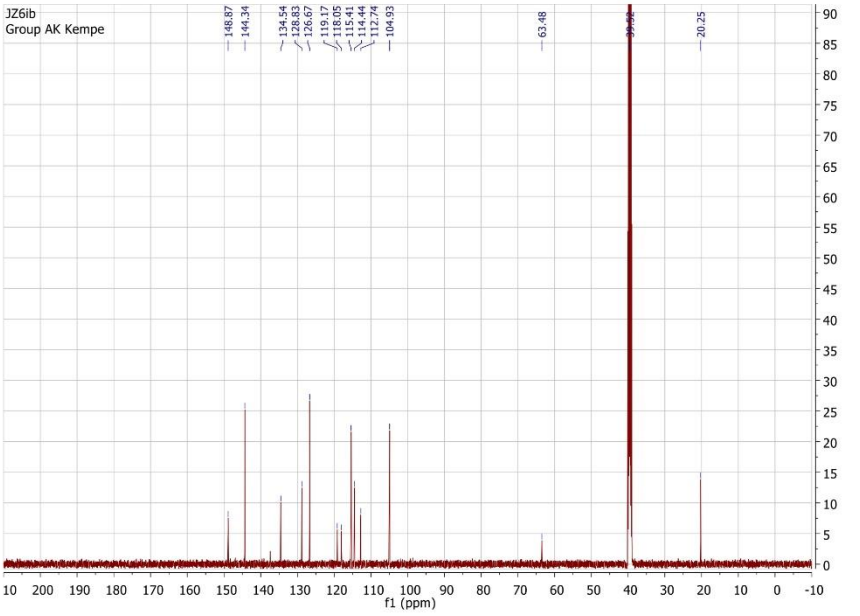


Supplementary Figure 32 ^{13}C NMR spectrum of compound **A1**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A2

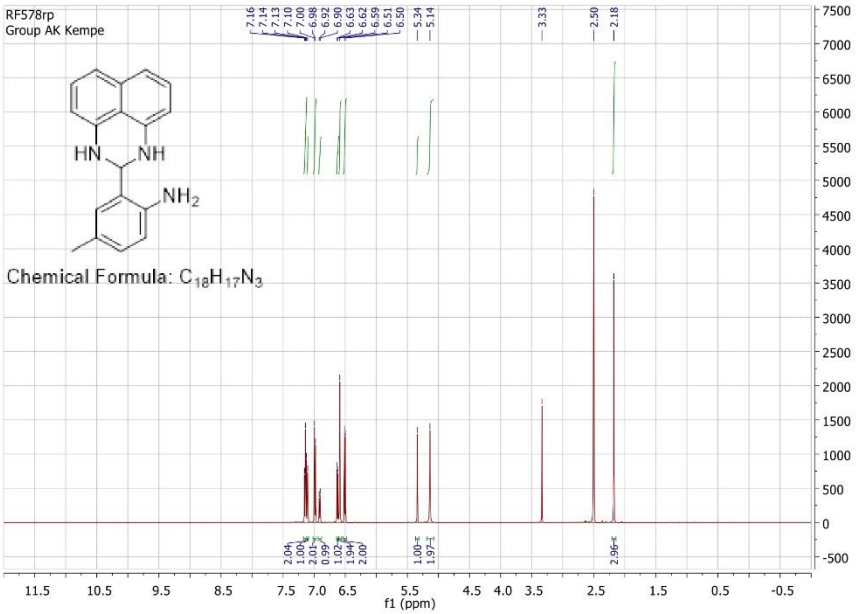


Supplementary Figure 33 ^{1}H NMR spectrum of compound **A2**. (500 MHz, 293 K, DMSO-d_6).

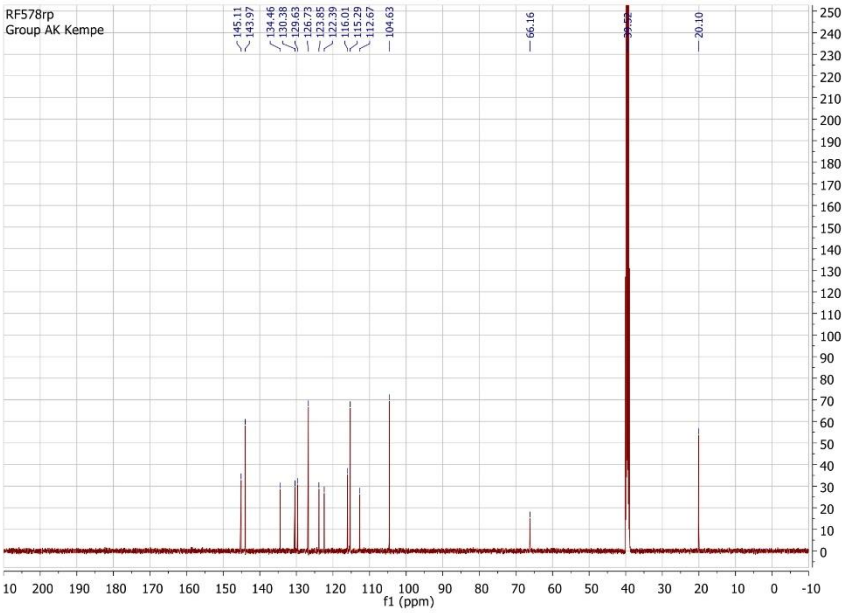


Supplementary Figure 34 ^{13}C NMR spectrum of compound **A2**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A3

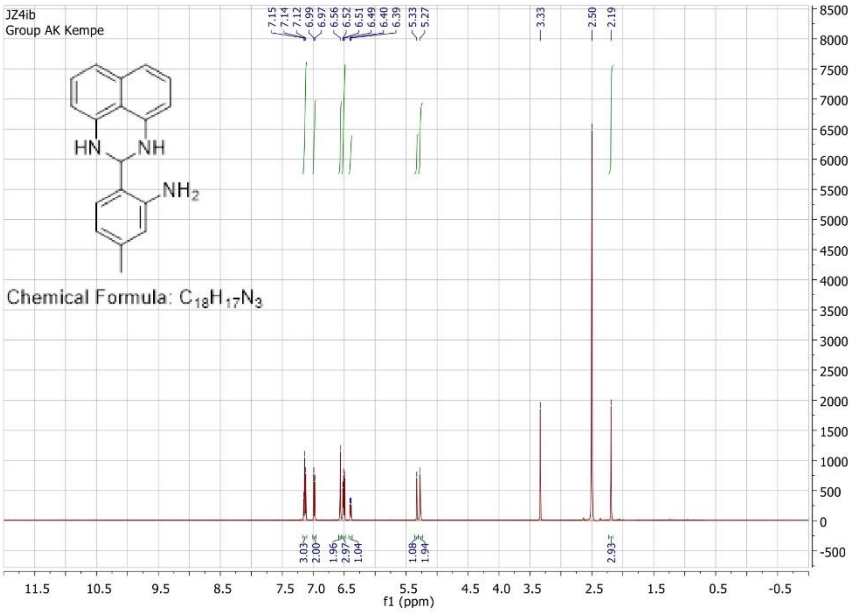


Supplementary Figure 35 ^{1}H NMR spectrum of compound **A3**. (500 MHz, 293 K, DMSO-d_6).

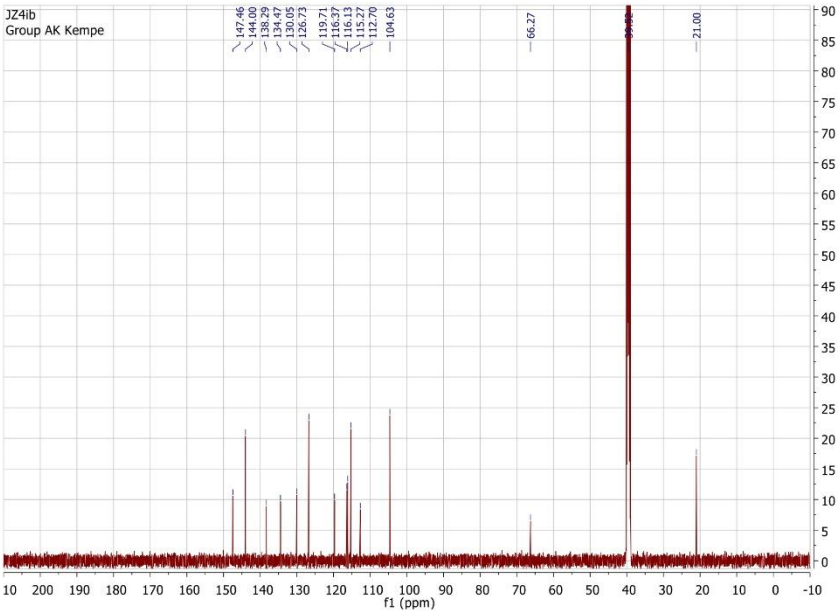


Supplementary Figure 36 ^{13}C NMR spectrum of compound **A3**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A4

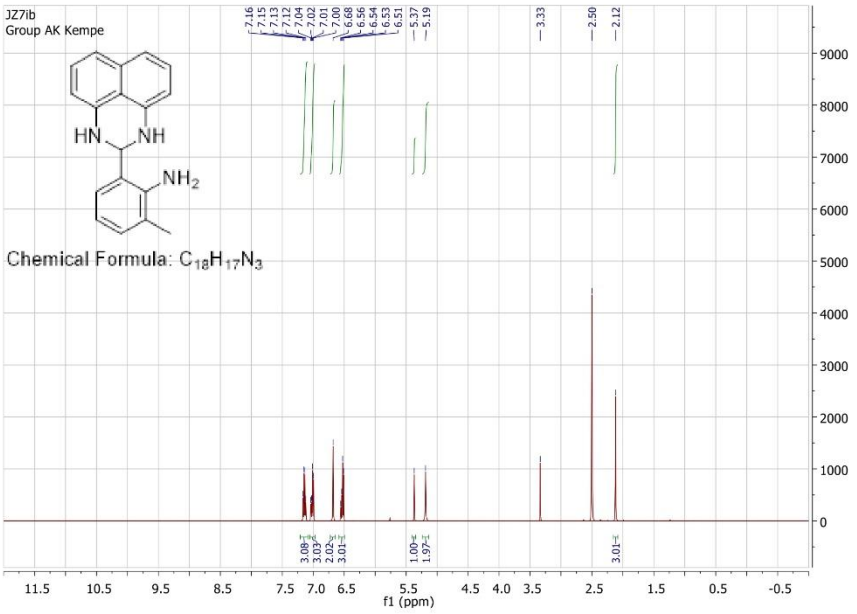


Supplementary Figure 37 ^{1}H NMR spectrum of compound **A4**. (500 MHz, 293 K, DMSO-d_6).

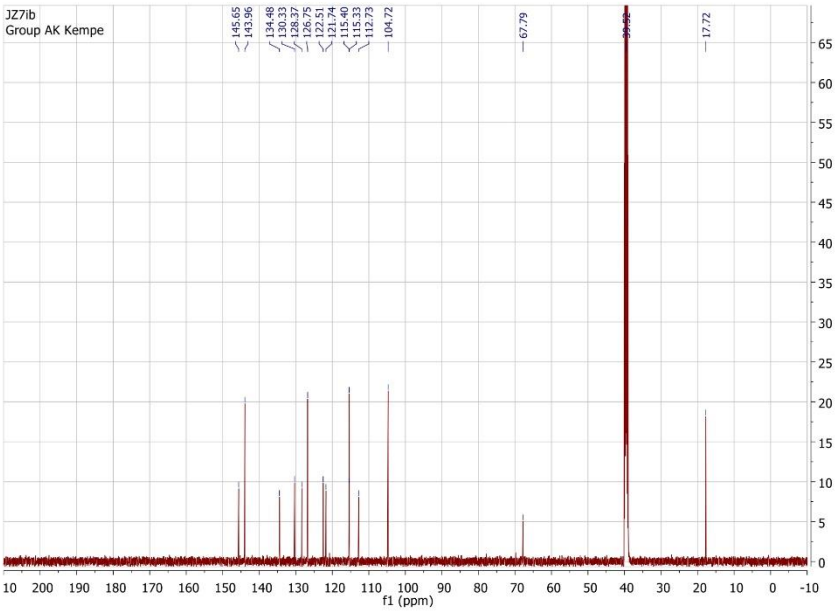


Supplementary Figure 38 ^{13}C NMR spectrum of compound **A4**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A5

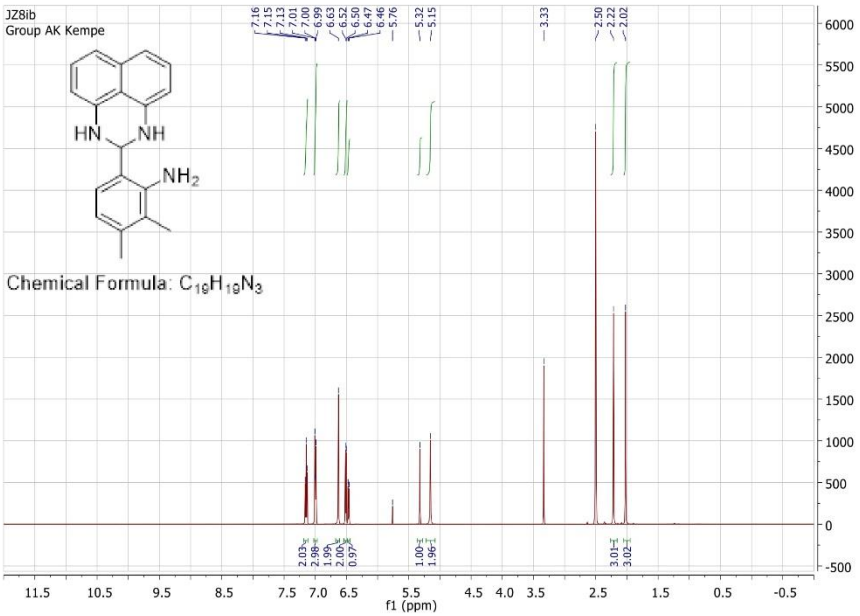


Supplementary Figure 39 ^{1}H NMR spectrum of compound **A5**. (500 MHz, 293 K, DMSO-d_6).

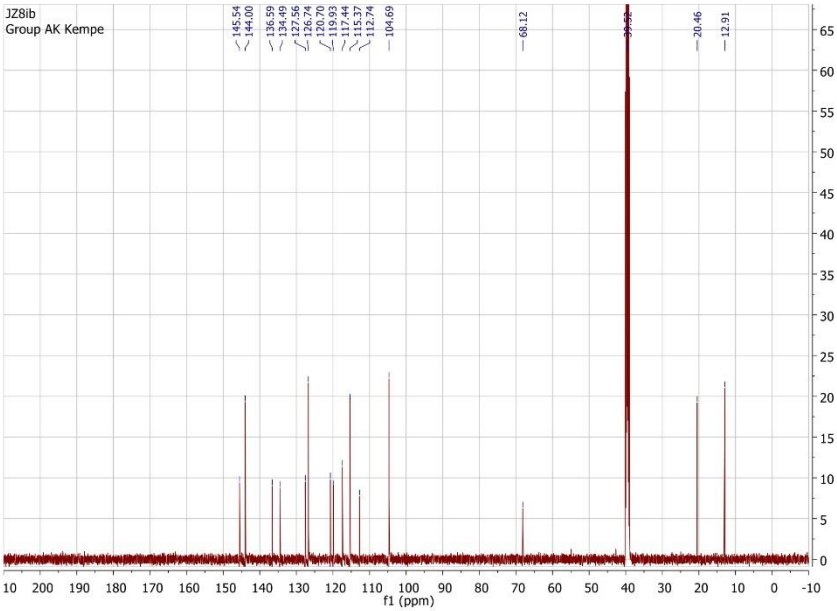


Supplementary Figure 40 ^{13}C NMR spectrum of compound **A5**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A6

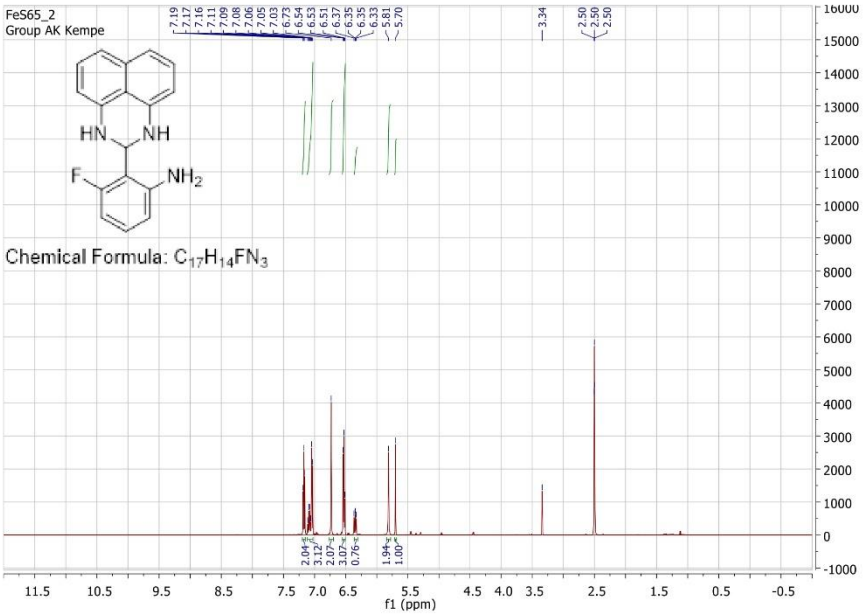


Supplementary Figure 41 ^{1}H NMR spectrum of compound **A6**. (500 MHz, 293 K, DMSO-d_6).

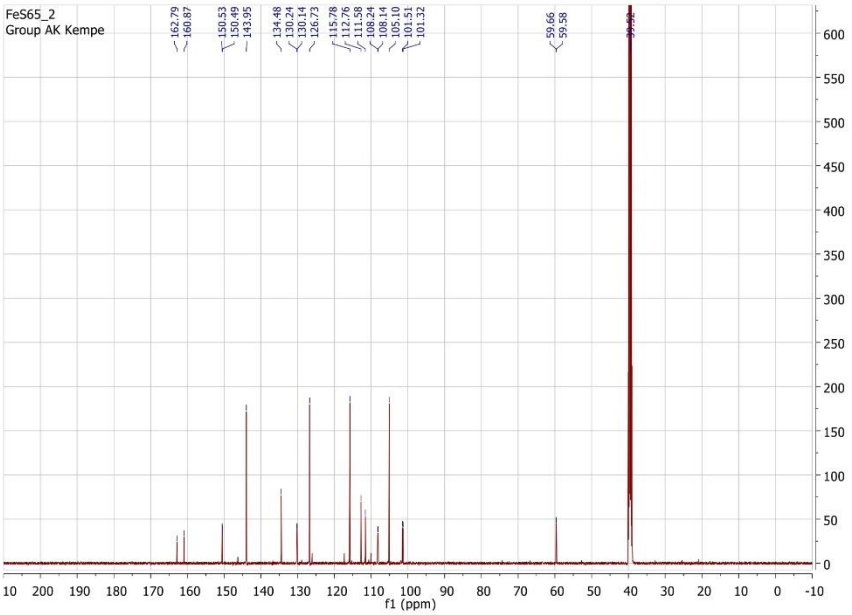


Supplementary Figure 42 ^{13}C NMR spectrum of compound **A6**. (125 MHz, 293 K, DMSO-d_6).

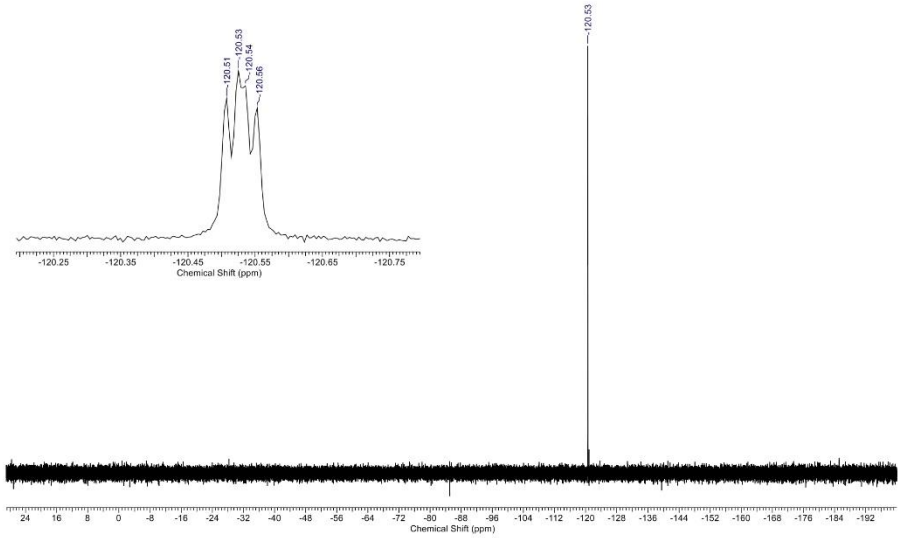
NMR spectra of A7



Supplementary Figure 43 ^{1}H NMR spectrum of compound **A7**. (500 MHz, 293 K, DMSO-d_6).

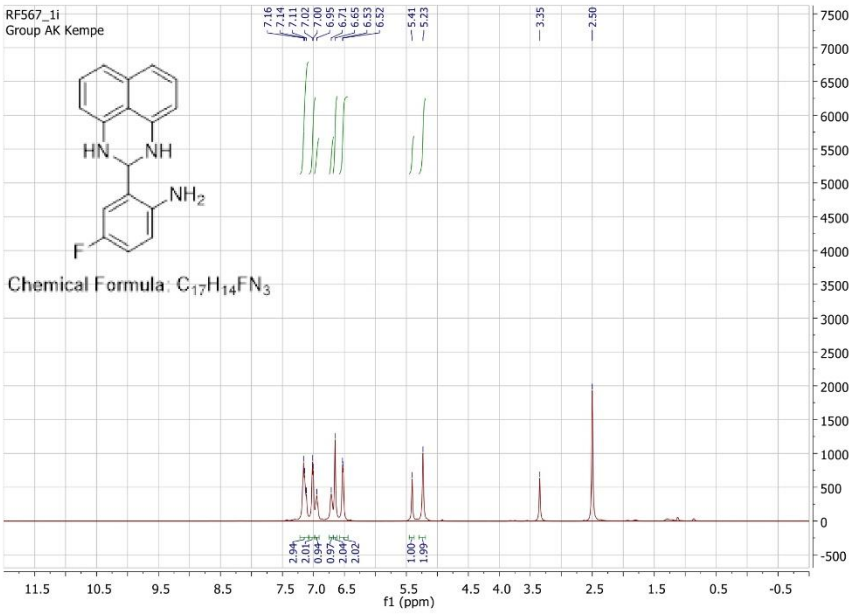


Supplementary Figure 44 ^{13}C NMR spectrum of compound **A7**. (125 MHz, 293 K, DMSO-d_6).

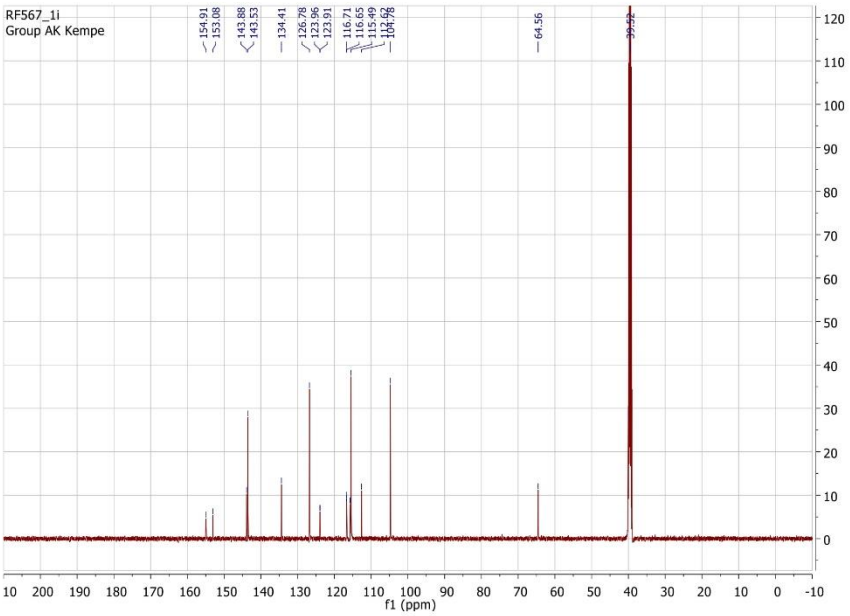


Supplementary Figure 45 ^{19}F NMR spectrum of compound **A7**. (376 MHz, 293 K, DMSO-d_6).

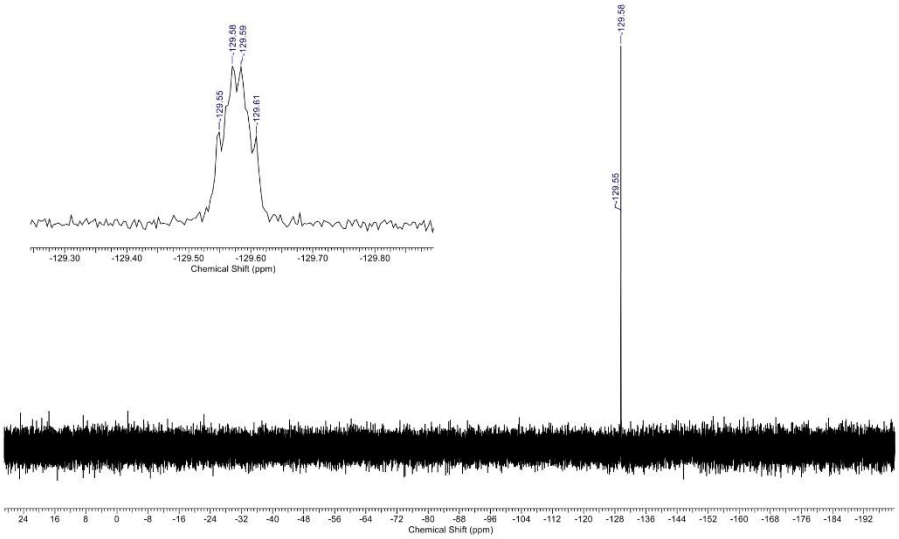
NMR spectra of A8



Supplementary Figure 46 ^{1}H NMR spectrum of compound **A8**. (500 MHz, 293 K, DMSO-d_6).

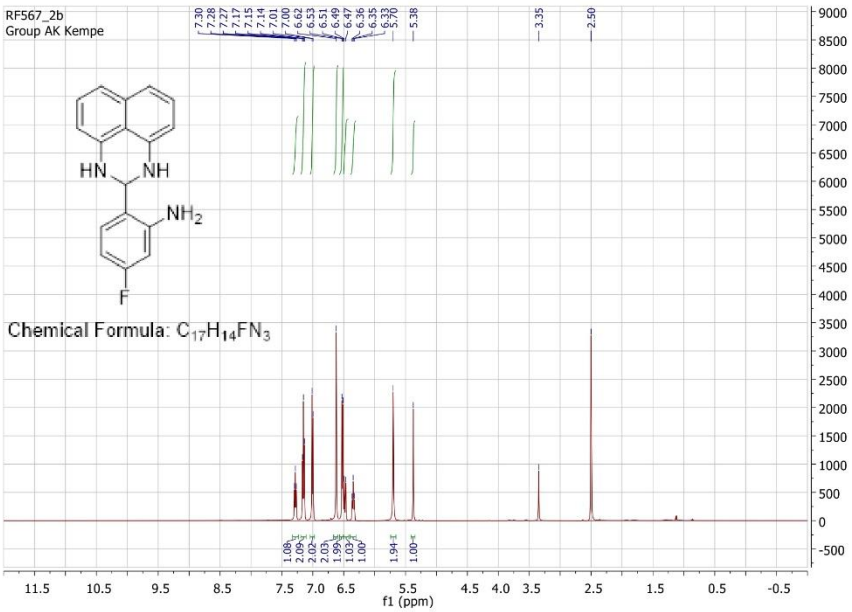


Supplementary Figure 47 ^{13}C NMR spectrum of compound **A8**. (125 MHz, 293 K, DMSO-d_6).

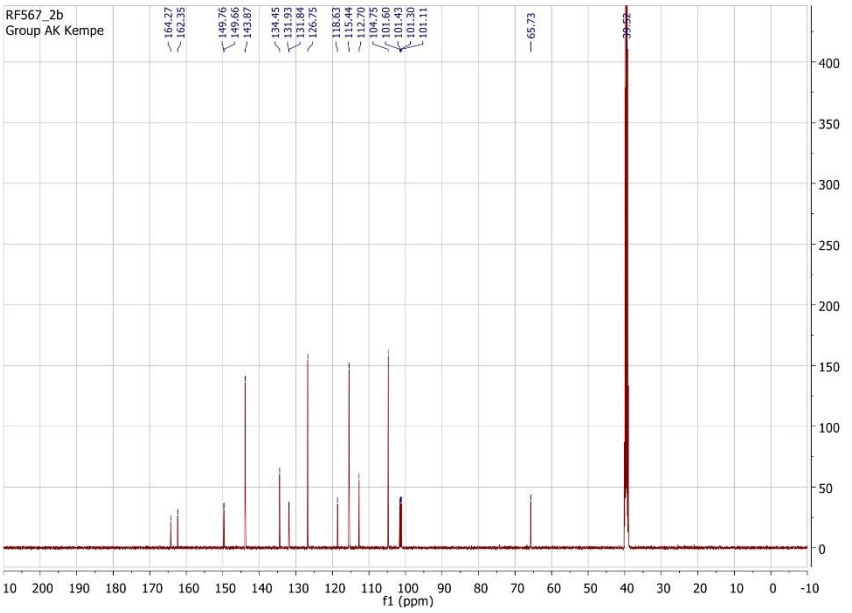


Supplementary Figure 48 ^{19}F NMR spectrum of compound **A8**. (376 MHz, 293 K, DMSO-d_6).

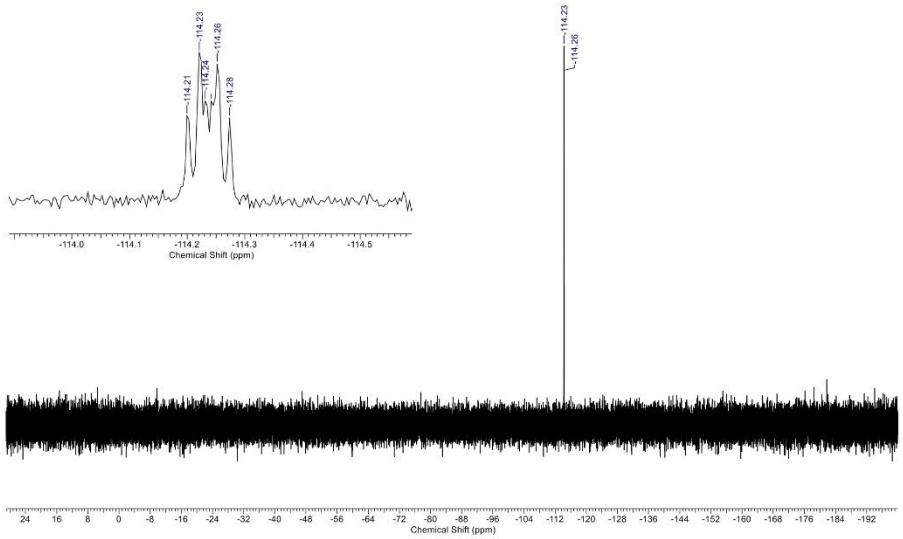
NMR spectra of A9



Supplementary Figure 49 ^{1}H NMR spectrum of compound **A9**. (500 MHz, 293 K, DMSO-d_6).

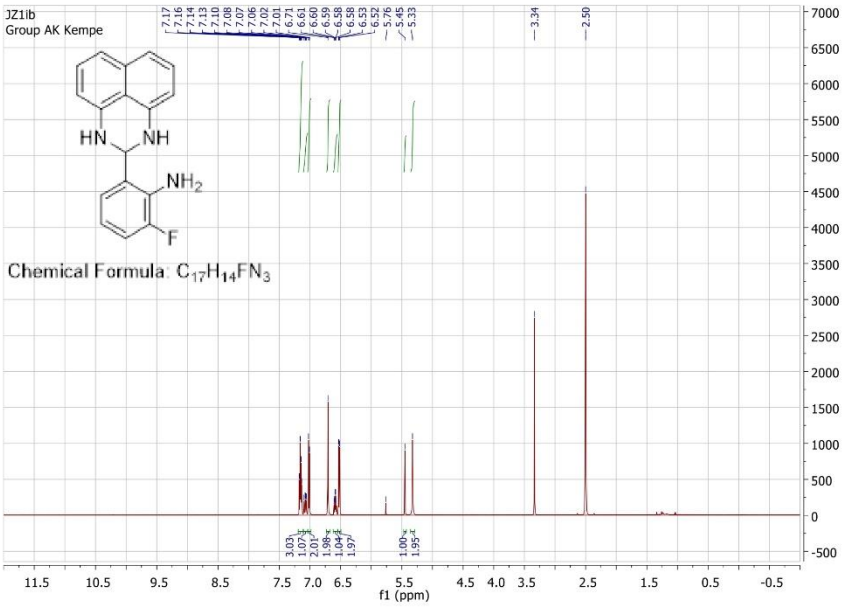


Supplementary Figure 50 ^{13}C NMR spectrum of compound **A9**. (125 MHz, 293 K, DMSO-d_6).

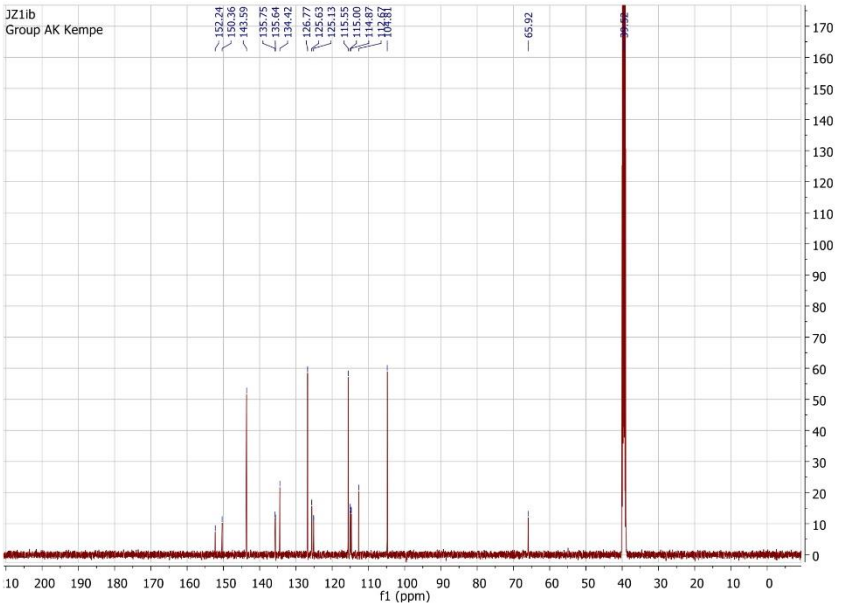


Supplementary Figure 51 ^{19}F NMR spectrum of compound **A9**. (376 MHz, 293 K, DMSO-d_6).

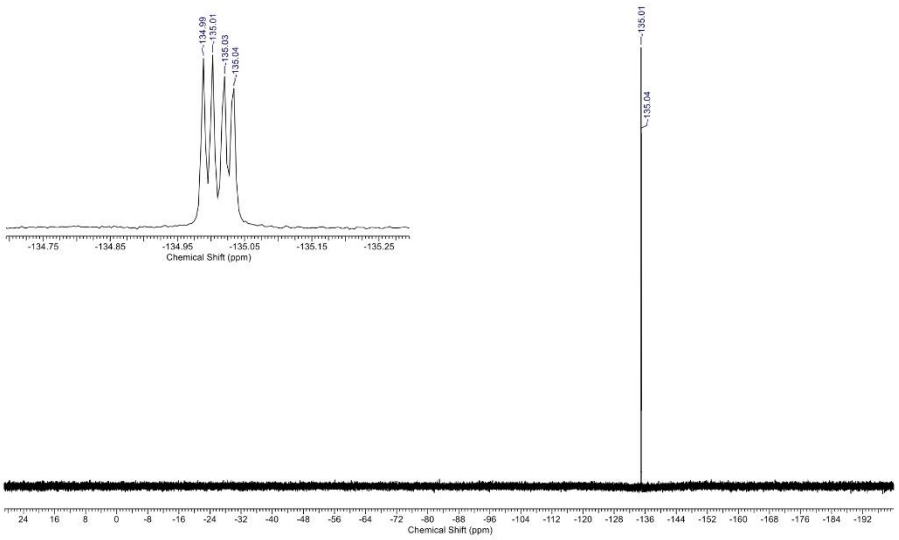
NMR spectra of A10



Supplementary Figure 52 ^{1}H NMR spectrum of compound **A10**. (500 MHz, 293 K, DMSO-d_6).

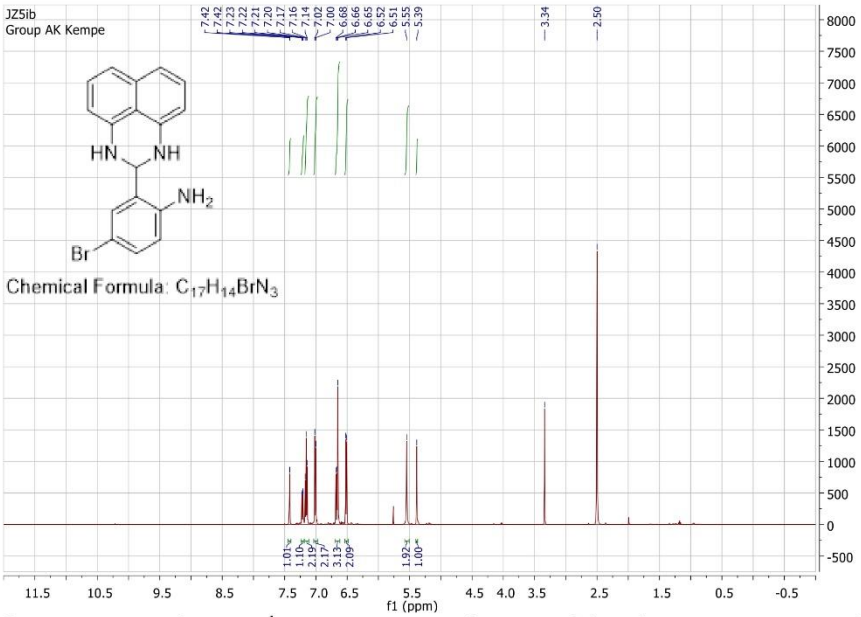


Supplementary Figure 53 ^{13}C NMR spectrum of compound **A10**. (125 MHz, 293 K, DMSO-d_6).

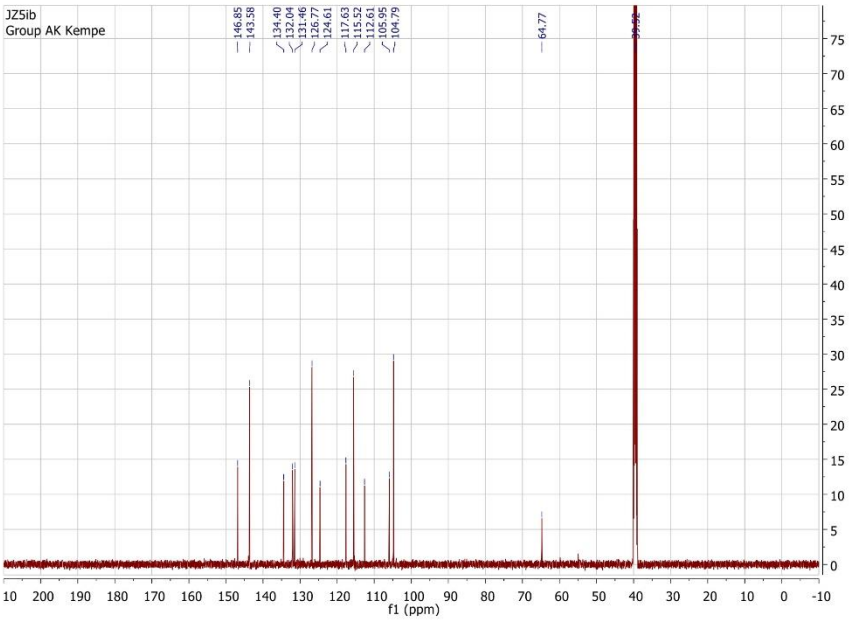


Supplementary Figure 54 ^{19}F NMR spectrum of compound **A10**. (376 MHz, 293 K, DMSO-d_6).

NMR spectra of A11

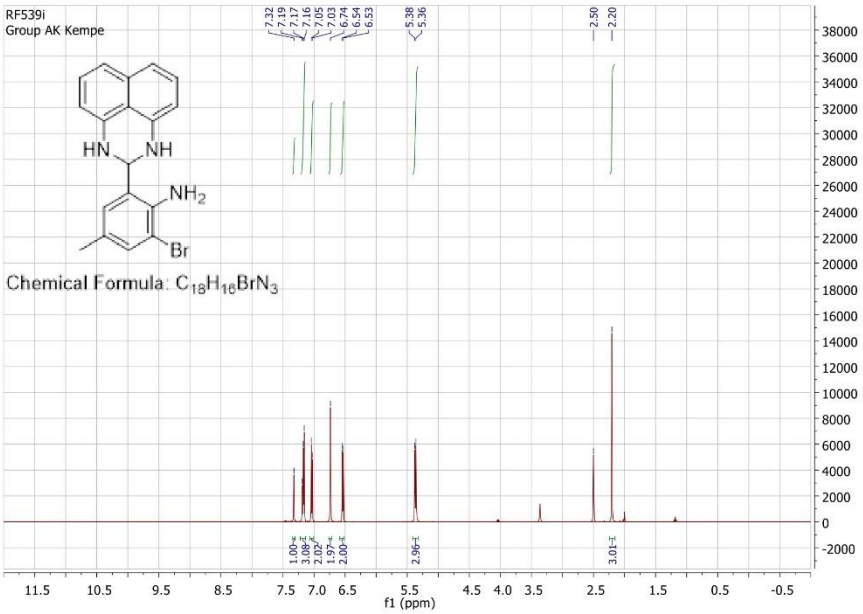


Supplementary Figure 55 ^{1}H NMR spectrum of compound **A11**. (500 MHz, 293 K, DMSO-d_6).

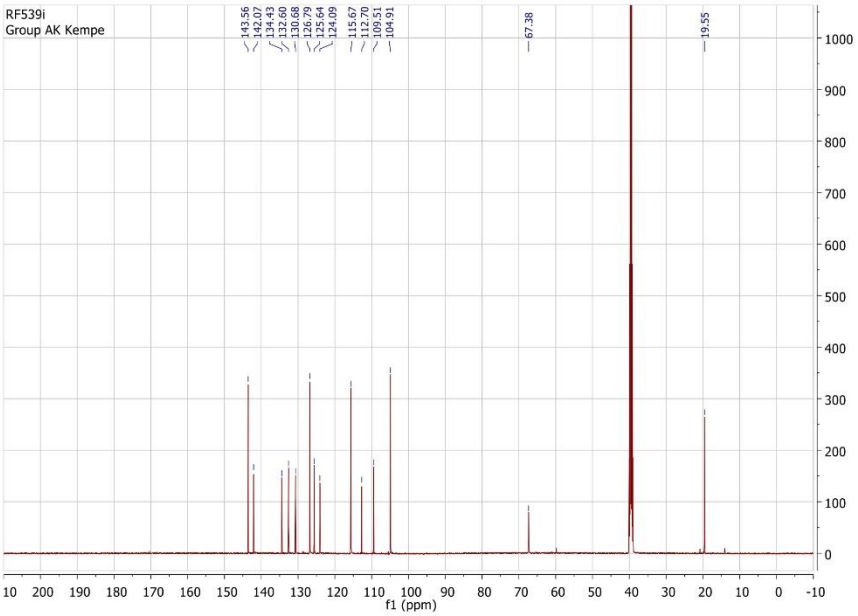


Supplementary Figure 56 ^{13}C NMR spectrum of compound **A11**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A12

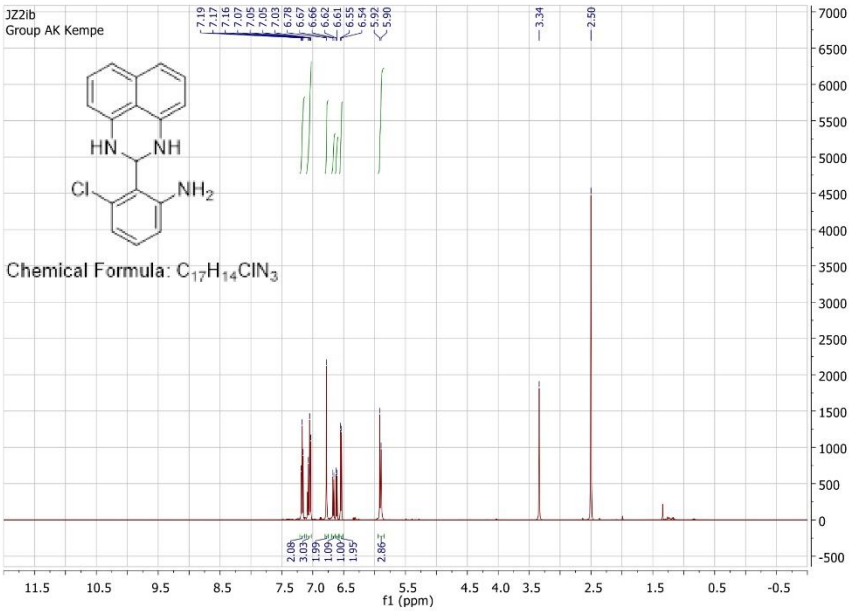


Supplementary Figure 57 ^{1}H NMR spectrum of compound **A12**. (500 MHz, 293 K, DMSO-d_6).

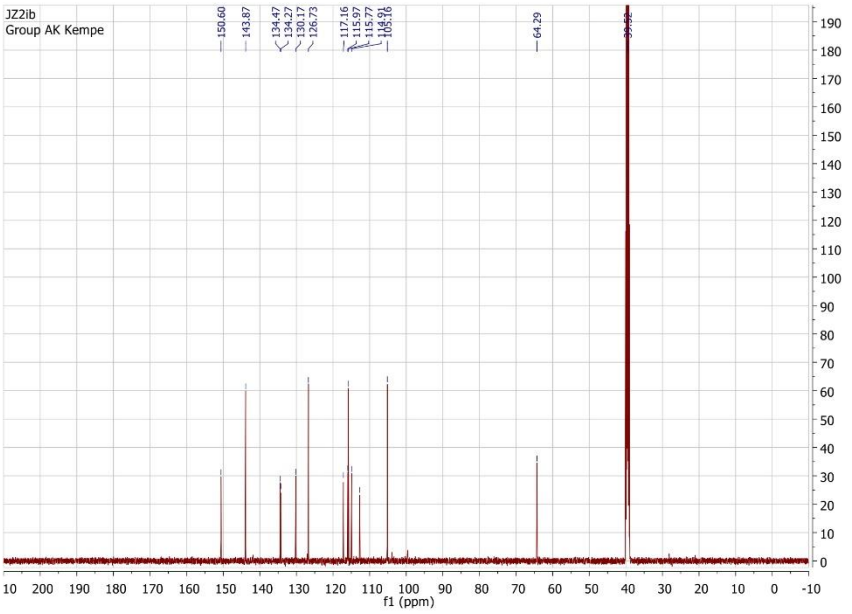


Supplementary Figure 58 ^{13}C NMR spectrum of compound **A12**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A13

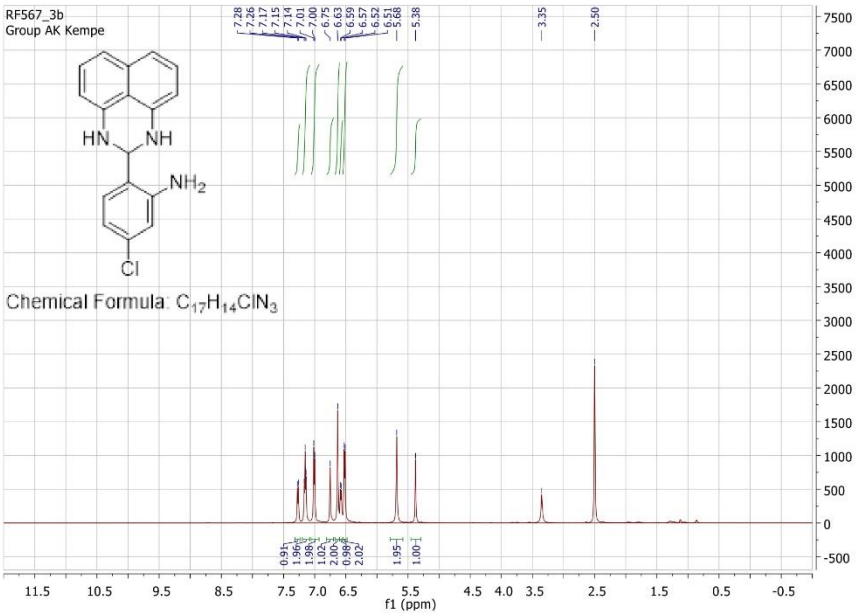


Supplementary Figure 59 ^{1}H NMR spectrum of compound **A13**. (500 MHz, 293 K, DMSO-d_6).

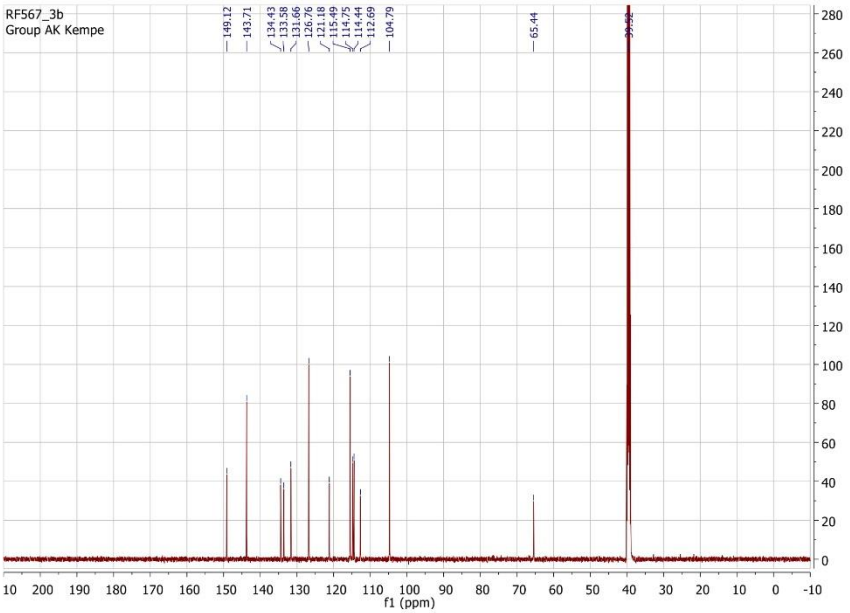


Supplementary Figure 60 ^{13}C NMR spectrum of compound **A13**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A14

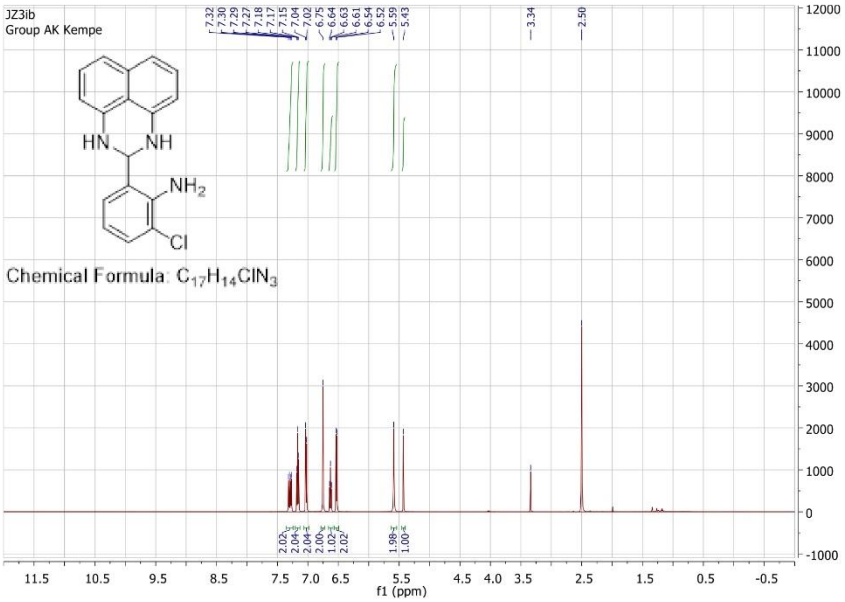


Supplementary Figure 61 ^{1}H NMR spectrum of compound **A14**. (500 MHz, 293 K, DMSO-d_6).

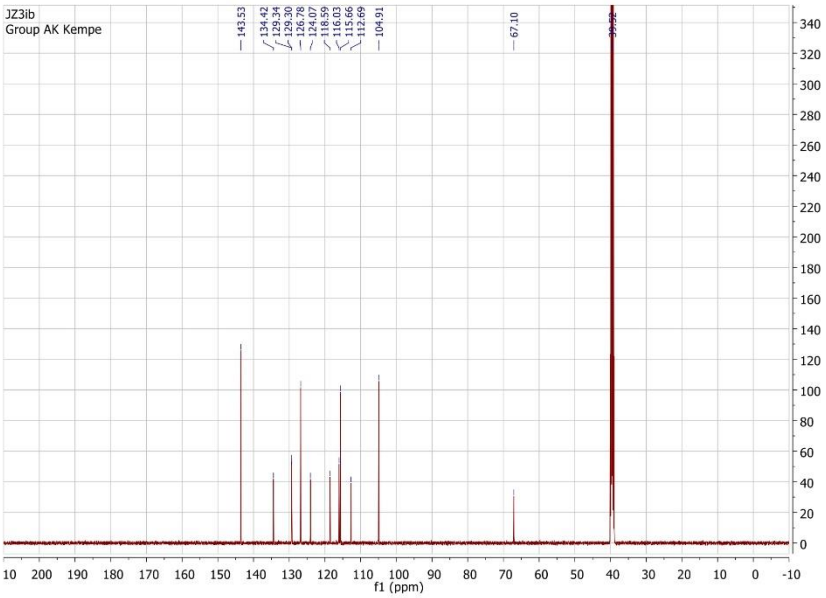


Supplementary Figure 62 ^{13}C NMR spectrum of compound **A14**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A15

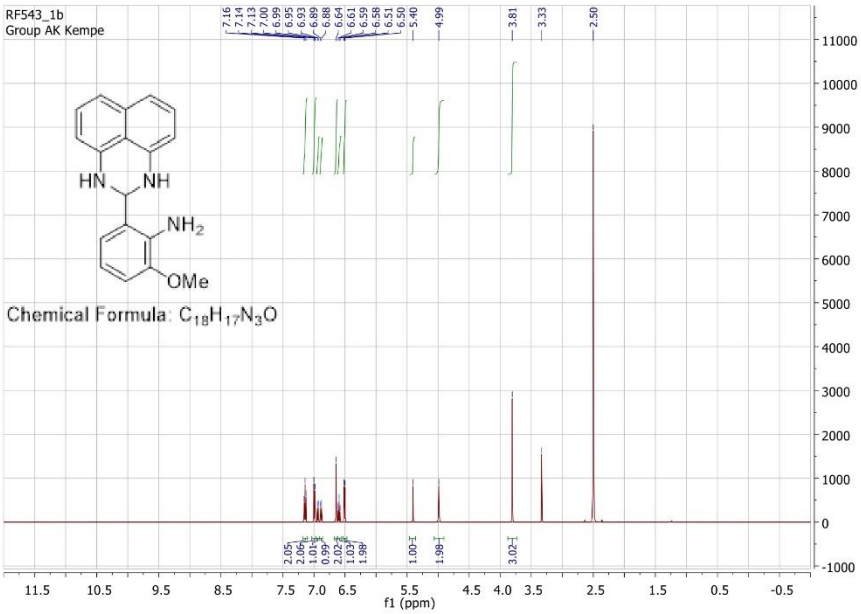


Supplementary Figure 63 ^{1}H NMR spectrum of compound **A15**. (500 MHz, 293 K, DMSO-d_6).

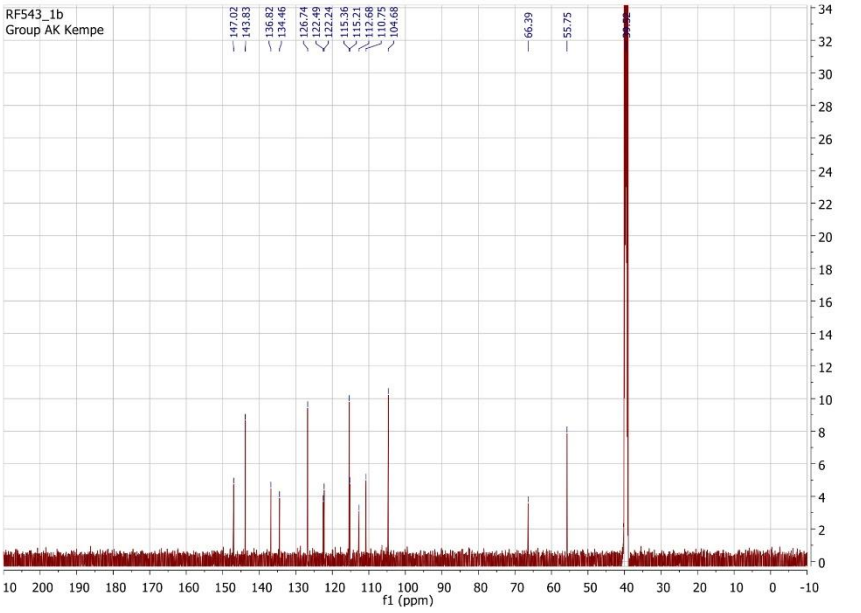


Supplementary Figure 64 ^{13}C NMR spectrum of compound **A15**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A16

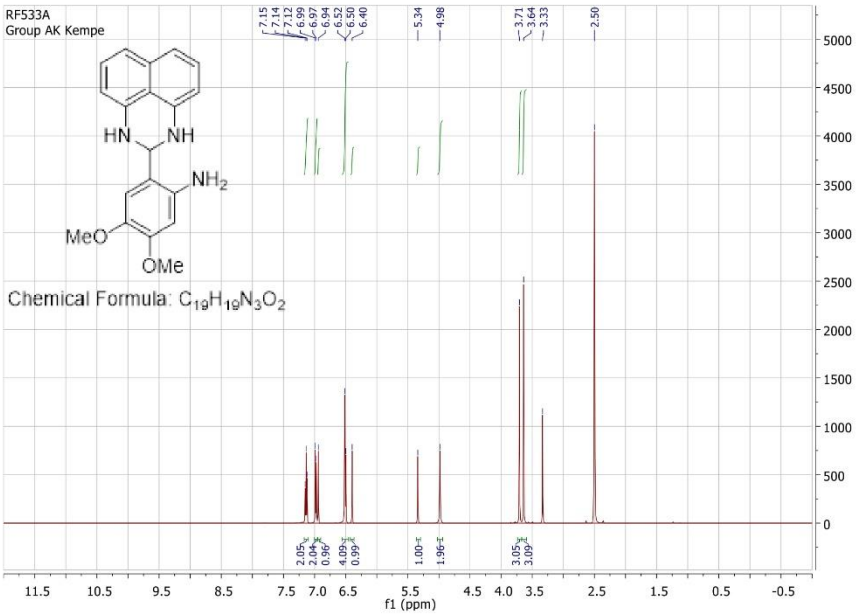


Supplementary Figure 65 ^{1}H NMR spectrum of compound **A16**. (500 MHz, 293 K, DMSO-d_6).

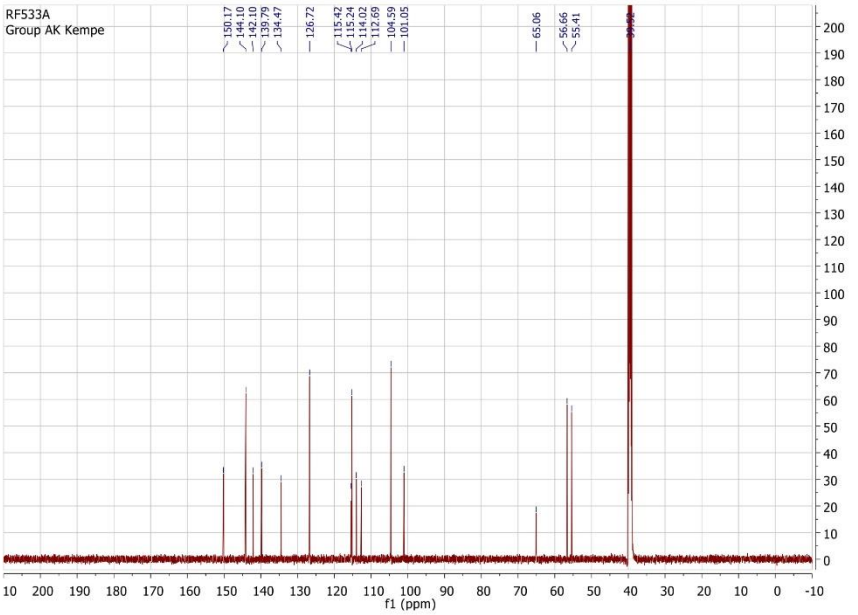


Supplementary Figure 66 ^{13}C NMR spectrum of compound **A16**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A17

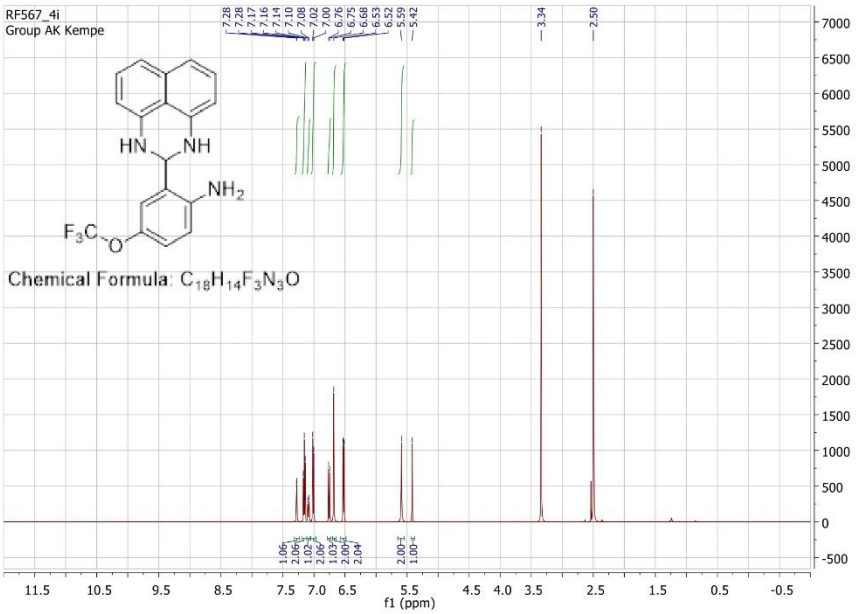


Supplementary Figure 67 ^{1}H NMR spectrum of compound **A17**. (500 MHz, 293 K, DMSO-d_6).

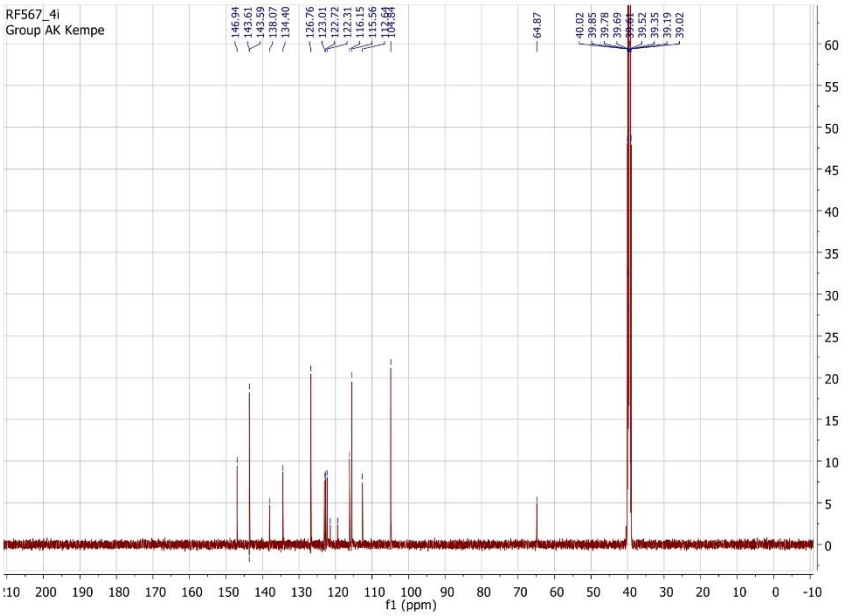


Supplementary Figure 68 ^{13}C NMR spectrum of compound **A17**. (125 MHz, 293 K, DMSO-d_6).

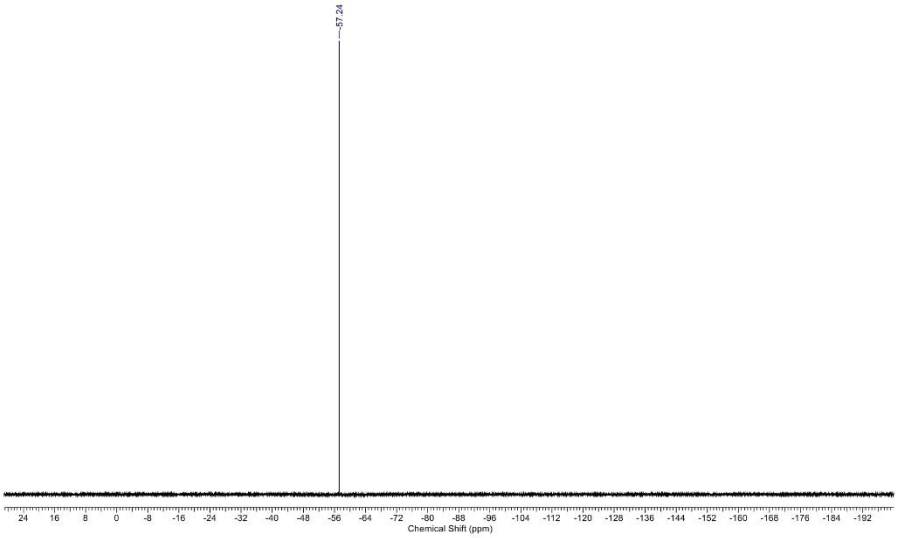
NMR spectra of A18



Supplementary Figure 69 ^{1}H NMR spectrum of compound **A18**. (500 MHz, 293 K, DMSO-d_6).

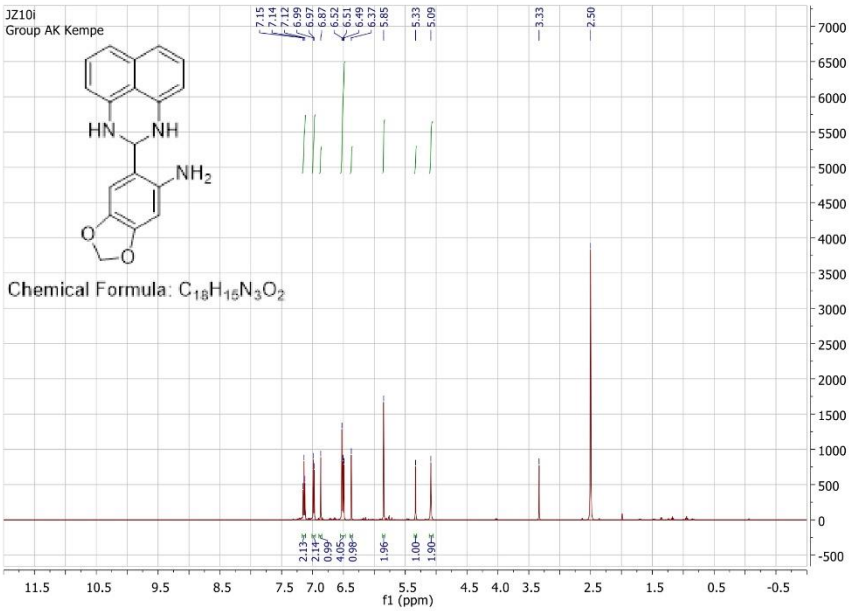


Supplementary Figure 70 ^{13}C NMR spectrum of compound **A18**. (125 MHz, 293 K, DMSO-d_6).

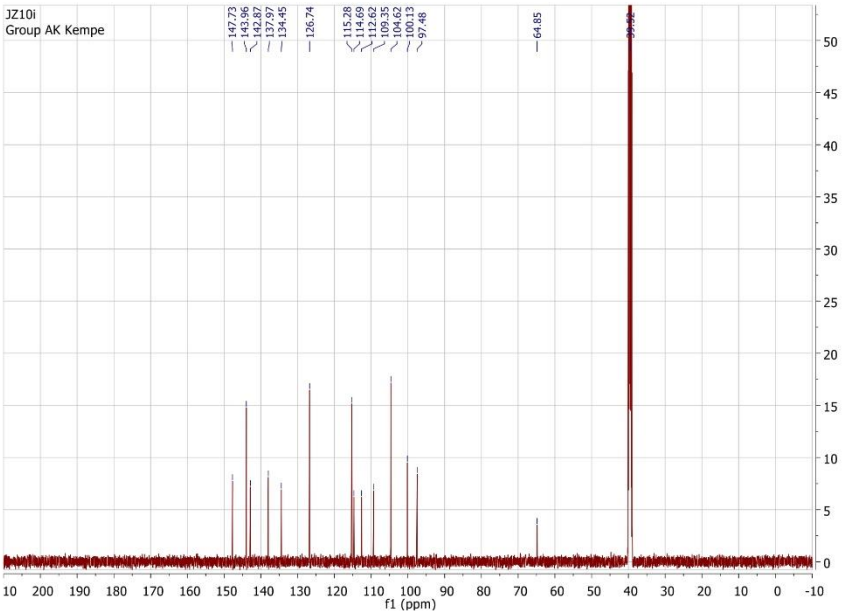


Supplementary Figure 71 ^{19}F NMR spectrum of compound **A18**. (376 MHz, 293 K, DMSO-d_6).

NMR spectra of A19

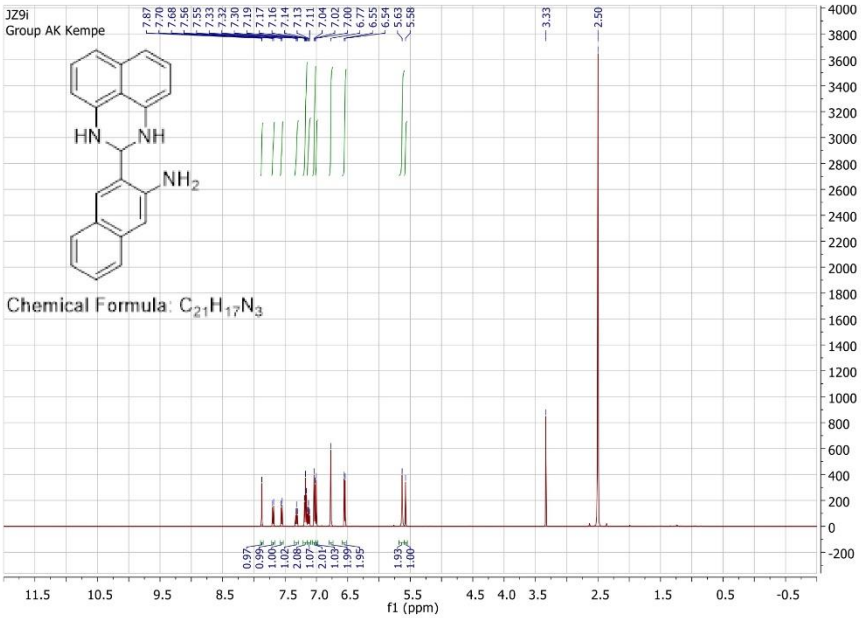


Supplementary Figure 72 ^{1}H NMR spectrum of compound **A19**. (500 MHz, 293 K, DMSO-d_6).

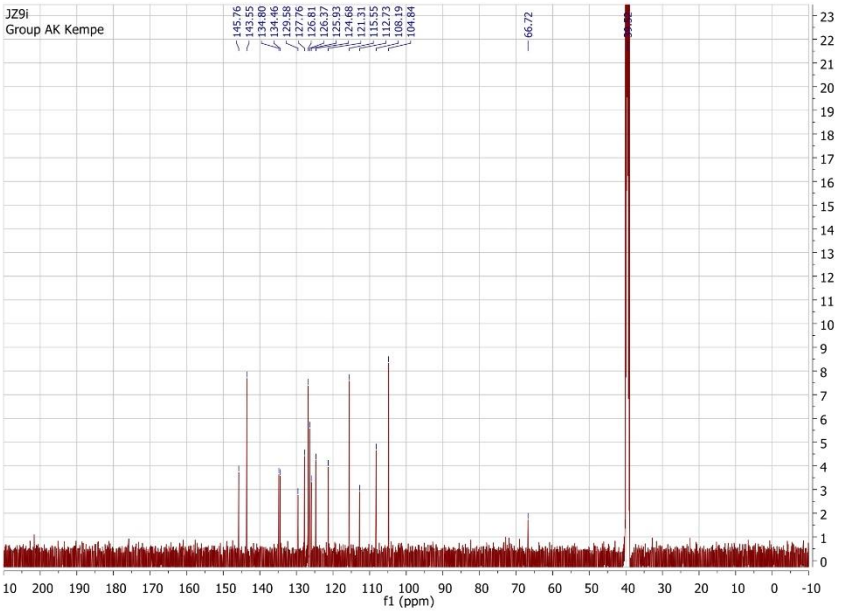


Supplementary Figure 73 ^{13}C NMR spectrum of compound **A19**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A20

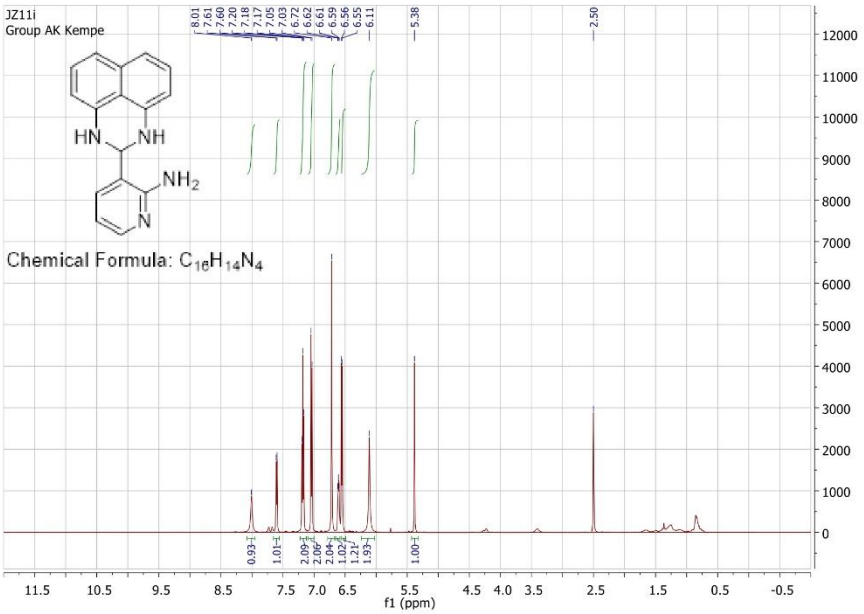


Supplementary Figure 74 ^{1}H NMR spectrum of compound **A20**. (500 MHz, 293 K, DMSO-d_6).

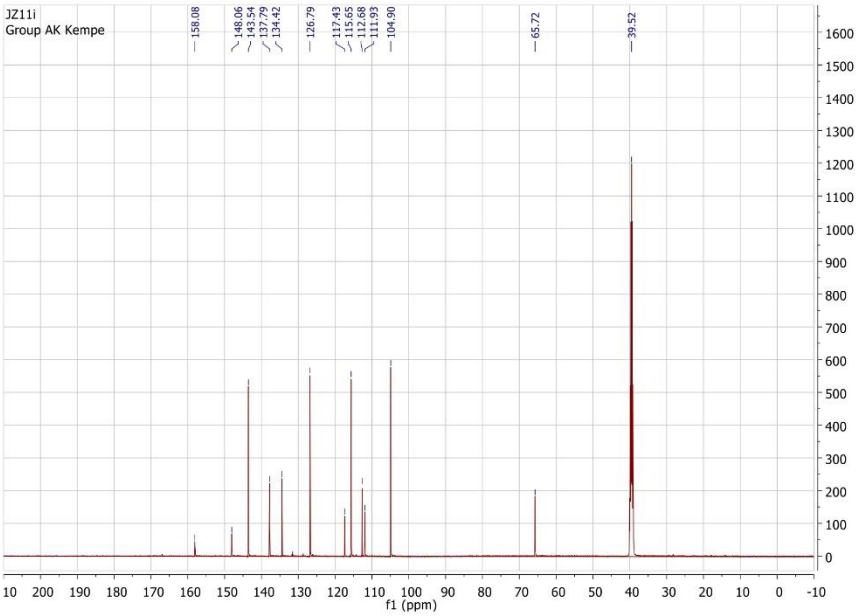


Supplementary Figure 75 ^{13}C NMR spectrum of compound **A20**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A21

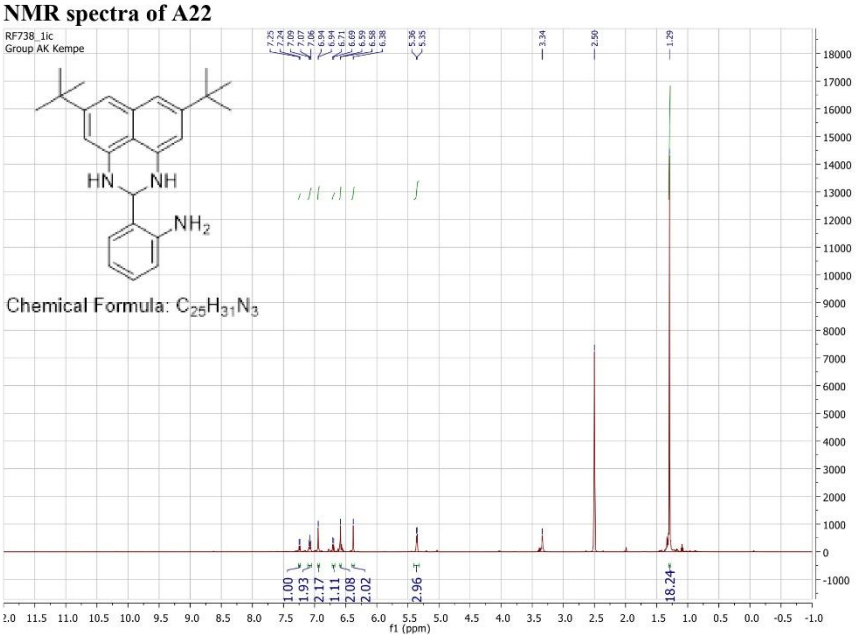


Supplementary Figure 76 ^{1}H NMR spectrum of compound **A21**. (500 MHz, 293 K, DMSO-d_6).

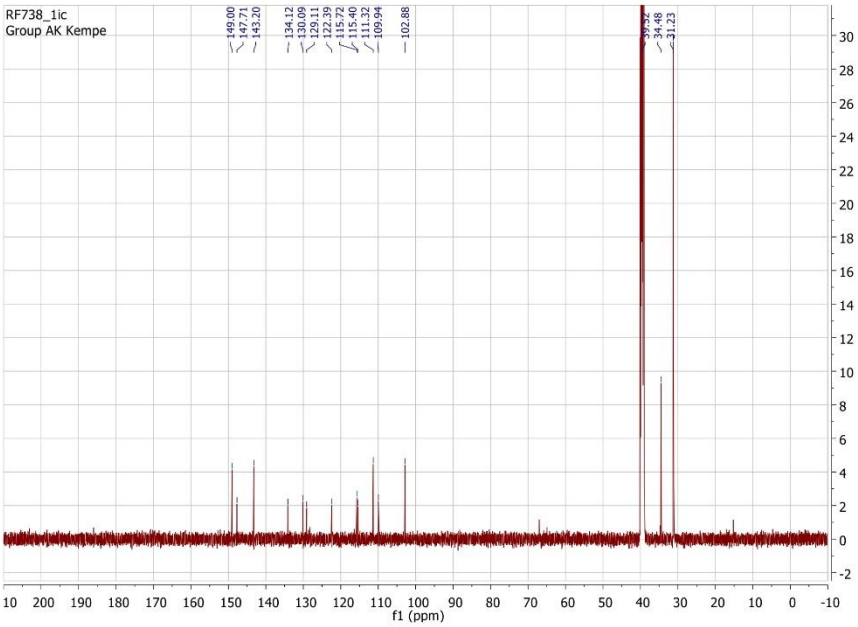


Supplementary Figure 77 ^{13}C NMR spectrum of compound **A21**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A22

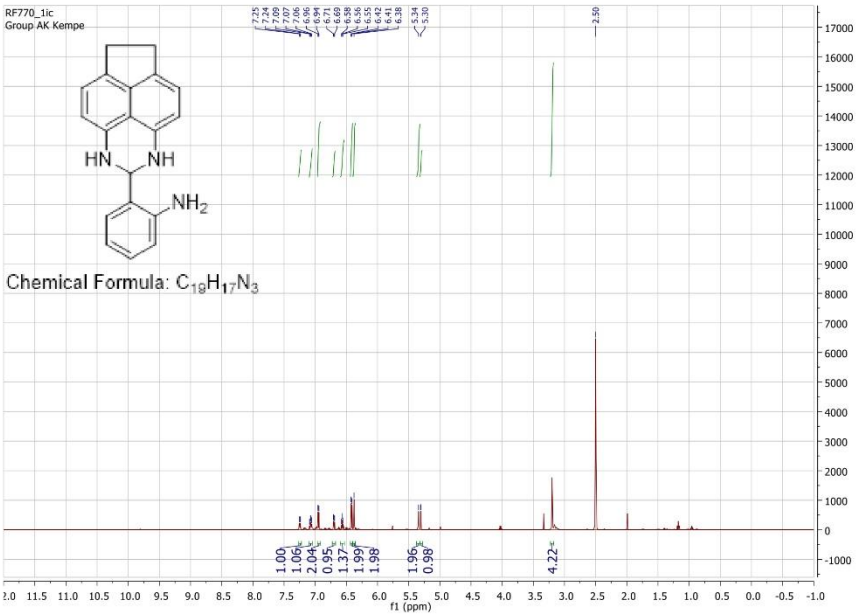


Supplementary Figure 78 ^{1}H NMR spectrum of compound **A22**. (500 MHz, 293 K, DMSO-d_6).

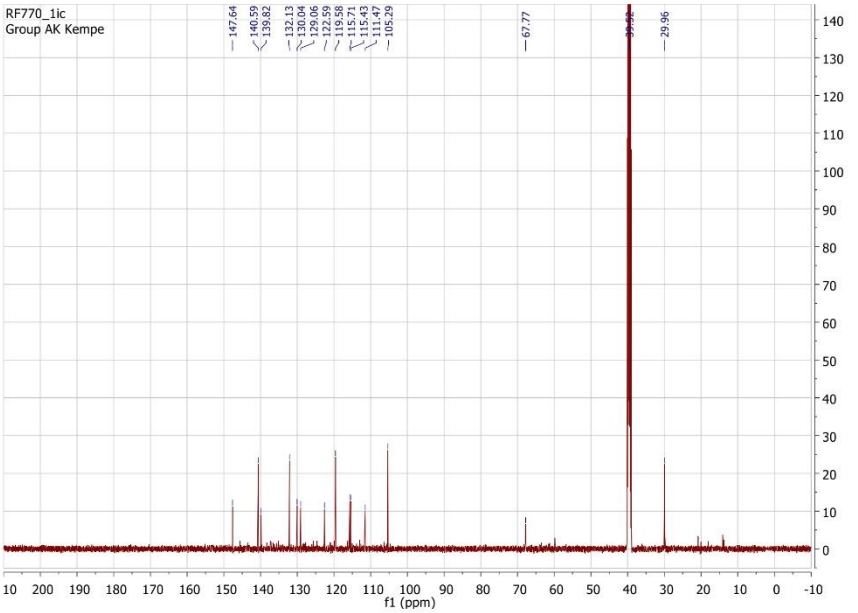


Supplementary Figure 79 ^{13}C NMR spectrum of compound **A22**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra A23

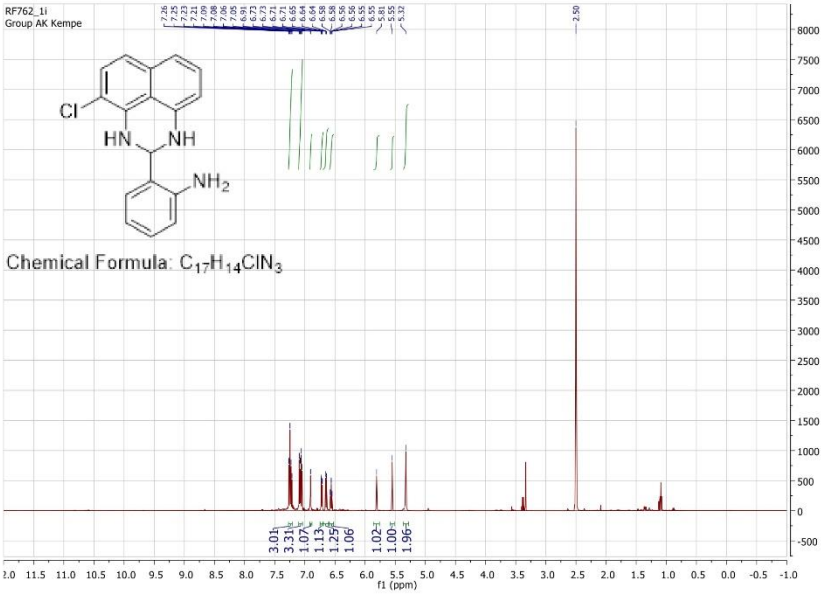


Supplementary Figure 80 ^{1}H NMR spectrum of compound **A23**. (500 MHz, 293 K, DMSO-d_6).

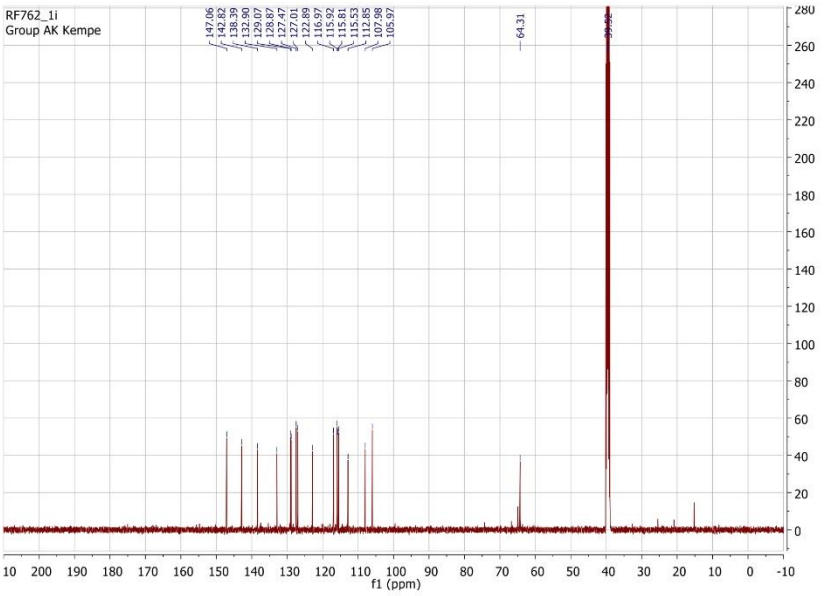


Supplementary Figure 81 ^{13}C NMR spectrum of compound **A23**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A24

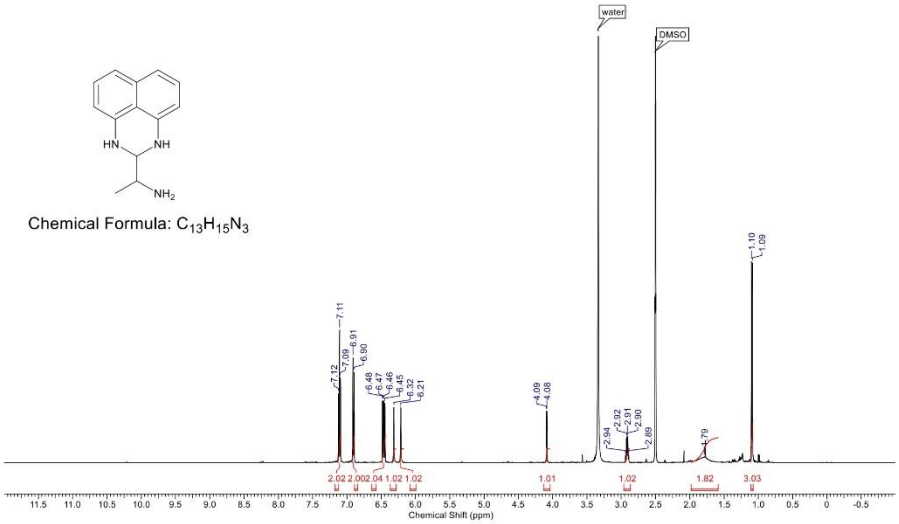


Supplementary Figure 82 ^{1}H NMR spectrum of compound **A24**. (500 MHz, 293 K, DMSO-d_6).

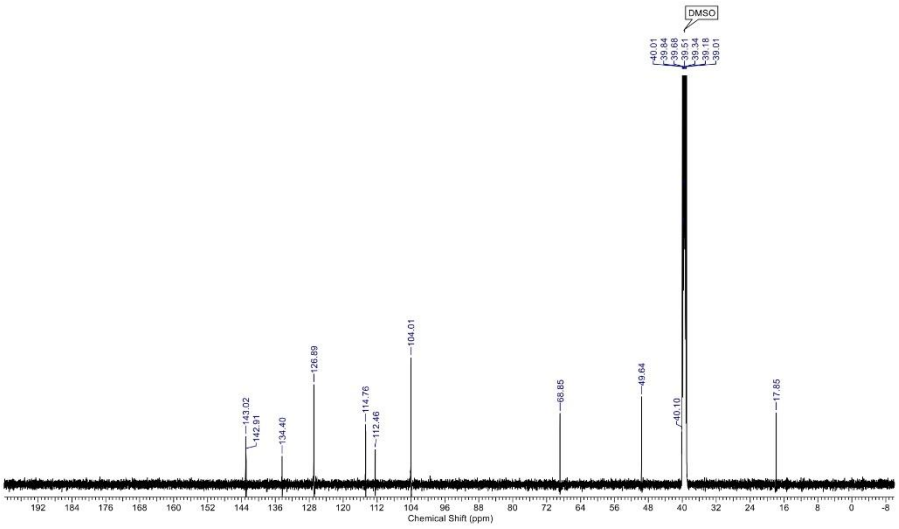


Supplementary Figure 83 ^{13}C NMR spectrum of compound **A24**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A25

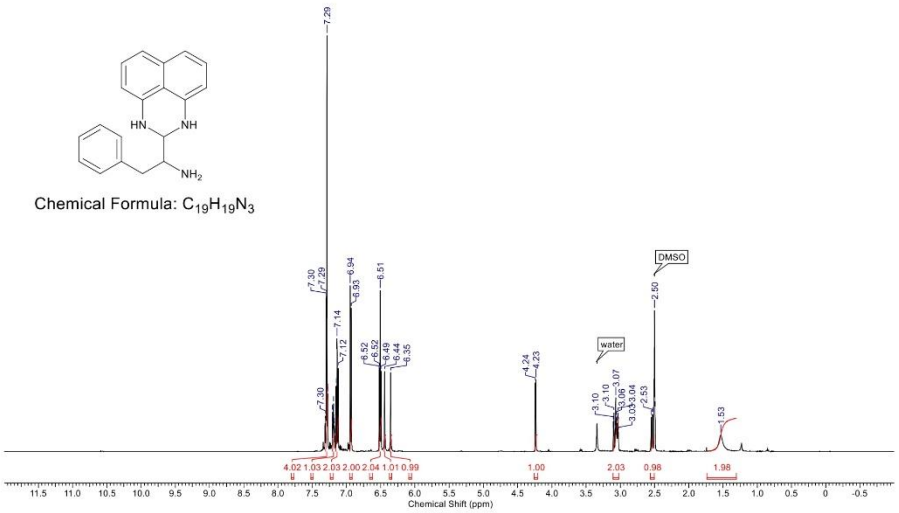


Supplementary Figure 84 ^{1}H NMR spectrum of compound **A25**. (500 MHz, 293 K, DMSO-d_6).

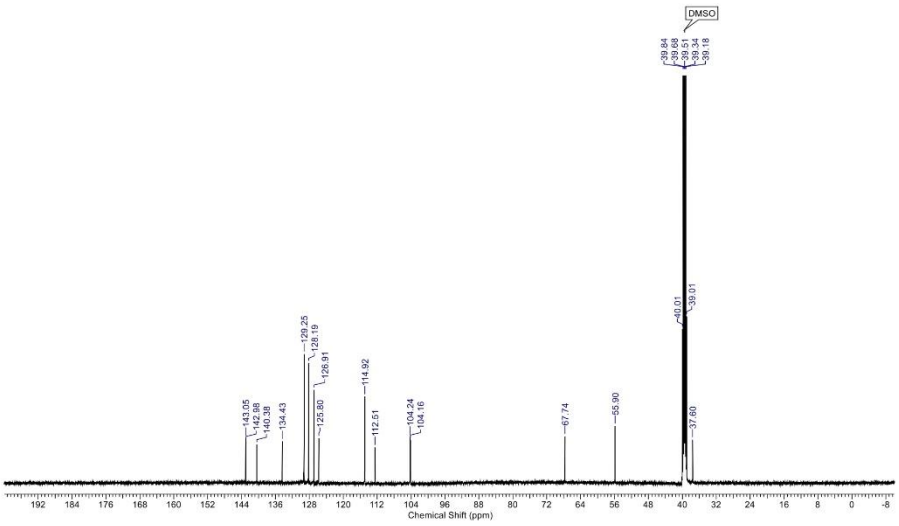


Supplementary Figure 85 ^{13}C NMR spectrum of compound **A25**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A26

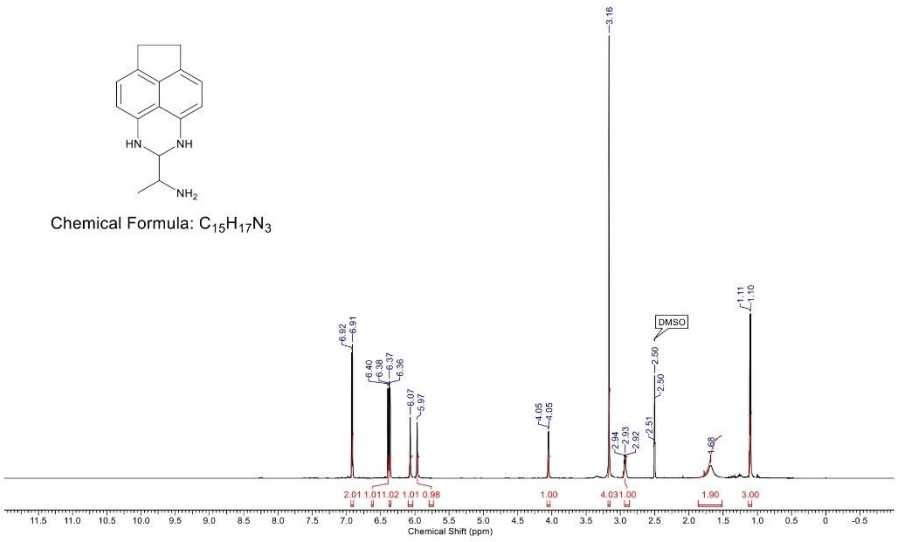


Supplementary Figure 86 ^{1}H NMR spectrum of compound **A26**. (500 MHz, 293 K, DMSO-d_6).

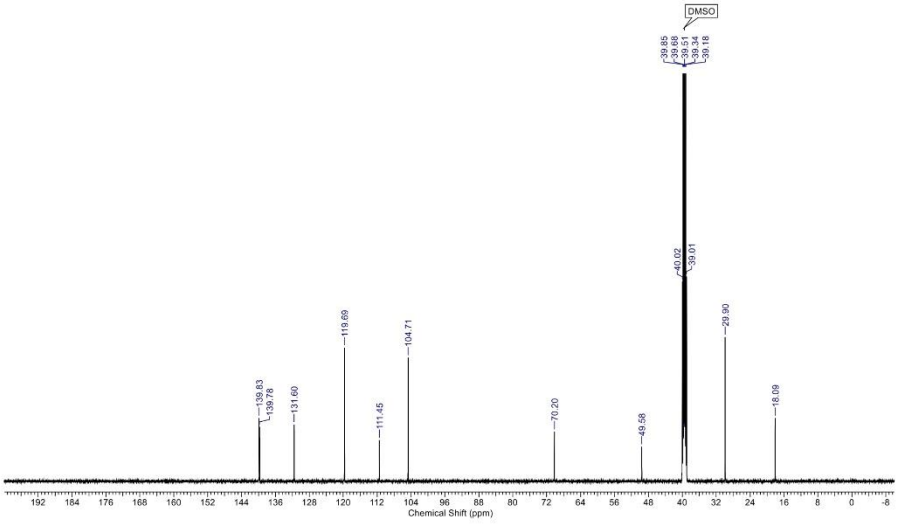


Supplementary Figure 87 ^{13}C NMR spectrum of compound **A26**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of A27

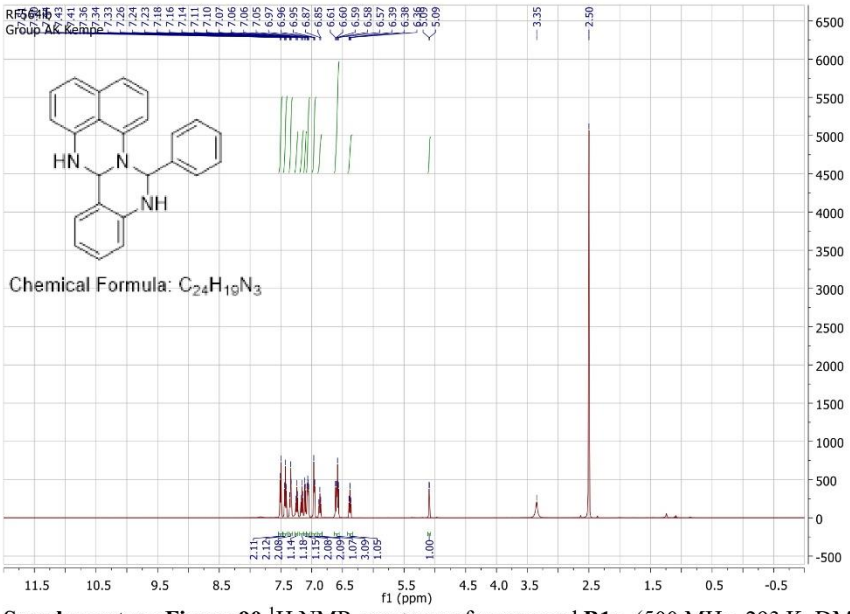


Supplementary Figure 88 ^{1}H NMR spectrum of compound **A27**. (500 MHz, 293 K, DMSO-d_6).

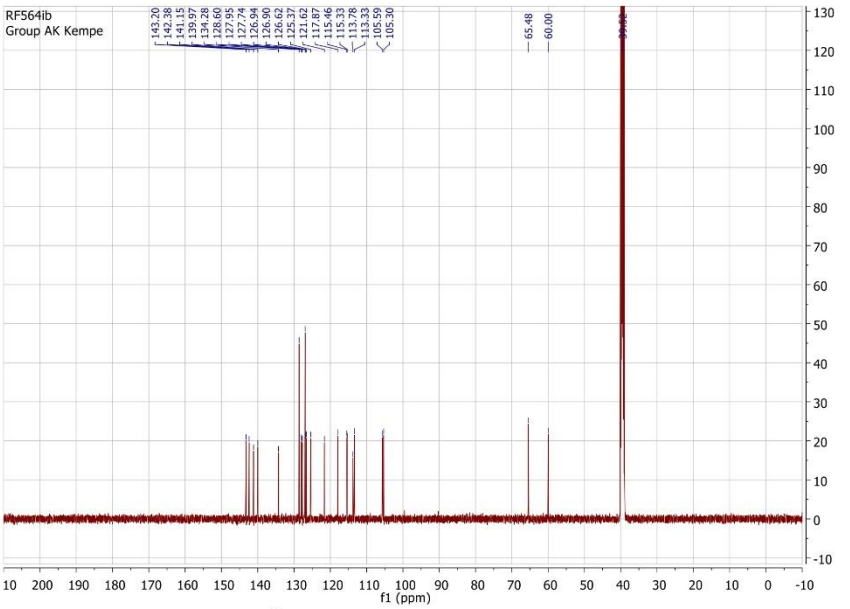


Supplementary Figure 89 ^{13}C NMR spectrum of compound **A27**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B1a

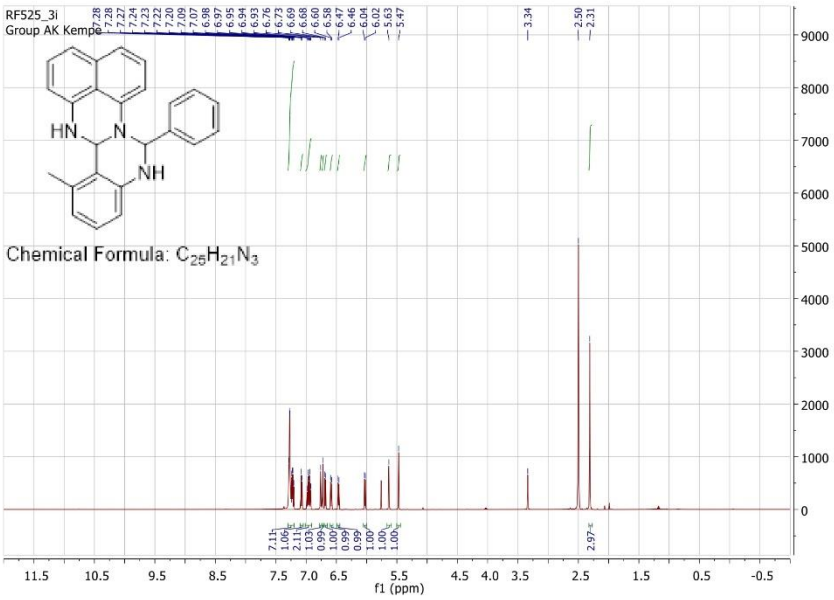


Supplementary Figure 90 ^{1}H NMR spectrum of compound **B1a**. (500 MHz, 293 K, DMSO-d_6).

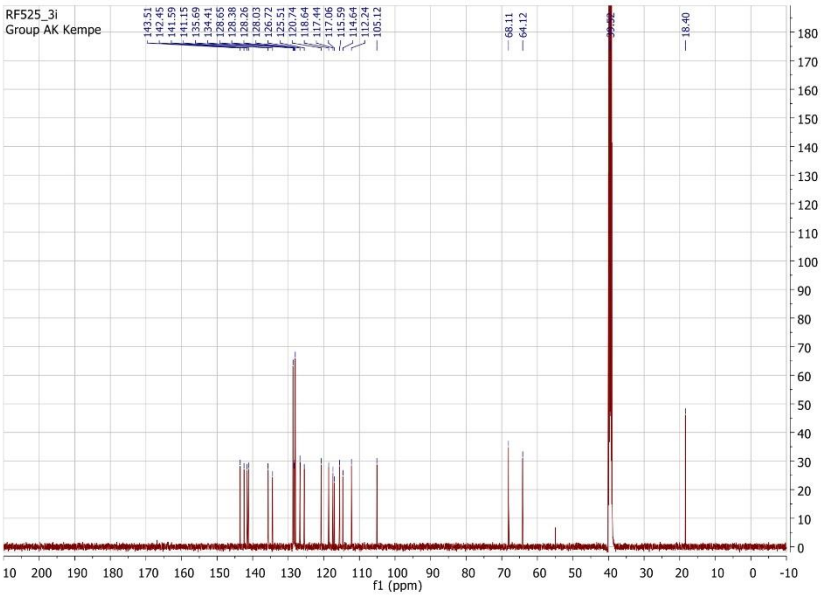


Supplementary Figure 91 ^{13}C NMR spectrum of compound **B1a**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B1b

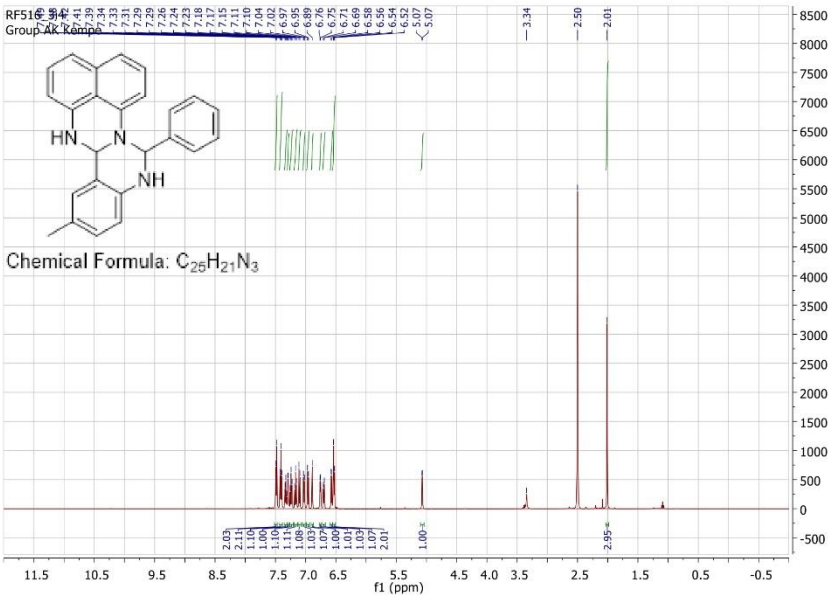


Supplementary Figure 92 ^{1}H NMR spectrum of compound **B1b**. (500 MHz, 293 K, DMSO-d_6).

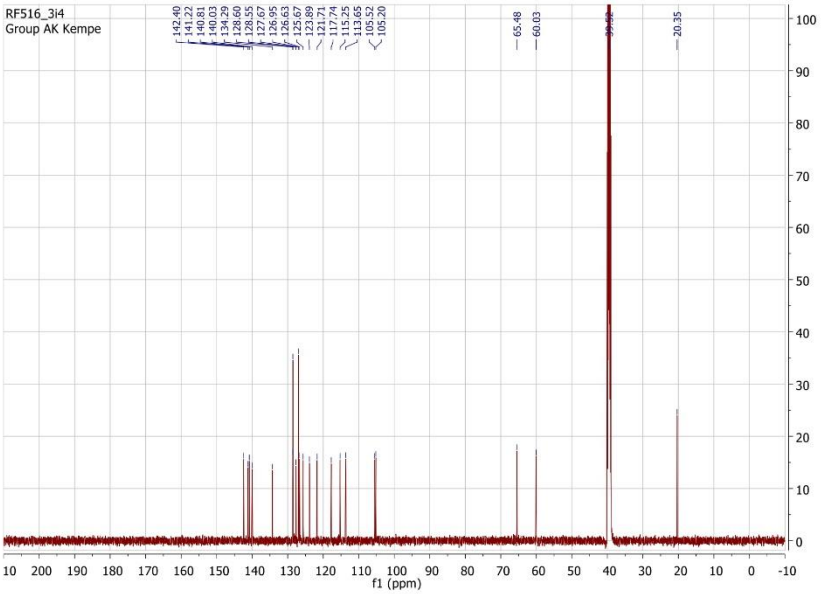


Supplementary Figure 93 ^{13}C NMR spectrum of compound **B1b**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B1c

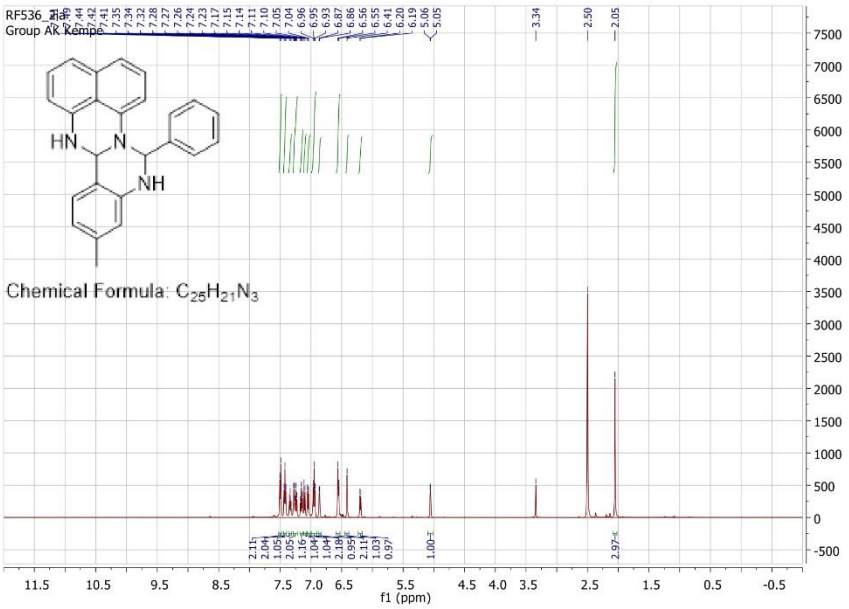


Supplementary Figure 94 ^{1}H NMR spectrum of compound **B1c**. (500 MHz, 293 K, DMSO-d_6).

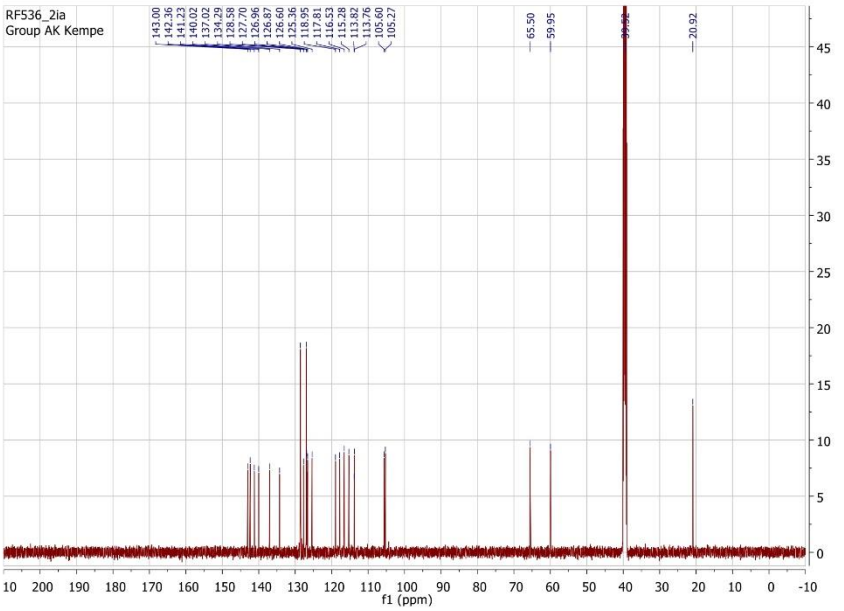


Supplementary Figure 95 ^{13}C NMR spectrum of compound **B1c**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B1d

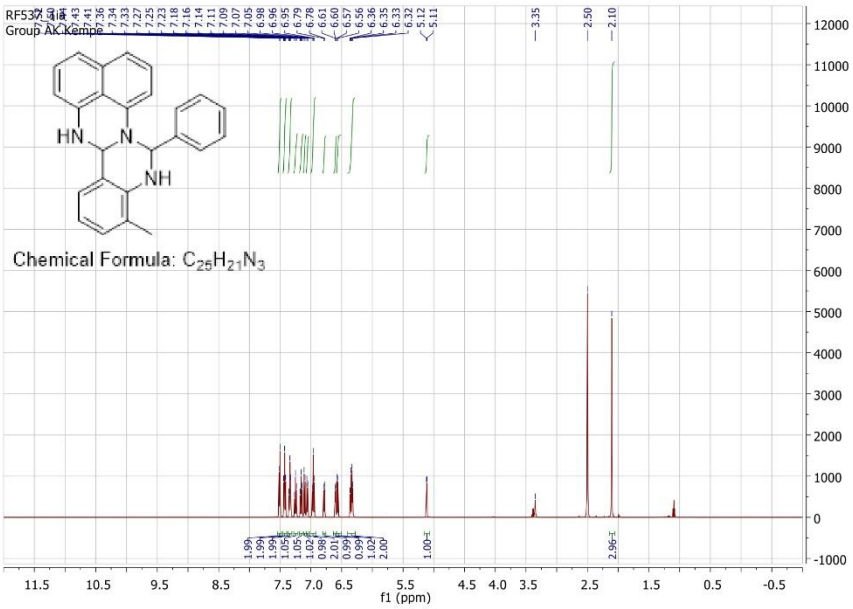


Supplementary Figure 96 ^{1}H NMR spectrum of compound **B1d**. (500 MHz, 293 K, DMSO-d_6).

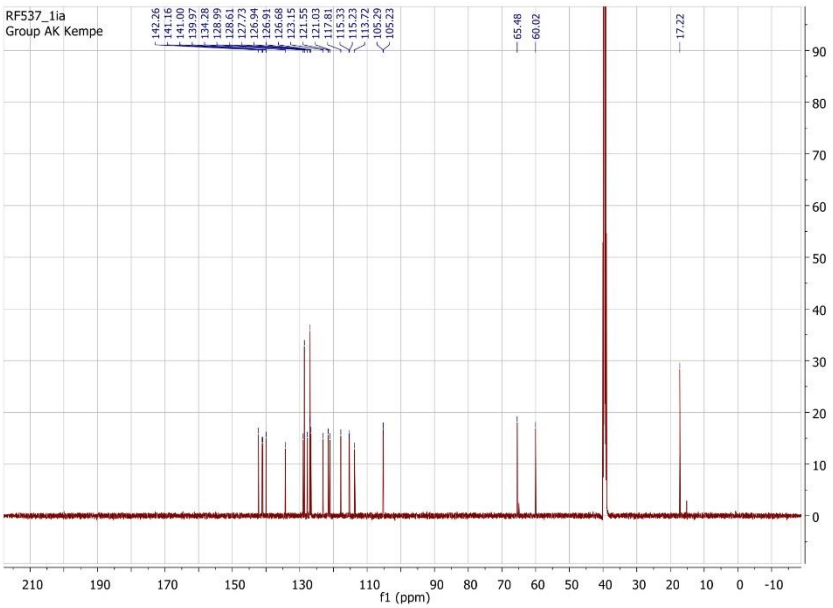


Supplementary Figure 97 ^{13}C NMR spectrum of compound **B1d**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B1e

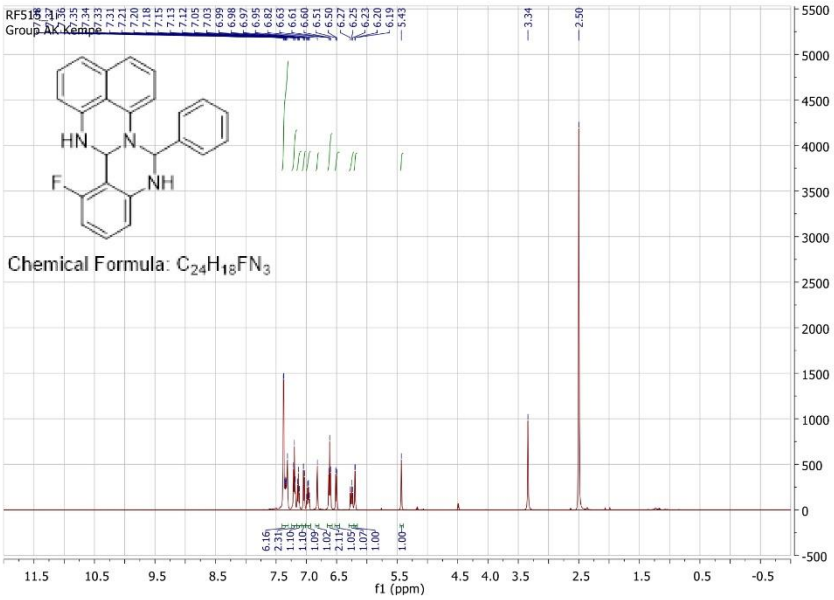


Supplementary Figure 98 ^{1}H NMR spectrum of compound **B1e**. (500 MHz, 293 K, DMSO-d_6).

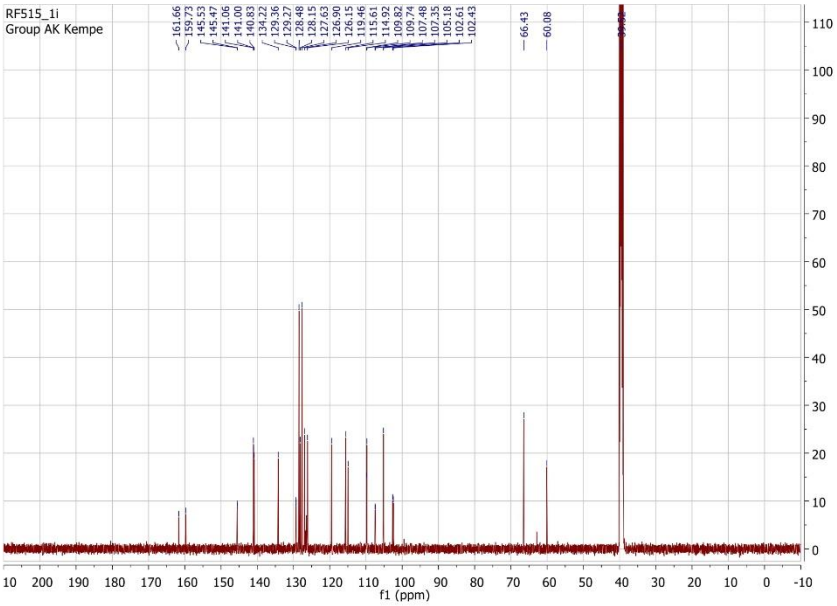


Supplementary Figure 99 ^{13}C NMR spectrum of compound **B1e**. (125 MHz, 293 K, DMSO-d_6).

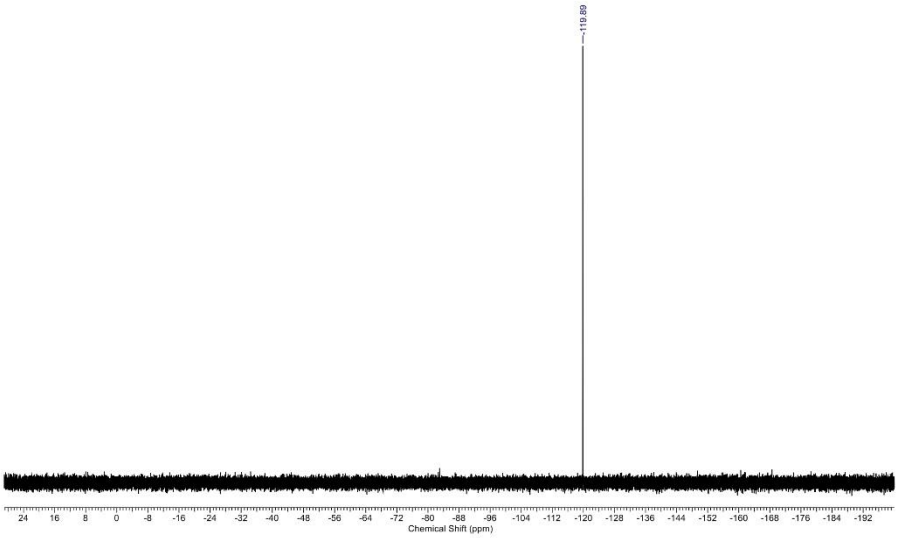
NMR spectra of B1f



Supplementary Figure 100 ^{1}H NMR spectrum of compound **B1f**. (500 MHz, 293 K, DMSO-d_6).

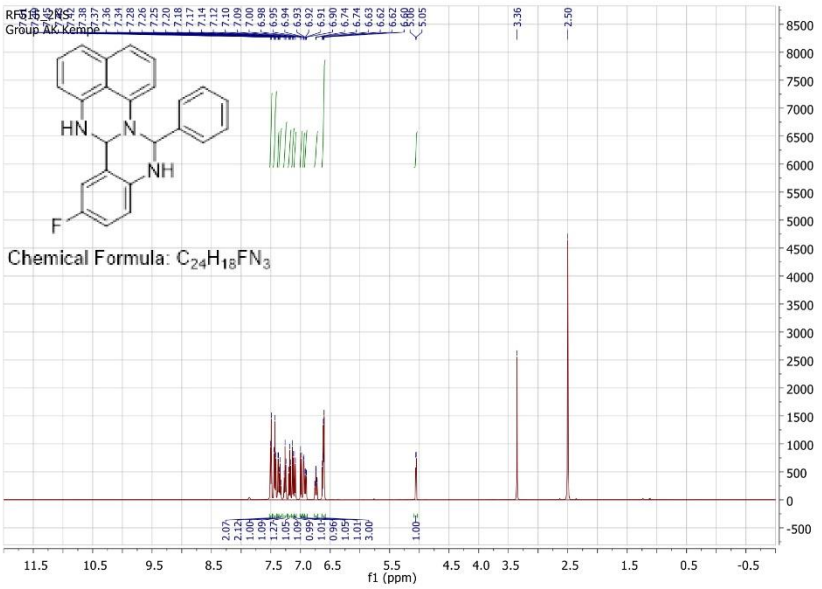


Supplementary Figure 101 ^{13}C NMR spectrum of compound **B1f**. (125 MHz, 293 K, DMSO-d_6).

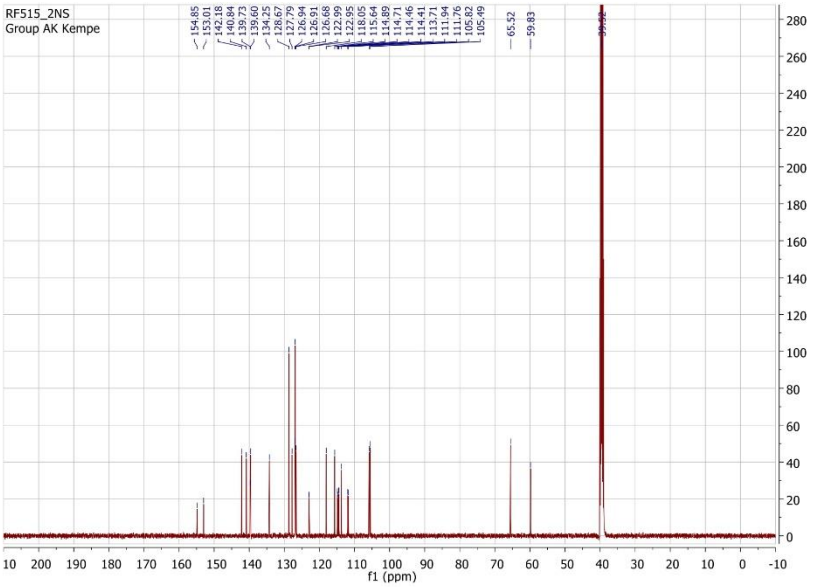


Supplementary Figure 102 ^{19}F NMR spectrum of compound **B1f**. (376 MHz, 293 K, DMSO-d_6).

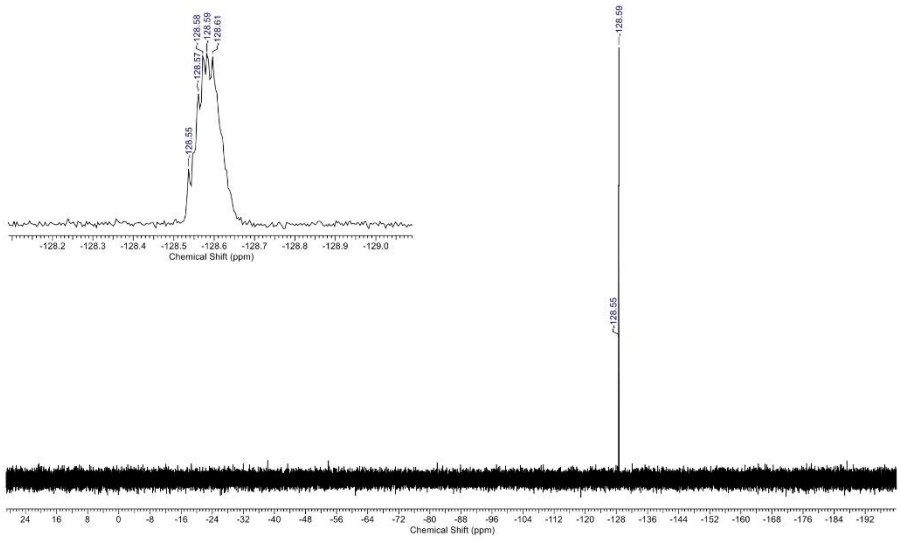
NMR spectra of B1g



Supplementary Figure 103 ^{1}H NMR spectrum of compound **B1g**. (500 MHz, 293 K, DMSO-d_6).

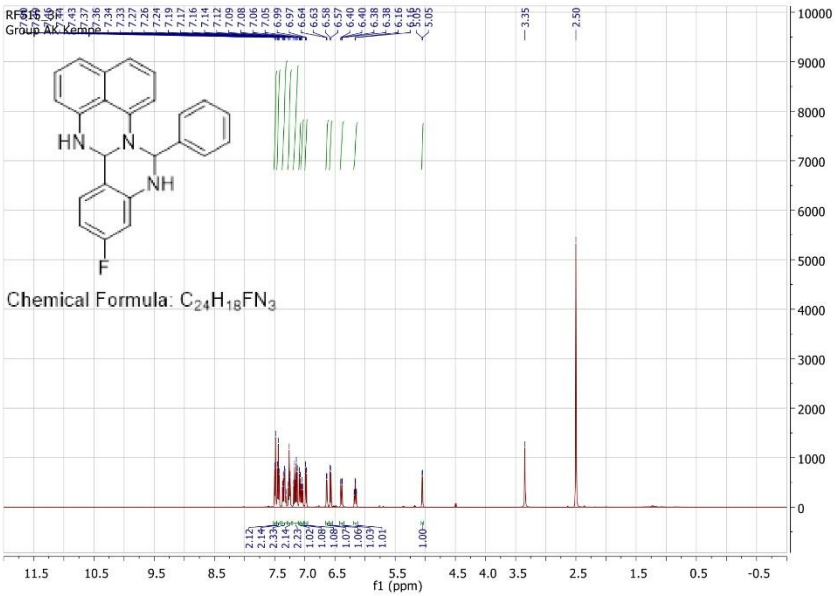


Supplementary Figure 104 ^{13}C NMR spectrum of compound **B1g**. (125 MHz, 293 K, DMSO-d_6).

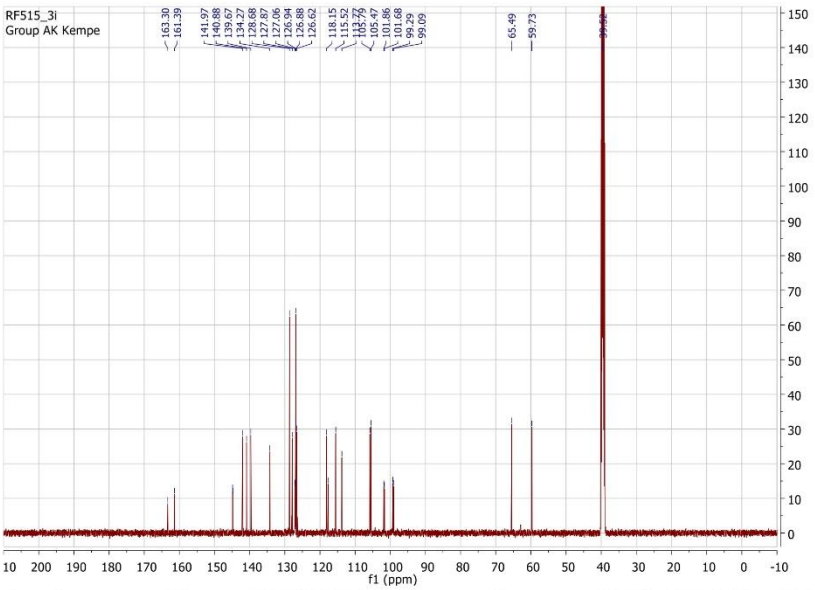


Supplementary Figure 105 ^{19}F NMR spectrum of compound **B1g**. (376 MHz, 293 K, DMSO-d_6).

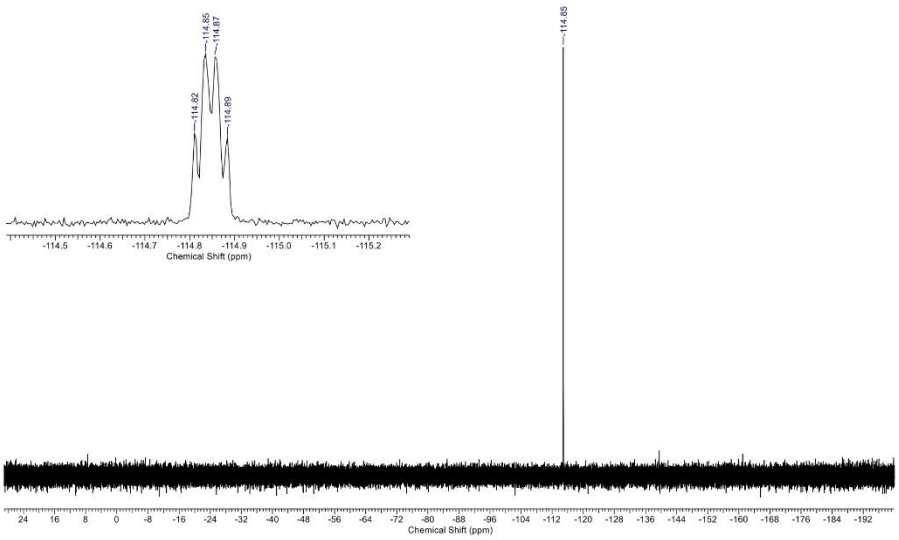
NMR spectra of B1h



Supplementary Figure 106 ^{1}H NMR spectrum of compound **B1h**. (500 MHz, 293 K, DMSO-d_6).

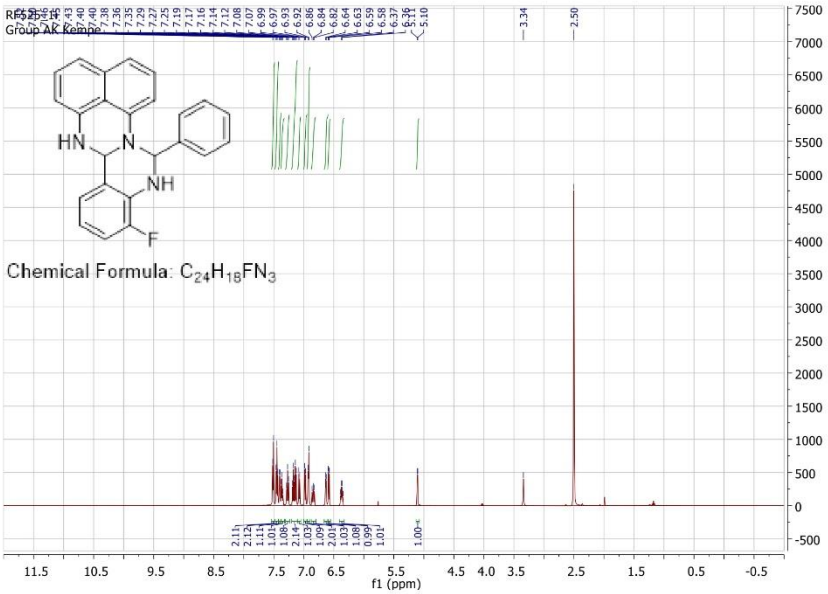


Supplementary Figure 107 ^{13}C NMR spectrum of compound **B1h**. (125 MHz, 293 K, DMSO-d_6).

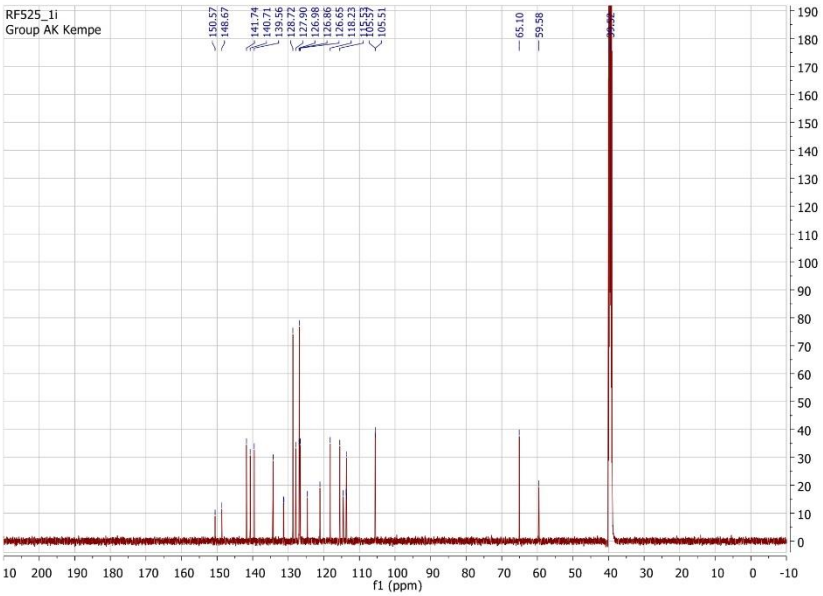


Supplementary Figure 108 ^{19}F NMR spectrum of compound **B1h**. (376 MHz, 293 K, DMSO-d_6).

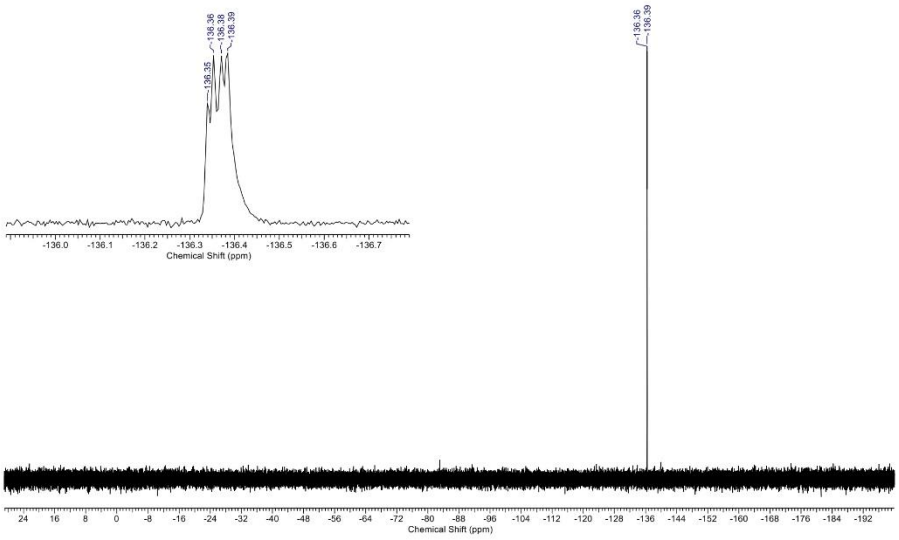
NMR spectra of B1i



Supplementary Figure 109 ^{1}H NMR spectrum of compound **B1i**. (500 MHz, 293 K, DMSO-d_6).

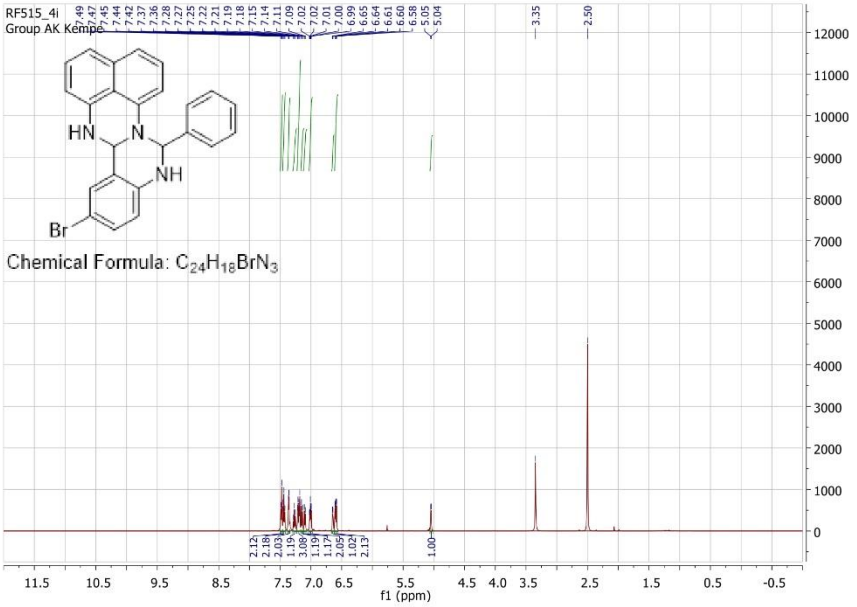


Supplementary Figure 110 ^{13}C NMR spectrum of compound **B1i**. (125 MHz, 293 K, DMSO-d_6).

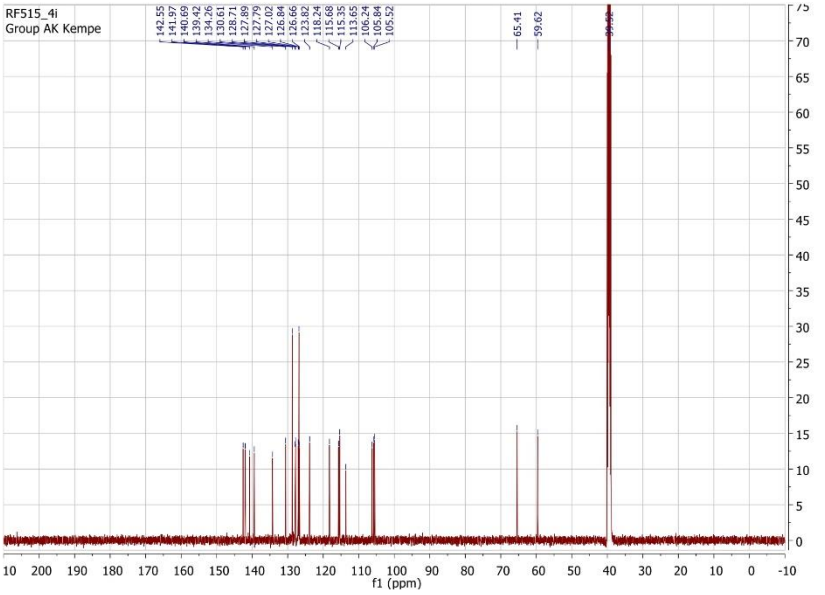


Supplementary Figure 111 ^{19}F NMR spectrum of compound **B1i**. (376 MHz, 293 K, DMSO-d_6).

NMR spectra of B1j

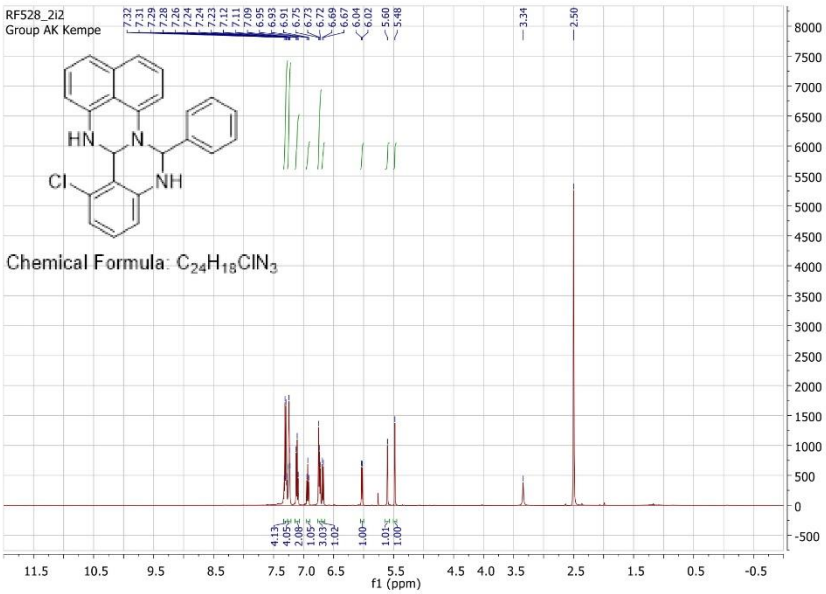


Supplementary Figure 112 ^{1}H NMR spectrum of compound **B1j**. (500 MHz, 293 K, DMSO-d_6).

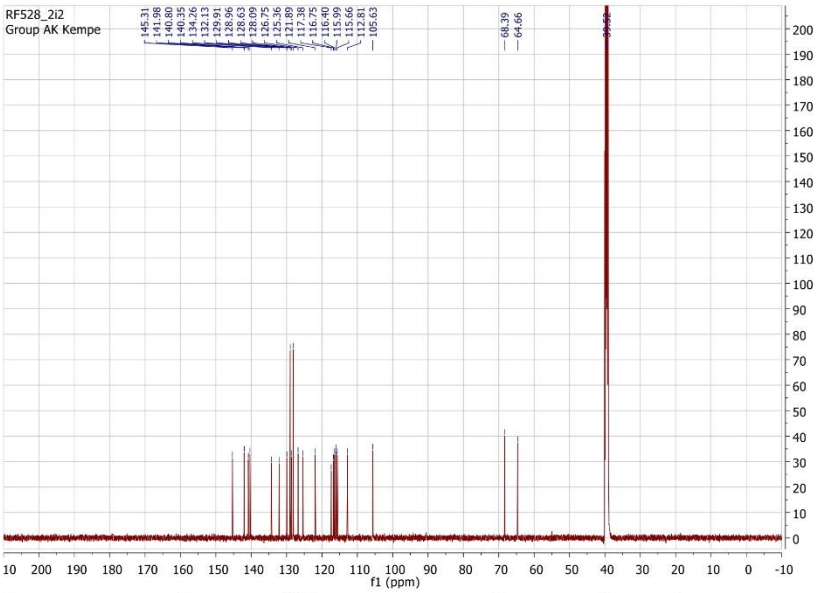


Supplementary Figure 113 ^{13}C NMR spectrum of compound **B1j**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B1k

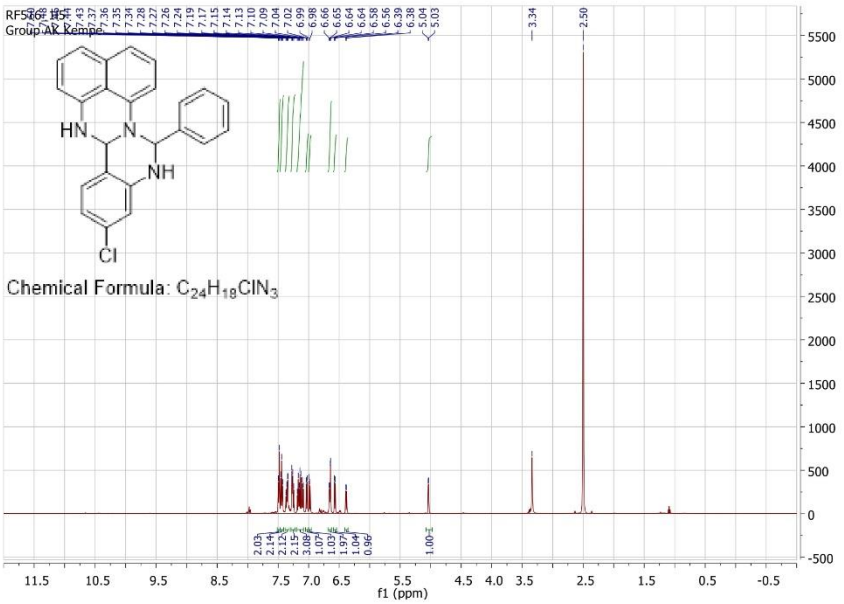


Supplementary Figure 114 ^{1}H NMR spectrum of compound **B1k**. (500 MHz, 293 K, DMSO-d_6).

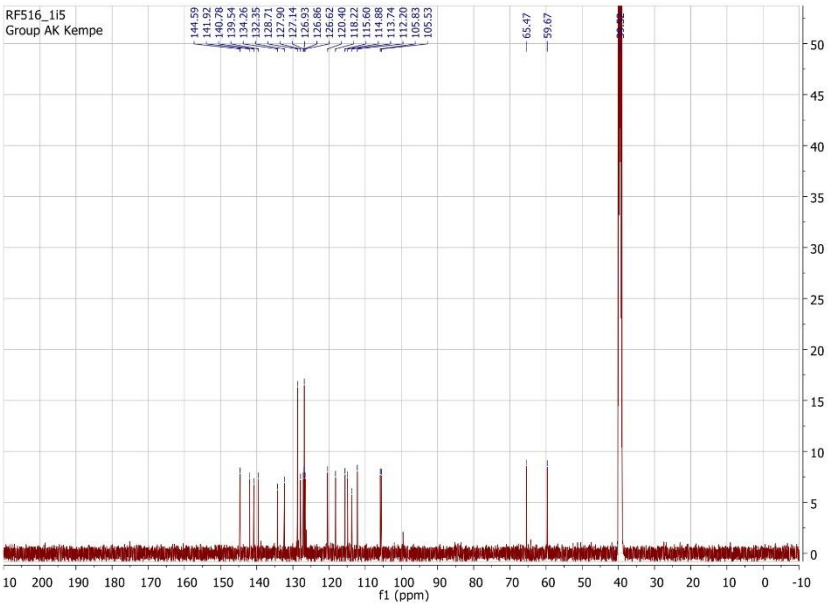


Supplementary Figure 115 ^{13}C NMR spectrum of compound **B1k**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B1l

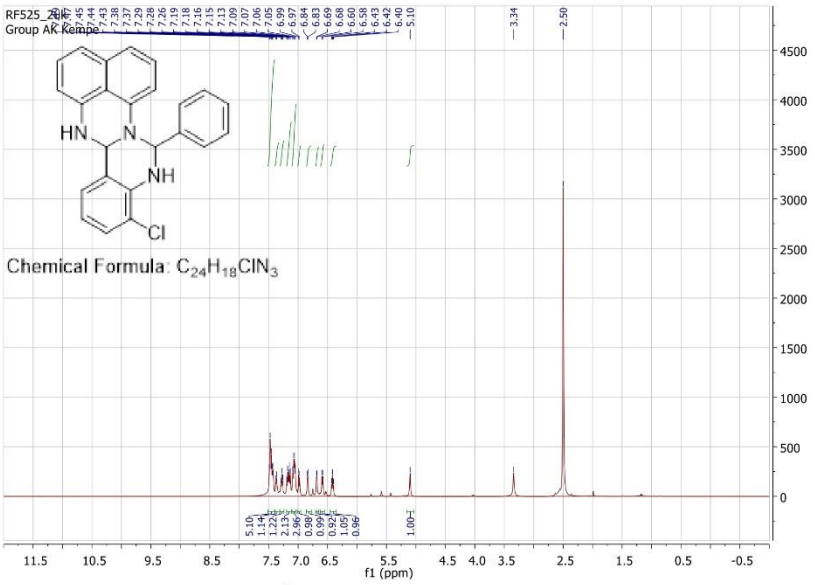


Supplementary Figure 116 ^{1}H NMR spectrum of compound **B1l**. (500 MHz, 293 K, DMSO-d$_6$).

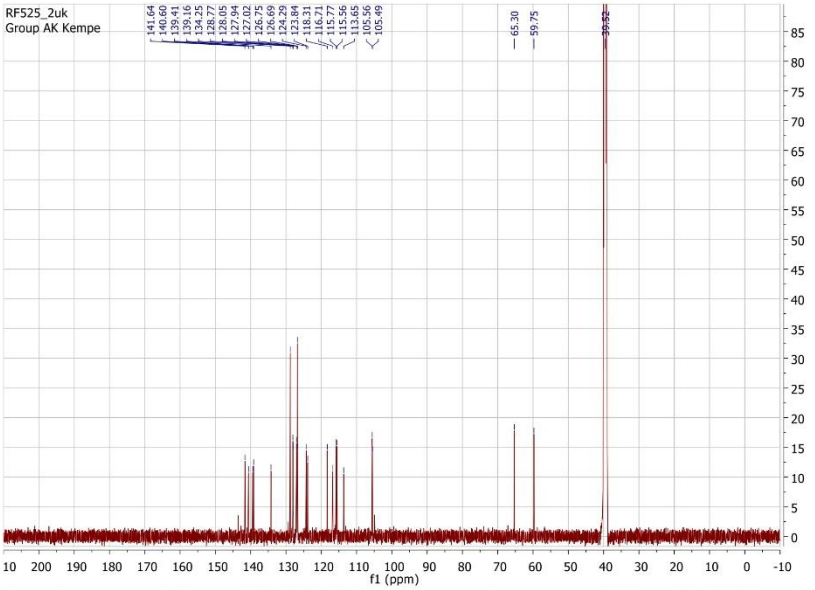


Supplementary Figure 117 ^{13}C NMR spectrum of compound **B1l**. (125 MHz, 293 K, DMSO-d$_6$).

NMR spectra of B1m

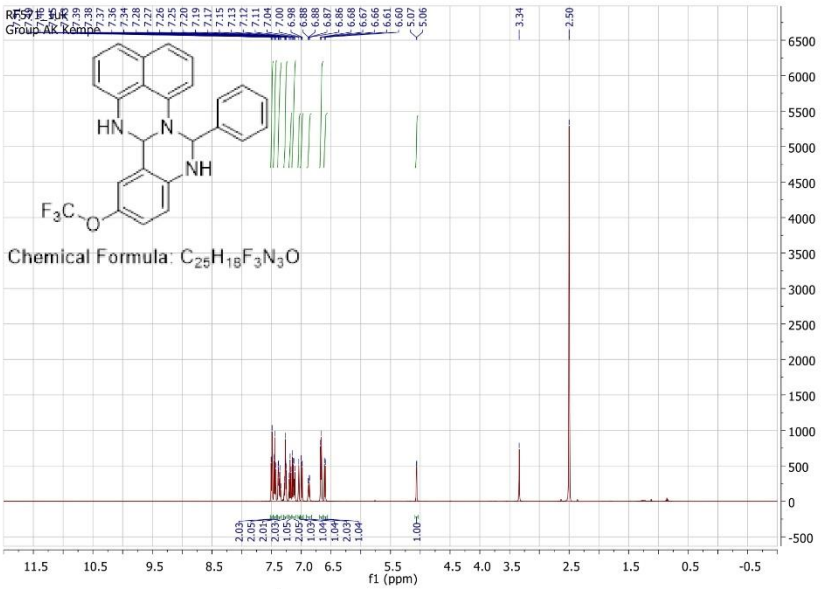


Supplementary Figure 118 ^{1}H NMR spectrum of compound **B1m**. (500 MHz, 293 K, DMSO-d_6).

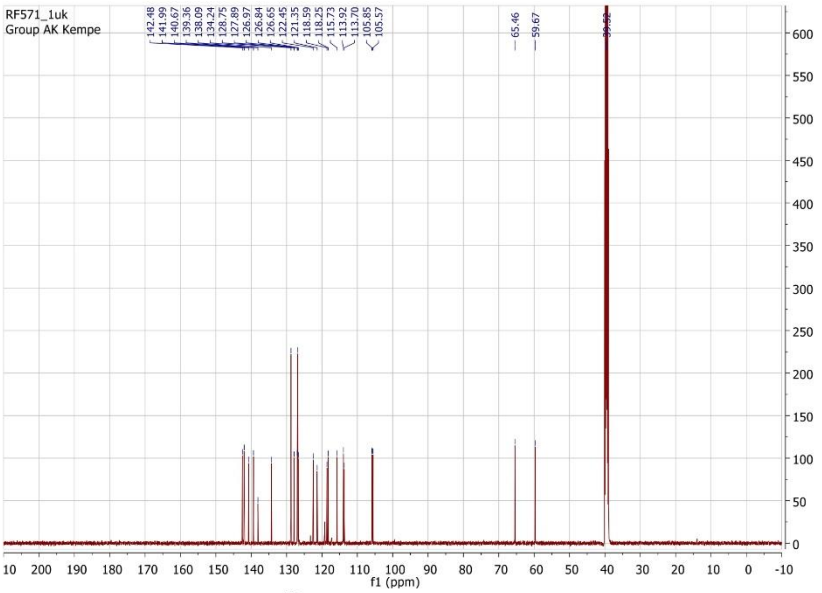


Supplementary Figure 119 ^{13}C NMR spectrum of compound **B1m**. (125 MHz, 293 K, DMSO-d_6).

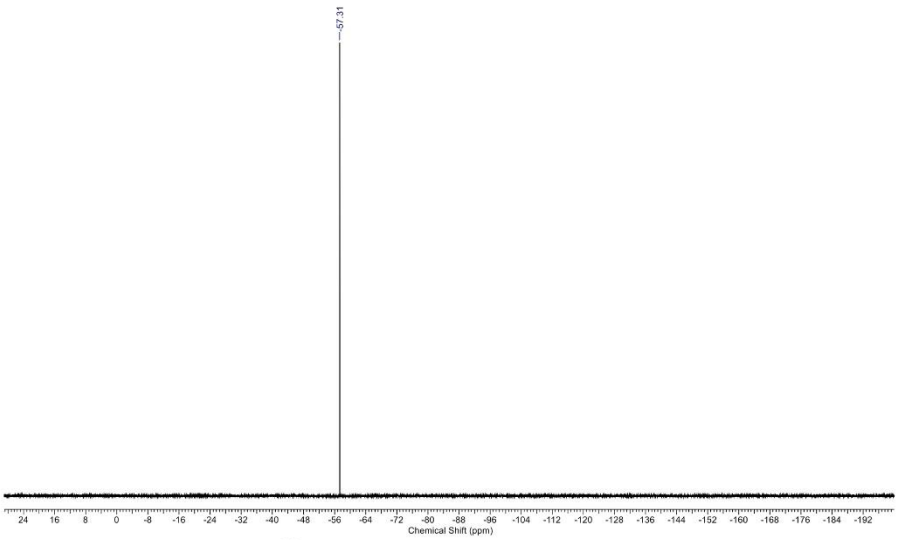
NMR spectra of B1n



Supplementary Figure 120 ^{1}H NMR spectrum of compound **B1n**. (500 MHz, 293 K, DMSO-d_6).

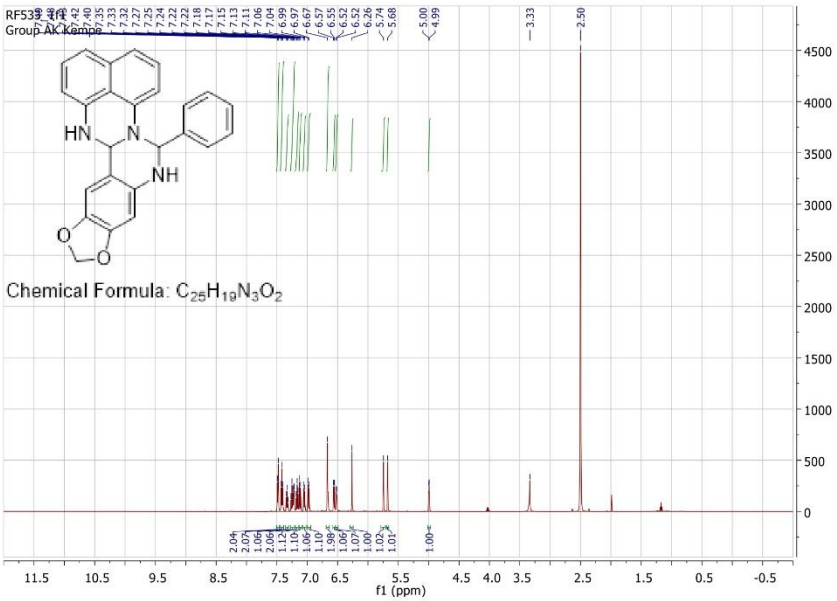


Supplementary Figure 121 ^{13}C NMR spectrum of compound **B1n**. (125 MHz, 293 K, DMSO-d_6).

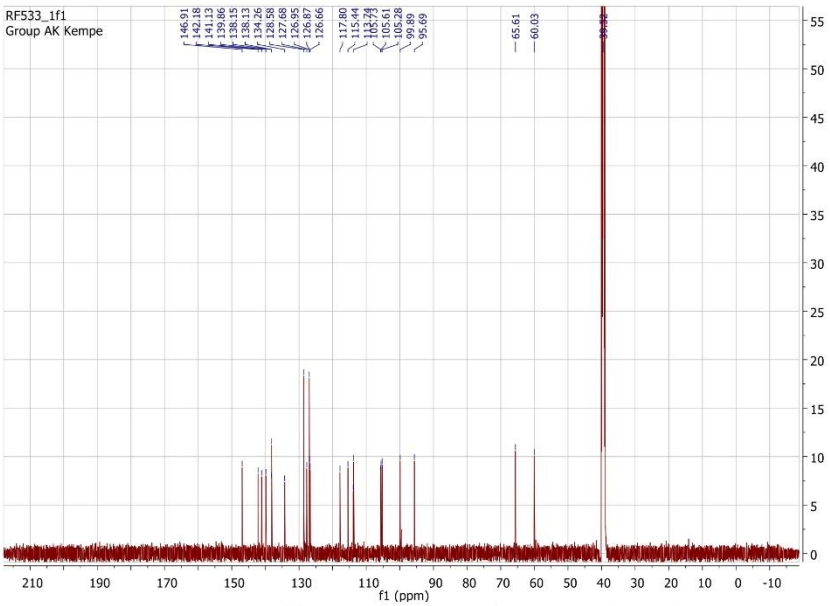


Supplementary Figure 122 ^{19}F NMR spectrum of compound **B1n**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B1o

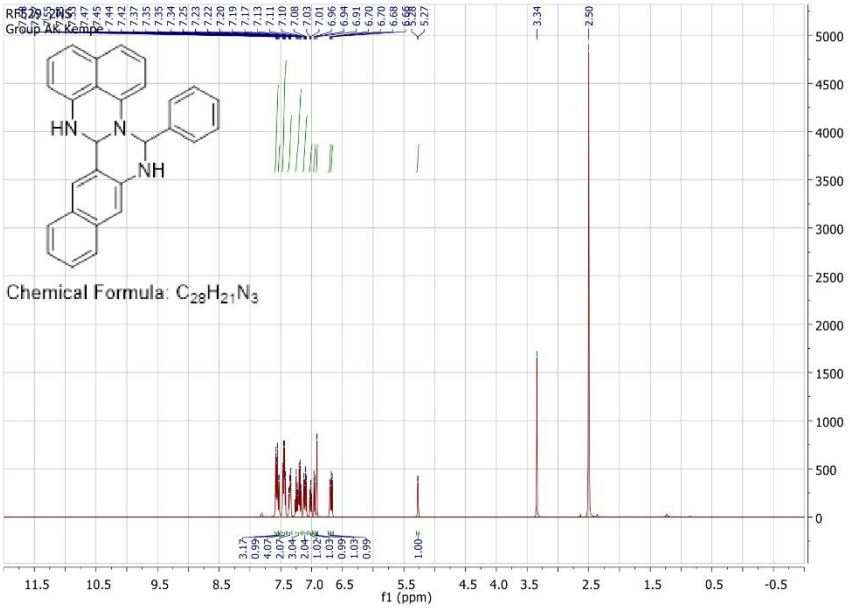


Supplementary Figure 123 ^{1}H NMR spectrum of compound **B1o**. (500 MHz, 293 K, DMSO-d_6).

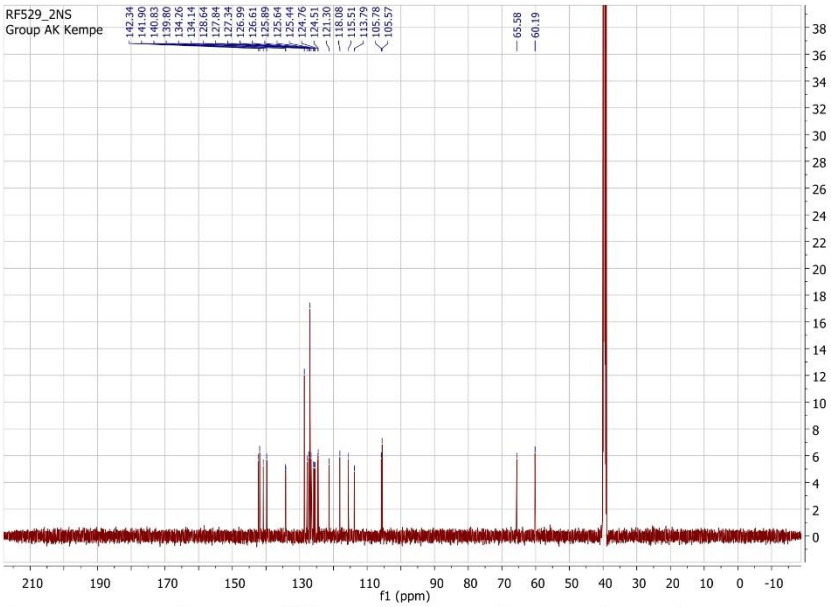


Supplementary Figure 124 ^{13}C NMR spectrum of compound **B1o**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B1p

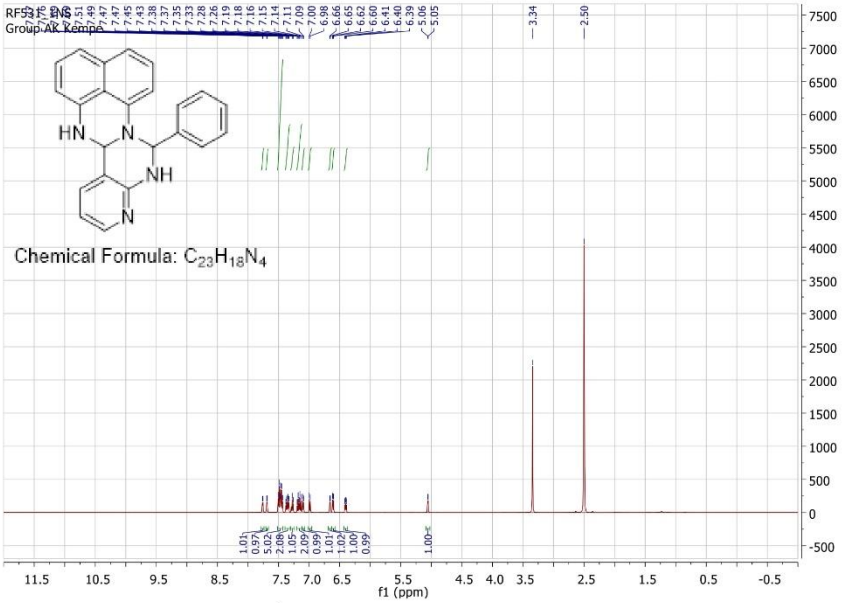


Supplementary Figure 125 ^{1}H NMR spectrum of compound **B1p**. (500 MHz, 293 K, DMSO-d_6).

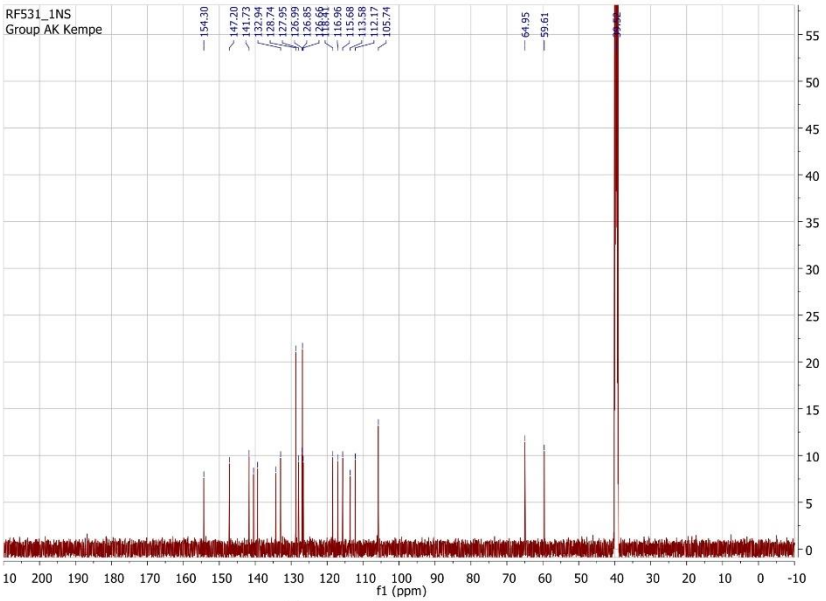


Supplementary Figure 126 ^{13}C NMR spectrum of compound **B1p**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B1q

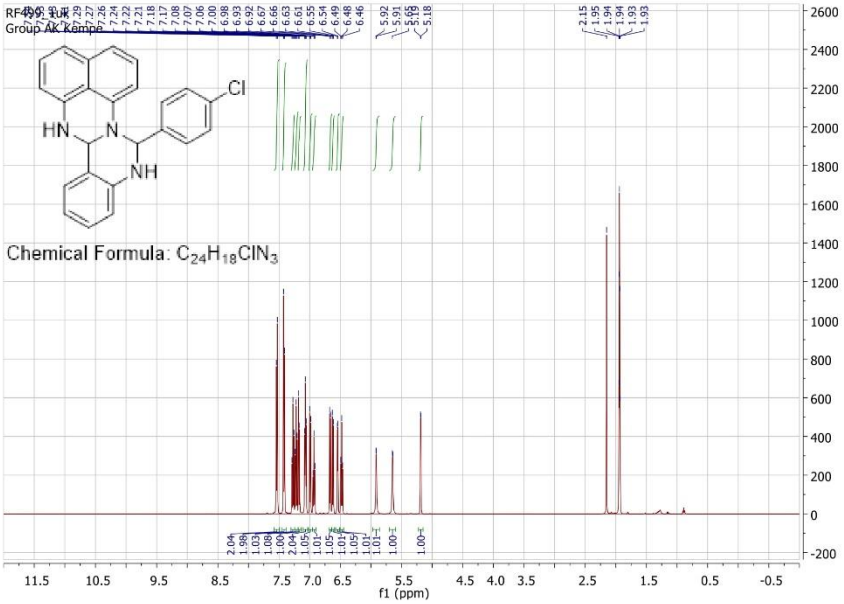


Supplementary Figure 127 ^{1}H NMR spectrum of compound **B1q**. (500 MHz, 293 K, DMSO-d_6).

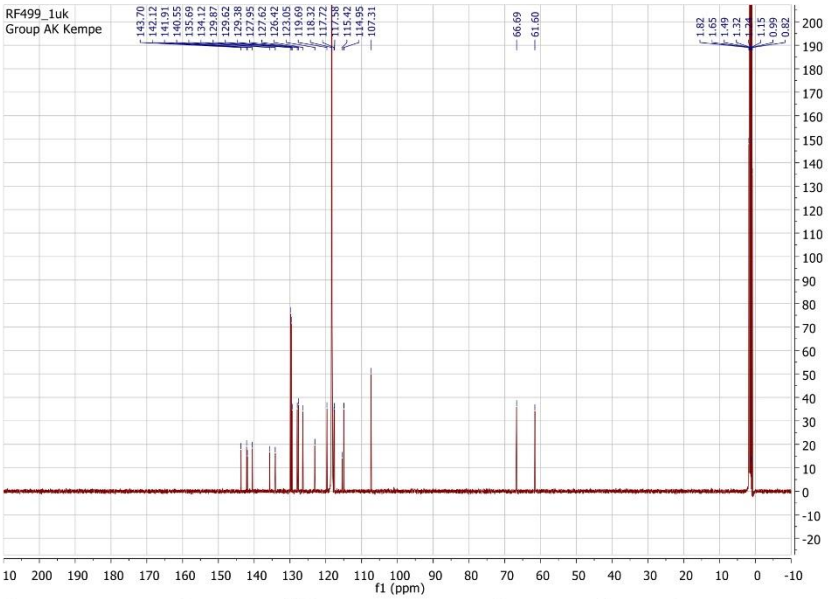


Supplementary Figure 128 ^{13}C NMR spectrum of compound **B1q**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2a

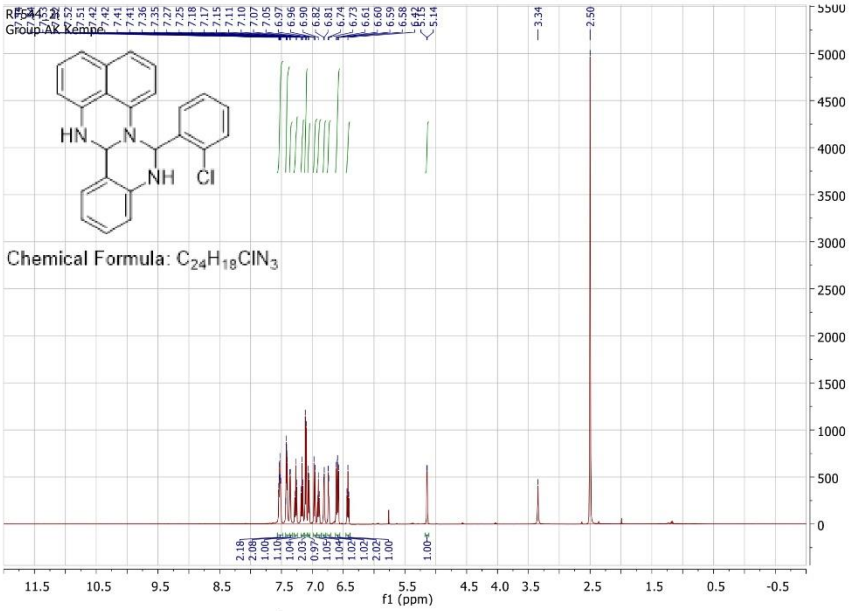


Supplementary Figure 129 ^{1}H NMR spectrum of compound **B2a**. (500 MHz, 293 K, DMSO-d_6).

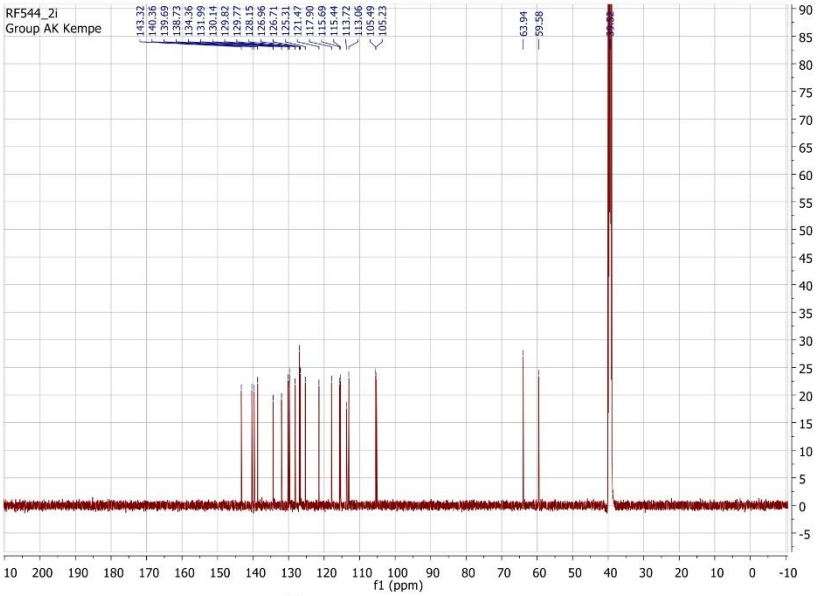


Supplementary Figure 130 ^{13}C NMR spectrum of compound **B2a**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2b

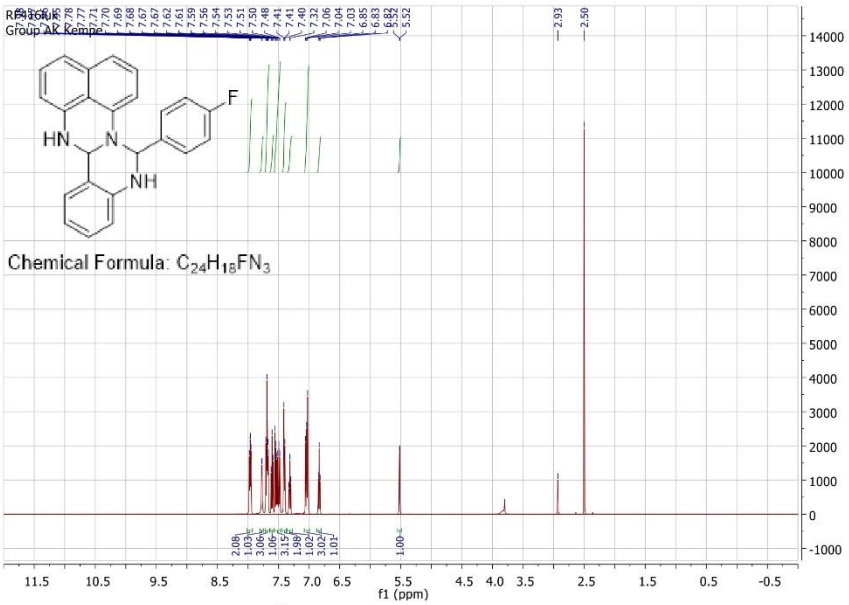


Supplementary Figure 131 ^{1}H NMR spectrum of compound **B2b**. (500 MHz, 293 K, DMSO-d_6).

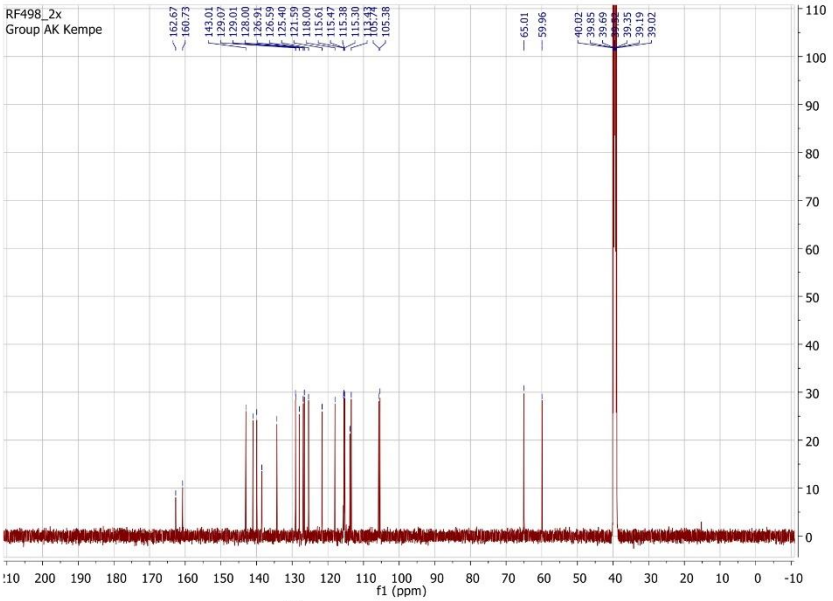


Supplementary Figure 132 ^{13}C NMR spectrum of compound **B2b**. (125 MHz, 293 K, DMSO-d_6).

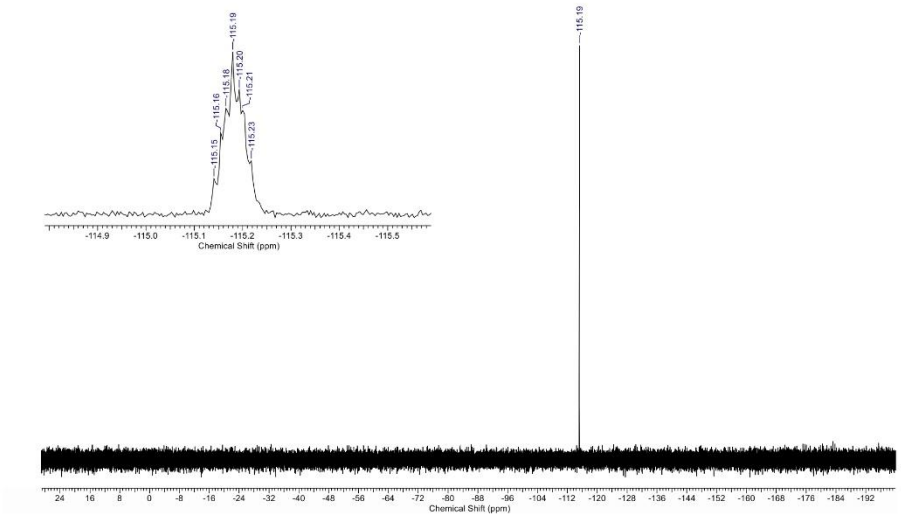
NMR spectra of B2c



Supplementary Figure 133 ^{1}H NMR spectrum of compound **B2c**. (500 MHz, 293 K, DMSO-d_6).

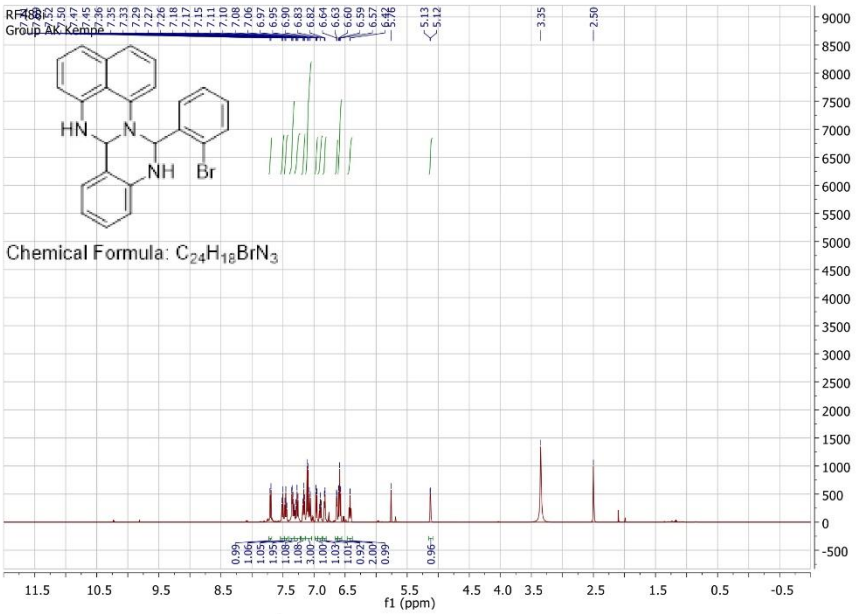


Supplementary Figure 134 ^{13}C NMR spectrum of compound **B2c**. (125 MHz, 293 K, DMSO-d_6).

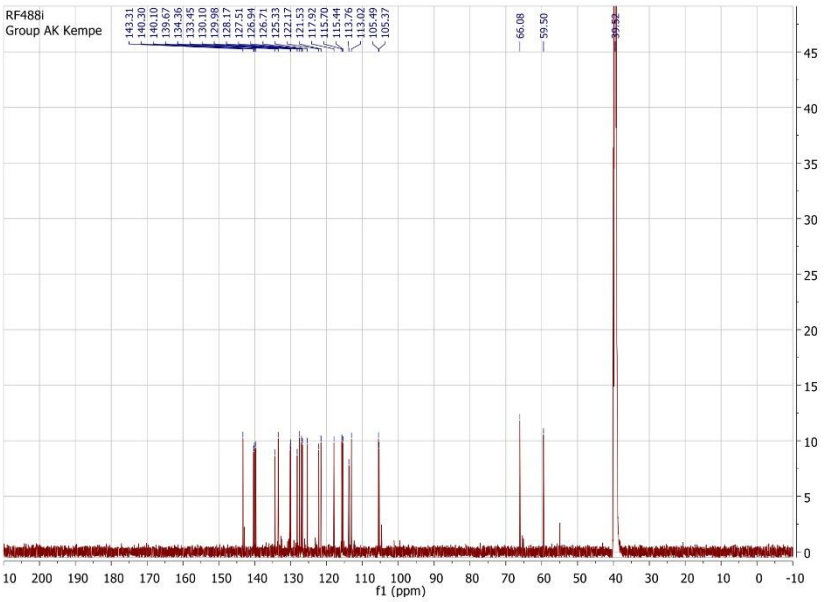


Supplementary Figure 135 ^{19}F NMR spectrum of compound **B2c**. (376 MHz, 293 K, DMSO-d_6).

NMR spectra of B2d

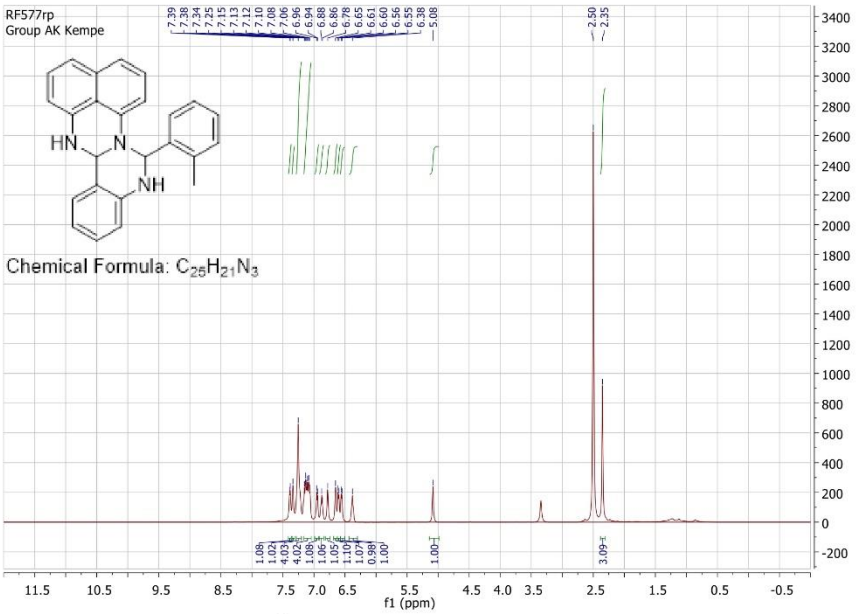


Supplementary Figure 136 ^{1}H NMR spectrum of compound **B2d**. (500 MHz, 293 K, DMSO-d_6).

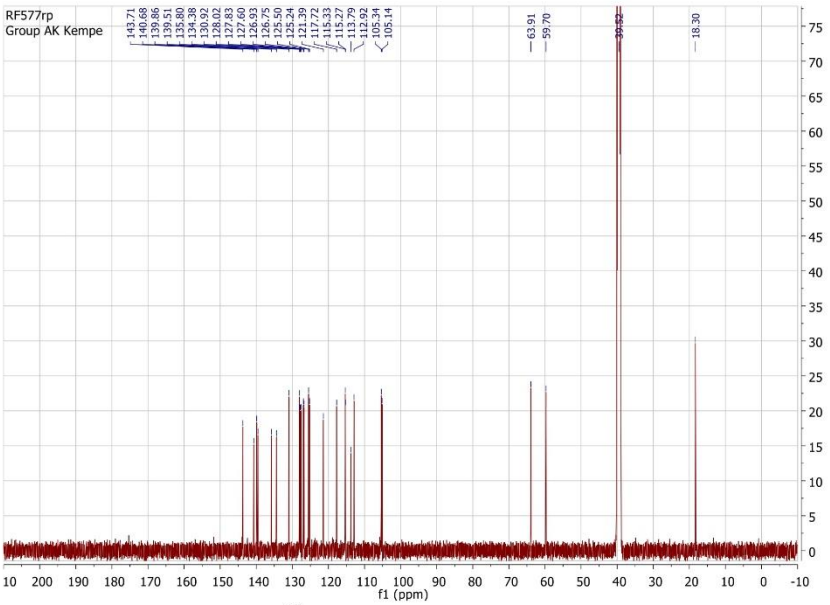


Supplementary Figure 137 ^{13}C NMR spectrum of compound **B2d**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2e

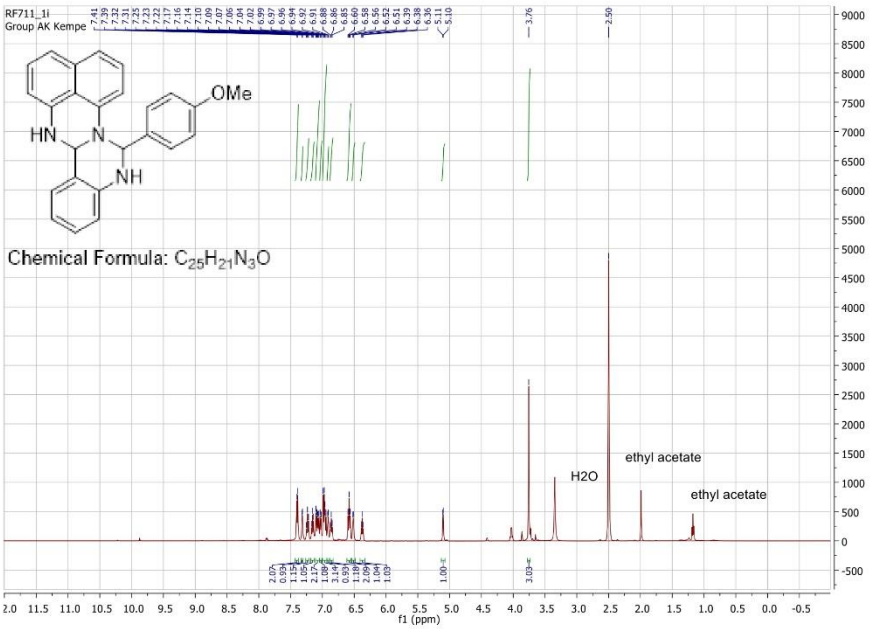


Supplementary Figure 138 ^{1}H NMR spectrum of compound **B2e**. (500 MHz, 293 K, DMSO-d_6).

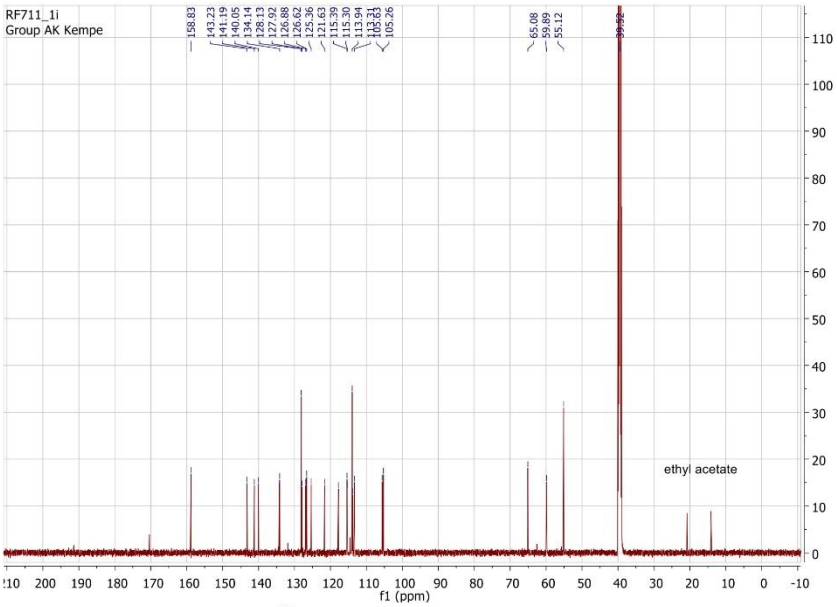


Supplementary Figure 139 ^{13}C NMR spectrum of compound **B2e**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2f

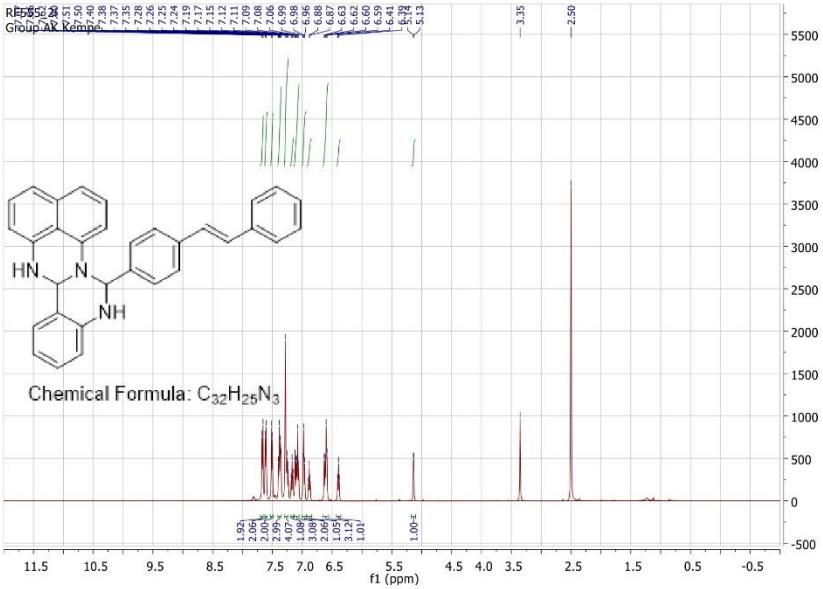


Supplementary Figure 140 ^{1}H NMR spectrum of compound **B2f**. (500 MHz, 293 K, DMSO-d_6).

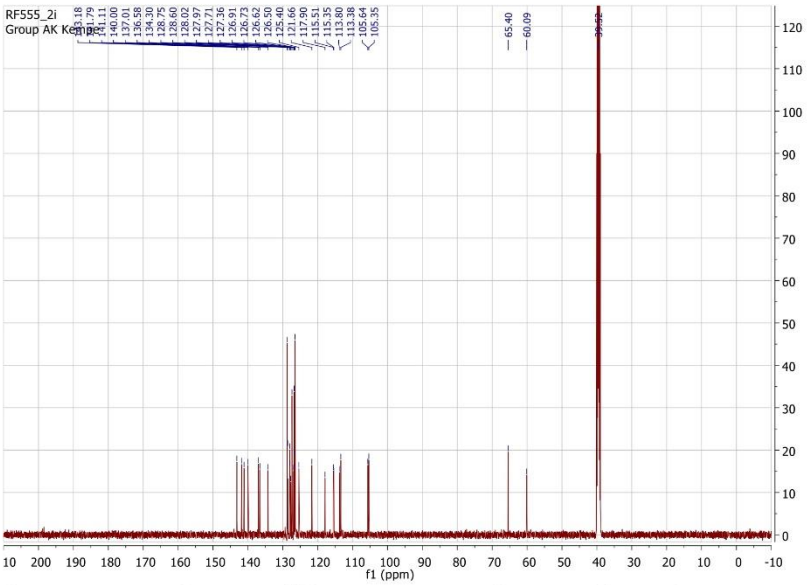


Supplementary Figure 141 ^{13}C NMR spectrum of compound **B2f**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2g

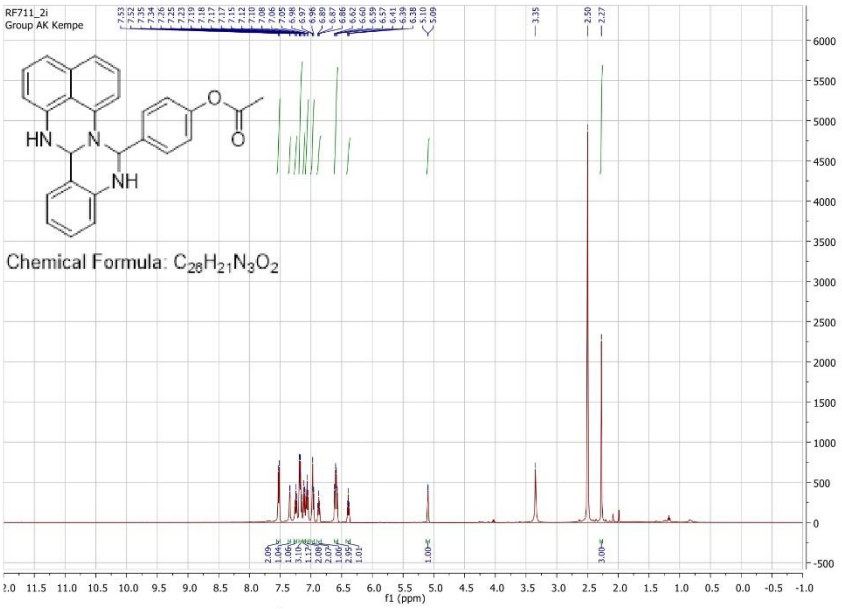


Supplementary Figure 142 ^{1}H NMR spectrum of compound **B2g**. (500 MHz, 293 K, DMSO-d_6).

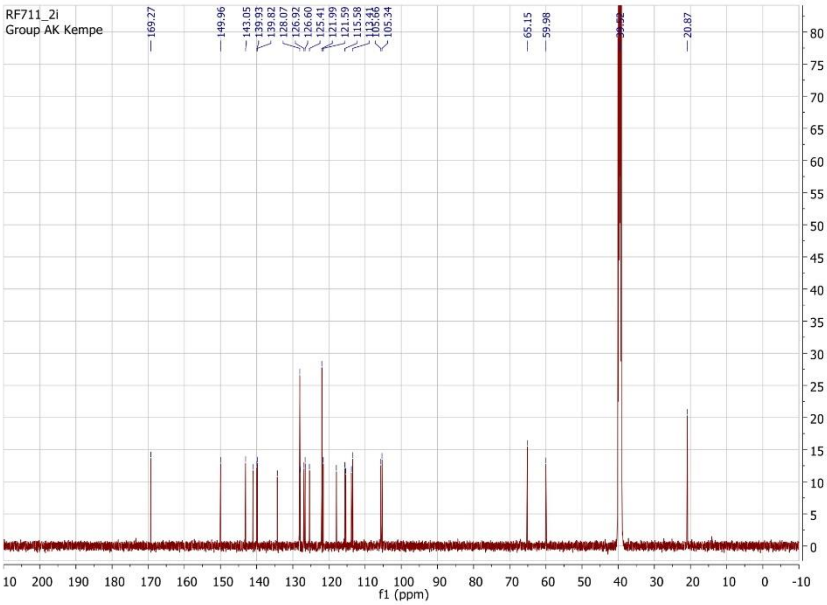


Supplementary Figure 143 ^{13}C NMR spectrum of compound **B2g**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2h

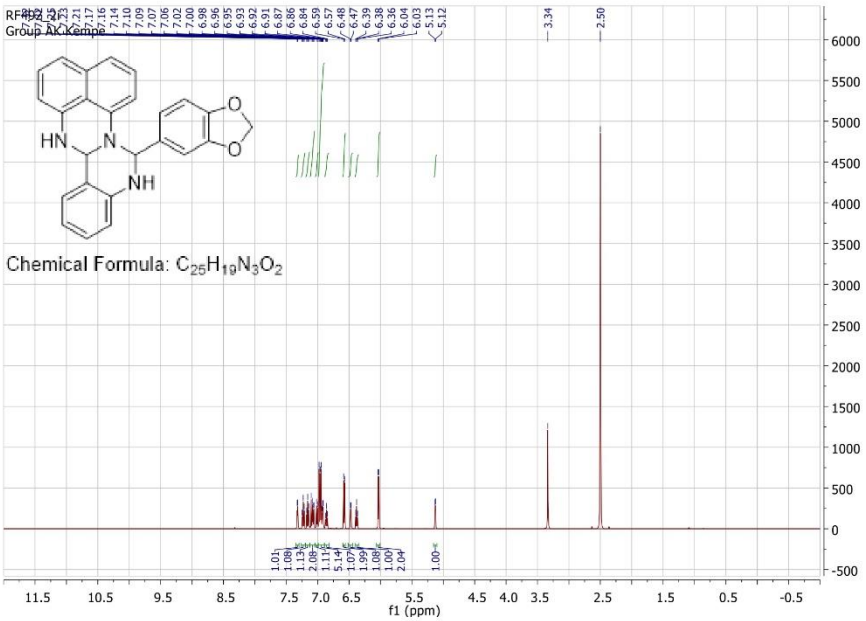


Supplementary Figure 144 ^{1}H NMR spectrum of compound **B2h**. (500 MHz, 293 K, DMSO-d_6).

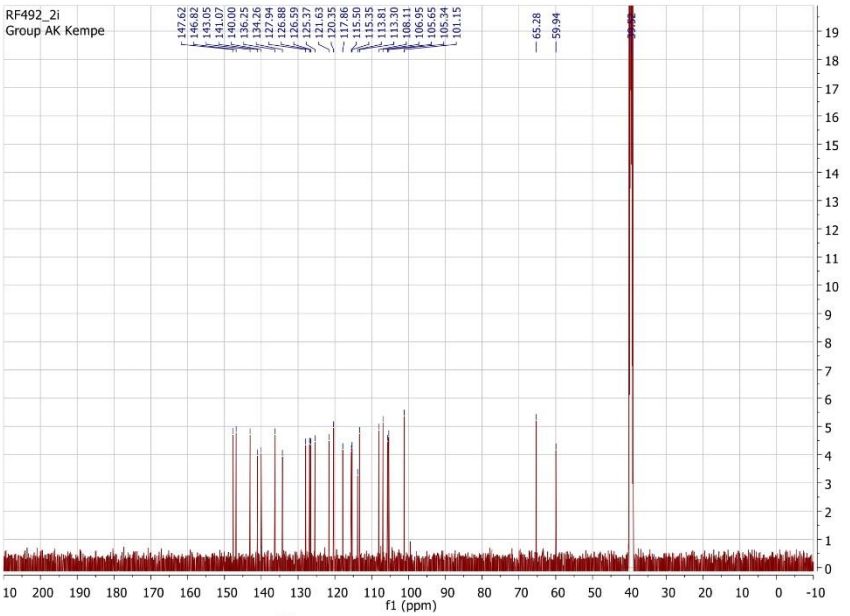


Supplementary Figure 145 ^{13}C NMR spectrum of compound **B2h**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2i

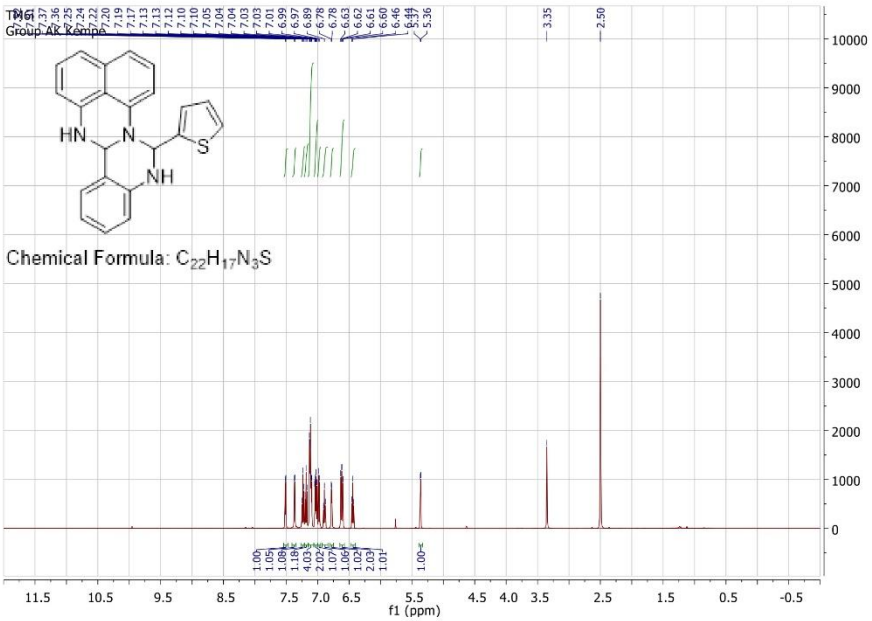


Supplementary Figure 146 ^{1}H NMR spectrum of compound **B2i**. (500 MHz, 293 K, DMSO-d_6).

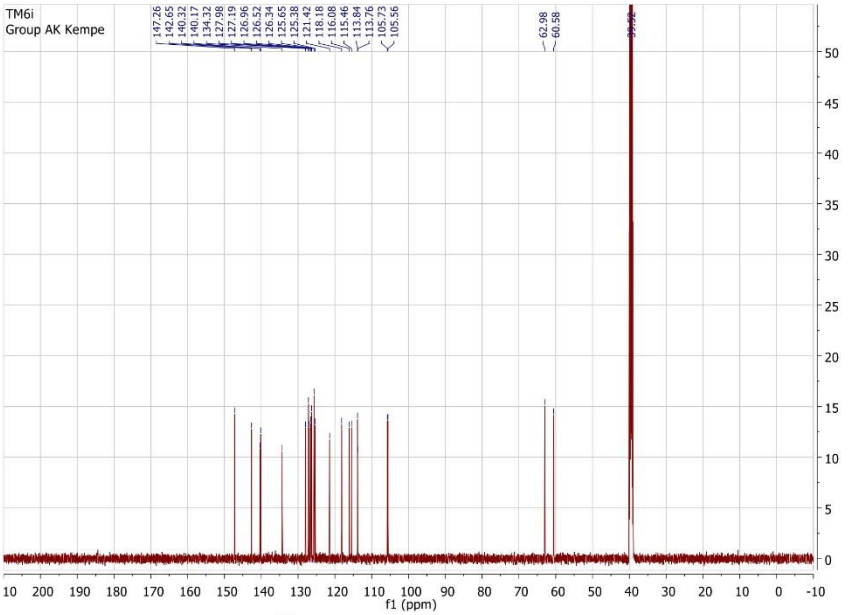


Supplementary Figure 147 ^{13}C NMR spectrum of compound **B2i**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2j

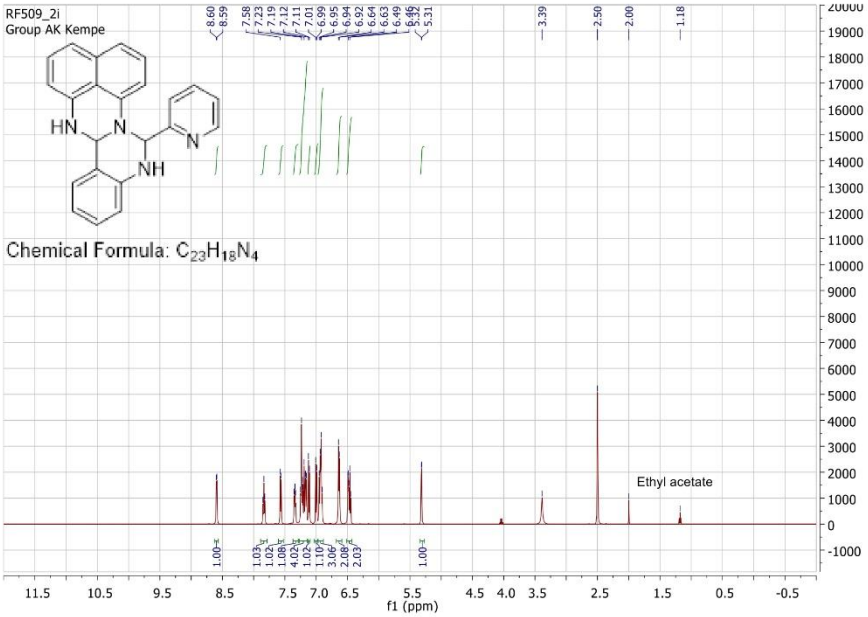


Supplementary Figure 148 ^{1}H NMR spectrum of compound **B2j**. (500 MHz, 293 K, DMSO-d_6).

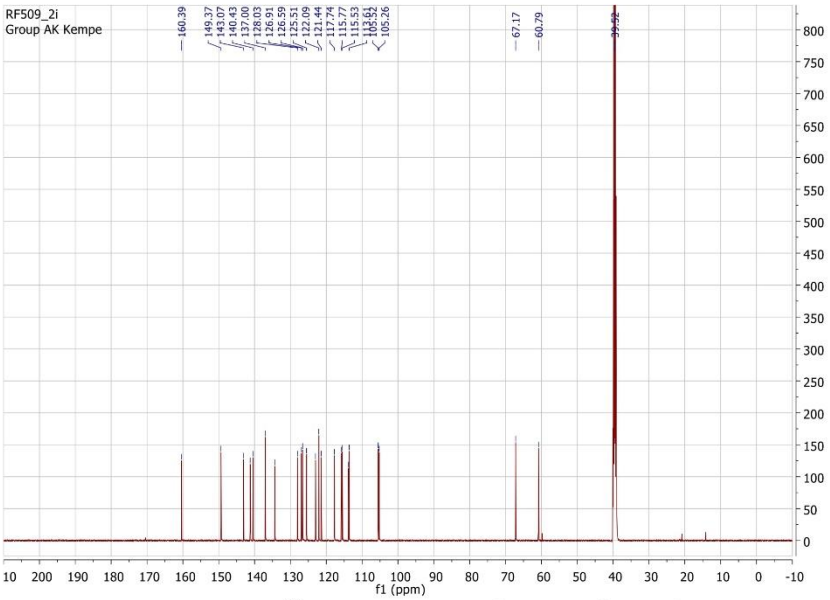


Supplementary Figure 149 ^{13}C NMR spectrum of compound **B2j**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2k

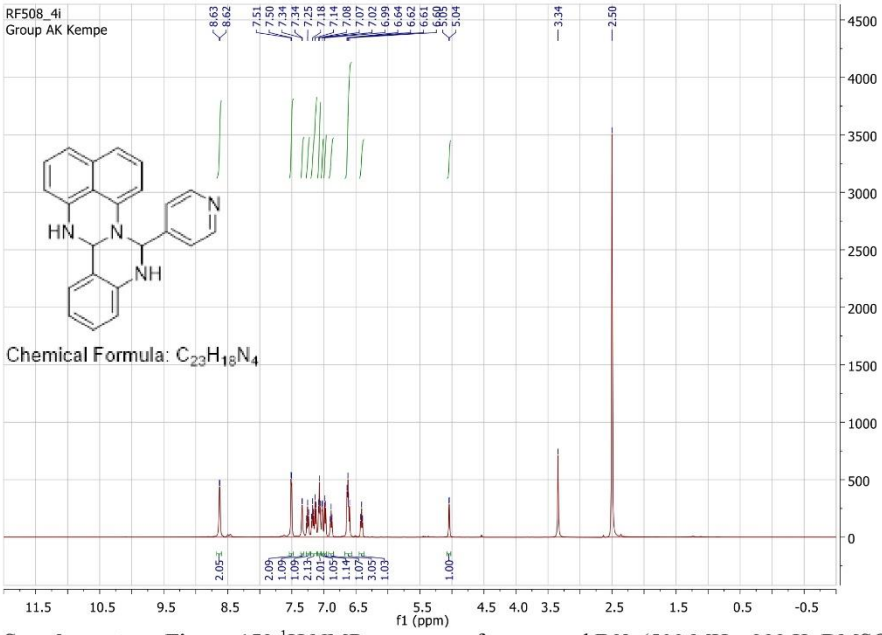


Supplementary Figure 150 ^{1}H NMR spectrum of compound **B2k**. (500 MHz, 293 K, DMSO-d_6).

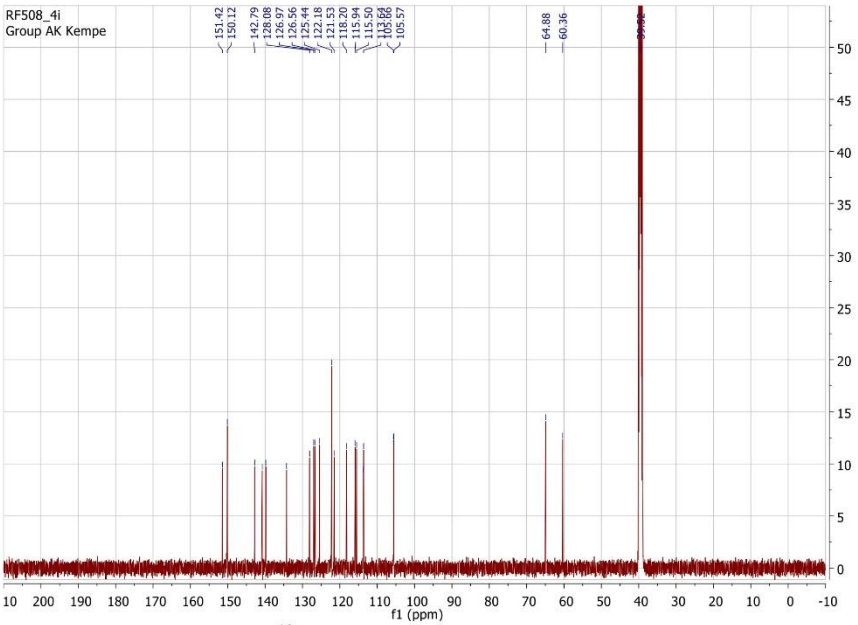


Supplementary Figure 151 ^{13}C NMR spectrum of compound **B2k**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2l

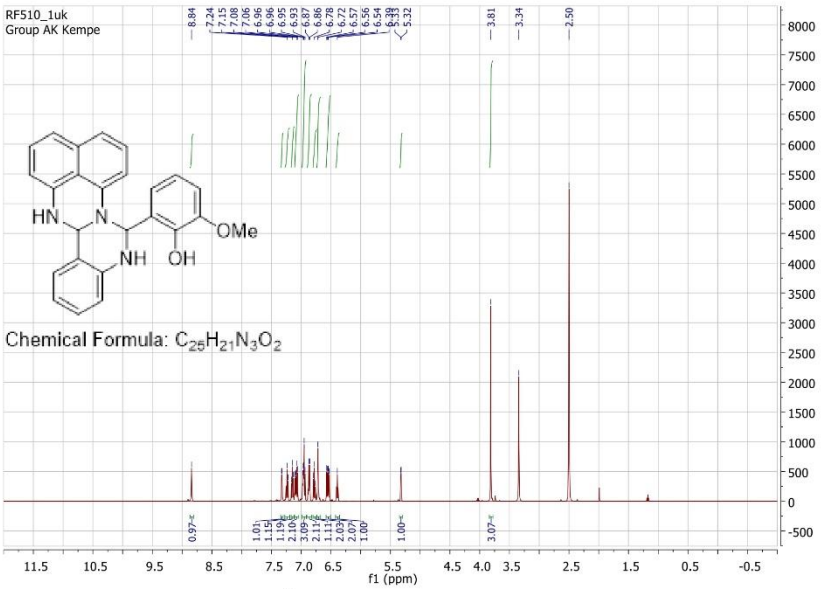


Supplementary Figure 152 ^{1}H NMR spectrum of compound **B2l**. (500 MHz, 293 K, DMSO-d_6).

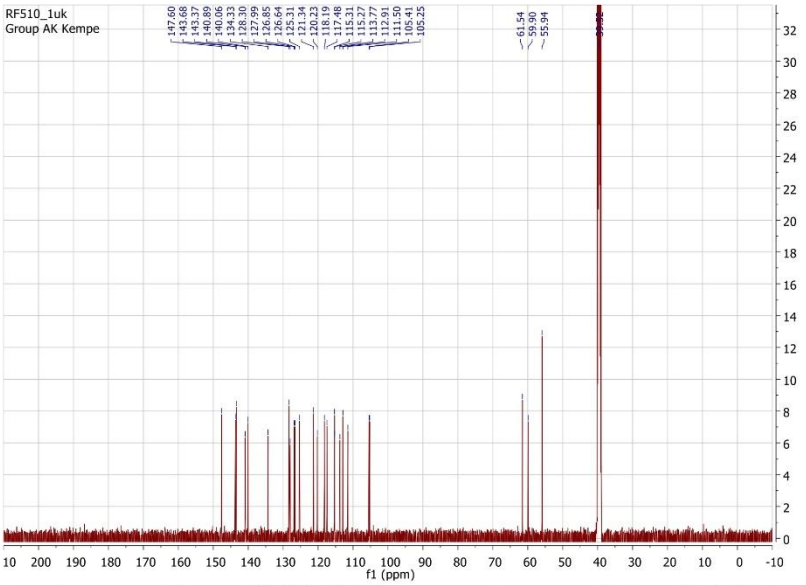


Supplementary Figure 153 ^{13}C NMR spectrum of compound **B2l**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2m

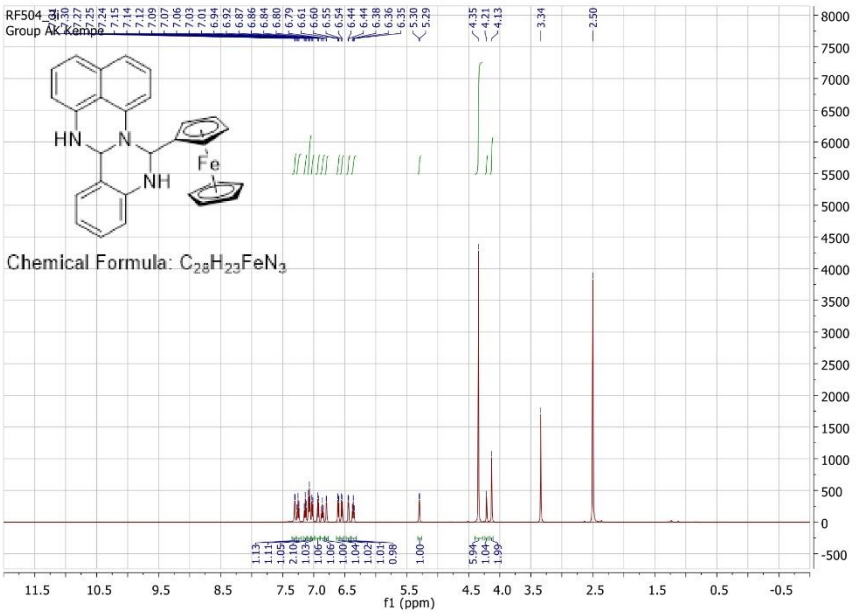


Supplementary Figure 154 ^{1}H NMR spectrum of compound **B2m**. (500 MHz, 293 K, DMSO-d_6).

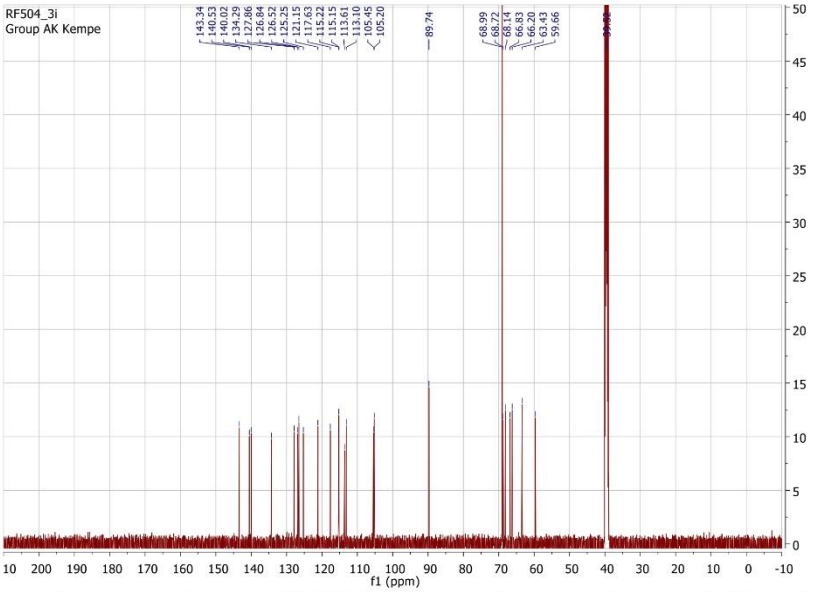


Supplementary Figure 155 ^{13}C NMR spectrum of compound **B2m**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2n

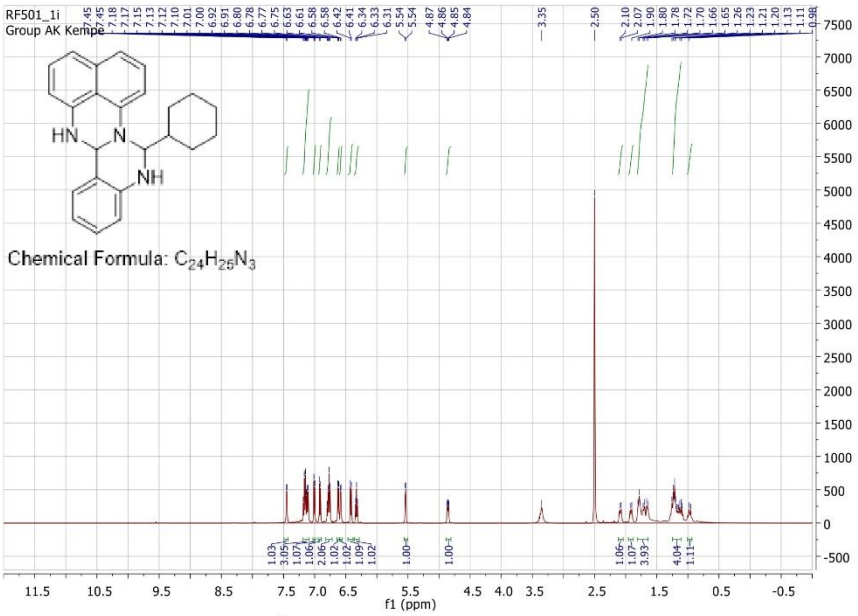


Supplementary Figure 156 ^{1}H NMR spectrum of compound **B2n**. (500 MHz, 293 K, DMSO-d_6).

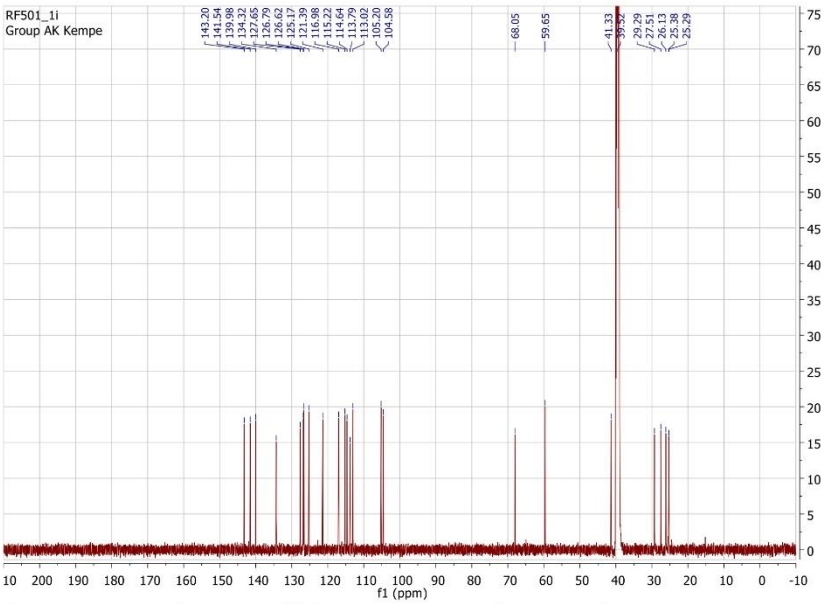


Supplementary Figure 157 ^{13}C NMR spectrum of compound **B2n**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2o

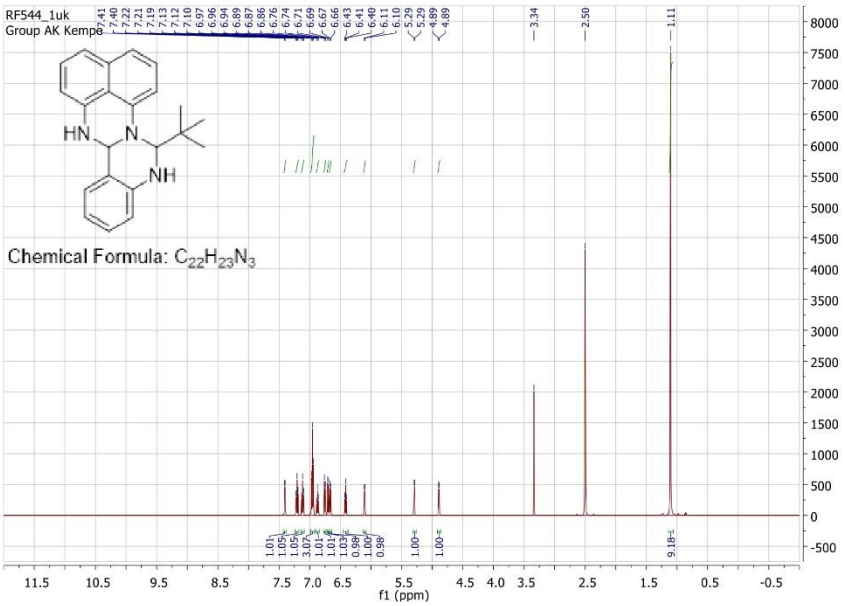


Supplementary Figure 158 ^{1}H NMR spectrum of compound **B2o**. (500 MHz, 293 K, DMSO-d_6).

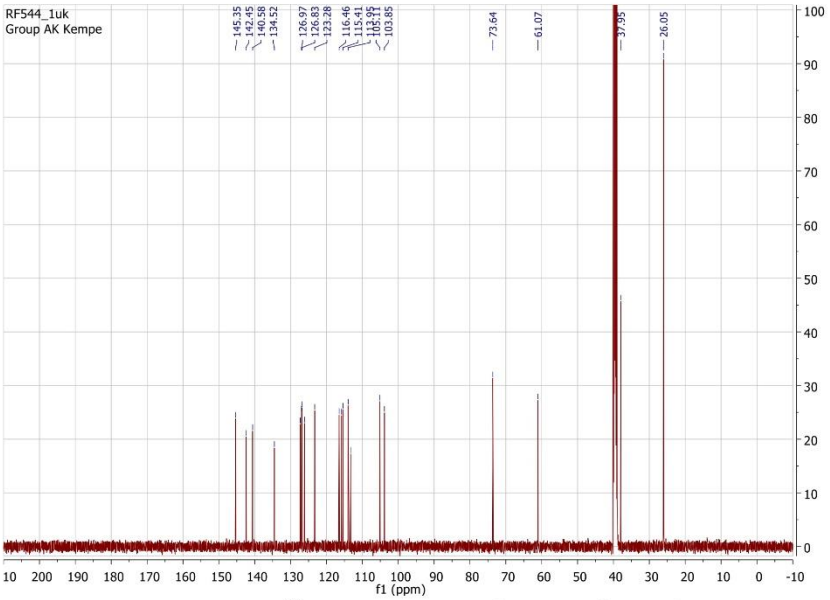


Supplementary Figure 159 ^{13}C NMR spectrum of compound **B2o**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B2p

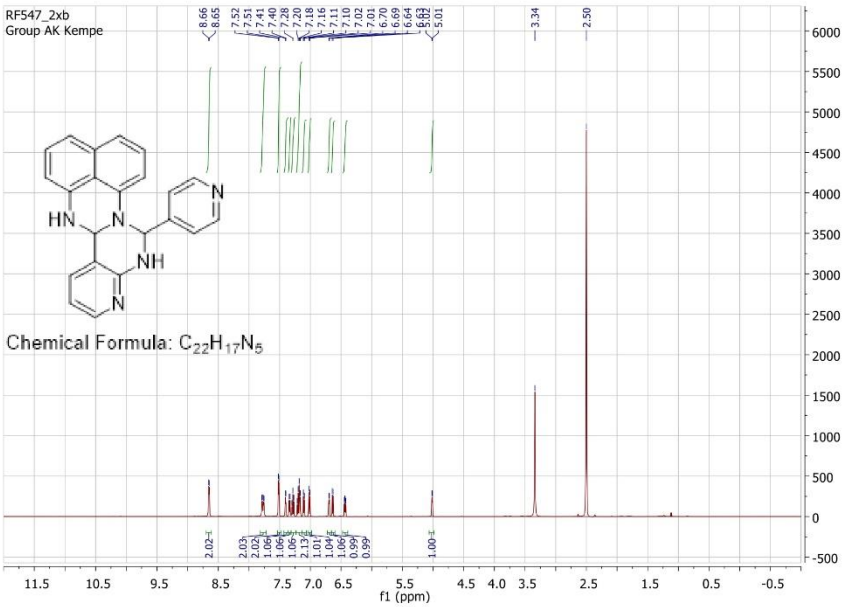


Supplementary Figure 160 ^{1}H NMR spectrum of compound **B2p**. (500 MHz, 293 K, DMSO-d_6).

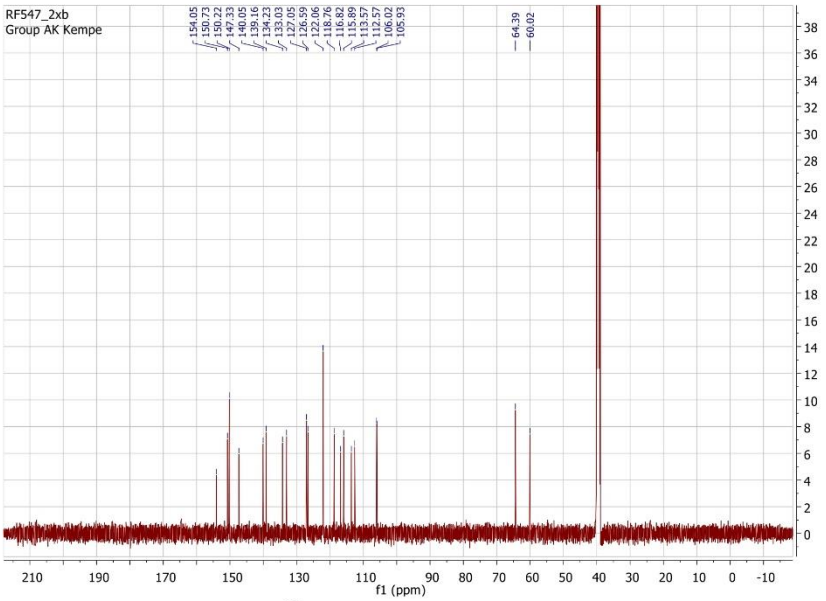


Supplementary Figure 161 ^{13}C NMR spectrum of compound **B2p**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B3a

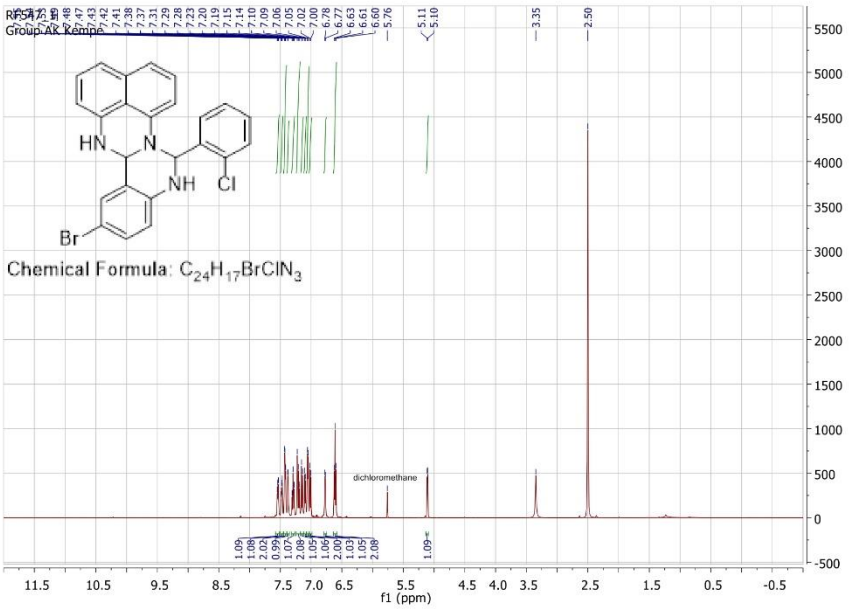


Supplementary Figure 162 ^{1}H NMR spectrum of compound **B3a**. (500 MHz, 293 K, DMSO-d_6).

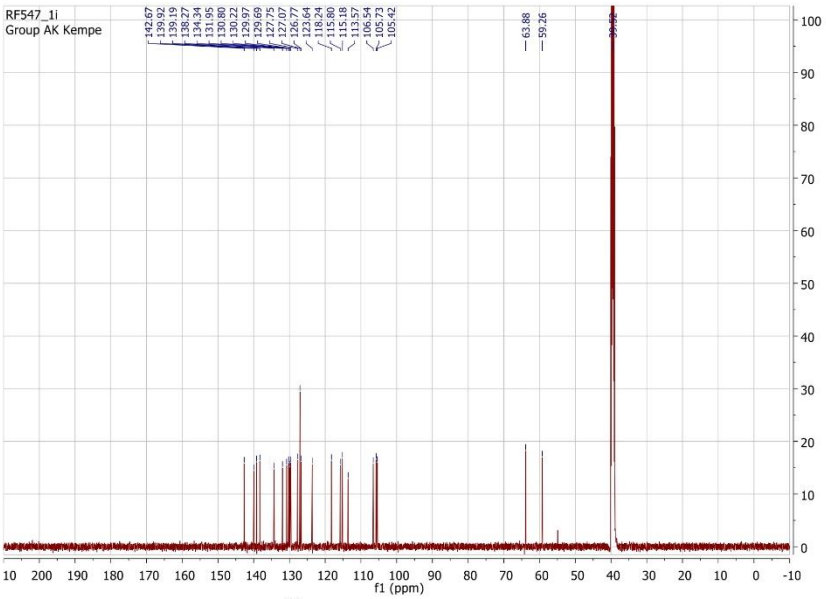


Supplementary Figure 163 ^{13}C NMR spectrum of compound **B3a**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B3b

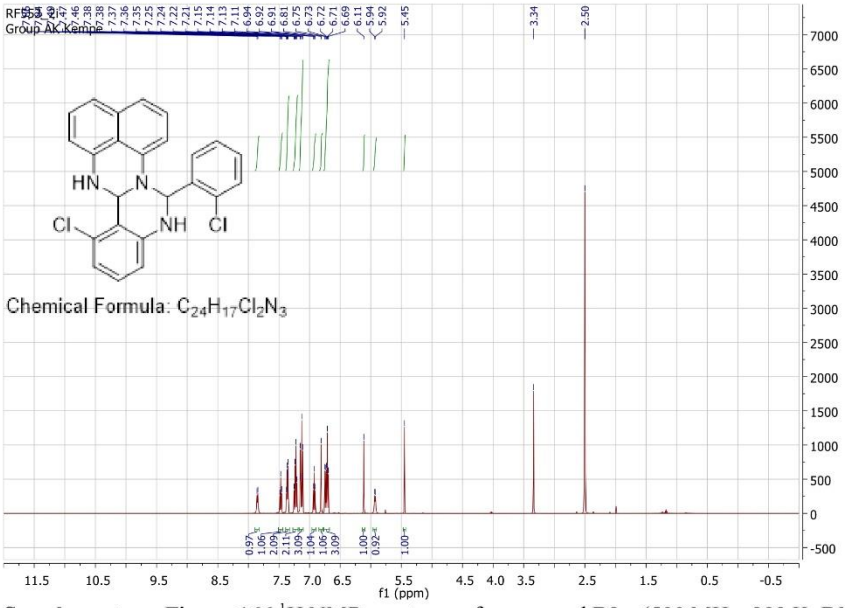


Supplementary Figure 164 ^{1}H NMR spectrum of compound **B3b**. (500 MHz, 293 K, DMSO-d_6).

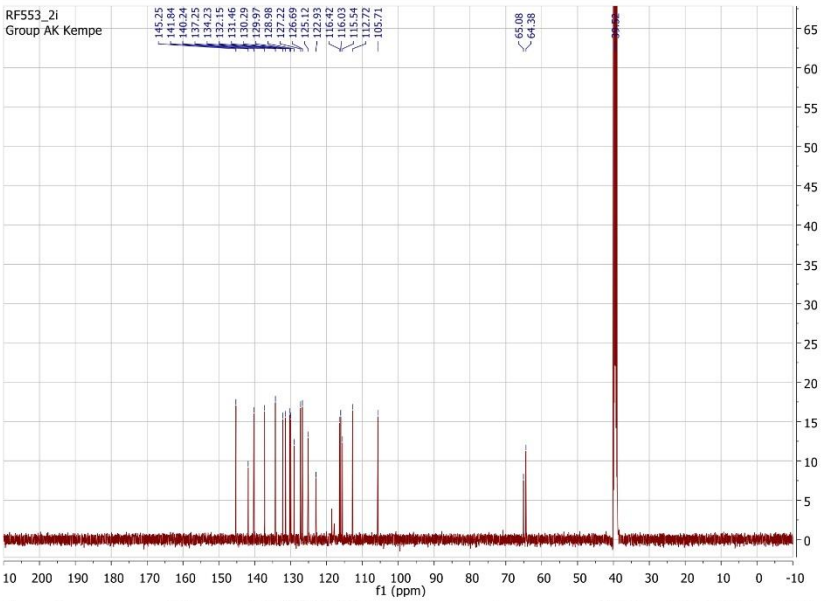


Supplementary Figure 165 ^{13}C NMR spectrum of compound **B3b**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B3c

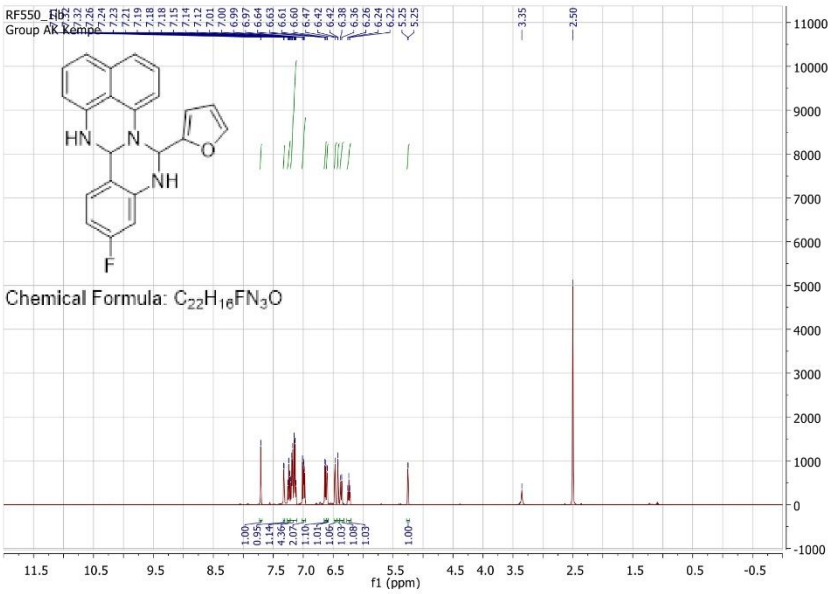


Supplementary Figure 166 ^{1}H NMR spectrum of compound **B3c**. (500 MHz, 293 K, DMSO-d_6).

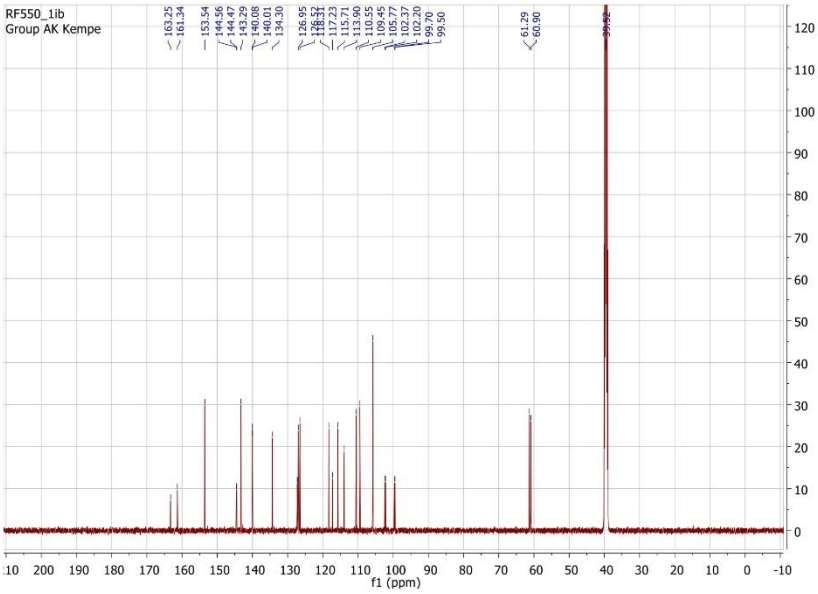


Supplementary Figure 167 ^{13}C NMR spectrum of compound **B3c**. (125 MHz, 293 K, DMSO-d_6).

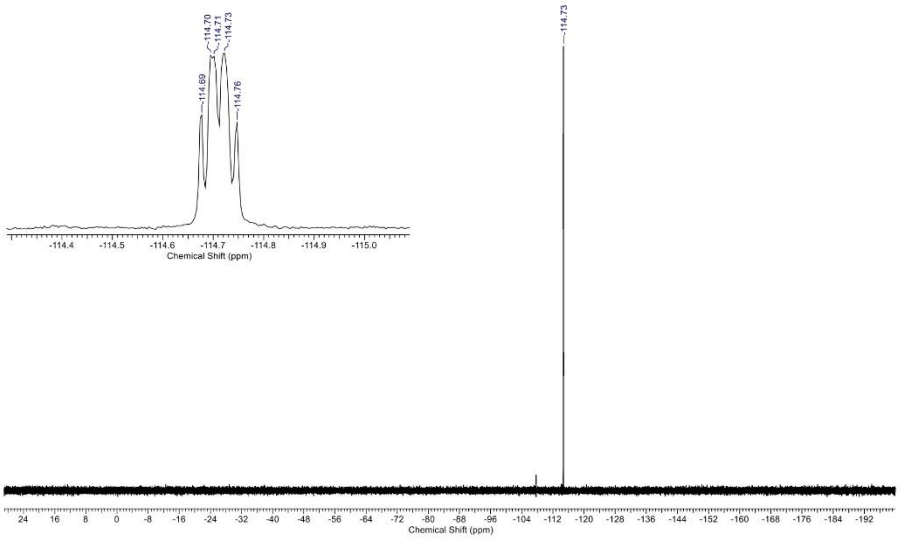
NMR spectra of B3d



Supplementary Figure 168 ^{1}H NMR spectrum of compound **B3d**. (500 MHz, 293 K, DMSO-d_6).

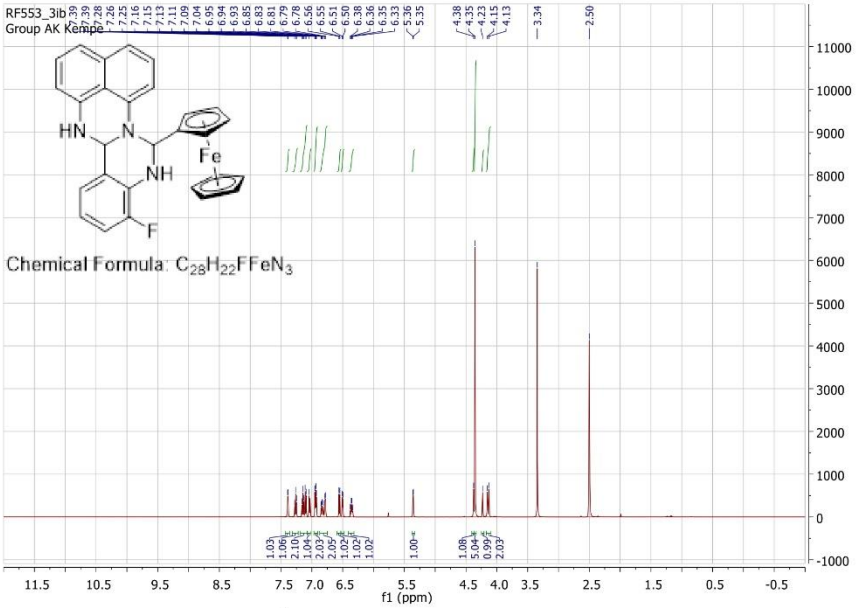


Supplementary Figure 169 ^{13}C NMR spectrum of compound **B3d**. (125 MHz, 293 K, DMSO-d_6).

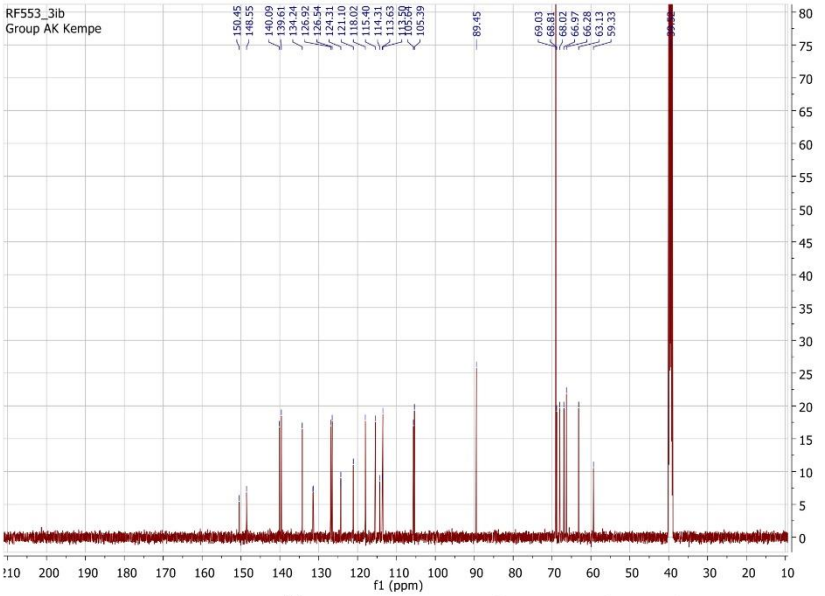


Supplementary Figure 170 ^{19}F NMR spectrum of compound **B3d**. (376 MHz, 293 K, DMSO-d_6).

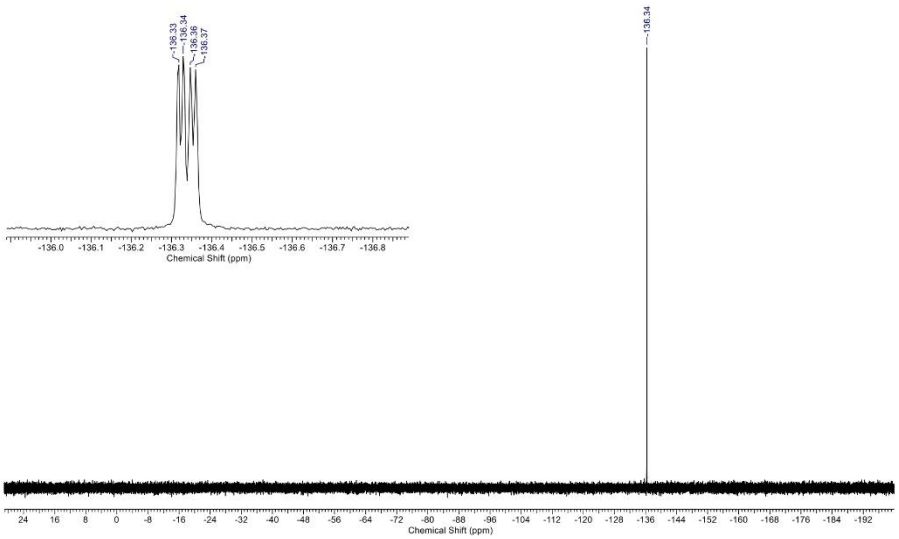
NMR spectra of B3e



Supplementary Figure 171 ^{1}H NMR spectrum of compound **B3e**. (500 MHz, 293 K, DMSO-d_6).

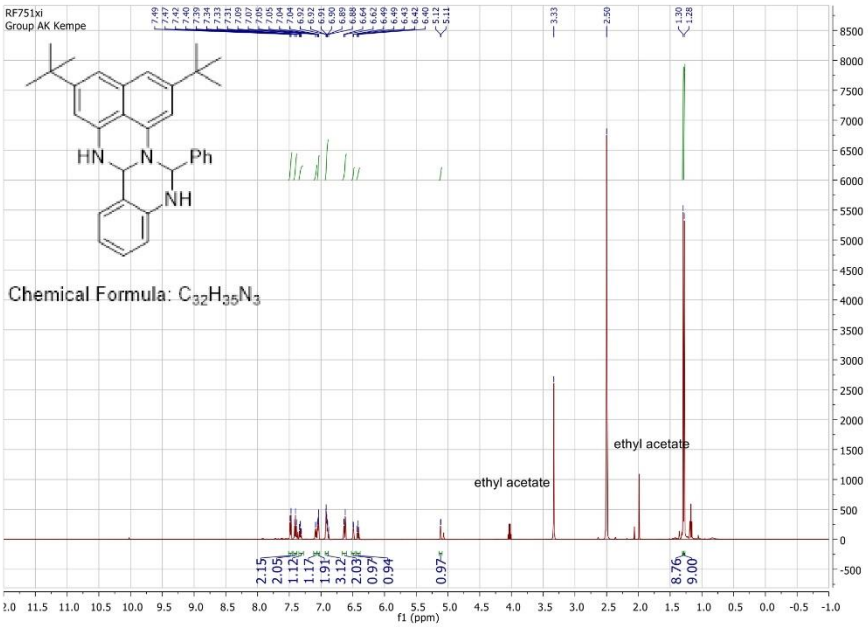


Supplementary Figure 172 ^{13}C NMR spectrum of compound **B3e**. (125 MHz, 293 K, DMSO-d_6).

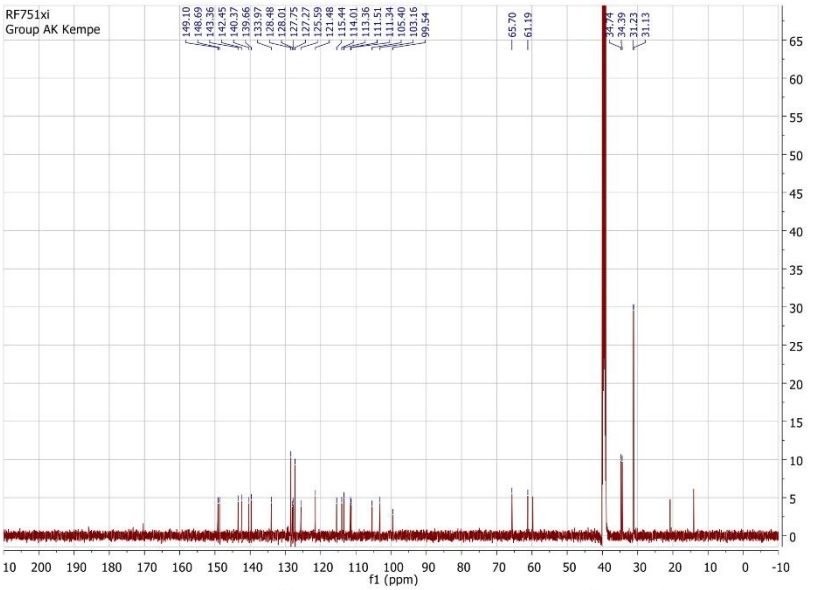


Supplementary Figure 173 ^{19}F NMR spectrum of compound **B3e**. (376 MHz, 293 K, DMSO-d_6).

NMR spectra of B4a

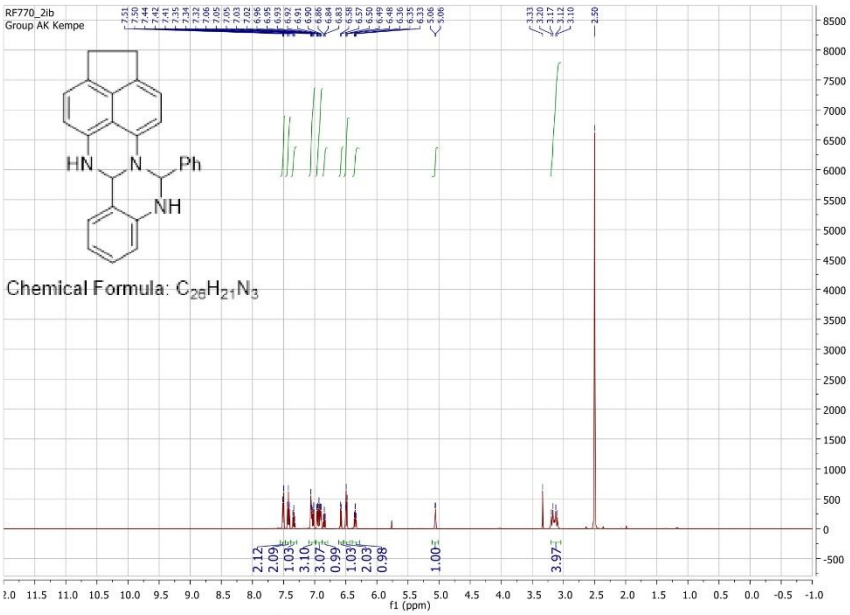


Supplementary Figure 174 ^{1}H NMR spectrum of compound **B4a**. (500 MHz, 293 K, DMSO-d_6).

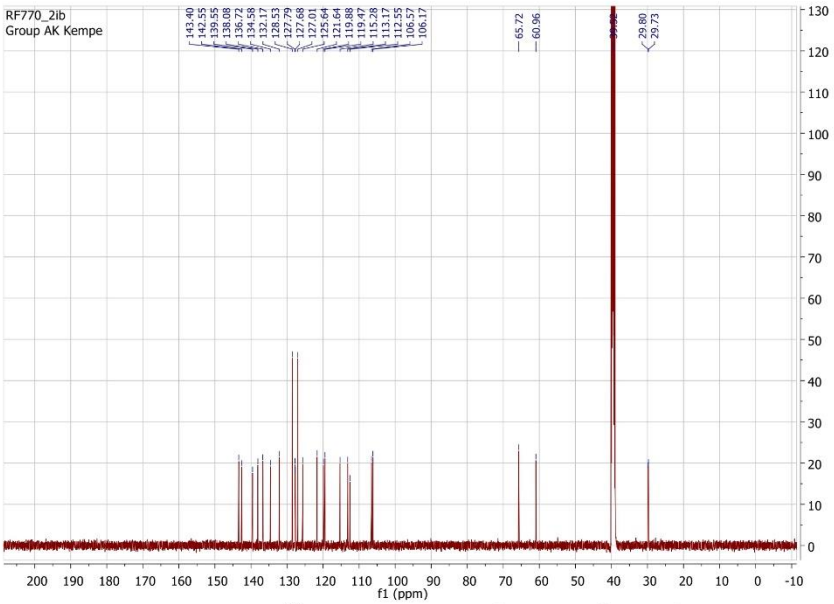


Supplementary Figure 175 ^{13}C NMR spectrum of compound **B4a**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B4b

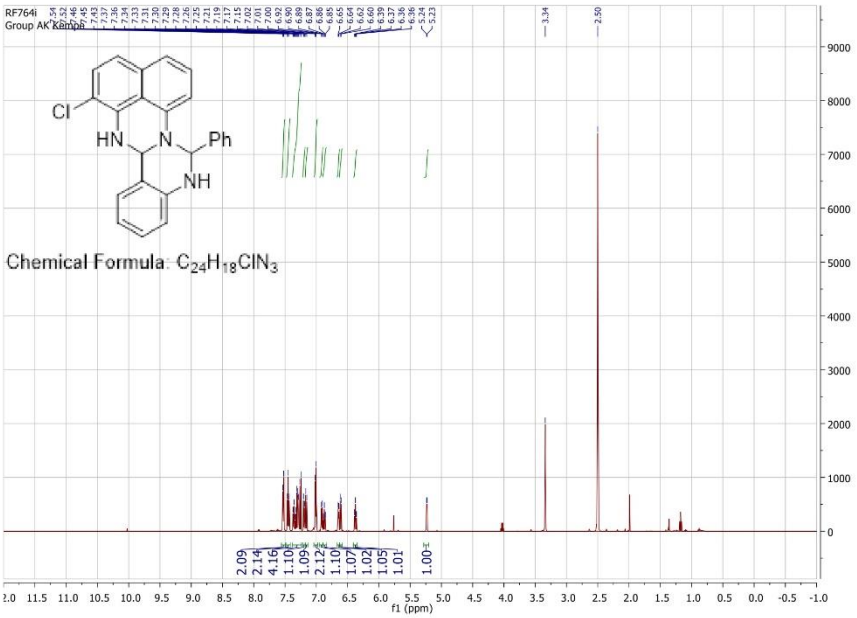


Supplementary Figure 176 ^{1}H NMR spectrum of compound **B4b**. (500 MHz, 293 K, DMSO-d_6).

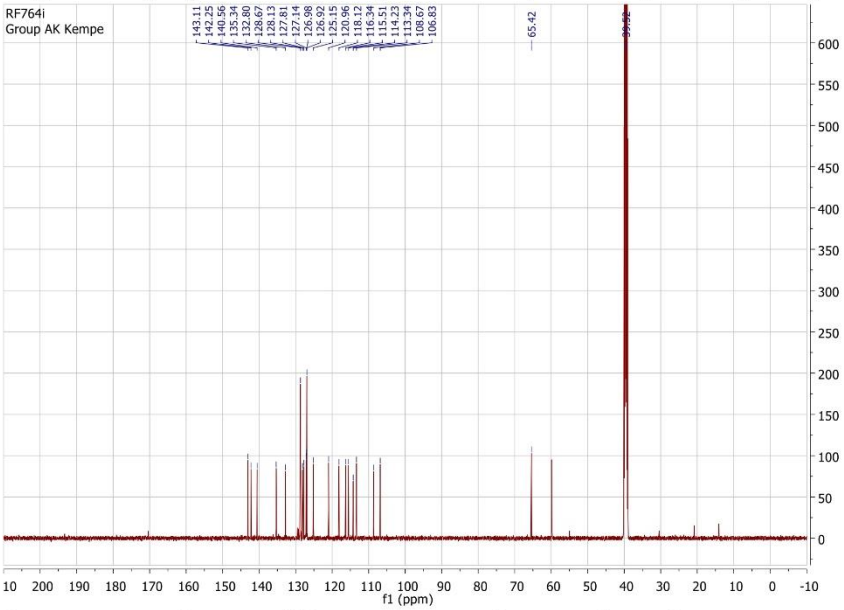


Supplementary Figure 177 ^{13}C NMR spectrum of compound **B4b**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B4c

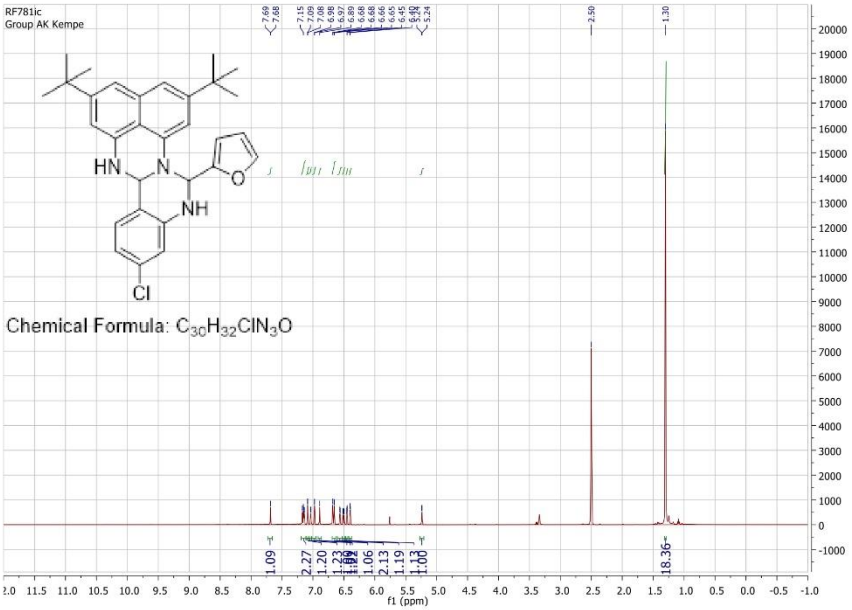


Supplementary Figure 178 ^{1}H NMR spectrum of compound **B4c**. (500 MHz, 293 K, DMSO-d_6).

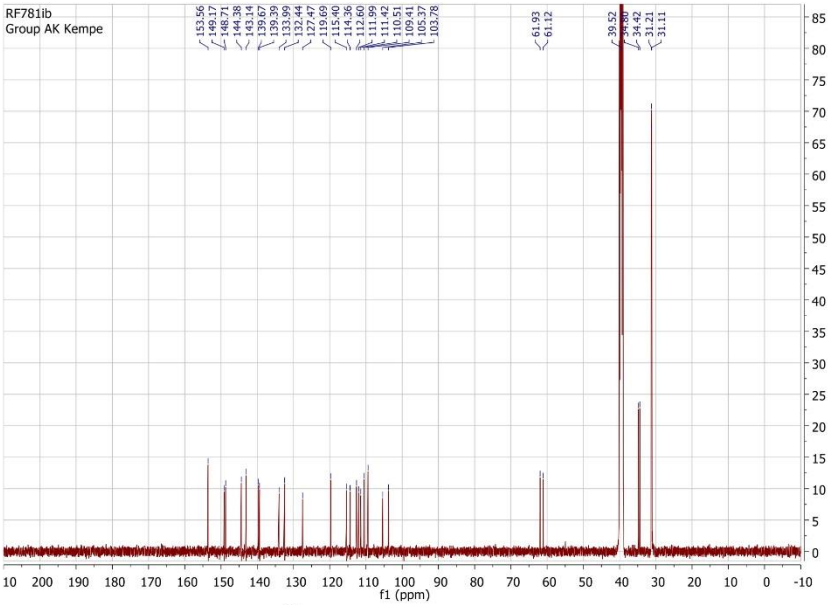


Supplementary Figure 179 ^{13}C NMR spectrum of compound **B4c**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B5a

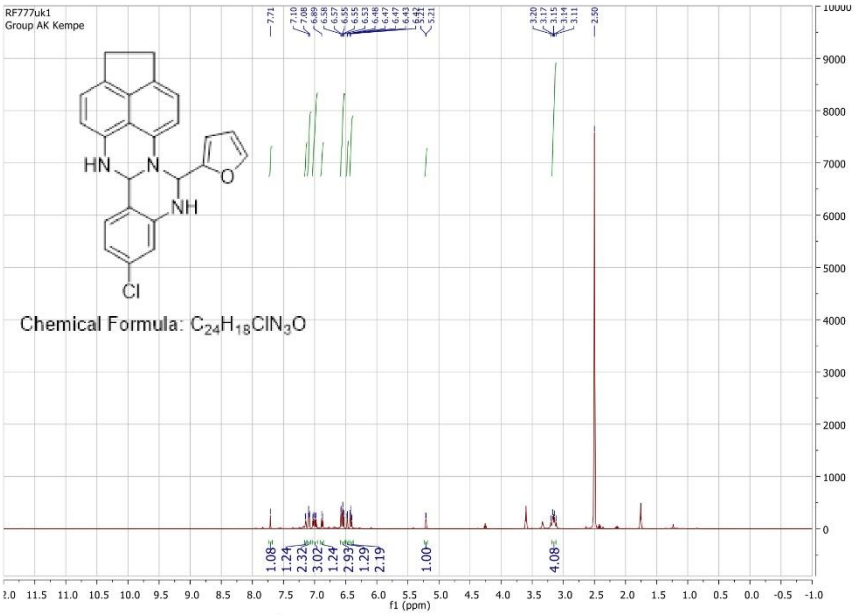


Supplementary Figure 180 ^{1}H NMR spectrum of compound **B5a**. (500 MHz, 293 K, DMSO-d_6).

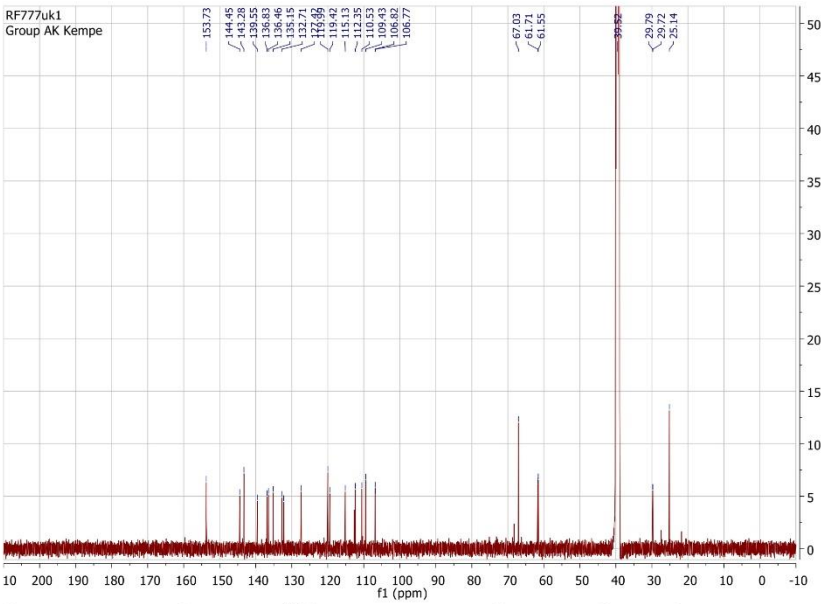


Supplementary Figure 181 ^{13}C NMR spectrum of compound **B5a**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B5b

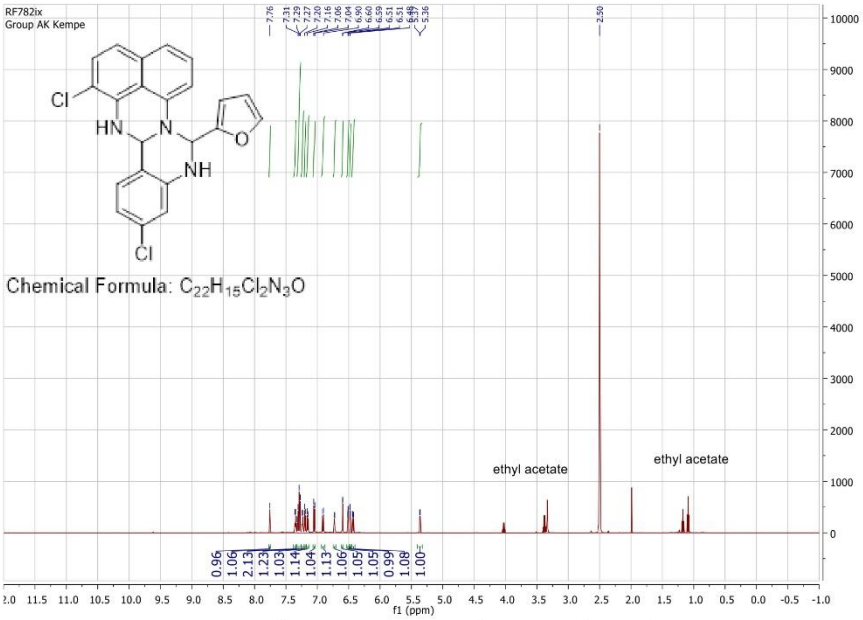


Supplementary Figure 182 ^{1}H NMR spectrum of compound **B5b**. (500 MHz, 293 K, DMSO-d_6).

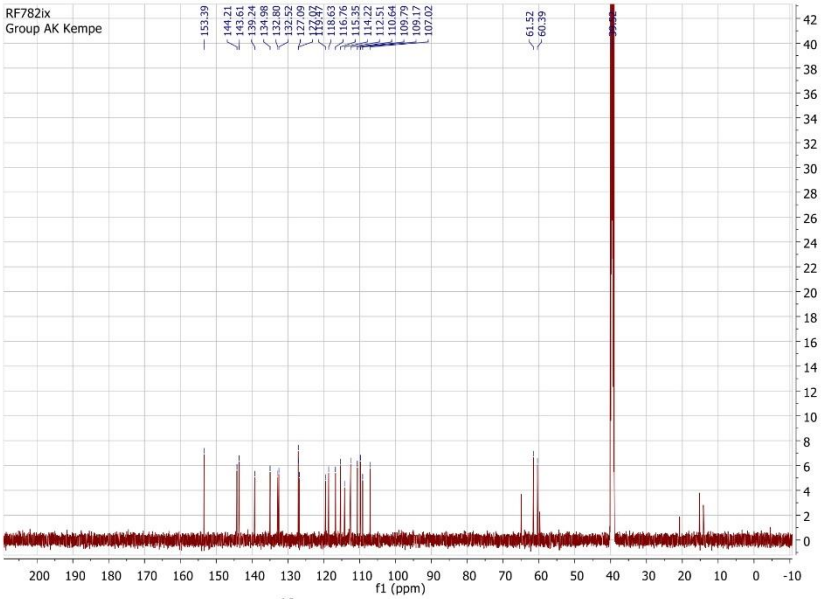


Supplementary Figure 183 ^{13}C NMR spectrum of compound **B5b**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B5c

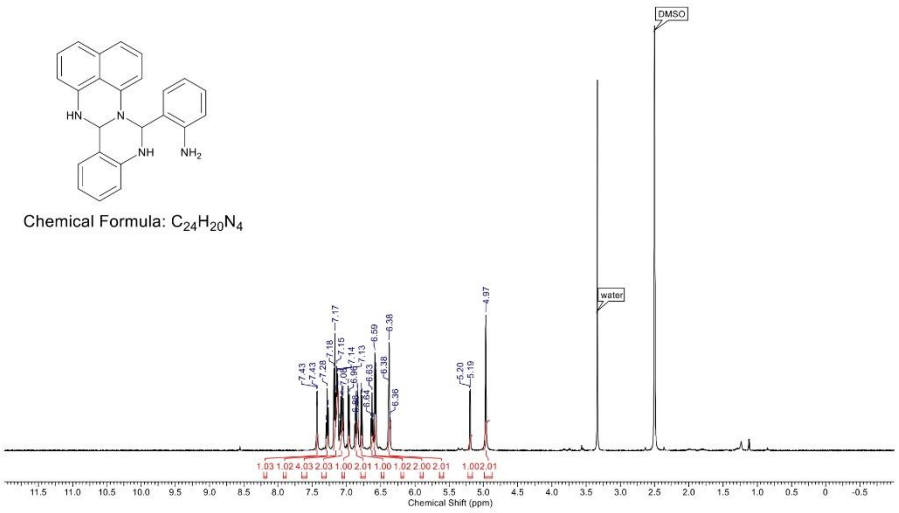


Supplementary Figure 184 ^{1}H NMR spectrum of compound **B5c**. (500 MHz, 293 K, DMSO-d_6).

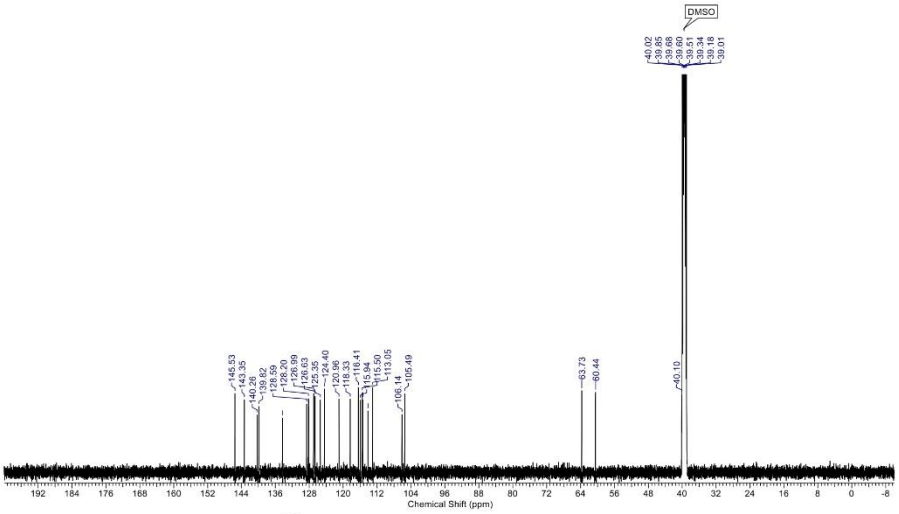


Supplementary Figure 185 ^{13}C NMR spectrum of compound **B5c**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B6a

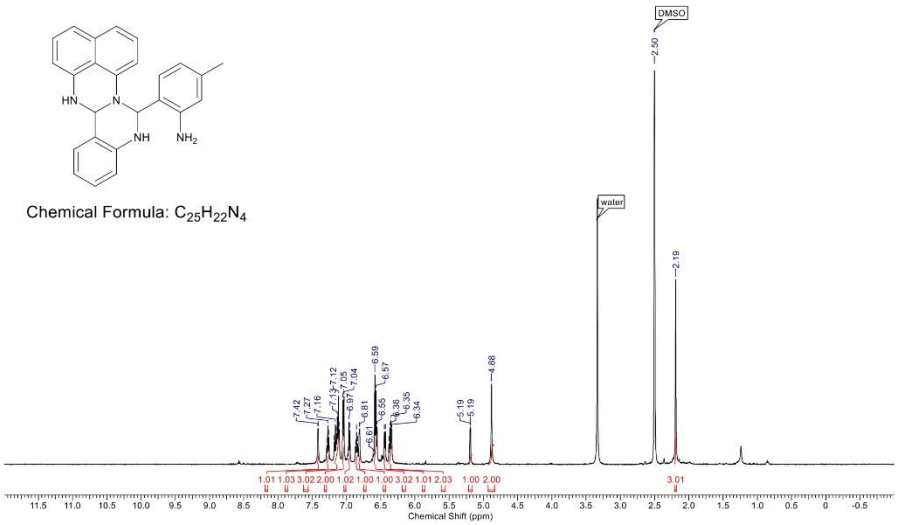


Supplementary Figure 186 ^{1}H NMR spectrum of compound **B6a**. (500 MHz, 293 K, DMSO-d_6).

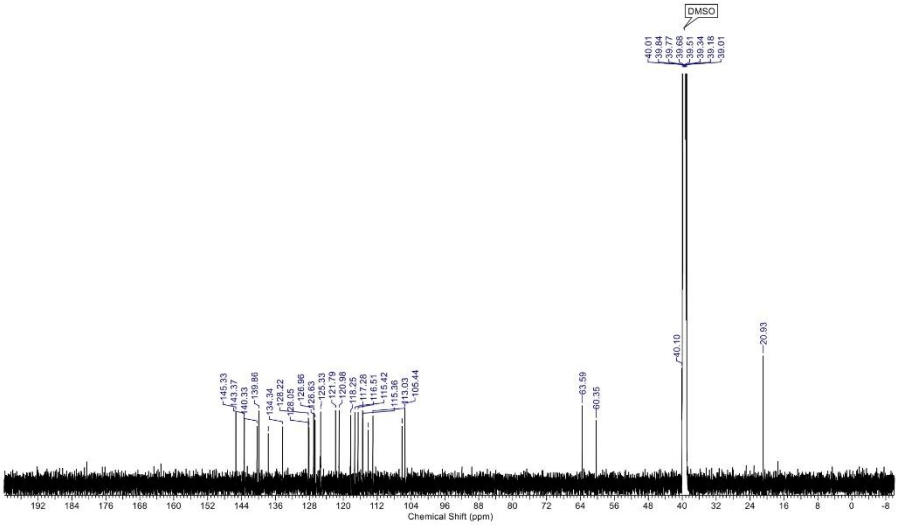


Supplementary Figure 187 ^{13}C NMR spectrum of compound **B6a**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B6b

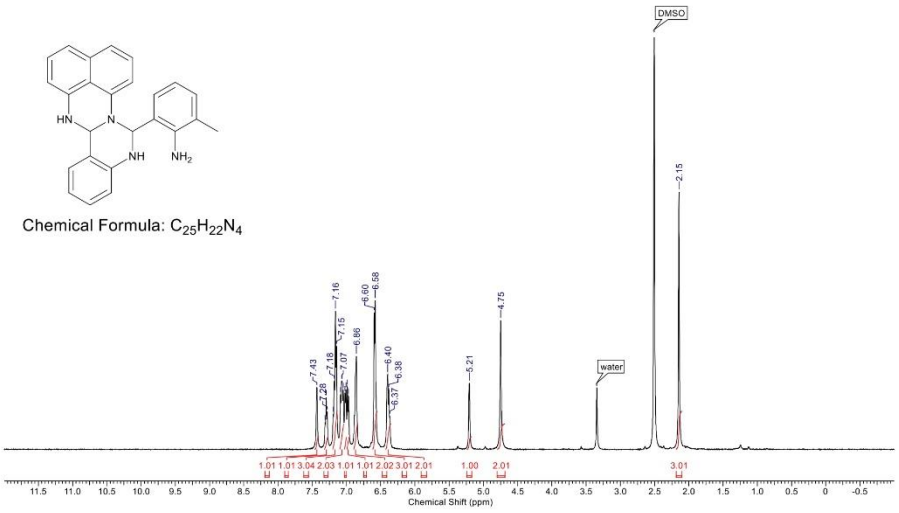


Supplementary Figure 188 ^{1}H NMR spectrum of compound **B6b**. (500 MHz, 293 K, DMSO-d_6).

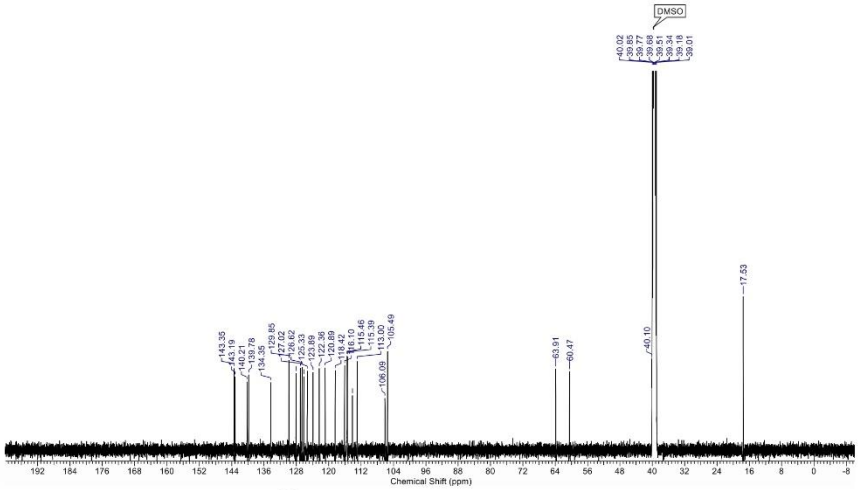


Supplementary Figure 189 ^{13}C NMR spectrum of compound **B6b**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of B6c

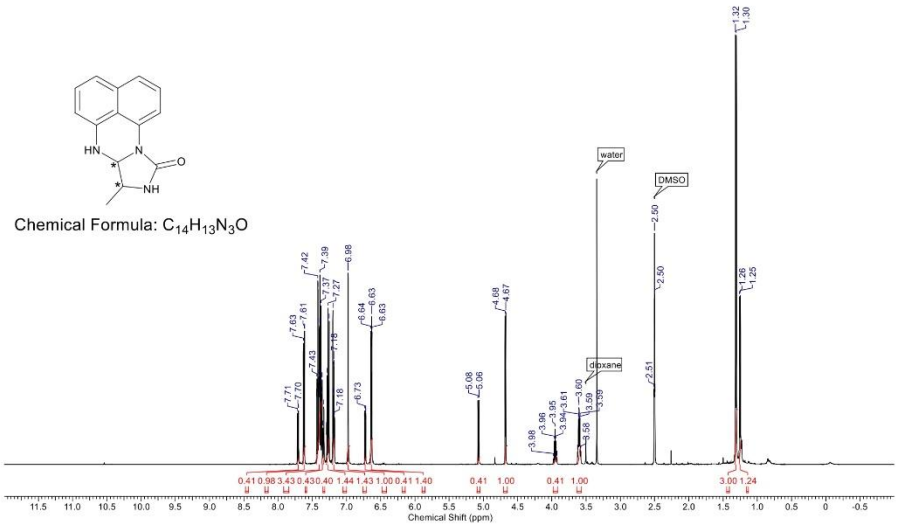


Supplementary Figure 190 ^{1}H NMR spectrum of compound **B6c**. (500 MHz, 293 K, DMSO-d_6).

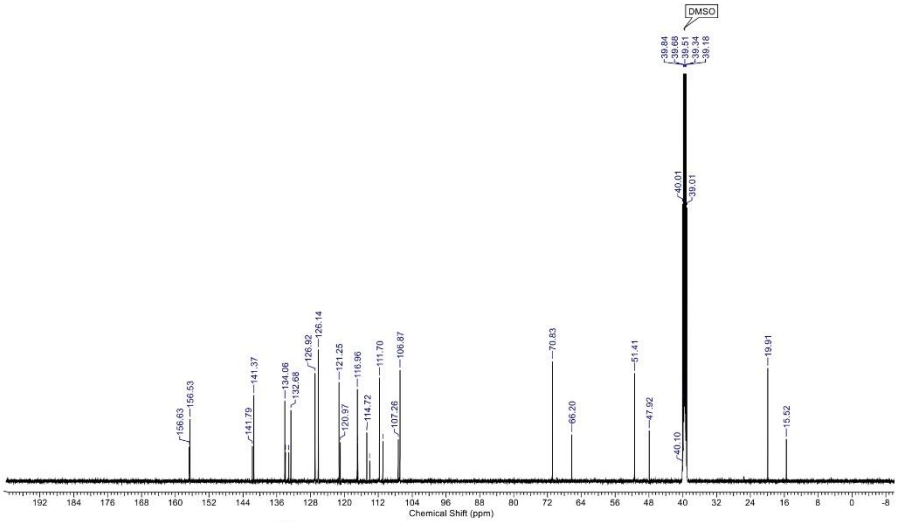


Supplementary Figure 191 ^{13}C NMR spectrum of compound **B6c**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of C1



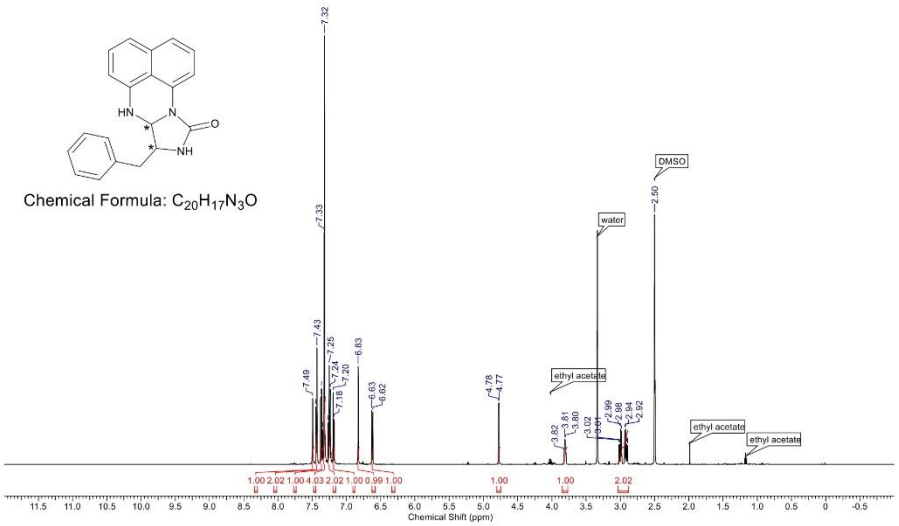
Supplementary Figure 192 ^{1}H NMR spectrum of compound **C1**. (500 MHz, 293 K, DMSO-d_6).



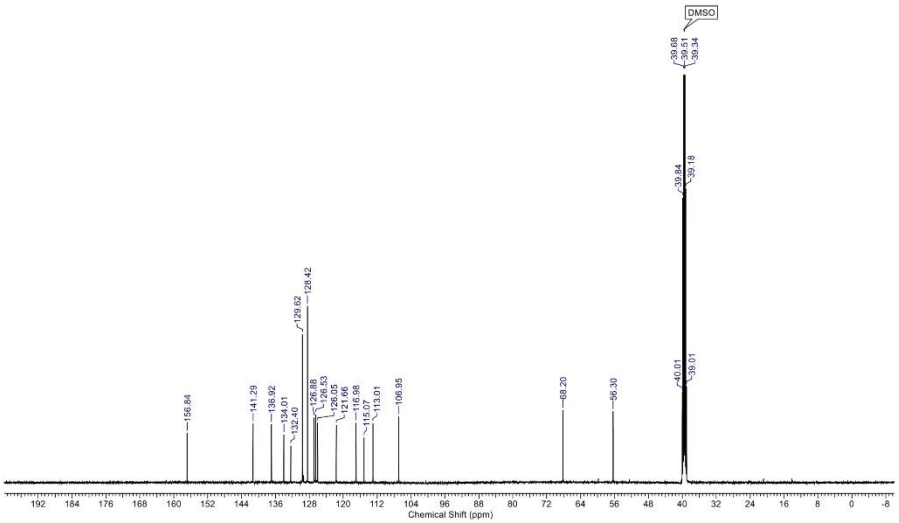
Supplementary Figure 193 ^{13}C NMR spectrum of compound **C1**. (125 MHz, 293 K, DMSO-d_6).

NMR spectra of C2

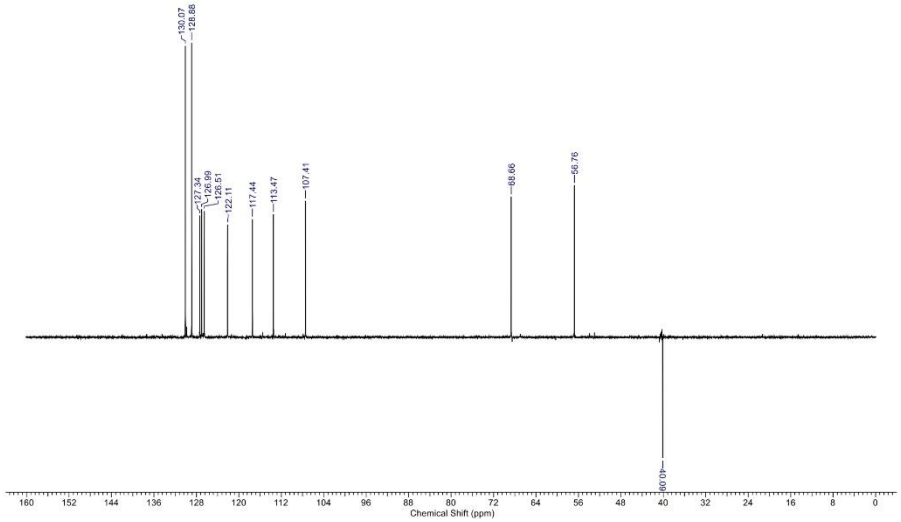
Main isomer of **C2**:



Supplementary Figure 194 ^{1}H NMR spectrum of the main isomer of compound **C2**. (500 MHz, 293 K, DMSO-d_6).

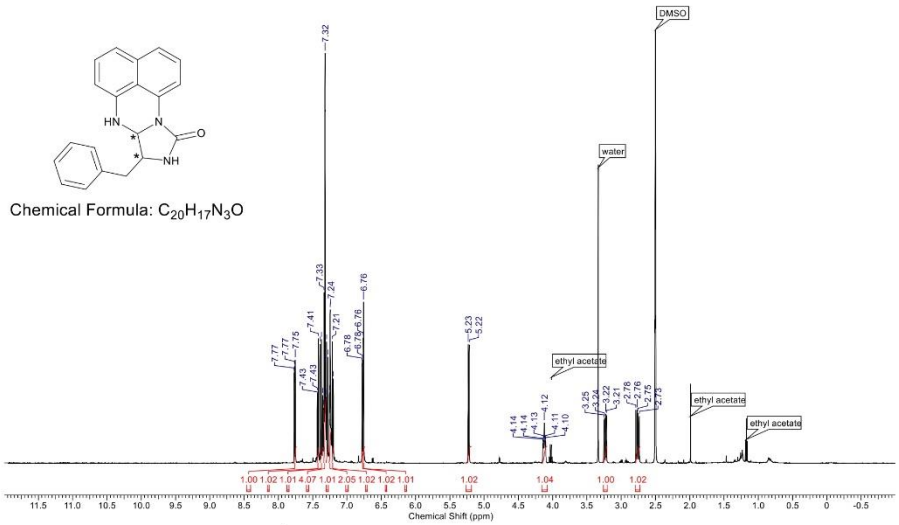


Supplementary Figure 195 ^{13}C NMR spectrum of the main isomer of compound **C2**. (125 MHz, 293 K, DMSO-d_6).

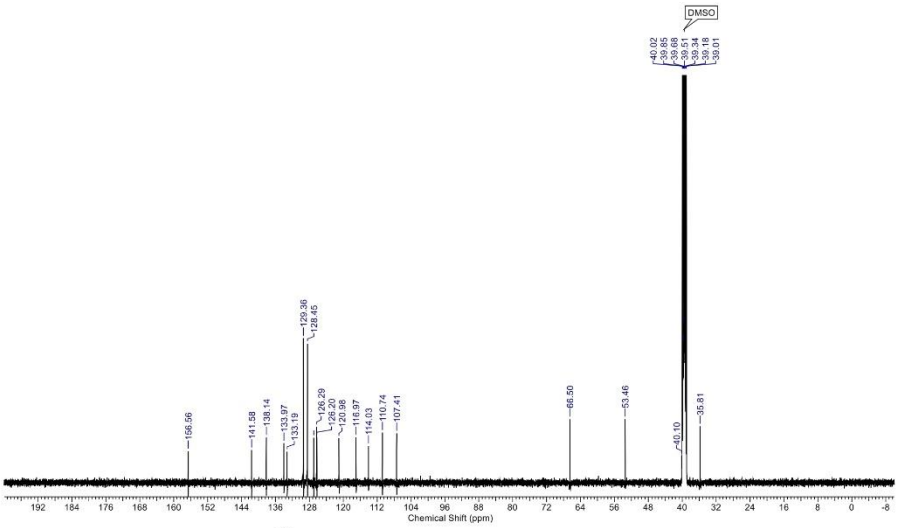


Supplementary Figure 196 DEPT 135 NMR spectrum of the main isomer of compound **C2**. (500 MHz, 293 K, DMSO-d_6).

Minor isomer of **C2**:



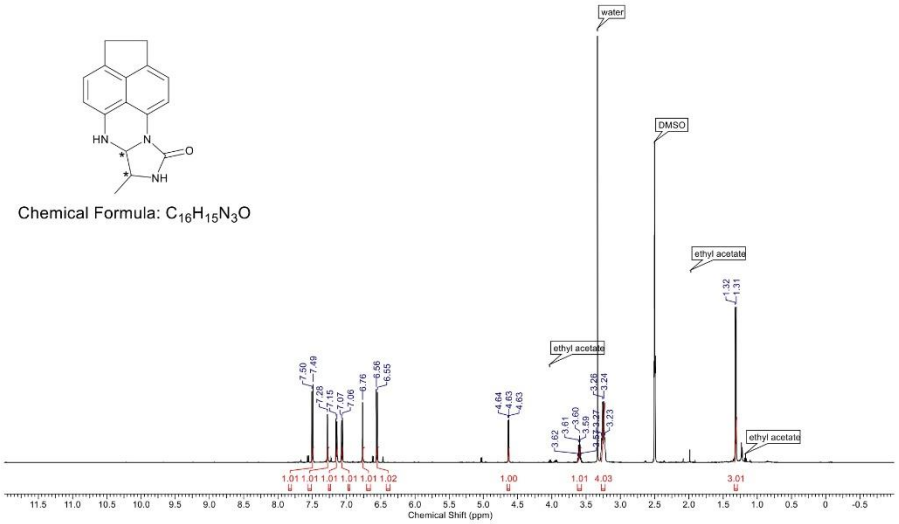
Supplementary Figure 197 ^{1}H NMR spectrum of the minor isomer of compound **C2**. (500 MHz, 293 K, DMSO-d_6).



Supplementary Figure 198 ^{13}C NMR spectrum of the minor isomer of compound **C2**. (125 MHz, 293 K, DMSO-d_6).

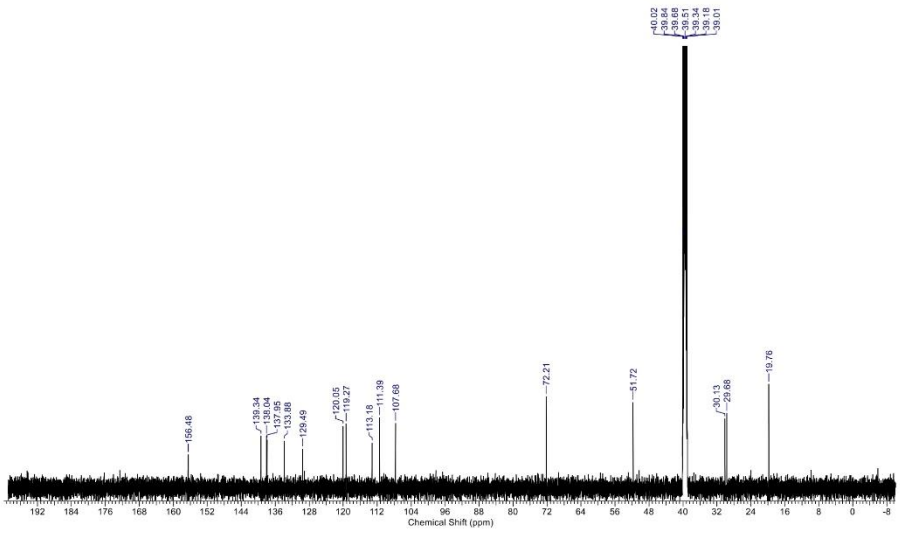
NMR spectra of C3

Main isomer of **C3**:



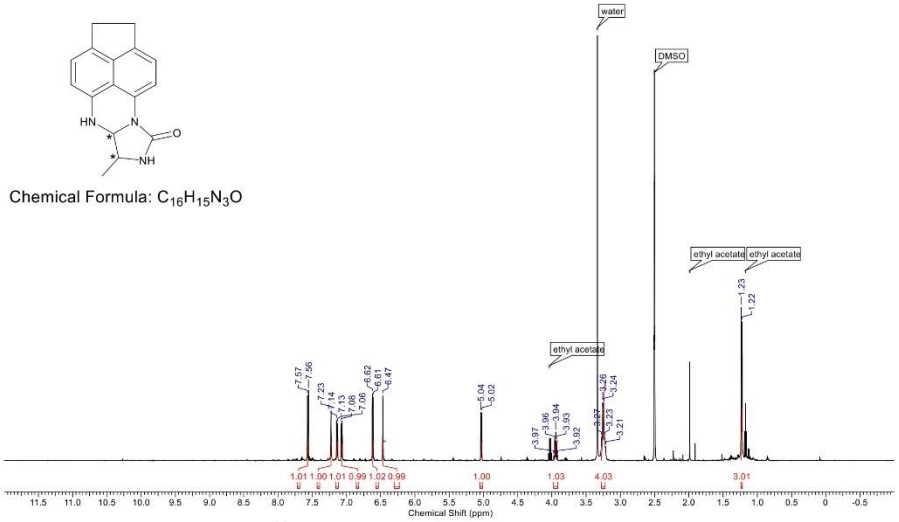
Chemical Formula: $C_{16}H_{15}N_3O$

Supplementary Figure 199 ^{1}H NMR spectrum of the main isomer of compound **C3**. (500 MHz, 293 K, DMSO-d_6).

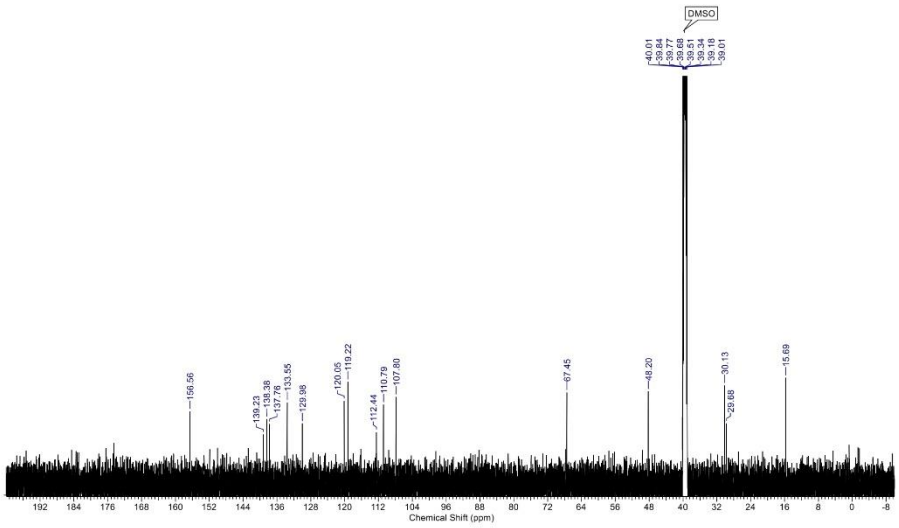


Supplementary Figure 200 ^{13}C NMR spectrum of the main isomer of compound **C3**. (125 MHz, 293 K, DMSO-d_6).

Minor isomer of **C3**:



Supplementary Figure 201 ^{1}H NMR spectrum of the minor isomer of compound **C3**. (500 MHz, 293 K, DMSO-d_6).



Supplementary Figure 202 ^{13}C NMR spectrum of the minor isomer of compound **C3**. (125 MHz, 293 K, DMSO-d_6).

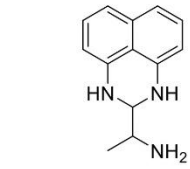
15. LC-HRMS spectra

General conditions

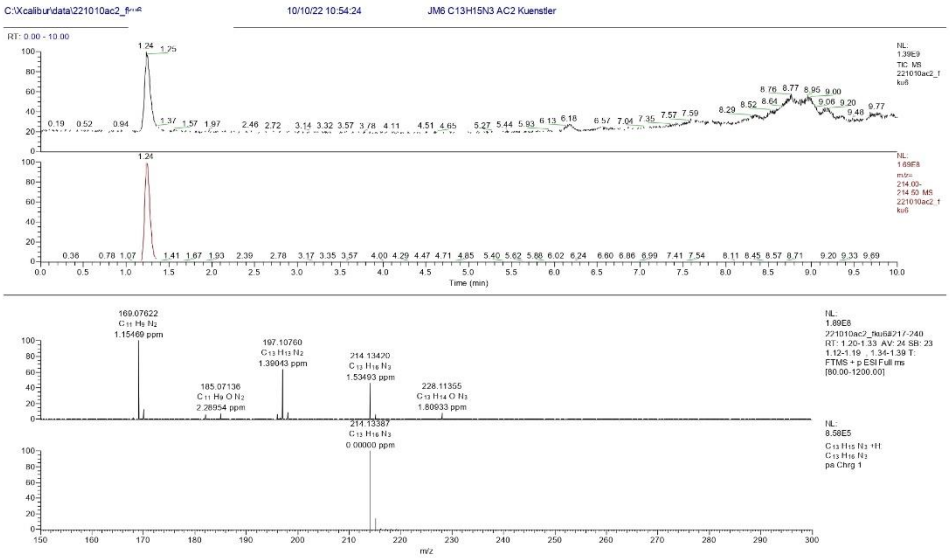
Liquid chromatography-high resolution mass spectra (LC-HRMS) were obtained from a Thermo Fisher scientific Q-Exactive instrument with a hybrid quadrupole orbitrap analyser in ESI+ mode. For liquid chromatography a Luna Omega PS C18 (100x2.1 mm, 1.6 µm) column was used with a solvent gradient from 30:70 MeCN/water to 90:10 MeCN/water. The samples were dissolved in ethanol or DMSO.

Due to the air sensitivity of most substances and specimen preparation under air the formation of nitrosamines occurred after short period of time, which is visible in traces in some of the spectra.

LC-HRMS of A25

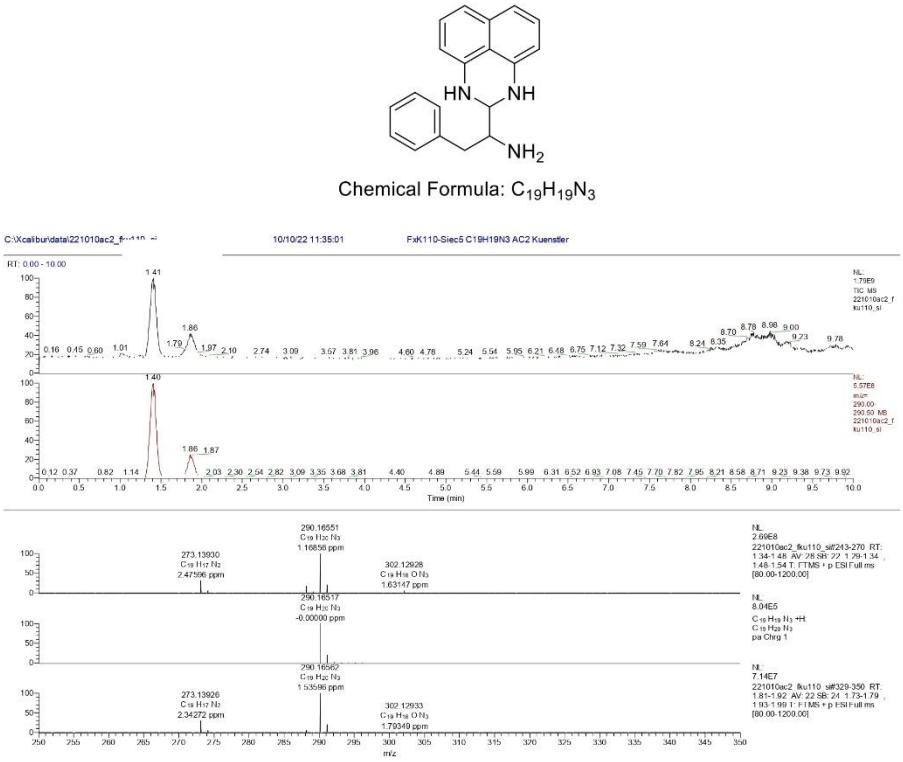


Chemical Formula: $C_{13}H_{15}N_3$



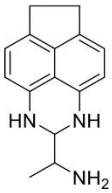
Supplementary Figure 203 LC-HRMS spectrum of compound **A25**.

LC-HRMS of A26

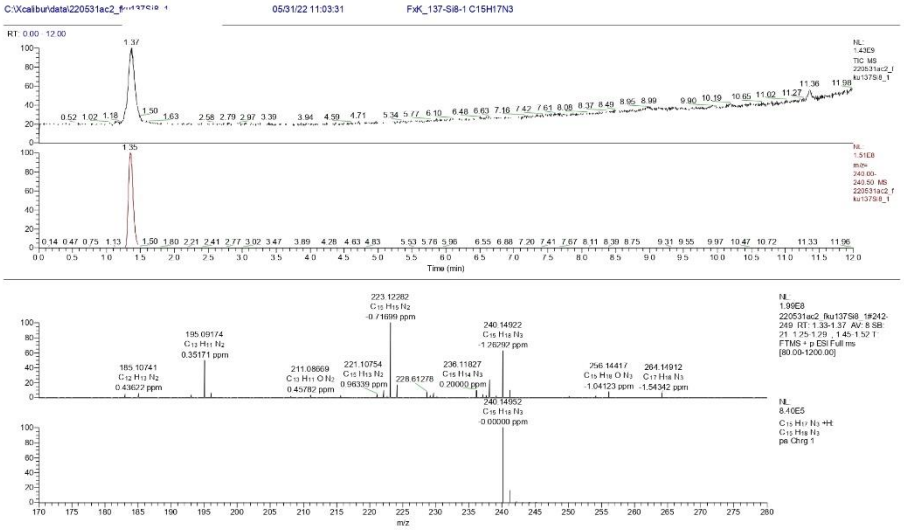


Supplementary Figure 204 LC-HRMS spectrum of compound **A26**.

LC-HRMS of A27

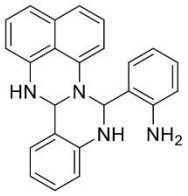


Chemical Formula: $C_{15}H_{17}N_3$

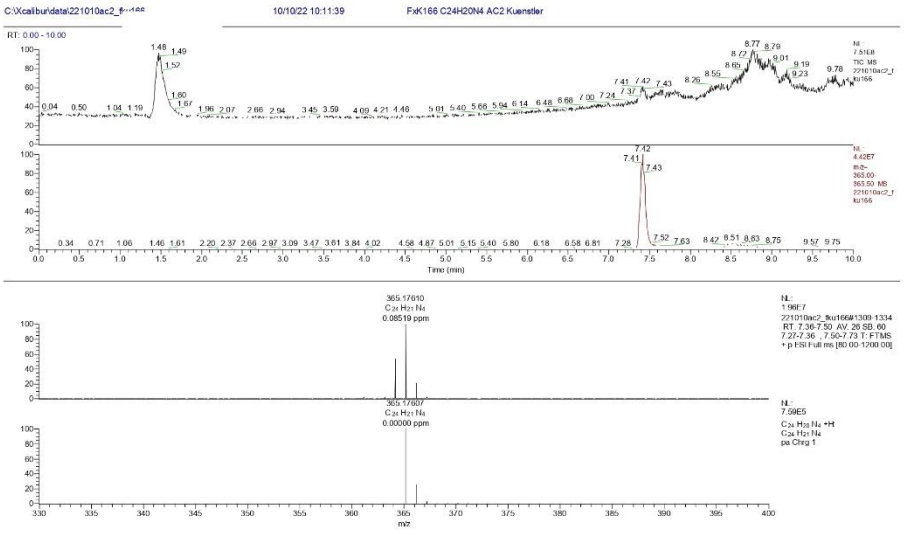


Supplementary Figure 205 LC-HRMS spectrum of compound **A27**.

LC-HRMS of B6a

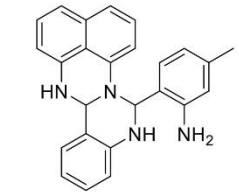


Chemical Formula: $C_{24}H_{20}N_4$

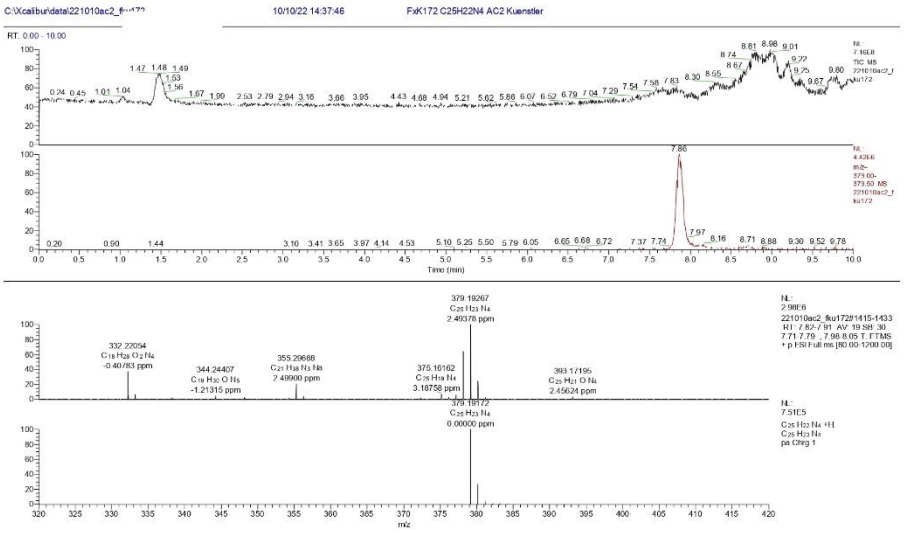


Supplementary Figure 206 LC-HRMS spectrum of compound **B6a**.

LC-HRMS of B6b

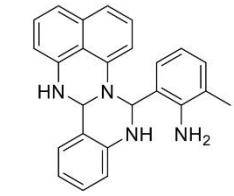


Chemical Formula: $C_{25}H_{22}N_4$

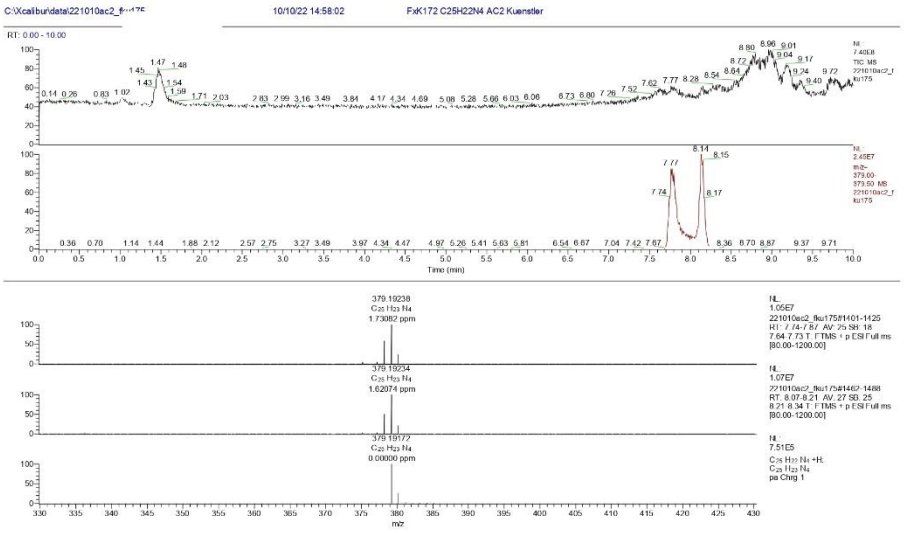


Supplementary Figure 207 LC-HRMS spectrum of compound **B6b**.

LC-HRMS of B6c

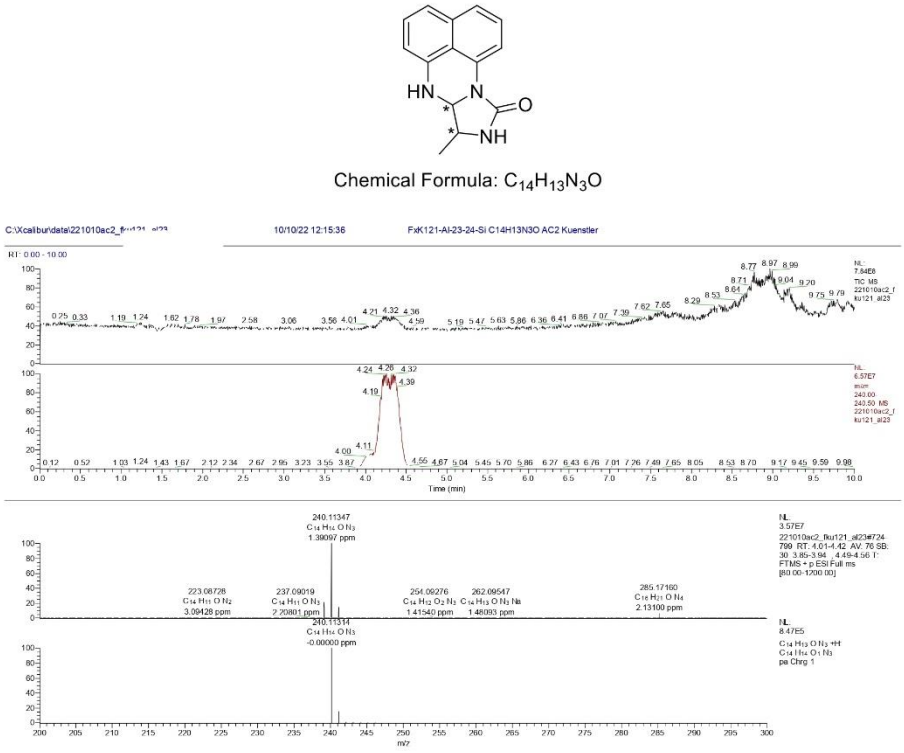


Chemical Formula: $C_{25}H_{22}N_4$



Supplementary Figure 208 LC-HRMS spectrum of compound **B6c**.

LC-HRMS of C1

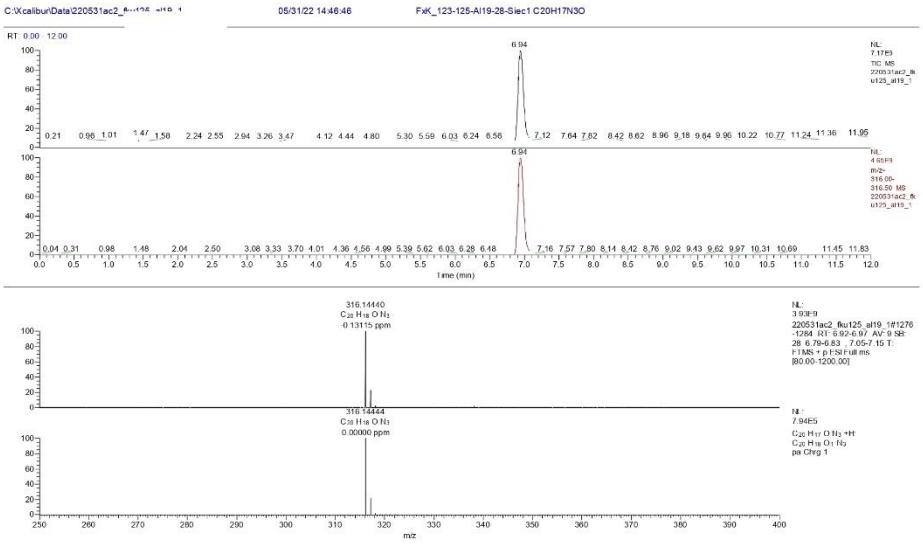


Supplementary Figure 209 LC-HRMS spectrum of compound **C1**.

LC-HRMS of C2

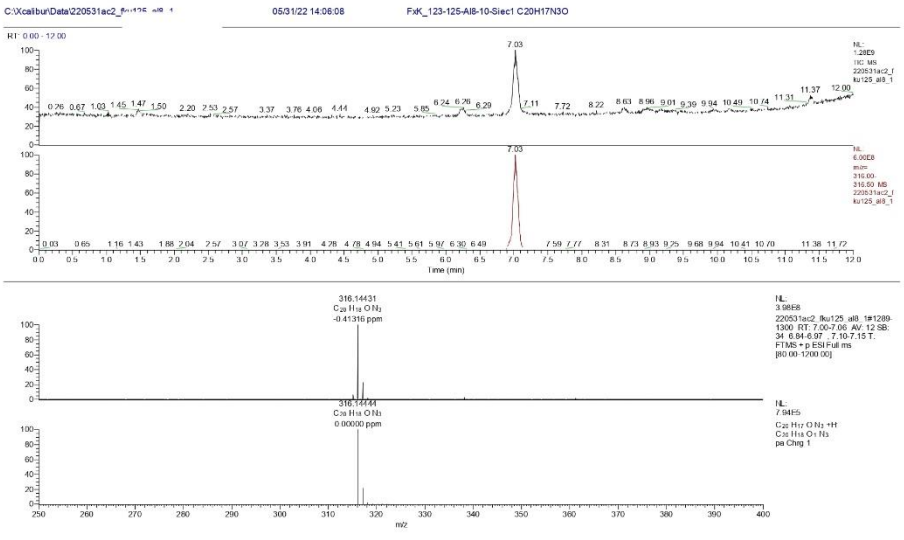
Chemical Formula: $C_{20}H_{17}N_3O$

main isomer of **C2**:



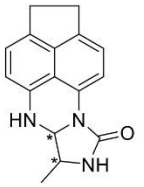
Supplementary Figure 210 LC-HRMS spectrum of the main isomer of compound **C2**.

minor isomer of **C2**:



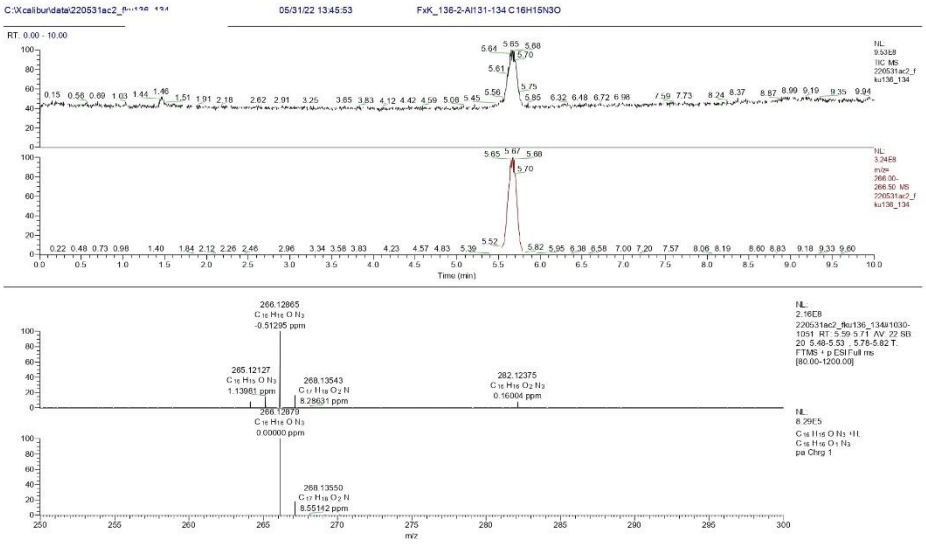
Supplementary Figure 211 LC-HRMS spectrum of the minor isomer of compound **C2**.

LC-HRMS of C3



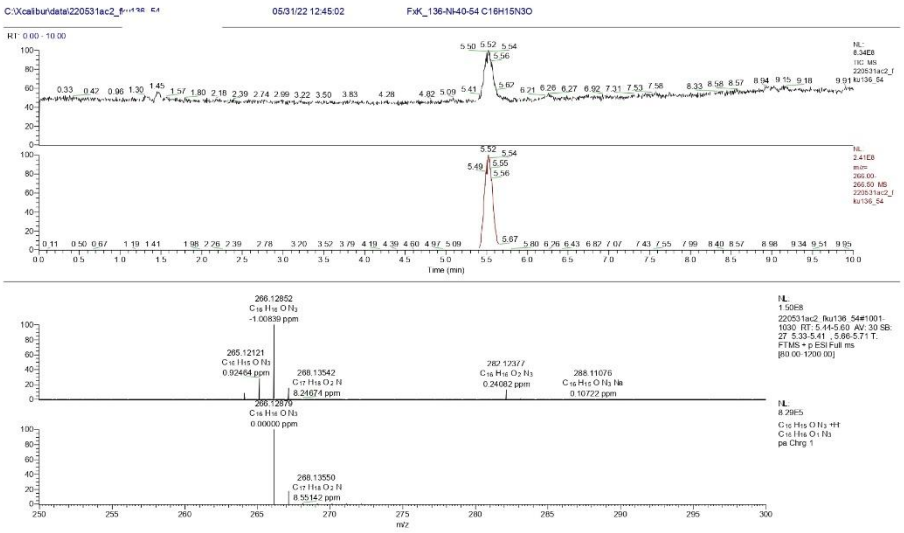
Chemical Formula: $C_{16}H_{15}N_3O$

main isomer of **C3**:



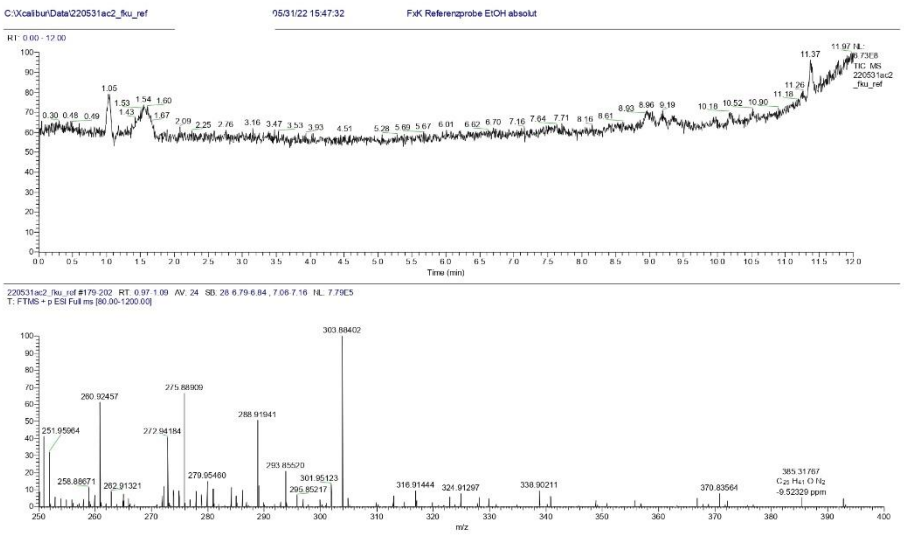
Supplementary Figure 212 LC-HRMS spectrum of the main isomer of compound **C3**.

minor isomer of **C3**:



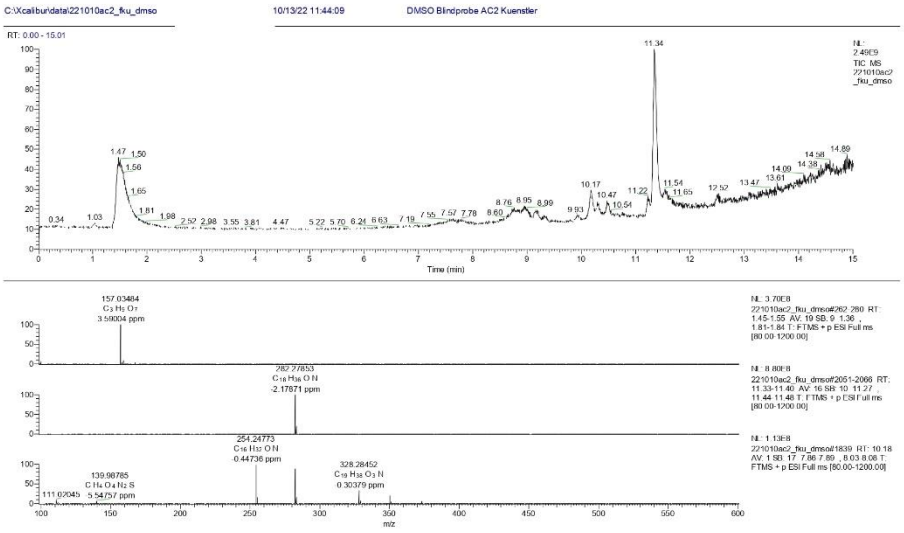
Supplementary Figure 213 LC-HRMS spectrum of the minor isomer of compound **C3**.

Blind sample of ethanol



Supplementary Figure 214 LC-HRMS spectrum of the used solvent ethanol.

Blind sample of DMSO



Supplementary Figure 215 LC-HRMS spectrum of the used solvent DMSO.

16. Crystallographic data

Supplementary Data 1: Crystallographic details of **A1** (CCDC number: 2084882).

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv481_1_te_i41_2

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv481_1_te_i41_2

Bond precision: C-C = 0.0051 A Wavelength=0.71073

Cell: a=22.690(3) b=22.690(3) c=10.320(2)
alpha=90 beta=90 gamma=90
Temperature: 133 K

	Calculated	Reported
Volume	5313.1(17)	5313.1(18)
Space group	I 41	I 41
Hall group	I 4bw	I 4bw
Moiety formula	C17 H15 N3	1.143(C17 H15 N3)
Sum formula	C17 H15 N3	C19.43 H17.14 N3.43
Mr	261.32	298.65
Dx,g cm-3	1.307	1.307
Z	16	14
Mu (mm-1)	0.079	0.079
F000	2208.0	2208.0
F000'	2208.70	
h,k,lmax	30,30,13	27,30,13
Nref	6770[3568]	4150
Tmin,Tmax	0.998,1.000	
Tmin'	0.996	

Correction method= Not given

Data completeness= 1.16/0.61 Theta(max)= 28.529

R(reflections)= 0.0507(3042) wR2(reflections)= 0.1234(4150)

S = 0.974 Npar= 369

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

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 Alert level B
PLAT417_ALERT_2_B Short Inter D-H..H-D       Hn1      ..Hn3B     .       1.94 Ang.
                                    -1/2+y,1-x,-1/4+z  =      4_464 Check

 Alert level C
STRVA01_ALERT_2_C           Chirality of atom sites is inverted?
          From the CIF: _refine_ls_abs_structure_Flack    5.000
          From the CIF: _refine_ls_abs_structure_Flack_su    4.000
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00508 Ang.
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N2       --Hn2      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N4       --Hn4      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N1       --Hn1      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N5       --Hn5      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N3       --Hn3B     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N3       --Hn3A     .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N6       --Hn6B     .     Please Check
PLAT601_ALERT_2_C Unit Cell Contains Solvent Accessible VOIDS of .         32 Ang**3
PLAT907_ALERT_2_C Flack x > 0.5, Structure Needs to be Inverted? .       5.00 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        21 Report

 Alert level G
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: check formula stoichiometry or atom site occupancies.
          From the CIF: _cell_formula_units_Z   14
          From the CIF: _chemical_formula_sum  C19.43 H17.14 N3.43
          TEST: Compare cell contents of formula and atom_site data

          atom    Z*formula  cif sites diff
          C        272.02    272.00    0.02
          H        239.96    240.00   -0.04
          N         48.02     48.00    0.02
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          6 Report
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .      4.000 Report
PLAT042_ALERT_1_G Calc. and Reported Moiety Formula Strings Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       1.14 Check
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          3 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          8 Note
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..         ! Info
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        173 Note
PLAT916_ALERT_2_G Hooft y and Flack x Parameter Values Differ by .       5.60 Check
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........       3.5 Low
PLAT950_ALERT_5_G Calculated (ThMax) and CIF-Reported Hmax Differ          3 Units

   0 ALERT level A = Most likely a serious problem - resolve or explain
   1 ALERT level B = A potentially serious problem, consider carefully
  12 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  14 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  12 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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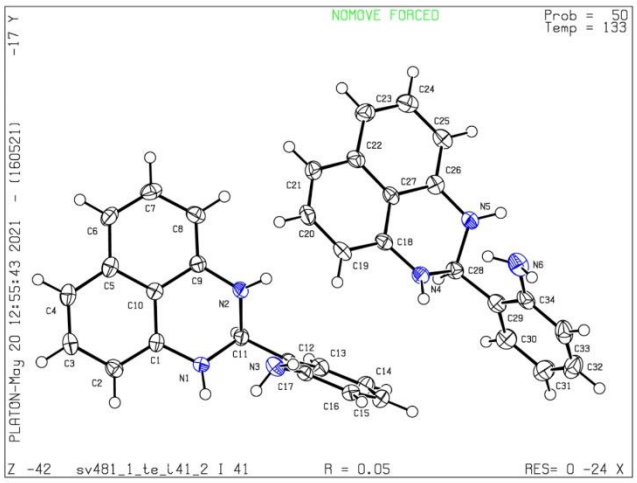
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 16/05/2021; check.def file version of 13/05/2021

Datablock sv481_1_te_i41_2 - ellipsoid plot



Supplementary Figure 216 Molecular structure of **A1**.

Supplementary Data 2: Crystallographic details of **B1a** (CCDC number: 2083140)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv499_1_m_p21c

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv499_1_m_p21c

Bond precision: C-C = 0.0020 A Wavelength=0.71073

Cell: a=5.7600(12) b=11.550(2) c=25.410(5)
alpha=90 beta=90.70(3) gamma=90
Temperature: 133 K

	Calculated	Reported
Volume	1690.4(6)	1690.4(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C24 H19 N3	C24 H19 N3
Sum formula	C24 H19 N3	C24 H19 N3
Mr	349.42	349.42
Dx,g cm-3	1.373	1.373
Z	4	4
Mu (mm-1)	0.082	0.082
F000	736.0	736.0
F000'	736.24	
h,k,lmax	7,15,34	7,15,33
Nref	4271	4090
Tmin,Tmax	0.995,0.997	
Tmin'	0.985	

Correction method= Not given

Data completeness= 0.958 Theta(max)= 28.448

R(reflections)= 0.0433(2915) wR2(reflections)= 0.1155(4090)

S = 1.039 Npar= 320

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
CRYSC01_ALERT_1_C The word below has not been recognised as a standard
           identifier.
           yellowish
PLAT222_ALERT_3_C NonSolvent Resd 1  H   Uiso(max)/Uiso(min) Range        7.0 Ratio
PLAT245_ALERT_2_C U(iso) H24       Smaller than U(eq) C24       by       0.015 Ang**2
PLAT410_ALERT_2_C Short Intra H...H Contact  H1       ..H8       .        1.96 Ang.
                                                    x,y,z  =      1_555 Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N1       --Hn1      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N3       --H5       .     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.149 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          7 Report
```

Alert level G

```
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          4 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          1 Note
PLAT793_ALERT_4_G Model has Chirality at C11         (Centro SPGR)         S Verify
PLAT793_ALERT_4_G Model has Chirality at C18         (Centro SPGR)         R Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        171 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........        3.2 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        17 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by         2 Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
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```

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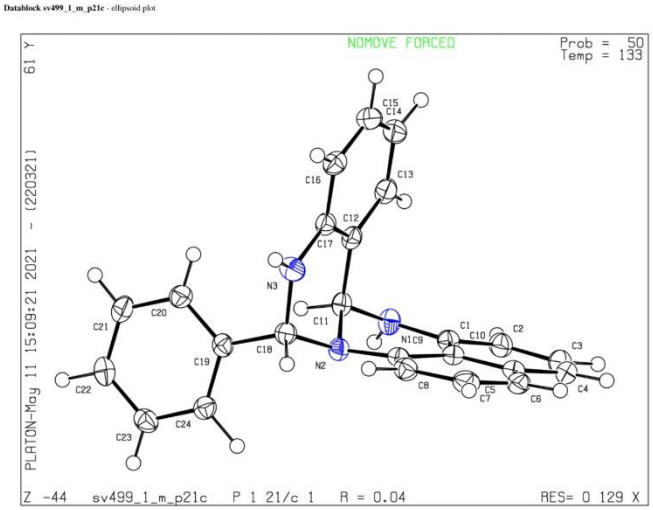

Supplementary Figure 217 Molecular structure of **B1a.**

Supplementary References

1. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **42**, 339–341 (2009).
2. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **71**, 3–8 (2015).
3. MacRae, C. F. *et al.* Mercury 4.0: From visualization to analysis, design and prediction. *J. Appl. Cryst.* **53**, 226–235 (2020).
4. Kallmeier, F., Dudziec, B., Irrgang, T. & Kempe, R. Manganese-Catalyzed Sustainable Synthesis of Pyrroles from Alcohols and Amino Alcohols. *Angew. Chem. Int. Ed.* **56**, 7261–7265 (2017).
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6. Mastalir, M. *et al.* Divergent Coupling of Alcohols and Amines Catalyzed by Isoelectronic Hydride Mn(I) and Fe(II) PNP Pincer Complexes. *Chem. Eur. J.* **22**, 12316–12320 (2016).
7. Freitag, F., Irrgang, T. & Kempe, R. Cobalt-Catalyzed Alkylation of Secondary Alcohols with Primary Alcohols via Borrowing Hydrogen/Hydrogen Autotransfer. *Chem. Eur. J.* **23**, 12110–12113 (2017).
8. Rösler, S., Ertl, M., Irrgang, T. & Kempe, R. Cobalt-Catalyzed Alkylation of Aromatic Amines by Alcohols. *Angew. Chem. Int. Ed.* **54**, 15046–15050 (2015).
9. Mastalir, M. *et al.* Air Stable Iron(II) PNP Pincer Complexes as Efficient Catalysts for the Selective Alkylation of Amines with Alcohols. *Adv. Synth. Catal.* **358**, 3824–3831 (2016).

7 Structure Investigations of Fertigines via X-Ray Crystallography

Robin Fertig, Torsten Irrgang, and Rhett Kempe*

Structure Investigations of Fertigines via X-Ray Crystallography.

*Inorganic Chemistry II - Catalyst Design, University of Bayreuth, 95440 Bayreuth, Germany

To be submitted

Structure Investigations of Fertigines via X-Ray Crystallography

Robin Fertig, Torsten Irrgang, and Rhett Kempe

Inorganic Chemistry II-Catalyst Design, University of Bayreuth, 95440 Bayreuth, Germany

Abstract

We reported here on the molecular structures of an unknown class of *N*-heterocycles, named fertigines. We gave an overview of their synthesis and crystallization method. Nine different fertigines have been crystallized and analyzed via single-crystal X-ray diffraction analysis. The influence of the substitution on the structural properties on the aminal-groups in the core region was investigated and the observed conformations in the crystal were discussed. The via ^{1}H-NMR analysis observed diastereoselectivity during synthesis was specified by determining the absolute configuration of the fertigines in the crystal.

Introduction

Recently, we have reported about a synthesis concept that enables the synthesis of an unknown class of *N*-heterocyclic compounds, named fertigines.[1] *N*-Heterocyclic compounds are of high importance as their motifs are found in many pharmaceuticals, natural products, and functional materials.[2] About 59 % of the FDA approved small-molecule drugs contain at least one nitrogen heterocycle, thus it is one of the most frequent motifs in pharmaceuticals.[3] One way to reduce the CO_2-emissions und to conservate the finite fossil carbon resources, is the development of reactions in which alcohols are converted into important chemical compounds, since they can be obtained from indigestible and abundantly available lignocellulose biomass.[4] The acceptorless dehydrogenative condensation (ADC) represents a concept that permits the catalytic synthesis of imines using alcohols and amines.[5] The selective linkage of these imine functionalities can lead to *N*-heterocycles. Relating to this concept, various noble-metal catalysts based on Ir or Ru have been developed for the synthesis of *N*-heterocycles like pyridines, pyrroles, pyrimidines, quinolines, indoles and quinazolines.[6–12] In recent years, there is the trend to a more sustainable catalysis by substitute these rare noble metals with abundantly available 3d metals like Fe,[13–15] Co,[16–19] and Mn.[20–22] Several groups showed the high applicability of such base-metal catalyst for the synthesis of *N*-heterocycles like pyrrole,[23,24] pyrimidine,[25,26] or benzimidazoles.[27] To overcome future challenges, it is important, not only to rest on the synthesis of already known (*N*-heterocyclic) compounds, but also to develop and investigate unreported *N*-heterocyclic compounds. Since previous work has intensively described the synthesis

and high functionalizability of fertigines, this work will focus on the description of their molecular structures. We will give better insights in the structure of nine different fertigines via single-crystal X-ray analysis and investigate the influence of different aldehyde substituents on the molecular structure of the fertigines.

Results and discussion

Figure 1 gives an overview of the reaction pathway for the synthesis of fertigines catalyzed by a Mn-precatalyst. Nine different fertigines were synthesized by using various aldehyde derivatives, substituted amino alcohols and 1,8-diaminonaphthalene derivatives.

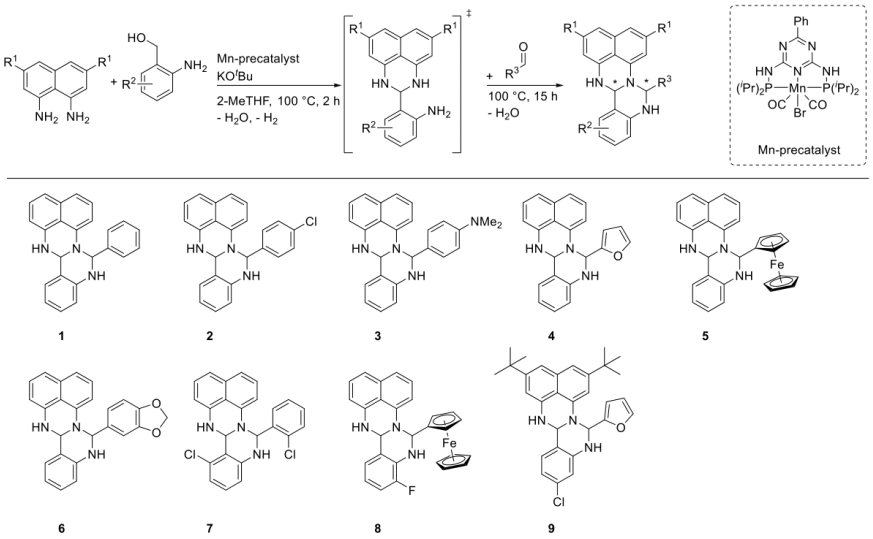


Figure 1: General procedure for the synthesis of the discussed fertigines **1** – **9**.

The synthesis of **1** was achieved by stirring a solution of 1,8-diaminonaphthalene, 2-aminobenzyl alcohol, KO^{t}Bu and Mn-precatalyst in 2-MeTHF at 100 °C (Figure 1). After heating the mixture for 2 h, benzaldehyde was added, and the reaction was stirred at 100 °C for 15 h. After workup, we obtained a white, air stable solid in 93 % yield (for detailed information see SI). This fertigine was previously characterized by elemental analysis, IR-spectroscopy and NMR-spectroscopy.[1] Ithough the fertigine contains two stereo centers, we did not observe all diastereomers via ^{1}H-NMR analysis (see SI), indicating a diastereoselectivity for the synthesis of fertigines. We determined the obtained pair of enantiomers by investigation of the molecular structure via X-ray crystallography. Crystals of **1** were obtained by dissolving **1** in a mixture of ethyl acetate and pentane (3/1) and storing the solution at -

8°C for 2 days. Figure 2 shows the molecular structure of **1** determined by single-crystal X-ray analysis with selected bond distances and angles in the caption.

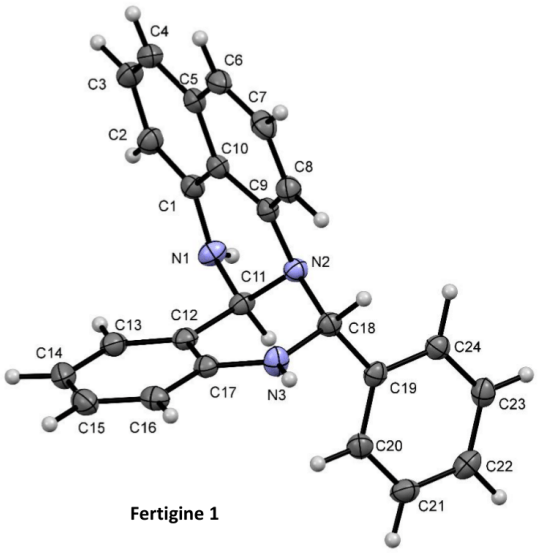


Figure 2: Molecular structure of **1** in the crystal (ORTEP drawing and atom labelling scheme with 50 % probability level). Selected bond lengths/Å and angles/°: N1-C11, 1.438(2); N2-C11, 1.490(2); N2-C18, 1.463(3); N3-C17, 1.377(2); N3-C18, 1.452(2); C11-C12, 1.525(2); C18-C19, 1.527(2). N1-C11-N2, 111.9(1); C11-N2-C18, 110.2(1); N2-C18-N3, 110.2(1); C18-N3-C17, 121.5(1).

The fertigine **1** crystallized in the monoclinic space group P 21/c having four independent molecules in the unit cell. The 3-dimensional molecular structure in the crystal shows an interesting shape, where all three aromatic regions of this molecule are almost perpendicular to each other (Figure 3). The angle between the naphthalene (red) and the annulated phenyl (blue) plane is α = 85.65 °, between the naphthalene (red) and the substituted phenyl (green) plane is β = 89.69 ° and between the annulated phenyl and the substituted phenyl plane is γ = 84.68 ° (for details see SI).

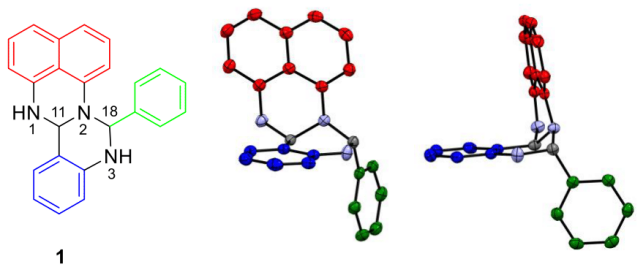
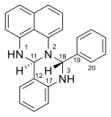
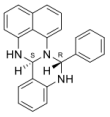
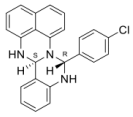
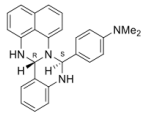
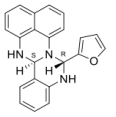
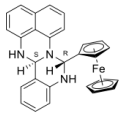


Figure 3: Orientation of the three aromatic regions (red, blue, green) of **1** in the crystal (ORTEP drawing and atom labelling scheme with 50 % probability level).

The absolute configuration of the molecular structure of **1** is $(S)_{C11}$, $(R)_{C18}$. Next, we investigated the structural properties of the core region around the nitrogen atoms of the fertigine. In literature,[28] the overall bond lengths of $C_{sp^3} - N_{sp^3}$ is 1.469 ± 0.014 Å. The bond lengths in **1** of the aminal belonging to C11 (C11-N1: 1.438(2) Å, C11-N2: 1.490(2) Å) are comparable to the values of a typically $C_{sp^3} - N_{sp^3}$-bond and are within the range of reported structures of 2,3-dihydro-1H-perimidines.[29,30] The C11-C12 bond length (1.525(2) Å) and C18-C19 bond length (1.527(2) Å) agree with reported $C_{arom.} - C_{sp^3}$ bond length.[28] The C_{aminal}-N lengths of C18 (C18-N2: 1.463(2) Å, C18-N3, 1.452(2) Å) are in line with the value in literature.[28] The angles C1-N1-C11: 117.4(1) ° and C11-N2-C18: 110.3(1) ° indicate a distorted trigonal pyramidal geometry for N1 and N2. According to the trigonal planar geometry of N3 (C17-N3-C18: 120.9(1) °) and to the bond length of N3-C17 (1.377(2) Å), N3 shows more the character of a sp^2-hybridization than of a sp^3-hybridization (lit.: $C_{arom.} - N_{sp^2}$: 1.353 ± 0.007 Å vs. $C_{arom.} - N_{sp^3}$: 1.419 ± 0.017).[28]

Table 1: Comparison of selected bond lengths, angles, and plane angles[a] of the fertigines **1** – **5**.

						
Distances/Å	**1**	**2**	**3**	**4**	**5**	
N1-C11	1.438(2)	1.450(4)	1.442(2)	1.461(5)	1.432(4)	
N2-C11	1.490(2)	1.466(4)	1.475(2)	1.466(5)	1.479(4	
N2-C18	1.463(2)	1.461(4)	1.469(2)	1.437(5)	1.469(4)	
N3-C17	1.377(2)	1.377(5)	1.379(2)	1.381(5)	1.384(4)	
N3-C18	1.452(2)	1.452(5)	1.448(2)	1.454(5)	1.459(4)	
C11-C12	1.525(2)	1.532(5)	1.530(3)	1.513(5)	1.529(6)	
C18-C19	1.527(2)	1.525(5)	1.516(3)	1.521(6)	1.506(4)	
Angles/°						
N1-C11-N2	111.9 (1)	108.8(3)	108.68(2)	106.5(3)	108.7(3)	
C11-N2-C18	110.20(1)	110.2(3)	109.01(1)	115.3(3)	109.8(2)	
N2-C18-N3	110.2 (1)	110.5(3)	109.56(1)	108.5(3)	110.9(3)	
C17-N3-C18	121.5(1)	121.4(3)	120.40(2)	117.4(3)	120.3(3)	
Plane angles/°						
α	85.65	86.68	82.16	37.71	88.76	
β	89.69	82.98	77.96	67.40	81.67	
γ	84.68	80.34	89.85	79.38	89.09	

[a] α is the angle between the planes of the naphthalene and the annulated phenyl plane. β is the angle between the planes of the naphthalene and the substituted phenyl moiety. γ is the angle between the planes of the annulated and the substituted phenyl moiety.

Next, we investigated the influence of the substituent at C18 on the molecular structure of the core region of the fertigines (Table 1, for atom labelling see structure on the top left side). Using 4-chloro-benzaldehyde for fertigine synthesis, we obtained the fertigine **2** (Figure 4a). It crystallized in the orthorhombic space group P 21 21 21 with 4 fertigines plus 4 acetonitriles in the unit cell (for more crystallographic details of **2** see SI). The aminal bond length of C11 and C18 are of comparable values

to **1**, only the bond length difference on C11 diminishes. Regarding the other bond lengths and angles of **2**, no significant difference to **1** could be observed, the almost orthogonality of the conformation remains. While the measured crystals of **1**,**2** and **4**,**5** are the $(S)_{C11}$,$(R)_{C18}$-enantiomers, the molecular structure of **3**, a fertigine with an electron-donating substituent at C18, is the only example in table 1 showing the $(R)_{C11}$,$(S)_{C18}$-enantiomer. It crystallized in the monoclinic space group P 21/n containing of 4 independent molecules in the unit cell (for more crystallographic details see SI). The structural properties (bond lengths, angles) of **3** are similar to **1**, only β shrinks to 77.96°, leading to a more pincer-shaped structure of **3**. Using furfural as aldehyde for synthesis, we obtained the fertigine **4**. There are 8 independent molecules in the unit cell, the orthorhombic space group is P b c a. Interestingly, the obtained molecular structure in the crystal has a different conformation than the fertigines before. Instead of an almost perpendicular orientation of the aromatic regions, especially the values of α and β shrink (Table 1), leading to a more flatten-twisted structure of the core region (Figure 5a). The aminal bond lengths and the $C_{arom.}-C_{sp^3}$ length are within the range of before reported fertigines (**1** - **3**). The angles in the core region are of same values compared to **1**, remaining the distorted trigonal pyramidal geometry of N1 and N2, as well as the trigonal planar geometry of N3. If C18 is substituted with ferrocene (fertigine **5**), it crystallized in the monoclinic space group Cc with 4 independent molecules (for more crystallographic details of **5** see SI). Regarding the bond lengths and angles, no significant impact on the structural properties could be observed, only the C18-C19-length is shorter (1.506(4) Å). The plane angles α, β and γ proof the almost perpendicular conformation, which is observed in two thirds of the investigated crystals. The N3-C17 bond length of all discussed fertigines vary between 1.377(2) – 1.384(4) Å, the C17-N3-C18 angle vary between 117.4(3) – 121.5(1) °. Thus, the hybridization of the N3 of all discussed fertigines is somewhere between sp^3 and sp^2, but closer to sp^2.

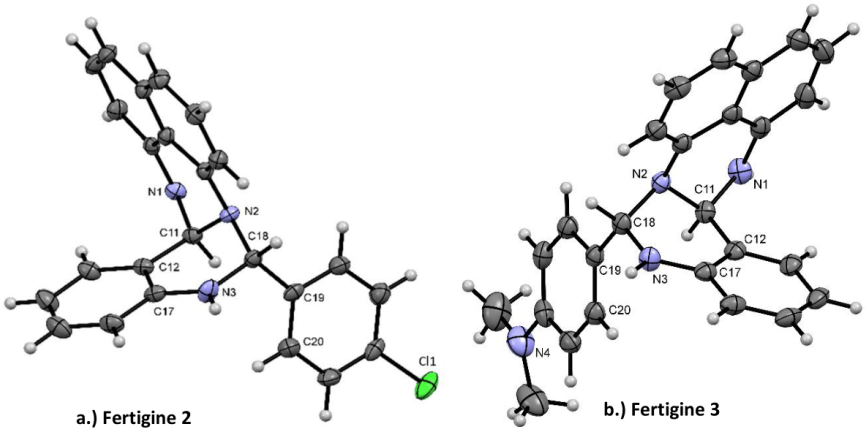


Figure 4: Molecular structure of **2** and **3** in the crystal (ORTEP drawing and atom labelling scheme with 50 % probability level). Both structures clearly show a conformation where the aromatic regions are almost perpendicular to each other. While **2** is the $(S)_{C11}$,$(R)_{C18}$-enantiomer, is **3** the $(R)_{C11}$,$(S)_{C18}$-enantiomer.

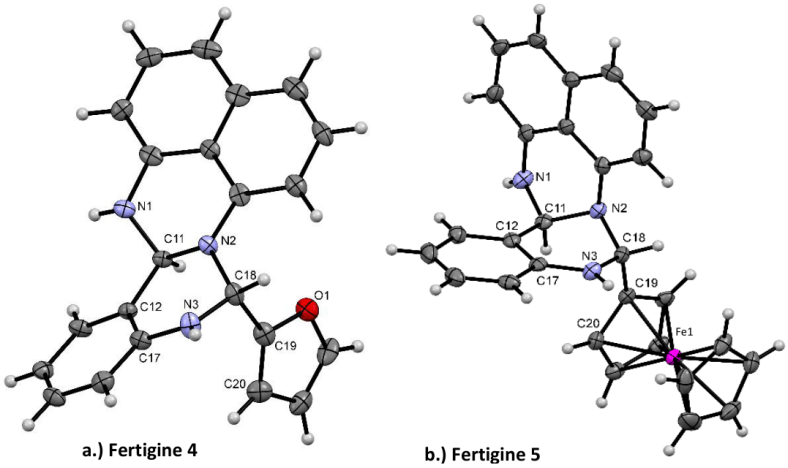
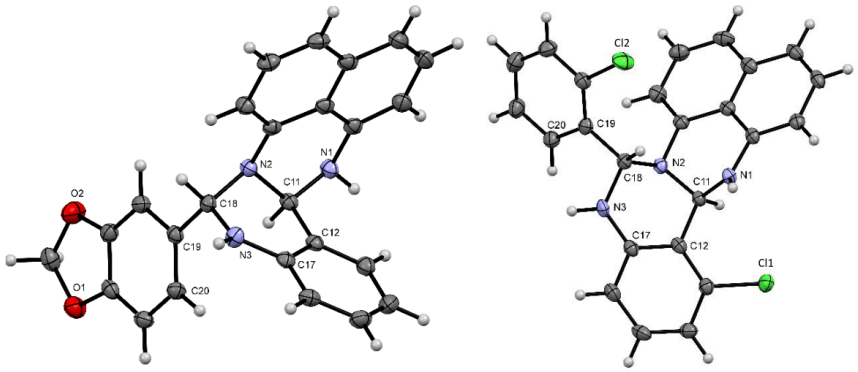


Figure 5: Molecular structure of **4** and **5** in the crystal (ORTEP drawing and atom labelling scheme with 50 % probability level

In Figure 6 and Figure 7 more molecular structures are presented. Figure 6a shows the molecular structure of the fertigine **6** in the mainly observed almost perpendicular conformation (α = 89.22°, β = 85.02°, γ = 89.51°). The fertigine **6** crystallized in the triclinic space group P -1 with 2 independent molecules in the unit cell (for more crystallographic details of **6** see SI). Regarding the absolute configuration of the molecular structure in the crystal, the more rarely observed $(R)_{C11}$,$(S)_{C18}$-enantiomer was obtained. The piperonyl-moiety causes no difference on the structural

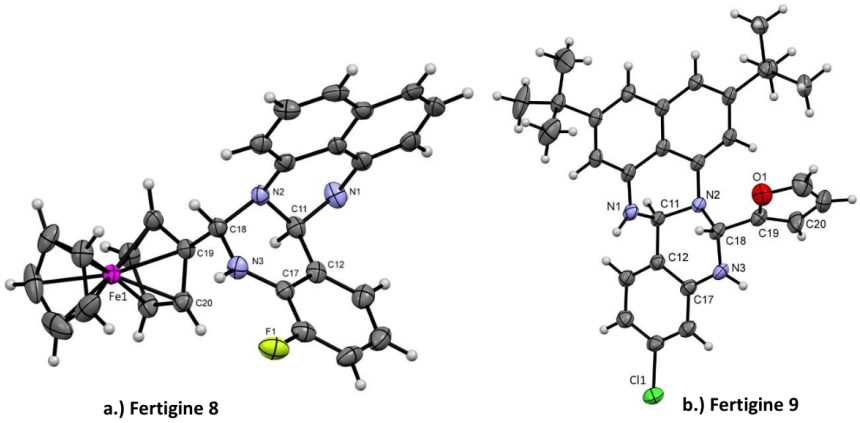
properties (bond lengths, angles) of the fertigine compared to **1**. Figure 6b shows the molecular structure of a dichloro-fertigine (fertigine **7**), with one chloro-substituent on the annulated and one on the substituted phenyl moiety. **7** crystallized in the orthorhombic space group P n a 21 consisting of 2 independent molecules per unit cell (for more crystallographic details of **7** see SI). Interestingly, the molecular structure of this fertigine has a more flatten-twisted conformation, whereby all three planar angles shrink to lower values (α = 47.50°, β = 50.72°, γ = 63.63°). The obtained enantiomer shows an absolute configuration of $(R)_{C11}$,$(S)_{C18}$.



a.) Fertigine 6 **b.) Fertigine 7**

Figure 6: **a.)** Molecular structure of **6** in the crystal (ORTEP drawing and atom labelling scheme with 50 % probability level) with selected bond lengths/Å, angles/° and plane angles/°: N1-C11, 1.441(2); N2-C11, 1.485(2); N2-C18, 1.464(2); N3-C17, 1.393(2); N3-C18, 1.446(2); C11-C12, 1.524(2); C18-C19, 1.522(2). N1-C11-N2, 112.21(13); C11-N2-C18, 109.60(12); N2-C18-N3, 109.26(13); C18-N3-C17, 119.76(13). α = 89.22, β = 85.02, γ = 89.51. **b.)** Molecular structure of **7** in the crystal (ORTEP drawing and atom labelling scheme with 50 % probability level) with selected bond lengths/Å, angles/° and plane angles/°: N1-C11, 1.467(4); N2-C11, 1.470(4); N2-C18, 1.493(4); N3-C17, 1.493(4); N3-C18, 1.460(4); C11-C12, 1.506(4); C18-C19, 1.513(4). N1-C11-N2, 110.4(2); C11-N2-C18, 110.8(2); N2-C18-N3, 106.4(2); C18-N3-C17, 120.3(2). α = 47.50, β = 50.72, γ = 63.63.

The fertigine **8** (Figure 7a) has a similar molecular structure like fertigine **5**, the only difference is a fluoro-substitution on the annulated phenyl group. It crystallized in the same monoclinic space group as **5** (Cc) and has 4 independent molecules in the unit cell. Crystallographic details of **8** are shown in table 4. It has in an almost perpendicular conformation (α = 87.26°, β = 83.38°, γ = 88.20°). The bond lengths, angles, and the absolute configuration ($(S)_{C11}$,$(R)_{C18}$-enantiomer) are the same compared to **5**. The fertigine **9** is the only crystallized fertigine with a substituted naphthalene-moiety. The monoclinic space group is P 21/n with 4 independent molecules in the unit cell (for more crystallographic details of **9** see SI). Regarding the plane angles (α = 58.51°, β = 40.62°, γ = 58.90°) of fertigine **9** (Figure 7b), the crystallized conformation of the $(S)_{C11}$,$(R)_{C18}$-enantiomer has a flatten-twisted structure. The structural properties (bond length and angles) are of comparable values like fertigine **1**.



a.) Fertigine 8 **b.) Fertigine 9**

Figure 7: **a.)** Molecular structure in the crystal of **8** (ORTEP drawing and atom labelling scheme with 50 % probability level) with selected bond lengths/Å, angles/° and plane angles/°: N1-C11, 1.434(5); N2-C11, 1.476(5); N2-C18, 1.468(5); N3-C17, 1.381(5); N3-C18, 1.438(5); C11-C12, 1.514(6); C18-C19, 1.511(5). N1-C11-N2, 109.5(3); C11-N2-C18, 109.6(3); N2-C18-N3, 110.6(3); C18-N3-C17, 119.4(3). α = 87.26, β = 83.38, γ = 88.20. **b.)** Molecular structure of **9** in the crystal (ORTEP drawing and atom labelling scheme with 50 % probability level) with selected bond lengths/Å, angles/° and plane angles/°: N1-C11, 1.470(4); N2-C11, 1.461(4); N2-C18, 1.493(4); N3-C17, 1.379(5); N3-C18, 1.452(4); C11-C12, 1.493(5); C18-C19, 1.494(5). N1-C11-N2, 111.1(3); C11-N2-C18, 109.9(3); N2-C18-N3, 107.4(3); C18-N3-C17, 119.5(3). α = 58.51, β = 40.62, γ = 58.90.

Conclusion

In summary, we have presented the molecular structures in the crystal of 9 different fertigines obtained by X-ray crystallography. The influence of a substitution at C18 on the structural properties was investigated with 5 different substituted fertigines (fertigine **1** – **5**). Furthermore, we have discussed the molecular structure in the crystal of fertigines with substitutions on the three aromatic moieties as well as multiple substitutions (fertigines **7** – **9**). We mainly observed a conformation of the fertigines in the crystal, where all aromatic planar regions are almost perpendicular to each other. The via ^{1}H-NMR spectroscopy observed diastereoselectivity was specified by analysing the absolute configuration, transpiring that only the (R),(S)- and (S),(R)-enantiomers could be found in crystals.

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Supplementary Information

Structure Investigations of Fertigines via X-Ray Crystallography

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1 General

All reactions and manipulations with air sensitive compounds being present were performed under dry argon (Ar 5.0) or nitrogen (N_2 5.0), using Schlenk and glove box techniques. Nonhalogenated solvents were dried over sodium benzophenone, 2-methyltetrahydrofuran (2-MeTHF) was dried over calcium hydride, and halogenated solvents were dried over P_2O_5. Deuterated solvents were bought from Cambridge Isotope Laboratories, distilled accordingly, and stored over molecular sieves (3 Å). 1,8-Diaminonaphthalene was sublimated before use. Other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were collected on a Varian INOVA 400 MHz spectrometer or on a Bruker Avance III HD 500 MHz. Chemical shifts (δ) are reported in ppm relative to residual solvent signal ($CDCl_3$: 7.26 ppm (^1H), 77.16 ppm (^{13}C); DMSO-D_6: 2.50 ppm (^1H), 39.51 ppm (^{13}C); C_6D_6: 7.16 ppm (^1H), 128.39 ppm (^{13}C)). Coupling constants (J) are given in Hz (coupling patterns: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet). GC analyses were carried out using an Agilent Technologies 6890N system equipped with a Macherey-Nagel (MN) Optima 5 HT column (30 m, 320 µm, 0.25 µm) or an Agilent Technologies 6850 system equipped with a MN Optima 17 column (30 m, 320 µm, 0.25 µm). GC/MS analyses were carried out on an Agilent 7890A/MSD 5975C system equipped with a HP-5MS column (30 m, 320 µm, 0.25 µm). For column chromatography, Alox N (90 Å pore withdraw, 50 – 200 µm particle size) from Macherey-Nagel was used. For X-Ray analysis a STOE STADIVARI [λ(Mo Kα) = 0.71073 Å] equipped with a dectris (Pilatus 200 K – 20 Hz) detector and an Oxford Cryostream low temperature unit was used. All organic compounds were characterized by 1H and 13C NMR analysis. Unknown compounds or compounds with incomplete spectroscopic literature data were further analyzed via elemental analysis. The ligands were synthesized according to literature procedures[1] and the precatalysts were also synthesized similar to literature procedures,[2] in thf under reflux for 1.5 h and subsequent removal of the solvent.

General reaction conditions for the synthesis of fertigines:

In a glovebox, 2 mmol 1,8-naphthalenediamin and 2 mmol 2-aminobenzyl alcohol derivatives are dissolved in 1 mL 2-MeTHF and added to a Schlenk tube. 0.5 mL of a 0.02 mmol/mL stock solution of the Mn-precatalyst and 0.5 mL of a 1.2 mmol/mL KO^{t}Bu stock solution is added to the Schlenk tube. 1 mL 2-MeTHF is added, and the reaction mixture is heated at 100 °C using an open system consisting of a return condenser and a bubble counter. After 2 hours reaction time, 2 mmol of various aldehydes are added to the reaction. For this, the aldehyde is dissolved in at least 0.5 mL 2-MeTHF and added to the reaction mixture through a septum with a syringe. After 15 h, the reaction is stopped by cooling down to room temperature. The work-up depends on the used substrates. Usually, 2 mL H_2O is added, and the reaction mixture is extracted with dichloromethane (3x10 mL). The organic layers were dried with Na_2SO_4 and the solvent is removed in vacuo. The crude product is purified by column chromatography using Alox N as stationary phase. Using some substrates, the product precipitates during reaction. If this is the case, 5 mL water is added, the reaction mixture is diluted with pentane and filtrated. After washing the residue with H_2O and pentane, it is dried in vacuo at 70 °C to obtain the product.

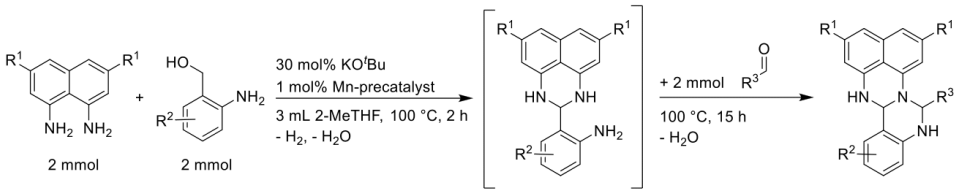
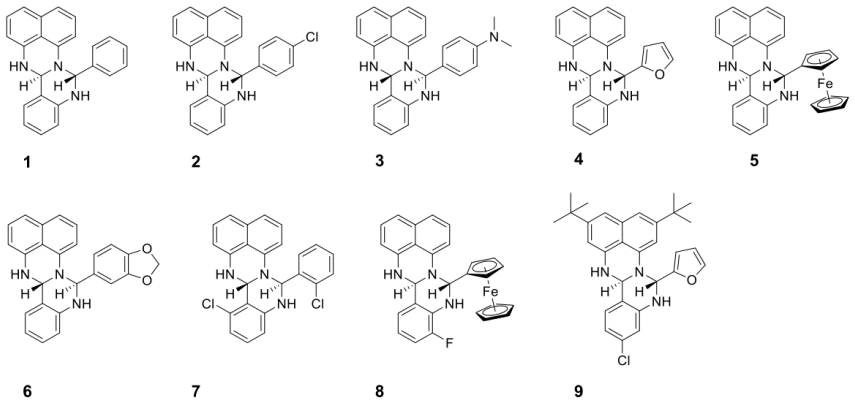


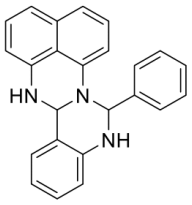
Figure S 1: General reaction conditions for the synthesis of fertigines.

Overview of the synthesized and via x-ray analysis characterized fertigines.



Synthesis and characterization of the investigated fertigines 1 – 9.

Synthesis of **1**



Chemical Formula: $C_{24}H_{19}N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-precatalyst (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a return condenser and a bubble counter. After 2 hours reaction time, benzaldehyde (2 mmol, 203 µl) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as a white solid (648 mg, 1.86 mmol, 93 %). Single crystals of **1** were grown in ethyl acetate / pentane (3/1) at – 8 °C.

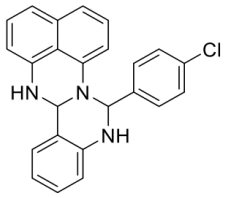
^{1}H NMR (DMSO-d6, 500 MHz, 293 K): δ = 7.50 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.24 (t, J = 7.9 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 7.06 (dd, J = 7.3, 4.0 Hz, 2H), 6.98 – 6.94 (m, 2H), 6.87 (t, J = 7.6 Hz, 1H), 6.64 – 6.55 (m, 3H), 6.38 (t, J = 7.4 Hz, 1H), 5.09 (d, J = 3.4 Hz, 1H) ppm.

^{13}C NMR (DMSO-d6, 125 MHz, 293 K): δ = 143.20, 142.38, 141.15, 139.97, 134.28, 128.60, 127.95, 127.74, 126.94, 126.90, 126.62, 125.37, 121.62, 117.87, 115.46, 115.33, 113.78, 113.33, 105.59, 105.30, 65.48, 60.00 ppm.

Elemental analysis calculated: C 82.49, H 5.48, N 12.03

Elemental analysis found: C 82.68, H 5.39, N 11.99

Synthesis of **2**



Chemical Formula: $C_{24}H_{18}ClN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-precatalyst (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a return condenser and a bubble counter. After 2 hours reaction time, 4-chlorobenzaldehyde (2 mmol, 281 mg) is diluted in 0.7 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3x10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate 5:1) and obtained as a yellow solid (537 mg, 1.40 mmol, 70 %). Single crystals of **2** were obtained by dissolving the product in very less acetonitrile and slow diffusion of pentane in the solution.

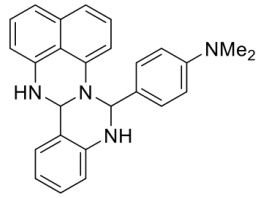
^{1}H NMR (CD_3CN, 500 MHz, 293 K): δ = 7.54 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.27 (t, J = 7.9 Hz, 1H), 7.27 (t, J = 7.9 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.07 (t, J = 6.5 Hz, 2H), 6.99 (d, J = 7.7 Hz, 1H), 6.93 (t, J = 7.7 Hz, 1H), 6.67 (d, J = 7.4 Hz, 1H), 6.67 (d, J = 7.4 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.54 (d, J = 4.8 Hz, 1H), 6.48 (t, J = 7.5 Hz, 1H), 6.48 (t, J = 7.5 Hz, 1H), 5.91 (d, J = 3.2 Hz, 1H), 5.65 (d, J = 4.4 Hz, 1H), 5.19 (d, J = 3.9 Hz, 1H) ppm.

^{13}C NMR (CD_3CN, 125 MHz, 293 K): δ = 143.87, 142.28, 142.08, 140.71, 135.85, 134.29, 130.04, 129.79, 129.54, 128.11, 127.78, 126.59, 123.21, 119.85, 117.89, 117.75, 115.58, 115.11, 107.48, 66.85, 61.77 ppm

Elemental analysis calculated: C 75.09, H 4.73, N 10.95

Elemental analysis found: C 74.82, H 5.04, N 10.80

Synthesis of **3**



Chemical Formula: $C_{26}H_{24}N_4$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^tBu (0.6 mmol, 67 mg, 30 mol%), Mn-precatalyst (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a return condenser and a bubble counter. After 2 hours reaction time, 4-dimethylaminobenzaldehyde (2 mmol, 298.38 mg) is diluted in 0.7 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3x10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by recrystallization in hot ethyl acetate and obtained as yellow crystals (502 mg, 1.28 mmol, 64 %).

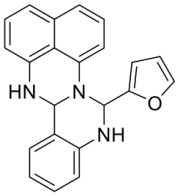
^{1}H NMR (DMSO-D6, 400 MHz, 293 K): δ = 7.33 – 7.27 (m, 3H), 7.23 (t, J = 7.9 Hz, 1H), 7.18 – 7.11 (m, 1H), 7.07 (t, J = 7.7 Hz, 2H), 7.01 (d, J = 7.7 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 6.85 (td, J = 6.9, 1.2 Hz, 2H), 6.75 (d, J = 8.9 Hz, 2H), 6.57 (dd, J = 7.7, 4.6 Hz, 2H), 6.46 (d, J = 4.1 Hz, 1H), 6.36 (t, J = 7.4 Hz, 1H), 5.14 (d, J = 3.8 Hz, 1H), 2.89 (s, 6H) ppm.

^{13}C NMR (DMSO-D6, 101 MHz, 293 K): δ = 149.98, 143.39, 141.33, 140.12, 134.27, 129.32, 127.81, 127.53, 126.82, 126.61, 125.30, 121.65, 117.58, 115.18, 113.82, 113.18, 112.31, 105.51, 105.14, 93.24, 65.13, 59.83, 54.93 ppm.

Elemental analysis calculated: C, 79.56; H, 6.16; N, 14.27

Elemental analysis found: C 79.29, H 6.04, N 14.54

Synthesis of **4**



Chemical Formula: $C_{22}H_{17}N_3O$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-precatalyst (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a return condenser and a bubble counter. After 2 hours reaction time, furfural (2 mmol, 166 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:0.5) and obtained as a yellow solid (577 mg, 1.70 mmol, 85 %). Single crystals of **4** were obtained by recrystallisation in ethyl acetate / pentane (3/1) at – 8 °C.

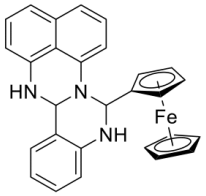
^{1}H NMR (DMSO-d6, 400 MHz, 293 K): δ = 7.68 (s, 1H), 7.28 (d, J = 3.4 Hz, 1H), 7.26 – 7.10 (m, 4H), 6.99 (d, J = 7.7 Hz, 1H), 6.96 – 6.84 (m, 3H), 6.64 (d, J = 7.4 Hz, 1H), 6.59 (d, J = 7.3 Hz, 1H), 6.54 (d, J = 4.2 Hz, 1H), 6.50 – 6.42 (m, 2H), 6.38 (d, J = 3.2 Hz, 1H), 5.30 (d, J = 3.2 Hz, 1H) ppm.

^{13}C NMR (DMSO-d6, 101 MHz, 293 K): δ = 153.93, 143.08, 142.78, 140.38, 134.32, 128.00, 126.91, 126.51, 125.46, 121.06, 118.01, 116.05, 115.56, 113.91, 113.75, 110.48, 109.23, 105.64, 105.48, 93.25, 61.26 ppm.

Elemental analysis calculated: C 77.86, H 5.05, N 12.38

Elemental analysis found: C 76.99, H 5.04, N 12.13

Synthesis of **5**



Chemical Formula: $C_{28}H_{23}FeN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-precatalyst (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a return condenser and a bubble counter. After 2 hours reaction time, ferrocenecarboxaldehyde (2 mmol, 428 mg) is diluted in 1.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature. The product precipitates during reaction. For purification it was filtrated, washed with H_2O and cold diethyl ether and dried at 70 °C in vacuo. The product is obtained as a pink solid (659 mg, 1.44 mmol, 72 %). Single crystals were grown in ethyl acetate / pentane (3/1) at – 8 °C.

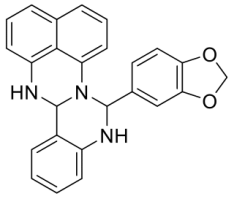
^{1}H NMR (DMSO-d6, 500 MHz, 293 K): δ = 7.30 (d, J = 3.6 Hz, 1H), 7.25 (t, J = 7.9 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.07 (t, J = 7.0 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 4.2 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 7.3 Hz, 1H), 6.44 (d, J = 4.1 Hz, 1H), 6.36 (t, J = 7.4 Hz, 1H), 5.30 (d, J = 3.4 Hz, 1H), 4.35 (s, 3H), 4.21 (s, 1H), 4.13 (s, 1H) ppm.

^{13}C NMR (DMSO-d6, 126 MHz, 293 K): δ = 143.34, 140.53, 140.02, 134.29, 127.86, 126.84, 126.52, 125.25, 121.15, 117.63, 115.22, 115.15, 113.61, 113.10, 105.45, 105.20, 89.74, 68.99, 68.72, 68.14, 66.83, 66.20, 63.43, 59.66 ppm.

Elemental analysis calculated: C 73.53, H 5.07, N 9.19

Elemental analysis found: C 72.78, H 5.05, N 9.02

Synthesis of **6**



Chemical Formula: $C_{25}H_{19}N_3O_2$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-aminobenzyl alcohol (2 mmol, 247 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-precatalyst (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a return condenser and a bubble counter. After 2 hours reaction time, piperonal (2 mmol, 301 mg) is diluted in 0.7 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via recrystallization in ethyl acetate at - 4 °C and obtained as yellow crystals (621 mg, 1.58 mmol, 79 %).

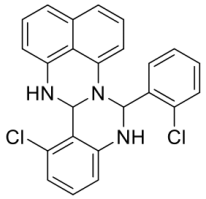
^{1}H NMR (DMSO-d6, 500 MHz, 293 K): δ = 7.32 (d, J = 3.8 Hz, 1H), 7.23 (t, J = 7.9 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.08 (dd, J = 13.7, 7.9 Hz, 2H), 7.01 (d, J = 7.8 Hz, 1H), 6.98 – 6.92 (m, 4H), 6.86 (t, J = 7.5 Hz, 1H), 6.58 (d, J = 7.7 Hz, 2H), 6.47 (d, J = 4.3 Hz, 1H), 6.38 (t, J = 7.4 Hz, 1H), 6.03 (d, J = 5.2 Hz, 2H), 5.13 (d, J = 3.7 Hz, 1H) ppm.

^{13}C NMR (DMSO-d6, 125 MHz, 293 K): δ = 147.62, 146.82, 143.05, 141.07, 140.00, 136.25, 134.26, 127.94, 126.88, 126.59, 125.37, 121.63, 120.35, 117.86, 115.50, 115.35, 113.81, 113.30, 108.11, 106.95, 105.65, 105.34, 101.15, 65.28, 59.94 ppm.

Elemental analysis calculated: C 76.32, H 4.87, N 10.68

Elemental analysis found: C 75.61, H 4.79, N 11.18

Synthesis of **7**



Chemical Formula: $C_{24}H_{17}Cl_2N_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-6-chlorobenzyl alcohol (2 mmol, 315 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-precatalyst (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a return condenser and a bubble counter. After 2 hours reaction time, 2-chlorobenzaldehyde (2 mmol, 225 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:2) and obtained as a yellow solid (594 mg, 1.42 mmol, 71 %). Single crystals were grown in ethyl acetate / pentane (3/1) at – 8 °C.

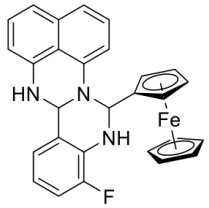
^{1}H NMR (DMSO-d6, 500 MHz, 293 K): δ = 7.85 (d, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.23 (dd, J = 15.5, 7.8 Hz, 2H), 7.13 (dd, J = 13.9, 5.5 Hz, 3H), 6.92 (t, J = 7.8 Hz, 1H), 6.81 (s, 1H), 6.77 – 6.69 (m, 3H), 6.11 (s, 1H), 5.93 (d, J = 7.1 Hz, 1H), 5.45 (s, 1H) ppm.

^{13}C NMR (DMSO-d6, 126 MHz, 293 K): δ = 145.25, 141.84, 140.24, 137.25, 134.23, 132.15, 131.46, 130.29, 129.97, 128.98, 127.22, 126.69, 125.12, 122.93, 116.42, 116.03, 115.54, 112.72, 105.71, 65.08, 64.38 ppm.

Elemental analysis calculated: C 68.91, H 4.10, N 10.05

Elemental analysis found: C 68.91, H 4.11, N 10.04

Synthesis of **8**



Chemical Formula: $C_{28}H_{22}FFeN_3$

In a glovebox, 1,8-diaminonaphthalene (2 mmol, 316 mg), 2-amino-4-fluorobenzyl alcohol (2 mmol, 228 mg), KO^{t}Bu (0.6 mmol, 67 mg, 30 mol%), Mn-precatalyst (0.02 mmol, 12 mg, 1 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a return condenser and a bubble counter. After 2 hours reaction time, furfural (2 mmol, 166 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3 x 10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1→5:3) and obtained as an orange solid (713 mg, 1.50 mmol, 75 %). Single crystals of **8** were obtained by dissolving the product in very less acetonitrile and slow diffusion of pentane in the solution.

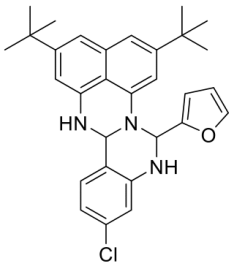
^{1}H NMR (DMSO-d6, 500 MHz, 293 K): δ = 7.39 (d, J = 4.0 Hz, 1H), 7.26 (t, J = 7.9 Hz, 1H), 7.18 – 7.08 (m, 1H), 7.07 (d, J = 24.0 Hz, 1H), 6.99 – 6.91 (m, 1H), 6.88 – 6.80 (m, 1H), 6.78 (d, J = 5.2 Hz, 1H), 6.55 (d, J = 7.4 Hz, 1H), 6.50 (d, J = 5.1 Hz, 1H), 6.36 (dd, J = 12.8, 7.8 Hz, 1H), 5.36 (d, J = 3.8 Hz, 1H), 4.38 (s, 1H), 4.35 (s, 2H), 4.23 (s, 1H), 4.14 (d, J = 11.9 Hz, 1H) ppm.

^{13}C NMR (DMSO-d6, 126 MHz, 293 K): δ = 150.45, 148.55, 140.09, 139.61, 134.24, 131.50, 131.40, 126.92, 126.54, 124.31, 124.28, 121.10, 118.02, 115.40, 114.31, 114.25, 113.63, 113.50, 105.64, 105.39, 89.45, 69.03, 68.81, 68.02, 66.97, 66.28, 63.13, 59.33, 39.52 ppm.

Elemental analysis calculated: C 70.75, H 4.67, N 8.84

Elemental analysis found: C 70.55, H 4.66, N 8.84

Synthesis of **9**



Chemical Formula: $C_{30}H_{32}ClN_3O$

In a glovebox, 1,8-diamino-4,6-di-*tert*-butyl-naphthalene (1 mmol, 270.5 mg), 2-amino-4-chloro-benzyl alcohol (1 mmol, 157 mg), KO^{t}Bu (0.3 mmol, 33 mg, 30 mol%), Mn-precatalyst (0.01 mmol, 6 mg, 2 mol%) and 3 mL 2-MeTHF are added to a Schlenk tube. The reaction mixture is heated at 100 °C using an open system consisting of a return condenser and a bubble counter. After 2 hours reaction time, furfural (1 mmol, 83 µL) is diluted in 0.5 mL 2-MeTHF and added with a syringe to the reaction mixture via a septum. After stirring for 15 h, the mixture is cooled down to room temperature and 2 mL H_2O is added. The aqueous phase is extracted with dichloromethane (3x10 mL), the organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via column chromatography over Alox N (pentane/ethyl acetate: 5:1) and obtained as an orange solid (354 mg, 0.73 mmol, 73 %). Single crystals were grown in ethyl acetate / pentane (3/1) at – 8 °C.

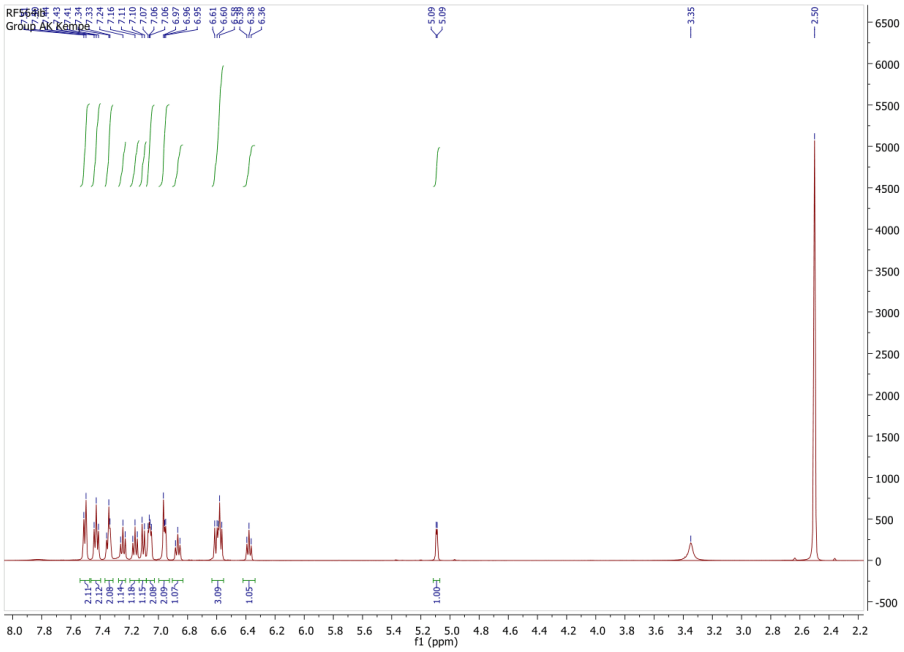
^{1}H NMR (DMSO-D6, 500 MHz, 293 K): δ = 7.68 (d, J = 0.7 Hz, 1H), 7.15 (dd, J = 9.9, 6.0 Hz, 2H), 7.09 (d, J = 0.8 Hz, 1H), 7.03 (d, J = 3.0 Hz, 1H), 6.97 (d, J = 1.5 Hz, 1H), 6.89 (s, 1H), 6.67 (dd, J = 10.2, 1.8 Hz, 2H), 6.56 (d, J = 3.6 Hz, 1H), 6.50 (dd, J = 8.2, 2.0 Hz, 1H), 6.45 (dd, J = 3.1, 1.8 Hz, 1H), 6.40 (d, J = 3.2 Hz, 1H), 5.24 (d, J = 2.9 Hz, 1H), 1.30 (s, 21H) ppm.

^{13}C NMR (CD_3CN, 125 MHz, 293 K): δ = 153.56, 149.17, 148.71, 144.38, 143.14, 139.67, 139.39, 133.99, 132.44, 127.47, 119.69, 115.40, 114.36, 112.60, 111.99, 111.42, 110.51, 109.41, 105.37, 103.78, 61.93, 61.12, 34.80, 34.42, 31.21, 31.11 ppm.

Elemental analysis calculated: C 74.13; H 6.64; N, 8.65

Elemental analysis found: C 74.42, H 6.35, N 8.72

^{1}H-NMR of fertigine 1, clearly showing one dataset in the spectrum indicating a diastereoselectivity of the synthesis.



2 X-ray crystallography of fertigines 1 – 9.

The obtained single crystals were mounted on a cryoloop (MiTeGen) with a layer of fomblin YR-1800 (CAS: 69991-67-9). All measurements were performed on a STOE STADIVARI [λ(Mo Kα) = 0.71073 Å] equipped with a dectris (Pilatus 200 K – 20 Hz) detector and an Oxford Cryostream low temperature unit. Structure solution and refinement was accomplished with OlexSys2,[3] SHELXL-2014,[4] WinGX,[5] and Mercury 2020.1.[6] Non-hydrogen atoms were anisotropically refined, hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. In table S 1 – table S2 are shown crystallographic details of the investigated fertigines **1** – **9**. The figures S 2 - S 6 show graphically the planes used for the calculations of the plane angles α, β, γ of the three different aromatic regions of the fertigines. Crystallographic data for the structures of all discussed compounds have been deposited in the Cambridge Crystallographic Data Centre and can be accessed with the respective CCDC number.

Table S 1: Crystallographic details of fertigines **1** - **3**.

Crystal	**1**	**2**	**3**
CCDC No.	2083140	2083142	2083143
Empirical	C24 H19 N3	C26 H21 Cl1 N4	C26 H24 N4
M/g mol^{-1}	349.42	424.92	392.49
Crystal	monoclinic	orthorhombic	monoclinic
Space	P 21/c	P 21 21 21	P 21/n
a/Å	5.7600(12)	8.9900(18)	9.860(2)
b/Å	11.550(2)	14.420(3)	9.1400(18)
c/Å	25.410(5)	16.840(3)	23.000(5)
α/°	90	90	90
β/°	90.70(3)	90	101.10(3)
γ/°	90	90	90
V/Å^3	1690.4(6)	2183.1(7)	2034.0(8)
Z	4	4	4
Crystal	0.18x0.049x0.031	0.065x0.051x0.047	0.056x0.034x0.009
ρ/(g cm^3)	1.373	1.293	1.282
μ/mm^{-1}	0.082	0.196	0.077
T/K	133	133	133
θ range/°	1.935-28.51	2.825-28.63	2.405-28.565
No. of	2915	3746	2714
No. of	4090	4160	4747
R_{int}	0.0246	0.0798	0.0468
wR_2 (all	0.1155	0.1775	0.1330
R_1	0.0433	0.0561	0.0544

Table S 2: Crystallographic details of fertigines **4** - **9**.

Compound	**4**	**5**	**6**
CCDC No.	2083141	2083149	2083146
Empirical formula	C22 H17 N3 O1	C28 H23 Fe1 N3	C25 H19 N3 O2
M/g mol^{-1}	339.39	457.34	393.43
Crystal system	orthorhombic	monoclinic	triclinic
Space group	P b c a	Cc	P -1
a/Å	16.580(3)	16.060(3)	5.5100(11)
b/Å	8.5600(17)	13.120(3)	9.770(2)
c/Å	22.590(5)	9.870(2)	16.910(3)
α/°	90	90	91.00(3)
β/°	90	97.60(3)	92.80(3)
γ/°	90	90	97.30(3)
V/Å^3	3206.1(11)	2061.4(8)	901.6(3)
Z	8	4	2
Crystal size	0.049x0.035x0.02	0.134x0.127x0.001	0.204x0.128x0.055
ρ/(g cm^3)	1.406	1.474	1.449
μ/mm^{-1}	0.089	0.754	0.094
T/K	133	133	133
θ range/°	2.826-28.439	3.740-28.502	3.16-28.48
No. of refl. unique	1670	3194	2962
No. of refl. obs.	3799	3514	4208
R_{int}	0.1330	0.0256	0.0311
wR_2 (all data)	0.2722	0.0993	0.1580
R_1	0.0948	0.0358	0.0520
Compound	**7**	**8**	**9**
CCDC No.	2083153	2083151	2083155
Empirical formula	C24 H17 Cl2 N3	C28 H22 F1 Fe1 N3	C30 H32 Cl1 N3 O1
M/g mol^{-1}	418.31	475.34	486.04
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	P n a 21	Cc	P 21/n
a/Å	10.240(2)	16.150(3)	14.530(3)
b/Å	23.510(5)	13.450(3)	8.4200(17)
c/Å	8.0200(16)	9.7400(19)	20.820(4)
α/°	90	90	90
β/°	90	97.90(3)	95.30(3)
γ/°	90	90	90
V/Å^3	1930.8(7)	2095.6(7)	2536.3(9)
Z	4	4	4
Crystal size	0.19x0.033x0.006	0.053x0.047x0.035	0.069x0.009x0.006
ρ/(g cm^3)	1.439	1.507	1.273
μ/mm^{-1}	0.352	0.751	0.179
T/K	133	200	133
θ range/°	2.17-28.52	3.02-27.965	2.795-28.825
No. of refl. unique	3514	2505	3770
No. of refl. obs.	3919	2909	6088
R_{int}	0.0376	0.0266	0.0611
wR_2 (all data)	0.1127	0.0861	0.2972
R_1	0.0417	0.0337	0.0858

Visualization of the planes for the calculation of the respective plane angles

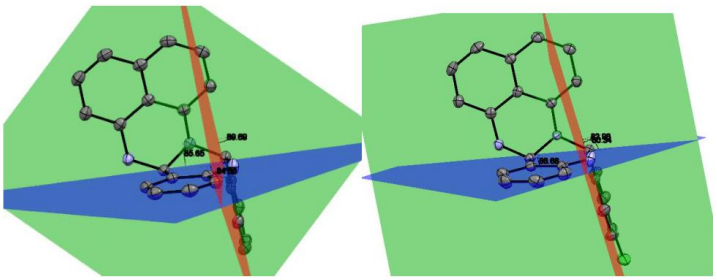


Figure S 2: Planes of the aromatic regions used for the calculation of the plane angles α, β, γ of **1** and **3**.

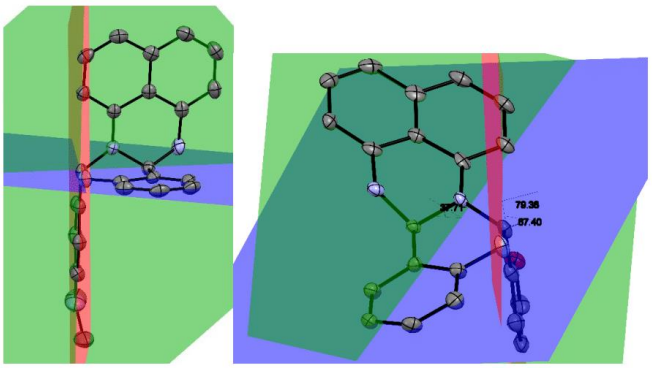


Figure S 3: Planes of the aromatic regions used for the calculation of the plane angles α, β, γ of **3** and **4**.

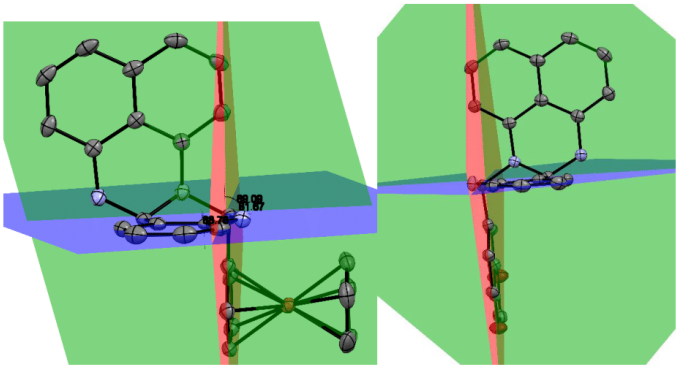


Figure S 4: Planes of the aromatic regions used for the calculation of the plane angles α, β, γ of **5** and **6**.

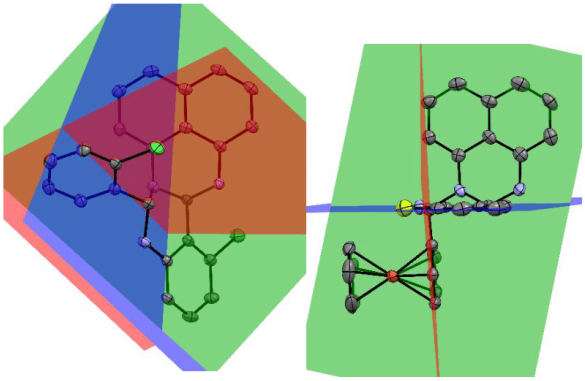


Figure S 5: Planes of the aromatic regions used for the calculation of the plane angles α, β, γ of **7** and **8**.

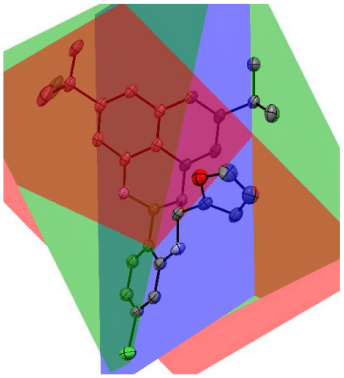


Figure S 6: Planes of the aromatic regions used for the calculation of the plane angles α, β, γ of **9**.

CheckCif reports

Fertigine 1

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv499_1_m_p21c

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv499_1_m_p21c

Bond precision: C-C = 0.0020 A Wavelength=0.71073

Cell: a=5.7600(12) b=11.550(2) c=25.410(5)
alpha=90 beta=90.70(3) gamma=90
Temperature: 133 K

	Calculated	Reported
Volume	1690.4(6)	1690.4(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C24 H19 N3	C24 H19 N3
Sum formula	C24 H19 N3	C24 H19 N3
Mr	349.42	349.42
Dx,g cm-3	1.373	1.373
Z	4	4
Mu (mm-1)	0.082	0.082
F000	736.0	736.0
F000'	736.24	
h,k,lmax	7,15,34	7,15,33
Nref	4271	4090
Tmin,Tmax	0.995,0.997	
Tmin'	0.985	

Correction method= Not given

Data completeness= 0.958 Theta(max)= 28.448

R(reflections)= 0.0433(2915) wR2(reflections)= 0.1155(4090)

S = 1.039 Npar= 320

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
CRYSC01_ALERT_1_C The word below has not been recognised as a standard
           identifier.
           yellowish
PLAT222_ALERT_3_C NonSolvent Resd 1  H   Uiso(max)/Uiso(min) Range        7.0 Ratio
PLAT245_ALERT_2_C U(iso) H24       Smaller than U(eq) C24       by      0.015 Ang**2
PLAT410_ALERT_2_C Short Intra H...H Contact  H1       ..H8       .       1.96 Ang.
                                             x,y,z  =      1_555 Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N1       --Hn1      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N3       --H5       .     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.149 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          7 Report
```

Alert level G

```
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          4 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          1 Note
PLAT793_ALERT_4_G Model has Chirality at C11         (Centro SPGR)         S Verify
PLAT793_ALERT_4_G Model has Chirality at C18         (Centro SPGR)         R Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        171 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........        3.2 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         17 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          2 Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   8 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   9 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   5 ALERT type 2 Indicator that the structure model may be wrong or deficient
   5 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

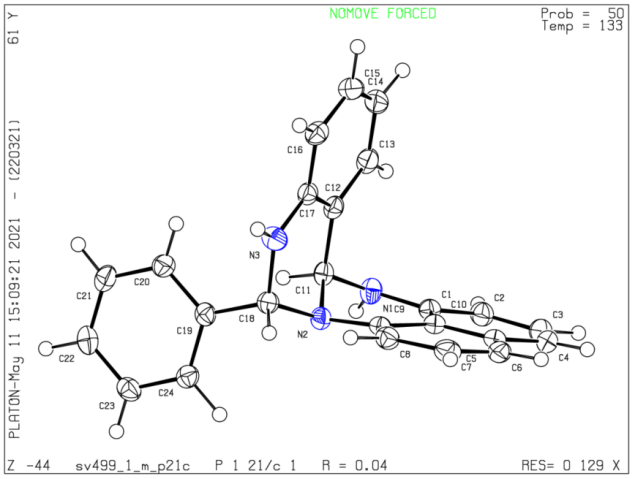
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 22/03/2021; check.def file version of 19/03/2021

Datablock sv499_1_m_p21c - ellipsoid plot



Fertigine 2

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv530_1_o_p212121

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv530_1_o_p212121

```
Bond precision:  C-C = 0.0052 A          Wavelength=0.71073

Cell:             a=8.9900(18)      b=14.420(3)      c=16.840(3)
                  alpha=90          beta=90          gamma=90
Temperature:      133 K

                 Calculated                Reported
Volume           2183.1(7)                 2183.1(8)
Space group      P 21 21 21                P 21 21 21
Hall group       P 2ac 2ab                 P 2ac 2ab
Moiety formula   C24 H18 Cl N3, C2 H3 N    C24 H18 Cl N3, C2 H3 N
Sum formula      C26 H21 Cl N4             C26 H21 Cl N4
Mr               424.92                    424.92
Dx,g cm-3        1.293                     1.293
Z                4                         4
Mu (mm-1)        0.196                     0.196
F000             888.0                     888.0
F000'            888.86
h,k,lmax         12,19,22                  12,19,22
Nref             5525[ 3119]               4160
Tmin,Tmax        0.988,0.991               0.086,0.992
Tmin'            0.987

Correction method= # Reported T Limits: Tmin=0.086 Tmax=0.992
AbsCorr = NUMERICAL

Data completeness= 1.33/0.75      Theta(max)= 28.480

R(reflections)= 0.0561( 3746)     wR2(reflections)= 0.1775( 4160)

S = 1.110                 Npar= 282
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without
          a literature citation. This should be contained in the
          _exptl_absorpt_process_details field.
          Absorption correction given as numerical
STRVA01_ALERT_2_C          Chirality of atom sites is inverted?
          From the CIF: _refine_ls_abs_structure_Flack    0.740
          From the CIF: _refine_ls_abs_structure_Flack_su    0.120
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00523 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H8       ..H18      .       1.94 Ang.
                                                    x,y,z  =      1_555 Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N3       --Hn3      .     Please Check
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
            C24 H18 Cl N3
PLAT907_ALERT_2_C Flack x > 0.5, Structure Needs to be Inverted? .       0.74 Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).          7 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         25 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .         12 Check
PLAT939_ALERT_3_C Large Value of Not (SHELXL) Weight Optimized S .      14.86 Check
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          2 Report
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero .      0.740 Note
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.12 Report
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          3 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          2 Note
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          2 Note
            C2 H3 N
PLAT791_ALERT_4_G Model has Chirality at C11         (Sohnke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C18         (Sohnke SpGr)          R Verify
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..          ! Info
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        186 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         20 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..........        2.2 Low
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
 11 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 12 ALERT level G = General information/check it is not something unexpected

  1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  6 ALERT type 2 Indicator that the structure model may be wrong or deficient
  6 ALERT type 3 Indicator that the structure quality may be low
  9 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

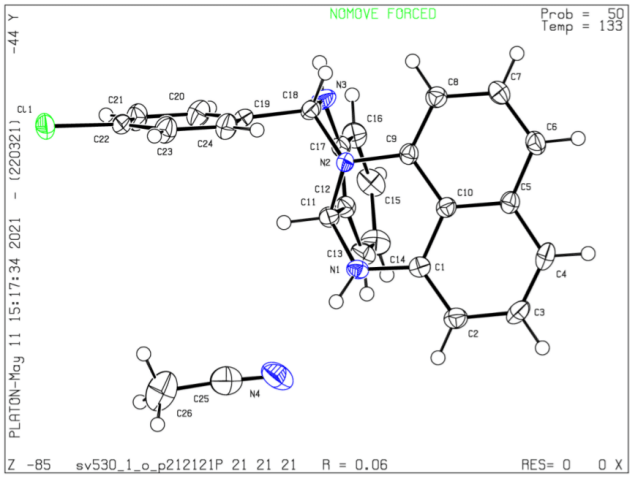
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 22/03/2021; check.def file version of 19/03/2021

Datablock sv530_1_o_p212121 - ellipsoid plot



Fertigine 3

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv539_1_m_p21n

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv539_1_m_p21n

```
Bond precision:  C-C = 0.0029 A          Wavelength=0.71073

Cell:             a=9.860(2)     b=9.1400(18)         c=23.000(5)
                  alpha=90       beta=101.10(3)       gamma=90
Temperature:      133 K

                 Calculated                Reported
Volume           2034.0(8)                 2034.0(7)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C26 H24 N4                C26 H24 N4
Sum formula      C26 H24 N4                C26 H24 N4
Mr               392.49                    392.49
Dx,g cm-3        1.282                     1.282
Z                4                         4
Mu (mm-1)        0.077                     0.077
F000             832.0                     832.0
F000'            832.27
h,k,lmax         13,12,30                  13,12,30
Nref             5114                      4747
Tmin,Tmax        0.997,0.999
Tmin'            0.996

Correction method= Not given

Data completeness= 0.928           Theta(max)= 28.429

R(reflections)= 0.0544( 2714)      wR2(reflections)= 0.1330( 4747)

S = 0.965                  Npar= 273
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N3       --Hn3      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N1       --Hn1      .     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      3.478 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         43 Report
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          2 Report
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          4 Note
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....        C26 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          2 Note
PLAT793_ALERT_4_G Model has Chirality at C11         (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C18         (Centro SPGR)          S Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        323 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          1 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        2.3 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          3 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          2 Check
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 12 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  3 ALERT type 2 Indicator that the structure model may be wrong or deficient
  5 ALERT type 3 Indicator that the structure quality may be low
  6 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

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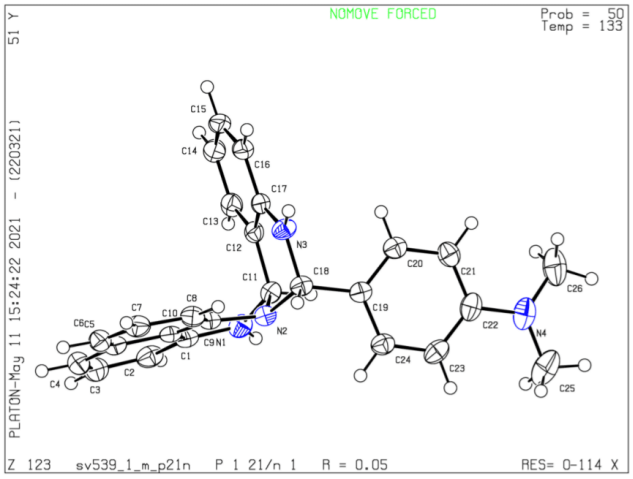
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 22/03/2021; check.def file version of 19/03/2021

Datablock sv539_1_m_p21n - ellipsoid plot



Fertigine 4

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv529_1_o_pbca

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv529_1_o_pbca

Bond precision: C-C = 0.0060 A Wavelength=0.71073

Cell: a=16.580(3) b=8.5600(17) c=22.590(5)
alpha=90 beta=90 gamma=90
Temperature: 133 K

	Calculated	Reported
Volume	3206.1(11)	3206.1(11)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C22 H17 N3 O	C22 H17 N3 O
Sum formula	C22 H17 N3 O	C22 H17 N3 O
Mr	339.39	339.38
Dx,g cm-3	1.406	1.406
Z	8	8
Mu (mm-1)	0.089	0.089
F000	1424.0	1424.0
F000'	1424.53	
h,k,lmax	22,11,30	21,11,29
Nref	4034	3799
Tmin,Tmax	0.996,0.998	
Tmin'	0.996	

Correction method= Not given

Data completeness= 0.942 Theta(max)= 28.439

R(reflections)= 0.0948(1670) wR2(reflections)= 0.2722(3799)

S = 0.884 Npar= 235

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
DIFMN02_ALERT_2_C  The minimum difference density is < -0.1*ZMAX*0.75
           _refine_diff_density_min given =     -0.612
           Test value =     -0.600
DIFMN03_ALERT_1_C  The minimum difference density is < -0.1*ZMAX*0.75
           The relevant atom site should be identified.
DIFMX02_ALERT_1_C  The maximum difference density is > 0.1*ZMAX*0.75
           The relevant atom site should be identified.
RINTA01_ALERT_3_C  The value of Rint is greater than 0.12
           Rint given   0.133
PLAT020_ALERT_3_C The Value of Rint is Greater Than 0.12 .........      0.133 Report
PLAT026_ALERT_3_C Ratio Observed / Unique Reflections (too) Low ..        44% Check
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ...................       0.27 Report
PLAT097_ALERT_2_C Large Reported Max.  (Positive) Residual Density       0.63 eA-3
PLAT098_ALERT_2_C Large Reported Min.  (Negative) Residual Density      -0.61 eA-3
PLAT213_ALERT_2_C Atom C2              has ADP max/min Ratio .....        3.1 oblate
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.3 Note
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00595 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor       N2       --H2       .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N3       --H3       .     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      3.136 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         22 Report
PLAT976_ALERT_2_C Check Calcd Resid. Dens.  0.95A   From N3             -0.56 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H3               -0.52 eA-3
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          2 Report
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.16 Report
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          3 Note
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O1             106.9 Degree
PLAT793_ALERT_4_G Model has Chirality at C13         (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C22         (Centro SPGR)          R Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        198 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          9 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          4 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
 18 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 10 ALERT level G = General information/check it is not something unexpected

  2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 13 ALERT type 2 Indicator that the structure model may be wrong or deficient
  8 ALERT type 3 Indicator that the structure quality may be low
  4 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

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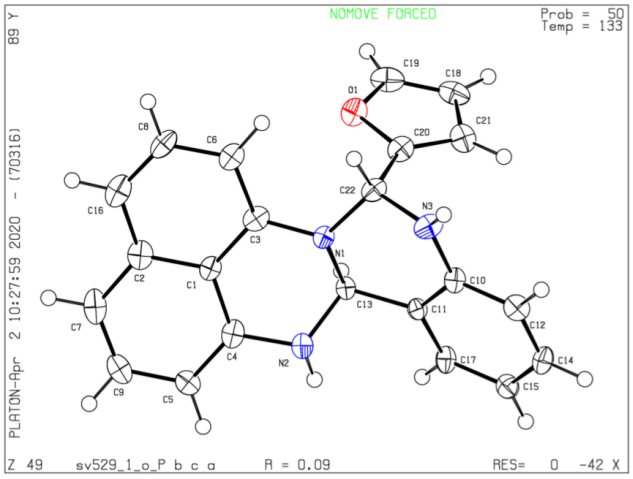
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 22/12/2019; check.def file version of 13/12/2019

Datablock sv529_1_o_pbca - ellipsoid plot



Fertigine 5

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv545_4_m_cc_a2

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv545_4_m_cc_a2

```
Bond precision:  C-C = 0.0050 A          Wavelength=0.71073

Cell:             a=16.060(3)      b=13.120(3)        c=9.870(2)
                  alpha=90         beta=97.60(3)      gamma=90
Temperature:      133 K

                 Calculated                Reported
Volume           2061.4(8)                 2061.4(7)
Space group      C c                       C 1 c 1
Hall group       C -2yc                    C -2yc
Moiety formula   C28 H23 Fe N3             C28 H23 Fe N3
Sum formula      C28 H23 Fe N3             C28 H23 Fe N3
Mr               457.34                    457.36
Dx,g cm-3        1.474                     1.474
Z                4                         4
Mu (mm-1)        0.754                     0.754
F000             952.0                     953.7
F000'            953.64
h,k,lmax         21,17,13                  20,17,12
Nref             5210[ 2609]               3514
Tmin,Tmax        0.903,0.999               0.995,0.998
Tmin'            0.903

Correction method= # Reported T Limits: Tmin=0.995 Tmax=0.998
AbsCorr = NUMERICAL

Data completeness= 1.35/0.67      Theta(max)= 28.500

R(reflections)= 0.0358( 3194)     wR2(reflections)= 0.0993( 3514)

S = 0.930                 Npar= 290
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without
          a literature citation. This should be contained in the
          _exptl_absorpt_process_details field.
          Absorption correction given as numerical
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low .      0.974 Why?
PLAT410_ALERT_2_C Short Intra H...H Contact  H10      ..H12      .       1.95 Ang.
                                             x,y,z  =      1_555 Check
PLAT420_ALERT_2_C D-H Without Acceptor       N2       --H2       .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N3       --H3A      .     Please Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).          5 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         12 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          1 Check
```

Alert level G

```
PLAT073_ALERT_1_G H-atoms ref, but _hydrogen_treatment Reported as     constr Check
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =           4 Note
PLAT792_ALERT_1_G Model has Chirality at C4          (Polar  SPGR)          S Verify
PLAT792_ALERT_1_G Model has Chirality at C12         (Polar  SPGR)          R Verify
PLAT794_ALERT_5_G Tentative Bond Valency for Fe1       (II)       .       2.15 Info
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..          ! Info
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         125 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          1 Note
PLAT916_ALERT_2_G Hooft y and Flack x Parameter Values Differ by .       0.11 Check
PLAT982_ALERT_1_G The Fe-f'=    0.3582 Deviates from  IT-value =       0.3463 Check
PLAT983_ALERT_1_G The Fe-f"=    0.8493 Deviates from  IT-Value =       0.8444 Check
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  8 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 11 ALERT level G = General information/check it is not something unexpected

  6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  4 ALERT type 2 Indicator that the structure model may be wrong or deficient
  5 ALERT type 3 Indicator that the structure quality may be low
  3 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

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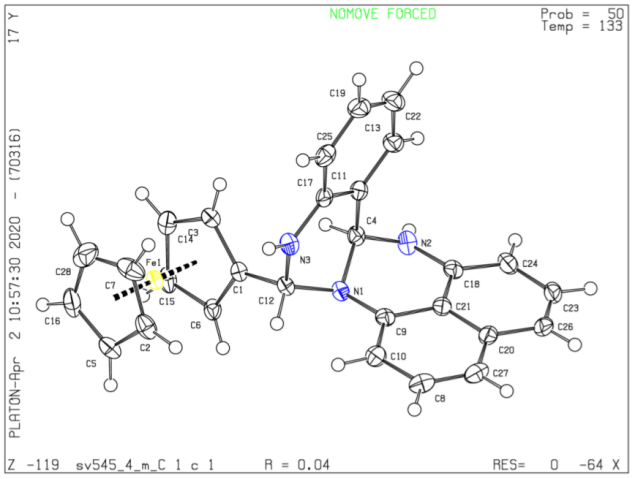
PLATON version of 22/12/2019; check.def file version of 13/12/2019

Datablock sv545_4_m_cc_a2 - ellipsoid plot



Fertigine 6

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv542_1_t_p-1

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv542_1_t_p-1

Bond precision: C-C = 0.0022 A Wavelength=0.71073

Cell: a=5.5100(11) b=9.770(2) c=16.910(3)
alpha=91.00(3) beta=92.80(3) gamma=97.30(3)
Temperature: 133 K

	Calculated	Reported
Volume	901.6(3)	901.6(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C25 H19 N3 O2	C25 H19 N3 O2
Sum formula	C25 H19 N3 O2	C25 H19 N3 O2
Mr	393.43	393.43
Dx,g cm-3	1.449	1.449
Z	2	2
Mu (mm-1)	0.094	0.094
F000	412.0	412.0
F000'	412.17	
h,k,lmax	7,13,22	7,12,22
Nref	4561	4208
Tmin,Tmax	0.986,0.995	0.987,0.996
Tmin'	0.981	

Correction method= # Reported T Limits: Tmin=0.987 Tmax=0.996
AbsCorr = NUMERICAL

Data completeness= 0.923 Theta(max)= 28.454

R(reflections)= 0.0520(2962) wR2(reflections)= 0.1580(4208)

S = 1.009 Npar= 271

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without
           a literature citation. This should be contained in the
           _exptl_absorpt_process_details field.
           Absorption correction given as numerical
PLAT410_ALERT_2_C Short Intra H...H Contact  H8       ..H15      .       1.94 Ang.
                                             x,y,z  =      1_555 Check
PLAT420_ALERT_2_C D-H Without Acceptor       N2       --H2       .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N3       --H3       .     Please Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).          5 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         35 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          2 Check
PLAT975_ALERT_2_C Check Calcd Resid. Dens.  0.97A   From N2              0.45 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H2               -0.53 eA-3
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............           2 Report
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large        0.11 Report
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)        0.03 Degree
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =           6 Note
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O1             105.8 Degree
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O2             106.0 Degree
PLAT793_ALERT_4_G Model has Chirality at C5          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C8          (Centro SPGR)          S Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        307 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          6 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         12 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          1 Check
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  9 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 13 ALERT level G = General information/check it is not something unexpected

  3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 10 ALERT type 2 Indicator that the structure model may be wrong or deficient
  3 ALERT type 3 Indicator that the structure quality may be low
  4 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

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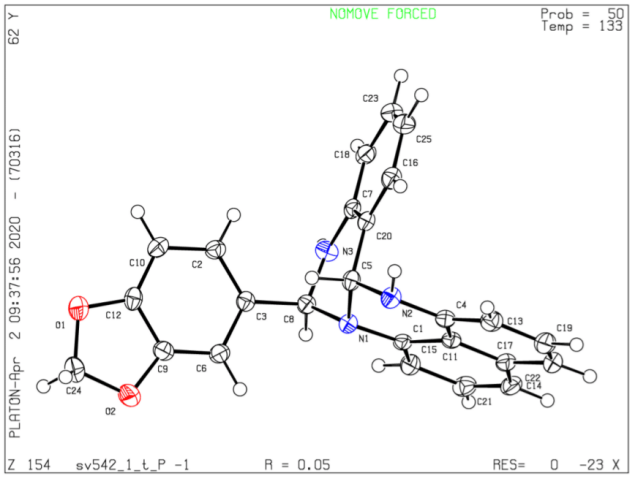
PLATON version of 22/12/2019; check.def file version of 13/12/2019

Datablock sv542_1_t_p-1 - ellipsoid plot



Fertigine 7

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv553_1_o_pna21

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv553_1_o_pna21

```
Bond precision:  C-C = 0.0046 A          Wavelength=0.71073

Cell:            a=10.240(2)      b=23.510(5)      c=8.0200(16)
                 alpha=90         beta=90          gamma=90
Temperature:     133 K

                Calculated                Reported
Volume          1930.8(7)                 1930.8(7)
Space group     P n a 21                  P n a 21
Hall group      P 2c -2n                  P 2c -2n
Moiety formula  C24 H17 Cl2 N3            C24 H17 Cl2 N3
Sum formula     C24 H17 Cl2 N3            C24 H17 Cl2 N3
Mr              418.31                    418.30
Dx,g cm-3       1.439                     1.439
Z               4                         4
Mu (mm-1)       0.352                     0.352
F000            864.0                     864.0
F000'           865.44
h,k,lmax        13,31,10                  13,31,10
Nref            4881[ 2610]               3919
Tmin,Tmax       0.986,0.998               0.967,0.990
Tmin'           0.935

Correction method= # Reported T Limits: Tmin=0.967 Tmax=0.990
AbsCorr = NUMERICAL

Data completeness= 1.50/0.80      Theta(max)= 28.481

R(reflections)= 0.0417( 3514)     wR2(reflections)= 0.1127( 3919)

S = 1.010                 Npar= 263
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without
           a literature citation. This should be contained in the
           _exptl_absorpt_process_details field.
           Absorption correction given as numerical
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00456 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor       N1       --H1       .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N3       --H3       .     Please Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          8 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          1 Check
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          2 Report
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          3 Note
PLAT792_ALERT_1_G Model has Chirality at C11         (Polar  SPGR)          R Verify
PLAT792_ALERT_1_G Model has Chirality at C18         (Polar  SPGR)          S Verify
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..          ! Info
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        107 Note
PLAT916_ALERT_2_G Hooft y and Flack x Parameter Values Differ by .       0.17 Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   8 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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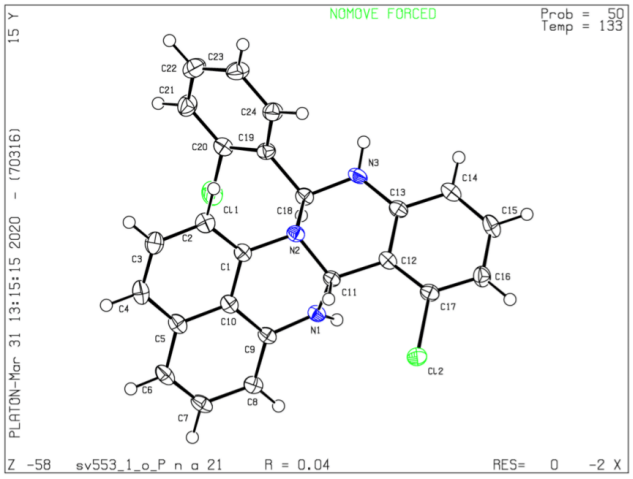
PLATON version of 22/12/2019; check.def file version of 13/12/2019

Datablock sv553_1_o_pna21 - ellipsoid plot



Fertigine 8

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv551_1_m_c2c

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv551_1_m_c2c

```
Bond precision:  C-C = 0.0067 A          Wavelength=0.71073

Cell:            a=16.150(3)     b=13.450(3)       c=9.7400(19)
                 alpha=90        beta=97.90(3)     gamma=90
Temperature:     200 K

                Calculated                Reported
Volume          2095.6(7)                 2095.6(7)
Space group     C c                       C 1 c 1
Hall group      C -2yc                    C -2yc
Moiety formula  C28 H22 F Fe N3           C28 H22 F Fe N3
Sum formula     C28 H22 F Fe N3           C28 H22 F Fe N3
Mr              475.34                    475.33
Dx,g cm-3       1.507                     1.507
Z               4                         4
Mu (mm-1)       0.751                     0.751
F000            984.0                     984.0
F000'           985.70
h,k,lmax        21,18,13                  21,17,13
Nref            5361[ 2685]               2909
Tmin,Tmax       0.961,0.974               0.969,0.984
Tmin'           0.961

Correction method= # Reported T Limits: Tmin=0.969 Tmax=0.984
AbsCorr = ANALYTICAL

Data completeness= 1.08/0.54      Theta(max)= 28.588

R(reflections)= 0.0337( 2505)     wR2(reflections)= 0.0861( 2909)

S = 1.035                 Npar= 299
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without
           a literature citation. This should be contained in the
           _exptl_absorpt_process_details field.
           Absorption correction given as analytical
PLAT241_ALERT_2_C High   MainMol Ueq as Compared to Neighbors of        C26 Check
PLAT241_ALERT_2_C High   MainMol Ueq as Compared to Neighbors of        C28 Check
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00672 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H3       ..H14      .      1.96 Ang.
                                                    x,y,z  =      1_555 Check
PLAT420_ALERT_2_C D-H Without Acceptor       N1       --H1       .     Please Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         22 Report
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          2 Report
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          4 Note
PLAT792_ALERT_1_G Model has Chirality at C4          (Polar  SPGR)          R Verify
PLAT792_ALERT_1_G Model has Chirality at C14         (Polar  SPGR)          S Verify
PLAT794_ALERT_5_G Tentative Bond Valency for Fe1       (II)      .       2.20 Info
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..          ! Info
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        165 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          1 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
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   3 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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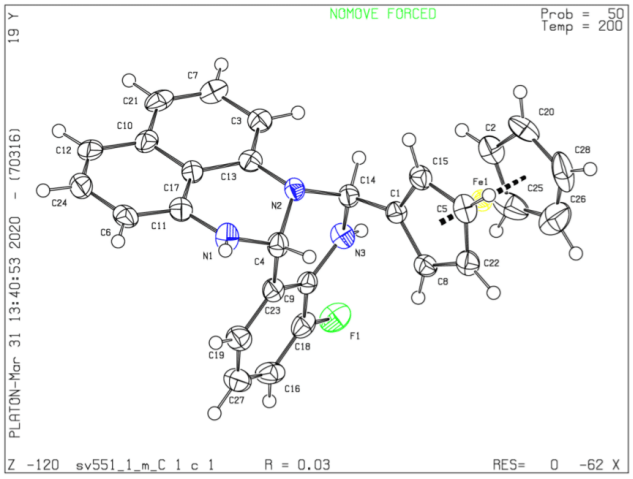
PLATON version of 22/12/2019; check.def file version of 13/12/2019

Datablock sv551_1_m_c2c - ellipsoid plot



Fertigine 9

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) sv586_1_m_p21n

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: sv586_1_m_p21n

```
Bond precision:  C-C = 0.0050 A          Wavelength=0.71073

Cell:             a=14.530(3)     b=8.4200(17)       c=20.820(4)
                  alpha=90        beta=95.30(3)      gamma=90
Temperature:      133 K

                 Calculated                Reported
Volume           2536.3(9)                 2536.3(9)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C30 H32 Cl N3 O           C30 H32 Cl N3 O
Sum formula      C30 H32 Cl N3 O           C30 H32 Cl N3 O
Mr               486.04                    486.03
Dx,g cm-3        1.273                     1.273
Z                4                         4
Mu (mm-1)        0.179                     0.179
F000             1032.0                    1032.0
F000'            1032.94
h,k,lmax         19,11,28                  19,11,27
Nref             6674                      6088
Tmin,Tmax        0.998,0.999
Tmin'            0.988

Correction method= Not given

Data completeness= 0.912          Theta(max)= 28.867

R(reflections)= 0.0858( 3770)     wR2(reflections)= 0.2972( 6088)

S = 1.059                 Npar= 326
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ...................       0.30 Report
PLAT222_ALERT_3_C NonSolvent Resd 1  H   Uiso(max)/Uiso(min) Range       10.0 Ratio
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C23 Check
PLAT245_ALERT_2_C U(iso) H18       Smaller than U(eq) C18       by      0.022 Ang**2
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00497 Ang.
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N3       --Hn3      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N1       --Hn1      .     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      4.634 Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).         6 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        62 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .         4 Check
PLAT975_ALERT_2_C Check Calcd Resid. Dens.  1.07A   From N1              0.57 eA-3
PLAT975_ALERT_2_C Check Calcd Resid. Dens.  0.97A   From N3              0.42 eA-3
PLAT975_ALERT_2_C Check Calcd Resid. Dens.  1.07A   From N3              0.42 eA-3
PLAT976_ALERT_2_C Check Calcd Resid. Dens.  1.03A   From N3             -0.55 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on Hn3              -0.39 eA-3
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............         2 Report
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large      0.17 Report
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =         4 Note
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O1           106.4 Degree
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........         2 Note
PLAT793_ALERT_4_G Model has Chirality at C11         (Centro SPGR)        S Verify
PLAT793_ALERT_4_G Model has Chirality at C18         (Centro SPGR)        R Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600       512 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...        18 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........       2.3 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         6 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
 16 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 11 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 13 ALERT type 2 Indicator that the structure model may be wrong or deficient
  8 ALERT type 3 Indicator that the structure quality may be low
  5 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

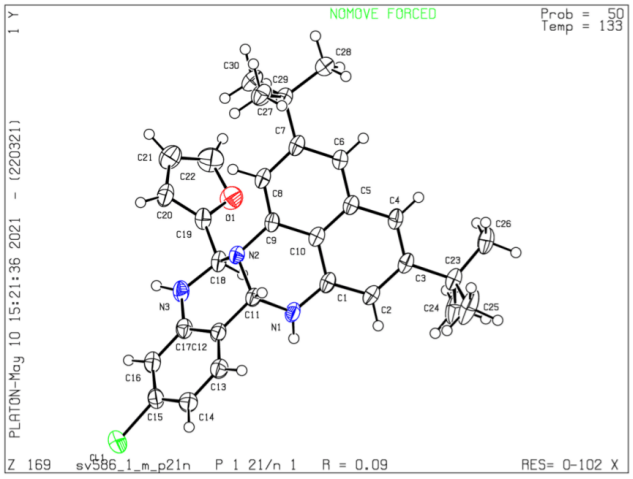
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 22/03/2021; check.def file version of 19/03/2021

Datablock sv586_1_m_p21n - ellipsoid plot



3 References

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8 List of Publications

The following publications were published, are submitted or are to be submitted during the work on this thesis:

- R. Fertig, T. Irrgang, F. Freitag, J. Zander, R. Kempe, Manganese-Catalyzed and Base-Switchable Synthesis of Amines or Imines via Borrowing Hydrogen or Dehydrogenative Condensation, *ACS Catal*. **2018**, *8*, 8525–8530.

- A. Noor, S. Qayyum, R. Fertig, Synthesis and structure of magnesium aminopyridinates and their attempted conversion to magnesium (I) derivatives, *Inorganica Chim. Acta* **2019**, *494*, 239-244,

- F. Kallmeier, R. Fertig, T. Irrgang, R. Kempe, Chromium-Catalyzed Alkylation of Amines by Alcohols, *Angew. Chem. Int. Ed.* **2020**, *59*, 11789.

- R. Fertig, T. Irrgang, R. Kempe, Rational design of N-heterocyclic compound classes via regenerative cyclization of diamines, *Submitted to Nat. Commun.* **2022**.

- R. Fertig, T. Irrgang, R. Kempe, Structure Investigations of Fertigines via X-Ray Crystallography, *to be submitted*

9 Acknowledgement/Danksagung

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10 (Eidesstattliche) Versicherungen und Erklärungen

(§ 8 Satz 2 Nr. 3 PromO Fakultät)

Hiermit versichere ich eidesstattlich, dass ich die Arbeit selbstständig verfasst und keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt habe (vgl. Art. 64 Abs. 1 Satz 6 BayHSchG).

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