

UNIVERSITÄT
BAYREUTH

Alkali Metal Assisted (De)Hydrogenation Catalysis

DISSERTATION

zur Erlangung des akademischen Grades
Doctor rerum naturalium (Dr. rer. nat.)

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Geboren in Lushnje (Albanien)

Universität Bayreuth
Bayreuther Graduiertenschule für Mathematik und Naturwissenschaften (BayNAT)
Anorganische Chemie II – Prof. Dr. Rhett Kempe

Bayreuth, 2025

Die vorliegende Arbeit wurde in der Zeit von Oktober 2022 bis September 2025 in Bayreuth am Lehrstuhl Anorganische Chemie II unter Betreuung von Herrn Professor Dr. Rhett Kempe angefertigt.

Vollständiger Abdruck der von der Bayreuther Graduiertenschule für Mathematik und Naturwissenschaften (BayNAT) der Universität Bayreuth genehmigten Dissertation zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften (Dr. rer. nat.).

Form der Dissertation: Kumulative Dissertation

Dissertation eingereicht am: 03.11.2025

Zulassung durch das Leitungsgremium: 25.11.2025

Wissenschaftliches Kolloquium: 01.06.2026

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Kjo punë i dedikohet familjes time, veçanërisht bashkëshortes sime Anës.

Të dua shumë.

...

Diese Arbeit ist meiner Familie gewidmet, im Besonderen meiner Frau Ana.

Ich liebe dich sehr.

Abbreviations

Å	Angstrom	RE	Reductive Elimination
COD	(1Z,5Z)-Cycloocta-1,5-diene	rt	Room temperature
d	doublet	s	singulett
DFT	Density functional theory	sep	septet
DMSO	Dimethylsulfoxide	sx	sextet
DOI	Digital object identifier	T	Temperature
GC	Gas Chromatography	t	triplet
IR	Infrared spectroscopy	<i>t</i> AmOH	<i>tert</i> -Amyl alcohol
K	Kelvin	THF	Tetrahydrofuran
m	multiplet	TOF	Turn over frequency
NMR	Nuclear magnetic resonance	TON	Turn over number
Nu	Nucleophile	v	Velocity
OA	Oxidative Addition	ΔE_Q	Quadrupole splitting
q	quartet	δ	Isomeric shift
quin	quintet	ν	Wavenumber

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1 Summary

The alkali metal assisted mechanism employing PN₅P-based catalyst systems in (de)hydrogenation reactions was investigated in this work. Three best performing catalysts based on iron, manganese and cobalt, which were equipped with PN₅P ligands, were investigated kinetically based on the Arrhenius equation. Emphasis was placed on the relationship between their catalytic activities and thermal stabilities (Figure 1).

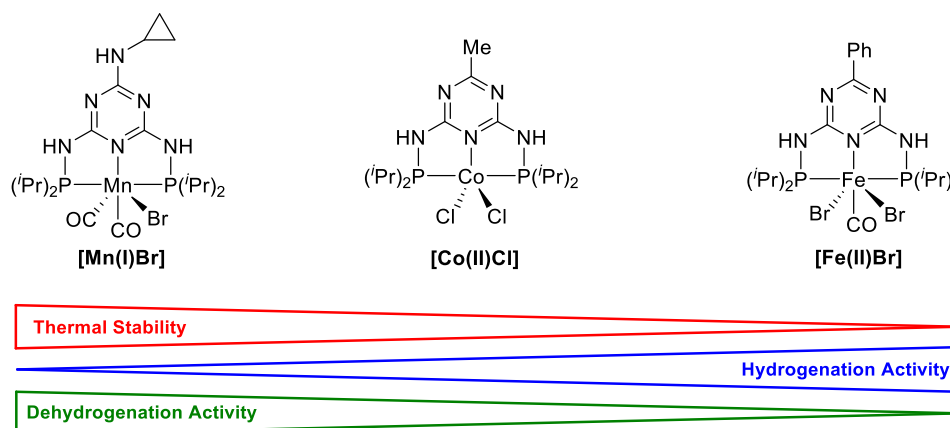


Figure 1. Schematic demonstration of the relationship between thermal stability and (de)hydrogenation activity for PN₅P-based iron, cobalt and manganese catalysts.

Since the manganese catalyst showed the highest thermal stability and the iron one the lowest, mechanistic investigations regarding their decomposition pathways were carried out. NMR spectroscopic analysis reveals that the manganese catalyst system does not decompose at temperatures where Arrhenius linearity breaks down, but instead undergoes an equilibrium transition into a dormant state (**[Mn(I)K]**; Figure 2). Once this equilibrium is set, catalysis is slower. This explains the deviation from Arrhenius linearity at temperatures above 130 °C. The high thermal stability of the Mn representative in comparison to the tested Fe and Co analogues explains, among other aspects, the broad usage of such catalysts.

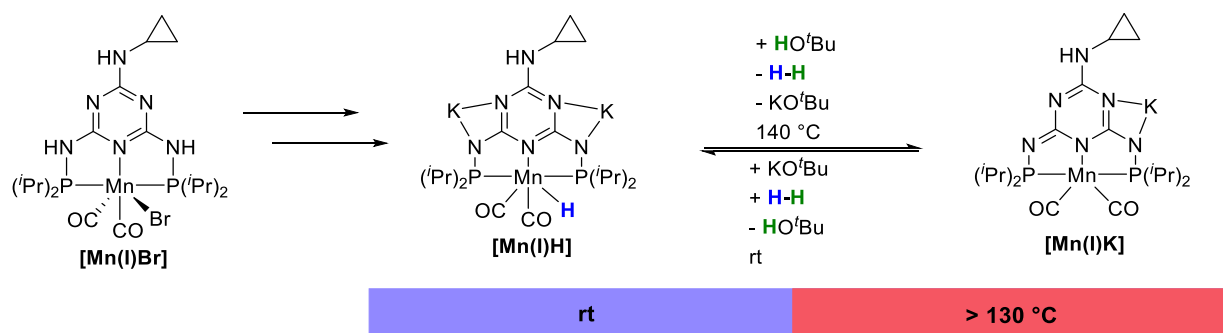


Figure 2. Equilibrium between the active hydride species **[Mn(I)H]** and the dormant species at high temperatures **[Mn(I)K]**.

The iron catalyst showed lower thermal stability and was therefore subjected to mechanistic examination. The activation pathway and catalytic cycle were discovered step-by-step. Interestingly, the active species turned to be an iron(I) complex, which is formed by disproportionation from the iron(II) precatalyst (Figure 3). The bimetallic iron(I) complex was characterized, among other methods by x-ray single-crystal analysis, and a potassium assisted mechanism was proposed for the hydrogenation of ketones. Numerous ketones (33), including many with hydrogenation-sensitive groups, were hydrogenated employing this catalyst, delivering the corresponding alcohols with high chemo selectivity.

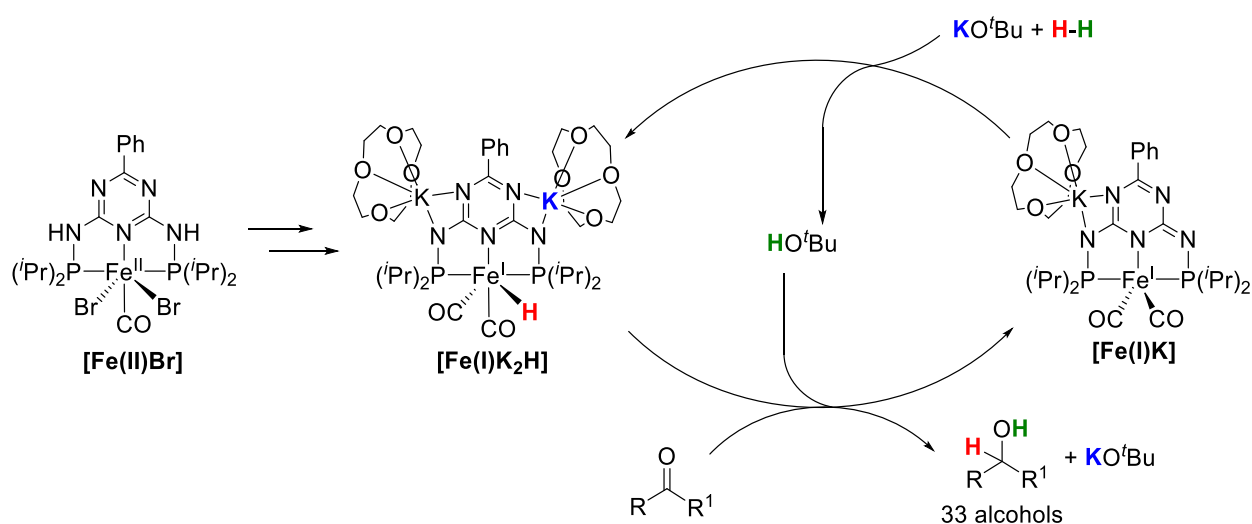


Figure 3. Synthesis of the iron(I) active species and proposed catalytic cycle for the iron(I)-mediated hydrogenation of carbonyl compounds.

Additionally, the iron(I) catalyst exhibited high chemo selectivity, which presumably comes as a result of the unusual oxidation state (+1). However, the 19 valence electron iron(I) hydride is very labile and tends to transform quickly into a more stable 18 valence electron iron(0) complex, which is catalytically inactive (Figure 4). This explains the low thermal stability of the iron catalyst system.

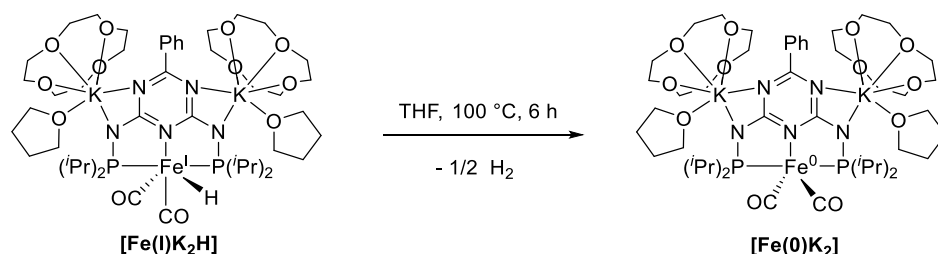


Figure 4. Transformation of the active iron(I) hydride to the inactive iron(0) complex.

Utilizing an Ir pincer catalyst, the potassium assisted mechanism, enabled by prior heterolytic cleavage of H₂ was compared with the classic pathway, consisting of oxidative addition (OA) of H₂, followed by substrate insertion to the metal and final reductive elimination (RE). Thereof derived active species permit selection between both mechanisms (Figure 5). The focus was set on the hydrogenation of multiple bonds. The dominant species (protonated or deprotonated /metalated) and, therefore, the mechanistic pathway could be selected desirably by the presence or absence of stoichiometric amounts of base. The catalytic activity could be switched on or off, accordingly. Contrary behavior of the catalytic activity was observed for compounds with polar and non-polar multiple bonds.



Figure 5. Proposed active species of a PN₅P-based Ir-complex for the efficient hydrogenation of non-polar (left) and polar unsaturated bonds (right).

2 Zusammenfassung

In dieser Arbeit wurde der Alkalimetall-assistierte Mechanismus unter Einsatz von PN_5P -basierten Katalysatorsystemen in (De-)Hydrierungsreaktionen untersucht. Drei leistungsstärkste Katalysatoren auf Basis von Eisen, Mangan und Kobalt, die mit PN_5P -Liganden ausgestattet waren, wurden kinetisch anhand der Arrhenius-Gleichung untersucht. Der Schwerpunkt lag auf der Beziehung zwischen ihren katalytischen Aktivitäten und thermischen Stabilitäten (Abbildung 1).

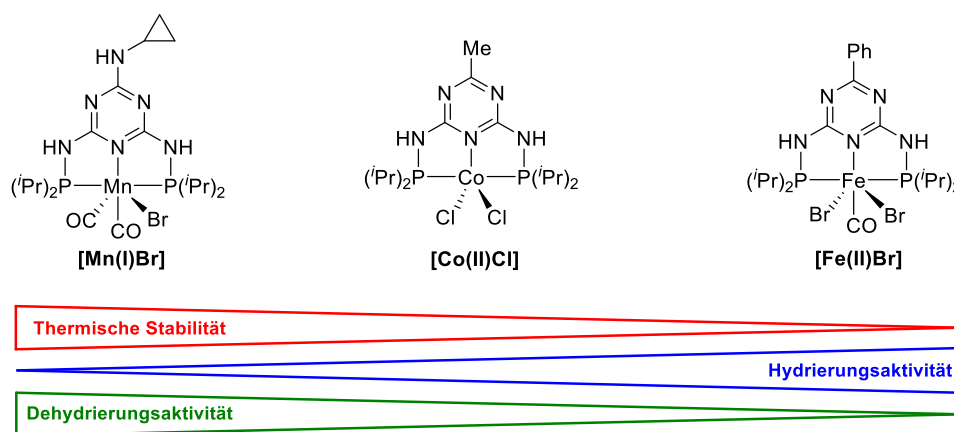


Abbildung 1. Schematische Darstellung der Beziehung zwischen thermischer Stabilität und (De-)Hydrieraktivität für PN_5P -basierte Eisen-, Kobalt- und Mangankatalysatoren.

Da der Mangankatalysator die höchste und der Eisenkatalysator die niedrigste thermische Stabilität aufwies, wurden mechanistische Untersuchungen zu den Zersetzungswegen durchgeführt. NMR-spektroskopische Analysen zeigen, dass sich das Mangankatalysatorsystem bei Temperaturen, bei denen die Arrhenius-Linearität zusammenbricht, nicht zersetzt, sondern stattdessen einen Gleichgewichtsübergang in einen inaktiven Zustand (**[Mn(I)K]**; Abbildung 2) durchläuft. Sobald sich dieses Gleichgewicht eingestellt hat, wird die Katalyse langsamer. Dies erklärt die Abweichung von der Arrhenius-Linearität bei Temperaturen über 130 °C. Die hohe thermische Belastbarkeit des Mn-Vertreters im Vergleich zu den Fe- und Co-Analoga erklärt, unter anderem, die breite Anwendung solcher Katalysatoren.

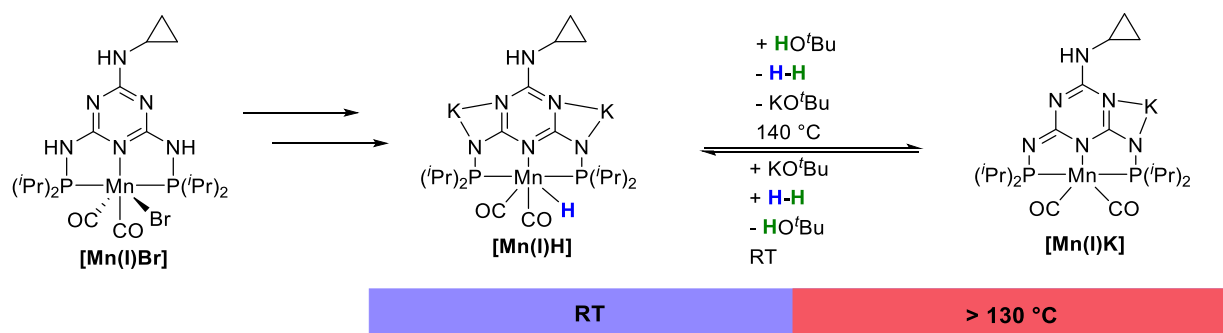


Abbildung 2. Gleichgewicht zwischen der aktiven Hydridspezies $[\text{Mn(I)H}]$ und der ruhenden Spezies bei hohen Temperaturen $[\text{Mn(I)K}]$.

Der Eisenkatalysator zeigte hingegen eine geringere thermische Stabilität und wurde daher mechanistisch untersucht. Der Aktivierungsweg und Katalysezyklus wurden schrittweise entdeckt. Interessanterweise stellte sich die aktive Spezies als Eisen(I)-Komplex heraus, der durch Disproportionierung aus dem Eisen(II)-Präkatalysator entsteht (Abbildung 3). Der bimetallische Eisen(I)-Komplex wurde, unter anderen Methoden, mittels Röntgenkristallstrukturanalyse charakterisiert und ein Kalium-assistierter Mechanismus wurde für die Hydrierung von Ketonen mittels dieses Katalysators vorgeschlagen. Zahlreiche Ketone(33), u.a. mit hydrierempfindlichen Gruppen, wurden mit diesem Katalysator zu den entsprechenden Alkoholen mit hoher Chemoselektivität hydriert.

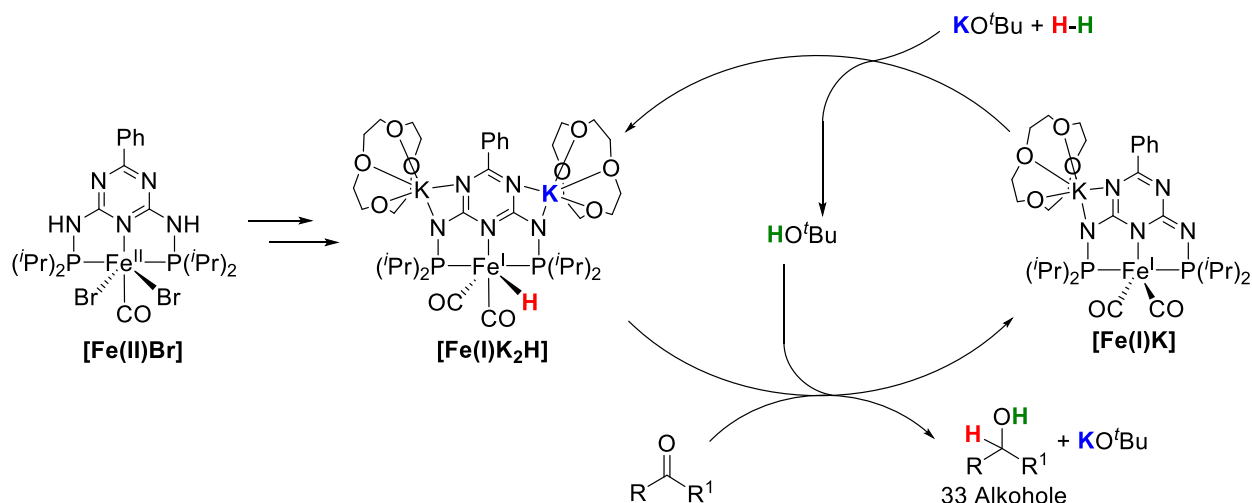


Abbildung 3. Synthese der aktiven Eisen(I)-Spezies und vorgeschlagener Katalysezyklus für die Eisen(I)-vermittelte Hydrierung von Carbonylverbindungen.

Darüber hinaus zeigte der Eisen(I)-Katalysator eine hohe Chemoselektivität, die vermutlich auf die ungewöhnliche Oxidationsstufe (+1) zurückzuführen ist. Das Eisen(I)-Hydrid mit 19 Valenzelektronen ist jedoch sehr labil und neigt dazu, sich schnell in einen stabileren Eisen(0)-Komplex mit 18 Valenzelektronen umzuwandeln, der katalytisch inaktiv ist (Abbildung 4). Dies erklärt die geringe thermische Stabilität des Eisenkatalysatorsystems.

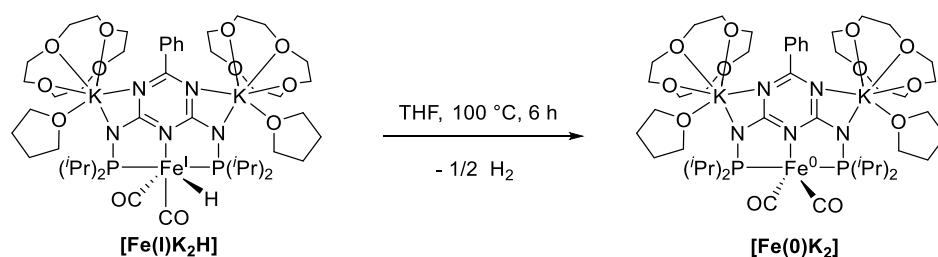


Abbildung 4. Umwandlung des aktiven Eisen(I)-hydrids in den inaktiven Eisen(0)-Komplex.

Unter Verwendung eines Ir-Pincerkatalysators wurde der Kalium-assistierte Mechanismus, der durch vorherige heterolytische Spaltung von H_2 ermöglicht wird, mit dem klassischen Mechanismus der oxidativen Addition (OA) von H_2 , gefolgt von Substratinsertion in das Metallzentrum und abschließender reduktiver Eliminierung (RE) verglichen. Die daraus abgeleiteten aktiven Spezies ermöglichen die Auswahl zwischen beiden Mechanismen (Abbildung 5). Der Fokus lag auf der Hydrierung von Mehrfachbindungen. Die dominante Spezies (protoniert oder deprotoniert/metalliert) und damit der mechanistische Pfad konnten durch Ab- oder Anwesenheit stöchiometrischer Mengen einer Kalium-Base beliebig gewählt werden. Die katalytische Aktivität konnte entsprechend ein- oder ausgeschaltet werden. Ein gegensätzliches Verhalten der katalytischen Aktivität wurde für Verbindungen mit polaren und unpolaren Mehrfachbindungen beobachtet.



Abbildung 5. Vorgeschlagene aktive Spezies des PN_5P -basierten Ir-Komplexes zur effizienten Hydrierung unpolarer (links) und polarer ungesättigter Bindungen (rechts).

3 Introduction

Catalysis is a powerful tool that plays a protagonist role in industry development.¹ A crucial aspect that underlines the potential of a catalyst is the occurring mechanism/catalytic cycle, which demonstrates the transformation of catalyst and substrate step-by-step.² Catalyst design is more efficient with adequate knowledge of the mechanistic pathway. Thus, further improvements to the already proposed mechanisms have yet to be made.

3.1 Pincer Chemistry

Catalysis performed by pincer complexes has been known and broadly utilized for decades,³ starting with the introduction of the concept “pincer chemistry” in 1976⁴. Basically, a pincer complex consists of a tridentate ligand and the metal core, which coordinates to all three anchors of the ligand (Figure 6). This alignment forms an almost planar geometry between the metal core and its coordination spots. A variety of atoms can undertake the role of the coordination anchor X, typically such as C,N,P and O. This constrained geometry provides significant stability for pincer complexes.⁵

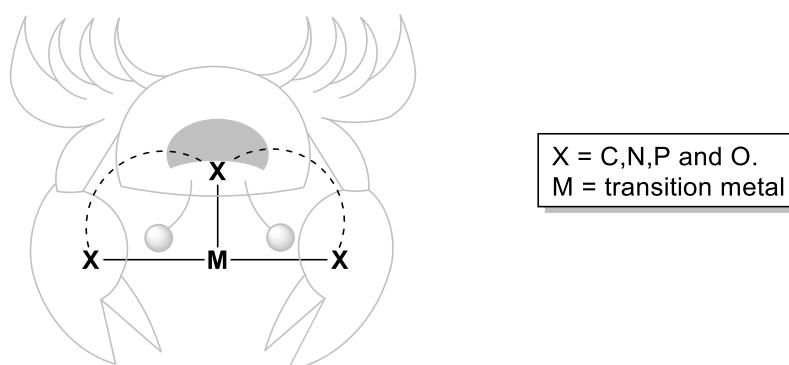


Figure 6. Illustration of a pincer complex.

3.2 Outer-sphere Mechanism in (De)Hydrogenation Reactions

Especially in (de)hydrogenation reactions, pincer catalysts have shown promising potential.^{6,7} This field has been developing rapidly, and findings show an increased popularity of the *outer-sphere* mechanism, often referred to as metal–ligand cooperation, which has been used to describe the main step of the catalytic cycle in (de)hydrogenation reactions.^{8,9,10,11,12,13} It takes place, when the transition metal M is coordinatively saturated, so that coordination of the substrate to the metal center (*inner-sphere*) is hindered. In hydrogenation reactions, when two hydrogen atoms of opposite polarity – one as a hydride and the other as a proton – are present within the catalyst, they can facilitate the proper alignment of the substrate in their vicinity. Usually, this formation is proposed as a six membered transition state (Figure 7). Hydride transfer reduces the corresponding unsaturated bond of the substrate.

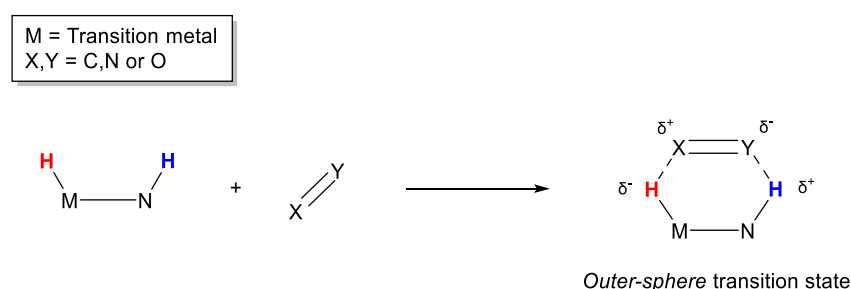


Figure 7. General illustration of the *outer-sphere* mechanism, involving the cooperation between the negatively polarized M–H and the positively polarized N–H function during hydrogenation reactions.

An honorable mention of the development of the *outer-sphere* mechanism is the work of the Nobel laureate Ryoji Noyori in 2000 as he proposed a metal-ligand bifunctional *outer-sphere* approach for asymmetric transfer hydrogenation of ketones.^{14,15,16,17,18} Ruthenium catalysts were used, equipped with two bidentate ligands (**[RuH]**, Figure 8). The diphosphine ligand is responsible for the stereoselectivity, while the diamine ligand enables the *outer-sphere* positioning of the ketone (acetophenone) close to the hydride. The ketone is positioned in alignment with one of the Ru–N bonds of **[RuH]** facing the hydride and the proton from up-close. Following hydride transfer gives rise to the corresponding alcohol, which in this case could be obtained in quantitative yields with up to 82% enantiomeric excess.

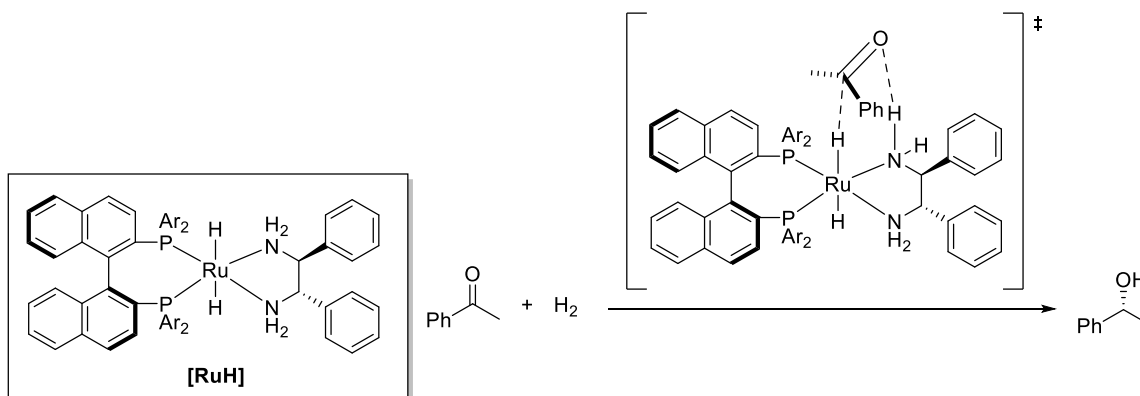


Figure 8. Hydrogenation of ketones using **[RuH]** and the occurring *outer-sphere* intermediate step prior to the hydride transfer, proposed by the Noyori group.

3.3 Alkali Metal Assisted Hydride Transfer

A modern approach to achieve higher catalytic activity is the replacement of the ligand proton with an alkali metal. Thus, the bifunctionality of pincer catalysts can be modified. Examples of proposed alkali metal assisted *outer-sphere* mechanisms are rare. The groundbreaking ones are demonstrated below.

Based on the available literature, Gordon and coworkers proposed for the first time in 2014 a DFT calculated potassium assisted pathway in the hydrogenation of acetophenone with the Noyori catalyst, in which each NH moiety is deprotonated forming a potassium amidate (Figure 9).¹⁹ A potassium assisted mechanism takes place if $X = K$. The key step involving an *outer-sphere* intermediate is shown in rectangular brackets. After the hydride transfer is accomplished, heterolytical cleavage of H_2 and simultaneous protonation of the alkoxide was proposed. Since the focus was laid on the hydride transfer herein, the diphosphine ligand was simplified for better illustration.

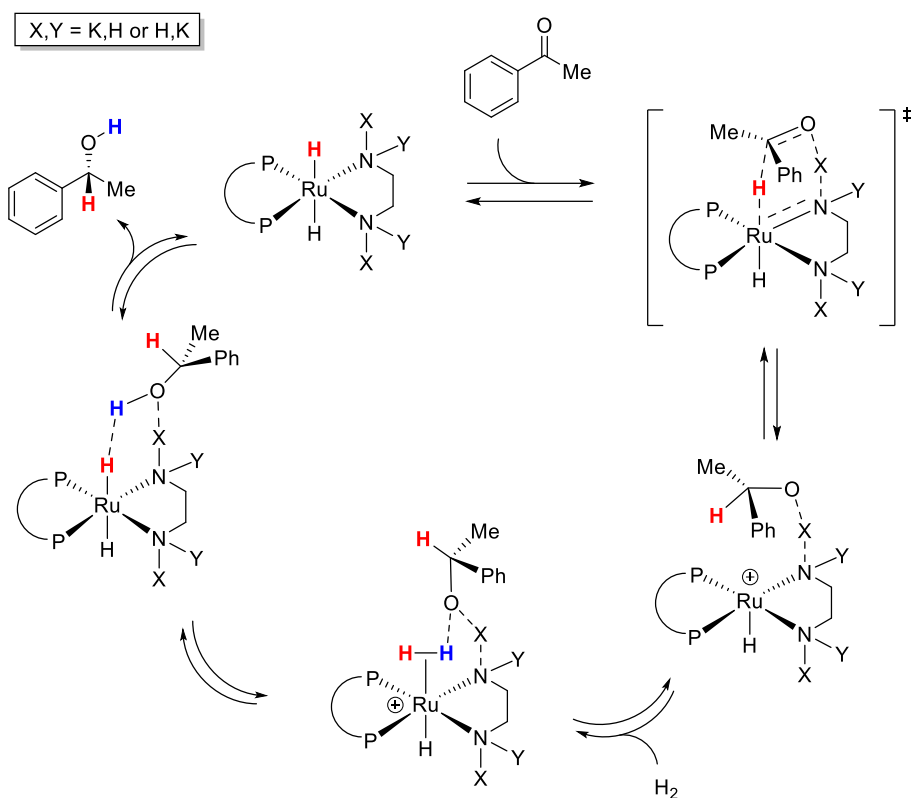


Figure 9. Proposed mechanism for the asymmetric hydrogenation of acetophenone employing Noyori's catalyst by Gordon and coworkers.¹⁹

Kitamura and coworkers were the firsts in 2018 to experimentally observe a bimetallic ruthenium hydride amidate with potassium/lithium as a counter ion (**[RuH(OMe)]**; Figure 10), shedding light to an intermediate of an alkali metal assisted mechanism.²⁰ The highlighted intermediate was detected by ¹H and ³¹P NMR spectroscopy. Heterolytical H₂ cleavage gives rise to the potassium amidate ruthenium dihydride. This species enables the *outer-sphere* transition state with the *tert*-butylmethylketone aligned next to the hydride and potassium ion. The hydride transfer and subsequent protonation by MeOH generate the desired alcohol and the highlighted ruthenium monohydride **[RuH(OMe)]**. If the amidate gets protonated during the cycle, the proton assisted mechanism (analog to the shown mechanism in Figure 10) takes over. The replacement of NH with NK, and *vice versa*, does not affect the stereoselectivity.

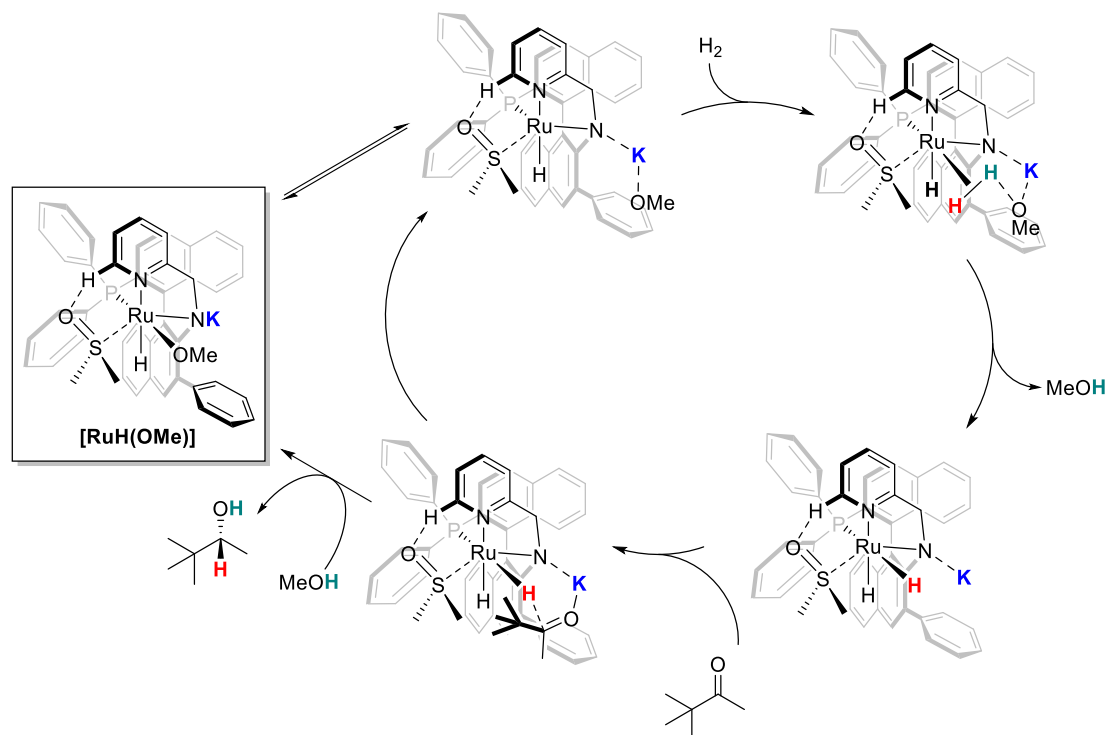


Figure 10. Proposed mechanism for the hydrogenation of *tert*-butylmethylketone by the ruthenium catalyst **[RuH(OMe)]** involving a potassium assisted *outer-sphere* hydride transfer.

In 2022, Liu and coworkers reported the first isolation of a manganese hydride complex bearing a lithium amidate moiety, which was subsequently employed as a direct catalyst for the hydrogenation of imines and ketones.²¹ The catalyst **[Mn(I)LiH]** consists of a lithium-compensated PNP ligand and a dicarbonyl manganese(I) hydride. The proposed intermediate prior to the hydride transfer is shown for 4-methoxybenzophenone in Figure 11 representatively, involving an *outer-sphere* positioning of the ketone next to the hydride and the lithium ion.

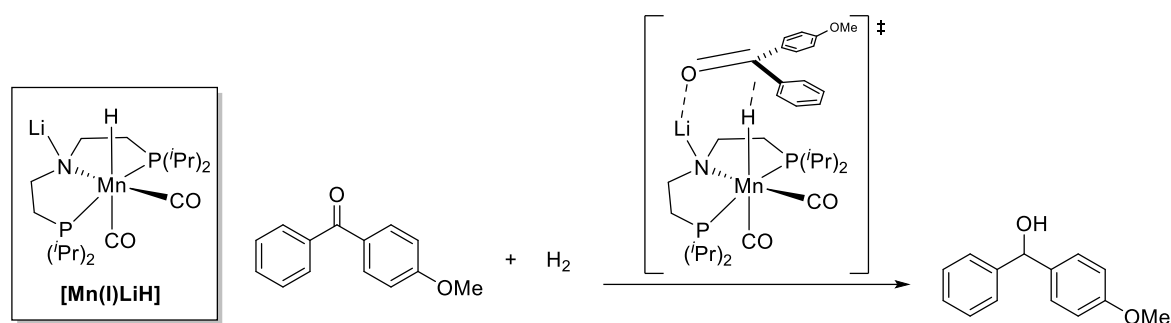


Figure 11. Hydrogenation of 4-methoxybenzophenone using **[Mn(I)LiH]** with gaseous H_2 by the group of Liu.²¹ The proposed intermediate state for the hydride transfer is shown over the arrow.

The groups of Bai, Lang, Li, and Zhang provided evidence for the formation of an iridium(III) dihydride species, in which sodium ions serve to compensate the negatively charged ligand.²² They utilized an OCN iridium(III) pincer complex **[Ir(III)H₂]** for this study and detected the deprotonated bimetallic species by several analytical methods. An *outer-sphere* hydride transfer for the hydrogenation of ketones was proposed, illustrated in Figure 12 with acetophenone as substrate. The latter has its carbonyl C-atom next to the upper hydride, since the bottom one is sterically covered by the *tert*-butyl and the cyclopentadienyl units, thus inducing stereoselectivity. The O-atom of the ketone can be coordinated to the sodium amidate or sodium alcoholate. Both transition states are possible, though coordination to the sodium alcoholate resulted to be energetically more favorable according to DFT studies. The difference in energy barrier amounted to significant 3.9 kcal/mol, making the transition state with the lower energy barrier the favored one. Astonishing *turn-over-numbers* of 13 million were achieved with this catalyst, underlining the potential of the alkali metal assisted hydride transfer.

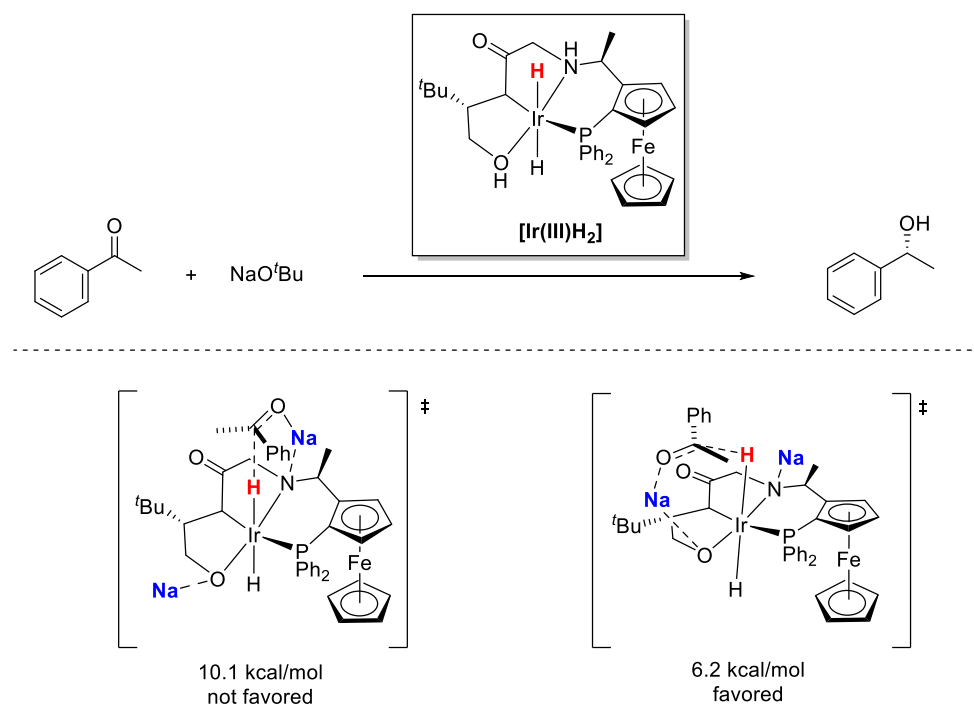


Figure 12. Proposed intermediates for the hydrogenation of acetophenone employing **[Ir(III)H₂]** by the groups of Bai, Lang, Li and Zhang.

3.4 Facilitation of the Alkali Metal Assisted Mechanism by PN_5P Complexes

In chapter 3.3 shown examples of the alkali metal assisted hydride transfer pathways, the alkali metal is bound to the ligand by coordination. This can be facilitated if an adequate multidentate cavity is provided from the ligand for the alkali metal to properly dock in. A guanamine derived pincer ligand offers a bidentate cavity, additional to the main tridentate pincer cavity (Figure 13). The chelating effect of the N,N-bidentate ligand should fixate alkali metals, stabilizing the resulting bimetallic complex.

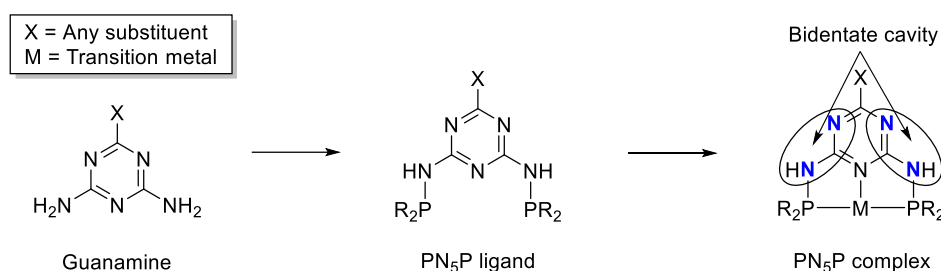


Figure 13. Conceptual synthetic approach of PN_5P complexes. The bidentate moieties for stabilization of alkali metals are highlighted.

Complexes of the PN_5P type have been habitually utilized in catalytic (de)hydrogenations by the group of Kempe.^{23,24,25,26,27,28,29,30,31,32,33} They investigated in 2018 the role of the alkali metal containing base in the coupling of primary amines with alcohols to obtain the corresponding amines or imines (Figure 14).³⁴ In dependence of the alkali metal of the base, the main product of the synthesis (amine/imine) could be adjusted desirably. They proposed a bimetallic species containing the alkali metal in the N,N-pocket cavity of the PN_5P ligand. The key step in this case seems to be the hydrogenation of the imine, which is formed in both cases. The hydride transfer ultimately delivers the amine. If the initial rate of the hydrogenation is too low ($\text{M} = \text{Na}$), the manganese(I) hydride reacts with a proton releasing H_2 gas. Presumably, the imine does not coordinate strongly to the sodium ion, due to the small surface³⁵ of the latter compared to potassium. Replacement by the bigger potassium ion favors the formation of the *outer-sphere* intermediate and increases the hydrogenation rate.

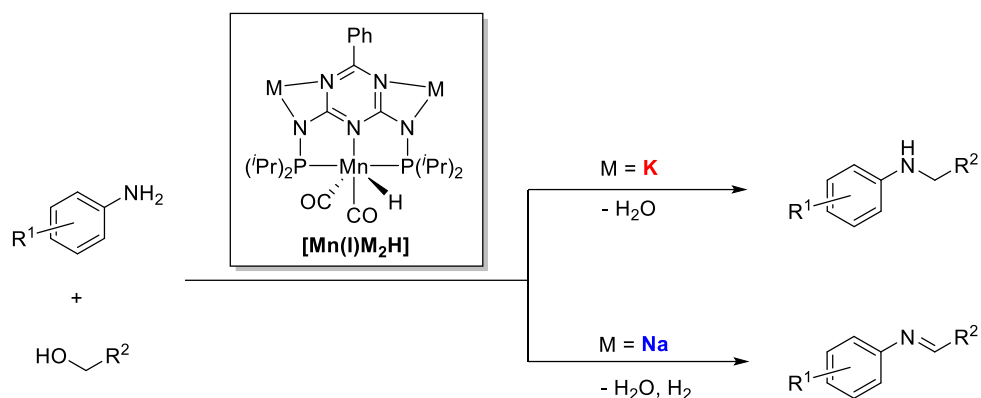


Figure 14. Base-switchable synthesis of amines or imines employing $[\text{Mn(I)M}_2\text{H}]$ as a catalyst.

The group of Kempe investigated the (de)hydrogenation steps employing $[\text{Mn(I)Br}]$ and thoroughly explained the transformation of the pre-catalyst to the bimetallic species $[\text{Mn(I)M}]$ (Figure 15).³⁶ This bimetallic species contains the alkali metal of the base in the N,N-cavity of the ligand. Conclusively, they proposed an *outer-sphere* mechanism for this reaction where the imine coordinates to the alkali metal *end-on*, maintaining an up-close position to the hydride (bottom transition state; Figure 15).

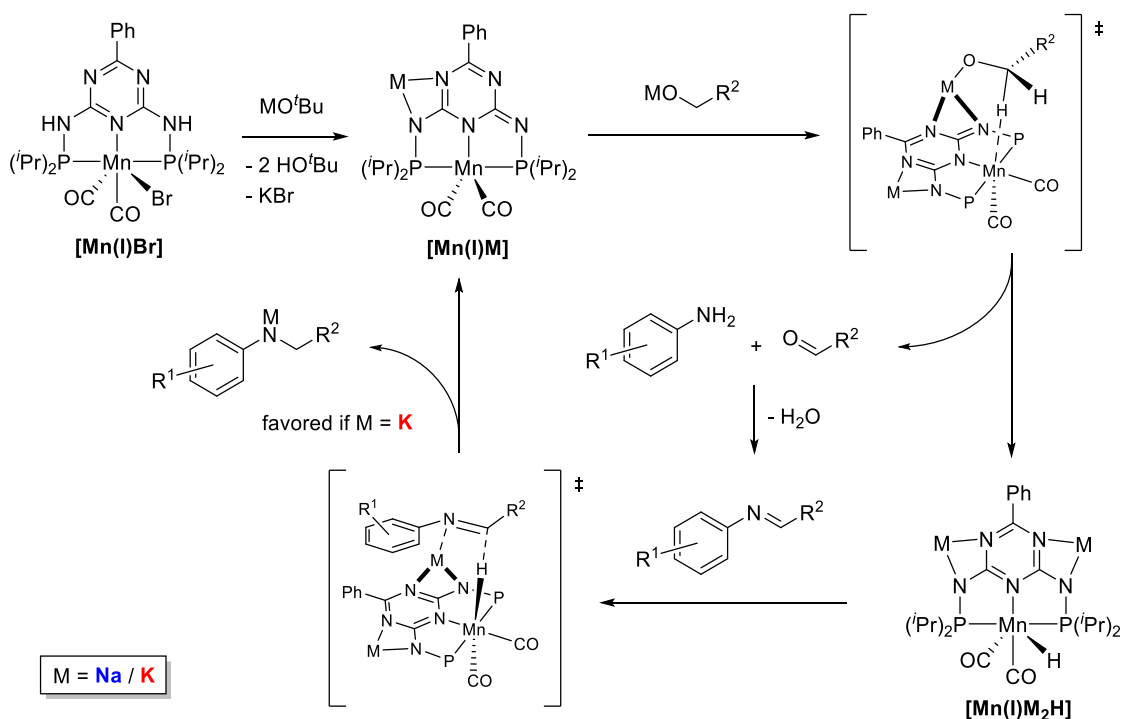


Figure 15. Activation and catalytic cycle of the hydrogenation of imines proposed by the group of Kempe.³⁶

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The corresponding Arrhenius plots shown in Figure 16 show the temperature-dependent activity and the thermal stability of the catalysts in the hydrogenation of acetophenone. The catalytic activity rises from manganese to iron, but the thermal stability seems to behave oppositely. Since the pincer ligands belong to the same compound class, the major influence on catalytic activity and thermal stability derives from the metal core.

The dehydrogenation of 1-phenylethanol was utilized to observe the behavior of the chosen catalyst systems in the counter reaction (Figure 17). The experiments were carried out in an opened system under inert atmosphere and investigated in a temperature range from 60 to 100 °C. For each catalyst were used same reaction conditions. In this case, manganese showed the highest activity followed by cobalt and ultimately iron, while their decomposition temperatures remained same as in the counter reaction (hydrogenation of acetophenone).

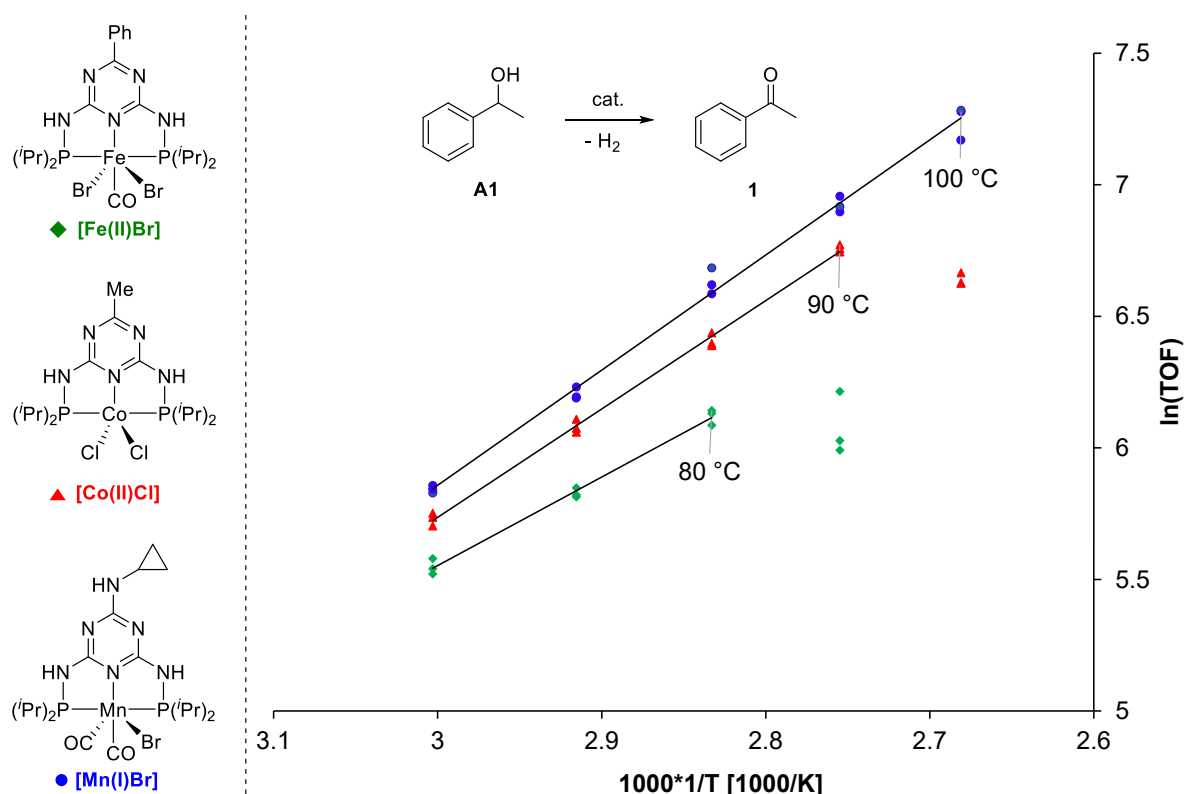


Figure 17. Arrhenius plots of the catalyst systems based on **[Fe(II)Br]**, **[Mn(I)Br]** and **[Co(II)Cl]** for the dehydrogenation of 1-phenylethanol. Reaction conditions: a) 1.00 mol% **[Fe(II)Br]**, 20.0 mol% KO^tBu, dioxane; b) 1.00 mol% **[Co(II)Cl]**, 4.00 mol% NaO^tBu, dioxane; c) 1.00 mol% **[Mn(I)Br]**, 10.0 mol% KO^tBu, dioxane.

A tendency of increasing catalytic activity from iron to manganese, with the exception of the iron catalyst system in ketone hydrogenation, can be observed from the maximal achieved TOF values (Figure 18). This was the case in both reactions (ketone hydrogenation and alcohol dehydrogenation). Additionally, the activation energies were determined from the slope of the corresponding Arrhenius linear regression. The activation energies also tend to rise from iron to manganese in both reactions. They represent the ability of the catalyst to efficiently utilize temperature. Thus, manganese is more suitable for high temperature demanding reactions.

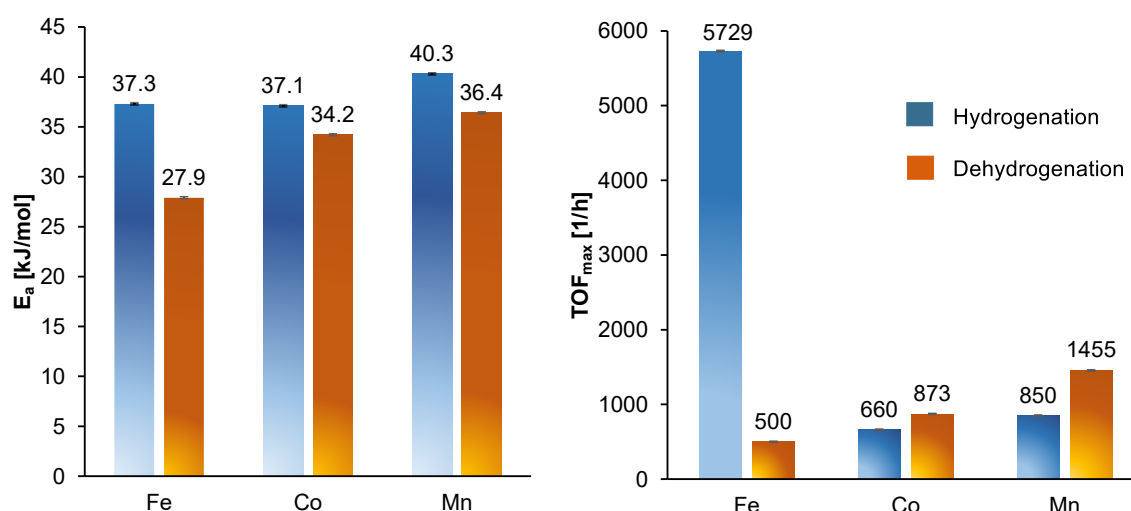


Figure 18. Activation energies and maximum turnover frequencies achieved of the three catalyst systems investigated in the hydrogenation of acetophenone and dehydrogenation of 1-phenylethanol. Activation energies were obtained from the corresponding Arrhenius plots.

Thorough investigation of catalyst decomposition at high temperatures was carried out for the manganese catalyst system. The active manganese hydride species was synthesized *in-situ* and analyzed by means of ^1H NMR spectroscopy at 140 °C. This temperature lies above the maximal temperature observed in the Arrhenius plot (Figure 16 and Figure 17), where the catalyst behaves according to the Arrhenius equation. The hydride signal (-5.6 ppm; Figure 19) of the manganese hydride almost completely disappears in 30 minutes and reappears only after cooling down to room temperature. In an hour the equilibrium between $[\text{Mn}(\text{I})\text{H}]$ and $[\text{Mn}(\text{I})\text{K}]$ could be shifted desirably by adjusting the temperature. This simulates the equilibrium during a catalytic reaction employing this catalyst and shows which species ($[\text{Mn}(\text{I})\text{H}]$ or $[\text{Mn}(\text{I})\text{K}]$) is the domi-

nant one at certain temperature regions. At temperatures above 130 °C, the equilibrium lies on the side of **[Mn(I)K]**, reducing the activity of the catalyst. However, this is no sign of decomposition, which underlines the potential of manganese catalysts to withstand high temperatures and be very suitable for a variety of high temperature demanding reactions.

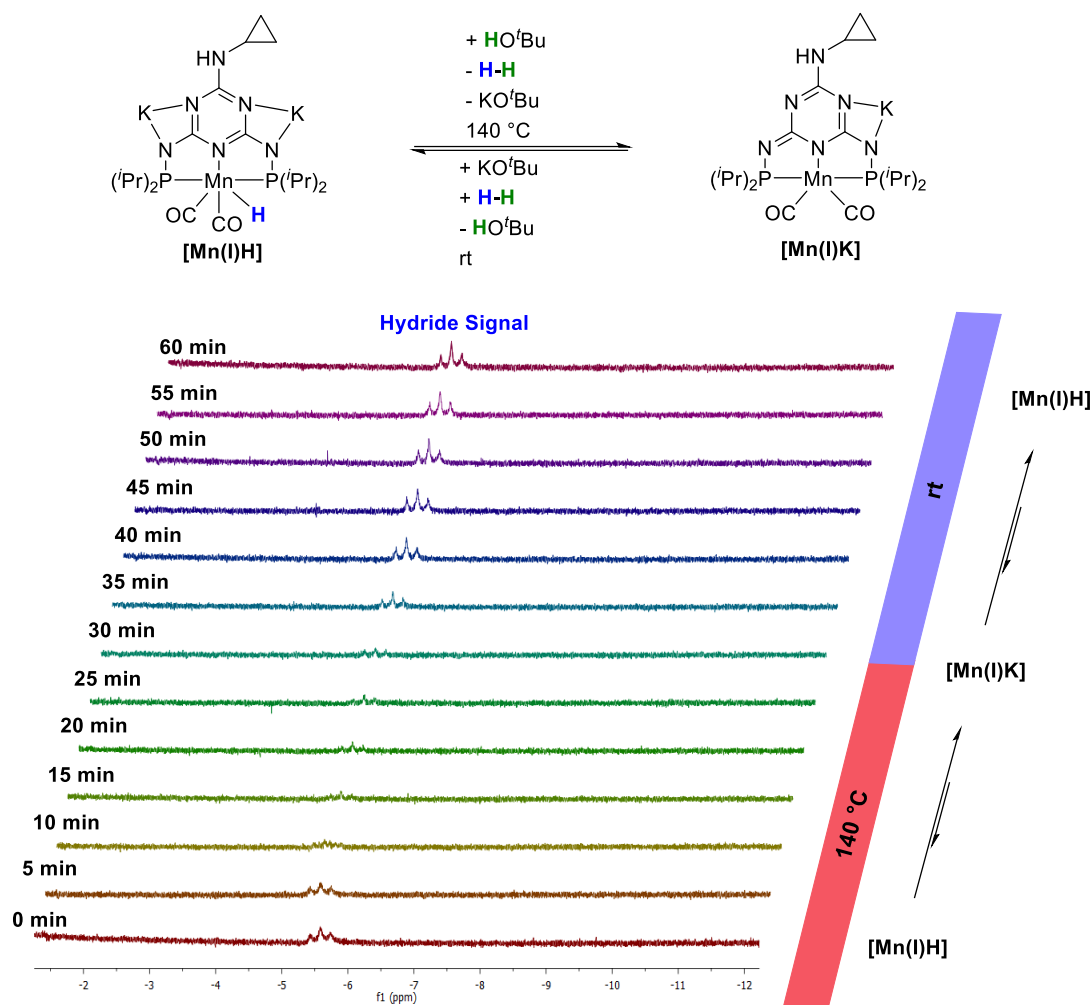
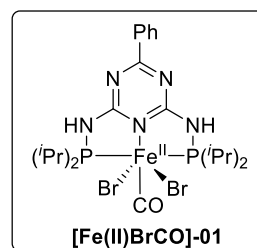
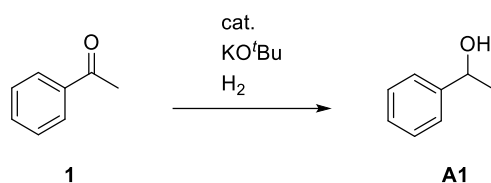


Figure 19. ¹H NMR investigation of the reversible formation of **[Mn(I)H]**. The dioxane-d₈ solution was heated at 140 °C for 30 minutes and then immediately cooled down to room temperature until the measurement was stopped. Reaction conditions: 10 eq. KO^tBu, 5 bar H₂, dioxane-d₈.

Interestingly, the iron catalyst system showed relatively low thermal stability. This leaned the attention toward the search for possible reasons for this behavior. To understand the decomposition path of a catalyst, its active species must be known. Therefore, the iron catalyst system was subjected to mechanistic investigations. The precatalyst is activated with addition of 3.00 eq. KO^tBu (Table 1).

Table 1. Screening of the KO^tBu amount.^[a]



Entry	KO ^t Bu	Yield of A1 [%]
1	0.20 mol% (1.00 eq.)	—
2	0.40 mol% (2.00 eq.)	—
3	0.46 mol% (2.30 eq.)	—
4	0.50 mol% (2.50 eq.)	—
5	0.54 mol% (2.70 eq.)	—
6	0.60 mol% (3.00 eq.)	97
7	0.80 mol% (4.00 eq.)	99
8	2.00 mol% (10.0 eq.)	99

^[a]Reaction conditions: 3.00 mmol acetophenone, 0.2 mol% **[Fe(II)BrCO]-01**, KO^tBu, 20 bar H₂, THF, 50 °C, 1 h. Yields determined by ¹H NMR.

Two equivalents of base are needed for deprotonation of the precatalyst, forming the dimeric species **[Fe(II)CO]** with bridging carbonyl ligands (Figure 20). In the presence of additional base amounts, the dimeric species starts to disproportionate delivering the active bimetallic iron(I) compound **[Fe(I)K]** and the stoichiometrically produced inactive iron(III) dimer **[Fe(III)]**. The formation of the iron(I) hydride **[Fe(I)K₂H]** takes place by heterolytical cleavage of H₂ from **[Fe(I)K]**. The crown ether 12-crown-4 was used to stabilize and coordinatively saturate the potassium ions as a chelating ligand.

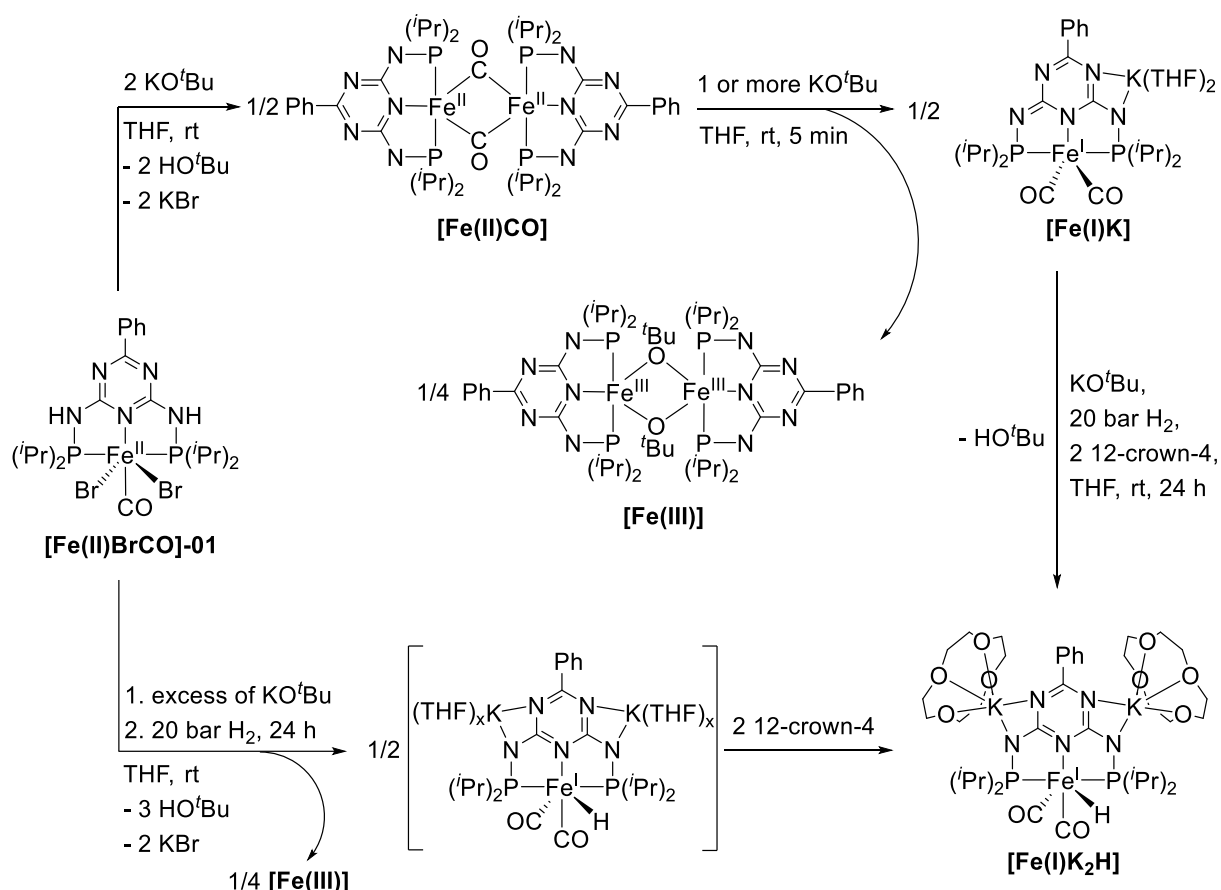


Figure 20. Formation of the iron(I) monohydride dicarbonyl complexes.

The changes in oxidation state and ligands were observed by zero-field ^{57}Fe Mössbauer spectroscopy by comparing the active iron(I) hydride **[Fe(I)K₂H]** with the iron(II) precatalyst **[Fe(II)BrCO]-01** (Figure 21). The isomeric shift is shifted towards lower velocities from **[Fe(II)BrCO]-01** to **[Fe(I)K₂H]** due to the highly covalent Fe–CO bonds, which is significant in the iron(I) hydride with two coordinating CO ligands. The increasing quadrupole splitting ΔE_Q is comprehended by the decreasing oxidation state and the number of uneven valence electrons in the iron(I) d^7 system ($\Delta E_Q = 2.125 \text{ mm}\cdot\text{s}^{-1}$), compared to the iron(II) d^6 system ($\Delta E_Q = 1.424 \text{ mm}\cdot\text{s}^{-1}$).

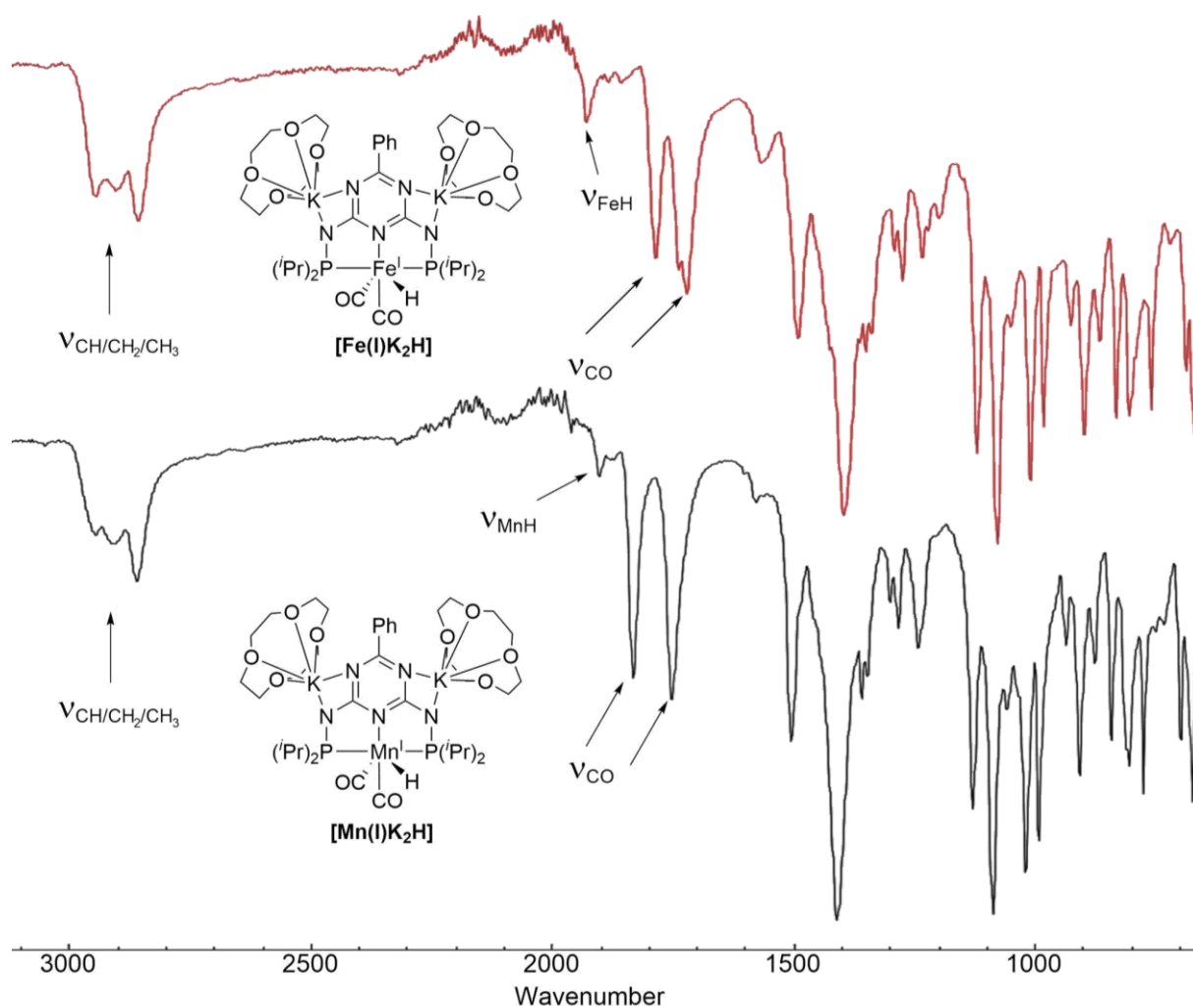


Figure 22. Stacked IR spectra of $[\text{Fe(I)K}_2\text{H}]$ (red) and $[\text{Mn(I)K}_2\text{H}]$ (black).

The crown ether was used not only for isolation but also for controlled crystallization of the manganese(I) hydride. Crystals of $[\text{Mn(I)K}_2\text{H}]$ were grown from the corresponding THF solution. X-ray single crystal structure analysis was performed for this compound, which revealed the expected molecular structure of the manganese(I) hydride. Both potassium ions of $[\text{Mn(I)K}_2\text{H}]$ are tilted towards the same direction of the hydride and each of them coordinates to one 12-crown-4 molecule. The crown ether helps fixating the potassium ions to the N,N-pocket cavity. The CO ligands stand almost orthogonal to the hydride and to each other.

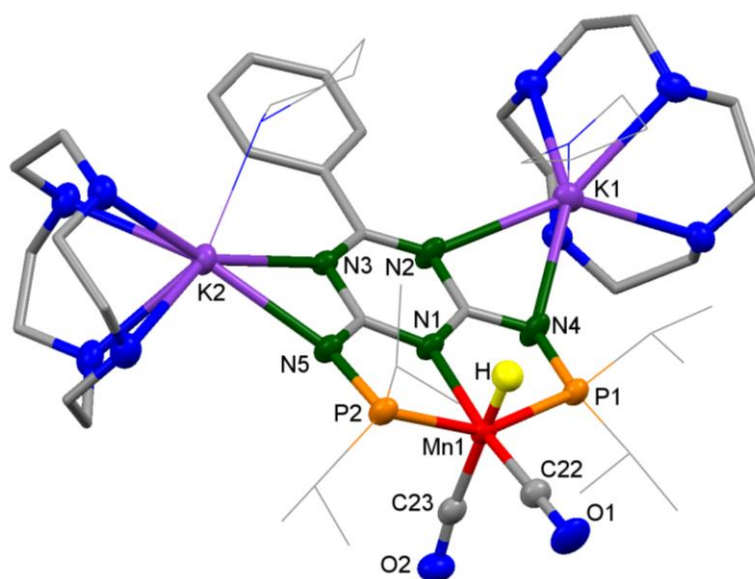


Figure 23. Molecular structure of **[Mn(I)K₂H]** with 50 % probability of thermal ellipsoids. All hydrogen atoms (except for hydride) are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Mn1–H 1.322 (3), Mn1–P1 2.228 (6), Mn1–P2 2.235 (6), Mn1–N1 2.050 (15), K1–N2 2.802 (19), K1–N4 2.729 (19), K2–N3 2.861 (17), K2–N5 2.721 (17); P1–Mn1–H 83.8 (12), P1–Mn1–P2 152.16 (2), P2–Mn1–H 77.9 (12), N1–Mn1–H 83.7 (12), N1–Mn1–P1 78.88 (5), N1–Mn1–P2 78.36 (5), C22–Mn1–N1 171.55 (9), C22–Mn1–C23 88.58 (10), C23–Mn1–H 175.7 (12), C23–Mn1–N1 99.86 (8), N4–K1–N2 49.59 (5), N5–K2–N3 48.98 (5).

A variety of ketones with different substituents, including hydrogenation sensitive ones, were hydrogenated with **[Fe(I)K₂H]** to the corresponding alcohols. A catalytic cycle for this reaction was constructed involving two iron(I) species (Figure 24). **[Fe(I)K]** cleaves H₂ heterolytically and generates the iron(I) hydride **[Fe(I)K₂H]**, which is ultimately responsible for the hydride transfer to the ketone. All evidence points to an *outer-sphere* mechanism, occurring as an intermediate step before the hydride transfer takes place. Thus, **[Fe(I)K]** is regenerated and a potassium alcoholate is formed. Protonation of the alcoholate delivers the desired alcohol.

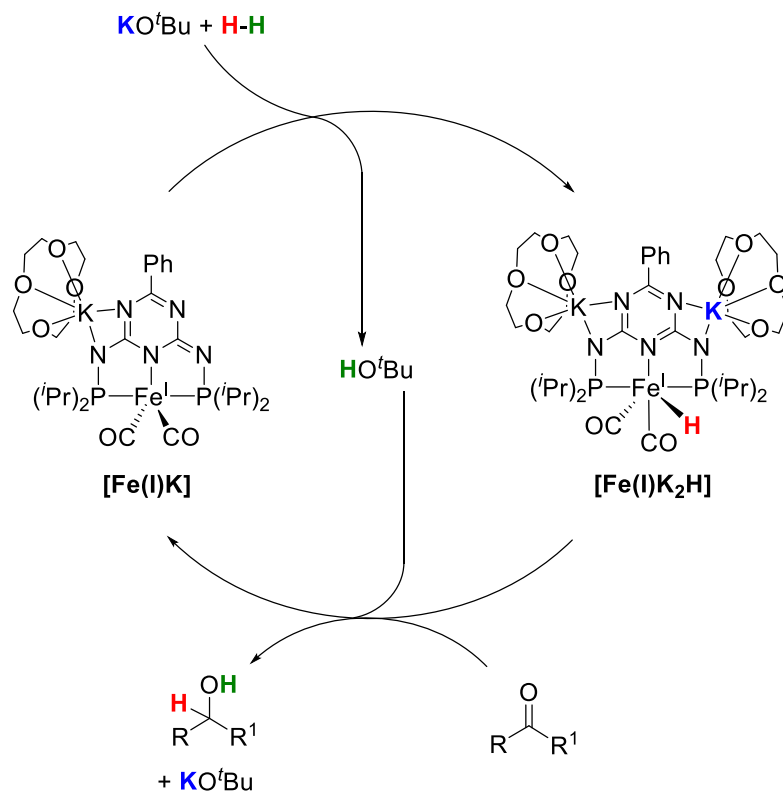


Figure 24. Proposed catalytic cycle for the iron(I)-mediated hydrogenation of carbonyl compounds.

The observed high chemo selectivity most probably originates from the unusual oxidation state of iron (+1). The presence of only one coordinative spot in the iron(I) core prohibits side reactions deriving from possible reductive elimination pathways. These pathways would be reasonable if an iron(II) dihydride were the active species.

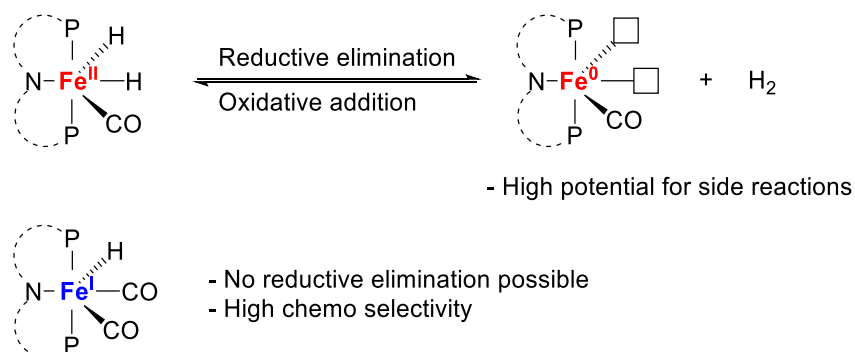


Figure 25. Proposed explanation of the high chemo selectivity of the iron(I) catalyst reported in this work.

The instability of the 19 valence electron iron(I) hydride is responsible for the low thermal stability of this catalyst system. Heating **[Fe(I)K₂H]** at 100 °C transforms the iron(I) hydride by reduction and liberation of gaseous H₂ to a catalytically inactive iron(0) complex (Figure 26). The chosen temperature to carry out this reaction lies above the observed maximal temperature region, where the catalyst still behaves according to the Arrhenius equation (Figure 16 and Figure 17).

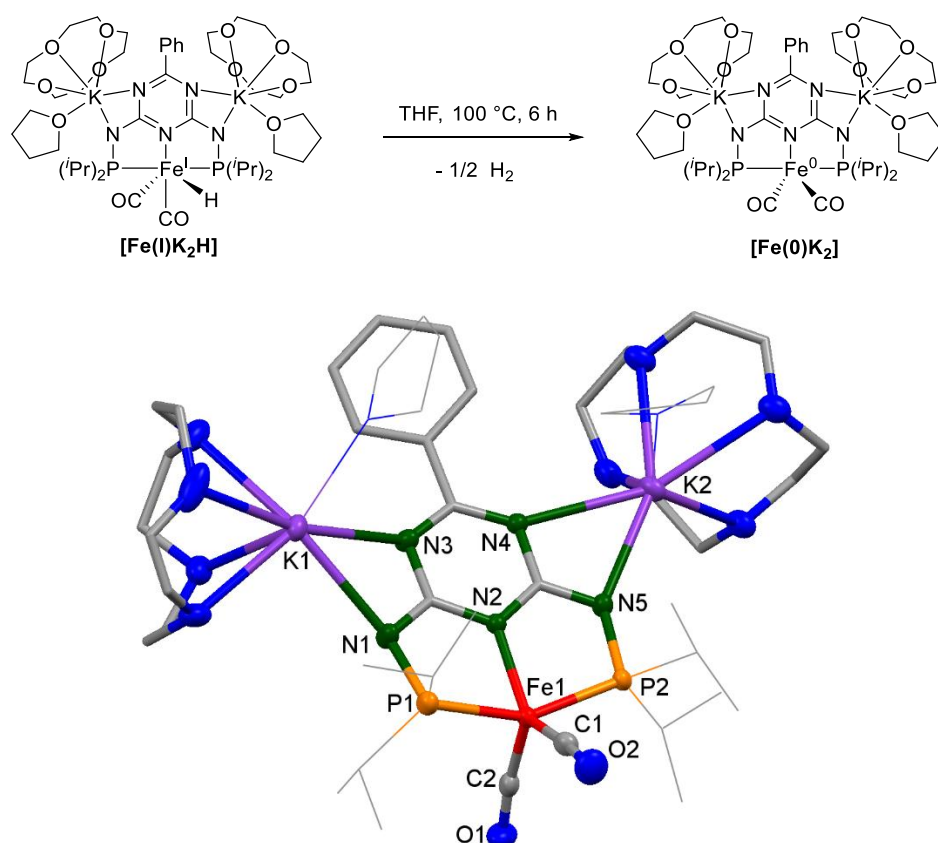


Figure 26. Formation of the iron(0) complex **[Fe(0)K₂]** from the iron(I) hydride **[Fe(I)K₂H]** and molecular structure of **[Fe(0)K₂]** with 50% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–C1 1.727 (4), Fe1–C2 1.1740 (3), Fe1–P2 2.202 (1), Fe1–P1 2.203 (1), Fe1–N2 2.034 (3), N1–K1 2.784 (3), N3–K1 2.813 (3), N4–K2 2.855 (2), N5–K2 2.749 (3); C1–Fe1–P2 95.3 (1), C1–Fe1–N2 133.5 (1), C2–Fe1–C1 113.3 (2), N2–Fe1–P2 78.87 (7), N2–Fe1–C2 113.3 (1), P1–Fe1–C2 98.3 (1), P1–Fe1–C2 102.2 (1), P1–Fe1–C1 91.6 (1), P1–Fe1–N2 77.98 (7), P1–Fe1–P2 153.69 (4), N1–K1–N3 49.04 (8), N5–K2–N4 48.82 (7).

The hydride transfer for the examples shown above is enabled by prior hydride formation utilizing heterolytic cleavage of dihydrogen, and the hydride transfer runs in a

concerted fashion, assisted by an alkali cation. This is an evolutionary approach of the classic pathway, enabled by oxidative addition (OA) of dihydrogen, followed by insertion of the substrate to the metal, and final reductive elimination (RE). Controlling both mechanisms by e.g. molecular switch is highly desirable. The iridium catalyst system **[Ir(COD)]** is able to react with hydrogen using both mechanisms and was used in this work to compare and control them (Figure 27). Switching of the catalytic hydrogenation activity was demonstrated (*vide infra*).

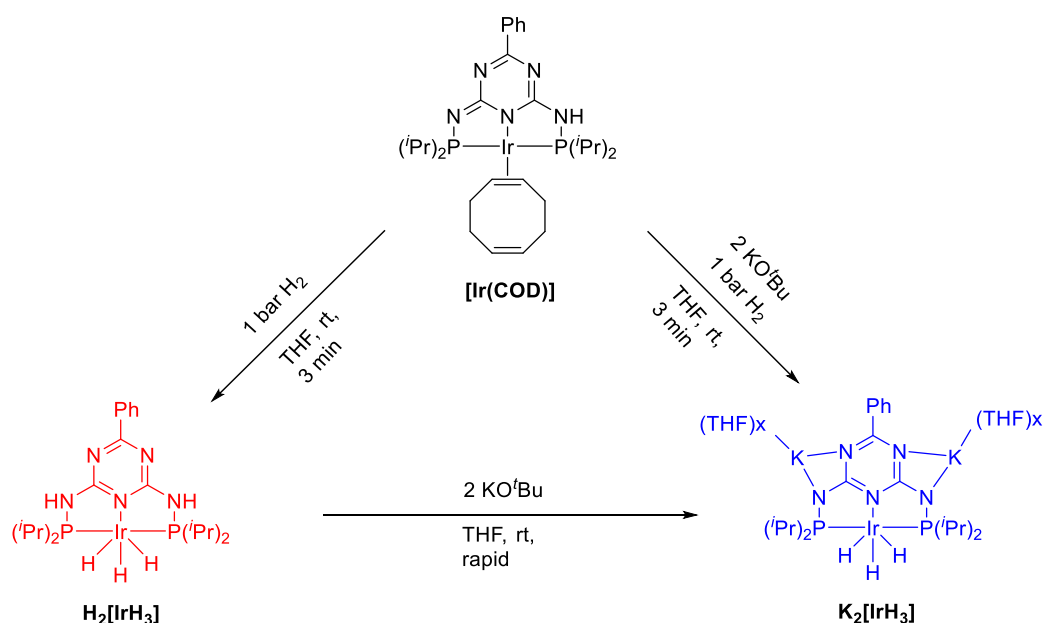


Figure 27. Synthesis of the active iridium(III) trihydride species.

The dominant species during a catalytic hydrogenation employing this **[Ir(COD)]** can be adjusted by the absence or addition of exactly 2.00 eq. KO^tBu. In the hydrogenation of benzophenone and diphenylacetylene, the catalytic activity could invertedly be switched on or off desirably (Figure 28A). The more suitable mechanism in the case of benzophenone with polar double bonds seems to be the potassium assisted one. Significantly (89 times) lower activity was observed, when no base was added to the reaction, making by OA and RE less favorable. Instead, the opposite behavior was observed in the hydrogenation of diphenylacetylene to 1,2-diphenylethane employing **[Ir(COD)]** (Figure 28B). The potassium assisted pathway seems to not be suitable in this case. Therefore, the classic OA-RE pathway appears to be the favored one, in which case the catalyst achieves 3802 times higher activity. Semi-hydrogenation product (cis-stilbene) was also formed up to 18% yield within the first hour (Supporting

Information) but was further converted to 1,2-diphenylethane throughout the reaction, leaving only traces of cis-stilbene (3.3 %) after 12 hours.

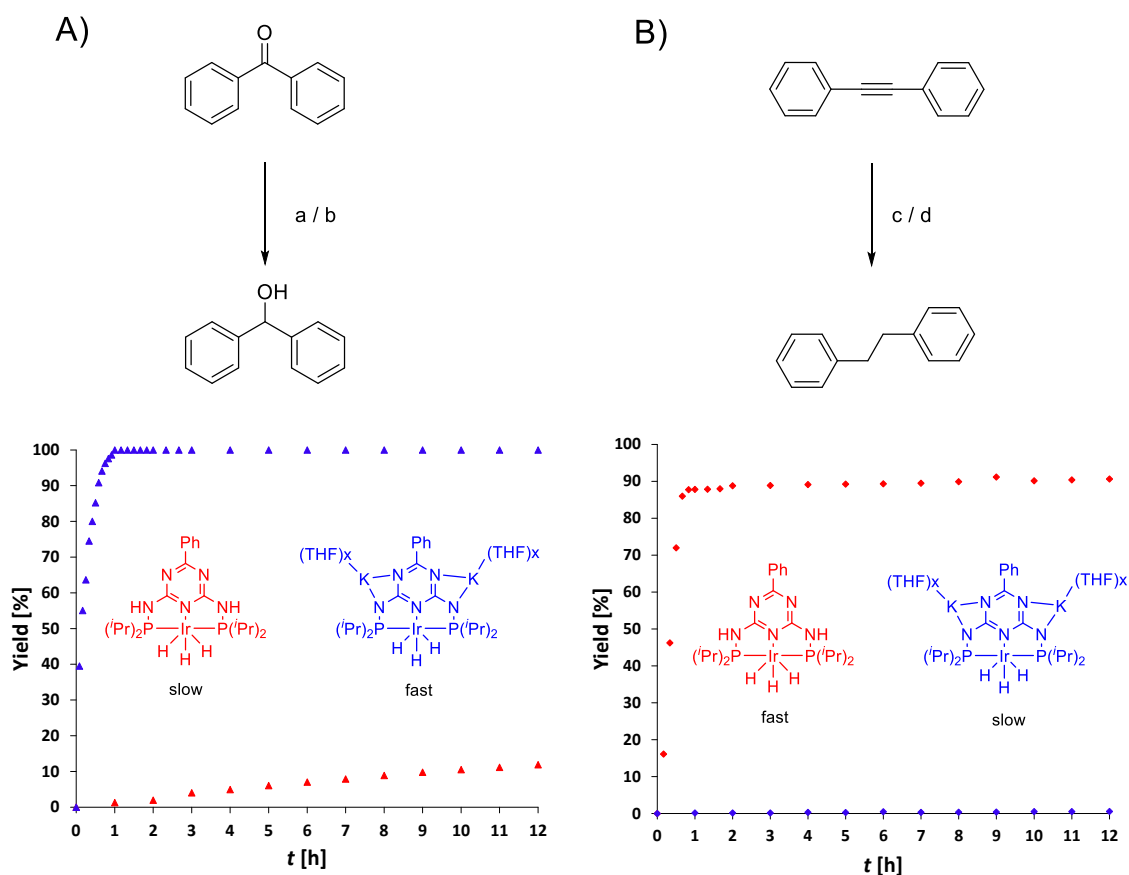


Figure 28. Time dependent yields of the hydrogenation of benzophenone (A) and diphenylacetylene (B) and without base (red) and utilizing 2.00 eq. KO^tBu (blue). Reaction conditions: a) 1.00 mol% **[Ir(COD)]**, 5 bar H₂, THF-d₈, 80 °C; b) 1.00 mol% **[Ir(COD)]**, 2.00 mol% KO^tBu, 5 bar H₂, THF-d₈, 80 °C; c) 1.00 mol% **[Ir(COD)]**, 8 bar H₂, THF-d₈, 80 °C; d) 1.00 mol% **[Ir(COD)]**, 2.00 mol% KO^tBu, 8 bar H₂, THF-d₈, 80 °C.

Furthermore, the switching of the catalytic activity utilizing **[Ir(COD)]** was tested for nitro compounds. 1-Methoxy-4-nitrobenzene was chosen as a representative for this purpose (Figure 29A). No reaction was observed, when the OA-RE hydrogenation was utilized without any base. The hydrogenation of the nitro compound to the corresponding amine could only be accomplished by the potassium assisted hydrogenation, utilizing 2.00 eq. of KO^tBu. This meets our expectations, similarly to the hydrogenation of ketones, since the nitro group is polar. To test the wide applicability of this concept to a variety of polar compounds with unsaturated bonds, imines were lastly investigated regarding switchable activity (Figure 29B). This reaction is an important step of the well-

known reductive amination. Similarly to the hydrogenation of ketones, the potassium assisted mechanism served better than the classic OA-RE pathway. The imine was hydrogenated 49 times faster utilizing the deprotonated/metalated active species than with the protonated one.

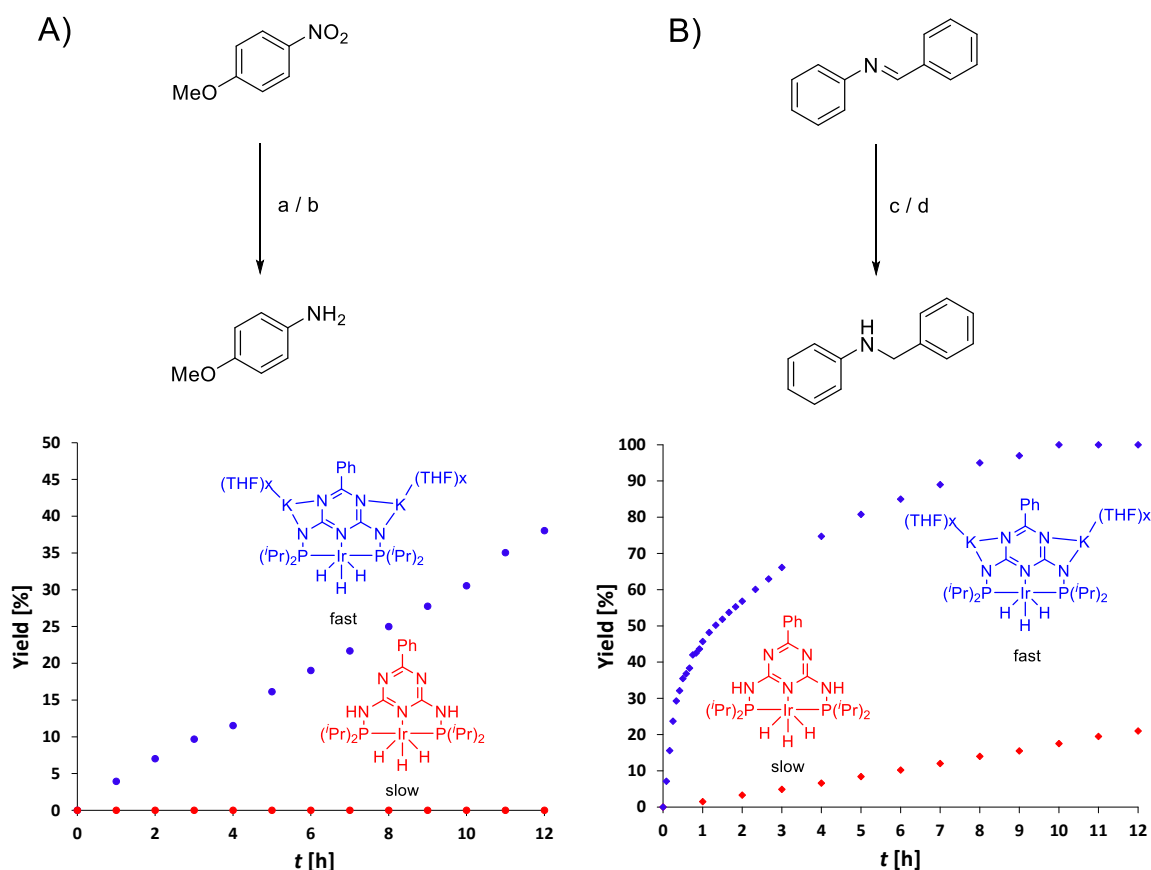


Figure 29. *In-situ* hydrogenation of *N*-phenylbenzylimine (A) and 1-methoxy-4-nitrobenzene (B) without base (red) and utilizing 2.00 eq. KO^tBu (blue). Yields were determined by ¹H NMR with 1,3,5-trimethoxybenzene as internal standard. Reaction conditions: a) 1.00 mol% [Ir(COD)], 5 bar H₂, THF-d₈, 80 °C; b) 1.00 mol% [Ir(COD)], 2.00 mol% KO^tBu, 5 bar H₂, THF-d₈, 80 °C; c) 5.00 mol% [Ir(COD)], 8 bar H₂, THF-d₈, 80 °C; d) 5.00 mol% [Ir(COD)], 10.00 mol% KO^tBu, 8 bar H₂, THF-d₈, 80 °C.

4.2 Individual Contribution to Joint Publications

The following scientific works are published, submitted or to be submitted in the future in collaboration with the named authors, as indicated below. The contributions of each author for each of the listed works below are described. The corresponding author is marked with an asterisk.

Chapter 5

This work was published in the journal *Organometallics* (*Organometallics* **2025**, *44* (20), 2434–2439) with the title “**The Special Thing about Mn (de)hydrogenation Catalysts**”.

Authors: Niko Sila, Tobias Schwarz, Andre Dickert, Torsten Irrgang, and Rhett Kempe*

Practical work in the laboratory was performed by me. I also contributed to the conceptualization of this project, by bringing innovative ideas and wrote the manuscript. Tobias Schwarz conducted part of the experiments. Andre Dickert performed x-ray single crystal crystallographic measurements. Dr. Torsten Irrgang gave helpful advice during the work and contributed in literature research and manuscript correction. Prof. Dr. Rhett Kempe conceptualized the project, helped me with scientific discussions and corrected the manuscript.

Chapter 6

This work was published in the Journal of the American Chemical Society (*J. Am. Chem. Soc.* **2024**, *146* (39), 26877–26883) with the title “**A Selective Iron(II) Hydrogenation Catalyst**”.

Authors: Niko Sila, Andreas Dürrmann, Birgit Weber, Frank W. Heinemann, Torsten Irrgang, and Rhett Kempe*

All practical work in the laboratory was performed by me. I also contributed to the conceptualization of this project, by bringing innovative ideas and wrote the manuscript. Andreas Dürrmann performed Mössbauer measurements and wrote together with me and Prof. Dr. Birgit Weber the paper section concerning Mössbauer spectroscopy. Dr. Frank W. Heinemann conducted x-ray single crystal crystallographic measurements

and structure solutions. Dr. Torsten Irrgang gave helpful advice during the work and contributed in literature research and manuscript correction. Prof. Dr. Rhett Kempe conceptualized the project, helped me with scientific discussions and corrected the manuscript.

Chapter 7

This work is to be submitted for publication in the future with the title “**Mechanistically Switchable Hydrogenation Catalysis**”.

Authors: Niko Sila, Torsten Irrgang, and Rhett Kempe*

All practical work in the laboratory was performed by me. I also contributed to the conceptualization of this project, by bringing innovative ideas and wrote the manuscript. Dr. Torsten Irrgang gave helpful advice during the work and contributed in literature research and manuscript correction. Prof. Dr. Rhett Kempe conceptualized the project, helped me with scientific discussions and corrected the manuscript.

5 The Special Thing About Mn (De)Hydrogenation Catalysts

Sila, N.; Schwarz, T.; Dickert, A.; Irrgang, T.; Kempe, R. The special thing about Mn (de)hydrogenation catalysts. *Organometallics* **2025**. 44 (20), 2434–2439.

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DOI: 10.1021/acs.organomet.5c00307

The Special Thing about Mn (de)hydrogenation Catalysts

Niko Sila, Tobias Schwarz, Andre Dickert, Torsten Irrgang, and Rhett Kempe*

Cite This: *Organometallics* 2025, 44, 2434–2439

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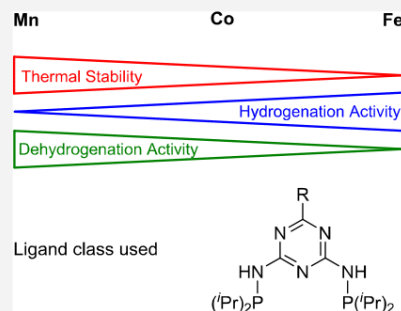
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ABSTRACT: Hydrogenation and dehydrogenation catalysis mediated by molecular Mn catalysts were discovered in 2016. Despite their late discovery (in comparison, for instance, to related Fe and Co catalysts), many novel catalysts and catalytic reactions have since been reported with a strong focus on dehydrogenation catalysis. Here, we try to find reasons why Mn-based (de)hydrogenation catalysis made such an impact despite its late discovery. We compare the temperature dependence of the rates of well-defined Mn, Fe, and Co catalysts in ketone hydrogenation and alcohol dehydrogenation via the liberation of H₂. The Mn catalyst showed an about 40–50 °C higher thermal stability in comparison to Fe and Co catalysts. In addition, details of the decomposition of Mn and Fe catalysts at the thermal limit are reported. While the PN₃P-based Mn catalyst decomposes reversibly, the PN₃P-based Fe catalyst does it irreversibly. Interestingly, all three catalysts (Mn, Fe, and Co) are active in alcohol dehydrogenation under very mild conditions, such as 60 °C, with Mn showing the highest activity at 100 °C



INTRODUCTION

Manganese hydrogenation catalysts, either homogeneous or heterogeneous, were not known prior to 2016. In this year, the groups of Milstein¹ and Kirchner² reported the first examples of Mn-based dehydrogenation catalysts able to liberate H₂, and the group of Beller³ and our group⁴ reported the first examples of hydrogenation catalysts. A part of the headline of our manuscript was “the importance of the multidentate ligand, the ancillary ligands, and the oxidation state,”⁴ providing guidance for the design of further Mn (de)hydrogenation catalysts.^{5–8} A comparison of molecular Mn (de)hydrogenation catalysts with related Fe and Co catalysts^{9–11} in similar reactions revealed early that the strength of Mn catalysts is the outstanding performance in alcohol dehydrogenation reactions (Figure 1A). In this context, it was demonstrated that dehydrogenation catalysis via the liberation of H₂, originally discovered employing Ru and Ir catalysts, could be matched with Mn catalysts.^{2,12–24} In addition, a variety of methodology developments involving dehydrogenation steps with the liberation of H₂ were reported.^{14,25–42} Very recently published examples by Beller⁴³ and Liu⁴⁴ still demonstrate the future potential of Mn (de)hydrogenation catalysts. The following question arose: Why did Mn (de)hydrogenation catalysts become so popular, despite their late discovery? We try to find answers to that question here. We investigated Mn, Fe, and Co catalysts stabilized by PN₃P pincer ligands (Figure 1B) and compared the temperature dependence of the rates in ketone hydrogenation and alcohol dehydrogenation via the liberation of H₂. The Mn catalyst showed about 40–50 °C higher thermal stability in comparison to Fe and Co catalysts. In addition, details of the decomposition of the Mn and Fe catalysts at the thermal limit are reported. While the Mn catalyst decomposes

A) State of the Art

- Mn, Fe and Co pincer complexes are efficient hydrogenation catalysts
- Mn pincer complexes are also efficient dehydrogenation catalysts

B) This Work

- Mn, Co and Fe pincer catalyst comparison

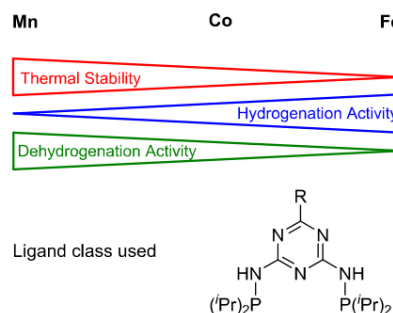
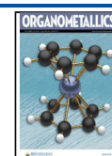


Figure 1. State of the art (A) and the work reported here (B).

Received: August 12, 2025
Revised: September 25, 2025
Accepted: September 26, 2025
Published: October 8, 2025



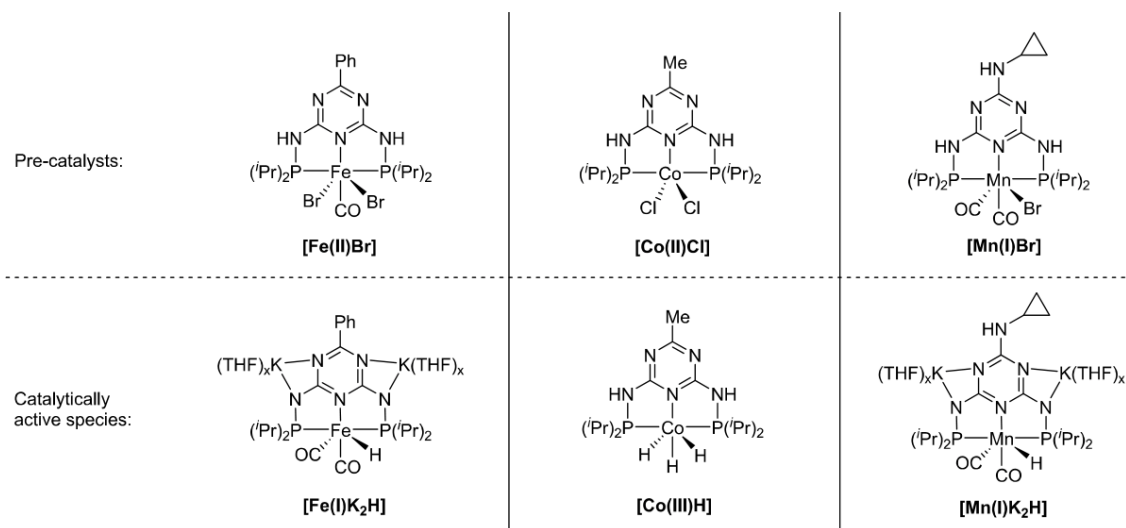


Figure 2. Structures of the precatalysts and the catalytically active species proposed.^{4,45–47}

reversibly via H_2 liberation, the Fe catalyst decomposes irreversibly and reductively by forming a catalytically inactive $\text{Fe}(0)$ complex. All three catalysts investigated (Mn, Fe, and Co) are active in alcohol dehydrogenation under very mild conditions, such as 60 °C, with Mn showing the highest activity at 100 °C.

RESULTS AND DISCUSSION

The three best-performing PN_3P -based iron, cobalt, and manganese complexes $[\text{Fe}(\text{II})\text{Br}]$, $[\text{Co}(\text{II})\text{Cl}]$, and $[\text{Mn}(\text{I})\text{Br}]$ (Figure 2) were used with their corresponding optimized reaction conditions^{4,45,46} for the comparison of the perform-

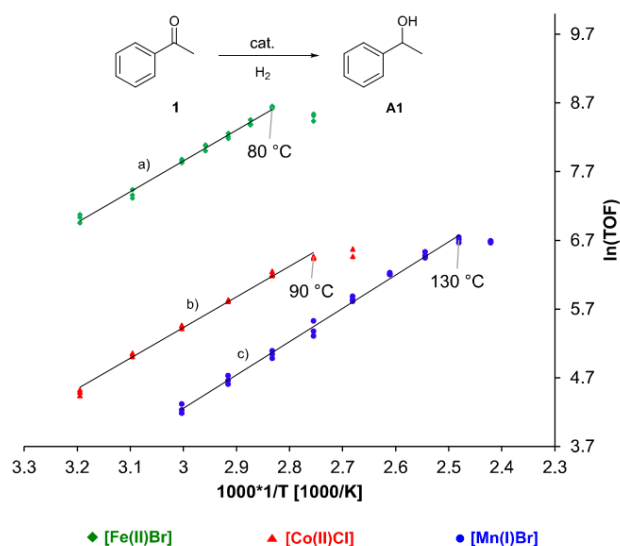


Figure 3. Arrhenius plots of the catalyst systems based on $[\text{Fe}(\text{II})\text{Br}]$, $[\text{Co}(\text{II})\text{Cl}]$, and $[\text{Mn}(\text{I})\text{Br}]$ for the hydrogenation of acetophenone. Each experiment was conducted three times. Yields were determined by GC with dodecane as the internal standard. Reaction conditions: (a) 0.007 mol % $[\text{Fe}(\text{II})\text{Br}]$, 0.14 mol % KO^tBu , 20 bar H_2 , tetrahydrofuran (THF); (b) 0.04 mol % $[\text{Co}(\text{II})\text{Cl}]$, 0.16 mol % NaO^tBu , 20 bar H_2 , *t*-AmOH; (c) 0.04 mol % $[\text{Mn}(\text{I})\text{Br}]$, 0.40 mol % KO^tBu , 20 bar H_2 , toluene.

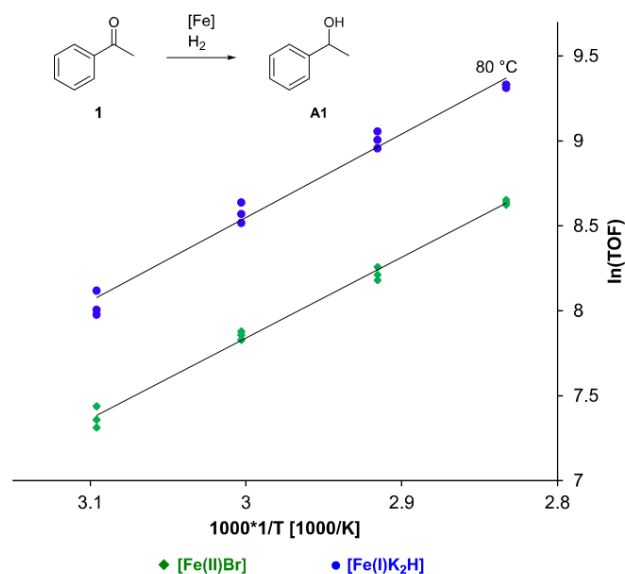


Figure 4. Arrhenius plots of the catalyst systems based on the $\text{Fe}(\text{II})$ precatalyst $[\text{Fe}(\text{II})\text{Br}]$ and the corresponding active species $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ for the hydrogenation of acetophenone. Each experiment was conducted three times. Yields were determined by GC with dodecane as the internal standard. Reaction conditions: 0.007 mol % $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ or $[\text{Fe}(\text{II})\text{Br}]$, 0.14 mol % KO^tBu , 20 bar H_2 , THF.

ance in (ketone) hydrogenation and alcohol dehydrogenation. All precatalysts are known, all perform well in the hydrogenation of acetophenone, and detailed information about the catalytically active species (Figure 2) has been proposed.^{4,45–47}

The catalytic activity of each catalyst system was determined by using the hydrogenation of acetophenone. The turnover frequencies (TOF) were determined and plotted logarithmically against the inverse temperatures to evaluate the linearity range based on the Arrhenius equation.⁴⁸ Arrhenius analysis is suitable for this study to determine the point where decomposition of the catalyst takes place, and therefore the TOF values no longer behave linearly. All runs were repeated three times to demonstrate the reliability of the method employed. All catalysts were performed in accordance with the

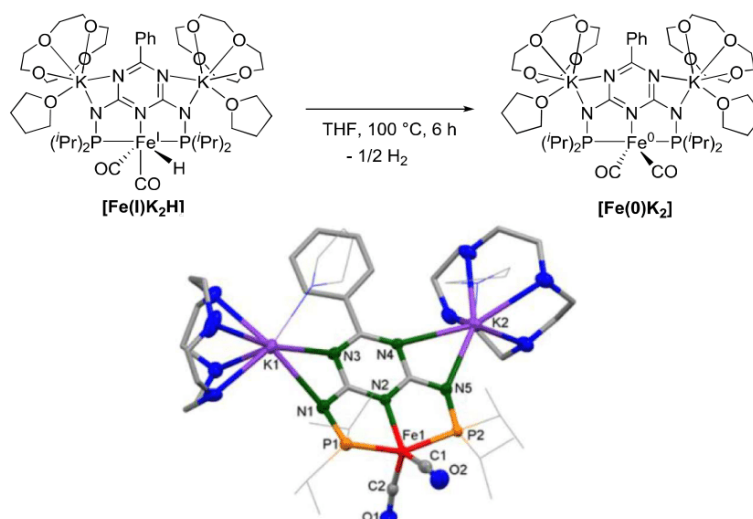


Figure 5. Formation of the Fe(0) complex $[\text{Fe}(\text{O})\text{K}_2]$ from the Fe(I) hydride $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ and the molecular structure of $[\text{Fe}(\text{O})\text{K}_2]$ with 50% probability of thermal ellipsoids.⁴⁹ Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1–C1 1.727 (4), Fe1–C2 1.1740 (3), Fe1–P2 2.202 (1), Fe1–P1 2.203 (1), Fe1–N2 2.034 (3), N1–K1 2.784 (3), N3–K1 2.813 (3), N4–K2 2.855 (2), N5–K2 2.749 (3); C1–Fe1–P2 95.3 (1), C1–Fe1–N2 133.5 (1), C2–Fe1–C1 113.3 (2), N2–Fe1–P2 78.87 (7), N2–Fe1–C2 113.3 (1), P1–Fe1–C2 98.3 (1), P1–Fe1–C2 102.2 (1), P1–Fe1–C1 91.6 (1), P1–Fe1–P2 77.98 (7), P1–Fe1–P2 153.69 (4), N1–K1–N3 49.04 (8), N5–K2–N4 48.82 (7).

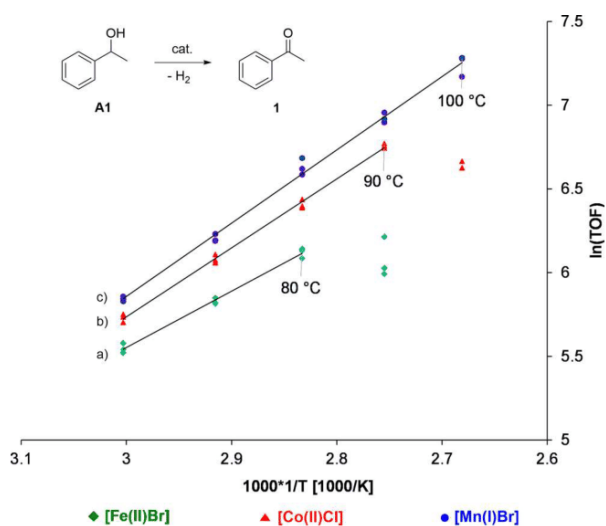


Figure 6. Arrhenius plots of the catalyst systems based on $[\text{Fe}(\text{II})\text{Br}]$, $[\text{Co}(\text{II})\text{Cl}]$, and $[\text{Mn}(\text{I})\text{Br}]$ for the dehydrogenation of 1-phenylethanol. Each experiment was conducted three times. Yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard. Reaction conditions: (a) 1.00 mol % $[\text{Fe}(\text{II})\text{Br}]$, 20.0 mol % KO^tBu , dioxane; (b) 1.00 mol % $[\text{Co}(\text{II})\text{Cl}]$, 4.00 mol % NaO^tBu , dioxane; (c) 1.00 mol % $[\text{Mn}(\text{I})\text{Br}]$, 10.0 mol % KO^tBu , dioxane.

Arrhenius equation at 60 °C, permitting a comparison of the activity. The iron catalyst showed the highest activity in the hydrogenation of acetophenone ($\text{TOF}_{60\text{ °C}} = 2609\text{ h}^{-1}$, $\text{TOF}_{80\text{ °C}} = 5667\text{ h}^{-1}$) under the conditions applied. The cobalt and manganese catalysts were 11 and 35 times less active, respectively, under these conditions ($[\text{Co}(\text{II})\text{Cl}]$: $\text{TOF}_{60\text{ °C}} = 245\text{ h}^{-1}$ $[\text{Mn}(\text{I})\text{Br}]$: $\text{TOF}_{60\text{ °C}} = 75\text{ h}^{-1}$). We propose that the maximum of the thermal stability of the catalysts investigated is identical to the temperature of the

highest $\ln(\text{TOF})$ value, still following the Arrhenius equation. The manganese catalyst reached an impressive 130 °C of maximum stability, while the cobalt catalyst reached 90 °C and the iron catalyst reached an even lower value of only 80 °C. A 40–50 °C higher thermal stability could provide a general explanation for the impressive performance of manganese pincer catalysts in dehydrogenation reactions. Thermal stability is essential here to push the hydrogenation-dehydrogenation equilibrium toward efficient hydrogen liberation. Looking at the structure of the catalytically active iron and manganese hydride catalysts proposed (Figure 2), we see that both complexes are isostructural, with the manganese complex being an 18-valence-electron compound and the iron complex a 19-valence-electron compound. The stability of the manganese catalyst system and the higher activity of the iron catalyst system could be explained by considering their valence electron numbers, which make the manganese catalyst more stable but less reactive regarding the hydride transfer and the iron catalyst vice versa. Since we used the precatalyst $[\text{Fe}(\text{II})\text{Br}]$ for the study shown in Figure 3, and the catalytically active species of the latter is known, we compared the Fe(II) precatalyst with its Fe(I) hydride species $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ (Figure 4). This 19-valence-electron complex is formed by a disproportionation reaction, which generates 0.5 equiv of an active Fe(I) hydride and 0.5 equiv of an inactive Fe(III) complex.⁴⁵ In this case, the catalytically active Fe(I) hydride $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ should provide twice the activity of the precatalyst $[\text{Fe}(\text{II})\text{Br}]$ over the temperature range investigated and the same slope in the Arrhenius plot (Figure 4).

We then became interested in the decomposition of the catalytically active hydride complex of an iron-based catalyst system. The iron hydride has been characterized in the past by our group,⁴⁵ and no additional direct evidence for the Fe hydride was collected during this work. $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ was refluxed for 6 h in tetrahydrofuran (THF) at 100 °C, which lies above the maximal temperature of Arrhenius linearity observed

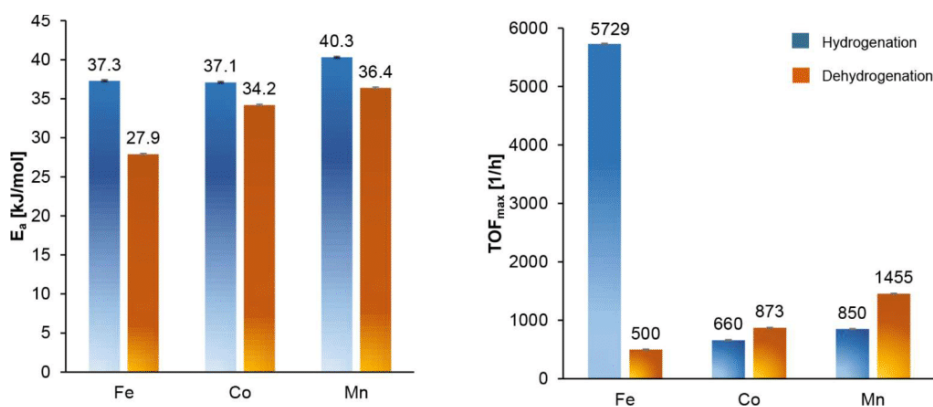


Figure 7. Activation energies and maximum turnover frequencies achieved by the three catalyst systems investigated in the hydrogenation of acetophenone and dehydrogenation of 1-phenylethanol. Activation energies were obtained from the corresponding Arrhenius plots.

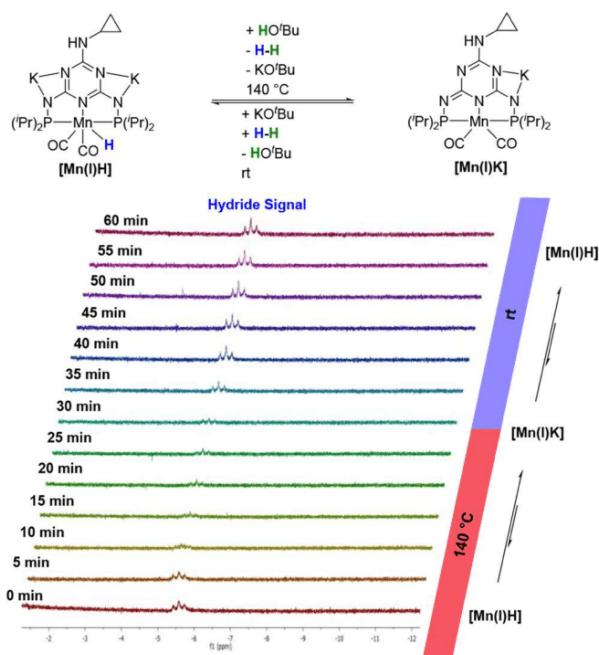


Figure 8. 1H NMR investigation of the reversible formation of $[Mn(I)H]$. The dioxane- d_8 solution was heated at 140 °C for 30 min and then immediately cooled down to room temperature until the measurement was stopped. The decrease and rise of the hydride signal show the formation of $[Mn(I)K]$ and the regeneration of $[Mn(I)H]$, respectively. Reaction conditions: 10 eq. KO^tBu , 5 bar of H_2 , dioxane- d_8 .

(80 °C; Figure 3), giving rise to the more stable 18-valence-electron $Fe(0)$ complex $[Fe(0)K_2]$ (Figure 5). We isolated $[Fe(0)K_2]$ in 57% yield by crystallization from the THF solution. The crystals obtained were orange in color in comparison to the blue of the $Fe(I)$ hydride. $[Fe(0)K_2]$ showed no catalytic activity in the hydrogenation of acetophenone. The formation of this catalytically inactive species is a possible deactivation pathway of iron hydride $[Fe(I)K_2H]$ at temperatures higher than 80 °C. The CO ligands and the pincer ligand of $[Fe(0)K_2]$ form a distorted trigonal bipyramidal geometry around the $Fe(0)$ central atom (Figure 5). This geometry leaves no space for a hydride ligand. The force for maintaining this structure is the 18-valence-

electron of the $Fe(0)$ complex in comparison to the 19-valence-electron of the $Fe(I)$ hydride. Both potassium ions are stabilized or coordinated by 12-crown-4 and compensate for the two negative charges of the PN_2P ligand. This serves as evidence for the oxidation state(0) of the iron core. The potassium ion K1 and the pincer ligand plane are positioned at a 19.8° angle, while the potassium ion K2 is found at a 7.8° angle to the pincer ligand plane. Both potassium ions are tilted in the same direction, adopting a *cis*-like arrangement with the pincer ligand plane.

Since we know the thermal stability windows of the iron, manganese, and cobalt catalyst systems investigated here, we became interested in the dehydrogenation of alcohols employing these catalysts in the temperature range where the catalysts are stable. The dehydrogenation of 1-phenylethanol was investigated. Dioxane was chosen as a solvent boiling at a high enough level, and dehydrogenation experiments were conducted in a temperature range from 60–100 °C. The same reaction conditions were used for each catalyst system (Figure 6) consistently with 3.0 mmol of 1-phenylethanol and 18.0 mL of dioxane. The precatalyst-to-base ratio was identical to that used during hydrogenation experiments. Based on the Arrhenius equation,⁴⁸ the $\ln(TOF)$ values calculated were plotted against the inverse temperature. Linearity was maintained until the corresponding degradation temperature for each catalyst system was reached (Figure 6). Experiments were conducted up to the boiling point of dioxane (101 °C). All data points were measured three times to confirm the reliability of the experiments carried out. The manganese catalyst system shows the highest activity at 100 °C in the dehydrogenation of 1-phenylethanol (Figure 7), although the differences in activity are significantly smaller than in ketone hydrogenation (Figure 3). All catalyst systems are active in the dehydrogenation of 1-phenylethanol via the liberation of H_2 , even at 60 °C. Thus, alcohol dehydrogenation can be carried out under very mild conditions, employing the catalyst families investigated here and presumably other related catalyst systems as well. The catalyst decomposition temperatures resulting from the hydrogenation catalysis (Figure 3) are identical to the corresponding values derived from dehydrogenation catalysis (Figure 6) for the Co and Fe catalysts investigated. The Fe catalyst showed the lowest activity ($TOF_{80\text{ °C}} = 500\text{ h}^{-1}$) and the Mn catalyst the highest activity ($TOF_{80\text{ °C}} = 1455\text{ h}^{-1}$) in alcohol dehydrogenation (Figure 7). Since the solvent used cannot be heated above 101 °C, the decomposition point of

the manganese catalysts could not be reached with the solvent used here. Furthermore, the activation energies for the catalysts examined were determined from the corresponding Arrhenius plots (Figures 3 and 6).

Finally, we performed an NMR decomposition experiment on the manganese catalyst system derived from $[\text{Mn}(\text{I})\text{Br}]$ (Figure 8). The precursor $[\text{Mn}(\text{I})\text{Br}]$ reacted with an excess of KO^tBu generating $[\text{Mn}(\text{I})\text{K}]$. The latter was converted to the active hydride species $[\text{Mn}(\text{I})\text{K}_2\text{H}]$ by adding 5 bar of H_2 pressure into the NMR tube.⁵⁰ A rapid color change from blue-green to colorless and the rise of a triplet at -5.5 ppm, after the addition of 5 bar of H_2 into the NMR tube, indicated the formation of the hydride species $[\text{Mn}(\text{I})\text{K}_2\text{H}]$ (Figure 8). The NMR tube was heated at 140°C for the first 30 min of the measurement and then cooled to room temperature to test the stability of $[\text{Mn}(\text{I})\text{K}_2\text{H}]$. A decrease in the hydride signal (-5.5 ppm) at 140°C and the formation of $[\text{Mn}(\text{I})\text{K}]$ were observed. The hydride signal reappeared after cooling to room temperature, demonstrating the regeneration of $[\text{Mn}(\text{I})\text{K}_2\text{H}]$. This experiment indicates that the “hydride decomposition” of the manganese catalyst system seems reversible, while $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ decomposes irreversibly (*vide supra*).

CONCLUSION

We conclude that the thermal stability of the PN_3P -based Mn catalyst investigated and the reversible formation of the catalytically active Mn hydride shown in Figure 8 could be key reasons for the intensive use of this specific and other related Mn catalysts in alcohol dehydrogenation reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.5c00307>.

Experimental procedures, spectroscopic, and crystallographic data (PDF)

Accession Codes

Deposition Number 2453020 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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<https://pubs.acs.org/doi/10.1021/acs.organomet.5c00307>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

This work was financially supported by the DFG (Deutsche Forschungsgemeinschaft), KE 756/31-2, and the University of Bayreuth.

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

NMR nuclear magnetic resonance
GC gas chromatography
TOF turnover frequency
THF tetrahydrofuran

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5.2 Supporting Information

The special thing about Mn (de)hydrogenation catalysts

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5.3 General considerations

All reactions were carried out in a glove box filled with nitrogen N₂ (5.0) or using Schlenk techniques. THF, dioxane and toluene were purified by distillation over drying agent (sodium or LiAlH₄) and stored over molecular sieves (3 Å). 2-Methyl-2-butanol and DMSO were dried over molecular sieves (3 Å). Dioxane-d₈ was dried by storing over KH for at least seven days. Other chemicals were purchased from commercial vendors, purified either by crystallization, sublimation or distillation and dried at least for 24 hours under high vacuum.

Yields for the hydrogenation experiments with acetophenone were determined by GC with dodecane as internal standard or by ¹H NMR with 1,3,5-trimethoxybenzene as internal standard. Gas chromatography measurements were carried out using an Agilent 6850 system equipped with a Machery-Nagel (MN) Optima 17 column (30 m, 320 μm, 0.25 μm).

Elementar *UNICUBE* (C/H/N) was used for elemental analysis measurements. Probes were weighed on a precision scale.

NMR measurements were performed on a *Varian* INOVA 300 or on a *Varian* INOVA 400. The chemical shift is given in the δ-scale. The signals were described using following symbols: s = singulett, d = doublet, t = triplet, q = quartet, quin = quintet, sx = sextet, sep = septet, m = multiplet. Coupling constants *J* were given in Hz. ¹³C and ³¹P NMR spectra were measured ¹H decoupled. High pressure NMR measurements were conducted using a Wilmad quick pressure valve NMR tube (5 mm diameter; max. 150 psi). The obtained spectra were processed with *Bruker* TopSpin 4.1.4¹ or MestRenova 6.1.0-6224².

Suitable single-crystals were covered by a Fomblin layer to protect from reacting with air. The desired single-crystal was observed under a light microscope, picked with a Nylon loop and measured on a STOE STADIVARI [λ(MoKα) = 0.71073 Å], equipped with an Oxford Cryostream low temperature unit. Structure solution and refinement were achieved using Olex 2-1.5^{3,4,5,6} and Mercury 4.2.0⁷.

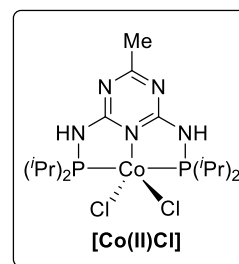
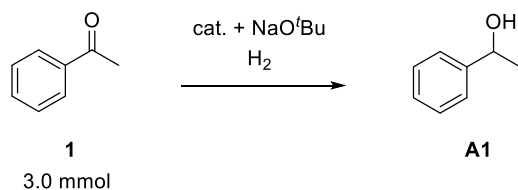
5.4 Experimental procedures

All pincer ligands and complexes **[Co(II)Cl]**, **[Mn(I)Br]**, **[Fe(II)Br]**, **[Fe(I)K₂H]** were synthesized according to the literature.^{8,9,10}

Hydrogenation reactions were carried out in PARR Instrument stainless steel autoclaves with suitable temperature controllers. A solution of catalyst and base in the corresponding solvent was prepared and acetophenone was added to the solution in a glass vial, which was placed in a suitable vial holder in the autoclave. The reaction was stopped by the addition of distilled water (20 mL). Afterwards, the internal standard was added, and the mixture was extracted with Et₂O (20 mL). The organic phase was filtered over 2 cm Si₂O plug and solvent was removed in a rotary evaporator. The yields were determined by GC or ¹H NMR analysis.

Dehydrogenation reactions were carried out using Schlenk technique. A solution of catalyst and base in dioxane was prepared and 1-phenylethanol was added to the solution in the Schlenk flask, which was equipped with a bubble counter and stirred at the desired temperatures. The reaction was stopped by the addition of distilled water (20 mL) and the solvent was removed in a rotary evaporator. Afterwards, the internal standard was added, and the mixture was extracted with Et₂O (20 mL). The organic phase was filtered over 2 cm Si₂O plug and the solvent was removed in a rotary evaporator. The yields were determined by GC or ¹H NMR analysis.

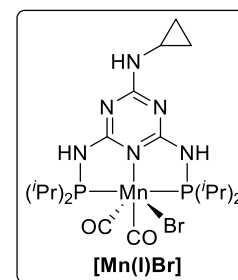
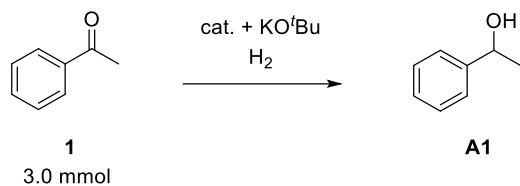
5.5 Hydrogenation experiments with [Co(II)Cl]



Entry	T [°C]	1/T [T ⁻¹]	Yield of A1 [%]	TOF [1/h]	ln(TOF)
1 ^a	40	0.00319	12.7	91	4.508
2 ^a	40	0.00319	11.9	85	4.443
3 ^a	40	0.00319	12.9	92	4.523
4 ^b	50	0.00309	12.7	159	5.067
5 ^b	50	0.00309	12.6	158	5.059
6 ^b	50	0.00309	12.0	150	5.011
7 ^b	60	0.00300	19.6	245	5.501
8 ^b	60	0.00300	18.8	235	5.460
9 ^b	60	0.00300	18.0	225	5.416
10 ^c	70	0.00291	21.0	350	5.858
11 ^c	70	0.00291	20.4	340	5.829
12 ^c	70	0.00291	20.0	333	5.809
13 ^d	80	0.00283	25.2	473	6.158
14 ^d	80	0.00283	27.6	518	6.249
15 ^d	80	0.00283	26.0	488	6.189
16 ^e	90	0.00275	26.4	660	6.492
17 ^e	90	0.00275	25.0	625	6.438
18 ^e	90	0.00275	25.5	638	6.458
19 ^e	100	0.00268	27.2	680	6.522
20 ^e	100	0.00268	25.7	643	6.465
21 ^e	100	0.00268	28.6	715	6.572

Reaction conditions: 0.04 mol% **[Co(II)Cl]**, 0.16 mol% NaOtBu, 20 bar H₂, 2.0 mL *t*AmOH. ^[a]3.5 h; ^[b]2.0 h; ^[c]1.5 h; ^[d]1.33 h; ^[e]1.0 h. Yields were determined by GC with dodecane as internal standard.

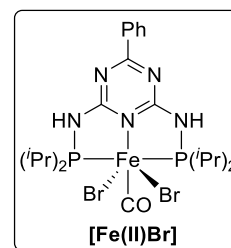
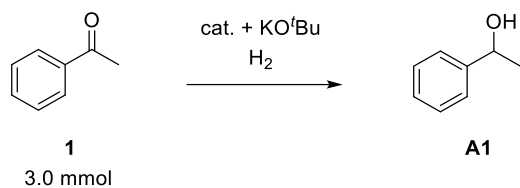
5.6 Hydrogenation experiments with [Mn(I)Br]



Entry	T [°C]	1/T [T ⁻¹]	Yield of A1 [%]	TOF [1/h]	ln(TOF)
1 ^a	60	0.00300	10.5	66	4.184
2 ^a	60	0.00300	11.0	69	4.230
3 ^a	60	0.00300	12.0	75	4.317
4 ^b	70	0.00291	13.6	113	4.730
5 ^b	70	0.00291	12.0	100	4.605
6 ^b	70	0.00291	12.7	106	4.662
7 ^c	80	0.00283	11.4	163	5.093
8 ^c	80	0.00283	10.8	154	5.039
9 ^c	80	0.00283	10.2	146	5.982
10 ^d	90	0.00275	12.6	252	5.529
11 ^d	90	0.00275	10.8	216	5.375
12 ^d	90	0.00275	10.1	202	5.308
13 ^d	100	0.00268	16.7	334	5.811
14 ^d	100	0.00268	17.2	344	5.841
15 ^d	100	0.00268	18.0	360	6.886
16 ^e	110	0.00261	20.3	508	6.229
17 ^e	110	0.00261	19.8	495	6.205
18 ^e	110	0.00261	19.7	493	6.199
19 ^e	120	0.00254	27.5	688	6.533
20 ^e	120	0.00254	25.1	628	6.442
21 ^e	120	0.00254	26.0	650	6.477
22 ^e	130	0.00248	32.8	820	6.709
23 ^e	130	0.00248	34.0	850	6.745
24 ^e	130	0.00248	31.4	785	6.666
25 ^e	140	0.00242	31.3	783	6.662
26 ^e	140	0.00242	32.3	808	6.694
27 ^e	140	0.00242	32.0	800	6.685

Reaction conditions: 0.04 mol% **[Mn(I)Br]**, 0.40 mol% KO^tBu, 20 bar H₂, 2.0 mL toluene. ^[a]3.5 h; ^[b]2.0 h; ^[c]1.5 h; ^[d]1.33 h; ^[e]1.0 h. Yields were determined by GC with dodecane as internal standard.

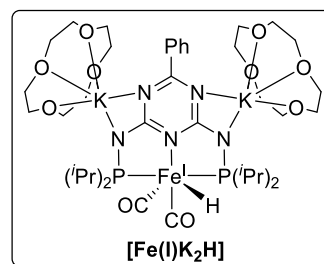
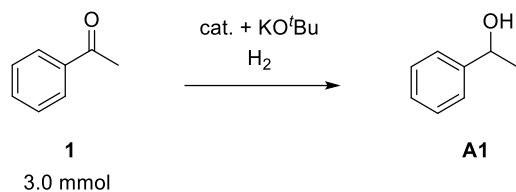
5.7 Hydrogenation experiments with [Fe(II)Br]



Entry	T [°C]	1/T [T ⁻¹]	Yield of A1 [%]	TOF [1/h]	ln(TOF)
1 ^a	40	0.00319	12.4	1181	7.074
2 ^a	40	0.00319	11.9	1133	7.033
3 ^a	40	0.00319	11.0	1048	6.954
4 ^b	50	0.00309	11.0	1571	7.360
5 ^b	50	0.00309	11.9	1700	7.438
6 ^b	50	0.00309	10.5	1500	7.313
7 ^b	60	0.00300	18.1	2562	7.859
8 ^b	60	0.00300	18.5	2609	7.877
9 ^b	60	0.00300	17.6	2491	7.831
10 ^b	65	0.00296	22.8	3223	8.089
11 ^b	65	0.00296	20.9	2952	8.001
12 ^b	65	0.00296	22.5	3176	8.074
13 ^b	70	0.00291	25.0	3530	8.179
14 ^b	70	0.00291	27.0	3813	8.257
15 ^b	70	0.00291	25.8	3648	8.212
16 ^b	75	0.00287	30.5	4309	8.379
17 ^b	75	0.00287	32.9	4652	8.455
18 ^b	75	0.00287	30.8	4357	8.390
19 ^b	80	0.00283	39.0	5514	8.625
20 ^b	80	0.00283	40.1	5667	8.653
21 ^b	80	0.00283	39.5	5584	8.638
22 ^b	90	0.00275	32.2	4557	8.435
23 ^b	90	0.00275	35.7	5041	8.536
24 ^b	90	0.00275	34.8	4923	8.512

Reaction conditions: 0.007 mol% **[Fe(II)Br]**, 0.14 mol% KO^tBu, 20 bar H₂, 2.0 mL THF.
^[a]1.5 h; ^[b]1.0 h. Yields were determined by GC with dodecane as internal standard.

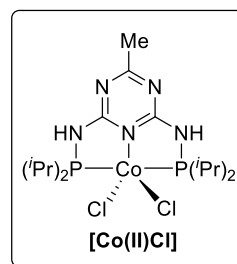
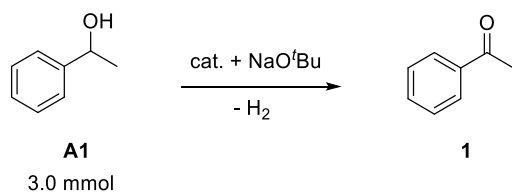
5.8 Hydrogenation experiments with [Fe(I)K₂H]



Entry	T [°C]	1/T [T ⁻¹]	Yield of A1 [%]	TOF [1/h]	ln(TOF)
1	50	0.00309	21.0	3000	8.006
2	50	0.00309	20.4	2914	7.977
3	50	0.00309	23.5	3357	8.118
4	60	0.00300	35.0	4428	8.395
5	60	0.00300	36.9	5271	8.570
6	60	0.00300	39.5	5642	8.638
7	70	0.00291	60.0	8571	9.056
8	70	0.00291	57.1	8157	9.007
9	70	0.00291	54.3	7757	8.956
10	80	0.00283	77.5	11071	9.312
11	80	0.00283	78.0	11142	9.318
12	80	0.00283	78.9	11271	9.330
13	90	0.00275	36.0	5142	8.545
14	90	0.00275	35.3	5042	8.525
15	90	0.00275	36.4	5200	8.556

Reaction conditions: 0.007 mol% **[Fe(I)K₂H]**, 0.14 mol% KO^tBu, 20 bar H₂, 2.0 mL THF, 1.0 h. Yields were determined by GC with dodecane as internal standard.

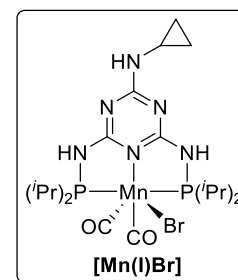
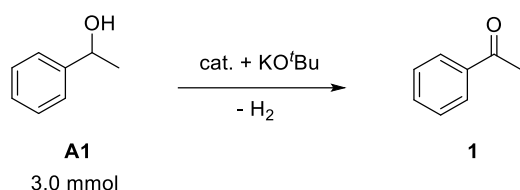
5.9 Dehydrogenation experiments with [Co(II)Cl]



Entry	T [°C]	1/T [T ⁻¹]	Yield of 1 [%]	TOF [1/h]	ln(TOF)
1	60	0.00300	6.0	300	5.704
2	60	0.00300	6.2	310	5.737
3	60	0.00300	6.3	315	5.753
4	70	0.00291	8.5	428	6.060
5	70	0.00291	8.7	435	6.075
6	70	0.00291	9.0	450	6.109
7	80	0.00283	12.0	600	6.397
8	80	0.00283	12.5	625	6.438
9	80	0.00283	11.9	595	6.389
10	90	0.00275	17.5	873	6.772
11	90	0.00275	17.0	850	6.745
12	90	0.00275	17.2	860	6.757
13	100	0.00268	15.1	755	6.627
14	100	0.00268	15.7	785	6.666
15	100	0.00268	15.1	755	6.627

Reaction conditions: 1.00 mol% **[Co(II)Cl]**, 4.00 mol% NaO^tBu, 18.0 mL Dioxane, 2.0 h. Yields were determined by ¹H NMR with 1,3,5-trimethoxybenzene as internal standard.

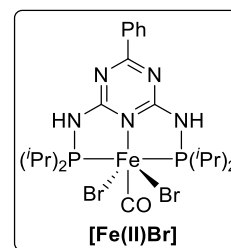
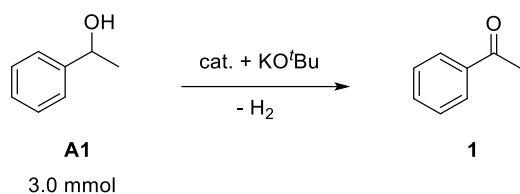
5.10 Dehydrogenation experiments with [Mn(I)Br]



Entry	T [°C]	1/T [T ⁻¹]	Yield of 1 [%]	TOF [1/h]	ln(TOF)
1	60	0.00300	7.0	350	5.857
2	60	0.00300	6.9	340	5.829
3	60	0.00300	6.8	345	5.844
4	70	0.00291	10.1	508	6.231
5	70	0.00291	9.8	490	6.194
6	70	0.00291	9.7	488	6.190
7	80	0.00283	15.0	750	6.620
8	80	0.00283	16.0	800	6.685
9	80	0.00283	14.5	725	6.586
10	90	0.00275	19.8	990	6.897
11	90	0.00275	20.2	1010	6.918
12	90	0.00275	21.0	1050	6.957
13	100	0.00268	28.9	1448	7.278
14	100	0.00268	29.1	1455	7.283
15	100	0.00268	26.0	1299	7.169

Reaction conditions: 1.00 mol% **[Mn(I)Br]**, 10.0 mol% KO^tBu, 18.0 mL Dioxane, 2.0 h. Yields were determined by ¹H NMR with 1,3,5-trimethoxybenzene as internal standard.

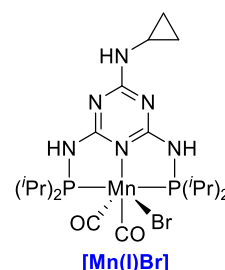
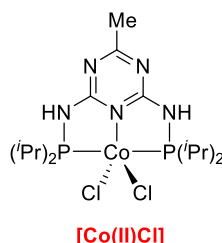
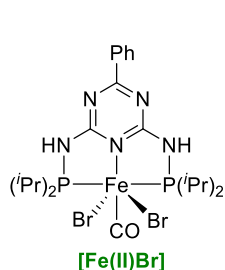
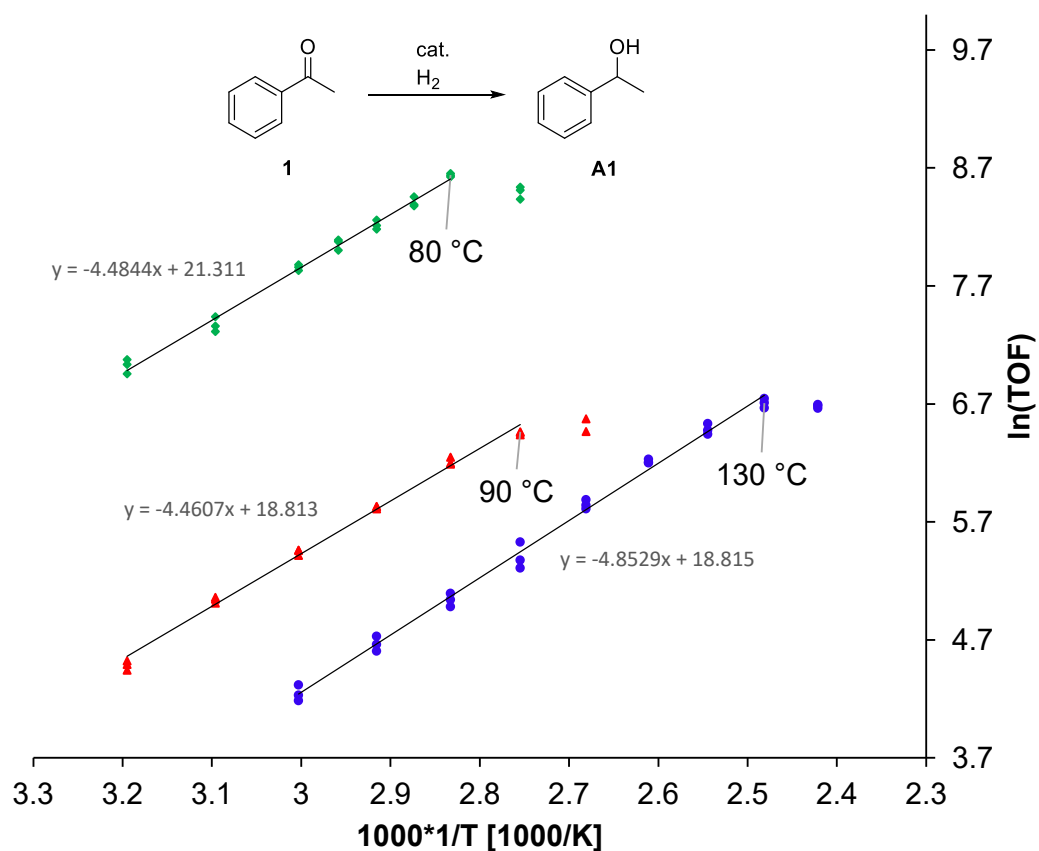
5.11 Dehydrogenation experiments with [Fe(II)Br]



Entry	T [°C]	1/T [T ⁻¹]	Yield of 1 [%]	TOF [1/h]	ln(TOF)
1	60	0.00300	5.3	265	5.579
2	60	0.00300	5.1	255	5.541
3	60	0.00300	5	250	5.521
4	70	0.00291	6.9	346	5.848
5	70	0.00291	6.7	335	5.814
6	70	0.00291	6.8	338	5.823
7	80	0.00283	9.3	465	6.142
8	80	0.00283	9.2	500	6.131
9	80	0.00283	8.8	440	6.087
10	90	0.00275	10	500	6.214
11	90	0.00275	8	400	5.991
12	90	0.00275	8.3	415	6.028

Reaction conditions: 1.00 mol% **[Fe(II)Br]**, 20.0 mol% KO^tBu, 18.0 mL Dioxane, 2.0 h. Yields were determined by ¹H NMR with 1,3,5-trimethoxybenzene as internal standard.

5.11.1 Determination of the activation energy for the hydrogenation of acetophenone



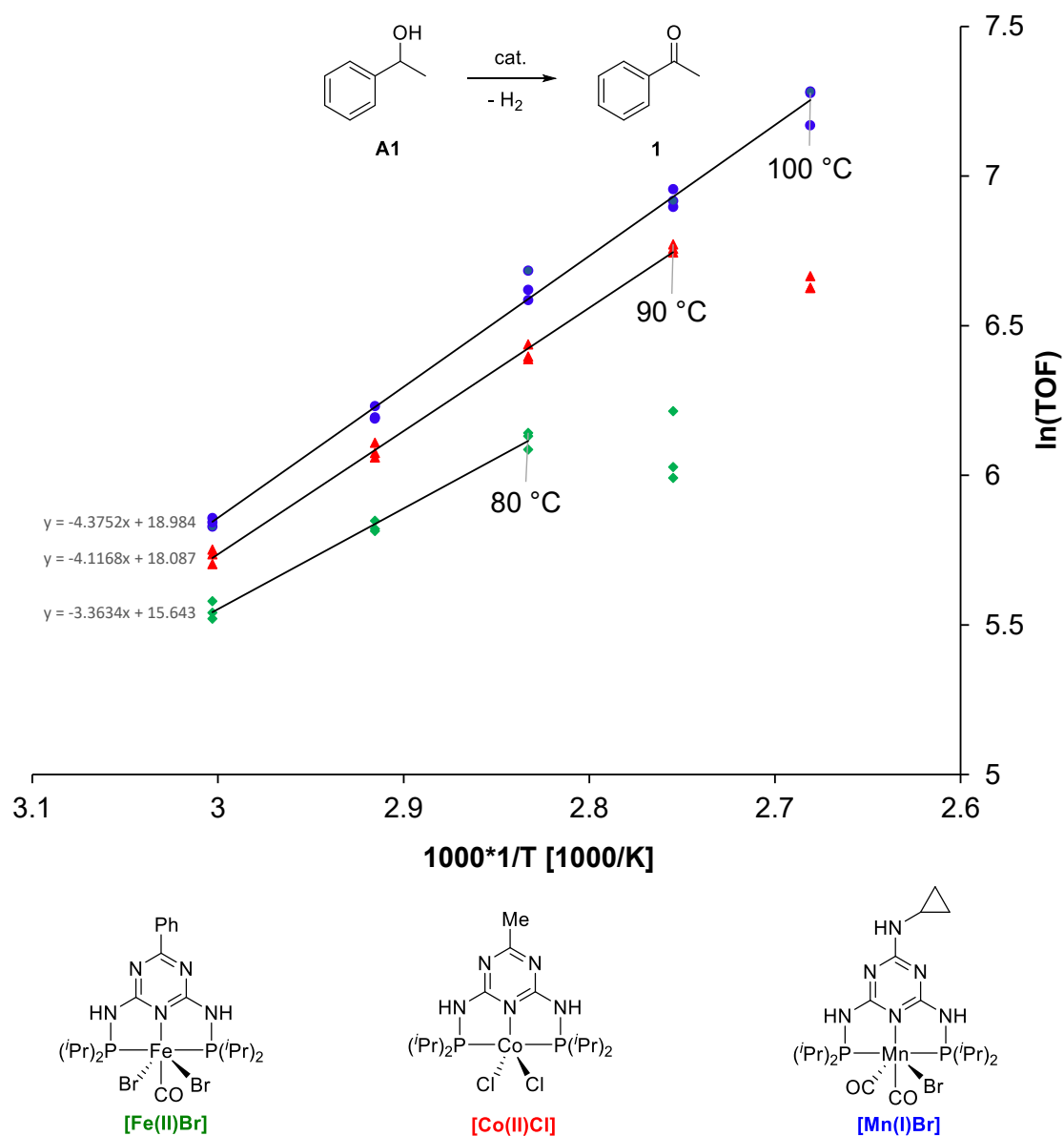
$$\ln(\text{TOF}) = -E_a/R \cdot (1/T) + \ln(A)$$

Supplementary Table 2. Arrhenius parameters for the hydrogenation of acetophenone.

Complex	Preexponential factor A [h ⁻¹]	Slope E _a /R [1000*K]	Activation energy E _a [kJ/mol]	Standard error σ _{Ea} [kJ/mol]
[FeBr(II)Br]	18.0*10 ⁸	− 4.484	37.28	± 0.03
[Co(II)Cl]	1.48*10 ⁸	− 4.461	37.08	± 0.03
[Mn(I)Br]	1.48*10 ⁸	− 4.853	40.35	± 0.05

R: Gas constant; E_a: Activation energy; A: Preexponential factor; σ: Standard error.¹¹

5.11.2 Determination of the activation energy for the dehydrogenation of 1-phenylethanol



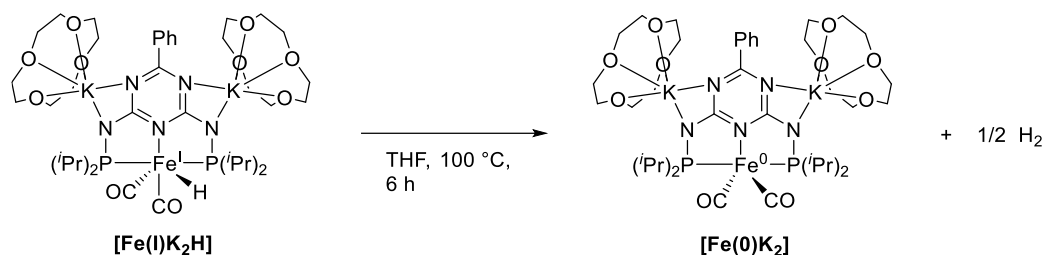
$$\ln(\text{TOF}) = -E_a/R \cdot (1/T) + \ln(A)$$

Supplementary Table 3. Arrhenius parameters for the dehydrogenation of 1-phenylethanol.

Complex	Preexponential factor A [s ⁻¹]	Slope E _a /R [1000*K]	Activation energy E _a [kJ/mol]	Standard error σ _{E_a} [kJ/mol]
[FeBr(II)Br]	1.76*10 ⁸	– 3.363	27.96	± 0.01
[Co(II)Cl]	7.16*10 ⁷	– 4.117	34.23	± 0.02
[Mn(I)Br]	6.22*10 ⁶	– 4.375	36.36	± 0.03

R: Gas constant; E_a: Activation energy; A: Preexponential factor; σ: Standard error.¹¹

5.11.3 Synthesis of the iron(0) complex $[\text{Fe}(0)\text{K}_2]$



Supplementary Figure 1. Reduction of the iron(I) hydride $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ to the iron(0) complex $[\text{Fe}(0)\text{K}_2]$.

A solution of $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ (250 mg; 260 μmol) in THF (10 mL) was refluxed at 100 $^\circ\text{C}$ for 6 hours. The solution was left to cool down and placed in the fridge at -35 $^\circ\text{C}$ to crystallize. After a week, the obtained red crystals were analyzed by single-crystal X-ray structure analysis. The remaining crystals were filtered from the solution and characterized by other methods.

Chemical formula obtained from X-ray structure analysis: $\text{C}_{47}\text{H}_{81}\text{FeK}_2\text{N}_5\text{O}_{12}\text{P}_2$; Molecular weight 959.96 g/mol.

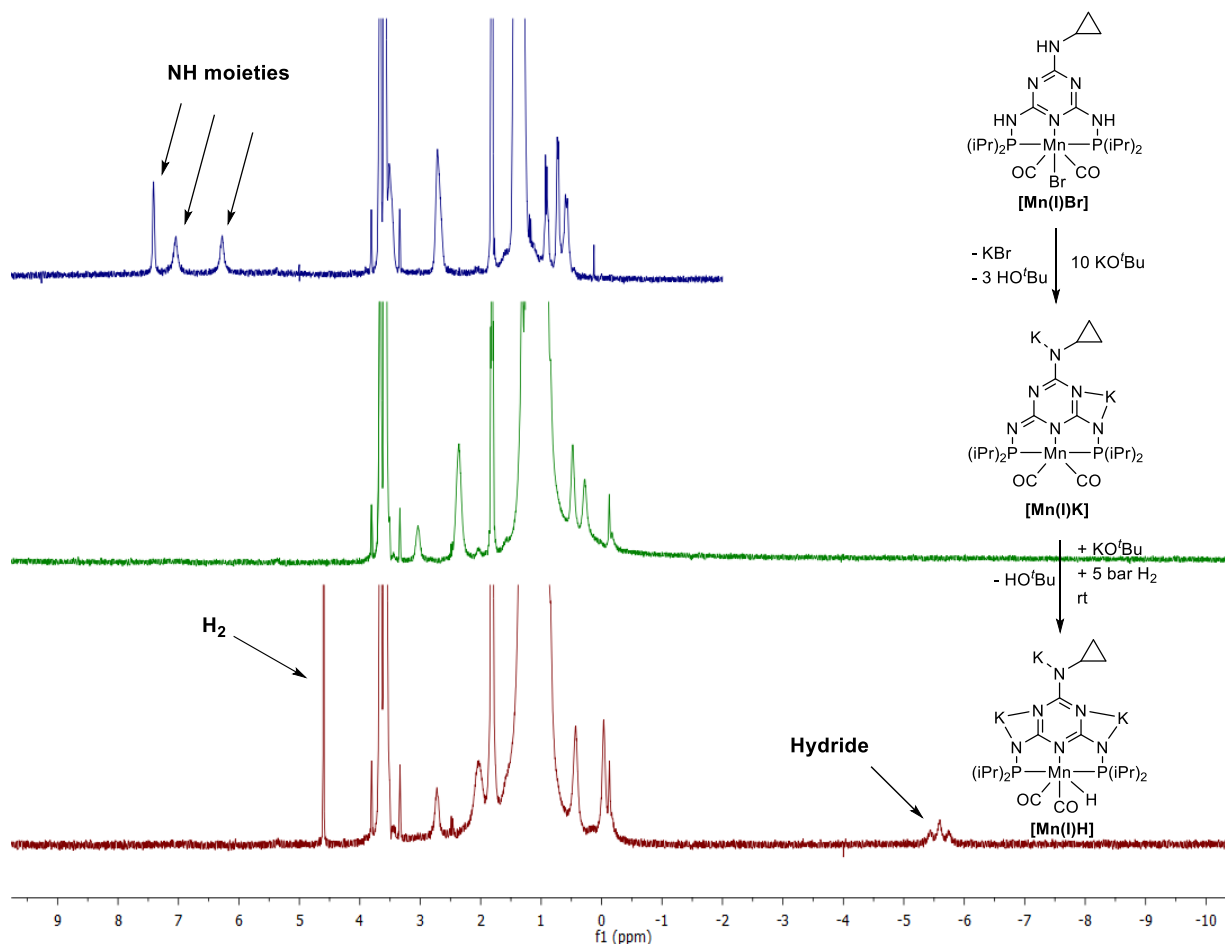
Yield: (57 %, 134 mg, 148 μmol) orange crystals.

^1H NMR (400 MHz, $\text{DMSO}-d_6$, 298 K): δ = 8.17–8.14 (m, 2H, Ar-*H*), 7.24–7.22 (m, 3H, Ar-*H*), 3.56 (m, 4H, THF-*H*), 3.53 (s, 28H, 12-crown-4-*H*), 1.73 (t, J = 3.2 Hz, 4H, THF-*H*), 1.91 (sep, J = 7.06 Hz, 4H, P-*CH*), 1.01–1.00 (m, 26H, P-*CH-CH*₃) ppm.

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 298 K): δ = 220.8, 206.7, 165.7, 142.7, 128.4, 128.0, 127.3, 76.4, 69.7, 67.4, 29.4, 27.3, 25.6, 20.4, 20.2, 19.6, 19.5 ppm.

Elemental analysis calculated for $\text{C}_{47}\text{H}_{81}\text{FeK}_2\text{N}_5\text{O}_{12}\text{P}_2$: C 51.13, H 7.39, N 6.34; found: C 50.92, H 7.24, N 6.13.

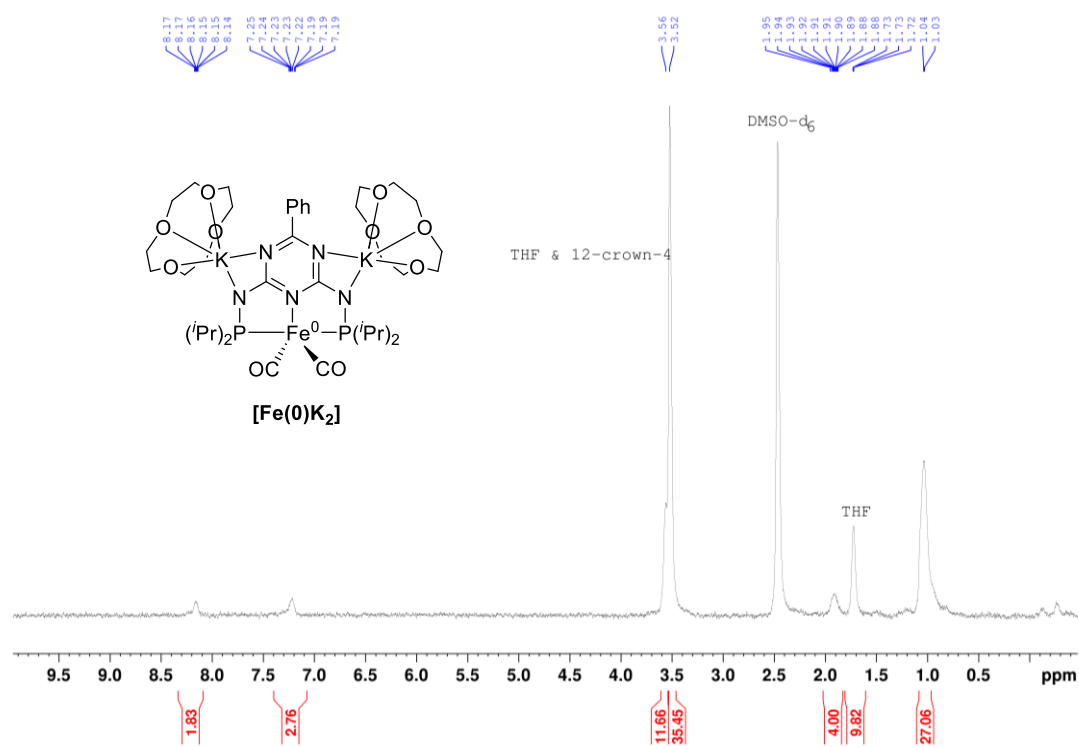
5.11.4 Temperature dependent reversible formation of [Mn(I)H]



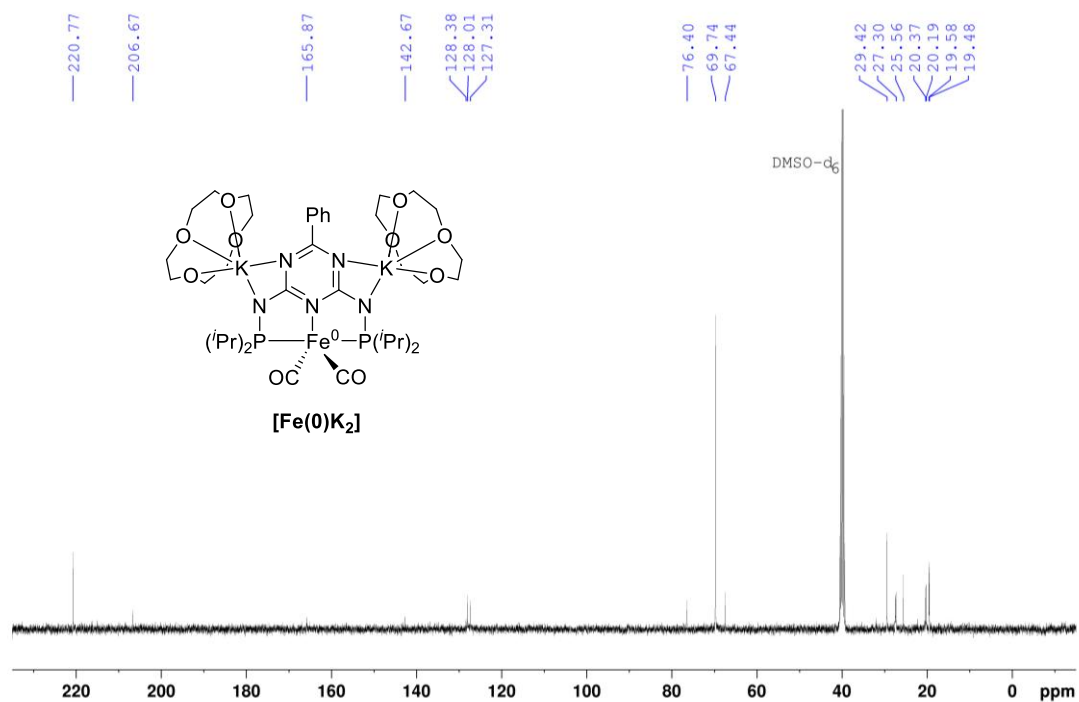
Supplementary Figure 2. *In-situ* formation of $[\text{Mn(I)H}]$ from $[\text{Mn(I)Br}]$ over $[\text{Mn(I)K}]$.

The precursor $[\text{Mn(I)Br}]$ (10.0 mg; 16.9 μmol) was dissolved in dioxane- d_8 (1.0 mL) and KO^tBu (19.0 mg, 169 μmol) was added to the solution, changing its color from yellow to dark blue-green. Afterwards the solution was transferred to a Wilmad quick pressure valve NMR tube (5 mm diam.) and the latter was first purged with H_2 and finally pressurized with 5 bar H_2 while rapidly changing the color to colorless. The tube was then inserted into a pre-heated Varian INOVA 300 NMR spectrometer and the measurement was performed at 140 $^\circ\text{C}$ during the first 30 minutes. The temperature was then set to 20 $^\circ\text{C}$ for the hydride to regenerate.

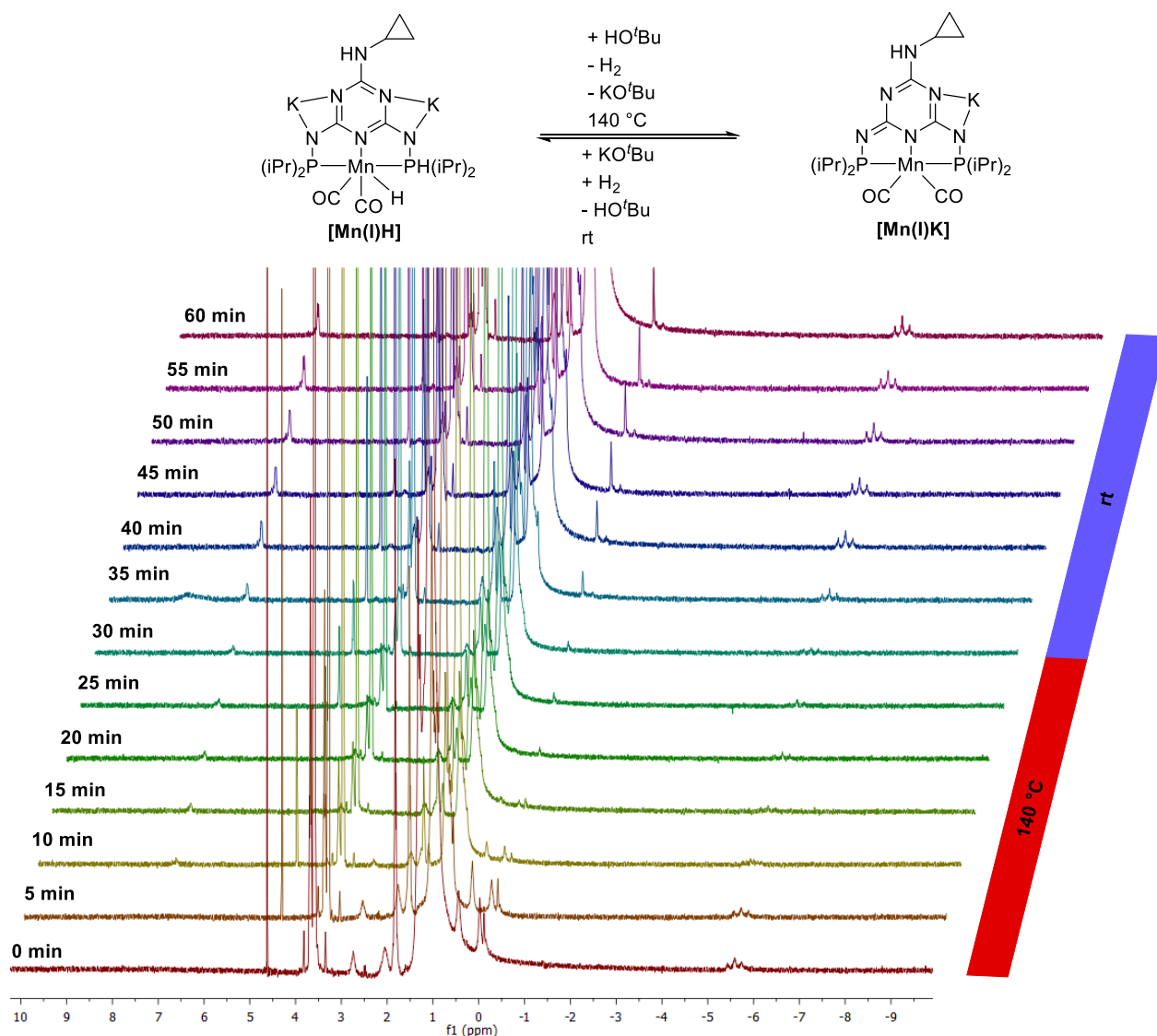
5.12 NMR spectra



Supplementary Figure 3. ^1H NMR spectra of the iron(0) complex **[Fe(0)K₂]**.



Supplementary Figure 4. ^{13}C NMR spectra of the iron(0) complex $[\text{Fe}(0)\text{K}_2]$.



Supplementary Figure 5. Reformation of **[Mn(I)H]** after heated 30 minutes at 140 °C and immediately after cooled down to room temperature. Protonation of the highlighted NK unit of the PN⁵P ligand was detected by the doublet signal at 7.4 ppm deriving from the rising NH proton.

5.13 References

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<https://www.bruker.com> (last checked: 21.05.2025).

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6 **A Selective Iron(I) Hydrogenation Catalyst**

Sila, N.; Dürrmann, A.; Weber, B.; Heinemann, F. W.; Irrgang, T.; Kempe, R. A Selective Iron(I) Hydrogenation Catalyst. *J. Am. Chem. Soc.* **2024**, *146* (39), 26877–26883.

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DOI: 10.1021/jacs.4c07959

A Selective Iron(I) Hydrogenation Catalyst

Niko Sila, Andreas Dürrmann, Birgit Weber, Frank W. Heinemann, Torsten Irrgang, and Rhett Kempe*

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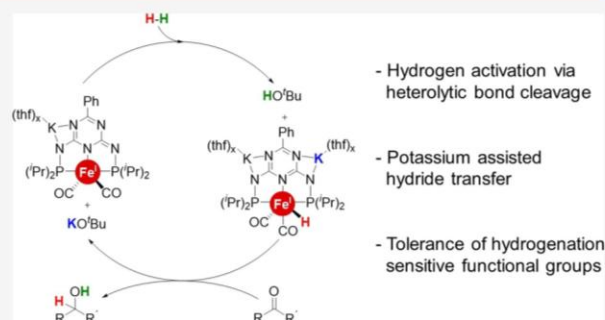


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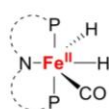
ABSTRACT: Iron is the most abundant transition metal of the Earth's crust, and the understanding of its function in key technologies, such as catalysis, is highly important. We report here on an iron(I) hydrogenation catalyst. Our catalyst activates hydrogen via heterolytic bond cleavage, forms a monohydride, and hydrogenates polar double bonds via a bimetallic pathway (potassium-assisted hydride transfer). The mechanism observed seems to exclude oxidative addition and reductive elimination pathways, permitting the tolerance of numerous hydrogenation-sensitive functional groups, as demonstrated for the hydrogenation of C=O bonds.



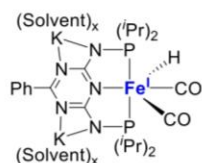
INTRODUCTION

Iron is the most abundant transition metal of the Earth's crust and the identification and understanding of its function in key

A) State of the art



B) Work reported here



- High chemo selectivity

Figure 1. State of the art and work reported here. (A) Generally proposed catalytically active iron(II) dihydride species for the hydrogenation of polar multiple bonds. (B) Iron(I) monohydride reported here.

technologies is highly important. Catalysis is a key technology and iron catalysts with impressive selectivity and/or activity have been discovered, for example, hydrogenation,^{1,2} dehydrogenation³ and tritiation catalysts.⁴ Iron(II) catalysts stabilized by pincer ligands have been introduced for the hydrogenation of aldehydes and ketones.^{5–12} Iron(II) dihydride complexes were proposed here as the catalytically active species (Figure 1A). A dihydride complex can undergo reductive elimination followed by oxidative addition pathways. A conceptually different approach would be stabilizing iron in a low oxidation state, such as iron(I) to suppress a reductive elimination pathway, because a monohydride is now formed. If oxidative addition can be avoided, for instance, by high coordination numbers, only the heterolytic bond cleavage can take place;

i.e., heterolytic hydrogen cleavage for hydrogenation catalysis. Oxidative addition and reductive elimination pathways can be excluded, and functional groups that are activated by those pathways, i.e., olefins,^{13–15} could be tolerated as a benefit of the redox inactivity. Examples of catalysis involving iron(I) complexes are proposed^{16–21} but in combination with oxidative addition (and reductive elimination) pathways. For recent progress in iron-based hydrogenation catalysis (homogeneous and heterogeneous) see refs 22–26.

We report here on an iron(I) hydrogenation catalyst. Our catalyst activates hydrogen via heterolytic bond cleavage, forms a monohydride and hydrogenates polar double bonds via a bimetallic pathway (potassium-assisted hydride transfer).^{27,28} The mechanism observed seems to exclude oxidative addition and reductive elimination pathways, permitting the tolerance of numerous hydrogenation-sensitive functional groups, as demonstrated for C=O bond hydrogenation.

RESULTS AND DISCUSSION

The precatalyst [Fe(II)BrCO]-01 (Figure 2) was synthesized by mixing equimolar amounts of the corresponding pincer ligand with FeBr₂ and the subsequent addition of gaseous CO following a procedure published by Kirchner and co-workers.²⁹ After the addition of 2 equiv KO^tBu to the solution of [Fe(II)BrCO]-01 in tetrahydrofuran (THF), rapid double deprotonation took place and the dimeric iron(II) species [Fe(II)CO] was formed (Figure 2, top). The oxidation state

Received: June 12, 2024

Revised: September 12, 2024

Accepted: September 13, 2024

Published: September 23, 2024



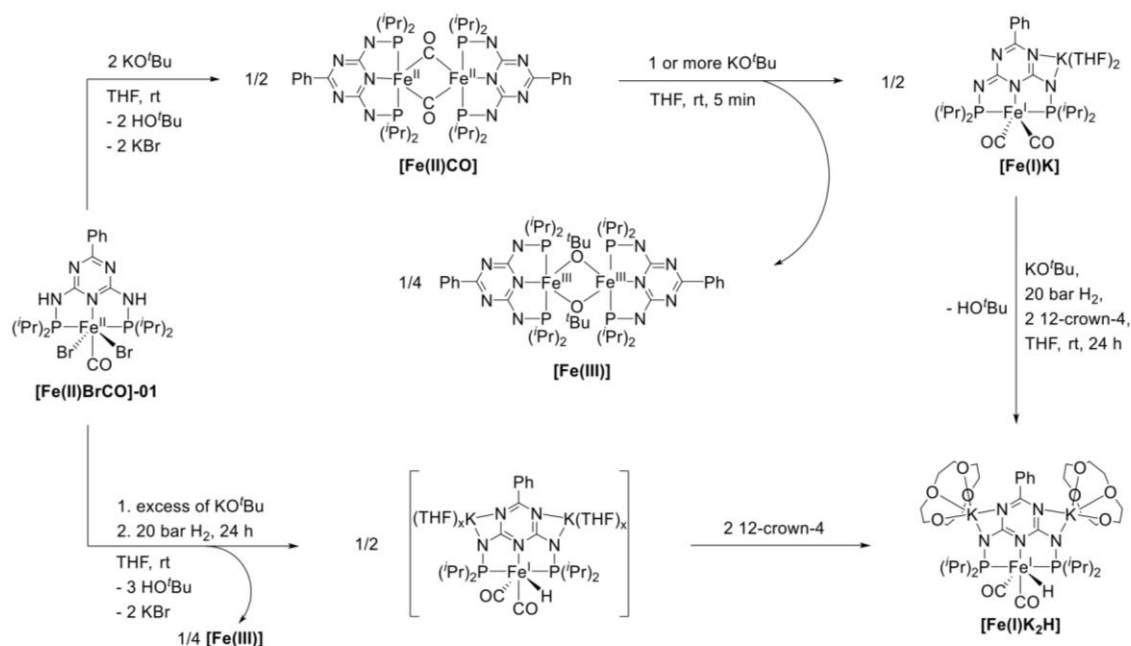


Figure 2. Formation of the iron(I) monohydride dicarbonyl complexes.

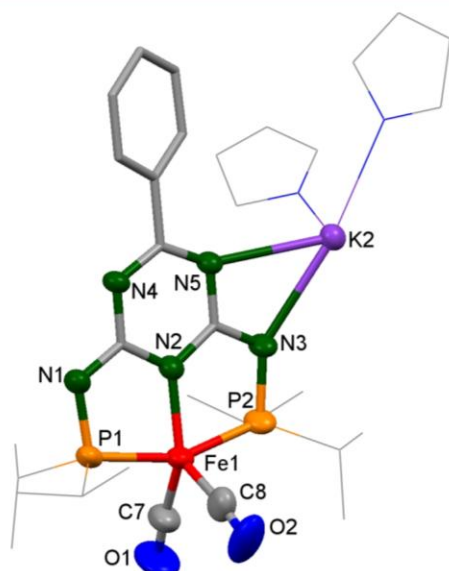
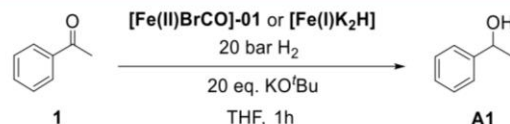


Figure 3. Molecular structure of the iron(I) complex $[\text{Fe}(\text{I})\text{K}]$ with 50% probability of thermal ellipsoids.³¹ Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1–C7 1.751 (5), Fe1–C8 1.761 (5), N2–Fe1 1.966 (3), P1–Fe1 2.237 (1), P2–Fe1 2.224 (1), N3–K2 2.759 (3), N5–K2 2.823 (3); P1–Fe1–N2 79.90 (8), N2–Fe1–P2 79.60 (8), N2–Fe1–C8 119.6 (2), C7–Fe1–N2 144.4 (2), Fe1–P2–N3 106.0 (1), N1–P1–Fe1 105.2 (1), C7–Fe1–C8 95.9 (2), P2–Fe1–P1 158.30 (4).

remains +2 until the further addition of at least 1 equiv KO^tBu , which leads to a disproportionation reaction. The third equivalent KO^tBu facilitates the formation of the bimetallic iron(I) complex $[\text{Fe}(\text{I})\text{K}]$ (Figure 2, top), which was characterized by numerous methods, including the determination of the solid-state structure by X-ray single crystal analysis (Figure 3). Two CO ligands coordinate the iron(I) ion forming a trigonal bipyramidal complex. The effective magnetic moment of $[\text{Fe}(\text{I})\text{K}]$ in solution $\mu_{\text{eff}} = 1.9 \mu_{\text{B}}$ (Evan's method)³⁰ corresponds with the expectations of a



Entry	T [°C]	Yield of A1 [%]		
		$[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$		$[\text{Fe}(\text{I})\text{K}_2\text{H}]$
		0.007 mol%	0.014 mol%	0.007 mol%
1	50	11	25	28
2	60	18	37	37

Figure 4. Comparison of the activity or initial rate of precursor $[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ after activation by KO^tBu (catalyst generated *in situ*) and the catalytically active species proposed, namely, $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, in the hydrogenation of acetophenone 1.

low-spin $3d^7$ system. Both disproportionation products, $[\text{Fe}(\text{I})\text{K}]$ and $[\text{Fe}(\text{III})]$, could be isolated. $[\text{Fe}(\text{I})\text{K}]$ possesses a Fe-to-K ratio of 1:1. The potassium ions in the crystal lattice bridge two $\text{N}_{\text{amido}}\text{N}_{\text{triazine}}$ pockets, creating a coordination polymer. Presumably, the noncharged pocket moiety remains free in solution. $[\text{Fe}(\text{I})\text{K}]$ permits the heterolytic cleavage of H_2 forming the iron(I) hydride $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ and HO^tBu . This was achieved by reacting $[\text{Fe}(\text{I})\text{K}]$ with 20 bar H_2 in the presence of KO^tBu (Figure 2). The iron(I) hydride $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ was isolated by precipitation with 12-crown-4 as a chelating ligand for the potassium ions. The iron(II) precursor $[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ disproportionates to $[\text{Fe}(\text{I})\text{K}]$ and $[\text{Fe}(\text{III})]$ in equal parts by the excess of KO^tBu at room temperature in roughly 5 min in THF (Figure 2, bottom). Each reaction step shown in Figure 2 is optically noticed by a color change of the corresponding solution ($[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ green, $[\text{Fe}(\text{II})\text{CO}]$ red, $[\text{Fe}(\text{I})\text{K}]$ and $[\text{Fe}(\text{III})]$ dark-green, $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ blue).

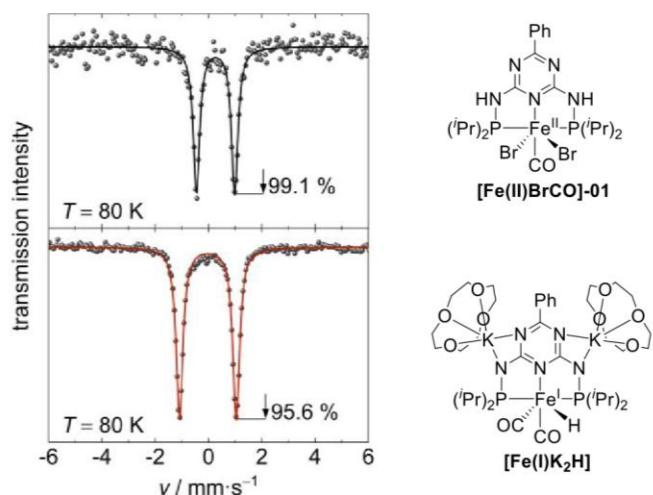


Figure 5. Zero-field ^{57}Fe Mössbauer spectra of $[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ (top) and $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ (bottom), recorded at $T = 80\text{ K}$. Symbols represent experimental data, and the solid line shows the corresponding Lorentzian fit.

We compared the catalytic activity of $[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ with $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ in the hydrogenation of acetophenone at 50 and 60 °C (Figure 4). Twice as much activity of $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ was observed when equimolar amounts of each complex were used. The activities of both iron(II) precursor and iron(I) hydride are identical when double amounts of $[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ are used. This study indicates that the catalytic activity is provided by $[\text{Fe}(\text{I})\text{K}_2\text{H}]$.

The electronic nature of the catalytic species was addressed by means of zero-field ^{57}Fe Mössbauer spectroscopy, which is a

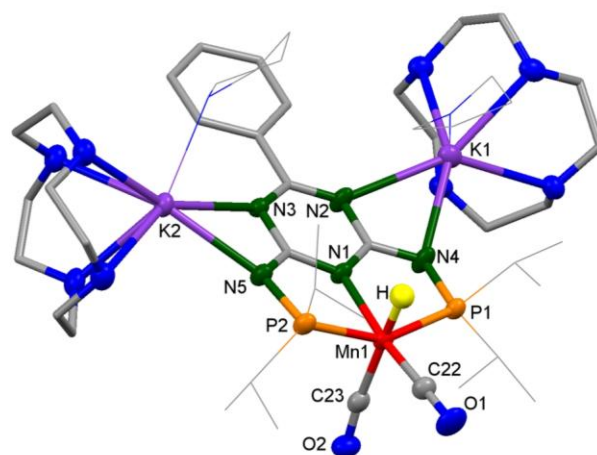


Figure 7. Molecular structure of $[\text{Mn}(\text{I})\text{K}_2\text{H}]$ with 50% probability of thermal ellipsoids.³⁶ All hydrogen atoms (except for hydride) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mn1–H 1.322 (3), Mn1–P1 2.228 (6), Mn1–P2 2.235 (6), Mn1–N1 2.050 (15), K1–N2 2.802 (19), K1–N4 2.729 (19), K2–N3 2.861 (17), K2–N5 2.721 (17); P1–Mn1–H 83.8 (12), P1–Mn1–P2 152.16 (2), P2–Mn1–H 77.9 (12), N1–Mn1–H 83.7 (12), N1–Mn1–P1 78.88 (5), N1–Mn1–P2 78.36 (5), C22–Mn1–N1 171.55 (9), C22–Mn1–C23 88.58 (10), C23–Mn1–H 175.7 (12), C23–Mn1–N1 99.86 (8), N4–K1–N2 49.59 (5), N5–K2–N3 48.98 (5).

diagnostic tool for probing oxidation states of iron. Figure 5 displays the spectra of the precatalyst $[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ and catalytically active $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ recorded at $T = 80\text{ K}$, while the corresponding spectrum of bimetallic intermediate $[\text{Fe}(\text{I})\text{K}]$ can be found in Supplementary Figure 4S, respectively. The pertinent parameters of the measurements are given in

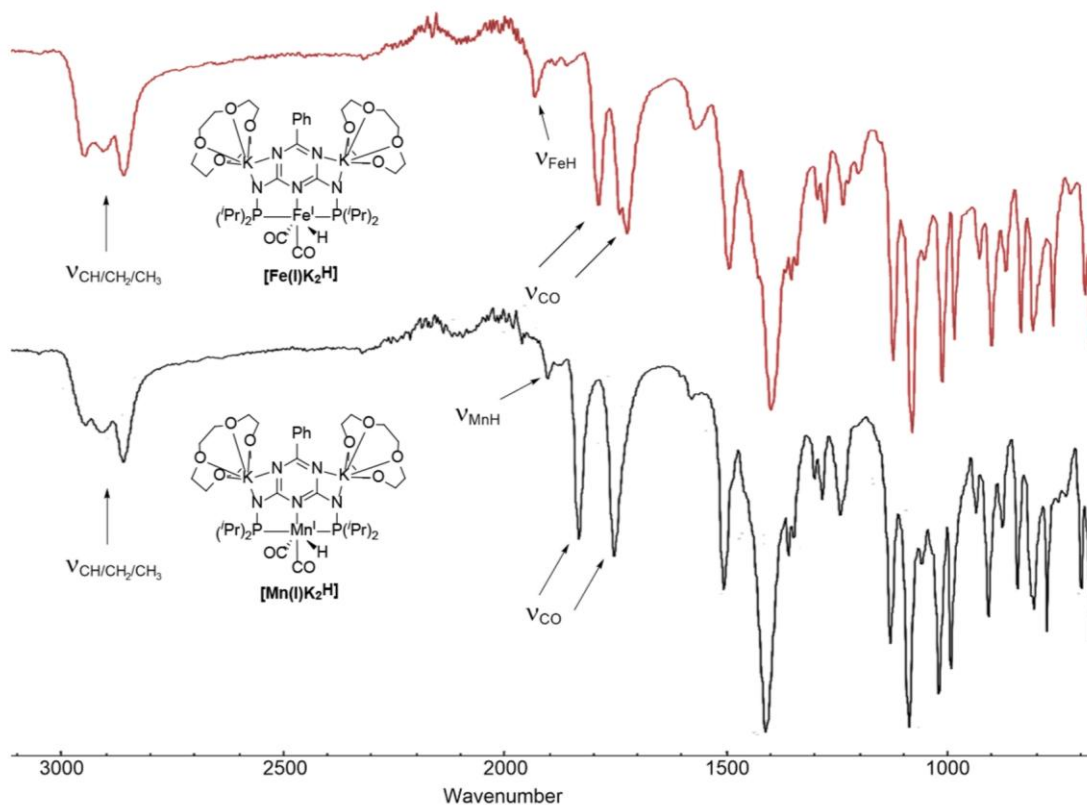


Figure 6. Stacked IR spectra of $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ (red) and $[\text{Mn}(\text{I})\text{K}_2\text{H}]$ (black).

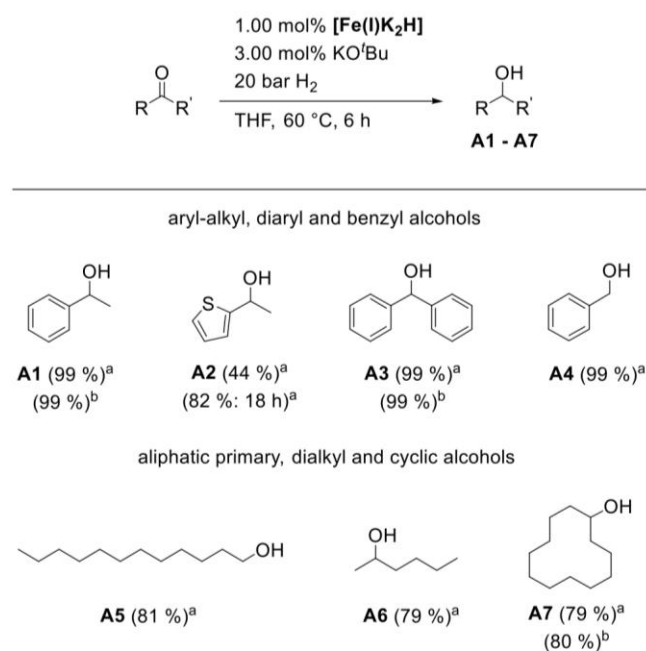


Figure 8. General scope of the hydrogenation of ketones and aldehydes. ^aIsolated products. ^bIsolated yields from upscaling with 30.0 mmol ketone. Reaction conditions: 1.00 mol % $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, 3.00 mol % KO^tBu, 20 bar H₂, THF, 60 °C, 6 h; ^cIsolated yields from upscaling with 30.0 mmol ketone.

Supplementary Tables 8 and 9 (Supporting Information). All spectra were fitted with Lorentzian lines to give well-defined doublets in the case of $[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ and $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, confirming the existence of one unique iron site for both compounds. By contrast, $[\text{Fe}(\text{I})\text{K}]$ delivers a slightly broadened resonance line, which we tentatively ascribe to dynamic processes and/or the existence of crystallographic inequivalent iron sites in the asymmetric unit (see Supporting Information for more details). In line with the results from Evan's method, Mössbauer parameters corroborate the existence of low-spin iron centers. It is important to note that the isomeric shifts observed for $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ ($\delta = -0.025 \text{ mm s}^{-1}$) and $[\text{Fe}(\text{I})\text{K}]$ ($\delta = 0.021 \text{ mm s}^{-1}$) are significantly smaller than for $[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ ($\delta = 0.228 \text{ mm s}^{-1}$). The isomeric shift values for low-valent iron should be considered with caution, as they depend on a range of different parameters and few examples are available.³² The shift of δ toward low Mössbauer velocities observed here can be attributed to a pronounced π -backbonding, which is prevalent in iron species of lower oxidation states, such as iron(I).³³ This reasonable assumption coincides well with results from vibrational spectroscopy (vide infra). The parameters of $[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ fall into the range of low-spin iron(II).³² The quadrupole splitting for $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ ($\Delta E_Q = 2.125 \text{ mm s}^{-1}$) exceeds that for $[\text{Fe}(\text{II})\text{BrCO}]\text{-01}$ ($\Delta E_Q = 1.424 \text{ mm s}^{-1}$). We explain this observation by the fact that a low-spin $3d^7$ system with one unpaired electron in the e_g^* orbitals, such as $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, comprises a less symmetric electron distribution around the ⁵⁷Fe nucleus. As a result, the overall contribution to the electric field gradient will be significantly larger. Although this argument also applies to a potential iron(III) species, the effect here would be less pronounced. We would like to emphasize that similar Mössbauer parameters have been reported for the scarce number of systems featuring iron in low oxidation states in related PNP³⁴ or N environments.³⁵

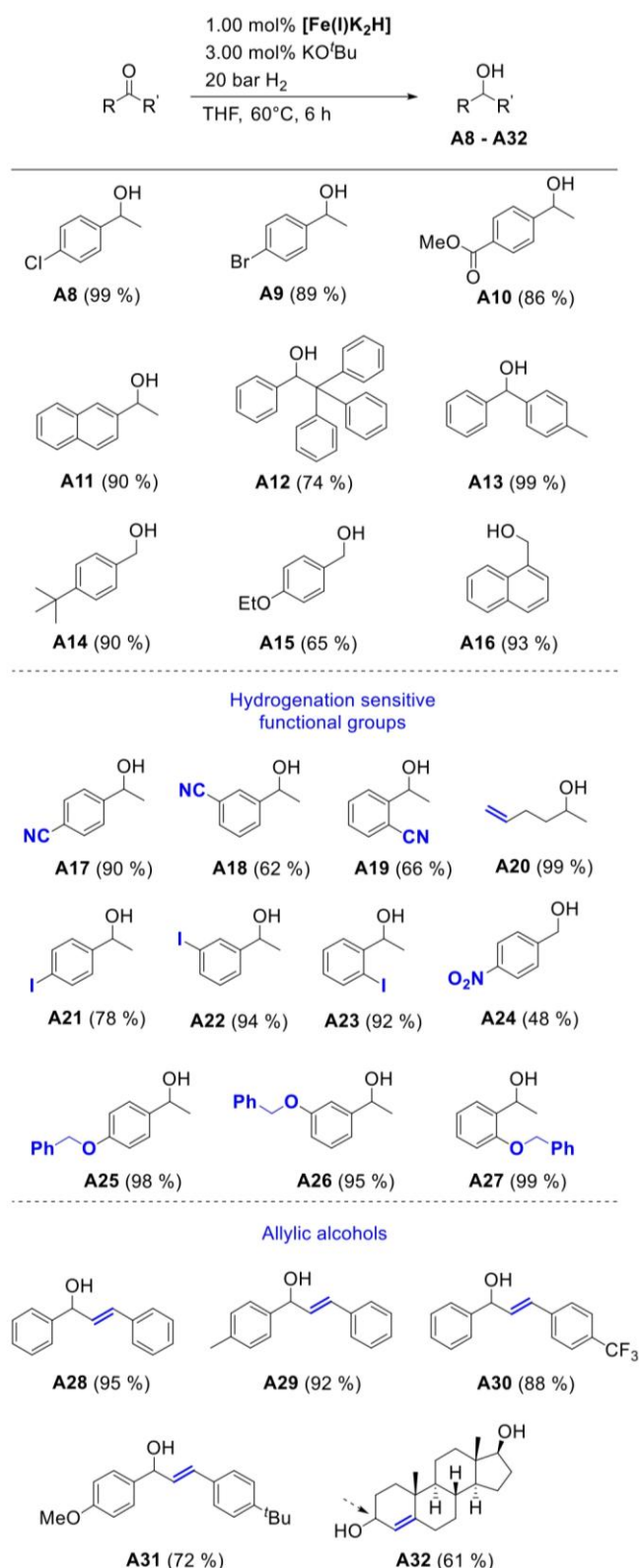


Figure 9. Hydrogenation of carbonyl compounds—electronic influence and hydrogenation-sensitive functional groups. All yields are of isolated products. Reaction conditions: 1.00 mol % $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, 3.00 mol % KO^tBu, 20 bar H₂, THF, 60 °C, 6 h.

Moreover, a low-spin $3d^7$ metal ion is expected to show a strong Jahn–Teller distortion, so that the large quadrupole splitting (and the reduced isomeric shift) for $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ is

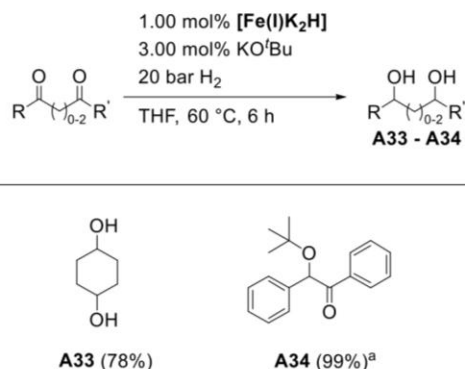


Figure 10. Hydrogenation of 1,2- and 1,4-diketones. All yields are of isolated products. Reaction conditions: 1.00 mol % $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, 3.00 mol % KO^tBu , 20 bar H_2 , THF, 60 °C, 6 h; ^a1.00 equiv KO^tBu .

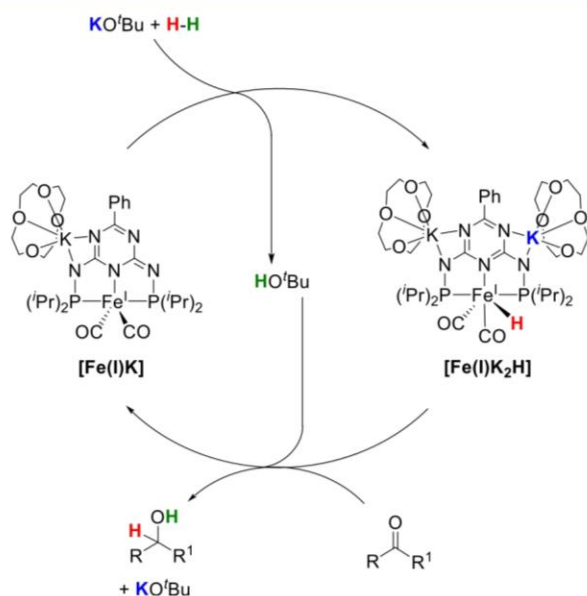


Figure 11. Proposed catalytic cycle for the iron(I)-mediated hydrogenation of carbonyl compounds.

the result of an interplay between electronic distortion and geometrical strains. X-ray crystallography gives clear evidence of iron(I) in the bimetallic compound $[\text{Fe}(\text{I})\text{K}]$ and, from the perspective of a close-to-ideal match of isomeric shift in $[\text{Fe}(\text{I})\text{K}]$ and $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, we also ascribe the formal oxidation state in catalytically active $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ to a low-valent iron(I) species. With respect to the nature of π -backbonding in $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, we compared the iron(I) complex with its manganese analog $[\text{Mn}(\text{I})\text{K}_2\text{H}]$, which we synthesized and characterized by numerous methods, including infrared (IR) spectroscopy (Figure 6). Both spectra reveal the presence of two intensive CO vibrations at $\nu([\text{Fe}(\text{I})\text{K}_2\text{H}]) = 1795 \text{ cm}^{-1}$; 1730 cm^{-1} and $\nu([\text{Mn}(\text{I})\text{K}_2\text{H}]) = 1835 \text{ cm}^{-1}$; 1755 cm^{-1} . As demonstrated by Mössbauer analysis, $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ features an electron-rich $3d^7$ metal center, capable of providing more electrons for π -backbonding than $[\text{Mn}(\text{I})\text{K}_2\text{H}]$ (19 VE vs. Eighteen VE; $3d^7$ vs. $3d^6$); i.e., the CO frequencies of $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ shift to lower wave numbers in comparison to $[\text{Mn}(\text{I})\text{K}_2\text{H}]$. The lower energy vibrations are, thus, a sign of a decrease of the formal bond order of CO. We interpret the more pronounced metal–carbonyl interaction as an additional hint of an iron(I) site in $[\text{Fe}(\text{I})\text{K}_2\text{H}]$. Another spectral feature

concerns the presence of the hydride: Next to the CO vibrations, we find a vibration with low intensity, though higher energy, at $\nu = 1930 \text{ cm}^{-1}$ in $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, which can also be observed in the corresponding IR spectrum of $[\text{Mn}(\text{I})\text{K}_2\text{H}]$ ($\nu = 1905 \text{ cm}^{-1}$). The analogy of the IR spectra indicates isostructural complexes. Note that $[\text{Mn}(\text{I})\text{K}_2\text{H}]$ is a stable 18 valence electron and $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ a sensitive 19 valence electron complex. Therefore, $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ is too unstable to survive a longer lasting crystallization procedure to obtain single crystals suitable for X-ray single crystal structural analysis. On the other hand, we could perform a single crystal X-ray structure analysis of $[\text{Mn}(\text{I})\text{K}_2\text{H}]$ (Figure 7).

Crystals of $[\text{Mn}(\text{I})\text{K}_2\text{H}]$ could be grown from a THF solution. An octahedral coordination sphere of the manganese(I) core can be observed (Figure 7). Each potassium ion coordinates to one 12-crown-4 molecule and both potassium ions of $[\text{Mn}(\text{I})\text{K}_2\text{H}]$ are tilted toward the same direction of the hydride. The CO ligands stand at an angle of 88.58° to each other and the hydride stands at an angle of 87.8° to the nearest C atom (almost orthogonal in both cases). A certain inhibition effect during the catalysis could be expected because 12-crown-4 was used as a chelating ligand to facilitate the isolation of $[\text{Fe}(\text{I})\text{K}_2\text{H}]$. Investigations of the hydrogenation activity of isolated $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, which is coordinated by 12-crown-4, revealed that this crown ether reduces the hydrogenation activity insignificantly if an excess of the potassium base relative to 12-crown-4 is used (Figure 4). By contrast, if an excess of 12-crown-4 is used in comparison to the base that is required for the formation of $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, a small decrease of the ketone hydrogenation activity is observed (Supplementary Table 7, Supporting Information). The inhibition rate of the crown ether is significant if crown ethers are used which are more specific for K^+ binding, such as 15-crown-5 and 18-crown-6 (Supplementary Table 7, Supporting Information). Similarly, the replacement of potassium by sodium or lithium reduces the catalytic activity significantly (Supplementary Table 2, Supporting Information).

After the optimization of the reaction conditions (1.00 mol % $[\text{Fe}(\text{I})\text{K}_2\text{H}]$, 3.00 mol % KO^tBu , 20 bar H_2 , THF, 60 °C, 6 h) for the hydrogenation of acetophenone as a standard substrate (Supporting Information), $[\text{Fe}(\text{I})\text{K}_2\text{H}]$ was used for the hydrogenation of a series of ketones and aldehydes containing aryl-alkyl, diaryl and dialkyl substituents (Figure 8). In addition, benzyl and purely aliphatic aldehydes were attained in a yield range of 79–99%. Upscaling of this reaction (30.0 mmol) was conducted for acetophenone, benzophenone and cyclododecanone, delivering similar yields of 99, 99, and 80%, respectively (Figure 8). Ketones and aldehydes with electron withdrawing and electron donor groups (A8–A16, Figure 9) were hydrogenated next. A high chemoselectivity was observed hydrogenating ketones and aldehydes with several hydrogenation-sensitive functional groups, such as nitrile, olefinic, iodide, nitro and benzyloxy groups (A17–A27, Figure 9). Various substituent positions of the aromatic unit (*ortho*, *meta* and *para*) were tested for the nitrile, iodide and benzyloxy carbonyl compounds. The selective hydrogenation of α,β -unsaturated ketones was carried out next. Note that the selective hydrogenation of α,β -unsaturated ketones employing well-defined iron catalysts is challenging.^{10,37} The corresponding allylic alcohols A28–A31 (Figure 9) were obtained with yields from 73 to 96%. Additionally, testosterone was hydrogenated, delivering 4-androstendiol A32 in a 61% yield. The alcohol unit which emerged is pointed out in Figure 9

with a dashed arrow. Based on the suggestion of one of the reviewers, the hydrogenation of 1,2-, 1,3- and 1,4-diketones was investigated (Figure 10). The hydrogenation of the 1,4-diketone proceeds under standard conditions and the formation of diols is observed (A33). More base had to be added for the 1,2-diketone to avoid potassium removal from the catalyst. The benzoin intermediate undergoes etherification with HO^tBu forming A34.³⁸ 1,3-Diketones could not be reduced.

Finally, a catalytic cycle for the hydrogenation of carbonyl compounds is proposed (Figure 11). Both [Fe(I)K] and [Fe(I)K₂H] are catalytically active species. [Fe(I)K] (17 valence electrons) heterolytically cleaves H₂ (Figure 2, bottom), generating the hydride [Fe(I)K₂H] (19 valence electrons) and HO^tBu, which serves as a protonation source. [Fe(I)K₂H] transfers the hydride and the potassium cation to the ketone, forming [Fe(I)K] and an intermediate potassium alcoholate. The oxidation state remains +1, permitting an exclusion of unwanted side reactions that depend on oxidative addition and reductive elimination pathways.

CONCLUSIONS

In conclusion, we report that an iron(I) complex can be a selective hydrogenation catalyst. Hydrogen activation takes

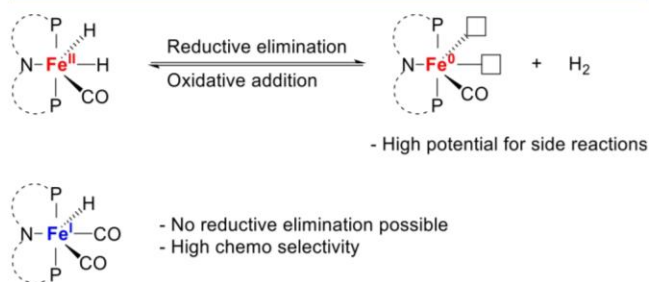


Figure 12. Proposed explanation of the high chemo selectivity of the iron(I) catalyst reported in this work.

place via heterolytic bond cleavage to form a catalytically active monohydride, and polar double bonds, such as those in ketones and aldehydes, are hydrogenated via a bimetallic pathway or potassium-assisted hydride transfer.^{20,39} The mechanism observed seems to exclude oxidative addition and reductive elimination pathways, permitting the tolerance of numerous hydrogenation-sensitive functional groups (Figure 12).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c07959>.

Experimental procedures and spectroscopic and crystallographic data (PDF)

Accession Codes

CCDC 2352638–2352640 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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<https://pubs.acs.org/doi/10.1021/jacs.4c07959>

Funding

This work was financially supported by the DFG (Deutsche Forschungsgemeinschaft), KE 756/31–2 and the University of Bayreuth. F.W.H. is grateful to the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU) for generous funding.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Johannes Porschke and Alexander Goller from Inorganic Chemistry II, University of Bayreuth for the single crystal X-ray measurements and Gerald Hörner from the Institute for Inorganic and Analytical Chemistry in Friedrich Schiller University Jena for the helpful discussions.

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6.2 Supporting Information

A Selective Iron(I) Hydrogenation Catalyst

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6.3 General considerations

All reactions were carried out in a glove box filled with nitrogen N₂ (5.0) or using Schlenk techniques. THF, dioxane, toluene and isopropanol were purified by distillation over drying agent (sodium or LiAlH₄) and stored over molecular sieves (3 Å). Dimethoxyethane, diglyme, 2-methyl-2-butanol, DMSO, 12-crown-4 and 15-crown-5 were dried over molecular sieves (3 Å). Other chemicals were purchased from commercial vendors, purified either by crystallization, sublimation or distillation and dried at least for 24 hours under high vacuum.

Probes for elemental analyses were weighed on a precision scale and the measurement was performed on an Elementar *UNICUBE* (C/H/N). IR spectra were collected in a glove box using a Cary 630 FTIR *Agilent* with an ATR crystal. The ordinate and coordinate axes represent the percentage transmission and the wave number in reciprocal centimeters, respectively.

NMR measurements were performed at room temperature, if not stated otherwise, on a *Varian* INOVA 300, *Varian* INOVA 400 or on a *Bruker* Avance III HD 500. The chemical shift is given in the δ -scale. Following symbols were used for the description of the signals: s = singulett, d = doublet, t = triplet, q = quartet, quin = quintet, sx = sextet, sep = septet, m = multiplet. Coupling constants *J* were given in Hz. ¹³C and ³¹P NMR spectra were measured ¹H decoupled. Magnetic susceptibility measurements were conducted using *Varian* INOVA 400 with an NMR tube containing a solution of the paramagnetic substance and trimethoxybenzene, and an additional inner tube containing a solution of trimethoxybenzene of same concentration. Evaluation was conducted using the Evan's method.¹ Spectra were processed with *Bruker* TopSpin 4.1.4.²

Suitable single-crystals were grown out of solutions and covered by a Fomblin layer before exposure to air. The desired single-crystal was observed under a light microscope, picked with a Nylon loop and measured on a STOE STADIVARI [$\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$] or on a Bruker-Nonius Kappa Photon II Duo diffractometer [$\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$], both equipped with an Oxford Cryostream low temperature unit. Structure solution and refinement were achieved using Olex 2-1.5^{3–6} and Mercury 3.3⁷.

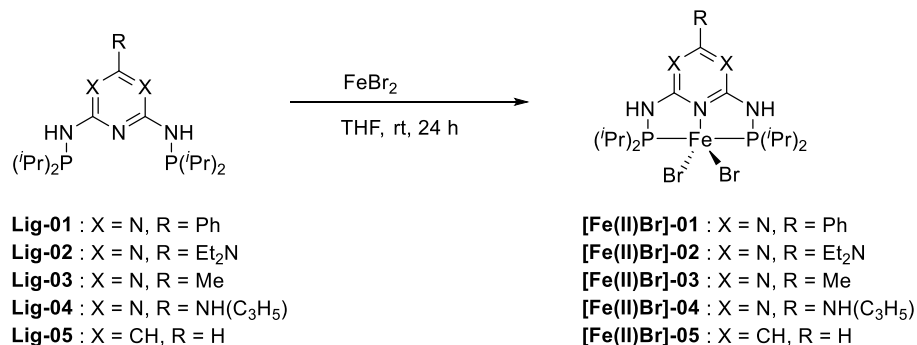
⁵⁷Fe Mössbauer spectra were recorded on a commercial Mössbauer spectrometer from WissEL (Wissenschaftliche Elektronik GmbH) in transmission geometry using constant acceleration mode. The ⁵⁷Co(Rh) source has a nominal activity of 50 mCi and

is stored at room temperature. Temperature control was achieved with a cryostat from CRYO Industries of America, Inc. connected to a temperature controller from Lake Shore Cryotronics, Inc. (Model 325). Polycrystalline material of the respective compound was filled in a PEEK container which was mounted on a copper block. Isomer shifts are reported relative to α -Fe foil at 298 K (without correction in terms of second-order Doppler shift). Suitable fit models could be obtained with the Recoil software package.⁸

6.4 Experimental procedures

All pincer ligands were synthesized according to the literature.^{9–11}

6.4.1 Synthesis of the paramagnetic Fe(II) complexes



Supplementary Figure 1. General synthesis of the paramagnetic Fe(II) complexes.

Under inert atmosphere the ligand and FeBr₂ were dissolved in THF and stirred for 24 hours at room temperature. The solvent was removed under high vacuum and the product was obtained as a powder.

[Fe(II)Br]-01:

Synthesized according to general procedure with ligand **Lig-01** (3.57 g, 8.51 mmol) and FeBr₂ (1.84 g, 8.51 mmol) in THF (300 mL).

Yield: (99%, 5.40 g, 8.51 mmol), yellow solid.

Chemical formula: C₂₁H₃₅Br₂FeN₅P₂; Molecular weight: 635.15 g/mol.

Elemental analysis calculated: C 39.7, H 5.55, N 11.0; found: C 39.6, H 5.30, N 11.0.

FT-IR (ATR): ν = 3200 (NH), 2960–2880 (CH_{1/3}) cm⁻¹.

[Fe(II)Br]-02:

Synthesized according to general procedure with ligand **Lig-02** (481 mg, 1.16 mmol) and FeBr₂ (250 mg, 1.16 mmol) in THF (60 mL).

Yield: (99%, 730 mg, 1.16 mmol) grey solid.

Chemical formula: C₁₉H₄₀Br₂FeN₆P₂; Molecular weight: 630.17 g/mol.

Elemental analysis calculated: C 36.21, H 6.40, N 13.34; found: C 35.85, H 6.37, N 13.00.

FT-IR (ATR): $\nu = 3250$ (NH), 2960–2880 ($\text{CH}_{1/3}$) cm^{-1} .

[Fe(II)Br]-03:

Synthesized according to general procedure with ligand **Lig-03** (414 mg, 1.16 mmol) and FeBr_2 (250 mg, 1.16 mmol) in THF (60 mL).

Yield: (99%, 664 mg, 1.16 mmol) red solid.

Chemical formula: $\text{C}_{16}\text{H}_{33}\text{Br}_2\text{FeN}_5\text{P}_2$; Molecular weight: 573.08 g/mol.

Elemental analysis calculated: C 33.53, H 5.80, N 12.22; found: C 33.85, H 6.03, N 12.08.

FT-IR (ATR): $\nu = 3200$ (NH), 2960–2880 ($\text{CH}_{1/3}$) cm^{-1} .

[Fe(II)Br]-04:

Synthesized according to general procedure with ligand **Lig-04** (462 mg, 1.16 mmol) and FeBr_2 (250 mg, 1.16 mmol) in THF (60 mL).

Yield: (99%, 712 mg, 1.16 mmol) yellow solid.

Chemical formula: $\text{C}_{18}\text{H}_{36}\text{Br}_2\text{FeN}_6\text{P}_2$; Molecular weight: 614.13 g/mol.

Elemental analysis calculated: C 35.20, H 5.91, N 13.68; found: C 34.89, H 5.78, N 13.55.

FT-IR (ATR): $\nu = 3170$ (NH), 2960–2880 ($\text{CH}_{1/2/3}$) cm^{-1} .

[Fe(II)Br]-05:

Synthesized according to general procedure with ligand **Lig-05** (396 mg, 1.16 mmol) and FeBr_2 (250 mg, 1.16 mmol) in THF (60 mL).

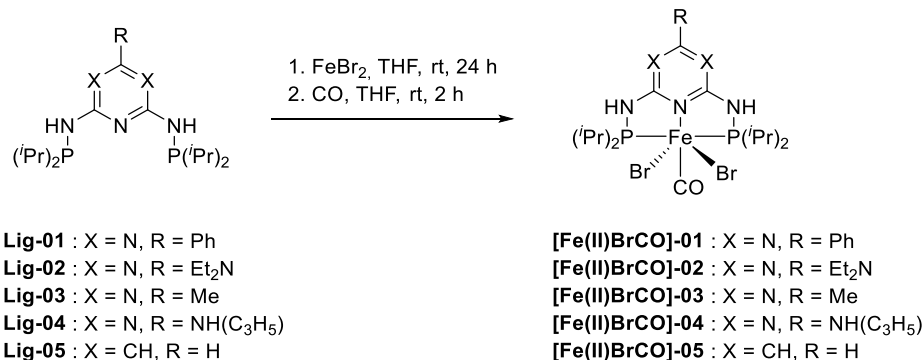
Yield: (99%, 645 mg, 1.16 mmol) grey solid.

Chemical formula: $\text{C}_{17}\text{H}_{33}\text{Br}_2\text{FeN}_3\text{P}_2$; Molecular weight: 557.07 g/mol.

Elemental analysis calculated: C 36.65, H 5.97, N 7.54; found: C 36.48, H 5.84, N 7.49.

FT-IR (ATR): $\nu = 3220\text{--}3195$ (NH), $2950\text{--}2890$ ($\text{CH}_{1/3}$) cm^{-1} .

6.4.2 General procedure for the precatalyst synthesis



Supplementary Figure 2. General synthesis of the Fe(II) precatalysts.

Under inert atmosphere the ligand and FeBr₂ were dissolved in THF and stirred for 24 hours at room temperature. CO gas was produced *in situ* by dropwise addition of HCOOH (20 mL) in pure H₂SO₄ (150 mL) at 0 °C. The generated gas was directed using Schlenk techniques to the stirring complex solution for approximately 2 hours. Afterwards, THF was removed under high vacuum and the residue was washed several times with a 1:1 mixture of pentane and toluene. The product was dried for 2 hours under high vacuum (otherwise loss of CO ligand) and obtained as a solid.

[Fe(II)BrCO]-01:

Synthesized according to general procedure with ligand **Lig-01** (3.57 g, 8.51 mmol) and FeBr₂ (1.84 g, 8.51 mmol) in THF (200 mL).

Chemical formula: C₂₂H₃₅Br₂FeN₅OP₂; Molecular weight 663.16 g/mol.

Yield: (89%, 5.05 g, 7.62 mmol) green solid.

¹H NMR (400 MHz, THF-d₈, 298 K): δ = 8.86 (s, 2H, NH), 8.43 (d, J = 7.60 Hz, 2H, CH), 7.51 (t, J = 7.06 Hz, 1H, CH), 7.45 (t, J = 7.65 Hz, 2H, CH), 3.25 (sep, 4H, J = 6.73 Hz, CH), 1.56 (q, 12H, J = 7.07 Hz, CH₃), 1.56 (q, 12H, J = 7.51 Hz, CH₃) ppm.

¹³C NMR (100 MHz, THF-d₈, 298 K): δ = 152.8, 151.2, 132.8, 129.3, 111.9, 28.0, 27.9, 27.8, 19.3, 18.9 ppm.

^{31}P NMR (162 MHz, THF- d_8 , 298 K): δ = 120.5, 104.9 (cis isomer) ppm.

FT-IR (ATR): ν = 3250 (NH), 2960–2880 ($\text{CH}_{1/3}$), 1960 (CO) cm^{-1} .

Elemental analysis calculated: C 39.85, H 5.32, N 10.56; found: C 39.95, H 5.21, N 10.30.

[Fe(II)BrCO]-02:

Synthesized according to general procedure with ligand **Lig-02** (829 mg, 2.00 mmol) and FeBr_2 (433 mg, 2.00 mmol) in THF (20 mL).

Chemical formula: $\text{C}_{20}\text{H}_{40}\text{Br}_2\text{FeN}_6\text{OP}_2$; Molecular weight: 658.18 g/mol.

Yield: (85%, 1.12 g, 1.70 mmol) blue solid.

^1H NMR (400 MHz, THF- d_8 , 298 K): δ = 7.99 (s, 1H, NH_2), 3.61 (q, J = 6.9 Hz, 4H, N- CH_2), 3.16 (sep, J = 5.8 Hz, 4H, P- CH), 1.50 (q, J = 6.9 Hz, 12H, P- $\text{CH}_2\text{-CH}_3$), 1.36 (q, J = 7.4 Hz, 12H, P- $\text{CH}_2\text{-CH}_3$), 1.15 (t, J = 6.9 Hz, 6H, N- $\text{CH}_2\text{-CH}_3$) ppm.

^{13}C NMR (100 MHz, THF- d_8 , 298 K): δ = 170.9, 41.1, 27.1, 26.9, 26.8, 20.7, 18.5, 17.5, 12.4 ppm.

^{31}P NMR (162 MHz, THF- d_8 , 298 K): δ = 117.51, 102.6 (cis isomer) ppm.

FT-IR (ATR): ν = 3280 (NH), 2960–2880 ($\text{CH}_{1/3}$), 1970 (CO) cm^{-1} .

Elemental analysis calculated: C 36.50, H 6.13, N 12.77; found: C 36.81, H 6.14, N 12.08.

[Fe(II)BrCO]-03:

Synthesized according to general procedure with ligand **Lig-03** (714 mg, 2.00 mmol) and FeBr_2 (433 mg, 2.00 mmol) in THF (20 mL).

Chemical formula: $\text{C}_{17}\text{H}_{33}\text{Br}_2\text{FeN}_5\text{OP}_2$; Molecular weight: 601.09 g/mol.

Yield: (92%, 1.10 g, 1.83 mmol) blue solid.

^1H NMR (400 MHz, THF- d_8 , 298 K): δ = 8.62 (s, 2H, NH), 3.10 (sep, J = 6.99 Hz, 4H, CH), 2.28 (s, 3H, Triaz- CH_3), 1.43 (1, J = 7.13 Hz, 12H, CH- CH_3), 1.28 (1, J = 7.44 Hz, 12H, CH- CH_3) ppm.

^{13}C NMR (100 MHz, THF- d_8 , 298 K): δ = 177.8, 173.4, 53.7, 28.5, 20.7, 19.9, 18.9 ppm.

^{31}P NMR (162 MHz, THF- d_8 , 298 K): δ = 119.8 ppm.

FT-IR (ATR): ν = 3200 (NH), 2960–2880 ($\text{CH}_{1/3}$), 1950 (CO) cm^{-1} .

Elemental analysis calculated: C 33.97, H 5.53, N 11.65; found: C 33.96, H 5.46, N 11.62.

[Fe(II)BrCO]-04:

Synthesized according to general procedure with ligand **Lig-04** (797 mg, 2.00 mmol) and FeBr_2 (433 mg, 2.00 mmol) in THF (20 mL).

Chemical formula: $\text{C}_{19}\text{H}_{36}\text{Br}_2\text{FeN}_6\text{OP}_2$; Molecular weight: 642.14 g/mol.

Yield: (97%, 1.19 g, 1.94 mmol) blue solid.

^1H NMR (400 MHz, THF- d_8 , 298 K): δ = 8.09 (s, 1H, NH), 7.75 (s, 1H, NH), 6.43 (s, 1H, NH), 3.04 (sep, J = 5.2 Hz, 4H, P–CH), 2.65 (s, br, 1H, Triaz–NH–CH), 1.36 (q, J = 6.0 Hz, 12H, CH_3), 1.24 (q, J = 8.0 Hz, 12H, CH_3) ppm.

^{13}C NMR (100 MHz, THF- d_8 , 298 K): δ = 225.6, 167.3, 27.1, 26.5, 25.5, 23.6, 18.5, 17.5, 6.3 ppm.

^{31}P NMR (162 MHz, THF- d_8 , 298 K): δ = 117.85, 103.6 (cis isomer) ppm.

FT-IR (ATR): ν = 3400 (NH), 3220 (NH), 2960–2880 ($\text{CH}_{1/3}$), 1960 (CO) cm^{-1} .

Elemental analysis calculated: C 35.54, H 5.65, N 13.09; found: C 35.28, H 5.60, N 12.92.

[Fe(II)BrCO]-05:

Synthesized according to general procedure with ligand **Lig-05** (682 mg, 2.00 mmol) and FeBr_2 (433 mg, 2.00 mmol) in THF (20 mL).

Chemical formula: $\text{C}_{18}\text{H}_{33}\text{Br}_2\text{FeN}_3\text{OP}_2$; Molecular weight: 585.08 g/mol.

Yield: (89%, 1.04 g, 1.78 mmol) blue solid.

^1H NMR (400 MHz, THF- d_8 , 298 K): δ = 7.48 (s, 2H, NH), 7.30 (t, J = 8.8 Hz, 1H, Ar- H), 6.36 (d, J = 7.9 Hz, 2H, Ar- H), 3.22 (sep, J = 6.2 Hz, 4H, P-CH), 1.52 (q, J = 6.7 Hz, 12H, CH_3), 1.39 (q, J = 8.2 Hz, 12H, CH_3) ppm.

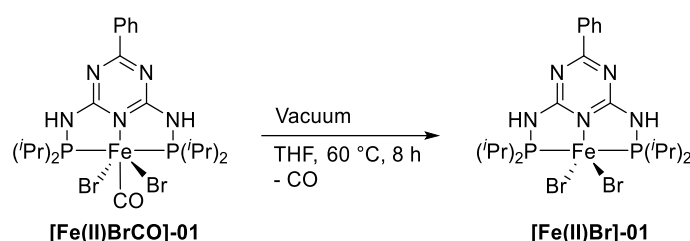
^{13}C NMR (100 MHz, THF- d_8 , 298 K): δ = 162.8, 138.6, 98.1, 29.6, 27.4, 18.6, 17.5 ppm.

^{31}P NMR (162 MHz, THF- d_8 , 298 K): δ = 123.1, 105.8 (cis isomer) ppm.

FT-IR (ATR): ν = 3260 (NH), 2960–2880 ($\text{CH}_{1/3}$), 1950 (CO) cm^{-1} .

Elemental analysis calculated: C 36.95, H 5.69, N 7.18; found: C 36.95, H 5.64, N 6.85.

6.4.3 CO removal with high vacuum



Supplementary Figure 3. Removal of the CO ligand under high vacuum.

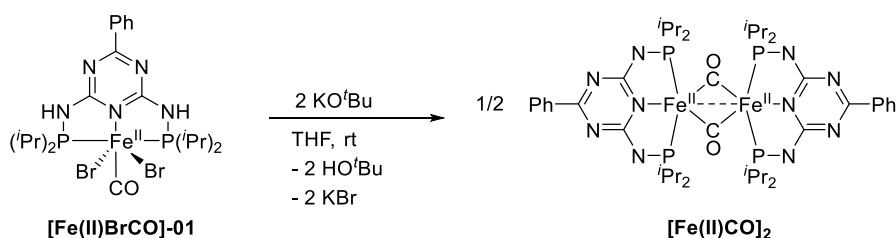
The diamagnetic Fe-complex **[Fe(II)BrCO]-01** (663 mg, 1.00 mmol) was left under high vacuum for 8 hours at 60 °C. During this time a slow color change from green to yellow could be observed. The paramagnetic Fe-complex **[Fe(II)Br]-01** was obtained as a yellow solid and analyzed using IR spectroscopy.

Chemical formula: $\text{C}_{21}\text{H}_{35}\text{Br}_2\text{FeN}_5\text{P}_2$; Molecular weight: 635.15 g/mol.

Yield: (99%, 663 mg, 0.99 mmol) yellow solid.

FT-IR (ATR): ν = 3220 (NH), 2860–2950 ($\text{CH}_{1/2/3}$) cm^{-1} .

6.4.4 Synthesis of the Fe(II) dimer [Fe(II)CO]₂



Supplementary Figure 4. Formation of the Fe(II) dimer **[Fe(II)CO]₂**.

Under inert atmosphere, KO^tBu (33.7 mg, 300 μ mol, 2.00 eq.) was added to a solution of Fe(II) precursor **[Fe(II)BrCO]-01** (100 mg, 150 μ mol) in THF (4 mL) and stirred rigorously for 1 minute at room temperature. After addition of the base an immediate change of color from olive green to dark red was observed. The generated KBr was left to precipitate and the solution was filtered. Pentane (6 mL) was added to the solution for precipitation of the complex. The residue was filtered and washed a couple of times with more pentane and dried under high vacuum for 2 hours.

Chemical formula: C₄₄H₆₆Fe₂N₁₀O₂P₄; Molecular weight: 1002.67 g/mol.

Yield: (90%, 67.6 mg, 67.5 μ mol) brown solid.

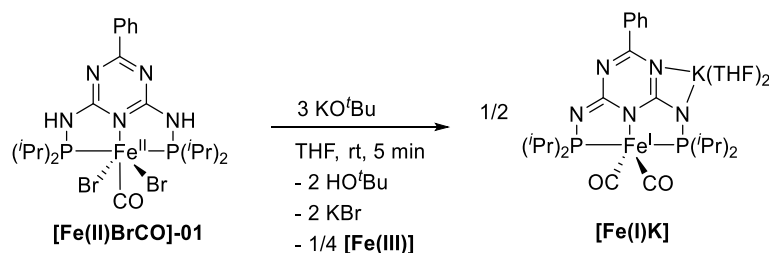
¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 8.29 (d, J = 6.68 Hz, 1H, Ar-*H*), 8.19 (d, J = 6.68 Hz, 1 H, Ar-*H*), 7.41 (m, 3 H, Ar-*H*), 2.11–2.40 (m, 2 H, P-*CH*), 1.46–0.61 (m, 26 H, P-*CH* & CH₃) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 137.10, 128.70, 128.46, 128.32, 128.25, 128.19, 127.98, 127.86, 20.67, 19.69, 19.61, 19.48, 19.27, 19.02, 18.94, 18.75, 18.67, 18.56, 18.07, 17.94, 17.56 ppm.

³¹P NMR (162 MHz, DMSO-d₆, 298 K): δ = 108.05 ppm.

FT-IR (ATR): ν = 2860–2950 (CH_{1/2/3}), 2000 (CO), 1950 (CO), 1890 (CO) cm⁻¹.

6.4.5 Synthesis of the Fe(I) coordination polymer [Fe(I)K]



Supplementary Figure 5. Formation of the Fe(I) coordination polymer **[Fe(I)K]**.

Under inert atmosphere, KO^tBu (1.50 mmol, 10 eq.) was added to a solution of Fe(II) precursor **[Fe(II)BrCO]-01** (150 μmol) in THF (4 mL) and stirred for 5 minutes at room temperature. After addition of the base an immediate change of color from olive green to dark red was observed, which changed in the next minutes to dark greenish. The solution was left at –20 °C for seven days and the resulting black crystals were filtered and dried for 2 hours under high vacuum.

Chemical formula: C₃₁H₄₉FeKN₅O₄P₂; Molecular weight: 712.65 g/mol.

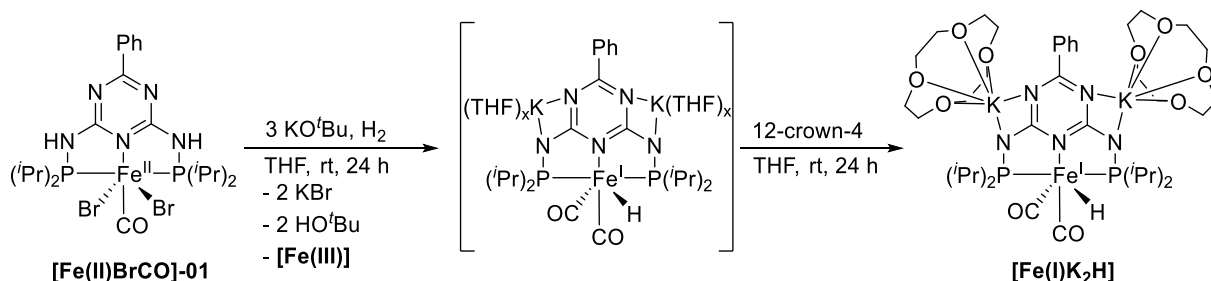
Yield: (43%, 45.9 mg, 64.5 μmol) black crystals.

FT-IR (ATR): ν = 2960 (CH_{1/2/3}), 2850 (CH_{1/2/3}), 1920 (CO), 1820 (CO) cm⁻¹.

Elemental analysis calculated: C 50.58, H 6.63, N 10.23; found: C 51.15, H 6.79, N 9.79.

Magnetic susceptibility (Evans' method)¹: μ_{eff} = 1.9 μ_B

6.4.6 Synthesis of the Fe(I) hydride [Fe(I)K₂H]



Supplementary Figure 6. Formation of the Fe(I) hydride **[Fe(I)K₂H]**.

Under inert atmosphere, KO^tBu (7.54 mmol, 10.0 eq.) was added to a solution of precursor **[Fe(II)BrCO]-01** (754 μmol) in THF (6 mL) and stirred at room temperature for

5 minutes. A fast color change from olive green to dark red and after some minutes to dark greenish was observable. The solution was placed in an autoclave, pressurized with 20 bar H₂ and stirred for 24 hours at room temperature. Afterwards, 12-crown-4 (3.77 mmol, 5.00 eq.) was added to the solution. The resulting mixture was left over night to precipitate, filtered and washed several times with THF. The product was obtained as a blue powder. The deuteride analogion was synthesized the same way with 8 bar D₂ pressure.

Chemical formula: C₃₉H₆₆FeK₂N₅O₁₀P₂; Molecular weight 960.97 g/mol.

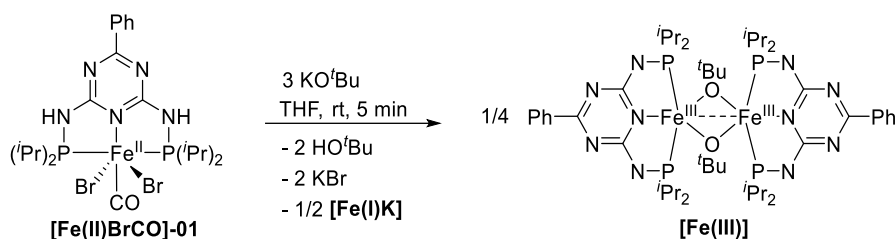
Yield: (44%, 317 mg, 330 μmol) blue powder.

FT-IR (ATR): ν = 2960–2870 (CH_{1/2/3}), 1930 (FeH), 1795 (CO), 1730 (CO) cm⁻¹.

Elemental analysis calculated: C 49.99, H 7.22, N 6.78; found: C 50.12, H 6.78, N 6.34.

Magnetic susceptibility (Evans' method)¹: $\mu_{\text{eff}} = 1.9 \mu_{\text{B}}$

6.4.7 Synthesis of the Fe(III) complex [Fe(III)]



Supplementary Figure 7. Formation of [Fe(III)].

Under inert atmosphere, KO^tBu (2.26 mmol, 3.00 eq.) was added to a solution of Fe(II) precursor **[Fe(II)BrCO]-01** (754 μmol) in THF (10 mL) and stirred for 5 minutes at room temperature. After addition of the base an immediate change of color from olive green to dark red was observed, which changed in the next minutes to dark greenish. The solution was left at –20 °C for several days and the crystallized **[Fe(I)K]** was removed by filtration. THF was evaporated from the green solution under high vacuum and the residue washed with pentane (2 x 50 mL). The obtained green solid was dried under high vacuum for 6 h.

Chemical formula: $C_{50}H_{86}Fe_2N_{10}O_2P_4$; Molecular weight: 1094.89 g/mol.

Yield: (66%, 140 mg, 249 μ mol) green solid.

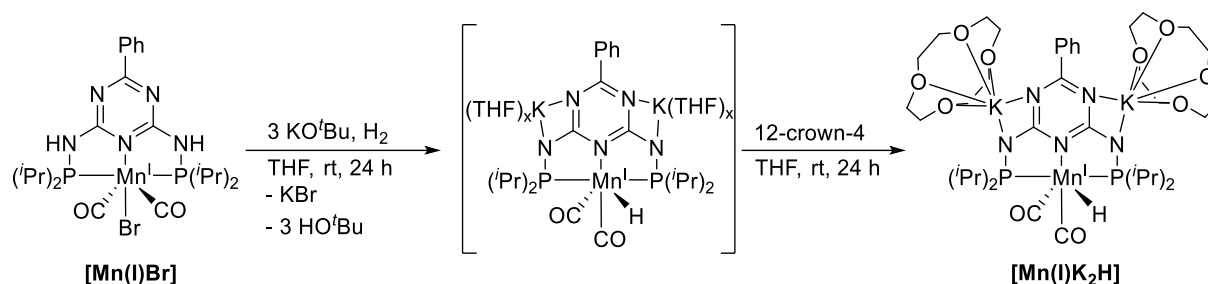
¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 8.28–8.02 (m, 2H, Ar-*H*), 7.36–7.31 (m, 3H, Ar-*H*), 2.04 (sep, *J* = 7.5 Hz, 2H, P-*CH*), 1.91 (sep, 7.8 Hz, 2H, P-*CH*), 1.66–1.15 (m, 8H, CH₃), 1.07 (s, 9H, O^{*t*}Bu), 1.08–0.62 (m, 16H, CH₃) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 127.94, 127.89, 127.85, 67.45, 67.24, 31.68, 27.40, 26.53, 25.56, 24.83, 24.19, 18.09, 16.46, 15.20 ppm.

³¹P NMR (162 MHz, DMSO-d₆, 298 K): δ = 102.3 ppm.

FT-IR (ATR): $\nu = 2960\text{--}2870$ ($\text{CH}_{1/2/3}$) cm^{-1} .

6.4.8 Synthesis of the Mn(I) hydride $[\text{Mn(I)}\text{K}_2\text{H}]$



Supplementary Figure 8. Formation of the Mn(I) hydride $[\text{Mn(I)}\text{K}_2\text{H}]$.

Under inert atmosphere, KO^tBu (7.54 mmol, 10.0 eq.) was added to a solution of precursor $[\text{Mn(I)Br}]$ (754 μmol) in THF (6 mL) and stirred at room temperature for 5 minutes. A fast color change from yellow to green was observed. The solution was placed in an autoclave, pressurized with 20 bar H_2 and stirred for 24 hours at room temperature. Afterwards, 12-crown-4 (3.77 mmol, 5.00 eq.) was added to the solution. The resulting mixture was left over night to precipitate, filtered and washed several times with THF. The product was obtained as red crystalline material.

Chemical formula: $\text{C}_{39}\text{H}_6\text{K}_2\text{MnN}_5\text{O}_{10}\text{P}_2$; Molecular weight 960.06 g/mol.

Yield: (44%, 317 mg, 330 μmol) red crystals.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 8.13 (dd, J = 3.2, 3.5 Hz, 2H, Ar- H), 7.26 (m, 3H, Ar- H), 3.60 (t, J = 5.9 Hz, 4H, THF- H), 3.55 (s, 32H, 12-crown-4- H), 2.00 (sx, J = 6.16 Hz, 2H, P- CH), 1.84–1.71 (m, 6H, THF- H & P- CH), 1.19 (dq, J = 6.5, 12.5 Hz, 14H, CH_3), 1.09 (q, J = 4.6 Hz, 7H, CH_3), 1.00 (q, J = 6.4 Hz, 7H, CH_3), – 5.68 (t, J = 46.9 Hz, 1H, Mn- H) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 173.4, 173.3, 164.6, 141.5, 128.7, 127.8, 127.6, 69.0, 67.5, 32.7, 32.6, 32.5, 32.0, 31.8, 31.7, 25.6, 19.8, 19.6, 19.2, 19.1 ppm.

^{31}P NMR (162 MHz, DMSO-d_6 , 298 K): δ = 153.7 ppm.

FT-IR (ATR): ν = 2960–2870 ($\text{CH}_{1/2/3}$), 1905 (MnH), 1835 (CO), 1755 (CO) cm^{-1} .

Elemental analysis calculated: C 50.04, H 7.23, N 6.79; found: C 49.73, H 6.81, N 6.20.

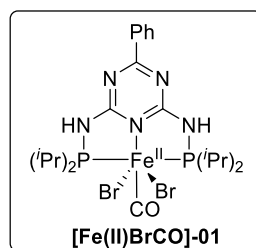
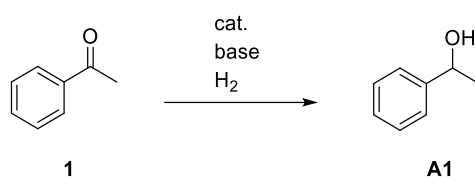
6.4.9 Optimization of reaction conditions

Supplementary Table 1. Screening of the precatalysts.^[a]

[Fe(II)BrCO] [Fe(II)Br]		
Entry	Precatalyst	Yield of A1 [%]
1	[Fe(II)BrCO]-01 (X=N, R=Ph)	99
2	[Fe(II)BrCO]-02 (X=N, R=NEt ₂)	85
3	[Fe(II)BrCO]-03 (X=N, R=Me)	59
4	[Fe(II)BrCO]-04 (X=N, R=NH(C ₃ H ₅))	32
5	[Fe(II)BrCO]-05 (X=CH, R=H)	38
6	[Fe(II)Br]-01 (X=N, R=Ph)	—
7	[Fe(II)Br]-02 (X=N, R=NEt ₂)	—
8	[Fe(II)Br]-03 (X=N, R=Me)	—
9	[Fe(II)Br]-04 (X=N, R=NH(C ₃ H ₅))	—
10	[Fe(II)Br]-05 (X=CH, R=H)	—

^[a]Reaction conditions: 3.00 mmol acetophenone, 0.2 mol% precatalyst, 2.0 mol%, KO^tBu, 20 bar H₂, THF, 50 °C, 1 h. Yields determined by ¹H NMR.

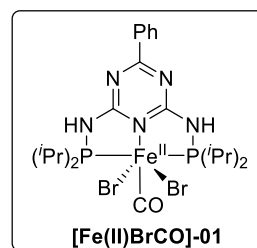
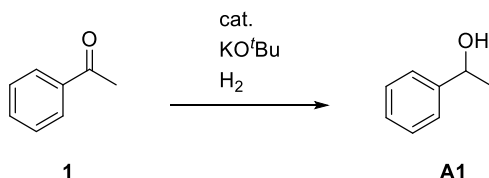
Supplementary Table 2. Screening of the base.^[a]



Entry	Base	Yield of A1 [%]
1	KO^tBu	76
2	NaO ^t Bu	65
3	LiO ^t Bu	—
4	Ba(O ^t Bu) ₂	—
5	Mg(O ^t Bu) ₂	—
6	KOH	—
7	NaOH	—

^[a]Reaction conditions: 3.00 mmol acetophenone, 0.06 mmol% **[Fe(II)BrCO]-01**, 0.6 mol% base, 20 bar H_2 , THF, 50 °C, 1 h. Yields determined by ^1H NMR.

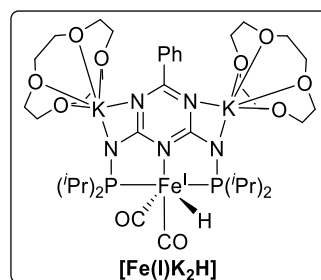
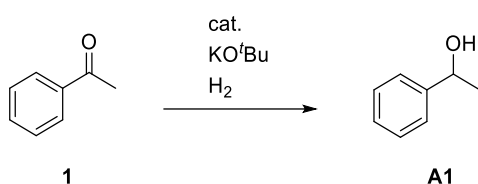
Supplementary Table 3. Screening of the KO^tBu amount.^[a]



Entry	KO ^t Bu	Yield of A1 [%]
1	0.20 mol% (1.00 eq.)	—
2	0.40 mol% (2.00 eq.)	—
3	0.46 mol% (2.30 eq.)	—
4	0.50 mol% (2.50 eq.)	—
5	0.54 mol% (2.70 eq.)	—
6	0.60 mol% (3.00 eq.)	97
7	0.80 mol% (4.00 eq.)	99
8	2.00 mol% (10.0 eq.)	99

^[a]Reaction conditions: 3.00 mmol acetophenone, 0.2 mol% **[Fe(II)BrCO]-01**, KO^tBu, 20 bar H_2 , THF, 50 °C, 1 h. Yields determined by ^1H NMR.

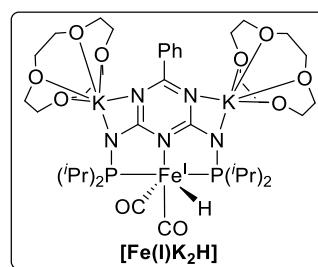
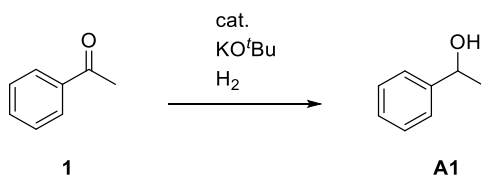
Supplementary Table 4. Screening of the H₂ pressure.^[a]



Entry	H ₂ pressure	Yield of A1 [%]
1	5 bar	traces
2	10 bar	20
3	15 bar	65
4	20 bar	72
4	25 bar	74

^[a]Reaction conditions: 3.00 mmol acetophenone, 0.03 mmol% **[Fe(I)K₂H]**, 0.06 mol% KO^tBu, THF, 50 °C, 1 h. Yields determined by ¹H NMR.

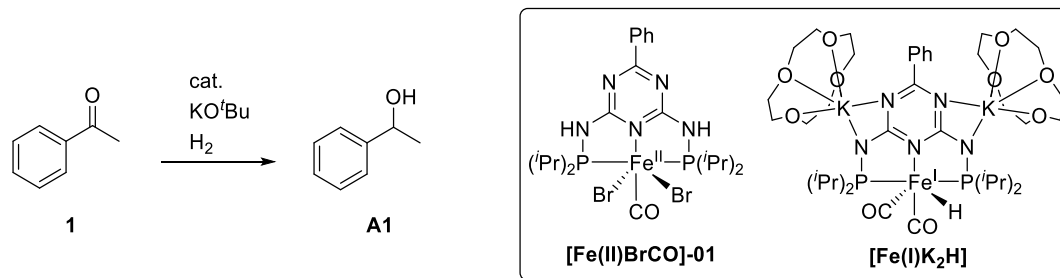
Supplementary Table 5. Screening of the solvent.^[a]



Entry	Solvent	Yield of A1 [%]
1	THF	72
2	Dioxane	57
3	Toluene	40
4	Diglyme	28
5	Dimethoxyethane	27
6	Isopropanol	—
7	2-Methyl-2-butanol	—

^[a]Reaction conditions: 3.00 mmol acetophenone, 0.03 mol% **[Fe(I)K₂H]**, 0.06 mol% KO^tBu, 20 bar H₂, 50 °C, 1 h. Yields determined by ¹H NMR.

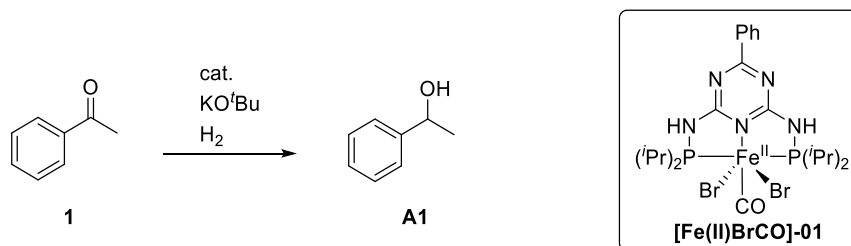
Supplementary Table 6. Comparison of the catalytic activity of **[Fe(II)BrCO]-01** and **[Fe(I)K₂H]**.^[a]



Entry	Temperature [°C]	Yield of A1 [%]		
		[Fe(II)BrCO]-01 0.007 mol%	[Fe(II)BrCO]-01 0.014 mol%	[Fe(I)K₂H] 0.007 mol%
1	50	11	25	28
2	60	18	37	37

^[a]Reaction conditions: 3.00 mmol acetophenone, **[Fe(II)BrCO]-01** / **[Fe(I)K₂H]**, 10.0 eq. KO^tBu, 20 bar H₂, THF, 1 h. Yields determined by ¹H NMR.

Supplementary Table 7. Inhibition experiments using crown ethers.^[a]



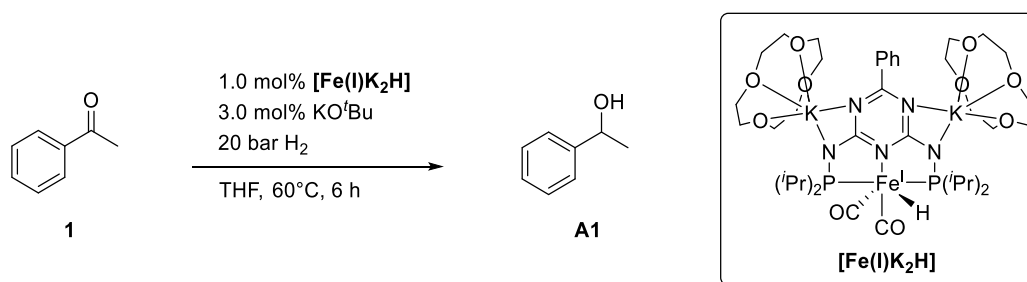
Entry	Ether	Yield of A1 [%]
1	4.0 mol% 18-crown-6	6
2	4.0 mol% 15-crown-5	38
3	4.0 mol% 12-crown-4	97
4	Dimethoxyethane as solvent	99
5	Diglyme as solvent	99

^[a]Reaction conditions: 3.00 mmol acetophenone, 0.2 mol% **[Fe(II)BrCO]-01**, 2.0 mol% KO^tBu, 20 bar H₂, THF, 50 °C, 1 h. Yields determined by ¹H NMR.

6.4.10 General procedure for the hydrogenation of ketones and aldehydes

Hydrogenation reactions were performed in PARR Instrument stainless steel autoclaves with suitable temperature controllers. As a standard procedure for the hydrogenation of ketones and aldehydes, a solution of catalyst and base in the corresponding solvent was prepared and the carbonyl compound was added to the solution in a glass vial, which was placed in a suitable vial holder in the autoclave. The autoclave was pressurized with 20 bar H₂, placed on a stirrer and the temperature was set desirably. After reaction completion the pressure was released and the catalyst solution was quenched by addition of water. Afterwards, 1 eq. 1,3,5-trimethoxybenzene was added as standard to the solution. Then CH₂Cl₂ or Et₂O was added and the organic phase was washed with water twice and dried over Na₂SO₄. The solvent was removed in a rotary evaporator and the resulting residue was analyzed by ¹H NMR to determine the yield.

Hydrogenation of 1



Supplementary Figure 9. Hydrogenation of 1.

Prepared according to the general procedure with acetophenone (100 mg, 97.8 μL, 832 μmol) as carbonyl compound. CH₂Cl₂ (10 mL) was added to the reaction mixture and the organic phase was washed with water (10 mL) twice. The organic phase was filtered with a 2 cm SiO₂-plug and dried over Na₂SO₄. The organic solvent was removed in a rotary evaporator and the product obtained as a colorless oil. Upscaling with 30.0 mmol acetophenone was conducted using the identical procedure.

Yield: (99%, 101 mg, 832 μmol) colorless oil.

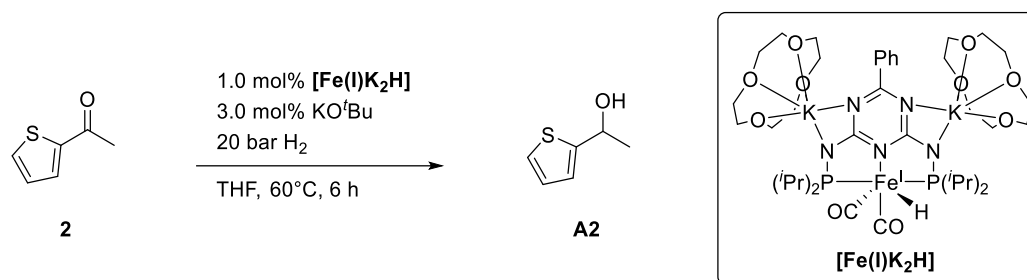
Upscaling yield: (99%, 3.66 g, 30.0 mmol) colorless oil.

Chemical formula: C₈H₁₀O; Molecular weight: 122.15 g/mol.

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.38 (m, 4H, Ar-*H*), 7.30 (m, 1H, Ar-*H*), 4.92 (q, J = 6.5 Hz, 1H, HO-*CH*), 2.00 (s, br, 1H, OH), 1.52 (d, J = 6.5 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 145.9, 128.5, 127.5, 125.4, 70.4, 25.2 ppm.

Hydrogenation of **2**



Supplementary Figure 10. Hydrogenation of **2**.

Prepared according to the general procedure with 1-(thiophen-2-yl)ethan-1-one (100 mg, 85.4 μL , 792 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a colorless oil.

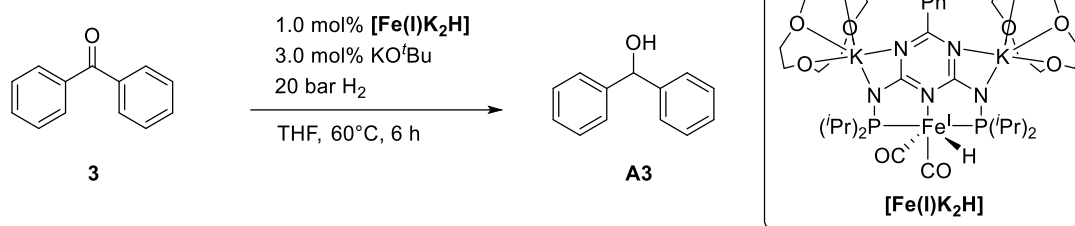
Yield: 44% (44.6 mg, 348 μmol) or 82% (18 h reaction time, 83.2 mg, 649 μmol) colorless oil.

Chemical formula: $\text{C}_6\text{H}_8\text{OS}$; Molecular weight: 128.17 g/mol.

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.22 (m, 1H, Ar-*H*), 6.95 (m, 2H, Ar-*H*), 5.08 (q, J = 6.2 Hz, 1H, HO-*CH*), 2.53 (s, 1H, OH), 1.57 (d, J = 6.2 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 149.9, 126.6, 124.4, 123.2, 66.1, 25.2 ppm.

Hydrogenation of 3



Supplementary Figure 11. Hydrogenation of **3**.

Prepared according to the general procedure with benzophenone (100 mg, 548 μmol) as carbonyl compound. CH_2Cl_2 (10 mL) was added to the reaction mixture and the organic phase was washed with water (10 mL) twice. The organic phase was filtered with a 2 cm SiO_2 -plug and dried over Na_2SO_4 . The eluent was removed in a rotary evaporator and product obtained as a white solid. Upscaling with 30.0 mmol benzophenone was conducted using the identical procedure.

Yield: (99%, 99.8 mg, 548 μmol) white solid.

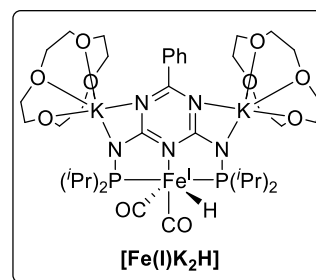
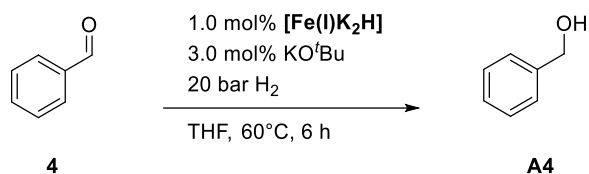
Upscaling yield: (99%, 5.51 g, 30.0 mmol) white solid.

Chemical formula: $\text{C}_{13}\text{H}_{12}\text{O}$; Molecular weight: 184.24 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 7.31 (d, J = 7.5 Hz, 3H, Ar- H), 7.23 (t, J = 7.5 Hz, 4H, Ar- H), 7.13 (t, J = 7.2 Hz, 3H, Ar- H), 5.82 (d, J = 3.9 Hz, 1H, OH), 5.63 (d, J = 3.9 Hz, 1H, HO-CH) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 146.1, 128.4, 127.1, 126.6, 74.6 ppm.

Hydrogenation of A4



Supplementary Figure 12. Hydrogenation of **4**.

Prepared according to the general procedure with benzaldehyde (100 mg, 96,2 μL , 942 μmol) as carbonyl compound. Et_2O (10 mL) was added to the reaction mixture and the organic phase was washed with water (10 mL) twice. The organic phase was filtered with a 2 cm SiO_2 -plug and dried over Na_2SO_4 . The eluent was removed in a rotary evaporator and product obtained as a colorless liquid.

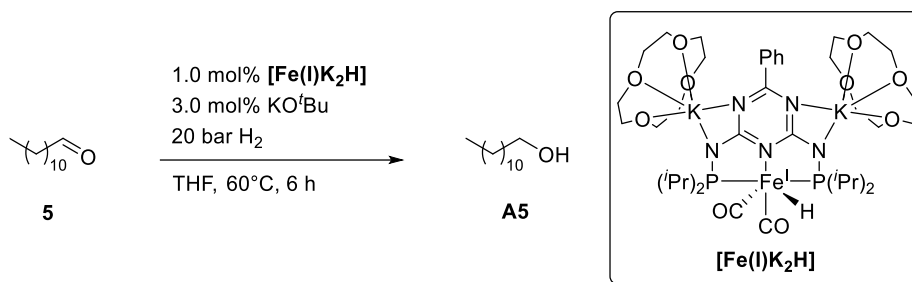
Yield: (99%, 101 mg, 940 μmol) colorless liquid.

Chemical formula: $\text{C}_7\text{H}_8\text{O}$; Molecular weight: 108.06 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 7.44–7.31 (m, 4H, Ar-*H*), 7.31–7.18 (m, 1H, Ar-*H*), 5.19 (t, J = 5.6 Hz, 1H, OH), 4.52 (d, J = 5.6 Hz, 2H, CH_2) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 143.0, 128.6, 127.2, 126.8, 63.4 ppm.

Hydrogenation of **5**



Supplementary Figure 13. Hydrogenation of **5**.

Prepared according to the general procedure with dodecanal (100 mg, 120 μL , 543 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a thick colorless oil.

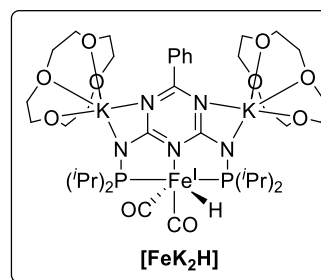
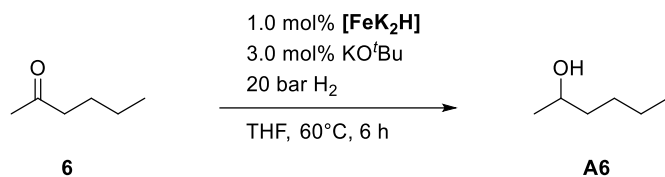
Yield: (81%, 81.9 mg, 440 μmol) colorless oil.

Chemical formula: $\text{C}_{12}\text{H}_{26}\text{O}$; Molecular weight: 186.36 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 4.33 (t, J = 5.1 Hz, 1H, OH), 3.39 (q, J = 6.4 Hz, 2H, HO- CH_2), 1.46–1.37 (m, 2H, HO- CH_2 - CH_2), 1.35–1.17 (m, 18H, CH_2), 0.88 (t, J = 6.3 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 61.2, 33.0, 31.8, 29.5, 29.2, 27.3, 26.0, 22.6, 14.3 ppm.

Hydrogenation of 6



Supplementary Figure 14. Hydrogenation of **6**.

Prepared according to the general procedure with 2-hexanone (100 mg, 123 μL , 998 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a colorless liquid.

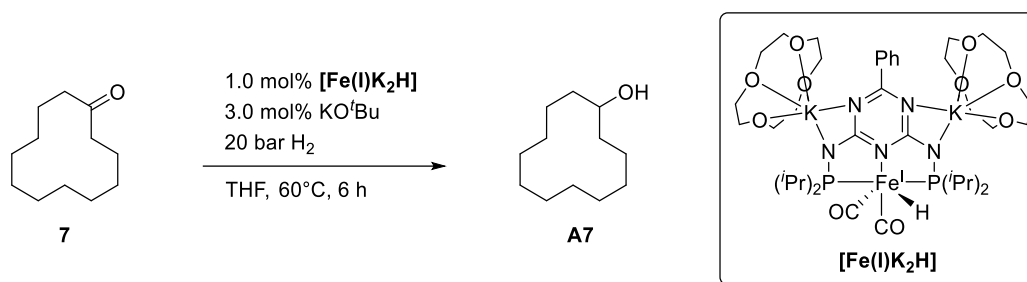
Yield: (79%, 80.6 mg, 788 μmol) colorless liquid.

Chemical formula: $\text{C}_6\text{H}_{14}\text{O}$; Molecular weight: 102.18 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 4.30 (d, J = 4.7 Hz, 1H, OH), 3.58 (sep, J = 5.0 Hz, 1H, HO-CH), 1.39–1.20 (m, 6H, CH_2), 1.05 (d, J = 6.1 Hz, 3H, HO-CH- CH_3), 0.89 (t, J = 6.4 Hz, 3H, CH_2 - CH_3) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 66.4, 36.4, 28.2, 24.1, 22.8, 14.6 ppm.

Hydrogenation of 7



Supplementary Figure 15. Hydrogenation of **7**.

Prepared according to the general procedure with cyclododecanone (100 mg, 549 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

Yield: (79%, 80.0 mg, 438 μmol) white solid.

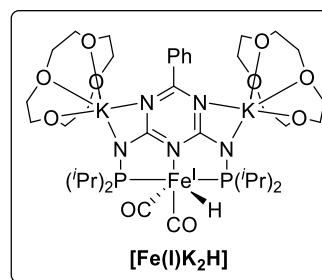
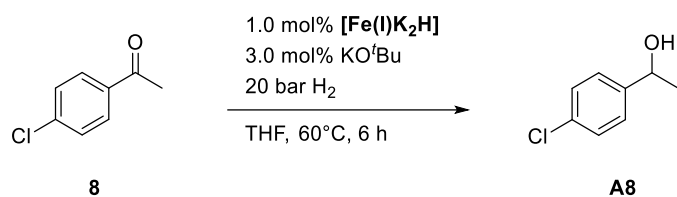
Upscaling yield: (80%, 4.44 g, 24.1 μmol) white solid.

Chemical formula: $\text{C}_{13}\text{H}_{24}\text{O}$; Molecular weight: 184.32 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 4.18 (d, J = 2.7 Hz, 1H, OH), 3.61–3.51 (m, 1H, HO–CH), 1.44 (sep, J = 6.2 Hz, 2H, CH_2), 1.35–1.17 (m, 20H, CH_2) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 67.0, 32.5, 24.2, 23.4, 23.3, 21.2 ppm.

Hydrogenation of 8



Supplementary Figure 16. Hydrogenation of **8**.

Prepared according to the general procedure with 4-chloroacetophenone (100 mg, 85.0 μL , 647 μmol) as carbonyl compound. CH_2Cl_2 (10 mL) was added to the reaction mixture and the organic phase was washed with water (10 mL) twice. The organic phase was filtered with a 2 cm SiO_2 -plug and dried over Na_2SO_4 . The organic solvent was removed in a rotary evaporator and the product obtained as a colorless oil.

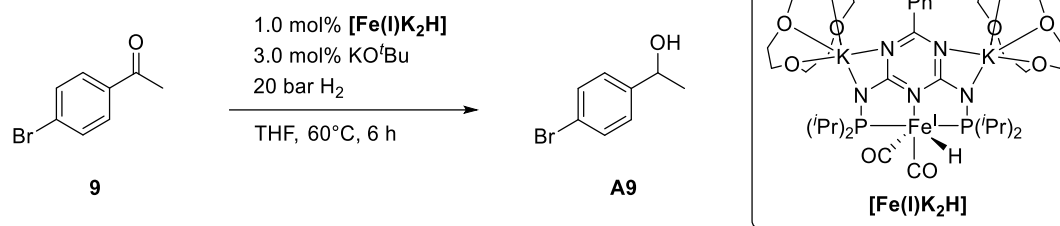
Yield: 99% (101 mg, 647 μmol) colorless oil.

Chemical formula: $\text{C}_8\text{H}_9\text{ClO}$; Molecular weight: 156.59 g/mol.

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.29 (m, 1H, Ar-*H*), 7.17 (m, 3H, Ar-*H*), 4.78 (q, J = 6.3 Hz, 1H, HO-*CH*), 2.12 (s, br, 1H, OH), 1.39 (d, J = 6.3 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 144.2, 133.0, 128.6, 126.8, 69.7, 25.2 ppm.

Hydrogenation of 9



Supplementary Figure 17. Hydrogenation of **9**.

Prepared according to the general procedure with 4-bromoacetophenone (100 mg, 502 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white powder.

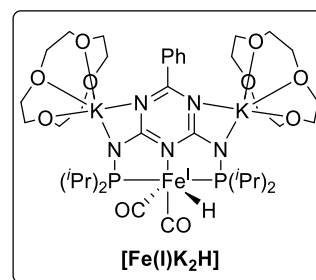
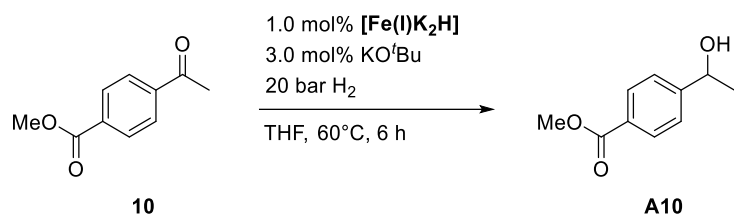
Yield: 89% (90.0 mg, 447 μmol) white powder.

Chemical formula: $\text{C}_8\text{H}_9\text{BrO}$; Molecular weight: 201.05 g/mol.

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.40 (dt, J = 1.7, 8.4 Hz, 2H, Ar- H), 7.18 (m, 2H, Ar- H), 4.79 (q, J = 6.4 Hz, 1H, HO- CH), 1.79 (s, 1H, OH), 1.39 (d, J = 6.5 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 44.8, 131.6, 127.2, 121.2, 69.8, 25.3 ppm.

Hydrogenation of **10**



Supplementary Figure 18. Hydrogenation of **10**.

Prepared according to the general procedure with methyl 4-acetylbenzoate (100 mg, 561 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a yellowish solid.

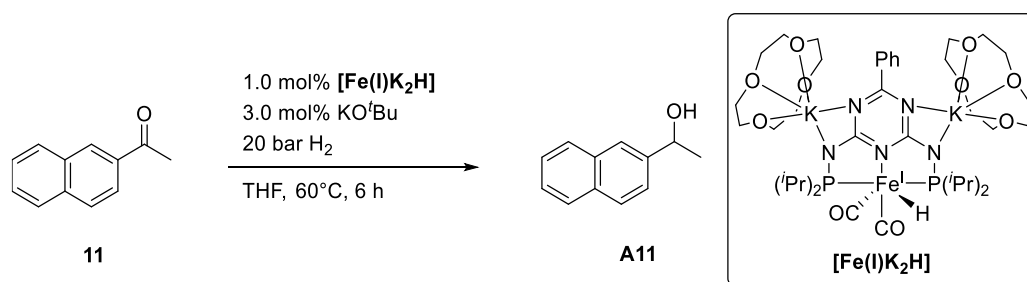
Yield: 86% (87.0 mg, 482 μmol) yellowish solid.

Chemical formula: $\text{C}_{10}\text{H}_{12}\text{O}_3$; Molecular weight: 180.23 g/mol.

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 8.00 (d, J = 8.1 Hz, 2H, Ar- H), 7.43 (d, J = 8.2 Hz, 2H, Ar- H), 4.95 (q, J = 6.5 Hz, 1H, HO- CH), 3.90 (s, 3H, COOCH_3), 1.94 (s, br, 1H, OH), 1.49 (d, J = 6.4 Hz, 3H, CH- CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 167.0, 150.9, 129.9, 129.2, 125.3, 70.0, 52.1, 25.3 ppm.

Hydrogenation of **11**



Supplementary Figure 19. Hydrogenation of **11**.

Prepared according to the general procedure with 1-(naphthalen-2-yl)ethan-1-one (100 mg, 588 μ mol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

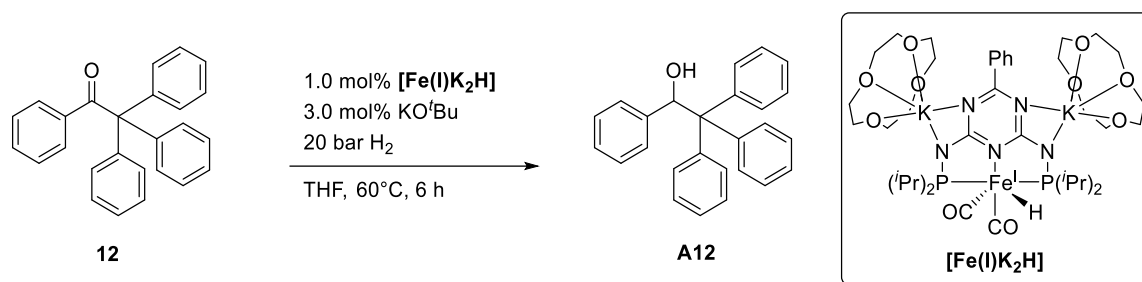
Yield: 90% (91.0 mg, 529 μ mol) white solid.

Chemical formula: C₁₂H₁₂O; Molecular weight: 172.23 g/mol.

¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 7.97–7.85 (m, 4H, Ar-*H*), 7.62–7.43 (m, 3H, Ar-*H*), 5.39 (d, *J* = 4.1 Hz, 1H, OH), 4.97 (dq, *J* = 4.3, 6.3 Hz, 1H, OH-CH), 1.49 (d, *J* = 6.3 Hz, 3H, CH₃) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 145.4, 133.4, 132.7, 128.2, 128.0, 127.9, 126.5, 125.9, 124.9, 123.7, 68.7, 26.3 ppm.

Hydrogenation of **12**



Supplementary Figure 20. Hydrogenation of **12**.

Prepared according to the general procedure with 1,2,2,2-tetraphenylethan-1-one (100 mg, 287 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

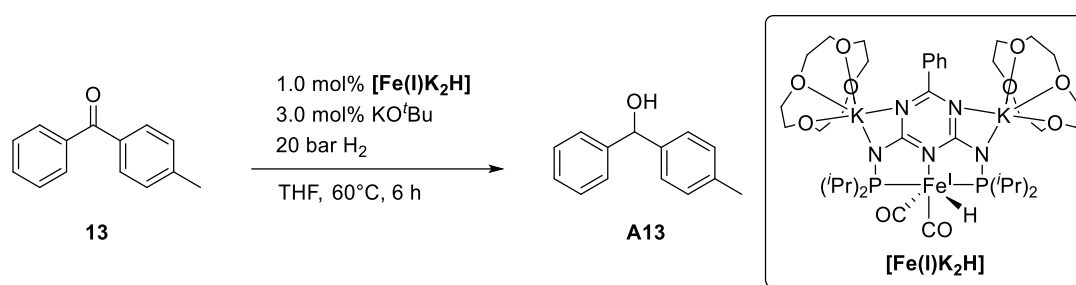
Yield: 74% (74.4 mg, 212 μmol) white solid.

Chemical formula: $\text{C}_{26}\text{H}_{22}\text{O}$; Molecular weight: 350.46 g/mol.

^1H NMR (400 MHz, $\text{DMSO}-d_6$, 298 K): δ = 7.32–7.23 (m, 6H, Ar-*H*), 7.21–7.09 (m, 9H, Ar-*H*), 7.03 (d, J = 7.0 Hz, 1H, Ar-*H*), 6.94 (t, J = 7.5 Hz, 2H, Ar-*H*), 6.75 (d, J = 7.5 Hz, 2H, Ar-*H*), 6.32 (d, J = 3.8 Hz, 1H, OH), 5.56 (d, J = 3.8 Hz, 1H, HO-CH) ppm.

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 298 K): δ = 145.3, 143.3, 131.2, 129.8, 127.3, 126.8, 126.1, 74.8, 64.1 ppm.

Hydrogenation of **13**



Supplementary Figure 21. Hydrogenation of **13**.

Prepared according to the general procedure with 4-methylbenzophenone (100 mg, 510 μmol) as carbonyl compound. Et_2O (10 mL) was added to the reaction mixture and the organic phase was washed with water (10 mL) twice. The organic phase was filtered with a 2 cm SiO_2 -plug and dried over Na_2SO_4 . The eluent was removed in a rotary evaporator and product obtained as a colorless liquid.

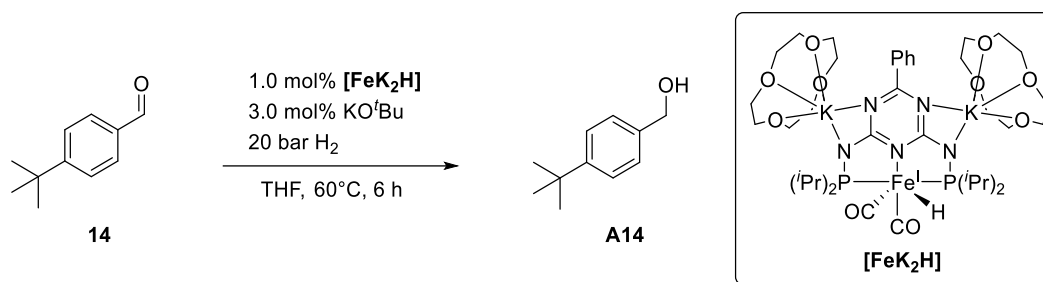
Yield: 99% (101 mg, 510 μmol) colorless liquid.

Chemical formula: $\text{C}_{14}\text{H}_{16}\text{O}$; Molecular weight: 200.27 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 7.44–7.37 (m, 2H, Ar-*H*), 7.36–7.26 (m, 4H, Ar-*H*), 7.26–7.18 (m, 1H, Ar-*H*), 7.17–7.09 (m, 2H, Ar-*H*), 5.88 (d, J = 4.0 Hz, 1H, OH), 5.70 (d, J = 4.0 Hz, 1H, HO-CH), 2.28 (s, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 146.3, 143.2, 136.2, 129.1, 128.5, 126.6, 74.8, 21.0 ppm.

Hydrogenation of **14**



Supplementary Figure 22. Hydrogenation of **14**.

Prepared according to the general procedure with 4-(*tert*-butyl)benzaldehyde (100 mg, 102 μ L, 616 μ mol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a colorless oil.

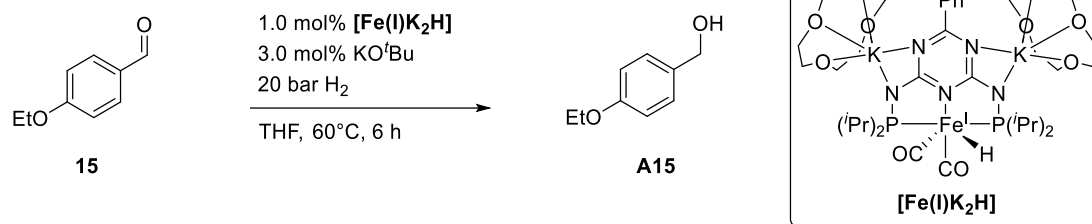
Yield: 90% (91.0 mg, 554 μ mol) colorless oil.

Chemical formula: C₁₁H₁₆O; Molecular weight: 164.25 g/mol.

¹H NMR (400 MHz, DMSO-*d*₆, 298 K): δ = 7.37 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.28 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 5.14 (t, *J* = 5.7 Hz, 1H, OH), 4.52 (d, *J* = 5.7 Hz, 2H, CH₂), 1.32 (s, 9H, CH₃) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆, 298 K): δ = 149.4, 140.0, 126.8, 125.2, 63.2, 34.6, 31.6 ppm.

Hydrogenation of **15**



Supplementary Figure 23. Hydrogenation of **15**.

Prepared according to the general procedure with 1-(4-ethoxyphenyl)ethan-1-one (100 mg, 609 μ mol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a colorless oil.

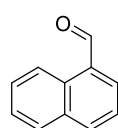
Yield: 65% (65.7 mg, 395 μ mol) colorless oil.

Chemical formula: C₁₀H₁₄O₂; Molecular weight: 166.22 g/mol.

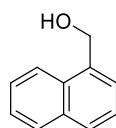
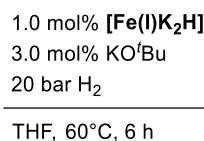
¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 7.25 (d, J = 8.5 Hz, 2H, Ar-*H*), 6.88 (d, J = 8.5 Hz, 2H, Ar-*H*), 5.08 (t, J = 5.7 Hz, 1H, OH), 4.47 (d, J = 5.7 Hz, 2H, HO-CH₂), 4.01 (q, J = 6.8 Hz, 2H, CH₂-CH₃), 1.34 (t, J = 6.8 Hz, 3H, CH₂-CH₃) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 157.9, 134.8, 128.4, 114.3, 63.3, 15.2 ppm.

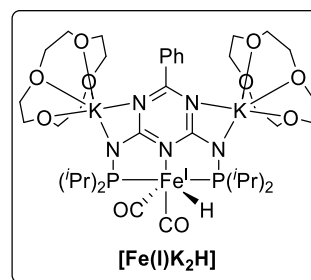
Hydrogenation of **16**



16



A16



Supplementary Figure 24. Hydrogenation of **16**.

Prepared according to the general procedure with 1-naphtaldehyde (100 mg, 640 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

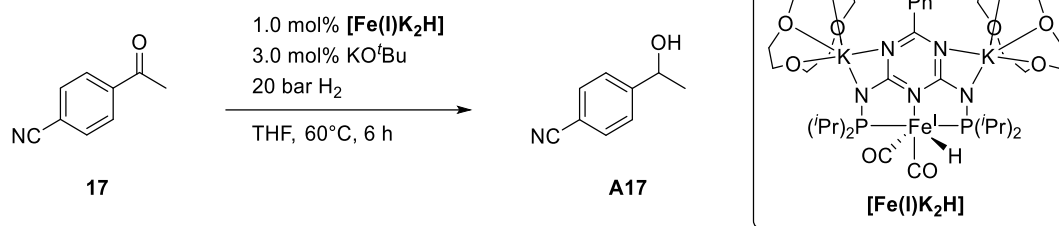
Yield: 93% (89.7 mg, 567 μmol) white solid.

Chemical formula: C₁₁H₁₀O; Molecular weight: 158.20 g/mol.

¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 8.10 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.92 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.82 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.63–7.42 (m, 4H, Ar-*H*), 5.36, (t, *J* = 5.1 Hz, 1H, OH), 5.01 (d, *J* = 5.0 Hz, 2H, CH₂) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 138.6, 133.9, 131.5, 129.1, 128.1, 126.6, 126.4, 126.2, 125.0, 124.5, 62.0 ppm.

Hydrogenation of **17**



Supplementary Figure 25. Hydrogenation of **17**.

Prepared according to the general procedure with 4-acetylbenzonitrile (100 mg, 689 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white yellowish powder.

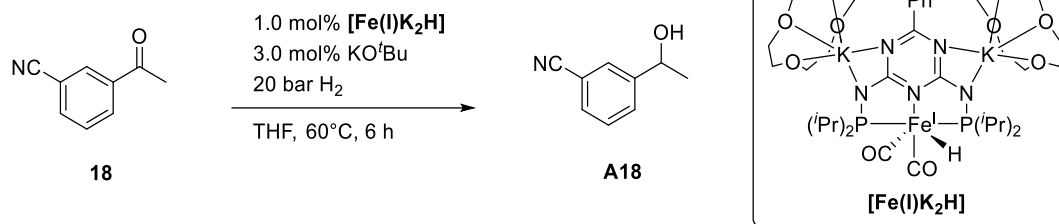
Yield: 90% (91.0 mg, 620 μmol) white yellowish solid.

Chemical formula: $\text{C}_9\text{H}_9\text{NO}$; Molecular weight: 147.16 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 7.80 (d, J = 8.1 Hz, 2H, Ar- H), 7.57 (d, J = 7.9 Hz, 2H, Ar- H), 5.46 (d, J = 4.1 Hz, 1H, OH), 4.83 (q, J = 5.7 Hz, 1H, HO- CH), 1.36 (d, J = 6.4 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 153.6, 132.6, 126.8, 119.5, 109.8, 68.1, 26.1 ppm.

Hydrogenation of **18**



Supplementary Figure 26. Hydrogenation of **18**.

Prepared according to the general procedure with 3-acetylbenzonitrile (100 mg, 689 μ mol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white powder.

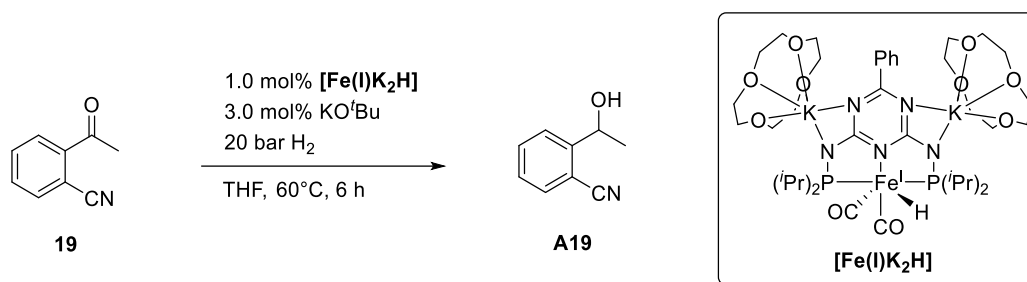
Yield: 62% (62.8 mg, 427 μ mol) white powder.

Chemical formula: C₉H₉NO; Molecular weight: 147.18 g/mol.

¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 7.82–7.76 (m, 1H, Ar-*H*), 7.74–7.66 (m, 2H, Ar-*H*), 7.59–7.50 (m, 1H, Ar-*H*), 5.42 (d, *J* = 4.2 Hz, 1H, OH), 4.81 (dq, *J* = 6.3, 4.5 Hz, 1H, HO-CH), 1.36 (d, *J* = 6.5 Hz, 3H, CH₃) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 149.4, 130.8, 129.4, 119.4, 111.5, 67.8, 26.1 ppm.

Hydrogenation of **19**



Supplementary Figure 27. Hydrogenation of **19**.

Prepared according to the general procedure with 2-acetylbenzonitrile (100 mg, 90.1 μ L, 689 μ mol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white powder.

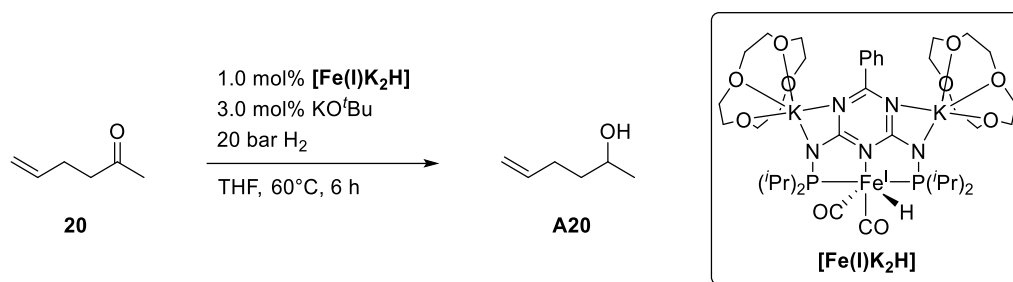
Yield: 66% (66.9 mg, 454 μ mol) white powder.

Chemical formula: C₉H₉NO; Molecular weight: 147.16 g/mol.

¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 7.86 (d, J = 7.5 Hz, 1H, Ar-*H*), 7.67–7.58 (m, 1H, Ar-*H*), 7.58–7.46 (m, 2H, Ar-*H*), 5.61 (q, J = 6.5 Hz, 1H, HO-*CH*), 1.51 (d, J = 6.5 Hz, 3H, *CH*₃) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 148.7, 132.4, 128.9, 123.6, 122.3, 109.9, 79.0, 21.3 ppm.

Hydrogenation of 20



Supplementary Figure 28. Hydrogenation of **20**.

Prepared according to the general procedure with hex-5-en-2-one (300 mg, 354 μL , 3.00 mmol) as carbonyl compound. CH_2Cl_2 (10 mL) was added to the reaction mixture and the organic phase was washed with water (10 mL) twice. The organic phase was filtered with a 2 cm SiO_2 -plug and dried over Na_2SO_4 . The organic solvent was removed in a rotary evaporator and the product obtained as a colorless oil.

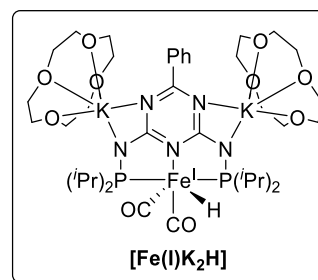
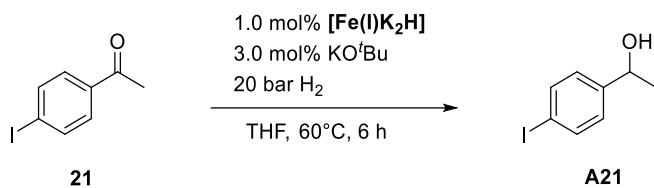
Yield: 99% (299 mg, 2.99 mmol) colorless oil.

Chemical formula: $\text{C}_6\text{H}_{12}\text{O}$; Molecular weight: 100.16 g/mol.

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 5.78 (ddt, J = 6.7, 10.2, 13.3 Hz, 1H, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2$), (dq, J = 1.57, 17.1 Hz, 1H, *trans*- $\text{H}(\text{H})\text{C}=\text{CH}$) 4.88 (d, J = 1.3, 10.2 Hz, 1H, *cis*- $\text{H}(\text{H})\text{C}=\text{CH}$), 3.72 (sep, J = 6.1 Hz, 1H, OH), 2.22 (d, J = 4.6 Hz, 1H, OH), 2.14–1.98 (m, 2H, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2$), 1.53–1.39 (m, 2H, $\text{CH}_2-\text{CH}-\text{CH}_3$), 1.11 (d, J = 6.1 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 138.4, 114.5, 67.4, 38.2, 30.0, 23.3 ppm.

Hydrogenation of **21**



Supplementary Figure 29. Hydrogenation of **21**.

Prepared according to the general procedure with 4-iodoacetophenone (100 mg, 406 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a light brown solid.

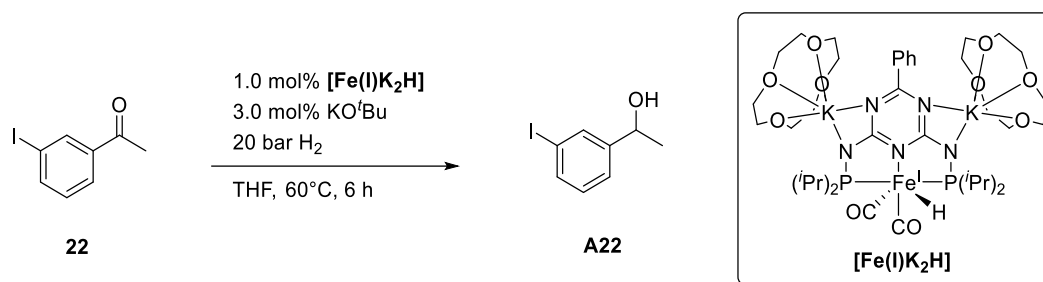
Yield: 78% (78.7 mg, 317 μmol) light brown solid.

Chemical formula: $\text{C}_8\text{H}_9\text{IO}$; Molecular weight: 248.06 g/mol.

^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 7.60 (d, J = 8.3 Hz, 2H, Ar- H), 7.06 (d, J = 8.2 Hz, 2H, Ar- H), 4.78 (q, J = 6.4 Hz, 1H, HO- CH), 1.73 (s, br, 1H, OH), 1.39 (d, J = 6.4 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 145.5, 137.5, 127.4, 92.7, 69.9, 25.3 ppm.

Hydrogenation of **22**



Supplementary Figure 30. Hydrogenation of **22**.

Prepared according to the general procedure with 3-iodoacetophenone (100 mg, 406 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

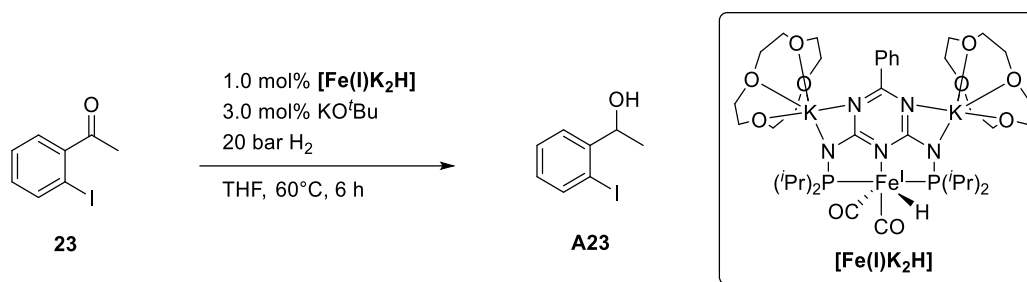
Yield: 94% (94.6 mg, 381 μmol) white solid.

Chemical formula: $\text{C}_8\text{H}_9\text{IO}$; Molecular weight: 248.06 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 7.80 (d, J = 7.9 Hz, 1H, Ar- H), 7.59 (d, J = 7.8 Hz, 1H, Ar- H), 7.43 (t, J = 7.5 Hz, 1H, Ar- H), 7.01 (t, J = 7.5 Hz, 1H, Ar- H), 5.43 (d, J = 3.4 Hz, 1H, OH), 4.82 (dq, J = 4.1, 5.9 Hz, HO- CH), 1.30 (d, J = 6.0 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 149.4, 139.1, 129.3, 129.0, 127.1, 127.1, 97.6, 72.4, 25.1 ppm.

Hydrogenation of **23**



Supplementary Figure 31. Hydrogenation of **23**.

Prepared according to the general procedure with 2-iodoacetophenone (100 mg, 406 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

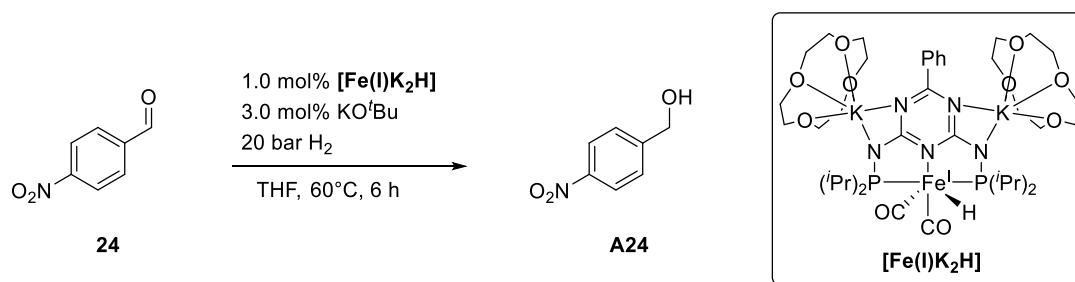
Yield: 92% (92.6 mg, 374 μmol) white solid.

Chemical formula: C₈H₉IO; Molecular weight: 248.06 g/mol.

¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 7.80 (dd, *J* = 0.8, 7.8 Hz, 1H, Ar-*H*), 7.59 (dd, *J* = 1.6, 7.8 Hz, 1H, Ar-*H*), 7.43 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 7.01 (dt, *J* = 1.6, 7.7 Hz, 1H, Ar-*H*), 5.43 (d, *J* = 4.0 Hz, 1H, OH), 4.82 (dq, *J* = 4.1, 6.2 Hz, 1H, HO-CH), 1.30 (d, *J* = 6.2 Hz, 3H, CH₃) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 149.4, 139.1, 129.3, 127.2, 97.6, 72.4, 25.0 ppm.

Hydrogenation of **24**



Supplementary Figure 32. Hydrogenation of **24**.

Prepared according to the general procedure with 4-nitrobenzaldehyde (100 mg, 662 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a yellowish solid.

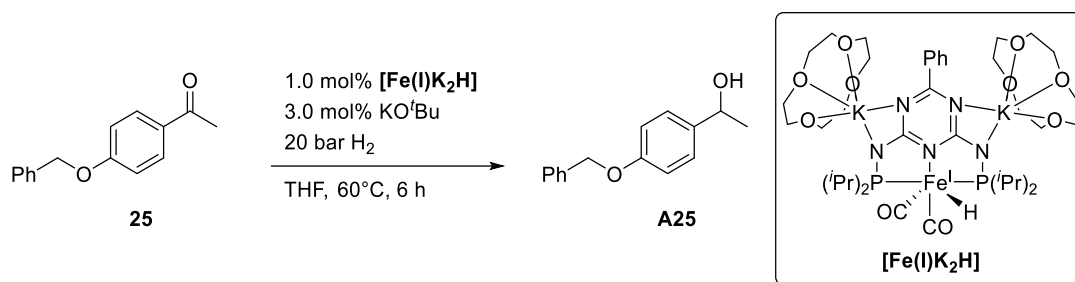
Yield: 48% (48.6 mg, 318 μmol) yellowish solid.

Chemical formula: $\text{C}_7\text{H}_7\text{NO}_3$; Molecular weight: 153.14 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 8.16 (d, J = 5.5 Hz, 2H, Ar- H), 7.56 (d, J = 5.5 Hz, 2H, Ar- H), 5.52 (s, 1H, OH), 4.62 (s, 4.62, 1H, CH_2) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 151.0, 146.5, 127.2, 123.5, 62.2 ppm.

Hydrogenation of 25



Supplementary Figure 33. Hydrogenation of **25**.

Prepared according to the general procedure with 4'-benzyloxyacetophenone (100 mg, 442 μmol) as carbonyl compound. Et_2O (10 mL) was added to the reaction mixture and the organic phase was washed with water (10 mL) twice. The organic phase was filtered with a 2 cm SiO_2 -plug and dried over Na_2SO_4 . The organic solvent was removed in a rotary evaporator and the product obtained as a white solid.

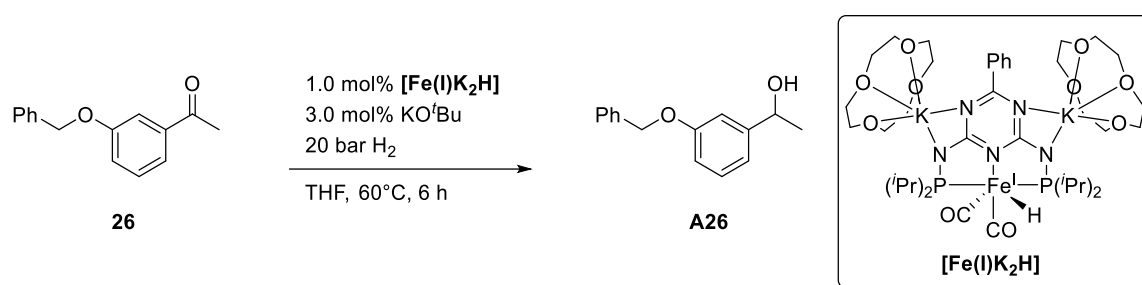
Yield: 98% (98.9 mg, 433 μmol) white solid.

Chemical formula: $\text{C}_{15}\text{H}_{16}\text{O}_2$; Molecular weight: 228.29 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 7.43 (m, 2H, Ar- H), 7.38 (m, 2H, Ar- H), 7.31 (m, 1H, Ar- H), 7.24 (m, 2H, Ar- H), 6.94 (m, 2H, Ar- H), 5.08 (s, 2H, Ph- CH-O-Ar), 5.02 (d, J = 4.2 Hz, 1H, OH), 4.66 (q, J = 4.2 Hz, 1H, HO- CH), 1.29 (d, J = 6.3 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 157.4, 140.1, 137.7, 128.8, 128.2, 128.0, 126.9, 114.7, 69.5, 68.0, 26.4 ppm.

Hydrogenation of 26



Supplementary Figure 34. Hydrogenation of **26**.

Prepared according to the general procedure with 3-benzyloxyacetophenone (100 mg, 442 μ mol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

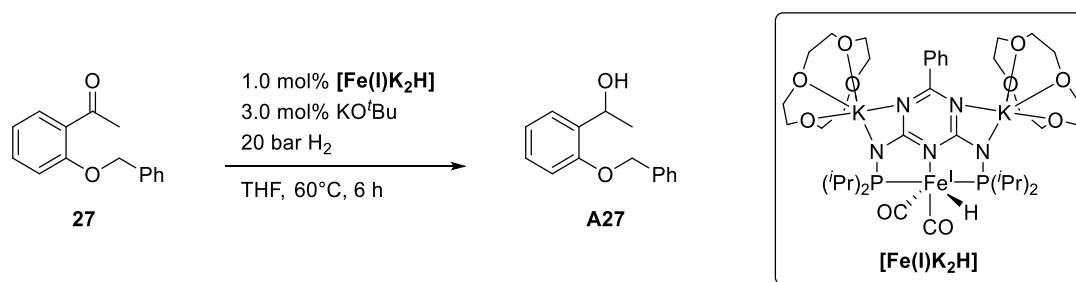
Yield: 95% (95.8 mg, 419 μ mol) white solid.

Chemical formula: C₁₅H₁₆O₂; Molecular weight: 228.29 g/mol.

¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 7.53–7.46 (m, 2H, Ar-*H*), 7.46–7.32 (m, 3H, Ar-*H*), 7.30–7.22 (m, 1H, Ar-*H*), 7.10–7.05 (m, 1H, Ar-*H*), 7.01–6.95 (m, 1H, Ar-*H*), 6.93–6.87 (m, 1H, Ar-*H*), 5.22 (d, *J* = 4.1 Hz, 1H, OH), 5.12 (s, 2H, Ar-O-CH₂), 4.75 (dq, *J* = 4.1, 6.2 Hz, 1H, HO-CH), 1.37 (d, *J* = 6.4 Hz, 3H, CH₃) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 158.8, 149.7, 137.7, 129.5, 128.8, 128.1, 118.3, 113.1, 112.4, 69.6, 68.5, 26.3 ppm.

Hydrogenation of 27



Supplementary Figure 35. Hydrogenation of **27**.

Prepared according to the general procedure with 2-benzyloxyacetophenone (100 mg, 442 μ mol) as carbonyl compound. Et₂O (10 mL) was added to the reaction mixture and the organic phase was washed with water (10 mL) twice. The organic phase was filtered with a 2 cm SiO₂-plug and dried over Na₂SO₄. The organic solvent was removed in a rotary evaporator and the product obtained as a white solid.

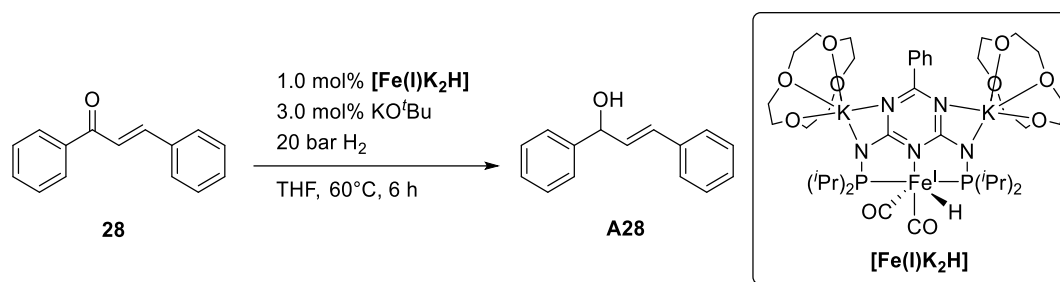
Yield: 99% (99.8 mg, 441 μ mol) white solid.

Chemical formula: C₁₅H₁₆O₂; Molecular weight: 228.29 g/mol.

¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 7.57–7.32 (m, 6H, Ar-*H*), 7.26–7.16 (m, 1H, Ar-*H*), 7.08–6.94 (m, 2H, Ar-*H*), 5.21–5.09 (m, 3H, Ar-O-CH₂ & HO-CH), 5.03 (d, *J* = 4.4 Hz, 1H, OH), 1.34 (d, *J* = 6.3 Hz, 3H, CH₃) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 154.7, 137.9, 136.3, 127.7, 126.0, 121.1, 112.1, 109.9, 69.7, 63.0, 25.2 ppm.

Hydrogenation of 28



Supplementary Figure 36. Hydrogenation of **28**.

Prepared according to the general procedure with *trans*-chalcone (100 mg, 480 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

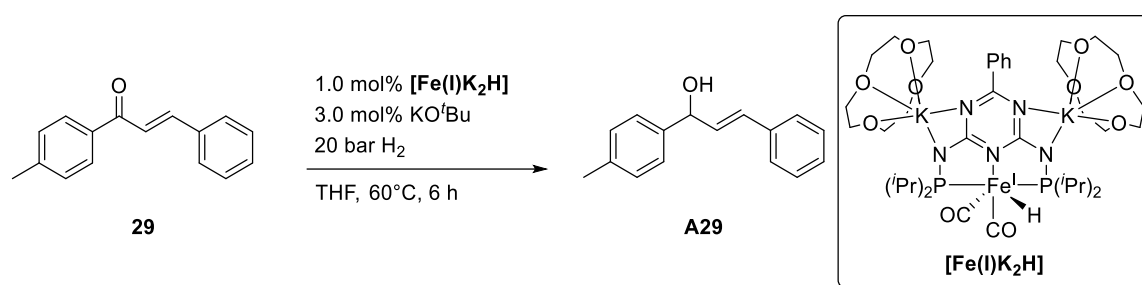
Yield: 95% (96.0 mg, 456 μmol) white solid.

Chemical formula: $\text{C}_{15}\text{H}_{14}\text{O}$; Molecular weight: 210.28 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 6.49 (m, 4H, Ar-*H*), 6.44–6.25 (m, 6H, Ar-*H*), 5.73 (d, J = 15.8 Hz, 1H, $\text{CH}=\text{CH}-\text{Ph}$), 5.48 (dd, J = 6.3, 15.8 Hz, 1H, $\text{CH}-\text{CH}=\text{CH}$), 4.75 (d, J = 4.2 Hz, 1H, OH), 4.36 (q, J = 3.9 Hz, 1H, HO-*CH*) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 144.9, 137.1, 134.2, 129.1, 128.63, 128.60, 127.8, 127.3, 126.8, 126.7, 73.7 ppm.

Hydrogenation of 29



Supplementary Figure 37. Hydrogenation of **29**.

Prepared according to the general procedure with *trans*-3-phenyl-1-(*p*-tolyl)prop-2-en-1-one (100 mg, 450 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

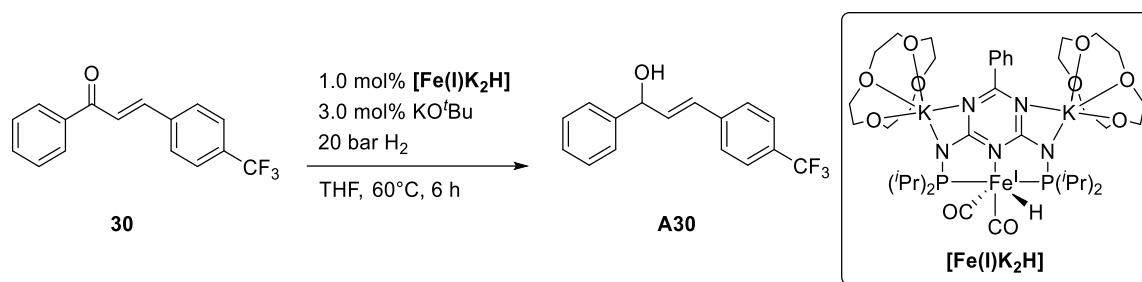
Yield: 92% (92.8 mg, 414 μmol) white solid.

Chemical formula: $\text{C}_{16}\text{H}_{16}\text{O}$; Molecular weight: 224.30 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 7.50–7.40 (m, 2H, Ar-*H*), 7.40–7.25 (m, 4H, Ar-*H*), 7.28–7.15 (m, 3H, Ar-*H*), 6.67 (d, J = 15.8 Hz, 1H, Ph-CH=CH), 6.43 (dd, J = 6.1, 15.8 Hz, 1H, Ph-CH=CH), 5.62 (d, J = 4.3 Hz, 1H, OH), 5.27 (t, J = 5.1 Hz, 1H, HO-CH), 2.31 (s, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 141.9, 137.2, 136.3, 134.3, 129.1, 128.4, 127.9, 126.7, 110.0, 73.5, 21.2 ppm.

Hydrogenation of 30



Supplementary Figure 38. Hydrogenation of **30**.

Prepared according to the general procedure with *trans*-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (100 mg, 362 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

Yield: 88% (88.6 mg, 319 μmol) white solid.

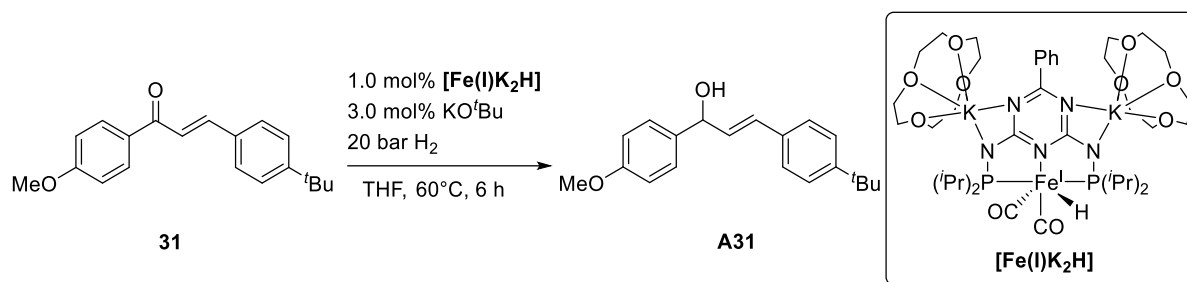
Chemical formula: $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}$; Molecular weight: 278.27 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 7.60 (s, 4H, Ar-*H*), 7.40–7.36 (m, 2H, Ar-*H*), 7.34–7.28 (m, 2H, Ar-*H*), 7.24–7.18 (m, 1H, Ar-*H*), 6.72 (d, J = 15.9 Hz, CH-CH=CH), 6.56 (dd, J = 15.9, 5.9 Hz, CH-CH=CH), 5.72 (d, J = 4.1 Hz, OH-CH), 5.26 (t, J = 4.6 Hz, OH-CH) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 144.0, 136.8, 129.1, 128.2, 127.0, 126.9, 126.6, 126.3, 125.8, 125.4 (q, J = 3.7 Hz, CF_3), 122.9, 72.9 ppm.

^{19}F NMR (376 MHz, DMSO-d_6 , 298 K): δ = 61.0 ppm.

Hydrogenation of 31



Supplementary Figure 39. Hydrogenation of **31**.

Prepared according to the general procedure with *trans*-3-(4-(*tert*-butyl)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (100 mg, 339 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

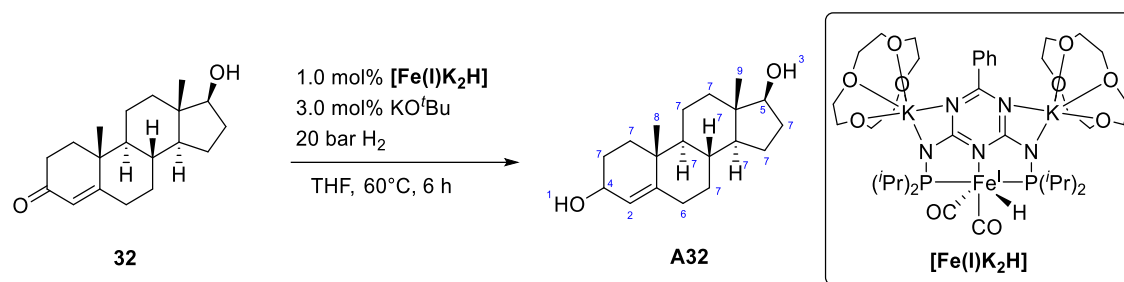
Yield: 72% (72.3 mg, 244 μmol) white solid.

Chemical formula: $\text{C}_{20}\text{H}_{24}\text{O}_2$; Molecular weight: 296.41 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 7.40–7.30 (m, 6H, Ar–H), 6.96–6.89 (d, J = 8.7 Hz, 2H, Ar–H), 6.61 (d, J = 15.9 Hz, 1H, Ar–CH=CH), 6.36 (dd, J = 6.0, 15.9 Hz, 1H, Ar–CH=CH), 5.53 (d, J = 4.2 Hz, 1H, OH), 5.23 (t, J = 4.6 Hz, 1H, HO–CH), 3.75 (s, 3H, OCH_3), 1.28 (s, 9H, Ar– $\text{C}(\text{CH}_3)_3$) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 158.7, 150.3, 137.0, 134.4, 133.6, 128.1, 127.8, 126.4, 125.7, 113.9, 109.8, 73.2, 55.7, 34.7, 31.5 ppm.

Hydrogenation of **32**



Supplementary Figure 40. Hydrogenation of **32**.

Prepared according to the general procedure with testosterone (100 mg, 347 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (1:9) ethyl acetate:pentane). The eluent was removed in a rotary evaporator.

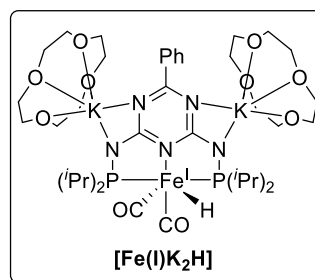
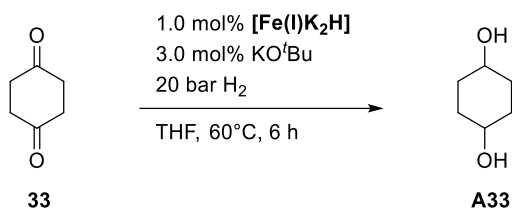
Yield: 61% (61.5 mg, 211 μmol) white solid.

Chemical formula: $\text{C}_{19}\text{H}_{30}\text{O}_2$; Molecular weight: 290.45 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 5.13 (d, J = 1.2 Hz, 1H, 1-*H*), 4.48 (d, J = 5.6 Hz, 1H, 2-*H*), 4.37 (d, J = 4.9 Hz, 1H, 3-*H*), 3.88–3.83 (m, 1H, 4-*H*), 3.37 (dt, J = 4.9, 8.9 Hz, 1H, 5-*H*), 2.46 (p, J = 1.8 Hz, 1H, 6-*H*) 2.13–2.24 (m, 1H, 7-*H*), 1.88 (dq, J = 2.3, 13.6 Hz, 1H, 7-*H*), 1.82–1.55 (m, 5H, 7-*H*), 1.47–1.36 (m, 2H, 7-*H*), 1.34–1.19 (m, 4H, 7-*H*), 1.17–1.07 (m, 2H, 7-*H*), 0.94 (s, 3H, 8-*H*), 0.92–0.72 (m, 3H, 7-*H*), 0.60 (s, 3H, 9-*H*) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 144.7, 125.9, 80.4, 66.4, 54.7, 50.7, 42.8, 37.2, 36.9, 36.0, 35.8, 32.8, 31.9, 30.2, 29.5, 23.5, 20.7, 18.9, 11.6 ppm.

Hydrogenation of **33**



Supplementary Figure 41. Hydrogenation of **33**.

Prepared according to the general procedure with cyclohexane-1,4-dione (100 mg, 892 μmol) as carbonyl compound. Purification was conducted using flash chromatography (silica gel, (3:7) methanol:pentane). The eluent was removed in a rotary evaporator and product obtained as a white solid.

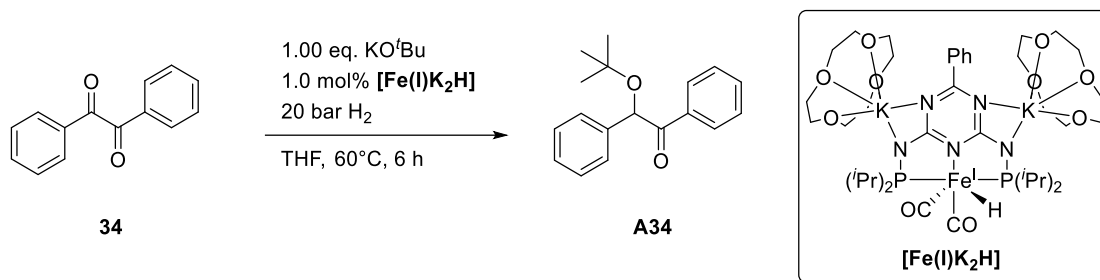
Yield: 78 % (81.0 mg, 695 μmol) white solid.

Chemical formula: $\text{C}_6\text{H}_{12}\text{O}_2$; Molecular weight: 116.08 g/mol.

^1H NMR (400 MHz, DMSO-d_6 , 298 K): δ = 4.26 (s, 2H, OH), 3.50–3.42 (m, 1H, *cis/trans*-CH-OH), 3.33–3.30 (m, 1H, *cis/trans*-CH-OH), 1.77–1.65 (m, 2H, CH_2), 1.57–1.45 (m, 2H, CH_2), 1.45–1.25 (m, 2H, CH_2), 1.13–1.02 (m, 2H, CH_2) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 , 298 K): δ = 68.6, 66.3, 63.1, 33.3, 30.7 ppm.

Hydrogenation of **34**



Supplementary Figure 42. Hydrogenation of **34**.

Prepared according to the general procedure with benzil (100 mg, 475 μ mol) as carbonyl compound and 1.00 eq KO^tBu (53.2 mg, 475 μ mol). Et₂O (10 mL) was added to the reaction mixture and the organic phase was washed with water (10 mL) twice. The organic phase was filtered with a 2 cm SiO₂-plug and dried over Na₂SO₄. The organic solvent was removed in a rotary evaporator and the product obtained as a yellow solid.

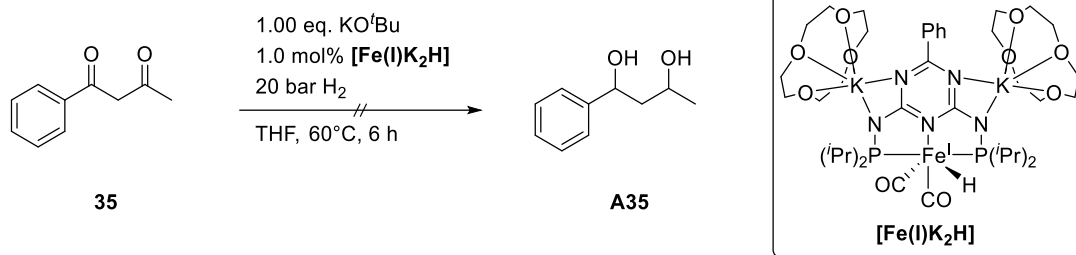
Yield: 99 % (126 mg, 473 μ mol) yellow solid.

Chemical formula: C₁₈H₂₀O₂; Molecular weight: 268.36 g/mol.

¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 7.43–7.28 (m, 10H, Ar–H), 6.39 (s, 1H, O–CH), 1.42 (s, 9H, C(CH₃)₃) ppm.

¹³C NMR (100 MHz, DMSO-d₆, 298 K): δ = 172.6, 144.1, 128.1, 127.5, 82.1, 81.1, 27.9 ppm.

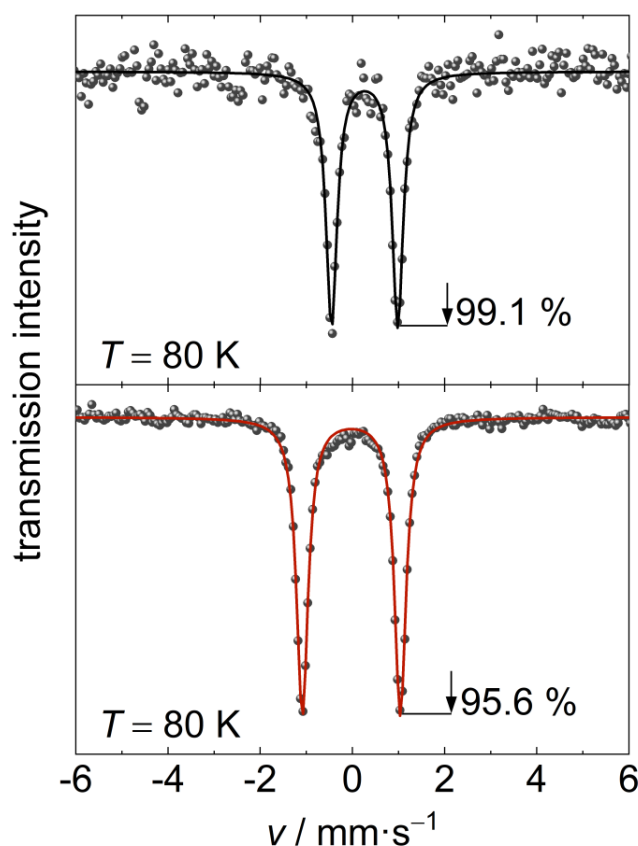
Hydrogenation of **35**



Supplementary Figure 43. Hydrogenation of **35**.

Prepared according to the general procedure with 1-phenylbutane-1,3-dione (100 mg, 616 μmol) as carbonyl compound and 1.00 eq KO^tBu (69.1 mg, 616 μmol). No reaction was observed.

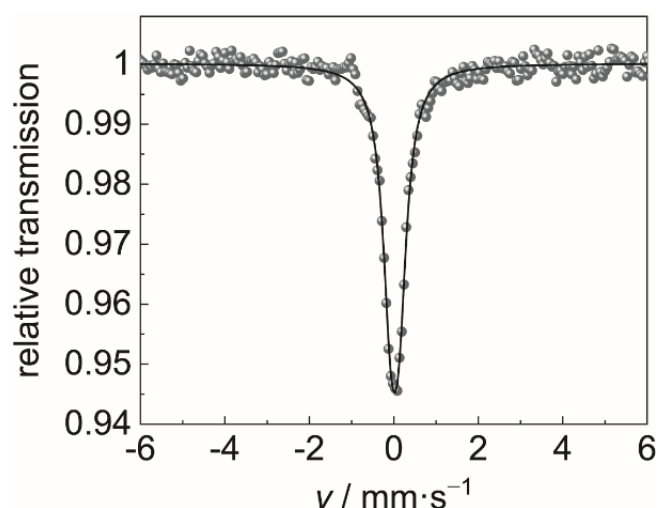
6.5 ^{57}Fe Mössbauer spectroscopy



Supplementary Figure 44. Zero-field ^{57}Fe Mössbauer spectrum of **[Fe(II)BrCO]-01** (top) and **[Fe(I)K₂H]** (bottom), recorded at $T = 80\text{ K}$. Symbols represent experimental data and solid line the corresponding Lorentzian fit.

Supplementary Table 8. Summary of ^{57}Fe Mössbauer parameters of **[Fe(II)BrCO]-01** and **[Fe(I)K₂H]**, determined from Lorentzian fits. δ denotes the isomer shift, ΔE_Q specifies the quadrupole splitting, Γ represents the full (Lorentzian) line width at half maximum (FWHM) and V the integral intensity of the component in the fit. Standard deviations are reported in brackets. A_2/A_1 is the ratio of relative intensities of a doublet which is usually expected to be $A_2/A_1 = 1$. It was therefore fixed in the fit (marked with an asterisk).

Entry	T [K]	δ [$\text{mm} \cdot \text{s}^{-1}$]	ΔE_Q [$\text{mm} \cdot \text{s}^{-1}$]	Γ_{FWHM} [$\text{mm} \cdot \text{s}^{-1}$]	A_2/A_1	V [%]
[Fe(II)BrCO]-01	80	0.228(7)	1.424(2)	0.309(20)	1*	100
[Fe(I)K₂H]	80	-0.025(2)	2.125(5)	0.304(8)	1*	100



Supplementary Figure 45. Zero-field ^{57}Fe Mössbauer spectrum of **[Fe(I)K]**, recorded at $T = 80$ K. Symbols represent experimental data and solid line the corresponding Lorentzian fit. We accounted for a small quadrupole splitting in our phenomenological fit model. The line width points towards dynamic processes on the experimental Mössbauer timescale which could be responsible for the collapse of a well-resolved quadrupole doublet (such case has already been observed before).¹² In addition, the asymmetric unit of single-crystalline **[Fe(I)K]** reveals crystallographic inequivalent iron sites. Both factors could cause the spectral appearance, i.e., the convolution of two (or more) individual sub-spectra to a single and broadened resonance signal. Nevertheless, the close-to-zero value of δ indicates the presence of a low-valent iron center in **[Fe(I)K]**, surrounded by carbonyl ligands. This fact agrees with the isomeric shift of **[Fe(I)K₂H]** shown in the manuscript (Figure 5).

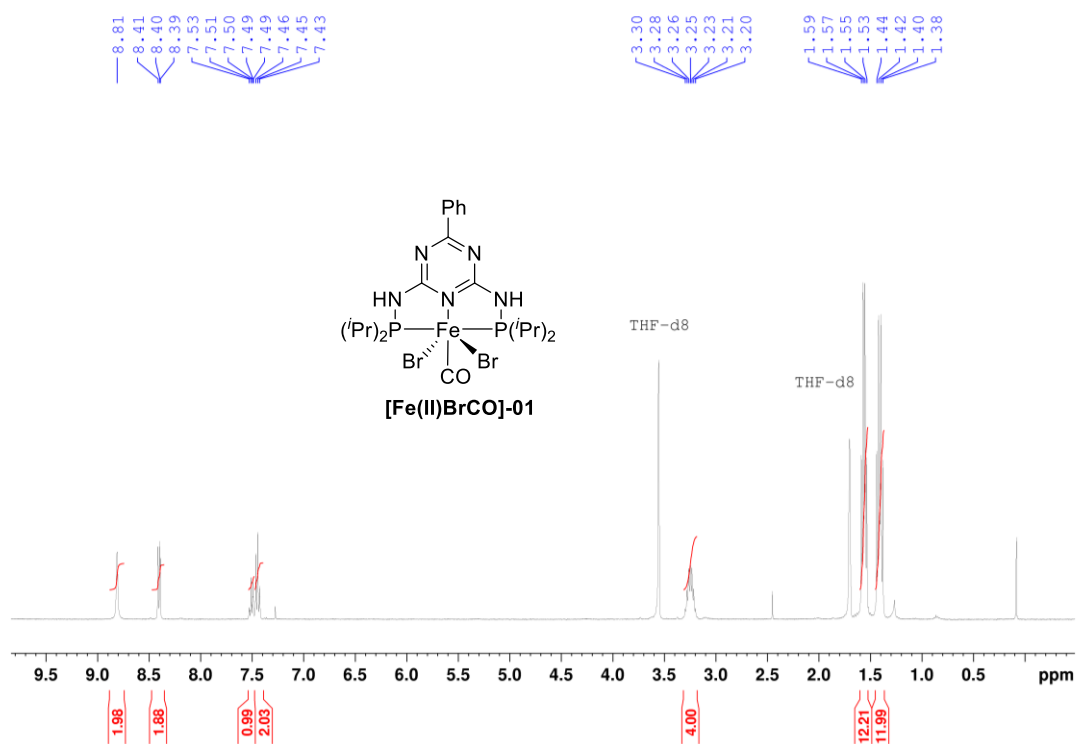
Supplementary Table 9. Summary of ^{57}Fe Mössbauer parameters of **[Fe(I)K]**, determined from Lorentzian fits. δ denotes the isomer shift, ΔE_Q specifies the quadrupole splitting, Γ represents the full (Lorentzian) line width at half maximum (FWHM) and V the integral intensity of the component in the fit. Standard deviations are reported in brackets. A_2/A_1 is the ratio of relative intensities of a doublet which is usually expected to be $A_2/A_1 = 1$. It was therefore fixed in the fit (marked with an asterisk).

Entry	T [K]	δ [mm·s ⁻¹]	ΔE_Q [mm·s ⁻¹]	Γ_{FWHM} [mm·s ⁻¹]	A_2/A_1	V [%]
[Fe(I)K]	80	0.021(9)	0.194(40)	0.464(44)	1*	100

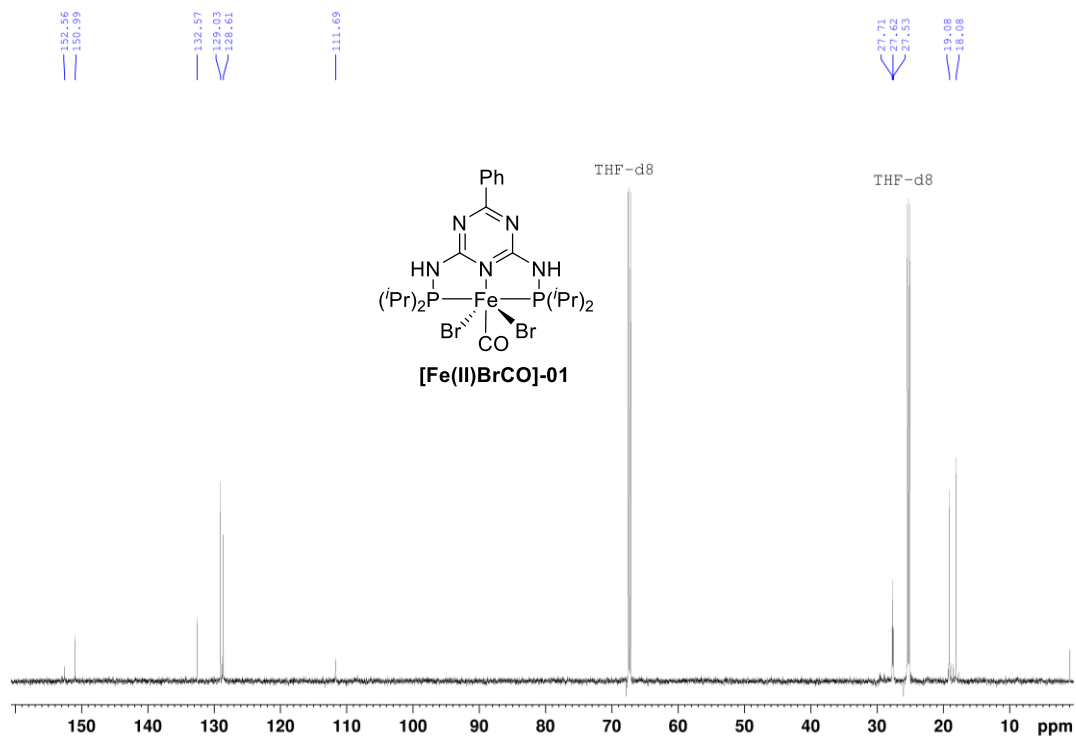
6.6 References

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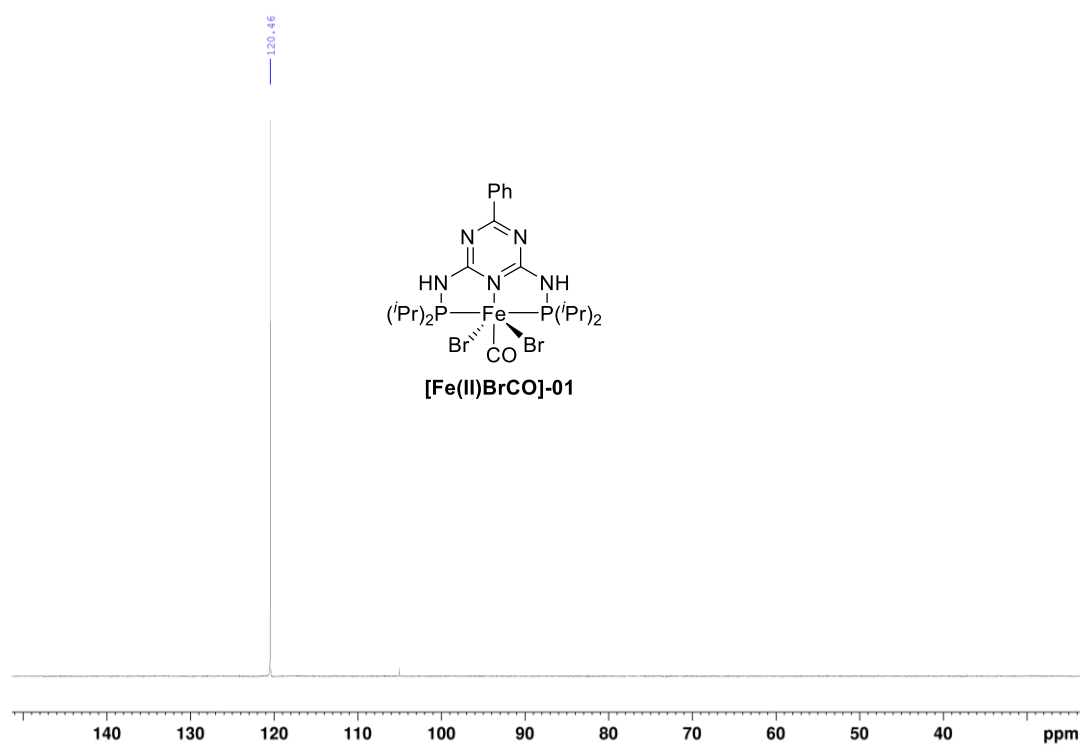
6.7 NMR spectra



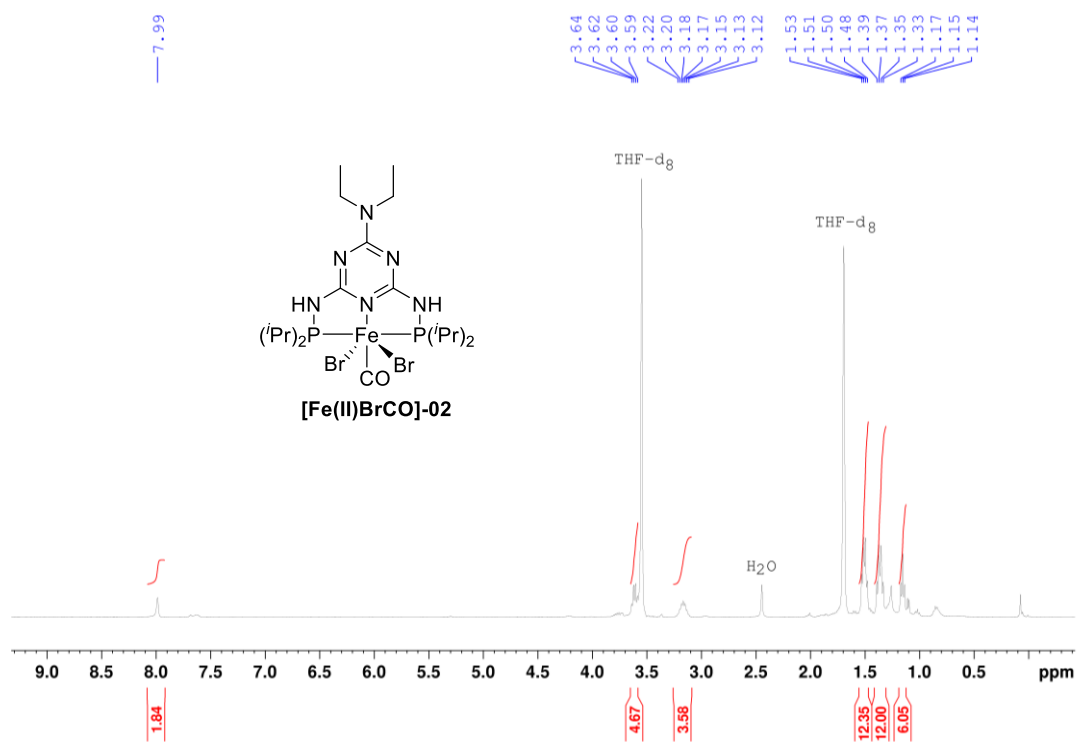
Supplementary Figure 46. ¹H NMR spectrum of [Fe(II)BrCO]-01.



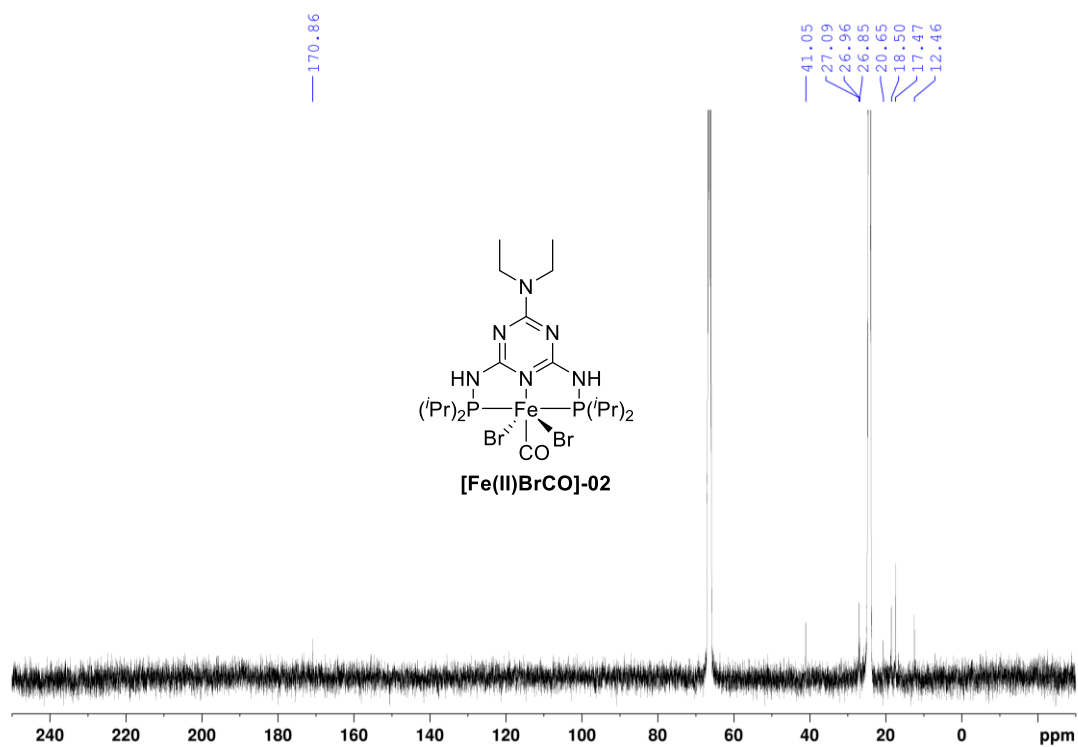
Supplementary Figure 47. ¹³C NMR spectrum of [Fe(II)BrCO]-01.



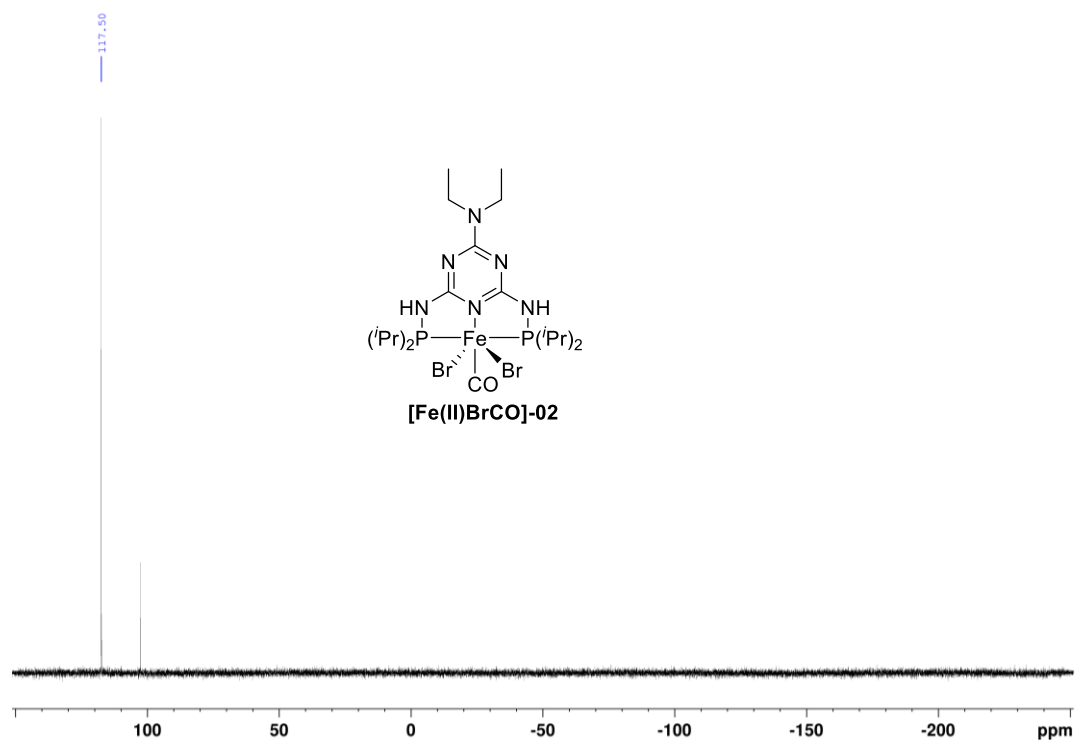
Supplementary Figure 48. ^{31}P NMR spectrum of **[Fe(II)BrCO]-01**.



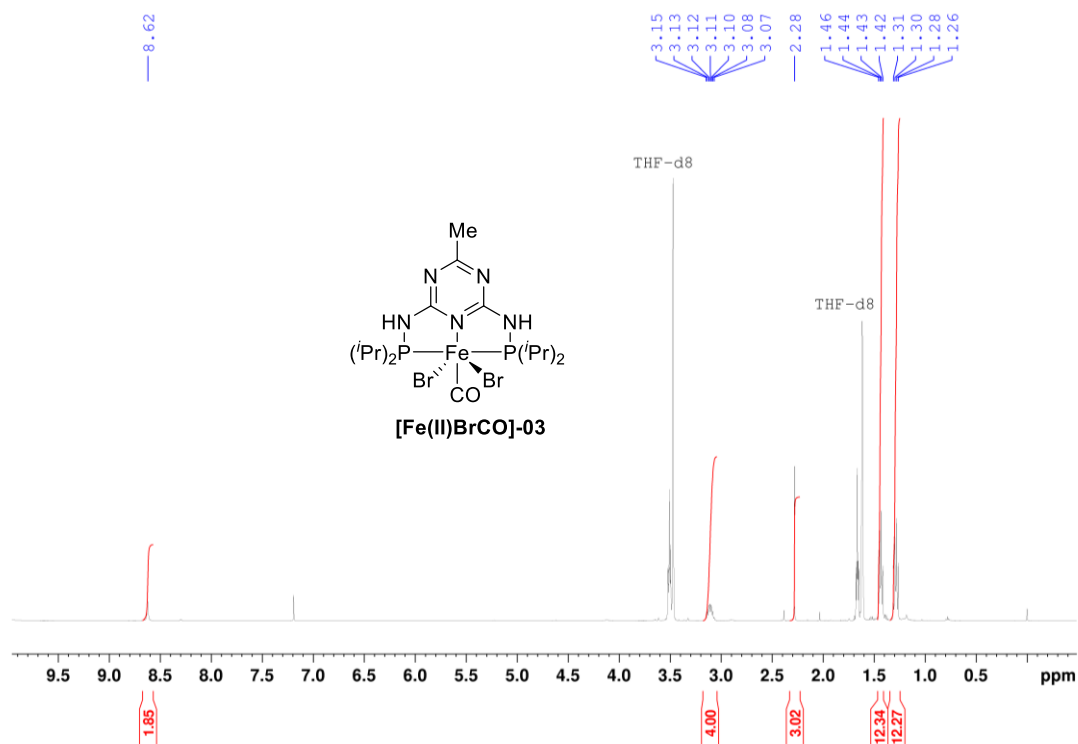
Supplementary Figure 49. ¹H NMR spectrum of **[Fe(II)BrCO]-02**.



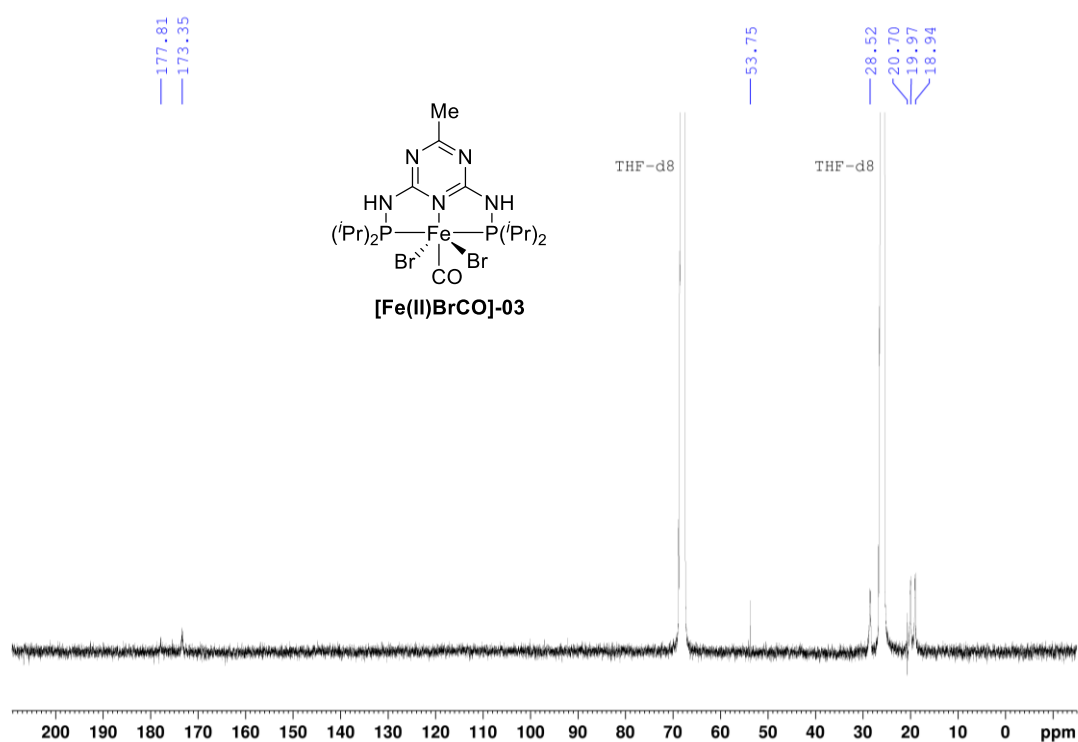
Supplementary Figure 50. ¹³C NMR spectrum of **[Fe(II)BrCO]-02**.



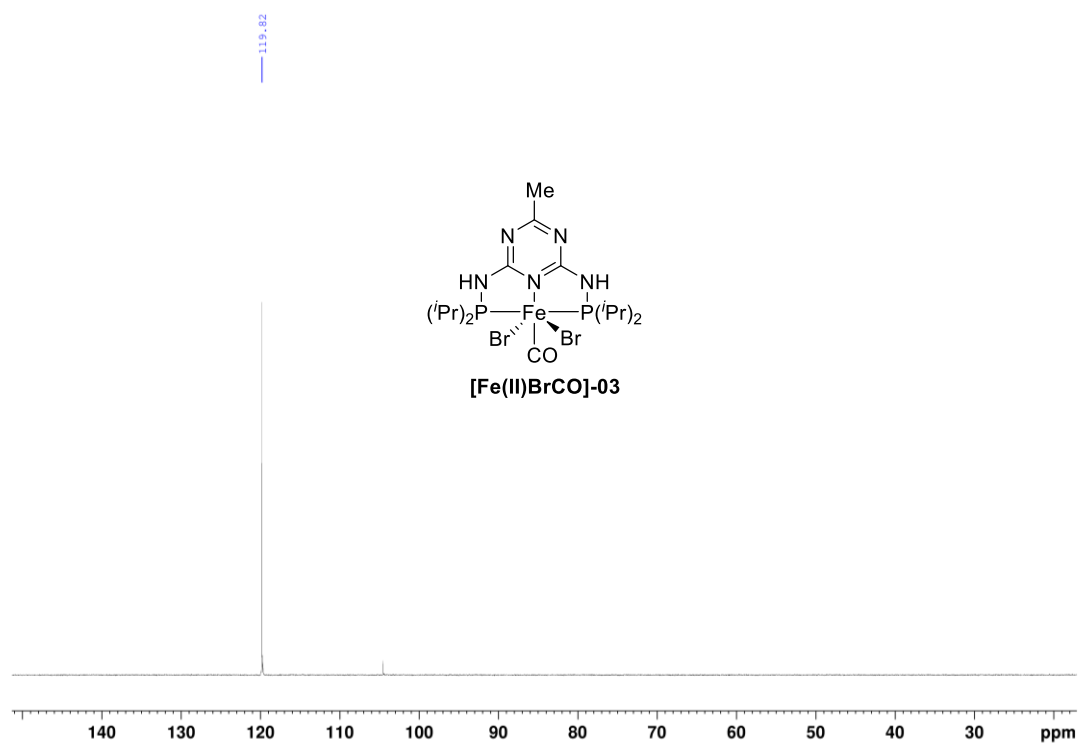
Supplementary Figure 51. ^{31}P NMR spectrum of **[Fe(II)BrCO]-02**.



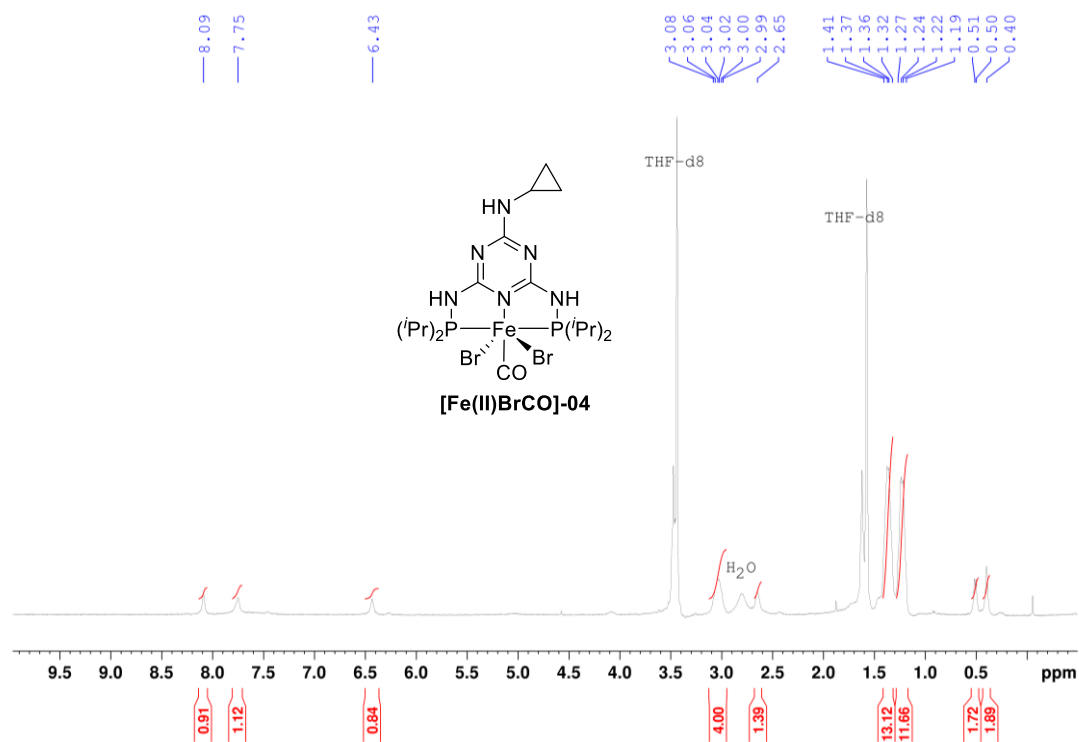
Supplementary Figure 52. ¹H NMR spectrum of **[Fe(II)BrCO]-03**.



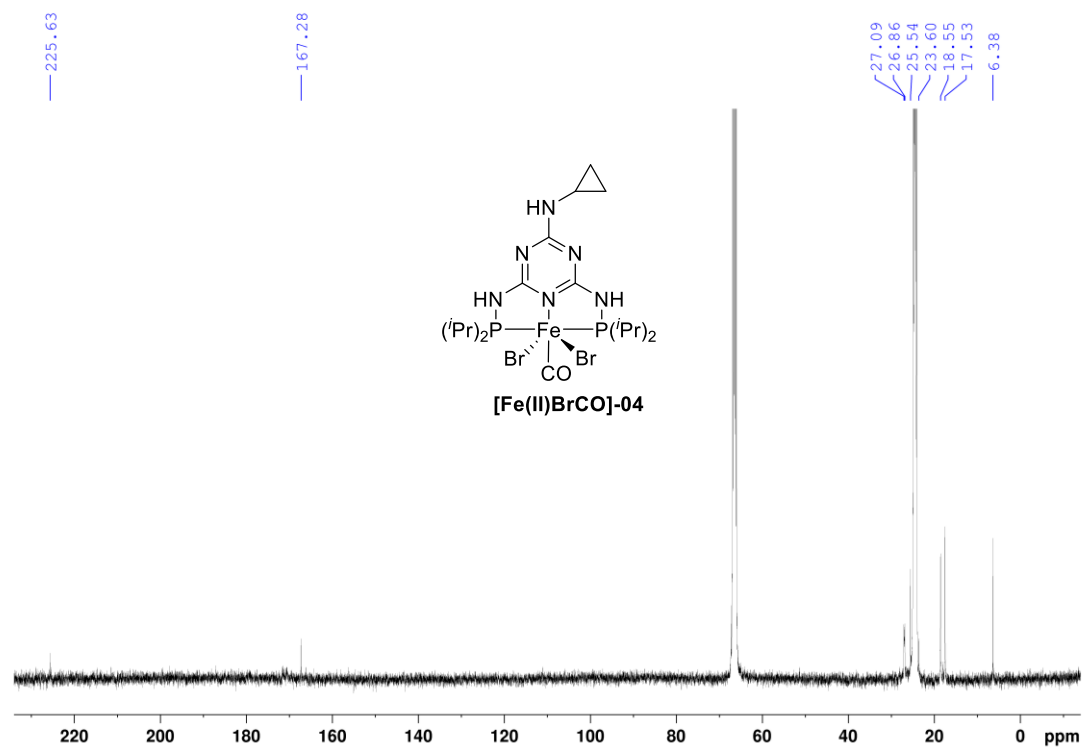
Supplementary Figure 53. ¹³C NMR spectrum of **[Fe(II)BrCO]-03**.



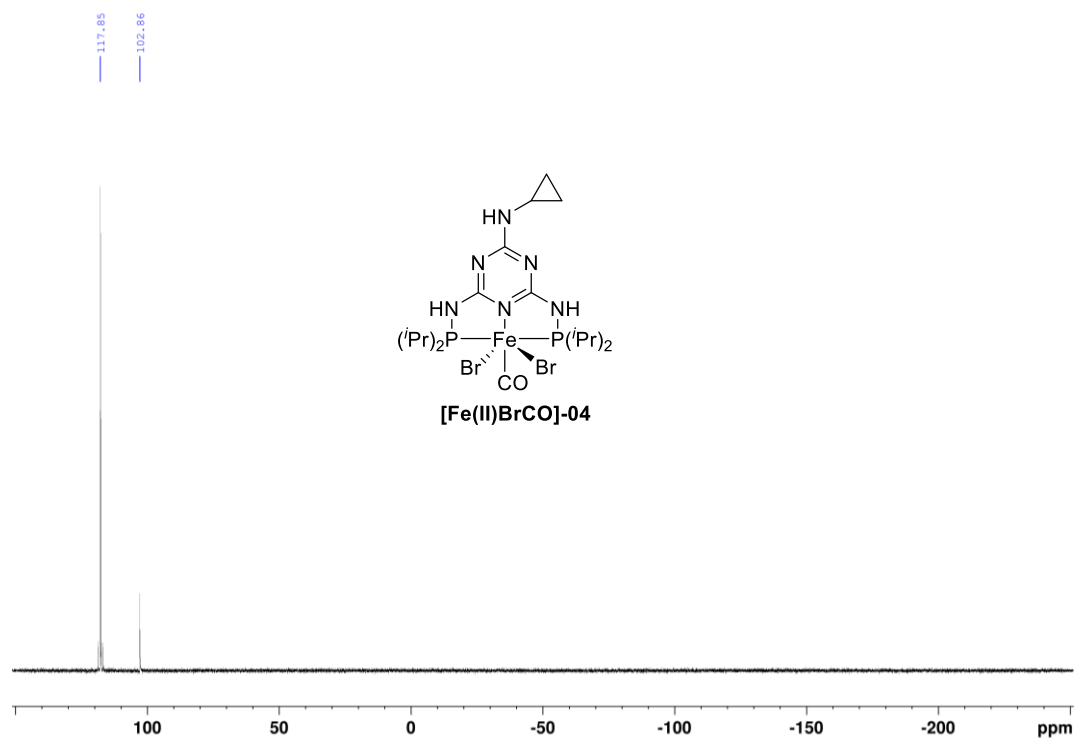
Supplementary Figure 54. ³¹P NMR spectrum of **[Fe(II)BrCO]-03**.



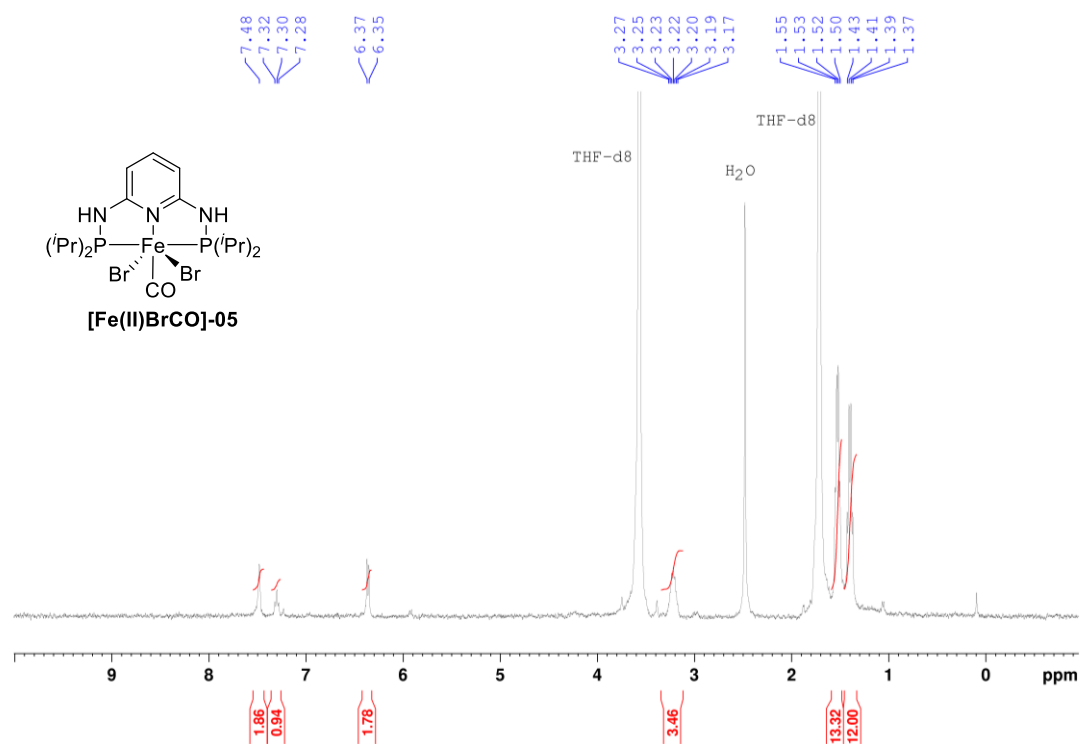
Supplementary Figure 55. ¹H NMR spectrum of **[Fe(II)BrCO]-04**.



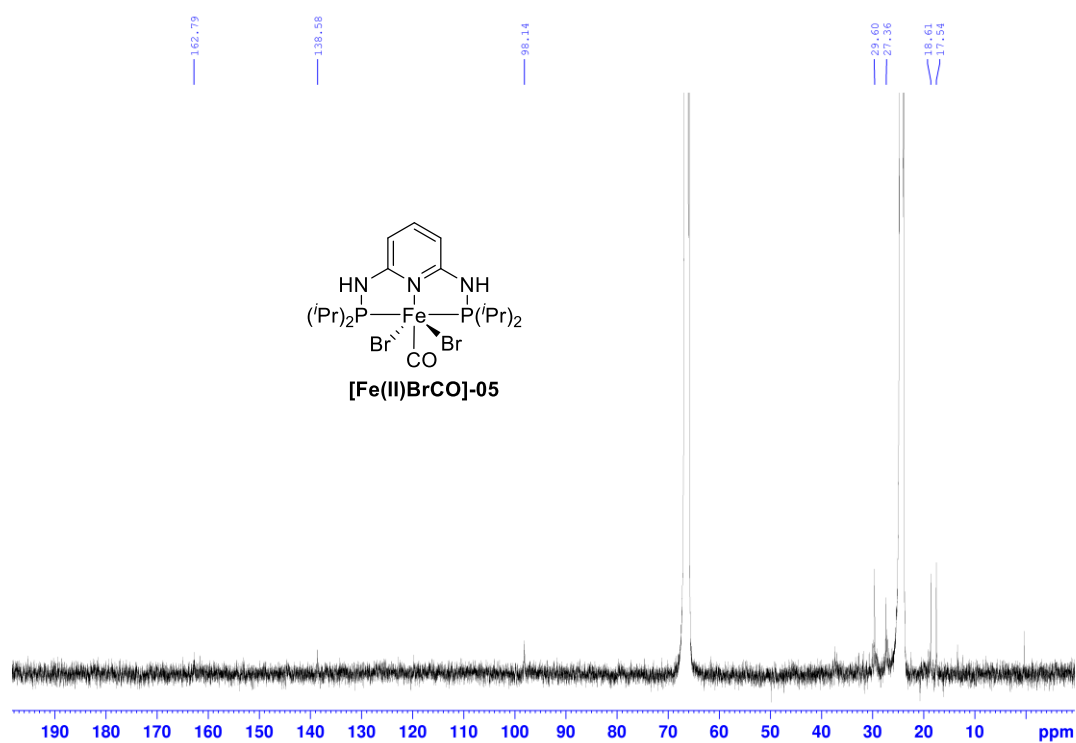
Supplementary Figure 56. ¹³C NMR spectrum of **[Fe(II)BrCO]-04**.



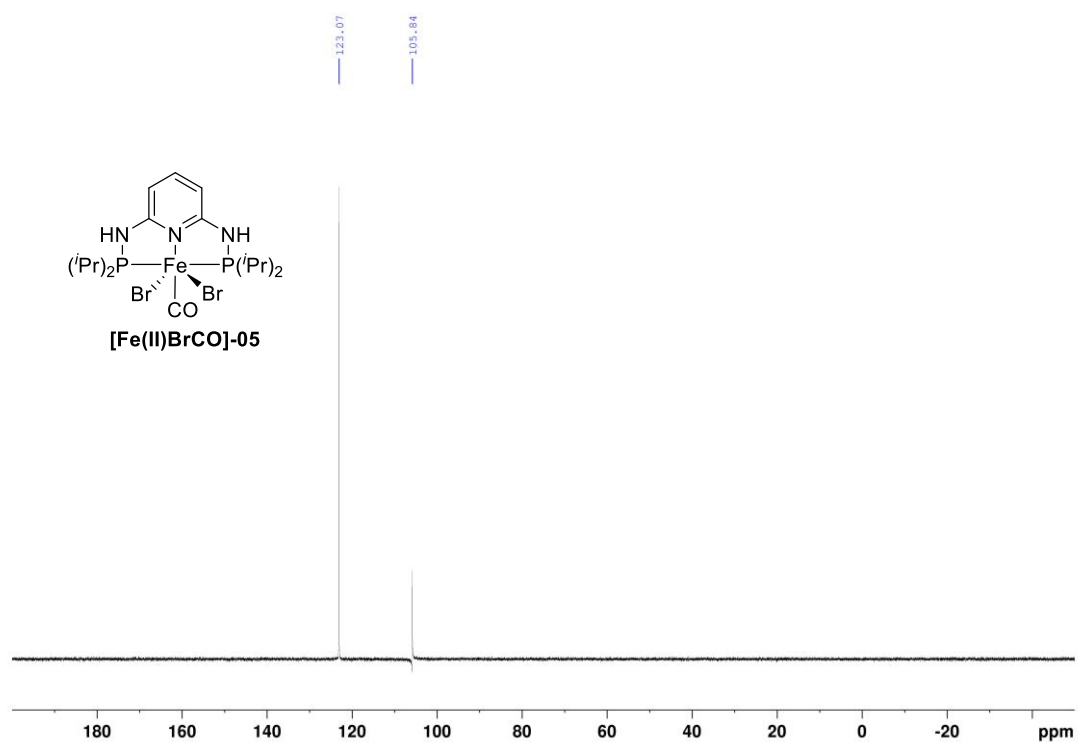
Supplementary Figure 57. ³¹P NMR spectrum of **[Fe(II)BrCO]-04**.



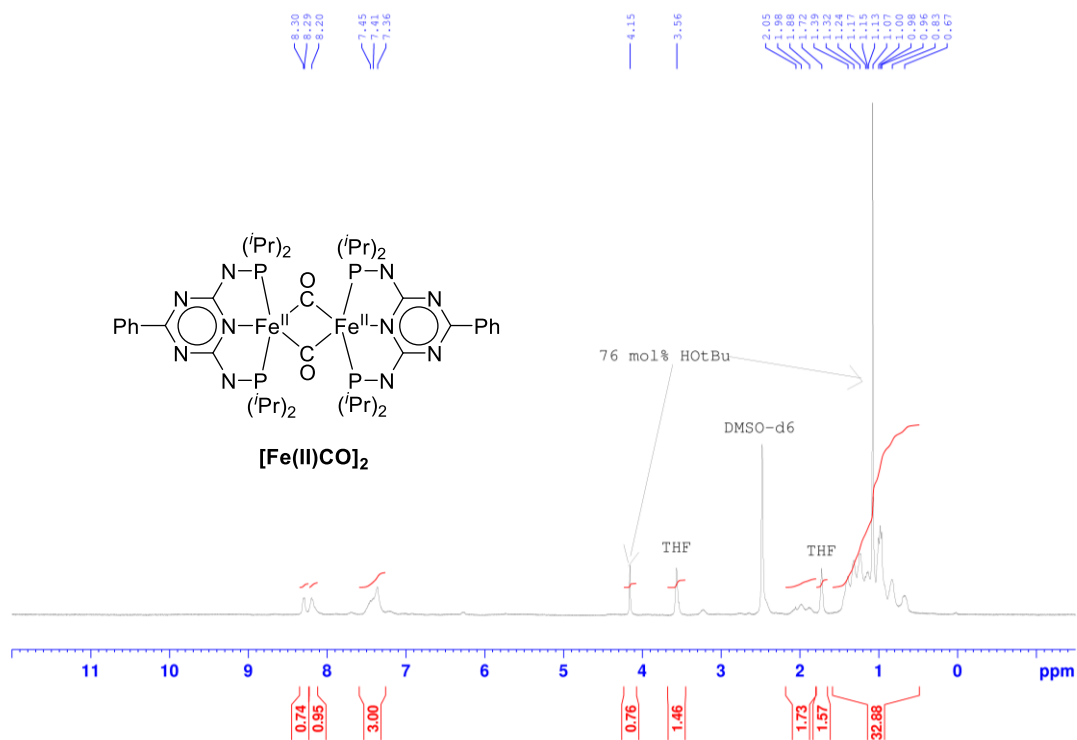
Supplementary Figure 58. ¹H NMR spectrum of **[Fe(II)BrCO]-05**.



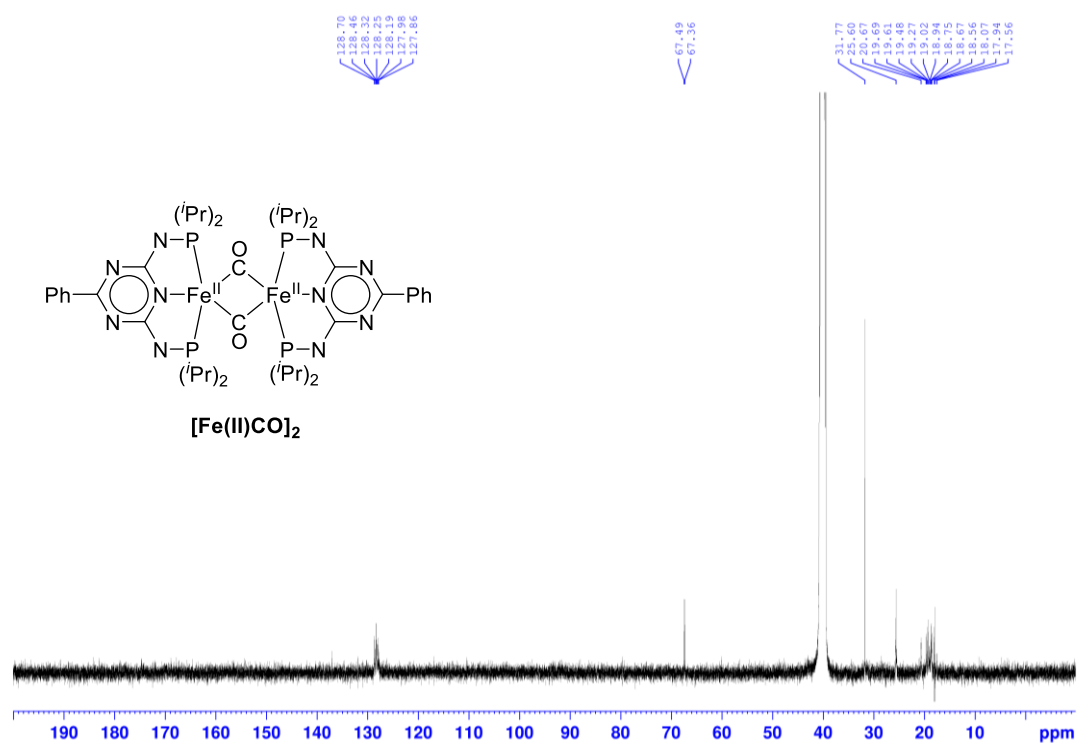
Supplementary Figure 59. ¹³C NMR spectrum of **[Fe(II)BrCO]-05**.



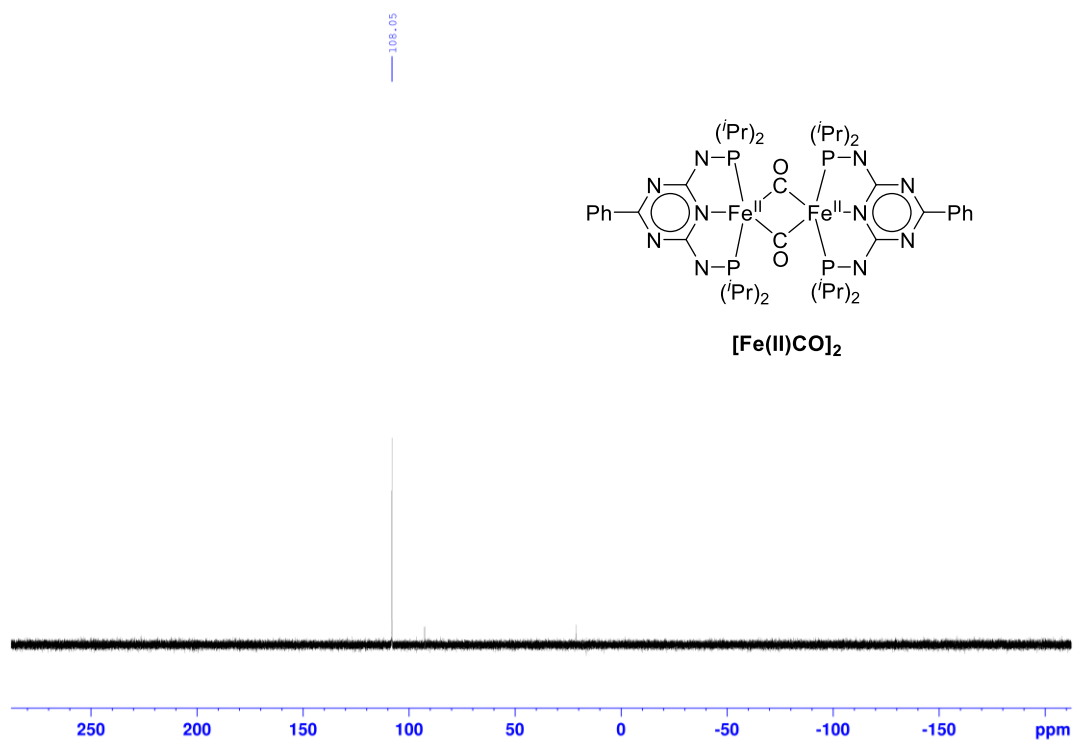
Supplementary Figure 60. ^{31}P NMR spectrum of **[Fe(II)BrCO]-05**.



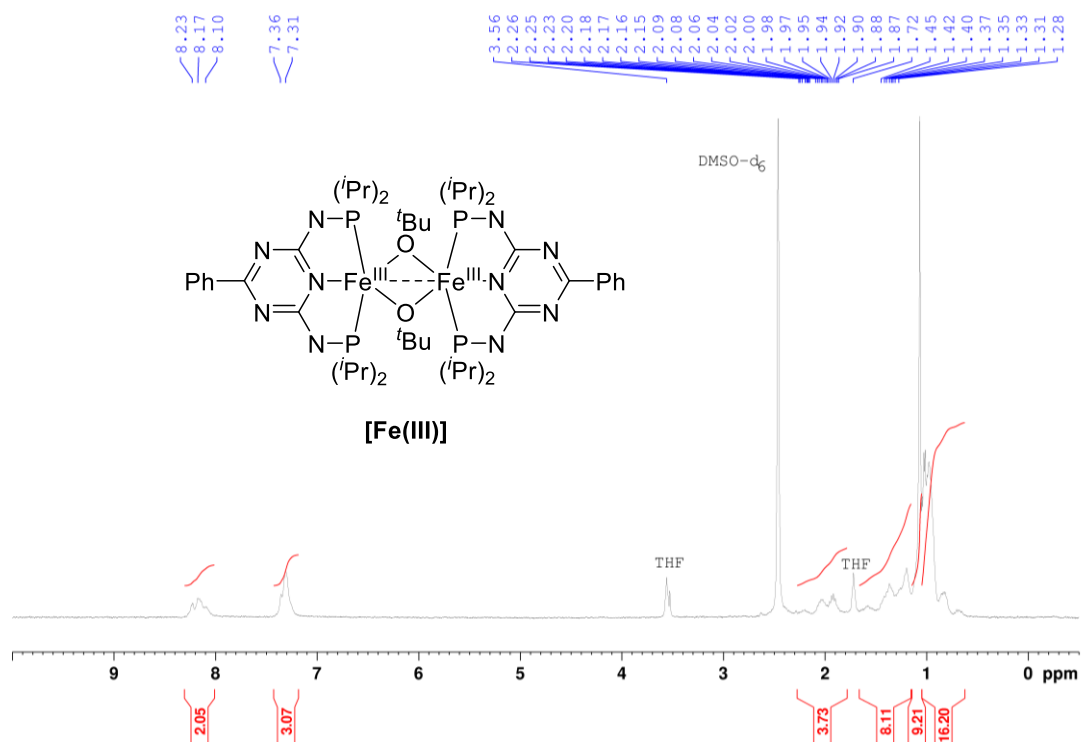
Supplementary Figure 61. ^1H NMR spectrum of $[\text{Fe}(\text{II})\text{CO}]_2$.



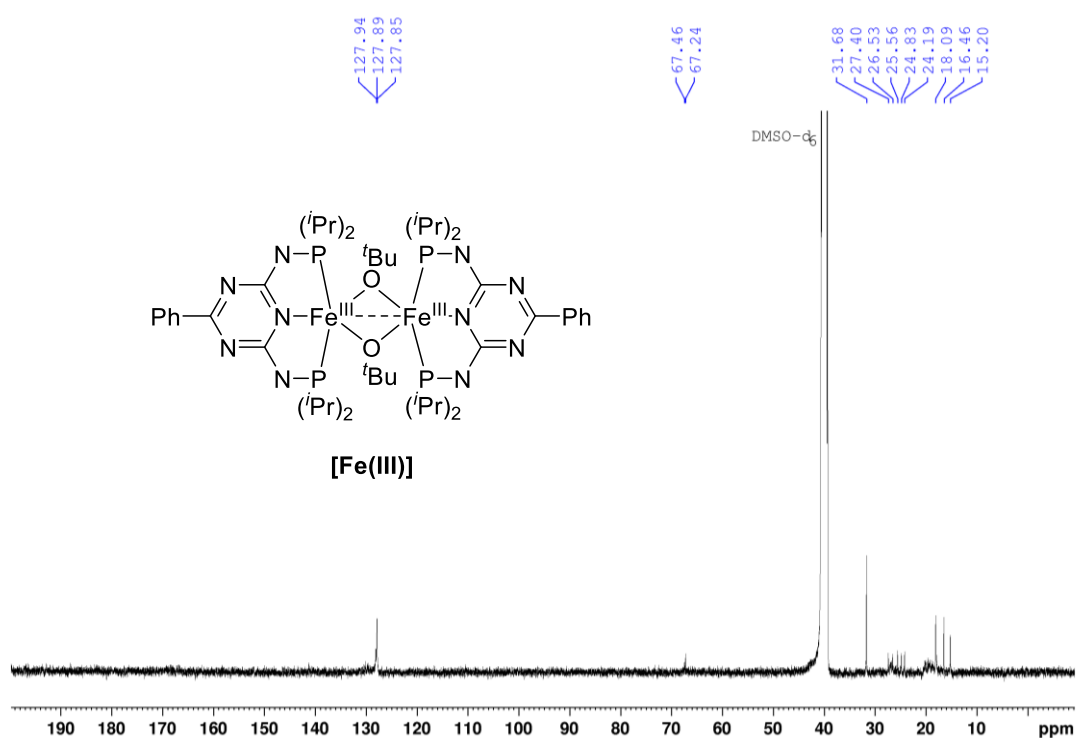
Supplementary Figure 62. ^{13}C NMR spectrum of $[\text{Fe}(\text{II})\text{CO}]_2$.



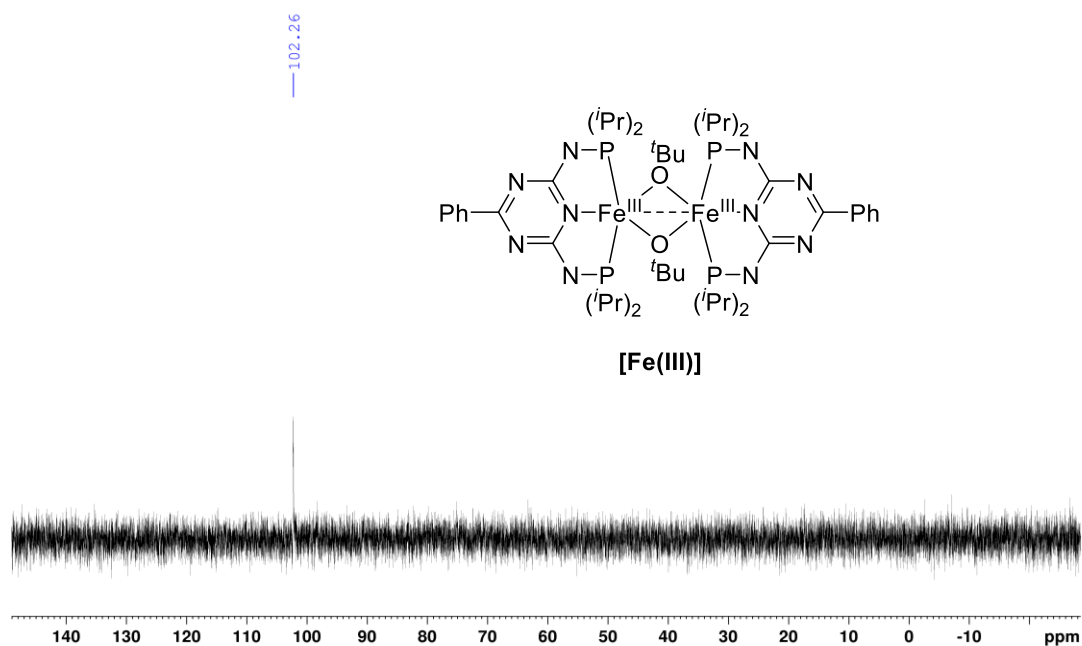
Supplementary Figure 63. ³¹P NMR spectrum of **[Fe(II)CO]₂**.



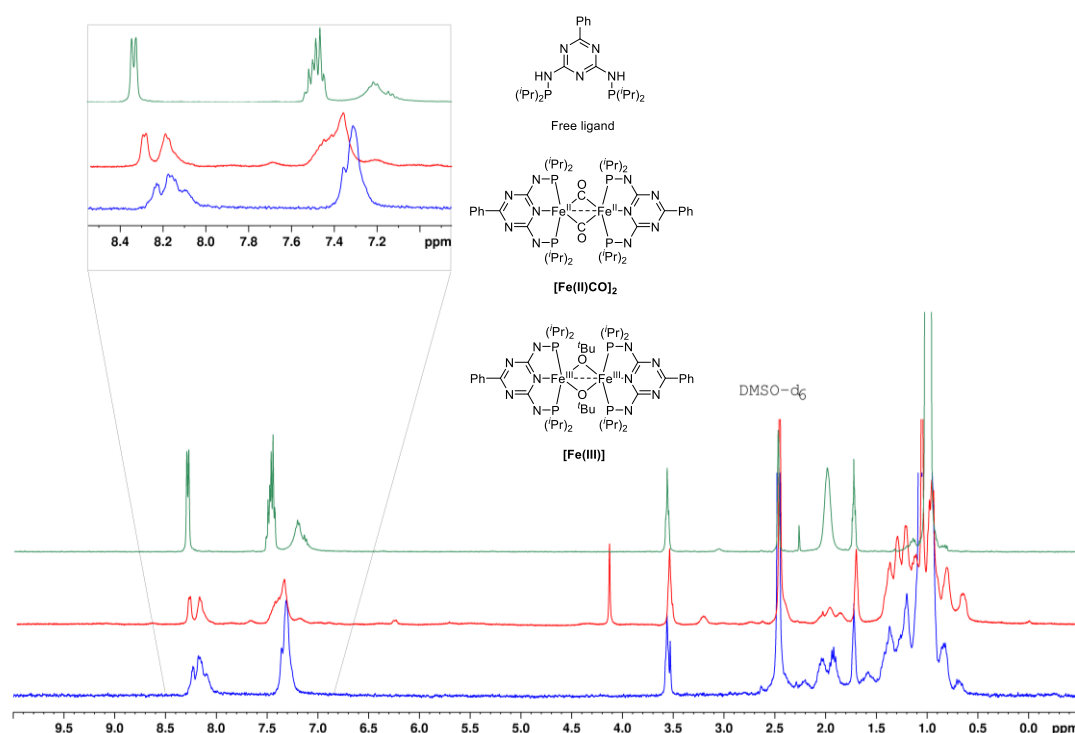
Supplementary Figure 64. ¹H NMR spectrum of **[Fe(III)]**.



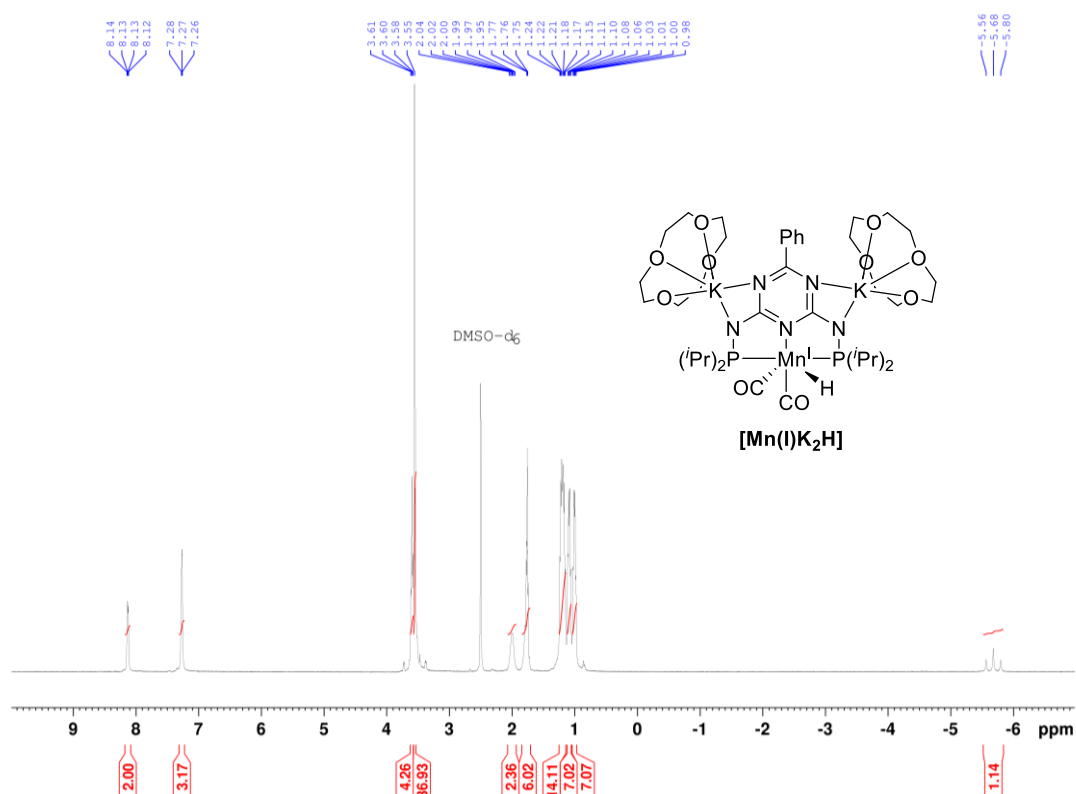
Supplementary Figure 65. ¹³C NMR spectrum of **[Fe(III)]**.



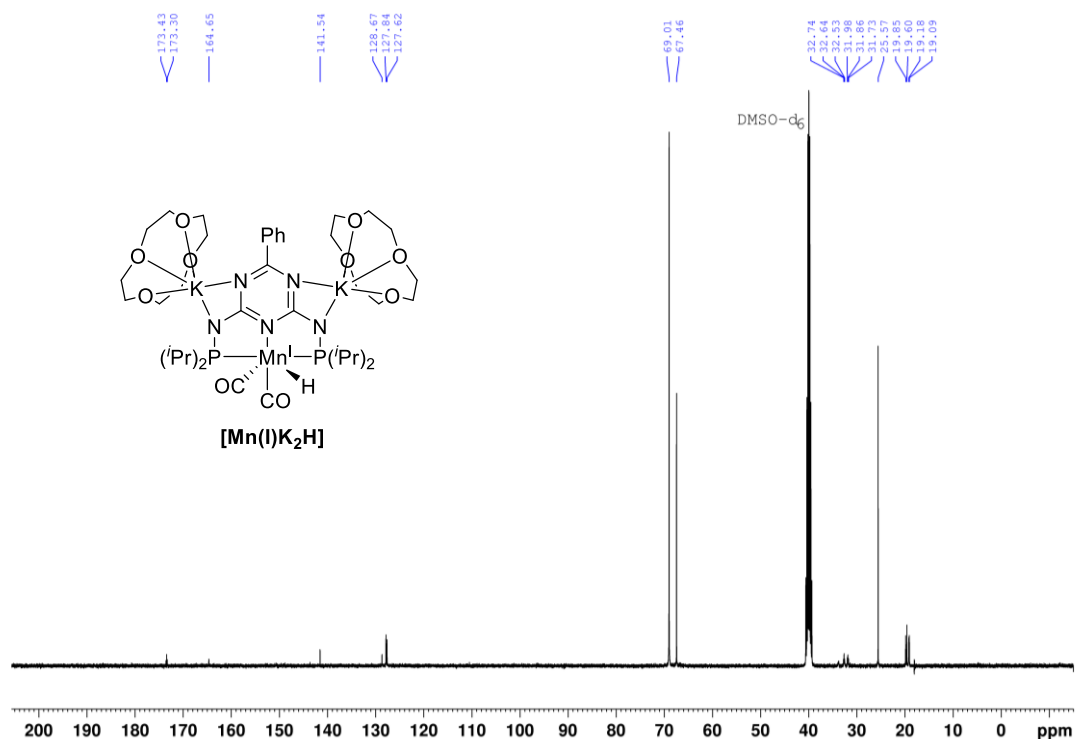
Supplementary Figure 66. ^{31}P NMR spectrum of **[Fe(III)]**.



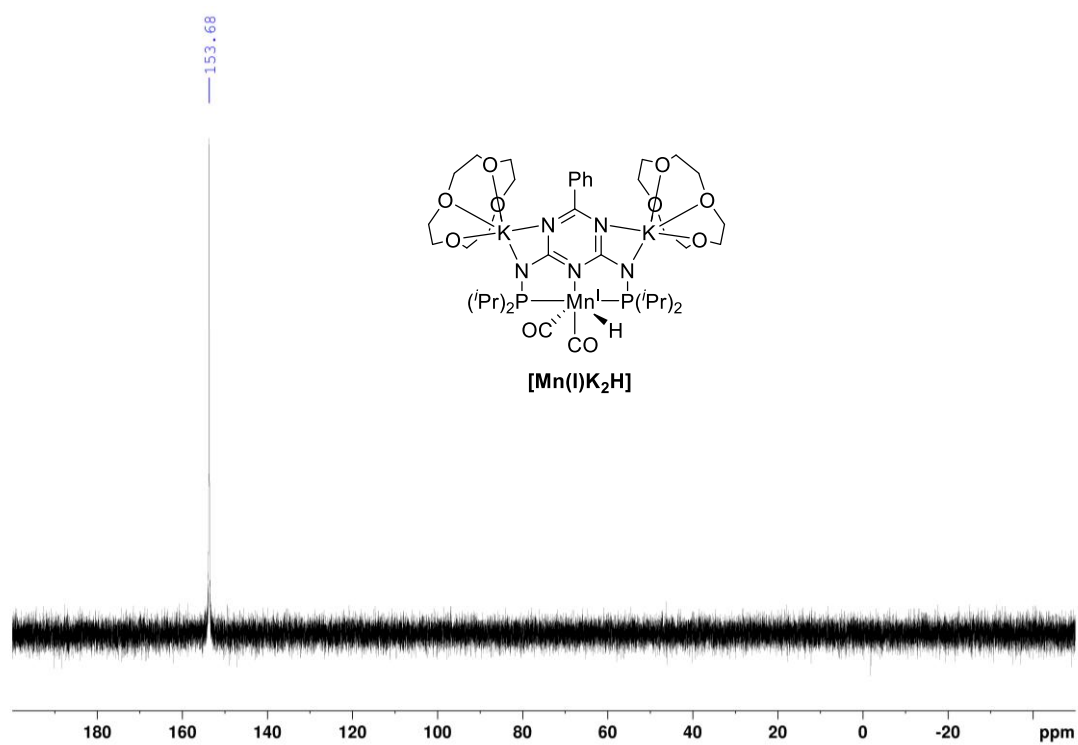
Supplementary Figure 67. Comparison of the ^1H NMR spectra of **[Fe(II)CO]₂** with **[Fe(III)]** and the free ligand. A difference in the chemical shift of the phenyl units is observed which most possibly results from the different oxidation states of the iron nuclei.



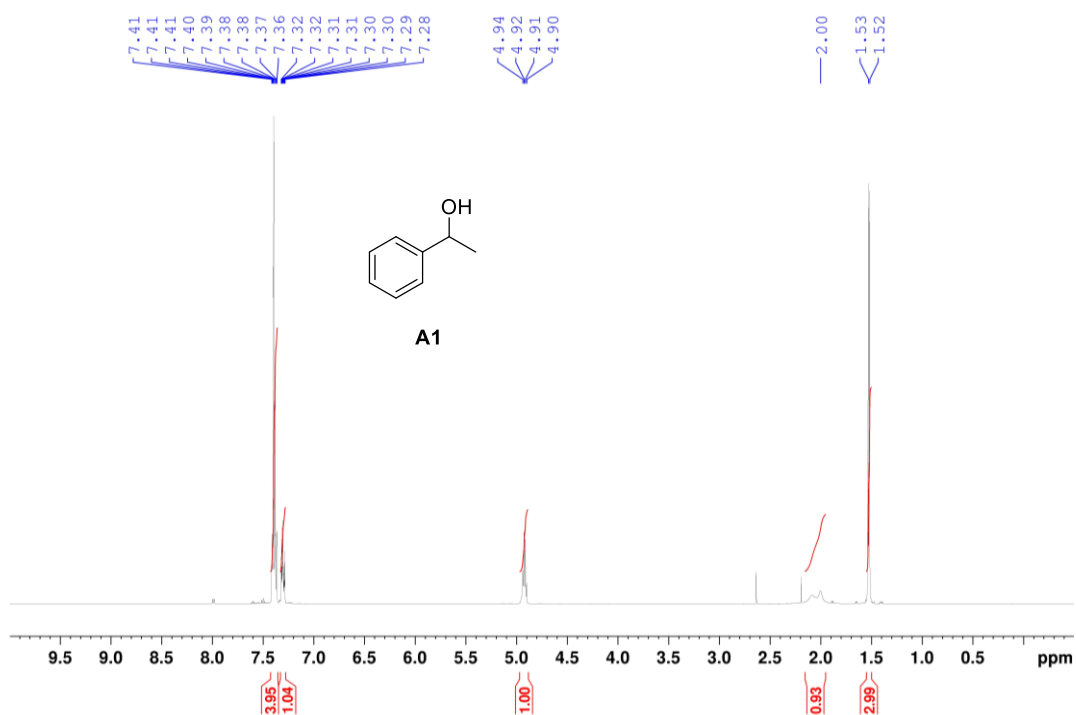
Supplementary Figure 68. ^1H NMR spectrum of $[\text{Mn}(\text{I})\text{K}_2\text{H}]$.



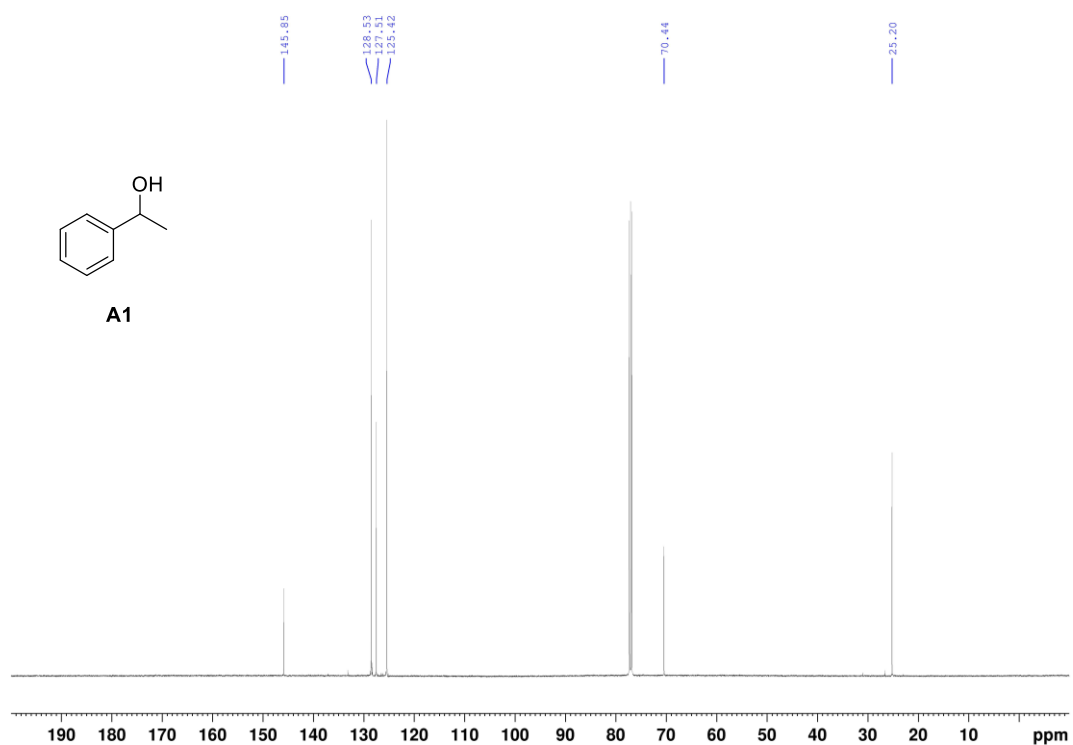
Supplementary Figure 69. ^{13}C NMR spectrum of $[\text{Mn}(\text{I})\text{K}_2\text{H}]$.



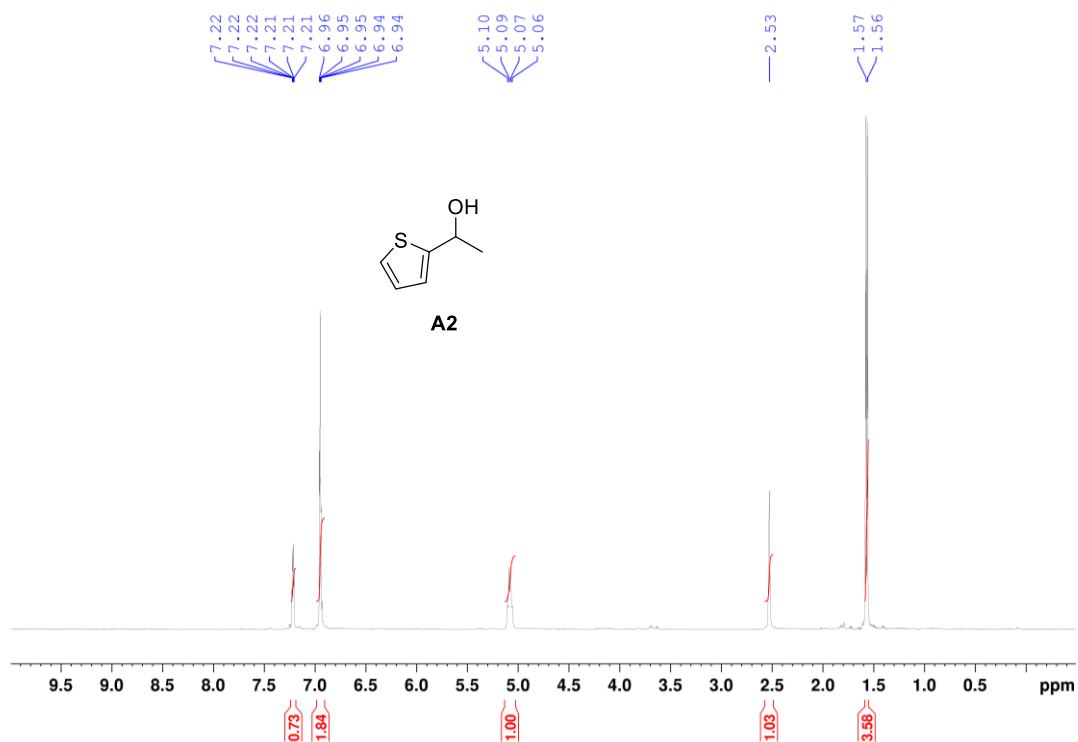
Supplementary Figure 70. ^{31}P NMR spectrum of $[\text{Mn(I)K}_2\text{H}]$.



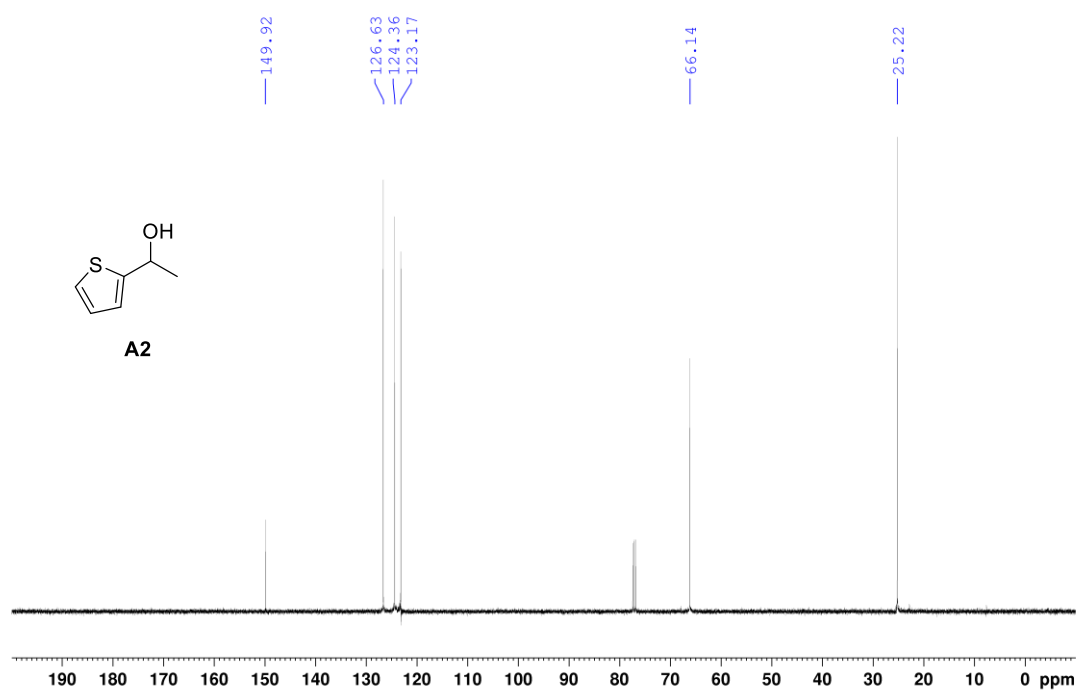
Supplementary Figure 71. ¹H NMR spectrum of 1-phenylethanol.



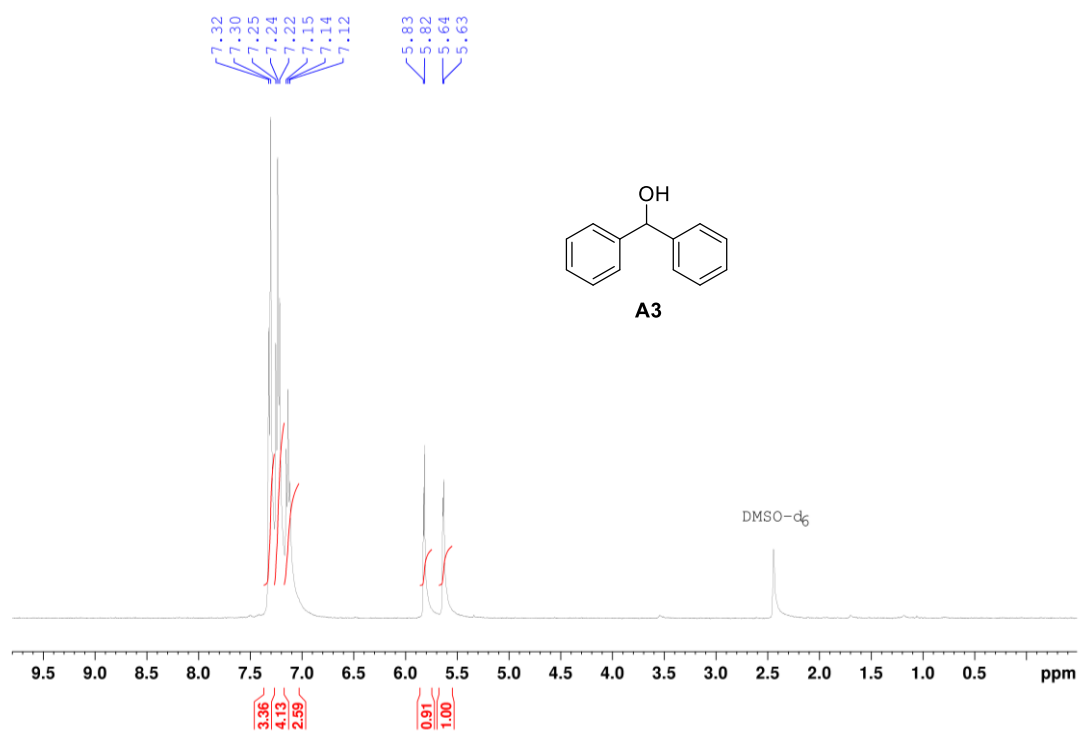
Supplementary Figure 72. ¹³C NMR spectrum of 1-phenylethanol.



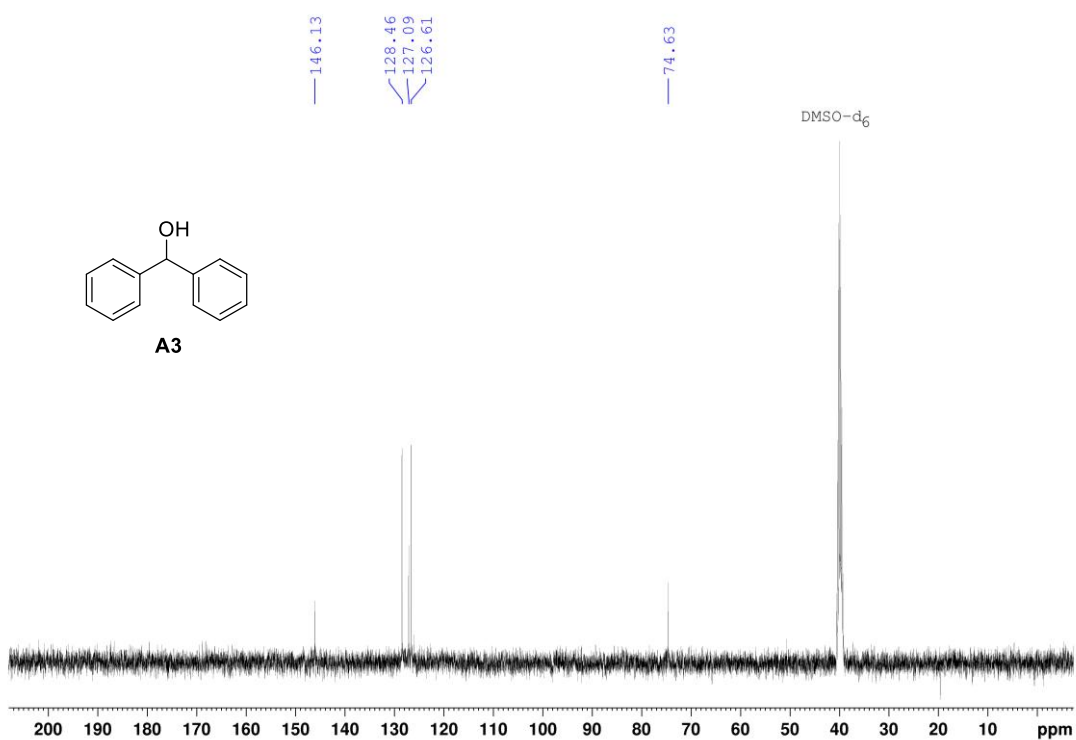
Supplementary Figure 73. ¹H NMR spectrum of 1-(thiophen-2-yl)ethan-1-ol.



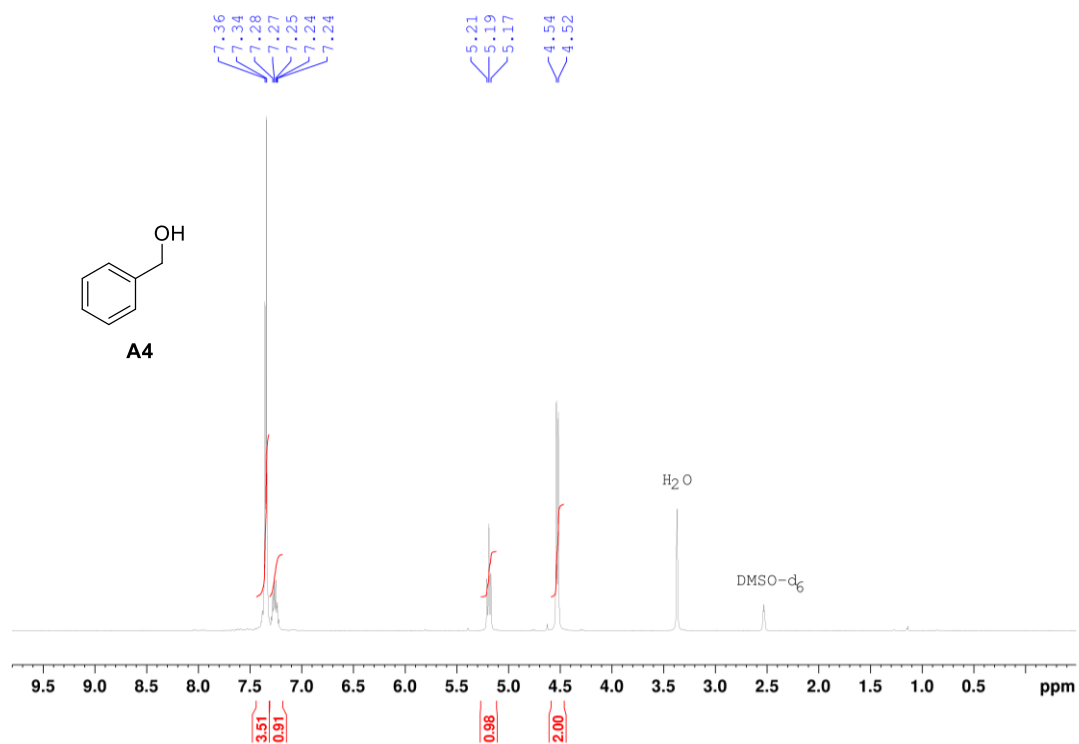
Supplementary Figure 74. ¹³C NMR spectrum of 1-(thiophen-2-yl)ethan-1-ol.



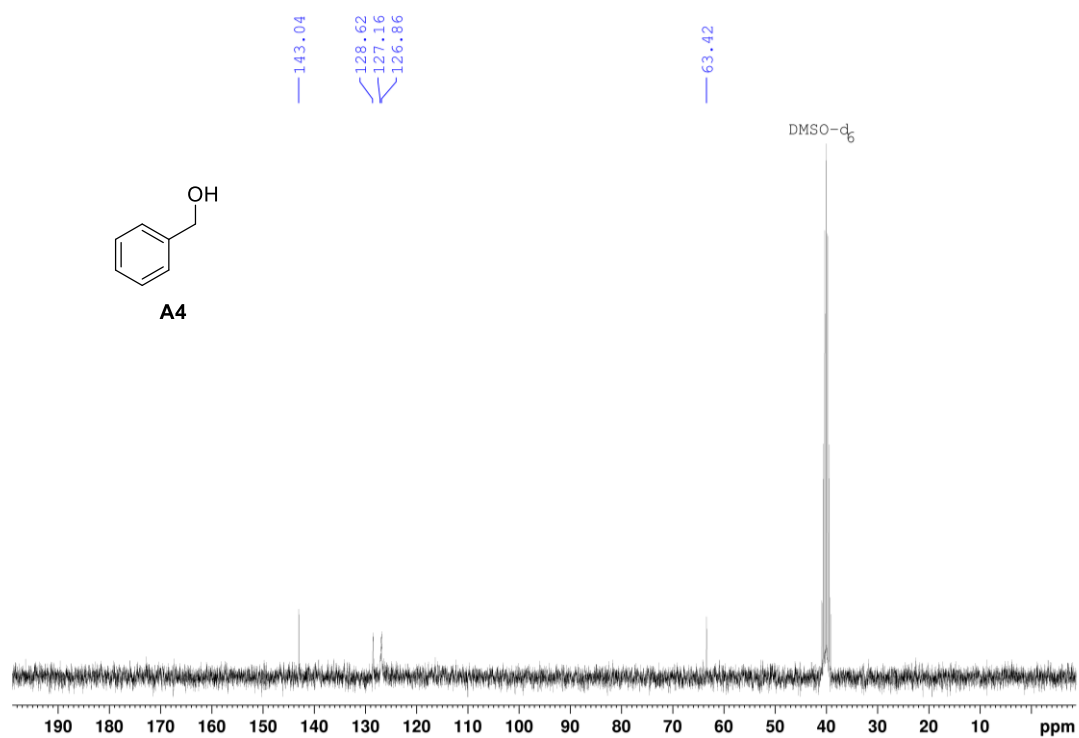
Supplementary Figure 75. ¹H NMR spectrum of diphenylmethanol.



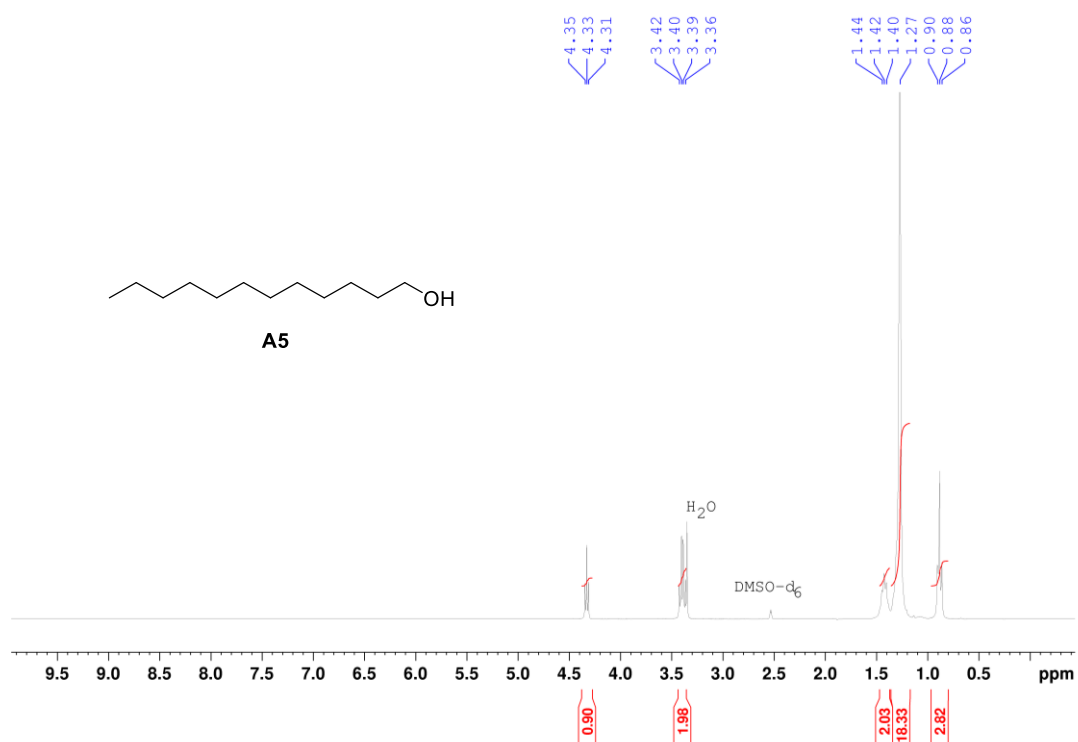
Supplementary Figure 76. ¹³C NMR spectrum of diphenylmethanol.



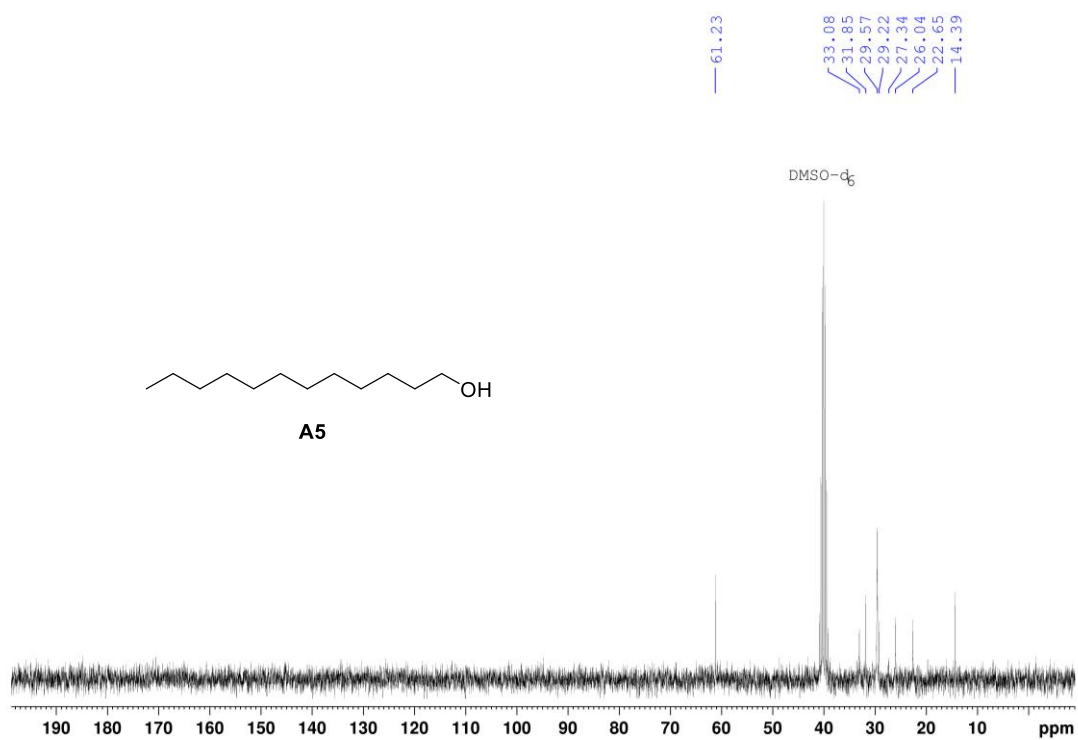
Supplementary Figure 77. ¹H NMR spectrum of benzyl alcohol.



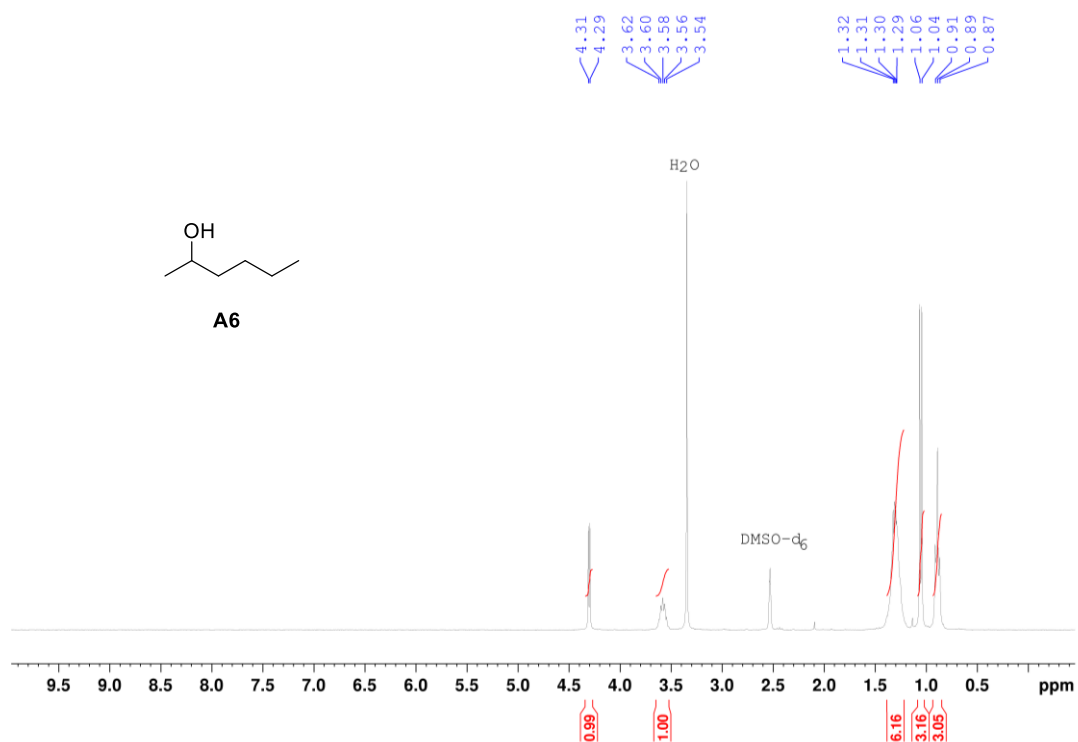
Supplementary Figure 78. ¹³C NMR spectrum of benzyl alcohol.



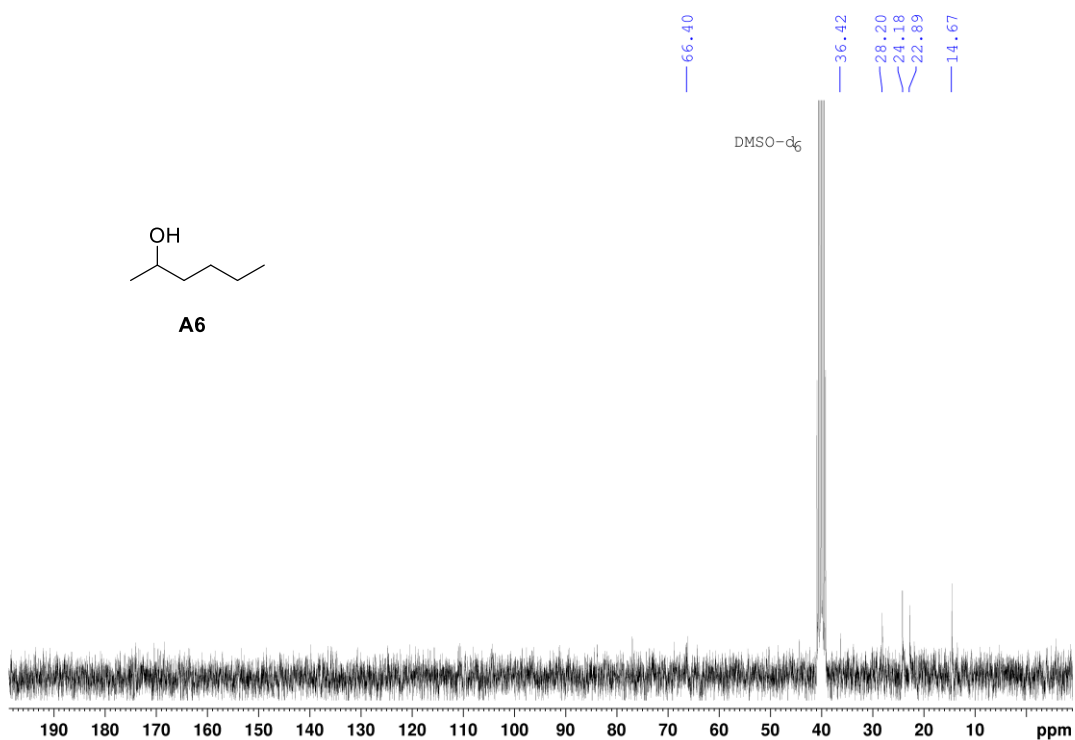
Supplementary Figure 79. ¹H NMR spectrum of 1-dodecanol.



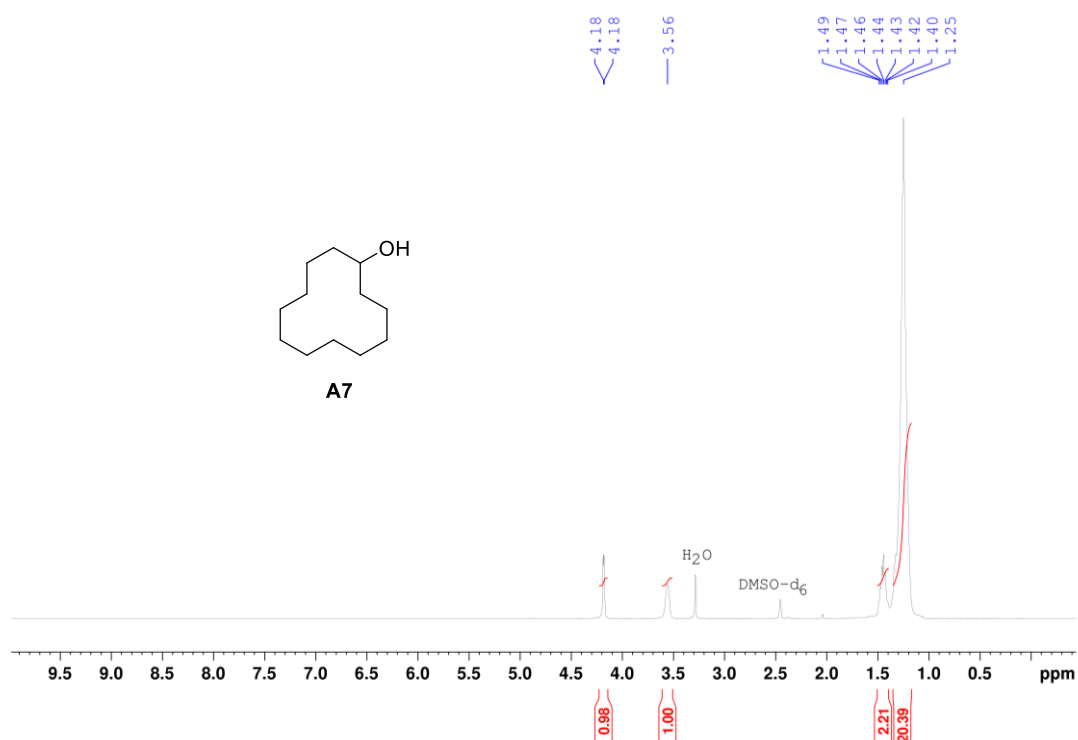
Supplementary Figure 80. ¹³C NMR spectrum of 1-dodecanol.



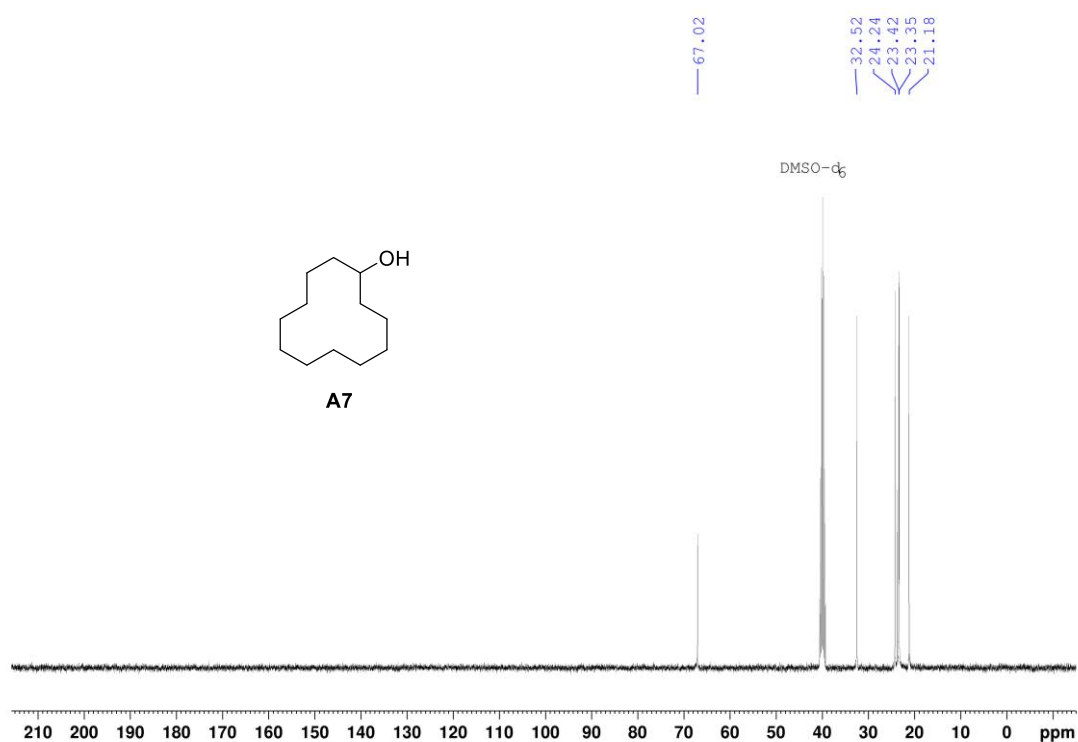
Supplementary Figure 81. ¹H NMR spectrum of 2-hexanol.



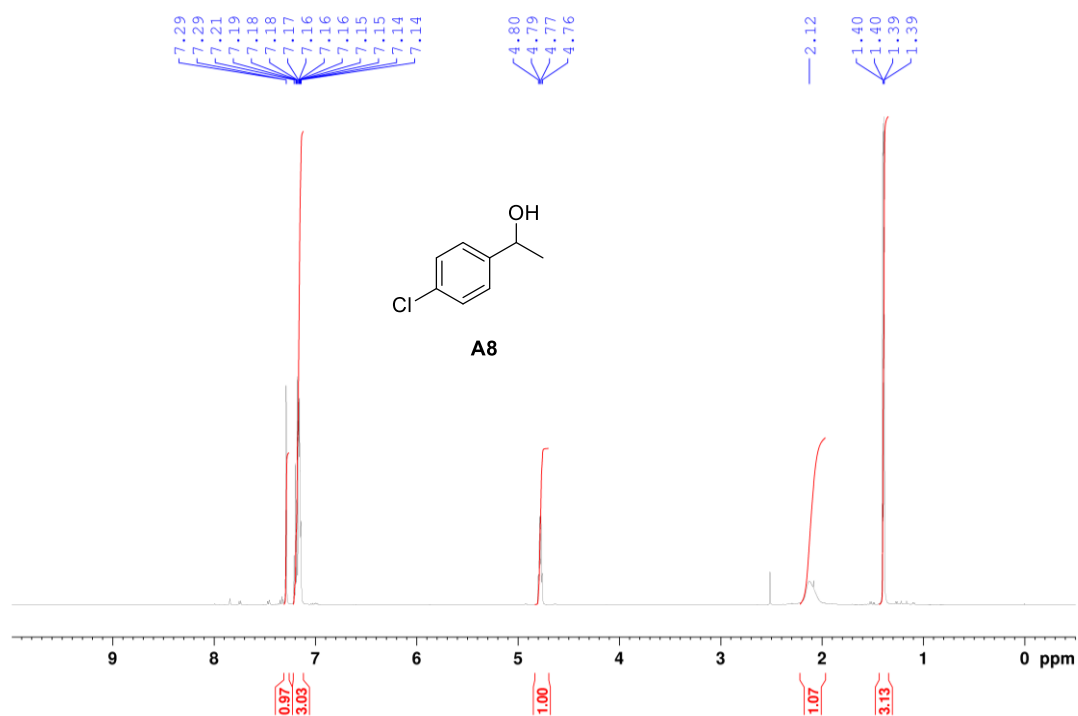
Supplementary Figure 82. ¹³C NMR spectrum of 2-hexanol.



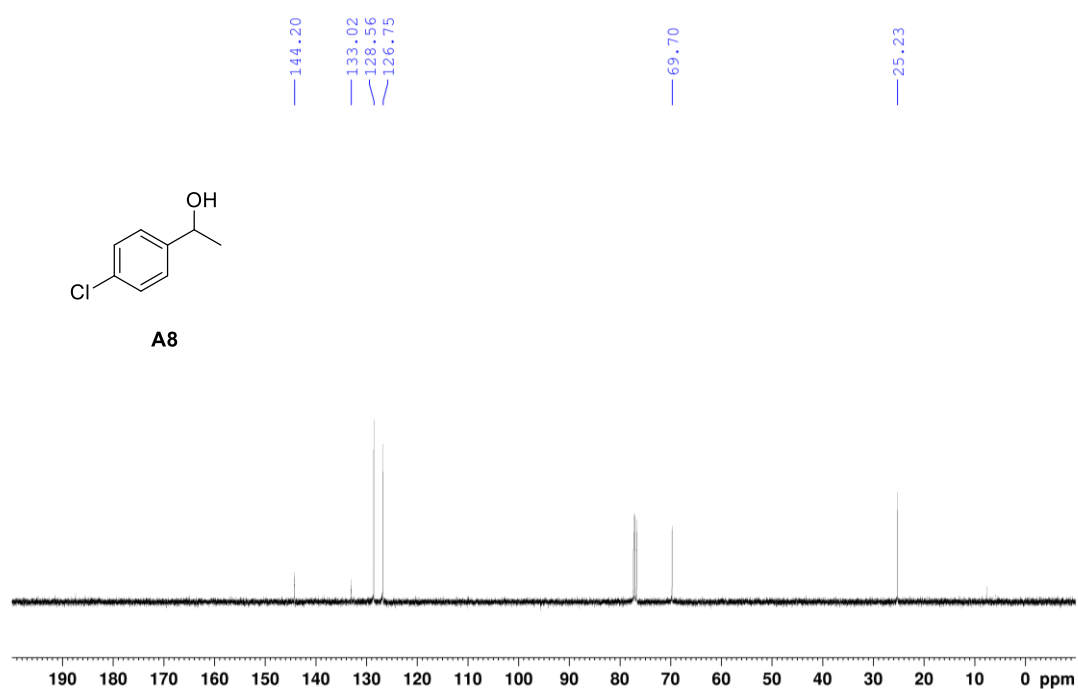
Supplementary Figure 83. ¹H NMR spectrum of cyclododecanol.



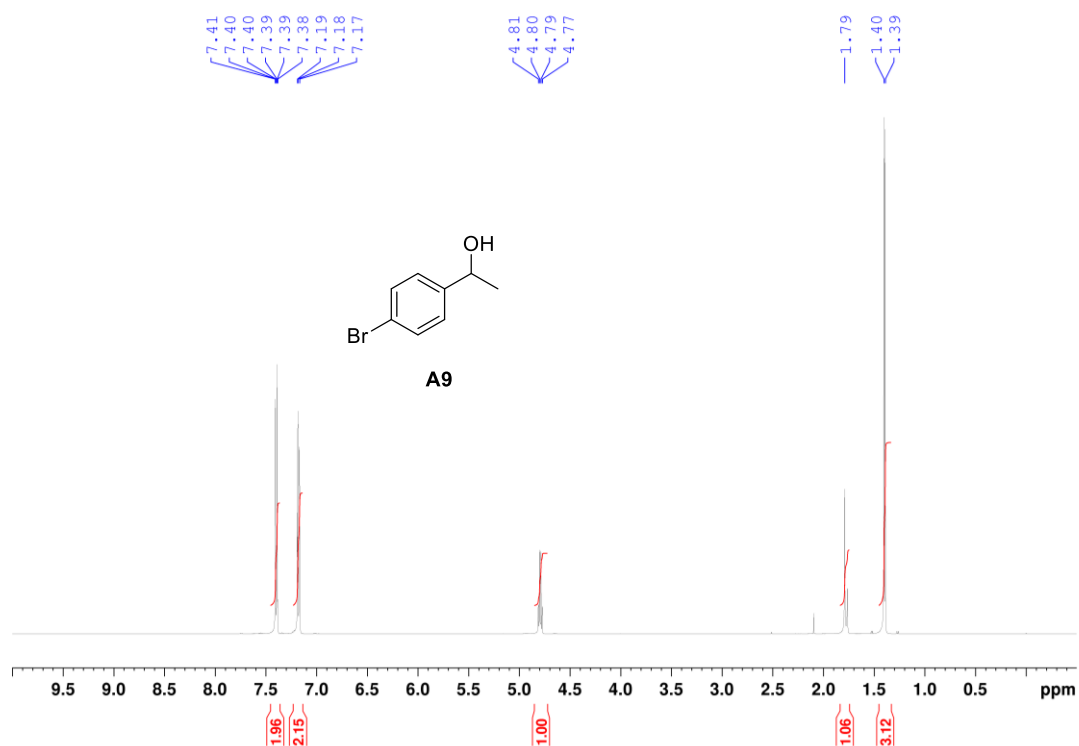
Supplementary Figure 84. ¹³C NMR spectrum of cyclododecanol.



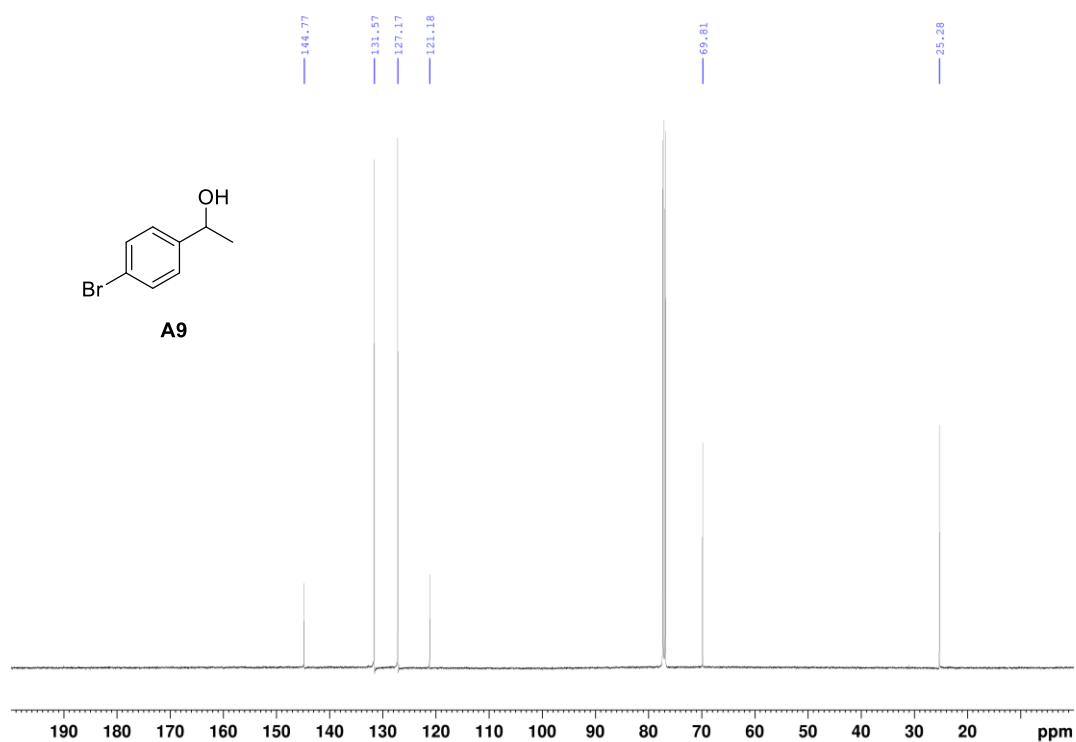
Supplementary Figure 85. ¹H NMR spectrum of 1-(4-chlorophenyl)ethan-1-ol.



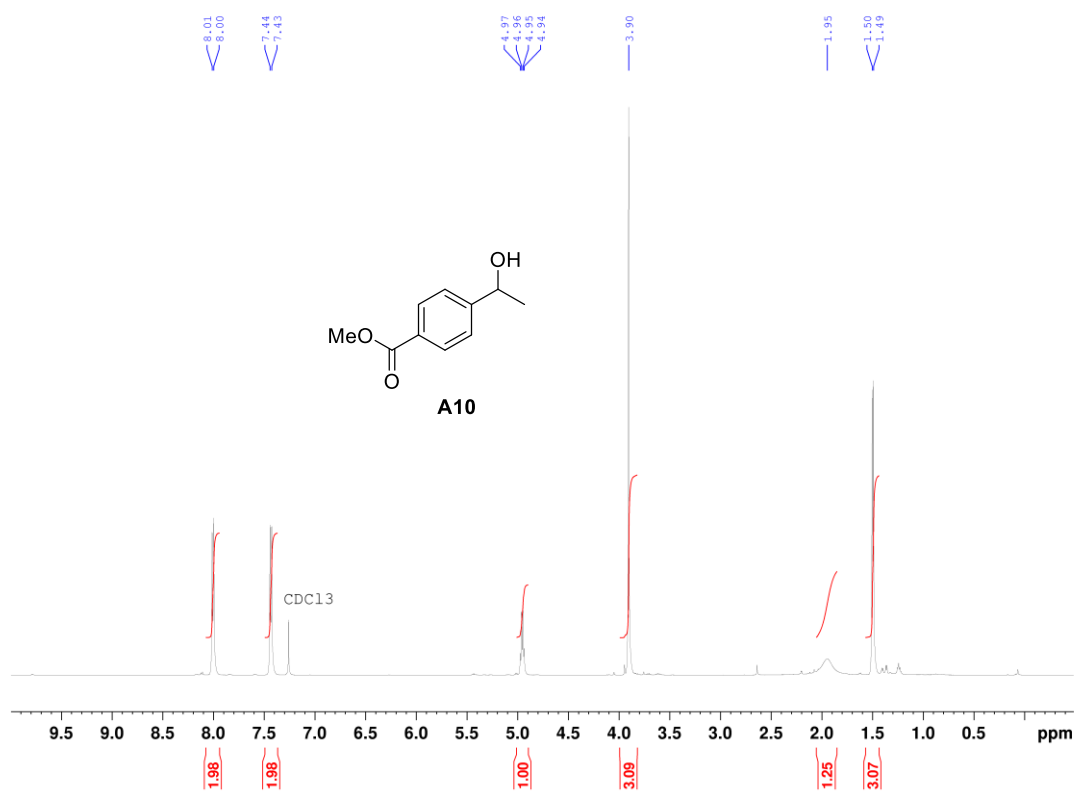
Supplementary Figure 86. ¹³C NMR spectrum of 1-(4-chlorophenyl)ethan-1-ol.



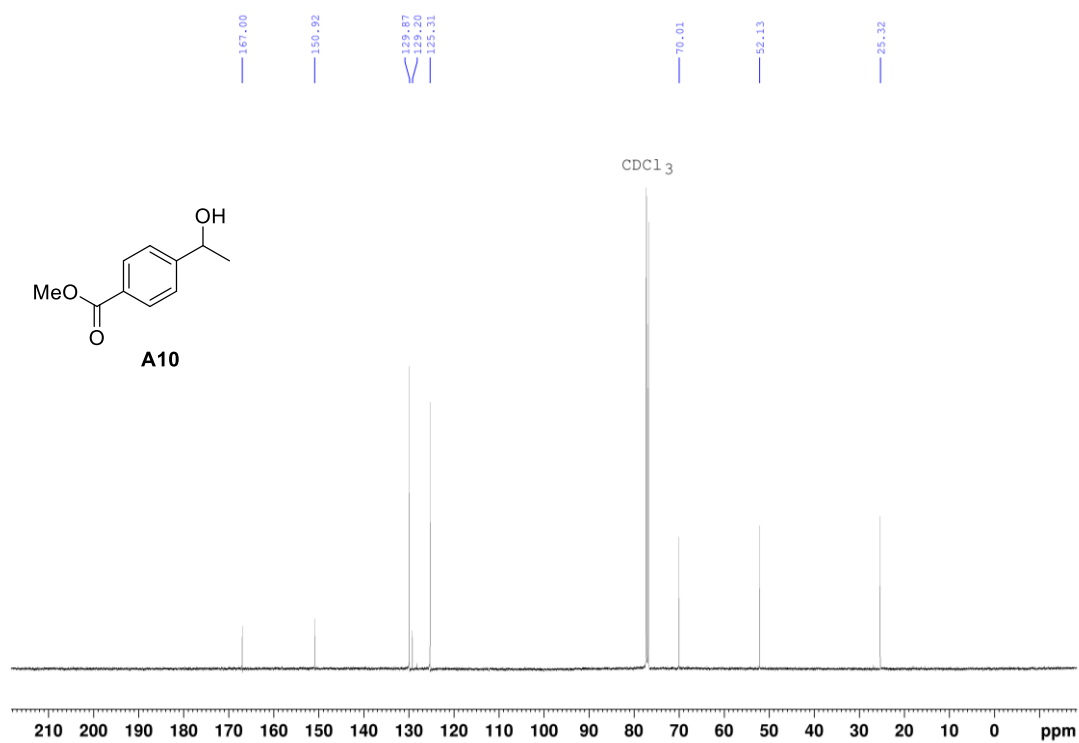
Supplementary Figure 87. ¹H NMR spectrum of 1-(4-bromophenyl)ethan-1-ol.



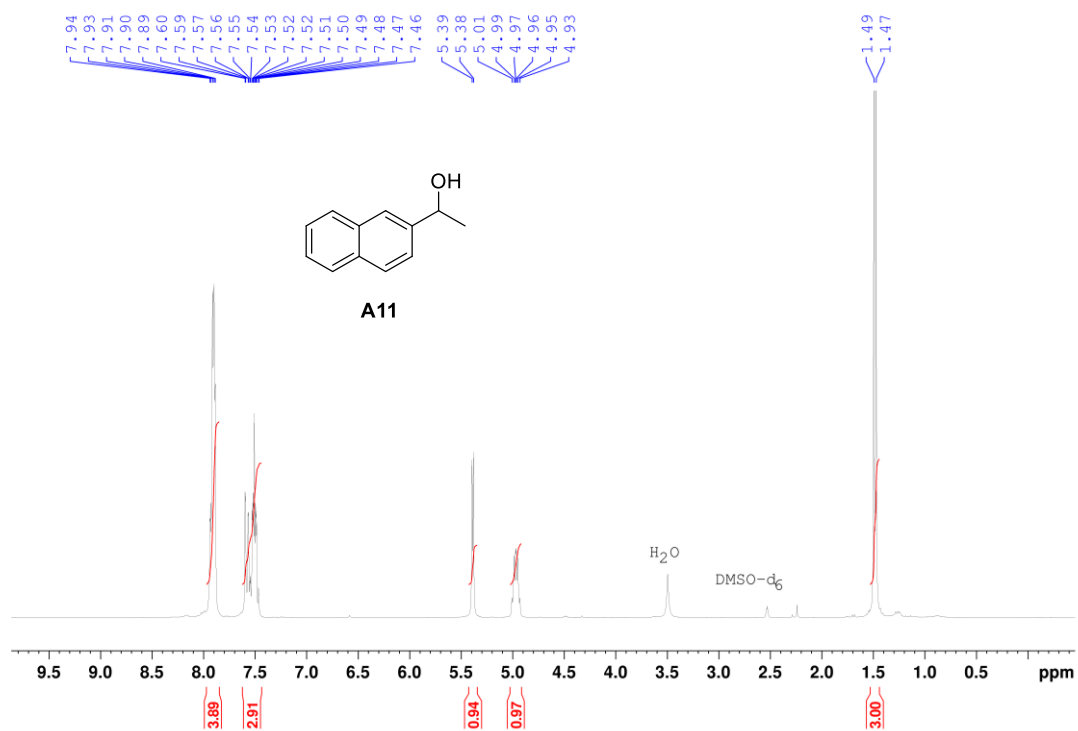
Supplementary Figure 88. ¹³C NMR spectrum of 1-(4-bromophenyl)ethan-1-ol.



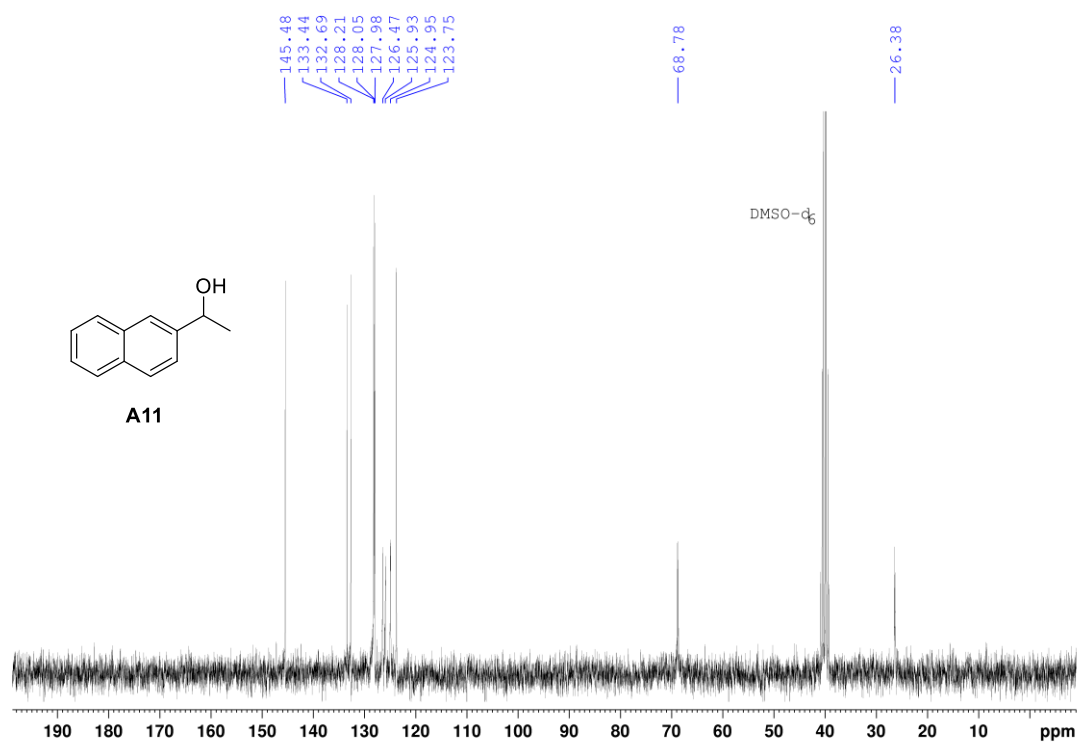
Supplementary Figure 89. ¹H NMR spectrum of 4-(1-hydroxyethyl)phenyl acetate.



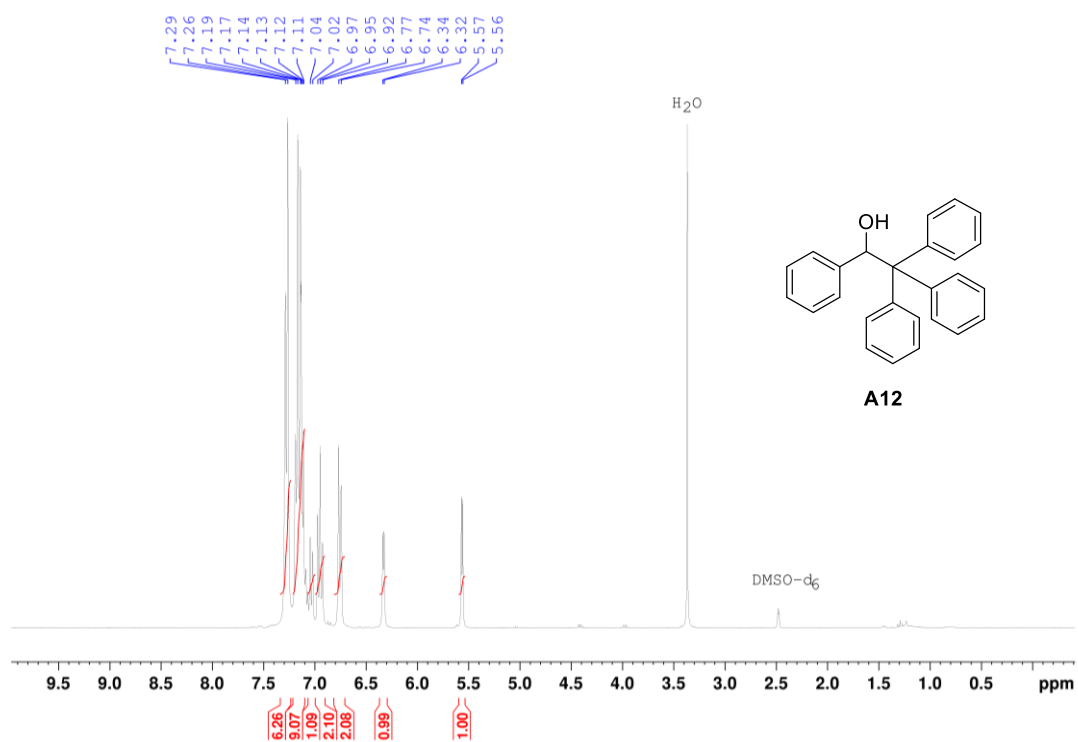
Supplementary Figure 90. ¹³C NMR spectrum of 4-(1-hydroxyethyl)phenyl acetate.



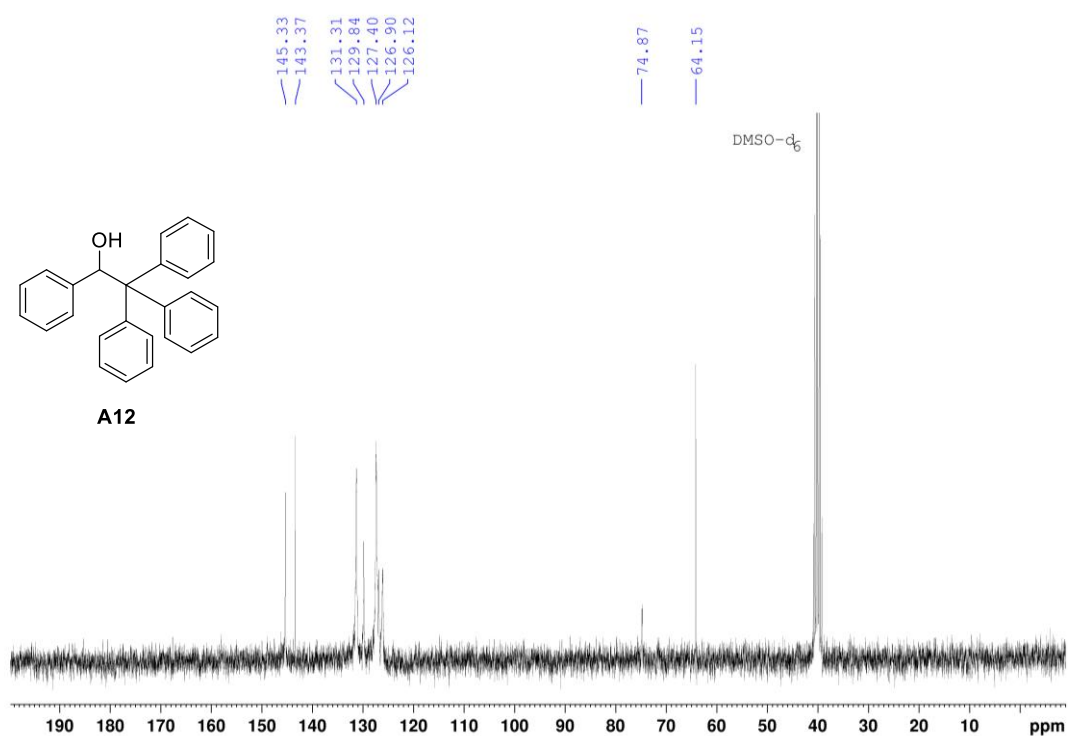
Supplementary Figure 91. ¹H NMR spectrum of 1-(naphthalen-2-yl)ethan-1-ol.



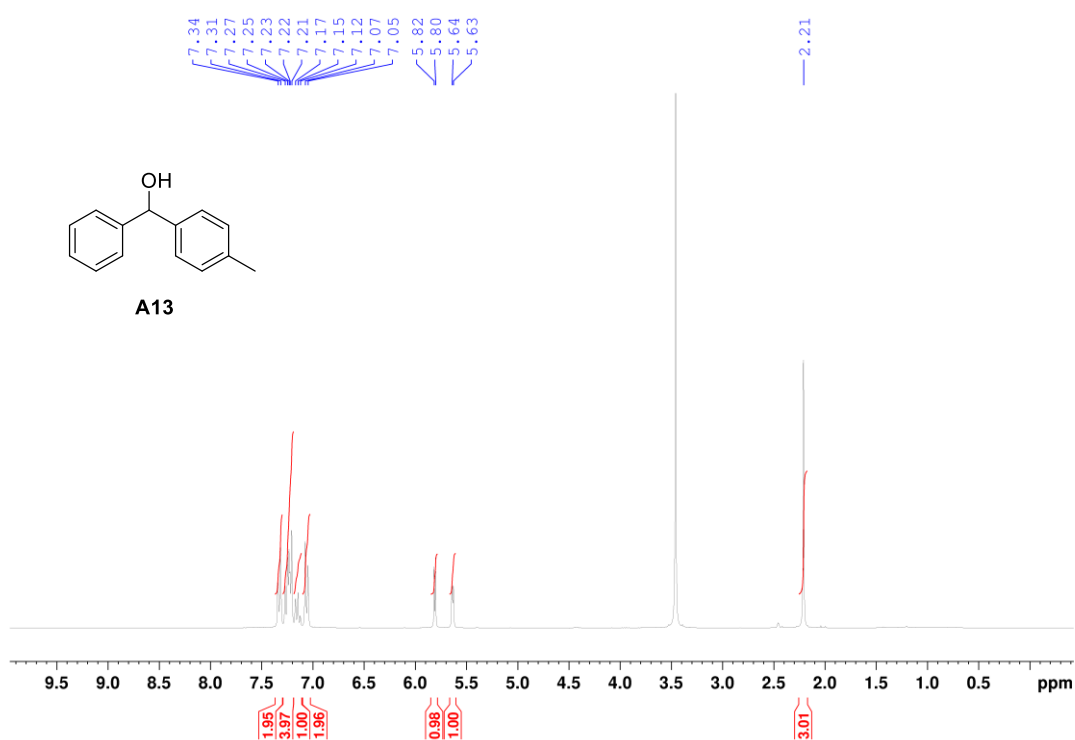
Supplementary Figure 92. ¹³C NMR spectrum of 1-(naphthalen-2-yl)ethan-1-ol.



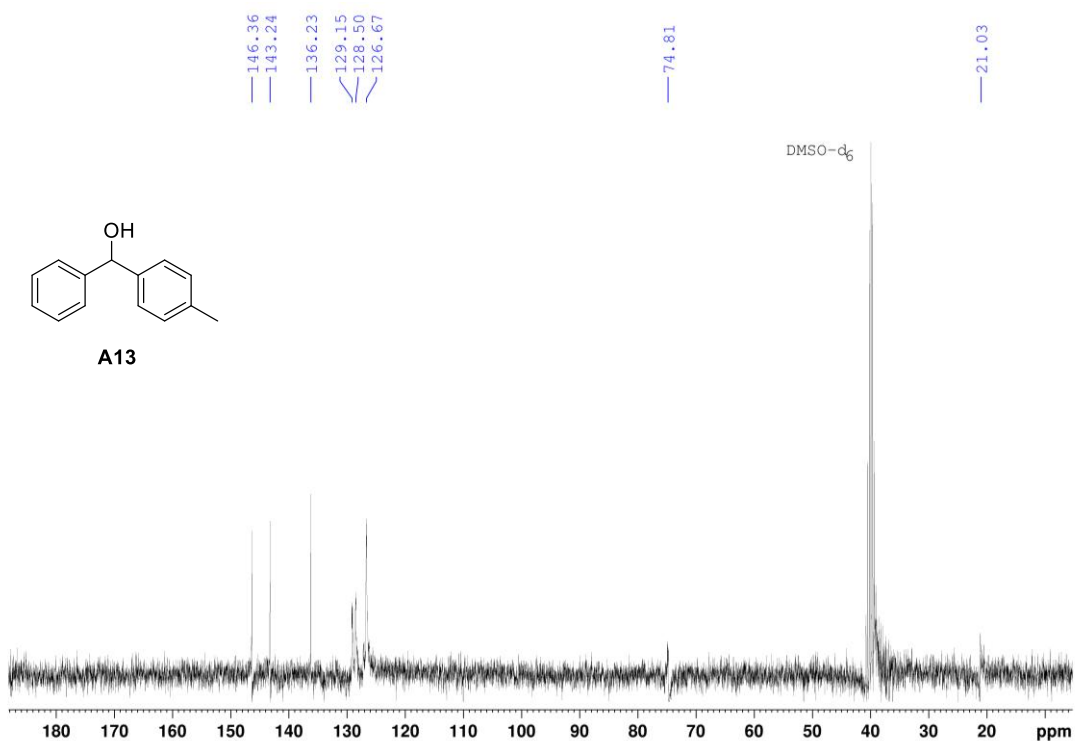
Supplementary Figure 93. ¹H NMR spectrum of 1,2,2,2-tetraphenylethan-1-ol.



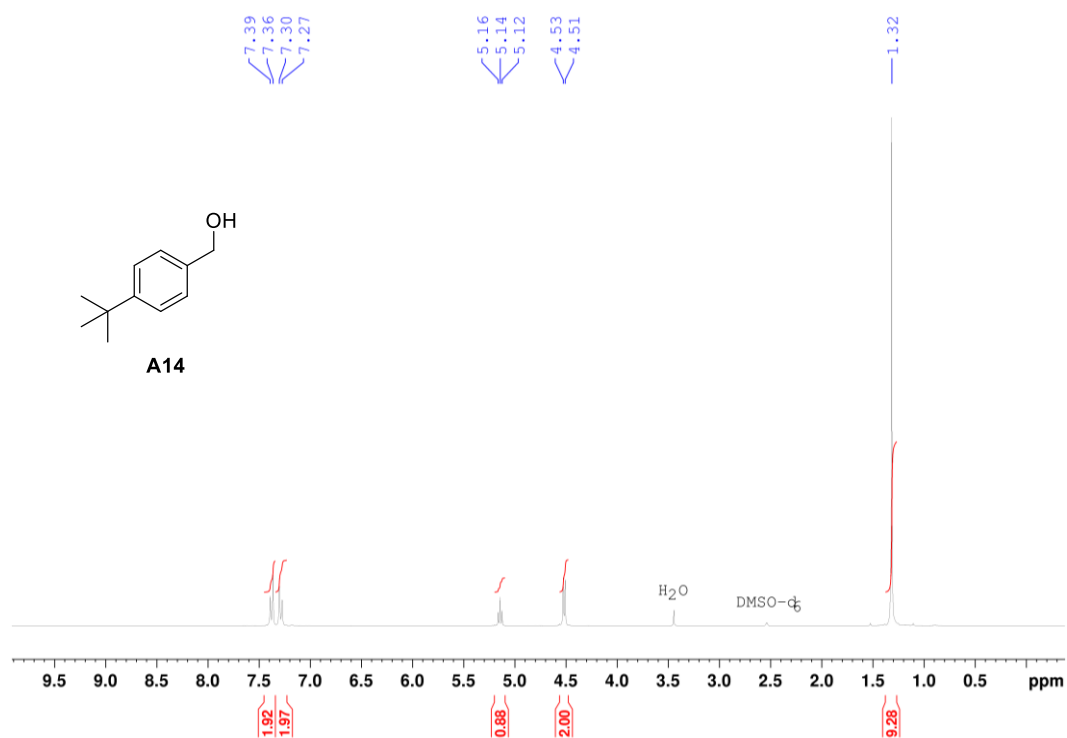
Supplementary Figure 94. ¹³C NMR spectrum of 1,2,2,2-tetraphenylethan-1-ol.



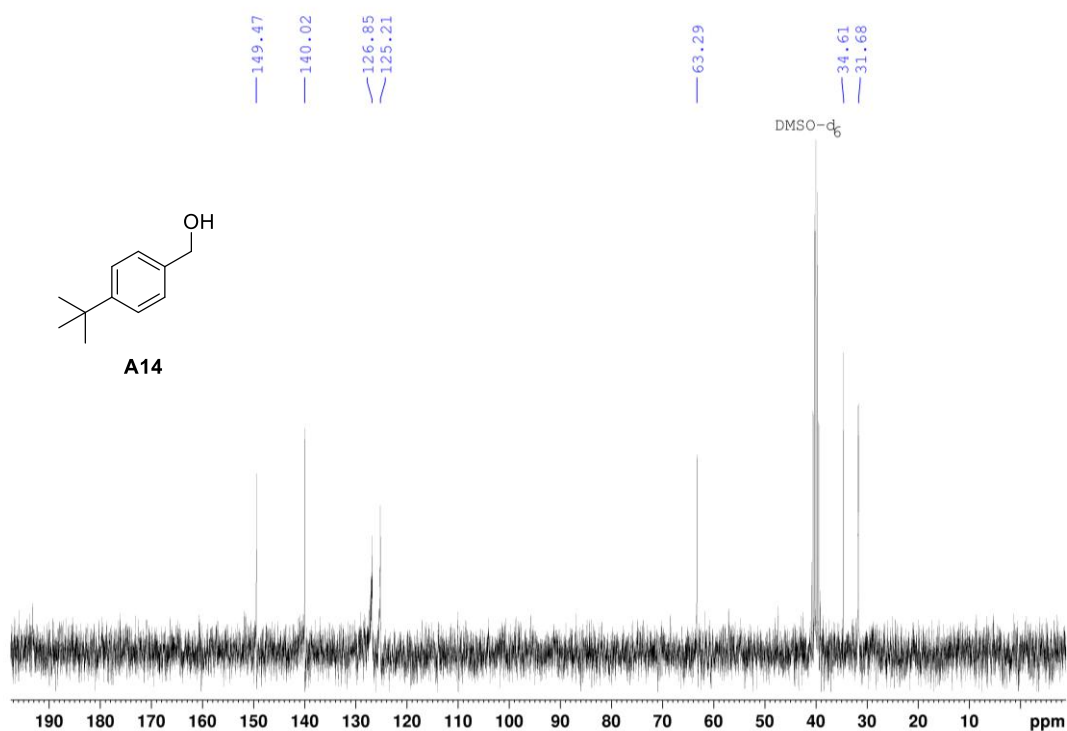
Supplementary Figure 95. ¹H NMR spectrum of phenyl(*p*-tolyl)methanol.



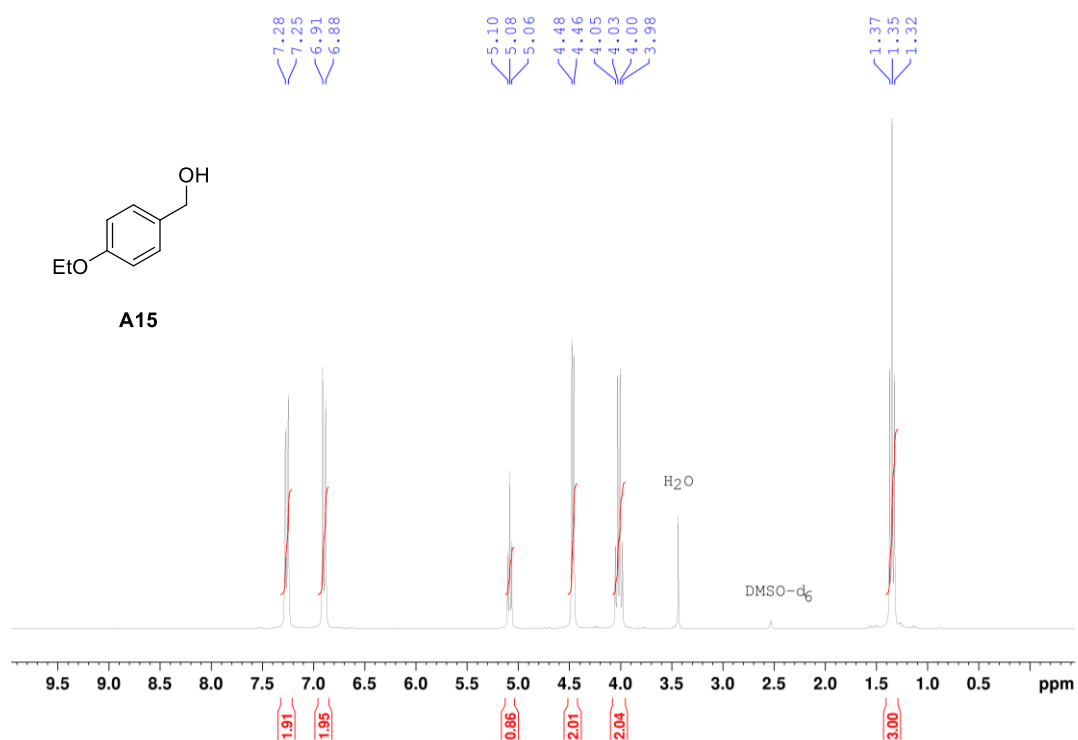
Supplementary Figure 96. ¹³C NMR spectrum of phenyl(*p*-tolyl)methanol.



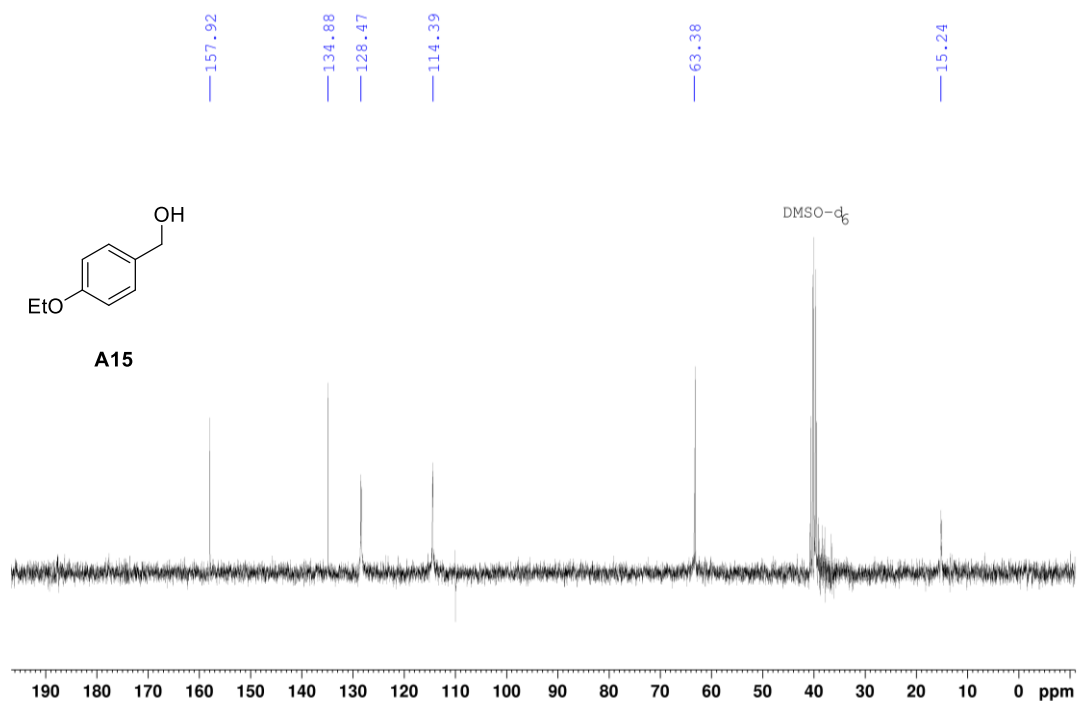
Supplementary Figure 97. ¹H NMR spectrum of (4-(*tert*-butyl)phenyl)methanol.



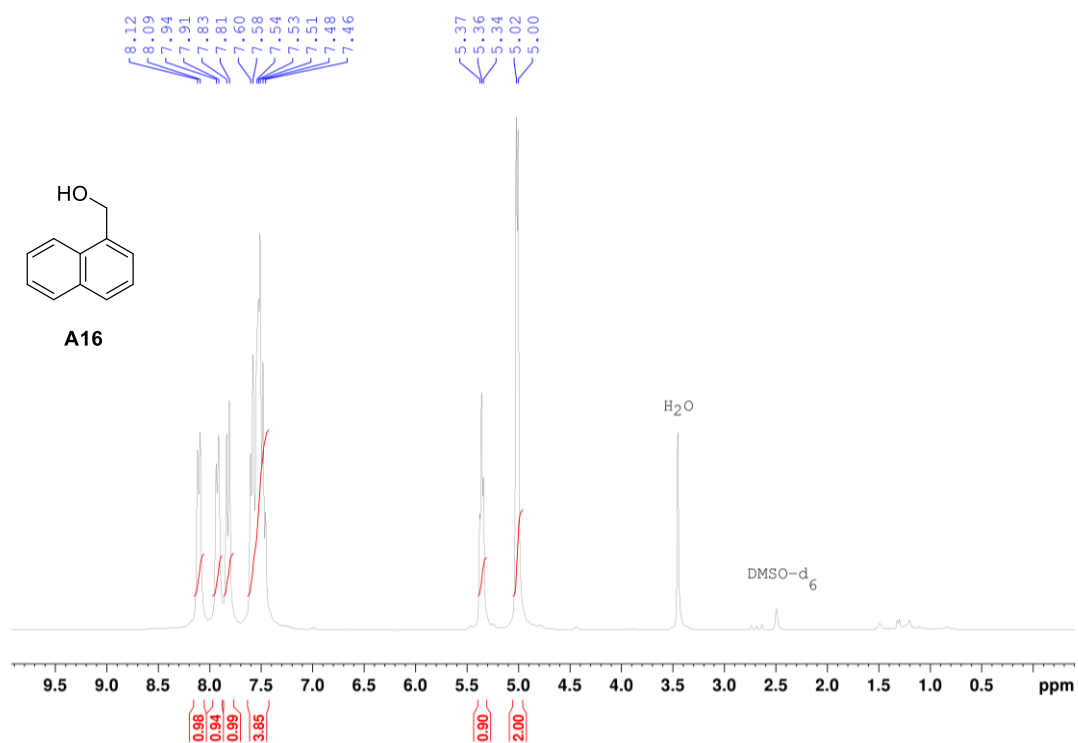
Supplementary Figure 98. ¹³C NMR spectrum of (4-(*tert*-butyl)phenyl)methanol.



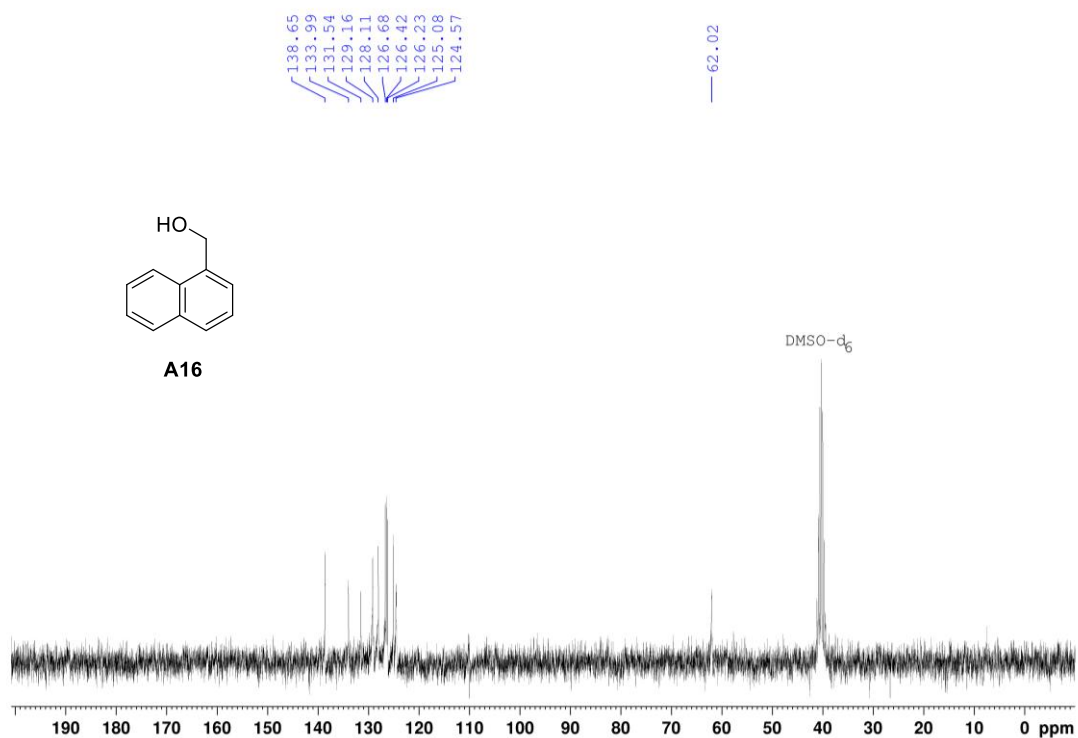
Supplementary Figure 99. ¹H NMR spectrum of (4-ethoxyphenyl)methanol.



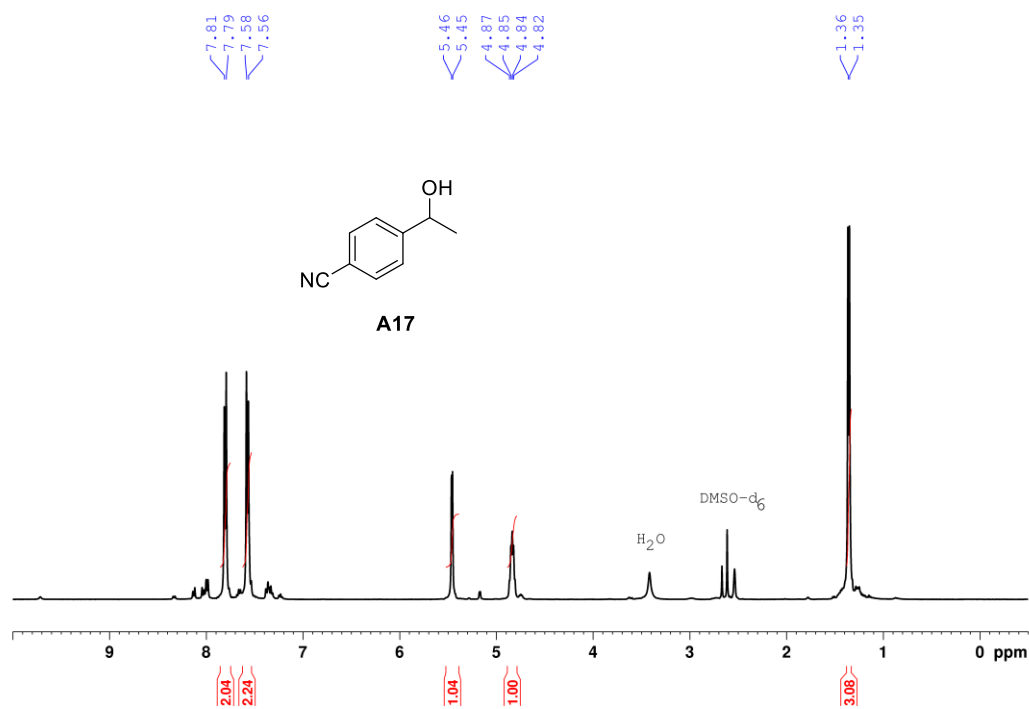
Supplementary Figure 100. ¹³C NMR spectrum of (4-ethoxyphenyl)methanol.



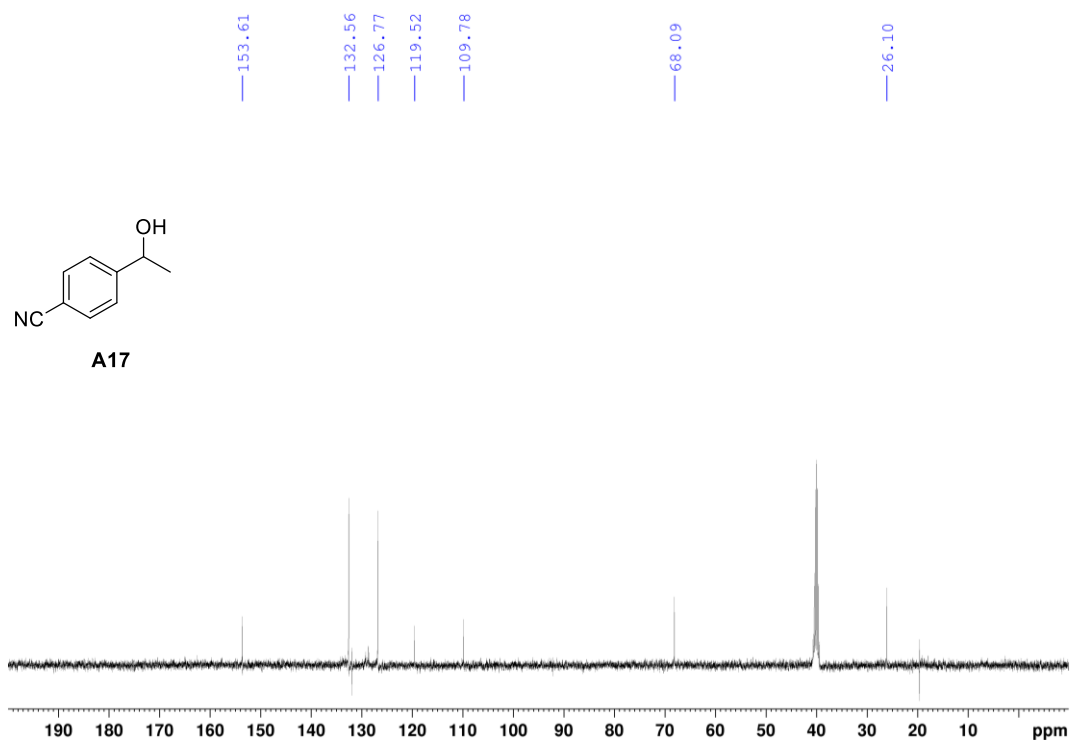
Supplementary Figure 101. ¹H NMR spectrum of naphthalen-1-ylmethanol.



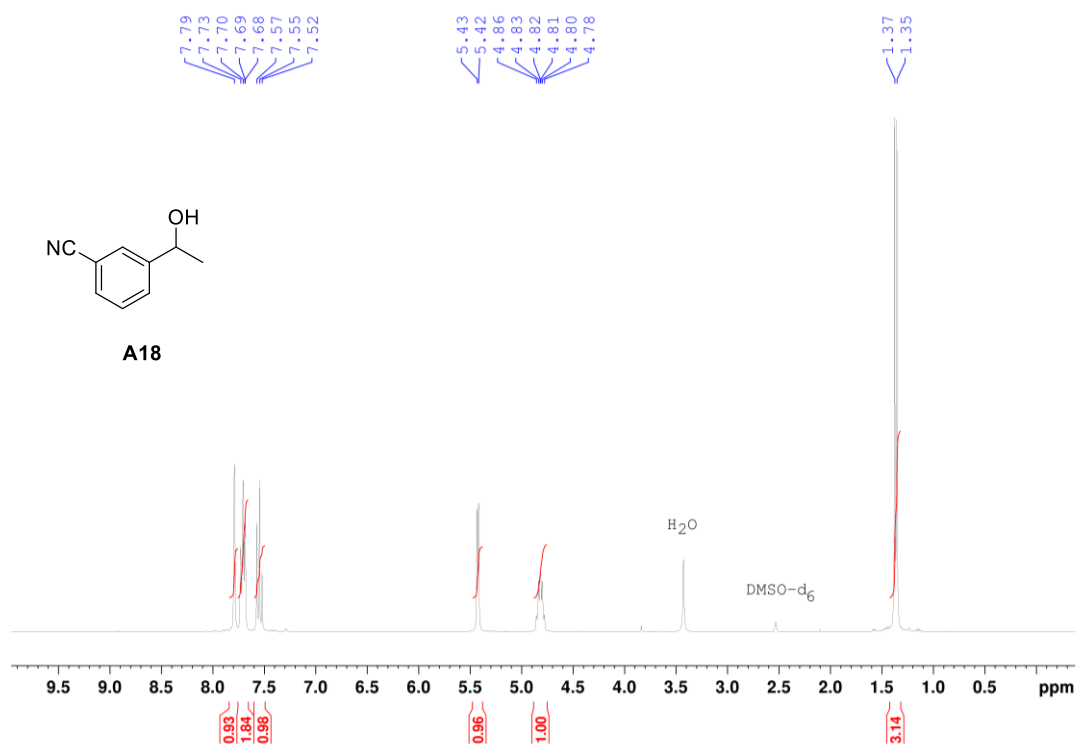
Supplementary Figure 102. ¹³C NMR spectrum of naphthalen-1-ylmethanol.



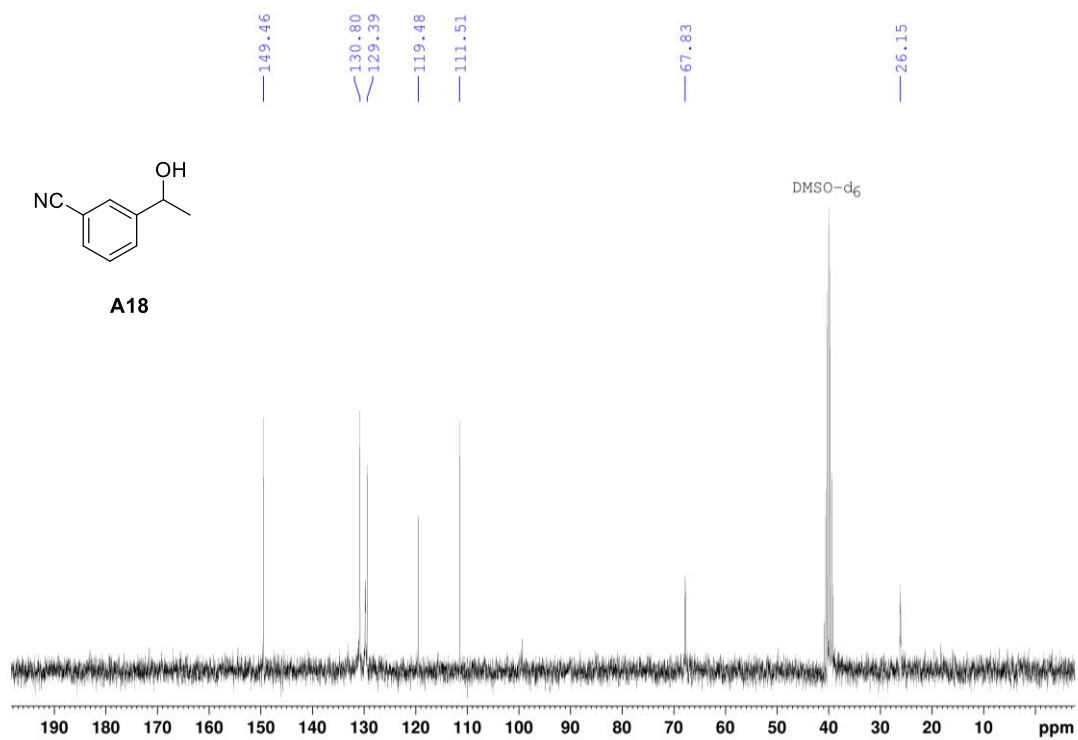
Supplementary Figure 103. ^1H NMR spectrum of 4-(1-hydroxyethyl)benzonitrile.



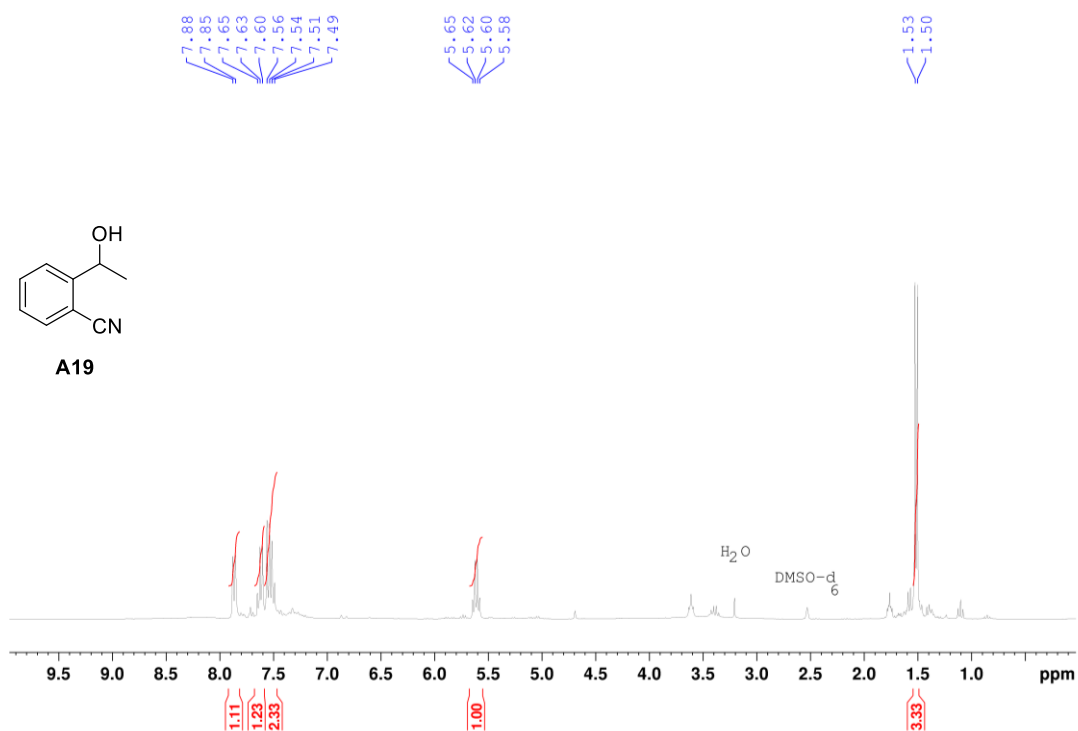
Supplementary Figure 104. ^{13}C NMR spectrum of 4-(1-hydroxyethyl)benzonitrile.



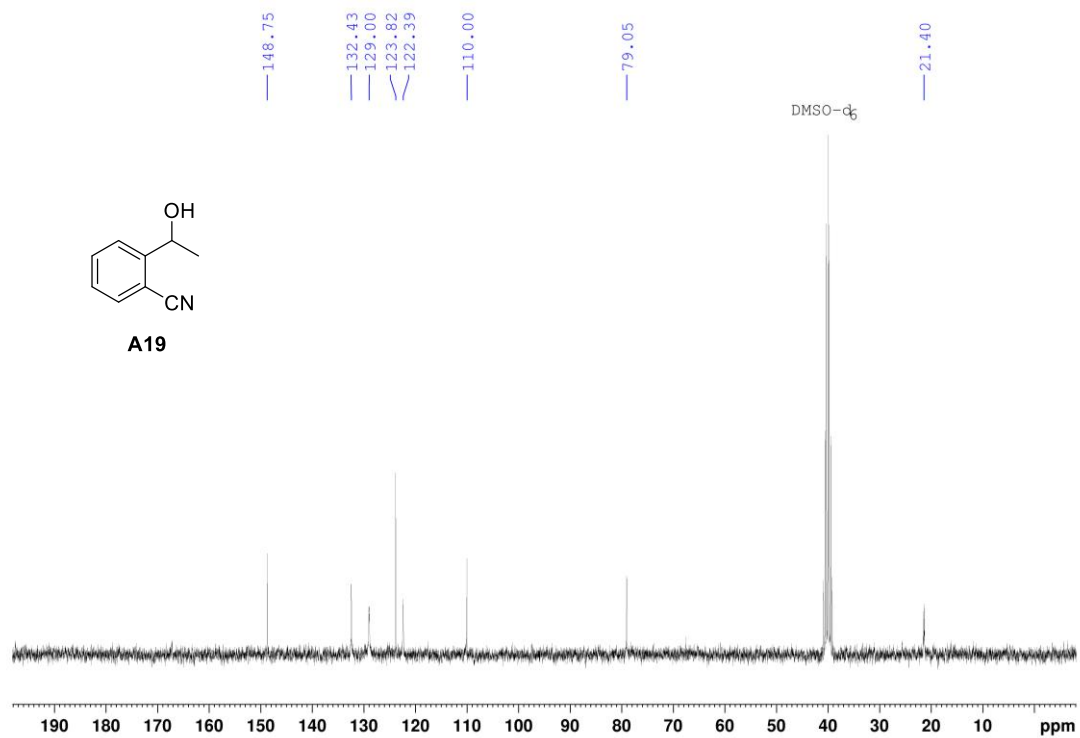
Supplementary Figure 105. ¹H NMR spectrum of 3-(1-hydroxyethyl)benzonitrile.



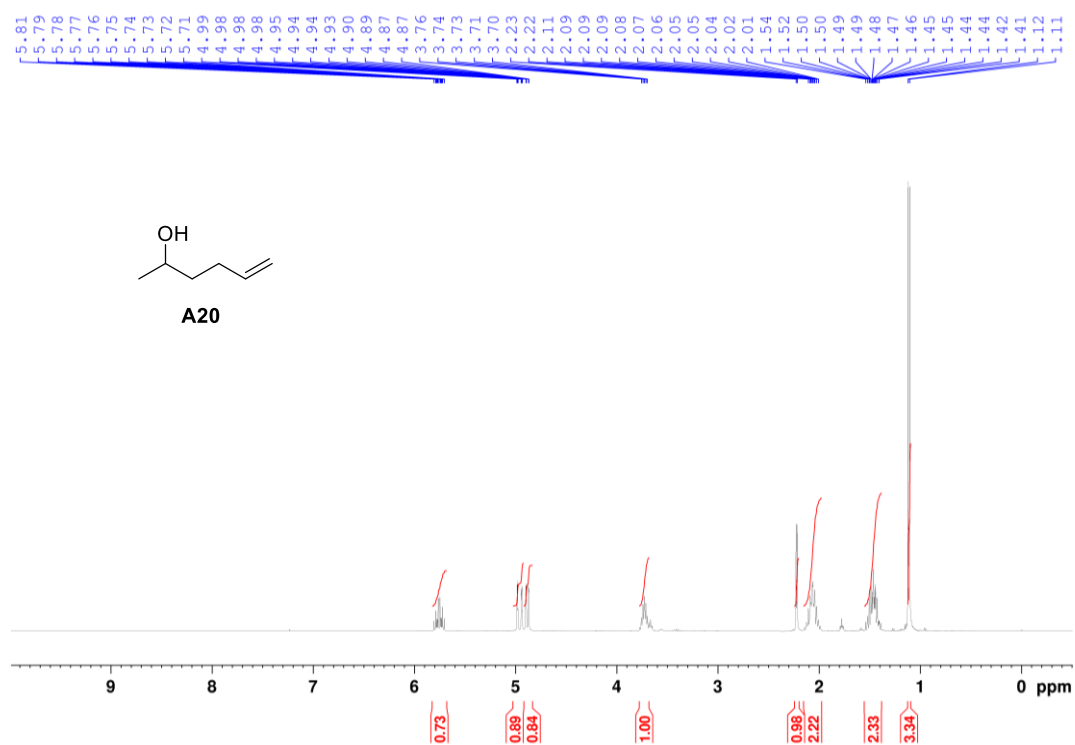
Supplementary Figure 106. ¹³C NMR spectrum of 3-(1-hydroxyethyl)benzonitrile.



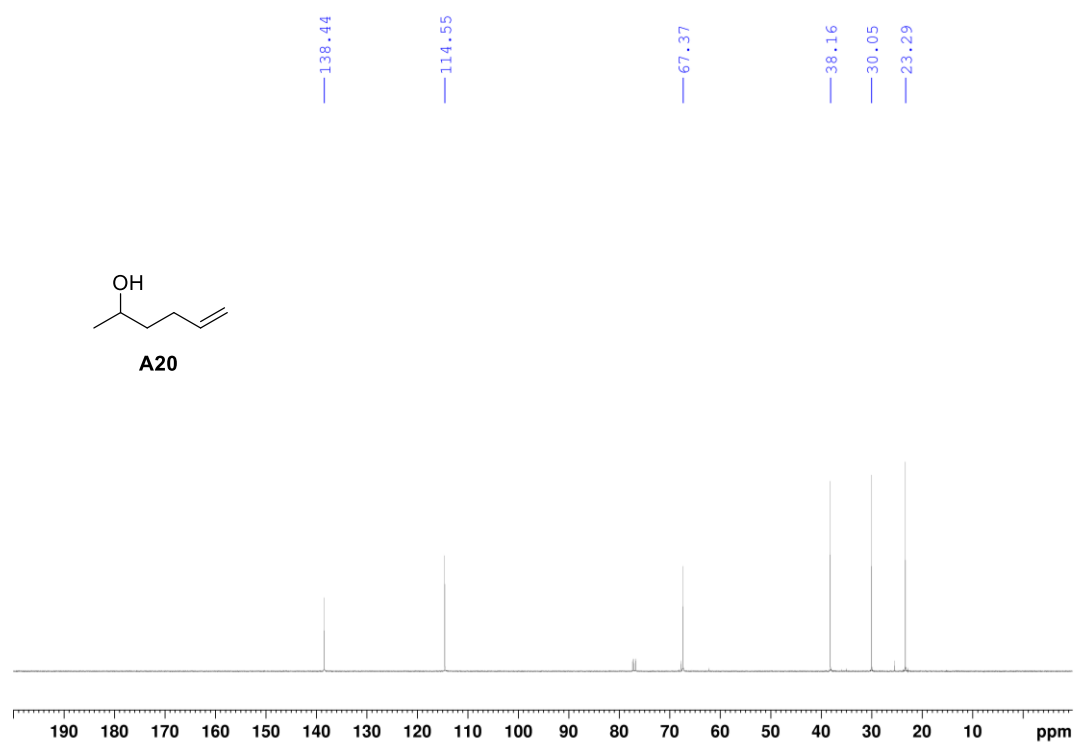
Supplementary Figure 107. ¹H NMR spectrum of 2-(1-hydroxyethyl)benzonitrile.



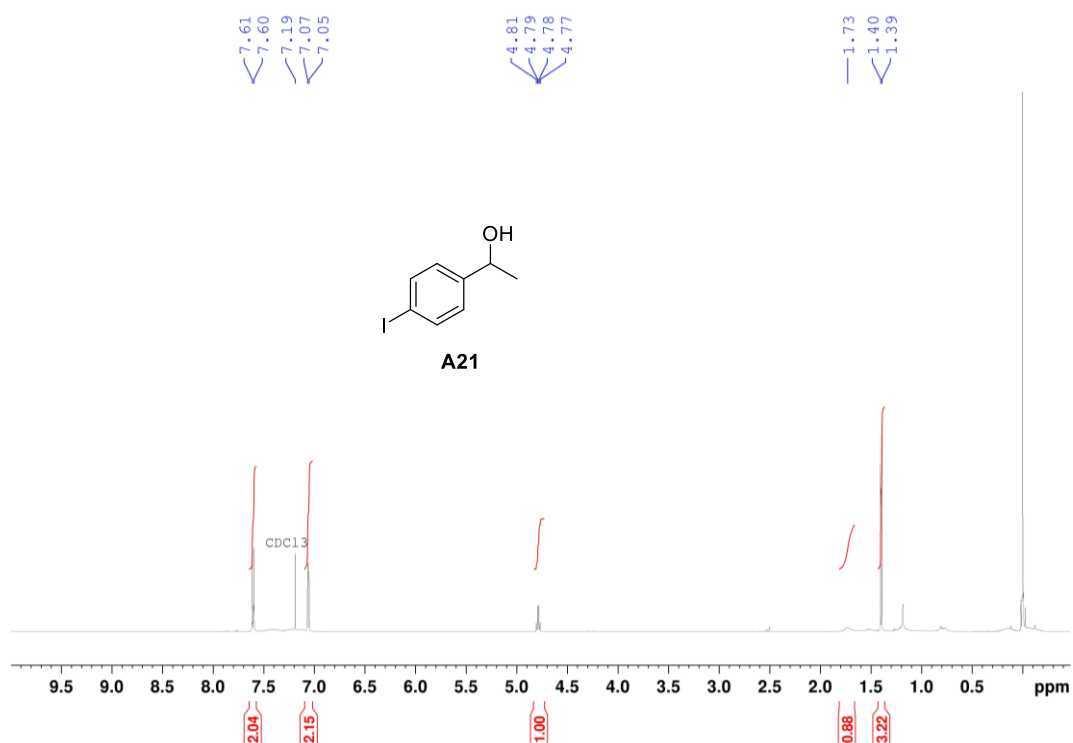
Supplementary Figure 108. ¹³C NMR spectrum of 2-(1-hydroxyethyl)benzonitrile.



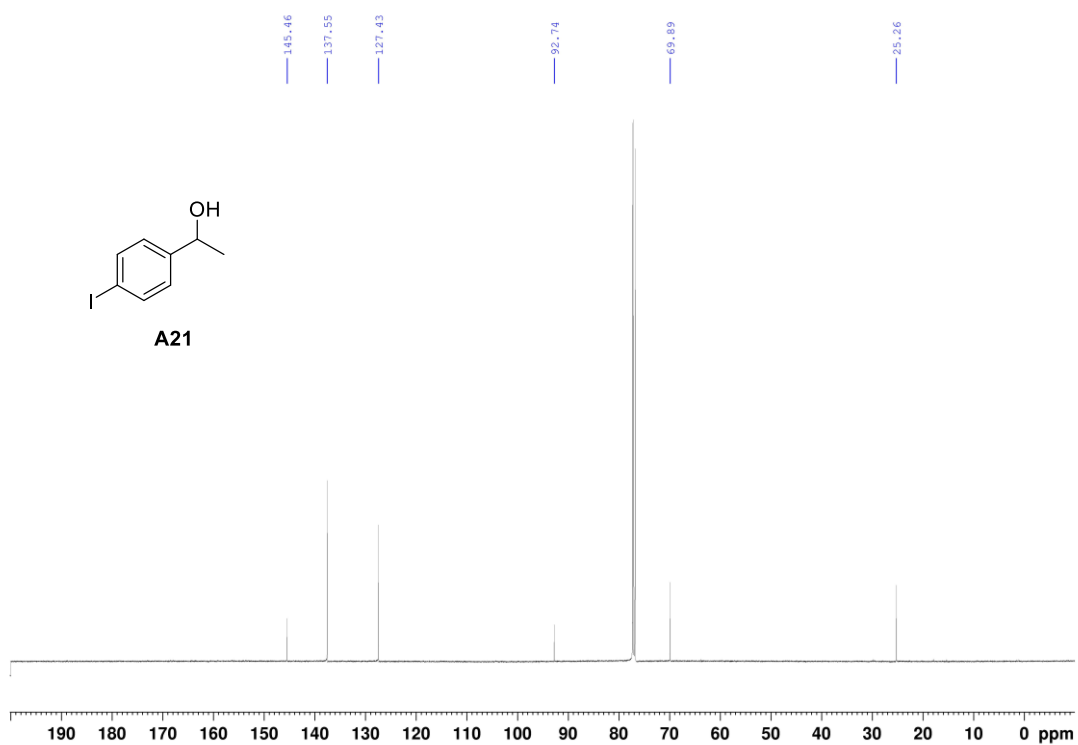
Supplementary Figure 109. ¹H NMR spectrum of hex-5-en-2-ol.



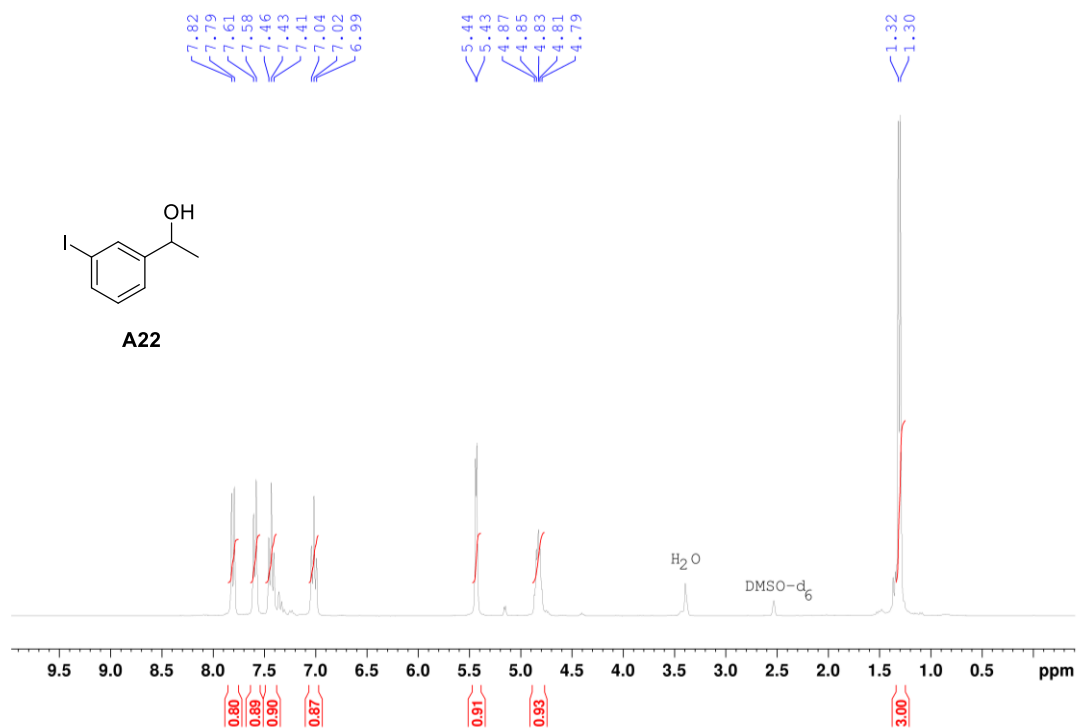
Supplementary Figure 110. ¹³C NMR spectrum of hex-5-en-2-ol.



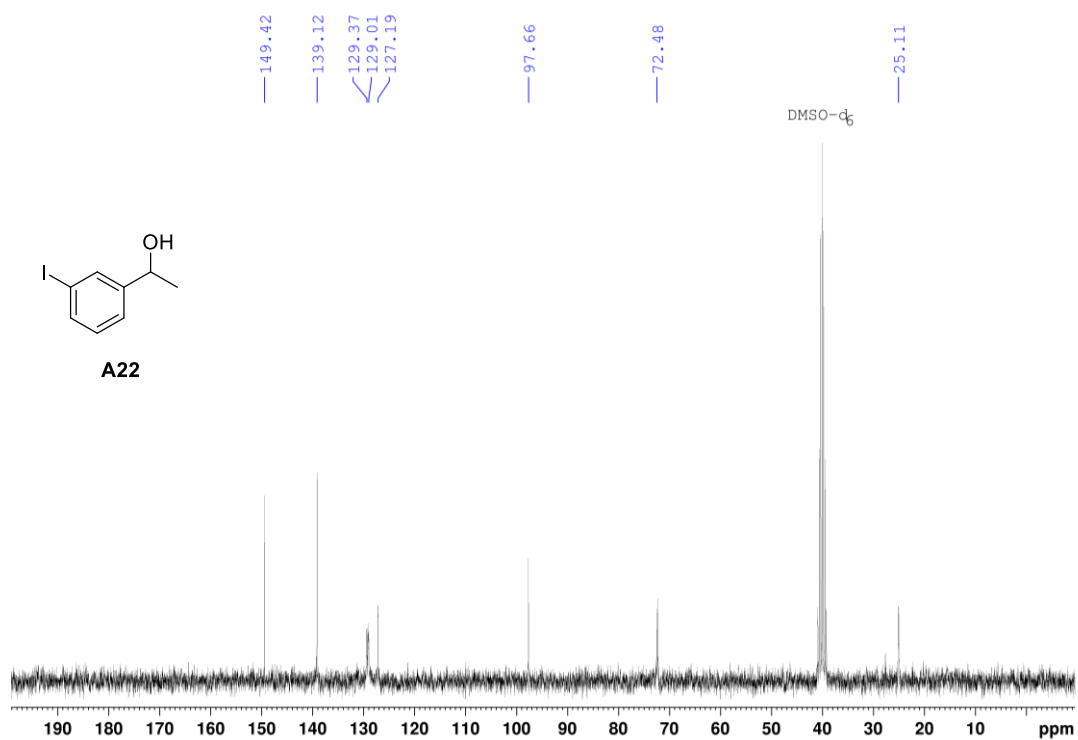
Supplementary Figure 111. ¹H NMR spectrum of 1-(4-iodophenyl)ethan-1-ol.



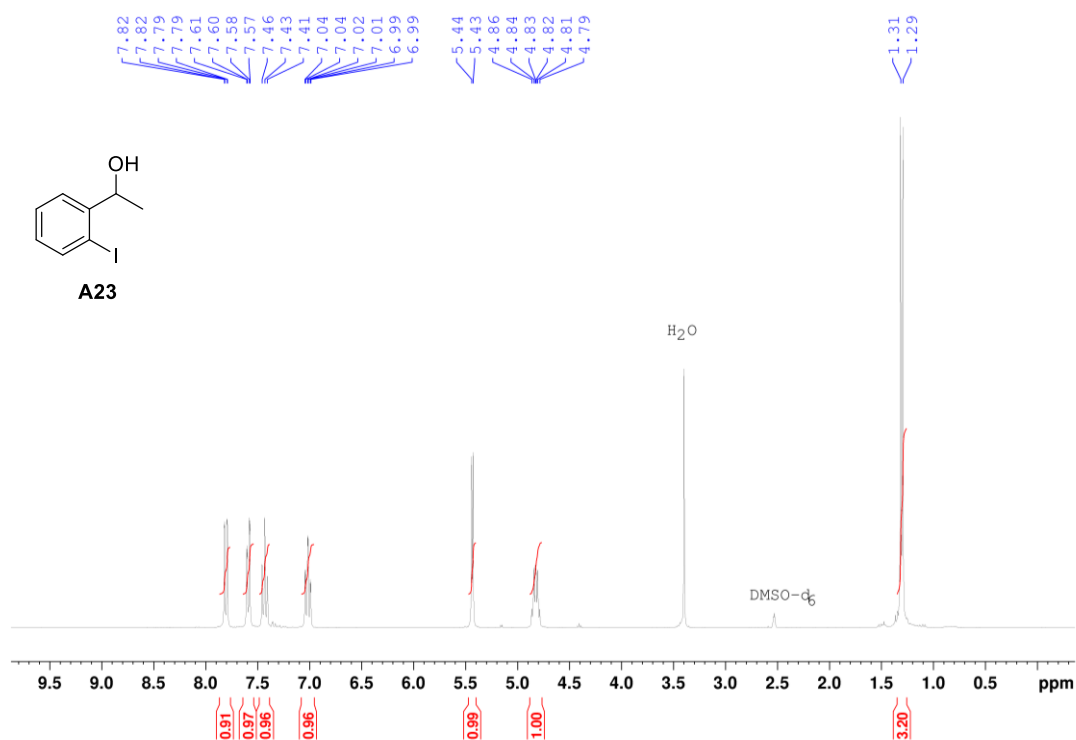
Supplementary Figure 112. ¹³C NMR spectrum of 1-(4-iodophenyl)ethan-1-ol.



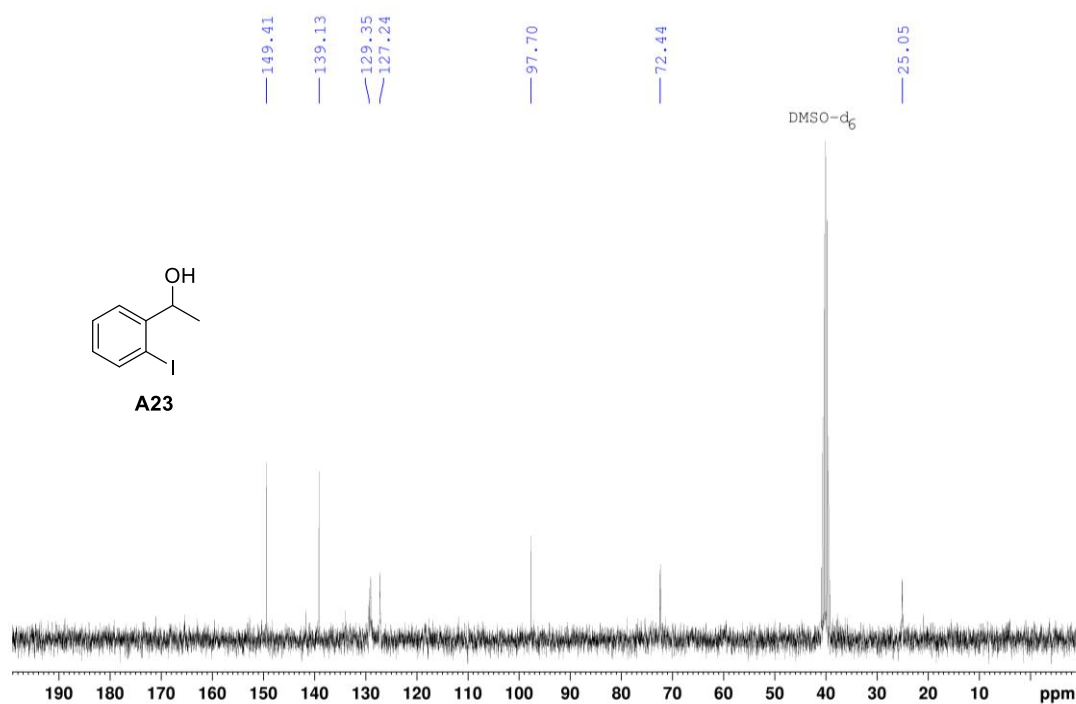
Supplementary Figure 113. ¹H NMR spectrum of 1-(3-iodophenyl)ethan-1-ol.



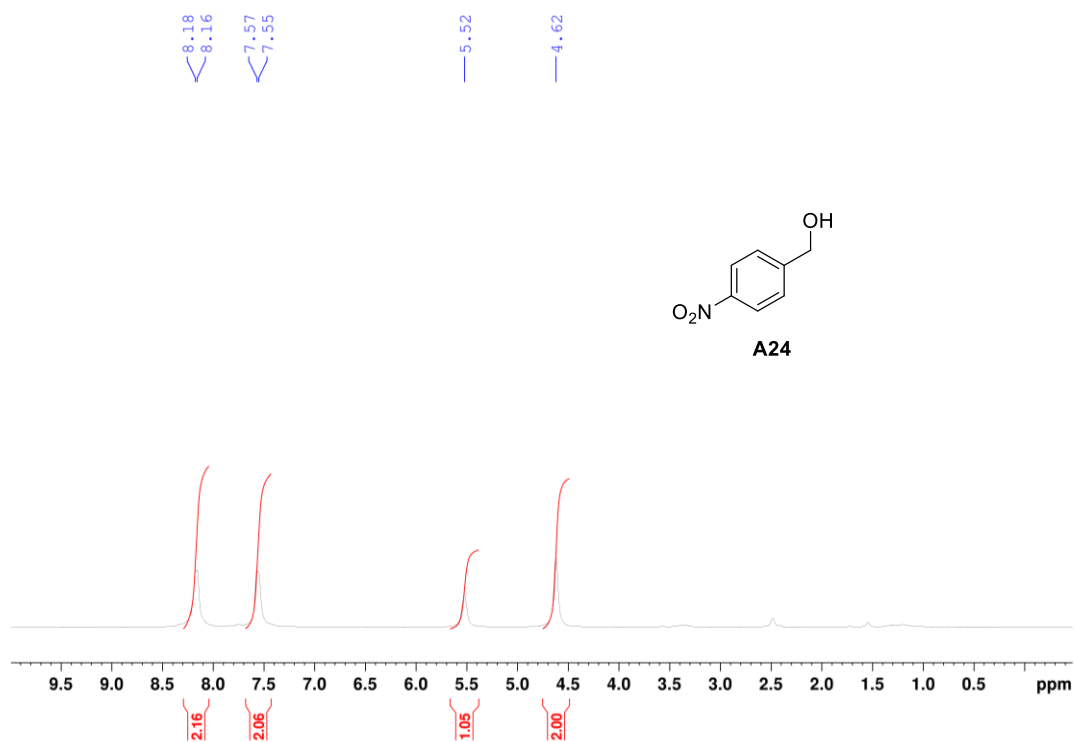
Supplementary Figure 114. ¹³C NMR spectrum of 1-(3-iodophenyl)ethan-1-ol.



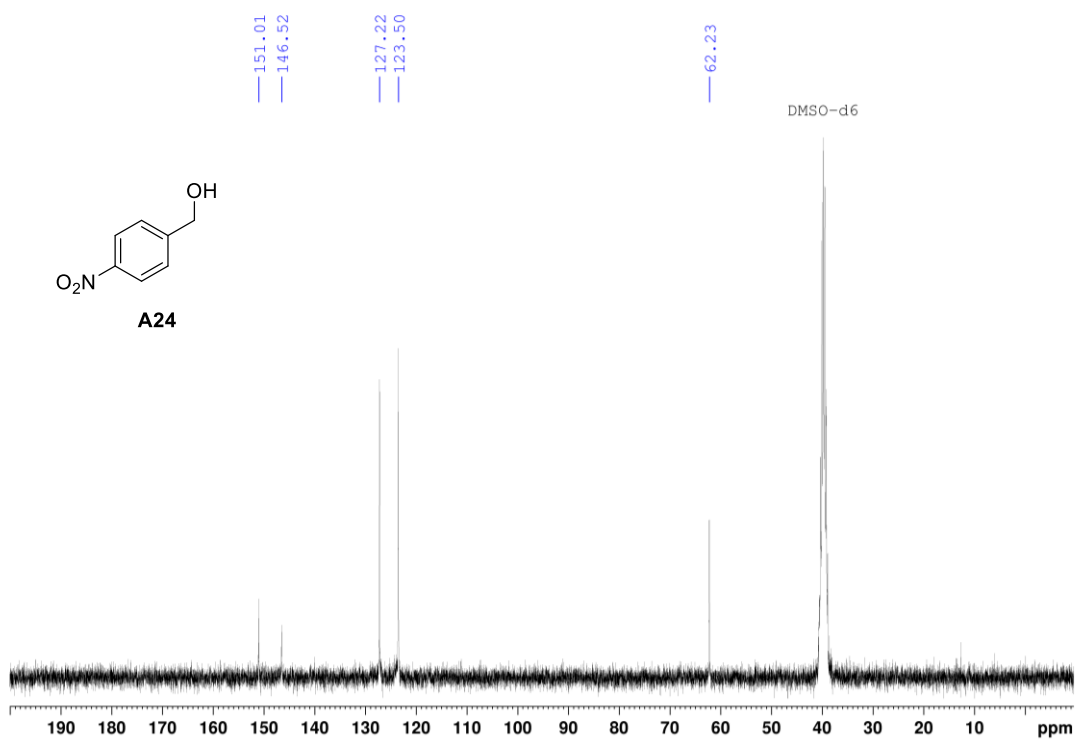
Supplementary Figure 115. ¹H NMR spectrum of 1-(2-iodophenyl)ethan-1-ol.



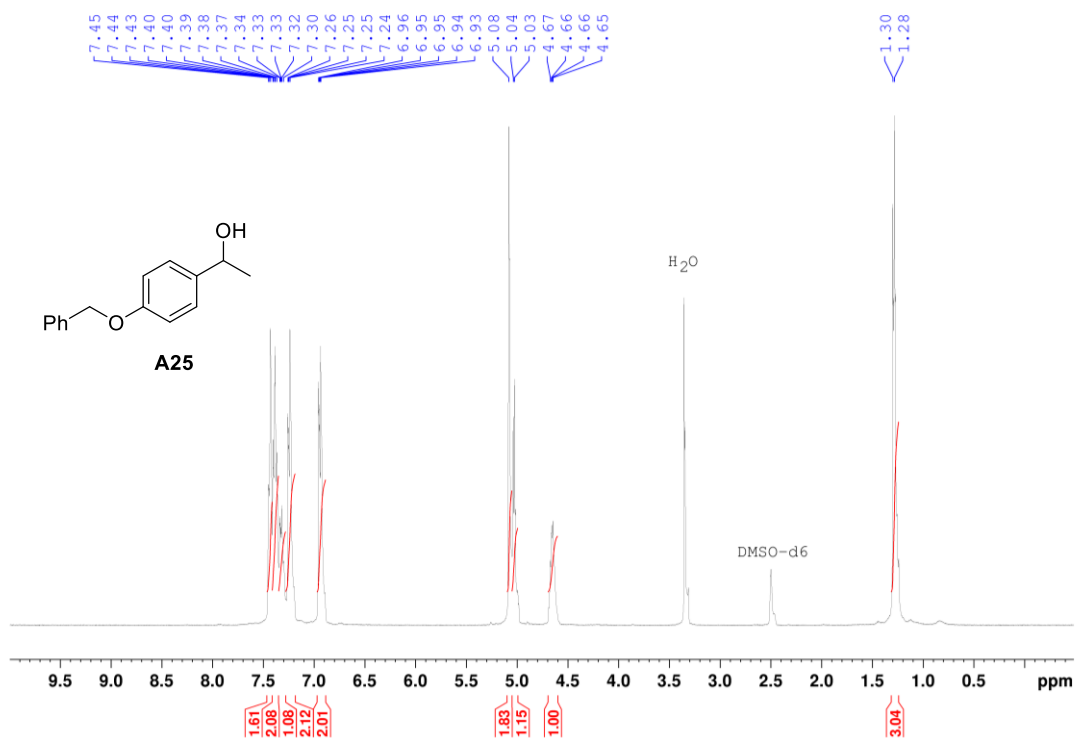
Supplementary Figure 116. ¹³C NMR spectrum of 1-(2-iodophenyl)ethan-1-ol.



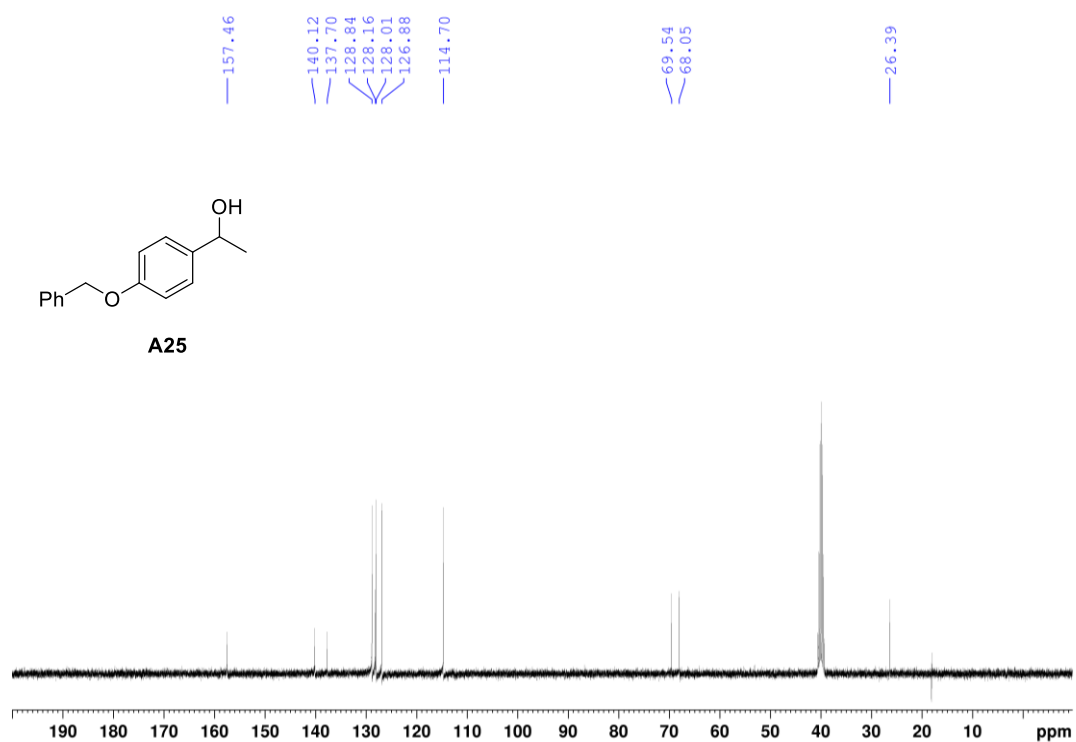
Supplementary Figure 117. ¹H NMR spectrum of 1-(4-nitrophenyl)ethan-1-ol.



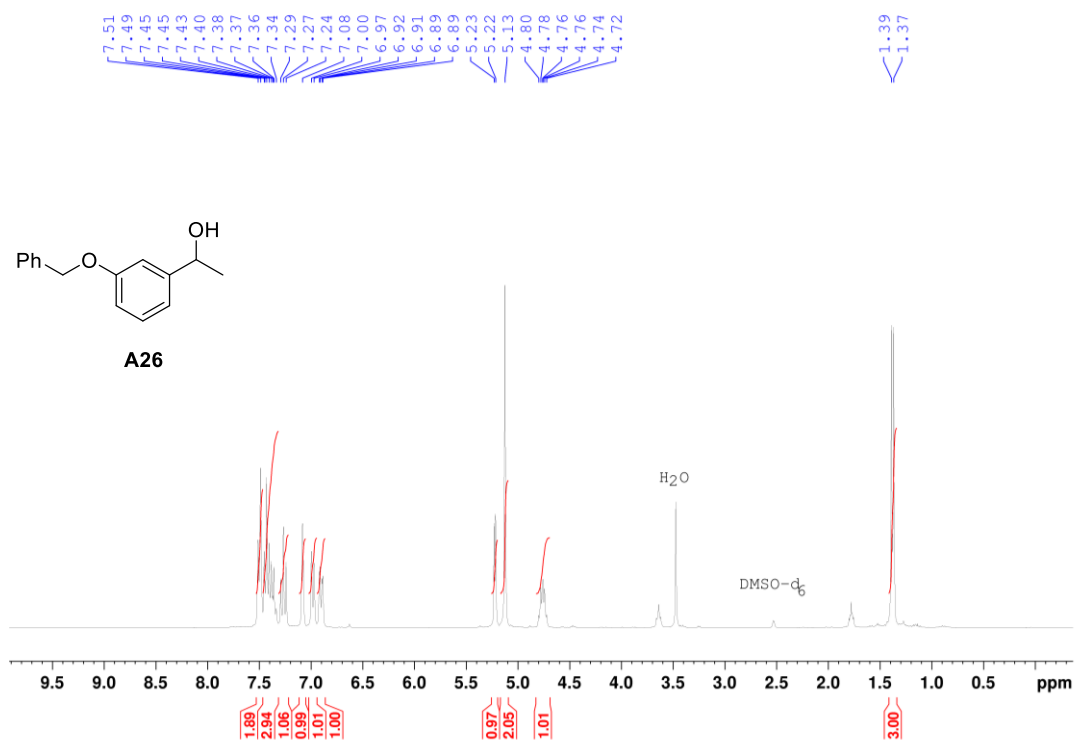
Supplementary Figure 118. ¹³C NMR spectrum of 1-(4-nitrophenyl)ethan-1-ol.



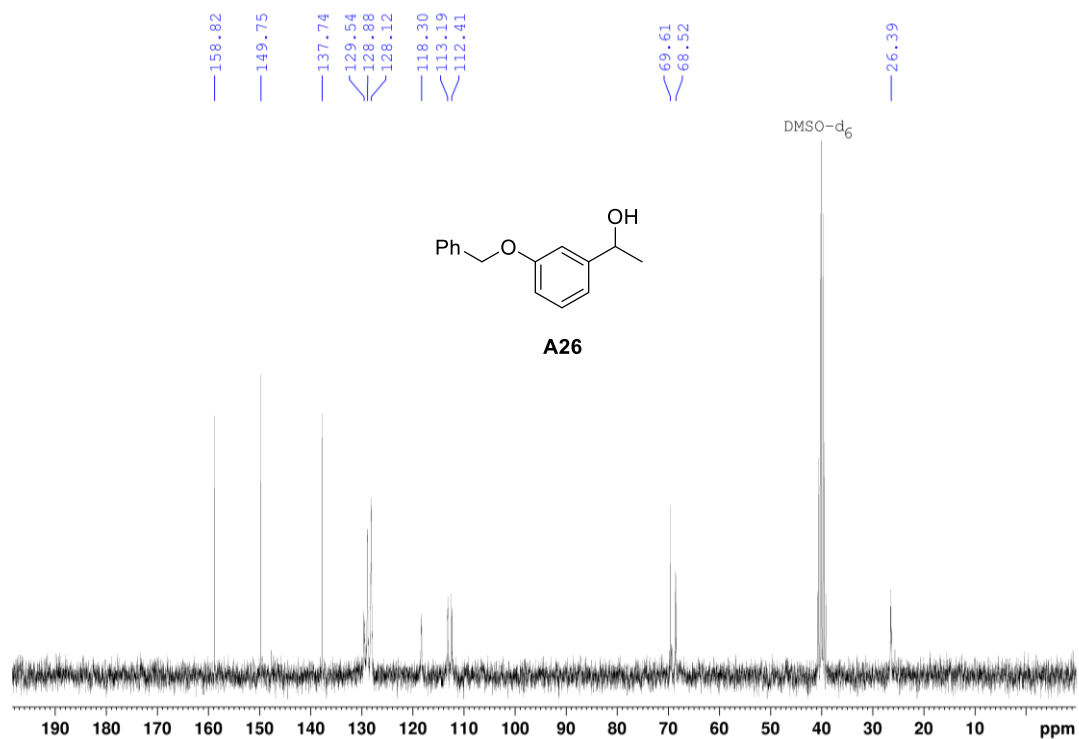
Supplementary Figure 119. ¹H NMR spectrum of 1-(4-(benzyloxy)phenyl)ethan-1-ol.



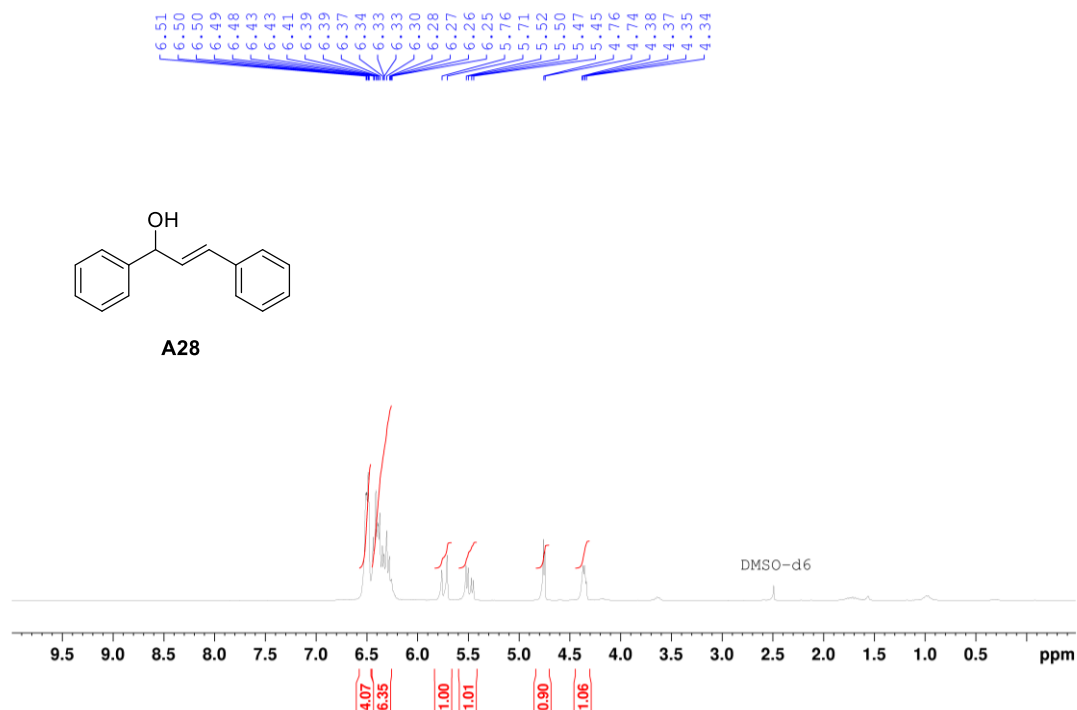
Supplementary Figure 120. ¹³C NMR spectrum of 1-(4-(benzyloxy)phenyl)ethan-1-ol.



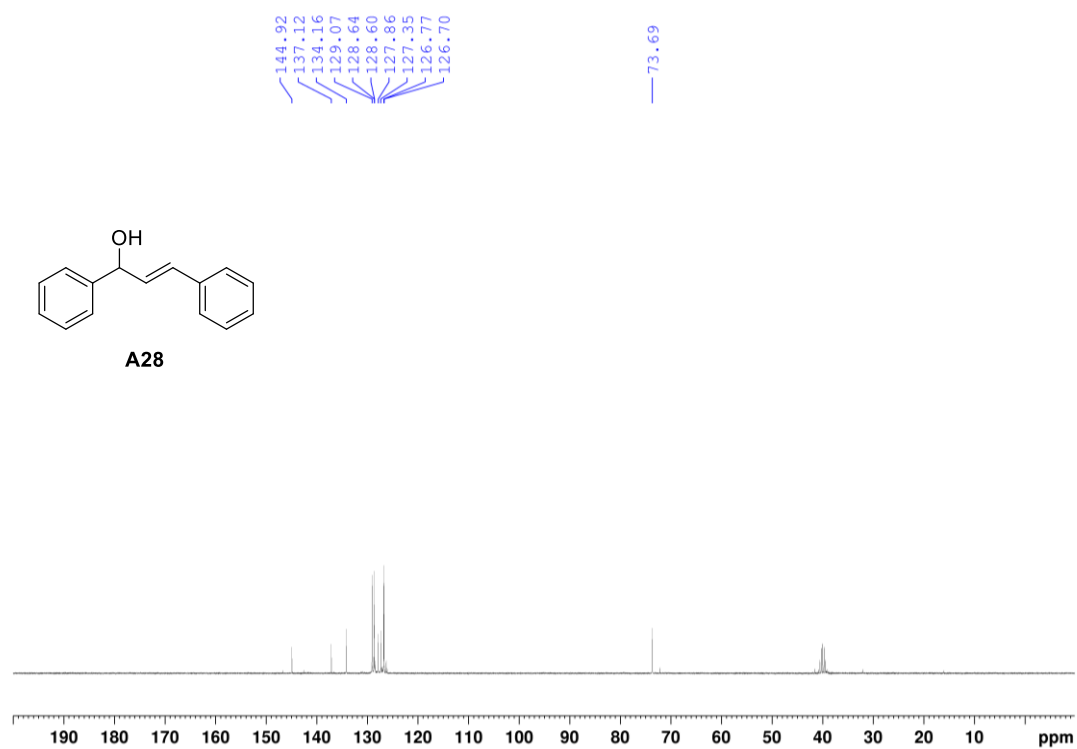
Supplementary Figure 121. ¹H NMR spectrum of 1-(3-(benzyloxy)phenyl)ethan-1-ol.



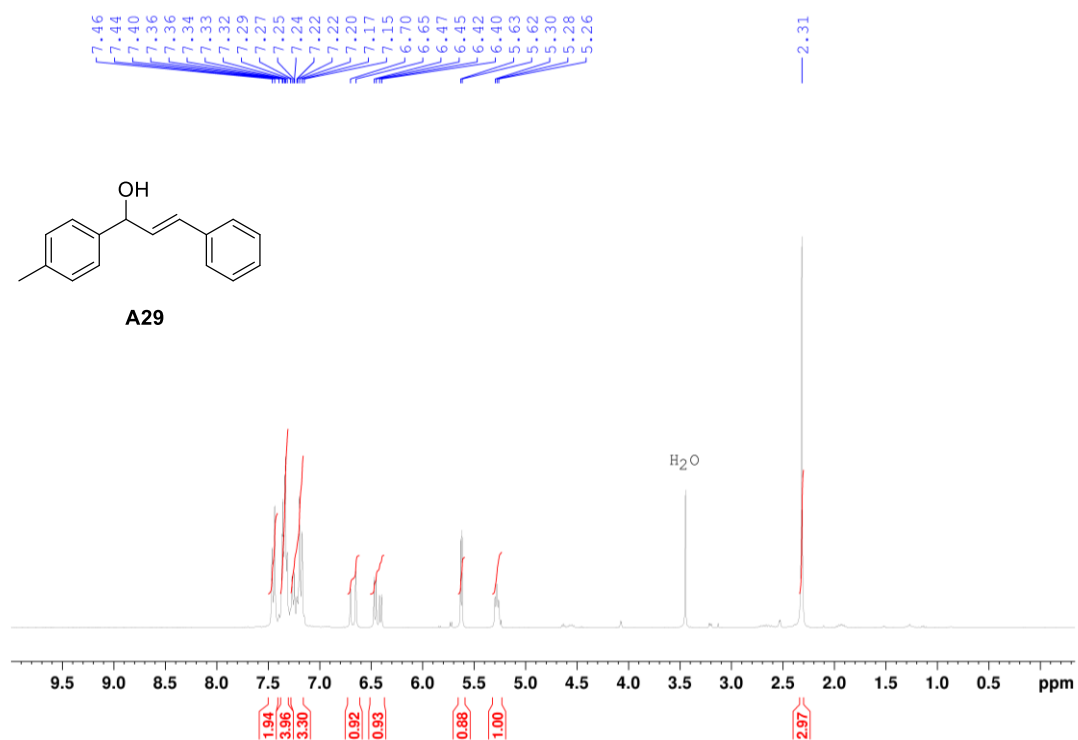
Supplementary Figure 122. ¹³C NMR spectrum of 1-(3-(benzyloxy)phenyl)ethan-1-ol.



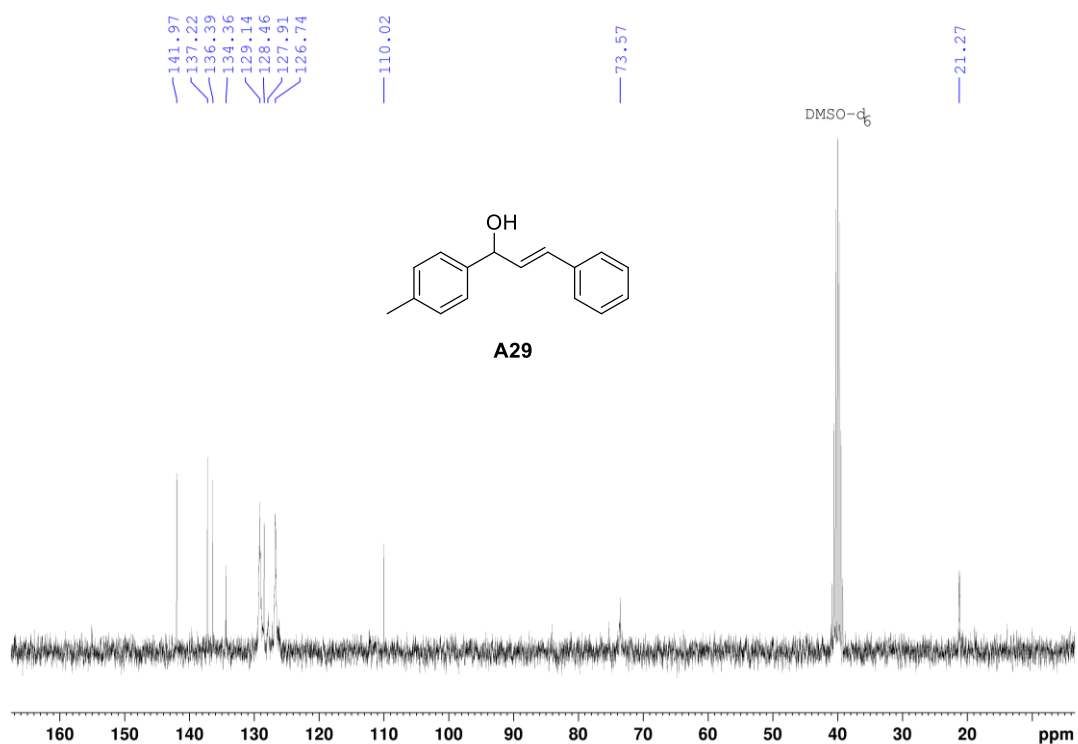
Supplementary Figure 123. ¹H NMR spectrum (*E*)-1,3-diphenylprop-2-en-1-ol.



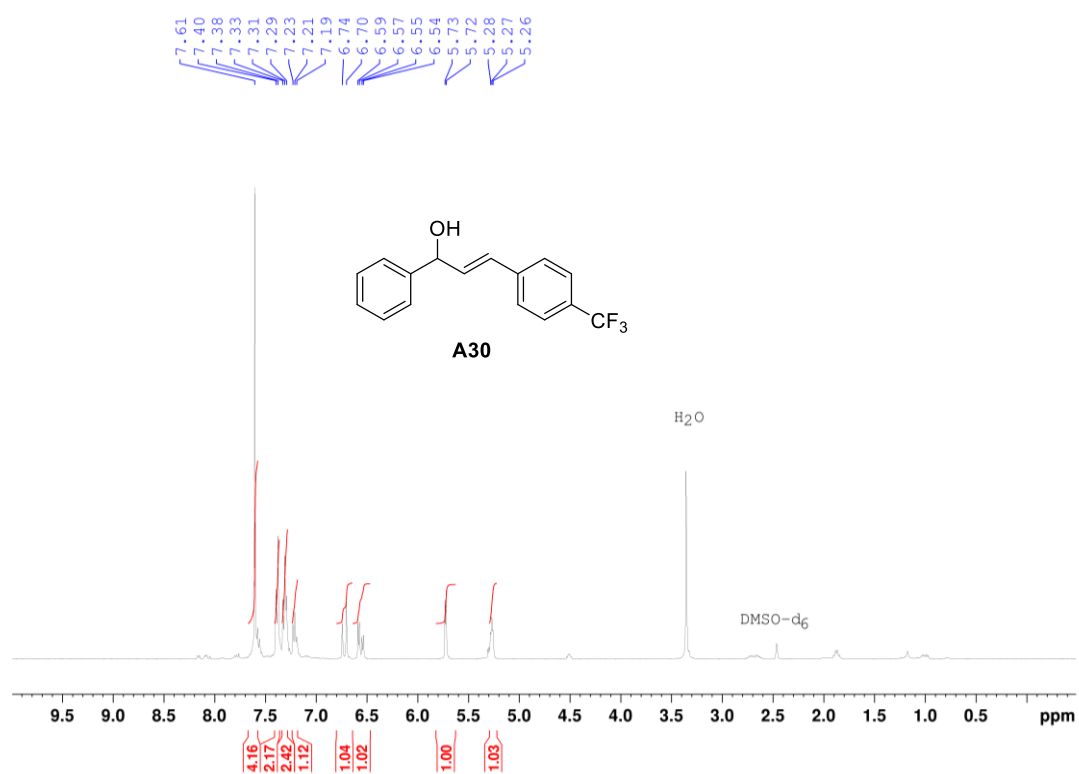
Supplementary Figure 124. ¹³C NMR spectrum of (*E*)-1,3-diphenylprop-2-en-1-ol.



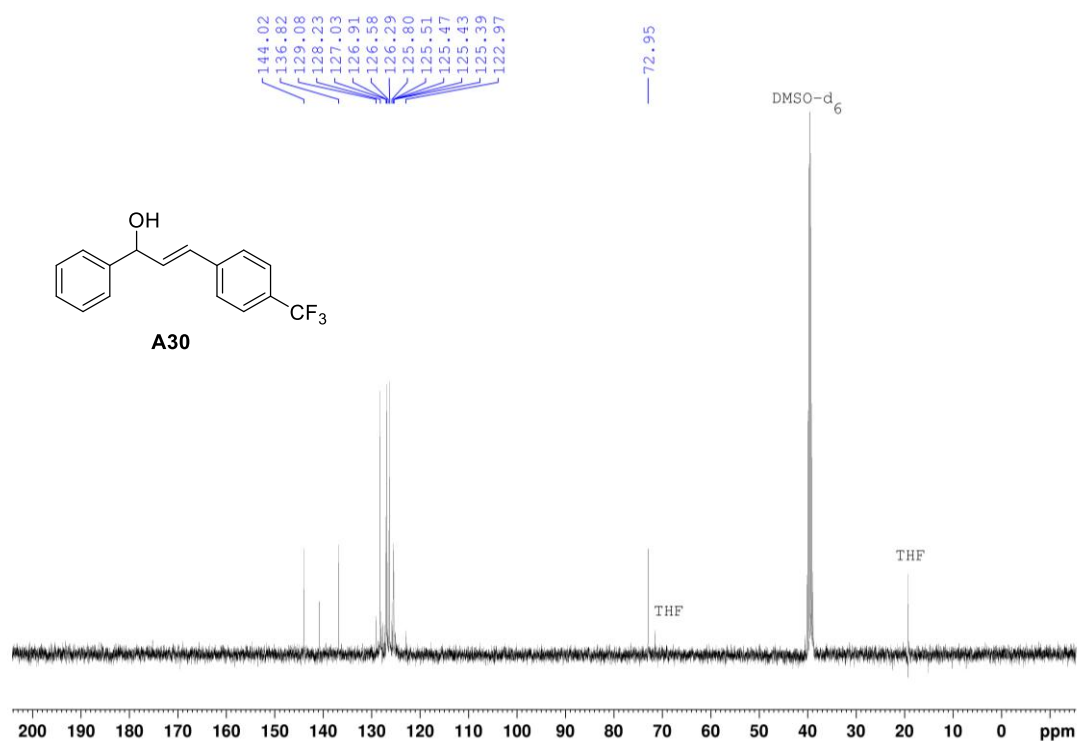
Supplementary Figure 125. ¹H NMR spectrum (E)-3-phenyl-1-(p-tolyl)prop-2-en-1-ol.



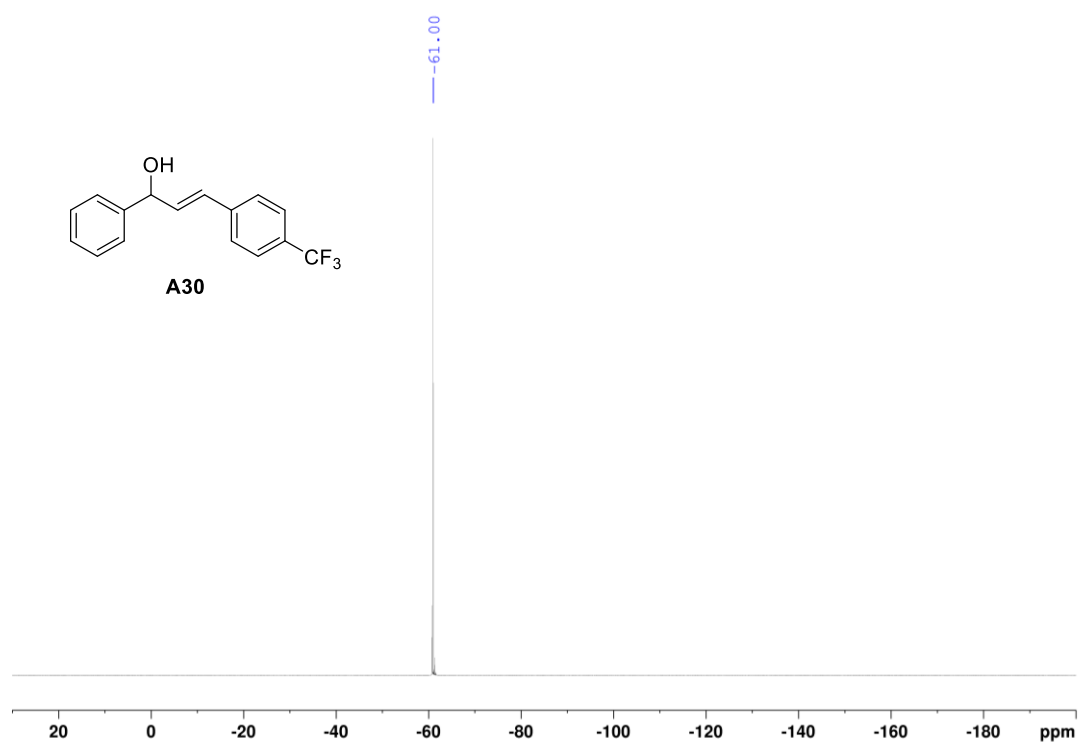
Supplementary Figure 126. ¹³C NMR spectrum (E)-3-phenyl-1-(p-tolyl)prop-2-en-1-ol.



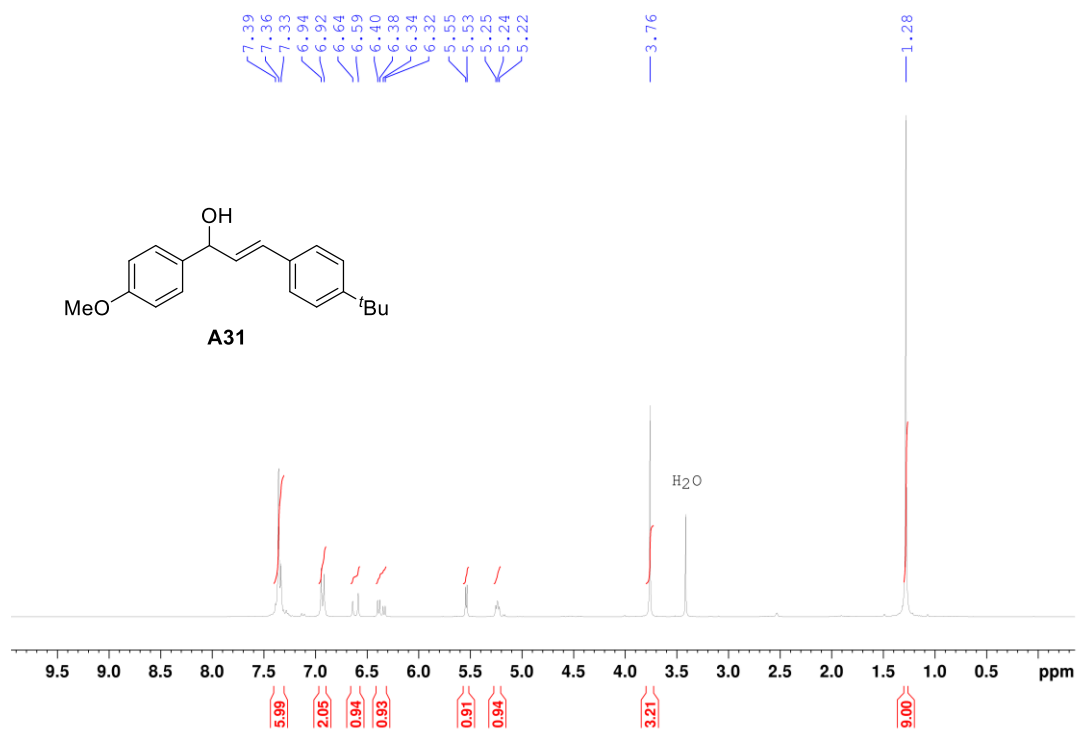
Supplementary Figure 127. ¹H NMR spectrum of (E)-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol.



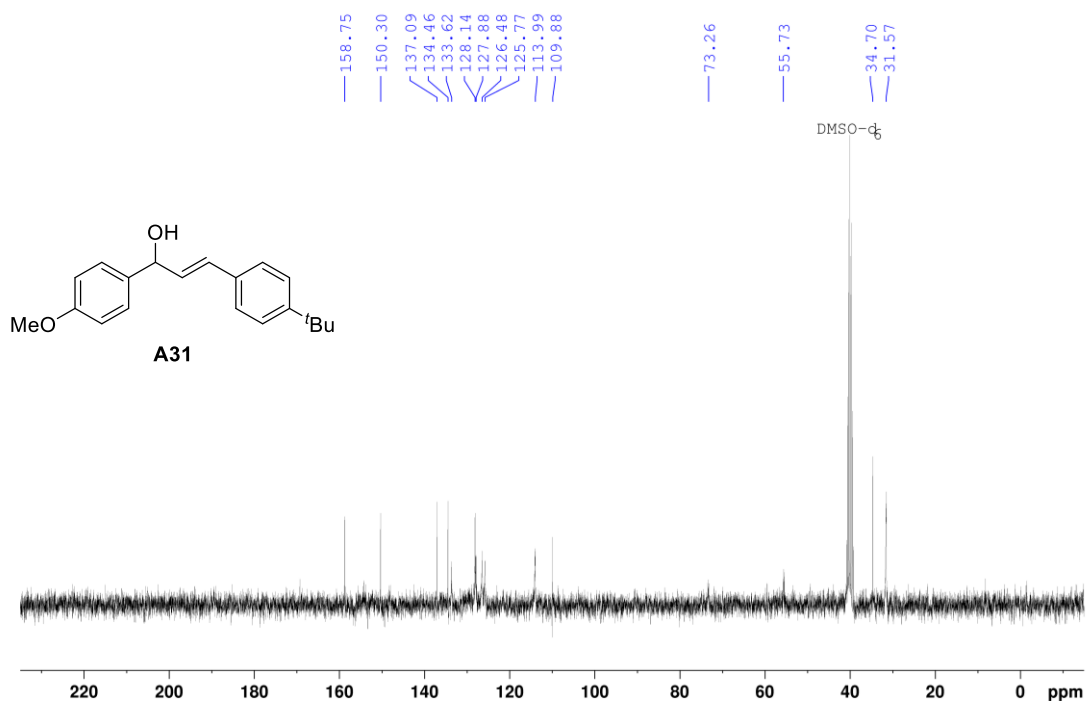
Supplementary Figure 128. ¹³C NMR spectrum of (E)-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol.



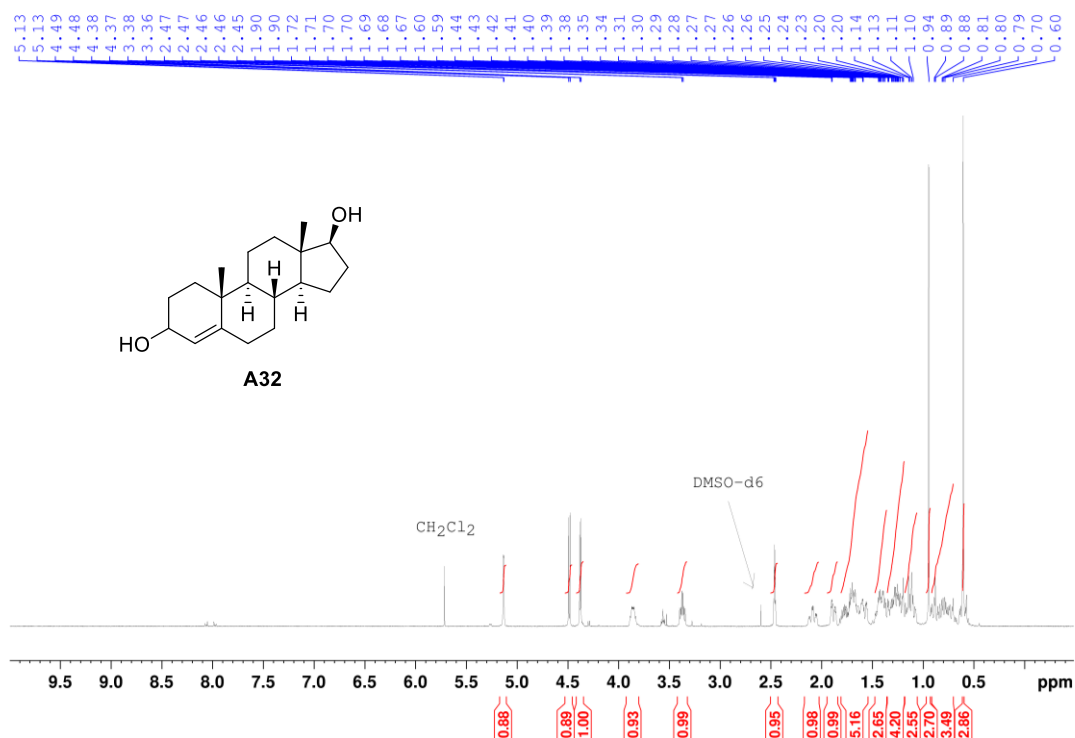
Supplementary Figure 129. ^{19}F NMR spectrum of (E)-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol.



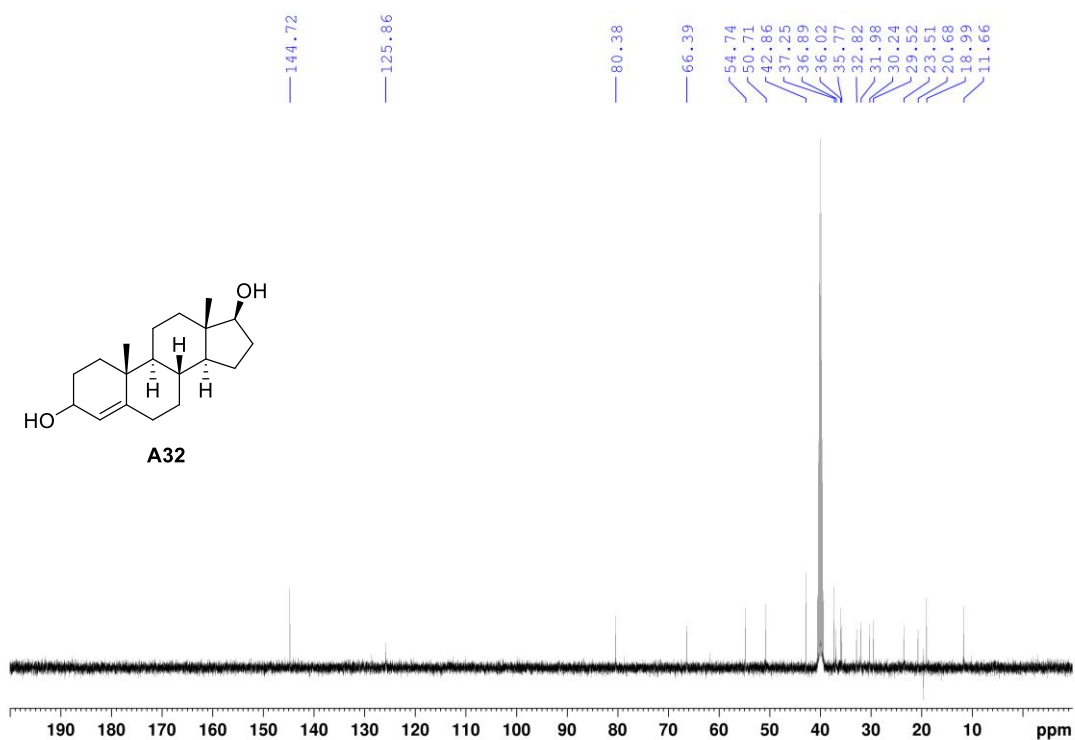
Supplementary Figure 130. ¹H NMR spectrum of (*E*)-3-(4-(*tert*-butyl)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-ol.



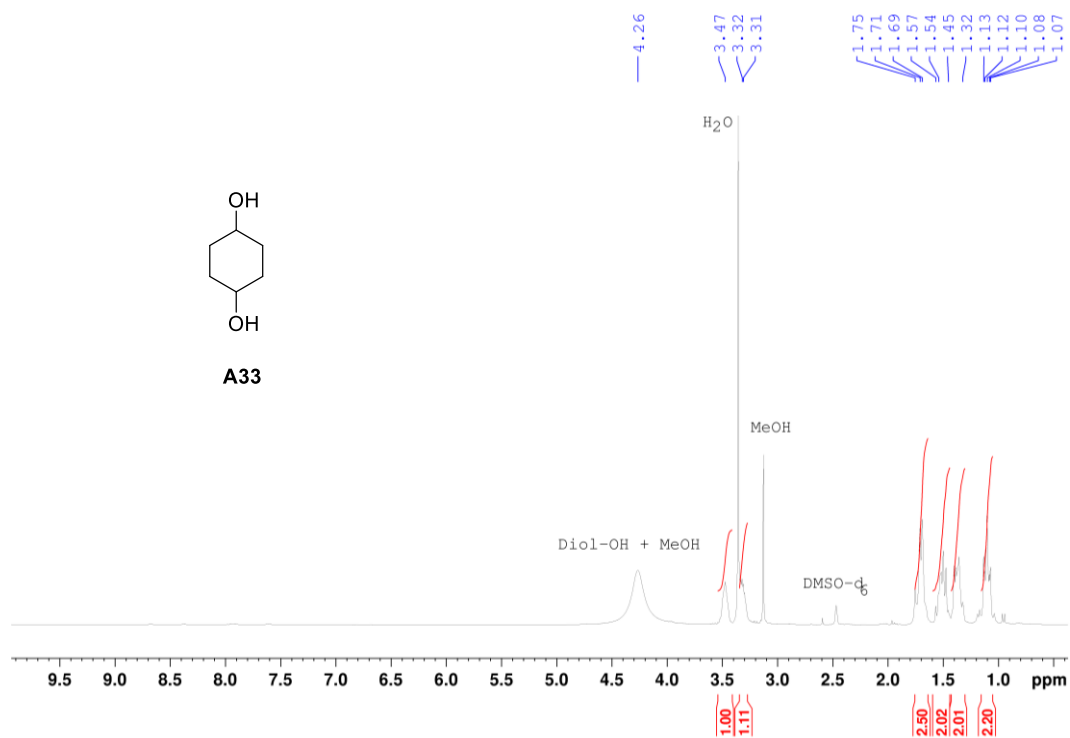
Supplementary Figure 131. ¹³C NMR spectrum of (*E*)-3-(4-(*tert*-butyl)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-ol.



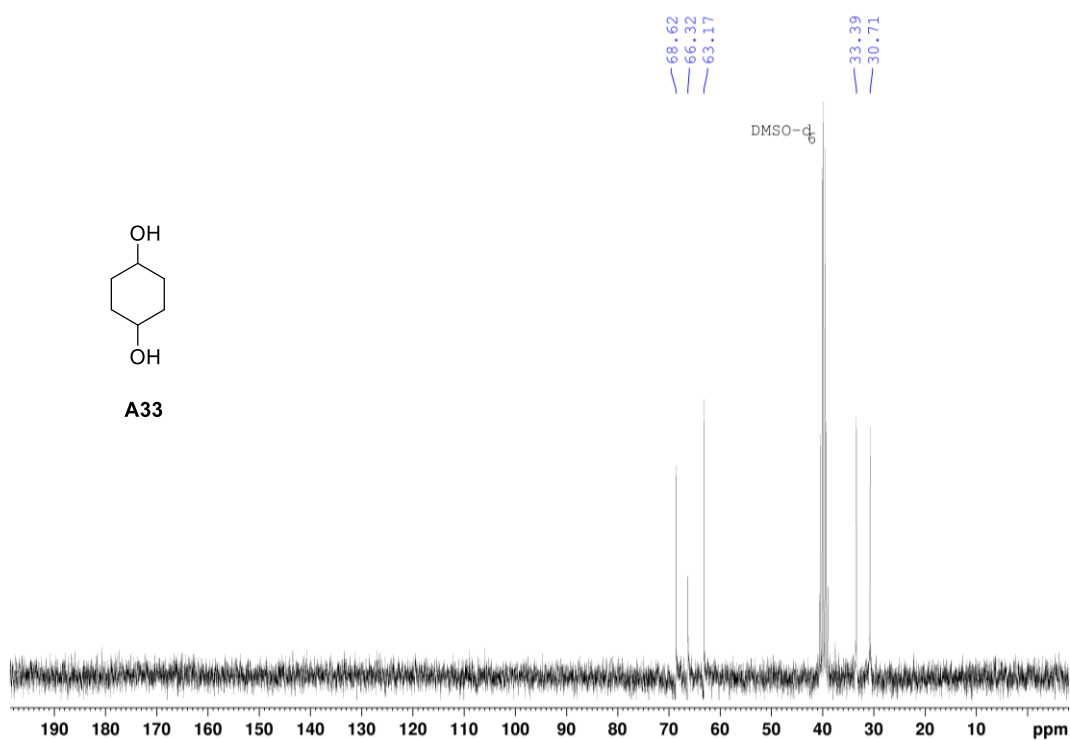
Supplementary Figure 132. ¹H NMR spectrum of Androstendiol.



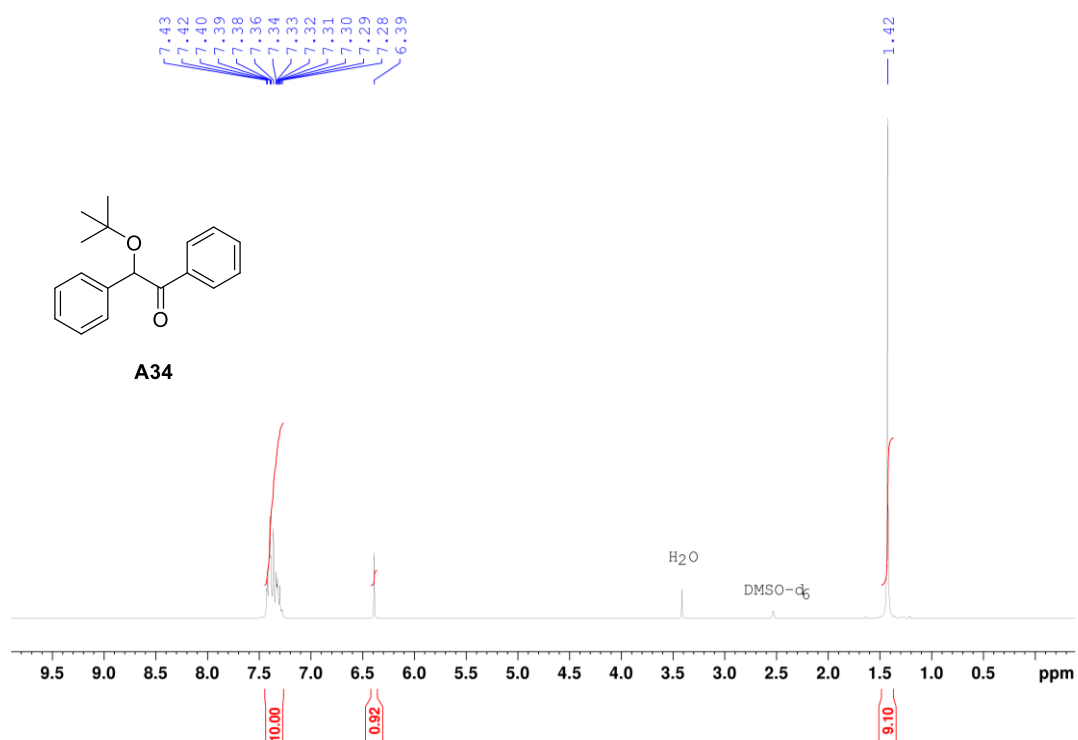
Supplementary Figure 133. ¹³C NMR spectrum of Androstendiol.



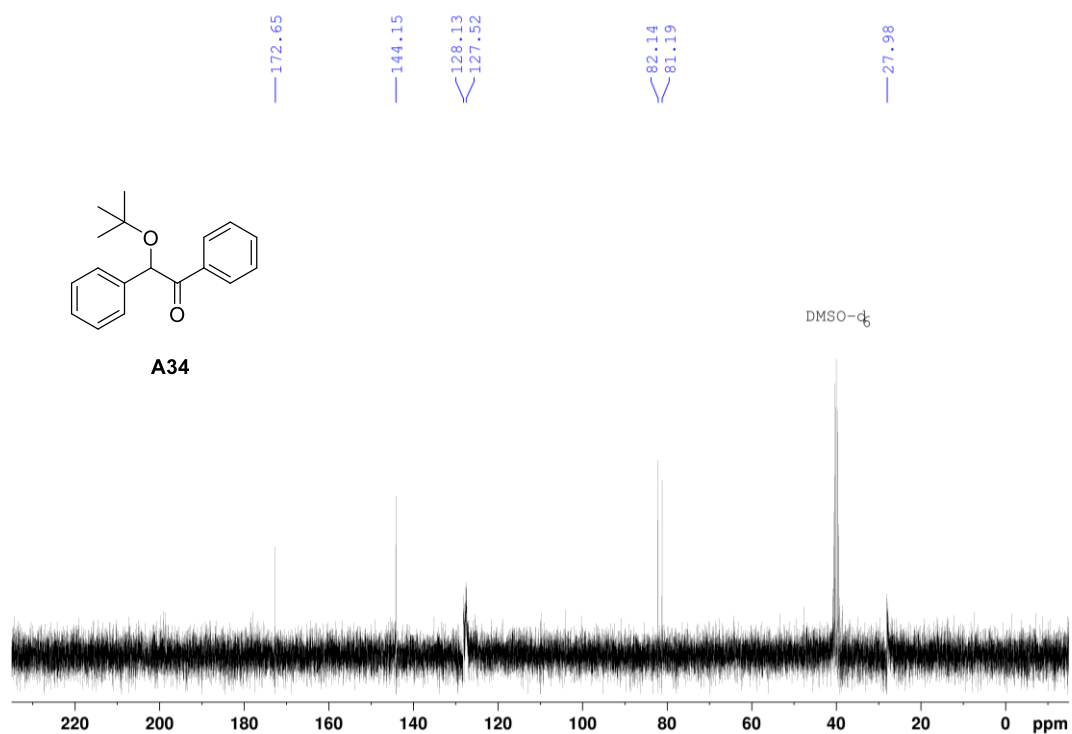
Supplementary Figure 134. ^1H NMR spectrum of 1,4-cyclohexanediol.



Supplementary Figure 135. ^{13}C NMR spectrum of 1,4-cyclohexanediol.

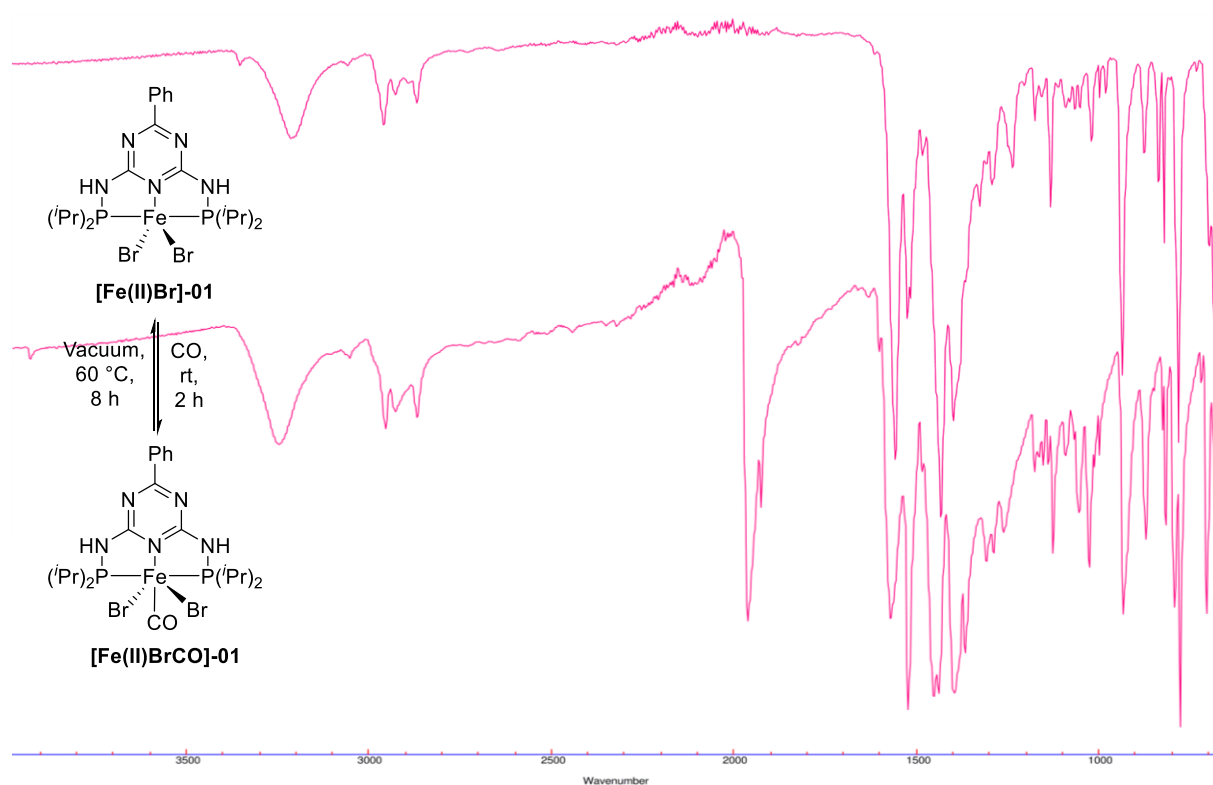


Supplementary Figure 136. ¹H NMR spectrum of 2-(*tert*-butoxy)-1,2-diphenylethan-1-one.



Supplementary Figure 137. ¹³C NMR spectrum of 2-(*tert*-butoxy)-1,2-diphenylethan-1-one.

6.8 IR spectra



Supplementary Figure 138. Comparative view of the IR spectra of **[Fe(II)Br]-01** and **[Fe(II)BrCO]-01**.



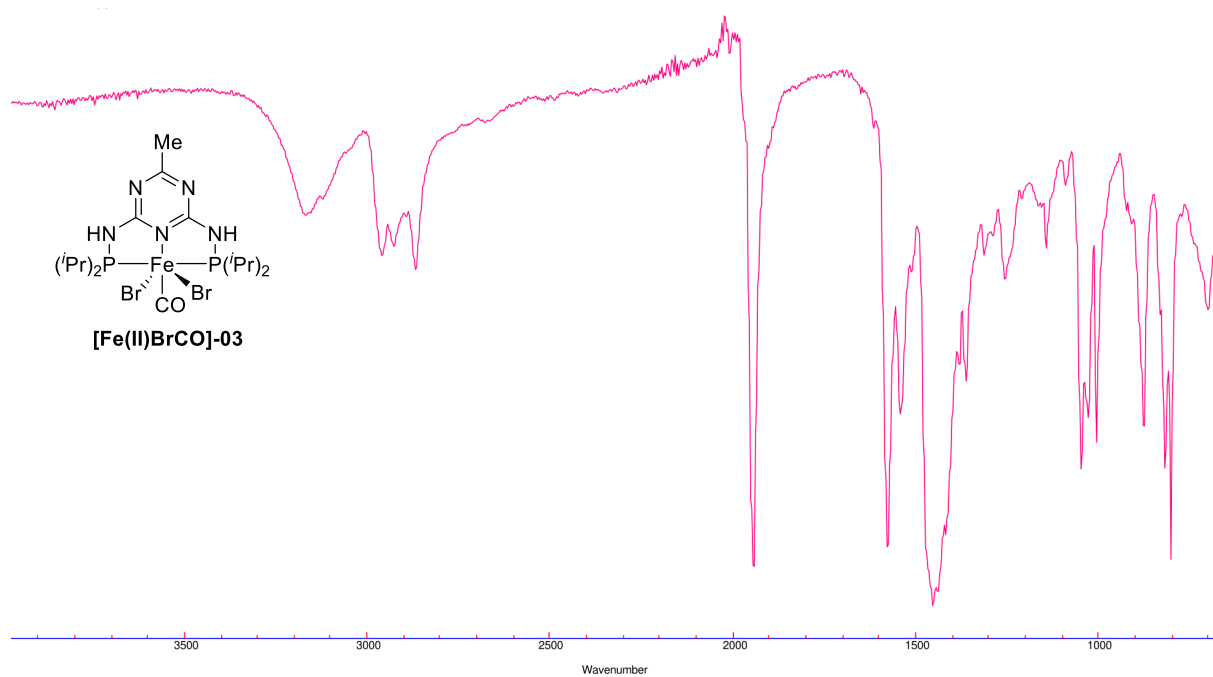
Supplementary Figure 139. IR spectrum of **[Fe(II)Br]-02**.



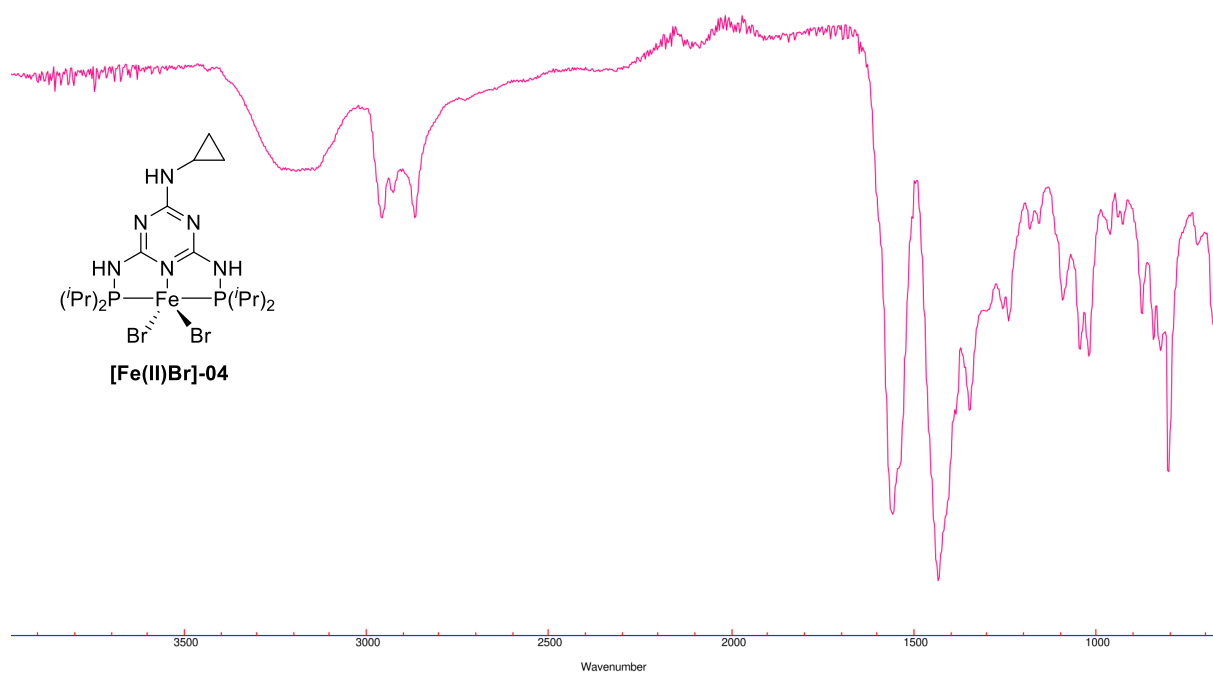
Supplementary Figure 140. IR spectrum of **[Fe(II)BrCO]-02**.



Supplementary Figure 141. IR spectrum of **[Fe(II)Br]-03**.



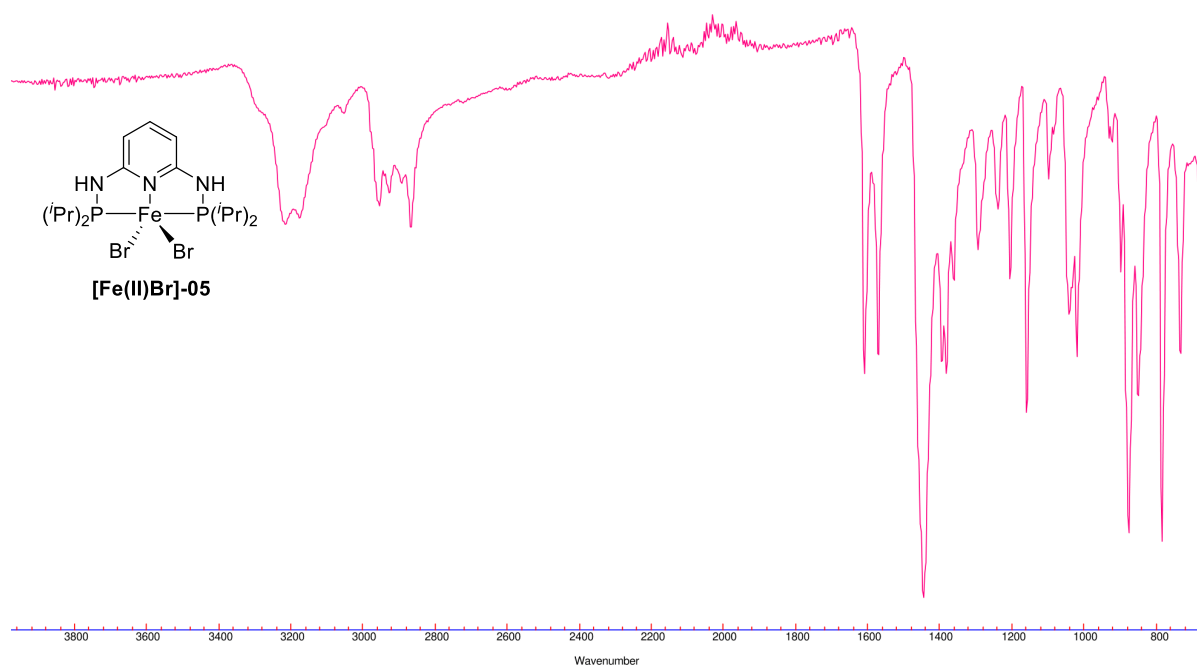
Supplementary Figure 142. IR spectrum of **[Fe(II)BrCO]-03**.



Supplementary Figure 143. IR spectrum of **[Fe(II)Br]-04**.



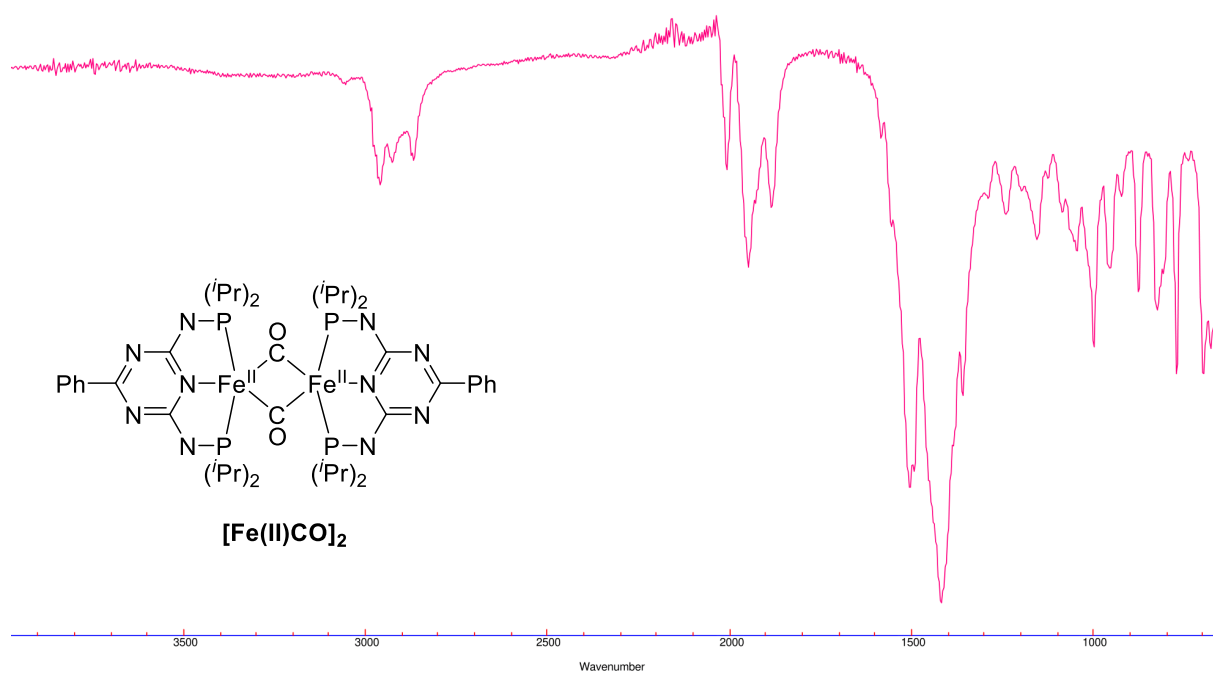
Supplementary Figure 144. IR spectrum of **[Fe(II)BrCO]-04**.



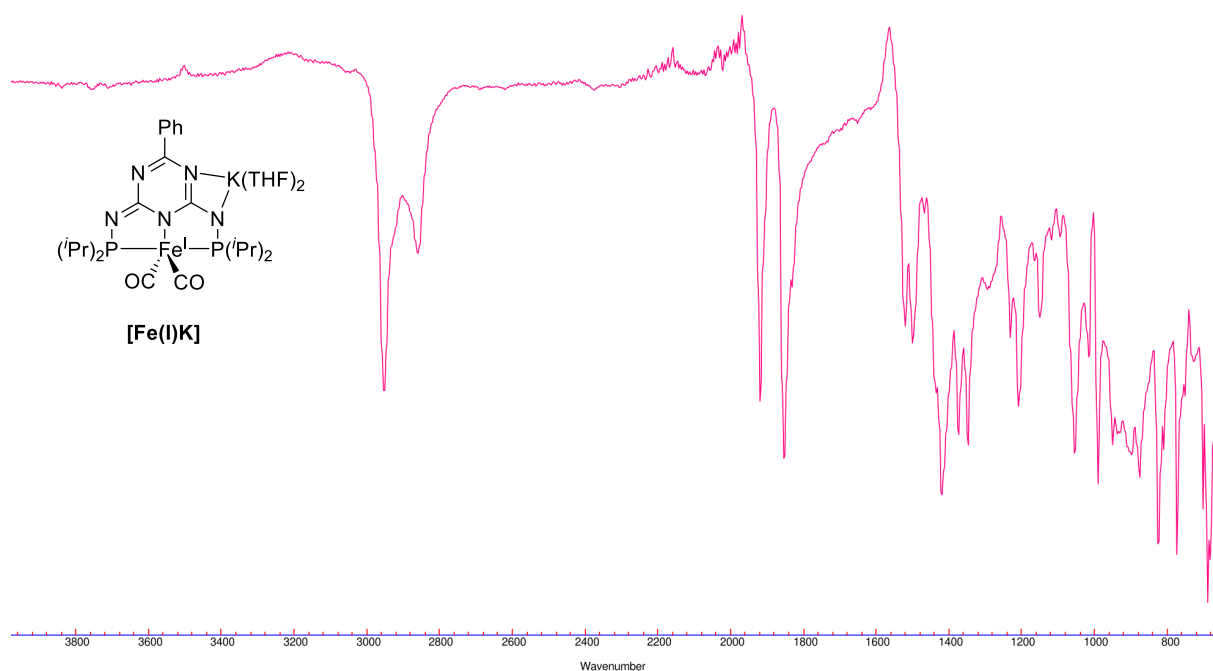
Supplementary Figure 145. IR spectrum of **[Fe(II)Br]-05**.



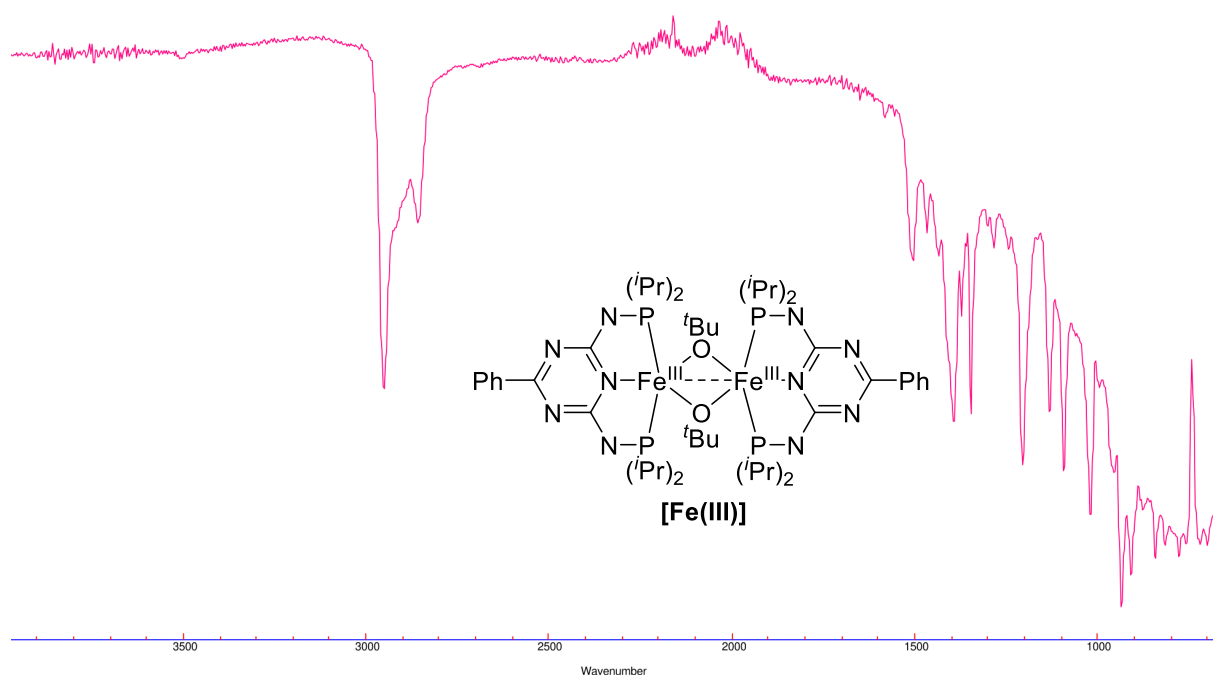
Supplementary Figure 146. IR spectrum of **[Fe(II)BrCO]-05**.



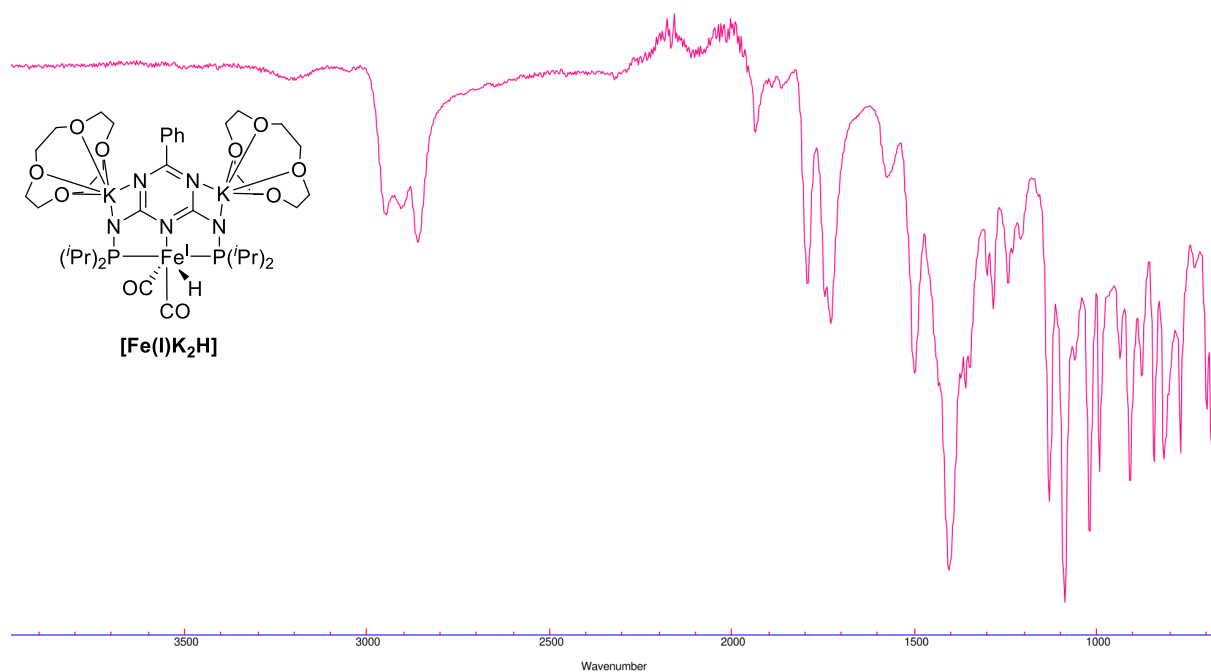
Supplementary Figure 147. IR spectrum of **[Fe(II)CO]₂**.



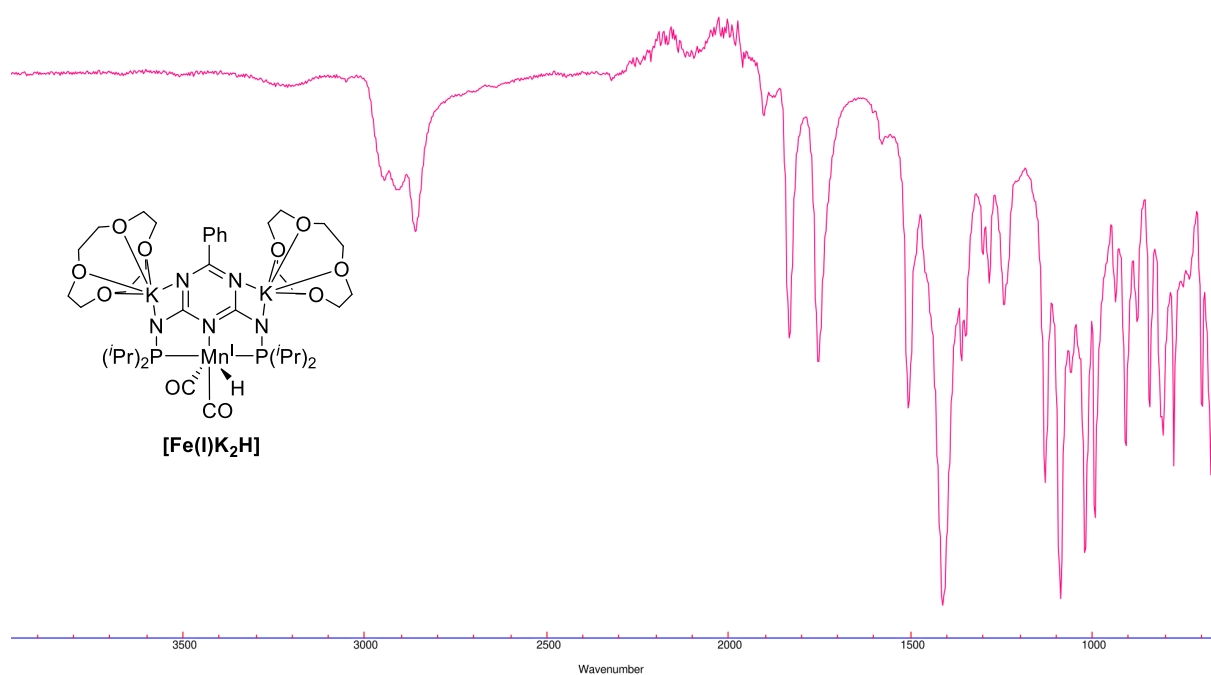
Supplementary Figure 148. IR spectrum of **[Fe(I)K]**.



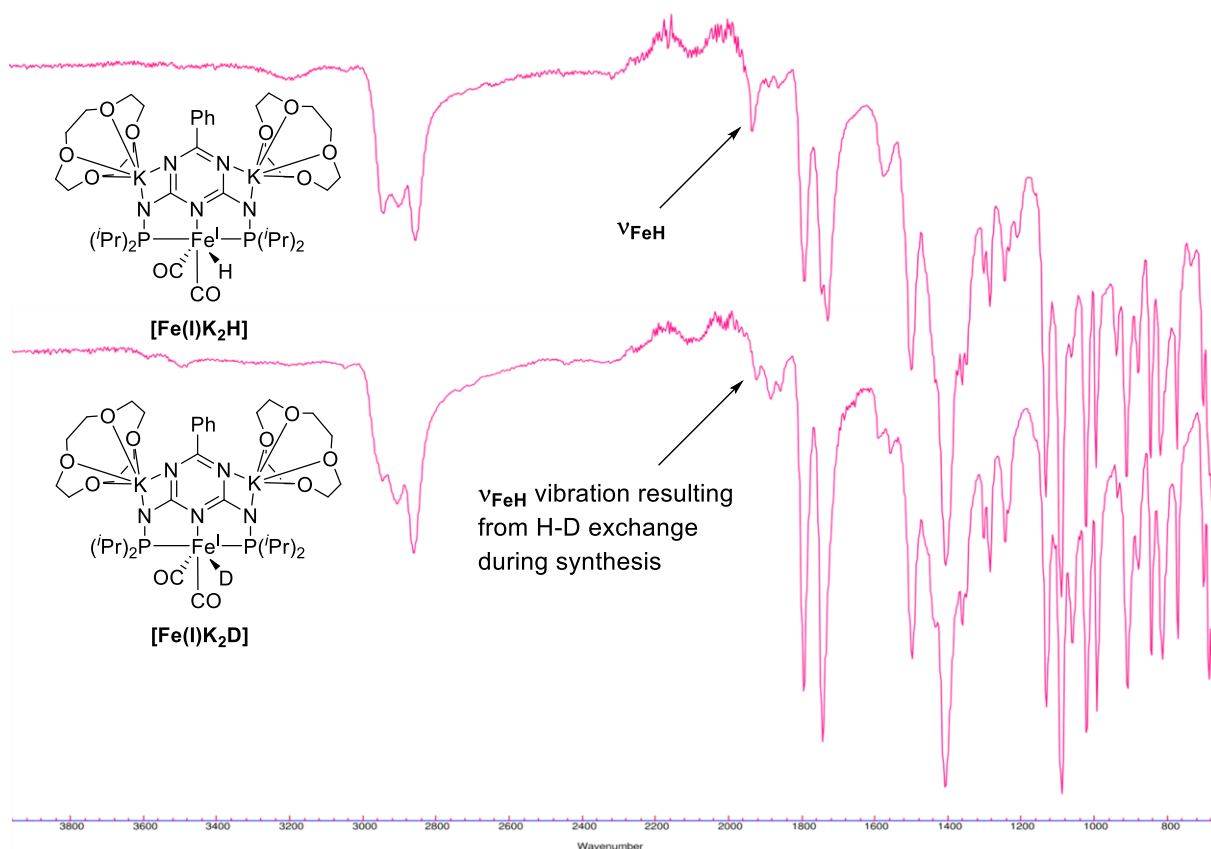
Supplementary Figure 149. IR spectrum of **[Fe(III)]**.



Supplementary Figure 150. IR spectrum of **[Fe(I)K₂H]**.



Supplementary Figure 151. IR spectrum of **[Mn(I)K₂H]**.



Supplementary Figure 152. Stacked spectra of **[Fe(I)K₂H]** and **[Fe(I)K₂D]**. Due to a possible H–D exchange during the synthesis of **[Fe(I)K₂D]** partial formation of the deuteride complex was observed using IR spectroscopy, since the FeH vibration was still visible. Nevertheless, the presumed FeH vibration had in the case of **[Fe(I)K₂D]** a considerably lower intensity, which indicates the presence of a mixture of iron(I) hydride and iron(I) deuteride. The emerged deuteride vibration could not be observed due to possible overlapping with other vibrations.

6.9 Crystallographic data

6.9.1 [Fe(I)K] (CCDC 2352638)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) p2_n

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: p2_n

Bond precision: C-C = 0.0072 Å Wavelength=0.71073

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 alpha=90 beta=96.50 (3) gamma=90

Temperature: 170 K

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Hall group	-P 2yac	-P 2yac
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Sum formula	C93 H147 Fe3 K3 N15 O12 P6 [+ solvent]	C31 H49 Fe K N5 O4 P2
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Dx, g cm ⁻³	1.197	1.197
Z	2	6
Mu (mm ⁻¹)	0.604	0.604
F000	2262.0	2262.0
F000'	2267.17	
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Nref	9876	9823
Tmin, Tmax	0.944, 0.954	
Tmin'	0.929	

Correction method= Not given

Data completeness= 0.995 Theta(max)= 24.500

R(reflections)= 0.0522 (6814)

wR2(reflections)=
0.1453 (9823)

S = 1.037

Npar= 610

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 B

PLAT220_ALERT_2_B NonSolvent Resd 1 C Ueq(max)/Ueq(min) Range 8.4 Ratio

Author Response: The structure suffered from poor data quality and solvent disorder. This large Ueq(max)/Ueq(min) range results from the fact that the three tetrahydrofuran molecules coordinated to the potassium atoms are likely disordered. Attempts were made to reasonably resolve this disorder but weren't successful.

PLAT910_ALERT_3_B Missing # of FCF Reflection(s) Below Theta(Min). 16 Note
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Author Response: Theta(min)=2.696. The theta values of the missing reflections are less than 2.696 deg. and therefore these reflections were excluded due to technical restrictions.

Alert level C

THETM01_ALERT_3_C The value of sine(theta_max)/wavelength is less than 0.590
Calculated sin(theta_max)/wavelength = 0.5835
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PLAT230_ALERT_2_C Hirshfeld Test Diff for C2 --C3 . 5.8 s.u.
PLAT230_ALERT_2_C Hirshfeld Test Diff for C01S --C01T . 5.3 s.u.
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PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C01S Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C39 Check
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● Alert level G

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PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
      Calc: C93 H147 Fe3 K3 N15 O12 P6
      Rep.: C31 H49 Fe K N5 O4 P2
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ... 0.333 Check
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Fe1 --C7 . 6.7 s.u.
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      H01F
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PLAT868_ALERT_4_G ALERTS Due to the Use of _smtbx_masks Suppressed ! Info
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0 ALERT level A = Most likely a serious problem - resolve or explain
2 ALERT level B = A potentially serious problem, consider carefully
22 ALERT level C = Check. Ensure it is not caused by an omission or oversight
19 ALERT level G = General information/check it is not something unexpected

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3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
22 ALERT type 2 Indicator that the structure model may be wrong or deficient
9 ALERT type 3 Indicator that the structure quality may be low
6 ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check

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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

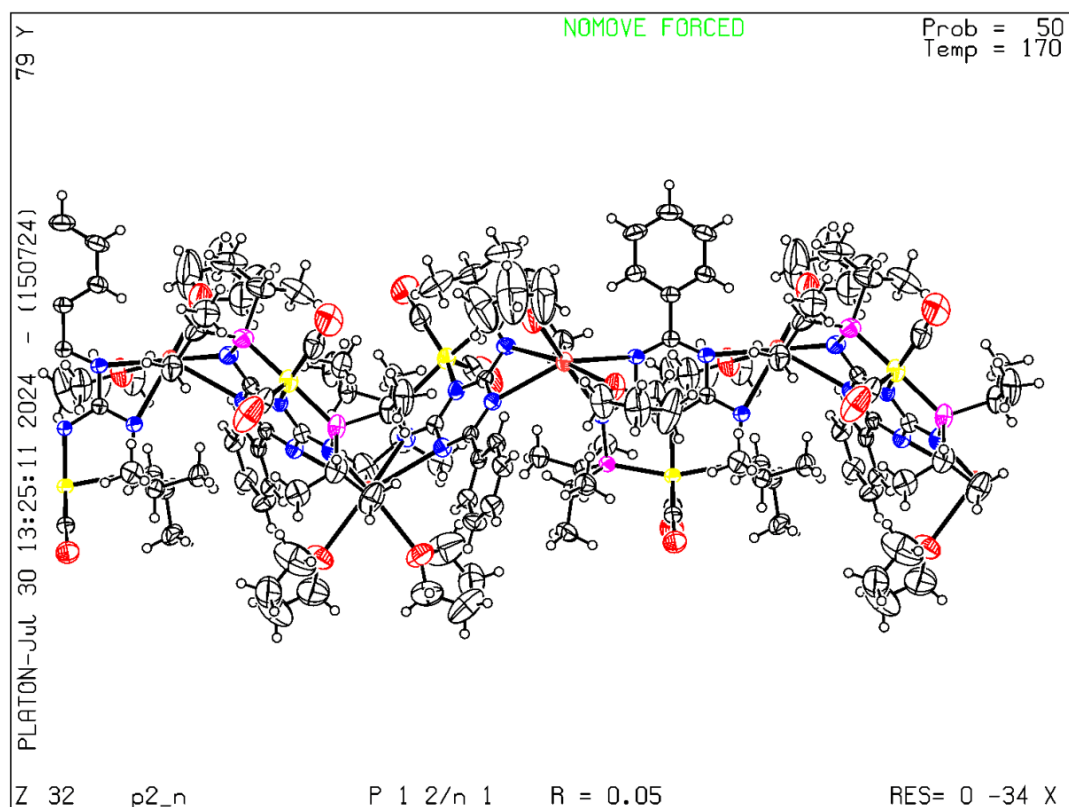
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Datablock p2_n - ellipsoid plot



6.9.2 [Fe(II)Br]-01 (CCDC 2352640)

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: p21_n

Bond precision:	C-C = 0.0063 Å	Wavelength=0.71073
Cell:	a=12.820 (3) alpha=90	b=13.100 (3) beta=90.80 (3) c=20.170 (4) gamma=90
Temperature:	133 K	
	Calculated	Reported
Volume	3387.1 (13)	3387.1 (12)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C21 H35 Br2 Fe N5 P2, C4 H8 O [+ solvent]	C21 H35 Br2 Fe N5 P2, C4 H8 O
Sum formula	C25 H43 Br2 Fe N5 O P2 [+ solvent]	C25 H43 Br2 Fe N5 O P2
Mr	707.23	707.25
Dx, g cm ⁻³	1.387	1.387
Z	4	4
Mu (mm ⁻¹)	2.923	2.923
F000	1448.0	1448.0
F000'	1448.28	
h,k,lmax	15,16,24	15,16,24
Nref	6662	6613
Tmin,Tmax	0.545,0.612	0.914,0.953
Tmin'	0.485	

Correction method= # Reported T Limits: Tmin=0.914 Tmax=0.953
AbsCorr = NONE

Data completeness= 0.993 Theta (max)= 26.000

R(reflections)= 0.0442(4614)

wR2(reflections)=
0.0954(6613)

S = 1.010

Npar= 333

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

PLAT057_ALERT_3_C	Correction for Absorption Required	RT(exp) ...	1.12	Do !
PLAT243_ALERT_4_C	High 'Solvent' Ueq as Compared to Neighbors of		C010	Check
PLAT341_ALERT_3_C	Low Bond Precision on C-C Bonds		0.00628	Ang.



Alert level G

PLAT007_ALERT_5_G	Number of Unrefined Donor-H Atoms	2	Report
PLAT012_ALERT_1_G	N.O.K. _shelx_res_checksum Found in CIF		Please Check
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 O006 .	106.5	Degree
PLAT605_ALERT_4_G	Largest Solvent Accessible VOID in the Structure	167	A**3
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels	74	Note
PLAT933_ALERT_2_G	Number of HKL-OMIT Records in Embedded .res File	5	Note
PLAT941_ALERT_3_G	Average HKL Measurement Multiplicity	4.0	Low
PLAT967_ALERT_5_G	Note: Two-Theta Cutoff Value in Embedded .res ..	52.0	Degree

- 0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
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- 1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
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4 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check
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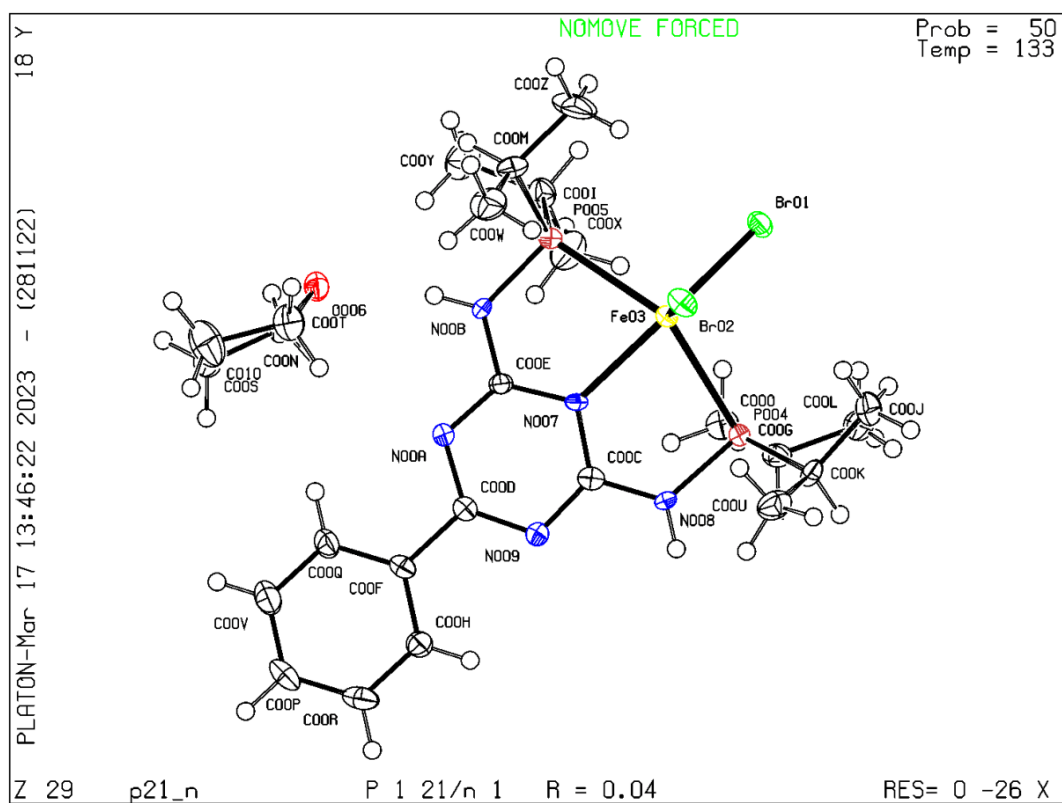
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6.9.3 [Mn(I)K₂H] (CCDC 2352639)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) rk2201

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: rk2201

Bond precision:	C-C = 0.0041 Å	Wavelength=0.71073
Cell:	a=40.308 (3)	b=13.4550 (9) c=23.6673 (16)
	alpha=90	beta=101.824 (3) gamma=90
Temperature:	100 K	
	Calculated	Reported
Volume	12563.5 (15)	12563.4 (15)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	2 (C47 H82 K2 Mn N5 O12 P2), 3 (C4 H8 O)	C47 H82 K2 Mn N5 O12 P2, 1.5 (C4 H8 O)
Sum formula	C106 H188 K4 Mn2 N10 O27 P4	C53 H94 K2 Mn N5 O13.50 P2
Mr	2424.83	1212.41
Dx, g cm ⁻³	1.282	1.282
Z	4	8
Mu (mm ⁻¹)	0.455	0.455
F000	5184.0	5184.0
F000'	5193.60	
h, k, lmax	55, 18, 32	55, 18, 32
Nref	17650	17645
Tmin, Tmax	0.872, 0.947	0.700, 0.746
Tmin'	0.872	

Correction method= # Reported T Limits: Tmin=0.700 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 29.573

R(reflections)= 0.0534 (14875)	wR2(reflections)= 0.1493 (17645)
S = 1.061	Npar= 1042

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

PLAT220_ALERT_2_C	NonSolvent	Resd 1	C	Ueq(max)/Ueq(min) Range	3.5	Ratio
PLAT234_ALERT_4_C	Large Hirshfeld Difference	C47	--C46A	.	0.16	Ang.
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of				C45	Check
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of				C47	Check
PLAT244_ALERT_4_C	Low 'Solvent' Ueq as Compared to Neighbors of				C201	Check
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance				2.672	Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L=	0.600			2	Report
PLAT976_ALERT_2_C	Check Calcd Resid. Dens.	0.51	Ang From O200	.	-0.67	eA-3
PLAT977_ALERT_2_C	Check Negative Difference Density on H10C	.			-0.32	eA-3

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite				73	Note
PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...				73	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 ...				0.500	Check
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large				25.77	Why ?
PLAT175_ALERT_4_G	The CIF-Embedded .res File Contains SAME Records				6	Report
PLAT178_ALERT_4_G	The CIF-Embedded .res File Contains SIMU Records				6	Report
PLAT186_ALERT_4_G	The CIF-Embedded .res File Contains ISOR Records				1	Report
PLAT230_ALERT_2_G	Hirshfeld Test Diff for	C32	--C33	.	5.5	s.u.
PLAT230_ALERT_2_G	Hirshfeld Test Diff for	C45	--C46	.	11.0	s.u.
PLAT232_ALERT_2_G	Hirshfeld Test Diff (M-X)	Mn1	--C22	.	7.9	s.u.
PLAT301_ALERT_3_G	Main Residue Disorder	(Resd 1)			46%	Note
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder	(Resd 2)			100%	Note
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder	(Resd 4)			100%	Note
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in		(Resd 2)		6.62	Check
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in		(Resd 4)		6.38	Check
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O110			.	99.1	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O200			.	109.7	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O100			.	103.6	Degree
PLAT411_ALERT_2_G	Short Inter H...H Contact	H20A	..H41C	.	2.09	Ang.
		1-x,1-y,1-z =			5_666	Check
PLAT412_ALERT_2_G	Short Intra XH3 .. XHn	H	..H12E	.	2.14	Ang.
		x,y,z =			1_555	Check
PLAT412_ALERT_2_G	Short Intra XH3 .. XHn	H9A	..H40D	.	2.11	Ang.
		x,y,z =			1_555	Check
PLAT412_ALERT_2_G	Short Intra XH3 .. XHn	H11B	..H15B	.	1.92	Ang.
		x,y,z =			1_555	Check
PLAT432_ALERT_2_G	Short Inter X...Y Contact	C1	..C28A	.	3.06	Ang.
		1/2-x,1/2+y,1/2-z =			4_555	Check
PLAT773_ALERT_2_G	Check long C-C Bond in CIF: C45	--C46A			1.73	Ang.
PLAT811_ALERT_5_G	No ADDSYM Analysis: Too Many Excluded Atoms				!	Info
PLAT860_ALERT_3_G	Number of Least-Squares Restraints				1227	Note
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			1	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.				2	Info

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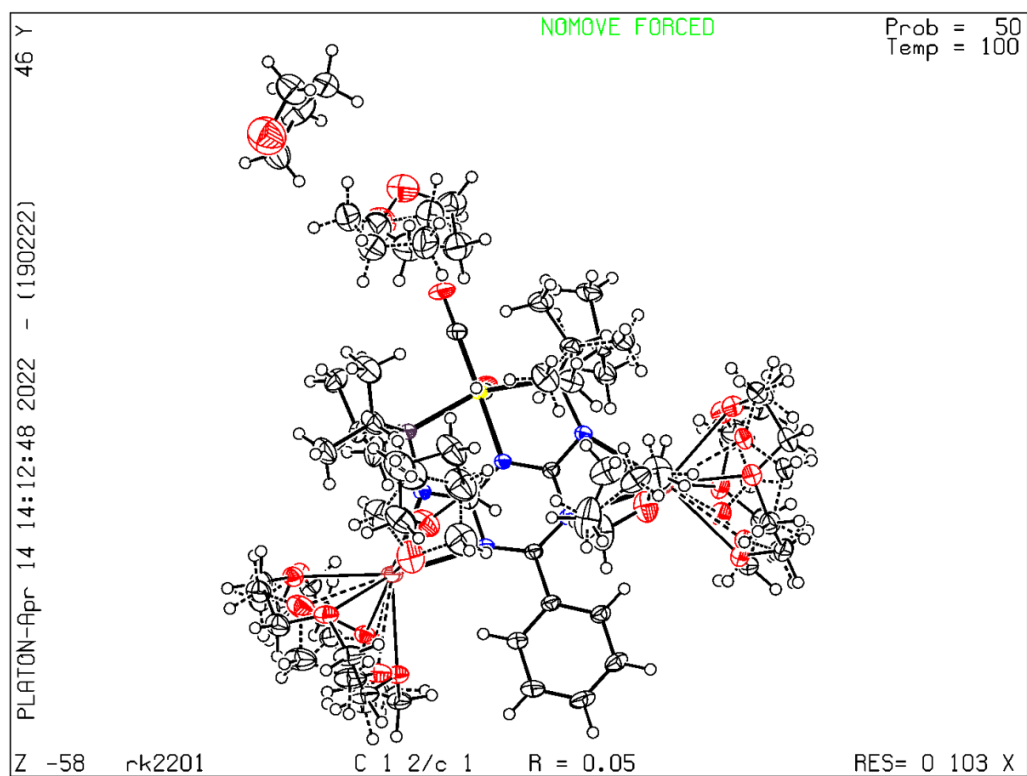
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7 Mechanistically Switchable Hydrogenation Catalysis

Niko Sila, Torsten Irrgang, and Rhett Kempe*

Inorganic Chemistry II – Catalyst Design, Sustainable Chemistry Center, University of Bayreuth, 95440 Bayreuth, Germany, email: kempe@uni-bayreuth.de

To be submitted.

Mechanistically Switchable Hydrogenation Catalysis

Niko Sila, Torsten Irrgang, and Rhett Kempe*

Chair Inorganic Chemistry II – Catalyst Design, Sustainable Chemistry Centre, University of Bayreuth, 95440 Bayreuth, Germany, email: kempe@uni-bayreuth.de

ABSTRACT: Hydrogenation catalysis plays a pivotal role in chemical industry and academic research, and two generally accepted mechanisms dominate. The oxidative addition of hydrogen in combination with reductive elimination operates if non-polar multiple bonds become hydrogenated, and the heterolytic cleavage of dihydrogen initially forming a proton and a hydride species followed by a concerted transfer of the hydride and the corresponding counter cation (proton or alkali metal cation) toward the substrate are relevant if hydrogen is added to polar multiple bonds. We recently reported on a molecular Ir catalyst that can activate hydrogen both ways, and demonstrate here that protonation or deprotonation of this catalyst permits a preference of the oxidative addition pathways or heterolytic dihydrogen cleavage, respectively. In addition, we report that important hydrogenation reactions, such as reductive amination employing hydrogen and nitro arene hydrogenation, can be preferred over the other in the protonated or deprotonated/metalated state. Both catalytically active species (protonated and deprotonated) are well defined and deprotonation can occur stoichiometrically exact with a potassium base.

INTRODUCTION

Hydrogenation catalysis plays a pivotal role in both chemical industrial and academic research,^{1,2} and two general mechanisms are known for the catalytic addition of hydrogen to multiple bonds. The hydrogenation of nonpolar multiple bonds can proceed via oxidative addition (OA) of H₂ to the catalyst forming a metal dihydride³ and, subsequently, a reaction of the metal dihydride with the nonpolar multiple bond takes place, followed by reductive elimination to regenerate the catalyst.⁴ By contrast, polar multiple bonds become hydrogenated via the heterolytic cleavage of dihydrogen. A proton and a metal hydride are formed initially, and bind to the catalyst. Hydride transfer to the polar multiple bond takes place next in a concerted fashion with the proton^{5–7} or a metal cation^{8–14} for charge compensation. Switching between both pathways would be highly desirable to permit more complex hydrogenation chemistry. There are numerous examples of ON-OFF switching of the catalytic activity,^{15–18} and groundbreaking works in temperature-induced chiral,¹⁹ photoredox,²⁰ and photochemistry.²¹ Feringa and coworkers developed a temperature and light-driven molecular motor for the thio-Michael addition in 2011.¹⁹ This motor enables an in-situ switching of the chiral preference of the catalyst system by a 360° unidirectional rotation. This controlled motion switches the configuration of the organocatalyst and enables control over stereoselectivity. Macmillan and coworkers demonstrated the mechanistic switching of the activity of a Ni(II) catalyst in the C–O cross-coupling between aryl bromides and alcohols.²⁰ Since the reductive elimination of the product is elusive with Ni(II) complexes, activation of this step was achieved by oxidation to Ni(III) by means of an Ir(II) photocatalyst. In 2020, Torres and coworkers reported on a dual light-driven Pd catalyst, whose activity in carbonylation reactions could be switched on by visible blue LED light.²¹

We reported recently on a Ir catalyst able to undergo both ways of hydrogen activation (oxidative addition and heterolytic dihydrogen cleavage, Figure 1B)²² and report here on the ability of this catalyst (family) to switch between these two types of mechanisms (Figure 1C). A symmetric alkyne (nonpolar C–C bond) is hydrogenated more than 1000 times faster in the protonated state than the deprotonated state and, inversely, benzophenone (polar C–O multiple bond) is hydrogenated more than 100 times faster in the deprotonated state. We switch between the two states by adding (or removing) two equivalents of a potassium base. The catalytically active species for both states are well-defined molecular Ir hydride compounds. Additionally, other important hydrogenation reactions, such as reductive amination employing hydrogen as the reducing agent²³ and the hydrogenation of nitroarenes, were investigated and different rates in the two states of the catalyst were observed.

RESULTS AND DISCUSSION

We used the Ir(I) pincer complex [Ir(COD)] as a precatalyst for this study (Figure 2). The synthesis of the protonated and metalated iridium(III) trihydride species (H₂[IrH₃] and K₂[IrH₃], respectively) were achieved at 1 bar H₂ at room temperature in a few minutes. H₂[IrH₃] was introduced by our group in 2013.²² The driving force which facilitates this reaction is the transformation of the 16 valence electron precursor [Ir(COD)] to a coordinately saturated 18 valence electron iridium(III) trihydride H₂[IrH₃]. This reaction is optically noticeable by a color change from red to yellow. Both NH functions of the ligand were deprotonated by the addition of 2.00 eq. KO^tBu, with potassium acting as a counter ion, delivering K₂[IrH₃]. The 12-crown-4-stabilized analogue of this complex was characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis (Supporting Information). The only difference between

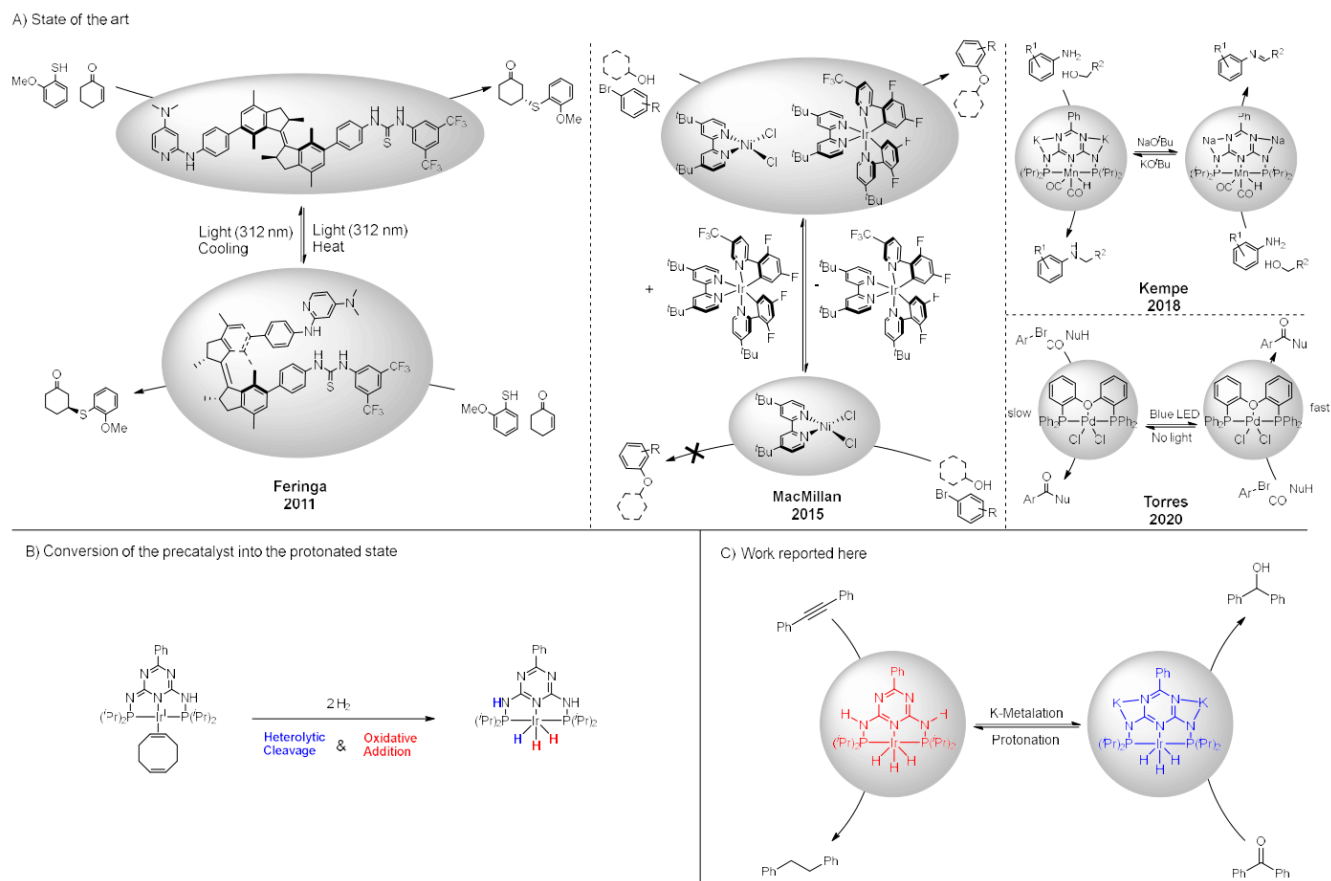


Figure 1. State of the art (A), conversion of the precatalyst into the protonated state (B), and work reported here (C).

$\text{H}_2[\text{IrH}_3]$ and $\text{K}_2[\text{IrH}_3]$ is the charge compensating atom (H or K) of the negatively charged pincer ligand. We conducted time conversion experiments to analyze the differences in catalytic activity between $\text{H}_2[\text{IrH}_3]$ and $\text{K}_2[\text{IrH}_3]$. Benzophenone was chosen as representative of compounds with a polar unsaturated bond (Figure 3A). The yields were determined by in-situ ^1H NMR measurements at the desired time tact and temperature. A Wilmad® quick pressure valve NMR tube (5 mm diameter; max. 150 psi) was used to carry out the reaction under H_2 pressure. Benzophenone was hydrogenated to diphenylmethanol without base in 11 % yield within 12 hours. Potassium-assisted hydrogenation with $\text{K}_2[\text{IrH}_3]$ was faster, achieving full conversion of the ketone in only one hour. The electrophilicity of an alkali metal is higher than that of a proton, attracting nucleophilic moieties (e.g. ketones by the O atom).^{11,13,14} Therefore, $\text{K}_2[\text{IrH}_3]$ facilitates the hydrogenation of polar compounds. It is possible to switch the activity on or off by adjusting the dominant active species ($\text{H}_2[\text{IrH}_3]$ or $\text{K}_2[\text{IrH}_3]$; Figure 2). In the case of $\text{H}_2[\text{IrH}_3]$, a solution of precatalyst and substrate was pressurized with H_2 to generate the active species. The switching of the catalytic activity from slow to fast was enabled by the prior addition of 2.00 eq. KO^tBu to the precatalyst and substrate solution. Pressurization with H_2 gas gives rise to the deprotonated/K-metalated active species $\text{K}_2[\text{IrH}_3]$, which boosts the reaction rate.

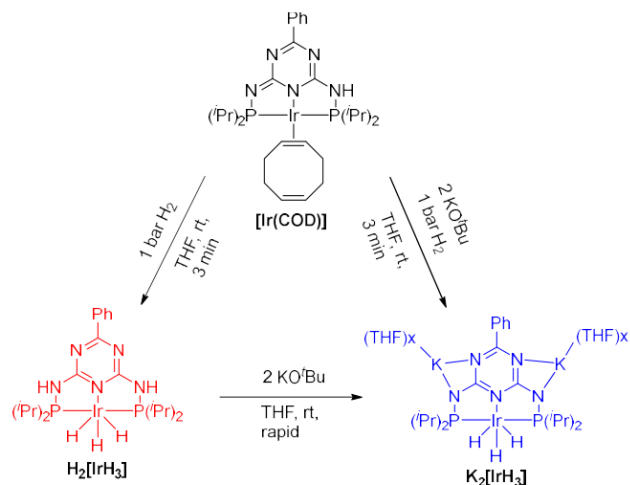


Figure 2. Synthesis of the active iridium(III) trihydride species.

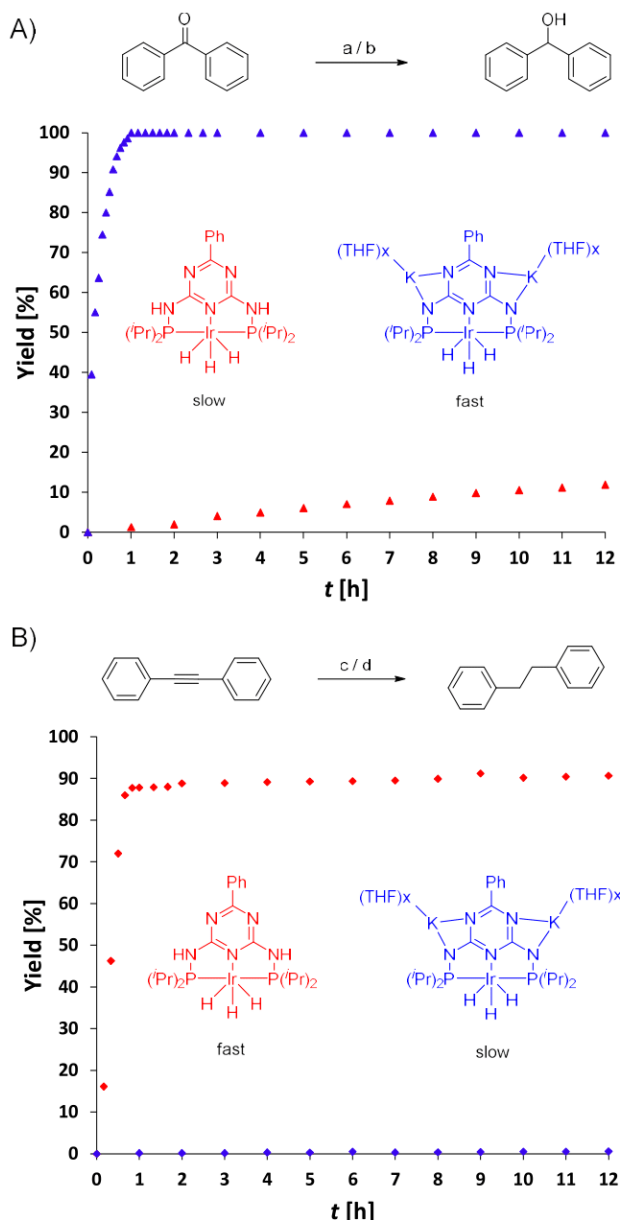


Figure 3. In-situ hydrogenation of benzophenone (A) and diphenylacetylene (B) without base (red) and utilizing 2.00 eq. KO^tBu (blue). Reaction conditions: a) 1.00 mol% [Ir(COD)], 5 bar H₂, THF-d₈, 80 °C; b) 1.00 mol% [Ir(COD)], 2.00 mol% KO^tBu, 5 bar H₂, THF-d₈, 80 °C; c) 1.00 mol% [Ir(COD)], 8 bar H₂, THF-d₈, 80 °C; d) 1.00 mol% [Ir(COD)], 2.00 mol% KO^tBu, 8 bar H₂, THF-d₈, 80 °C.

Furthermore, we aimed for the utilization of both catalysts in the hydrogenation of a nonpolar multiple bond and chose diphenylacetylene. The yield of the main product (1,2-diphenylethane) was plotted against the reaction time (Figure 3B). Semi-hydrogenation product (*cis*-stilbene) was also formed up to 18 % yield within the first hour (Supporting Information) but was further converted to 1,2-diphenylethane throughout the reaction, leaving only traces of *cis*-stilbene (3.3 %) after 12 hours. The activity dropped if KO^tBu was added prior to the reaction (Figure 3B; blue plot). We observed the opposite behavior of the catalyst here, compared to the hydrogenation of benzophenone. In

this scenario, the activity was switched off by metalation/deprotonation.

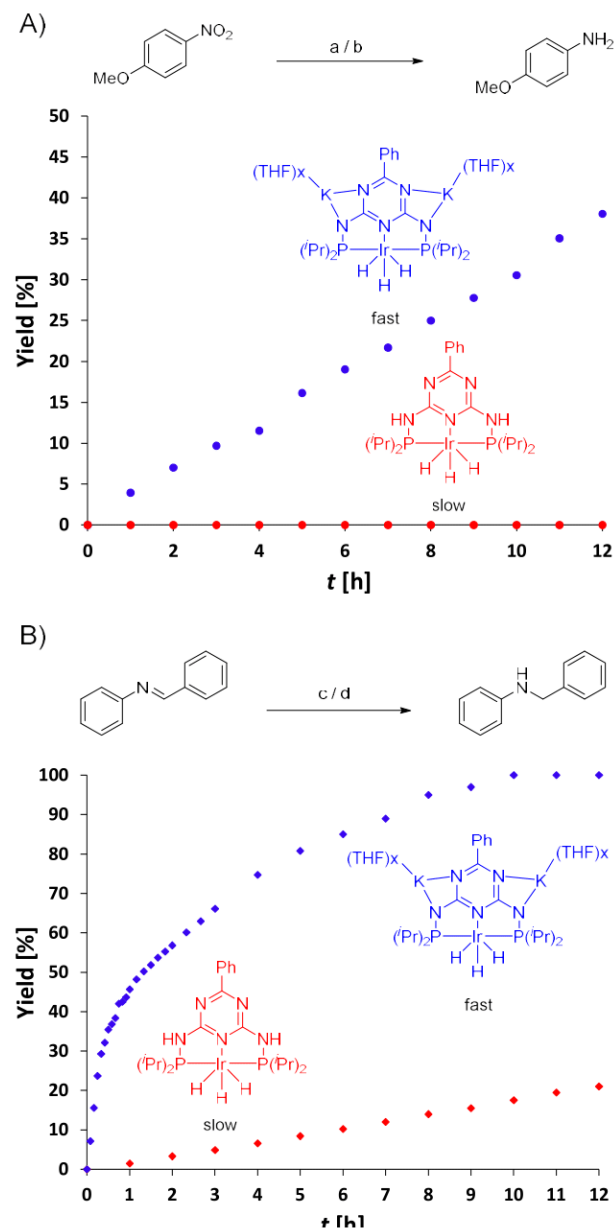


Figure 4. In-situ hydrogenation of 1-methoxy-4-nitrobenzene (A) and *N*-phenylbenzylimine (B) without base (red) and utilizing 2.00 eq. KO^tBu (blue). Yields were determined by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard. Reaction conditions: a) 5.00 mol% [Ir(COD)], 8 bar H₂, THF-d₈, 80 °C; b) 5.00 mol% [Ir(COD)], 2.00 mol% KO^tBu, 8 bar H₂, THF-d₈, 80 °C; c) 1.00 mol% [Ir(COD)], 5 bar H₂, THF-d₈, 80 °C; d) 1.00 mol% [Ir(COD)], 2.00 mol% KO^tBu, 5 bar H₂, THF-d₈, 80 °C.

The switching of the catalytic activity was also observed in the hydrogenation of 1-methoxy-4-nitrobenzene, which was chosen as a representative for nitro arenes (Figure 4A). In this case, the nitro compound could be hydrogenated to the corresponding amine only by the utilization of K₂[IrH₃], from which 38 % of the corresponding amine was formed

in 12 hours. No reaction occurred utilizing $\text{H}_2[\text{IrH}_3]$, where no base was added. This observation is comprehensible, since nitro groups are polar and better suited for hydrogenation by the potassium-assisted mechanism.

Another compound class with polar unsaturated double bonds is the imines. The hydrogenation of imines is an important reaction step of the reductive amination employing hydrogen. *N*-Phenylbenzylamine was chosen (Figure 4B). The activities observed look very similar to those from the hydrogenation of benzophenone (Figure 3A). Hydrogenation utilizing $\text{H}_2[\text{IrH}_3]$ delivered only 21 % *N*-benzylaniline in 12 hours, while full conversion was achieved utilizing $\text{K}_2[\text{IrH}_3]$ for the same reaction time.

Table 1. Comparison of the initial rates for the hydrogenation of benzophenone to diphenylmethanol, diphenylacetylene to diphenylethane, 1-methoxy-4-nitrobenzene to 4-methoxyaniline, and *N*-phenylbenzylamine to *N*-benzylaniline.

Product	Initial rate [$\mu\text{mol/h}$]	
	Base-free	2 mol% KO^tBu
Diphenylmethanol ^a	1.69 ± 0.07	150.63 ± 23.43
1,2-Diphenylethane ^b	190.10 ± 13.0	0.05 ± 0.01
4-Methoxyaniline ^c	–	4.31 ± 0.06
<i>N</i> -Benzylaniline ^a	2.28 ± 0.05	110.95 ± 8.23

Reaction conditions: a) 139 μmol substrate, 1.00 mol% $[\text{Ir}(\text{COD})]$, 5 bar H_2 , THF- d_8 , 80 °C; b) 139 μmol substrate, 1.00 mol% $[\text{Ir}(\text{COD})]$, 8 bar H_2 , THF- d_8 , 80 °C; c) 139 μmol substrate, 5.00 mol% $[\text{Ir}(\text{COD})]$, 8 bar H_2 , THF- d_8 , 80 °C.

The initial rates of the reactions investigated from Figures 3 and 4 were determined by linear regression of the initial points and are shown in Table 1. The activity differences are significant in each case of the reactions analyzed in Table 1. Ketone hydrogenation was 89 times and imine hydrogenation 49 times faster utilizing the potassium-assisted mechanism. The hydrogenation of diphenylacetylene was 3802 times faster catalyzed by OA and reductive elimination than by the potassium-assisted mechanism (Table 1).

CONCLUSION

A molecular Ir catalyst that can activate hydrogen by OA and heterolytic cleavage of H_2 and has two catalytically active stages: a protonated and a deprotonated/metalated state, was investigated. The deprotonated/metalated stage can be reached by the addition of two equivalents of KO^tBu to the protonated stage of the catalyst. The activity for a variety of hydrogenation reactions differs drastically in the two stages of the catalyst. Keton hydrogenation is very slow in the protonated state and more than 80 times faster in the deprotonated/metalated stage. By contrast, hydrogenation

of a symmetric nonpolar alkyne proceeds more than 3000 times faster in the protonated state. Assuming that the polar multiple C-O bond of a ketone is hydrogenated via the redox neutral heterolytic cleavage of H_2 and the nonpolar multiple C-C bond of an alkyne via redox active OA of H_2 , we conclude that the Ir catalyst investigated here is switchable between both mechanistic pathways (for selected substrates).

ASSOCIATED CONTENT

Experimental procedures, and spectroscopic and crystallographic data are found in the Supporting Information.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This work was financially supported by the DFG (Deutsche Forschungsgemeinschaft), KE 756/37-1 and the University of Bayreuth.

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

OA: Oxidative Addition;
RE: Reductive Elimination;
COD: Cyclooctadiene;
Nu: Nucleophile;
NMR: Nuclear Magnetic Resonance;
THF: Tetrahydrofuran.

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7.2 Supporting Information

Mechanistically Switchable Hydrogenation Catalysis

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7.3 General considerations

All reactions were carried out in a glove box filled with nitrogen N₂ (5.0) or using Schlenk techniques. THF was purified by distillation over drying agent (sodium or LiAlH₄) and stored over molecular sieves (3 Å). 12-crown-4 was dried over molecular sieves (3 Å). THF-d₈ was dried by storing over KH for at least seven days. Other chemicals were purchased from commercial vendors, purified either by crystallization, sublimation or distillation and dried at least for 24 hours under high vacuum.

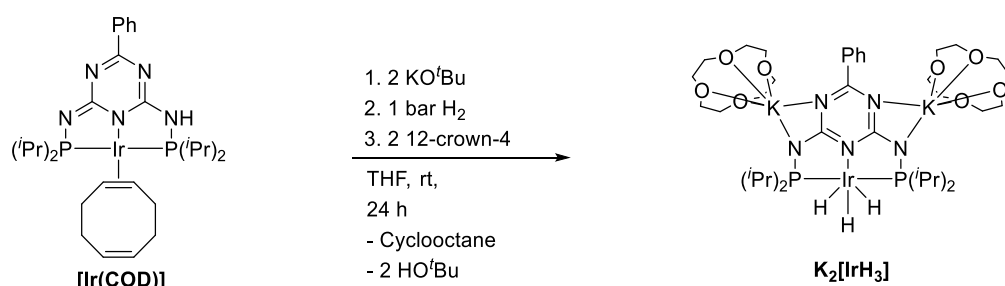
NMR measurements were performed at room temperature, if not stated otherwise, on a *Varian* INOVA 300 or on a *Varian* INOVA 400. The chemical shift is given in the δ -scale. Following symbols were used for the description of the signals: s = singulett, d = doublet, t = triplet, q = quartet, quin = quintet, sx = sextet, sep = septet, m = multiplet. Coupling constants *J* were given in Hz. ¹³C NMR spectra were measured ¹H decoupled.

High pressure NMR measurements were conducted using a Wilmad quick pressure valve NMR tube (5 mm diameter; max. 150 psi). Spectra were processed with MesstRenova 6.1.0-6224¹.

7.4 Experimental procedures

The iridium complexes **[Ir(COD)]** and **[IrH₃]** were synthesized according to literature.² All catalytic reactions were investigated using *in-situ* ¹H NMR measurements which were acquired with a desired time tact. The quantitative analysis was accomplished by integration of a selected product signal and referencing with one of the internal standard (1,3,5-trimethoxybenzene) signals. The NMR spectrometer was pre-heated at the desired temperature and the measurement was started immediately after insertion of the NMR tube.

7.4.1 Synthesis of K₂[IrH₃]



Supplementary Figure 2. Synthesis of **K₂[IrH₃]**.

A solution of precatalyst **[Ir(COD)]** (100 mg, 139 μmol) and KO^tBu (77.9 mg, 695 μmol) in THF (6.0 mL) was purged multiple times with H₂ in a Schlenk tube and a rapid color change from red to yellow could be observed. Subsequently 12-crown-4 (112 μL, 695 μmol) was added to the reaction mixture and the solution was left to precipitate at – 23 °C for 24 hours. The precipitated yellow solid was filtered and dried under high vacuum.

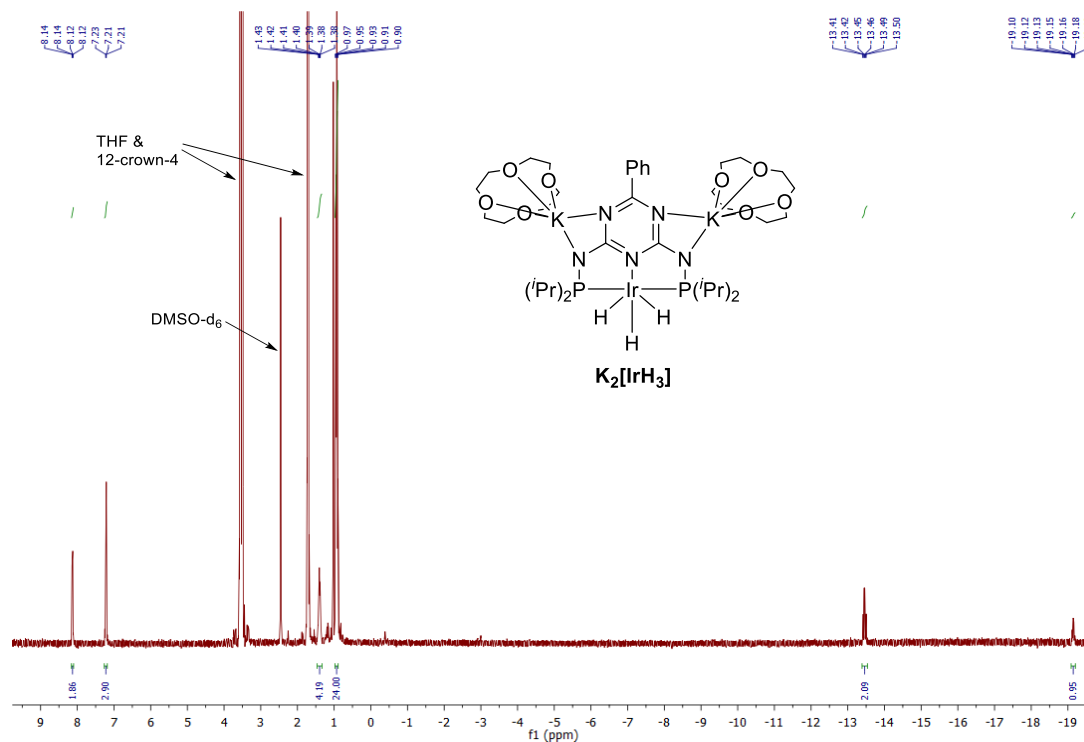
Yield: 80.0 mg (53 %, 74.3 μmol)

¹H NMR (300 MHz, DMSO-*d*₆, 298 K): δ = 8.13 (dd, *J* = 2.4, 7.3 Hz, 2H, Ar-*H*), 7.23–7.21 (m, 3H, Ar-*H*), 1.40 (sep, *J* = 6.8 Hz, 4H, P-*CH*), 0.93 (quin, *J* = 7.2 Hz, 24H, CH₃), – 13.45 (dt, *J* = 5.7, 15.7 Hz, 2H, Ir-*H*), – 19.50 (ddd, *J* = 5.6, 11.3, 18.0 Hz, 1H, Ir-*H*) ppm.

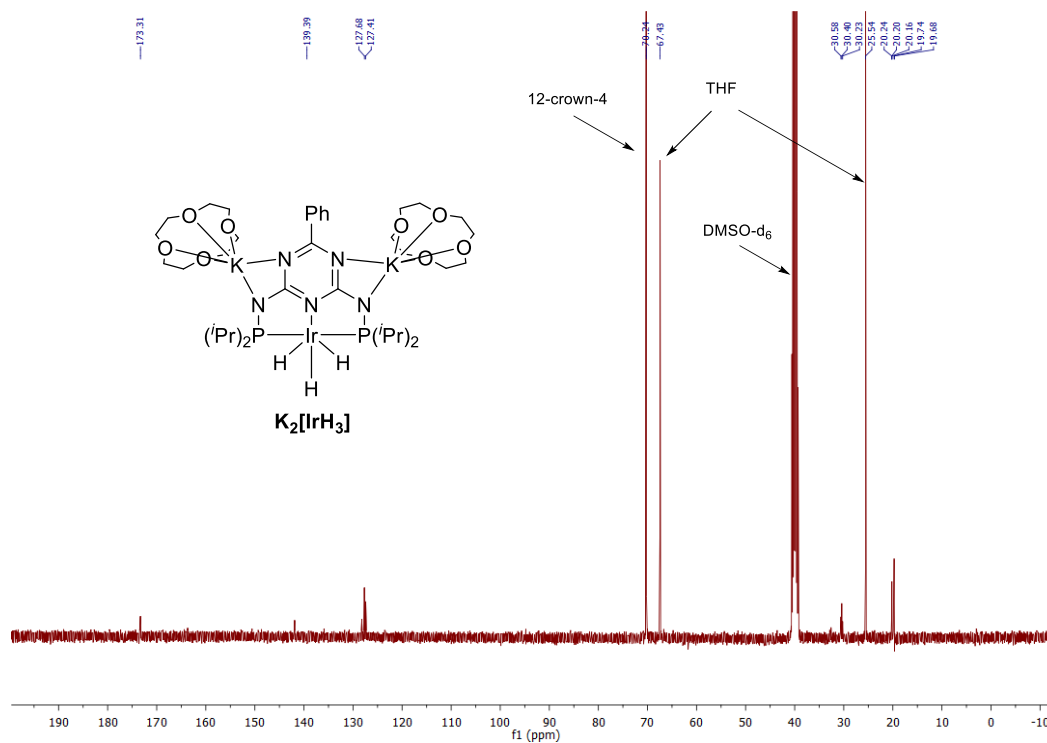
¹³C NMR (75.5 MHz, DMSO-*d*₆, 298 K): δ = 173.3, 139.3, 127.6, 127.4, 70.2, 67.4, 30.5, 30.4, 30.2, 25.5, 20.2, 20.2, 20.1, 19.7, 19.6 ppm.

Elemental analysis calculated: C 43.56, H 7.12, N 6.51; found: C 43.12, H 7.10, N 6.22.

7.5 Attachments

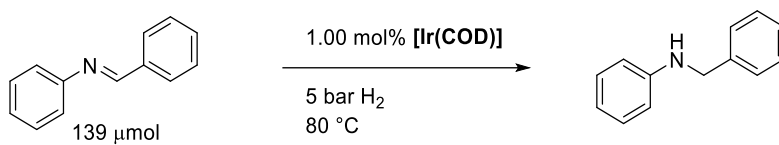


Supplementary Figure 5. 1H NMR spectrum of $K_2[IrH_3]$.



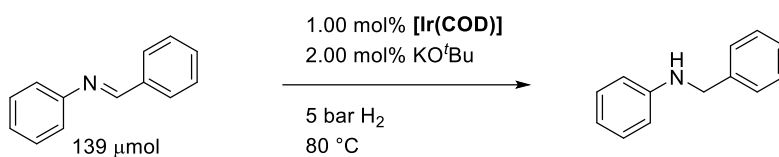
Supplementary Figure 6. ^{13}C NMR spectrum of $K_2[IrH_3]$.

Supplementary Table 1. Time-conversion data for the base-free imine hydrogenation.



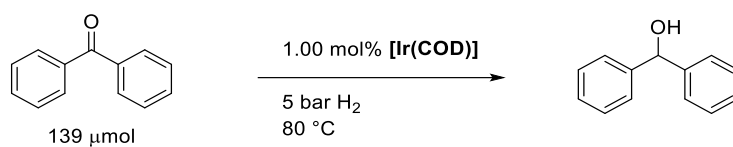
Entry	<i>t</i> [h]	Yield [%]	Yield [μmol]
1	0	0	0
2	1	1.5	2.1
3	2	3.3	4.6
4	3	4.9	6.8
5	4	6.6	9.2
6	5	8.4	11.7
7	6	10.2	14.2
8	7	12.0	16.7
9	8	14.0	19.5
10	9	15.5	21.5
11	10	17.5	24.3
12	11	19.5	27.1
13	12	21.0	29.2

Supplementary Table 2. Time-conversion data for the potassium assisted imine hydro-
genation.



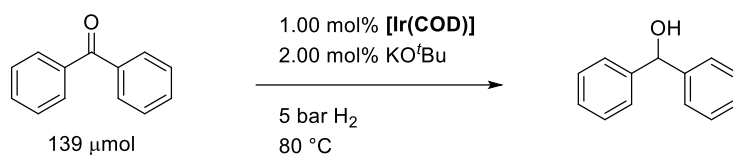
Entry	<i>t</i> [h]	Yield [%]	Yield [μmol]
1	0	0	0
2	0.083	7.1	9.9
3	0.166	15.5	21.6
4	0.250	23.7	32.9
5	0.333	29.3	40.7
6	0.416	32.1	44.7
7	0.500	35.5	49.3
8	0.583	36.8	51.1
9	0.666	38.3	53.3
10	0.750	42.0	58.3
11	0.833	42.5	59.1
12	0.916	43.6	60.6
13	1.000	45.7	63.5
14	1.166	48.2	67.0
15	1.333	50.2	69.8
16	1.500	51.8	72.0
17	1.666	53.7	74.7
18	1.833	55.3	76.8
19	2.000	56.8	79.0
20	2.333	60.1	83.5
21	2.666	62.9	87.5
22	3	66.1	91.9
23	4	74.7	103.9
24	5	80.8	112.3
25	6	84.9	118.1
26	7	89.0	123.7
27	8	95.0	132.1
28	9	97.0	134.8
29	10	99.9	139.0
30	11	99.9	138.9
31	12	99.9	139.9

Supplementary Table 3. Time-conversion data for the base-free ketone hydrogenation.



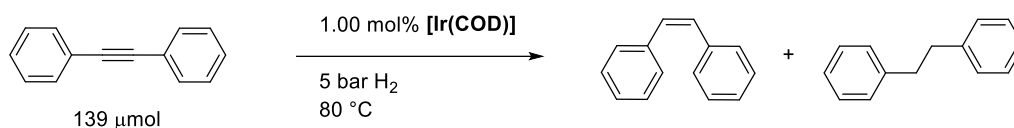
Entry	<i>t</i> [h]	Yield [%]	Yield [μmol]
1	0	0	0
2	1	1.3	1.8
3	2	2.0	2.7
4	3	4.0	5.6
5	4	4.9	6.9
6	5	6.0	8.4
7	6	7.0	9.8
8	7	7.9	11.0
9	8	8.9	12.3
10	9	9.8	13.6
11	10	10.5	14.6
12	11	11.1	15.5
13	12	11.8	16.5

Supplementary Table 4. Time-conversion data for the potassium assisted ketone hydrogenation.



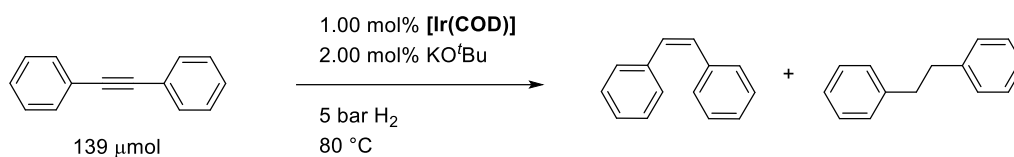
Entry	t [h]	Yield [%]	Yield [μmol]
1	0	0	0
2	0.083	39.5	54.9
3	0.166	55.0	76.5
4	0.250	63.7	88.5
5	0.333	74.5	103.5
6	0.416	80.0	111.2
7	0.500	85.2	118.4
8	0.583	90.8	126.3
9	0.666	94.1	130.8
10	0.750	96.3	133.8
11	0.833	97.5	135.6
12	0.916	98.6	137.1
13	1.000	99.9	138.9
14	1.166	99.9	138.9
15	1.333	99.9	138.9
16	1.500	99.9	138.9
17	1.666	99.9	138.9
18	1.833	99.9	138.9
19	2.000	99.9	138.9
20	2.333	99.9	138.9
21	2.666	99.9	138.9
22	3	99.9	138.9
23	4	99.9	138.9
24	5	99.9	138.9
25	6	99.9	138.9
26	7	99.9	138.9
27	8	99.9	138.9
28	9	99.9	138.9
29	10	99.9	138.9
30	11	99.9	138.9
31	12	99.9	139.9

Supplementary Table 5. Time-conversion data for the base-free alkyne hydrogenation.



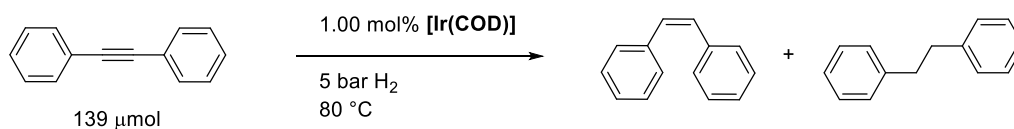
Entry	<i>t</i> [h]	<i>cis</i> -Stilbene		1,2-Diphenylethane	
		Yield [%]	Yield [μmol]	Yield [%]	Yield [μmol]
1	0	0	0	0	0
2	0.166	4.03	5.6	18.3	25.5
3	0.333	6.0	8.3	25.9	35.9
4	0.500	7.2	10.1	31.6	44.0
5	0.666	8.7	12.1	39.0	54.2
6	0.833	10.3	14.3	45.4	63.0
7	1.00	11.5	16.0	50.8	70.6
8	1.333	13.7	19.1	60.2	83.7
9	1.666	15.7	21.8	68.0	94.5
10	2	17.3	24.0	73.1	101.5
11	3	19.9	27.6	79.0	109.8
12	4	21.0	29.2	79.3	110.2
13	5	20.9	29.1	79.8	110.9
14	6	20.7	28.8	80.0	111.2
15	7	20.3	28.2	80.0	111.2
16	8	20.1	27.9	80.0	111.2
17	9	19.8	27.5	80.1	111.3
18	10	19.5	27.1	80.2	111.5
19	11	19.2	26.7	80.4	111.7
20	12	19.0	26.5	80.6	112.0

Supplementary Table 6. Time-conversion data for the potassium assisted alkyne hydrogenation.



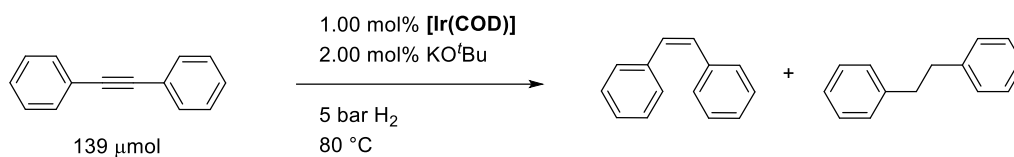
Entry	<i>t</i> [h]	<i>cis</i> -Stilbene		1,2-Diphenylethane	
		Yield [%]	Yield [μmol]	Yield [%]	Yield [μmol]
1	0	0	0	0	0
2	1	1.1	1.4	0.2	0.3
3	2	1.4	2.0	1.3	1.9
4	3	2.0	2.8	0.5	0.7
5	4	2.7	3.7	0.9	1.3
6	5	3.5	4.9	1.3	1.9
7	6	4.3	5.9	1.6	2.3
8	7	5.2	7.3	1.9	2.7
9	8	6.7	9.3	2.4	3.3
10	9	7.7	10.7	2.8	3.9
11	10	9.1	12.6	3.4	4.8
12	11	10.1	14.1	4.0	5.5
13	12	11.3	15.6	4.3	5.9

Supplementary Table 7. Time-conversion data for base-free alkyne hydrogenation.



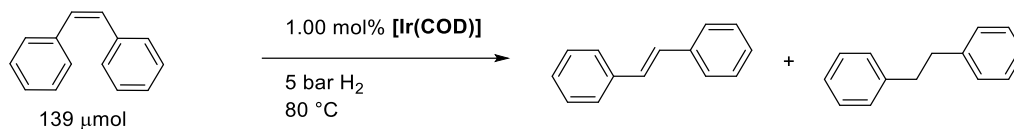
Entry	<i>t</i> [h]	<i>cis</i> -Stilbene		1,2-Diphenylethane	
		Yield [%]	Yield [μmol]	Yield [%]	Yield [μmol]
1	0	0	0	0	0
2	0.166	5.0	7.0	16.1	22.4
3	0.333	8.6	11.9	46.3	64.3
4	0.500	11.3	15.6	72.0	100.1
5	0.666	12.9	17.8	86.0	119.6
6	0.833	13.3	18.4	87.8	122.0
7	1.00	13.0	18.1	87.8	122.1
8	1.333	12.6	17.5	87.9	122.1
9	1.666	11.7	16.3	88.0	122.3
10	2	11.1	15.4	88.8	123.5
11	3	9.5	13.2	88.9	123.6
12	4	8.5	11.8	89.2	123.9
13	5	7.6	10.5	89.3	124.1
14	6	5.7	7.9	89.4	124.2
15	7	5.1	7.1	89.5	124.4
16	8	4.6	6.4	89.9	124.9
17	9	4.2	5.9	91.2	126.8
18	10	3.8	5.3	90.2	125.3
19	11	3.6	5.0	90.4	125.7
20	12	3.3	4.5	90.7	126.0

Supplementary Table 8. Time-conversion data for the potassium assisted alkyne hydrogenation.



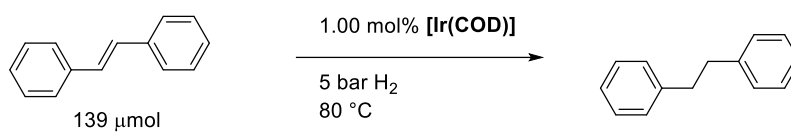
Entry	t [h]	<i>cis</i> -Stilbene		1,2-Diphenylethane	
		Yield [%]	Yield [μmol]	Yield [%]	Yield [μmol]
1	0	0	0	0	0
2	1	1.22	1.69	0.15	0.21
3	2	1.34	1.86	0.17	0.23
4	3	1.50	2.08	0.17	0.23
5	4	1.59	2.21	0.33	0.46
6	5	1.72	2.39	0.28	0.39
7	6	2.11	2.93	0.49	0.68
8	7	1.76	2.44	0.31	0.43
9	8	1.89	2.62	0.36	0.50
10	9	1.07	1.48	0.41	0.57
11	10	2.13	2.96	0.54	0.75
12	11	2.09	2.90	0.54	0.75
13	12	2.35	3.27	0.58	0.80

Supplementary Table 9. Time-conversion data for the base-free *cis*-Stilbene hydrogenation.



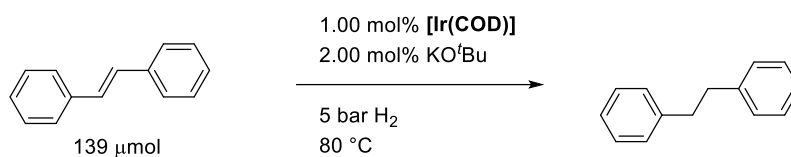
Entry	t [h]	<i>trans</i> -Stilbene		1,2-Diphenylethane	
		Yield [%]	Yield [μmol]	Yield [%]	Yield [μmol]
1	0	0	0	0	0
2	1	15.0	20.9	0.5	0.7
3	2	20.5	28.5	0.8	1.0
4	3	24.0	33.4	0.9	1.2
5	4	27.5	38.2	1.0	1.4
6	5	30.0	41.7	1.2	1.7
7	6	32.5	45.2	1.4	1.9
8	7	35.0	48.7	1.5	2.1
9	8	37.0	51.4	1.6	2.3
10	9	39.0	54.2	1.7	2.4
11	10	40.5	56.3	1.8	2.6
12	11	42.0	58.4	2.0	2.8
13	12	44.0	61.2	2.2	3.1

Supplementary Table 10. Time-conversion data for the base-free *trans-stilbene* hydrogenation.



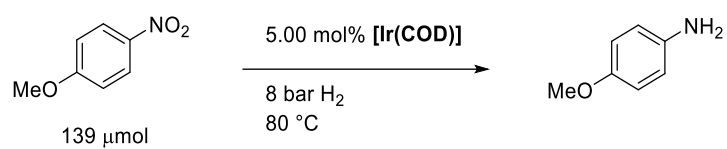
Entry	<i>t</i> [h]	Yield [%]	Yield [μmol]
1	0	0	0
2	1	1.8	2.4
3	2	1.9	2.6
4	3	2.1	2.9
5	4	2.2	3.1
6	5	2.4	3.8
7	6	2.5	3.5
8	7	2.6	3.7
9	8	2.9	4.0
10	9	2.9	4.1
11	10	3.1	4.3
12	11	3.2	4.4
13	12	3.3	4.6

Supplementary Table 11. Time-conversion data for the potassium assisted *trans*-stilbene hydrogenation.



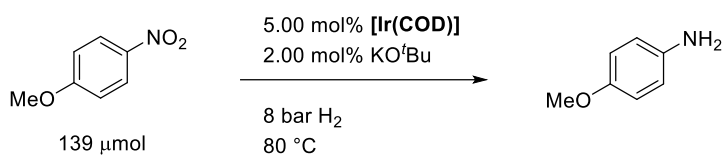
Entry	<i>t</i> [h]	Yield [%]	Yield [μmol]
1	0	0	0
2	1	0.7	0.9
3	2	0.8	1.2
4	3	0.8	1.2
5	4	0.9	1.2
6	5	0.9	1.3
7	6	1.0	1.3
8	7	1.1	1.5
9	8	1.1	1.5
10	9	1.2	1.6
11	10	1.2	1.7
12	11	1.2	1.7
13	12	1.3	1.9

Supplementary Table 12. Time-conversion data for the base-free 1-methoxy-4-nitrobenzene hydrogenation.



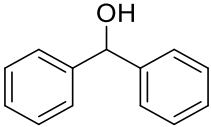
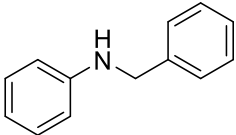
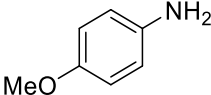
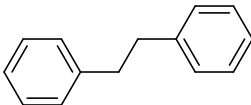
Entry	t [h]	Yield [%]	Yield [μmol]
1	0	0	0
2	1	0	0
3	2	0	0
4	3	0	0
5	4	0	0
6	5	0	0
7	6	0	0
8	7	0	0
9	8	0	0
10	9	0	0
11	10	0	0
12	11	0	0
13	12	0	0

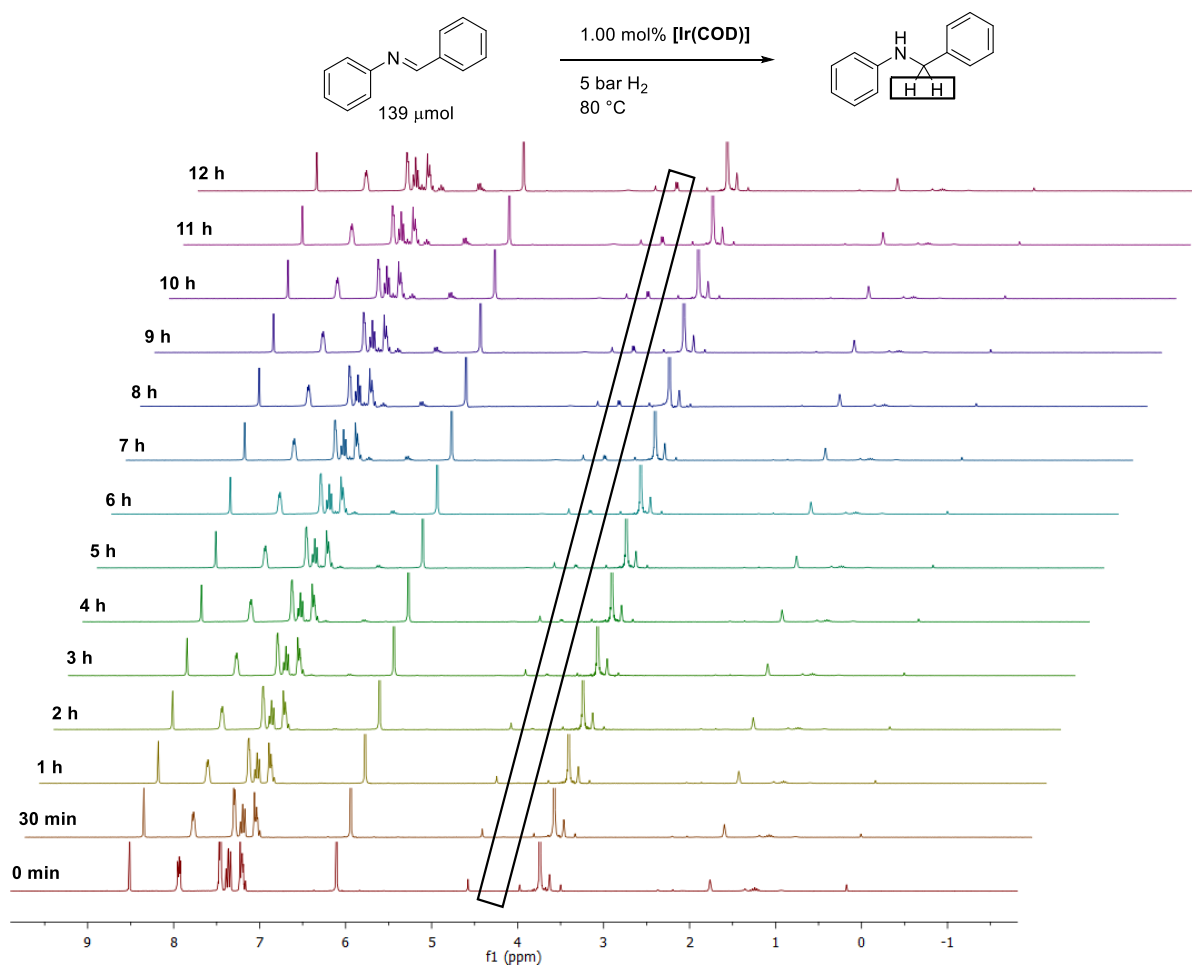
Supplementary Table 13. Time-conversion data for the potassium assisted 1-methoxy-4-nitrobenzene hydrogenation.



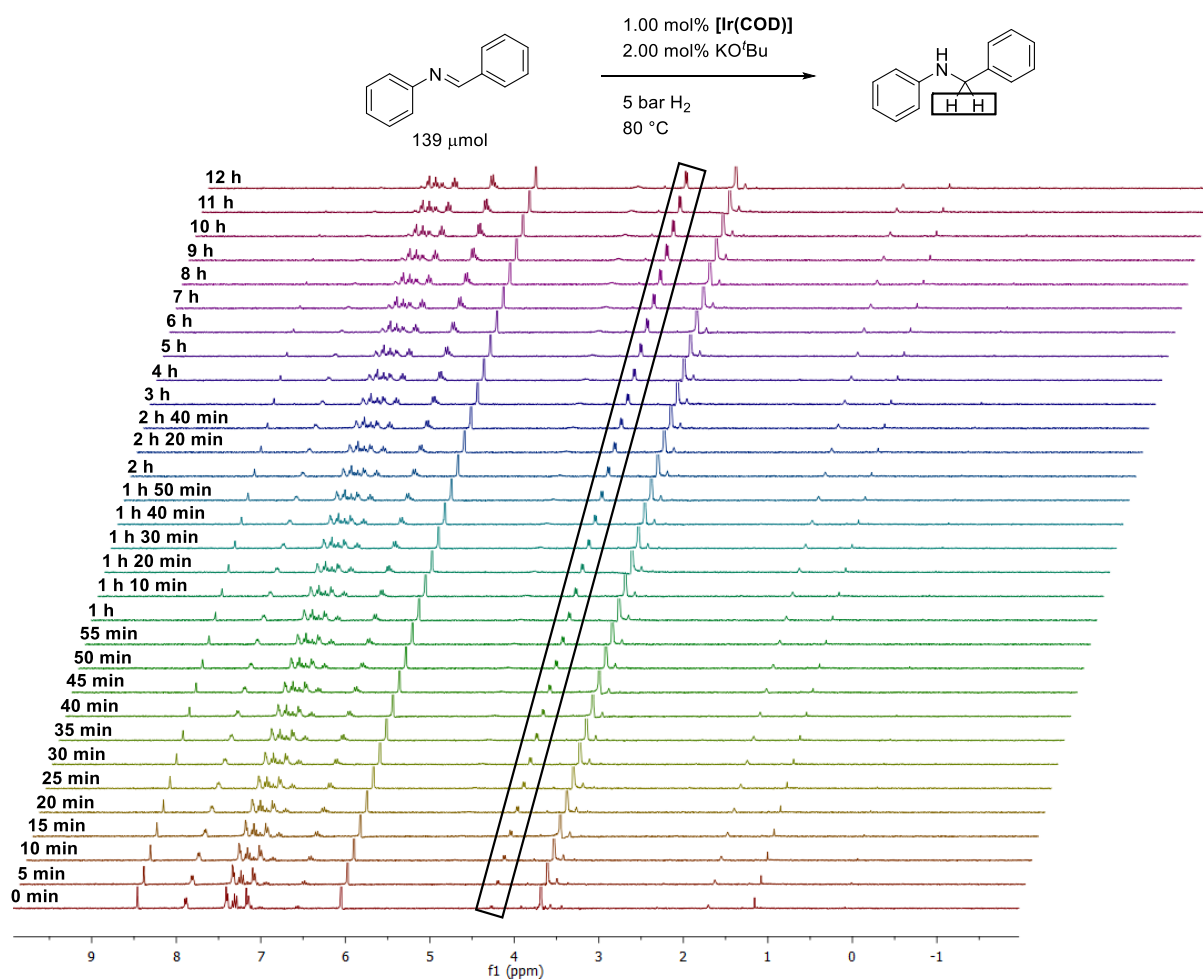
Entry	t [h]	Yield [%]	Yield [μmol]
1	0	0	0
2	1	3.94	5.47
3	2	7.02	9.75
4	3	9.67	13.44
5	4	11.52	16.01
6	5	16.13	22.42
7	6	19.01	26.42
8	7	21.67	30.12
9	8	24.98	34.72
10	9	27.75	38.57
11	10	30.54	42.45
12	11	35.03	48.69
13	12	38.04	52.87

Supplementary Table 14. Initial rates of the hydrogenation products.

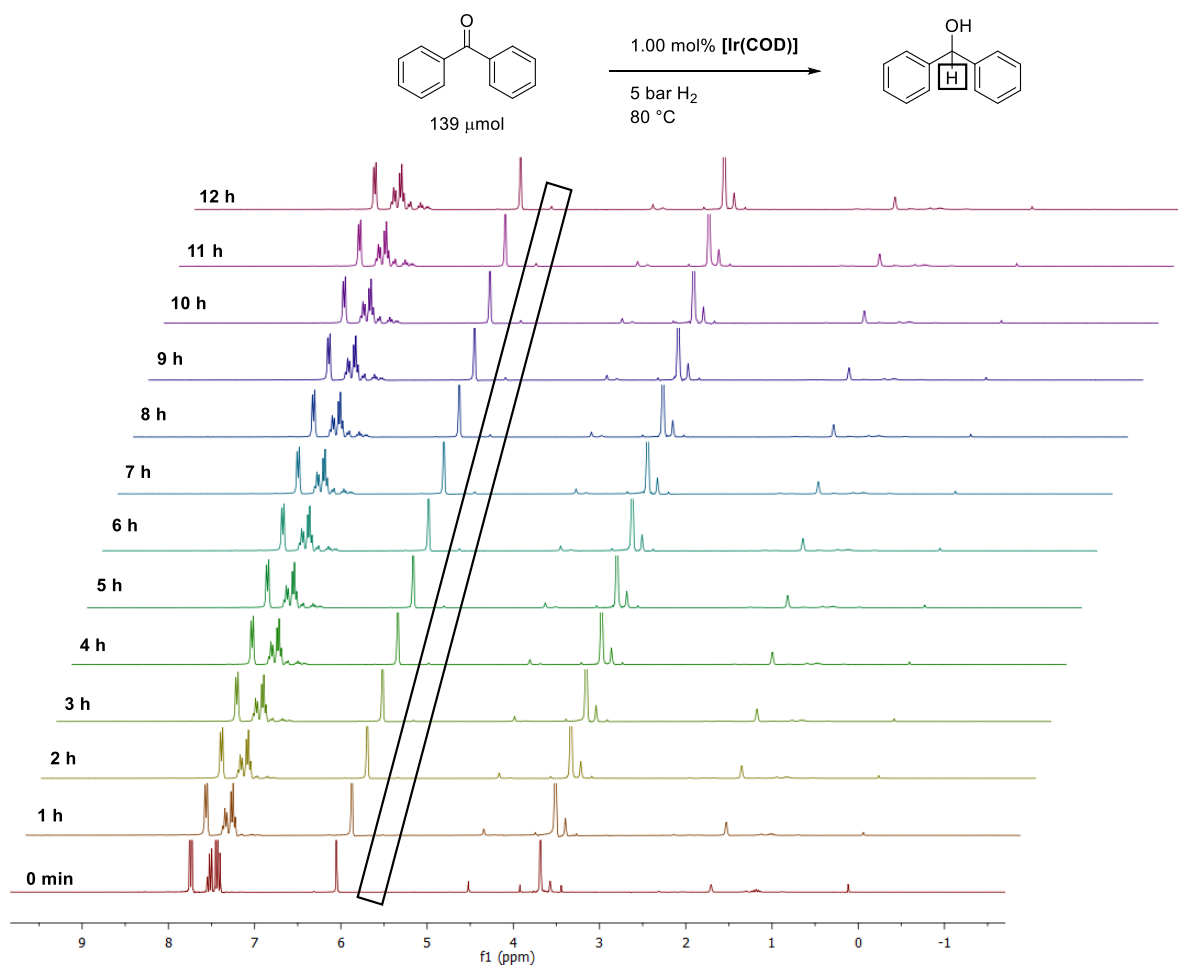
Hydrogenation Product	Base	Initial rate [$\mu\text{mol/h}$]	Error [$\mu\text{mol/h}$]
 Diphenylmethanol	—	1.69	± 0.07
 N-Benzylaniline	—	2.28	± 0.05
 4-Methoxyaniline	—	—	—
 1,2-Diphenylethane	—	190.10	± 13.0
	2.00 eq. KO ^t Bu	0.05	± 0.007



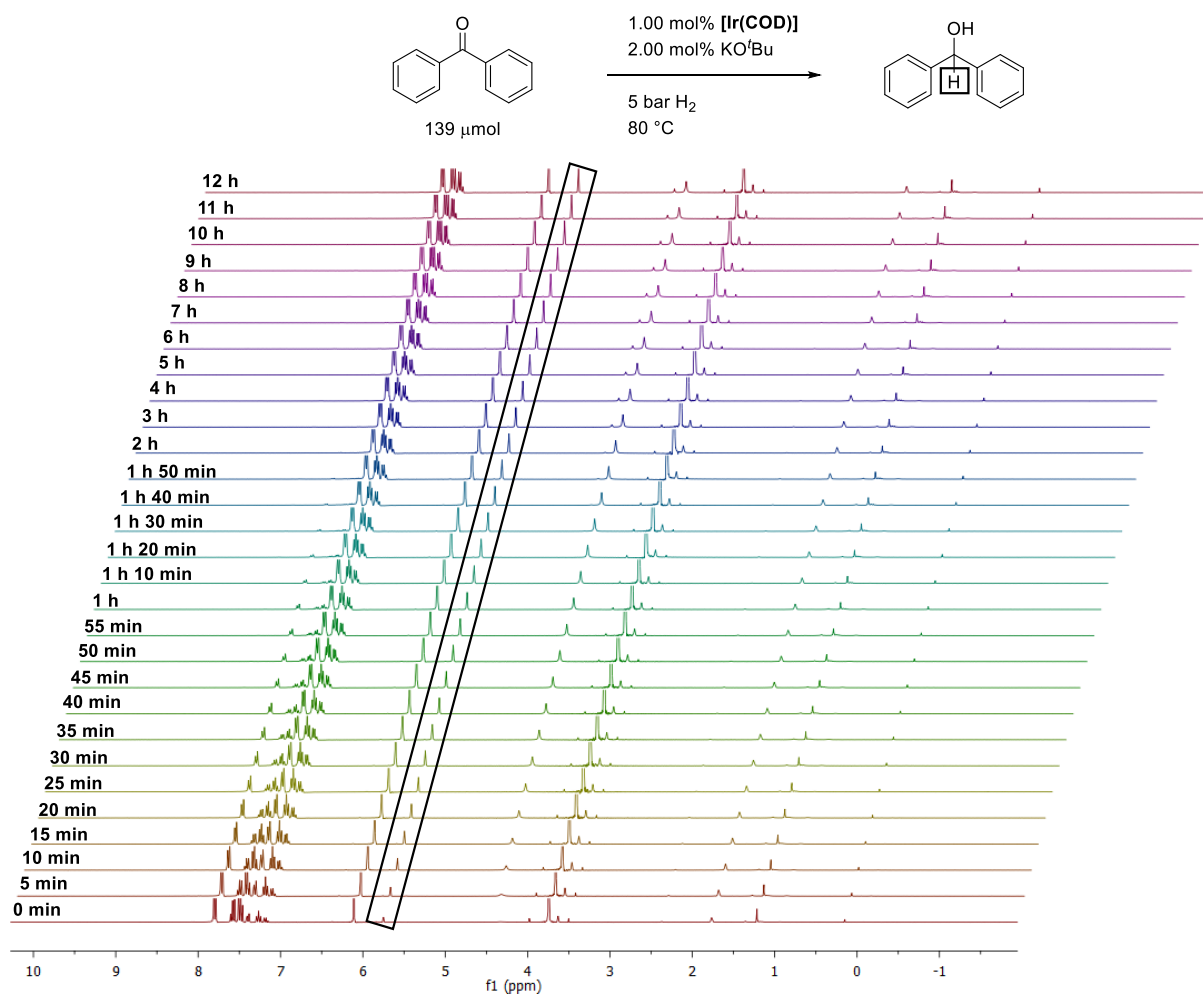
Supplementary Figure 7. Stacked ^1H NMR spectra of the *in-situ* hydrogenation of *N*-benzylideneaniline without base. One of the signals of the product was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



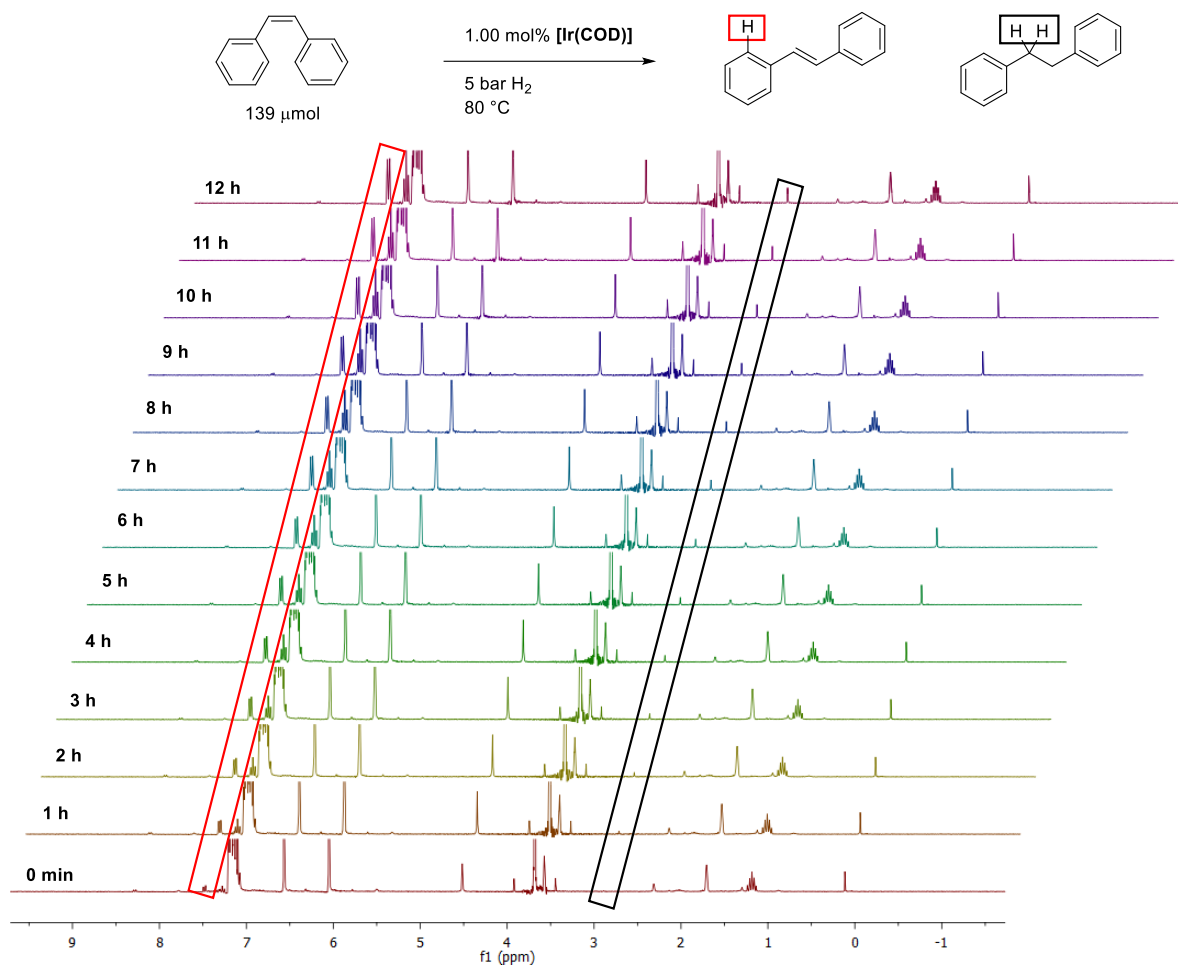
Supplementary Figure 8. Stacked ^1H NMR spectra of the *in-situ* hydrogenation of *N*-benzylideneaniline with 2 equivalents KO^tBu . One of the signals of the product was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



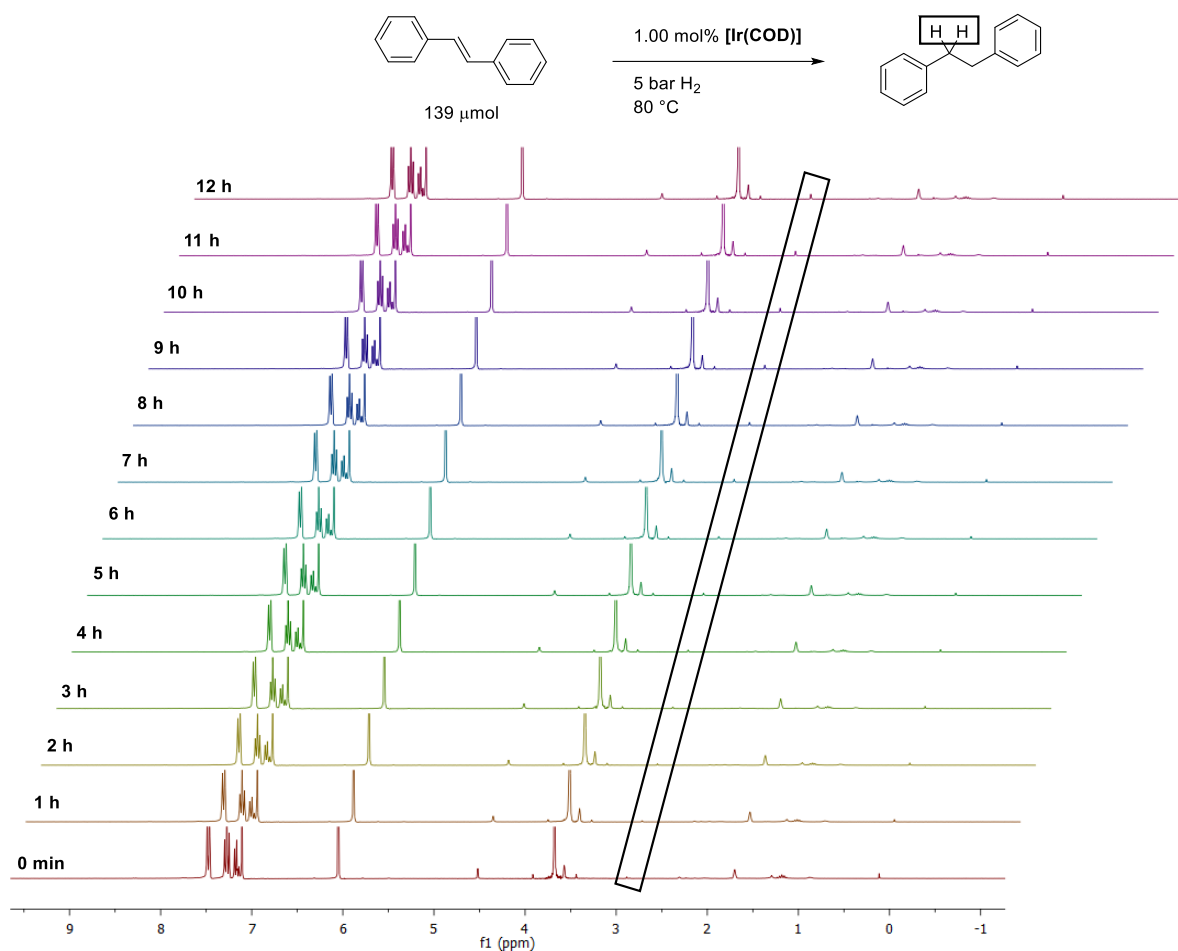
Supplementary Figure 9. Stacked ¹H NMR spectra of the *in-situ* hydrogenation of benzophenone without base. One of the signals of the product was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



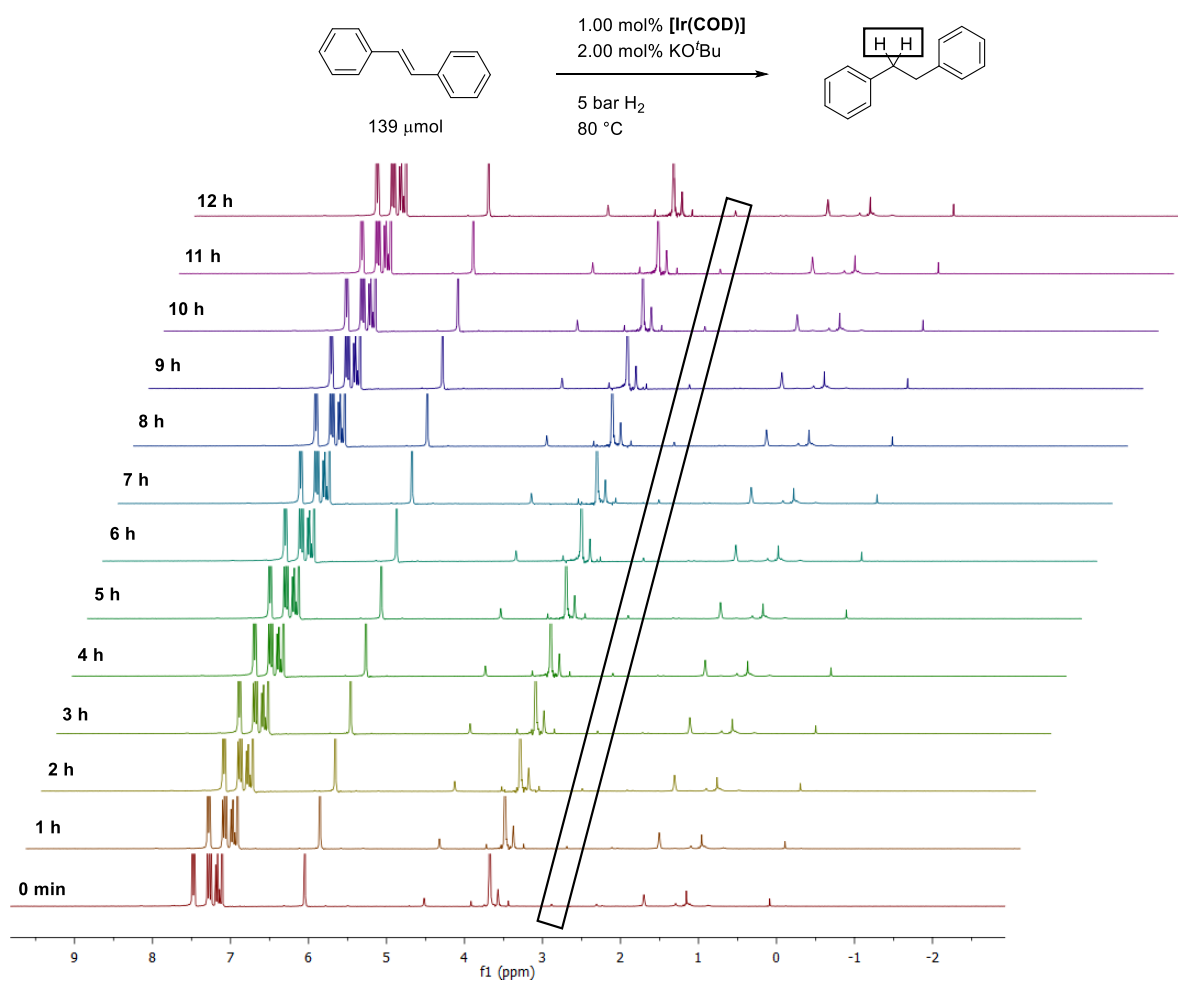
Supplementary Figure 10. Stacked ¹H NMR spectra of the *in-situ* hydrogenation of benzophenone with 2 equivalents KO^tBu. One of the signals of the product was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



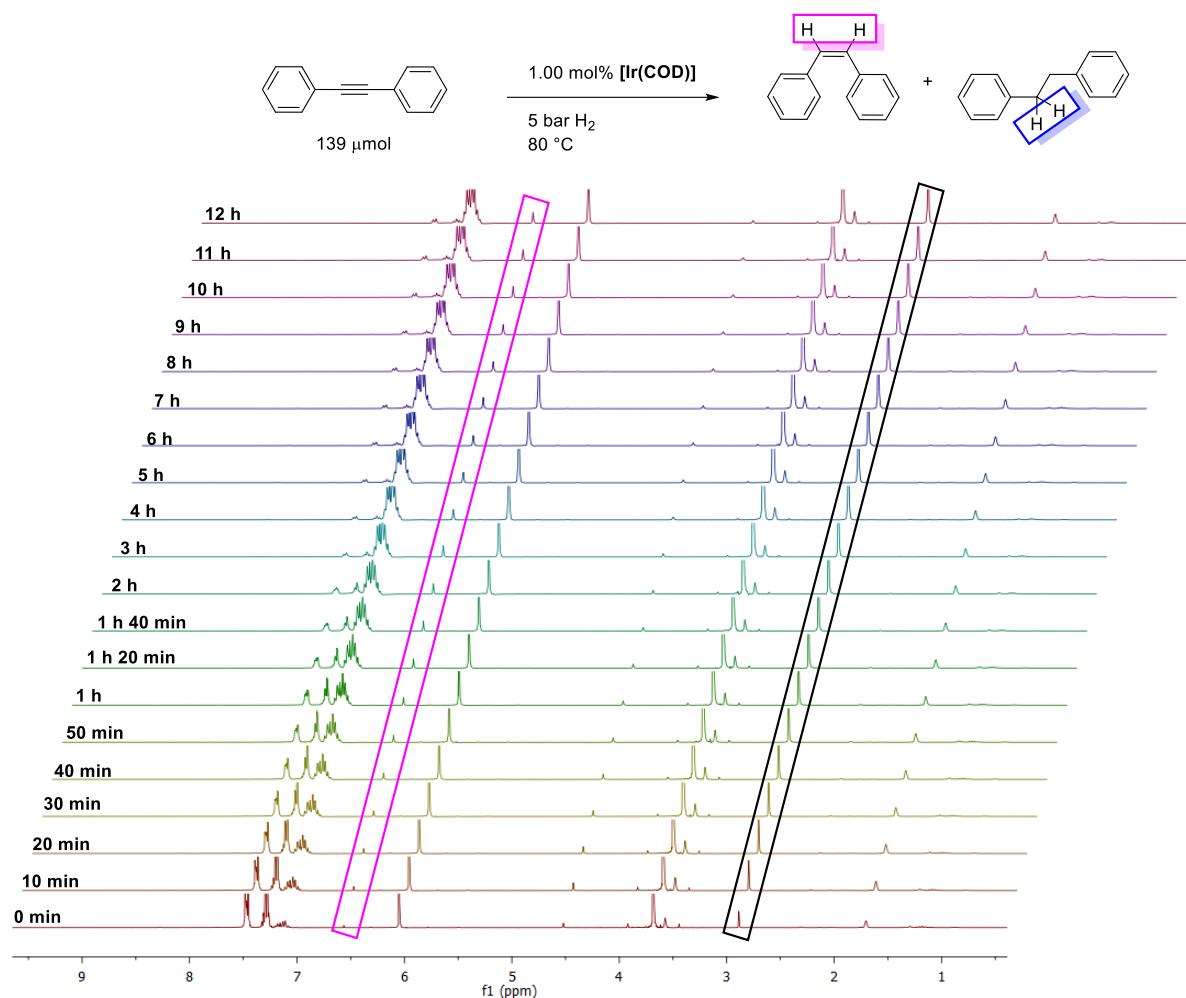
Supplementary Figure 11. Stacked ^1H NMR spectra of the *in-situ* hydrogenation of *cis*-stilbene without base. One of the signals of the product was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



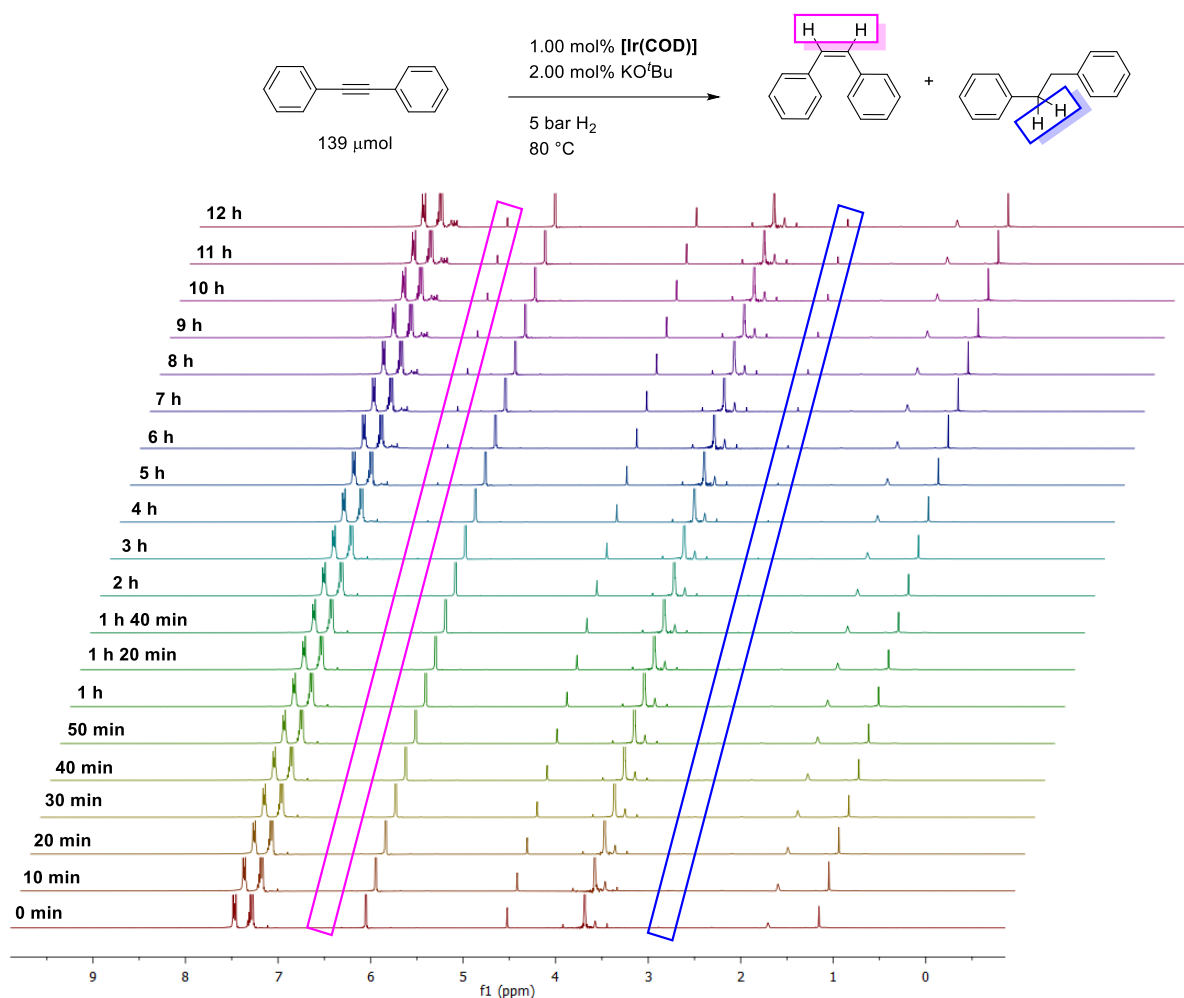
Supplementary Figure 12. Stacked ^1H NMR spectra of the *in-situ* hydrogenation of *trans*-stilbene without base. One of the signals of the product was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



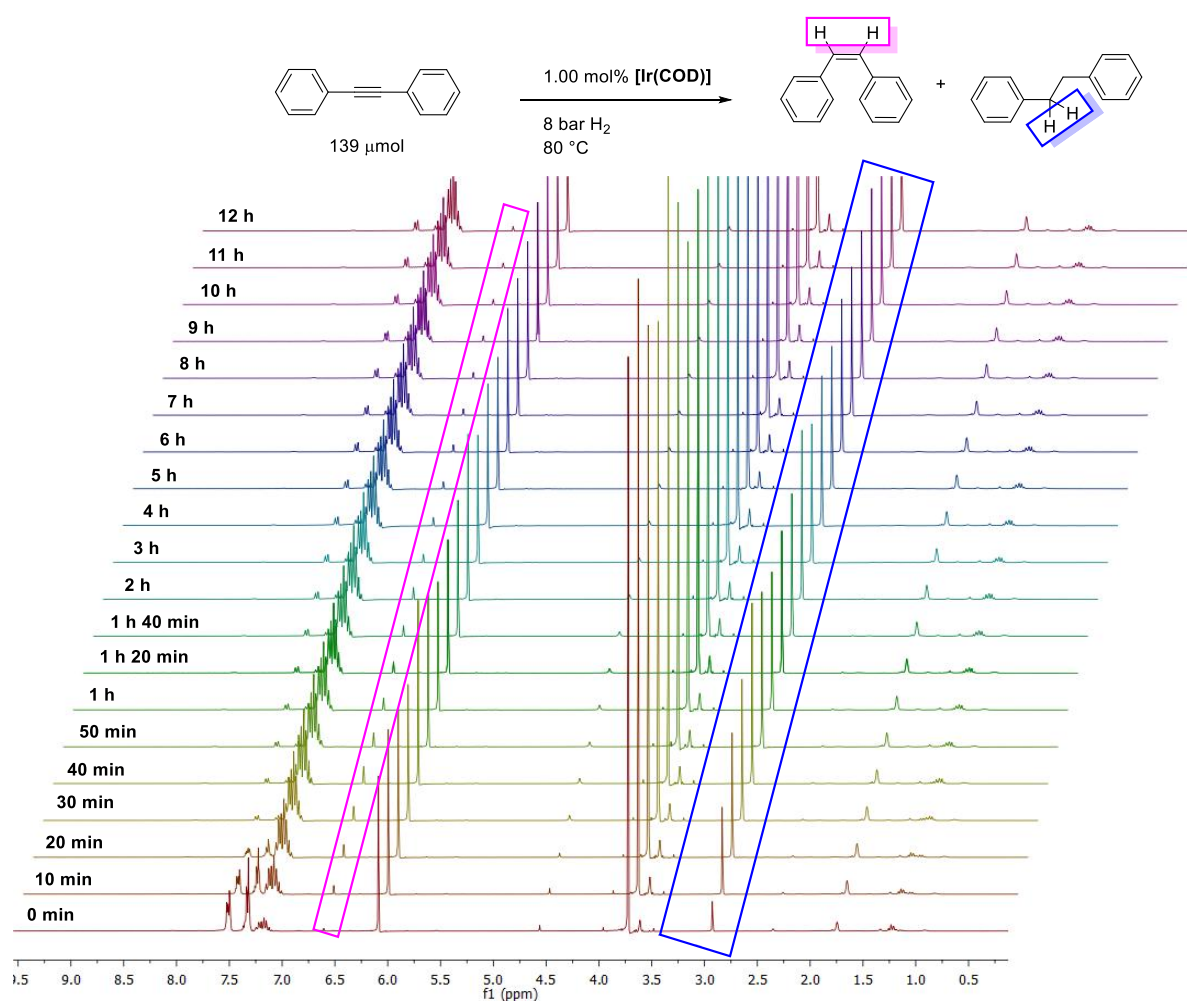
Supplementary Figure 13. Stacked ^1H NMR spectra of the *in-situ* hydrogenation of *trans*-stilbene with 2 equivalents KO^tBu . One of the signals of the product was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



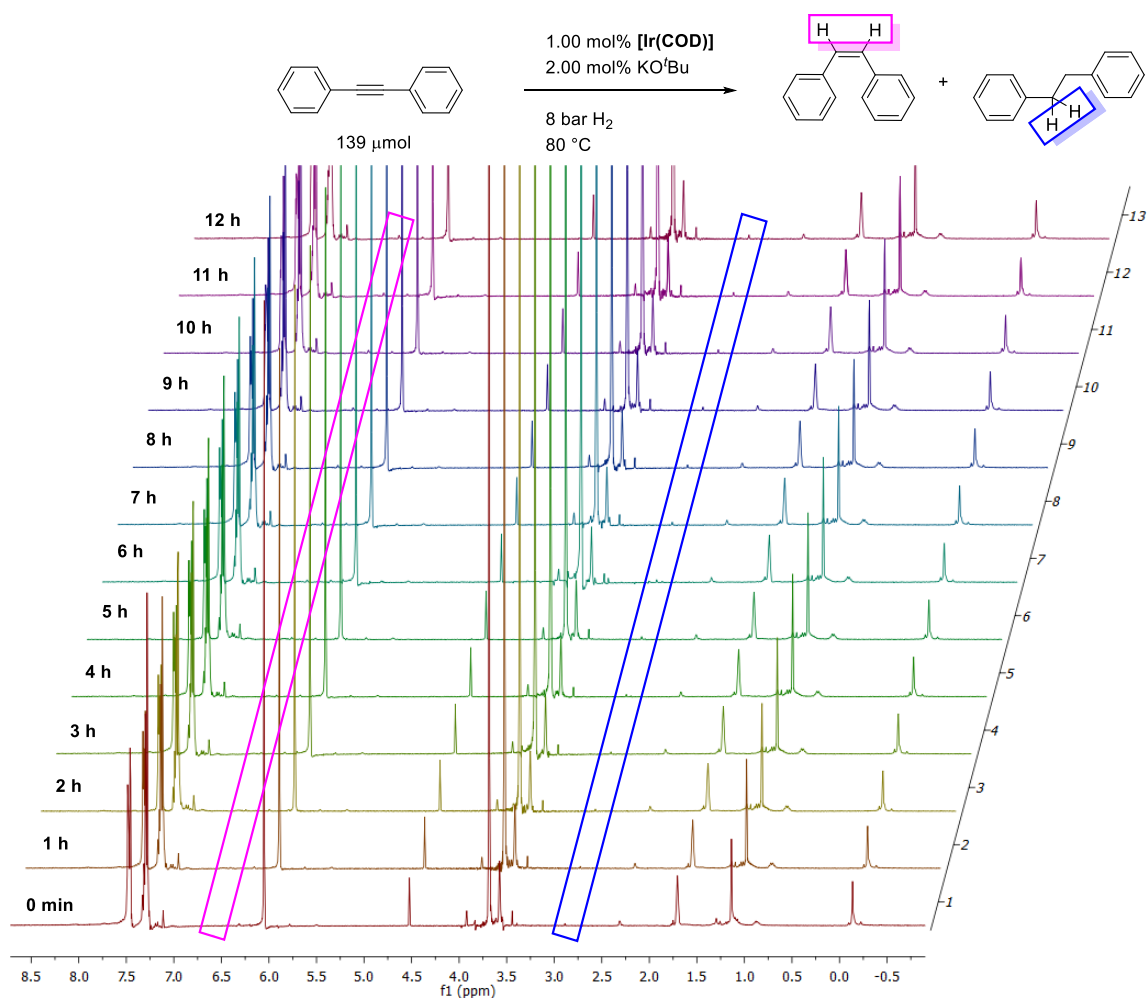
Supplementary Figure 14. Stacked ^1H NMR spectra of the *in-situ* hydrogenation of diphenylacetylene without base. One of the signals of the products was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



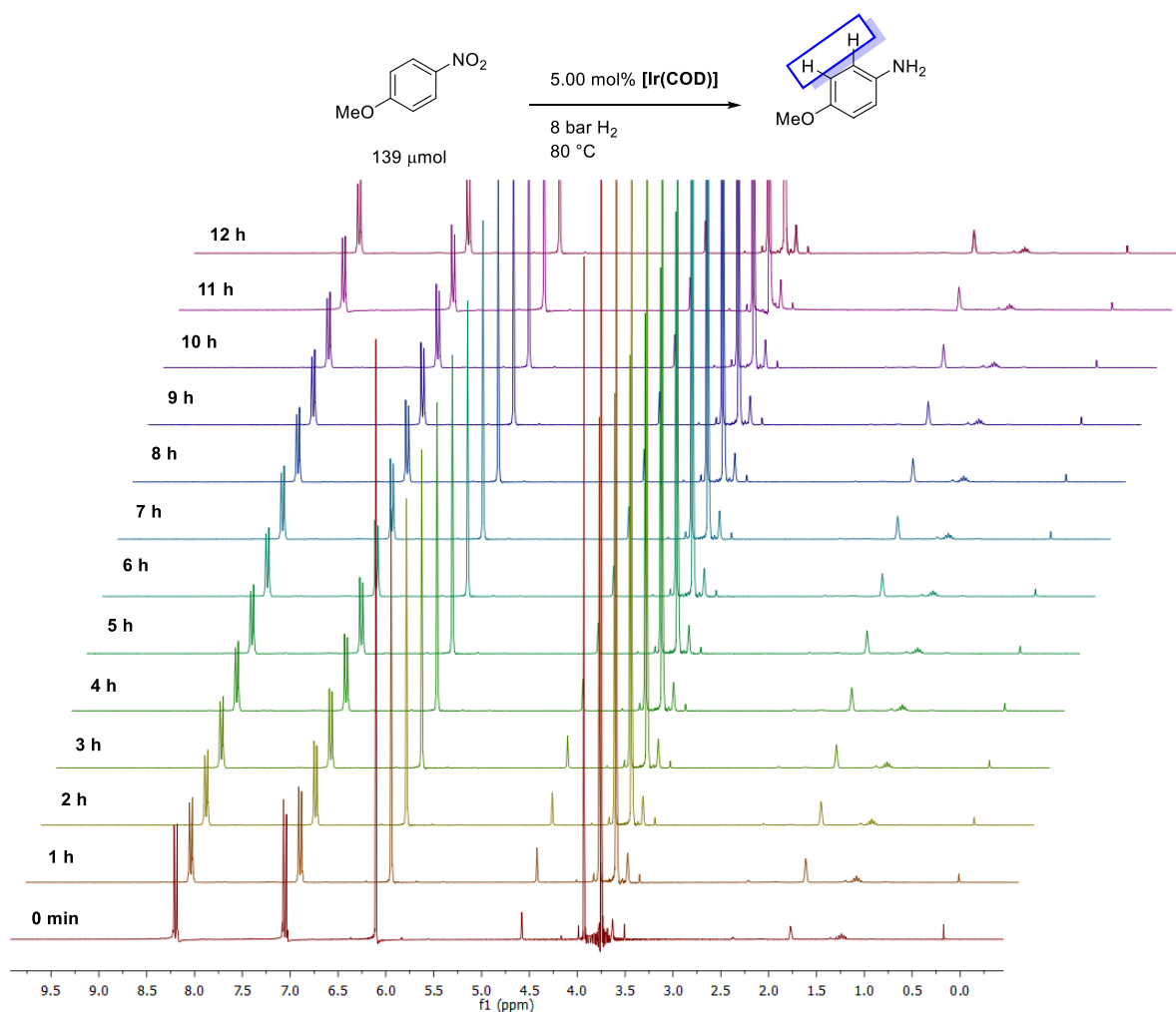
Supplementary Figure 15. Stacked ^1H NMR spectra of the *in-situ* hydrogenation of diphenylacetylene with 2 equivalents KO^tBu . One of the signals of the products was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



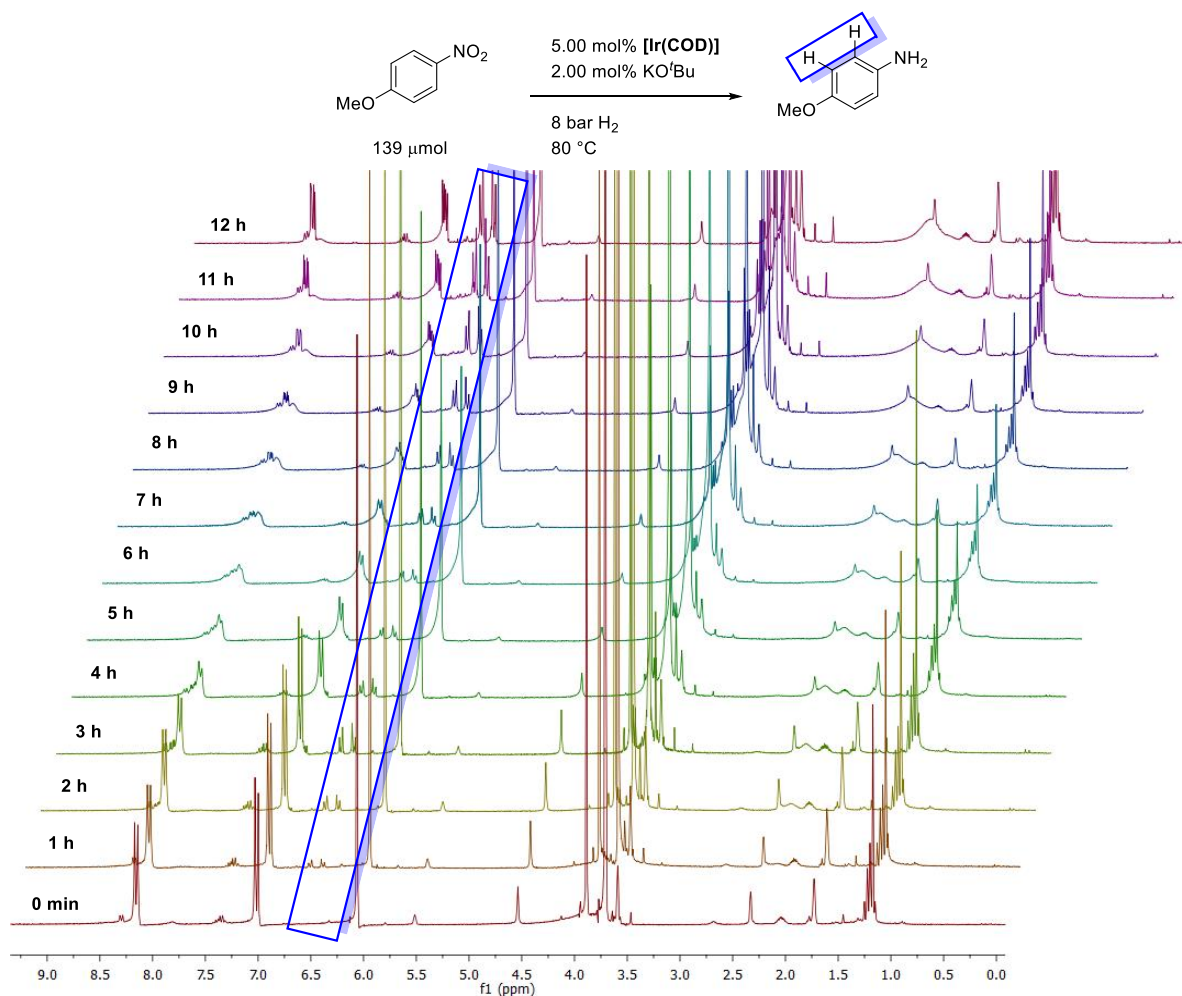
Supplementary Figure 16. Stacked ^1H NMR spectra of the *in-situ* hydrogenation of diphenylacetylene without base. One of the signals of the products was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



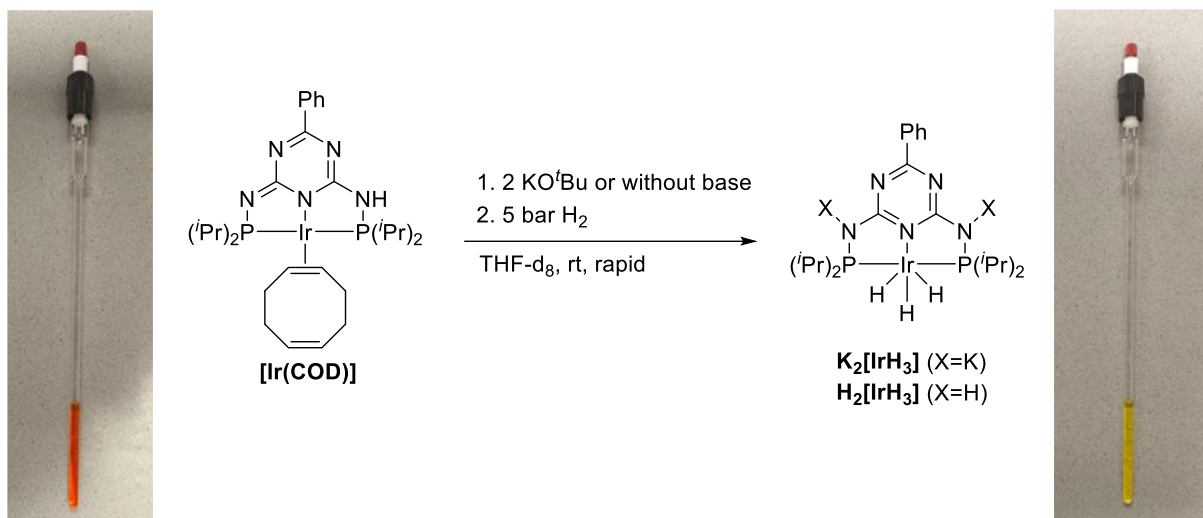
Supplementary Figure 153. Stacked ^1H NMR spectra of the *in-situ* hydrogenation of diphenylacetylene with 2 equivalents KO^tBu. One of the signals of the products was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



Supplementary Figure 18. Stacked ^1H NMR spectra of the *in-situ* hydrogenation of 1-methoxy-4-nitrobenzene without base. One of the signals of the products was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



Supplementary Figure 19. Stacked ¹H NMR spectra of the *in-situ* hydrogenation of 1-methoxy-4-nitrobenzene with 2 equivalents KO^tBu. One of the signals of the products was marked with a rectangle. Yields were determined by referencing with the internal standard (1,3,5-trimethoxybenzene) signal at 6.05 ppm.



Supplementary Figure 16. Wilmad[®] quick pressure valve NMR-tube (5 mm diam.) with the red precursor solution (left) and with the yellow hydride solution after H₂ pressurization (right).

7.6 References

¹ For information on the software MestRenova 6.1.0-6224 please check the website: <https://mestrelab.com> (last checked: 15.10.2025).

² Michlik, S.; Kempe, R. A sustainable catalytic pyrrole synthesis. *Nat. Chem.* **2013**, 5, 140–144.

8 List of Publications

The following publications were accepted/published or submitted during the work of this thesis:

Sila, N.; Dürrmann, A.; Weber, B.; Heinemann, F. W.; Irrgang, T.; Kempe, R.
A Selective Iron(I) Hydrogenation Catalyst.
J. Am. Chem. Soc. **2024**, *146* (39), 26877–26883.

Sila, N.; Schwarz, T.; Dickert, A.; Irrgang, T.; Kempe, R.
The Special Thing about Mn (de)hydrogenation Catalysts.
Organometallics **2025**, *44* (20), 2434–2439.

Sila, N.; Irrgang, T.; Kempe, R.
Mechanistically Switchable Hydrogenation Catalysis.
To be submitted.

9 Acknowledgements

Very special thanks go to my main supervisor Prof. Dr. Rhett Kempe for being a professional leader throughout this whole work. I appreciate his compassion for my work and his amazingly intelligent ideas. Under his supervision it was possible for me to develop a whole new understanding of science. Through our countless discussions I could get a better picture of the wonderful world of academia. I wish him pleasant remaining years as professor at the university of Bayreuth and a smooth transition into retirement.

A heartfelt thank goes to Dr. Torsten Irrgang for the astonishing supervision, his professionalism and for being available almost at any time needed. I also thank him for supporting me emotionally during this long journey. It has been a real pleasure being supervised by him.

I am very grateful for the help that Dr. Frank W. Heinmann gave me regarding single crystal x-ray crystallography and his kind persona. Huge appreciation goes to Prof. Dr. Birgit Weber and Andreas Dürrmann for the expertise in Mössbauer spectroscopy.

Last but definitely not least, I thank my family for supporting me financially and emotionally. This would have not been possible, especially not without the help of my mother – a woman I admire for her courage and big heart. Ultimately there is one last person, to whom I would like to give my well-deserved thanks – my beloved wife. Even an entire book would not be enough to thank her for understanding my complex personality, for supporting me every time, and, most and for all, for loving me unconditionally.

I am thankful to my fate for everything that happened to me!

10 Declaration / Eidesstaatliche Erklärung

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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. 97 Abs. 1 Satz 8 BayHIG).

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