Electronic Supporting Information for

From Imine to Amine: An Unexpected Left Turn. Cis-β Iron (II) PNNP' Precatalysts for the Asymmetric Transfer Hydrogenation of Acetophenone

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General considerations

All manipulations were performed under an inert atmosphere of argon using Schlenk or standard glovebox techniques, unless otherwise stated. Solvents and liquid substrates were dried and degassed via distillation prior to use. All solid substrates were heated to 80 °C under vacuum to remove any traces of water before being stored in the glovebox. Monotosylated DPEN was prepared according to literature procedure.[1] All phosphonium dimers were synthesized according to literature procedures.[2, 3] NMR spectra were recorded at ambient temperature and pressure using an Agilent DD2 700 MHz, 600 MHz, and 500 MHz spectrometer as well as Bruker Avance-III 400 MHz autosampler. The conversions and ee, using di-tert-butylbenzene as an external standard, for each reaction were obtained on a Perkin Elmer Clarus 400 Chromatograph equipped with a chiral column (CP chirasil-Dex CB 25 m x 2.5 mm), using hydrogen gas as the mobile phase. The infrared spectra were recorded on a Bruker Alpha with an ATR platinum diamond attachment. All experiments were repeated three times for accuracy.

Methods for Syntheses of the PNN Ligand (7, 8, and 9)

Synthesis of N-((1*S*,2*S*)-2-((2-fluorophenyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide (7, BenzoFTsDPEN): In a glovebox, bis(dibenzylideneacetone)palladium(0) (266 mg, 0.463 mmol, 10 mol%), *rac*-BINAP (577 mg, 0.926 mmol, 20 mol%), and sodium *tert*-butoxide (1.78 g, 18.5 mmol, 4 eq.) were dissolved in toluene (12 mL). This dark yellow solution was stirred for 1 h at 28 °C. Concurrently 2-bromofluorobenzene (890 mg, 5.09 mmol, 1.1 eq.) and monotosylated-(*S,S*)-DPEN (1.695 g, 4.63 mmol, 1 eq.) were dissolved in toluene (12 mL) and stirred for 1 h. The two solutions were combined in a 50 mL Schlenk flask and heated to reflux with a condenser on a Schlenk line under argon for 3 d. Toluene was then removed *in vacuo* and the brown residue was redissolved in DCM. A water/DCM extraction was performed extracting the water layer with DCM (30 mL x2), then the DCM was dried with magnesium sulphate and filtered through celite. The DCM was removed *in* vacuo, then the residue was redissolved in diethylether and filtered through celite to remove the palladium(0) impurities. The diethyl ether is removed *in vacuo* to yield a dark brown residue. A silica column is prepared using a gradient eluent (10:1 hexanes: ethyl acetate) to remove side-products then (3:1 hexanes:ethyl acetate, R_f = 0.46) to isolate a tan powder. Washing with hexanes removes other impurities to obtain the product as a white solid (1.60 g, 76%).

^{1}H NMR spectrum (500 MHz, $CDCl_3$) δ 7.52 – 7.37 (m, 2H, tosyl aromatic), 7.19 – 7.01 (m, 8H, overlapping tosyl aromatic and CH**Ph** aromatic) 7.01 - 6.85 (m, 3H, overlapping CH**Ph** aromatic and C_6**H**$_4$), 6.84 – 6.71 (m, 3H, overlapping CH**Ph** aromatic and C_6**H**$_4$), 6.65 – 6.51 (m, 1H, C_6**H**$_4$), 6.42 (td, *J* = 8, 2 Hz, 1H, C_6**H**$_4$), 5.37 (d, *J* = 6 Hz, 1H, C_6H_4N**H**), 4.67 (br, 1H, $CH_3C_6H_4SO_2$N**H**), 4.53 (m, 2H, two overlapping C**H**Ph), 2.34 (s, 3H, tosyl C**H**$_3$). ^{19}F NMR spectrum (377 MHz, $CDCl_3$): δ -134.84 (s). ESI+ Mass Spec $[M + H^+]^+$: calc.: 461.1694, actual: 461.1692. Elemental Analysis: calc.: 70.41% C, 5.47% H, 6.08% N; actual: 70.63% C, 5.46% H, 5.83% N.

Synthesis of N-((1*S*,2*S*)-2-((2-(diphenylphosphanyl)phenyl)amino)-1,2-diphenylethyl)-4-methylbenzenesulfonamide (8, BenzoPPh$_2$TsDPEN): In a glovebox, diphenylphosphine (1.76 g, 9.46 mmol, 3 eq.) was dissolved in THF (20 mL), then potassium hydride (0.380 g, 9.46 mmol, 3 eq.) was added potion-wise to the vial and the solution was stirred for an hour, until the solution turned bright orange. **7** (1.45 g, 3.155 mmol, 1 eq.) was dissolved in THF (40 mL) and placed in a 100 mL Schlenk flask. The $KPPh_2$ was placed in a syringe and capped with a rubber stopper. The Schlenk flask was removed from the glovebox and placed under argon on the Schlenk line. This solution was cooled to -78 °C, then the $KPPh_2$ was injected slowly. Once complete, the Schlenk flask was warmed to 28 °C, then the solution was refluxed for 3 days. The solution was removed from heat and allowed to cool to 28 °C before the solvent was removed *in vacuo*. The flask was then opened to air and a saturated solution of sodium bicarbonate (30 mL) was added. DCM (30 mL) was added to the flask, and the organic layer was separated. The aqueous layer was extracted with DCM (30 mL x2) and the organic layers were combined and dried with magnesium sulphate, then filtered through celite. The solvent was removed *in vacuo* and the residue was redissolved in ether (30 mL). This solution was stirred for 2 hours and the product was isolated by filtration to obtain an off-white powder (1.43 g, 75%).

^{1}H NMR spectrum (300 MHz, $CDCl_3$) δ 7.47 – 7.23 (m, 12H, overlapping tosyl aromatic and CH**Ph**), 7.22 – 6.94 (m, 9H, overlapping tosyl aromatic, CH**Ph**, and C_6**H**$_4$), 6.85 – 6.67 (m, 5H, overlapping CH**Ph**, C_6**H**$_4$), 6.59 (t, *J* = 7 Hz, 1H, C_6**H**$_4$), 6.35 (dd, *J* = 8, 5 Hz, 1H, C_6**H**$_4$), 5.21 – 4.89 (m, 2H, both N**H**), 4.66 (t, *J* = 6 Hz, 1H, C**H**Ph), 4.37 (t, *J* = 6 Hz, 1H, C**H**Ph), 2.34 (s, 3H, tosyl C**H**$_3$). ^{31}P NMR spectrum (121 MHz, $CDCl_3$) δ -21.61 (s). ESI+ Mass Spec $[M + O + H^+]^+$: calc: 643.2179, actual: 643.2173. Elemental Analysis: calc.: 74.74% C, 5.63% H, 4.47% N; actual: 74.36% C, 5.60% H, 4.34% N.

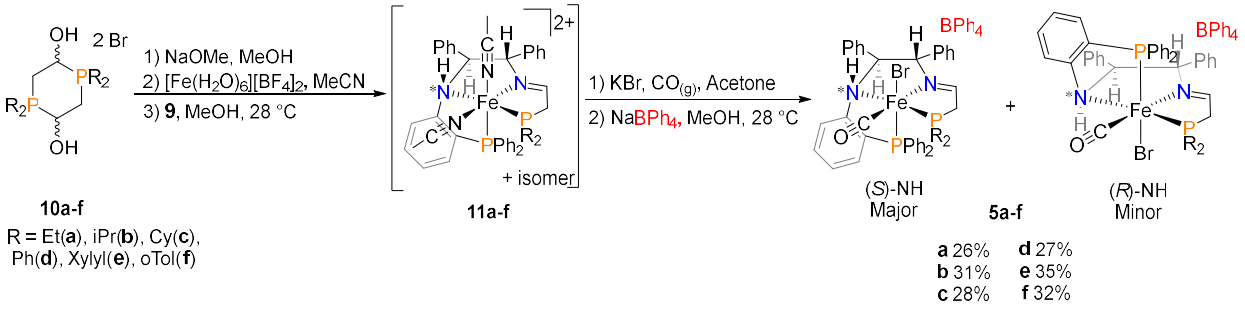
Note: This product was air stable and only oxidized under ESI mass spec conditions.

Synthesis of (1*S*,2*S*)-N1-(2-(diphenylphosphanyl)phenyl)-1,2-diphenylethane-1,2-diamine (9, BenzoPPh$_2$DPEN): In a glovebox, **8** (200 mg, 0.32 mmol, 1 eq.) was dissolved in a solution of SmI_2 (0.2 M, 12 mL, 3.20 mmol, 10 eq.)

and placed in a 100 mL Schlenk flask. This was placed under argon on the Schlenk Line while stirring the solution. Immediately, water (168 µL, 9.57 mmol, 30 eq.) then pyrrolidine (510 µL, 6.38 mmol, 20 eq.) was injected to form a metallic green solution. The flask was opened to air, then Ether (24 mL) was injected followed by 10% w/v sodium tartrate and 10% w/v potassium carbonate solution (50 mL). The organic phase was separated, and the aqueous phase was extracted with ether (50 mL x2). The organic layers were combined, dried with magnesium sulphate, filtered through celite, and concentrated under reduced pressure to yield a crude product. This was redissolved in Ether (20 mL) and filtered to remove an orange impurity. The oil was redissolved in MeCN/MeOH (1:1), then filtered to remove any grease. The solvent was removed to yield a colourless oil (151 mg, >99%). This was used in subsequent steps without further purification.

^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ 7.52 – 7.04 (m, 20H, aromatic), 7.01 – 6.90 (m, 1H, $C_6\mathbf{H}_4$), 6.69 (m, 1H, $C_6\mathbf{H}_4$), 6.50 – 6.41 (m, 1H $C_6\mathbf{H}_4$), 6.33 (t, *J* = 8 Hz, 1H $C_6H_4N\mathbf{H}$), 6.19 (m, 1H, $C_6\mathbf{H}_4$), 4.51 (dd, *J* = 8 Hz, 4 Hz, 1H, $C_6H_4NHC\mathbf{H}Ph$), 4.24 (d, *J* = 4 Hz, 1H, $C\mathbf{H}PhNH_2$); No NH_2 peaks were observed. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) δ -21.67. ESI+ Mass Spec $[M + H^+]^+$: calc: 473.2141, actual: 473.2146.

Experimental Protocol for the Synthesis of Imine Iron Precatalysts (5a-f)



Synthesis of bisdiphenylphosphine imine iron precatalyst [FeBr(CO)($PPh_2C_6H_4NHCHPhCHPh$-$NCHCH_2PPh_2$)]BPh_4 (5d): In a vial in the glovebox, **10d** (73 mg, 0.138 mmol, 1 eq.) and sodium methoxide (15 mg, 0.275 mmol, 2 eq.) were stirred together in methanol (10 mL) for 2 minutes. A solution of iron (II) hexaqua bis(tetrafluoroborate) (116 mg, 0.344 mmol, 2.5 eq.) in methanol (2 mL) was then added, followed by a solution of **9** (130 mg, 0.275 mmol, 2 eq.) in acetonitrile (10 mL). The solution immediately turned purple. This solution was placed in a Schlenk flask, placed on the Schlenk line under argon, and heated to 50 °C for 16 h. The pink solution was concentrated *in vacuo* to yield a pink residue. Potassium bromide (131 mg, 1.10 mmol, 4 eq.) was added to the Schlenk flask and the flask was placed under vacuum for 1 h. The flask was placed under CO (g) then acetone (5 mL) was injected. The pink solution turned yellow immediately. The flask was stirred under CO(g) overnight. In the morning, the solution turned a dark yellow/brown, then the solution was removed *in vacuo*. The residue was redissolved in DCM, then filtered through celite to remove any salts. The DCM was removed *in vacuo* to yield a dark yellow residue. The residue was dissolved in minimal MeOH (1 mL) and a solution of sodium tetraphenylborate (99 mg, 0.289 mmol, 2.1 eq.) in minimal MeOH (0.5 mL) was added dropwise to precipitate a tan powder. This powder was collected by filtration and washed with MeOH (0.5 mL) then ether (2 mL), and dried *in vacuo* to yield a tan powder. This was stirred in Ether (10 mL) for 20 h, then filtered out and washed with Ether (2x2 mL). The product was dried under vacuum for several hours to isolate the product as a tan powder (87 mg, 27%). Crystals suitable for single crystal X-ray diffraction were grown via slow diffusion of diethylether into a concentrated solution of **5d** in DCM to obtain red crystals.

^{1}H NMR spectrum (500 MHz, CD_2Cl_2) δ 7.88 (m, 1H, CH_2**H**C=NCHPh), 7.84 – 6.67 (m, 50H, aromatics), 6.44 (ddd, *J* = 8, 4, 1 Hz, 1H, C_6**H**$_4$), 6.26 (m, 1H, C_6H_4N**H**), 6.00 (d, *J* = 8, 1H, C_6**H**$_4$), 5.71 (m, 1H, HC=NC**H**Ph), 4.38 (m, 1H, PC**H**$_2$), 3.89 (dd, *J* = 13, 11 Hz, 1H, C_6H_4NHC**H**Ph), 3.83 (ddt, overlapping with the CHPh peak, 1H, PC**H**$_2$). ^{31}P NMR spectrum (162 MHz, CD_2Cl_2) δ 69.76 (d, $^2J_{PP}$ = 43 Hz), 65.85 (d, $^2J_{PP}$ = 43 Hz). The 2D ^{1}H-^{13}C HSQC spectrum (500 MHz, CD_2Cl_2) showing CH correlations for the CHPh peaks at (5.69, 77.0) and (3.90, 78.8), as well as the CH_2 correlations for the Ph_2PCH_2 at (4.41, 41.6) and (3.86, 42.2). The 2D ^{1}H-^{1}H COSY displays an interesting 5-bond cross peak between the C**H**Ph (5.71ppm) and the PC**H**$_2$ (4.38 ppm). This is likely due to an optimal dihedral angle between these two protons. IR Stretch (CO Ligand): 1969 cm^{-1}. ESI+ Mass Spec [M -BPh_4]$^+$: calc.: 845.1149, actual: 845.1147. Elemental Analysis [M + 0.5 Ether + 0.25 DCM]: calc.: 71.88% C, 5.39% H, 2.29% N; actual: 76.23% C, 5.73% H, 2.40% N. See Fig. S7 for NMR Spectra.

Synthesis of (R= Et, 5a): Follow the procedure as stated in the section titled "Synthesis of Bisdiphenylphosphine Imine Iron Precatalyst" using BenzoPPh_2DPEN (55 mg, 0.116 mmol, 2 eq.) and the ethyl-based cyclic phosphonium dimer dibromide (25 mg, 0.058 mmol, 1 eq.) instead. Product was isolated as a tan powder. Yield: 32 mg (26%). ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) δ 73.76 (d, $^2J_{PP}$ = 48 Hz), 74.45 (d, $^2J_{PP}$ = 48 Hz), IR Stretch (CO Ligand): 1970 cm^{-1}.

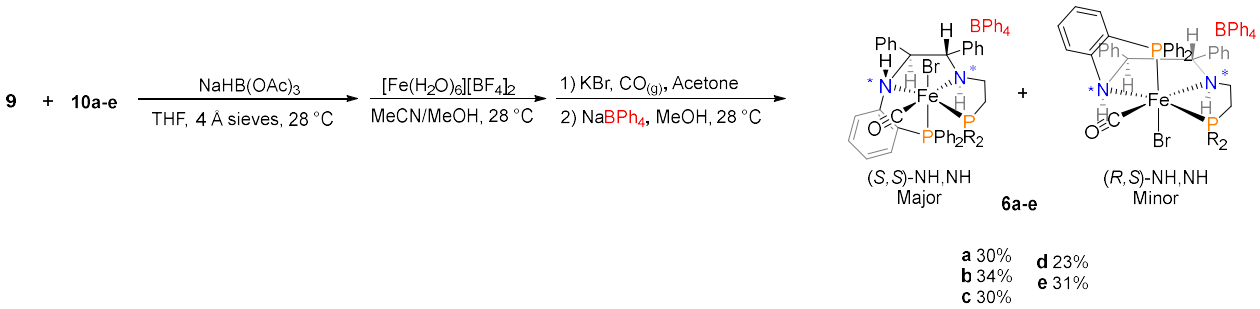
Synthesis of (R= iPr, 5b): Follow the procedure as stated in the section titled "Synthesis of Bisdiphenylphosphine Imine Iron Precatalyst" using BenzoPPh_2DPEN (55 mg, 0.116 mmol, 2 eq.) and the isopropyl-based cyclic phosphonium dimer dibromide (28 mg, 0.058 mmol, 1 eq.) instead. Product was isolated as a tan powder. Yield: 40 mg (31%). ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) δ 70.71 (d, $^2J_{PP}$ = 43 Hz), 83.38 (d, $^2J_{PP}$ = 43 Hz), IR Stretch (CO Ligand): 1968 cm^{-1}.

Synthesis of (R= Cy, 5c): Follow the procedure as stated in the section titled "Synthesis of Bisdiphenylphosphine Imine Iron Precatalyst" using BenzoPPh$_2$DPEN (55 mg, 0.116 mmol, 2 eq.) and the cyclohexyl-based cyclic phosphonium dimer dibromide (38 mg, 0.058 mmol, 1 eq.) instead. Product was isolated as a tan powder. Yield: 38 mg (28%). ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) δ 71.25 (d, $^2J_{PP}$ = 42 Hz), 76.86 (d, $^2J_{PP}$ = 42 Hz), IR Stretch (CO Ligand): 1967 cm^{-1}.

Synthesis of (R= Xylyl, 5e): Follow the procedure as stated in the section titled "Synthesis of Bisdiphenylphosphine Imine Iron Precatalyst" using BenzoPPh$_2$DPEN (60 mg, 0.127 mmol, 2 eq.) and the xylyl-based cyclic phosphonium dimer dibromide (46 mg, 0.064 mmol, 1 eq.) instead. Product was isolated as a tan powder. Yield: 55 mg (35%). ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) δ 71.27 (d, $^2J_{PP}$ = 42 Hz), 76.89 (d, $^2J_{PP}$ = 42 Hz), IR Stretch (CO Ligand): 1968 cm^{-1}.

Synthesis of (R= oTol, 5f): Follow the procedure as stated in the section titled "Synthesis of Bisdiphenylphosphine Imine Iron Precatalyst" using BenzoPPh$_2$DPEN (55 mg, 0.116 mmol, 2 eq.) and the orthotolyl-based cyclic phosphonium dimer dibromide (30 mg, 0.058 mmol, 1 eq.) instead. Product was isolated as a tan powder. Yield: 45 mg (32%). ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) δ 68.70 (d, $^2J_{PP}$ = 44 Hz), 70.75 (d, $^2J_{PP}$ = 44 Hz), IR Stretch (CO Ligand): 1968 cm^{-1}.

Experimental Protocol for the Synthesis of Amine Iron Precatalysts (6a-e)



Synthesis of bisdiphenylphosphine amine iron precatalyst [FeBr(CO)($PPh_2C_6H_4NHCHPhCHPh$-$NHCH_2CH_2PPh_2$)]BPh_4 via the intermediate tetradentate PPh_2-NH-NH-PPh_2 ligand 12d (6d):

Step 1: **10d** (68 mg, 0.128 mmol, 0.6 eq.) and sodium tris(acetoxy)borohydride (100 mg, 0.471 mmol, 2.2 eq.) were dissolved in THF (10 mL) and stirred for 2 minutes. A solution of **9** (101 mg, 0.214 mmol, 1 eq.) in THF (1 mL) was added to the solution as well as molecular sieves. This cloudy reaction was stirred for 24 h. The solvent was removed *in vacuo*. The residue was redissolved in DCM (20 mL), and filtered to remove any salts and any broken down molecular sieves. The Schlenk flask was brought out on the Schlenk line under argon, and an air-free extraction was performed. A saturated ammonium chloride solution (15 mL, degassed) was added to the Schlenk flask then removed by syringe, followed by addition of water (15 mL, distilled, degassed). The bottom DCM layer was removed via syringe and injected into a new Schlenk flask under argon. This Schlenk flask was opened under a large pressure of argon and sodium sulphate was added until the DCM was dry. The solvent was removed *in vacuo* and the flask was brought back into the glovebox. The product was extracted from the sodium sulphate with DCM. The DCM was filtered through celite then removed *in* vacuo. The residue was redissolved in MeOH/MeCN (1:1) and filtered to remove any grease. The solvent was removed *in vacuo* to obtain crude **12d** as a tan oil. This was used in subsequent steps without further purification. ^{31}P NMR (121 MHz, CD_2Cl_2) δ -20.25 (s), -21.49 (s).

Step 2: **12d** (crude, 54 mg, 0.078 mmol, 1 eq.) was dissolved in MeCN (1 mL) and the iron(II) hexaqua tetrafluoroborate (26 mg, 0.078 mmol, 1 eq.) in MeOH (1 mL) was added. This solution immediately turned pink, then was stirred for 16 h. The solvent was removed *in vacuo* to yield a pink residue. Potassium bromide (10 mg, 0.086 mmol, 1.1 eq.) was added to the flask, then the flask was placed under $CO_{(g)}$ on the Schlenk line. Upon addition of acetone (5 mL), this pink solution turned yellow immediately. This solution was stirred for 16 h at which point the solvent was removed *in vacuo* and the flask was placed back in the glovebox. The brown/yellow residue was redissolved in DCM and filtered through celite to remove any salts, then the solvent was removed *in vacuo*. This residue was dissolved in minimal MeOH (1 mL) and a saturated solution of sodium tetraphenylborate (25 mg, 0.078 mmol, 1 eq.) in minimal MeOH (0.2 mL) was added dropwise to cause the precipitation of a tan powder, which was isolated via filtration, washed with MeOH (0.5 mL), then washed with diethyl ether (2 x 5 mL) and dried *in vacuo* to obtain the product 21 mg, 23%) as a slightly red powder. Crystals were grown via a slow diffusion of diethylether into a concentrated solution of **6d** in DCM.

^{1}H NMR spectrum (400 MHz, CD_2Cl_2) δ 7.95-6.82 (m, 52H, aromatics), 6.38 (m, 1H, $C_6\mathbf{H}_4$), 6.35 (m, 1H, overlapped, $C_6H_4N\mathbf{H}$), 6.03 (m, 1H, aromatic), 5.08 (pseudo triplet, J = 12 Hz, 1H, $CH_2NHC\mathbf{H}Ph$), 4.93 (m, 1H, $CH_2N\mathbf{H}$), 3.60 (m, 1H, $PC\mathbf{H}_2$), 3.45 (pseudo triplet, J = 11 Hz, 1H, $C_6H_4NHC\mathbf{H}Ph$), 3.31 (m, 1H, $PC\mathbf{H}_2$), 3.27 (m, 1H, $C\mathbf{H}_2NH$), 3.00 (m, 1H, $C\mathbf{H}_2NH$). ^{31}P NMR spectrum (162 MHz, CD_2Cl_2) δ 75.35 (d, $^2J_{PP}$ = 42 Hz), 65.56 (d, $^2J_{PP}$ = 42 Hz). The 2D ^{1}H-^{13}C HSQC spectrum (400 MHz, CD_2Cl_2) showing CH correlations for the C**H**Ph peaks at (5.09, 71.01) and (3.46, 79.95) as well as the CH_2 correlations for the $Ph_2PC\mathbf{H}_2$ at (3.60, 46.95) and (3.31, 47.10), and the $NHC\mathbf{H}_2$ at (3.27, 29.10) and (3.00, 28.81). IR Stretch (CO Ligand): 1964 cm^{-1}. ESI+ Mass Spec [M-BPh4]$^+$: calc.: 847.1305, actual: 847.1295. Elemental

Analysis [M + 0.5 Ether + 0.25 DCM]: calc.: 71.76% C, 5.55% H, 2.28% N; actual: 71.22% C, 5.27% H, 2.31% N. See Fig. S9 for the NMR Spectra.

Synthesis of (R= Et, 6a): Follow the experimental procedure as stated in the section titled "Synthesis of Bisdiphenylphosphine Amine Iron Precatalysts *via* the Intermediate Tetradentate PPh_2-NH-NH-PPh_2 Ligand". For step 1: use BenzoPPh_2DPEN (109 mg, 0.231 mmol, 1 eq.), the ethyl-based cyclic phosphonium dimer dibromide (59 mg, 0.138 mmol, 0.6 eq.), and sodium tris(acetoxy)borohydride (108 mg, 0.508 mmol, 2.2 eq.) instead. For step 2: in the iron template reaction, use iron(II) hexaqua tetrafluoroborate (78 mg, 0.231 mmol, 1 eq.). In the CO ligand addition, use potassium bromide (30 mg, 0.254 mmol, 1.1 eq.). Product was isolated as a slightly red powder. Yield: 74 mg (30%). Crystals suitable for single crystal x-ray diffraction were grown *via* a slow diffusion of pentane into a concentrated solution of iron precatalyst in tetrahydrofuran. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) δ 7.99-6.82 (m, 42H, aromatics), 6.38 (dd, *J* = 8, 4 Hz, 1H, $C_6\mathbf{H}_4$), 6.22 (m, 1H, $C_6H_4N\mathbf{H}$), 6.03 (d, *J* = 8 Hz, 1H, aromatic), 4.99 (dd, *J* = 12, 1 Hz, 1H, $CH_2NHC\mathbf{H}Ph$), 4.83 (m, 1H, $CH_2N\mathbf{H}$), 3.46 (dd, *J* = 12, 10 Hz, 1H, $C_6H_4NHC\mathbf{H}Ph$), 3.30 (dddd, *J* = 19, 12, 10, 5 Hz, 1H, $C\mathbf{H}_2NH$), 3.09-3.01 (ddt, *J* = 37, 11, 5 Hz 1H, $C\mathbf{H}_2NH$), 2.35 (td, *J* = 15, 8 Hz, 1H, $PEt_2C\mathbf{H}_2$), 2.24 (m, overlapped, 1H, PEt_2's $C\mathbf{H}_2$), 2.03 (tdd, *J* = 15, 7, 5 Hz, 1H, $PEt_2C\mathbf{H}_2$), 1.83 (m, 1H, PEt_2's $C\mathbf{H}_2$), 1.54 (m, overlapped, 1H, PEt_2's $C\mathbf{H}_2$), 1.33 (m, overlapped, 1H, PEt_2's $C\mathbf{H}_2$), 1.20 (m, overlapped, 3H, PEt_2's CH_3), 0.66 (dt, *J* = 15, 8 Hz, 3H, PEt_2's CH_3). ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) δ 72.83 (d, $^2J_{PP}$ =44 Hz), 77.72 (d, $^2J_{PP}$ = 44 Hz). The ^{1}H-^{13}C Heteronuclear Single Quantum Coherence spectrum (HSQC, 500 MHz, CD_2Cl_2) showing CH correlations for the CHPh peaks at (4.99, 70.97) and (3.46, 79.15) as well as the CH_2 correlations for the $NHCH_2$ at (3.30, 46.90) and (3.09-3.01, 46.76), the Et_2PCH_2 at (2.35, 30.00) and (2.03, 30.00), and the PEt_2's CH_2 at (2.24, 19.42), as well as the PEt_2's CH_3 at (1.20, 7.29), and (0.66, 7.24). The rest of the peaks were assigned based on the COSY and NOESY spectra. IR Stretch (CO Ligand): 1960 cm^{-1}. ESI+ Mass Spec $[M\text{-}BPh_4]^+$: calc.: 751.1305; actual: 751.1293. Elemental Analysis: calc.: 70.61% C, 5.83% H, 2.61% N; actual: 71.08% C, 5.92% H, 2.57% N. For NMR Spectra see Fig. S10.

Synthesis of (R= iPr, 6b): Follow the experimental procedure as stated in the section titled "Synthesis of Bisdiphenylphosphine Amine Iron Precatalysts *via* the Intermediate Tetradentate PPh_2-NH-NH-PPh_2 Ligand". For step 1: use BenzoPPh_2DPEN (109 mg, 0.231 mmol, 1 eq.), the isopropyl-based cyclic phosphonium dimer dibromide (67 mg, 0.138 mmol, 0.6 eq.), and sodium tris(acetoxy)borohydride (108 mg, 0.508 mmol, 2.2 eq.) instead. For step 2: in the iron template reaction, use iron(II) hexaqua tetrafluoroborate (78 mg, 0.231 mmol, 1 eq.). In the CO ligand addition, use potassium bromide (30 mg, 0.254 mmol, 1.1 eq.). Product was isolated as a slightly red powder. Yield: 86 mg (34%), ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) δ 74.28 (d, $^2J_{PP}$ = 45 Hz), 80.30 (d, $^2J_{PP}$ = 45 Hz), IR Stretch (CO Ligand): 1964 cm^{-1}.

Synthesis of (R= Cy, 6c): Follow the experimental procedure as stated in the section titled "Synthesis of Bisdiphenylphosphine Amine Iron Precatalysts *via* the Intermediate Tetradentate PPh_2-NH-NH-PPh_2 Ligand". For step 1: use BenzoPPh_2DPEN (109 mg, 0.231 mmol, 1 eq.), the cyclohexyl-based cyclic phosphonium dimer dibromide (89 mg, 0.138 mmol, 0.6 eq.), and sodium tris(acetoxy)borohydride (108 mg, 0.508 mmol, 2.2 eq.) instead. For step 2: in the iron template reaction, use iron(II) hexaqua tetrafluoroborate (78 mg, 0.231 mmol, 1 eq.). In the CO ligand addition, use potassium bromide (30 mg, 0.254 mmol, 1.1 eq.). Product was isolated as a slightly red powder. Yield: 83 mg (30%), ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) δ 73.78 (d, $^2J_{PP}$ = 39 Hz), 74.43 (d, $^2J_{PP}$ = 39 Hz), IR Stretch (CO Ligand): 1962 cm^{-1}.

Synthesis of (R= Xylyl, 6e): Follow the experimental procedure as stated in the section titled "Synthesis of Bisdiphenylphosphine Amine Iron Precatalysts *via* the Intermediate Tetradentate PPh_2-NH-NH-PPh_2 Ligand". For step 1: use BenzoPPh2DPEN (109 mg, 0.231 mmol, 1 eq.), the xylyl-based cyclic phosphonium dimer dibromide (101 mg, 0.138 mmol, 0.6 eq.), and sodium tris(acetoxy)borohydride (108 mg, 0.508 mmol, 2.2 eq.) instead. For step 2: use iron(II) hexaqua tetrafluoroborate (78 mg, 0.231 mmol, 1 eq.). In the CO ligand addition, use potassium bromide (30 mg, 0.254 mmol, 1.1 eq.). Product was isolated as a slightly red powder. Yield: 89 mg (31%), ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) δ 63.69 (d, $^2J_{PP}$ = 41 Hz), 75.43 (d, $^2J_{PP}$ = 41 Hz), IR Stretch (CO Ligand): 1963 cm^{-1}.

Experimental Protocols for ATH, Base and Hydride Studies, and Crystallization of 16d.

General procedure for ATH of acetophenone in optimized conditions (see Figure 6 and 7 in the manuscript).

Stock Solution 1 (SS1): An iron precatalyst ($6.48x10^{-3}$ mmol) was dissolved in cold DCM (1 mL) and quickly placed into a 1 mL syringe. A new vial was charged with a magnetic stir bar and then 0.1 mL of SS1. The solvent was removed *in vacuo* to obtain $6.48x10^{-4}$ mmol of iron precatalyst. This vial was charged with acetophenone (39 mg, 0.324 mmol, 500 eq.) and iPrOH (6.63 g). Stock Solution 2 (SS2): KOtBu (10 mg, 0.089 mmol) in iPrOH (1.02 g) was prepared. A new vial was charged with 0.06 g of SS2, then diluted with iPrOH (0.501 g). This basic solution was added to the vial charged with precatalyst to start the catalytic run. Samples were taken at 1, 2, 3, 4, 5, 10, 30, 60 minutes to create the reaction profiles by placing 0.1 mL of the reaction mixture into gas chromatography autosampler vials filled with oxygenated iPrOH to quench the reactivity of the iron catalyst.

Note: The final concentrations were $7.2x10^{-5}$ M of iron precatalyst, 0.037 M of acetophenone, $5.74x10^{-4}$ M of KOtBu, and 13.1 M iPrOH.

General procedure for iron precatalyst activation with 1 eq. of KOtBu

An iron precatalyst ($5.15x10^{-2}$ mmol) and KOtBu (5.8 mg, $5.15x10^{-2}$ mmol, 1 eq.) was placed in a vial charged with a stir bar. THF (10 mL) was added and the resultant solution was stirred rapidly for 5 minutes. The solvent was removed *in vacuo* and the residue was redissolved in benzene then filtered through a 25 mm syringe filter (o.45 µm, PTFE). The benzene was removed *in vacuo* and an IR spectrum was taken of the residue. The remaining residue was redissolved in C_6D_6 for NMR analysis (^{31}P, ^{1}H, 2D ^{1}H-1H COSY, 2D ^{1}H-^{1}H NOESY, 2D ^{1}H-^{13}C HSQC, and IR Spectra).

Crystallization of 16d:

Follow the procedure entitled "General Procedure for Iron Precatalyst Activation with 1 eq. of KOtBu" with **5d**. Crystals suitable for single crystal X-ray diffraction were obtained by slow diffusion of diethylether into a solution of the residue in benzene. Dark purple crystals form in a green supernatant.

^{1}H NMR spectrum (600 MHz, CD_2Cl_2) δ 7.59-6.65 (m, 54H, aromatic), 6.72 (d, overlapped, 1H, H_2C**H**C=N), 5.36 (br, 1H, C_6H_4NHC**H**Ph), 5,10 (br, 1H, HC=NC**H**Ph), 3.08 (ddd, *J* = 19, 14, 3 Hz, 1H, Ph_2PC**H**$_2$), 2.37 (dd, *J* = 19, 7 Hz, 1H, Ph_2PC**H**$_2$). ^{31}P NMR spectrum (243 MHz, CD_2Cl_2) δ 65.32 (d, $^{2}J_{PP}$ = 32 Hz), 85.84 (d, $^{2}J_{PP}$ = 32 Hz). The 2D ^{1}H-^{13}C HSQC spectrum (600 MHz, CD_2Cl_2) showing CH correlations for the C**H**Ph peaks at (5.36, 75.41) and (5.10, 83.70) as well as the CH_2 correlations for the Ph_2PC**H**$_2$ at (3.08, 45.65) and (2.37, 45.47). IR Stretch (CO Ligand): 1937 cm^{-1}. ESI+ Mass Spec $[M\text{-}BPh_4]^+$: calc.: 765.1887, actual: 765.1871. Elemental Analysis: calc.: 78.61% C, 5.48% H, 2.58% N; actual: 78.60% C, 5.53% H, 2.48% N.

General procedure for iron precatalyst activation with 8 eq. of KOtBu

An iron precatalyst ($5.15x10^{-2}$ mmol) and KOtBu (46.2 mg, $4.12x10^{-1}$ mmol, 8 eq.) was placed in a vial charged with a stir bar. THF (10 mL) was added and the resultant solution was stirred rapidly for 5 minutes. The solvent was removed *in vacuo* and the residue was redissolved in benzene then filtered through a 25 mm syringe filter (o.45 µm, PTFE). The benzene was removed *in vacuo* and an IR spectrum was taken. No NMR data was taken due to the formation of paramagnetic material.

General procedure for hydride studies

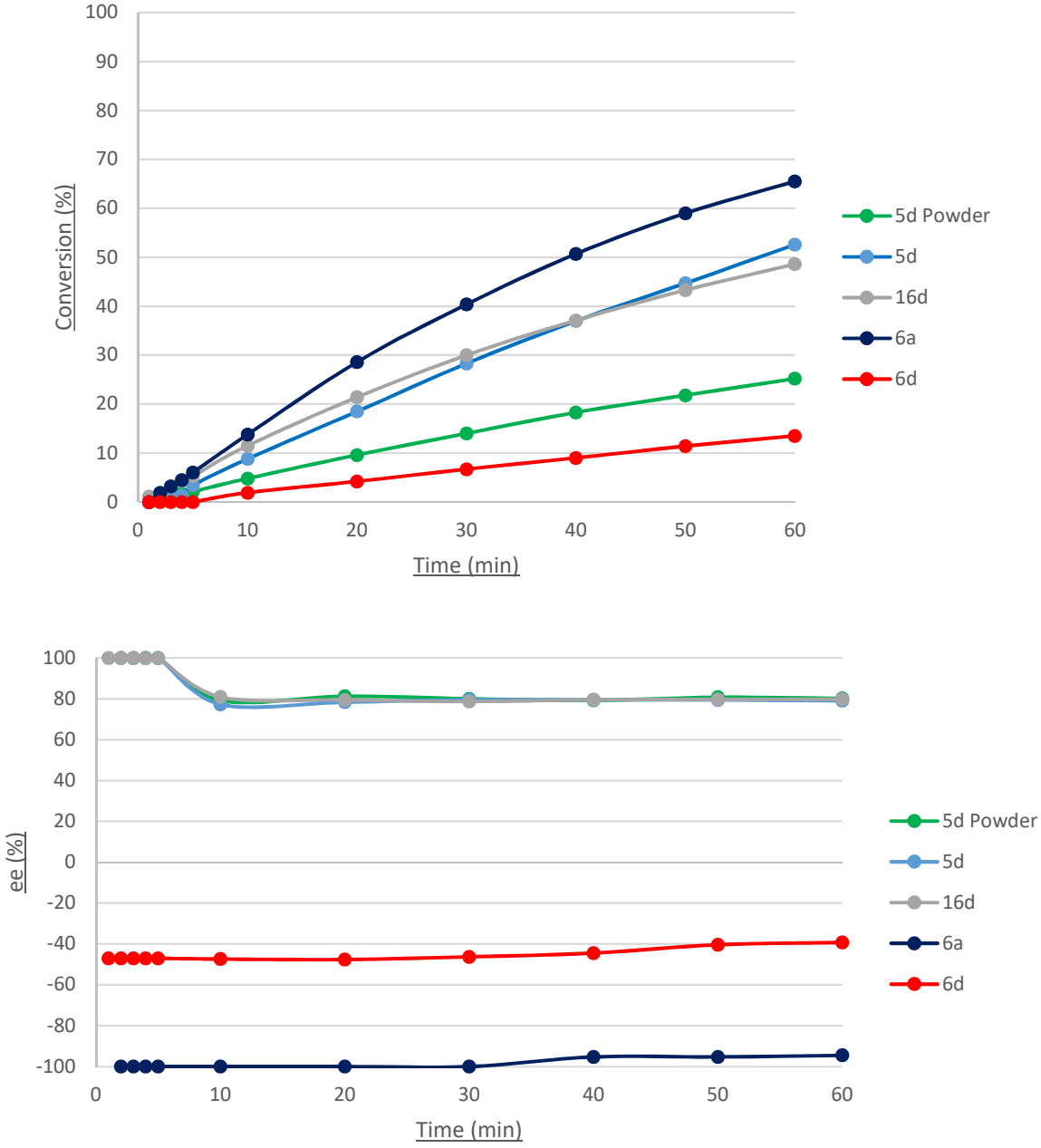
An iron precatalyst ($5.15x10^{-2}$ mmol) and KOtBu (46.2 mg, $4.12x10^{-1}$ mmol, 8 eq.) was placed in a vial charged with a stir bar. THF (10 mL) was added and the resultant solution was stirred rapidly for 5 minutes. The solvent was removed *in vacuo* and the residue was redissolved in iPrOH and stirred rapidly for at least 20 minutes. The solvent was removed *in vacuo*, redissolved in benzene, then filtered through a 25 mm syringe filter (o.45 µm, PTFE). The benzene was removed *in vacuo* and an IR spectrum was taken of the residue. The remaining residue was redissolved in C_6D_6 for NMR analysis (^{31}P, ^{1}H, 2D ^{1}H-^{1}H COSY, 2D ^{1}H-^{1}H NOESY, 2D ^{1}H-^{13}C HSQC, and IR Spectra). These spectra can be found in the corresponding section below.

Table S1 Summary of ^{31}P Chemical Shifts, $^{2}J_{PP}$ Coupling Constants, IR CO Stretch, and Suggested Structures

Precat.	Label	^{31}P δ (ppm)	$^{2}J_{pp}$ (Hz)	$\Delta^{31}P$ δ (ppm)	CO Stretch (cm^{-1})[a]	Structure Analysis[b]
5d	**5d**	70.00, 71.17	44	1.17	1969	6, *cis-β*, precatalyst
	14d	55.53, 61.45	35	5.92	1928	6, *trans*, singly deprotonated
	***cis-beta*-15d**	62.7, 82.04	59	19.34	-	5, *cis-β*, cationic
	16d	65.32, 85.84	32	20.52	1937	5, *trans*, cationic
	17d	78.4, 85.38	27	6.98	-	6, *trans*, hydride
	18d	78.34, 85.10	33	6.76	1910	5, *trans*, doubly deprotonated
	19d	73.81, 76.81	38	3	1845	6, *trans*, alkoxide
6d	**6d**	65.56, 75.35	42	9.79	1964	6, *cis-β*, precatalyst
	20d	55.66, 58.98	32	3.32	1939	6, *trans*, singly deprotonated
6a	**6a**	73.06, 77.95	44	4.89	1960	6, *cis-β*, precatalyst
	18a	81.92, 83.08	33	1.16	1893	5, *trans*, doubly deprotonated
	19a	74.02, 76.70	36	2.68	-	6, *trans*, alkoxide
	20a	56.95, 60.08	30	3.13	1924	6, *trans*, singly deprotonated
	***cis-beta*-20a**	75.59, 84.07	43	8.48	-	6, *cis-β*, singly deprotonated
	21a	77.24, 81.41	26	4.17	-	6, *trans*, hydride

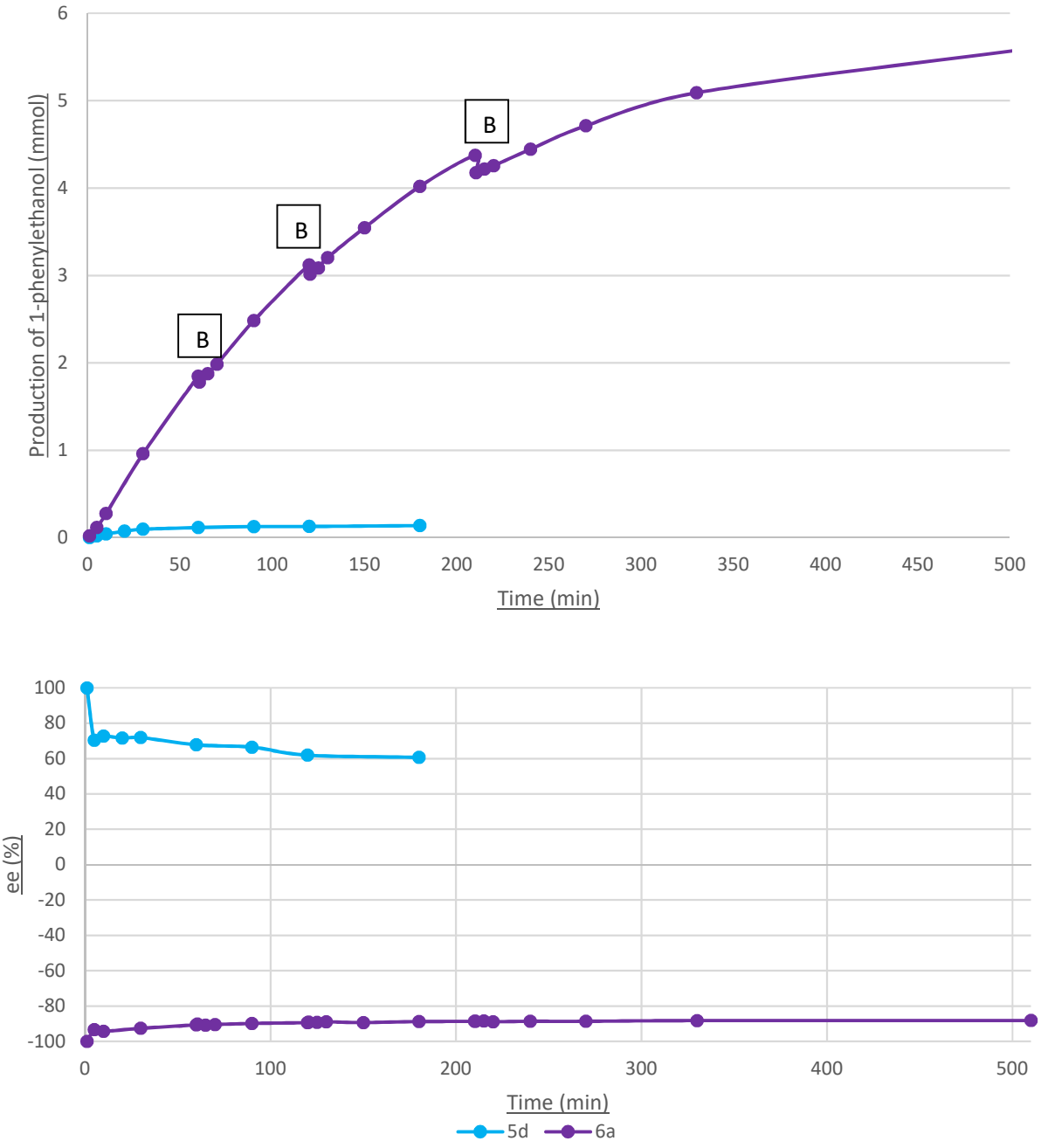
[a] IR stretch could not be assigned. [b]Labeled as coordinate number, *cis-β* or *trans* complex, complex information.

Fig. S1 Reaction Profiles for the ATH of Acetophenone in Optimized Conditions. Conversion (top), ee (bottom).[a]



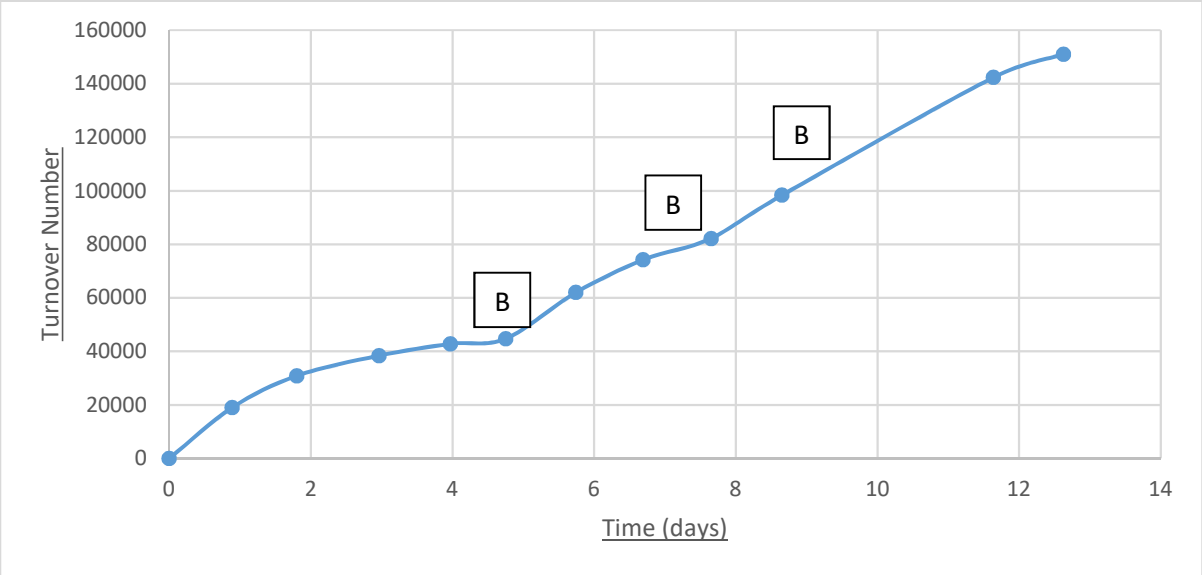
[a] Reactions performed under argon at 28 °C. Acetophenone:KOtBu:precatalyst ratio was 500:8:1. Volume of iPrOH = 9 mL. Final concentrations: [Acetophenone] = 0.037 M; [KOtBu] = 5.7 x 10^{-4} M; [Fe] = 7.2 x 10^{-5} M; [iPrOH] = 13.1 M.

Fig. S2 Reaction Profiles for the ATH of Acetophenone at 75 °C with a 6121:1 substrate:precatalyst ratio. Conversion (top), ee (bottom).[a] An Additional 6121 eq. of Acetophenone, 9 mL of iPrOH, and 8eq. of KOtBu was added to the reaction flask at B.



[a] Reactions performed under argon at 75 °C. Acetophenone:KOtBu:precatalyst ratio was 6121:8:1. Volume of iPrOH = 9 mL. Initial reaction concentrations: [Acetophenone] = 0.453 M; [KOtBu] = 5.7 x 10^{-4} M; [Fe] = 7.2 x 10^{-5} M; [iPrOH] = 12.4 M.

Fig. S3 Reaction Profiles for the ATH of Acetophenone at 85 °C with an initial substrate:precatalyst ratio of 54000:1. Conversion (top), ee (bottom).[a] An Additional 54000 eq. of Acetophenone of KOtBu was added to the reaction flask at B.

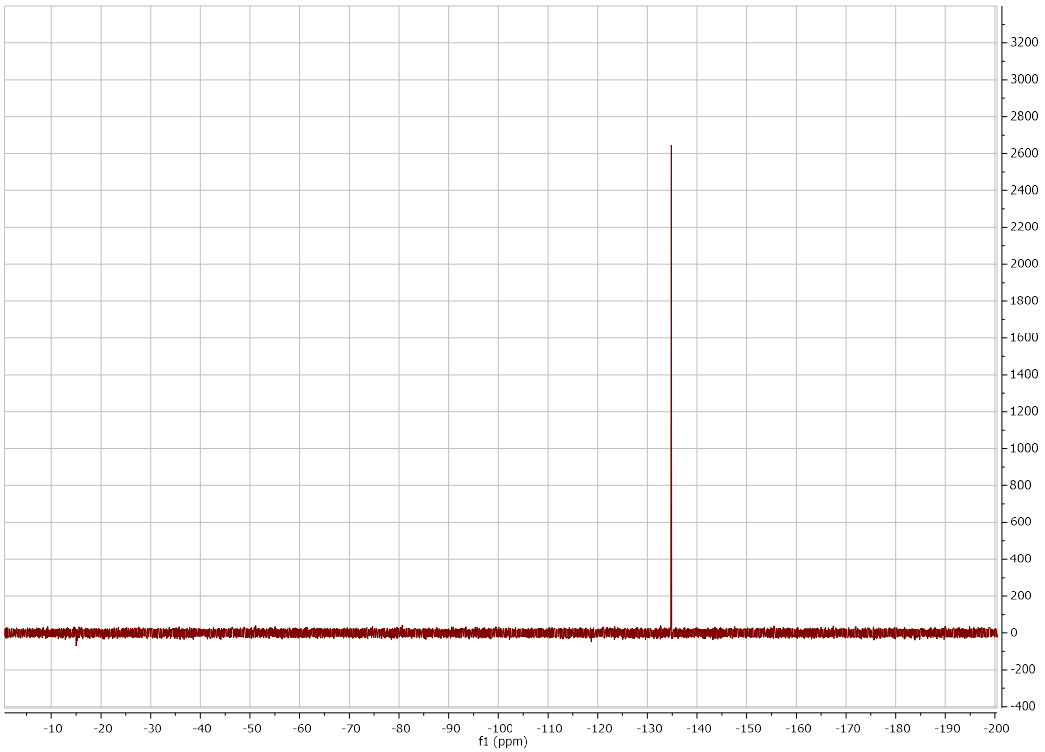


[a] Reactions performed under argon at 85 °C. Initial acetophenone:KOtBu:precatalyst ratio was 54000:4140:1. Volume of iPrOH = 81 mL. Initial reaction concentrations: [Acetophenone] = 0.429 M; [KOtBu] = 3.28 x 10^{-2} M; [Fe] = 8.0 x 10^{-6} M; [iPrOH] = 12.4 M.

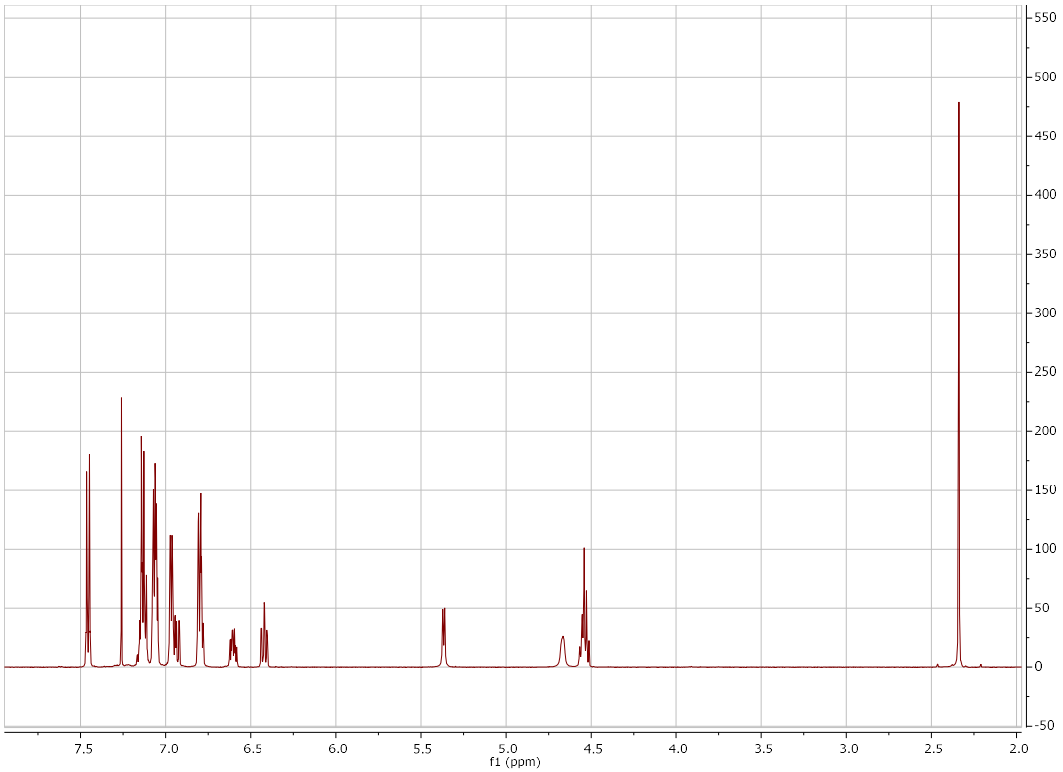
Note: The ee degraded quickly due to the high concentration of 1-phenylethanol in solution as the reaction proceeded.

Fig. S4 NMR Spectroscopy for BenzoFTsDPEN (**7**).

(a) ^{19}F NMR spectrum (377 MHz, $CDCl_3$):



(b) ^{1}H NMR spectrum (500 MHz, $CDCl_3$):



(c) 2D ^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$):

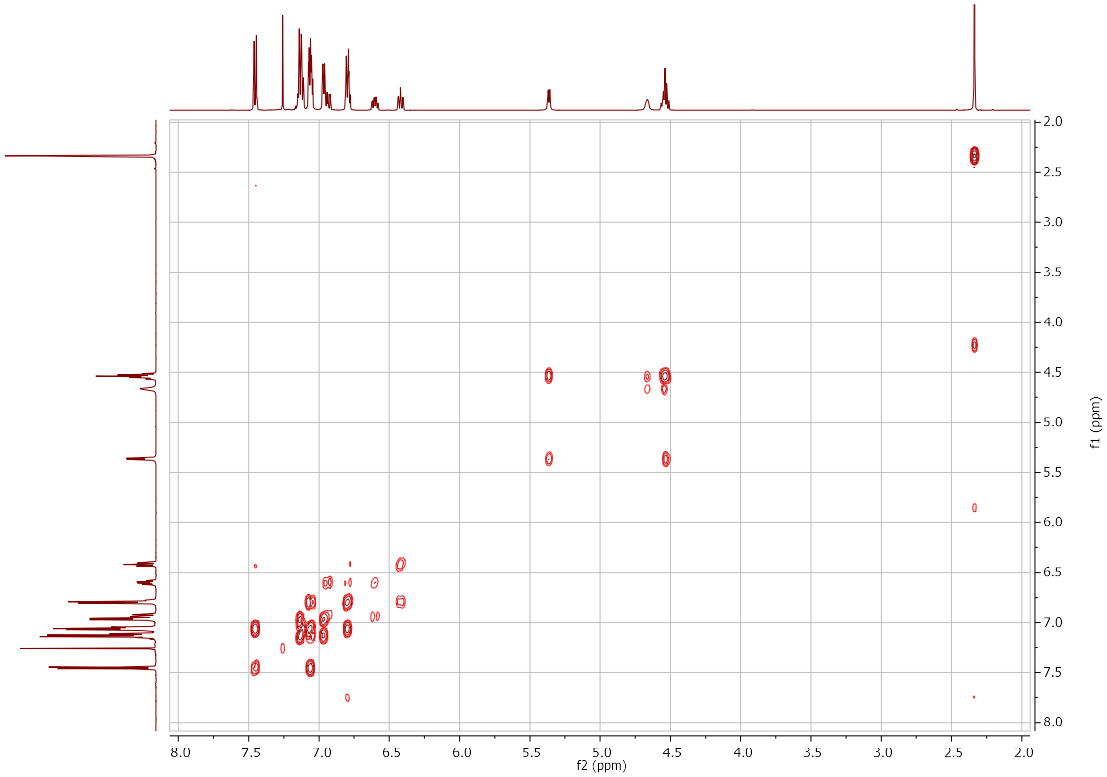
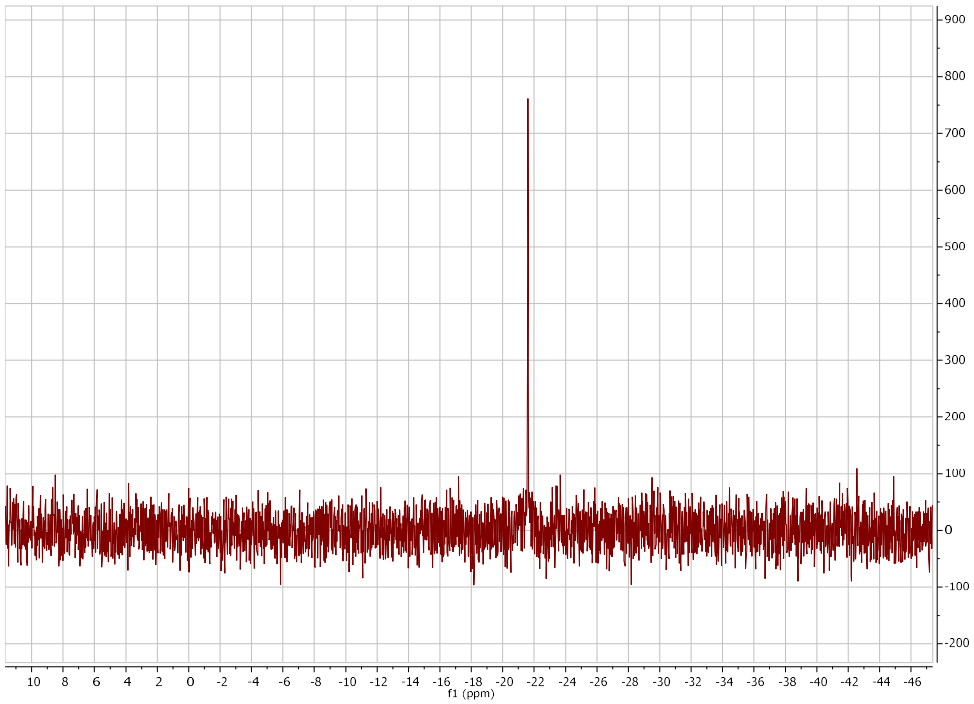
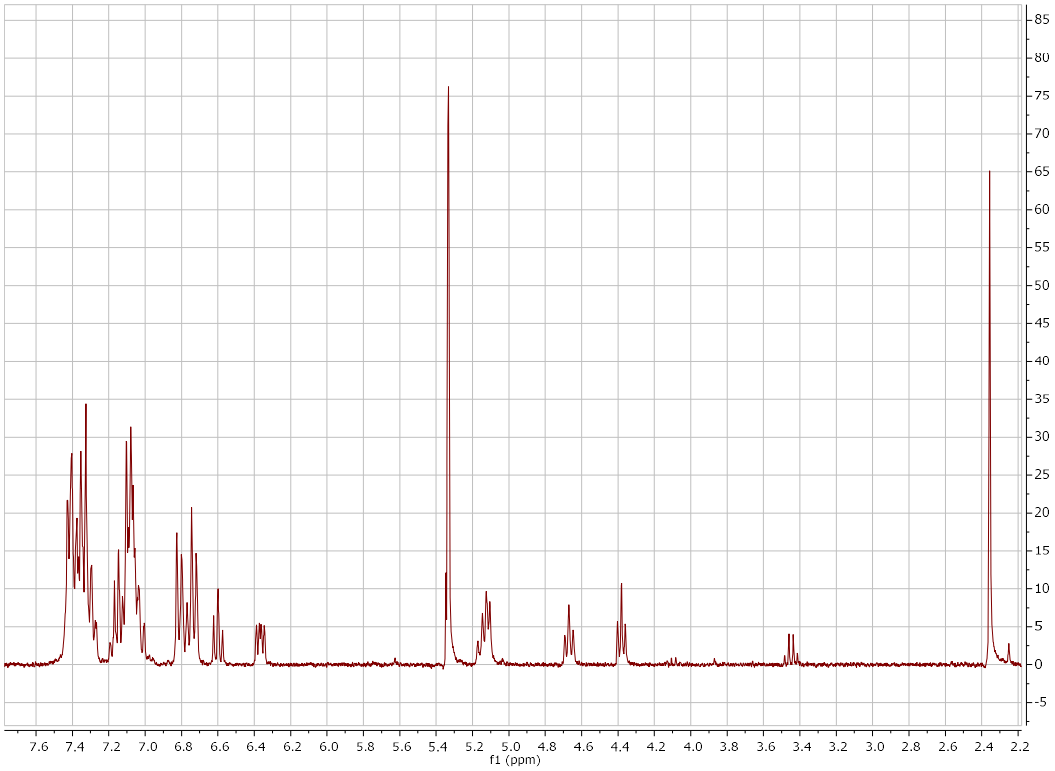


Fig. S5 NMR Spectroscopy for BenzoPPh$_2$TsDPEN (**8**).

(a) ^{31}P NMR spectrum (121 MHz, $CDCl_3$):



(b) ^{1}H NMR spectrum (300 MHz, $CDCl_3$):



(c) 2D ^{1}H-^{1}H COSY spectrum (300 MHz, $CDCl_3$):

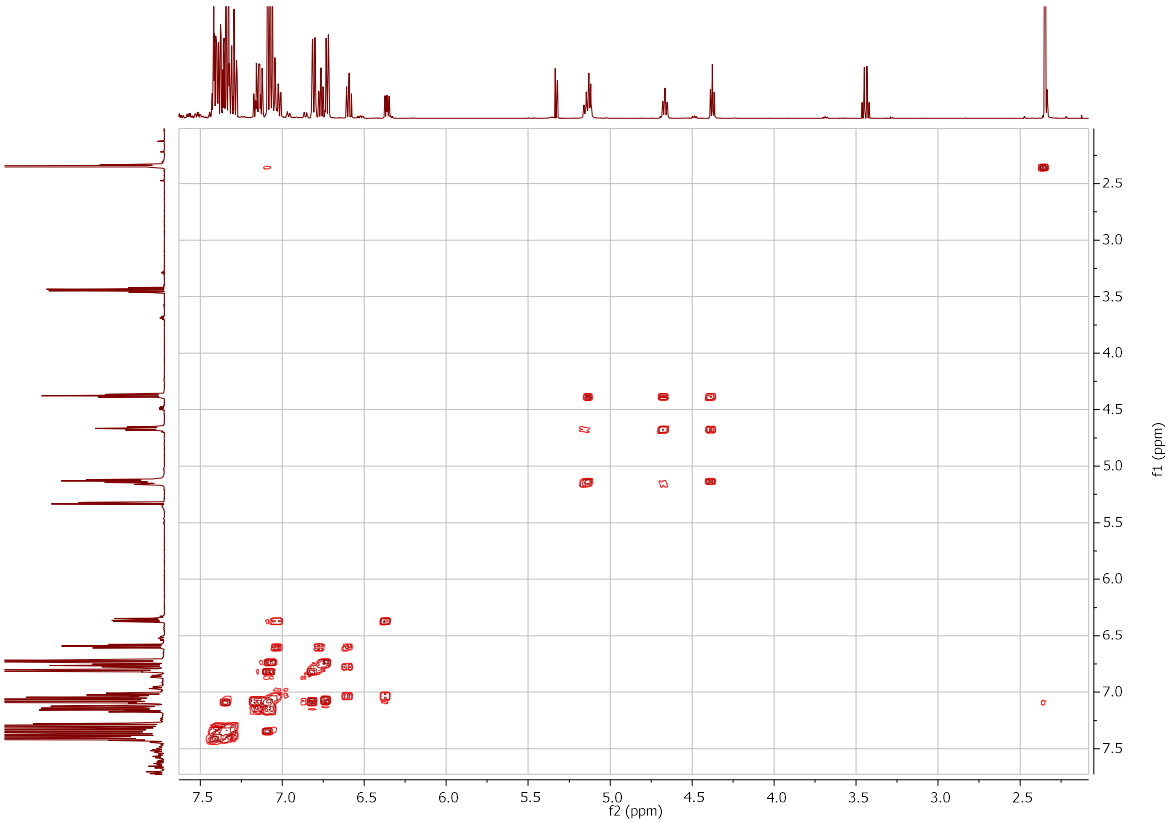
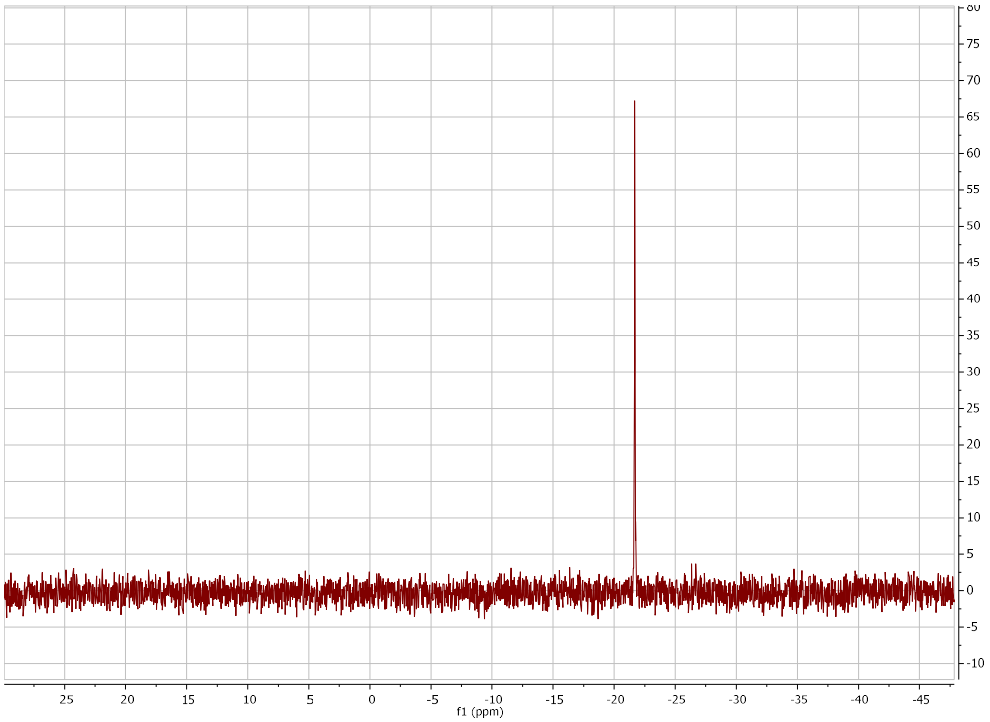
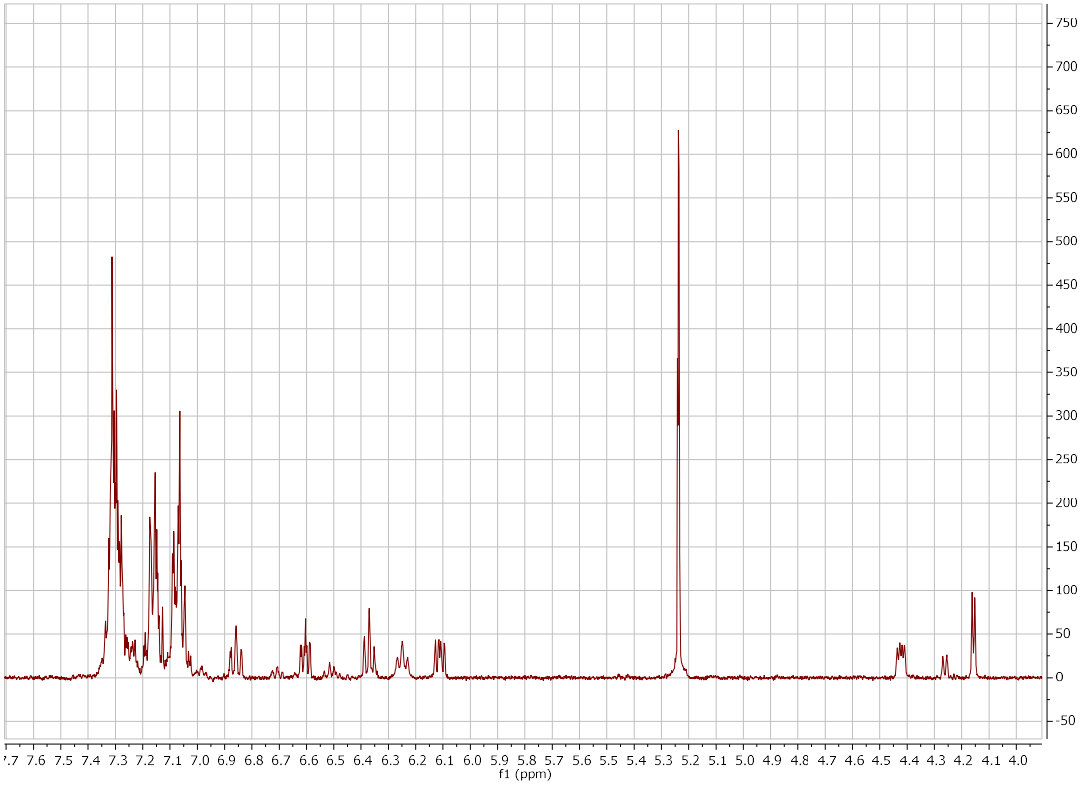


Fig. S6 NMR Spectroscopy for BenzoPPh$_2$DPEN (**9**).

(a) ^{31}P NMR spectrum (162 MHz, $CDCl_3$):



(b) ^{1}H NMR spectrum (400 MHz, $CDCl_3$):



(c) 2D ^{1}H-^{1}H COSY spectrum (400 MHz, $CDCl_3$):

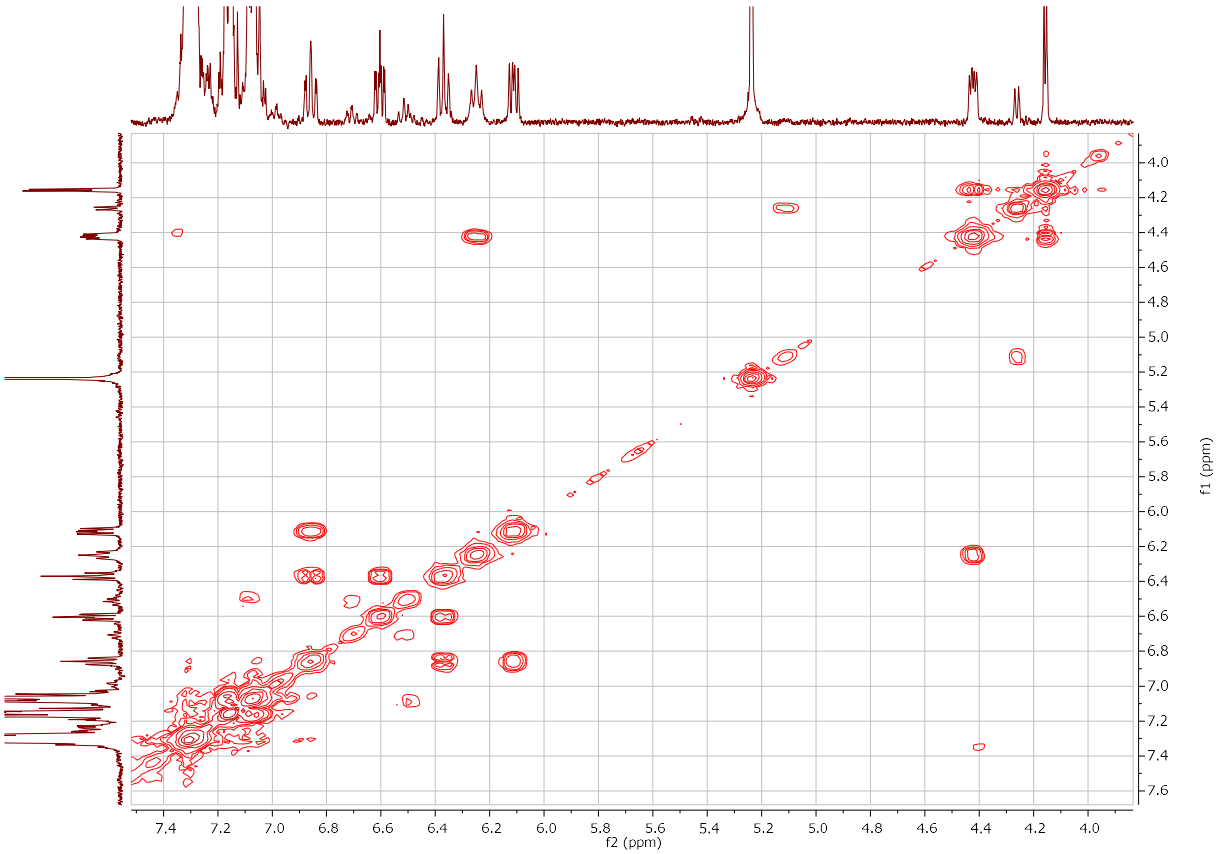
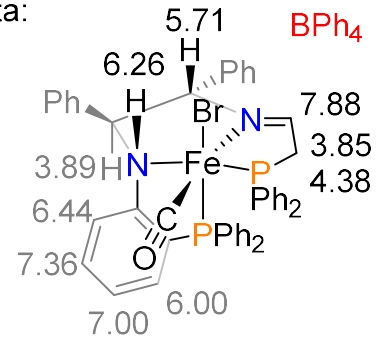
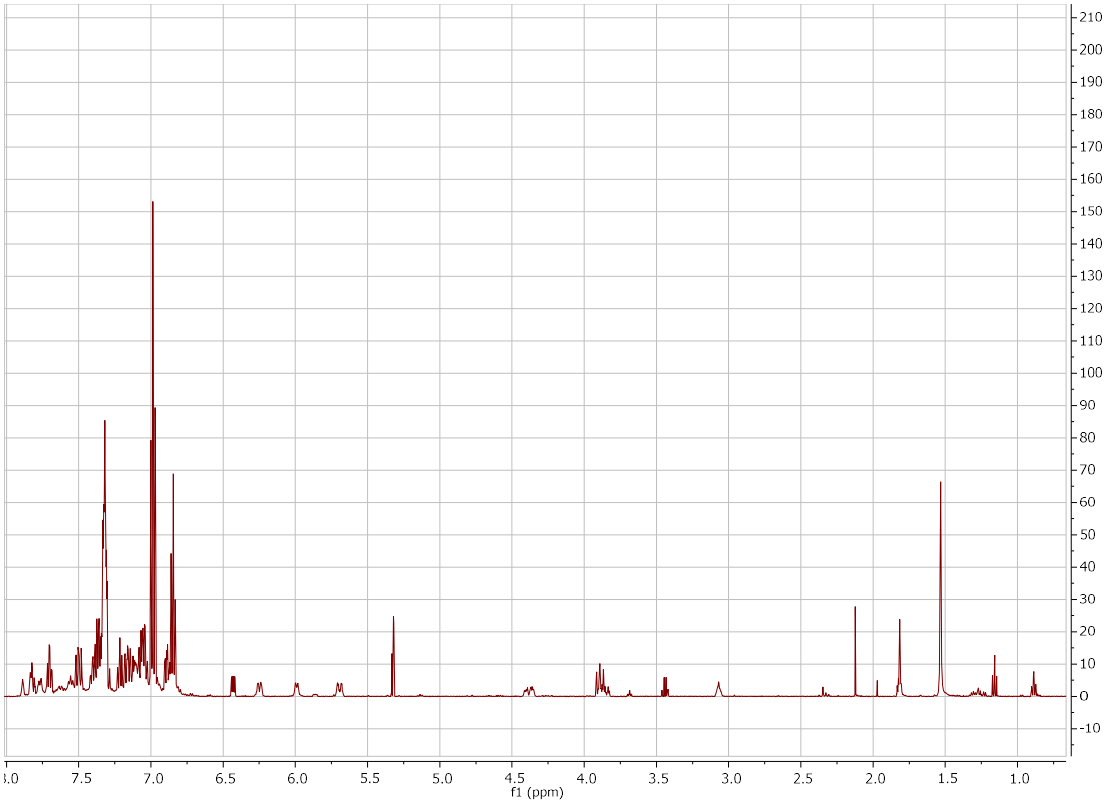


Fig. S7 NMR and IR Spectroscopy for Imine Iron Precatalyst (**5d**). Major diastereomer **(*S*)-NH** is shown below.

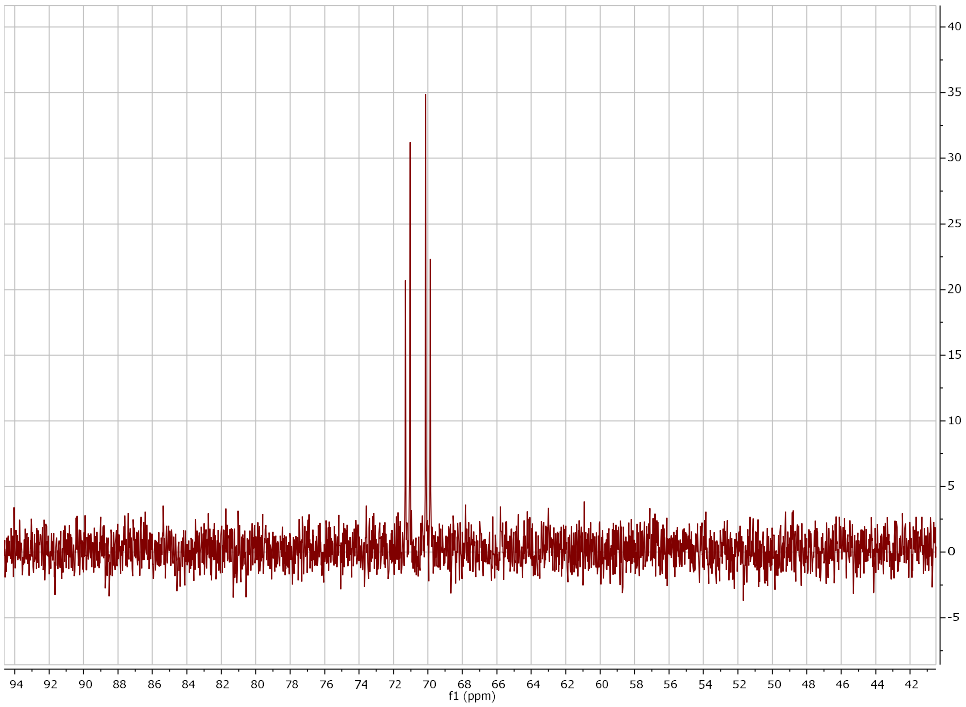
^{1}H NMR Data:



(a) ^{1}H NMR spectrum (500 MHz, CD_2Cl_2):

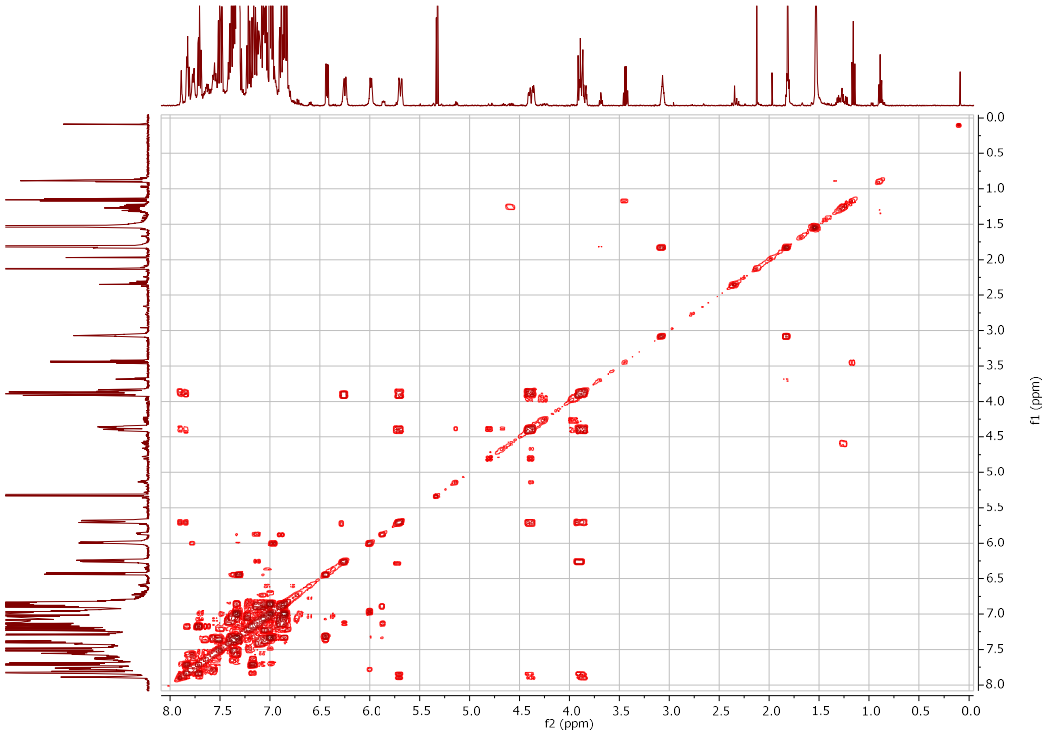


(b) ^{31}P NMR spectrum (162 MHz, CD_2Cl_2): (*S*)-NH-**5d** displays a doublet at 70.0 ppm and 71.2 ppm ($^2J_{PP}$ = 44 Hz).

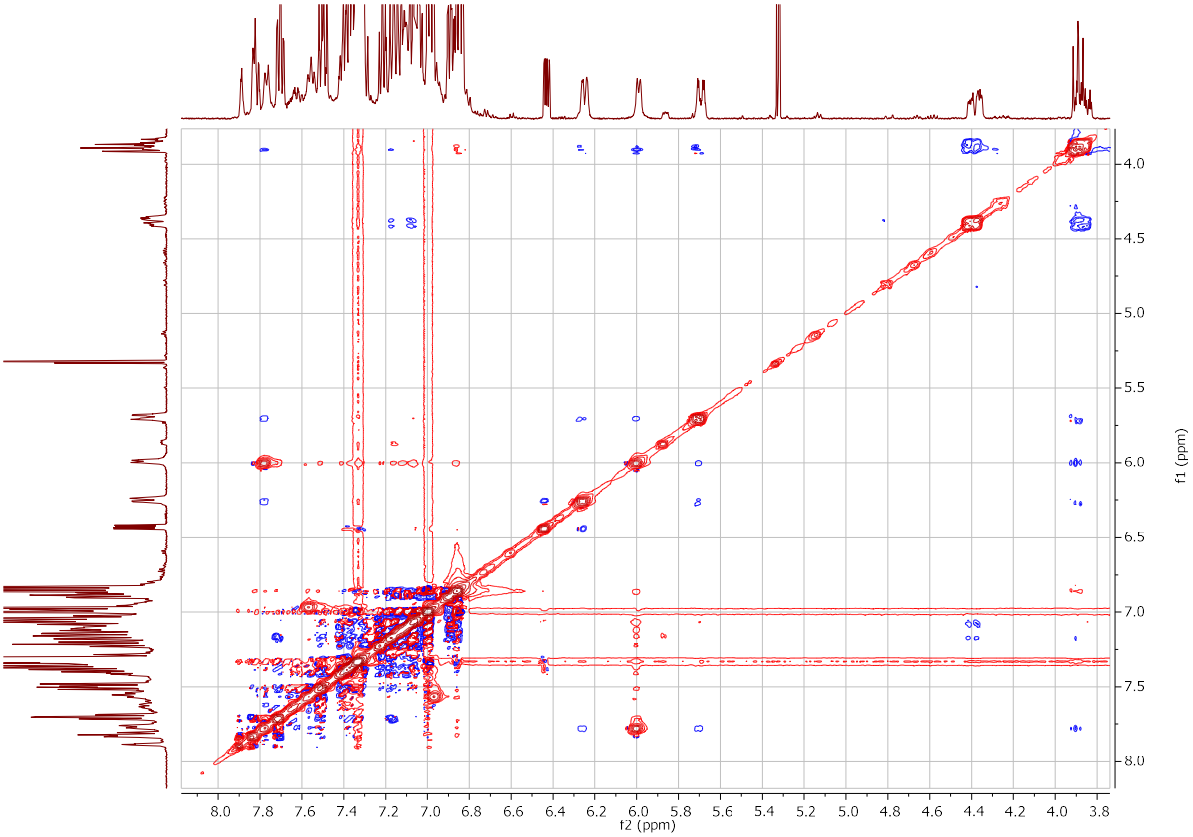


(c) 2D ^{1}H-^{1}H COSY spectrum (500 MHz, CD_2Cl_2):

Note: There is an interesting cross peak between the C**H**Ph at 5.71 ppm and the C**H**$_2$ at 4.38 ppm, which spans 5 bonds. In the crystal structure these two protons are anti, which lead to an optimal dihedral angle.

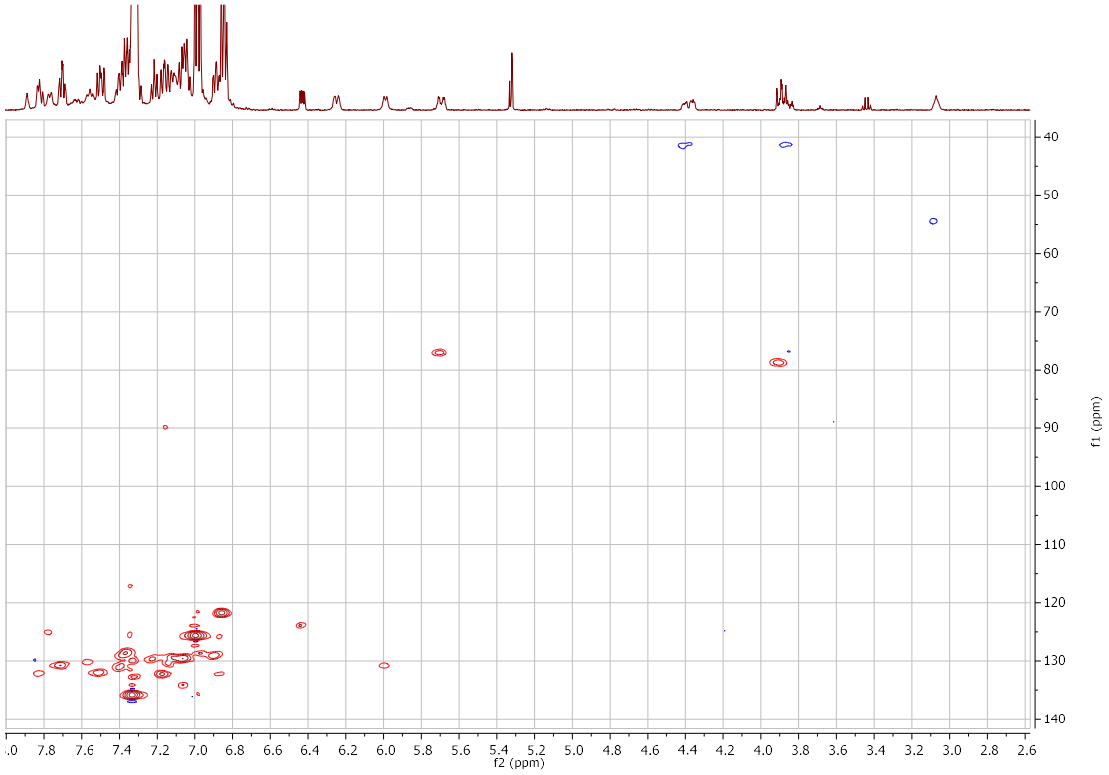


(d) 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, CD_2Cl_2):



(e) 2D ^{1}H-^{13}C HSQC Spectrum (500 MHz, CD_2Cl_2):

The C**H**Ph of **(*S*)-NH-5d** are found at (5.71, 77.08) and (3.89, 78.78), and the two protons of the C**H₂** of the imine arm at (4.38, 41.32) and (3.85, 41.32). There is no cross peak from the proton at 6.26 ppm, thus it is an NH proton.



(f) IR Spectrum:

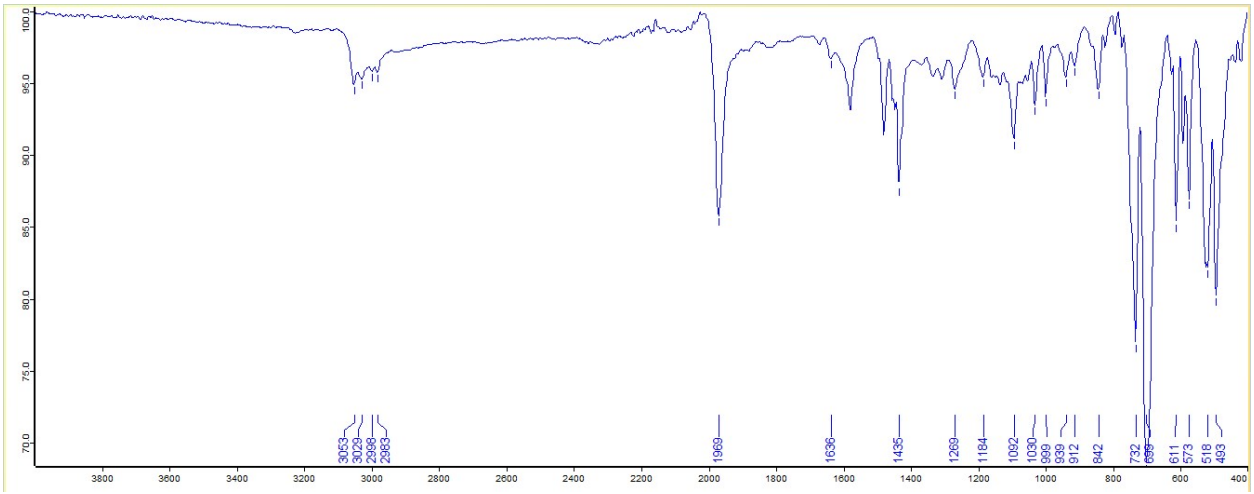
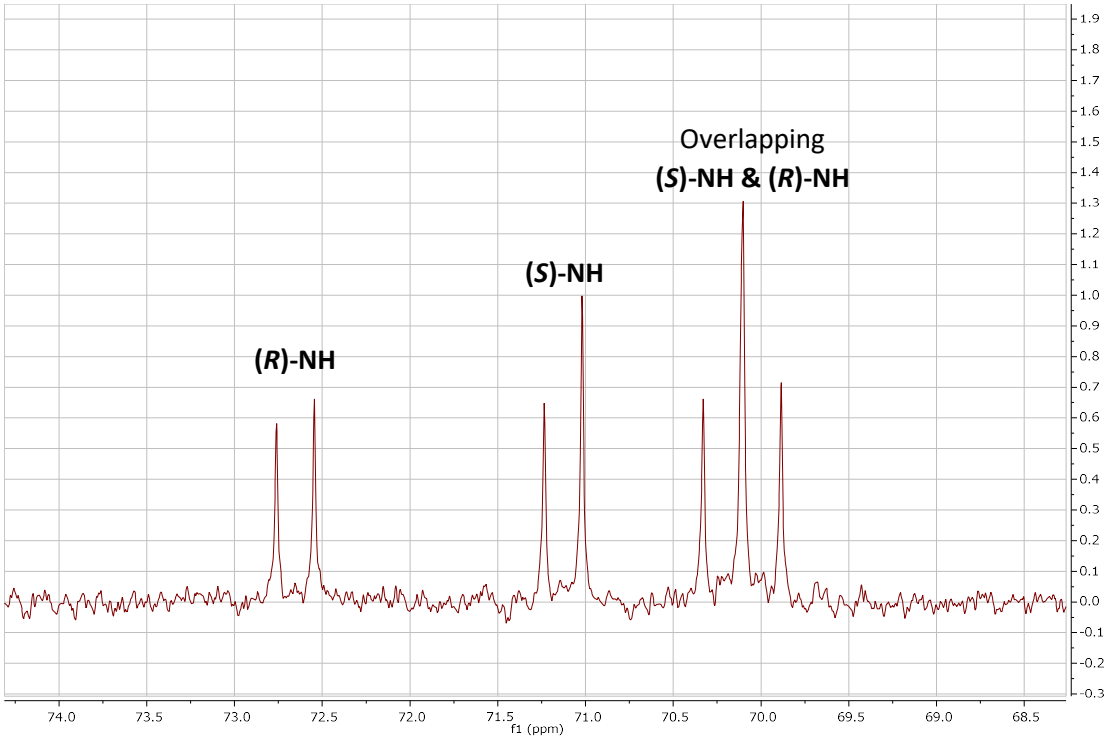


Fig. S8 NMR Spectroscopy of Crystals of Imine Iron Precatalyst **5d** (1:1 mixture of (*S*)-NH:(*R*)-NH).

(a) ^{31}P NMR spectrum (202 MHz, CD_2Cl_2):
Major species **(*S*)-NH** at 70.0 ppm and 71.2 ppm ($^2J_{PP}$ = 44 Hz), and the minor species **(*R*)-NH** at 70.21 ppm and 72.67 ppm ($^2J_{PP}$ = 44 Hz).



(b) ^1H NMR spectrum (500 MHz, CD_2Cl_2):

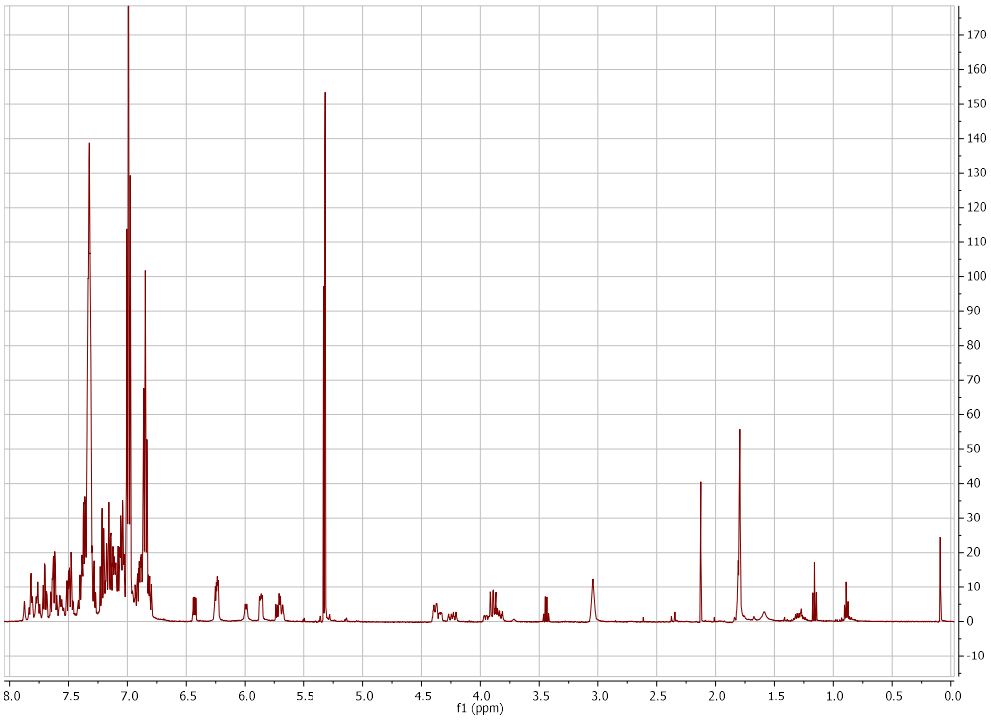
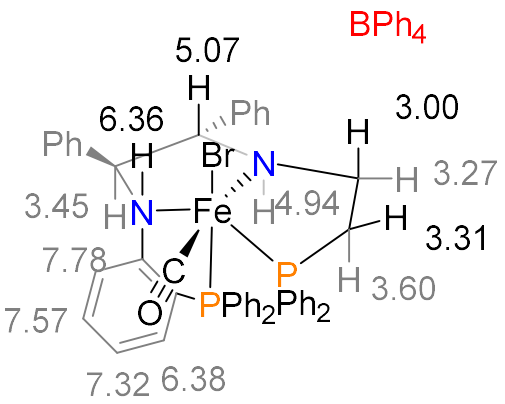
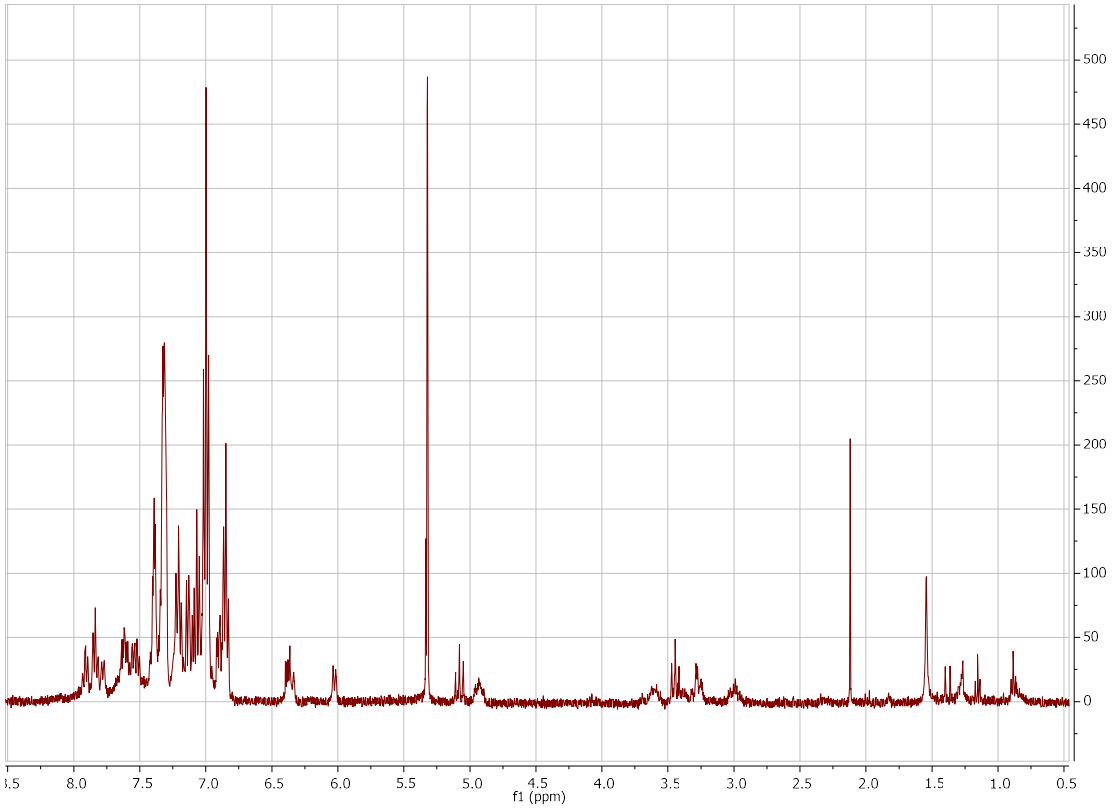


Fig. S9 NMR and IR Spectroscopy of Crystals (*S,S*)-NH,NH Amine Iron Precatalyst (**6d**).

^{1}H NMR Data:

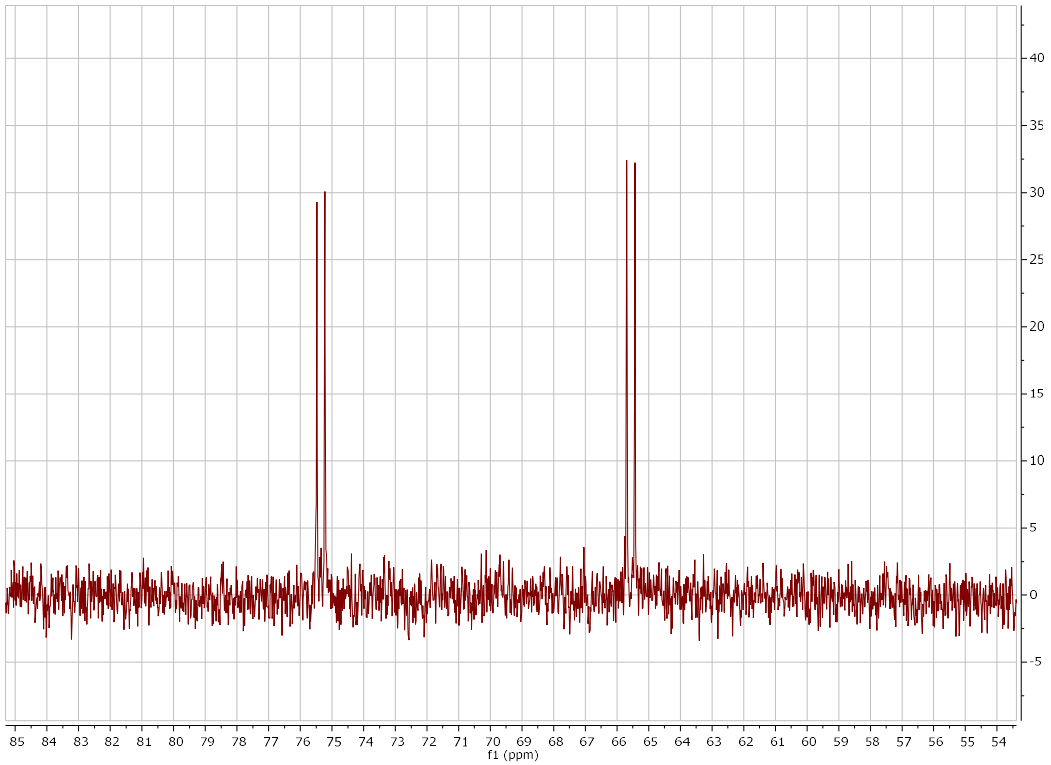


(a) ^{1}H NMR spectrum (400 MHz, CD_2Cl_2):

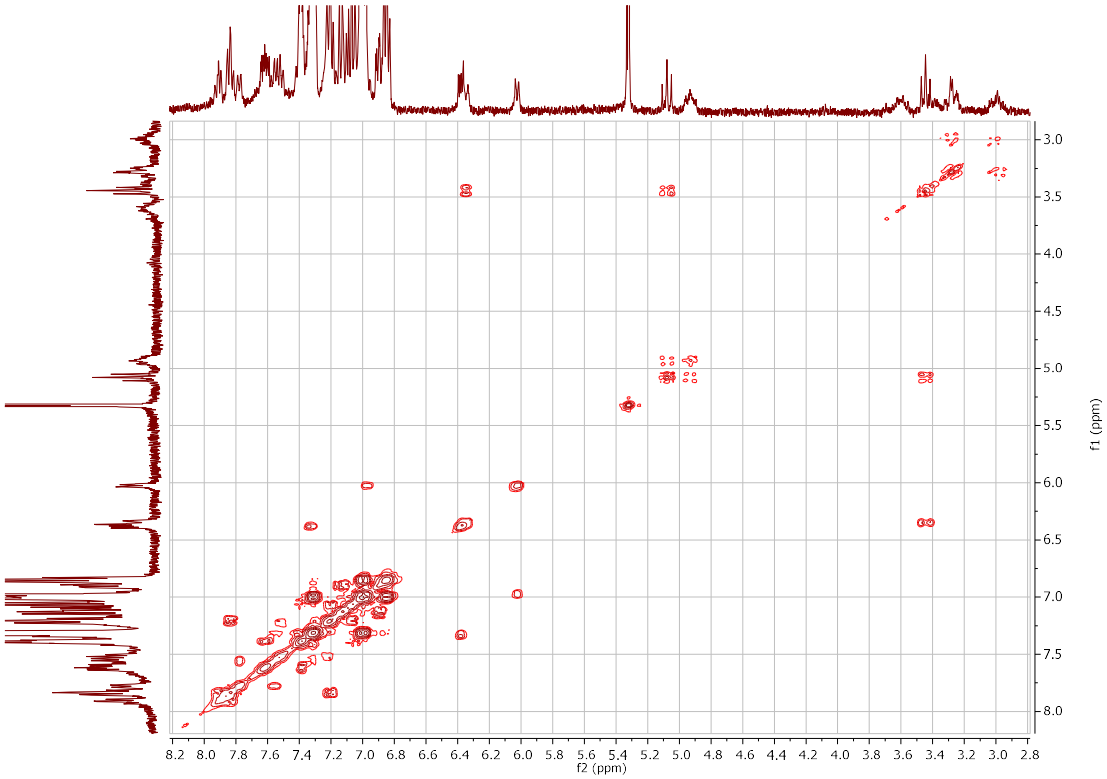


(b) ^{31}P NMR spectrum (162 MHz, CD_2Cl_2):

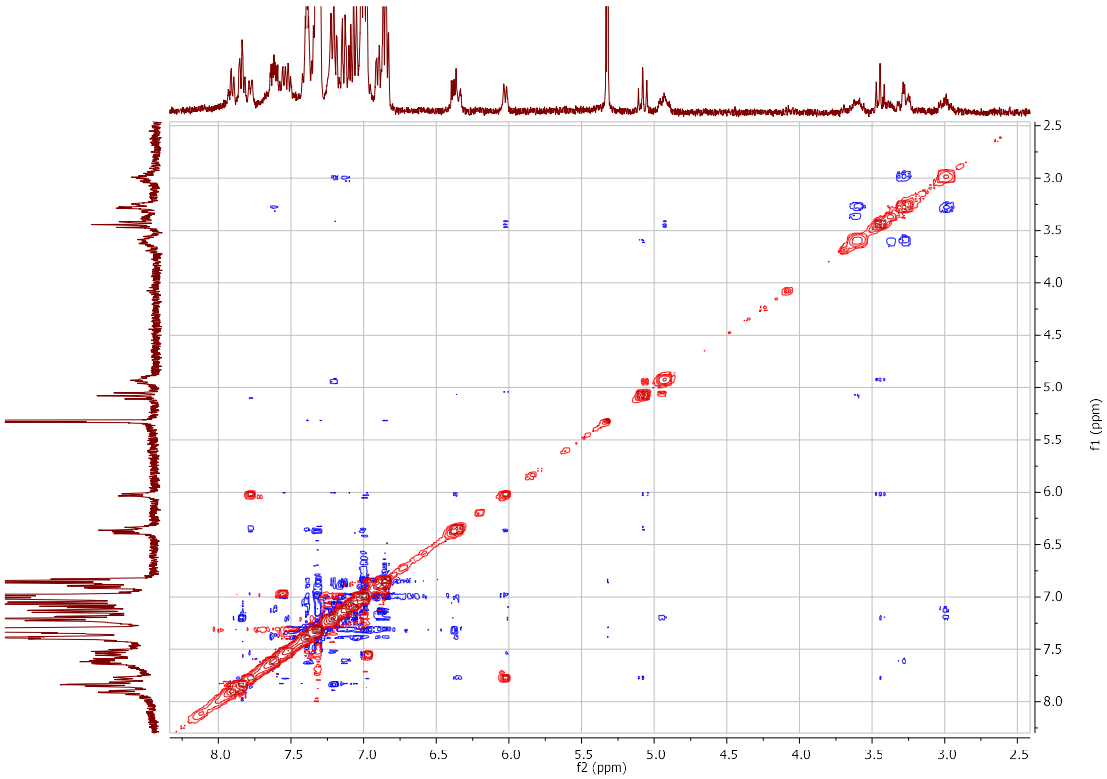
The ^{31}P NMR spectrum for **6d** displays a doublet at 65.56 ppm and 75.35 ppm ($^2J_{PP}$ = 42 Hz).



(c) 2D ^1H-^1H COSY spectrum (400 MHz, CD_2Cl_2):

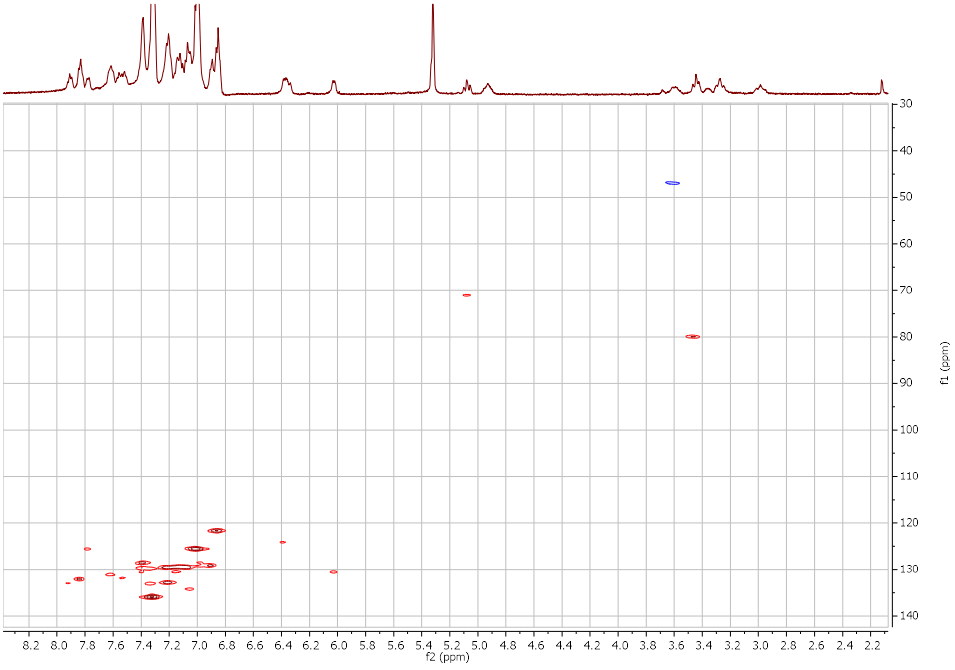


(d) 2D ^{1}H-^{1}H NOESY spectrum (400 MHz, CD_2Cl_2):



(e) 2D ^{1}H-^{13}C HSQC spectrum (400 MHz, CD_2Cl_2):

The C**H**Ph of **(*S*, *S*)-NH-6d** are found at (5.07, 71.00) and (3.45, 80.73). There is no crosspeak for the protons at 6.36 ppm and 4.94 ppm thus they are NH protons. The HSQC shows a cross peak for the proton at 6.38 ppm (not the NH proton at 6.36 ppm), which corresponds to a C_6**H**$_4$ aromatic proton.



(f) IR Spectrum:

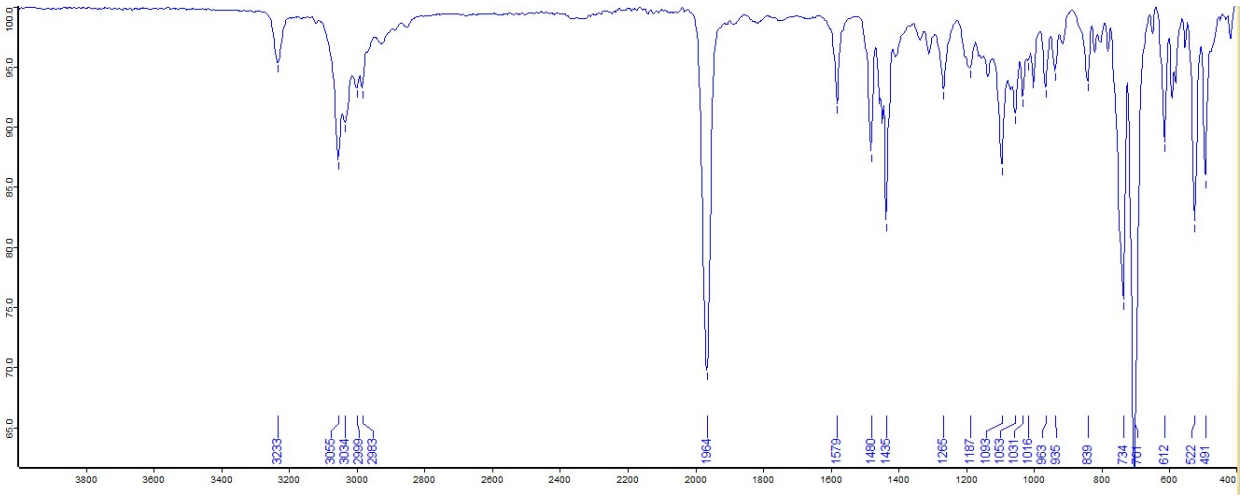
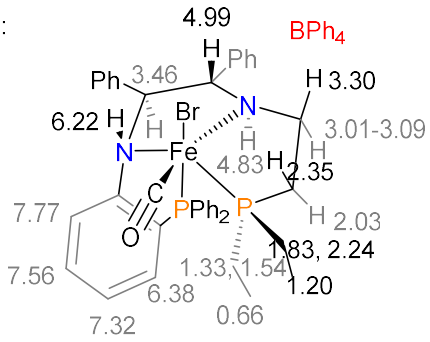
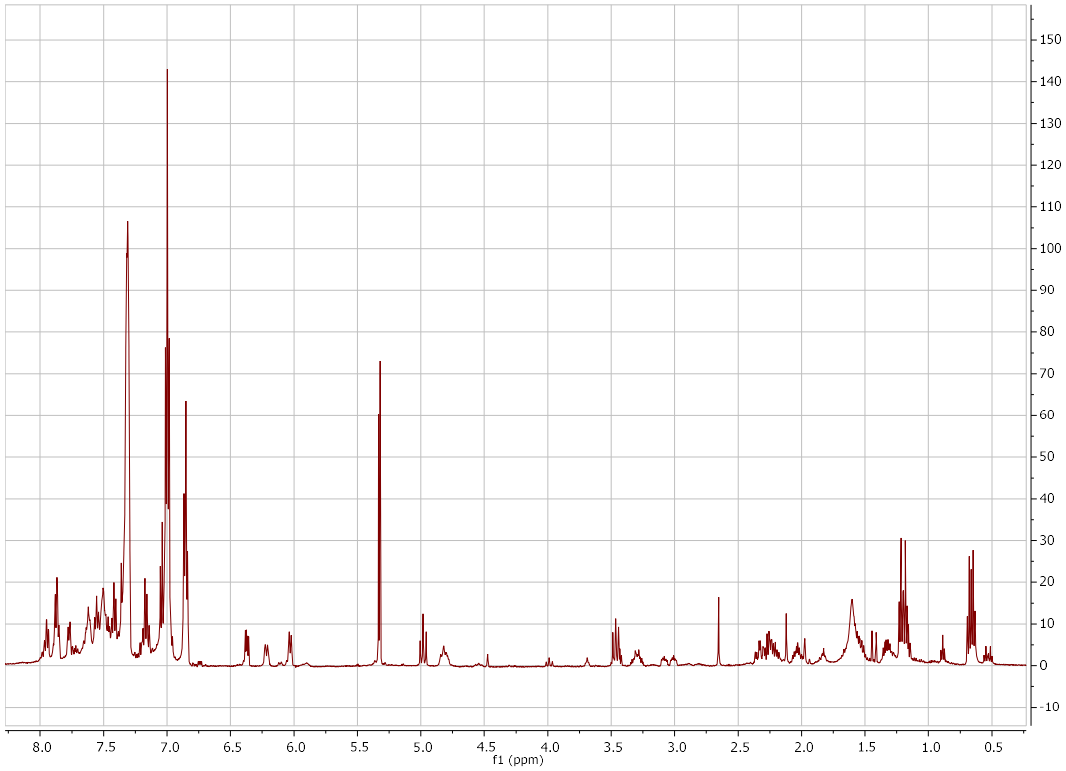


Fig. S10 NMR and IR Spectroscopy of Powder of Amine Iron Precatalyst (**6a**) Containing (*S*,*S*)-NH,NH and (*R*,*S*)-NH,NH.

^{1}H NMR Data:

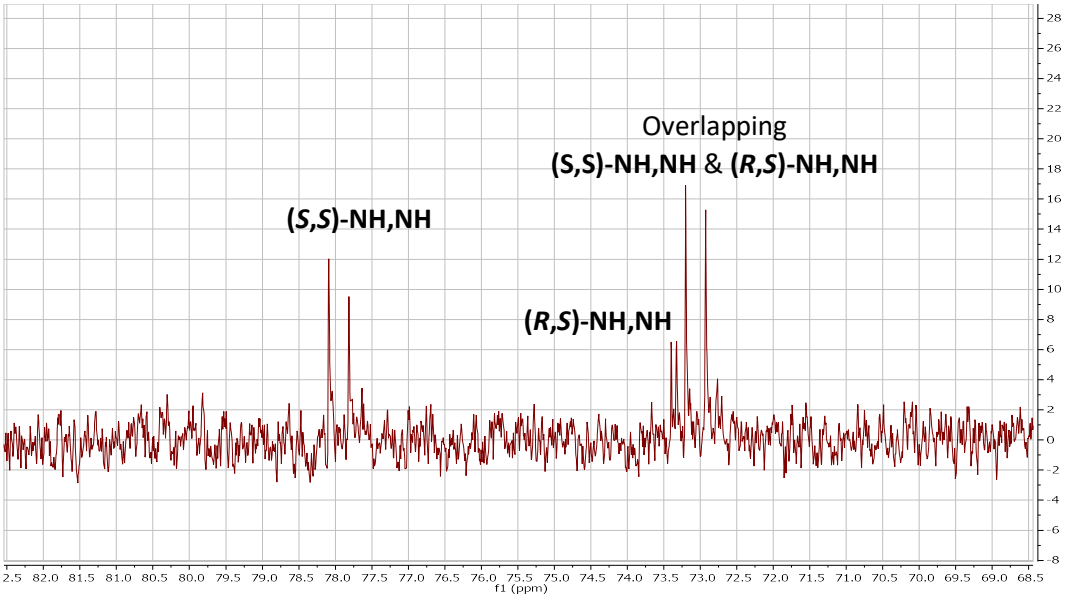


(a) ^{1}H NMR spectrum (500 MHz, CD_2Cl_2):

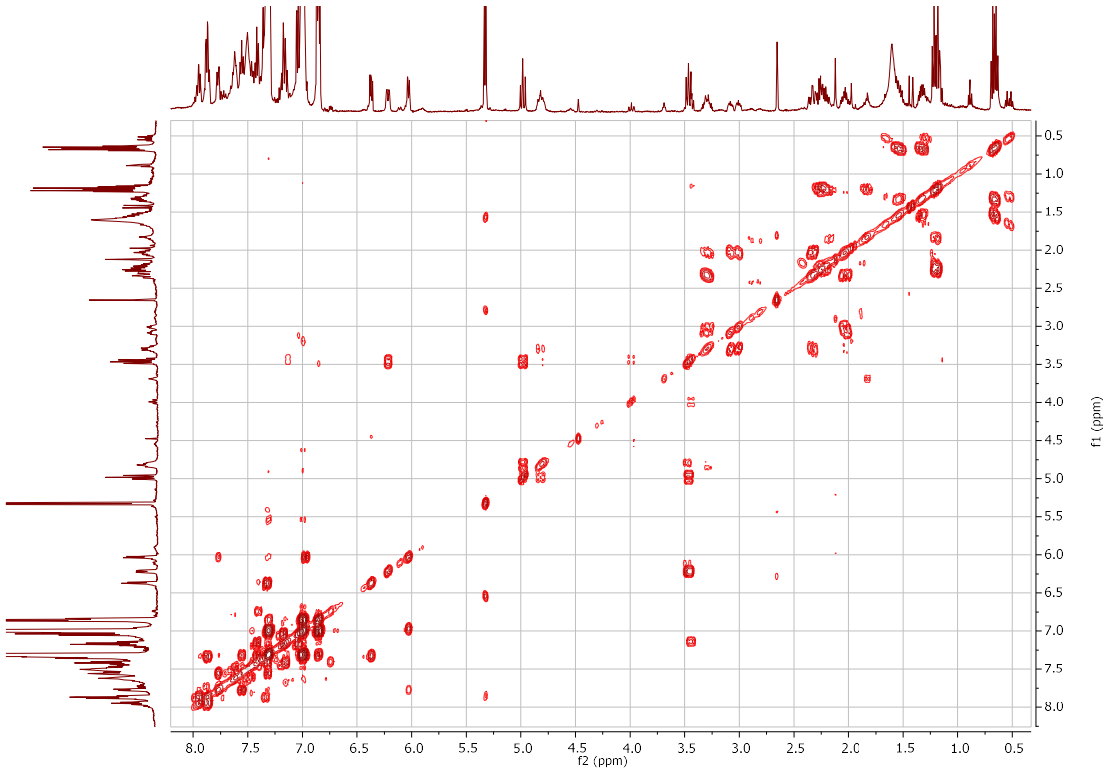


(b) ^{31}P NMR spectrum (202 MHz, CD_2Cl_2):

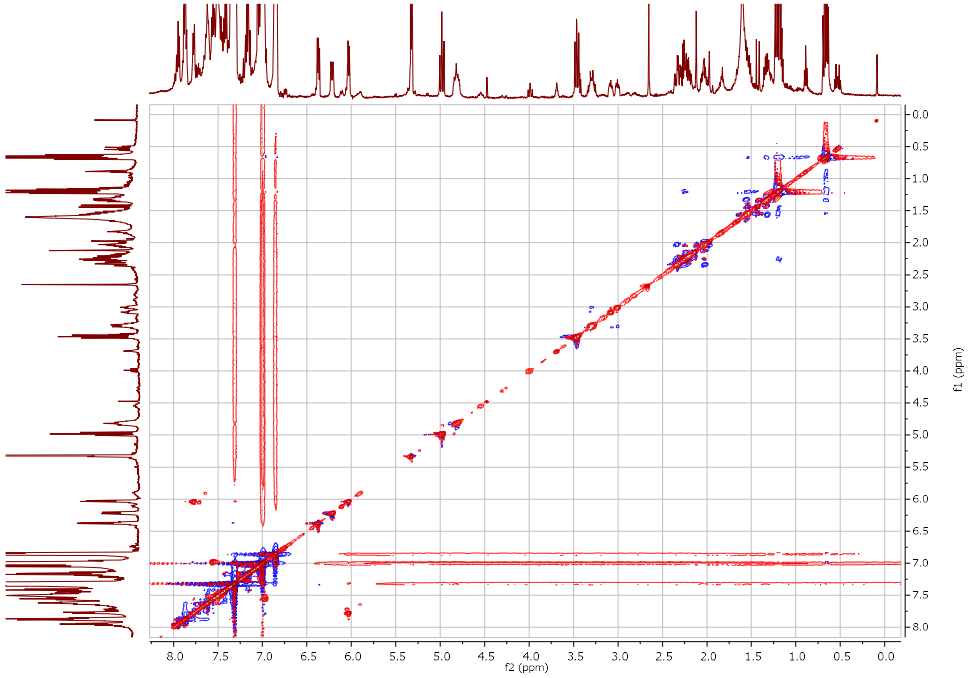
Major species (*S,S*)-NH,NH displaying doublets at 73.06 ppm and 77.95 ppm in the ^{31}P NMR spectrum. The minor species displays one doublet at 73.36 ppm and the other was overlapping with the major species.



(c) 2D ^{1}H-^{1}H COSY spectrum (500 MHz, CD_2Cl_2):

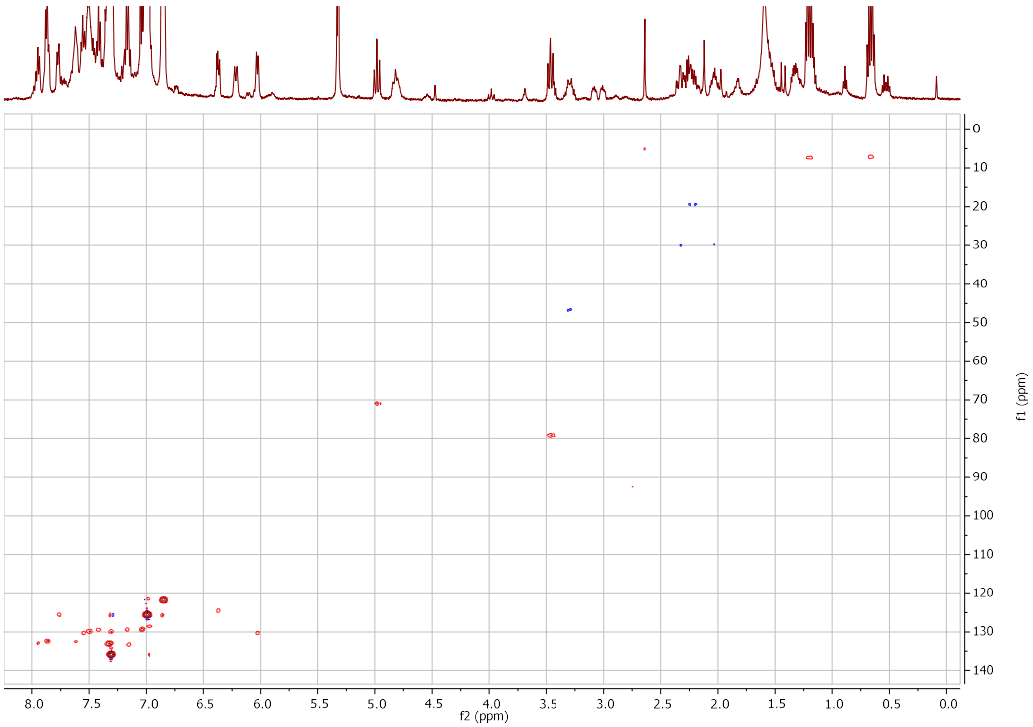


(d) 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, CD_2Cl_2):

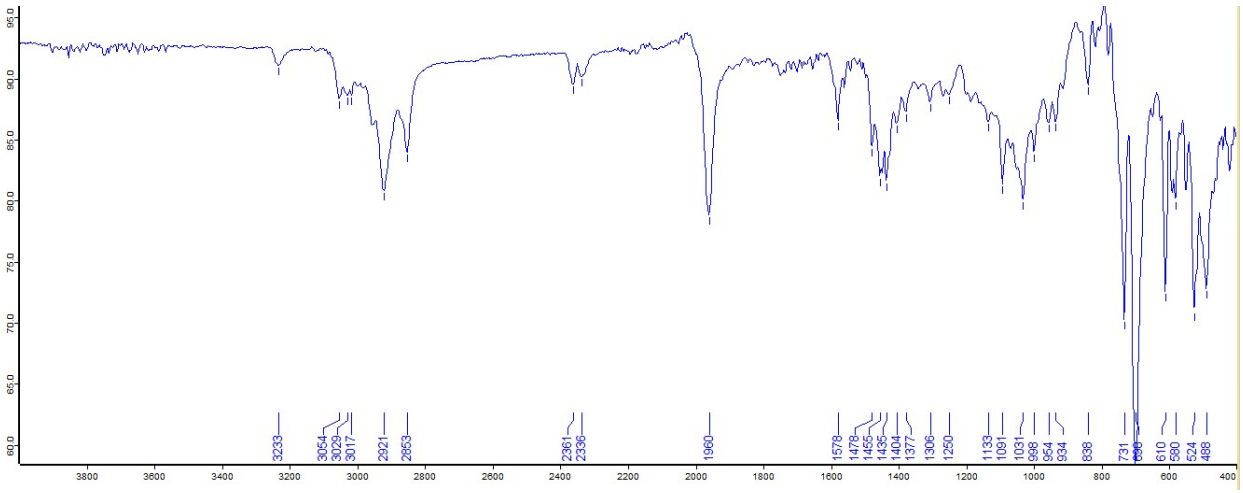


(e) 2D ^{1}H-^{13}C HSQC spectrum (500MHz, CD_2Cl_2):

2D ^{1}H-^{13}C HSQC spectrum displays the C**H**Ph at (4.99, 70.97) and (3.46, 79.15), the protons of the two CH_2 of the amine arm at (3.30, 46.90), (3.09, 46.36), (2.35, 29.99), and (2.03, 29.79), the protons of the two CH_2 of the diethylphosphine which are overlapping at (2.24, 19.42), (1.84,19.55), (1.54, 23.09), and (1.33, 22.93), and the protons of the two CH_3 of the diethylphosphine at (1.20,7.29), and (0.66, 7.24).



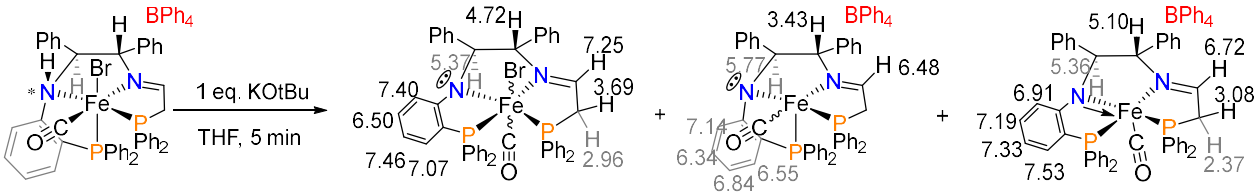
(f) IR Spectrum:



A Note on Solving NMR in the Following Studies:

2D ^{1}H-^{13}C HSQC spectrum was used to locate the two C**H**Ph o the DPEN backbone in the ^{13}C range of 70-90 ppm, using the intensity in the ^{1}H to discern the major species, medium species, and minor species. The 2D ^{1}H-^{1}H COSY spectrum was used to discern the connectivity of the DPEN backbone to the imine or amine side arm, verifying how many protons were attached to each carbon through the HSQC. CH protons were red in colour while CH_2 protons were blue. The 2D ^{1}H-^{1}H NOESY spectrum was used to place the protons on either the top or bottom of the plane formed by the PNNP ligand, using the DPEN C**H**Ph as an anchor. The *cis-β* or *trans* structure was based on the $^{2}J_{PP}$ coupling constants of each complex, wherein a coupling constant >40 Hz as found in the precatalysts denoted a *cis-β* structure and a coupling constant <40 Hz, as found in crystal **16d**, was assigned as a trans complex. The amino proton next to the ethylene linker was usually in the ^{1}H range of 3.80-4.50 ppm, verified by the COSY connection of the adjacent CH_2. This was important to discern if the complex was five- or six-coordinate, as the protonation of this amido requires the addition of another anionic ligand (alkoxide or hydride) to form a neutral iron complex. Unfortunately, the alkoxide protons could not be discerned from the ^{1}H NMR. The ^{1}H NMR chemical shifts for each complex is shown when known.

Fig. S11 Base Activation Studies of **5d** with 1 eq. of KOtBu.



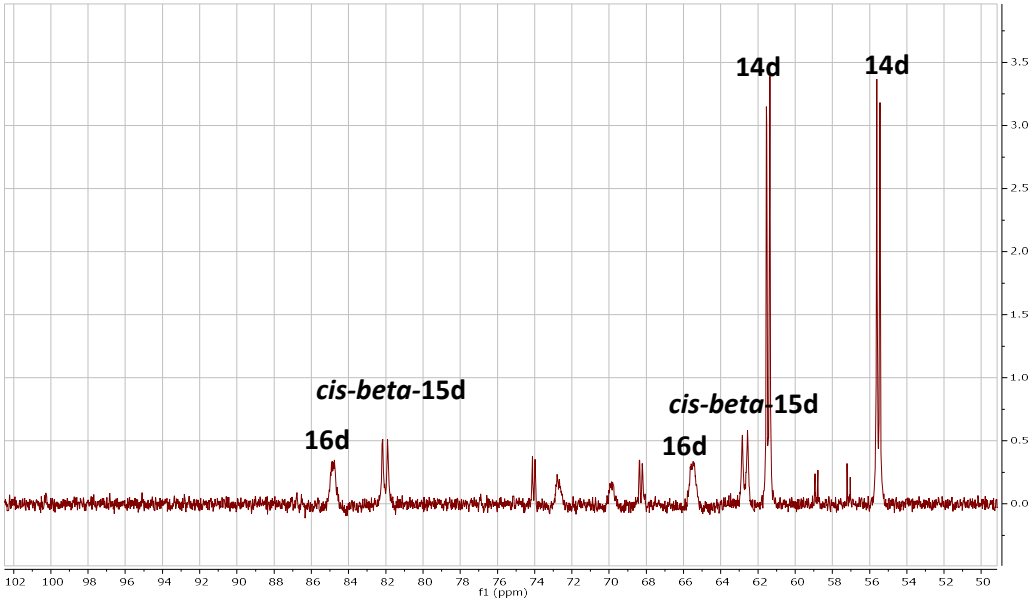
5d-(*S*)-NH
95%

14d
60% (5 min)
100% (5 d)

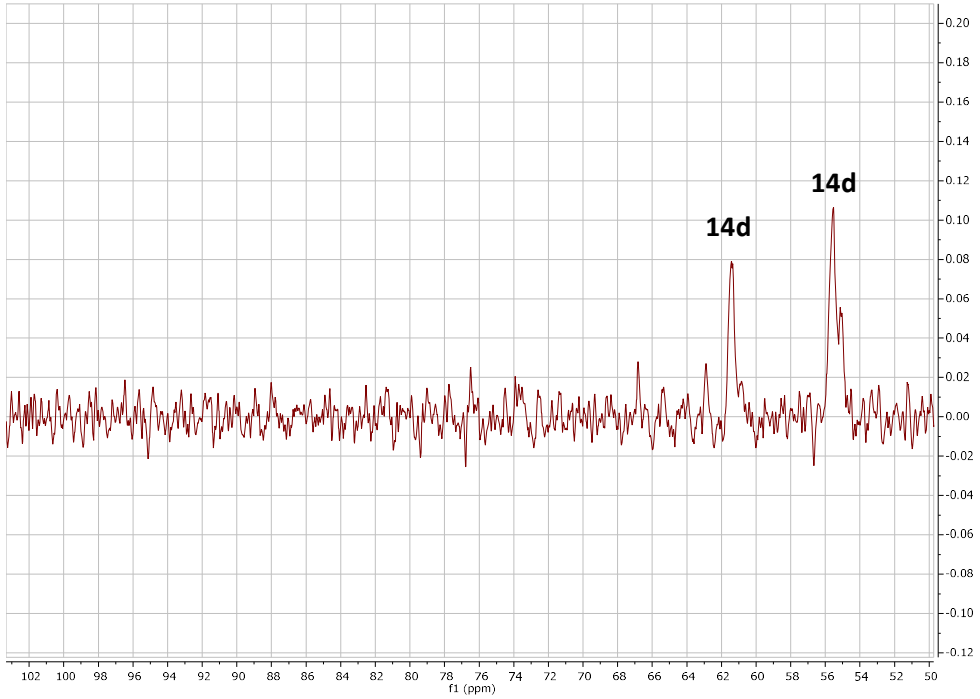
***cis-beta*-15d**
15% (5 min)
0% (5 d)

16d
25% (5 min)
0% (5 d)

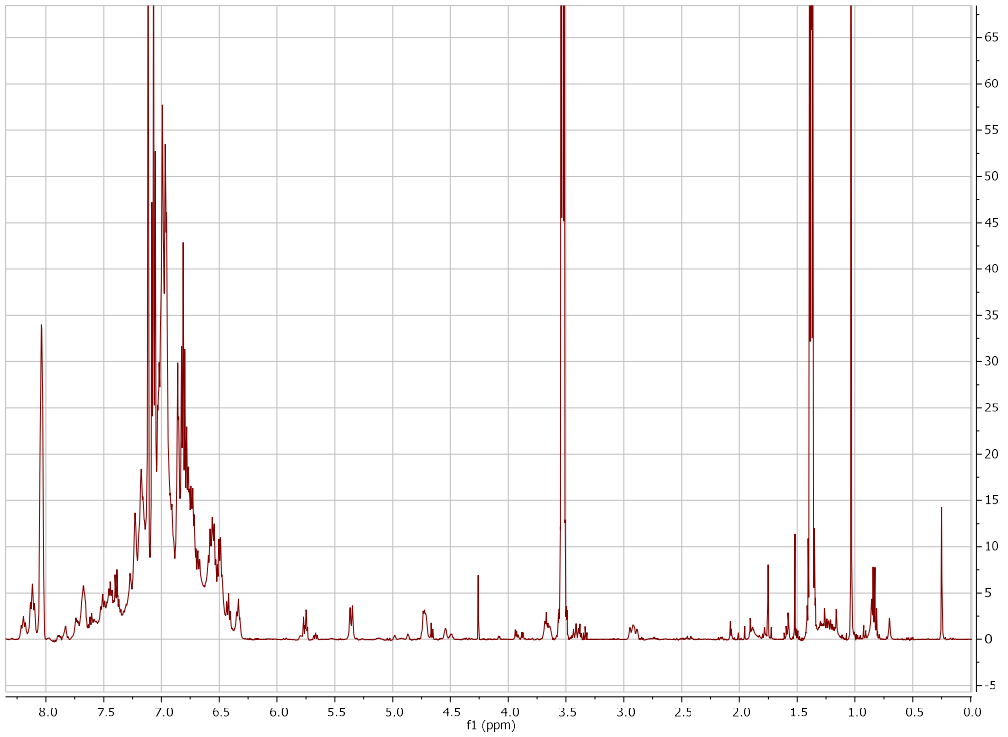
(a) ^{31}P NMR spectrum (202 MHz, C_6D_6). Spectrum taken after 5 minutes:
Complex **16d** displays two broad peaks at 65.42 ppm and 84.92 ppm ($^2J_{PP}$ = 32 Hz), with a large spacing between the two chemical shifts. Upon isolation of the crystals of **16d**, we discern that the cationic five-coordinate complex with an open site was only slightly soluble in C_6D_6. Redissolution of the crystals in CD_2Cl_2 yielded more resolved spectra as shown in a later section. **Cis-beta-15d** displays two small doublets at 62.70 ppm and 82.04 ppm ($^2J_{PP}$ of 59 Hz). This large coupling constant suggests a *cis-β* structure, while the large spacing between the doublets suggests a similar five-coordinate cationic iron complex which was observed in the crystal of **16d**. Six-coordinate complex **14d** was the major species as shown in the ^{31}P NMR spectrum at 55.53 ppm and 61.45 ppm ($^2J_{PP}$ was 35 Hz). There were also three extra iron complexes which could not be discerned.



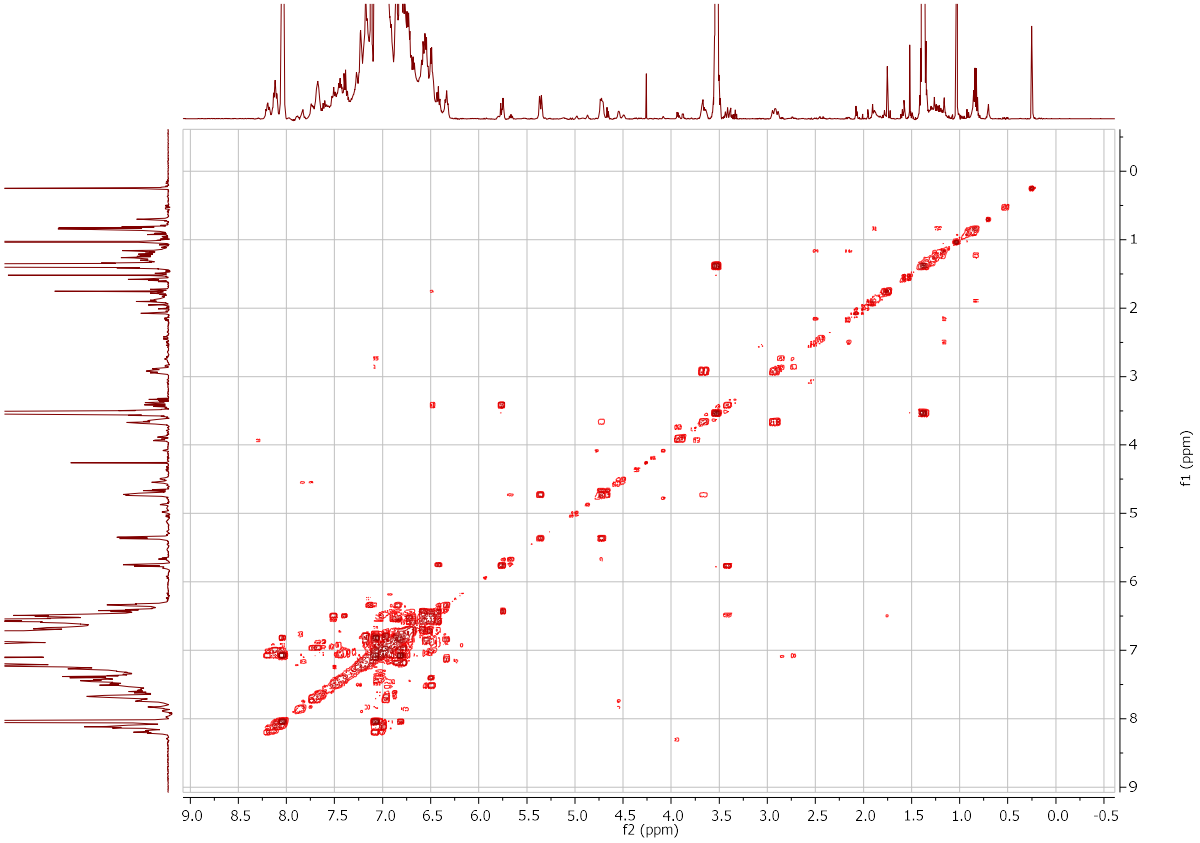
(b) ^{31}P NMR spectrum after 5 d (202 MHz, C_6D_6):



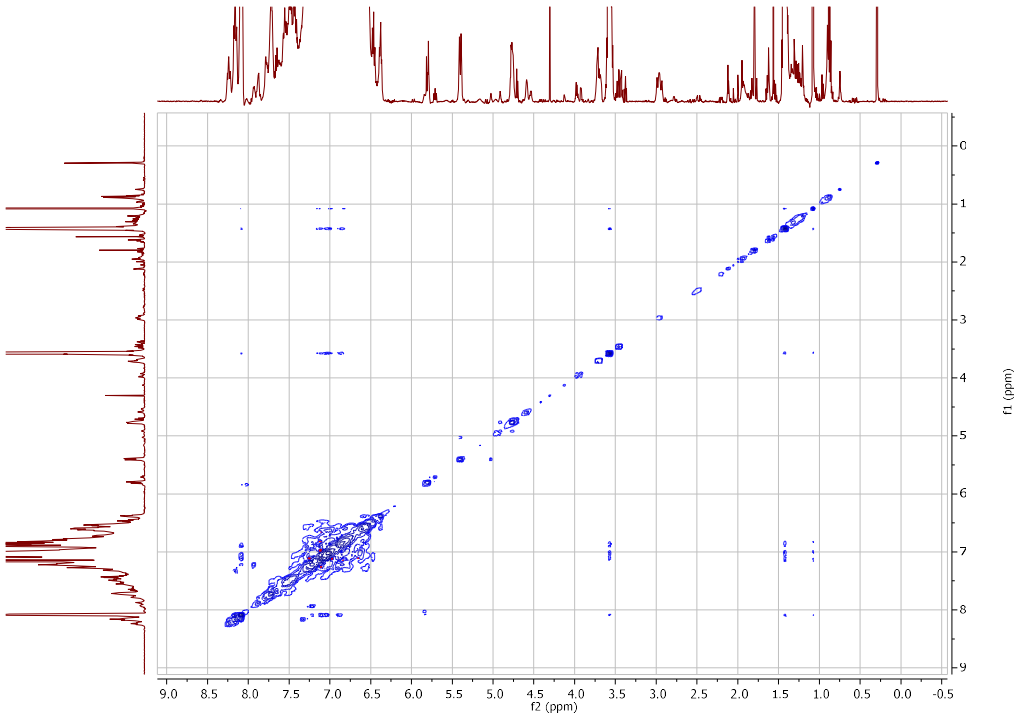
(c) ^{1}H NMR spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:



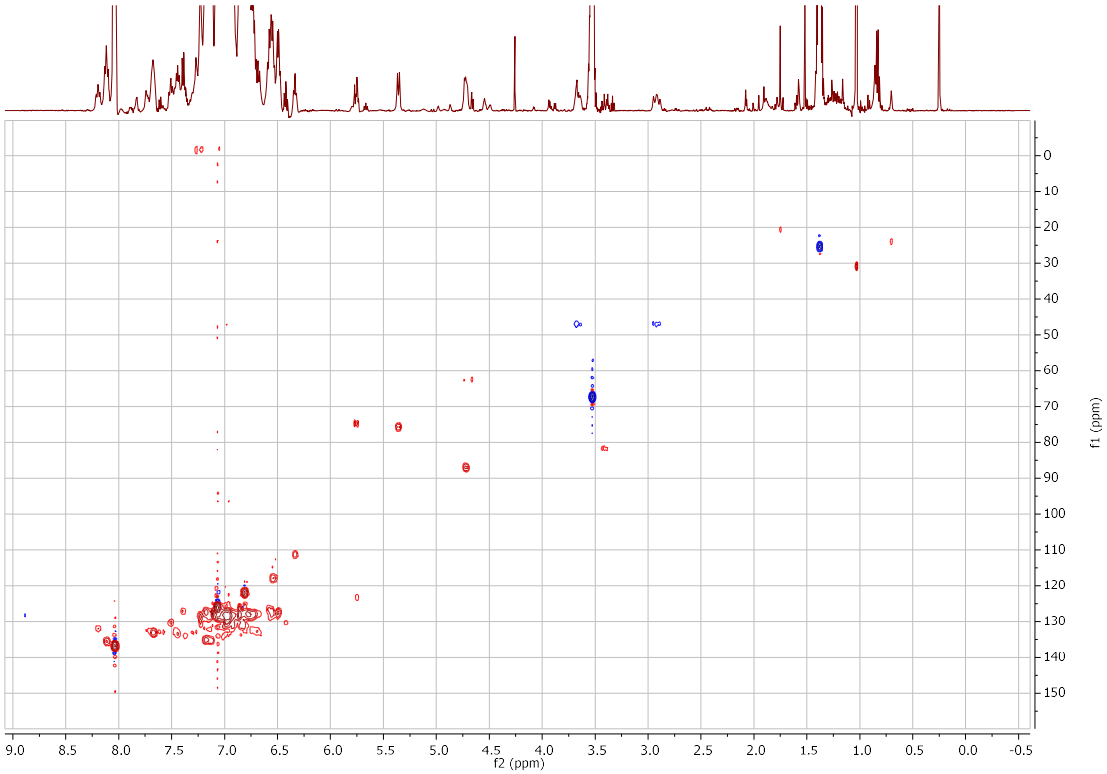
(d) 2D ^{1}H-^{1}H COSY spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:



(e) 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:



(f) 2D ^{1}H-^{13}C HSQC spectrum (500MHz, C_6D_6). Spectrum taken after 5 minutes:
The C**H**Ph of major species **14d** at (5.37, 75.75) and (4.72, 86.99), the two protons of the CH_2 of the imine arm at (3.69, 47.06) and (2.96, 47.03). The information for **16d** can be found in Fig. S12.



(g) IR Spectrum:
The broad CO stretch of **14d** at 1920 cm^{-1} was overlapping with the stretch of **16d** found at 1937 cm^{-1} (Fig. S11) and the stretch of the doubly deprotonated species at 1910 cm^{-1} (Fig. S13).

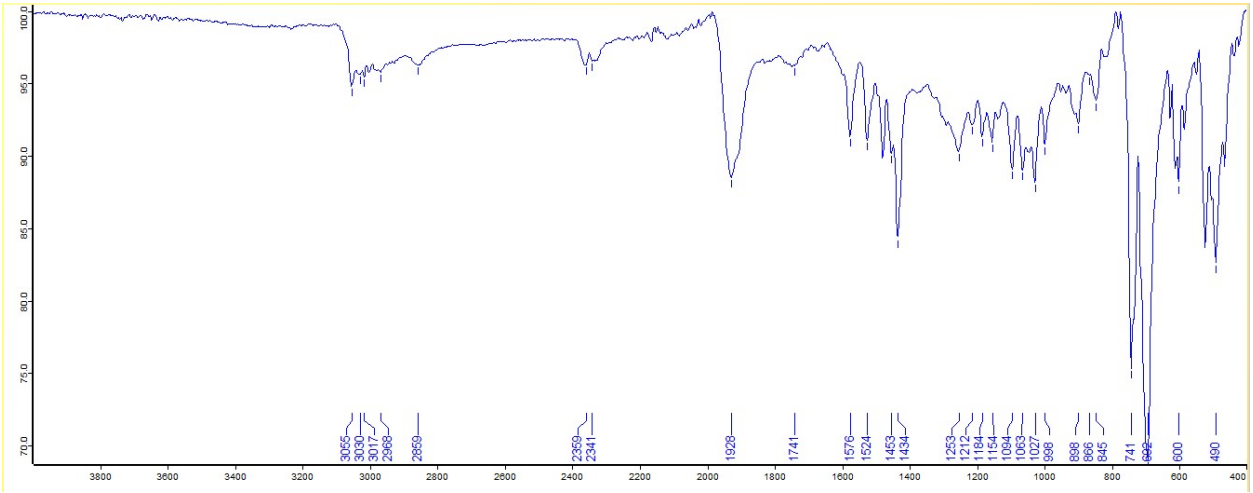
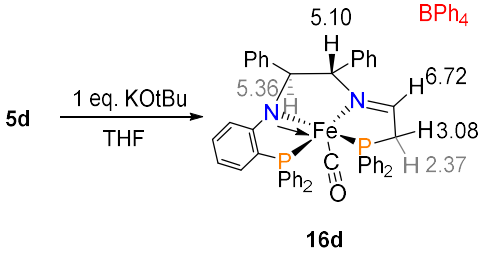
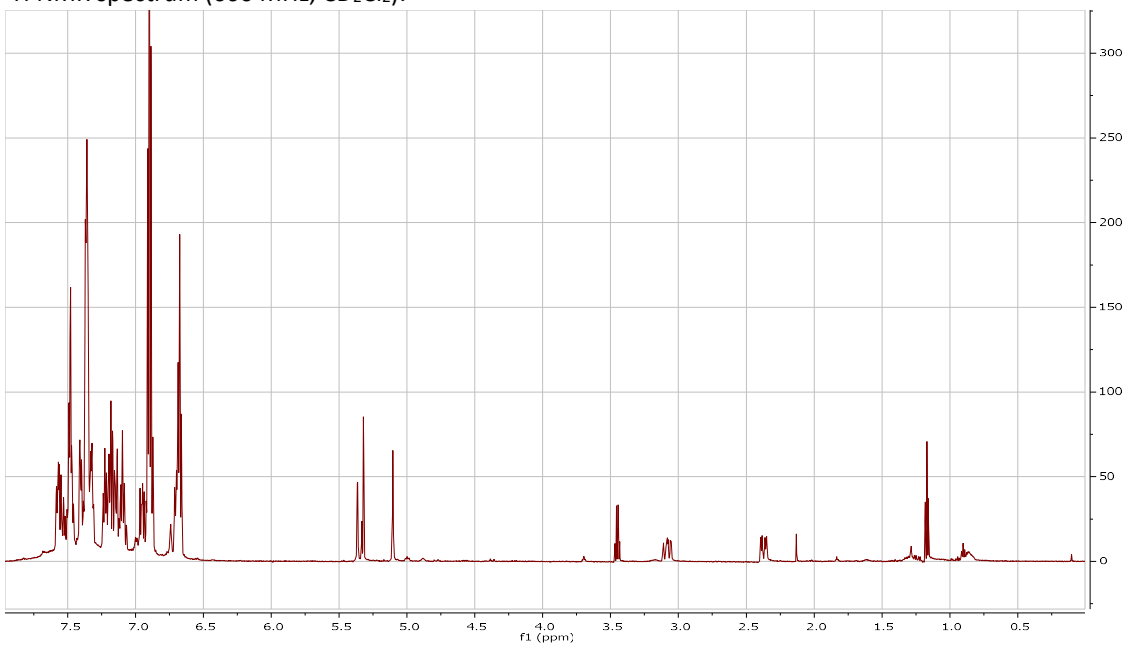


Fig. S12 NMR and IR Spectroscopy of Crystals of **16d**.



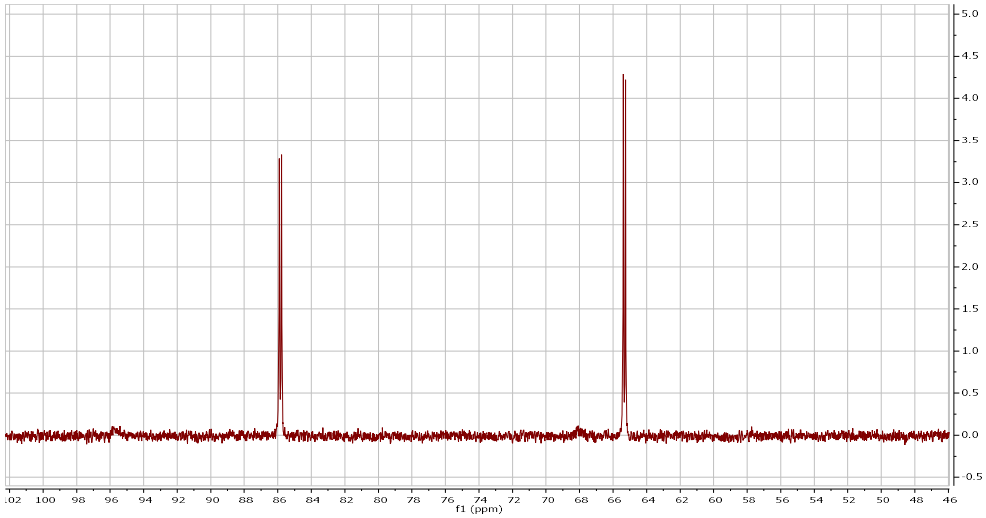
16d

(a) ^{1}H NMR spectrum (600 MHz, CD_2Cl_2):

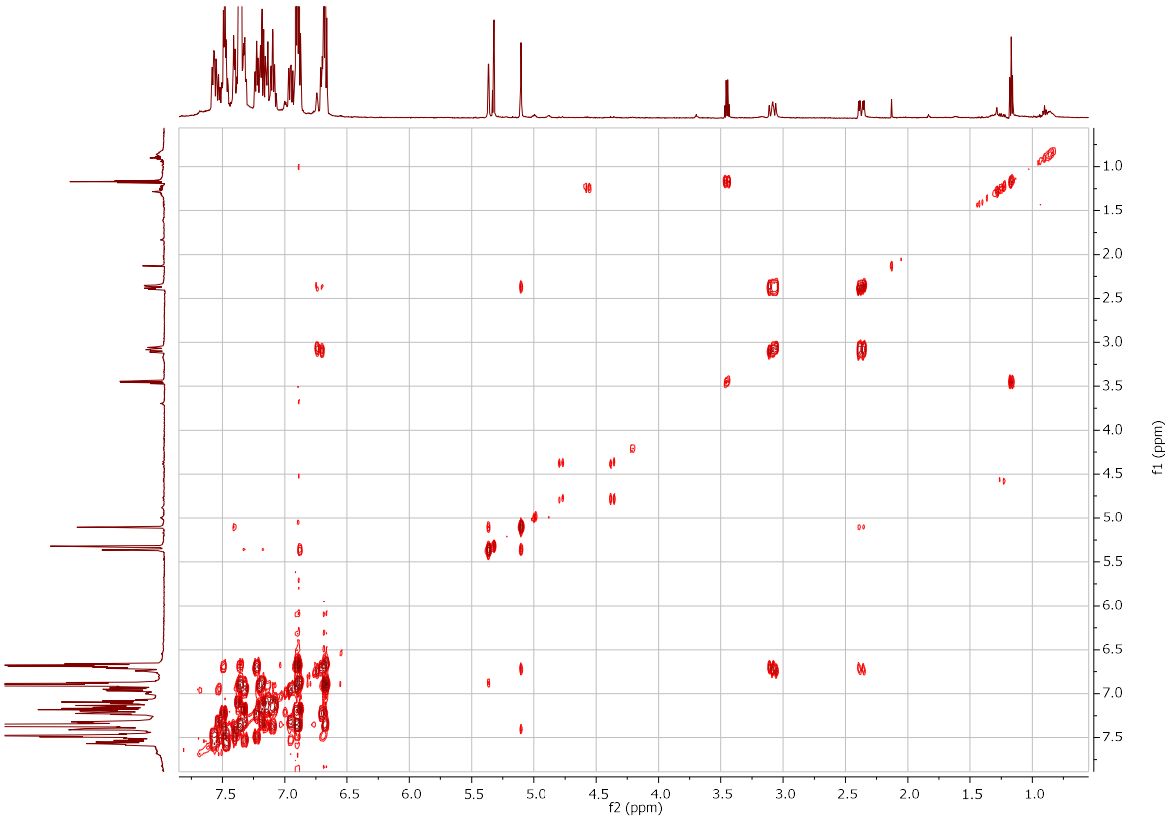


(b) ^{31}P NMR spectrum (243 MHz, CD_2Cl_2):

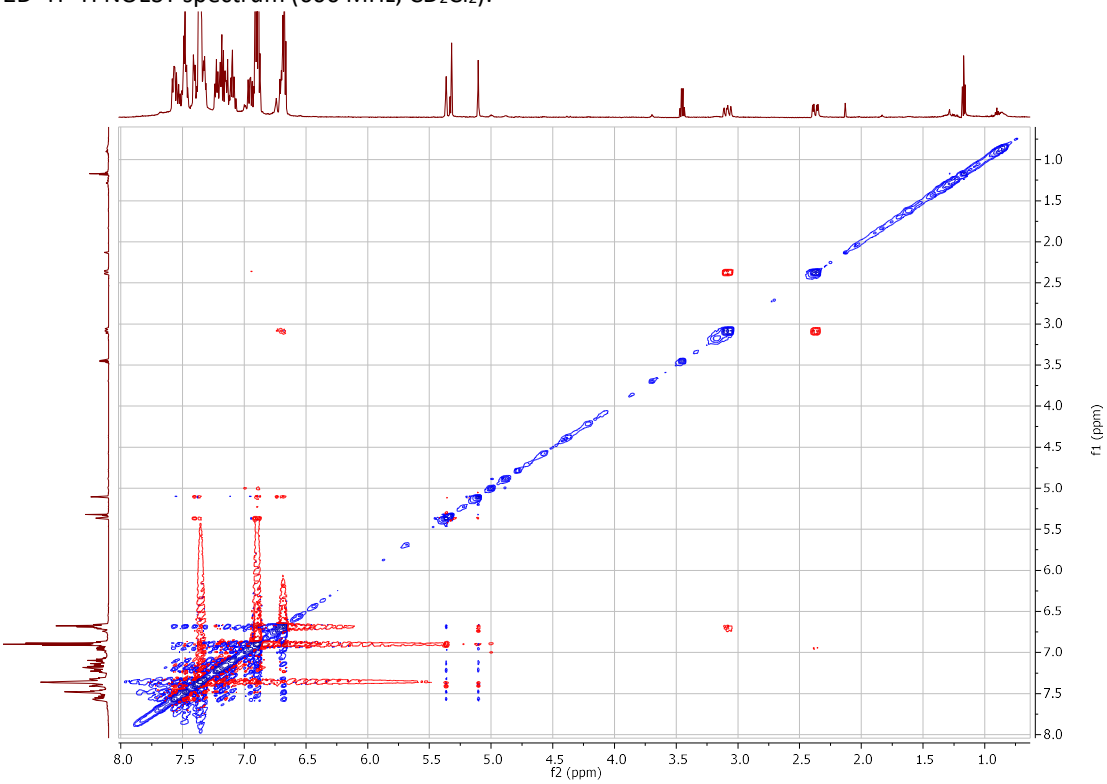
The ^{31}P NMR spectrum of **16d** displays a doublet at 65.32 ppm and 85.84 ppm ($^{2}J_{PP}$ = 32 Hz).



(c) 2D ^{1}H-^{1}H COSY spectrum (600 MHz, CD_2Cl_2):

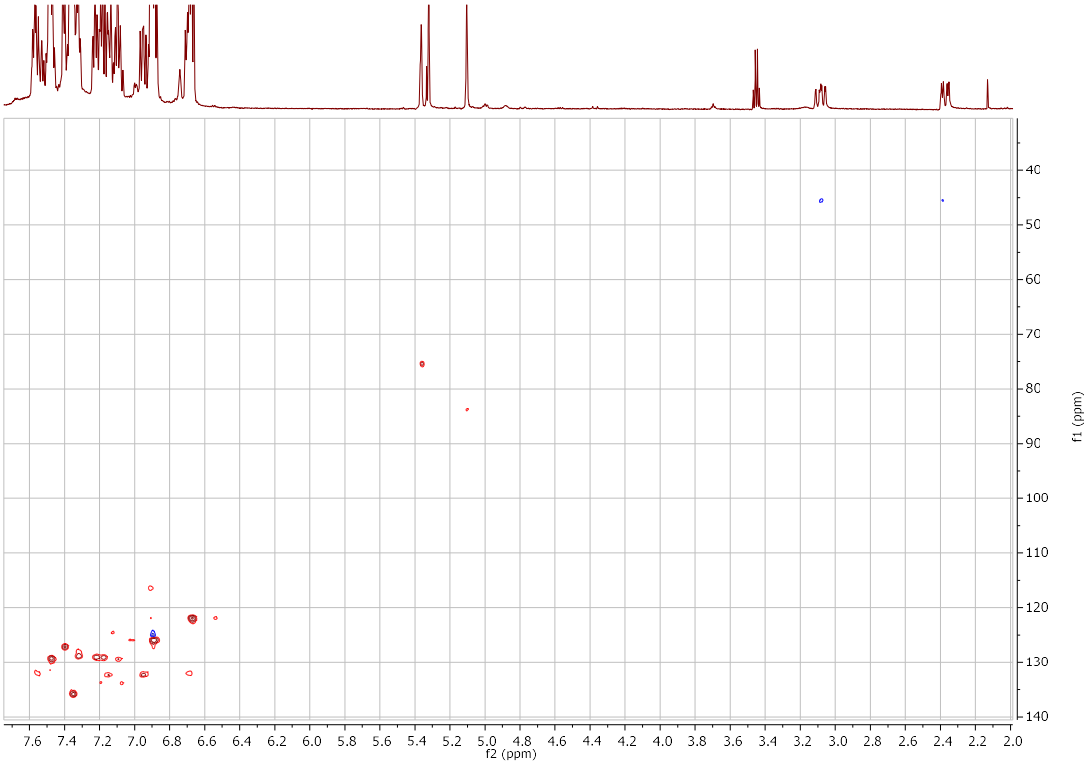


(d) 2D ^{1}H-^{1}H NOESY spectrum (600 MHz, CD_2Cl_2):



(e) 2D ^{1}H-^{13}C HSQC spectrum (600MHz, CD_2Cl_2):

The C**H**Ph at (5.36, 75.75) and (5.10, 83.70), the two protons of the CH_2 of the imine arm at (3.08, 45.67) and (2.37, 45.47).



(f) IR Spectrum:

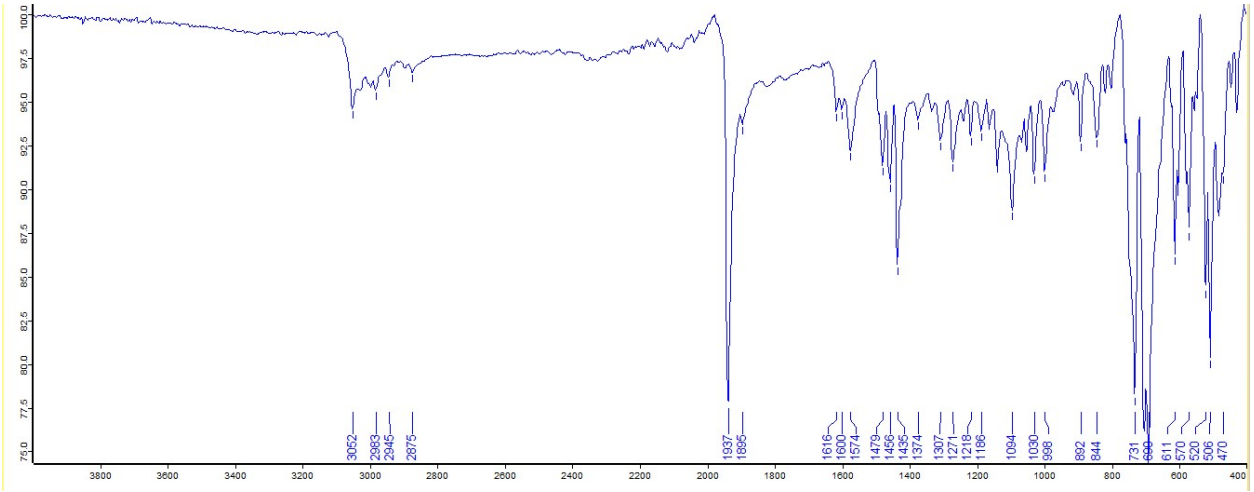
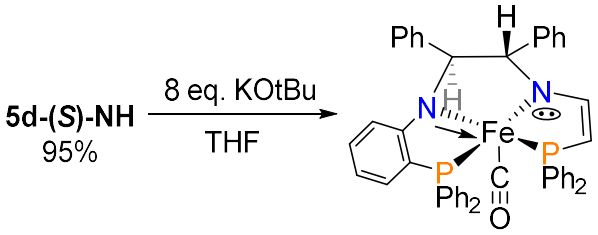
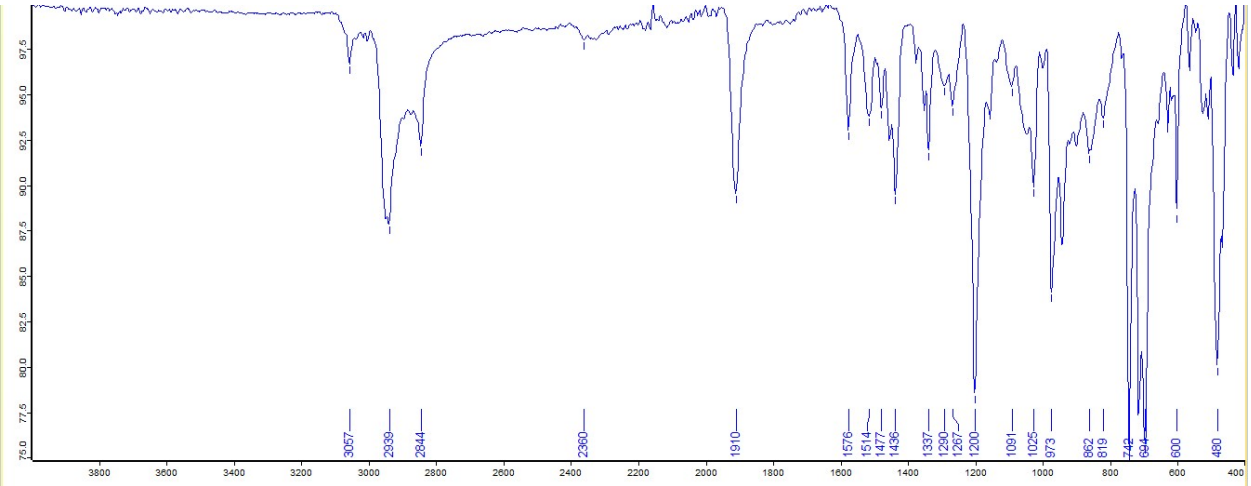


Fig. S13 Base Studies of Imine Precatalyst **5d** with 8 eq. of KOtBu.



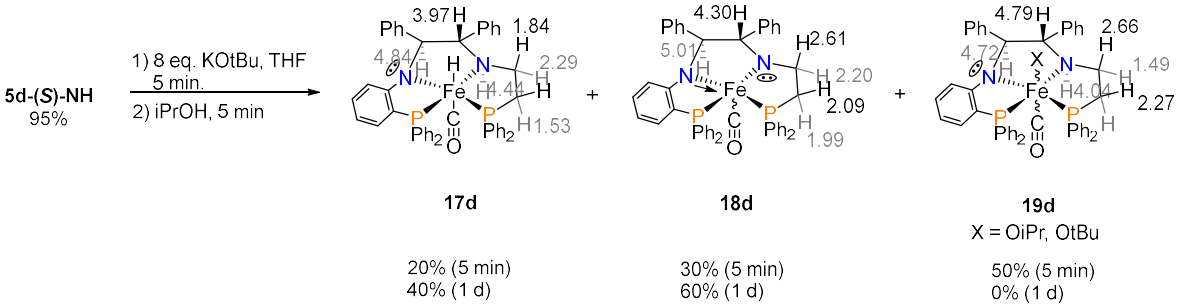
(a) IR Spectrum:

The proposed structure displays a CO stretch at 1910 cm^{-1} and a carbon-carbon double bond stretch at 1514 cm^{-1}.

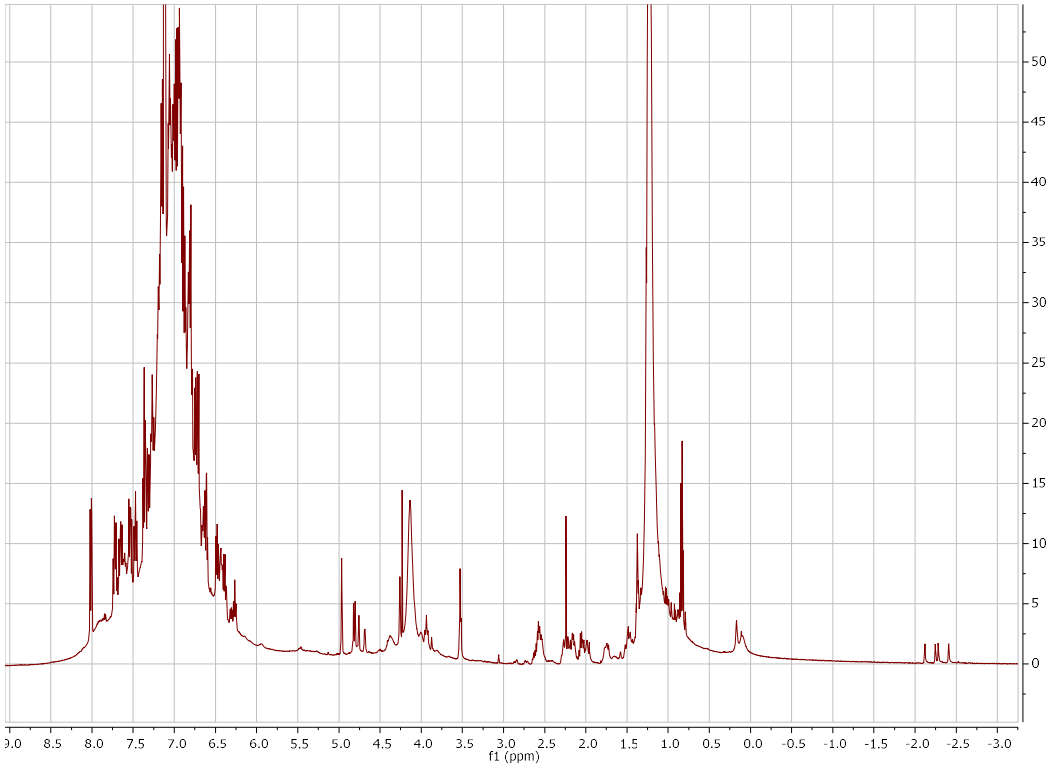


Note: No NMR data was available as some paramagnetic material is formed. By stirring in iPrOH, the paramagnetic compound is converted to diamagnetic compounds.

Fig. S14 Base Activated Hydride Studies with Imine Precatalyst **5d**. Full characterization of the alkoxide complex **19d** can be found in Fig. S17.

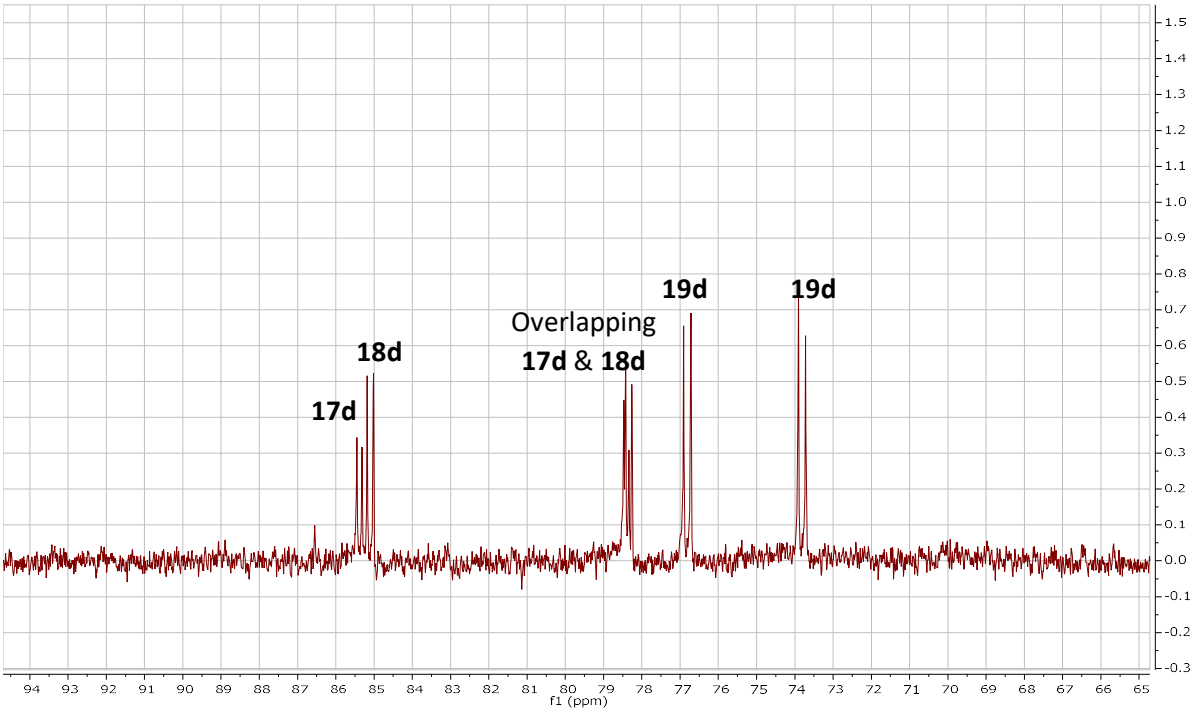


(a) ^{1}H NMR spectrum (500 MHz, C_6D_6). Spectrum was taken after 5 minutes:



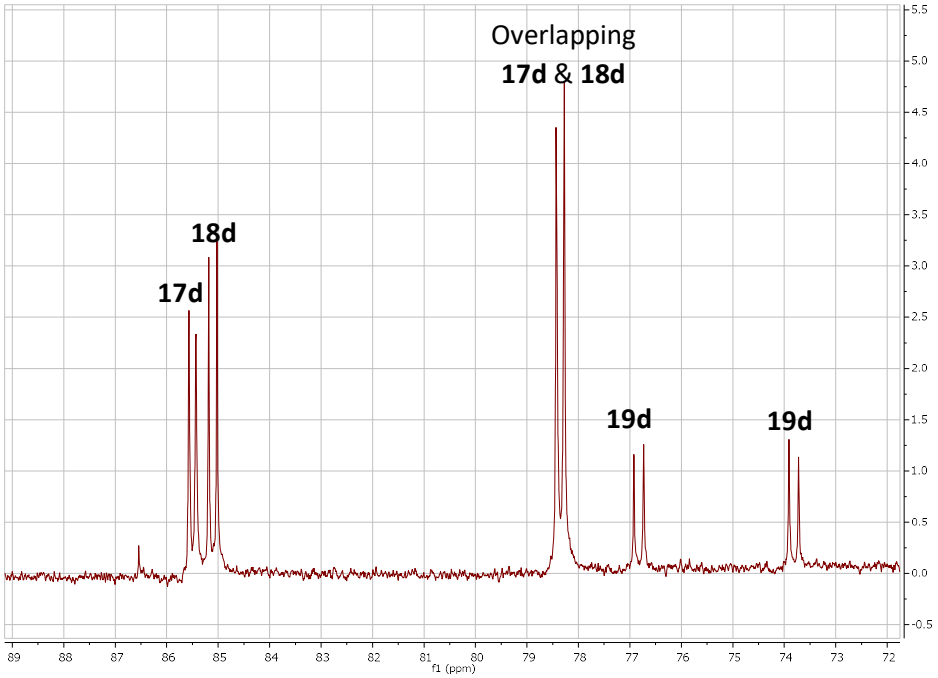
(b) A well resolved ^{31}P NMR spectrum (202 MHz, C_6D_6):

This ^{31}P NMR spectrum was specifically chosen to display the fully resolved doublets. The actual ^{31}P NMR spectrum, in terms of correct ratios of products, can be found below.

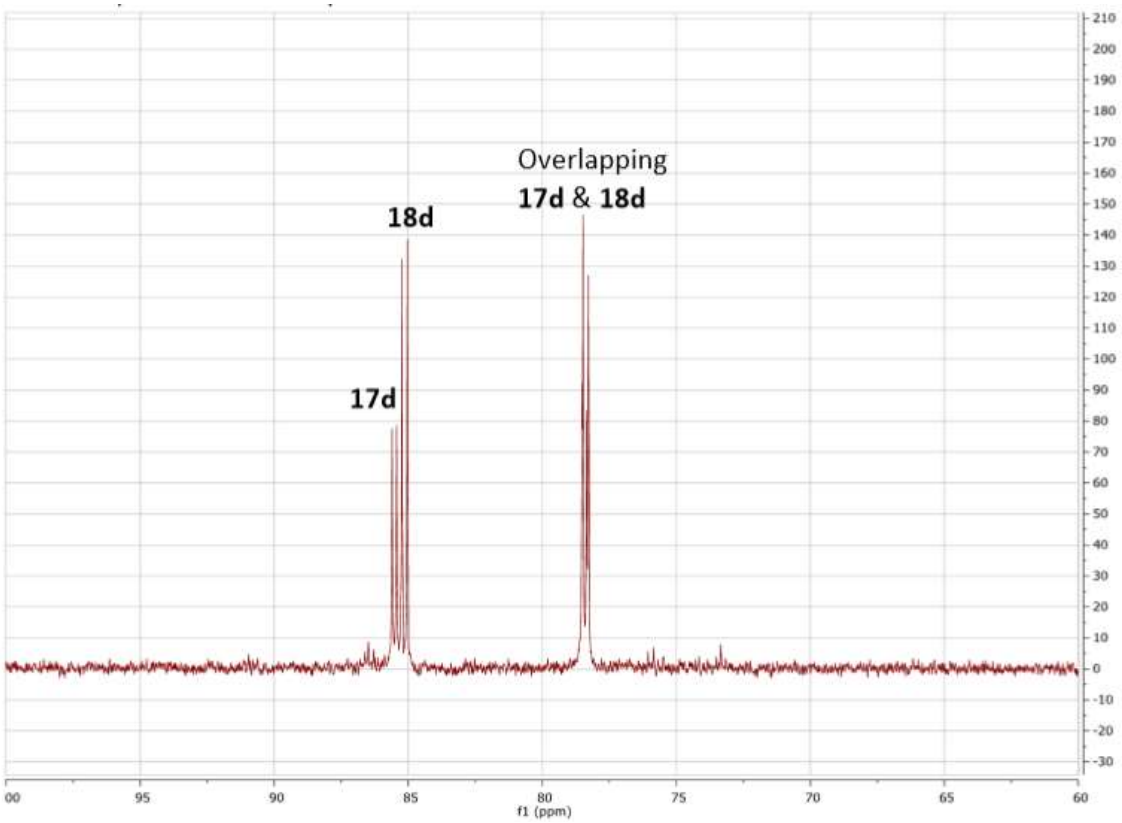


(c) ^{31}P NMR spectrum (202 MHz, C_6D_6) with the correct product ratio. Spectrum taken after 5 minutes:

The formation of the iron hydride complex **17d** at 78.4 ppm and 85.4 ppm ($^2J_{PP}$ = 27 Hz), the doubly deprotonated iron complex **18d** at 78.3 ppm and 85.1 ppm ($^2J_{PP}$ = 33 Hz), and the iron alkoxide complex **19d** at 73.8 ppm and 76.8 ppm ($^2J_{PP}$ = 38 Hz). The ^1H NMR of **18d** displays the hydride signal at -2.22 ppm ($^2J_{HP}$ = 64, 81 Hz).

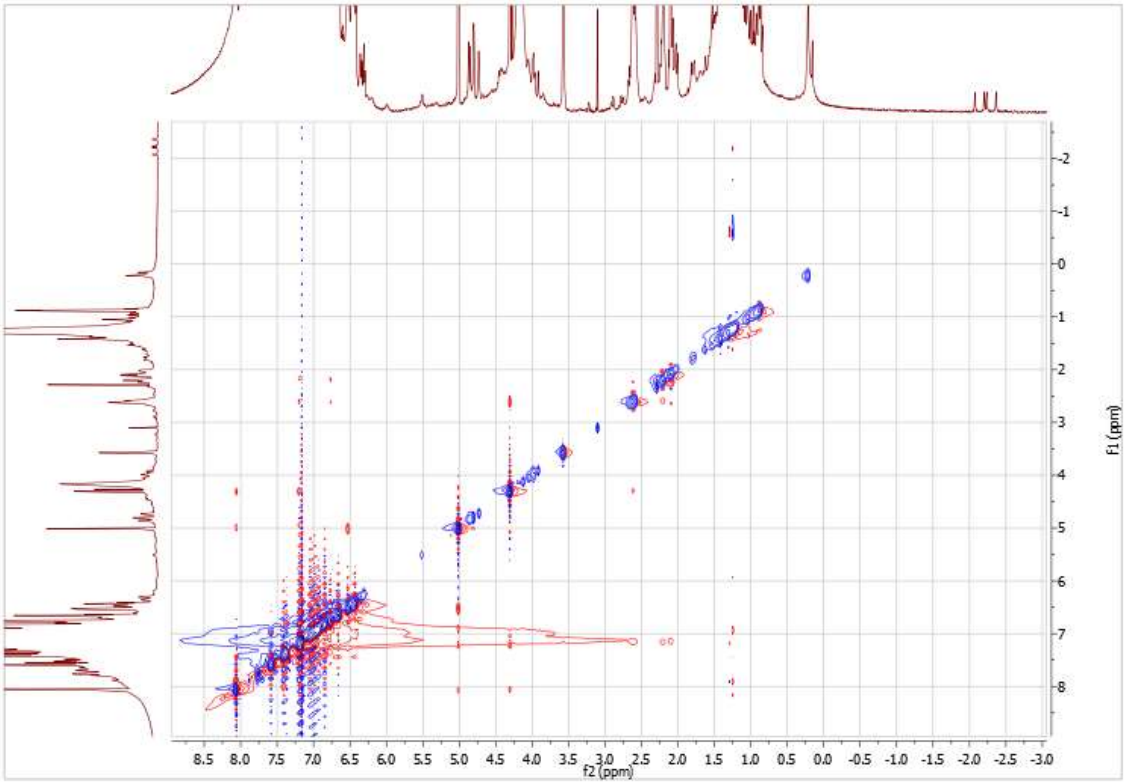


(d) ^{31}P NMR spectrum after 1 day:

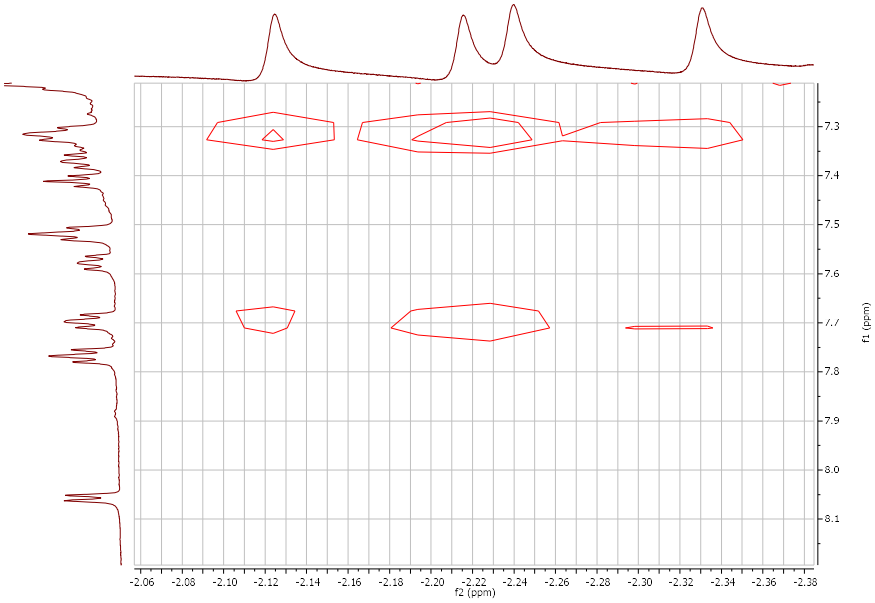


(e) 2D ^{1}H-^{1}H COSY spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:

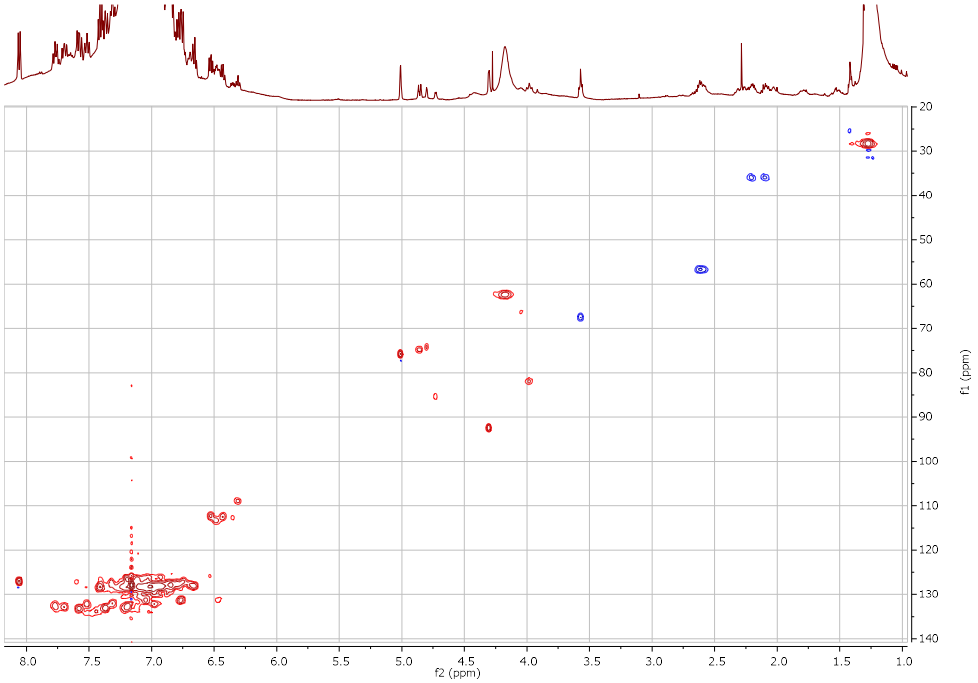
(f) 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, C_6D_6). Spectrum was taken after 5 minutes:



(g) Expanded region in the 2D ^{1}H-^{1}H NOESY NMR spectrum. Spectrum was taken after 5 minutes:
The hydride cross-peak displaying a correlation to only two aromatic protons at 7.70 ppm and 7.32 ppm. For this reason, we suggest that the hydride is not on the same side of the PNNP ligand as the amine proton.



(h) 2D ^{1}H-^{13}C HSQC spectrum (500MHz, C_6D_6). Spectrum taken after 5 minutes:
The reduced imine side arm of **17d** displaying the C**H**Ph at (4.84, 74.79) and (3.97, 81.94), the protons of the two CH_2 of the amine arm at (2.29, 37.59), (1.84, 49.49), and (1.54, 37.63). **18d** displaying the C**H**Ph at (5.01, 75.75) and (4.30, 92.41), the protons of the two CH_2 of the amine arm at (2.61, 56.70), (2.20, 35.96), and (2.09, 35.96). **19d** displaying the C**H**Ph at (4.79, 74.18) and (4.72, 85.36), the protons of the two CH_2 of the amine arm at (2.66, 35.14).



(i) IR Spectrum taken after 5 minutes:
The CO stretch of the doubly deprotonated complex with the reduced side arm (**18d**) is at 1901 cm^{-1}.

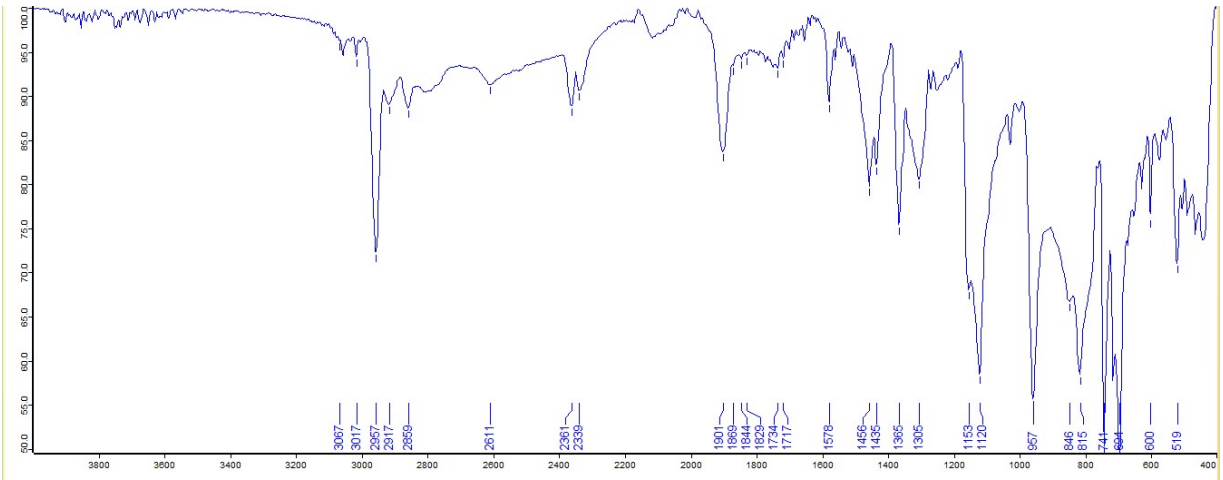
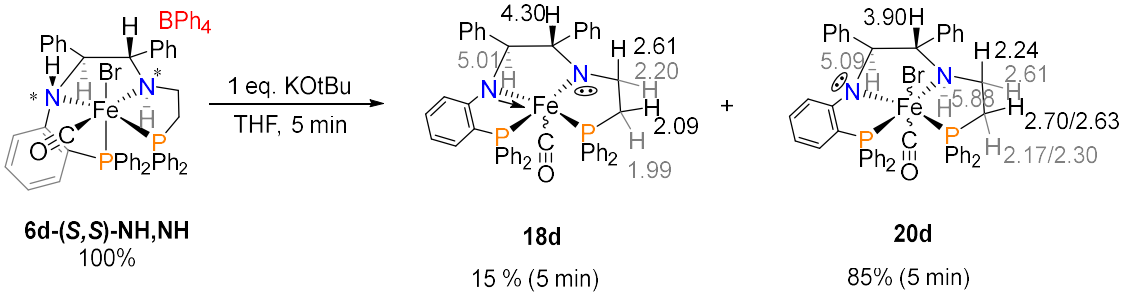


Fig. S15 Base Activation Studies of Amine Catalyst **6d** with 1 eq. of KOtBu.

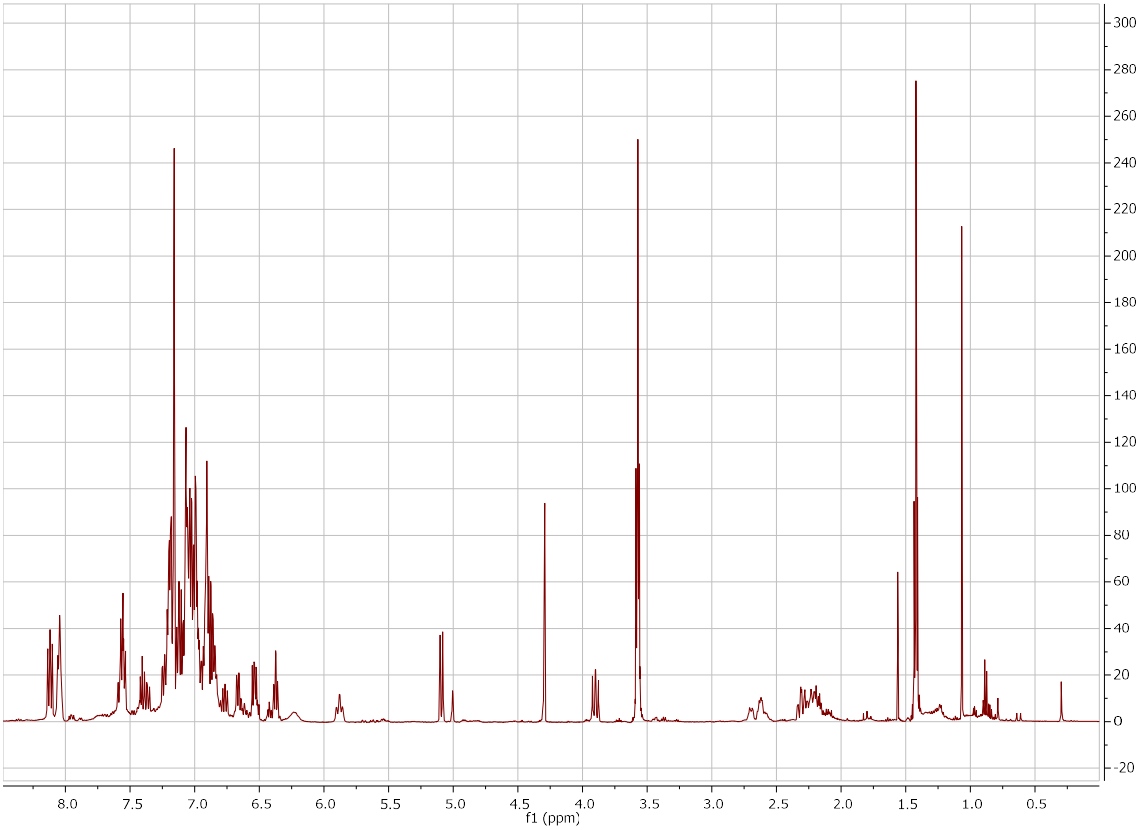


6d-(*S*,*S*)-NH,NH
100%

18d
15 % (5 min)

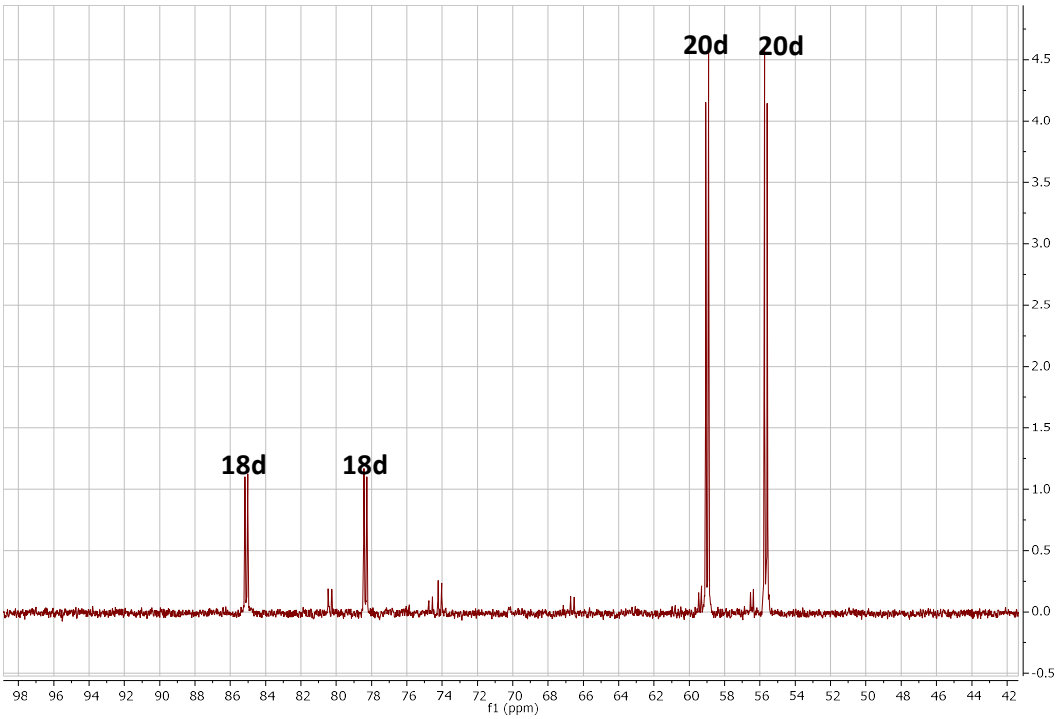
20d
85% (5 min)

(a) ^{1}H NMR spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:

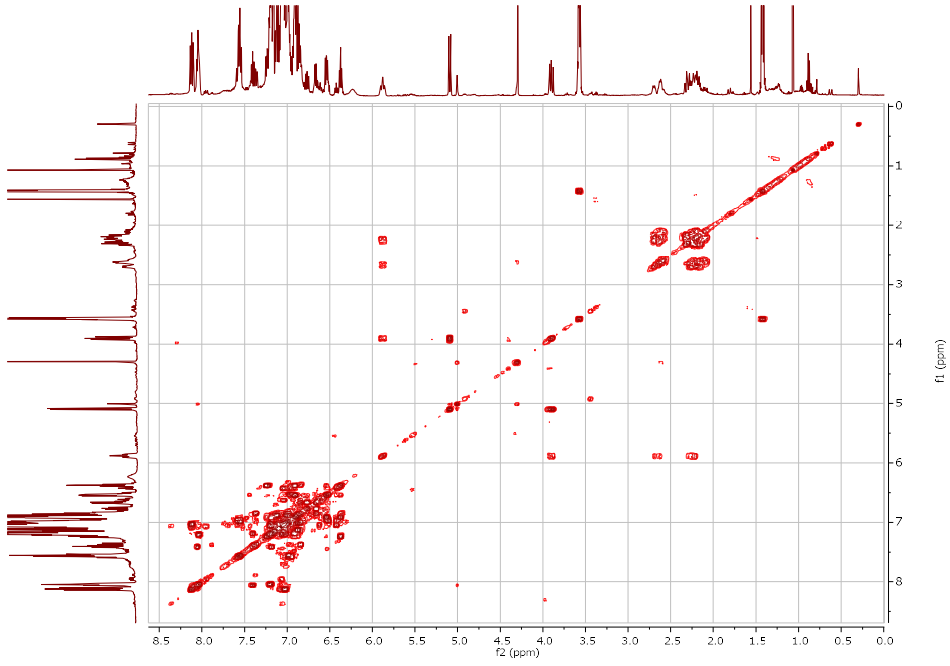


(b) ^{31}P NMR spectrum (202 MHz, C_6D_6). Spectrum taken after 5 minutes:

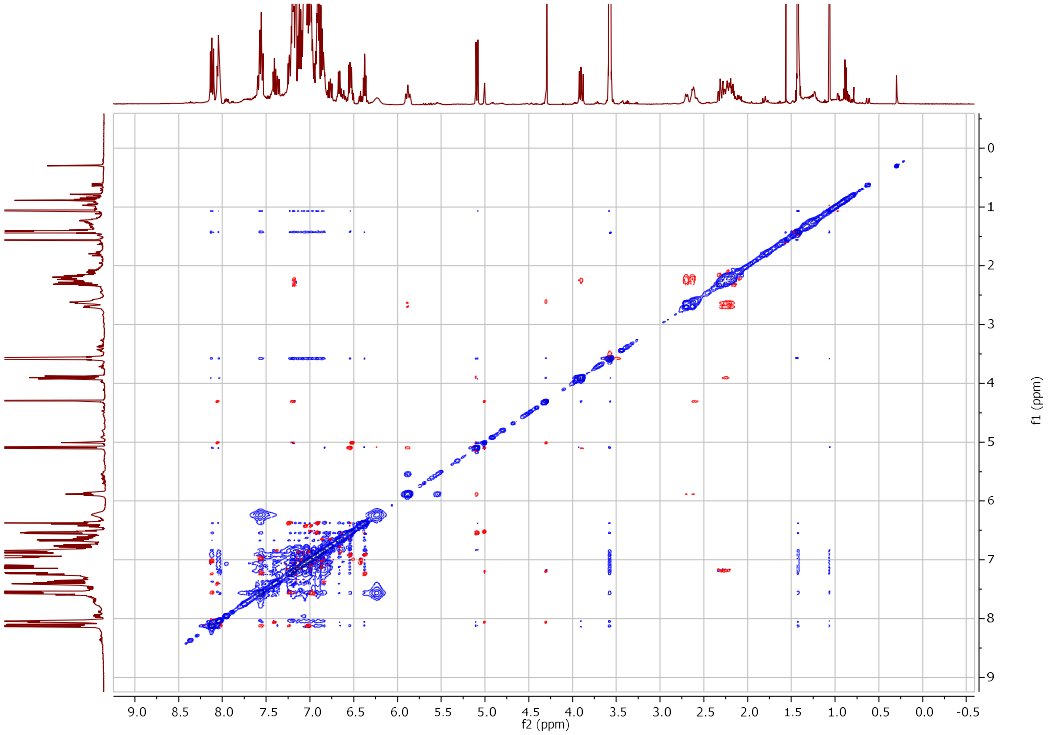
The doubly deprotonated iron complex **18d** at 78.3 ppm and 85.1 ppm ($^2J_{PP}$ = 33 Hz), and the singly deprotonated iron complex **20d** at 55.66 ppm and 58.98 ppm ($^2J_{PP}$ = 32 Hz). The formation of the doubly deprotonated species with the reduced side **18d** arm appearing in this study as well as in the hydride studies using **5d**, verifies the reduction of the imine side arm upon addition of iPrOH in basic conditions.



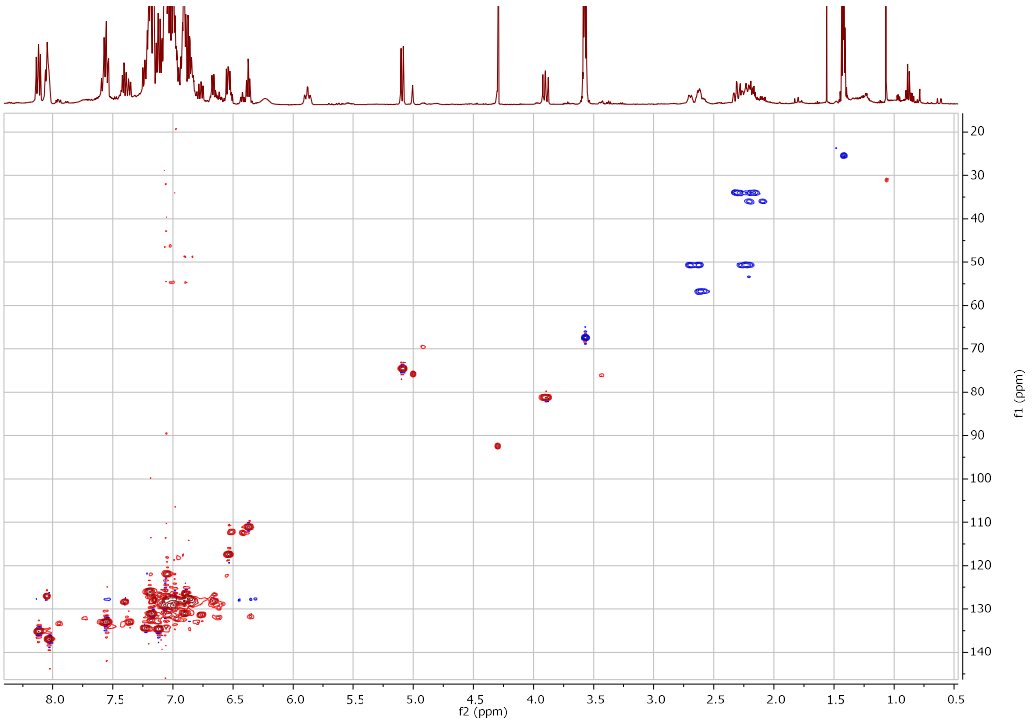
(c) 2D ^1H-^1H COSY spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:



(d) 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:



(e) 2D ^{1}H-^{13}C HSQC spectrum (500MHz, C_6D_6). Spectrum was taken after 5 minutes:
The formation of **18d** as shown in Fig. S14A as well as the singly deprotonated **20d** displaying the C**H**Ph at (5.09, 74.55) and (3.90, 81.22), the protons of the two CH_2 of the amine arm at (2.70-2.63, 50.74), (2.61, 56.74), (2.24, 50.64), and (2.30-2.17, 34.01).



(f) IR Spectrum taken after 5 minutes:

The CO stretch of **20d** is at 1939 cm^{-1}. The CO stretches at 1895 cm^{-1} and 1962 cm^{-1}, for **18d** and **6d** respectively, were within the specified error of the Bruker Alpha with an ATR platinum diamond attachment.

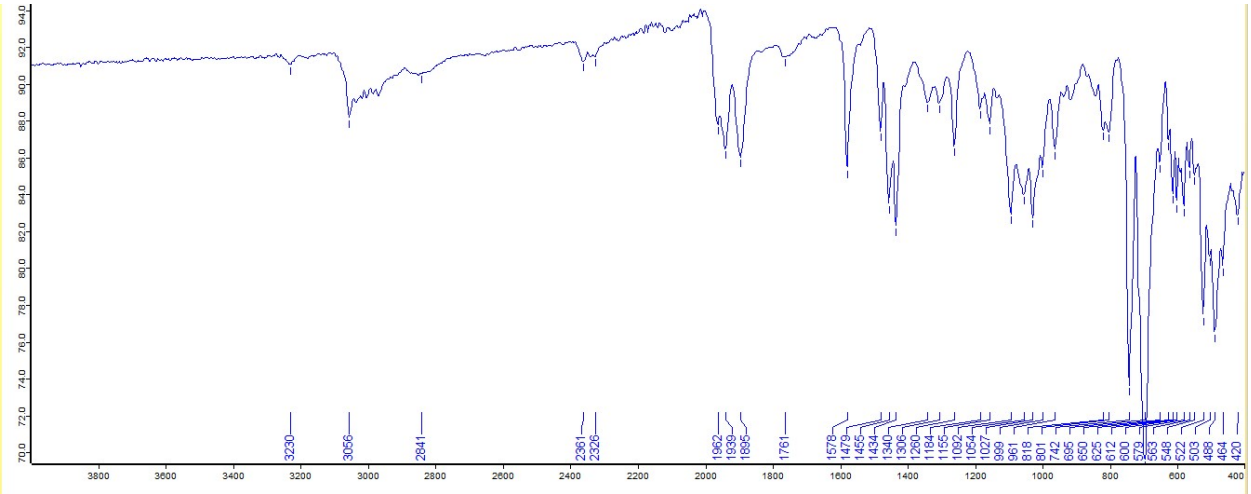
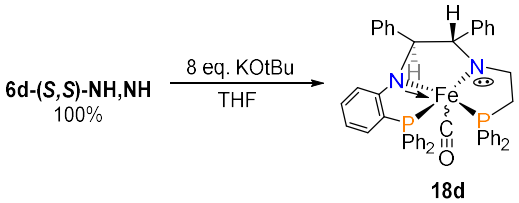


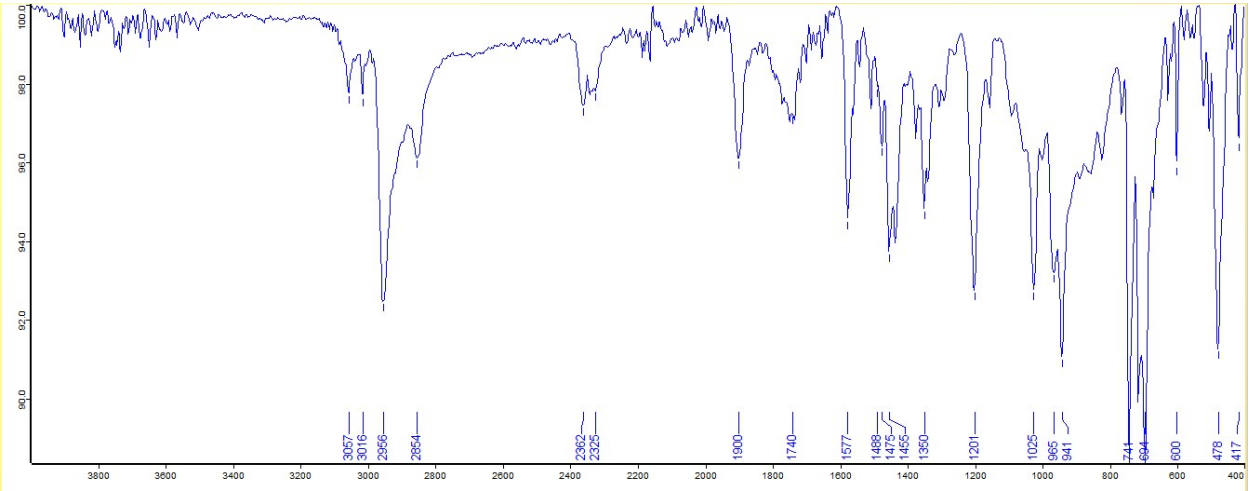
Fig. S16 Base Activation Studies of Amine Precatalyst **6d** with 8 eq. of KOtBu.



18d

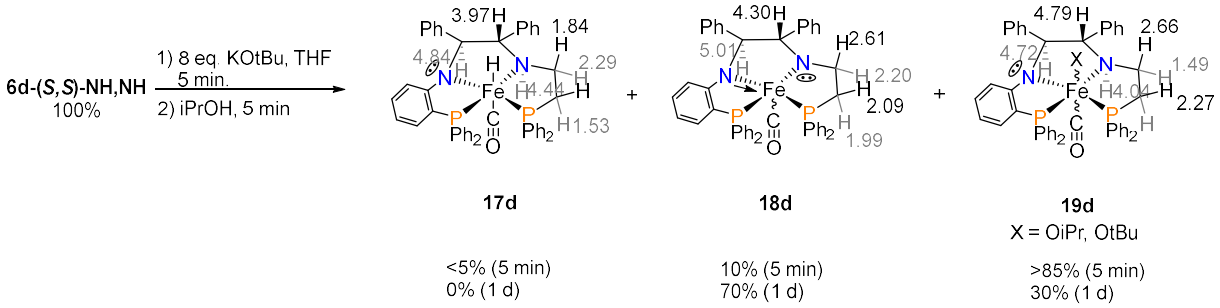
(a) IR Spectrum:

The proposed structure **18d** displays a CO stretch at 1900 cm^{-1}.

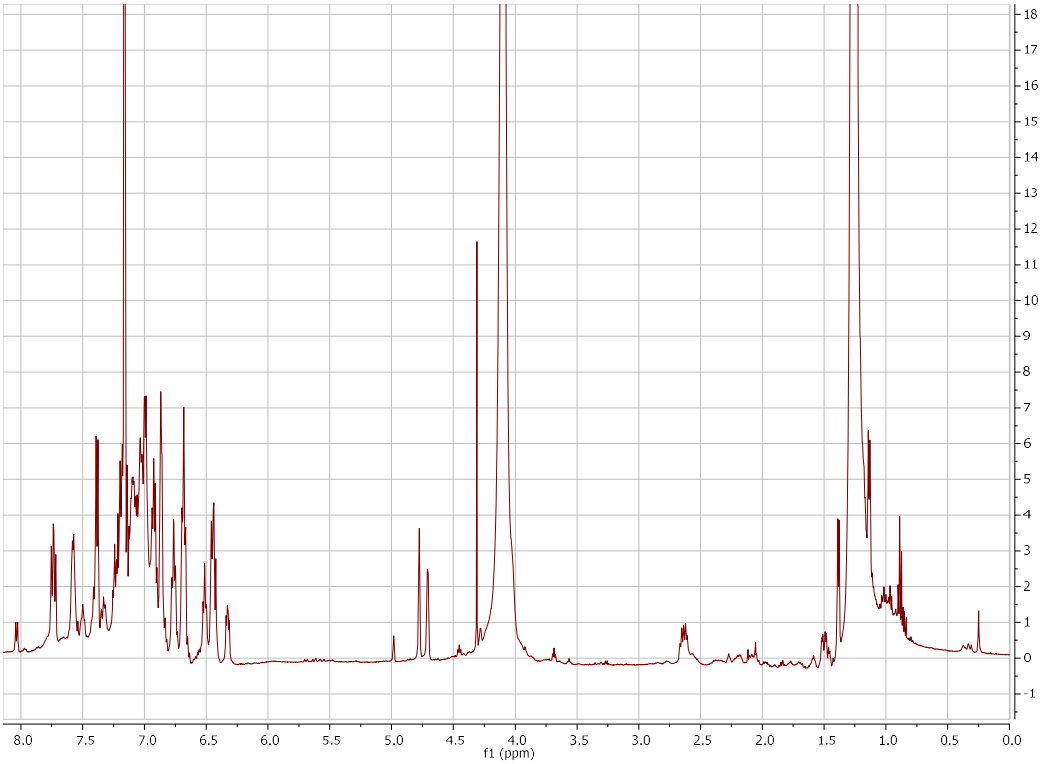


Note: No NMR Data was available as some paramagnetic material is formed. By stirring in iPrOH, the paramagnetic compound is converted to a diamagnetic compound.

Fig. S17 Base Activated Hydride Studies with Amine Precatalyst **6d**. All spectra were taken after 5 minutes. See Fig. S18 for the spectra after 1 day.

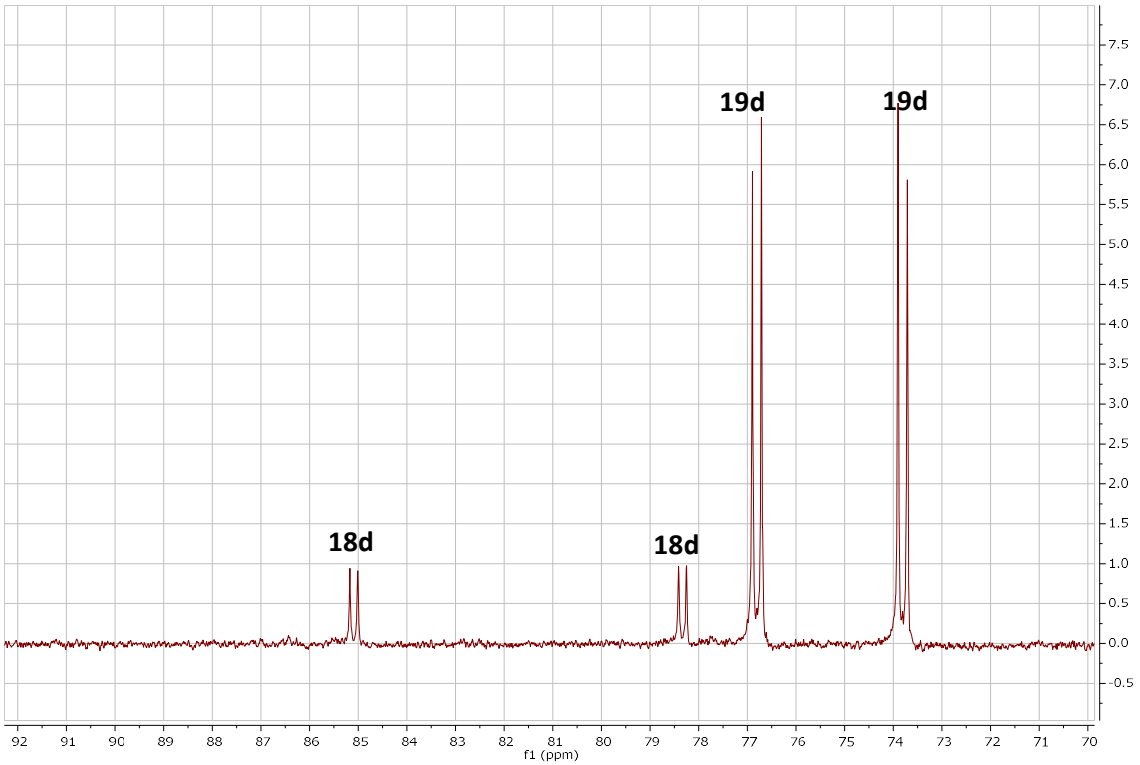


(a) ^{1}H NMR spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:

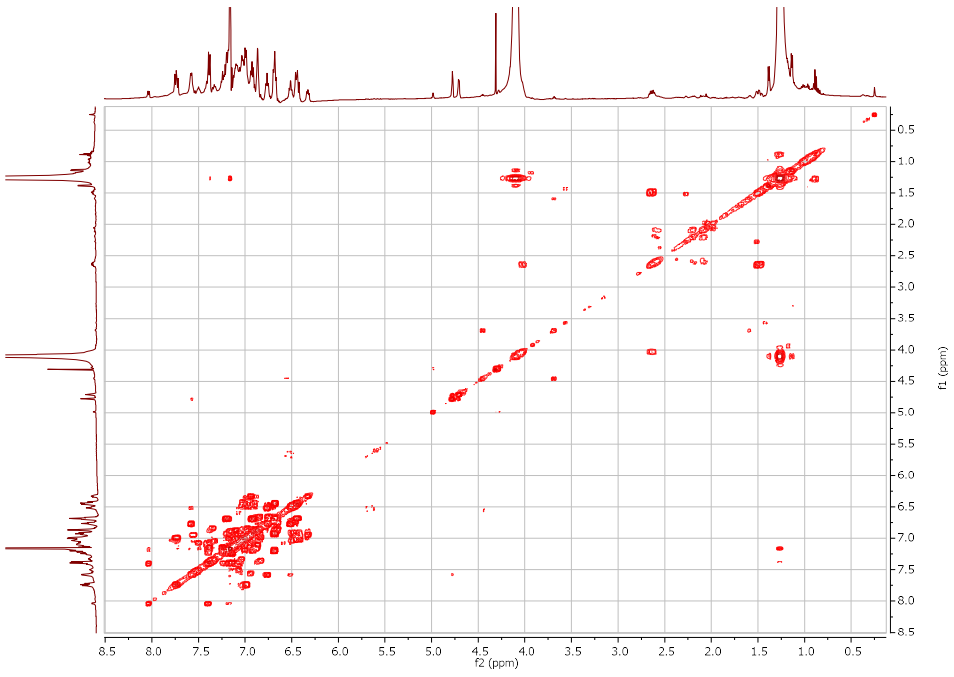


(b) ^{31}P NMR spectrum (202 MHz, C_6D_6). Spectrum taken after 5 minutes:

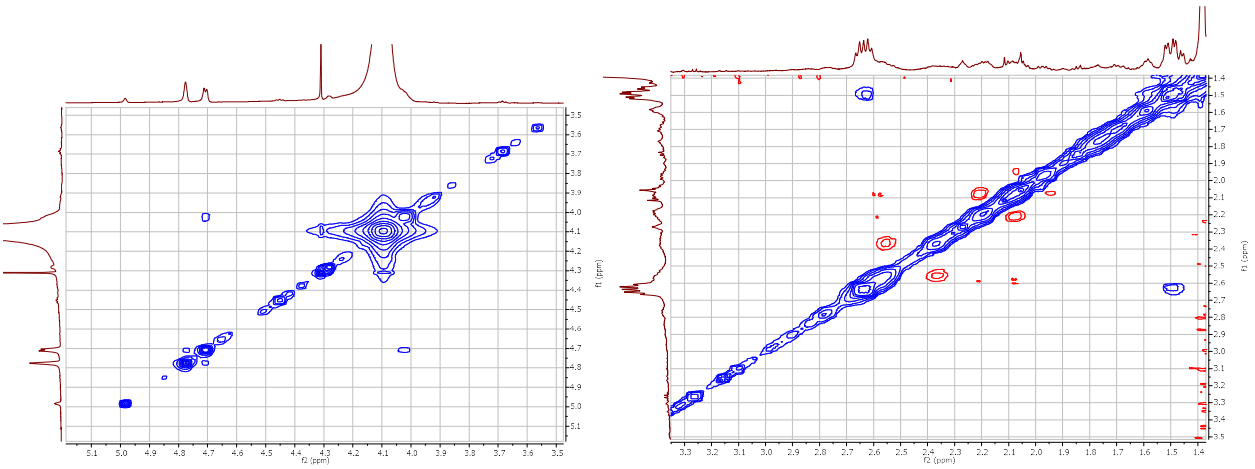
A much lower concentration of the hydride species **17d** was observed upon activation of **6d**, leading to a decreased activity compared to the imine precatalyst **5d**. The major species formed immediately was the alkoxide complex **19d** which shifts to the doubly deprotonated complex **18d** slowly over time as shown in Fig. S18.



(c) 2D ^{1}H-^{1}H COSY spectrum (500 MHz, C_6D_6). Spectrum was taken after 5 minutes:



(d) 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, C_6D_6). Spectrum was taken after 5 minutes:
Left: displays the correlation between the CHPh of the DPEN backbone to the amine proton of the alkoxide complex at 4.04 ppm. It is usually buried under the iPrOH peak. Right: The connectivity of the ethylene linker of **19d,** which is similar to the hydride complex.



(e) IR Spectrum taken after 5 minutes:
Again, **18d** displays a CO stretch at 1900 cm^{-1} and alkoxide complex **19d** displays a CO stretch at 1845 cm^{-1}.

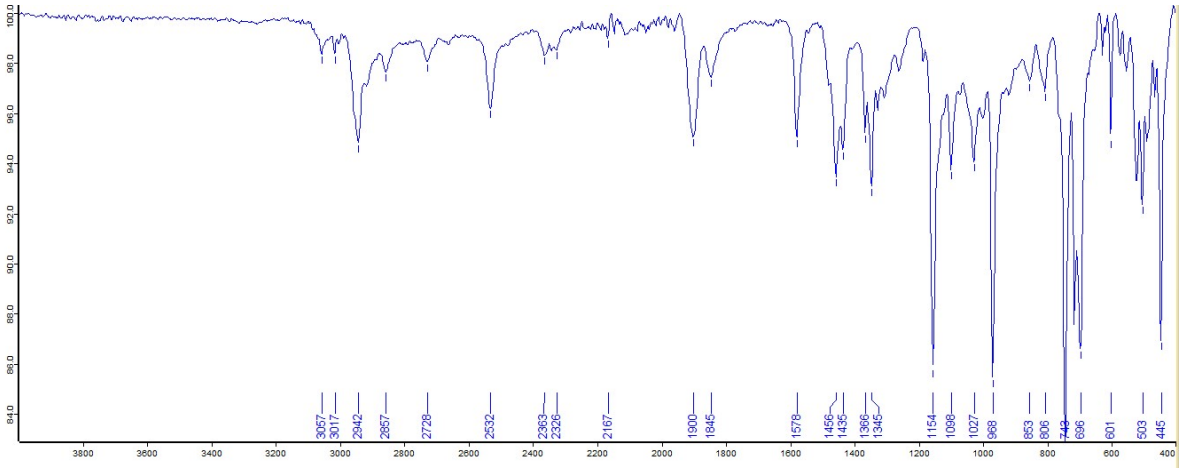
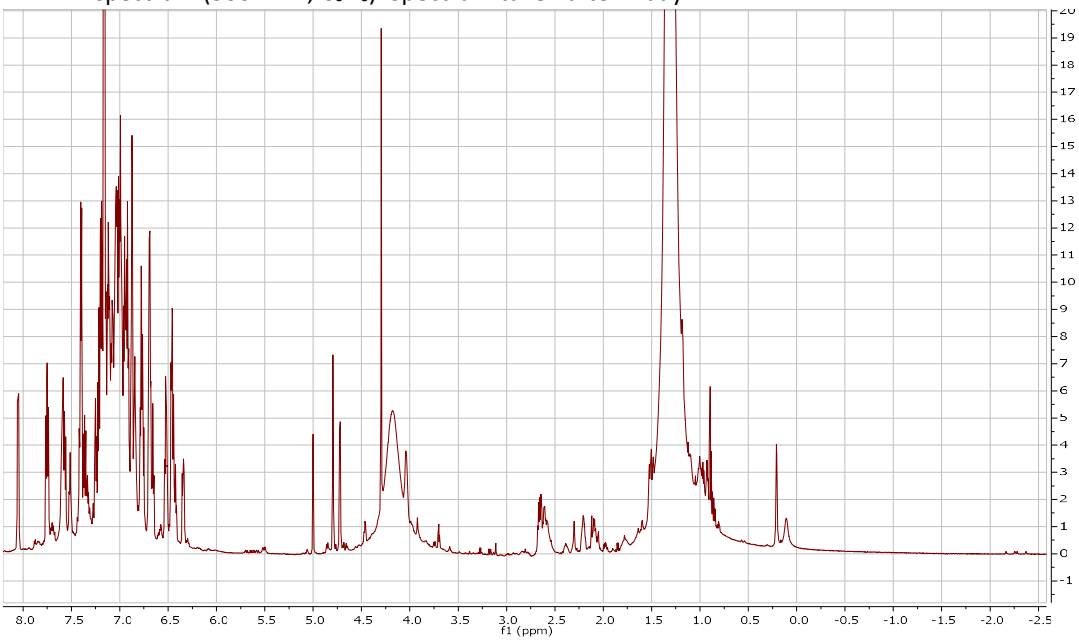


Fig. S18 Base Activated Hydride Studies with Amine Precatalyst **6d** After One Day.

(a) ^{1}H NMR spectrum (500 MHz, C_6D_6). Spectrum taken after 1 day:



(b) ^{31}P NMR spectrum (202 MHz, C_6D_6). Spectrum taken after 1 day:

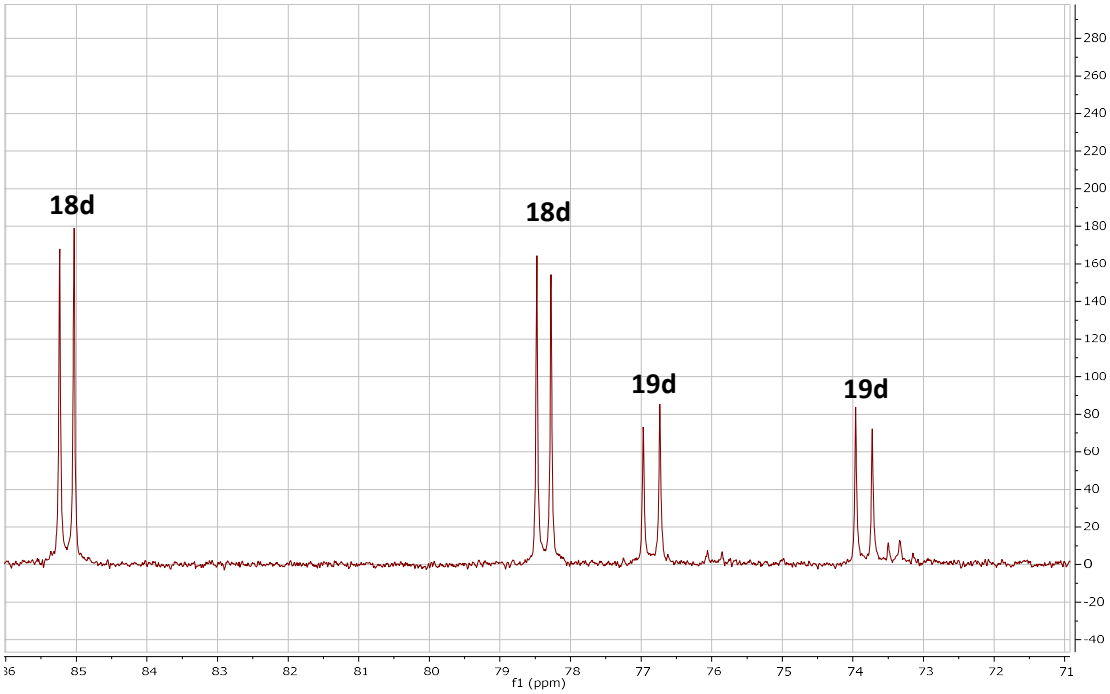
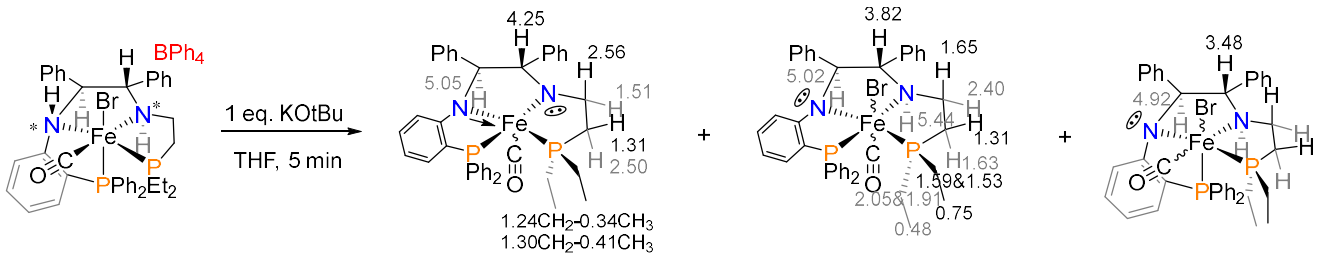


Fig. S19 Base Studies of Amine Catalyst **6a** with 1 eq. of KOtBu.



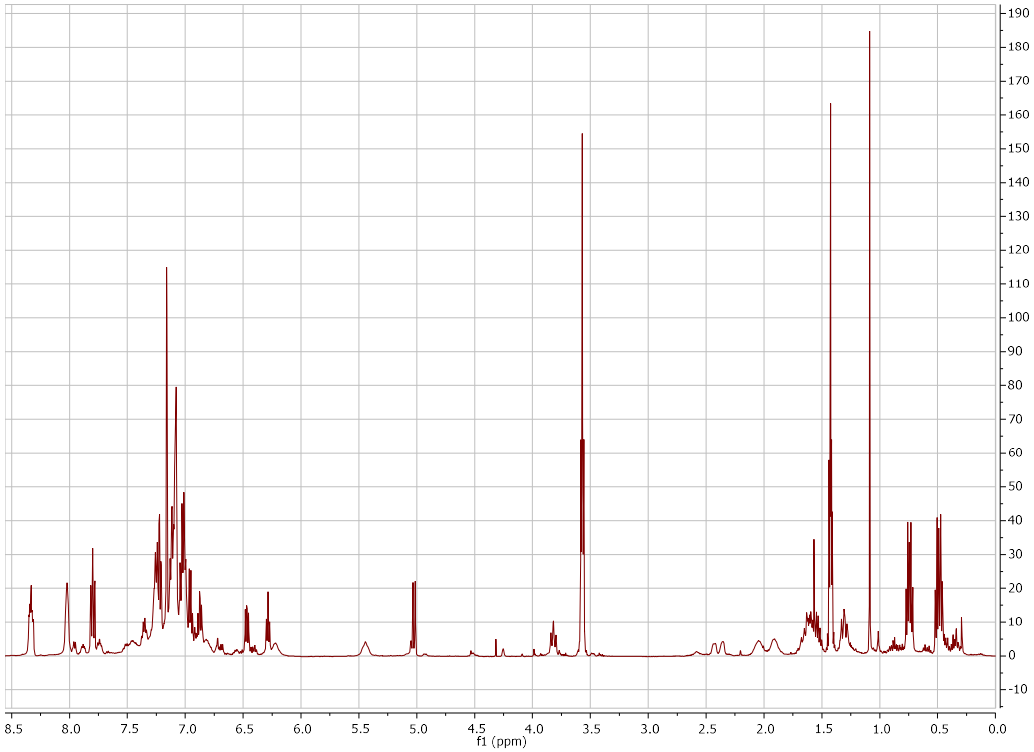
6a-(*S,S*)-NH,NH
100%

18a
10% (5 min)
10% (5 d)

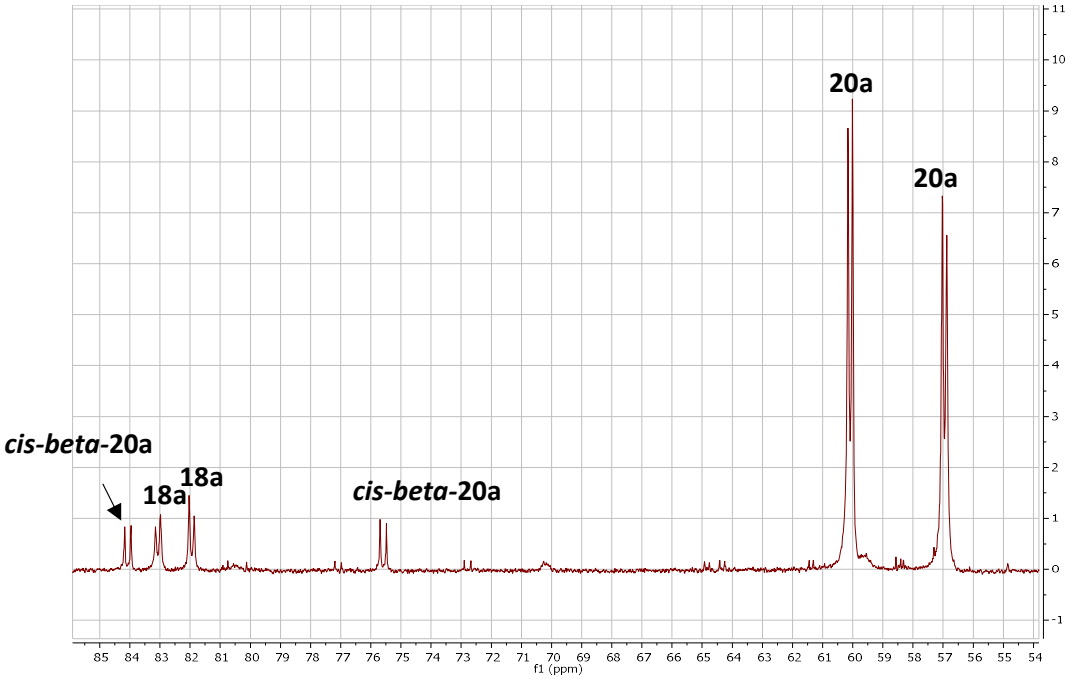
20a
85% (5 min)
85% (5 d)

***cis-beta*-20a**
5% (5 min)
5% (5 d)

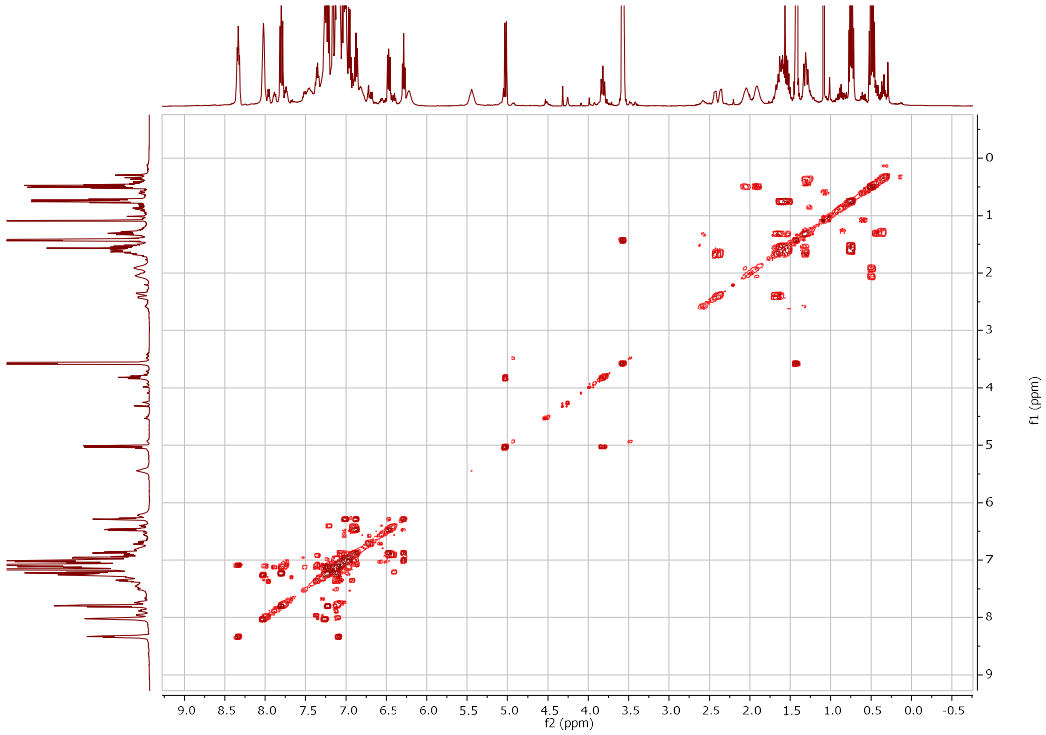
(a) ^{1}H NMR spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:



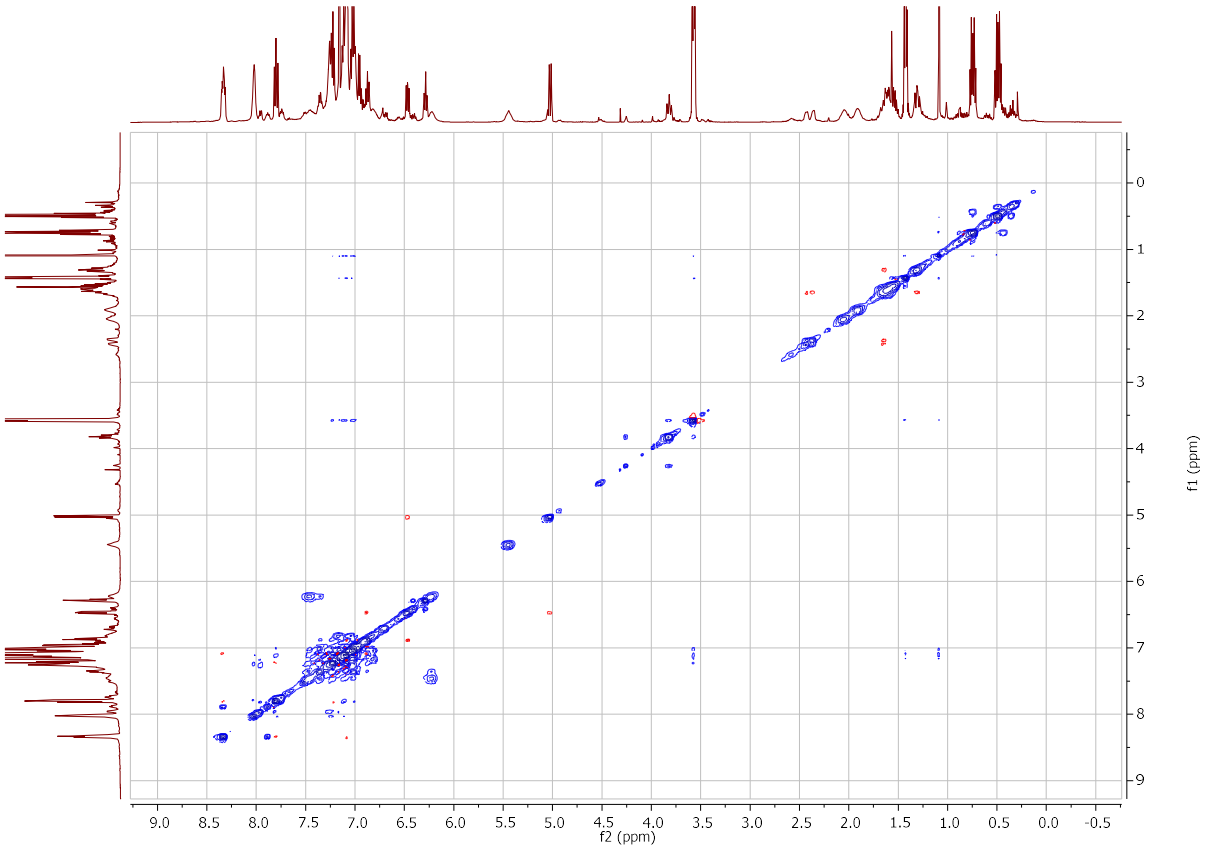
(b) ^{31}P NMR spectrum (202 MHz, C_6D_6). Spectrum taken after 5 minutes:
The singly deprotonated **20a** as the major species displaying a doublet at 56.95 ppm and 60.08 ppm ($^2J_{PP}$ = 30 Hz), doubly deprotonated **18a** displaying a doublet at 81.95 ppm and 83.07 ppm ($^2J_{PP}$ = 33 Hz), a small amount of singly deprotonated and potentially *cis-β* complex ***cis-beta*-20a** at 75.59 ppm and 84.07 ppm ($^2J_{PP}$ = 43 Hz). The spectrum taken after 1 day was similar.



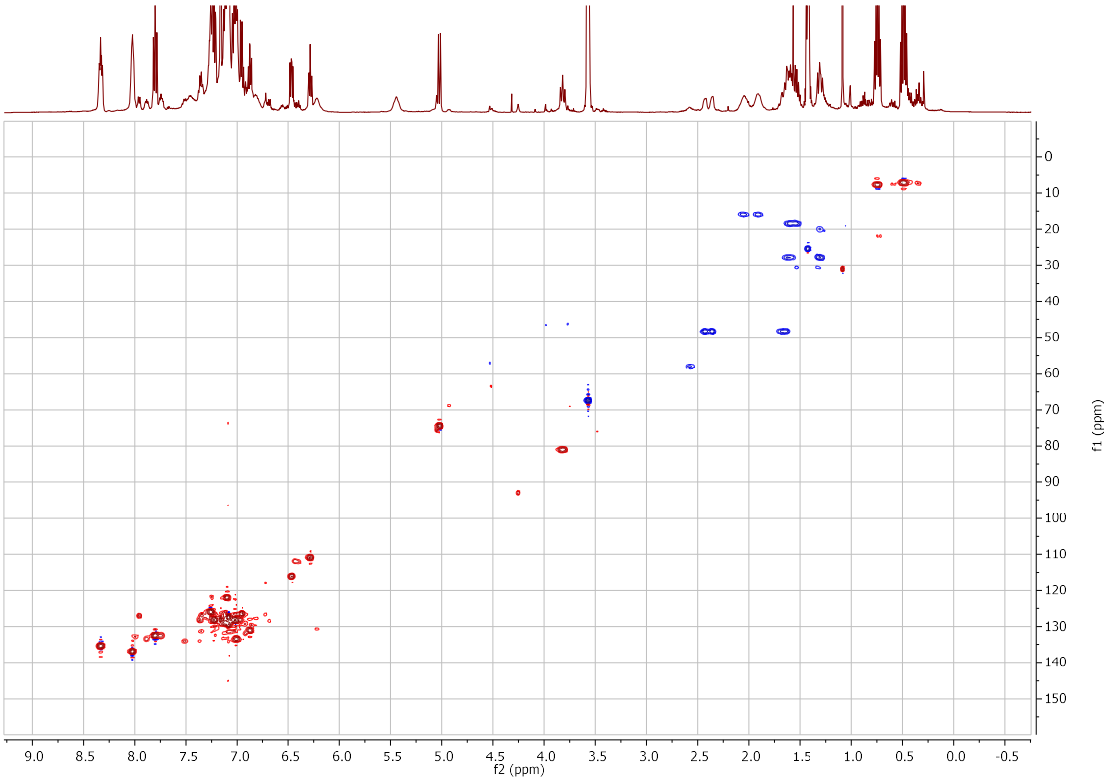
(c) 2D ^{1}H-^{1}H COSY spectrum (500 MHz, C_6D_6). Spectrum was taken after 5 minutes:



(d) 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, C_6D_6). Spectrum was taken after 5 minutes:



(e) 2D ^{1}H-^{13}C HSQC spectrum (500MHz, C_6D_6). Spectrum taken after 5 minutes:
The formation of **18a** with the C**H**Ph at (5.05, 75.55) and (4.25, 92.92), the protons of the two CH_2 of the amine arm at (2.56, 58.05), (2.50, 58.05), (1.51, 30.61), and (1.31, 30.61), the protons of the two CH_2 of the diethylphosphine which are overlapping at (1.30, 19.87), and (1.24, 19.87), and the protons of the two CH_3 of the diethylphosphine at (0.41, 7.09), and (0.34, 7.09). Complex **20a** with the C**H**Ph at (5.02, 74.43) and (3.82, 81.08), the protons of the two CH_2 of the amine arm at (2.40, 48.29), (1.65, 48.30), (1.63, 27.82), and (1.31, 27.81), the protons of the two CH_2 of the diethylphosphine at (2.05, 15.94), (1.91, 15.94), (1.59, 18.46), and (1.53, 18.46), and the protons of the two CH_3 of the diethylphosphine at (0.75, 7.70), and (0.48, 7.09). Complex ***cis-beta*-20a** with the C**H**Ph at (4.92, 68.78) and (3.48, 81.08). The other protons could not be assigned as this complex was formed in very low concentrations.



(f) IR Spectrum taken after 5 minutes:
18a displays a CO stretch at 1894 cm^{-1} and **20a** displays a CO stretch at 1924 cm^{-1}.

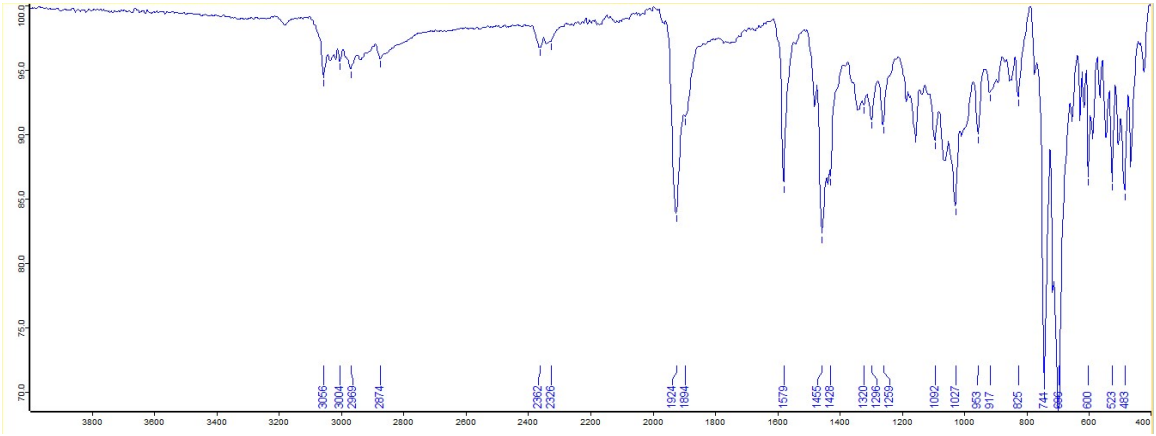
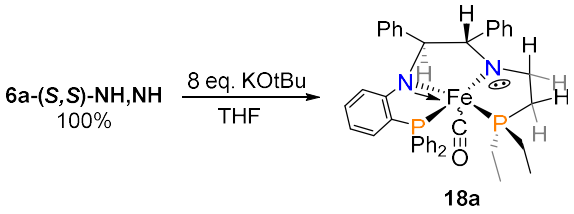


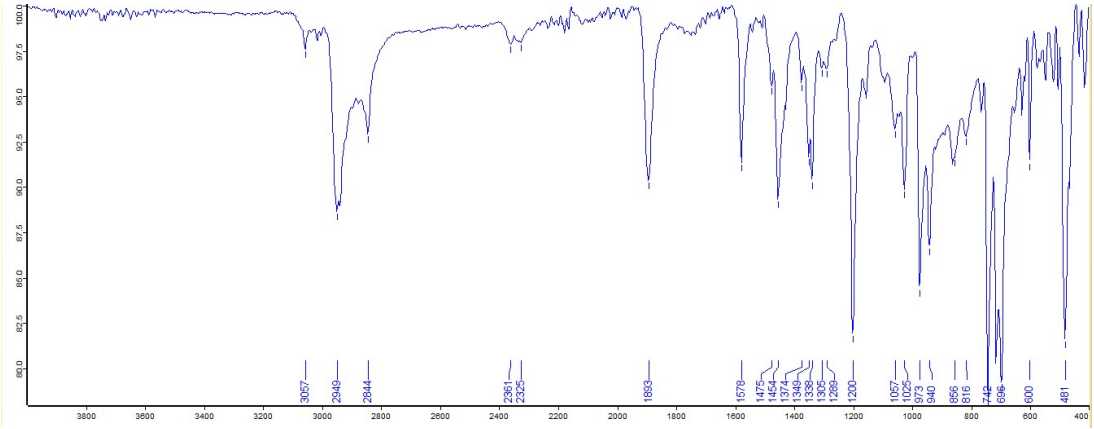
Fig. S20 Base Activation Studies of Amine Catalyst **6a** with 8 eq. of KOtBu.



18a

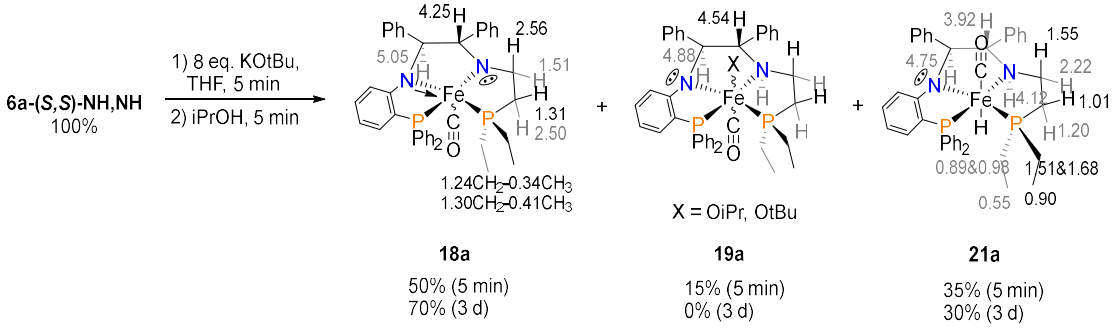
(a) IR Spectrum:

Again, **18a** displays a CO stretch at 1893 cm^{-1}, which was the specified error of the Bruker Alpha with an ATR platinum diamond attachment.

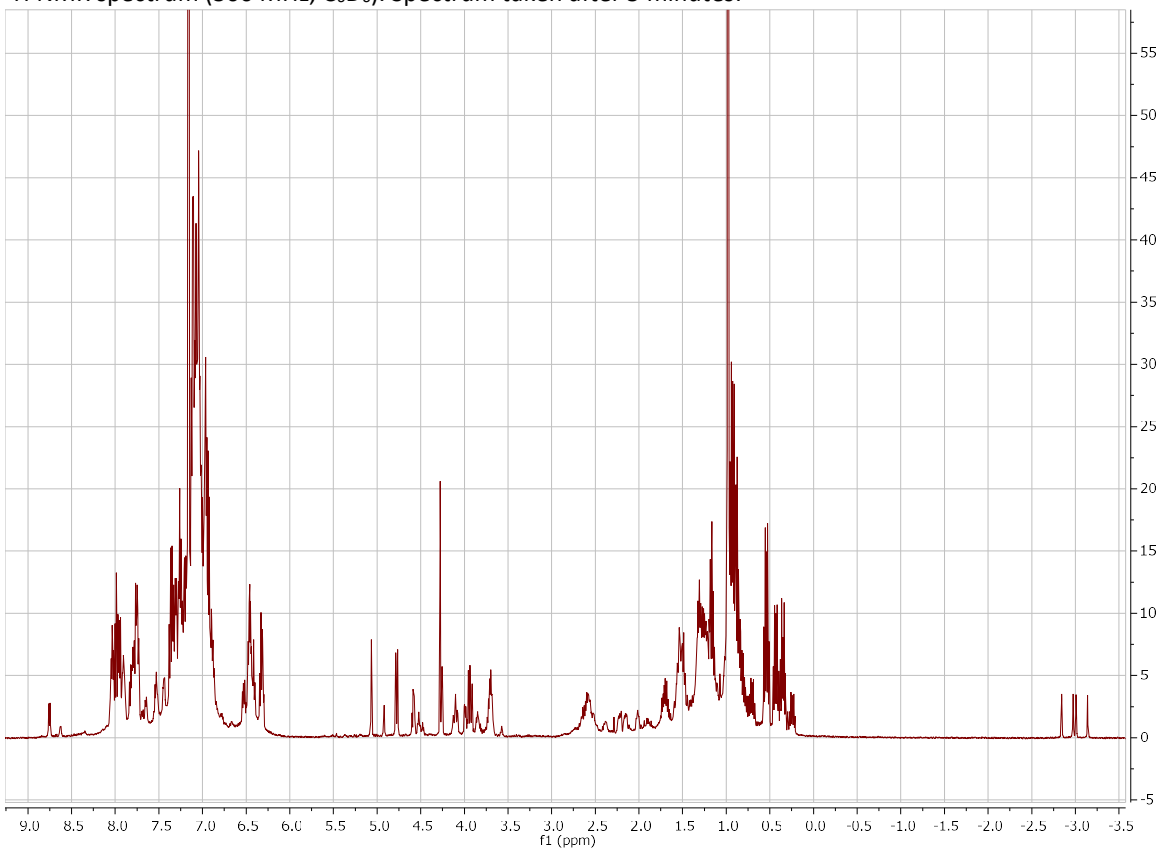


Note: No NMR Data was available as some paramagnetic material is formed. By stirring in *i*PrOH, the paramagnetic compound is converted to a diamagnetic compound.

Fig. S21 Base Activated Hydride Studies with Amine Precatalyst **6a**.

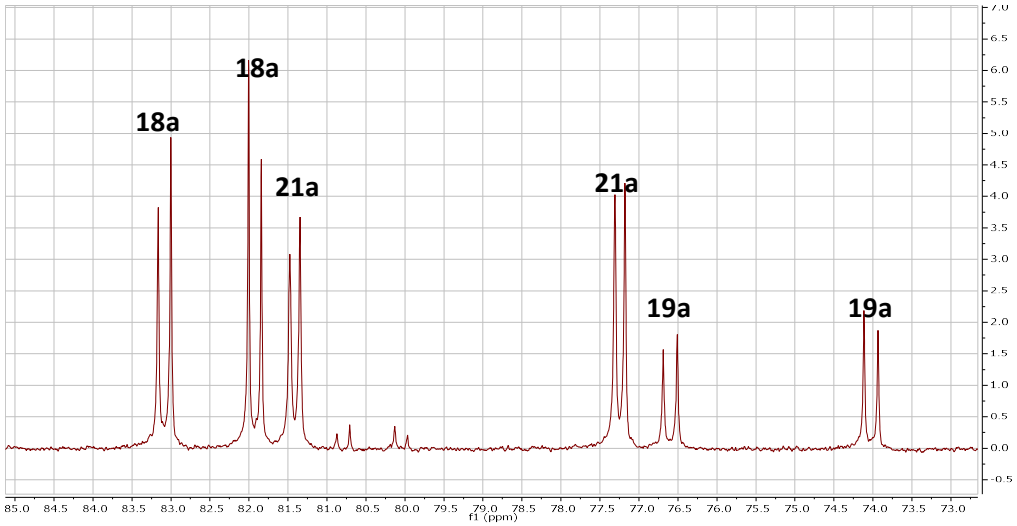


(a) ^{1}H NMR spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:

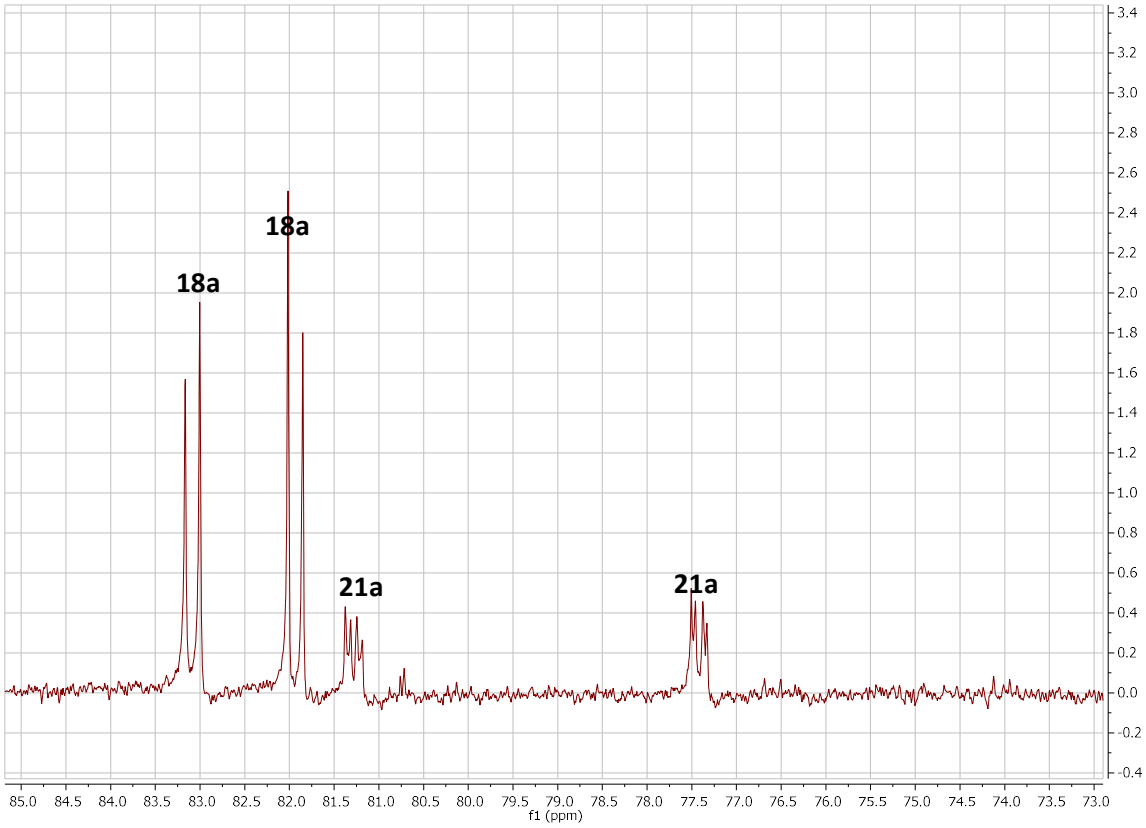


(b) ^{31}P NMR spectrum (202 MHz, C_6D_6). Spectrum was taken after 5 minutes:

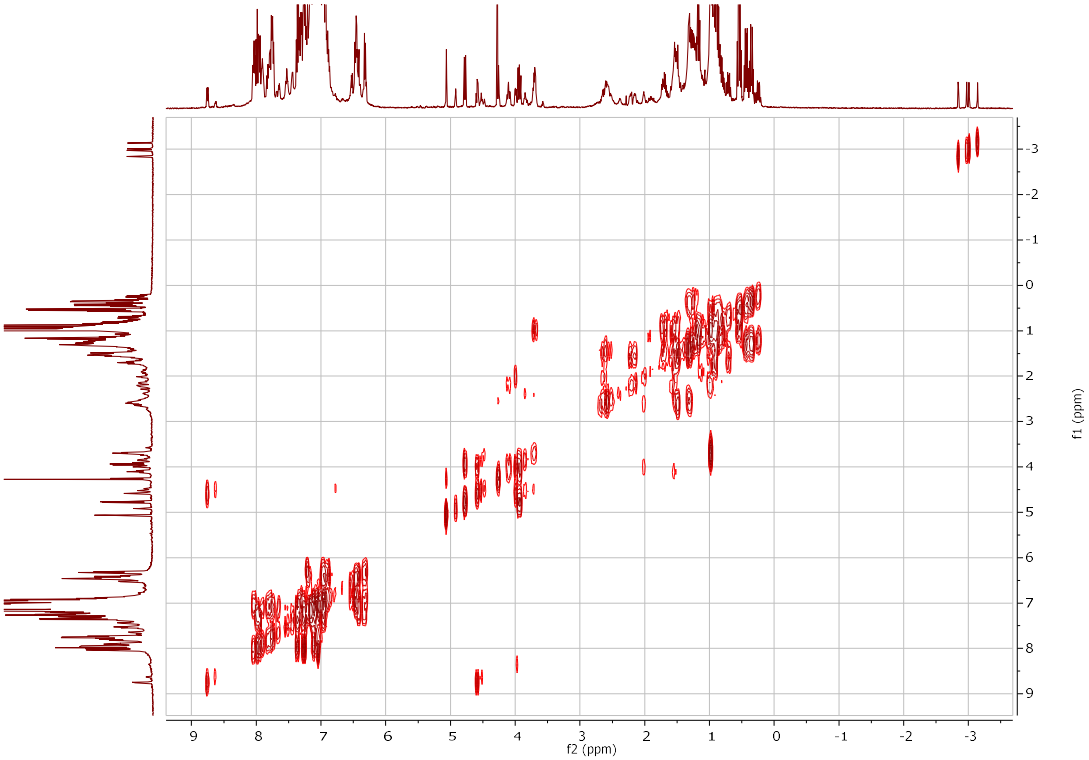
The formation of the **18a** as the major species and hydride complex **21a** at 77.24 ppm and 81.41 ppm ($^2J_{PP}$ = 26 Hz). The hydride signal in the ^1H NMR comes in at -3.07 ppm ($^2J_{HP}$ = 65 Hz and 83 Hz). We propose an alkoxide complex **21a** displaying a doublet at 74.02 ppm and 76.60 ppm ($^2J_{PP}$ = 36 Hz), in this case the amino proton could not be found due to noise, but the $^2J_{PP}$ coupling constant was similar to alkoxide complex **19d**.



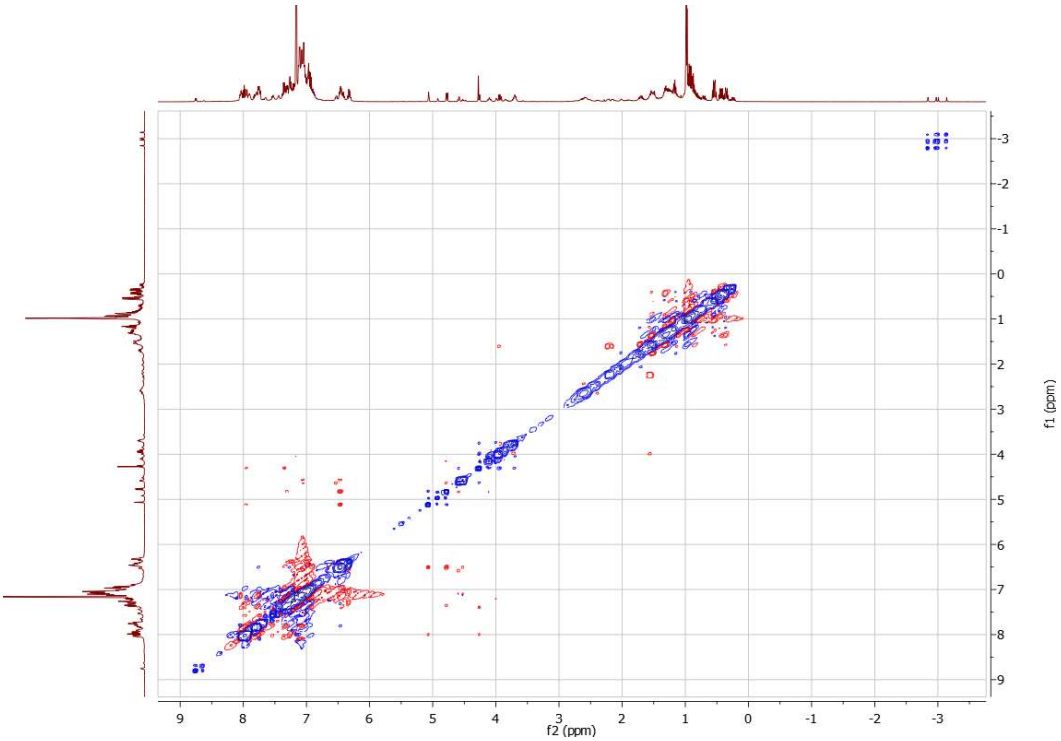
(c) ^{31}P NMR spectrum (202 MHz, C_6D_6) taken after 3 days:



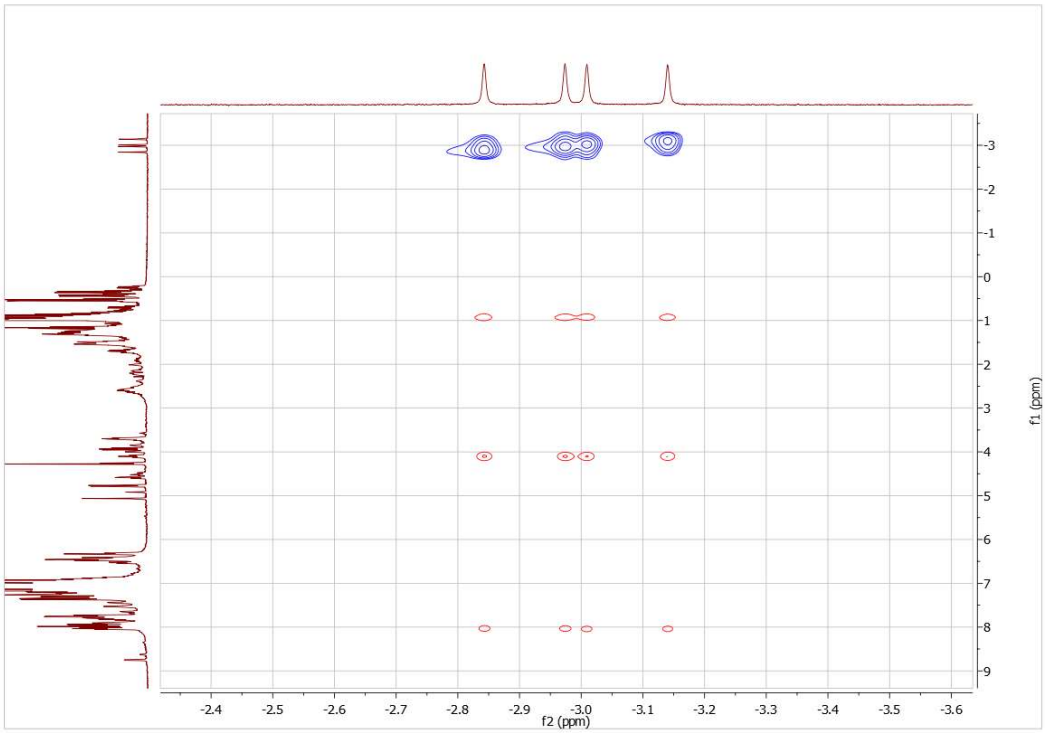
(d) 2D ^{1}H-^{1}H COSY spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:



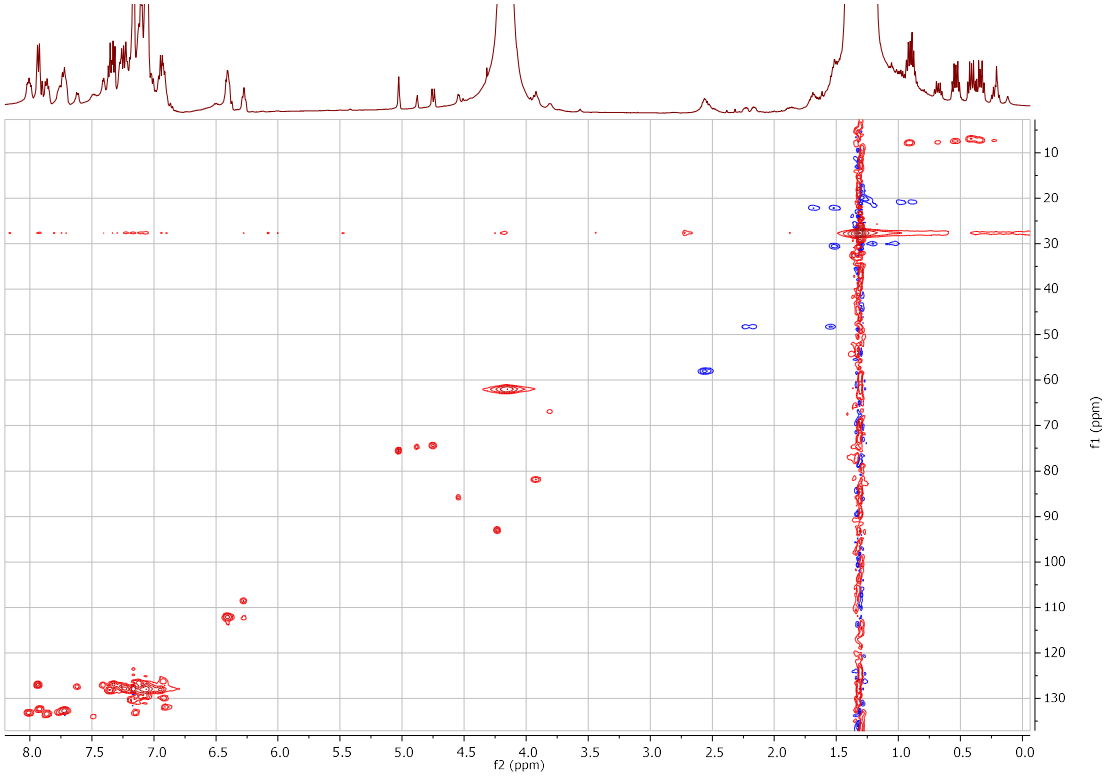
(e) 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, C_6D_6). Spectrum taken after 5 minutes:



(f) Expanded 2D ^{1}H-^{1}H NOESY NMR spectrum. Spectrum was taken after 5 minutes:
For **19a**, the hydride signal correlates to the amino proton at 4.12 ppm, demonstrating that they are on the same side of the PNNP ligand.



(g) 2D ^{1}H-^{13}C HSQC spectrum (500MHz, C_6D_6). Spectrum was taken after 5 minutes:
The formation of **18a** as before. The proposed alkoxide complex **19a** displays the C**H**Ph at (4.88, 74.65) and (4.54, 85.78). The hydride complex **21a** displays the C**H**Ph at (4.75, 74.39) and (3.92, 81.85), the protons of the two CH_2 of the amine arm at (2.22, 48.27), (1.55, 48.26), (1.20, 30.01), and (1.01, 29.90), the protons of the two CH_2 of the diethylphosphine at (1.68, 22.14), (1.51, 22.09), (0.98, 20.91), and (0.89, 20.85), and the protons of the two CH_3 of the diethylphosphine at (0.90, 7.82), and (0.55, 7.41).



(h) IR Spectrum taken after 5 minutes:
Again, **18a** displays a CO stretch at 1892 cm^{-1}, which was the specified error of the Bruker Alpha with an ATR platinum diamond attachment. **21a** CO Stretch could not be discerned.

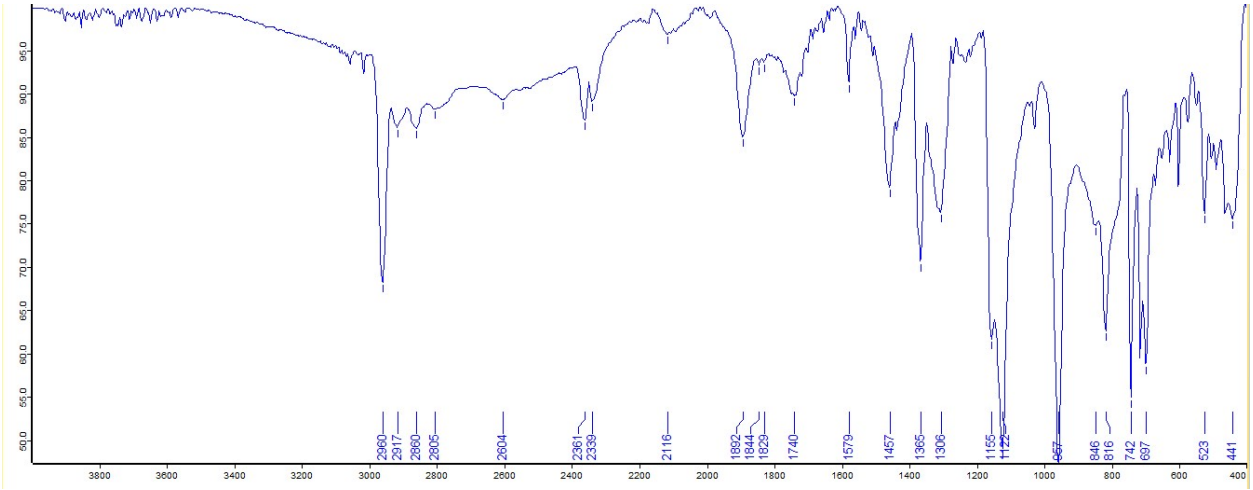
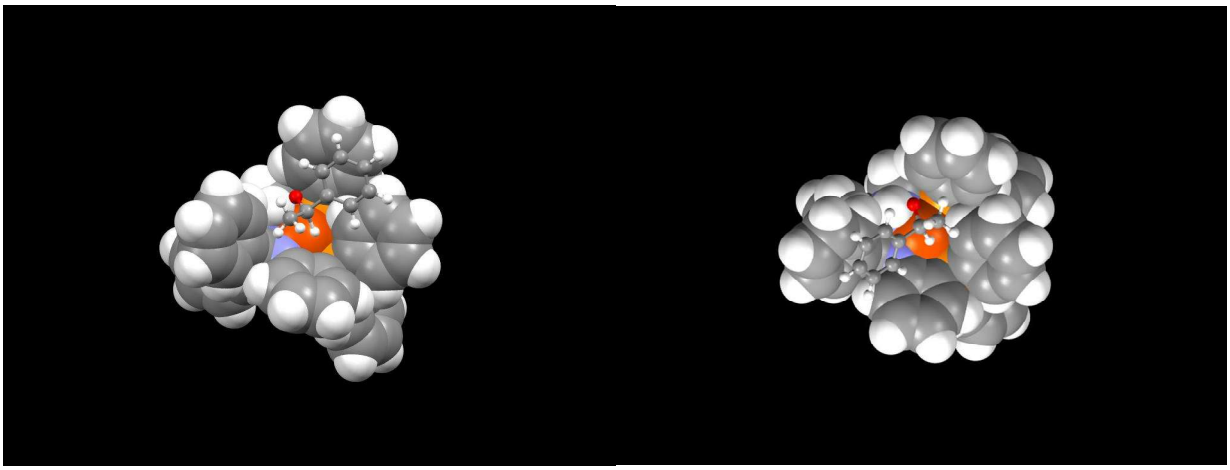
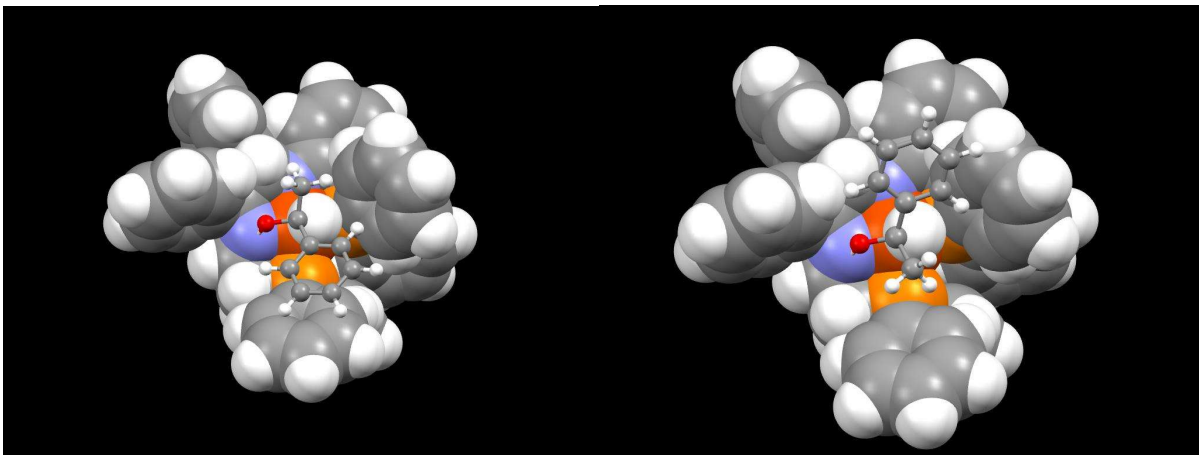


Fig. S22 3D Space-Filling Model of $\mathbf{TS_{23,22}}$ Forming (*R*)-1-phenylethanol (Left) and (*S*)-1-phenylethanol (Right) with R=Ph. This is a view from the top of the PNNP ligand.



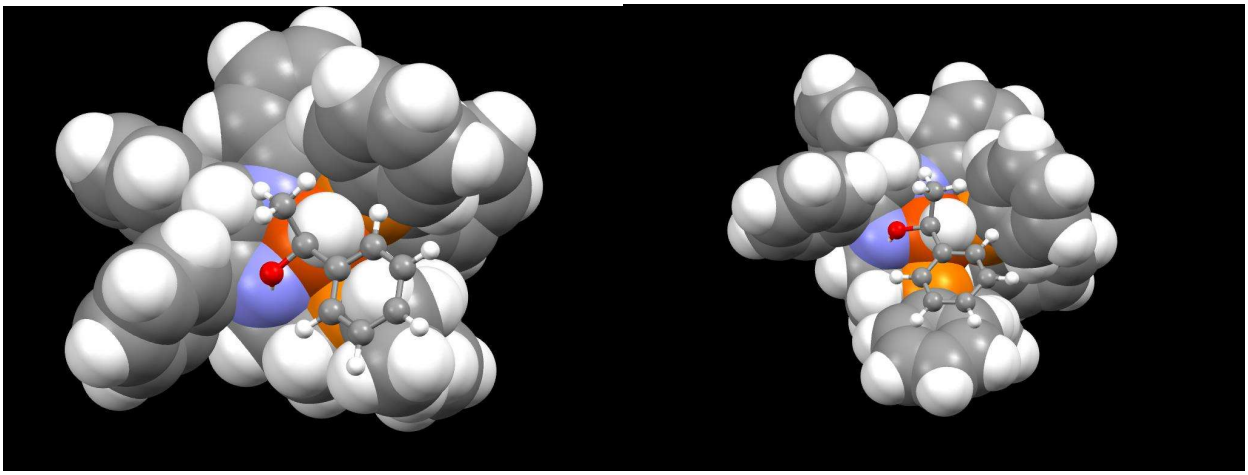
In this case, the favored product was (*R*)-1-phenylethanol. The active site was quite sterically encumbered due to the orthophenylene linker, leading to lower activities compared to previous iron precatalysts **1a,b** and **4**. The (*S*)-1-phenylethanol places the phenyl group towards the phenyl of the DPEN backbone. From the crystal structure of **16d**, we know that the CHPh of the DPEN backbone and the ethyldiphenylphosphine donor partially block the open site of the iron complex as shown in Fig. 8 in the manuscript, but the ethyldiphenylphosphine is more flexible. The (*R*)-1-phenylethanol places the phenyl group in the less sterically encumbered location, as the ethyldiphenylphosphine donor tend to bend to compensate for the approaching acetophenone.

Fig. S23 3D Space-Filling Model of **$TS_{21,CO\text{-}Up\text{-}18}$** Forming (*S*)-1-phenylethanol (Left) and (*R*)-1-phenylethanol (Right) with R=Ph. This is a view from the bottom of the PNNP ligand.



The major product in **$TS_{21,CO\text{-}Up\text{-}18}$** was (*S*)-1-phenylethanol. The left-hand side of the fig. displays that the phenyl of the product was placed above the ethyldiphenylphosphine instead of over the phenyl of the C**H**Ph backbone of the DPEN as was observed in the previous example shown above. The orthophenylene creates a steric wall, which the acetophenone could not place the phenyl group passed. Production of the (*R*)-1-phenylethanol, as shown on the right-hand side, was too sterically encumbered.

Fig. S24 3D Space-Filling Model of $\mathbf{TS_{21,Co\text{-}Up\text{-}18}}$ Forming (*S*)-1-phenylethanol with R=Et (Left) and (*S*)-1-phenylethanol (Right) with R=Ph. This is a view from the bottom of the PNNP ligand.



Since the phenyl of the approaching acetophenone is placed over the ethyldiphenylphospshine donor, changing the R-group at this location leads to a large change in enantioselectivity and activity of these catalysts. On the left-hand side, the phosphine donor with R = Et (**6a**) leads to a less sterically-hindered area for the phenyl of the acetophenone. As we increase the size of the R group to Ph, as shown on the right-hand side, the site for the phenyl of (*S*)-1-phenylethanol becomes energetically-less favorable.

The trend for increasing the size of the R group to activity or enantioselectivity was not evident, as the ethylene linker may bend to compensate for the alterations to the R group and the thermodynamics of the active hydride complex also dictates whether the acetophenone will approach from the top or the bottom of the iron catalyst.

Fig. S25 Crystal Data for Imine Iron Precatalyst **5d** Containing the Two Diastereomers.

Empirical formula	C71 H60 B Br Fe N2 O P2
Formula weight	1165.72
Temperature	151(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 11.301(2) Å; α = 110.941(5)°
	b = 14.448(3) Å; β = 97.709(6)°
	c = 19.278(4) Å; γ = 101.330(5)°
Volume	2809.8(9) $Å^3$
Z	2
Density (calculated)	1.378 Mg/m^3
Absorption coefficient	1.085 mm^{-1}
F(000)	1208
Crystal size	0.120 x 0.100 x 0.100 mm^3
Theta range for data collection	1.536 to 27.617°
Index ranges	-14<=h<=14, -18<=k<=18, -25<=l<=25
Reflections collected	92778
Independent reflections	25756 [R(int) = 0.1305]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6670
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	25756 / 3 / 1423
Goodness-of-fit on F^2	0.939
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.0715
R indices (all data)	R1 = 0.1340, wR2 = 0.0881
Absolute structure parameter	0.000(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.537 and -0.701 $e.Å^{-3}$

Select bond lengths and angles were placed in the manuscript under the Fig. 4. The rest of the crystal data may be obtained in the cif file.

Fig. S26 Crystal Data for Amine Iron Precatalyst **6a**.

Empirical formula	C67 H70 B Br Fe N2 O2 P2
Formula weight	1143.76
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 10.9864(4) Å; α = 90°
	b = 12.9194(4) Å; β = 90°
	c = 40.2053(14) Å; γ = 90°
Volume	5706.6(3) $Å^3$
Z	4
Density (calculated)	1.331 Mg/m^3
Absorption coefficient	3.829 mm^{-1}
F(000)	2392
Crystal size	0.150 x 0.030 x 0.010 mm^3
Theta range for data collection	2.198 to 67.391°
Index ranges	-12<=h<=13, -15<=k<=15, -47<=l<=47
Reflections collected	111385
Independent reflections	10120 [R(int) = 0.1096]
Completeness to theta = 25.242°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7344 and 0.5700
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10120 / 15 / 700
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1173
R indices (all data)	R1 = 0.0534, wR2 = 0.1211
Absolute structure parameter	0.017(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.407 and -0.683 $e.Å^{-3}$

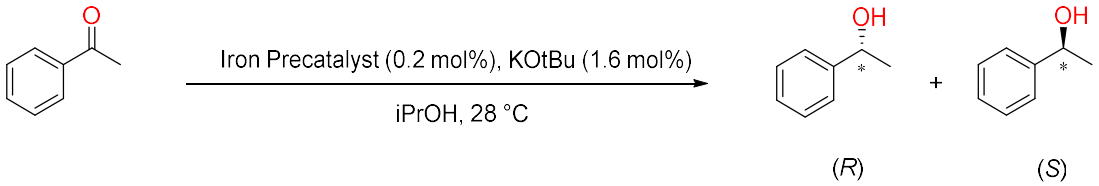
Select bond lengths and angles were placed in the manuscript under the Fig. 5. The rest of the crystal data may be obtained in the cif file.

Fig. S27 Crystal Data Base Activated Iron Complex **16d**.

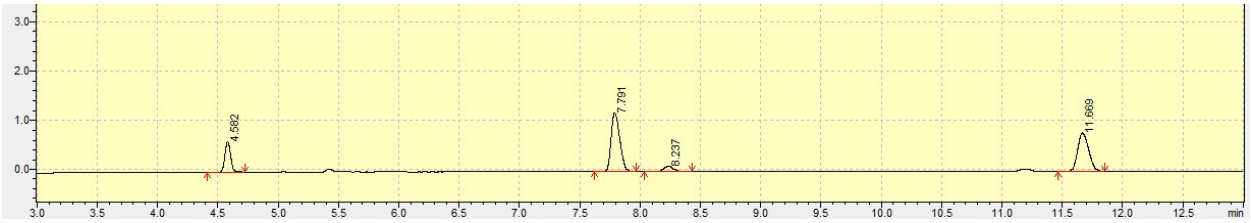
Empirical formula	C71 H59 B Fe N2 O P2
Formula weight	1084.80
Temperature	150(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 10.7598(6) Å; α = 90°
	b = 17.9842(9) Å; β = 99.782(4)°
	c = 14.3349(8) Å; γ = 90°
Volume	2733.6(3) $Å^3$
Z	2
Density (calculated)	1.318 Mg/m^3
Absorption coefficient	3.137 mm^{-1}
F(000)	1136
Crystal size	0.120 x 0.060 x 0.030 mm^3
Theta range for data collection	3.128 to 67.438°
Index ranges	-12<=h<=12, -21<=k<=21, -17<=l<=17
Reflections collected	37029
Independent reflections	9158 [R(int) = 0.2584]
Completeness to theta = 25.242°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7529 and 0.4287
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9158 / 1 / 704
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0752, wR2 = 0.1616
R indices (all data)	R1 = 0.1438, wR2 = 0.1978
Absolute structure parameter	0.077(11)
Extinction coefficient	n/a
Largest diff. peak and hole	0.502 and -0.696 $e.Å^{-3}$

Select bond lengths and angles were placed in the manuscript under the Fig. 8. The rest of the crystal data may be obtained in the cif file.

Fig. S28A Gas Chromatograph Readout for the Asymmetric Transfer Hydrogenation of Acetophenone with **5d**.

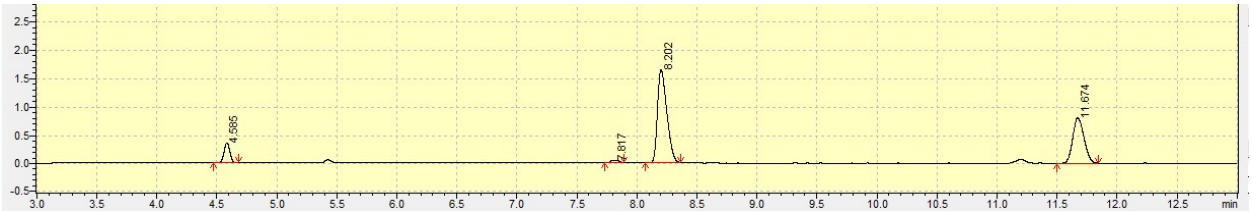


Oven Temperature: 130 °C



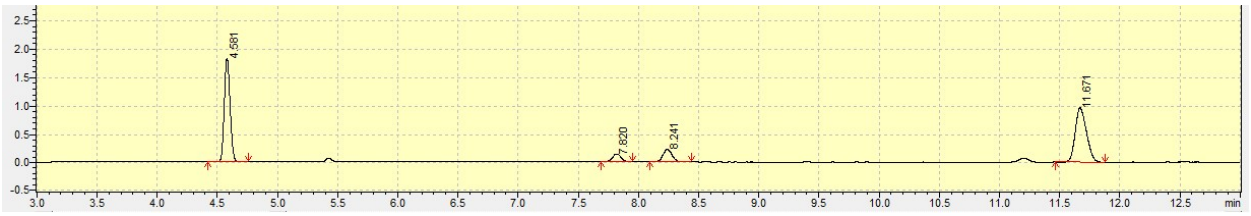
Retention time: acetophenone: 4.582 min.; (*R*)-1-phenylethanol: 7.791 min.; (*S*)-1-phenylethanol: 8.237 min.; di-tert-butylbenzene (external standard): 11.669 min..

Fig. S28B Gas Chromatograph Readout for the Asymmetric Transfer Hydrogenation of Acetophenone with **6a**.



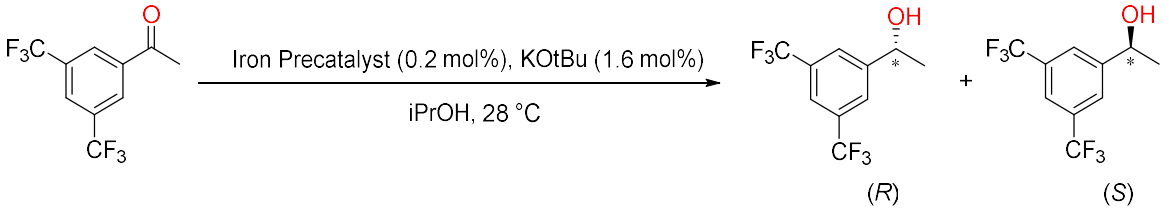
Retention time: acetophenone: 4.582 min.; (*R*)-1-phenylethanol: 7.791 min.; (*S*)-1-phenylethanol: 8.237 min.; di-tert-butylbenzene (external standard): 11.669 min..

Fig. S28C Gas Chromatograph Readout for the Asymmetric Transfer Hydrogenation of Acetophenone with **6d**.

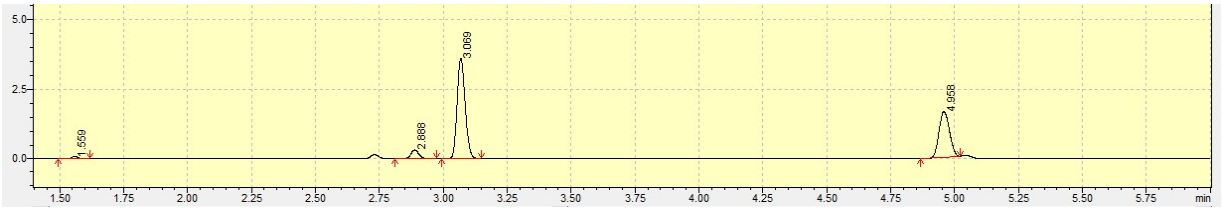


Retention time: acetophenone: 4.582 min.; (*R*)-1-phenylethanol: 7.791 min.; (*S*)-1-phenylethanol: 8.237 min.; di-tert-butylbenzene (external standard): 11.669 min..

Fig. S29A Gas Chromatograph Readout for the Asymmetric Transfer Hydrogenation of 3',5'-bis(trifluoromethyl)acetophenone with **5d**.

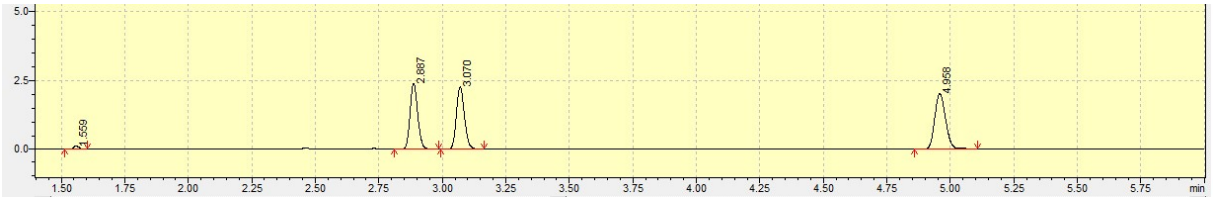


Oven Temperature: 110 °C



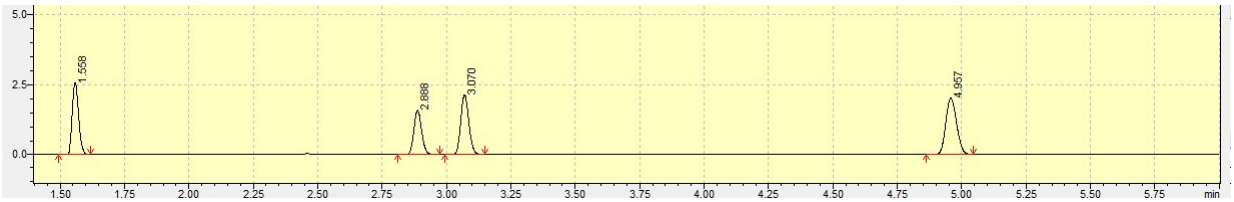
Retention time: 3',5'-bis(trifluoromethyl)acetophenone: 1.559 min.; (*S*)- 1-(3',5'-bis(trifluoromethyl)phenyl)ethanol: 2.888 min.; (*R*)-1-(3',5'-bis(trifluoromethyl)phenyl)ethanol: 3.069 min.; di-tert-butylbenzene (external standard): 4.958 min..

Fig. S29B Gas Chromatograph Readout for the Asymmetric Transfer Hydrogenation of 3',5'-bis(trifluoromethyl)acetophenone with **6a**.



Retention time: 3',5'-bis(trifluoromethyl)acetophenone: 1.559 min.; (*S*)- 1-(3',5'-bis(trifluoromethyl)phenyl)ethanol: 2.888 min.; (*R*)-1-(3',5'-bis(trifluoromethyl)phenyl)ethanol: 3.069 min.; di-tert-butylbenzene (external standard): 4.958 min..

Fig. S29C Gas Chromatograph Readout for the Asymmetric Transfer Hydrogenation of 3',5'-bis(trifluoromethyl)acetophenone with **6d**.



Retention time: 3',5'-bis(trifluoromethyl)acetophenone: 1.559 min.; (*S*)- 1-(3',5'-bis(trifluoromethyl)phenyl)ethanol: 2.888 min.; (*R*)-1-(3',5'-bis(trifluoromethyl)phenyl)ethanol: 3.069 min.; di-tert-butylbenzene (external standard): 4.958 min..

References:

1. L. F. Tietze, Y. Zhou and E. Topken, *Eur. J. Org. Chem.,* 2000, 2247-2252.
2. A. A. Mikhailine, P. O. Lagaditis, P. E. Sues, A. J. Lough and R. H. Morris, *J. Organomet. Chem.,* 2010, ***695***, 1824-1830.
3. P. E. Sues, A. J. Lough and R. H. Morris, *Organometallics,* 2011, ***30***, 4418-4431.