Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

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Supporting Information

1. General Information

All manipulations were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were dried and degassed before use, with the exception of octafluorotoluene which was degassed only. *N*-Methylpyrrolidine, triethylamine, toluene-d_8 and $CDCl_3$ were also dried and degassed before use. (*S*)-*N*,*N*-Dimethyl-1-ferrocenyl-ethylamine *L*-tartrate salt was provided by Eastman Chemical Company. All other chemicals were purchased commercially and used as received. Propene/CO/H_2 (10/45/45) was obtained from BOC. Flash column chromatography was performed using dry and degassed solvents under an inert atmosphere using either Merck Geduran Si 60 (40-63 μm) silica gel or Sigma Aldrich activated neutral Brockmann I alumina.

NMR spectra were recorded on a Bruker Advance 300, 400 or 500 MHz instrument. Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvent. Signal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a combination of the above. Where appropriate coupling constants (*J*) are quoted in Hz and are reported to the nearest 0.1 Hz. All spectra were recorded at room temperature (unless otherwise stated) and the solvent for a particular spectrum is given in parentheses. NMR of compounds containing phosphorus were recorded under an inert atmosphere in dry and degassed solvent. High pressure NMR was recorded under a CO/H_2 atmosphere using a Norell S-5-500-HW-HPV-7 NMR tube.

Infrared spectroscopy was recorded using a MIRacle^{TM} single reflection horizontal ATR accessory from Pike (ZnSe single crystal) to analyse solids (neat). High pressure infrared spectroscopy was performed in a Parr pressure vessel. The high pressure IR spectra were recorded using an Avatar 360 FT-IR.

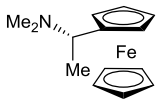
Mass spectrometry data was performed on a Micromass GCT spectrometer, Micromass LCT spectrometer, Waters ZQ4000, Thermofisher LTQ Orbitrap XL or Finnigan MAT 900 XLT instruments.

Gas chromatography was performed on an Agilent Technologies 7820A machine. Gas chromatography – mass spectrometry was performed on an Agilent Technologies 6890 machine with 5973 mass selective detector. An Agilent column (HP-1) was used, 30 m length, 0.248 mm diameter and 0.25 μm film. Optical rotation measurements were taken on a Perkin Elmer 341 polarimeter.

Hydroformylation reactions of propene and 1-octene were performed in a Parr 4590 Micro Reactor fitted with a gas entrainment stirrer; comprising of holes which gives better gas dispersion throughout the reaction mixture. The pressure vessel also had the ability to add more gas to the reaction as gas is used up, thus maintaining the reactor at a specific pressure; this ability was used to measure reaction kinetics.

2. Synthesis of ligands and ligand precursors

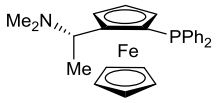
(*S*)-*N*,*N*-dimethyl-1-ferrocenyl-ethylamine (5)



5

Amine **5** was prepared using a different method from the literature, but displayed spectroscopic data that was consistent with those reported previously.[1,2] Water (30 mL) was added to (*S*)-*N*,*N*-dimethyl-1-ferrocenyl-ethylamine *L*-tartrate salt (10.20 g, 25.16 mmol). Potassium hydroxide was then added until the pH was 10. Diethyl ether (20 mL) was added and the layers were separated. The aqueous layer was washed twice with diethyl ether (5 mL). The organic layers were combined and dried over magnesium sulfate and concentrated *in vacuo* to give amine **5** as an orange oil (5.81 g, 22.59 mmol, 90%). $[\alpha]_D^{20}$ –11 (*c* 1.50, ethanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.09-4.15 (4H, m, $C_5\mathbf{H}_4$), 4.11 (5H, s, $C_5\mathbf{H}_5$), 3.56-3.63 (1H, m, NC**H**), 2.06 (6H, s, $N(C\mathbf{H}_3)_2$), 1.45 (3H, d, *J* = 6.9 Hz, $CHC\mathbf{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 87.4 ($\mathbf{C}_{Fc}$), 69.5 ($\mathbf{C}_{Fc}$H), 68.7 (5 x $\mathbf{C}_{Fc}$H), 67.5 ($\mathbf{C}_{Fc}$H), 67.3 ($\mathbf{C}_{Fc}$H), 67.0 ($\mathbf{C}_{Fc}$H), 58.8 (N**C**H), 40.9 (2 x $N\mathbf{C}H_3$), 16.2 ($NCH\mathbf{C}H_3$); HRMS (ESI^+) $C_{14}H_{20}NFe$ $[M+H]^+$: calc. 258.0940, found: 258.0937.

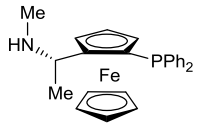
(*S*)-*N*,*N*-Dimethyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine (6)



6

Amine **6** was prepared using a different method from the literature, but displayed spectroscopic data that was consistent with those reported previously.[2] Amine **5** (14.30 g, 55.61 mmol) was dissolved in tert-butyl methyl ether (85 mL) under argon. To this was added *n*-BuLi slowly (1.6 M solution, 22.6 mL, 66.73 mmol) and reaction was stirred at room temperature for 1 hour. The solution was then purged with argon for 30 minutes. Chlorodiphenylphosphine (12.0 mL, 66.73 mmol) in tert-butyl methyl ether (10 mL) was added slowly, and reaction was stirred at room temperature for 4 hours. The reaction was cooled to 0 °C, and saturated sodium bicarbonate solution was added (57 mL) followed by water (45 mL). The layers were separated and the aqueous layer washed with toluene. The organic layer was dried over magnesium sulfate, filtered and washed with ethanol. Solution was concentrated, and recrystallised from ethanol (45 mL) to give amine **6** as an orange solid (9.16 g, 20.75 mmol, 31%). mp 136-138 °C (hexane); $[\alpha]_D^{20}$ +338 (*c* 0.32, ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.61 (2H, m, Ar**H**), 7.34-7.37 (3H, m, Ar**H**), 7.16-7.23 (5H, m, Ar**H**), 4.36-4.37 (1H, m, $C_5\mathbf{H}_3$), 4.24-4.25 (1H, m, $C_5\mathbf{H}_3$), 4.12-4.18 (1H, m, $C_5\mathbf{H}_3$), 3.94 (5H, s, $C_5\mathbf{H}_5$), 3.85-3.86 (1H, m, NC**H**), 1.77 (6H, s, $N(C\mathbf{H}_3)_2$), 1.25 (3H, d, *J* = 6.7 Hz, $CHC\mathbf{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9 (d, *J* = 14.3 Hz, $\mathbf{C}_{Ar}$), 139.0 (d, *J* = 15.7 Hz, $\mathbf{C}_{Ar}$), 135.2 (d, *J* = 34.3 Hz, 2 x $\mathbf{C}_{Ar}$H), 132.4 (d, *J* = 31.4 Hz, 2 x $\mathbf{C}_{Ar}$H), 128.8 ($\mathbf{C}_{Ar}$H), 128.0 (d, *J* = 12.9 Hz, 2 x $\mathbf{C}_{Ar}$H), 127.4 (d, *J* = 11.3 Hz, 2 x $\mathbf{C}_{Ar}$H), 127.2 ($\mathbf{C}_{Ar}$H), 97.0 (d, *J* = 15.8 Hz, $\mathbf{C}_{Fc}$), 71.9 (d, *J* = 5.6 Hz, $\mathbf{C}_{Fc}$H), 71.2 ($\mathbf{C}_{Fc}$), 69.8 (5 x $\mathbf{C}_{Fc}$H), 69.4 (d, *J* = 3.7 Hz, $\mathbf{C}_{Fc}$H), 68.3 ($\mathbf{C}_{Fc}$H), 57.3 (d, *J* = 6.8 Hz, N**C**H), 39.1 (2 x $N\mathbf{C}H_3$), 9.4 ($NCH\mathbf{C}H_3$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ –22.9; HRMS (ESI^+) $C_{26}H_{29}NPFe$ $[M+H]^+$: calc. 442.1382, found: 442.1373.

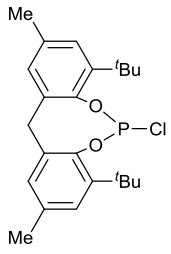
(*S*)-*N*-Methyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine (**7**)



7

Amine **7** was prepared following a literature procedure for the (*R*, *S*)-amine and displayed spectroscopic data that was consistent with those reported previously.[3] Amine **6** (7.622 g, 17.27 mmol) and acetic anhydride (5.46 mL, 57.85 mmol) were combined under N_2. The reaction was heated to 90 °C (at which the solution became homogeneous) and held at this temperature for 3.5 hours.[i] *iso*-Propanol (20 mL) was added to the reaction mixture, and this solution was added to 40% wt methylamine solution (30 mL, 347.13 mmol) in *iso*-propanol (10 mL). The reaction was stirred at 50 °C for 2 days. The reaction was cooled to room temperature and water was added (88 mL), which resulted in a precipitate. The reaction was stirred for 30 minutes, before being filtered and washed with water (10 mL) to give amine **7** as an orange solid (6.58 g, 15.40 mmol, 89%). mp 109-111 °C (hexane); $[\alpha]_D^{20}$ +311 (*c* 0.38, ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.57 (2H, m, Ar**H**), 7.37-7.39 (3H, m, Ar**H**), 7.27-7.29 (5H, m, Ar**H**), 4.47-4.49 (1H, m, $C_5\mathbf{H}_3$), 4.29-4.30 (1H, m, $C_5\mathbf{H}_3$), 4.03 (5H, s, $C_5\mathbf{H}_5$), 3.95-3.98 (1H, m, NC**H**), 3.79-3.80 (1H, m, $C_5\mathbf{H}_3$), 1.95 (3H, s, NC$\mathbf{H}_3$), 1.57 (1H, br.s, N**H**), 1.47 (3H, d, *J* = 6.7 Hz, CHC$\mathbf{H}_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.9 (d, *J* = 10.0 Hz, $\mathbf{C}_{Ar}$), 137.0 (d, *J* = 8.3 Hz, $\mathbf{C}_{Ar}$), 134.9 (d, *J* = 20.6 Hz, 2 x $\mathbf{C}_{Ar}$H), 132.8 (d, *J* = 19.6 Hz, 2 x $\mathbf{C}_{Ar}$H), 129.1 ($\mathbf{C}_{Ar}$H), 128.54 ($\mathbf{C}_{Ar}$H), 128.49 ($\mathbf{C}_{Ar}$H), 128.4 ($\mathbf{C}_{Ar}$H), 128.3 ($\mathbf{C}_{Ar}$H), 128.2 ($\mathbf{C}_{Ar}$H), 97.4 (d, *J* = 22.7 Hz, $\mathbf{C}_{Fc}$), 75.4 (d, *J* = 7.0 Hz, $\mathbf{C}_{Fc}$), 71.2 (d, *J* = 4.8 Hz, $\mathbf{C}_{Fc}$H), 69.7 (5 x $\mathbf{C}_{Fc}$H), 69.4 (d, *J* = 4.5 Hz, $\mathbf{C}_{Fc}$H), 69.0 ($\mathbf{C}_{Fc}$H), 52.5 (d, *J* = 10.0 Hz, N**C**H), 32.7 (N**C**H_3), 18.7 (NCH**C**H_3); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ –24.8; HRMS (ESI$^+$) $C_{25}H_{27}NPFe$ $[M+H]^+$: calc. 428.1225, found: 428.1221.

2,2'-Methylenebis(6-*tert*-butyl-4-methyl-*o*-phenylene)chlorophosphite (8a)

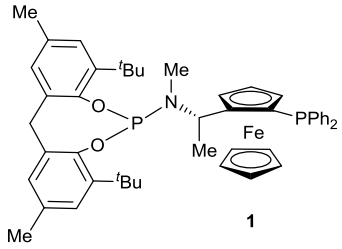


8a

Chlorophosphite **8a** was prepared by a different procedure to the literature, but displayed ^{31}P{^{1}H}spectroscopic data that was consistent with those reported previously.[4] 2,2'-Methylenebis(6-*tert*-butyl-4-methylphenol) (2.98 g, 8.75 mmol) was dissolved in toluene (40 mL) under N_2, and to this was added PCl_3 (1.15 mL, 13.13 mmol) and *N*-methylpyrrolidine (2.73 mL, 26.25 mmol). The reaction mixture was stirred at room temperature for 40 hours and was then filtered and the resulting filtrate concentrated *in vacuo* to give chlorophosphite **8a** as off-white solid (2.63 g, 6.50 mmol, 74%) that was extremely sensitive to moisture was characterised by NMR only. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (2H, s, Ar**H**), 7.00 (2H, s, Ar**H**), 4.32 (1H, dd, $^2J_{H\text{-}H}$ = 13.9, $^5J_{H\text{-}P}$ = 3.2 Hz, ArC**H**H), 3.32 (1H, d, *J* =13.0 Hz, ArCH**H**), 2.28 (6H, s, 2 x ArC$\mathbf{H}_3$), 1.38 (18H, s, 2 x C(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5 (2 x $\mathbf{C}_{Ar}$), 141.8 (d, *J* = 3.3 Hz, 2 x $\mathbf{C}_{Ar}$), 135.3 (d, *J* = 3.4 Hz, 2 x $\mathbf{C}_{Ar}$), 134.7 (2 x $\mathbf{C}_{Ar}$), 129.0 (2 x $\mathbf{C}_{Ar}$H), 127.1 (2 x $\mathbf{C}_{Ar}$H), 35.0 ($\mathbf{C}H_2$), 34.9 (2 x $\mathbf{C}$(CH$_3$)$_3$), 30.91 (C($\mathbf{C}$H$_3$)$_3$), 30.88 (C($\mathbf{C}$H$_3$)$_3$), 21.3 (2 x Ar$\mathbf{C}H_3$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 150.7 (br s).

[i] TLC (4:1 heptane:ethyl acetate, triethytlamine deactivated) could be used to monitor consumption of starting material.

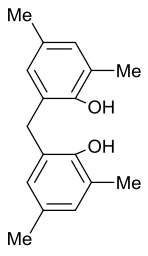
Ligand (1)



1

Amine **7** (0.30 g, 0.70 mmol) was dissolved in ethyl acetate (1.5 mL) and *N*-methylpyrrolidine (0.11 mL, 1.07 mmol) under argon. The solution was cooled to 0 °C and was purged with argon for 15 minutes, then chlorophosphite **8a** (0.340 g, 0.85 mmol) in CH_2Cl_2 (2 mL) was added. The reaction mixture was stirred at 0 °C for 1 hour, then warmed to room temperature and stirred for 16 hours. The solution was concentrated *in vacuo* to afford a crude solid. The solid was purified by flash column chromatography on silica (pre-treated with a solution of 95:5 toluene:Et_3N) using 30:1 hexane:ethyl acetate as eluent under N_2 to give phosphine-phosphoramidite ligand **1** as an orange solid (0.38 g, 0.48 mmol, 69%). mp 252-253 °C (hexane); $[\alpha]_D^{20}$ +94 (*c* 0.51, toluene); Elemental analysis found C, 72.48; H, 6.90; N, 1.85%. $C_{48}H_{55}FeNO_2P_2$ requires C, 72.45; H, 6.97; N, 1.76%; IR 2949, 1435, 1213, 1159, 1107, 989, 932, 905, 814, 795 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.53 (2H, m, Ar**H**), 7.38-7.40 (3H, m, Ar**H**), 7.05-7.20 (7H, m, Ar**H**), 6.96-6.97 (2H, m, Ar**H**), 4.71-4.73 (1H, m, $C_5\mathbf{H}_3$), 4.44-4.52 (1H, m, NC**H**), 4.26-4.28 (1H, m, $C_5\mathbf{H}_3$), 4.19 (5H, s, $C_5\mathbf{H}_3$), 4.06 (1H, dd, $^2J_{H\text{-}H}$ = 12.4, $^5J_{H\text{-}P}$ = 2.3 Hz, ArC**H**H), 3.58-3.59 (1H, m, $C_5\mathbf{H}_3$), 3.14-3.19 (4H, m, 1H ArCH**H** + 3H NC$\mathbf{H}_3$), 2.28 (3H, s, ArC$\mathbf{H}_3$), 2.27 (3H, s, ArC$\mathbf{H}_3$), 2.10 (3H, dd, *J* = 6.8, 1.1 Hz, CC$\mathbf{H}_3$), 1.35 (9H, s, C(C$\mathbf{H}_3$)$_3$), 1.30 (9H, s, C(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8-147.1 (m, 2 x $\mathbf{C}_{Ar}$), 141.5-141.6 (2 x $\mathbf{C}_{Ar}$), 137.5-137.8 (m, 2 x $\mathbf{C}_{Ar}$), 136.5-136.8 (m, 2 x $\mathbf{C}_{Ar}$), 134.9 (d, *J* = 20.3 Hz, 2 x $\mathbf{C}_{Ar}$H), 132.9 (d, *J* = 19.7 Hz, 2 x $\mathbf{C}_{Ar}$H), 132.8 (2 x $\mathbf{C}_{Ar}$), 129.1 ($\mathbf{C}_{Ar}$H), 128.2-128.4 (m, 7 x $\mathbf{C}_{Ar}$H), 126.3 (d, *J* = 7.9 Hz, 2 x $\mathbf{C}_{Ar}$H), 99.7 (dd, *J* = 19.5 Hz, 5.5 Hz, $\mathbf{C}_{Fc}$), 73.5 (d, *J* = 10.7 Hz, $\mathbf{C}_{Fc}$), 72.5 ($\mathbf{C}_{Fc}$H), 70.8 (d, *J* = 3.2 Hz, $\mathbf{C}_{Fc}$H), 69.5 (5 x $\mathbf{C}_{Fc}$H), 67.5 ($\mathbf{C}_{Fc}$H), 49.2 (d, *J* = 29.3 Hz, N**C**H), 35.01 (**C**(CH$_3$)$_3$), 34.96 (**C**(CH$_3$)$_3$), 34.7 (**C**H$_2$), 31.2 (d, *J* = 5.1 Hz, C(**C**H$_3$)$_3$), 31.0 (d, *J* = 5.1 Hz, C(**C**H$_3$)$_3$), 28.5 (d, *J* = 14.2 Hz, N**C**H$_3$), 22.2 (dd, *J* = 15.0, 3.8 Hz, NCH**C**H$_3$), 21.2 (Ar**C**H$_3$); 21.1 (Ar**C**H$_3$); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 143.1, –20.6; HRMS (EI$^+$) $C_{48}H_{55}NO_2P_2FeNa$ $[M+Na]^+$: calc. 818.2955, found: 818.2965.

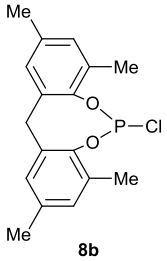
2,2'-Methylenebis(4,6-dimethylphenol) (8bi)



8bi

Isolated intermediate in synthesis of chlorophosphite **8b**. Diol **8bi** was prepared following a literature procedure and displayed spectroscopic data that was consistent with those reported previously.[5] 2,4-Dimethylphenol (6 mL, 49.12 mmol) was added to 5% w/w aqueous NaOH solution (47 mL, 60.91 mmol) and 37% w/w aqueous formaldehyde (7.6 mL, 98.24 mmol). The solution was heated to reflux and held and this temperature for 4 hours. The solution was cooled to room temperature and neutralised with glacial acetic acid (6 mL). The precipitate was filtered and washed with water and dried under vacuum. The crude product was then recrystallised from 1:1 chloroform:petroleum ether 40-60 to give diol **8bi** as an off-white solid (3.95 g, 15.41 mmol, 31%). mp 145-147 °C (hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 6.94 (2H, d, *J* = 2.1 Hz, Ar**H**), 6.80 (2H, d, *J* = 1.5, 0.5 Hz, Ar**H**), 5.90 (2H, br.s, O**H**), 3.84 (2H, s, C$\mathbf{H}_2$), 2.22 (6H, s, ArC$\mathbf{H}_3$), 2.20 (6H, s, ArC$\mathbf{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0 (2 x $\mathbf{C}_{Ar}$), 130.2 (2 x $\mathbf{C}_{Ar}$), 130.1 (2 x $\mathbf{C}_{Ar}$H), 129.0 (2 x $\mathbf{C}_{Ar}$H), 126.2 (2 x $\mathbf{C}_{Ar}$), 123.9 (2 x $\mathbf{C}_{Ar}$), 31.3 (**C**H$_2$), 20.6 (2 x Ar**C**H$_3$), 16.2 (2 x Ar**C**H$_3$); m/z (ESI$^+$): 279.14 $[M+Na]^+$.

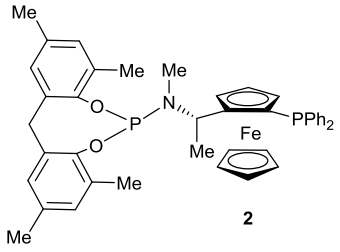
2,2'-Methylenebis(4,6-dimethyl-o-phenylene)chlorophosphite (8b)



8b

2,2'-Methylenebis(4,6-dimethylphenol) (2.99 g, 11.66 mmol) was dissolved in toluene (40 mL) under N_2, and to this was added PCl_3 (1.53 mL, 17.49 mmol) and *N*-methylpyrrolidine (3.64 mL, 34.98 mmol). The reaction mixture was stirred at room temperature for 40 hours then filtered and the solution was removed *in vacuo* to give chlorophosphite **8b** as an orange solid (2.24 g, 6.98 mmol, 60%) that is extremely sensitive to moisture and was characterised by NMR only. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (2H, s, Ar**H**), 6.86 (2H, s, Ar**H**), 4.32 (1H, dd, $^2J_{H\text{-}H}$ = 12.8 Hz, $^5J_{H\text{-}P}$ = 1.8 Hz, ArC**H**H), 3.38 (1H, d, *J* = 12.9 Hz, ArCH**H**), 2.29 (6H, s, 2 x ArC**H**$_3$), 2.21 (6H, s, 2 x ArC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8 (d, *J* = 15.9 Hz, 2 x **C**$_{Ar}$), 134.9 (2 x **C**$_{Ar}$), 133.7 (2 x **C**$_{Ar}$), 130.6 (d, *J* = 2.5 Hz, 2 x **C**$_{Ar}$), 130.2 (2 x **C**$_{Ar}$H), 128.0 (2 x **C**$_{Ar}$H), 34.1 (**C**H$_2$), 20.9 (2 x Ar**C**H$_3$), 17.1 (2 x Ar**C**H$_3$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 126.0.

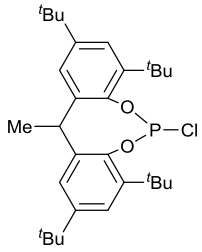
Ligand (2)



2

Amine **7** (0.30 g, 0.70 mmol) was dissolved in ethyl acetate (1.5 mL) and *N*-methylpyrrolidine (0.11 mL, 1.07 mmol) under argon. The solution was cooled to 0 °C and was purged with argon for 15 minutes then chlorophosphite **8b** (0.27 g, 0.85 mmol) in CH_2Cl_2 (2 mL) was added. The reaction mixture was stirred at 0 °C for 1 hour, warmed to room temperature and stirred for 16 hours. The solution was concentrated *in vacuo* to afford a crude solid. The solid was purified by flash column chromatography on silica (pre-treated with a solution of 95:5 toluene:Et_3N) using 10:1 hexane:diethyl ether as eluent under N_2 to give phosphine-phosphoramidite ligand **2** as an orange solid (0.15 g, 0.21 mmol, 30%). mp 200-201 °C (hexane); $[\alpha]_D^{20}$ +136 (*c* 0.55, toluene); Elemental analysis found C, 70.76; H, 6.18; N, 2.05%. $C_{42}H_{43}FeNO_2P_2$ requires C, 70.89; H, 6.09; N, 1.97%; IR 2922, 1476, 1435, 1206, 1042, 905, 844, 814 785, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.73 (2H, m, Ar**H**), 7.45-7.41 (3H, m, Ar**H**), 7.07-7.16 (5H, m, Ar**H**), 6.93 (1H, s, Ar**H**), 6.89 (1H, s, Ar**H**), 6.81 (1H, s, Ar**H**), 6.68 (1H, s, Ar**H**), 5.02-5.14 (1H, m, NC**H**), 4.64 (1H, br s, C_5**H**$_3$), 4.38-4.40 (1H, m, C_5**H**$_3$), 4.32 (1H, dd, $^2J_{H\text{-}H}$ = 12.5, $^5J_{H\text{-}P}$ = 2.3 Hz, ArC**H**H), 4.03 (1H, br s, C_5**H**$_3$), 3.92 (5H, s, C_5**H**$_5$), 3.31 (1H, d, *J* = 12.6 Hz, ArCH**H**), 2.67 (3H, d, *J* = 6.7 Hz, NC**H**$_3$), 2.19-2.24 (9H, m, 3 x ArC**H**$_3$), 1.92 (3H, d, *J* = 6.9 Hz, NCHC**H**$_3$), 1.73 (3H, s, ArC**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2 (dd, *J* = 12.4 Hz, 3.9 Hz, **C**$_{Ar}$), 141.8 (**C**$_{Ar}$), 141.7 (**C**$_{Ar}$), 139.2 (d, *J* = 9.4 Hz, **C**$_{Ar}$), 135.9 (d, *J* = 22.4 Hz, 2 x **C**$_{Ar}$H), 135.8 (d, *J* = 1.9 Hz, **C**$_{Ar}$), 135.4 (d, *J* = 2.6 Hz, **C**$_{Ar}$), 133.0-133.1 (m, 2 x **C**$_{Ar}$), 132.1 (d, *J* = 15.8 Hz, 2 x **C**$_{Ar}$H), 131.2 (d, *J* = 3.1 Hz, **C**$_{Ar}$), 130.7 (d, *J* = 2.9 Hz, **C**$_{Ar}$), 129.8 (d, *J* = 0.4 Hz, **C**$_{Ar}$H), 129.6 (d, *J* = 0.7 Hz, **C**$_{Ar}$H), 129.4 (d, *J* = 1.0 Hz, **C**$_{Ar}$H), 128.2 (**C**$_{Ar}$H), 128.1 (**C**$_{Ar}$H), 127.8 (**C**$_{Ar}$H), 127.74 (**C**$_{Ar}$H), 127.72 (**C**$_{Ar}$H), 127.5 (d, *J* = 1.3 Hz, **C**$_{Ar}$H), 127.2 (**C**$_{Ar}$H), 97.2 (dd, *J* = 26.4, 11.8, Hz, **C**$_{Fc}$), 75.8 (d, *J* = 13.4 Hz, **C**$_{Fc}$), 71.9 (d, *J* = 5.0 Hz, **C**$_{Fc}$H) 70.6-70.7 (m, **C**$_{Fc}$H), 69.8 (5 x **C**$_{Fc}$H), 69.5 (**C**$_{Fc}$H), 51.2 (dd, *J* = 32.4, 7.7 Hz, N**C**H), 34.1 (**C**H$_2$), 26.2 (d, *J* = 2.0 Hz, N**C**H$_3$), 20.8 (d, *J* = 2.9 Hz, 2 x Ar**C**H$_3$), 19.6-19.7 (m, NCH**C**H$_3$), 18.0-18.1 (m, Ar**C**H$_3$), 16.8-16.9 (m, Ar**C**H$_3$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 139.1 (d, *J* = 14.6 Hz), –23.0 (d, *J* = 14.6 Hz); HRMS (ESI$^+$) $C_{42}H_{43}NO_2P_2FeNa$ $[M+Na]^+$: calc. 734.2016, found: 734.2031.

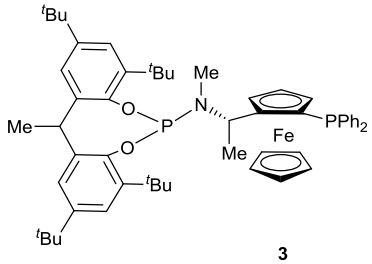
2,2'-Ethyldiene(4,6-di-*tert*-butyl-o-phenylene) (8c)



8c

2,2'-Ethylidene-bis(4,6-di-*tert*-butylphenol) (3.01 g, 6.86 mmol) was dissolved in toluene (40 mL) under N_2, and to this was added PCl_3 (0.90 mL, 10.29 mmol) and *N*-methylpyrrolidine (2.14 mL, 20.58 mmol). The reaction mixture was stirred at room temperature for 40 hours and was then filtered and the resulting filtrate concentrated *in vacuo* to give chlorophosphite **8c** as off-white solid (2.94 g, 5.74 mmol, 85%) that was extremely sensitive to moisture was characterised by NMR only in a diastereomeric ratio of ~4:1 ratio (A:B) by ^{1}H NMR.[ii] Species A: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (2H, d, *J* = 2.1 Hz, 2 x Ar**H**), 7.30 (2H, d, *J* = 2.0 Hz, 2 x Ar**H**), 4.97-5.03 (1H, m, ArC**H**CH_3); 1.68 (3H, d, *J* = 7.6 Hz, ArCHC**H**$_3$), 1.46 (18H, s, 2 x C(C**H**$_3$)$_3$), 1.36 (18H, s, 2 x C(C**H**$_3$)$_3$), ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0 (d, *J* =1.9 Hz, 2 x **C**$_{Ar}$), 146.3 (d, *J* = 9.4 Hz, 2 x **C**$_{Ar}$), 141.5 (d, *J* = 4.3 Hz, 2 x **C**$_{Ar}$), 140.4 (d, *J* = 4.3 Hz, 2 x **C**$_{Ar}$), 122.8 (2 x **C**$_{Ar}$H), 121.5 (d, *J* = 1.4 Hz, 2 x **C**$_{Ar}$H), 35.2 (2 x **C**(CH$_3$)$_3$), 35.0 (2 x **C**(CH$_3$)$_3$), 32.0 (Ar**C**HCH$_3$), 31.6 (2 x C(**C**H$_3$)$_3$), 30.80 (C(**C**H$_3$)$_3$) 30.76 (C(**C**H$_3$)$_3$), 20.1 (ArCH**C**H$_3$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 166.1; Species B: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (2H, d, *J* = 2.0 Hz, 2 x Ar**H**), 7.25 (2H, d, *J* = 2.2 Hz, 2 x Ar**H**), 4.78 (1H, m, ArC**H**CH_3); 1.64-1.71 (3H, m, ArCHC**H**$_3$), 1.45 (18H, s, 2 x C(C**H**$_3$)$_3$), 1.36 (18H, s, 2 x C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8 (2 x **C**$_{Ar}$), 147.1 (2 x **C**$_{Ar}$), 139.7-139.8 (m, 2 x **C**$_{Ar}$), 138.1 (d, *J* = 0.4 Hz, 2 x **C**$_{Ar}$), 122.7 (2 x **C**$_{Ar}$H), 122.2 (br s, 2 x **C**$_{Ar}$H), 35.4 (2 x **C**(CH$_3$)$_3$), 34.9 (2 x **C**(CH$_3$)$_3$), 31.7 (2 x C(**C**H$_3$)$_3$), 31.6 (2 x C(**C**H$_3$)$_3$), 20.6 (ArCH**C**H$_3$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 134.1 (br.s).

Ligand (3)



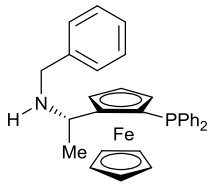
3

Amine **7** (0.30 g, 0.70 mmol) was dissolved in ethyl acetate (1.5 mL) and *N*-methylpyrrolidine (0.11 mL, 1.07 mmol) under argon. The solution was cooled to 0 °C and was purged with argon for 15 minutes then chlorophosphite **8c** (0.423 g, 0.85 mmol) in CH_2Cl_2 (2 mL) was added. The reaction mixture was stirred at 0 °C for 1 hour, then warmed to room temperature and stirred for 16 hours. The solution was concentrated *in vacuo* to afford a crude solid. The solid was purified by flash column chromatography on silica (pre-treated with a solution of 95:5 toluene:Et_3N) using 30:1 hexane:ethyl acetate as eluent under N_2 to give phosphine-phosphoramidite ligand **3** as an orange solid (0.28 g, 0.35 mmol, 44%). mp 238-240 °C (hexane); $[\alpha]_D^{20}$ +70 (*c* 0.55, toluene); Elemental analysis found C, 74.05; H, 7.66; N, 1.64%. $C_{55}H_{69}FeNO_2P_2$ requires C, 73.90; H, 7.78; N, 1.57%; IR 2959, 1215, 1200, 1130, 1105, 989, 850, 831, 806, 776 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.47-7.51 (2H, m, Ar**H**), 7.38-7.39 (5H, m, Ar**H**), 7.07-7.17 (7H, m, Ar**H**), 4.77-4.83 (1H, m, ArC**H**CH_3), 4.72 (1H, s, C_5**H**$_3$), 4.38-4.42 (1H, m, NC**H**), 4.26-4.27 (1H, m, C_5**H**$_3$), 4.18 (s, 5H, C_5**H**$_5$), 3.57 (1H, m, C_5**H**$_3$), 3.20 (3H, d, *J* = 7.7 Hz, NC**H**$_3$), 2.10 (3H, d, *J* = 6.8 Hz, NCHC**H**$_3$), 1.52 (3H, d, *J* = 7.1 Hz, ArCHC**H**$_3$), 1.28-1.34 (36H, m, 4 x C(C**H**$_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.5-147.7 (m, **C**$_{Ar}$) 145.67-145.70 (m, **C**$_{Ar}$), 140.3-140.6 (m, 4 x **C**$_{Ar}$), 137.6-137.9 (m, 4 x **C**$_{Ar}$), 134.9 (d, *J* = 21.3 Hz, 2

[ii] For some signals only the major species could be clearly identified due to overlap. One CH peak in the ^{13}C NMR for the minor species (B) could not be found.

x $\mathbf{C}_{Ar}$H), 132.8 (d, *J* = 18.7 Hz, 2 x $\mathbf{C}_{Ar}$H), 129.1 ($\mathbf{C}_{Ar}$H), 128.2-128.4 (m, 5 x $\mathbf{C}_{Ar}$H), 121.9 (d, *J* = 7.6 Hz, 2 x $\mathbf{C}_{Ar}$H), 120.8 (d, *J* = 7.6 Hz, 2 x $\mathbf{C}_{Ar}$H) 99.4-99.7 (m, $\mathbf{C}_{Fc}$), 77.4 (d, *J* = 10.2 Hz, $\mathbf{C}_{Fc}$), 72.7 (d, *J* = 3.6 Hz, $\mathbf{C}_{Fc}$H), 71.0 (d, *J* = 2.9 Hz, $\mathbf{C}_{Fc}$H), 69.5 (5 x $\mathbf{C}_{Fc}$H), 67.6 ($\mathbf{C}_{Fc}$H), 49.8 (N**C**H), 35.37 (**C**$(CH_3)_3$), 35.36 (**C**$(CH_3)_3$), 35.31 (**C**$(CH_3)_3$), 35.30 (**C**$(CH_3)_3$), 31.69 (C(**C**$H_3)_3$), 31.68 (C(**C**$H_3)_3$), 31.1-31.3 (m, 2 x C(**C**$H_3)_3$ and Ar**C**HCH_3), 28.1 (d, *J* = 10.6 Hz, N**C**H_3), 21.9-22.2 (m, NCH**C**H_3), 19.9 (ArCH**C**H_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 143.0, –20.2; HRMS (ESI^+) $C_{55}H_{69}NO_2P_2Fe$ $[M]^+$: calc. 893.4153, found: 893.4148.

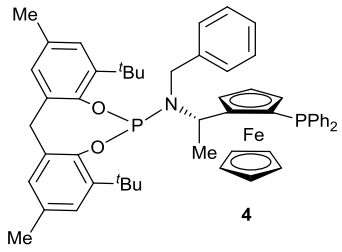
(*S*)-*N*-Benzyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine (4i)



4i

Isolated intermediate in the synthesis of ligand **4**: Amine **6** (1.00 g, 2.27 mmol) was added to flask with acetic anhydride (0.86 mL, 9.06 mmol) under argon. The reaction was heated to 90 °C, at which the solution became homogeneous, and held for 4 hours. Benzylamine (6.19 mL, 56.75 mmol) in *iso*-propanol (10 mL) was added. The reaction was stirred at 60 °C for 4 days. The reaction was cooled to room temperature and water was added (18 mL), which resulted in a precipitate. The reaction was stirred for 30 minutes, before being filtered and washed with water to afford a crude solid. The solid was purified by flash column chromatography on alumina using 4:1 hexanes:ethyl acetate as eluent to give amine intermediate as an orange solid (0.50 g, 0.99 mmol, 44%). mp 131-133 °C (hexane); $[\alpha]_D^{20}$ +266 (*c* 0.43, toluene); IR 2965, 1474, 1447, 1431, 1362, 1107, 1026, 999, 820, 800 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56-7.59 (2H, m, Ar**H**), 7.39-7.40 (3H, m, Ar**H**), 7.26-7.30 (2H, m, Ar**H**), 7.21-7.22 (3H, m, Ar**H**), 7.07-7.11 (3H, m, Ar**H**), 6.72-6.73 (2H, m, Ar**H**), 5.57 (1H, s, $C_5\mathbf{H}_3$), 4.32-4.33 (1H, m, $C_5\mathbf{H}_3$), 4.16-4.21 (1H, m, NC**H**), 4.05 (5H, s, $C_5\mathbf{H}_5$), 3.83 (1H, s, $C_5\mathbf{H}_3$), 3.52 (2H, m, NC$\mathbf{H}_2$), 1.59 (3H, d, *J* = 7.2 Hz, CC$\mathbf{H}_3$), 1.17 (1H, br s, N**H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0 (d, *J* = 9.1 Hz, $\mathbf{C}_{Ar}$) 139.4 ($\mathbf{C}_{Ar}$), 137.2 (d, *J* = 9.1 Hz, $\mathbf{C}_{Ar}$), 135.1 (d, *J* = 20.9 Hz, 2 x $\mathbf{C}_{Ar}$H), 132.6 (d, *J* = 18.7 Hz, 2 x $\mathbf{C}_{Ar}$H), 129.2 (d, *J* = 0.8 Hz, $\mathbf{C}_{Ar}$H), 128.6 ($\mathbf{C}_{Ar}$H), 128.5 ($\mathbf{C}_{Ar}$H), 128.4 ($\mathbf{C}_{Ar}$H), 128.2 ($\mathbf{C}_{Ar}$H), 128.12 ($\mathbf{C}_{Ar}$H), 128.09 (2 x $\mathbf{C}_{Ar}$H), 128.0 (2 x $\mathbf{C}_{Ar}$H), 126.4 ($\mathbf{C}_{Ar}$H), 97.8 (d, *J* = 23.9 Hz, $\mathbf{C}_{Fc}$), 75.0 (d, *J* = 7.2 Hz, $\mathbf{C}_{Fc}$), 71.3 (d, *J* = 4.6 Hz, $\mathbf{C}_{Fc}$H), 69.7 (5 x $\mathbf{C}_{Fc}$H), 69.5 (d, *J* = 3.7 Hz, $\mathbf{C}_{Fc}$ H), 69.2 ($\mathbf{C}_{Fc}$ H), 51.4 (d, *J* = 9.8 Hz, N**C**H), 41.4 (N$\mathbf{C}H_2$), 19.4 (NCH**C**H_3); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$,) δ –25.3; HRMS (NSI^+) $C_{31}H_{31}NFeP$ $[M+H]^+$: calc. 504.1538, found: 504.1528.

Ligand (4)

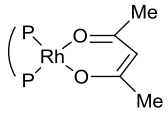


4

Isolated intermediate amine **4i** (0.12 g, 0.24 mmol) was dissolved in CH_2Cl_2 (3 mL) and triethylamine (0.07 mL, 0.49 mmol) under argon. The solution was cooled to 0 °C and PCl_3 (0.02 mL, 0.27 mmol) was added. The reaction was warmed to room temperature and stirred for 16 hours. The solution was concentrated *in vacuo*, then washed with CH_2Cl_2 and concentrated again *in vacuo*. The solid was dissolved in CH_2Cl_2 (3 mL) and triethylamine (0.07 mL, 0.485 mmol), and was cooled to 0 °C. 2,2'-methylenebis(6-tert-butyl-4-methylphenol) (0.08 g, 0.24 mmol) in CH_2Cl_2 (2 mL) was added. The reaction was warmed to room temperature and stirred for 16 hours. The solution was concentrated *in vacuo* to afford a crude

solid. The solid was purified by flash column chromatography on alumina using 30:1 hexane:ethyl acetate as eluent under N_2 to give phosphine-phosphoramidite ligand **4** as an orange solid (0.14 g, 0.16 mmol, 64%). mp 125-127 °C (hexane); $[\alpha]_D^{20}$ +110 (*c* 0.38, toluene); Elemental analysis found C, 74.28; H, 6.87; N, 1.71%. $C_{54}H_{59}FeNO_2P_2$ requires C, 74.39; H, 6.82; N, 1.61%; IR 2953, 2920, 1433, 1215, 1200, 1107, 1026, 1001, 864, 810 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (2H, d, *J* = 7.6 Hz, Ar**H**), 7.56-7.62 (2H, m, Ar**H**), 7.20-7.45 (8H, m, Ar**H**), 6.99-7.14 (m, 7H, Ar**H**), 4.82-4.92 (m, 2H, NC$\mathbf{H}_2$Ph), 4.82 (1H, s, $C_5\mathbf{H}_3$), 4.61-4.70 (1H, m, C**H**CH_3), 4.33-4.35 (1H, m, $C_5\mathbf{H}_3$), 4.11 (5H, s, $C_5\mathbf{H}_5$), 3.87 (1H, dd, $^2J_{H\text{-}H}$ = 12.3, $^5J_{H\text{-}P}$ = 2.1 Hz, ArC**H**H), 3.77 (1H, s, $C_5\mathbf{H}_3$), 2.99 (1H, d, *J* = 12.6 Hz, ArCH**H**), 2.31 (6H, s, 2 x Ar$C\mathbf{H}_3$), 2.27 (3H, d, *J* = 6.8 Hz, CC$\mathbf{H}_3$), 1.45 (9H, s, ArC($C\mathbf{H}_3)_3$), 1.32 (9H, s, ArC($C\mathbf{H}_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4-141.5 (m, 2 x $\mathbf{C}_{Ar}$), 140.0-140.1 (m, 2 x $\mathbf{C}_{Ar}$), 138.1-138.5 (m, 3 x $\mathbf{C}_{Ar}$), 136.99-137.02 (m, 3 x $\mathbf{C}_{Ar}$) 135.2 (d, *J* = 21.6 Hz, 2 x $\mathbf{C}_{Ar}$H), 132.8 ($\mathbf{C}_{Ar}$), 132.5 (d, *J* = 18.4 Hz, 2 x $\mathbf{C}_{Ar}$H), 130.0 (2 x $\mathbf{C}_{Ar}$H), 129.2 ($\mathbf{C}_{Ar}$H), 128.0-128.3 (m, 9 x $\mathbf{C}_{Ar}$H), 127.1 ($\mathbf{C}_{Ar}$H), 126.3 (d, *J* = 12.6 Hz, 2 x $\mathbf{C}_{Ar}$H), 101.1 (dd, *J* = 22.3, 2.6 Hz, $\mathbf{C}_{Fc}$), 73.5 (d, *J* = 11.0 Hz, $\mathbf{C}_{Fc}$), 72.1 (d, *J* = 3.3 Hz, $\mathbf{C}_{Fc}$H), 70.7 (d, *J* = 3.3 Hz, $\mathbf{C}_{Fc}$H), 69.6 (5 x $\mathbf{C}_{Fc}$H), 68.2 ($\mathbf{C}_{Fc}$H), 49.9 (dd, *J* = 25.5, 4.7 Hz, N**C**H), 48.2 (d, *J* = 10.8 Hz, N$\mathbf{C}H_2$), 35.09 (d, *J* = 0.9 Hz, $\mathbf{C}(CH_3)_3$), 35.0 (d, *J* = 0.9 Hz, $\mathbf{C}(CH_3)_3$), 34.4-34.5 (m, Ar$\mathbf{C}H_2$), 31.4-31.6 (m, 2 x C($\mathbf{C}H_3)_3$), 25.1-25.3 (m, NCH$\mathbf{C}H_3$), 21.1 (d, *J* = 2.3 Hz, 2 x Ar$\mathbf{C}H_3$); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 143.2, –22.6; HRMS (EI^+) $C_{54}H_{59}FeNO_2P_2$ $[M]^+$: calc. 871.3370, found: 871.3366.

3. Synthesis of Complex



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[Rh(acac)$(CO)_2$] (0.016 g, 0.062 mmol) and ligand **1** (0.050 g, 0.062 mmol) were dissolved in toluene (4 mL) under argon, and were stirred at room temperature for 2 hours. The solution was concentrated *in vacuo*, and dissolved in minimal hexane. Product precipitated from hexane at 0 °C to give complex **15** as an orange solid (0.059 g, 0.058 mmol, 94%). mp 178-180 °C_{dec} (hexane); $[\alpha]_D^{20}$ +49 (*c* 0.28, $CHCl_3$); IR 2959, 1581, 1514, 1432, 1400, 1215, 1108, 1044, 890, 852 cm^{-1}; ^1H NMR (300 MHz, C_7D_8) δ 8.31-8.39 (1H, m, ArC$\mathbf{H}_2$), 7.91-8.02 (4H, m, Ar**H**), 7.79-7.84 (1H, m, NC**H**), 6.68-7.17 (9H, m, Ar**H**), 6.45 (1H, s, Ar**H**), 5.24 (1H, s, OCH(CH_3)C**H**), 4.30 (1H, s, $C_5\mathbf{H}_3$), 4.00-4.09 (2H, m, 1H $C_5\mathbf{H}_3$ + 1H ArC**H**H), 3.48 (5H, s, $C_5\mathbf{H}_5$), 3.10 (1H, d, *J* = 14.9 Hz, ArCH**H**), 2.85 (3H, d, *J* = 7.3 Hz, NC$\mathbf{H}_3$), 2.20 (3H, s, Ar$C\mathbf{H}_3$), 1.88 (3H, s, Ar$C\mathbf{H}_3$), 1.67 (3H, s, OCHC$\mathbf{H}_3$), 1.60 (3H, d, *J* = 7.2 Hz, CC$\mathbf{H}_3$), 1.54 (9H, s, C($C\mathbf{H}_3)_3$), 1.32 (3H, s, OCC$\mathbf{H}_3$), 1.19 (9H, s, C($C\mathbf{H}_3)_3$); ^{13}C NMR (75 MHz, C_7D_8)[iii] δ 202.7 (RhO**C**), 185.2 (RhO**C**), 184.3 ($\mathbf{C}_{Ar}$), 183.7 ($\mathbf{C}_{Ar}$), 153.3 ($\mathbf{C}_{Ar}$), 151.8 ($\mathbf{C}_{Ar}$), 135.9 (d, *J* = 11.5 Hz, 2 x $\mathbf{C}_{Ar}$H), 135.5 (d, *J* = 12.6 Hz, 2 x $\mathbf{C}_{Ar}$H), 132.3 ($\mathbf{C}_{Ar}$H), 130.6 ($\mathbf{C}_{Ar}$H), 130.5 ($\mathbf{C}_{Ar}$), 130.2 (2 x $\mathbf{C}_{Ar}$), 129.6 (2 x $\mathbf{C}_{Ar}$), 129.4 (2 x $\mathbf{C}_{Ar}$H), 126.7 ($\mathbf{C}_{Ar}$H) 127.2 ($\mathbf{C}_{Ar}$H), 126.9 ($\mathbf{C}_{Ar}$H), 126.5 ($\mathbf{C}_{Ar}$H), 126.5 ($\mathbf{C}_{Ar}$H), 125.80 ($\mathbf{C}_{Ar}$H) 125.78 ($\mathbf{C}_{Ar}$), 100.3 (OC**C**H), 96.8 (d, *J* = 17.5 Hz, $\mathbf{C}_{Fc}$), 72.5 ($\mathbf{C}_{Fc}$H), 70.5 (5 x $\mathbf{C}_{Fc}$H), 70.3 ($\mathbf{C}_{Fc}$), 68.4 (d, *J* = 5.9 Hz, $\mathbf{C}_{Fc}$H), 66.7 ($\mathbf{C}_{Fc}$H), 50.9 (d, *J* = 4.5 Hz, N**C**H), 42.7 ($\mathbf{C}H_2$), 35.8 ($\mathbf{C}(CH_3)_3$), 34.8 ($\mathbf{C}(CH_3)_3$), 33.0 (C($\mathbf{C}H_3)_3$), 30.6 (C($\mathbf{C}H_3)_3$), 29.6 (d, *J* = 6.0 Hz, N$\mathbf{C}H_3$), 27.2 (d, *J* = 8.2 Hz, Ar$\mathbf{C}H_3$), 25.7 (d, *J* = 5.1 Hz, Ar$\mathbf{C}H_3$), 20.5 (RhOC$\mathbf{C}H_3$), 20.1 (RhOC$\mathbf{C}H_3$), 18.7 (d, *J* = 13.5 Hz, NCH$\mathbf{C}H_3$); $^{31}P\{^1H\}$ NMR

[iii] Due to large toluene-d_8 peaks, some complex peaks (e.g. 202.7 ppm) could not be identified in ^{13}C NMR, and could only be identified using GHSCQ and GHMBC; therefore multiplicity of these signals could not be determined.

(121 MHz, C_7D_8) δ 134.6 (dd, *J* = 81.2, 289.6 Hz), 33.9 (dd, *J* = 80.1, 187.5 Hz); HRMS (ESI^+) $C_{53}H_{61}O_4NFeP_2Rh$ $[M-H]^+$: calc. 996.2476, found: 996.2468.

4. General Procedures - Catalysis

4.1 Hydroformylation of propene

Ligand (6.40 µmol (Rh:L 1:1.25)) was added to a schlenk tube, which was then purged with nitrogen (or argon). [Rh(acac)$(CO)_2$] (5.12 µmol) was added in a toluene stock solution (2 mg/mL). Toluene was then added to make up to 20 mL total volume (though a different solvent was used at this stage during solvent screen).Internal standard 1-methylnaphthalene (0.2 mL) was added. The solution was transferred via syringe to the pressure vessel (which had been purged with CO/H_2) through the injection port. CO/H_2(1:1) (20 bar) was added and the heating jacket set to 90 °C while stirring. Once the temperature reached 90 °C, the reaction was stirred for 1 hour to fully activate the catalyst. Then pressure was then slowly released and replaced with propene/CO/H_2 (20 bar). The reaction was then run for 1 hour. After this time, stirring was stopped and pressure vessel was cooled using a basin of cold water. The pressure was released and the crude sample was analysed immediately by GC (in CH_2Cl_2).

The GC method was run on a DB-5 Agilent column; with length 30 m, diameter 0.250 mm and film 0.25µm. The oven was initially held at 25 °C for 6 minutes, then increased to 60 °C at a rate of 10 °C per minute, the ramp was then increased to 20 °C per minute until the temperature reached 300°C. The products could be identified with the following retention times; *iso*-butanal (1.99 min); *n*-butanal (2.20 min) and 1-methylnaphthalene (15.08 min). The GC was calibrated for propene and 1-octene hydroformylation using (1-methylnaphthalene) as an internal standard. Both the linear (butanal) and branched (*iso*-butanal) products were calibrated against the internal standard and against each other.

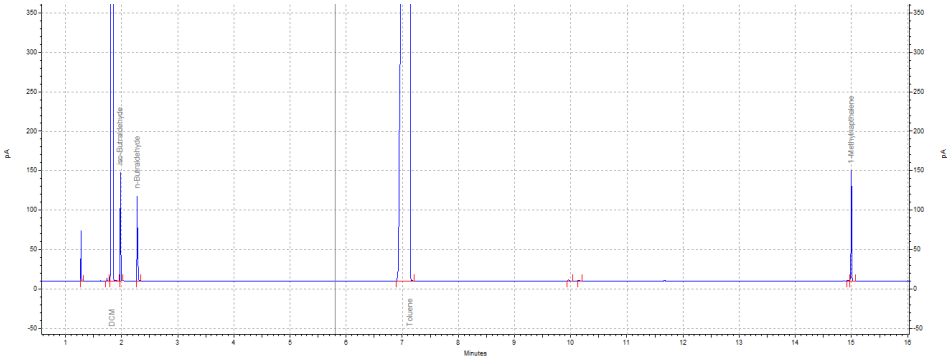


Figure 1: GC spectra of propene hydroformylation

4.2 Hydroformylation of 1-octene

Ligand (0.013 mmol (Rh:L 1:1.25)) was added to a schlenk tube, which was then purged with nitrogen (or argon). [Rh(acac)$(CO)_2$] (0.010 mmol) was added in a toluene stock solution (2 mg/mL). Toluene was then added to make up to 20 ml total volume (though a different solvent was used at this stage during solvent screen). Internal standard 1-methylnaphthalene (0.2 mL) was added. The solution was transferred via syringe to the pressure vessel (which had been purged with CO/H_2) through the injection port. CO/H_2 was (20 bar) was added and the heating jacket set to 90 °C while stirring. Once the temperature reached 90 °C, the reaction was stirred for 1 hour to fully activate the catalyst. Then pressure was then slowly released and 1-octene (16 mmol) was added and CO/H_2 (20 bar). The reaction was then run for

desired time before stirring was stopped and pressure vessel was cooled using a basin of cold water. The pressure was released and the crude sample was analysed immediately by GC (in CH_2Cl_2).

The GC analysis was ran on a DB-5 Aglient column; with length 30 m, diameter 0.250 mm and film 0.25µm. The oven was initially held at 25 °C for 6 minutes, then increased to 60 °C at a rate of 10 °C per minute, the ramp was then increased to 20 °C per minute until the temperature reached 300°C. 3-octene and octane were found to have the same retention time; and some alkenes observed two peaks due to *E*- and *Z*-alkenes. Identities were confirmed by either comparison with purchased pure sample or analysis of reaction mixture by GCMS. The reaction components could be identified with the following retention times; 1-octene (8.04 min), 4-octene (8.23 min), 3-octene and octane (8.34 min), 2-octene (8.56 min and 8.79 min), 2-propyl hexanal (12.69 min), 2-ethyl heptanal (12.78 min), 2-methyl octanal (12.87 min), nonanal (13.27 min) and 1-methylnaphthalene (15.02 min).

Only the linear product (nonanal) was calibrated against the internal standard. It was assumed that the branched product (2-methyl octanal) as well as branched products arising from internal alkenes (2-ethyl heptanal and 2-propyl hexanal) would have the same response factor in the GC. 1-octene was also calibrated against the internal standard, and it was assumed that all isomers of the substrate would also have a similar response by GC. Unfortunately the complex mixture of aldehydes could not be individually isolated, nor separated cleanly by chiral methods therefore the resultant enantioselectivity of the *iso*-product was not determined.

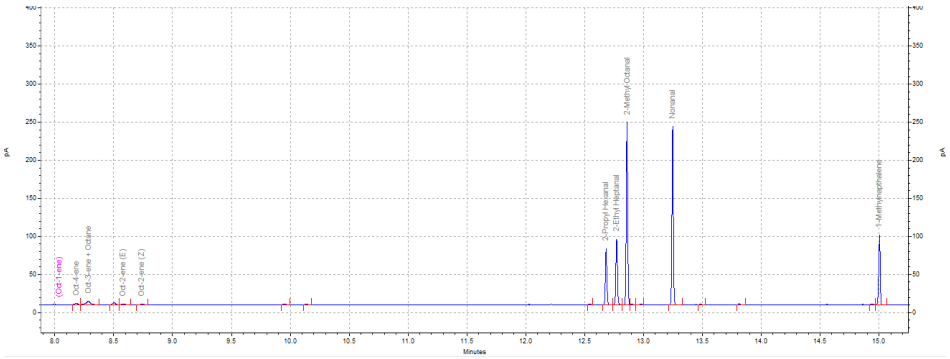


Figure 2: GC spectra of 1-octene hydroformylation (toluene and dichloromethane at lower retention times are not shown)

4.3 Kinetics of 1-octene hydroformylation

The gas uptake of the hydroformylation of 1-octene was monitored at constant pressure. The reaction was allowed to continue until gas uptake ceased; assuming this was at or at least near full conversion, this was found to be ~4.8 bar. A pressure measurement was recorded every 99 seconds, but, the data was only to 1 decimal point. A calculation was then used (**Equation 1**) to convert gas uptake to "conversion to aldehydes" in order to plot a kinetics curve (**Figure 3**).

Loss of gas in burette over time = gas consumed by reaction
Mol fraction = gas consumed / total gas consumed
% conversion to aldehydes = mol fraction ×100

Equation 1: Calculation of conversion for kinetics

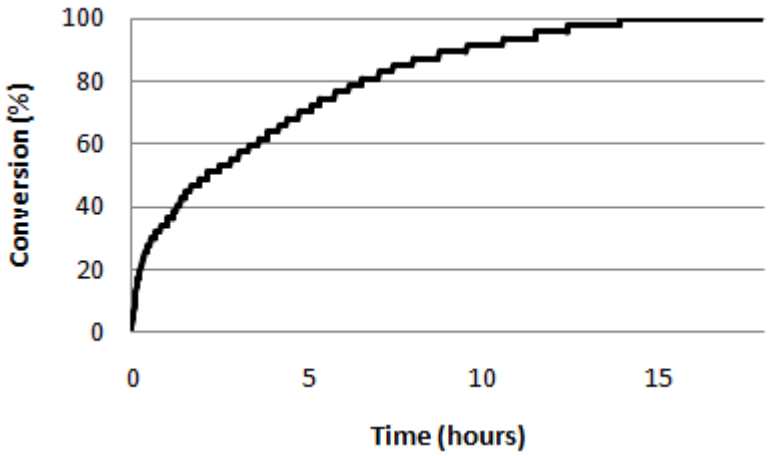


Figure 3: Kinetics curve for 1-octene hydroformylation with ligand **1**

Reaction performed in pressure vessel 2. [Rh(acac)$(CO)_2$] 0.010 mmol and ligand 0.013 mmol (Rh:L 1:1.25) stirred in toluene (20 mL) at 90 °C under CO/H_2 (20 bar) for 1 hour, prior to running reaction with 1-octene 16.00 mmol under CO/H_2 (20 bar). Products determined by GC using 1-methylnaphthalene as an internal standard.

The results could then be analysed further to establish that the reaction is first order. The natural log (alkene concentration) was calculated and plotted against time (**Figure 4**). This graph resulted in a straight line; therefore the reaction is first order with respect to substrate.

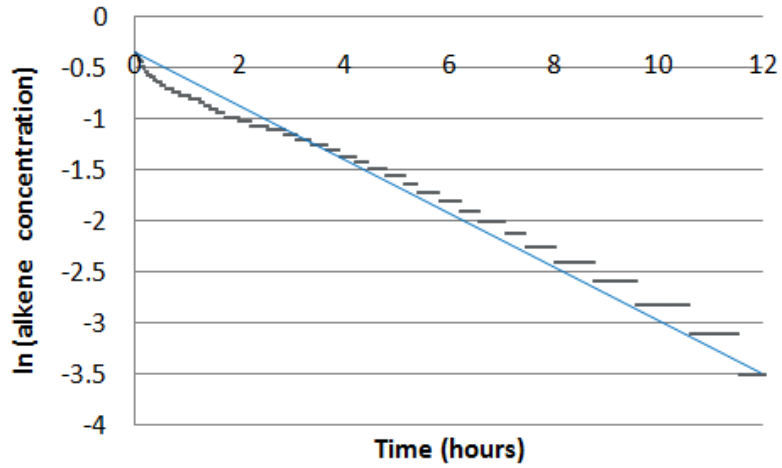


Figure 4: First order reaction for 1-octene hydroformylation with ligand **1**

4.4 Possibility of dehydroformylation

It was questioned whether the aldehyde products could be converted under the hydroformylation conditions. If this was the case; it could mean that although *iso*-butanal is being produced, it may be converted back through the reversible catalytic cycle to *n*-butanal. To test this theory, a 1-octene hydroformylation was performed with a sample of *iso*-butanal present in the reaction mixture. A one hour activation was carried out, before the addition of 1-octene and *iso*-butanal. The reaction was performed at 90 °C for 19 hours and analysed by GC (**Figure 5**). The majority of 1-octene had been converted to aldehydes, though some isomers of 1-octene were still present. *Iso*-butanal was still clearly visible and no *n*-butanal was observed. This suggests that conversion from *iso*-butanal to *n*-butanal is not occurring under the reaction conditions.

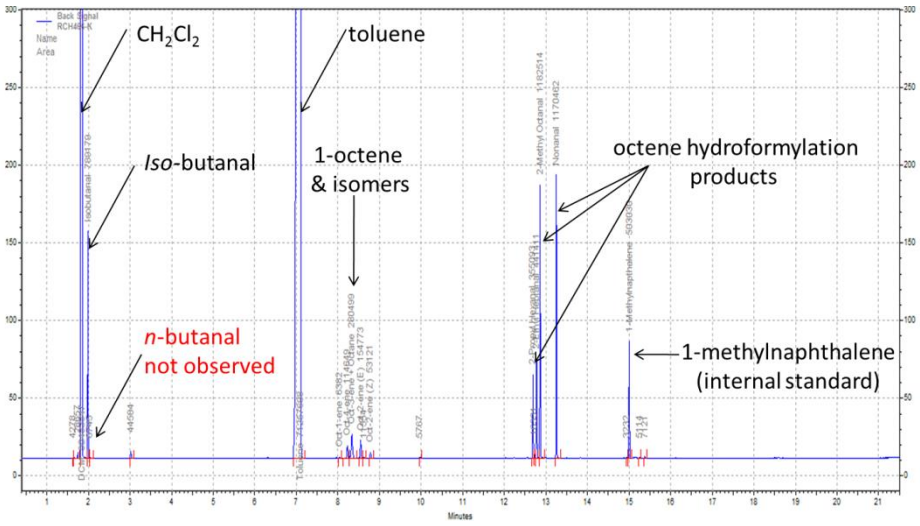


Figure 5: No dehydroformylation occurring

4.5 Asymmetric hydroformylation

Ligands **1**-**4** were tested in the hydroformylation of allyl cyanide and styrene. These ligands contain both planar chirality and a stereocentre. However, in all cases low enantioselectivity was obtained. The reactions were performed in a microwave vial (Biotage 10 mL glass microwave vials) inside a portable pressure vessel, which could hold 4 vials at one time.

General asymmetric procedure: Ligand (5.0 μmol (Rh:L 1:1.25)) was added to a microwave vial, which was then sealed with a cap and purged with nitrogen (or argon) through a needle. [Rh(acac)$(CO)_2$] (4.0 μmol) was added in a toluene stock solution (2 mg/mL). Toluene was then added to make up to 1.75 mL total volume. The vial was then transported to a portable pressure vessel which had been purged with CO/H_2. Two small needles were placed in the cap to allow transfer of gas into the vial. CO/H_2 was (20 bar) was added and the pressure vessel was placed in an oil bath, pre-set to 50 °C. The reaction was stirred for 1 hour to fully activate the catalyst. After this time, the pressure vessel was cooled by placing it in cold water. The pressure was released, and the vials removed from the pressure vessel while under a nitrogen atmosphere (via needle). Substrate (0.5 mmol) was then added with internal standard tetraethylsilane (0.02 mL). The reaction was stirred and a t_0 sample was taken for analysis by ^{1}H NMR. The vials were then placed back in the pressure vessel which was sealed and purged with CO/H_2. The pressure was then set to 10 bar CO/H_2, and the pressure vessel was again placed in the oil bath at 50 °C. The reaction was stirred at this temperature for 17 hours. The pressure vessel was then cooled, and pressure released. A sample of the reaction mixture was then analysed by ^{1}H NMR to determine conversion (using t_0) and regioselectivity. Analysis of enantioselectivity varied depending on substrate.

Determination of enantioselectivity for styrene: The toluene was then removed and the aldehydes dissolved in ethanol and excess $NaBH_4$ was added to reduce the aldehyde to alcohols. After workup, enantioselectivity could be analysed by chiral HPLC. The samples were ran on an AS-H column, using hexane:*iso*-propanol 95:5 and a flow rate of 0.5 mL/minute. The enantiomers of the branched product were

found to have retention times of 17.01 minutes and 18.35 minutes, while the linear product was observed at 19.66 minutes.

Determination of enantioselectivity for allyl cyanide: The enantiomeric excess was determined using the method developed by Chi *et. al.*[6] 0.1 ml reaction mixture was added to an NMR tube with ~0.5 mL $CDCl_3$. To this was added (*R*)-1-phenylpropan-1-amine (40 µL) to make the imine as diastereomers. The NMR tube was inverted a number of times to mix the reagents and was left to stand for ~15 minutes before being analysed by ^{1}H NMR. In the ^{1}H NMR spectra, the ratio of signals at δ 1.16 and 1.20 was used to determine the diastereomeric ratio.

Table 2: Hydroformylation of allyl cyanide

Entry	Ligand	Conversion %	iso %	ee %
1	1	34	76	16
2	2	93	77	< 5
3	3	52	78	< 5
4	4	91	77	13

[Rh(acac)$(CO)_2$] 4.0 µmol and ligand 5.0 µmol (Rh:L 1:1.25) stirred at 500 RPM in toluene (1.75 mL) at 50 °C under CO/H_2 (20 bar) for 1 hour, prior to running reaction with allyl cyanide (0.50 mmol) for 17 hours under CO/H_2 (10 bar). Conversion and B:L ratio determined by ^{1}H NMR using tetraethylsilane as an internal standard. Enantioselectivity determined by ^{1}H NMR after reaction with (R)-(+)-1-phenylpropylamine.

Table 3: Hydroformylation of styrene

Entry	Ligand	Conversion %	iso %	ee %
1	1	60	92	< 5
2	2	74	91	< 5
3	3	11	95	< 5
4	4	23	90	6

[Rh(acac)$(CO)_2$] 4.0 µmol and ligand 5.0 µmol (Rh:L 1:1.25) stirred at 500 RPM in toluene (1.75 mL) at 50 °C under CO/H_2 (20 bar) for 1 hour, prior to running reaction with styrene (0.50 mmol) for 17 hours under CO/H_2 (10 bar). Conversion and B:L ratio determined by ^{1}H NMR using tetraethylsilane as an internal standard. Enantioselectivity determined by HPLC.

5. General Procedures – Catalyst Characterisation

5.1 NMR

[Rh(acac)$(CO)_2$] (0.020 mmol) and ligand (0.020 mmol (Rh:L 1:1)) were added to a microwave vial (Biotage 10 mL glass microwave vials), which was then sealed with a cap and purged with nitrogen (or argon) through a needle. Toluene-d_8 (1 mL) was added to dissolve the compound. The microwave vial was then transported to a portable pressure vessel (which could hold 4 microwave vials) which had been purged with CO/H_2. Two small needles were placed in the cap to allow transfer of gas into the vial. CO/H_2 was (20 bar) was added and the pressure vessel was placed in an oil bath, pre-set to 90 °C. After stirring at 90 °C for 1 hour, the pressure vessel was cooled and pressure released. The reaction mixture was then transferred to an NMR tube under nitrogen *via* syringe and was analysed immediately and room temperature and low temperature (–70 °C).

In a separate reaction with ligand **3**, the reaction mixture was transferred *via* syringe to a high pressure NMR tube under CO/H_2 (1 bar). The NMR tube was then pressurised to 9 bar CO/H_2 and analysed immediately.

The ^{1}H NMR (hydride region) and ^{31}P{^{1}H}NMR was found to give better resolution at -70 °C compared to room temperature. In the ^{31}P{^{1}H}NMR only two peaks were fully resolved, while four peaks were at -70 °C. In the ^{1}H NMR one of the hydride peaks is a broad singlet at room temperature and an apparent triplet at –70 °C, **Figures 9** and **10** respectively).

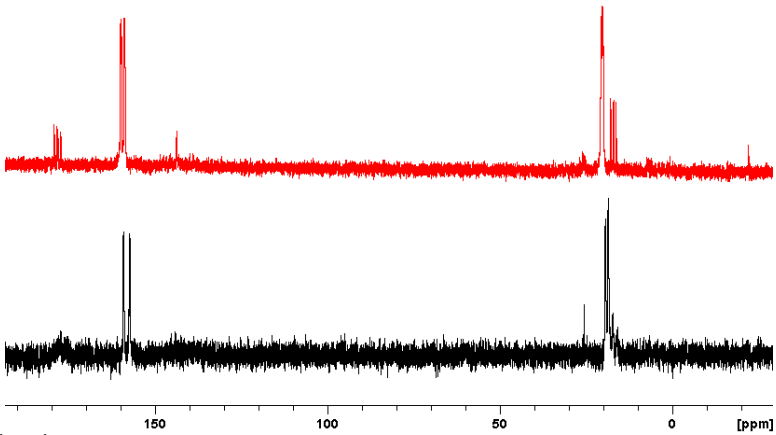


Figure 9: ^{31}P{^{1}H} NMR of catalyst with ligand **1** at 20 °C (black) and –70 °C (red)

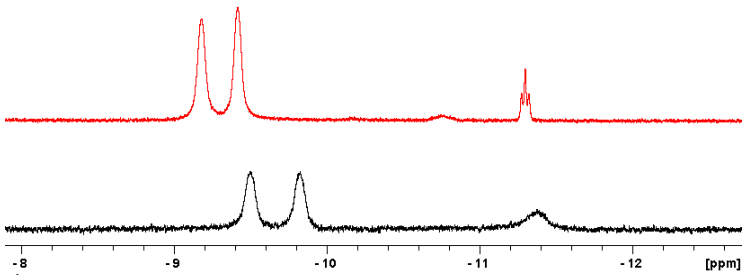


Figure 10: ^{1}H NMR of catalyst with ligand **1** at 20 °C (black) and –70 °C (red)

The 119 Hz coupling in the ^{1}H NMR major peak was confirmed to be from the hydride-phosphorus (as opposed to hydride-rhodium), as the doublet disappeared in the ^{1}H{^{31}P}NMR spectrum (**Figure 11**). The coupling from hydride to the other

phosphorus was too small to see and the hydride-rhodium coupling was also very small.

This was also confirmed in figure **12** by the phosphorus NMR. The $^{31}P\{^{1}H\}$ NMR (black) and ^{31}P NMR (red) spectra were compared for all peaks. In three of the signals these was no change in the spectra; however for the major phosphine, the peak shape changes due to large $^{2}J_{P\text{-}H}$ coupling.

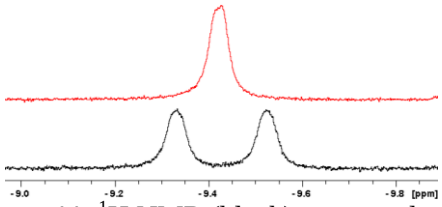


Figure 11: ^{1}H NMR (black) compared with $^{1}H\{^{31}P\}$NMR (red) of catalyst with ligand **1**

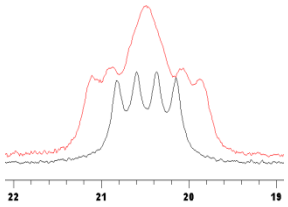


Figure 12: Signal of major phosphine species of catalyst with ligand **1** $^{31}P\{^{1}H\}$ NMR (black) and ^{31}P NMR (red)

5.2 HPIR

$[Rh(acac)(CO)_2]$ (0.06 mmol) and ligand (0.075 mmol (Rh:L 1:1.25)) was added to a schlenk tube, which was then purged with nitrogen (or argon). Hexane (30 mL) was added to dissolve rhodium and ligand. Reaction mixture was then transferred *via* syringe to the pressure vessel (which had been purged with CO/H_2) through the injection port. CO/H_2 (1:1, 20 bar) was added and the heating jacket set to 70 °C while stirring. Once the vessel reached 70 °C a spectrum was recorded, and then every 15 minutes for 90 minutes in total. A background spectrum of hexanes at 70 °C and under CO/H_2 (20 bar) was subtracted from the spectra for analysis. Spectra showing the carbonyl region of activated catalysts formed with ligands **1-4** are given in **Figures 13-24**.

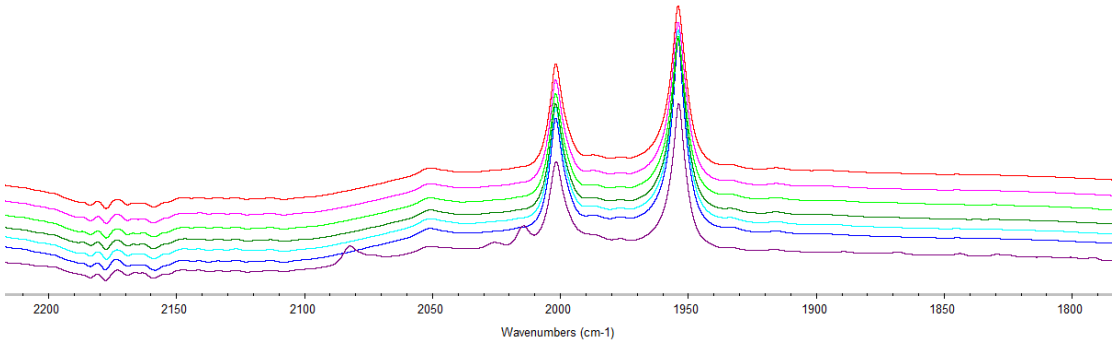


Figure 13: Staggered HPIR carbonyl region for catalyst with ligand **2** at 70 °C in hexane. Spectra recorded every 15 minutes, for 90 minutes. No unmodified catalyst detected. Colours in spectra: 0 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes, 90 minutes.

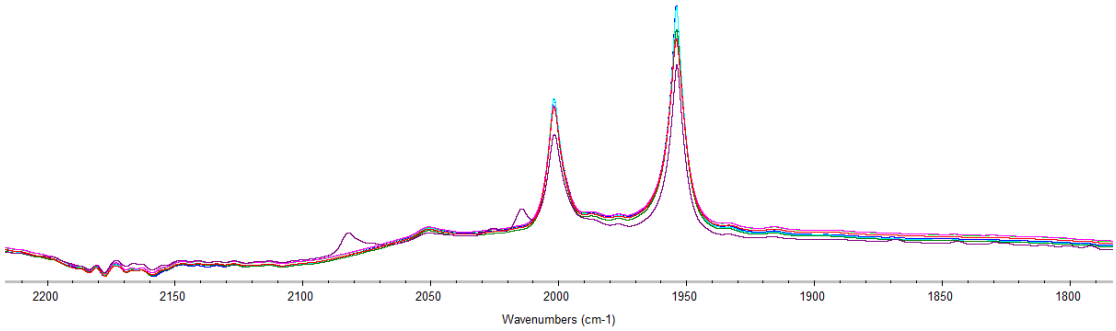


Figure 14: Overlaid HPIR carbonyl region for catalyst with ligand **2** at 70 °C in hexane. Spectra recorded every 15 minutes, for 90 minutes. No change in spectra over time. Colours in spectra: 0 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes, 90 minutes.

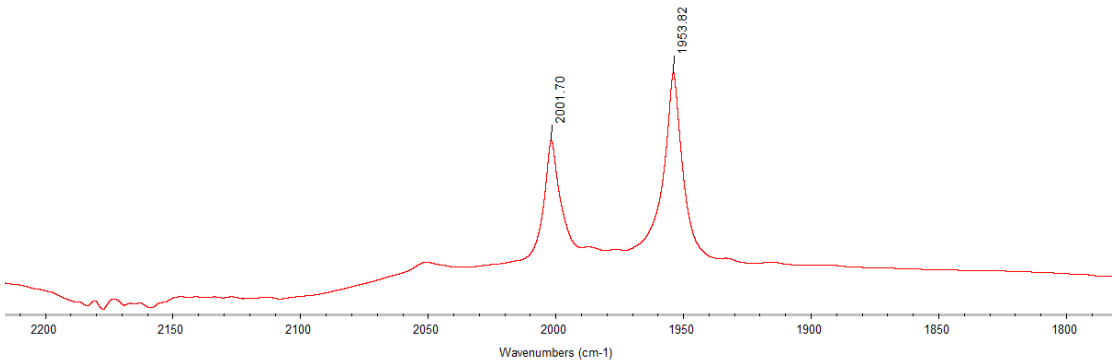


Figure 15: HPIR carbonyl region for catalyst with ligand **2** after 90 minutes
Only axial-equatorial by NMR

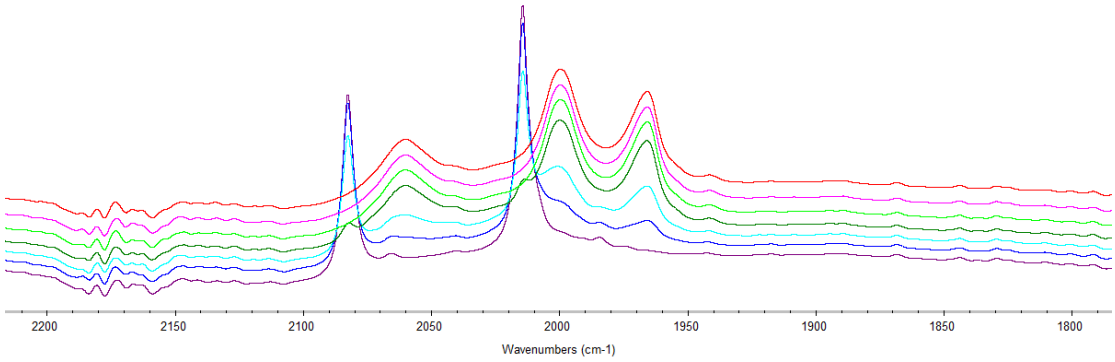


Figure 16: Staggered HPIR carbonyl region for catalyst with ligand **3** at 70 °C in hexane. Spectra recorded every 15 minutes, for 90 minutes. Unmodified catalyst detected at 0 minutes, 15 minutes, 30 minutes and 45 minutes. Colours in spectra: 0 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes, 90 minutes.

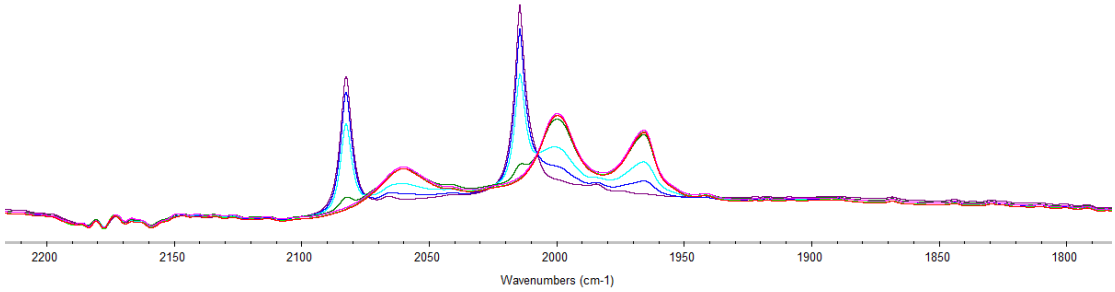


Figure 17: Overlaid HPIR carbonyl region for catalyst with ligand **3** at 70 °C in hexane. Spectra recorded every 15 minutes, for 90 minutes. Unmodified catalyst detected at 0 minutes, 15 minutes, 30 minutes and 45 minutes. Colours in spectra: 0 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes, 90 minutes.

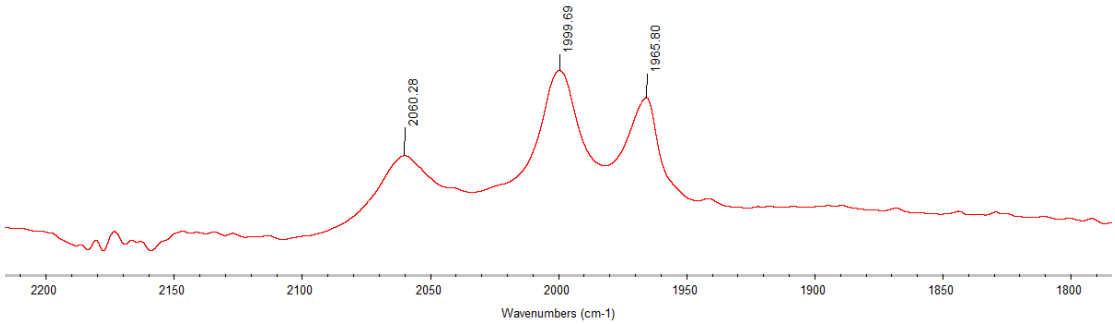


Figure 18: HPIR carbonyl region for catalyst with ligand **3** after 90 minutes
Only bis-equatorial by NMR

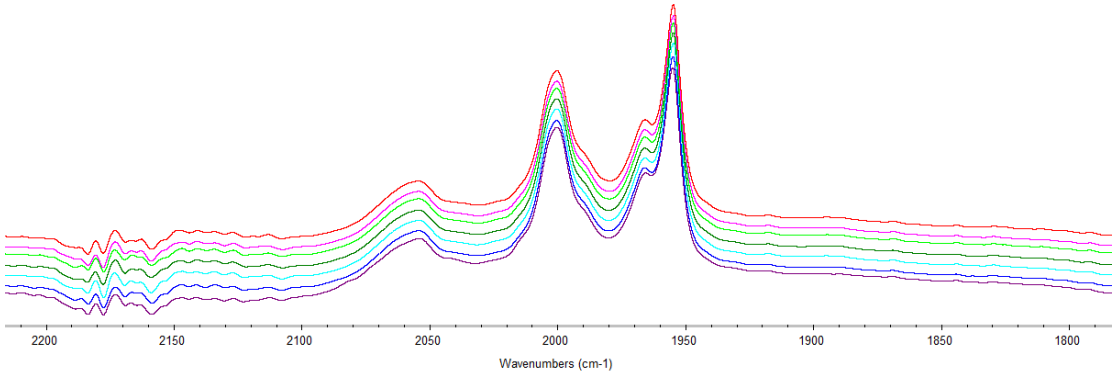


Figure 19: Staggered HPIR carbonyl region for catalyst with ligand **1** at 70 °C in hexane
Spectra recorded every 15 minutes, for 90 minutes. No unmodified catalyst detected. Colours in spectra: 0 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes, 90 minutes.

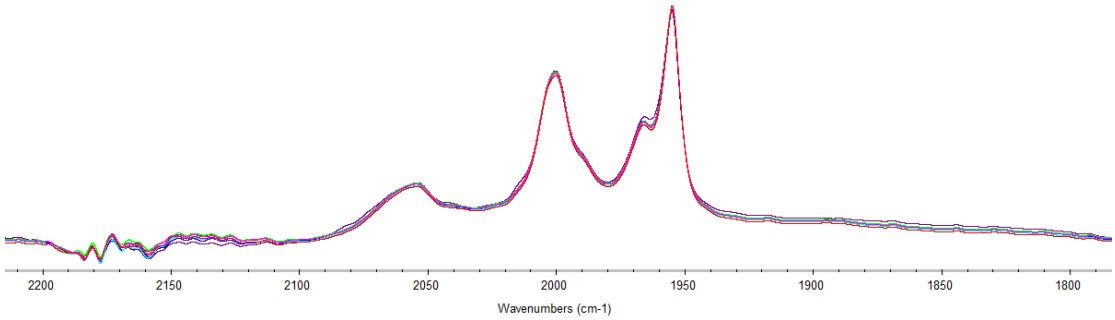


Figure 20: Overlaid HPIR carbonyl region for catalyst with ligand **1** at 70 °C in hexane. Spectra recorded every 15 minutes, for 90 minutes. No change in spectra over time. No unmodified catalyst detected. Colours in spectra: 0 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes, 90 minutes.

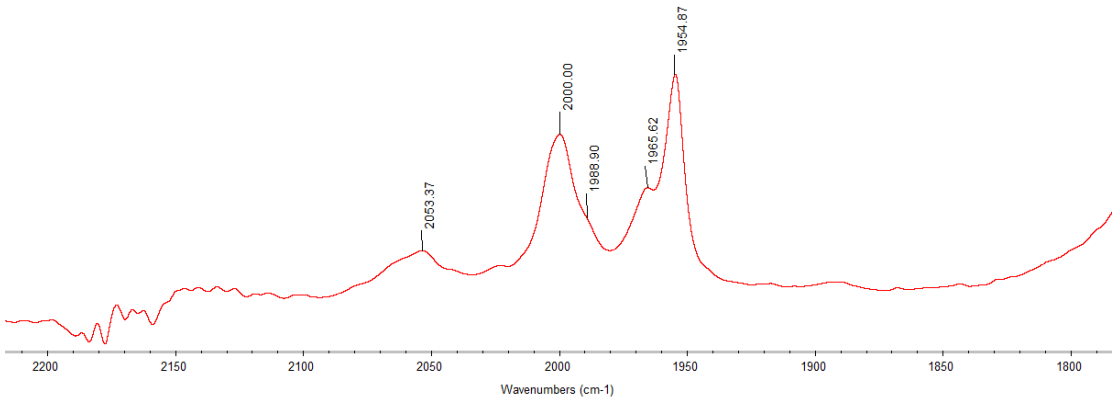


Figure 21: HPIR carbonyl region for catalyst with ligand **1** after 90 minutes
Mix of axial-equatorial and bis-equatorial ~9:1 by NMR

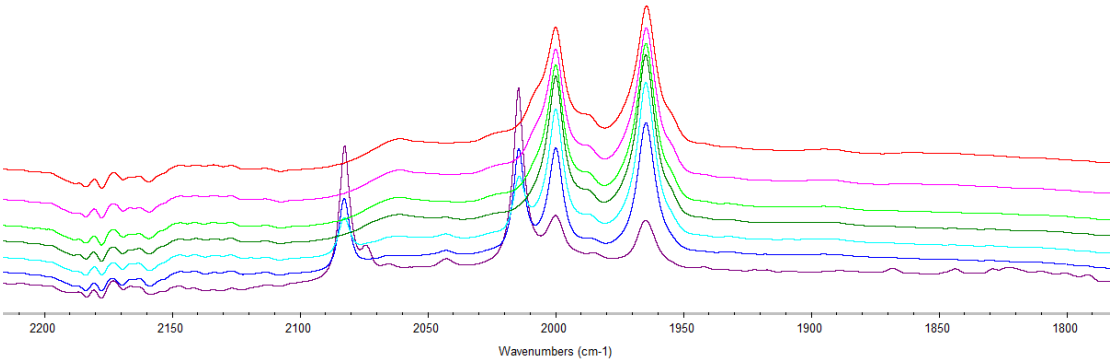


Figure 22: Staggered HPIR carbonyl region for catalyst with ligand **4** at 70 °C in hexane. Spectra recorded every 15 minutes, for 90 minutes. Unmodified catalyst detected at 0 minutes, 15 minutes and 30 minutes. Colours in spectra: 0 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes, 90 minutes.

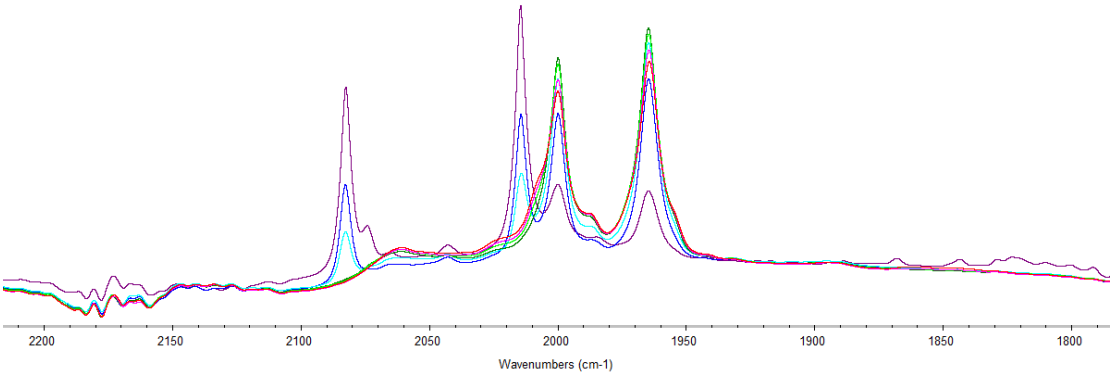


Figure 23: Overlaid HPIR carbonyl region for catalyst with ligand **4** at 70 °C in hexane. Spectra recorded every 15 minutes, for 90 minutes. Unmodified catalyst detected at 0 minutes, 15 minutes and 30 minutes. Colours in spectra: 0 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes, 90 minutes.

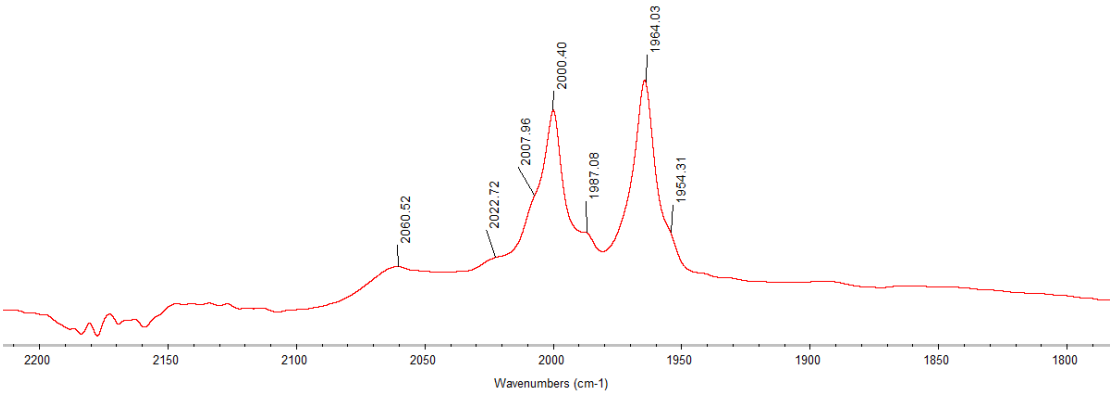


Figure 24: HPIR carbonyl region for catalyst with ligand **4** after 90 minutes
Mix of axial-equatorial and bis-equatorial ~1:3 by NMR

6. NMR Spectra of Ligands and Ligand Precursors

NMR spectra are provided for novel compounds, as well as through which have been synthesised before but not all NMR data was provided. All NMR spectra shown here was recorded under an inert atmosphere in dry and degassed solvent.

In the study of active catalysts (**Section 7**), no ^{13}C NMR was obtained and only the rhodium-hydride region of the ^{1}H NMR was studied.

Figure 25: ^{1}H NMR (400 MHz, $CDCl_3$) of **8a**

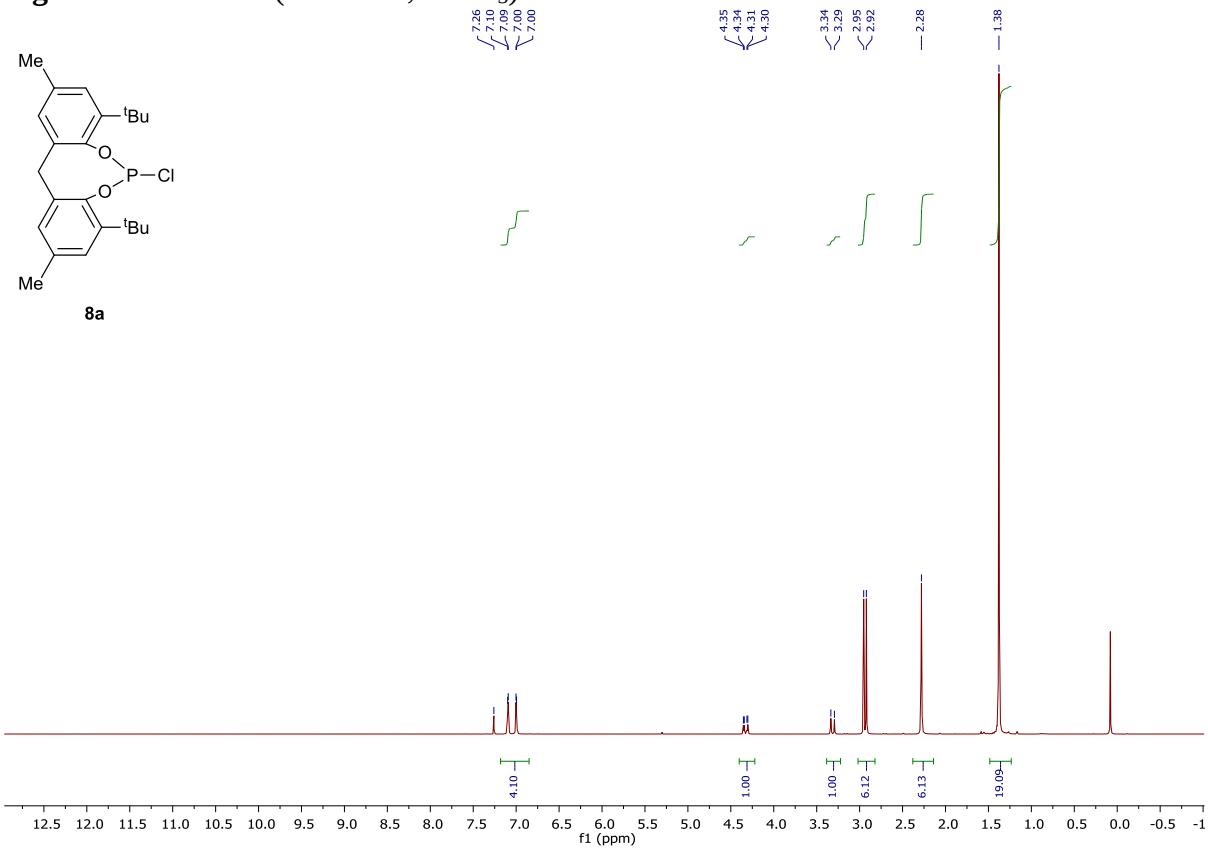


Figure 26: DEPTQ-135 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) of **8a**

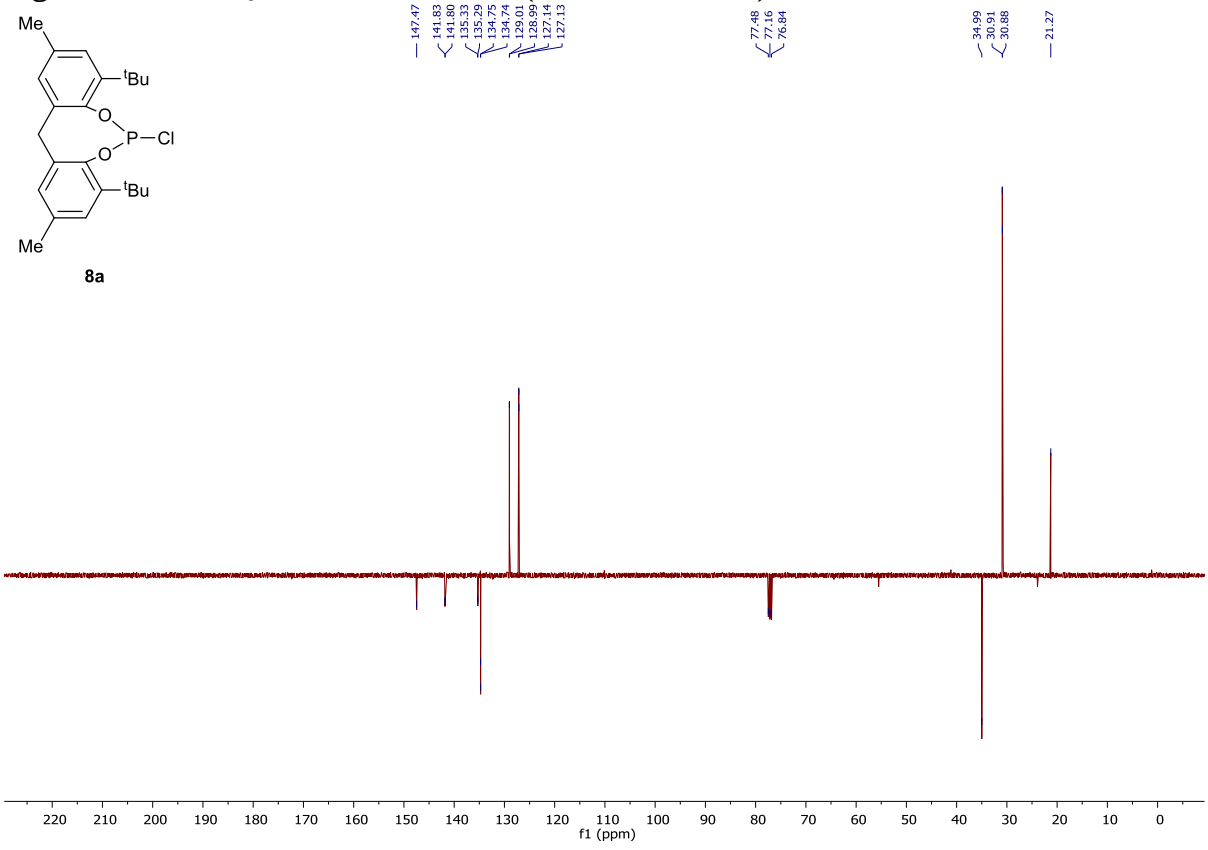
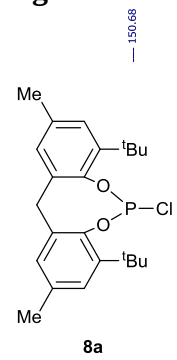
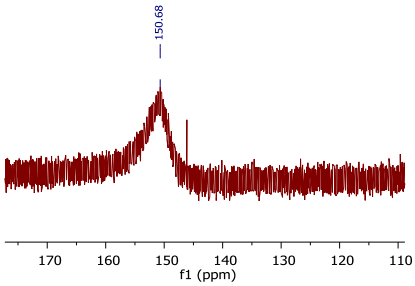


Figure 27: $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) of **8a**



8a



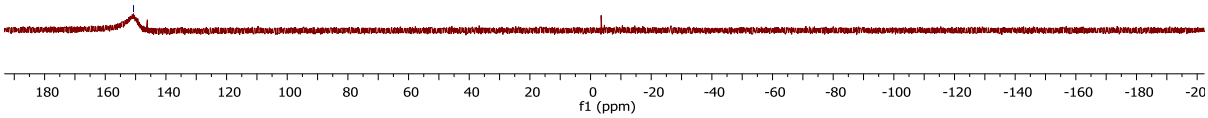


Figure 28: ^{1}H NMR (400 MHz, $CDCl_3$) of **1**

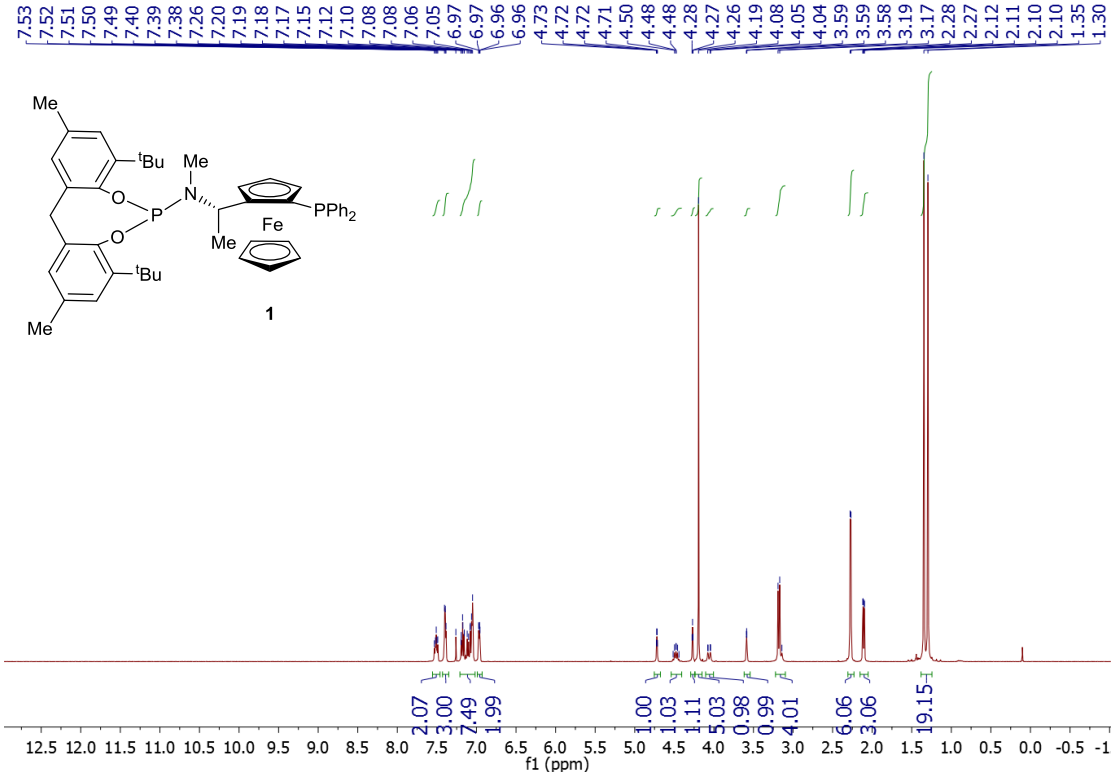


Figure 29: DEPTQ-135 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) of **1**

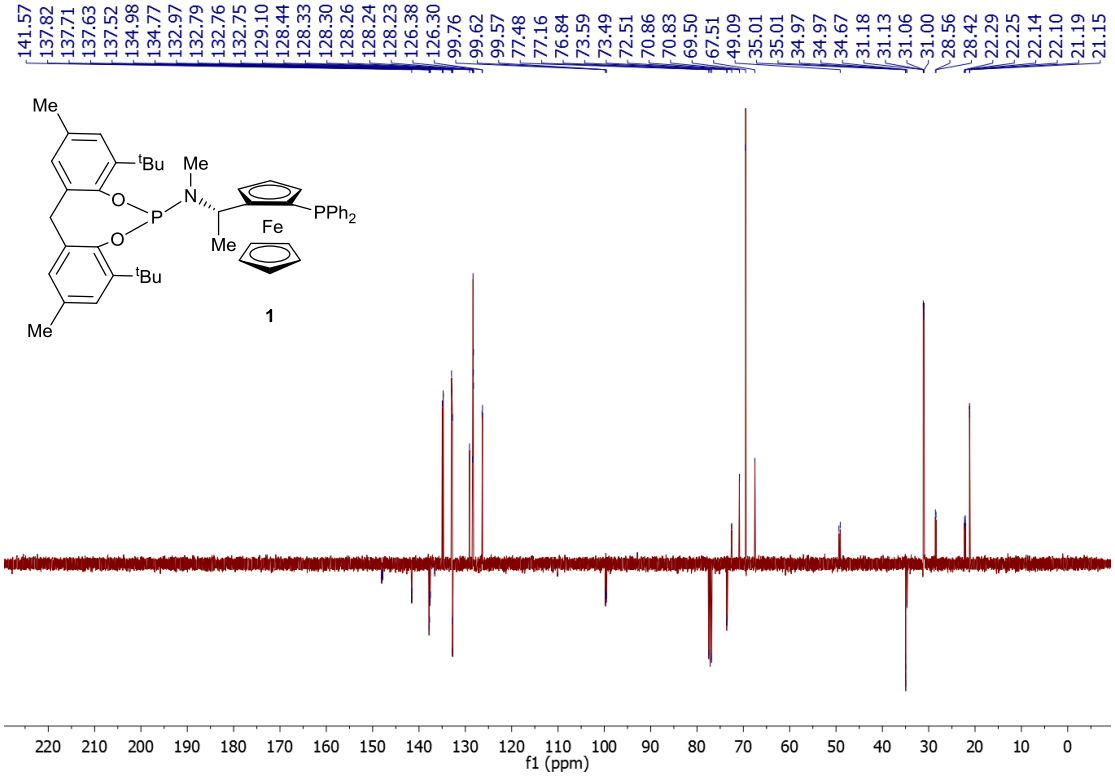


Figure 30: $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **1**

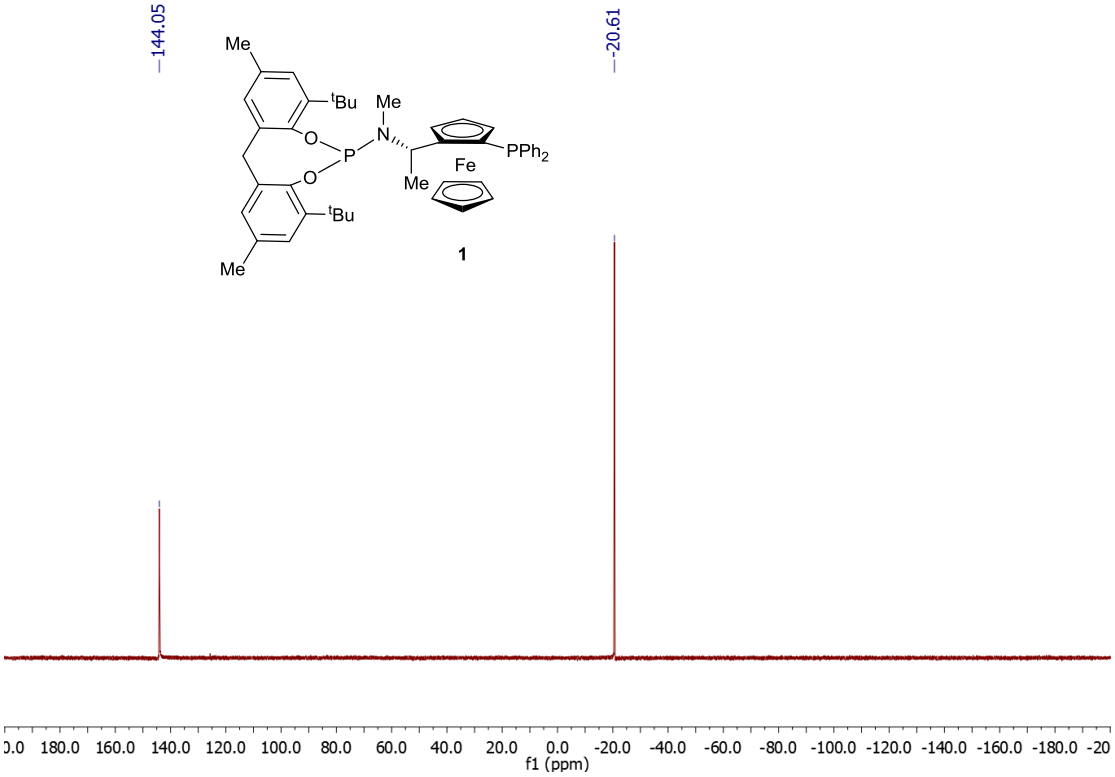


Figure 31: ^{1}H NMR (400 MHz, $CDCl_3$) of **8b**

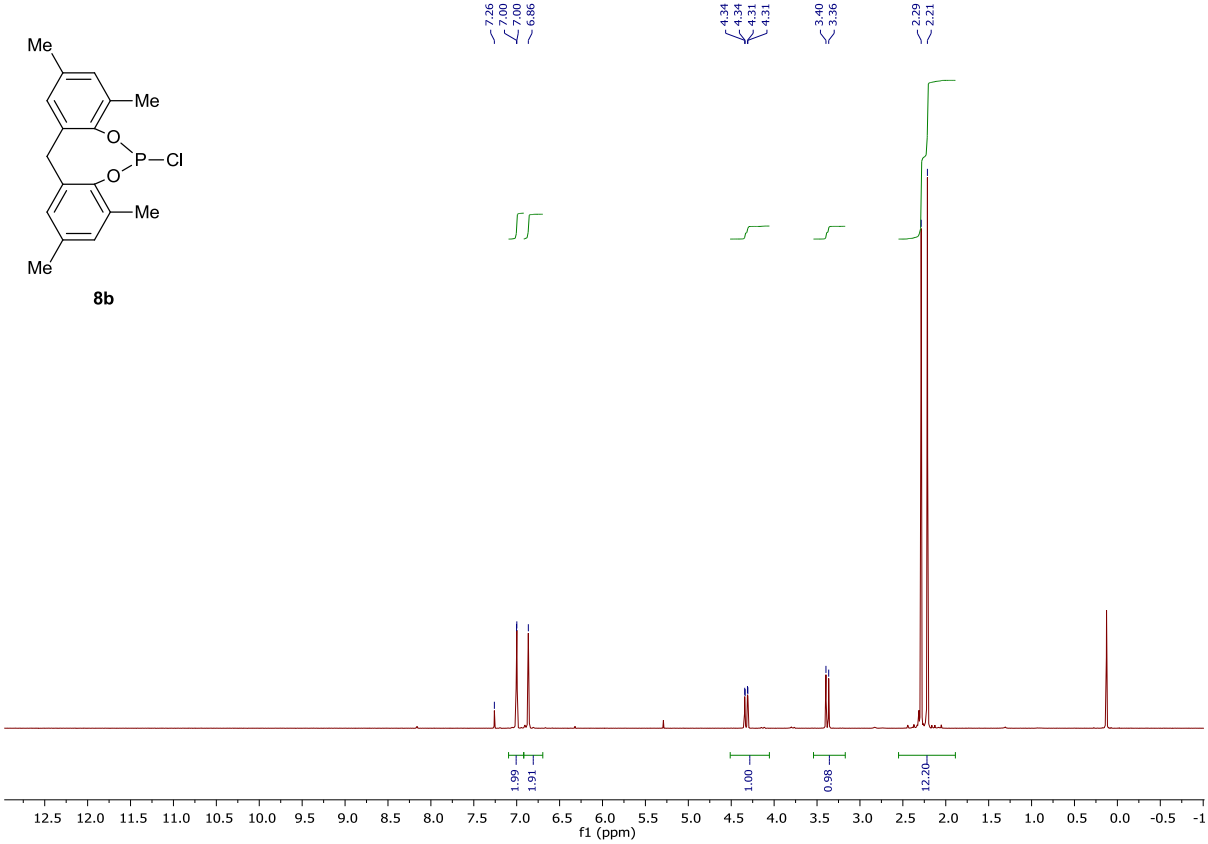


Figure 32: DEPTQ-135 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) of **8b**

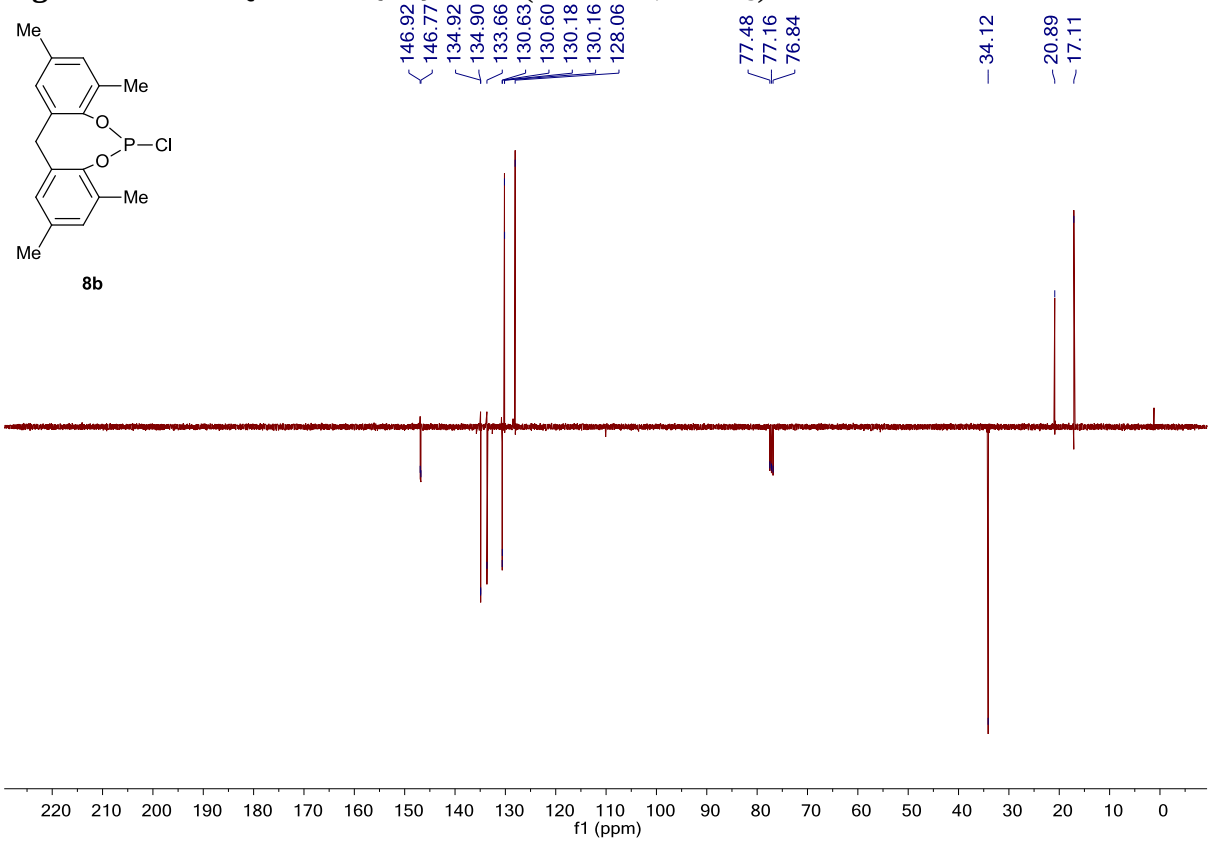


Figure 33: $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) of **8b**

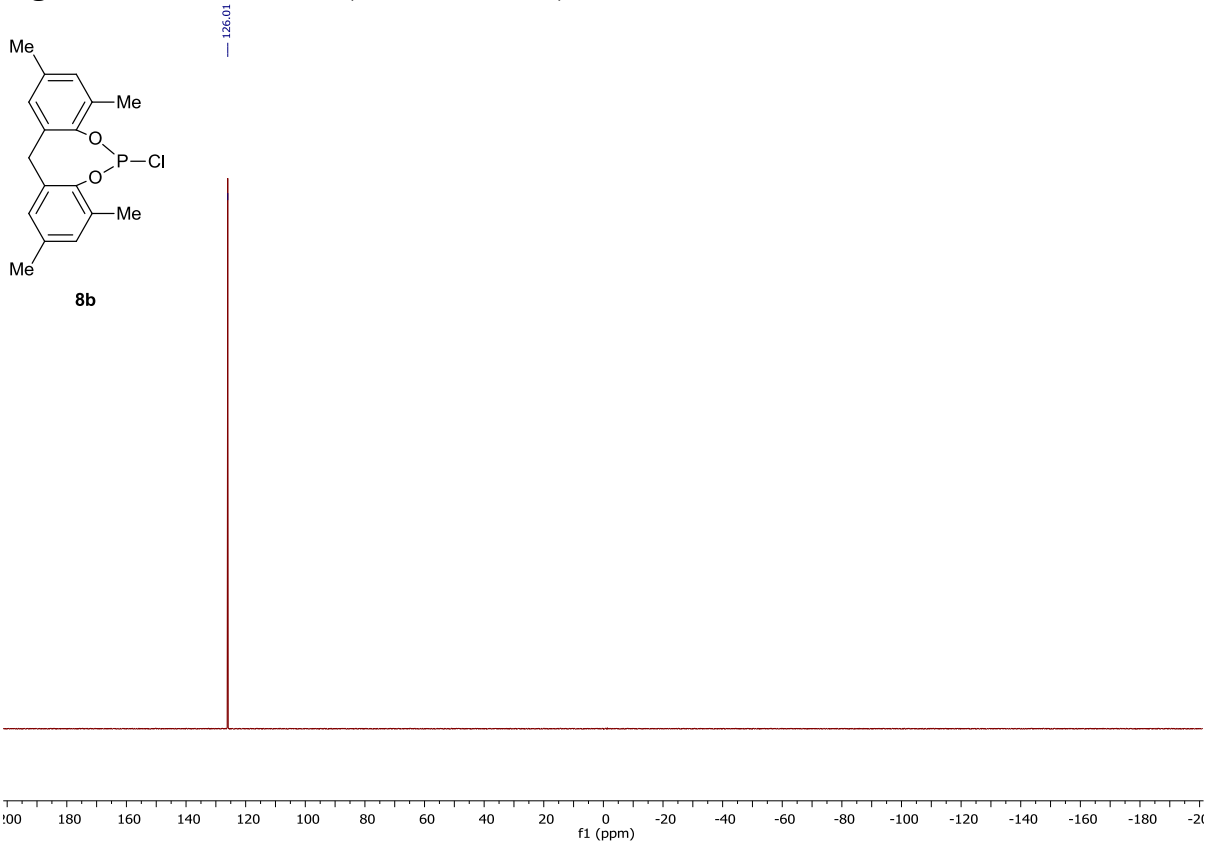


Figure 34: ^{1}H NMR (300 MHz, $CDCl_3$) of **2**
(trace grease and hexanes present below 1.5 ppm)

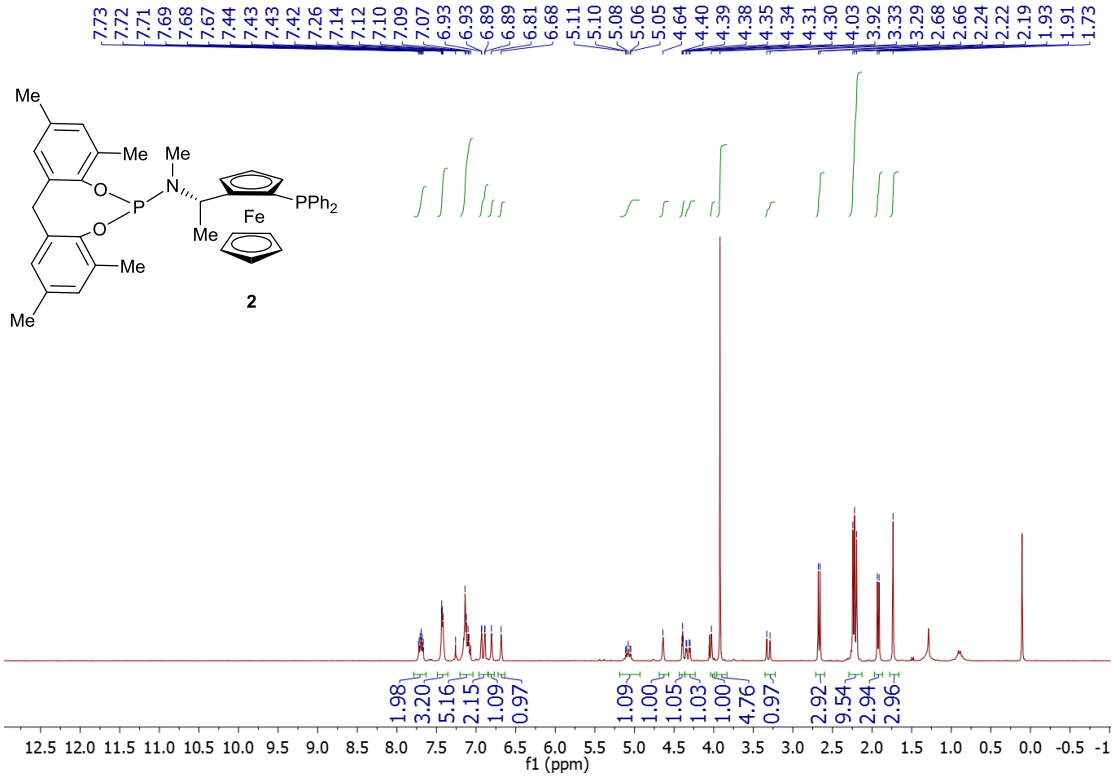


Figure 35: DEPTQ-135 ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of **2**

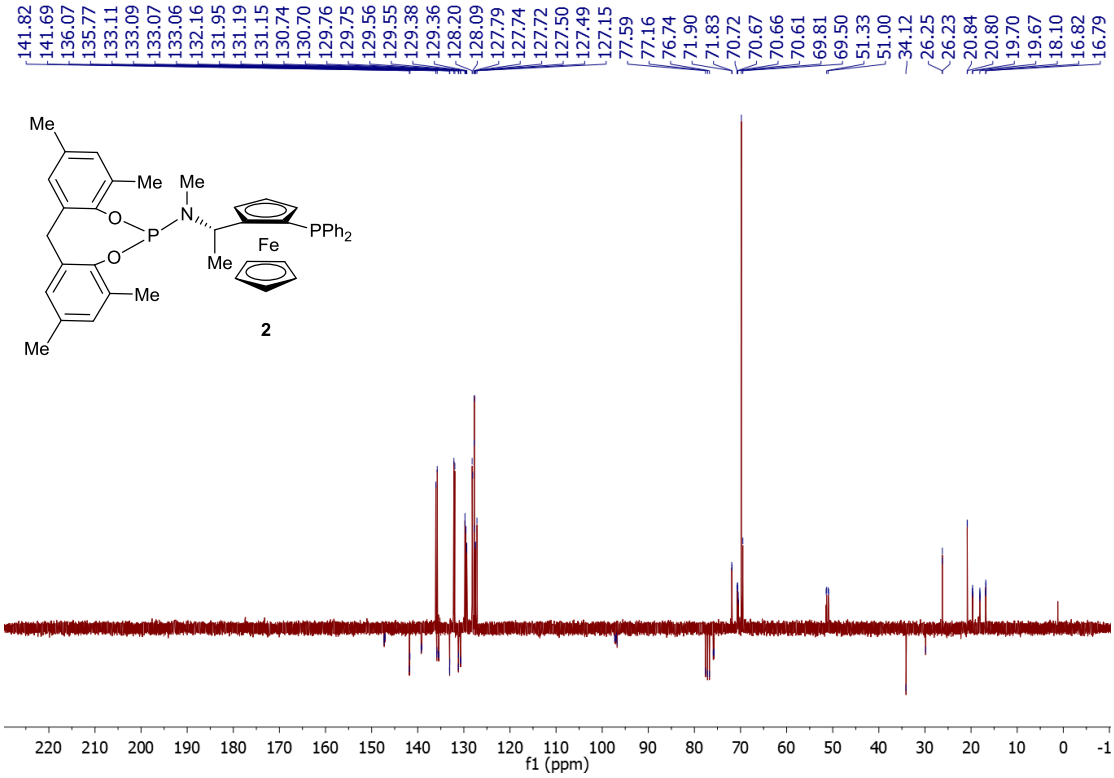


Figure 36: $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **2**

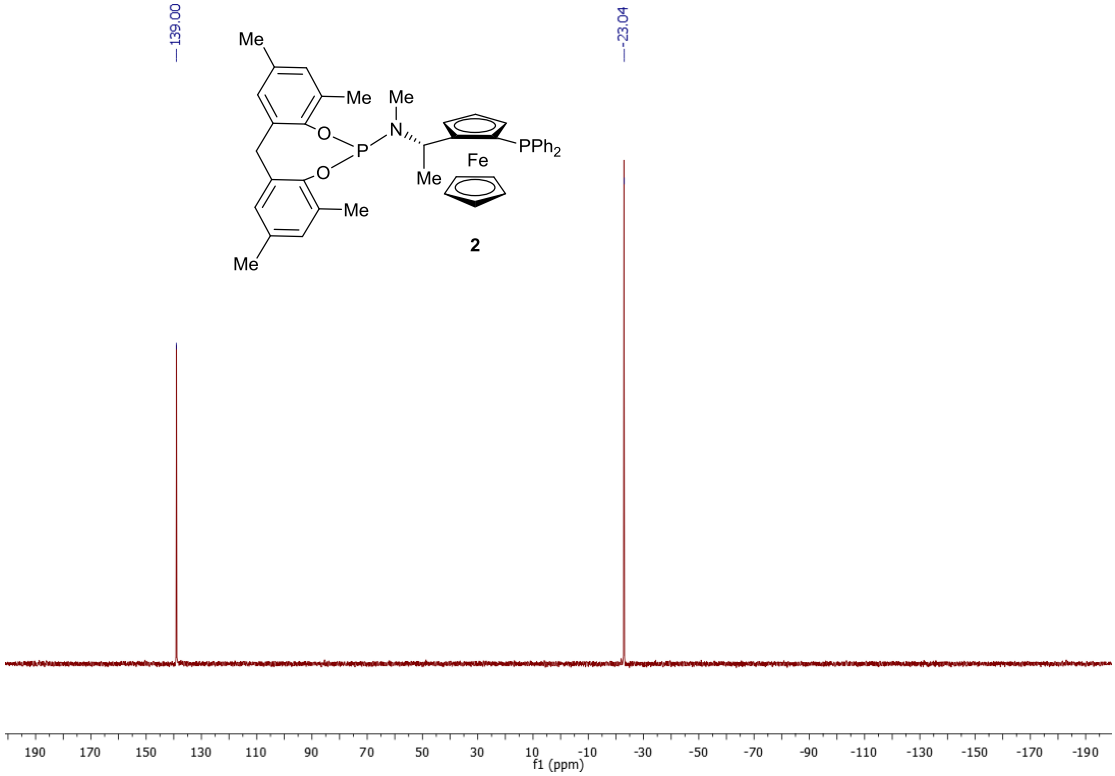


Figure 37: ^{1}H NMR (400 MHz, $CDCl_3$) of **8c** (2 species observed)

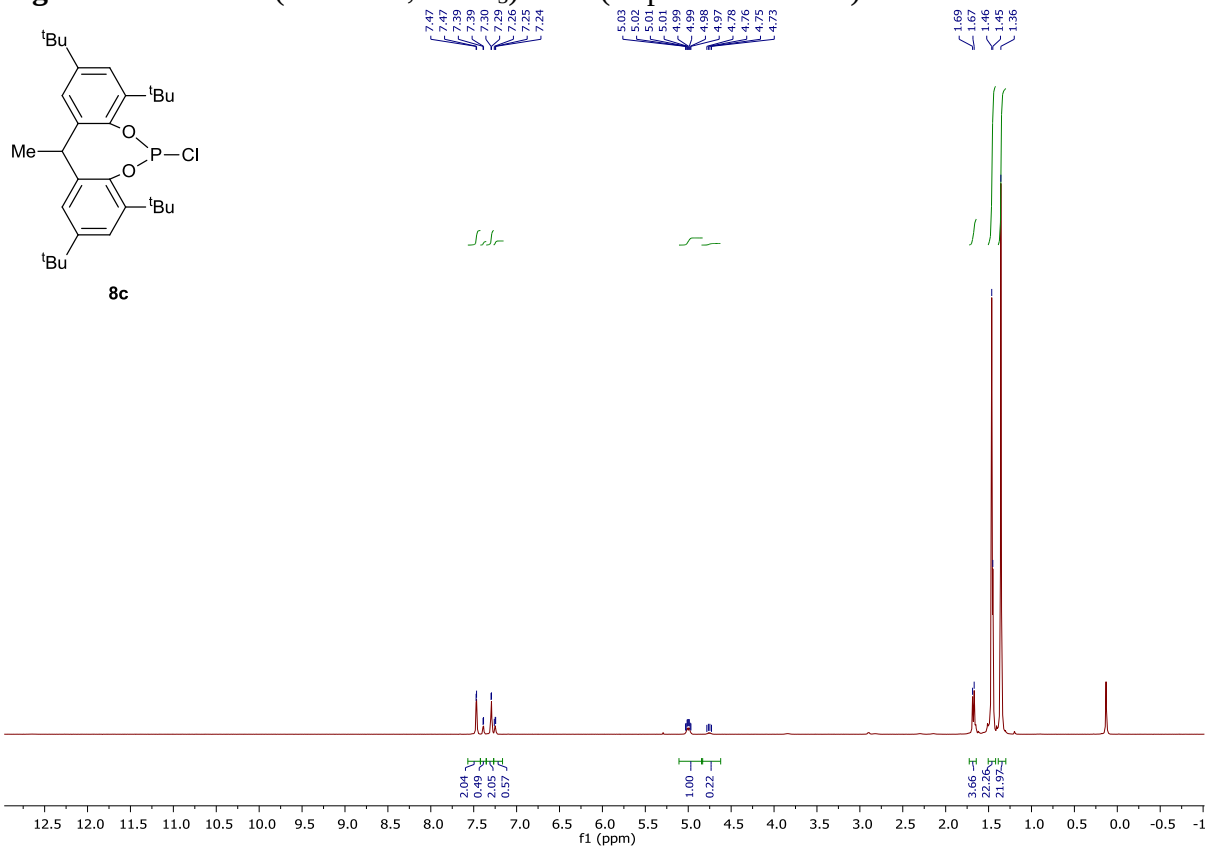


Figure 38: DEPTQ-135 ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) of **8c** (2 species observed)

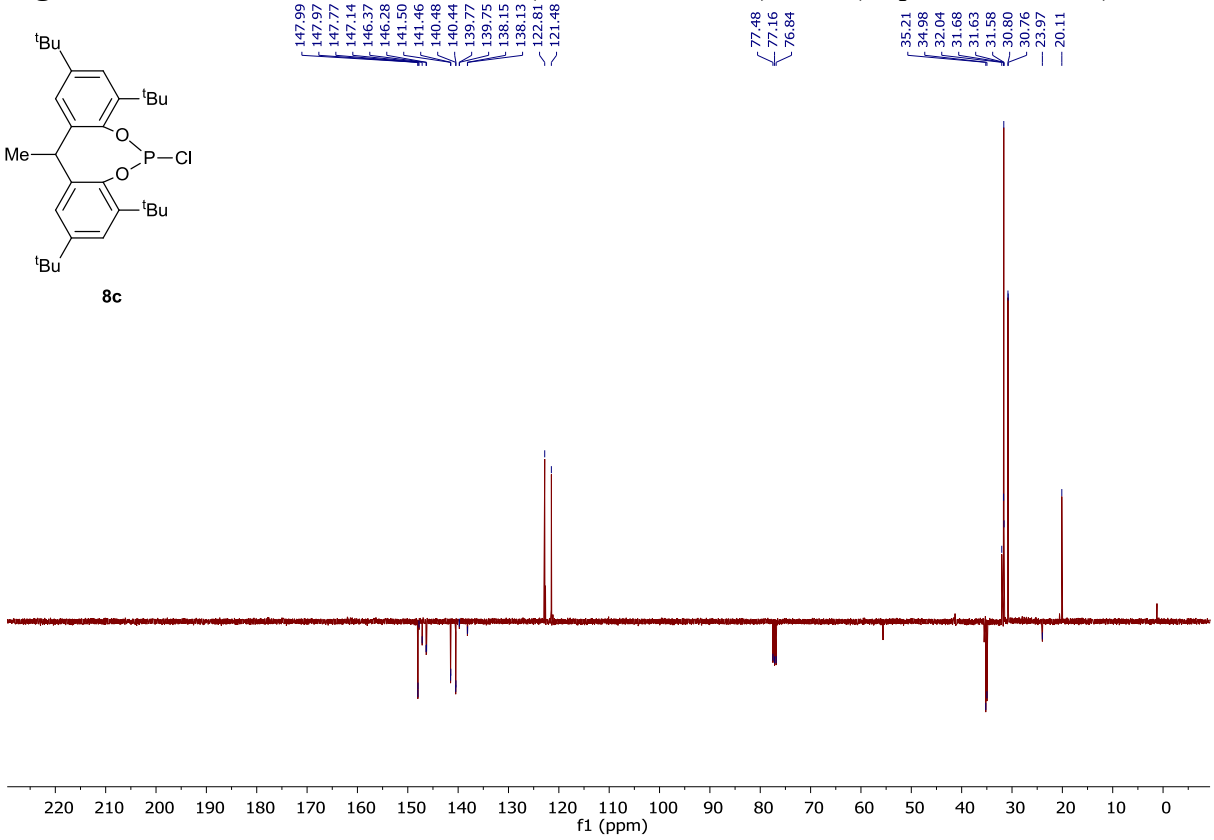


Figure 39: $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) of **8c** (2 species observed)

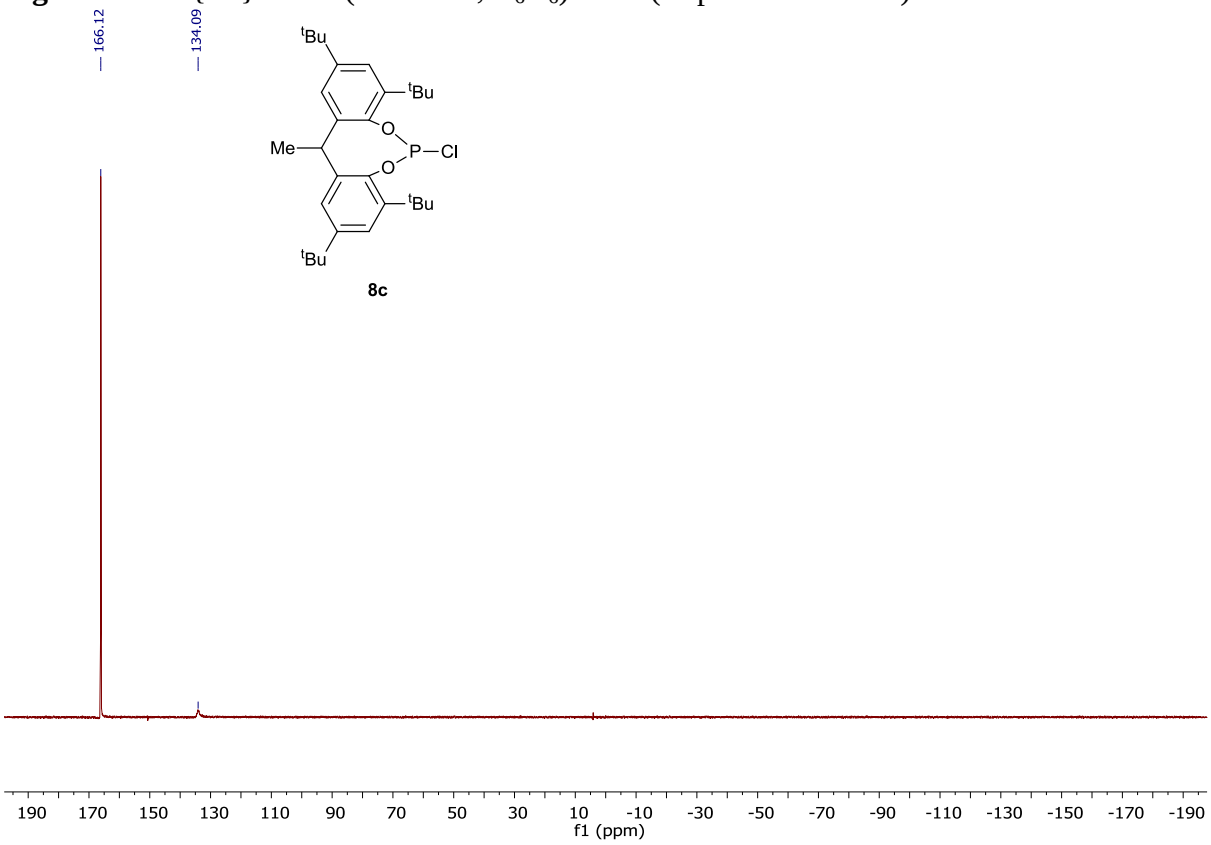


Figure 40: ^{1}H NMR (300 MHz, $CDCl_3$) of **3**

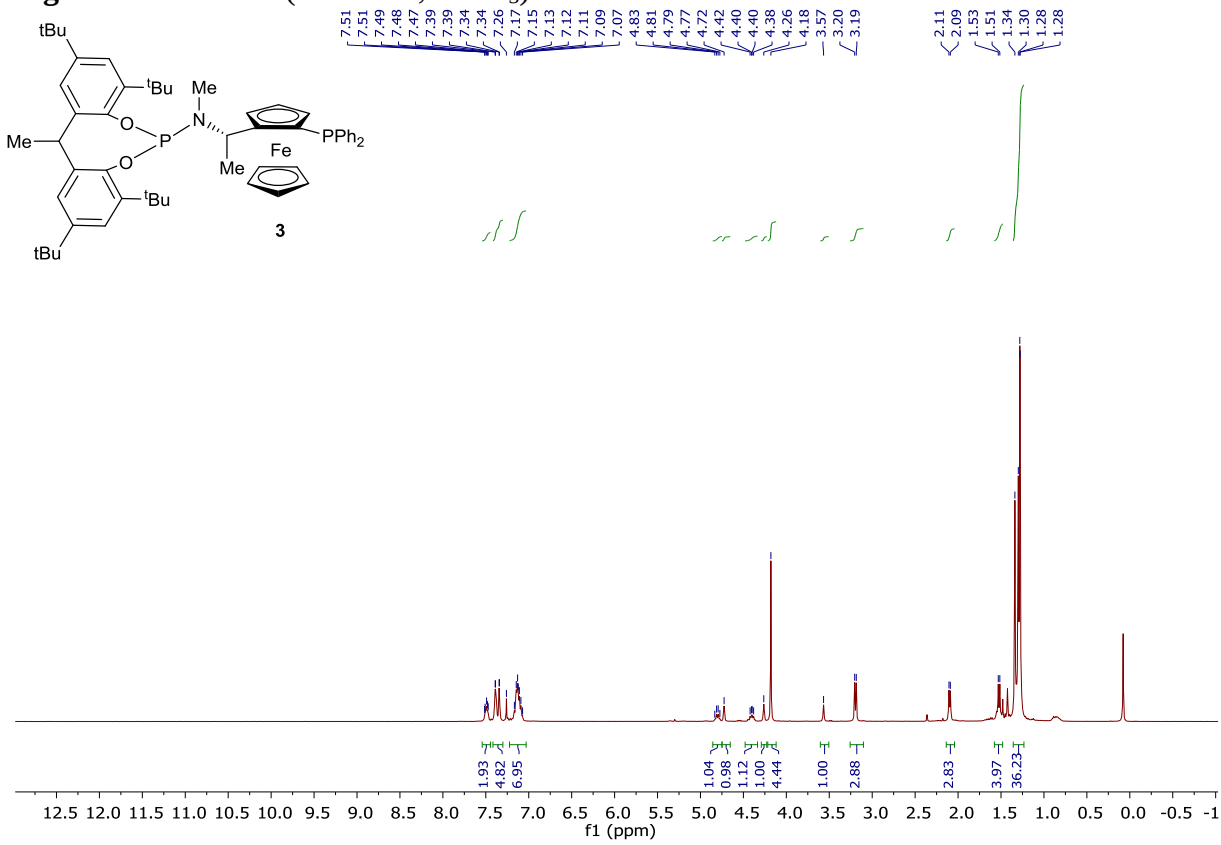


Figure 41: DEPTQ-135 ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of **3**

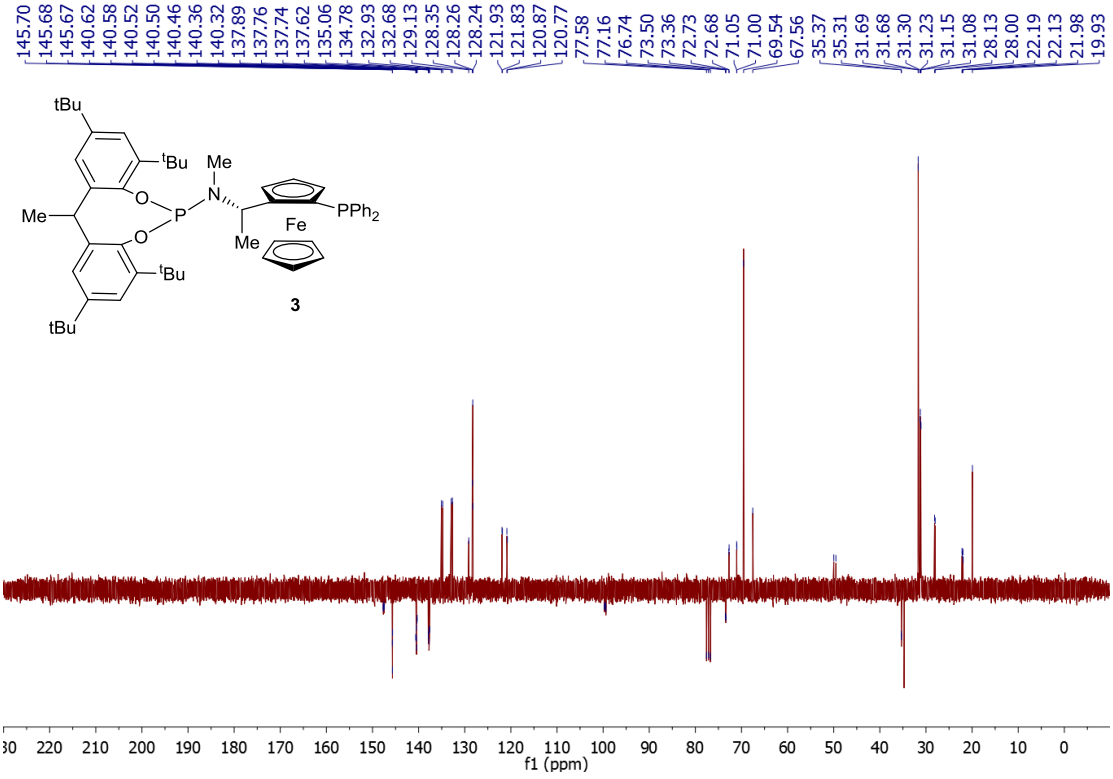


Figure 42: $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **3**

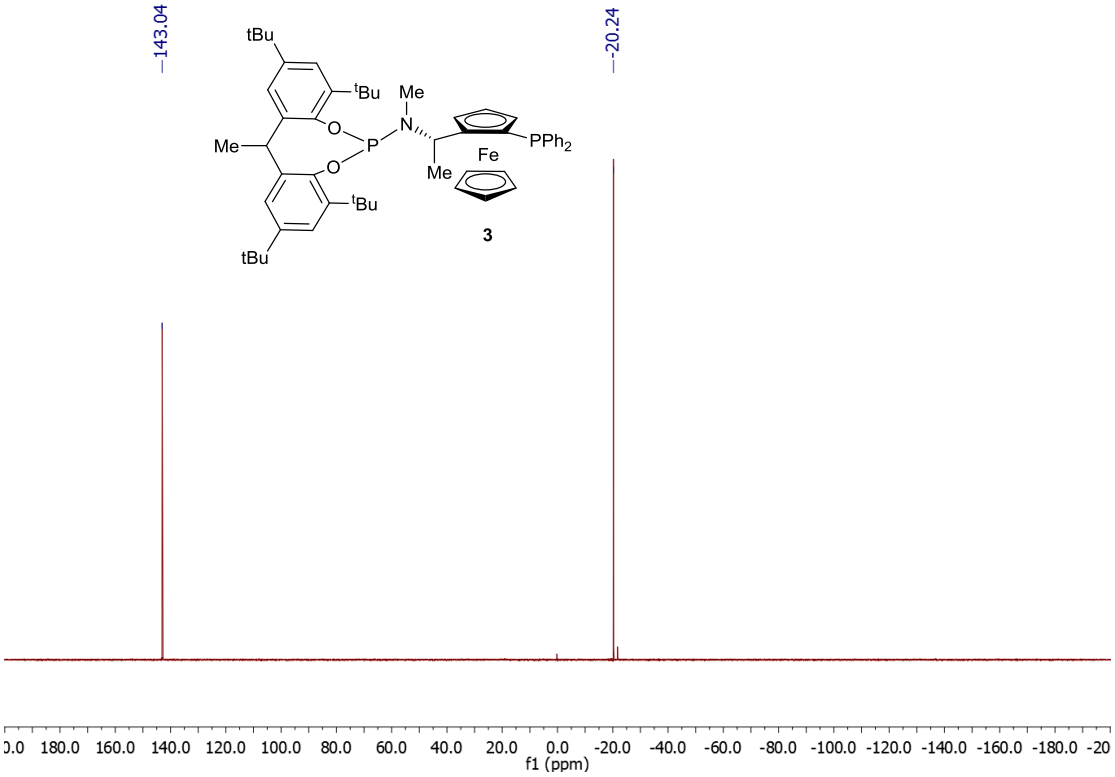


Figure 43: ^{1}H NMR (500 MHz, $CDCl_3$) of **4i**

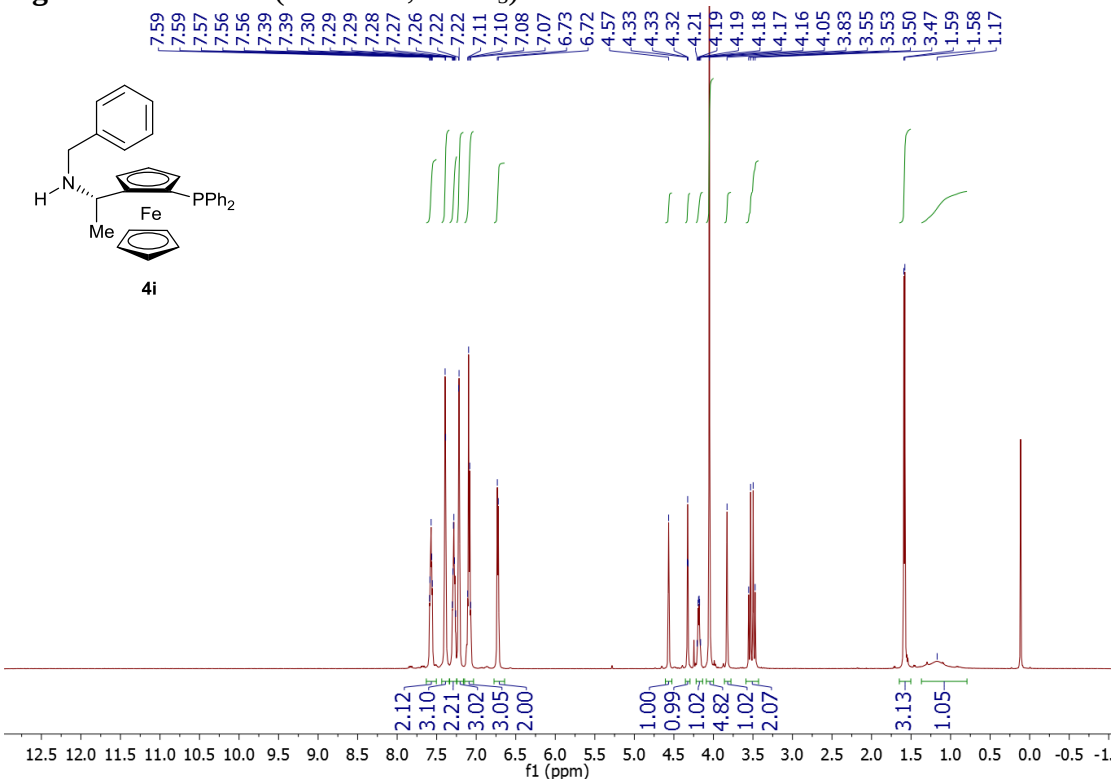


Figure 44: DEPTQ-135 ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) of **4i**

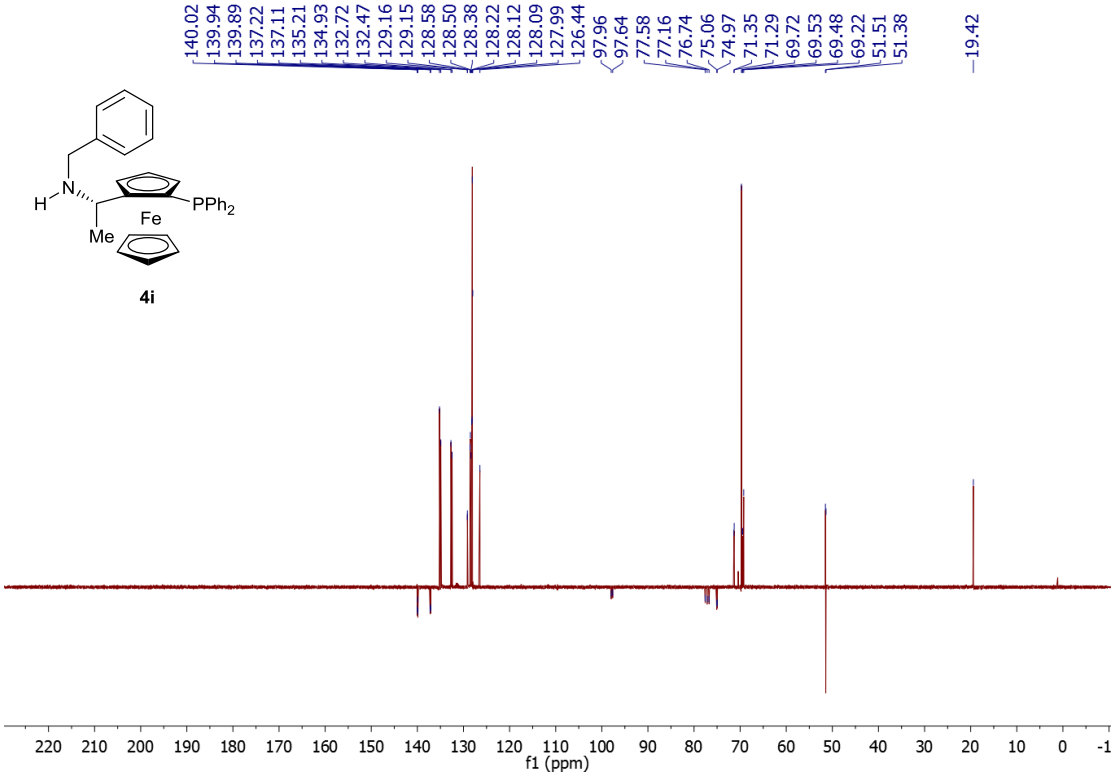


Figure 45: $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) of **4i**

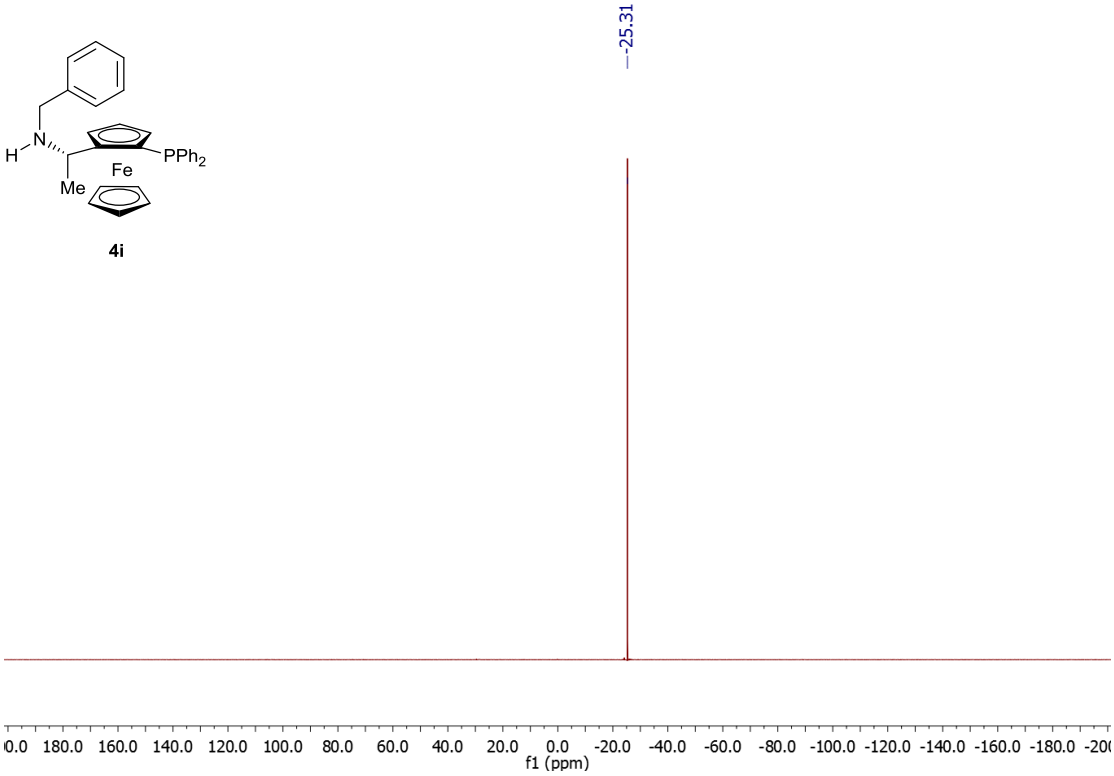


Figure 46: ^{1}H NMR (300 MHz, $CDCl_3$) of **4**

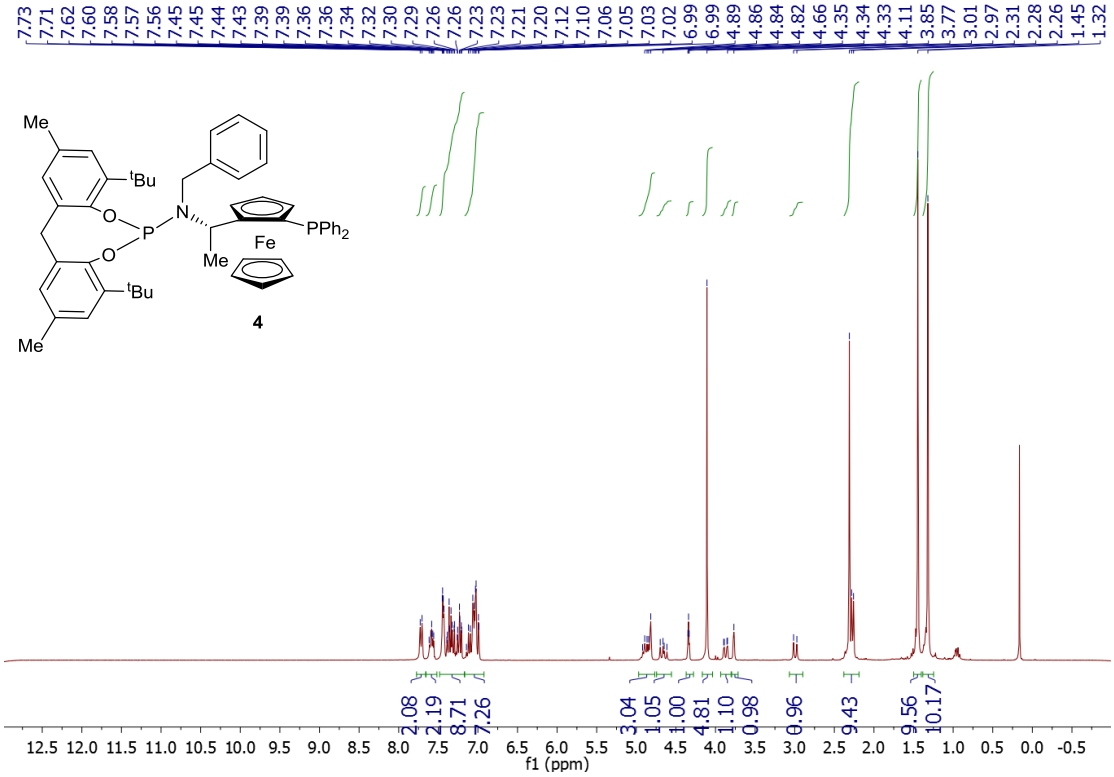


Figure 47: DEPTQ-135 ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) of **4**

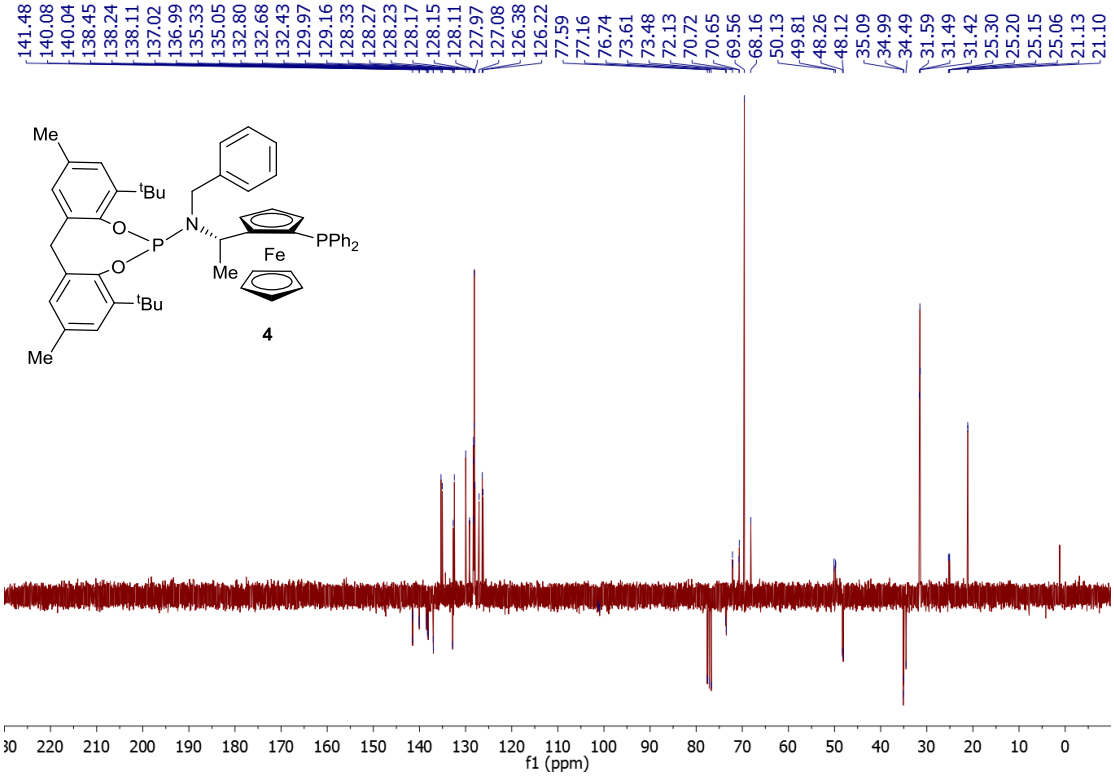
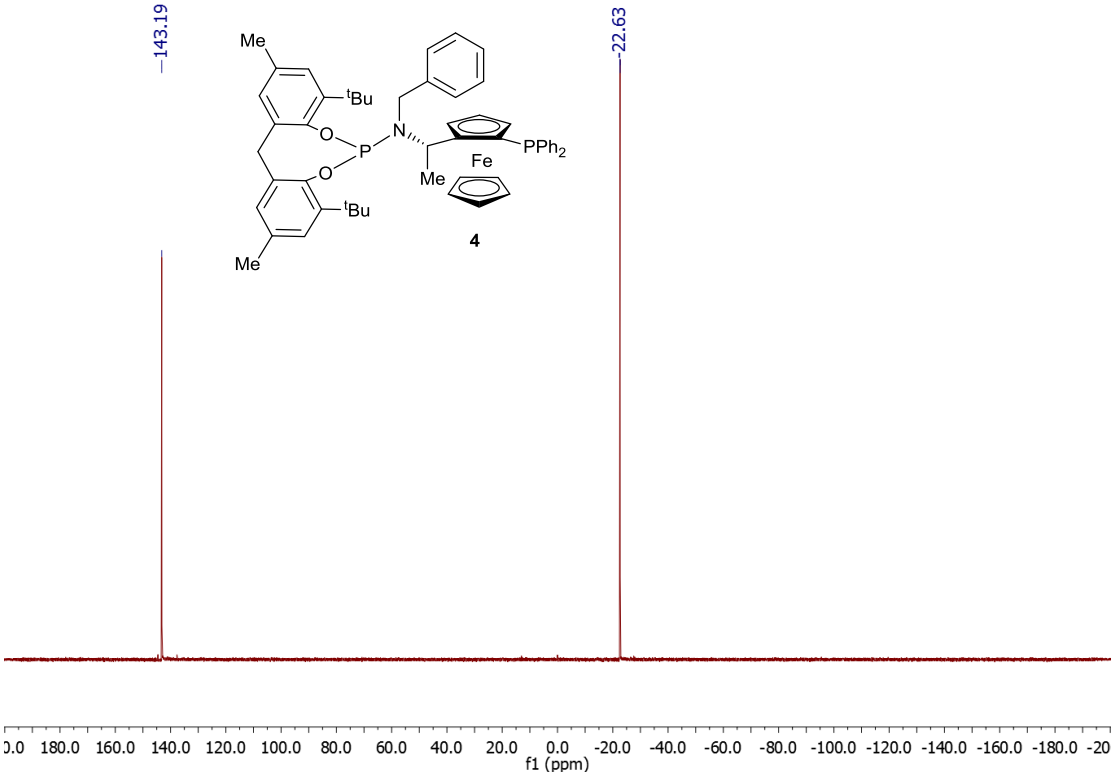


Figure 48: $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **4**



7. NMR Spectra of Complexes and Active Catalysts

Figure 49: ^{1}H NMR (300 MHz, C_7D_8) of **15**

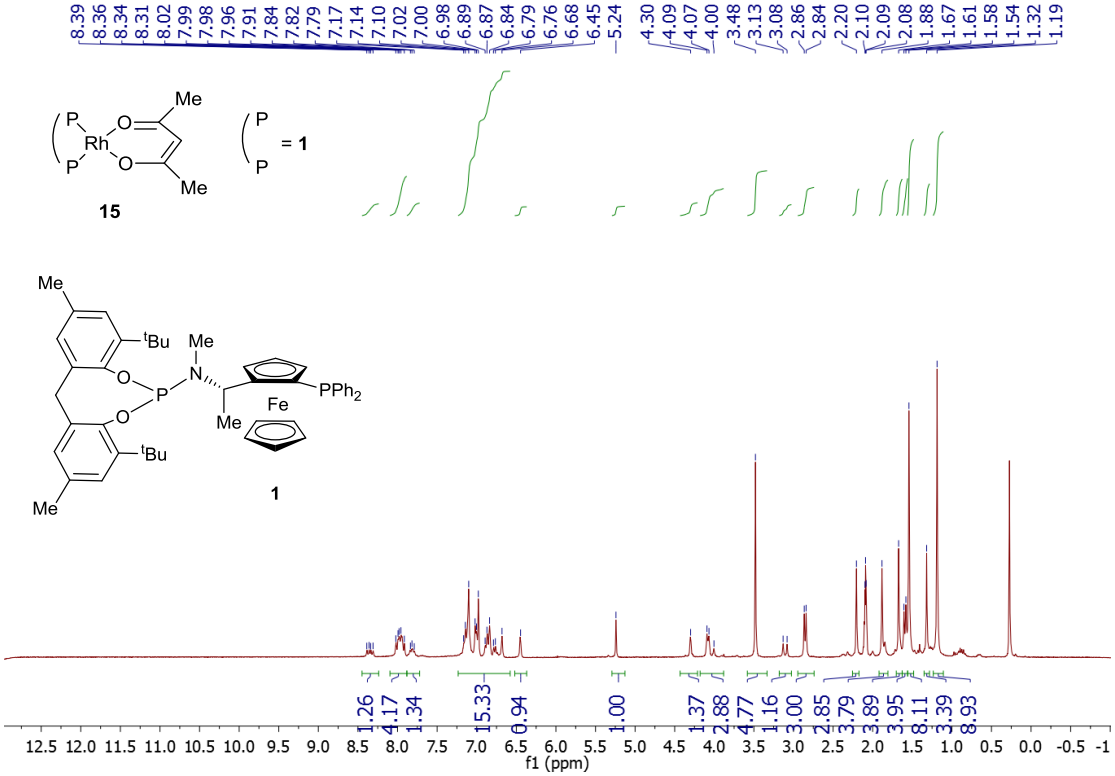


Figure 50: $^{13}C\{^{1}H\}$ NMR (75 MHz, C_7D_8) of **15**
(Signal at 202.7 ppm only observed by GHMBC)

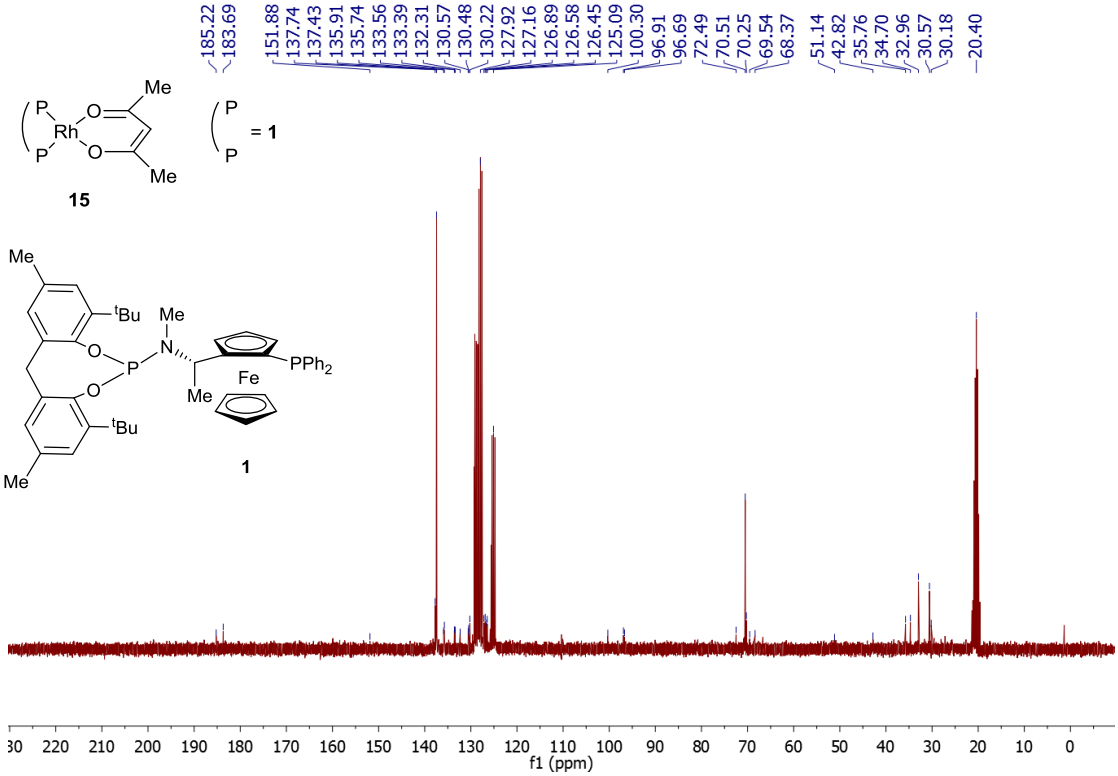


Figure 51: GHSQC (300 MHz ^{1}H, 75 MHz ^{13}C, C_7D_8) of **15**

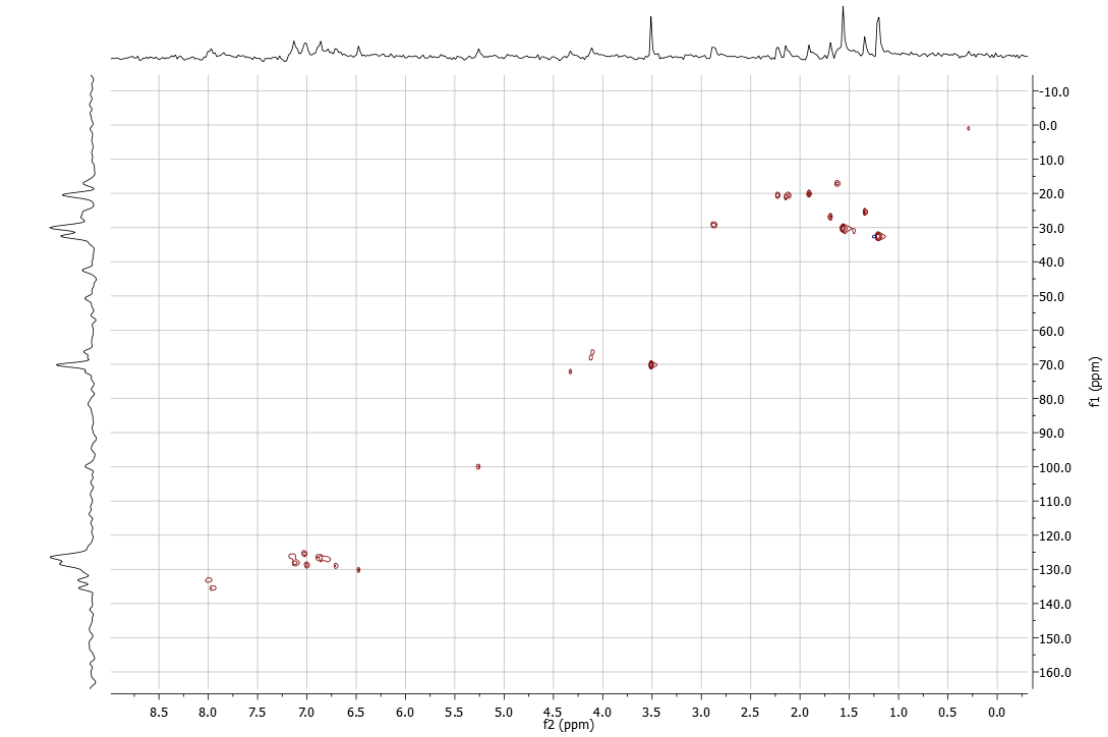


Figure 52: GHMBC (300 MHz ^{1}H, 75 MHz ^{13}C, C_7D_8) of **15**

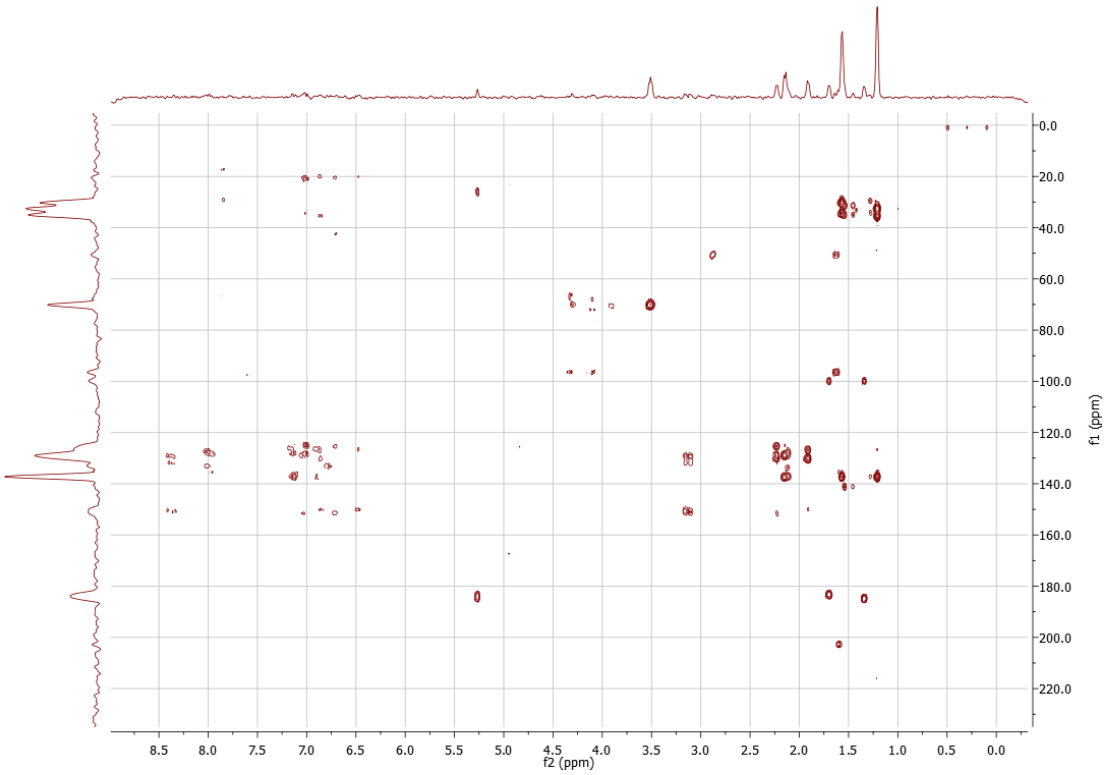


Figure 53: $^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8) of **15**

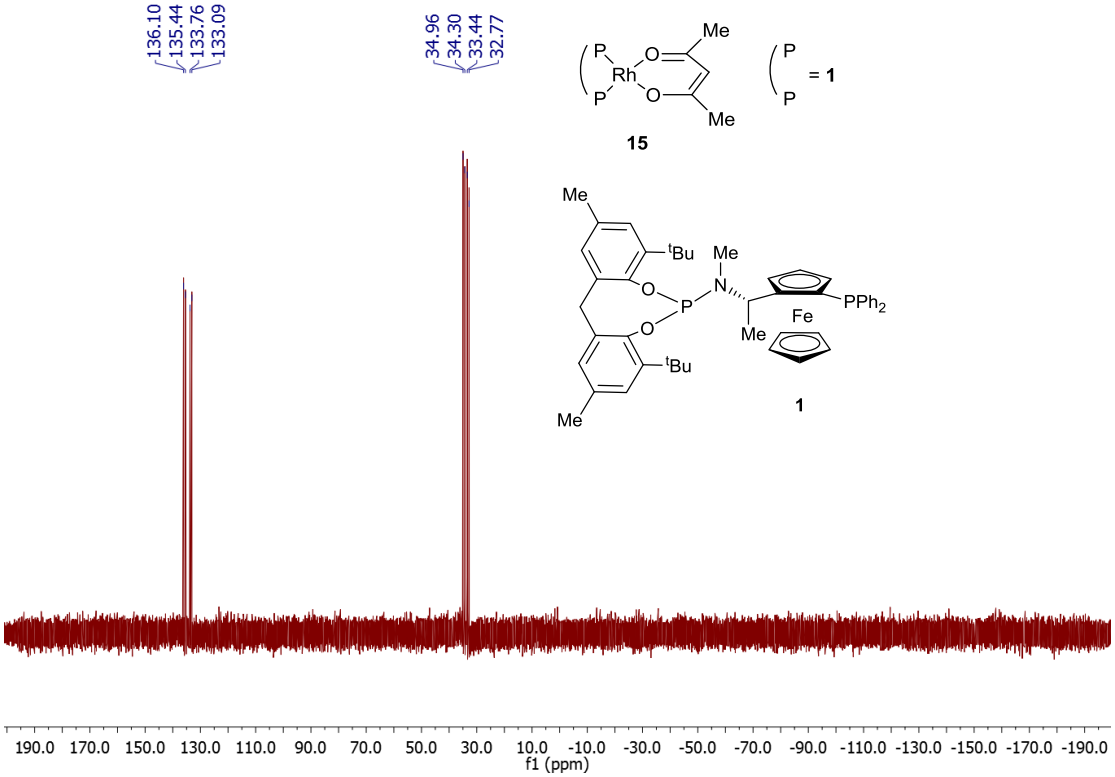


Figure 54: ^{1}H NMR (300 MHz, C_7D_8) of activated catalyst (Rh-H region) with **1** at 20 °C

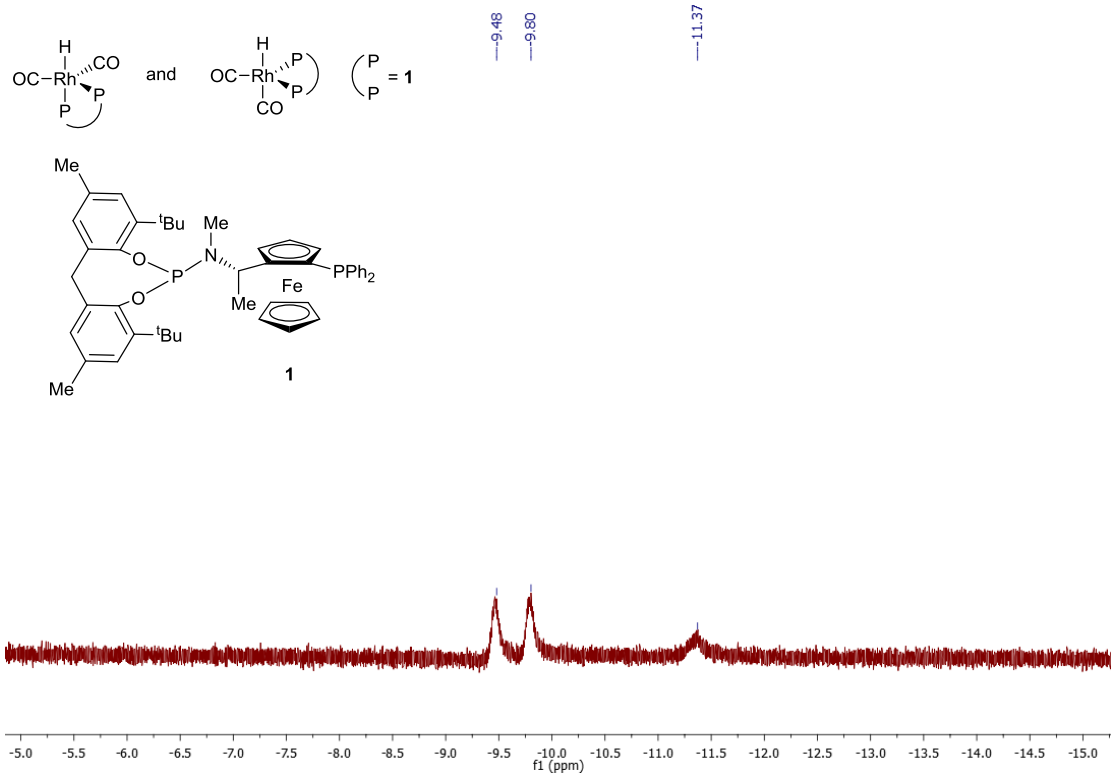


Figure 55: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_7D_8) of activated catalyst with **1** at 20 °C

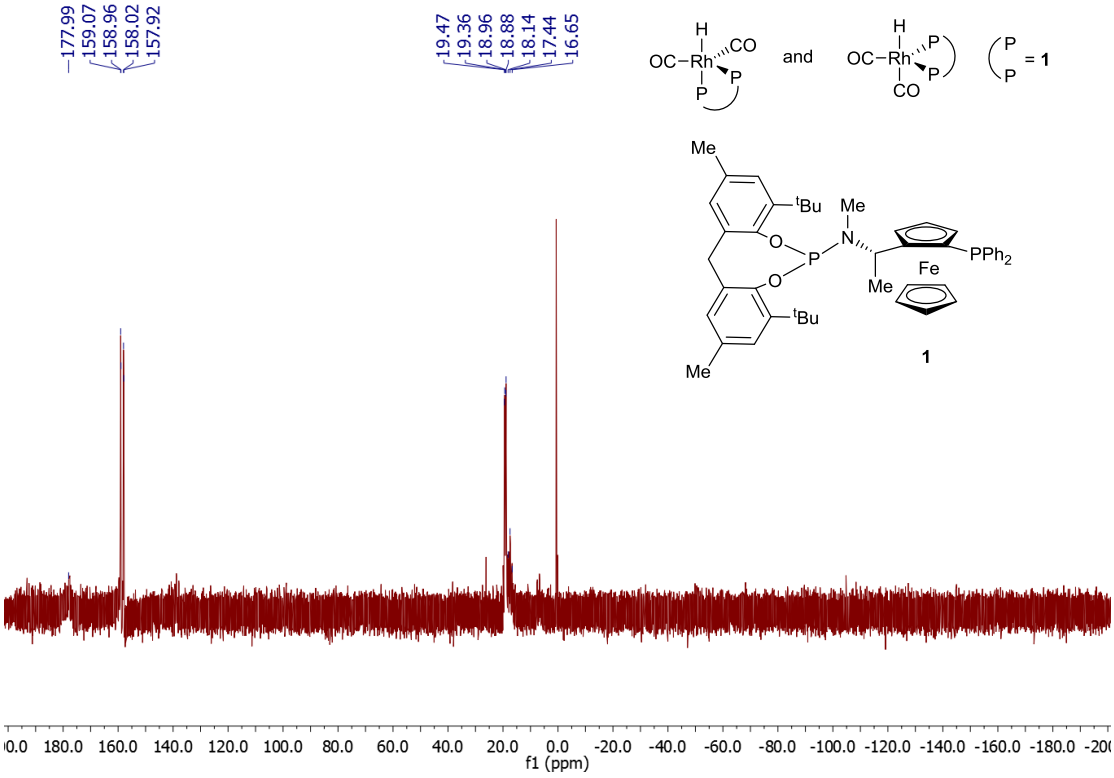


Figure 56: ^{1}H NMR (500 MHz, C_7D_8) of activated catalyst (Rh-H region) with **1** at –70 °C

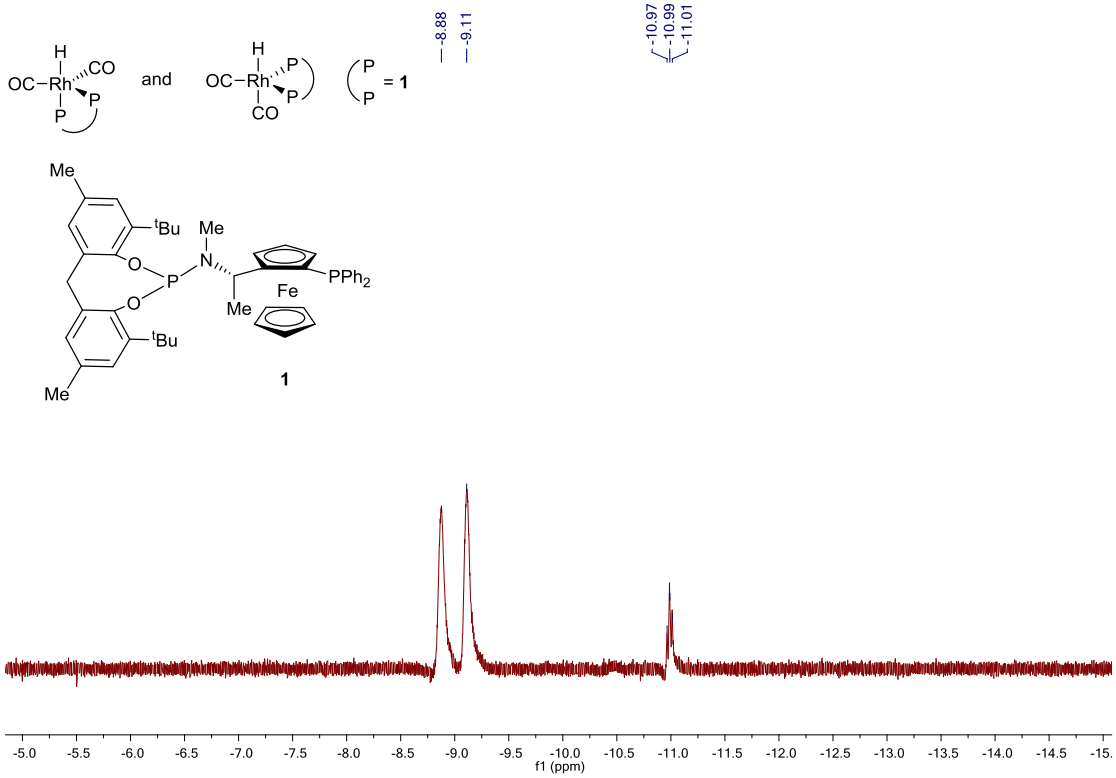


Figure 57: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_7D_8) of activated catalyst with **1** at –70 °C

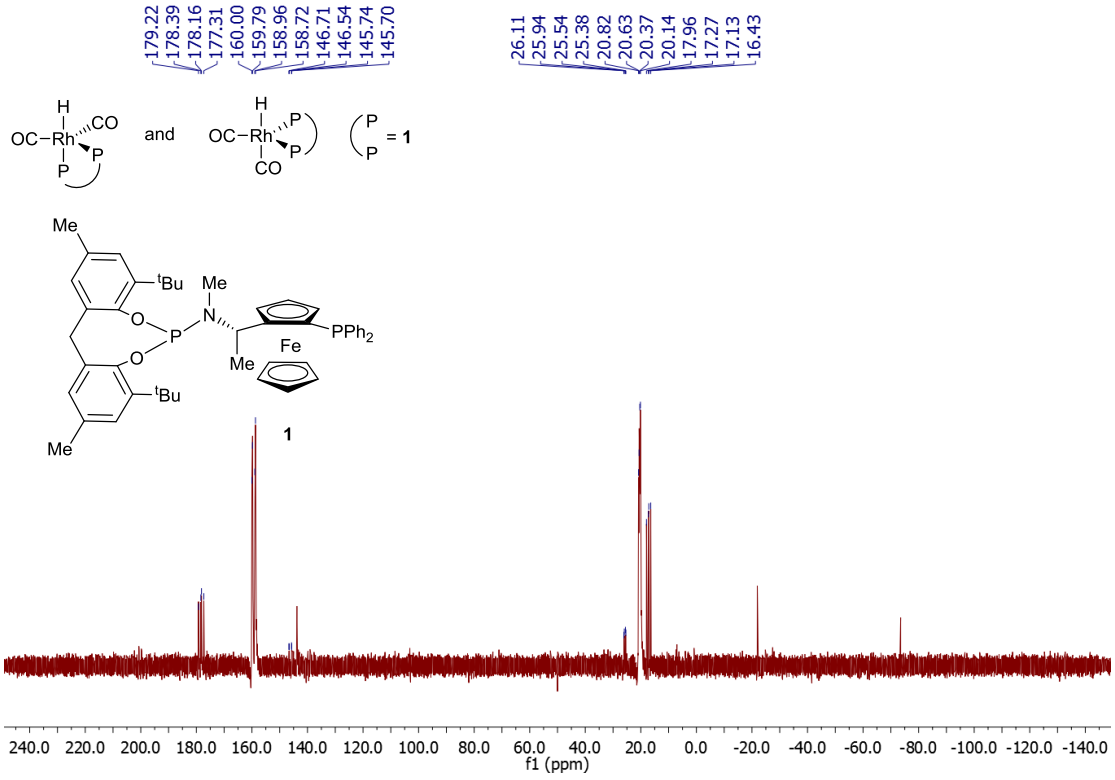


Figure 58: ^{31}P NMR (202 MHz, C_7D_8) of activated catalyst with **1** at –70 °C

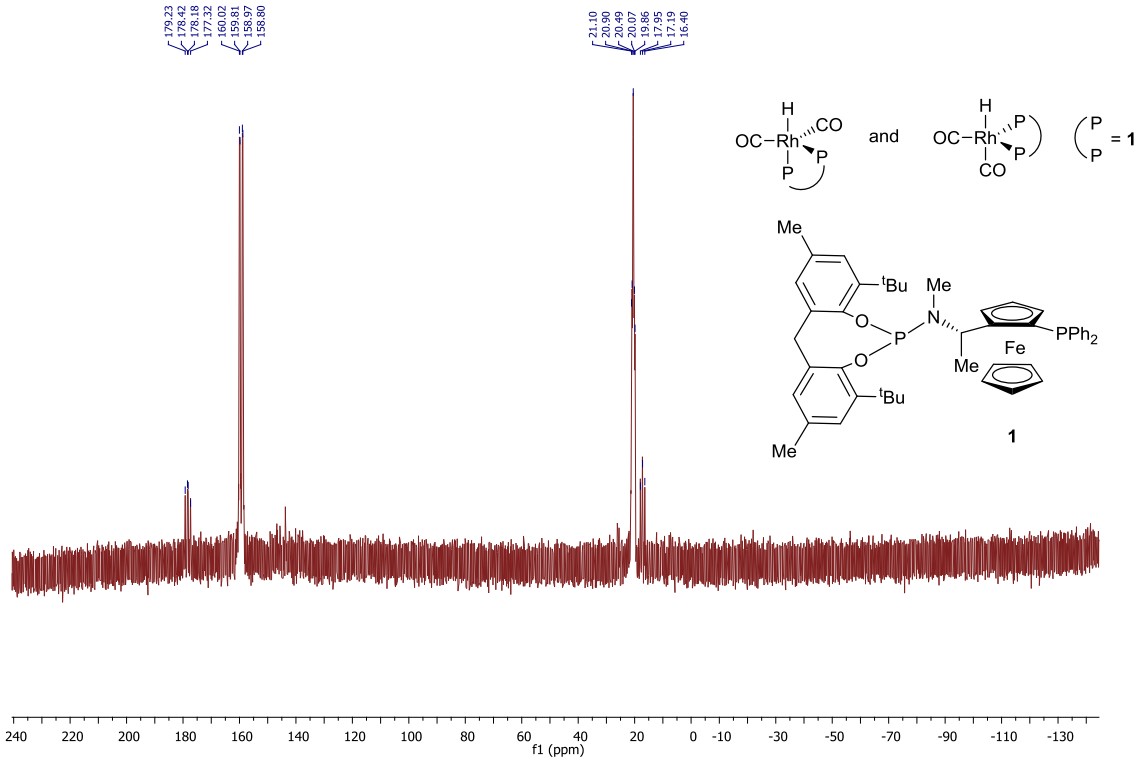


Figure 59: ^{1}H NMR (300 MHz, C_7D_8) of activated catalyst (Rh-H region) with **1** at +70 °C

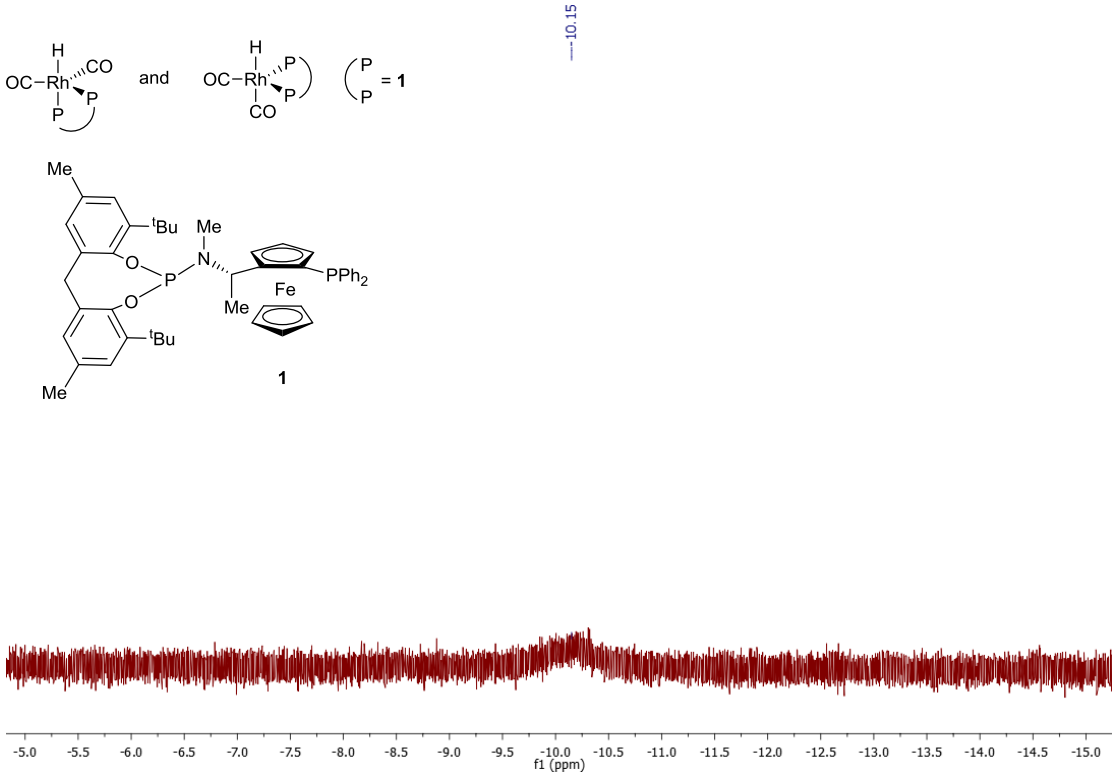


Figure 60: $^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8) of activated catalyst with **1** at +70 °C

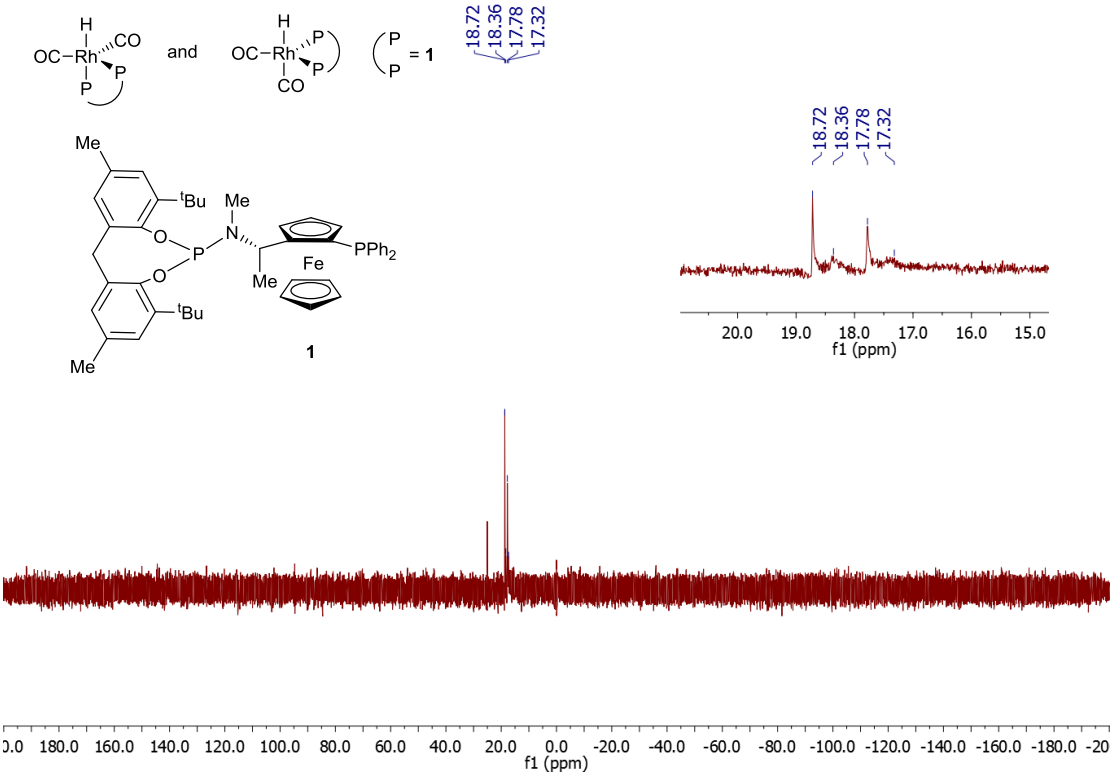


Figure 61: ^{1}H NMR (500 MHz, C_7D_8) of activated catalyst (Rh-H region) with **2** at 20 °C

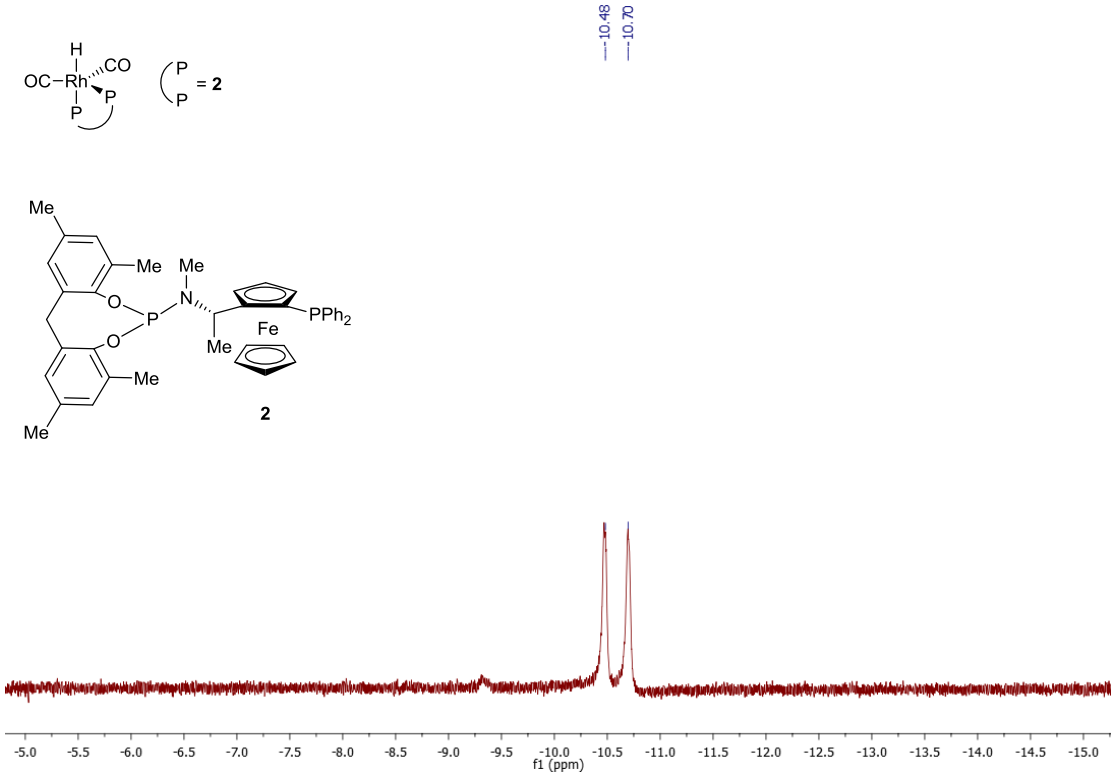


Figure 62: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_7D_8) of activated catalyst with **2** at 20 °C

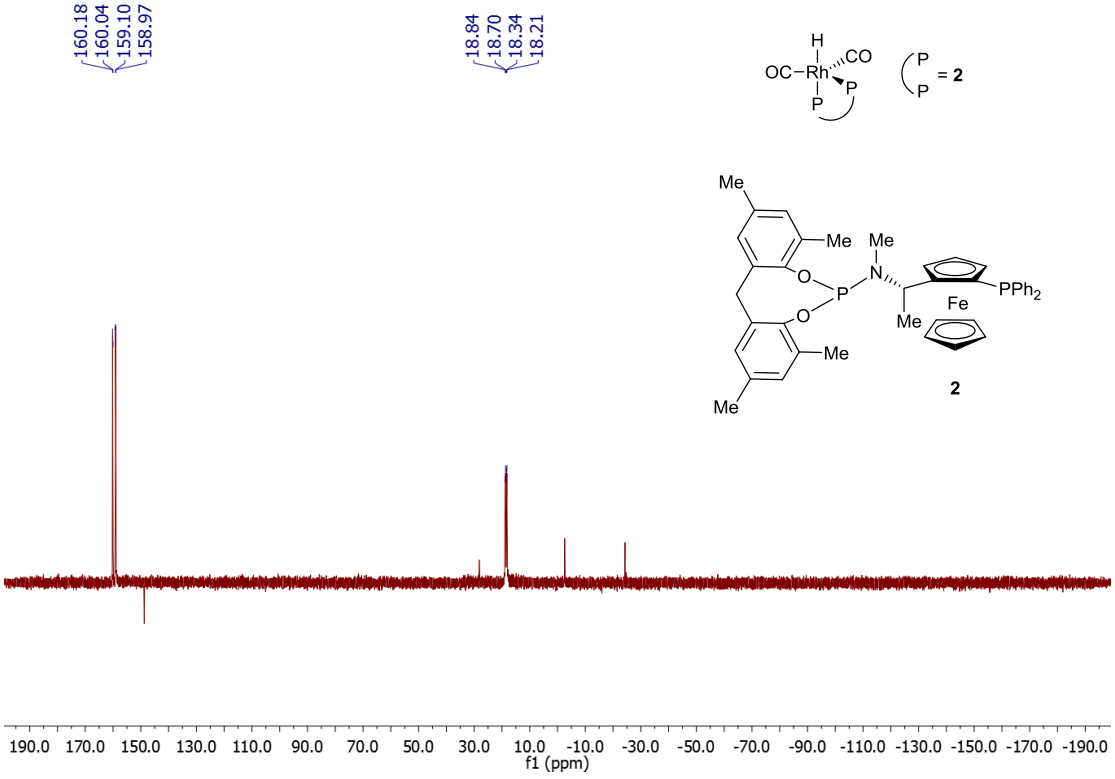


Figure 63: ^{1}H NMR (500 MHz, C_7D_8) of activated catalyst (Rh-H region) with **2** at –70 °C

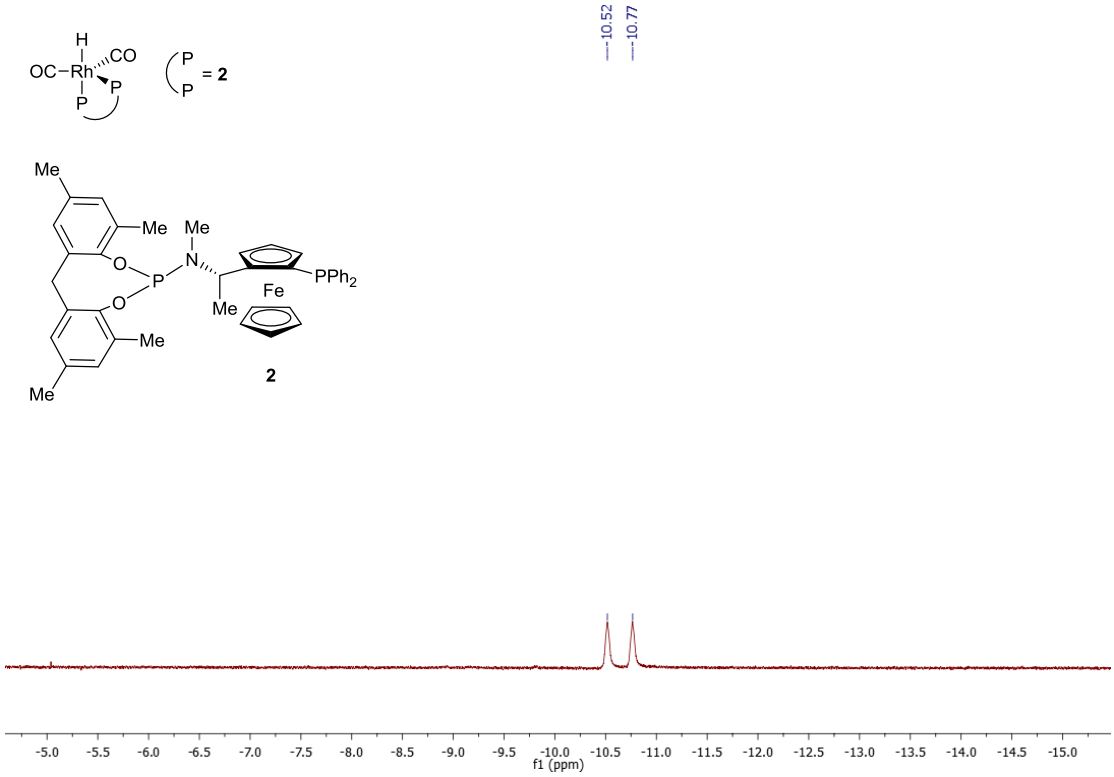


Figure 64: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_7D_8) of activated catalyst with **2** at –70 °C

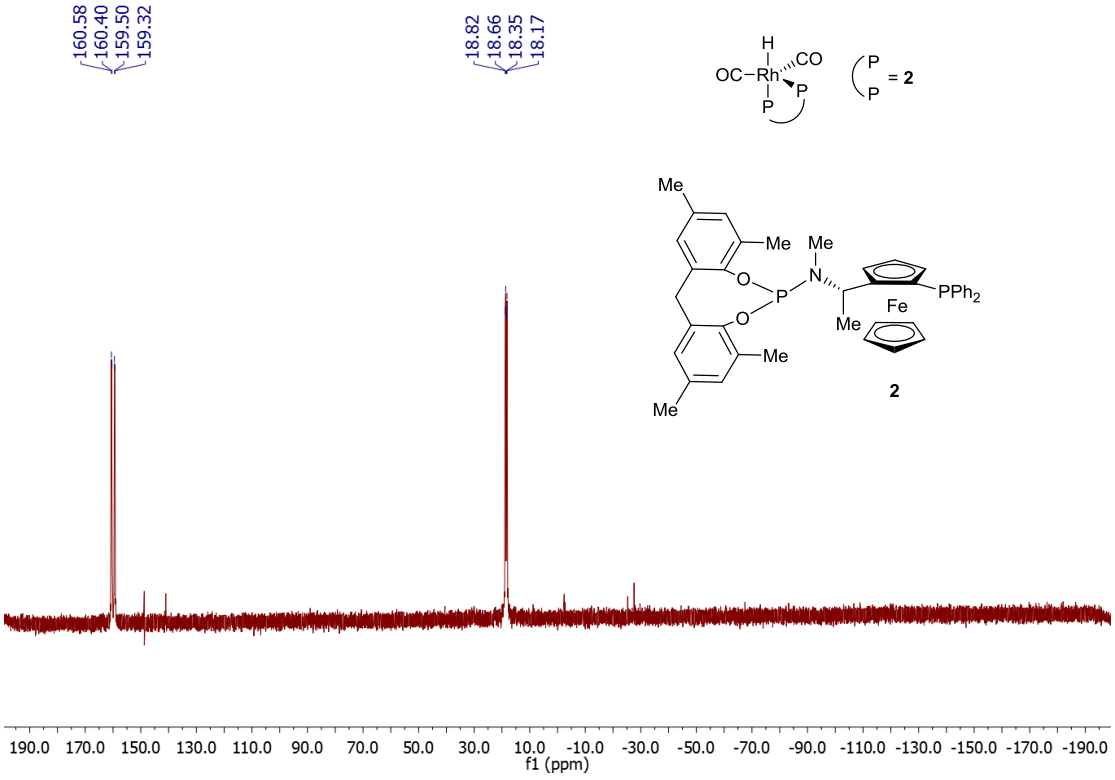


Figure 65: ^{31}P NMR (202 MHz, C_7D_8) of activated catalyst with **2** at –70 °C

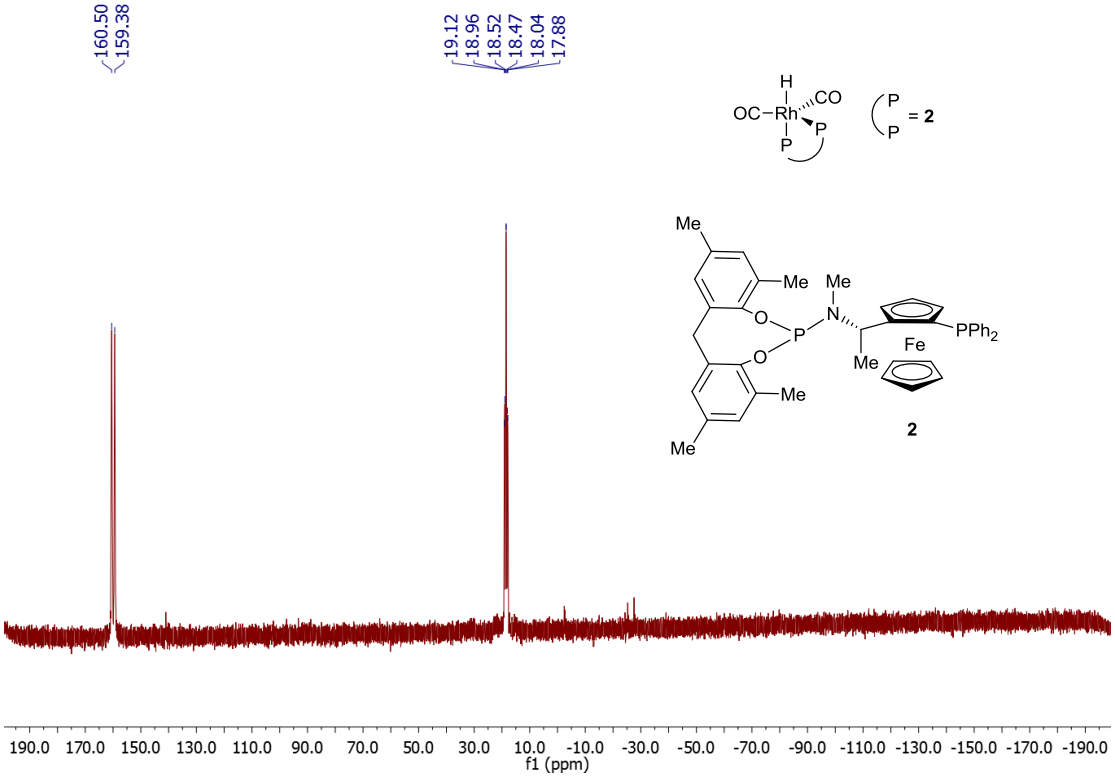


Figure 66: ^{1}H NMR (500 MHz, C_7D_8) of activated catalyst (Rh-H region) with **3** at 20 °C

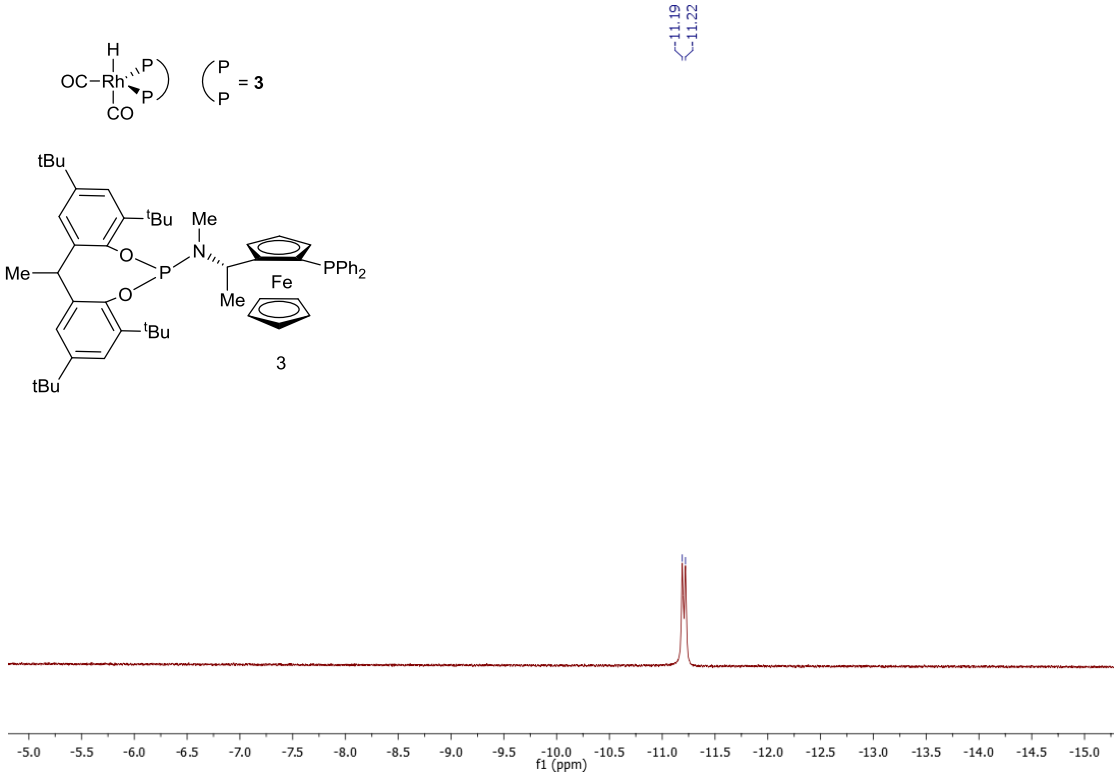


Figure 67: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_7D_8) of activated catalyst with **3** at 20 °C

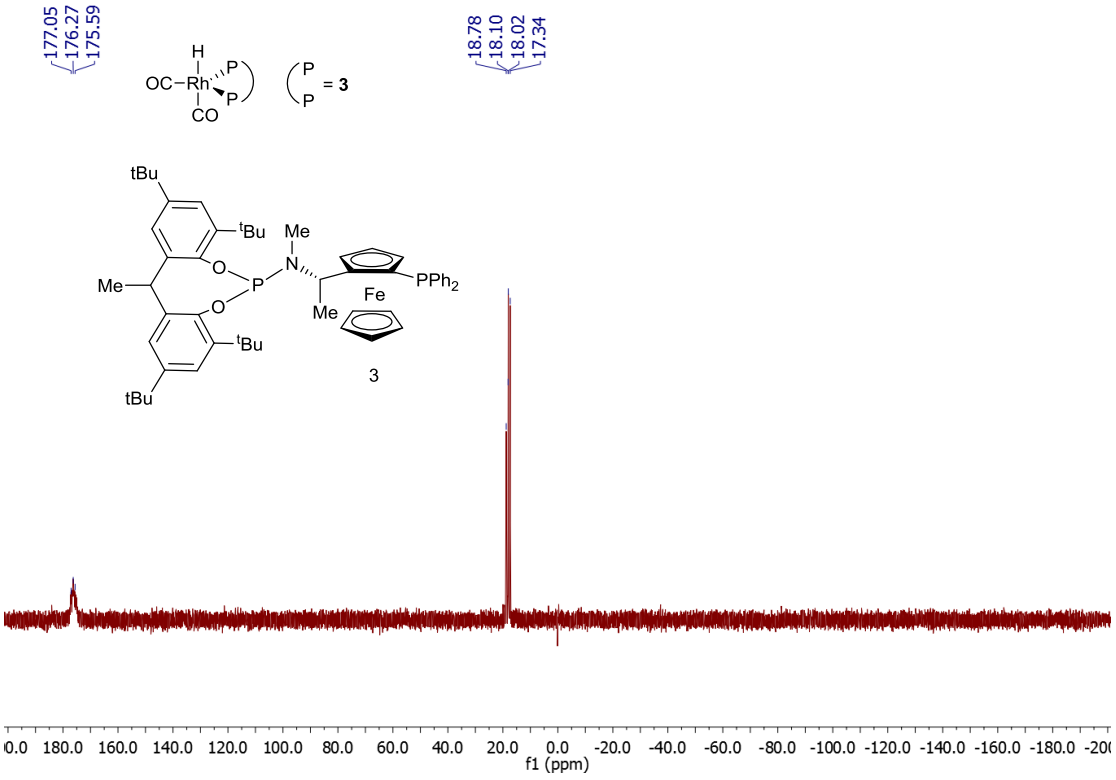


Figure 68: ^{1}H NMR (500 MHz, C_7D_8) of activated catalyst (Rh-H region) with **3** at –70 °C

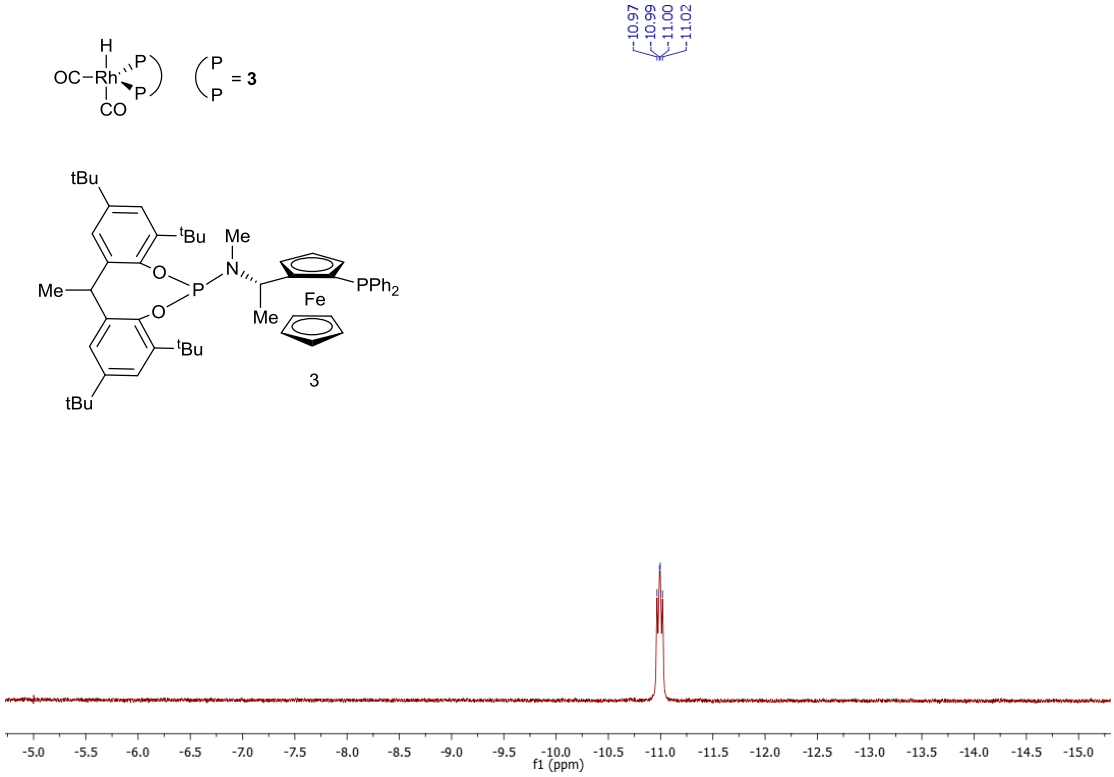


Figure 69: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_7D_8) of activated catalyst with **3** at –70 °C

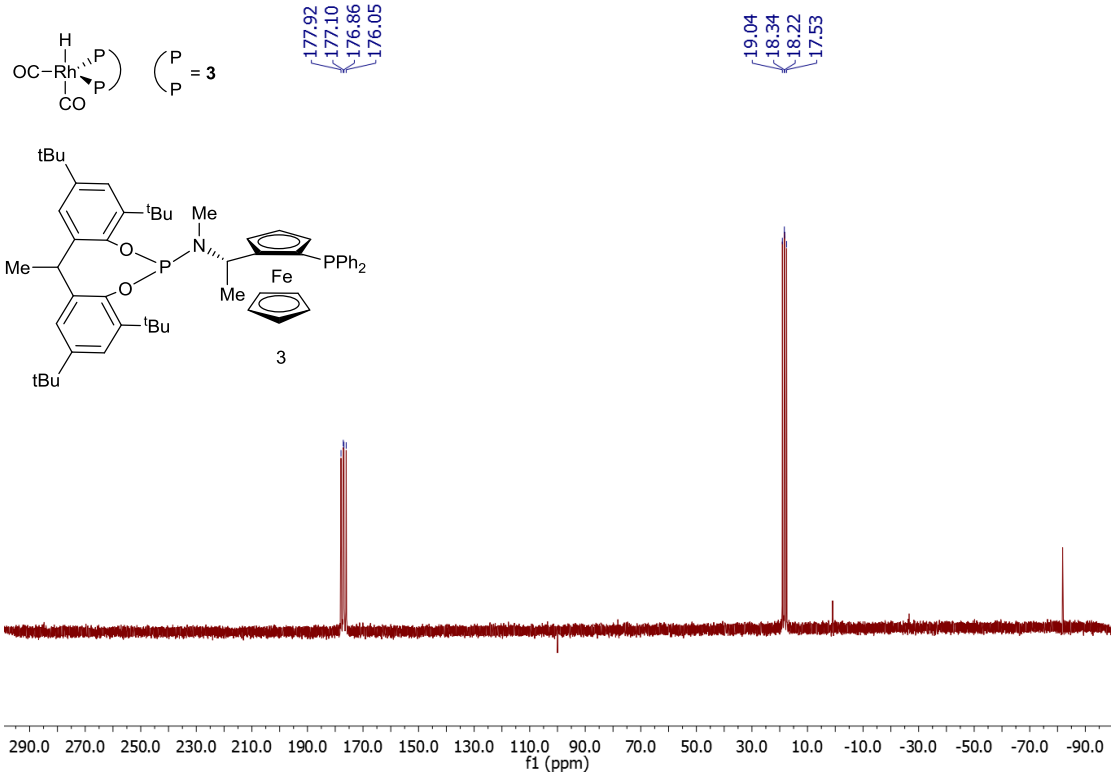


Figure 70: ^{31}P NMR (202 MHz, C_7D_8) of activated catalyst with **3** at –70 °C

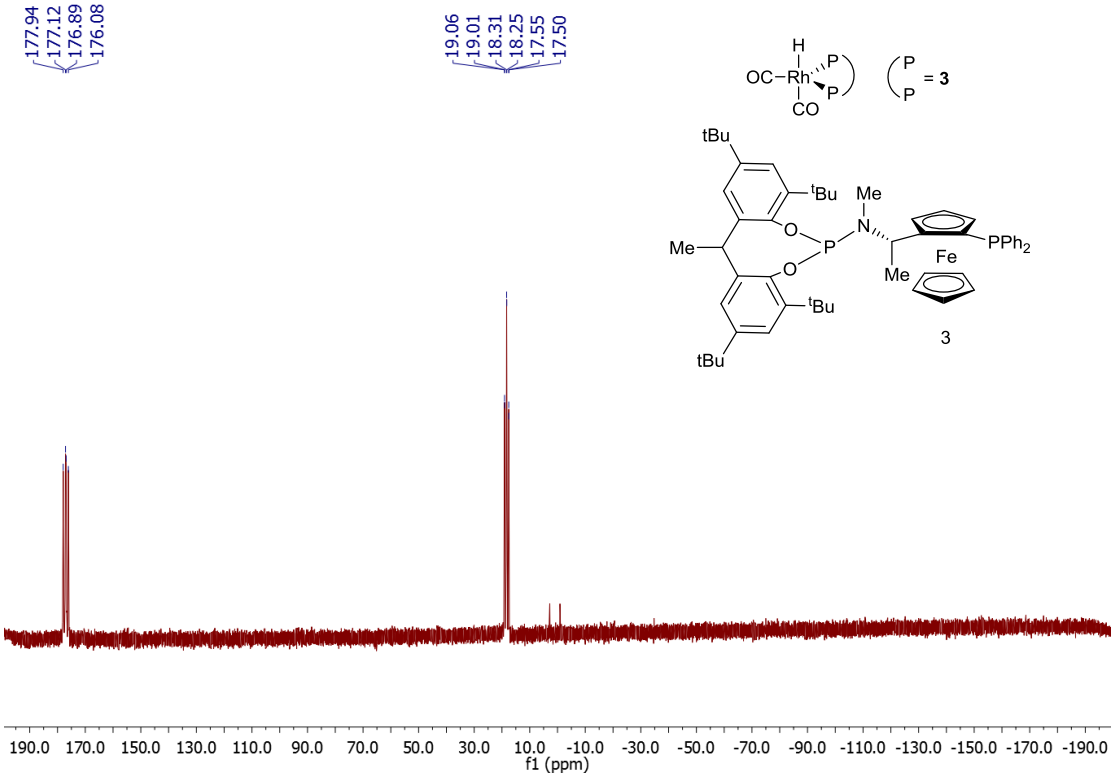


Figure 71: ^{1}H NMR (300 MHz, C_7D_8) of activated catalyst (Rh-H region) with **3** at 20 °C under CO/H_2 (1:1) (8 bar)

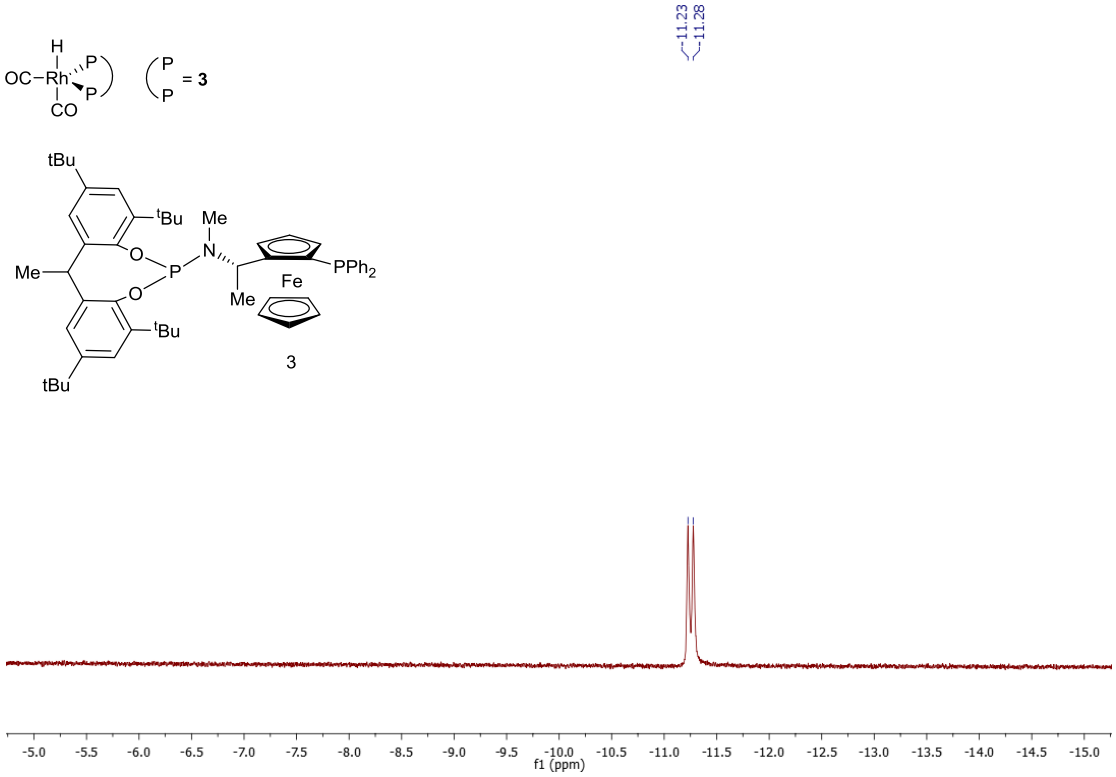


Figure 72: $^{31}P\{^{1}H\}$ NMR (121 MHz, C_7D_8) of activated catalyst with **3** at 20 °C under CO/H_2 (1:1) (8 bar)

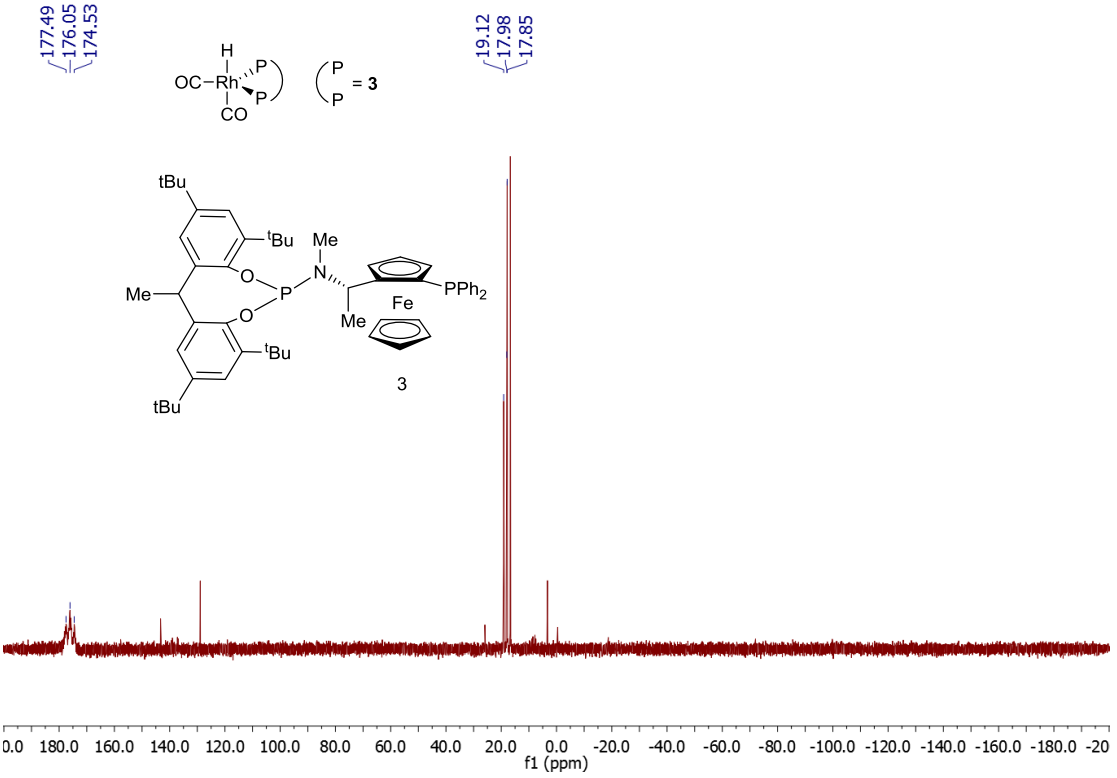


Figure 73: ^{1}H NMR (400 MHz, C_7D_8) of activated catalyst (Rh-H region) with **4** at 20 °C

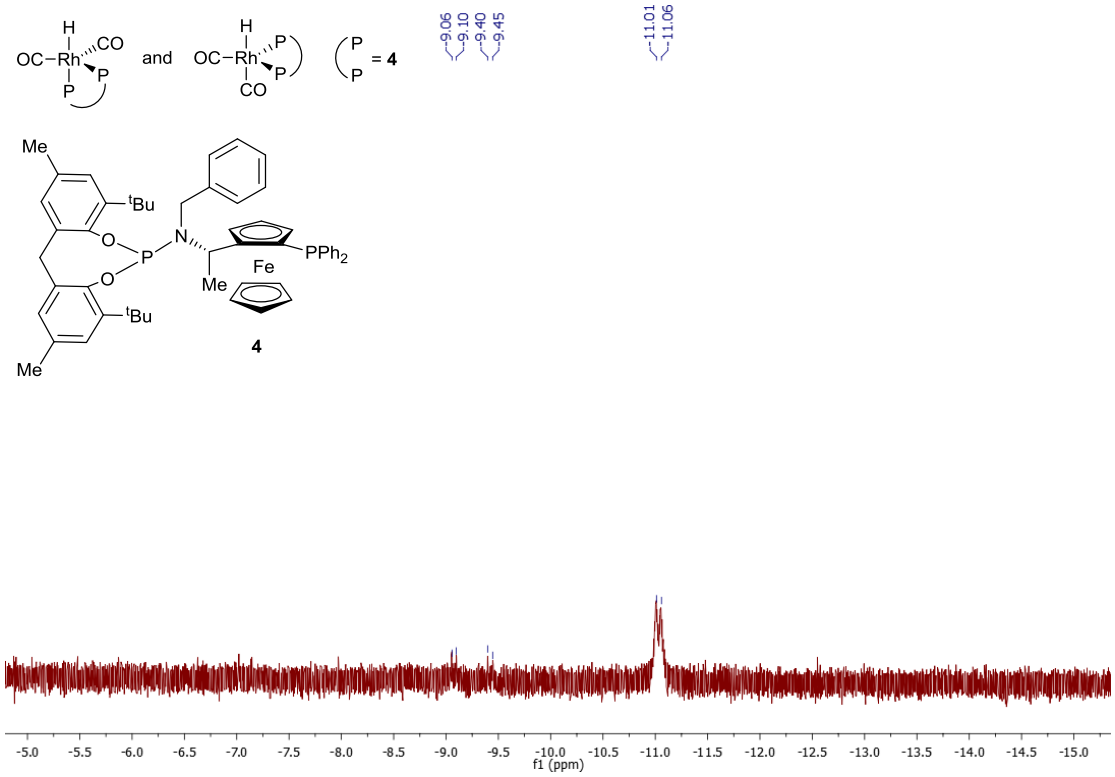


Figure 74: $^{31}P\{^{1}H\}$ NMR (162 MHz, C_7D_8) of activated catalyst with **4** at 20 °C

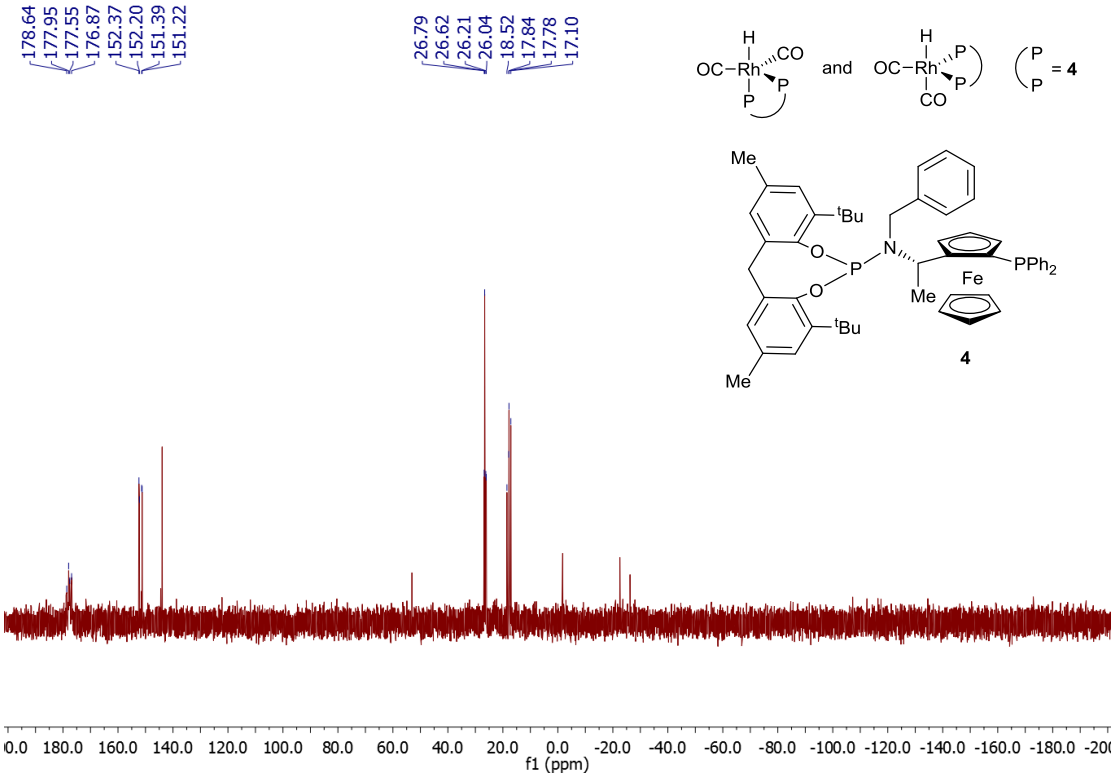


Figure 75: ^{1}H NMR (500 MHz, C_7D_8) of activated catalyst (Rh-H region) with **4** at –70 °C

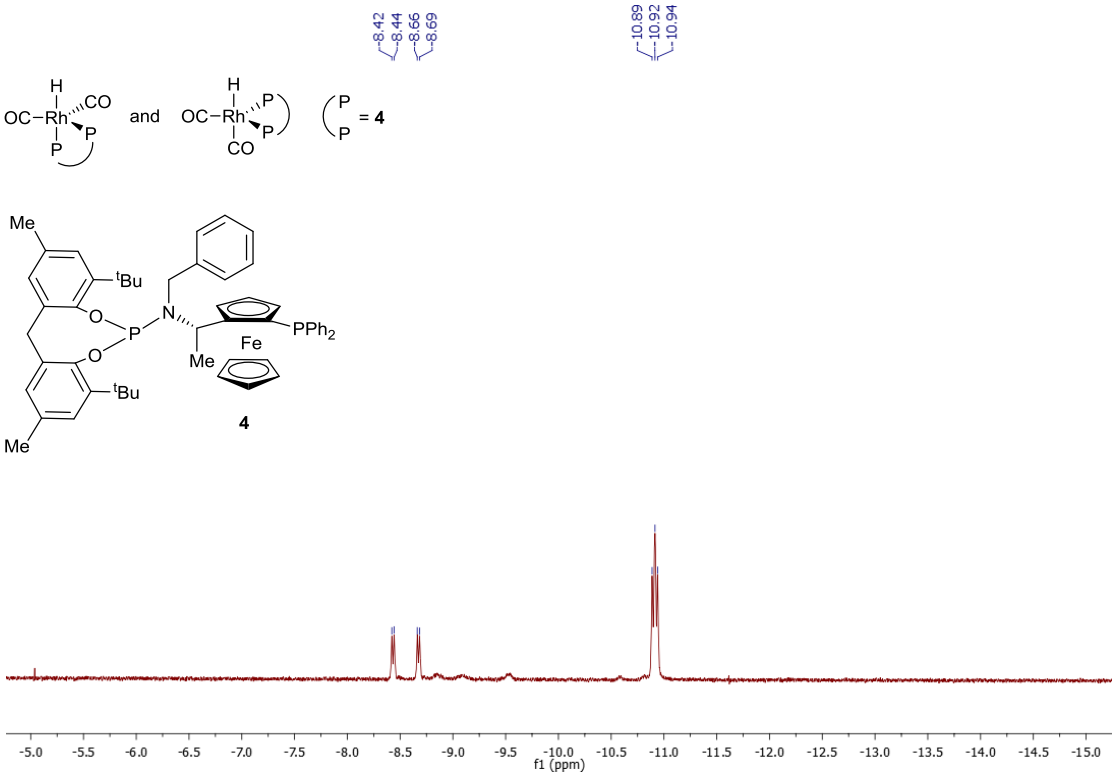


Figure 76: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_7D_8) of activated catalyst with **4** at –70 °C

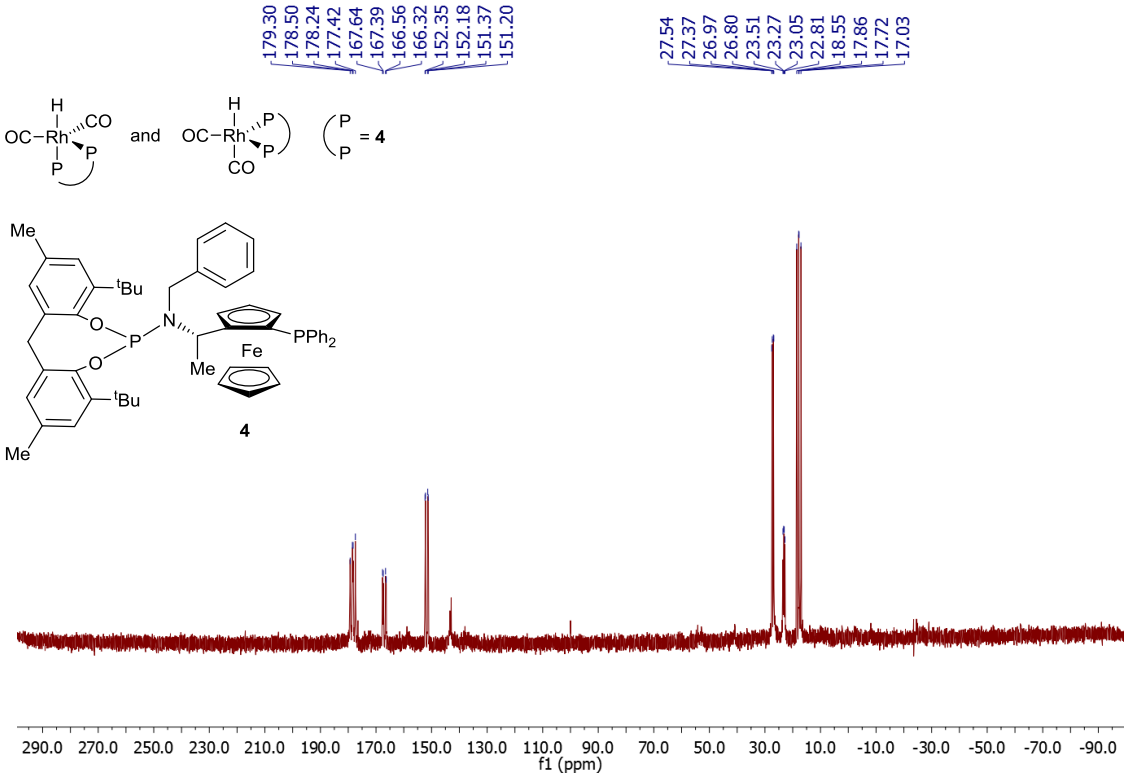
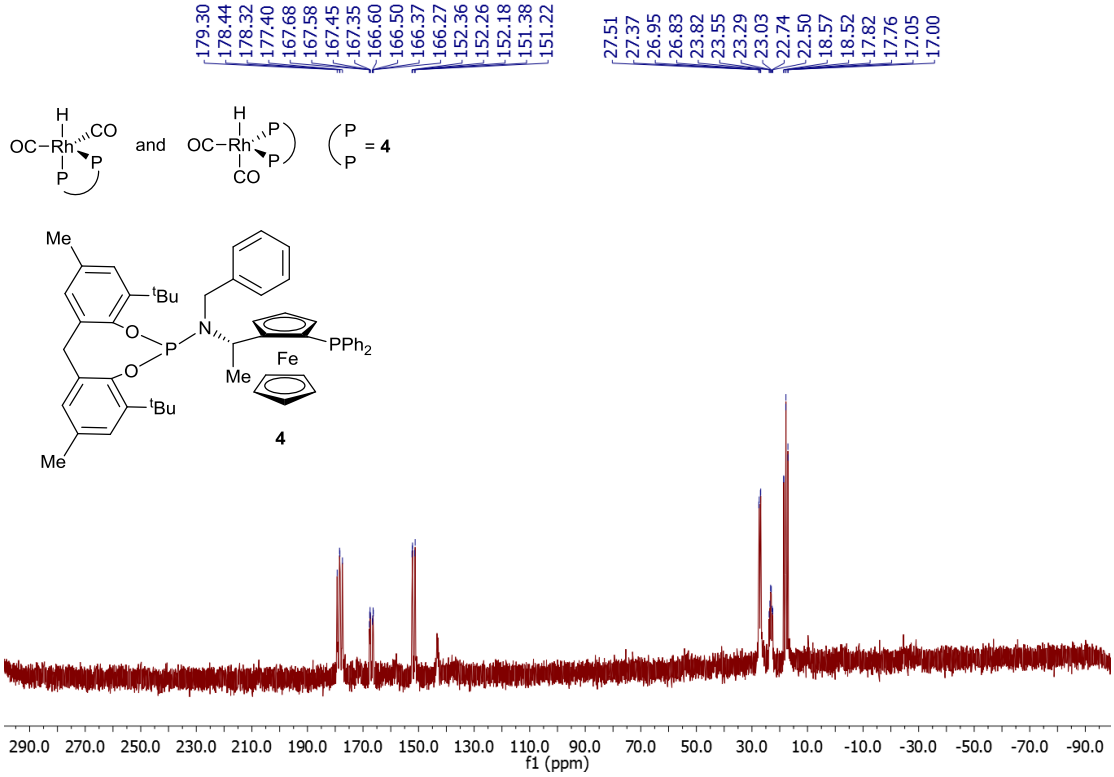


Figure 77: ^{31}P NMR (202 MHz, C_7D_8) of activated catalyst (Rh-H region) with **4** at –70 °C



8. References

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