Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Planar Chiral Palladacycle Precatalysts for Asymmetric Synthesis

Ross A. Arthurs, David L. Hughes and Christopher J. Richards*

School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ, U.K.

Chris.Richards@uea.ac.uk

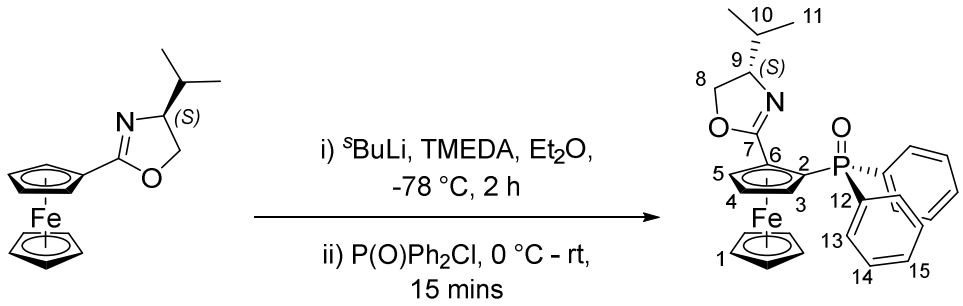
Index

1. Experimental procedures

General information

Tetrahydrofuran were distilled over sodium and benzophenone ketyl and dichloromethane distilled over calcium hydride. All reactions were carried out under an inert atmosphere of either nitrogen or argon. Silica gel (60 Å pore size, 40 - 63 µm technical grade) was used for chromatography. All starting materials not commercially available are specifically referenced. Alkyllithium was not titrated prior to use. TMEDA was dried with 4 Å MS. Shimadzu™ LC-20AB liquid chromatogram with a SPD-M20A detector used for HPLC. All protons and carbons were assigned using 2D NMR techniques including HSQC, HMBC, NOESY and COESY. Carbons and hydrogens denoted with a prime (*e.g.* $C^{2'}$) indicate the most deshielded carbon/hydrogen when there are two carbons/hydrogens with the same number on the structure. Carbons denoted with two superscripts (*e.g.* $C^{2/3}$) indicate where two environments cannot be readily distinguished from one another. For ^{1}H NMR ap = apparent (e.g. aptd = apparent triple doublet).

Preparation of (S,S_p)-7

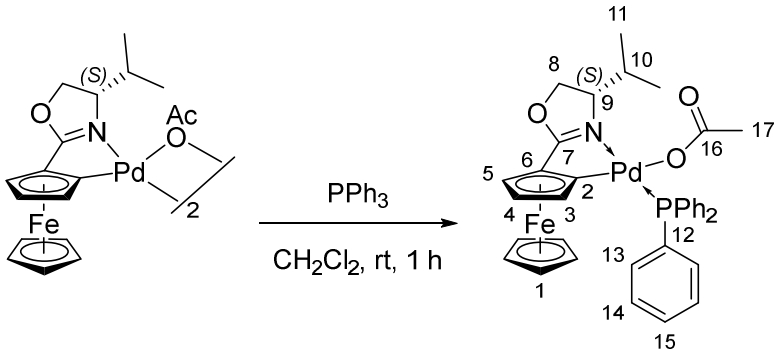


(*S*)-**1**[1] (0.059 g, 0.2 mmol) was added to a flame dried Schlenk tube under an atmosphere of argon and dissolved in dry THF (5 mL). The subsequent orange solution was cooled to -78 °C and stirred for 5 mins after which *n*-butyl lithium (2.5 M in hexanes) (0.11 mL, 0.28 mmol) was slowly added. After stirring for 2 hours the mixture was warmed to 0 °C and chlorodiphenylphosphine oxide (0.076 mL, 0.4 mmol) was added and the reaction was allowed to warm to room temperature. After an additional 15 mins, the reaction was diluted with diethyl ether and then quenched with saturated sodium hydrogen carbonate solution. The organics were separated with H_2O, washed with brine, dried over $MgSO_4$ and the solvent removed *in vacuo* giving a crude product containing a 2:1 mixture of diastereoisomers. The diastereoisomers were separated by column chromatography (SiO_2, 2

% MeOH in Et_2O) yielding the desired product as a yellow brown solid (0.0255 g, 26%): mp 197 - 198 °C; R_f 0.34 (2 % MeOH in Et_2O); $[\alpha]_D^{19.4°C}$ = +114 (*c* = 0.2, chloroform); HRMS (ES) $[M+H]^+$ $C_{28}H_{28}FeNO_2P+H^+$, Calc. 498.1280, Obs. 498.1263; ν_{max} (film)/cm^{-1} 3080, 3062, 2963, 2930, 2871, 1648 (C=N), 1120 (P=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 - 7.71 (2H, m, Ph-$H^{13'}$), 7.69 - 7.64 (2H, m, Ph-H^{13}), 7.50 - 7.46 (1H, m, Ph-$H^{15'}$), 7.45 - 7.36 (5H, m, Ph-$H^{14',14+15}$), 5.06 (1H, dt, *J* = 2.6 + 1.4 Hz, Cp-H^5), 4.49 (5H, s, CpH), 4.45 (1H, dd, *J* = 4.4, 2.4 Hz, Cp-H^4), 4.22 - 4.18 (1H, m, C*H*H), 3.93 (1H, dd, *J* = 3.9, 2.5 Hz, Cp-H^3), 3.72 (1H, td, *J* = 9.3, 6.3 Hz, CH), 3.13 (1H, t, *J* = 8.8 Hz, CH*H*), 1.53 - 1.47 (1H, m, ^{i}Pr-H), 0.81 (3H, d, *J* = 6.8 Hz, ^{i}Pr-CH_3), 0.61 (3H, d, *J* = 6.8 Hz, ^{i}Pr-CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.57 (C^7), 134.86 (d, *J* = 107 Hz, $C^{12'}$), 134.82 (d, *J* = 110.4 Hz, C^{12}), 131.63 (d, *J* = 9.3 Hz, $C^{13'}$), 131.35 (d, *J* = 9.7 Hz, C^{13}), 131.26 (d, *J* = 2.6 Hz, $C^{15'}$), 130.97 (d, *J* = 2.9 Hz, C^{15}), 128.23 (d, *J* = 4.3 Hz, $C^{14'}$), 128.13 (d, *J* = 4.8 Hz, C^{14}), 78.54 (d, *J* = 14.6 Hz, C^3), 75.72 (d, *J* = 109.9 Hz, C^2), 74.49 (d, *J* = 9.1 Hz, C^6), 73.47 (d, *J* = 8.2 Hz, C^5), 72.41 (C^9), 71.54 (d, *J* = 10.9 Hz, C^4), 71.37 (C^1), 70.08 (C^8), 32.30 (C^{10}), 19.16 ($C^{11'}$), 17.97 (C^{11}); ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.4 (P(O)Ph_2).

(*S*,S_p)-**7** was also obtained by the oxidation of (*S*,S_p)-**3**[1] (0.0591 g, 0.123 mmol) with H_2O_2 (2 mL) at room temperature for 1 h after which the reaction was quenched with 10 % sodium thiosulphate solution. The reaction mixture was washed with CH_2Cl_2 and dried with Na_2SO_4. Purification by column chromatography (SiO_2, 1 % MeOH in Et_2O) yielded a yellow brown solid as a single diastereoisomer (0.0248 g, 41 %). Matches data reported above.

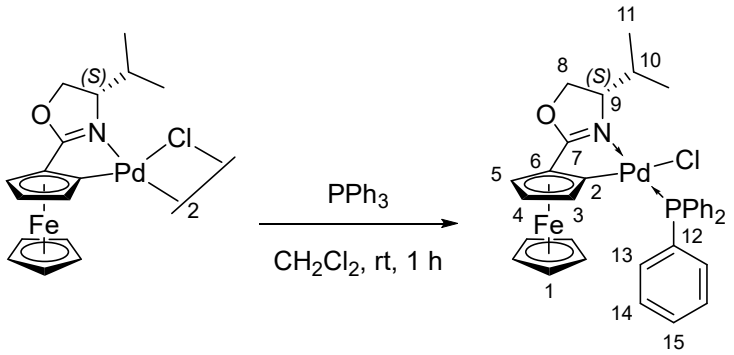
Preparation of (S,S_p)-5a



(S,S_p)-**2a**[2] (0.025 g, 0.029 mmol) and triphenylphosphine (0.015 g, 0.057 mmol) were added to a flame dried Schlenk tube and dissolved in dichloromethane (1 mL) and stirred at room temperature for 1 hour. The solvent was removed *in vacuo* yielding a deep orange solid (0.034 g, 83 %): mp 136 - 137 °C (under argon), ν_{max} (film)/cm^{-1} 3052, 2961, 2925, 2871, 1615 (C=N), 1582 (C=O), 1499; $[\alpha]_D^{23.5°C}$ = -572 (*c* = 0.55, MeCN); MS (EI) $[M]^+$ $C_{36}H_{36}FeNO_3PPd^+$, Calc. 723.1, Obs. 723.1; ^{1}H NMR (500 MHz, MeCN-d^3) δ 7.78 - 7.72, (6H, m, Ph-H^{13}), 7.52 - 7.48 (3H, m, Ph-H^{15}), 7.46 - 7.41 (6H, m, Ph-H^{14}), 4.63 (1H, t, *J* = 9.5 Hz, C*H*H), 4.59 - 4.55 (1H, m, CH*H*), 4.45 (1H, d, *J* = 1.9 Hz, Cp-H^5), 4.07 (1H, ddd, *J* 10.0, 7.5, 4.2 Hz, CH), 4.02 (1H, t, *J* = 2.2 Hz, Cp-H^4), 3.90 (5H, s, CpH), 3.30 (1H, d, *J* = 2.2 Hz, Cp-H^3), 2.34 - 2.26 (1H, m, ^{i}Pr(H)), 1.25 (3H, s, OAc), 1.03 (3H, d, *J* = 6.9 Hz, ^{i}Pr(Me)), 0.88 (3H, d, *J* = 7.2 Hz, ^{i}Pr(Me)); ^{13}C NMR (125 MHz, MeCN-d^3) δ 179.8 (C^7), 176.3 (C^{16}), 135.7 (d, *J* = 12.0 Hz, C^{13}), 132.1 (d, *J* = 50.3 Hz, C^{12}), 131.5 (d, *J* = 2.4 Hz, C^{15}), 129.1 (d, *J* = 10.7 Hz, C^{14}), 90.2 (d, *J* = 8.6 Hz, C^2), 77.3 (d, *J* = 9.0 Hz, C^3), 73.8 (d, *J* = 1.3 Hz, C^6), 73.1 (d, *J* = 3.0 Hz, C^8), 70.9 (C^1), 69.7 (d, *J* = 2.6 Hz, C^4), 68.3 (d, *J* = 3.3 Hz, C^9), 65.6 (C^5), 29.3 (C^{10}), 23.9 (C^{17}), 19.3 (C$^{11'}$), 15.7 (C^{11}); ^{31}P NMR (202 MHz, MeCN-d^3) δ 36.48 (PPh_3).

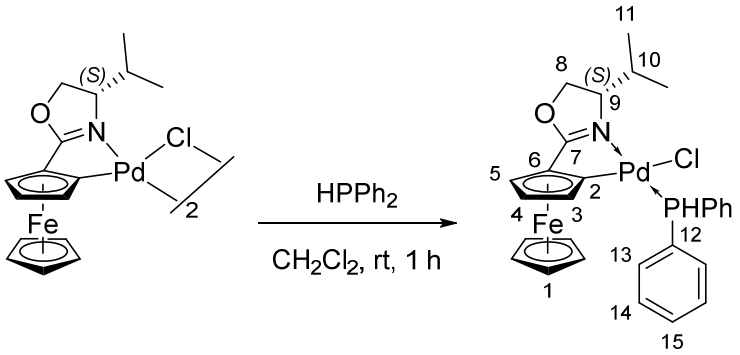
Note: Performing the NMR in $CDCl_3$ showed a slow conversion into the chloride (see Figure S7). It was not possible to obtain the HRMS due to a mixture of isotopologues and weak monoisotopic peaks.

Preparation of (S,S_p)-5b



(S,S_p)-**2b**[3] (0.025 g, 0.029 mmol) and triphenylphosphine (0.015 g, 0.057 mmol) were added to a flame dried Schlenk tube and dissolved in dichloromethane (1 mL) and stirred at room temperature for 1 hour. The solvent was removed *in vacuo* and purification by column chromatography (SiO_2, 20 % EtOAc in hexane) yielded a deep orange solid (0.038 g, 95 %): R_f 0.21 (20 % EtOAc in hexane); mp decomposed ~230 °C (under argon), ν_{max} (film)/cm^{-1} 3077, 3052, 2958, 2925, 2867, 1618 (C=N), 1503; $[\alpha]_D^{22.8°C}$ = -825 (c = 0.26, MeCN); HRMS (AS) [M-Cl]$^+$ $C_{34}H_{33}FeNOPPd^+$, Calc. 664.0699, Obs. 664.0711; ^{1}H NMR (500 MHz, MeCN-d^3) δ 7.78 - 7.72 (6H, m, Ph-H^{13}), 7.53 - 7.49 (3H, m, Ph-H^{15}), 7.48 - 7.43 (6H, m, Ph-H^{14}), 4.67 - 4.57 (2H, m, C*H*H + CH*H*), 4.47 (1H, d, J = 1.9 Hz, Cp-H^5), 4.18 (1H, ddd, J = 10.2, 6.3, 4.2 Hz, CH), 4.02 (1H, t, J = 2.1 Hz, Cp-H^4), 3.97 (5H, s, CpH), 3.04 (1H, brs, Cp-H^3), 2.87 (1H, brs, ^{i}Pr(H)), 1.06 (3H, d, J = 6.9 Hz, ^{i}Pr(Me)), 0.92 (3H, d, J = 7.2 Hz, ^{i}Pr(Me)); ^{13}C NMR (125 MHz, MeCN-d^3) δ 179.9 (C^7), 135.6 (d, J = 11.7 Hz, C^{13}), 132.9 (d, J = 51.3 Hz, C^{12}), 131.6 (C^{15}), 129.1 (d, J = 10.8 Hz, C^{14}), 94.6 (C^2), 75.9 (d, J = 8.7 Hz, C^3), 74.2 (C^6), 73.3 (C^8), 70.9 (C^1), 69.4 (C^4), 68.0 (d, J = 3.1 Hz, C^9), 65.6 (C^5), 29.4 (C^{10}), 19.2 (C$^{11'}$), 15.5 (C^{11}); ^{31}P NMR (202 MHz, MeCN-d^3) δ 37.49 (PPh_3).

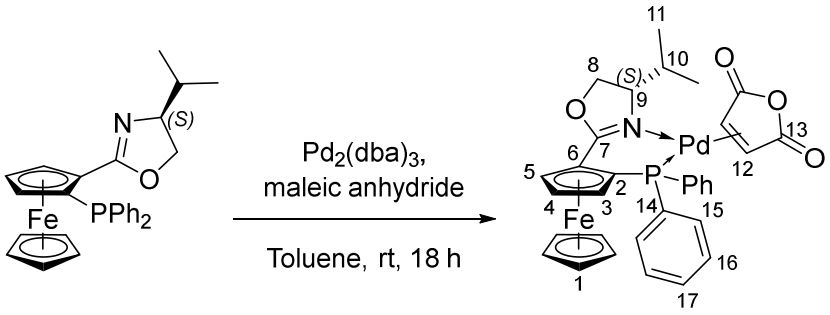
Preparation of (S,S_p)-6b



(S,S_p)-**2b**[3] (0.025 g, 0.029 mmol) and diphenylphosphine (9.92 µl, 0.057 mmol) were added to a flame dried Schlenk tube and dissolved in dichloromethane (1 mL) and stirred at room temperature for 1 hour. The solvent was removed *in vacuo* yielding a deep orange solid (0.025 g, 73 %): mp 110 - 112 °C (under argon), ν_{max} (film)/cm^{-1} 3077, 3055, 2961, 2929, 2871, 1615 (C=N), 1503; $[\alpha]_D^{22.8°C}$ = -882 (c = 0.20, MeCN); MS (EI) $[M]^+$ $C_{28}H_{29}ClFeNOPPd^+$, Calc. 623.0, Obs. 623.0; ^{1}H NMR (500 MHz, MeCN-d^3) δ 8.05 (2H, dd, J = 12.0, 7.4 Hz, Ph-H$^{13'}$), 7.88 (2H, dd, J = 12.7, 7.3 Hz, Ph-H^{13}), 7.58 - 7.49 (4H, m, Ph-H$^{14',15',15}$), 7.47 (2H, td, J = 7.3, 2.0 Hz, Ph-H^{14}), 6.56 (1H, d, J = 388.9 Hz, PH), 4.64 (1H, dd, J = 9.0, 6.2 Hz, C*H*H), 4.57 (1H, t, J = 9.7 Hz, CH*H*), 4.54 (1H, d, J = 2.2 Hz, Cp-H^5), 4.45 (1H, brs, Cp-H^3), 4.37 (1H, t, J = 2.4 Hz, Cp-H^4), 4.17 - 4.12 (1H, m, CH), 4.07 (5H, s, CpH), 2.90 (1H, brs, ^{i}Pr(H)), 1.04 (3H, d, J = 5.9 Hz, ^{i}Pr(Me)), 0.90 (3H, d, J = 7.0 Hz, ^{i}Pr(Me)); ^{13}C NMR (125 MHz, MeCN-d^3) δ 179.9 (C^7), 135.2 (d, J = 11.1 Hz, C$^{13'}$), 134.8 (d, J = 11.4 Hz, C^{13}), 132.2 (d, J = 2.6 Hz, C$^{15'}$), 132.0 (d, J = 2.6 Hz, C^{15}), 129.9 (d, J = 10.8 Hz, C$^{14'}$), 129.7 (d, J = 11.0 Hz, C^{14}), 129.5 (d, J = 51.2 Hz, C$^{12'}$), 129.5 (d, J = 52.8 Hz, C^{12}), 91.6 (d, J = 8.0 Hz, C^2), 74.8 (d, J = 1.0 Hz, C^6), 73.8 (d, J = 15.7 Hz, C^3), 73.2 (d, J = 3.2 Hz, C^8), 70.7 (C^1), 70.2 (d, J = 4.5 Hz, C^4), 68.0 (d, J = 3.4 Hz, C^9), 66.8 (C^5), 29.2 (C^{10}), 19.1 (C$^{11'}$), 15.1 (C^{11}); ^{31}P NMR (202 MHz, MeCN-d^3) δ 8.44 ($HPPh_2$).

Note: It was not possible to obtain the HRMS due to a mixture of isotopologues and weak monoisotopic peaks.

Preparation of (S,S_p)-4

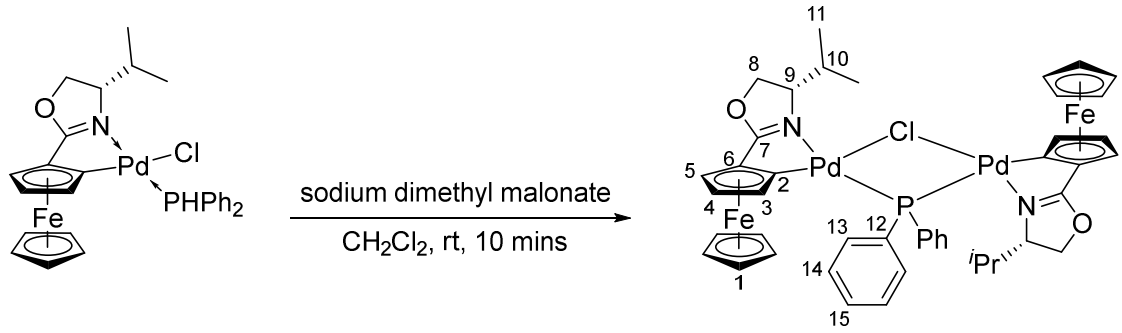


(S,S_p)-**3**[1] (0.087 g, 0.18 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.076 g, 0.08 mmol) and maleic anhydride (0.024 g, 0.24 mmol) were added to a flame dried Schlenk tube and dissolved in toluene (15 mL). The resulting deep purple solution was stirred vigorously overnight resulting in the formation of a dark suspension. The reaction was filtered through Celite™ using toluene as the eluent and the solvent removed *in vacuo*. Purification by column chromatography (SiO_2, 40 % EtOAc in hexane) yielded an orange solid (0.07 g, 61 %): mp decomposed ~200 °C (under argon), ν_{max} (film)/cm^{-1} 3056, 3016, 2960, 2923, 2873, 1790 (C=O), 1723 (C=O), 1626 (C=N); $[\alpha]_D^{20.5°C}$ = -538 (c = 0.46, $CHCl_3$); HRMS (AS) $[M+H]^+$ $C_{32}H_{30}FeNO_4PPd+H^+$, Calc. 686.0389, Obs. 686.0389; Major isomer ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (2H, ddd, J = 11.6, 7.8, 1.5 Hz, Ph-H$^{15'}$), 7.56 - 7.46 (3H, m, Ph-H$^{16',17'}$), 7.33 - 7.27 (3H, m, Ph-H^{16,17}), 7.08 (2H, ddd, J = 11.0, 6.6, 3.2 Hz, Ph-H^{15}), 5.04 (1H, brs, Cp-H^5), 4.70 (1H, t, J = 2.6 Hz, Cp-H^4), 4.41 - 4.38 (1H, m, Cp-H^3), 4.35 (1H, t, J = 3.7 Hz, C-H$^{12'}$), 4.33 - 4.21 (3H, m, C*H*H, CH*H*, C-H^9), 4.07 (1H, dd, J = 10.5, 3.8 Hz, C-H^{12}), 3.96 (5H, s, CpH), 2.80 (1H, dtd, J = 13.8, 6.9, 3.3 Hz, ^{i}Pr(H)), 1.07 (3H, d, J = 7.1 Hz, ^{i}Pr(Me)), 0.99 (3H, d, J = 6.9 Hz, ^{i}Pr(Me)); Minor isomer ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 - 7.68 (2H, m, Ph-H$^{15'}$), 7.56 - 7.46 (3H, m, Ph-H$^{16',17}$), 7.33 - 7.27 (3H, m, Ph-H^{16,17}), 7.21 - 7.14 (2H, m, Ph-H^{15}), 5.04 (1H, brs, Cp-H^5), 4.72 (1H, t, J = 2.6 Hz, Cp-H^4), 4.50 - 4.46 (1H, m, Cp-H^3), 4.33 - 4.21 (3H, m, C*H*H, CH*H*, C-H^9), 3.86 (5H, s, CpH), 3.87 - 3.79 (2H, m, C-H$^{12',12}$), 2.67 (1H, dtd, J = 13.7, 6.9, 3.4 Hz, ^{i}Pr(H)), 1.04 (3H, d, J = 7.0 Hz, ^{i}Pr(Me)), 0.95 (3H, d, J = 6.8 Hz, ^{i}Pr(Me)); Major isomer ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6 (d, J = 2.0 Hz, C$^{13'}$), 171.5 (d, J = 5.2 Hz, C^{13}), 169.1 (C^7), 135.5 (d, J = 36.7 Hz, C$^{14'}$), 134.9 (d, J = 16.7 Hz, C$^{15'}$), 134.7 (d, J = 40.1 Hz, C^{14}), 131.6 (d, J = 13.3 Hz, C^{15}), 131.2 (d, J = 2.0 Hz, C$^{17'}$), 129.4 (d, J = 1.6 Hz, C^{17}), 128.6 (d, J = 10.8 Hz, C$^{16'}$), 128.5 (d, J = 9.7 Hz, C^{16}), 75.5 (d, J = 2.6 Hz, C^3), 74.0 (d, J = 2.3 Hz, C^4), 73.5 (d, J = 46.2 Hz, C^2), 73.4 (d, J = 1.5 Hz, C^5), 73.1 (C^6), 71.8 (d, J = 0.5 Hz, C^9), 71.4 (C^1), 67.7 (C^8), 47.4 (d, J = 31.7 Hz, C$^{12'}$), 46.4 (d, J = 1.8 Hz, C^{12}), 29.2 (C^{10}), 19.2 (C$^{11'}$), 14.7 (C^{11}); Minor isomer ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9 (d,

J = 1.5 Hz, $C^{13'}$), 171.2 (d, *J* = 5.0 Hz, C^{13}), 169.1 (C^{7}), 137.3 (d, *J* = 37.8 Hz, $C^{14'}$), 135.1 (d, *J* = 16.6 Hz, $C^{15'}$), 133.7 (d, *J* = 40.2 Hz, C^{14}), 131.4 (d, *J* = 13.1 Hz, C^{15}), 131.4 (d, *J* = 2.1 Hz, $C^{17'}$), 129.1 (d, *J* = 1.5 Hz, C^{17}), 128.8 (d, *J* = 11.2 Hz, $C^{16'}$), 128.5 (d, *J* = 9.7 Hz, C^{16}), 75.9 (d, *J* = 2.7 Hz, C^{3}), 75.1 (d, *J* = 1.8 Hz, C^{9}), 74.0 (d, *J* = 33.0 Hz, C^{2}), 74.0 (d, *J* = 2.1 Hz, C^{4}), 73.4 (d, *J* = 1.3 Hz, C^{5}), 73.1 (C^{6}), 71.6 (C^{1}), 67.7 (C^{8}), 47.8 (d, *J* = 1.7 Hz, $C^{12'}$), 46.7 (d, *J* = 32.7 Hz, C^{12}), 29.2 (C^{10}), 19.2 ($C^{11'}$), 14.9 (C^{11}); Major isomer ^{31}P NMR (202 MHz, $CDCl_3$) δ 14.44 (PPh_2); Minor isomer ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.83 (PPh_2).

Note: compound exists as a 1 : 1.6 ratio of isomers.

Preparation of (*S*,*S*,*S*$_p$,*S*$_p$)-8b

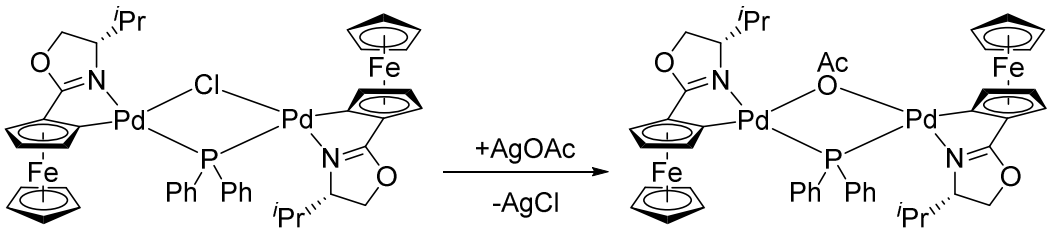


In a flame dried Schlenk tube (tube-1), sodium *tert*-butoxide solution (2M in THF) (0.05 mL, 0.10 mmol) was added to a solution of dimethyl malonate (22.6 µl, 0.20 mmol) in THF (1 mL) at 0 °C and allowed to stir for 30 mins and then the solvent was removed under high vacuum to give a beige residue. In a separate flame dried Schlenk tube (tube-2), (*S*,*S*$_p$)-**6b** (0.0125 g, 0.020 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and then the contents of Schlenk tube (2) were transferred to Schlenk tube (1) and stirred at room temperature for 10 mins. The solvent was then removed *in vacuo* and the residue purified by column chromatography (SiO_2, 10 % EtOAc in hexane) to give an orange solid (0.007 g, 70 %): R_f 0.26 (20 % Et_2O in Hexane); mp >230 °C (under argon), ν_{max} (film)/cm^{-1} 3096, 2958, 2923, 2967, 1617 (C=N), 1495; $[\alpha]_D^{20.1^\circ C}$ = -2000 (*c* = 0.23, $CHCl_3$); HRMS (AS) $[M\text{-}Cl]^+$ $C_{44}H_{46}Fe_2N_2O_2PPd_2^+$, Calc. 991.0103, Obs. 991.0093; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 - 8.05 (4H, m, Ph-H^{13}), 7.38 - 7.34 (6H, m, Ph-H^{14+15}), 4.49 - 4.47 (4H, m, C*H*H + CH*H*), 4.36 (2H, d, *J* = 1.8 Hz, Cp-H^5), 4.08 (2H, td, *J* = 8.0, 4.6 Hz, CH), 4.04 (10H, s, CpH), 4.02 (2H, t, *J* = 2.3 Hz, Cp-H^4), 3.22 (2H, d, *J* = 1.6 Hz, Cp-H^3), 2.51 - 2.43 (2H, m, ^{i}Pr(H)), 1.06 (6H, d, *J* = 6.8 Hz, ^{i}Pr(Me)), 0.97 (6H, d, *J* = 7.0 Hz, ^{i}Pr(Me)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.9 (C^7), 137.2 (d, *J* = 32.8 Hz, C^{12}), 135.4 (d, *J* = 12.7 Hz, C^{13}), 128.8 (C^{15}), 127.8 (d, *J* = 10.5 Hz, C^{14}), 91.4 (d, *J* = 2.9 Hz, C^2), 75.1 (d, *J* = 8.6 Hz, C^3),

73.3 (d, J = 1.6 Hz, C^6), 72.2 (C^8), 70.0 (C^1), 69.0 (C^4), 66.9 (C^9), 64.5 (C^5), 29.3 (C^{10}), 19.6 ($C^{11'}$), 16.0 (C^{11}); ^{31}P NMR (202 MHz, $CDCl_3$) δ 23.40 (PPh_2).

See Figure S28 for the X-ray structure.

Note: Addition of excess AgOAc to an NMR tube containing (S,S,S_p,S_p)-**8b** showed the formation of acetate bridged palladacycle (S,S,S_p,S_p)-**8a** (see Figures S20-22 for the NMR spectra).



ν_{max} (film)/cm^{-1} 3096, 2958, 2919, 2849, 1621 (C=N), 1556 (C=O), 1495; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 - 7.97 (4H, m, Ph-H), 7.33 - 7.27 (6H, m, Ph-H), 4.51 - 4.46 (4H, m, C*H*H + CH*H*), 4.34 (2H, brs, Cp-H), 4.09 - 4.03 (2H, m, CH), 4.00 (10H, s, CpH), 3.97 (2H, brs, Cp-H), 3.00 (2H, brs, Cp-H^3), 2.70 - 2.60 (2H, m, ^{i}Pr(H)), 2.01 (3H, brs, OAc), 1.04 (6H, d, J = 6.8 Hz, ^{i}Pr(Me)), 0.95 (6H, d, J = 7.1 Hz, ^{i}Pr(Me)); ^{31}P NMR (202 MHz, $CDCl_3$) δ 55.63 (PPh_2).

Note: after filtering off the excess AgOAc and precipitated AgCl a ^{1}H NMR was obtained in $CDCl_3$ and this showed the conversion back to **8b** as a result of ligand exchange (see Figure S23)

2. Phosphine insertion ^{31}P NMR studies

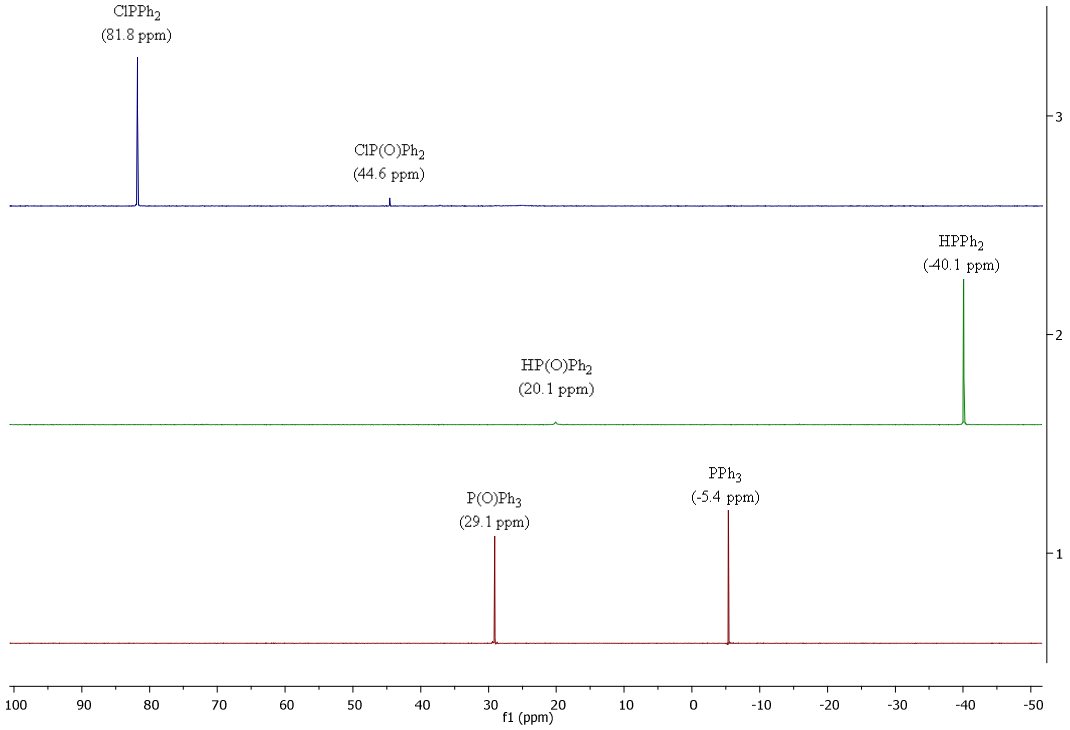
Phosphine reference compounds

a) PPh_3 & $P(O)Ph_3$ (red spectrum), $HPPh_2$ & $HP(O)Ph_2$ (green spectrum) and $ClP(O)Ph_2$ & $ClPPh_2$ (blue spectrum).

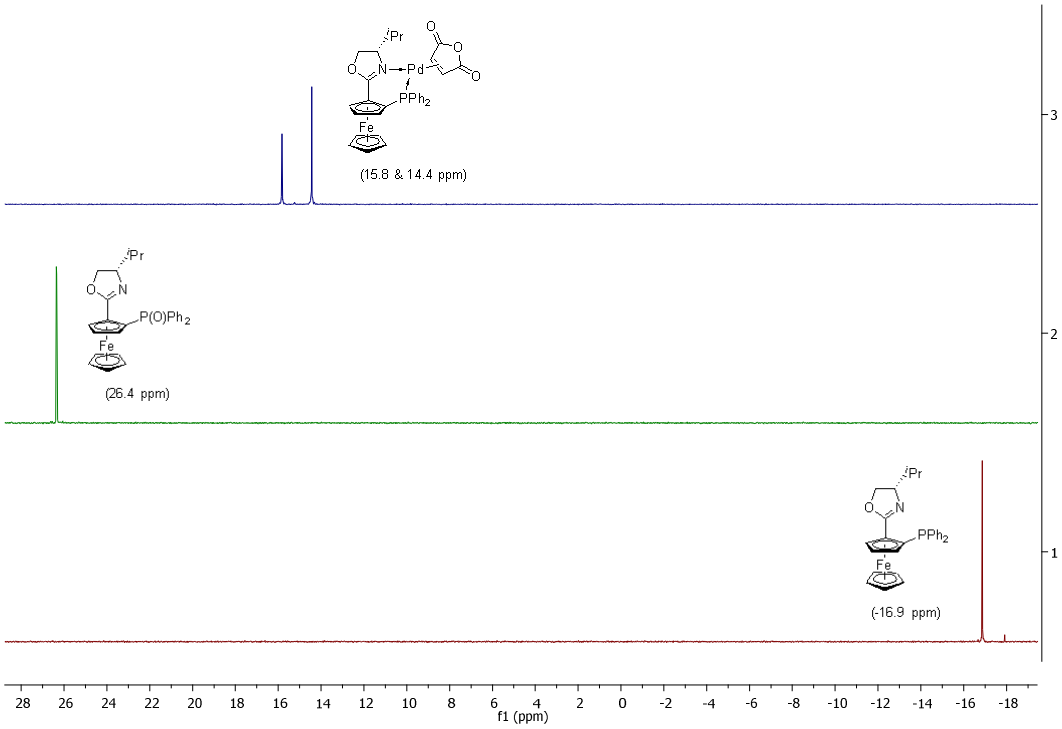
b) (*S*,*S*$_p$)-**3** (red spectrum), (*S*,*S*$_p$)-**7** (green spectrum) and (*S*,*S*$_p$)-**4** (blue spectrum).

c) (*S*,*S*$_p$)-**5a** (red spectrum), (*S*,*S*$_p$)-**5b** (green spectrum) and (*S*,*S*$_p$)-**6b** (blue spectrum).

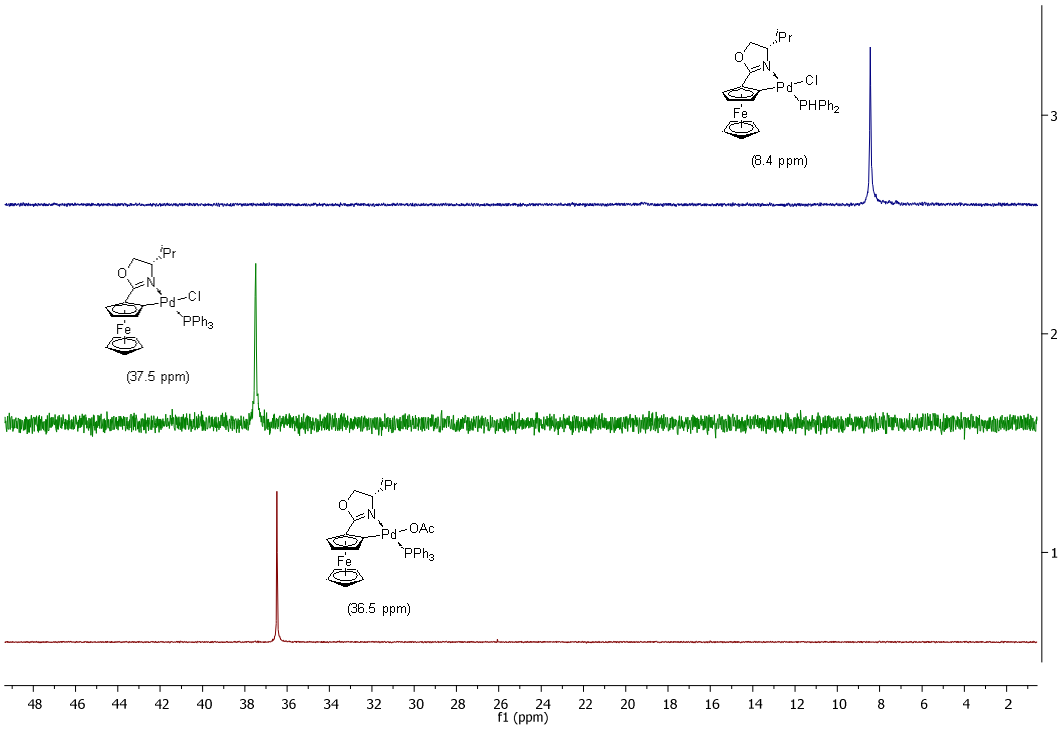
a) Phosphine reference compounds - ^{31}P NMR (202 MHz, $CDCl_3$)



b) Phosferrox reference compounds - ^{31}P NMR (202 MHz, $CDCl_3$)



c) Palladacycle reference compounds - ^{31}P NMR (202 MHz, MeCN-d^3)

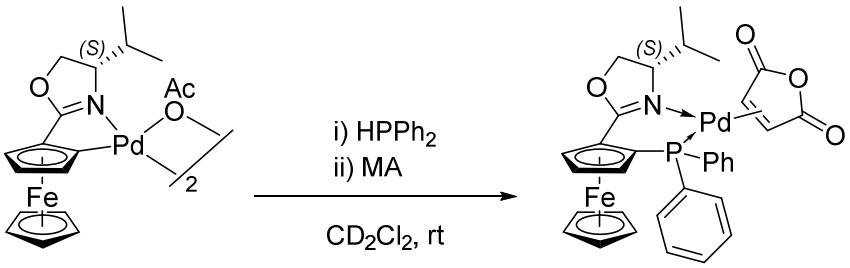


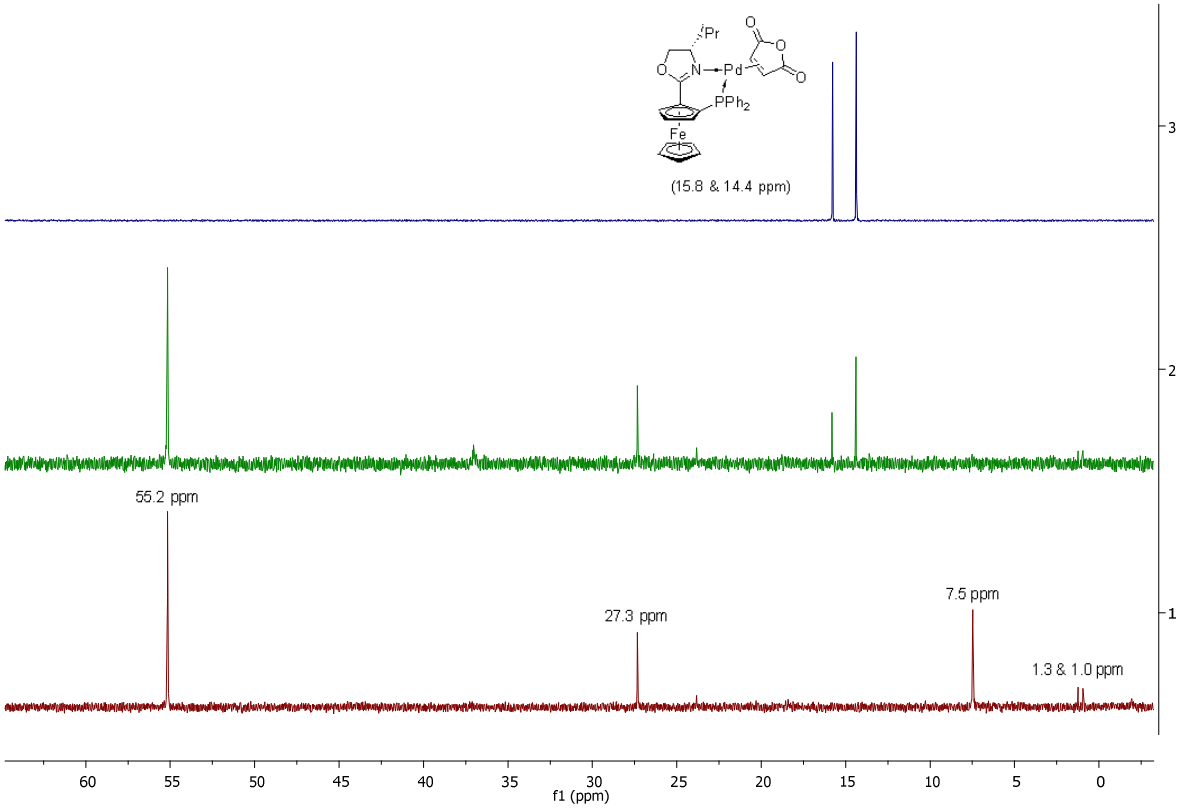
Phosphine insertion studies (A-D)

All peaks are labelled starting from the lowest spectra (red). Only new peaks that appear on the spectra above are labelled. For all, the top spectrum is the (*S*,S_p)-**4**. A short description is shown below the spectral comparison. Experiments performed with 0.01 mmol of either acetate bridged palladacycle (*S*,S_p)-**2a** or chloride bridged palladacycle (*S*,S_p)-**2b** dissolved in 0.7 mL CD_2Cl_2 in an NMR tube with a J. Young valve under an inert atmosphere. After addition of reagents approximately 10 minutes elapsed before NMR experiments were ran. A glove box was used for the preparation of samples.

MA = maleic anhydride, DMM = dimethyl malonate & NaDMM = sodium dimethyl malonate.

A. Addition of $HPPh_2$ to (S,S_p)-**2a** followed by addition of MA - ^{31}P NMR (202 MHz, CH_2Cl_2).

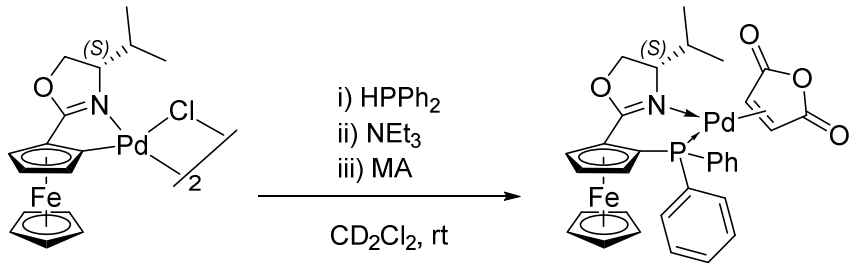


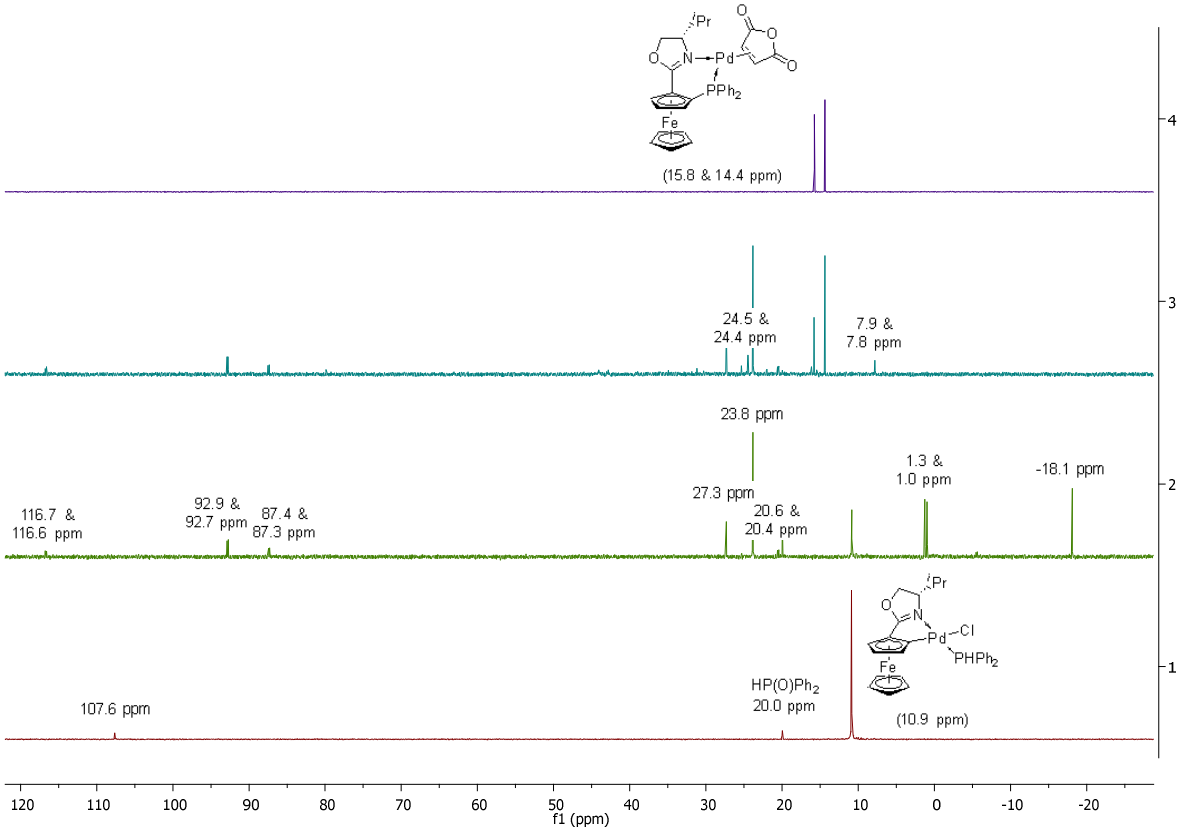


Orange solution of (S,S_p)-**2a** went very dark (almost black) upon addition of 2 eq. $HPPh_2$ (red spectrum), no colour change upon addition of 2 eq. MA (green spectrum).

See Figure S24 for integration of {^{31}P} NMR spectrum (after the addition of MA).

B. Addition of $HPPh_2$ to (S,S_p)-**2b**, followed by addition of NEt_3 then MA - ^{31}P NMR (202 MHz, CH_2Cl_2).

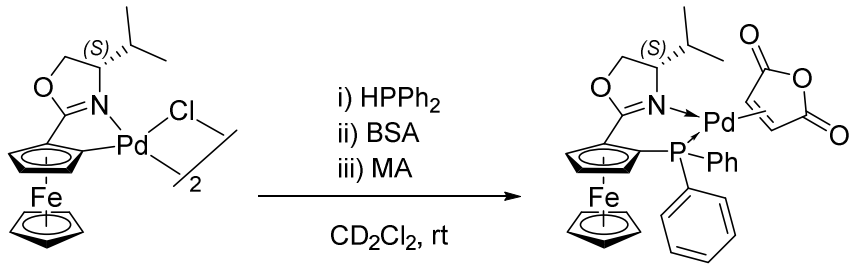


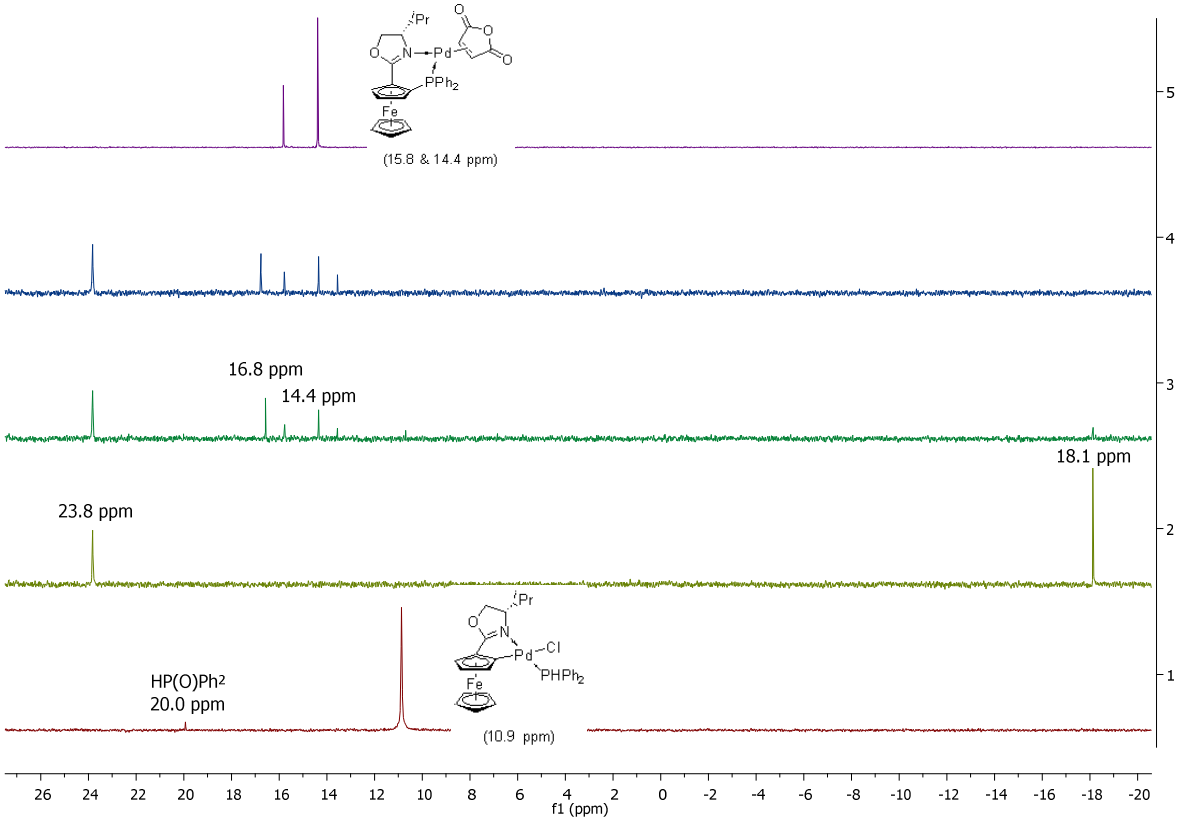


Addition of 2 eq. $HPPh_2$ to an orange solution of (S,S_p)-**2b** showed the formation of the previously characterised complex (S,S_p)-**6b** ($HPPh_2$ used contained a small amount of oxidised phosphine - red spectrum). 2 eq. triethylamine was added, causing the deep orange solution to darken considerably (green spectrum) followed by 4 eq. MA (blue spectrum).

See Figure S25 for integration of {^{31}P} NMR spectrum (after the addition of MA).

C. Addition of BSA to a mixture of (S,S_p)-**2b** and $HPPh_2$ followed by addition of MA - ^{31}P NMR (202 MHz, CH_2Cl_2).

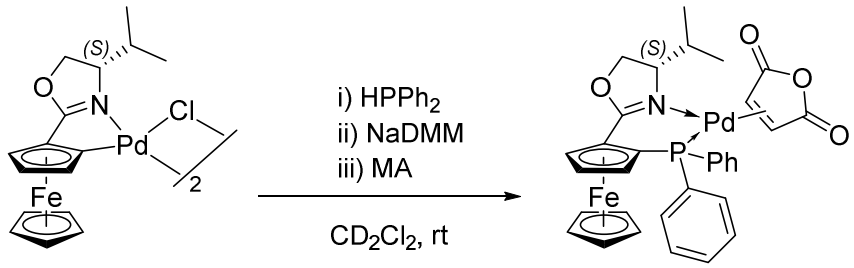


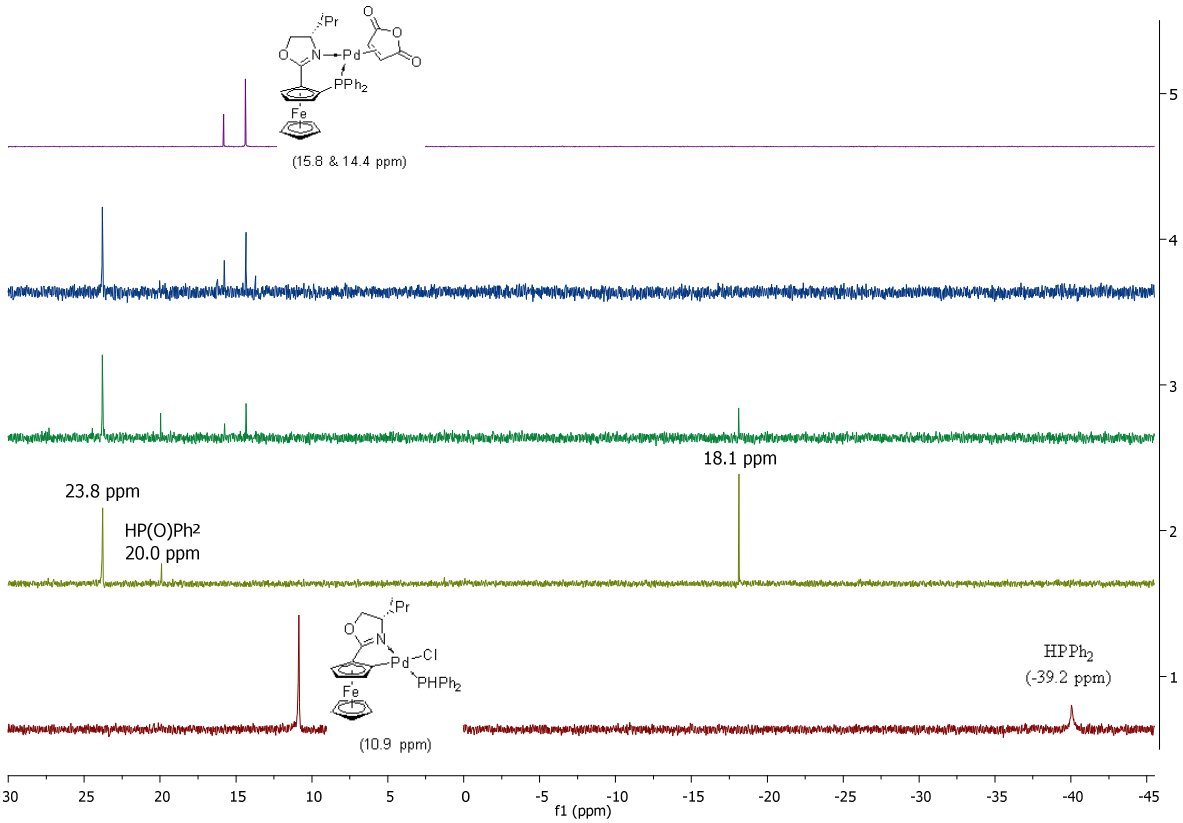


2 eq. $HPPh_2$ was added to (S,S_p)-**2b** (red spectrum). BSA (10 eq.) was added in one go causing the solution to go very dark red (lime green spectrum). Addition of 2 eq. MA showed no apparent colour change (green spectrum). Leaving the sample overnight showed complete loss of the signal at 18.1 ppm (blue spectrum).

See Figure S26 for integration of {^{31}P} NMR spectrum (after the addition of MA – blue spectrum).

D. Addition of a mixture of (S,S_p)-**2b** and $HPPh_2$ to NaDMM salt followed by addition of MA - ^{31}P NMR (202 MHz, CH_2Cl_2).





2 eq. $HPPh_2$ was added to (S,S_p)-**2b** (red spectrum). This solution was then added to pre prepared NaDMM salt (10 eq.) which went very dark within 1 min (lime green spectrum). Addition of 2 eq. MA showed no apparent colour change and formation of (S,S_p)-**3** (18.1 ppm) and (S,S,S_p,S_p)-**8b** (23.8 ppm) (green spectrum). Addition of a further 2 eq. of MA resulted in the loss of the signal at 18.1 ppm (blue spectrum) to leave (S,S_p)-**4** and (S,S,S_p,S_p)-**8b** in solution.

See Figure S27 for integration of {^{31}P} NMR spectrum (after the addition of MA - blue spectrum).

3. Methods of Pd(0) Generation and Catalysis

Catalysis experiments

Conditions A

(I) In a flame dried Schlenk tube, (S,S_p)-**3** (0.0120 g, 0.025 mmol) and $[Pd(C_3H_5)Cl]_2$ (0.0037 g, 0.010 mmol) dissolved in CH_2Cl_2 (1.7 mL) and stirred for 30 mins. 1,3-Diphenylallyl acetate (0.252 g, 1.0 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and added to the reaction vessel. This was followed sequentially by dimethyl malonate (0.34 mL, 3.0 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (0.74 mL, 3.0 mmol) and potassium acetate (0.002 g, 0.02 mmol) and the reaction allowed to stir at room temperature.

(II) In a flame dried Schlenk tube, (S,S_p)-**4** (0.0069 g, 0.010 mmol) dissolved in CH_2Cl_2 (1.7 mL). 1,3-Diphenylallyl acetate (0.252 g, 1.0 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and added to the reaction vessel. This was followed sequentially by dimethyl malonate (0.34 mL, 3.0 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (0.74 mL, 3.0 mmol) and potassium acetate (0.002 g, 0.02 mmol) and the reaction allowed to stir at room temperature.

(III) In a flame dried Schlenk tube, (S,S_p)-**2a** (0.0092 g, 0.010 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and $HPPh_2$ (3.48 µl, 0.020 mmol) was added and stirred for 10 mins. 1,3-Diphenylallyl acetate (0.252 g, 1.0 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and added to the reaction vessel. This was followed sequentially by dimethyl malonate (0.34 mL, 3.0 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (0.74 mL, 3.0 mmol) and potassium acetate (0.002 g, 0.02 mmol) and the reaction allowed to stir at room temperature.

(IV) In a flame dried Schlenk tube, (S,S_p)-**2b** (0.0088 g, 0.010 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and $HPPh_2$ (3.48 µl, 0.020 mmol) was added and stirred for 10 mins. 1,3-Diphenylallyl acetate (0.252 g, 1.0 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and added to the reaction vessel. This was followed sequentially by dimethyl malonate (0.34 mL, 3.0 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (0.74 mL, 3.0 mmol) and potassium acetate (0.002 g, 0.02 mmol) and the reaction allowed to stir at room temperature.

Conditions B

(V) In a flame dried Schlenk tube, (S,S_p)-**3** (0.0120 g, 0.025 mmol) and $[Pd(C_3H_5)Cl]_2$ (0.0037 g, 0.010 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and stirred for 30 mins. 1,3-

Diphenylallyl acetate (0.252 g, 1.0 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and added to the reaction vessel followed by sodium dimethyl malonate (3 mmol) and allowed to stir at room temperature. Sodium dimethyl malonate was prepared by addition of sodium *tert*-butoxide solution (2M in THF) (1.50 mL, 3.0 mmol) to a solution of dimethyl malonate (0.34 mL, 3.0 mmol) in THF (2.5 mL) at 0 °C and allowed to stir for 30 mins and then the solvent was removed under high vacuum to give a beige powder.

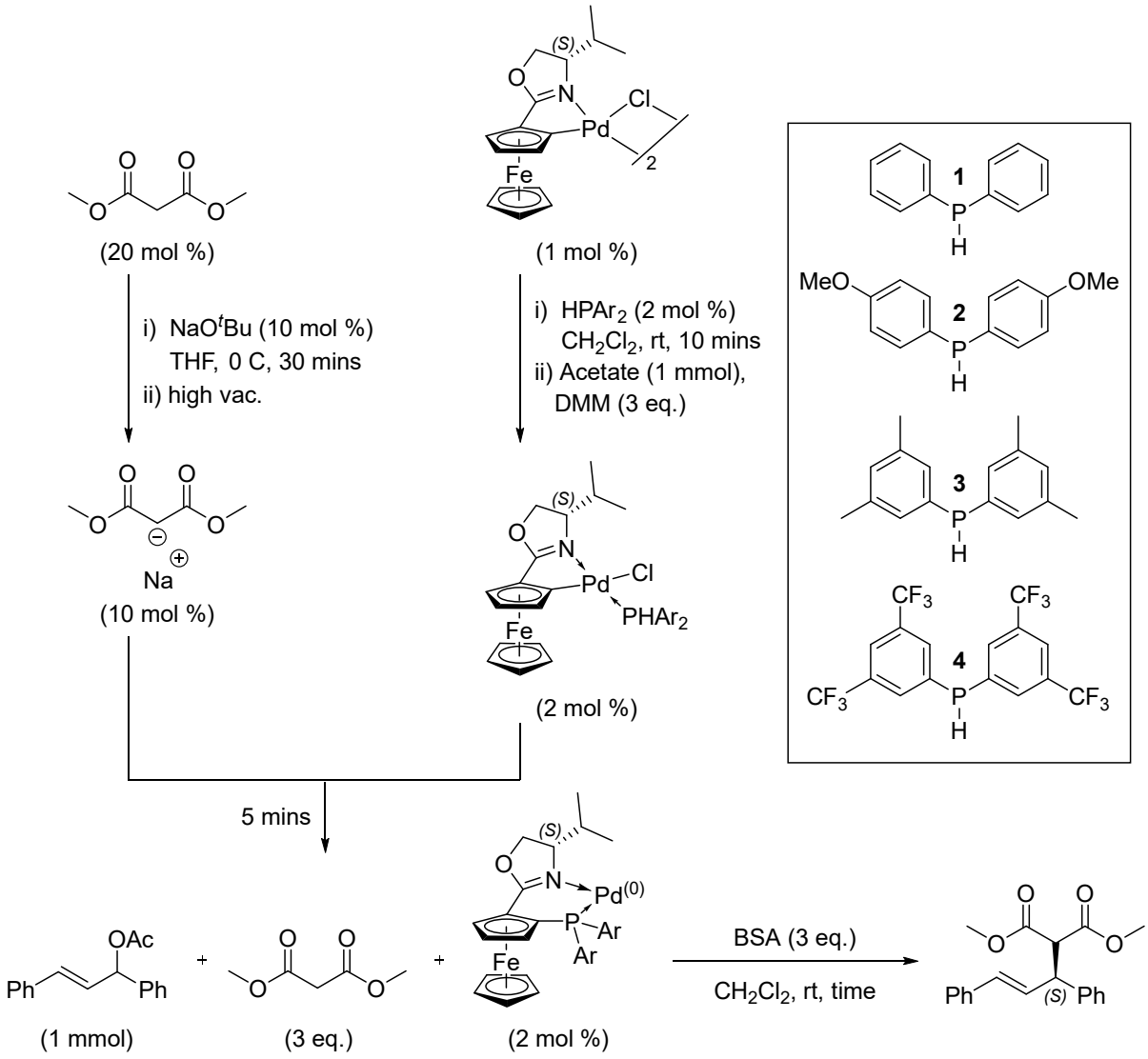
(VI) In a flame dried Schlenk tube, (S,S_p)-**2b** (0.0088 g, 0.010 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and $HPPh_2$ (3.48 µl, 0.020 mmol) was added and stirred for 10 mins. 1,3-Diphenylallyl acetate (0.252 g, 1.0 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and added to the reaction vessel followed by sodium dimethyl malonate (3 mmol) and allowed to stir at room temperature. Sodium dimethyl malonate was prepared by addition of sodium *tert*-butoxide solution (2M in THF) (1.50 mL, 3.0 mmol) to a solution of dimethyl malonate (0.34 mL, 3.0 mmol) in THF (2.5 mL) at 0 °C and allowed to stir for 30 mins and then the solvent was removed under high vacuum to give a beige powder.

Table S1. Catalysis optimisation.

Entry	Method	Reaction time	Conversion (%)	ee %[a]
1	**(I)**	< 1 h	100 %	95%
2	**(II)**	4 days	6 %	86%
3	**(III)**	4 days	51 %	85%
4	**(IV)**	4 days	77 %	85%
5	**(IV)**[b]	4 days	20 %	94%
6	**(IV)**[c]	4 days	0 %	-
7	**(IV)**[d]	4 days	0 %	-
8	**(V)**	3.5 h	100 %	88%
9	**(VI)**	2.5 h	100 %	77%

a = Major enantiomer has the *S* configuration, b = at 3rd of the scale with no KOAc added, c = THF used as the solvent, d = toluene used as the solvent.

Final catalytic experimental procedure (Conditions C)



In a flame dried Schlenk tube (tube-1), sodium *tert*-butoxide solution (2M in THF) (0.05 mL, 0.10 mmol) was added to a solution of dimethyl malonate (22.6 µl, 0.20 mmol) in THF (1 mL) at 0 °C and allowed to stir for 30 mins and then the solvent was removed under high vacuum to give a beige residue. In a separate flame dried Schlenk tube (tube-2), (*S*,*S*$_p$)-**2b** (0.0088 g, 0.010 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and phosphine (0.020 mmol) was added and stirred for 10 mins. 1,3-Diphenylallyl acetate (0.252 g, 1.0 mmol) was dissolved in CH_2Cl_2 (1.7 mL) and then added to Schlenk tube (2) followed by dimethyl malonate (0.34 mL, 3.0 mmol). The contents of Schlenk tube (2) were transferred to Schlenk tube (1) and stirred for 5 mins after which *N*,*O*-bis(trimethylsilyl)acetamide (0.74 mL, 3.0 mmol) was added and the reaction allowed to stir at room temperature. After completion or 24 hours (whichever came first), the reaction was quenched with saturated ammonium chloride, separated with

diethyl ether, dried with magnesium sulphate and the solvent removed *in vacuo*. A ^{1}H NMR was performed at this point to determine the conversion. Purification by column chromatography (SiO_2, 5 % EtOAc in hexane) gave the product as a colourless oil which was subjected to chiral HPLC analysis. See Table S2 for results.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 - 7.27 (8H, m, Ph-H), 7.26 - 7.18 (2H, m, Ph-H), 6.48 (1H, d, *J* = 15.7 Hz, C=C-H), 6.33 (1H, dd, *J* = 15.7, 8.6 Hz, C=C-H), 4.27 (1H, dd, *J* = 10.8, 8.7 Hz, CH), 3.96 (1H, d, *J* = 10.9 Hz, CH), 3.71 (3H, s, OCH_3), 3.52 (3H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 167.9, 140.3, 137.0, 132.0, 129.3, 128.9, 128.6, 128.0, 127.7, 127.3, 126.5, 57.8, 52.8, 52.6, 49.3. Matches previously reported data.[5, 6]

Enantiomeric excess was determined by chiral HPLC analysis using a CHIRALCEL OD-H; Eluent = 98:2 (Hexane:IPA); Flow rate = 0.5 mL min^{-1}; Concentration = 0.0015 gmL^{-1}, Injection volume = 5 µl, wavelength = 254 nm. (*S*)-enantiomer RT = 20.5 min, (*R*)-enantiomer RT = 18.9 min.

Note: when the phosphine used is a solid, a stock solution was prepared in a glove box with CH_2Cl_2 and the volume used subtracted from the volume of CH_2Cl_2 used to dissolve (S,S_p)-**2b**.

Table S2. Allylic alkylation results.

Entry	$HPAr_2$	Reaction time	Conversion (%)	ee %[a]
1	**1**	1 h	98.6 %	86%
2	**2**	24 h	100 %	83%
3	**3**	24 h	100 %	84%
4	**4**	24 h	18.0 %	85%

a = Major enantiomer has the *S* configuration.

See Figures S29-32 for HPLC traces of the product.

4. ^{1}H, ^{13}C and ^{31}P spectra for new compounds

Figure S1. **7** - ^{1}H NMR (500 MHz, $CDCl_3$).

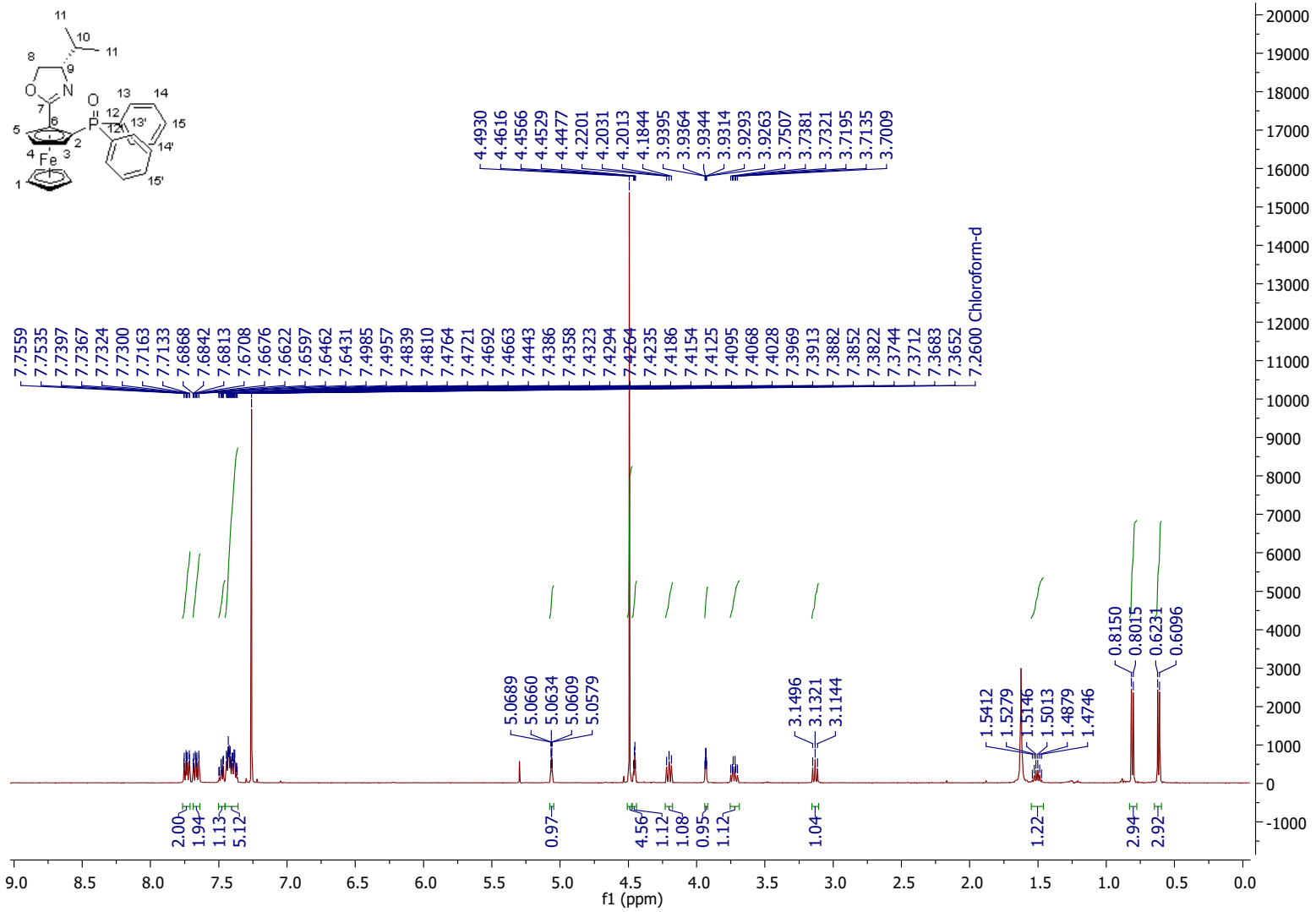


Figure S2. **7** - ^{13}C NMR (125 MHz, $CDCl_3$).

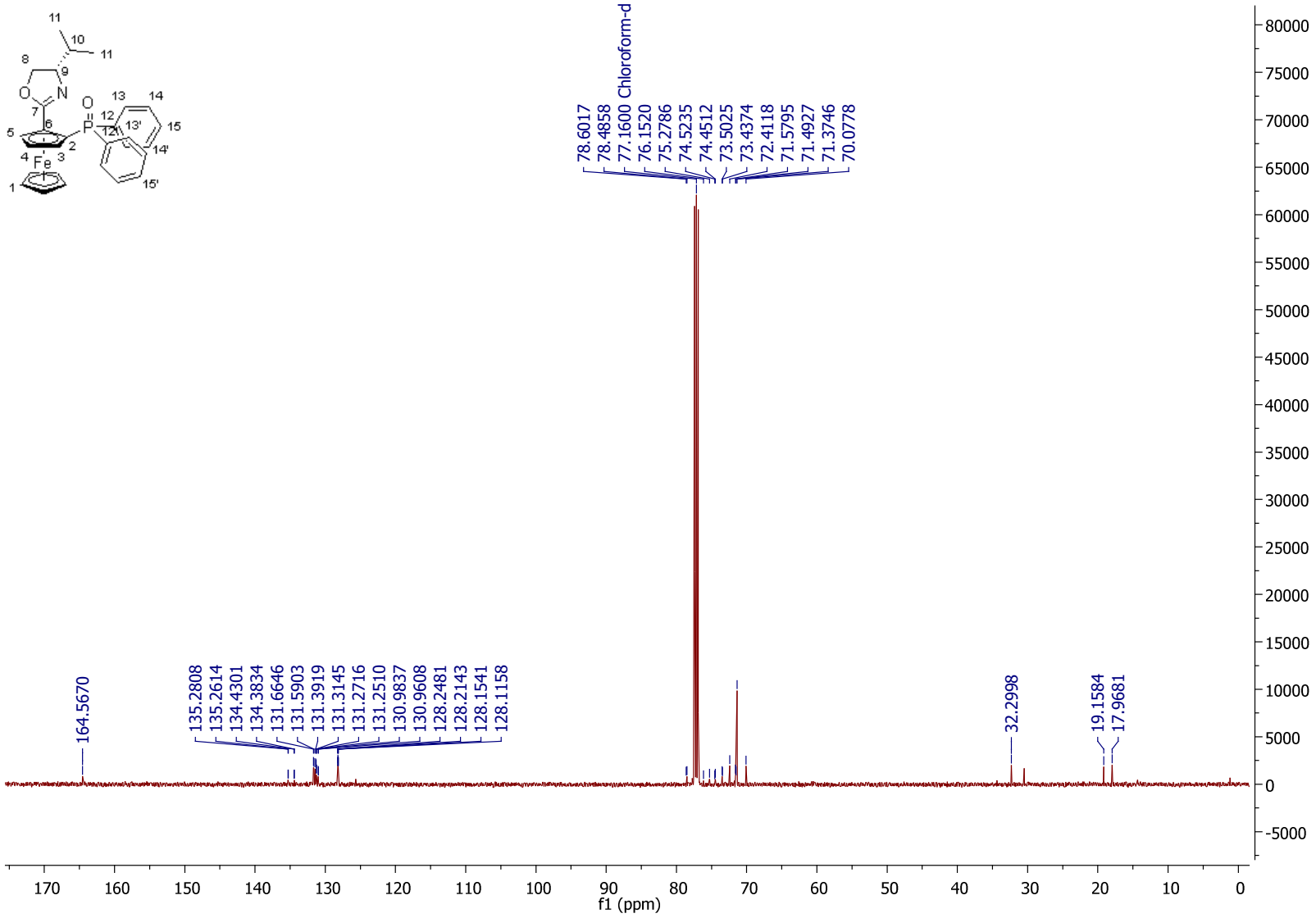


Figure S3. **7** - ^{31}P NMR (202 MHz, $CDCl_3$).

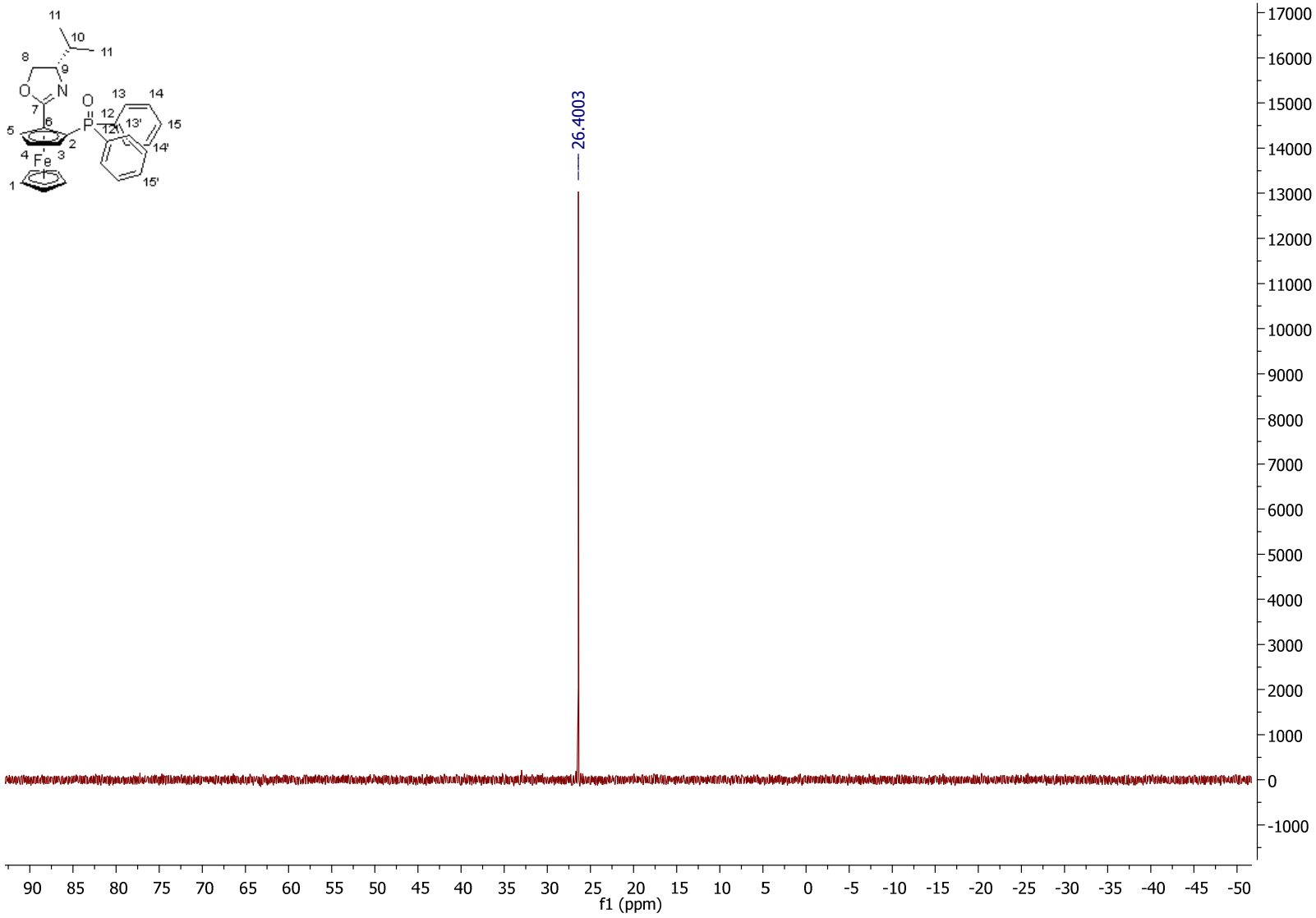


Figure S4. **5a** - ^{1}H NMR (500 MHz, MeCN-d^{3}).

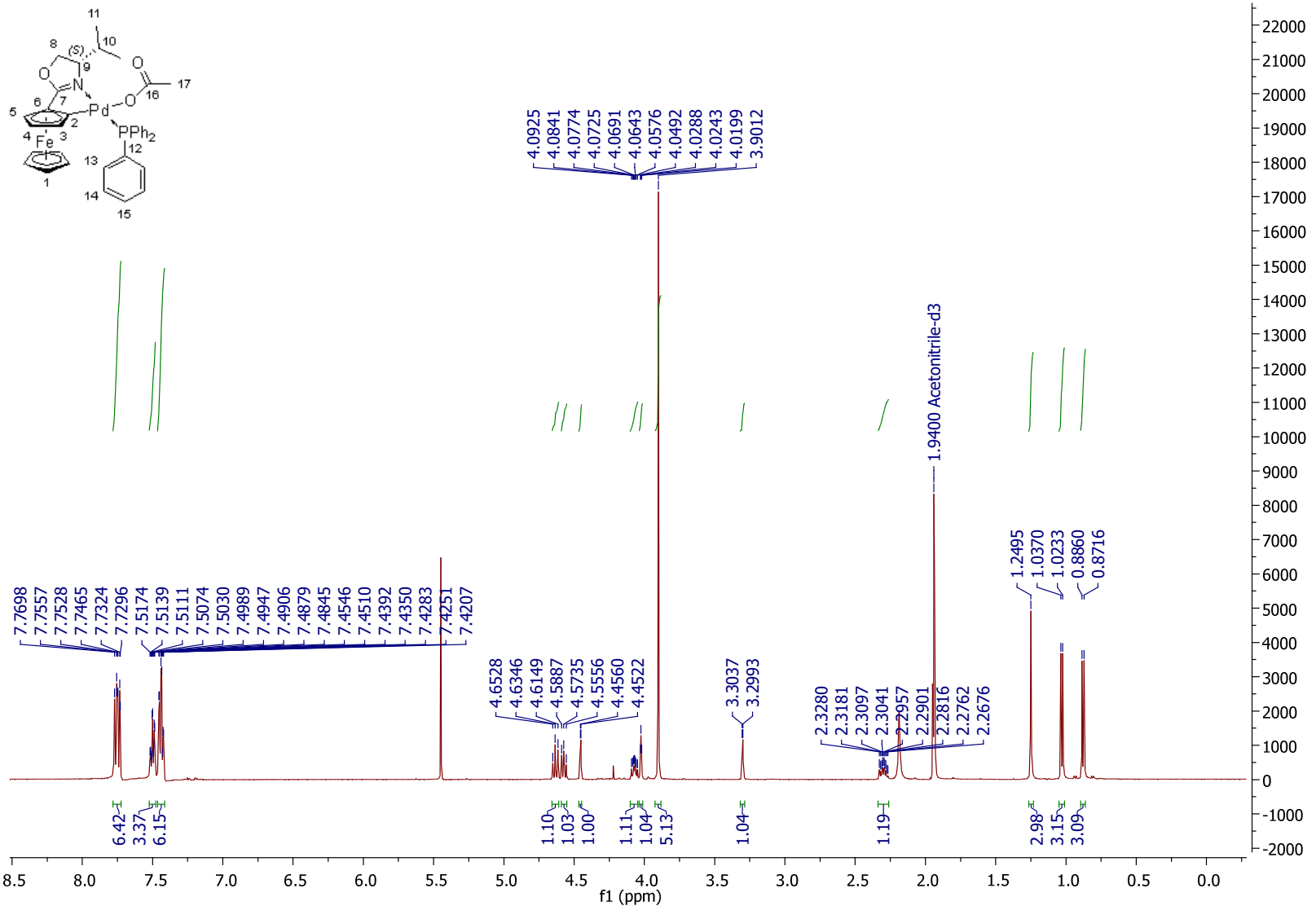


Figure S5. **5a** - ^{13}C NMR (125 MHz, MeCN-d^3).

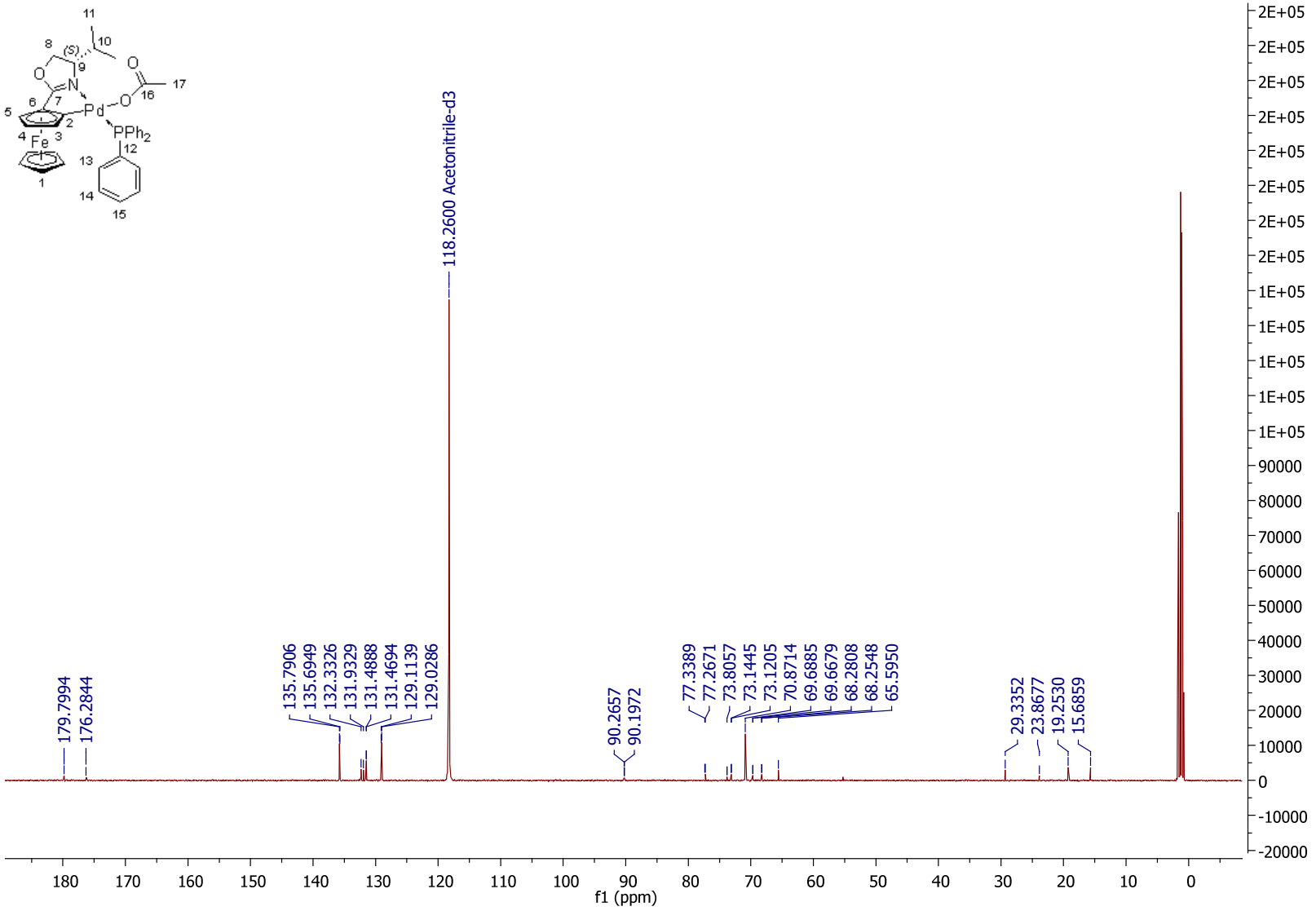


Figure S6. **5a** - ^{31}P NMR (202 MHz, MeCN-d^3).

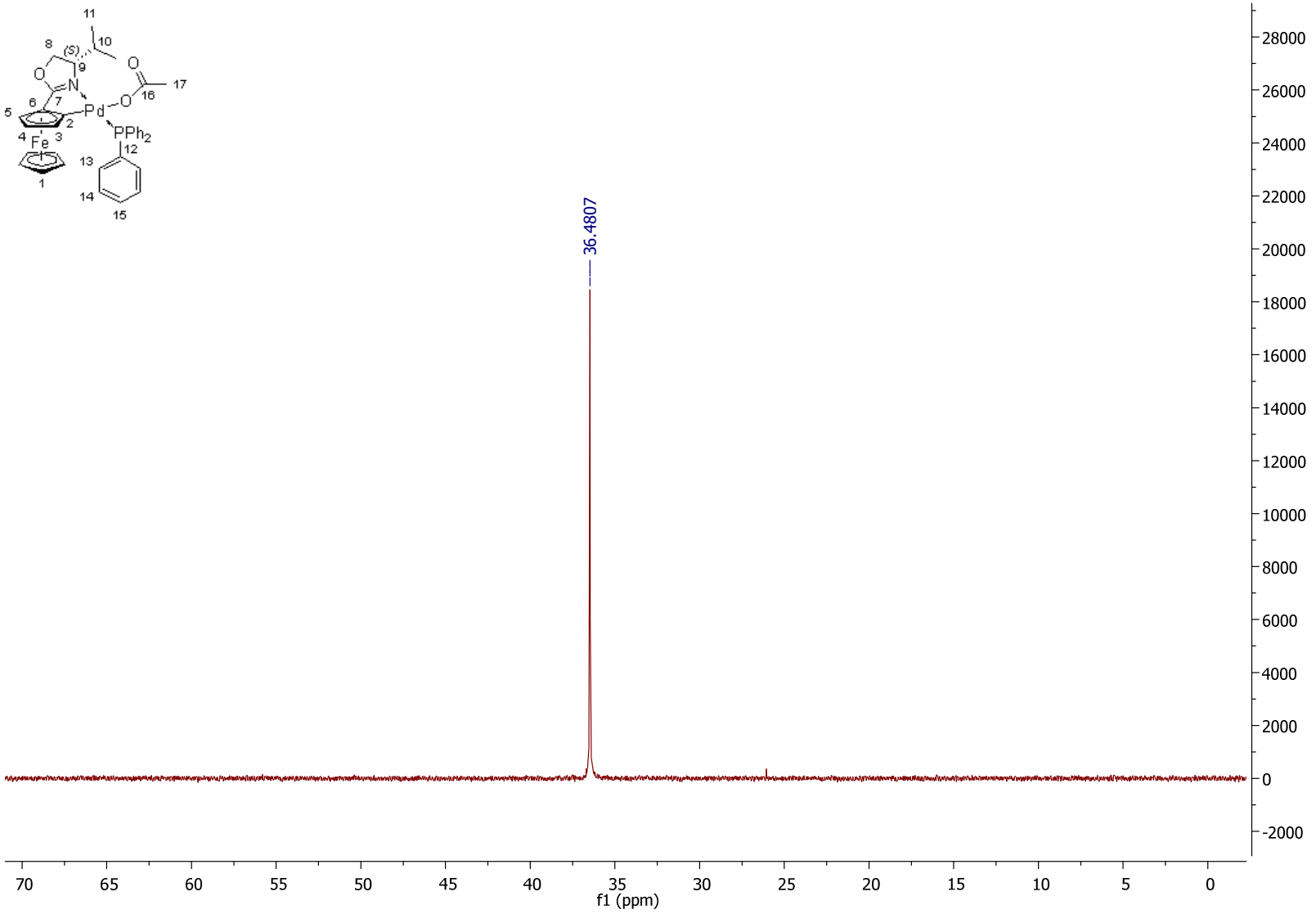


Figure S7. **Conversion of 5a (green spectrum - major component) into 5b (red and purple spectra)** - ^{1}H NMR (500 MHz, $CDCl_3$).

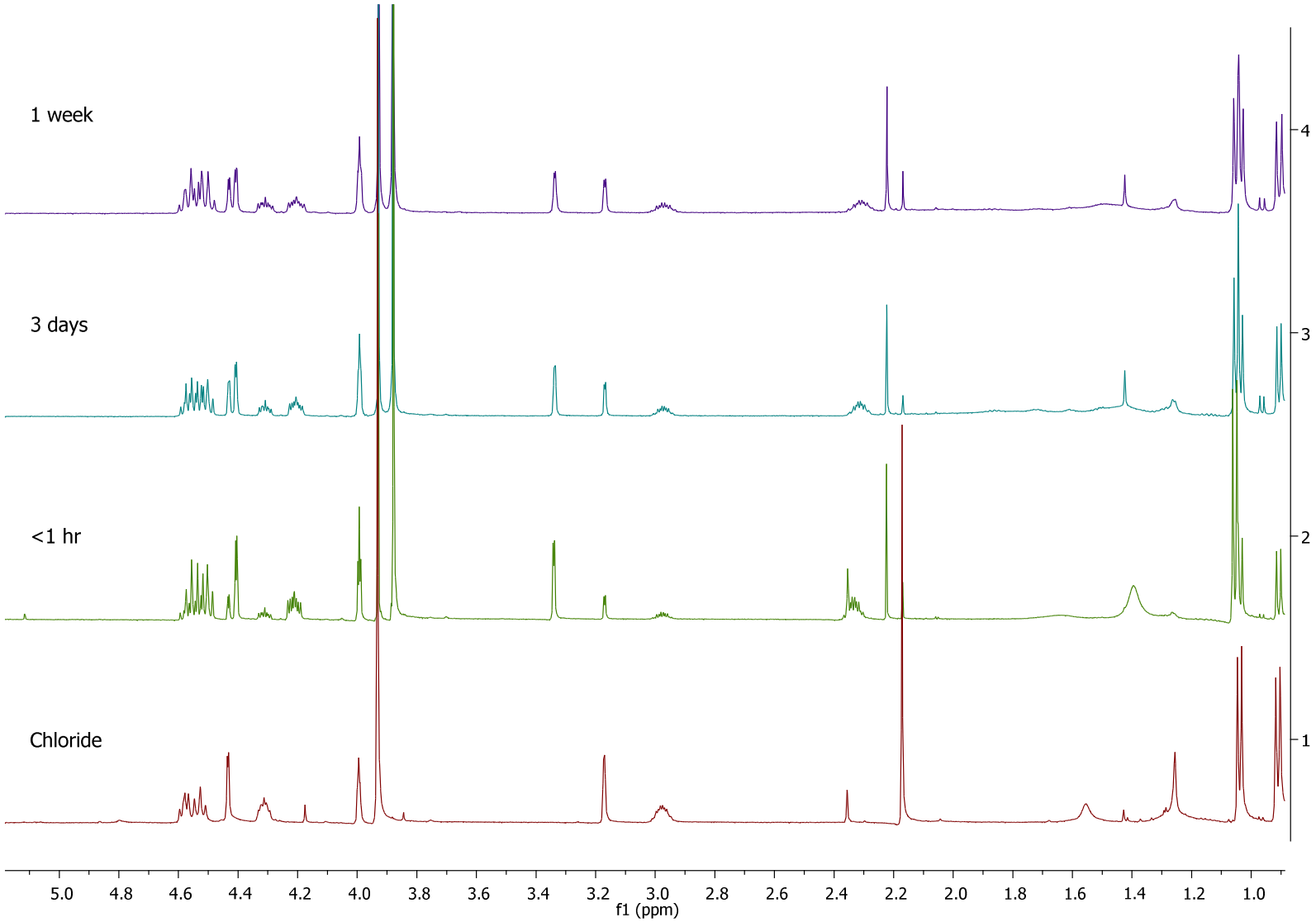


Figure S8. **5b** - ^{1}H NMR (500 MHz, MeCN-d^{3}).

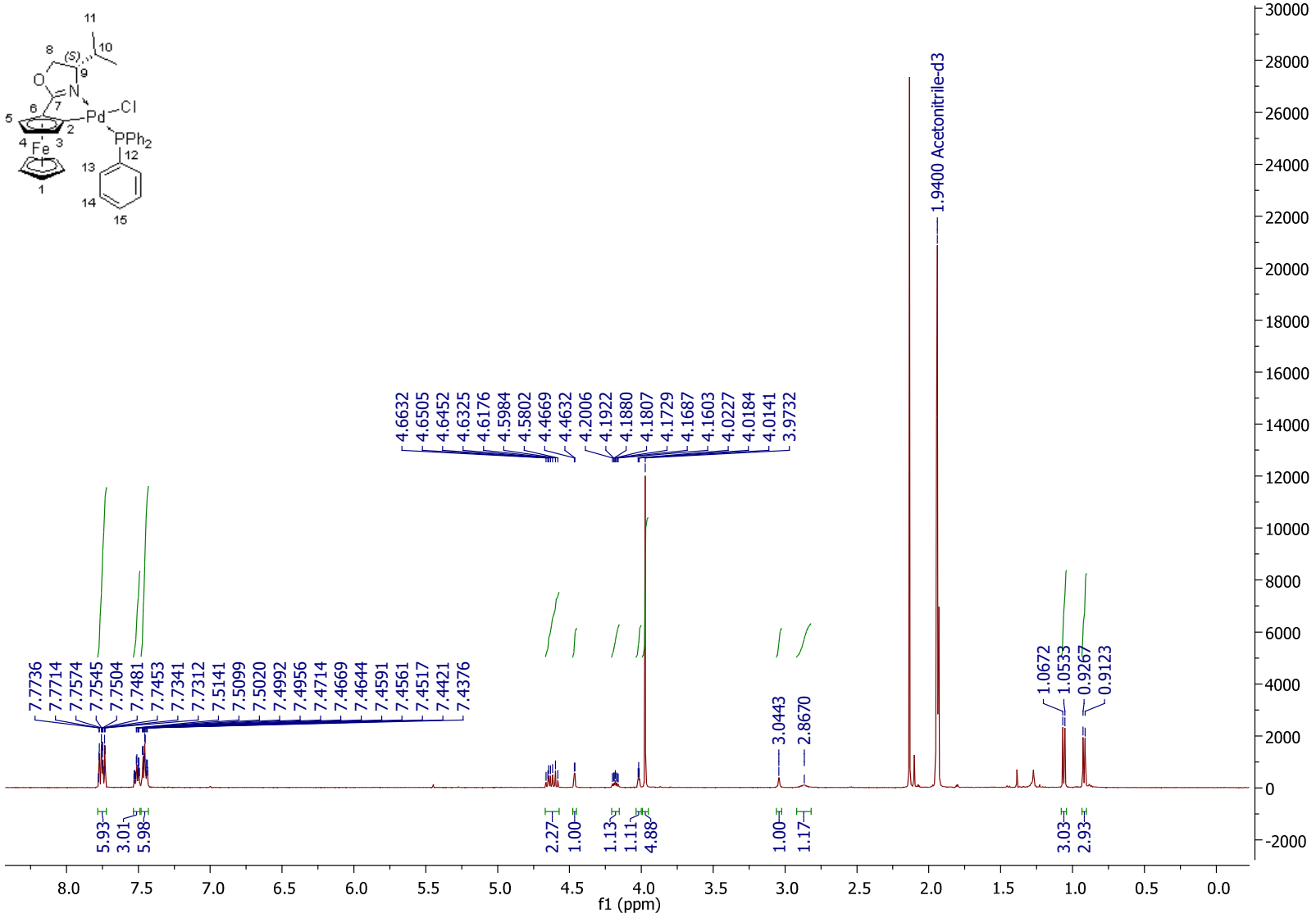


Figure S9. **5b** - ^{13}C NMR (125 MHz, MeCN-d^3).

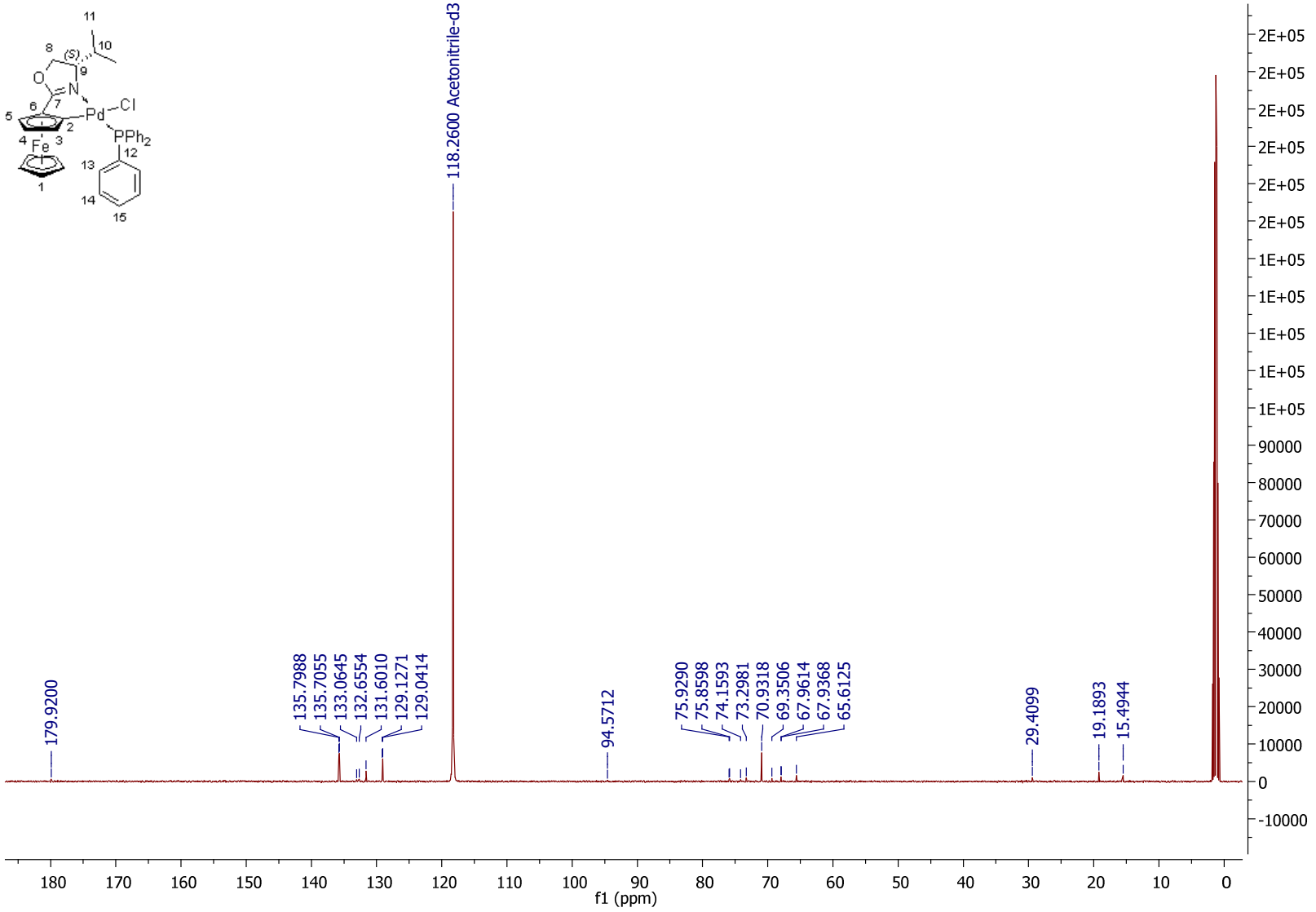


Figure S10. **5b** - ^{31}P NMR (202 MHz, MeCN-d^3).

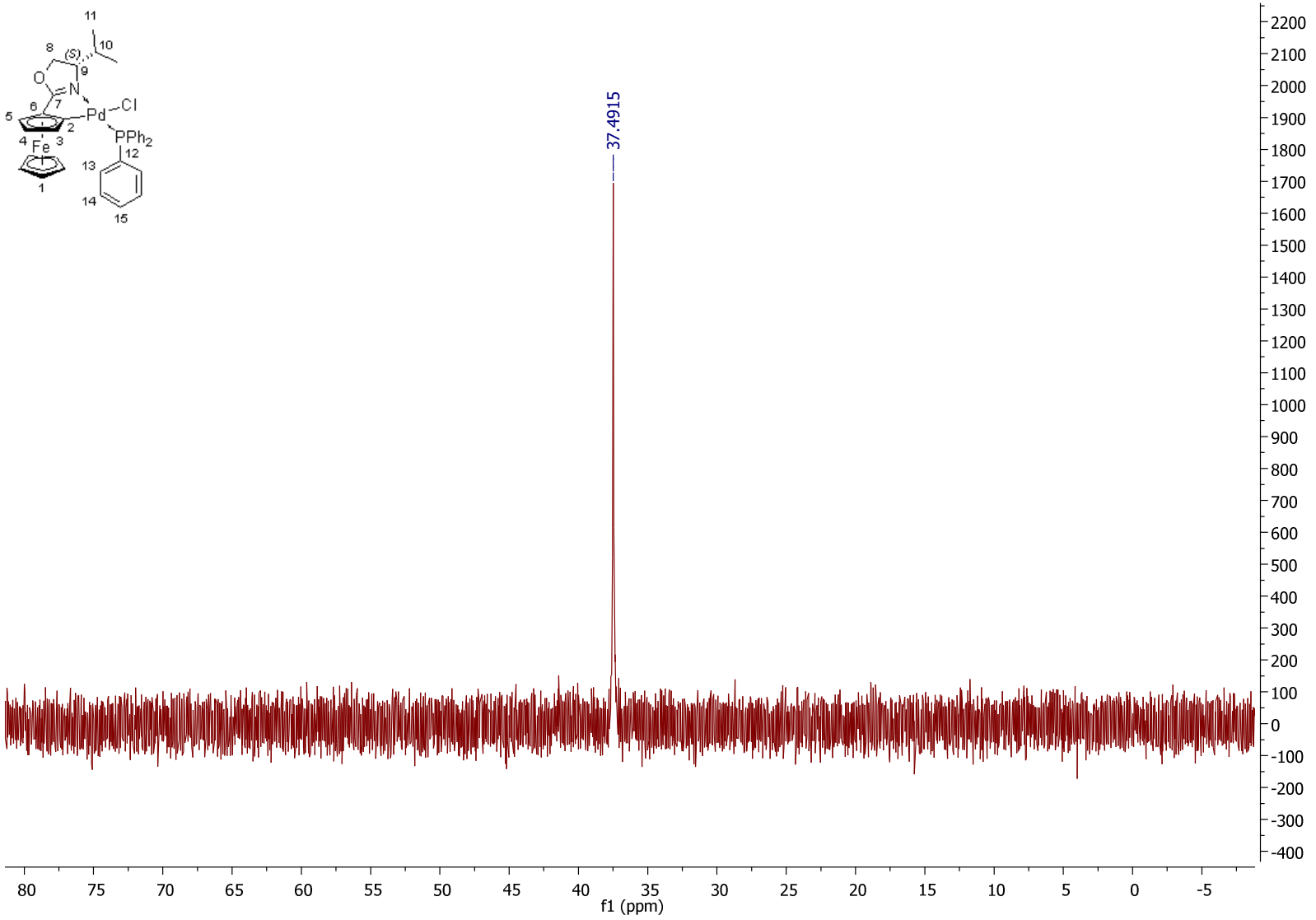


Figure S11. **6b** - ^{1}H NMR (500 MHz, MeCN-d^{3}).

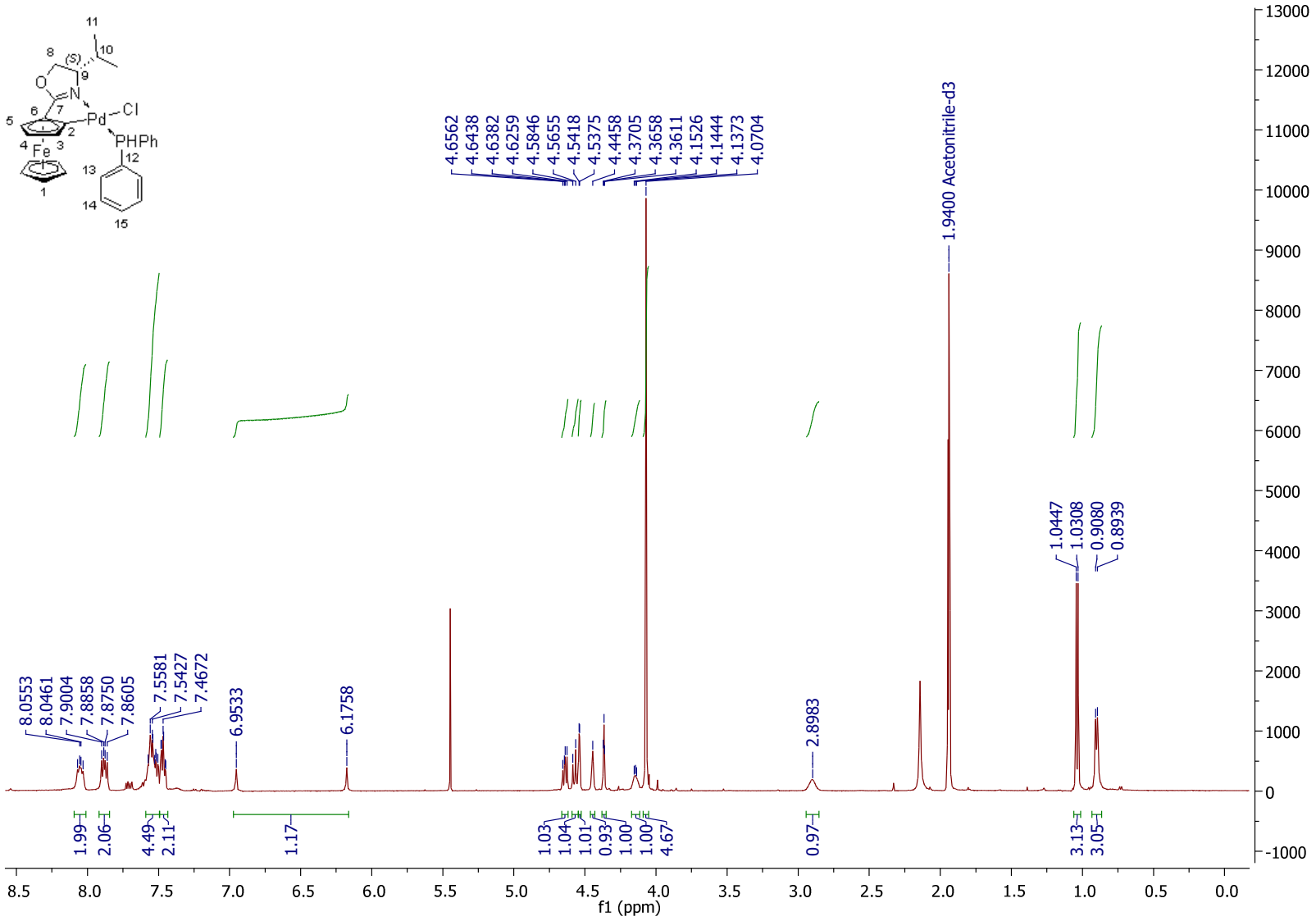


Figure S12. **6b** - ^{13}C NMR (125 MHz, MeCN-d^3).

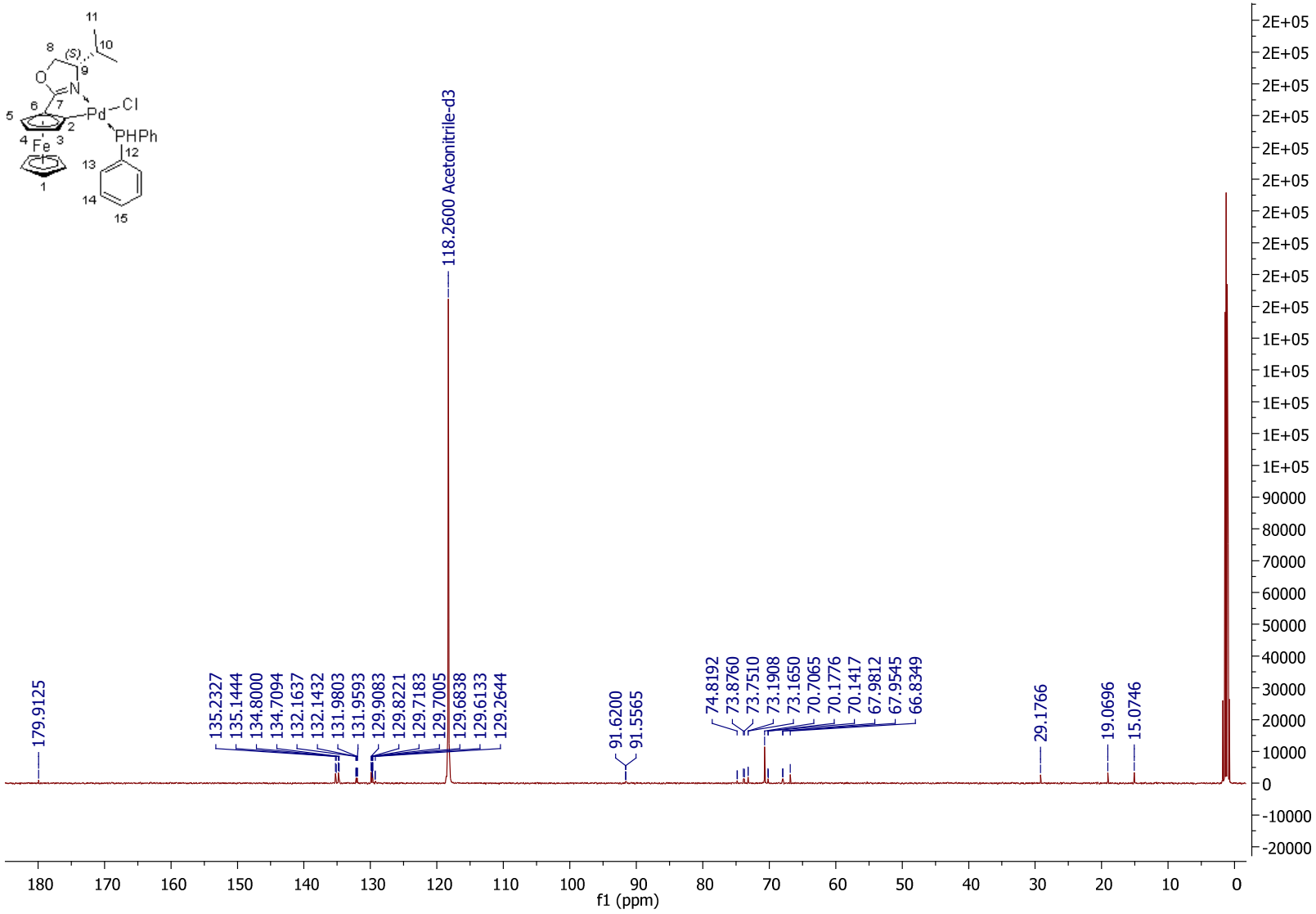


Figure S13. **6b** - ^{31}P NMR (202 MHz, MeCN-d^3).

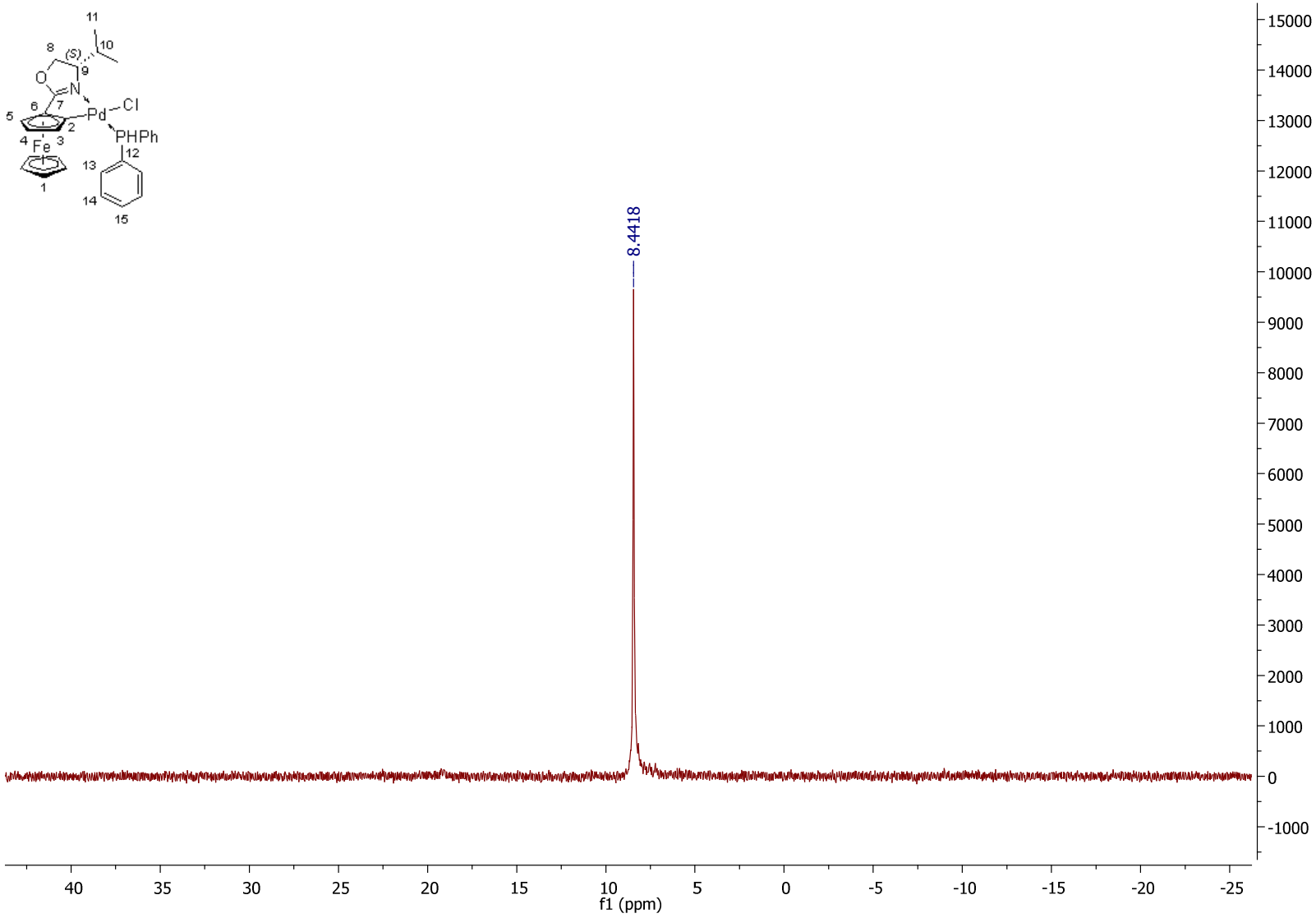


Figure S14. **4** - ^{1}H NMR (500 MHz, $CDCl_3$).

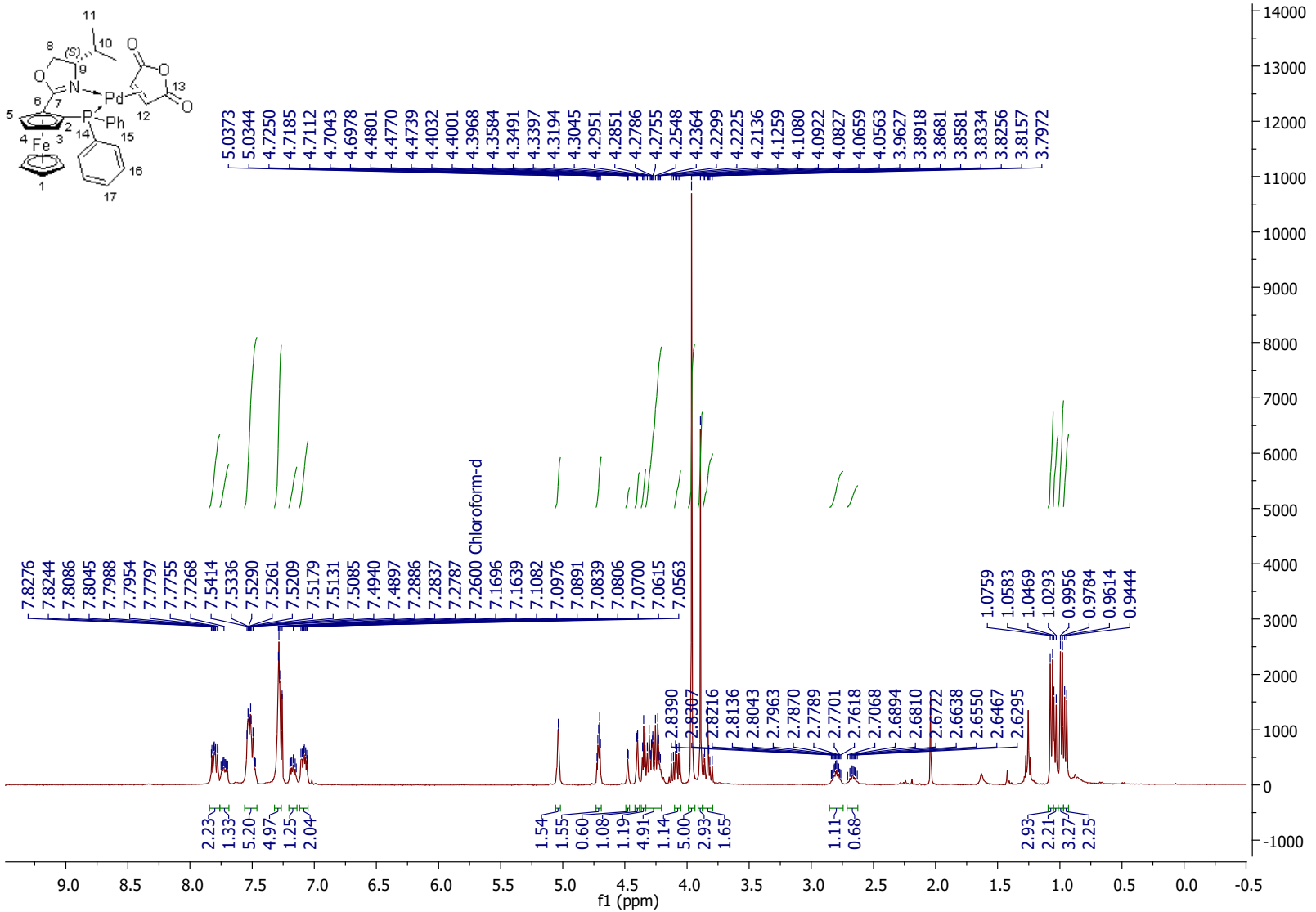


Figure S15. **4** - ^{13}C NMR (125 MHz, $CDCl_3$).

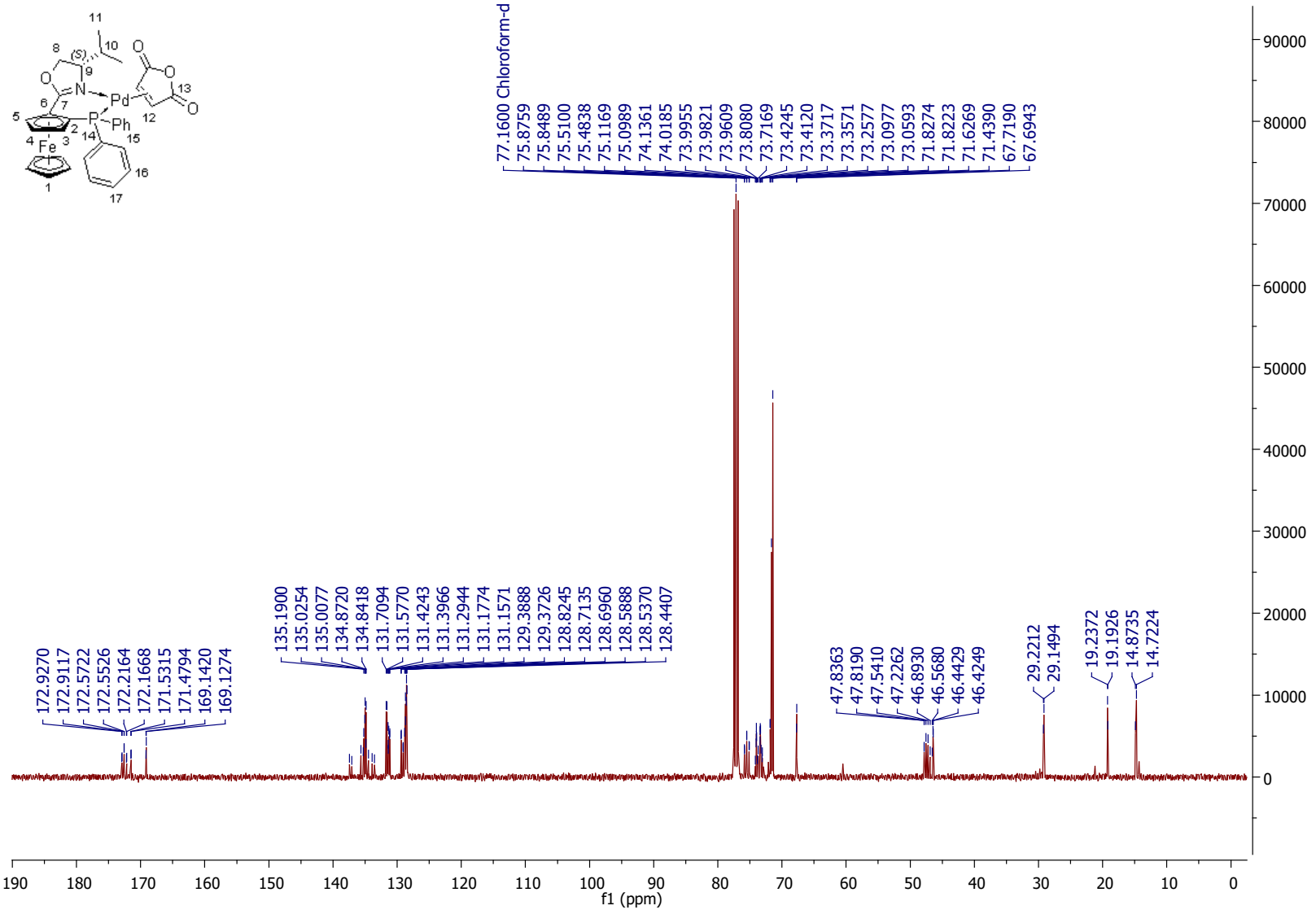


Figure S16. **4** - ^{31}P NMR (202 MHz, $CDCl_3$).

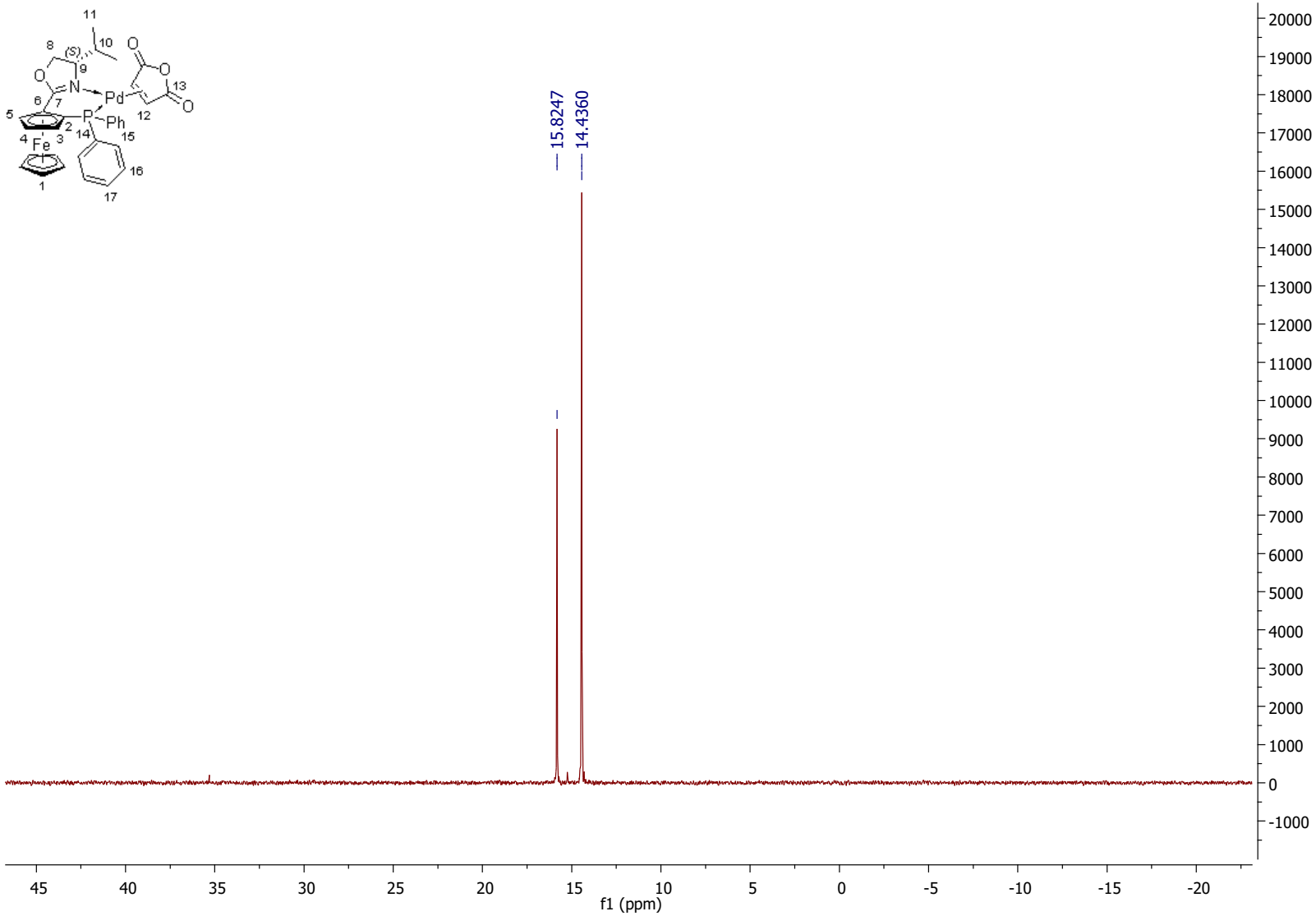


Figure S17. **8b** - ^{1}H NMR (500 MHz, $CDCl_3$).

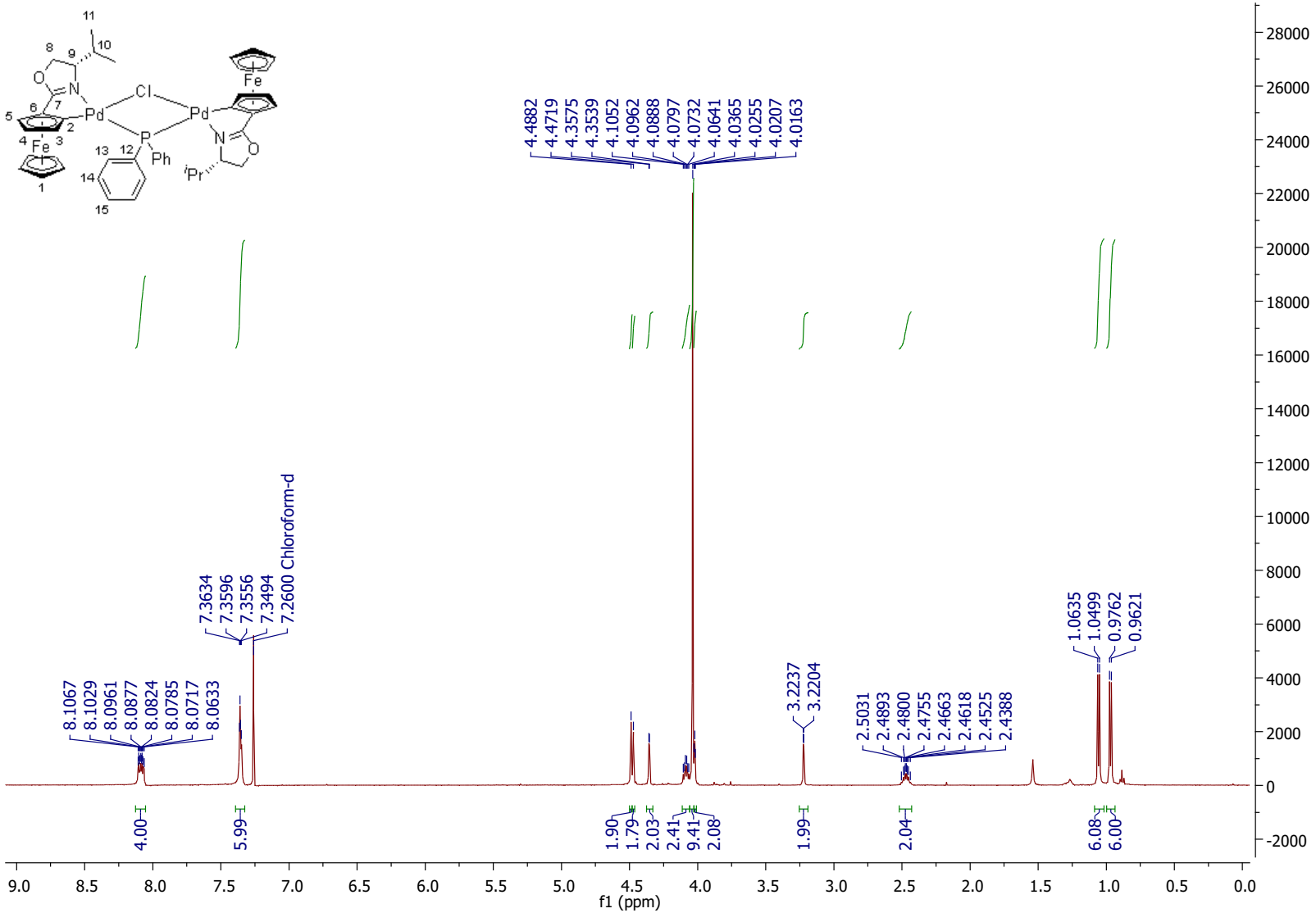


Figure S18. **8b** - ^{13}C NMR (125 MHz, $CDCl_3$).

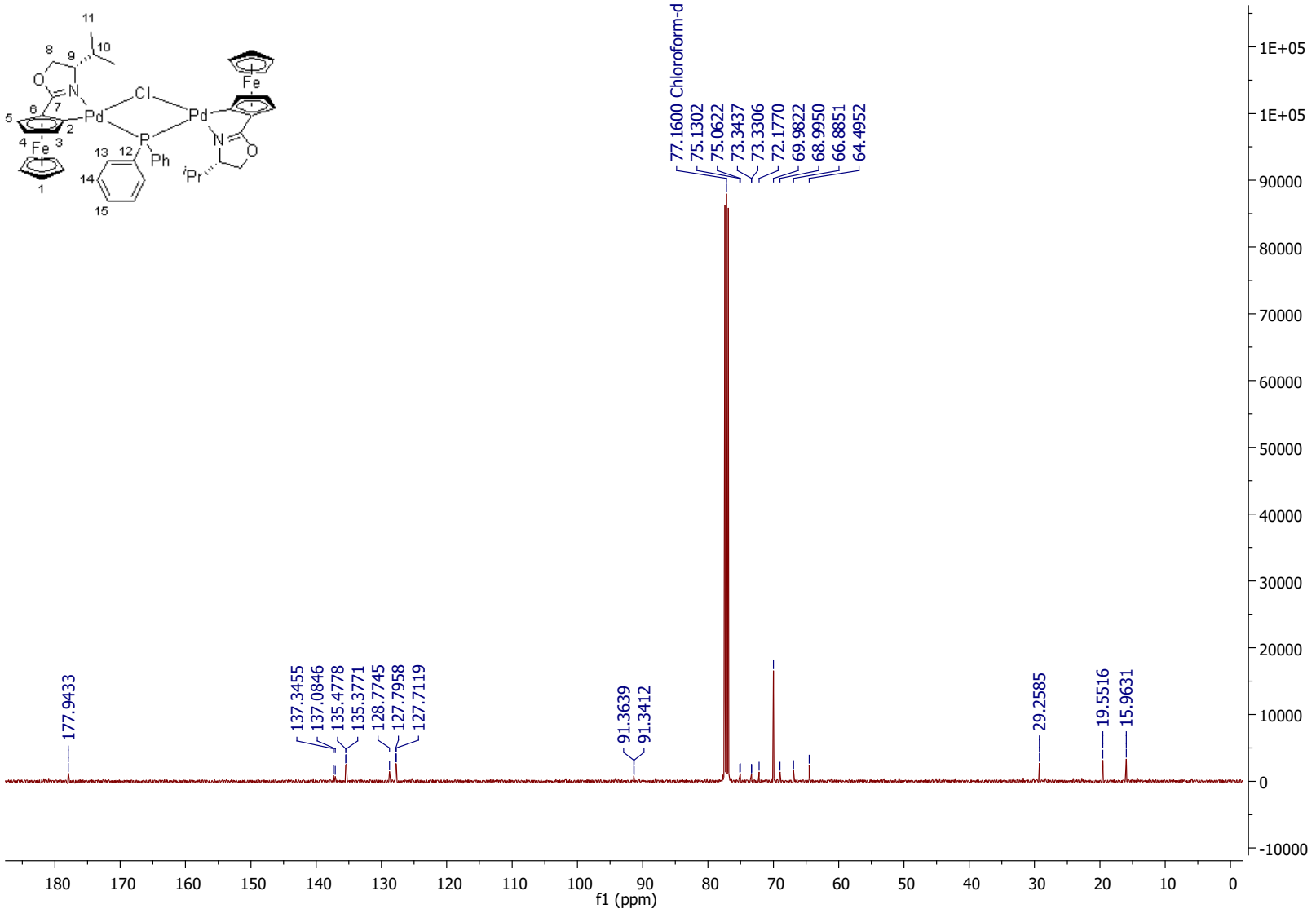


Figure S19. **8b** - ^{31}P NMR (202 MHz, $CDCl_3$).

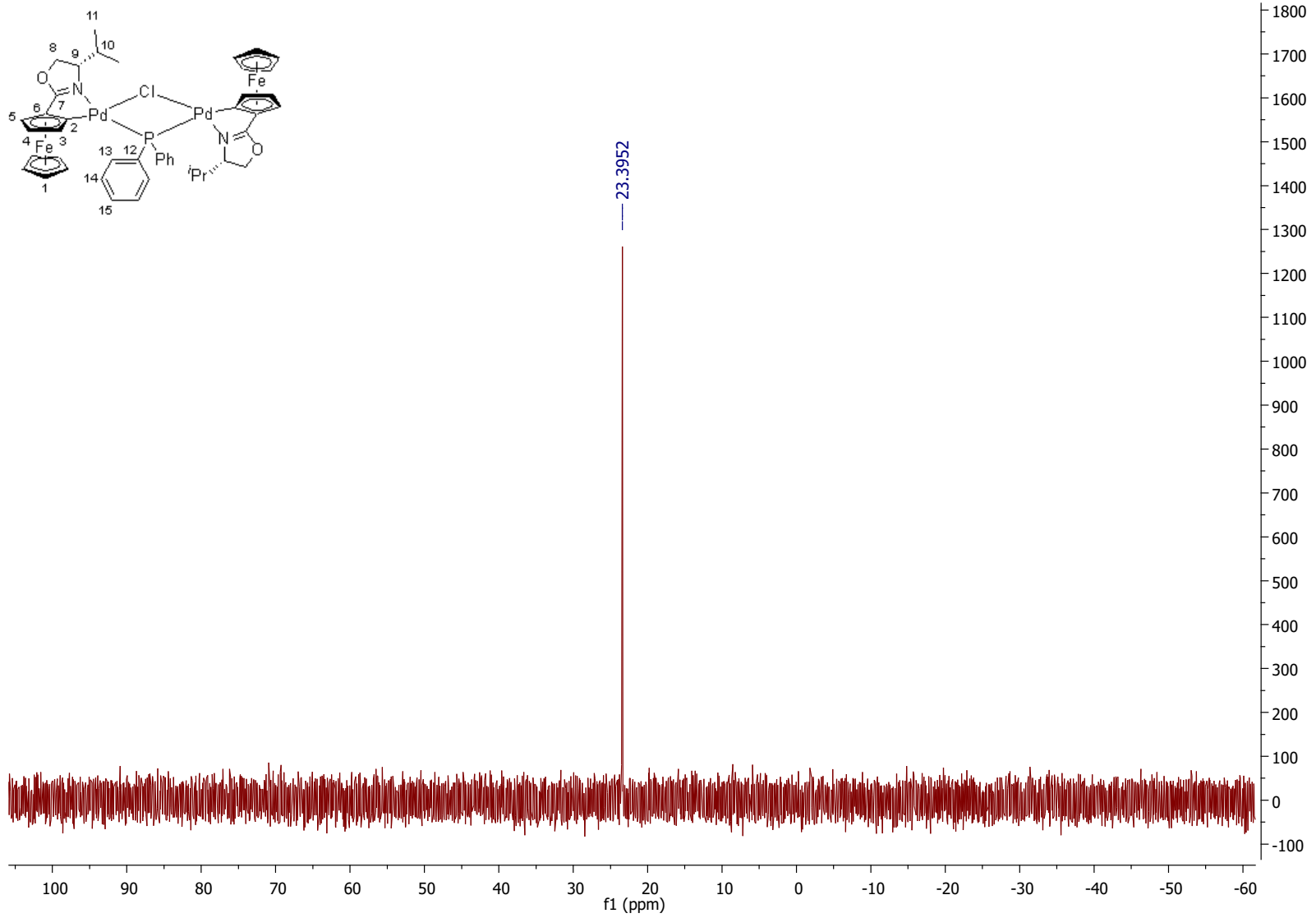


Figure S20. Addition of AgOAc to **8b** (red) to give **8a** (purple) - ^{31}P NMR (202 MHz, $CDCl_3$).

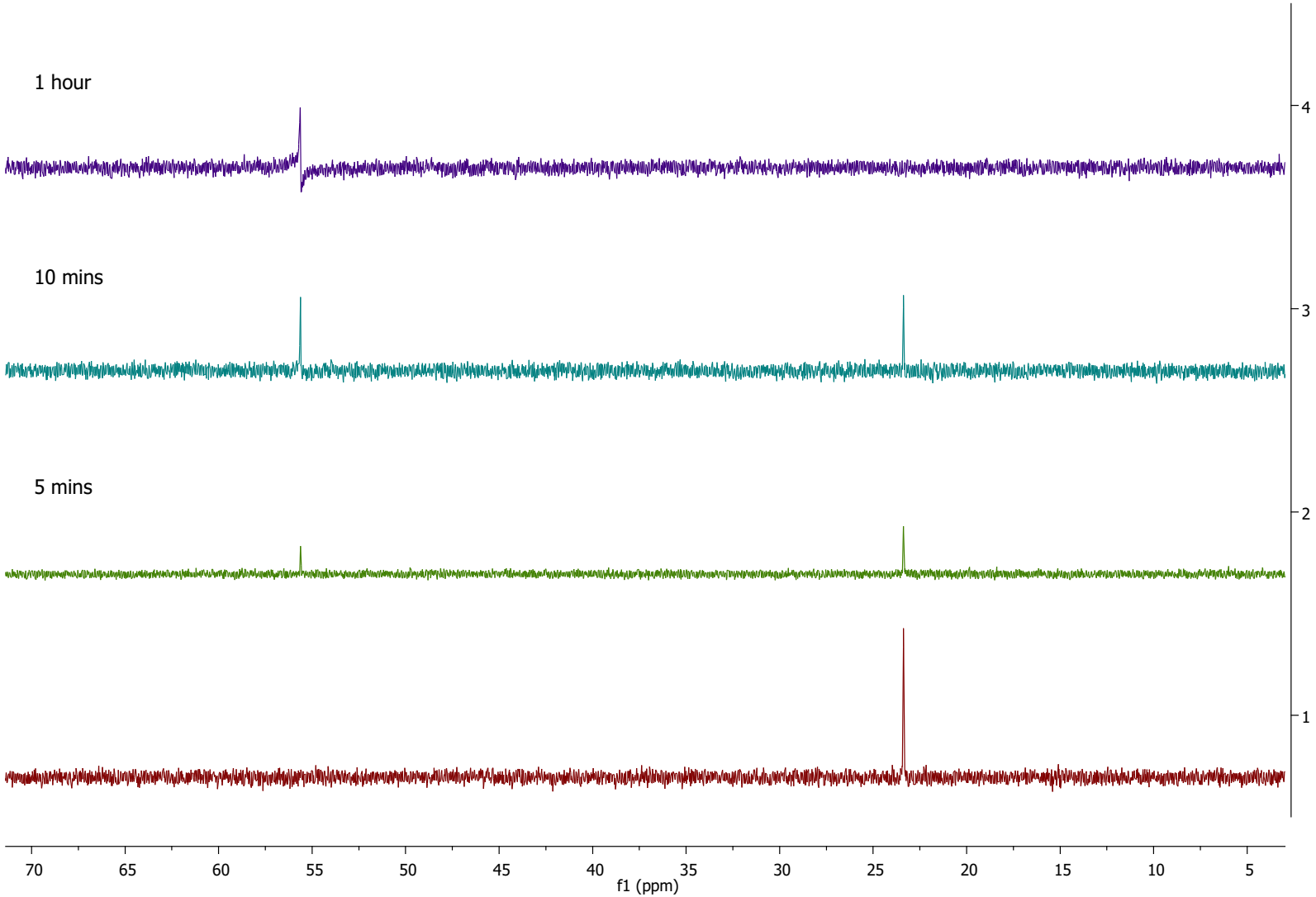


Figure S21. **8a** - ^{1}H NMR (500 MHz, $CDCl_3$).

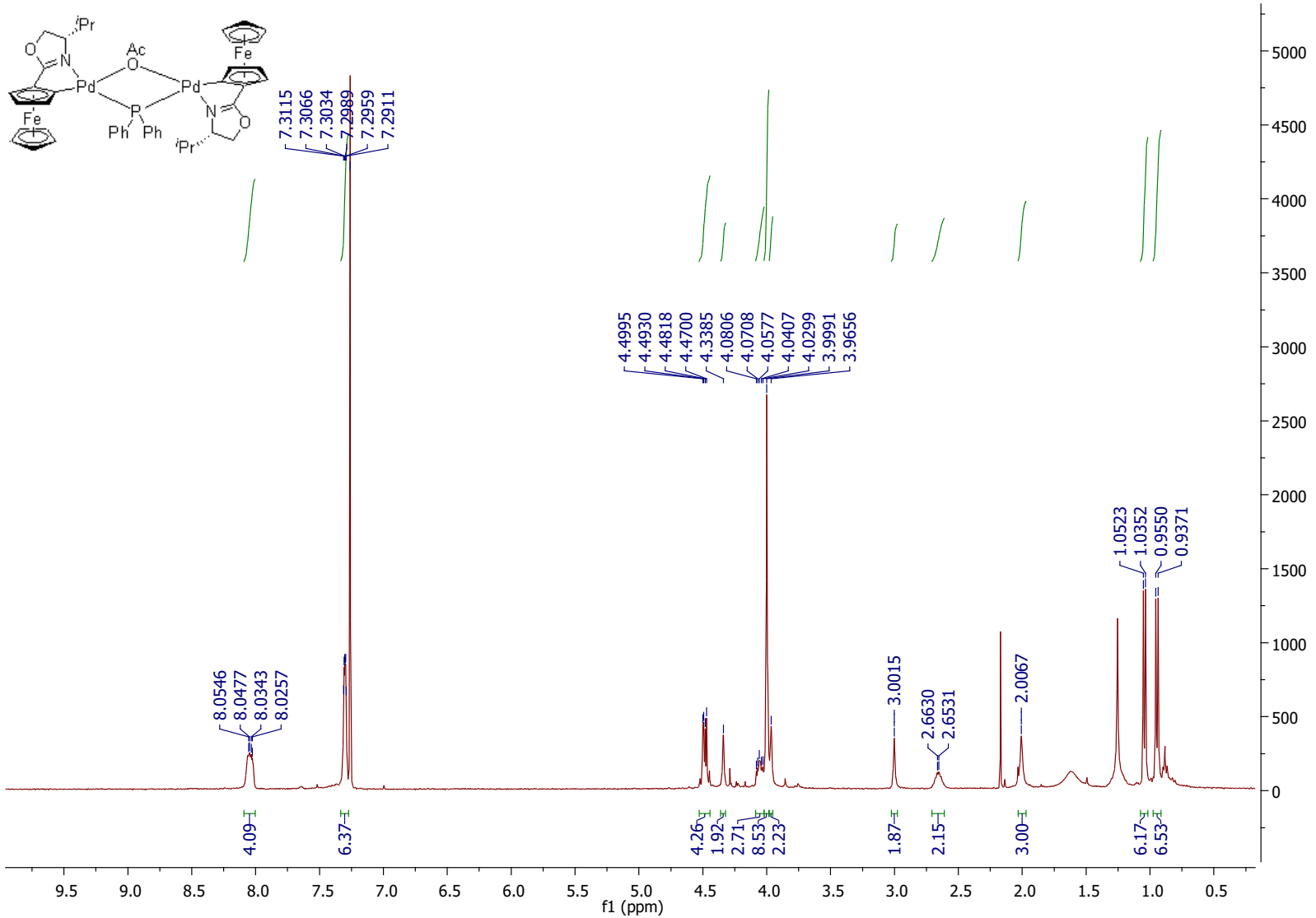


Figure S22. **8a** - ^{31}P NMR (202 MHz, $CDCl_3$).

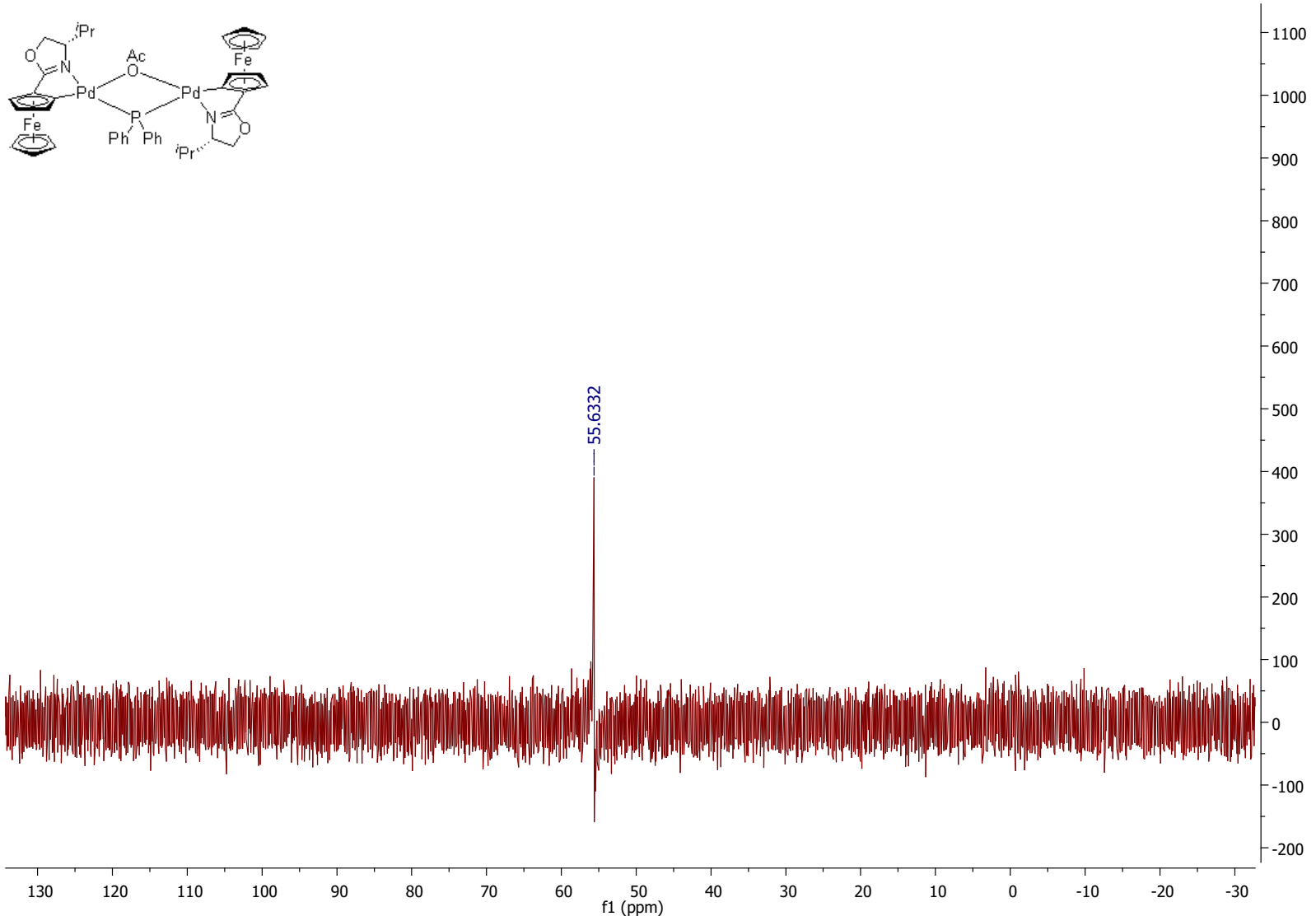


Figure S23. After filtering **8a** (red) signals indicated by arrows (green) show the formation of **8b** (blue) - ^{1}H NMR (500 MHz, $CDCl_3$).

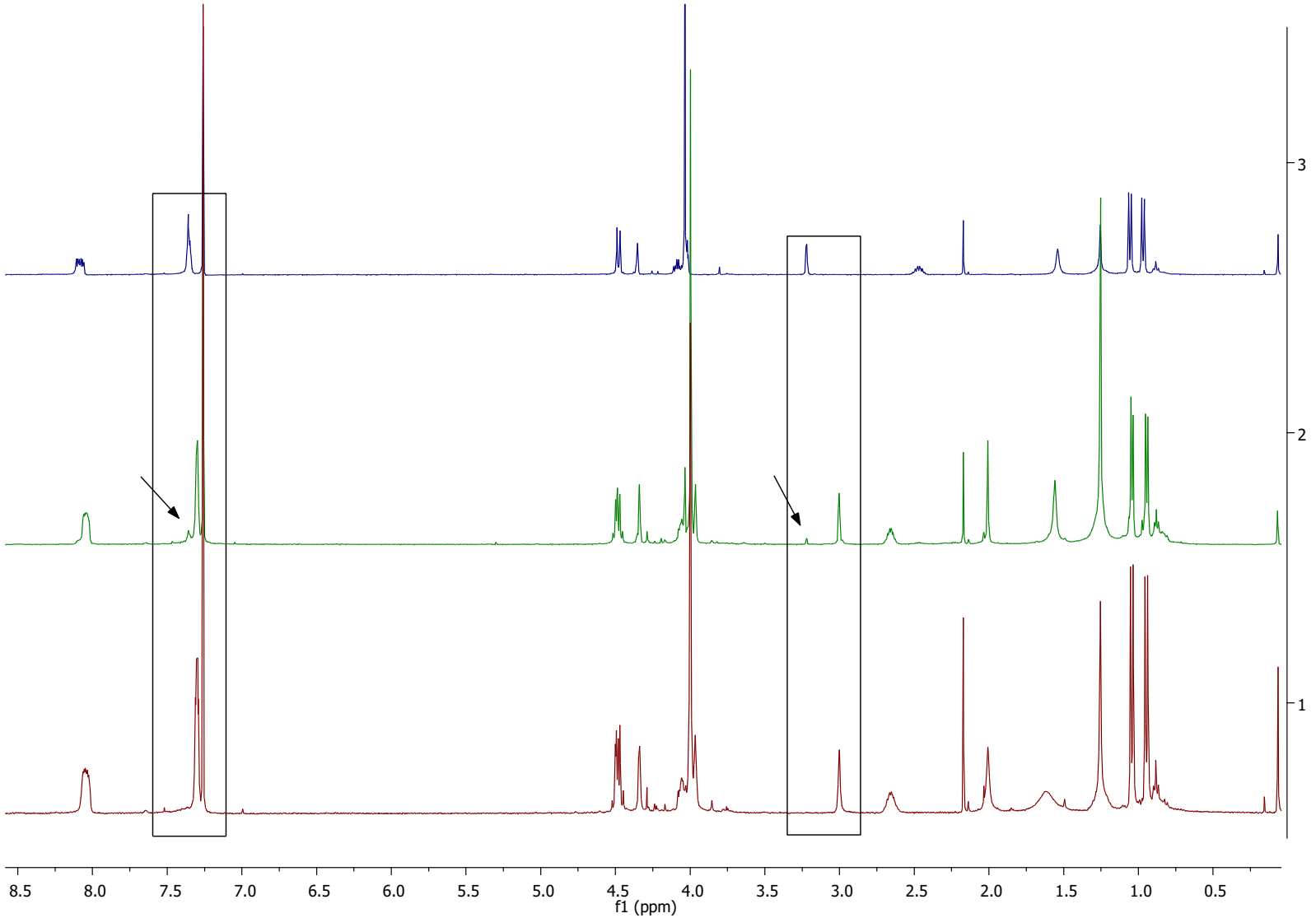


Figure S24. Phosphine insertion study **A** - ^{31}P NMR (202 MHz, CD_2Cl_2).

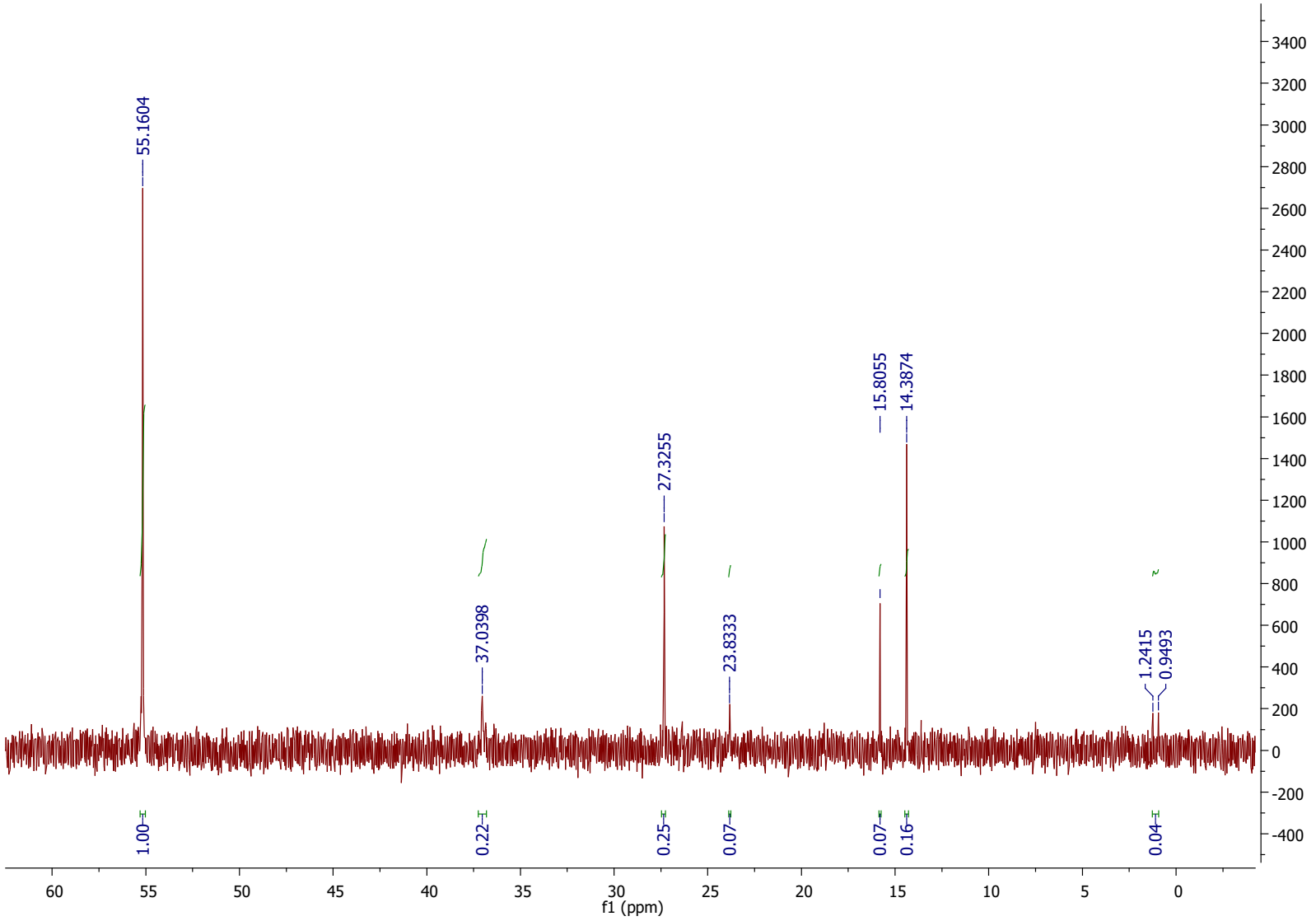


Figure S25. Phosphine insertion study **B** - ^{31}P NMR (202 MHz, CD_2Cl_2).

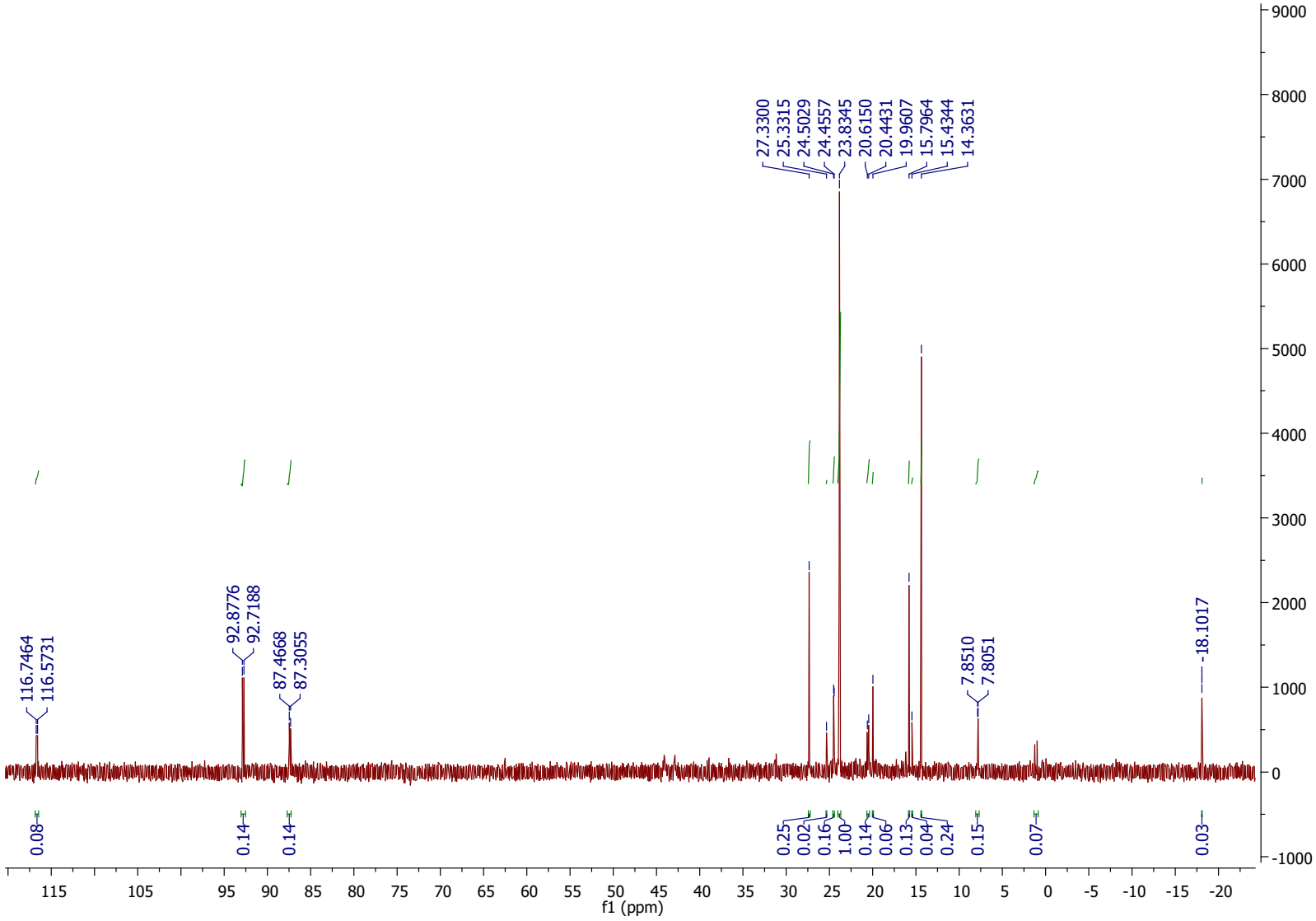


Figure S26. Phosphine insertion study **C** - ^{31}P NMR (202 MHz, CD_2Cl_2).

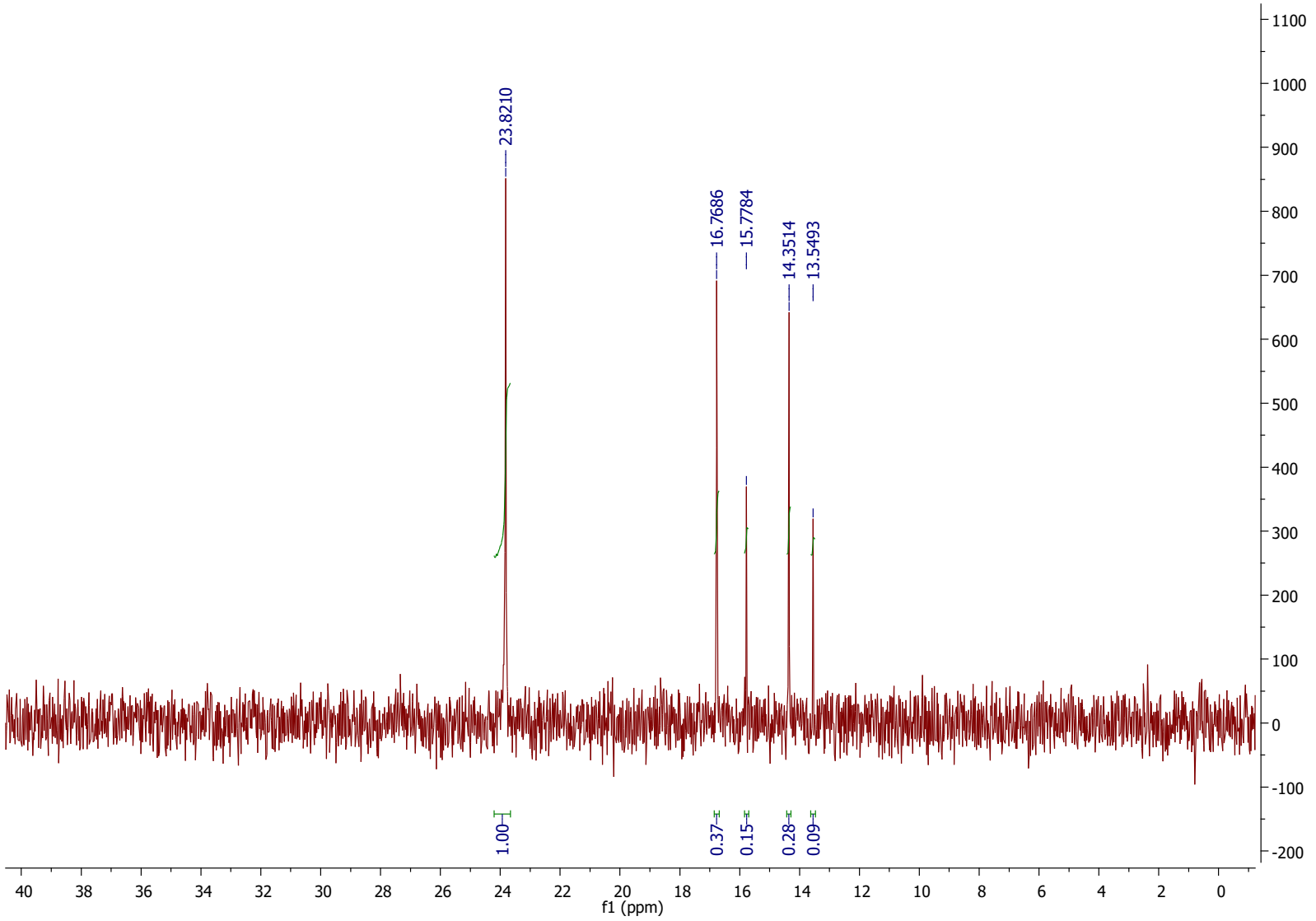
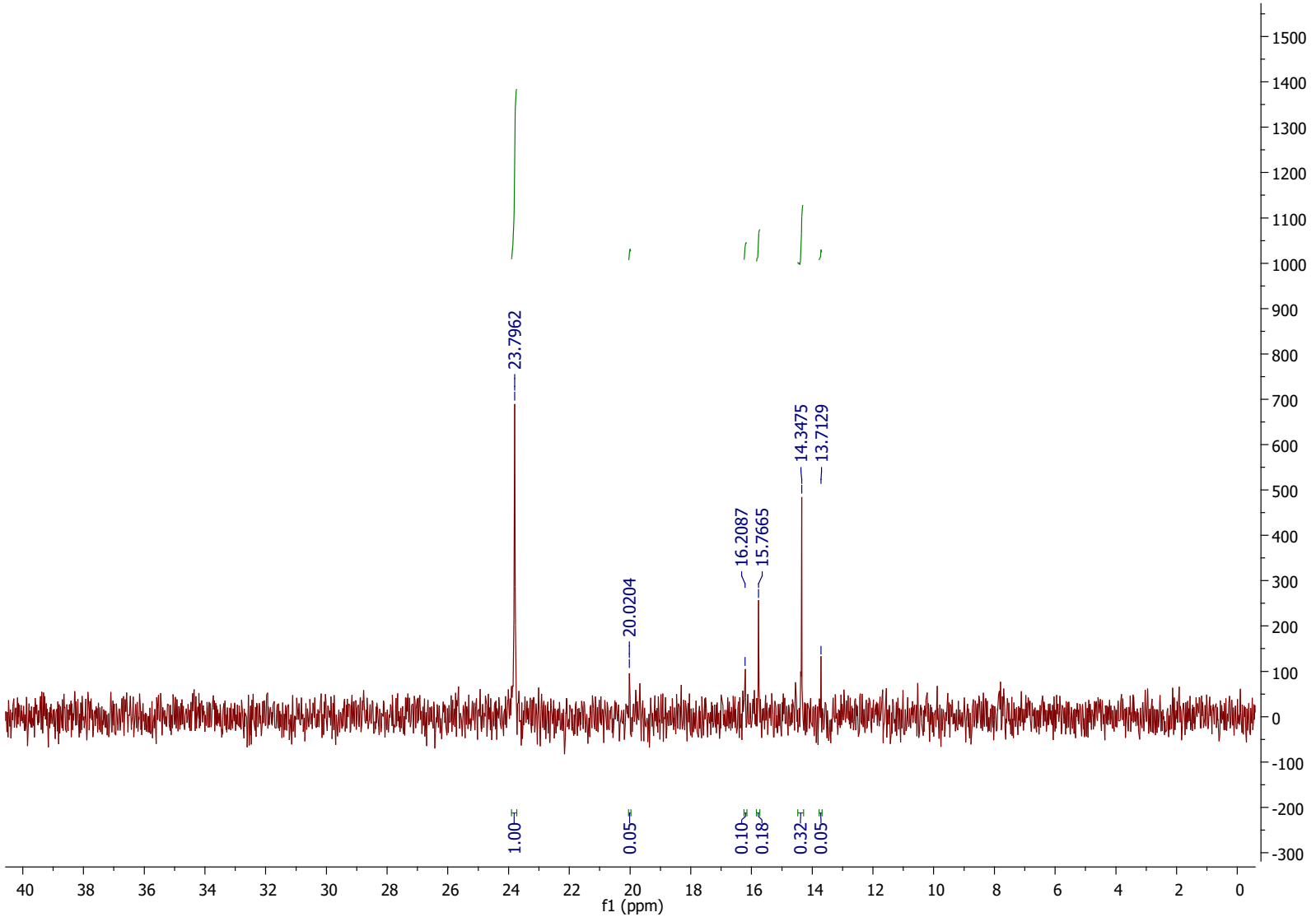


Figure S27. Phosphine insertion study **D** - ^{31}P NMR (202 MHz, CD_2Cl_2).



5. X-ray Crystallography

Crystal structure analysis - (*S*,*S*,*S*$_p$,*S*$_p$)-**8b**

Crystal data: $C_{44}H_{46}ClFe_2N_2O_2PPd_2$, M = 1025.75. Orthorhombic, space group $P2_12_12_1$ (no. 19), a = 12.18010(12), b = 12.77485(10), c = 25.8213(2) Å, V = 4017.77(5) Å^3. Z = 4, Dc = 1.696 g cm^{-3}, F(000) = 2064, T = 100.01(10) K, μ(Mo-Kα) = 17.35 cm^{-1}, λ(Mo-Kα) = 0.71073 Å.

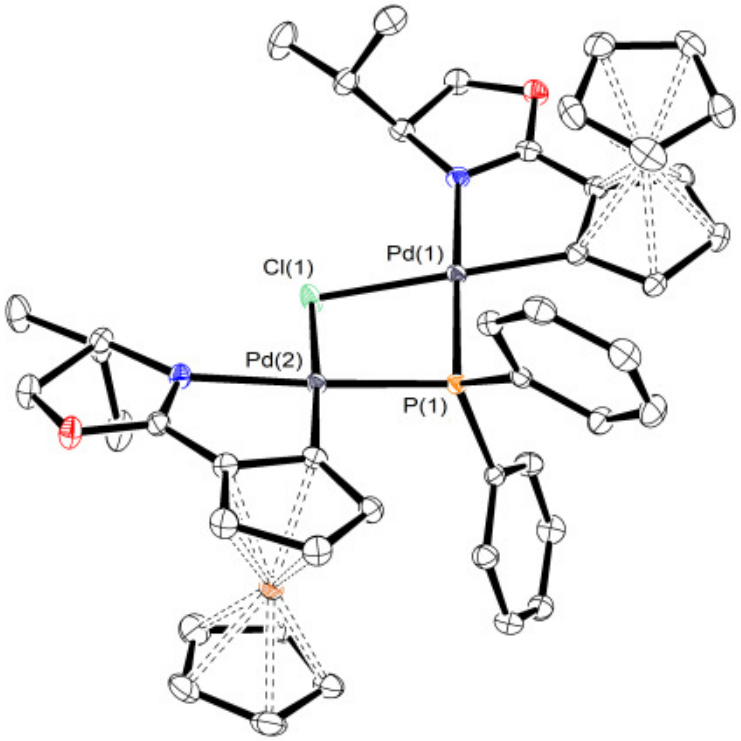
The crystals were red plates. One, *ca* 0.11 x 0.125 x 0.135 mm, was mounted on a small loop and fixed in the cold nitrogen stream on a Rigaku Oxford Diffraction XtaLAB Synergy diffractometer, equipped with Mo-Kα radiation, HyPix detector and mirror monochromator. Intensity data were measured by thin-slice ω-scans. Total no. of reflections recorded, to θ_{max} = 27.5°, was 138243 of which 9215 were unique (Rint = 0.055); 9126 were 'observed' with $I > 2\sigma_I$.

Data were processed using the CrysAlisPro-CCD and -RED programs[7]. The structure was determined by the intrinsic phasing routines in the SHELXT program[8] and refined by full-matrix least-squares methods, on F^2's, in SHELXL[9]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in idealised positions and their Uiso values were set to ride on the Ueq values of the parent carbon atoms. At the conclusion of the refinement, wR_2 = 0.038 and R_1 = 0.015 (2B) for all 9215 reflections weighted $w = [\sigma^2(F_o^2) + (0.0199\ P)^2 + 1.350\ P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$. The absolute structure parameter, x = -0.002(5) with the structure as shown in the Figures.

In the final difference map, the highest peak (*ca* 0.5 eÅ^{-3}) was near Pd(2).

Scattering factors for neutral atoms were taken from reference 10. Computer programs used in this analysis have been noted above, and were run through WinGX[11] on a Dell Optiplex 780 PC at the University of East Anglia.

Figure S28. (S,S,S_p,S_p)-**8b**



Identification code	**rossa26 / RAA18.1360e / (S,S,S_p,S_p)-8b**
Empirical formula	$C_{44}H_{46}ClFe_2N_2O_2PPd_2$
Formula weight	1025.75
Crystal system, Space Group	Orthorhombic, $P2_12_12_1$ (no. 19)
Unit cell dimensions	a = 12.18010(12) Å α = 90°
	b = 12.77485(10) Å β = 90°
	c = 25.8213(2) Å γ = 90°
Volume	4017.77(5) Å^3
Z, Density (calculated)	4, 1.696 Mg / m^3
$F(000)$	2064
Absorption coefficient	1.735 mm^{-1}
Temperature	100.01(10) K
Wavelength	0.71073 Å
Crystal colour, shape	Red, Plate
Crystal size	0.11 × 0.125 × 0.135 mm
Crystal mounting	on a small loop, in oil, fixed in cold N_2 stream
θ range for data collection	1.849 – 27.498°
Limiting indices: h, k, l	$-15 \le h \le 15$, $-16 \le k \le 16$, $-33 \le l \le 33$
Completeness of data: θ, %	25.242°, 100.0%
Absorption correction	Semi–empirical from equivalents
Max. and min. transmission	1.00000 and 0.91293
Reflections collected	138243
No. of unique reflections, R(int)	9215, 0.055
No. of 'obsd' reflections (I > 2σI)	9126
Structure determined by:	dual methods, in SHELXT
Refinement	Full-matrix least-squares on F^2, in SHELXL
Data / restraints / parameters	9215 / 0 / 487
Goodness-of-fit on F^2	1.068
Final R indices ('obsd' data)	$R1$ = 0.015, $wR2$ = 0.038
Final R indices (all data)	$R1$ = 0.015, $wR2$ = 0.038
Reflections weighted: w = where P=(Fo^2+2Fc^2)/3	$[\sigma^2(Fo^2)+(0.0199P)^2+1.3500P]^{-1}$
Absolute structure parameter	-0.002(5)
Largest diff. peak and hole, location	0.49 and -0.31 e Å^{-3}, near Pd(2) centre

6. HPLC Traces

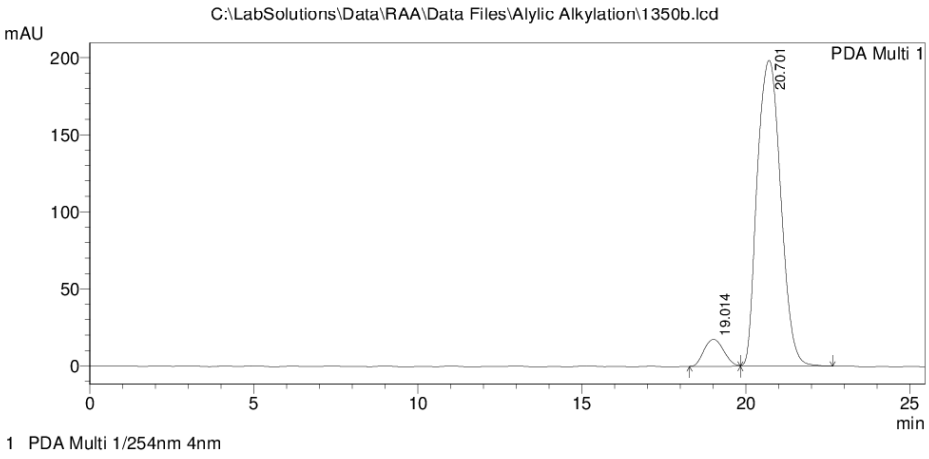
Figure S29. Results from Table S2 Entry 1.

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\RAA\Data Files\Alylic Alkylation\1350b.lcd

Acquired by	: Admin
Sample Name	: RAA18.1350b
Sample ID	: RAA18.1350b
Tray#	: 1
Vail #	: 50
Injection Volume	: 5 uL
Data File Name	: 1350b.lcd
Method File Name	: 98-2 Hex-IPA 0.5ml per min.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 12/2/2019 3:14:30 PM
Data Processed	: 12/2/2019 4:44:21 PM

<Chromatogram>



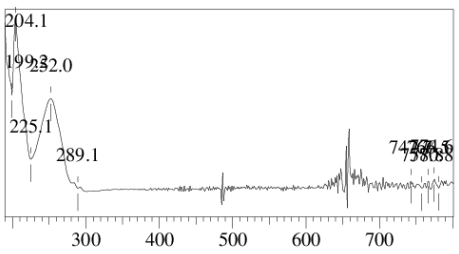
1 PDA Multi 1/254nm 4nm

Quantitative Results

PDA

ID#	Name	Ret. Time	Area	Height	Conc.
1	RT19.014	19.014	738954	17519	6.928
2	RT20.701	20.701	9927954	198561	93.072

Peak 1



Peak 2

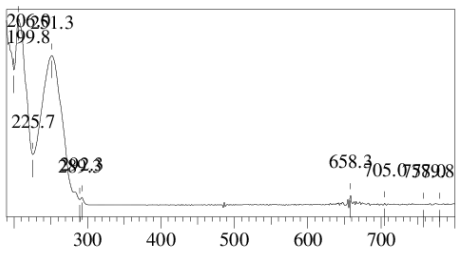


Figure S30. Results from Table S2 Entry 2.

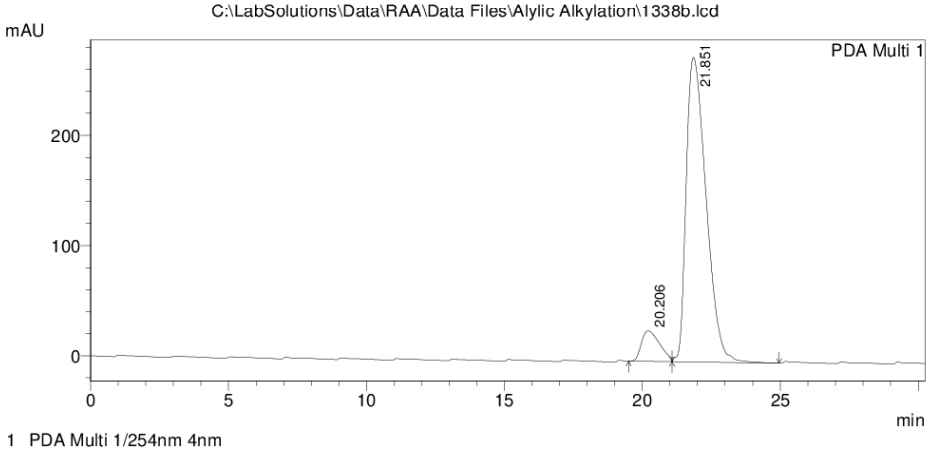
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\RAA\Data Files\Alylic Alkylation\1338b.lcd

Acquired by	: Admin
Sample Name	: RAA18.1338b
Sample ID	: RAA18.1338b
Tray#	: 1
Vail #	: 38
Injection Volume	: 5 uL
Data File Name	: 1338b.lcd
Method File Name	: 98-2 Hex-IPA 0.5ml per min.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/29/2019 2:14:30 PM
Data Processed	: 7/29/2019 4:07:50 PM

<Chromatogram>

C:\LabSolutions\Data\RAA\Data Files\Alylic Alkylation\1338b.lcd



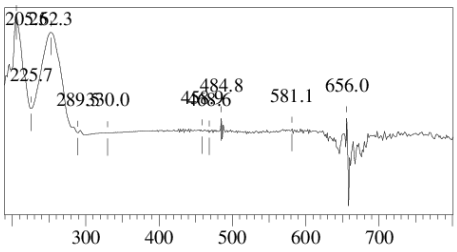
1 PDA Multi 1/254nm 4nm

Quantitative Results

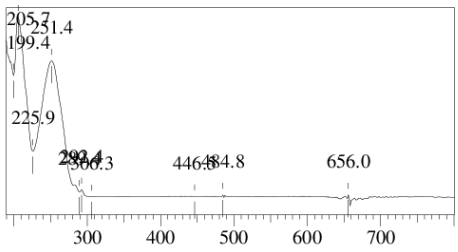
PDA

ID#	Name	Ret. Time	Area	Height	Conc.
1	RT20.206	20.206	1276461	27749	8.417
2	RT21.851	21.851	13889094	276542	91.583

Peak 1



Peak 2



C:\LabSolutions\Data\RAA\Data Files\Alylic Alkylation\1338b.lcd

Figure S31. Results from Table S2 Entry 3.

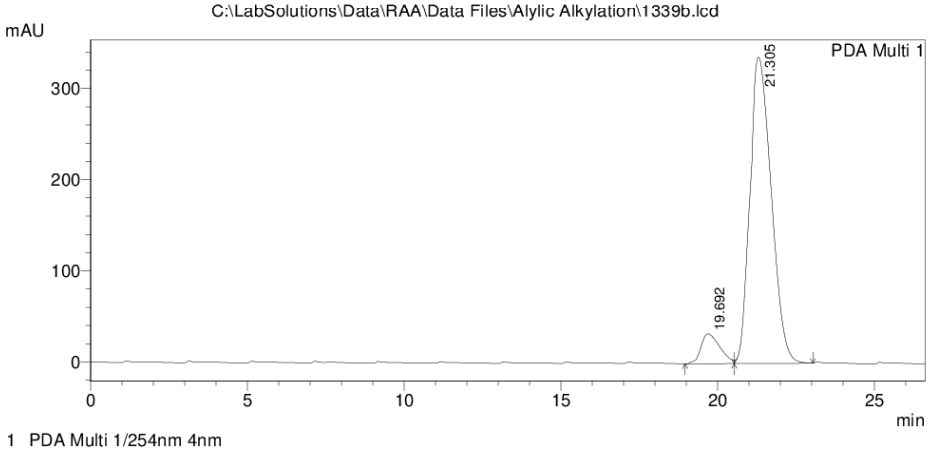
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\RAA\Data Files\Alylic Alkylation\1339b.lcd

Acquired by	: Admin
Sample Name	: RAA18.1339b
Sample ID	: RAA18.1339b
Tray#	: 1
Vail #	: 39
Injection Volume	: 5 uL
Data File Name	: 1339b.lcd
Method File Name	: 98-2 Hex-IPA 0.5ml per min.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/29/2019 2:46:38 PM
Data Processed	: 7/30/2019 1:58:51 PM

<Chromatogram>

C:\LabSolutions\Data\RAA\Data Files\Alylic Alkylation\1339b.lcd



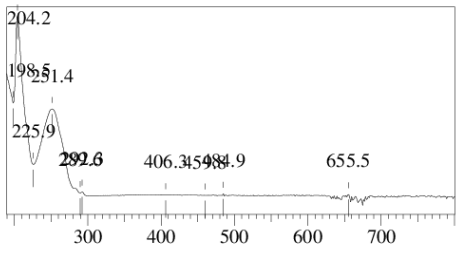
1 PDA Multi 1/254nm 4nm

Quantitative Results

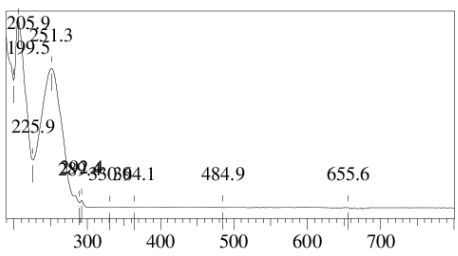
PDA

ID#	Name	Ret. Time	Area	Height	Conc.
1	RT19.692	19.692	1365494	32621	7.893
2	RT21.305	21.305	15935386	335848	92.107

Peak 1



Peak 2



C:\LabSolutions\Data\RAA\Data Files\Alylic Alkylation\1339b.lcd

Figure S32. Results from Table S2 Entry 4.

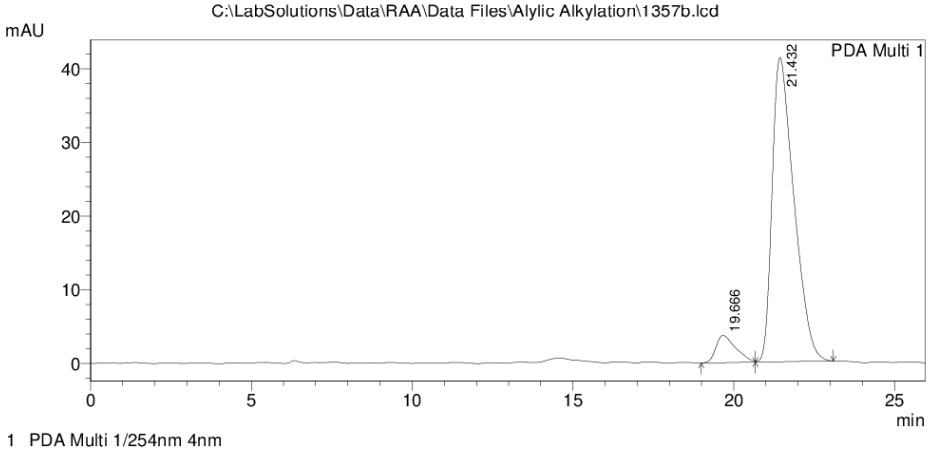
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\RAA\Data Files\Alylic Alkylation\1357b.lcd

Acquired by	: Admin
Sample Name	: RAA18.1357b
Sample ID	: RAA18.1357b
Tray#	: 1
Vail #	: 57
Injection Volume	: 3 uL
Data File Name	: 1357b.lcd
Method File Name	: 98-2 Hex-IPA 0.5ml per min.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 12/11/2019 6:44:59 PM
Data Processed	: 12/11/2019 7:11:28 PM

<Chromatogram>

C:\LabSolutions\Data\RAA\Data Files\Alylic Alkylation\1357b.lcd



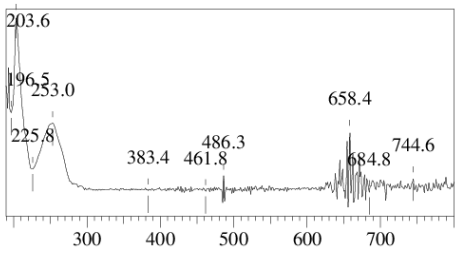
1 PDA Multi 1/254nm 4nm

Quantitative Results

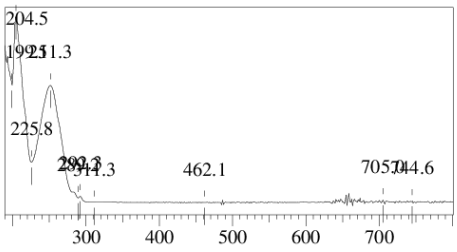
PDA

ID#	Name	Ret. Time	Area	Height	Conc.
1	RT19.666	19.666	158915	3709	7.553
2	RT21.432	21.432	1945095	41322	92.447

Peak 1



Peak 2



7. References

1. T. Sammakia, H. A. Latham and D. R. Schaad, *J. Org. Chem*., 1995, **60**, 10-11.
2. J.-B. Xia and S.-L. You, *Organometallics*, 2007, **26**, 4869-4871.
3. R. A. Arthurs, D. L. Hughes and C. J. Richards, *Organometallics*, 2019, **38**, 4271-4279.
4. C. J. Richards and A. W. Mulvaney, *Tetrahedron: Asymmetry*, 1996, **7**, 1419-1430.
5. Y. Tanaka, T. Mino, K. Akita, M. Sakamoto and T. Fujita, *J. Org. Chem.*, 2004, **69**, 6679-6687.
6. D. Liu, F. Xie and W. Zhang, *J. Org. Chem.*, 2007, **72**, 6992-6997.
7. Programs CrysAlisPro, *Oxford Diffraction Ltd., Oxford Diffraction Ltd., Abingdon, UK* 2018.
8. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8
9. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122 & 2015, **C71**, 3-8
10. *'International Tables for X-ray Crystallography'*, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, pp. 500, 219 and 193.
11. L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849-854.