Computational and Carbon-13 NMR Studies of Pt-C Bonds in P-C-P Pincer Complexes

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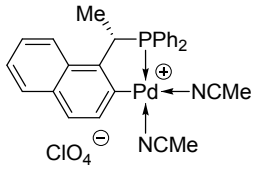
Electronic Supporting Information

General Information

All reactions were carried out under a positive pressure of nitrogen using standard Schlenk technique. Solvents were purchased from their respective companies (DCM, THF: Fisher, toluene, n-hexanes: Avantor, Acetone: Sigma-Aldrich) and used as supplied. Where necessary, solvents were degassed prior to use. A Low Temp Pairstirrer PSL-1800 was used for controlling low temperature reactions. Column chromatography was done on Silica gel 60 (Merck). Melting points were measured using SRS Optimelt Automated Point System SRS MPA100. Optical rotation were measured with Atago automatic polarimeter (AP-300) in the specified solvent in a 0.1 dm cell at 589 nm. NMR spectra were recorded on Bruker AV 300, and AV 400 spectrometers at 300 K. Chemical shifts were reported in ppm and referenced to an internal $SiMe_4$ standard (0 ppm) or chloroform-d (7.26 ppm) for ^1H NMR, chloroform-d (77.23 ppm) for ^{13}C NMR, and an external 85% H_3PO_4 for $^{31}P\{^1H\}$ NMR. All other reactants and reagents were used as supplied. The X-ray crystallographic examination and data collection were performed with Mo Kα radiation on a Bruker Kappa CCD spectrometer. Structure solution and refinement were done on a computer using the SHELX package.[1]

The PC-cyclometalated catalyst **A**,[2] complexes **9a** and **10a**[3] were prepared according to literature methods. The pincer complexes **6a-8a** were prepared by the combination of a hydrophosphination protocol[2] and a metalation procedure.[4]



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Caution! *Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.*

Experimental Section

General procedure for the synthesis of complex 6a, 7a and 8a

To a solution of $HPPh_2$ (0.218 mmol, 1.0 eq.) in THF (3 mL) was added catalyst **A** (0.0109 mmol, 5 mol%). The reaction mixture was stirred for a complete dissolution and cooled to -80° C. Dienone (0.107 mmol, 0.49 equiv.) was added, followed by a solution of NEt_3 (0.218 mmol, 1.0 equiv.) in THF (1 mL) dropwise. The reaction mixture was stirred overnight and monitored by $^{31}P\{^1H\}$NMR for its completion. Upon completion, the reaction mixture was allowed to room temperature and solvent was removed under reduced pressure protected by nitrogen. The residue was dissolved in chloroform (10 mL) and $PtCl_2(PPh_3)_2$ (0.107 mmol, 0.49 eq.) was added. The reaction was stirred at reflux overnight. The reaction mixture was condensed to 2 mL and diluted with acetone (8 mL). KCl (0.214 mmol, 0.99 equiv.) and sulfur (0.214

mmol, 0.99 equiv.) were added. The mixture was refluxed for 2 h and evaporated under reduced pressure to give the crude product, which was then purified by silica gel column chromatography to afford the pure complex.

Complex 6a Yellow solid. Yield 72%. Mp: 157-158 °C. $[\alpha]^{26}_D$ = -327° (*c* 0.49, CH_2Cl_2), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-6.80 (m, 33H, aromatics), 5.07-4.96 (m, 2H, C*H*PPh$_2$), 3.27-3.07 (m, 4H, C*H*$_2$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 46.5 (s, J_{PtP} = 2967.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.7 (t, $^3J_{PC}$ = 4.0 Hz, 2C, *C*O), 151.5-123.9 (m, 41C, aromatics), 146.0 (s, $^1J_{PtC}$ = 935.8 Hz, 1C, Pt*C*), 47.5 (t, $^1J_{PC}$ = 18.6 Hz, 2C, *C*HPPh$_2$), 44.4 (s, 2C, *C*H$_2$). HRMS (+ESI) *m/z*: (M-Cl)$^+$ calcd for $C_{48}H_{39}O_2P_2Pt$, 904.2073; found, 904.2081.

Complex 7a Yellow solid. Yield 71%. Mp: 148-150°C. $[\alpha]^{26}_D$ = -245° (*c* 0.49, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-6.89 (m, 35H, aromatics), 5.04-5.00 (m, 2H, C*H*PPh$_2$), 3.20 (q, 4H, $^3J_{PH}$ = $^3J_{HH}$ = 6.4 Hz, C*H*$_2$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 46.9 (s, J_{PtP} = 2973.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.4 (t, $^3J_{PC}$ = 4.0 Hz, 2C, *C*O), 151.5-124.7 (m, 41C, aromatics), 142.0 (s, $^1J_{PtC}$ = 943.9 Hz, 1C, Pt*C*), 47.1 (t, $^1J_{PC}$ = 18.1 Hz, 2C, *C*HPPh$_2$), 44.3 (s, 2C, *C*H$_2$), 20.9 (s, 1C, *C*H$_3$). HRMS (+ESI) *m/z*: (M-Cl)$^+$ calcd for $C_{49}H_{41}O_2P_2Pt$, 918.2230; found, 918.2227.

Complex 8a Yellow solid. Yield 60%. Mp: 167-169°C. $[\alpha]^{26}_D$ = -269° (*c* 0.52, CH_2Cl_2), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-7.17 (m, 32H, aromatics), 5.05-4.94 (m, 2H, C*H*PPh$_2$), 3.25-3.09 (m, 4H, C*H*$_2$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 46.7 (s, J_{PtP} = 2935.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.8 (t, $^3J_{PC}$ = 3.5 Hz, 2C, *C*O), 153.9-118.8 (m, 41C, aromatics), 145.1 (s, $^1J_{PtC}$ = 954.9 Hz, 1C, Pt*C*), 47.0 (t, $^1J_{PC}$ = 18.1 Hz, 2C, *C*HPPh$_2$), 44.2 (s, 2C, *C*H$_2$). HRMS (+ESI) *m/z*: (M-Cl)$^+$ calcd for $C_{48}H_{38}O_2P_2BrPt$, 982.1178; found, 982.1176.

General procedure for the synthesis of complexes 6b, 7b and 8b

To a solution of the pincer-Pt-Cl complex **6a**, **7a** or **8a** (0.0505 mmol, 1.0 equiv.) in DCM (5 mL) and water (1 mL) was added PPh_3 (0.0505 mmol, 1.0 equiv.) and $AgClO_4$ (0.101 mmol, 2.0 equiv.) The reaction mixture was stirred for 2 h. The residue was removed and the filtrate washed with water (2 X 20 mL), dried over Na_2SO_4 and concentrated to give the crude product, which was purified by silica gel column chromatography.

Complex 6b Brown solid. Yield 98%. Mp: 117-119°C. $[\alpha]^{26}_D$ = -116° (*c* 0.43, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-6.69 (m, 48H, aromatics), 5.29-5.28 (m, 2H, C*H*PPh$_2$), 3.49-3.42 (m, 2H, C*H*$_2$), 3.17-3.09 (m, 2H, C*H*$_2$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 54.1 (d, $^2J_{PP}$ = 19.4 Hz, J_{PtP} = 2768.2 Hz), 18.3 (t, $^2J_{PP}$ = 19.4 Hz, J_{PtP} = 2055.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.4 (t, $^3J_{PC}$ = 4.5 Hz, 2C, *C*O), 157.8 (d, $^2J_{PC}$ = 89.7 Hz, J_{PtC} = 687.6 Hz, 1C, Pt*C*), 147.8-123.0 (m, 59C, aromatics), 49.1 (td, $^1J_{PC}$ = 18.1 Hz, $^3J_{PC}$ = 7.0, 2C, *C*HPPh$_2$), 40.11 (s, 2C, *C*H$_2$). HRMS (+ESI) *m/z*: (M-ClO_4)$^+$ calcd for $C_{66}H_{54}O_2P_3Pt$, 1166.2985; found, 1166.3007.

Complex 7b Brown solid. Yield 99%. Mp: 103-105°C. $[\alpha]^{26}_D$ = -113° (*c* 0.53, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-6.52 (m, 47H, aromatics), 5.24-5.23 (m, 2H, C*H*PPh$_2$), 3.46-3.39 (m, 2H, C*H*$_2$), 3.20-3.12 (m, 2H, C*H*$_2$), 1.97 (s, 3H, C*H*$_3$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 53.5 (d, $^2J_{PP}$ = 19.4 Hz, J_{PtP} = 2775.5 Hz), 18.3 (t, $^2J_{PP}$ = 19.4 Hz, J_{PtP} = 2057.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.5 (t, $^3J_{PC}$ = 4.5 Hz, 2C, *C*O), 154.6 (d, $^2J_{PC}$ = 90.1 Hz, J_{PtC} = 687.8 Hz, 1C, Pt*C*), 148.1-124.0 (m, 59C, aromatics), 49.4 (td, $^1J_{PC}$ = 16.7 Hz, $^3J_{PC}$ = 7.0, 2C, *C*HPPh$_2$), 40.49 (s, 2C, *C*H$_2$), 21.28 (s, 1C, *C*H$_3$). HRMS (+ESI) *m/z*: $(M+H)^+$ HRMS (+ESI) *m/z*: $(M-ClO_4)^+$ calcd for $C_{67}H_{56}O_2P_3Pt$, 1180.3141; found, 1180.3142.

Complex 8b Brown solid. Yield 97%. Mp: 128-130°C. $[\alpha]^{26}_D$ = -78° (*c* 0.51, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-6.86 (m, 47H, aromatics), 5.24-5.23 (m, 2H, C*H*PPh$_2$), 3.42-3.36 (m, 2H, C*H*$_2$), 3.27-3.19 (m, 2H, C*H*$_2$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 53.2 (d, $^2J_{PP}$ = 19.4 Hz, J_{PtP} = 2742.9 Hz), 17.6 (t, $^2J_{PP}$ = 19 Hz, J_{PtP} = 2085.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.1 (s, 2C, *C*O), 157.0 (d, $^2J_{PC}$ = 91.1 Hz, J_{PtC} = 702.9 Hz, 1C, Pt*C*), 150.5-122.1 (m, 59C, aromatics), 49.2 (td, $^1J_{PC}$ = 18.1 Hz, $^3J_{PC}$ = 7.0, 2C, *C*HPPh$_2$), 40.5 (s, 2C, *C*H$_2$). HRMS (+ESI) *m/z*: $(M+H)^+$ HRMS (+ESI) *m/z*: $(M-ClO_4)^+$ calcd for $C_{66}H_{53}O_2P_3BrPt$, 1244.2090; found, 1244.2084.

General procedure for the synthesis of complexes 6c, 7c and 8c

To a mixture of the pincer-Pt-Cl complex **6a**, **7a** or **8a** (0.042 mmol, 1.0 equiv.) in DCM (5 mL) and water (1 mL) was added AgCN (0.084 mmol, 2.0 equiv.). The reaction mixture was stirred overnight, filtered through celite and the filtrate was washed with water, dried over Na_2SO_4 and concentrated to give the crude product, which was purified by silica gel column chromatography.

Complex 6c White solid. Yield 92%. Mp: 160-162°C. $[\alpha]^{26}_D$ = -326° (*c* 0.43, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-6.88 (m, 33H, aromatics), 5.30-5.19 (m, 2H, C*H*PPh$_2$), 3.19-3.09 (m, 2H, C*H*$_2$), 3.03-2.95 (m, 2H, C*H*$_2$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 49.3 (s, J_{PtP} = 2781.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.6 (t, $^3J_{PC}$ = 5.1 Hz, 2C, *C*O), 159.5 (s, J_{PtC} = 676.3 Hz, 1C, Pt*C*), 153.7-123.5 (m, 42C, aromatics and *C*N), 49.9 (t, $^1J_{PC}$ = 18.6 Hz, 2C, *C*HPPh$_2$), 44.7 (s, 2C, *C*H$_2$). HRMS (+ESI) *m/z*: $(M+H)^+$ calcd for $C_{49}H_{40}NO_2P_2Pt$, 931.2182; found, 931.2177.

Complex 7c White solid. Yield 83%. Mp: 228-230°C (dec). $[\alpha]^{26}_D$ = -325° (*c* 0.40, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-6.96 (m, 32H, aromatics), 5.27-5.15 (m, 2H, C*H*PPh$_2$), 3.23-2.98 (m, 4H, C*H*$_2$), 2.00 (s, 3H, C*H*$_3$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 49.5 (s, J_{PtP} = 2789.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.6 (t, $^3J_{PC}$ = 4.5 Hz, 2C, *C*O), 155.9 (s, J_{PtC} = 677.0 Hz, 1C, Pt*C*), 153.9-124.4 (m, 42C, aromatics and *C*N), 49.7 (t, $^1J_{PC}$ = 19.1 Hz, 2C, *C*HPPh$_2$), 44.9 (s, 2C, *C*H$_2$), 21.4 (s, 1C, *C*H$_3$). HRMS (+ESI) *m/z*: $(M+H)^+$ calcd for $C_{50}H_{42}NO_2P_2Pt$, 945.2339; found, 945.2327.

Complex 8c White solid. Yield 89%. Mp: 152-154 °C. $[\alpha]^{26}_D$ = -239° (*c* 0.49, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.17 (m, 32H, aromatics), 5.28-5.17 (m, 2H,

C*H*PPh$_2$), 3.07 (q, $^3J_{PH} = {}^3J_{HH} = 6.8$ Hz, 4H, CH_2); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 49.2 (s, $J_{PtP} = 2756.8$ Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.8 (t, $^3J_{PC} = 4.5$ Hz, 2C, *C*O), 158.7 (t, $^2J_{PC} = 2.0$ Hz, $J_{PtC} = 687.6$ Hz, 1C, Pt*C*) 156.1-120.4 (m, 42C, aromatics and *C*N), 49.3 (t, $^1J_{PC} = 19.1$ Hz, 2C, *C*HPPh$_2$), 44.6 (s, 2C, *C*H$_2$). HRMS (+ESI) *m/z*: (M+H)$^+$ calcd for $C_{49}H_{39}NO_2P_2BrPt$, 1009.1287; found, 1009.1295.

General procedure for the synthesis of complexes 6d, 7d and 8d

To a solution of the pincer-Pt-Cl complex **6a**, **7a** or **8a** (0.213 mmol, 1.0 equiv.) in chloroform (10 mL) and water (2 mL) was added $AgNO_3$ (0.850 mmol, 4.0 equiv.) The reaction mixture was stirred overnight. Residue was removed by filtration and the filtrate was washed with water, dried over Na_2SO_4 and concentrated to give the pure product.

Complex 6d Yellow solid. Yield 82%. Mp: 123-125°C. $[\alpha]^{26}_D = -238°$ (*c* 6.3, CH_2Cl_2). ^{1}H NMR (400 MHz, acetone-d^6): δ 8.26-6.77 (m, 33H, aromatics), 5.08-5.05 (m, 2H, C*H*PPh$_2$), 3.51-3.42 (m, 2H, CH_2), 3.28-3.20 (m, 2H, CH_2); ^{31}P{^{1}H} NMR (162 MHz, acetone-d^6): δ 49.8 (s, $J_{PtP} = 3085.6$ Hz); ^{13}C NMR (101 MHz, acetone-d^6): δ 197.3 (t, $^3J_{PC} = 4.0$ Hz, 2C, *C*O), 152.4-124.9 (m, 41C, aromatics), 135.3 (s, $J_{PtC} = 951.1$ Hz, 1C, Pt*C*), 47.8 (t, $^1J_{PC} = 18.6$ Hz, 2C, *C*HPPh$_2$), 44.9 (s, 2C, *C*H$_2$). HRMS (+ESI) *m/z*: (M-NO$_3$)$^+$ calcd for $C_{48}H_{39}O_2P_2Pt$, 904.2073; found, 904.2087.

Complex 7d Yellow solid. Yield 87%. Mp: 134-136°C. $[\alpha]^{26}_D = -194°$ (*c* 6.7, CH_2Cl_2). ^{1}H NMR (400 MHz, acetone-d^6): δ 8.26-6.84 (m, 32H, aromatics), 5.00-4.99 (m, 2H, C*H*PPh$_2$), 3.45-3.37 (m, 2H, CH_2), 3.28-3.21 (m, 2H, CH_2), 1.90 (s, 3H, CH_3); ^{31}P{^{1}H} NMR (162 MHz, acetone-d^6): δ 49.9 (s, $J_{PtP} = 3099.4$ Hz); ^{13}C NMR (101 MHz, acetone-d^6): δ 197.3 (t, $J_{PC} = 4.0$ Hz, 2C, *C*O), 152.3-125.8 (m, 40C, aromatics), 131.3 (s, $J_{PtC} = 947.4$ Hz, 1C, Pt*C*), 47.8 (t, $^1J_{PC} = 18.1$ Hz, 2C, *C*HPPh$_2$), 45.0 (s, 2C, *C*H$_2$), 21.0 (s, 2C, *C*H$_3$). HRMS (+ESI) *m/z*: (M-NO$_3$)$^+$ calcd for $C_{49}H_{41}O_2P_2Pt$, 918.2230; found, 918.2230.

Complex 8d Yellow solid. Yield 99%. Mp: 141-143°C. $[\alpha]^{26}_D = -204°$ (*c* 0.49, CH_2Cl_2). ^{1}H NMR (400 MHz, acetone-d^6): δ 8.29-7.24 (m, 32H, aromatics), 5.12-4.98 (m, 2H, C*H*PPh$_2$), 3.54-3.45 (m, 2H, CH_2), 3.36-3.27 (m, 2H, CH_2); ^{31}P{^{1}H} NMR (162 MHz, acetone-d^6): δ 49.9 (s, $J_{PtP} = 3057.2$ Hz); ^{13}C NMR (101 MHz, acetone-d^6): δ 196.9 (t, $^3J_{PC} = 4.0$ Hz, 2C, *C*O), 154.6-119.8 (m, 41C, aromatics), 134.9 (s, $J_{PtC} = 965.6$ Hz, 1C, Pt*C*), 47.6 (t, $^1J_{PC} = 18.6$ Hz, 2C, *C*HPPh$_2$), 44.8 (s, 2C, *C*H$_2$). HRMS (+ESI) *m/z*: (M-NO$_3$)$^+$ calcd for $C_{48}H_{38}O_2P_2BrPt$, 982.1178; found, 982.1187.

Synthesis of complex 6e

To a solution of the pincer-Pt-Cl complex **6a** (0.213 mmol, 1.0 equiv.) in DCM (10 mL) and was added AgOAc (0.320 mmol, 1.5 equiv.) The reaction mixture was stirred overnight, filtered through a plug of silca gel and extracted into DCM (25 mL). The organic layer was washed with water (2 X 25 mL), dried over Na_2SO_4 and concentrated to give the pure product **6e**.

Complex 6e White solid. Yield 95%. Mp: 145-147°C. $[\alpha]^{26}_{D}$ = -311° (*c* 1.00, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11-8.08 (m, 4H, aromatics), 7.90-7.85 (m, 4H, aromatics), 7.45-7.35 (m, 18H, aromatics), 7.14-7.09 (m, 4H, aromatics), 6.94 (d, J_{HH} = 7.5 Hz, 2H, aromatics), 6.69 (t, J_{HH} = 7.3 Hz, 1H, aromatics), 4.96-4.77 (m, 2H, C*H*PPh_2), 3.45-3.36 (m, 2H, CH_2), 3.06-2.95 (m, 2H, CH_2); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 48.8 (s, J_{PtP} = 3097.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6 (t, $^3J_{PC}$ = 5.1 Hz, 2C, *C*O), 176.5 (s, 1C, *C*OMe), 151.0-123.5 (m, 41C, aromatics), 139.0 (s, J_{PtC} = 882.9 Hz, 1C, Pt*C*), 47.9 (t, $^1J_{PC}$ = 18.3 Hz, 2C, *C*HPPh_2), 43.8 (s, 2C, *C*H_2), 24.2 (s, 1C, O*C*H_3). HRMS (+ESI) *m/z*: $(M\text{-}OAc)^+$ calcd for $C_{48}H_{39}O_2P_2Pt$, 904.2073; found, 904.2077.

General Procedure for Catalytic Addition of Diphenylphosphine to Chalcone

The catalyst **6e** (25 umol, 5 mol %) was added to a solution of diphenylphosphine (0.5 mmol, 1.0 equiv) in DCM (1 mL) and stirred at RT followed by the subsequent addition of chalcone **11** (0.5 mmol, 1.0 equiv). Completion of the reaction was determined by the disappearance of the phosphorous signal attributed to diphenylphosphine (-40 ppm) in the ^{31}P{^{1}H} NMR spectrum. Upon completion of the reaction, aq. H_2O_2 (0.1 mL, 31% v/v) was added to form the respective product. The volatiles were removed under reduced pressure and the crude product was directly loaded onto silica gel column (3 EA : 2 *n*-hexane) to afford the pure product. The data obtained is consistent with literature.[5] The *ee* of the oxide product was determined on a Daicel Chiralpak IC column with *n*-hexane/2-propanol = 80/20, flow = 0.8 mL/min, wavelength = 240 nm. Retention times: 16.7 min, 24.0 min.

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NMR spectra

Complex **6a**

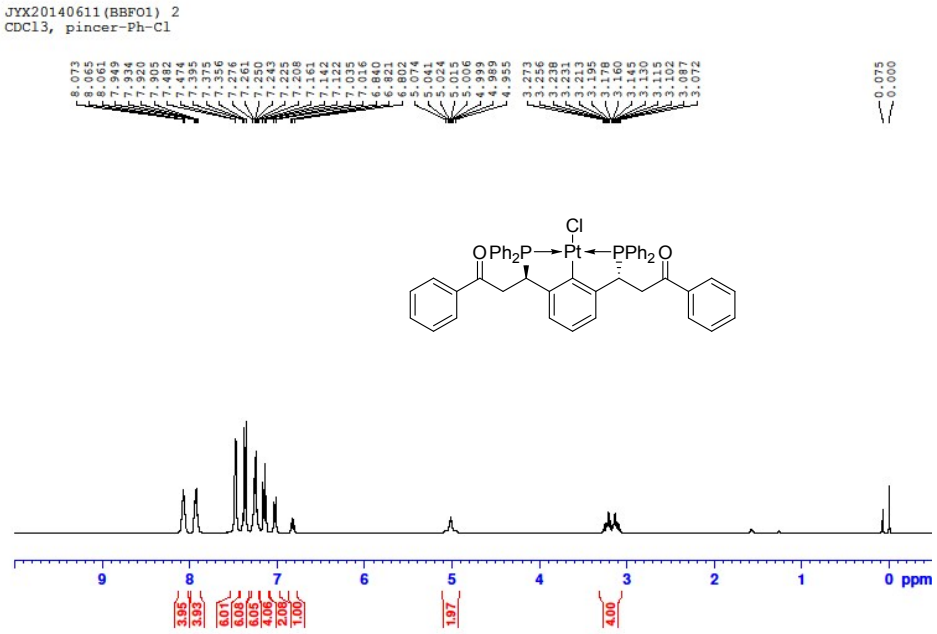


Figure 1. ^{1}H NMR spectrum of complex **6a**.

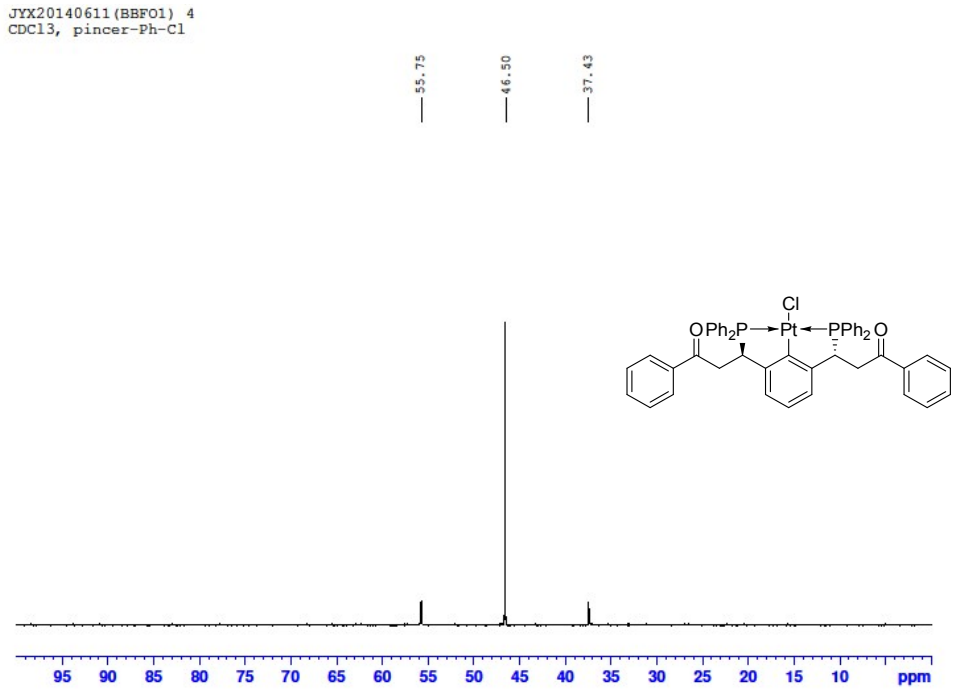


Figure 2. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6a**.

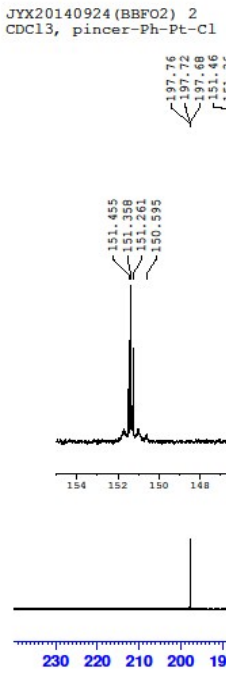


Figure 3. ^{13}C NMR spectrum of complex **6a**.

Complex **7a**

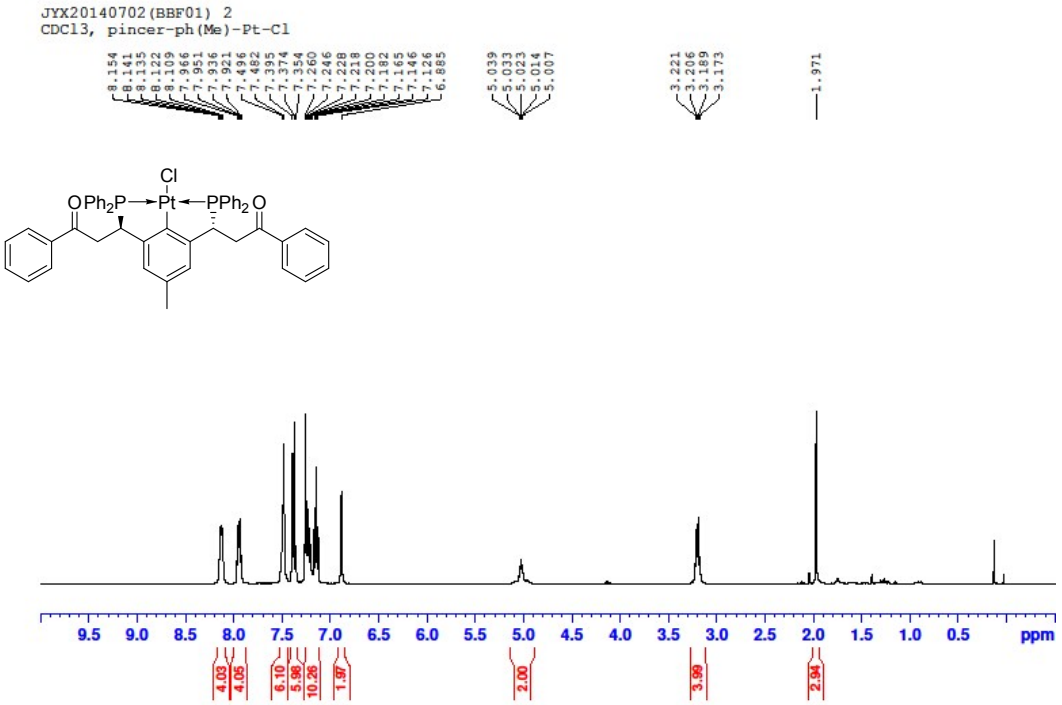


Figure 4. ^{1}H NMR spectrum of complex **7a**.

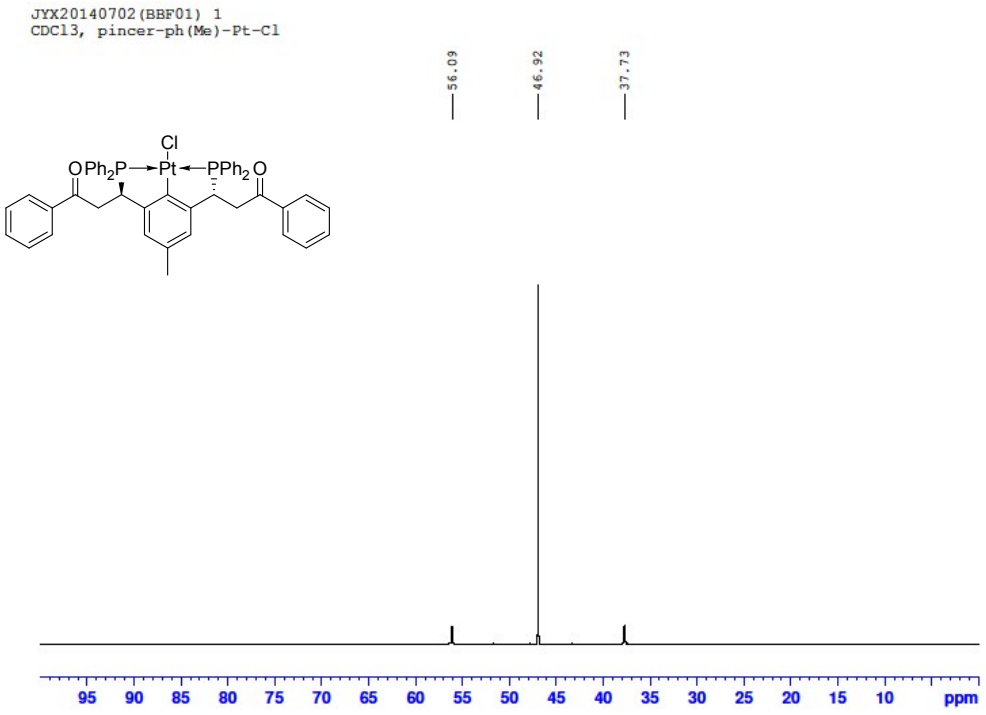


Figure 5. $^{31}P\{^{1}H\}$ NMR spectrum of complex **7a**.

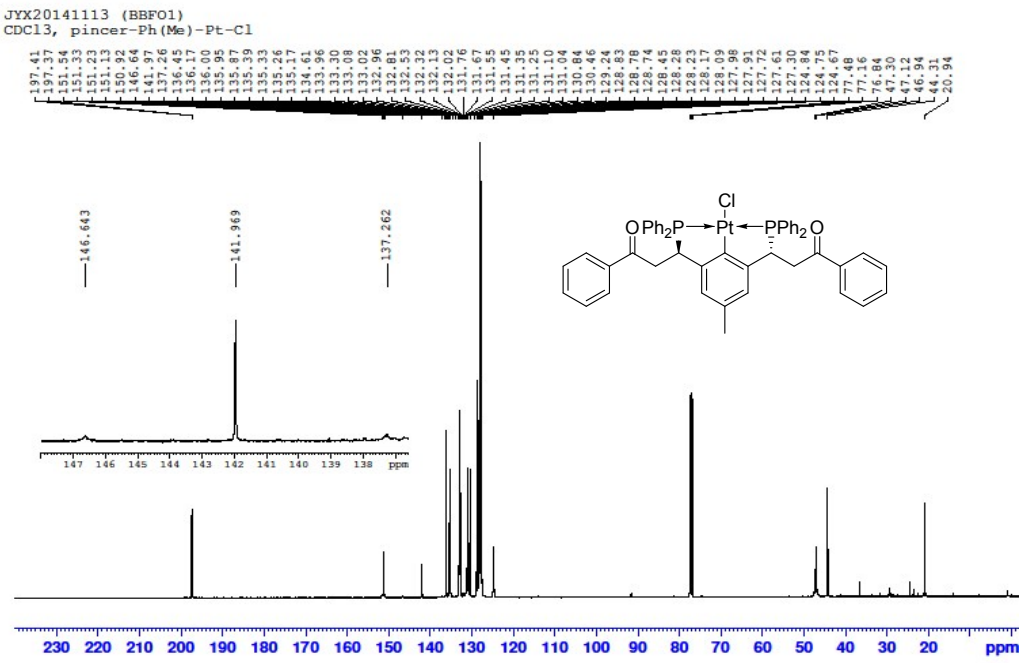


Figure 6. ^{13}C NMR spectrum of complex **7a**.

Complex **8a**

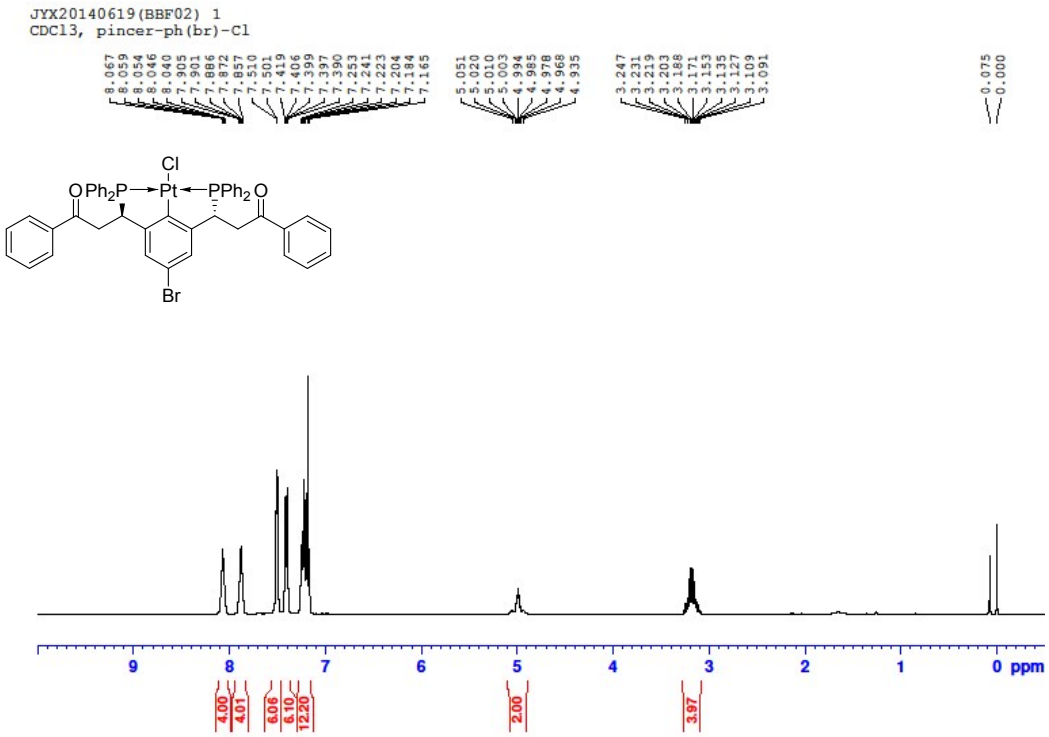


Figure 7. ^{1}H NMR spectrum of complex **8a**.

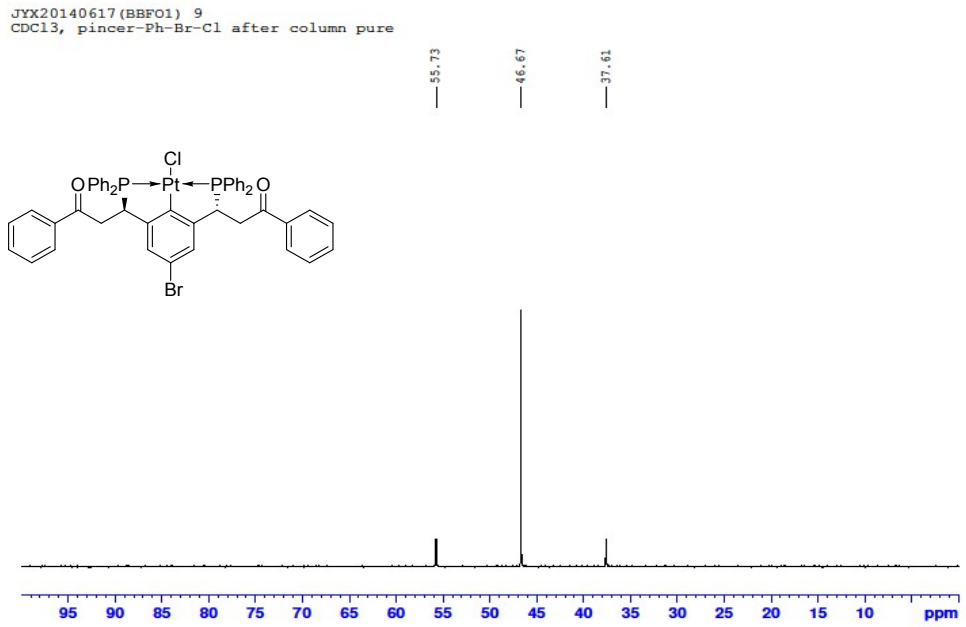


Figure 8. $^{31}P\{^{1}H\}$ NMR spectrum of complex **8a**.

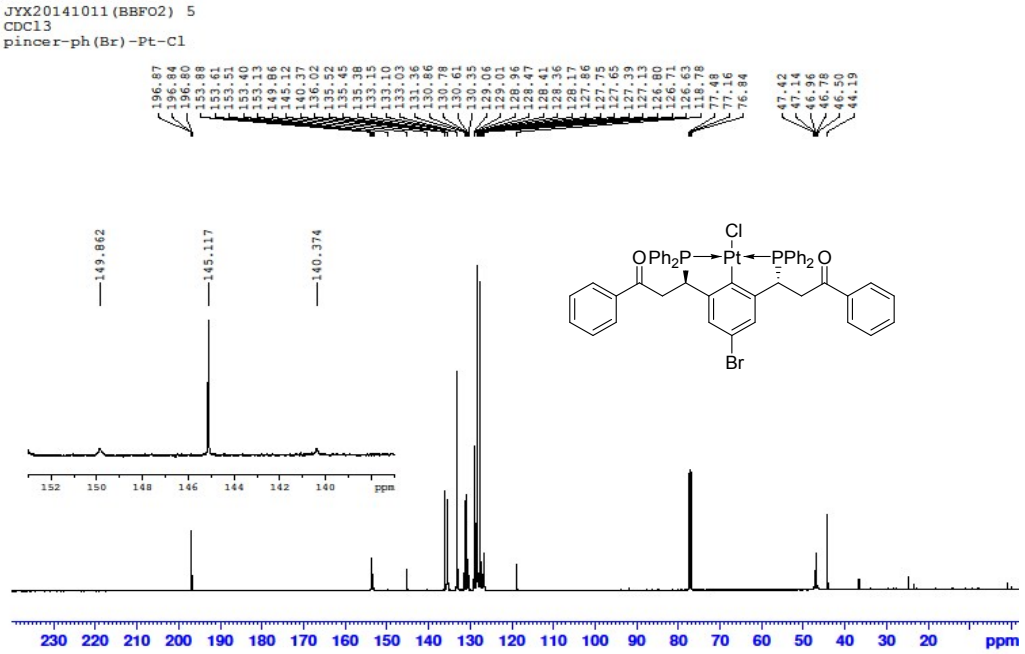


Figure 9. ^{13}C NMR spectrum of complex **8a**.

Complex **6b**

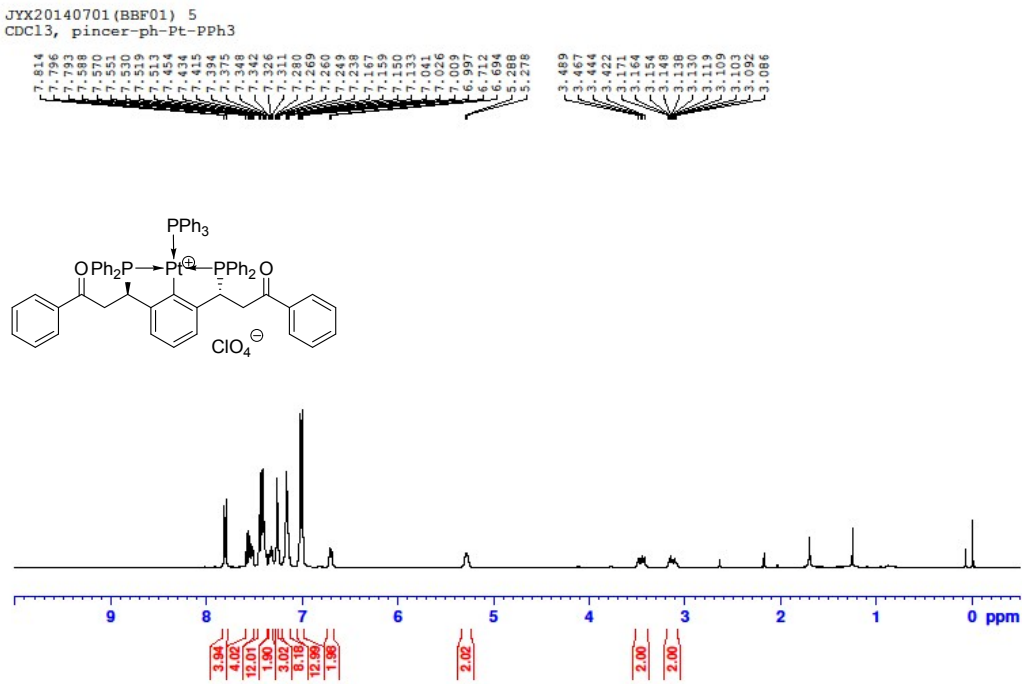


Figure 10. ^{1}H NMR spectrum of complex **6b**.

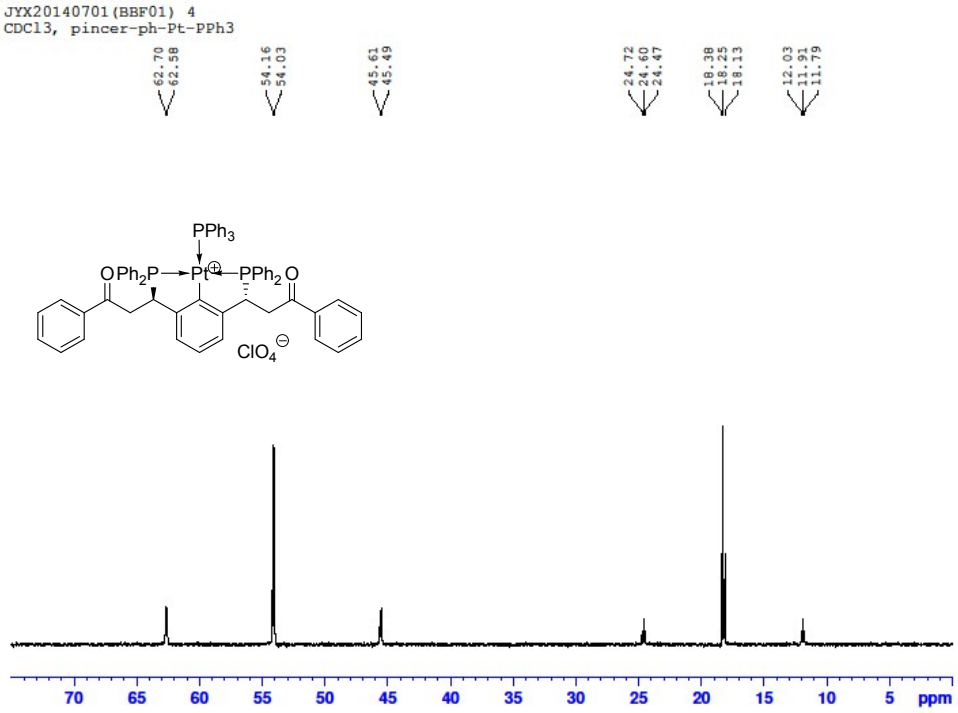


Figure 11. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6b**.

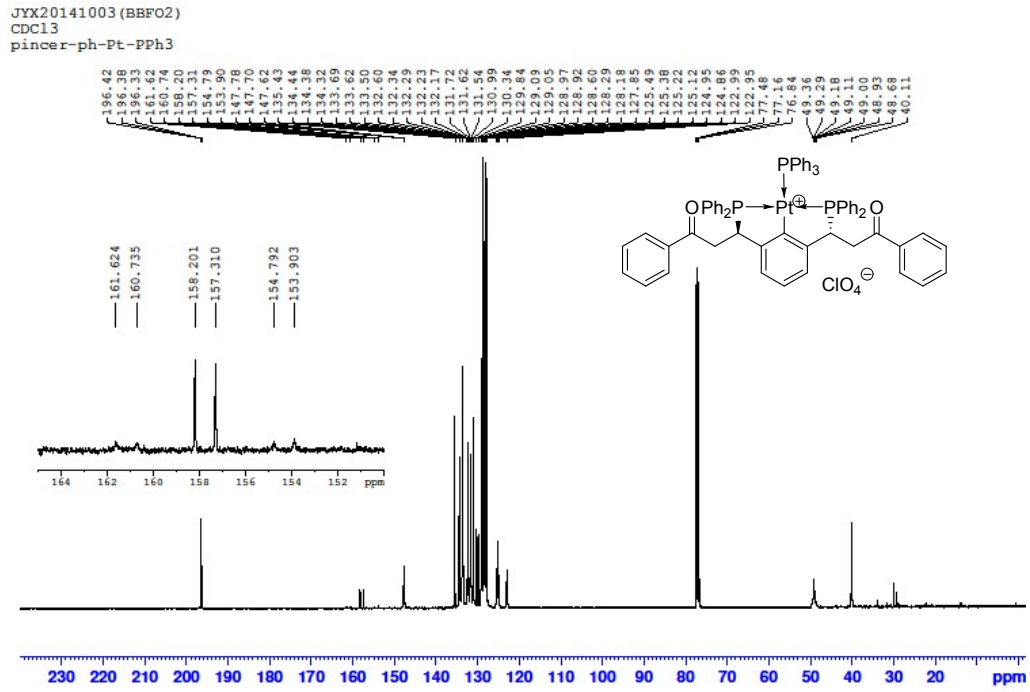


Figure 12. ^{13}C NMR spectrum of complex **6b**.

Complex **7b**

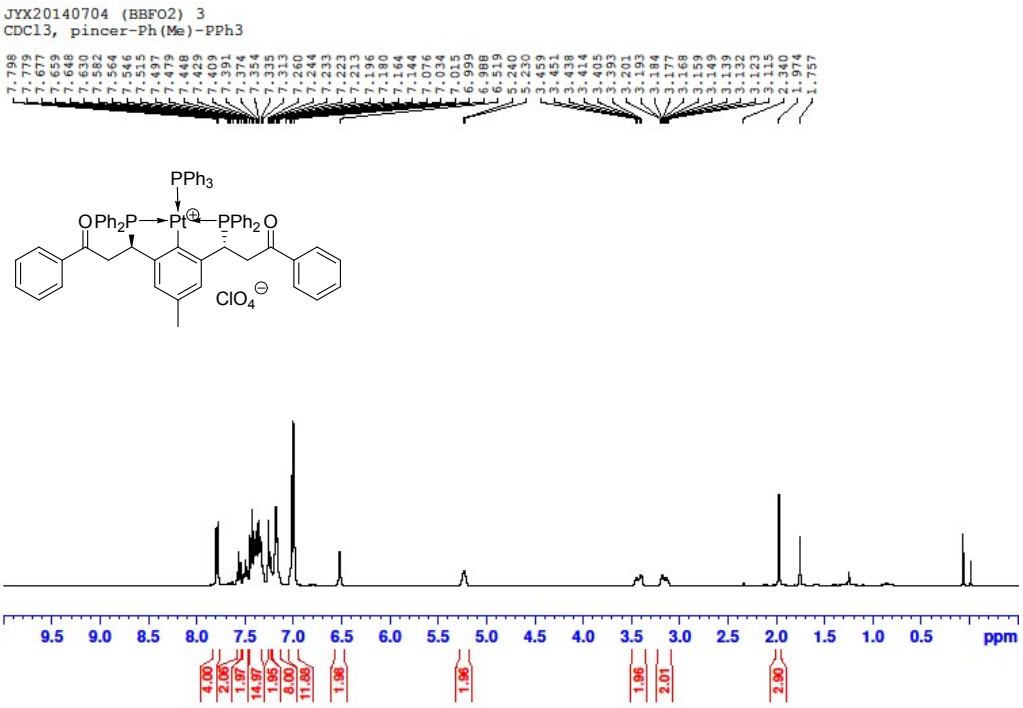


Figure 13. ^{1}H NMR spectrum of complex **7b**.

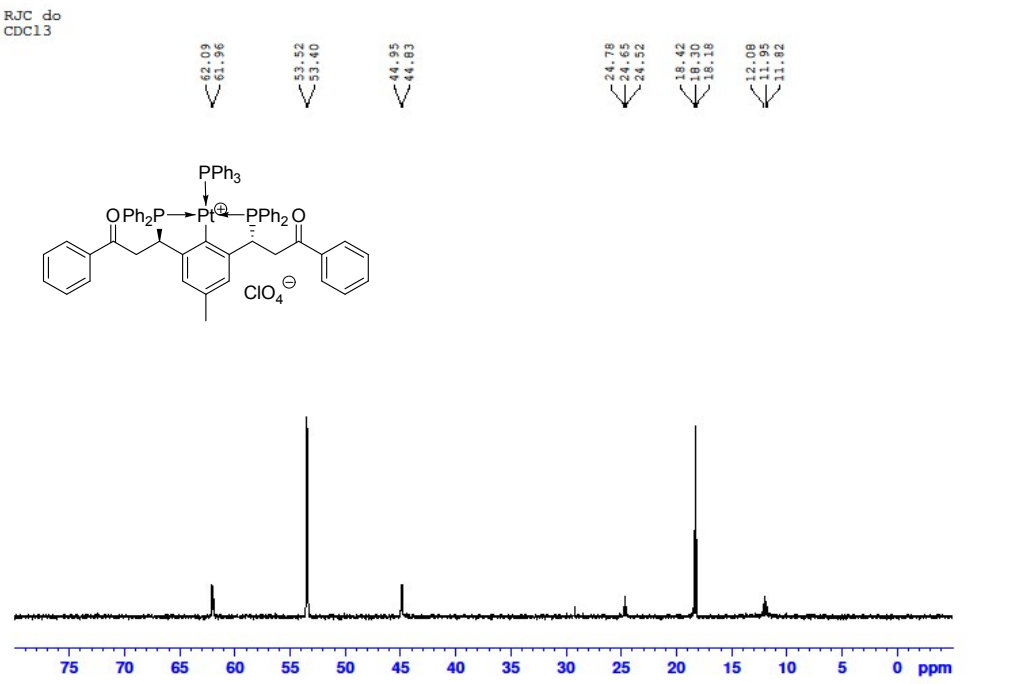


Figure 14. ^{31}P{^{1}H} NMR spectrum of complex **7b**.

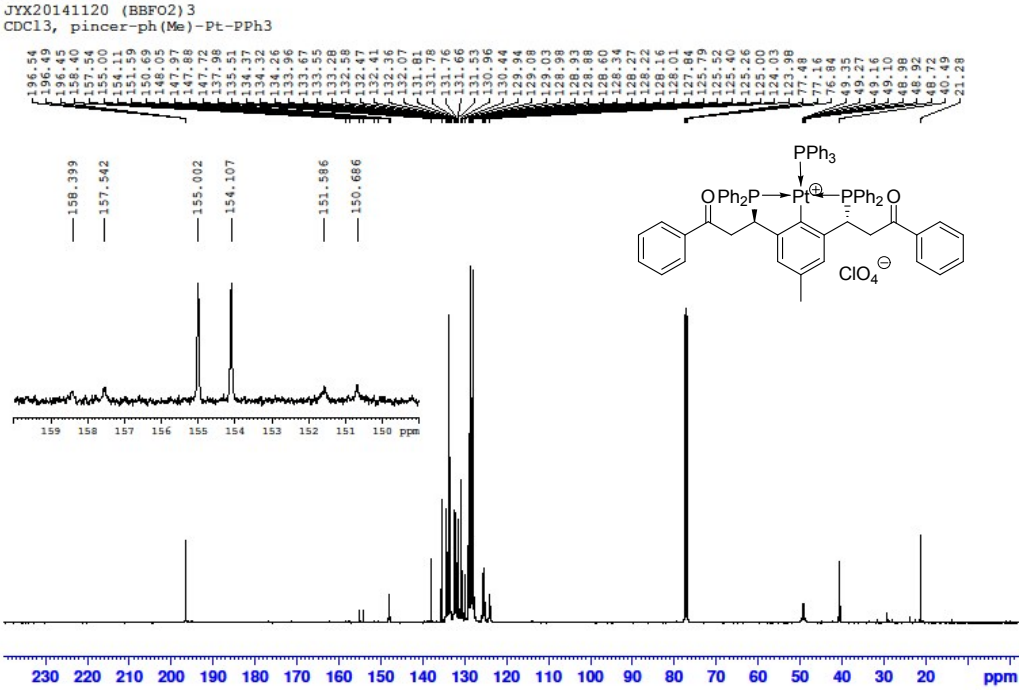


Figure 15. ^{13}C NMR spectrum of complex **7b**.

Complex **8b**

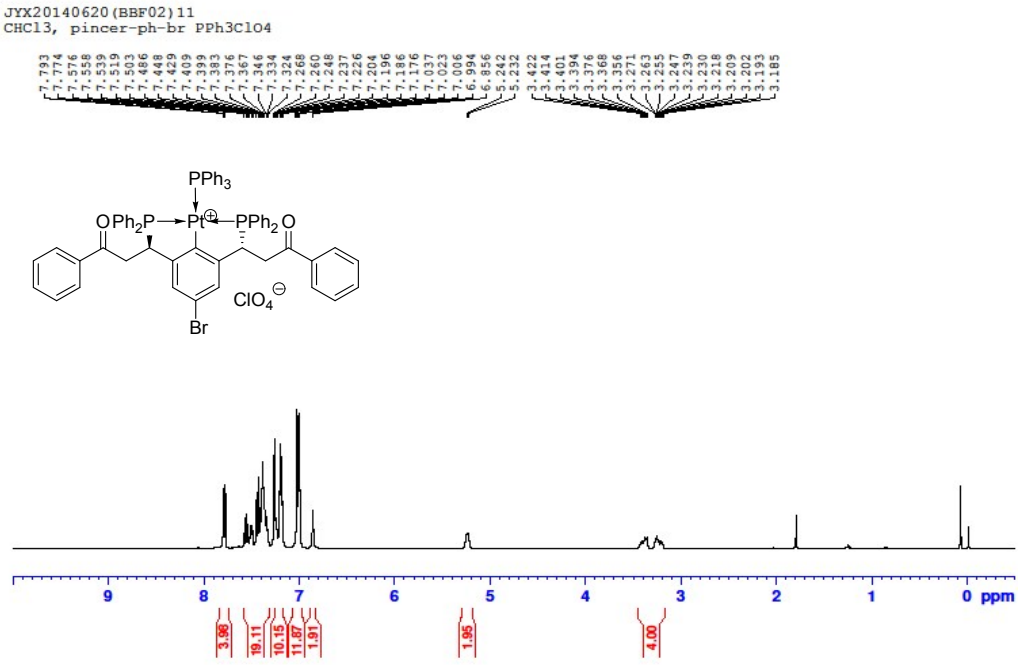


Figure 16. ^{1}H NMR spectrum of complex **8b**.

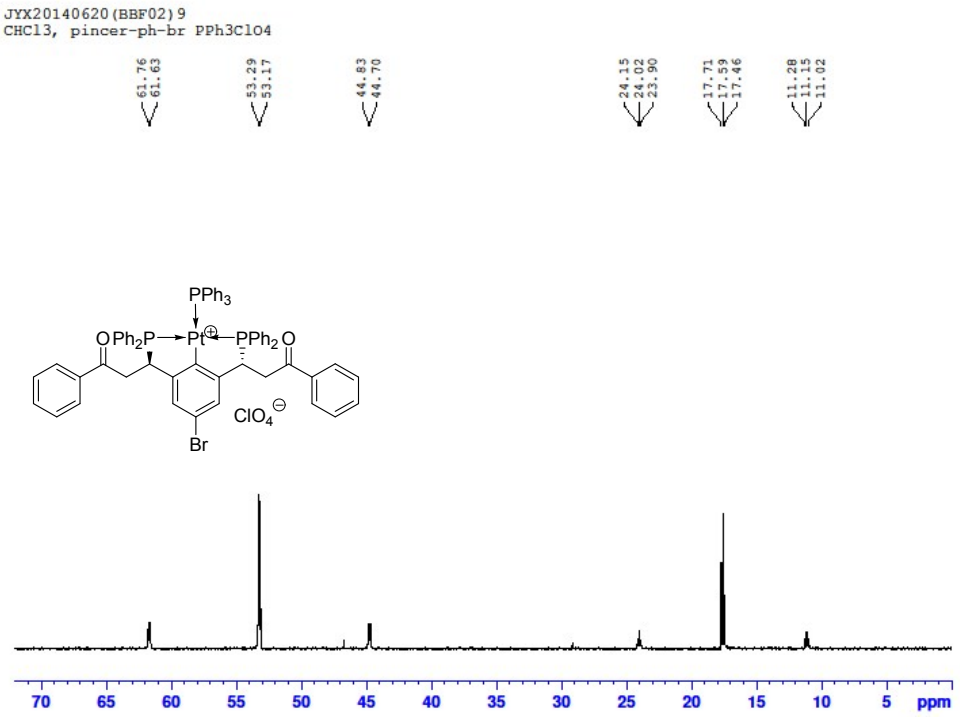


Figure 17. $^{31}P\{^{1}H\}$ NMR spectrum of complex **8b**.

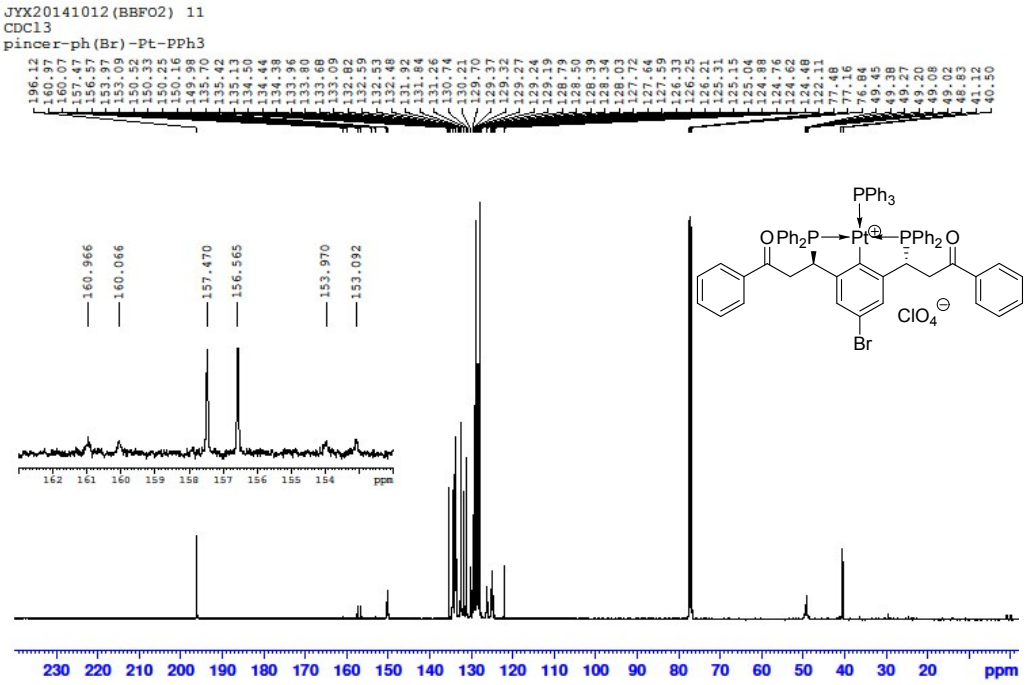


Figure 18. ^{13}C NMR spectrum of complex **8b**.

Complex **6c**

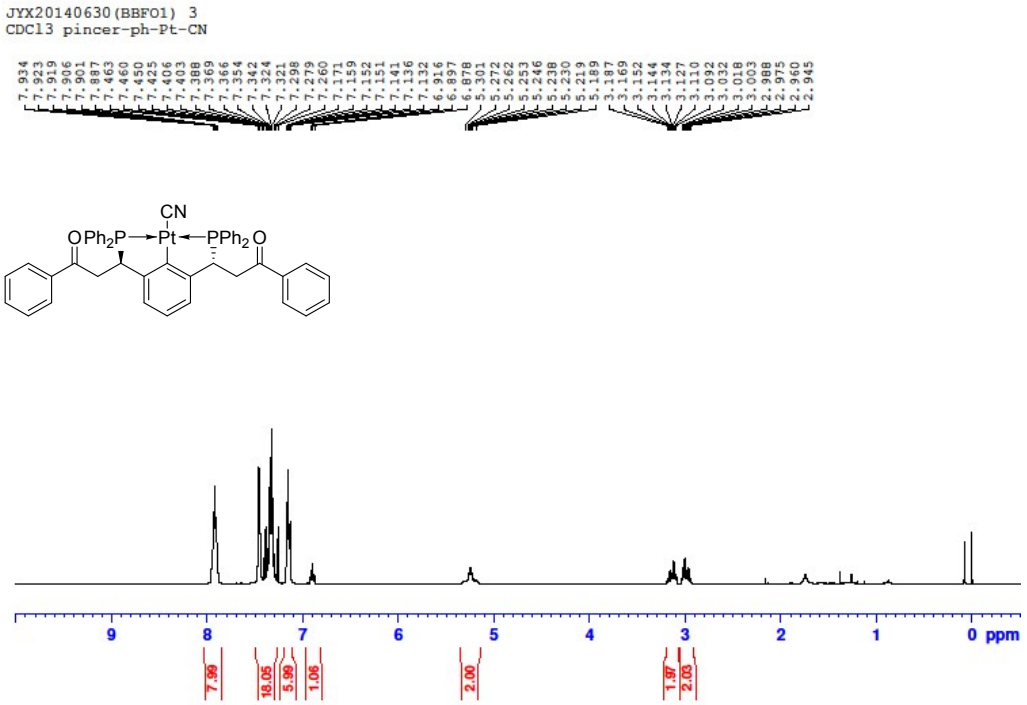


Figure 19. ^{1}H NMR spectrum of complex **6c**.

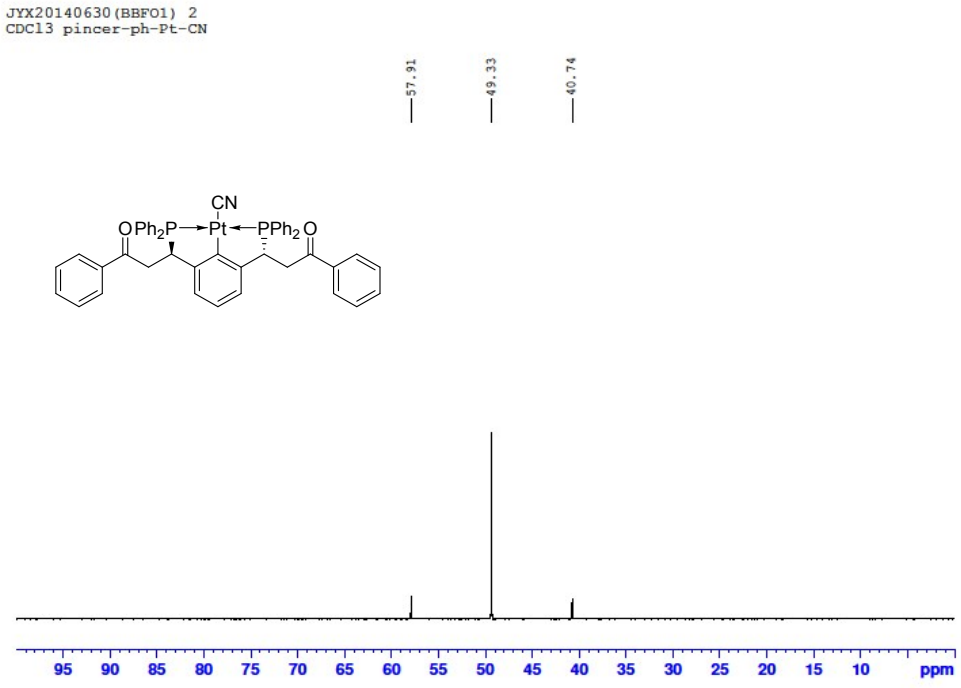


Figure 20. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6c**.

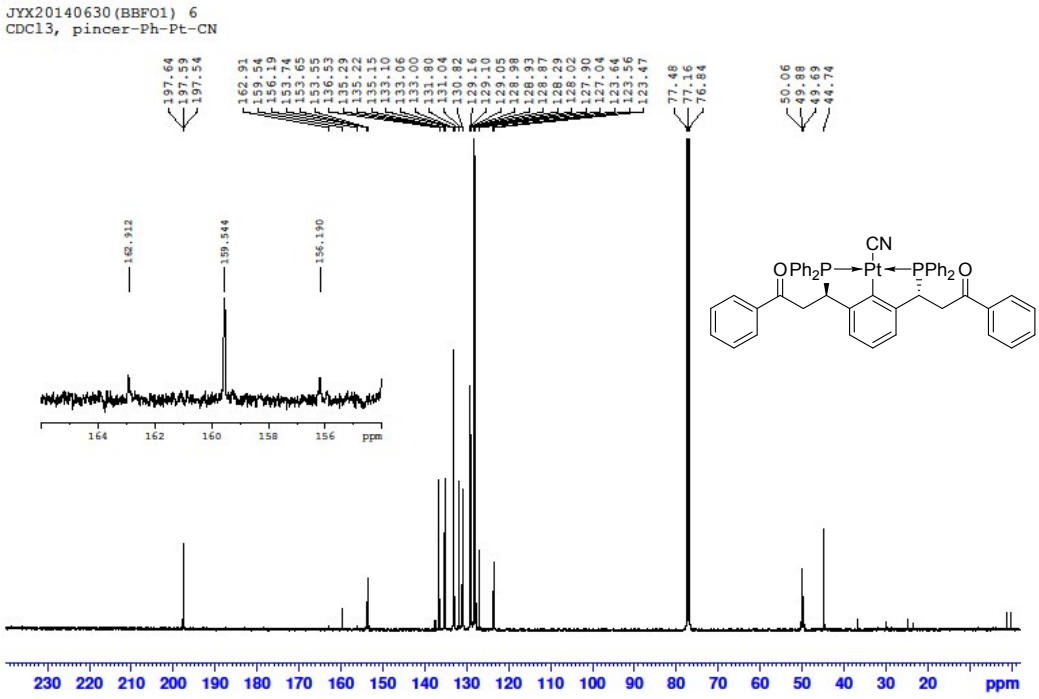


Figure 21. ^{13}C NMR spectrum of complex **6c**.

Complex **7c**

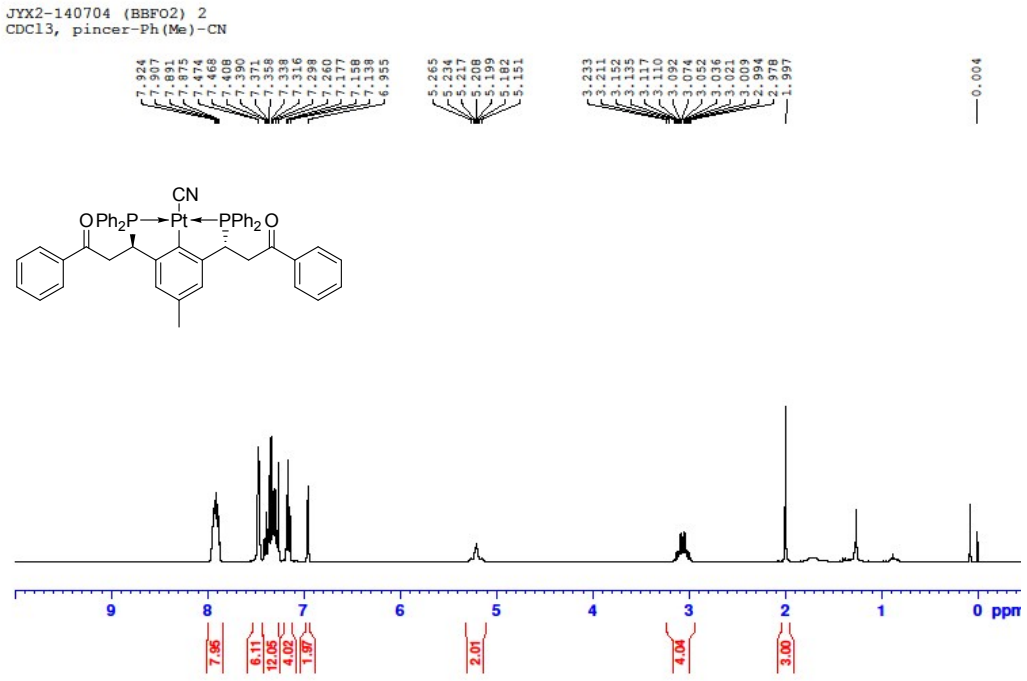


Figure 22. ^{1}H NMR spectrum of complex **7c**.

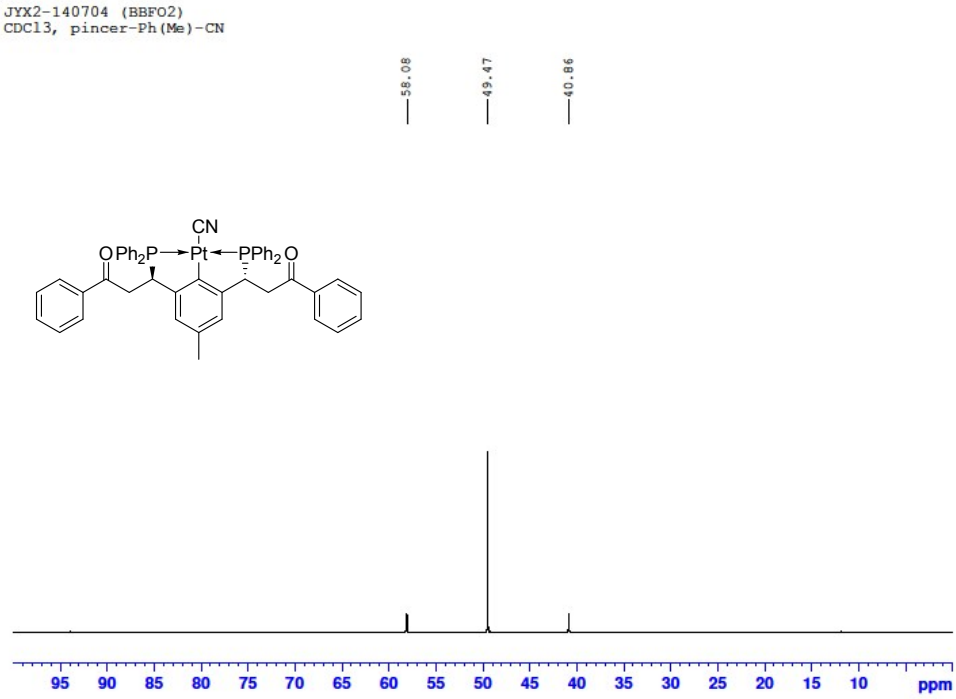


Figure 23. $^{31}P\{^{1}H\}$ NMR spectrum of complex **7c**.

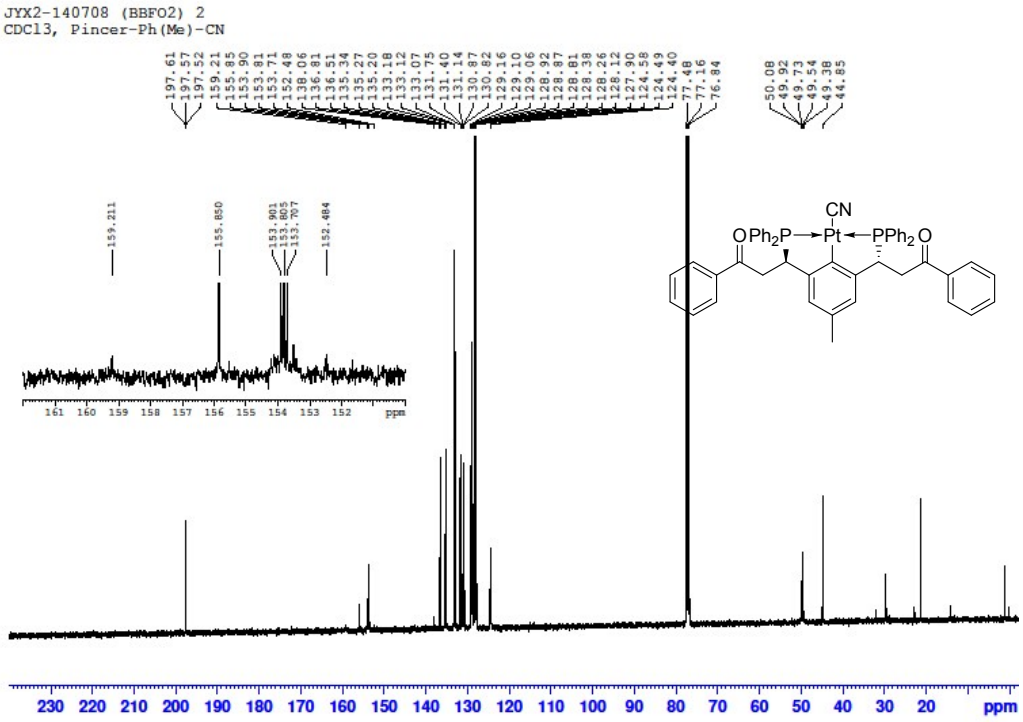


Figure 24. ^{13}C NMR spectrum of complex **7c**.

Complex **8c**

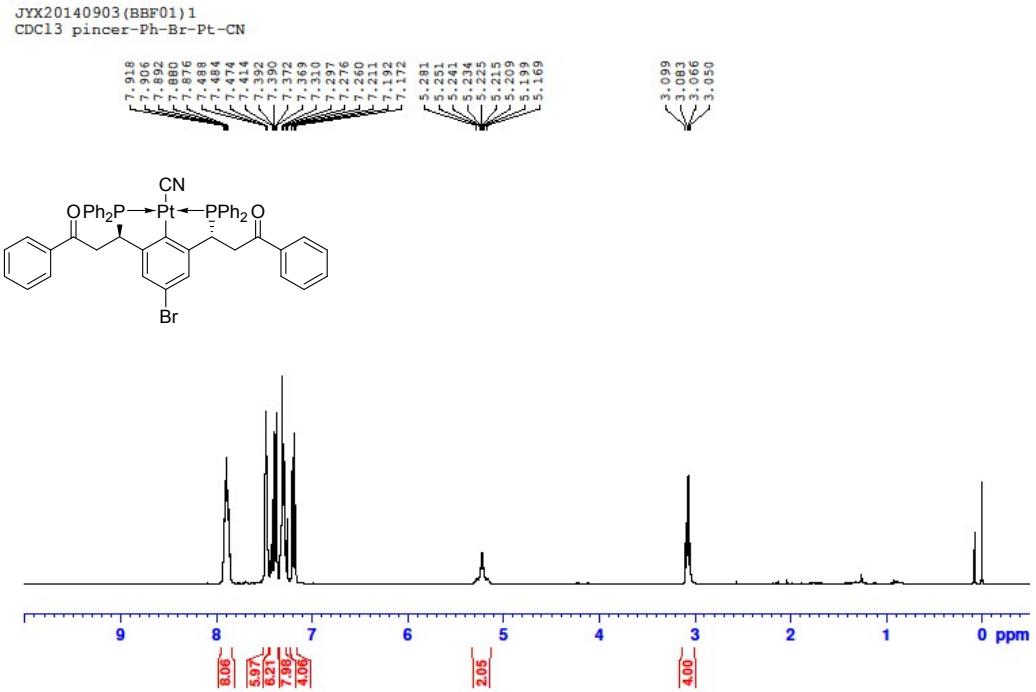


Figure 25. ^{1}H NMR spectrum of complex **8c**.

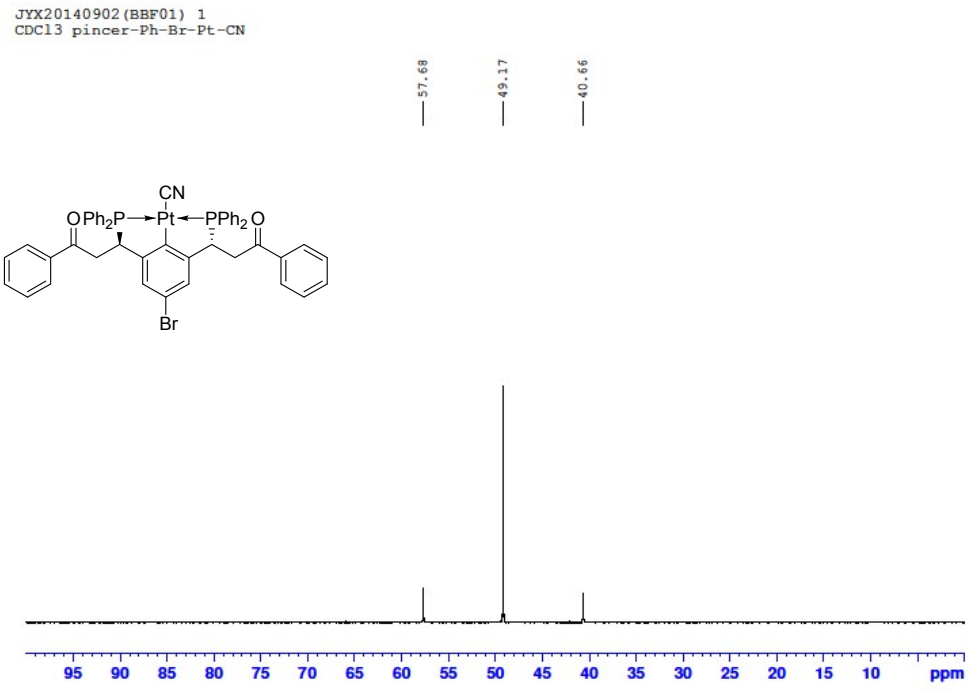


Figure 26. $^{31}P\{^{1}H\}$ NMR spectrum of complex **8c**.

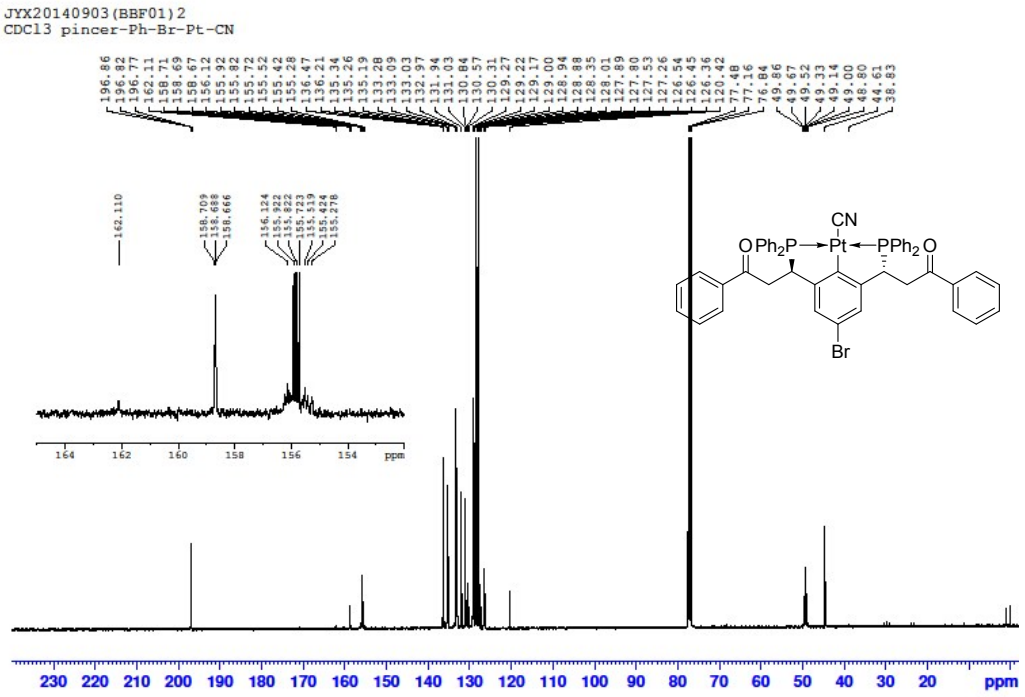


Figure 27. ^{13}C NMR spectrum of complex **8c**.

Complex **6d**

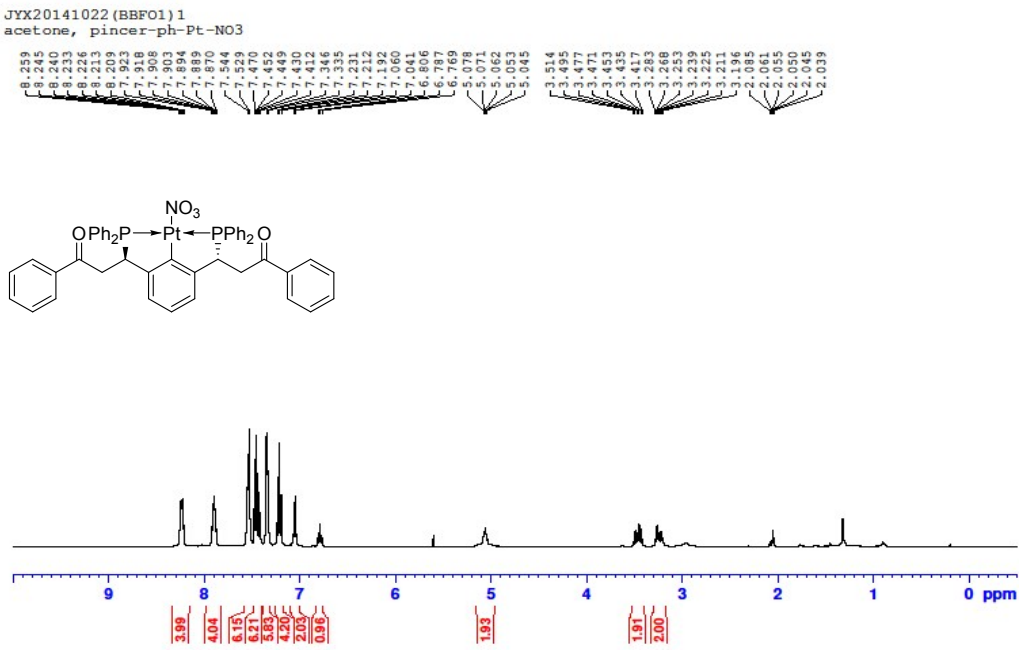


Figure 28. ^{1}H NMR spectrum of complex **6d**.

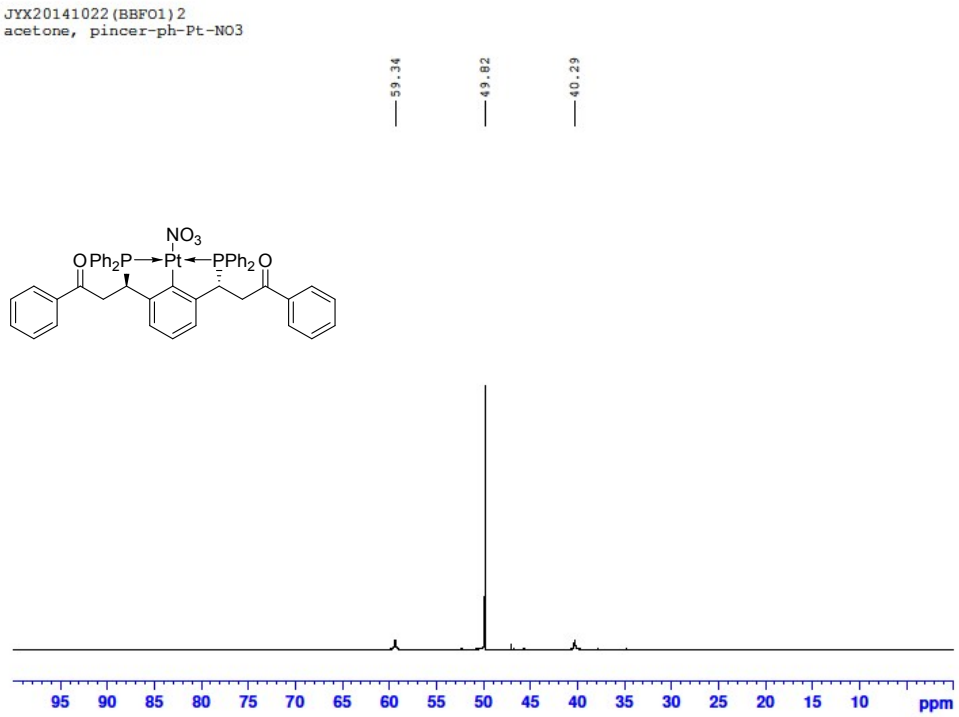


Figure 29. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6d**.

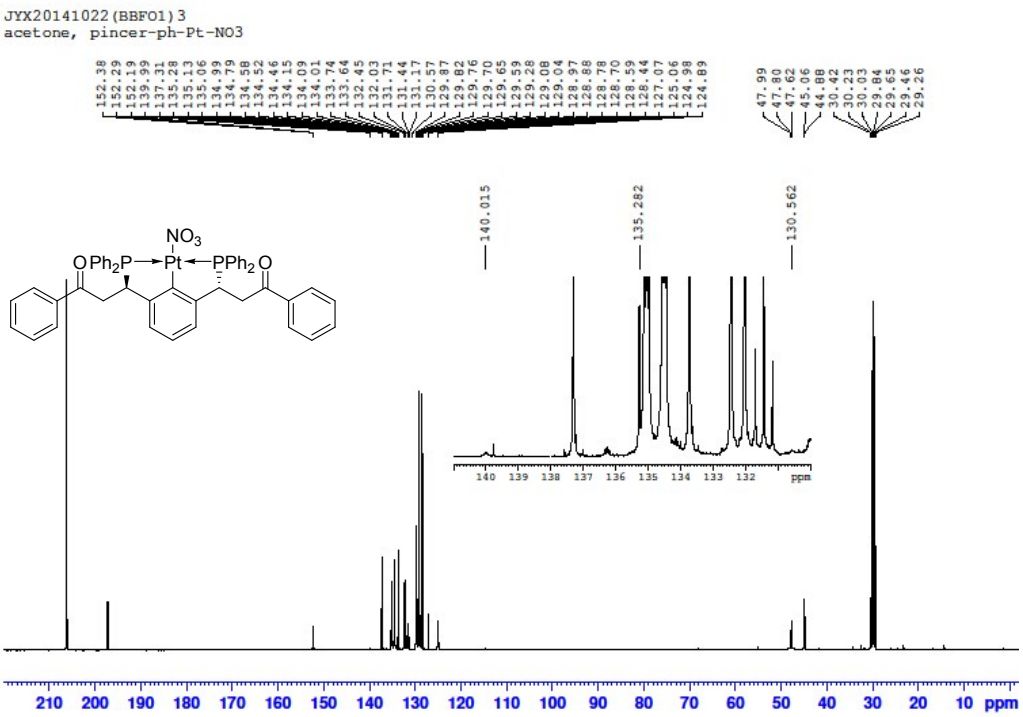


Figure 30. ^{13}C NMR spectrum of complex **6d**.

Complex **7d**

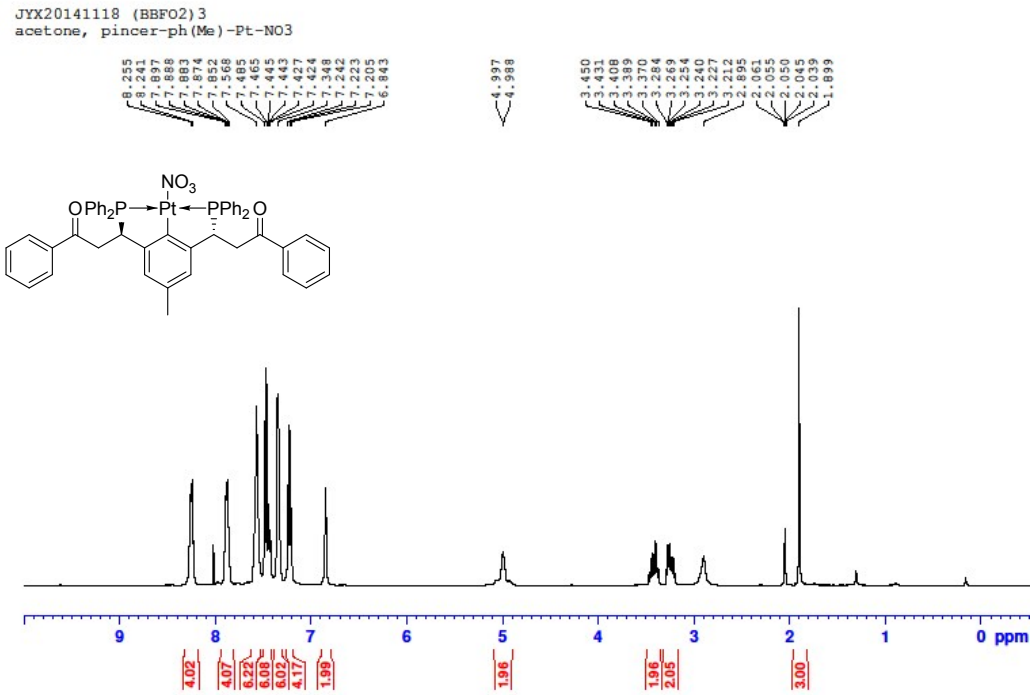


Figure 31. ^{1}H NMR spectrum of complex **7d**.

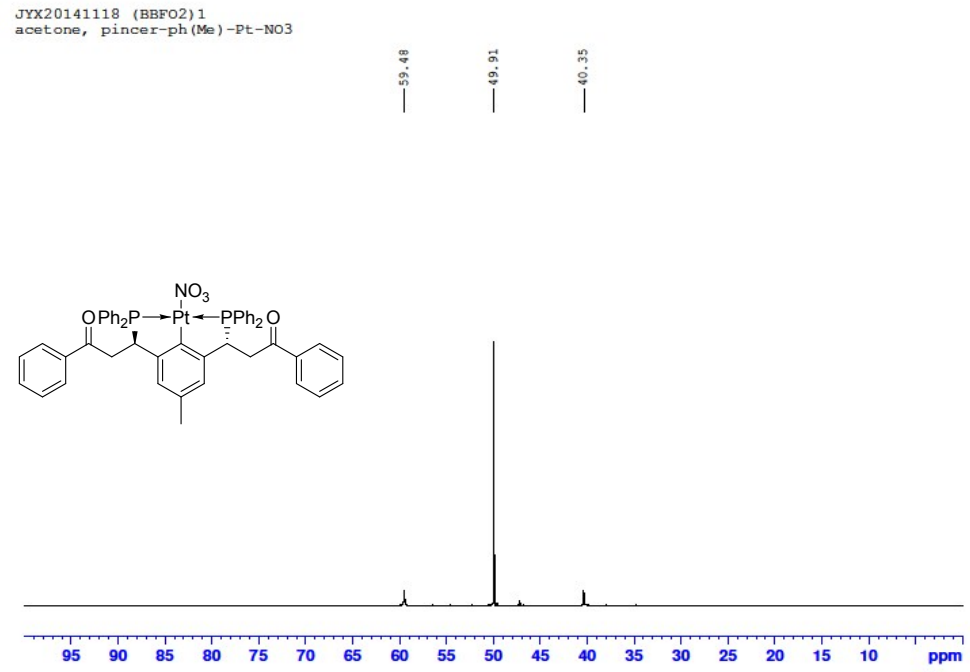


Figure 32. ^{31}P{^{1}H} NMR spectrum of complex **7d**.

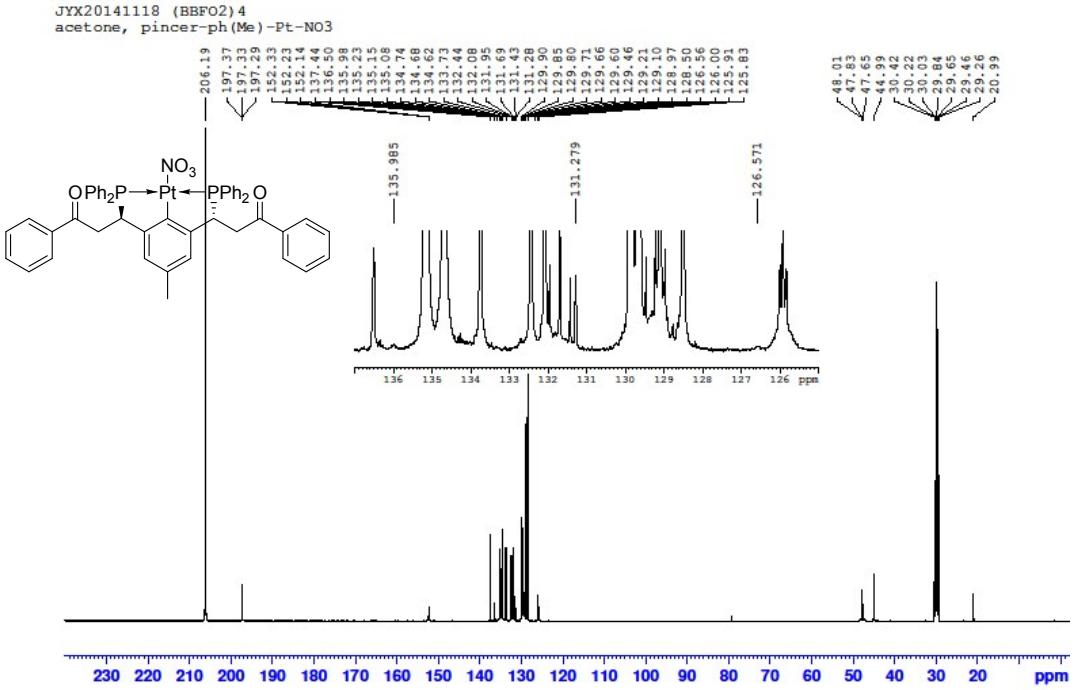


Figure 33. ^{13}C NMR spectrum of complex **7d**.

Complex **8d**

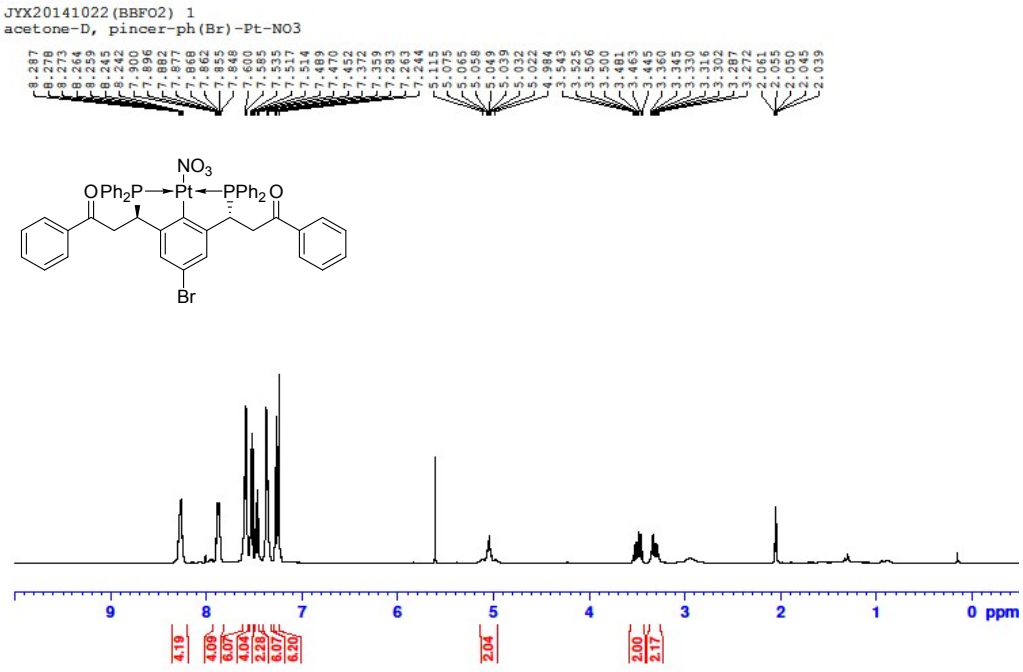


Figure 34. ^{1}H NMR spectrum of complex **8d**.

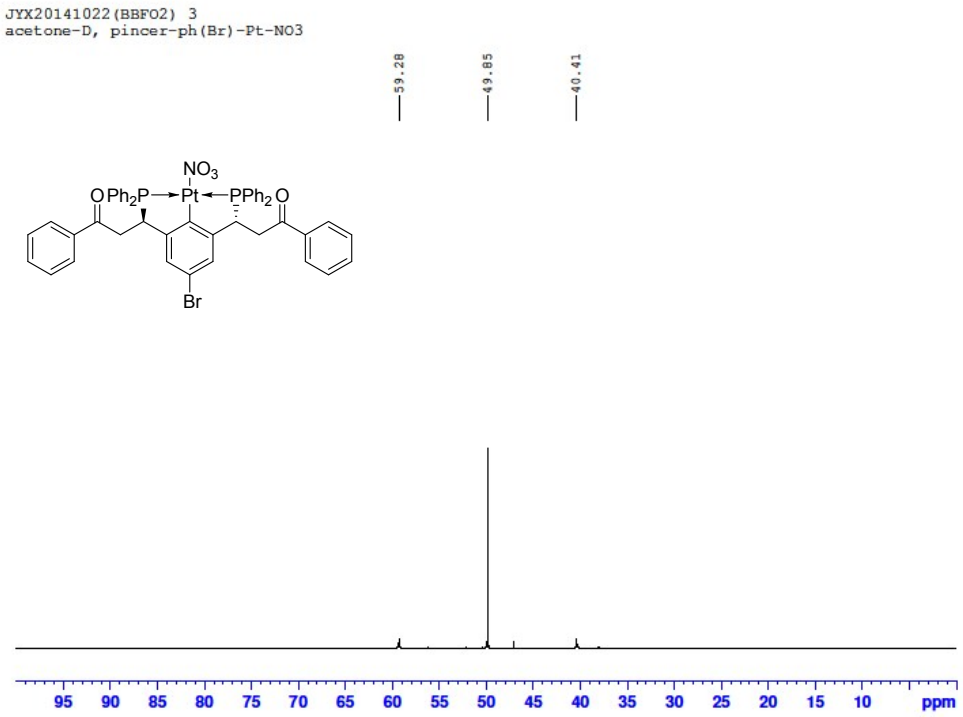


Figure 35. $^{31}P\{^{1}H\}$ NMR spectrum of complex **8d**.

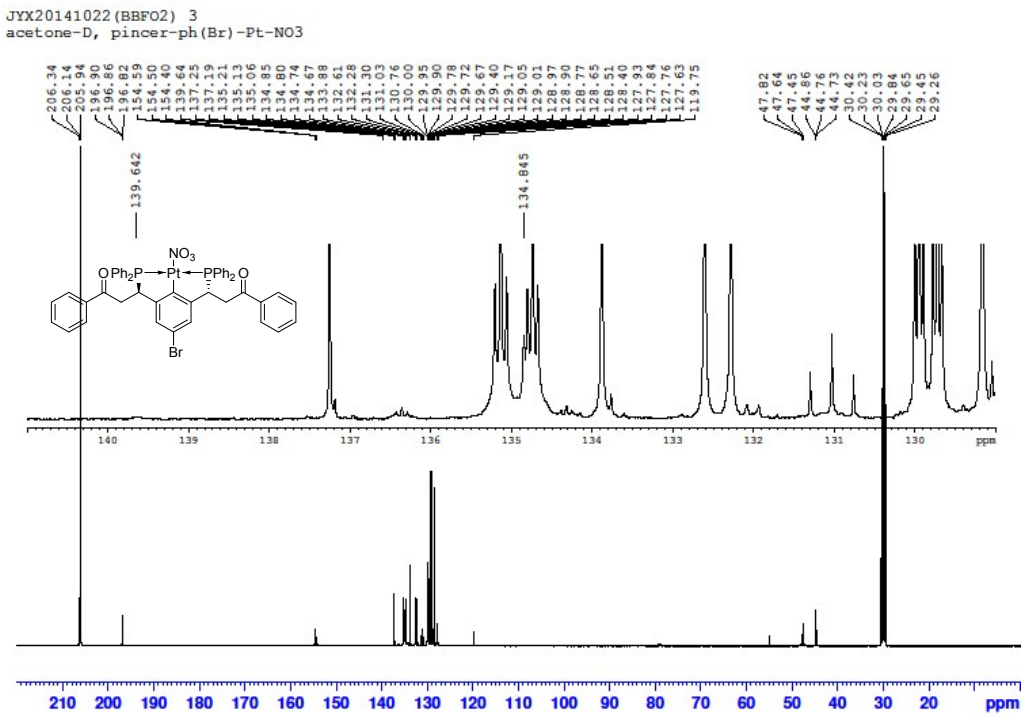


Figure 36. ^{13}C NMR spectrum of complex **8d**.

Complex **9a**

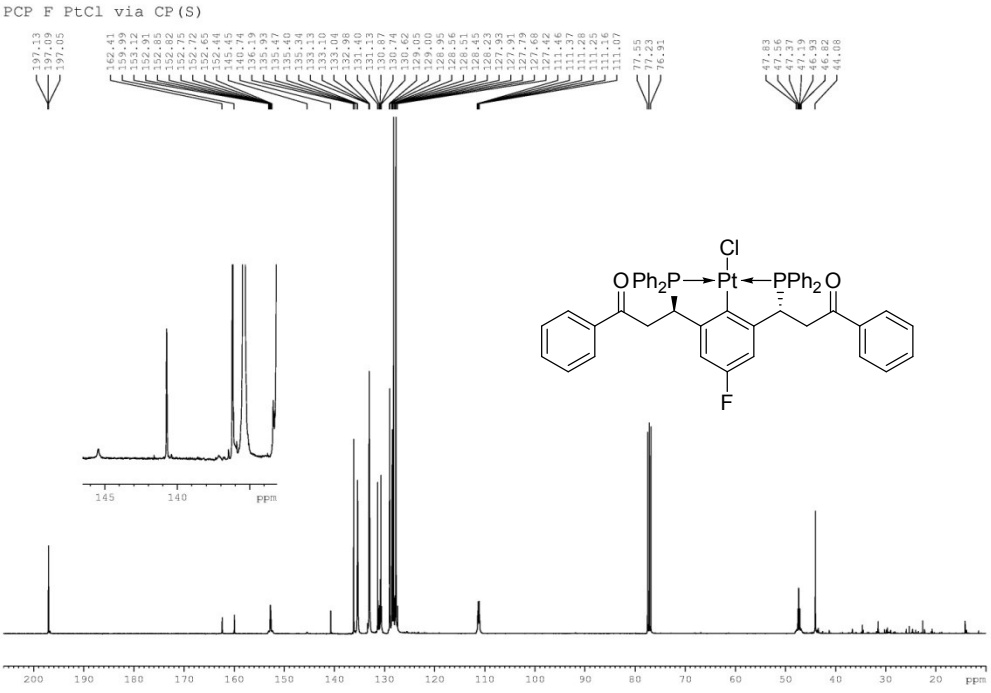


Figure 37. ^{13}C NMR spectrum of complex **9a**.

Complex **10a**

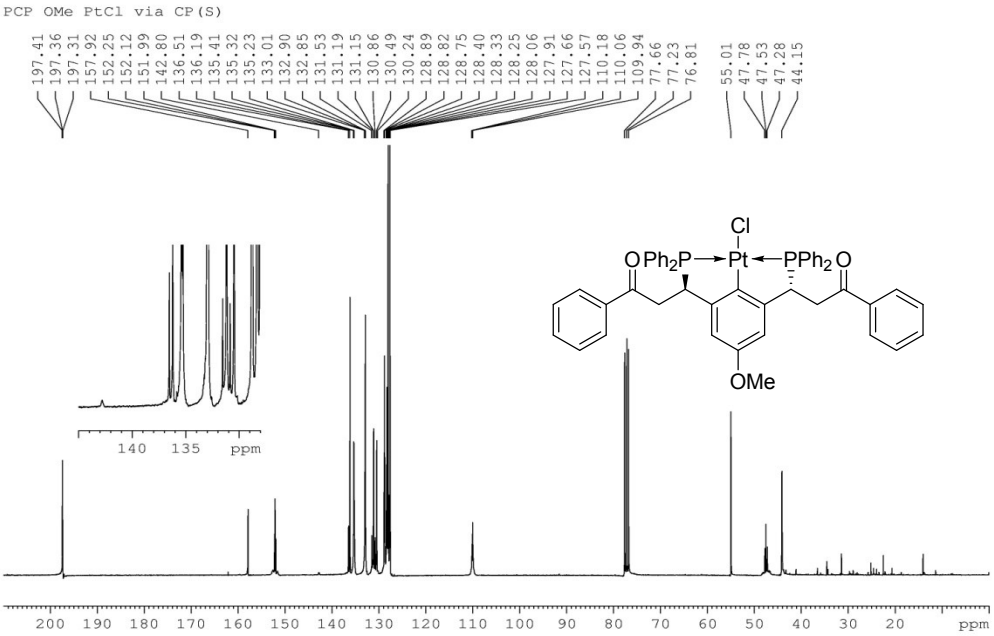


Figure 38. ^{13}C NMR spectrum of complex **10a**.

Complex **6e**

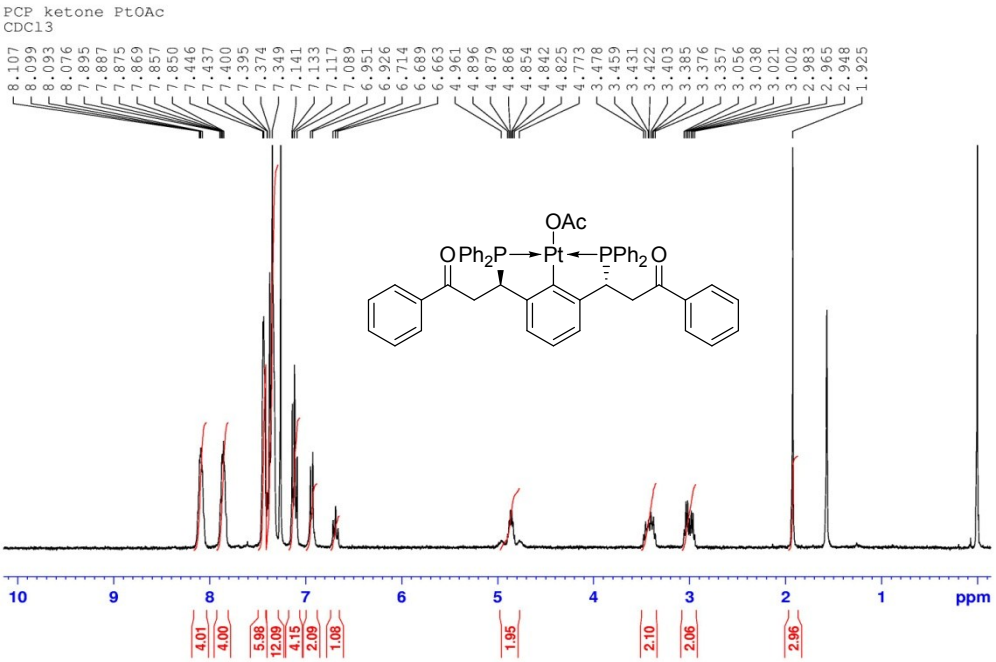


Figure 39. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6e**.

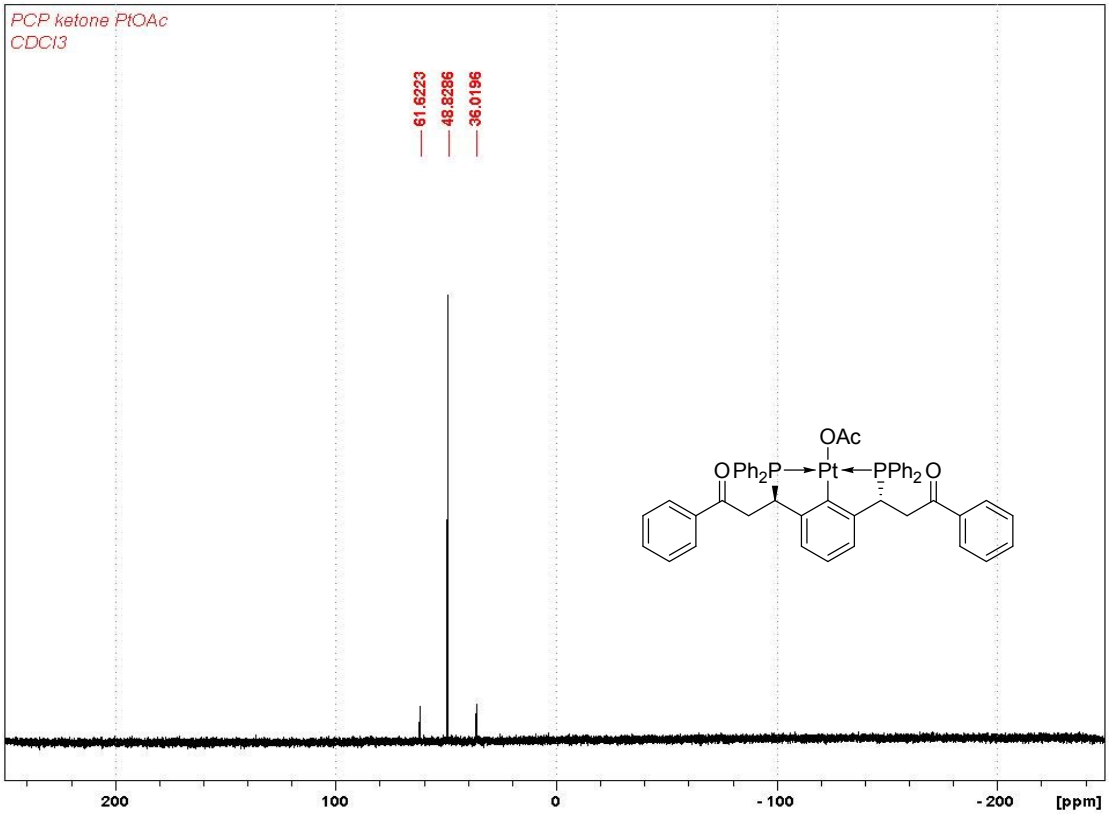


Figure 40. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6e**.

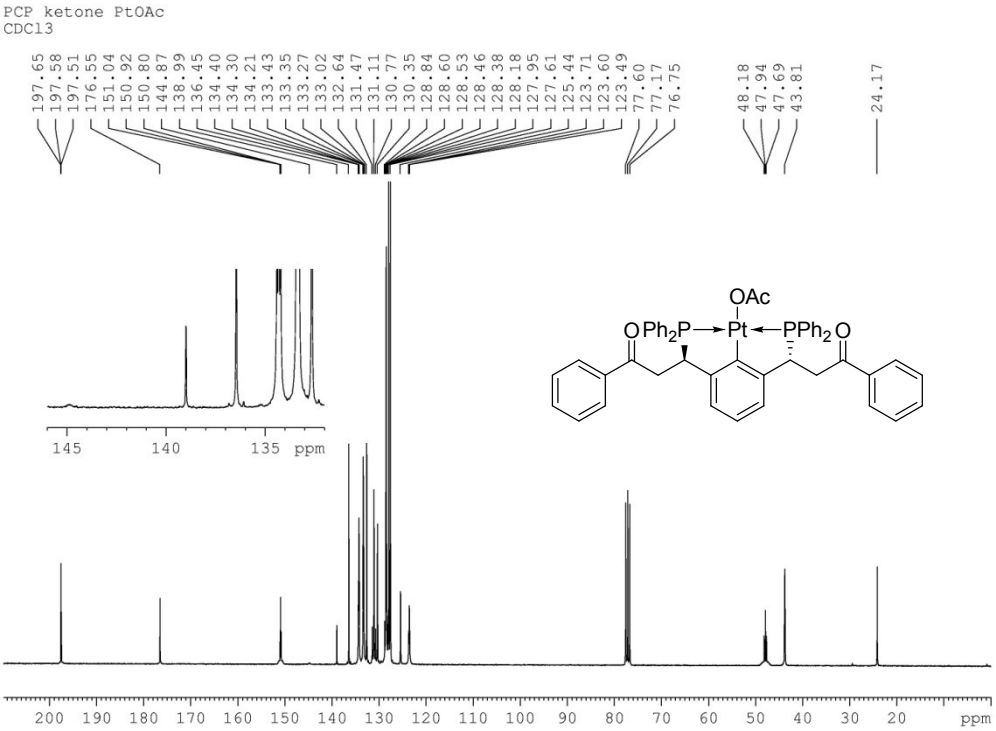


Figure 41. ^{13}C NMR spectrum of complex **6e**.

^{1}H and $^{31}P\{^{1}H\}$ NMR Studies of Complex 6e

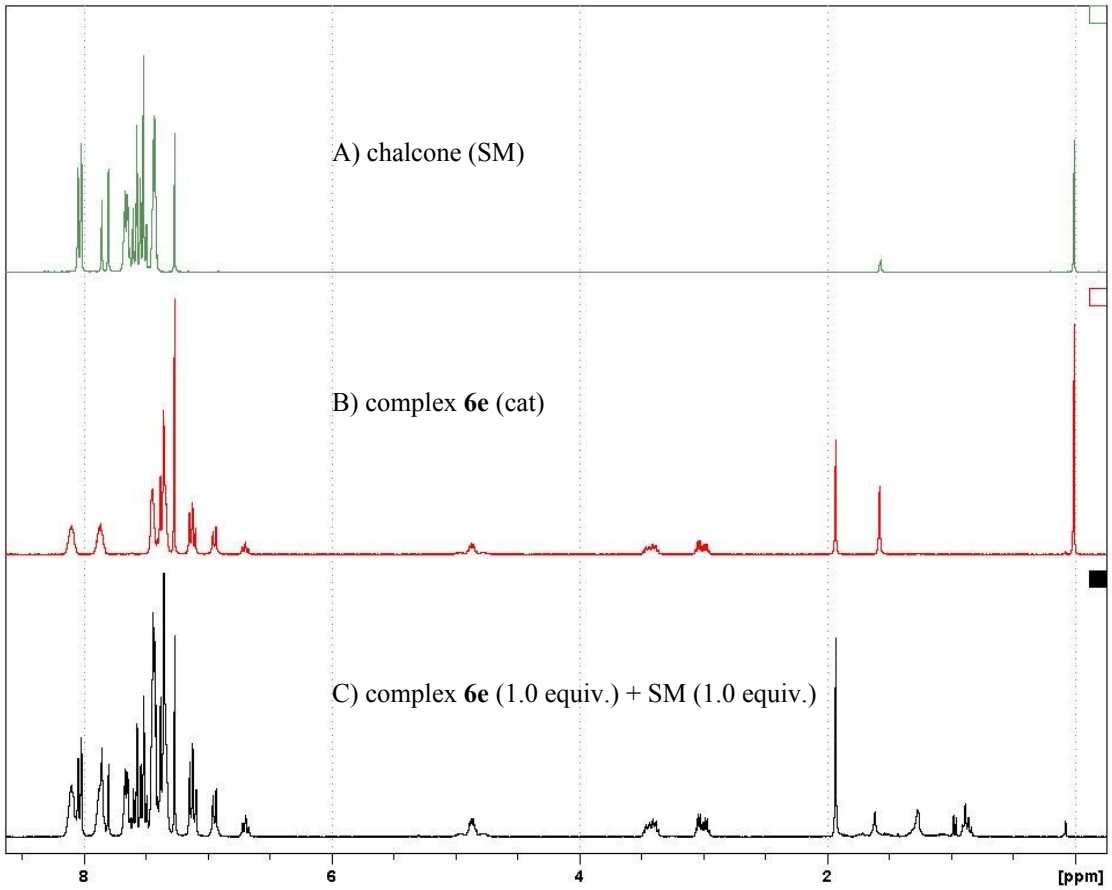


Figure 42. ^{1}H NMR studies of complex **6e**.

Due to the fact that the pincer complex **6e** offers only one easily accessible coordination site, it is necessary for it to adopt an intermolecular mechanism, hence the catalytic hydrophosphination (HP) reaction could either be triggered by the P→Pd or carbonyl-O→Pd interactions with the pincer complex. In order to determine which mode of activation is indeed involved in this catalytic P-H addition process, a series of closely monitored ^{1}H and $^{31}P\{^{1}H\}$ NMR experiments were conducted.

On the basis of the ^{1}H NMR results (Fig. 42), it was conclusively determined that the carbonyl O of chalcone is unable to coordinate to complex **6e** by virtue of the following observations: (1) the ^{1}H spectrum (Fig. 42, spectrum C) exhibits clearly discernible proton signals arising from both the substrate and the pincer complex, and (2) the signal at 1.92 ppm in the ^{1}H spectra (Fig. 42, spectra B and C) attributed to -OAc remains unchanged upon the addition of chalcone, which indicates that the Pd-OAc bond is unaffected by the substrate.

Similarly, the $^{31}P\{^{1}H\}$ spectra (Fig. 43, spectrum F) of stoichiometric amount of chalcone added to complex **6e** shows no visible changes in the chemical shift of the pincer complex at 48.0 ppm.

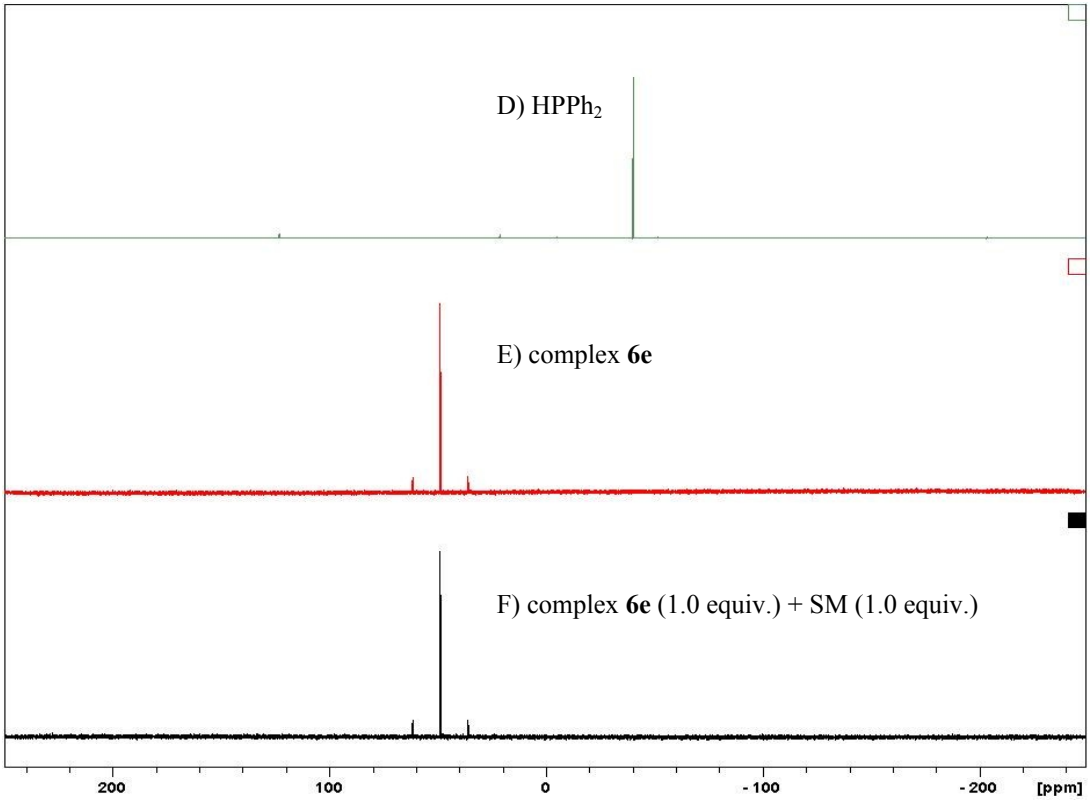


Figure 43. $^{31}P\{^{1}H\}$ NMR spectra of mechanistic study.

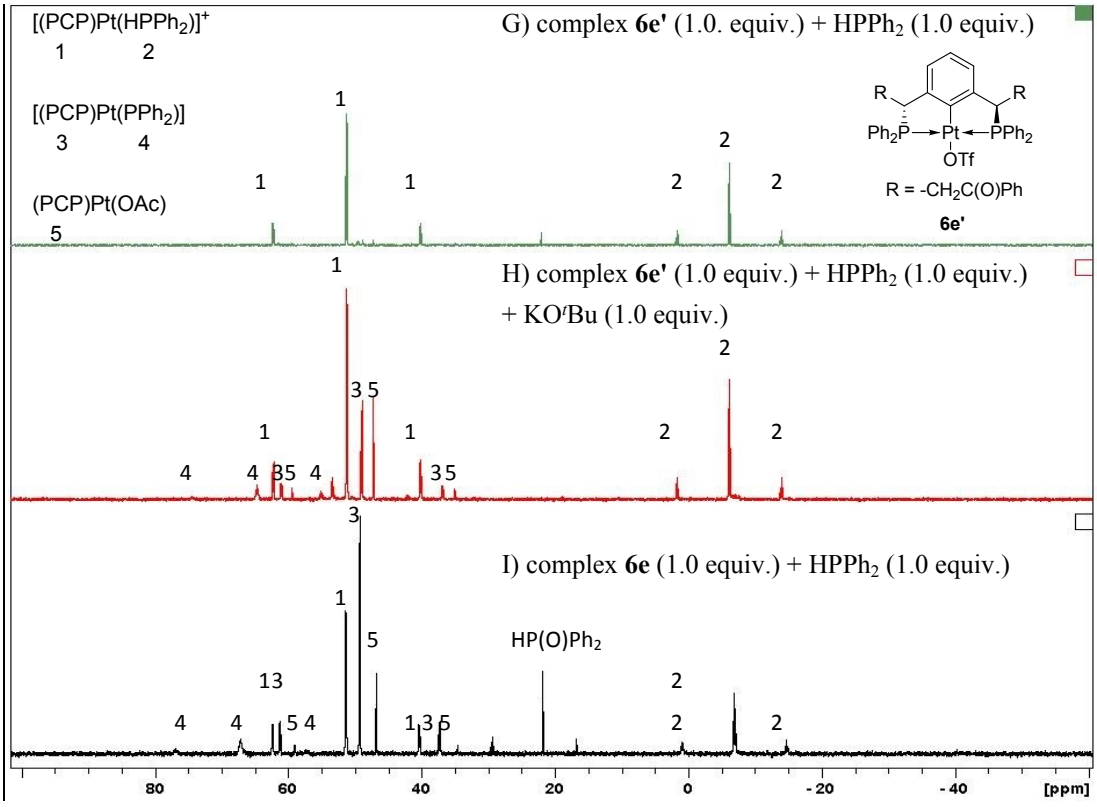


Figure 44. $^{31}P\{^{1}H\}$ NMR spectra of mechanistic study.

However, on the addition of $HPPh_2$ to complex **6e** (Fig. 44, spectrum I), significant changes in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture were noted in Table 1 below:

Table 1. $^{31}P\{^1H\}$ NMR signals observed in spectrum I (complex **6e** + $HPPh_2$) and their assignments.

δ (ppm)	multiplicity	$^2J_{P\text{-}P}$ (Hz)	Satellite peaks (ppm)	$^1J_{Pt\text{-}P}$ (Hz)	Species
-6.2	triplet	21.0	1.7, -14.0	1895.4	$[(PCP)Pt(\underline{HPPh_2})]^+$
50.0	doublet	23.7	62.0, 38.1	2902.1	$(\underline{PCP})Pt(PPh_2)$
52.1	doublet	20.4	63.1, 41.1	2663.5	$[(\underline{PCP})Pt(HPPh_2)]^+$
67.9	broad signal	-	77.9, 58.0	2401.3	$(PCP)Pt(\underline{PPh_2})$
48.0	singlet	-	60.2, 35.8	2952.4	$(\underline{PCP})Pt(OAc)$
22.9	singlet	-	-	-	$HP(O)Ph_2$

The assignments of the various signals (with the Pt satellites) was confirmed by a similar $^{31}P\{^1H\}$ NMR experiment conducted on the analogous complex **6e'** (Fig. 44, spectrum G), in which the counteranion (TfO^-) differs from that of catalyst **6e** (AcO^-). An acetate anion is able to deprotonate the coordinated $HPPh_2$, but the less basic triflate anion is unable to do so. As such, a mixture of **6e'** with $HPPh_2$ will result in the formation of only the $[(PCP)Pt(HPPh_2)]^+$ species. The observed $^{31}P\{^1H\}$ NMR signals of the reaction between **6e'** and stoichiometric amount of $HPPh_2$ in $CDCl_3$ for 10 mins is summarized in Table 2 below.

Table 2. $^{31}P\{^1H\}$ NMR signals observed in spectrum G (complex **6e'** + $HPPh_2$) and their assignments.

δ (ppm)	multiplicity	$^2J_{P\text{-}P}$ (Hz)	Satellite peaks (ppm)	$^1J_{Pt\text{-}P}$ (Hz)	Species
-6.2	triplet	20.7	1.7, -14.0	1890.0	$[(PCP)Pt(\underline{HPPh_2})]^+$
52.1	doublet	20.3	63.1, 41.1	2664.5	$[(\underline{PCP})Pt(HPPh_2)]^+$

Subsequently, stoichiometric amount of KO^{t}Bu was added to the reaction mixture and stirred for 10 mins. The $^{31}P\{^1H\}$ NMR signals (Fig. 44, spectrum H) are compiled in Table 3 below.

Table 3. $^{31}P\{^1H\}$ NMR signals observed in spectrum H (complex **6e'** + $HPPh_2$ + KO^{t}Bu).

δ (ppm)	multiplicity	$^2J_{P\text{-}P}$ (Hz)	Satellite peaks (ppm)	$^1J_{Pt\text{-}P}$ (Hz)	Species
-6.1	triplet	21.0	1.7, -13.9	1889.8	$[(PCP)Pt(\underline{HPPh_2})]^+$
50.0	doublet	23.6	62.1, 38.0	2925.2	$(\underline{PCP})Pt(PPh_2)$
52.1	doublet	20.4	63.1, 41.1	2663.5	$[(\underline{PCP})Pt(HPPh_2)]^+$
64.9	broad triplet	23.1	74.4, 55.1	2375.3	$(PCP)Pt(\underline{PPh_2})$
48.2	singlet	-	60.4, 35.9	2955.4	$(\underline{PCP})Pt(OAc)$

We are unable to explain the difference (3.0 ppm) in the chemical shift of PPh_2 in the $[(PCP)Pt(PPh_2)]$ species observed in Figs. 44 spectra H and I. It could possibly be due to the use of a different base (*i.e.* KO^{t}Bu. KOAc was used initially but due to the poor

solubility in $CDCl_3$, the reaction occurred extremely slowly).

In conclusion, this NMR study has positively shown that in the case of pincer complex **6e**, the catalytic HP reaction proceeds *via* the activation of the P-H bond on $HPPh_2$ rather than the carbonyl O of chalcone.

Crystallographic Data of Complexes 6a and 6c

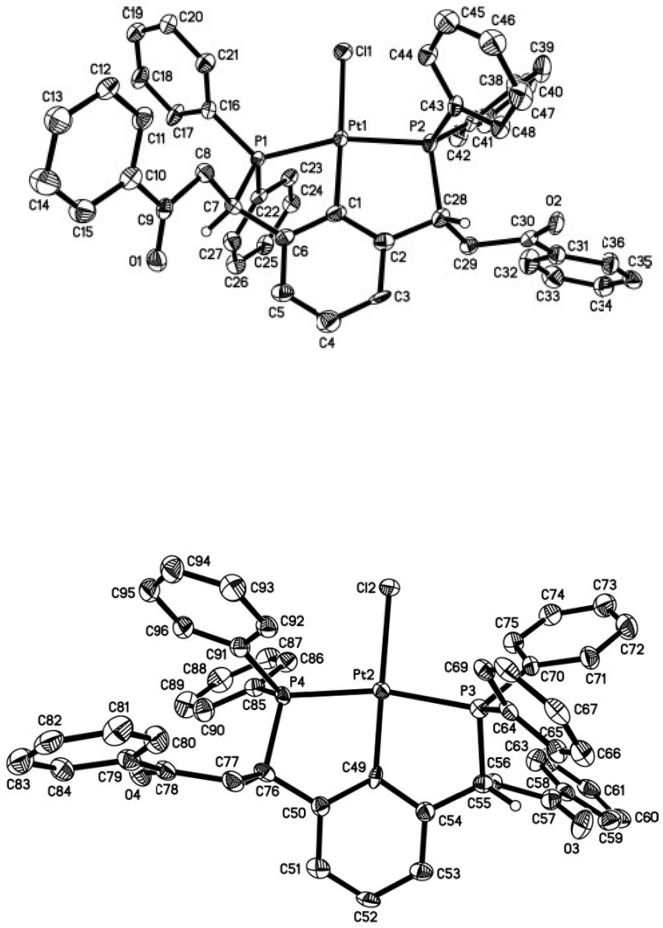


Figure 45. Molecular structures and absolute stereochemistry of complex **6a** with 50% thermal ellipsoids shown. Hydrogen atoms except those on the chiral center are omitted for clarity.

Table 4. Crystal data and structure refinement for complex **6a**.

Chemical formula	$C_{48}H_{39}ClO_2P_2Pt$	
Formula weight	940.27 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.120 x 0.400 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 11.7981(10) Å	α = 90°
	b = 26.540(2) Å	β = 96.6405(12)°

	c = 12.7246(11) Å	γ = 90°
Volume	3957.6(6) Å^3	
Z	4	
Density (calculated)	1.578 g/cm^3	
Absorption coefficient	3.733 mm^{-1}	
F(000)	1872	
Theta range for data collection	2.81 to 30.54°	
Index ranges	-16<=h<=16, -37<=k<=37, -18<=l<=18	
Reflections collected	24179	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7540 and 0.3170	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	24179 / 2269 / 973	
Goodness-of-fit on F^2	1.048	
Δ/σ_{max}	0.001	
Final R indices	17737 data; I>2σ(I)	R1 = 0.0701, wR2 = 0.1416
	all data	R1 = 0.1014, wR2 = 0.1540
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0654P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.0(0)	
Largest diff. peak and hole	5.249 and -3.046 eÅ^{-3}	
R.M.S. deviation from mean	0.242 eÅ^{-3}	

Table 5. Bond lengths (**Å**) for complex **6a**.

Pt1-C1	2.022(13)	Pt1-P1	2.274(3)	C44-C45	1.40(2)	C45-C46	1.36(2)
Pt1-P2	2.278(3)	Pt1-Cl1	2.388(3)	C46-C47	1.39(2)	C47-C48	1.401(18)
Pt2-C49	2.001(12)	Pt2-P4	2.280(3)	C49-C54	1.415(18)	C49-C50	1.429(17)
Pt2-P3	2.285(4)	Pt2-Cl2	2.399(3)	C50-C51	1.424(18)	C50-C76	1.499(19)
C1-C2	1.386(18)	C1-C6	1.424(19)	C51-C52	1.37(2)	C52-C53	1.385(18)
C2-C3	1.425(18)	C2-C28	1.518(19)	C53-C54	1.377(18)	C54-C55	1.517(18)
C3-C4	1.36(2)	C4-C5	1.34(2)	C55-C56	1.540(18)	C55-P3	1.851(13)
C5-C6	1.411(18)	C6-C7	1.516(18)	C56-C57	1.52(2)	C57-O3	1.204(18)
C7-C8	1.560(18)	C7-P1	1.842(13)	C57-C58	1.49(2)	C58-C63	1.39(2)
C8-C9	1.519(19)	C9-O1	1.230(17)	C58-C59	1.41(2)	C59-C60	1.40(2)
C9-C10	1.485(19)	C10-C11	1.40(2)	C60-C61	1.35(2)	C61-C62	1.39(2)
C10-C15	1.42(2)	C11-C12	1.388(18)	C62-C63	1.401(19)	C64-C69	1.398(19)
C12-C13	1.39(2)	C13-C14	1.38(2)	C64-C65	1.40(2)	C64-P3	1.817(14)

C14-C15	1.40(2)	C16-C21	1.38(2)	C65-C66	1.41(2)	C66-C67	1.39(2)
C16-C17	1.425(19)	C16-P1	1.783(14)	C67-C68	1.37(2)	C68-C69	1.386(19)
C17-C18	1.381(19)	C18-C19	1.37(2)	C70-C75	1.392(19)	C70-C71	1.417(18)
C19-C20	1.40(2)	C20-C21	1.398(19)	C70-P3	1.806(13)	C71-C72	1.39(2)
C22-C27	1.39(2)	C22-C23	1.428(19)	C72-C73	1.40(2)	C73-C74	1.37(2)
C22-P1	1.801(14)	C23-C24	1.395(18)	C74-C75	1.390(19)	C76-C77	1.527(19)
C24-C25	1.37(2)	C25-C26	1.38(2)	C76-P4	1.867(13)	C77-C78	1.50(2)
C26-C27	1.363(19)	C28-C29	1.545(19)	C78-O4	1.219(17)	C78-C79	1.513(19)
C28-P2	1.871(14)	C29-C30	1.515(19)	C79-C80	1.39(2)	C79-C84	1.41(2)
C30-O2	1.219(17)	C30-C31	1.51(2)	C80-C81	1.38(2)	C81-C82	1.36(2)
C31-C32	1.39(2)	C31-C36	1.399(19)	C82-C83	1.42(2)	C83-C84	1.39(2)
C32-C33	1.37(2)	C33-C34	1.40(2)	C85-C86	1.380(19)	C85-C90	1.393(19)
C34-C35	1.35(2)	C35-C36	1.40(2)	C85-P4	1.822(14)	C86-C87	1.39(2)
C37-C42	1.40(2)	C37-C38	1.41(2)	C87-C88	1.38(2)	C88-C89	1.39(2)
C37-P2	1.815(15)	C38-C39	1.40(2)	C89-C90	1.40(2)	C91-C96	1.38(2)
C39-C40	1.41(3)	C40-C41	1.40(2)	C91-C92	1.41(2)	C91-P4	1.818(14)
C41-C42	1.38(2)	C43-C48	1.372(17)	C92-C93	1.39(2)	C93-C94	1.38(2)
C43-C44	1.399(19)	C43-P2	1.825(13)	C94-C95	1.37(2)	C95-C96	1.39(2)

Table 6. Bond angles (°) for complex **6a**.

C1-Pt1-P1	81.7(4)	C1-Pt1-P2	83.7(4)	C52-C51-C50	120.5(12)	C51-C52-C53	119.7(12)
P1-Pt1-P2	163.90(12)	C1-Pt1-Cl1	176.3(5)	C54-C53-C52	121.6(13)	C53-C54-C49	120.7(13)
P1-Pt1-Cl1	97.85(12)	P2-Pt1-Cl1	97.13(13)	C53-C54-C55	119.2(12)	C49-C54-C55	120.1(12)
C49-Pt2-P4	83.2(3)	C49-Pt2-P3	83.1(3)	C54-C55-C56	111.0(11)	C54-C55-P3	106.1(9)
P4-Pt2-P3	165.93(12)	C49-Pt2-Cl2	178.0(5)	C56-C55-P3	111.5(9)	C57-C56-C55	113.4(12)
P4-Pt2-Cl2	97.25(12)	P3-Pt2-Cl2	96.55(12)	O3-C57-C58	121.2(14)	O3-C57-C56	119.8(14)
C2-C1-C6	120.2(12)	C2-C1-Pt1	120.2(10)	C58-C57-C56	118.3(13)	C63-C58-C59	119.3(14)
C6-C1-Pt1	119.6(9)	C1-C2-C3	118.7(13)	C63-C58-C57	123.1(14)	C59-C58-C57	117.6(14)
C1-C2-C28	122.8(12)	C3-C2-C28	118.5(12)	C60-C59-C58	119.1(17)	C61-C60-C59	120.6(18)
C4-C3-C2	120.4(12)	C5-C4-C3	121.3(14)	C60-C61-C62	121.6(16)	C61-C62-C63	118.9(17)
C4-C5-C6	121.8(14)	C5-C6-C1	117.6(12)	C58-C63-C62	120.2(16)	C69-C64-C65	119.4(13)
C5-C6-C7	122.2(12)	C1-C6-C7	120.2(12)	C69-C64-P3	119.1(11)	C65-C64-P3	121.5(10)
C6-C7-C8	113.3(11)	C6-C7-P1	104.2(9)	C64-C65-C66	119.7(14)	C67-C66-C65	119.3(15)
C8-C7-P1	109.1(9)	C9-C8-C7	114.3(11)	C68-C67-C66	120.8(14)	C67-C68-C69	120.5(14)
O1-C9-C10	121.1(13)	O1-C9-C8	121.4(12)	C68-C69-C64	120.2(14)	C75-C70-C71	118.1(12)
C10-C9-C8	117.4(12)	C11-C10-C15	120.1(14)	C75-C70-P3	119.7(10)	C71-C70-P3	122.2(10)
C11-C10-C9	122.9(14)	C15-C10-C9	117.0(13)	C72-C71-C70	120.7(14)	C71-C72-C73	119.2(15)
C12-C11-C10	120.1(16)	C11-C12-C13	120.0(16)	C74-C73-C72	120.7(14)	C73-C74-C75	120.0(14)
C14-C13-C12	120.5(16)	C13-C14-C15	120.8(17)	C74-C75-C70	121.1(14)	C50-C76-C77	113.3(11)

C14-C15-C10	118.5(16)	C21-C16-C17	117.7(13)	C50-C76-P4	106.4(9)	C77-C76-P4	114.2(10)
C21-C16-P1	121.0(10)	C17-C16-P1	121.1(11)	C78-C77-C76	115.1(12)	O4-C78-C77	120.9(13)
C18-C17-C16	121.3(14)	C19-C18-C17	119.9(14)	O4-C78-C79	120.5(13)	C77-C78-C79	118.5(12)
C18-C19-C20	120.2(14)	C19-C20-C21	119.9(15)	C80-C79-C84	119.1(14)	C80-C79-C78	123.8(13)
C16-C21-C20	121.0(13)	C27-C22-C23	118.0(12)	C84-C79-C78	117.0(13)	C81-C80-C79	120.9(15)
C27-C22-P1	125.4(11)	C23-C22-P1	116.6(10)	C82-C81-C80	120.0(16)	C81-C82-C83	121.5(16)
C24-C23-C22	119.3(13)	C25-C24-C23	120.9(13)	C84-C83-C82	118.2(15)	C83-C84-C79	120.3(15)
C24-C25-C26	119.5(13)	C27-C26-C25	121.3(15)	C86-C85-C90	120.4(13)	C86-C85-P4	119.2(11)
C26-C27-C22	121.0(14)	C2-C28-C29	112.9(11)	C90-C85-P4	120.4(10)	C85-C86-C87	120.6(15)
C2-C28-P2	105.8(9)	C29-C28-P2	113.6(10)	C88-C87-C86	118.8(15)	C87-C88-C89	121.6(15)
C30-C29-C28	114.1(12)	O2-C30-C31	119.9(13)	C88-C89-C90	118.9(16)	C85-C90-C89	119.7(15)
O2-C30-C29	121.2(13)	C31-C30-C29	118.7(12)	C96-C91-C92	118.3(13)	C96-C91-P4	124.4(12)
C32-C31-C36	118.6(14)	C32-C31-C30	122.1(13)	C92-C91-P4	117.3(11)	C93-C92-C91	119.7(14)
C36-C31-C30	119.2(13)	C33-C32-C31	121.8(15)	C94-C93-C92	120.5(15)	C95-C94-C93	119.8(15)
C32-C33-C34	119.0(16)	C35-C34-C33	120.2(15)	C94-C95-C96	120.3(15)	C91-C96-C95	121.4(15)
C34-C35-C36	121.4(14)	C31-C36-C35	119.1(14)	C16-P1-C22	105.2(6)	C16-P1-C7	109.2(6)
C42-C37-C38	120.1(14)	C42-C37-P2	119.0(11)	C22-P1-C7	104.6(6)	C16-P1-Pt1	122.2(5)
C38-C37-P2	120.8(11)	C39-C38-C37	119.2(15)	C22-P1-Pt1	112.1(4)	C7-P1-Pt1	102.3(4)
C38-C39-C40	119.8(16)	C41-C40-C39	120.2(16)	C37-P2-C43	105.5(7)	C37-P2-C28	110.6(7)
C42-C41-C40	119.5(17)	C41-C42-C37	121.0(16)	C43-P2-C28	105.8(6)	C37-P2-Pt1	113.0(4)
C48-C43-C44	121.5(12)	C48-C43-P2	120.9(10)	C43-P2-Pt1	118.6(4)	C28-P2-Pt1	103.1(4)
C44-C43-P2	117.5(10)	C43-C44-C45	118.7(13)	C70-P3-C64	104.8(6)	C70-P3-C55	108.6(6)
C46-C45-C44	119.7(14)	C45-C46-C47	121.9(14)	C64-P3-C55	105.8(6)	C70-P3-Pt2	121.6(5)
C46-C47-C48	119.0(14)	C43-C48-C47	119.3(13)	C64-P3-Pt2	113.3(5)	C55-P3-Pt2	101.6(5)
C54-C49-C50	117.5(12)	C54-C49-Pt2	120.5(9)	C91-P4-C85	107.4(7)	C91-P4-C76	106.8(6)
C50-C49-Pt2	121.8(9)	C51-C50-C49	119.7(12)	C85-P4-C76	105.0(6)	C91-P4-Pt2	115.7(5)
C51-C50-C76	119.3(11)	C49-C50-C76	120.9(11)	C85-P4-Pt2	116.6(5)	C76-P4-Pt2	104.3(4)

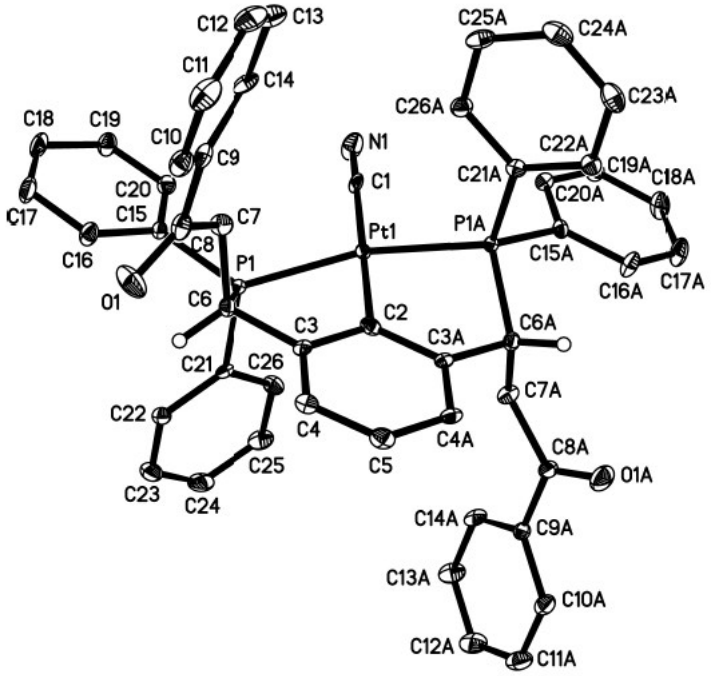


Figure 46. Molecular structure and absolute stereochemistry of complex **6c** with 50% thermal ellipsoids shown. Hydrogen atoms except those on the chiral center are omitted for clarity.

Table 7. Crystal data and structure refinement for complex **6c**.

Empirical formula	C49 H39 N O2 P2 Pt	
Formula weight	930.84	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P 41 21 2	
Unit cell dimensions	a = 9.4921(4) Å	α = 90°.
	b = 9.4921(4) Å	β = 90°.
	c = 43.0304(17) Å	γ = 90°.
Volume	3877.0(4) $Å^3$	
Z	4	
Density (calculated)	1.595 Mg/m^3	
Absorption coefficient	3.744 mm^{-1}	
F(000)	1856	
Crystal size	0.340 x 0.240 x 0.230 mm^3	
Theta range for data collection	2.862 to 33.305°.	
Index ranges	-14<=h<=11, -14<=k<=14, -63<=l<=40	
Reflections collected	47640	
Independent reflections	6862 [R(int) = 0.0363]	
Completeness to theta = 27.000°	99.8 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.48 and 0.40
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6862 / 0 / 251
Goodness-of-fit on F^2	1.180
Final R indices [I>2sigma(I)]	R1 = 0.0294, wR2 = 0.0555
R indices (all data)	R1 = 0.0336, wR2 = 0.0564
Absolute structure parameter	0.029(3)
Extinction coefficient	n/a
Largest diff. peak and hole	1.481 and -1.025 e.Å^{-3}

Table 8. Bond lengths (**Å**) for complex **6c**.

C(1)-N(1)	1.150(7)	C(7)-H(7A)	0.9900	C(14)-H(14)	0.9500	C(21)-C(22)	1.399(5)
C(1)-Pt(1)	2.029(5)	C(7)-H(7B)	0.9900	C(15)-C(20)	1.395(5)	C(21)-P(1)	1.825(4)
C(2)-C(3)	1.411(4)	C(8)-O(1)	1.215(5)	C(15)-C(16)	1.400(5)	C(22)-C(23)	1.383(5)
C(2)-C(3)#1	1.411(4)	C(8)-C(9)	1.500(5)	C(15)-P(1)	1.816(4)	C(22)-H(22)	0.9500
C(2)-Pt(1)	2.062(5)	C(9)-C(14)	1.389(5)	C(16)-C(17)	1.393(5)	C(23)-C(24)	1.379(6)
C(3)-C(4)	1.399(5)	C(9)-C(10)	1.405(5)	C(16)-H(16)	0.9500	C(23)-H(23)	0.9500
C(3)-C(6)	1.511(5)	C(10)-C(11)	1.385(6)	C(17)-C(18)	1.389(6)	C(24)-C(25)	1.399(6)
C(4)-C(5)	1.386(4)	C(10)-H(10)	0.9500	C(17)-H(17)	0.9500	C(24)-H(24)	0.9500
C(4)-H(4)	0.9500	C(11)-C(12)	1.383(6)	C(18)-C(19)	1.389(5)	C(25)-C(26)	1.384(5)
C(5)-C(4)#1	1.386(4)	C(11)-H(11)	0.9500	C(18)-H(18)	0.9500	C(25)-H(25)	0.9500
C(5)-H(5)	0.9500	C(12)-C(13)	1.389(6)	C(19)-C(20)	1.386(5)	C(26)-H(26)	0.9500
C(6)-C(7)	1.549(5)	C(12)-H(12)	0.9500	C(19)-H(19)	0.9500	P(1)-Pt(1)	2.285(9)
C(6)-P(1)	1.848(4)	C(13)-C(14)	1.383(5)	C(20)-H(20)	0.9500	Pt(1)-P(1)#1	2.2859(9)
C(6)-H(6)	1.0000	C(13)-H(13)	0.9500	C(21)-C(26)	1.397(5)	C(21)-C(22)	1.399(5)

Table 9. Bond angles (°) for complex **6c**.

C(3)#1-C(2)-Pt(1)	121.1(2)	C(12)-C(11)-H(11)	120.0	C(23)-C(22)-C(21)	119.7(4)
C(4)-C(3)-C(2)	120.8(4)	C(10)-C(11)-H(11)	120.0	C(23)-C(22)-H(22)	120.1
C(4)-C(3)-C(6)	121.9(3)	C(11)-C(12)-C(13)	120.5(4)	C(21)-C(22)-H(22)	120.1
C(2)-C(3)-C(6)	117.1(3)	C(11)-C(12)-H(12)	119.8	C(24)-C(23)-C(22)	120.3(4)
C(5)-C(4)-C(3)	120.1(4)	C(13)-C(12)-H(12)	119.8	C(24)-C(23)-H(23)	119.9
C(5)-C(4)-H(4)	119.9	C(14)-C(13)-C(12)	119.8(4)	C(22)-C(23)-H(23)	119.9
C(3)-C(4)-H(4)	119.9	C(14)-C(13)-H(13)	120.1	C(23)-C(24)-C(25)	120.8(4)
C(4)#1-C(5)-C(4)	120.2(4)	C(12)-C(13)-H(13)	120.1	C(23)-C(24)-H(24)	119.6
C(4)#1-C(5)-H(5)	119.9	C(13)-C(14)-C(9)	120.4(4)	C(25)-C(24)-H(24)	119.6
C(4)-C(5)-H(5)	119.9	C(13)-C(14)-H(14)	119.8	C(26)-C(25)-C(24)	119.1(4)
C(3)-C(6)-C(7)	109.3(3)	C(9)-C(14)-H(14)	119.8	C(26)-C(25)-H(25)	120.5
C(3)-C(6)-P(1)	105.0(2)	C(20)-C(15)-C(16)	119.7(3)	C(24)-C(25)-H(25)	120.5

C(7)-C(6)-P(1)	107.5(2)	C(20)-C(15)-P(1)	119.8(3)	C(25)-C(26)-C(21)	120.4(4)
C(3)-C(6)-H(6)	111.6	C(16)-C(15)-P(1)	120.6(3)	C(25)-C(26)-H(26)	119.8
C(7)-C(6)-H(6)	111.6	C(17)-C(16)-C(15)	120.1(4)	C(21)-C(26)-H(26)	119.8
P(1)-C(6)-H(6)	111.6	C(17)-C(16)-H(16)	120.0	C(15)-P(1)-C(21)	102.20(16)
C(8)-C(7)-C(6)	114.0(3)	C(15)-C(16)-H(16)	120.0	C(15)-P(1)-C(6)	105.44(17)
C(8)-C(7)-H(7A)	108.7	C(18)-C(17)-C(16)	119.8(4)	C(21)-P(1)-C(6)	110.76(15)
C(6)-C(7)-H(7A)	108.7	C(18)-C(17)-H(17)	120.1	C(15)-P(1)-Pt(1)	126.46(12)
C(8)-C(7)-H(7B)	108.8	C(16)-C(17)-H(17)	120.1	C(21)-P(1)-Pt(1)	110.89(12)
C(6)-C(7)-H(7B)	108.7	C(17)-C(18)-C(19)	120.2(4)	C(6)-P(1)-Pt(1)	100.70(12)
H(7A)-C(7)-H(7B)	107.6	C(17)-C(18)-H(18)	119.9	C(1)-Pt(1)-C(2)	180.00(14)
O(1)-C(8)-C(9)	121.4(4)	C(19)-C(18)-H(18)	119.9	C(1)-Pt(1)-P(1)#1	99.93(11)
O(1)-C(8)-C(7)	121.3(4)	C(20)-C(19)-C(18)	120.4(4)	C(2)-Pt(1)-P(1)#1	80.07(8)
C(9)-C(8)-C(7)	117.3(3)	C(20)-C(19)-H(19)	119.8	C(1)-Pt(1)-P(1)	99.93(11)
C(14)-C(9)-C(10)	119.4(4)	C(18)-C(19)-H(19)	119.8	C(2)-Pt(1)-P(1)	80.07(8)
C(14)-C(9)-C(8)	122.0(3)	C(19)-C(20)-C(15)	119.9(4)	P(1)#1-Pt(1)-P(1)	160.15(4)
C(10)-C(9)-C(8)	118.6(3)	C(19)-C(20)-H(20)	120.1		
C(11)-C(10)-C(9)	120.0(4)	C(15)-C(20)-H(20)	120.1		
C(11)-C(10)-H(10)	120.0	C(26)-C(21)-C(22)	119.8(3)		
C(9)-C(10)-H(10)	120.0	C(26)-C(21)-P(1)	118.1(3)		
C(12)-C(11)-C(10)	119.9(4)	C(22)-C(21)-P(1)	121.9(3)		

Computational Methods

DFT calculations and NBO analyses were performed on complexes **6a** and **6c**, which show distinct C-Pt bond lengths. The B3LYP functional was used in conjunction with the SDD effective core potential basis set (for Pt) and the 6-31G* basis set (for the other atoms).[6] This level of theory is referred to here as B3LYP/[SDD(Pt),6-31G*(others)]. Calculations were performed using the Gaussian 09 software package.[7] The NBO analysis were perfomed on the DFT optimized geometries using the NBO program version 3.1 implemented in Gaussian 09.

NBOs corresponding to π-type Pt-C interaction and their delocalization energies for 6a and 6c

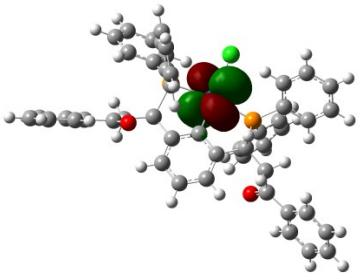
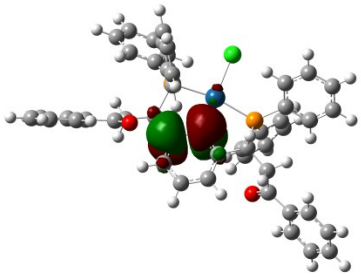
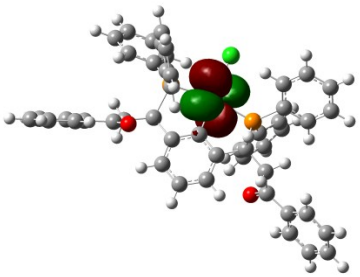
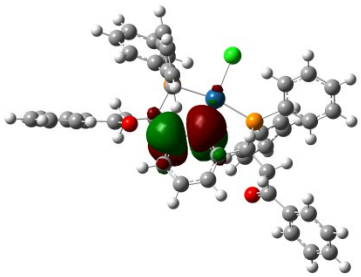
Donor	Acceptor	Interaction energy (kcal/mol)
 #194	 #750	2.46
 #196	 #750	5.56
sum		**8.02**

Figure 47. NBOs corresponding to π-type Pt-C interaction and their delocalization energies for **6a**. The ID numbers of the NBOs, as provided in the Gaussian output file, are also shown. If we assume that the Pt-C bond is on the x-axis, and that the z-axis is perpendicular to the benzene ring, the d orbitals may be viewed as mixtures of d_{xz} and d_{xy}. The acceptor orbital is a C-C(π*) orbital.

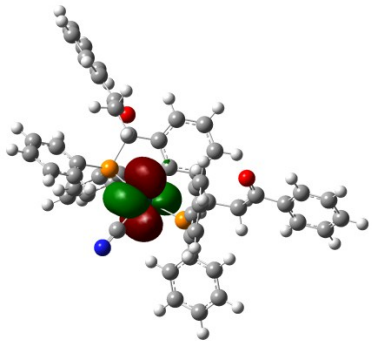
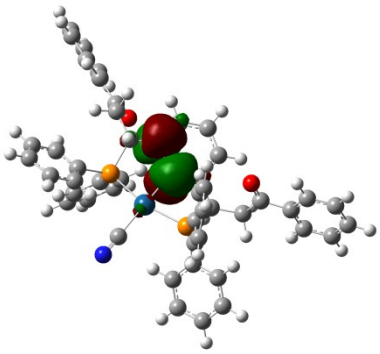
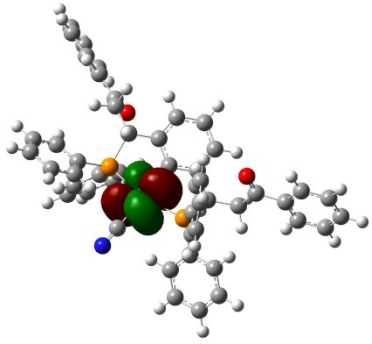
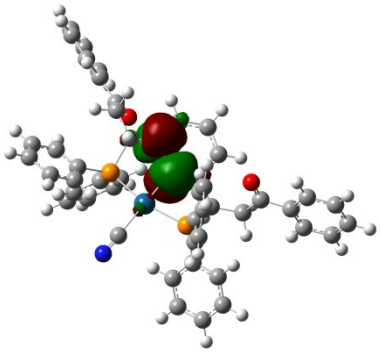
Donor	Acceptor	Interaction energy (kcal/mol)
 #196	 #757	2.91
 #197	 #757	3.74
sum		**6.65**

Figure 48. NBOs corresponding to π-type Pt-C interaction and their delocalization energies for **6c**. The ID numbers of the NBOs, as provided in the Gaussian output file, are also shown. If we assume that the Pt-C bond is on the x-axis, and that the z-axis is perpendicular to the benzene ring, the d orbitals may be viewed as mixtures of d_{xz} and d_{xy}. The acceptor orbital is a C-C(π*) orbital.

Table 10. XYZ coordinates of optimized geometry (in Å) of Complex **6a**.

Pt	23.041906	11.811508	9.097872
C	21.751586	13.259118	9.747622
C	21.108681	14.124238	8.827495
C	20.221837	15.105824	9.282815
H	19.731088	15.773834	8.581468
C	19.960913	15.246316	10.643973
C	20.586507	14.405977	11.562251
H	20.366793	14.525346	12.618712
C	21.476638	13.417849	11.128790
C	22.250707	12.548498	12.113389
H	23.266010	12.975394	12.149139
C	21.817564	12.517760	13.588521
H	22.551870	11.930854	14.151944
H	21.908083	13.537104	13.994869
C	20.418092	12.025292	13.942251
C	20.083967	11.840467	15.396494
C	18.803892	11.357258	15.715112
H	18.121986	11.139018	14.899919
C	18.429339	11.165113	17.041356
H	17.437437	10.788243	17.275526
C	19.328660	11.457916	18.071601
H	19.036929	11.309157	19.107893
C	20.602449	11.942128	17.767759
H	21.303059	12.172602	18.565595
C	20.979915	12.131134	16.437935
H	21.973597	12.510150	16.221845
C	24.128234	10.310570	12.223134
C	23.936046	9.732054	13.491611
H	22.931650	9.568618	13.872545
C	25.030417	9.339451	14.262706
H	24.868428	8.890413	15.239103
C	26.328285	9.518408	13.776902
H	27.180252	9.209320	14.376833
C	26.526945	10.084847	12.517501
H	27.533303	10.212381	12.128486
C	25.435130	10.478804	11.740172
H	25.589705	10.888164	10.747257
C	21.424315	9.649277	11.257768
C	20.115616	9.974186	10.860643
H	19.852528	11.003609	10.650445
C	19.146642	8.978698	10.754952
H	18.135653	9.246982	10.460652
C	19.470591	7.645667	11.021245

H	18.712791	6.871587	10.932632
C	20.773025	7.312077	11.390836
H	21.039471	6.276782	11.586119
C	21.747738	8.306056	11.505649
H	22.760520	8.027461	11.775491
C	21.342998	13.884461	7.340004
H	20.741191	12.997149	7.084528
C	20.878004	14.942011	6.325047
H	21.045517	14.548842	5.315620
H	19.784296	15.039637	6.405727
C	21.453212	16.352321	6.403920
C	21.107957	17.315610	5.302372
C	20.247909	16.997015	4.239129
H	19.789270	16.015509	4.175785
C	19.965223	17.941743	3.252248
H	19.295988	17.685418	2.435634
C	20.540865	19.212197	3.314241
H	20.321355	19.946176	2.543419
C	21.398939	19.538979	4.369072
H	21.847915	20.527218	4.419366
C	21.677784	18.598622	5.355980
H	22.338630	18.830603	6.184632
C	22.928295	12.265742	5.493750
C	22.994798	13.016509	4.305340
H	23.201546	14.082519	4.342406
C	22.821538	12.396918	3.067643
H	22.878780	12.986881	2.156724
C	22.581390	11.021989	3.001434
H	22.449640	10.539439	2.036517
C	22.521638	10.269292	4.174675
H	22.350723	9.197346	4.128113
C	22.695597	10.883726	5.417292
H	22.683396	10.292216	6.327115
C	24.451096	14.225584	7.076173
C	25.504588	14.020278	6.171718
H	25.446866	13.225907	5.435588
C	26.644754	14.825419	6.221113
H	27.451974	14.653751	5.514098
C	26.748537	15.836968	7.175481
H	27.635765	16.463737	7.212798
C	25.710746	16.034658	8.090276
H	25.785475	16.817203	8.840481
C	24.573636	15.230212	8.051376
H	23.775980	15.393397	8.765484

O	19.575494	11.804755	13.086918
O	22.156414	16.712727	7.334545
P	22.724011	10.945660	11.225301
P	23.034949	13.059122	7.145962
H	19.270418	16.011194	10.989156
Cl	24.582385	10.070124	8.316408

Table 11. XYZ coordinates of optimized geometry (in Å) of Complex **6c**.

Pt	23.070568	11.783691	9.086649
C	21.753883	13.261578	9.745666
C	21.109797	14.124021	8.825560
C	20.221619	15.107160	9.275543
H	19.728151	15.773209	8.574002
C	19.962484	15.249858	10.637514
C	20.588646	14.413401	11.560068
H	20.368891	14.537341	12.616212
C	21.478775	13.425443	11.125265
C	22.258704	12.553574	12.105044
H	23.277348	12.973344	12.128645
C	21.842865	12.529186	13.585201
H	22.584288	11.947421	14.144635
H	21.936183	13.551752	13.982736
C	20.448042	12.036746	13.956450
C	20.128515	11.861316	15.414898
C	18.854869	11.371698	15.749311
H	18.166734	11.142338	14.942420
C	18.494303	11.187210	17.080497
H	17.507414	10.805128	17.326987
C	19.401164	11.494459	18.099855
H	19.120245	11.351767	19.139952
C	20.668544	11.985270	17.780292
H	21.374905	12.227031	18.569647
C	21.032208	12.166331	16.445561
H	22.021142	12.550568	16.217173
C	24.082931	10.257538	12.219385
C	23.861263	9.685767	13.486254
H	22.849364	9.565432	13.863246
C	24.934350	9.241820	14.258913
H	24.749310	8.797773	15.233428
C	26.240438	9.361099	13.776542
H	27.075537	9.010655	14.377303
C	26.468460	9.919830	12.518856
H	27.479962	10.000049	12.130963
C	25.397488	10.365914	11.740707

H	25.578160	10.772597	10.751398
C	21.373685	9.678531	11.221444
C	20.075759	10.039465	10.820396
H	19.837847	11.077369	10.622836
C	19.085415	9.067627	10.693701
H	18.082928	9.362893	10.396193
C	19.377002	7.724077	10.943764
H	18.602528	6.968819	10.838761
C	20.668429	7.355681	11.319083
H	20.909616	6.312174	11.502698
C	21.664581	8.325303	11.454506
H	22.668276	8.019966	11.729475
C	21.349771	13.873643	7.339508
H	20.756460	12.979358	7.088905
C	20.878799	14.919256	6.315012
H	21.046160	14.519763	5.308007
H	19.784772	15.010720	6.397923
C	21.446503	16.333281	6.382766
C	21.087275	17.289613	5.279911
C	20.220532	16.961519	4.224968
H	19.766741	15.977237	4.169680
C	19.925061	17.900208	3.236004
H	19.250791	17.636657	2.425848
C	20.494481	19.174001	3.287778
H	20.265011	19.903334	2.515449
C	21.359130	19.510110	4.334328
H	21.803200	20.500922	4.376515
C	21.650779	18.575778	5.323213
H	22.316999	18.815077	6.145423
C	22.987397	12.287035	5.494083
C	23.052599	13.055303	4.316579
H	23.228827	14.126039	4.370980
C	22.920157	12.447576	3.068152
H	22.976785	13.051176	2.166190
C	22.723013	11.066916	2.979697
H	22.624044	10.593616	2.006387
C	22.665721	10.296943	4.141569
H	22.530367	9.220945	4.078664
C	22.797975	10.900255	5.394533
H	22.782308	10.293312	6.293568
C	24.460599	14.243289	7.125099
C	25.531803	14.053264	6.237923
H	25.493071	13.266170	5.492663
C	26.665405	14.865175	6.316118

H	27.486413	14.705383	5.622445
C	26.744813	15.868012	7.281933
H	27.627244	16.499673	7.341787
C	25.688763	16.051094	8.178411
H	25.744335	16.827255	8.936804
C	24.557403	15.240371	8.110850
H	23.745272	15.392331	8.810830
O	19.598596	11.807074	13.110275
O	22.155895	16.700847	7.305740
P	22.706791	10.941287	11.215268
P	23.053549	13.064041	7.155719
H	19.271436	16.015204	10.980887
C	24.356710	10.341404	8.438039
N	25.096386	9.514629	8.063344