Inductive Modulation of Tris(phosphinomethyl)phenylborate Donation at Group VI Metals via Borate Phenyl Substituent Modification

Supplementary Information

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I. General Procedures

All operations were performed under an atmosphere of 99.5% argon further purified by passage through a column of activated Aceto Corp. catalyst R3-11 and 10 Å molecular sieves. The plumbing components of the gas purification systems were made of glass and copper. Ultra-Torr® and Swagelock® fittings were employed to provide connections between glass and copper tubing that are impermeable to air. Solutions were routinely transferred via stainless steel cannulas. Gastight syringes equipped with stainless steel three-way stopcocks and needles were used to transfer solutions when necessary. Standard Schlenk techniques were employed with double manifold vacuum lines.[S1] Solids were handled in a glove box. Solvents were purified by standard procedures and stored under argon.

Literature procedures were employed to prepare $Cr(CO)_3(C_{10}H_8)$, $Tl[PhBP^{Ph}_3]$, $M'(CO)_3(RCN)_3$, $[Li(THF)][PhBP^{iPr}_3]$, $M(CO)_3$(triphos), $[Li(TMEDA)][Ph_2PCH_2]$, **4**-**6**, **10**-**11**, **15**-**17**, dichloro(2,4,6-trimethylphenyl)borane, dichloro(pentafluorophenyl)borane, dichloro(3,5-dimethylphenyl)borane and dichloro(3,5-bis(trifluoromethyl)phenyl)borane.[S2-S12] Other reagents were obtained from Aldrich and Strem and used as received. Alumina (activated, neutral, ~150 mesh) and Celite were treated prior to the introduction of organometallic complexes: alumina/celite (~10 cm^3) was first poured hot onto a medium porosity frit. The filter flask was then evacuated and maintained under dynamic vacuum until the powder had cooled to ambient temperature.

Solution infrared spectra were acquired on a Nicolet Magna 550 FTIR spectrometer with samples sealed in 0.1 mm gastight NaCl cells. Nujol (mineral oil) mulls for IR spectra were prepared in the glove box. NMR samples were sealed under argon into 5 mm tubes and were analyzed on a Bruker 400 MHz FT-NMR spectrometer at ambient temperature. ^1H and ^{13}C chemical shifts are reported in parts per million (δ) and are given with reference to residual ^1H and ^{13}C solvent references relative to TMS (C_4D_8O: $\delta(^1H)$: 1.73, 3.58; $\delta(^{13}C)$: 25.37, 67.57). ^{31}P chemical shifts are reported in parts per million (δ) and are given with reference to 80% H_3PO_4. ^{11}B chemical shifts are reported in parts per million (δ) and are given with reference to $BF_3{\bullet}OEt_2$. Melting points (uncorrected) were determined under argon in sealed capillary tubes on a Laboratory Devices Mel-Temp apparatus. Microanalyses were carried out by ALS Environmental Services, Tucson, Arizona.

References

S1. (a) D. F. Shriver and M. A. Drezdon, *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986. (b) J. E. Ellis, *ACS Symp*. *Ser*. 1987, *No*. **357**, 34.

S2. $Cr(CO)_3(C_{10}H_8)$: M. Uemura, T. Minami, K. Hirotsu and Y. Hayashi, *J. Org. Chem.* 1989, **54**, 469.

S3. $Tl[PhBP_3]$: J. C. Peters, J. C. Thomas, J. A. Dupont and C. G. Riordan, *Inorg. Synth.* 2004, **34**, 8.

S4. $M'(CO)_3(RCN)_3$ (M' = Cr, Mo, W): G. J. Kubas and L. S. Van der Sluys, *Inorg. Synth*. 1990, **28**, 29.

S5. $[Li(THF)][PhBP^{iPr}{}_3]$: (a) L. Turculet, J. D. Feldman and T. D. Tilley, *Organometallics*, 2003, **22**, 4627. (b) L. Turculet, J. D. Feldman and T. D. Tilley, *Organometallics*, 2004, **23**, 2488.

S6. $M(CO)_3$(triphos): (a) O. Walter, T. Klein, G. Huttner and L. Zsolnai, *J. Organomet. Chem.*, 1993, **458**, 63. (b) V. Zanotti, V. Rutar and R. J. Angelici, *J. Organomet. Chem.*, 1991, **414**, 177.

S7. $[Li(TMEDA)][Ph_2PCH_2]$: G. Fraenkel, W.R. Winchester and P. G. Williard, *Organometallics*, 1989, **8**, 2308

S8. **4-6**, **10-11**, **15-17**: P. J. Fischer, A. B. Weberg, T. D. Bohrmann, H. Xu and V. G. Young, Jr., *Dalton Trans.*, 2015, **44**, 3737.

S9. Dichloro(2,4,6-trimethylphenyl)borane: K. Fujimoto, H. Yorimitsu and A. Osuka, *Chem. Eur. J.*, 2015, **21**, 11311.

S10. Dichloro(pentafluorophenyl)borane: A. Sundararaman and F. Jäkle, *J. Organomet. Chem.* 2003, **681**, 134.

S11. Dichloro(3,5-dimethylphenyl)borane: P. A. Deck, C. L. Beswick and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 1772.

S12. Dichloro(3,5-bis(trifluoromethyl)phenyl)borane: M. T. Gieseler and M. Kalesse, *Org. Lett.*, 2014, **16**, 548.

II. Synthesis Descriptions and Characterization Data

[PPN][Cr(CO)$_3$(PhBP$^{iPr}_3$)] (1). THF (40 mL) was added to [Li(THF)][PhBP$^{iPr}_3$] (0.300 g, 0.534 mmol) and Cr(CO)$_3$(CH$_3$CN)$_3$ (0.132 g, 0.509 mmol). The orange solution was refluxed (1.5 hr). An IR spectrum (IR (THF) υ(CO): 1887 (s), 1794 (m), 1778 (m, sh), 1711 (m) cm^{-1}) indicated complete consumption of Cr(CO)$_3$(CH$_3$CN)$_3$ and formation of a contact ion-pair. The solvent was removed in vacuo leaving an oily yellow residue. A solution of PPNCl (0.322 g, 0.560 mmol) in CH$_2$Cl$_2$ (40 mL) was added; the suspension was stirred (1 hr). The LiCl precipitate was separated by filtration through Celite, and the CH$_2$Cl$_2$ of the filtrate was removed in vacuo leaving a pale yellow solid. This solid was dissolved in CH$_3$CN (40 mL) and the solution filtered through alumina. Most of the filtrate solvent was removed in vacuo. Addition of pentane (50 mL) affected the precipitation of a pale yellow solid that was isolated by filtration, washed with pentane (3 * 10 mL) and dried in vacuo. Pentane diffusion into a THF solution provided pale yellow microcrystals (0.401 g, 68%). Anal. Calcd for C$_{66}$H$_{83}$BCrNO$_3$P$_5$: C, 68.57; H, 7.24; N, 1.21. Found C, 68.31; H, 7.21; N, 1.20. Mp. 205 – 207 °C (dec). IR (CH$_2$Cl$_2$) υ(CO) 1876 (s), 1762 (m) cm^{-1}; (CH$_3$CN) υ(CO) 1878 (s), 1765 (m) cm^{-1}; (THF) υ(CO) 1886 (s), 1780 (m) cm^{-1}; (nujol) υ(CO) 1886 (s), 1769 (s) cm^{-1}. ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 52.8 (s, CrP), 21.1 (s, PPN). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -15.2 (s). ^{1}H NMR (400 MHz, C$_4$D$_8$O): 7.70 – 7.48 (m, 30H, PPN), 7.41 (m, 2H, *o*-H, BPh), 6.94 (app. t, *J* = 7.4 Hz, 2H, *m*-H, BPh), 6.71 (app. t, *J* = 7.2 Hz, 1H, *p*-H, BPh), 1.94 (septet, *J* = 7.2 Hz, 6H, P(C*H*(CH$_3$)$_2$)$_2$), 1.46 (m, 18H, C*H*$_3$), 1.23 (m, 18H, C*H*$_3$), 0.46 (s, br, 6H, BC*H*$_2$). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ 235.2 (m, CO), 134.7 (s, *p*-C, PPN), 133.4 (m, *m*-C, PPN), 132.5 (s, BPh), 130.6 (m, *o*-C, PPN), 128.5 (d, $^1J_{PC}$ = 108 Hz, *i*-C, PPN), 126.8 (m, BPh), 122.3 (s, BPh), 35.6 (s, br, P(*C*H(CH$_3$)$_2$)$_2$), 22.1 (s, P(CH(*C*H$_3$)$_2$)$_2$), 20.7 (s, P(CH(*C*H$_3$)$_2$)$_2$), 18.2 (m, B*C*H$_2$).

[PPN][Mo(CO)$_3$(PhBP$^{iPr}_3$)] (2). THF (40 mL) was added to [Li(THF)][PhBP$^{iPr}_3$] (0.300 g, 0.534 mmol) and Mo(CO)$_3$(CH$_3$CH$_2$CN)$_3$ (0.176 g, 0.510 mmol). The yellow solution was refluxed (1.5 hr). An IR spectrum (IR (THF) υ(CO): 1901 (s), 1807 (m), 1789 (m, sh), 1717 (m) cm^{-1}) indicated complete consumption of Mo(CO)$_3$(CH$_3$CH$_2$CN)$_3$ and formation of a contact ion-pair. The solvent was removed in vacuo leaving an oily yellow residue. A solution of PPNCl (0.322 g, 0.560 mmol) in CH$_2$Cl$_2$ (40 mL) was added; the resulting suspension was stirred (1 hr). The LiCl precipitate was separated by filtration through Celite, and the CH$_2$Cl$_2$ was removed in vacuo from the filtrate leaving a pale yellow solid. This solid was dissolved in CH$_3$CN (40 mL) and the solution filtered through alumina. Most of the filtrate solvent was removed in vacuo. Addition of pentane (50 mL) affected the precipitation of a pale yellow solid that was isolated by filtration, washed with pentane (3 * 10 mL) and dried in vacuo. Pentane diffusion into a THF solution provided off-white microcrystals (0.441 g, 75%). Anal. Calcd for C$_{66}$H$_{83}$BMoNO$_3$P$_5$: C, 66.06; H, 6.97; N, 1.17. Found C, 66.00; H, 7.09; N, 1.09. Mp. 223 – 224 °C (dec). IR (CH$_2$Cl$_2$) υ(CO) 1890 (s), 1772 (m) cm^{-1}; (CH$_3$CN) υ(CO) 1892 (s), 1776 (m) cm^{-1}; (nujol) υ(CO) 1900 (s), 1788 (s, sh) 1779 (s) cm^{-1}. ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 36.2 (s, MoP), 21.1 (s, PPN). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -14.4 (s). ^{1}H NMR (400 MHz, C$_4$D$_8$O): 7.70 – 7.48 (m, 30H, PPN), 7.42 (m, 2H, *o*-H, BPh), 6.94 (t, *J* = 7.4 Hz, 2H, *m*-H, BPh), 6.72 (t, *J* = 7.2 Hz, 1H, *p*-H, BPh), 1.88 (septet, *J* = 7.0 Hz, 6H, P(C*H*(CH$_3$)$_2$)$_2$), 1.37 (m, 18H, C*H*$_3$), 1.21 (m, 18H, C*H*$_3$), 0.52 (m, 6H, BC*H*$_2$). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ 225.9 (m, CO), 134.7 (s, *p*-C, PPN), 133.3 (m, *m*-C, PPN), 132.3 (s, BPh), 130.5 (m, *o*-C, PPN), 128.5 (d, $^1J_{PC}$ = 109 Hz, *i*-C, PPN), 126.8 (m, BPh), 122.3 (s, BPh), 34.0 (s, br, P(*C*H(CH$_3$)$_2$)$_2$), 22.1 (s, P(CH(*C*H$_3$)$_2$)$_2$), 20.2 (s, P(CH(*C*H$_3$)$_2$)$_2$), 17.6 (m, B*C*H$_2$).

[PPN][W(CO)$_3$(PhBP$^{iPr}_3$)] (3). THF (40 mL) was added to [Li(THF)][PhBP$^{iPr}_3$] (0.299 g, 0.533 mmol) and W(CO)$_3$(CH$_3$CH$_2$CN)$_3$ (0.220 g, 0.508 mmol). The pale orange solution was refluxed (1.5 hr). An IR spectrum (IR (THF) υ(CO): 1895 (s), 1800 (m), 1784 (m, sh), 1713 (m) cm^{-1}) indicated complete consumption of W(CO)$_3$(CH$_3$CH$_2$CN)$_3$ and formation of a contact ion-pair. The solvent was removed in vacuo leaving a pale yellow residue. A solution of PPNCl (0.321 g, 0.558 mmol) in CH$_2$Cl$_2$ (40 mL) was added; the resulting suspension was stirred (1 hr). The LiCl precipitate was separated by filtration through Celite, and the CH$_2$Cl$_2$ was removed in vacuo from the filtrate leaving a pale yellow solid. This solid was dissolved in CH$_3$CN (40 mL) and the solution filtered through alumina. Most of the filtrate solvent was removed in vacuo. Addition of pentane

(40 mL) affected the precipitation of a pale yellow solid that was isolated by filtration, washed with pentane (3 * 10 mL) and dried in vacuo. Pentane diffusion into a THF solution provided off-white microcrystals (0.451 g, 69%). Anal. Calcd for $C_{66}H_{83}BNO_3P_5W$: C, 61.55; H, 6.50; N, 1.09. Found C, 61.33; H, 6.74; N, 1.03. Mp. 215 – 217 °C (dec). IR (CH_2Cl_2) υ(CO) 1884 (s), 1767 (m) cm^{-1}; (CH_3CN) υ(CO) 1886 (s), 1770 (m) cm^{-1}; (THF) υ(CO) 1894 (s), 1785 (m) cm^{-1}; (nujol) υ(CO) 1893 (s), 1772 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 21.1 (s, PPN), 18.5 (s, br, ^{31}P-^{183}W satellites: 19.1 (br), 17.9 (br), $^1J_{PW}$ = 194 Hz, WP). ^{11}B NMR (128 MHz, C_4D_8O): δ -13.3 (s). ^1H NMR (400 MHz, C_4D_8O): 7.70 – 7.49 (m, 30H, PPN), 7.43 (m, 2H, *o*-H, BPh), 6.96 (t, J = 7.4 Hz, 2H, *m*-H, BPh), 6.75 (t, J = 7.2 Hz, 1H, *p*-H, BPh), 1.96 (septet, J = 6.5 Hz, 6H, $P(CH(CH_3)_2)_2$), 1.37 (m, 18H, CH_3), 1.22 (m, 18H, CH_3), 0.60 (m, br, 6H, BCH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 218.0 (m, CO), 134.8 (s, *p*-C, PPN), 133.4 (m, *m*-C, PPN), 132.5 (s, BPh), 130.5 (m, *o*-C, PPN), 128.5 (d, $^1J_{PC}$ = 109 Hz, *i*-C, PPN), 126.9 (m, BPh), 122.4 (s, BPh), 34.9 (m, $P(CH(CH_3)_2)_2$), 22.2 (s, $P(CH(CH_3)_2)_2$), 20.3 (s, $P(CH(CH_3)_2)_2$), 17.7 (m, BCH_2).

[PPN][$Cr(CO)_3\{\eta^6$-$(PhBP^{iPr}{}_3)Cr(CO)_3\}$] (7). THF (40 mL) was added to **1** (0.300 g, 0.259 mmol) and $Cr(CO)_3(C_{10}H_8)$ (0.137 g, 0.519 mmol) affording a deep red solution. The intensity of this color decreased while the solution was stirred at ambient temperature (15 hr). The solution was filtered through alumina. Solvent removal from the filtrate in vacuo revealed orange oil. Addition of Et_2O (40 mL) resulted in the precipitation of a sticky bright yellow solid. Trituration freed the solid from the flask wall. The yellow solid was isolated by filtration, washed generously with Et_2O (4 * 15 mL) until the rinses were colorless (and free of excess $Cr(CO)_3(C_{10}H_8)$), and dried in vacuo. Pentane diffusion into a THF solution provided bright yellow microcrystals (0.193 g, 58%). Anal. Calcd for $C_{69}H_{83}BCr_2NO_6P_5$: C, 64.14; H, 6.47; N, 1.08. Found C, 64.03; H, 6.58; N, 0.99. Mp. 207 – 209 °C (dec). IR (THF) υ(CO) 1946 (s) 1889 (s), 1863 (s), 1783 (s) cm^{-1}; (nujol) υ(CO) 1947 (s), 1883 (s, sh), 1868 (s, sh), 1857 (s), 1779 (s), 1751 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 52.6 (s, br, CrP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C_4D_8O): δ -15.5 (s). ^1H NMR (400 MHz, C_4D_8O): 7.69 – 7.52 (m, 30H, PPN), 5.56 (s, br, 2H, *o*-H, BPh), 5.24 (s, br, 1H, *p*-H, BPh), 5.16 (s, br, 2H, *m*-H, BPh), 1.92 (s, br, 6H, $P(CH(CH_3)_2)_2$), 1.46 (m, 18H, CH_3), 1.26 (m, 18H, CH_3), 0.52 (s, br, 6H, BCH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 237.6 (s, arene-bound $Cr(CO)_3$), 235.0 (m, phosphine-bound $Cr(CO)_3$), 134.8 (s, *p*-C, PPN), 133.4 (m, *m*-C, PPN), 130.5 (m, *o*-C, PPN), 128.5 (d, $^1J_{PC}$ = 108 Hz, *i*-C, PPN), 101.1 (m, BPh), 94.1 (s, BPh), 93.8 (s, BPh), 36.3 (m, $P(CH(CH_3)_2)_2$), 22.0 (s, $P(CH(CH_3)_2)_2$), 20.5 (m, $P(CH(CH_3)_2)_2$), 17.7 (m, BCH_2).

[PPN][$Cr(CO)_3\{\eta^6$-$(PhBP^{iPr}{}_3)Mo(CO)_3\}$] (8). THF (40 mL) was added to **2** (0.300 g, 0.250 mmol) and $Cr(CO)_3(C_{10}H_8)$ (0.132 g, 0.500 mmol) affording a deep red solution. The intensity of this color decreased while the solution was stirred at ambient temperature (19 hr). The solution was filtered through alumina. Solvent removal from the filtrate in vacuo revealed orange oil. Addition of Et_2O (40 mL) resulted in the precipitation of a sticky yellow/orange solid. Trituration freed the solid from the flask wall. The yellow solid was isolated by filtration, washed generously with Et_2O (4 * 15 mL) until the rinses were colorless (and free of excess $Cr(CO)_3(C_{10}H_8)$), and dried in vacuo. Pentane diffusion into a THF solution provided bright yellow microcrystals (0.193 g, 58%). Anal. Calcd for $C_{69}H_{83}BCrMoNO_6P_5$: C, 62.03; H, 6.26; N, 1.05. Found C, 62.01; H, 6.30; N, 0.99. Mp. 217 – 218 °C (dec). IR (THF) υ(CO) 1946 (s) 1902 (s), 1863 (s), 1794 (s) cm^{-1}; (nujol) υ(CO) 1947 (s), 1897 (s, sh), 1869 (s, sh), 1857 (s), 1790 (s), 1764 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 35.9 (s, MoP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C_4D_8O): δ -14.9 (s). ^1H NMR (400 MHz, C_4D_8O): 7.70 – 7.50 (m, 30H, PPN), 5.55 (app. d, J = 5.9 Hz, 2H, *o*-H, BPh), 5.24 (app. t, J = 6.0 Hz, 1H, *p*-H, BPh), 5.17 (app. t, J = 6.2 Hz, 2H, *m*-H, BPh), 1.86 (septet, J = 7.0 Hz, 6H, $P(CH(CH_3)_2)_2$), 1.36 (m, 18H, CH_3), 1.23 (m, 18H, CH_3), 0.45 (m, br, 6H, BCH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 237.5 (s, arene-bound $Cr(CO)_3$), 225.5 (m, phosphine-bound $Mo(CO)_3$), 134.8 (s, *p*-C, PPN), 133.4 (m, *m*-C, PPN), 130.5 (m, *o*-C, PPN), 128.5 (dd, $^1J_{PC}$ = 108 Hz, J = 1.6 Hz, *i*-C, PPN), 101.0 (s, BPh), 94.3 (s, BPh), 93.6 (s, BPh), 34.1 (m, $P(CH(CH_3)_2)_2$), 22.1 (s, $P(CH(CH_3)_2)_2$), 20.1 (s, $P(CH(CH_3)_2)_2$), 17.7 (m, BCH_2).

[PPN][$Cr(CO)_3\{\eta^6$-$(PhBP^{iPr}{}_3)W(CO)_3\}$] (9). THF (40 mL) was added to **3** (0.428 g, 0.332 mmol) and $Cr(CO)_3(C_{10}H_8)$ (0.176 g, 0.665 mmol) affording a deep red solution. The intensity of this color decreased while the solution was stirred at ambient temperature (15 hr). The solution was filtered through alumina. Solvent removal from the filtrate in vacuo revealed orange oil. Addition of Et_2O (40 mL) resulted in the precipitation of a pale yellow solid that was isolated by filtration, washed generously with Et_2O (4 * 15 mL) until the rinses were colorless (and free of excess $Cr(CO)_3(C_{10}H_8)$), and dried in vacuo. Pentane diffusion into a THF solution provided pale yellow microcrystals (0.347 g, 73%). Anal. Calcd for $C_{69}H_{83}BCrNO_6P_5W$: C, 58.20; H, 5.88; N, 0.98. Found C, 58.68; H, 6.01; N, 0.91. Mp. 207 – 209 °C (dec). IR (THF) υ(CO) 1946 (s) 1896 (s), 1863 (s), 1789 (s) cm^{-1}; (nujol) υ(CO) 1947 (s), 1891 (s), 1869 (s, sh), 1857 (s), 1785 (s), 1760 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 21.0 (s, PPN), 18.2 (s, ^{31}P-^{183}W satellites: 18.8, 17.6, $^1J_{PW}$ = 197 Hz, WP)). ^{11}B NMR (128 MHz, C_4D_8O): δ -13.7 (s). ^1H NMR (400 MHz, C_4D_8O): 7.71 – 7.50 (m, 30H, PPN), 5.56 (app. d, *J* = 5.8 Hz, 2H, *o*-H, BPh), 5.25 (app. t, *J* = 6.0 Hz, 1H, *p*-H, BPh), 5.18 (app. t, *J* = 6.2 Hz, 2H, *m*-H, BPh), 1.94 (m, 6H, $P(CH(CH_3)_2)_2$), 1.36 (m, 18H, CH_3), 1.24 (m, 18H, CH_3), 0.52 (m, br, 6H, BCH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 237.5 (s, arene-bound $Cr(CO)_3$), 217.5 (m, phosphine-bound $W(CO)_3$), 134.8 (s, *p*-C, PPN), 133.4 (m, *m*-C, PPN), 130.5 (m, *o*-C, PPN), 128.5 (d, $^1J_{PC}$ = 108 Hz, *i*-C, PPN), 101.1 (s, BPh), 94.2 (s, BPh), 93.7 (s, BPh), 35.0 (m, $P(CH(CH_3)_2)_2$), 22.1 (s, $P(CH(CH_3)_2)_2$), 20.2 (s, $P(CH(CH_3)_2)_2$), 17.6 (m, BCH_2).

$[PPN][W(CO)_3\{\eta^6\text{-}(PhBP^{iPr}_3)Cr(CO)_3\}]$ (12). THF (40 mL) was added to **1** (0.374 g, 0.324 mmol) and $W(CO)_3(CH_3CH_2CN)_3$ (0.280 g, 0.647 mmol) affording an orange solution. The solution turned dark brown while under reflux (1.5 hr). The solution was filtered through alumina. Solvent removal from the filtrate in vacuo revealed a sticky yellow residue that solidified upon addition of Et_2O (40 mL). The golden solid was isolated by filtration, washed with Et_2O (2 * 10 mL), and dried in vacuo. Pentane diffusion into a THF solution provided bright golden microcrystals (0.356 g, 77%). Anal. Calcd for $C_{69}H_{83}BCrNO_6P_5W$: C, 58.20; H, 5.88; N, 0.98. Found C, 58.90; H, 6.10; N, 0.94. Mp. 207 – 209 °C (dec). IR (THF) υ(CO) 1944 (s) 1889 (s), 1855 (s), 1784 (s) cm^{-1}; (nujol) υ(CO) 1946 (s), 1883 (s), 1867 (s, sh), 1853 (s), 1780 (s), 1752 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 52.9 (s, CrP), 21.1 (s, PPN) ^{11}B NMR (128 MHz, C_4D_8O): δ -15.7 (s). ^1H NMR (400 MHz, C_4D_8O): 7.71 – 7.49 (m, 30H, PPN), 5.68 (app. d, *J* = 5.7 Hz, 2H, *o*-H, BPh), 5.44 – 5.38 (m, 3H, *m*/*p*-H, BPh), 1.91 (septet, *J* = 7.2 Hz, 6H, $P(CH(CH_3)_2)_2$), 1.44 (m, 18H, CH_3), 1.25 (m, 18H, CH_3), 0.32 (s, br, 6H, BCH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 235.0 (m, phosphine-bound $Cr(CO)_3$), 214.4 (s, ^{13}C-^{183}W satellites: 215.38, 213.51, $^1J_{CW}$ = 189 Hz, arene-bound $W(CO)_3$), 134.8 (s, *p*-C, PPN), 133.4 (m, *m*-C, PPN), 130.5 (m, *o*-C, PPN), 128.5 (dd, $^1J_{PC}$ = 108 Hz, *J* = 1.5 Hz, *i*-C, PPN), 99.0 (m, BPh), 93.4 (s, BPh), 92.0 (s, BPh), 35.5 (m, $P(CH(CH_3)_2)_2$), 22.0 (s, $P(CH(CH_3)_2)_2$), 20.7 (m, $P(CH(CH_3)_2)_2$), 18.1 (m, BCH_2).

$[PPN][W(CO)_3\{\eta^6\text{-}(PhBP^{iPr}_3)Mo(CO)_3\}]$ (13). THF (40 mL) was added to **2** (0.325 g, 0.271 mmol) and $W(CO)_3(CH_3CH_2CN)_3$ (0.117 g, 0.271 mmol) affording a yellow solution. The solution turned dark orange/brown while under reflux (1.5 hr). The solution was filtered through alumina. Solvent removal from the filtrate in vacuo revealed a sticky yellow residue that solidified upon addition of Et_2O (40 mL). Trituration freed the solid from the flask wall. The solid was isolated by filtration, washed with Et_2O (4 * 10 mL), and dried in vacuo. Pentane diffusion into a THF solution provided yellow microcrystals (0.249 g, 63%). Anal. Calcd for $C_{69}H_{83}BMoNO_6P_5W$: C, 56.46; H, 5.70; N, 0.95. Found C, 56.71; H, 5.81; N, 0.90. Mp. 176 – 178 °C (dec). IR (THF) υ(CO) 1944 (s) 1902 (s), 1858 (s), 1794 (s) cm^{-1}; (nujol) υ(CO) 1947 (s), 1897 (s), 1867 (s, sh), 1853 (s), 1791 (s), 1765 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 36.2 (s, MoP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C_4D_8O): δ -15.0 (s). ^1H NMR (400 MHz, C_4D_8O): 7.71 – 7.49 (m, 30H, PPN), 5.68 (app. d, *J* = 5.3 Hz, 2H, *o*-H, BPh), 5.46 – 5.39 (m, 3H, *m*/*p*-H, BPh), 1.85 (septet, *J* = 7.0 Hz, 6H, $P(CH(CH_3)_2)_2$), 1.36 (m, 18H, CH_3), 1.22 (m, 18H, CH_3), 0.39 (s, br, 6H, BCH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 225.4 (m, phosphine-bound $Mo(CO)_3$), 214.4 (s, ^{13}C-^{183}W satellites: 215.34, 213.46, $^1J_{CW}$ = 190 Hz, arene-bound $W(CO)_3$), 134.8 (s, *p*-C, PPN), 133.4 (m, *m*-C, PPN), 130.5 (m, *o*-C, PPN), 128.5 (dd, $^1J_{PC}$ = 108 Hz, *J* = 1.6 Hz, *i*-C, PPN), 98.9 (s, BPh), 93.5 (s, BPh), 91.8 (s, BPh), 34.0 (m, $P(CH(CH_3)_2)_2$), 22.0 (s, $P(CH(CH_3)_2)_2$), 20.1 (s, $P(CH(CH_3)_2)_2$), 18.2 (m, BCH_2).

$[PPN][W(CO)_3\{\eta^6\text{-}(PhBP^{iPr}_3)W(CO)_3\}]$ (14). THF (40 mL) was added to **3** (0.300 g, 0.233 mmol) and $W(CO)_3(CH_3CH_2CN)_3$ (0.202 g, 0.466 mmol) affording a yellow solution. The solution turned dark brown while under reflux (1.5 hr). The solution was filtered through alumina. Solvent removal from the filtrate in vacuo revealed a sticky yellow residue that solidified upon addition of Et_2O (40 mL). Trituration freed the solid from the flask wall. The solid was isolated by filtration, washed with Et_2O (4 * 10 mL), and dried in vacuo. Pentane diffusion into a THF solution provided bright yellow microcrystals (0.242 g, 67%). Anal. Calcd for $C_{69}H_{83}BNO_6P_5W_2$: C, 53.27; H, 5.38; N, 0.90. Found C, 53.36; H, 5.48; N, 0.92. Mp. 216 – 217 °C (dec). IR (THF) υ(CO) 1945 (s) 1896 (s), 1857 (s), 1789 (s) cm^{-1}; (nujol) υ(CO) 1947 (s), 1892 (s), 1867 (s, sh), 1855 (s), 1786 (s), 1761 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 21.1 (s, PPN), 18.4 (s, br, ^{31}P-^{183}W satellites: 19.1 (br), 17.8 (br), $^1J_{PW}$ = 198 Hz, WP)). ^{11}B NMR (128 MHz, C_4D_8O): δ -13.8 (s). ^1H NMR (400 MHz, C_4D_8O): 7.70 – 7.49 (m, 30H, PPN), 5.68 (app. d, J = 5.7 Hz, 2H, *o*-H, BPh), 5.47 – 5.40 (m, 3H, *m*/*p*-H, BPh), 1.92 (septet, J = 6.7 Hz, 6H, $P(CH(CH_3)_2)_2$), 1.36 (m, 18H, CH_3), 1.23 (m, 18H, CH_3), 0.45 (m, br, 6H, BCH_2). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 217.4 (m, phosphine-bound $W(CO)_3$), 214.4 (s, ^{13}C-^{183}W satellites: 215.32, 213.45, $^1J_{CW}$ = 189 Hz, arene-bound $W(CO)_3$), 134.8 (s, *p*-C, PPN), 133.4 (m, *m*-C, PPN), 130.5 (m, *o*-C, PPN), 128.5 (d, $^1J_{PC}$ = 108 Hz, *i*-C, PPN), 99.0 (m, BPh), 93.5 (s, BPh), 92.0 (s, BPh), 35.1 (m, $P(CH(CH_3)_2)_2$), 22.1 (s, $P(CH(CH_3)_2)_2$), 20.2 (s, $P(CH(CH_3)_2)_2$), 18.1 (m, BCH_2).

[((3,5-Me)C_6H_3)$BP^{Ph}{}_3$]Tl (18). Et_2O (350 mL) was added to [Li(TMEDA)][Ph_2PCH_2] (20.96 g, 65.02 mmol); the pale yellow suspension was cooled to -78 °C. A solution of freshly distilled ((3,5-Me)C_6H_3)BCl_2 (4.05 g, 21.67 mmol) in toluene (20 mL) was added dropwise to this cold suspension over 30 minutes. The reaction mixture was stirred while slowly warming to ambient temperature (20 hr). Pentane (320 mL) was added and the suspension was cooled to -78 °C with vigorous stirring. At this point, stirring was stopped, and the mixture was allowed to stand at -78 °C for ~30 minutes until nearly all the solid had deposited at the bottom of the round bottom flask. The filtrate was carefully decanted; the remaining solids were brought to ambient temperature and dried *in vacuo*. The remainder of the procedure was carried out efficiently in air. Hexanes (200 mL) were added to the solids; the suspension was filtered and the separated solids washed thoroughly with hexanes (2 * 100 mL). The solids were mixed with CH_3OH (150 mL); the suspension was filtered through Celite. The colorless filtrate was concentrated *in vacuo* revealing a white sticky solid. The mass of this crude [Li(TMEDA)][((3,5-Me)C_6H_3)$BP^{Ph}{}_3$] (14.77 grams) was determined by difference while being transferred as a solution in methanol (80 mL) into a 250 mL Erlenmeyer flask. An aqueous solution (50 mL) of $TlPF_6$ (7.57 g, 21.67 mmol) was added dropwise over 10 minutes to the stirring solution of crude [Li(TMEDA)][((3,5-Me)C_6H_3)$BP^{Ph}{}_3$] resulting in a white suspension that was stirred for an additional 10 minutes once the $TlPF_6$ addition was complete. The product was extracted into CH_2Cl_2 (2 * 150 mL); the combined extracts were filtered through Celite, and the solvent removed *in vacuo* revealing a white solid. This solid was washed with hexanes (3 * 40 mL) and Et_2O (40 mL), and transferred to a 500 mL Erlenmeyer flask. Benzene (200 mL) and anhydrous $MgSO_4$ were added; the suspension was stirred (2 hr). The insolubles were removed via filtration; the filtrate was concentrated *in vacuo* revealing a white solid. Diffusion of pentane into a nearly saturated benzene solution resulted in white microcrystals (8.64 g, 43%). Anal. Calcd for $C_{47}H_{45}BP_3Tl$: C, 61.50; H, 4.94. Found: C, 62.03; H, 4.90. Mp. 214 °C (dec). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 20.6 (d, $^1J_{TlP}$ = 5124 Hz). ^{11}B NMR (128 MHz, C_4D_8O): δ -11.2 (s). ^1H NMR (400 MHz, C_4D_8O): δ 7.23 (m, 14H, *o*-H, (3,5-Me)C_6H_3 and PPh), 7.06 (m, 18H, *m*/*p*-H, PPh), 6.64 (s, br, *p*-H, (3,5-Me)C_6H_3), 2.29 (s, 6H, Me), 1.68 (m, 6H, BCH_2P). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 140.1 (m, *i*-C, PPh), 135.6 (s, *o*-C, (3,5-Me)C_6H_3), 132.6 (s, br, *o*-C, PPh), 130.1 (s, *m*-C, (3,5-Me)C_6H_3), 129.2 (s, *p*-C, PPh), 128.9 (m, *m*-C, PPh), 125.5 (s, *p*-C, (3,5-Me)C_6H_3), 22.2 (s, Me), 16.9 (m, BCH_2P).

[((3,5-CF_3)C_6H_3)$BP^{Ph}{}_3$]Tl (19). Et_2O (250 mL) was added to [Li(TMEDA)][Ph_2PCH_2] (13.00 g, 40.31 mmol); the pale yellow suspension was cooled to -78 °C. A solution of freshly distilled ((3,5-CF_3)C_6H_3)BCl_2 (3.96 g, 13.43 mmol) in toluene (50 mL) was added dropwise to this cold suspension over 45 minutes. The reaction mixture was stirred while slowly warming to ambient temperature (24 hr); the color of the mixture changed from pale yellow to dark brown. Pentane (250 mL) was added and the suspension was cooled to -78 °C with vigorous stirring. At this point, stirring was stopped, and the mixture was allowed to stand at -78 °C for ~30 minutes until nearly all the solid had deposited at the bottom of the round bottom flask. The filtrate was carefully decanted; the remaining solids were brought to ambient temperature and dried *in vacuo*. The remainder of the procedure was carried out efficiently in air. Hexanes (2 * 100 mL) were used to transfer the solid onto a filter funnel; the filtrate was discarded. CH_3OH (250 mL) was added to the brown solid, and the solution was filtered through Celite. The light brown filtrate was concentrated *in vacuo* revealing a brown sticky solid. The mass of this crude [Li(TMEDA)][((3,5-CF_3)C_6H_3)$BP^{Ph}{}_3$] (9.52 grams) was determined by difference while being transferred as a solution in methanol (50 mL) into a 250 mL Erlenmeyer flask. An aqueous solution (25 mL) of $TlPF_6$ (3.52 g, 10.08 mmol) was added dropwise over 10 minutes to the stirring solution of crude [Li(TMEDA)][((3,5-CF_3)C_6H_3)$BP^{Ph}{}_3$] resulting in a brown suspension that was stirred for an additional 10 min once the $TlPF_6$ addition was complete. The product was extracted into CH_2Cl_2 (2 * 150 mL); the combined extracts were filtered through Celite, and the solvent was removed *in vacuo* revealing a brown solid. This solid was washed with hexanes (2 * 90 mL) and Et_2O (30 mL) and dried *in vacuo*. The solid was transferred to a 250 mL Erlenmeyer flask; benzene (150 mL) and anhydrous $MgSO_4$ were added. The suspension was stirred (2 hr). The suspension was filtered through Celite; the filtrate was concentrated in vacuo revealing a brown solid. Diffusion of pentane into a nearly saturated benzene solution resulted in light brown microcrystals (5.32 g, 39%). Anal. Calcd for $C_{47}H_{39}BF_6P_3Tl$: C, 55.02; H, 3.83. Found: C, 55.45; H, 4.01. Mp. 245 °C (dec). $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 19.0 (d, $^1J_{TlP}$ = 4903 Hz). ^{11}B NMR (128 MHz, C_4D_8O): δ -11.2 (s). $^{19}F\{^1H\}$ NMR (376 MHz, C_4D_8O) δ -62.9 (s). ^1H NMR (400 MHz, C_4D_8O): δ 8.12 (s, br, 2H, *o*-H, (3,5-CF_3)C_6H_3), 7.62 (s, br, 1H, *p*-H, (3,5-CF_3)C_6H_3), 7.24 (m, 12H, *o*-H, PPh), 7.14 – 7.05 (m, 18H, *m*/*p*-H, PPh), 1.64 (m, 6H, BCH_2P). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 139.5 (m, *i*-C, PPh), 132.6 (s, br, *o*-C, PPh), 132.0 (s, br, *o*-C, (3,5-CF_3)C_6H_3), 129.2 (s, *p*-C, PPh), 129.1 (m, *m*-C, PPh), 125.9 (q, $^1J_{CF}$ = 274 Hz, $\mathit{C}F_3$), 117.8 (m, *m*-C, (3,5-CF_3)C_6H_3), 16.6 (m, $B\mathit{C}H_2P$).

[PPN][Cr(CO)$_3$(((3,5-Me)C_6H_3)$BP^{Ph}{}_3$)] (20). CH_3CN (40 mL) was added to [(3,5-Me)C_6H_3)$BP^{Ph}{}_3$]Tl (0.539 g, 0.587 mmol) and $Cr(CO)_3(CH_3CN)_3$ (0.145 g, 0.560 mmol). The yellow solution was refluxed (1.5 hr), and the solvent was removed *in vacuo*. THF (40 mL) was added to the yellow residue, and the resulting suspension was added to PPNCl (0.353 g, 0.615 mmol); the mixture was stirred (1 hr). The suspension was filtered through alumina; most of the yellow filtrate solvent was removed *in vacuo*. Addition of Et_2O (30 mL) affected the precipitation of a yellow solid that was isolated by filtration, washed with Et_2O (3 * 10 mL) and dried *in vacuo*. Pentane diffusion into a nearly saturated Et_2O:THF solution provided yellow microcrystals (0.462 g, 60%). Anal. Calcd for $C_{86}H_{75}BCrNO_3P_5$: C, 74.41; H, 5.45; N, 1.01. Found: C, 74.06; H, 5.71; N, 0.91. Mp. 242 °C (dec). IR (THF) υ(CO) 1903 (s), 1805 (m) cm^{-1}; (CH_3CN) υ(CO) 1899 (s), 1794 (m) cm^{-1}; (nujol) υ(CO) 1902 (s), 1793 (s, br) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 46.5 (s, CrP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C_4D_8O): δ -14.6 (s). ^1H NMR (400 MHz, C_4D_8O): δ 7.65 – 7.53 (m, 30H, PPN), 7.45 (m, 12H, *o*-H, PPh), 6.96 (s, br, 2H, *o*-H, (3,5-Me)$C_6\mathit{H}_3$), 6.93 – 6.85 (m, 18H, *m*/*p*-H, PPh), 6.43 (s, br, 1H, *p*-H, (3,5-Me)$C_6\mathit{H}_3$), 2.16 (s, 6H, Me), 1.14 (s, br, 6H, $BC\mathit{H}_2P$). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 234.3 (m, CO), 146.5 (m, *i*-C, PPh), 134.4 (s, *p*-C, PPN), 133.3 (m, *m*-C, PPN), 133.0 (m, *o*-C PPN), 130.2 (m, *o*-C, PPh), 128.1 (dd, $^1J_{PC}$ = 108 Hz, J = 1.7 Hz, *i*-C, PPN), 127.2 (m, *m*-C, PPh), 126.8 (s, *p*-C, PPh), 124.2 (s, *p*-C, (3,5-Me)C_6H_3), 22.0 (s, Me), 18.5 (m, $B\mathit{C}H_2P$).

[PPN][Mo(CO)$_3$(((3,5-Me)C_6H_3)$BP^{Ph}{}_3$)] (21). CH_3CN (40 mL) was added to [((3,5-Me)C_6H_3)$BP^{Ph}{}_3$]Tl (0.488 g, 0.532 mmol) and $Mo(CO)_3(CH_3CH_2CN)_3$ (0.175 g, 0.506 mmol). The yellow solution was refluxed (1.5 hr), and the solvent was removed *in vacuo*. THF (40 mL) was added to the yellow residue, and the resulting suspension was added to PPNCl (0.320 g, 0.557 mmol); the mixture was stirred (1 hr). The suspension was filtered through alumina; most of the yellow filtrate solvent was removed *in vacuo*. Addition of Et_2O (30 mL) affected the precipitation of a yellow solid that was isolated by filtration, washed with Et_2O (3 * 10 mL) and dried *in vacuo*. Pentane diffusion into a nearly saturated Et_2O:THF solution provided pale yellow microcrystals (0.498 g, 69%). Anal. Calcd for $C_{86}H_{75}BMoNO_3P_5$: C, 72.12; H, 5.28; N, 0.98. Found: C, 71.96; H, 5.35; N, 0.89. Mp. 238 °C (dec). IR (THF) υ(CO) 1915 (s), 1815 (m) cm^{-1}; (CH_3CN) υ(CO) 1911 (s), 1805 (m) cm^{-1}; (nujol) υ(CO) 1914 (s), 1800 (s, br) cm^{-1}. $^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O): δ 28.1 (s, MoP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C_4D_8O): δ -14.1 (s). ^1H NMR (400 MHz, C_4D_8O): δ 7.65 – 7.50 (m, 30H, PPN), 7.45 (m, 12H, *o*-H, PPh), 6.98 (s, br, 2H, *o*-H, (3,5-Me)$C_6\mathit{H}_3$), 6.95 – 6.86 (m, 18H, *m*/*p*-H, PPh), 6.44 (s, br, 1H, *p*-H, (3,5-Me)$C_6\mathit{H}_3$), 2.17 (s, 6H, Me), 1.18 (s, br, 6H, $BC\mathit{H}_2P$). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): δ 225.4 (m, CO), 145.8 (m, *i*-C, PPh), 134.6 (s, *p*-C, PPN), 133.6 (m, *m*-C, PPN), 133.2 (m, *o*-C PPN), 130.3 (m, *o*-C, PPh), 128.3 (dd, $^1J_{PC}$ = 109 Hz, *J* = 1.7 Hz, *i*-C, PPN), 127.5 (m, *m*-C, PPh), 127.2 (s, *p*-C, PPh), 124.4 (s, *p*-C, (3,5-Me)C$_6$H$_3$), 22.2 (s, Me), 19.3 (m, B*C*H$_2$P).

[PPN][W(CO)$_3$(((3,5-Me)C$_6$H$_3$)BP$^{Ph}{}_3$)] (22). CH$_3$CN (40 mL) was added to [((3,5-Me)C$_6$H$_3$)BP$^{Ph}{}_3$]Tl (0.488 g, 0.532 mmol) and W(CO)$_3$(CH$_3$CH$_2$CN)$_3$ (0.219 g, 0.506 mmol). The yellow solution was refluxed (1.5 hr), and the solvent was removed *in vacuo*. THF (40 mL) was added to the yellow residue, and the resulting suspension was added to PPNCl (0.320 g, 0.557 mmol); the mixture was stirred (1 hr). The suspension was filtered through alumina; most of the yellow filtrate solvent was removed *in vacuo*. Addition of Et$_2$O (30 mL) affected the precipitation of a yellow solid that was isolated by filtration, washed with Et$_2$O (3 * 10 mL) and dried *in vacuo*. Pentane diffusion into a nearly saturated Et$_2$O:THF solution provided pale yellow microcrystals (0.502 g, 65%). Anal. Calcd for C$_{86}$H$_{75}$BNO$_3$P$_5$W: C, 67.95; H, 4.97; N, 0.92. Found: C, 67.78; H, 5.09; N, 0.87. Mp. 231 °C (dec). IR (THF) υ(CO) 1910 (s), 1810 (s) cm^{-1}; (CH$_3$CN) υ(CO) 1906 (s), 1801 (s) cm^{-1}; (nujol) υ(CO) 1908 (s), 1793 (s, br) cm^{-1}. ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 21.0 (s, PPN), 10.5 (s, br, ^{31}P-^{183}W satellites: 11.2 (br), 9.9 (br), $^1J_{PW}$ = 204 Hz, WP). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -13.1 (s). ^{1}H NMR (400 MHz, C$_4$D$_8$O): δ 7.63 – 7.49 (m, 30H, PPN), 7.46 (m, 12H, *o*-H, PPh), 6.97 (s, br, 2H, *o*-H, (3,5-Me)C$_6$*H*$_3$), 6.94 – 6.86 (m, 18H, *m*/*p*-H, PPh), 6.44 (s, br, 1H, *p*-H, (3,5-Me)C$_6$*H*$_3$), 2.16 (s, 6H, Me), 1.28 (s, br, 6H, BC*H*$_2$P). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ 216.4 (m, CO), 145.4 (m, *i*-C, PPh), 134.6 (s, *p*-C, PPN), 133.7 (m, *m*-C, PPN), 133.2 (m, *o*-C PPN), 130.3 (m, *o*-C, PPh), 128.3 (dd, $^1J_{PC}$ = 108 Hz, J = 1.6 Hz, *i*-C, PPN), 127.5 (m, *m*-C, PPh), 127.3 (s, *p*-C, PPh), 124.4 (s, *p*-C, (3,5-Me)C$_6$H$_3$), 22.1 (s, Me), 19.2 (m, B*C*H$_2$P).

[PPN][Cr(CO)$_3$(((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}{}_3$)] (23). THF (40 mL) was added to [C$_6$H$_3$(3,5-CF$_3$)BP$^{Ph}{}_3$]Tl (0.360 g, 0.350 mmol) and Cr(CO)$_3$(CH$_3$CN)$_3$ (0.096 g, 0.334 mmol). The pale yellow solution was refluxed (1.5 hr). The resulting yellow-brown solution was added to PPNCl (0.211 g, 0.368 mmol); the mixture was stirred (2 hr). The suspension was filtered through alumina; most of the yellow filtrate solvent was removed *in vacuo*. Addition of Et$_2$O (20 mL) affected the precipitation of a yellow solid that was isolated by filtration, washed with Et$_2$O (3 * 10 mL) and dried *in vacuo*. Pentane diffusion into a nearly saturated Et$_2$O:THF solution provided yellow microcrystals (0.276 g, 55%). Anal. Calcd for C$_{86}$H$_{69}$BCrF$_6$NO$_3$P$_5$: C, 69.04; H, 4.65; N, 0.94. Found: C, 68.35; H, 4.73; N, 0.89. Mp. 236 °C (dec). IR (THF) υ(CO) 1906 (s), 1809 (m) cm^{-1}; (CH$_3$CN) υ(CO) 1901 (s), 1798 (m) cm^{-1}; (nujol) υ(CO) 1903 (s), 1798 (s, br) cm^{-1}. ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 45.6 (s, br, CrP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -14.4 (s). ^{19}F{^{1}H} NMR (376 MHz, C$_4$D$_8$O) δ -62.8 (s). ^{1}H NMR (400 MHz, C$_4$D$_8$O): δ 7.87 (m, 2H, *o*-H, (3,5-CF$_3$)C$_6$*H*$_3$), 7.66 – 7.50 (m, 30H, PPN), 7.46 (m, 12H, *o*-H, PPh), 7.41 (s, br, 1H, *p*-H, (3,5-CF$_3$)C$_6$*H*$_3$), 6.98 – 6.88 (m, 18H, *m*/*p*-H, PPh), 1.16 (m, 6H, BC*H*$_2$P). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ 234.1 (m, CO), 146.1 (m, *i*-C, PPh), 134.6 (s, *p*-C, PPN), 133.3 (m, *m*-C, PPN), 133.1 (m, *o*-C PPN), 132.2 (s, br, *o*-C, (3,5-CF$_3$)C$_6$*H*$_3$), 130.3 (m, *o*-C, PPh), 128.3 (dd, $^1J_{PC}$ = 108 Hz, *J* = 1.7 Hz, *i*-C, PPN), 127.6 (s br, *m*-C, PPh), 127.3 (s, *p*-C, PPh), 116.7 (m, *m*-C, (3,5-CF$_3$)C$_6$*H*$_3$), 18.6 (m, B*C*H$_2$P).

[PPN][Mo(CO)$_3$(((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}{}_3$)] (24). THF (40 mL) was added to [((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}{}_3$]Tl (0.350 g, 0.341 mmol) and Mo(CO)$_3$(CH$_3$CH$_2$CN)$_3$ (0.112 g, 0.325 mmol). The pale yellow solution was refluxed (1.5 hr). The resulting yellow-brown solution was added to PPNCl (0.206 g, 0.356 mmol); the mixture was stirred (2 hr). The suspension was filtered through alumina; most of the yellow filtrate solvent was removed *in vacuo*. Addition of Et$_2$O (40 mL) resulted in a residual amount of Mo(CO)$_3$ salt precipitation. The mixture was stirred (30 min) before the solvent was removed *in vacuo*. Pentane (50 mL) was added. Vigorous trituration affected the formation of a tan solid that was isolated by filtration, washed with pentane (3 * 10 mL) and dried *in vacuo*. Slow evaporation of a Et$_2$O:THF solution resulted in tan microcrystals (0.225 g, 45%). Anal. Calcd for C$_{86}$H$_{69}$BF$_6$MoNO$_3$P$_5$: C, 67.07; H, 4.52; N, 0.91. Found: C, 67.06; H, 4.56; N, 0.93. Mp. 203 °C (dec). IR (THF) υ(CO) 1919 (s), 1820 (m) cm^{-1}; (CH$_3$CN) υ(CO) 1914 (s), 1809 (m) cm^{-1}; (nujol) υ(CO) 1916 (s), 1810 (s, br) cm^{-1}. ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 27.0 (q, $^2J_{PC}$ = 5.0 Hz, MoP), 21.0 (s, PPN). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -13.9 (s). ^{19}F{^{1}H} NMR (376 MHz, C$_4$D$_8$O) δ -62.8 (s). ^{1}H NMR (400 MHz, C$_4$D$_8$O): δ 7.88 (s, br, 2H, *o*-H, (3,5-CF$_3$)C$_6$*H*$_3$), 7.66 – 7.51 (m, 30H, PPN), 7.46 (m, 12H, *o*-H, PPh), 7.42 (s, br, 1H, *p*-H, (3,5-

CF$_3$)C$_6$*H*$_3$), 6.99 – 6.90 (m, 18H, *m*/*p*-H, PPh), 1.18 (m, 6H, BC*H*$_2$P). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ 224.1 (m, CO), 145.0 (m, *i*-C, PPh), 134.6 (s, *p*-C, PPN), 133.4 (m, *m*-C, PPN), 133.2 (m, *o*-C, PPN), 132.2 (s, br, *o*-C, (3,5-CF$_3$)C$_6$*H*$_3$), 130.3 (m, *o*-C, PPh), 128.3 (dd, $^1J_{\mathrm{PC}}$ = 108 Hz, *J* = 1.7 Hz, *i*-C, PPN), 127.7 (m, *m*-C, PPh), 127.4 (s, *p*-C, PPh), 126.0 (q, $^1J_{CF}$ = 273 Hz, *C*F$_3$), 116.7 (m, *m*-C, (3,5-CF$_3$)C$_6$H$_3$), 19.2 (m, B*C*H$_2$P).

[PPN][W(CO)$_3$(((3,5-CF$_3$)C$_6$H$_3$)BP$^{\mathrm{Ph}}{}_3$)] (25). THF (40 mL) was added to [((3,5-CF$_3$)C$_6$H$_3$)BP$^{\mathrm{Ph}}{}_3$]Tl (0.330 g, 0.322 mmol) and W(CO)$_3$(CH$_3$CH$_2$CN)$_3$ (0.133 g, 0.307 mmol). The pale brown solution was refluxed (1.5 hr). The resulting yellow-brown solution was added to PPNCl (0.194 g, 0.338 mmol); the mixture was stirred (2 hr). The suspension was filtered through alumina; most of the pale yellow filtrate solvent was removed *in vacuo*. Et$_2$O (15 mL) was added and the oily residue was triturated. The solvent was removed *in vacuo* and pentane (50 mL) was added to the oily residue. Trituration resulted in a tan solid that was isolated by filtration, washed with pentane (3 * 10 mL) and dried *in vacuo*. Slow evaporation of a Et$_2$O:THF solution resulted in tan microcrystals (0.276 g, 55%). Anal. Calcd for C$_{86}$H$_{69}$BF$_6$NO$_3$P$_5$W: C, 63.45; H, 4.27; N, 0.86. Found: C, 63.51; H, 4.23; N, 0.83. Mp. 205 °C (dec). IR (THF) υ(CO) 1914 (s), 1815 (s) cm^{-1}; (CH$_3$CN) υ(CO) 1908 (s), 1803 (s) cm^{-1}; (nujol) υ(CO) 1906 (s), 1792 (s, br) cm^{-1}. ^{31}P{^{1}H} NMR (162 MHz, C$_4$D$_8$O): δ 21.0 (s, PPN), 9.37 (q, $^2J_{PC}$ = 5.0 Hz, ^{31}P-^{183}W satellites: 10.00 (m), 8.73 (m), $^1J_{PW}$ = 206 Hz, WP). ^{11}B NMR (128 MHz, C$_4$D$_8$O): δ -12.9 (s). ^{19}F{^{1}H} NMR (376 MHz, C$_4$D$_8$O) δ -62.8 (s). ^{1}H NMR (400 MHz, C$_4$D$_8$O): δ 7.87 (s, br, *o*-H, (3,5-CF$_3$)C$_6$*H*$_3$, 7.66 – 7.44 (m, 42H, (PPN, *o*-H, PPh)), 7.42 (s, 1H, *p*-H, (3,5-CF$_3$)C$_6$*H*$_3$), 6.99 – 6.90 (m, 18H, *m*/*p*-H, PPh), 1.29 (m, 6H, BC*H*$_2$P). ^{13}C{^{1}H} NMR (101 MHz, C$_4$D$_8$O): δ 215.9 (m, CO), 144.6 (m, *i*-C, PPh), 134.6 (s, *p*-C, PPN), 133.6 (m, *m*-C, PPN), 133.2 (m, *o*-C PPN), 132.3 (s, br, *o*-C, (3,5-CF$_3$)C$_6$H$_3$), 130.3 (m, *o*-C, PPh), 128.3 (dd, $^1J_{\mathrm{PC}}$ = 108 Hz, *J* = 1.7 Hz, *i*-C, PPN), 127.7 (m, *m*/*p*-C, PPh), 126.0 (q, $^1J_{CF}$ = 273 Hz, *C*F$_3$), 116.8 (m, *m*-C, (3,5-CF$_3$)C$_6$H$_3$), 19.0 (m, B*C*H$_2$P).

III. Thermal Ellipsoid Drawings

Figure S1: Molecular Structure of [PPN][Cr(CO)$_3$(PhBP$^{iPr}{}_3$)] (1)

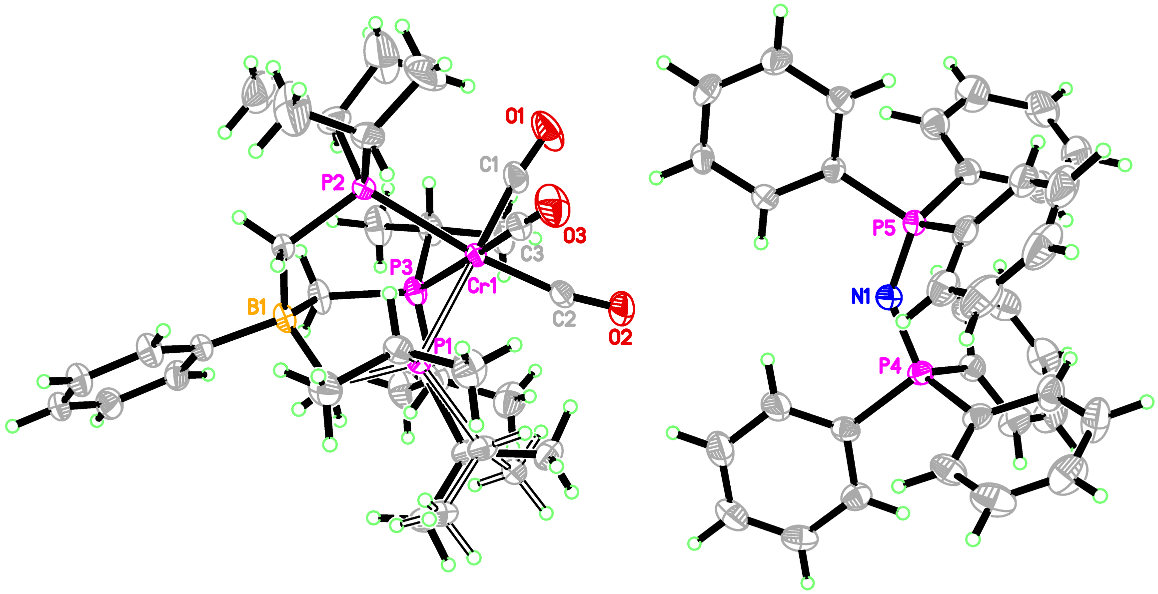


Figure S2: Molecular Structure of the Anion of [PPN][Mo(CO)$_3$(PhBP$^{iPr}{}_3$)] (2)

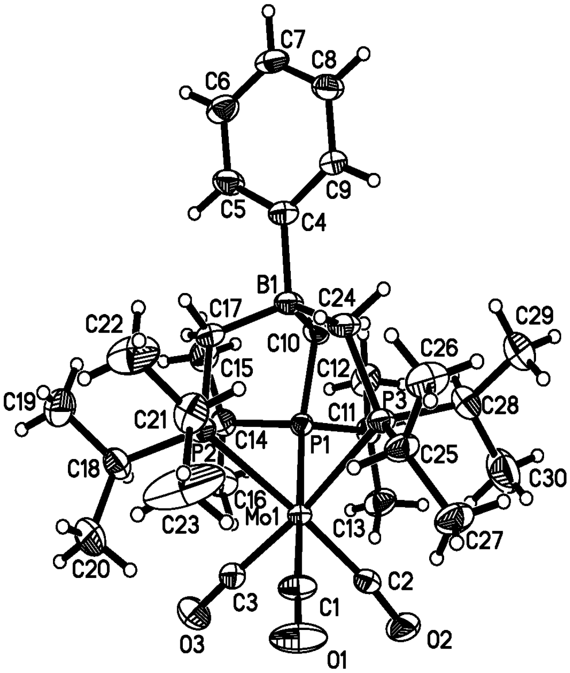


Figure S3: Molecular Structure of [PPN][W(CO)$_3$(PhBP$^{iPr}{}_3$)] (3)

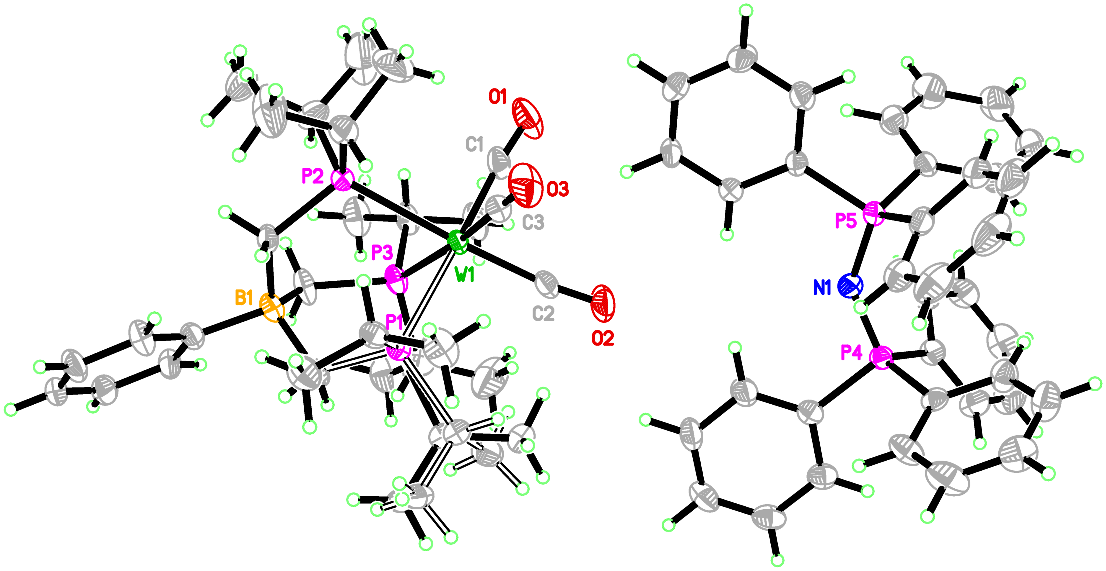


Figure S4: Molecular Structure of [PPN][Cr(CO)$_3${η^6-(PhBP$^{iPr}{}_3$)Cr(CO)$_3$}] (7)

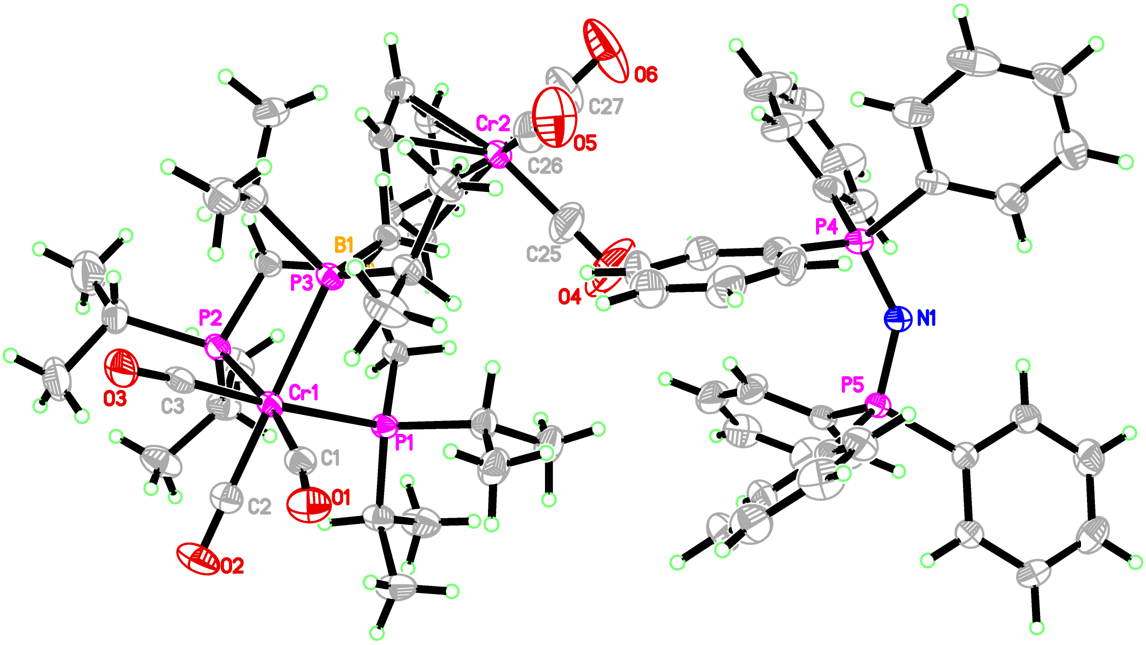


Figure S5: Molecular Structure of [PPN][Cr(CO)$_3${η^6-(PhBP$^{iPr}{}_3$)Mo(CO)$_3$}] (8)

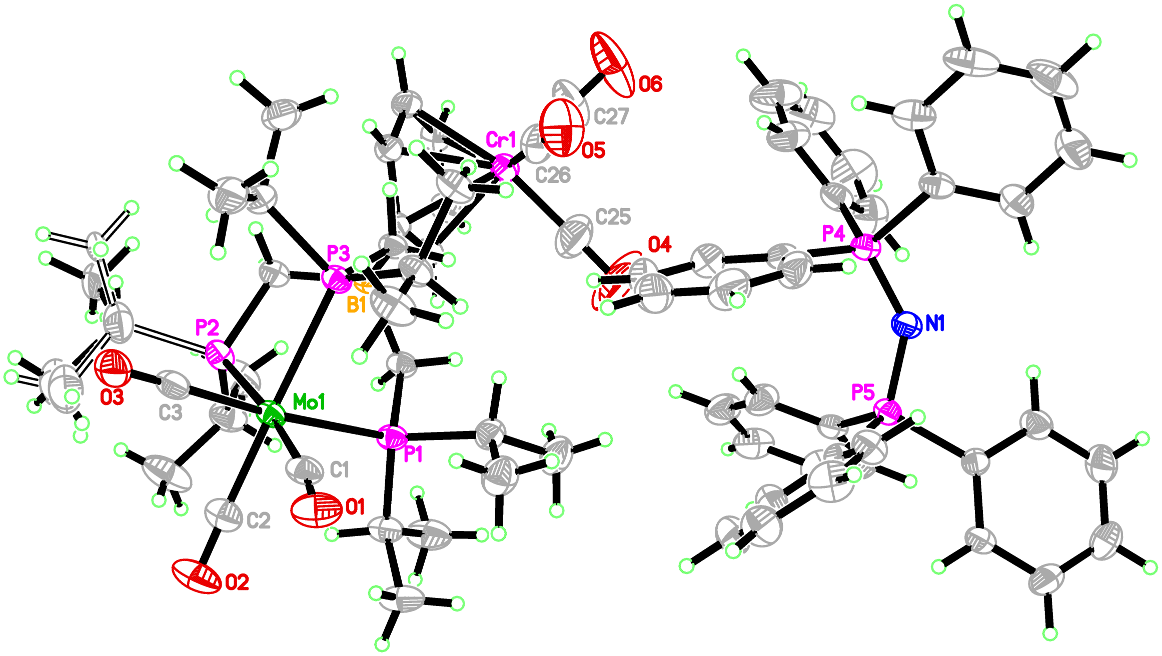


Figure S6: Molecular Structure of [PPN][Cr(CO)$_3${η^6-(PhBP$^{iPr}{}_3$)W(CO)$_3$}] (9)

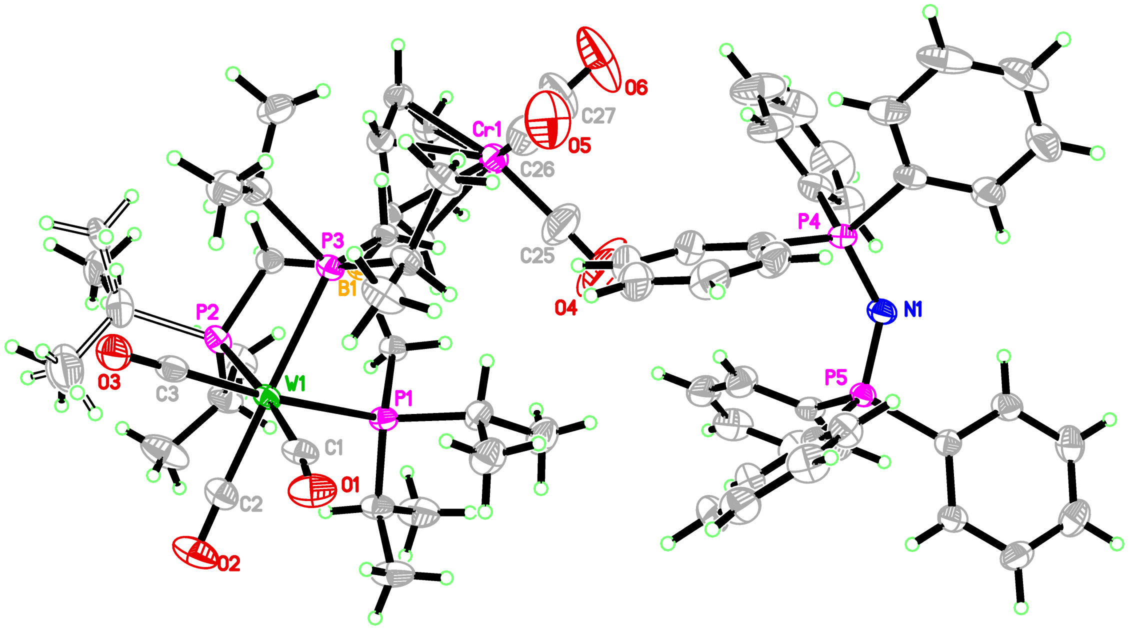


Figure S7: Molecular Structure of $[PPN][W(CO)_3\{\eta^6\text{-}(PhBP^{iPr}_3)Cr(CO)_3\}]$ (12)

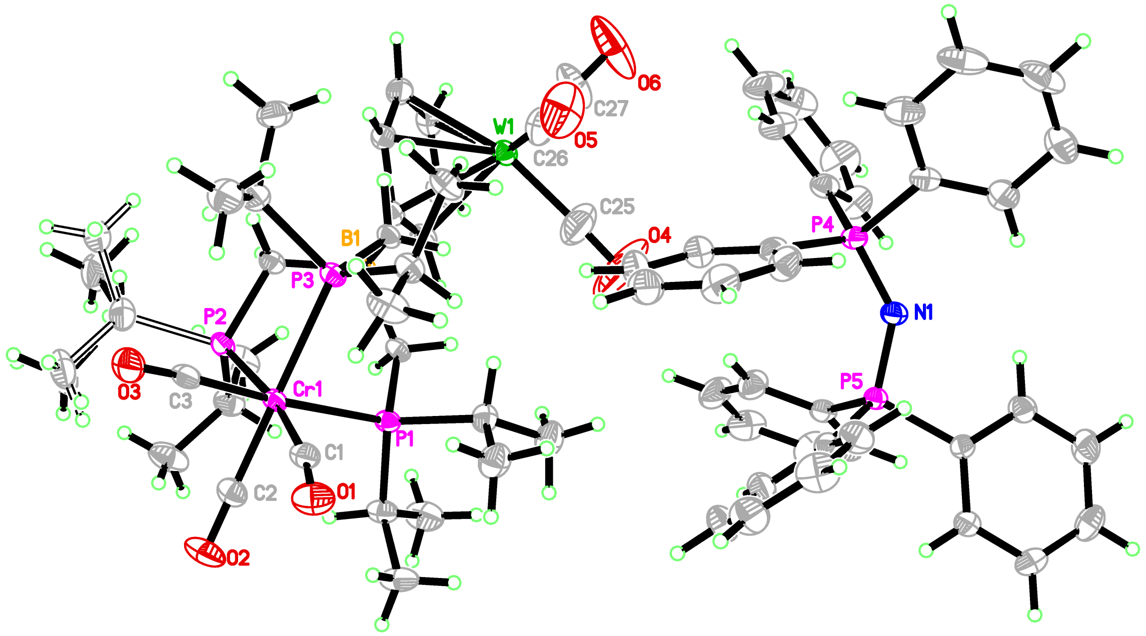


Figure S8: Molecular Structure of $[PPN][W(CO)_3\{\eta^6\text{-}(PhBP^{iPr}_3)Mo(CO)_3\}]$ (13)

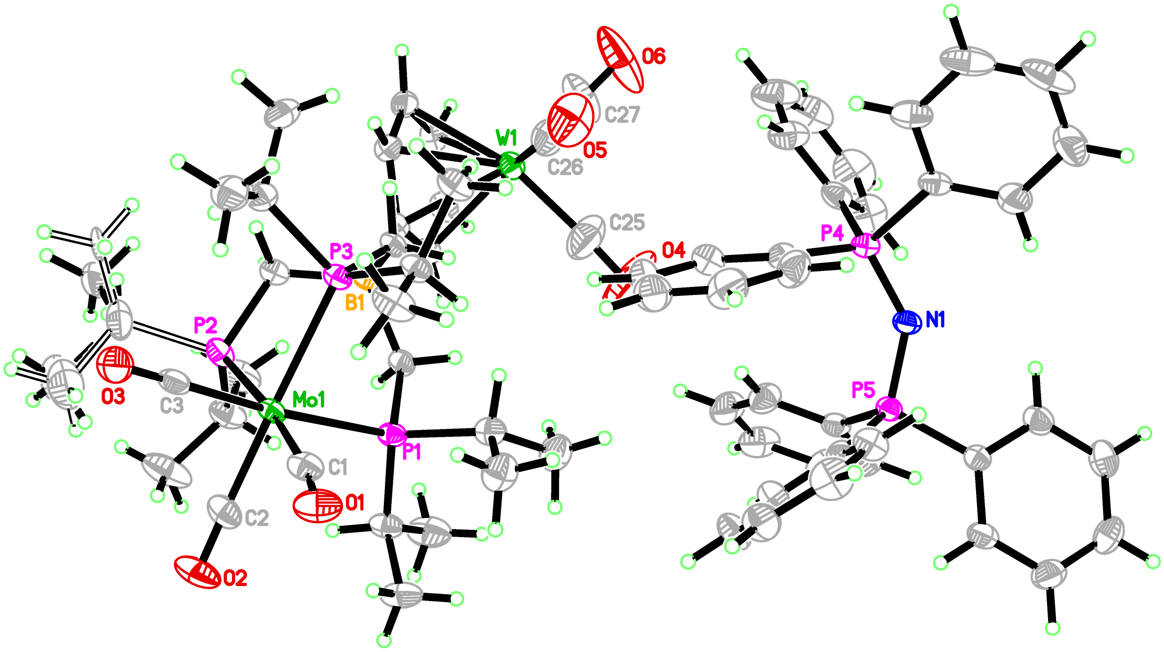


Figure S9: Molecular Structure of [PPN][W(CO)$_3${η^6-(PhBP$^{iPr}{}_3$)W(CO)$_3$}] (14)

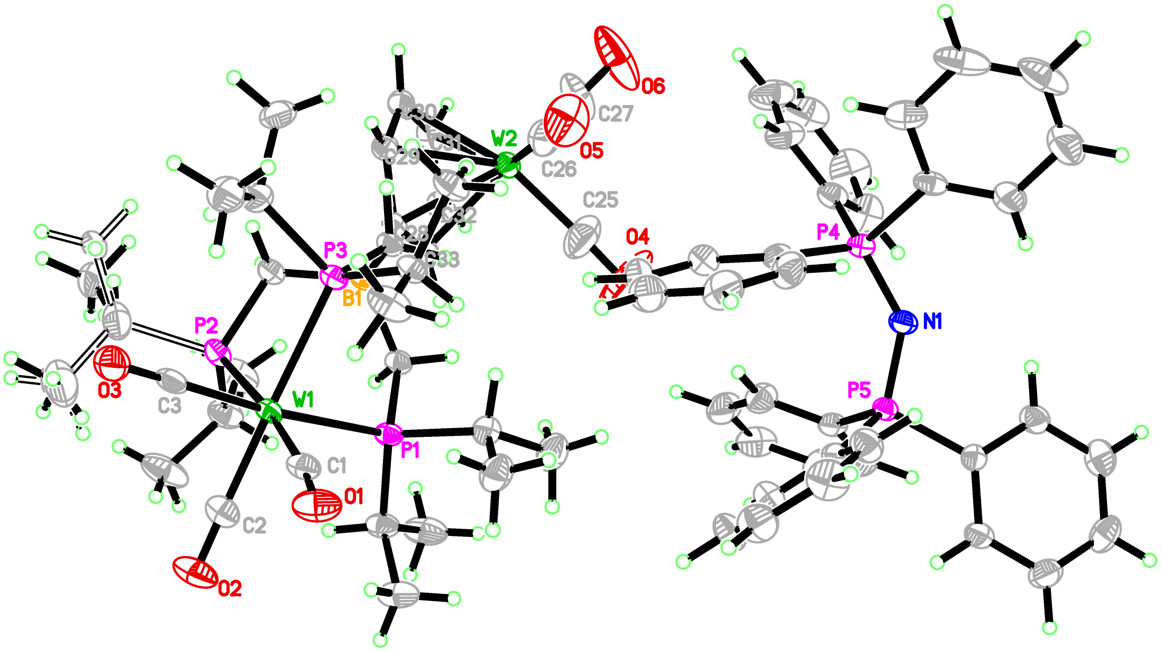


Figure S10: Molecular Structure of [((3,5-Me)C$_6$H$_3$)BP$^{Ph}{}_3$]Tl (18)

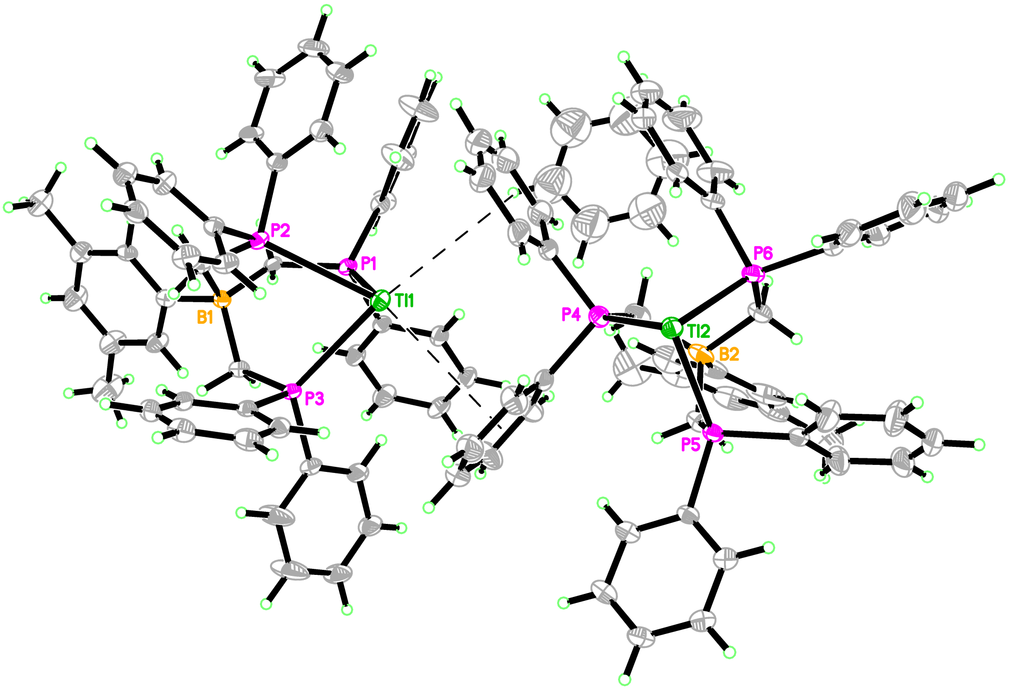


Figure S11: Molecular Structure of $[((3,5\text{-}CF_3)C_6H_3)BP^{Ph}{}_3]Tl$ (19)

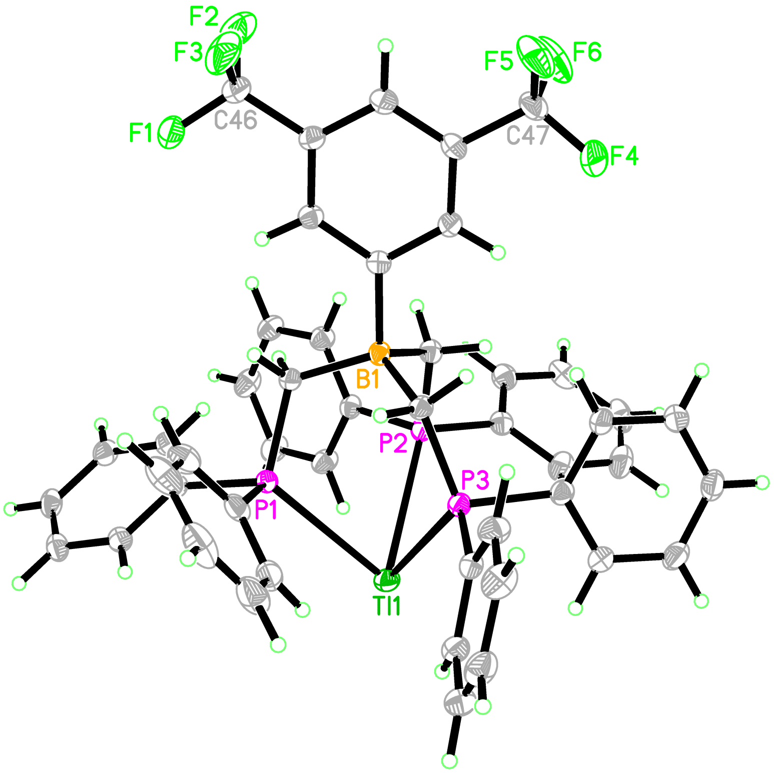


Figure S12: Molecular Structure of $[PPN][Cr(CO)_3(((3,5\text{-}Me)C_6H_3)BP^{Ph}{}_3)]$ (20)

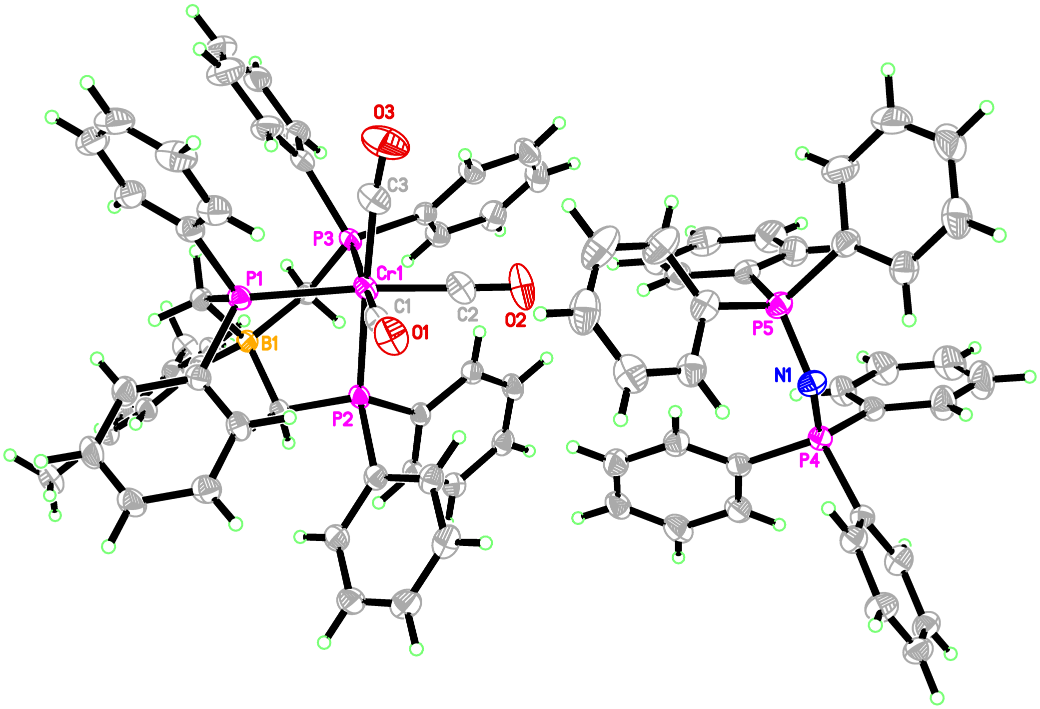


Figure S13: Molecular Structure of the Anion of $[PPN][Mo(CO)_3(((3,5\text{-}Me)C_6H_3)BP^{Ph}{}_3)]$ (21)

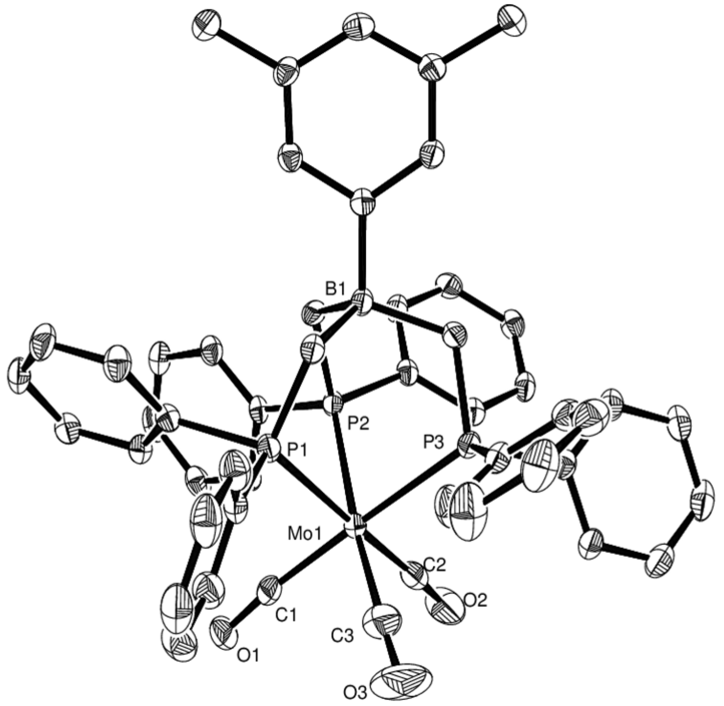


Figure S14: Molecular Structure of the Anion of $[PPN][W(CO)_3(((3,5\text{-}Me)C_6H_3)BP^{Ph}{}_3)]$ (22)

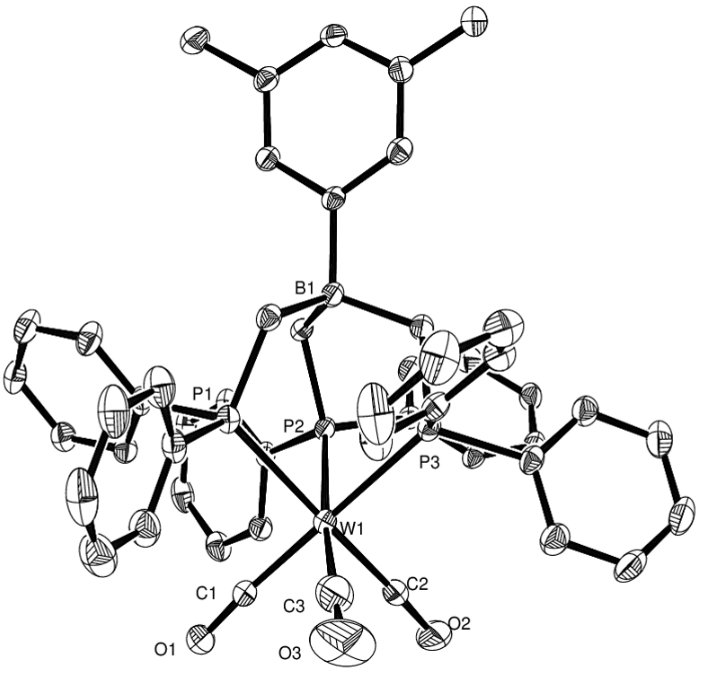


Figure S15: Molecular Structure of the Anion of $[PPN][Cr(CO)_3(((3,5\text{-}CF_3)C_6H_3)BP^{Ph}{}_3)]$ (23)

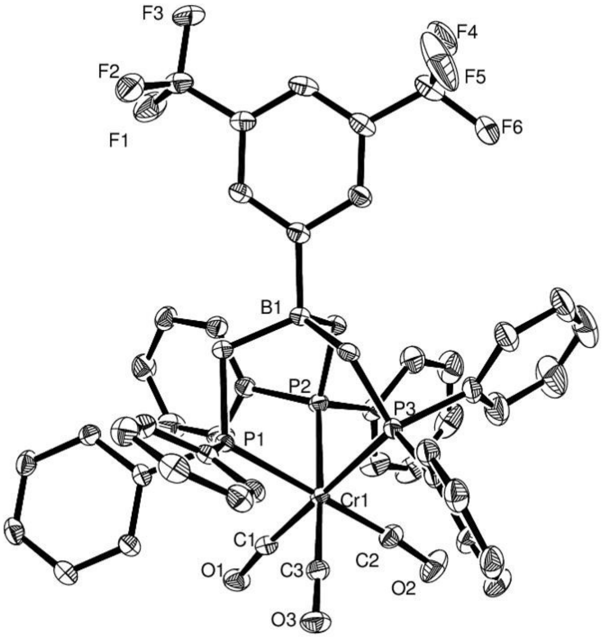


Figure S16: Molecular Structure of $[PPN][Mo(CO)_3(((3,5\text{-}CF_3)C_6H_3)BP^{Ph}{}_3)]$ (24)

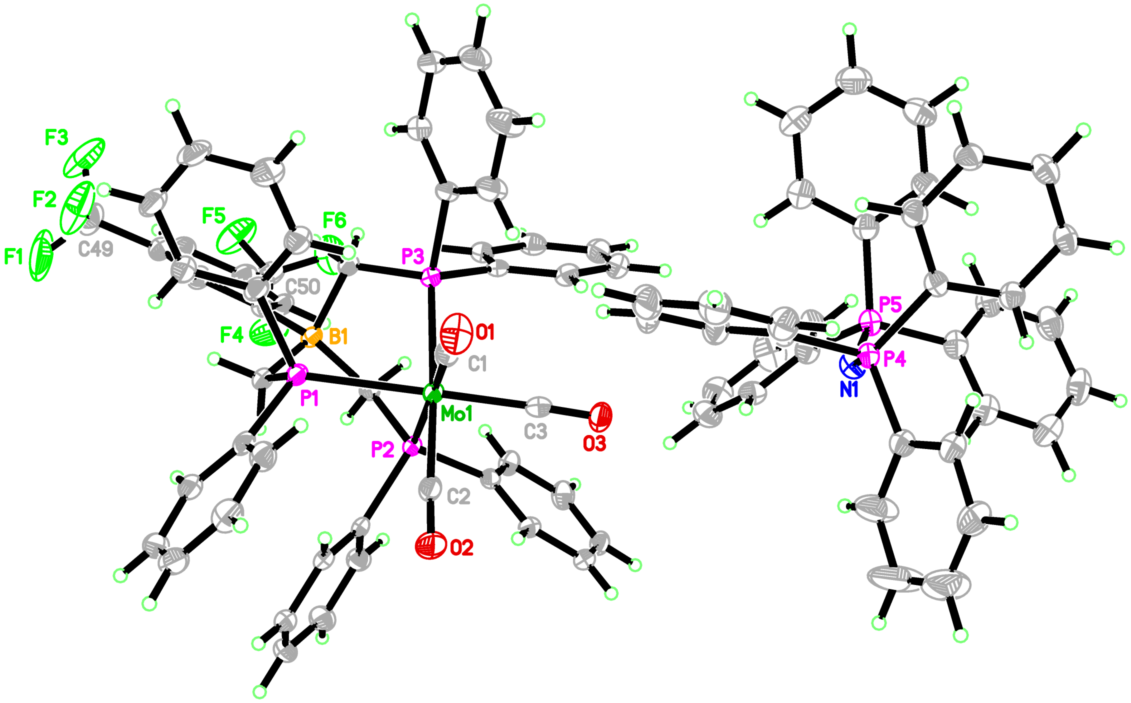
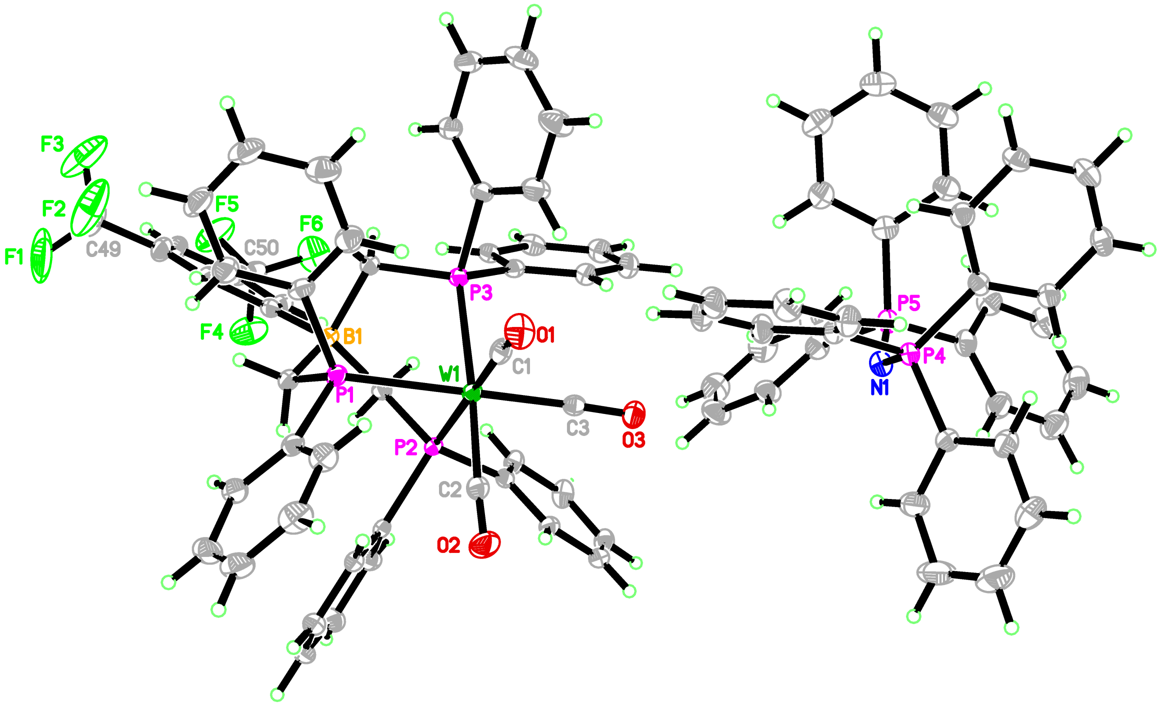


Figure S17: Molecular Structure of [PPN][W(CO)$_3$(((3,5-CF$_3$)C$_6$H$_3$)BP$^{Ph}{}_3$)] (25)



IV. X-ray Crystallographic Collection and Refinement Details; Thermal Ellipsoid Drawings

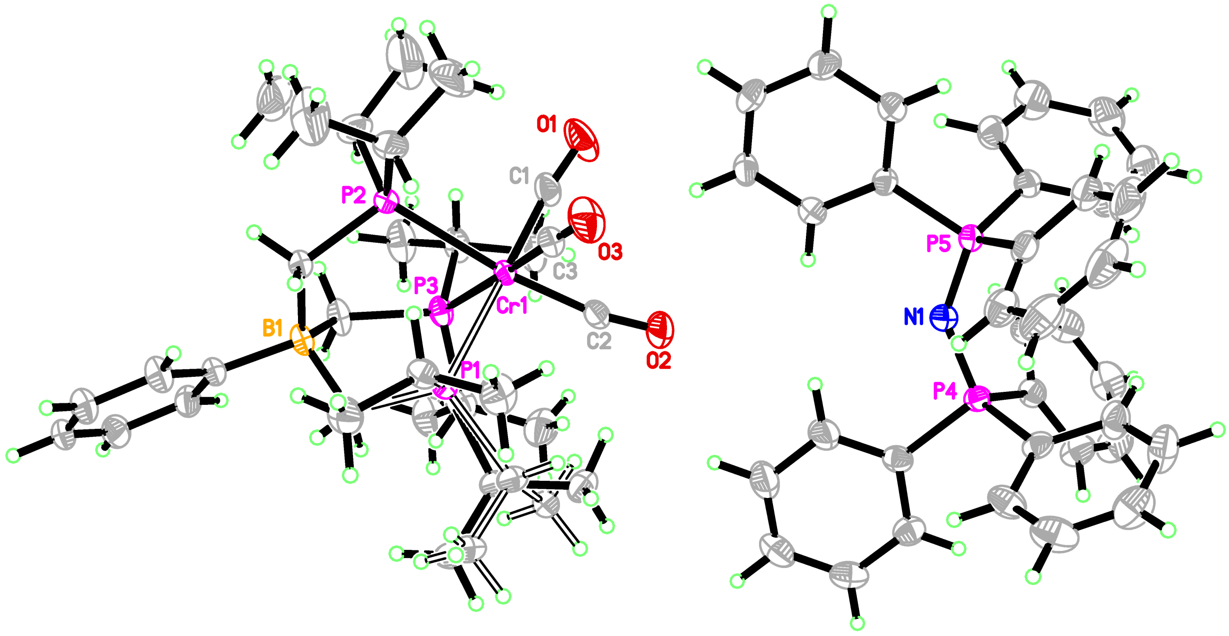
REFERENCE NUMBER: 16168z

CRYSTAL STRUCTURE REPORT

$C_{66}H_{83}BCrNO_3P_5$
or
$[C_{36}H_{30}NP_2]^+[C_{30}H_{53}BCrO_3P_3]^-$

Report prepared for:
Prof. P. Fischer / Macalester University

August 30, 2016



Victor G. Young, Jr.
X-Ray Crystallographic Laboratory
Department of Chemistry
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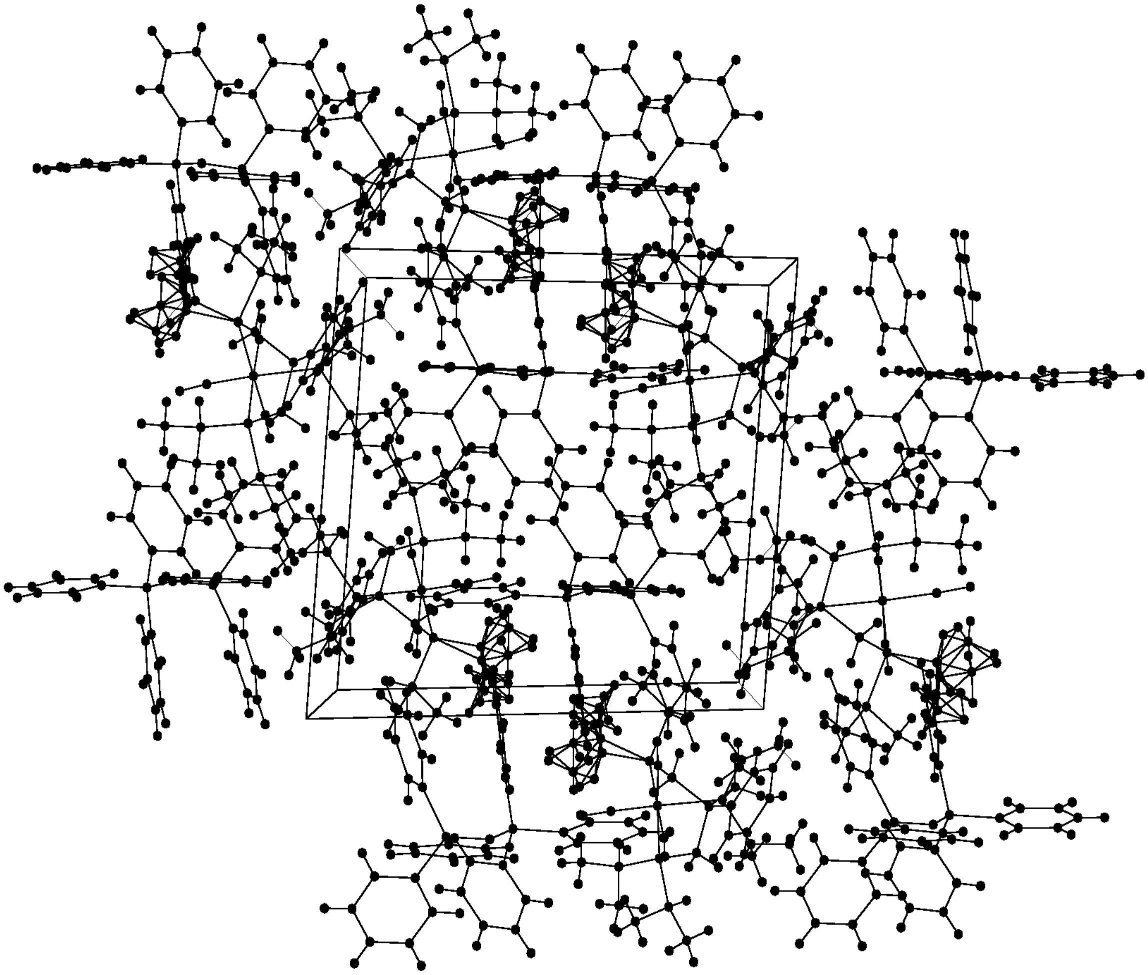
Minneapolis, MN 55455



Data collection

A crystal (approximate dimensions 0.450 x 0.320 x 0.080 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX-II CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 235 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 30 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.30° steps in ω at four different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 1367 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/ (Sheldrick, 2014)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0395$ and $wR2 = 0.0974$ (F^2, all data).

Structure description

The structure is the one suggested. The crystal was twinned by non-merohedry: further information is provided in the CIF. One isopropyl group is disordered and its minor component produced an A-alert and a B-alert that are explained in the CIF.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\mathrm{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

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[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2012).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Table S1. Crystal data and structure refinement for 16168z.

Identification code	16168z	
Empirical formula	$C_{66}H_{83}BCrNO_3P_5$	
Formula weight	1155.99	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	*a* = 13.399(5) Å	α = 93.923(5)°
	b = 14.737(6) Å	β = 104.751(5)°
	c = 16.319(7) Å	γ = 91.952(5)°
Volume	3104(2) $Å^3$	
Z	2	
Density (calculated)	1.237 Mg/m^3	
Absorption coefficient	0.358 mm^{-1}	
F(000)	1228	
Crystal color, morphology	Yellow, Plate	
Crystal size	0.450 x 0.320 x 0.080 mm^3	
Theta range for data collection	1.761 to 27.593°	
Index ranges	$-17 \le h \le 16$, $-19 \le k \le 19$, $0 \le l \le 21$	
Reflections collected	13924	
Independent reflections	13924 [*R*(int) = 0.0339]	
Observed reflections	11475	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.745553 and 0.679026	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13924 / 716 / 725	
Goodness-of-fit on F^2	1.005	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0395, *wR*2 = 0.0890	
R indices (all data)	*R*1 = 0.0539, *wR*2 = 0.0974	
Largest diff. peak and hole	0.680 and -0.647 e.$Å^{-3}$	

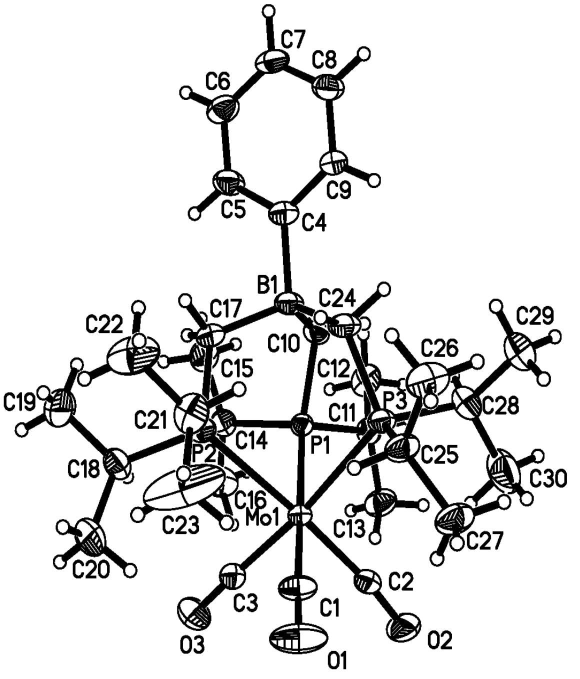
REFERENCE NUMBER: 16151a

CRYSTAL STRUCTURE REPORT

$C_{66}H_{83}BMoNO_3P_5$
Or
$[C_{36}H_{30}NP_2]^+[C_{66}H_{83}BMoNO_3P_5]^-$

Report prepared for:
Prof. P. Fischer - Macalester University

June 13, 2016



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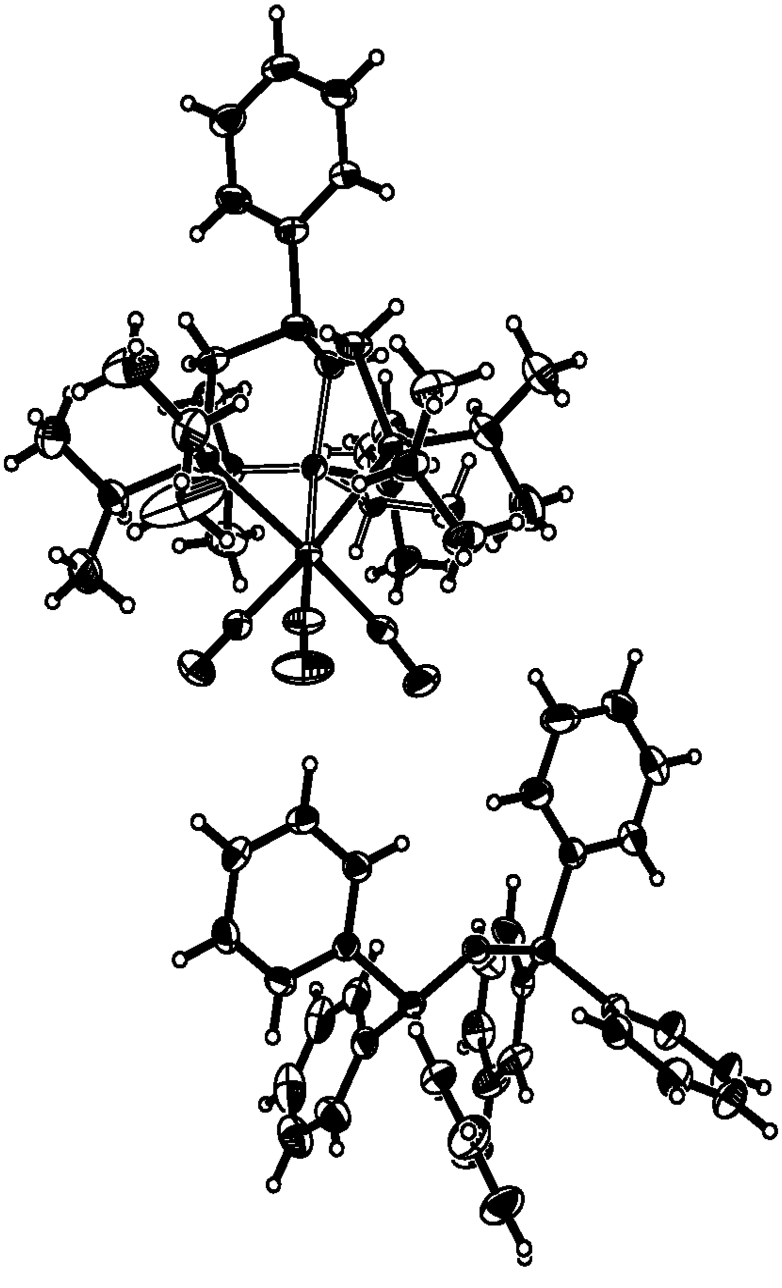
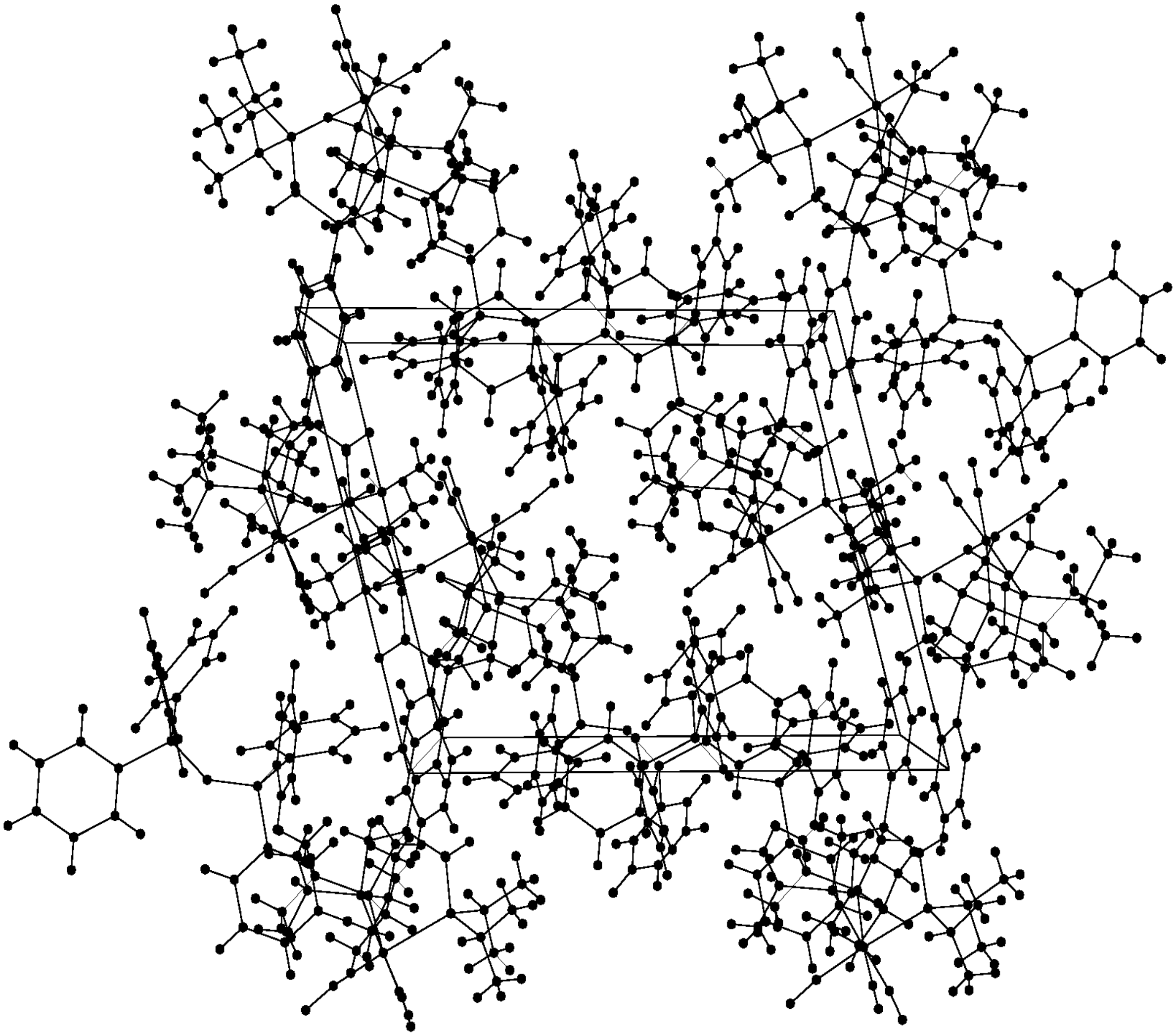




Data collection

A crystal (approximate dimensions 0.400 x 0.250 x 0.120 mm^3) was placed onto the tip of a Mitegen mount and mounted on a Bruker APEX-II CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 139 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 6 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.30° steps in ω at four different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2925 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/ (Sheldrick, 2014)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0407$ and $wR2 = 0.0939$ (F^2, all data).

Structure description

The structure is the one suggested. One isopropyl group is rotationally disordered.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

---

[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2014); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\mathrm{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table S2. Crystal data and structure refinement for 16151a.

Identification code	16151a	
Empirical formula	$C_{66}H_{83}BMoNO_3P_5$	
Formula weight	1199.93	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.389(8) Å	α = 94.448(7)°
	b = 14.789(8) Å	β = 104.751(7)°
	c = 16.369(9) Å	γ = 92.076(7)°
Volume	3120(3) $Å^3$	
Z	2	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	0.384 mm^{-1}	
$F(000)$	1264	
Crystal color, morphology	yellow, Plate	
Crystal size	0.400 x 0.250 x 0.120 mm^3	
Theta range for data collection	1.575 to 27.470°	
Index ranges	$-17 \le h \le 17$, $-19 \le k \le 19$, $-21 \le l \le 21$	
Reflections collected	36465	
Independent reflections	14016 [R(int) = 0.0425]	
Observed reflections	10806	
Completeness to theta = 25.242°	99.8%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7455 and 0.6717	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14016 / 716 / 724	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	$R1$ = 0.0407, $wR2$ = 0.0854	
R indices (all data)	$R1$ = 0.0577, $wR2$ = 0.0939	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.760 and -0.706 e.$Å^{-3}$	

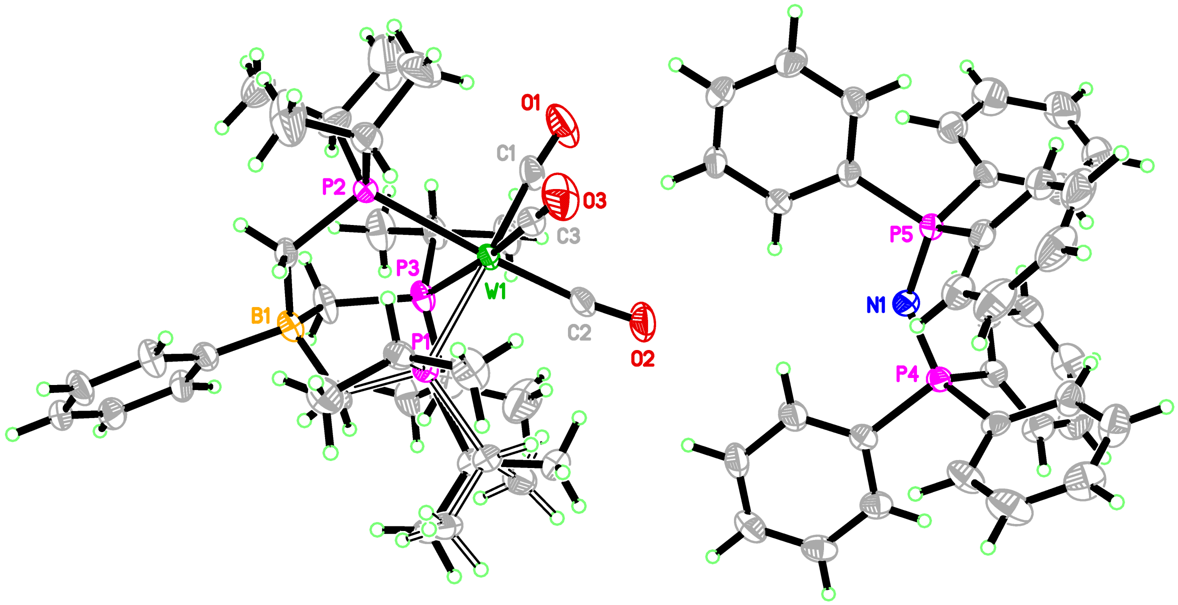
REFERENCE NUMBER: 16185z

CRYSTAL STRUCTURE REPORT

$C_{66}H_{83}BNO_3P_5W$
or
$[C_{36}H_{30}NP_2]^+[C_{30}H_{53}BO_3P_3W]^-$

Report prepared for:
Prof. P. Fischer / Macalester University

August 30, 2016



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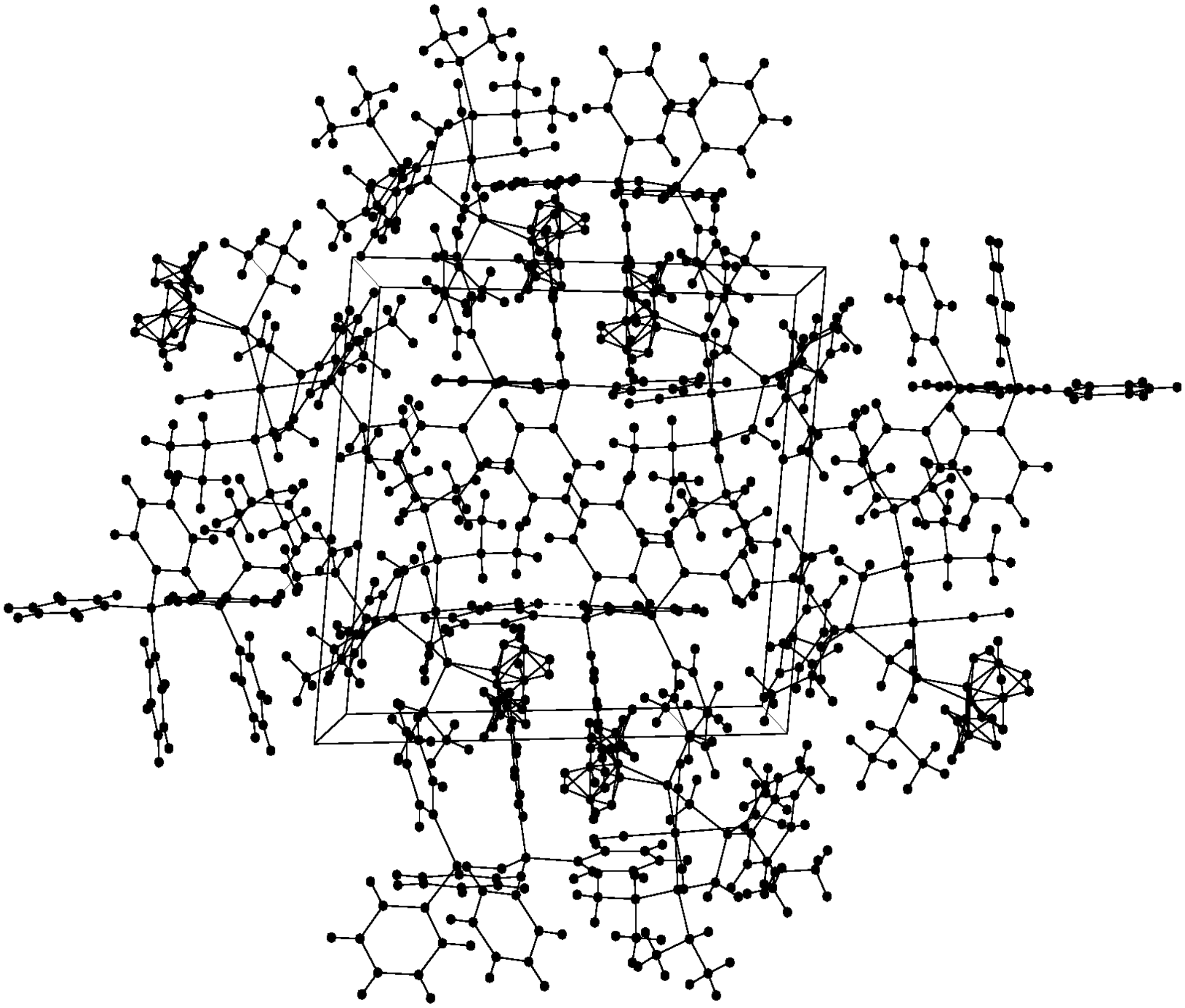

Data collection

A crystal (approximate dimensions 0.450 x 0.320 x 0.080 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX-II CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 657 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 5 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 9970 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/ (Sheldrick, 2014)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0394$ and $wR2 = 0.0767$ (F^2, all data).

Structure description

The structure is the one suggested. One isopropyl group is disordered.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\,|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, \Sigma\,[w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, (n-p)]^{1/2}$$

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[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2012).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Table S3. Crystal data and structure refinement for 16185z.

Identification code	16185z	
Empirical formula	$C_{66}H_{83}BNO_3P_5W$	
Formula weight	1287.84	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.374(4) Å	α = 94.317(4)°
	b = 14.778(4) Å	β = 104.773(3)°
	c = 16.383(5) Å	γ = 92.027(3)°
Volume	3117.1(15) $Å^3$	
Z	2	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	2.027 mm^{-1}	
$F(000)$	1328	
Crystal color, morphology	Yellow, Plate	
Crystal size	0.450 x 0.320 x 0.080 mm^3	
Theta range for data collection	1.577 to 27.483°	
Index ranges	$-17 \le h \le 17$, $-19 \le k \le 19$, $-21 \le l \le 21$	
Reflections collected	36709	
Independent reflections	14145 [R(int) = 0.0537]	
Observed reflections	11434	
Completeness to theta = 25.242°	99.7%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7456 and 0.5878	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14145 / 716 / 724	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	$R1$ = 0.0394, $wR2$ = 0.0705	
R indices (all data)	$R1$ = 0.0544, $wR2$ = 0.0767	
Largest diff. peak and hole	1.526 and -0.764 e.$Å^{-3}$	

REFERENCE NUMBER: 16173z

CRYSTAL STRUCTURE REPORT

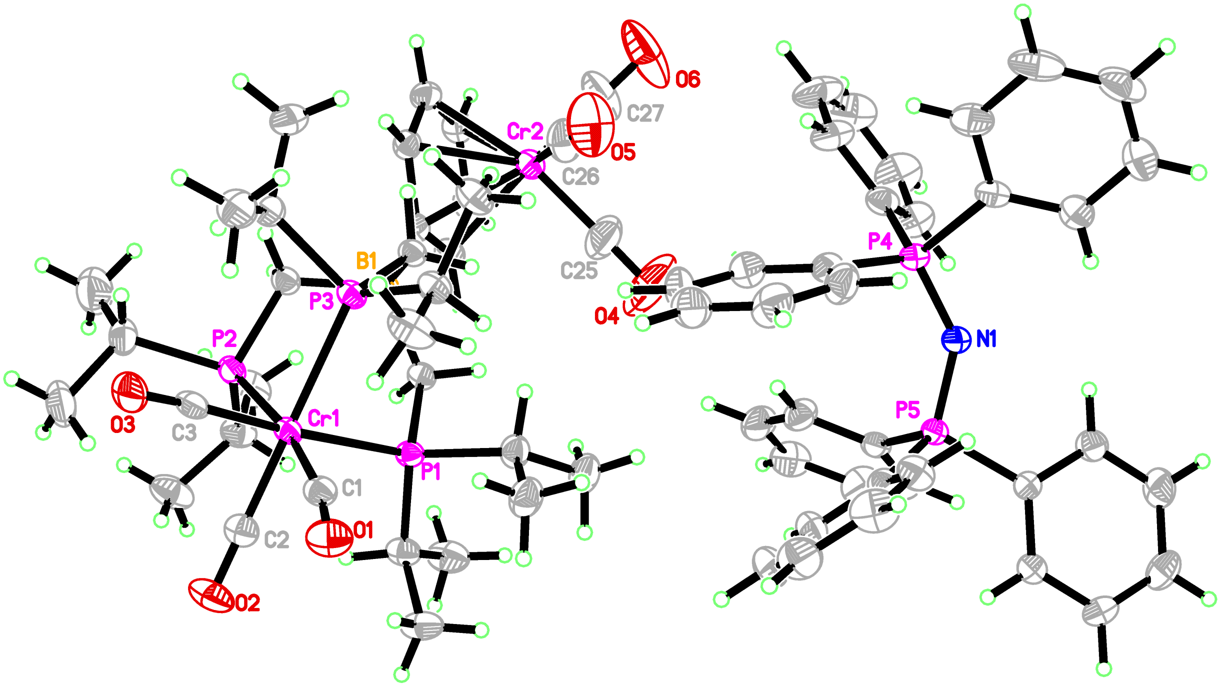
$C_{69}\ H_{83}\ B\ Cr_2\ N\ O_6\ P_5$

or

$[C_{36}\ H_{30}\ N\ P_2]^+\ [C_{33}\ H_{53}\ B\ Cr_2\ O_6\ P_3]^-$

Report prepared for:
Prof. P. Fischer / Macalester University

August 24, 2016



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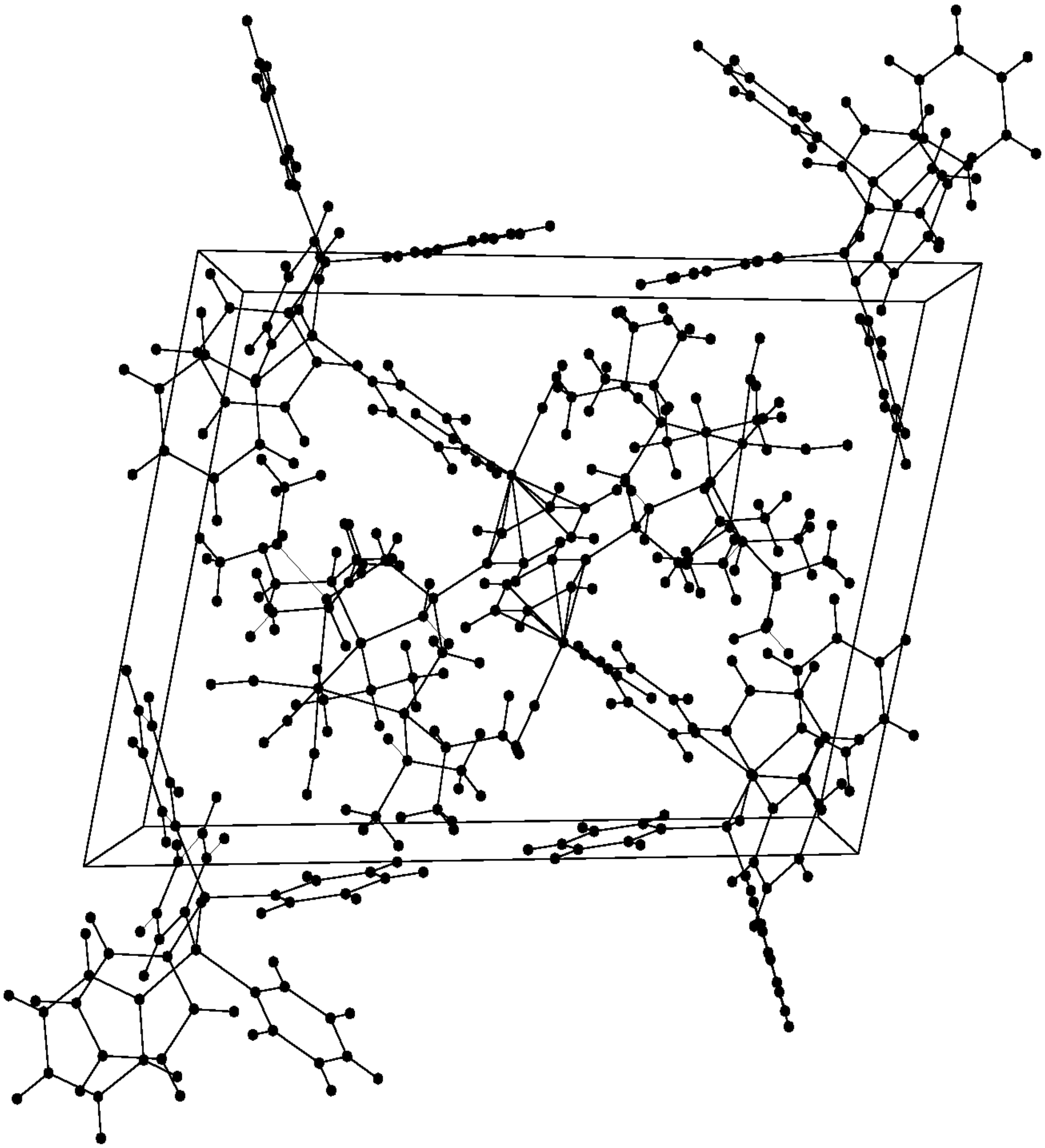

Data collection

A crystal (approximate dimensions 0.450 x 0.250 x 0.220 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX-II CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 91 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.50º steps in ω at four different ϕ settings and a detector position of -28º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated 9911 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXS-97 (Sheldrick, 2008)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0454$ and $wR2 = 0.1195$ (F^2, all data).

Structure description

The structure is the one suggested. There was an insignificant amount of disorder in the isopropyl group C15/C16/C17, therefore this was not modeled as was done for the other five crystal structures completed in this series.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

Some equations of interest:

$$R_{\text{int}} = \Sigma\,|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, \Sigma\,[w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2(F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, (n-p)]^{1/2}$$

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[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2012).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Table S4. Crystal data and structure refinement for 16173z.

Identification code	16173z	
Empirical formula	$C_{69} H_{83} B Cr_2 N O_6 P_5$	
Formula weight	1292.02	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	*a* = 12.031(4) Å	α = 100.819(4)°
	b = 14.432(4) Å	β = 99.989(4)°
	c = 19.966(6) Å	γ = 95.851(4)°
Volume	3321.0(18) $Å^3$	
Z	2	
Density (calculated)	1.292 Mg/m^3	
Absorption coefficient	0.498 mm^{-1}	
F(000)	1360	
Crystal color, morphology	Yellow, Prism	
Crystal size	0.450 x 0.250 x 0.220 mm^3	
Theta range for data collection	1.451 to 27.559°	
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-25 \leq l \leq 25$	
Reflections collected	39142	
Independent reflections	15053 [*R*(int) = 0.0418]	
Observed reflections	10790	
Completeness to theta = 25.242°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7455 and 0.6740	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15053 / 0 / 769	
Goodness-of-fit on F^2	1.045	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0454, *wR*2 = 0.1059	
R indices (all data)	*R*1 = 0.0691, *wR*2 = 0.1195	
Largest diff. peak and hole	0.836 and -0.535 e.$Å^{-3}$	

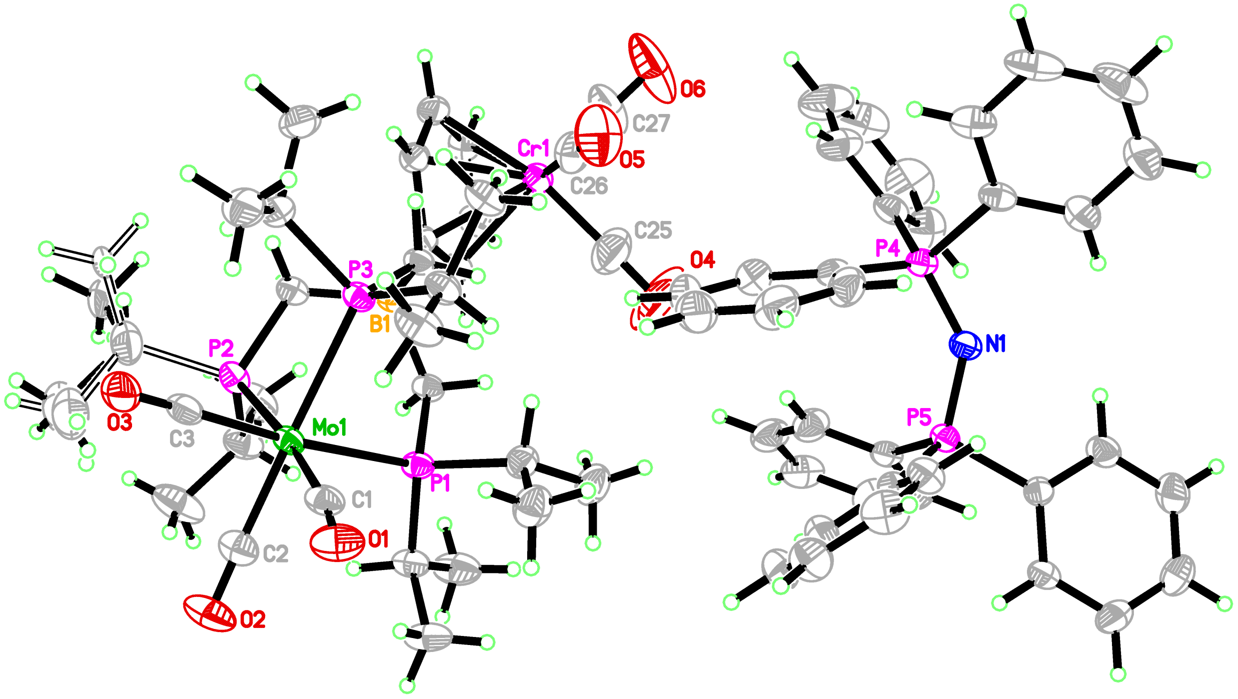
REFERENCE NUMBER: 16178z

CRYSTAL STRUCTURE REPORT

$C_{69}H_{83}BCrMoNO_6P_5$
Or
$[C_{36}H_{30}NP_2]^+[C_{33}H_{53}BCrMoO_6P_3]^-$

Report prepared for:
Prof. P. Fischer / Macalester University

August 24, 2016



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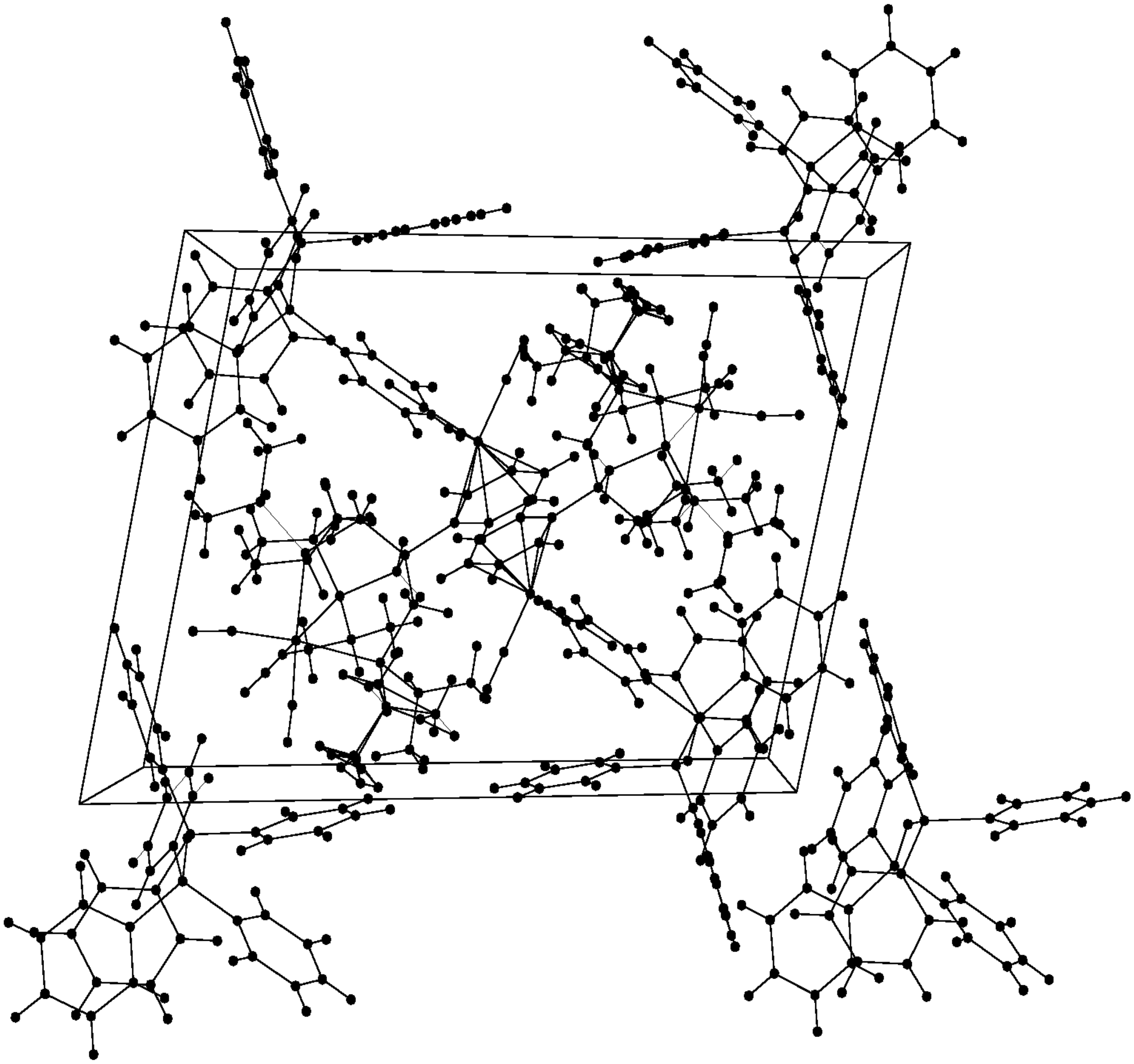

Data collection

A crystal (approximate dimensions 0.450 x 0.420 x 0.400 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX-II CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 131 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 4 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from the xyz centroids of 9976 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXS-97 (Sheldrick, 2008)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0442$ and $wR2 = 0.1051$ (F^2, all data).

Structure description

The structure is the one suggested. The isopropyl group with atoms C15/C16/C17 is disordered over two positions. Appropriate restraints and constraints were applied to these atoms for refinement.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

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[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2012).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Table S5. Crystal data and structure refinement for 16178z.

Identification code	16178z	
Empirical formula	$C_{69}H_{83}BCrMoNO_6P_5$	
Formula weight	1335.96	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	*a* = 12.036(5) Å	α = 100.817(5)°
	b = 14.602(6) Å	β = 100.202(5)°
	c = 20.034(8) Å	γ = 95.829(5)°
Volume	3370(2) Å^3	
Z	2	
Density (calculated)	1.316 Mg/m^3	
Absorption coefficient	0.516 mm^{-1}	
F(000)	1396	
Crystal color, morphology	Yellow, Block	
Crystal size	0.450 x 0.420 x 0.400 mm^3	
Theta range for data collection	1.434 to 27.485°	
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-26 \leq l \leq 26$	
Reflections collected	39756	
Independent reflections	15296 [*R*(int) = 0.0477]	
Observed reflections	11055	
Completeness to theta = 25.242°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7456 and 0.6756	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15296 / 130 / 784	
Goodness-of-fit on F^2	1.047	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0442, *wR*2 = 0.0932	
R indices (all data)	*R*1 = 0.0685, *wR*2 = 0.1051	
Largest diff. peak and hole	0.415 and -0.436 e.Å^{-3}	

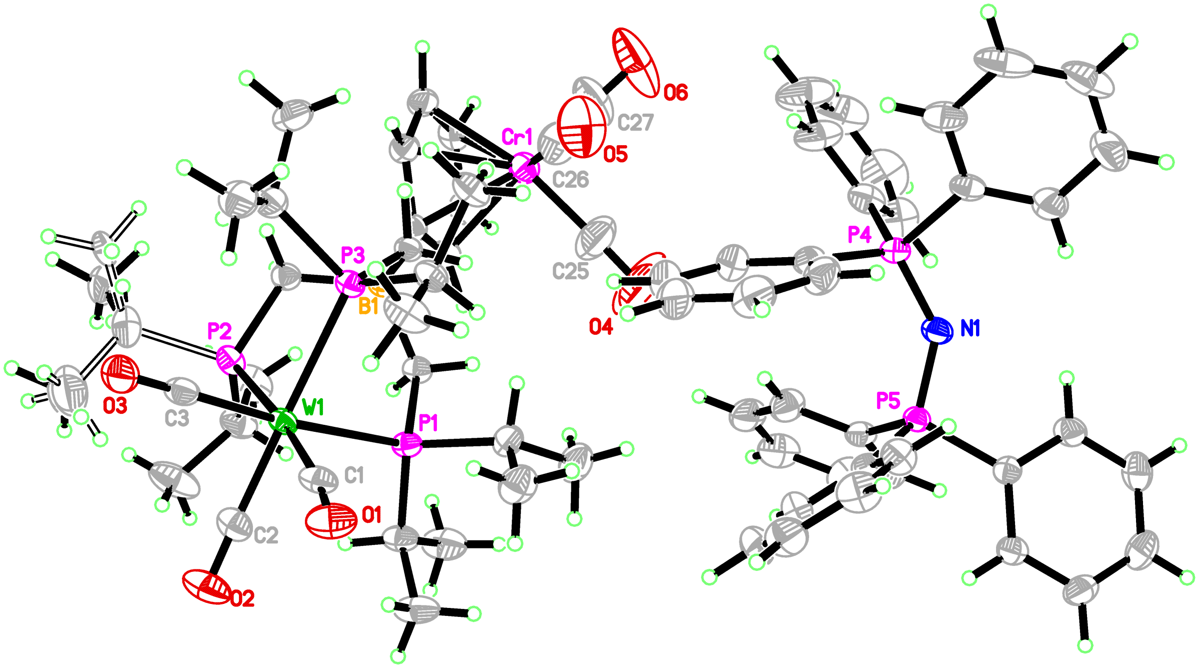
REFERENCE NUMBER: 16175z

CRYSTAL STRUCTURE REPORT

$C_{69} H_{83} B\ Cr\ N\ O_6\ P_5\ W$
or
$[C_{36}H_{30}NP_2]^+ [C_{33}H_{53}BCrO_6P_3W]^-$

Report prepared for:
Prof. P. Fischer / Macalester University

August 24, 2016



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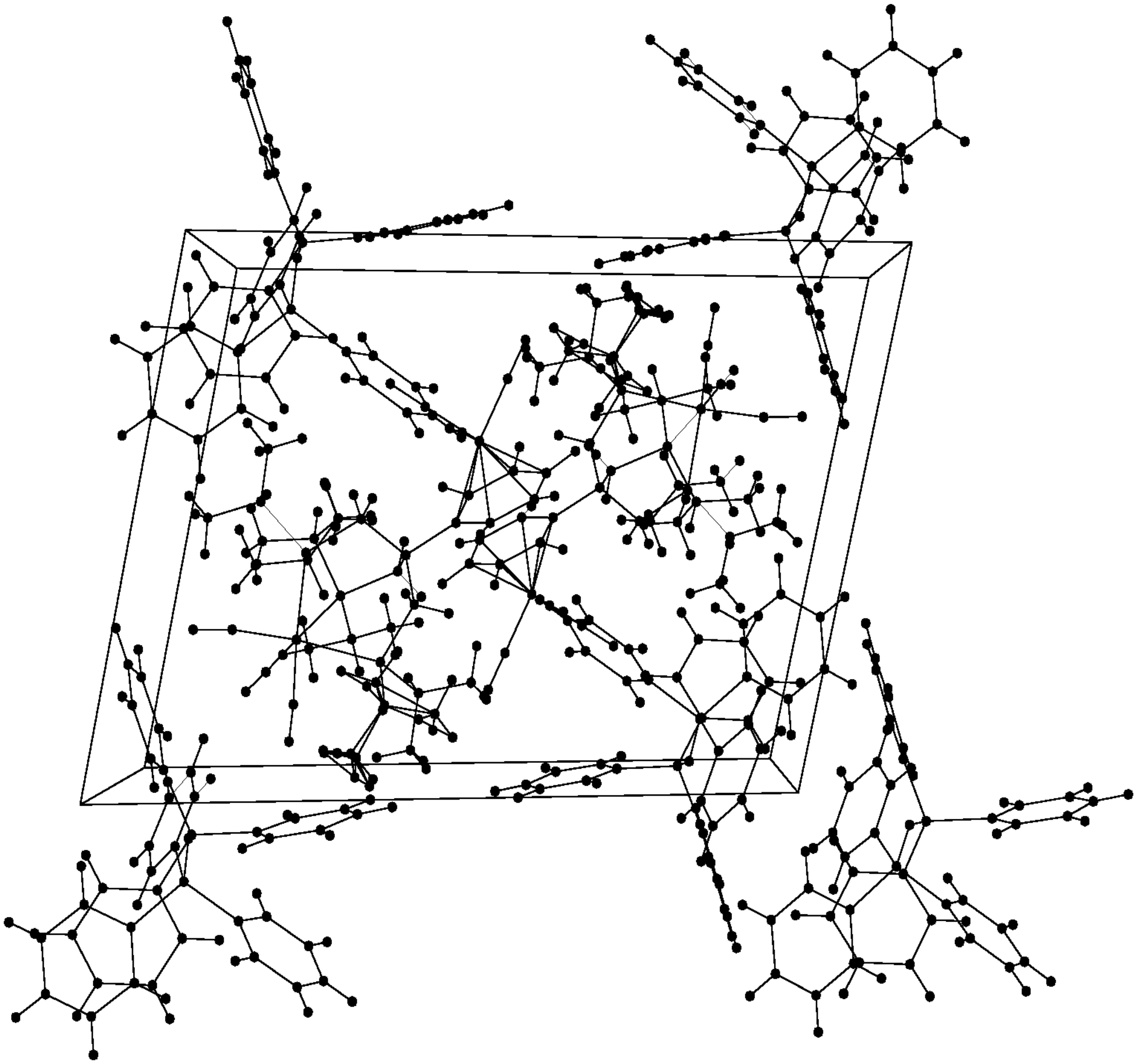

Data collection

A crystal (approximate dimensions 0.450 x 0.250 x 0.220 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX-II CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 203 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 9890 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXS-97 (Sheldrick, 2008)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0328$ and $wR2 = 0.0817$ (F^2, all data).

Structure description

The structure is the one suggested. The isopropyl group with atoms C15/C16/C17 is disordered over two positions. Appropriate restraints and constraints were applied to these atoms for refinement.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

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[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2012).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

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Some equations of interest:

$$R_{\text{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table S6. Crystal data and structure refinement for 16175z.

Identification code	16175z	
Empirical formula	$C_{69} H_{83} B Cr N O_6 P_5 W$	
Formula weight	1423.87	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.019(4) Å	α = 100.765(4)°
	b = 14.605(5) Å	β = 100.228(4)°
	c = 19.963(7) Å	γ = 95.750(4)°
Volume	3355(2) $Å^3$	
Z	2	
Density (calculated)	1.409 Mg/m^3	
Absorption coefficient	2.044 mm^{-1}	
$F(000)$	1460	
Crystal color, morphology	Yellow, Block	
Crystal size	0.450 x 0.250 x 0.220 mm^3	
Theta range for data collection	1.433 to 27.564°	
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-25 \leq l \leq 25$	
Reflections collected	39635	
Independent reflections	15256 [R(int) = 0.0338]	
Observed reflections	13233	
Completeness to theta = 25.242°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7456 and 0.6295	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15256 / 130 / 784	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	$R1$ = 0.0328, $wR2$ = 0.0770	
R indices (all data)	$R1$ = 0.0411, $wR2$ = 0.0817	
Largest diff. peak and hole	0.683 and -1.274 e.$Å^{-3}$	

REFERENCE NUMBER: 16183zz

CRYSTAL STRUCTURE REPORT

$C_{69} H_{83} B Cr N O_6 P_5 W$

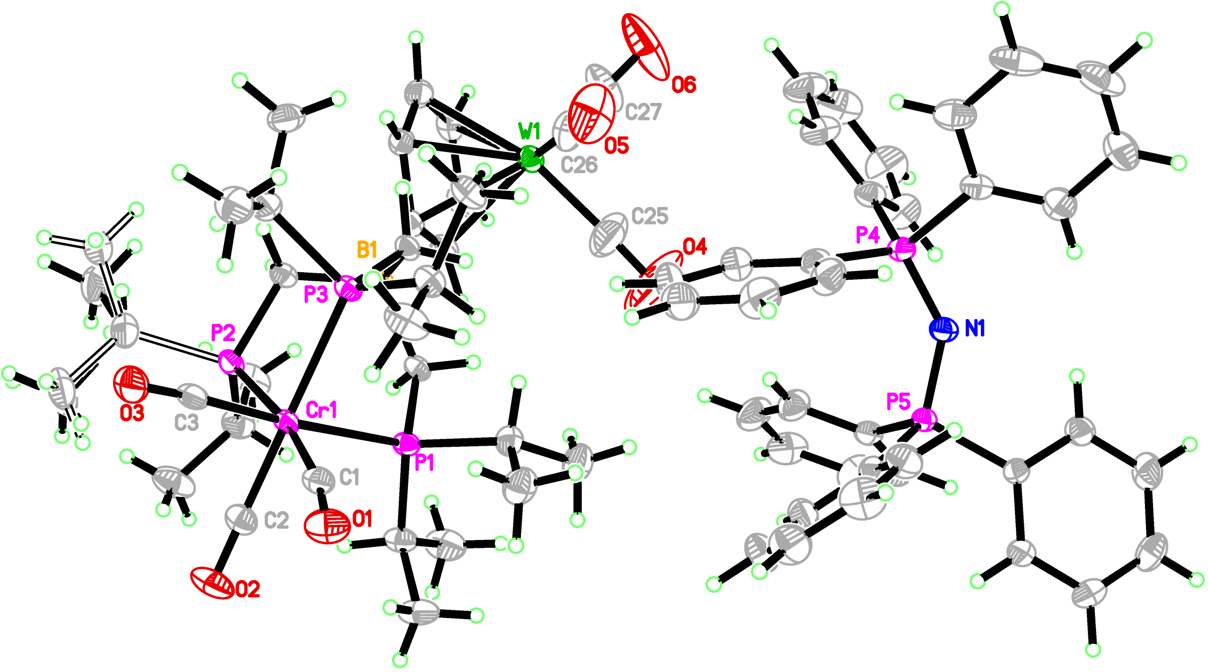
or

$[C_{33}H_{53}BCrO_6P_3W][C_{36}H_{30}NP_2]$

Report prepared for:

Prof. P. Fischer / Macalester University

August 24, 2016



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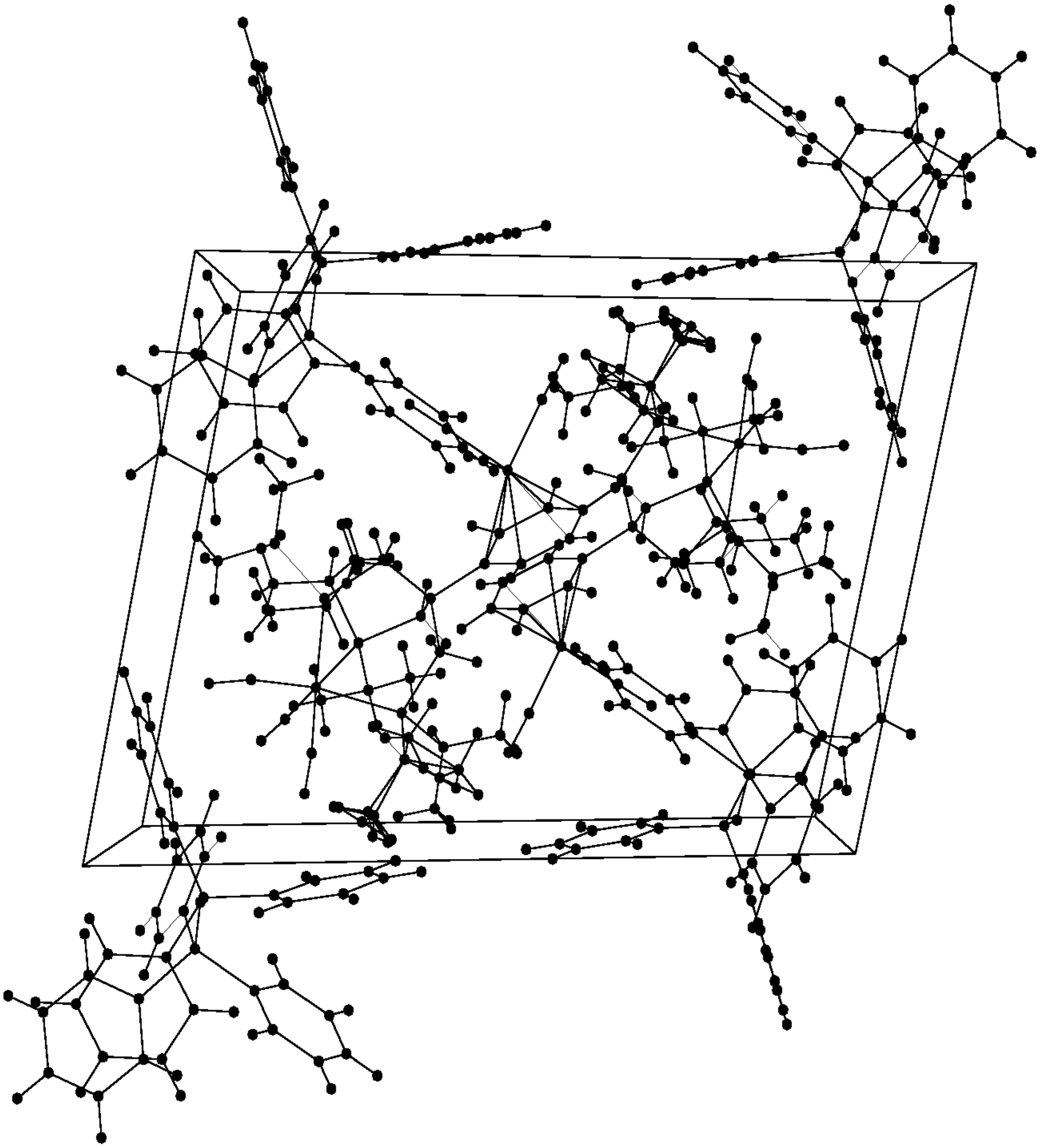

Data collection

A crystal (approximate dimensions 0.450 x 0.430 x 0.390 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX-II CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 438 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 5 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 9910 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXS-97 (Sheldrick, 2008)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0249$ and $wR2 = 0.0594$ (F^2, all data).

Structure description

The structure is the one suggested. The isopropyl group with atoms C15/C16/C17 is disordered over two positions. Appropriate restraints and constraints were applied to these atoms for refinement. In addition, the hydrogen atoms for C17 and C17' were converted to a strict riding model since convergence was difficult for just this disordered methyl group.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

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[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2012).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\,|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, \Sigma\,[w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\mathrm{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table S7. Crystal data and structure refinement for 16183zz.

Identification code	16183zz	
Empirical formula	$C_{69}H_{83}BCrNO_6P_5W$	
Formula weight	1423.87	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.069(3) Å	α = 100.665(3)°
	b = 14.458(4) Å	β = 99.911(3)°
	c = 19.962(5) Å	γ = 95.693(3)°
Volume	3340.8(14) $Å^3$	
Z	2	
Density (calculated)	1.415 Mg/m^3	
Absorption coefficient	2.053 mm^{-1}	
$F(000)$	1460	
Crystal color, morphology	Yellow, Block	
Crystal size	0.450 x 0.430 x 0.390 mm^3	
Theta range for data collection	1.447 to 27.498°	
Index ranges	$-15 \le h \le 15$, $-18 \le k \le 18$, $-25 \le l \le 25$	
Reflections collected	39359	
Independent reflections	15148 [R(int) = 0.0252]	
Observed reflections	13717	
Completeness to theta = 25.242°	99.7%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5862	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15148 / 130 / 782	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	$R1$ = 0.0249, $wR2$ = 0.0571	
R indices (all data)	$R1$ = 0.0296, $wR2$ = 0.0594	
Largest diff. peak and hole	0.691 and -0.838 e.$Å^{-3}$	

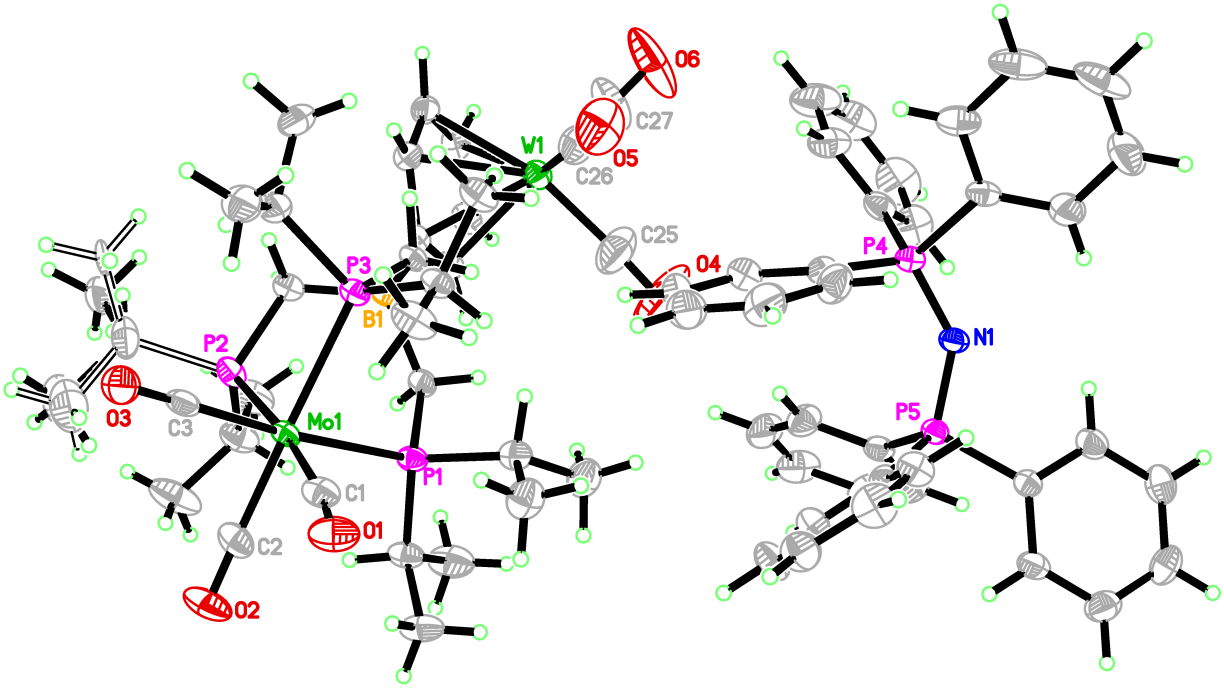
REFERENCE NUMBER: 16177z

CRYSTAL STRUCTURE REPORT

C_{69} H_{83} B Mo N O_6 P_5 W
or
$[C_{36}H_{30}NP_2]^+[C_{33}H_{53}BMoO_6P_3W]^-$

Report prepared for:
Prof. P. Fischer / Macalester University

August 24, 2016



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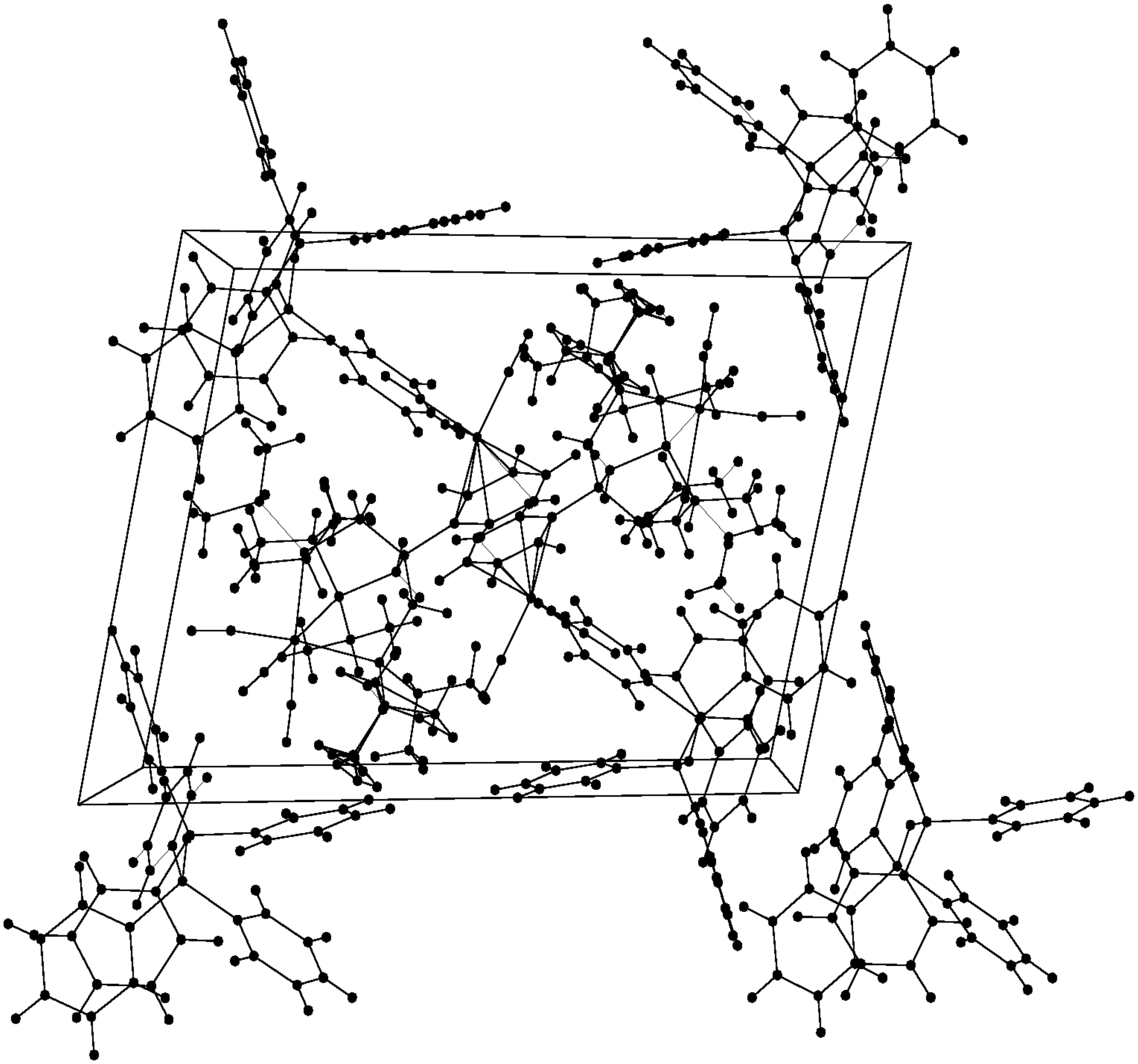

Data collection

A crystal (approximate dimensions 0.400 x 0.300 x 0.130 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX-II CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 266 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 6 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.30° steps in ω at four different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from the xyz centroids of 9858 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXS-97 (Sheldrick, 2008)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0368$ and $wR2 = 0.0819$ (F^2, all data).

Structure description

The structure is the one suggested. The isopropyl group with atoms C15/C16/C17 is disordered over two positions. Appropriate restraints and constraints were applied to these atoms for refinement.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

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[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2012).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\mathrm{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table S8. Crystal data and structure refinement for 16177z.

Identification code	16177z	
Empirical formula	$C_{69} H_{83} B Mo N O_6 P_5 W$	
Formula weight	1467.81	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.067(5) Å	α = 100.676(5)°
	b = 14.620(6) Å	β = 100.089(5)°
	c = 20.030(9) Å	γ = 95.678(5)°
Volume	3387(2) Å^3	
Z	2	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	2.050 mm^{-1}	
F(000)	1496	
Crystal color, morphology	Yellow, Plate	
Crystal size	0.400 x 0.300 x 0.130 mm^3	
Theta range for data collection	1.431 to 27.567°	
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-25 \leq l \leq 25$	
Reflections collected	39734	
Independent reflections	15353 [R(int) = 0.0428]	
Observed reflections	12073	
Completeness to theta = 25.242°	99.7%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7456 and 0.5821	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15353 / 130 / 784	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	$R1$ = 0.0368, $wR2$ = 0.0746	
R indices (all data)	$R1$ = 0.0536, $wR2$ = 0.0819	
Largest diff. peak and hole	1.147 and -0.923 e.Å^{-3}	

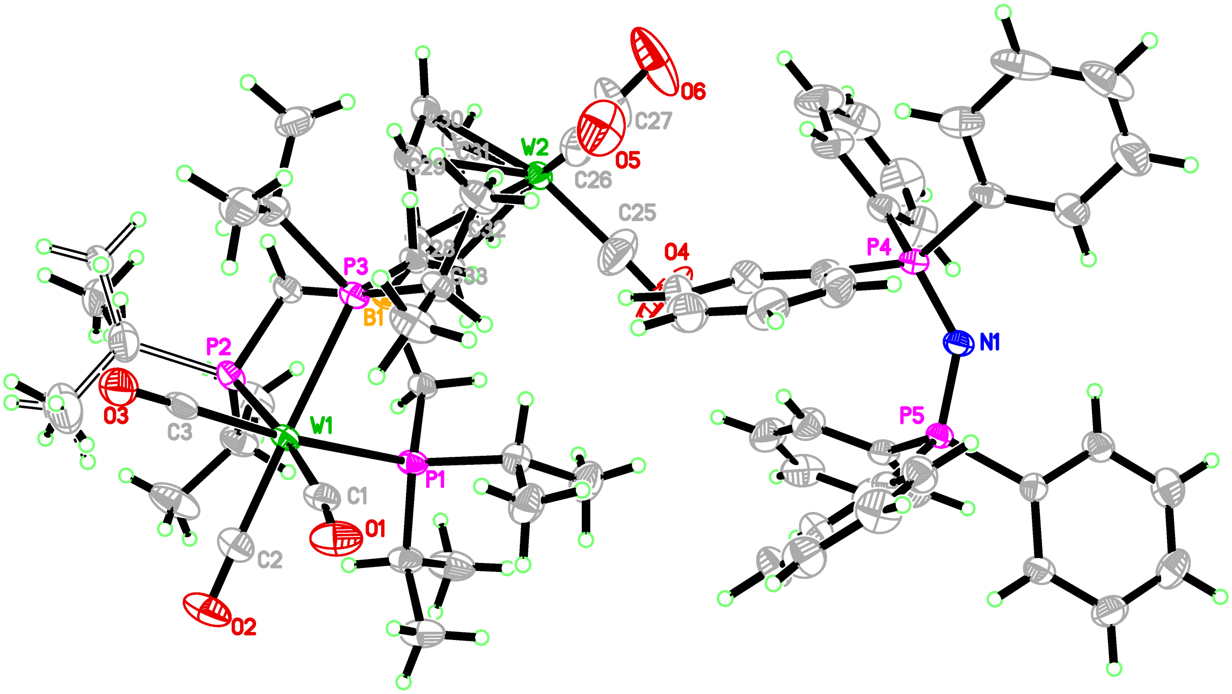
REFERENCE NUMBER: 16176z

CRYSTAL STRUCTURE REPORT

$C_{69} H_{83} B N O_6 P_5 W_2$
Or
$[C_{36}H_{30}NP_2]^+[C_{33}H_{53}BO_6P_3W_2]^-$

Report prepared for:
Prof. P. Fischer / Macalester University

August 24, 2016



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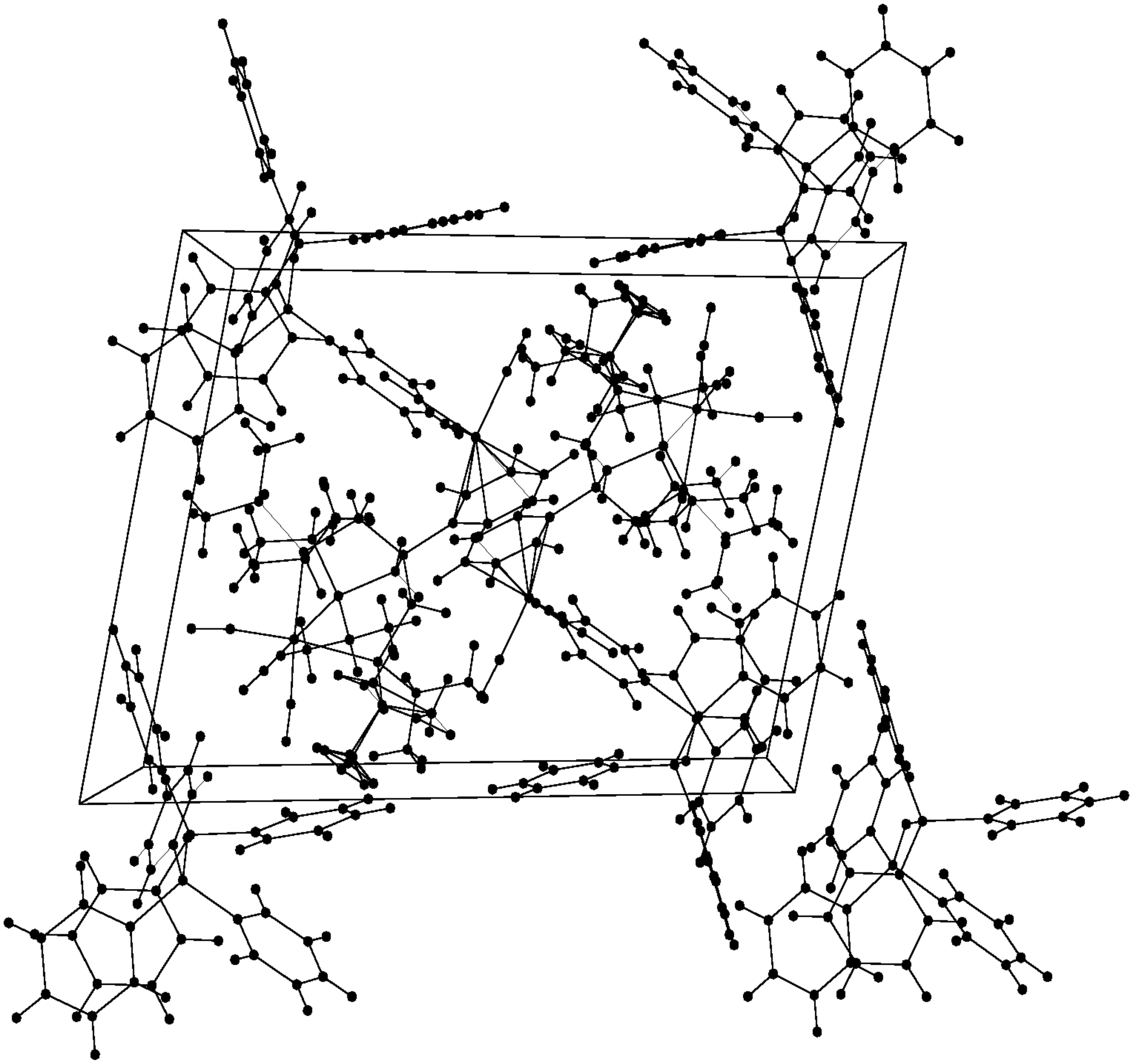

Data collection

A crystal (approximate dimensions 0.400 x 0.270 x 0.120 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX-II CCD diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 342 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 6.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 9925 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXS-97 (Sheldrick, 2008)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0220$ and $wR2 = 0.0522$ (F^2, all data).

Structure description

The structure is the one suggested. The isopropyl group with atoms C15/C16/C17 is disordered over two positions. Appropriate restraints and constraints were applied to these atoms for refinement.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

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[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2012).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table S9. Crystal data and structure refinement for 16176z.

Identification code	16176z	
Empirical formula	$C_{69} H_{83} B N O_6 P_5 W_2$	
Formula weight	1555.72	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.0622(17) Å	α = 100.618(2)°
	b = 14.568(2) Å	β = 100.221(2)°
	c = 19.949(3) Å	γ = 95.626(2)°
Volume	3359.5(8) $Å^3$	
Z	2	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	3.591 mm^{-1}	
$F(000)$	1560	
Crystal color, morphology	Yellow, Block	
Crystal size	0.400 x 0.270 x 0.120 mm^3	
Theta range for data collection	1.435 to 27.526°	
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-25 \leq l \leq 25$	
Reflections collected	39611	
Independent reflections	15278 [R(int) = 0.0224]	
Observed reflections	13196	
Completeness to theta = 25.242°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7456 and 0.5287	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15278 / 130 / 784	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	$R1$ = 0.0220, $wR2$ = 0.0493	
R indices (all data)	$R1$ = 0.0285, $wR2$ = 0.0522	
Largest diff. peak and hole	0.988 and -0.856 e.$Å^{-3}$	

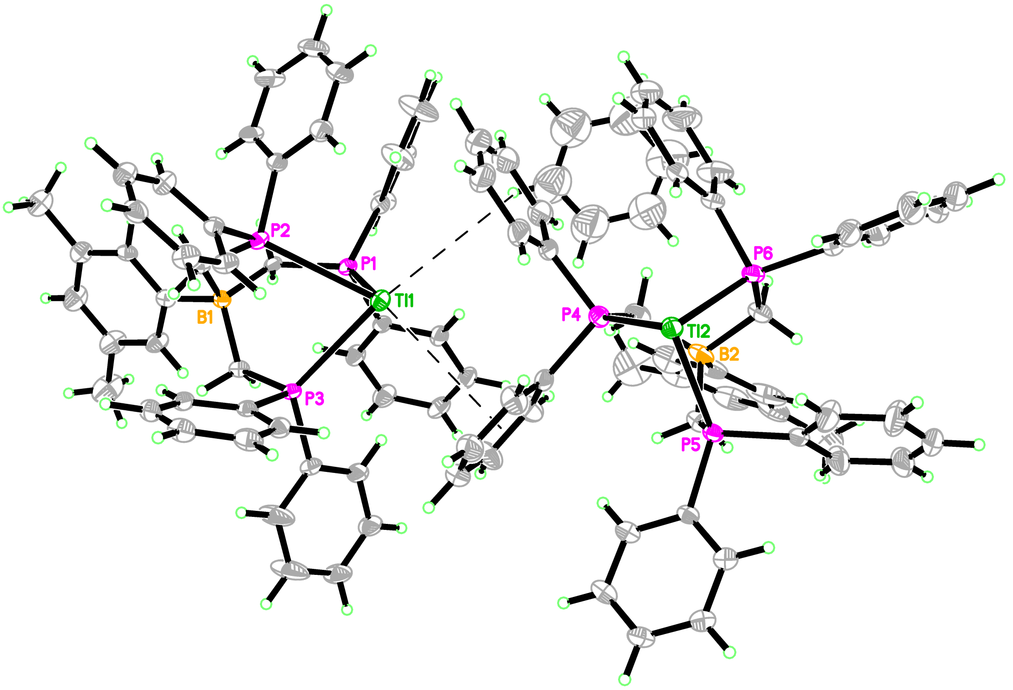
REFERENCE NUMBER: 17144z

CRYSTAL STRUCTURE REPORT

$C_{100} H_{96} B_2 P_6 Tl_2$
Or
$2(C_{47}H_{45}BP_3Tl), C_6H_6$

Report prepared for:
Prof. P. Fischer / McCalester Univ.

September 25, 2017



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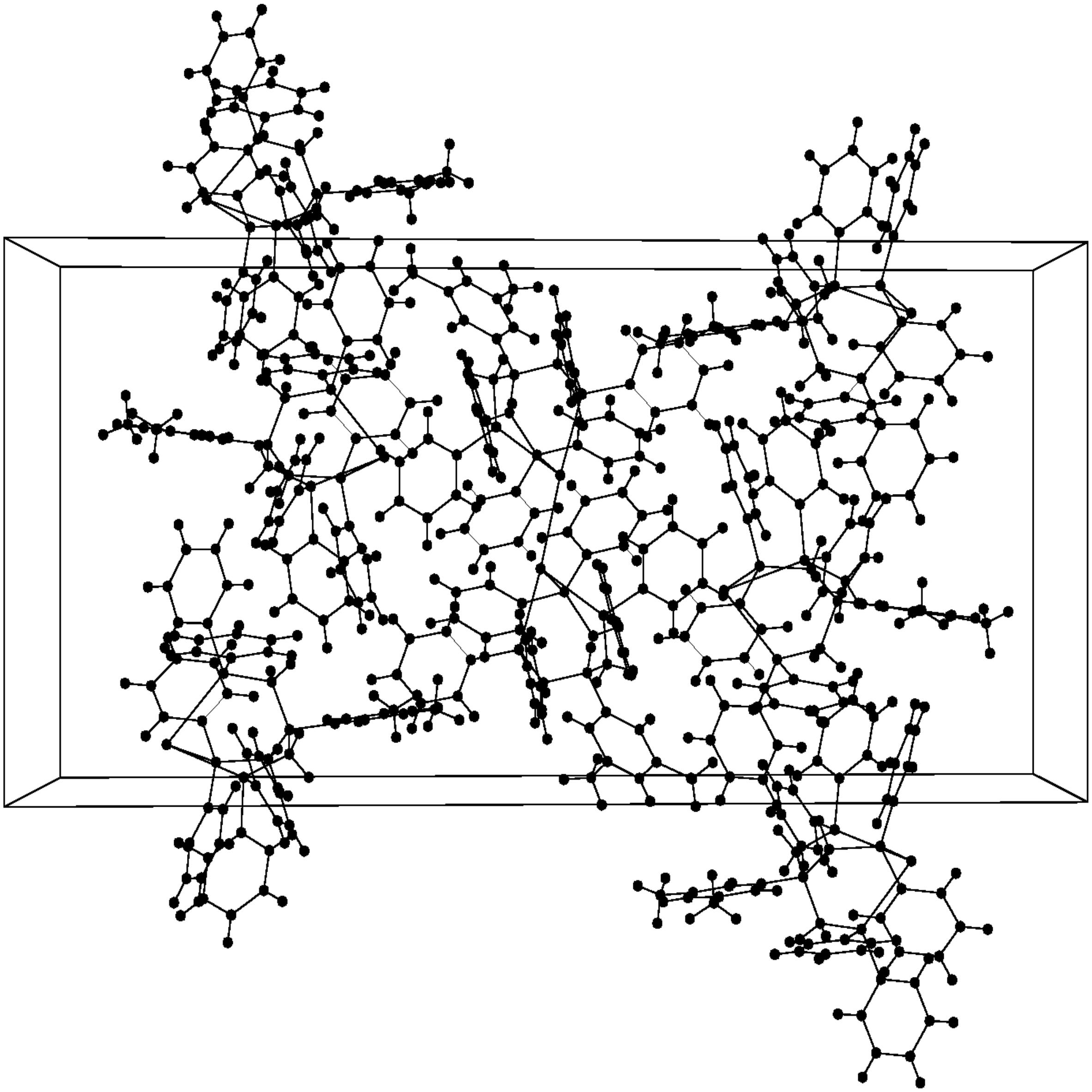

Data collection

A crystal (approximate dimensions 0.200 x 0.090 x 0.060 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker VENTURE PHOTON-II diffractometer for a data collection at 100(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 1786 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.78 Å. All major sections of frames were collected with 0.80° steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2737 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group $P2_1/c$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0470$ and $wR2 = 0.0917$ (F^2, obs. data).

Structure description

The structure is the one suggested. The individual formula units are arranged as thus. Two Tl complexes have a non-bonded contact 3.534Å through symmetry equivalents of Tl2. Tl1 has two π-interactions with phenyl rings from the Tl1 molecule. These Tl complexes have different environments. Finally, there is ½ molecule of benzene per asymmetric unit.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

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[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{\text{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table S10. Crystal data and structure refinement for 17144z.

Identification code	17144z	
Empirical formula	$C_{100}H_{96}B_2P_6Tl_2$	
Formula weight	1913.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.1041(18) Å	α = 90°
	b = 18.327(3) Å	β = 92.754(4)°
	c = 38.204(5) Å	γ = 90°
Volume	8465(2) $Å^3$	
Z	4	
Density (calculated)	1.502 Mg/m^3	
Absorption coefficient	3.964 mm^{-1}	
$F(000)$	3832	
Crystal color, morphology	Colorless, Needle	
Crystal size	0.200 x 0.090 x 0.060 mm^3	
Theta range for data collection	2.245 to 27.103°	
Index ranges	$-9 \leq h \leq 15$, $-23 \leq k \leq 19$, $-48 \leq l \leq 48$	
Reflections collected	51299	
Independent reflections	18619 [R(int) = 0.0324]	
Observed reflections	16716	
Completeness to theta = 25.242°	99.6%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7471 and 0.5949	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18619 / 936 / 995	
Goodness-of-fit on F^2	1.257	
Final R indices [I>2sigma(I)]	$R1$ = 0.0470, $wR2$ = 0.0917	
R indices (all data)	$R1$ = 0.0543, $wR2$ = 0.0937	
Largest diff. peak and hole	2.828 and -1.872 e.$Å^{-3}$	

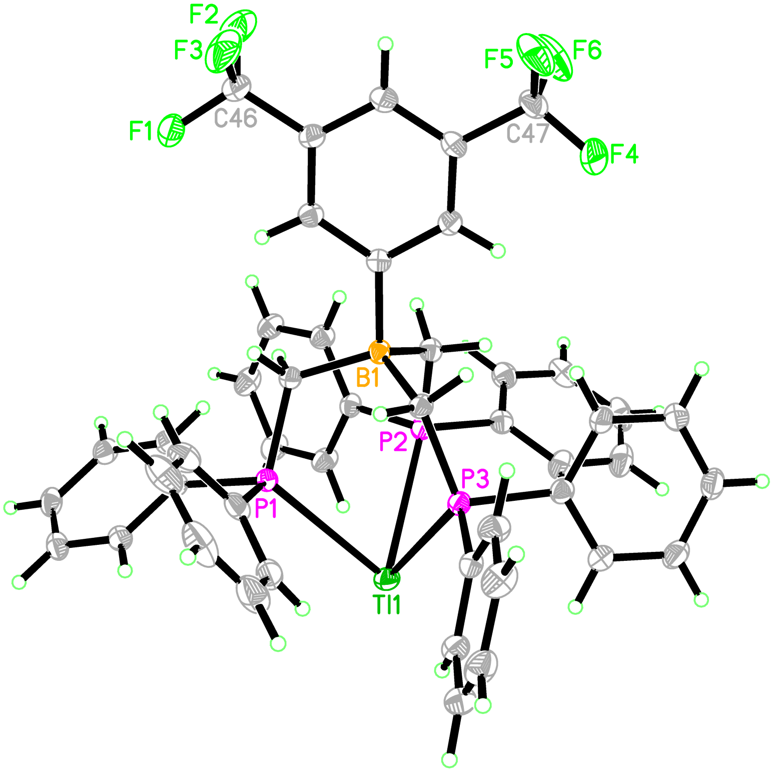
REFERENCE NUMBER: 17163z

CRYSTAL STRUCTURE REPORT

$C_{47}H_{39}BF_6P_3Tl$

Report prepared for:
Prof. P. Fischer / Macalester College

September 25, 2017



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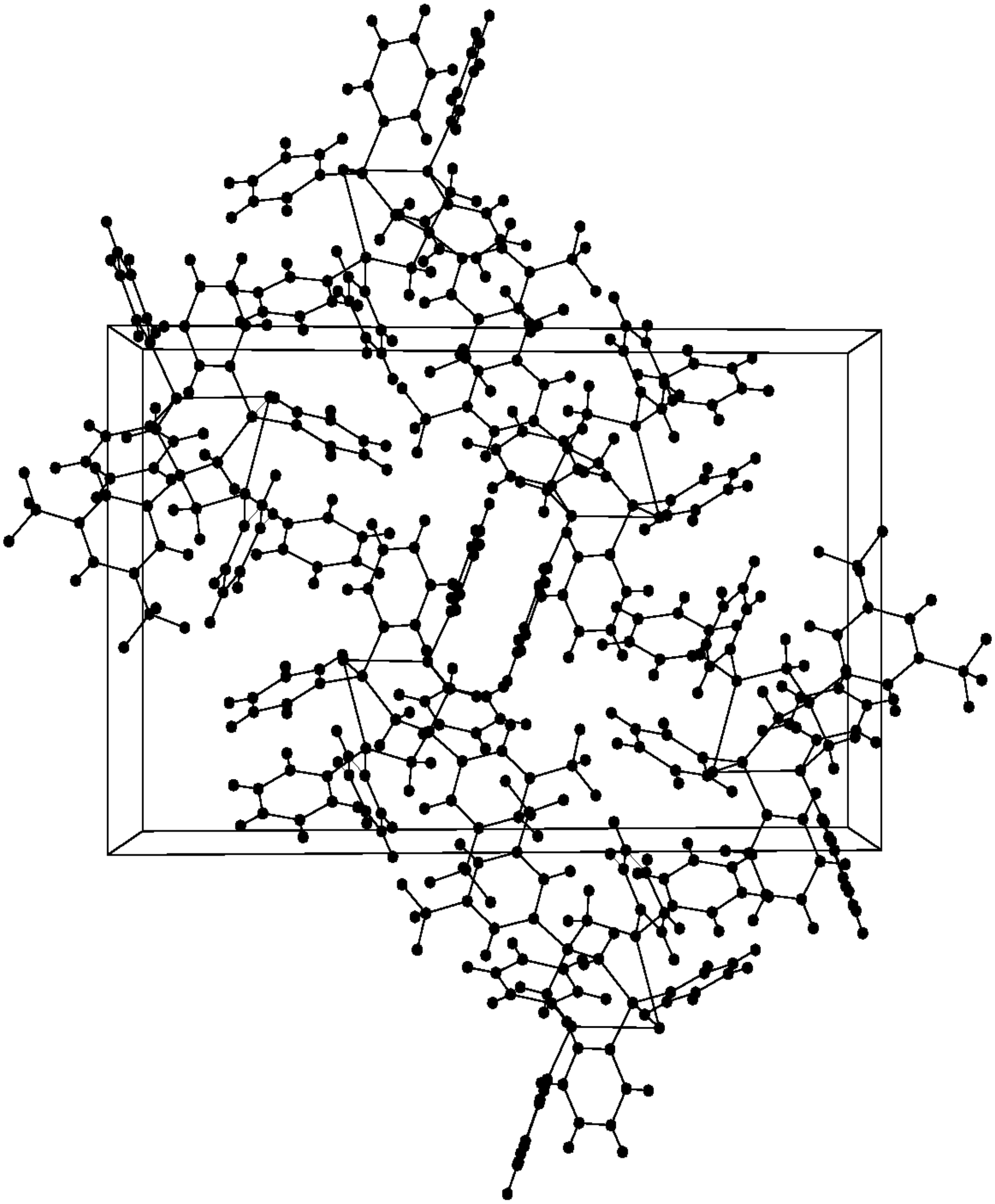

Data collection

A crystal (approximate dimensions 0.180 x 0.110 x 0.080 mm^3) was placed onto the tip of a 0.1 mm diameter Mitegen loop and mounted on a Bruker VENTURE PHOTON-II diffractometer for a data collection at 100(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 595 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 8 seconds and a detector distance of 4.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.65 Å. All major sections of frames were collected with 1.20° steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2965 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXL-2014/5 (Sheldrick, 2014)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group $P2_1/n$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0290$ and $wR2 = 0.0566$ (F^2, obs. data).

Structure description

The structure is the one suggested.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

Some equations of interest:

$$R_{\text{int}} = \Sigma\ |F_o^2 - < F_o^2 >| / \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma\ [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q / [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$$

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[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Table S11. Crystal data and structure refinement for 17163z.

Identification code	17163z	
Empirical formula	$C_{47}H_{39}BF_6P_3Tl$	
Formula weight	1025.87	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.1861(4) Å	α = 90°
	b = 15.8699(9) Å	β = 94.474(2)°
	c = 25.4574(11) Å	γ = 90°
Volume	4102.7(3) $Å^3$	
Z	4	
Density (calculated)	1.661 Mg/m^3	
Absorption coefficient	4.115 mm^{-1}	
$F(000)$	2024	
Crystal color, morphology	block, yellow	
Crystal size	0.180 x 0.110 x 0.080 mm^3	
Theta range for data collection	2.381 to 33.185°	
Index ranges	$-15 \leq h \leq 15$, $-19 \leq k \leq 24$, $-39 \leq l \leq 26$	
Reflections collected	37688	
Independent reflections	15439 [R(int) = 0.0284]	
Observed reflections	12246	
Completeness to theta = 25.242°	99.4%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.1044 and 0.0620	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15439 / 0 / 523	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	$R1$ = 0.0290, $wR2$ = 0.0566	
R indices (all data)	$R1$ = 0.0448, $wR2$ = 0.0609	
Largest diff. peak and hole	1.216 and -1.242 e.$Å^{-3}$	

REFERENCE NUMBER: 17164z

CRYSTAL STRUCTURE REPORT

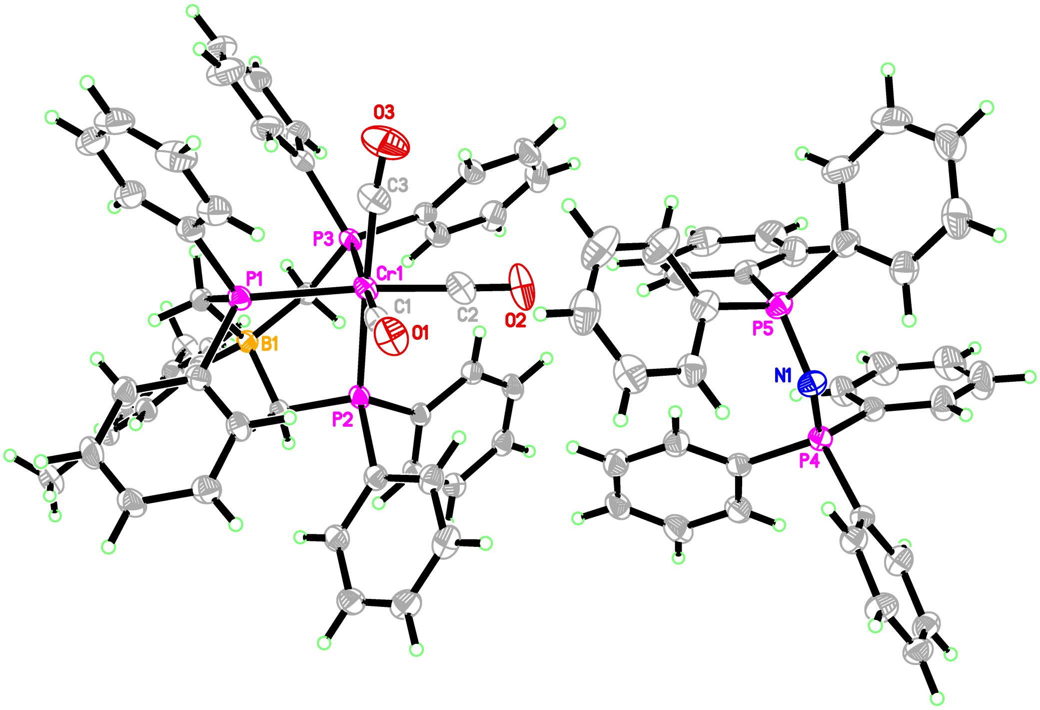
$C_{92.50}H_{90.08}BCrNO_4P_5$

or

$[C_{36}H_{30}NP_2]\ [C_{50}H_{45}BCrO_3P_3] \cdot 0.5(C_5H_{12}) \cdot 0.54(C_4H_{10}O) \cdot 0.46(C_4H_8O)$

Report prepared for:
Prof. P. Fischer / Macalester College

September 26, 2017



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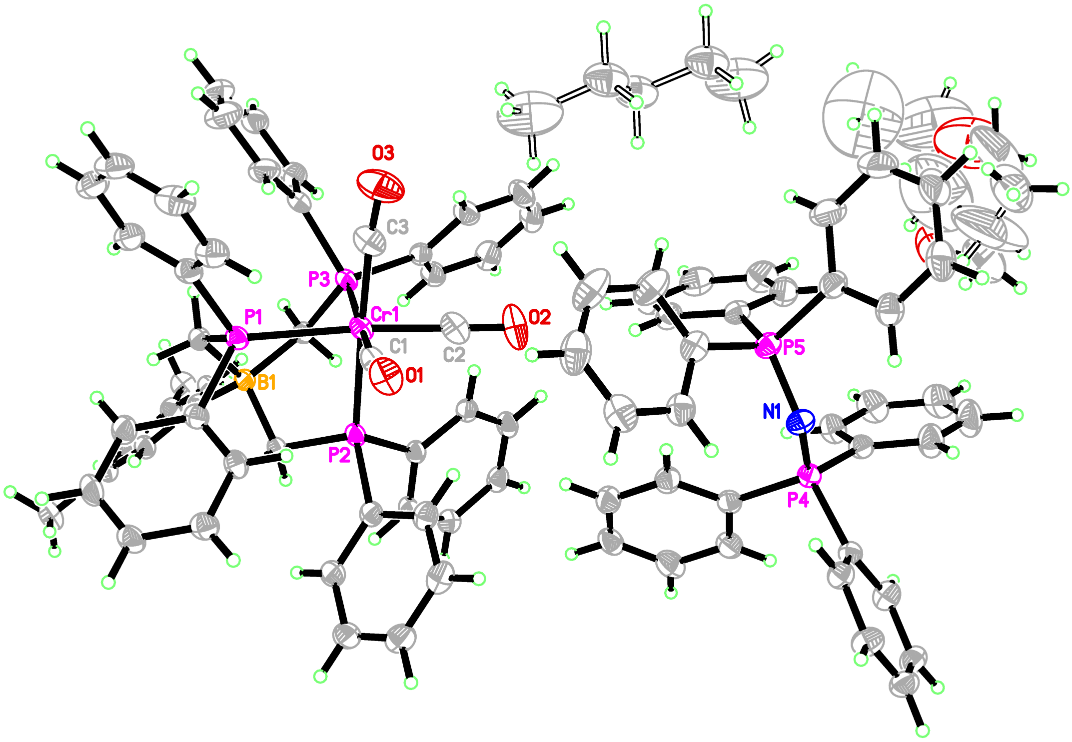
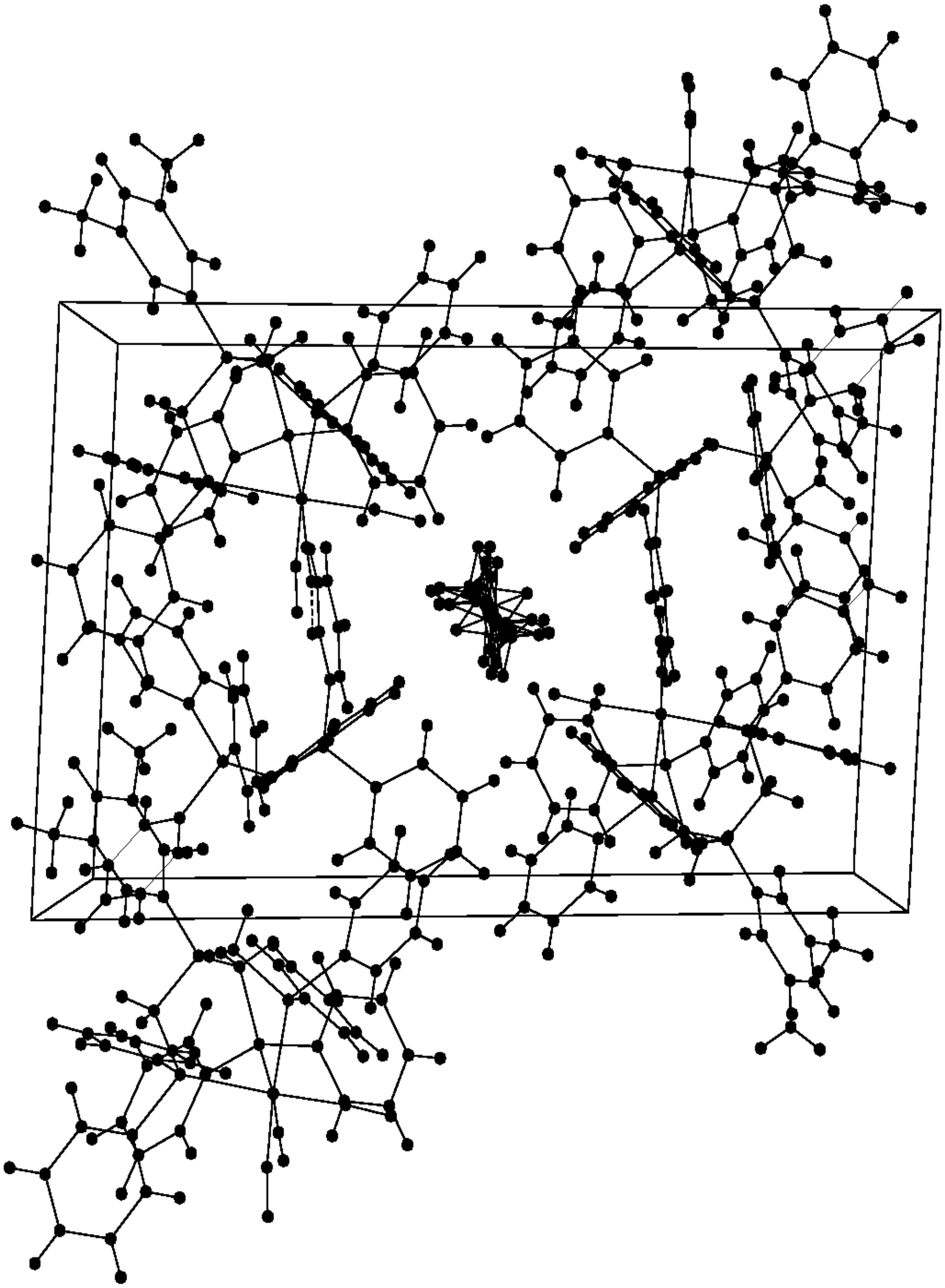

O3
C3
P3
Cr1
P1
O2
C1
C2
B1
O1
P2
P5
N1
P4



Data collection

A crystal (approximate dimensions 0.140 x 0.100 x 0.020 mm^3) was placed onto the tip of a 0.1 mm diameter Mitegen loop and mounted on a Bruker AVENTURE PHOTON-II diffractometer for a data collection at 100(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 227 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 30 seconds and a detector distance of 4.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.80 Å. All major sections of frames were collected with 1.20° steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2895 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0536$ and $wR2 = 0.1168$ (F^2, obs. data).

Structure description

The structure is the one suggested. There is one *n*-pentane located on an inversion center and compositional disorder of a THF and diethylether in a 0.46:0.54 ratio on a general site. These solvents could be refined with restraints to a sensible result.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

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[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

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Some equations of interest:

$$R_{\text{int}} = \Sigma\,|F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, \Sigma\,[w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2(F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table S12. Crystal data and structure refinement for 17164z.

Identification code	17164z	
Empirical formula	$C_{92.50}H_{90.08}BCrNO_4P_5$	
Formula weight	1497.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	*a* = 13.241(3) Å	α = 92.848(8)°
	b = 13.693(3) Å	β = 96.030(7)°
	c = 21.408(4) Å	γ = 92.184(8)°
Volume	3851.3(13) $Å^3$	
Z	2	
Density (calculated)	1.291 Mg/m^3	
Absorption coefficient	0.307 mm^{-1}	
F(000)	1576	
Crystal color, morphology	yellow, plate	
Crystal size	0.140 x 0.100 x 0.020 mm^3	
Theta range for data collection	2.295 to 26.372°	
Index ranges	$-16 \le h \le 16$, $-17 \le k \le 17$, $-26 \le l \le 26$	
Reflections collected	75317	
Independent reflections	15712 [*R*(int) = 0.0650]	
Observed reflections	12257	
Completeness to theta = 25.242°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7457 and 0.5579	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15712 / 61 / 995	
Goodness-of-fit on F^2	1.088	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0536, *wR*2 = 0.1168	
R indices (all data)	*R*1 = 0.0750, *wR*2 = 0.1287	
Extinction coefficient	0.0069(4)	
Largest diff. peak and hole	0.690 and -0.609 e.$Å^{-3}$	

REFERENCE NUMBER: 17174

CRYSTAL STRUCTURE REPORT

C92.50 H89.90 B Mo N O4 P5

Report prepared for: Paul Fischer
July 31, 2017

James T. Moore
X-Ray Crystallographic Laboratory
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207 Pleasant St. S.E.
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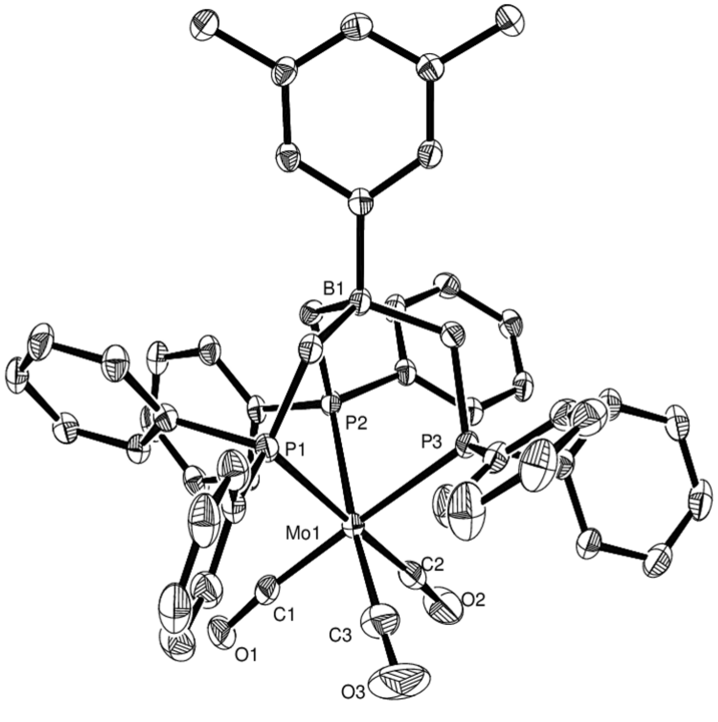

Data collection

A crystal (approximate dimensions 0.140 x 0.100 x 0.020 mm was placed onto the tip of a 0.150 mm MiTeGen loop and mounted on a Bruker PHOTON-II CMOS diffractometer for a data collection at 100(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from two sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 424 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.78 Å. Four major sections of frames were collected with 1.0° steps in ω at four different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay.[2] Final cell constants were calculated from the xyz centroids of 9378 strong reflections from the actual data collection after integration.[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT 2014/5 (Sheldrick, 2014)[4] and refined using SHELXL-2016/6 (Sheldrick, 2016).[5] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0510$ and $wR2 = 0.1154$ (F^2, all data).

Structure description

The structure is the one suggested. The packing in the unit cell is identical to that of the W derivative. In the structure, one molecule of pentane appears to be disordered over the inversion center. This solvent was modelled using the Shelx PART -1 instruction with 50% occupancy over both sides of the inversion center. The EADP constraint was used to make the anisotropic displacement parameters equal for the atoms related by the inversion symmetry.

The other solvent appears to suffer from substitutional disorder between diethyl ether and tetrahydrofuran. The total occupancy for the solvent was constrained to one. In this model, the anisotropic displacement parameters for both solvents were restrained using the RIGU instruction. Additionally, the atoms overlapping in space were treated with the EADP constraint. The final refinement yielded a 0.55:0.45 ratio of tetrahydrofuran to diethyl ether in the unit cell.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

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[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2004).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2004).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2004).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

[5] SHELXL 2016/6; G. M. Sheldrick, *Acta Cryst.* **C71**, 3-8 (2015).

Some equations of interest:

$$R_{\text{int}} = \Sigma \, |F_o^2 - \langle F_o^2 \rangle| \, / \, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \, / \, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \, / \, [\sigma^2 (F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \, / \, (n-p)]^{1/2}$$

Table S13. Crystal data and structure refinement for 17174.

Identification code	17174	
Empirical formula	C92.50 H89.90 B Mo N O4 P5	
Formula weight	1541.15	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.2924(6) Å	α = 93.002(2)°
	b = 13.7468(6) Å	β = 96.659(2)°
	c = 21.6431(10) Å	γ = 92.057(2)°
Volume	3919.2(3) Å^3	
Z	2	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.323 mm^{-1}	
F(000)	1612	
Crystal color, morphology	colourless, Plate	
Crystal size	0.140 x 0.100 x 0.020 mm^3	
Theta range for data collection	2.187 to 27.103°	
Index ranges	$-13 \leq h \leq 17$, $-17 \leq k \leq 17$, $-27 \leq l \leq 27$	
Reflections collected	43977	
Independent reflections	17203 [R(int) = 0.0507]	
Observed reflections	11938	
Completeness to theta = 25.242°	99.5%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17203 / 51 / 970	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	$R1$ = 0.0510, $wR2$ = 0.1026	
R indices (all data)	$R1$ = 0.0891, $wR2$ = 0.1154	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.726 and -0.563 e.Å^{-3}	

REFERENCE NUMBER: 17175

CRYSTAL STRUCTURE REPORT

$C_{92.50} H_{89.89} B N O_4 P_5 W$

Report prepared for: Paul Fischer
July 31, 2017

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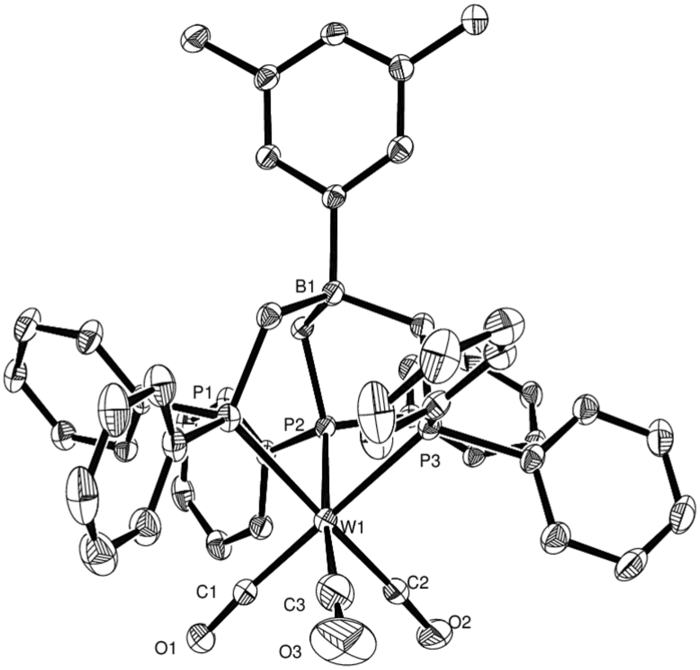
207 Pleasant St. S.E.
Minneapolis, MN 55455



Data collection

A crystal (approximate dimensions 0.130 x 0.080 x 0.010 mm was placed onto the tip of a 0.150 mm MiTeGen loop and mounted on a Bruker PHOTON-II CMOS diffractometer for a data collection at 100(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from two sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 257 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 45 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.71 Å. Five major sections of frames were collected with 1.0° steps in ω at four different ϕ settings and a detector position of -15.7° in 2θ. The intensity data were corrected for absorption and decay.[2] Final cell constants were calculated from the xyz centroids of 9049 strong reflections from the actual data collection after integration.[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT 2014/5 (Sheldrick, 2014)[4] and refined using SHELXL-2016/6 (Sheldrick, 2016).[5] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0496$ and $wR2 = 0.0962$ (F^2, all data).

Structure description

The structure is the one suggested. The packing in the unit cell is identical to that of the Mo derivative. In the structure, one molecule of pentane appears to be disordered over the inversion center. This solvent was modelled using the Shelx PART -1 instruction with 50% occupancy over both sides of the inversion center. The EADP constraint was used to make the anisotropic displacement parameters equal for the atoms related by the inversion symmetry.

The other solvent appears to suffer from substitutional disorder between diethyl ether and tetrahydrofuran. The total occupancy for the solvent was constrained to one. In this model, the anisotropic displacement parameters for both solvents were restrained using the RIGU instruction. Additionally, the atoms overlapping in space were treated with the EADP constraint. The final refinement yielded a 0.56:0.44 ratio of tetrahydrofuran to diethyl ether in the unit cell.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

---

[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2004).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2004).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2004).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

[5] SHELXL 2016/6; G. M. Sheldrick, *Acta Cryst.* **C71**, 3-8 (2015).

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\mathrm{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table S14. Crystal data and structure refinement for 17175.

Identification code	17175	
Empirical formula	C92.50 H89.89 B N O4 P5 W	
Formula weight	1629.05	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	*a* = 13.2825(6) Å	α = 93.123(2)°
	b = 13.7240(6) Å	β = 96.668(2)°
	c = 21.6196(11) Å	γ = 91.892(2)°
Volume	3905.5(3) $Å^3$	
Z	2	
Density (calculated)	1.385 Mg/m^3	
Absorption coefficient	1.635 mm^{-1}	
F(000)	1676	
Crystal color, morphology	colourless, plate	
Crystal size	0.130 x 0.080 x 0.010 mm^3	
Theta range for data collection	2.267 to 30.034°	
Index ranges	$-18 \le h \le 18$, $-16 \le k \le 19$, $-30 \le l \le 30$	
Reflections collected	81140	
Independent reflections	22801 [*R*(int) = 0.0601]	
Observed reflections	17648	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22801 / 51 / 974	
Goodness-of-fit on F^2	1.067	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0496, *wR*2 = 0.0884	
R indices (all data)	*R*1 = 0.0768, *wR*2 = 0.0962	
Largest diff. peak and hole	3.135 and -1.759 e.$Å^{-3}$	

REFERENCE NUMBER: 17173

CRYSTAL STRUCTURE REPORT

C94 H86.43 B Cr F6 N O5 P5

Report prepared for: Paul Fischer
August 1, 2017

James T. Moore
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Department of Chemistry
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207 Pleasant St. S.E.
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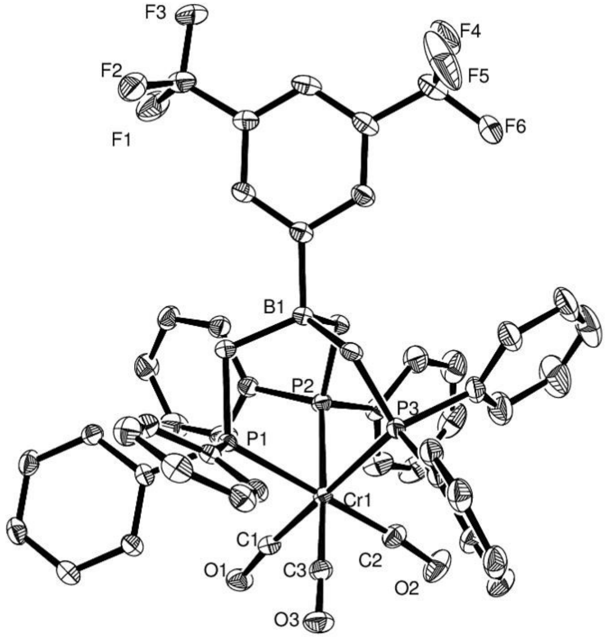

Data collection

A crystal (approximate dimensions 0.244 x 0.090 x 0.088 mm was placed onto the tip of a 0.15 mm MiTeGen loop and mounted on a Bruker PHOTON-II CMOS diffractometer for a data collection at 100(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from two sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 699 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.70 Å. Six major sections of frames were collected with 1.0° steps in ω at six different ϕ settings and a detector position of 15.7° in 2θ. The intensity data were corrected for absorption and decay.[2] Final cell constants were calculated from the xyz centroids of 9912 strong reflections from the actual data collection after integration.[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT 2014/5 (Sheldrick, 2014)[4] and refined using SHELXL-2016/6 (Sheldrick, 2016).[5] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. One -CF_3 group in the anion appears to be rotationally disordered. The fluorine atoms were split over two positions, and the total occupancy of each fluorine atom was constrained to 1. The anisotropic displacement parameters for the disordered fluorine atoms were also constrained using the EADP instruction. One solvent appears to suffer from substitutional disorder between diethyl ether and tetrahydrofuran. The total occupancy for the solvent was constrained to one, and the anisotropic displacement parameters for the ellipsoids occupying the same space were constrained using the EADP instruction. The final refinement yielded a 0.71:0.29 ratio of diethyl ether to tetrahydrofuran. In addition, another tetrahydrofuran molecule was heavily disordered. The molecule was split over three positions, and the total occupancy for the three molecules was set to 1 using the SUMP restraint. Once again, the anisotropic displacement parameters for the atoms occupying the same space were made equal using the EADP constraint. Eleven reflections below θ_{min} were not observed in the experiment. These low-resolution reflections were most likely hidden behind the beamstop. The final full matrix least squares refinement converged to

$R1 = 0.0504$ and $wR2 = 0.1298$ (F^2, all data).

Structure description

The structure is the one suggested. Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

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[1] APEX2, Bruker Analytical X-ray Systems, Madison, WI (2004).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2004).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2004).

[4] SHELXTL 2008, Bruker Analytical X-Ray Systems, Madison, WI (2008); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

[5] SHELXL 2016/6; G. M. Sheldrick, *Acta Cryst.* **C71**, 3-8 (2015).

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2(F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

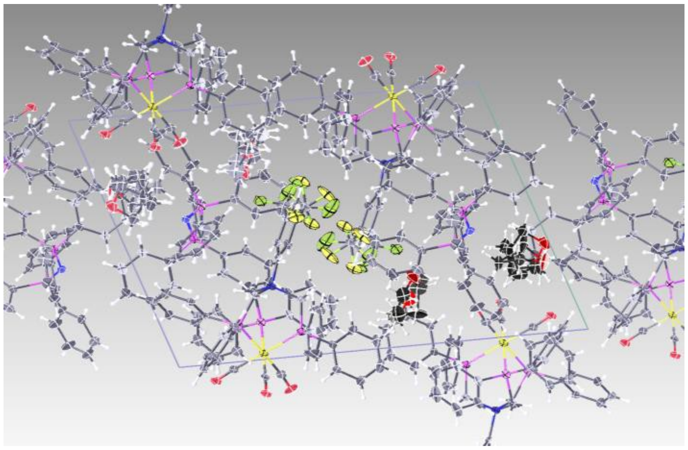


Figure 1. Packing diagram of 17173, viewed along the a-axis.

Table S15. Crystal data and structure refinement for 17173.

Identification code	17173	
Empirical formula	$C_{94}H_{86.43}BCrF_6NO_5P_5$	
Formula weight	1641.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.8112(5) Å	α = 71.3030(10)°
	b = 14.6992(5) Å	β = 80.2710(10)°
	c = 21.4270(8) Å	γ = 80.1950(10)°
Volume	4029.6(3) $Å^3$	
Z	2	
Density (calculated)	1.353 Mg/m^3	
Absorption coefficient	0.311 mm^{-1}	
$F(000)$	1711	
Crystal color, morphology	yellow, block	
Crystal size	0.244 x 0.090 x 0.088 mm^3	
Theta range for data collection	2.236 to 30.546°	
Index ranges	$-19 \le h \le 19$, $-20 \le k \le 20$, $-30 \le l \le 30$	
Reflections collected	108170	
Independent reflections	24636 [R(int) = 0.0485]	
Observed reflections	18534	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	24636 / 1 / 1121	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	$R1$ = 0.0504, $wR2$ = 0.1154	
R indices (all data)	$R1$ = 0.0754, $wR2$ = 0.1298	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.823 and -0.566 e.$Å^{-3}$	

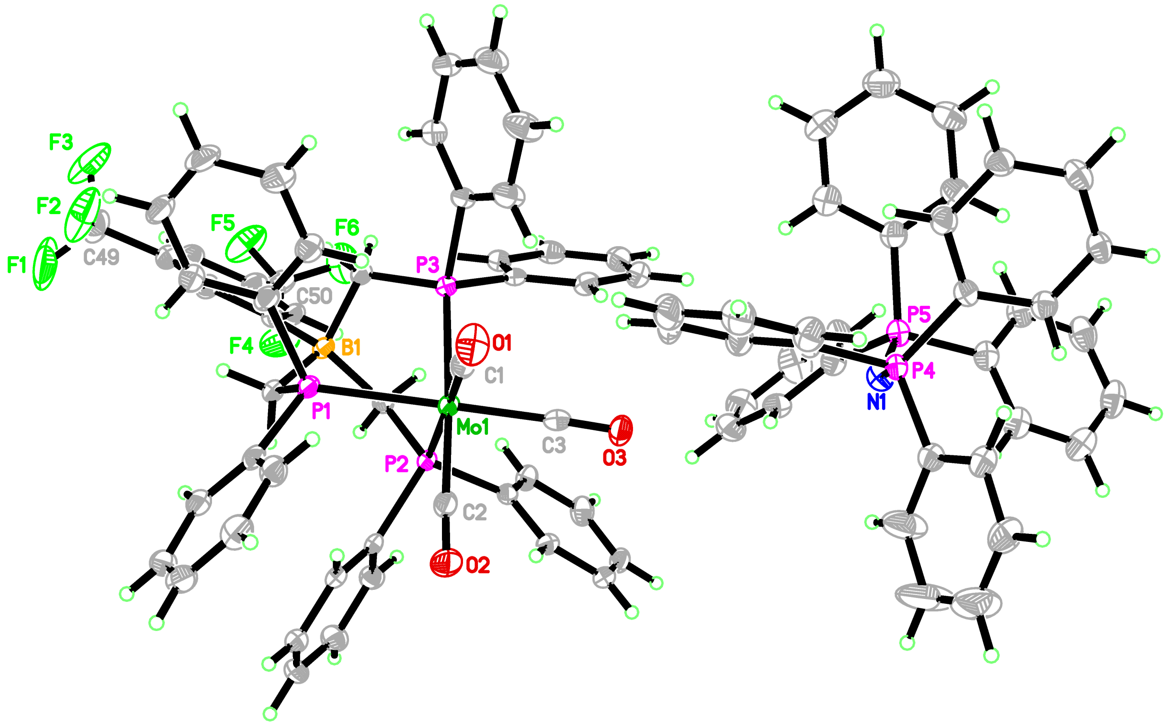
REFERENCE NUMBER: 17157zz

CRYSTAL STRUCTURE REPORT

$C_{86}H_{69}BF_6MoNO_3P_5$

Report prepared for:
Prof. P. Fischer / Macalester College

September 25, 2017



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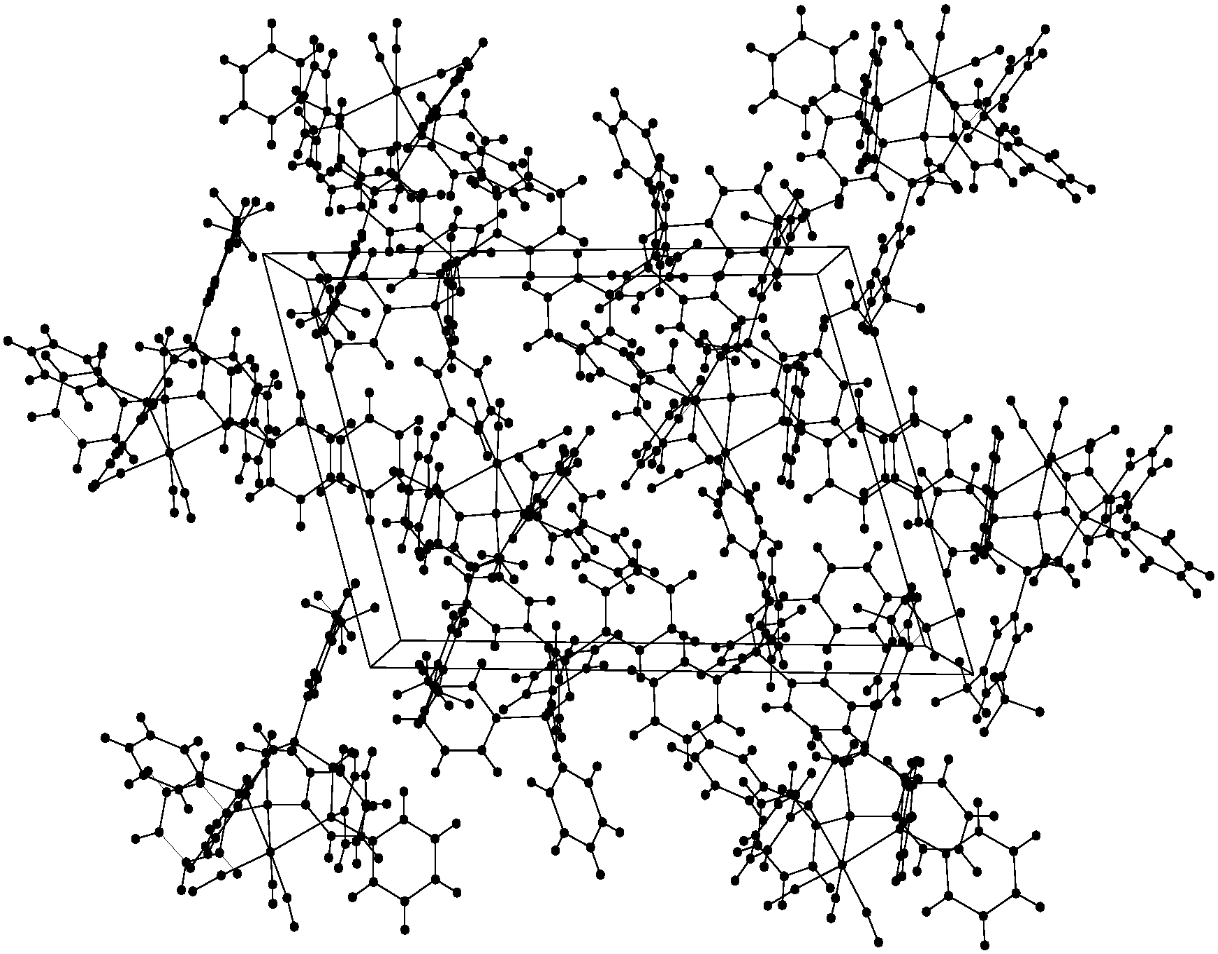

Data collection

A crystal (approximate dimensions 0.140 x 0.080 x 0.050 mm[3]) was placed onto the tip of a 0.1 mm diameter Mitegen loop and mounted on a Bruker VENTURE PHOTON-II diffractometer for a data collection at 100(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 240 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 45 seconds and a detector distance of 4.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.80 Å. All major sections of frames were collected with 1.20° steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2954 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0399$ and $wR2 = 0.0894$ (F^2, obs. data).

Structure description

The structure is the one suggested. The structure contains void regions that contain some mixer of diethylether and THF solvent as analyzed by Platon/Squeeze.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

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[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{\mathrm{int}} = \Sigma\, |F_o^2 - \langle F_o^2 \rangle| \,/\, \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\mathrm{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table S16. Crystal data and structure refinement for 17157zz.

Identification code	17157zz	
Empirical formula	$C_{86} H_{69} B F_6 Mo N O_3 P_5$	
Formula weight	1540.02	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.7990(13) Å	α = 72.406(4)°
	b = 14.3427(15) Å	β = 81.517(4)°
	c = 21.051(2) Å	γ = 81.554(4)°
Volume	3904.8(7) Å^3	
Z	2	
Density (calculated)	1.310 Mg/m^3	
Absorption coefficient	0.334 mm^{-1}	
F(000)	1584	
Crystal color, morphology	Colourless, Block	
Crystal size	0.140 x 0.080 x 0.050 mm^3	
Theta range for data collection	2.159 to 26.419°	
Index ranges	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-26 \leq l \leq 26$	
Reflections collected	71923	
Independent reflections	16015 [R(int) = 0.0424]	
Observed reflections	12798	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6685	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16015 / 882 / 928	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.0894	
R indices (all data)	R1 = 0.0553, wR2 = 0.0947	
Largest diff. peak and hole	1.393 and -0.895 e.Å^{-3}	

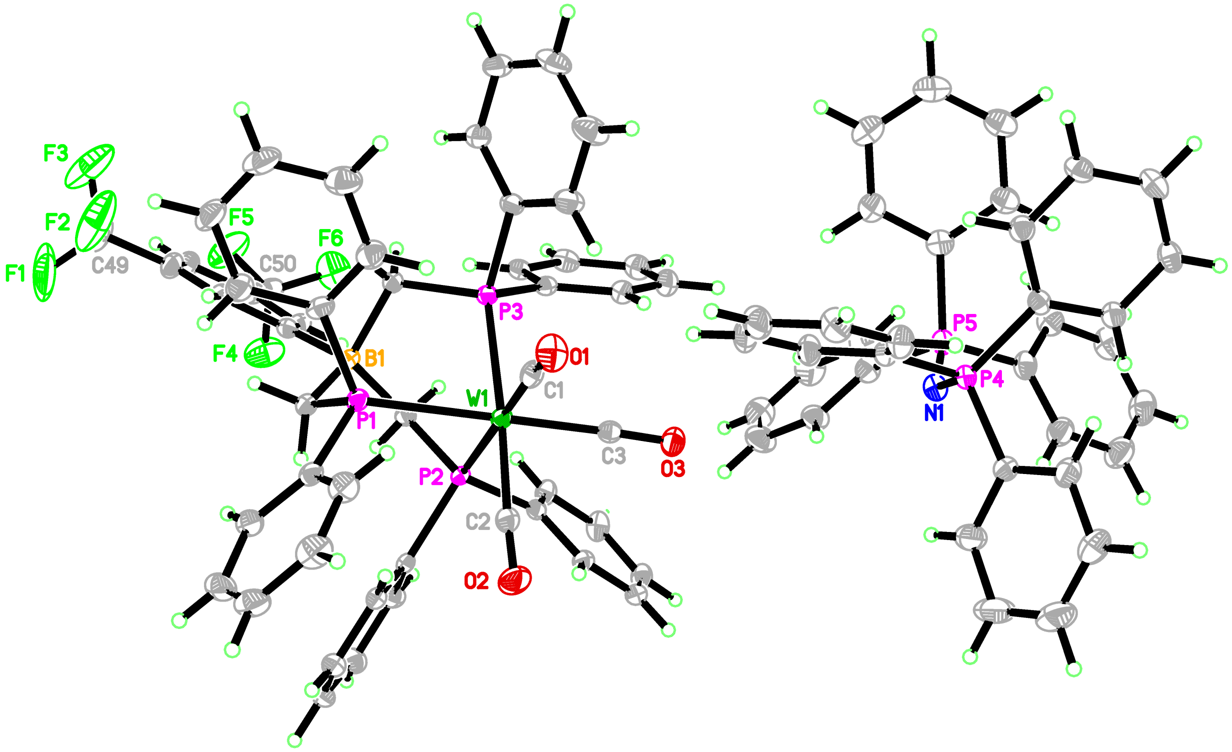
REFERENCE NUMBER: 17158z

CRYSTAL STRUCTURE REPORT

$C_{86}H_{69}BF_6NO_3P_5W$

Report prepared for:
Prof. P. Fischer / McCalester Univ.

September 25, 2017



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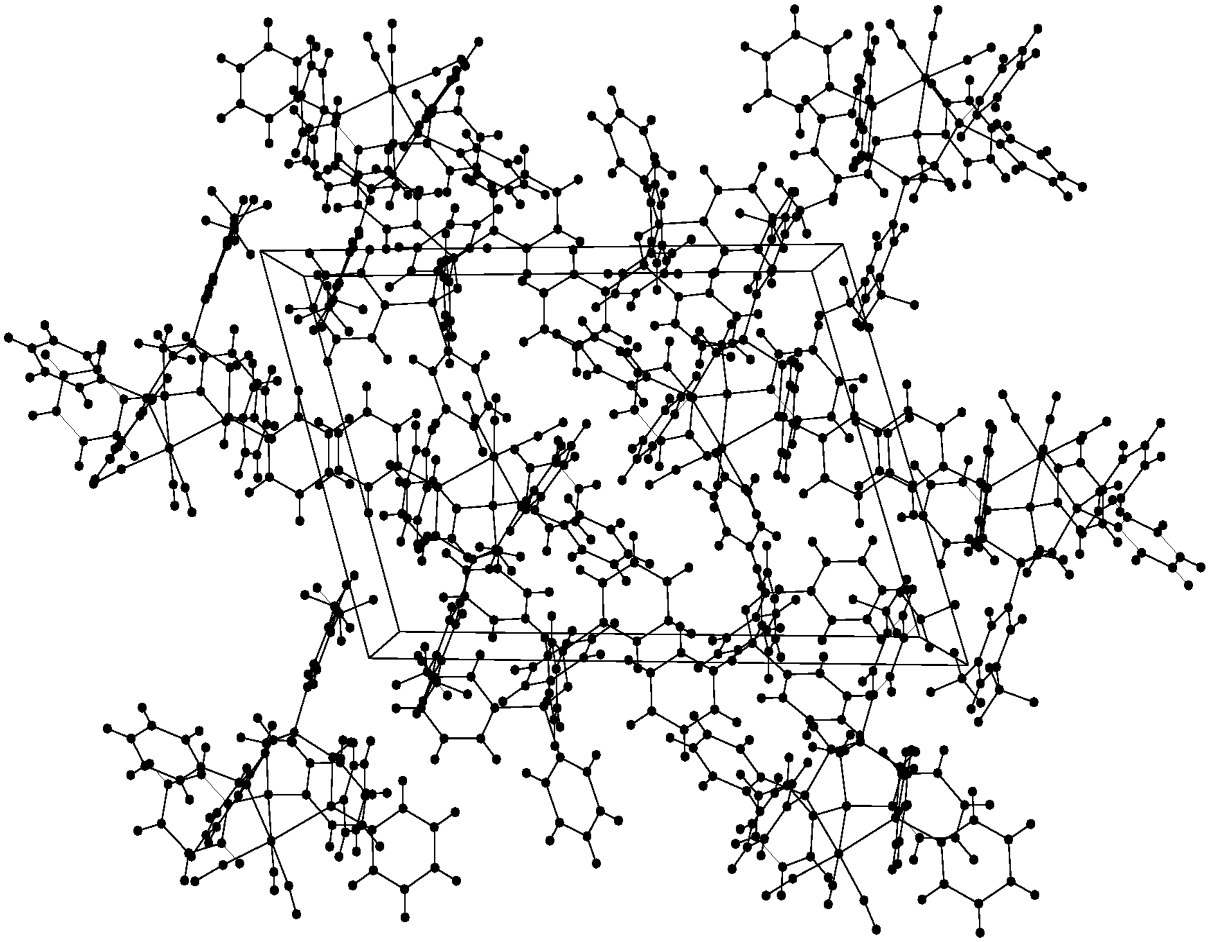

Data collection

A crystal (approximate dimensions 0.140 x 0.080 x 0.050 mm^3) was placed onto the tip of a 0.1 mm diameter Mitegen loop and mounted on a Bruker VENTURE PHOTON-II diffractometer for a data collection at 100(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 509 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 20 seconds and a detector distance of 4.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2872 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2014/5 (Sheldrick, 2014)[4] and refined using SHELXL-2014/6 (Sheldrick, 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0360$ and $wR2 = 0.0737$ (F^2, obs. data).

Structure description

The structure is the one suggested. The structure contains void regions that contain some mixer of diethylether and THF solvent as analyzed by Platon/Squeeze.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

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[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

[7] A. L. Spek, *Acta. Cryst.* **D65**, 148-155 (2009). PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.

Some equations of interest:

$$R_{\text{int}} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^{\,2}|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^{\,2})^2] \,/\, \Sigma\, [w(F_o^2\,)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2\,(F_o^2) + (a{*}P)^2 + b{*}P + d + e{*}\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^{\,2})^2] \,/\, (n\text{-}p)]^{1/2}$$

Table S17. Crystal data and structure refinement for 17158z.

Identification code	17158z	
Empirical formula	$C_{86} H_{69} B F_6 N O_3 P_5 W$	
Formula weight	1627.93	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.8107(8) Å	α = 72.168(2)°
	b = 14.2859(9) Å	β = 81.547(2)°
	c = 21.0859(11) Å	γ = 81.991(2)°
Volume	3897.6(4) Å^3	
Z	2	
Density (calculated)	1.387 Mg/m^3	
Absorption coefficient	1.648 mm^{-1}	
F(000)	1648	
Crystal color, morphology	Colourless, Block	
Crystal size	0.140 x 0.080 x 0.050 mm^3	
Theta range for data collection	2.228 to 30.560°	
Index ranges	$-19 \leq h \leq 19$, $-20 \leq k \leq 20$, $-30 \leq l \leq 21$	
Reflections collected	83727	
Independent reflections	23811 [R(int) = 0.0425]	
Observed reflections	19757	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7461 and 0.6795	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23811 / 882 / 928	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0737	
R indices (all data)	R1 = 0.0490, wR2 = 0.0772	
Largest diff. peak and hole	2.043 and -1.268 e.Å^{-3}	

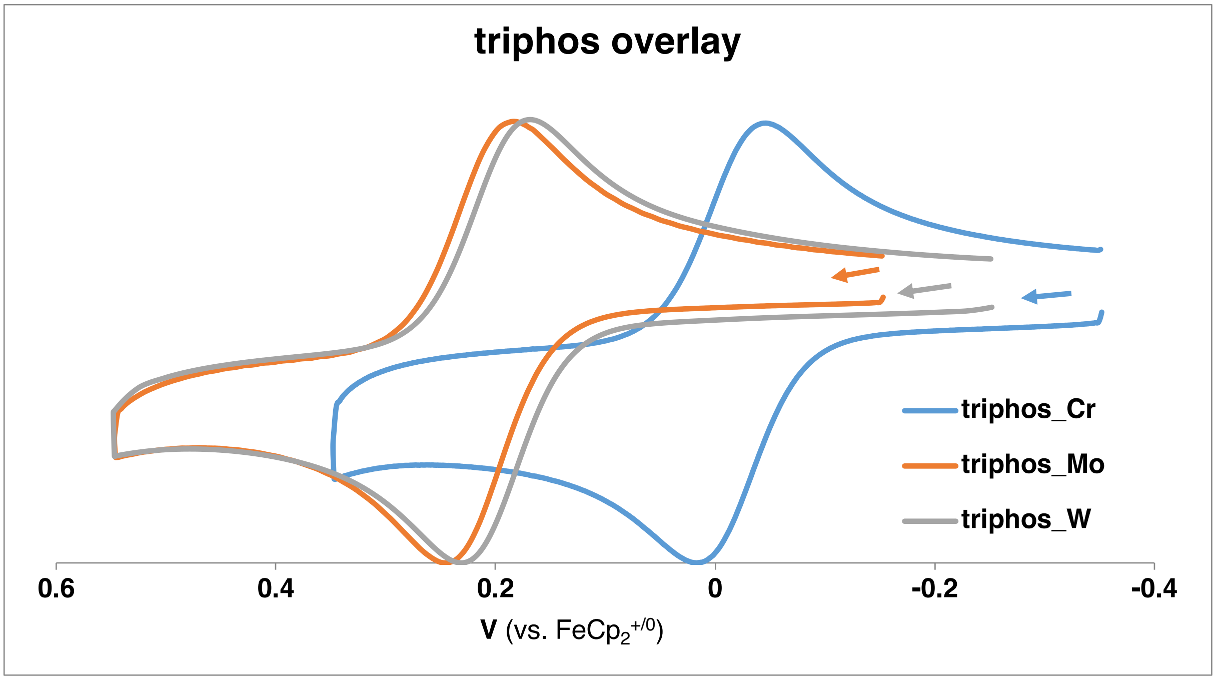
V. Cyclic Voltammetry Data and Plots

All data, organized by metal based redox event. All measurements performed in a 0.4 M [TBA][PF_6] solution of CH_3CN with ~1.5 mM of analyte. The CV scans were normalized for the sake of the overlays.

	Cr Complexes						
	Metal	Borate	Phosphine	Salt	$E_{1/2}$ vs $Fc^{+/0}$ (V)	$\Delta(E_{pc}\text{-}E_{pa})$	I_{pc}/I_{pa}
1	Cr	Ph	^{i}Pr	Et_4N	-0.691	69	1.03
7	Cr	$PhCr(CO)_3$	^{i}Pr	PPN	-0.635	66	1.06
12	Cr	$PhW(CO)_3$	^{i}Pr	Et_4N	-0.627	64	1.03
20	Cr	3,5-Me	Ph	PPN	-0.385	77	1.08
4	Cr	Ph	Ph	Et_4N	-0.370	67	1.06
10	Cr	$PhCr(CO)_3$	Ph	Et_4N	-0.354	66	1.11
15	Cr	$PhW(CO)_3$	Ph	Et_4N	-0.341	66	1.24
23	Cr	3,5-CF_3	Ph	PPN	-0.336	89	1.06
--	Cr	Triphos			-0.015	63	1.05

	Mo Complexes						
	Metal	Borate	Phosphine	Salt	$E_{1/2}$ vs Fc (V)	$\Delta(E_{pc}\text{-}E_{pa})$	I_{pc}/I_{pa}
2	Mo	Ph	^{i}Pr	Et_4N	-0.422	68	1.07
21	Mo	3,5-Me	Ph	PPN	-0.134	86	1.26
5	Mo	Ph	Ph	Et_4N	-0.132	68	1.16
24	Mo	3,5-CF_3	Ph	PPN	-0.088	85	1.09
--	Mo	Triphos			0.215	61	1.11

	W Complexes						
	Metal	Borate	Phosphine	Salt	$E_{1/2}$ vs Fc (V)	$\Delta(E_{pc}\text{-}E_{pa})$	I_{pc}/I_{pa}
3	W	Ph	^{i}Pr	Et_4N	-0.411	67	1.12
22	W	3,5-Me	Ph	PPN	-0.151	86	1.33
6	W	Ph	Ph	Et_4N	-0.133	70	0.99
25	W	3,5-CF_3	Ph	PPN	-0.106	86	1.07
--	W	Triphos			0.200	64	1.07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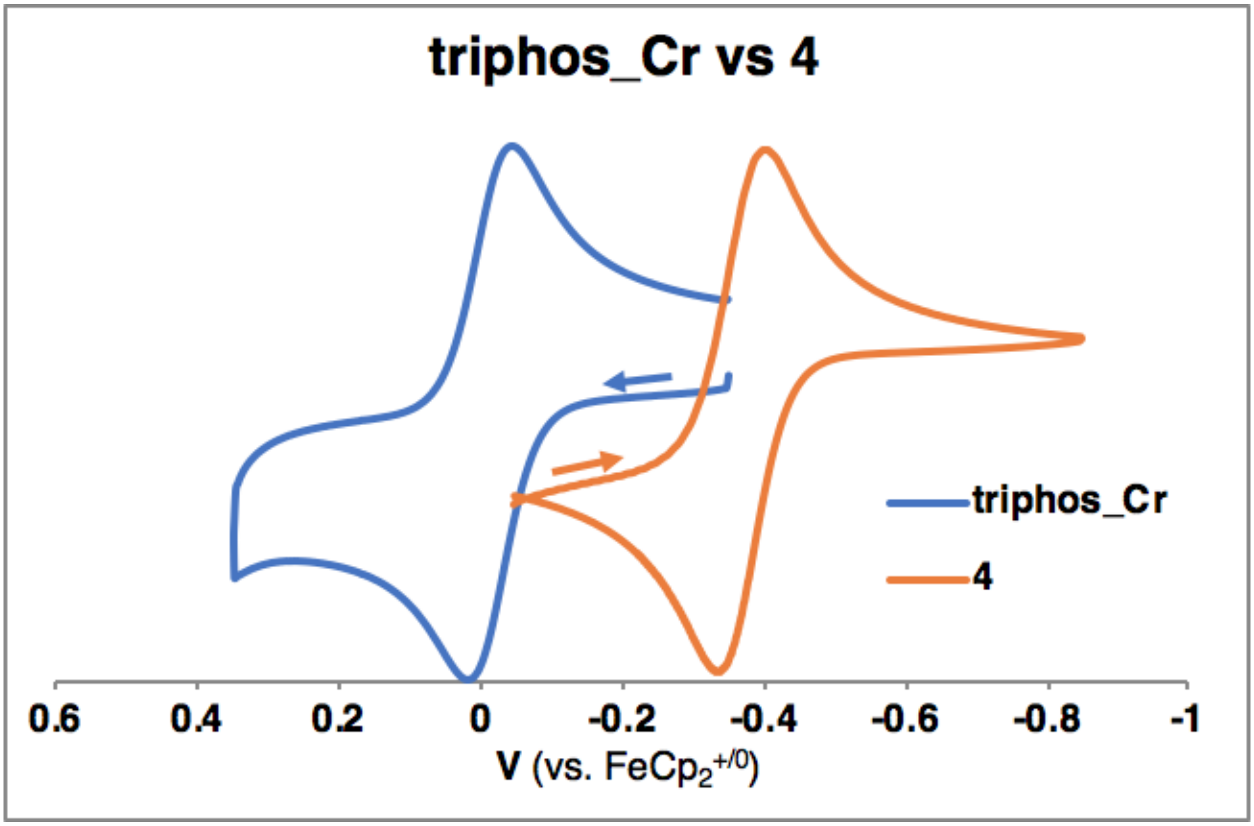
triphos_Cr
triphos_Mo
triphos_W
0.6
0.4
0.2
0
-0.2
-0.4
V (vs. FeCp$_2$$^{+/0}$)


triphos_Cr vs 4
triphos_Cr
4
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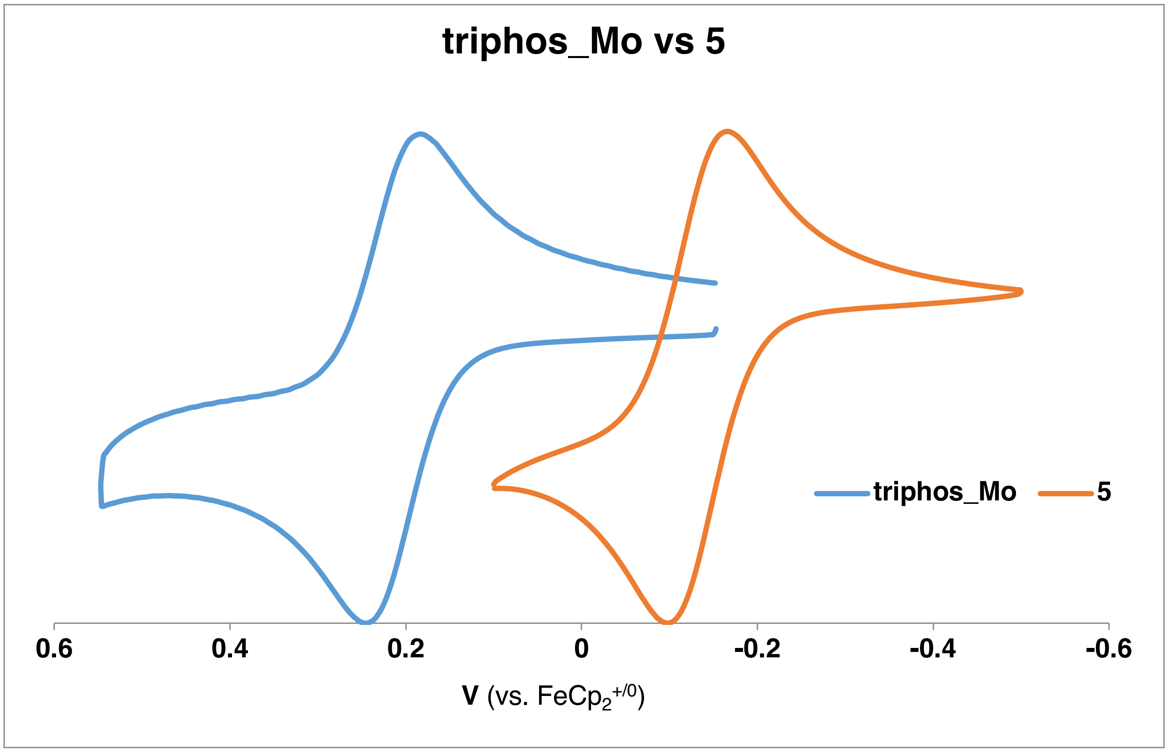
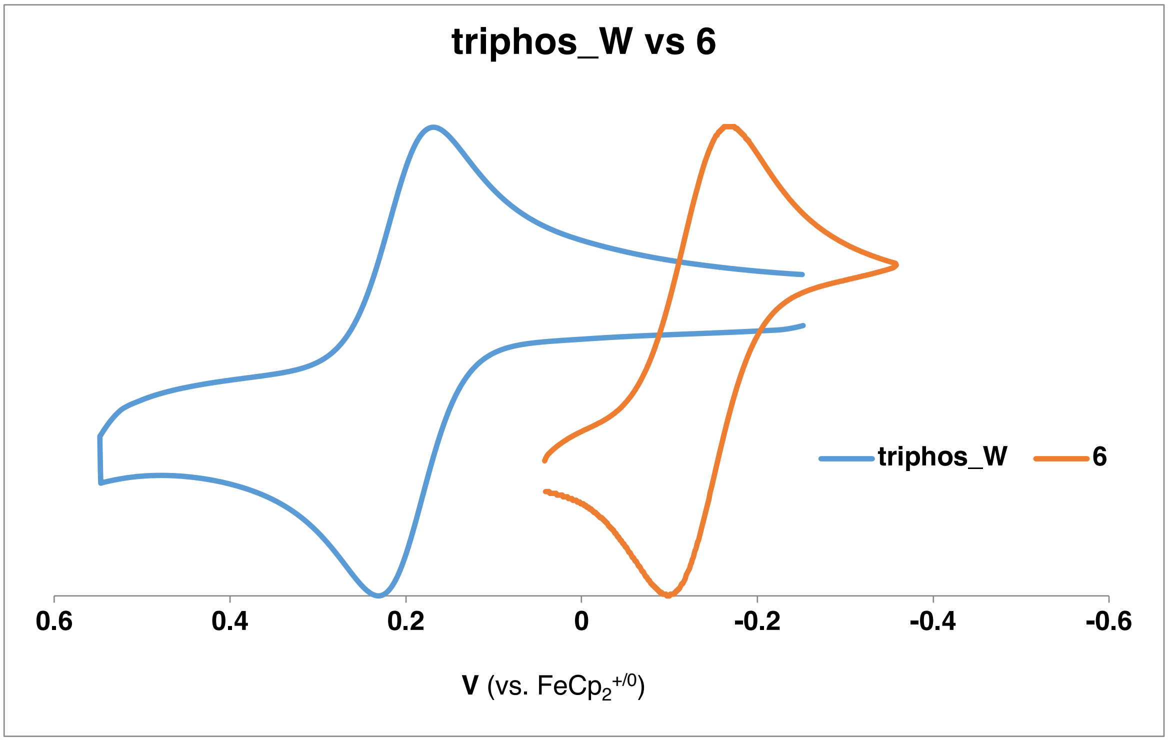
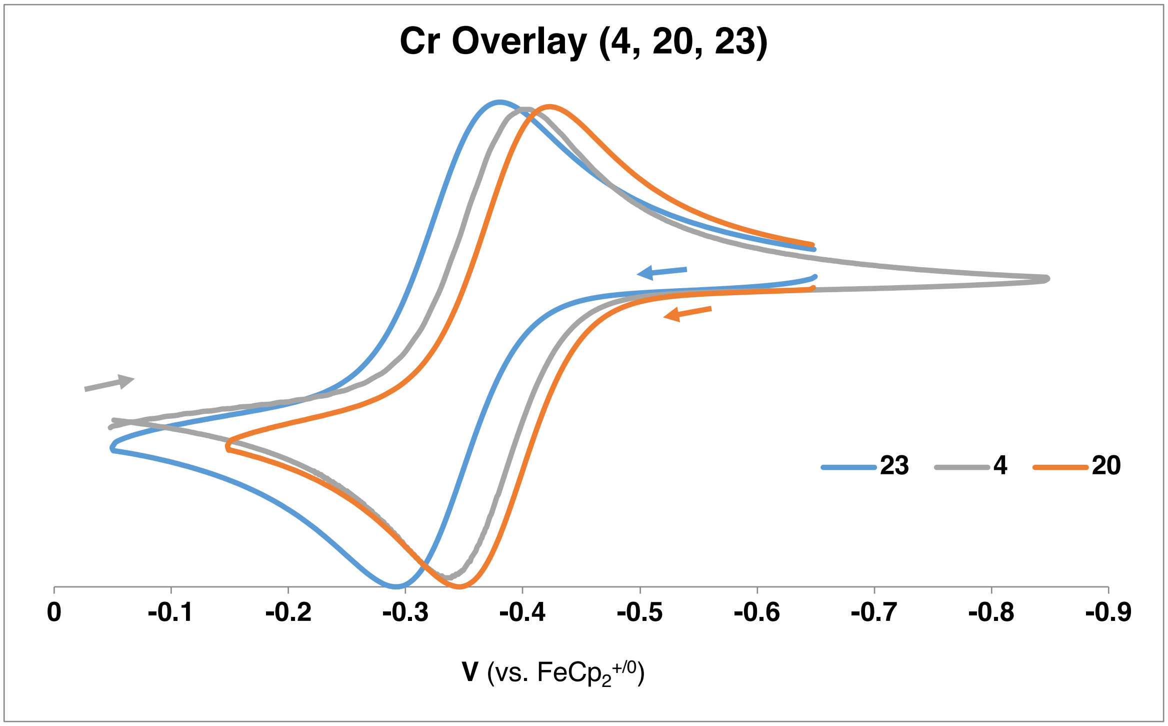
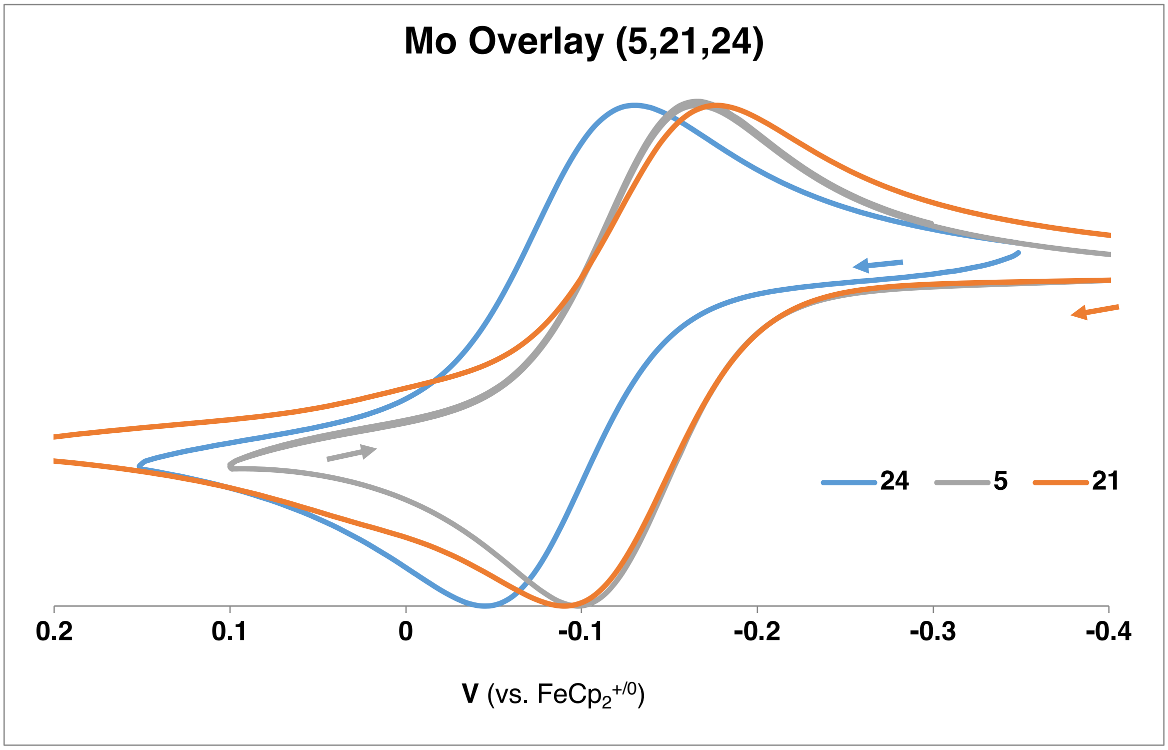
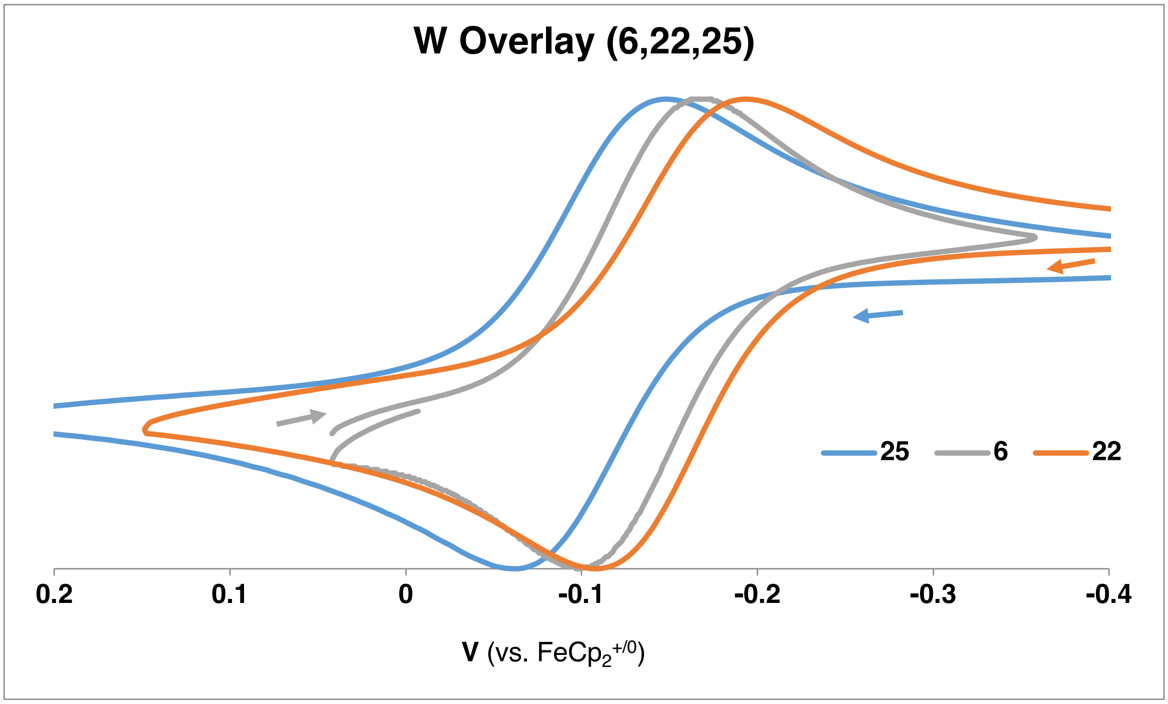
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
V (vs. FeCp$_2$$^{+/0}$)

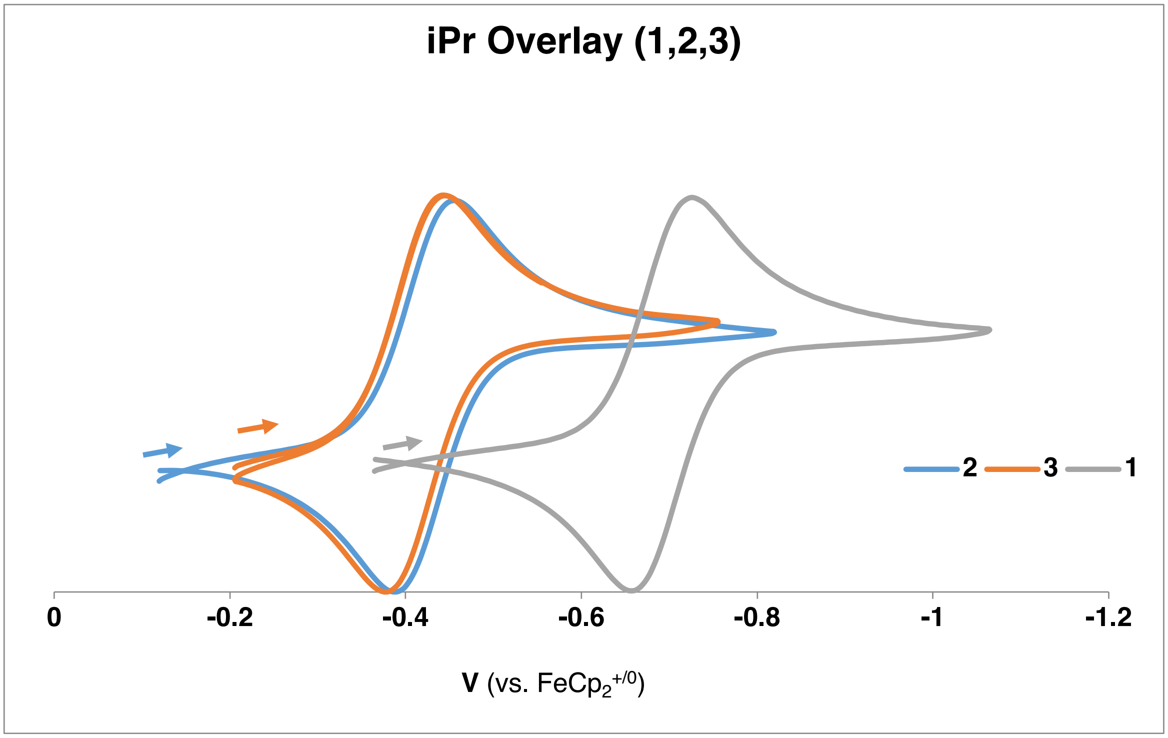

triphos_Mo vs 5
triphos_Mo
5
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
V (vs. FeCp$_2$$^{+/0}$)

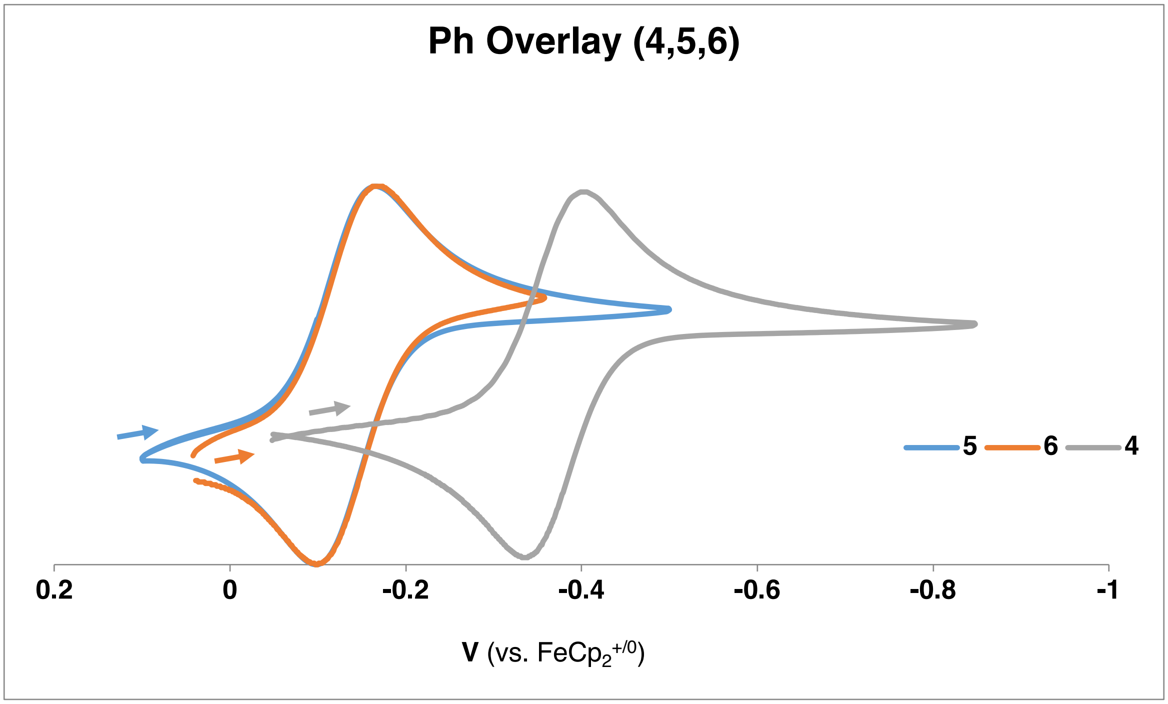

triphos_W vs 6
triphos_W
6
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
V (vs. FeCp$_2$$^{+/0}$)

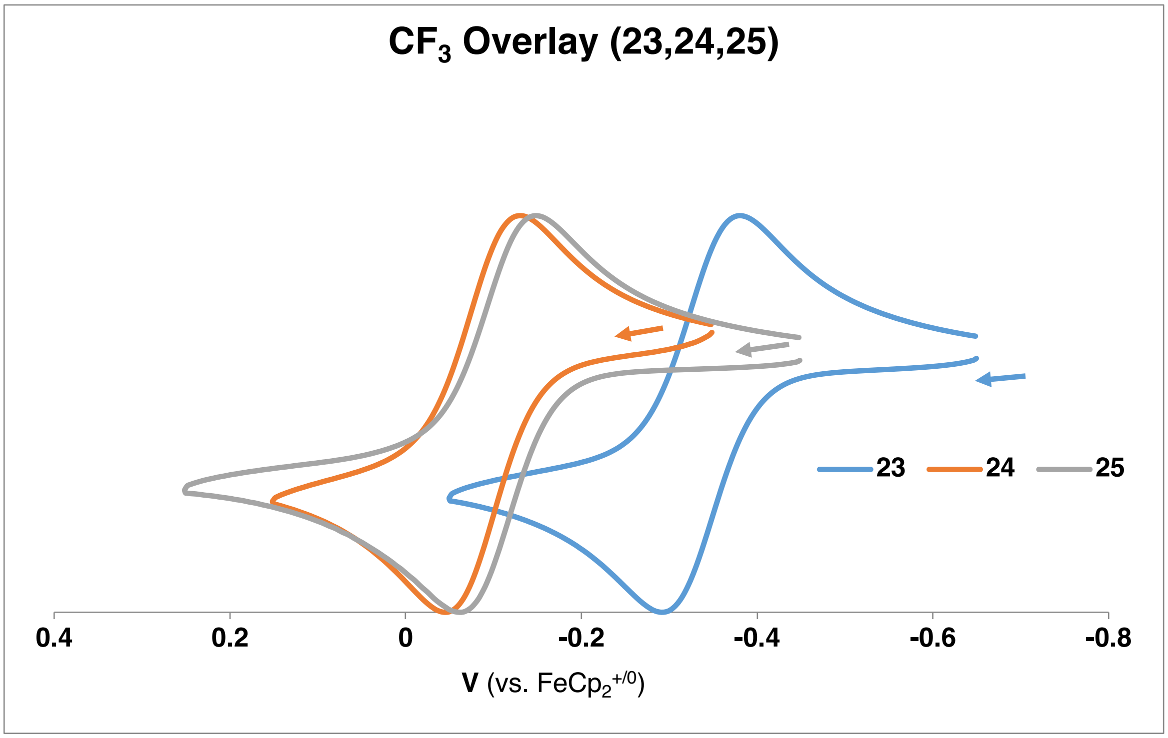

Cr Overlay (4, 20, 23)
23
4
20
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
V (vs. FeCp$_2$$^{+/0}$)

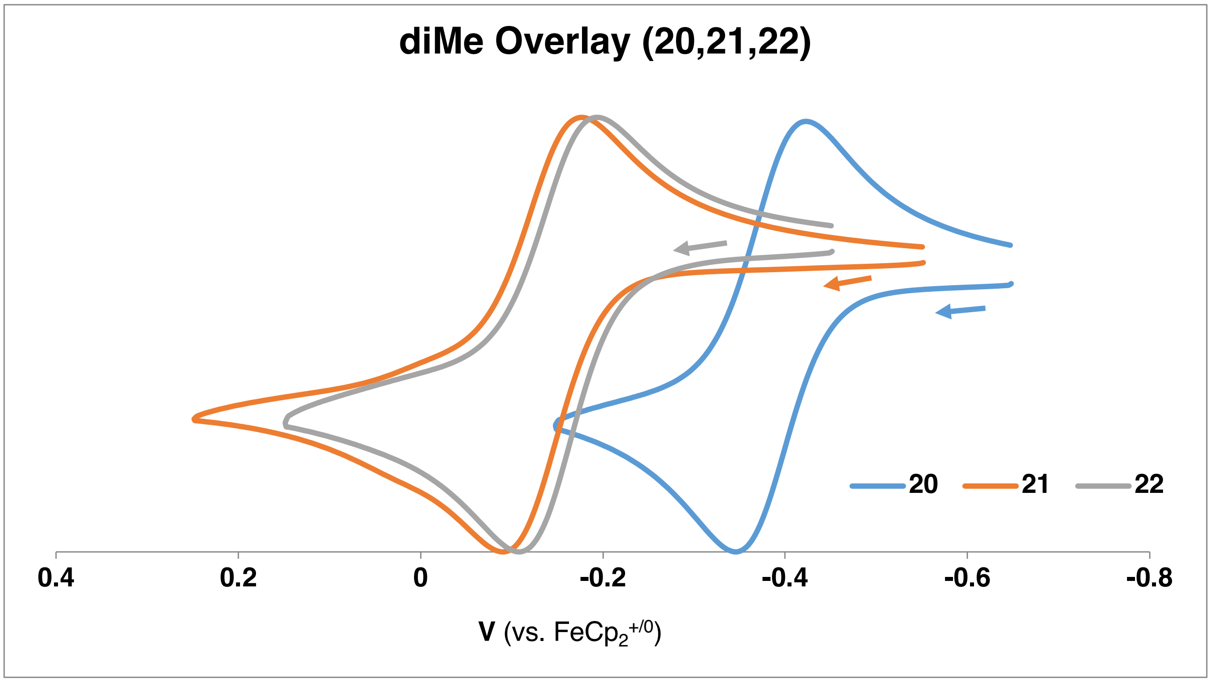

Mo Overlay (5,21,24)
24
5
21
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
V (vs. FeCp$_2$$^{+/0}$)

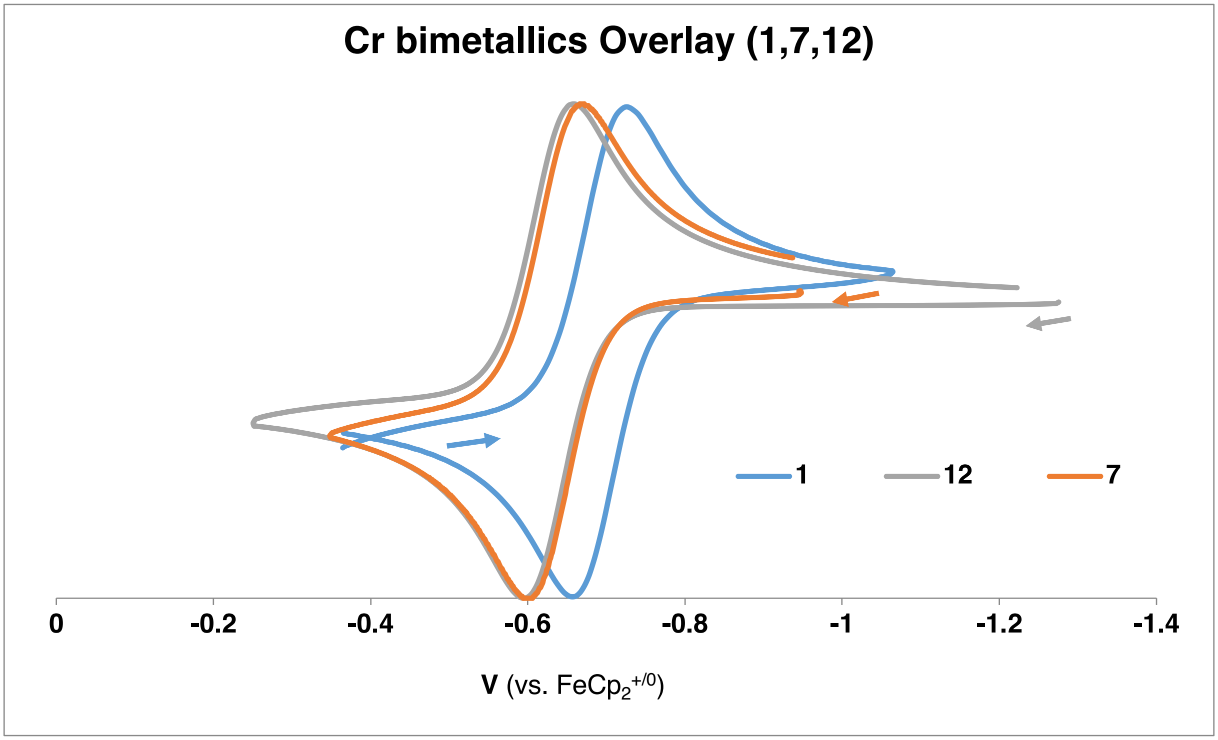

W Overlay (6,22,25)
25
6
22
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
V (vs. FeCp$_2^{+/0}$)

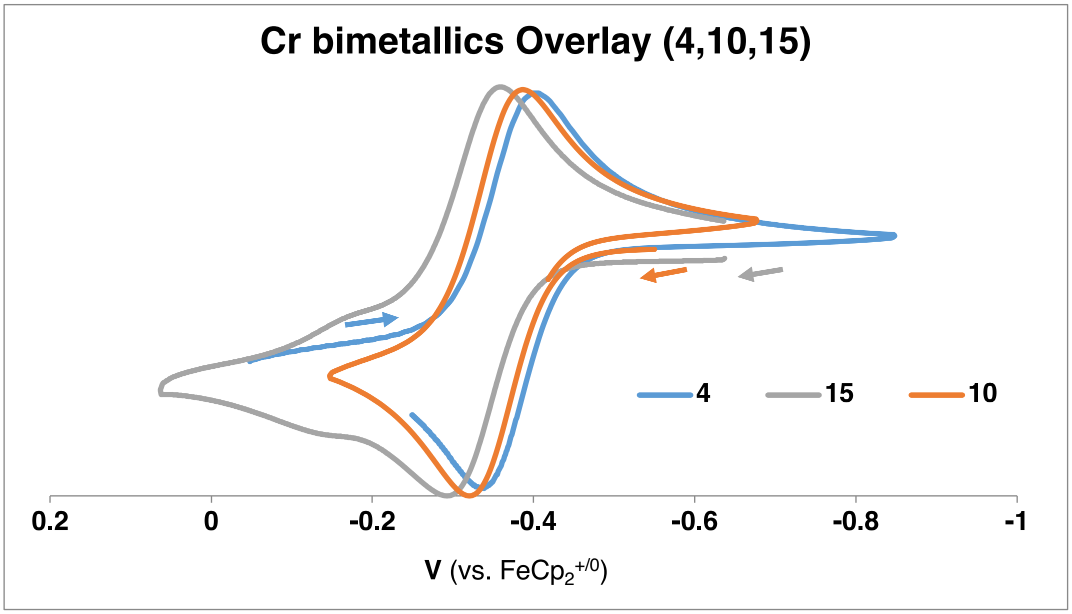

iPr Overlay (1,2,3)
2
3
1
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
V (vs. FeCp$_2^{+/0}$)


Ph Overlay (4,5,6)
5
6
4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
V (vs. $FeCp_2^{+/0}$)

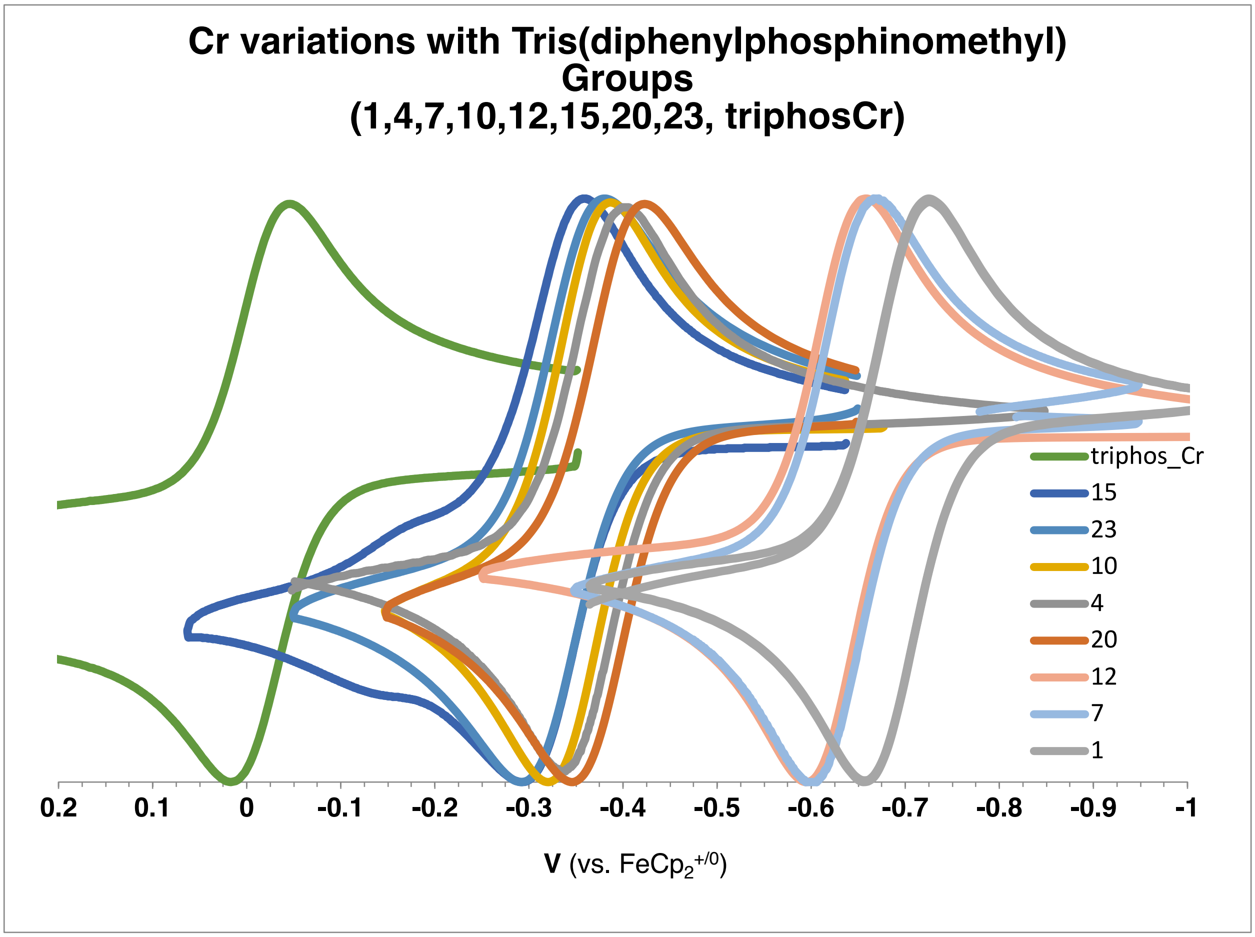

CF_3 Overlay (23,24,25)
23
24
25
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
V (vs. $FeCp_2^{+/0}$)

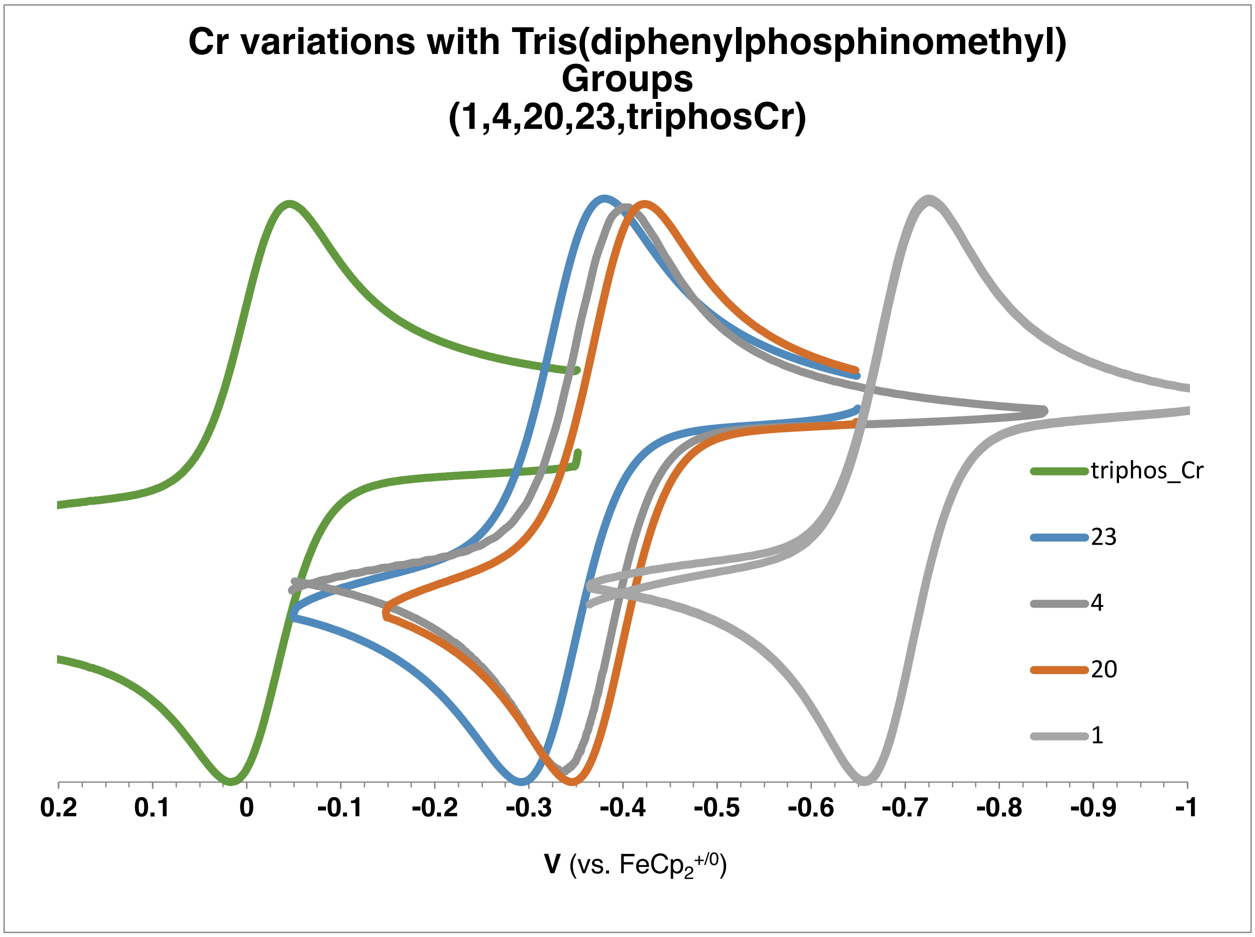

diMe Overlay (20,21,22)
20
21
22
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
V (vs. FeCp$_2^{+/0}$)


Cr bimetallics Overlay (1,7,12)
1
12
7
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
V (vs. FeCp$_2^{+/0}$)

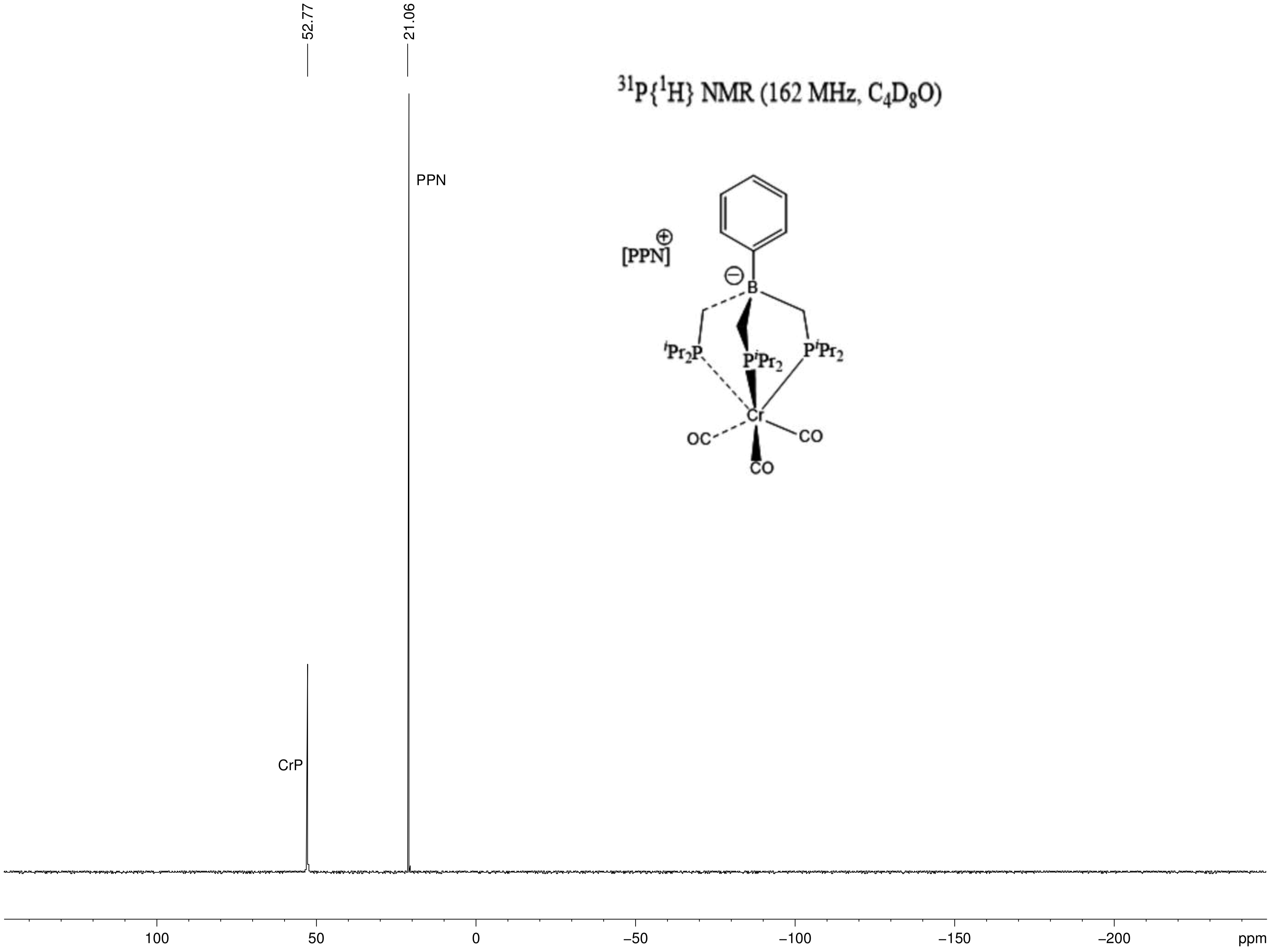


The apparently reversible process between 0.000 and -0.200 V in the scan of **15** is tentatively assigned to the oxidation of a $P_3W(CO)_3$ complex due to η^6-phenyl $W(CO)_3$ lability in CH_3CN and the thermodynamic stability of W-P relative Cr-P bonds. Further work is necessary to unambiguously identify this impurity that was observed at the electrode even when analytically pure samples of **15** were employed.



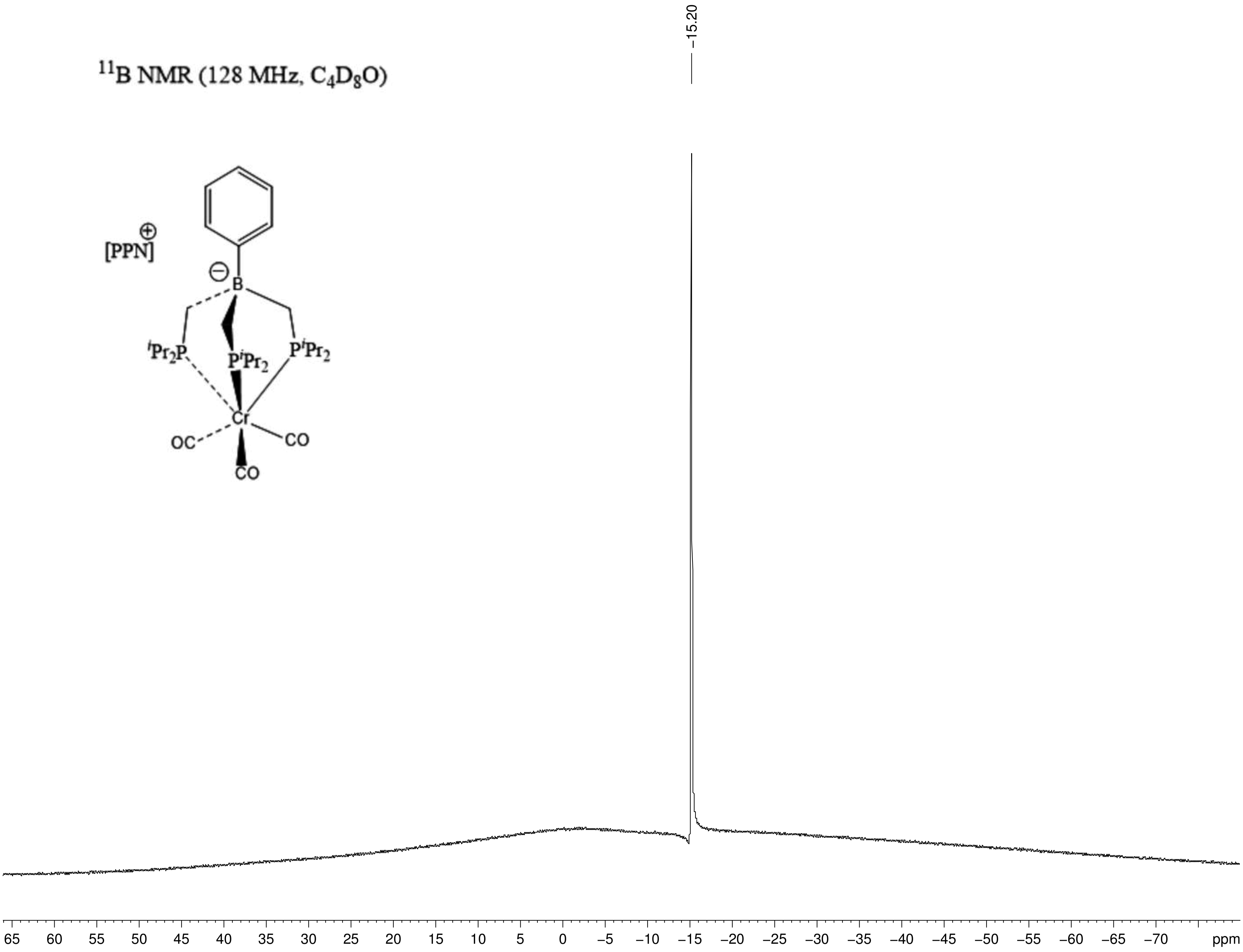

Cr variations with Tris(diphenylphosphinomethyl) Groups
(1,4,20,23,triphosCr)
triphos_Cr
23
4
20
1
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
V (vs. FeCp2+/0)

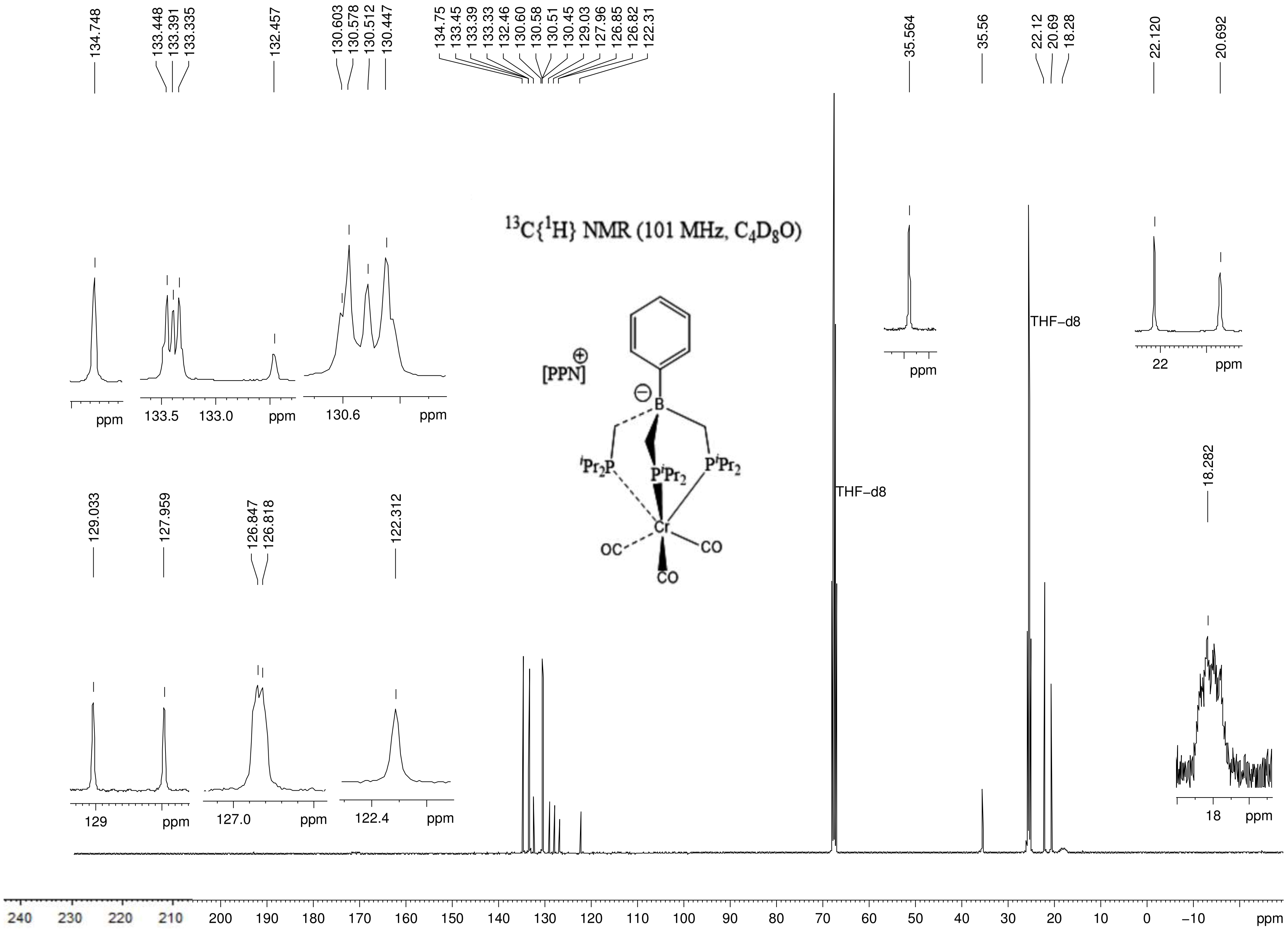
VI. Annotated $^{31}P\{^{1}H\}$, ^{11}B, ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra



$^{31}P\{^{1}H\}$ NMR (162 MHz, C_4D_8O)

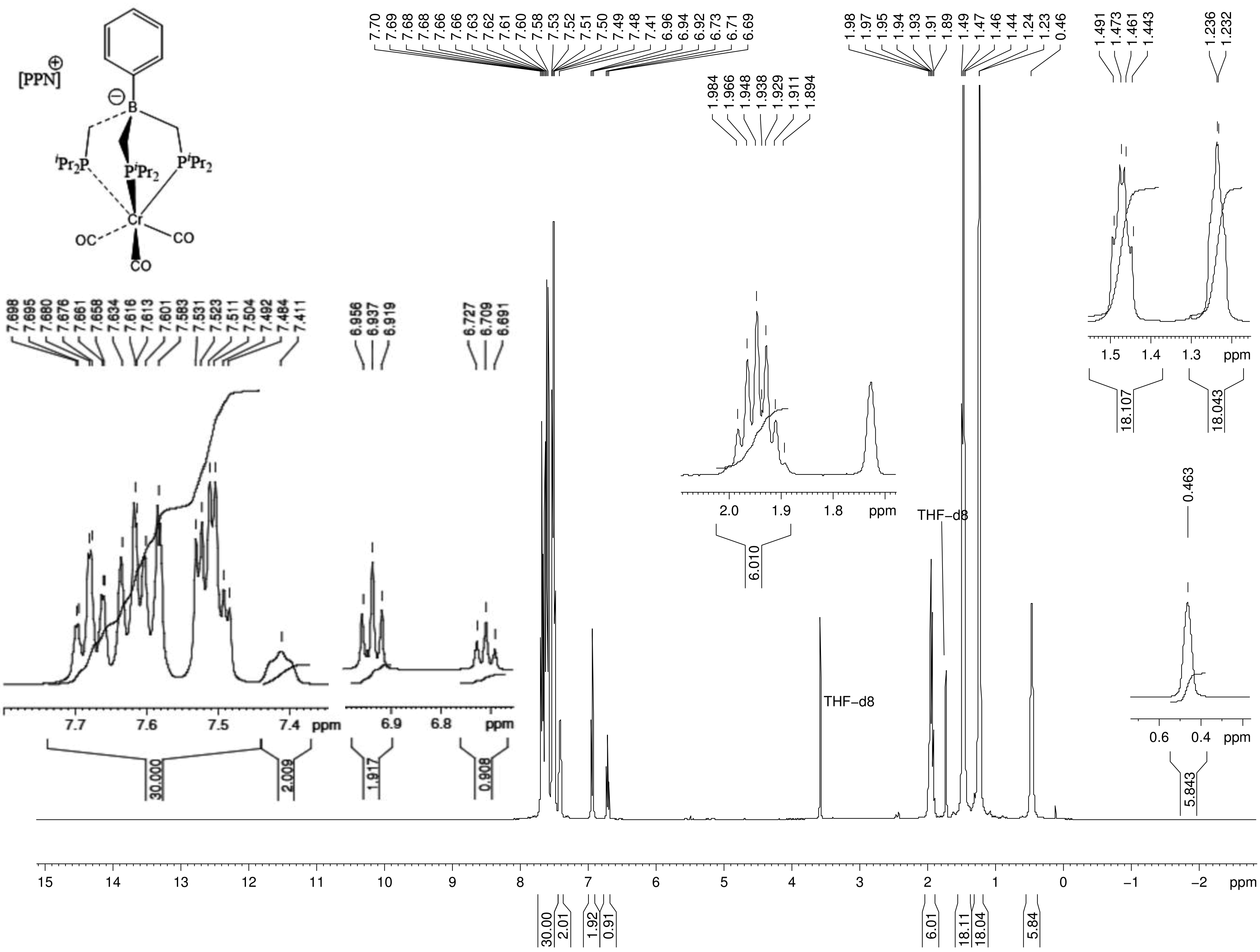
^{11}B NMR (128 MHz, C_4D_8O)



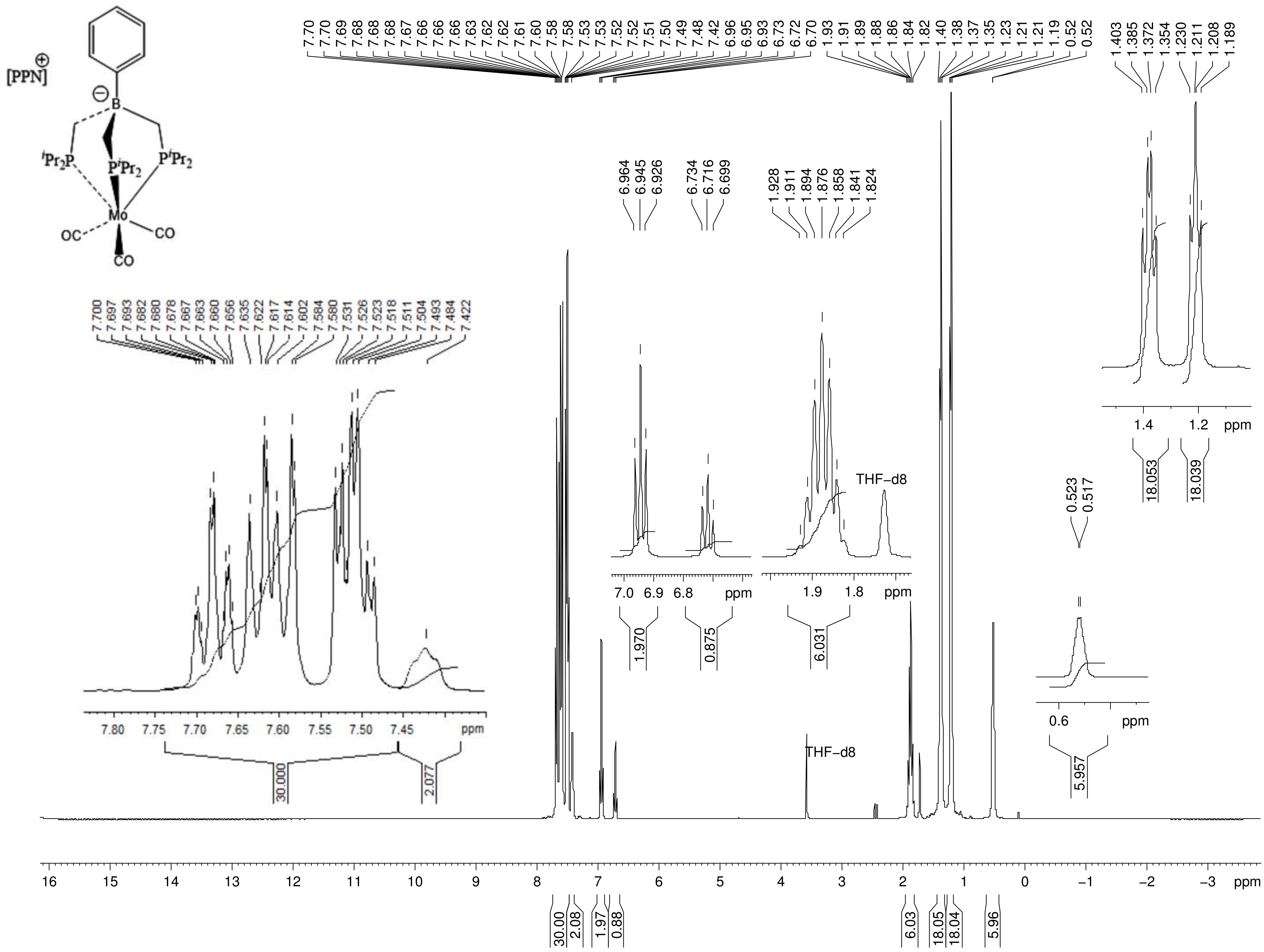


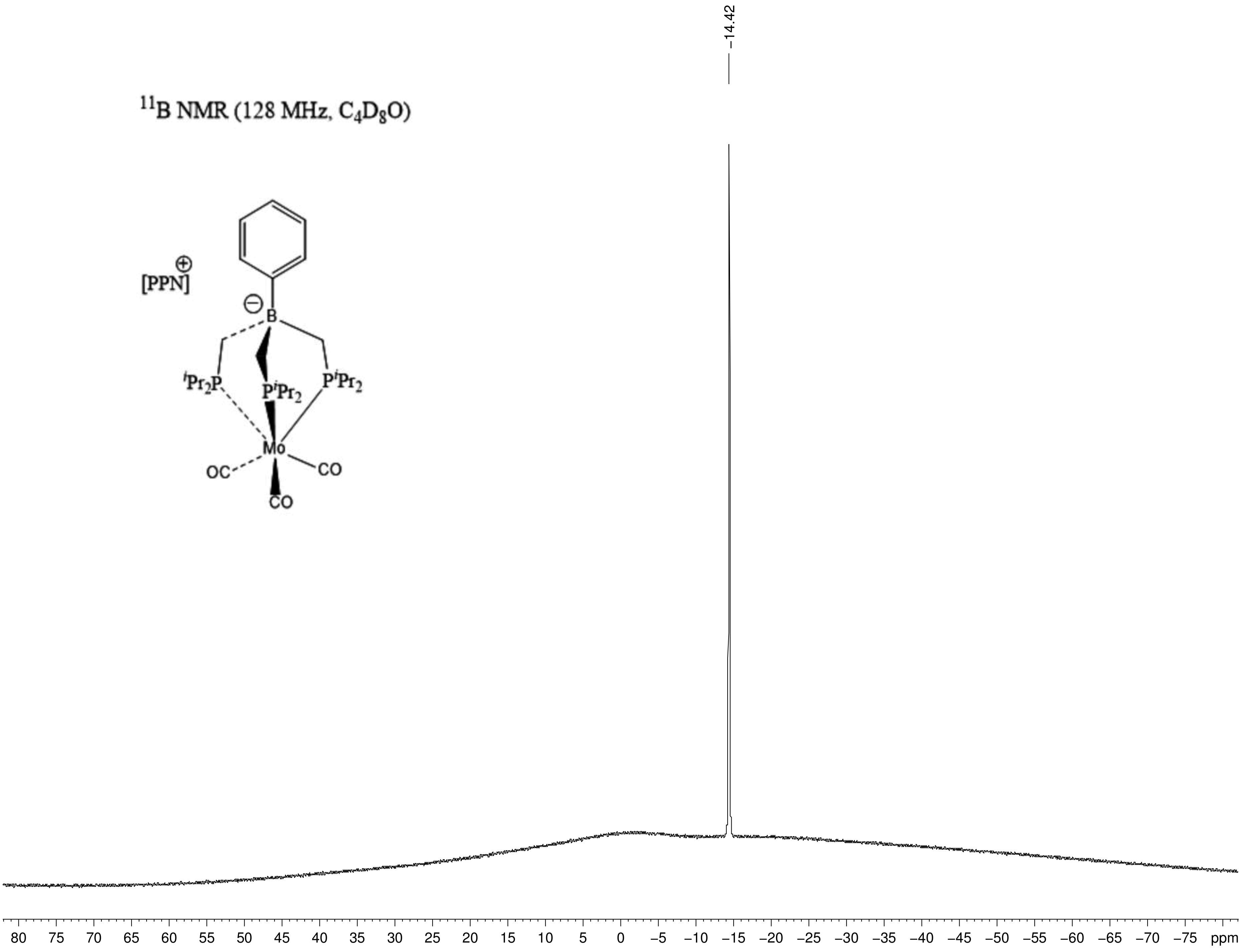
^{13}C{^{1}H} NMR (101 MHz, C_4D_8O)

^{1}H NMR (400 MHz, C_4D_8O)



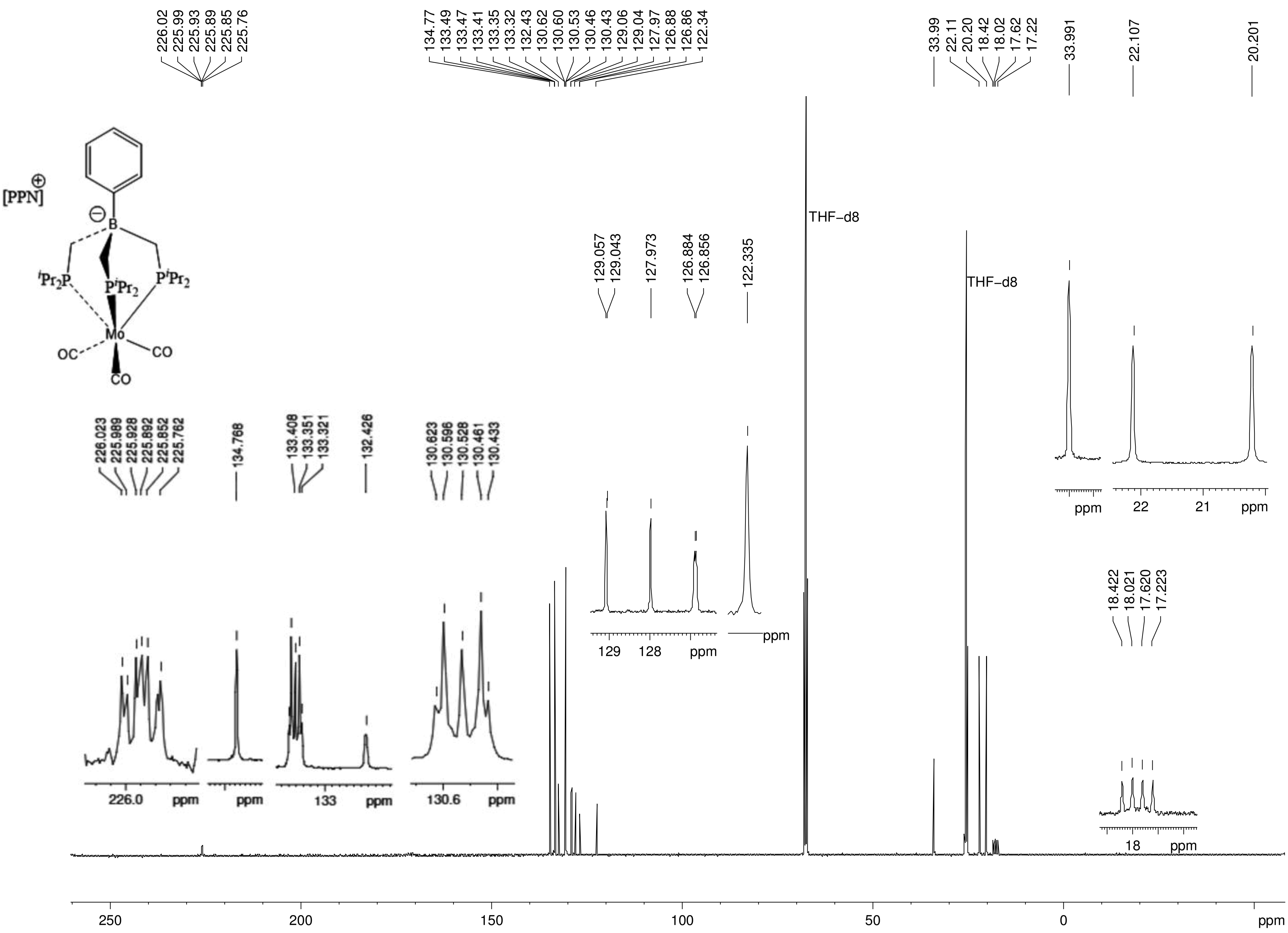
^1H NMR (400 MHz, C_4D_8O)

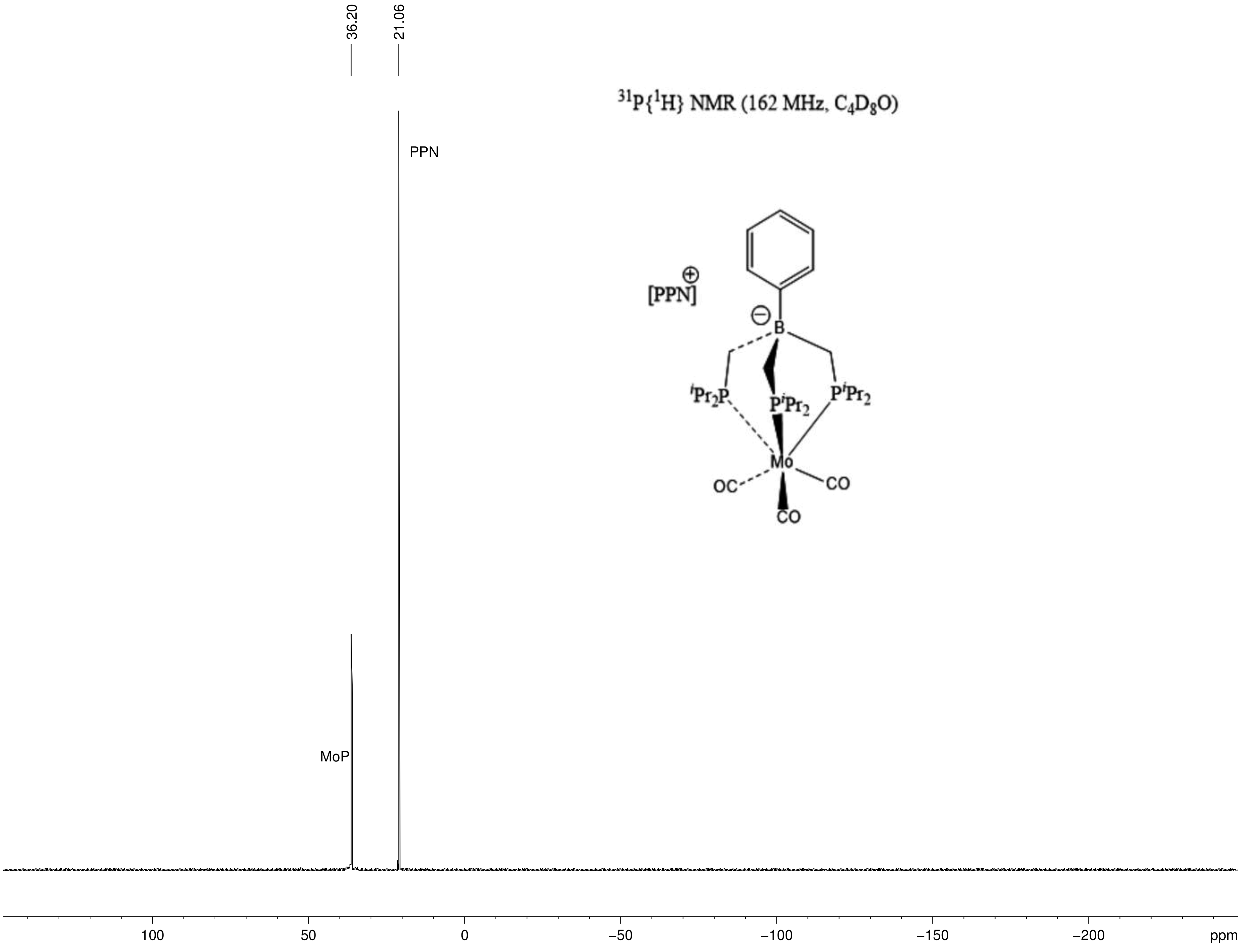




^{11}B NMR (128 MHz, C_4D_8O)

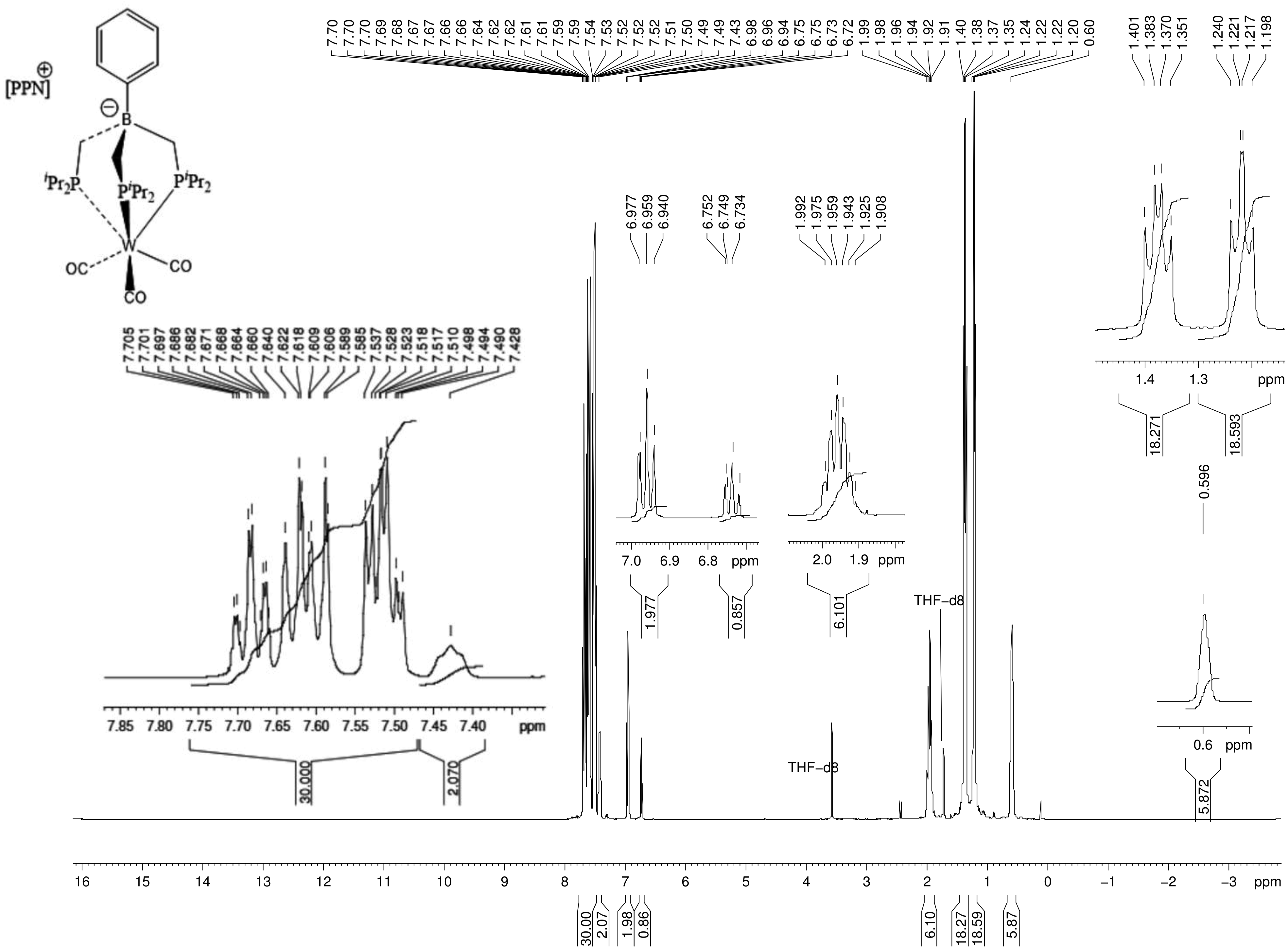
$^{13}C\{^{1}H\}$ NMR (101 MHz, C_4D_8O)



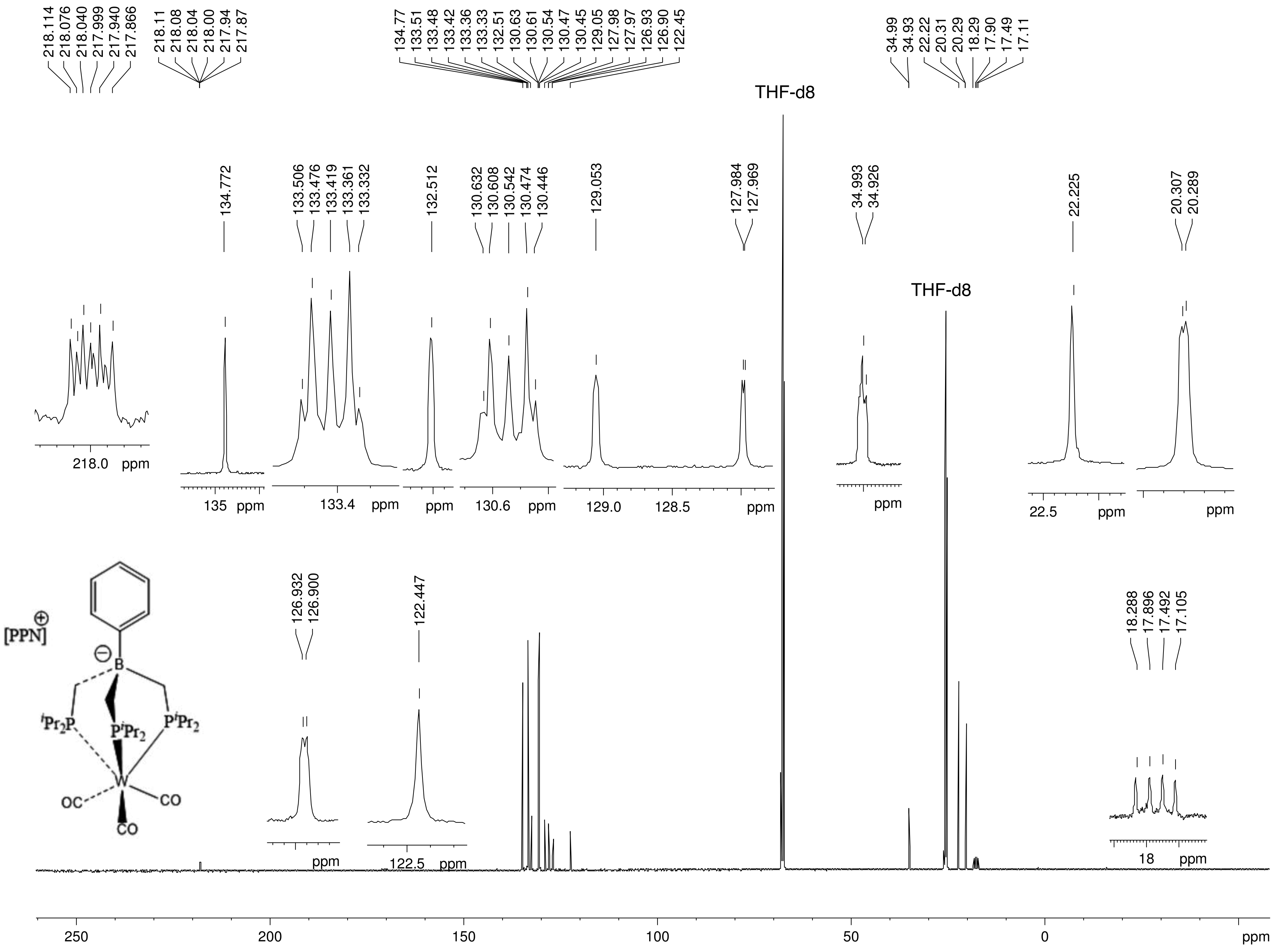


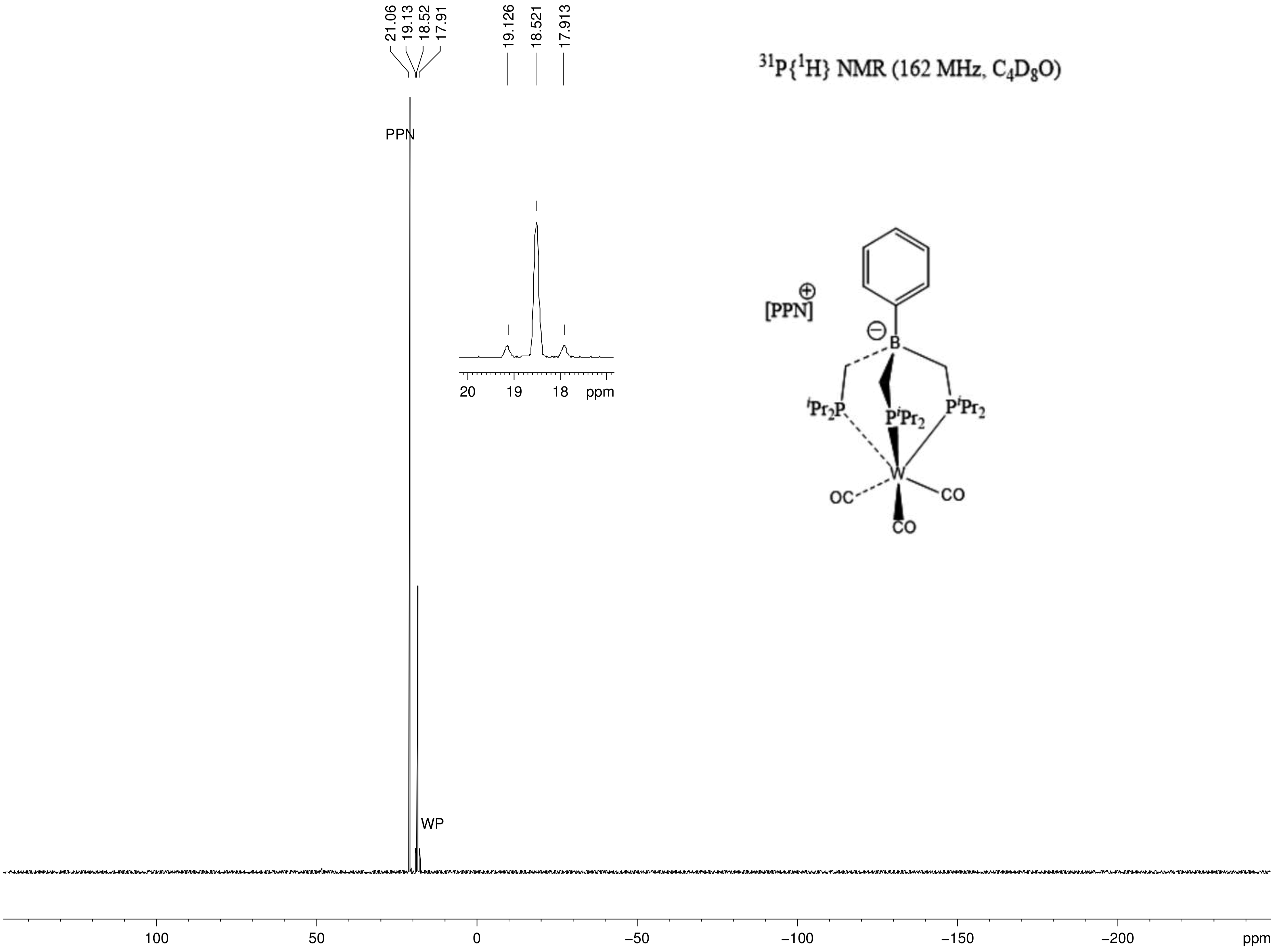
$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)

^{1}H NMR (400 MHz, C_4D_8O)



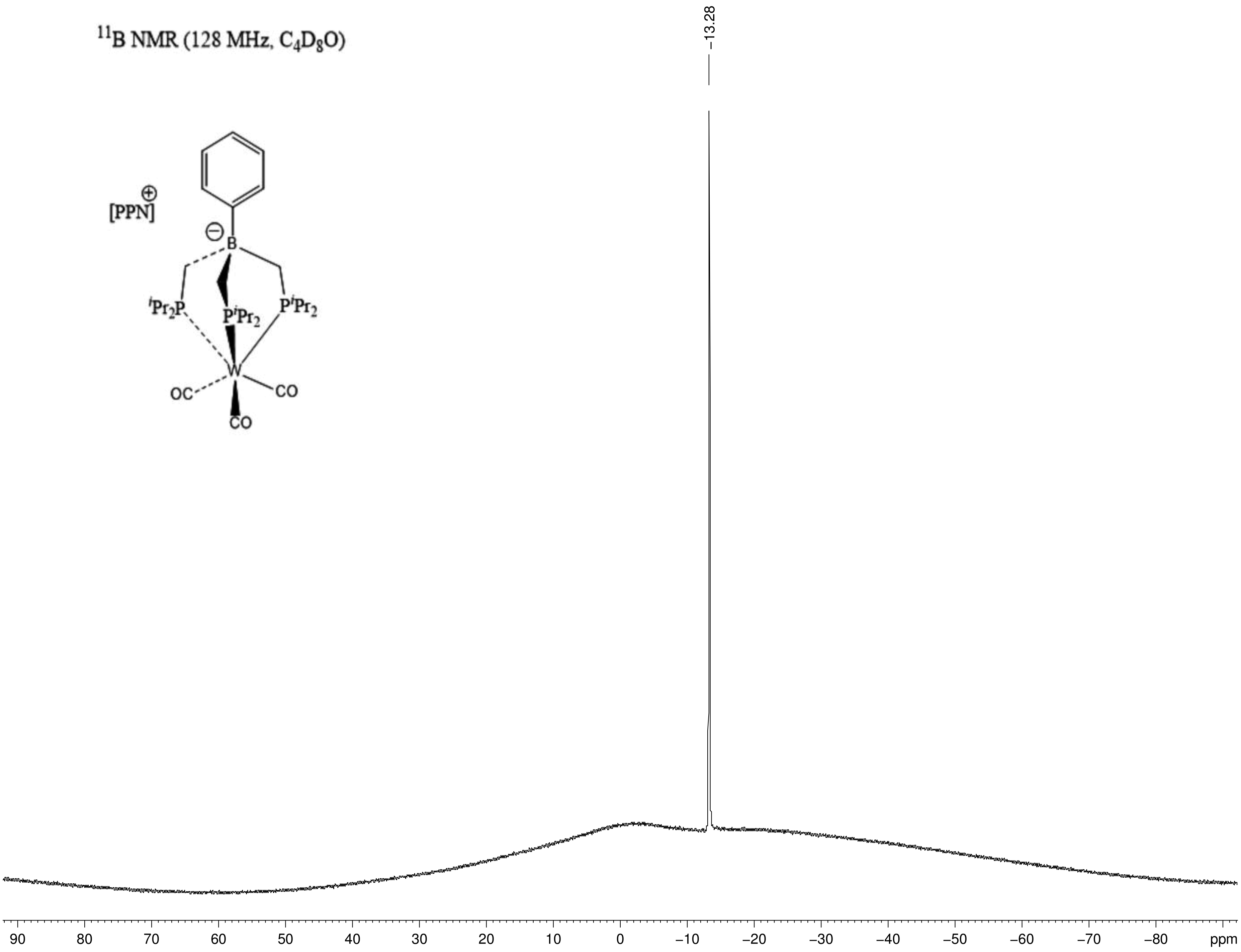
$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)

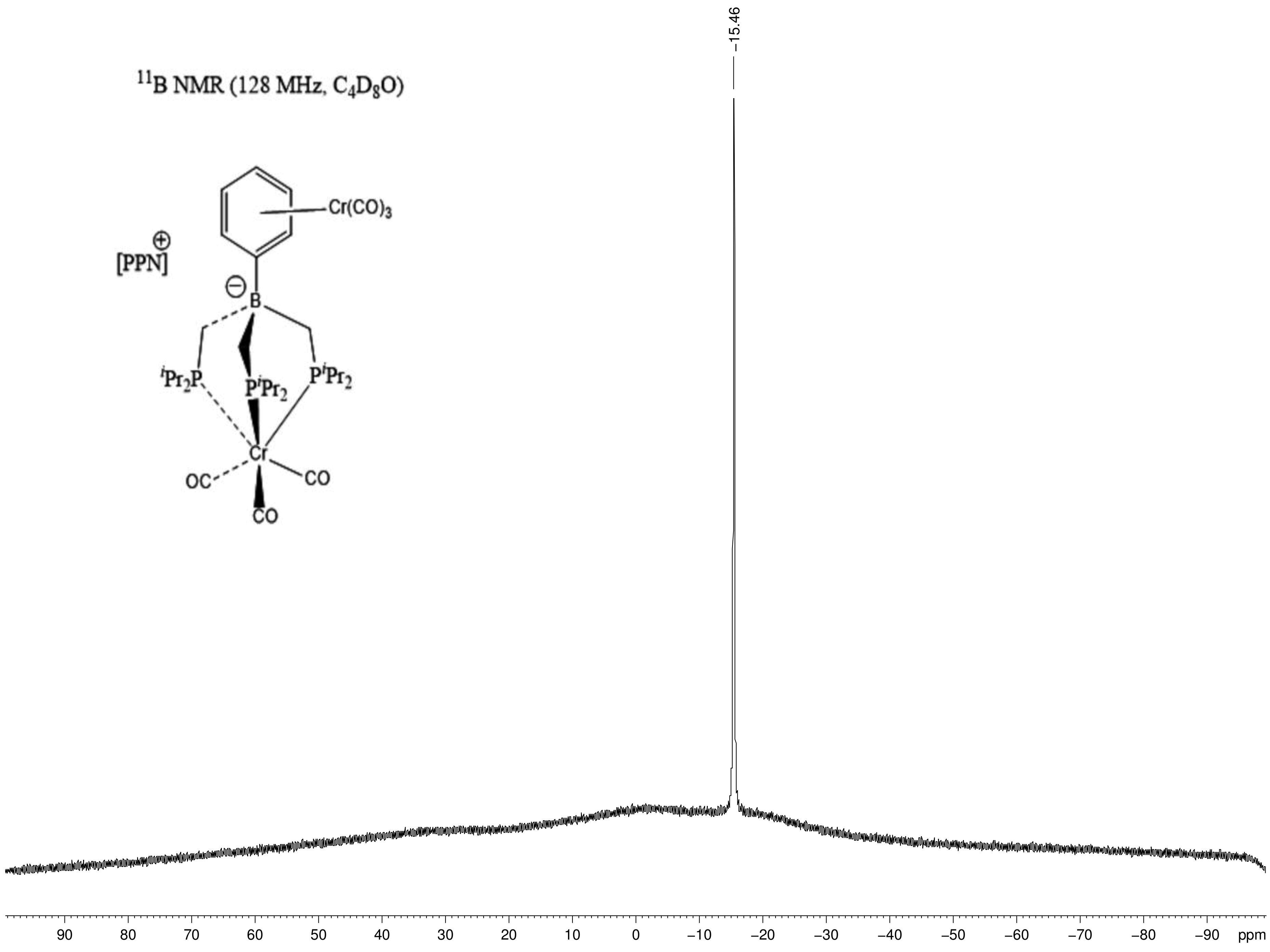




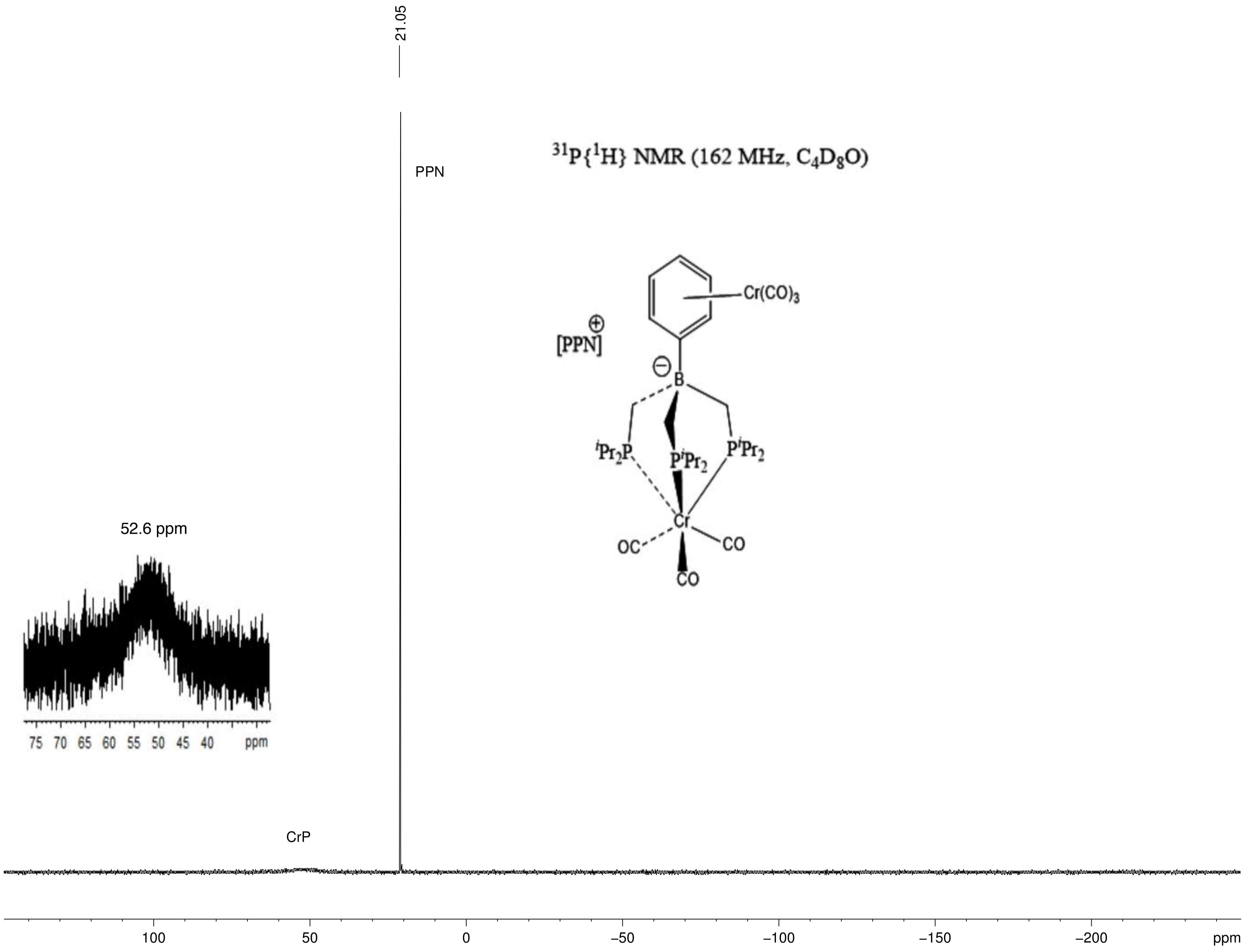
$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)

^{11}B NMR (128 MHz, C_4D_8O)

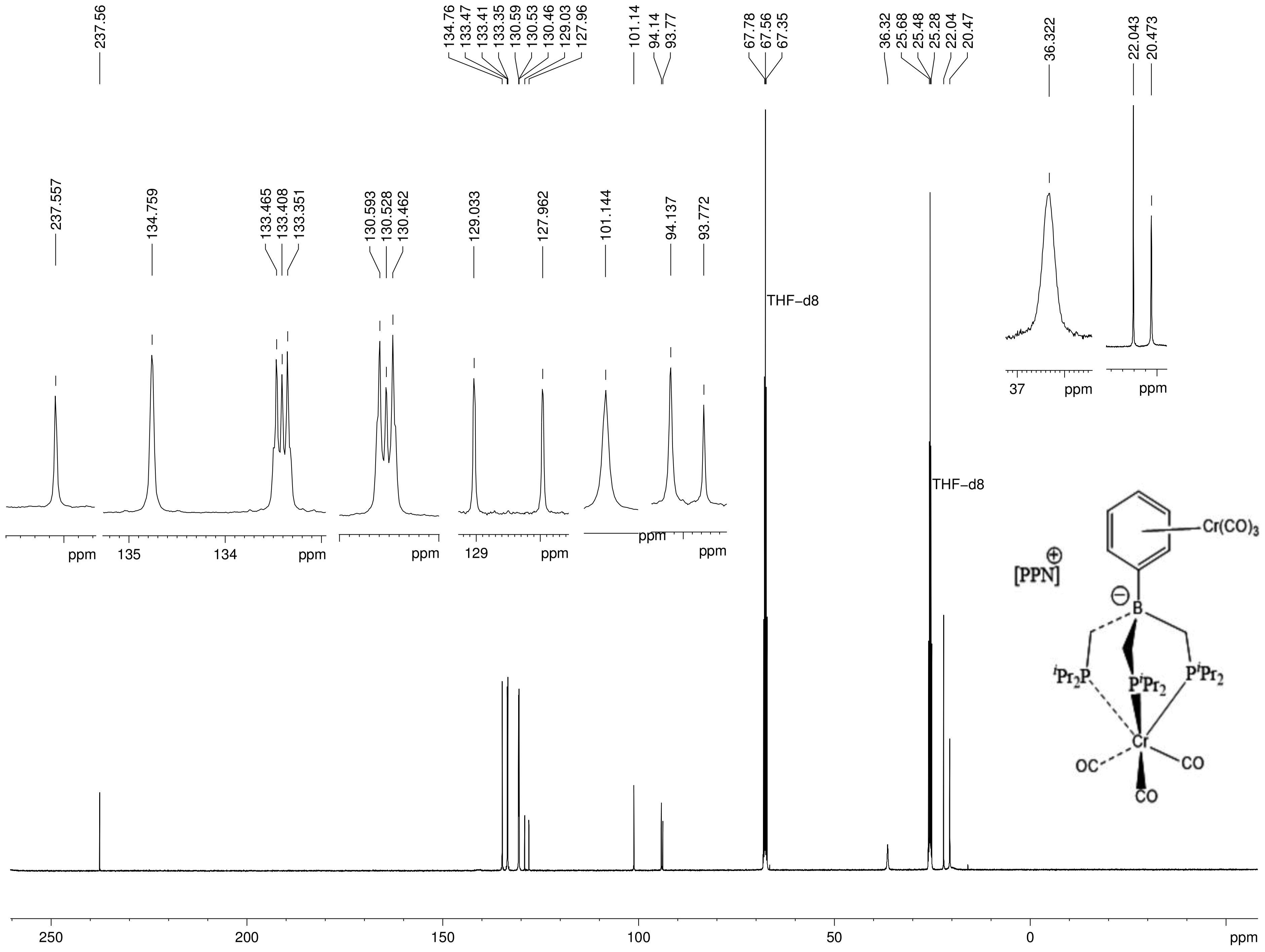




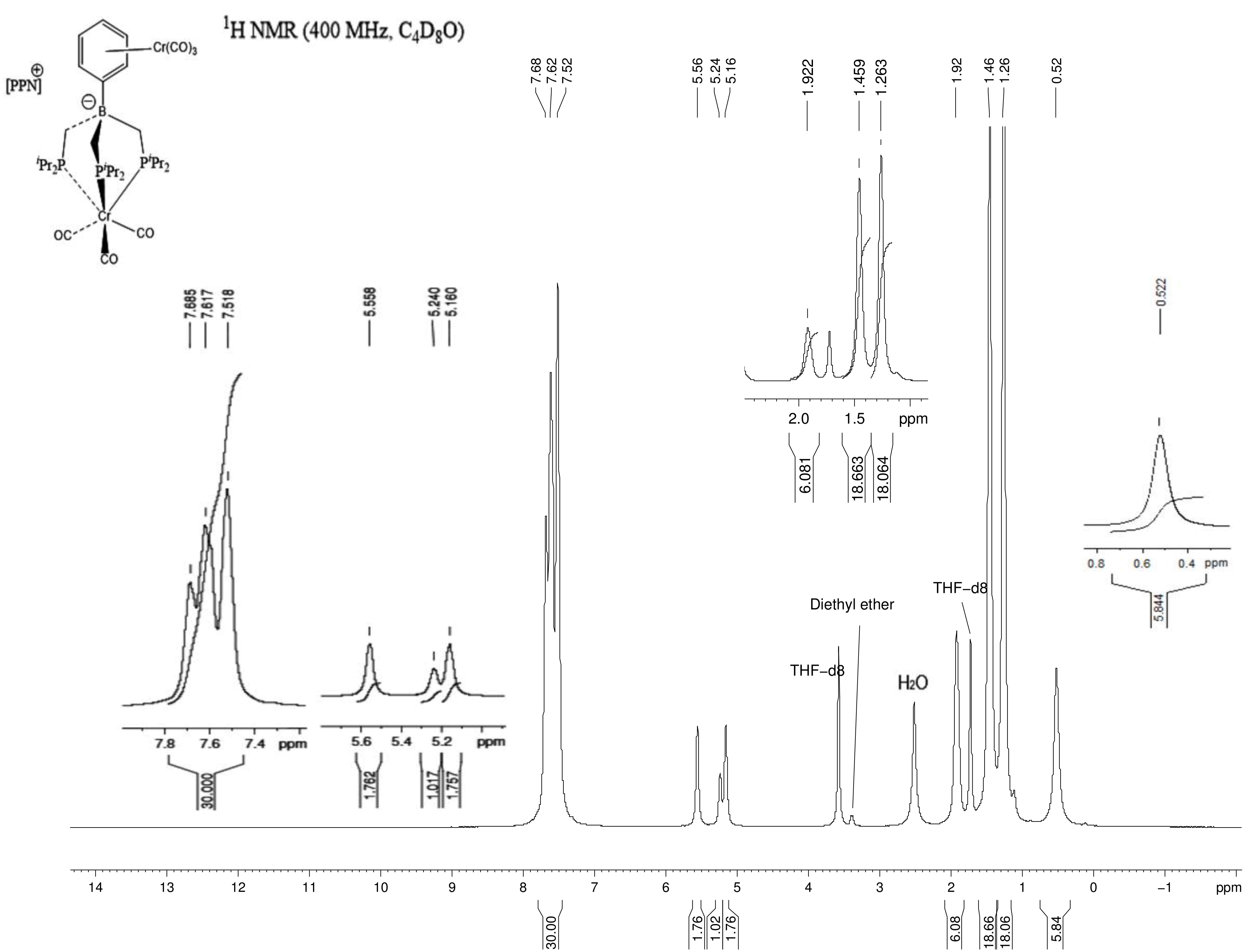
^{11}B NMR (128 MHz, C_4D_8O)

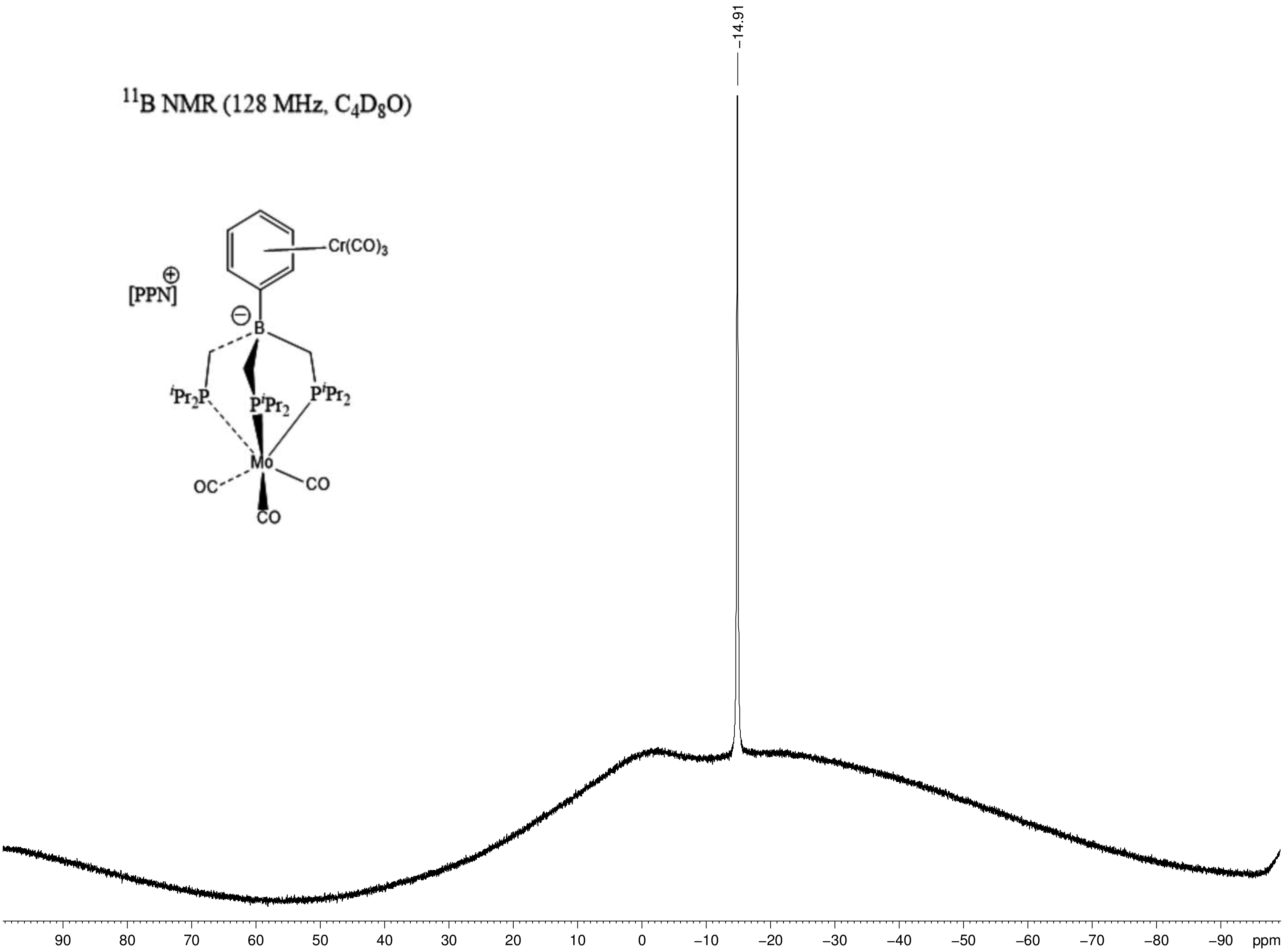
21.05
³¹P{¹H} NMR (162 MHz, C₄D₈O)
PPN
[PPN]⊕
⊖B
Cr(CO)₃
ⁱPr₂P
PⁱPr₂
PⁱPr₂
Cr
OC
CO
CO
52.6 ppm
75
70
65
60
55
50
45
40
ppm
CrP
100
50
0
−50
−100
−150
−200
ppm

$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)



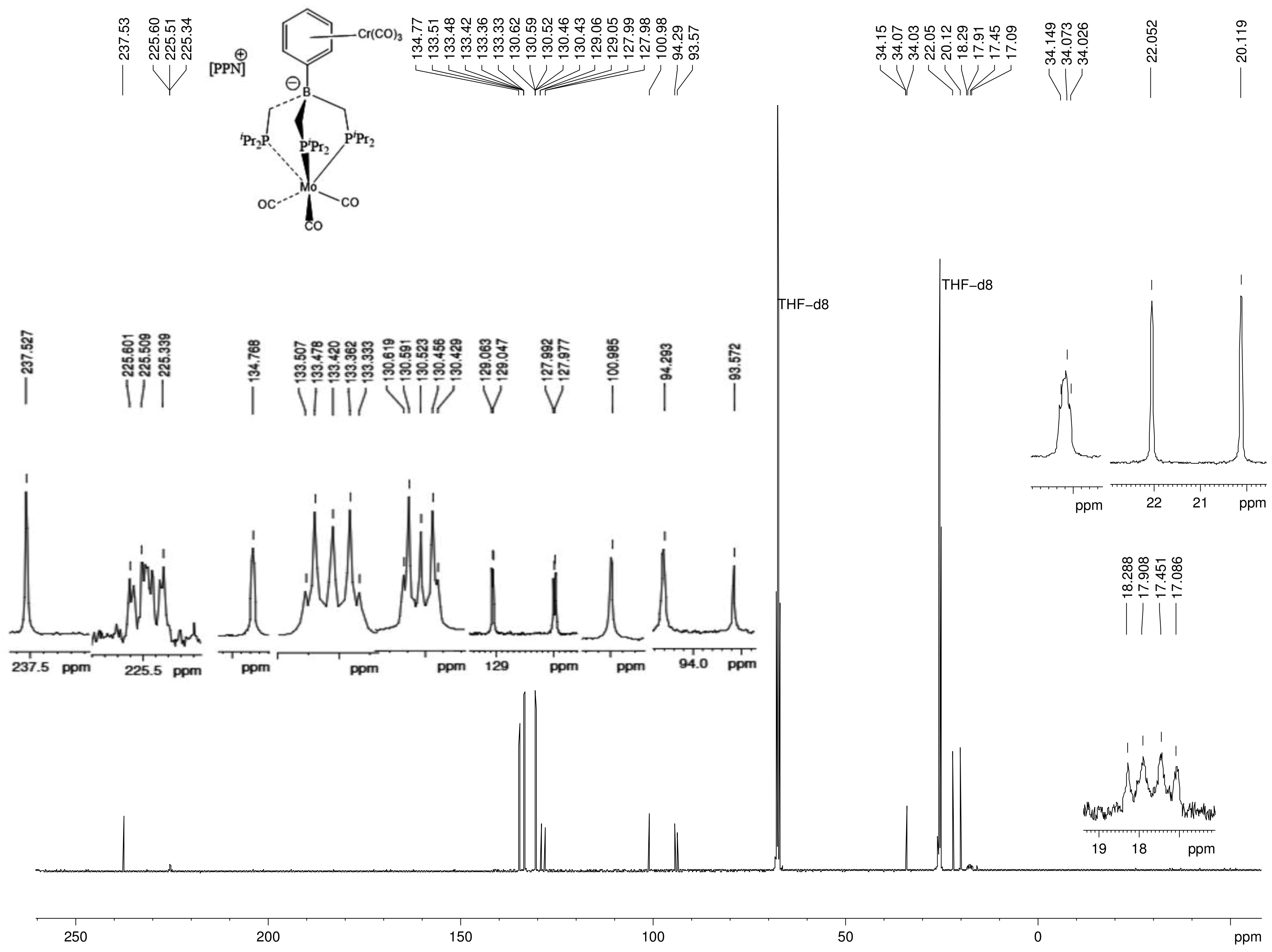
^{1}H NMR (400 MHz, C_4D_8O)



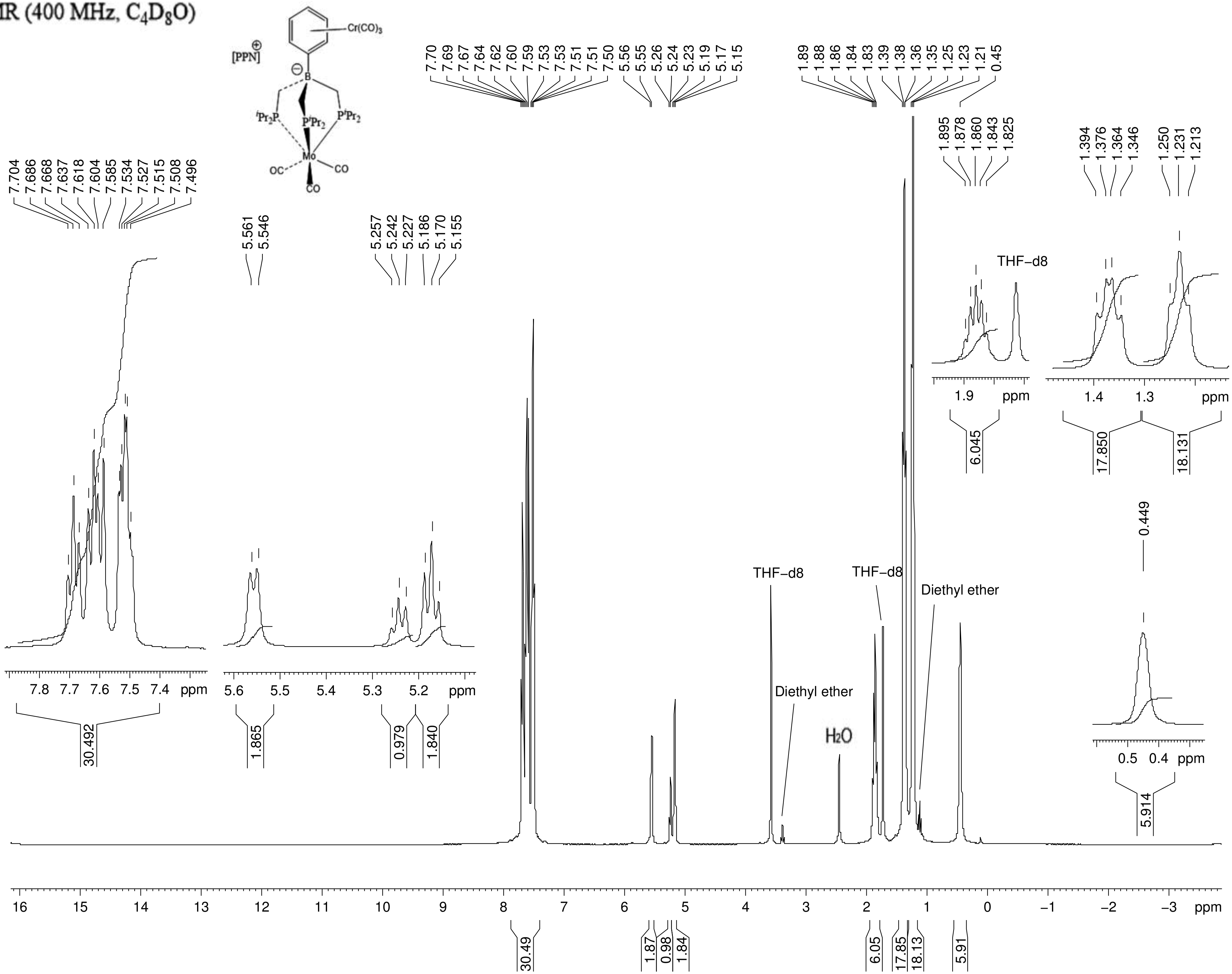


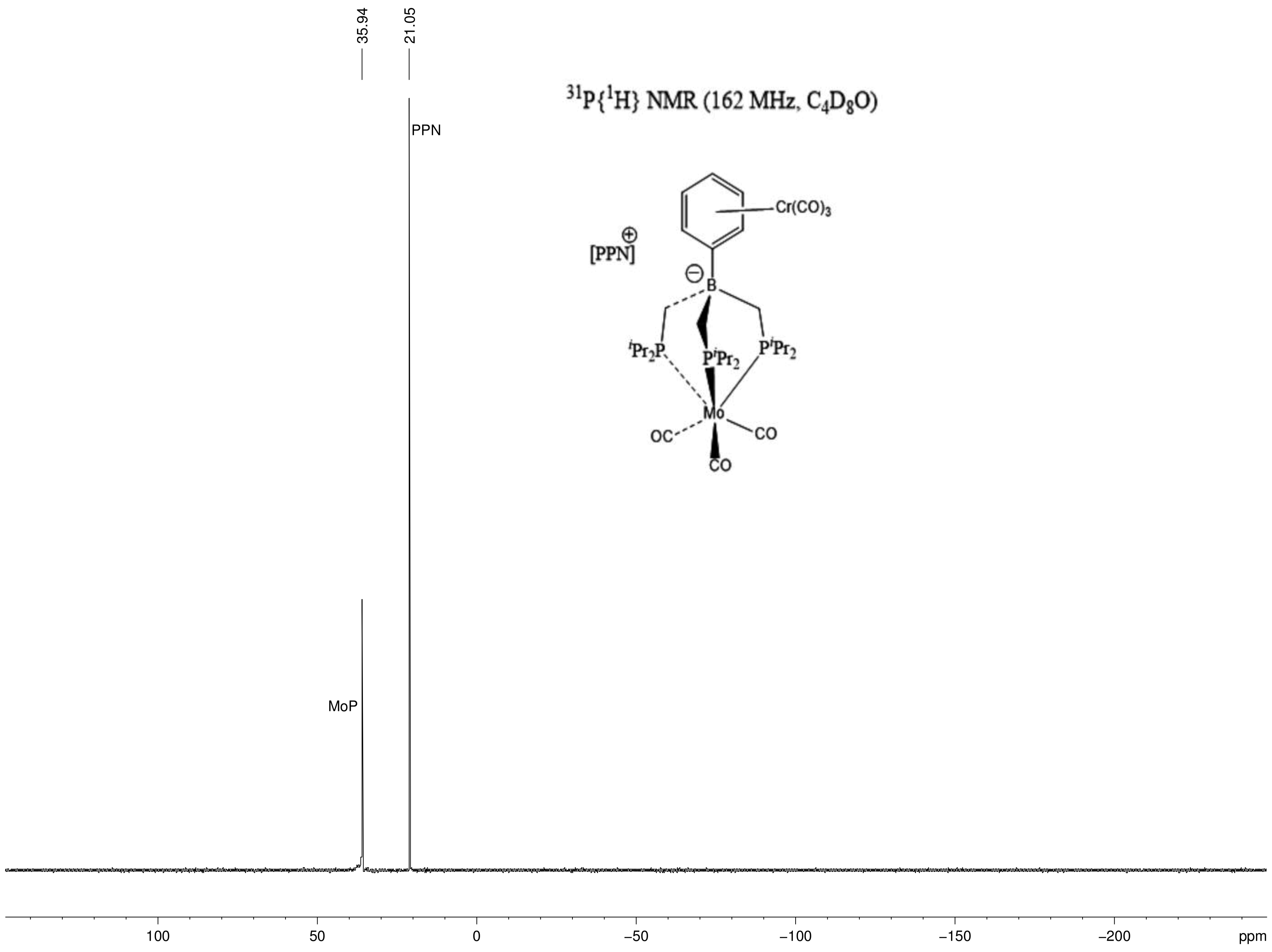
^{11}B NMR (128 MHz, C_4D_8O)

$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)

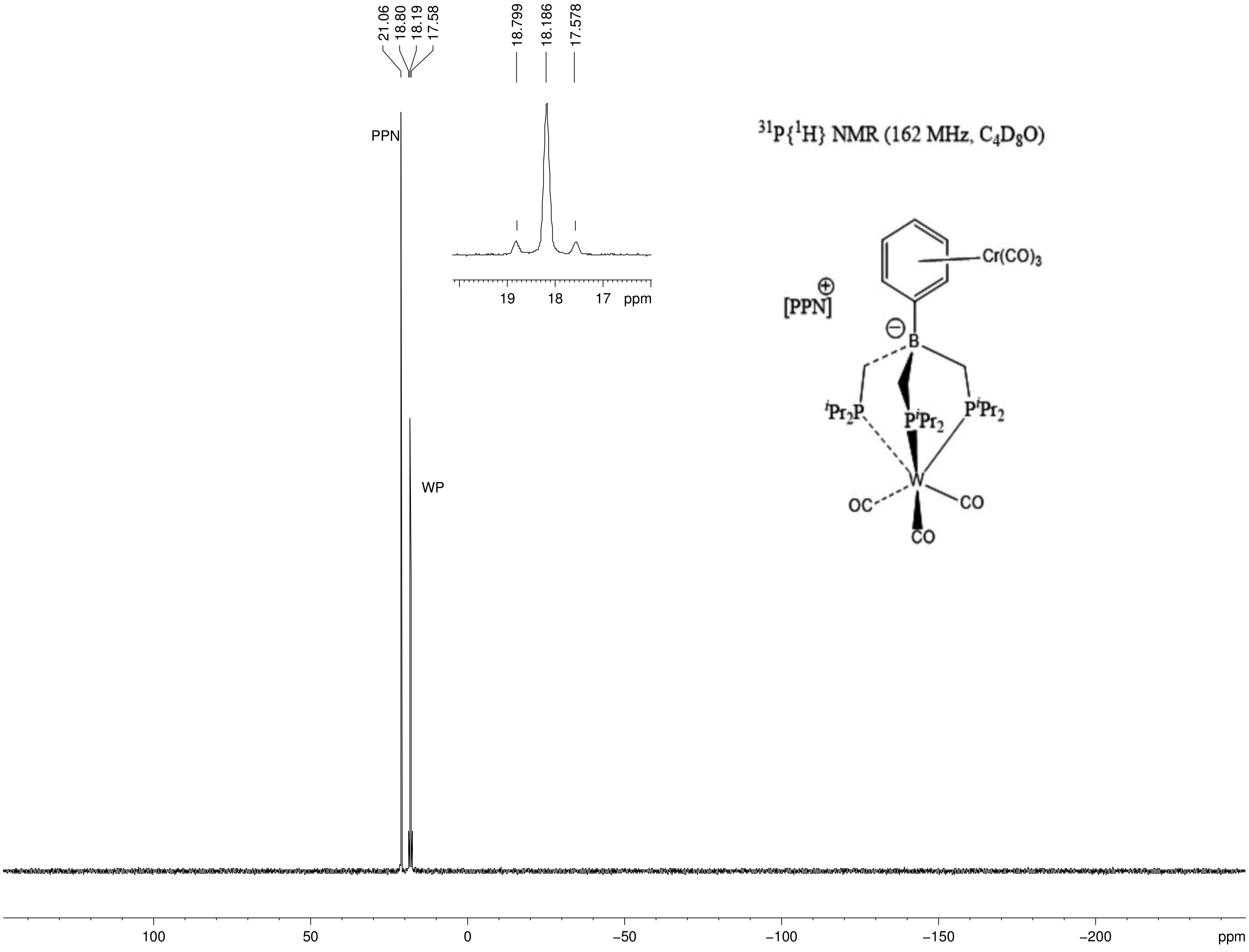


^{1}H NMR (400 MHz, C_4D_8O)



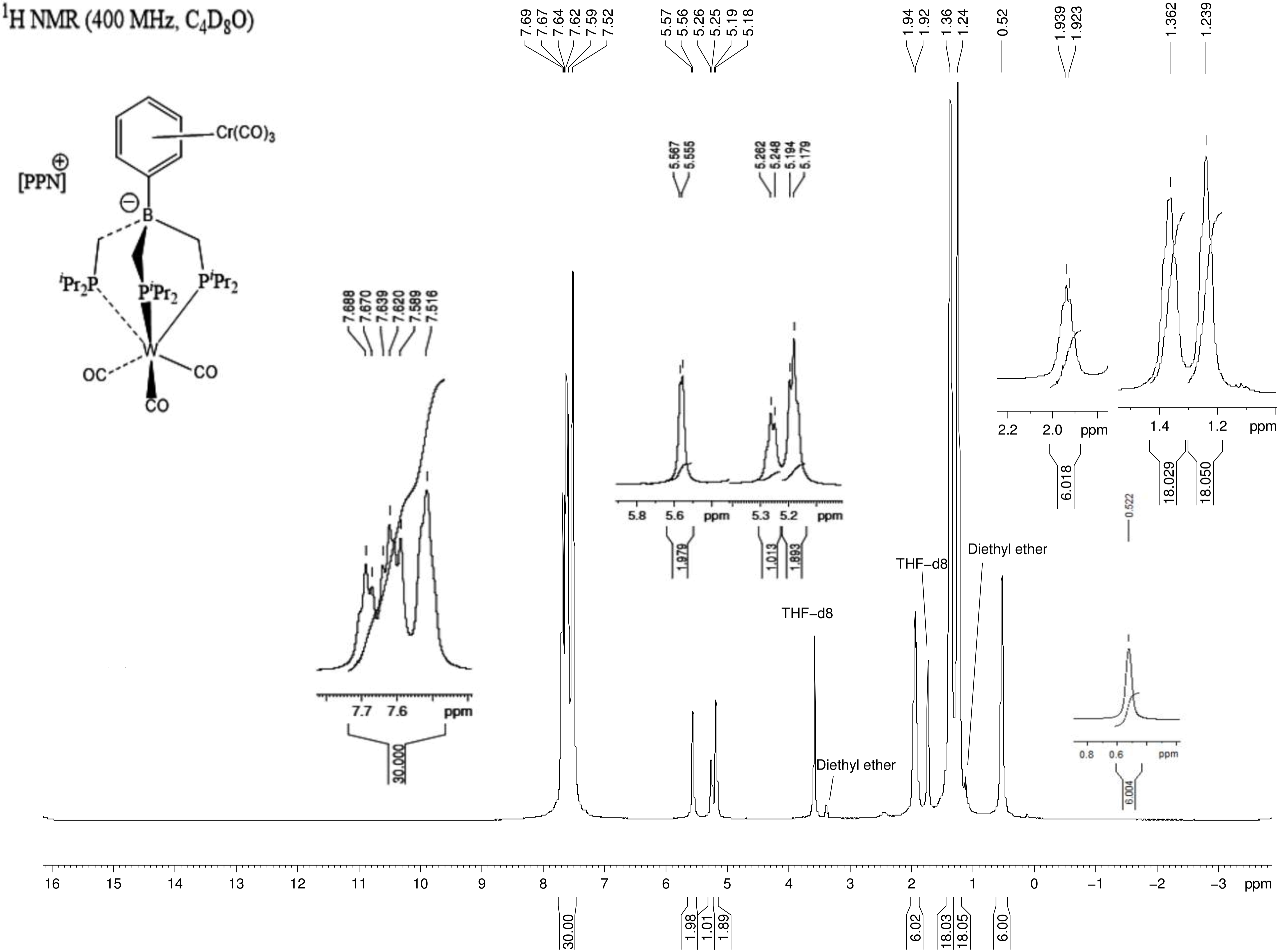


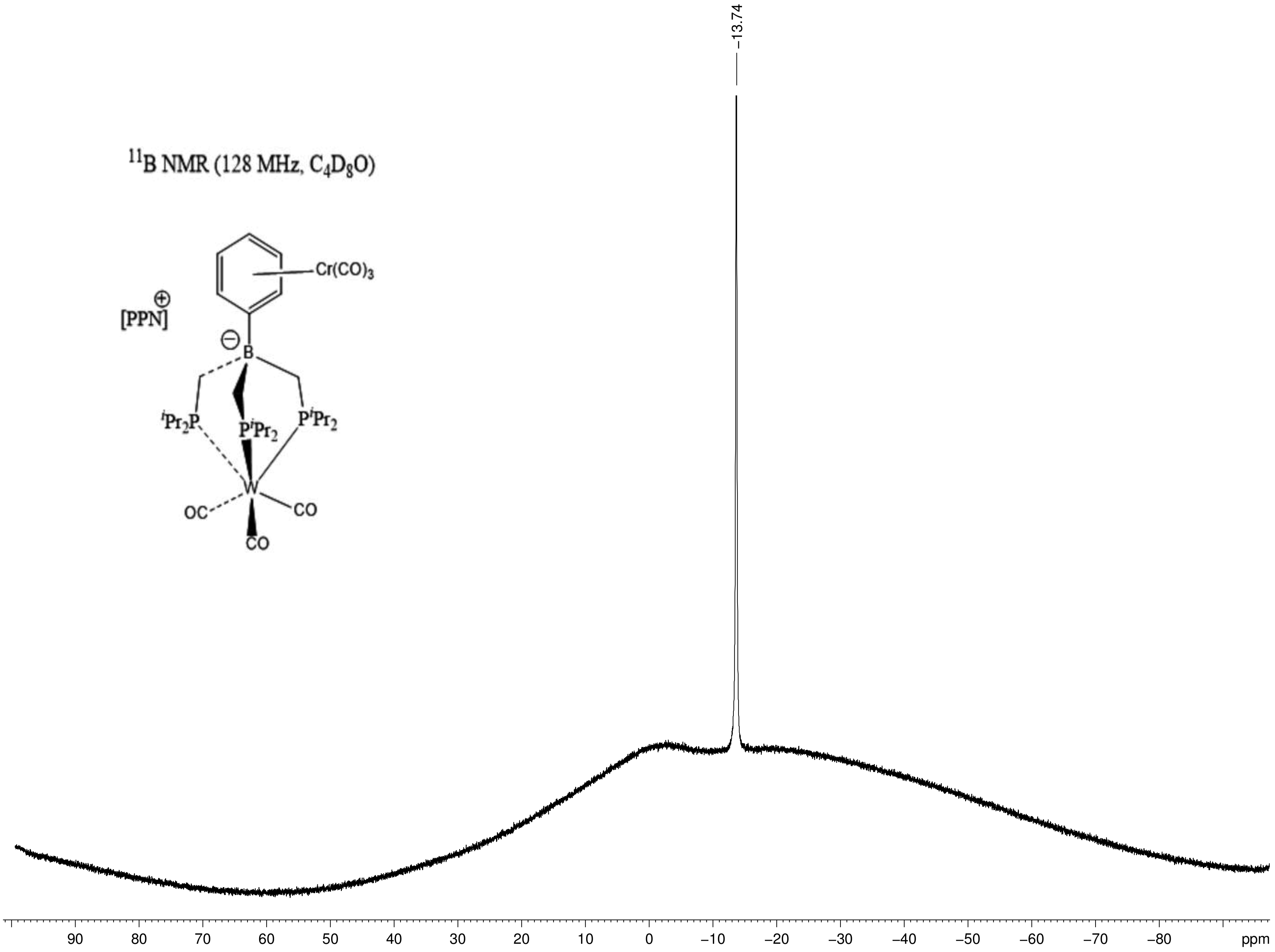
$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)



$^{31}P\{^{1}H\}$ NMR (162 MHz, C_4D_8O)

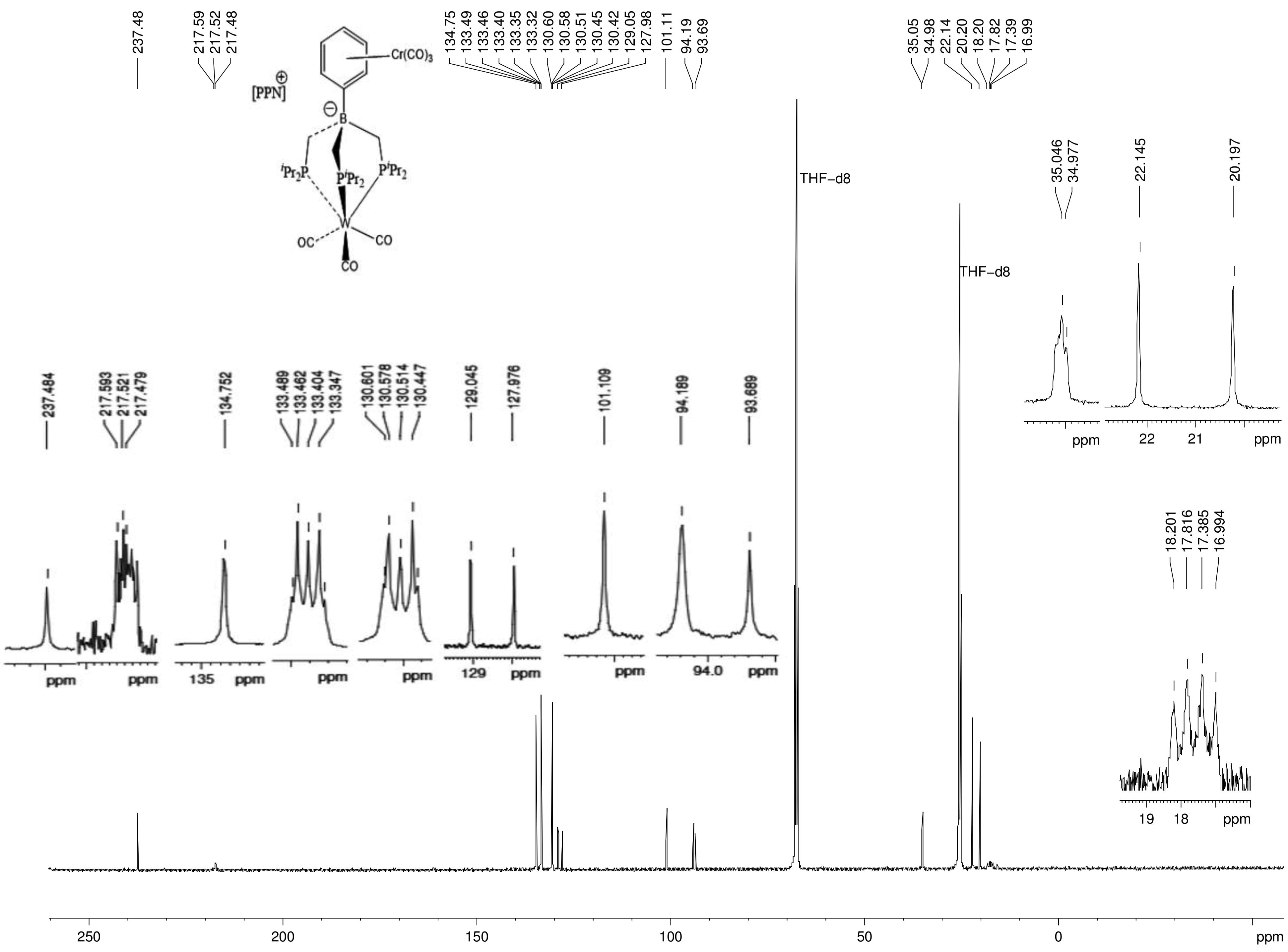
^{1}H NMR (400 MHz, C_4D_8O)

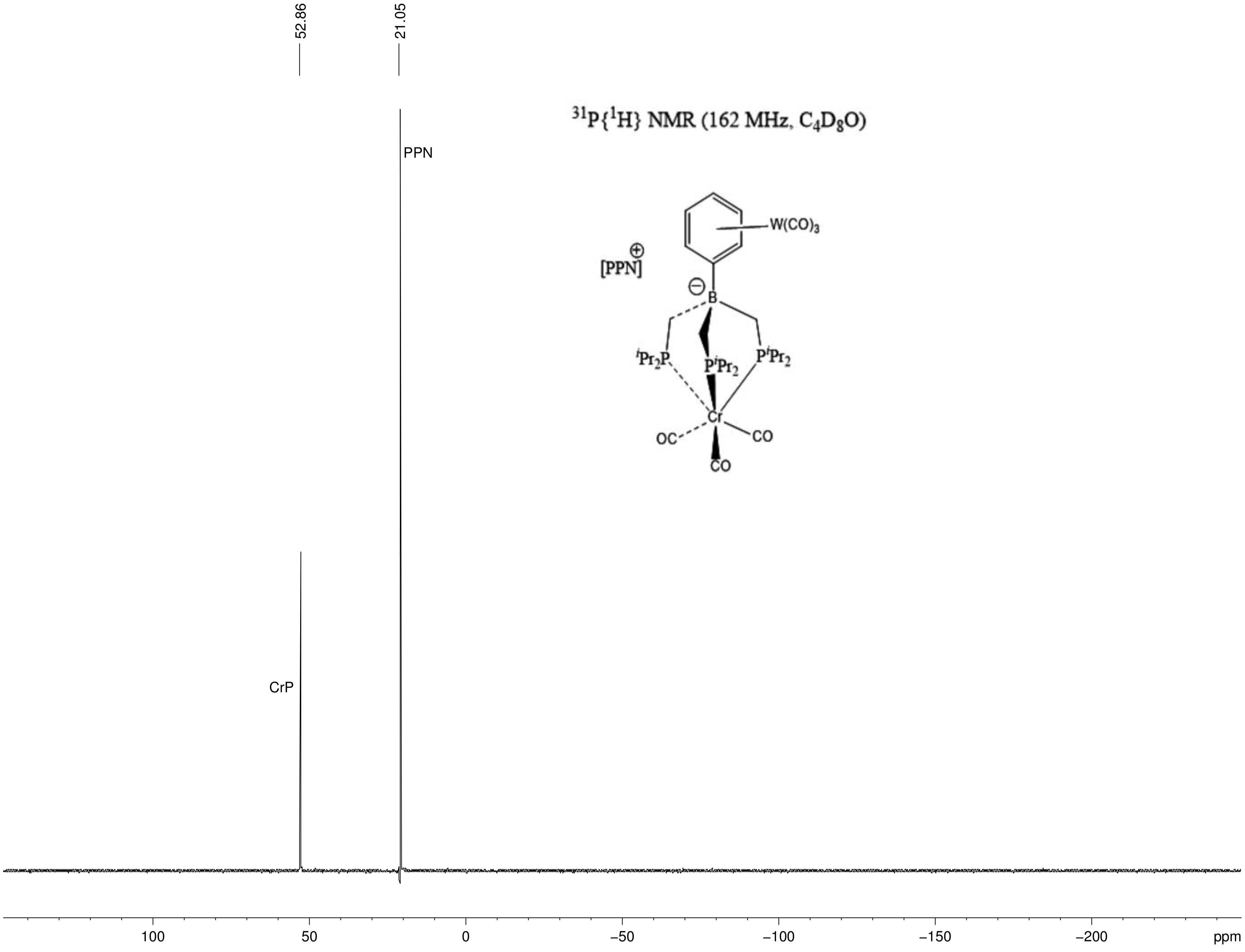




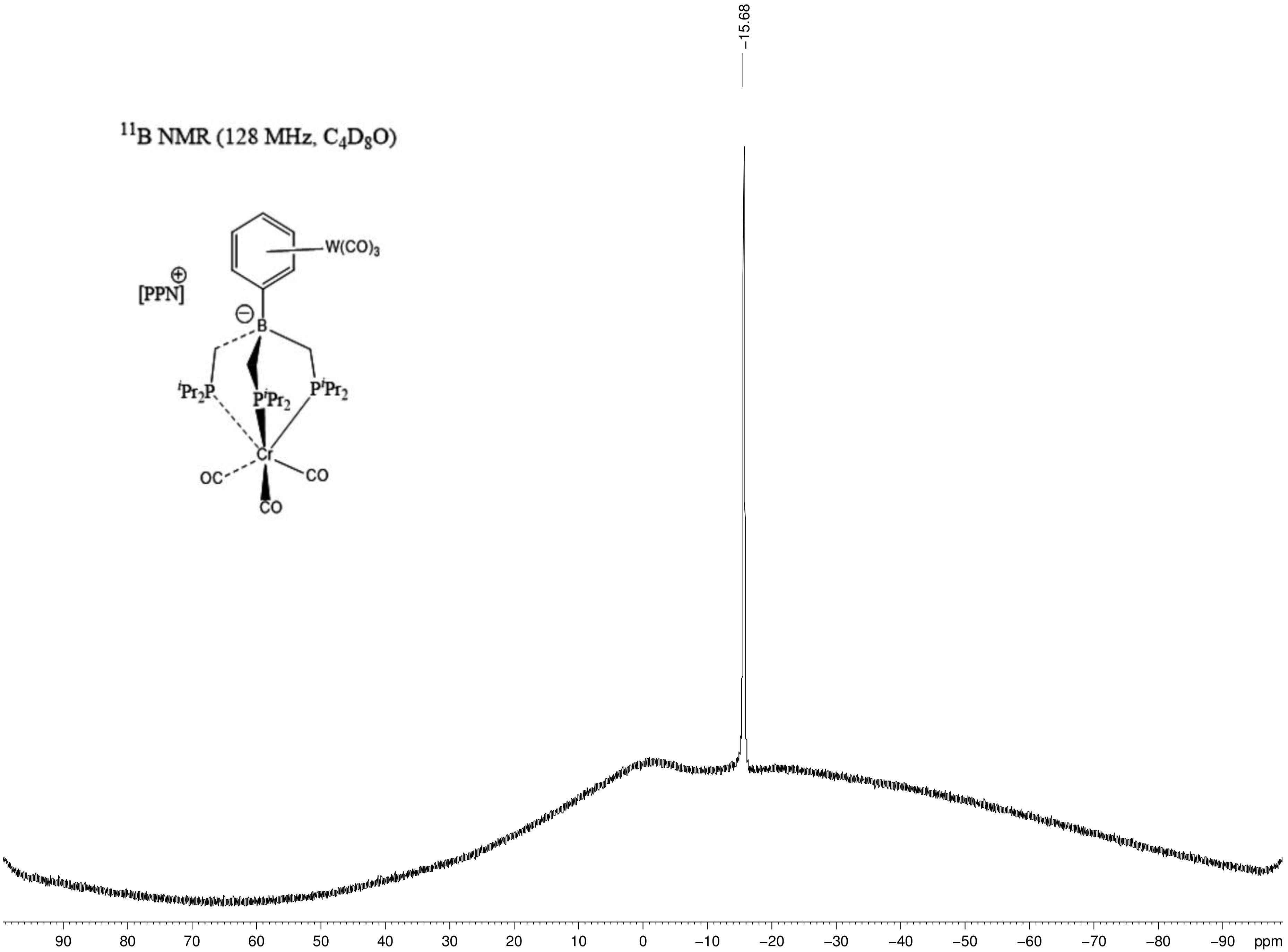
^{11}B NMR (128 MHz, C_4D_8O)

$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)



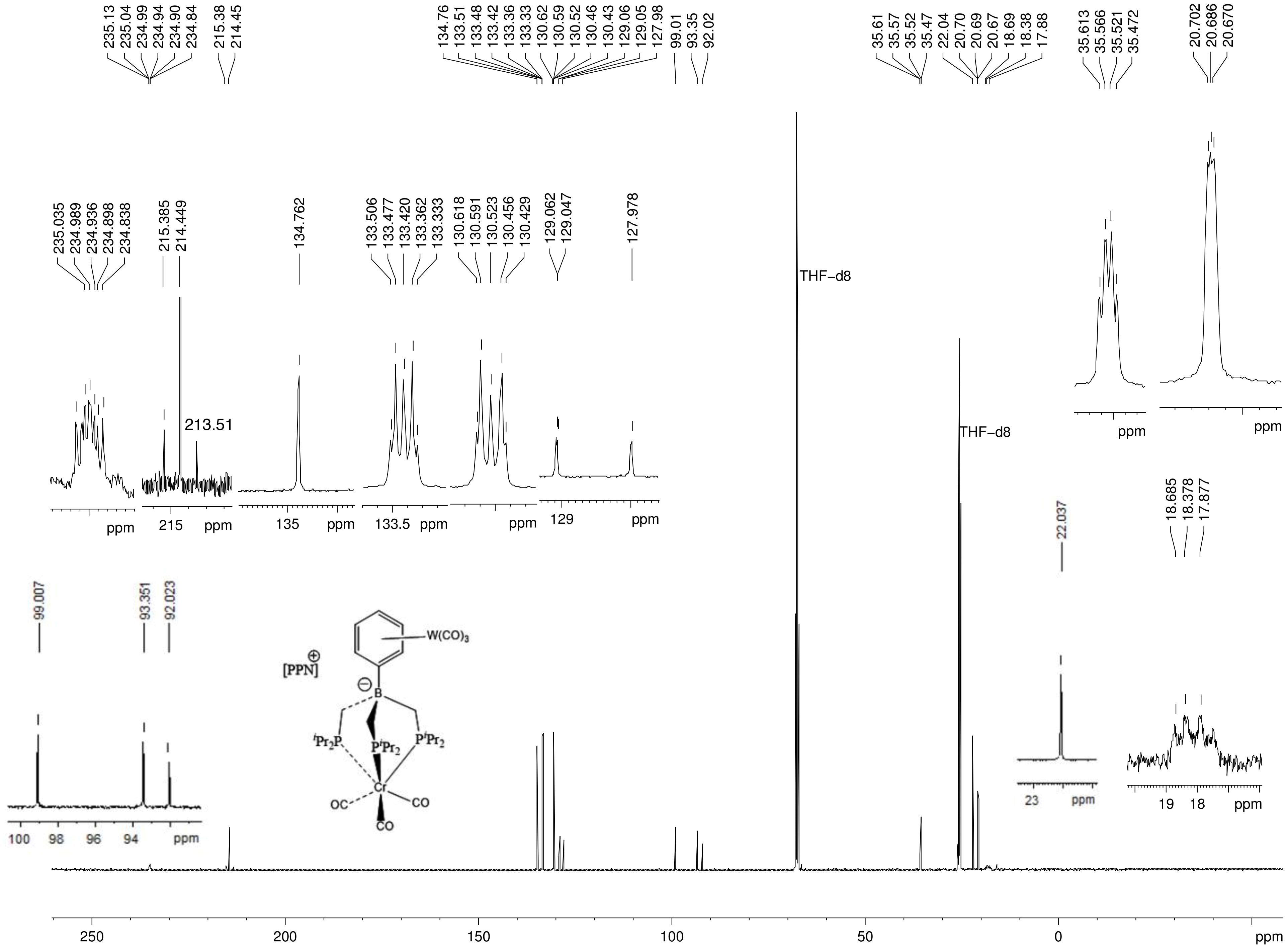


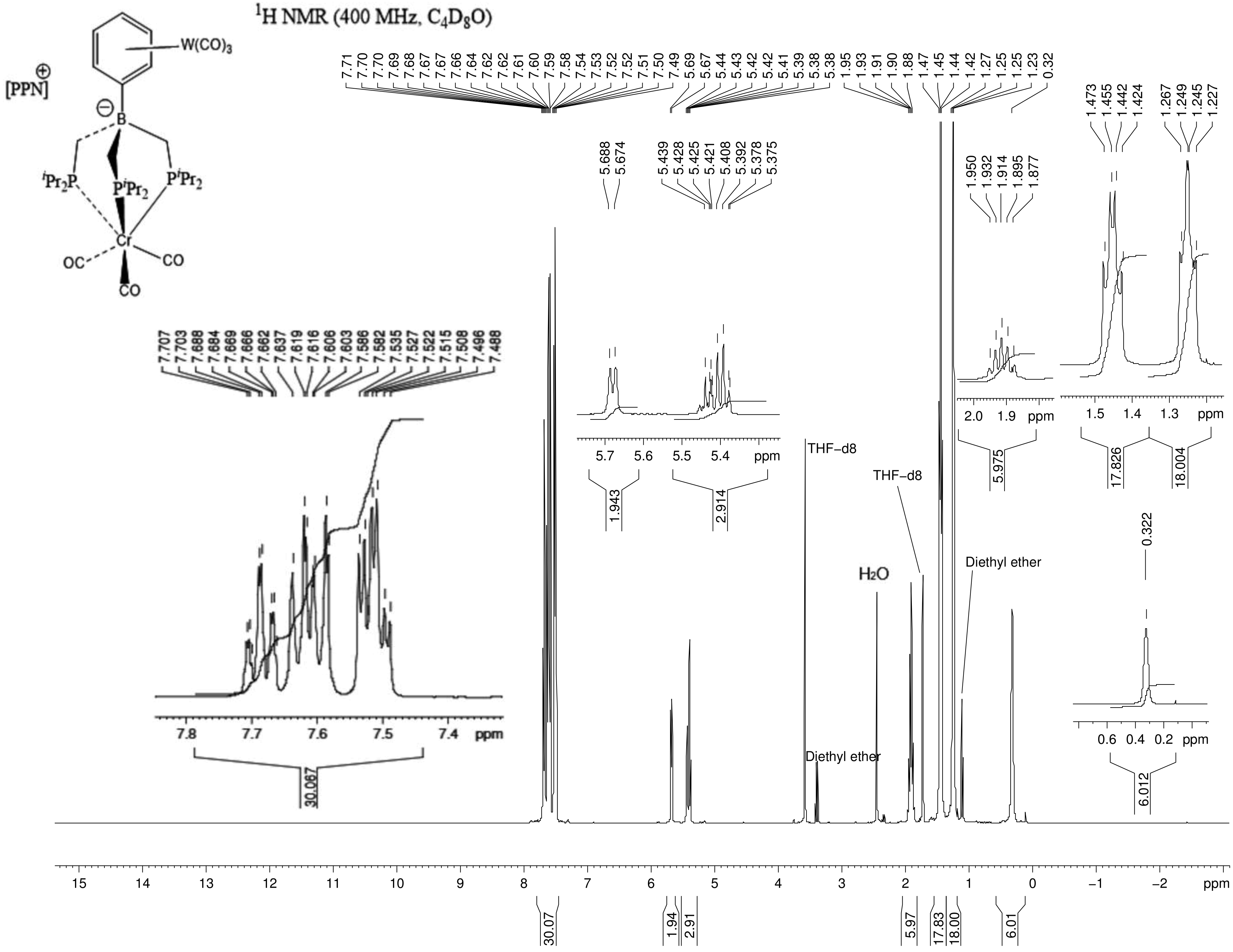
$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)



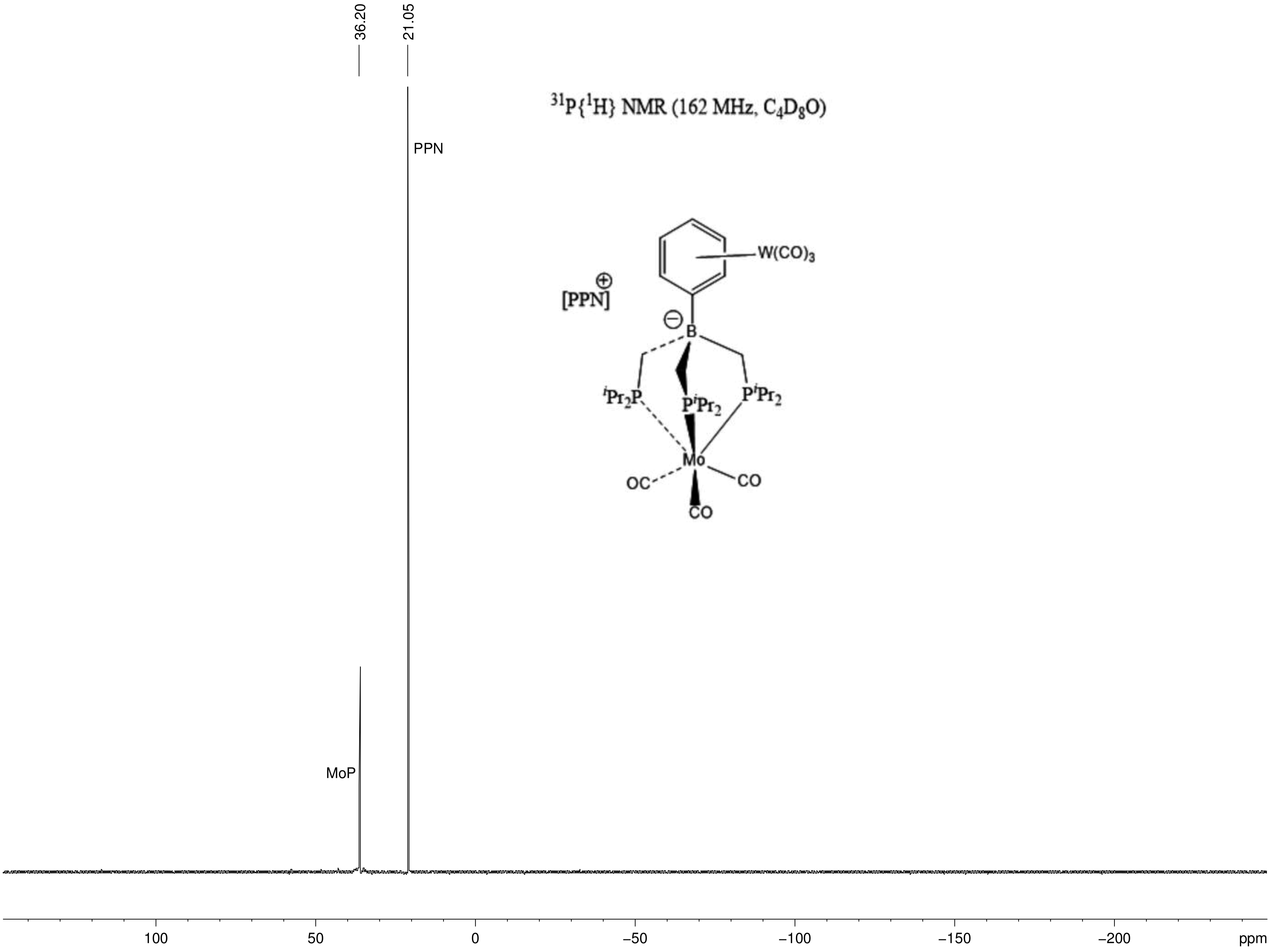
^{11}B NMR (128 MHz, C_4D_8O)

$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)



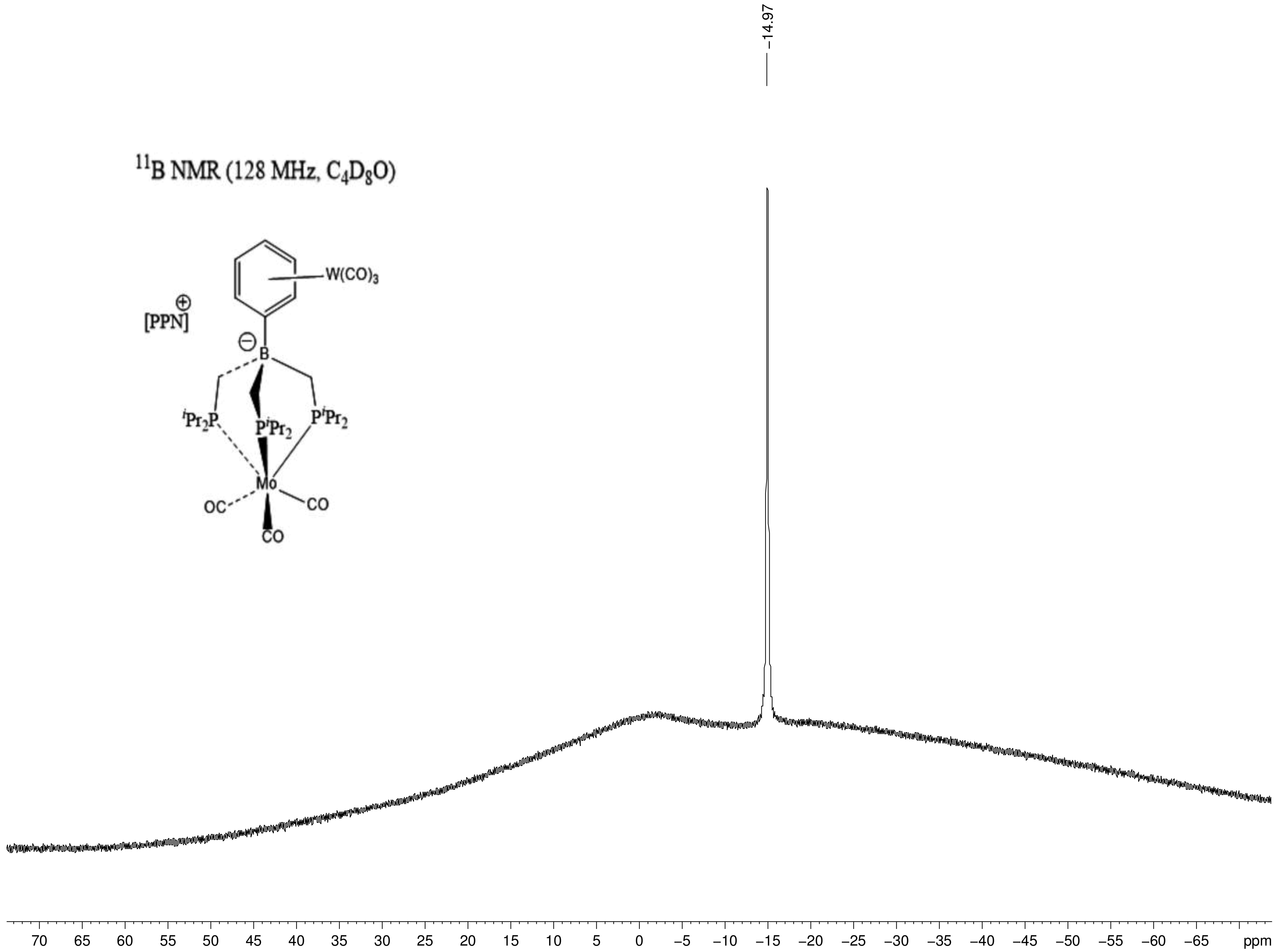


^{1}H NMR (400 MHz, C_4D_8O)

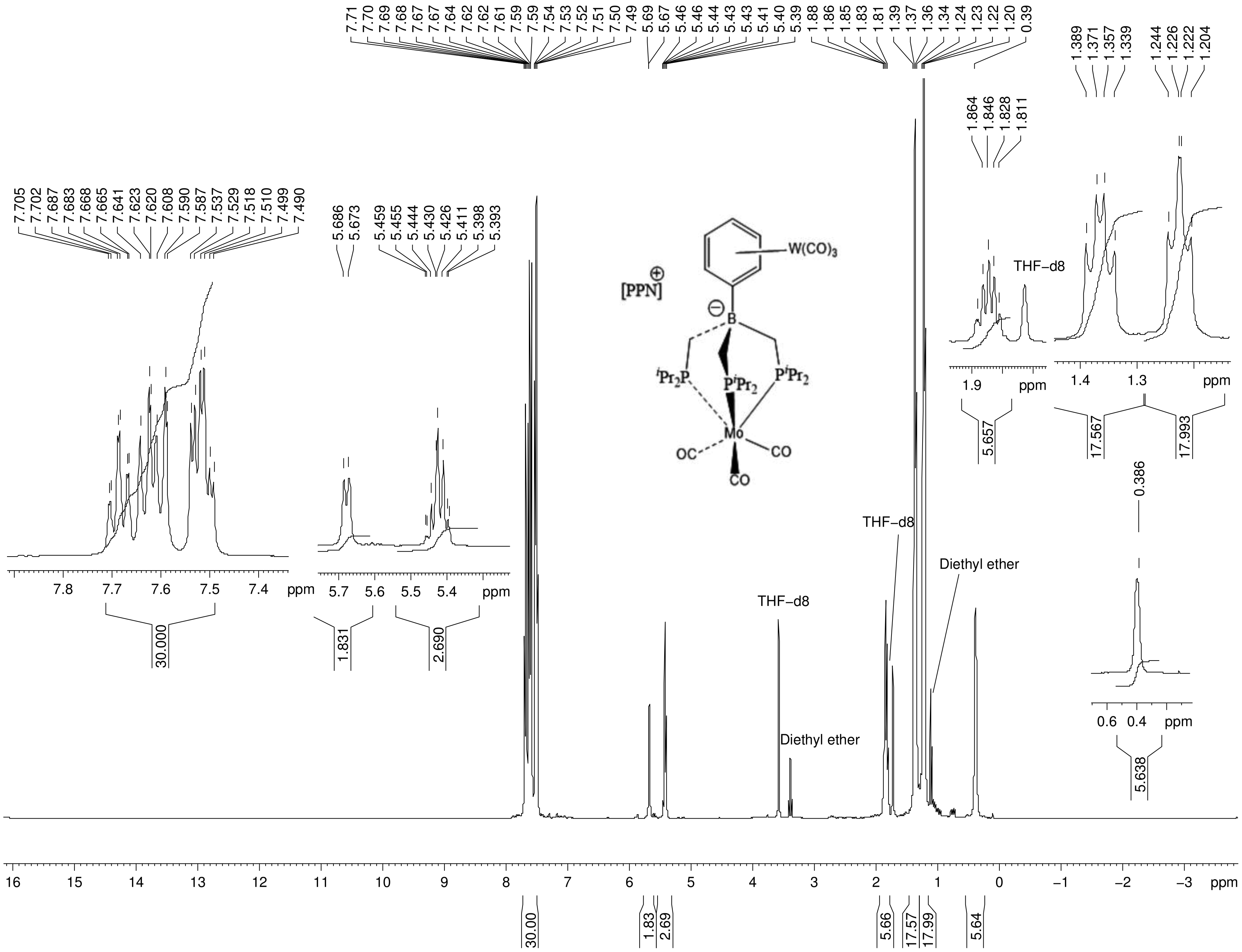


$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)

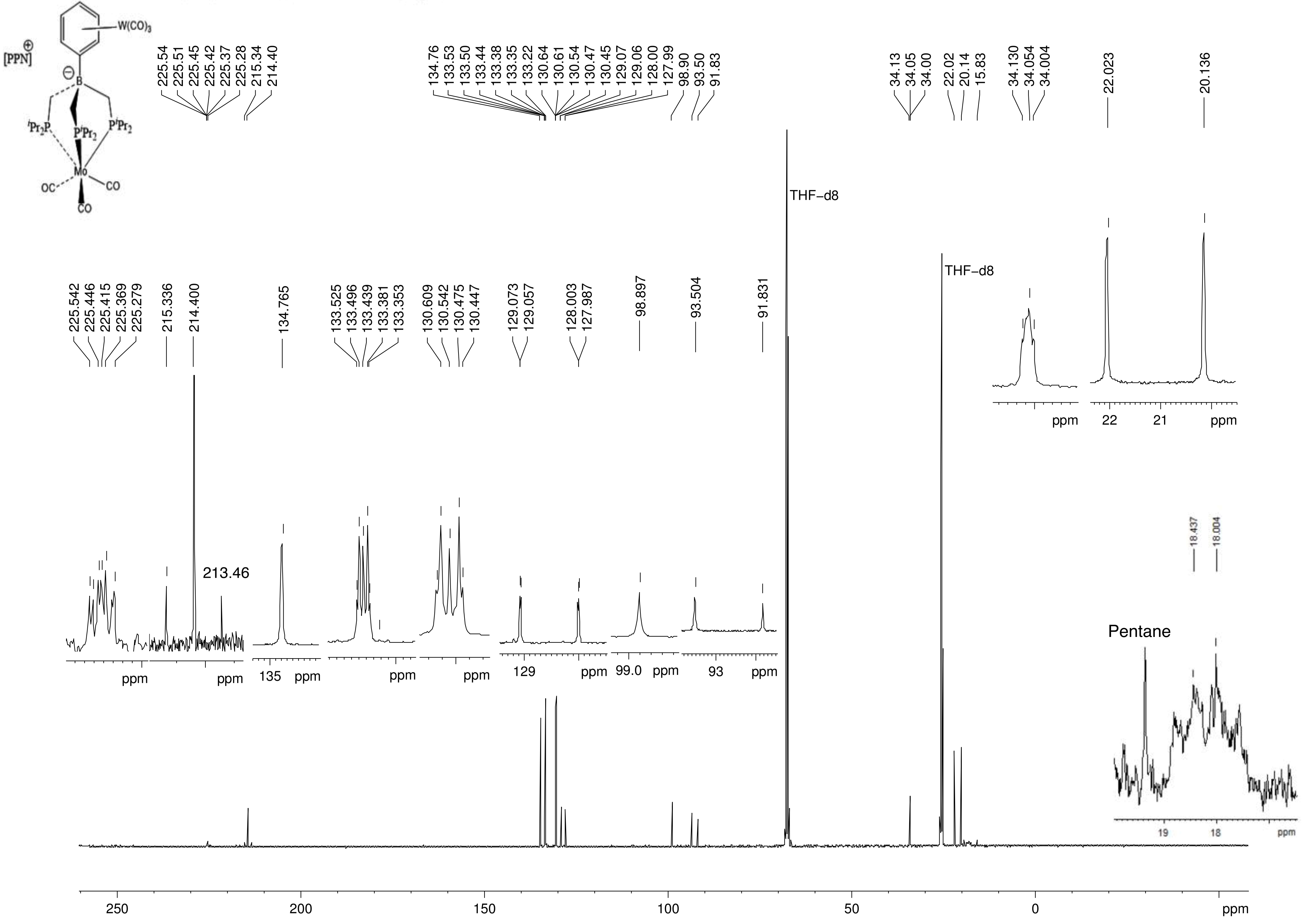
^{11}B NMR (128 MHz, C_4D_8O)



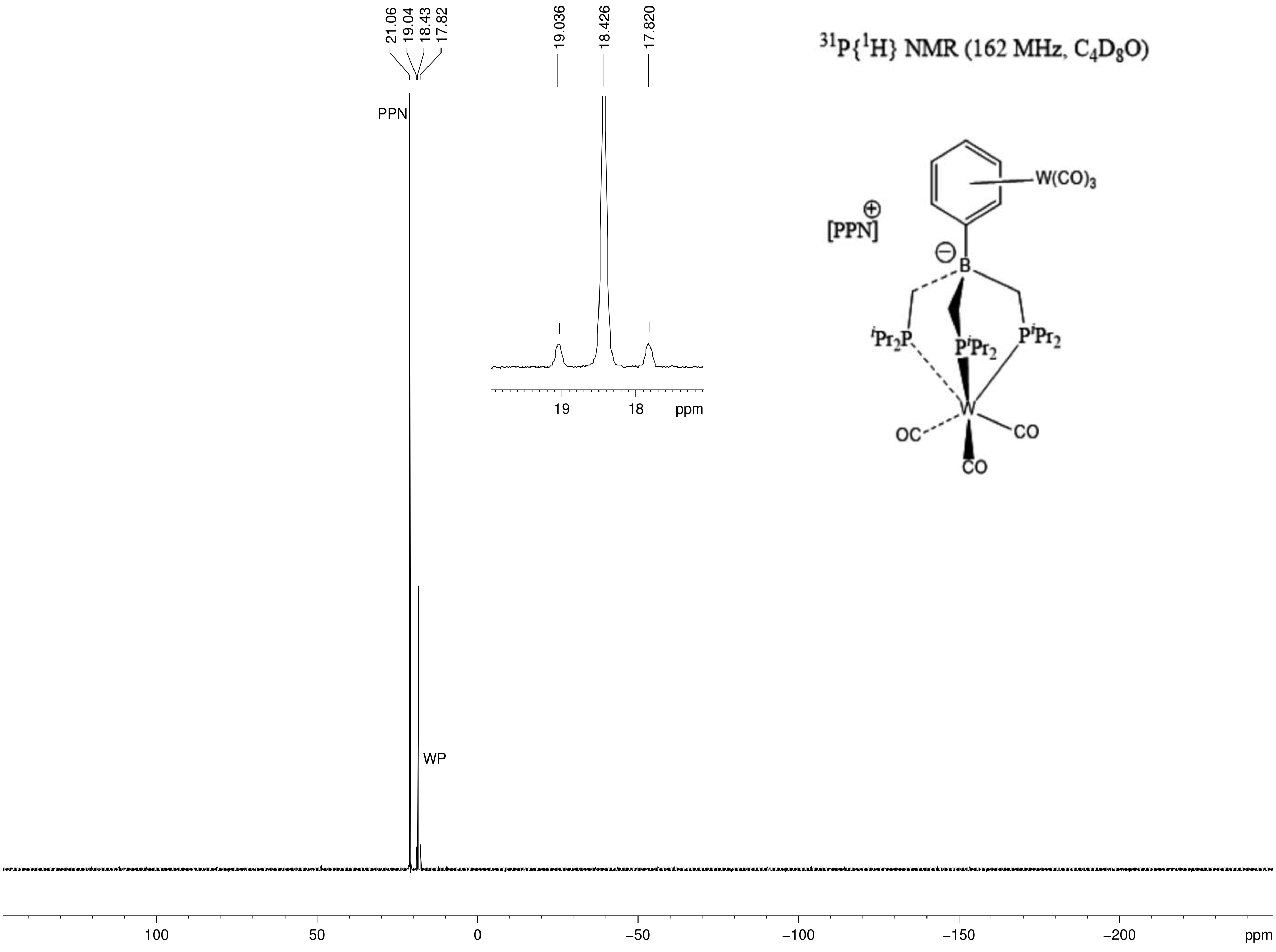
^{1}H NMR (400 MHz, C_4D_8O)



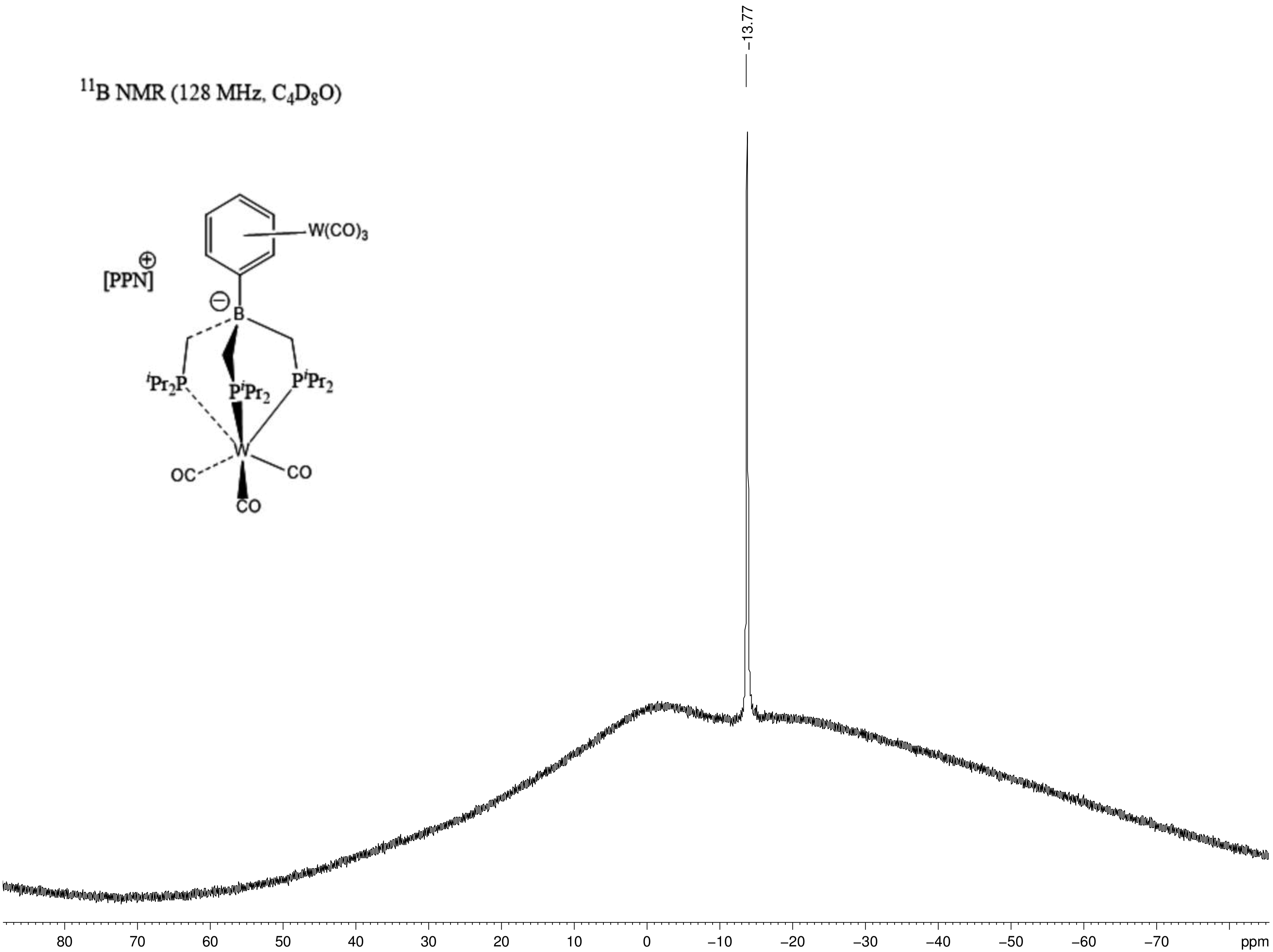
$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)



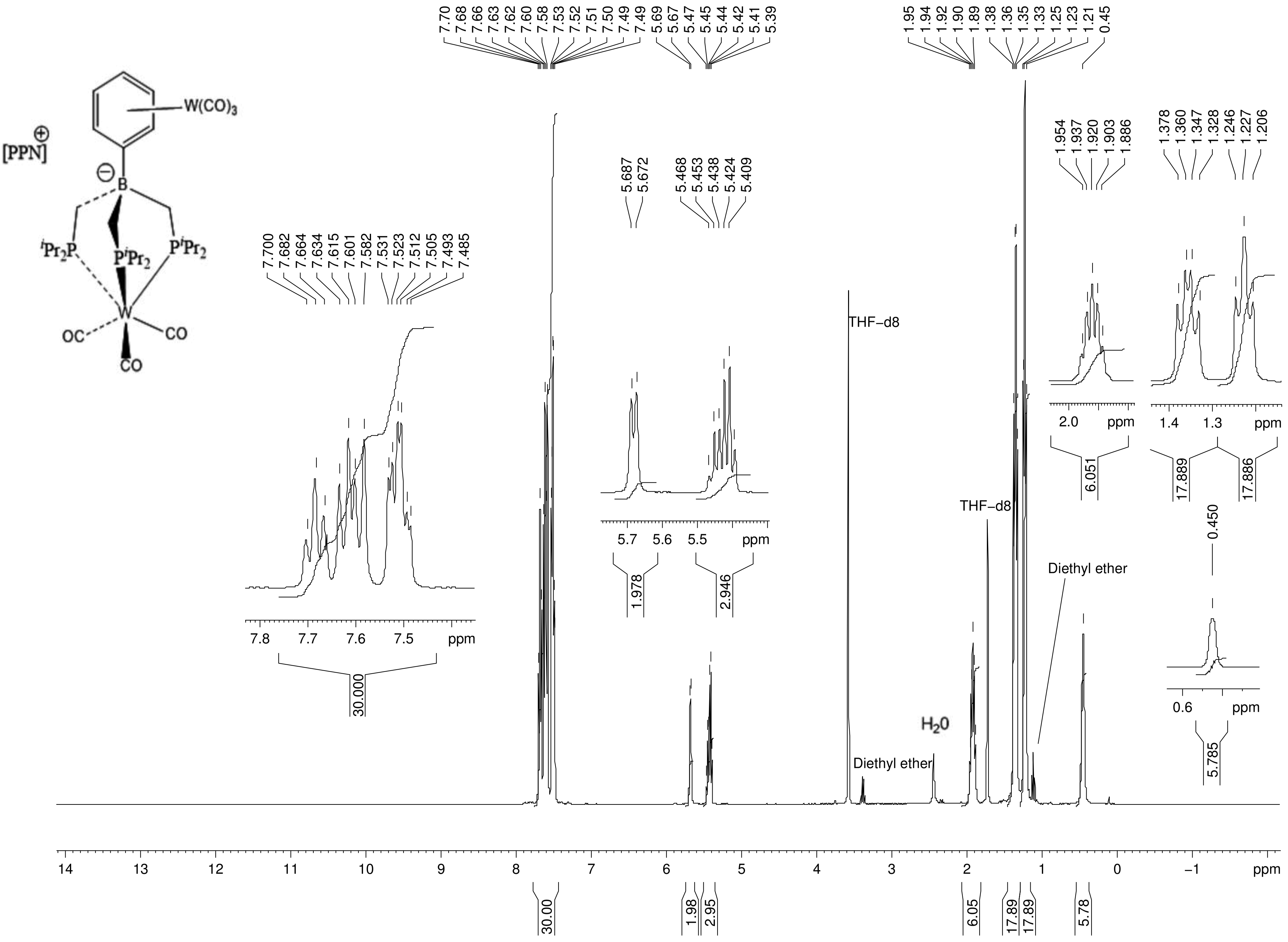
$^{31}P\{^{1}H\}$ NMR (162 MHz, C_4D_8O)



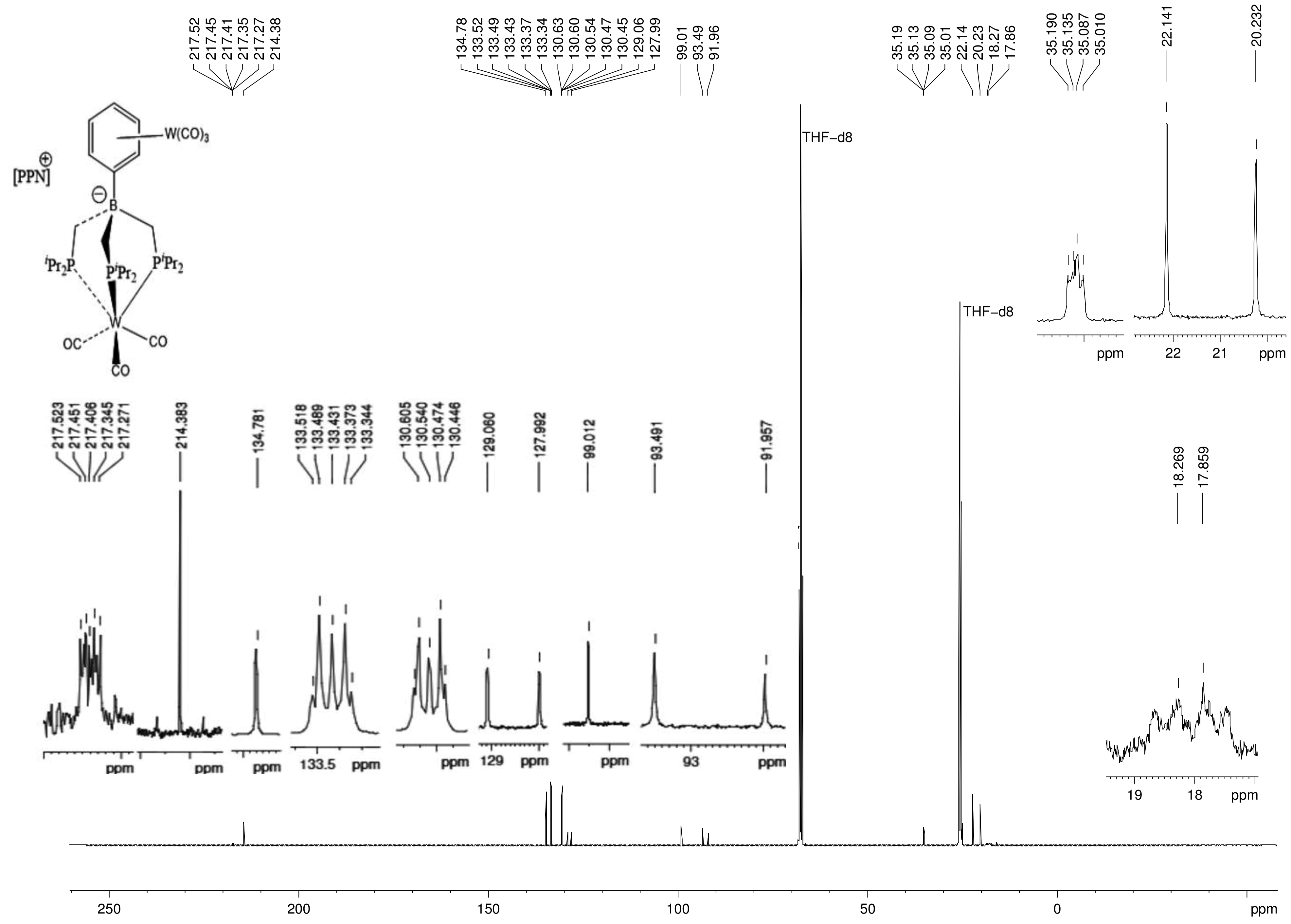
^{11}B NMR (128 MHz, C_4D_8O)



^{1}H NMR (400 MHz, C_4D_8O)

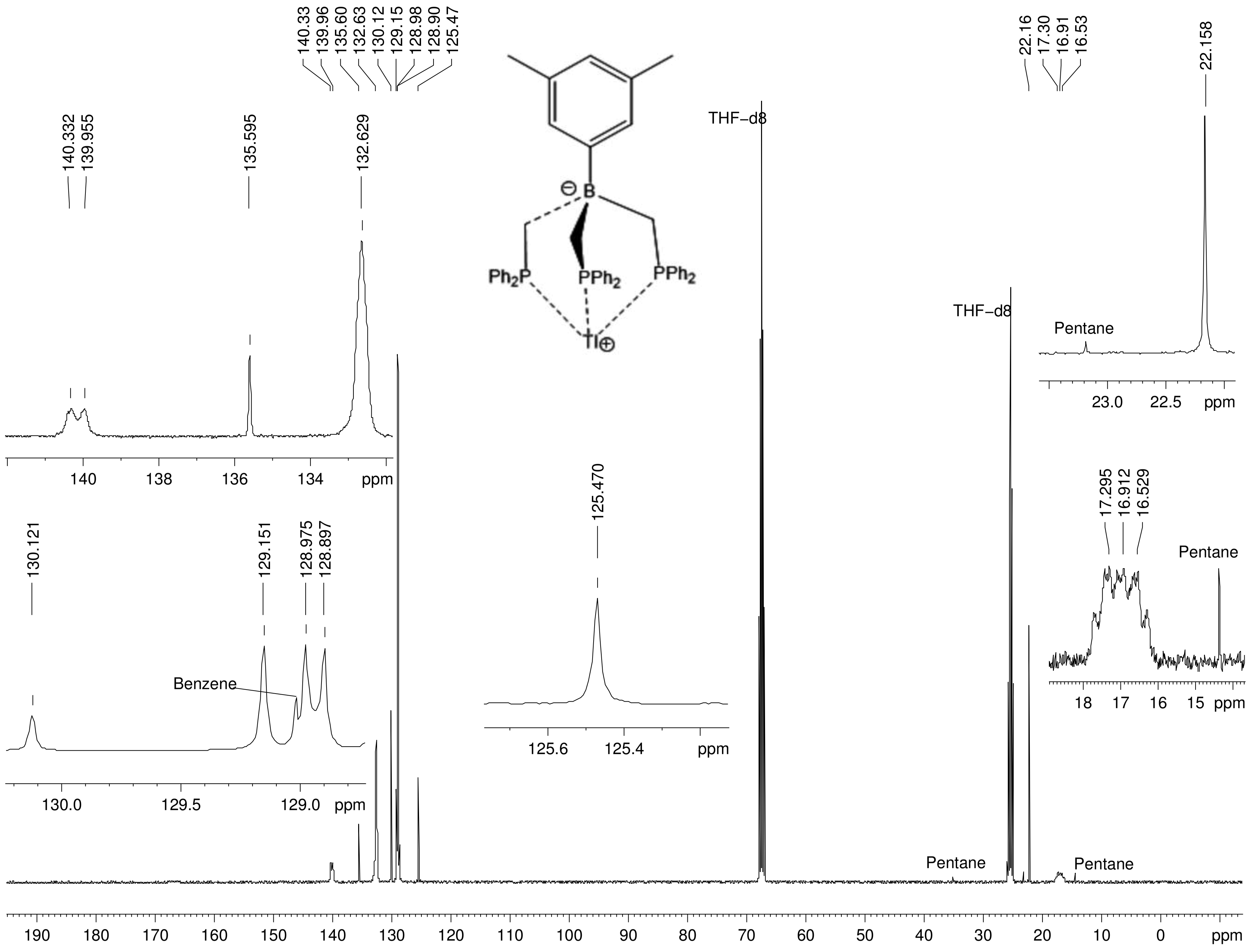


$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)

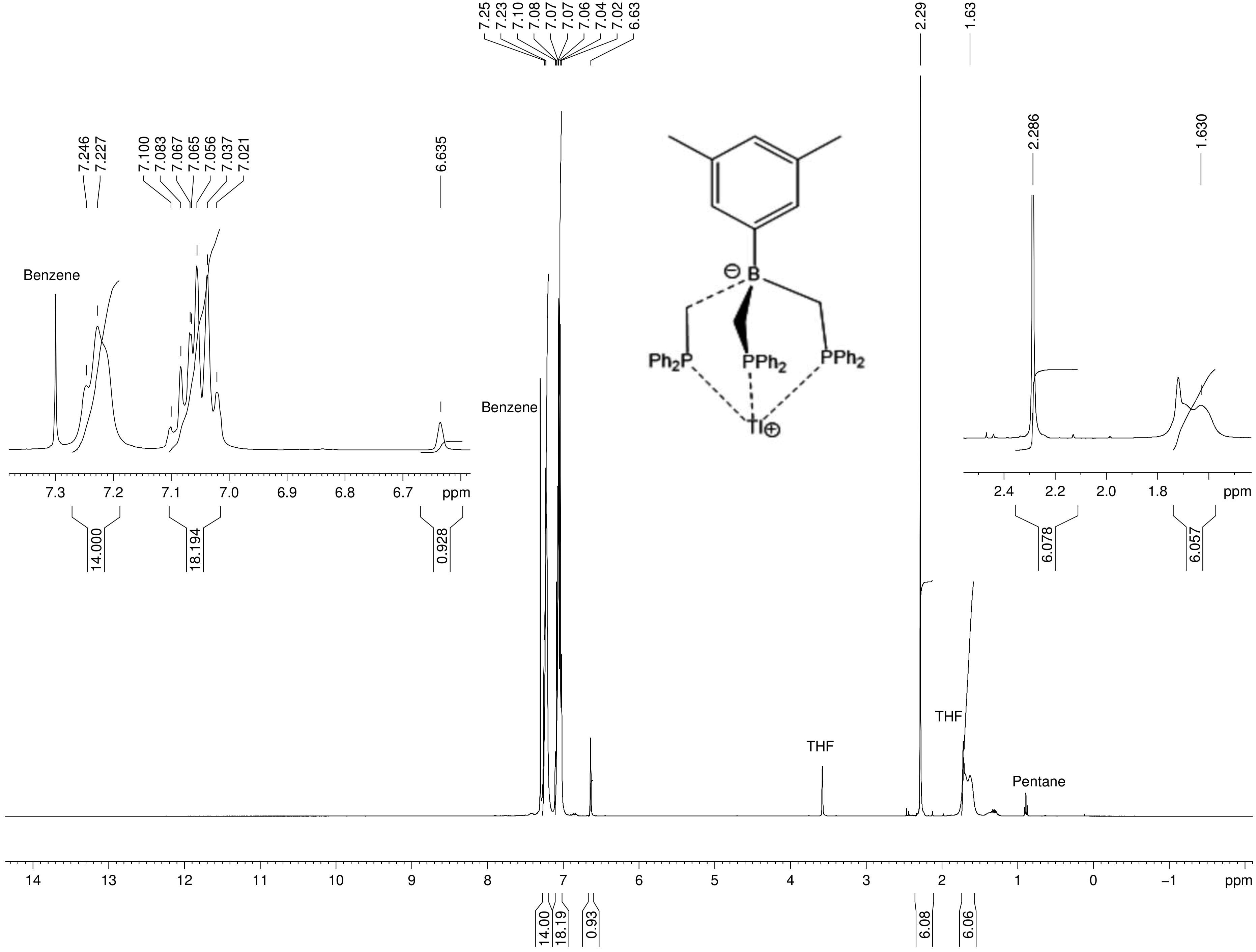


^{11}B NMR (128 MHz, C_4D_8O)

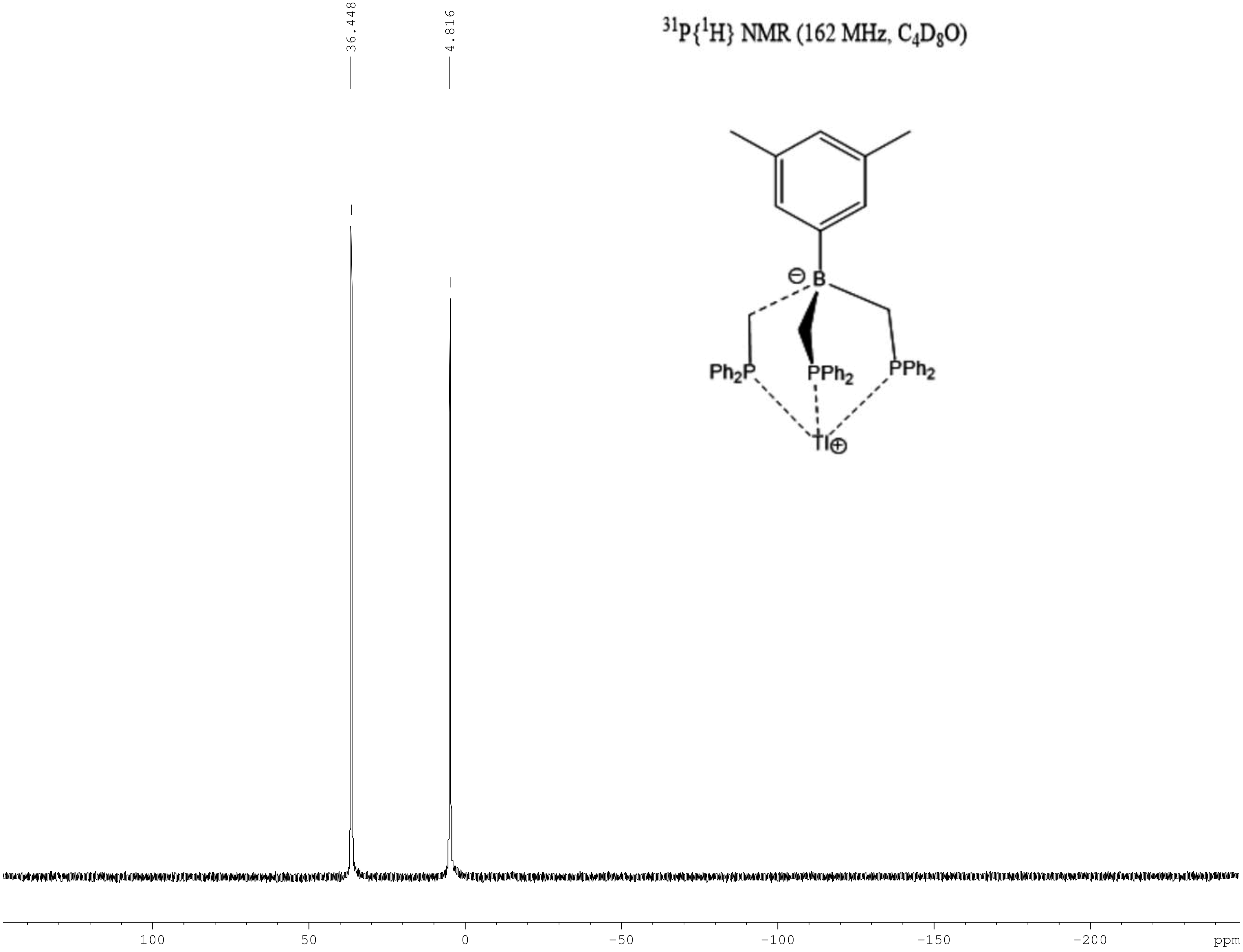
$^{13}C\{^{1}H\}$ NMR (101 MHz, C_4D_8O)



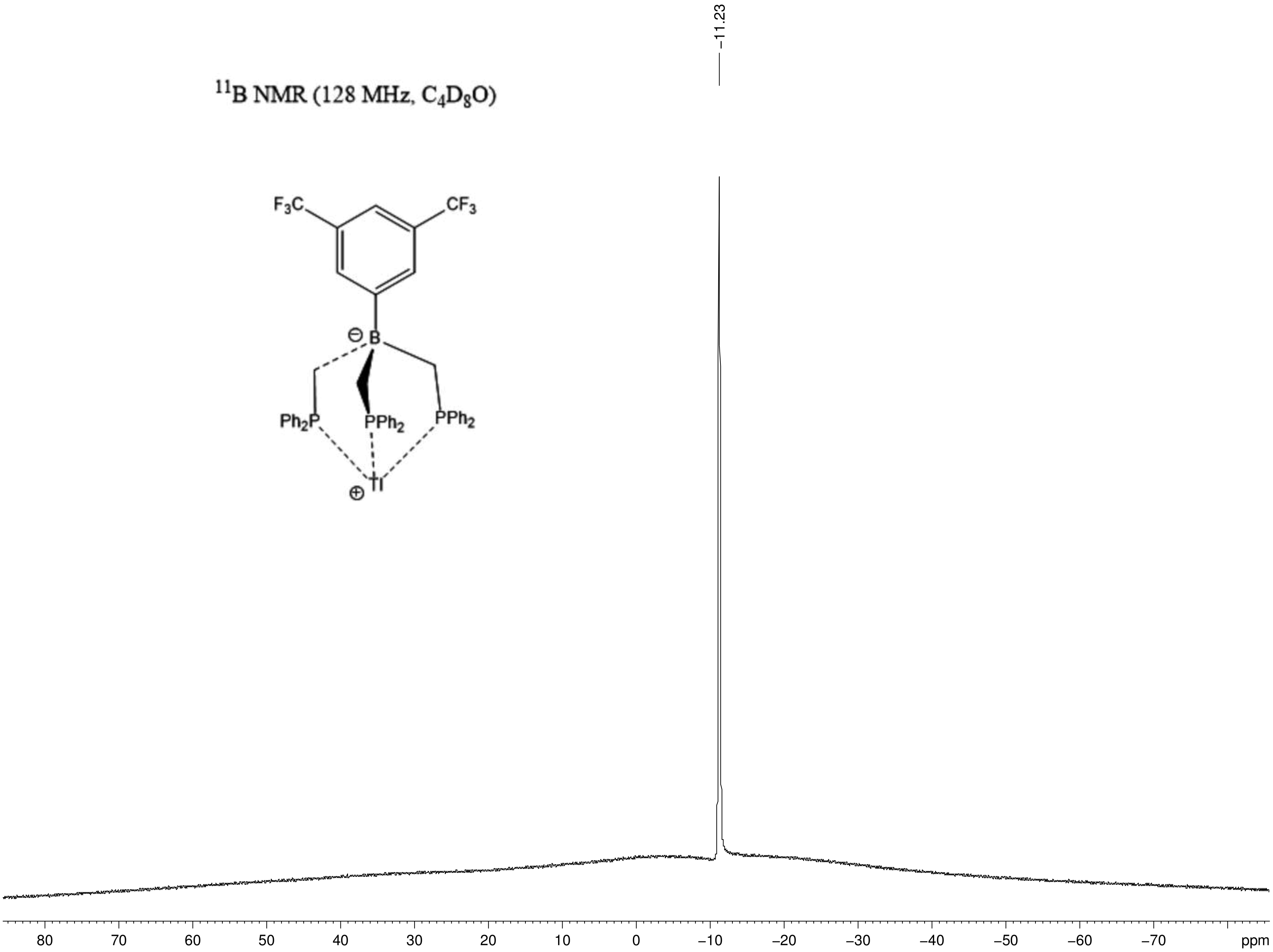
¹H NMR (400 MHz, C_4D_8O)



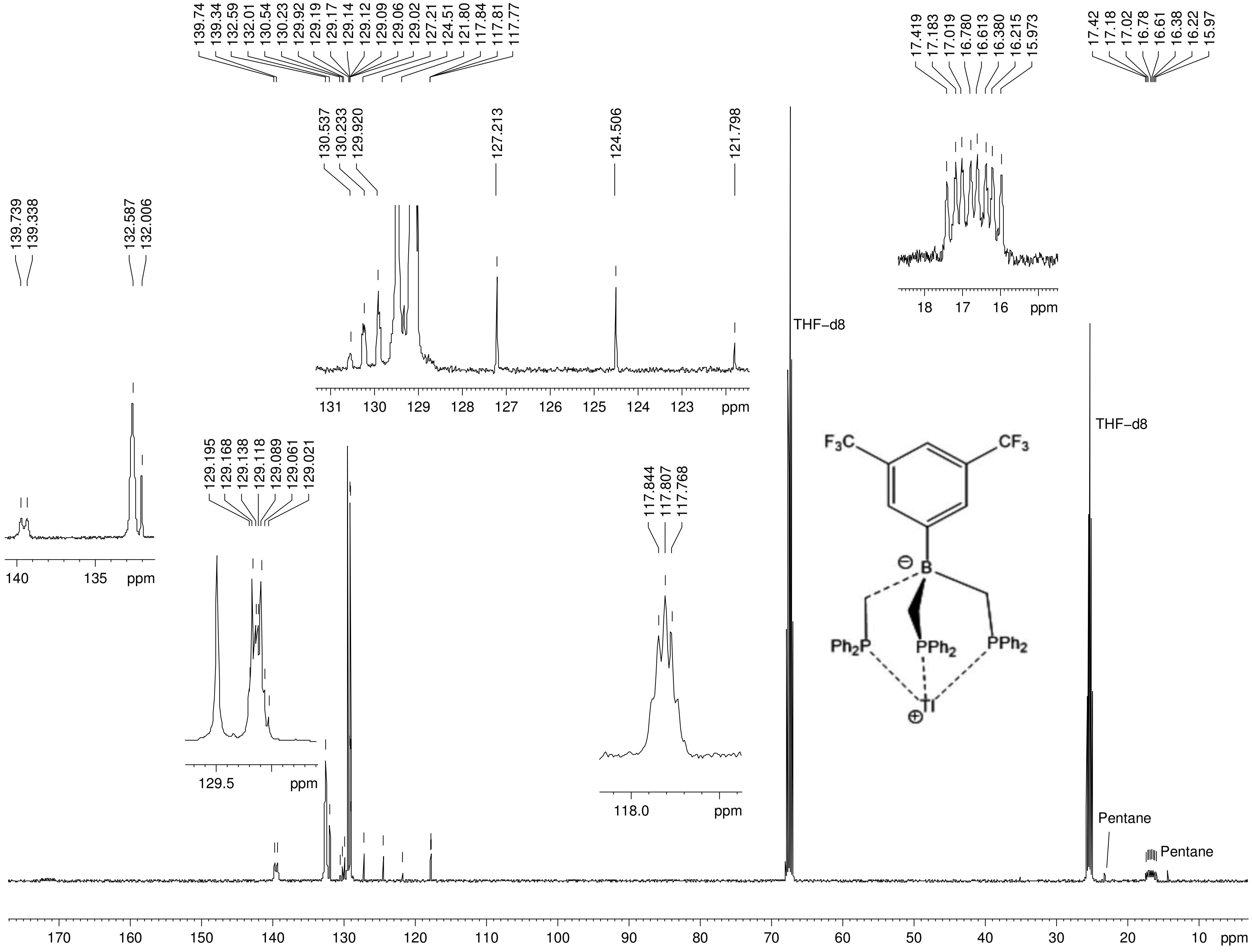
$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)

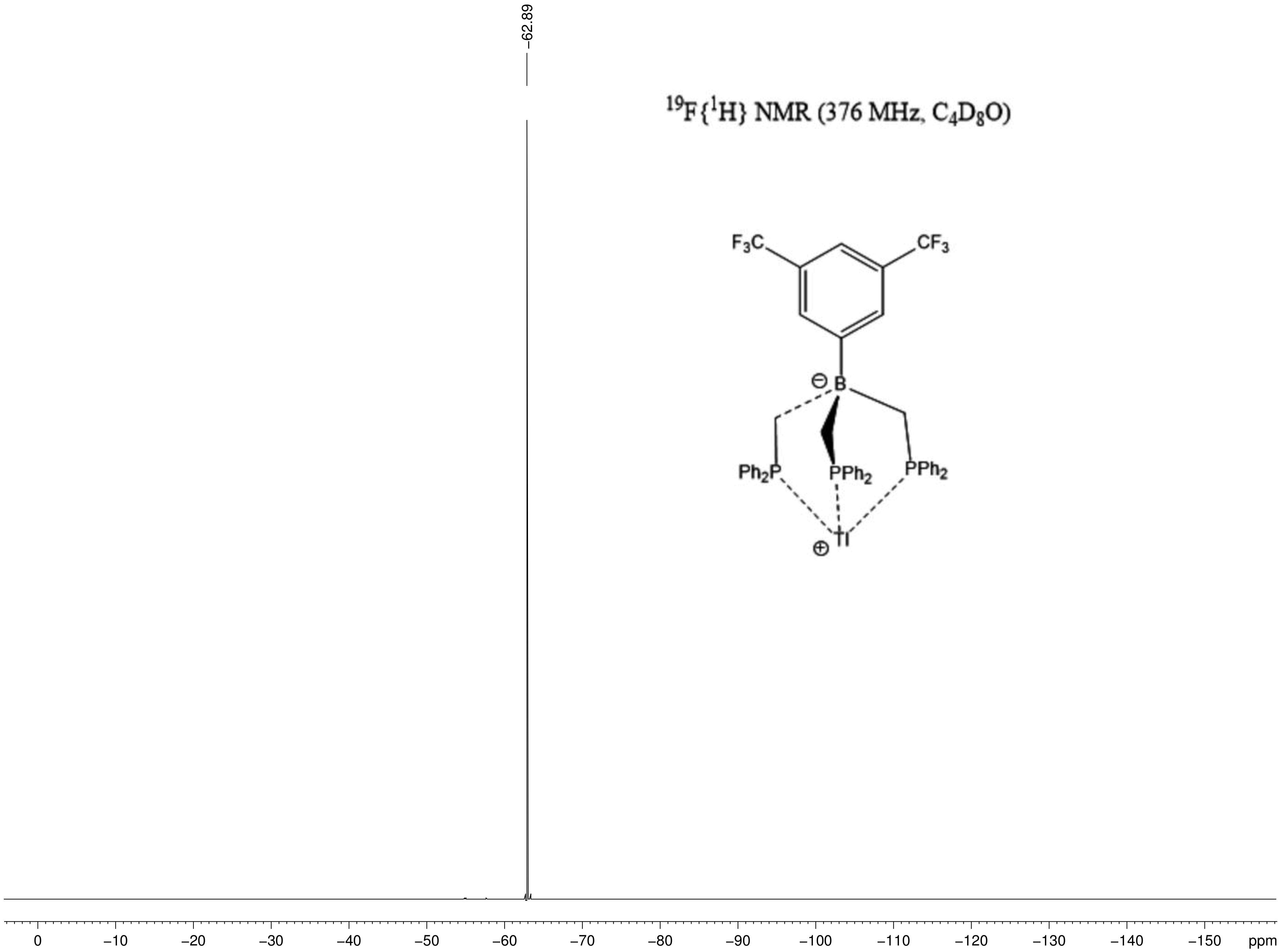


^{11}B NMR (128 MHz, C_4D_8O)

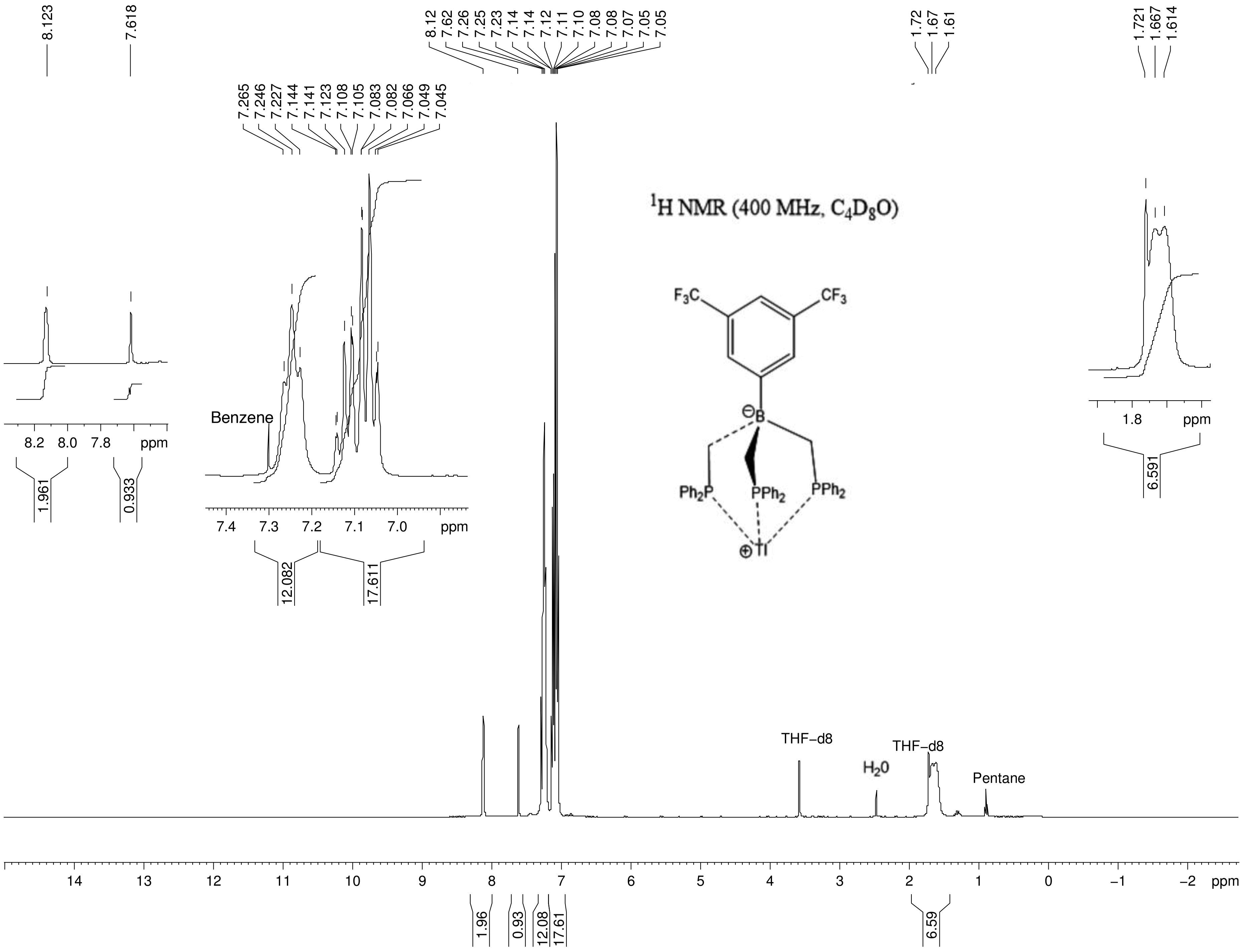


$^{13}C\{^{1}H\}$ NMR (101 MHz, C_4D_8O)

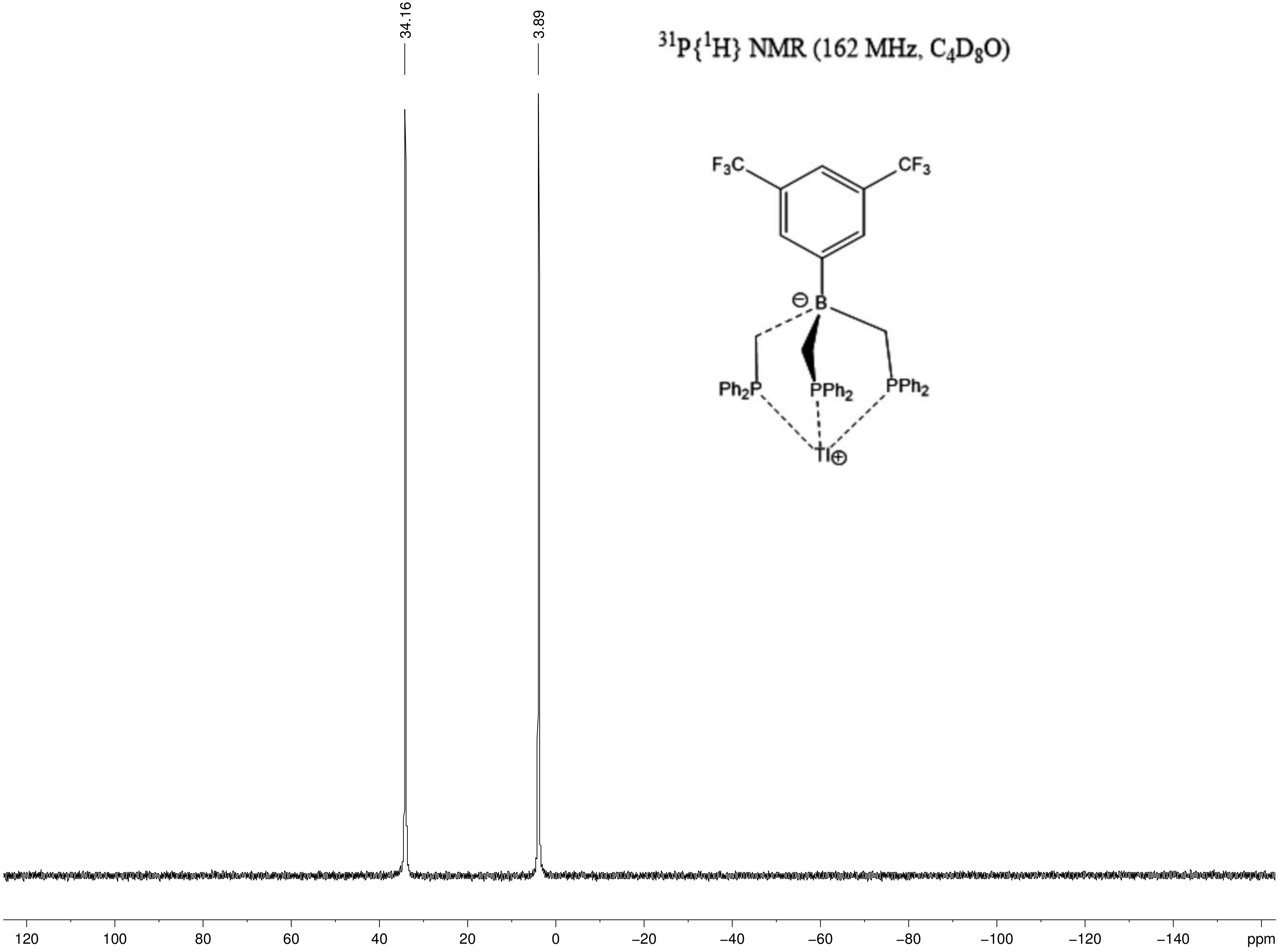




$^{19}F\{^1H\}$ NMR (376 MHz, C_4D_8O)

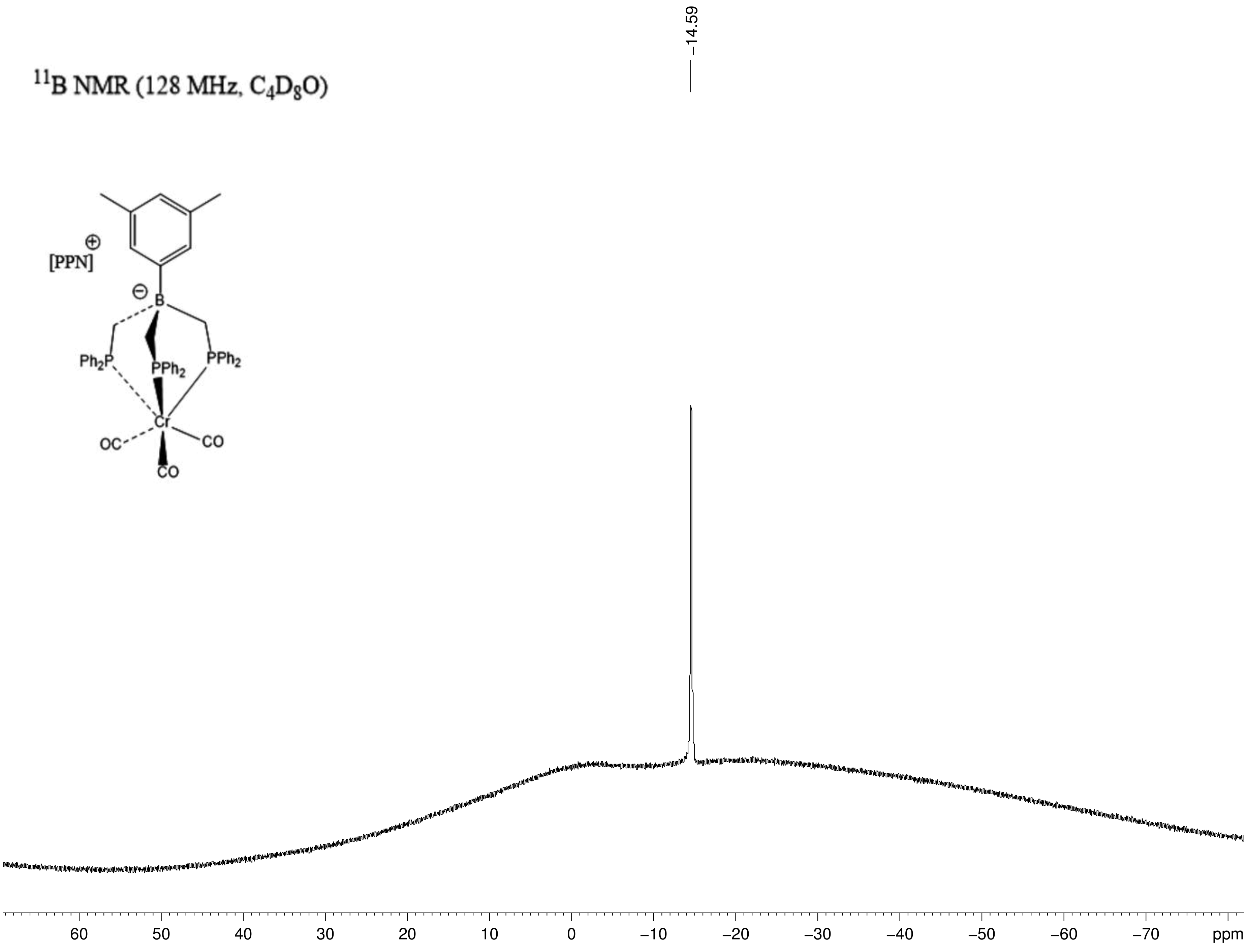


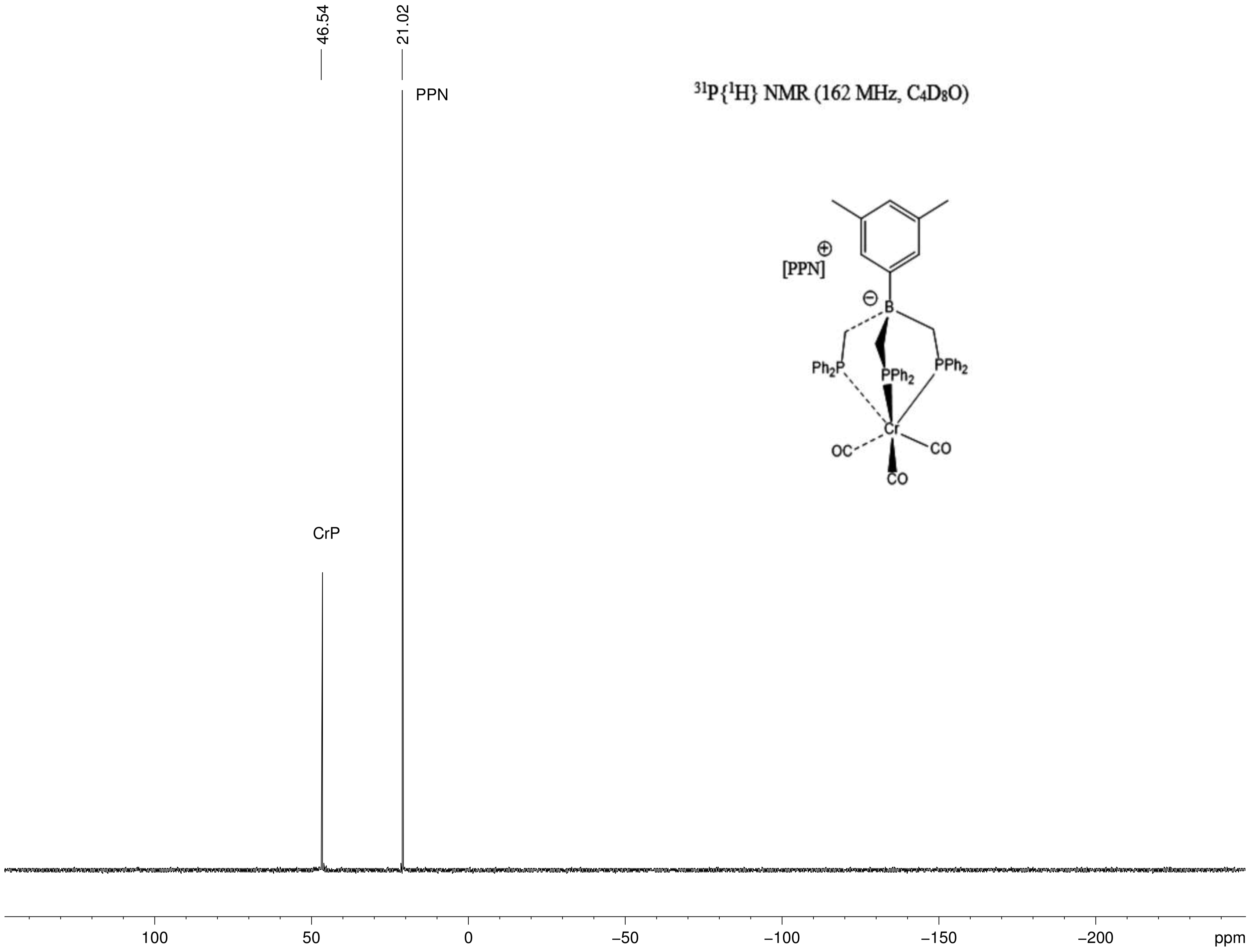
^{1}H NMR (400 MHz, C_4D_8O)



$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)

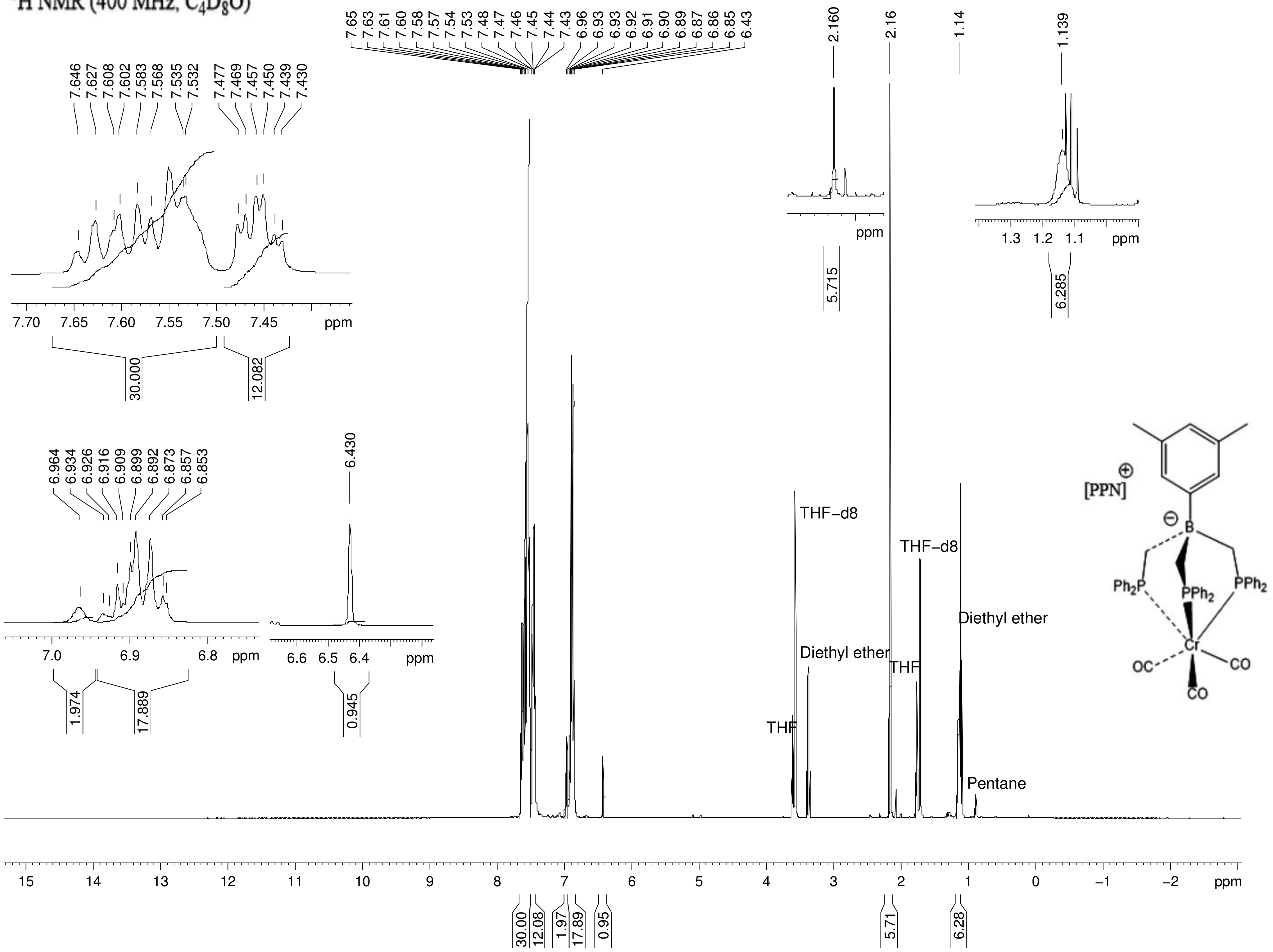
^{11}B NMR (128 MHz, C_4D_8O)



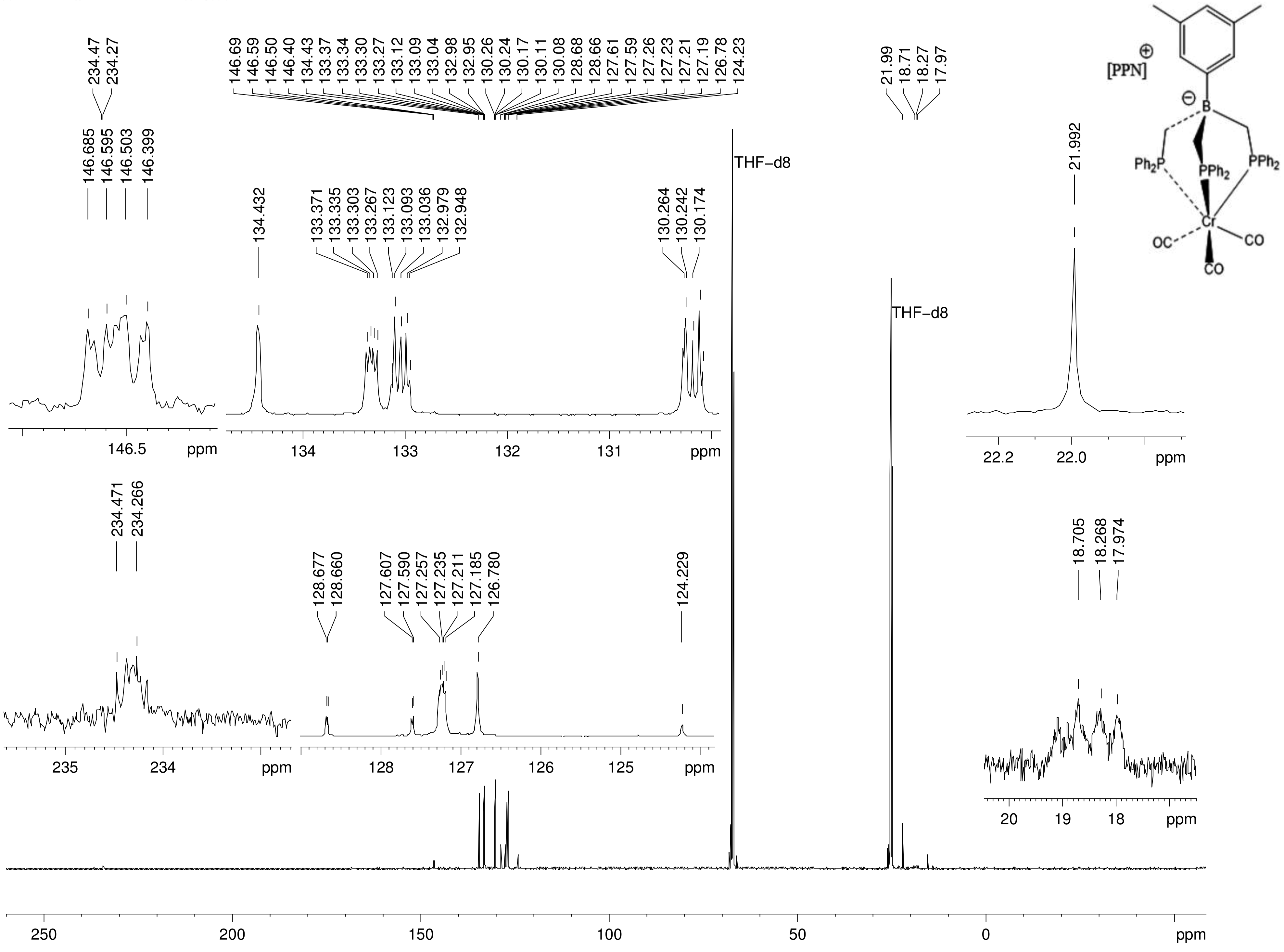


$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)

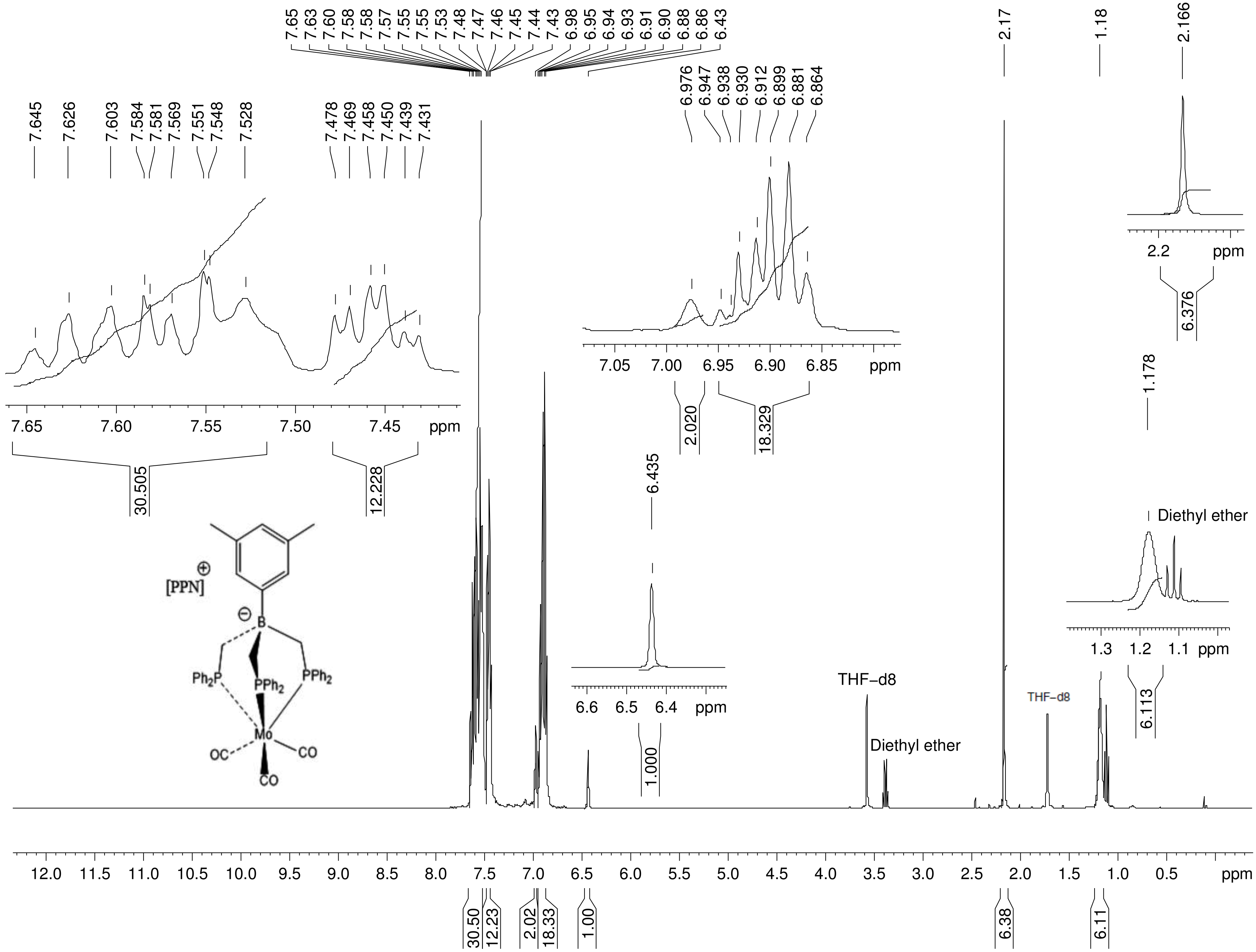
^{1}H NMR (400 MHz, C_4D_8O)



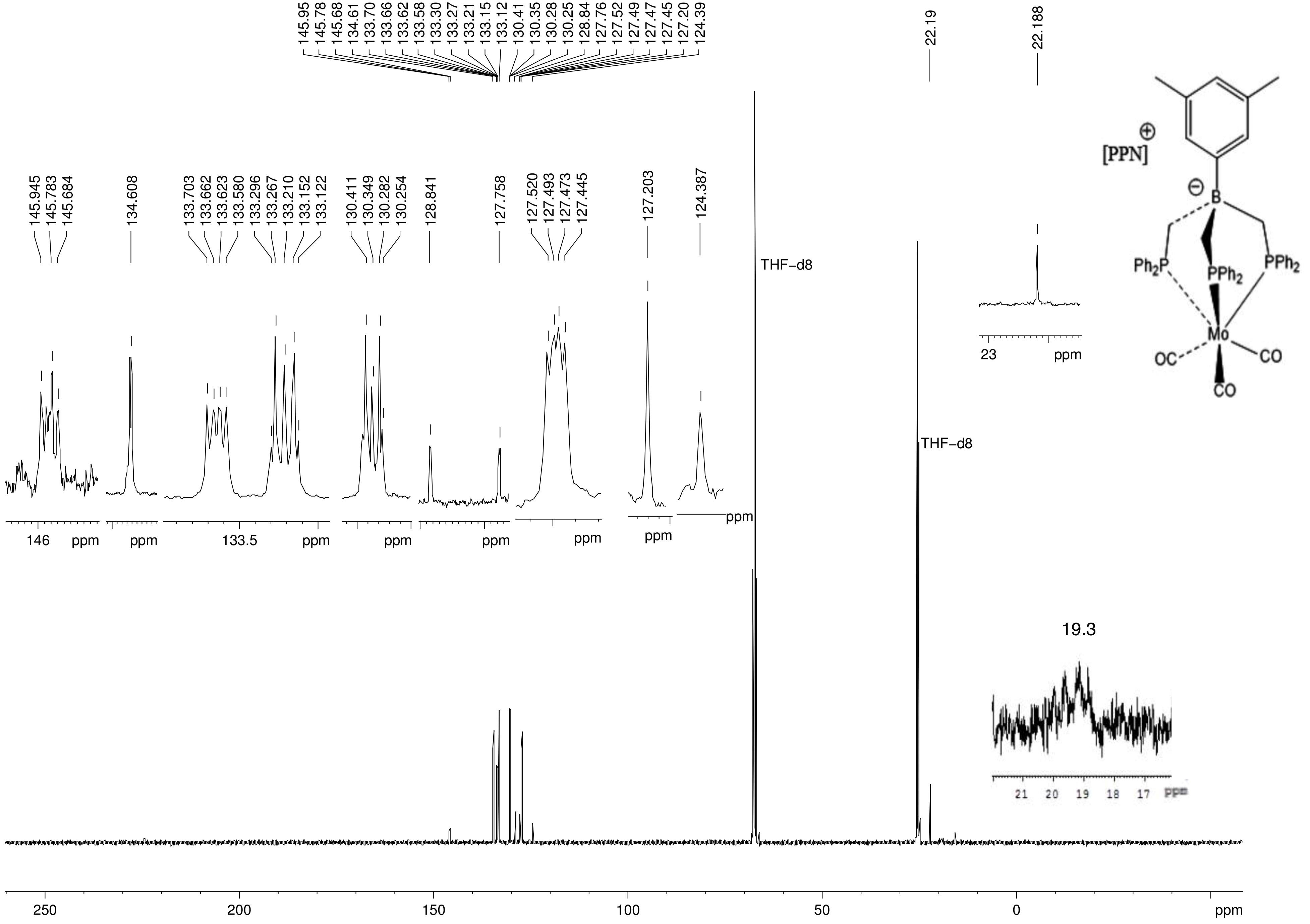
$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)



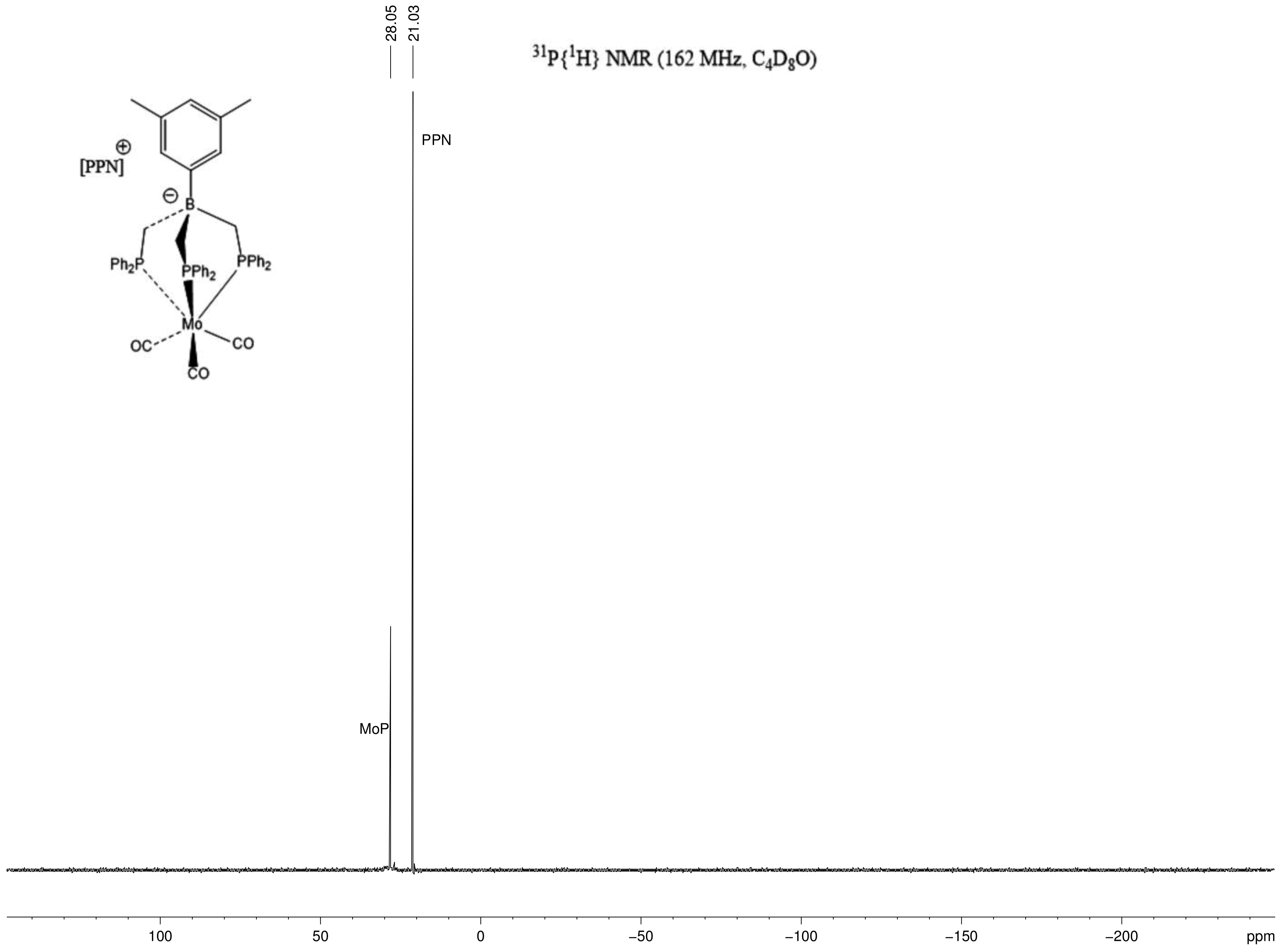
^1H NMR (400 MHz, C_4D_8O)



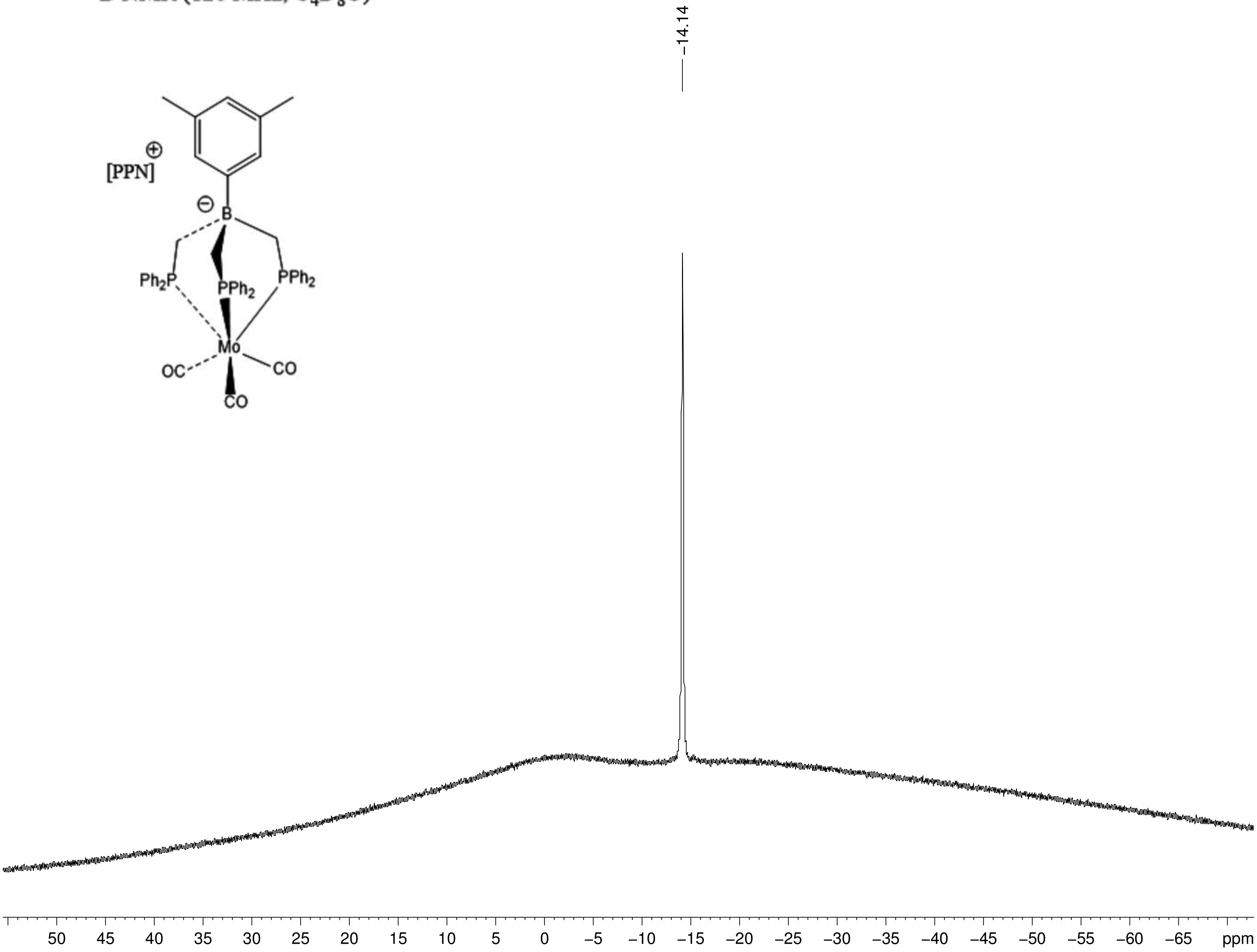
$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)



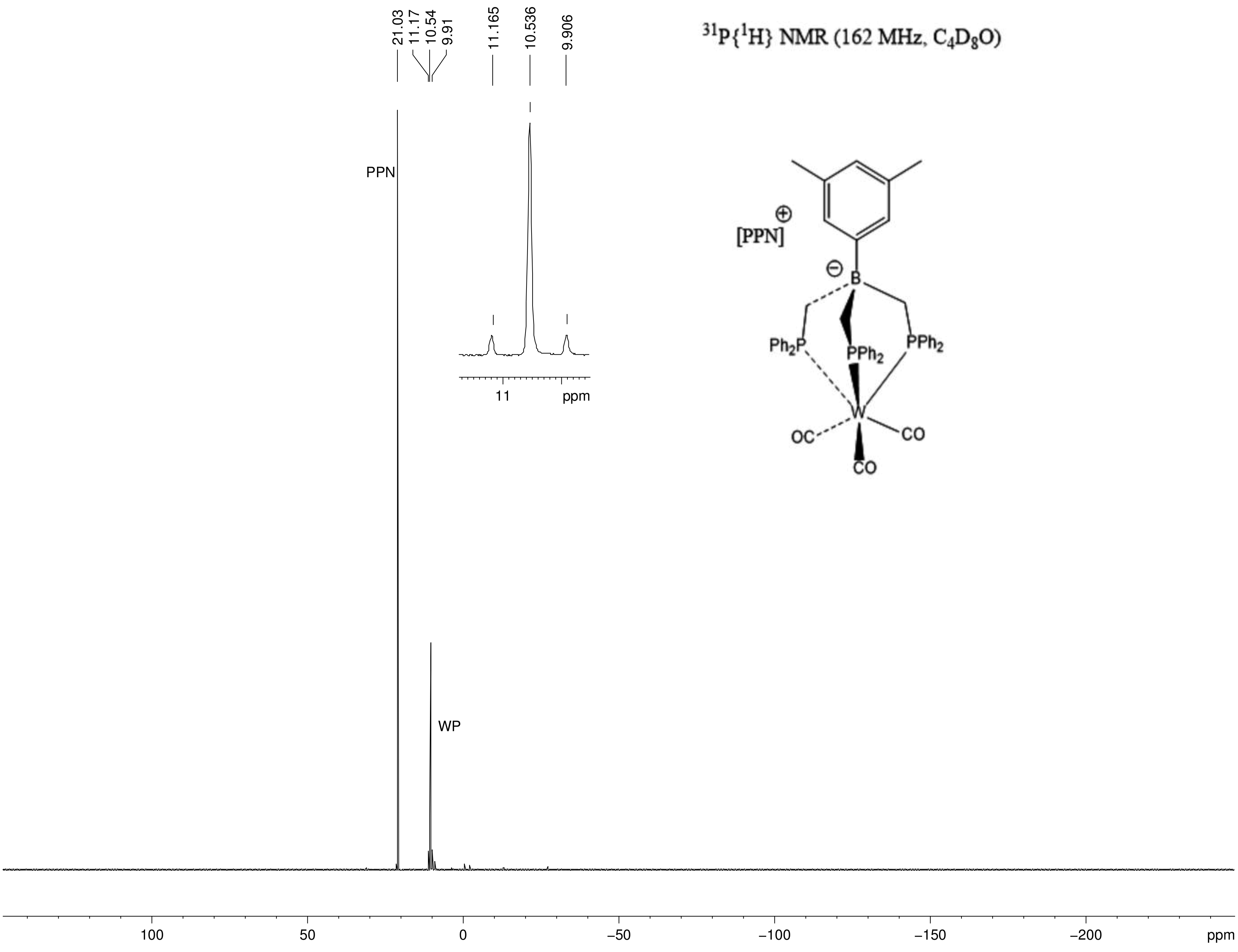
$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)



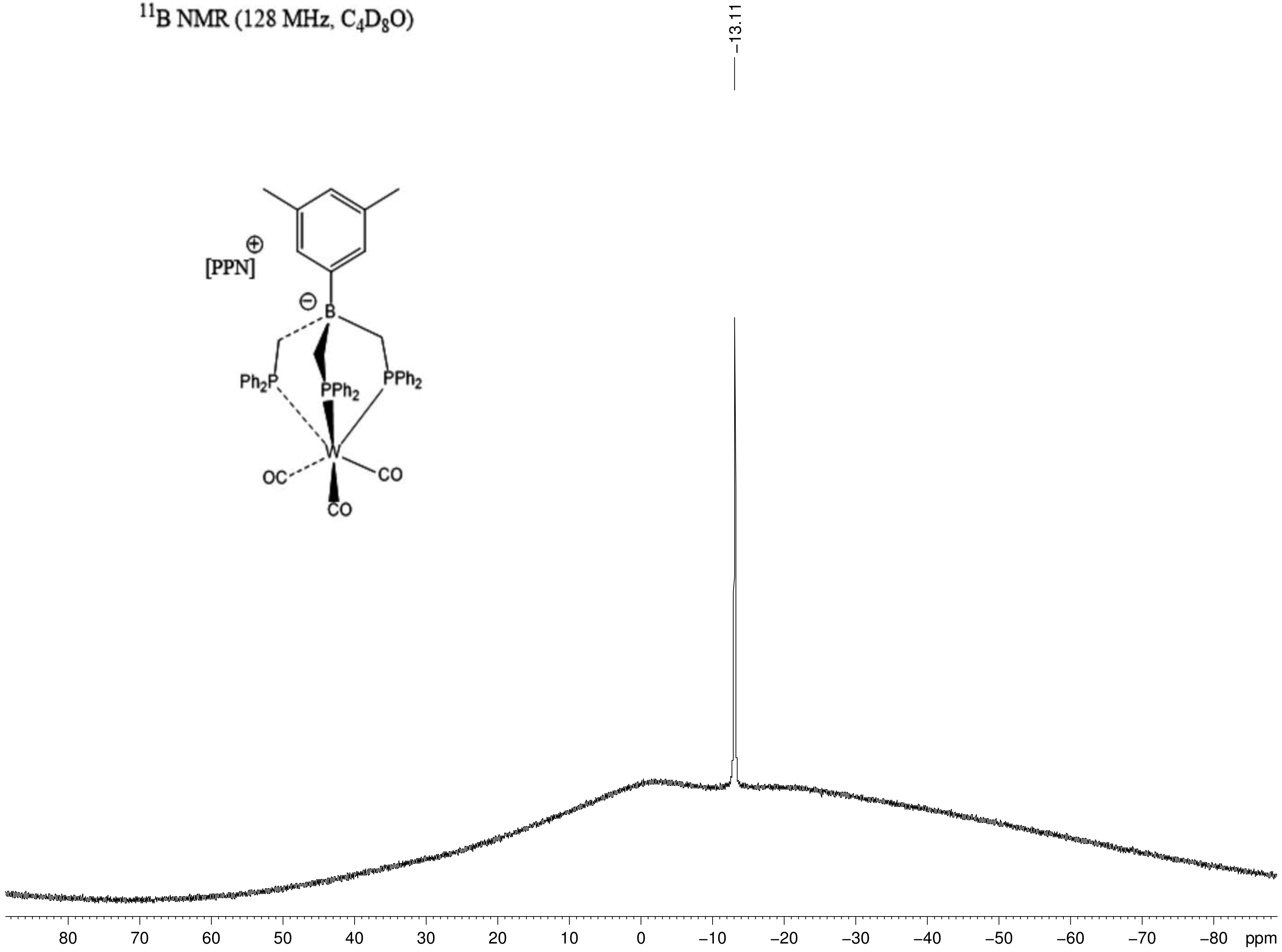
^{11}B NMR (128 MHz, C_4D_8O)



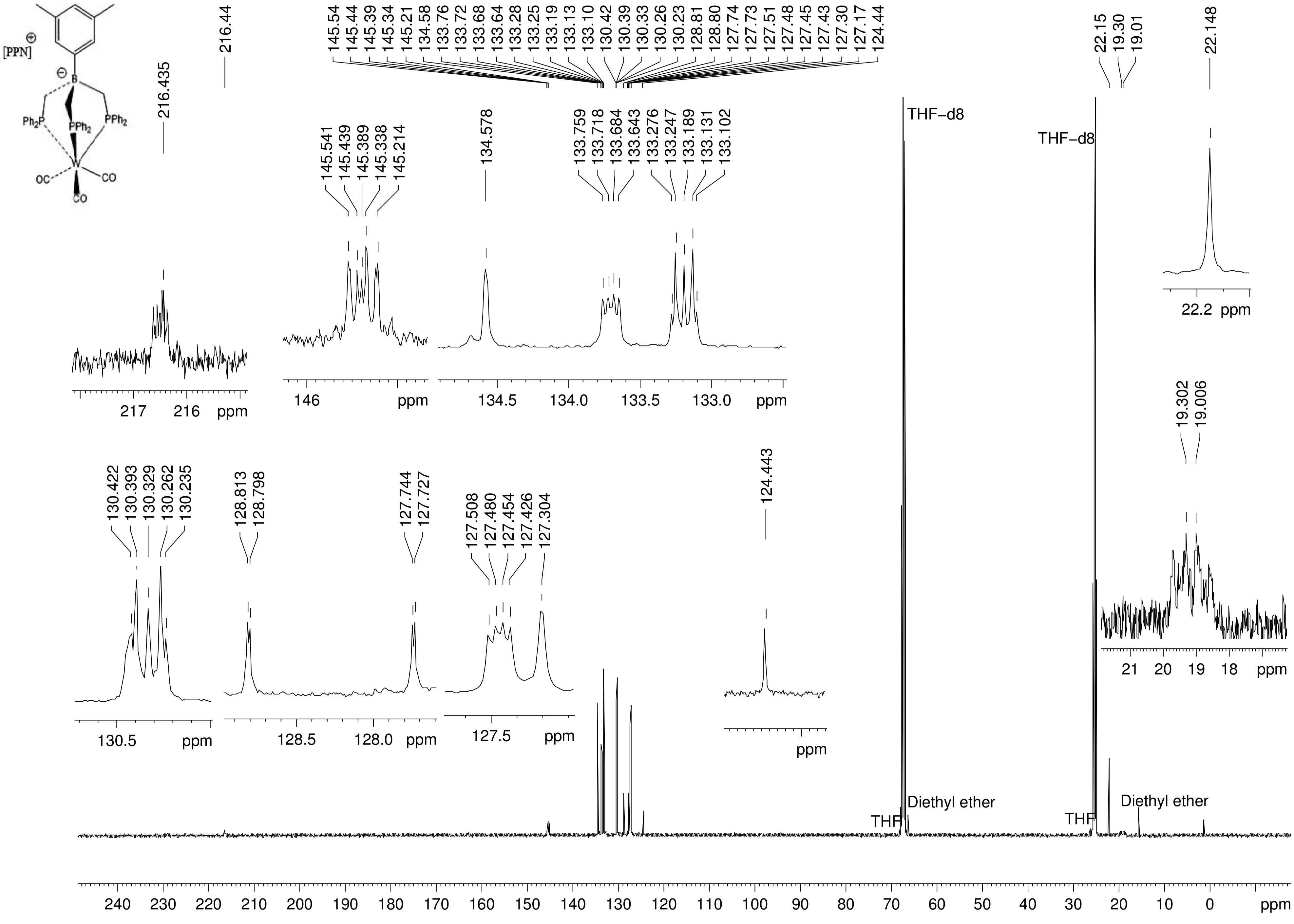
$^{31}P\{^{1}H\}$ NMR (162 MHz, C_4D_8O)



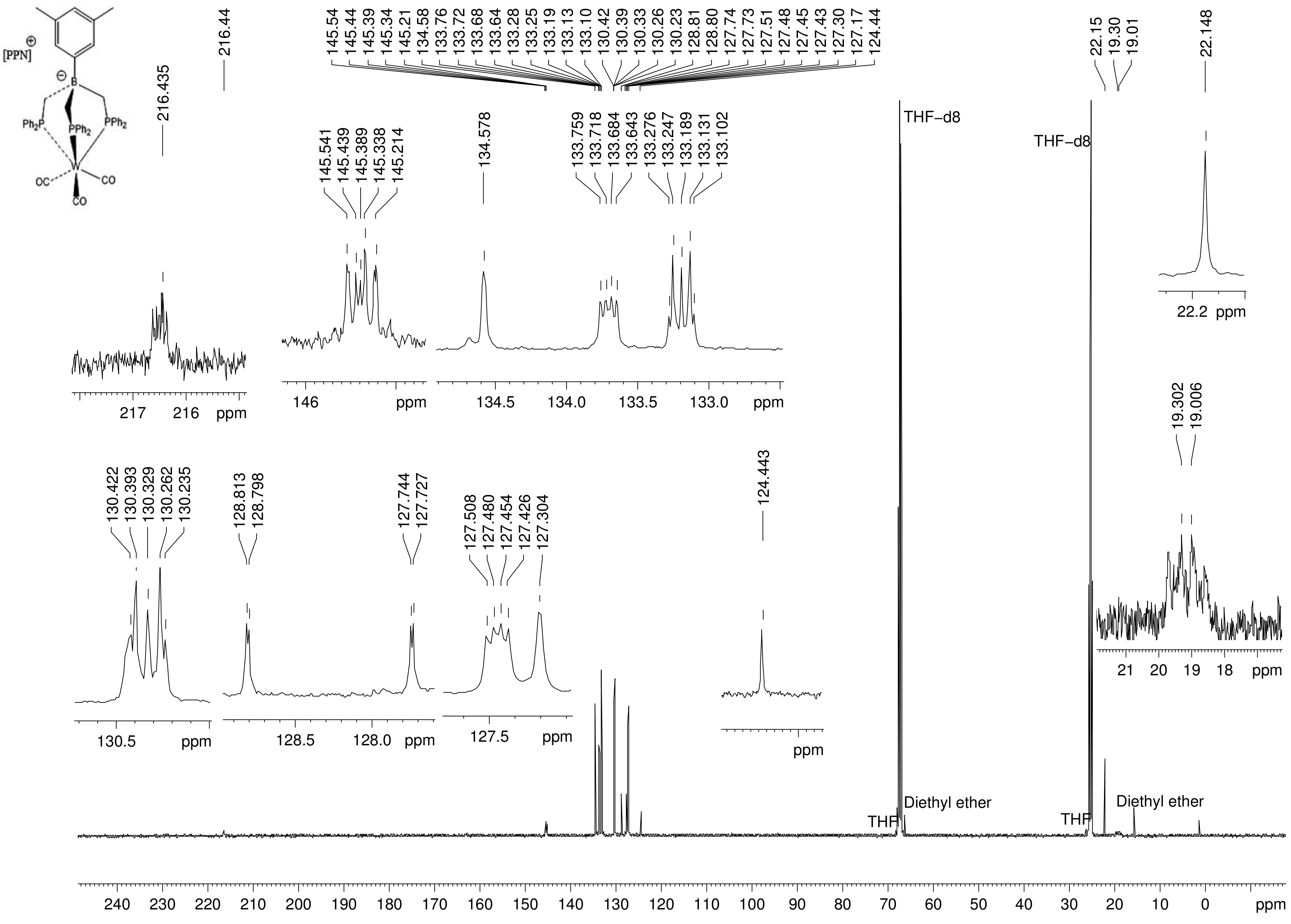
^{11}B NMR (128 MHz, C_4D_8O)

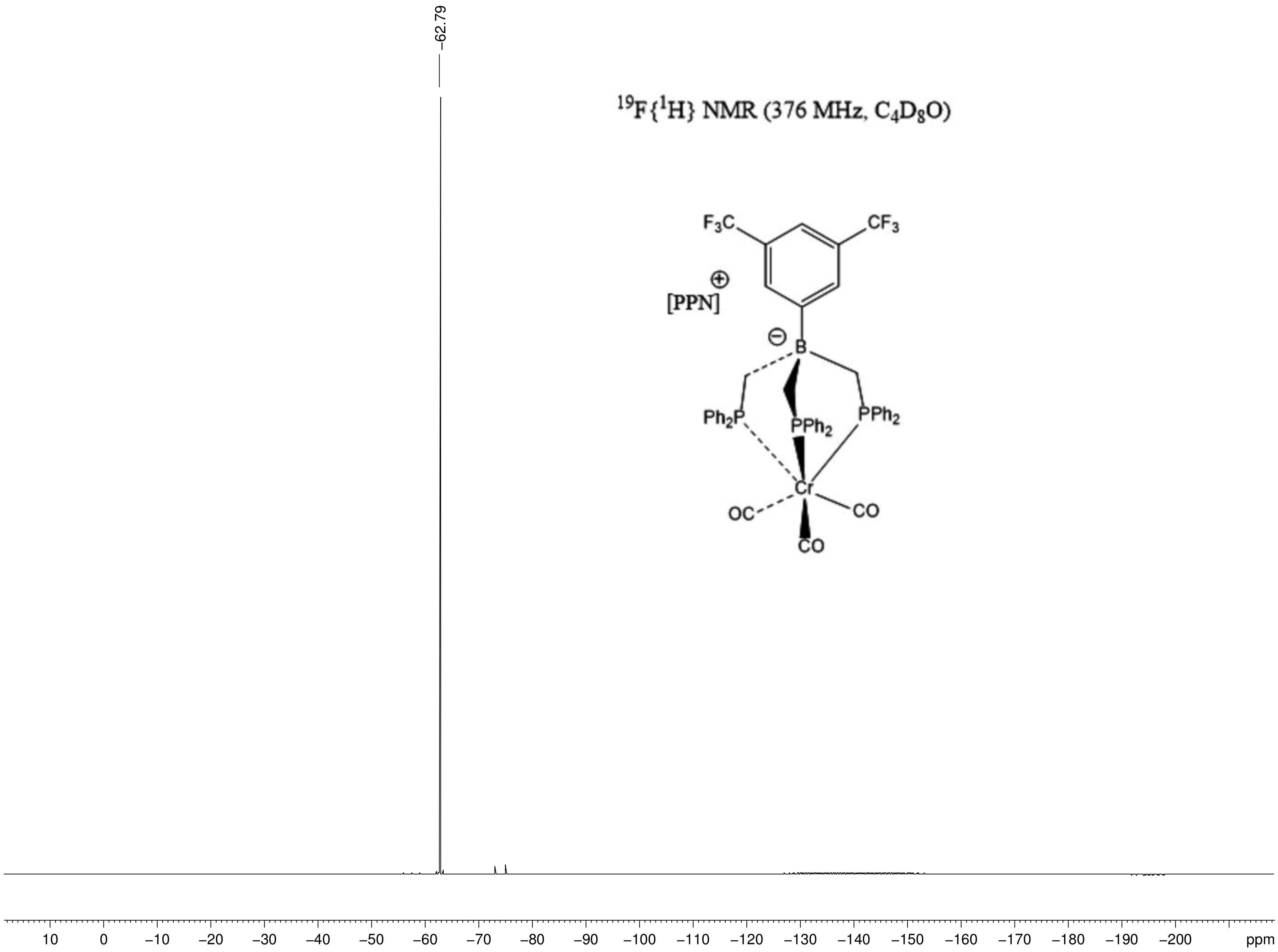


$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)

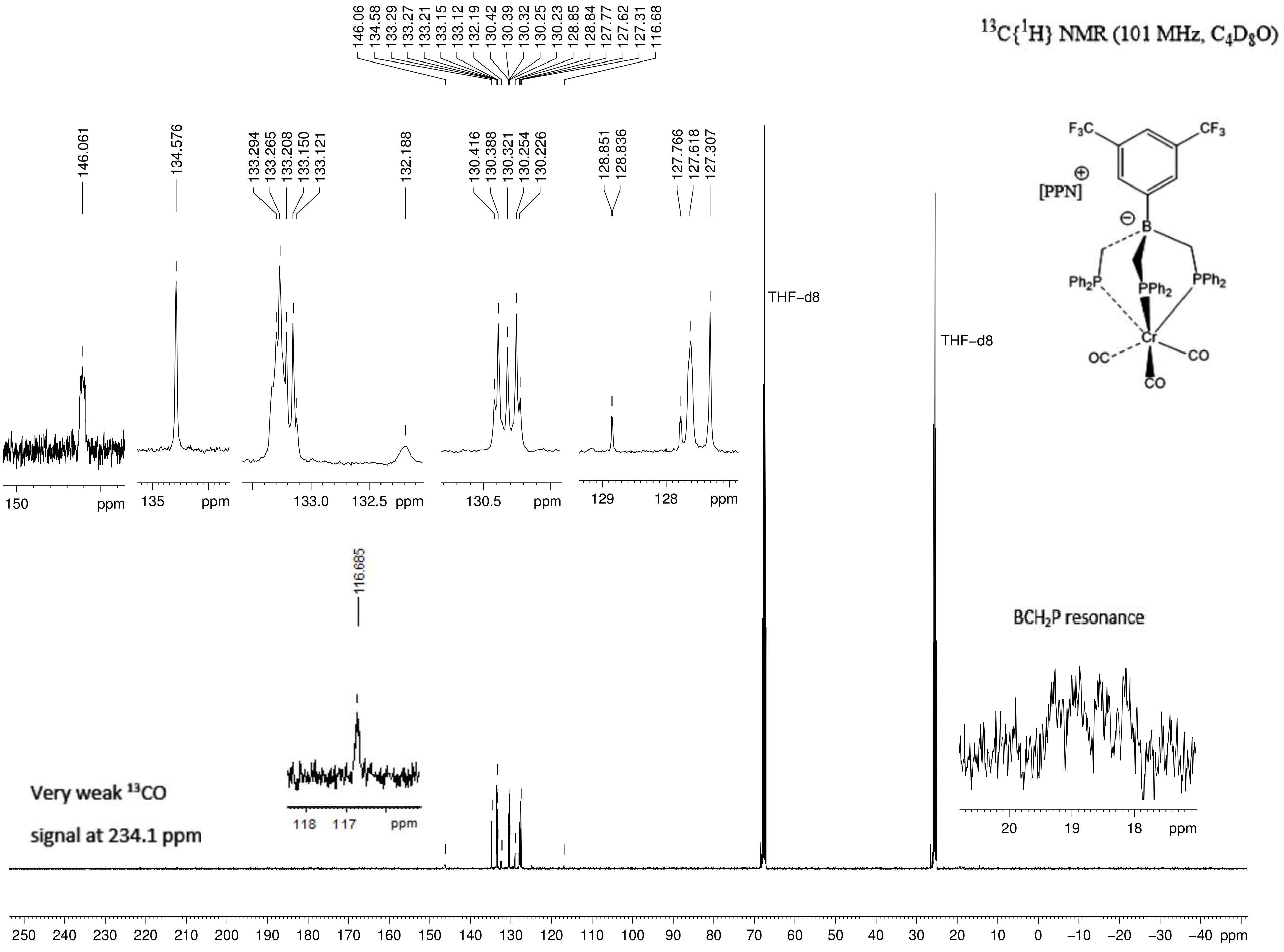


$^{13}C\{^{1}H\}$ NMR (101 MHz, C_4D_8O)

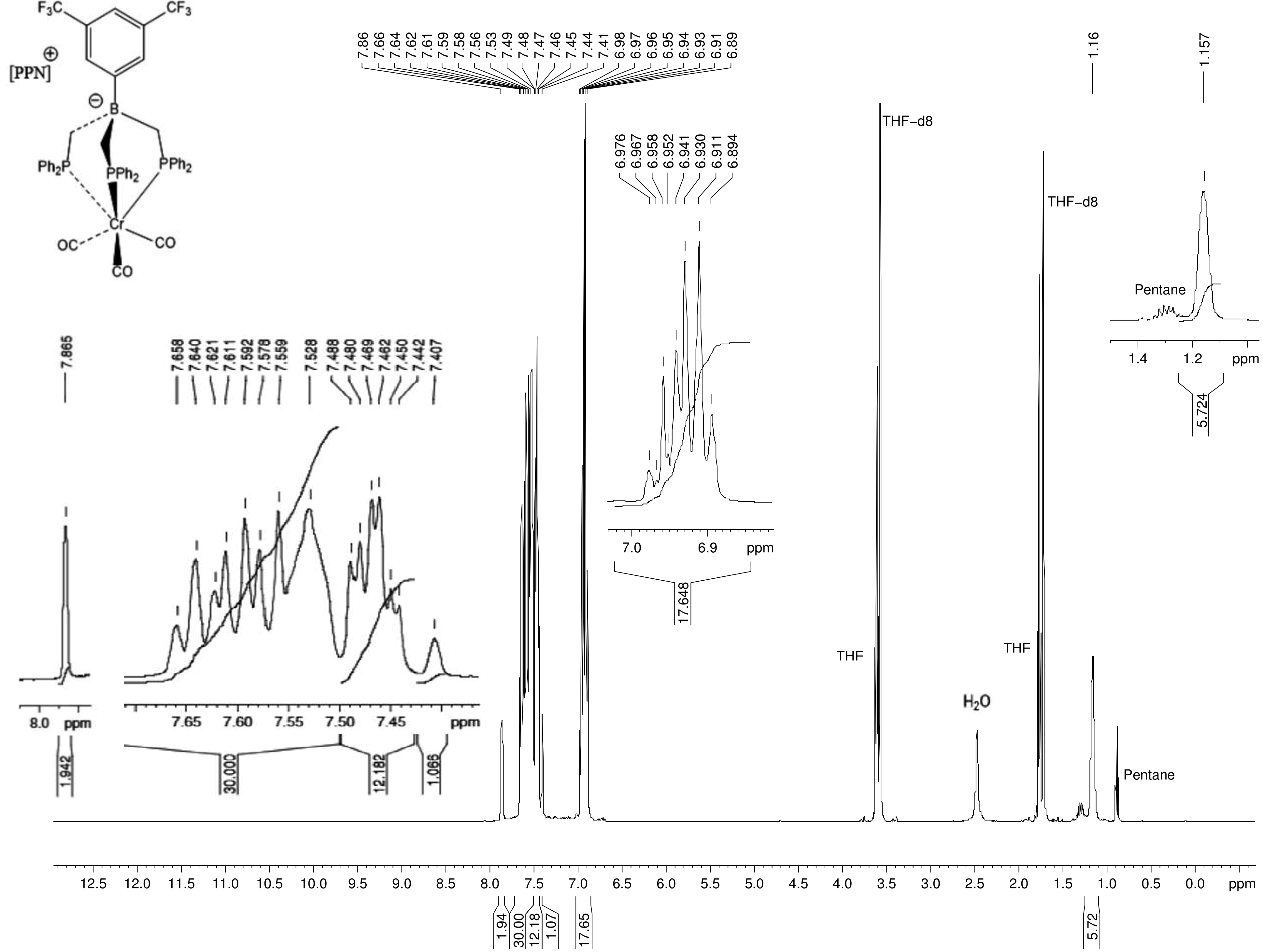




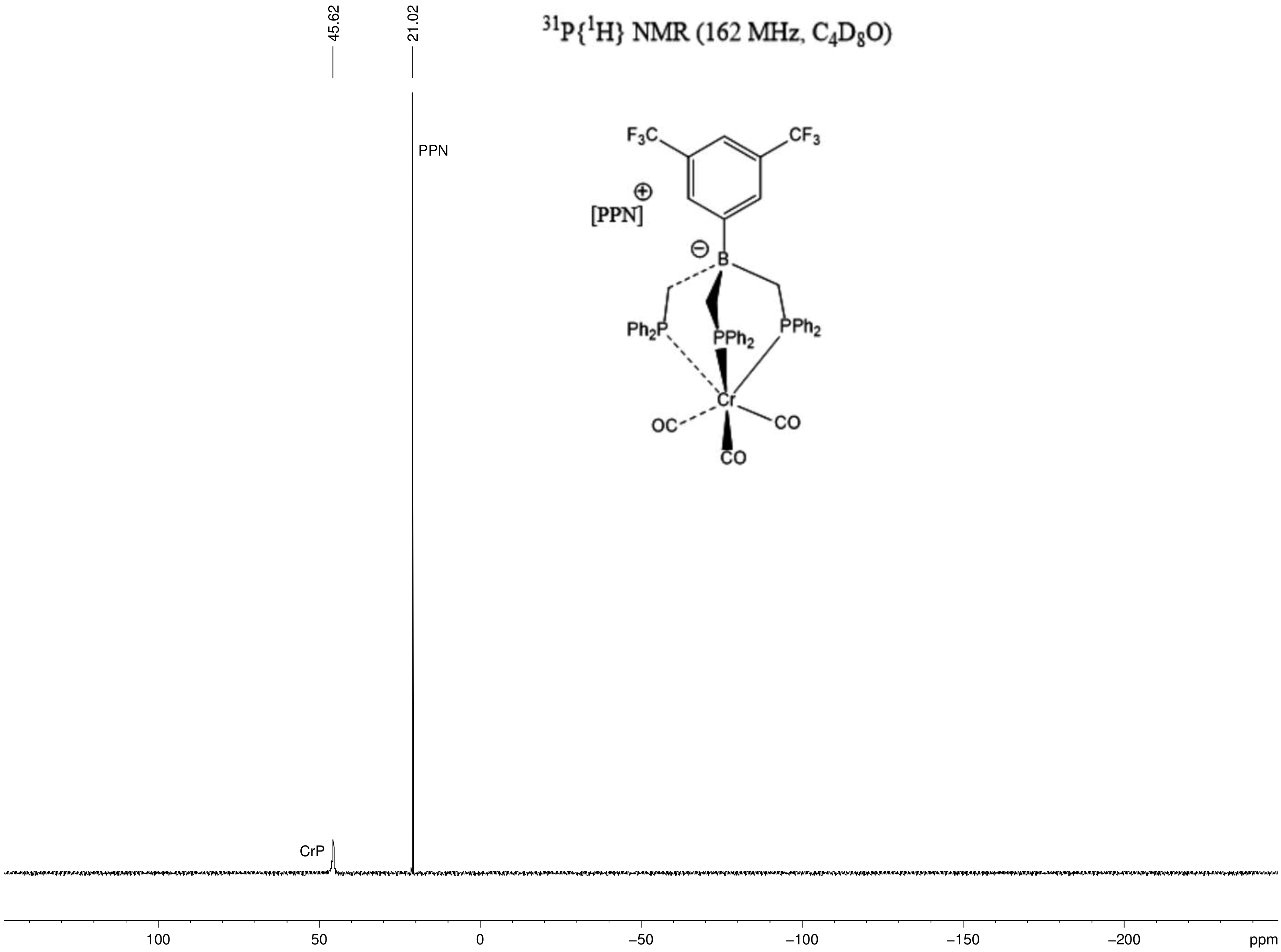
^{19}F{^{1}H} NMR (376 MHz, C_4D_8O)


$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)

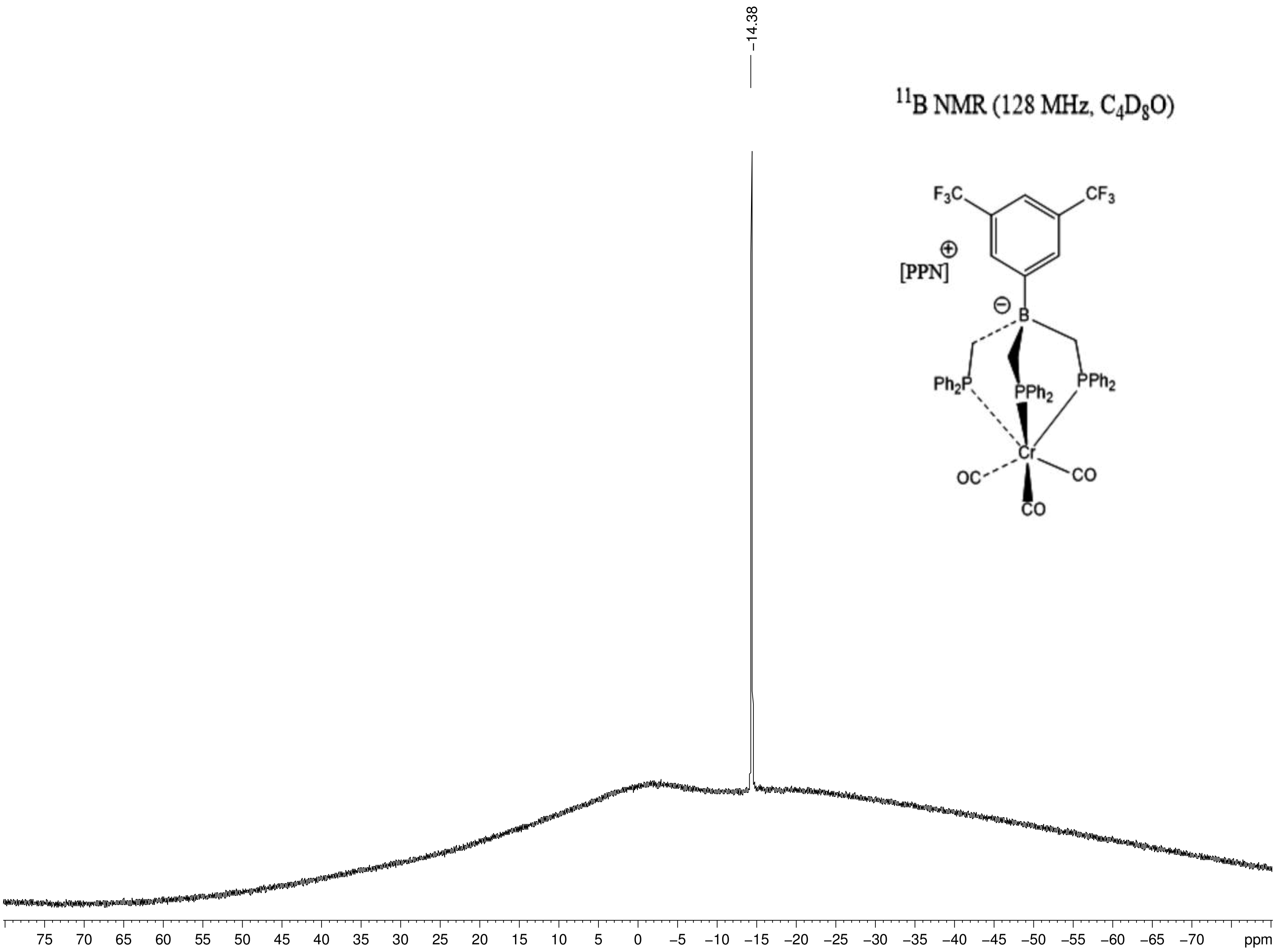
^{1}H NMR (400 MHz, C_4D_8O)

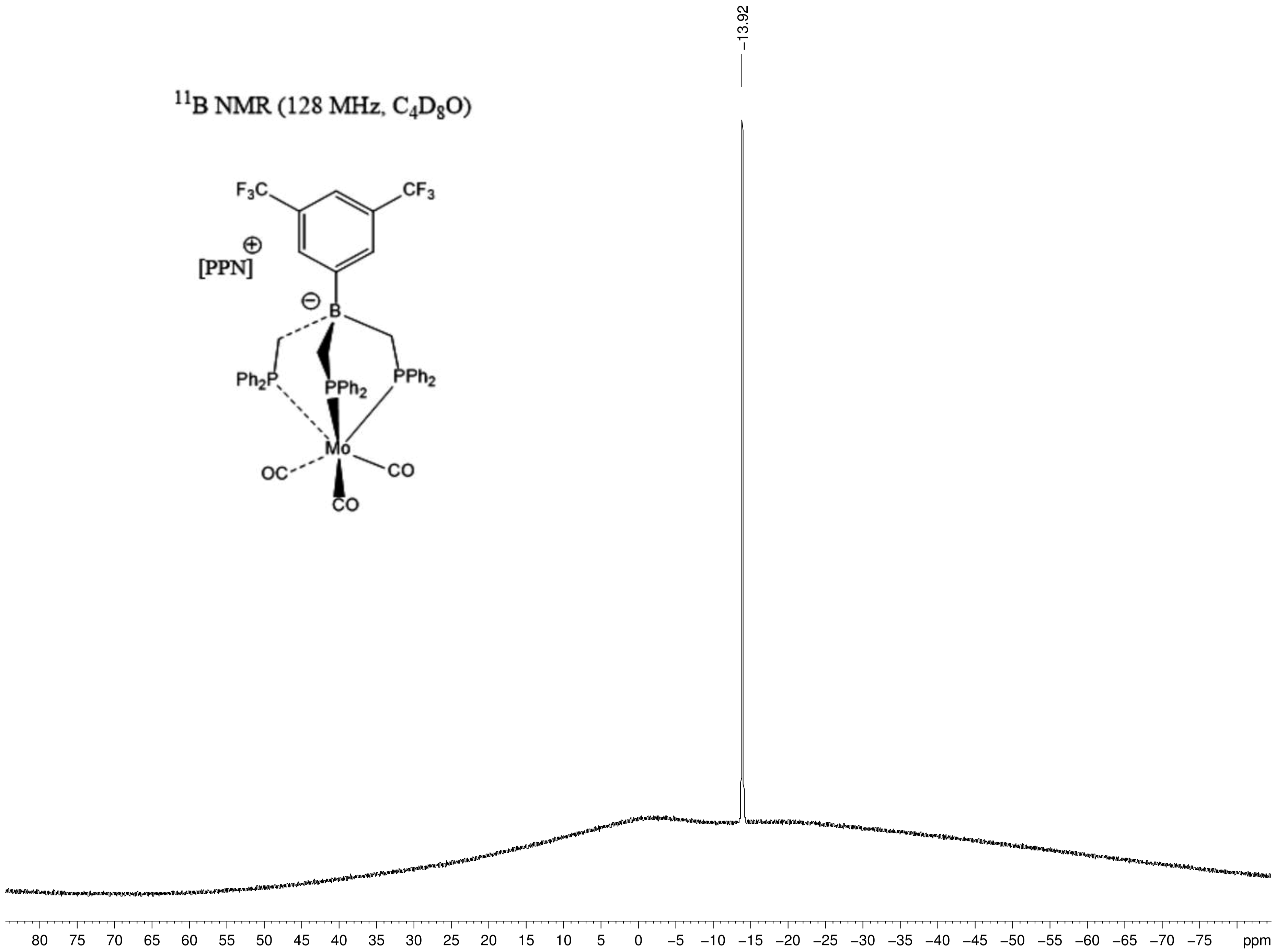


$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)

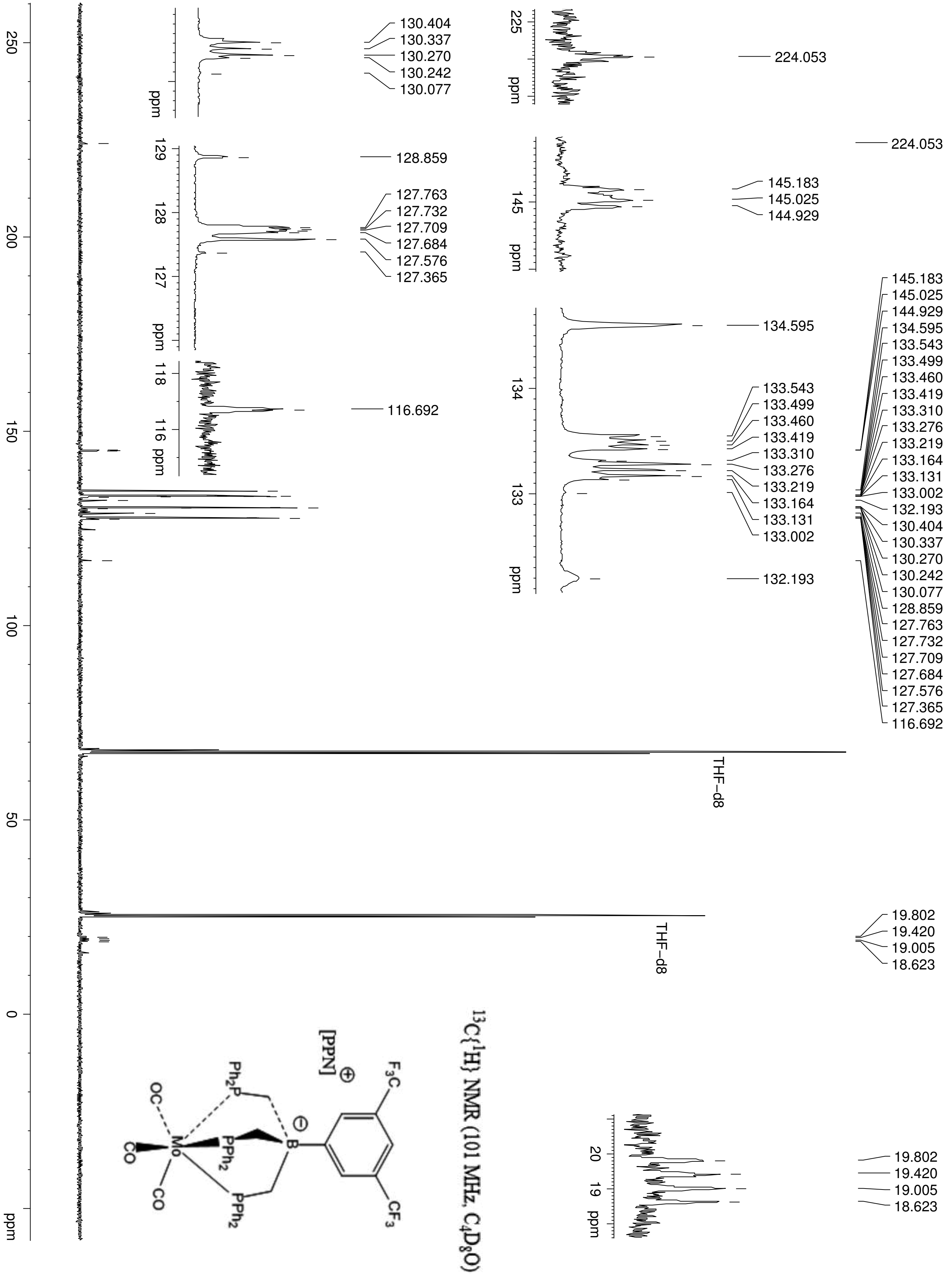


^{11}B NMR (128 MHz, C_4D_8O)

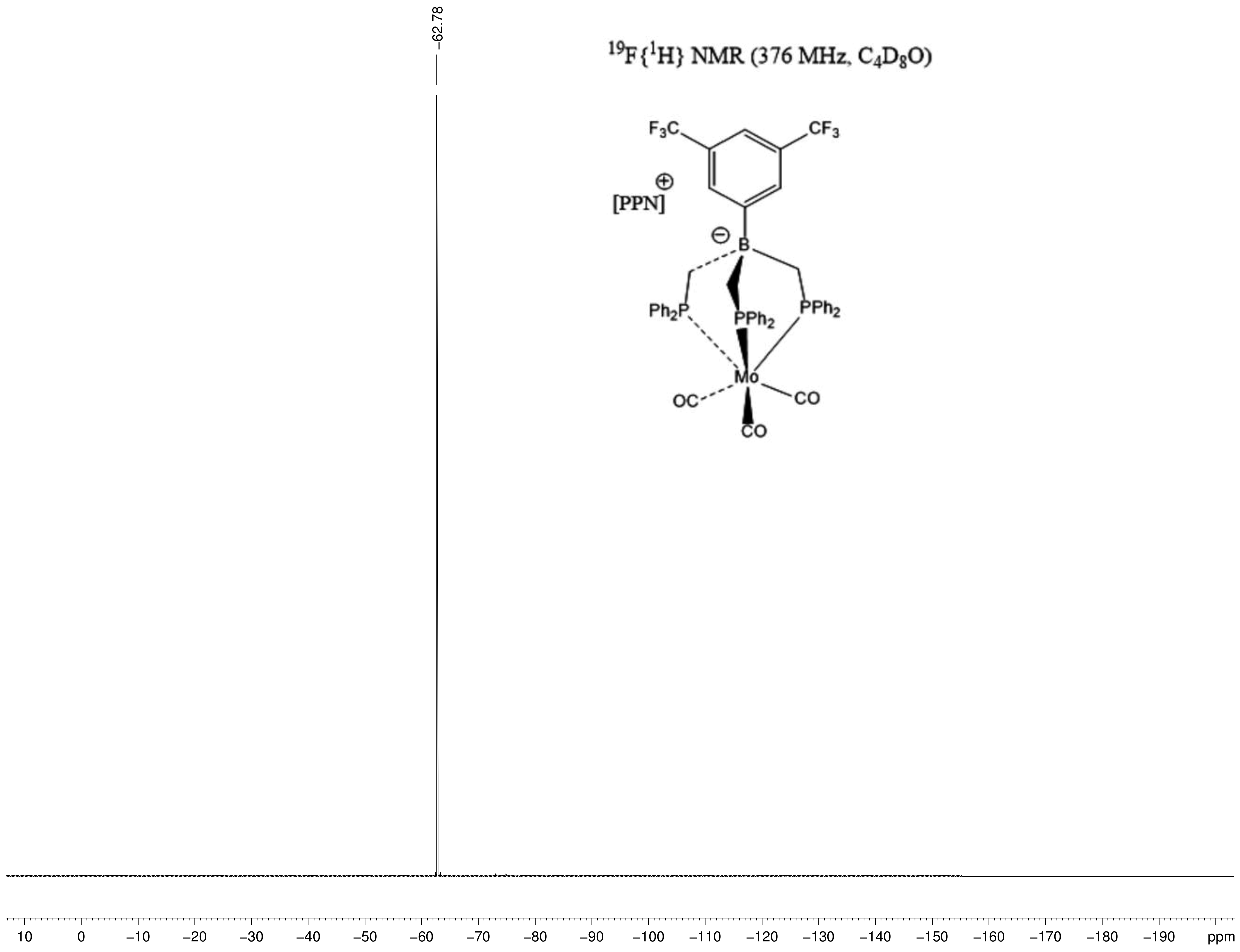




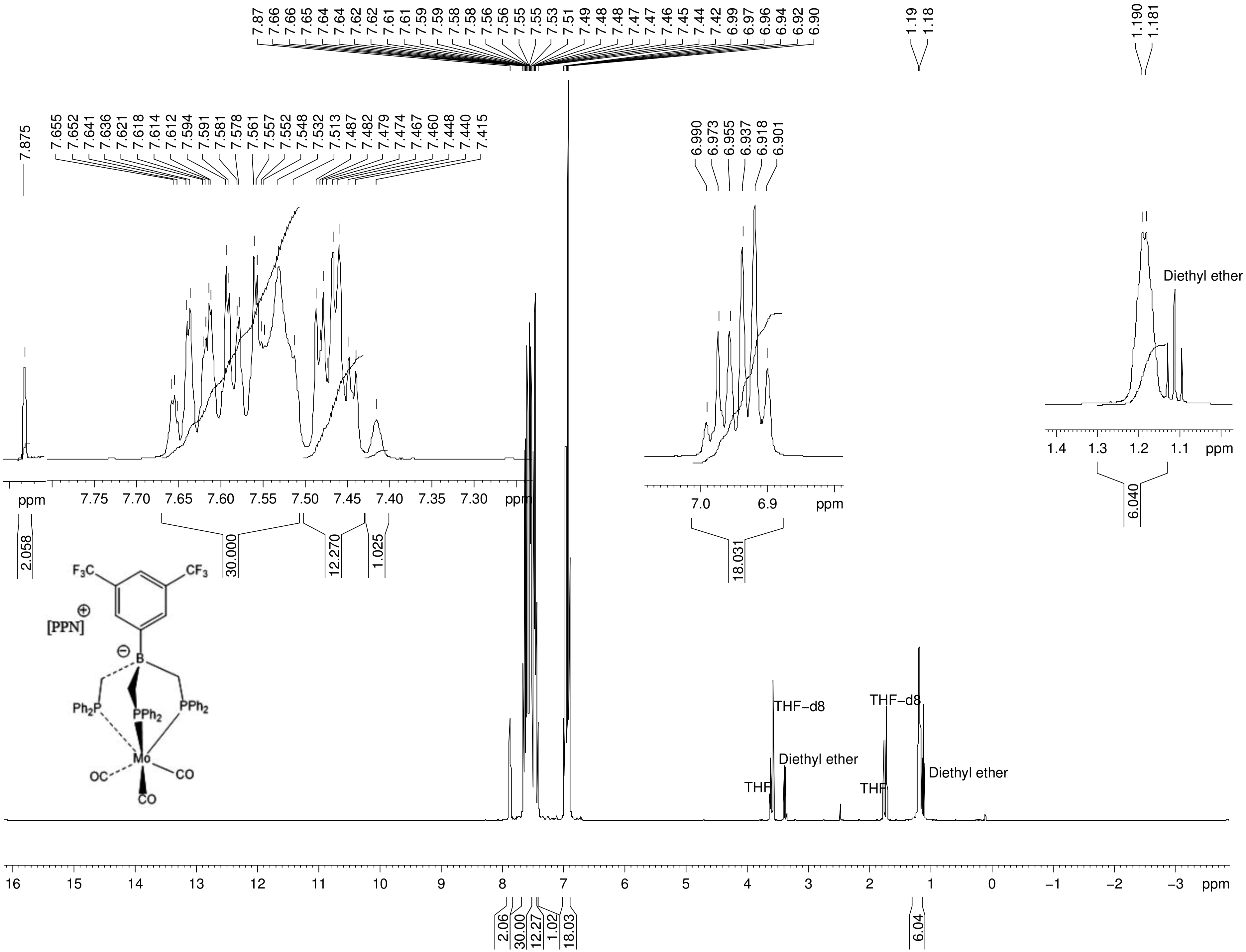
^{11}B NMR (128 MHz, C_4D_8O)



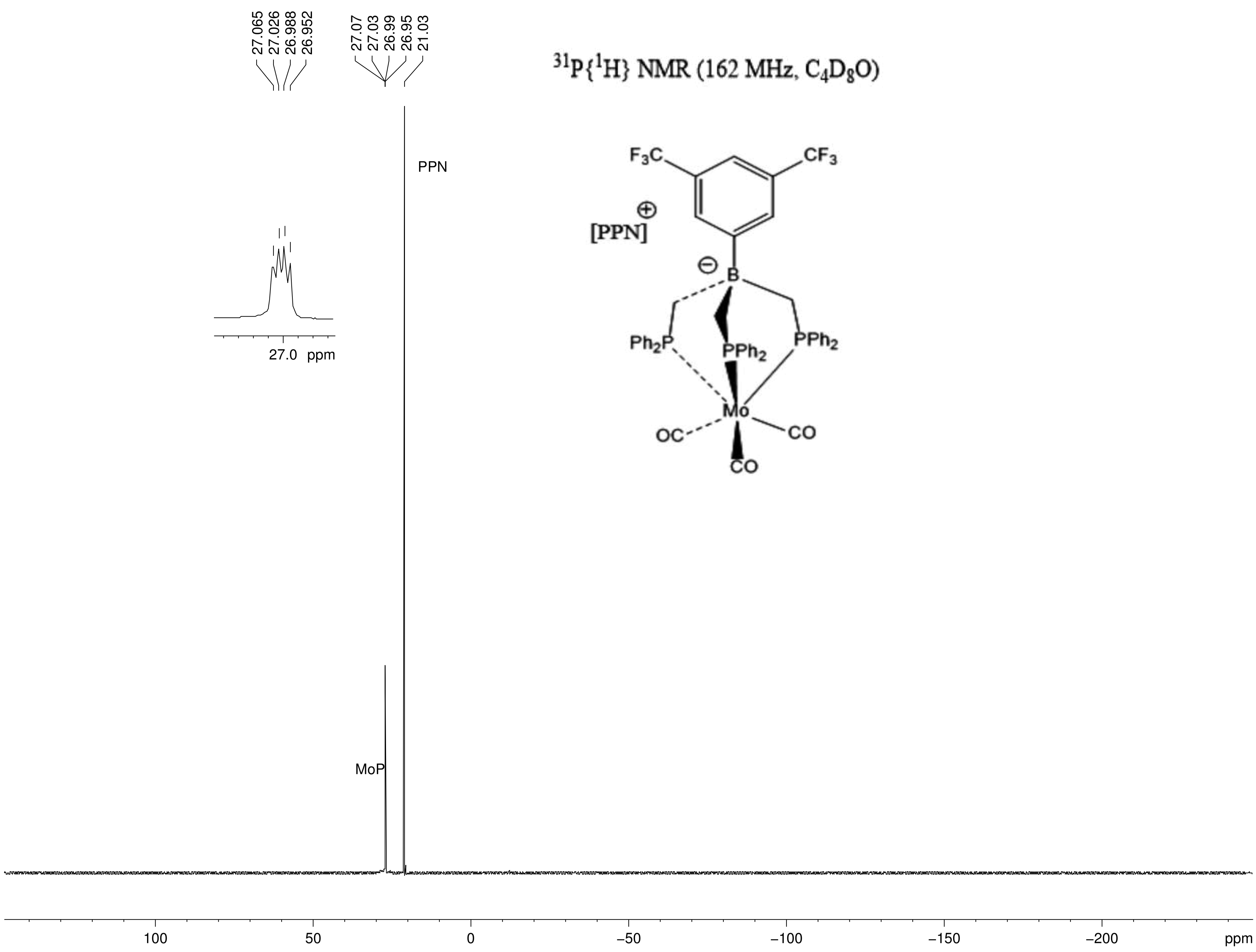
$^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O)

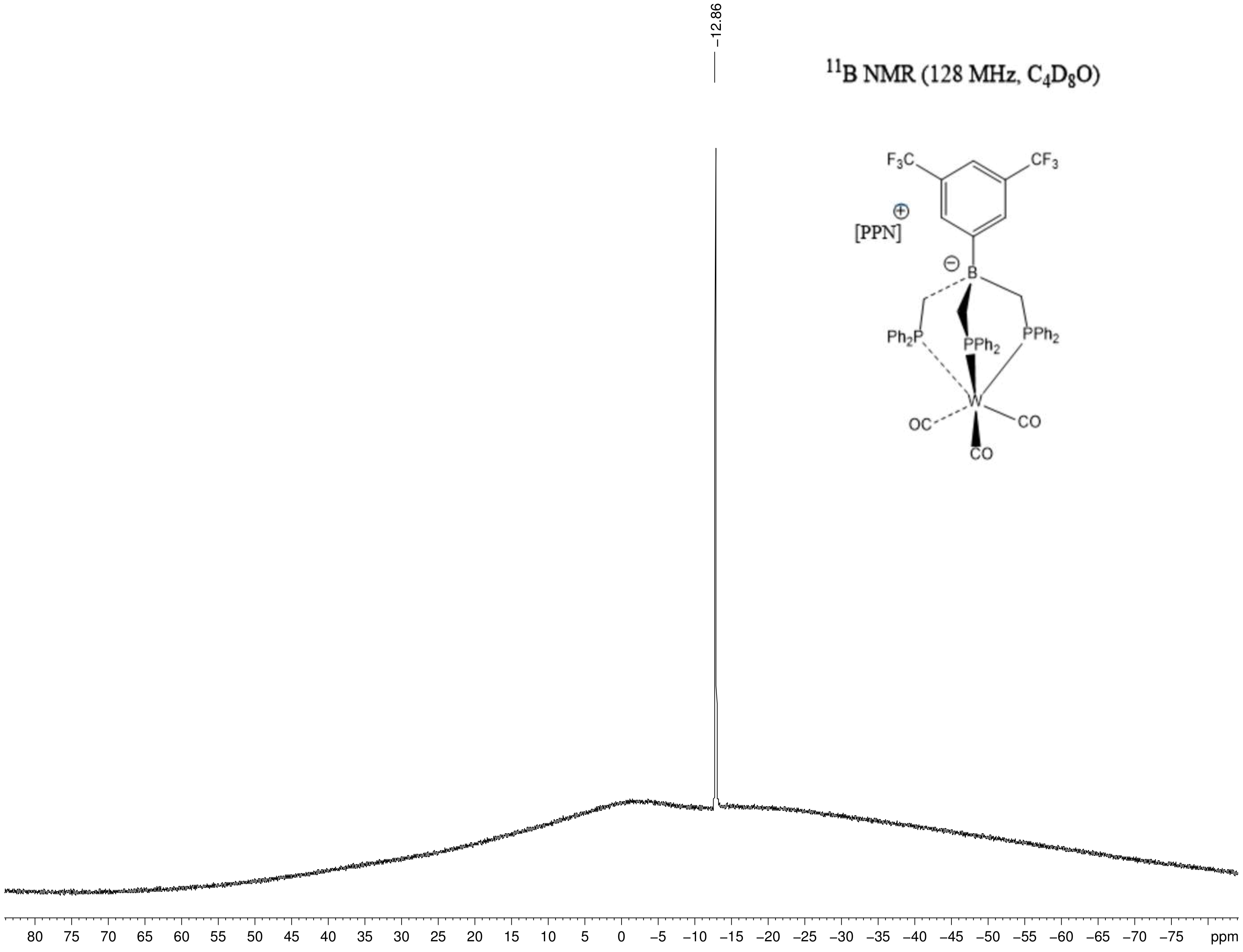

$^{19}F\{^{1}H\}$ NMR (376 MHz, C_4D_8O)

^{1}H NMR (400 MHz, C_4D_8O)



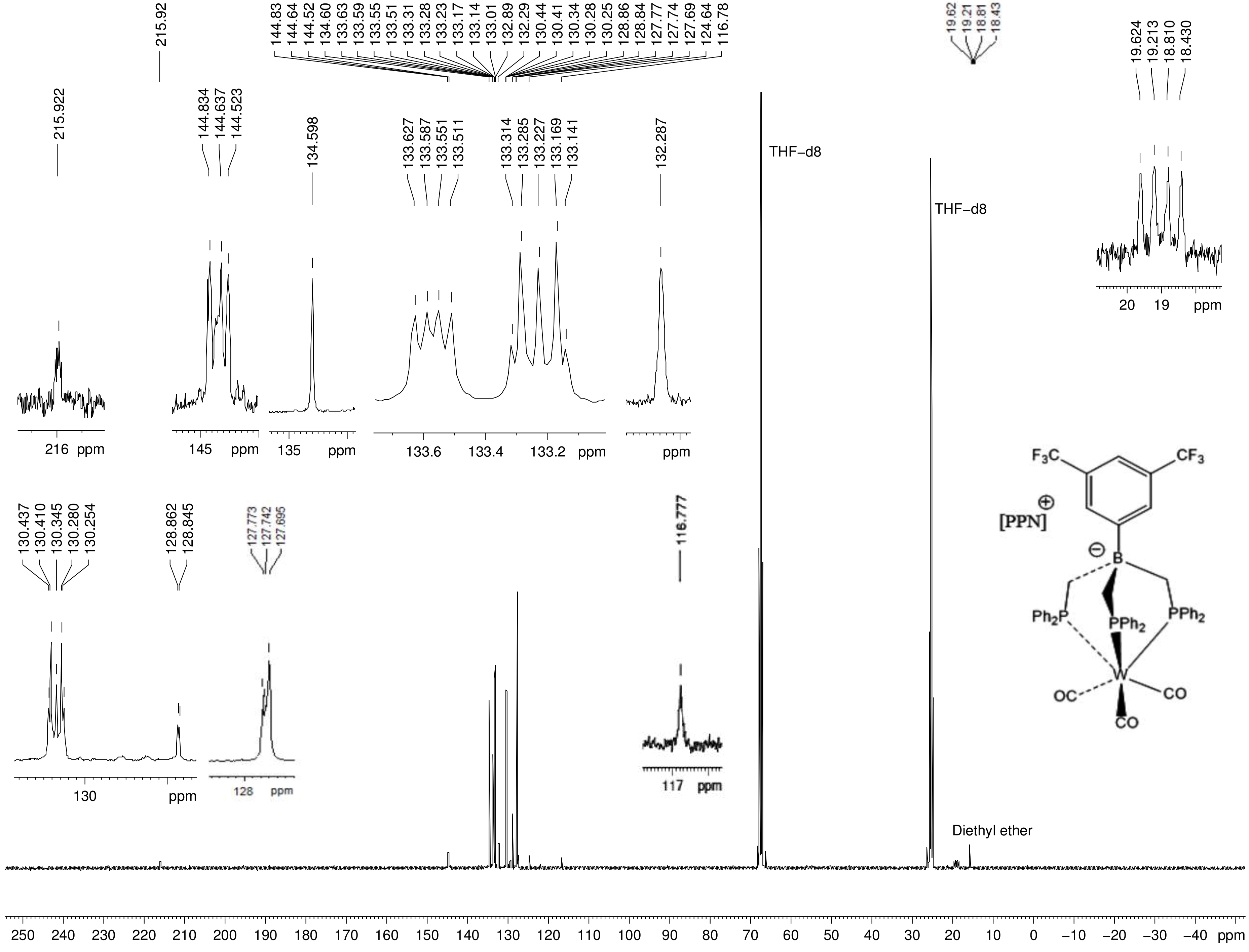
$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)

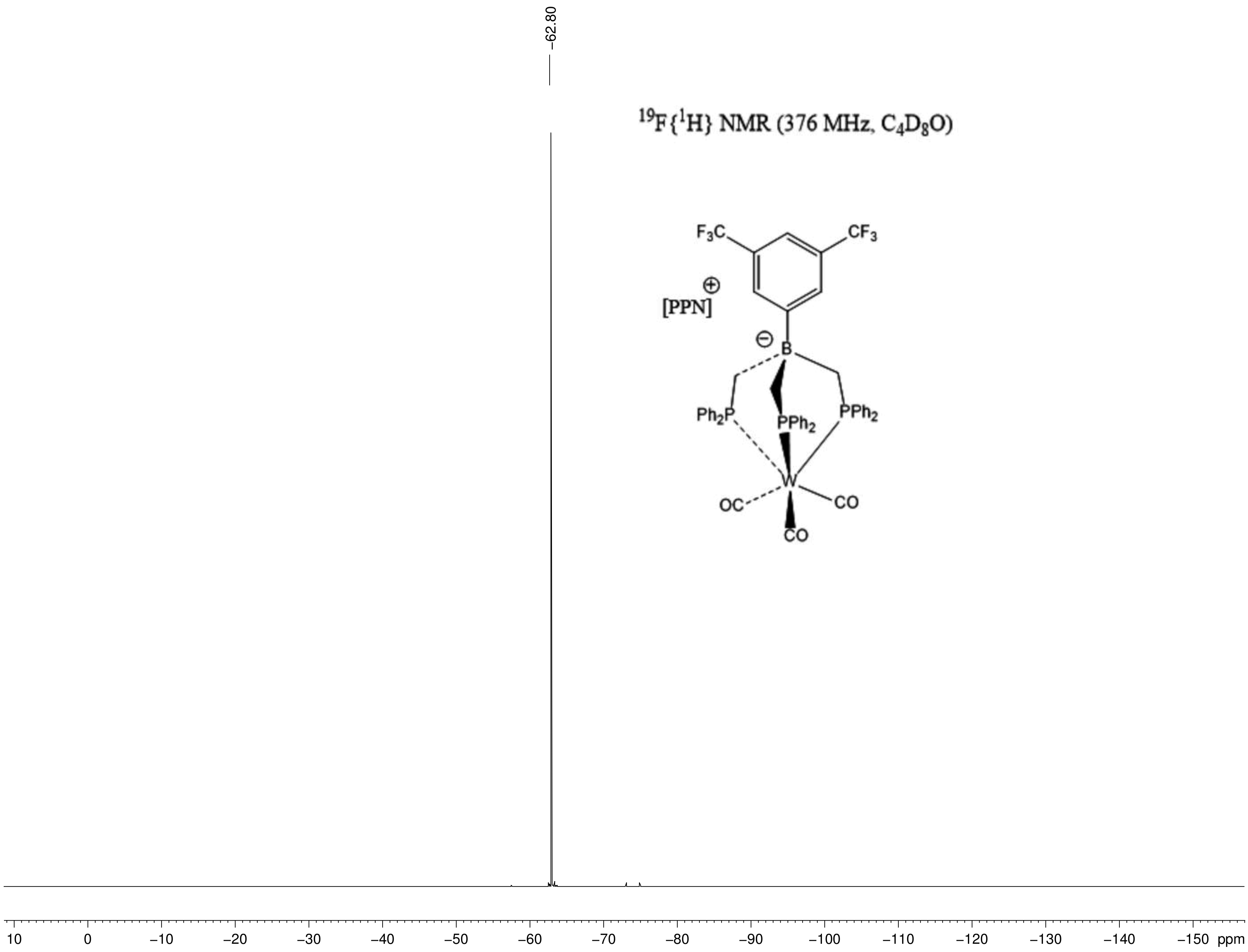




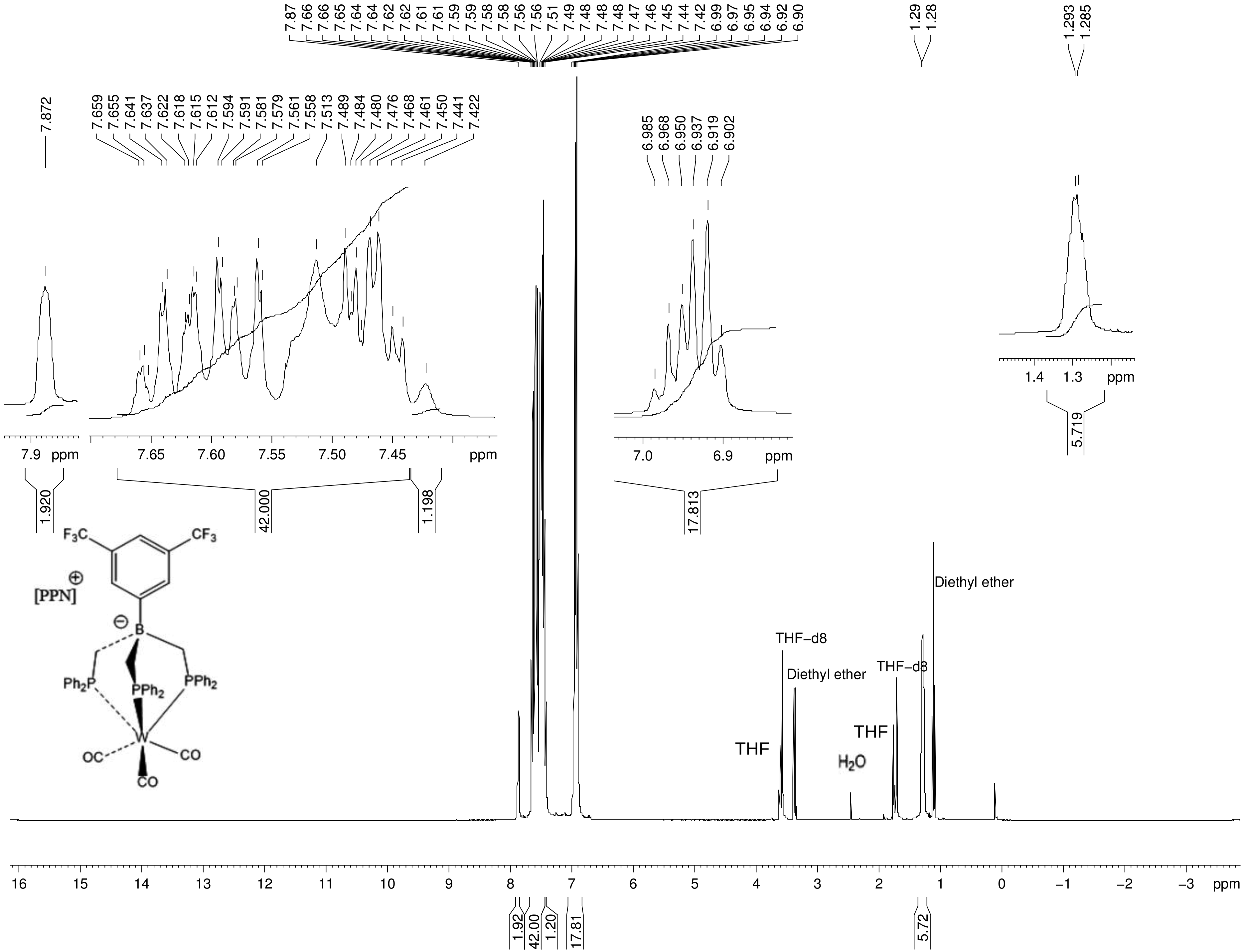
^{11}B NMR (128 MHz, C_4D_8O)

$^{13}C\{^{1}H\}$ NMR (101 MHz, C_4D_8O)




−62.80
$^{19}F\{^1H\}$ NMR (376 MHz, C_4D_8O)
F_3C
CF_3
[PPN]
⊕
⊖
B
Ph_2P
PPh_2
PPh_2
W
OC
CO
CO
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
ppm

^{1}H NMR (400 MHz, C_4D_8O)



$^{31}P\{^1H\}$ NMR (162 MHz, C_4D_8O)