

## SUPPORTING INFORMATION

for

### **Modifying Phosphorus(III) Substituents to Activate Remote Ligand-Centered Reactivity in Triaminoborane Ligands**

Kyoungsoon Lee,<sup>†</sup> Johnathan D. Culpepper,<sup>†</sup> Riffat Parveen,<sup>‡</sup> Dale C. Swenson,<sup>†</sup> Bess Vlasisavljevic,<sup>‡\*</sup> Scott R. Daly<sup>†\*</sup>

Email: scott-daly@uiowa.edu, Bess.Vlasisavljevic@usd.edu

<sup>†</sup>The University of Iowa, Department of Chemistry, E331 Chemistry Building, Iowa City, IA 52242, United States

<sup>‡</sup>The University of South Dakota, Department of Chemistry, 414 E. Clark Street, Vermillion, SD 57069, United States

#### TABLE OF CONTENTS

Experimental	pp. S2 – S7
Molecular Structures of <b>1</b> , <b>2</b> , <b>5</b> , <b>6</b> , and <b>8</b>	pp. S8 – S9
Tabulated Crystallographic Data	pp. S10
NMR Spectra	pp. S11 – S3
Supporting Information References	pp. S54

## Experimental

**General Considerations.** Reactions were carried out under an atmosphere of N<sub>2</sub> or Ar using glovebox or standard Schlenk techniques unless stated otherwise. Glassware used for reactions performed under inert conditions was dried in an oven at 150 °C for at least 1.5 h and allowed to cool under vacuum before use. Solvents used under anhydrous conditions were dried and deoxygenated using a Pure Process Technologies Solvent Purification System. Reagents were purchased from commercial vendors and used without further purification. MeOH was refluxed over Mg and distilled before use. NEt<sub>3</sub> was distilled and stored over KOH. 1,8,10,9-triazaboradecalin (TBD),<sup>1</sup> CIP(OMe)<sub>2</sub>,<sup>2</sup> and <sup>Ph</sup>TBDPhos<sup>1</sup> were prepared as previously described.

<sup>1</sup>H, <sup>19</sup>F, and <sup>31</sup>P NMR data were recorded on a Bruker AVANCE-300 or DPX-300 instrument operating at 300 MHz for <sup>1</sup>H, 282.2 MHz for <sup>19</sup>F, and 121.4 MHz for <sup>31</sup>P. <sup>11</sup>B and <sup>13</sup>C NMR data were acquired on a Bruker AVANCE-400 or DRX-400 instrument operating at 128.3 and 75.5 MHz, respectively. Chemical shifts are reported in  $\delta$  units in ppm referenced to residual solvent peaks (<sup>1</sup>H and <sup>13</sup>C), 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P;  $\delta$  0.0 ppm), 0.05 % C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> (<sup>19</sup>F;  $\delta$  -62.9 ppm), or BF<sub>3</sub>·Et<sub>2</sub>O (<sup>11</sup>B;  $\delta$  0.0 ppm). Microanalysis data (CHN) were collected using an EAI CE-440 Elemental Analyzer at the University of Iowa. IR spectra were collected on a Thermo Scientific Nicolet iS5 using KBr pellets or an attenuated total reflection (ATR) accessory in an N<sub>2</sub>-filled glovebox. HR-EI mass spectra were recorded on a Waters GCT Premier TOF MS instrument.

**MeOTBDPhos.** To a stirring solution of TBD (5.00 g, 36.0 mmol) and NEt<sub>3</sub> (7.29 g, 72.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added CIP(OMe)<sub>2</sub> (9.25 g, 72.0 mmol). The reaction was stirred overnight, evaporated to dryness under vacuum, and extracted with THF (300 mL). The filtrate was evaporated to dryness under vacuum and dissolved in pentane (40 mL). Cooling the solution to -30 °C yielded a white precipitate. Yield: 9.05 g (78%). Anal. Calcd for C<sub>10</sub>H<sub>24</sub>BN<sub>3</sub>O<sub>4</sub>P<sub>2</sub>: C, 37.2; H, 7.49; N, 13.0. Found: C, 37.0; H, 7.33; N, 13.0. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  1.77 (quint, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 2.86 (t, NCH<sub>2</sub>, 4H), 3.15 (m, NCH<sub>2</sub>, 4H), 3.50 (t, OCH<sub>3</sub>, 12H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  24.7 (br s, FWHM = 220 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  27.9 (s, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 36.9 (s, NCH<sub>2</sub>), 48.3 (s, NCH<sub>2</sub>), 51.9 (t, *J* = 11 Hz, OCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  145.6 (s). MS (EI) *m/z*: calcd for C<sub>10</sub>H<sub>24</sub>BN<sub>3</sub>O<sub>4</sub>P<sub>2</sub> 323.1335; found 323.1351. IR (ATR, cm<sup>-1</sup>): 2978 w, 2951 w, 2925 m, 2861 w, 2822 m, 1527w, 1513 m, 1470 m, 1442 m, 1371 s, 1360 w, 1349 w, 1322 m, 1310 w, 1295 s, 1229 w, 1209 m, 1166 m, 1113 m, 1098 m, 1019 vs, 972 m, 917 vw, 903 w, 879 m, 846 vw, 814 m, 798 vw, 764 w, 754 w, 745 w, 738 w, 695 vs, 684 vw, 671 vw, 661 m, 651 m.

**Et<sup>r</sup>TBDPhos.** To a stirring solution of TBD (0.20 g, 1.4 mmol) and NEt<sub>3</sub> (0.29 g, 2.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added CIPEt<sub>2</sub> (0.36 g, 2.9 mmol). The reaction was stirred overnight, evaporated to dryness under vacuum, and extracted with THF (40 mL). The filtrate was evaporated to dryness under vacuum and dissolved in pentane (5 mL). The solution was cooled to -30 °C to yield colorless needles. Yield: 0.18 g (40%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  1.01 (m, -CH<sub>2</sub>-CH<sub>3</sub>, 12H), 1.34 (m, -CH<sub>2</sub>-CH<sub>3</sub>, 4H), 1.64 (m, -CH<sub>2</sub>-CH<sub>3</sub>, 4H), 1.70 (m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 2.83 (t, NCH<sub>2</sub>, 4H), 2.93 (m, NCH<sub>2</sub>, 4H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  25.9 (br s, FWHM = 220 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  9.9 (s, -CH<sub>2</sub>-CH<sub>3</sub>), 20.5 (s, -CH<sub>2</sub>-CH<sub>3</sub>), 28.4 (s, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 40.1 (s, NCH<sub>2</sub>), 48.7 (s, NCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  43.3 (s).

**(<sup>Ph</sup>TBDPhos)PtCl<sub>2</sub> (1).** To a stirring solution of (COD)PtCl<sub>2</sub> (0.68 g, 1.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added a solution of <sup>Ph</sup>TBDPhos (0.50 g, 1.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The reaction was stirred overnight, and hexane was added to induce formation of a white precipitate. The precipitate

was isolated by filtration, dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and crystallized by vapor diffusion with Et<sub>2</sub>O. Yield: 0.92 g (89%). Anal. Calcd for C<sub>30</sub>H<sub>32</sub>BCl<sub>2</sub>N<sub>3</sub>P<sub>2</sub>Pt·2CH<sub>2</sub>Cl<sub>2</sub>: C, 40.8; H, 3.85; N, 4.46. Found: C, 40.8; H, 3.66; N, 4.60. The two molecules of CH<sub>2</sub>Cl<sub>2</sub> included in the EA are present in the XRD structure and observed in the <sup>1</sup>H NMR spectrum. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C): δ 1.54 (m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 2.81 – 2.93 (m, NCH<sub>2</sub>, 8H), 7.33 – 7.47 (m, Ph, 12H), 7.70 – 7.81 (m, Ph, 8H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C): δ 24.4 (br s, FWHM = 460 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 26.0 (s, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 47.0 (s, NCH<sub>2</sub>), 48.3 (s, NCH<sub>2</sub>), 128.3 (t, *J* = 6.0 Hz, Ph), 131.1 (s, Ph), 133.1 (t, *J* = 5.3 Hz, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 43.9 (s with doublet satellites, <sup>1</sup>*J*<sub>PtP</sub> = 3730 Hz). MS (EI) *m/z*: calcd for C<sub>30</sub>H<sub>32</sub>BCl<sub>2</sub>N<sub>3</sub>P<sub>2</sub>Pt 772.1189; found 772.1248. IR (ATR, cm<sup>-1</sup>): 3050 w, 2979 vw, 2945 w, 2859 vw, 1588 vw, 1536 m, 1519 s, 1481 w, 1466 w, 1448 vw, 1432 s, 1384 m, 1363 m, 1348 w, 1324 m, 1298 m, 1280 m, 1268 w, 1258 w, 1210 s, 1172 m, 1119 vw, 1097 s, 1058 w, 1027 s, 1011 vw, 997 w, 917 m, 892 m, 833 m, 788 m, 743 s, 722 s, 715 vw, 690 vs, 639 m, 629 w, 620 m, 605 s, 581 s, 576 m, 559 w, 555 s.

(<sup>MeO</sup>TBDPhos)PtCl<sub>2</sub> (**2**). To a stirring solution of (COD)PtCl<sub>2</sub> (0.38 g, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added a solution of <sup>MeO</sup>TBDPhos (0.33 g, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The reaction was stirred overnight, reduced to 5 mL, and crystallized by vapor diffusion with Et<sub>2</sub>O to yield colorless needles. Yield: 0.57 g (95%). Anal. Calcd for C<sub>10</sub>H<sub>24</sub>BCl<sub>2</sub>N<sub>3</sub>O<sub>4</sub>P<sub>2</sub>Pt: C, 20.4; H, 4.11; N, 7.13. Found: C, 20.5; H, 3.93; N, 6.84. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C): δ 1.85 (quint, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 2.94 (t, NCH<sub>2</sub>, 4H), 3.23 (m, NCH<sub>2</sub>, 4H), 3.86 (t, OCH<sub>3</sub>, 12H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C): δ 22.7 (br s, FWHM = 260 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 26.0 (s, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 40.5 (s, NCH<sub>2</sub>), 48.6 (s, NCH<sub>2</sub>), 54.6 (s, OCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 69.9 (s with doublet satellites, <sup>1</sup>*J*<sub>PtP</sub> = 4895 Hz). MS (EI) *m/z*: calcd for C<sub>10</sub>H<sub>24</sub>BCl<sub>2</sub>N<sub>3</sub>O<sub>4</sub>P<sub>2</sub>Pt 588.0360; found 588.0389. IR (ATR, cm<sup>-1</sup>): 3003 w, 2904 w, 2880 w, 2853 w, 1524 vw, 1509 m, 1466 vw, 1454 w, 1445 vw, 1428 vw, 1390 m, 1364 m, 1351 w, 1322 m, 1306 w, 1293 vw, 1285 m, 1207 m, 1169 m, 1113 vw, 1088 m, 1064 vw, 1054 vw, 1024 vw, 1004 vs, 922 s, 890 w, 875 vw, 864 vw, 856 vw, 837 w, 811 s, 775 s, 749 vw, 741 vw, 730 w, 722 w, 713 vw, 703 vw, 693 vw, 698 vw, 683 w, 673 w, 665 w, 655 m, 646 m, 637 s, 630 s, 621 s, 612 s.

(<sup>Et</sup>TBDPhos)PtCl<sub>2</sub> (**3**). To a stirring solution of <sup>Et</sup>TBDPhos (0.14 g, 0.44 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (7 mL) was added (COD)PtCl<sub>2</sub> (0.17 g, 0.45 mmol). The reaction was stirred overnight, reduced to ~4 mL, and crystallized by vapor diffusion with Et<sub>2</sub>O to yield colorless needles. Yield: 0.18 g (71%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C): δ 1.19 (m, -CH<sub>2</sub>-CH<sub>3</sub>, 12H), 1.83 (m, -CH<sub>2</sub>-CH<sub>3</sub>, 4H), 2.00 (m, -CH<sub>2</sub>-CH<sub>3</sub>, 4H), 2.61 (m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 2.93 (t, NCH<sub>2</sub>, 4H), 3.10 (m, NCH<sub>2</sub>, 4H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C): δ 24.1 (br s, FWHM = 292 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 8.9 (-CH<sub>2</sub>-CH<sub>3</sub>), 20.5 (m, -CH<sub>2</sub>-CH<sub>3</sub>), 26.7 (s, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 42.5 (s, NCH<sub>2</sub>), 48.8 (s, NCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 58.9 (s with doublet satellites, <sup>1</sup>*J*<sub>PtP</sub> = 3692 Hz).

(<sup>Ph</sup>TBDPhos)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**4**). To a stirring solution of **1** (0.10 g, 0.13 mmol) and excess NEt<sub>3</sub> (0.5 mL) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added a solution of 1,2-benzenedithiol (0.018 g, 0.13 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The reaction was stirred overnight, evaporated to dryness under vacuum, and extracted with THF (10 mL). The solution was evaporated to dryness under vacuum and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). Vapor diffusion with Et<sub>2</sub>O yielded green-yellow blocks. Yield: 0.080 g (73%). Anal. Calcd for C<sub>36</sub>H<sub>36</sub>BN<sub>3</sub>P<sub>2</sub>PtS<sub>2</sub>: C, 51.3; H, 4.31; N, 4.99. Found: C, 51.2; H, 4.22; N, 4.57. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C): δ 1.62 (quint, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 2.84 – 3.02 (m, NCH<sub>2</sub>, 8H), 6.57 – 6.69 (m, Ar, 2H), 7.18 – 7.37 (m, Ar, 14H), 7.48 – 7.65 (m, Ar, 8H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C): δ 24.9 (br s, FWHM = 510 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 26.4 (s, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 47.2 (s, NCH<sub>2</sub>), 48.6 (s, NCH<sub>2</sub>), 121.0 (s, Ar), 127.7 (t, *J* = 5.9 Hz, Ar), 129.3 (s, Ar), 130.6 (s, Ar), 131.4 (s, Ar),

132.1 (s, Ar), 133.1 (t,  $J = 6.0$  Hz, Ar), 146.4 (m, Ar).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 20 °C):  $\delta$  53.3 (s with doublet satellites,  $^1J_{\text{PtP}} = 2917$  Hz). MS (EI)  $m/z$ : calcd for  $\text{C}_{36}\text{H}_{36}\text{BN}_3\text{P}_2\text{PtS}_2$  842.1567; found 842.1433. IR (ATR,  $\text{cm}^{-1}$ ): 3049 vw, 2949 vw, 1559 vw, 1548 vw, 1514 w, 1506 m, 1466 w, 1481 w, 1443 w, 1432 m, 1417 w, 1383 m, 1360 w, 1348 w, 1323 m, 1298 w, 1266 m, 1236 vw, 1225 vw, 1207 m, 1171 m, 1095 s, 1029 m, 997 w, 937 w, 905 w, 891 w, 830 m, 779 m, 741 w, 729 s, 710 m, 687 vs, 663 w, 656 w, 635 m, 625 vw, 618 w, 612 vw, 601 vw, 596 m, 581 vw, 569 m, 556 vw, 551 vw. UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 250 ( $5.16 \times 10^4$ ), 326 ( $7.80 \times 10^3$ ).

**(<sup>MeO</sup>TBDPhos)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (5).** To a stirring solution of **2** (1.00 g, 1.70 mmol) and excess  $\text{NEt}_3$  (5 mL) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was added a solution of 1,2-benzenedithiol (0.24 g, 1.7 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL). The reaction was stirred overnight, evaporated to dryness under vacuum, and extracted with THF (100 mL). The solution was evaporated to dryness under vacuum and dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL). A pale-yellow precipitate was obtained by adding excess  $\text{Et}_2\text{O}$  to the solution. The precipitate was dissolved in  $\text{CH}_2\text{Cl}_2$  and crystals were grown by vapor diffusion with  $\text{Et}_2\text{O}$ . Yield: 0.82 g (73%). Anal. Calcd for  $\text{C}_{16}\text{H}_{28}\text{BN}_3\text{O}_4\text{P}_2\text{PtS}_2$ : C, 29.2; H, 4.29; N, 6.38. Found: C, 29.3; H, 4.23; N, 6.38.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 20 °C):  $\delta$  1.89 (m,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ , 4H), 2.97 (t,  $\text{NCH}_2$ , 4H), 3.28 (m,  $\text{NCH}_2$ , 4H), 3.72 – 3.84 (m,  $\text{OCH}_3$  12H), 6.78 – 6.89 (m, Ar, 2H), 7.57 – 7.67 (m, Ar, 2H).  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 20 °C):  $\delta$  23.2 (br s, FWHM = 410 Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 20 °C):  $\delta$  26.1 (s,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 39.5 (s,  $\text{NCH}_2$ ), 48.9 (s,  $\text{NCH}_2$ ), 53.9 (m,  $\text{OCH}_3$ ), 121.9 (s, Ar), 129.8 (s, Ar), 144.8 (m, Ar).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 20 °C):  $\delta$  97.7 (s with doublet satellites,  $^1J_{\text{PtP}} = 3918$  Hz). MS (EI)  $m/z$ : calcd for  $\text{C}_{16}\text{H}_{28}\text{BN}_3\text{O}_4\text{P}_2\text{PtS}_2$  658.0737; found 658.0807. IR (ATR,  $\text{cm}^{-1}$ ): 3016 w, 2937 w, 2872 w, 2834 w, 1535 vw, 1521 m, 1474 w, 1444 m, 1417 w, 1386 m, 1368 m, 1325 m, 1299 w, 1280 s, 1239 vw, 1232 vw, 1210 m, 1176 m, 1121 w, 1096 m, 1065 w, 1029 s, 1000 vs, 949 vw, 938 w, 921 m, 899 vw, 891 vw, 834 m, 805 w, 789 s, 760 s, 743 s, 699 vw, 665 w, 654 vw. UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 249 ( $4.58 \times 10^4$ ), 320 ( $1.10 \times 10^4$ ).

**(<sup>MeO</sup>TBDPhos-MeOH)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (5-MeOH).** To a stirring solution of **5** (0.10 g, 0.15 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added MeOH (1 mL) and  $\text{NEt}_3$  (0.5 mL) in air. The reaction was shaken several times, filtered, and crystallized by vapor diffusion with  $\text{Et}_2\text{O}$  to yield colorless blocks and needles. Yield: 0.089 g (85%). Anal. Calcd for  $\text{C}_{17}\text{H}_{32}\text{BN}_3\text{O}_5\text{P}_2\text{PtS}_2$ : C, 29.6; H, 4.67; N, 6.09. Found: C, 29.5; H, 4.43; N, 5.51.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 20 °C):  $\delta$  1.66 – 1.94 (m, 4H), 2.80 – 3.05 (m, 4H), 3.06 – 3.16 (m, 2H), 3.18 (s,  $\text{B-OCH}_3$ , 3H), 3.59 – 3.71 (m, 2H), 3.71 – 3.83 (m,  $\text{P(OCH}_3)_2$ , 12H), 6.78 (m, Ar, 2H), 7.03 (m, NH, 1H), 7.61 (m, Ar, 2H).  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 20 °C):  $\delta$  1.7 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 20 °C):  $\delta$  27.8 (s), 38.3 (s), 47.0 (s), 50.5 (s), 54.2 (s), 121.5 (s, Ar), 129.8 (s, Ar), 145.4 (s, Ar).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 20 °C):  $\delta$  97.3 (s with doublet satellites,  $^1J_{\text{PtP}} = 3954$  Hz). IR (ATR,  $\text{cm}^{-1}$ ): 2929 w, 2880 w, 2823 m, 1546 w, 1535 vw, 1529 vw, 1512 w, 1501 vw, 1493 vw, 1484 vw, 1460 w, 1444 m, 1396 w, 1359 m, 1343 w, 1293 m, 1243 m, 1184 m, 1138 s, 1103 s, 1079 m, 1041 w, 1019 vs, 973 vw, 909 m, 879 s, 834 m, 802 s, 766 vw, 743 vw, 672 vw, 663 m, 636 vw, 609 w, 600 w, 584 w, 571 m, 554 s.

**(<sup>Et</sup>TBDPhos)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (6).** To a stirring solution of (<sup>Et</sup>TBDPhos)PtCl<sub>2</sub> (0.15 g, 0.26 mmol) and  $\text{NEt}_3$  (72  $\mu\text{L}$ , 0.52 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was added a solution of 1,2-benzenedithiol (0.037 g, 0.26 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL). The reaction was stirred overnight, evaporated to dryness under vacuum, and extracted with THF (20 mL). The solution was then evaporated to dryness under vacuum and dissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL). Vapor diffusion with  $\text{Et}_2\text{O}$  yielded greenish-yellow blocks. Yield: 0.11 g (66%). In some reactions it was found that **3** co-crystallizes with **6** if present.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 20 °C):  $\delta$  1.20 (m,  $-\text{CH}_2\text{-CH}_3$ , 12H), 1.85 (m,  $-\text{CH}_2\text{-CH}_3$ , 4H), 2.19 (m,  $-\text{CH}_2\text{-CH}_3$ , 4H), 2.45 (m,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ , 3H), 2.60 (m,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ , 1H), 2.90 (m,  $\text{NCH}_2$ , 4H), 3.07

(m, NCH<sub>2</sub>, 4H), 6.77 – 6.79 (m, Ar, 2H), 7.48 – 7.49 (m, Ar, 2H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C): δ 24.2 (br s, FWHM = 390 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 8.8 (–CH<sub>2</sub>–CH<sub>3</sub>), 24.5 (m, –CH<sub>2</sub>–CH<sub>3</sub>), 26.8 (s, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>), 42.5 (s, NCH<sub>2</sub>), 51.0 (s, NCH<sub>2</sub>), 121.9 (s, Ar), 129.7 (s, Ar), 143.8 (m, Ar). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 61.2 (s with doublet satellites, <sup>1</sup>J<sub>PP</sub> = 2912 Hz).

**(<sup>MeO</sup>TBDPhos)Mo(CO)<sub>4</sub> (8).** A mixture of Mo(CO)<sub>6</sub> (1.00 g, 3.79 mmol) and <sup>MeO</sup>TBDPhos (1.23 g, 3.81 mmol) in THF (50 mL) was heated to reflux overnight. The resulting pale-yellow solution was evaporated to dryness under vacuum and extracted with Et<sub>2</sub>O (50 mL). The pale-yellow solution was allowed to cool to RT, evaporated to dryness under vacuum, and the residue was dissolved in Et<sub>2</sub>O (3 mL). Layering the solution with pentane formed an off-white precipitate after 2 days. The solution was filtered through a Celite column and stored at -30 °C to yield colorless blocks. Yield: 0.90 g (45%). Anal. Calcd for C<sub>14</sub>H<sub>24</sub>BMoN<sub>3</sub>O<sub>8</sub>P<sub>2</sub>: C, 31.7; H, 4.56; N, 7.91. Found: C, 31.8; H, 4.47; N, 7.82. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C): δ 1.79 (quint, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>, 4H), 2.92 (t, NCH<sub>2</sub>, 4H), 3.24 (m, NCH<sub>2</sub>, 4H), 3.50 – 3.57 (m, OCH<sub>3</sub>, 12 H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C): δ 24.2 (br s, FWHM = 320 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 26.6 (s, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>), 39.8 (s, NCH<sub>2</sub>), 49.5 (s, NCH<sub>2</sub>), 51.5 (s, OCH<sub>3</sub>), 208.6 (t, CO, *J* = 13 Hz), 213.7 (vt, CO, *J* = 10 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 165.4 (s with sextet satellites, <sup>1</sup>J<sub>MoP</sub> = 194 Hz). MS (EI) *m/z*: calcd for C<sub>14</sub>H<sub>24</sub>BMoN<sub>3</sub>O<sub>8</sub>P<sub>2</sub> 533.0186; found 533.0201. IR (KBr, cm<sup>-1</sup>): 2941 m, 2889 m, 2851 m, 2837 m, 2025 vs (CO), 1924 vs (CO), 1903 vs, (CO) 1889 vs (CO), 1507 s, 1473 m, 1463 vw, 1443 m, 1391 m, 1366 m, 1352 m, 1320 w, 1297 w, 1277 s, 1228 w, 1207 s, 1169 s, 1121 w, 1093 m, 1065 w, 1024 vs, 938 m, 909 m, 893 m, 828 s, 788 s, 751 w, 727 s, 664 w, 645 m, 606 s, 596 w, 567 m, 546 m.

**[(<sup>MeO</sup>TBDPhos-H)Mo(CO)<sub>4</sub>]NTf<sub>2</sub> (8-HNTf<sub>2</sub>).** To a stirring solution of **8** (0.10 g, 0.19 mmol) in Et<sub>2</sub>O (1 mL) was added a solution of HNTf<sub>2</sub> (0.053 g, 0.19 mmol) in Et<sub>2</sub>O (1 mL). The solution turned pale yellow after stirring overnight and was evaporated to dryness under vacuum to yield a colorless, analytically-pure powder. Anal. Calcd for C<sub>16</sub>H<sub>25</sub>BF<sub>6</sub>MoN<sub>4</sub>O<sub>12</sub>P<sub>2</sub>S<sub>2</sub>: C, 23.7; H, 3.10; N, 6.90. Found: C, 23.8; H, 3.09; N, 6.82. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C): δ 1.97 (m, 2H), 2.15 (m, 2H), 2.98 (m, 2H), 3.31 (m, 2H), 3.54 – 3.73 (m, 16H), 7.08 (br s, NH, 1H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C): δ 27.8 (br s, FWHM = 400 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 20 °C): δ -79.3 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 167.0 (s). IR (KBr, cm<sup>-1</sup>): 3116 m (NH), 2982 w, 2949 m, 2847 w, 2042 vs (CO), 1947 vw (CO), 1915 vs (CO), 1479 m, 1449 m, 1435 m, 1345 s, 1322 s, 1302 vw, 1275 vw, 1262 vw, 1241 vw, 1193 s, 1135 m, 1099 m, 1059 s, 1029 s, 929 w, 915 vw, 890 vw, 820 vw, 764 s, 741 s, 669 vw, 653 w, 611 m, 594 m, 570 m, 539 w, 508 m.

**(<sup>MeO</sup>TBDPhos-MeOH)Mo(CO)<sub>4</sub> (8-MeOH).** To a stirring solution of **8** (0.10 g, 0.19 mmol) in Et<sub>2</sub>O (1 mL) was added MeOH (0.5 mL) and NEt<sub>3</sub> (0.1 mL) in air. The colorless solution was stirred overnight. Colorless blocks were obtained by slowly allowing the solution to evaporate in air. The resulting crystals were isolated by filtration and washed with hexane (10 mL). Yield: 0.089 g (84%). Anal. Calcd for C<sub>15</sub>H<sub>28</sub>BMoN<sub>3</sub>O<sub>9</sub>P<sub>2</sub>: C, 32.0; H, 5.01; N, 7.46. Found: C, 32.0; H, 4.89; N, 7.74. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C): δ 1.61 (m, 2H), 1.79 (m, 2H), 2.80 (m, 4H), 3.06 (m, 3H), 3.15 (s, BOCH<sub>3</sub>, 3H), 3.43 – 3.59 (m, P(OCH<sub>3</sub>)<sub>2</sub> 12H), 3.71 (m, 2H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C): δ 2.7 (br s, FWHM = 80 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 28.3 (s, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>), 38.3 (vt, NCH<sub>2</sub>, *J* = 2 Hz), 46.9 (s, NCH<sub>2</sub>), 51.2 (s, P(OCH<sub>3</sub>)<sub>2</sub>), 51.3 (s, P(OCH<sub>3</sub>)<sub>2</sub>), 51.9 (s, BOCH<sub>3</sub>), 209.5 (t, CO, *J* = 13 Hz), 210.3 (t, CO, *J* = 13 Hz), 214.5 (vt, CO, *J* = 10 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 20 °C): δ 165.3 (s with sextet satellites, <sup>1</sup>J<sub>MoP</sub> = 192 Hz). IR (KBr, cm<sup>-1</sup>): 3266 m (NH), 2970 m, 2956 m, 2940 m, 2885 m, 2832 m, 2820 m, 2018 vs (CO), 1933 vs (CO), 1909 vs (CO), 1872 vs (CO), 1463 m, 1438 m, 1404 w, 1365 m, 1343 w, 1295 m, 1242 m, 1194 m, 1180 vw, 1141 s, 1108 s,

1092 s, 1081 s, 1060 s, 1038 s, 1026 s, 1010 s, 963 m, 951 vw, 918 m, 874 m, 832 w, 791 vw, 779 m, 743 m, 728 m, 709 m, 676 vw, 661 vw, 647 vw, 619 s, 599 s, 566 m, 535 vw, 527 m, 515 vw, 501 vw.

**Crystallographic studies.** Single crystals were obtained from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (**1**, **2**, **5** and **6**), CH<sub>2</sub>Cl<sub>2</sub>/MeOH/NEt<sub>3</sub>/Et<sub>2</sub>O (**5-MeOH**), Et<sub>2</sub>O/hexane (**8**), or Et<sub>2</sub>O/MeOH/NEt<sub>3</sub> (**8-MeOH**) and mounted on a MiTeGen micromount using ParatoneN oil in air. The data collection, structural solution, and refinement were carried out as reported previously.<sup>3</sup> Briefly, the structures were solved with Direct Methods (SHELXT)<sup>4</sup> and the positions of the non-hydrogen atoms were confirmed by subsequent least-squares refinement (SHELXL).<sup>5</sup> The positional disorder of the P(OMe)<sub>2</sub> groups in **5-MeOH** was modeled by refining each atom over two positions and setting the sum of the site occupancy factor equal to one. The disordered TBD subunit in **6** was modeled similarly. The positions of all hydrogen atoms were idealized and allowed to ride on the attached atom. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution and refinement were performed with Olex<sup>2</sup> and publication figures were generated with Olex<sup>2</sup> or Mercury.<sup>6</sup>

**DFT Calculations.** Geometry optimizations were performed using the M06-L density functional and the def2-SVP basis set for main group elements while the def2-TZVP and its corresponding ECP were used for Pt.<sup>7</sup> Calculations were performed at room temperature and using CH<sub>2</sub>Cl<sub>2</sub> as the solvent. All DFT calculations were performed using the Gaussian 16 software package. We also tested the choice of the meta-GGA M06-L functional against the hybrid B3LYP functional.<sup>8</sup> For the B3LYP functional, the choice of basis set and ECP remain the same, however a dispersion correction (Grimme's D3 correction with Becke-Johnson damping)<sup>9</sup> was incorporated. Free energies of reaction for (R<sub>2</sub>TBDPhos)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) with CH<sub>3</sub>OH were computed with both M06L and B3LYP functionals. After computing geometries from different initial guesses, we chose the most stable conformer for reactant and product. The supplemental file *optimized-geometries.xyz* contains the computed Cartesian coordinates of the molecules reported in this study. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, <http://www.ccdc.cam.ac.uk/pages/Home.aspx>)<sup>6b</sup> for visualization and analysis.

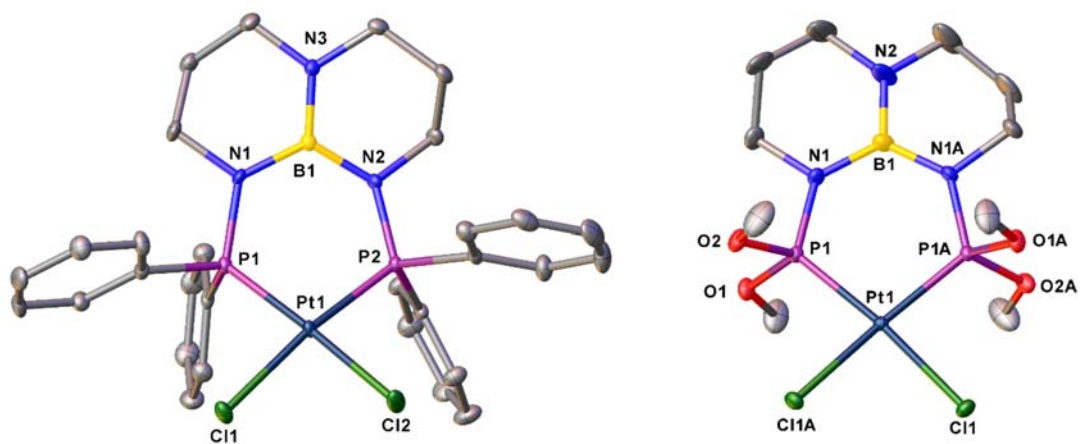
**Table S1.** Calculated  $\Delta G$  of reaction computed using the M06-L and B3LYP functionals for  $(^R\text{TBDPhos})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4) + \text{MeOH} \rightarrow (^R\text{TBDPhos-MeOH})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$ .

R	M06-L	B3LYP
OMe	-5.79	-9.01
OEt	-3.98	-8.39
Me	-1.83	-6.09
Ph	-0.93	-4.01
Et	2.46	0.74
<sup>i</sup> Pr	6.59	2.58

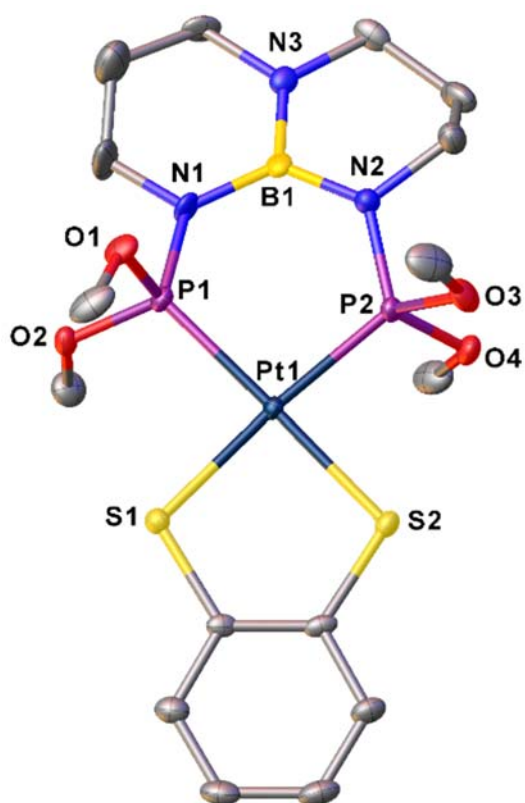
**Table S2.** DFT calculated Gibbs free energies of  $(^R\text{TBDPhos})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$  (reactant) and  $(^R\text{TBDPhos-MeOH})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$  (product) using the M06L functional. Calculations for Product 1 and Product 2 were performed using different starting orientations of the OMe groups on the TBD backbone. Product 1 started with OMe pointing towards Pt (as observed in the XRD structure of **5-MeOH**) whereas Product 2 started with OMe pointing away from Pt.

R =	Complex	M06L			
		SCF (a.u)	Total Energy (a.u)	Gibbs Free energy (a.u)	$\Delta G$ (kcal/mol) <sup>†</sup>
<b>Me</b>	Reactant	-2413.3690	-2412.9084	-2412.9957	
	Product 1	-2529.0151	-2528.4957	-2528.5877	-1.83
	Product 2*	-2529.0151	-2528.4957	-2528.5877	-1.84
<b>OMe</b>	Reactant	-2714.0174	-2713.5305	-2713.6300	
	Product 1	-2829.6688	-2829.1231	-2829.2283	-5.79
	Product 2*	-2829.6688	-2829.1240	-2829.2254	-3.95
<b><sup>i</sup>Pr</b>	Reactant	-2727.5917	-2726.8918	-2726.9969	
	Product 1	-2843.2242	-2842.4655	-2842.5755	6.59
	Product 2	-2843.2209	-2842.4629	-2842.5726	8.39
<b>Ph</b>	Reactant	-3179.6944	-3179.0065	-3179.1235	
	Product 1	-3295.3383	-3294.5916	-3294.7141	-0.93
	Product 2	-3295.3278	-3294.5812	-3294.7030	6.02
<b>OEt</b>	Reactant	-2871.1665	-2870.5617	-2870.6733	
	Product 1	-2986.8171	-2986.1531	-2986.2688	-3.98
	Product 2*	-2986.8171	-2986.1531	-2986.2687	-3.96
<b>Et</b>	Reactant	-2570.4781	-2569.8967	-2569.9939	
	Product 1	-2686.1162	-2685.4759	-2685.5791	2.46
	Product 2	-2686.1048	-2685.46415	-2685.56658	10.34
	<b>MeOH</b>	-2413.3690	-2412.9084	-115.5891	

\*Product 2 converges to a structure that is similar to Product 1. <sup>†</sup> $\Delta G = G(\text{Product}) - G(\text{Reactant} + \text{MeOH})$

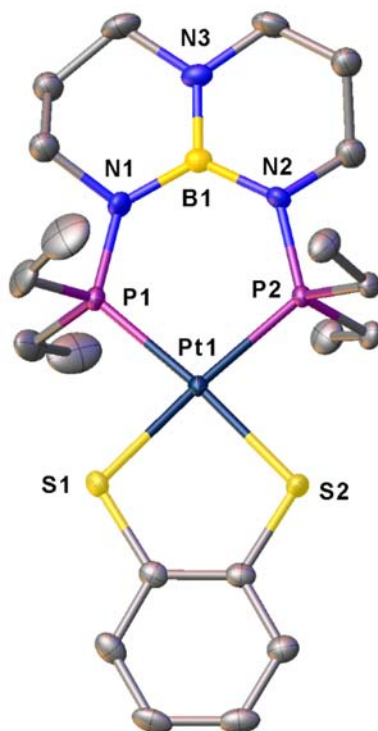


**Figure S1.** Molecular structures of  $(^{\text{Ph}}\text{TBDPhos})\text{PtCl}_2$  (**1**; *left*) and  $(^{\text{MeO}}\text{TBDPhos})\text{PtCl}_2$  (**2**; *right*) with thermal ellipsoids drawn at the 35% probability level. Co-crystallized solvent molecules and hydrogen atoms were omitted from the figure.



**Figure S2.** Molecular structure of  $(^{\text{MeO}}\text{TBDPhos})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$  (**5**) with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms were omitted from the figure.





**Figure S3.** Molecular structure of (<sup>Et</sup>TBDPhos)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**6**) with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms and disordered fragments were omitted from the figure.



**Figure S4.** Molecular structure of (<sup>MeO</sup>TBDPhos)Mo(CO)<sub>4</sub> (**8**) with thermal ellipsoids drawn at the 35% probability level. Hydrogen atoms were omitted from the figure.

**Table S3.** Crystallographic data for (<sup>Ph</sup>TBDPhos)PtCl<sub>2</sub> (**1**), (<sup>MeO</sup>TBDPhos)PtCl<sub>2</sub> (**2**), (<sup>MeO</sup>TBDPhos)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**5**), (<sup>MeO</sup>TBDPhos-MeOH)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**5-MeOH**), (<sup>Et</sup>TBDPhos)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**6**), (<sup>MeO</sup>TBDPhos)Mo(CO)<sub>4</sub> (**8**), and (<sup>MeO</sup>TBDPhos-MeOH)Mo(CO)<sub>4</sub> (**8-MeOH**).

	<b>1</b>	<b>2</b>	<b>5</b>	<b>5-MeOH</b>	<b>6</b>	<b>8</b>	<b>8-MeOH</b>
formula	C <sub>32</sub> H <sub>36</sub> BCl <sub>6</sub> N <sub>3</sub> P <sub>2</sub> Pt	C <sub>10</sub> H <sub>24</sub> BCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> P <sub>2</sub> Pt	C <sub>16</sub> H <sub>28</sub> BN <sub>3</sub> O <sub>4</sub> P <sub>2</sub> PtS <sub>2</sub>	C <sub>17</sub> H <sub>32</sub> BN <sub>3</sub> O <sub>5</sub> P <sub>2</sub> PtS <sub>2</sub>	C <sub>20</sub> H <sub>36</sub> BN <sub>3</sub> P <sub>2</sub> PtS <sub>2</sub>	C <sub>14</sub> H <sub>24</sub> BMoN <sub>3</sub> O <sub>8</sub> P <sub>2</sub>	C <sub>15</sub> H <sub>28</sub> BMoN <sub>3</sub> O <sub>9</sub> P <sub>2</sub>
FW (g mol <sup>-1</sup> )	943.18	589.06	658.38	690.41	640.48	531.05	563.09
crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic
space group	P-1	Pbcn	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Cc	C2/c	P2 <sub>1</sub> /n	P-1
a (Å)	9.4060(9)	14.9159(15)	9.0210(9)	15.9347(16)	18.4280(18)	10.4009(10)	9.2443(9)
b (Å)	12.2212(12)	11.3340(11)	9.4970(9)	10.2361(10)	17.5106(18)	13.3405(13)	10.2295(10)
c (Å)	16.9381(17)	11.3449(11)	26.448(2)	14.7399(15)	17.6481(18)	15.7314(16)	13.0524(13)
α (deg)	88.129(5)	90	90	90	90	90	97.427(5)
β (deg)	76.895(5)	90	90	92.306(5)	117.543(5)	96.242(5)	104.798(5)
γ (deg)	72.751(5)	90	90	90	90	90	100.202(5)
volume (Å <sup>3</sup> )	1809.8(3)	1917.9(3)	2265.9(4)	2402.3(4)	5049.4(9)	2169.8(4)	1154.6(2)
Z	2	4	4	4	8	4	2
ρ <sub>calc</sub> (g cm <sup>-3</sup> )	1.731	2.040	1.930	1.909	1.711	1.626	1.620
μ (mm <sup>-1</sup> )	4.436	7.779	6.546	6.182	5.862	0.797	0.757
F(000)	928	1136	1288	1360	2576	1080	576
θ range (deg)	2.33/26.49	2.73/27.89	2.39/27.91	2.56/26.43	2.56/26.38	2.24/27.82	2.34/28.02
R(int)	0.0400	0.0230	0.0375	0.0284	0.0352	0.0281	0.0249
data/restraints/parameters	7446/0/406	2261/0/108	5380/0/267	4021/30/278	6248/12/261	5155/0/266	5086/0/286
GOF	1.038	1.146	1.105	1.002	1.049	1.039	1.064
R <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0260	0.0199	0.0254	0.0231	0.0203	0.0224	0.0234
wR <sub>2</sub> (all data) <sup>b</sup>	0.0528	0.0323	0.0486	0.0449	0.0456	0.0544	0.0537
Ext. Coeff	-	-	-	-	-	-	-
Largest Peak/Hole (e <sup>-</sup> Å <sup>-3</sup> )	1.560/-1.717	0.313/-0.803	0.961/-1.131	0.666/-0.905	0.764/-0.804	0.928/-0.506	0.358/-0.357
Temp (K)	190(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)

<sup>a</sup>R<sub>1</sub> =  $\sum |F_o| - |F_c|$  /  $\sum |F_o|$  for reflections with  $F_o^2 > 2 \sigma(F_o^2)$ .

<sup>b</sup>wR<sub>2</sub> =  $[\sum w(F_o^2 - F_c^2)^2 / \sum (F_o^2)^2]^{1/2}$  for all reflections.

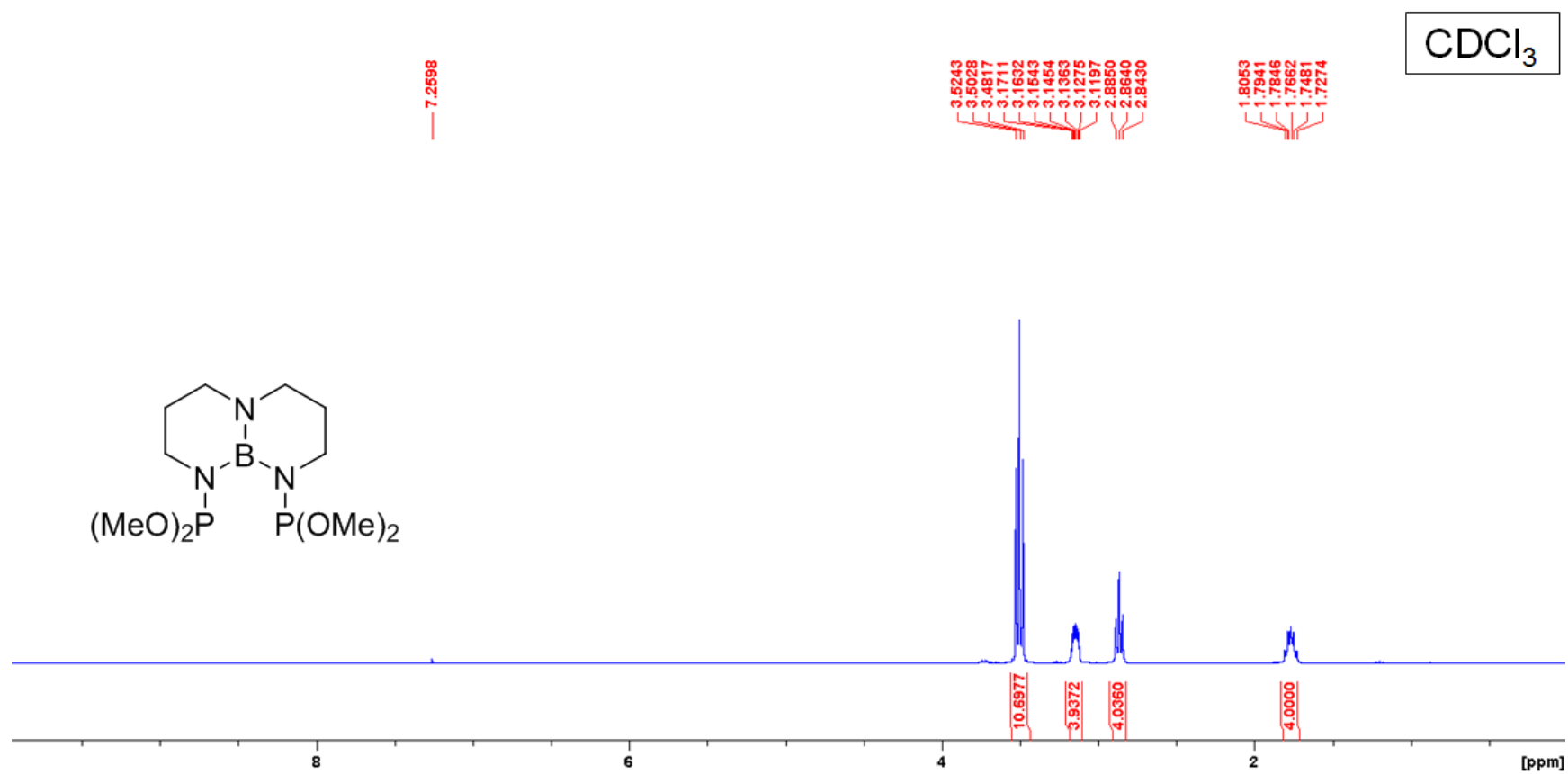
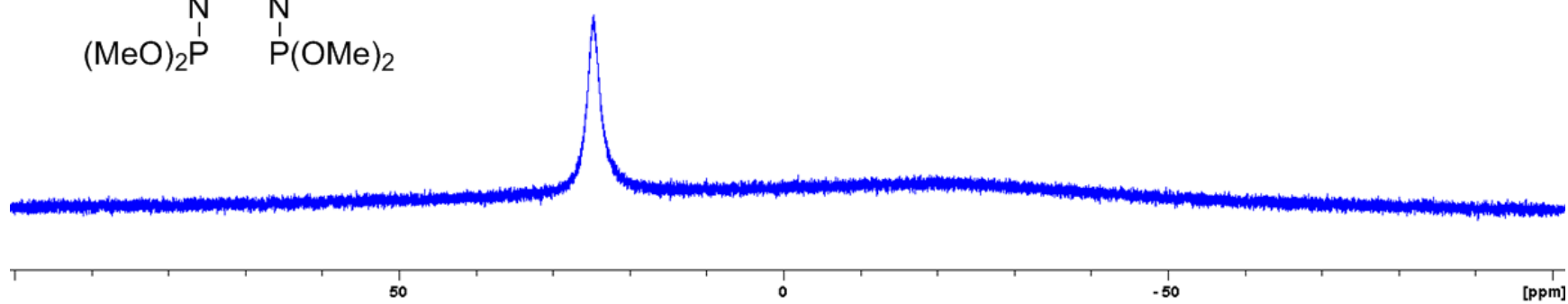
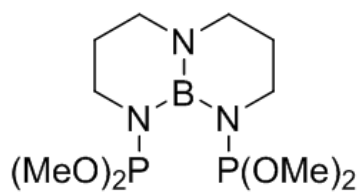


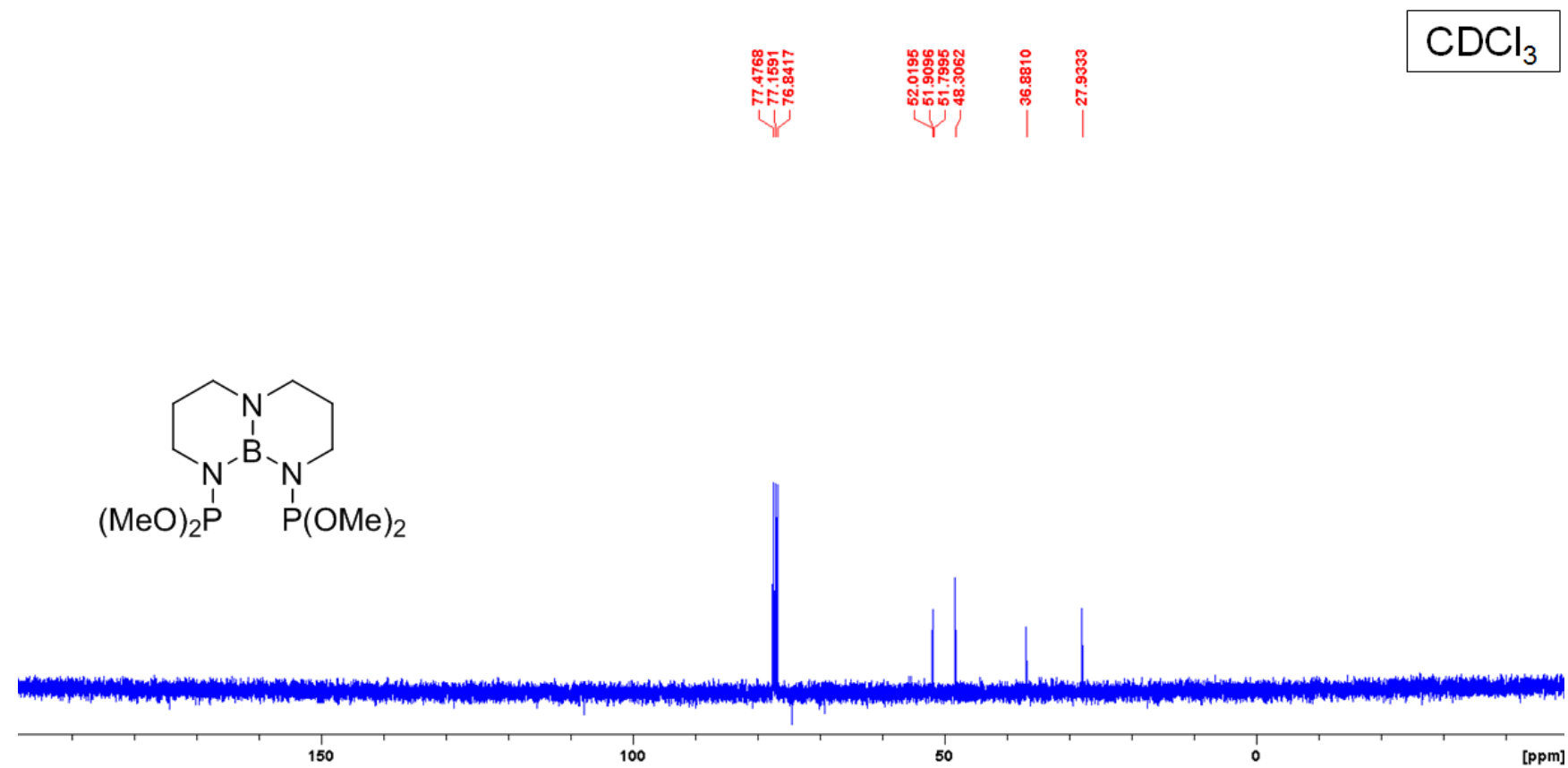
Figure S5. <sup>1</sup>H NMR spectrum of <sup>18</sup>O-TBDPhos.

CDCl<sub>3</sub>

— M 24.7084



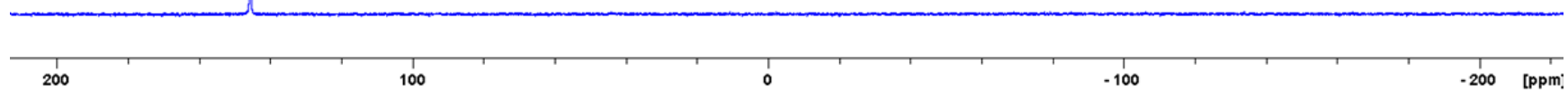
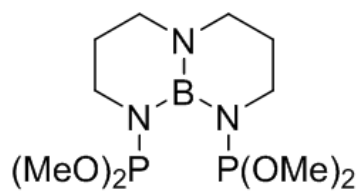
**Figure S6.** <sup>11</sup>B NMR spectrum of <sup>MeO</sup>TBDPhos.



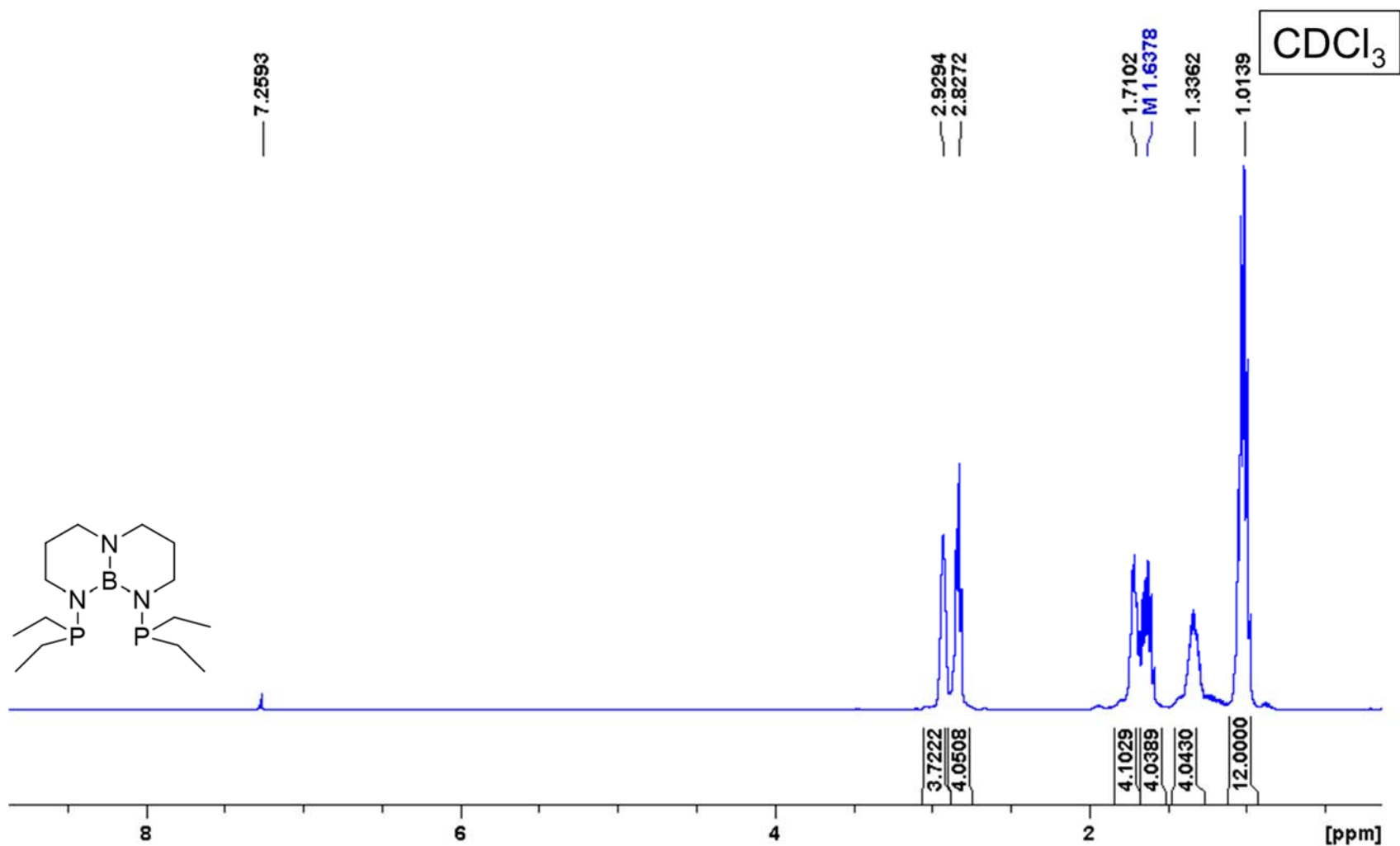
**Figure S7.** <sup>13</sup>C NMR spectrum of <sup>MeO</sup>TBDPhos.

CDCl<sub>3</sub>

— 145.6662



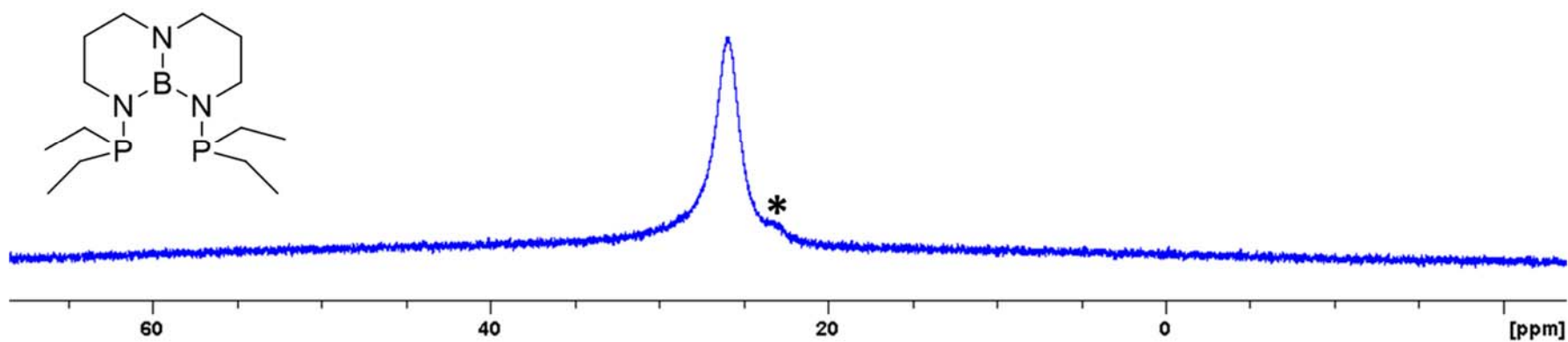
**Figure S8.** <sup>31</sup>P NMR spectrum of <sup>MeO</sup>TBDPhos.



**Figure S9.** <sup>1</sup>H NMR spectrum of EtTBDPhos. Additional minor resonances in the baseline are assigned to the ligand with only one PEt<sub>2</sub> arm, which is a minor impurity that co-crystallizes with EtTBDPhos.

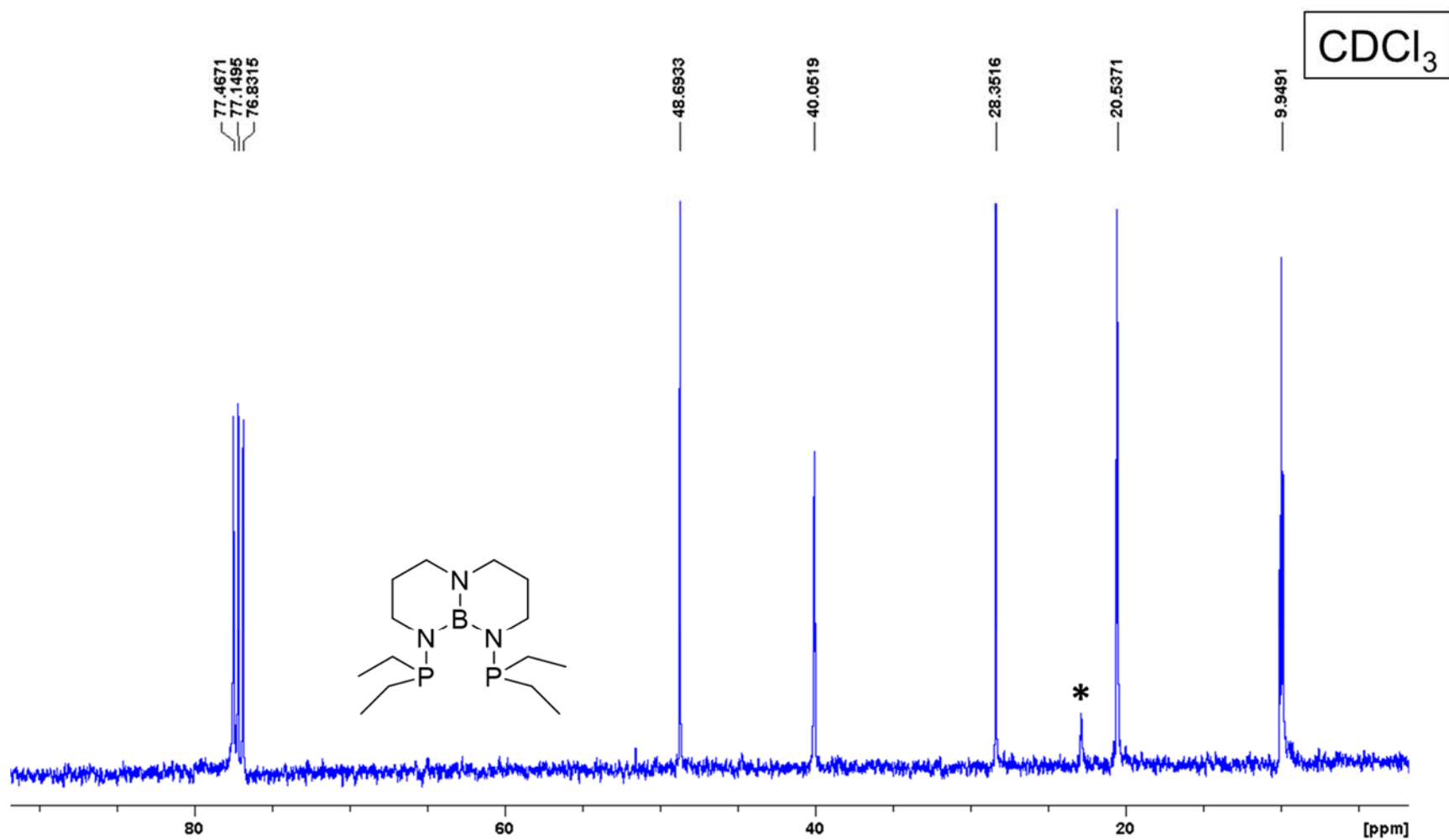
CDCl<sub>3</sub>

— 25.9058



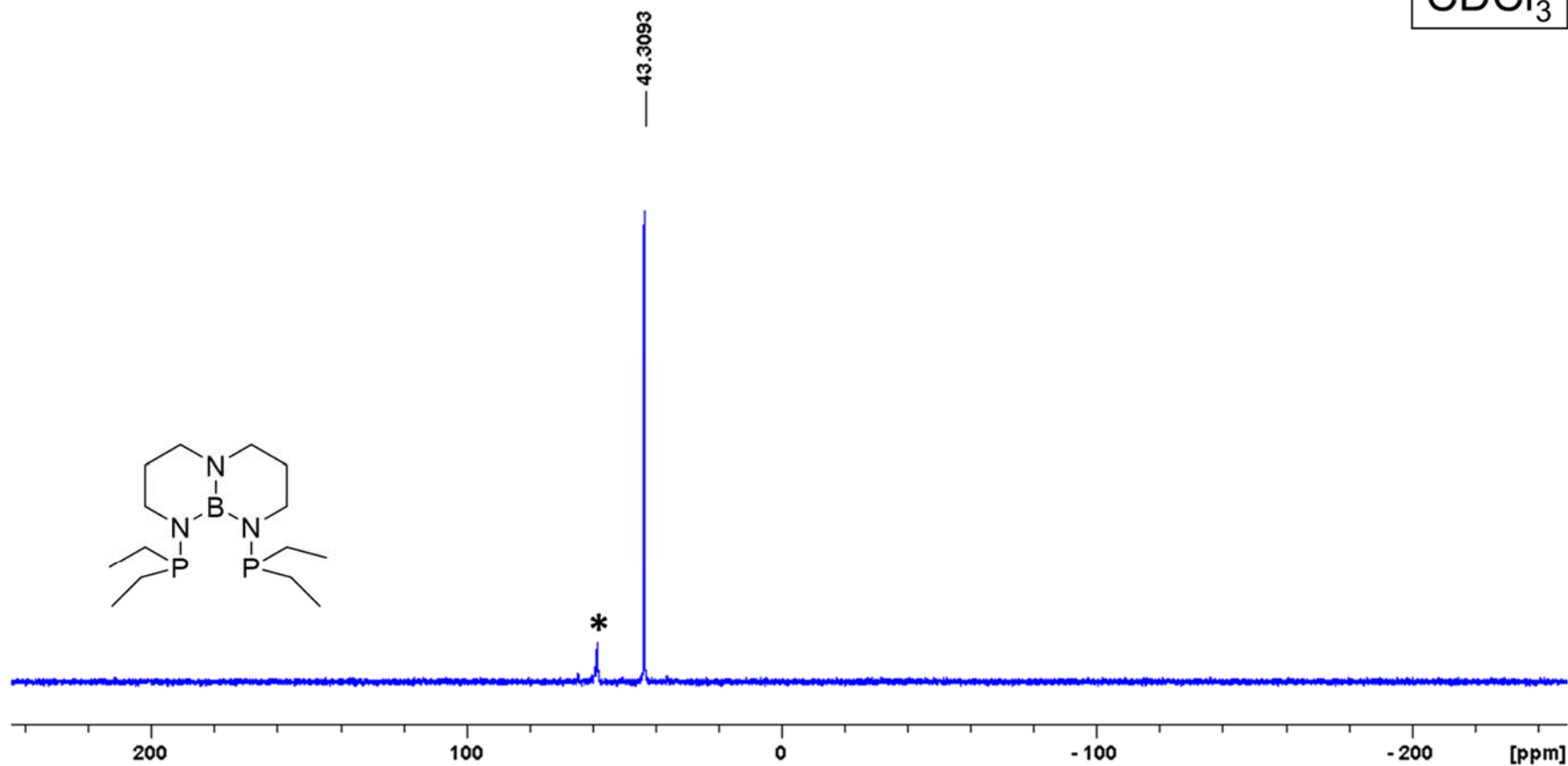
**Figure S10.** <sup>11</sup>B NMR spectrum of <sup>Et</sup>TBDPhos. The \* indicates the resonance assigned to the ligand with only one PEt<sub>2</sub> arm, which is a minor impurity that co-crystallizes with <sup>Et</sup>TBDPhos.



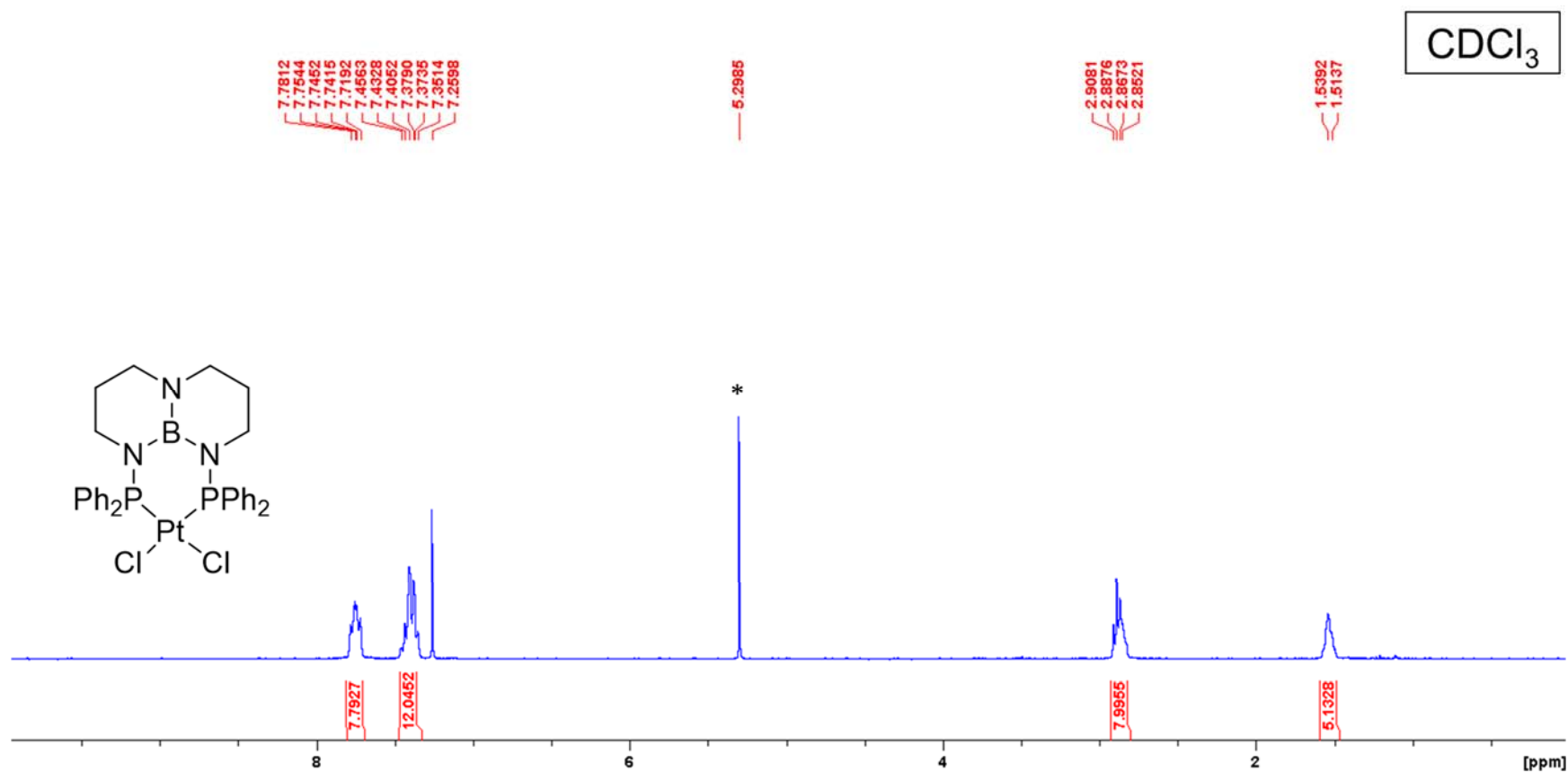


**Figure S11.**  $^{13}\text{C}$  NMR spectrum of  $^{\text{Et}}\text{TBDPhos}$ . The \* indicates the minor resonance assigned to the ligand with only one  $\text{PEt}_2$  arm, which is an impurity that co-crystallizes with  $^{\text{Et}}\text{TBDPhos}$ .

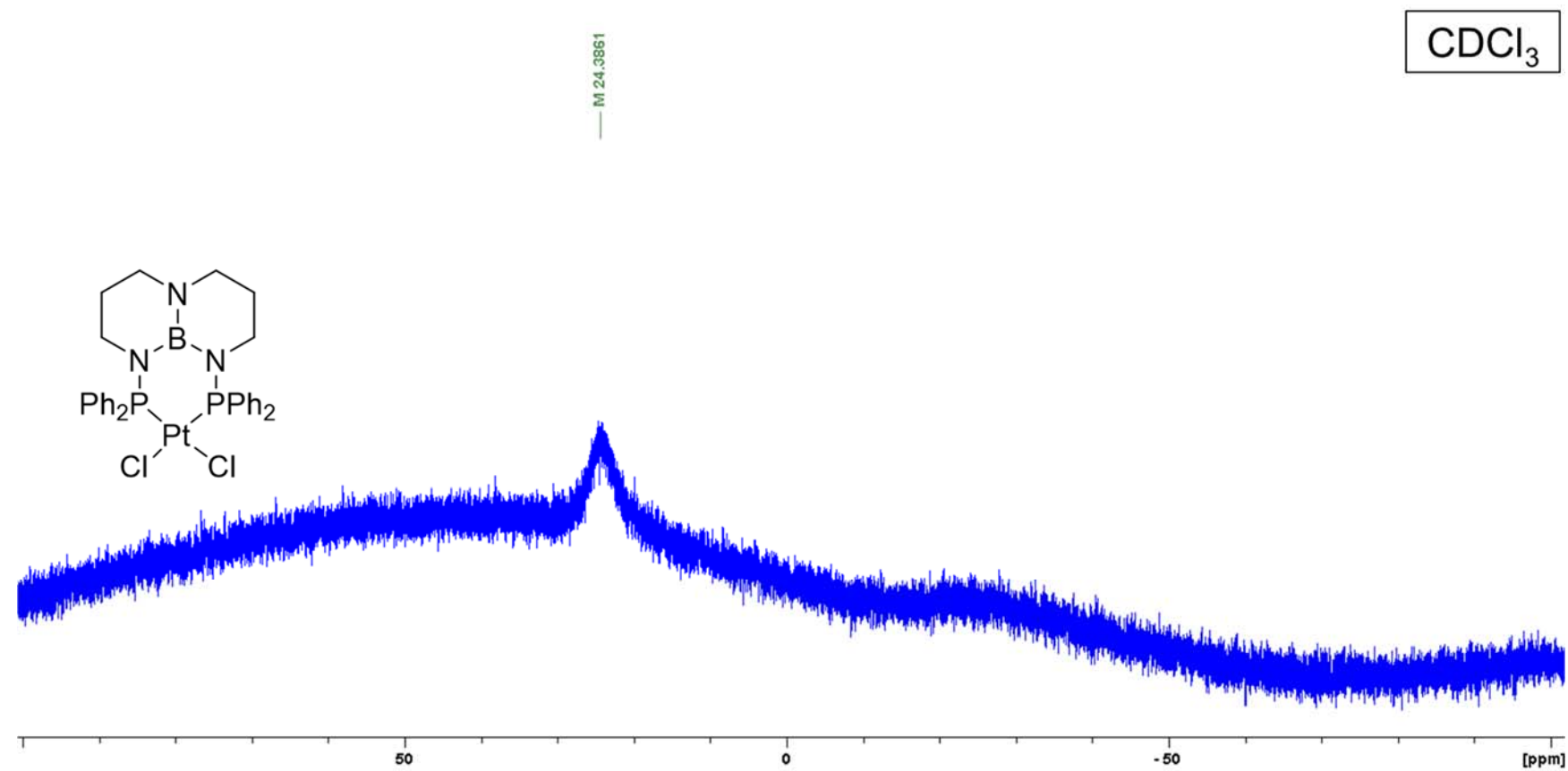
CDCl<sub>3</sub>



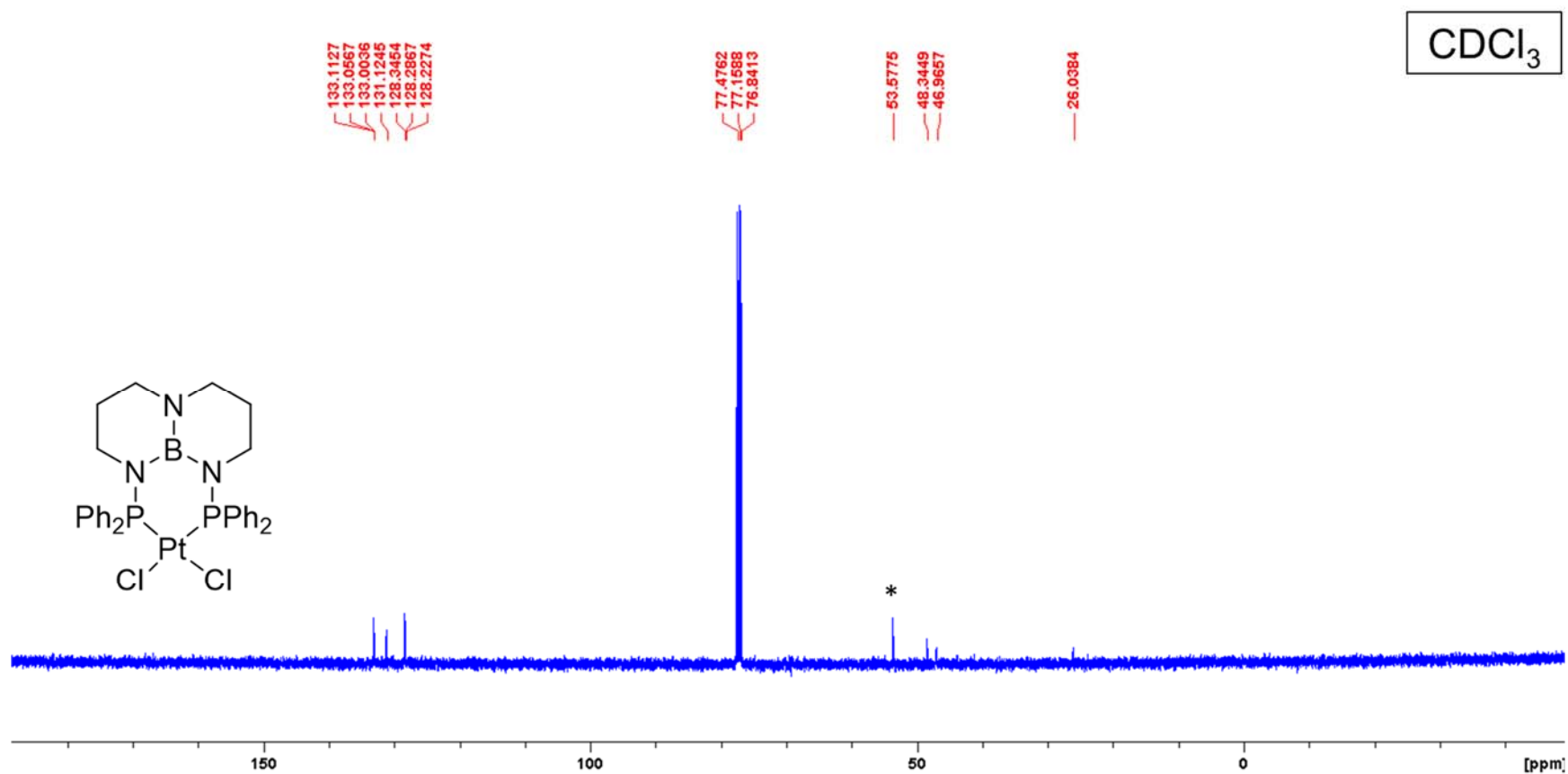
**Figure S12.** <sup>31</sup>P NMR spectrum of EtTBDPhos. The \* indicates the minor resonance assigned to the ligand with only one PEt<sub>2</sub> arm, which is an impurity that co-crystallizes with EtTBDPhos.



**Figure S13.**  $^1\text{H}$  NMR spectrum of  $(^{\text{Ph}}\text{TBDPhos})\text{PtCl}_2$  (**1**). The \* is the resonance assigned to  $\text{CH}_2\text{Cl}_2$  that co-crystallizes with **1**.



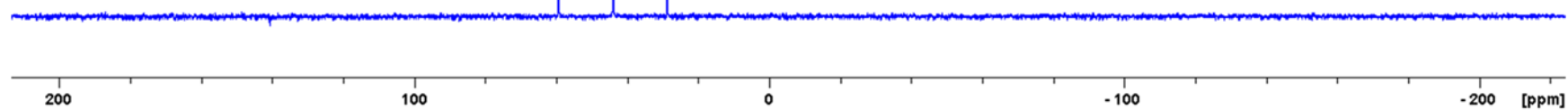
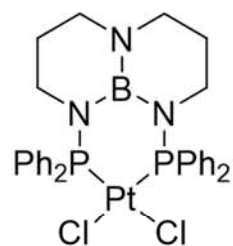
**Figure S14.** <sup>11</sup>B NMR spectrum of (PhTBDPhos)PtCl<sub>2</sub> (1).



**Figure S15.**  $^{13}\text{C}$  NMR spectrum of  $(^{\text{Ph}}\text{TBDPhos})\text{PtCl}_2$  (**1**). The \* is the resonance assigned to  $\text{CH}_2\text{Cl}_2$  that co-crystallizes with **1**.

CDCl<sub>3</sub>

59.2626  
43.9174  
28.5726



**Figure S16.** <sup>31</sup>P NMR spectrum of (PhTBDPhos)PtCl<sub>2</sub> (**1**).

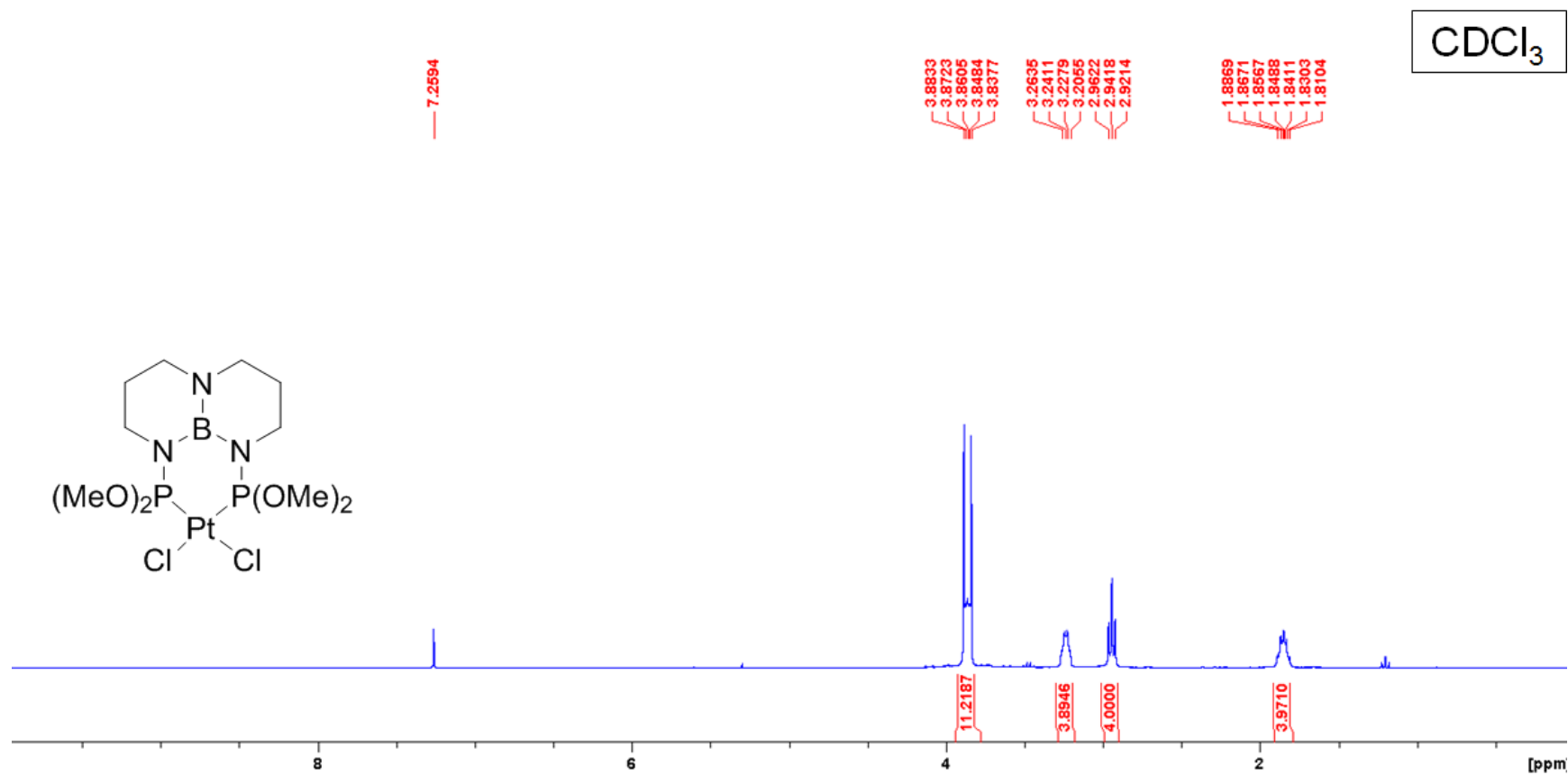
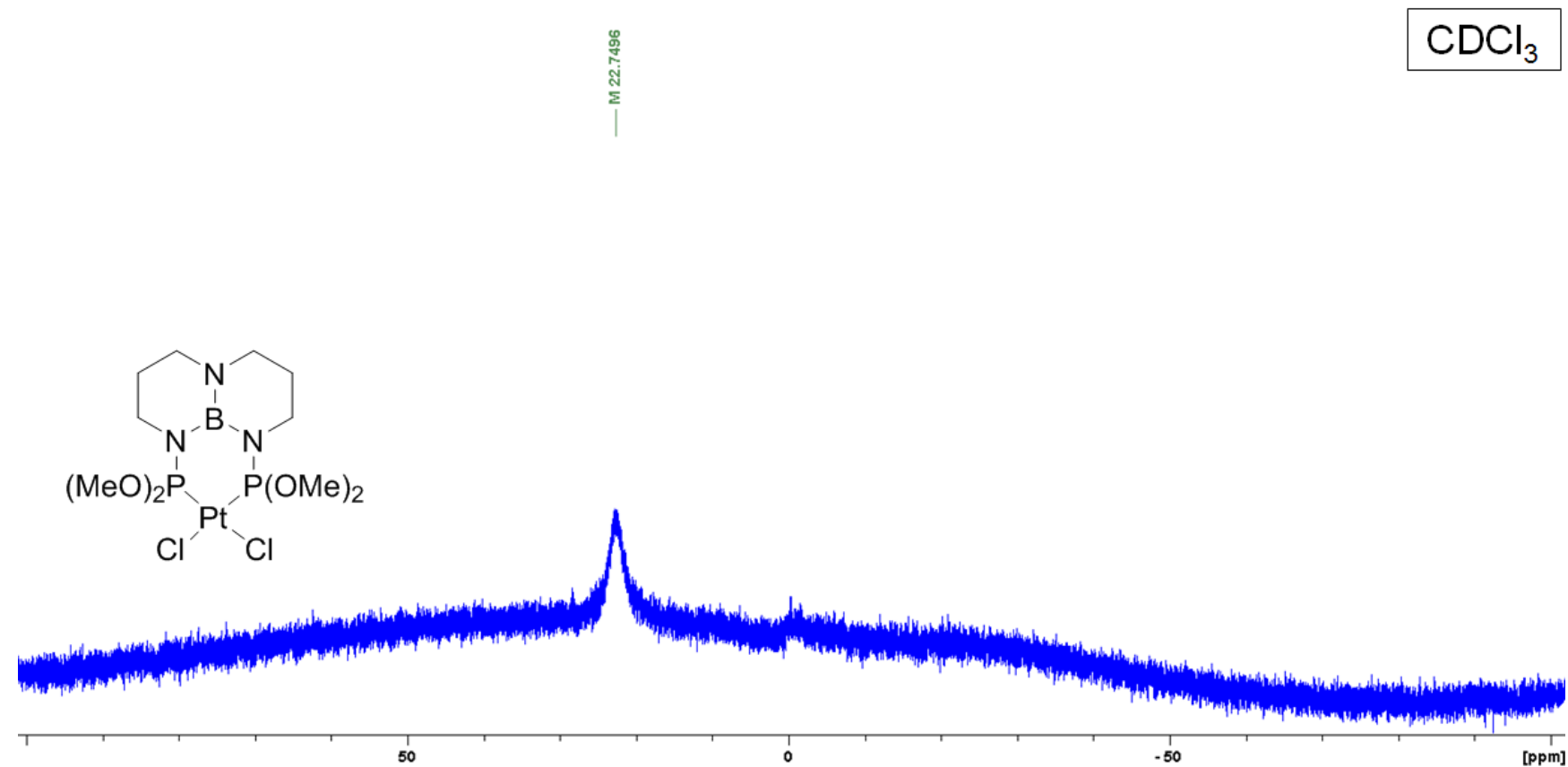
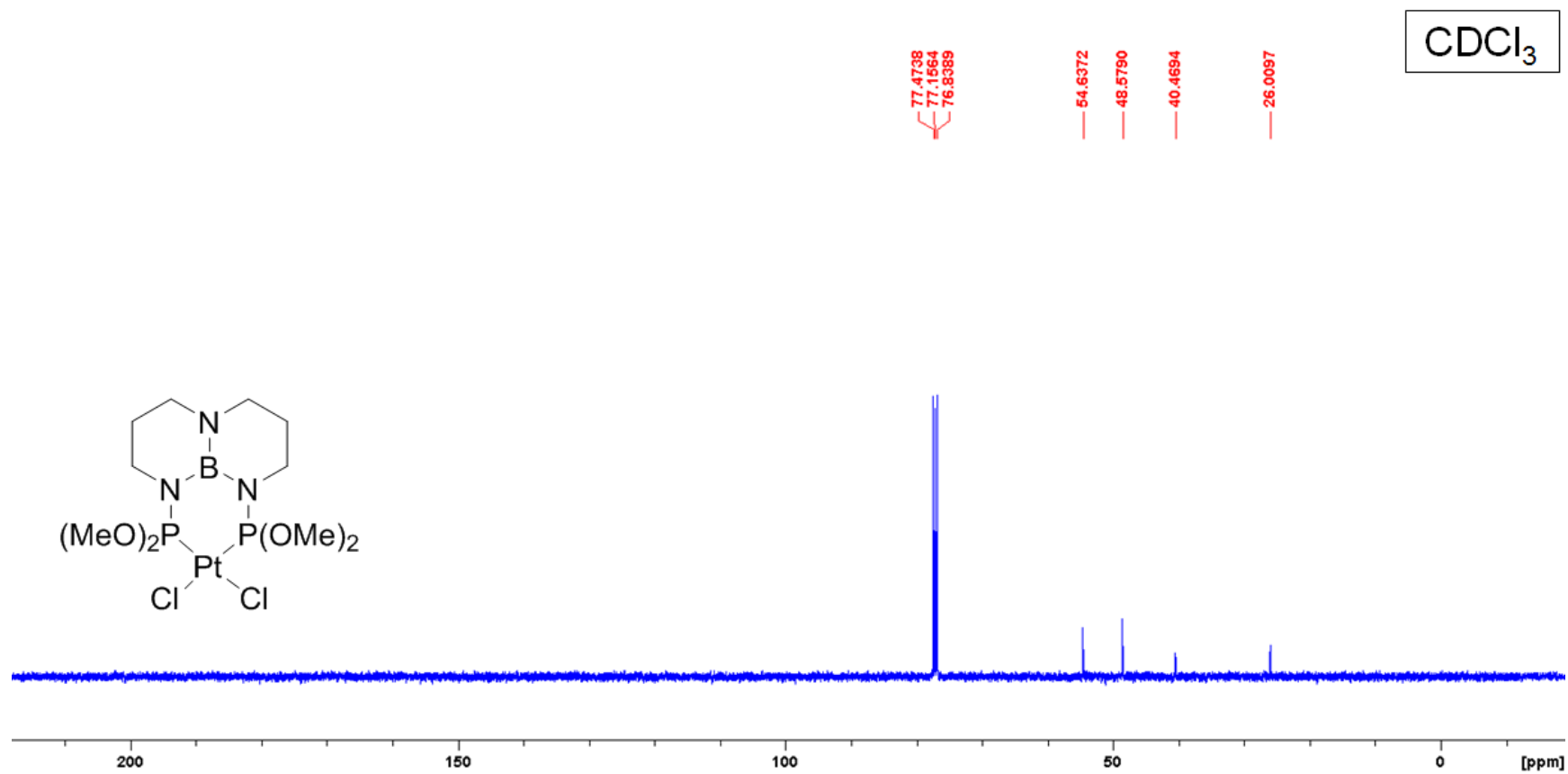


Figure S17. <sup>1</sup>H NMR spectrum of (MeO)<sup>t</sup>TBDPhosPtCl<sub>2</sub> (2).



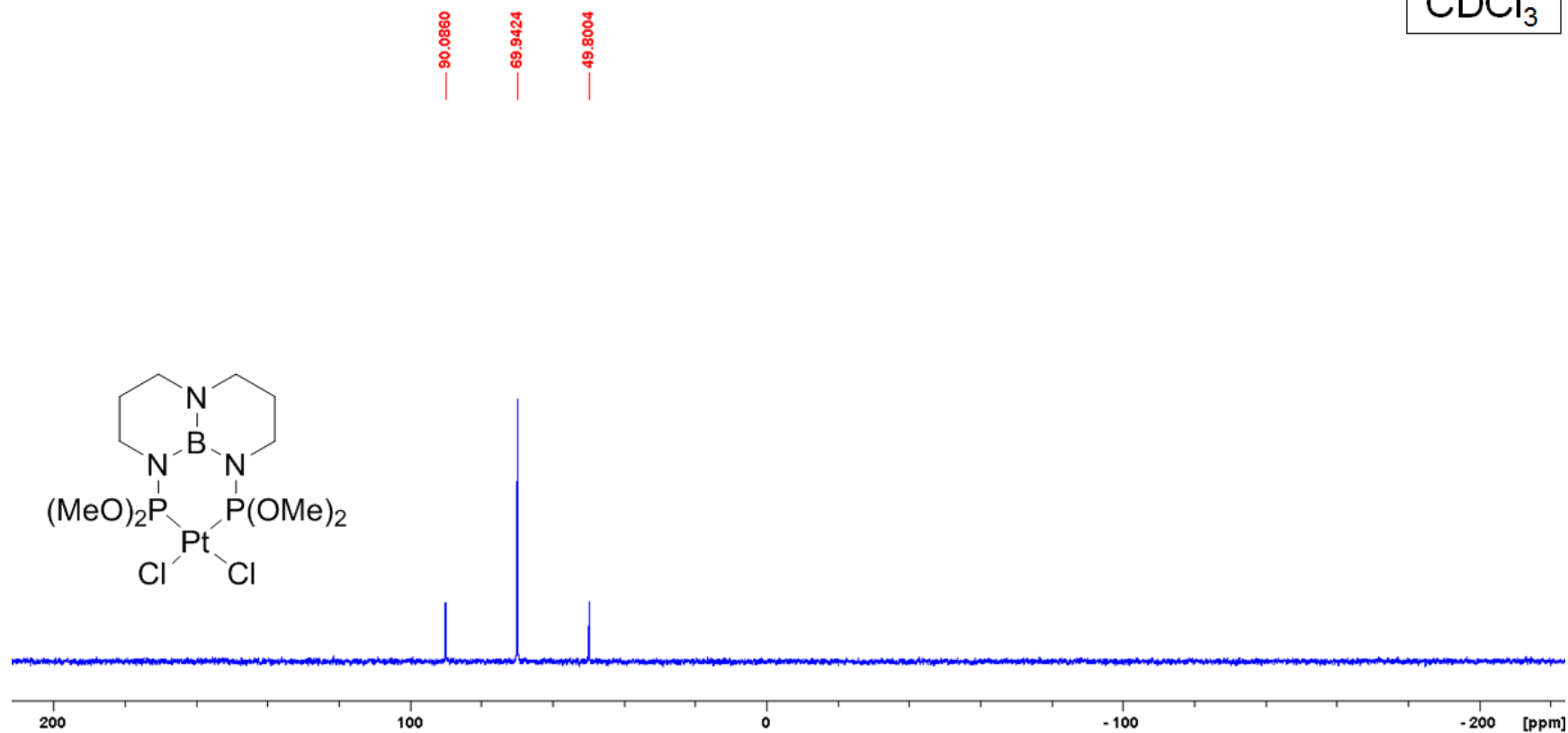
**Figure S18.** <sup>11</sup>B NMR spectrum of (MeOTBDPhos)PtCl<sub>2</sub> (**2**).



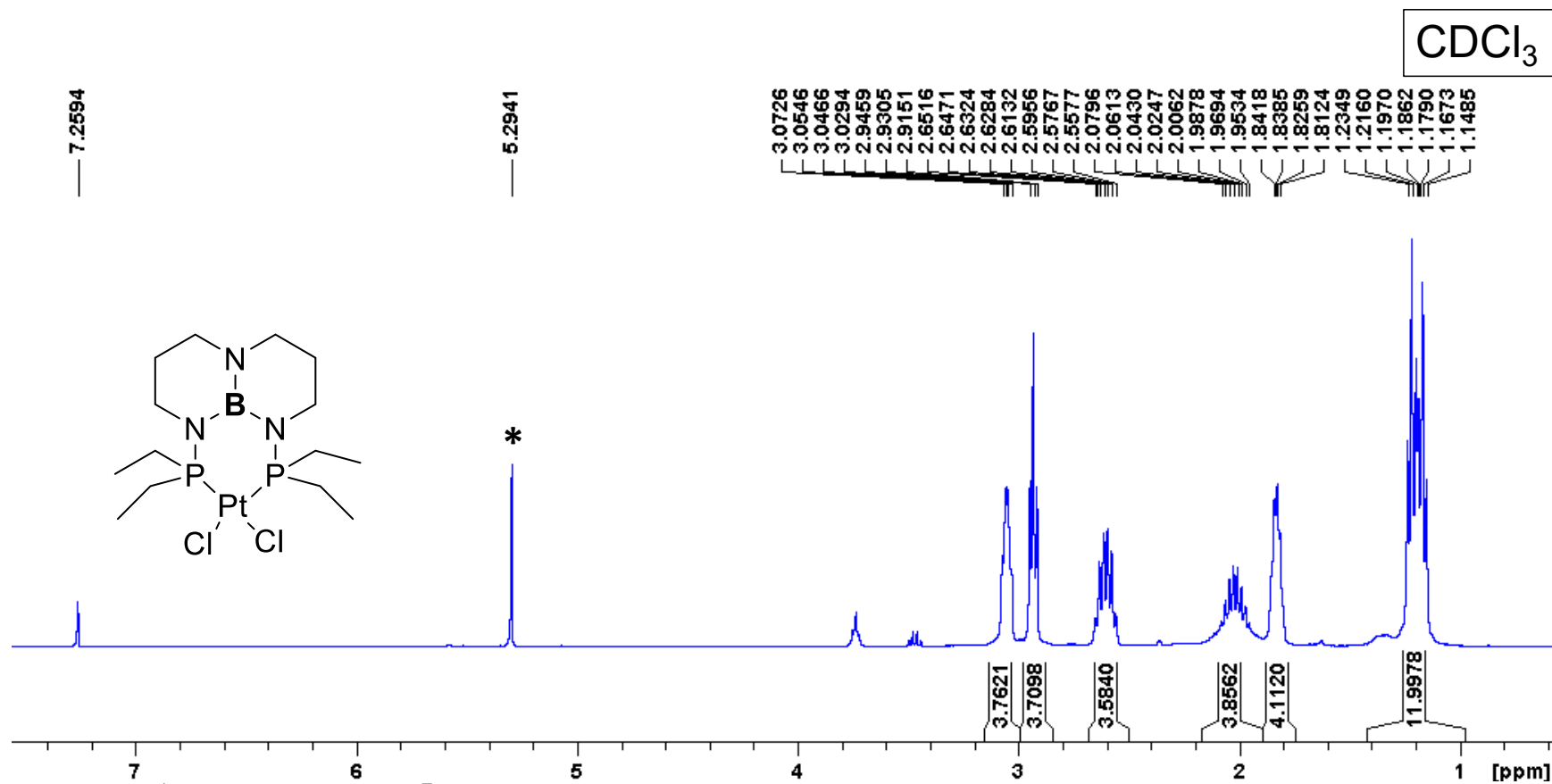


**Figure S19.**  $^{13}\text{C}$  NMR spectrum of  $(^{\text{MeO}}\text{TBDPhos})\text{PtCl}_2$  (**2**).

CDCl<sub>3</sub>



**Figure S20.** <sup>31</sup>P NMR spectrum of (MeOTBDPhos)PtCl<sub>2</sub> (**2**).



**Figure S21.**  $^1\text{H}$  NMR spectrum of  $(^{\text{Et}}\text{TBDPhos})\text{PtCl}_2$  (**3**). The \* symbol is assigned to  $\text{CH}_2\text{Cl}_2$ , which likely co-crystallizes **3** as it does for **1**.

CDCl<sub>3</sub>

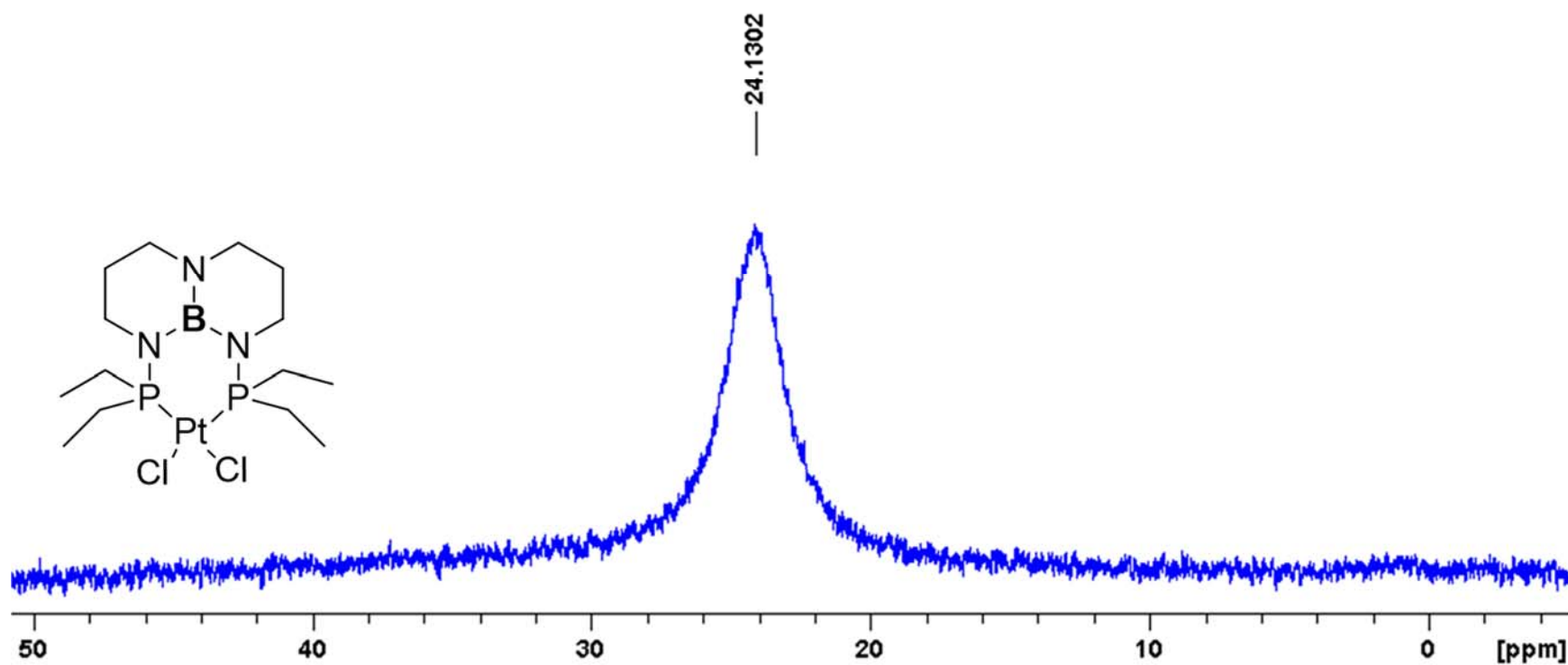


Figure S22. <sup>11</sup>B NMR spectrum of (EtTBDPhos)PtCl<sub>2</sub> (3).

CDCl<sub>3</sub>

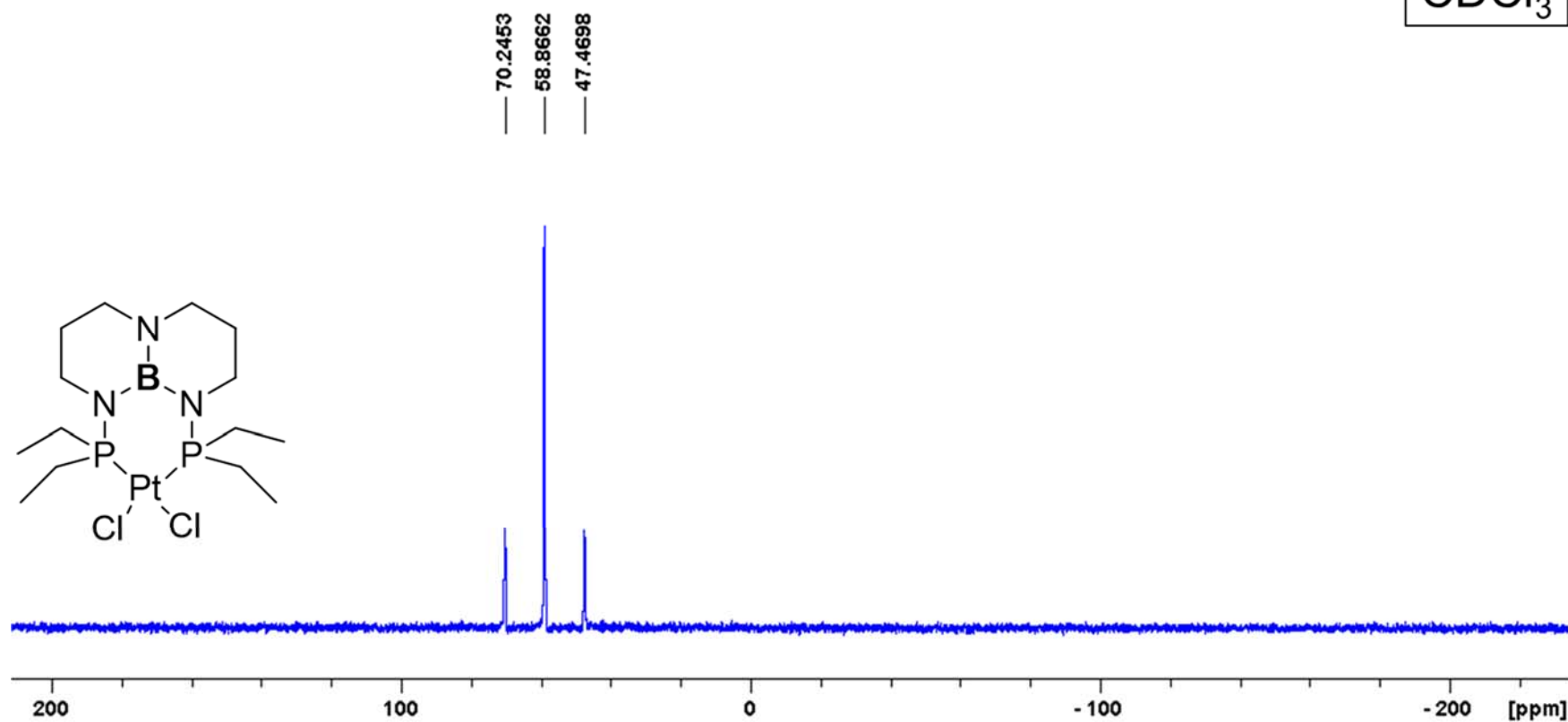
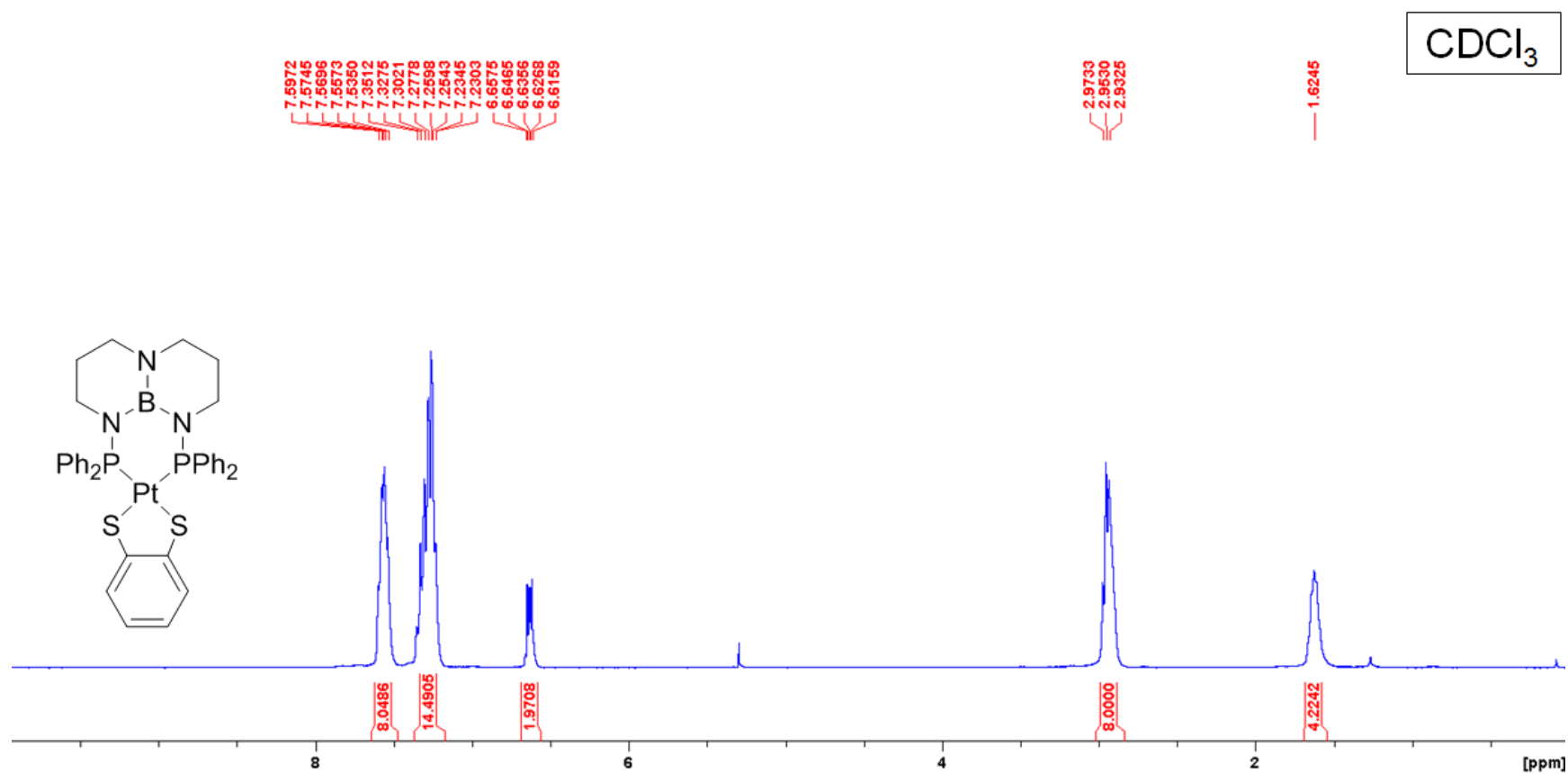


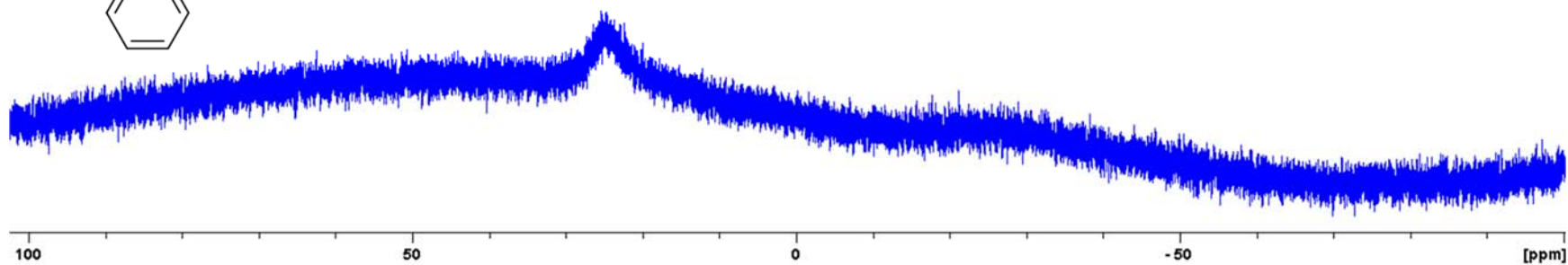
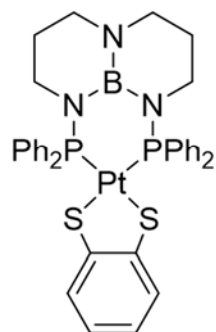
Figure S23. <sup>31</sup>P NMR spectrum of (EtTBDPhos)PtCl<sub>2</sub> (3).



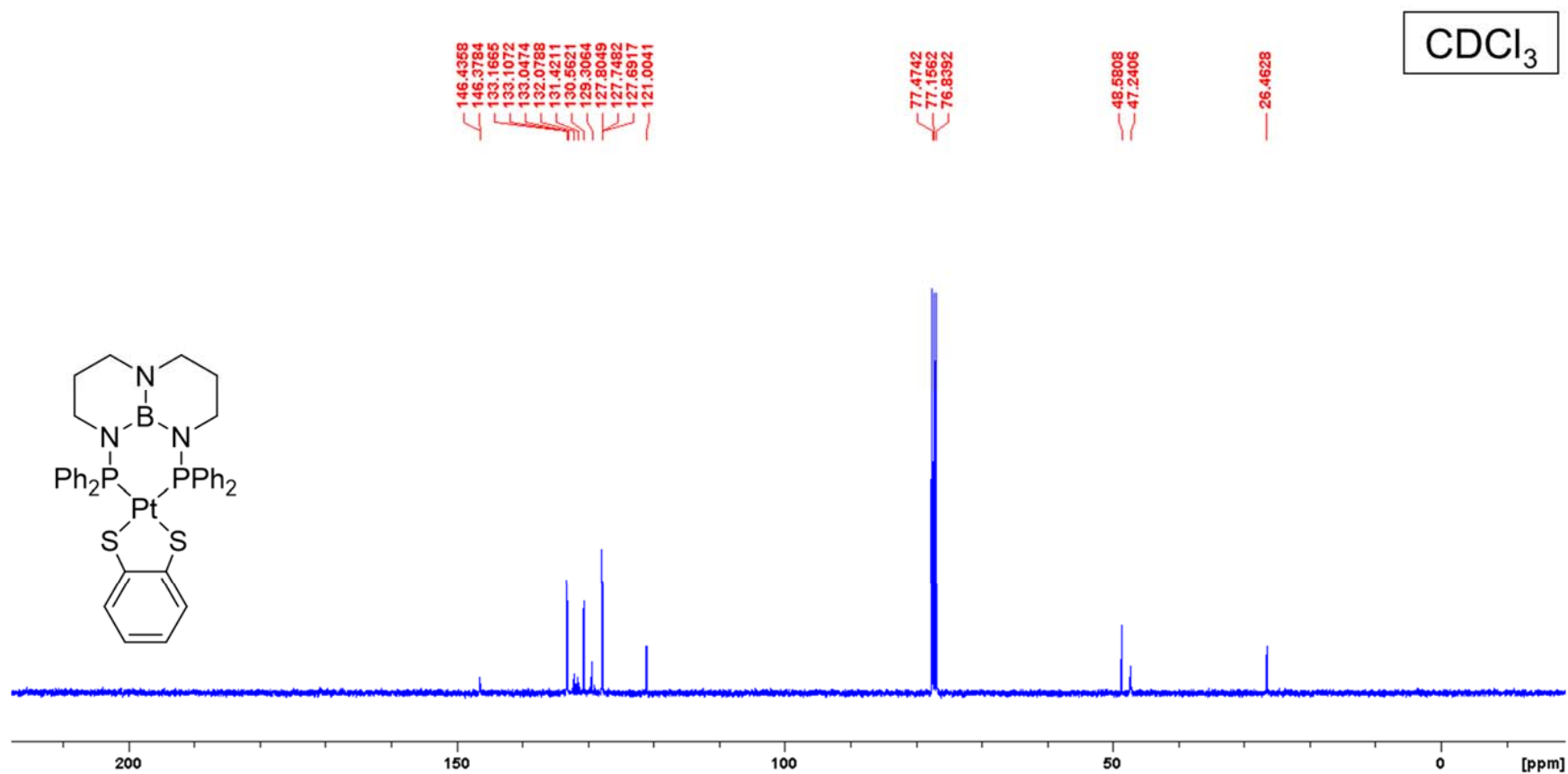
**Figure S24.** <sup>1</sup>H NMR spectrum of (PhTBDPhos)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (4).

CDCl<sub>3</sub>

— M 24.9084



**Figure S25.** <sup>11</sup>B NMR spectrum of (PhTBDPhos)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**4**).

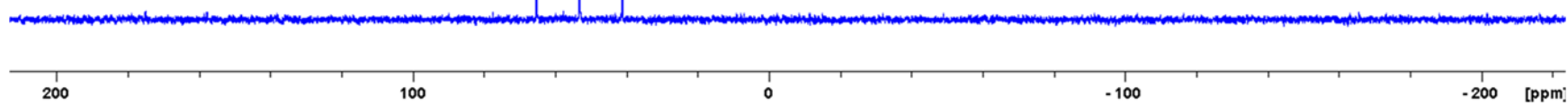
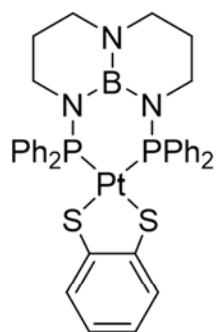


**Figure S26.**  $^{13}\text{C}$  NMR spectrum of  $(^{\text{Ph}}\text{TBDPhos})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$  (4).

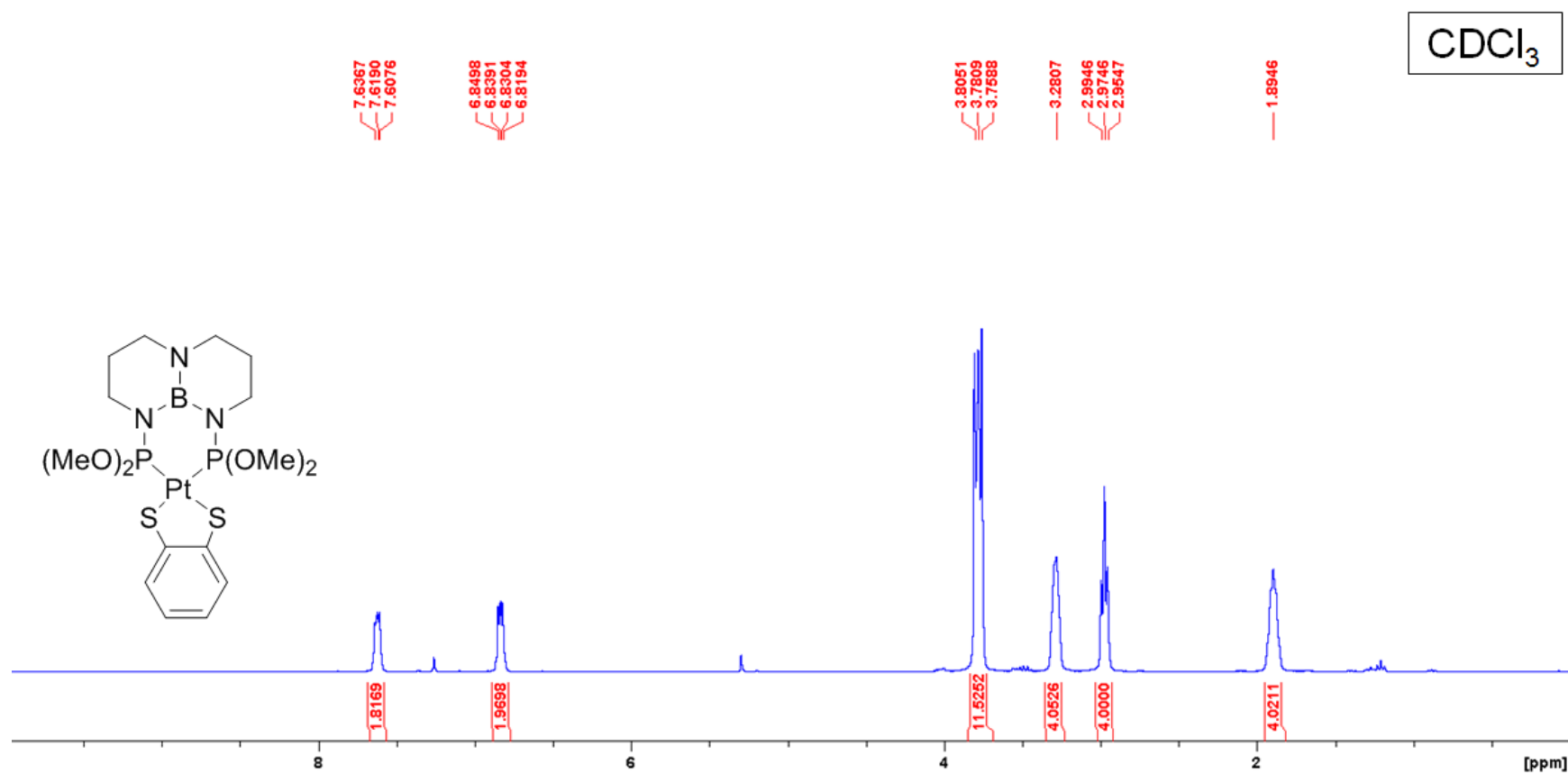


CDCl<sub>3</sub>

— 65.2566  
— 53.2516  
— 41.2475



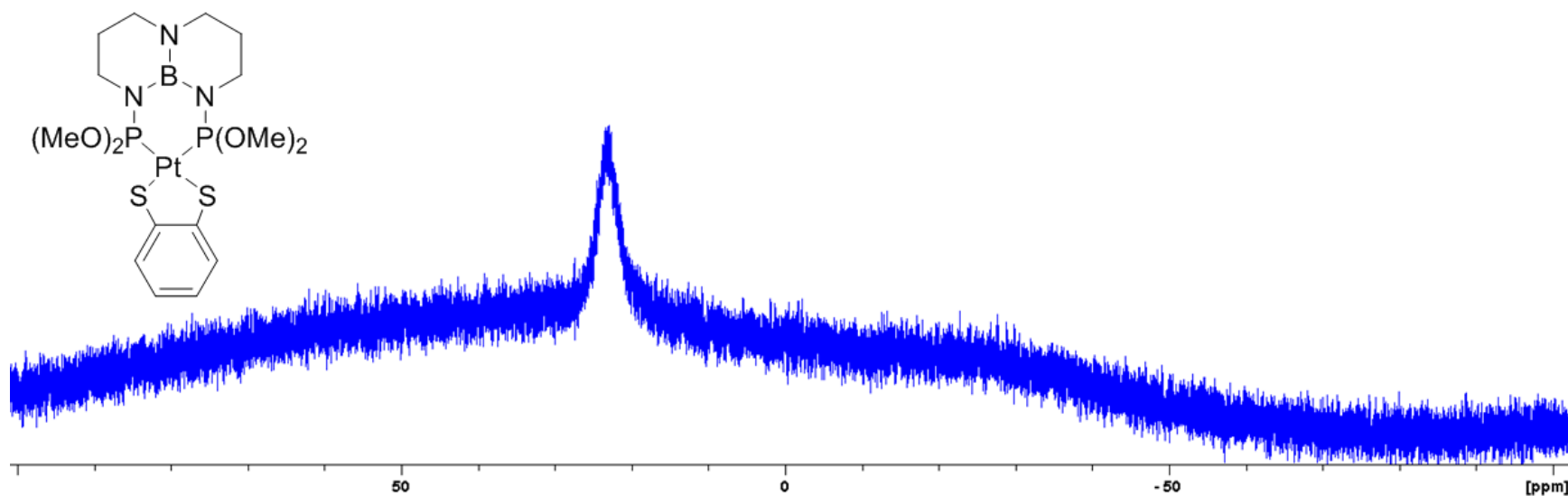
**Figure S27.**  $^{31}\text{P}$  NMR spectrum of  $(^{\text{Ph}}\text{TBDPhos})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$  (**4**).



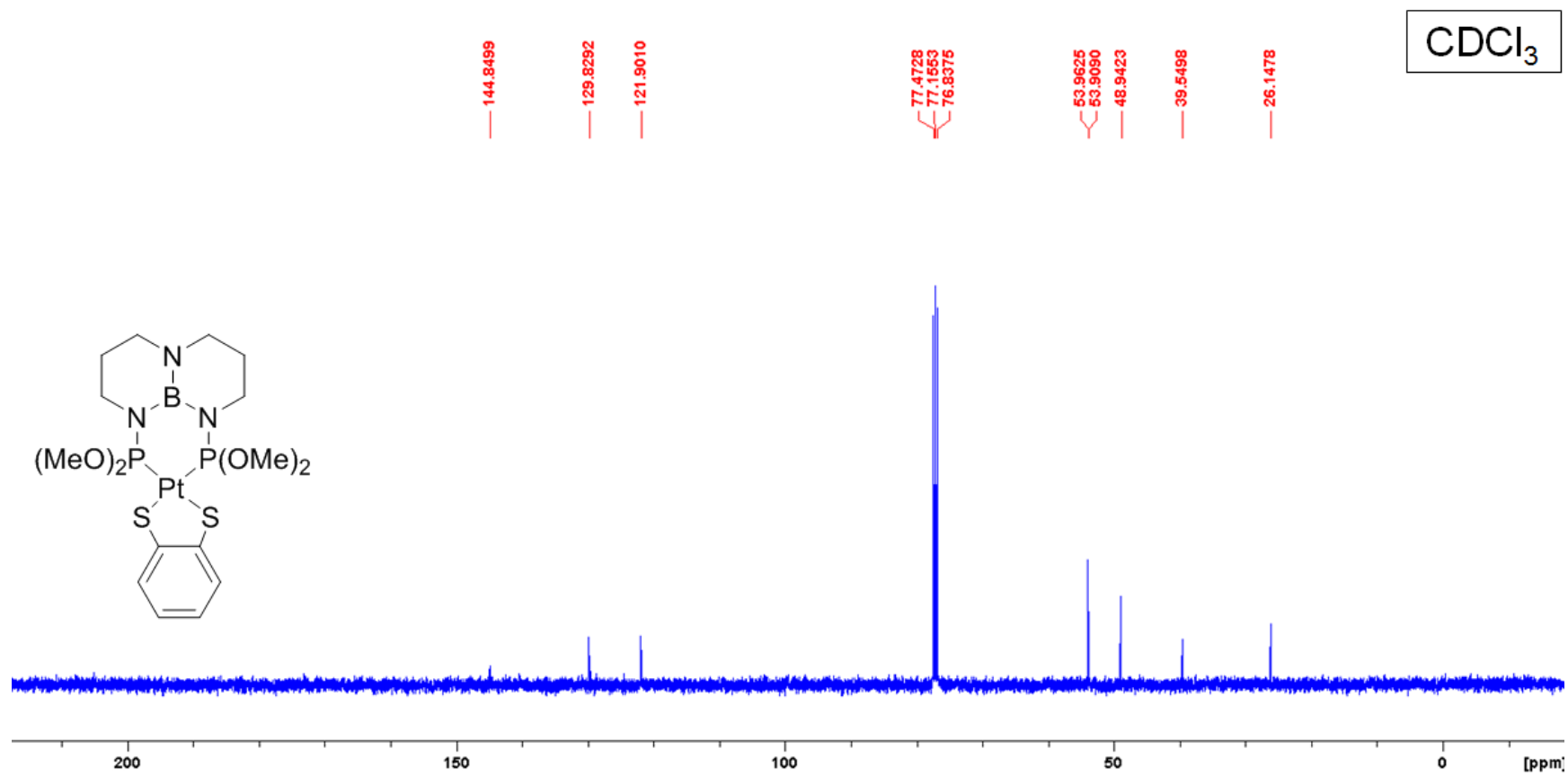
**Figure S28.** <sup>1</sup>H NMR spectrum of (<sup>MeO</sup>TBDPhos)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**5**).

CDCl<sub>3</sub>

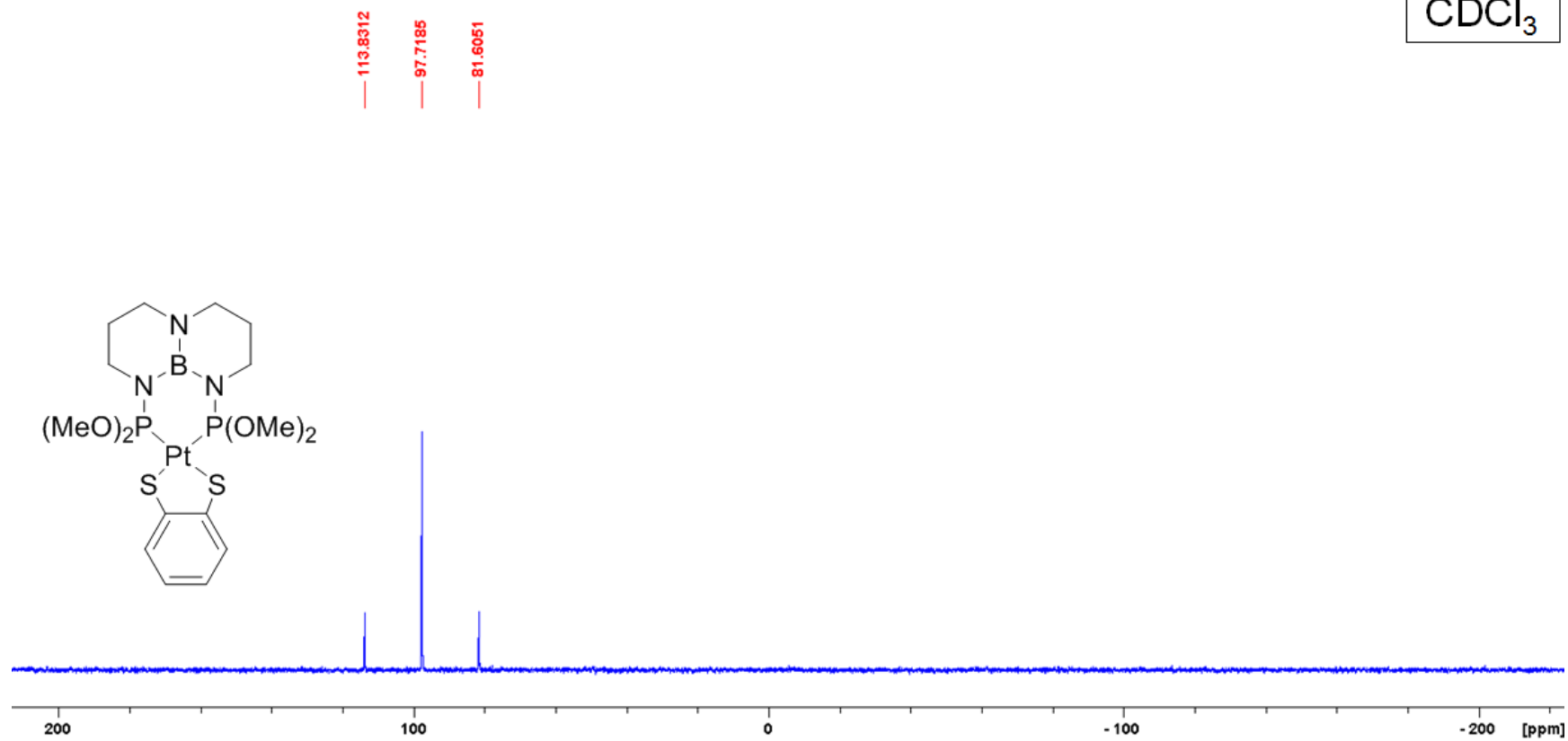
— M 23.1957



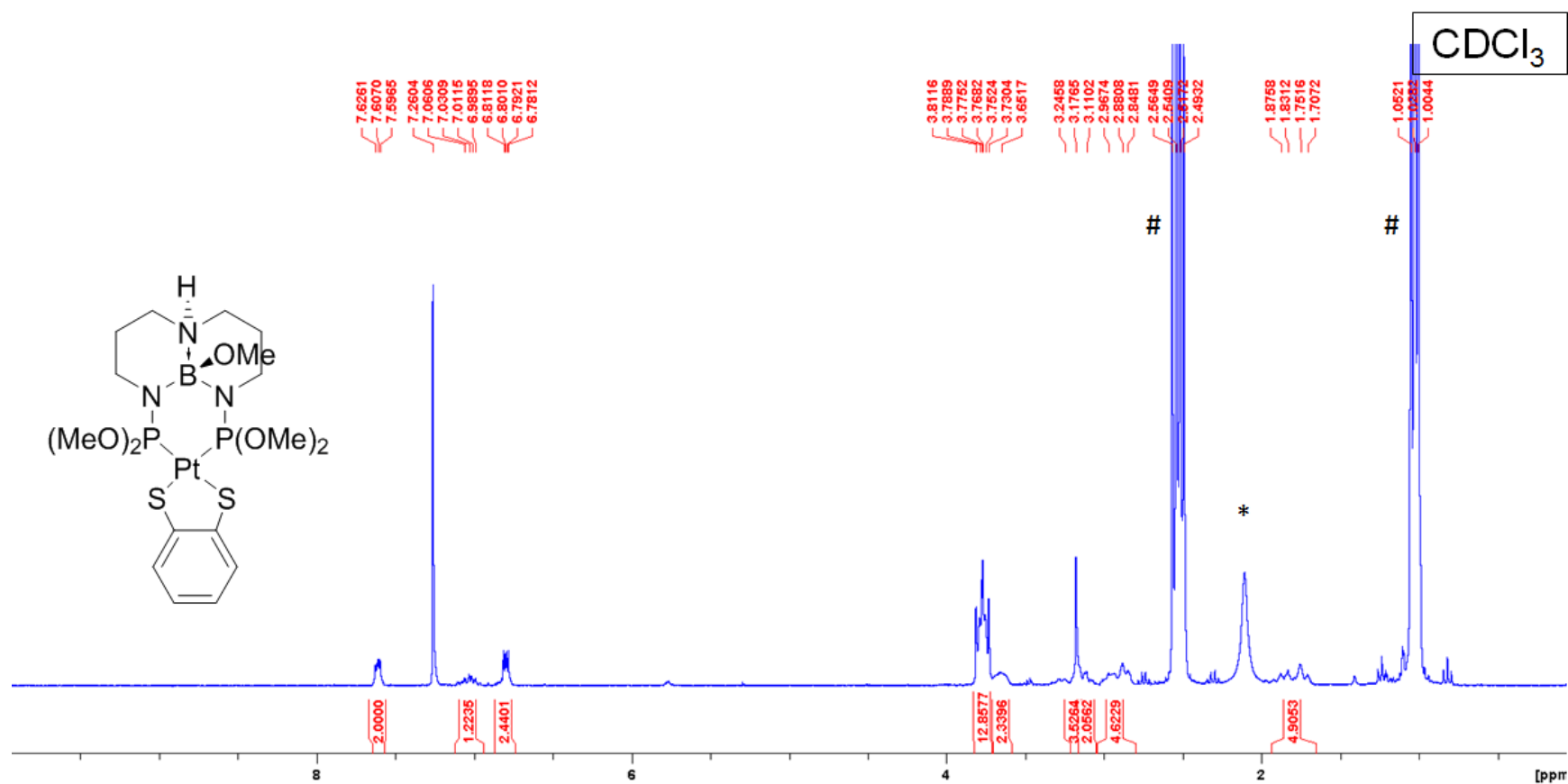
**Figure S29.** <sup>11</sup>B NMR spectrum of (MeO)<sup>t</sup>BDPPhosPt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**5**).



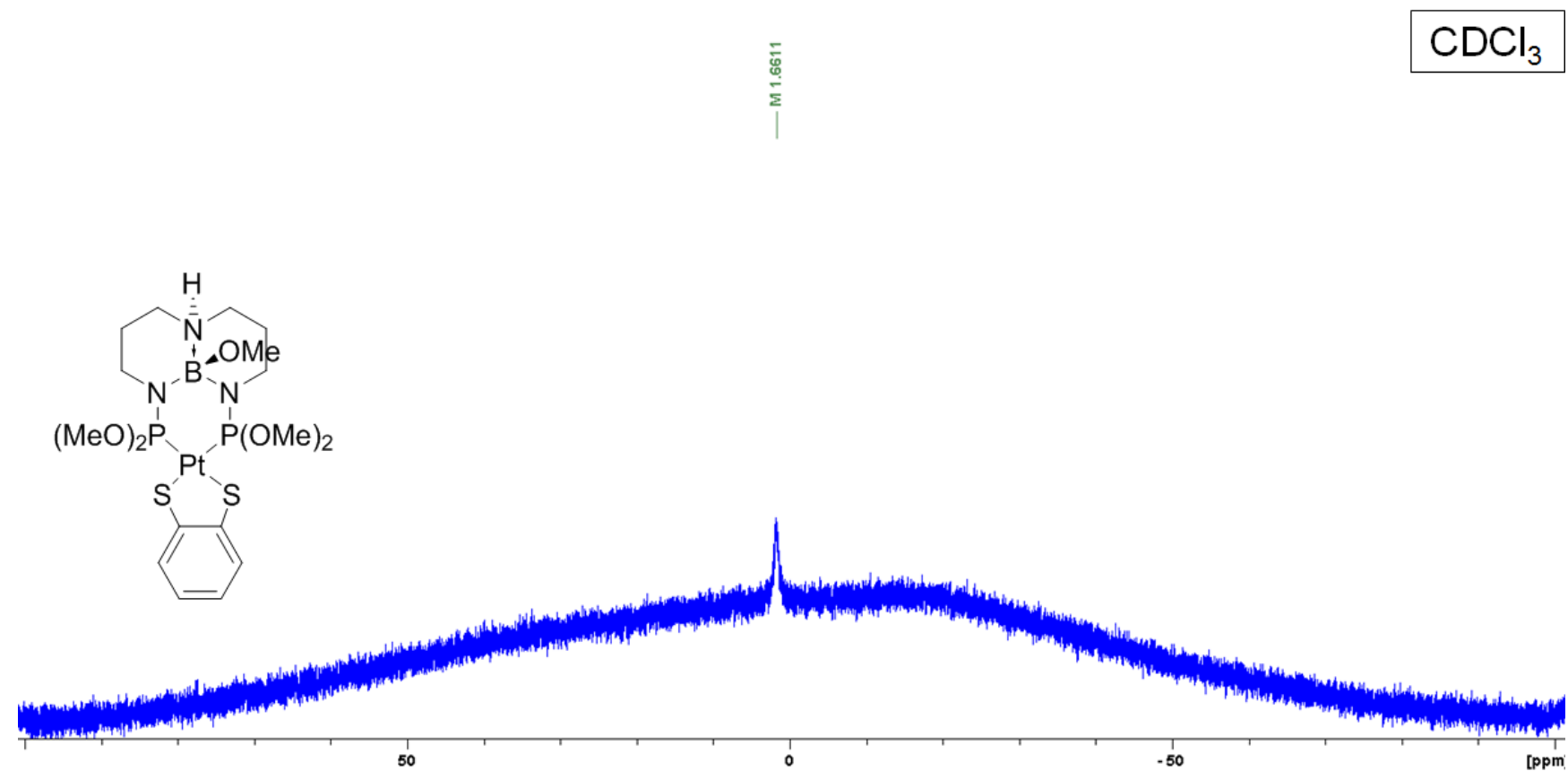
**Figure S30.**  $^{13}\text{C}$  NMR spectrum of  $(^{\text{MeO}}\text{TBDPhos})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$  (**5**).

$\text{CDCl}_3$ 

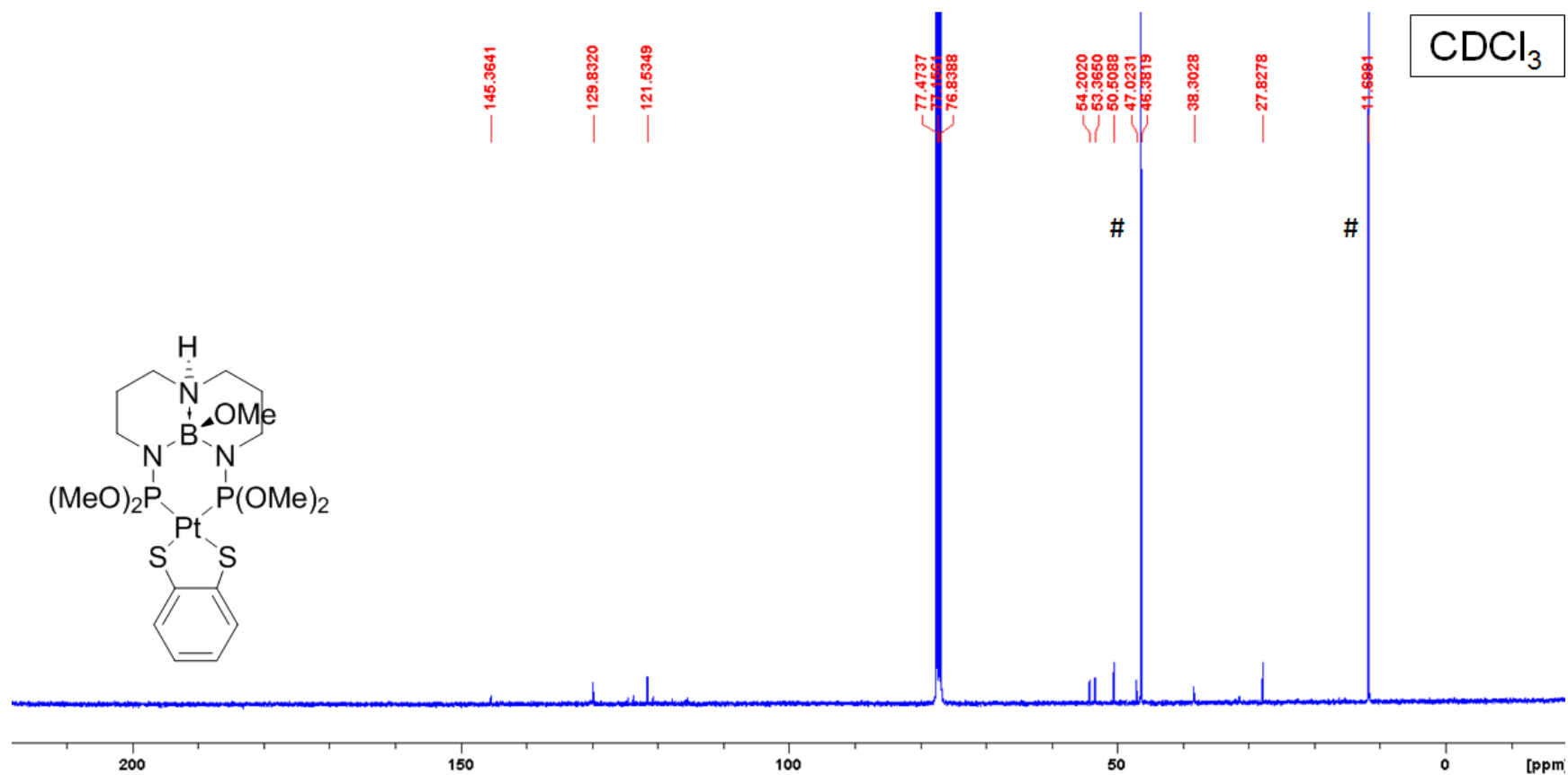
**Figure S31.**  $^{31}\text{P}$  NMR spectrum of  $(^{\text{MeO}}\text{TBDPhos})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$  (**5**).



**Figure S32.**  $^1\text{H}$  NMR spectrum of  $(\text{MeOTBDPhos-MeOH})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$  (**5-MeOH**).  $\text{NEt}_3$  was added to help dissolve the complex. The \* and # symbols indicate resonances assigned to residual  $\text{H}_2\text{O}$  and added  $\text{NEt}_3$ , respectively.



**Figure S33.** <sup>11</sup>B NMR spectrum of (MeOTBDPhos-MeOH)Pt(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**5-MeOH**). NEt<sub>3</sub> was added to help dissolve the complex.

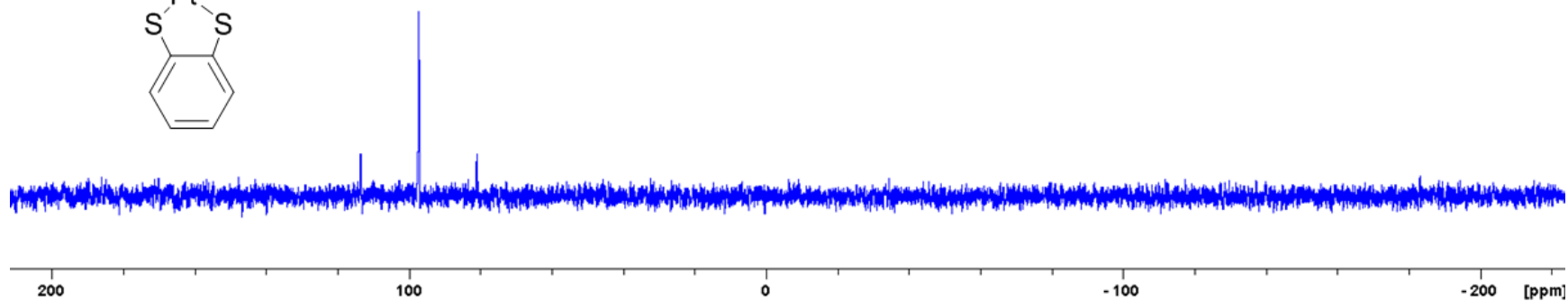
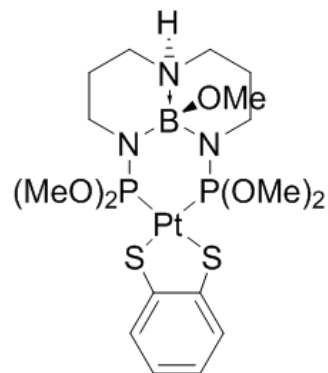


**Figure S34.**  $^{13}\text{C}$  NMR spectrum of  $(^{\text{MeO}}\text{TBDPhos-MeOH})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$  (**5-MeOH**). NEt<sub>3</sub> was added to help dissolve the complex. The # symbol indicates resonances assigned to added NEt<sub>3</sub>.

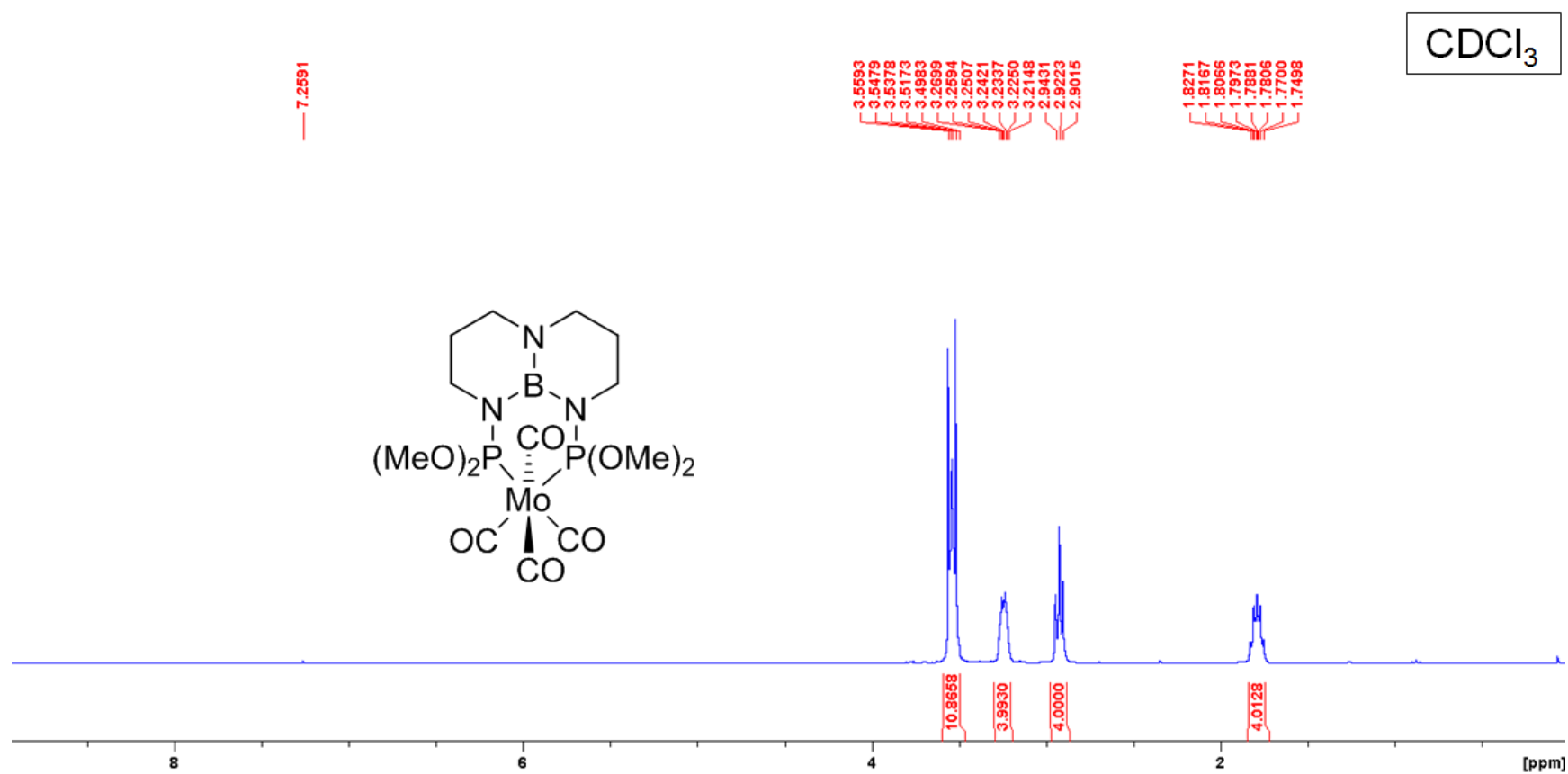


CDCl<sub>3</sub>

113.6203  
97.3195  
81.0880



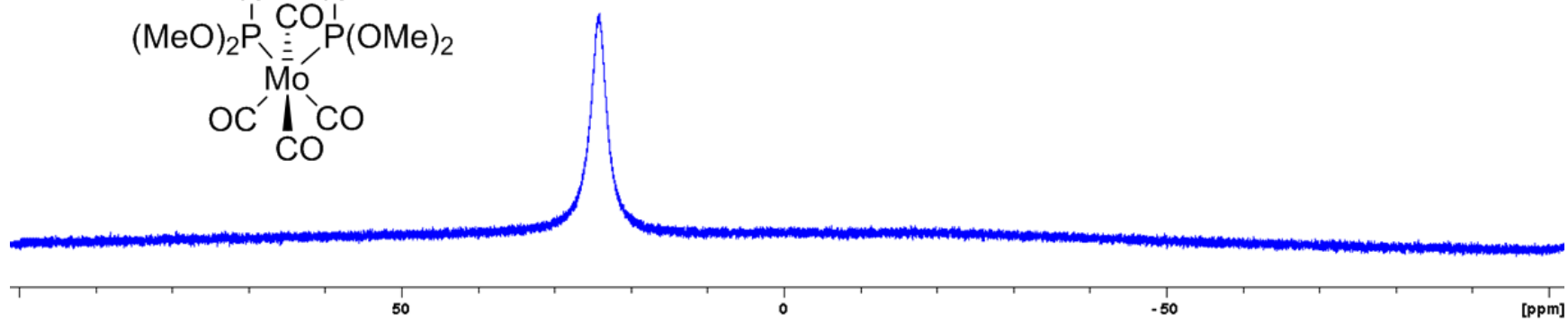
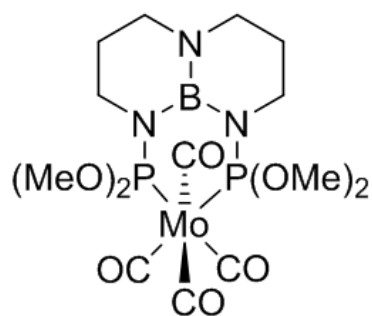
**Figure S35.**  $^{31}\text{P}$  NMR spectrum of  $(^{\text{MeO}}\text{TBDPhos-MeOH})\text{Pt}(\text{S}_2\text{C}_6\text{H}_4)$  (**5-MeOH**).  $\text{NEt}_3$  was added to help dissolve the complex.



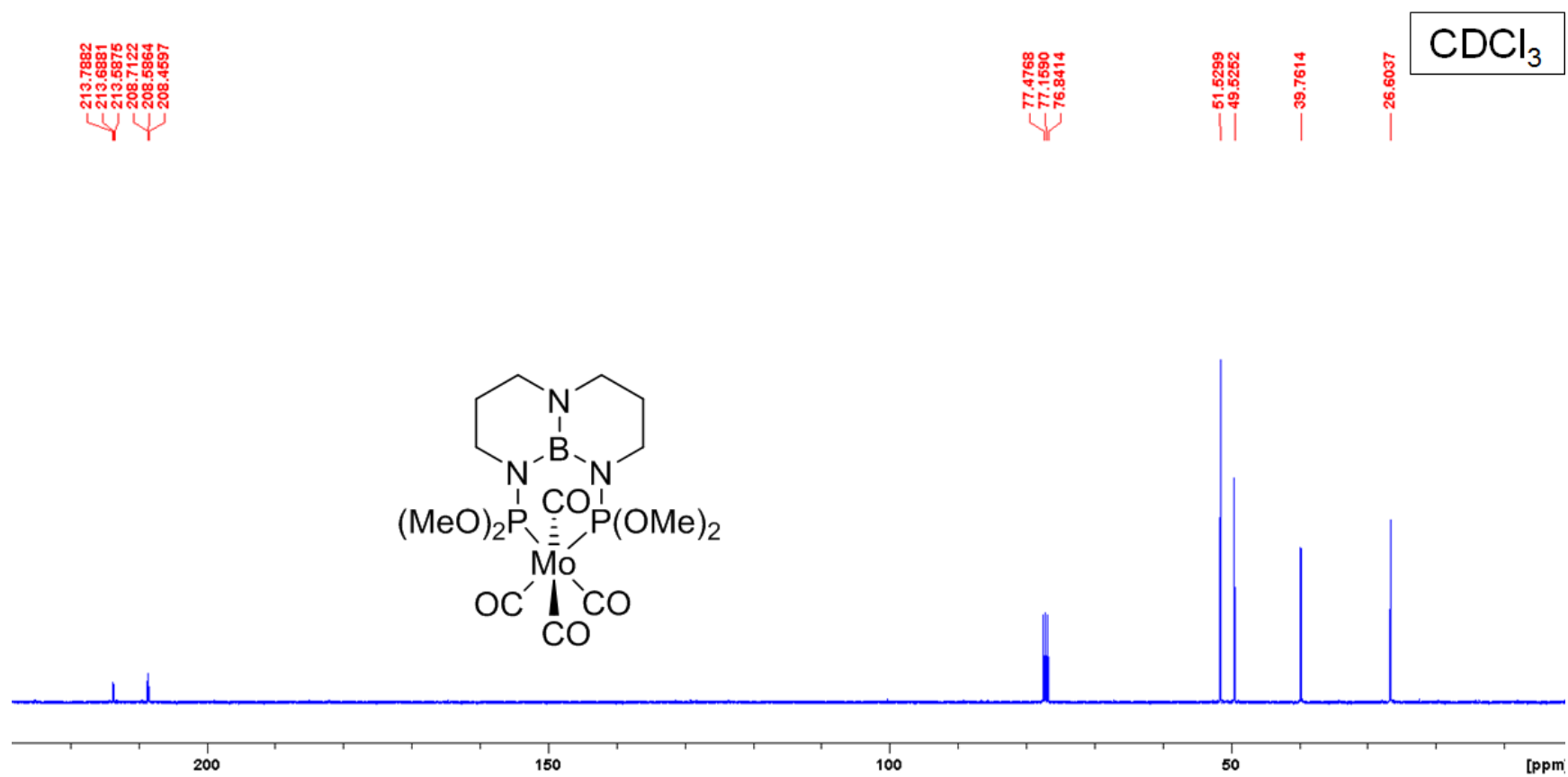
**Figure S36.** <sup>1</sup>H NMR spectrum of (<sup>MeO</sup>TBDPhos)Mo(CO)<sub>4</sub> (**8**).

CDCl<sub>3</sub>

— M 24.2245



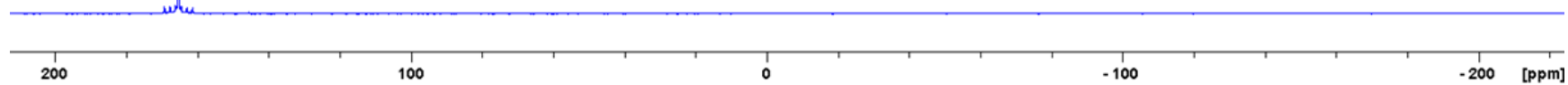
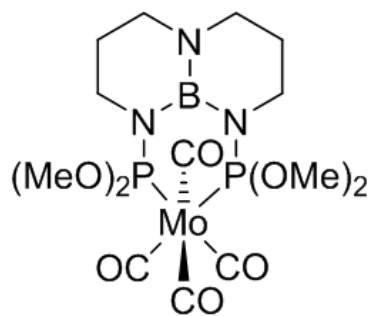
**Figure S37.** <sup>11</sup>B NMR spectrum of (MeO)TBDPhos)Mo(CO)<sub>4</sub> (**8**).



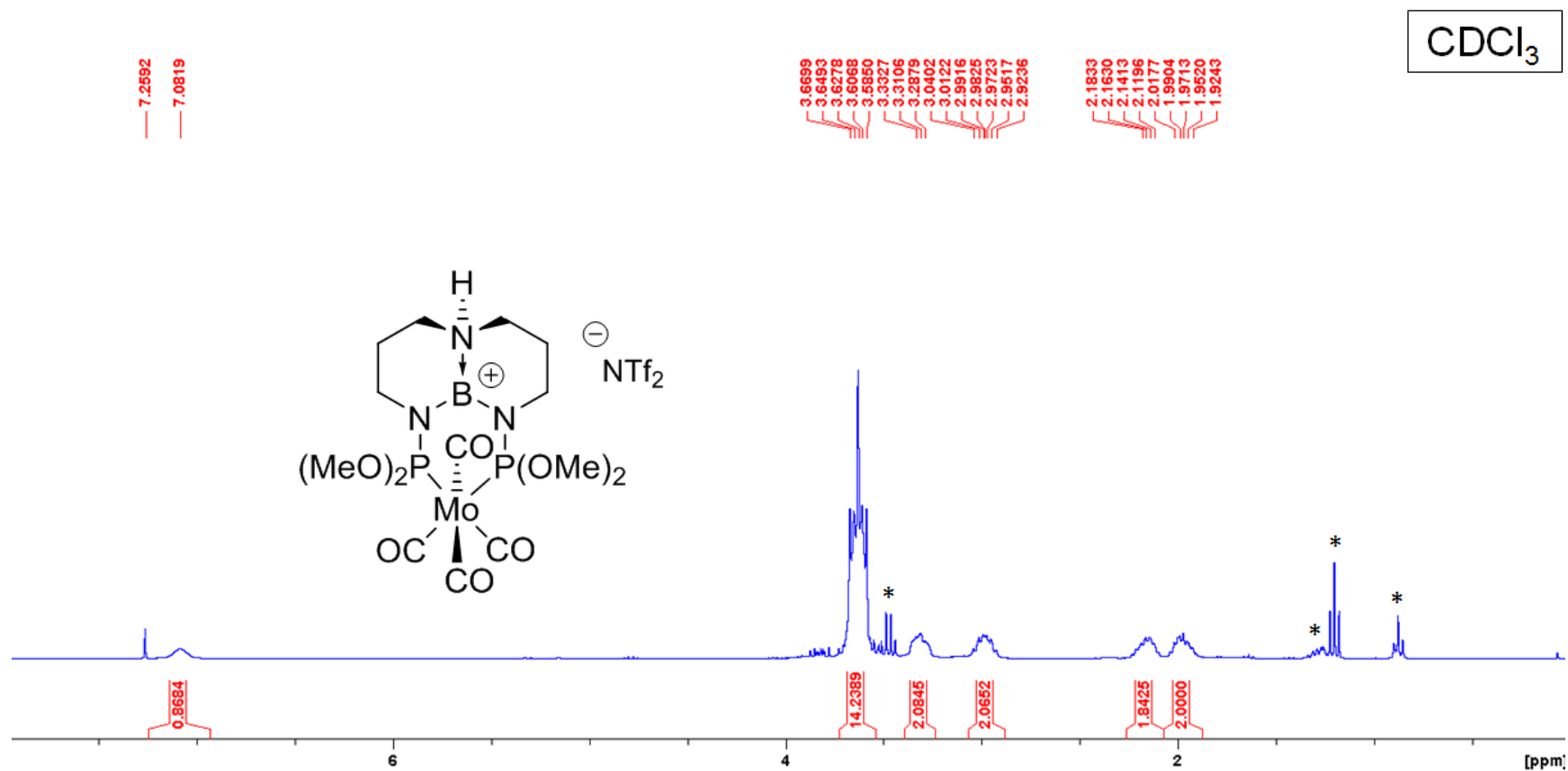
**Figure S38.**  $^{13}\text{C}$  NMR spectrum of  $(^{\text{MeO}}\text{TBDPhos})\text{Mo}(\text{CO})_4$  (**8**).

CDCl<sub>3</sub>

169.3925  
167.7946  
166.1977  
165.4026  
164.6049  
163.0146  
161.4193



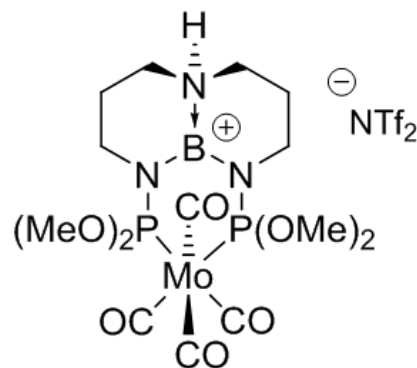
**Figure S39.** <sup>31</sup>P NMR spectrum of (<sup>Me</sup>O TBDPhos)Mo(CO)<sub>4</sub> (**8**).



**Figure S40.** <sup>1</sup>H NMR spectrum of (<sup>MeO</sup>TBDPhos-HNTf<sub>2</sub>)Mo(CO)<sub>4</sub> (**8-HNTf<sub>2</sub>**). The \* symbol indicates resonances assigned to residual Et<sub>2</sub>O and pentane.

CDCl<sub>3</sub>

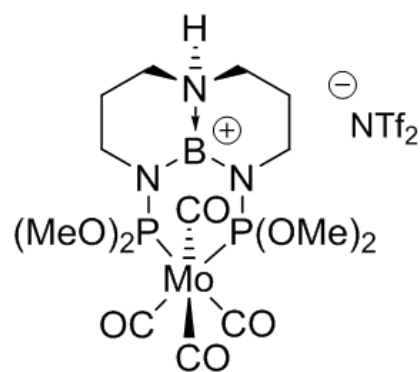
— 27.7929



**Figure S41.**  $^{11}\text{B}$  NMR spectrum of  $(\text{MeO})\text{TBDPhos-HNTf}_2\text{Mo(CO)}_4$  (**8-HNTf<sub>2</sub>**).

CDCl<sub>3</sub>

-79.2674



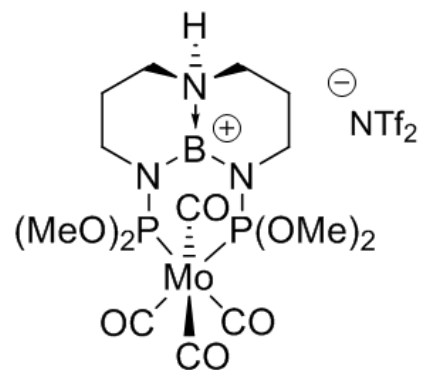
0 0 -50 -100 -150 -200 [ppm]

**Figure S42.**  $^{19}\text{F}$  NMR spectrum of  $(^{\text{MeO}}\text{TBDPhos-HNTf}_2)\text{Mo(CO)}_4$  (**8-HNTf<sub>2</sub>**).



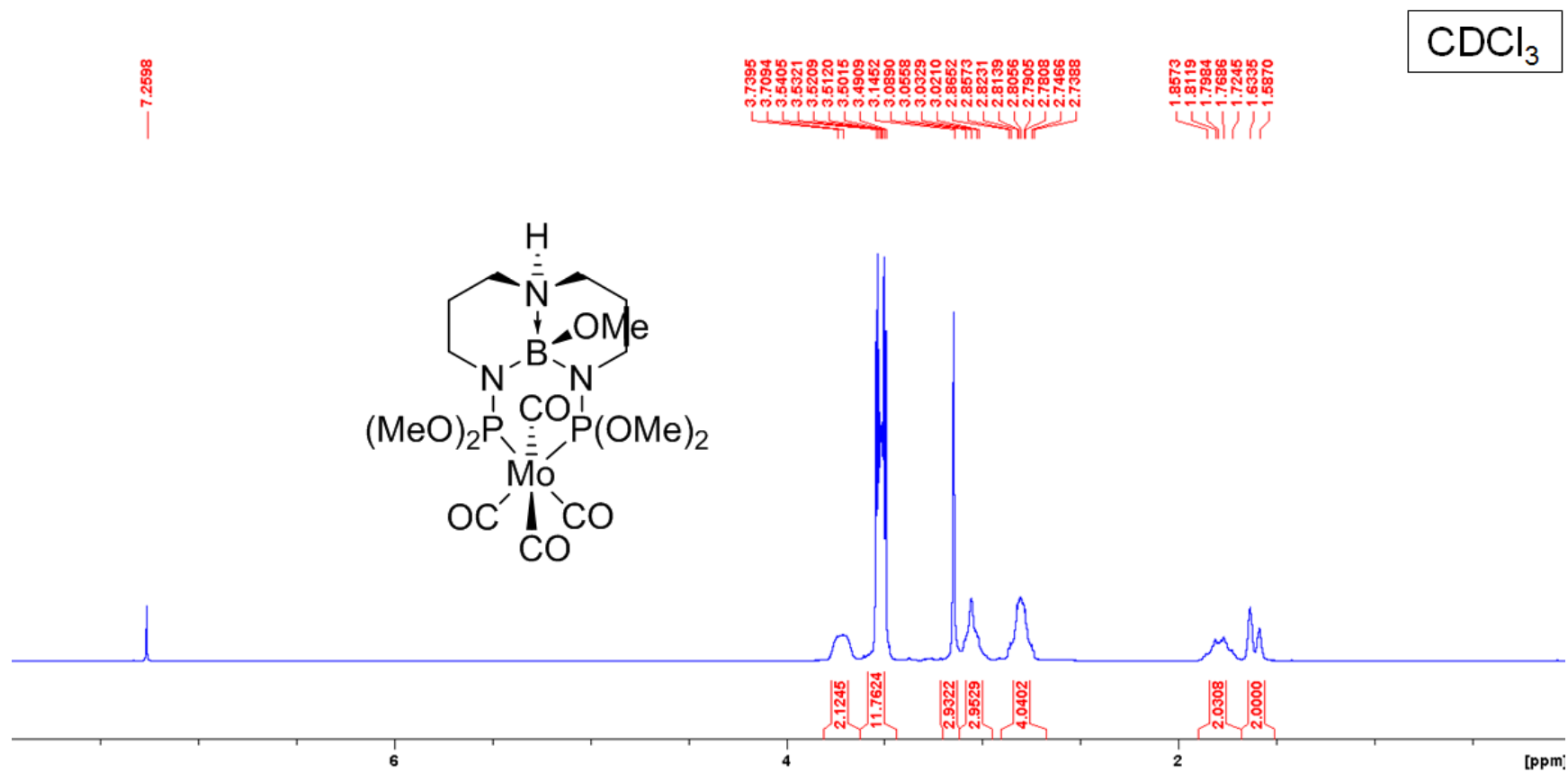
CDCl<sub>3</sub>

— 166.9731



200 100 0 -100 -200 [ppm]

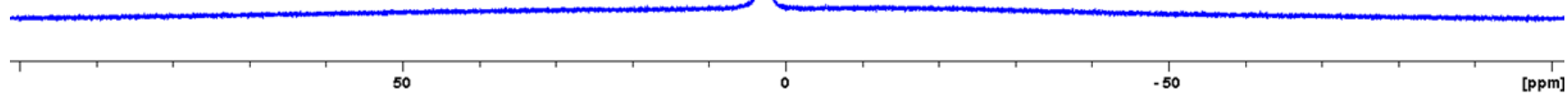
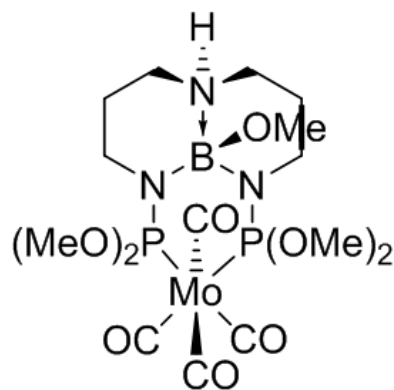
**Figure S43.**  $^{31}\text{P}$  NMR spectrum of  $(^{\text{MeO}}\text{TBDPhos-HNTf}_2)\text{Mo(CO)}_4$  (**8-HNTf<sub>2</sub>**).



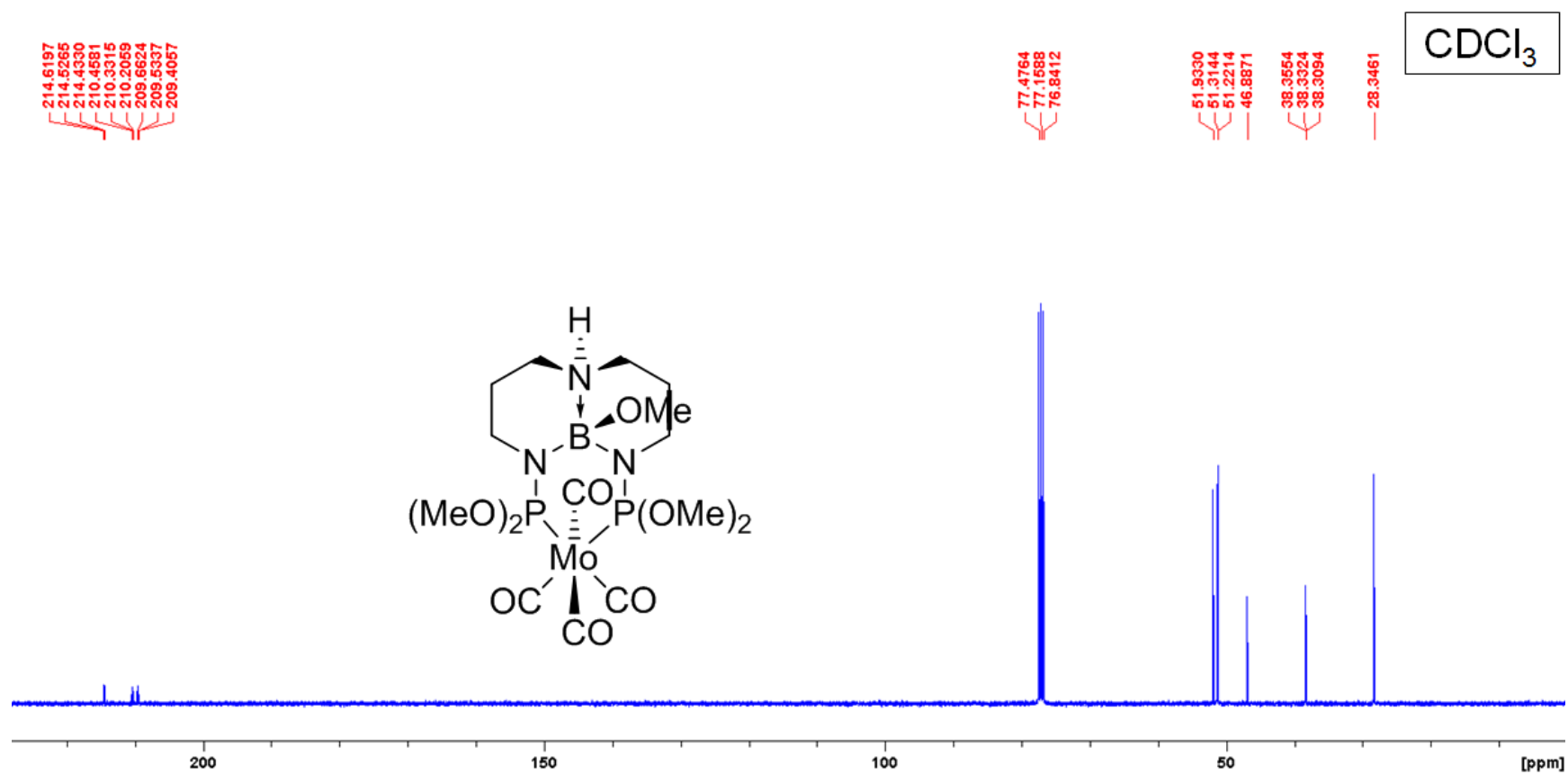
**Figure S44.**  $^1\text{H}$  NMR spectrum of  $(\text{MeOTBDPhos-MeOH})\text{Mo}(\text{CO})_4$  (8-MeOH).

CDCl<sub>3</sub>

— 2.6810



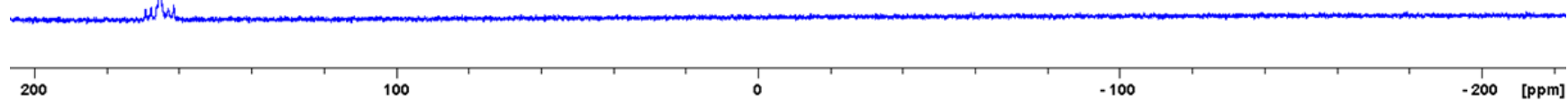
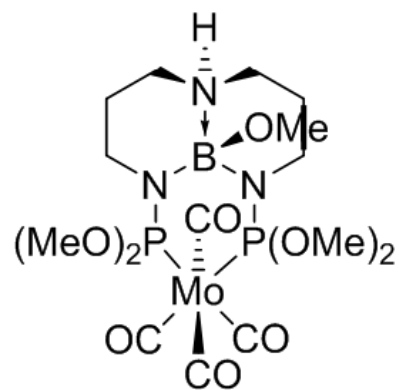
**Figure S45.** <sup>11</sup>B NMR spectrum of (<sup>MeO</sup>TBDPhos-MeOH)Mo(CO)<sub>4</sub> (**8-MeOH**).



**Figure S46.**  $^{13}\text{C}$  NMR spectrum of  $(^{\text{MeO}}\text{TBDPhos-MeOH})\text{Mo}(\text{CO})_4$  (**8-MeOH**).

CDCl<sub>3</sub>

169.1884  
167.5909  
165.2573  
162.8549  
161.4077



**Figure S47.** <sup>31</sup>P NMR spectrum of (<sup>MeO</sup>TBDPhos-MeOH)Mo(CO)<sub>4</sub> (**8-MeOH**).

### Supporting Information References

- (1) Lee, K.; Donahue, C. M.; Daly, S. R. Triaminoborane-bridged diphosphine complexes with Ni and Pd: coordination chemistry, structures, and ligand-centered reactivity. *Dalton Trans.* **2017**, 46, 9394-9406.
- (2) Mazour, Z. Substituted phosphorochloridous acid. Ger. Offen. DE 2643442, April 7, 1977.
- (3) Lee, K.; Wei, H.; Blake, A. V.; Donahue, C. M.; Keith, J. M.; Daly, S. R. Ligand K-edge XAS, DFT, and TDDFT analysis of pincer linker variations in Rh(I) PNP complexes: reactivity insights from electronic structure. *Dalton Trans.* **2016**, 45, 9774-9785.
- (4) Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A Found. Adv.* **2015**, 71, 3-8.
- (5) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C Struct. Chem.* **2015**, 71, 3-8.
- (6) (a) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, 42, 339-341. (b) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* **2008**, 41, 466-470.
- (7) (a) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, 7, 3297-3305. (b) Zhao, Y.; Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **2006**, 125, 194101/194101-194101/194118.
- (8) Becke, A. D. A new mixing of Hartree-Fock and local-density-functional theories. *J. Chem. Phys.* **1993**, 98, 1372-1377.
- (9) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, 132, 154104/154101-154104/154119.