Supporting Information for

Development of Highly Productive Nickel-Sodium Phenoxyphosphine Ethylene Polymerization Catalysts and Their Reaction Temperature Profiles

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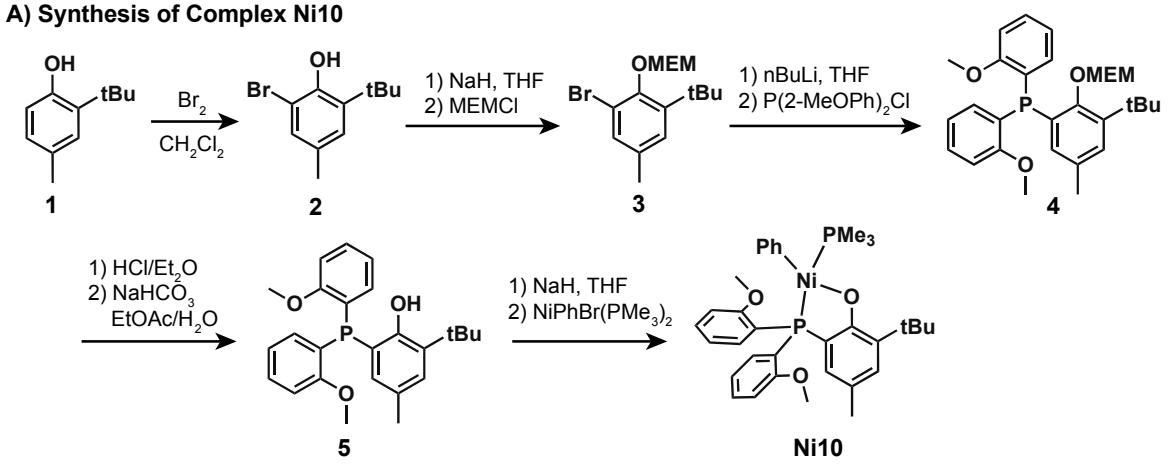
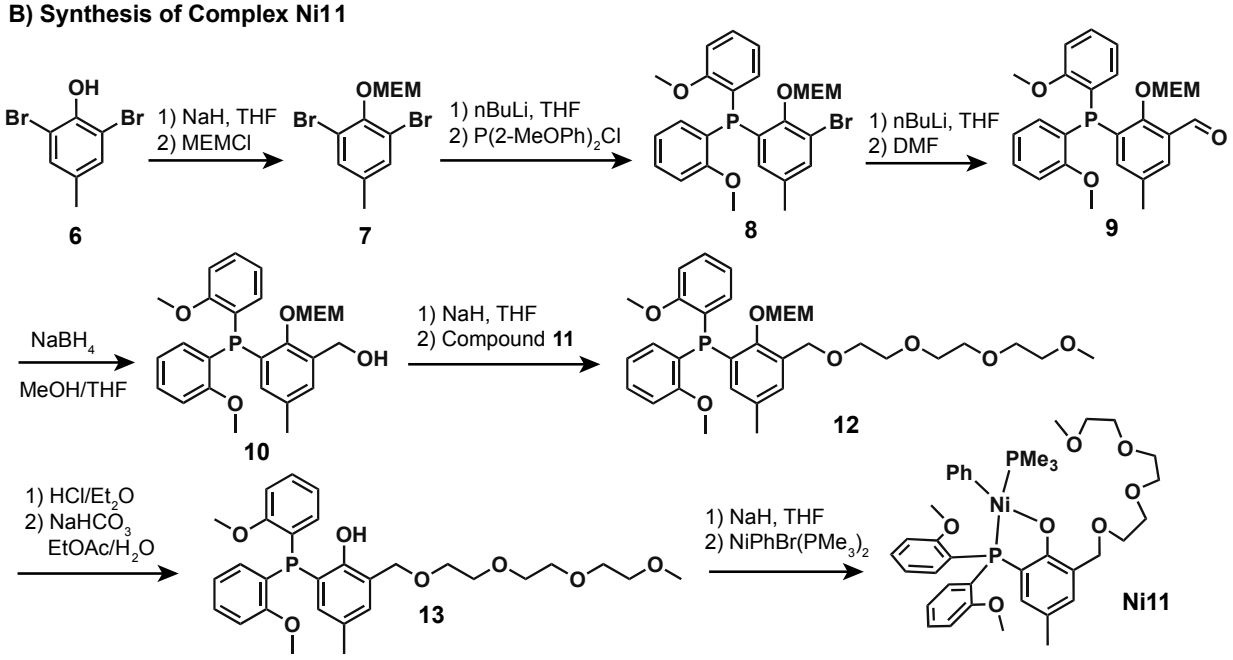
Experimental

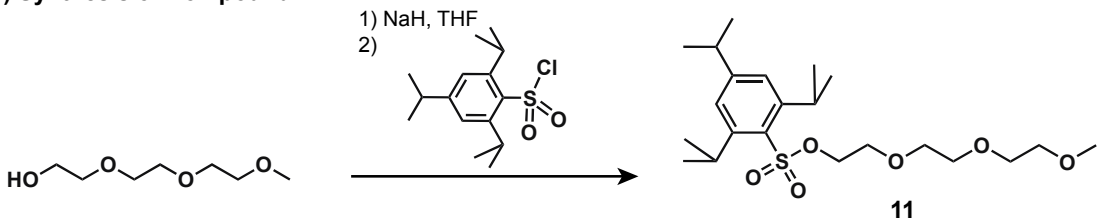
A) Synthesis of Complex Ni10



B) Synthesis of Complex Ni11



C) Synthesis of Compound 11



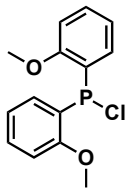
Scheme S1. Procedures for the synthesis of **Ni10**, **Ni11**, and **11**.

General Procedures

Commercial reagents were used as received. All air- and water-sensitive manipulations were performed using standard Schlenk techniques or under a nitrogen atmosphere using a drybox. Anhydrous solvents were obtained from an Innovative Technology solvent drying system saturated with argon. High-purity polymer grade ethylene was obtained from Matheson TriGas without further purification. The $NaBAr^F_4$ salt was prepared according to a literature procedure.[1] NMR spectra were acquired using JEOL spectrometers (ECA-400, -500, and -600) and referenced using residual solvent peaks. All ^{13}C NMR spectra were proton decoupled. ^{31}P NMR spectra were referenced to phosphoric acid. ^1H NMR spectroscopic characterization of polymers: each NMR sample contained ~20 mg of polymer in 0.5 mL of 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2) and was recorded on a 500 MHz spectrometer using standard acquisition parameters at 120 °C. High-resolution mass spectra were obtained from the mass spectral facility at the University of Houston. Elemental analyses were performed by Atlantic Microlab. Gel permeation chromatography (GPC) data were obtained using a Malvern high temperature GPC instrument equipped with refractive index, viscometer, and light scattering detectors at 150 °C with 1,2,4-trichlorobenzene (stabilized with 125 ppm BHT) as the mobile phase. A calibration curve was established using polystyrene standards in triple detection mode. All molecular weights reported are based on the triple detection method.

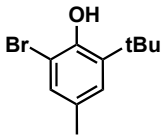
Synthesis and Characterization

Preparation of $P(2\text{-}MeOPh)_2Cl$. This synthesis was modified from a reported procedure.[2] A



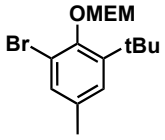
200 mL Schlenk flask was charged with magnesium turnings (1.2 g, 50 mmol, 2.5 equiv.) under nitrogen in 50 mL of dry THF. The compound 2-bromoanisole (5.2 mL, 40 mmol, 2.0 equiv.) was added to the reaction mixture and then stirred at RT for 3 h until the solution turned dark gray. The resulting Grignard reagent was slowly cannula transferred over a period of 45 min to a solution of PCl_3 (1.6 mL, 20 mmol, 1.0 equiv.) in 100 mL of dry THF at -78 °C. After the addition was complete, the heterogeneous mixture was continued stirring and allowed to warm up to RT overnight. Finally, the solvent was removed under vacuum and the crude product was used in the next step without further purification. ^{31}P NMR ($CDCl_3$, 162 MHz): δ (ppm)= 69.94 (s), 62.56 (s).

Preparation of Compound 2. This synthesis was modified from a literature procedure.[3] The

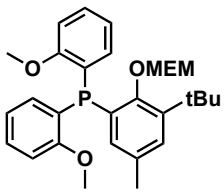


compound 2-*tert*-butyl-4-cresol (6.73 g, 40.95 mmol, 1.05 equiv.) was dissolved in 100 mL of dry DCM in a 200 mL Schlenk flask. The flask was covered with aluminum foil and cooled to 0 °C. Bromine (2 mL, 39 mmol, 1.00 equiv.) was added dropwise to the reaction flask and the mixture was allowed to warm to RT and stirred overnight. The reaction was quenched by the slow addition of cold H_2O (75 mL) and was then extracted into DCM (2×150 mL). The organic layers were combined, washed with aqueous $NaHCO_3$ (2×100 mL), H_2O (2×100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (20:1 hexane: ethyl acetate) to afford a white solid (9.50 g, 39.07 mmol, 95%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.16 (s, 1H), 7.01 (s, 1H), 5.64 (s, 1H), 2.26 (s, 3H), 1.40 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ (ppm) = 148.21, 137.24, 130.30, 129.69, 127.46, 111.97, 35.36, 29.47, 20.68.

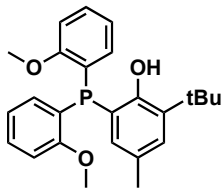
Preparation of Compound 3. To a mixture of **2** (9.50 g, 39.07 mmol, 1.0 equiv.) in 100 mL of dry THF in a 200 mL Schlenk flask under nitrogen at -0 °C, small aliquots of NaH (60%, 2.34 g, 58.6 mmol, 1.5 equiv.) were added and the mixture was stirred at RT for 2 h. The reagent 2-methoxyethoxymethyl chloride (MEMCl) (5.5 mL, 44.93 mmol, 1.15 equiv.) was added and the solution was stirred overnight. The reaction was quenched by the slow addition of H_2O and the product was extracted into Et_2O (2×150 mL). The organic layers were combined, washed with H_2O (2×75 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (20:1 hexane: ethyl acetate) to afford a colorless oil (6.91 g, 20.86 mmol, 53%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.22 (d, J_{HH} = 1.8 Hz, 1H), 7.07 (d, J_{HH} = 1.8 Hz, 1H), 5.27 (s, 2H), 4.05 (m, 2H), 3.65 (m, 2H), 3.41 (s, 3H), 2.26 (s, 3H), 1.40 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ (ppm) = 150.46, 145.06, 134.56, 132.14, 127.69, 117.74, 98.21, 71.72, 69.45, 59.18, 35.65, 30.94, 20.83. HRMS–ESI(+): Calc. for $C_{15}H_{23}BrO_3$ $[M+Na]^+$ = 353.0728, Found = 353.0853.



Preparation of Compound 4. To a solution of compound **3** (6.62 g, 20 mmol, 1.0 equiv.) in 50 mL of dry THF in a 100 mL Schlenk flask under nitrogen at -78 °C, nBuLi (1.6 M in hexanes, 12.8 mL, 20.5 mmol, 1.02 equiv.) was added dropwise using a syringe pump. The reaction mixture was stirred at -78 °C for 40 min. A solution of P(2-MeOPh)$_2$Cl (5.05 g, 18 mmol, 0.9 equiv.) in 50 mL of dry THF was cannula transferred into the reaction mixture and stirred for another 40 min. The reaction was quenched by the slow addition of H_2O and the product was extracted into Et_2O (3×75 mL). The organic layers were combined, washed with H_2O (2×50 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (4:1 hexane: ethyl acetate) to afford a colorless oil (4.02 g, 8.09 mmol, 40%). This compound was used directly in the next step without further purification.



Preparation of Compound 5. Compound **4** (1.24 g, 2.5 mmol, 1.0 equiv.) was dissolved in 100 mL of MeOH and then 10 mL solution of 2 M HCl in Et_2O was added. The reaction mixture was stirred at RT overnight and then dried to remove solvent. The product was dissolved in 200 mL of EtOAc along and then combined with 50 mL of 1 M aqueous $NaHCO_3$. The mixture was stirred at RT for 30 min and the product was extracted into Et_2O (2×100 mL). The organic layers were combined, washed with H_2O (2×100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (4:5 hexane: ethyl acetate) to afford a white solid (0.69 g, 1.68 mmol, 67%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.40 (d, J_{HH} = 11.5 Hz, 1H), 7.19 (ddd, J_{HH} = 7.4, 5.6, 1.7 Hz, 2H), 7.13 (d, J_{HH} = 1.8 Hz, 1H), 7.02 (td, J_{HH} = 8.1, 1.5 Hz, 2H), 6.97 (dd, J_{HH} = 5.4, 1.6 Hz, 1H), 6.70 (t, J_{HH} = 7.5 Hz, 2H), 6.37 (dd, J_{HH} = 8.1, 5.1 Hz, 2H), 3.07 (s, 6H), 1.92 (s, 3H), 1.51 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 161.04 (d, J_{CP} = 15.1 Hz), 156.56 (d, J_{CP} = 19.7 Hz), 135.36, 133.23, 133.0.3 (d, J_{CP} = 3.2 Hz), 130.24, 129.53, 128.42, 123.09 (d, J_{CP} = 2.8 Hz), 120.96, 119.28, 110.30, 55.71, 34.79, 29.54, 20.88. ^{31}P NMR ($CDCl_3$, 162 MHz): δ (ppm) = -51.71. HRMS–ESI(+): Calc. for $C_{25}H_{29}O_3P$ $[M+Na]^+$ = 431.1752, Found = 431.1887.

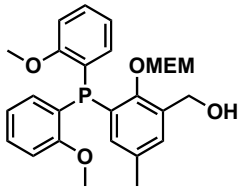


Preparation of Compound 7. Solid 2,6-dibromo-4-methylphenol (6.65 g, 25 mmol, 1.0 equiv.) was dissolved in 100 mL of dry THF in a Schlenk flask under nitrogen and cooled to 0 °C. Small aliquots of NaH (60%, 1.48 g, 37 mmol, 1.5 equiv.) were added and the mixture was stirred at room temperature for 1 h. The reagent 2-methoxyethoxymethyl chloride (MEMCl) was added and the resulting solution was stirred overnight. The reaction was quenched by the slow addition of H_2O and the products were extracted into Et_2O (2×100 mL). The organic layers were combined, washed with H_2O (2×50 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (2:1 hexane: ethyl acetate) to afford a clear oil (7.66 g, 21.64 mmol, 86%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.29 (s, 2H), 5.20 (s, 2H), 4.08 (m, 2H), 3.61 (m, 2H), 3.38 (s, 3H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) = 149.04, 136.91, 133.35, 117.97, 98.36, 71.77, 69.89, 59.19, 20.29. HRMS–ESI(+): Calc. for $C_{11}H_{14}Br_2O_3$ $[M+Na]^+$ = 374.9202, Found = 374.9332.

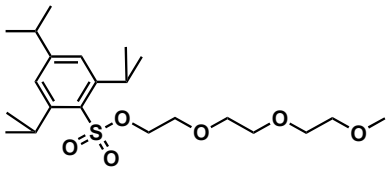
Preparation of Compound 8. To a solution of **7** (7.08 g, 20 mmol, 1.0 equiv.) in 50 mL of dry THF in a Schlenk flask under nitrogen at -78 °C, nBuLi (1.6 M in hexanes, 12.8 mL, 20.5 mmol, 1.02 equiv.) was added dropwise using a syringe pump. The reaction mixture was then stirred at -78 °C for 40 min. A solution of P(2-MeOPh)$_2$Cl (5.05 g, 18 mmol, 0.9 equiv.) in 50 mL of dry THF was cannula transferred to the reaction mixture and stirred for another 40 min. The reaction was quenched by the slow addition of H_2O and the products were extracted into Et_2O (3×75 mL). The organic layers were combined, washed with H_2O (2×50 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (3:1 hexane: ethyl acetate) to afford a colorless oil (6.82 g, 13.16 mmol, 73%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.36 (s, 1H), 7.32 (t, J_{HH} = 7.5 Hz, 2H), 6.86 (m, 3H), 6.83 (d, J_{HH} = 5.2 Hz, 1H), 6.63 (m, 2H), 6.49 (m, 1H), 5.30 (s, 2H), 4.02 (t, J_{HH} = 4.8 Hz, 2H), 3.72 (s, 6H), 3.52 (t, J_{HH} = 4.5 Hz, 2H), 3.34 (s, 3H), 2.12 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) = 161.33 (d, J_{CP} = 16.5 Hz), 161.20 (d, J_{CP} = 20.9), 154.24, 154.07, 135.61, 134.78, 134.50, 133.86, 132.94 (d, J_{CP} = 17.4 Hz), 132.81, 130.34, 124.31, 124.20 (d, J_{CP} = 13.7 Hz), 121.18, 117.34, 117.32, 110.22, 98.75 (d, J_{CP} = 9.4 Hz), 98.68, 71.81, 69.52 (d, J_{CP} = 4.3 Hz), 59.07, 55.75, 20.66. ^{31}P NMR ($CDCl_3$, 162 MHz): δ (ppm) = -35.90. HRMS–ESI(+): Calc. for $C_{25}H_{30}BrO_5P$ $[M+Na]^+$ = 541.0750, Found = 541.0940.

Preparation of Compound 9. To a solution of **8** (6 g, 11.58 mmol, 1.0 equiv.) in 50 mL of dry THF in a Schlenk flask under nitrogen at -78 °C, nBuLi (1.6 M in hexanes, 8.4 mL, 13.44 mmol, 1.16 equiv.) was added dropwise using a syringe pump. The reaction mixture was stirred at -78 °C for 40 min. Dry DMF (5 mL, 65 mmol, 5.6 equiv.) was added to the reaction mixture and stirred for another 40 min. The reaction was quenched by the slow addition of H_2O and the product was extracted into Et_2O (3×75 mL). The organic layers were combined, washed with H_2O (2×50 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (3:2 hexane: ethyl acetate) to afford a light yellow oil (4.67 g, 9.98 mmol, 86%). This compound was used directly in the next step without further purification.

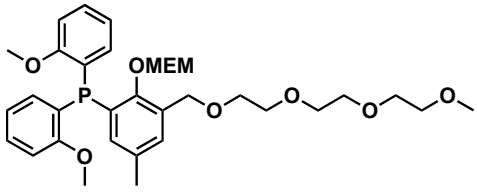
Preparation of Compound 10. Compound **9** (4.67 g, 9.98 mmol, 1.0 equiv.) was dissolved in 400 mL of MeOH and 80 mL of THF. Small aliquots of $NaBH_4$ (2 g, 54 mmol, 5.4 equiv.) were added and the mixture was stirred at RT overnight. The reaction solvent was removed under vacuum and the residue was redissolved in Et_2O (100 mL). The ether layer was washed with H_2O (2×100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (1:3 hexane: ethyl acetate) to afford a white solid (3.8 g, 8.08 mmol, 81%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 7.33 (t, J_{HH} = 7.6 Hz, 2H), 7.20, (s, 1H), 6.87 (dd, J_{HH} = 8.4, 5.5 Hz, 2H), 6.84 (t, J_{HH} = 7.4 Hz, 2H), 6.62 (m, 2H), 6.51 (m, 1H), 5.29 (s, 2H), 4.62 (s, 2H), 3.88 (m, 2H), 3.72 (s, 6H), 3.57 (m, 2H), 3.36 (s, 3H), 2.14 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) = 161.21 (d, J_{CP} = 16.6 Hz), 157.74 (d, J_{CP} = 20.6 Hz), 135.24, 134.73, 134.37, 133.78, 132.59, 130.25, 129.79 (d, J_{CP} = 12.2 Hz), 124.29 (d, J_{CP} = 12.3 Hz), 121.08, 110.15, 99.92 (d, J_{CP} = 13.1 Hz), 71.50, 69.16, 61.02, 59.11, 55.74, 20.94. ^{31}P NMR ($CDCl_3$, 162 MHz): δ (ppm) = -38.50. HRMS–ESI(+): Calc. for $C_{14}H_{20}O_6$ $[M+Na]^+$ = 493.1751, Found = 493.1925.



Preparation of Compound 11. Triethylene glycol monomethyl ether (2.63 g, 16 mmol, 1.0 equiv.) was dissolved in 100 mL of dry THF in a Schlenk flask under nitrogen and cooled to 0 °C. Small aliquots of NaH (60%, 1 g, 25 mmol, 1.56 equiv.) were added and the mixture was stirred at RT for 1 h. The reagent 2,4,6-triisopropylbenzenesulfonyl chloride (6.1 g, 20 mmol, 1.25 equiv.) was added and the solution was stirred overnight. The reaction was quenched by the slow addition of H_2O and the product was extracted into Et_2O (2×100 mL). The organic layers were combined, washed with H_2O (3×50 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (5:1 hexane: ethyl acetate to 1:3 hexane: ethyl acetate) to afford a colorless oil (5.14 g, 11.95 mmol, 75%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.16 (s, 2H), 4.14 (m, 4H), 3.71 (t, J_{HH} = 4.8 Hz, 2H), 3.59 (m, 6H), 3.50 (m, 2H), 3.34 (s, 3H), 2.89 (sep, J_{HH} = 6.9 Hz, 1H), 1.24 (m, 18H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) = 153.77, 150.93, 129.35, 123.84, 71.96, 70.78, 70.64, 68.87, 68.22, 59.12, 34.34, 29.67, 24.80, 23.65. HRMS–ESI(+): Calc. for $C_{22}H_{38}O_6S$ $[M+Na]^+$ = 453.2287, Found = 453.2442.



Preparation of Compound 12. To a mixture of **11** (3.8 g, 8.08 mmol, 1 equiv.) in 100 mL of dry THF in a Schlenk flask under nitrogen at -0 °C, small aliquots of NaH (60%, 1.3 g, 32.4 mmol, 4 equiv.) was added. The reaction mixture stirred at RT for 1 h. A solution of compound **11** (5.23 g, 12.15 mmol, 1.5 equiv.) in 50 mL of THF was cannula transferred into the reaction mixture and then stirred at RT overnight. The reaction was quenched by the slow addition of cold H_2O and the product was extracted into Et_2O (3×100 mL). The organic layers were combined, washed with H_2O (2×75 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (1:1 hexane: ethyl acetate to 1:4 hexane: ethyl acetate) to afford a colorless oil (3.95 g, 6.07 mmol, 75%). This compound was used directly in the next step without further purification.



Preparation of Compound 13. Compound **12** (3.95 g, 6.07 mmol, 1 equiv.) was dissolved in 100 mL of MeOH and then treated with 10 mL of 2 M HCl in Et_2O. The reaction mixture was stirred at RT overnight. The solvent was removed under vacuum and the product was dissolved in 200 mL of EtOAc. A 50 mL solution of 1 M $NaHCO_3$ in H_2O was then added. The mixture was stirred at RT for 30 min and the product was extracted into Et_2O (2×100 mL). The organic layers were combined, washed with H_2O (2×100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude material was purified by silica gel column chromatography (1:3 hexane: ethyl acetate) to afford a white waxy solid (2.9 g, 5.49 mmol, 90%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.32 (td, J_{HH} = 7.7, 1.5 Hz, 2H), 7.23 (d, J_{HH} = 1Hz, 1H), 6.97 (d, J_{HH} = 1.7 Hz, 1H), 6.85 (m, 4H), 6.77 (m, 2H), 6.52 (m, J_{HH} = 5.1, 1.9 Hz, 1H), 4.66 (s, 2H), 3.73 (s, 6H), 3.68 (m, 2H), 3.66 (m, 2H), 3.60 (m, 2H), 3.58 (m, 4H), 3.49 (m, 2H), 3.35 (s, 3H), 2.11 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) = 161.53 (d, J_{CP} = 26.8 Hz), 161.40 (d, J_{CP} = 5.5 Hz), 155.96 (d, J_{CP} = 29.7 Hz), 155.87, 134.34, 133.74 (d, J_{CP} = 6.6 Hz), 130.62, 130.22, 129.04 (d, J_{CP} = 9.6 Hz), 123.91, 122.57 (d, J_{CP} = 6.1 Hz), 121.04, 110.32, 71.98, 70.99, 70.76, 70.61, 70.40, 69.73, 59.11, 55.81, 20.71. ^{31}P NMR ($CDCl_3$, 162 MHz): δ (ppm) = -44.09. HRMS–ESI(+): Calc. for $C_{29}H_{39}O_7P$ $[M+Na]^+$ = 551.2175, Found = 551.2362.

Preparation of Complex NiPhBr(PMe$_3$)$_2$. This synthesis was modified from a literature procedure.[4] Inside the glovebox, Ni[COD]$_2$ (1.10 g, 4 mmol, 1 equiv.) and PMe_3 (1 M in THF, 10 mL, 10 mmol, 2.5 equiv.) were dissolved in 50 mL of dry Et_2O. PhBr (0.94 g, 6.0 mmol, 1.5 equiv.) was added and the reaction mixture was stirred at RT for 6 h. The solution was filtered to remove a black solid and the filtrate was then dried completely under vacuum. The crude material was washed with cold Et_2O (-30 °C, 4×4 mL) to afford a bright orange solid (1.02 g, 3.17 mmol, 79%). ^{1}H NMR (C_6D_6, 500 MHz): δ (ppm) = 7.28 (dd, J_{HH} = 7.7, 1.1 Hz, 2H), 6.91 (t, J_{HH} = 7.5 Hz, 2H), 6.75 (m, 1H), 0.78 (t, J_{HH} = 3.9 Hz, 18H). ^{31}P NMR (C_6D_6, 202 MHz): δ (ppm) = -14.78.

Preparation of Complex Ni10. Inside the glovebox, ligand **15** (0.164 g, 0.4 mmol, 1.0 equiv.) was dissolved in 10 mL of THF. Small aliquots of NaH (60%, 0.32 g, 0.8 mmol, 2.0 equiv.) were added and the mixture was stirred at RT for 2 h. The solution was filtered to remove excess NaH and then combined with a solution of NiPhBr(PMe$_3$)$_2$ (0.122 g, 0.38 mmol, 0.95 equiv.) in 5 mL of benzene. The resulting mixture was stirred at RT overnight. The precipitate formed was removed by filtration and the filtrate was dried under vacuum. The crude material was dissolved in a mixture of 15 mL of pentane and 2 mL of toluene and the solution was filtered once again before evaporating to dryness. Finally, the resulting solid was washed with pentane (3×2 mL) and dried under vacuum to afford a yellow powder (0.11 g, 0.17 mmol, 45%). ^{1}H NMR (C_6D_6, 500 MHz): δ (ppm) = 7.56 (ddd, J_{HH} = 11.1, 7.5, 1.3 Hz, 2H), 7.23 (d, J_{HH} = 7.5 Hz, 2H), 7.14 (d, J_{HH} = 2.0 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.97 – 6.92 (m, 1H), 6.71 (t, J_{HH} = 7.4 Hz, 2H), 6.63 (t, J_{HH} = 7.5 Hz, 2H), 6.58 (d, J_{HH} = 7.3 Hz, 1H), 6.38 (dd, J_{HH} = 8.1, 4.4 Hz, 2H), 2.98 (s, 6H), 2.04 (s, 3H), 1.69 (s, 9H), 0.81 (d, J_{HH} = 8.8 Hz, 9H). ^{13}C NMR (C_6D_6, 152 MHz): δ (ppm) = 174.11 (d, J_{CP} = 26.3 Hz), 160.74 (d, J_{CP} = 5.5 Hz), 150.92 (d, J_{CP} = 32.6 Hz), 137.70 (d, J_{CP} = 9 Hz), 137.09 (d, J_{CP} = 2.8 Hz), 133.99 (d, J_{CP} =

5.4 Hz), 130.85, 130.72, 130.47, 125.22, 121.86 (d, J_{CP} = 6.8 Hz), 120.47 (d, J_{CP} = 8.3 Hz), 120.29, 119.86, 118.69, 118.20, 110.66 (d, J_{CP} = 4.4 Hz), 54.88, 35.13, 29.54, 20.60, 12.47 (d, J_{CP} = 23.8 Hz). ^{31}P NMR (C_6D_6, 202 MHz): δ (ppm) = 15.08 (d, J_{PP} = 320.9 Hz), -13.64 (d, J_{PP} = 320.7 Hz). Anal. Calcd for $C_{34}H_{42}NiO_3P_2$: C, 65.94; H, 6.84. Found: 65.68; 6.99.

Preparation of Complex Ni11. Inside the glovebox, ligand **13** (1.12 g, 2.11 mmol, 1.0 equiv.) was dissolved in 50 mL of dry THF. Small aliquots of NaH (60%, 0.17g, 4.22 mmol, 2.0 equiv.) were added and the mixture was stirred at RT for 2 h. The mixture was filtered to remove excess NaH and then a solution of $NiPhBr(PMe_3)_2$ (0.65 g, 2.02 mmol, 0.96 equiv.) in 20 mL of benzene was added. The resulting mixture was stirred at RT overnight. The next day, the solution was filtered to remove the precipitate and the filtrate was dried completely under vacuum. The crude material was dissolved in a mixture of 40 mL of pentane and 4 mL of benzene. Another filtration was performed to remove the precipitate and the filtrate was dried once again. Finally, the resulting solid was washed with pentane (3×5 mL) and dried to under vacuum to afford a yellow powder (1.12 g, 1.51 mmol, 75%). ^{1}H NMR (C_6D_6, 500 MHz): δ (ppm) = 7.64 (m, 2H), 7.37 (d, J_{HH} = 1.7 Hz, 1H), 7.24 (d, J_{HH} = 7.7 Hz, 2H), 7.06 (dd, J_{HH} = 8.0, 4.4 Hz, 1H), 7.02 (m, 2H), 6.74 (t, J_{HH} = 7.4 Hz, 2H), 6.66 (t, J_{HH} = 7.5 Hz, 2H), 6.61 (m, 1H), 4.87 (s, 2H), 3.74 (m, 2H), 3.60 (m, 2H), 3.50 (m, 2H), 3.44 (m, 4H), 3.30 (m, 2H), 3.07 (s, 3H), 2.95 (s, 6H), 2.03 (s, 3H), 0.81 (d, 9H). ^{13}C NMR (C_6D_6, 152 MHz): δ (ppm) = 173.39 (d, J_{CP} = 26.8 Hz), 160.77 (d, J_{CP} = 4.8 Hz), 150.91 (d, J_{CP} = 29.7 Hz), 137.05, 133.93 (d, J_{CP} = 6.3 Hz), 132.86, 131.74, 131.00, 127.16 (d, J_{CP} = 9.5 Hz), 125.22, 120.46, 120.39, 120.31, 120.07, 119.71, 117.92, 117.54, 110.52 (d, J_{CP} = 3.8 Hz), 72.09, 70.99, 70.85, 70.80, 70.63, 69.89, 69.82, 58.42, 54.81, 20.45, 11.50 (d, J_{CP} = 24.7 Hz). ^{31}P NMR (C_6D_6, 202 MHz): δ (ppm) = 13.74 (J_{PP} = 319.5 Hz), -12.74 (J_{PP} = 318.1 Hz). Anal. Calcd for $C_{38}H_{52}NiO_7P_2$: C, 61.72; H, 6.82. Found: 61.63; 6.96.

Metal-Binding Studies

***UV-Vis Absorption Spectroscopy: Metal Titration*.** Stock solutions of **Ni11** and $NaBAr^F{}_4$ were prepared inside an inert nitrogen-filled glovebox. A 500 μM stock solution of **Ni11** were obtained by dissolving 25 μmol of **Ni11** in 50 mL of Et_2O. A 10 mL aliquot of this 500 μM solution was diluted to 50 mL using a volumetric flask to give a final concentration of 100 μM. The 3.0 mM stock solution of $NaBAr^F{}_4$ was obtained by dissolving 30 μmol of $NaBAr^F{}_4$ in 10 mL of Et_2O using a volumetric flask. A 3.0 mL solution of **Ni11** was transferred to a 1 cm quartz cuvette and then sealed with a septum screw cap. A 100 μL airtight syringe was loaded with the 3.0 mM solution of $NaBAr^F{}_4$. The cuvette was placed inside a UV-vis spectrophotometer and the spectrum of the **Ni11** solution was recorded. Aliquots containing 0.1 equiv. of $NaBAr^F{}_4$ (10 μL), relative to the nickel complex, were added and the solution was allowed to reach equilibrium before the spectra were measured (about 20−30 min). The titration experiments were stopped after the addition of up to 1.0 equiv. of $NaBAr^F{}_4$.

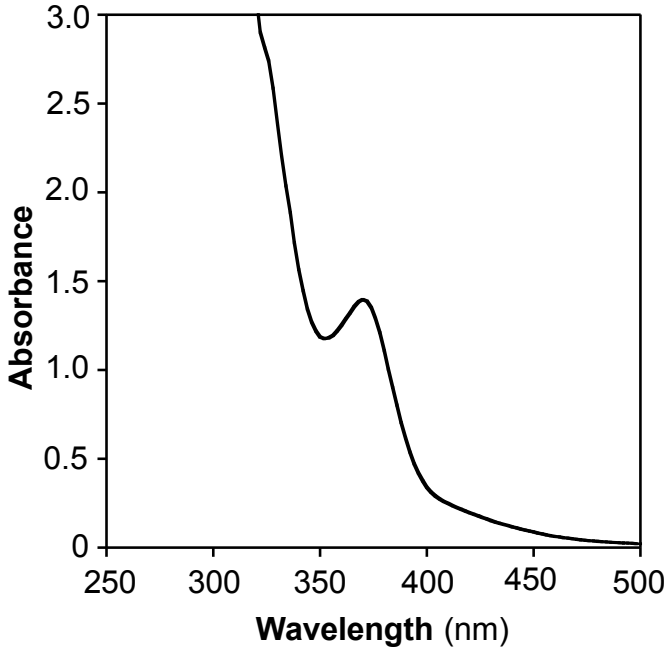


Figure S1. UV-vis absorbance spectra of complex **Ni10 (**100 μM in Et_2O) after the addition of 4 equiv. of $NaBAr^F{}_4$. The starting trace of **Ni10** before and after the addition of Na^+ are identical, suggesting that sodium does not bind to the nickel complex.

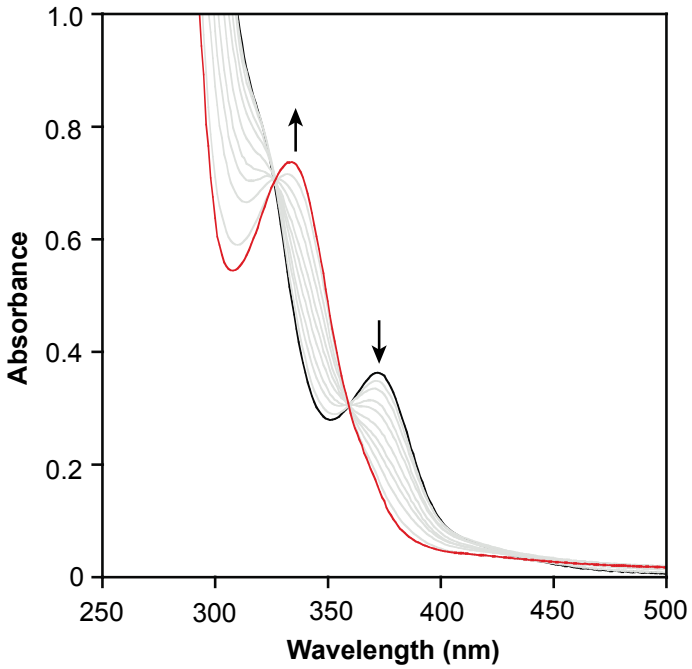


Figure S2. UV-vis absorbance spectra of complex **Ni11 (**100 μM in Et_2O) after the addition of various aliquots of $NaBAr^F_4$. The starting trace of **Ni11** is shown in black and the final trace (+ 1.0 equiv. of Na^+ relative to Ni) is shown in red.

UV-Vis Absorption Spectroscopy: Job Plot Studies. Stock solutions of **Ni11** (500 μM) and $NaBAr^F_4$ (500 μM) in Et_2O were prepared in separate volumetric flasks inside the drybox. Stock solutions of **Ni11** and $NaBAr^F_4$ were combined in different ratios to give 10 different samples, each having a final volume of 3.0 mL. The samples were recorded by UV-vis absorption spectroscopy at RT.

The UV-vis spectral data were analyzed according to the method reported by Hirose.[5] In our case, the host (H) is **Ni11**, the guest (g) is Na^+, and the complex (C) is **Ni11**-Na. Since the sodium salt has no absorption in the 300-500 nm range, we used this simplified expression to analyze the data: $A_{obs} - \varepsilon_h \cdot [H]_t = (\varepsilon_C - a \cdot \varepsilon_h) \cdot [C]$, where A_{obs} = observed absorbance, a = constant, ε_h = molar absorptivity of host **Ni11**, ε_C = molar absorptivity of **Ni11**-Na, $[H]_t$ = starting concentration of host **Ni11**, and [C] = observed concentration of **Ni11**-Na. Since [C] is proportional to $A_{obs} - \varepsilon_h \cdot [H]_t$, a Job Plot was constructed by plotting $A_{obs} - \varepsilon_h \cdot [H]_t$ vs. χ_{Ni} (the mole ratio of **Ni11** = [**Ni11**]/([**Ni11**]+[Na^+])).

Table S1. Data and Calculations Used for Job Plot[a]

χ_{Ni}	**Volume of Stock Soln of H** (mL)	**Amount of H Added** (mol)	**Final Conc. of H** (M)	A_h (calculated)	A_{obs} (@330 nm)	A_{obs}-A_h
1.0	3.000E-03	1.500E-06	5.000E-04	2.663E+00	2.663E+00	-2.040E-04
0.9	2.700E-03	1.350E-06	4.500E-04	2.396E+00	2.350E+00	4.576E-02
0.8	2.400E-03	1.200E-06	4.000E-04	2.130E+00	1.966E+00	1.637E-01
0.7	2.100E-03	1.050E-06	3.500E-04	1.864E+00	1.653E+00	2.108E-01
0.6	1.800E-03	9.000E-07	3.000E-04	1.598E+00	1.308E+00	2.896E-01
0.5	1.500E-03	7.500E-07	2.500E-04	1.331E+00	1.008E+00	3.234E-01
0.4	1.200E-03	6.000E-07	2.000E-04	1.065E+00	8.275E-01	2.375E-01
0.3	9.000E-04	4.500E-07	1.500E-04	7.988E-01	6.497E-01	1.491E-01
0.2	6.000E-04	3.000E-07	1.000E-04	5.325E-01	4.393E-01	9.315E-02
0.1	3.000E-04	1.500E-07	5.000E-05	2.663E-01	2.714E-01	-5.174E-03

[a]The molar absorptivity of H (ε_h) at 330 nm = 5325 $M^{-1}cm^{-1}$. Stock solution of H is 500 μM.

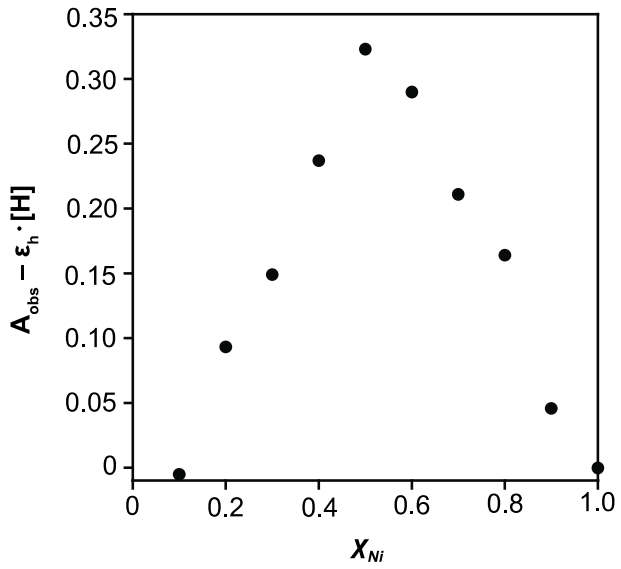


Figure S3. Job Plot showing the coordination interactions between complex **Ni11** and $NaBAr^F{}_4$. The peak maximum occurs at $\chi_{Ni} = 0.5$, which suggests that the optimal nickel:sodium binding stoichiometry is 1:1. The y-axis value ($A_{obs} - \varepsilon_h \cdot [H]_t$) is proportional to the concentration of the nickel-sodium complex **Ni11**-Na. The x-axis is the molar ratio of nickel (χ_{Ni} = [**Ni11**]/([**Ni11**]+[Na^+])). The full data is given in Table S1.

Polymerization Studies

General Procedure for Ethylene Polymerization. Inside the drybox, the nickel complex **Ni11** (0.5 μmol) and $NaBAr^F{}_4$ (1 μmol) were dissolved in 10 mL of toluene in a 20 mL vial and stirred for 10 min. Solid $Ni(COD)_2$ (4 μmol) was added and stirred until a clear solution was obtained (4 – 5 min). The mixture was loaded into a 10 mL syringe equipped with an 8-inch stainless steel needle. The loaded syringe was sealed by sticking the needle tip into a rubber septum and brought outside of the drybox. To prepare the polymerization reactor, 90 mL of dry toluene was placed in an empty autoclave. The autoclave was pressurized with ethylene to 80 psi, stirred for 5 min, and then the reactor pressure was reduced to 5 psi. This process was repeated 3 times to remove trace amounts of oxygen inside the reaction vessel. The reactor was then heated to the desired temperature and the catalyst solution was injected into the autoclave through a side arm. The autoclave was sealed and purged with ethylene at 40 psi (no stirring) three times. Finally, the reactor pressure was increased to the desired pressure, and the contents were stirred vigorously. To stop the polymerization, the autoclave was vented and cooled in an ice bath. A solution of MeOH (600 mL) was added to precipitate the polymer. The polymer was collected by vacuum filtration, rinsed with MeOH, and dried under vacuum at 80 °C overnight. The reported yields are average values obtained from duplicate or triplicate runs.

*Special Notes**:***

- To obtain consistent polymer yields from run to run, the amount of catalyst used in each run must be kept as consistent as possible. Since 0.5 μmol of the **Ni11** catalyst weighs only 0.37 mg, it is extremely difficult to weigh out exactly this amount using a standard analytical balance. To minimize errors due to weighing inconsistencies, we used a batch catalyst preparation method. First, we weighed out 37 mg (50 μmol) of the catalyst and then dissolved it into 50 mL of toluene. This solution was divided equally into 10 vials so that each vial contained 5 μmol of catalyst. Next, we combined each 5 μmol of catalyst with 20 mL of toluene and partitioned this 25 mL mixture into 10 vials so that each vial contained 0.5 μmol of catalyst. Finally, each vial was dried completely under vacuum and stored in a refrigerator inside the drybox until ready for use.
- For all polymerization reactions, except ones that were performed to determine the temperature profiles, the reaction temperature was controlled by manual cooling of the reactor with an air stream when the reactor increases more than 5°C above the starting temperature.
- To clean the Parr reactor, the vessel was washed with hot toluene (80 °C) to remove the polymer sample from the previous run and rinsed with acetone before drying under vacuum for at least 1 h to remove trace amounts of water.

Table S2. Comparison of Nickel Catalyst Activity[a]

Catalyst	Yield (g)				Activity (kg PE/mol Ni·h)
	Run 1	Run 2	Run 3	Average	
Ni10	0.89	1.22	-	1.06	2120
Ni10/NaBAr$^F_4$	1.17	0.72	-	0.94	1880
Ni10/NaBAr$^F_4$/ 15-crown-5	1.05	0.86	-	0.96	1920
Ni11	0	0	0	0	0
Ni11/NaBAr$^F_4$	8.95	8.85	9.41	9.07	18100

[a]Polymerization conditions: Ni catalyst (0.5 μmol), NaBAr$^F_4$ (1 μmol, if any), Ni(COD)$_2$ (4 μmol), 100 mL toluene, 450 psi ethylene, 30°C for 1 h.

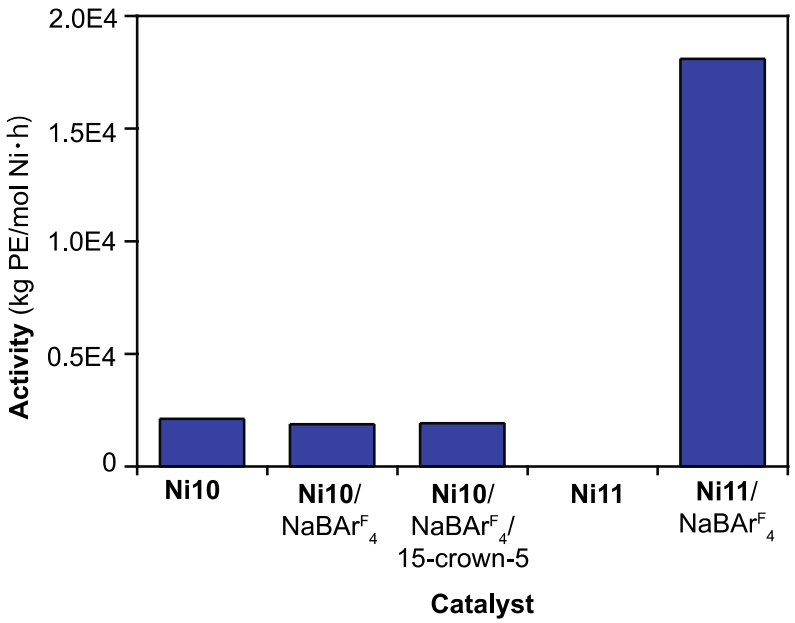


Figure S4. Comparison of catalyst activity between **Ni10** and **Ni11** with and without the addition of NaBAr$^F_4$. Full data shown in Table S2.

Table S3. Pressure Study of Ethylene Polymerization by **Ni11**-Na[a]

Pressure (psi)	**Yield** (g)				**Activity** (kg PE/mol Ni·h)
	Run 1	Run 2	Run 3	Average	
150	2.34	1.81	1.52	1.89	3780
300	4.77	4.86	3.62	4.42	8840
450	4.59	5.72	5.91	5.41	10800

[a]Polymerization conditions: Ni catalyst (0.5 μmol), $NaBAr^{F}_{4}$ (1 μmol), $Ni(COD)_2$ (4 μmol), 100 mL toluene, 20°C for 1 h at various ethylene pressures. Temperature controlled by manual external cooling when necessary.

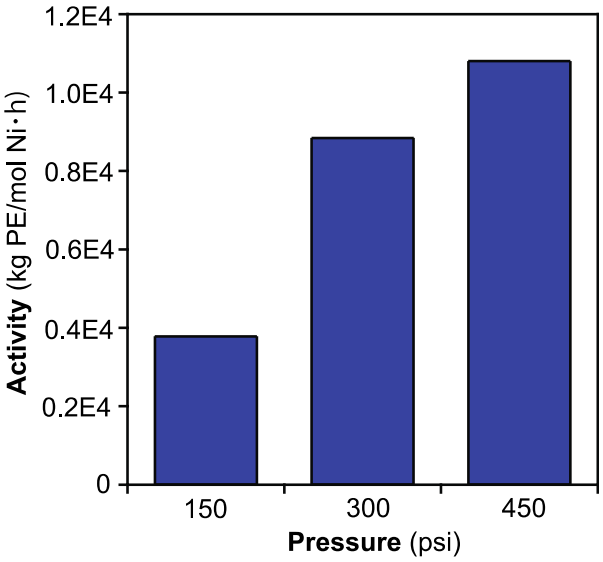


Figure S5. Activity vs. pressure plot of catalyst **Ni11**-Na in ethylene polymerization at 450 psi. The highest activity was observed at 450 psi. Full data shown in Table S3.

Table S4. Time Study of Ethylene Polymerization by **Ni11**-Na at 150 psi[a]

Time	Yield (g)				Activity (kg PE/mol Ni·h)	M_n[b] ($\times 10^3$)	M_w/M_n[b]
	Run 1	Run 2	Run 3	Average			
0.25 h	0.425	0.418	0.356	0.400	3200	1420	1.4
1 h	2.34	1.81	1.52	1.89	3780	1590	1.4
2 h	3.08	3.75	3.19	3.34	3340	1550	1.5
3 h	4.21	3.63	5.45	4.43	2950	1580	1.4

[a]Polymerization conditions: Ni catalyst (0.5 μmol), $NaBAr^F_4$ (1 μmol), $Ni(COD)_2$ (4 μmol), 100 mL toluene, 150 psi ethylene, 20°C for various times as indicated. Temperature controlled by manual external cooling when necessary.
[b]Determined by GPC in trichlorobenzene at 150°C.

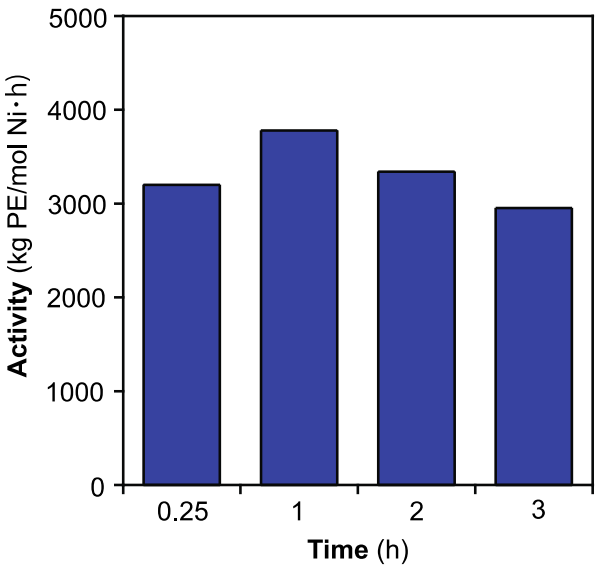


Figure S6. Activity vs. time plot of catalyst **Ni11**-Na in ethylene polymerization at 150 psi. The activity remained relatively constant over a 3 h time course. Full data shown in Table S4.

Table S5. Time Study of Ethylene Polymerization by **Ni11**-Na at Optimal Reaction Conditions[a]

Time	Yield (g)				Activity (kg PE/mol Ni·h)
	Run 1	Run 2	Run 3	Average	
0.5 h	6.92	5.71	-	6.32	25300
1 h	8.95	8.85	9.41	9.07	18100
2 h	14.37	15.80	-	15.08	15080

[a]Polymerization conditions: Ni catalyst (0.5 μmol), $NaBAr^F_4$ (1 μmol), $Ni(COD)_2$ (4 μmol), 100 mL toluene, 450 psi ethylene at 30 °C for various times as indicated. Temperature controlled by manual external cooling when necessary.

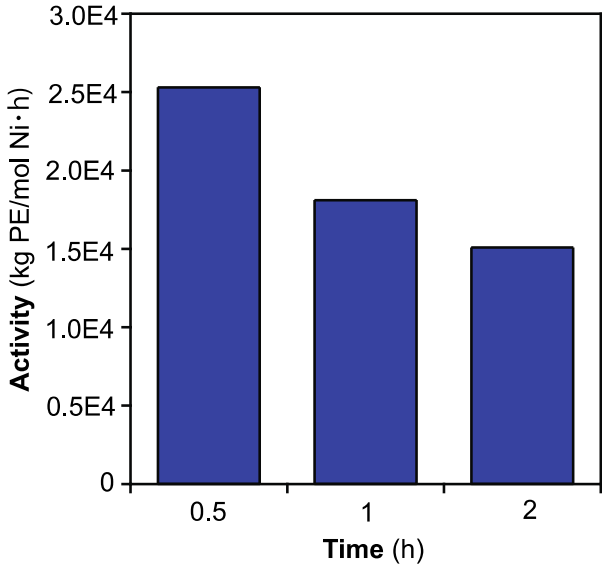


Figure S7. Activity vs. time plot of catalyst **Ni11**-Na in ethylene polymerization at optimal reaction conditions. The activity decreased gradually over the 2 h time course. Full data shown in Table S5.

Table S6. Temperature Study of Ethylene Polymerization by **Ni11**-Na at 150 psi[a]

Temperature (°C)	**Yield** (g)				**Activity** (kg PE/mol Ni·h)	M_n[b] ($\times 10^3$)	M_w/M_n[b]
	Run 1	Run 2	Run 3	Average			
RT	2.34	1.81	1.52	1.89	3780	1590	1.4
30	4.06	4.14	2.86	3.69	7380	1400	1.3
40	3.81	3.63	4.26	3.90	7800	1380	1.4
50	4.27	5.24	4.21	4.57	9140	850	1.6
60	2.52	3.86	3.14	3.17	6340	830	1.7

[a]Polymerization conditions: Ni catalyst (0.5 μmol), $NaBAr^F_4$ (1 μmol), $Ni(COD)_2$ (4 μmol), 100 mL toluene, 150 psi ethylene, 1 h at various temperatures. Temperature controlled by manual external cooling when necessary.
[b]Determined by GPC in trichlorobenzene at 150°C.

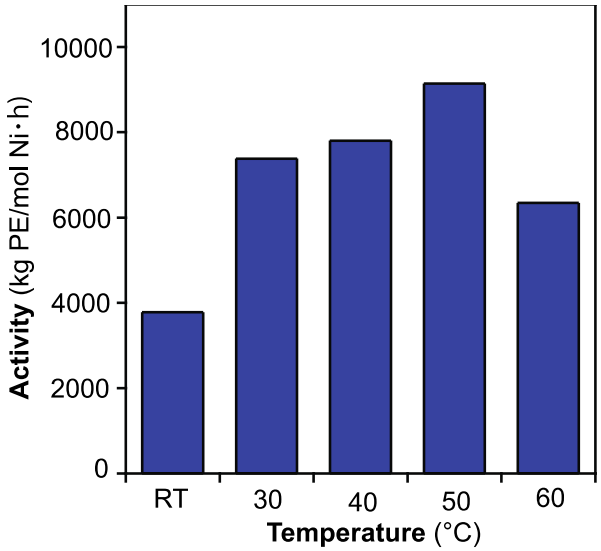


Figure S8. Activity vs. temperature plot of catalyst **Ni11**-Na in ethylene polymerization at 150 psi. The activity was optimal at ~50°C. Full data shown in Table S6.

Table S7. Temperature Study of Ethylene Polymerization by **Ni11**-Na at 450 psi[a]

Temperature (°C)	**Yield** (g)				**Activity** (kg PE/mol Ni·h)	M_n[b] ($\times 10^3$)	M_w/M_n[b]
	Run 1	Run 2	Run 3	Average			
RT	4.59	5.72	5.91	5.41	10800	1550	1.4
30	9.41	8.95	8.85	9.07	18100	1710	1.5
40	6.89	6.64	8.51	7.35	14700	1210	1.5
50	6.32	6.29	6.96	6.52	13000	1260	1.4
60	4.91	4.63	4.53	4.69	9380	1090	1.2

[a]Polymerization conditions: Ni catalyst (0.5 μmol), $NaBAr^F_4$ (1 μmol), $Ni(COD)_2$ (4 μmol), 100 mL toluene, 450 psi ethylene, 1 h at various temperatures. Temperature controlled by manual external cooling when necessary.
[b]Determined by GPC in trichlorobenzene at 150°C.

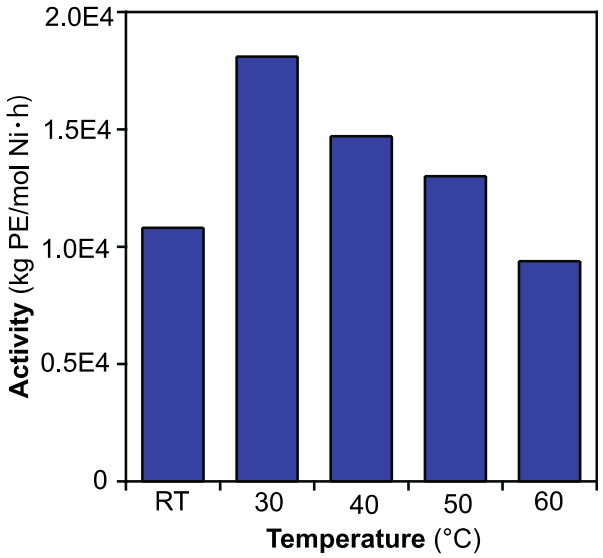


Figure S9. Activity vs. temperature plot of catalyst **Ni11**-Na in ethylene polymerization at 450 psi. The activity was optimal at ~30°C. Full data shown in Table S7.

Table S8. Time-Dependent Catalyst Activity of **Ni11**-Na (100 μM)[a]

Time (min)	**Temperature** (°C)	**Yield** (g)			**Activity** (kg PE/mol Ni·h)
		Run 1	Run 2	Average	
4	159	10.80	9.90	10.35	31050
60	29	10.97	11.70	11.34	2268

[a]Polymerization conditions: Ni catalyst (5.0 μmol), $NaBAr^F_4$ (10.0 μmol), $Ni(COD)_2$ (20.0 μmol), 50 mL toluene, 450 psi ethylene, start reaction at 20°C. Temperature *was not* controlled by manual external cooling.

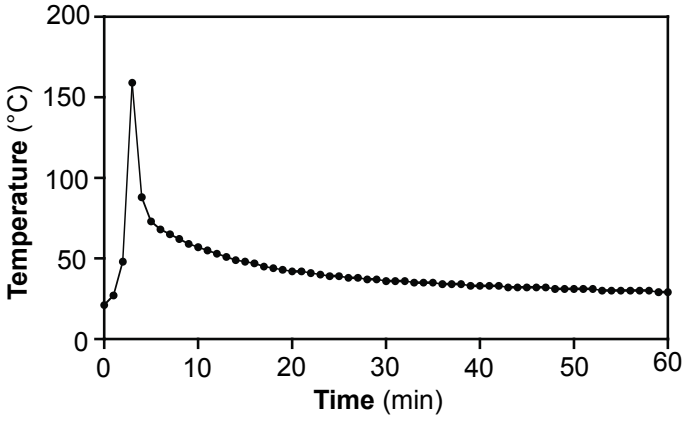


Figure S10. Temperature profile of ethylene polymerization (450 psi) by **Ni11**-Na (100 μM) over the course of 1 h. The temperature values represent the internal reactor temperatures and were recorded manually by reading the digital temperature gauge.

Table S9. Time-Dependent Catalyst Activity of **Ni11**-Na (50 μM)[a]

Time (min)	**Temperature** (°C)	**Yield** (g)			**Activity** (kg PE/mol Ni·h)
		Run 1	Run 2	Average	
4	60	5.60	6.30	5.95	17800
5	122	11.70	13.30	12.50	30000
5.5	110	13.70	14.90	14.30	31200
7	98	18.90	21.50	20.20	34630
60	35	20.70	18.80	19.75	3950

[a]Polymerization conditions: Ni catalyst (5.0 μmol), $NaBAr^F_4$ (10.0 μmol), $Ni(COD)_2$ (20.0 μmol), 100 mL toluene, 450 psi ethylene, start reaction at 20°C. Temperature *was not* controlled by manual external cooling.

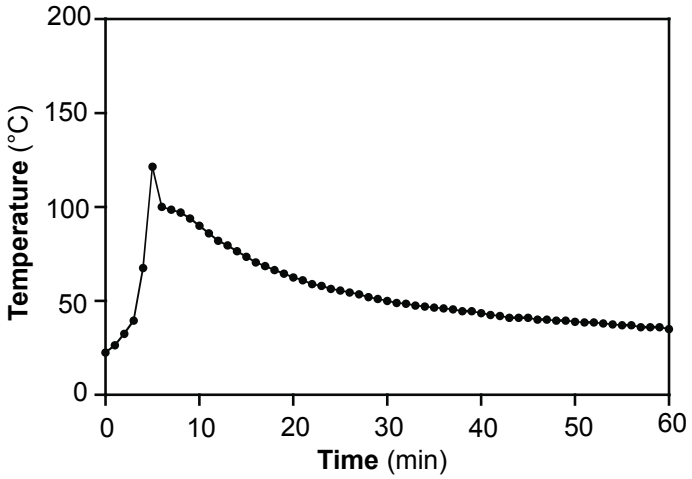
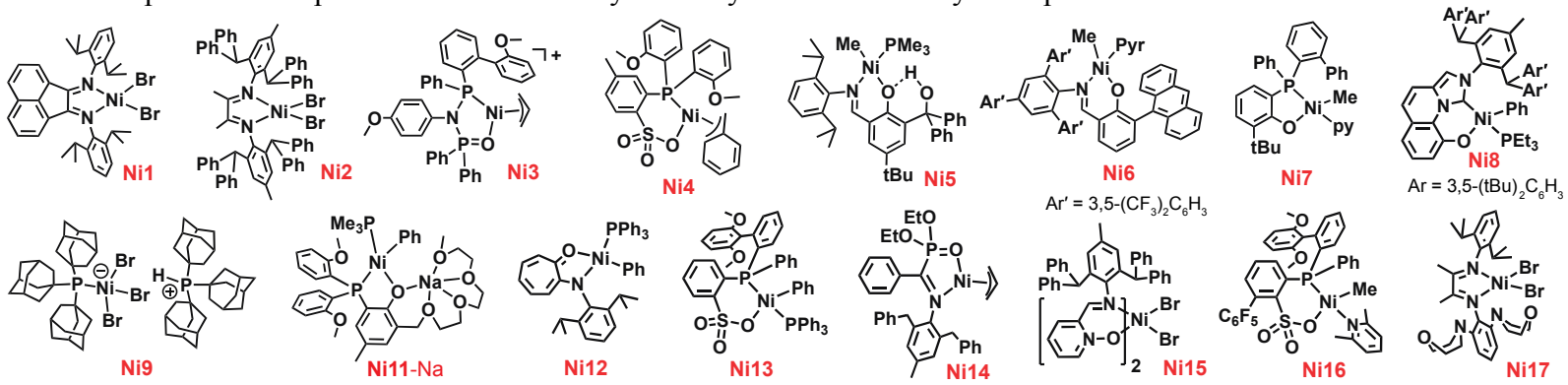


Figure S11. Temperature profile of ethylene polymerization (450 psi) by **Ni11**-Na (50 μM) over the course of 1 h. The temperature values represent the internal reactor temperatures and were recorded manually by reading the digital temperature gauge.

Table S10. Comparison of Representative Nickel Ethylene Polymerization Catalysts Reported in the Literature



Complex (conc.)	**C_2H_4 Pressure** (psi)	**Temp.** (°C)	**Time** (min)	**Activity** (kg PE/mol Ni·h)	**TON** (×10³ mol ethylene/ mol Ni)	***M*$_n$**	***M*$_w$/*M*$_n$**	**Reference** (Compound name in original reference)
Ni1 (0.83 μmol in 200 mL)	200	35	10	67200	400	337000	1.8	Brookhart (**4g**)[6]
Ni2 (1.57 μmol in 100 mL)	100	100	10	2856	17	422000	1.2	Long (**2b**)[7]
Ni3 (5.00 μmol in 20 mL)	118	25	60	260	9	188900	2.5	Chen (**Ni4**)[8]
Ni4 (20.0 μmol in 30 mL)	300	25	120	163	12	1500		Jordan (**4a**)[9]
Ni5 (10.0 μmol in 25 mL)	118	25	40	1184	28	6700	1.8	Marks (**1b**)[10]
Ni6 (5.00 μmol in 100 mL)	580	30	40	1218	29	466100	1.6	Mecking (**2-CF_3/Py**)[11]
Ni7 (5.00 μmol in 100 mL)	145	30	20	2100	25	398000	1.5	Li (**2c**)[12]
Ni8 (2.5 μmol in 8.5 mL)	580	30	30	1000	18	84000	2.0	Nozaki (**7c**)[13]
Ni9 (0.50 μmol in 150 mL)	400	10	3.5	103600	216	1390000	1.4	Daugulis/Brookhart (**6**)[14]
Ni11-Na (0.50 μmol in 100 mL)	450	30	60	18100	646	1710	1.5	This work
Ni12 (7.6 μmol in 200 mL)	400	80	60	1500	54	119000	1.8	Brookhart (**3**)[15]
Ni13 (10 μmol in 80 mL)	400	90	20	7028	84	10000	2.2	Scott (**3b**)[16]
Ni14 (10 μmol in 20 mL)	118	60	60	540	19	2800	2.4	Chen (**Ni2-Ar***)[17]
Ni15 (1 μmol in 20 mL)	118	20	30	11700	209	4000	2.2	Chen (**Ni-Ph**)[18]
Ni16 (2 μmol in 50 mL)	118	80	30	4500	80	4700	2.7	Chen (**4**)[19]
Ni17 (2 μmol in 50 mL)	118	RT	180	2000	214	6500	2.6	Chen (**NO-*i*Pr-Ni**) [20]

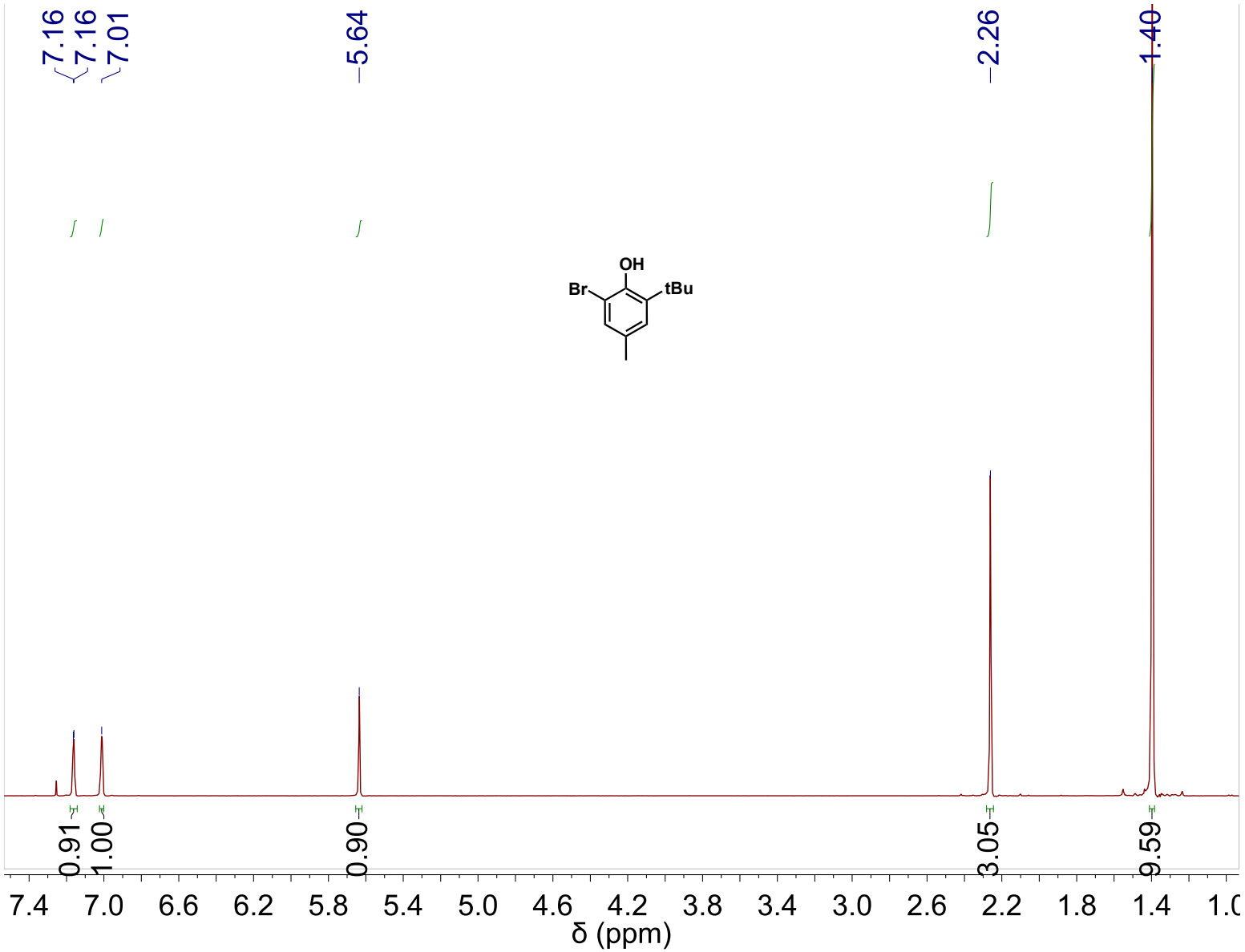


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **2**.

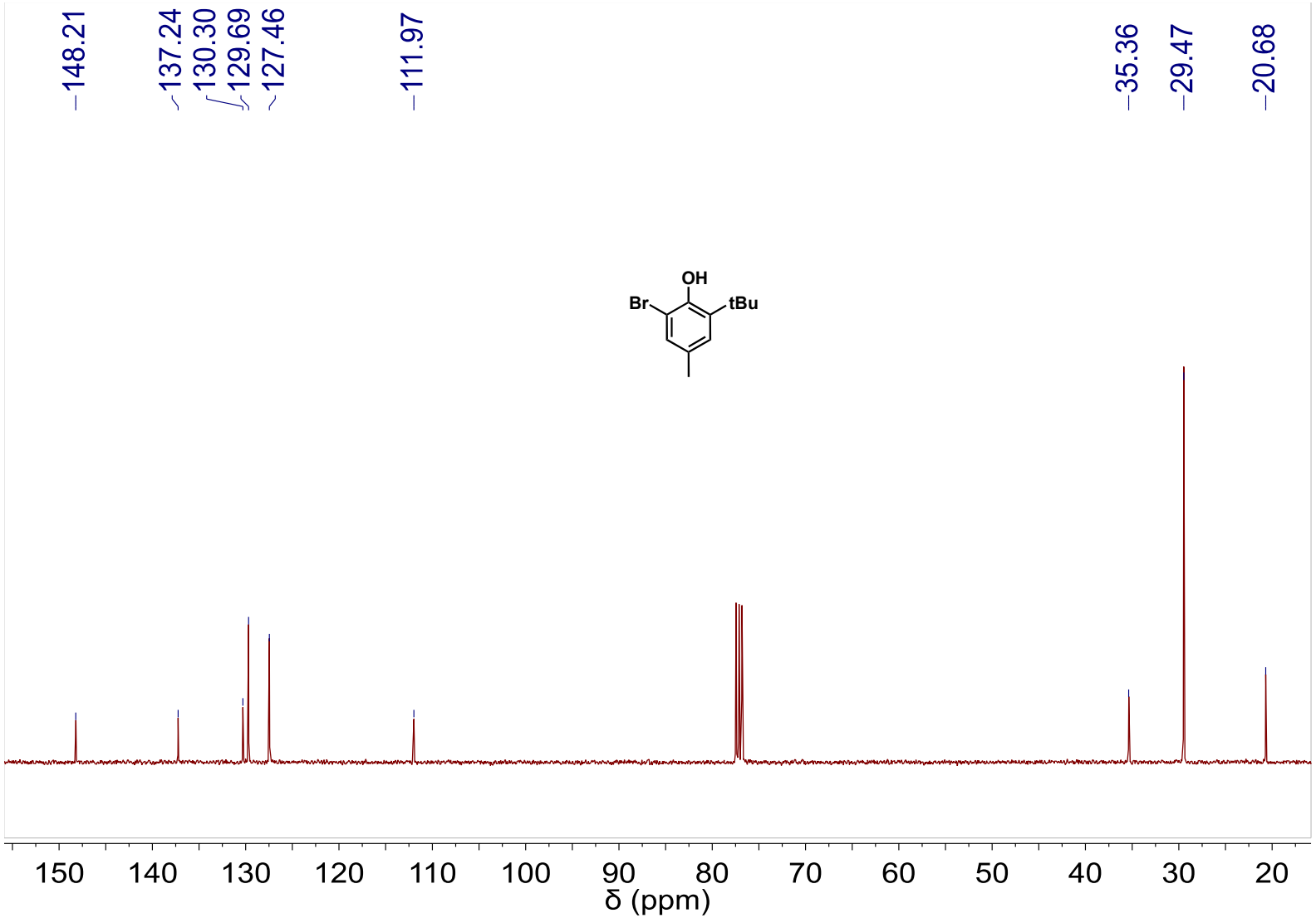


Figure S13. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **2**.

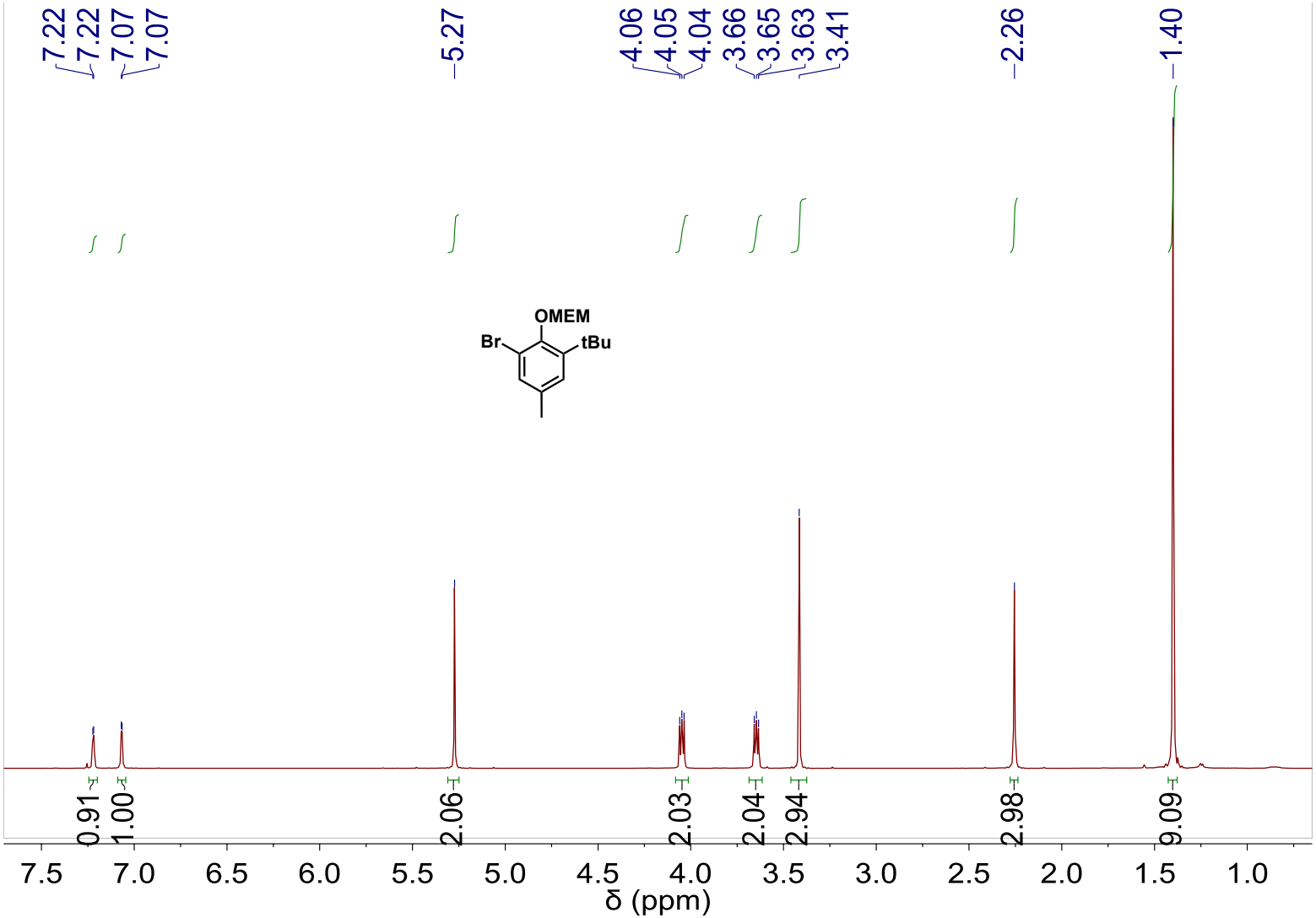


Figure S14. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **3**.

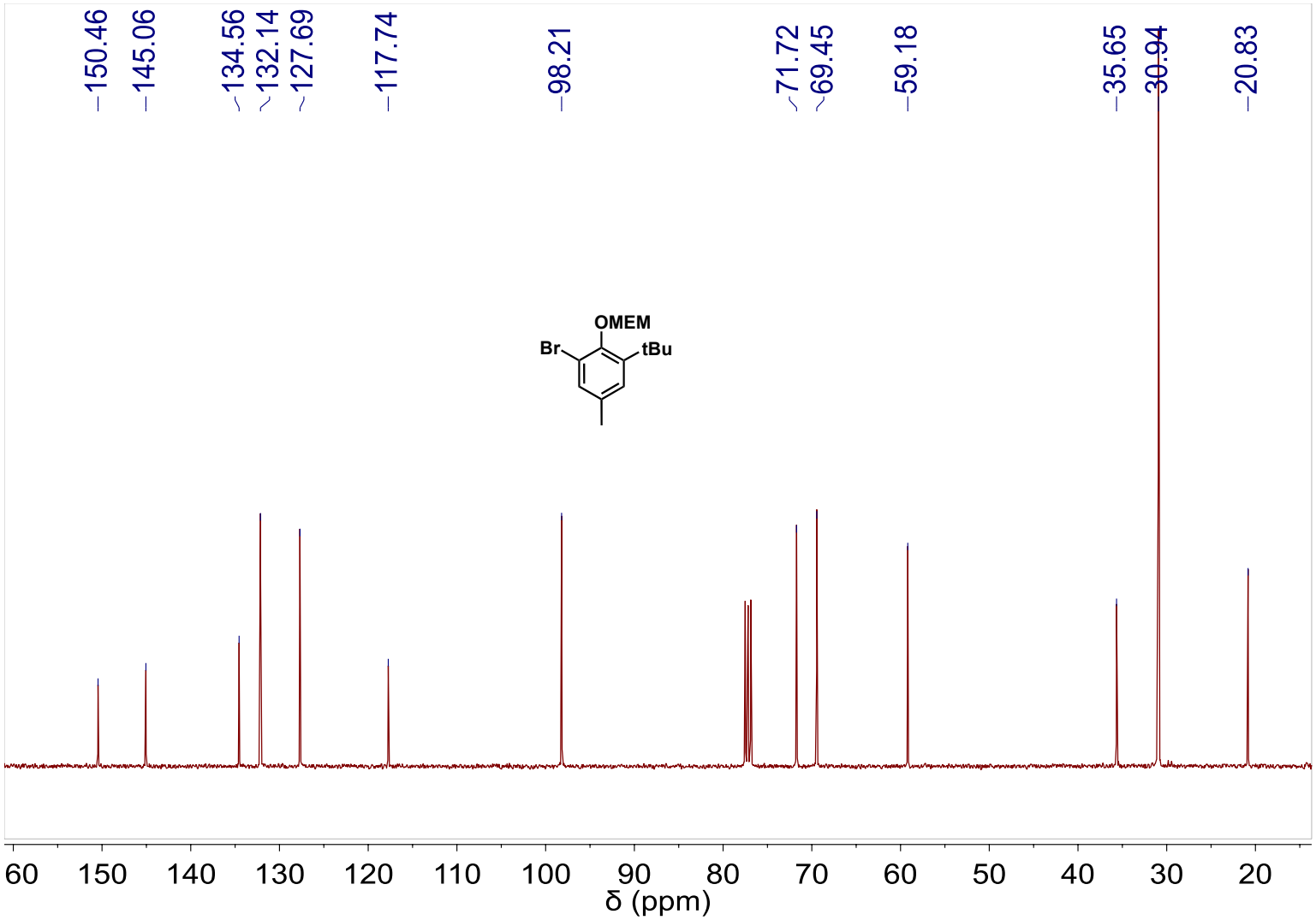


Figure S15. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **3**.

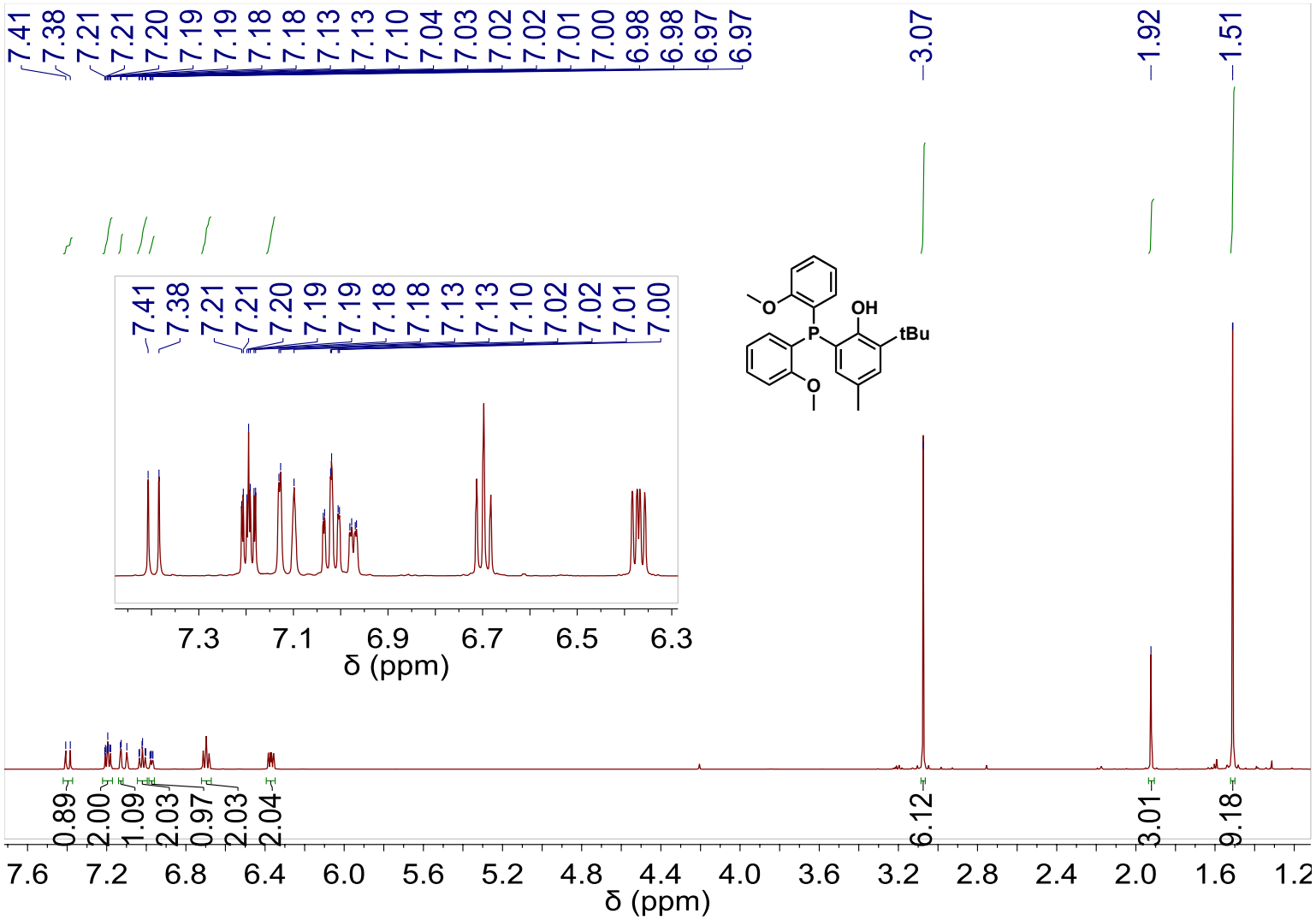


Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **5**.

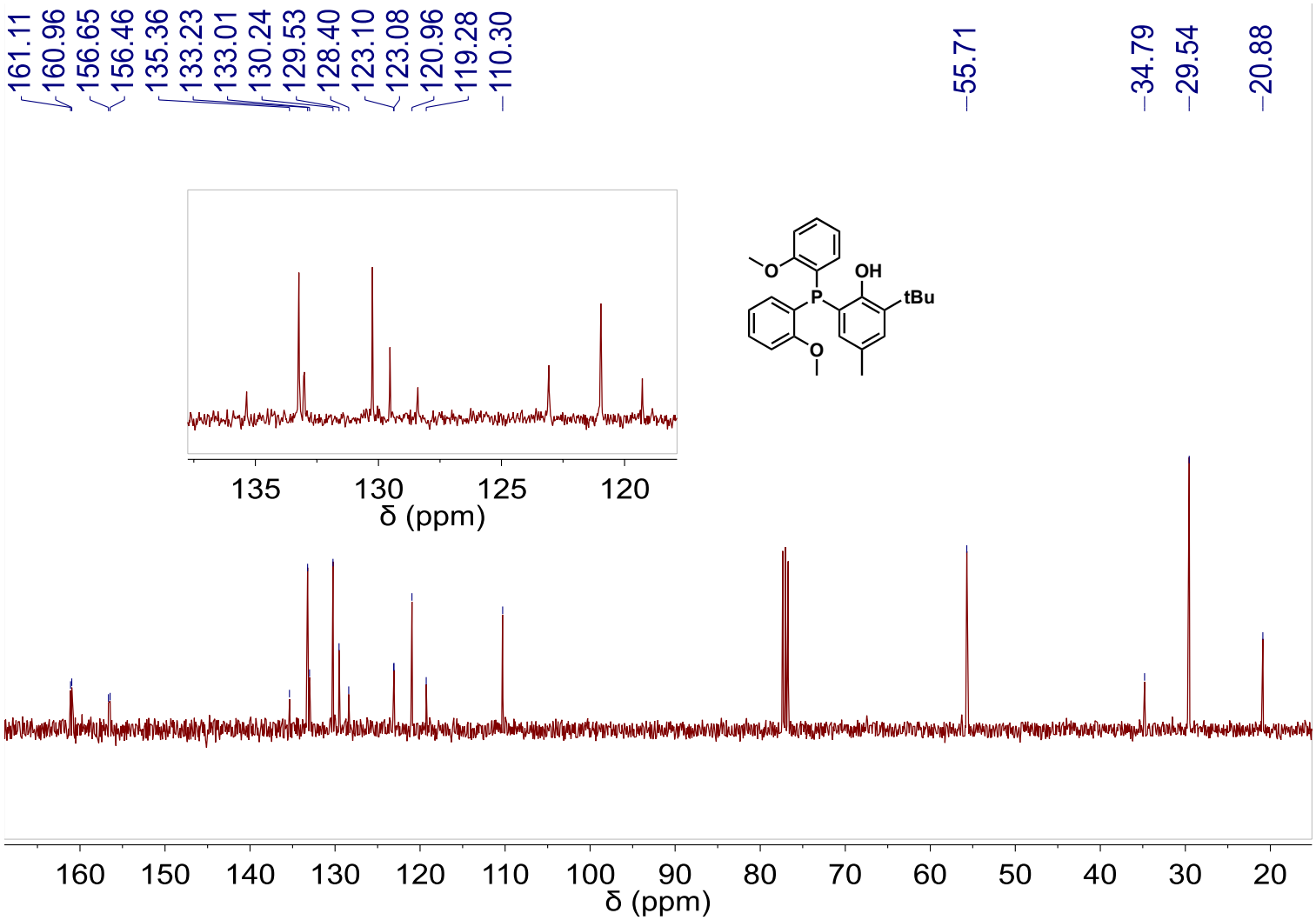


Figure S17. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of compound **5**.

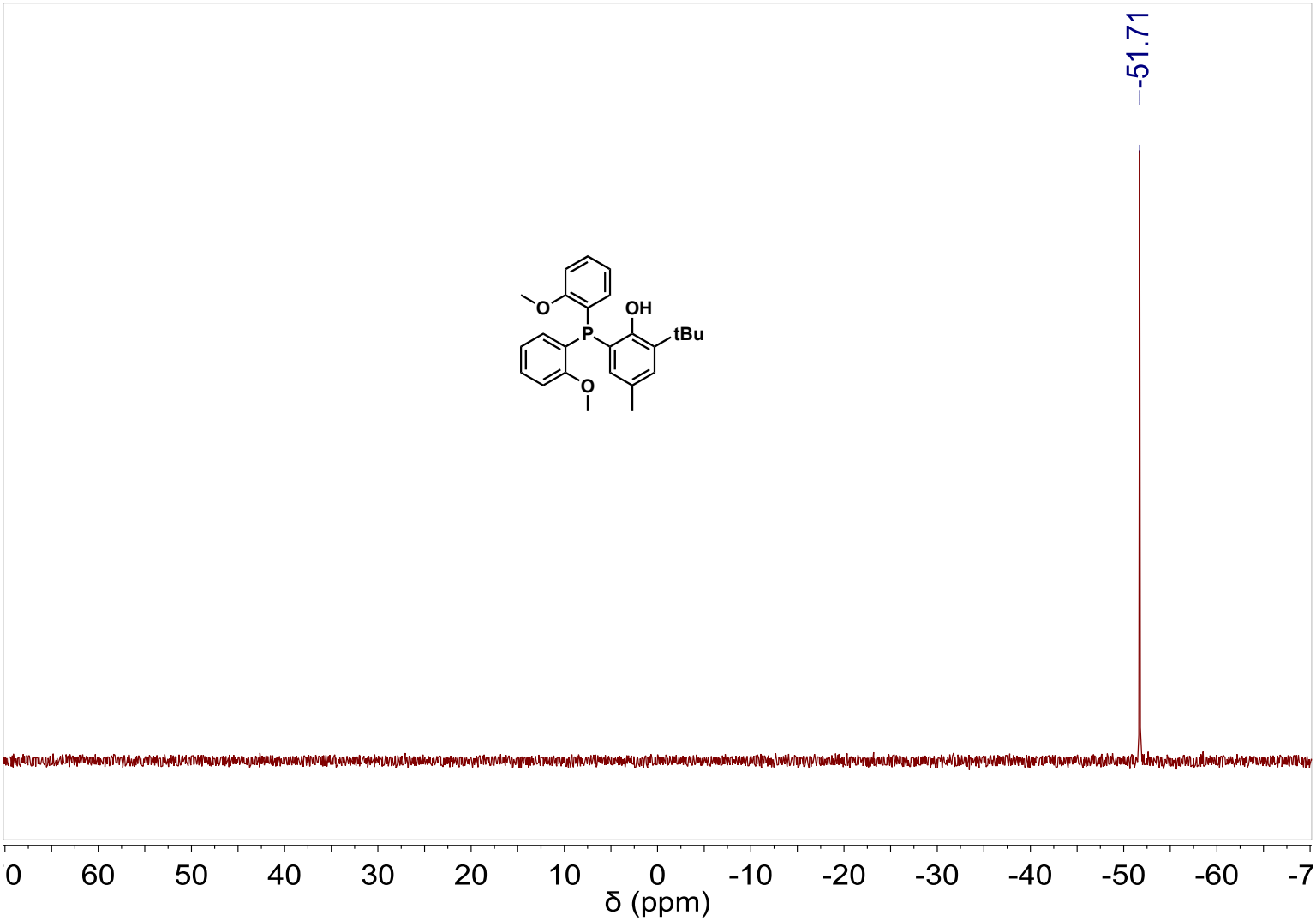


Figure S18. ^{31}P NMR spectrum ($CDCl_3$, 202 MHz) of compound **5**.

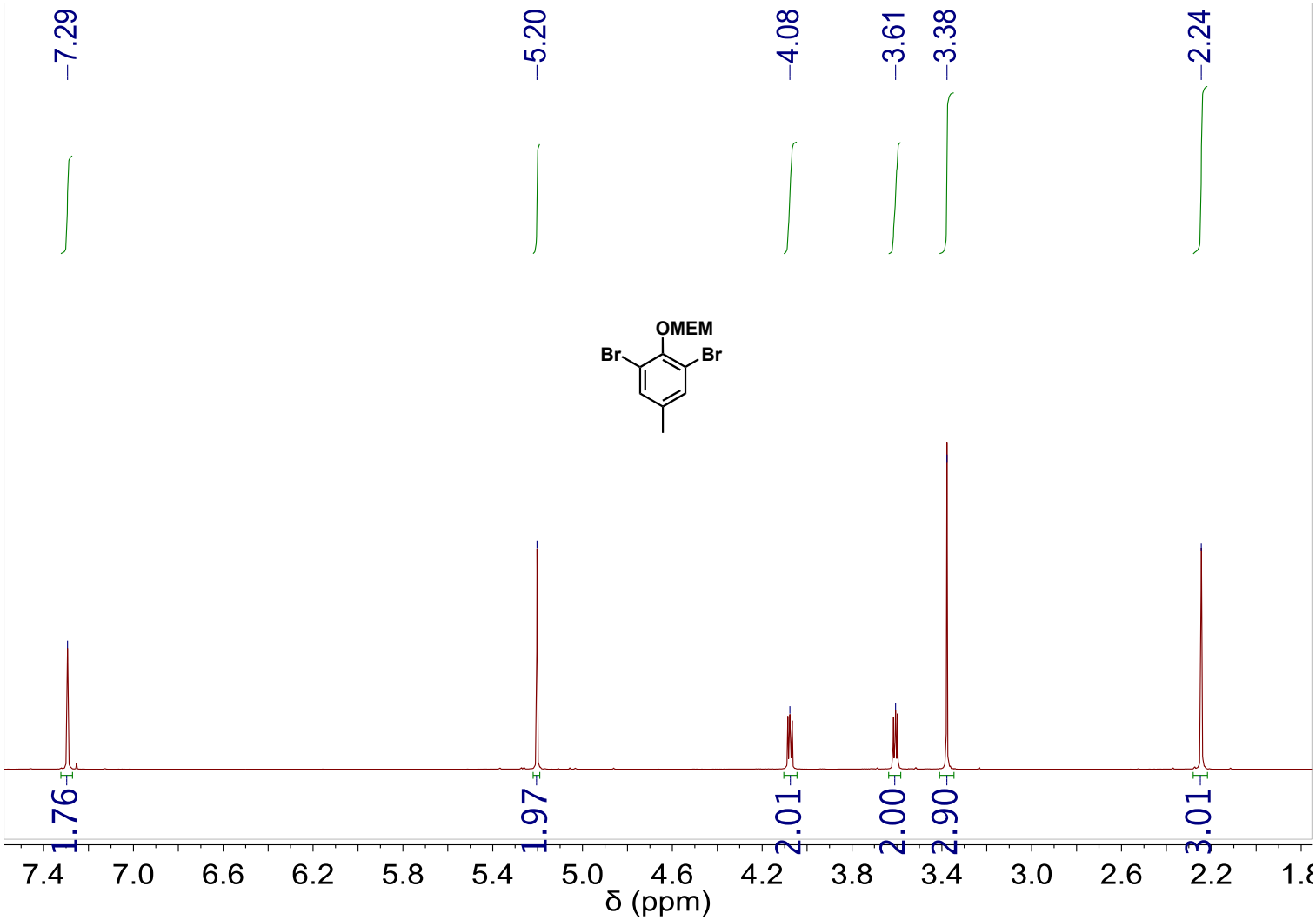


Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **7**.

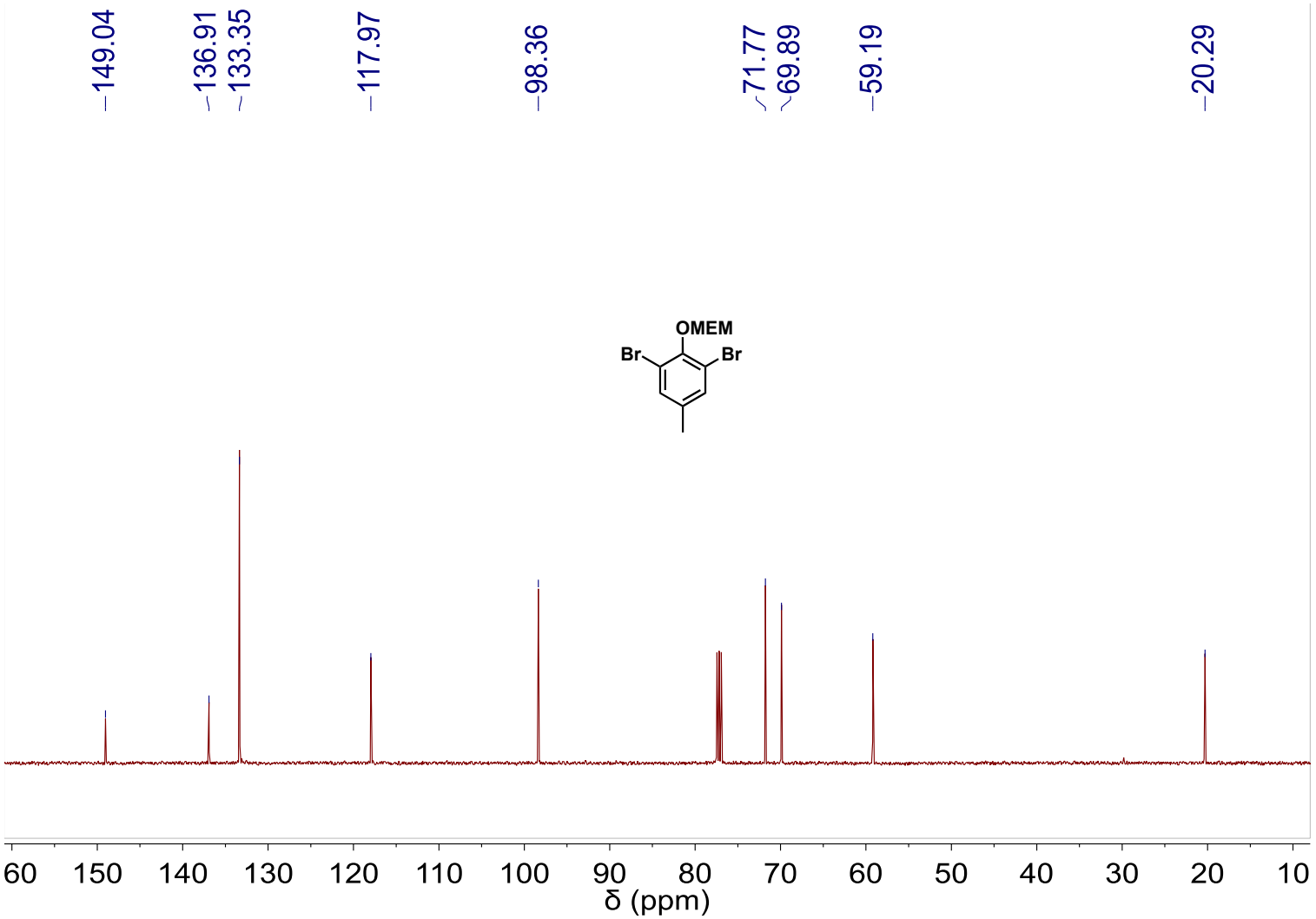


Figure S20. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of compound **7**.

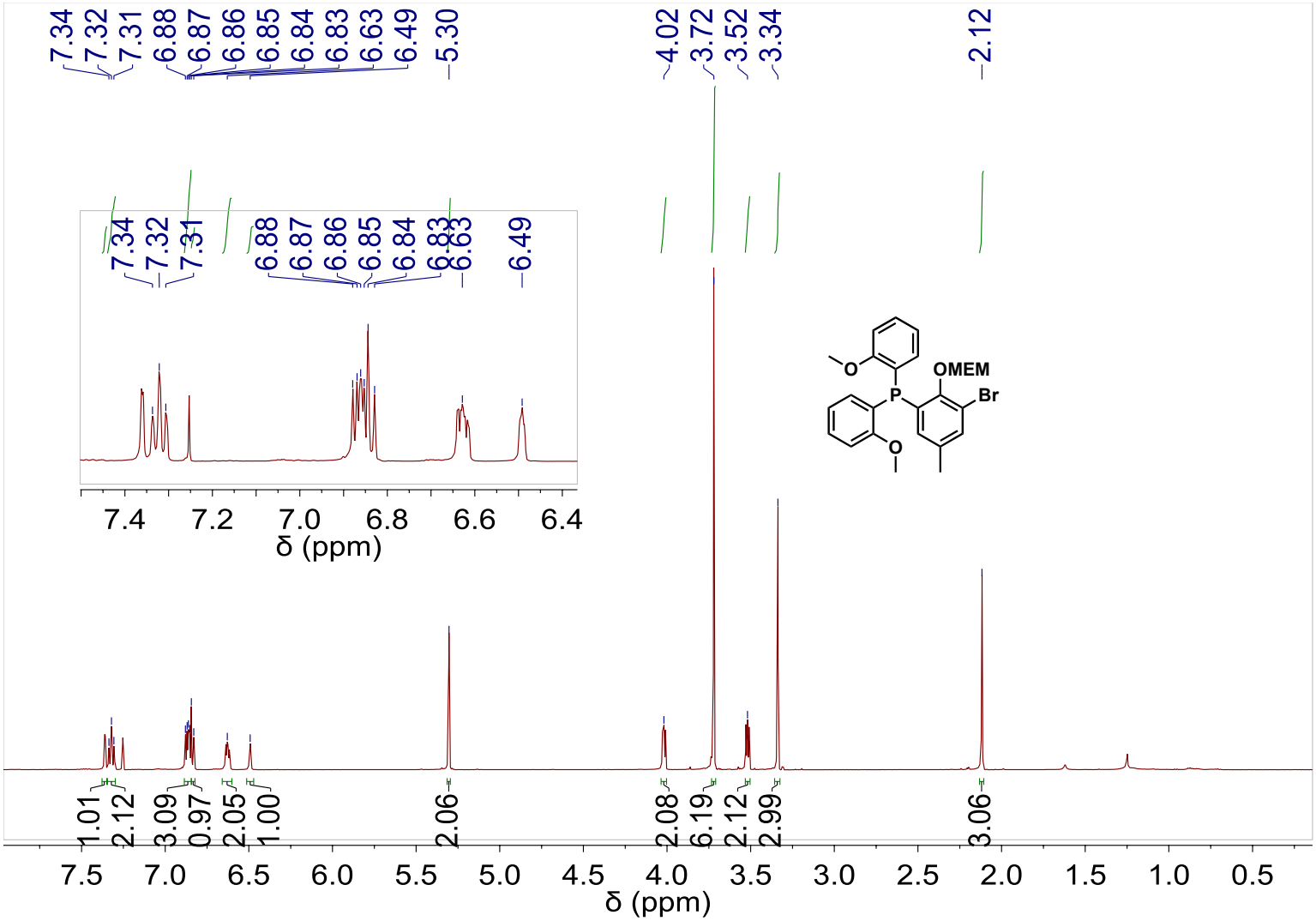


Figure S21. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **8**.

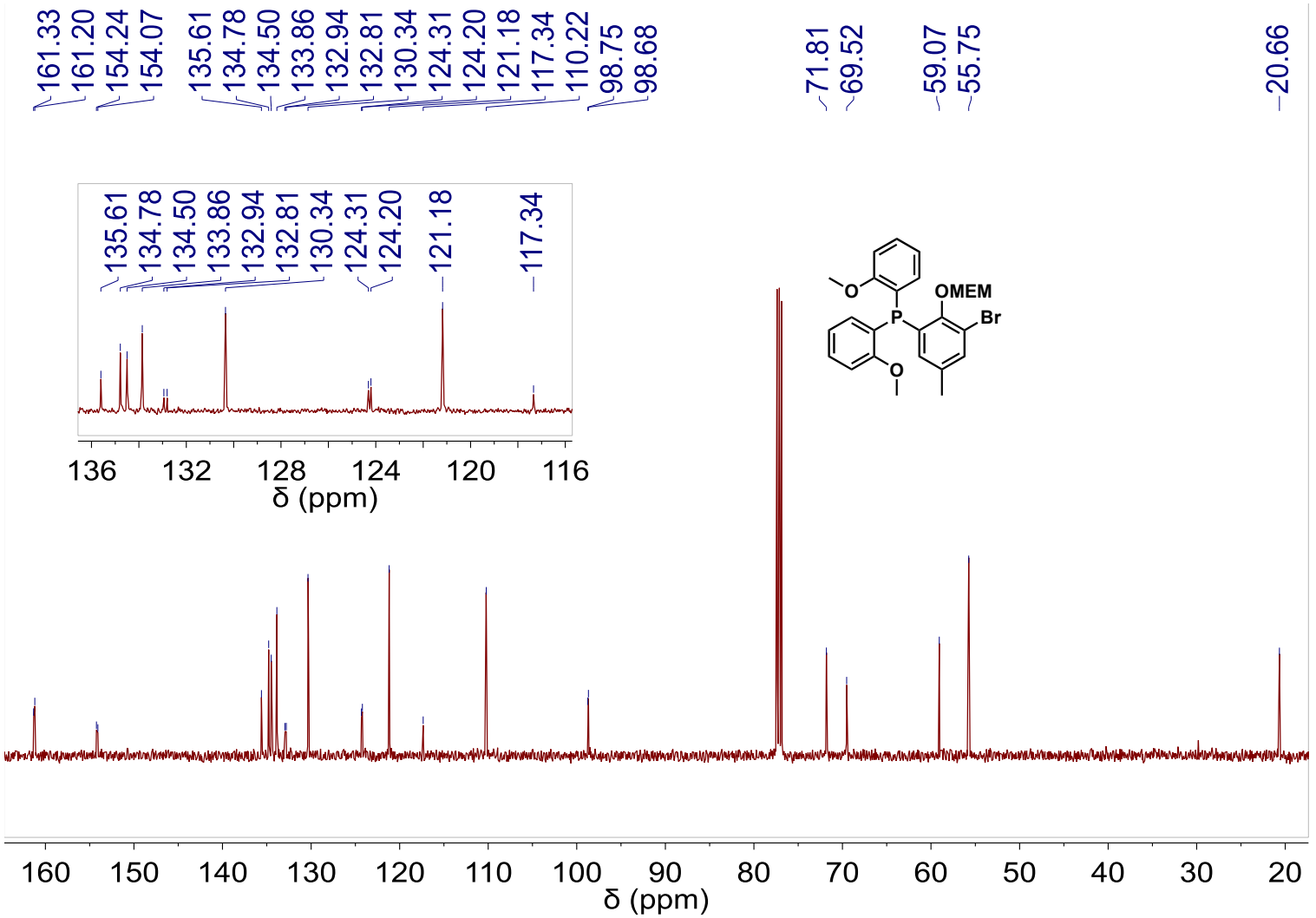


Figure S22. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of compound **8**.

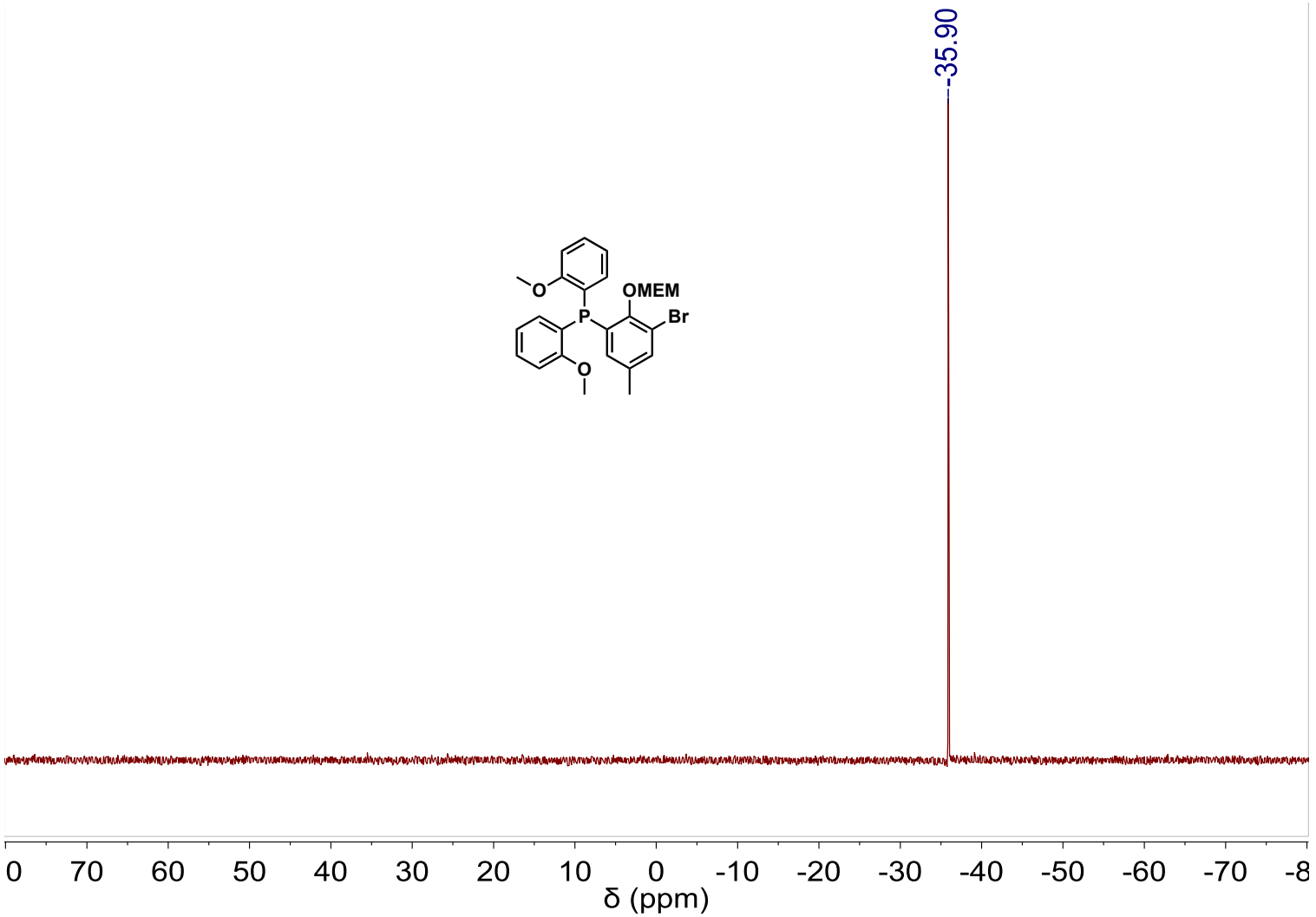


Figure S23. ^{31}P NMR spectrum ($CDCl_3$, 202 MHz) of compound **8**.

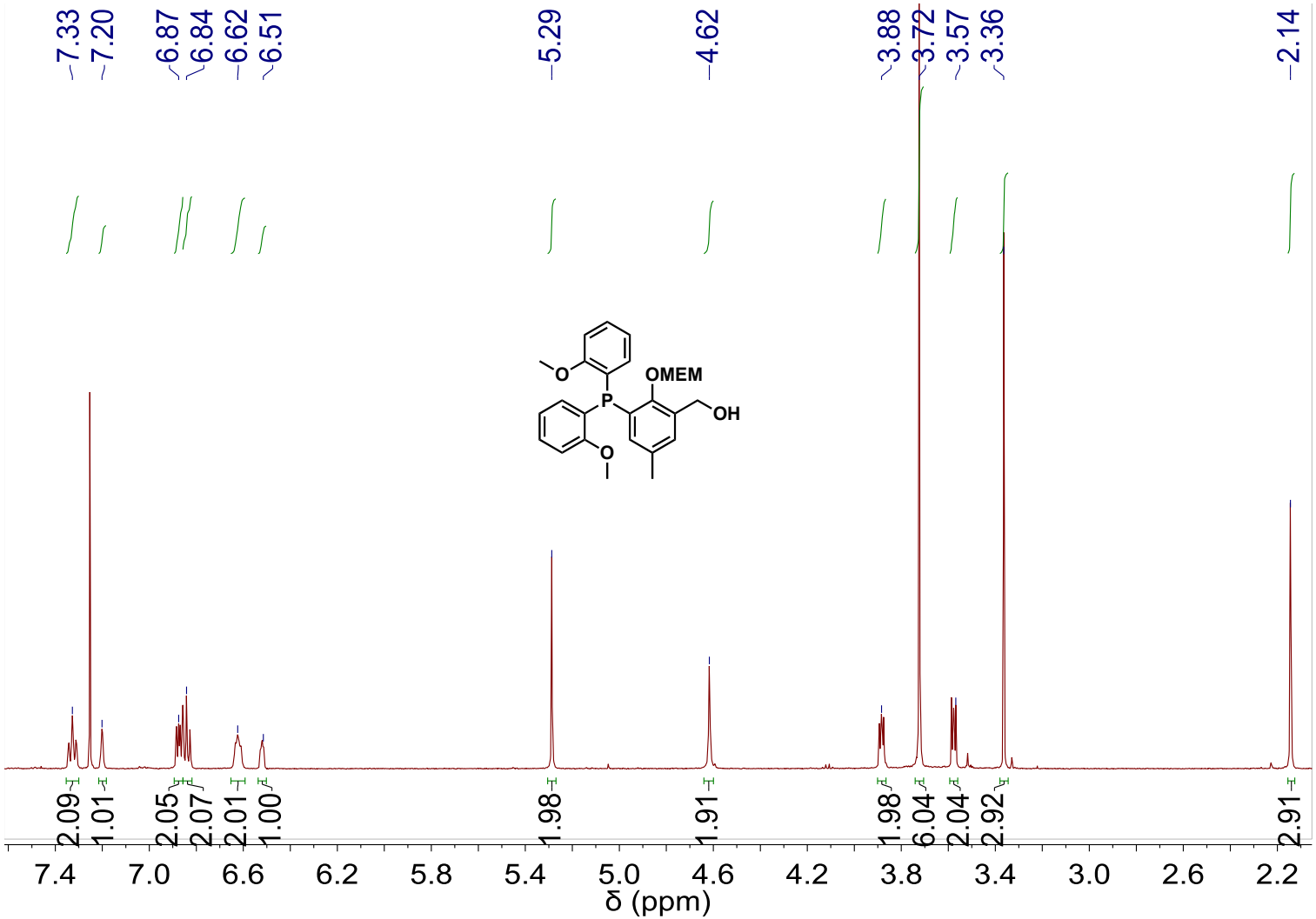


Figure S24. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **10**.

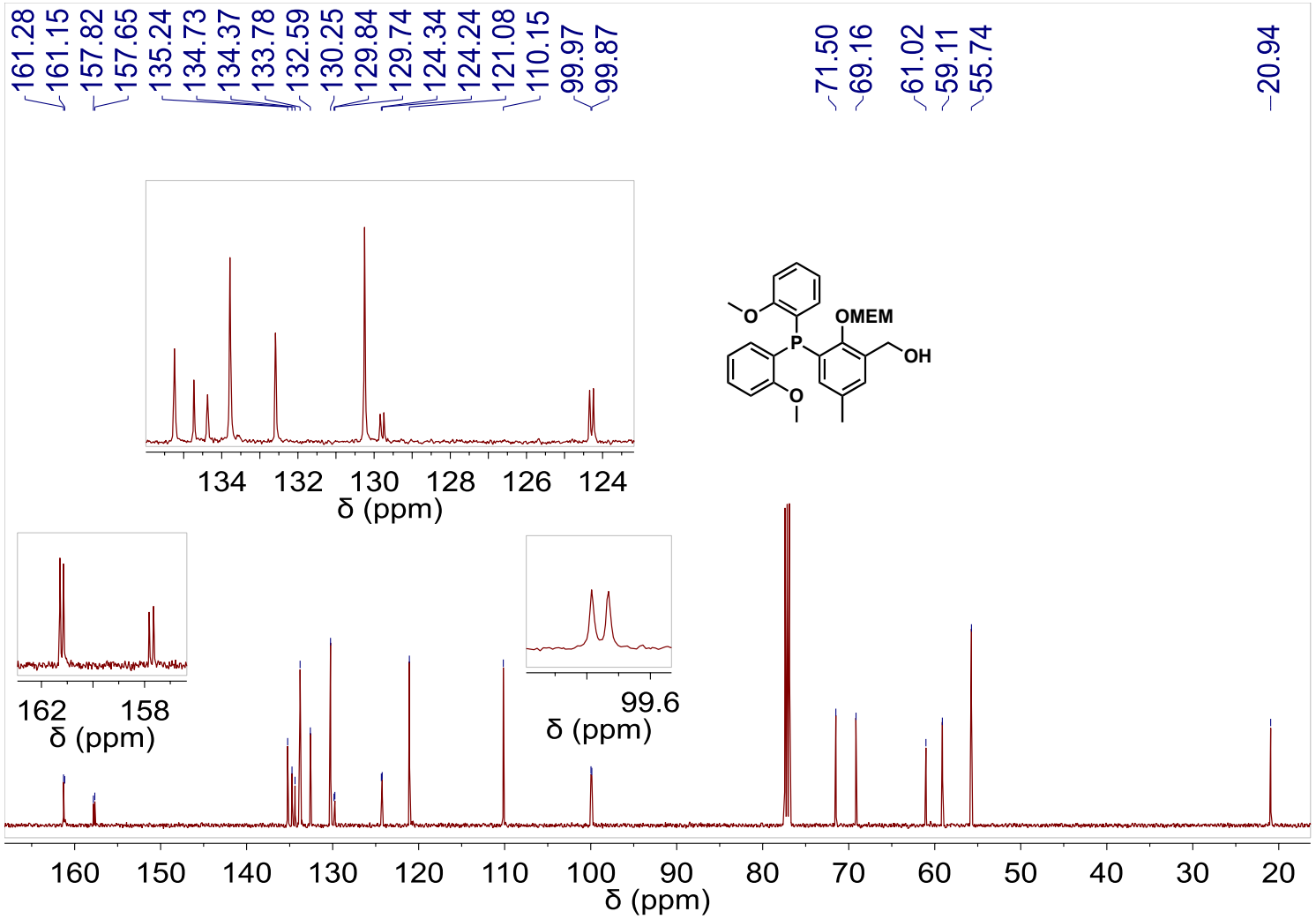


Figure S25. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of compound **10**.

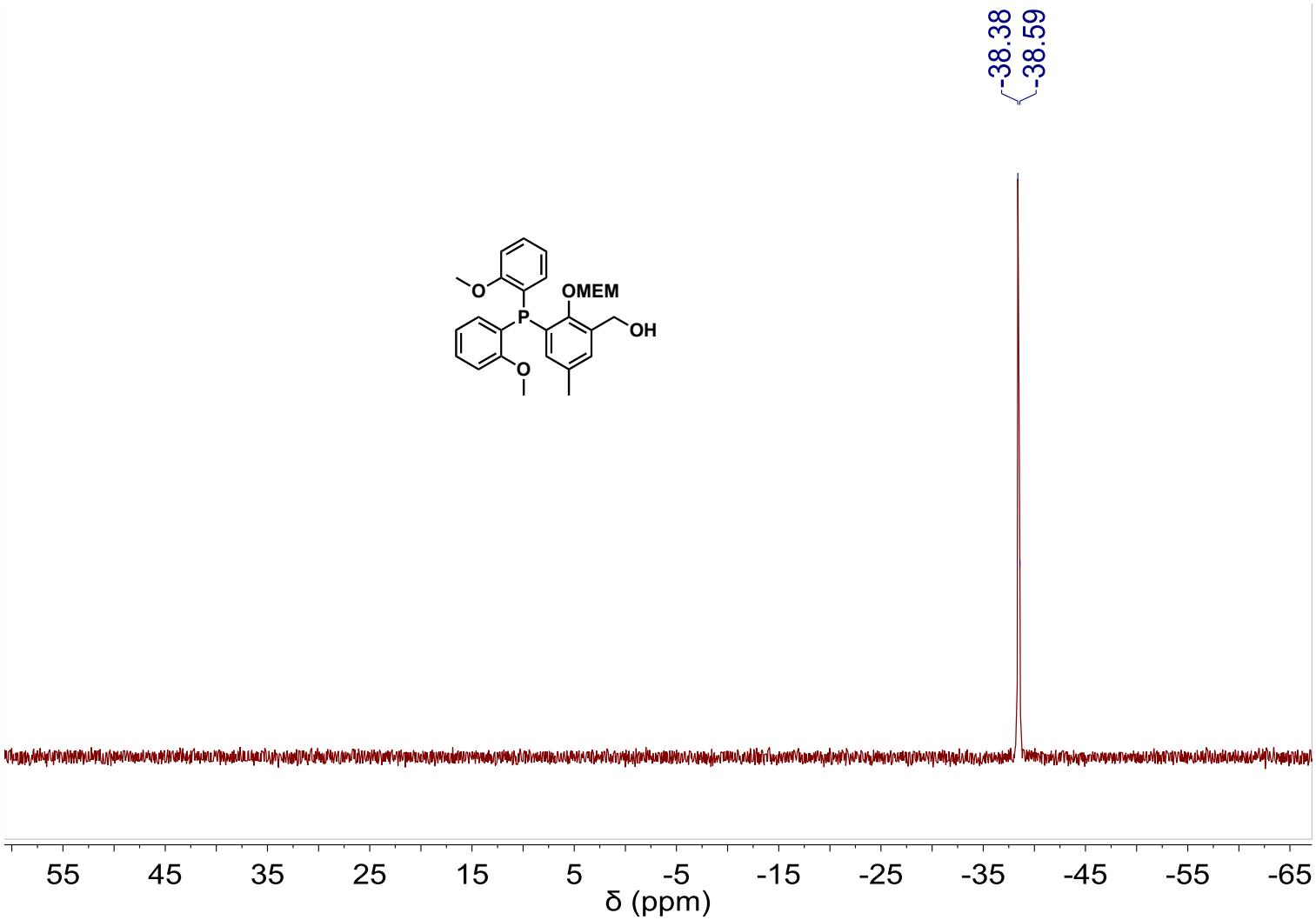


Figure S26. ^{31}P NMR spectrum ($CDCl_3$, 202 MHz) of compound **10**.

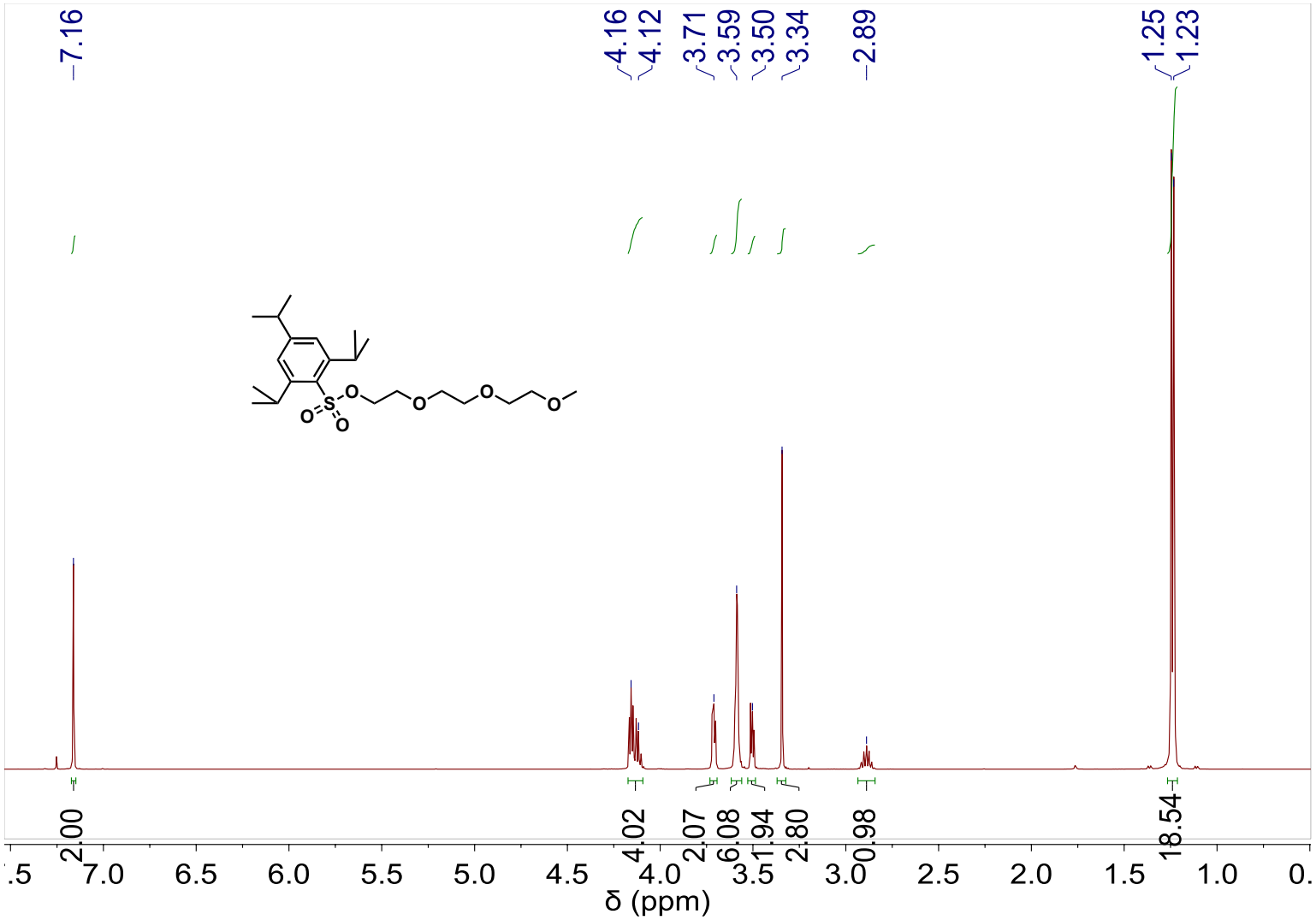


Figure S27. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **11**.

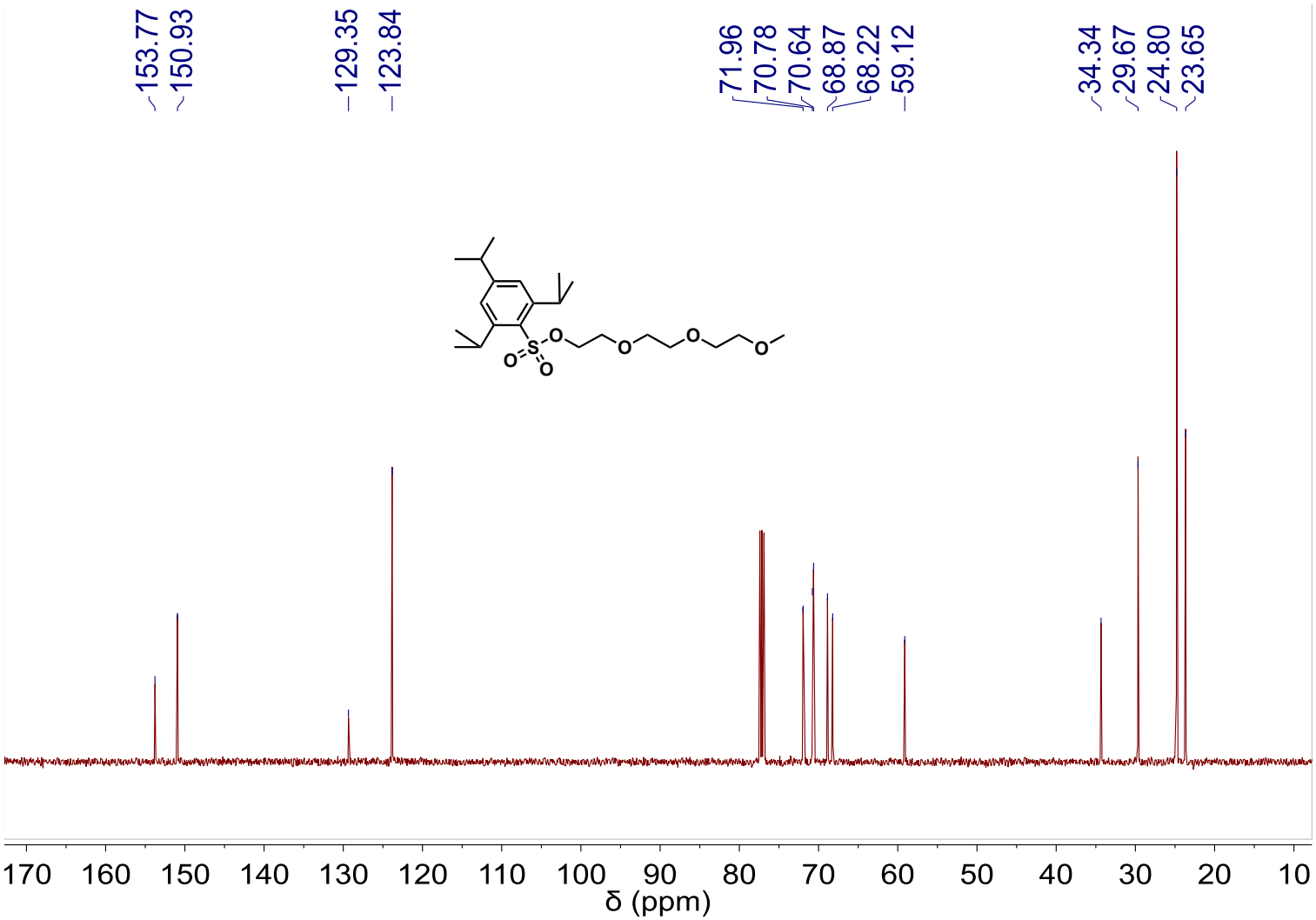


Figure S28. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of compound **11**.

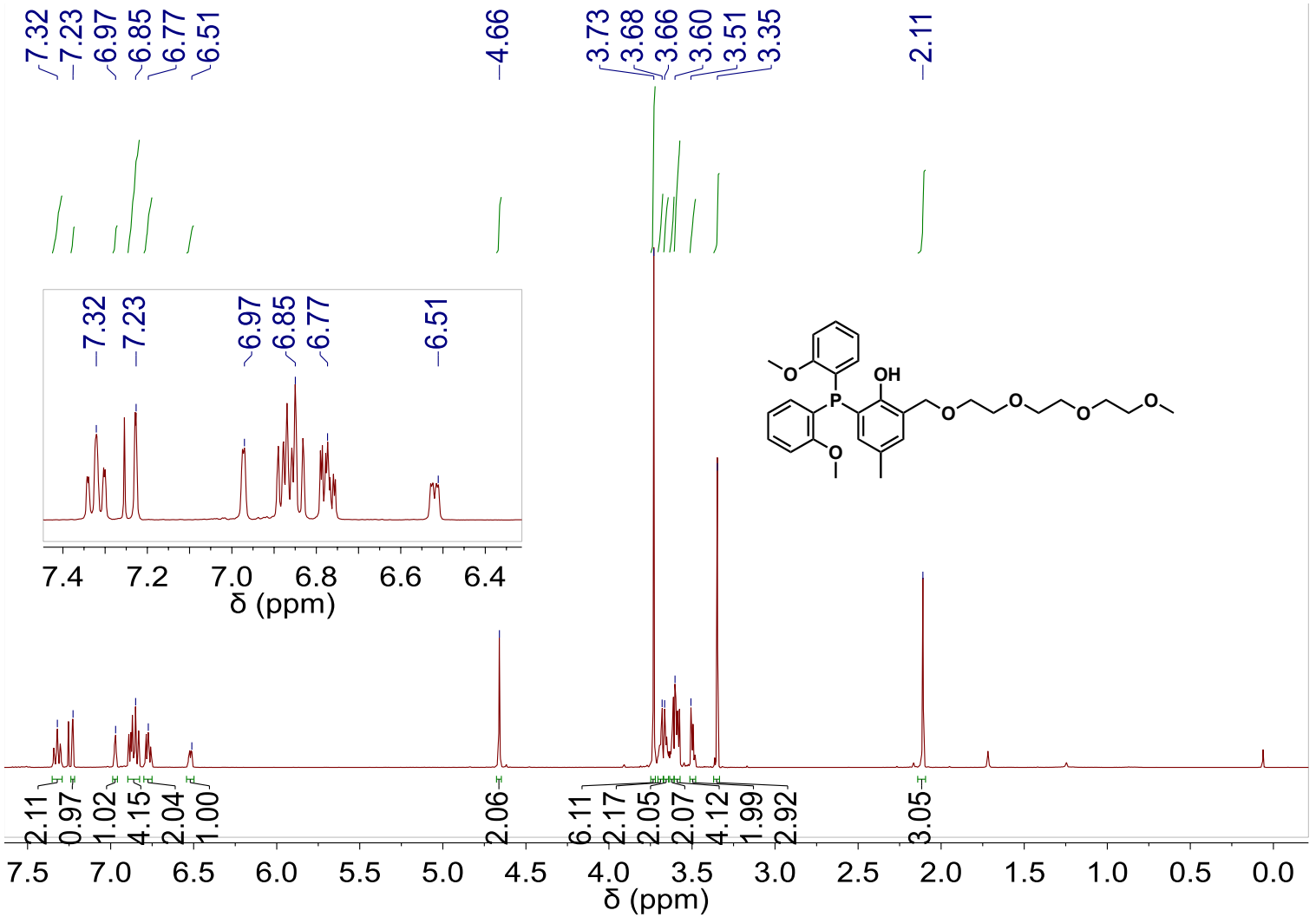


Figure S29. ^{1}H NMR spectrum ($CDCl_3$, 126 MHz) of compound **13**.

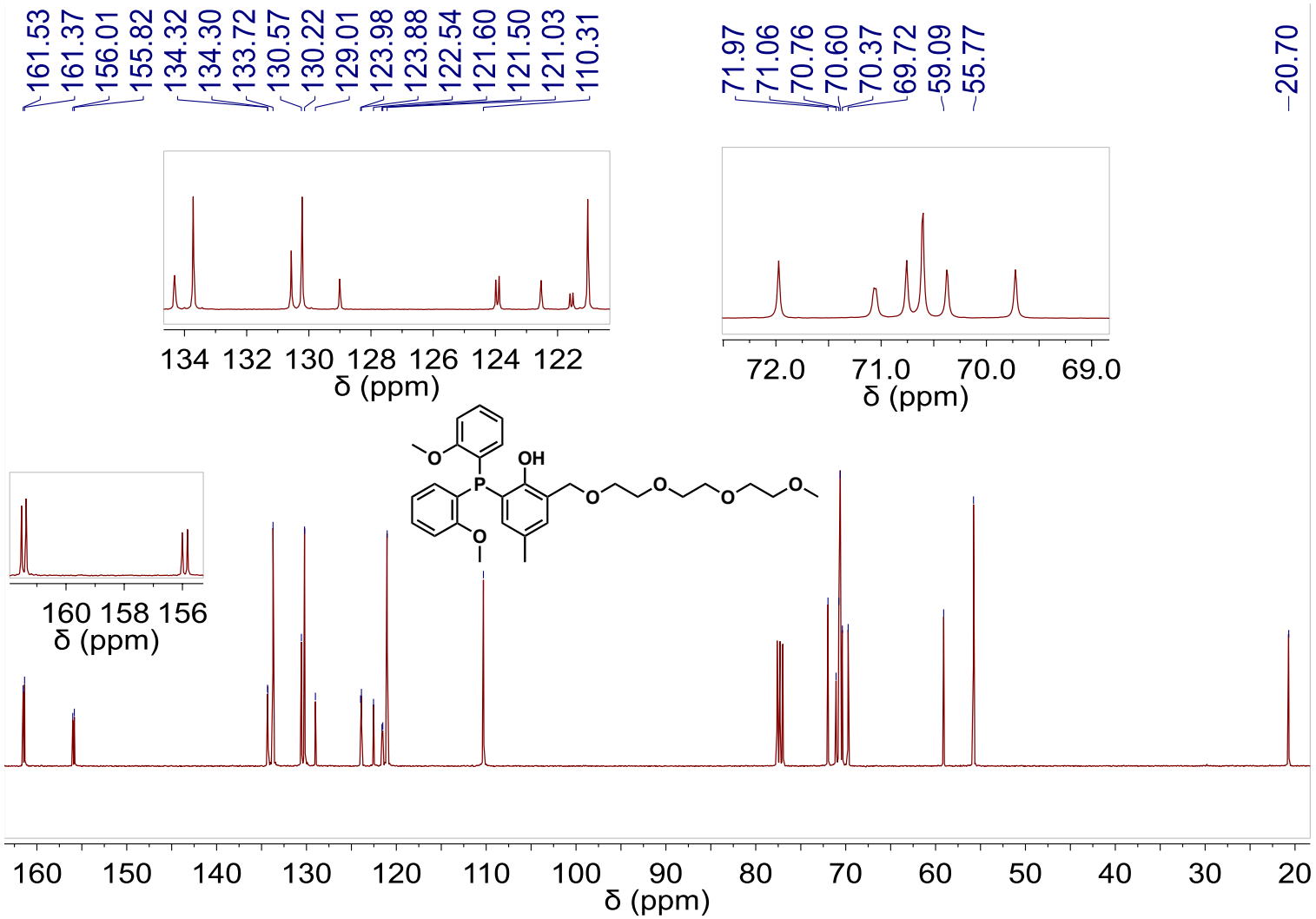


Figure S30. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of compound **13**.

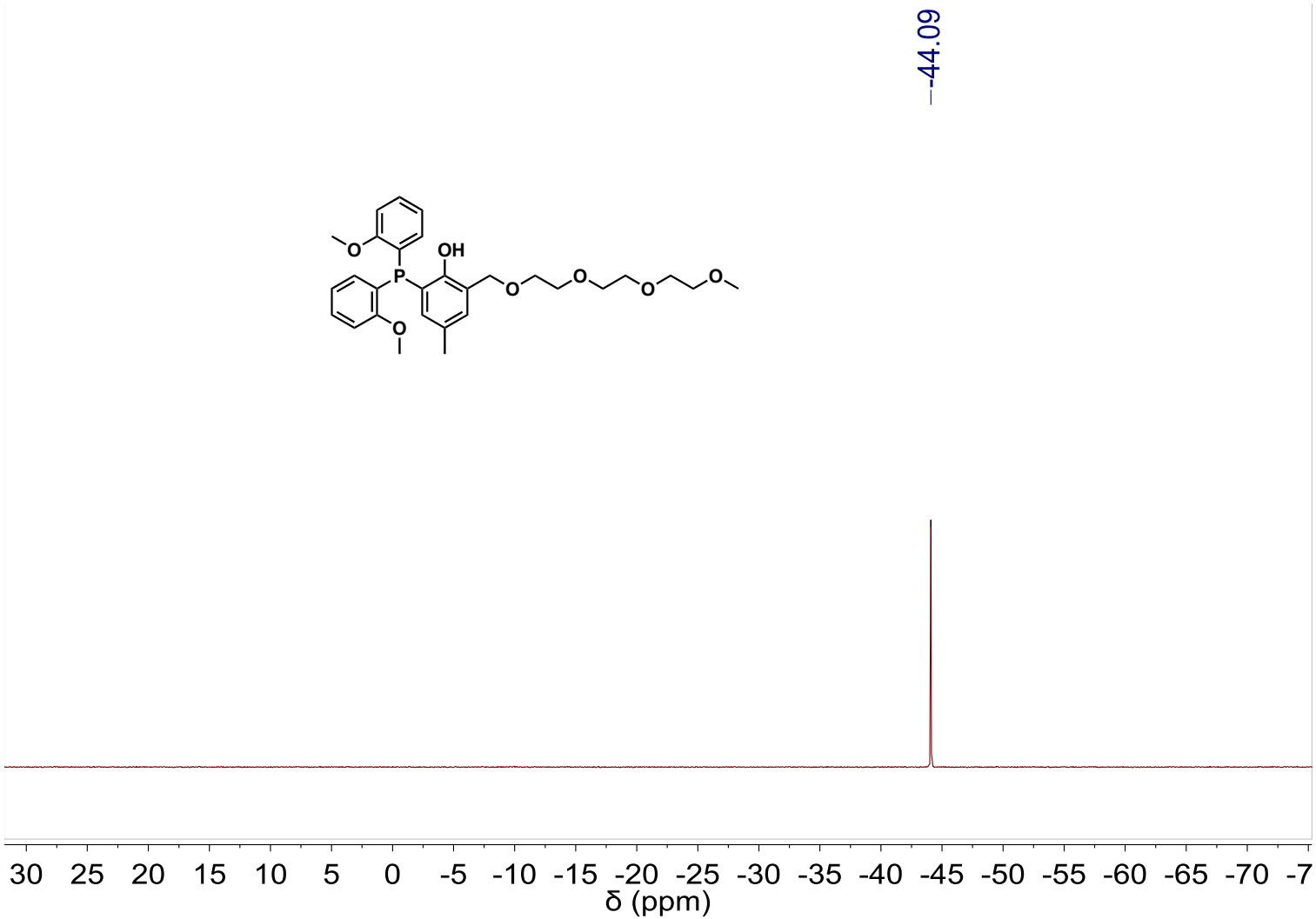


Figure S31. ^{31}P NMR spectrum ($CDCl_3$, 162 MHz) of compound **13**.

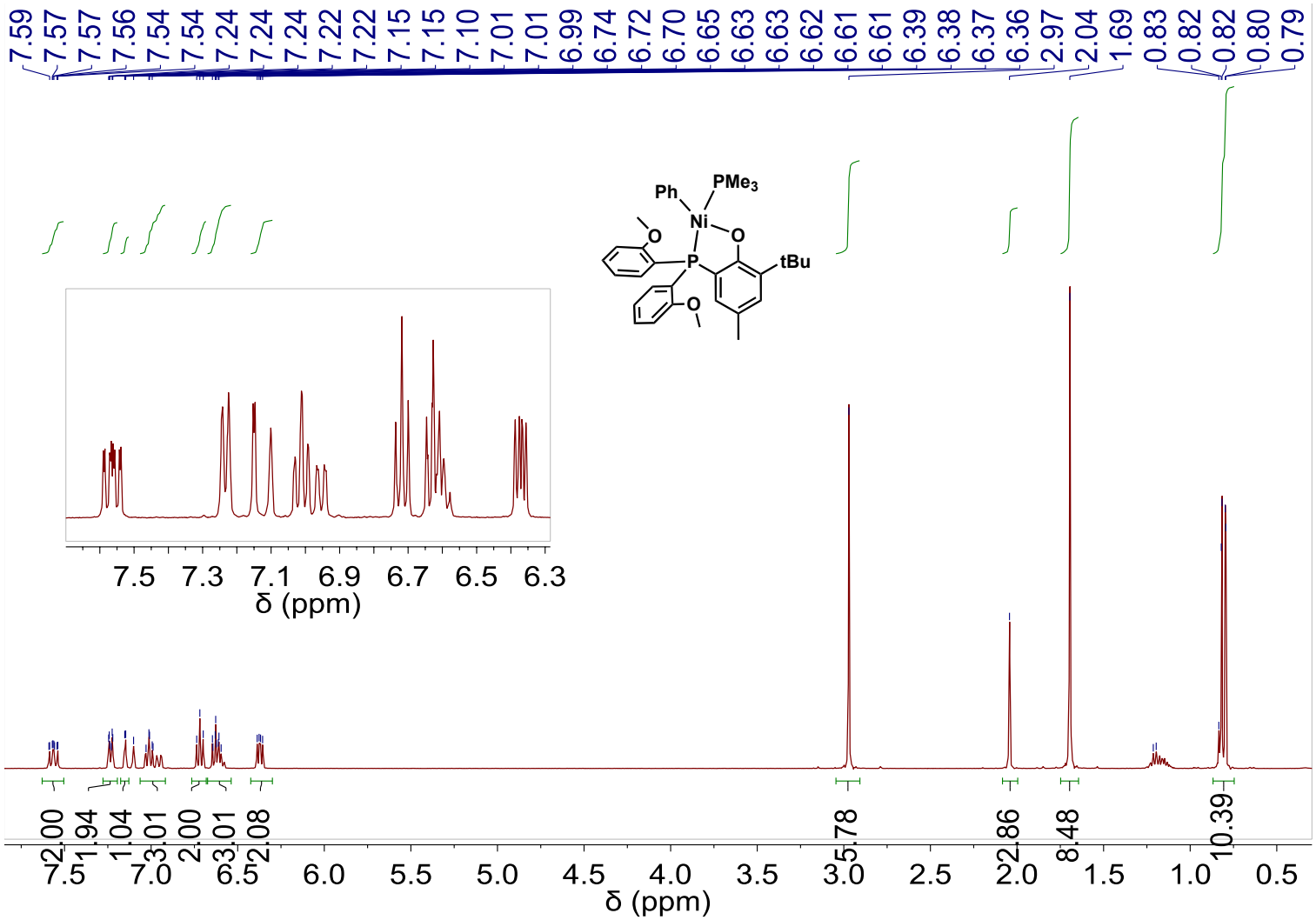


Figure S32. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of complex **Ni10**.

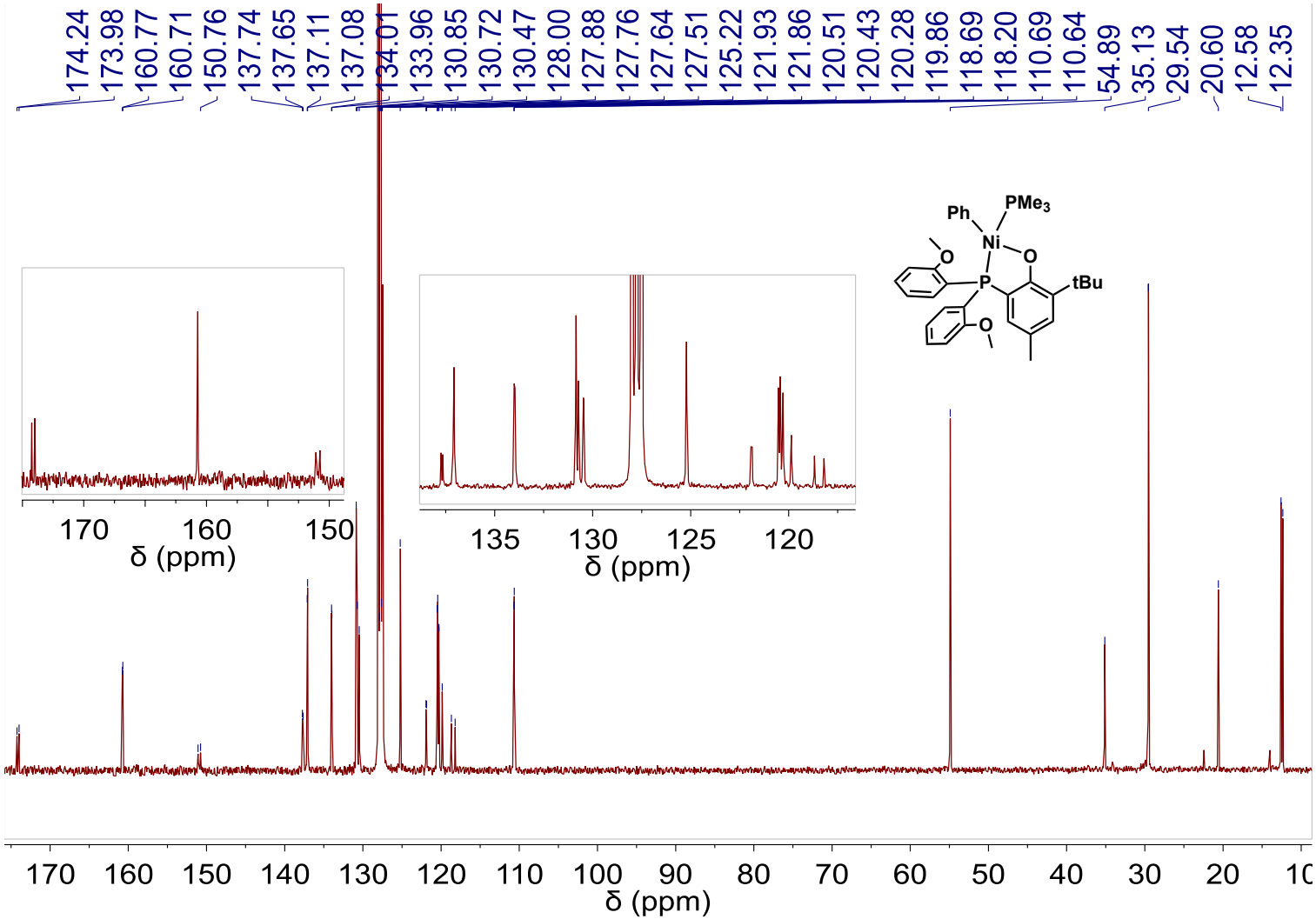


Figure S33. ^{13}C NMR spectrum (C_6D_6, 100 MHz) of complex **Ni10**.

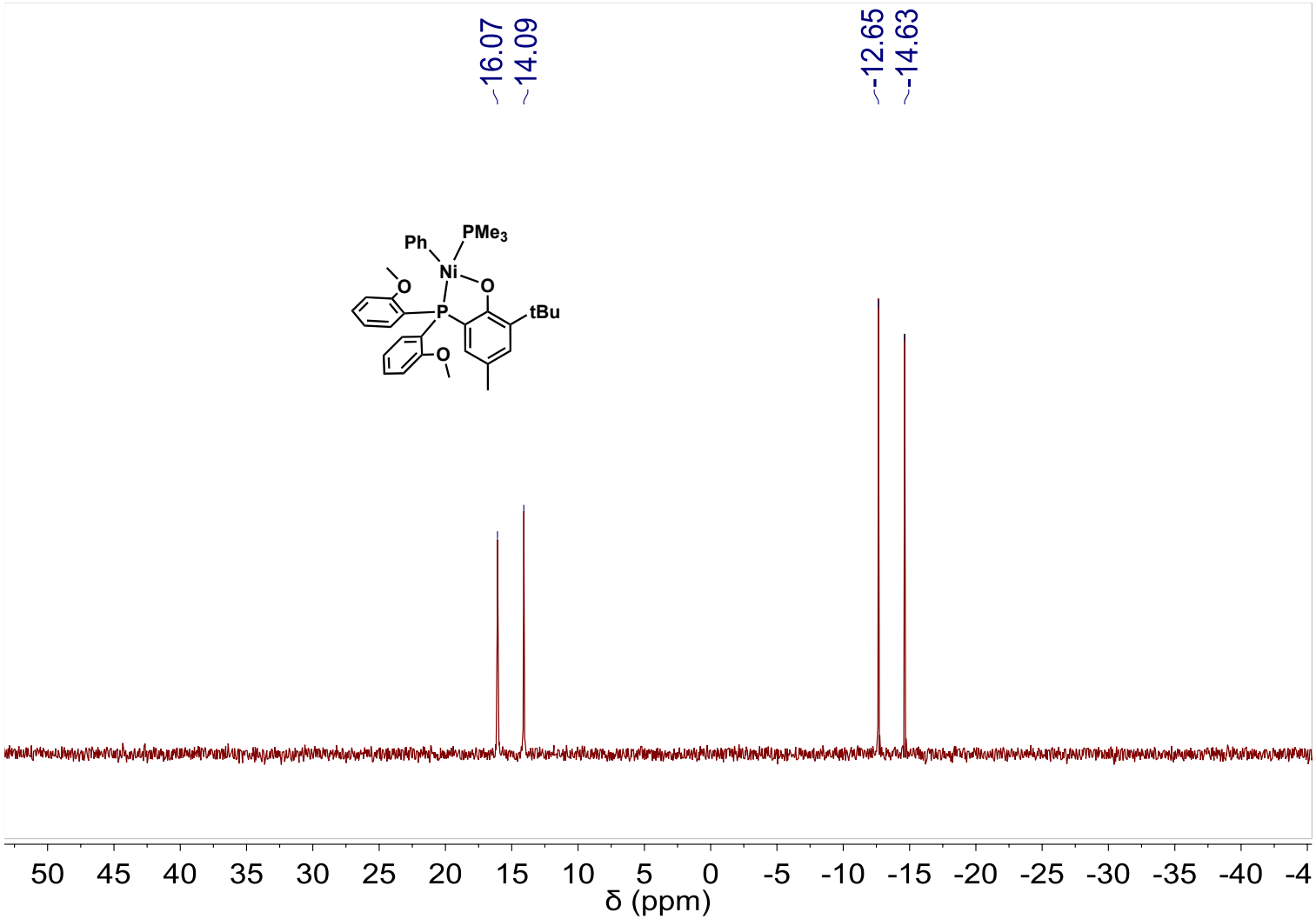


Figure S34. ^{31}P NMR spectrum (C_6D_6, 162 MHz) of complex **Ni10**.

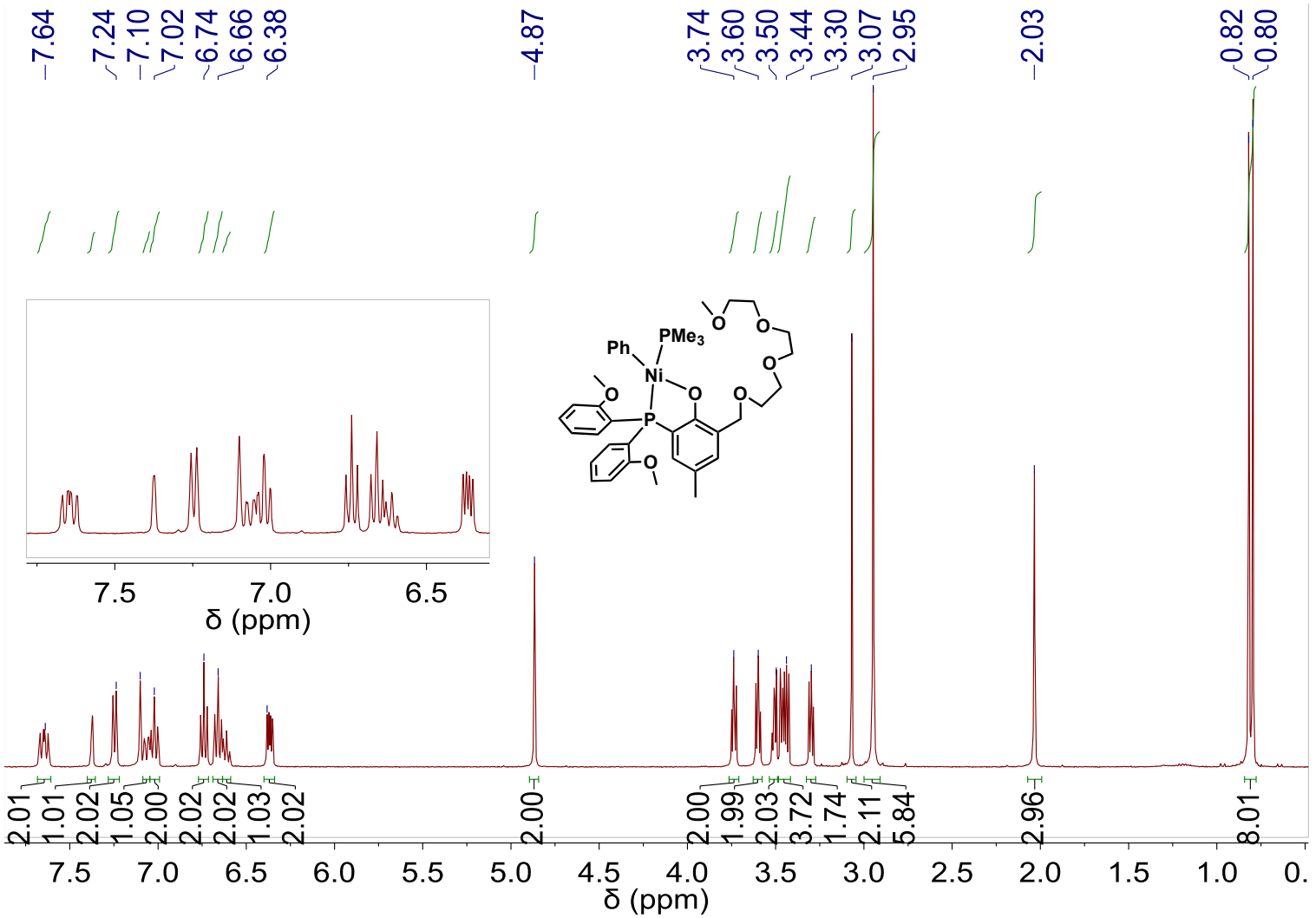


Figure S35. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of complex **Ni11**.

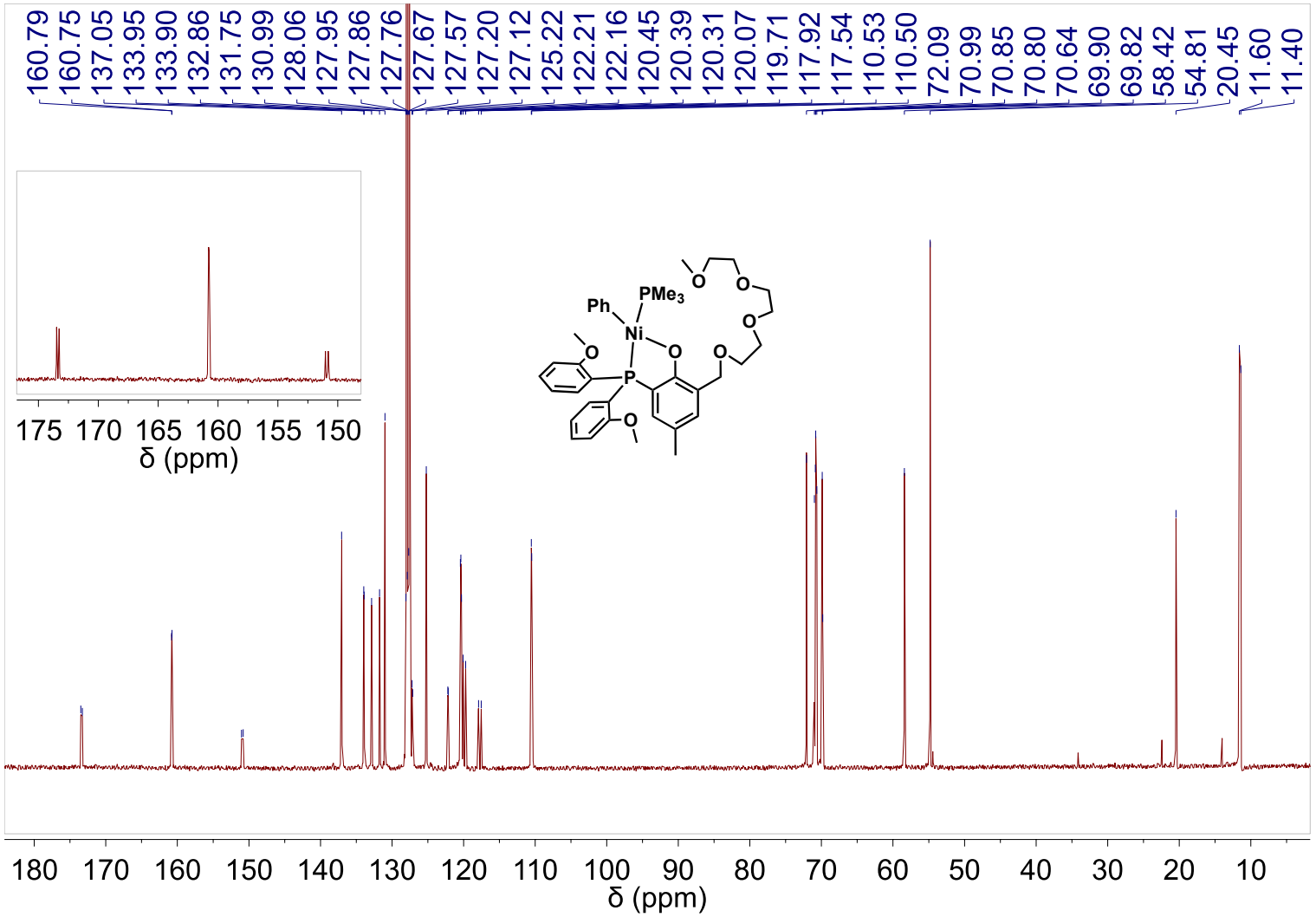


Figure S36. ^{13}C NMR spectrum (C_6D_6, 126 MHz) of complex **Ni11**.

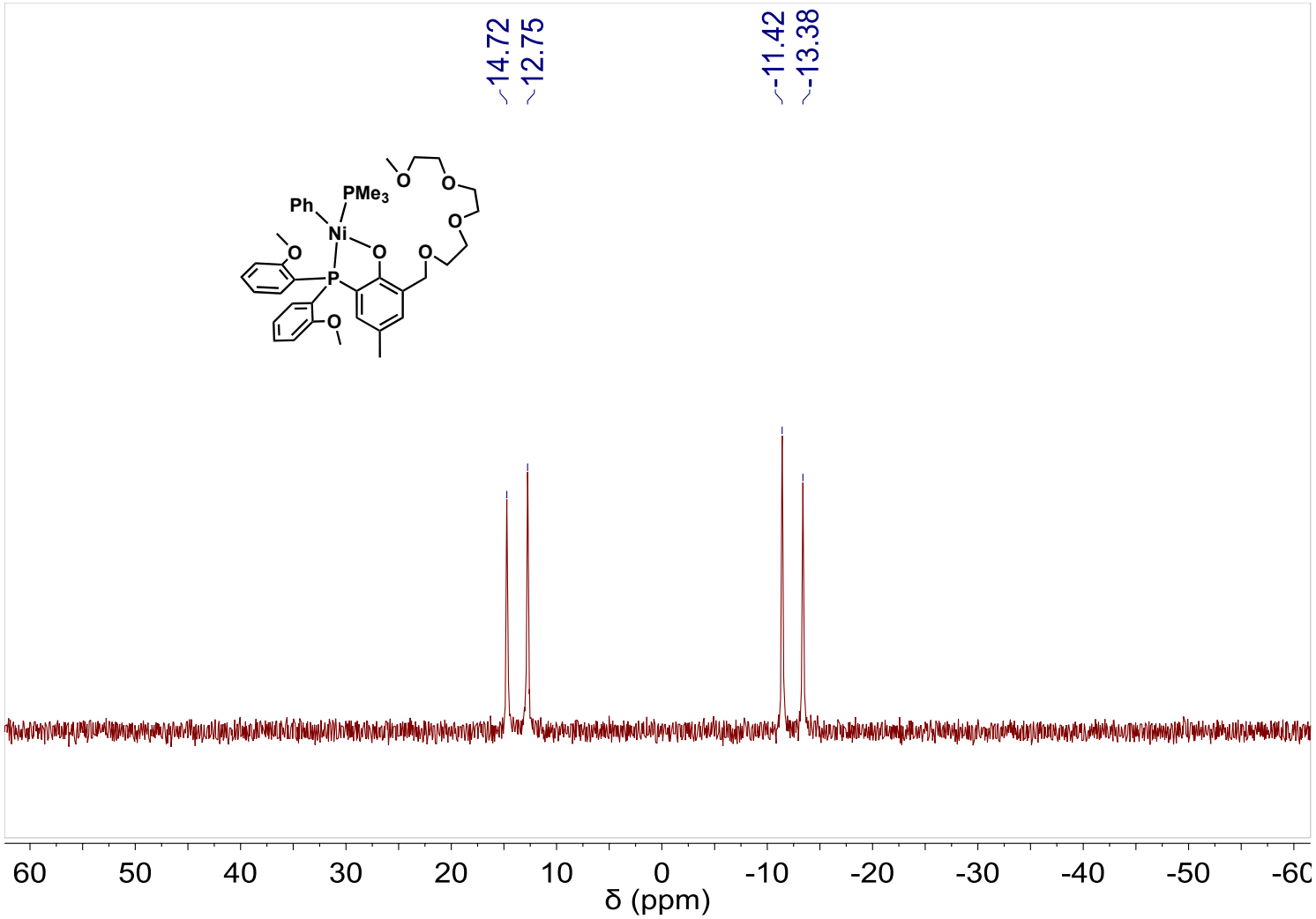


Figure S37. ^{31}P NMR spectrum (C_6D_6, 162 MHz) of complex **Ni11**.

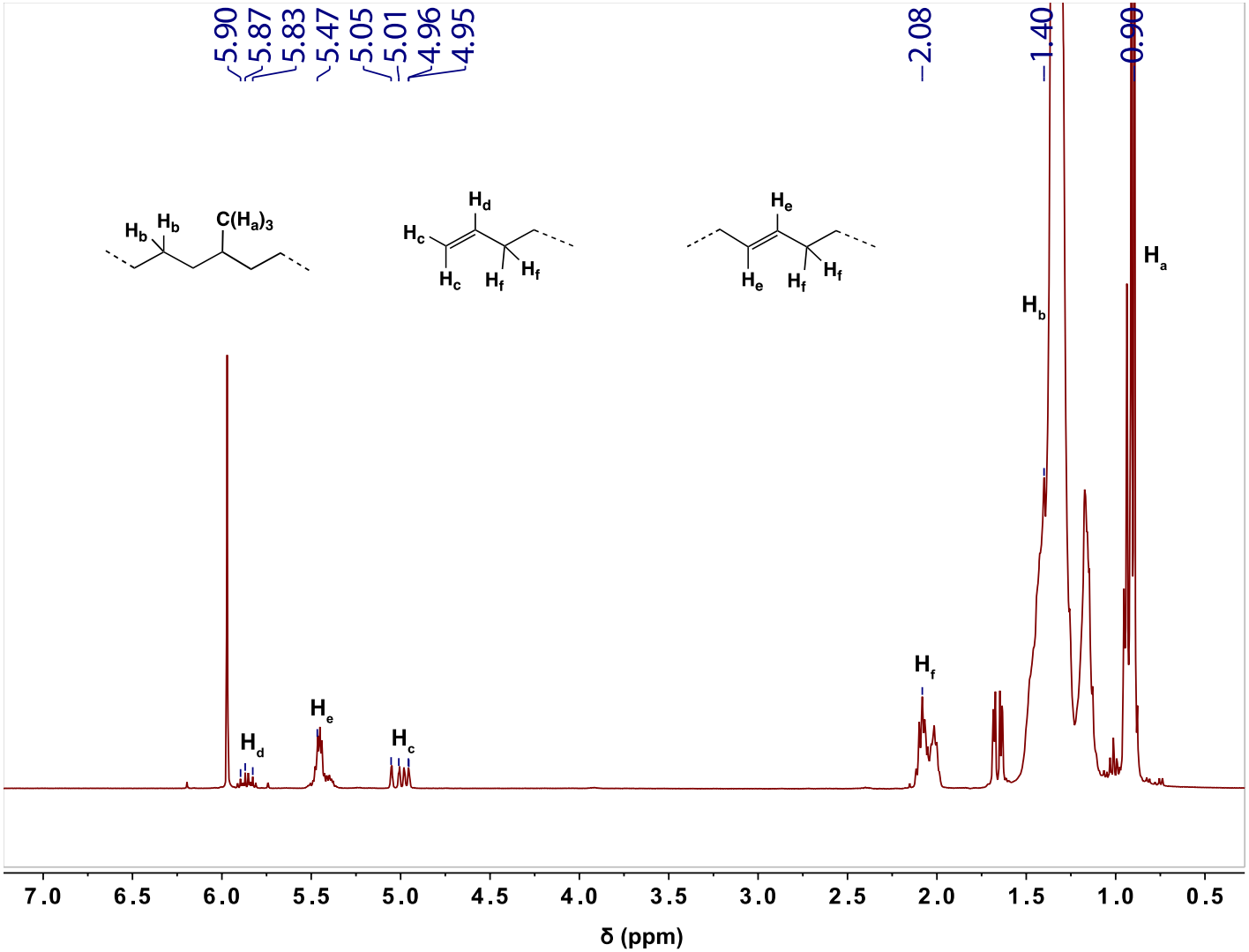


Figure S38. ^{1}H NMR spectrum (TCE-d_2, 500 MHz, 120°C) of polyethylene obtained from the reaction of **Ni11**-Na/Ni(COD)$_2$ with 150 psi of ethylene at 20°C for 1 h (see Table 1, Entry 5).

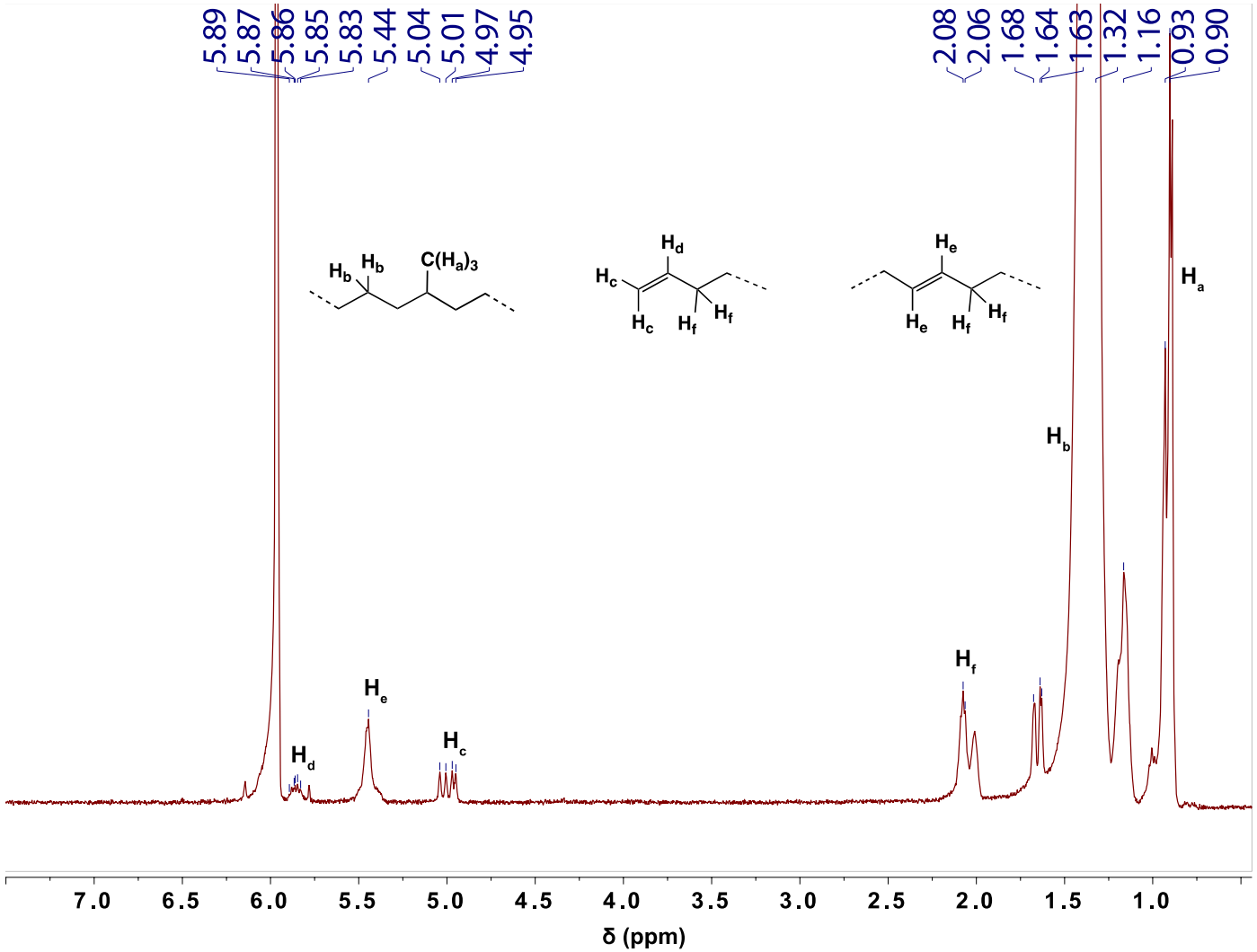


Figure S39. ^{1}H NMR spectrum (TCE-d_2, 500 MHz, 120°C) of polyethylene obtained from the reaction of **Ni11**-Na/Ni(COD)$_2$ with 450 psi of ethylene at 30°C for 1 h (see Table 1, Entry 9).

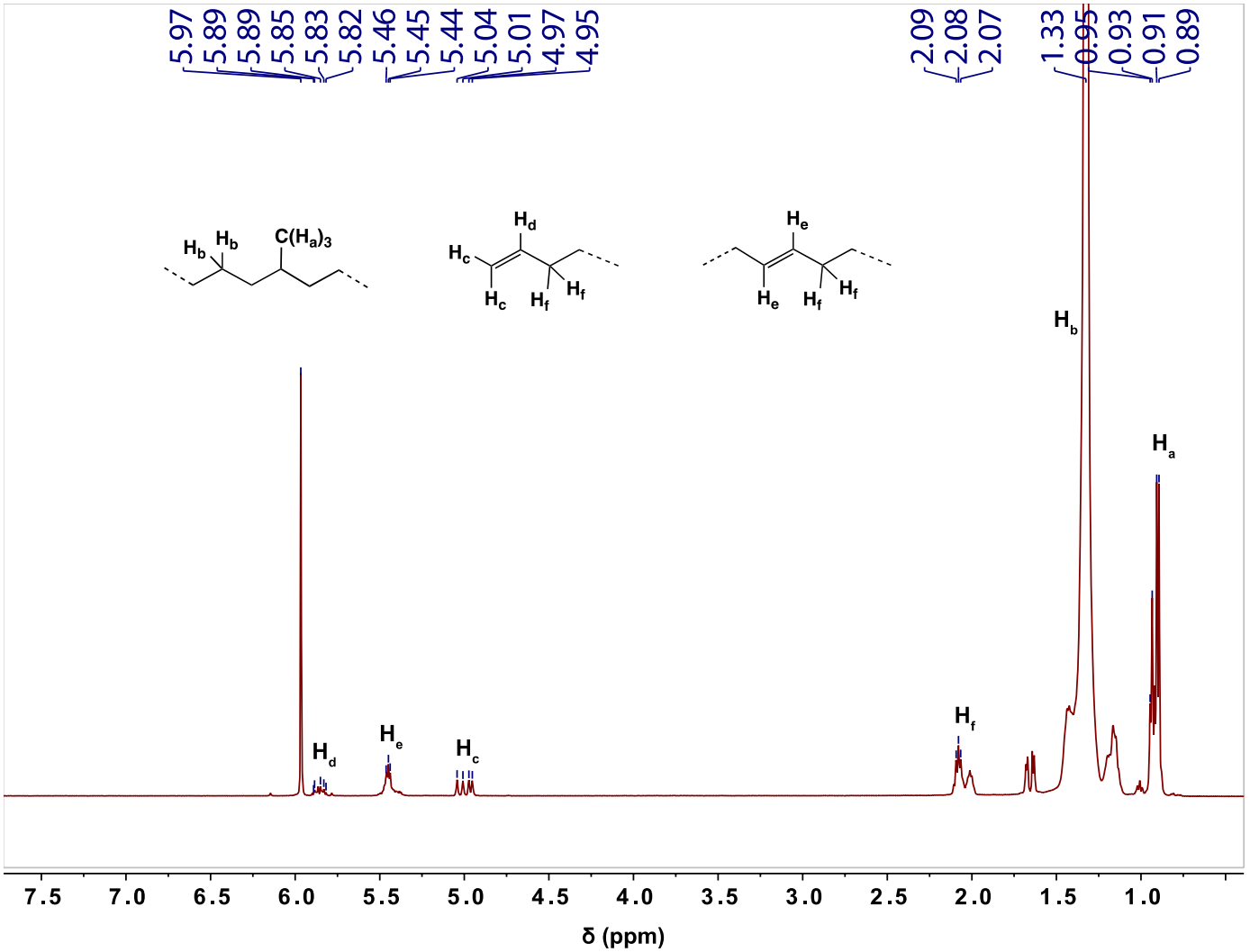


Figure S40. ^{1}H NMR spectrum (TCE-d_2, 500 MHz, 120°C) of polyethylene obtained from the reaction of **Ni11**-Na/Ni(COD)$_2$ with 450 psi of ethylene at 60°C for 1 h (see Table 1, Entry 14).

X-ray Data Collection and Refinement

Single crystals suitable for X-ray diffraction studies were picked out of the crystallization vials and mounted onto Mitogen loops using Paratone oil. The crystals were collected at a 6.0 cm detector distance at –150°C on a Brucker Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using the program SHELXT and refined by SHELXLE. Hydrogen atoms connected to carbon were placed at idealized positions using standard riding models and refined isotropically. All non-hydrogen atoms were refined anisoptriocally.

Crystals of complex **Ni10** were grown by layering of pentane into a solution of the complex in toluene at -30 ^{o}C. The three methyl carbons (C32-C34) attached to the phosphine atom were refined in two parts due to positional disorder. The solvent molecule pentane was refined successfully without the use of any structural restraints.

Crystals of complex **Ni11** were grown by layering of pentane into a solution of the complex and $NaBAr^{F}_{4}$ in a mixture of toluene and Et_2O at -30 ^{o}C. The fluorine atoms attached to carbons C54, C61, and C69 were refined using positional disorder due to free rotation of the CF_3 groups.

Table S11. Crystal Data and Structure Refinement for **Ni10** and **Ni11**-Na

	Ni10·C_5H_{12}	**Ni11**-Na
Empirical Formula	$NiC_{34}H_{42}O_3P_2 \cdot C_5H_{12}$	$NiNaC_{38}H_{30}O_7P_2(BC_{32}H_{12}F_{24})$
Formula Weight	691.47	1625.64
Temperature (°C)	-150	-150
Wavelength (Å)	0.71073	0.71073
Crystal System	Triclinic	Monoclinic
Space Group	P_{-1}	$P2_1/c$
Unit Cell Dimensions		
a (Å)	11.0922(13)	21.7805(17)
b (Å)	11.6999(14)	17.3222(14)
c (Å)	15.9470(19)	19.7901(16)
α (°)	72.2620(10)	90
β (°)	71.2670(10)	102.5400(10)
γ (°)	81.6330(10)	90
Volume (Å^3)	1864.1(4)	7288.4(10)
Z, Calculated Density (Mg/m^3)	2, 1.232	4, 1.481
Absorption Coefficient (mm^{-1})	0.640	0.429
F(000)	740	3312
Theta Range for Data Collection (°)	1.403 to 25.027	1.516 to 27.554
Limiting Indices	$-13 \le h \le 10$	$-23 \le h \le 28$
	$-13 \le k \le 13$	$-24 \le k \le 22$
	$-18 \le l \le 18$	$-25 \le l \le 25$
Reflections Collected/ Unique	9114/ 6404	43028/16670
	[R(int) = 0.0106]	[R(int) = 0.0181]
Data/ Restraints/ Parameters	6404 / 30 / 418	16670 / 57 / 944
Goodness of Fit on F²	1.085	1.053
Final R Indices	$R_1 = 0.0466$	$R_1 = 0.0666$
[I > 2σ(I)]	$wR_2 = 0.1590$	$wR_2 = 0.1861$
R Indices (All Data)*	$R_1 = 0.0556$	$R_1 = 0.0779$
	$wR_2 = 0.2051$	$wR_2 = 0.2007$
Largest Diff. Peak and Hole (e Å^{-3})	1.339 and -0.821	1.893 and -1.533

*$R_1 = \Sigma \, ||F_o|-|F_o||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)_2]]^{1/2}$; GOF = $[\Sigma[w(F_o^2 - F_c^2)_2]/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined

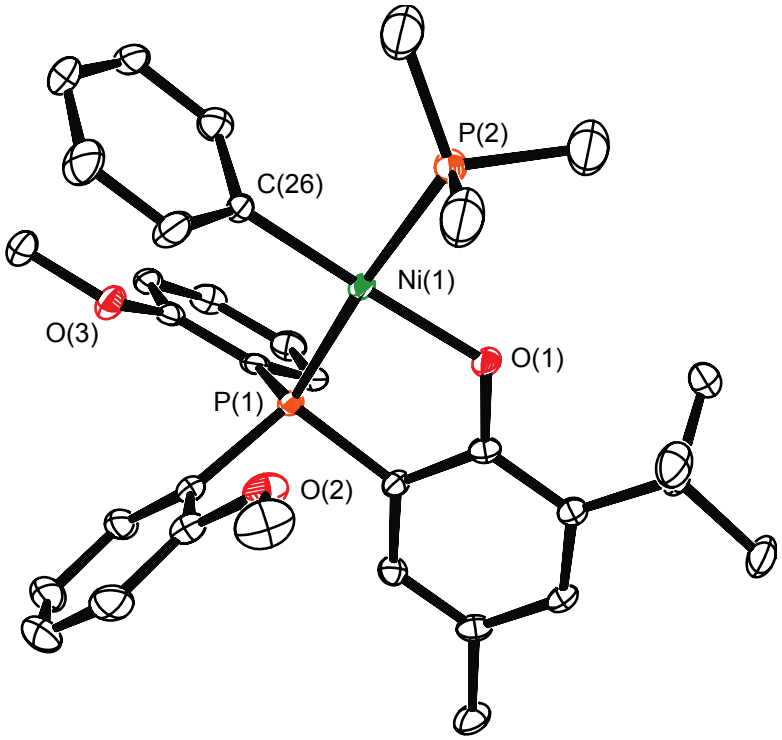


Figure S41. X-ray structure of complex **Ni10** (ORTEP view, displacement ellipsoids drawn at 50% probability level). Hydrogen atoms and pentane solvent have been omitted for clarity. Atom colors: green = nickel, orange = phosphorus, red = oxygen, black = carbon.

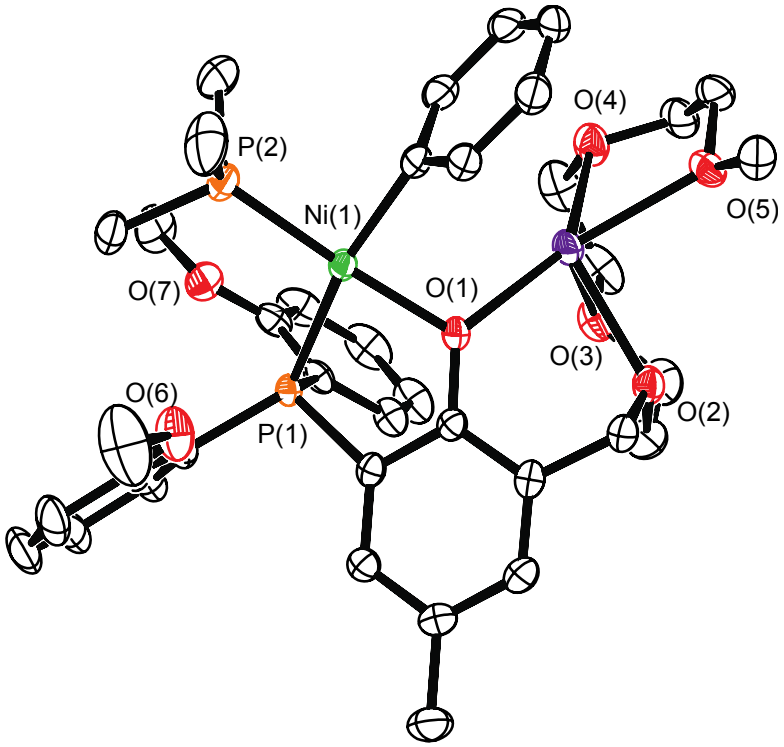


Figure S42. X-ray structure of complex **Ni11**-Na (ORTEP view, displacement ellipsoids drawn at 50% probability level). Hydrogen atoms and the $BAr^{F}_{4}^{-}$ anion have been omitted for clarity. Atom colors: green = nickel, orange = phosphorus, purple = sodium, red = oxygen, black = carbon.

References

(1) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920-3922.
(2) Mokhadinyana, M. S.; Maumela, M. C.; Mogorosi, M. M.; Overett, M. J.; Van Den Berg, J.-A.; Janse Van Rensburg, W.; Blann, K. Tetramerisation of Ethylene. Int. Patent WO/2014/181250, November 12, 2014.
(3) Egami, H.; Ide, T.; Kawato, Y.; Hamashima, Y. *Chem. Commun.* **2015**, *51*, 16675-16678.
(4) Carmona, E.; Paneque, M.; Poveda, M. L. *Polyhedron* **1989**, *8*, 285-291.
(5) Hirose, K. *J. Incl. Phenom. Marocycl. Chem.* **2001**, *39*, 193-209.
(6) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320-2334.
(7) Rhinehart, J. L.; Brown, L. A.; Long, B. K. *J. Am. Chem. Soc.* **2013**, *135*, 16316-16319.
(8) Chen, M.; Chen, C. *Angew. Chem. Int. Ed.* **2018**, *57*, 3094-3098.
(9) Zhou, X.; Bontemps, S.; Jordan, R. F. *Organometallics* **2008**, *27*, 4821-4824.
(10) Delferro, M.; McInnis, J. P.; Marks, T. J. *Organometallics* **2010**, *29*, 5040-5049.
(11) Kenyon, P.; Mecking, S. *J. Am. Chem. Soc.* **2017**, *139*, 13786-13790.
(12) Zhang, Y.; Mu, H.; Pan, L.; Wang, X.; Li, Y. *ACS Catal.* **2018**, *8*, 5963-5976.
(13) Tao, W.-j.; Nakano, R.; Ito, S.; Nozaki, K. *Angew. Chem. Int. Ed.* **2016**, *55*, 2835-2839.
(14) Kocen, A.; Brookhart, M.; Daugulis, O. *Nat. Commun.* **2019**, *10*, 438.
(15) Hicks, F. A.; Brookhart, M. *Organometallics* **2001**, *20*, 3217-3219.
(16) Perrotin, P.; McCahill, J. S. J.; Wu, G.; Scott, S. L. *Chem. Commun.* **2011**, *47*, 6948-6950.
(17) Gao, J.; Yang, B.; Chen, C. *J. Catal.* **2019**, *369*, 233-238.
(18) Zou, C.; Dai, S.; Chen, C. *Macromolecules* **2018**, *51*, 49-56.
(19) Chen, M.; Chen, C. *ACS Catal.* **2017**, *7*, 1308-1312.
(20) Li, M.; Wang, X.; Luo, Y.; Chen, C. *Angew. Chem. Int. Ed.* **2017**, *56*, 11604-11609.