Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

N-Bridged Strategy Enables Hemilabile Phosphine-Carbonyl Palladium and Nickel Catalysts to Mediate Ethylene Polymerization and Copolymerization with Polar Vinyl Monomers

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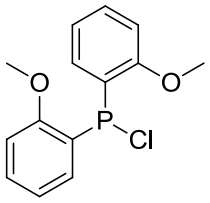
Contents

General Procedures and Materials: All syntheses involving air and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of nitrogen. All solvents were purified from the MBraun SPS system. NMR spectra for the ligands, complexes, and polymers were recorded on a Bruker AV400 (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{31}P: 162 MHz, ^{19}F: 376 MHz) or a Bruker AV500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{31}P: 202 MHz, ^{19}F: 470 MHz). The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 ℃. Melting points (T_m) of polyethylenes and polymers were measured through DSC analyses, which were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere at heating and cooling rates of 20 ℃/min (temperature range: 40-250 ℃).

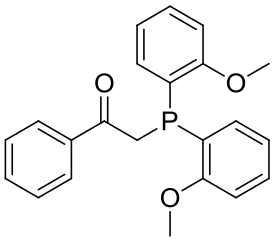
Materials: (COD)PdMeCl[1] and [Ni(allyl)Cl]$_2$[2] were prepared according to the literature procedures. The following polar monomers were commercially available and used after distillation under vacuum: methyl acrylate (MA), butyl vinyl ether (BVE), acrylic acid (AA). All other reagents were commercially available and used as received.

X-Ray diffraction: Data collections were performed at −100 ℃ on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54178 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.[3] The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[4] All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXTL or Olex2.[5] Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

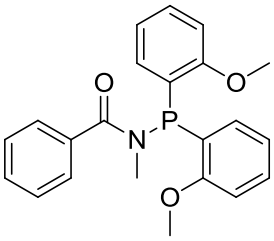
Preparation of ligands and catalysts



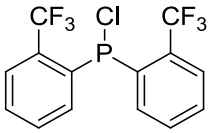
Chlorobis(2,6-dimethoxyphenyl)phosphine: 2-bromoanisole 27 g (0.144 mol) was dissolved in 150 mL ether under nitrogen, 60 mL *n*-BuLi (2.5 M in hexane, 0.144 mmol) was droped at -78 ^{o}C. After 2 h, 12.1 g (0.07 mol) Et_2NPCl_2 prepared was added to the solution and stirred overnight at room temperature. Subsequently, 69 mL HCl/Et_2O (2 M, 0.07 mol) was added at room temperature and stirred overnight. The resulting was filtered over celite and the solvent was removed under vacuum to yield a white solid chlorobis(2,6-dimethoxyphenyl)phosphine (15 g, 76%)[6]. ^{31}P NMR (202 Hz, $CDCl_3$): 69.34.



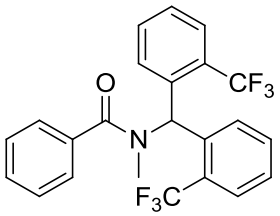
L1: To a solution of diisopropylamine (0.36 g, 14 mmol) in THF (10 mL) was added dropwiseat -78 ℃ with *n*-BuLi (2.3 mL, 1.6 M, 3.7 mmol) under nitrogen. After the mixture was stirred for 0.5 h, a solution of acetophenone (0.43 g, 3.6 mmol) in THF (10 mL) was added dropwise. The mixture was stirred for 2 h at -78 ℃ and then transferred into a schlenk flask containing chlorobis(2,6-dimethoxyphenyl)phosphine (1 g, 3.5 mmol) in THF (10 mL). After the mixture was stirred for 12 h at room temperature, the solvent was removed in vacuo. The residue was treated with chloroform, and the resulting suspension was filtered in order to remove LiCl. The filtrate was then evaporated to dryness, and the residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:10). The ligand was isolated by recrystallization (chloroform/petroleum ether) as a white solid **L1** (0.8 g, 63%)[7]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12-8.08 (m, 2H), 7.56-7.51 (m, 1H), 7.46-7.41 (m, 2H), 7.37-7.31 (m, 2H), 7.24-7.19 (m, 2H), 6.97-6.91 (t, 2H), 6.88-6.83 (dd, *J* = 4.31 Hz, 2H), 3.80 (s, 2H, -***CH$_2$***-), 3.72 (s, 6H, ***OMe***). ^{13}C NMR (125 MHz, $CDCl_3$): δ 185.65 (d, *J* = 17.38 Hz), 161.66 (dd, *J* = 47.15Hz, *J* = 51.37Hz), 160.40 (s), 135.63 (s), 134.78 (s), 133.22 (s), 131.91 (s), 129.27 (s), 129.00 (s), 128.75 (s), 127.43 (s), 125.61 (s), 133.44 (s), 122.37 (d, *J* = 8.31Hz), 117.46 (s), 116.54 (s), 112.06 (d, *J* = 5.41Hz), 56.00 (s, ***OMe***), 35.95 (d, *J*= 2.62Hz, -***CH$_2$***-). ^{31}P NMR (202 MHz, $CDCl_3$): δ -29.76.



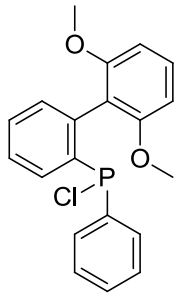
L2: N-methylbenzamide (2.02 g, 15 mmol) was dissolved in THF (30 mL) at -10 ^{o}C under nitrogen. A solution of 9.4ml *n*-BuLi (1.6 M) in hexane was added dropwise. The white suspension was stirred at this temperature for1.5 h and subsequently allowed to room temperature. Chlorobis (2,6-dimethoxyphenyl)phosphine (2.13 g, 7.59 mmol) in THF (20mL) was added and the clear solution was stirred for 12 h at ambient temperature. The mixture was evaporated to dryness and subsequently suspended in$CHCl_3$ (40 mL). After that, the suspension was filtered through Celite. The ligand was isolated by recrystallization (THF) as a white solid **L2** (1.9 g, 70.4%)[8]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53-7.50 (m, 2H), 7.43-7.37 (m, 3H), 7.35-7.31 (m, 2H), 7.18-7.09 (m, 2H), 6.92-6.88 (m, 2H), 3.74 (s, 6H, ***OMe***), 2.78 (s, 3H, ***N-Me***). ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.91 (d, *J* = 28.87 Hz), 160.88 (d, *J* = 15.83 Hz), 137.34 (d, *J* = 3.21), 131.67 (d, *J* = 2.90), 131.06 (s), 130.15 (s), 128.05 (s), 127.69 (d, *J* = 7.36), 122.76 (d, *J* = 12.34), 110.27 (s), 55.63 (s, ***OMe***), 33.73 (s, ***N-Me***). ^{31}P NMR (202 MHz, $CDCl_3$): δ 43.36.



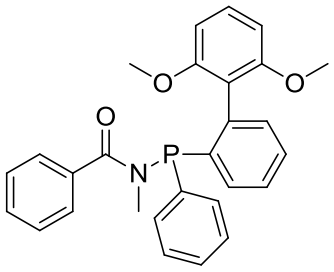
Chlorobis(2-(trifluoromethyl)phenyl)phosphine: 11 mL *n*-BuLi (2.4 M in hexane, 26 mmol) was added dropwise to a solution of 5.9 g 2-bromobenzotrifluoride (26 mmol) in Et_2O (100 mL) at -78 ^{o}C under nitrogen. The reaction mixture was allowed to warm to room temperature. The solution was cooled to -78 ^{o}C and a solution of 2.3 g Cl_2PNEt_2 (13 mmol) in Et_2O (15 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 h, meanwhile a white precipitate formed. The reaction mixture was cooled to 0 ℃ and 13 mL HCl (2 M, 26 mmol) was added. The reaction mixture was allowed to warm to room temperature and the resulting slurry was stirred for 2 days. The precipitate was filtered off over celite and washed with Et_2O.The solvent was removed under vacuum to yield white solid (3.6g, 78%)[9]. ^{31}P NMR (202 MHz, $CDCl_3$): δ 72.60.



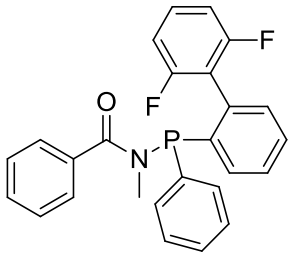
L3: N-methylbenzamide (0.5 g, 3.75 mmol) was dissolved in THF (20 mL) at -10 °C under nitrogen. A solution of 2.4 mL *n*-BuLi (1.6 M, 3.84 mmol) in hexanes was added dropwise. The white suspension was stirred with cooling for 1.5 h and subsequently allowed to room temperature. Chlorobis(2-(trifluoromethyl)phenyl)-phosphine (1.34 g, 3.79 mmol) in THF (20mL) was added and the clear solution was stirred for 12 h at ambient temperature. The mixture was evaporated to dryness and subsequently suspended in $CHCl_3$ (40 mL). After that, the suspension was filtered through Celite. The ligand was isolated by recrystallization (THF/petroleum ether) as a white solid **L3** (1.45 g, 85.3%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79-7.75 (m, 2H), 7.66-7.52 (m, 4H), 7.49-7.23 (m, 7H), 2.82 (s, 3H, ***N-Me***). ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.22 (d, *J* = 37.38 Hz), 136.27 (d, *J* = 3.55 Hz), 134.34 (d, *J* = 35.36 Hz), 133.45 (d, *J* = 28.49 Hz), 131.93 (s), 130.38 (s), 130.13 (s), 128.03 (s), 127.43 (d, *J* = 8.35 Hz), 125.10 (d, *J* = 1.94 Hz), 33.85 (s, ***NMe***). ^{31}P NMR (202 MHz, $CDCl_3$): δ 46.26.



(2',6'-dimethoxybiphenyl-2-yl)phenylphosphine chloride: 1.46 g (5 mmol) 2-Bromo-2',6'-dimethoxybiphenyl was dissolved in 30 mL THF, 2.3 mL *n*-BuLi (2.4 M in hexane, 11 mmol) was added dropwise at -10 °C under nitrogen. After stirred for 3 h at room temperature, the reaction suspension was slowly transferred into the solution of $PPhCl_2$ (0.89 g, 5 mmol) in 15 mL THF, and the reaction mixture was stirred for 7 h. The resulting precipitate was filtered over off celite and the solvent was removed under vacuum to yield a white solid (1.5 g, 69%)[10]. ^{31}P NMR (202 MHz, $CDCl_3$): δ 46.26 (80% purity without further purification).

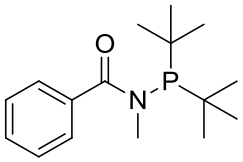


L4: N-methylbenzamide (0.25 g, 1.85 mmol) was dissolved in THF (20 mL) at -10 °C under nitrogen. A solution of 1.2 mL*n*-BuLi (1.6 M, 1.92 mmol) in hexanes was added dropwise. The white suspension was stirred with cooling for 1.5 h and subsequently allowed to room temperature. (2',6'-dimethoxybiphenyl-2-yl)-phenylphosphine chloride (1.06 g, 1.85 mmol, 80% purity) in THF (20 mL) was added and the clear solution was stirred for 12 h at ambient temperature. The mixture was evaporated to dryness and subsequently suspended in $CHCl_3$ (40 mL). After that, the suspension was filtered through Celite. The ligand was isolated by recrystallization (THF/hexane) as a white solid **L4** (0.8 g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49-7.44 (m, 1H), 7.41-7.34 (m, 3H), 7.32-7.17 (m, 8H), 7.16-7.09 (m, 2H), 7.01-6.97 (m, 2H), 6.64 (d, *J* = 9.96 Hz, 1H), 6.33 (d, *J* = 10.53 Hz, 1H), 3.67 (s, 3H, ***OMe***), 3.46 (s, 3H, ***OMe***), 2.87 (s, 3H, ***N-Me***). ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.03 (d, *J* = 34.35 Hz), 158.37 (s), 157.26 (s), 141.33 (d, *J* = 32.67 Hz), 136.63 (s), 136.55 (d, *J* = 15.61 Hz), 135.89 (d, *J* = 17.36 Hz), 132.51 (d, *J* = 2.88 Hz), 131.73 (d, *J* = 6.02 Hz), 131.04 (d, *J* = 20.43 Hz), 130.08 (s), 129.55 (d, *J* = 12.83 Hz), 128.60 (s), 128.49 (d, *J* = 6.81 Hz), 127.87 (d, *J* = 6.81 Hz), 127.40 (s), 127.32 (s), 117.92 (d, *J* = 6.14 Hz), 104.06 (d, *J* = 16.12 Hz), 55.82 (s, ***OMe***), 32.71 (s, ***N-Me***). ^{31}P NMR (202 MHz, $CDCl_3$): δ 51.96.

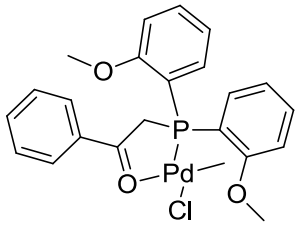


L5: 1.9 g 2-bromo-2',6'-difluorobiphenyl (7.06 mmol) was dissolved in 20 mL THF, 4.2 ml *n*-BuLi (2.4 M in hexane, 8.47 mmol) was added dropwise at -78 °C under nitrogen. After stirring for 2 h at -78 °C, the reaction suspension was slowly transferred into the solution of $PPhCl_2$ (1.26 g, 7.06 mmol) in 15 mL THF, and the reaction mixture (A) was further stirred for 12 h at -30 °C. N-methylbenzamide (0.87 g, 6.5 mmol) was dissolved in THF (20 mL) at -10 °C. A solution of 4.9 mL *n*-BuLi (1.6 M, 7.8 mmol) in hexanes was added dropwise. The white suspension was stirred with cooling for 1.5 h and subsequently allowed to room temperature. After that, the

reaction mixture A was transferred to the resulting suspension and stirred at room temperature overnight. The solution was filtered over celite and the solvent was removed under vacuum. The ligand was isolated by recrystallization (THF/hexane) as a white solid **L5** (0.5 g, 17% yield, 74% purity without further purification)[10]. ^{31}P NMR (202 MHz, $CDCl_3$): δ 50.53.

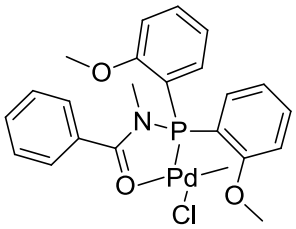


L6: N-methylbenzamide (1.01 g, 7.4 mmol) was dissolved in THF (20 mL) at -10 °C under nitrogen. A solution of 4.7 mL *n*-BuLi (1.6 M, 7.52 mmol) in hexanes was added dropwise. The white suspension was stirred with cooling for 1.5 h and subsequently allowed to room temperature. Di-tert-butylchlorophosphane (1.37 g, 7.58 mmol) in THF (20 mL) was added and the clear solution was refluxed for 12 h. The mixture was evaporated to dryness and subsequently suspended in $CHCl_3$ (40 mL). After that, the suspension was filtered through Celite. The solvent was removed under vacuum and crystallized (THF/ether) to remove white solid. The product was isolated by removed the solvent as a yellow viscous liquid **L6**. (1.6 g, 78% yield, 83% content without further purification)[11]. ^{31}P NMR (202 MHz, $CDCl_3$): δ 95.59.

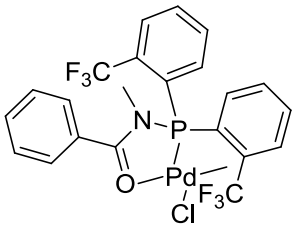


Pd1: A mixture of **L1** (168.4 mg, 0.46 mmol) and (COD)PdMeCl (122.4 mg, 0.46 mmol) in 15mL of CH_2Cl_2 was stirred at room temperature for 12 h. The resulting mixture was evaporated and the residue was washed by Et_2O. The solid was collected by filtration to give **Pd1** as a white solid (200 mg, 83.4%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08-7.84 (m, 2H), 7.69-7.53 (m, 3H), 7.52-7.34 (m, 4H), 7.02-6.97 (m, 2H), 6.95-6.87 (m, 2H), 4.30 (d, *J* = 19.08 Hz, 2H, ***-CH$_2$-***), 3.73 (s, 6H, ***OMe***), 0.80 (s, 3H, Pd-***CH$_3$***). ^{13}C NMR (125 MHz, $CDCl_3$): it cannot be characterized due to a very poor solubility. ^{31}P NMR (202 MHz, $CDCl_3$): δ 24.64.

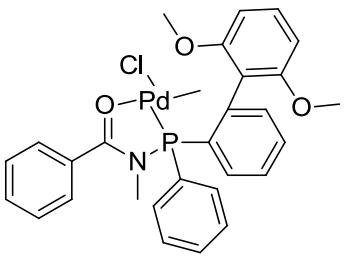
Elemental analysis: Anal. Calcd for $C_{23}H_{24}ClO_3PPd$:C, 52.99; H, 4.64. Found: C, 53.06; H, 4.68.



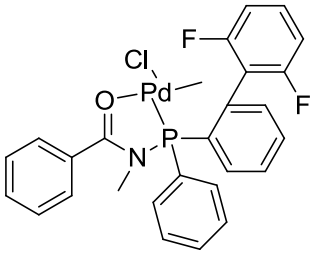
Pd2: Similar procedure was employed with mixing **L2** (379.4 mg, 1.0 mmol) and (COD)PdMeCl (265 mg, 1.0 mmol). **Pd2** was obtained as a gray solid (450 mg, 83.9%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66-7.55 (m, 4H), 7.51-7.46 (m, 3H), 7.45-7.40 (m, 2H), 3.81 (s, 6H, ***OMe***), 2.93 (d, *J* = 7.51, 3H, ***NMe***), 0.81 (d, *J* = 2.86 Hz, 3H, Pd-***Me***). ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.56 (d, *J* = 11.13 Hz), 160.83 (d, *J* = 4.40 Hz), 135.24 (d, *J* = 12.04 Hz), 134.48 (d, *J* = 2.56 Hz), 133.22 (d, *J* = 4.14 Hz), 131.42 (s), 128.70 (s), 127.57 (s), 121.45 (d, *J* = 11.30 Hz), 115.24 (d. *J* = 51.99 Hz), 111.79 (d, *J* = 9.61 Hz), 55.99 (s, ***OMe***), 37.31 (d, *J* = 5.03 Hz, ***NMe***), -5.18 (s, Pd-***Me***). ^{31}P NMR (202 MHz, $CDCl_3$): δ 88.80.
Elemental analysis: Anal. Calcd for $C_{23}H_{25}ClNO_3PPd$: C, 51.51; H, 4.70; N, 2.61. Found: C, 51.70; H, 4.64; N, 2.65.



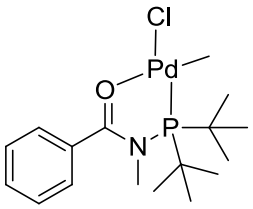
Pd3: Similar procedure was employed with mixing **L3** (227.7 mg, 0.5 mmol) and (COD)PdMeCl (132.5 mg, 0.5 mmol). **Pd3** was obtained as a white solid (250 mg, 81.7%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04-7.94 (m, 2H), 7.83-7.70 (m, 4H), 7.69-7.56 (m, 2H), 7.53-7.47 (m, 1H), 7.47-7.41 (m, 4H), 2.74 (d, *J* = 7.31 Hz, ***NMe***), 1.06 (d, *J* = 3.15 Hz, Pd-***Me***). ^{13}C NMR (125 MHz, $CDCl_3$): it cannot be characterized due to a very poor solubility.^{31}P NMR (202 MHz, $CDCl_3$): δ 88.30.
Elemental analysis: Anal. Calcd for $C_{23}H_{19}ClF_6NOPPd$: C, 45.12; H, 3.31; N, 2.29. Found: C, 45.30; H, 3.29; N, 2.20.



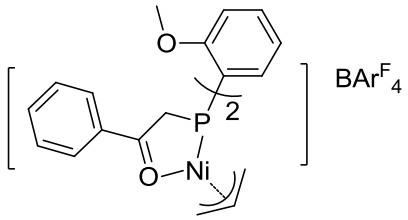
Pd4: Similar procedure was employed with mixing **L4** (136.6 mg, 0.3 mmol) and (COD)PdMeCl (79.5 mg, 0.3 mmol). **Pd4** was obtained as a white solid (150 mg, 81.7%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00-7.93 (m, 2H), 7.65-7.59 (m, 2H), 7.58-7.53 (m, 2H), 7.44-7.38 (m, 4H), 7.38-7.34 (m,1H), 7.32-7.28 (t, 2H), 7.15-7.11 (m, 2H), 6.81 (d, *J* = 8.89 Hz, 1H), 6.54 (d, *J* = 10.41 Hz, 1H), 4.00 (s, 3H, ***OMe***), 3.53 (s, 3H, ***OMe***), 2.77 (d, *J* = 4.79 Hz, 3H, ***NMe***), 0.75 (d, *J* = 3.20 Hz, 3H, Pd-***Me***). ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.29 (d, *J* = 11.54 Hz), 157.67 (d, *J* = 71.45 Hz), 140.77 (d, *J* = 19.24 Hz), 134.70 (d, *J* = 16.46 Hz), 134.35 (d, *J* = 8.60 Hz), 133.64 (d, *J* = 10.85 Hz), 132.28 (d, *J* = 53.36 Hz), 132.28 (d, *J* = 4.42 Hz), 131.42 (s), 130.80 (s), 129.18 (d, *J* = 51.92 Hz), 129.18 (d, *J* = 10.61 Hz), 128.37 (s), 128.06 (s), 127.03 (d, *J* = 11.40 Hz), 126.05 (d, *J* = 51.28 Hz), 116.63 (d, *J* = 4.76 Hz), 105.09 (s), 103.77 (s), 56.75 (s, ***OMe***), 55.99 (s, ***OMe***), 36.28 (d, *J* = 4.18 Hz, ***NMe***), -4.52 (s, Pd-***Me***). ^{31}P NMR (202 MHz, $CDCl_3$): δ 93.24.
Elemental analysis: Anal. Calcd for $C_{29}H_{29}ClNO_3PPd$: C, 56.88; H, 4.77; N, 2.29. Found: C, 56.71; H, 4.68; N, 2.21.



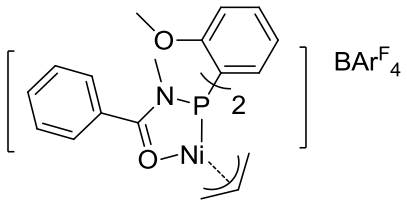
Pd5: Similar procedure was employed with mixing **L5** (129.3 mg, 0.25 mmol actually) and (COD)PdMeCl (66.3 mg, 0.25 mmol). **Pd5** was obtained as a white solid (80 mg, 54.4%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80-7.73 (m, 1H), 7.62-7.54 (m, 6H), 7.52-7.43 (m, 7H), 7.26-7.20 (m, 2H), 7.01 (t, 1H), 2.96 (d, *J* = 5.35 Hz, 3H, ***NMe***), 0.59 (s, 3H, ***Pd-Me***). ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.44 (d, *J* = 12.23 Hz), 160.83 (dd, *J* = 9.31 Hz, *J* = 7.93 Hz), 158.87 (dd, *J* = 8.96 Hz, *J* = 10.00 Hz), 137.28 (d, *J* = 20.36 Hz), 134.70 (d, *J* = 5.30 Hz), 133.77 (d, *J* = 9.91 Hz), 133.27 (d, *J* = 4.34 Hz), 132.95 (d, *J* = 4.65 Hz), 131.77, 131.50 (d, *J* = 3.72 Hz), 131.42 (s), 130.61 (d, *J* = 12.70 Hz), 129.45 (d, *J* = 10.84 Hz), 128.59 (s), 128.52 (d, *J* = 6.20 Hz), 128.15 (s), 127.72 (s), 127.53 (d, *J* = 3.41 Hz), 126.39 (d, *J* = 45.85 Hz), 113.17 (dd, *J* = 3.80 Hz, *J* = 4.70 Hz), 111.32 (dd, *J* = 3.36 Hz, *J* = 4.47 Hz), 35.77 (***NMe***), -5.20 (d, *J* = 3.39 Hz, ***Pd-Me***). ^{31}P NMR (202 MHz, $CDCl_3$): δ 83.23. ^{19}F NMR (470 MHz, $CDCl_3$): δ -108.46, -113.76.
Elemental analysis: Anal. Calcd for $C_{27}H_{23}ClF_2NOPPd$: C, 55.12; H, 3.94; N, 2.38. Found: C, 55.00; H, 3.89; N, 2.31.



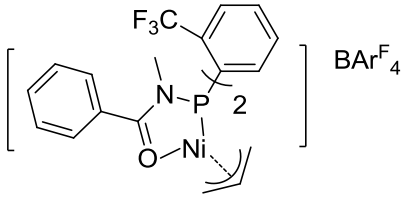
Pd6: Similar procedure was employed with mixing **L6** (100 mg, 0.28 mmol actually) and (COD)PdMeCl (74 mg, 0.28 mmol). **Pd6** was obtained as a white solid (100 mg, 81.8%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49-7.40 (m, 3H), 7.35-7.29 (m, 2H), 3.19 (d, *J* = 3.33 Hz, 3H, ***NMe***), 1.56 (d, *J* = 15.07 Hz, 18H, ***-C(CH$_3$)$_3$***), 1.03 (d, *J* = 1.2 0 Hz, 3H, Pd-***Me***). ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.77 (d, *J* = 7.04 Hz), 133.23 (d, *J* = 4.14 Hz), 131.25 (s), 128.97 (s), 126.74 (s), 40.94 (d, *J* = 8.60 Hz), 40.47 (d, *J* = 4.02 Hz), 30.12 (d, *J* = 6.52 Hz, ***NMe***), -7.49 (s, Pd-***Me***). ^{31}P NMR (202 MHz, $CDCl_3$): δ 138.2.
Elemental analysis: Anal. Calcd for $C_{17}H_{29}ClNOPPd$: C, 46.80; H, 6.70; N, 3.21. Found: C, 46.74; H, 6.64; N, 3.19.



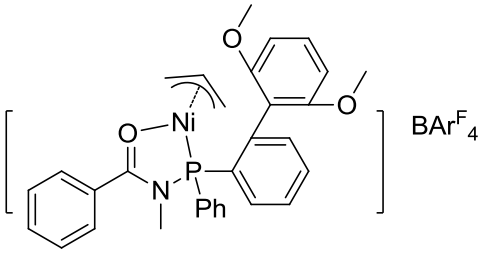
Ni1: A mixture of **L1**(182.2 mg, 0.5 mmol), $[Ni(allyl)Cl]_2$ (67.5 mg, 0.25 mmol), and NaBAF (443 mg, 0.5 mmol) in 15 mL CH_2Cl_2 was stirred at room temperature for 12 h. The resulting mixture was filtrated and evaporated. The resulting solid was recrystallized from CH_2Cl_2 and hexane solution to give **Ni1** as a bright yellow solid (450 mg, 67.8%)[12]. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.13-8.04 (m, 2H), 7.84-7.78 (m, 1H), 7.76-7.69 (m, 9H), 7.65-7.52 (m, 8H), 7.26-7.16 (m, 2H), 7.11-7.03 (m, 4H), 5.83 (br, 1H, **allyl-*CH*-**), 4.24 (d, *J* = 12.94Hz, 2H, ***-CH$_2$-***), 4.13-3.89 (m, 1.69H, ***allyl -CH$_2$-*)**, 3.83 (s, 6H, ***OMe***), 3.03-2.53 (m, 1.69H, ***allyl -CH$_2$-***). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 213.76 (d, *J* = 11.44 Hz), 162.17 (dd, *J* = 49.40 Hz, *J* = 50.95 Hz), 160.77 (s), 137.95 (s), 135.21 (s), 133.41 (d, *J* = 4.06 Hz), 131.29 (s), 130.09 (s), 129.66 (br), 129.41 (br), 129.16 (br), 128.91 (br), 128.25 (s), 126.09 (s), 123.92 (s), 122.19 (d, *J* = 11.96Hz), 121.76 (s), 117.88 (br), 116.99 (s), 112.05 (d, *J* = 4.17), 56.36 (s, ***OMe***), 44.03 (d, *J* = 27.28, ***-CH$_2$-***).^{31}P NMR (202 MHz, CD_2Cl_2): δ 15.49.
Elemental analysis: Anal. Calcd for $C_{57}H_{38}BF_{24}NiO_3P$: C, 51.58; H, 2.89. Found: C, 51.44; H, 2.88.



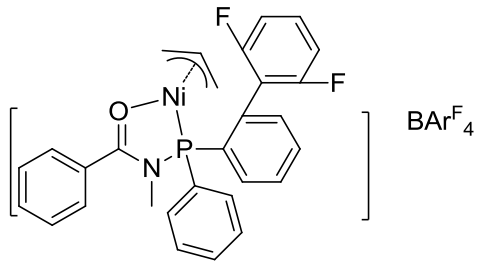
Ni2: Similar procedure was employed with mixing **L2** (124.6 mg, 0.328 mmol), [Ni(allyl)Cl]$_2$ (44 mg, 0.164 mmol) and NaBAF (291 mg, 0.328 mmol). **Ni2** was obtained as a bright yellow solid (300 mg, 68.2%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78-7.64 (m, 8H), 7.64-7.56 (m, 3H), 7.54-7.41 (m, 7H), 7.22-7.01 (m, 6H), 5.55 (br, 1H, **allyl-*CH*-**), 4.87-4.39 (m, 0.64H, ***allyl -CH$_2$-***), 3.57-3.08 (m, 1.52H, ***allyl -CH$_2$-***), 3.87 (s, 6H, ***OMe***), 2.90 (d, *J* = 3.35, 3H, ***NMe***), 2.41-2.72 (m, 0.71H, ***allyl -CH$_2$-***). ^{13}C NMR (125 MHz, $CDCl_3$): δ 185.81 (d, *J* = 17.51), 161.84 (dd, *J* = 52.98, *J* = 52.98), 135.79 (s), 134.94 (s), 133.38 (s), 132.07 (s), 130.34 (s), 129.43 (s), 129.04 (d, *J* = 26.29), 127.59 (s), 125.77 (s), 123.60 (s), 122.54 (d, *J* = 12.45), 121.43 (s), 117.60 (d, *J* = 6.21), 116.70 (s), 112.22 (d, *J* = 8.37), 56.13 (s, ***OMe***), 36.11 (d, *J* = 2.87, ***NMe***).^{31}P NMR (202 MHz, $CDCl_3$): δ 86.37.
Elemental analysis: Anal. Calcd for $C_{57}H_{39}BF_{24}NNiO_3P$: C, 51.00; H, 2.93; N, 1.04. Found: C, 50.88; H, 2.99; N, 1.02.



Ni3: Similar procedure was employed with mixing **L3** (149.5 mg, 0.328 mmol), [Ni(allyl)Cl]$_2$ (44 mg, 0.164 mmol) and NaBAF (291 mg, 0.328 mmol) **Ni3** was obtained as a bright yellow solid (390 mg, 83.8%). ^{1}H NMR (125 MHz, $CDCl_3$): δ 8.10-7.89 (m, 2H), 7.85-7.71 (m, 3H), 7.70-7.66 (m, 8H), 7.65-7.59 (m, 2H), 7.53-7.46 (m, 6H), 7.41-7.31 (m, 3H), 5.83 (br, 0.78H, **allyl-*CH*-**), 4.97-4.80 (m, 0.78H, ***allyl -CH$_2$-***), 3.82-3.60 (m, 0.34H, ***allyl -CH$_2$-***), 3.55-3.44 (m, 0.48H, ***allyl -CH$_2$-***), 3.39-3.27 (m, 0.31H, ***allyl -CH$_2$-***), 2.80 (d, *J* = 4.81, 3H, ***NMe***), 2.51-2.31 (m, 0.28H, ***allyl -CH$_2$-***), 2.15-2.01 (m, 0.44H, ***allyl -CH$_2$-***). ^{13}C NMR (125 MHz, $CDCl_3$): δ 186.74 (d, *J* = 19.40), 161.82 (dd, *J* = 51.68, *J* = 45.70), 134.92 (s), 134.63 (s), 133.94 (d, *J* = 28.06), 132.90 (d, *J* = 9.62), 130.41 (d, *J* = 5.00), 129.55 (s), 129.16 (br), 128.92 (br), 127.91 (s), 127.41 (s), 125.74 (s), 123.57 (s), 121.41 (s), 117.62 (br), 36.37 (s, ***NMe***). ^{31}P NMR (202 MHz, $CDCl_3$): δ 90.34, 89.11.
Elemental analysis: Anal. Calcd for $C_{54}H_{28}BF_{30}NNiOP$: C, 47.09; H, 2.05; N, 1.02. Found: C, 47.20; H, 2.09; N, 1.05.

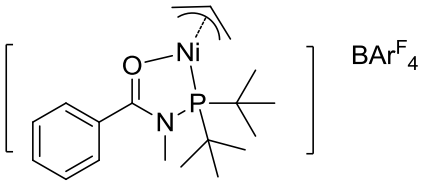


Ni4: Similar procedure was employed with mixing **L4** (99.6 mg, 0.219 mmol), [Ni(allyl)Cl]$_2$ (29.3 mg, 0.11 mmol) and NaBAF (193.7 mg, 0.219 mmol). **Ni4** was obtained as a bright yellow solid (210 mg, 67.7%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78-7.66 (m, 9H), 7.65-7.42 (m, 16H), 7.42-7.29 (m, 2H), 6.72 (m, 2H), 5.35 (br, 0.4H, **allyl-*CH*-**), 4.57-4.39 (m, 0.78H, ***allyl* -*CH*$_2$-**), 4.25 (br, 0.35H, **allyl-*CH*-**), 3.75 (s, 3H, ***OMe***), 3.36 (s, 3H, ***OMe***), 3.16 (s, 3H, ***NMe***), 2.86-2.76 (m, 0.38H, **allyl -*CH*$_2$-**), 2.53-2.31 (m, 0.83H, **allyl -*CH*$_2$-**), 1.45-1.35 (m, 0.46H, **allyl -*CH*$_2$-**). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.84 (dd, *J* = 49.60, *J* = 44.70), 134.94 (s), 134.52 (s), 134.04 (s), 133.79 (d, *J* = 3.80), 132.58 (s), 131.34 (s), 130.47 (d, *J* = 9.70), 130.20 (d, *J* = 16.02), 129.64 (d, *J* = 2.89), 129.28 (s), 129.15 (br), 128.90 (s), 128.22 (br), 127.94 (s), 126.25 (s), 125.85 (s), 125.77 (s), 123.61 (s), 121.44 (s), 117.60 (br), 105.15 (s), 56.25 (s, ***OMe***), 35.58 (s, ***NMe***). ^{31}P NMR (202 MHz, $CDCl_3$): δ 91.82, 90.66.
Elemental analysis: Anal. Calcd for $C_{63}H_{43}BF_{24}NNiO_3P$: C, 53.34; H, 3.06; N, 0.99. Found: C, 53.20; H, 3.01; N, 0.94.



Ni5: Similar procedure was employed with mixing **L5** (160 mg, 0.28 mmol, actually), [Ni(allyl)Cl]$_2$ (26.5 mg, 0.14 mmol) and NaBAF (175.4 mg, 0.28 mmol). **Ni5** was obtained as a bright yellow solid (150 mg, 38.3%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84-7.76 (m, 1H), 7.72-7.67 (m, 11H), 7.66-7.57 (m, 6H), 7.55-7.46 (m, 11H), 5.38 (br, 0.39H, **allyl-*CH*-**), 4.81-4.71 (m, 0.35H, ***allyl* -*CH*$_2$-**), 4.60-4.53 (m, 0.31H, allyl **-*CH*$_2$-**), 4.35 (br, 0.41H, **allyl-*CH*-**), 3.37-3.29 (m, 0.43H, ***allyl* -*CH*$_2$-**), 3.12 (s, 3H, ***NMe***), 3.07-3.00 (m, 1H, ***allyl* -*CH*$_2$-**), 2.72-2.65 (m, 0.39H, **allyl -*CH*$_2$-**), 2.49-2.41 (m, 0.34H, **allyl -*CH*$_2$-**), 1.60-1.52 (m, 0.38H, ***allyl* -*CH*$_2$-**),1.48-1.40 (m, 0.46H, **allyl -*CH*$_2$-**). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.84 (dd, *J* = 49.60, *J* = 50.16), 136.40 (s), 136.24 (s), 134.96 (s), 133.79 (3), 133.11 (s), 131.98 (q), 130.73 (br), 130.14 (d, *J* = 11.24), 129.56 (s), 129.43 (m), 129.15 (br), 128.90 (br), 128.64 (br), 127.94 (s),

126.76 (s), 125.84 (s), 125.22 (s), 124.85 (s), 123.61 (s), 121.44 (s), 117.59 (br), 35.58 (s, ***NMe***).^{31}P NMR (202 MHz, $CDCl_3$): δ 90.98, 89.83.
Elemental analysis: Anal. Calcd for $C_{61}H_{37}BF_{26}NNiOP$: C, 52.54; H, 2.67; N, 1.00. Found: C, 52.40; H, 2.60; N, 0.97.



Ni6: Similar procedure was employed with mixing **L6** (100 mg, 0.28 mmol, actually), $[Ni(allyl)Cl]_2$ (26.5 mg, 0.14 mmol) and NaBAF (175.4 mg, 0.28 mmol). **Ni6** was obtained as a bright yellow solid (180 mg, 51.8%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73-7.67 (m, 89H), 7.62-7.58 (m, 1H), 7.53-7.46 (m, 6H), 7.35-7.29 (m, 2H), 5.63 (br, 1H, **allyl-*CH*-**), 4.78-4.72 (m, 1H, ***allyl -CH$_2$-***), 3.59 (dd, *J* = 6.84, *J* = 6.40, 1H, ***allyl -CH$_2$-***)), 3.31 (m, 1H, ***allyl -CH$_2$-***), 3.29 (d, *J* = 2.45, 1H, ***NMe***), 2.02 (d, *J* = 12.92, 1H, ***allyl -CH$_2$-***), 1.55 (d, *J* = 17.84, 9H), 1.36 (d, *J* = 16.29, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.11 (d, *J* = 11.19), 161.85 (dd, *J* = 48.99, *J* = 48.99), 134.93 (s), 133.32 (s), 130.12 (s), 129.61 (s), 129.44 (br), 129.18 (br), 128.93 (br), 128.68 (br), 127.94 (s), 126.81 (s), 125.77 (s), 123.61 (s), 121.44 (s), 117.63 (br), 117.22 (s), 79.33 (d, *J* = 19.48), 46.48 (d, *J* = 2.22), 39.70 (d, *J* = 3.68), 39.36 (dd, J = 7.26, J = 6.99), 29.39 (dd, J = 5.96, J = 6.77). ^{31}P NMR (202 MHz, $CDCl_3$): δ 146.16.
Elemental analysis: Anal. Calcd for $C_{51}H_{43}BF_{24}NNiOP$: C, 49.31; H, 3.49; N, 1.13. Found: C, 49.17; H, 3.43; N, 1.10.

General produces for the polymerization

Homopolymerization of ethylene: In a typical experiment, a 150 mL glass pressure reactor connected with a high pressure gas line was added 48 mL of toluene, then adjusted to the desired polymerization temperature. The desired amount of catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe under N_2. With a rapid stirring, the reactor was pressurized and maintained at 8 atm of ethylene. After the desired amount of time, the pressure reactor was vented and the polymer was precipitated in ethanol, filtered and dried at 50 ℃ for at least 24 h under vacuum.

Copolymerization of ethylene and polar monomers: a 150 mL glass pressure reactor connected with a high pressure gas line was added 17 mL of toluene, then adjusted to the desired polymerization temperature. The desired amount of polar monomers and catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system respectively via syringe under N_2. With a rapid stirring, the reactor was pressurized and maintained at 8 atm of ethylene. After the desired amount of time, the pressure reactor was vented and the polymer was precipitated in ethanol, filtered and dried at 50 ℃ for at least 24 h under vacuum.

NMR figures of ligands and catalysts

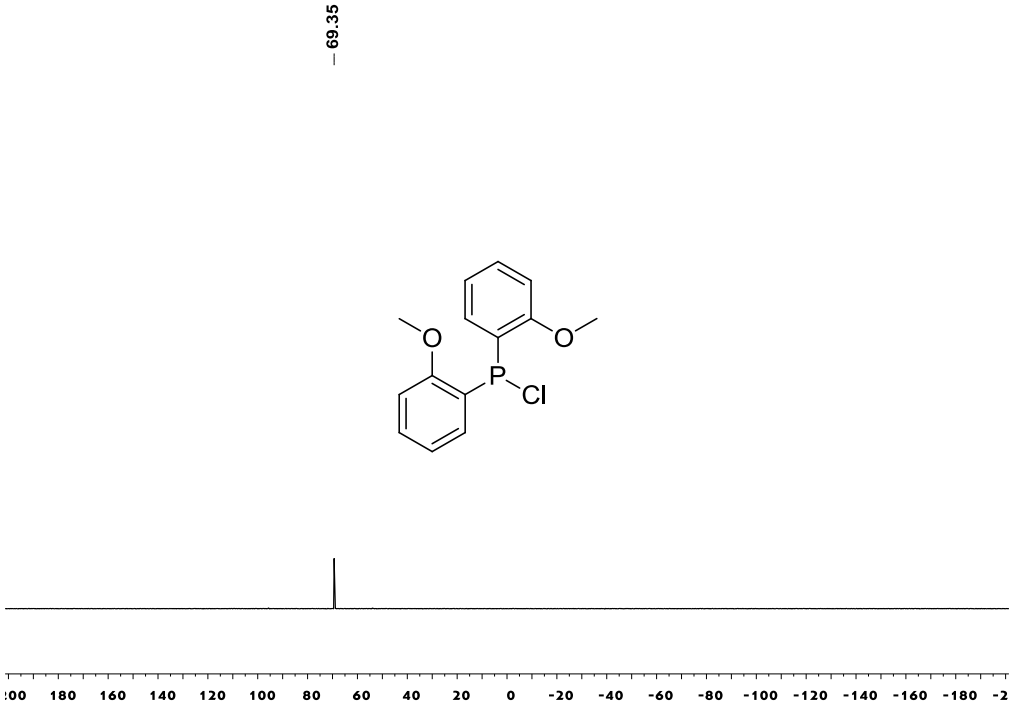


Figure S1. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of Chlorobis(2,6-dimethoxyphenyl)phosphine

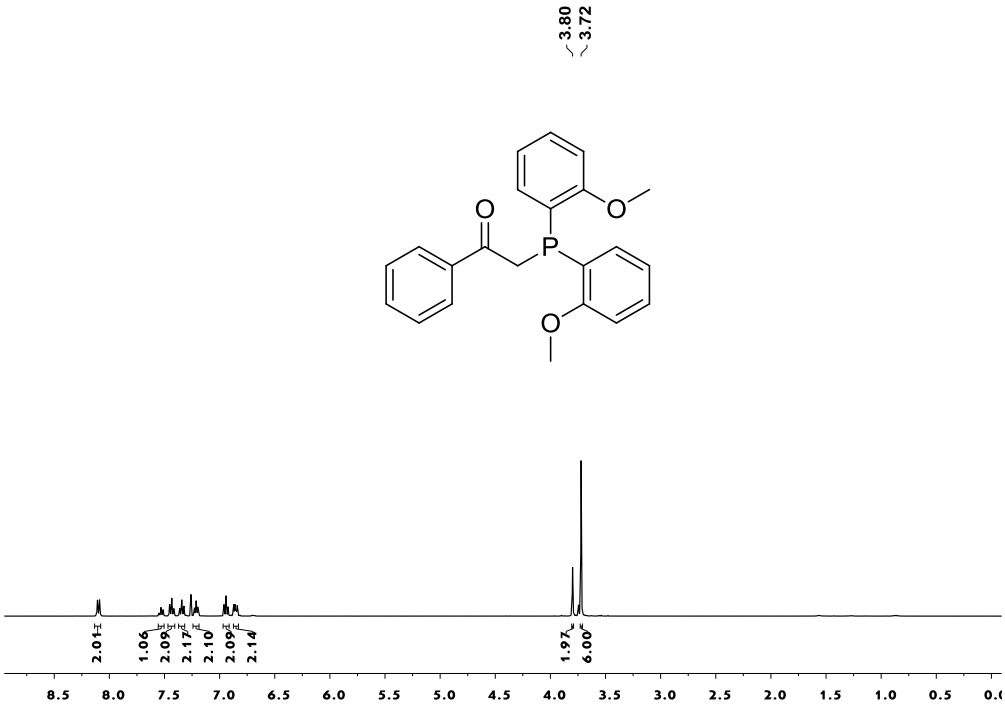


Figure S2. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **L1**

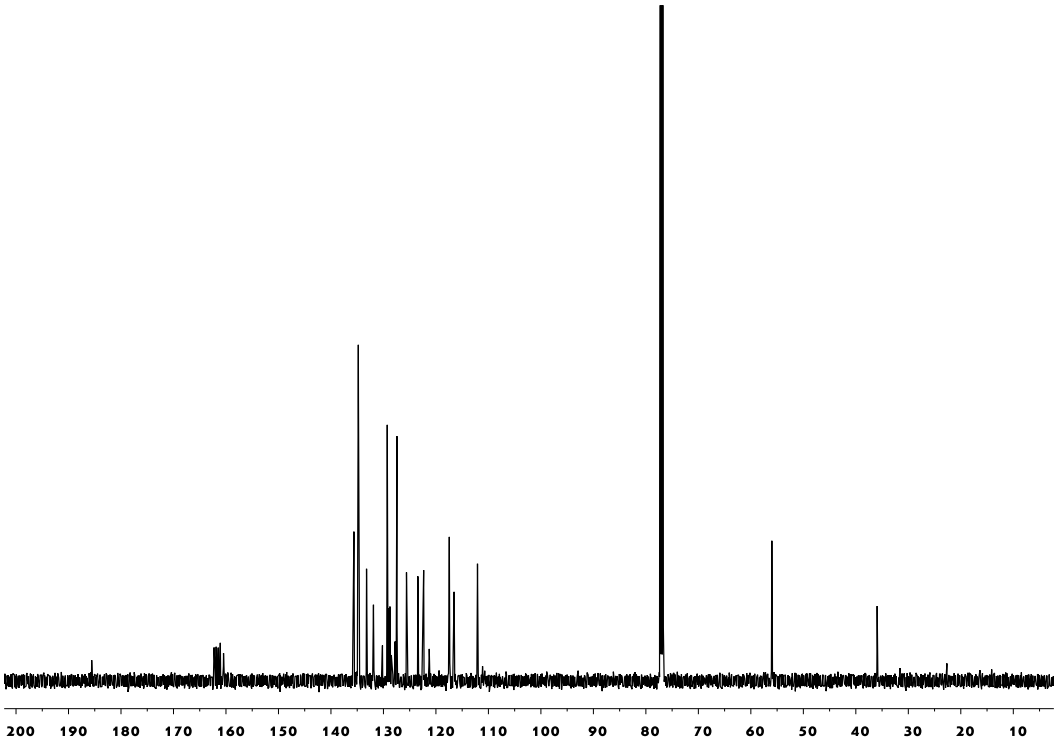


Figure S3. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **L1**

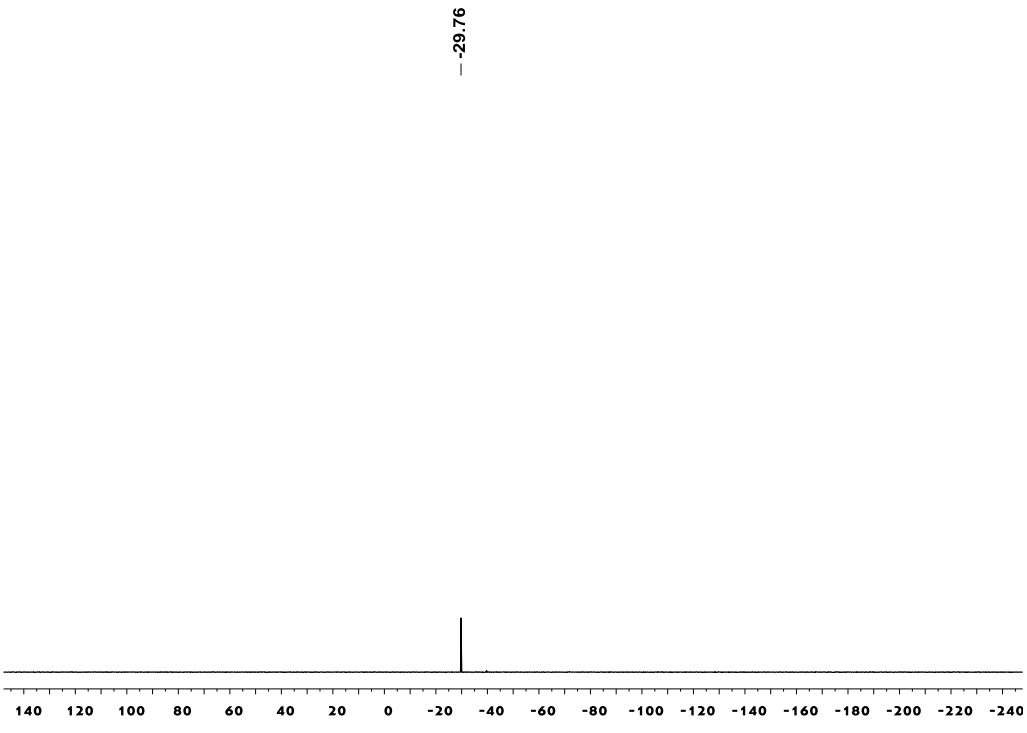


Figure S4. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **L1**

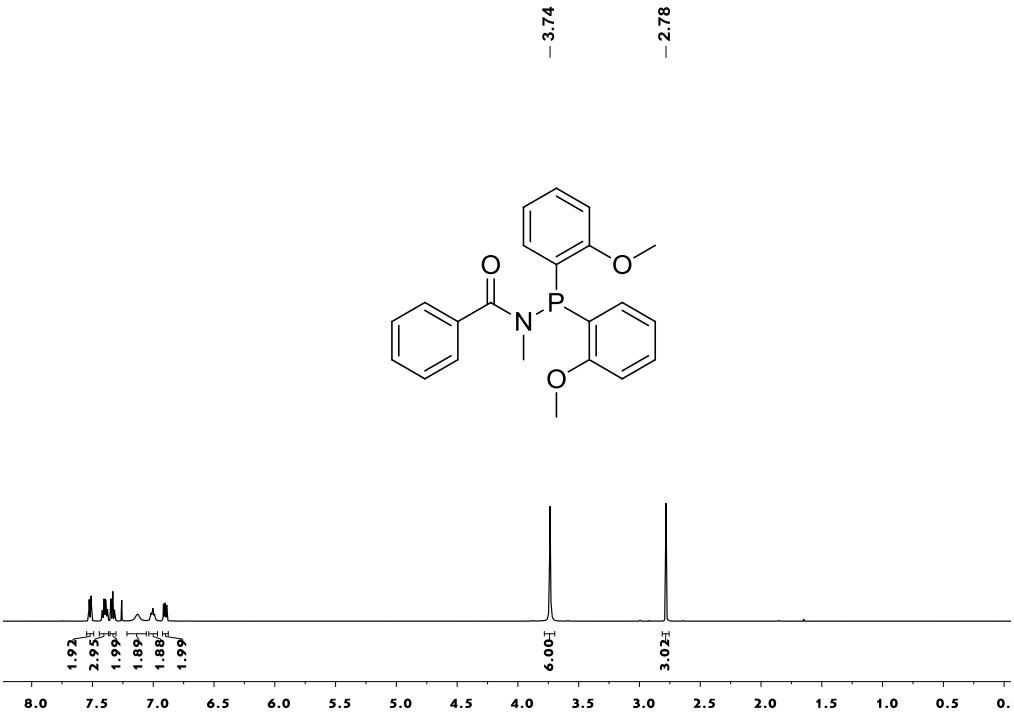


Figure S5. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **L2**

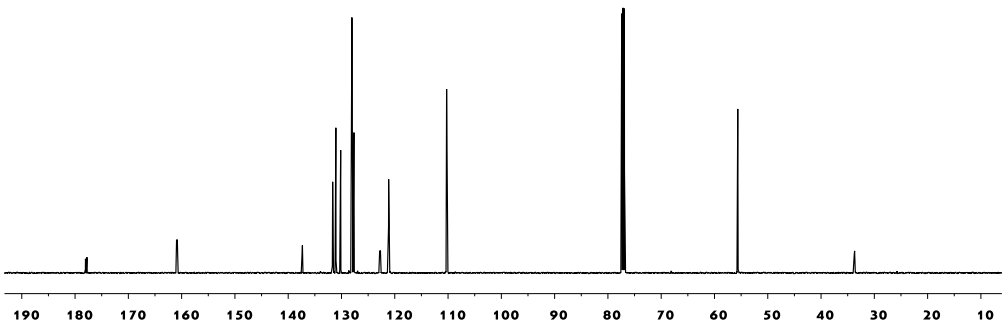


Figure S6. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **L2**

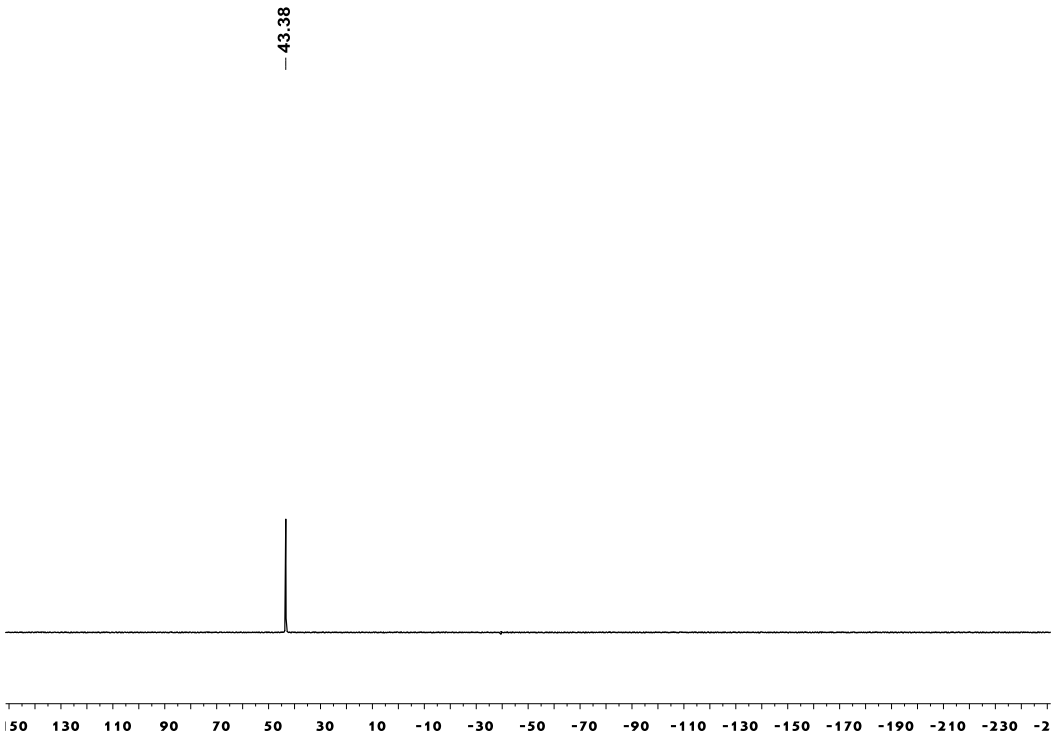


Figure S7. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **L2**

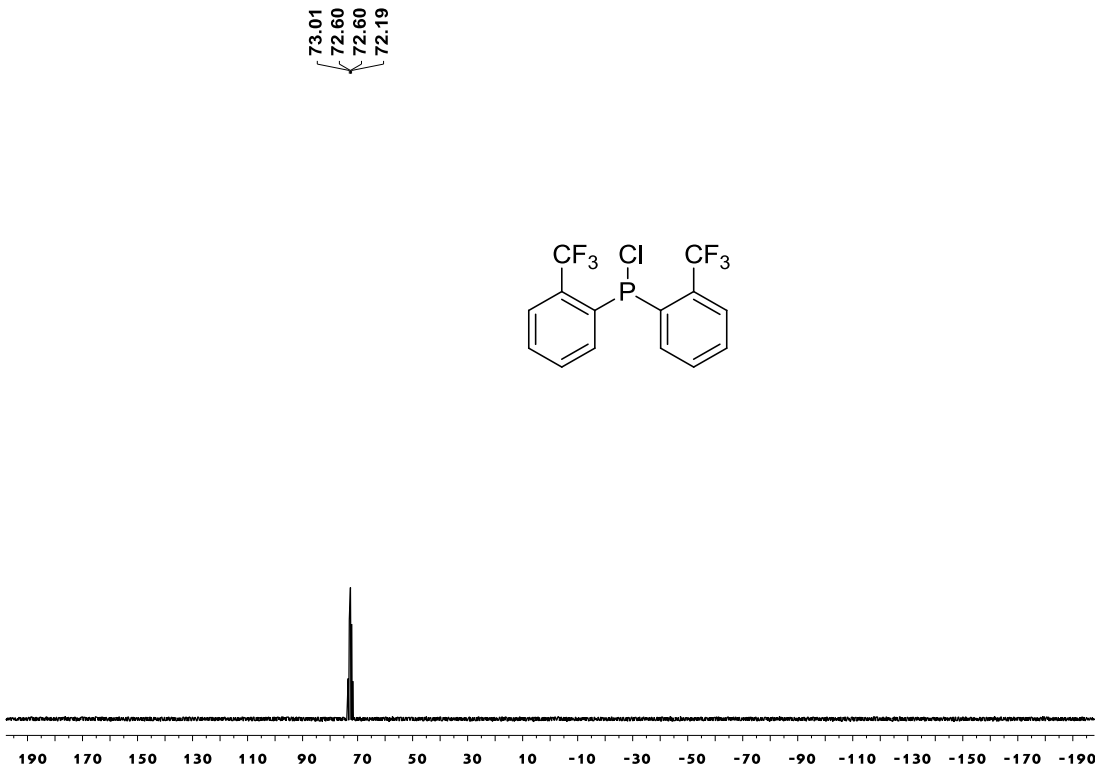


Figure S8. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of Chlorobis(2-(trifluoromethyl)phenyl)phosphine

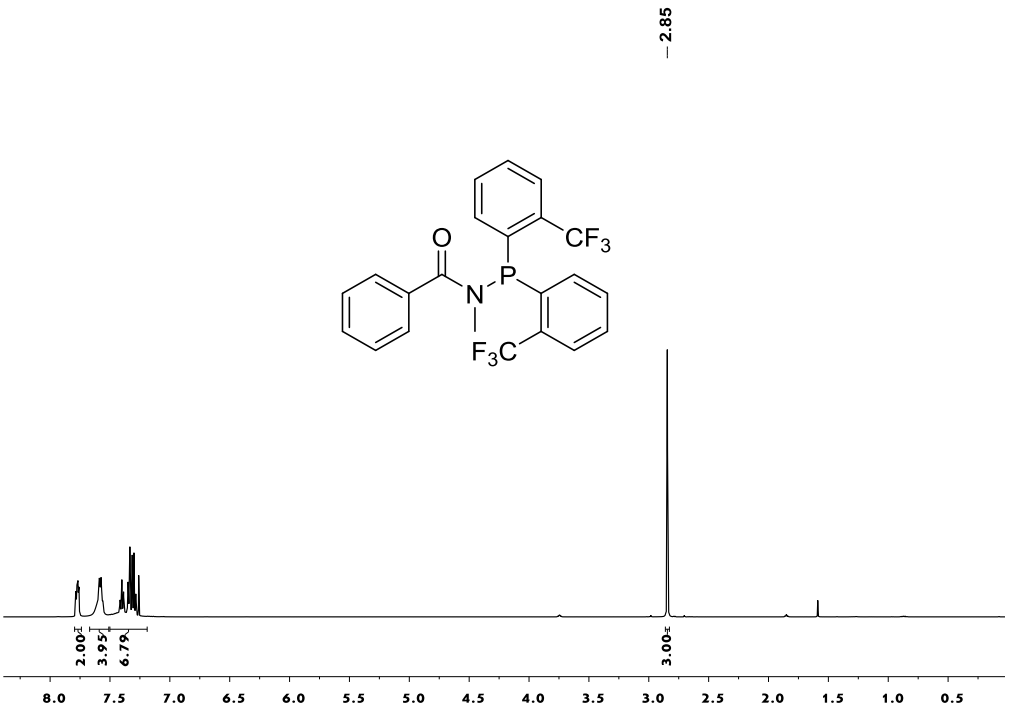


Figure S9. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **L3**

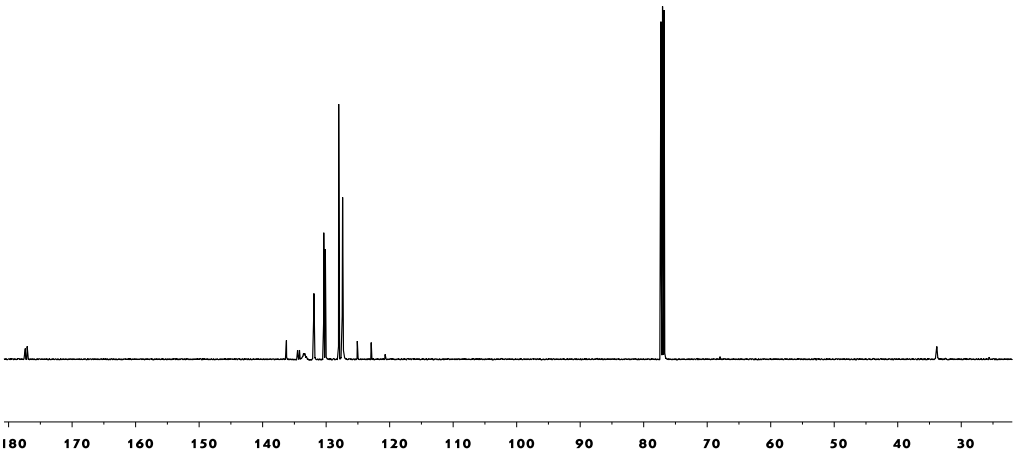


Figure S10. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **L3**

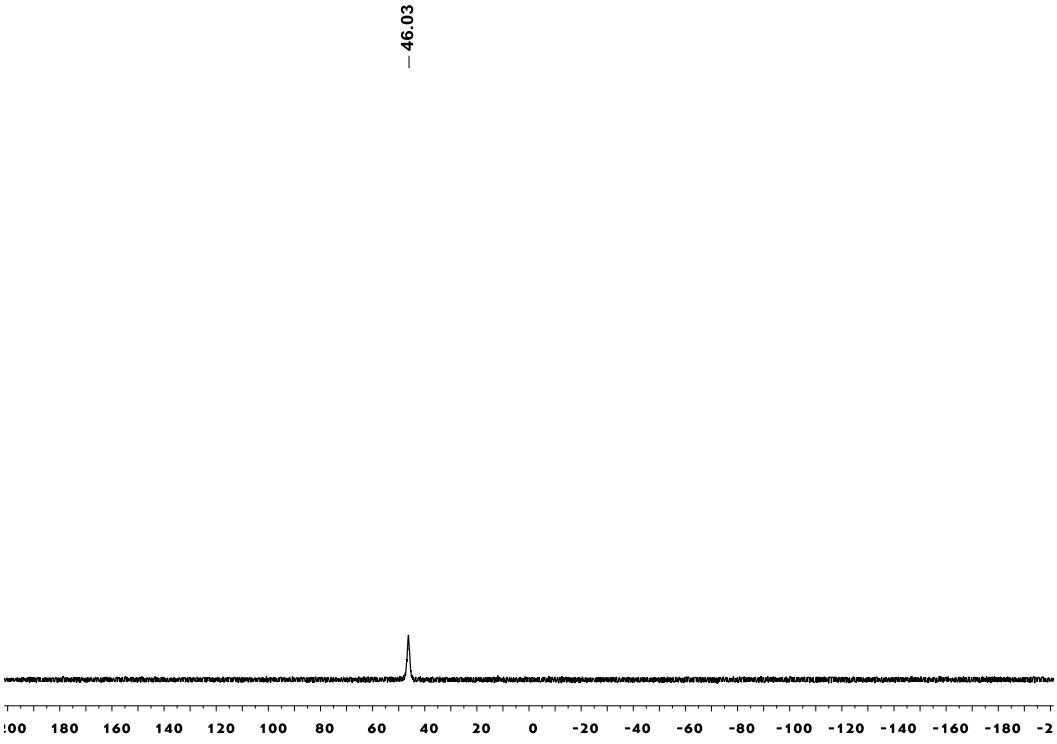


Figure S11. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **L3**

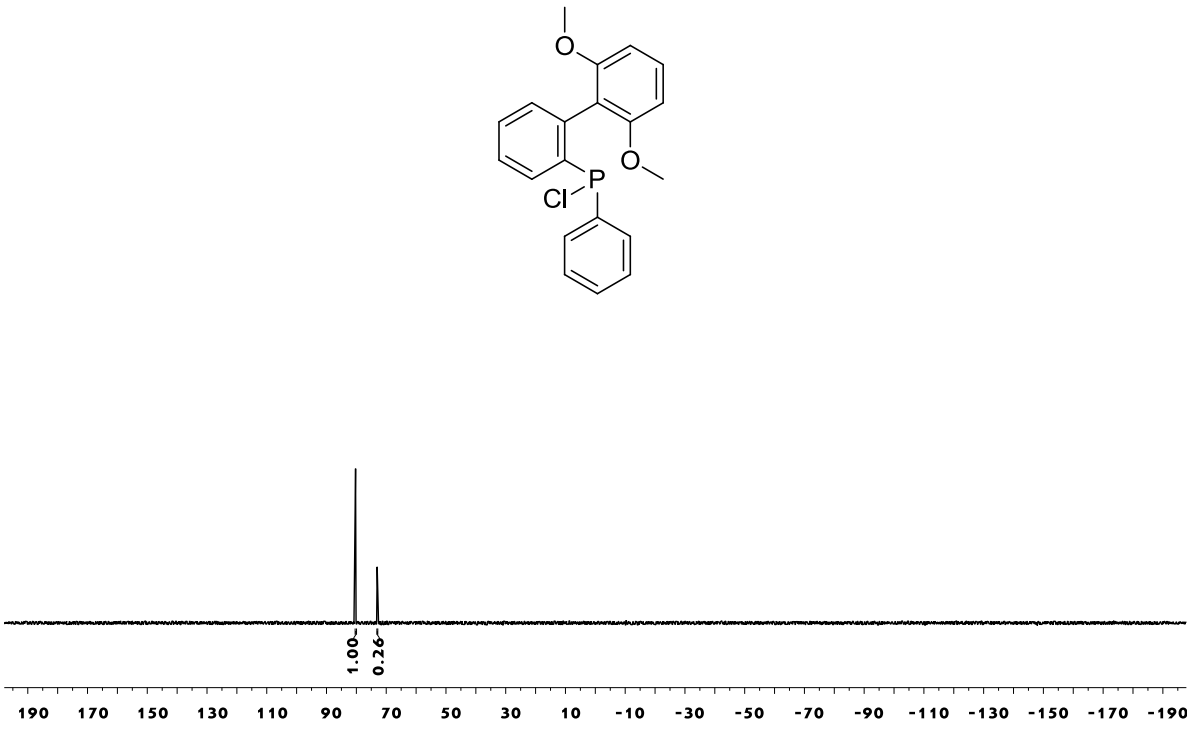


Figure S12. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of (2', 6'-dimethoxybiphenyl-2-yl)phenylphosphine chloride

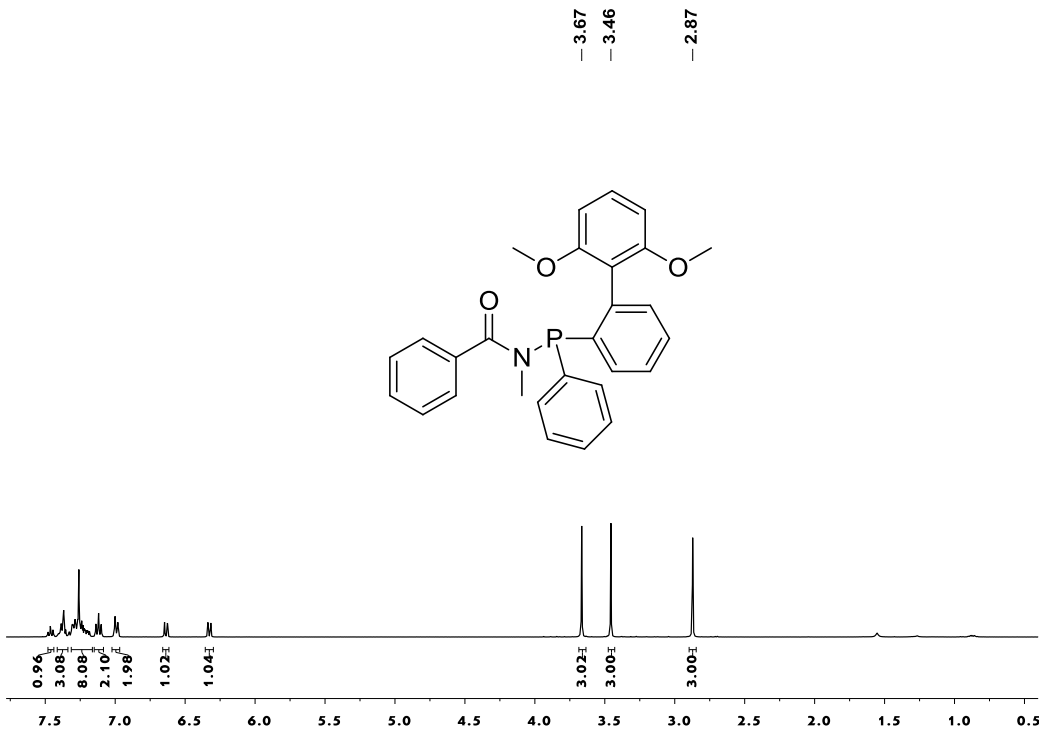


Figure S13. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **L4**

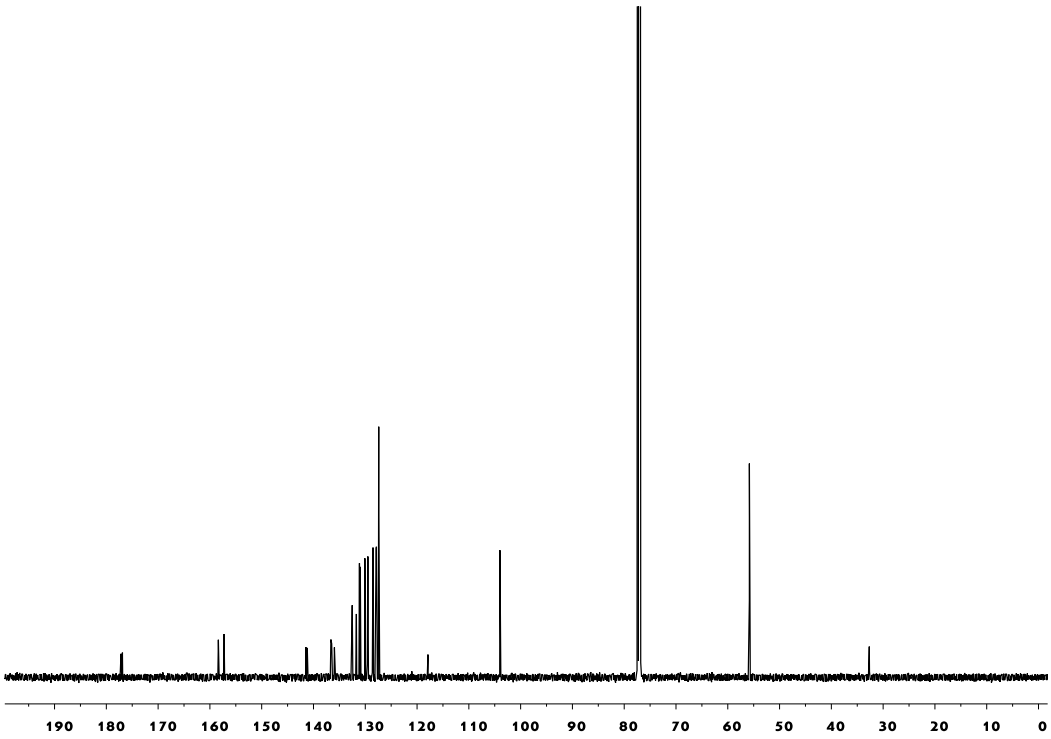


Figure S14. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **L4**

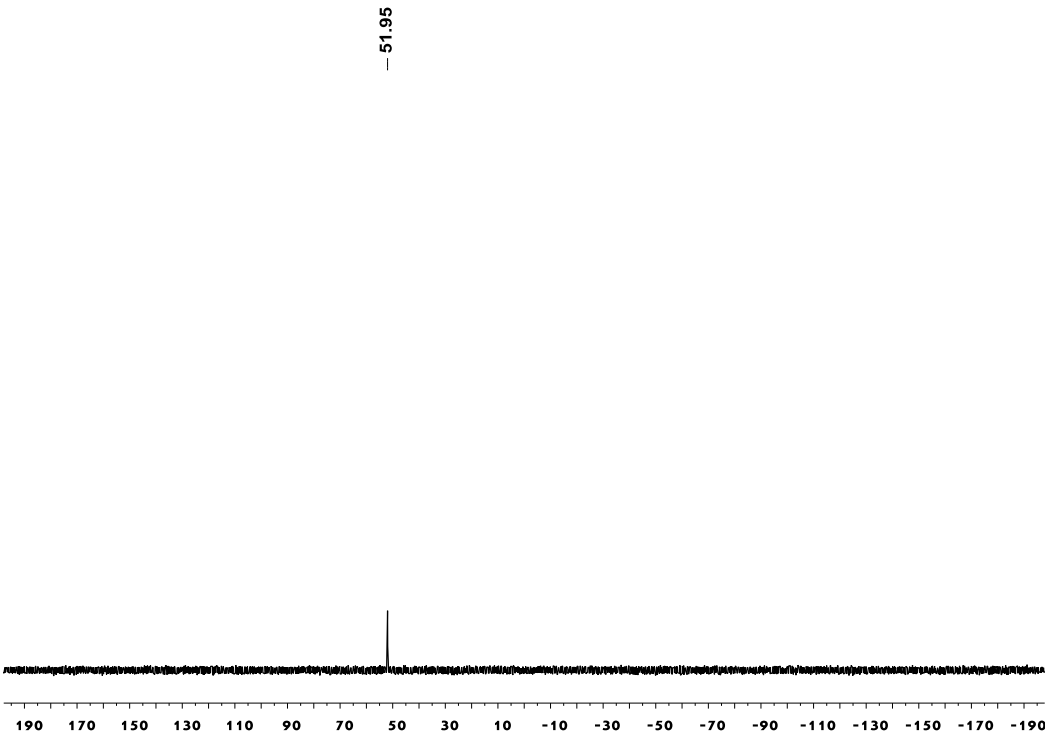


Figure S15. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **L4**

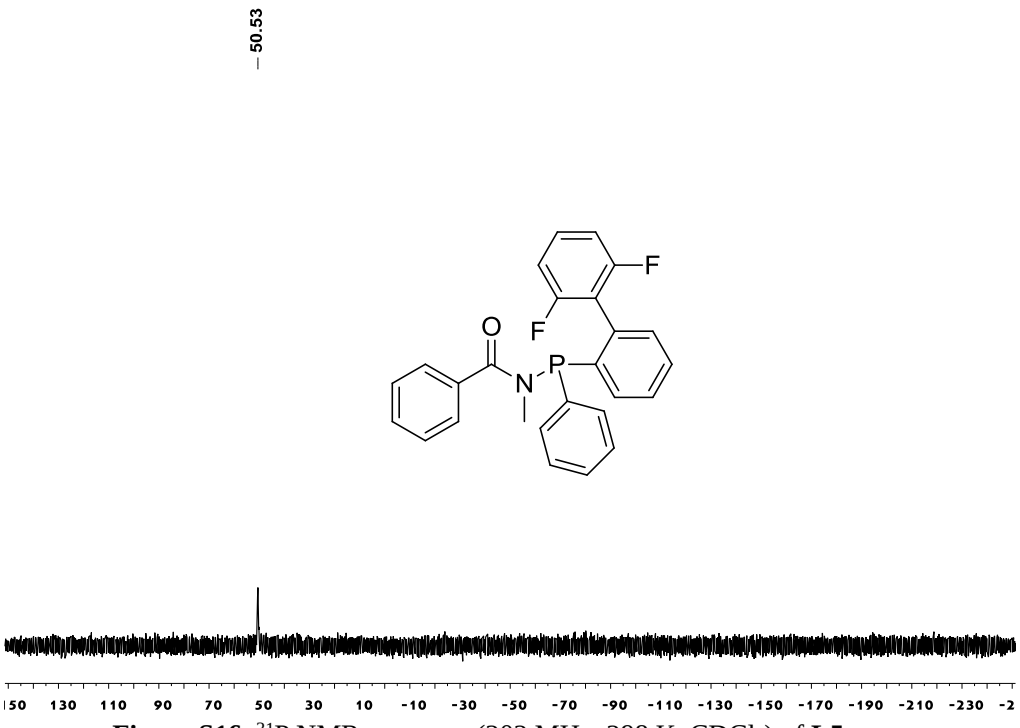


Figure S16. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **L5**

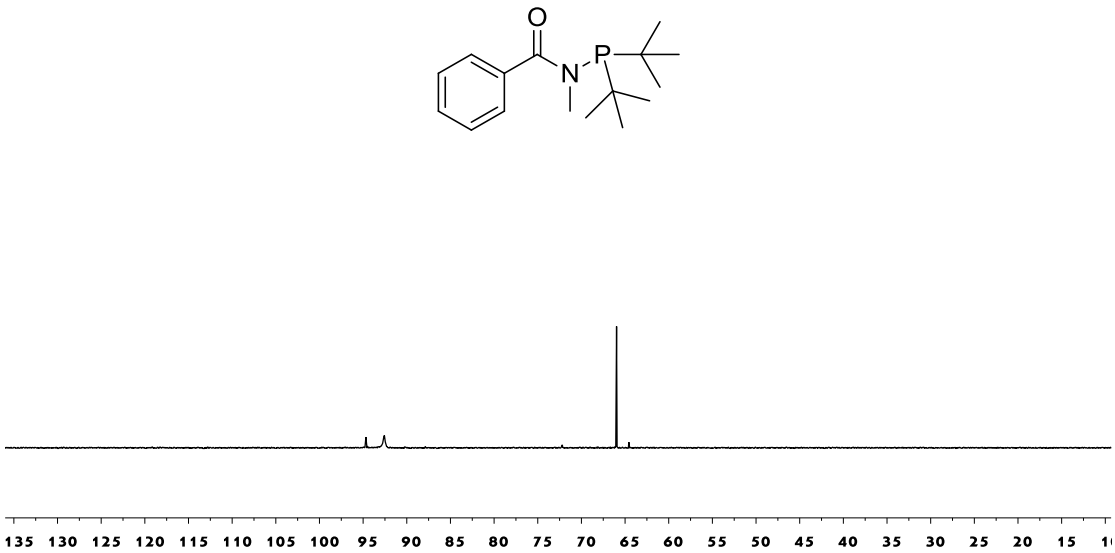


Figure S17. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **L6**

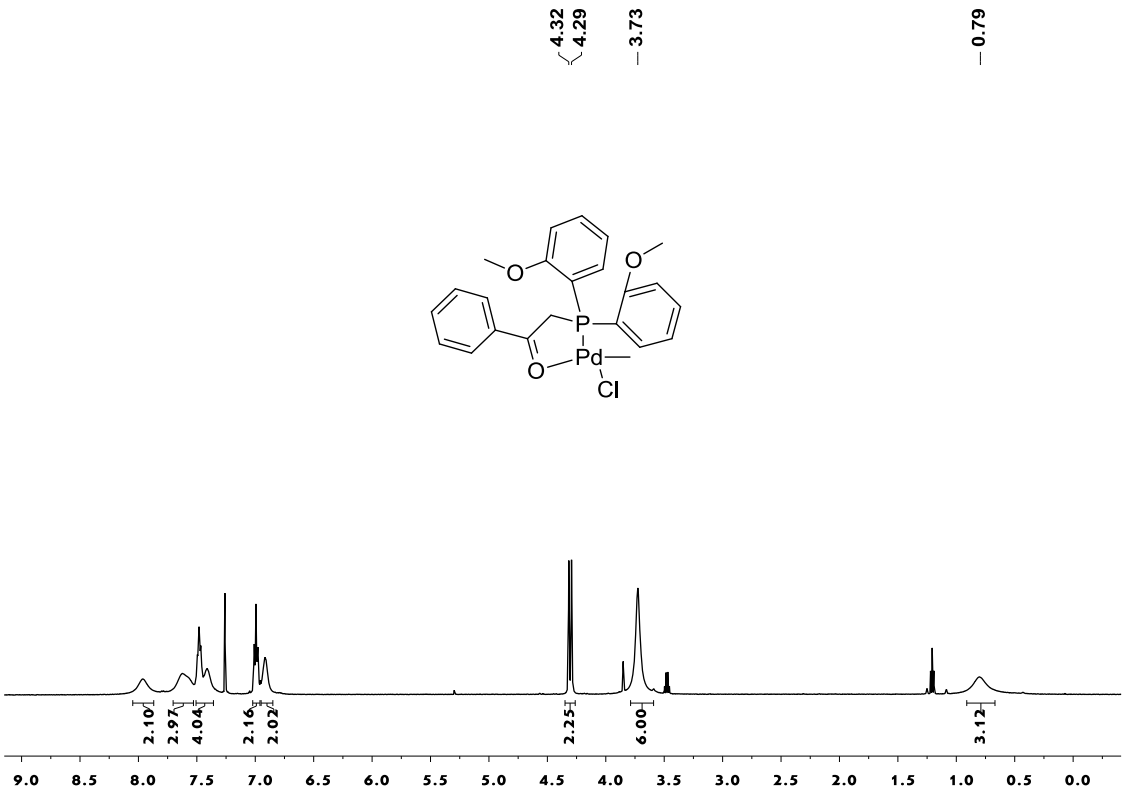


Figure S18. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **Pd1**

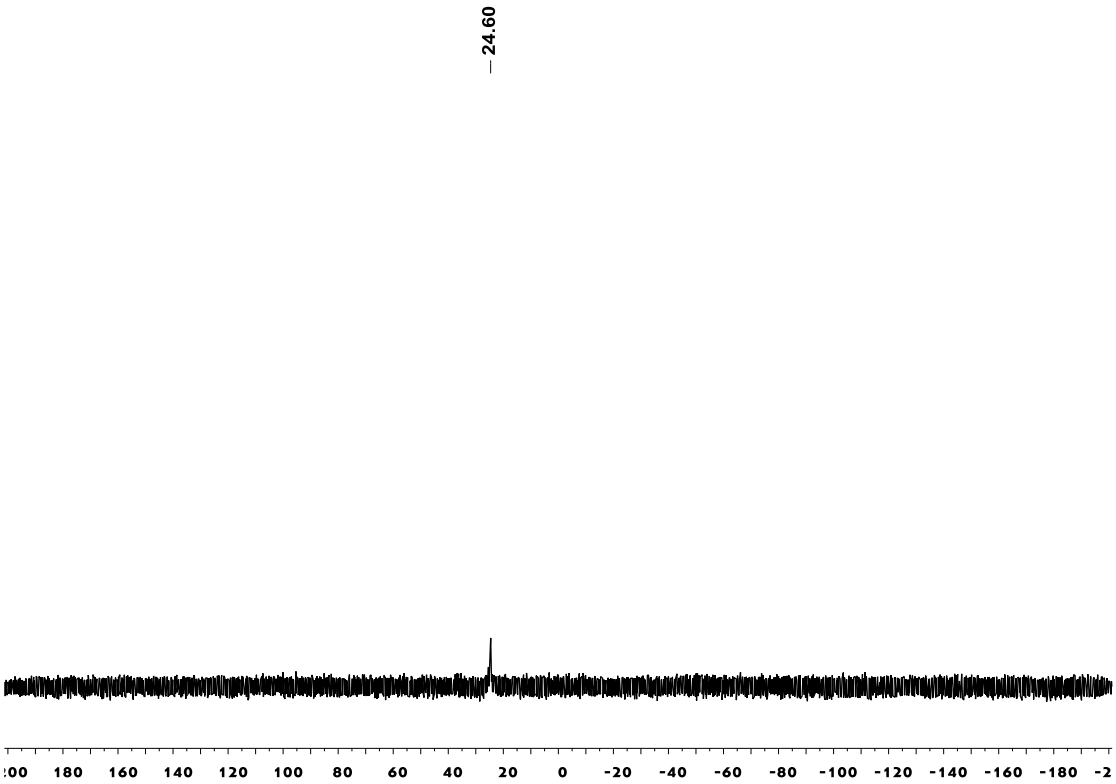


Figure S19. ^{31}P NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **Pd1**

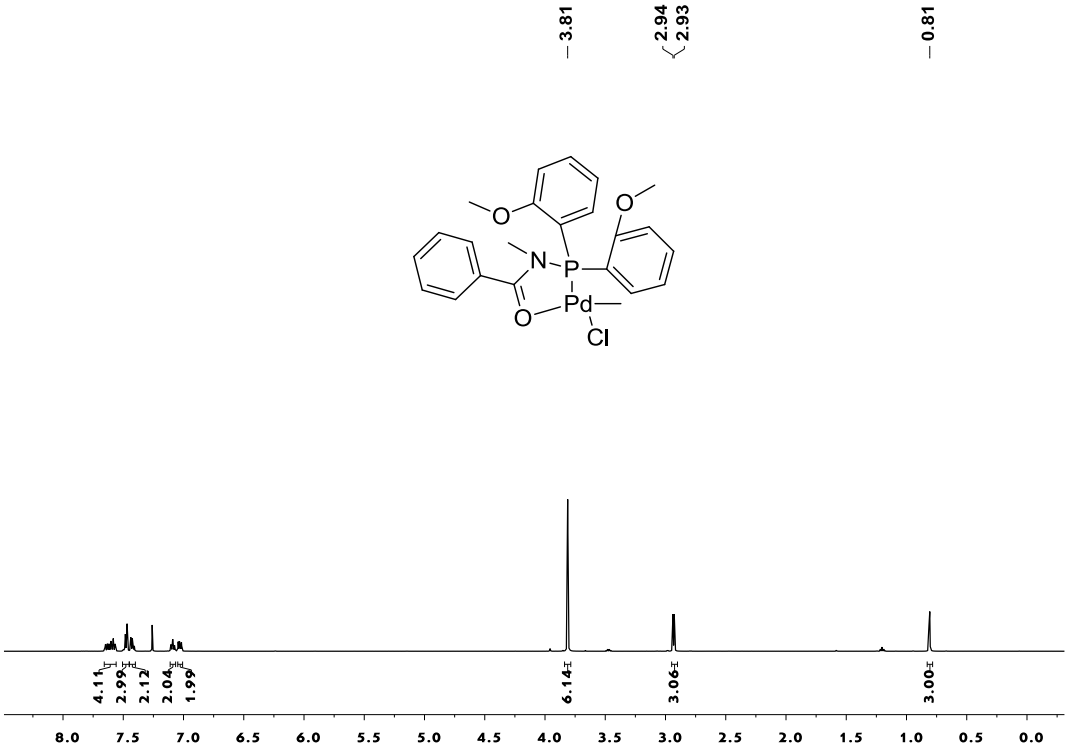


Figure S20. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **Pd2**

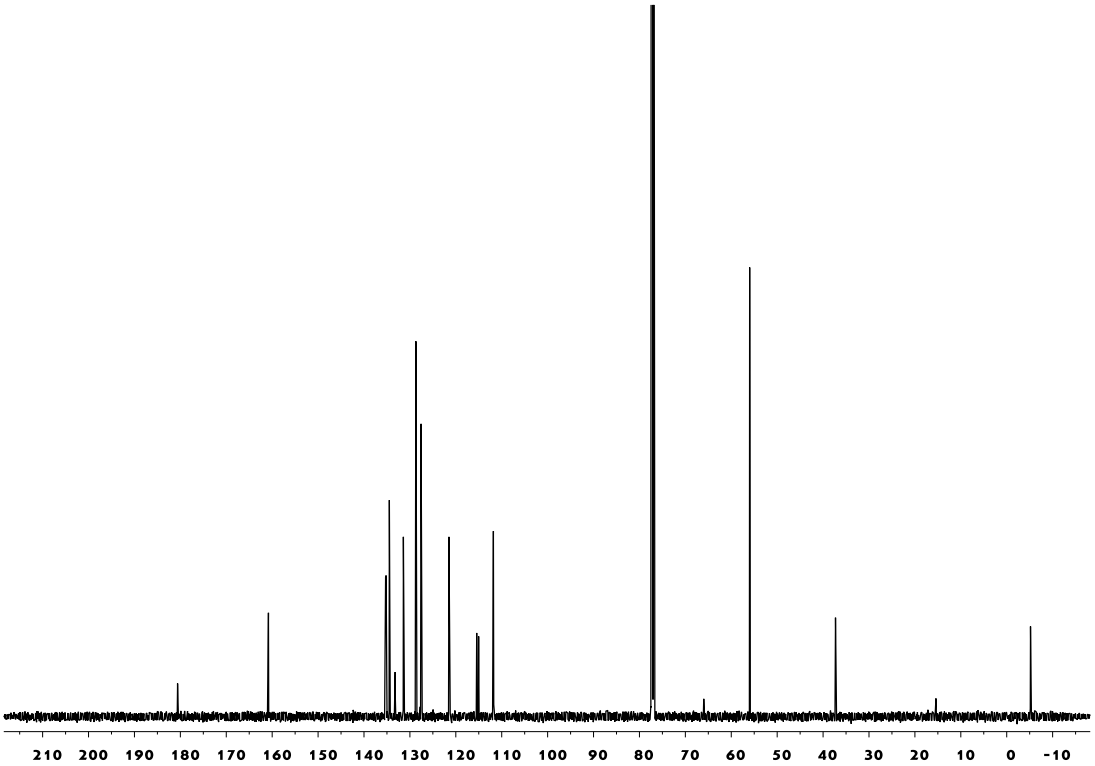


Figure S21. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **Pd2**

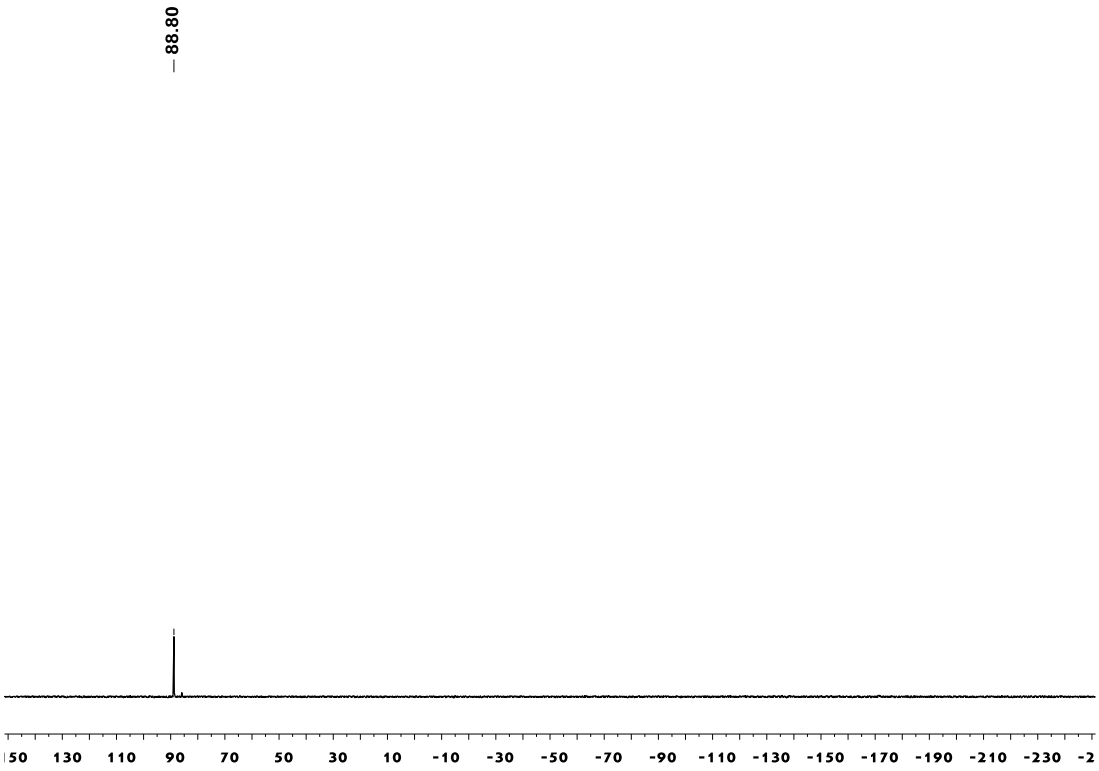


Figure S22. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Pd2**

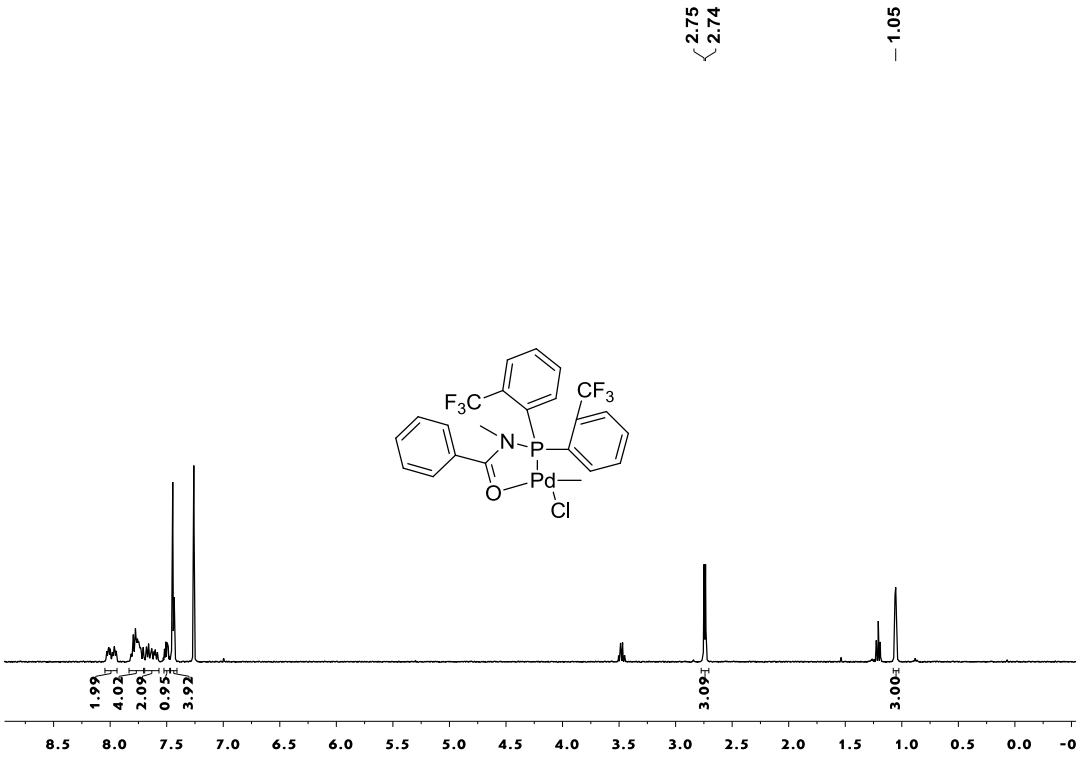


Figure S23. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **Pd3**

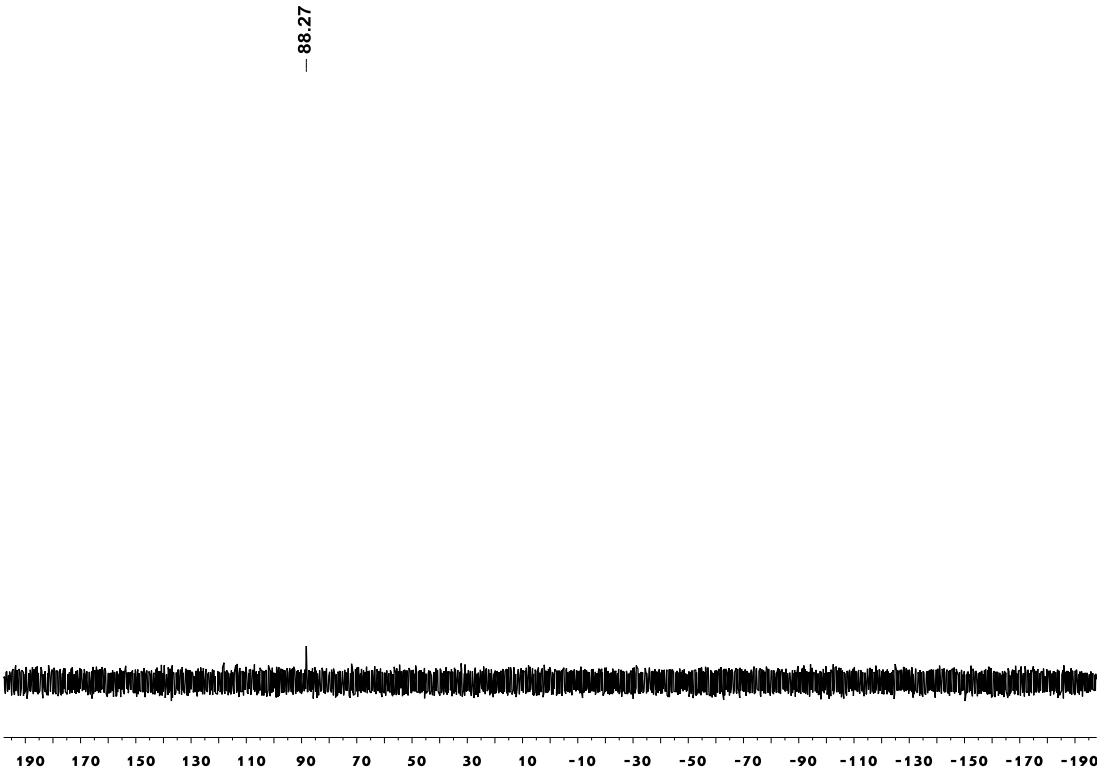


Figure S24. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Pd3**

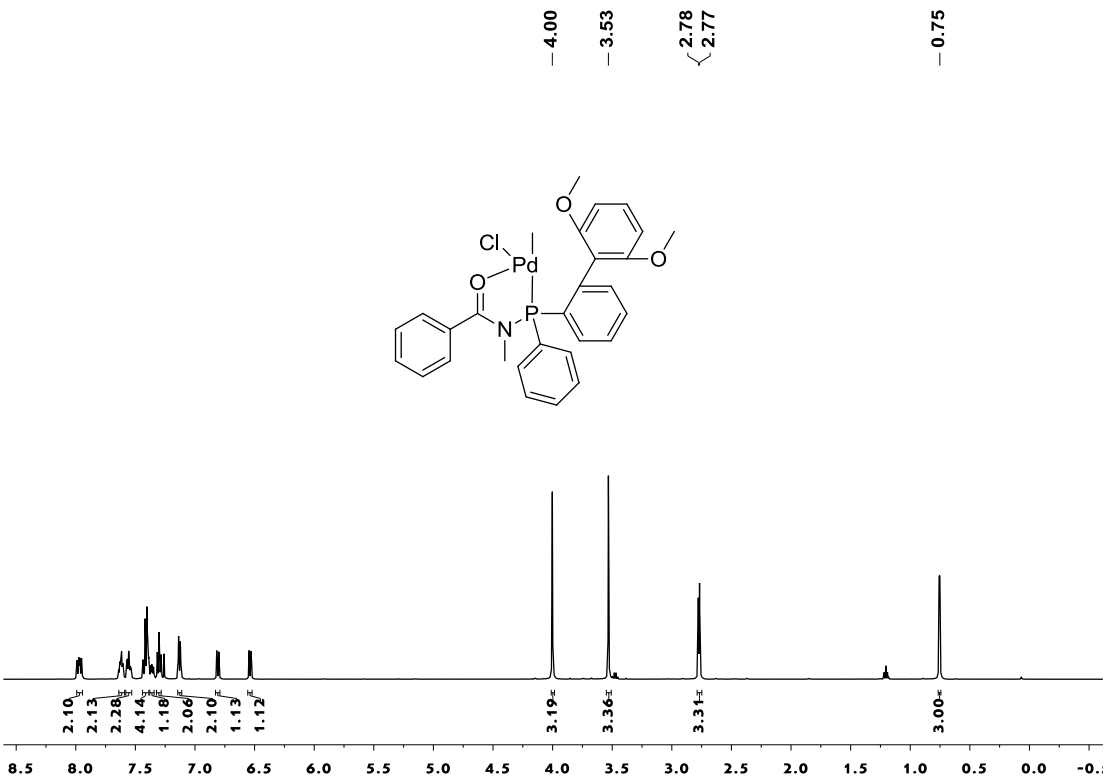


Figure S25. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **Pd4**

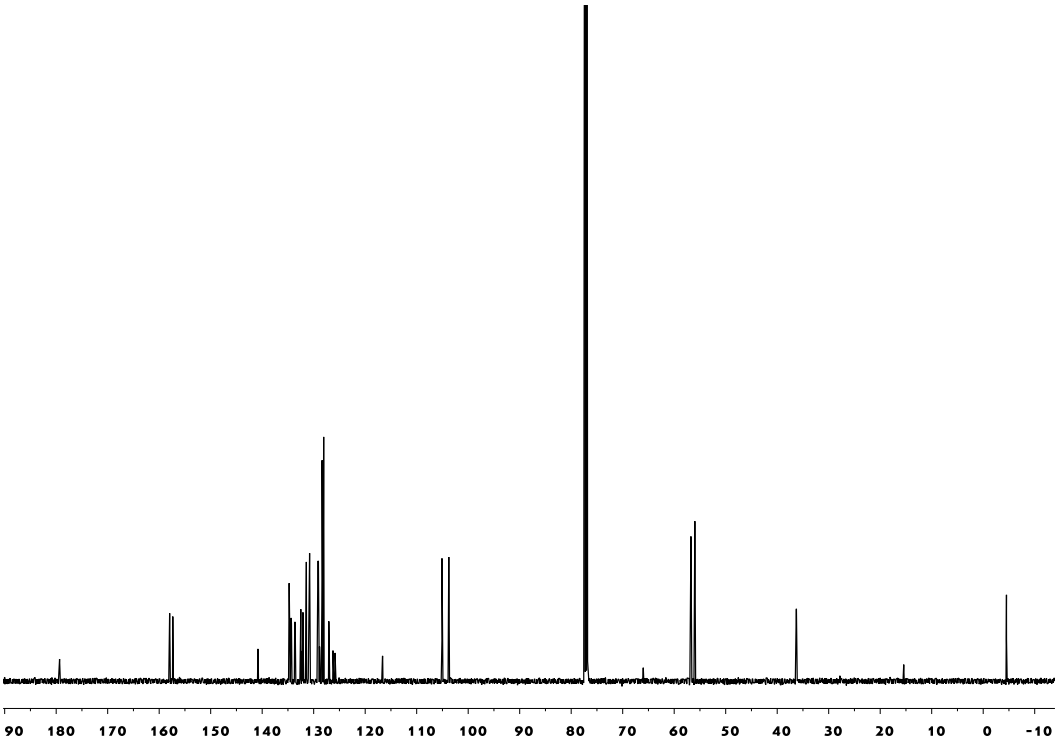


Figure S26. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **Pd4**

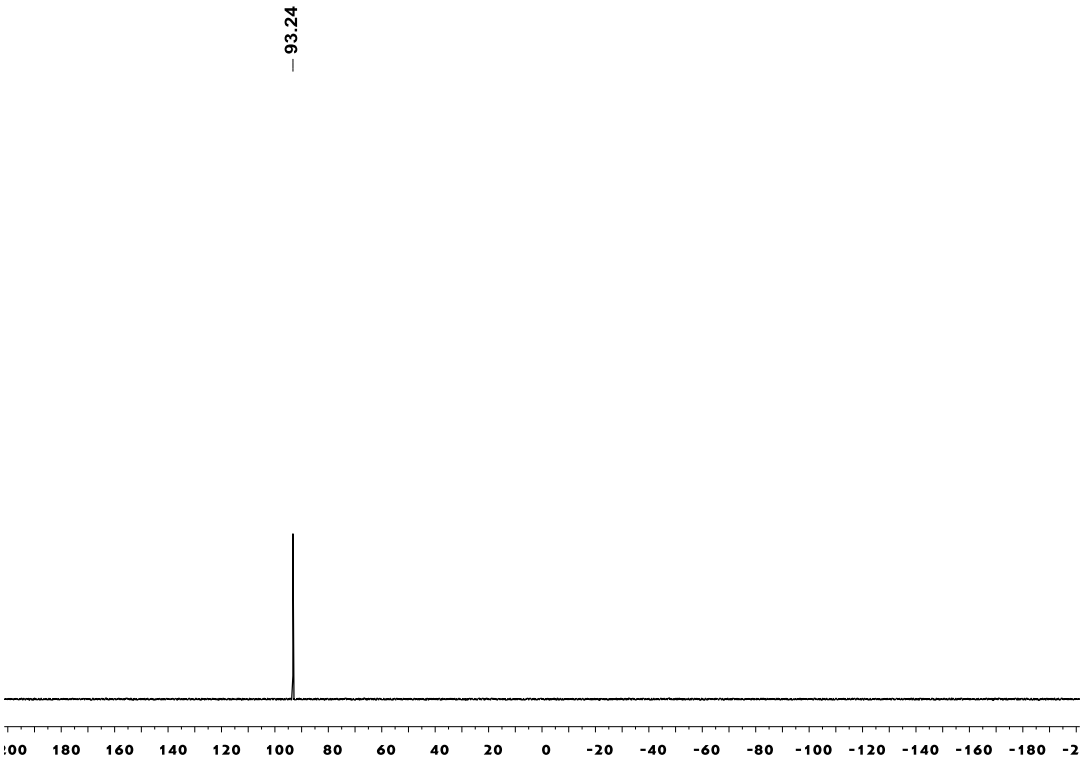


Figure S27.[31]P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Pd4**

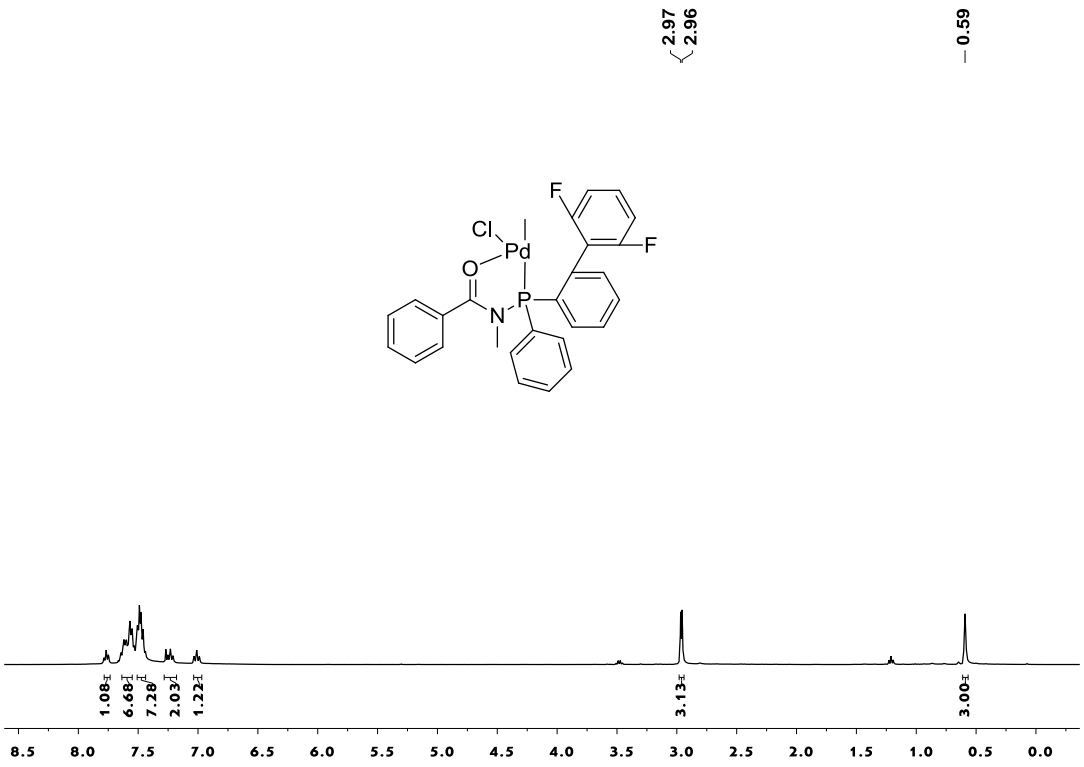


Figure S28. [1]H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **Pd5**

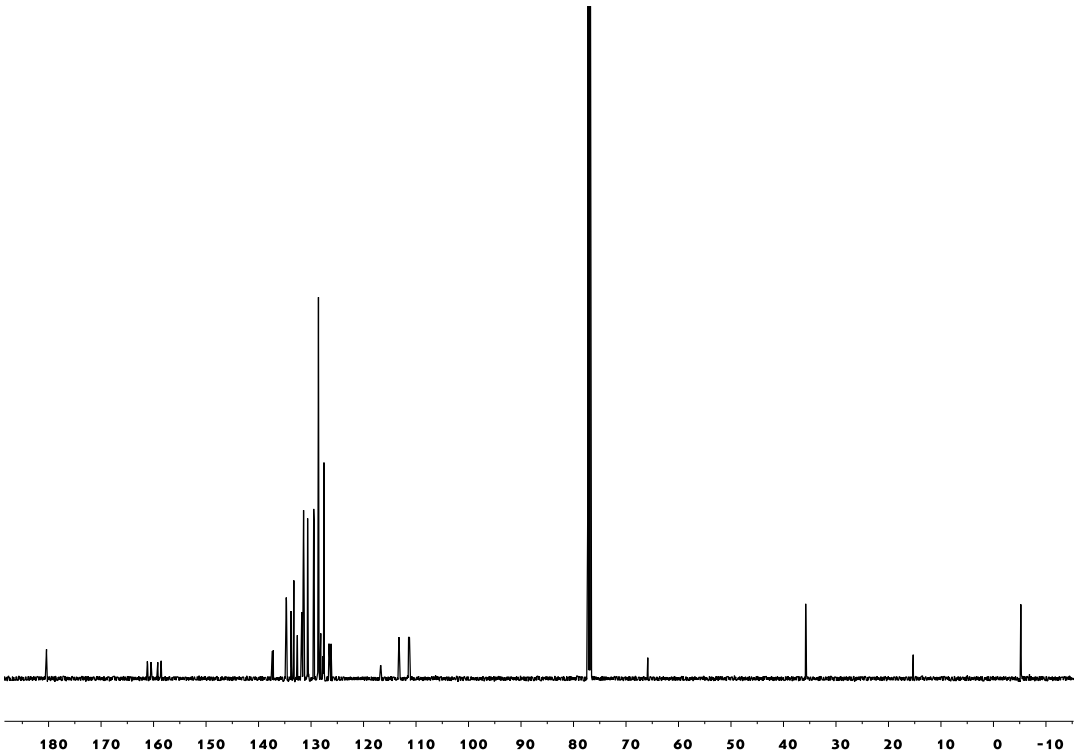


Figure S29. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **Pd5**

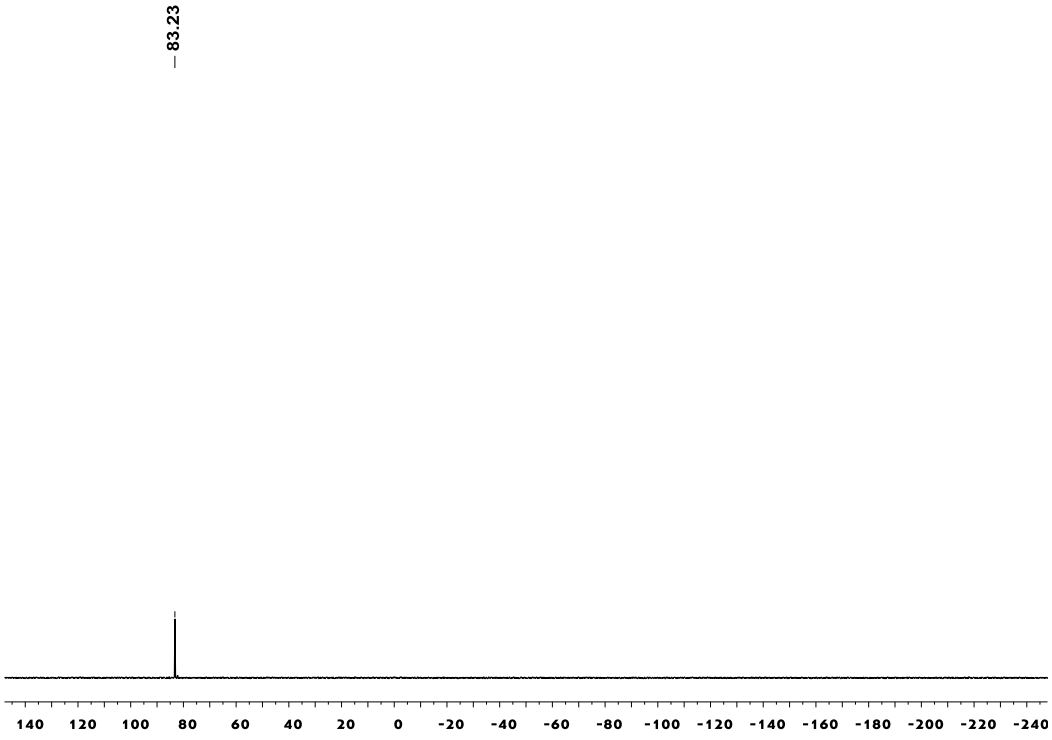


Figure S30. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Pd5**

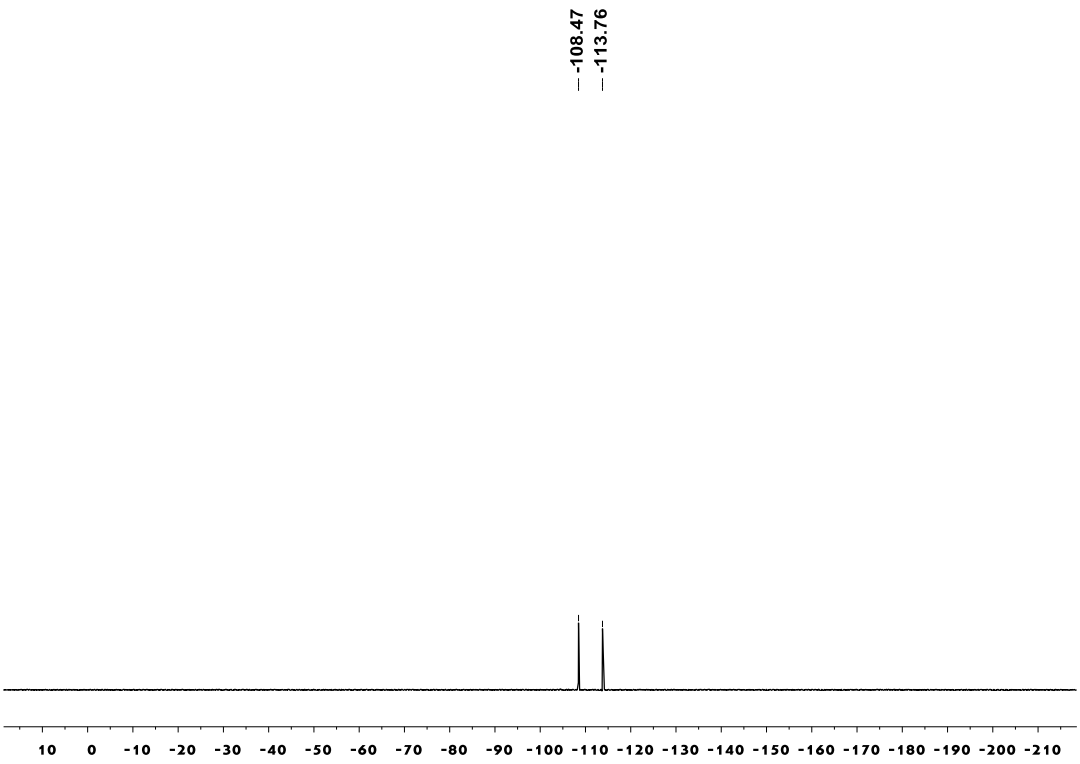


Figure S31. ^{19}F NMR spectrum (470 MHz, 298 K, $CDCl_3$) of **Pd5**

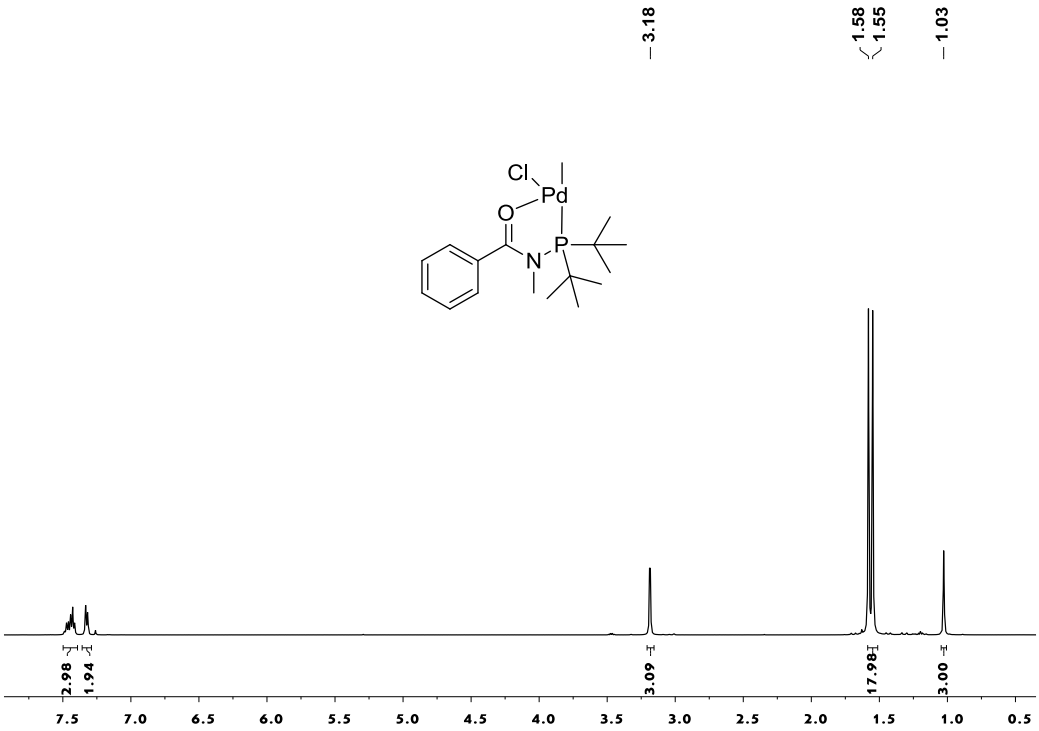


Figure S32. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **Pd6**

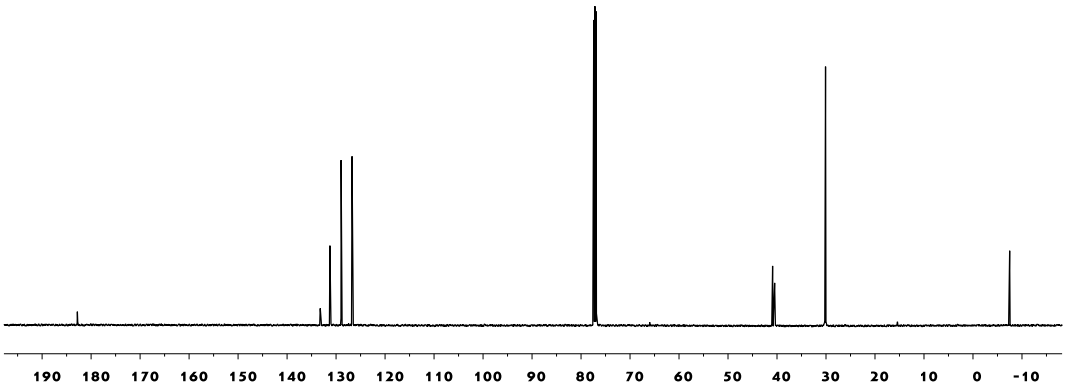


Figure S33. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **Pd6**

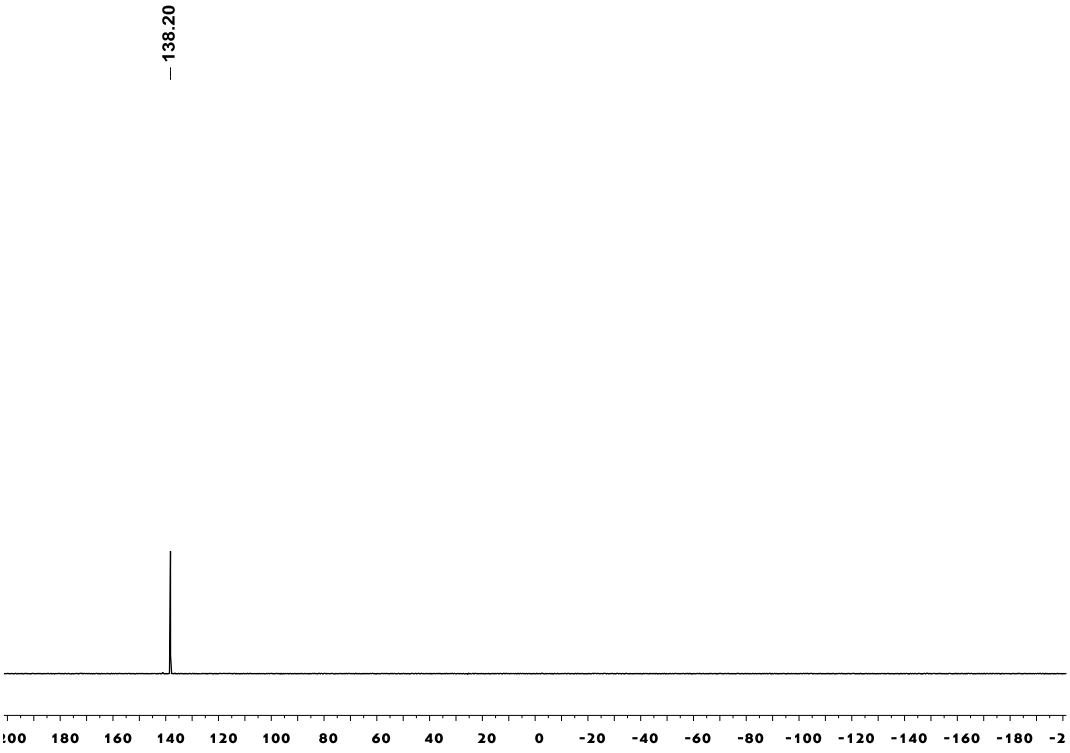


Figure S34. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Pd6**

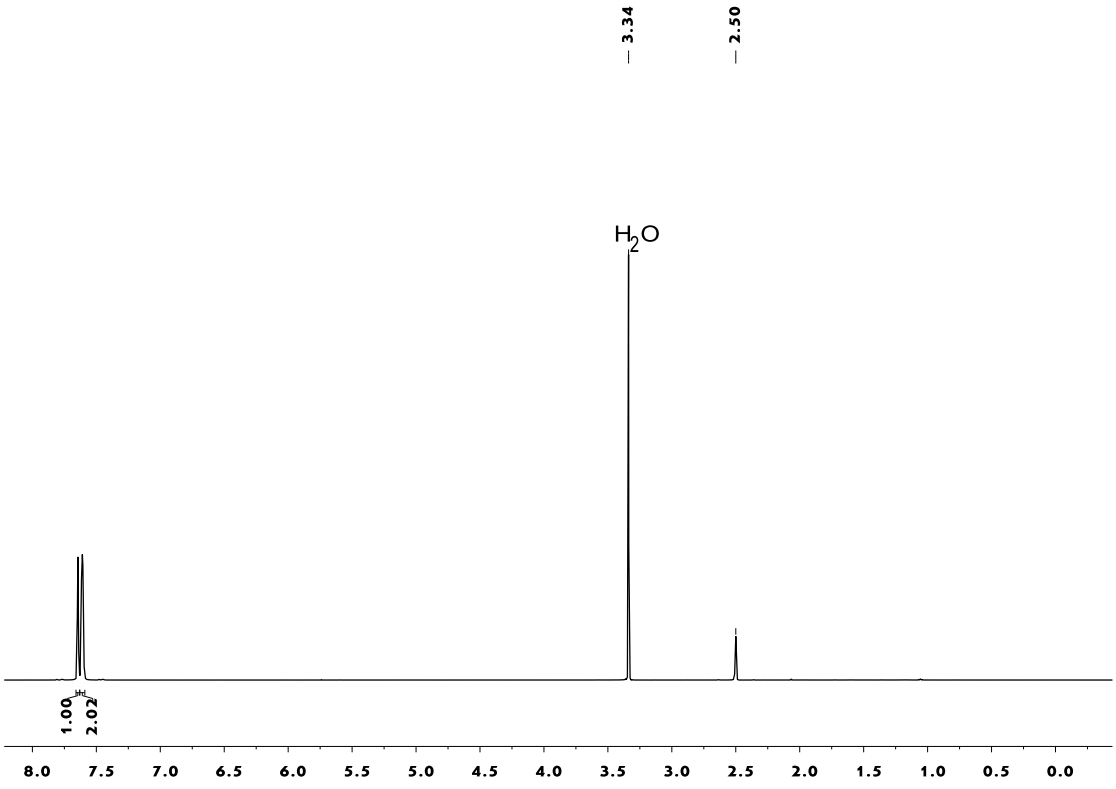


Figure S35. ^{1}H NMR spectrum (500 MHz, 298 K, $(CD_3)SO$) of **NaBAr$^{F}_{4}$**

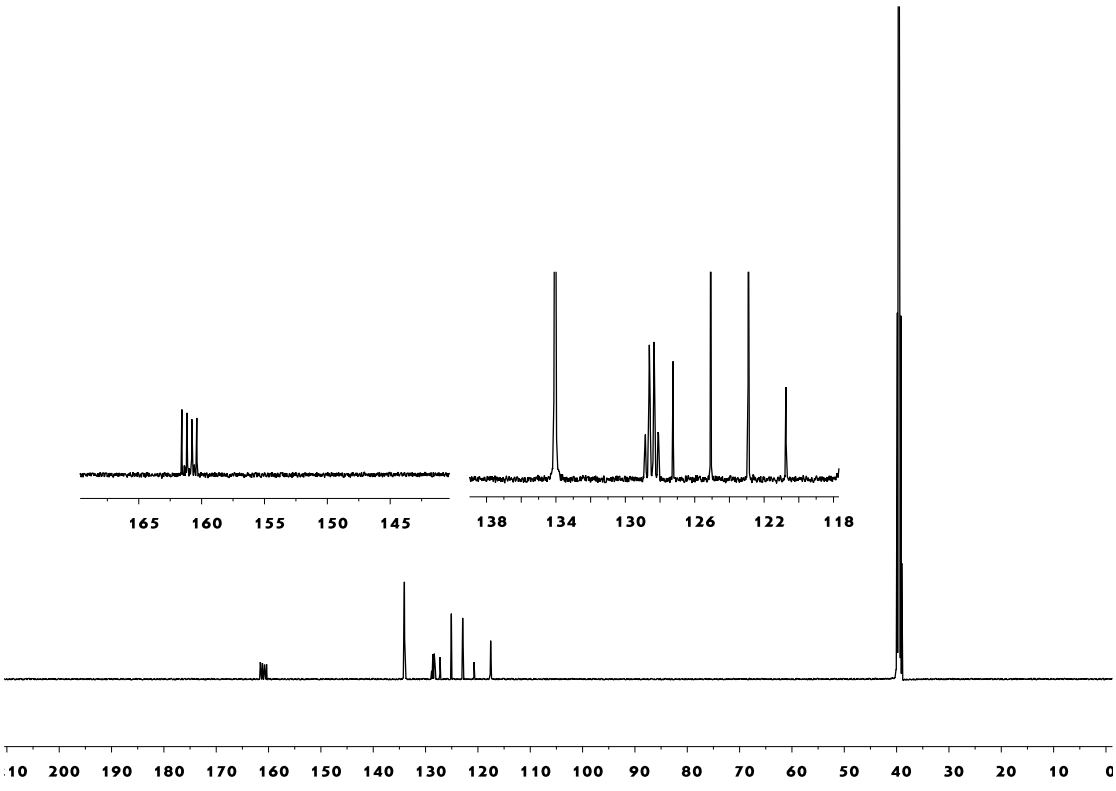


Figure S36. ^{13}C NMR spectrum (125 MHz, 298 K, $(CD_3)SO$) of **NaBAr$^{F}_{4}$**

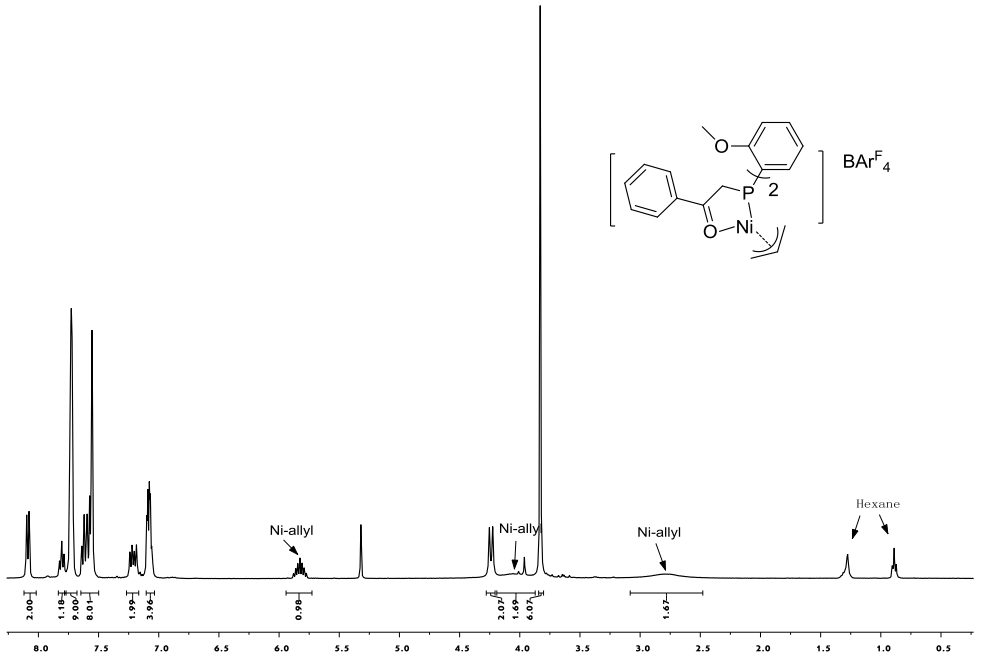


Figure S37. ^{1}H NMR spectrum (500 MHz, 298 K, CD_2Cl_2) of **Ni1**

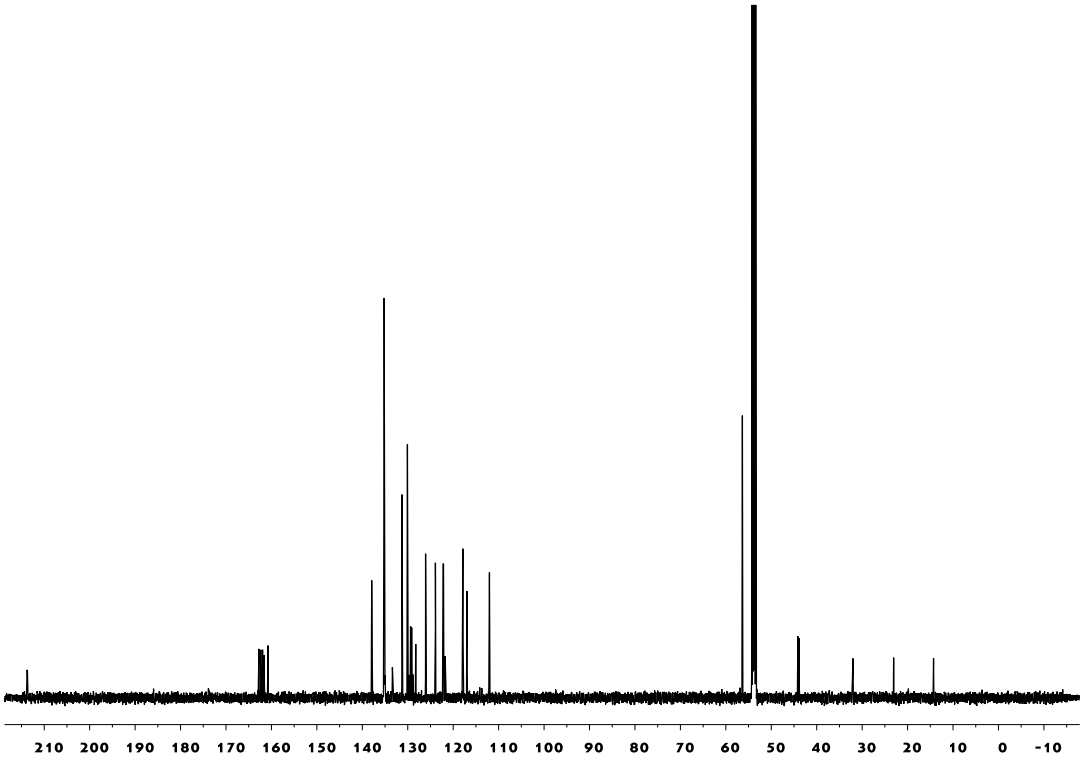


Figure S38. ^{13}C NMR spectrum (125 MHz, 298 K, CD_2Cl_2) of **Ni1**

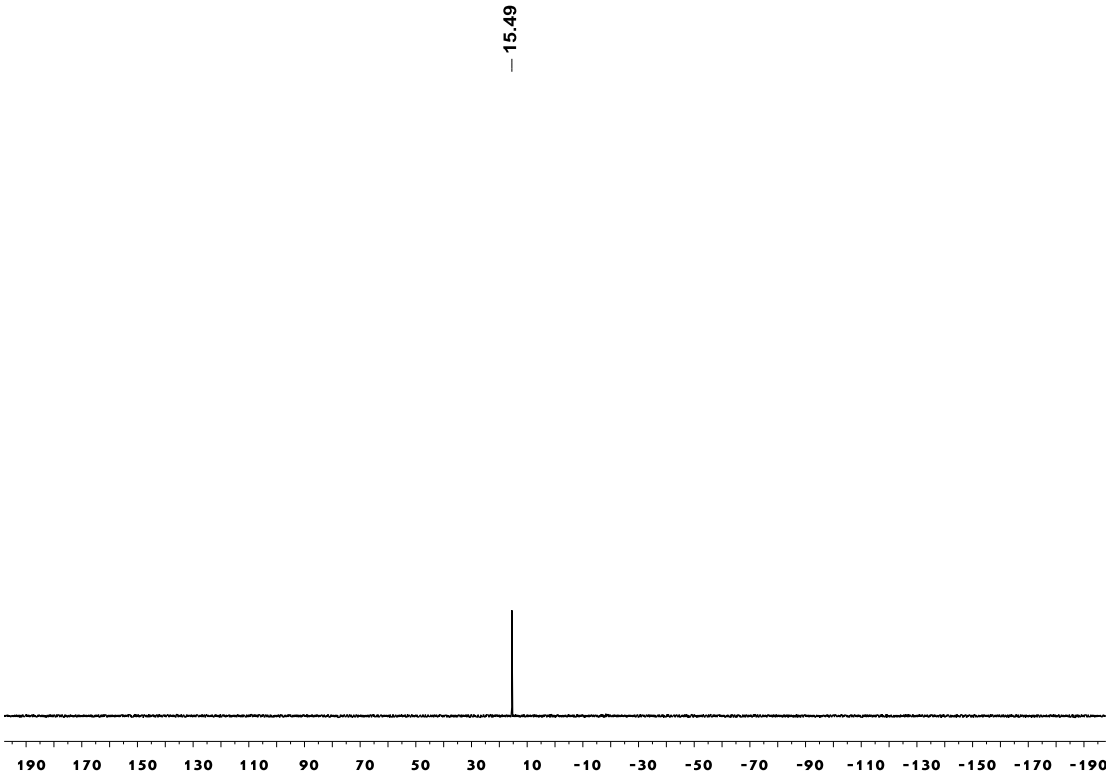


Figure S39. ^{31}P NMR spectrum (202 MHz, 298 K, CD_2Cl_2) of **Ni1**

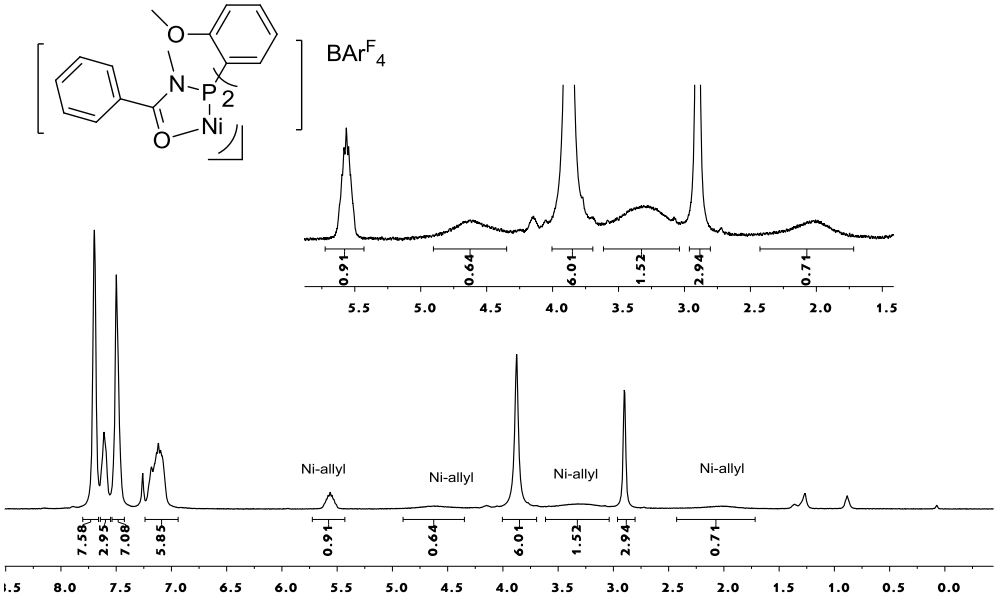


Figure S40. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **Ni2**

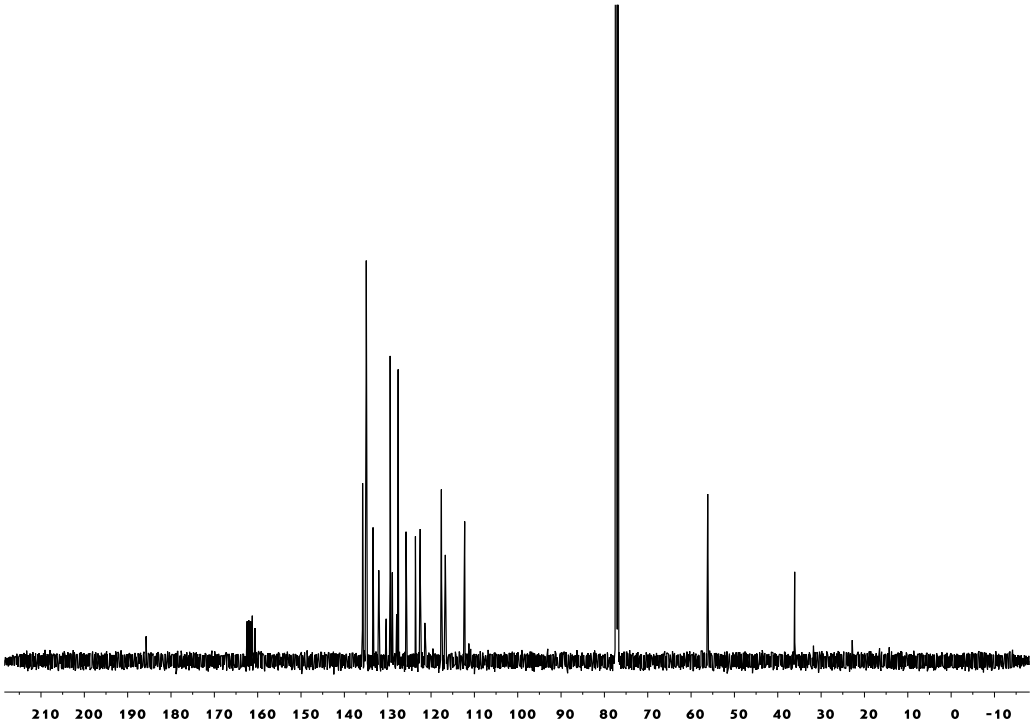


Figure S41. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **Ni2**

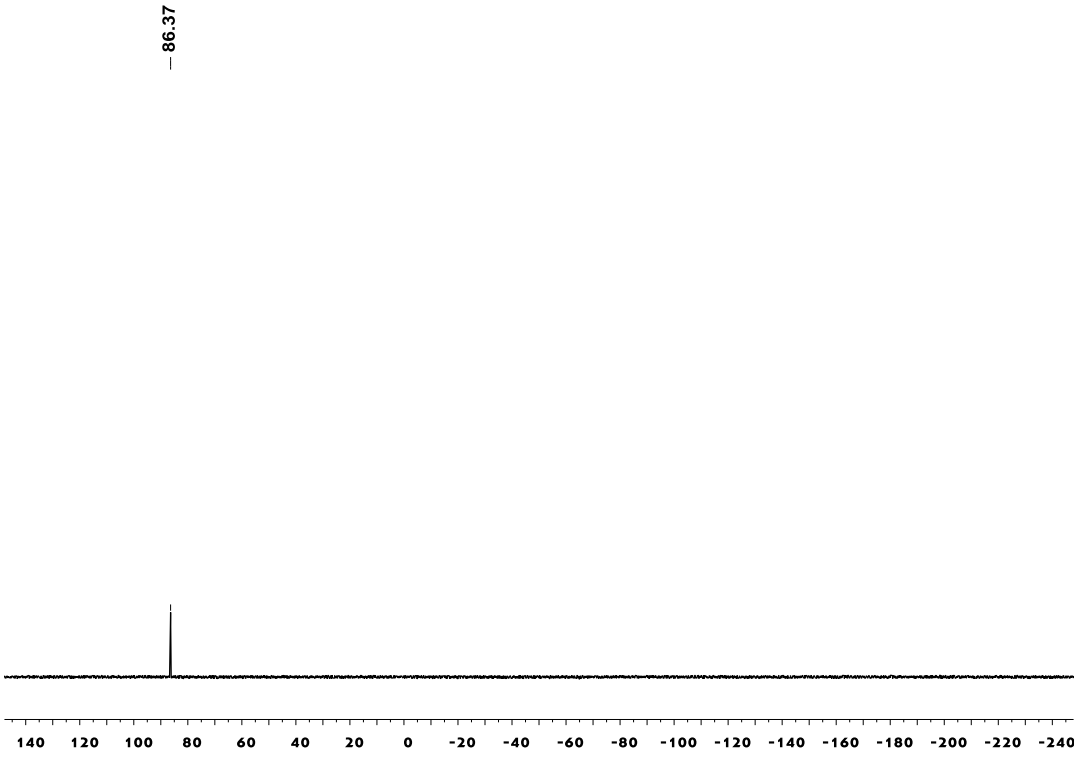


Figure S42. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Ni2**

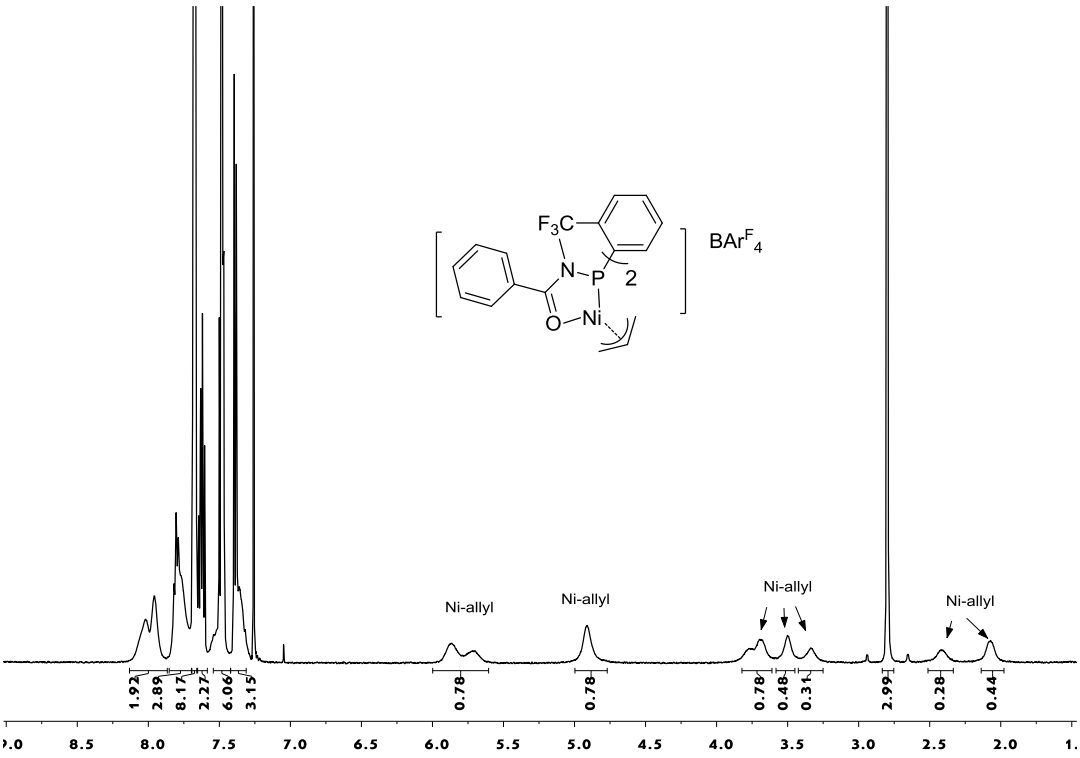


Figure S43. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **Ni3**

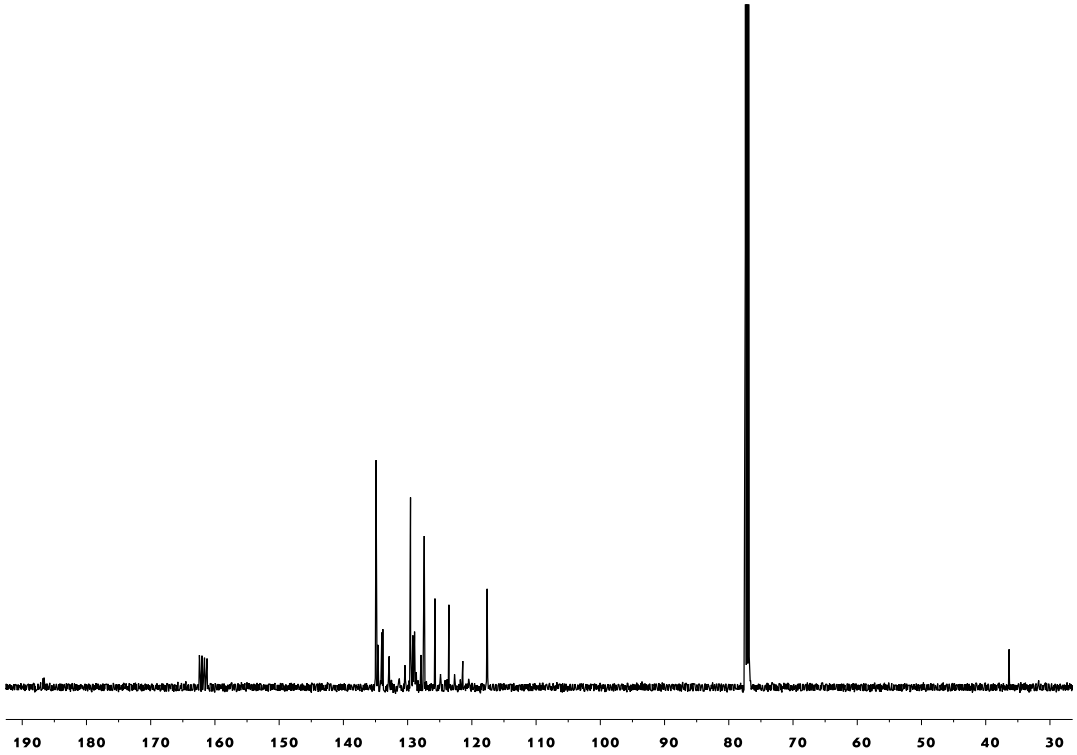


Figure S44. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **Ni3**

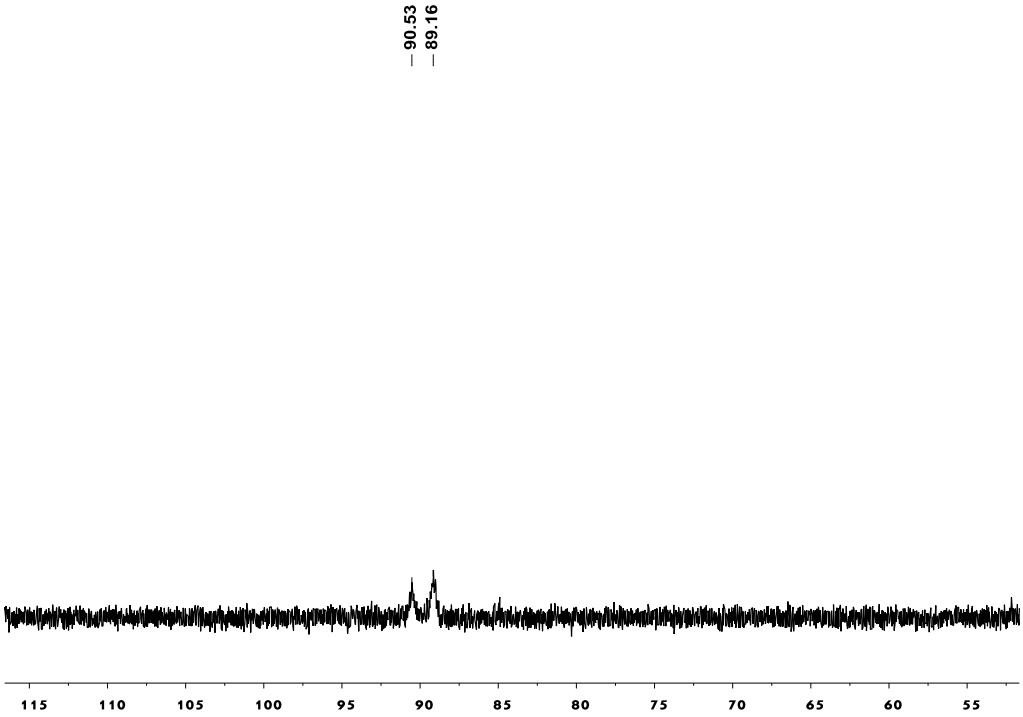


Figure S45. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Ni3**

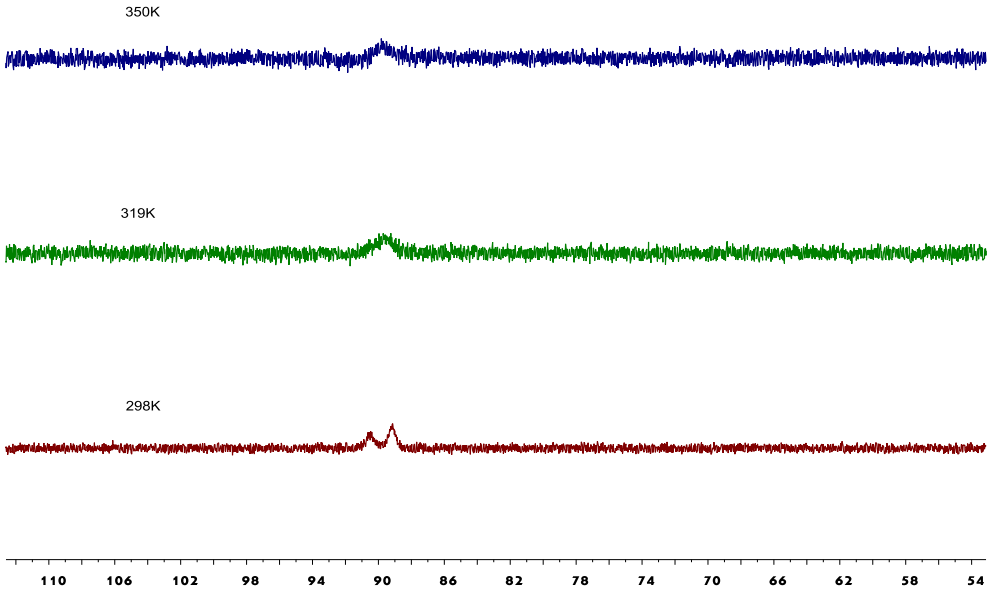


Figure S46. ^{31}P NMR spectra (202MHz, $C_2D_2Cl_4$) of **Ni3** at 298K, 319K, 350K

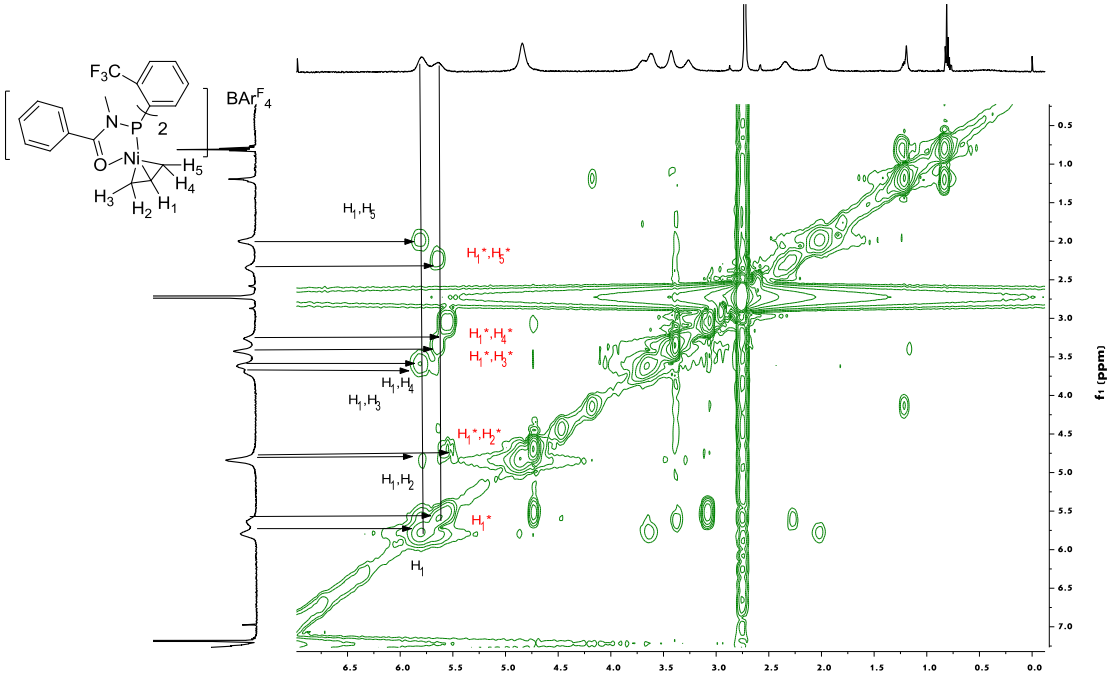


Figure S47. COSY spectrum (400 MHz, $CDCl_3$) of **Ni3**

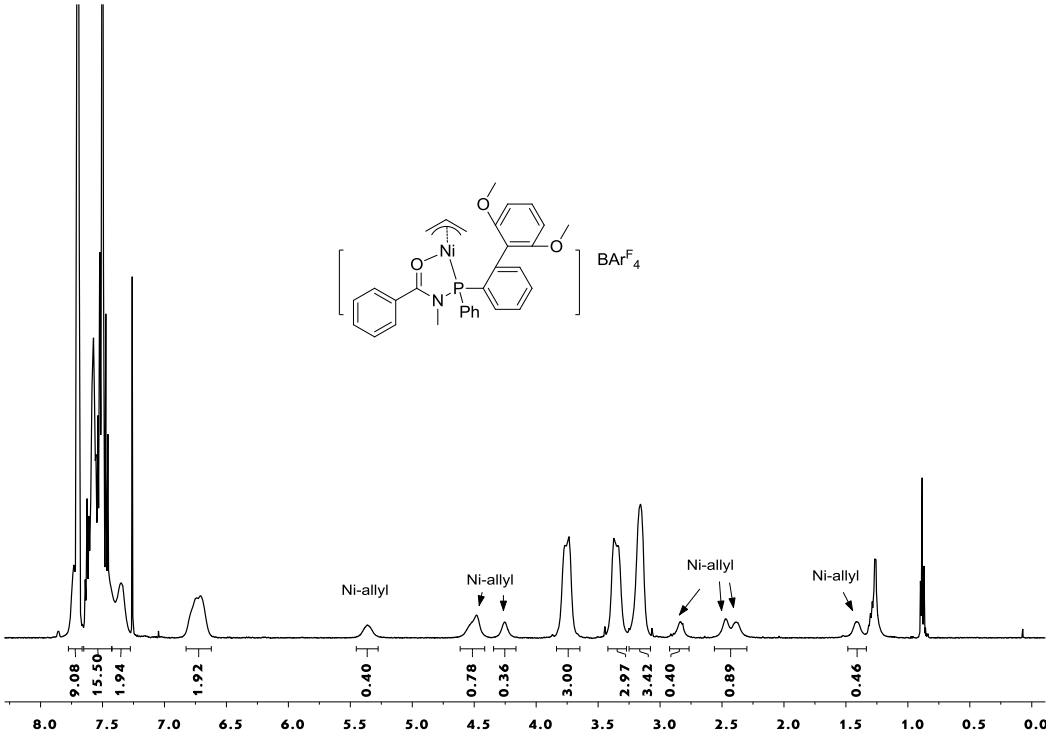


Figure S48. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **Ni4**

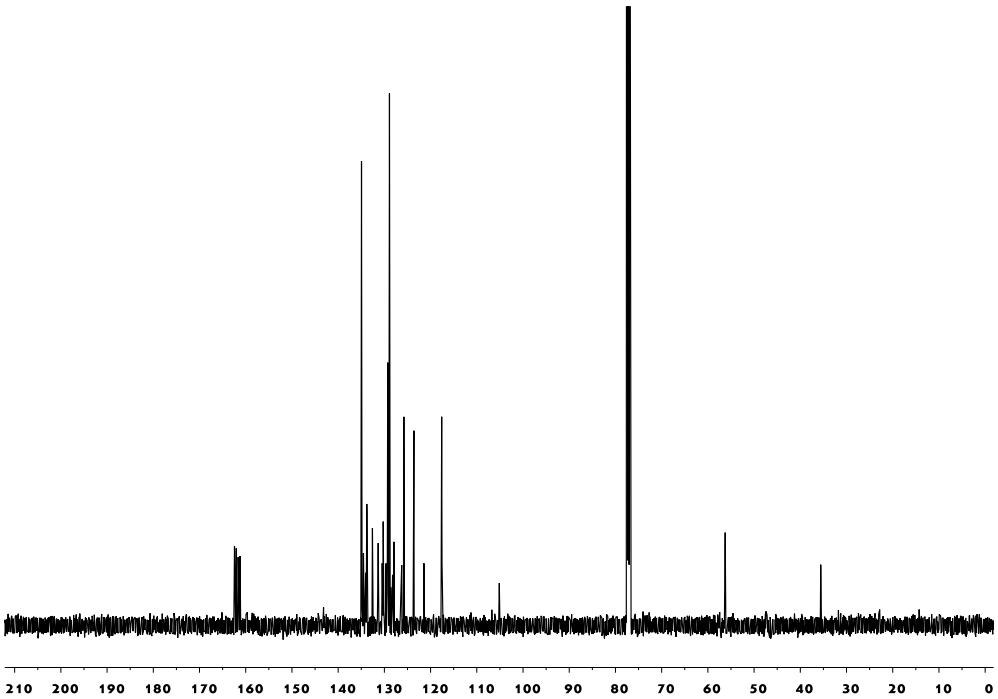


Figure S49. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **Ni4**

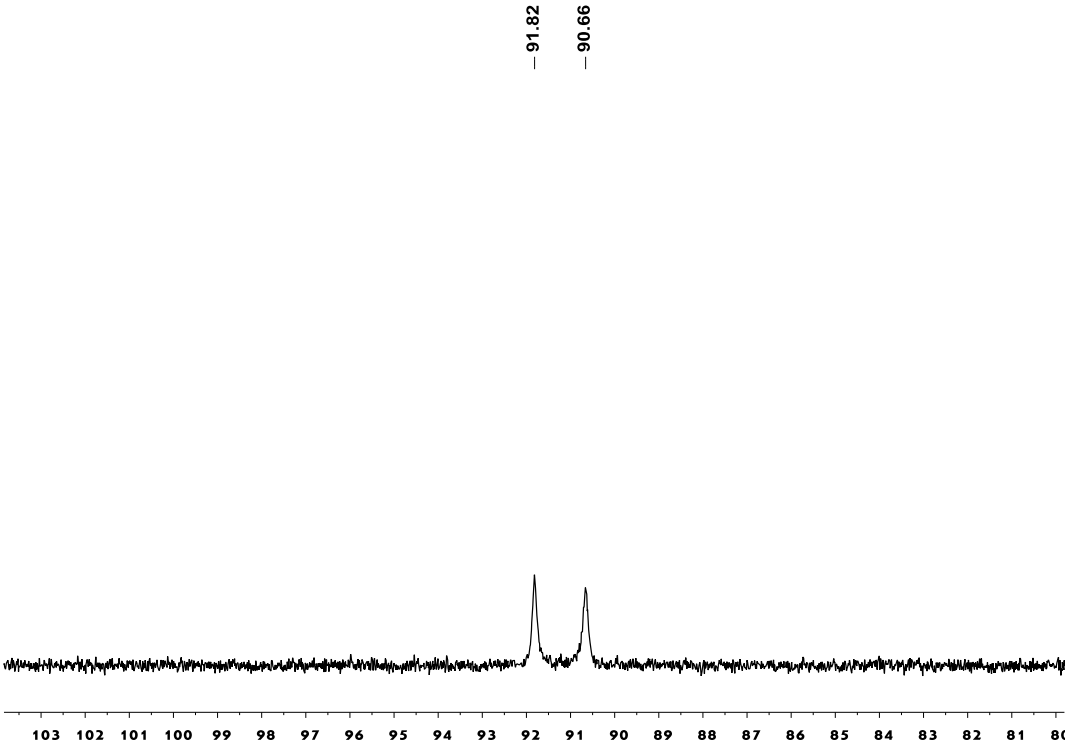


Figure S50. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Ni4**

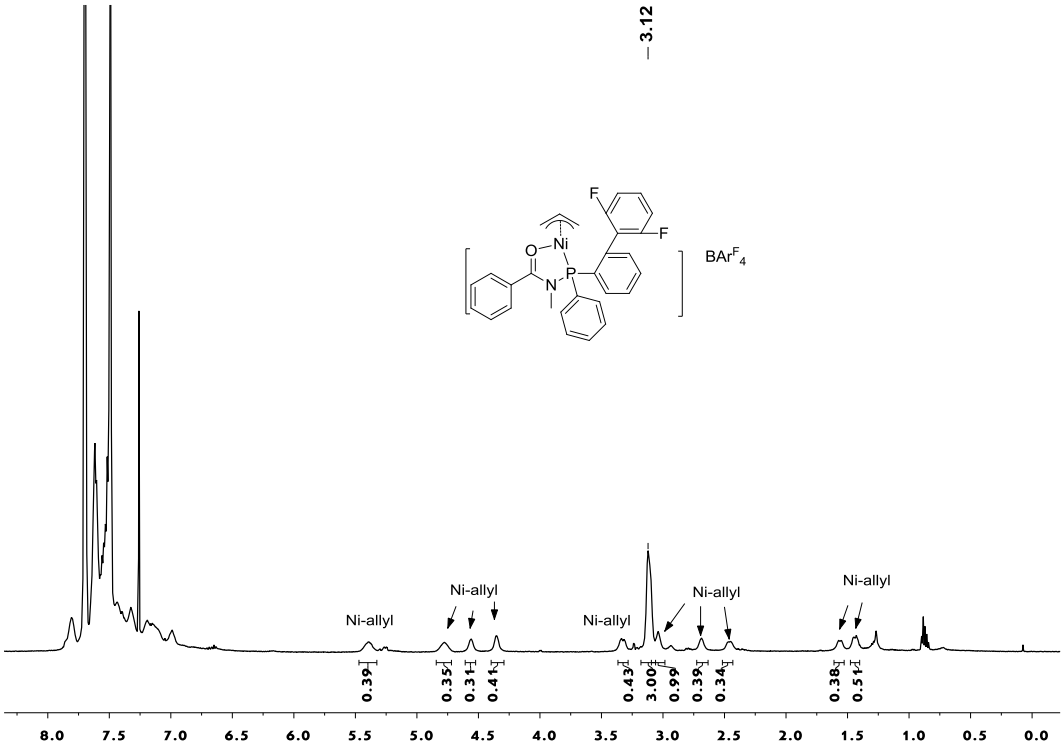


Figure S51. ^{1}H NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Ni5**

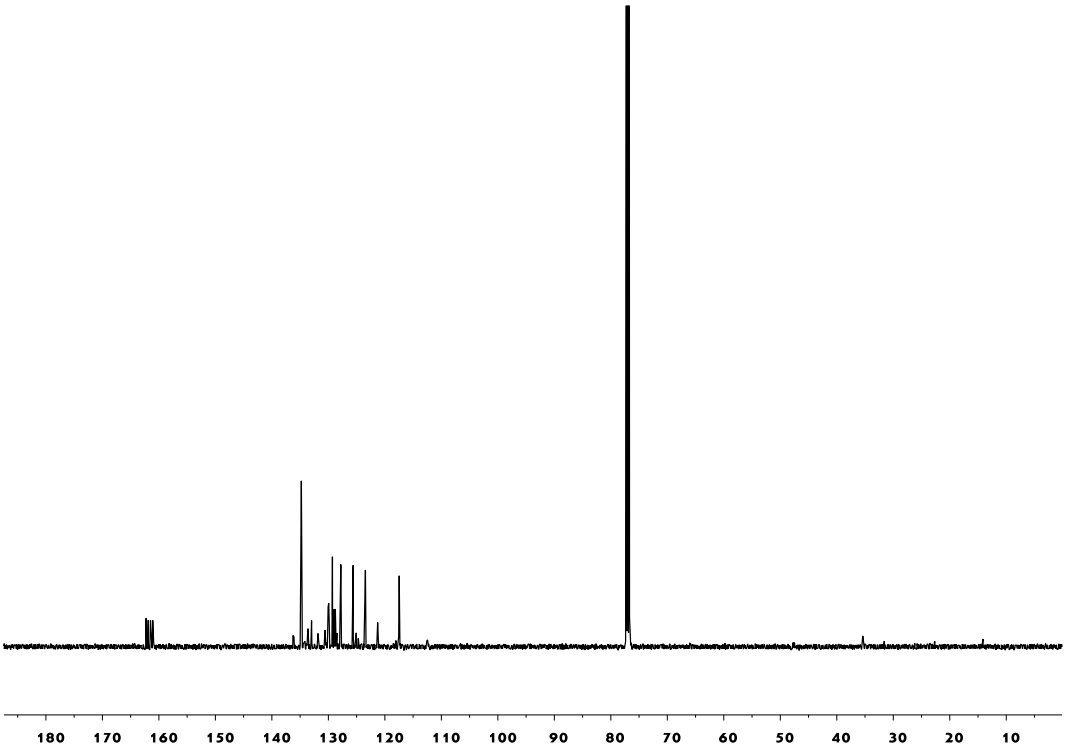


Figure S52. ^{31}C NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Ni5**

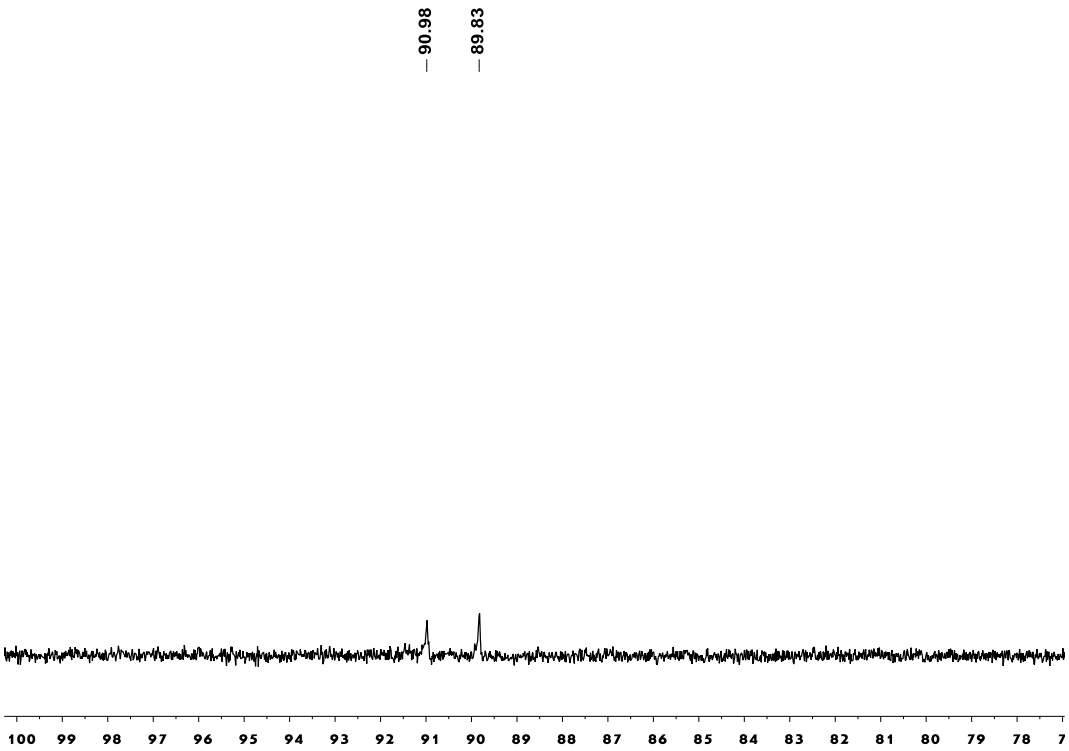


Figure S53. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Ni5**

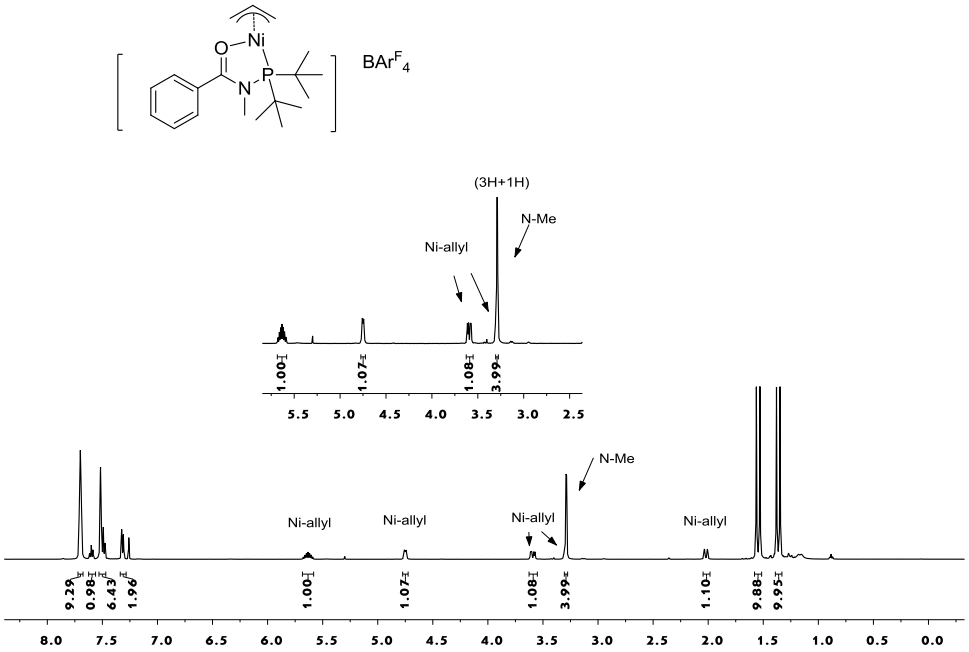


Figure S54. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **Ni6**

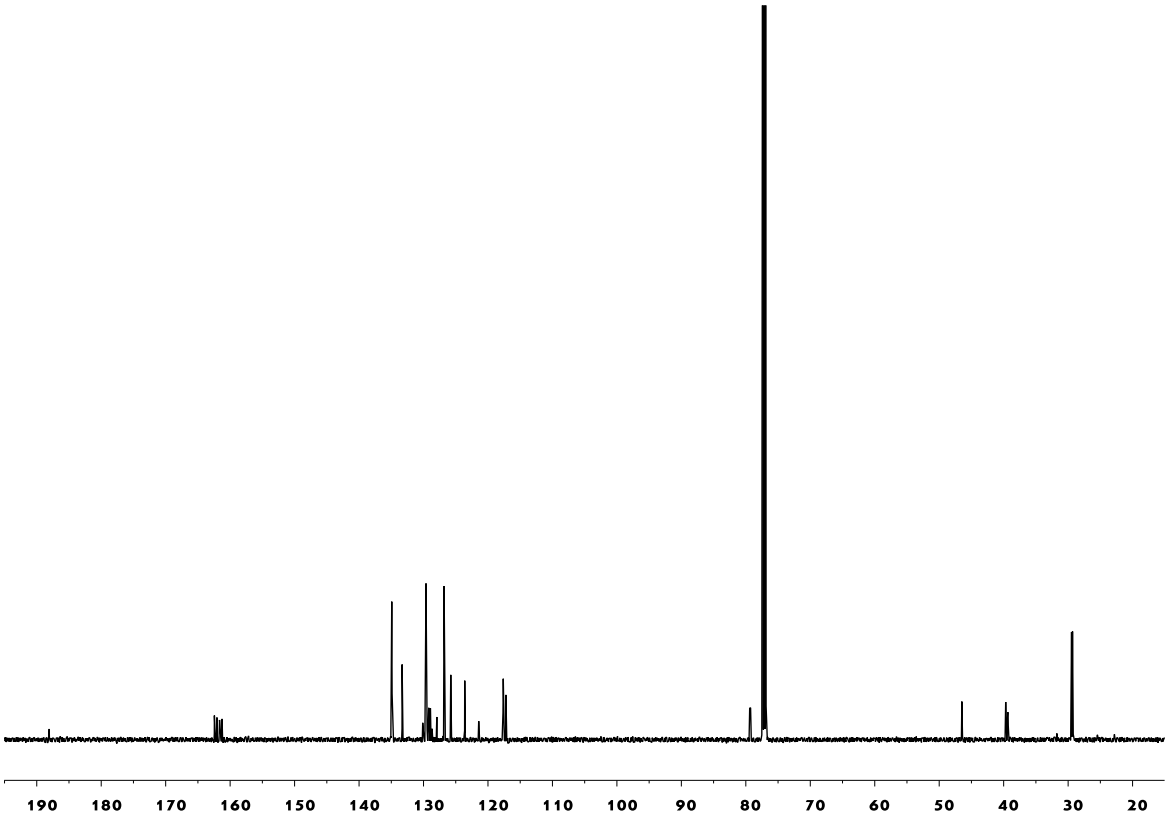


Figure S55. ^{13}C NMR spectrum (125 MHz, 298 K, $CDCl_3$) of **Ni6**

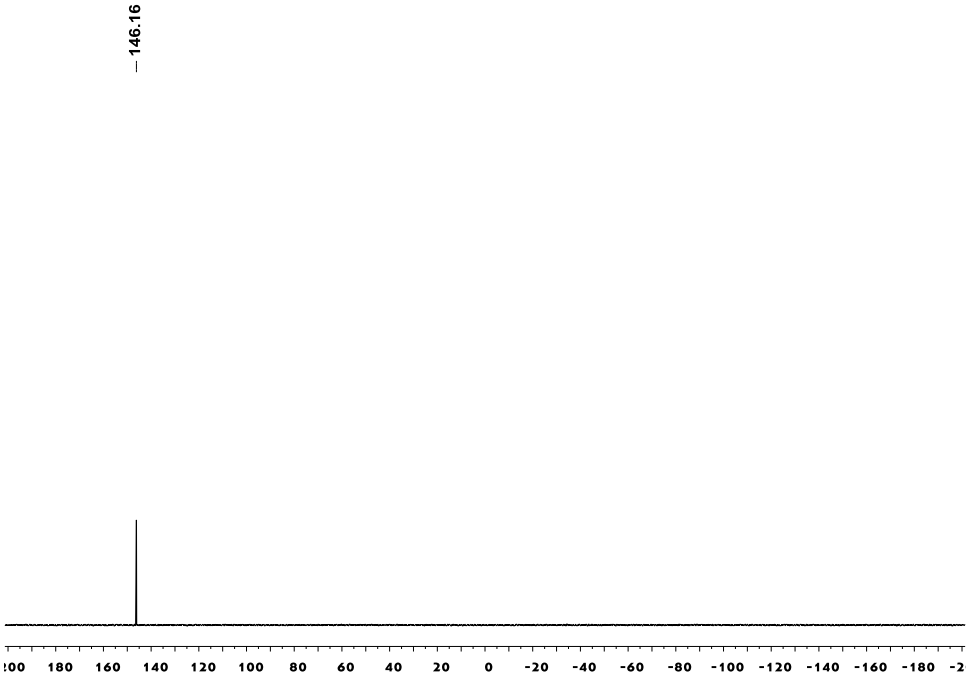


Figure S56. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of **Ni6**

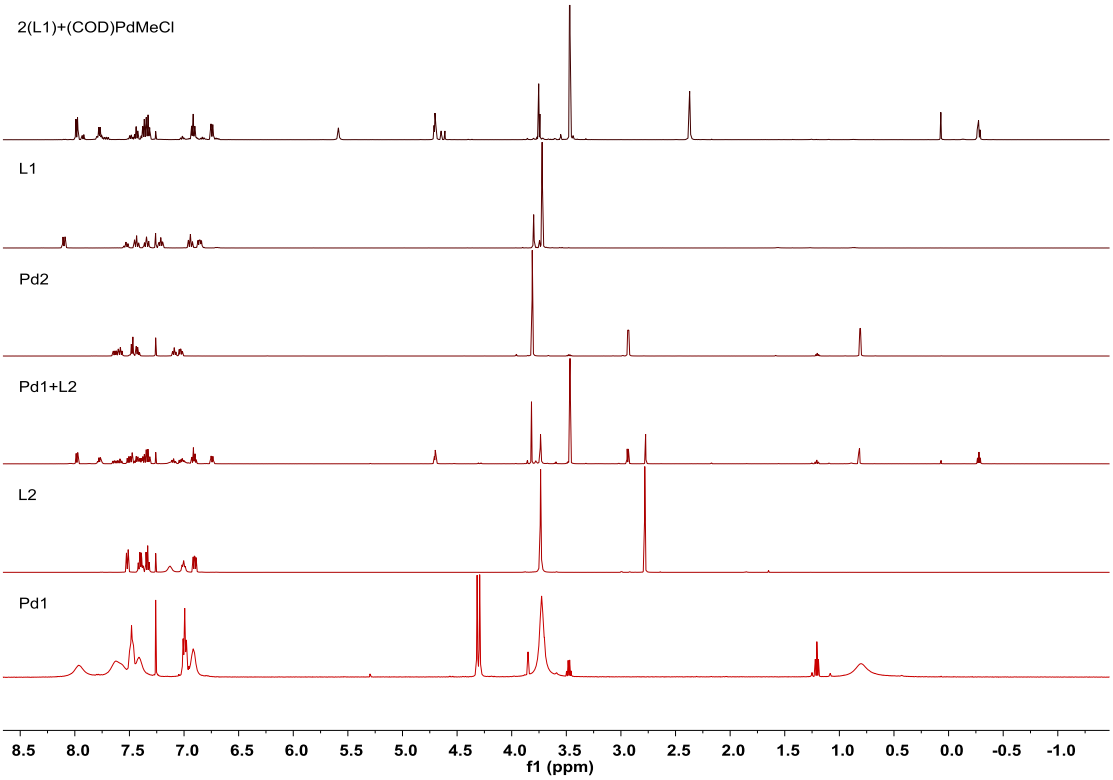


Figure S57. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of Ligands and catalysts

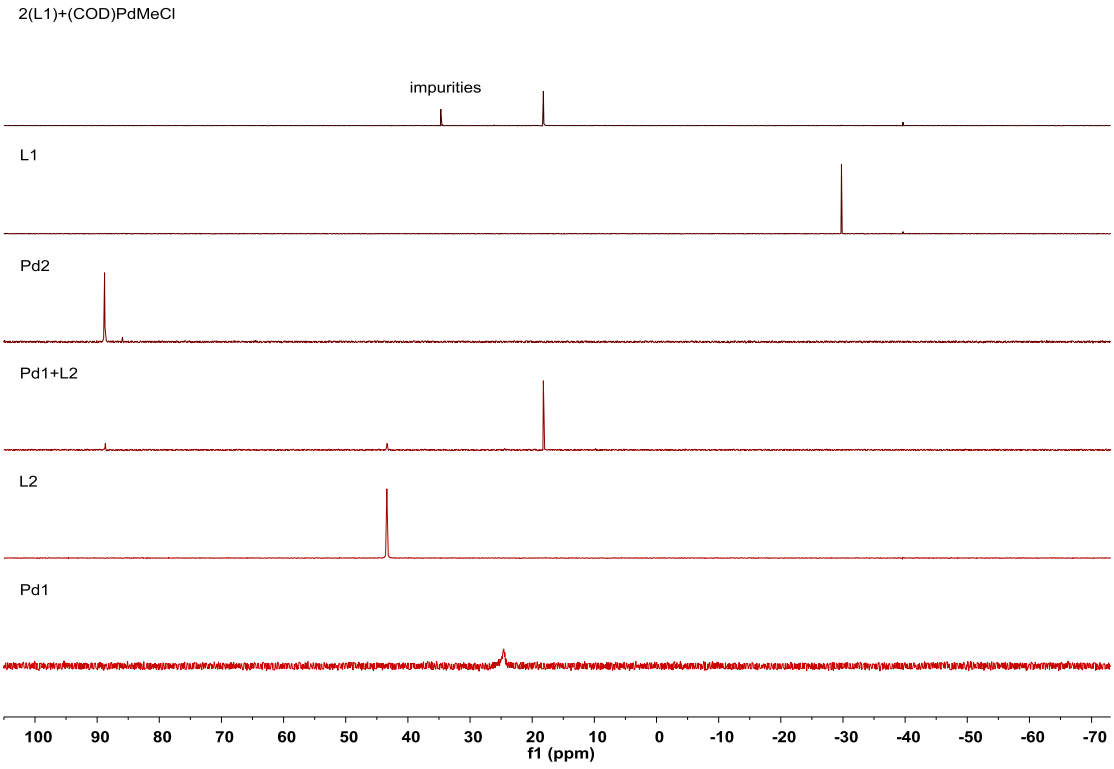


Figure S58. ^{31}P NMR spectrum (202 MHz, 298 K, $CDCl_3$) of Ligands and catalysts

NMR Spectra of polymers

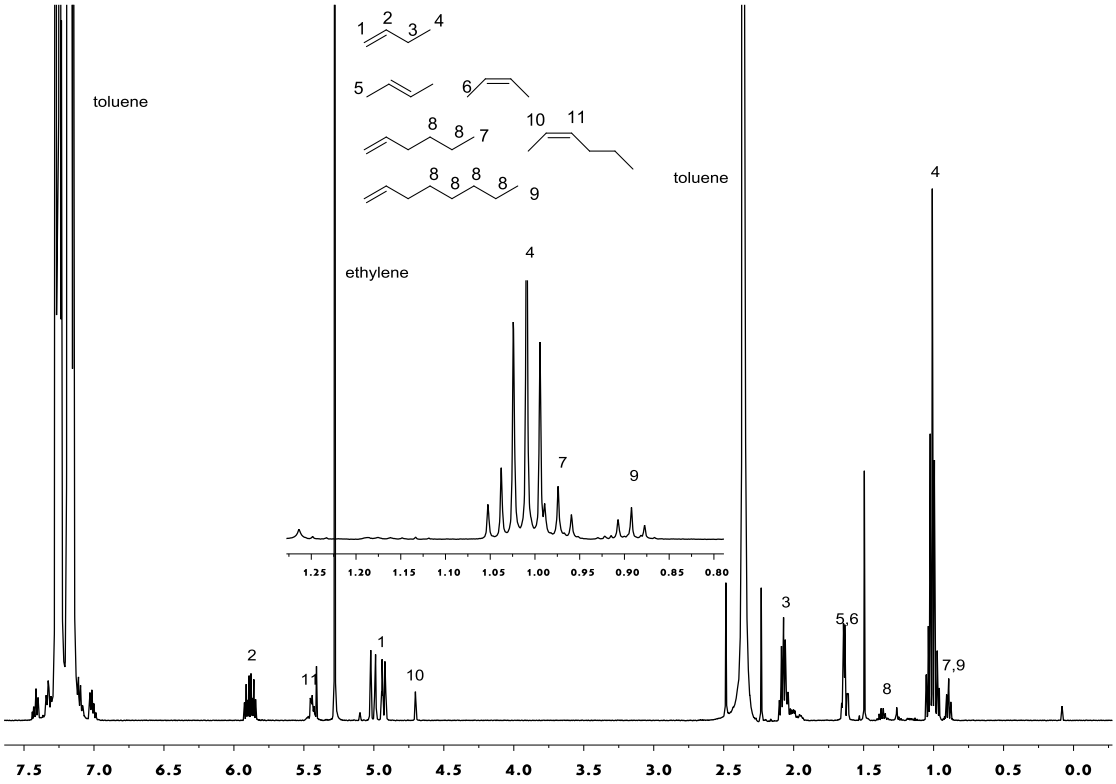


Figure S59. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of ethylene oligomer (**Pd 1, 80 ℃**) from table 1, entry 1.

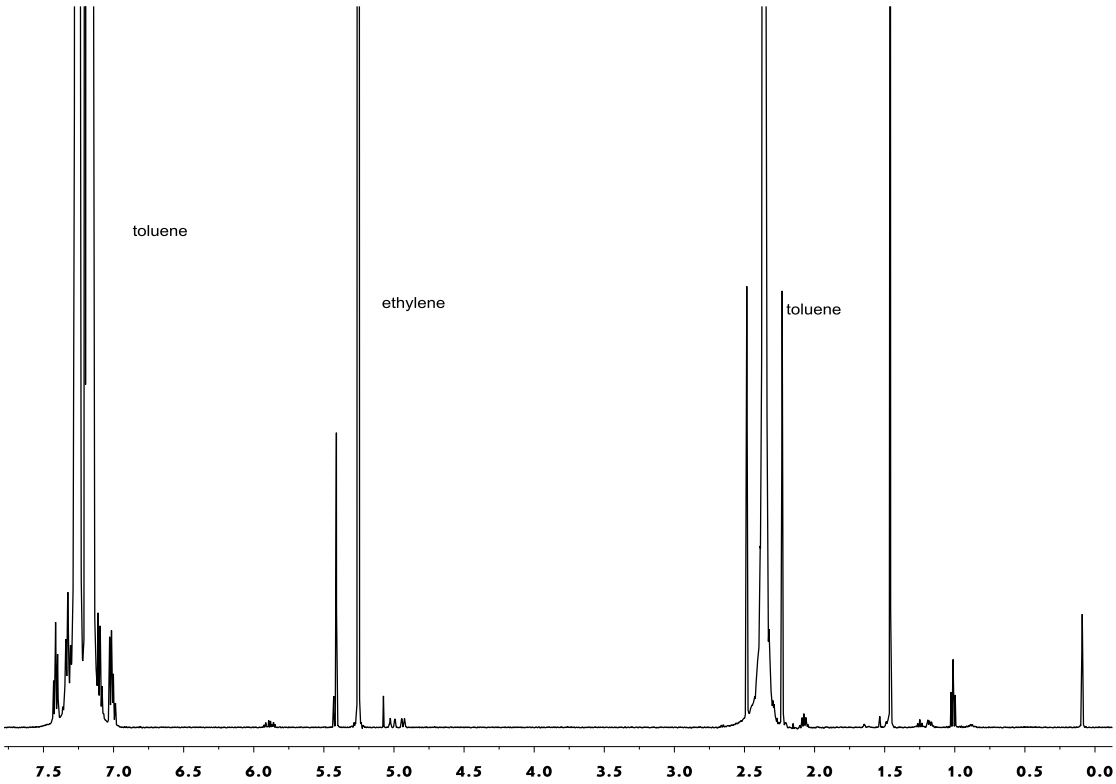


Figure S60. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of ethylene oligomer (**Pd 1, 30 ℃**) from table 1, entry 2

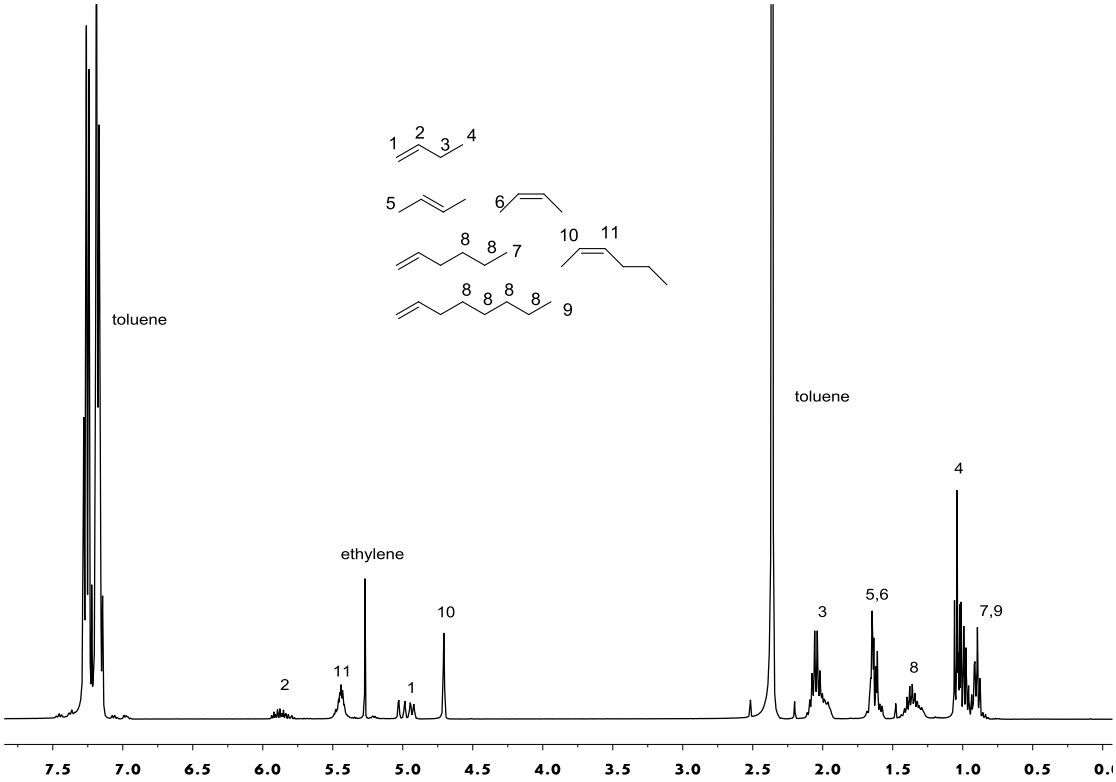


Figure S61. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of ethylene oligomer (**Ni 1, 80 ℃**) from table 1, entry 13

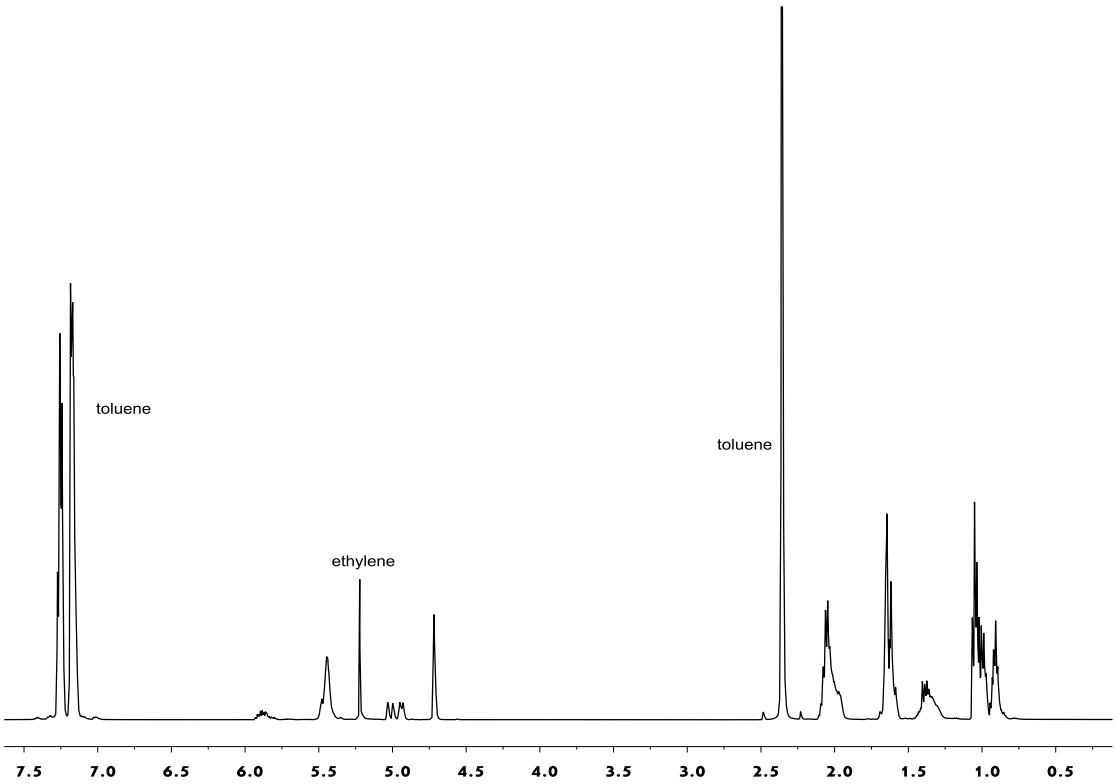


Figure S62. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of ethylene oligomer (**Ni 1, 30 ℃**) from table 1, entry 14

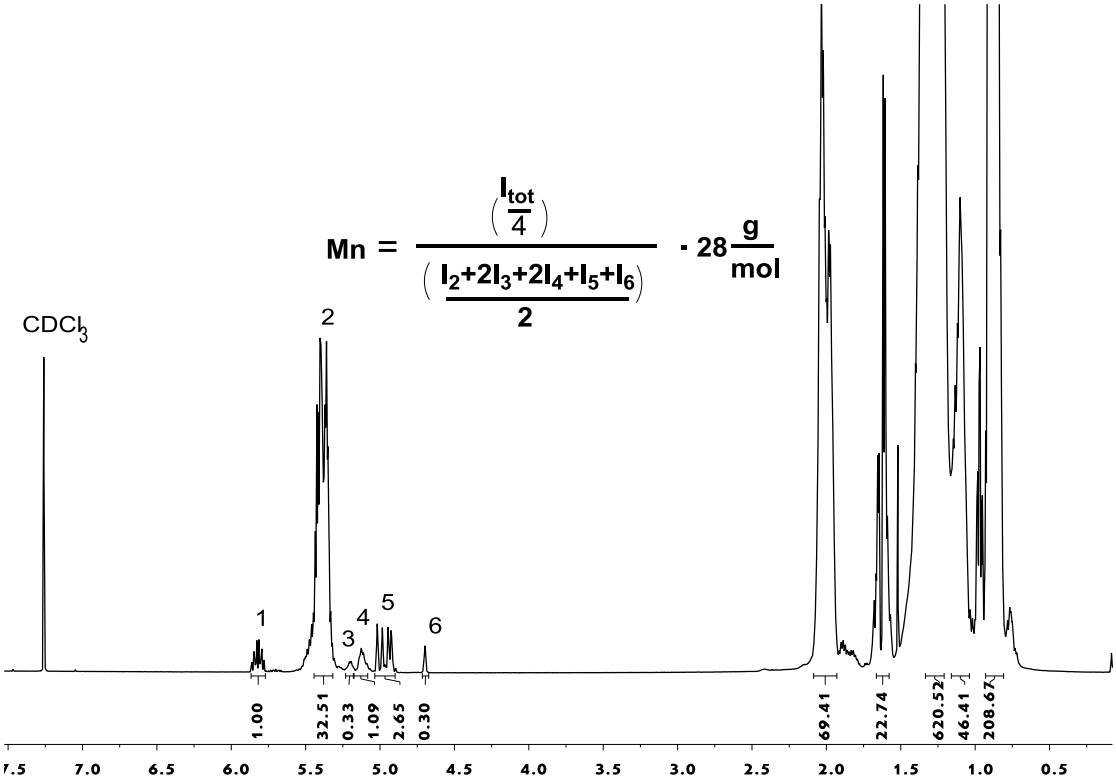


Figure S63. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of ethylene oligomer (**Ni 3, 80 ℃**) from table 1, entry 17

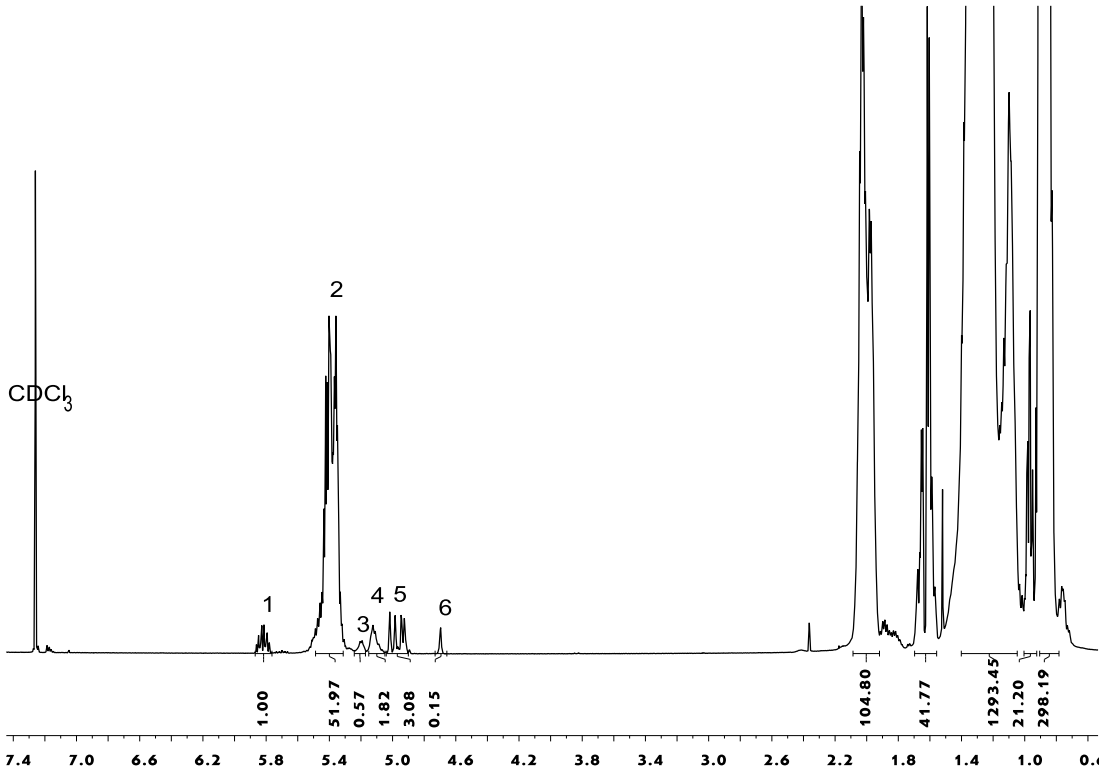


Figure S64. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of ethylene oligomer (**Ni 3, 30 ℃**) from table 1, entry 18

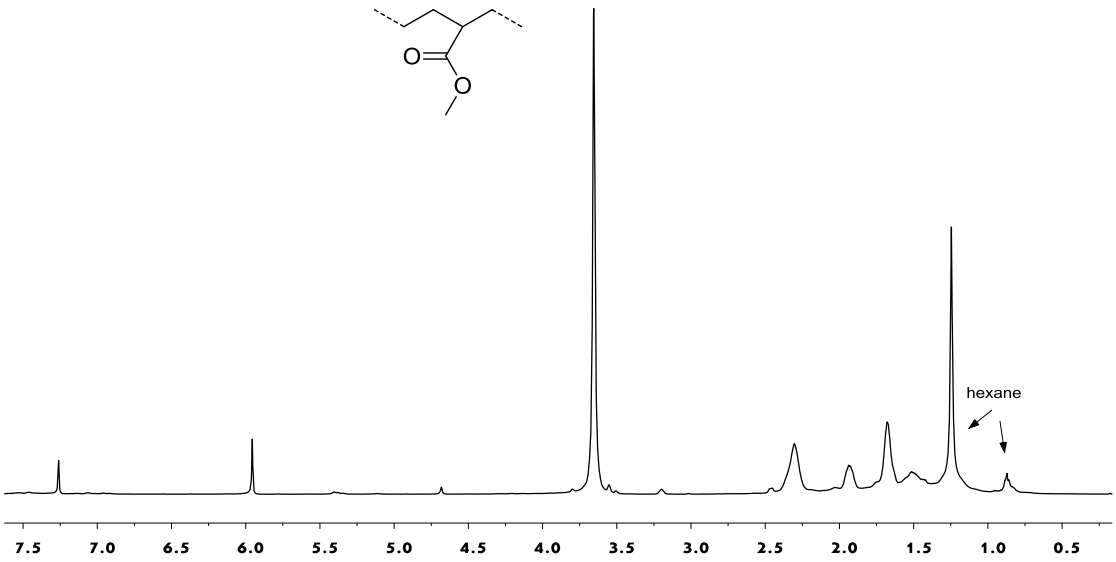


Figure S65. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of **PMA**

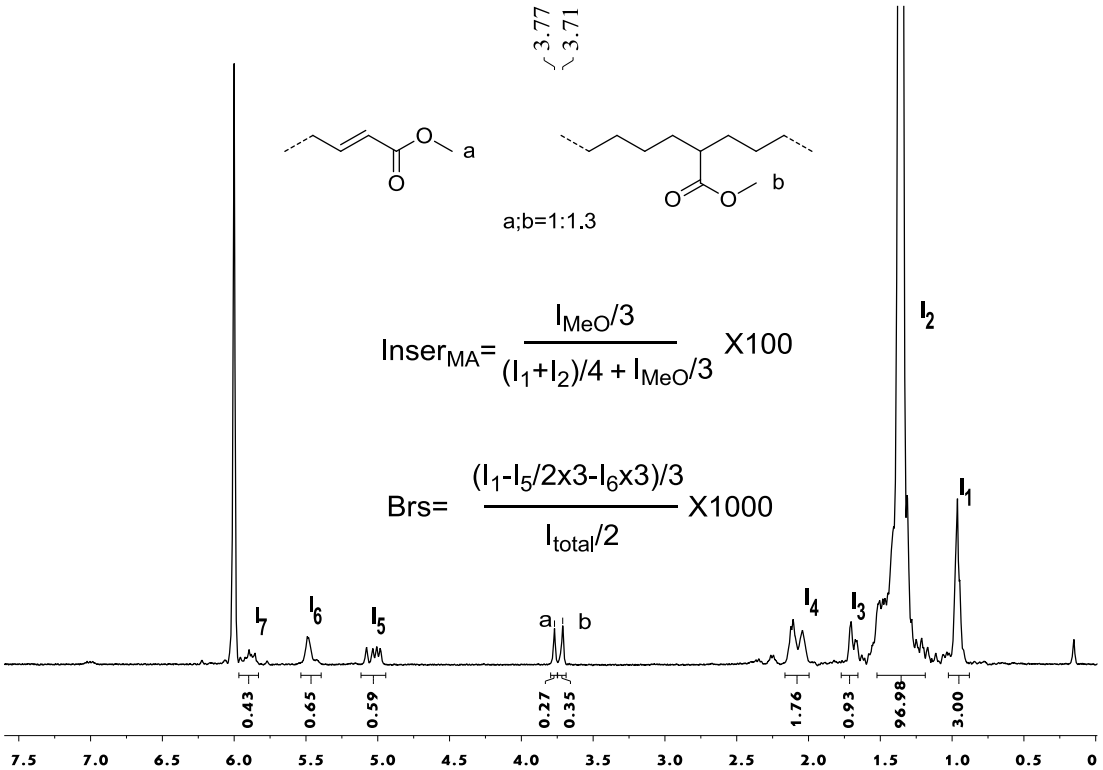


Figure S66. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-methyl acrylate copolymer from table 2, entry 3.

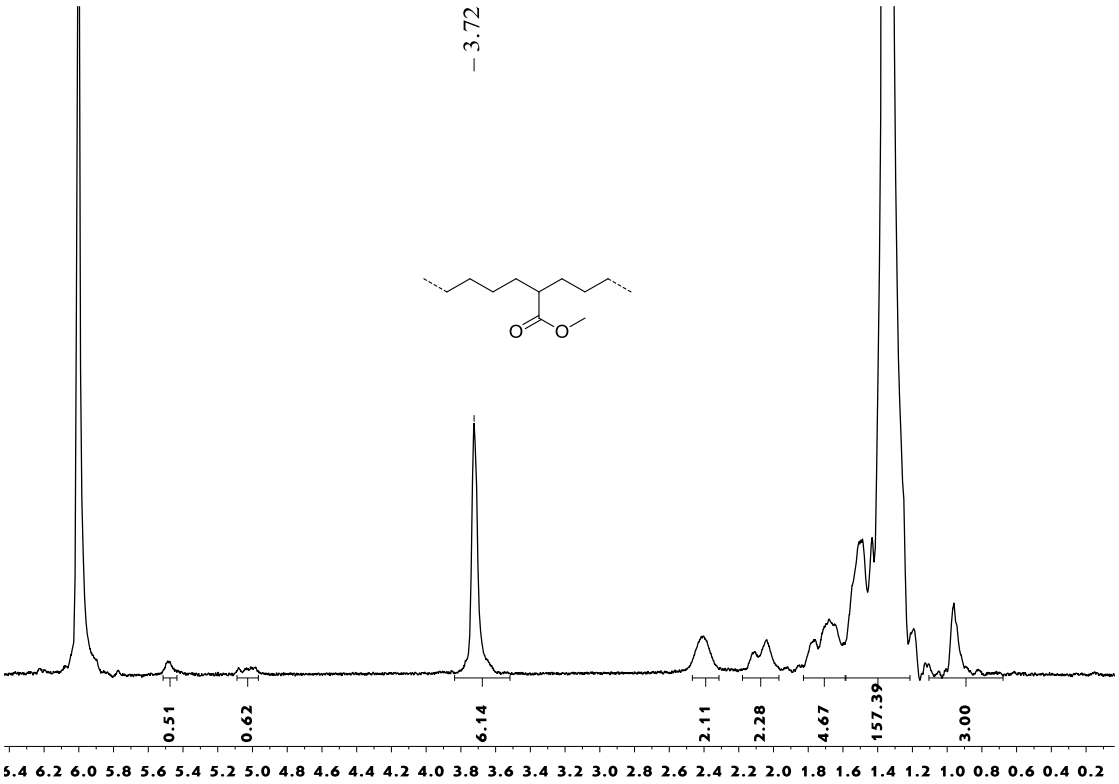


Figure S67. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-methyl acrylate copolymer from table 2, entry 4.

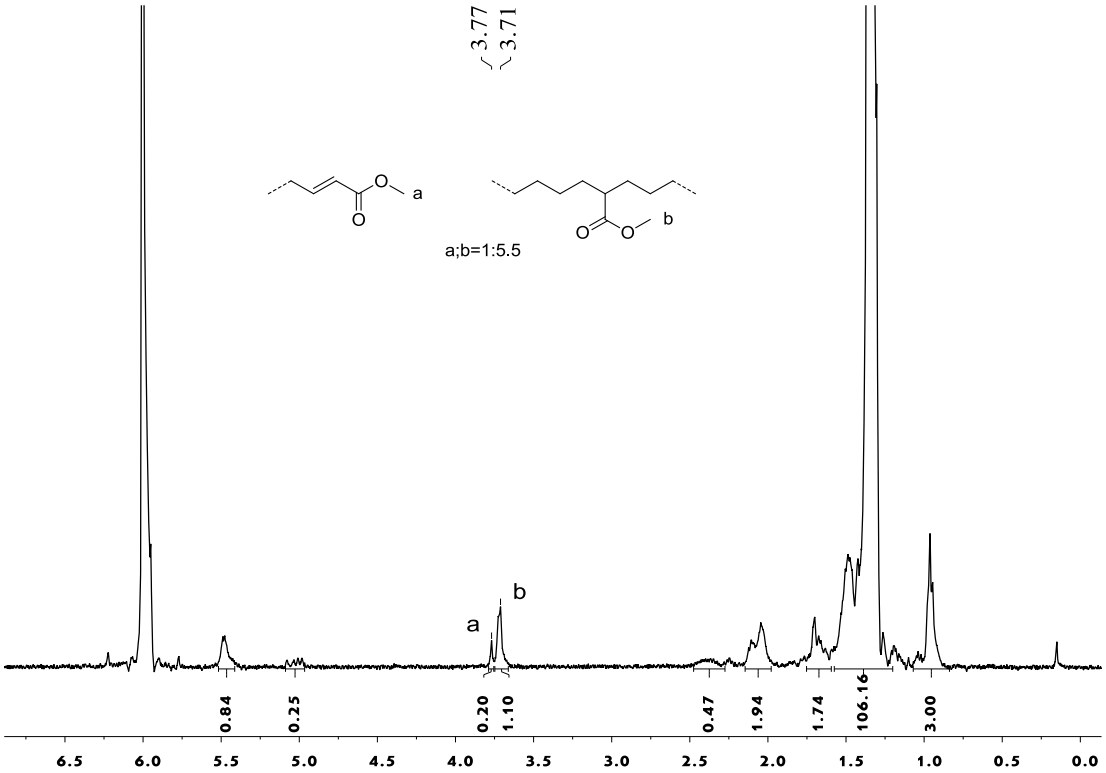


Figure S68. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-methyl acrylate copolymer from table 2, entry 5.

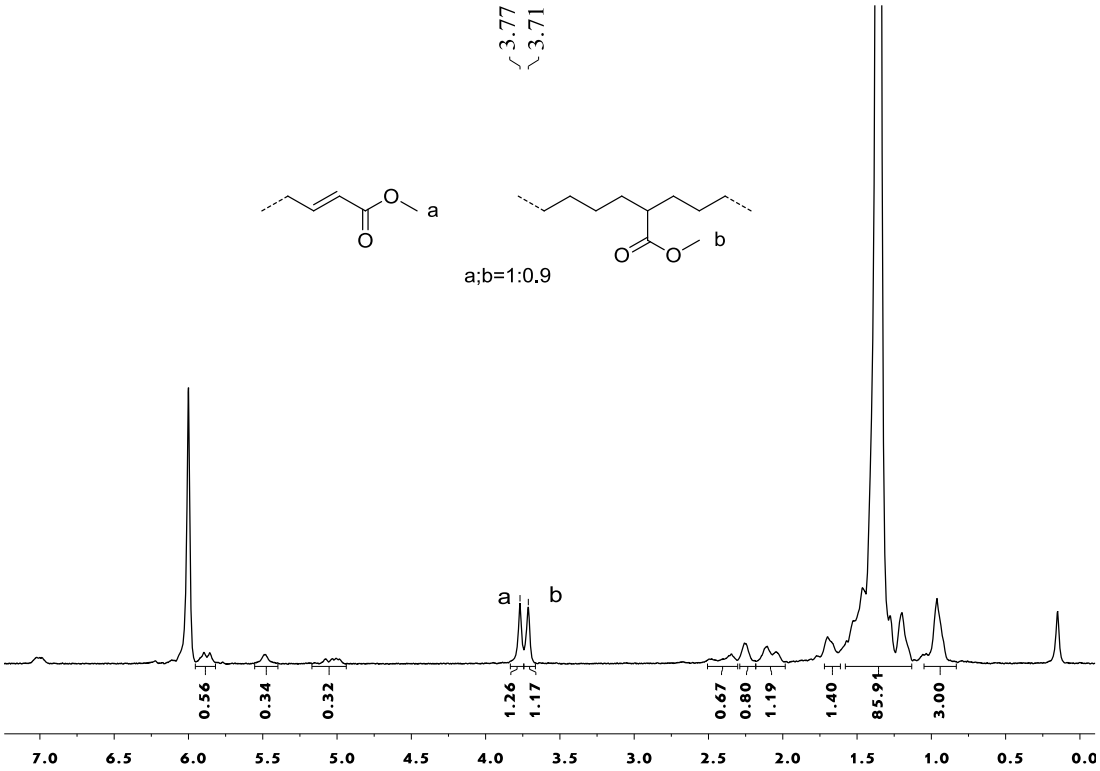


Figure S69. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-methyl acrylate copolymer from table 2, entry 8.

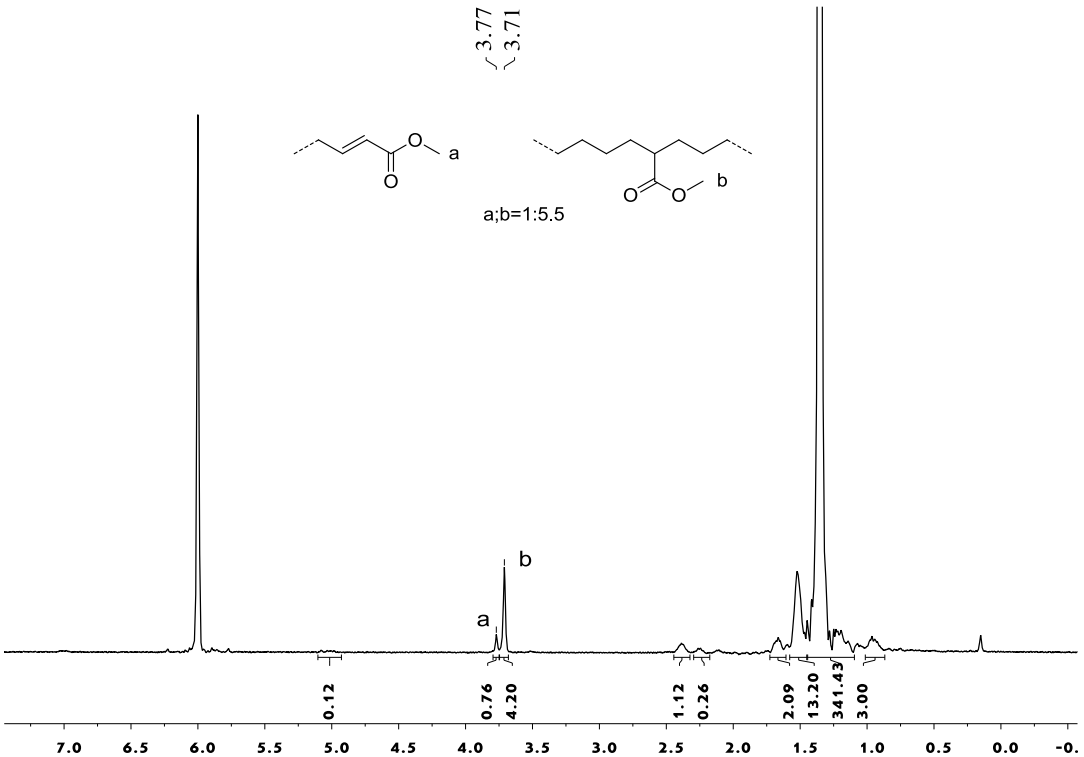


Figure S70. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-methyl acrylate copolymer from table 2, entry 10.

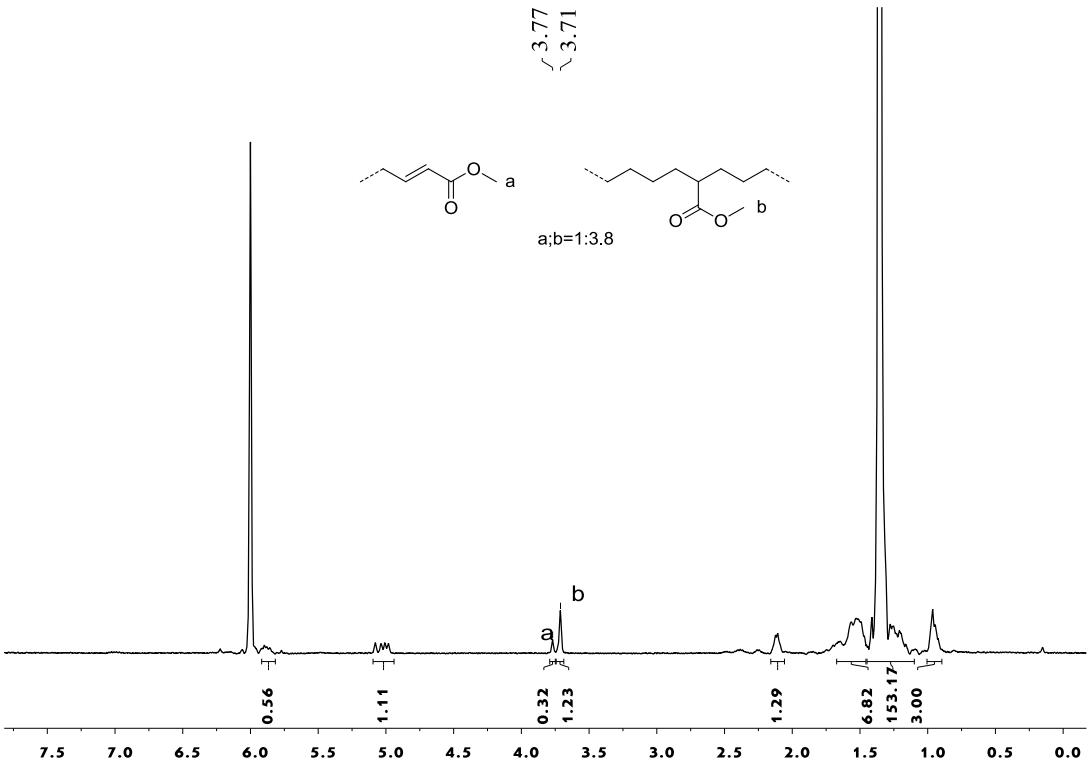


Figure S71. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-methyl acrylate copolymer from table 2, entry 11.

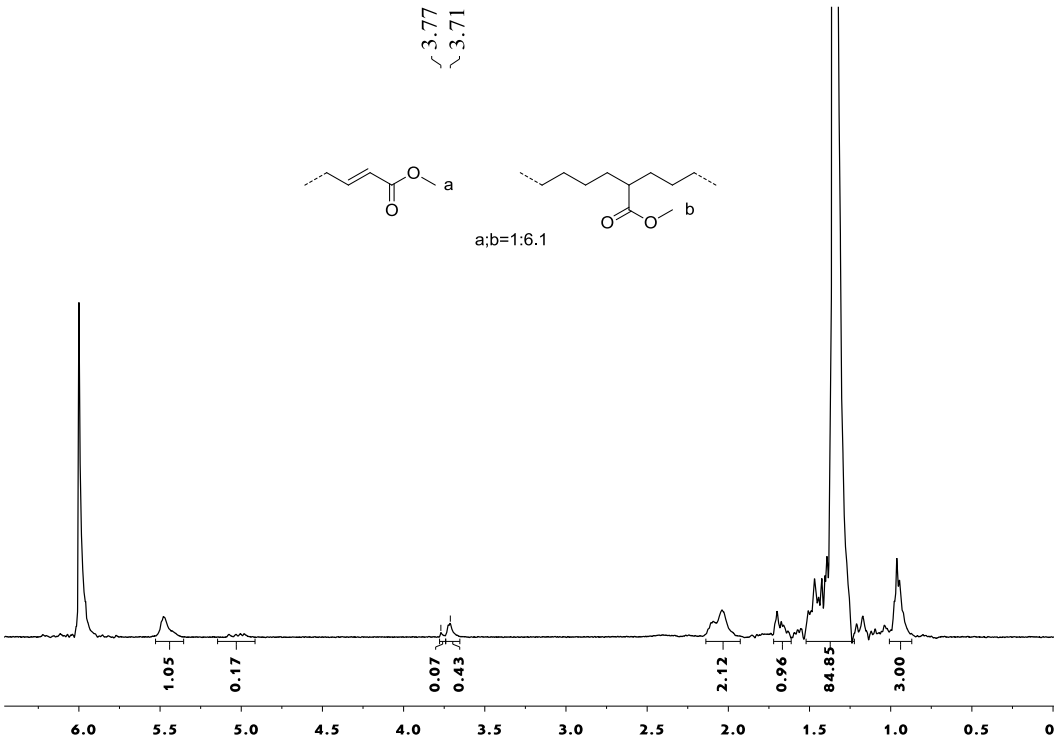


Figure S72. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-methyl acrylate copolymer from table 2, entry 13.

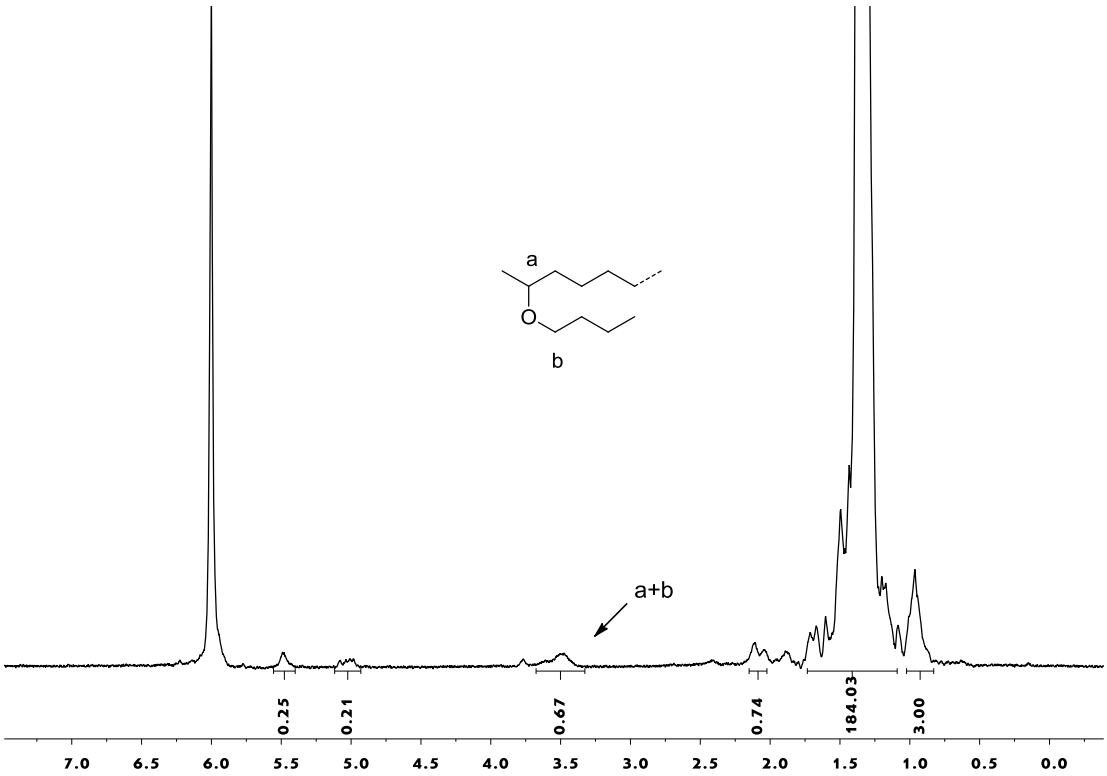


Figure S73-H. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-vinyl n-butyl ether copolymer from table 2, entry 14.

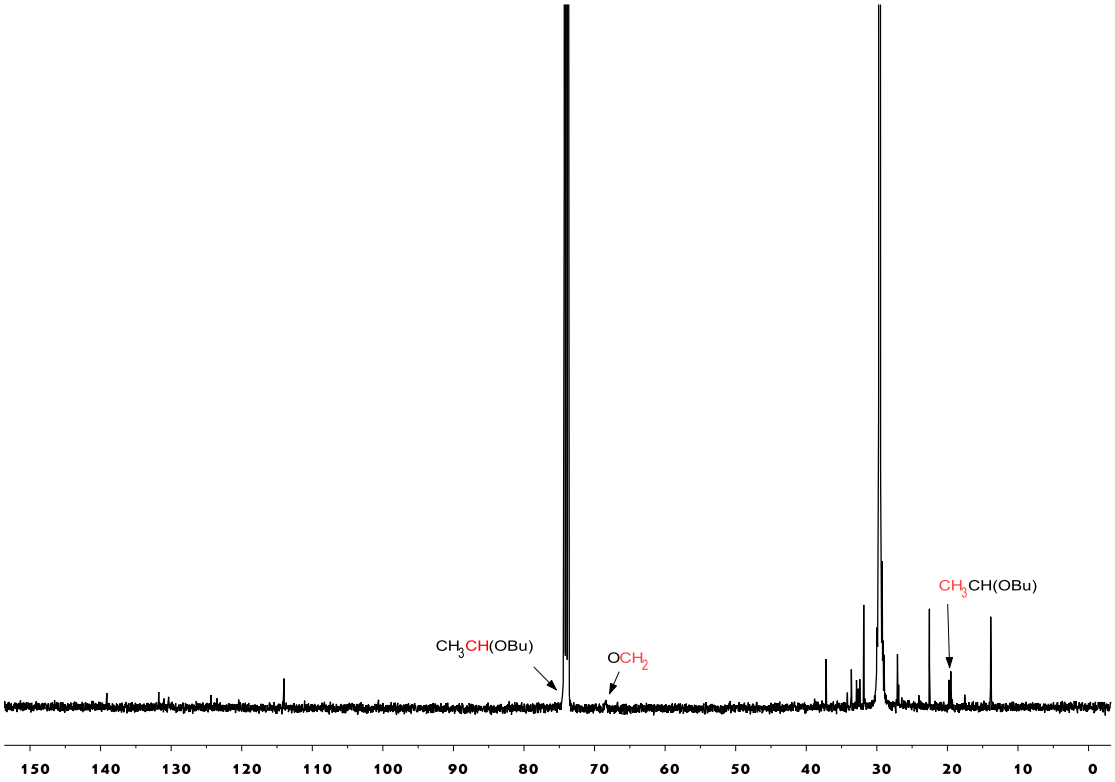


Figure S73-C. ^{13}C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-vinyl n-butyl ether copolymer from table 2, entry 14.

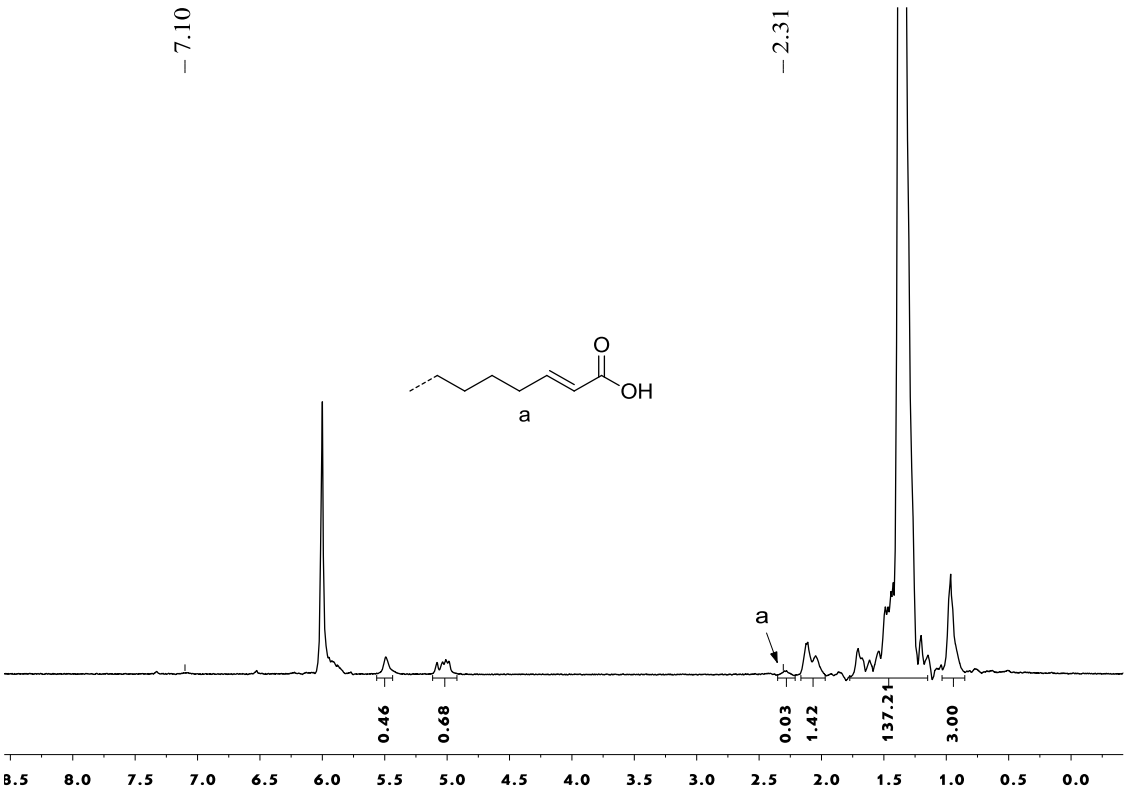


Figure S74. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene- acrylic acid copolymer from table 2, entry 15.

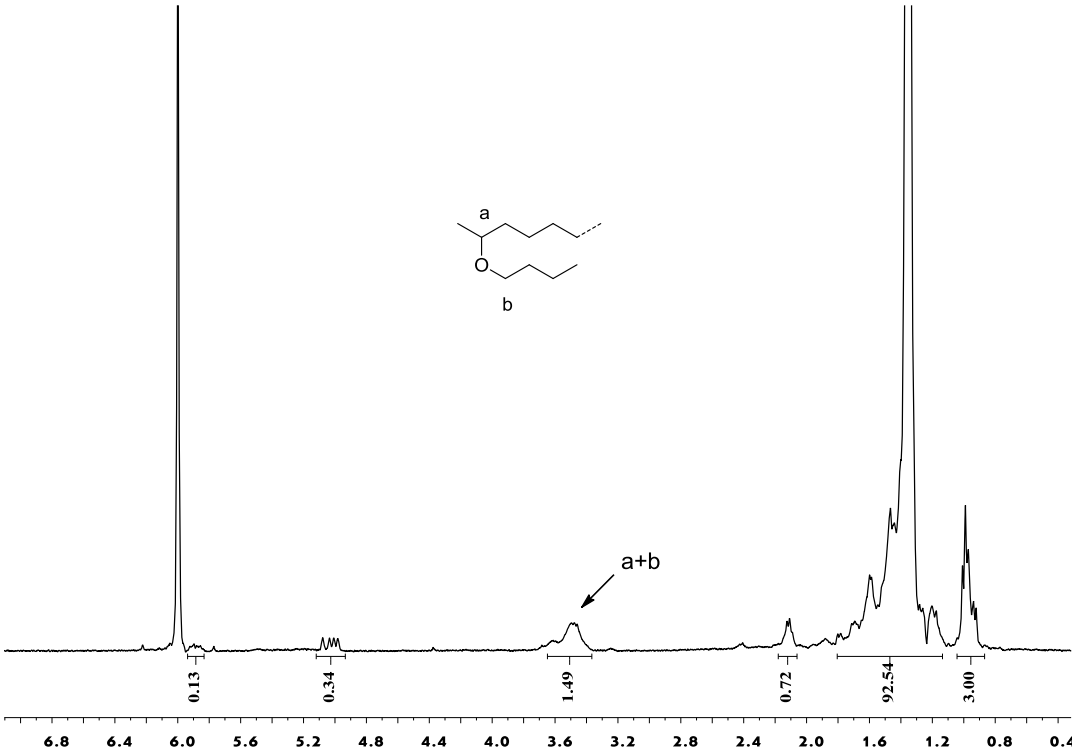


Figure S75. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-vinyl n-butyl ether copolymer from table 2, entry 16.

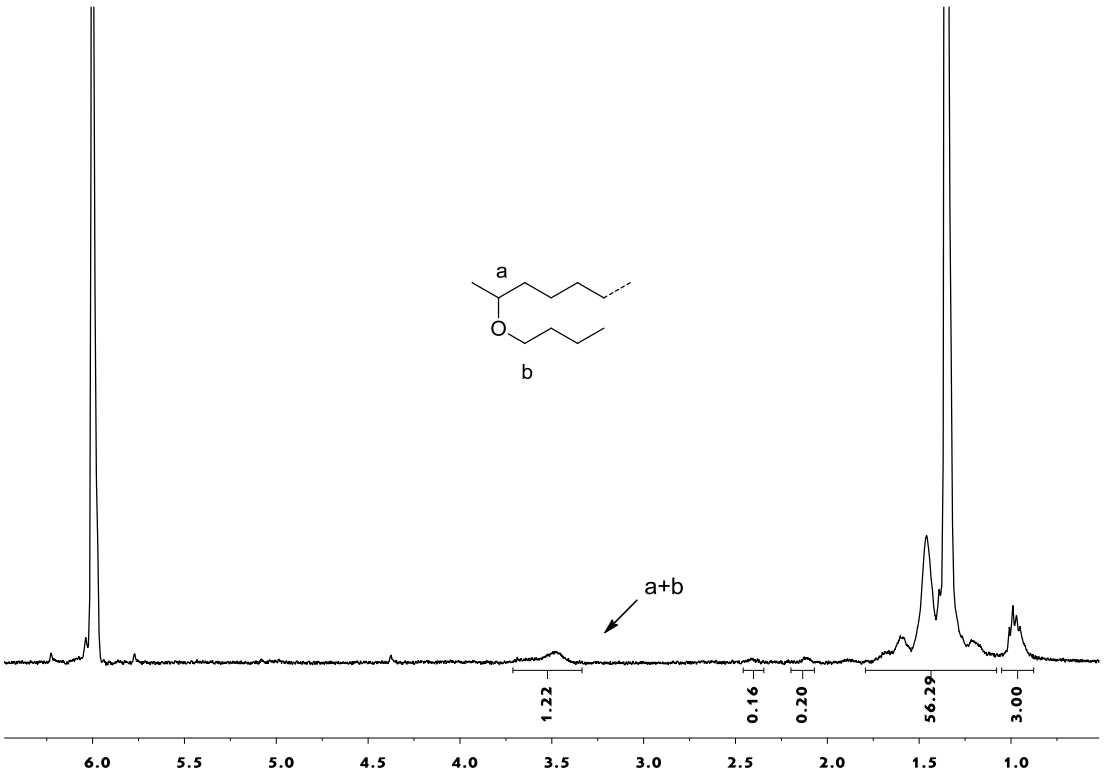
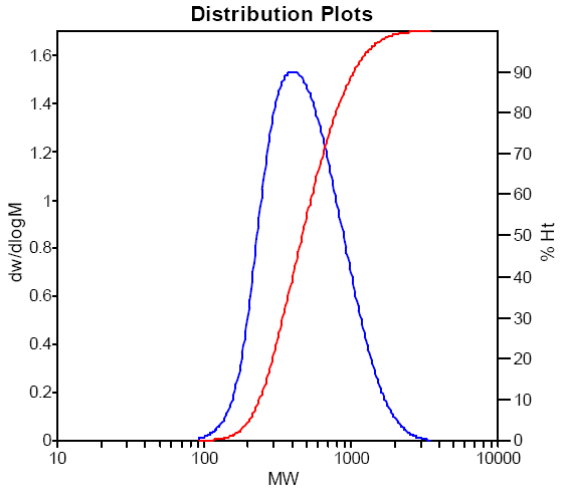


Figure S76. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of ethylene-vinyl n-butyl ether copolymer from table 2, entry 17.

GPC traces and DSC data of (co)polymers



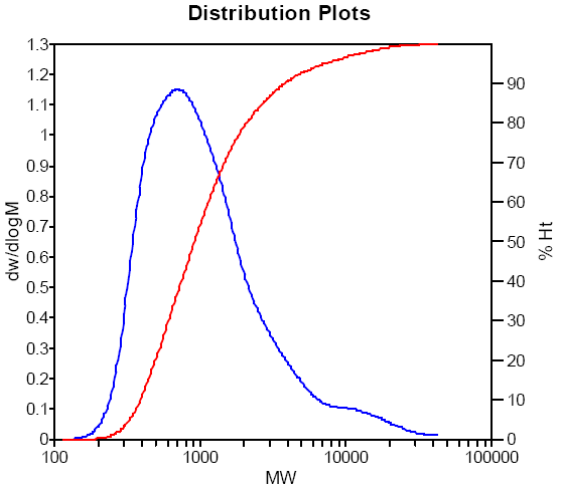
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	405	410	565	797	1097	539	1.37805

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		22.83	25.03	26.55	-231.205	0	21533.5	100

Figure S77. GPC trace of the polymer from table 1, entry 3.



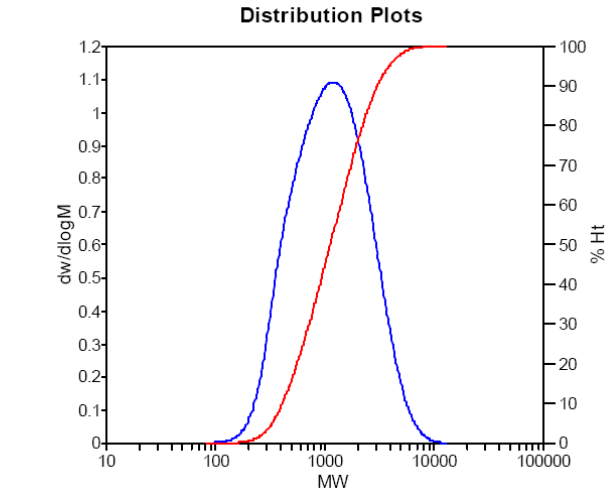
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	700	771	1944	8284	18978	1602	2.5214

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		20.23	24.45	26.33	-134.043	100	16659.4	100

Figure S78. GPC trace of the polymer from table 1, entry 4.



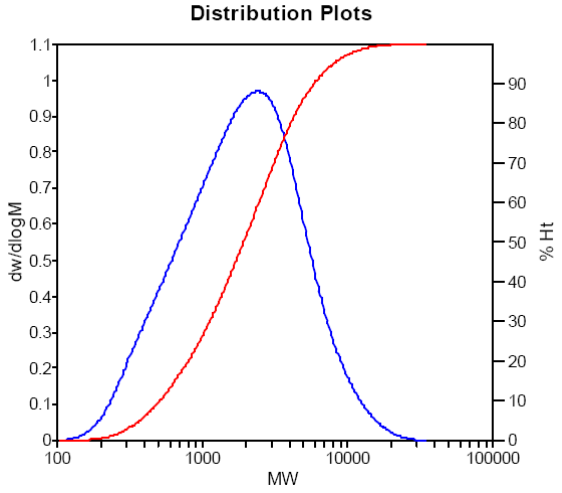
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1212	839	1473	2440	3583	1365	1.75566

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		21.47	23.90	26.68	-86.7325	100	11350.4	100

Figure S79. GPC trace of the polymer from table 1, entry 5.



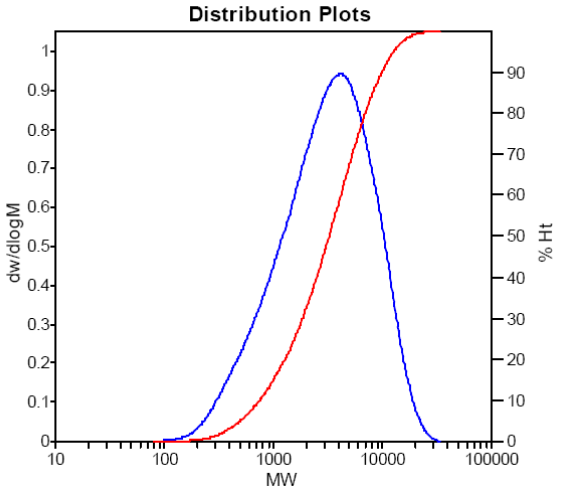
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2424	1182	2729	5442	9098	2455	2.3088

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		20.42	23.18	26.42	-107.101	100	15796.4	100

Figure S80. GPC trace of the polymer from table 1, entry 6.



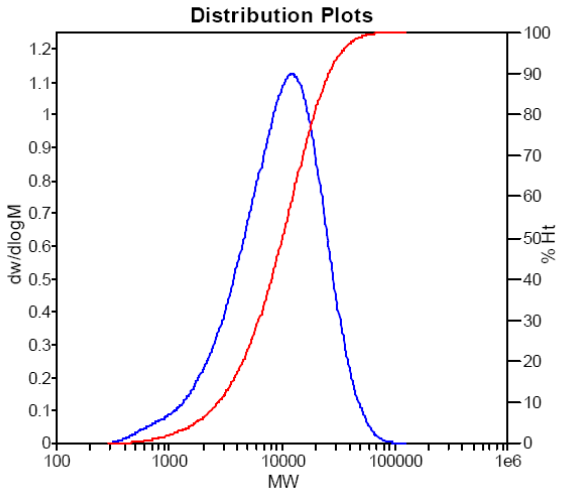
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4127	1742	4417	7983	11465	3997	2.53559

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		20.47	22.63	26.70	-93.2797	100	14153.4	100

Figure S81. GPC trace of the polymer from table 1, entry 7.



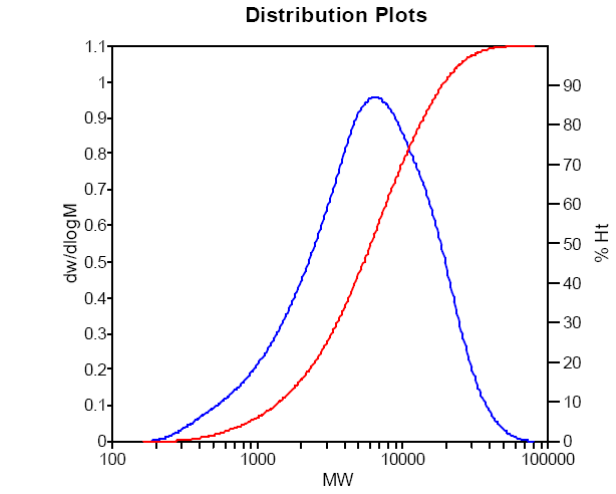
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12155	5614	12647	21074	30253	11643	2.25276

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.10	21.52	25.40	-58.758	100	7464.37	100

Figure S82. GPC trace of the polymer from table 1, entry 8.



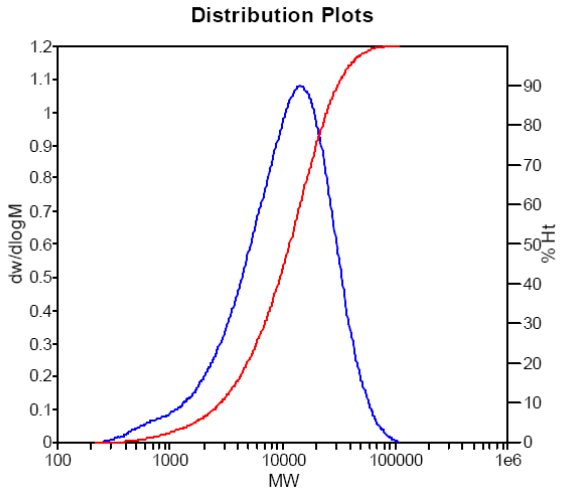
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6481	3168	8447	15898	24038	7610	2.66635

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.57	22.17	25.95	-71.9912	100	10739.8	100

Figure S83. GPC trace of the polymer from table 1, entry 9.



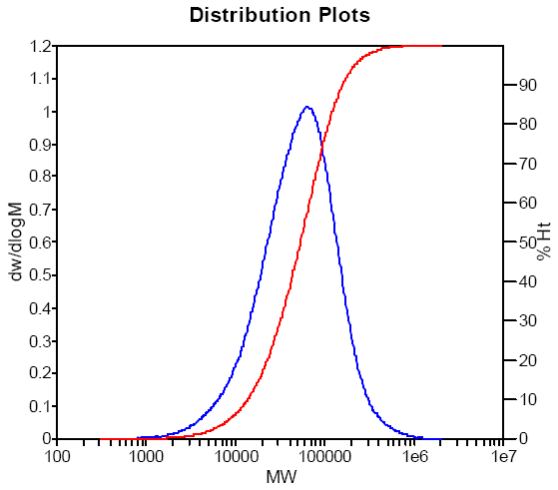
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14422	5734	14682	25133	36133	13315	2.56052

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.43	21.48	25.77	-17.7193	100	2308.94	100

Figure S84. GPC trace of the polymer from table 1, entry 10.



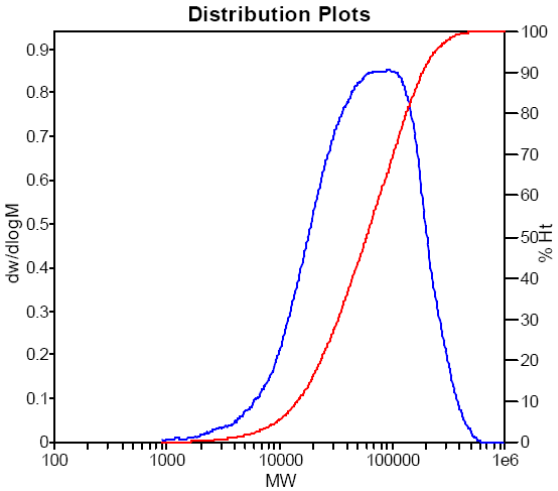
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	64876	27825	76256	169700	346965	67303	2.74056

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.40	19.97	25.48	-26.2568	100	3689.6	100

Figure S85. GPC trace of the polymer from table 1, entry 11.



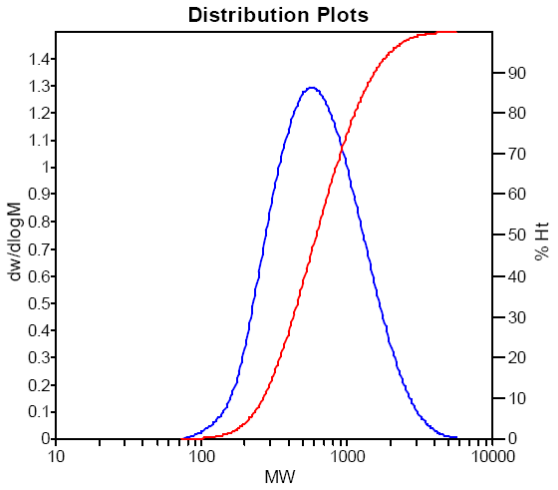
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	92032	29881	83186	154019	223373	74936	2.78391

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.93	19.43	24.25	-10.4607	100	1768.41	100

Figure S86. GPC trace of the polymer from table 1, entry 12



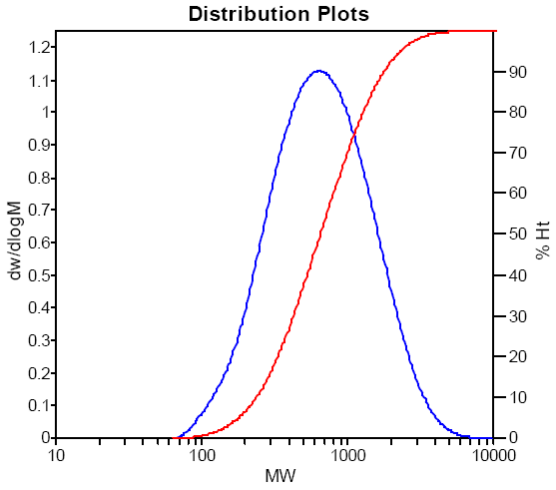
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	577	500	786	1234	1809	738	1.572

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		22.32	24.67	26.78	-192.939	0	21269.7	100

Figure S87. GPC trace of the polymer from table 1, entry 15



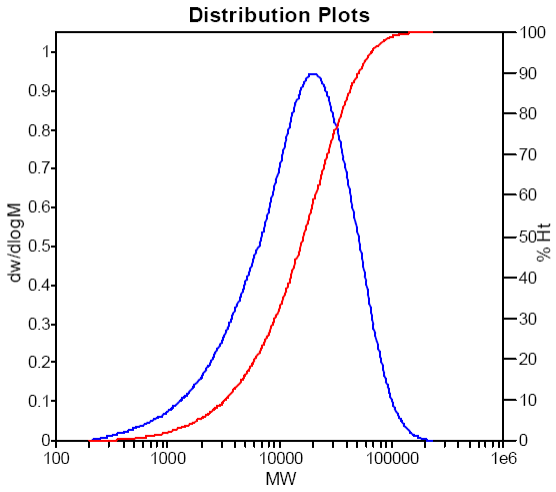
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	646	482	862	1455	2188	798	1.78838

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		21.67	24.57	26.93	-122.708	0	15532.2	100

Figure S88. GPC trace of the polymer from table 1, entry 16



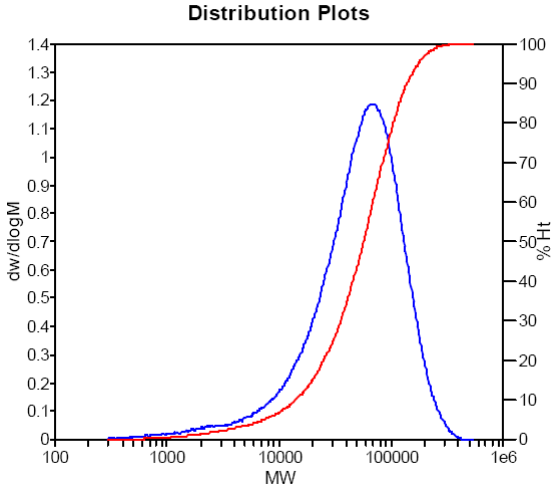
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	20035	6849	22569	43258	65806	20215	3.29523

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.45	21.00	25.77	-84.7559	100	12832	100

Figure S89. GPC trace of the polymer from table 1, entry 19



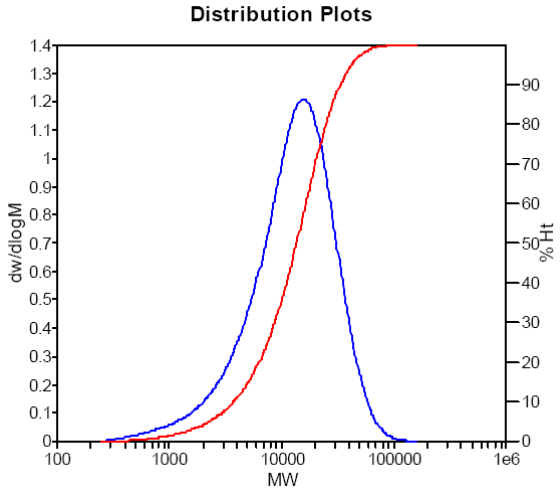
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	70181	21407	68490	110087	151442	63183	3.19942

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.60	19.77	25.43	-18.9308	100	2302.98	100

Figure S90. GPC trace of the polymer from table 1, entry 20



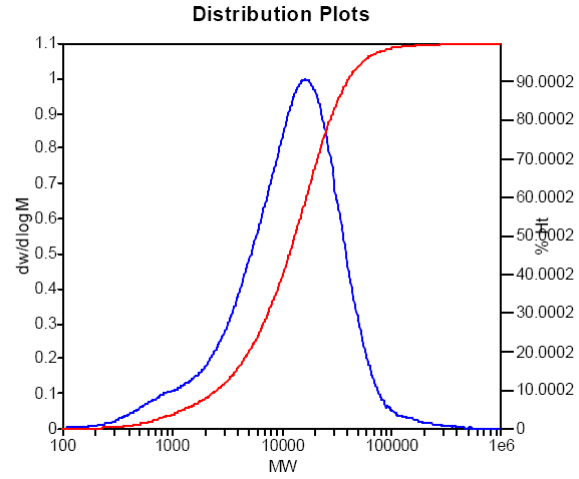
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	15731	7240	16601	26919	38737	15360	2.29296

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.83	21.25	25.53	-101.293	0	11964.2	100

Figure S91. GPC trace of the polymer from table 1, entry 22



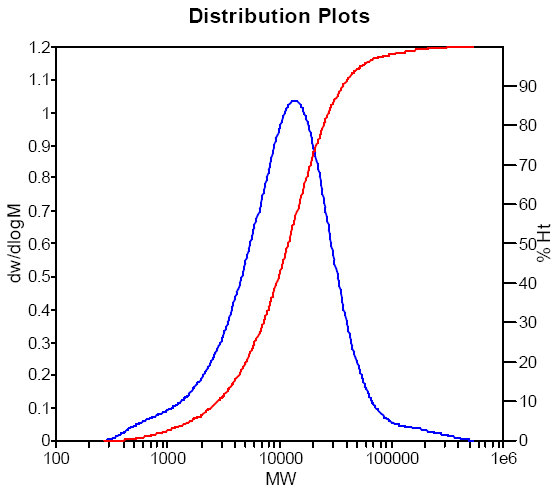
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	16186	4988	19257	56770	185809	16772	3.86067

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.98	21.25	26.60	-23.11	100	3346.64	100

Figure S92. GPC trace of the polymer from table 1, entry 23



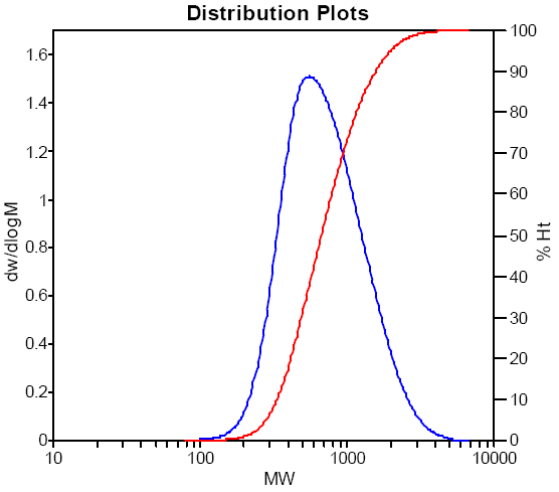
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	13828	5824	18999	66374	186871	16254	3.26219

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.58	21.38	25.45	-101.617	0	14009.6	100

Figure S93. GPC trace of the polymer from table 1, entry 24



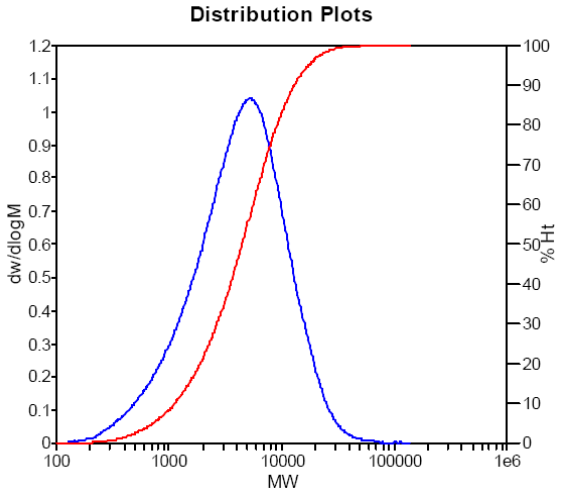
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	559	585	832	1223	1758	790	1.42222

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		22.17	24.77	26.82	-42.1321	100	4032.77	100

Figure S94. GPC trace of the polymer from table 2, entry 3



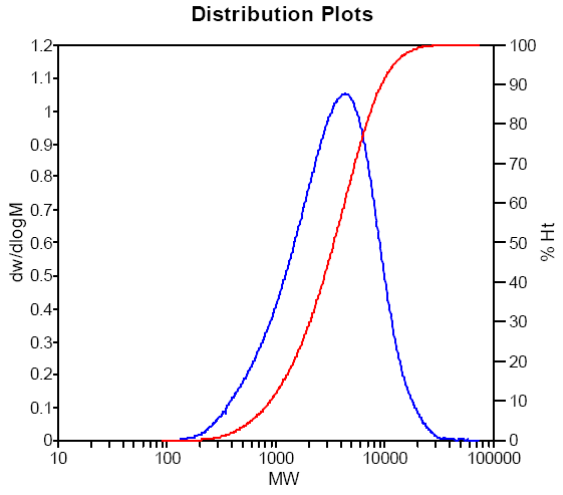
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	5386	2448	6132	12554	25480	5522	2.5049

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.02	22.40	26.55	-18.4702	100	2568.56	100

Figure S95. GPC trace of the polymer from table 2, entry 4



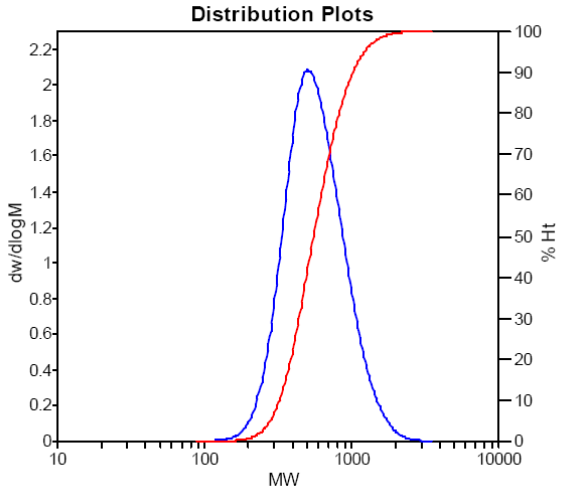
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4309	1980	4474	8077	13096	4081	2.2596

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.67	22.63	26.65	-19.2107	100	2637.73	100

Figure S96. GPC trace of the polymer from table 2, entry 5



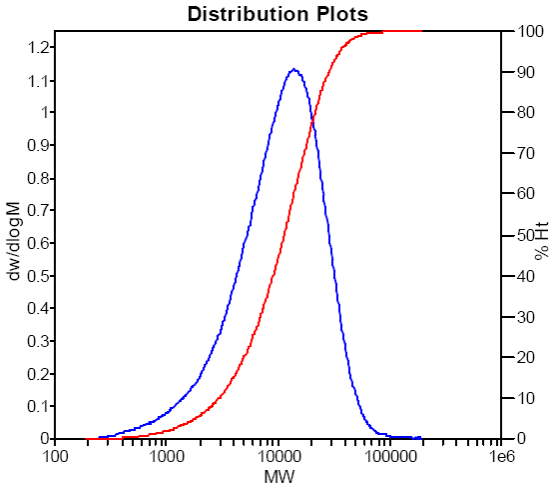
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	508	509	622	773	967	604	1.222

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		22.85	24.87	26.68	-37.2661	100	2581.21	100

Figure S97. GPC trace of the polymer from table 2, entry 8



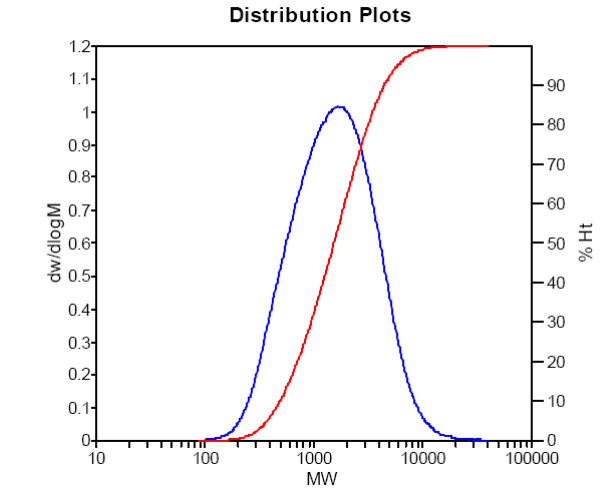
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14022	5989	14068	24013	38682	12938	2.34897

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.67	21.40	25.90	-25.698	100	3273.92	100

Figure S98. GPC trace of the polymer from table 2, entry 10



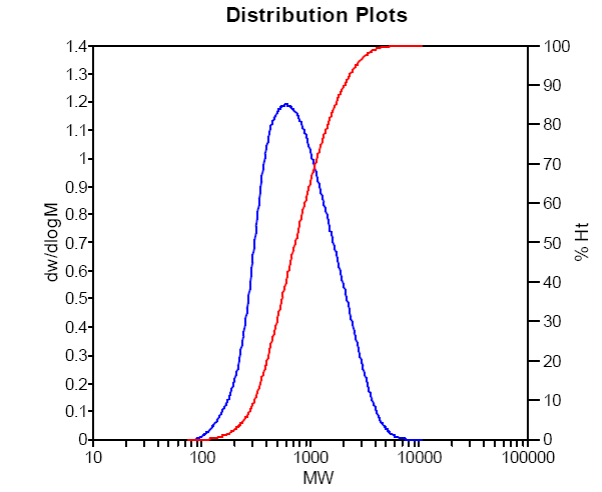
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1655	1055	2125	4144	7828	1932	2.01422

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		20.32	23.63	26.68	-26.51	100	3770.42	100

Figure S99. GPC trace of the polymer from table 2, entry 11



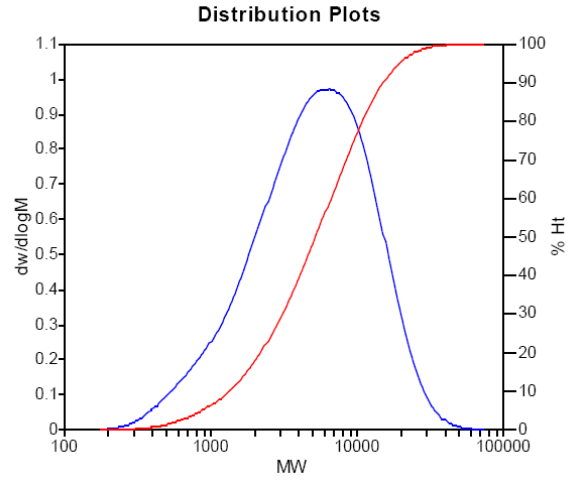
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	606	586	985	1643	2472	915	1.68089

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		21.70	24.68	26.87	-37.4321	0	4540.62	100

Figure S100. GPC trace of the polymer from table 2, entry 13



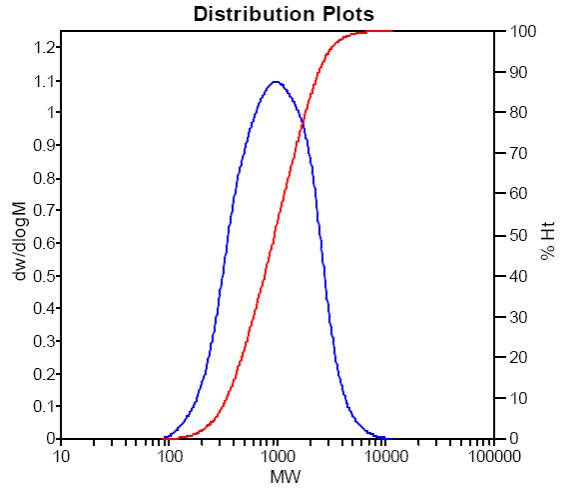
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6424	2957	6985	12492	18613	6354	2.36219

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.25	14.90	17.33	-42.1422	100	4054.99	100

Figure S101. GPC trace of the polymer from table 2, entry 14



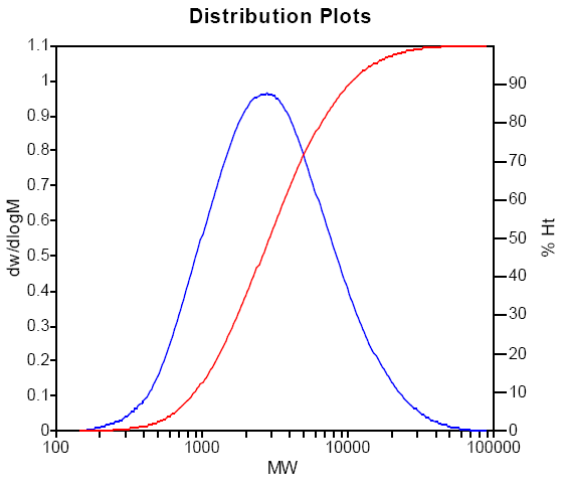
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	947	692	1202	1939	2838	1119	1.73699

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		21.63	24.22	26.68	-32.1113	0	4235.5	100

Figure S102. GPC trace of the polymer from table 2, entry 15



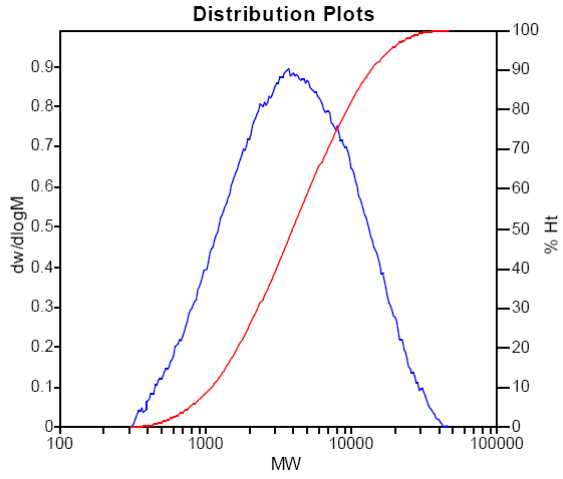
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2781	1932	4604	11006	21397	4061	2.38302

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.12	15.47	17.45	-22.3232	100	2165.48	100

Figure S103. GPC trace of the polymer from table 2, entry 16



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3737	2480	5945	11689	17627	5325	2.39718

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.57	15.27	16.95	-1.79885	100	187.886	100

Figure S104. GPC trace of the polymer from table 2, entry 17

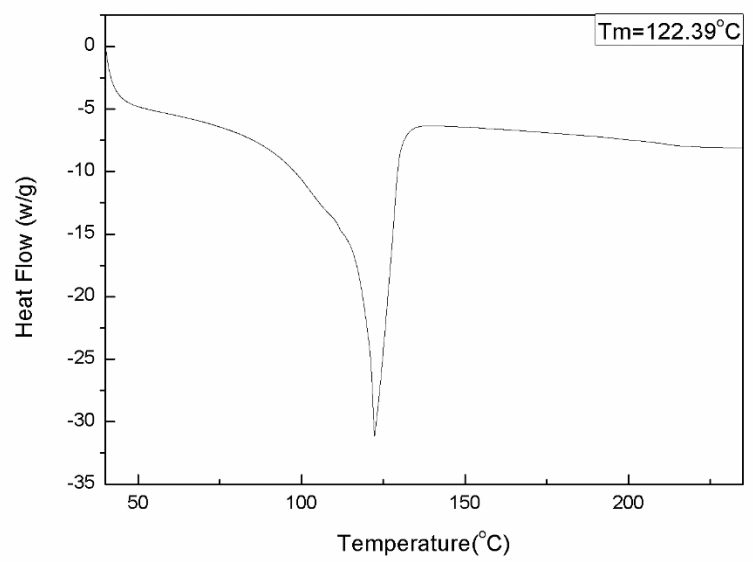


Figure S105. DSC data of the polymer from table 1, entry 7

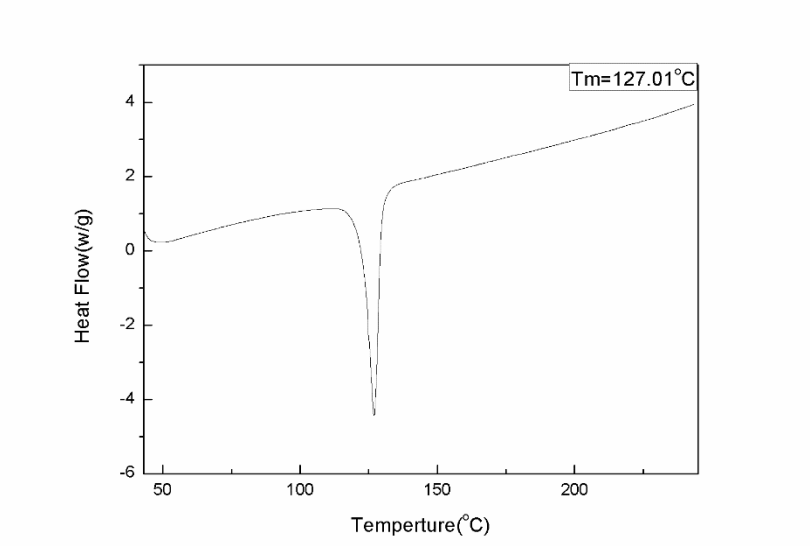


Figure S106. DSC data of the polymer from table 1, entry 8

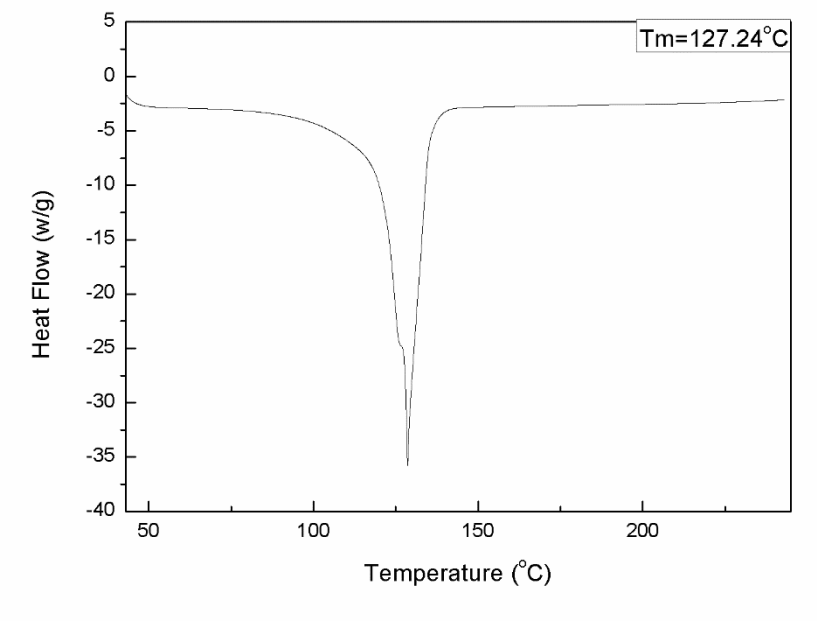


Figure S107. DSC data of the polymer from table 1, entry 9

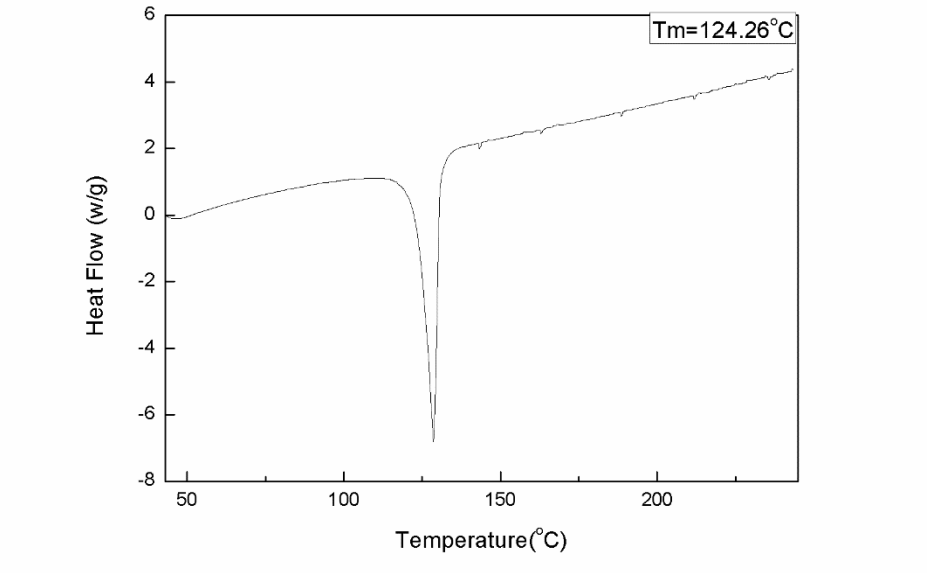


Figure S108. DSC data of the polymer from table 1, entry 10

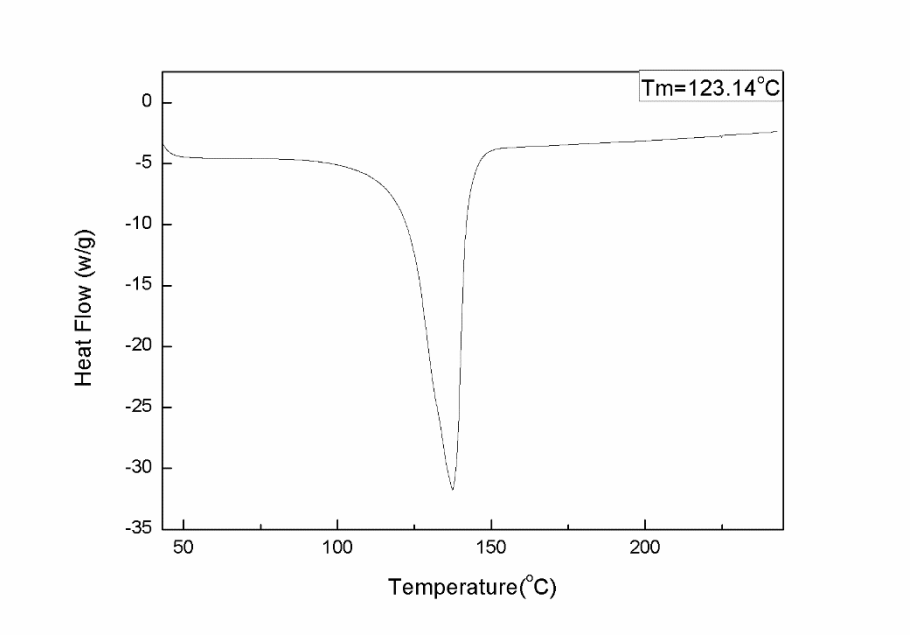


Figure S109. DSC data of the polymer from table 1, entry 12

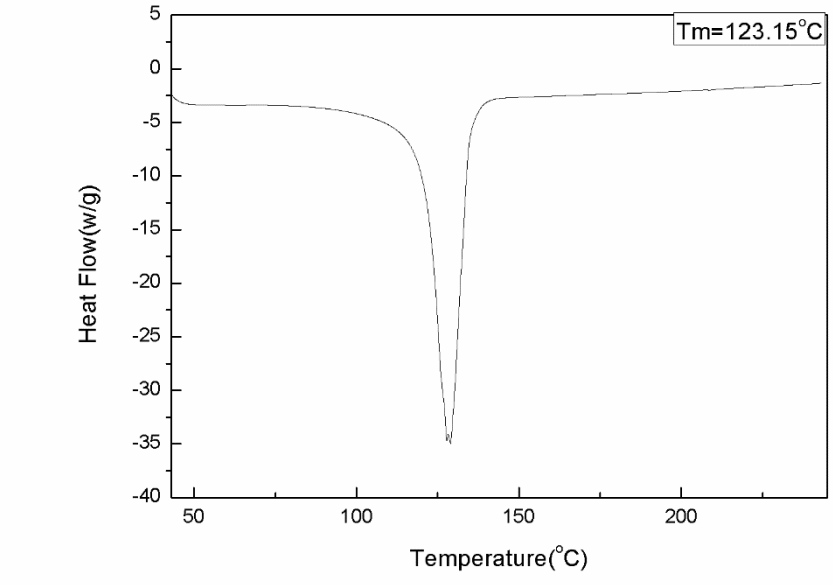


Figure S110. DSC data of the polymer from table 1, entry 22

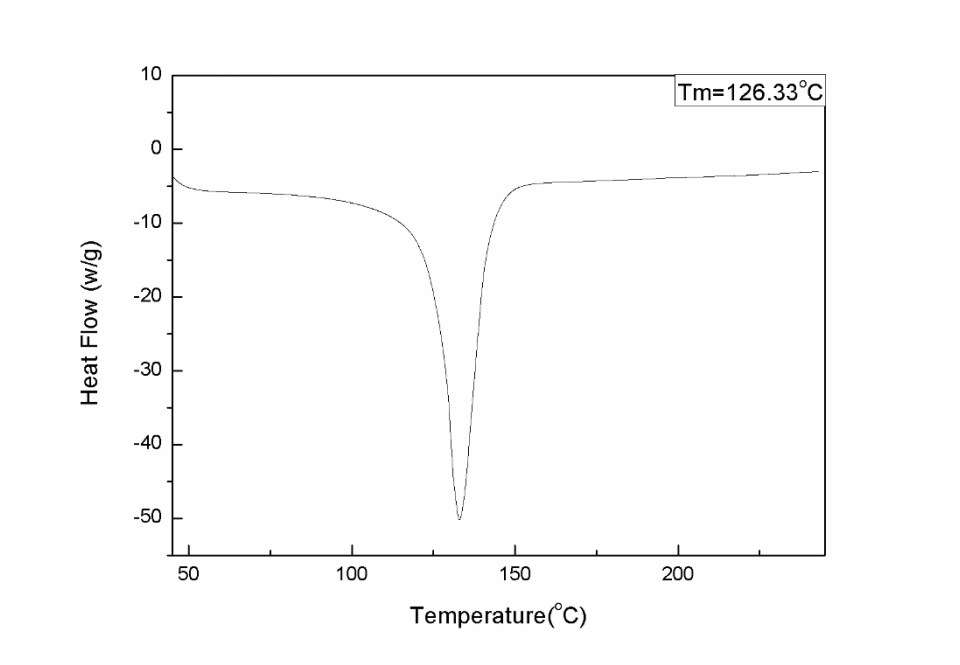


Figure S111. DSC data of the polymer from table 1, entry 23

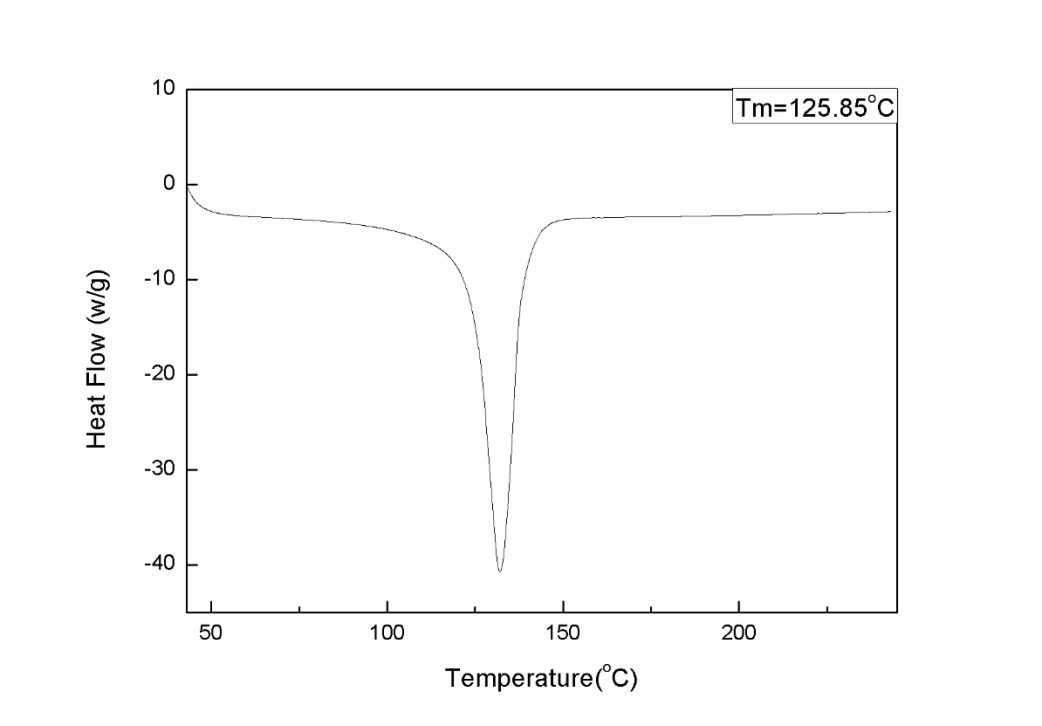


Figure S112. DSC data of the polymer from table 1, entry 24

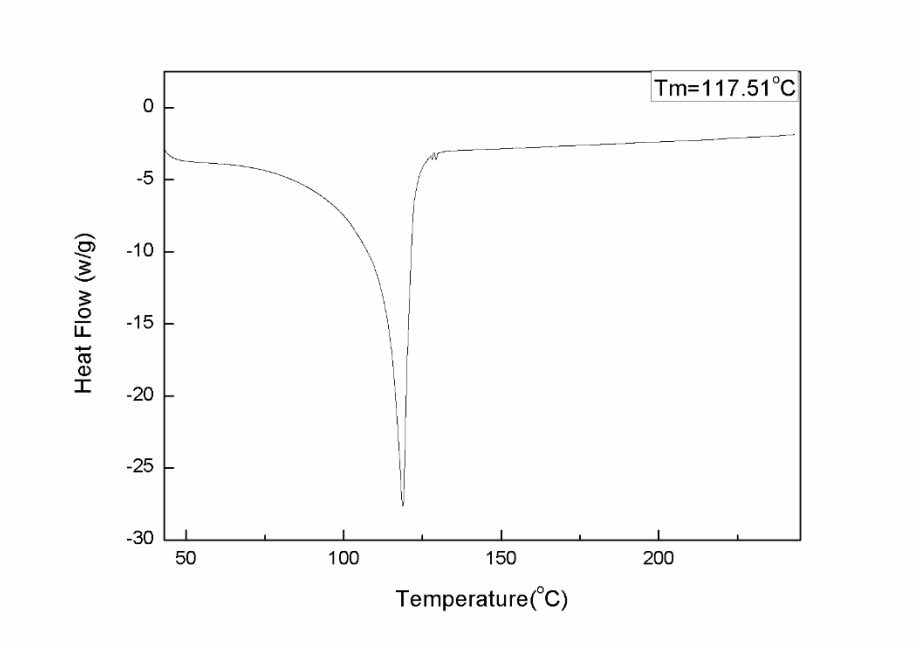


Figure S113. DSC data of the polymer from table 2, entry 4

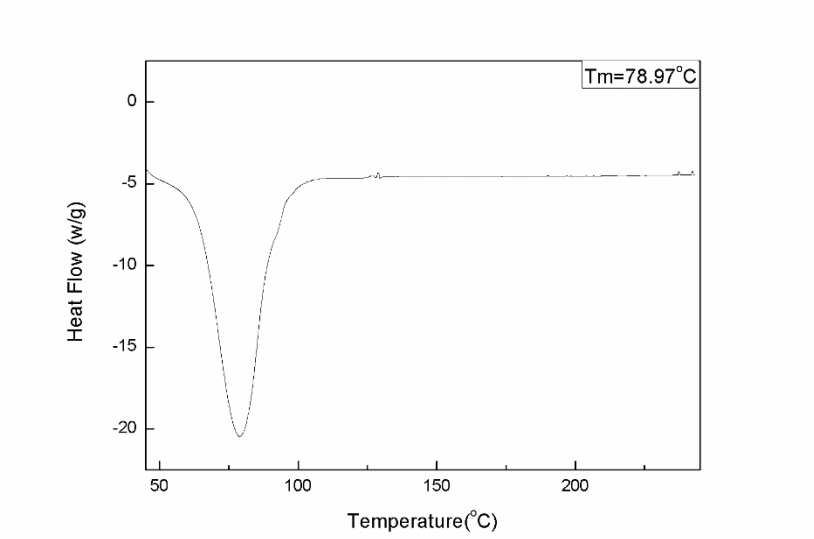


Figure S114. DSC data of the polymer from table 2, entry 8

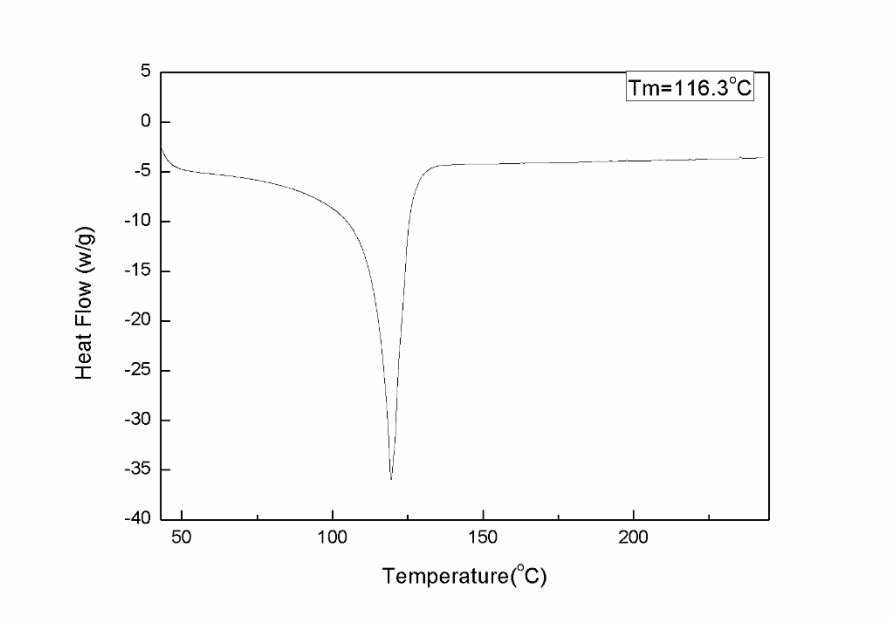


Figure S115. DSC data of the polymer from table 2, entry 10

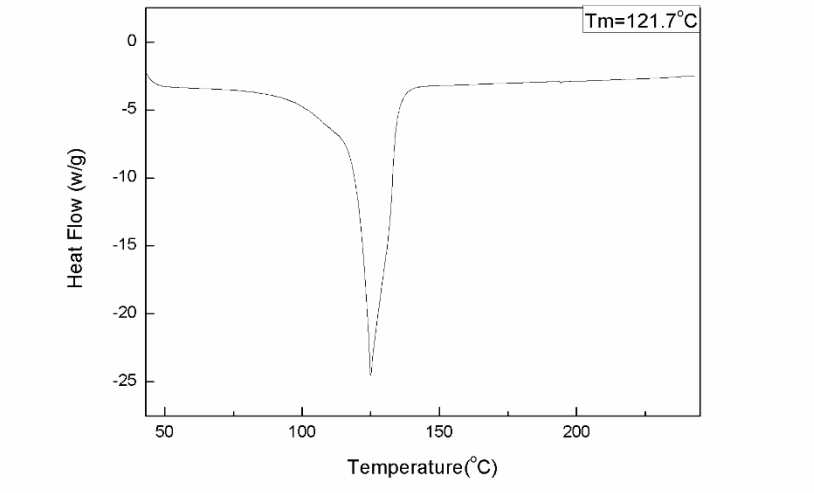


Figure S116. DSC data of the polymer from table 2, entry 14

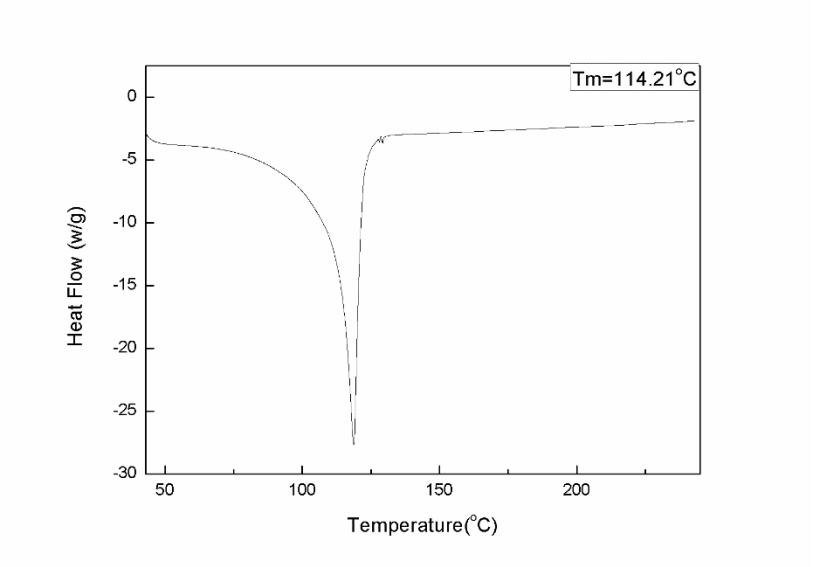


Figure S117. DSC data of the polymer from table 2, entry 16

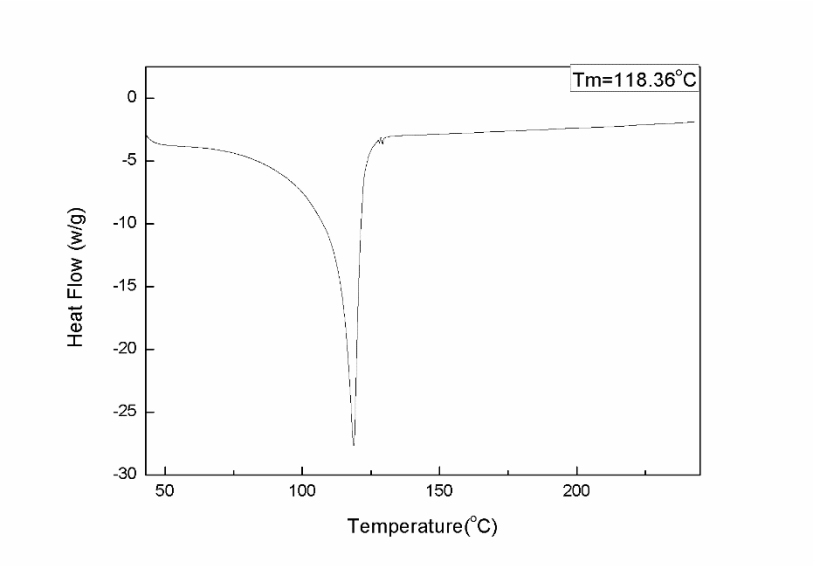


Figure S118. DSC data of the polymer from table 2, entry 17

X-ray Crystallography

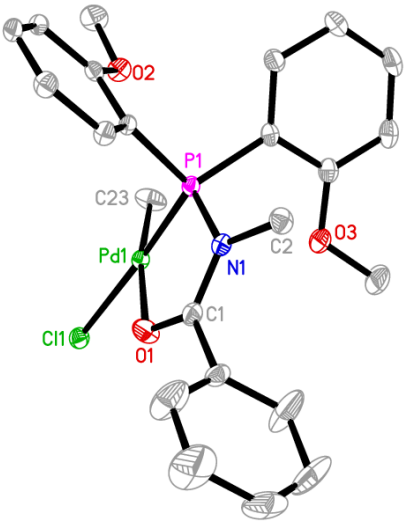


Figure S119. Molecular structures of catalysts **Pd2** Hydrogen atoms were omitted for clarity.Selected bond lengths (Å) and angles (deg) for **Pd2**: Pd1-P1 = 2.1850(8), Pd1-C23 =2.033(4), Pd1-O1 = 2.189(2), Pd1-Cl1 = 2.3590(8), C23- Pd1-Cl1 = 91.49(12), O1- Pd1-P1 = 80.29(7).

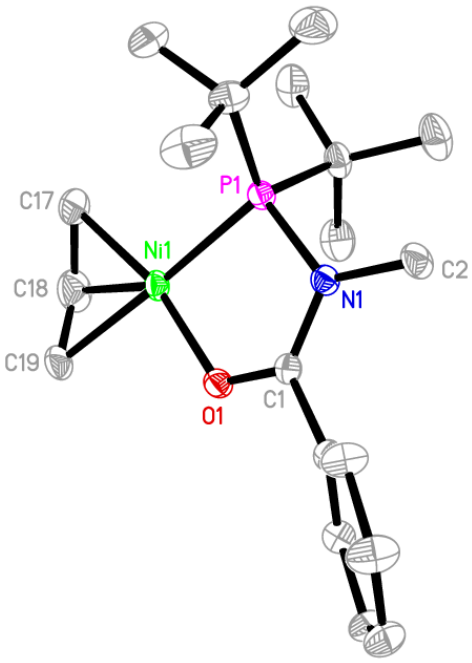


Figure S120. Molecular structures of catalysts **Ni6**. Hydrogen atoms and the BAr^F_4 groups were omitted for clarity. Selected bond lengths (Å) and angles (deg) for **Ni6**: Ni1-P1 = 2.1707(10), Ni1-C17 = 1.998(4), Ni1- C18 = 2.014(4), Ni1- C19 = 2.034(4), Ni1-O1 = 1.894(2),O1-Ni1-P1 = 86.13(7), C17-Ni1-C19 = 72.73(17).

Table S1. Crystallographic data for **Pd2** and **Ni6**

	Pd2	**Ni6**
Formula	$C_{23}H_{25}ClNO_3PPd$	$C_{51}H_{43}BF_{24}NNiOP$
Formula weight	536.26	1242.35
Crystal dimensions (mm^3)	0.26 ×0.18 ×0.11	0.32 ×0.21 ×0.18
Crystal system	triclinic	Monoclinic
Space group	P -1	-P 2ybc
a (Å)	8.6330(4)	12.6795(3)
b (Å)	10.4214(5)	19.6724(4)
c (Å)	16.3267(8)	21.4947(4)
α (°)	78.0730(10)	90
β (°)	86.9240(10)	97.3710(10)
γ (°)	70.4470(10)	90
Volume ($Å^3$)	1354.10(11)	5317.25(19)
Z	2	4
T (K)	173(2)	173(2)
D_{calcd} (g cm^{-3})	1.315	1.552
μ (mm^{-1})	0.863	1.935
F (000)	544	2512
No. of rflns. collected	28327	23694
No. of indep. rflns. /R_{int}	6106 / 0.0271	7465 / 0.0313
No. of obsd. rflns. [$I_0 > 2\sigma(I_0)$]	5680	6441
Data / restraints / parameters	6106 / 0 / 271	7465 / 72 / 749
R_1 / wR_2 [$I_0 > 2\sigma(I_0)$]	0.0408 / 0.1023	0.0553 / 0.1392
R_1 / wR_2 (all data)	0.0441 / 0.1050	0.0632 / 0.1475
GOF (on F^2)	0.996	1.003
Largest diff. peak and hole (e $Å^{-3}$)	4.511 / –0.669	1.073 / –0.733
CCDC No.	1973964	1973963

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