Supporting Information:

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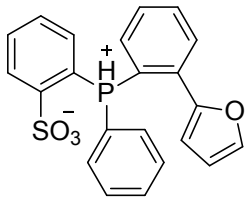
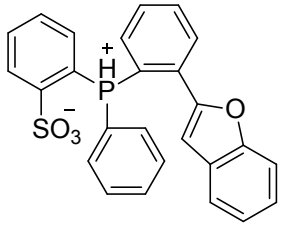
1. General methods.

All experiments were carried out under dry Nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded a Bruker AscendTm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane; the ^{31}P NMR spectra were referenced to an external 85% H_3PO_4 solution. Coupling constants are in Hz. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. X-ray Diffraction data were collected at 298 (2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) with a PL 210 equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 140 ^{o}C using trichlorobenzene as a solvent, and the calibration was made using polystyrene standard and are corrected for linear polyethylene by universal calibration using the Mark–Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ cm^3/g and R = 0.67 for polystyrene and $K = 5.90 \times 10^{-2}$ cm^3/g and R = 0.69 for polyethylene. Dichloromethane, THF, and hexanes were purified by solvent purification systems. 2-(2-bromophenyl)furan,[1] 2-(2-bromophenyl)thiophene,[1] 2-(2-bromophenyl)-1-benzofuran,[2] 2-(2-bromophenyl)-1-benzothiophene,[3] and 2-(2- bromophenyl)-1-methyl-1H-pyrrole,[4] were prepared according to literature procedures.

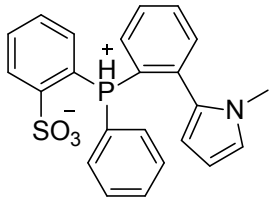


Preparation of Ligand L1： At 0 °C, ^{n}BuLi (2.5 M, 8 mL, 20 mmol) was added slowly to a solution of benzenesulfonic acid (1.58 g, 10 mmol) in THF (50 mL). The suspension was stirred for 1 h and added to a solution of dichlorophenyl-phosphine (1.35 mL, 10.0 mmol) in THF (30 mL) at -78 °C. The mixture was stirred for another 12 h at room temperature to yield a solution of lithium [chloro(phenyl)phosphino]benzenesulfonate. In a separate Schlenk flask, 2-(2-bromophenyl)furan (2.2 g, 10 mmol) was dissolved in dry THF (100 mL) under nitrogen and cooled to -78 °C. ^{n}BuLi (2.5 M in hexane, 4 mL, 10 mmol) was added dropwise. The resulting red solution was stirred for 1.0 h at -78 °C before the lithium [chloro(phenyl)phosphino]benzenesulfonate was added dropwise. The mixture was stirred for another 24 h at room temperature. The volatiles were removed, and the residue was taken up in distilled water (150 mL). The mixture was acidified to pH ~2 with concentrated HCl/H_2O solution, and extracted three times with CH_2Cl_2 (total volume 250 mL). The extracts were combined, dried over $MgSO_4$, and concentrated under vacuum. The crude product was recrystallized from dichloromethane/ether at room temperature. The resulting white crystals were filtered and dried to give the

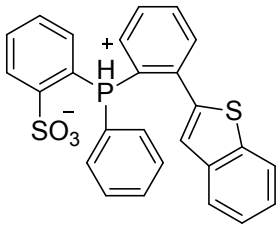
desired ligand **L1**(2.7 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (br, 1H), 7.89 – 7.63 (m, 4H), 7.62-7.43 (m, 5H), 7.42 – 7.32 (m, 2H), 7.20 – 7.07 (m, 2H), 6.73 (s, 1H), 6.32 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ 151.1 (d, J = 4 Hz), 149.2 (d, J = 7 Hz), 143.2 (s), 134.9 (d, J = 12 Hz), 133.9 (d, J = 6 Hz), 133.8 (s), 132.6 (s), 132.4 (d, J = 6 Hz), 132.2 (d, J = 9 Hz), 131.5 (s), 130.4 (s), 129.5 (d, J = 13 Hz), 129.2 (d, J = 9 Hz), 129.0 (d, J = 9 Hz), 128.6 (s), 128.4 (d, J = 12 Hz), 127.5 (s), 127.2 (d, J = 13 Hz), 126.9 (s), 125.8(s). ^{31}P NMR (162 MHz, DMSO): δ -13.22. ESI-MS (m/z): $[M-H]^-$ Calcd for $C_{22}H_{16}O_4PS$, 407.0507; Found: 407.0502.



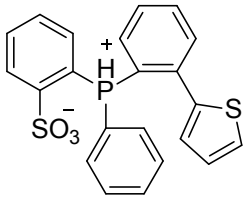
Preparation of Ligand L2. Similar procedure as above was employed except 2-(2-bromophenyl)-1-benzofuran was used. **L2** was obtained as a light white solid (3.3 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (br, 1H), 7.97 (br, 1H), 7.78 (d, J = 5.9 Hz, 2H), 7.57 – 7.48 (m, 8H), 7.37-7.35 (d, J = 7.6 Hz 2H), 7.20-7.19 (d, J = 7.3 Hz, 2H), 7.10 (s, 2H). ^{13}C NMR (100 MHz, DMSO) of **L2**: δ 153.9 (s), 151.8 (s), 151.6 (s), 138.3 (d, J = 13 Hz), 137.2 (s), 137.0 (s), 135.0 (d, J = 11 Hz), 134.3 (s), 134.1 (s), 133.8 (s), 133.6 (s), 133.4 (s), 133.2 (s), 129.6 (s), 129.2 (d, J = 6 Hz), 128.8 (s), 128.6 (s), 128.4 (s), 128.3 (s),127.7 (s), 124.8 (s), 123.1 (s), 121.6 (s), 111.2 (s), 108.1 (d, J = 18 Hz). ^{31}P NMR (162 MHz, DMSO): δ -13.82. ESI-MS (m/z): $[M-H]^-$ Calcd for $C_{26}H_{18}O_4$ PS , 457.0663; Found: 457.0656.



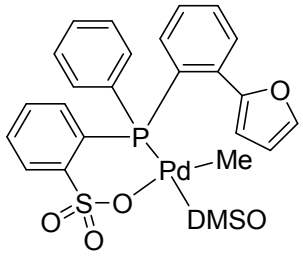
Preparation of Ligand L3. Similar procedure as above was employed except 2-(2-bromophenyl)-1-methyl-1H-pyrrole was used. **L3** was obtained as a light white solid (1.9 g, 45%). Solubility of **L3** in common organic solvent is very low, so only ^{1}H and ^{31}P NMR spectra were recorded. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.96 – 7.66 (m, 4H), 7.59 (s, 2H), 7.48 (d, J = 6.1 Hz, 3H), 7.43 – 7.21 (m, 3H), 7.09 (dd, J = 13.9, 7.8 Hz, 1H), 6.58 (s, 1H), 5.97 (s, 1H), 3.35 (s, 3H).^{31}P NMR (162 MHz, DMSO): δ -14.55. ESI-MS (m/z): $[M-H]^-$ Calcd for $C_{23}H_{19}NO_3PS$, 420.0823; Found: 420.0831



Preparation of Ligand L4. Similar procedure as above was employed except 2-(2-bromophenyl)-1-benzothiophene was used. **L4** was obtained as a light white solid (3.8 g, 80%). Solubility of **L4** in common organic solvent is very low, so only ^{1}H and ^{31}P NMR spectra were recorded. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (br, 1H), 7.77 (br, 3H), 7.67 (br, 3H), 7.56 (br, 1H), 7.74-7.28 (m, 9H), 7.12 (br, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 2.04. ESI-MS (m/z): $[M-H]^-$ Calcd for $C_{26}H_{18}O_3PS_2$, 473.0435; Found: 473.0417.

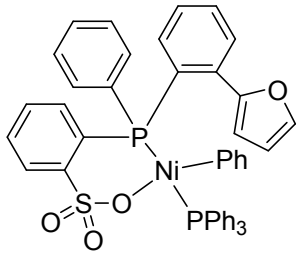


Preparation of Ligand L5. Similar procedure as above was employed except 2-(2-bromophenyl)thiophene was used. **L5** was obtained as a light white solid (1.9 g, 45%). Solubility of **L5** in common organic solvent is very low, so only ^{1}H and ^{31}P NMR spectra were recorded. ^{1}H NMR (400 MHz, DMSO): δ 7.86 (s, 1H), 7.58 (d, 2H), 7.52 (s, 1H), 7.47-7.34 (m, 4H), 7.29 (s, 4H), 7.17 (d, 3H), 7.05 (s, 1H). ^{31}P NMR (162 MHz, DMSO): δ -24.82 (s). ESI-MS (m/z): $[M-H]^-$ Calcd for $C_{22}H_{16}O_3PS_2$, 423.0278; Found: 423.0281.

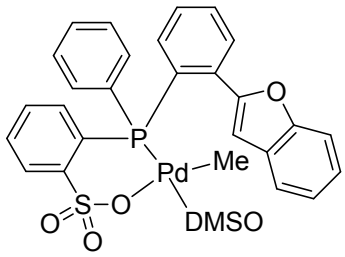


Preparation of catalyst Pd1. Ligand **L1** (490 mg,1.2 mmol) was suspended in THF (10 mL). $(TMEDA)PdMe_2$ (303 mg, 1.2 mmol) was added at room temperature. After 5 min the evolution of gas stopped and the suspension turned clear. The solution was stirred overnight at -5 °C. The resulting white precipitate was filtered, washed with diethyl ether and dried under reduced pressure to yield a tmeda-bridged dimer **1-TMEDA** according to literature.[5] **1-TMEDA** was dispersed in 10 mL DMSO at room temperature. The solvent was removed under reduced pressure at 70 °C. The **1-TMEDA** complex is only slightly soluble in DMSO, therefore complete dissolution of the solid indicate complete conversion of the starting material. After removal of DMSO under reduced pressure, the resulting solid was dispersed in diethyl ether, and

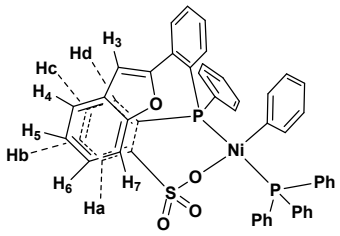
isolated by filtration to yield a white solid **Pd1** (487 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29-8.26 (m, 1H), 7.78 – 7.75 (m, 1H), 7.61-7.48 (m, 5H), 7.45 – 7.36 (m, 4H), 7.32 – 7.28 (t, *J* = 7.7 Hz, 3H), 7.21 – 7.16 (m, 1H), 7.08 – 7.03 (m, 1H), 6.38 (s, 2H), 2.96 (s, 6H, DMSO), 0.42 (s, 3H, Pd-*Me*). ^{13}C NMR (100 MHz, DMSO): δ 150.91 (d, *J* = 4.3 Hz), 147.51 (s), 147.37 (s), 143.56 (s), 134.81 (d, *J* = 13.1 Hz), 134.16 (d, *J* = 3.4 Hz), 134.03 (s), 133.63 (s), 131.25 (s), 131.15 (d, *J* = 3.3 Hz), 130.26 (d, *J* = 6.7 Hz), 129.81 (d, *J* = 8.3 Hz), 129.31 (s), 128.79 (d, *J* = 11.2 Hz), 128.54 (s), 128.05 (s), 126.70 (s), 126.20 (s), 111.62 (s), 111.26 (s), 40.43 (s, DMSO), -0.66 (s, Pd-*Me*). ^{31}P NMR (162 MHz, DMSO): δ 26.56. Anal. Calcd. for $C_{25}H_{25}O_5PPdS_2$: C, 49.47; H, 4.15. Found: C, 48.97; H, 4.28.



Preparation of catalyst Ni1. A suspension of **L1** (200 mg, 0.49 mmol) and Na_2CO_3 (156 mg, 1.47 mmol) in 15 mL Dichloromethane was stirred for 6 h at room temperature. *trans*-[$(PPh_3)_2$Ni(Cl)Ph] (340mg, 0.49 mmol) was added in small portions. Dichloromethane was added until the volume of the solution reached 20 mL, and the reaction mixture was stirred for 24 h at room temperature. The resulting yellow-orange mixture was filtered over Celite and the volatiles were removed under vacuum. Toluene (3 mL) was added to the orange residue to afford a slurry, then hexanes (5 mL) were added and the mixture was stirred for 5 mins. The precipitate was recovered by filtration, washed with hexanes (3 x 10 mL) and dried for 20 h under dynamic vacuum to yield a yellow solid **Ni1** (237 mg, 60%).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.83 (s, 1H), 7.64 (s, 2H), 7.49 (d, *J* = 8.3 Hz, 8H), 7.39 (d, *J* = 15.9 Hz, 6H), 7.26 (br, 8H), 7.13 – 6.94 (m, 2H), 6.79 (br, 1H), 6.71 (br, 1H), 6.59 (br, 1H), 6.46 (br, 1H), 6.21 (br, 2H), 6.16 (br, 1H), 5.85 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.17 (s), 145.94 (d, *J* = 13.5 Hz), 143.50 (s), 138.03 (s), 137.38 (s), 136.66 (d, *J* = 12.4 Hz), 135.10 (d, *J* = 5.1 Hz), 134.44 (d, *J* = 10.6 Hz), 133.64 (d, *J* = 7.3 Hz), 131.44 (s), 130.80 (s), 129.97 (s), 129.88 (d, *J* = 6.1 Hz), 129.72 (s), 129.55 (d, *J* = 4.9 Hz), 129.43 (s), 129.28 (s), 128.16 (d, *J* = 9.6 Hz), 127.95 (d, *J* = 7.5 Hz), 127.55 (s), 127.28 (d, *J* = 6.5 Hz), 127.09 (s), 126.80 (d, *J* = 8.0 Hz), 126.16 (s), 125.69 (s), 121.09 (s), 111.69 (s), 109.08 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.48 (d, J_{PP} = 283 Hz), 3.64 (J_{PP} = 283 Hz). Anal. Calcd. for $C_{46}H_{36}NiO_4P_2S$: C, 68.59; H, 4.50. Found: C, 68.26; H, 4.11.

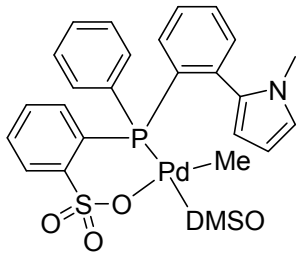


Preparation of catalyst Pd2. Similar procedure was employed as catalyst **Pd1** except **L2** (200 mg, 0.44 mmol) was used. **Pd2** was obtained as a white solid (202 mg, 70%). ^{1}H NMR (400 MHz, DMSO): δ 8.02 (d, *J* = 3.2 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.65 – 7.48 (m, 9H), 7.29 – 7.17 (m, 5H), 7.00 – 6.93 (m, 1H), 2.54 (s, 6H, DMSO), 0.17 (s, 3H, Pd-*Me*). ^{13}C NMR (100 MHz, DMSO): δ 154.29 (s), 154.16 (d, *J* = 3.6 Hz), 147.29 (d, *J* = 14.0 Hz), 134.92 (d, *J* = 13.1 Hz), 134.54 (d, *J* = 4.5 Hz), 133.85 (s), 133.67 (d, *J* = 11.1 Hz), 131.46 (s), 130.94 (d, *J* = 3.8 Hz), 130.84 (s), 130.32 (d, *J* = 6.7 Hz), 129.41 (s), 129.21 (s), 128.93 (d, *J* = 11.1 Hz), 128.62 (d, *J* = 8.3 Hz), 128.03 (s), 127.91 (s), 127.35 (d, *J* = 8.3 Hz), 124.67 (s), 123.22 (s), 121.30 (s), 111.71 (s), 106.74 (s), 40.43 (s, DMSO), -0.54 (s, Pd-*Me*). ^{31}P NMR (162 MHz ,DMSO): δ 27.93. Anal. Calcd. for $C_{29}H_{27}O_5PPdS_2$: C, 53.01; H, 4.14. Found: C, 53.31; H, 4.26.

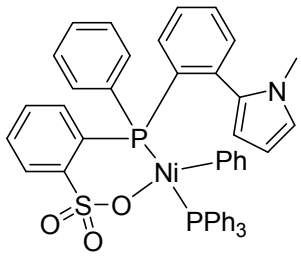


Preparation of catalyst Ni2. Similar procedure was employed as catalyst **Ni1** except **L2** (200 mg, 0.44 mmol) was used. **Ni2** was obtained as a yellow powder (242 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 – 8.29 (m, 1H, H_a), 7.77 (dd, *J* = 7.7, 3.9 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.50 (dd, *J* = 9.7, 8.4 Hz, 6H), 7.43 (dd, *J* = 4.7, 2.2 Hz, 4H, H_b), 7.32 (dt, *J* = 17.9, 9.0 Hz, 5H), 7.24 – 7.08 (m, 10H, H_c), 6.92 (dt, *J* = 14.5, 7.3 Hz, 2H, H_d), 6.74 (dd, *J* = 16.4, 7.7 Hz, 2H, H_7), 6.45 (d, *J* = 7.8 Hz, 1H, H_4), 6.27 – 6.21 (m, 1H), 6.19 (d, *J* = 3.6 Hz, 1H, H_5), 6.20 (d, *J* = 2.4 Hz, 1H, H_6), 5.84 (dd, *J* = 11.0, 5.5 Hz, 1H, H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.15 (d, *J* = 1.6 Hz), 155.01 (s), 146.02 (s, *J* = 13.9 Hz), 145.88 (s), 137.98 (s), 137.26 (s), 136.94 (s), 136.82 (s), 135.53 (d, *J* = 5.0 Hz), 134.54 (d, *J* = 10.6 Hz), 133.40 (d, *J* = 7.1 Hz), 130.95 (s, *J* = 10.4 Hz), 130.84 (s), 130.07 (d, *J* = 2.0 Hz), 129.93 (d, *J* = 1.3 Hz), 129.65 (d, *J* = 3.9 Hz), 129.55 (d, *J* = 5.0 Hz), 129.39 (s), 128.69 (d, *J* = 7.3 Hz), 128.35 (s), 128.25 (s), 127.78 (s, *J* = 8.1 Hz), 127.70 (s), 127.12 (d, *J* = 6.6 Hz), 126.38 (s), 125.95 (s), 125.10 (s), 123.20 (s), 121.13 (s), 120.78 (s), 112.82 (s), 106.13 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.66(d, J_{PP} = 283 Hz), 4.55 (d, J_{PP} = 283 Hz). Key ^{1}H-^{1}H COSY correlations ($CDCl_3$): δ/δ 8.31 (H_a)/7.40 (H_b), 7.40 (H_b)/7.10 (H_c), 7.10 (H_c)/6.89 (H_d), 6.76 (H_7)/6.18 (H_6), 6.18(H_6)/5.85 (H_5), 5.85 (H_5)/6.45 (H_4). Key ^{1}H-^{1}H NOESY correlations ($CDCl_3$): δ/δ

8.31 (H_a)/6.18 (H_6), 8.31 (H_a)/6.76 (H_7), 8.31 (H_a)/7.10 (H_c), 8.31 (H_a)/7.40 (H_b). Anal. Calcd. for $C_{50}H_{38}NiO_4P_2S$: C,70.19; H, 4.48. Found: C, 69.73; H, 4.27.

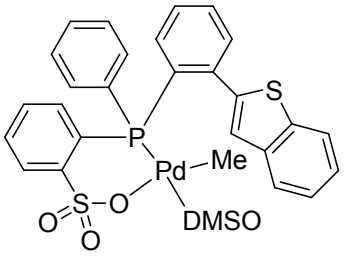


Preparation of catalyst Pd3. Similar procedure was employed as catalyst **Pd1** except **L3** (200 mg, 0.47 mmol) was used. **Pd3** was obtained as a white solid (176 mg, 60%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.62 – 7.34 (m, 11H), 6.99 (s, 1H), 6.74 (s, 1H), 6.11 (s, 1H), 5.49 (s, 1H), 3.48 (s, 3H), 2.92 (s, 6H, DMSO), 0.44 (s, 3H, Pd-*Me*). ^{13}C NMR (100 MHz, DMSO): δ 147.62 (s), 147.48 (s), 136.81 (d, *J* = 12.9 Hz), 134.45 (d, *J* = 6.4 Hz), 134.12 (d, *J* = 12.4 Hz), 133.94 (s), 133.02 (d, *J* = 7.6 Hz), 130.72 (s), 130.56 (s, *J* = 15.6 Hz), 130.02 (s), 129.69 (d, *J* = 6.3 Hz), 129.55 (d, *J* = 6.4 Hz), 128.81 (s), 128.35 (d, *J* = 4.3 Hz), 128.26 (s), 127.28 (d, *J* = 8.1 Hz), 126.80 (d, *J* = 8.5 Hz), 123.57 (s), 112.15 (d, *J* = 1.7 Hz), 106.95 (s), 40.43 (s), 34.06 (s, DMSO), -0.52 (s, Pd-*Me*). ^{31}P NMR (162 MHz DMSO): δ 22.15 (s). Anal. Calcd. for $C_{26}H_{28}NO_4PPdS_2$: C, 50.37; H, 4.55; N, 2.26. Found: C, 50.09; H, 4.73; N, 2.17.

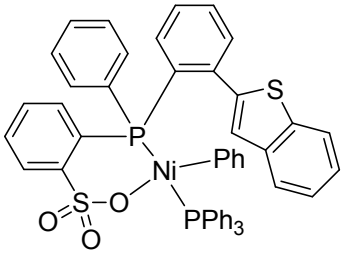


Preparation of catalyst Ni3. Similar procedure was employed as catalyst **Ni1** except **L3** (200 mg, 0.47 mmol) was used. **Ni3** was obtained as a yellow powder (236 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.84 (m, 1H), 7.75 (s, 3H), 7.49 – 7.43 (m, 6H), 7.36 (d, *J* = 6.6 Hz, 7H), 7.32 – 7.27 (m, 7H), 7.17 (dd, *J* = 15.9, 8.3 Hz, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.78 (s, 1H), 6.58 (s, 1H), 6.40 (d, *J* = 7.5 Hz, 1H), 6.32 (d, *J* = 7.3 Hz, 2H), 6.23 (t, *J* = 7.1 Hz, 1H), 6.09 – 6.02 (m, 1H), 5.96 (t, *J* = 7.3 Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.75 (d, *J* = 13.5 Hz), 139.99 (s), 139.64 (s), 139.32 (s), 138.43 (s), 137.60 (s), 136.39 (d, *J* = 10.3 Hz), 135.75 (d, *J* = 11.5 Hz), 134.90 (d, *J* = 5.3 Hz), 134.30 (d, *J* = 10.4 Hz), 132.14 (s), 131.92 (d, *J* = 6.8 Hz), 131.55 (d, *J* = 4.6 Hz), 130.24 (s), 129.88 (d, *J* = 1.8 Hz), 129.70 (s), 129.50 (s), 129.30 (d, *J* = 10.5 Hz), 128.63 (d, *J* = 4.3 Hz), 128.08 (d, *J* = 9.6 Hz), 127.78 (d, *J* = 10.2 Hz), 127.03 (d, *J* = 6.4 Hz), 126.66 (d, *J* = 8.1 Hz), 125.88 (d, *J* = 19.1 Hz), 123.46 (s), 121.39 (s), 111.15 (s), 108.32 (s), 34.11 (s, N-*Me*). ^{31}P NMR (162 MHz, $CDCl_3$): δ 15.01(d, J_{PP} = 172 Hz), -0.38(d, J_{PP} = 172 Hz). Anal.

Calcd. for $C_{47}H_{39}NNiO_3P_2S$: C, 68.97; H, 4.80; N, 1.71. Found: C, 69.13; H, 5.24; N, 1.60.



Preparation of catalyst Pd4. Similar procedure was employed as catalyst **Pd1** except **L4** (200 mg, 0.42 mmol) was used. **Pd4** was obtained as a white solid (209 mg, 74%). Solubility of **Pd4** in common organic solvent is very low, so only ^{1}H and ^{31}P NMR spectra were recorded. ^{1}H NMR (400 MHz, DMSO): δ 7.96 (d, *J* = 17.5 Hz, 2H), 7.72 (s, 3H), 7.62 (s, 1H), 7.53 (s, 6H), 7.30 (dd, *J* = 21.9, 13.0 Hz, 4H), 7.14 – 7.07 (m, 1H), 6.77 (s, 1H), 2.54 (s, 6H), 0.29 (s, 3H). ^{31}P NMR (162 MHz, DMSO): δ 21.97 (s). Anal. Calcd. for $C_{29}H_{27}O_4PPdS_3$: C, 51.75; H, 4.04. Found: C, 52.11; H, 4.31.



Preparation of catalyst Ni4. Similar procedure was employed as catalyst **Ni1** except **L4** (200mg, 0.42 mmol) was used. **Ni4** was obtained as a yellow powder (249 mg, 68%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.73 (m, 2H), 7.61 (dd, *J* = 13.7, 7.5 Hz, 4H), 7.53 (d, *J* = 6.7 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 4H), 7.38 (s, 1H), 7.34 (d, *J* = 8.2 Hz, 4H), 7.31 (s, 2H), 7.28 (s, 4H), 7.24 (s, 3H), 7.21 (s, 3H), 7.20 (s, 1H), 7.17 (s, 1H), 7.15 (s, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.64 – 6.57 (m, 1H), 6.38 (dd, *J* = 15.5, 7.6 Hz, 2H), 6.25 (t, *J* = 7.0 Hz, 1H), 6.00 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100MHz, CDCl3): δ 146.28 (d, *J* = 12.8 Hz), 141.73 (d, *J* = 3.0 Hz), 139.63 (d, *J* = 7.1 Hz), 139.08 (s), 138.75 (s), 138.59 (s), 138.41 (s), 138.25 (s), 138.18 (d, *J* = 3.6 Hz), 135.64 (d, *J* = 10.9 Hz), 134.52 (d, *J* = 4.7 Hz), 134.13 (d, *J* = 10.3 Hz), 132.85 (s), 132.30 (d, *J* = 7.3 Hz), 130.30 (s), 129.74 (s), 129.61 (s), 129.31 (s), 129.20 (s), 128.68 (s), 128.51 (d, *J* = 9.8 Hz), 128.23 (s), 127.99 (d, *J* = 9.7 Hz), 127.69 (d, *J* = 10.1 Hz), 127.35 (d, *J* = 7.4 Hz), 126.60 (d, *J* = 6.6 Hz), 126.20 (s), 125.79 (s), 125.55 (s), 124.60 (d, *J* = 6.3 Hz), 124.15 (s), 121.63 (d, *J* = 8.0 Hz). ^{31}P NMR (162MHz, CDCl3): δ 14.50(d, J_{PP} = 277 Hz), 0.79(d, J_{PP} = 277 Hz). Anal. Calcd. for $C_{50}H_{38}NiO_3P_2S_2$: C,68.90; H, 4.39. Found: C, 69.13; H, 4.01.

Procedure for ethylene homopolymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with 19 mL toluene, 4 μmol of metal complex in 1 mL CH_2Cl_2 and a magnetic stir bar in a glovebox. The pressure vessel was connected to a high pressure line and the solution was degassed. The vessel was warmed to 80 °C using an oil bath (water bath for the case of polymerization at room temperature) and allowed to equilibrate for 15 min. With rapid stirring, the reactor was pressurized and maintained at 8.0 atm of ethylene. After a desired amount of time, the pressure vessel was vented and the polymer was precipitated in acidified methanol (methanol/HCl = 50/1) and dried at 50 °C for 24 h under vacuum. Analysis of Polymer Branching by ^{1}H NMR Spectroscopy. BD = $1000\times2(I_{CH3})/3(I_{CH2+CH}+I_{CH3})$. CH_3 (m, 0.77-0.95 ppm); CH_2 and CH (m, ca. 1.0-1.45 ppm).

Procedure for ethylene-polar monomer copolymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with toluene and polar monomer in total 19 mL and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high pressure line and the solution was degassed. The vessel was warmed to 80 °C using an oil bath (water bath for the case of polymerization at room temperature) and allowed to equilibrate for 15 min. Complex in 1 mL CH_2Cl_2 was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized and maintained at 8.0 atm of ethylene. After 1 h, the pressure vessel was vented and the polymer was precipitated in acidified methanol (methanol/HCl = 50/1) and dried at 80 °C for 24 h under vacuum.

2. NMR and ESI-MS of ligand L1-L5 and catalyst Pd1~Pd4, Ni1~Ni4.

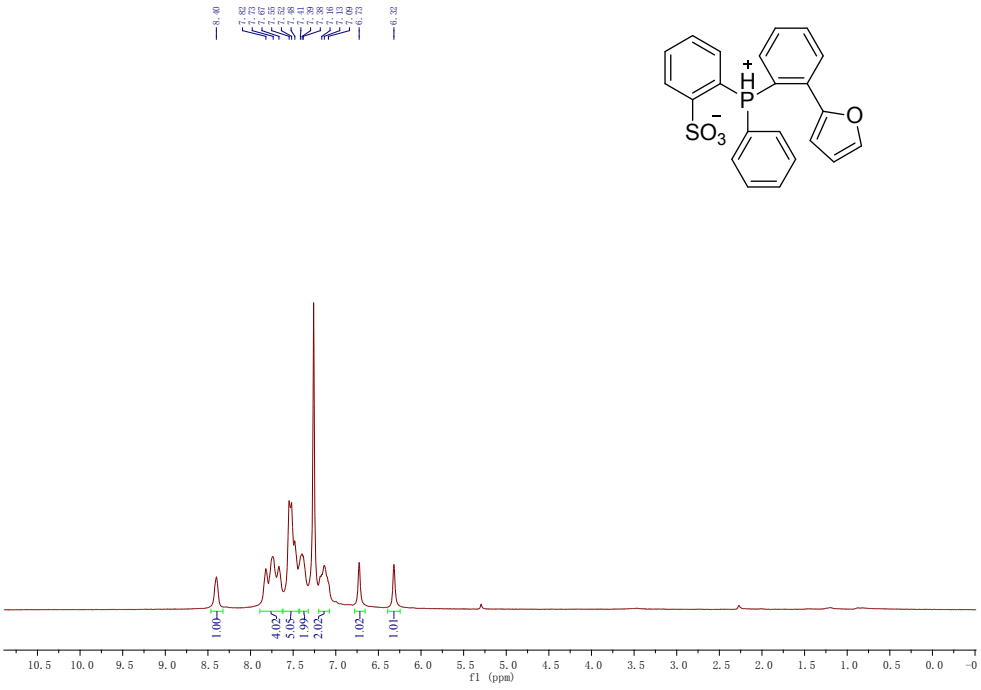


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **L1**.

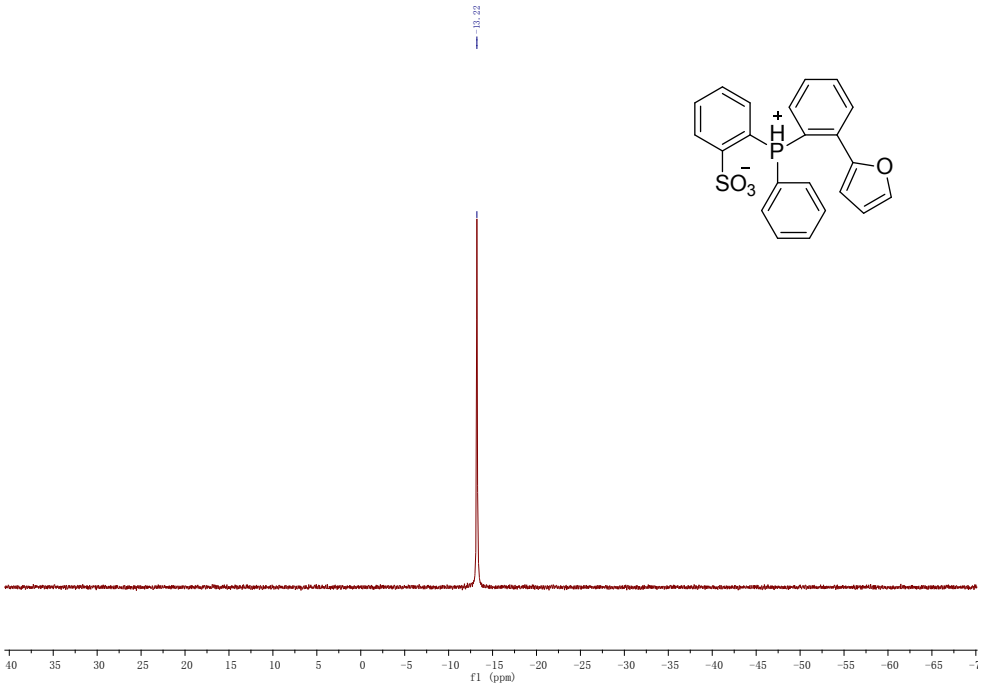


Figure S2. ^{31}P NMR spectrum (162 MHz, DMSO) of **L1**.

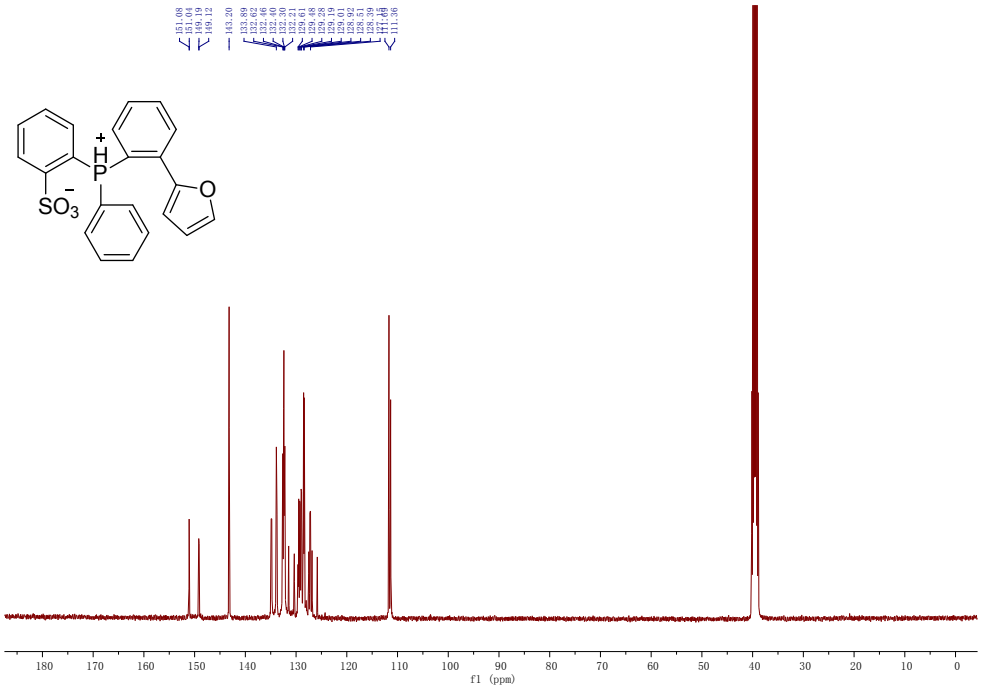


Figure S3. ^{13}C NMR spectrum (100 MHz, DMSO) of **L1.**

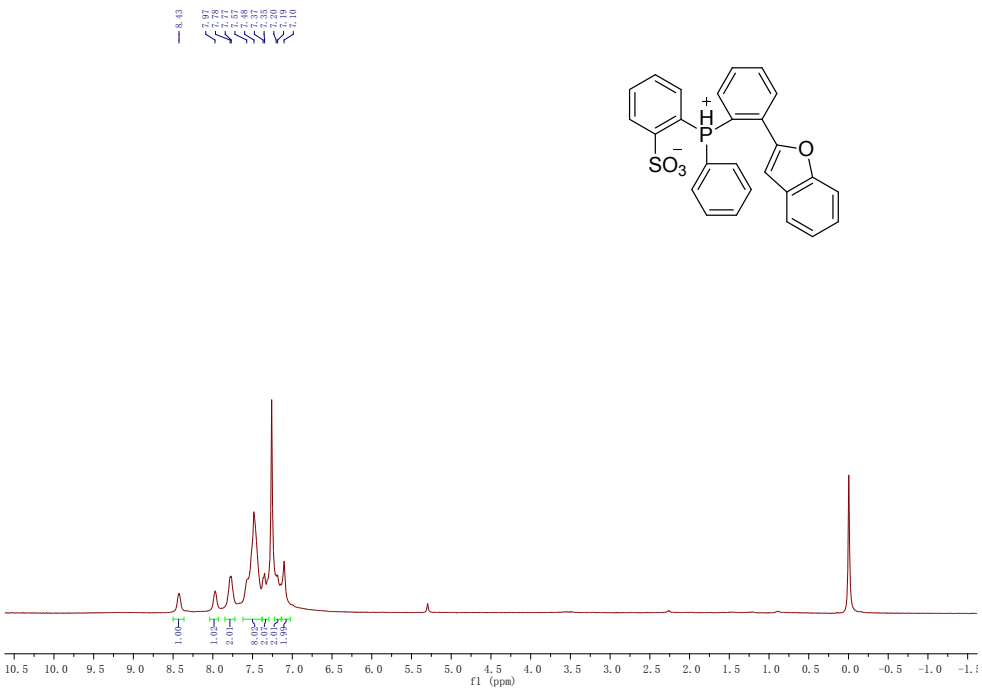


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **L2**.

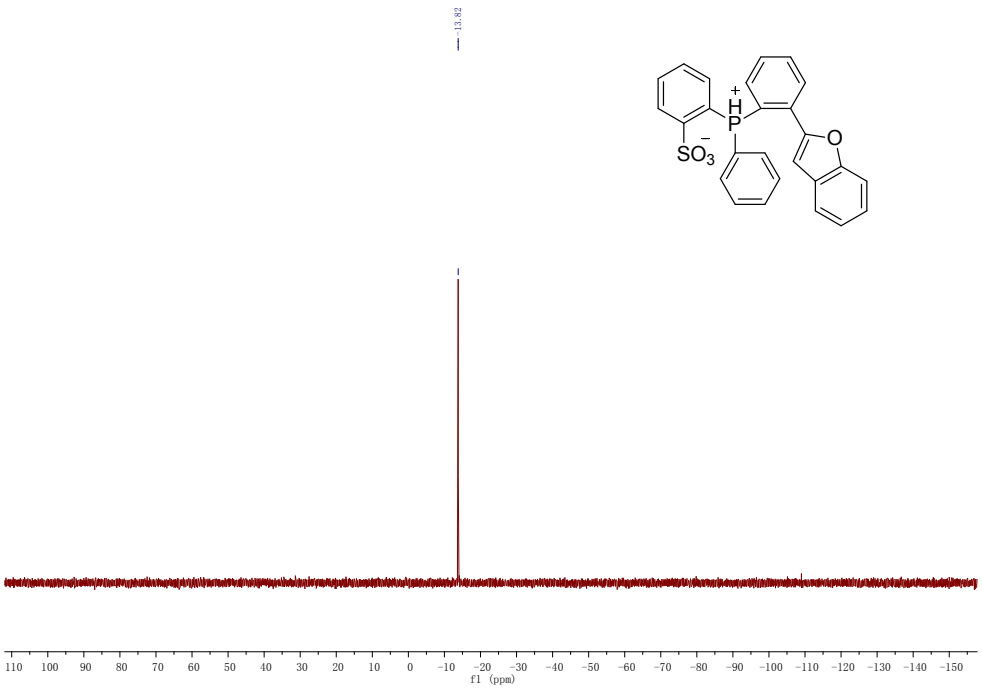


Figure S5.^{31}P NMR spectrum (162 MHz, DMSO) of **L2**

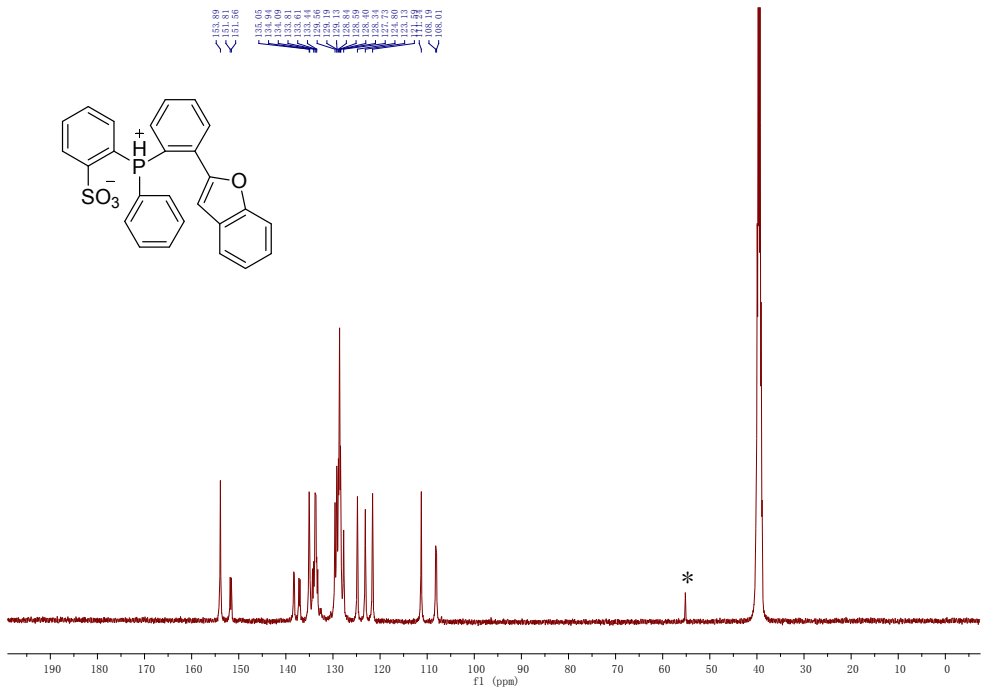


Figure S6. ^{13}C NMR spectrum (100 MHz, DMSO) of **L2** (* is dichloromethane) .

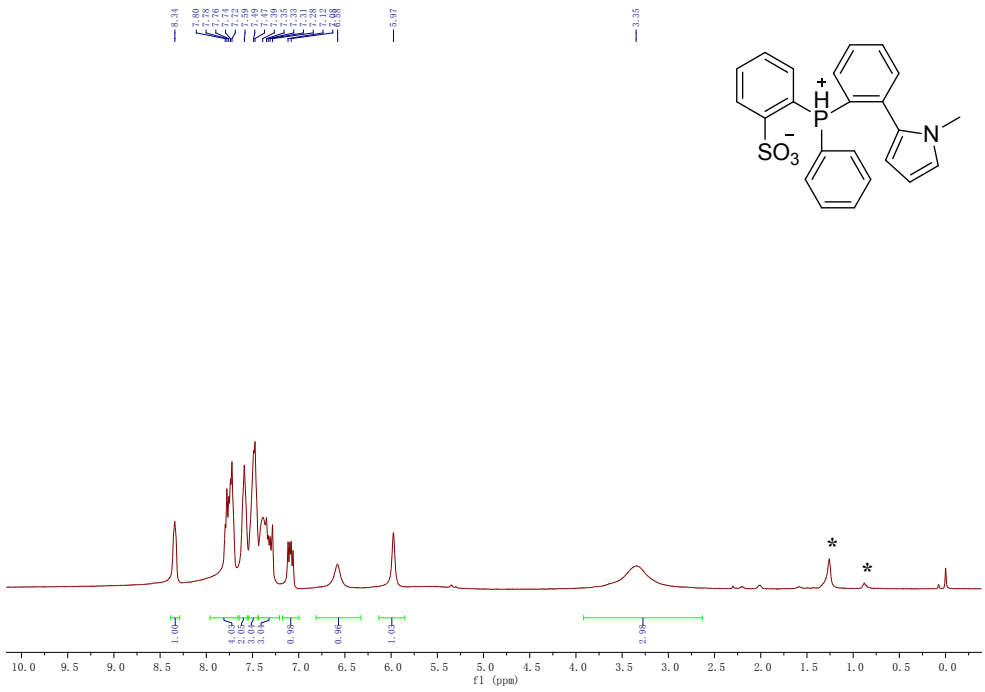


Figure S7.^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **L3.** (*is hexanes)

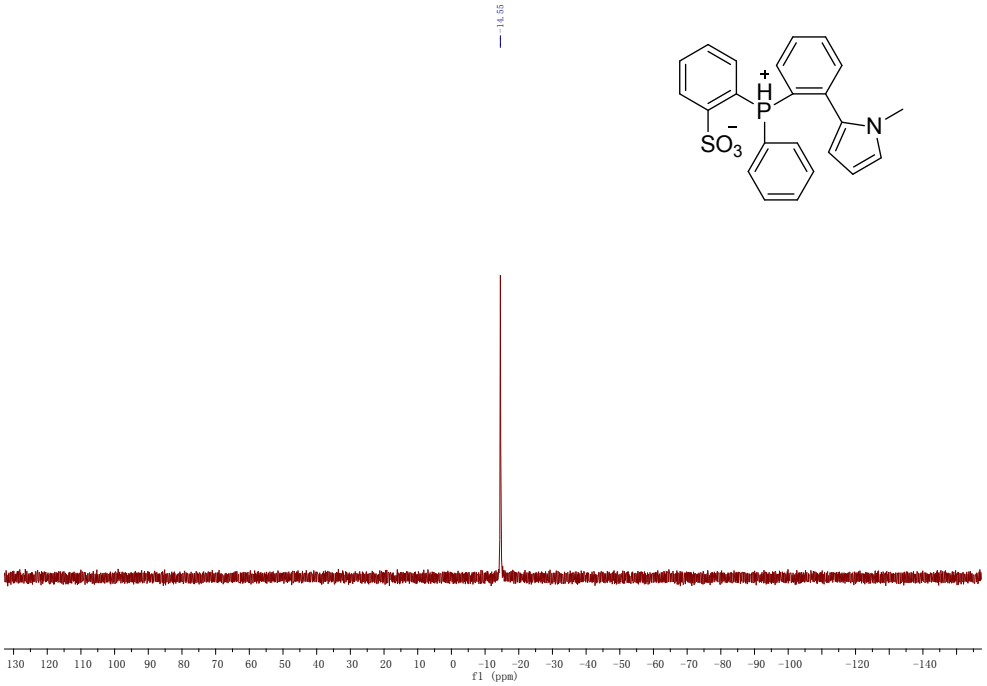


Figure S8.^{31}P NMR spectrum (162 MHz, DMSO) of **L3**

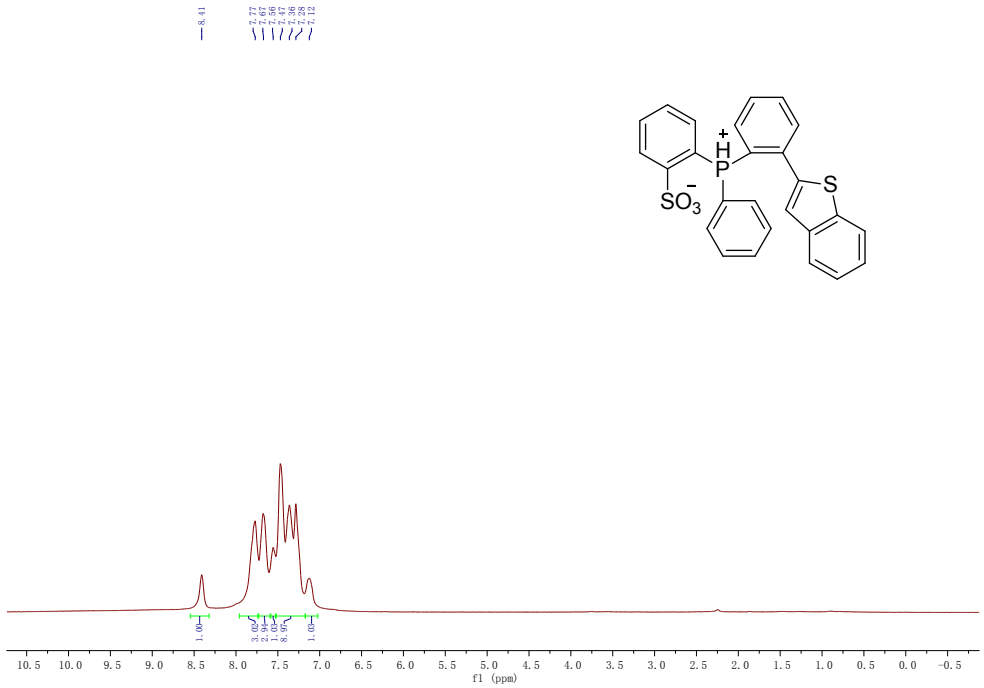


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **L4**

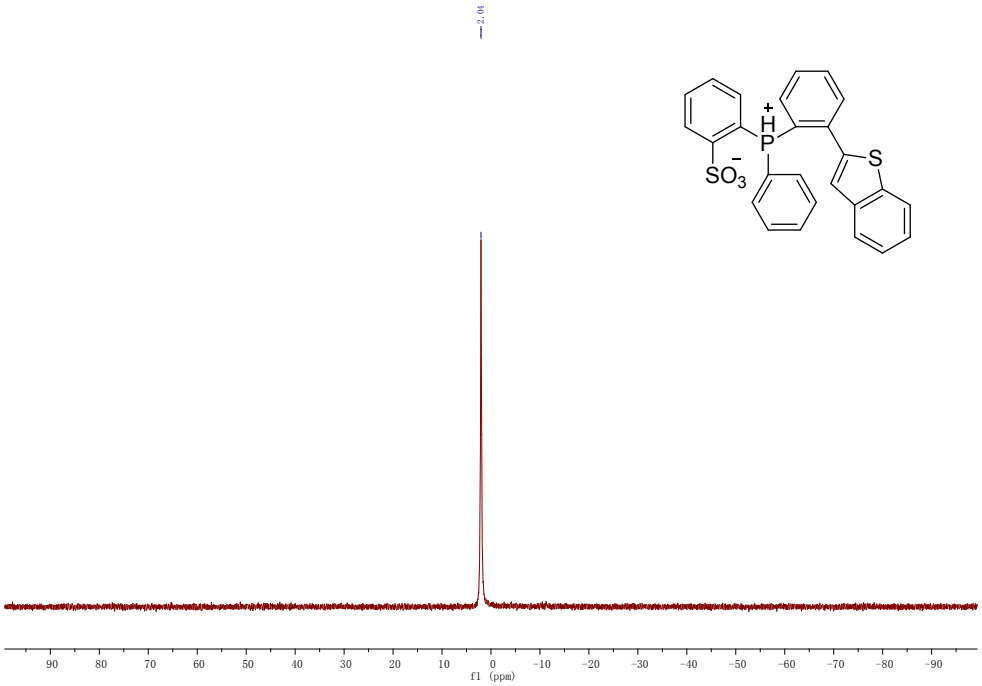


Figure S10.^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **L4**

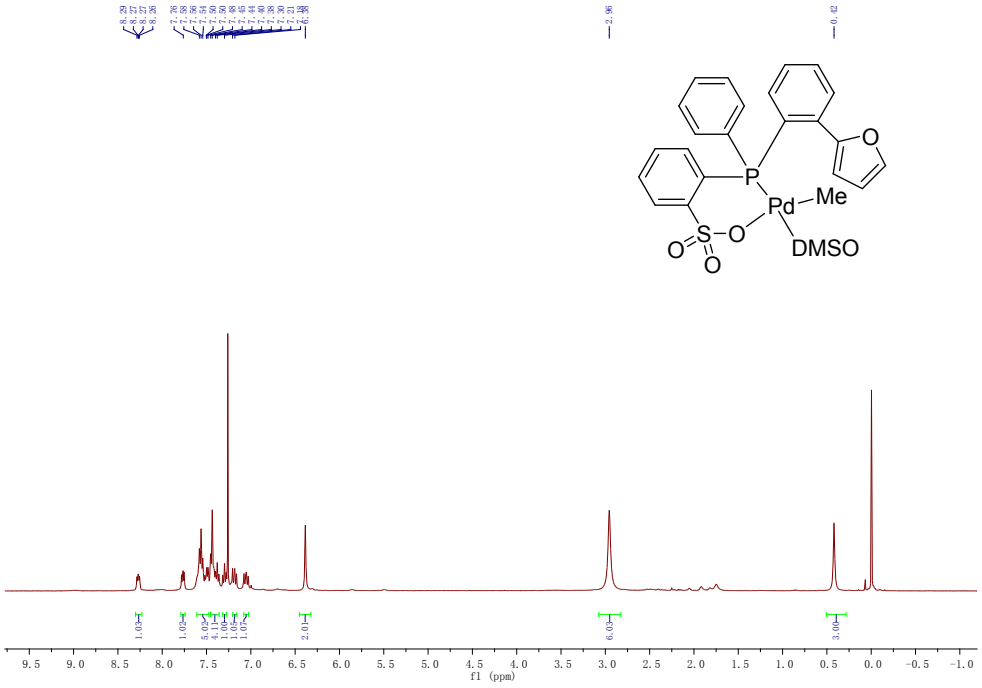


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of catalyst **Pd1**.

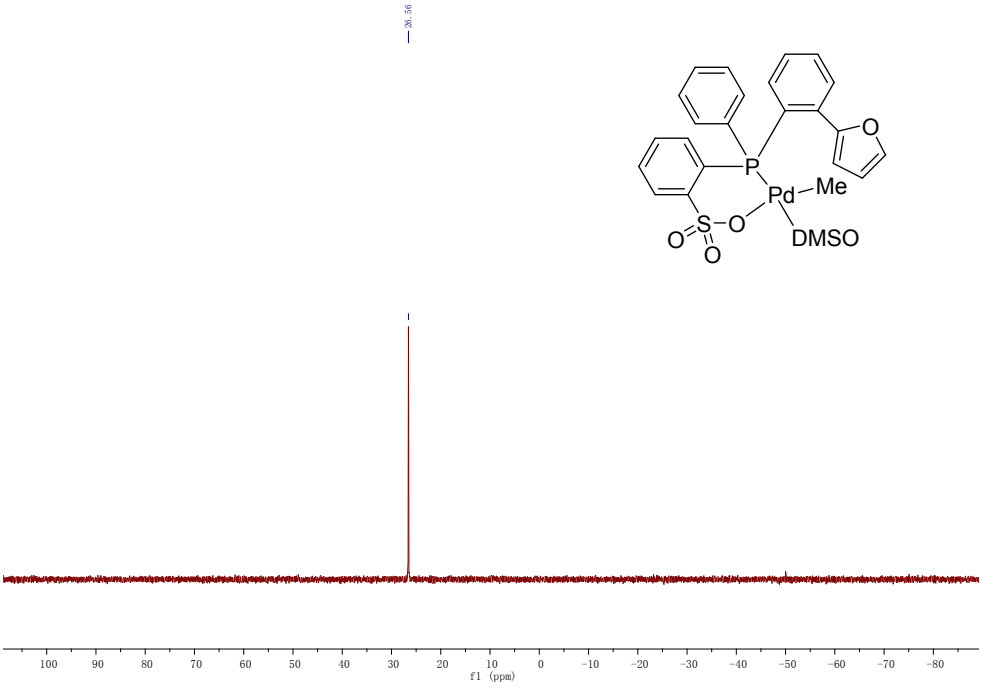


Figure S12.[31]P NMR spectrum (162 MHz, DMSO) of catalyst **Pd1.**

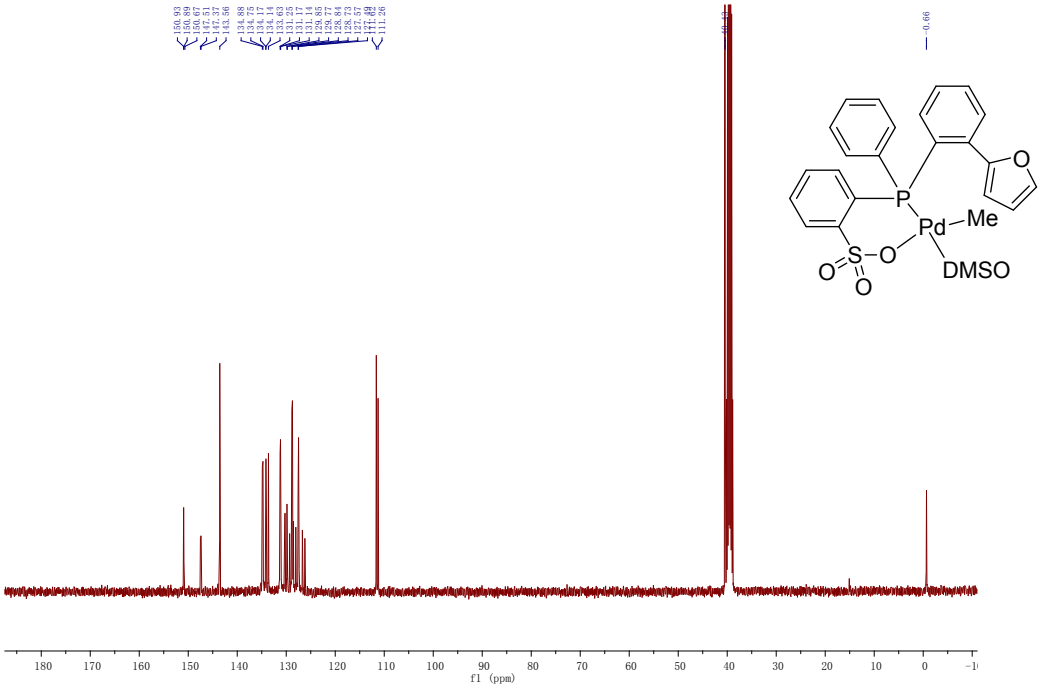


Figure S13.[13]C NMR spectrum (100 MHz, DMSO) of catalyst **Pd1.**

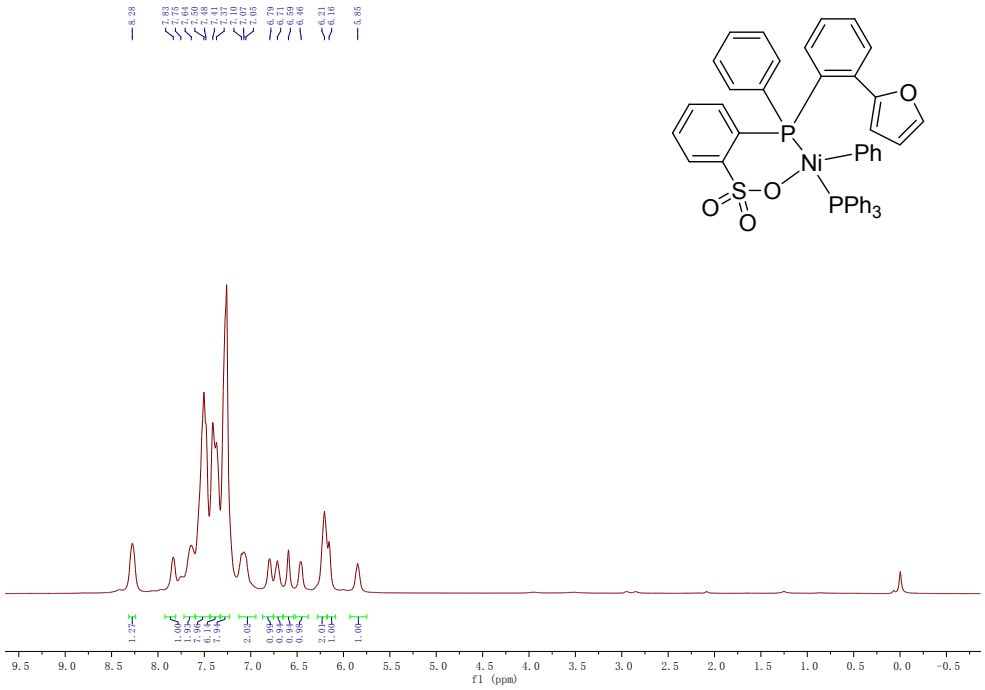


Figure S14.[1]H NMR spectrum (400 MHz, $CDCl_3$) of catalyst **Ni1.**

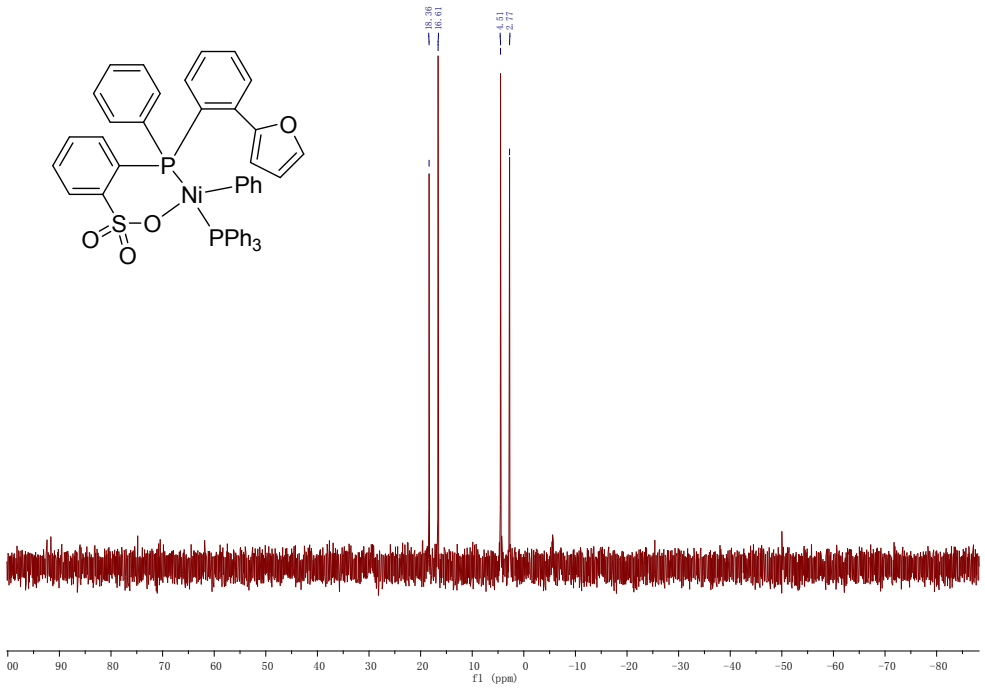


Figure S15.[31]P NMR spectrum (162 MHz, $CDCl_3$) of catalyst **Ni1.**

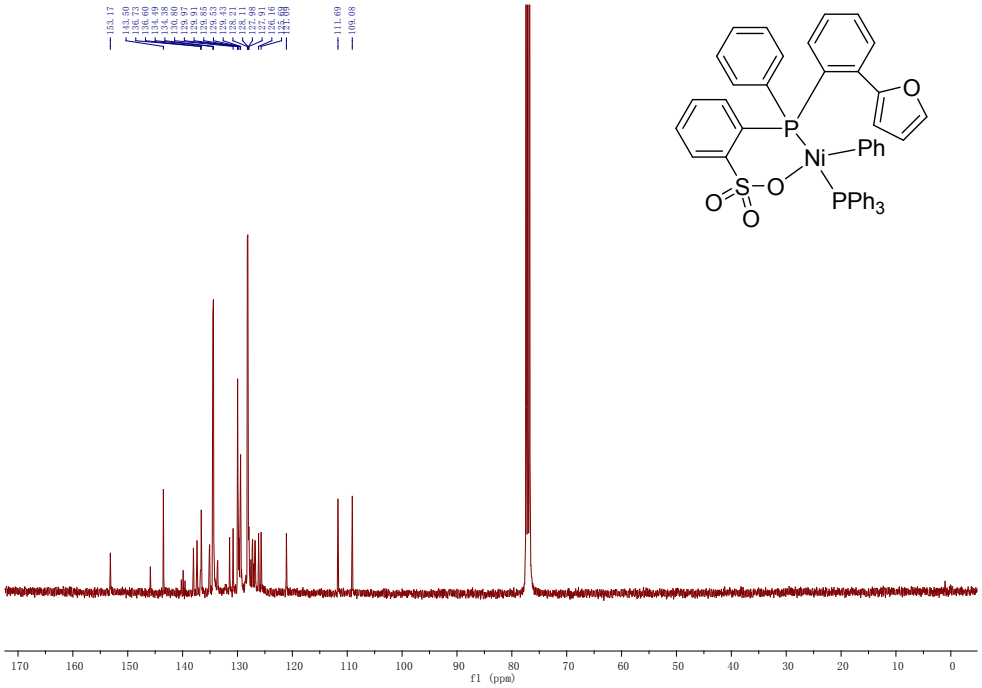


Figure S16.^{13}C NMR spectrum (100 MHz, $CDCl_3$) of catalyst **Ni1.**

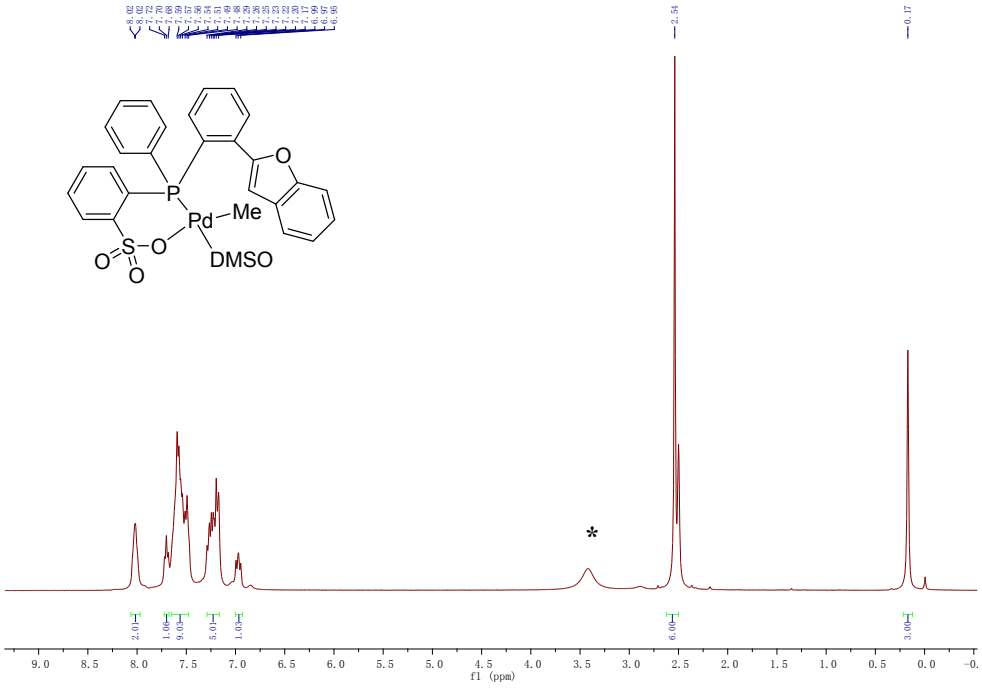


Figure S17.^{1}H NMR spectrum (400 MHz, DMSO) of **catalyst Pd2**. (* is H2O)

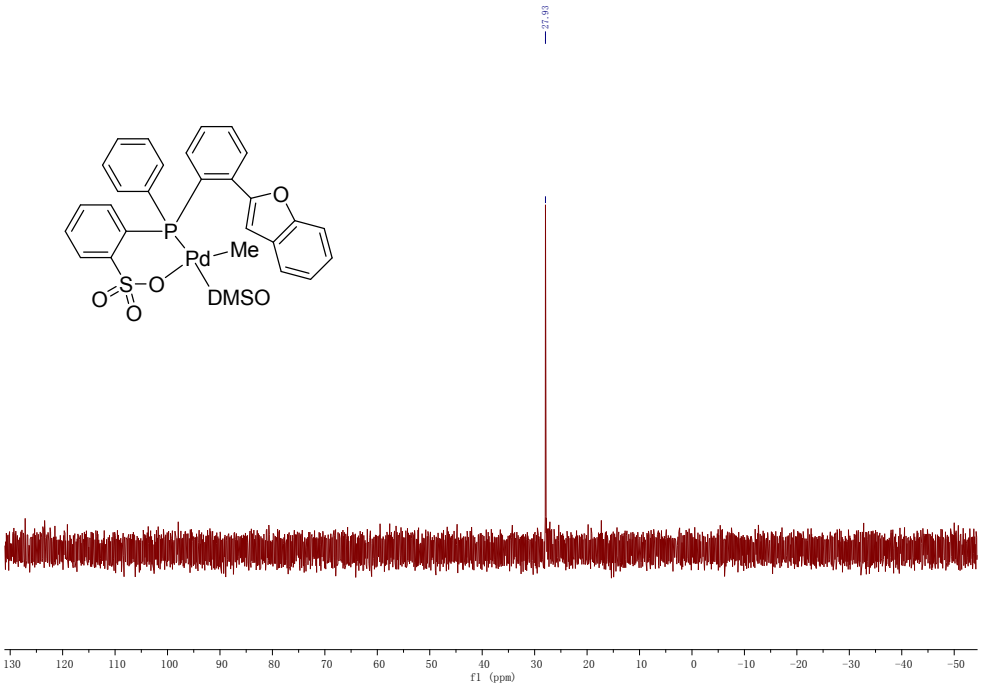


Figure S18.^{31}P NMR spectrum (162 MHz, DMSO) of catalyst **Pd2.**

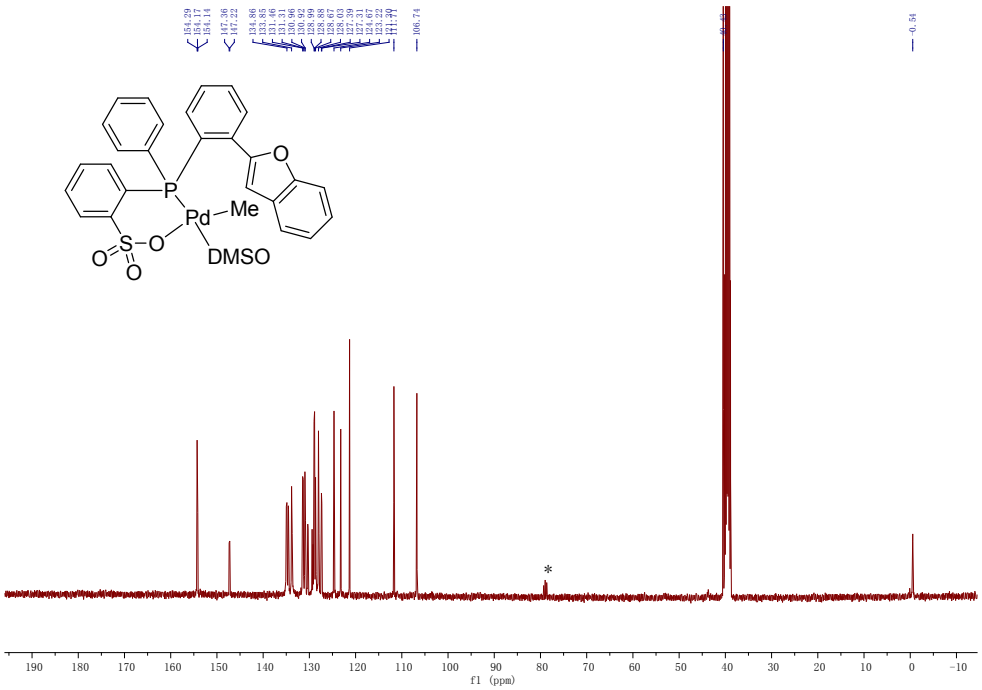


Figure S19.^{13}C NMR spectrum (100 MHz, DMSO) of catalyst **Pd2.**（＊ is $CDCl_3$）

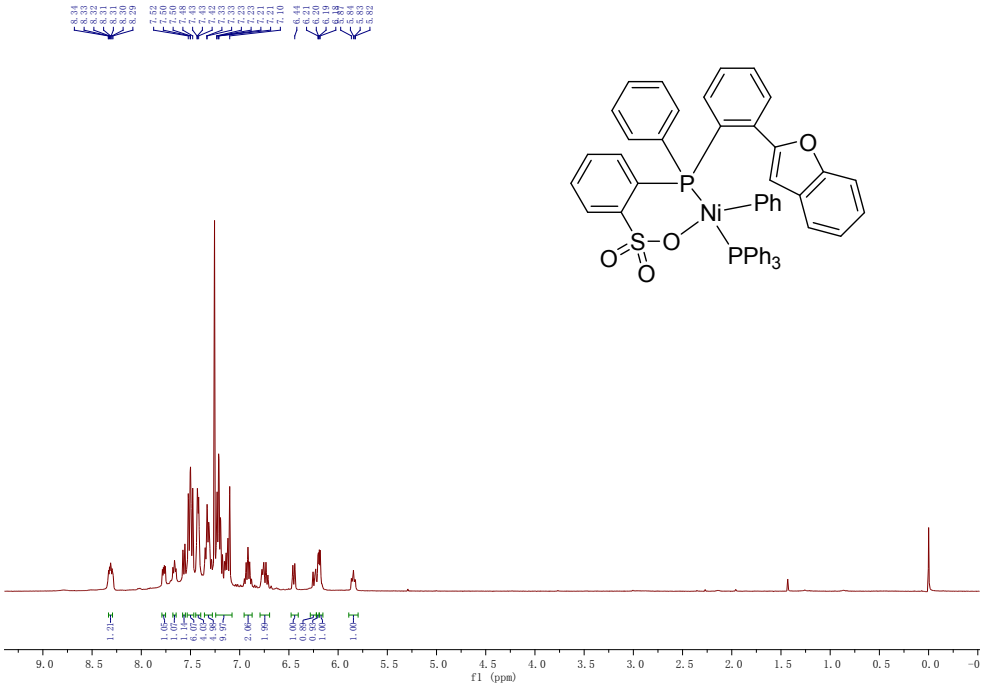


Figure S20.[1]H NMR spectrum (400 MHz, $CDCl_3$) of catalyst **Ni2.**

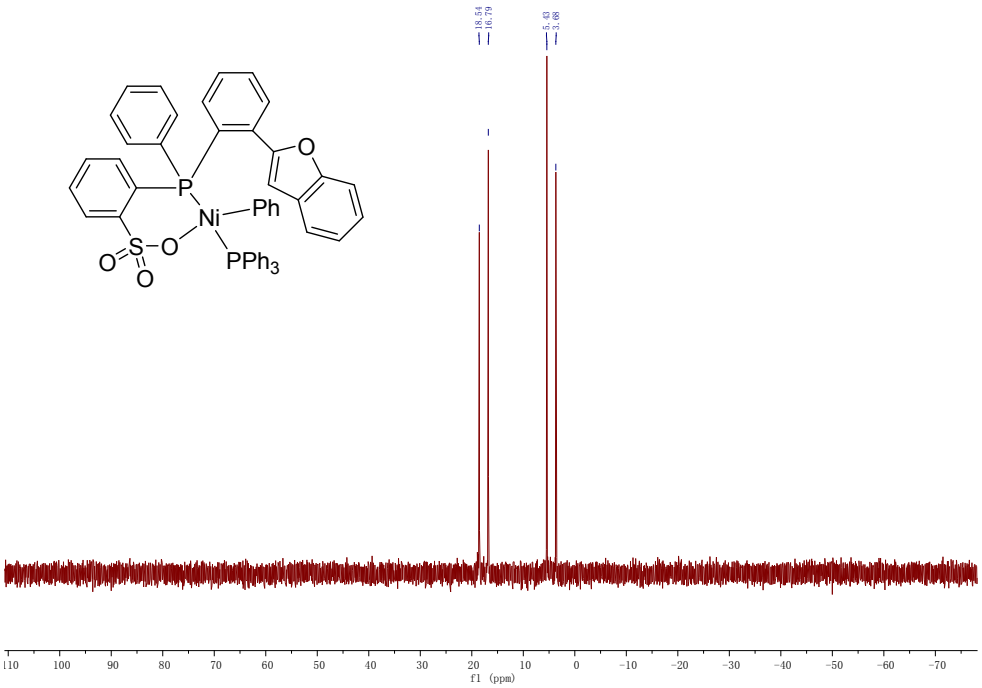


Figure S21.[31]P NMR spectrum (162 MHz, $CDCl_3$) of catalyst **Ni2.**

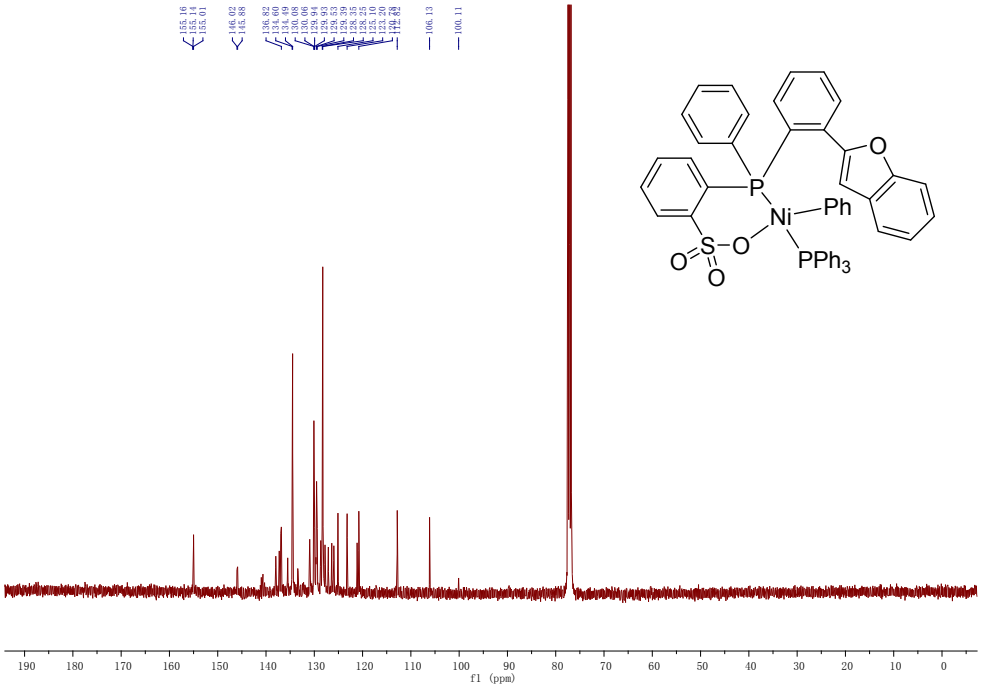


Figure S22. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of catalyst **Ni2.**

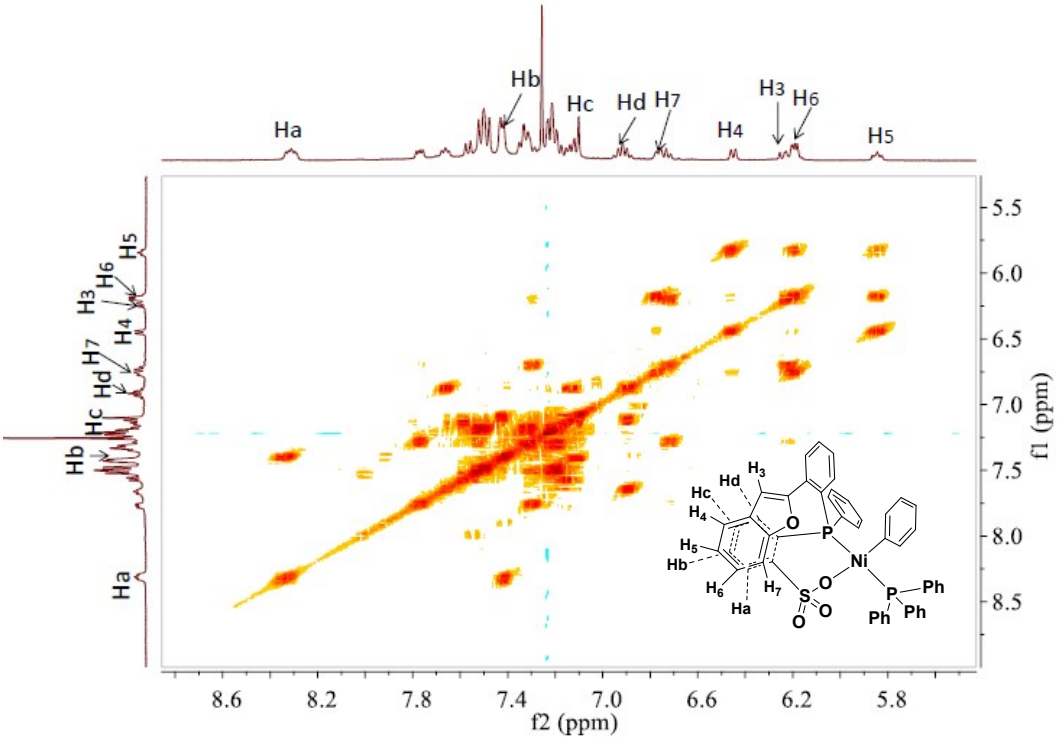


Figure S23. ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$) of catalyst **Ni2**.

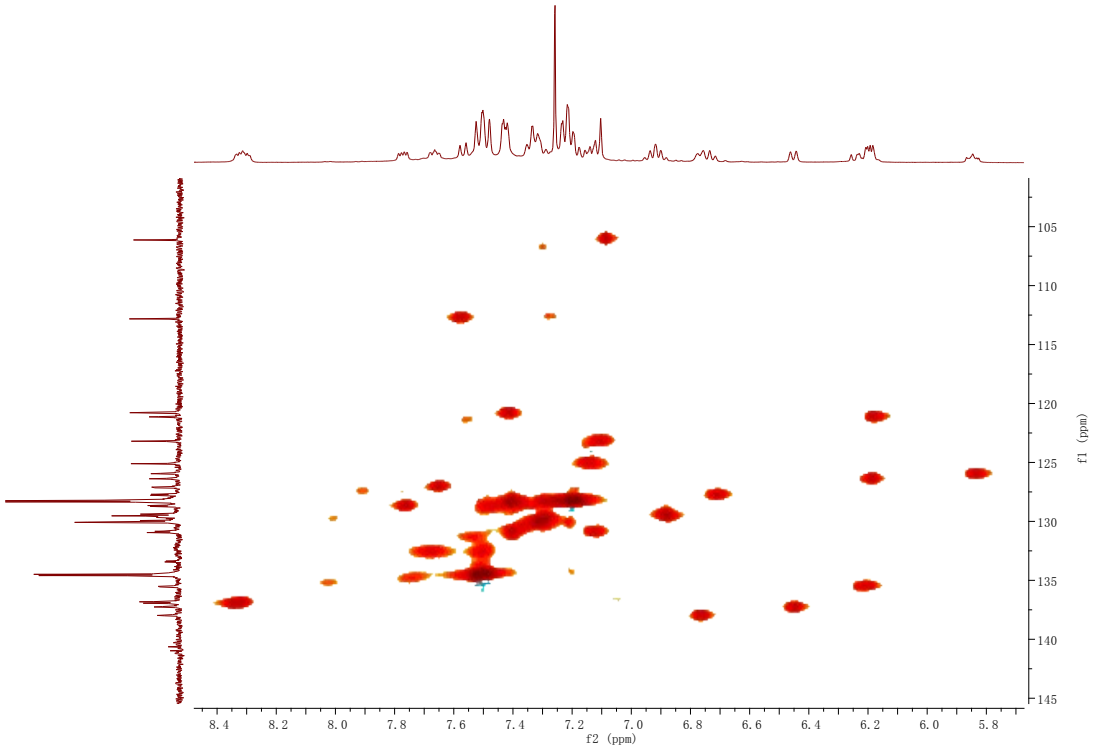


Figure S24. ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) of catalyst **Ni2**

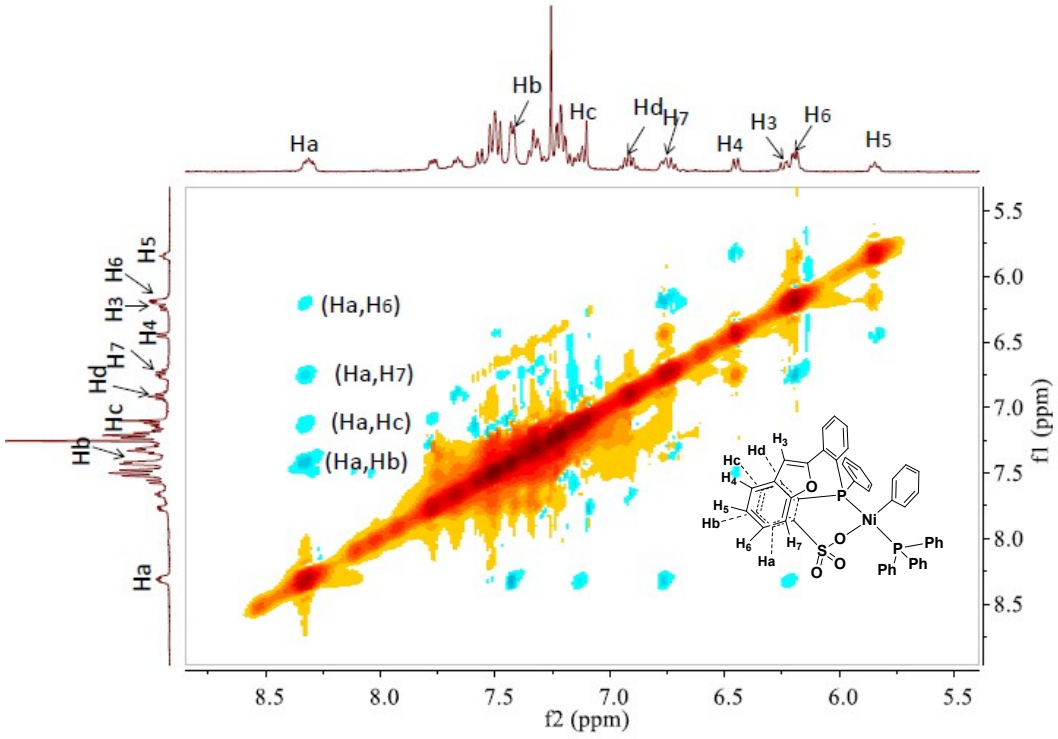


Figure S25. ^{1}H-^{1}H NOESY NMR spectrum ($CDCl_3$) of catalyst **Ni2**.

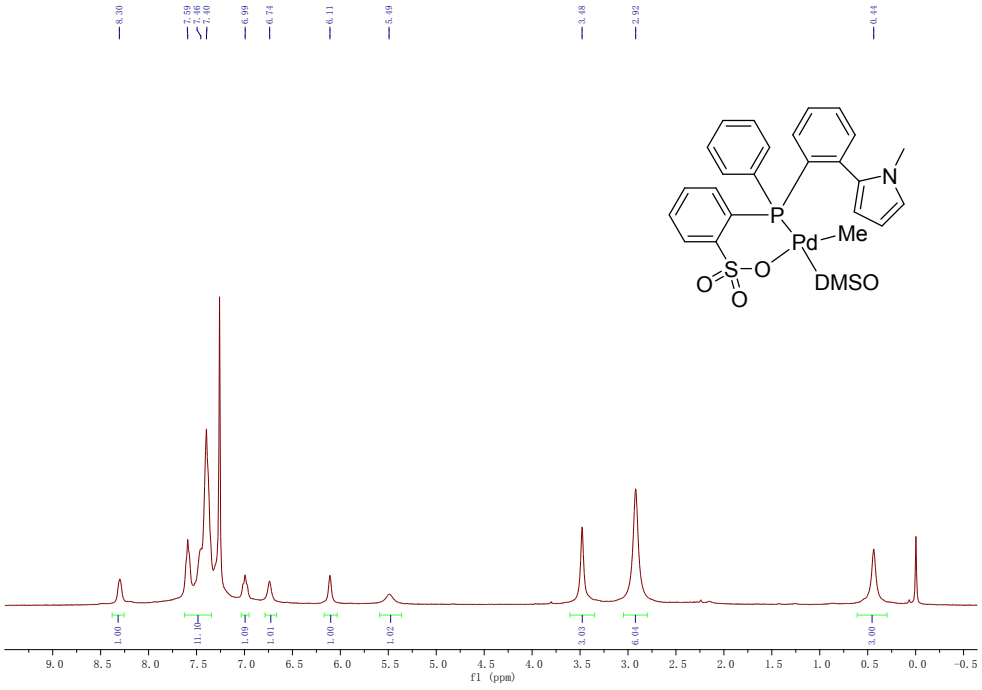


Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of catalyst **Pd3.**

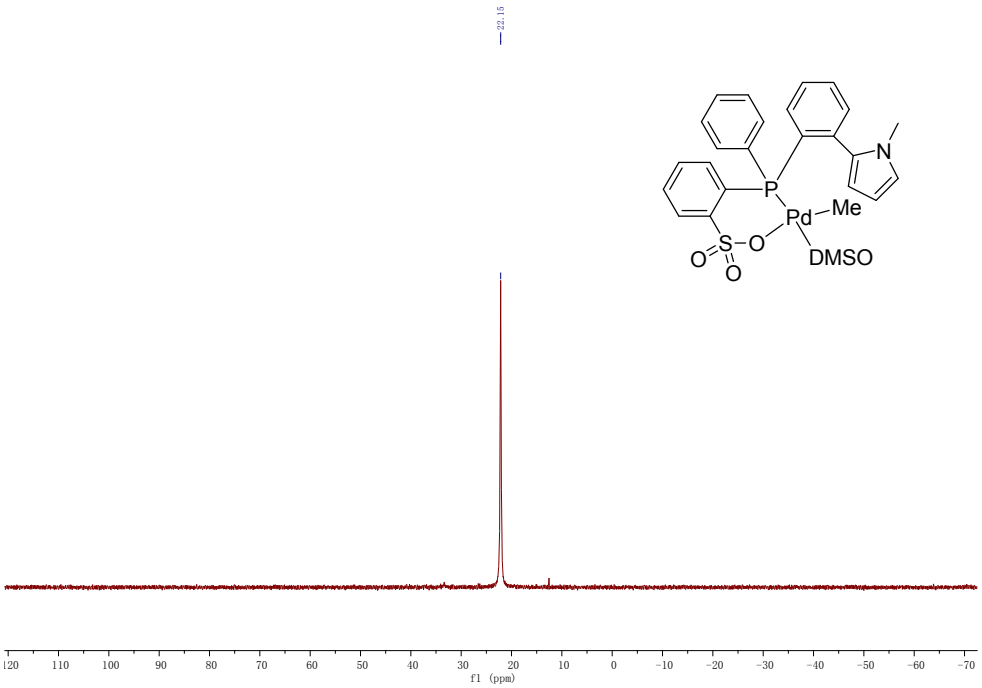


Figure S27.^{13}P NMR spectrum (162 MHz, DMSO) of catalyst **Pd3.**

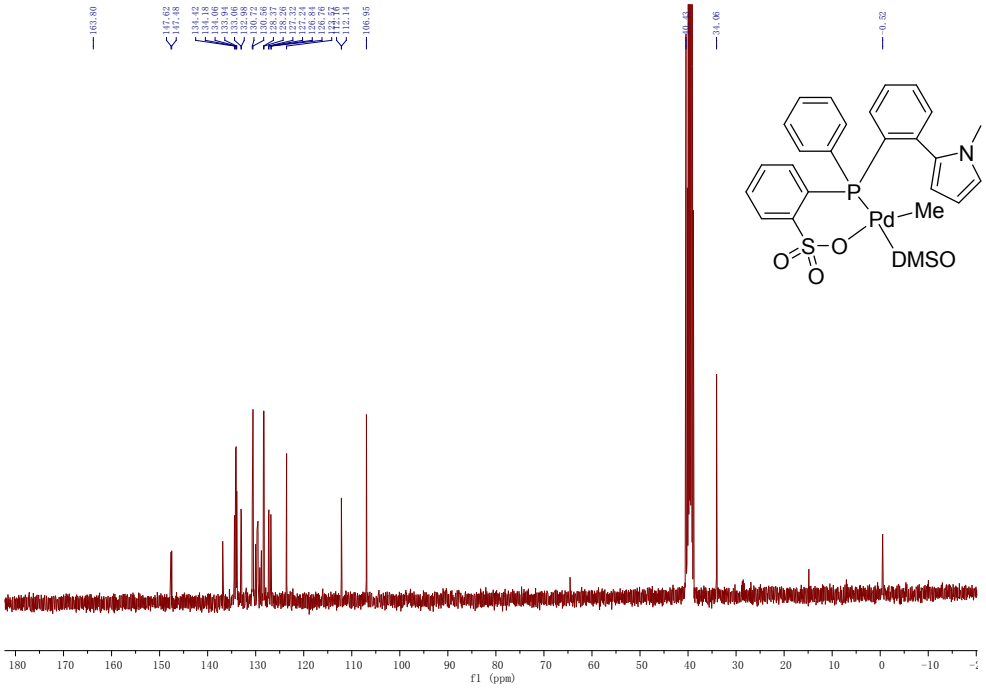


Figure S28. ^{13}C NMR spectrum (100 MHz, DMSO) of catalyst **Pd3.**

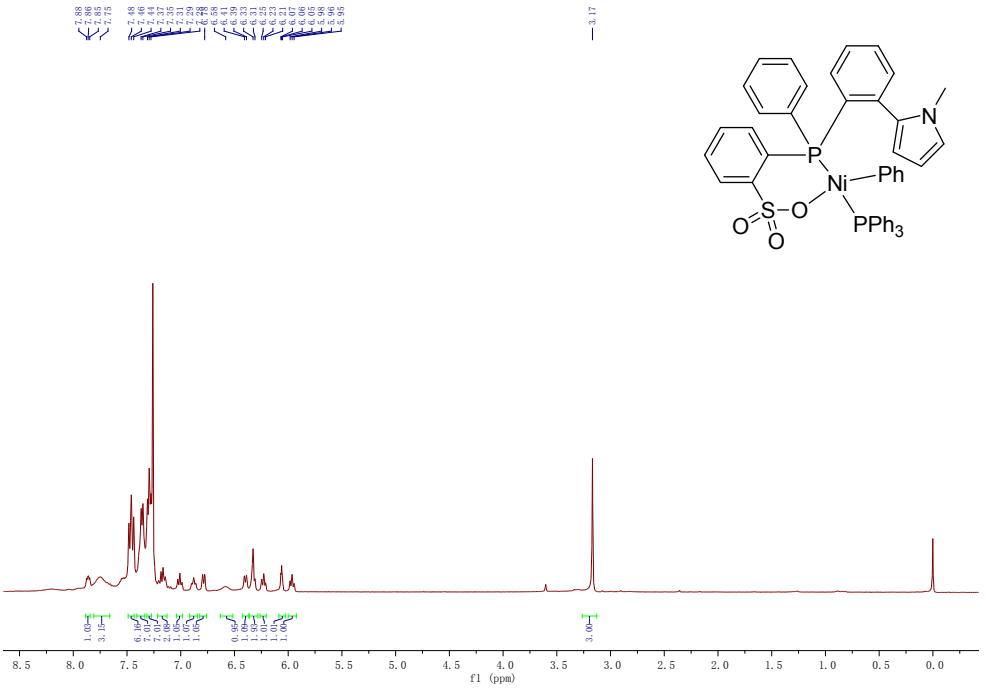


Figure S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of catalyst **Ni3.**

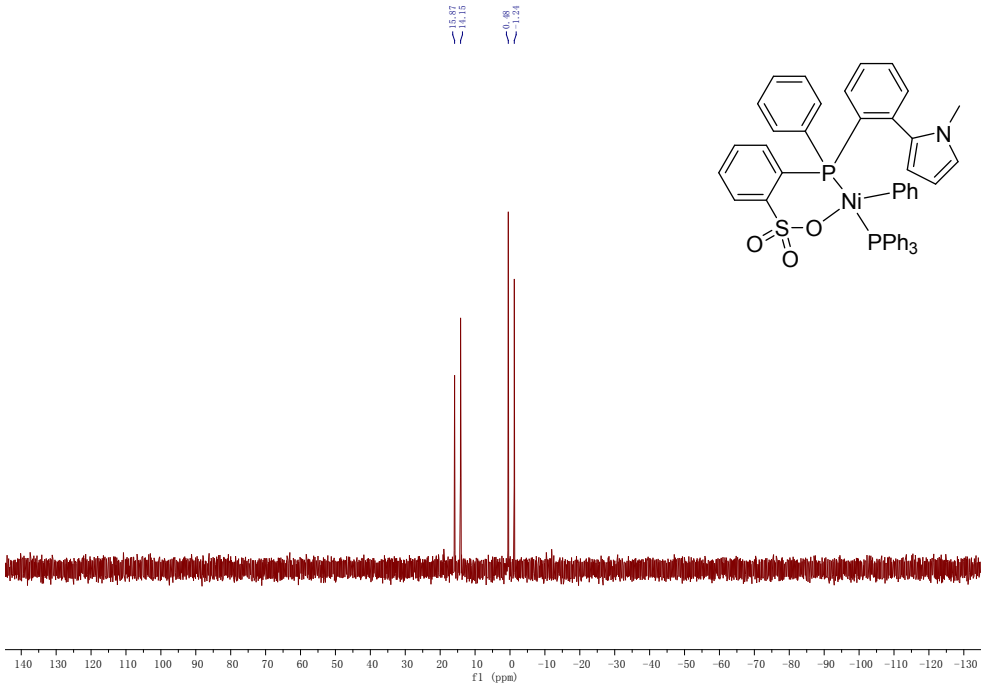


Figure S30. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of catalyst **Ni3.**

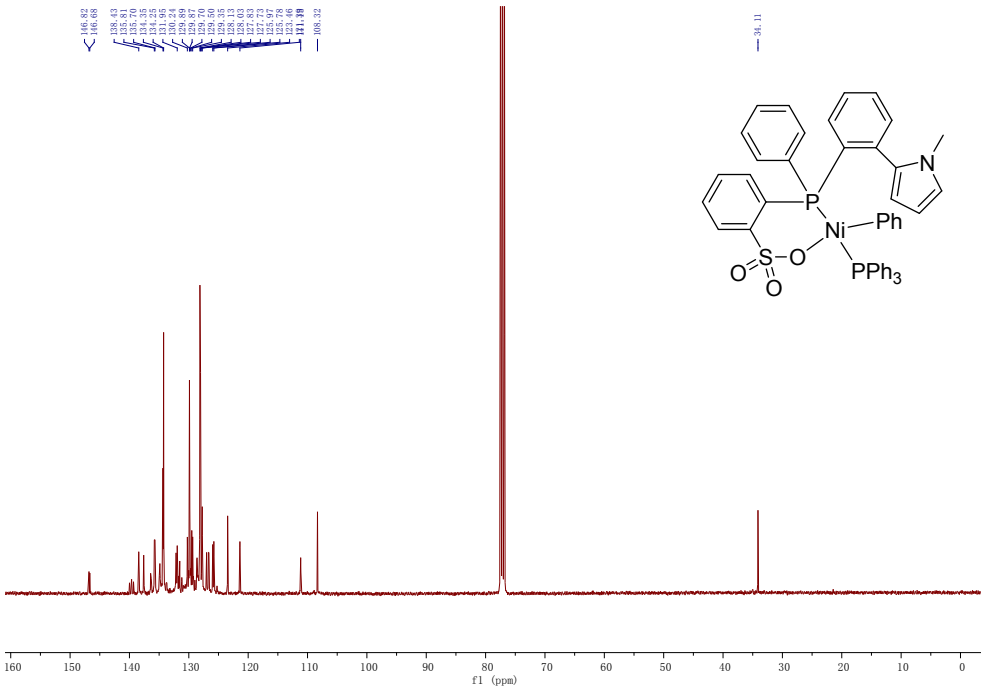


Figure S31. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of catalyst **Ni3.**

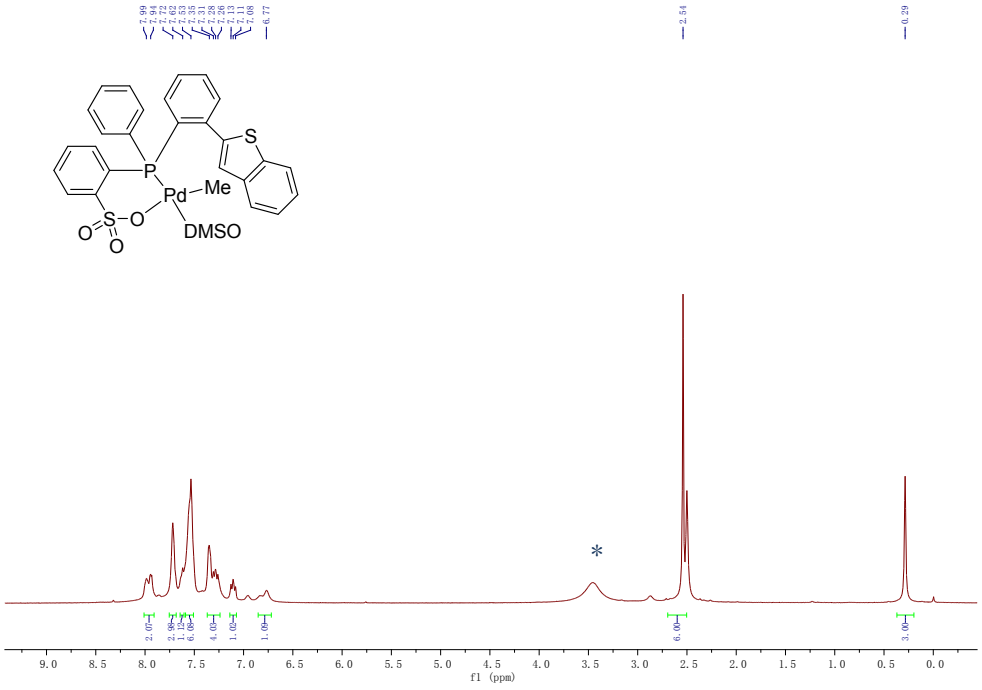


Figure S32. ^{1}H NMR spectrum (400 MHz, DMSO) of catalyst **Pd4**.(* is H_2O)

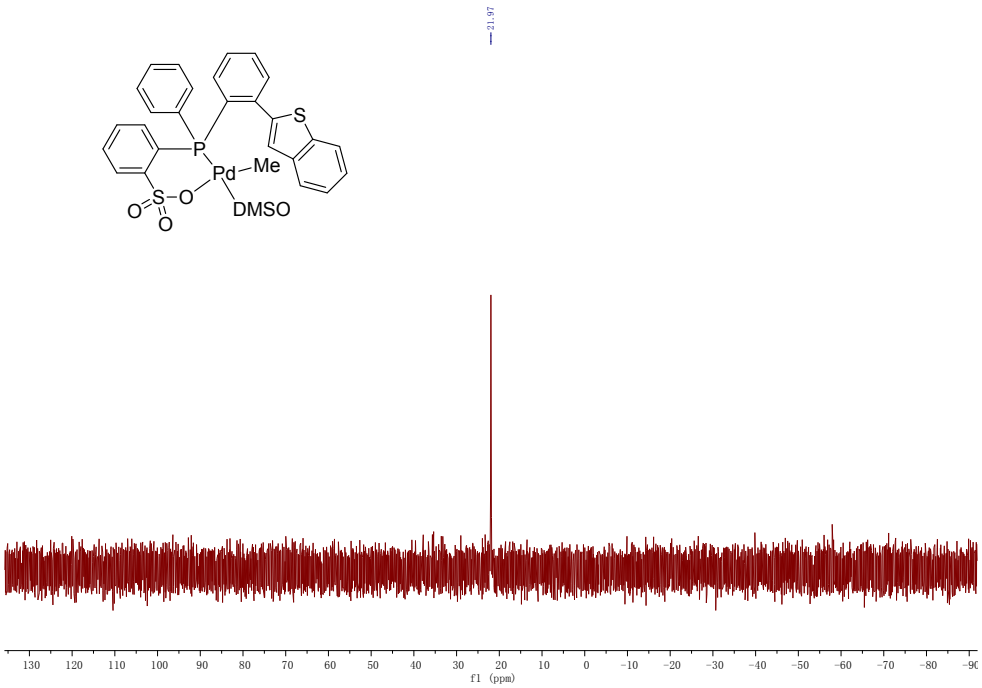


Figure S33. ^{31}P NMR spectrum (162 MHz, DMSO) of catalyst **Pd4.**

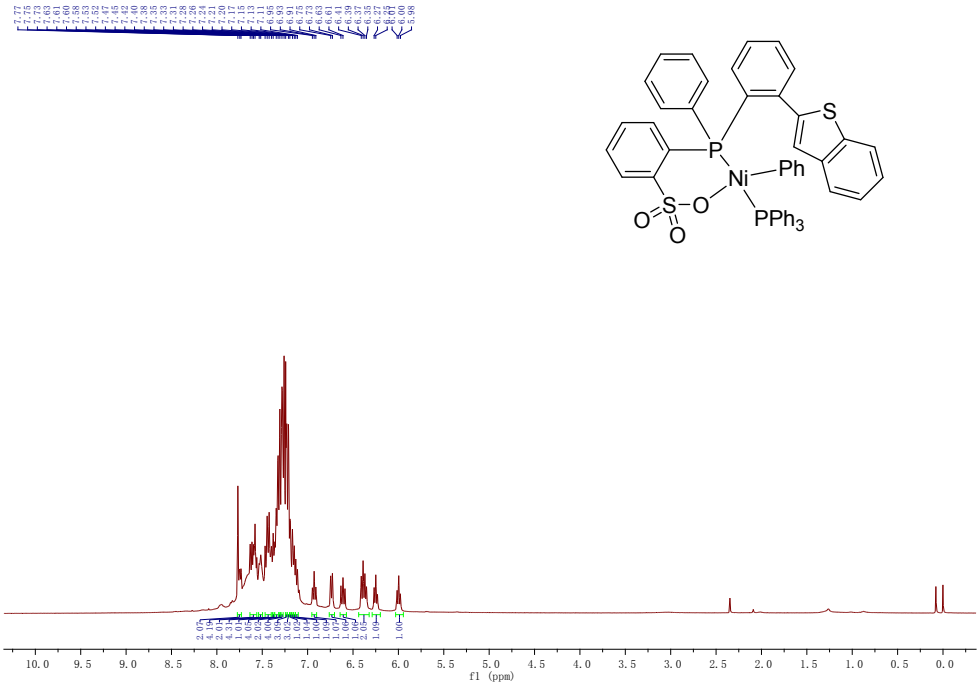


Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of catalyst **Ni4.**

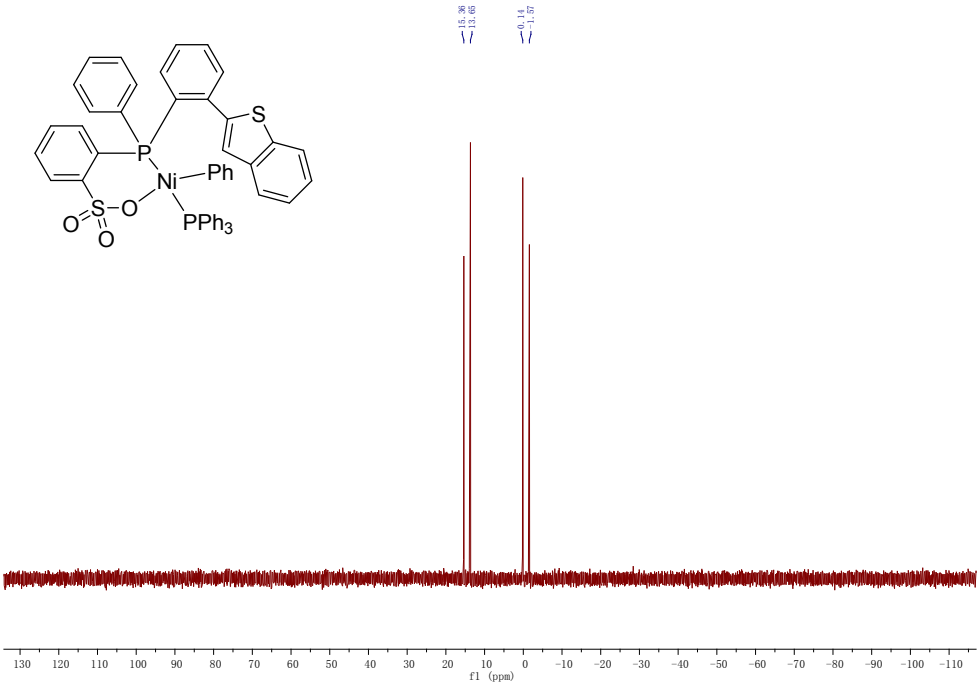


Figure S35. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of catalyst **Ni4.**

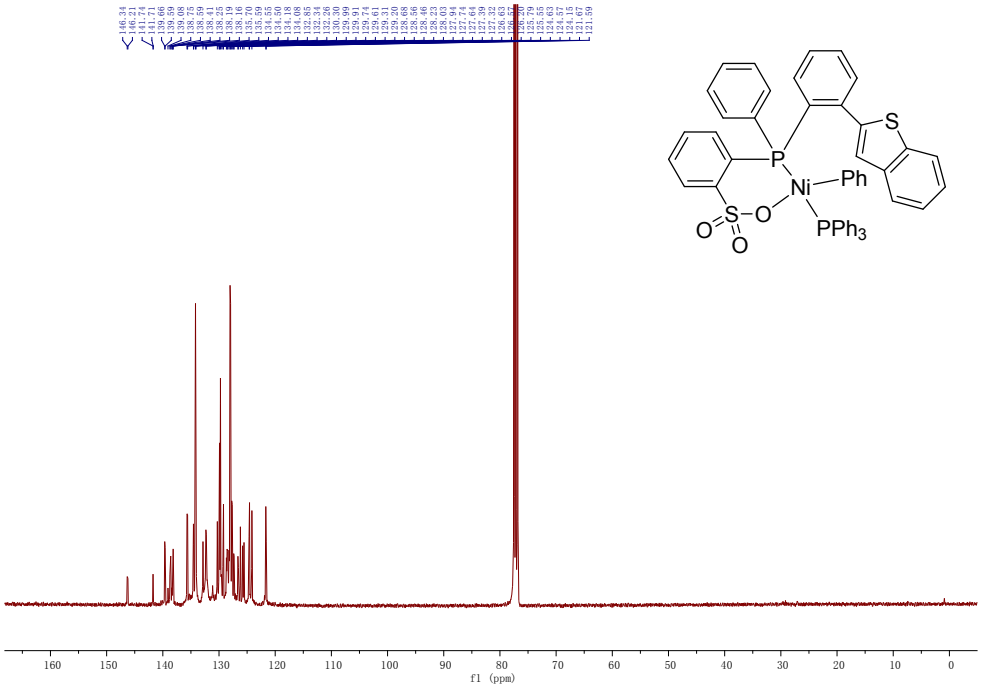


Figure S36. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of catalyst **Ni4.**

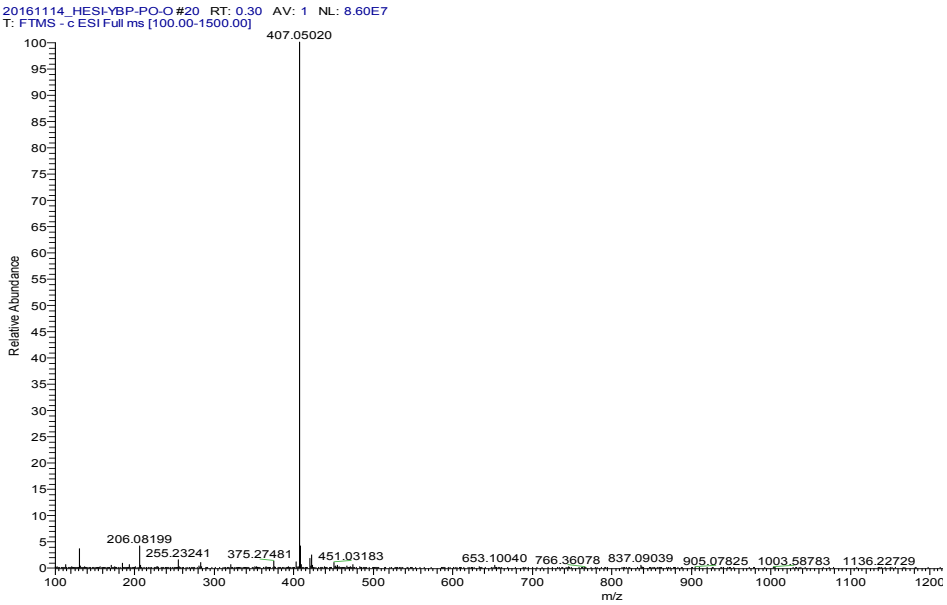


Figure S37. ESI-MS of **L1**.

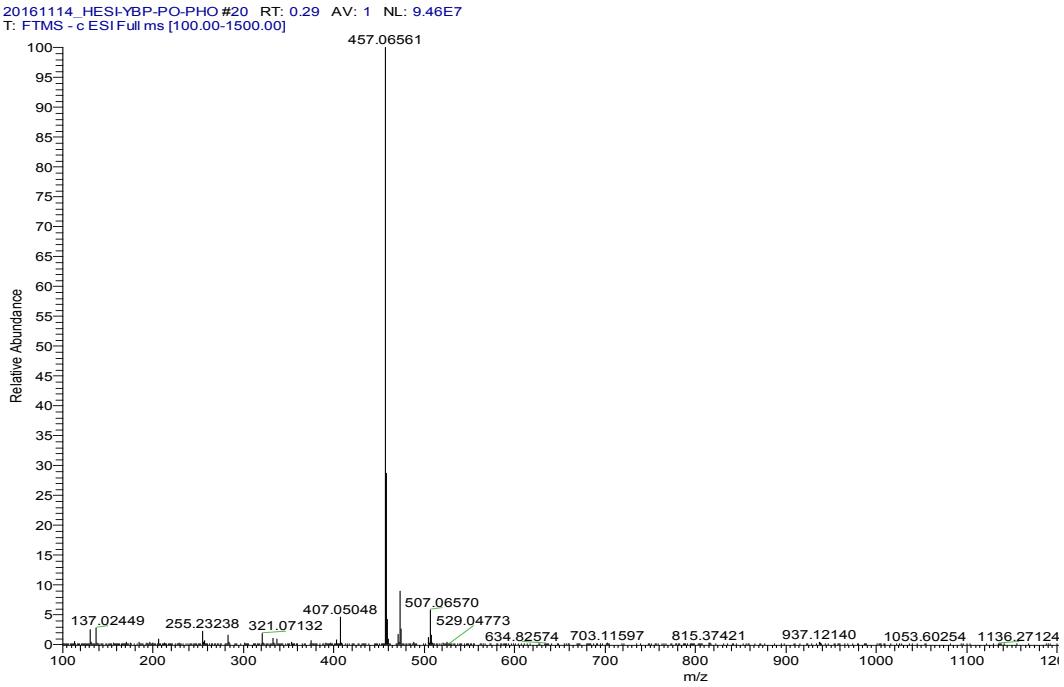


Figure S38. ESI-MS of **L2**.

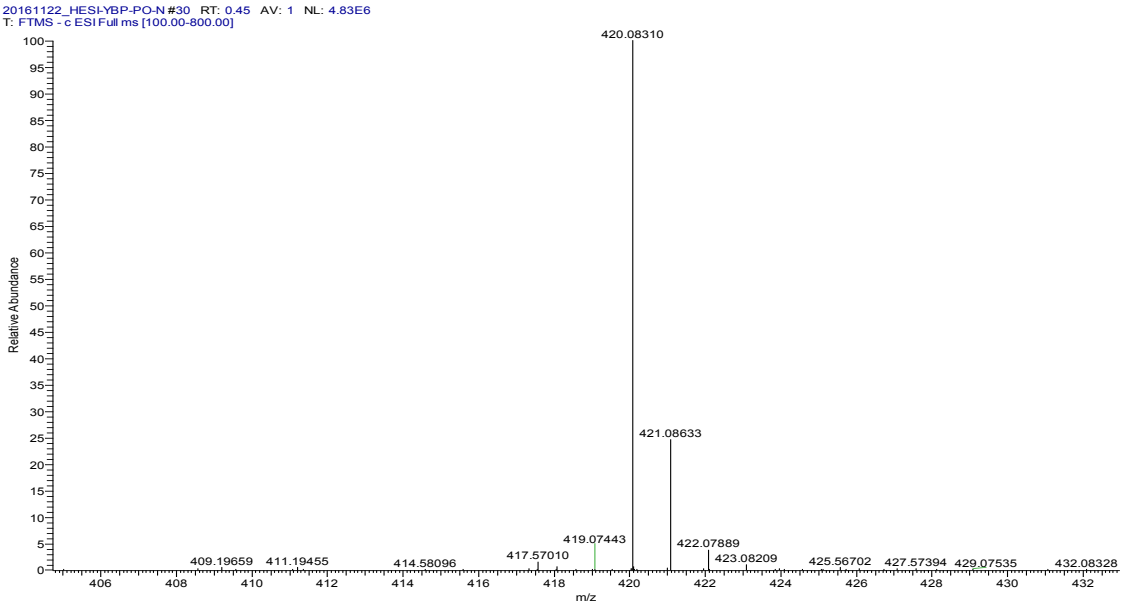


Figure S39. ESI-MS of **L3**.

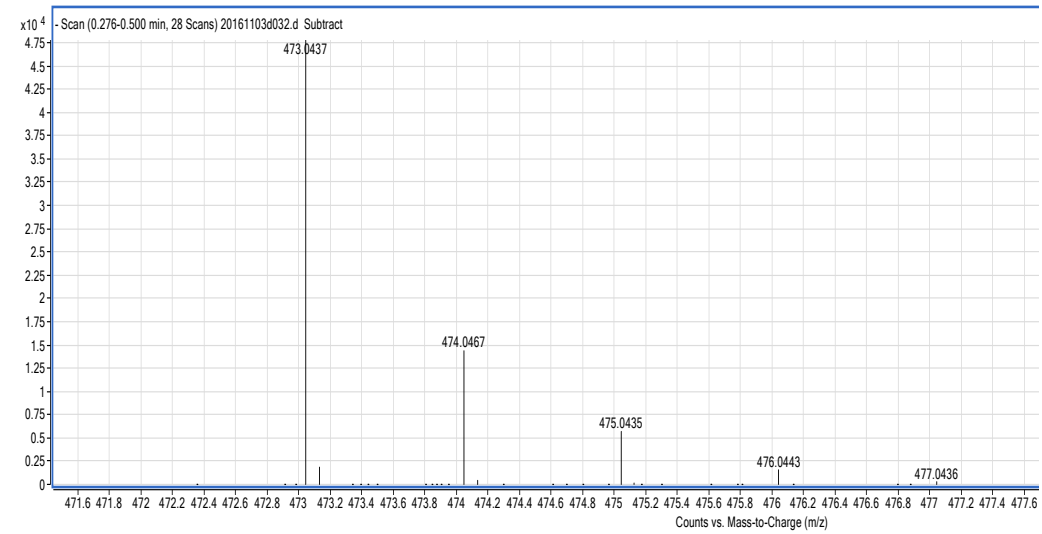


Figure S40 ESI-MS of **L4**.

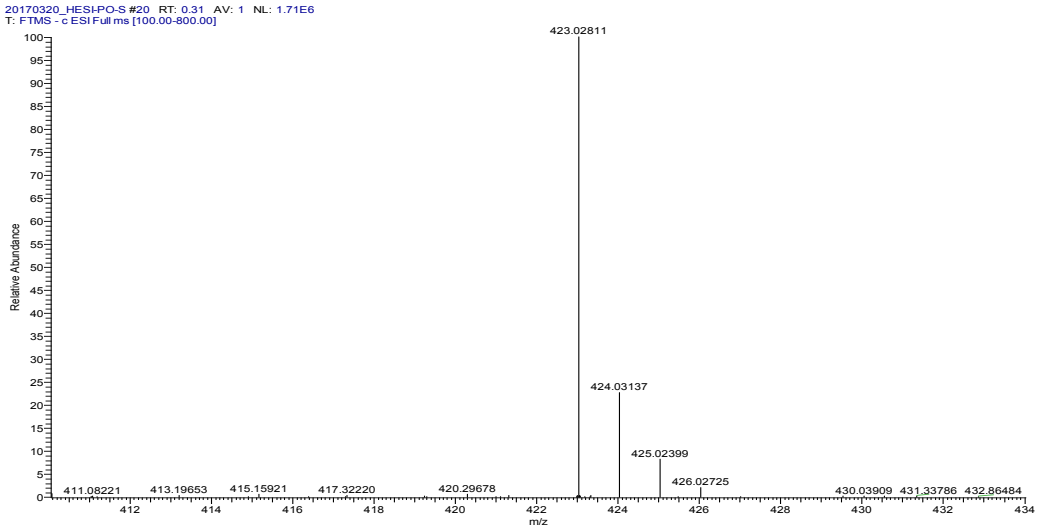


Figure S41. ESI-MS of **L5.**

3. NMR figures of (co)polymers.

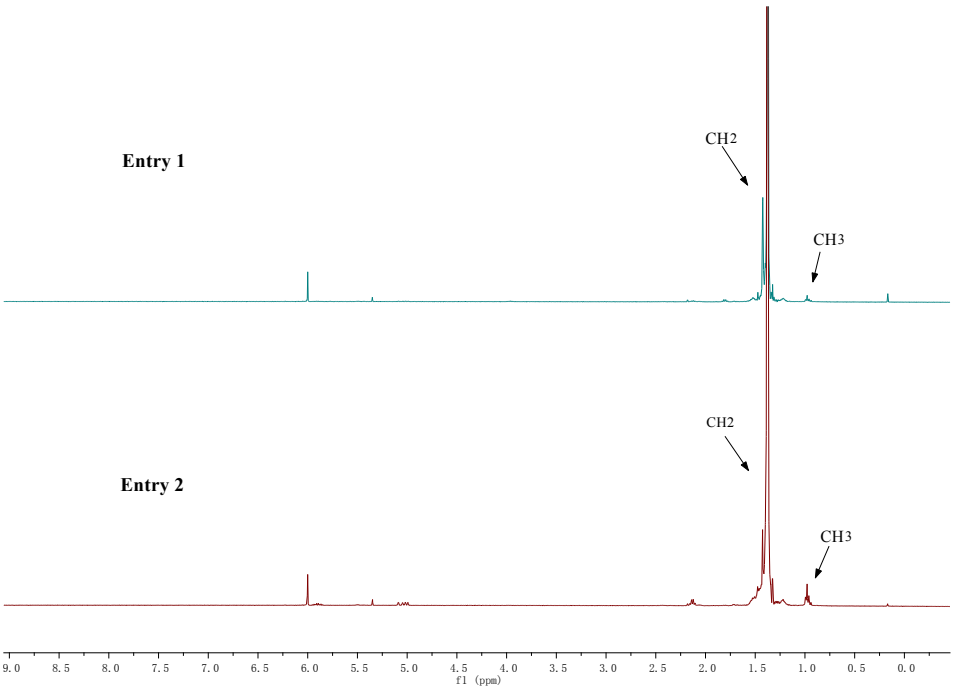


Figure S42. ^{1}H NMR spectrum of the PE from table 1. ($C_2D_2Cl_4$, 120^{o}C).

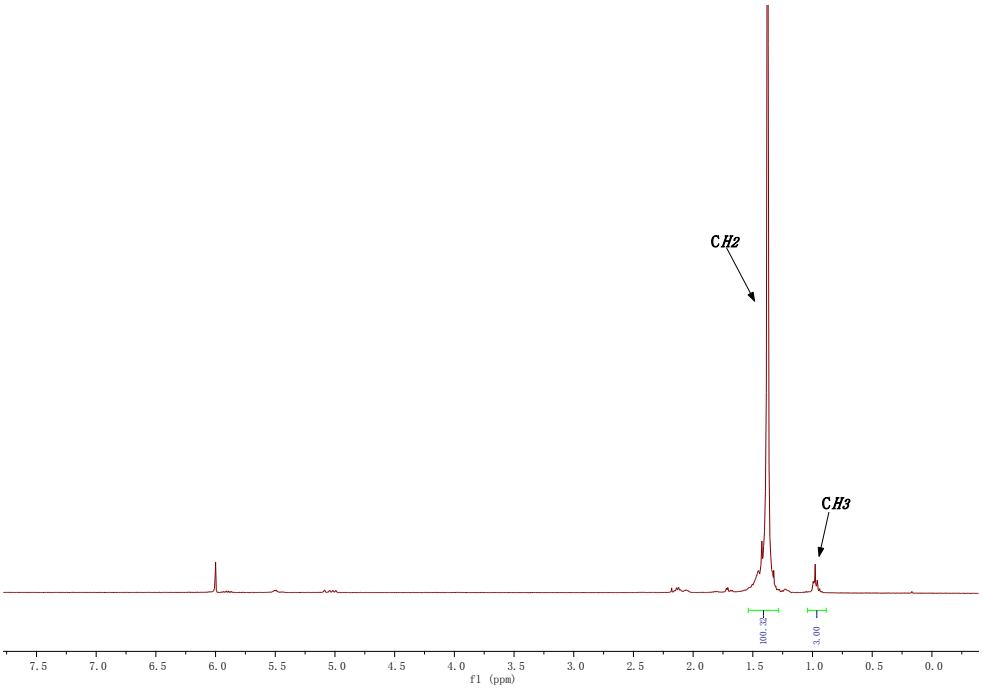


Figure S43. ^{1}H NMR spectrum of the PE from table 1, entry 3. ($C_2D_2Cl_4$, 120^{o}C).

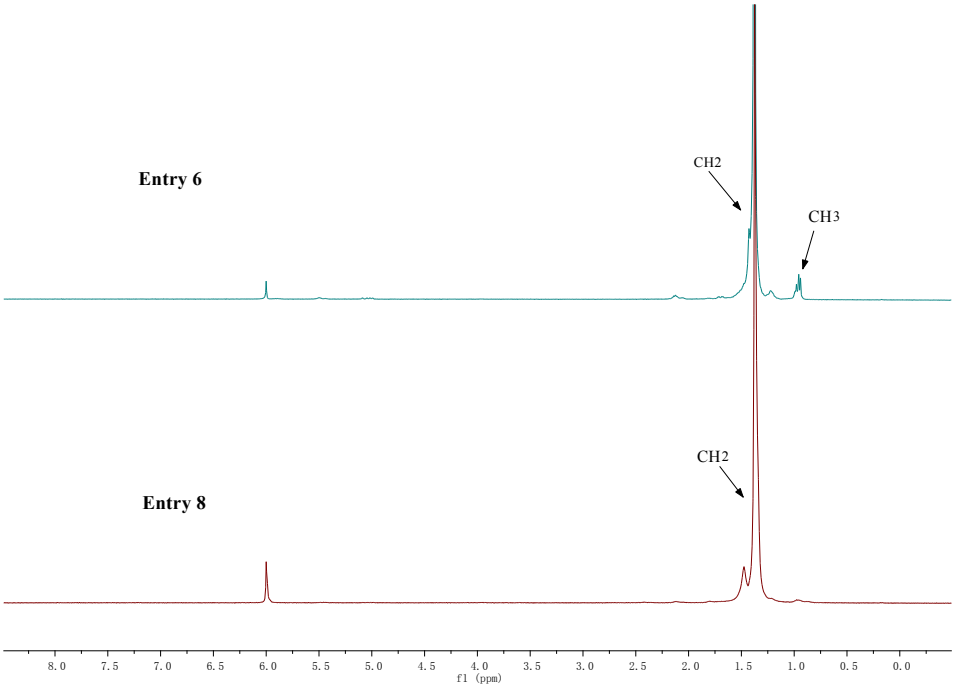


Figure S44. ^{1}H NMR spectrum of the PE from table 1. ($C_2D_2Cl_4$, 120^{o}C).

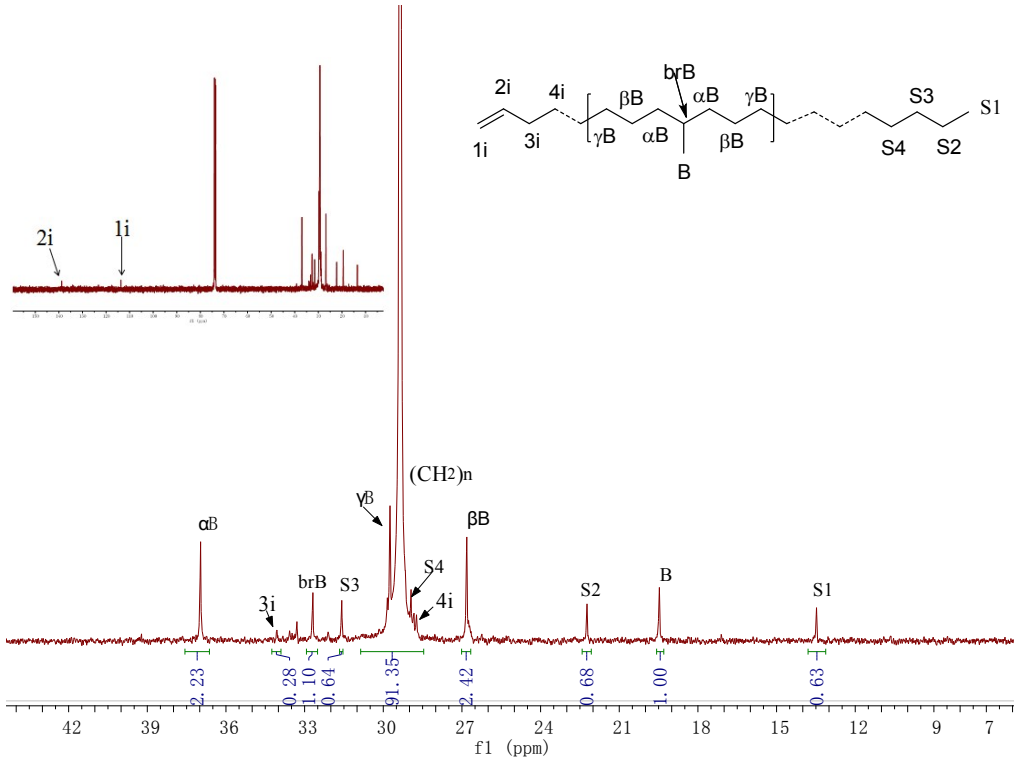


Figure S45. ^{13}C NMR spectrum of the PE from table 1, entry 6. ($C_2D_2Cl_4$, 120^{o}C)

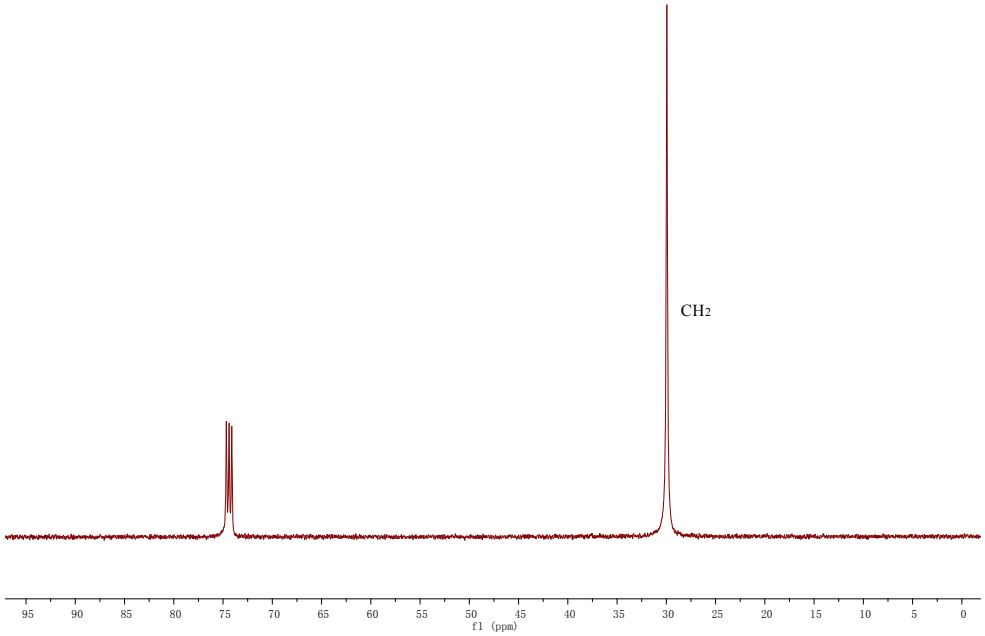


Figure S46. ^{13}C NMR spectrum of the PE from table 1, entry 8. ($C_2D_2Cl_4$, 120°C)

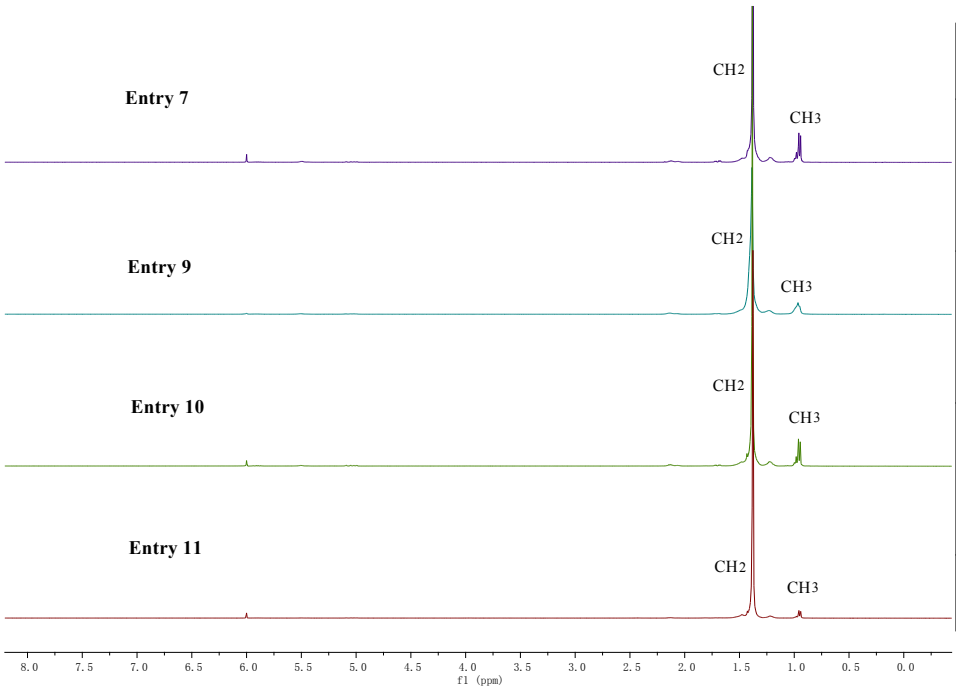


Figure S47. ^{1}H NMR spectrum of the PE from table 1. ($C_2D_2Cl_4$, 120°C).

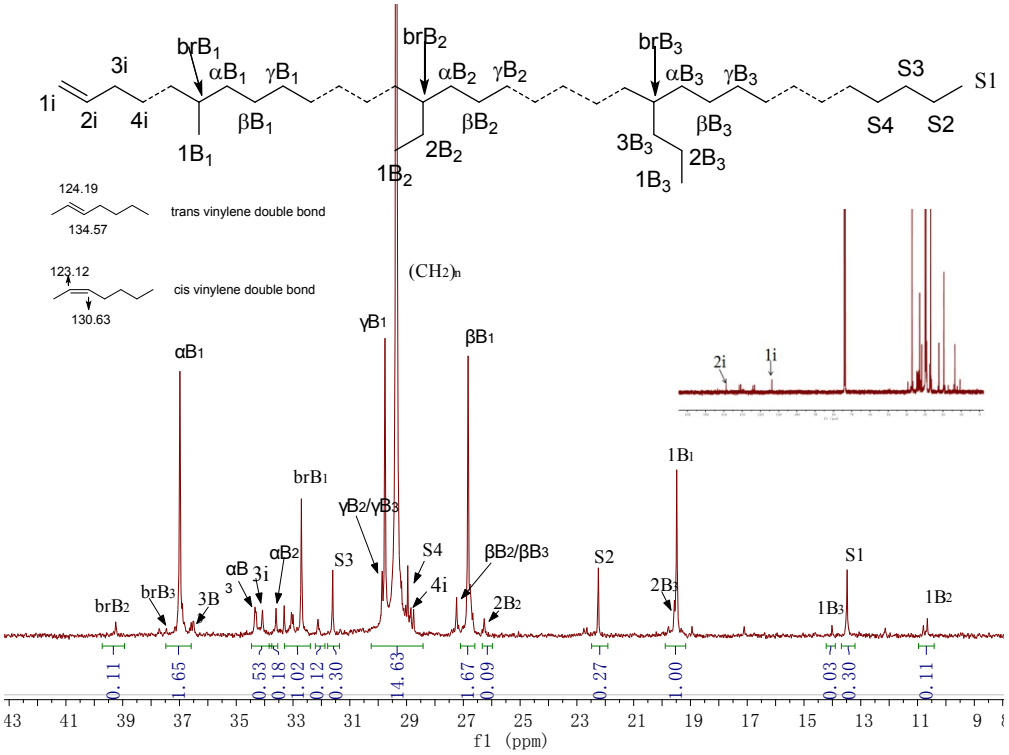


Figure S48. ^{13}C NMR spectrum of the PE from table 1, entry 7. ($C_2D_2Cl_4$, 120°C).

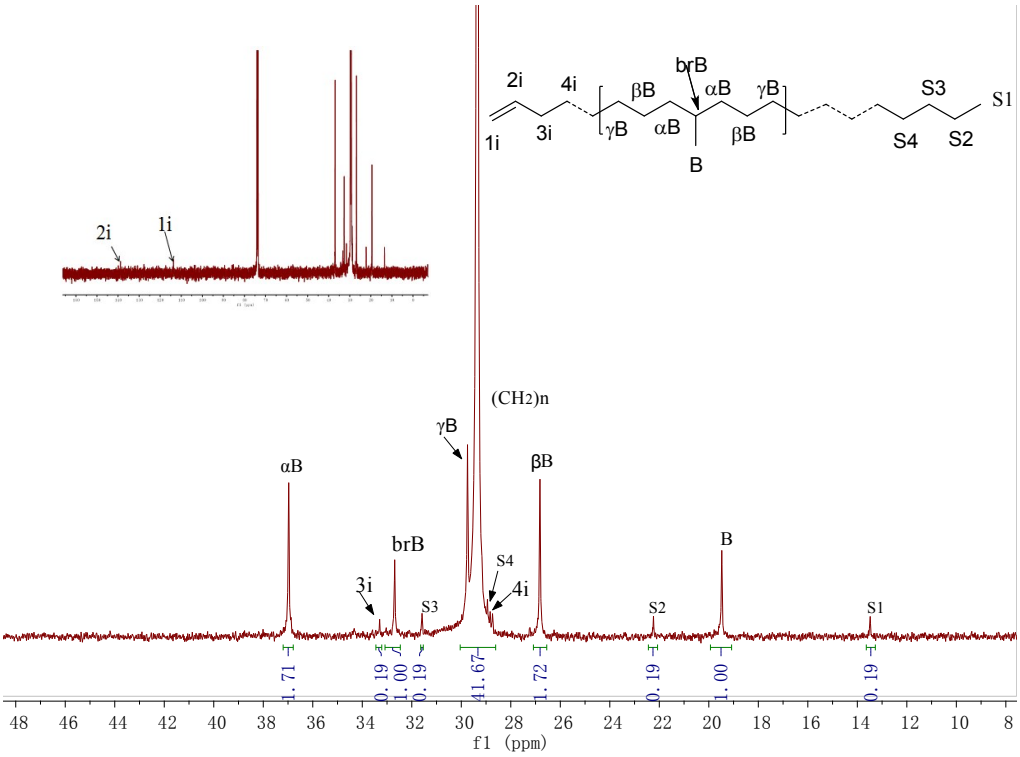


Figure S49. ^{13}C NMR spectrum of the PE from table 1, entry 11. ($C_2D_2Cl_4$, 120°C)

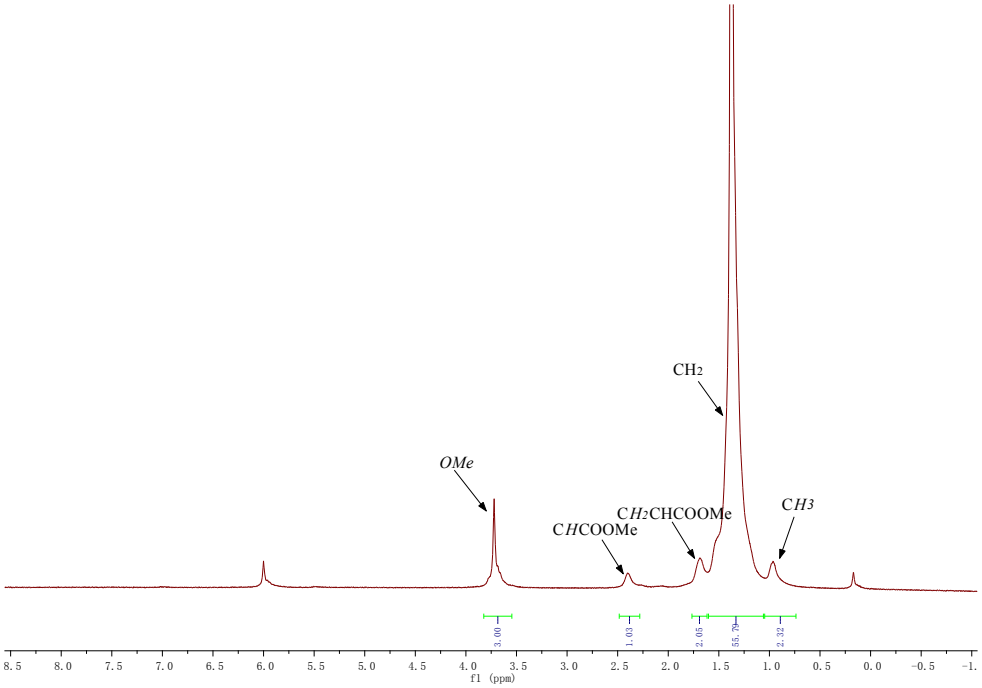


Figure S50. ^{1}H NMR spectrum of the polymer from table 2, entry 1. ($C_2D_2Cl_4$, 120^{o}C).

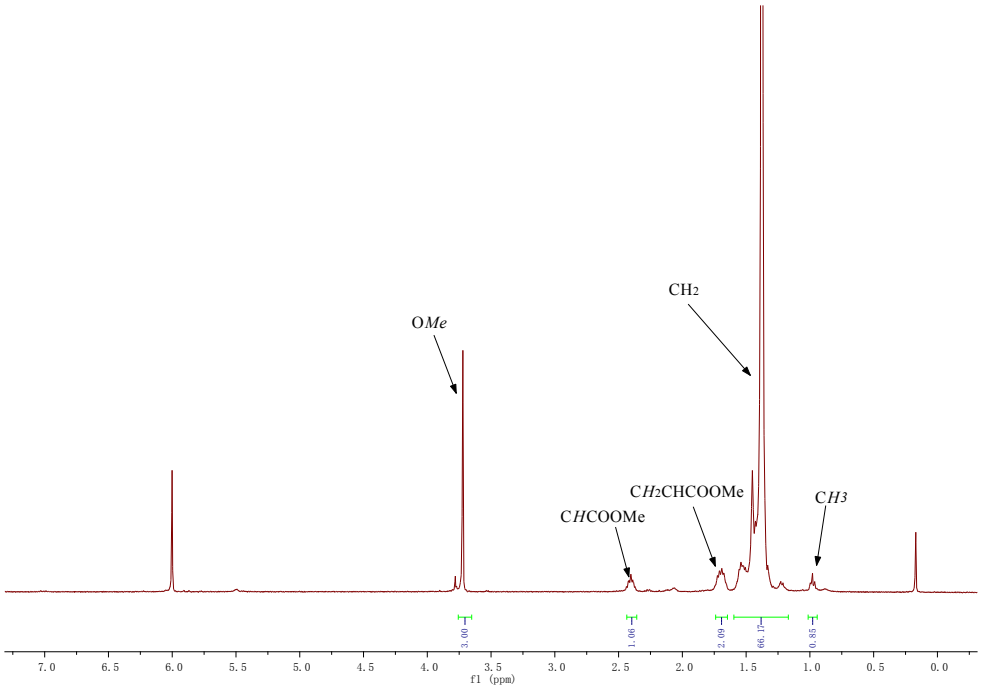


Figure S51. ^{1}H NMR spectrum of the polymer from table 2, entry 2. ($C_2D_2Cl_4$, 120^{o}C).

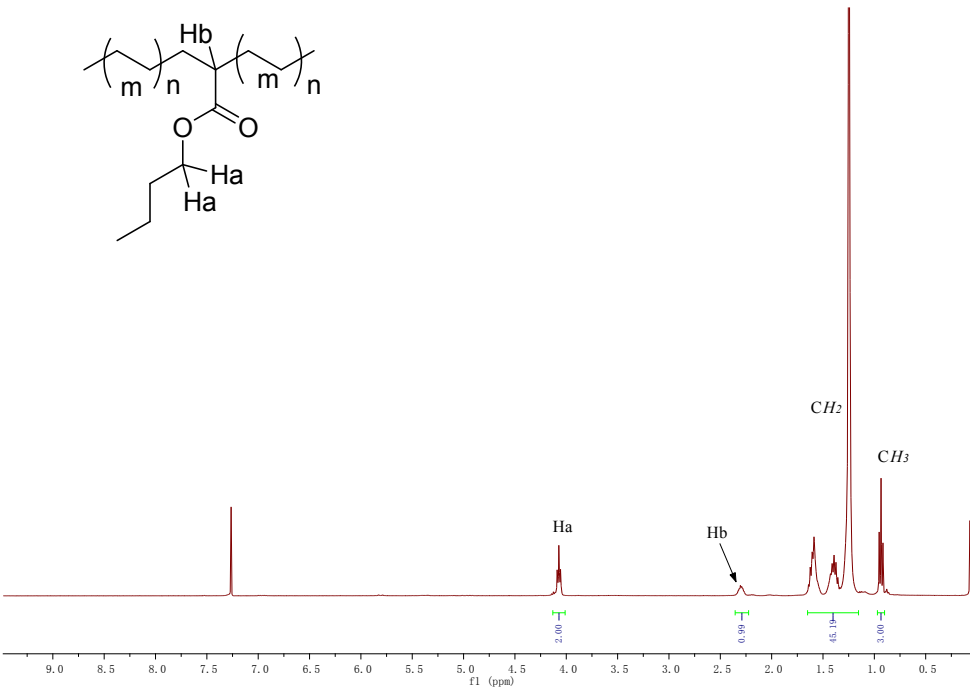


Figure S52. ^{1}H NMR spectrum of the polymer from table 2, entry 3. ($CDCl_3$).

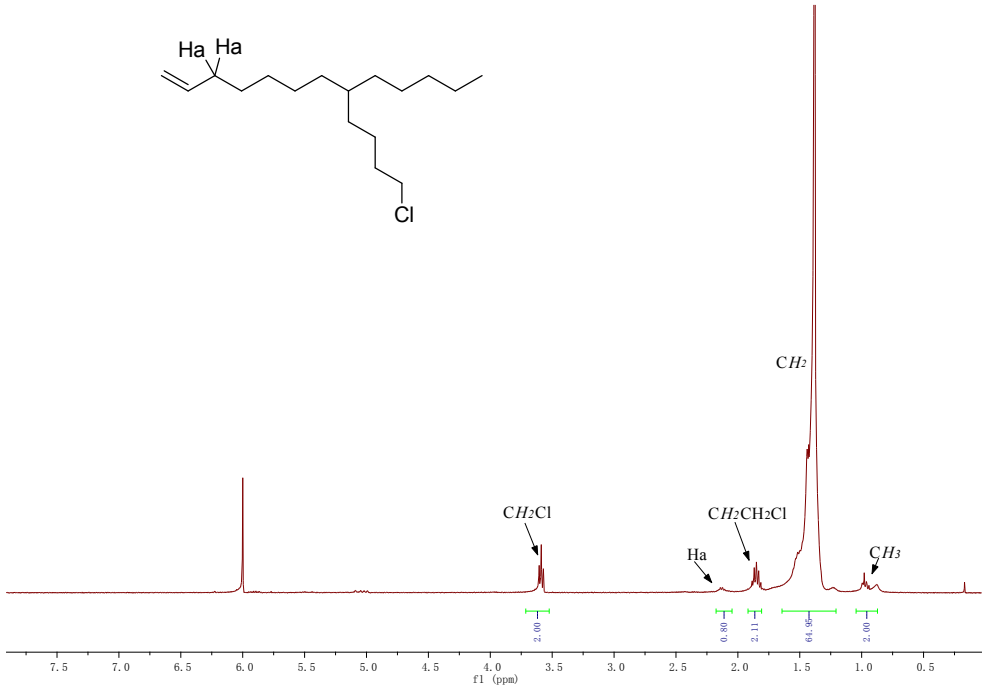


Figure S53. ^{1}H NMR spectrum of the polymer from table 2, entry 4. ($C_2D_2Cl_4$, 120^{o}C).

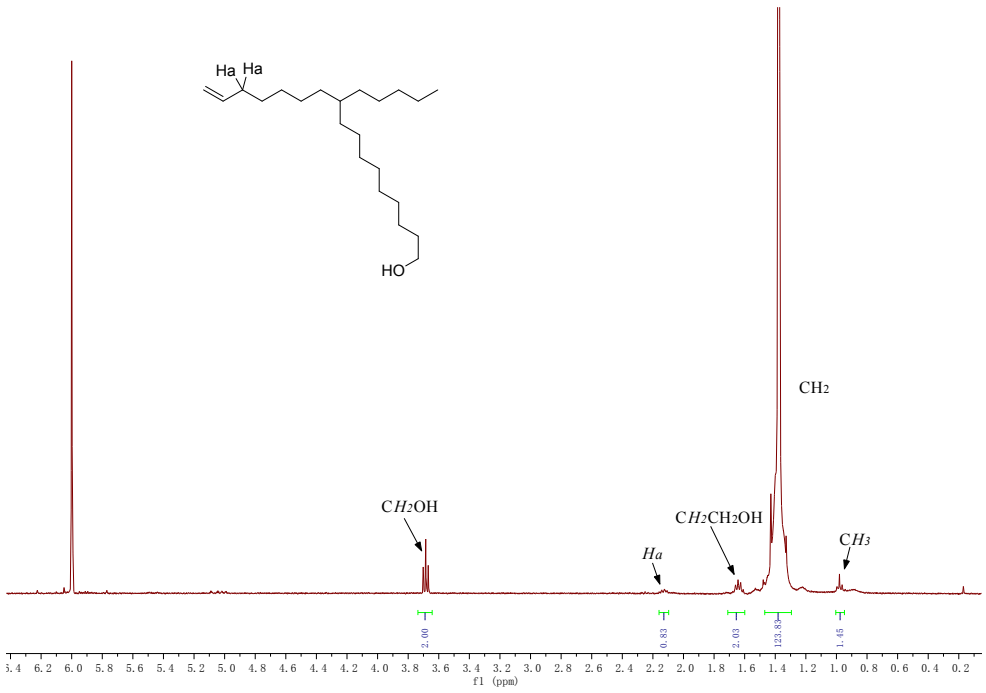


Figure S54. ^{1}H NMR spectrum of the polymer from table 2, entry 5. ($C_2D_2Cl_4$, 120^{o}C).

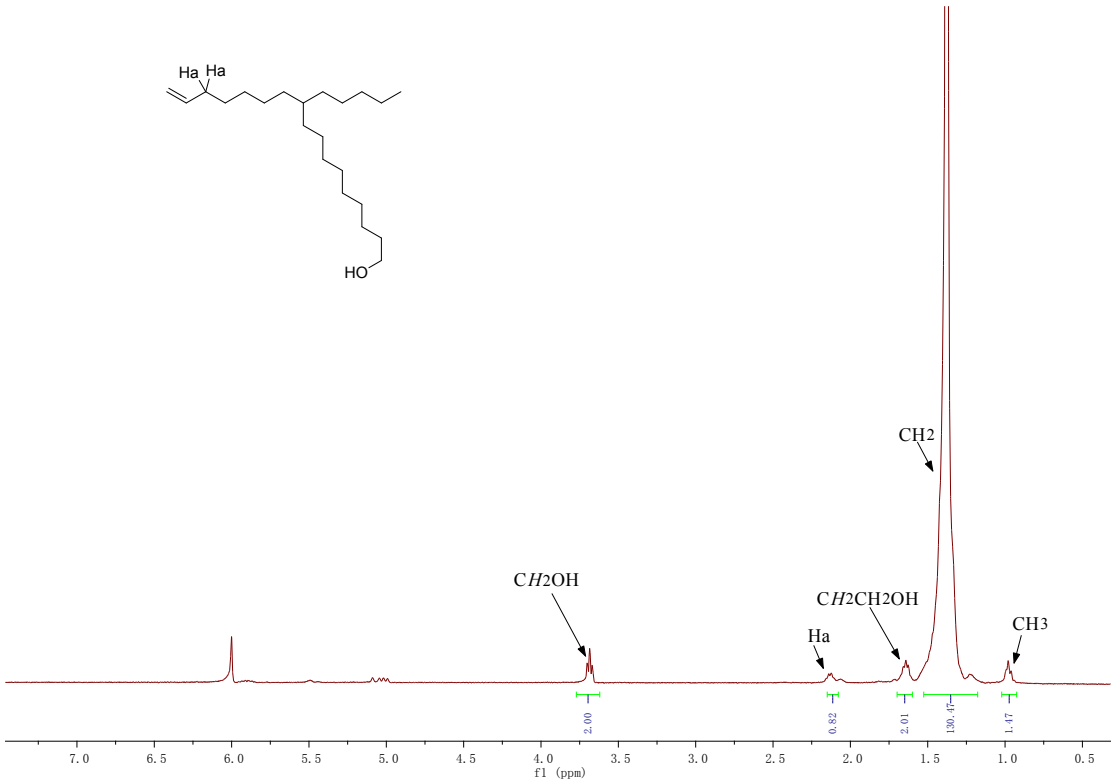


Figure S55. ^{1}H NMR spectrum of the polymer from table 2, entry 6. ($C_2D_2Cl_4$, 120^{o}C).

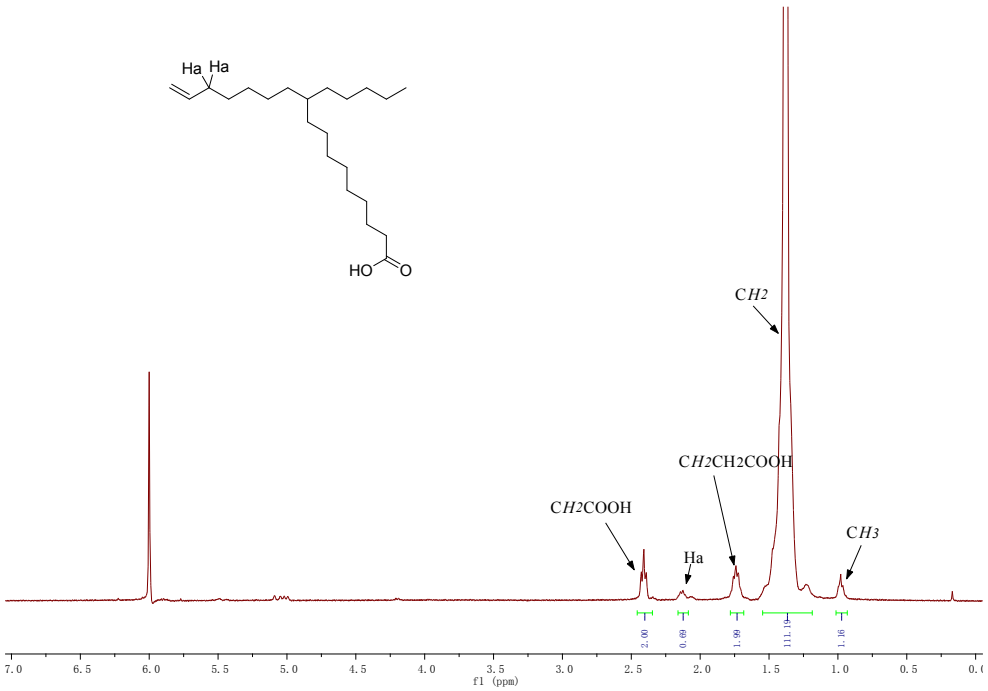


Figure S56. ^{1}H NMR spectrum of the polymer from table 2, entry 7. ($C_2D_2Cl_4$, 120^{o}C).

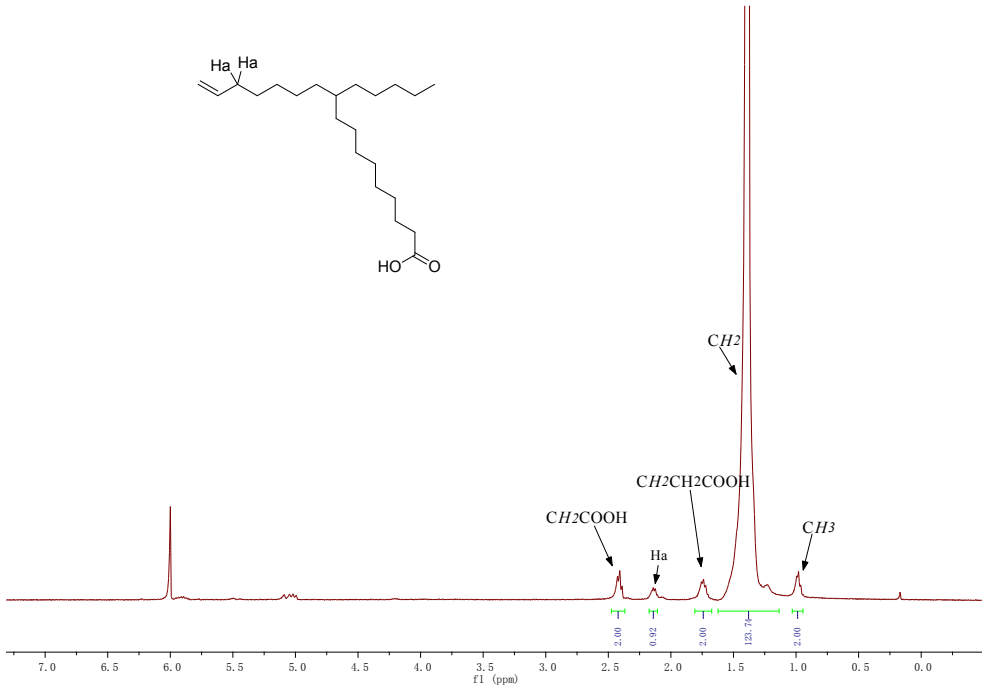


Figure S57. ^{1}H NMR spectrum of the polymer from table 2, entry 8. ($C_2D_2Cl_4$, 120^{o}C).

4. DSC and GPC traces of (co)polymers.

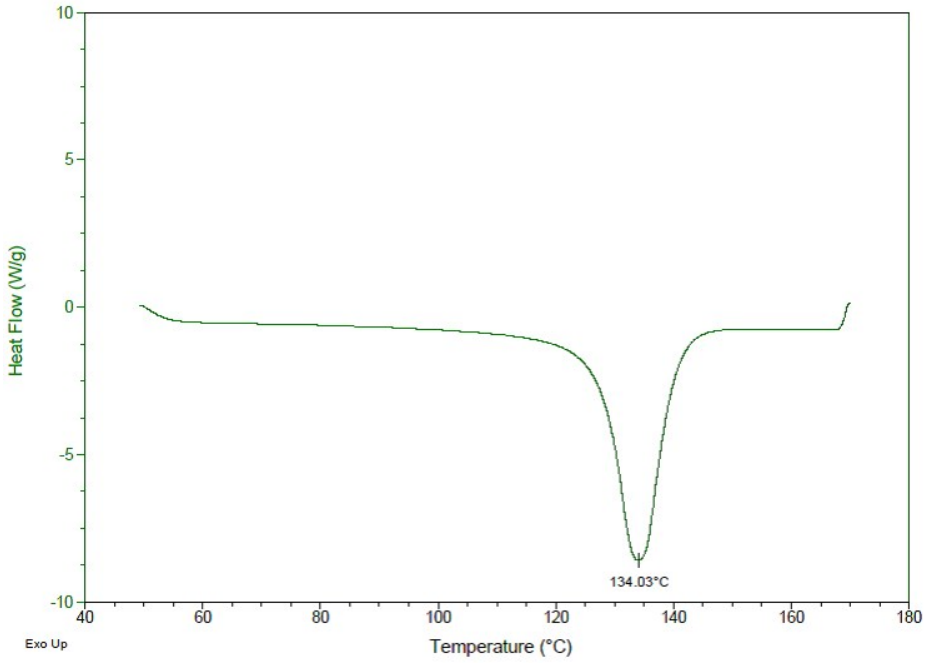


Figure S58. DSC data of the polymer from table 1, entry 1.

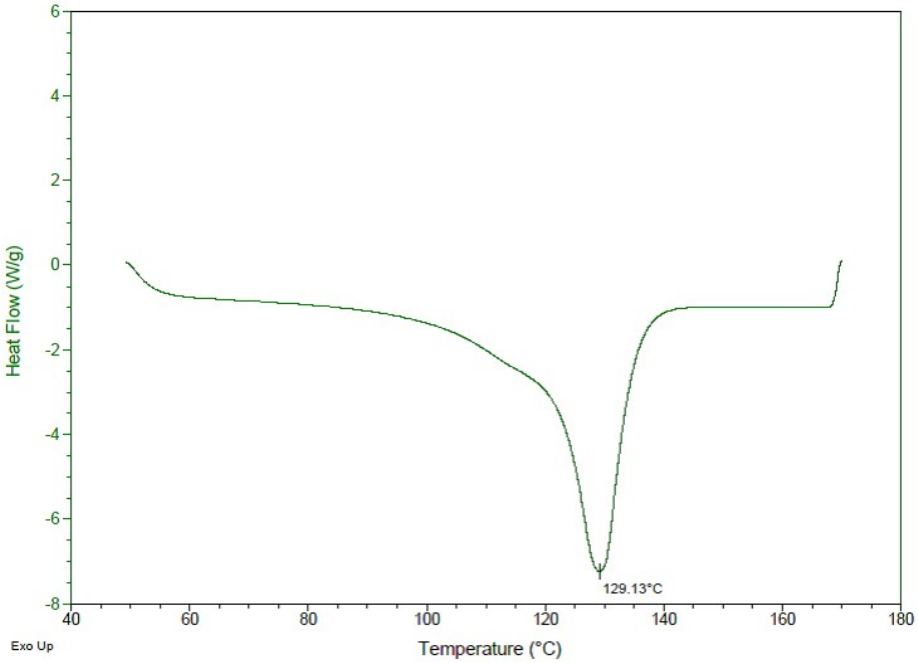


Figure S59. DSC data of the polymer from table 1, entry 2.

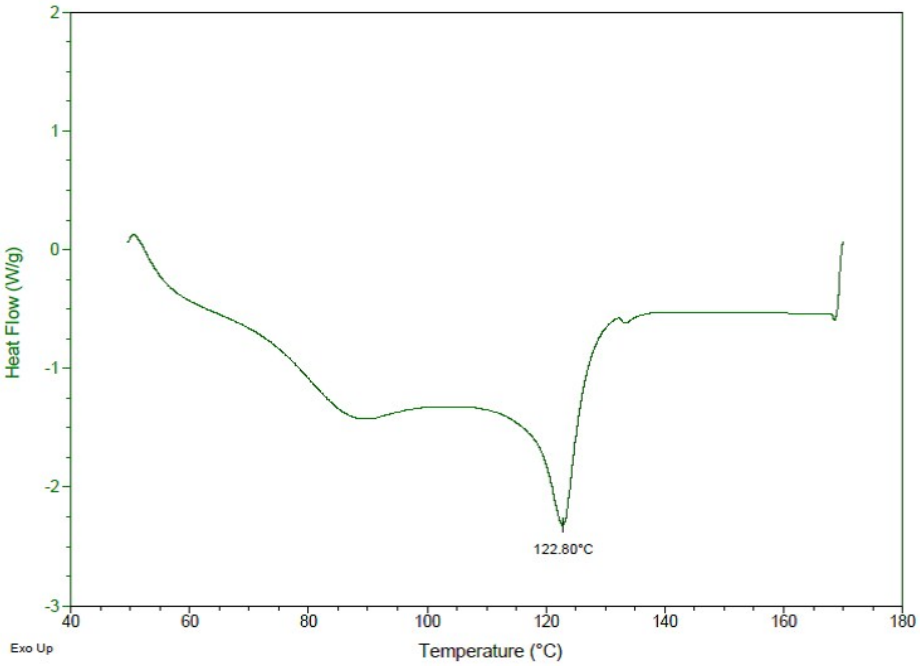


Figure S60. DSC data of the polymer from table 1, entry 3.

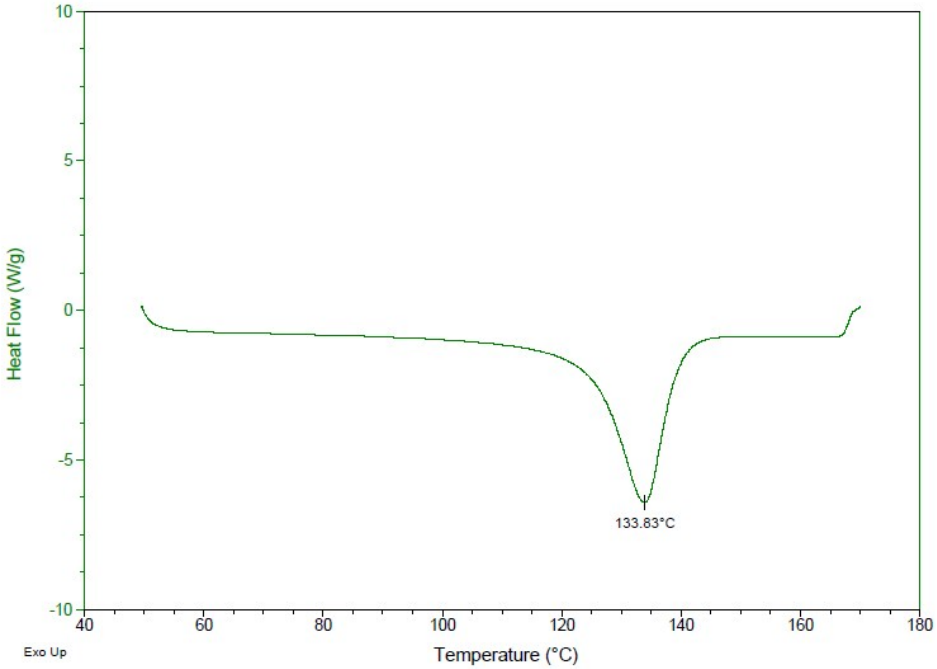


Figure S61. DSC data of the polymer from table 1, entry 8.

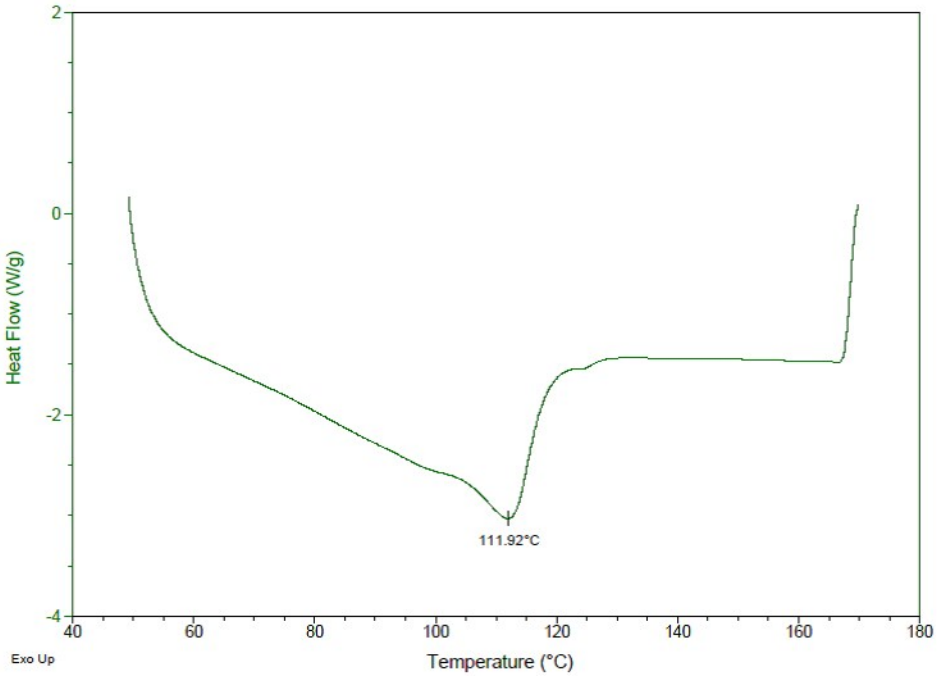


Figure S62. DSC data of the polymer from table 1, entry 11.

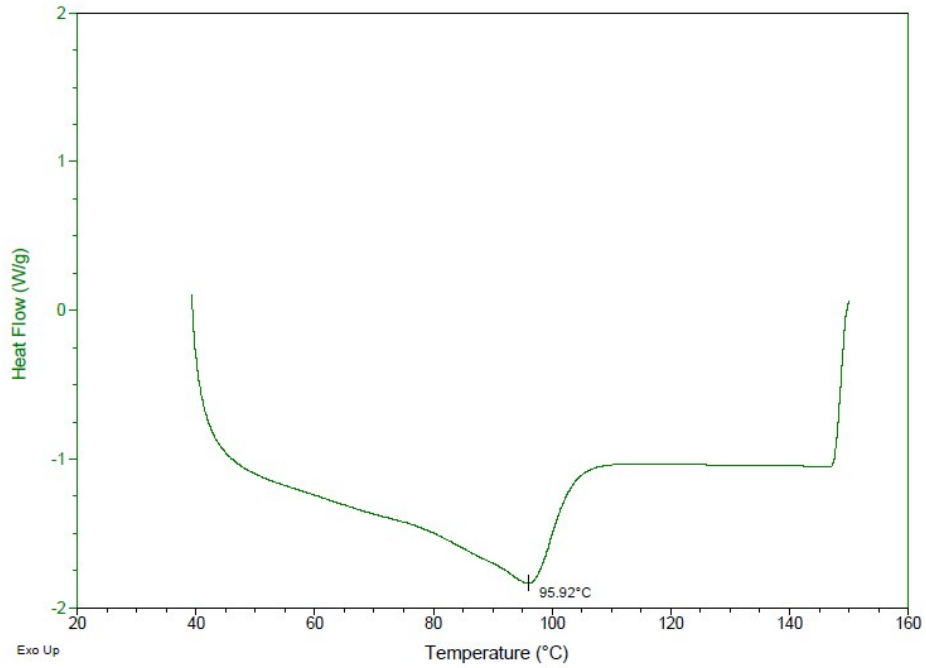


Figure S63. DSC data of the polymer from table 2, entry 1.

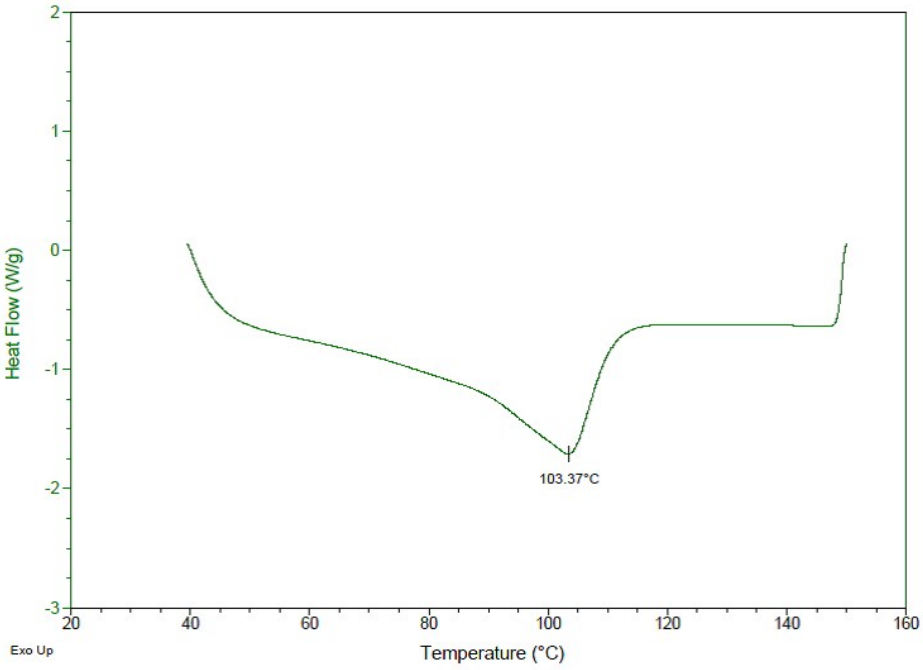


Figure S64. DSC data of the polymer from table 2, entry 2.

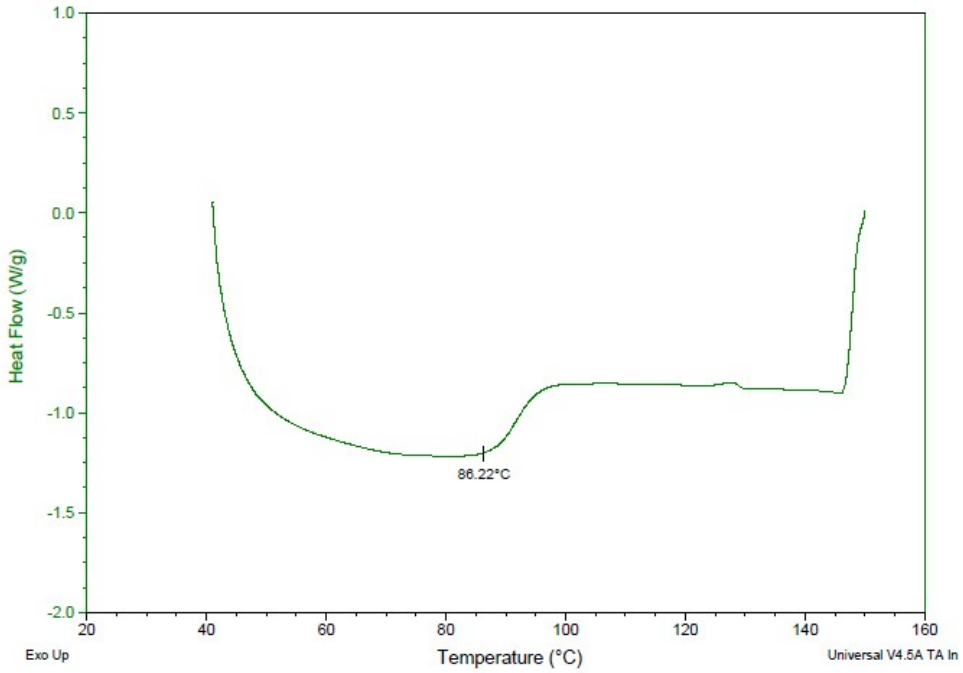


Figure S65. DSC data of the polymer from table 2, entry 3.

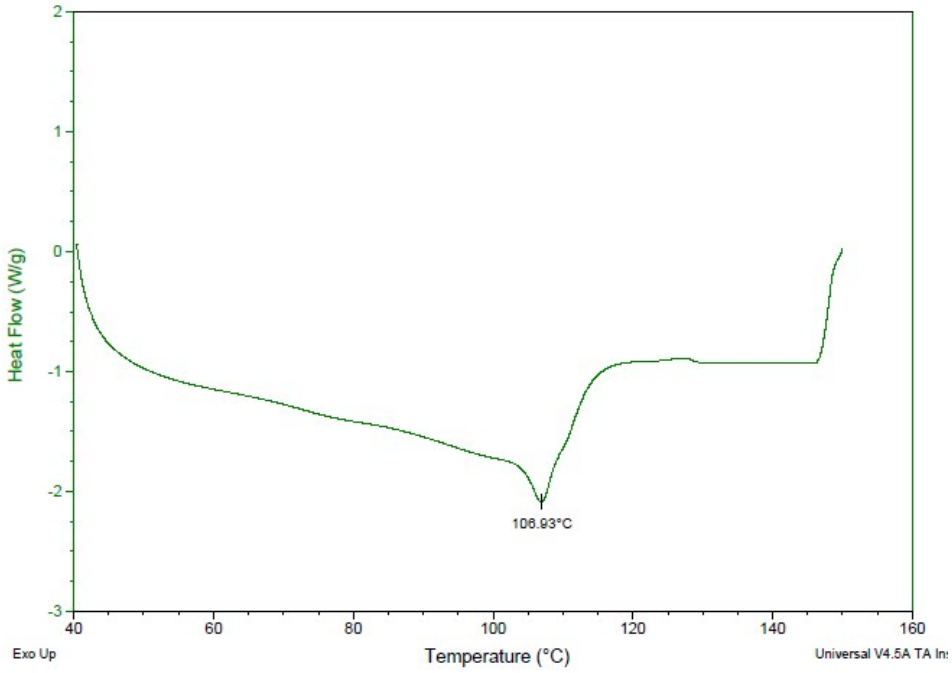


Figure S66. DSC data of the polymer from table 2, entry 4.

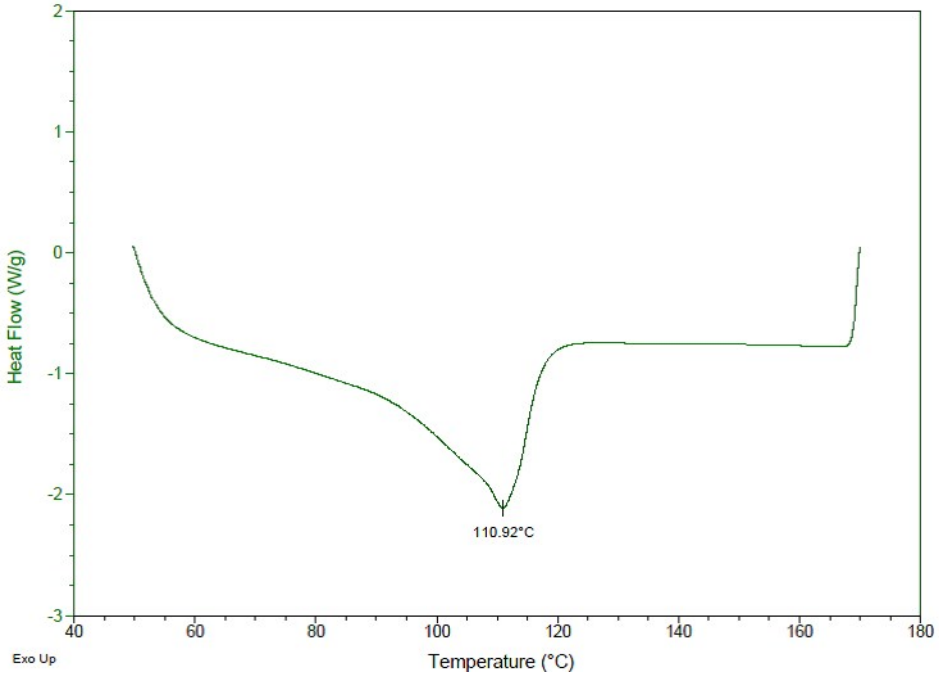


Figure S67. DSC data of the polymer from table 2, entry 5.

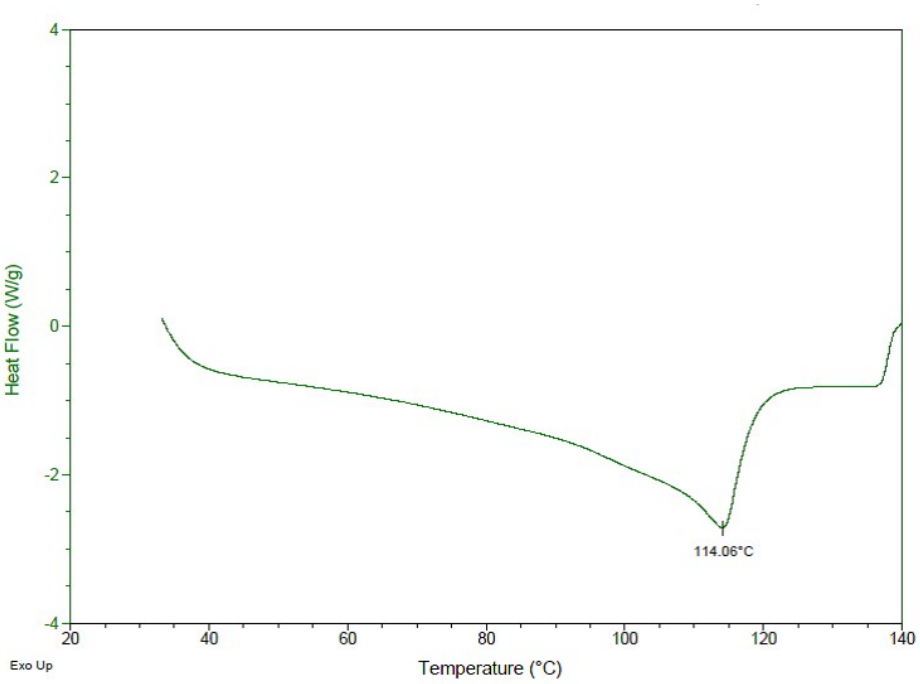


Figure S68. DSC data of the polymer from table 2, entry 6.

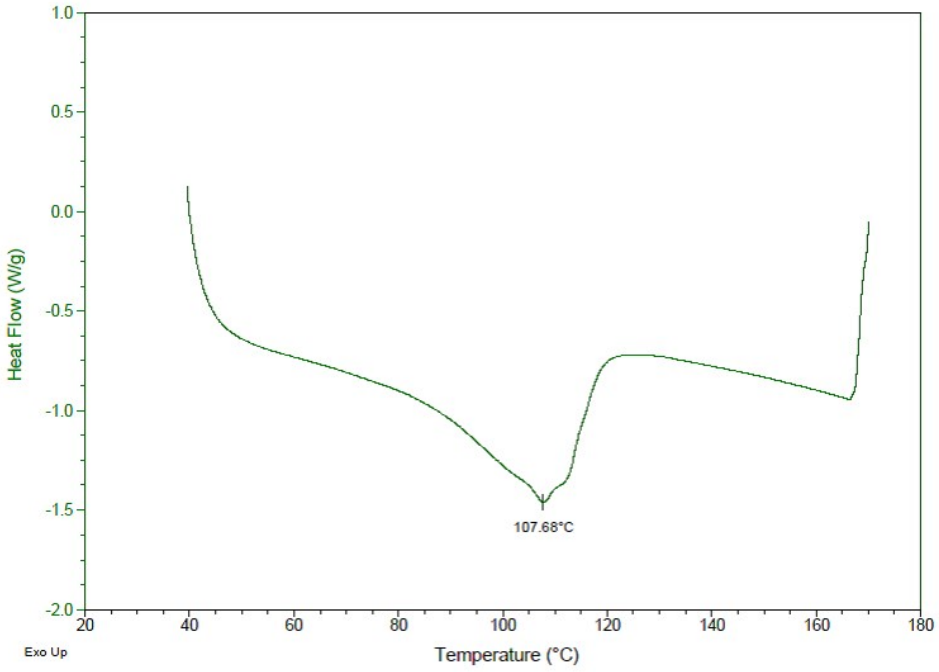


Figure S69. DSC data of the polymer from table 2, entry 7.

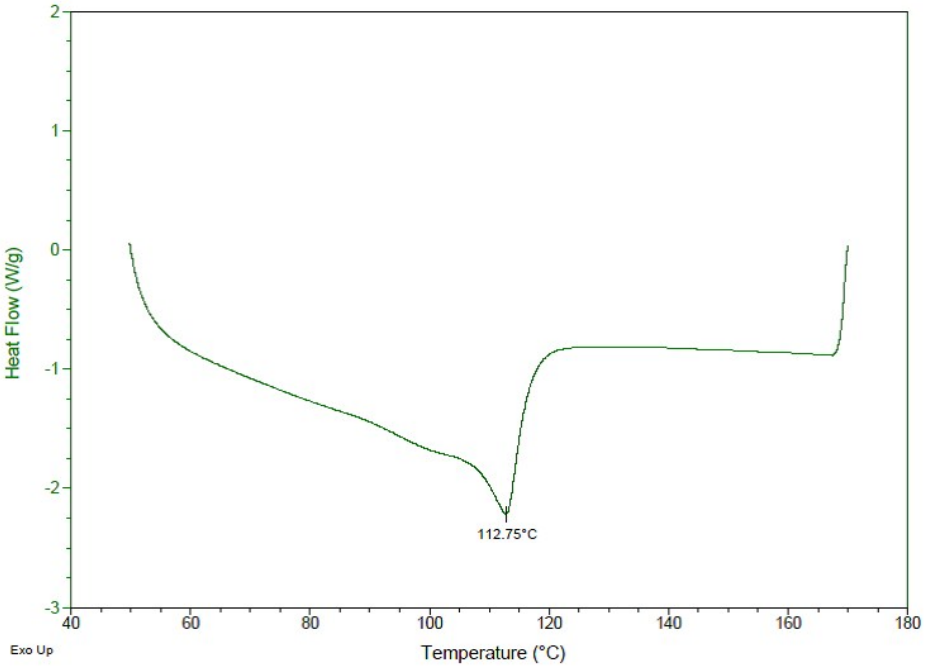


Figure S70. DSC data of the polymer from table 2, entry 8.

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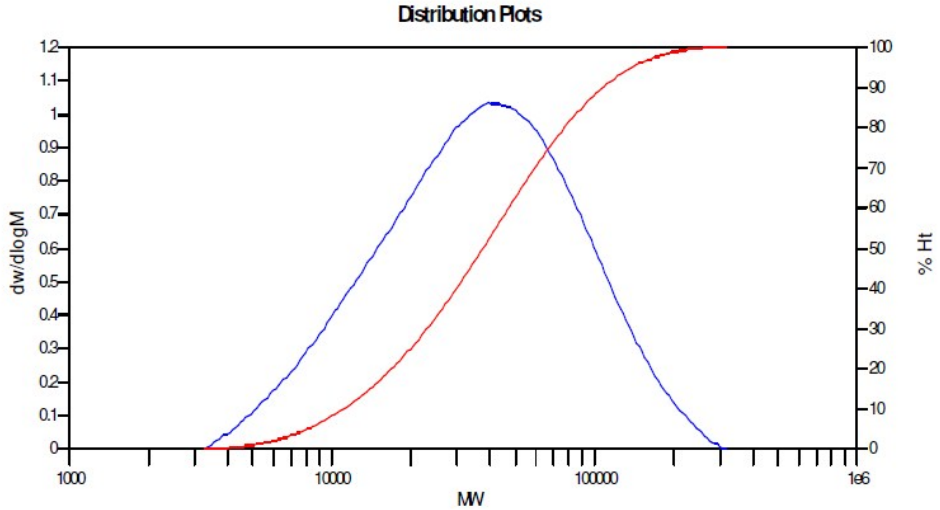
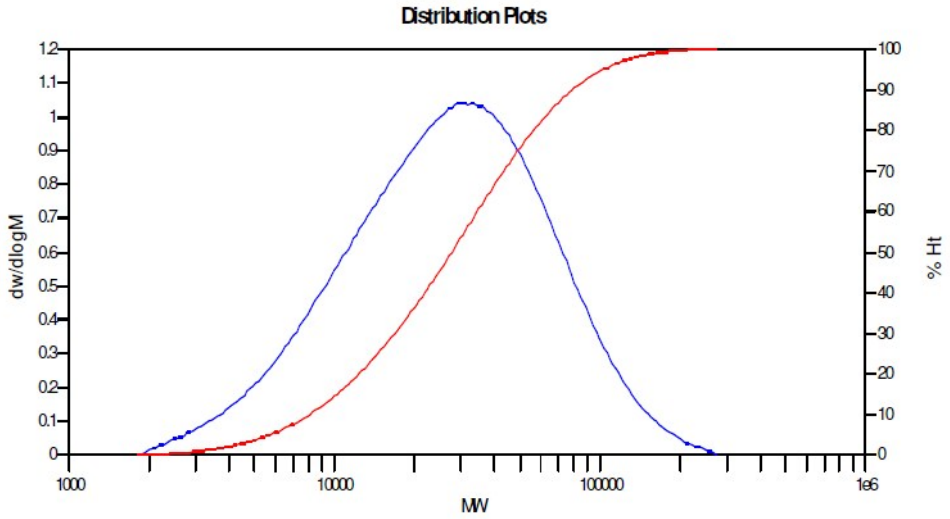


MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	39462	24605	50019	86370	124131	45329	2.03288

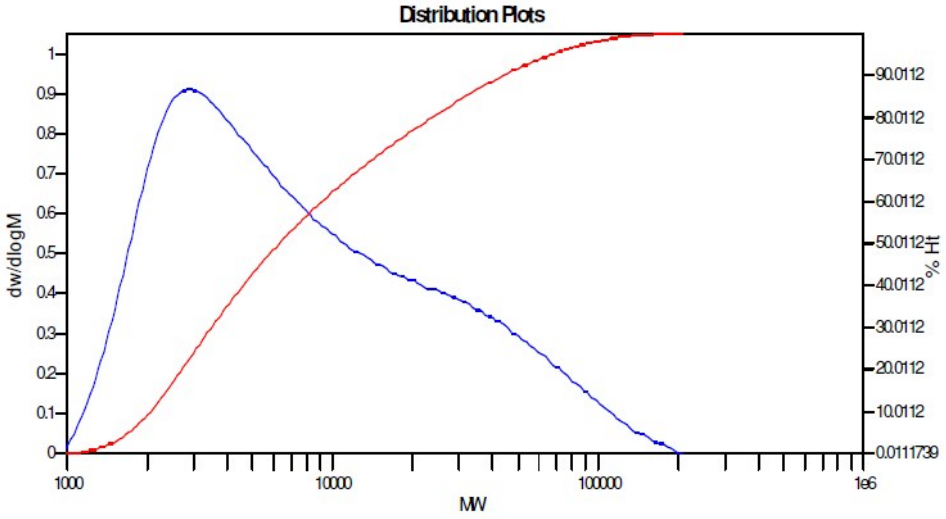
Figure S71. GPC trace of the polymer from table 1, entry 1.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	30425	17555	36918	65626	98592	33342	2.10299

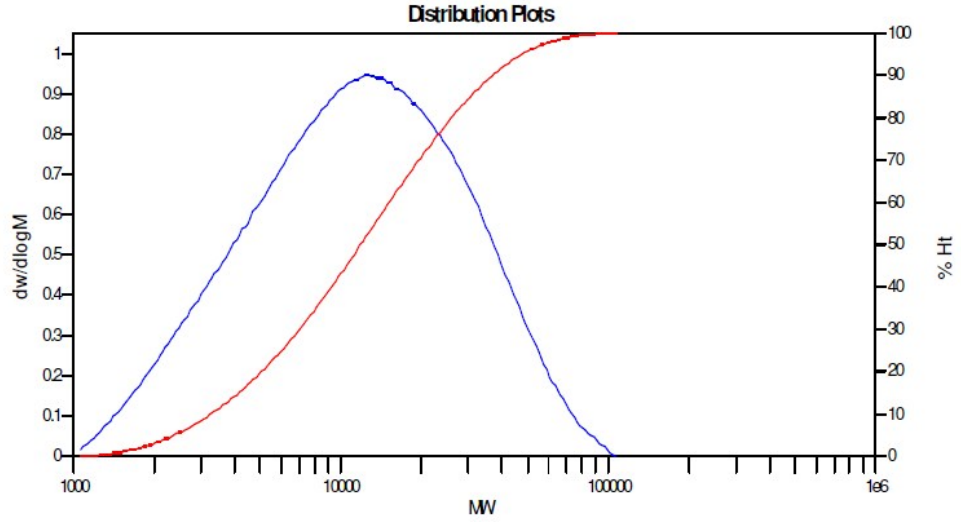
Figure S72. GPC trace of the polymer from table 1, entry 2.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2860	4645	15994	50493	85054	12786	3.44327

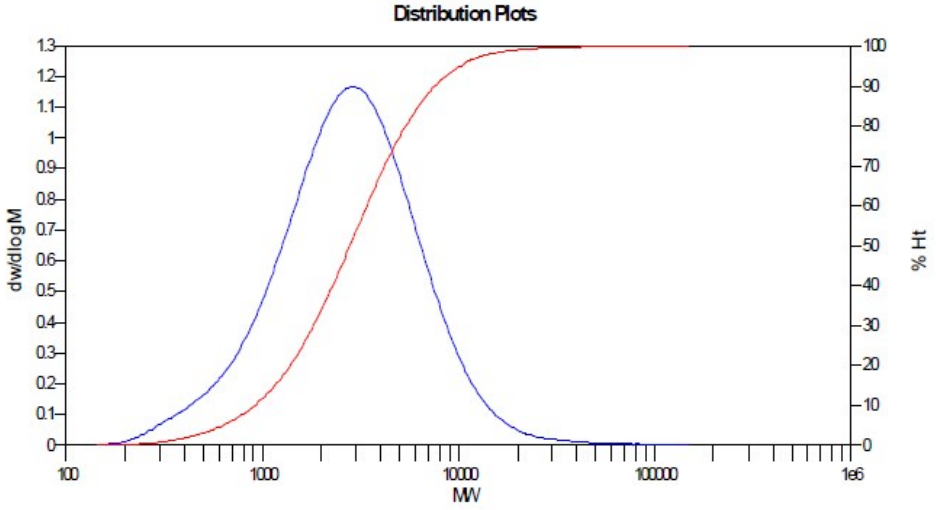
Figure S73. GPC trace of the polymer from table 1, entry 3.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12389	7486	16475	29740	42946	14772	2.20077

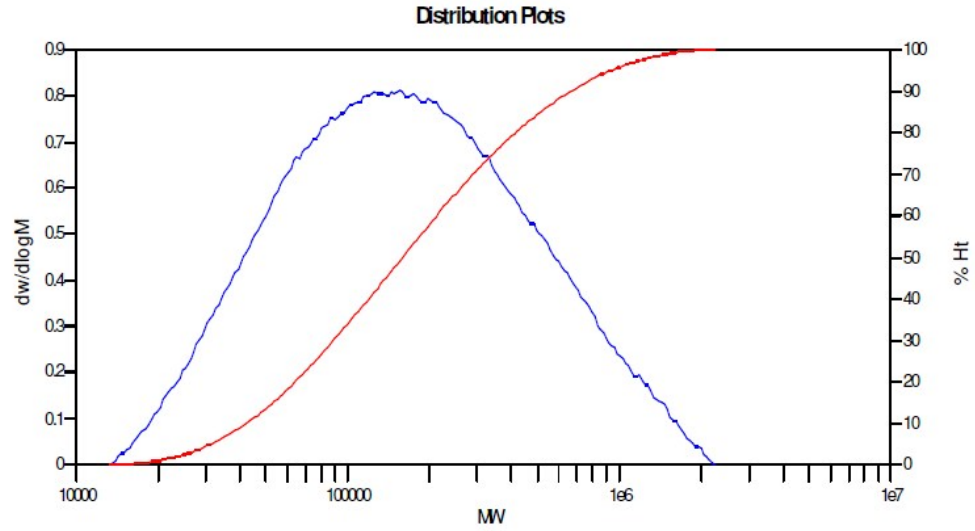
Figure S74. GPC trace of the polymer from table 1, entry 6.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2887	1858	3852	9261	30636	3435	2.0732

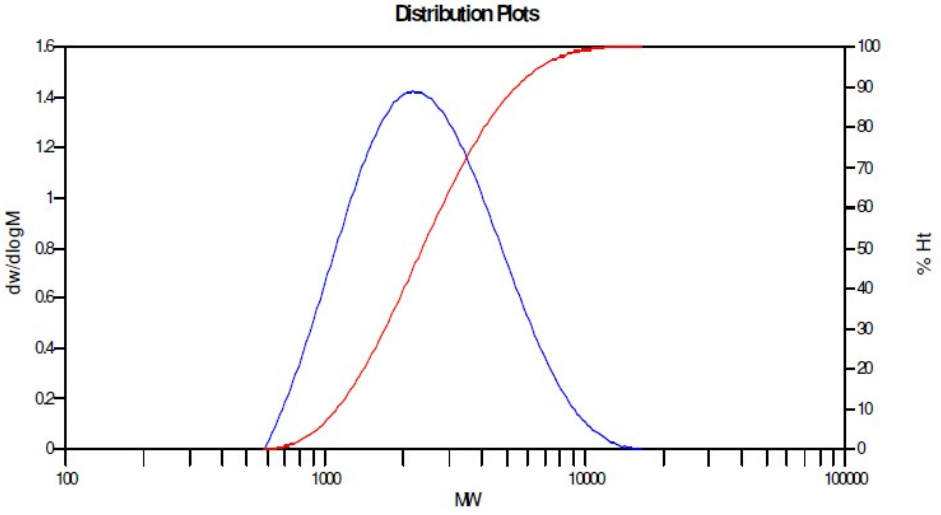
Figure S75. GPC trace of the polymer from table 1, entry 7.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	155503	99567	269603	611270	965384	231575	2.70775

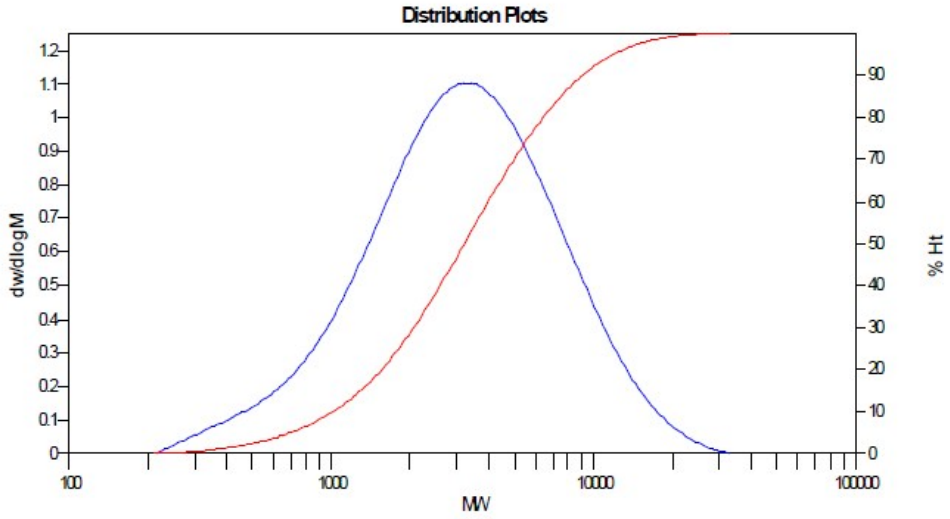
Figure S76. GPC trace of the polymer from table 1, entry 8.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2167	2015	2867	4092	5537	2713	1.42283

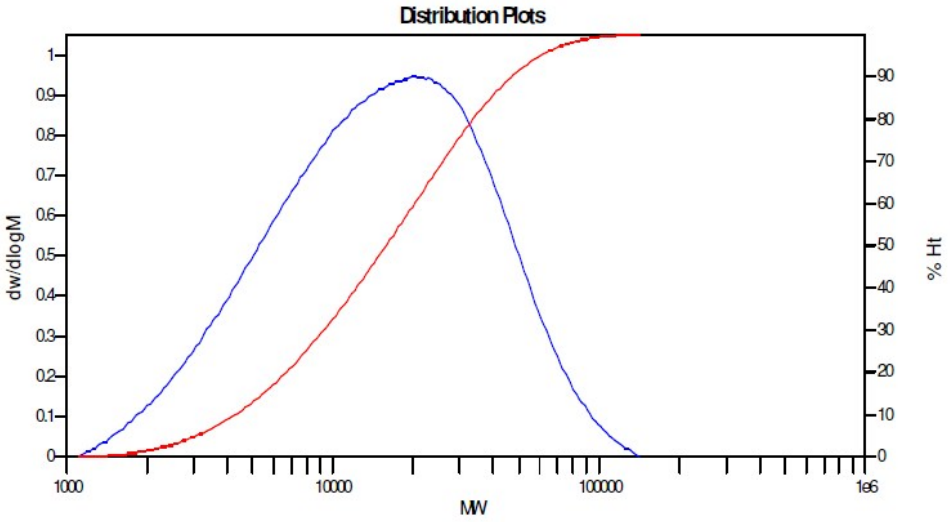
Figure S77. GPC trace of the polymer from table 1, entry 9.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3335	2106	4284	7515	11325	3885	2.03419

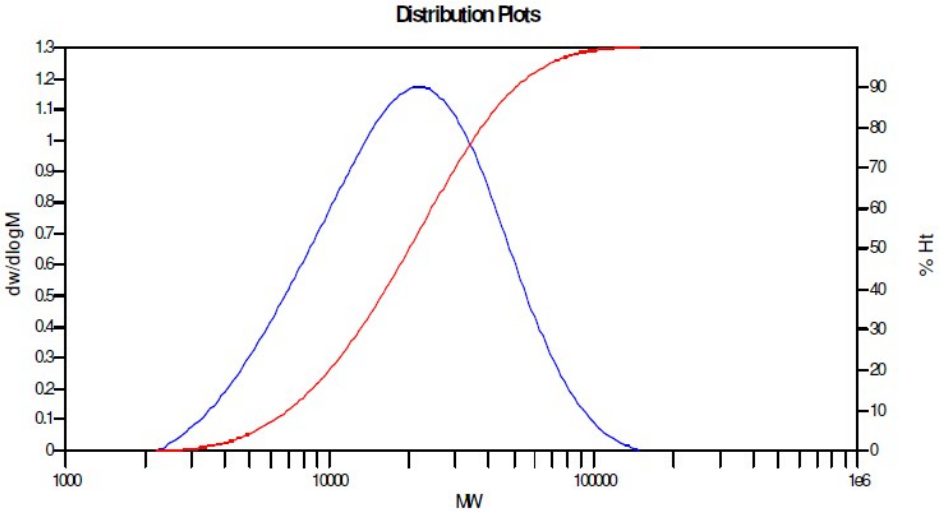
Figure S78. GPC trace of the polymer from table 1, entry 10.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	19879	9747	21425	37955	54664	19274	2.19811

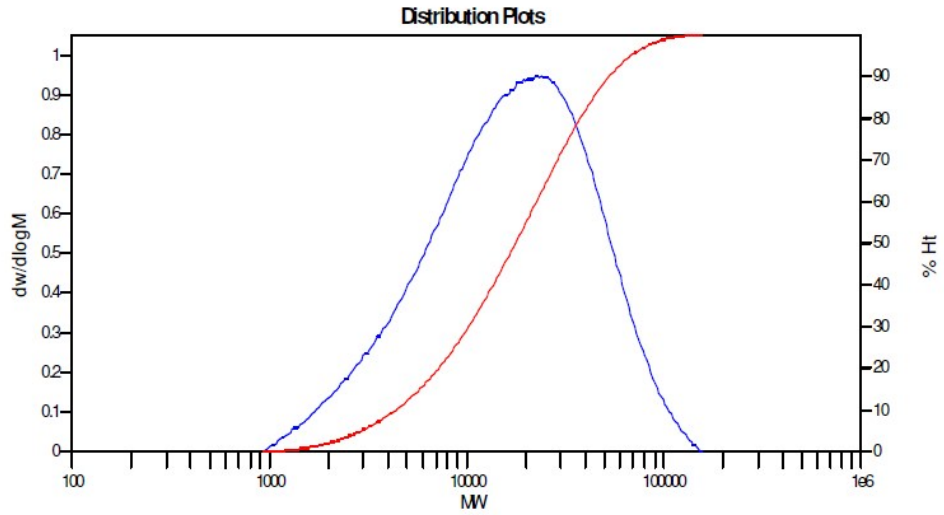
Figure S79. GPC trace of the polymer from table 1, entry 11.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	21191	14357	24946	39361	55080	23111	1.73755

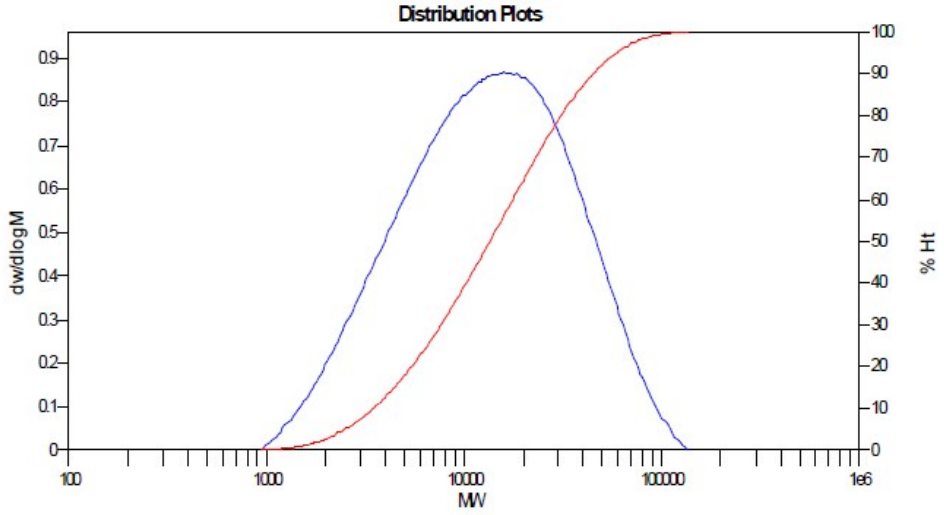
Figure S80. GPC trace of the polymer from table 2, entry 1.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	24019	10017	23917	42826	61442	21427	2.38764

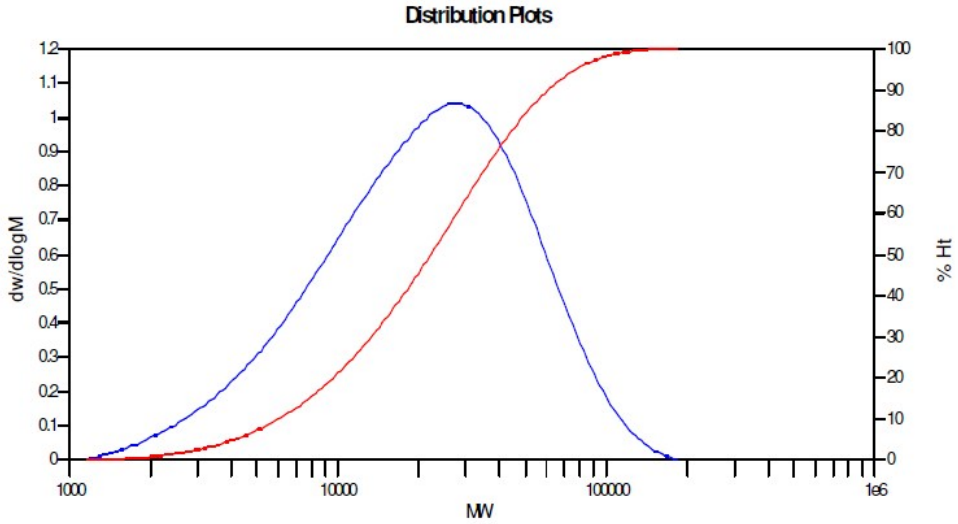
Figure S81. GPC trace of the polymer from table 2, entry 2.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	15956	8102	19567	37287	54811	17337	2.41508

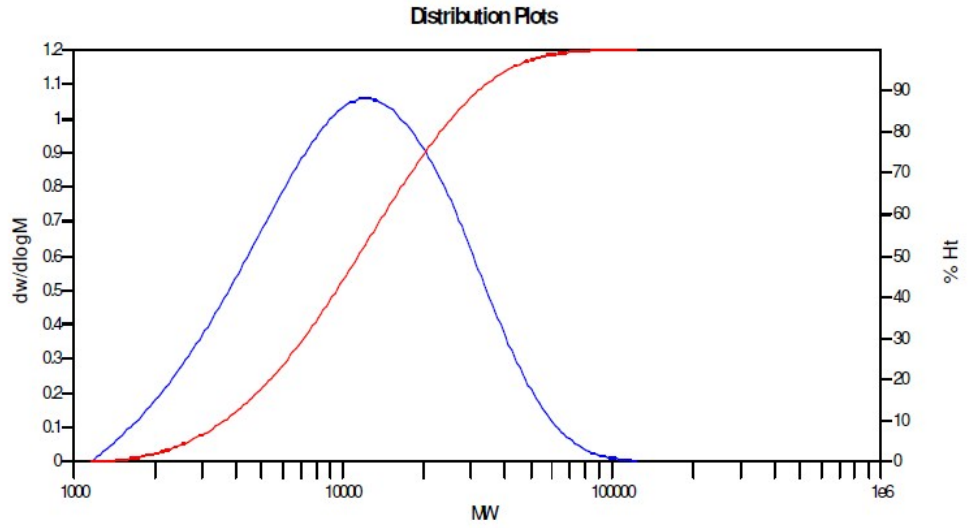
Figure S82. GPC trace of the polymer from table 2, entry 4.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	26401	13296	28548	48128	67733	25913	2.14711

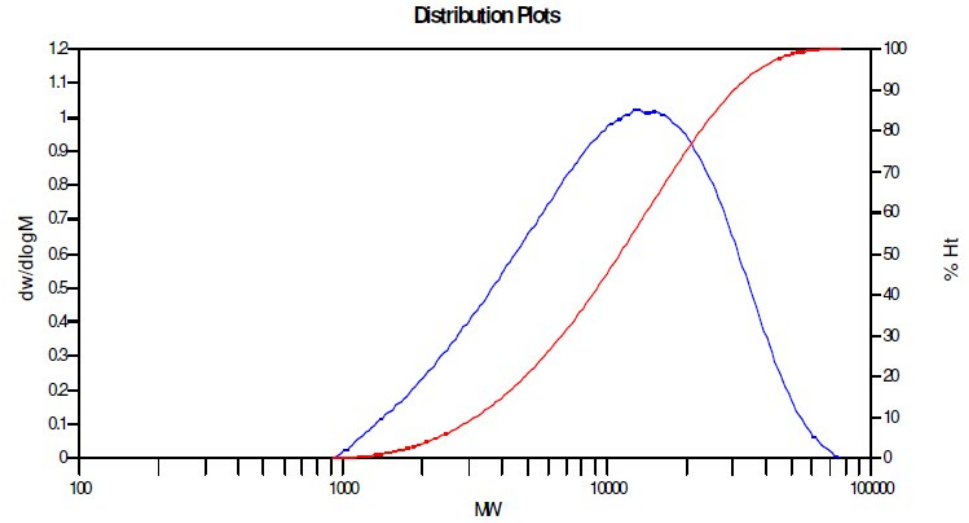
Figure S83. GPC trace of the polymer from table 2, entry 5.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12099	7841	15063	25679	37717	13719	1.92106

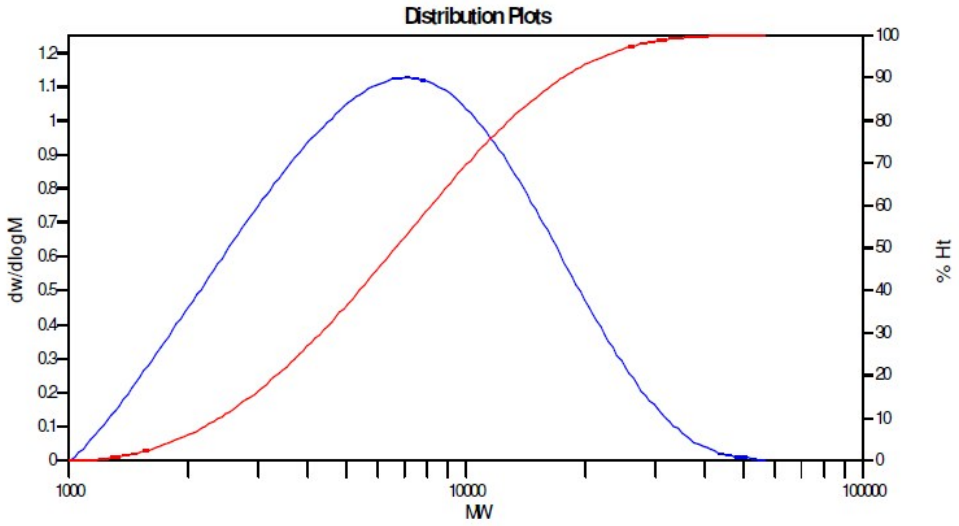
Figure S84. GPC trace of the polymer from table 2, entry 6.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12989	7089	14274	23198	31358	13030	2.01354

Figure S85. GPC trace of the polymer from table 2, entry 7.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	7024	4957	8506	13587	19123	7847	1.71596

Figure S86. GPC trace of the polymer from table 2, entry 8.

5. X-ray crystallography data

Crystal data and structure refinement for **Ni1**

Data	Ni-O
Formula	C46 H36 Ni O4 P2 S
Formula weight	805.46
Temperature[K]	298(2)
λ(Mo-Kα)[Å]	0.71073
Crystal system	Monoclinic
Space group	Cc
a[Å]	10.2889(9)
b[Å]	20.9035(18)
c[Å]	18.3345(17)
α[°]	90.00
β[°]	102.106(2)
γ[°]	90.00
Volume[Å^3]	3855.6(6)
Z	4
D(calc)[g·cm^{-3}]	1.388
μ[mm^{-1}]	0.685
F(000)	1672
θ min-max (º)	2.319-26.119
h	-11→12
k	-20→24
l	-21→11
Reflections collected	11436
Reflections unique	4299
R(int)	0.0417
Data / restraints / parameters	4299 / 2 / 488
Final R indices [I>2σ(I)]	R_1 = 0.0539 wR_2 = 0.1368
R indices (all data)	R_1 = 0.0700 wR_2 = 0.1457
GOF on F^2	1.046

Crystal data and structure refinement for **Ni2**

Formula	C51H40Cl2NiO4P2S
Formula weight	940.44
Temperature[K]	298(2)
λ(Mo-Kα)[Å]	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
a[Å]	18.0878(16)
b[Å]	13.8845(13)
c[Å]	17.3793(15)
α[°]	90.00
β[°]	101.127(2)
γ[°]	90.00
Volume[Å3]	4282.6(7)
Z	4
D(calc)[g·cm-3]	1.459
μ[mm-1]	0.749
F(000)	1944
θ min-max (º)	2.299- 22.453
h	-21-21
k	-16-15
l	-16-20
Reflections collected	21422
Reflections unique	7530
R(int)	0.0884
Data / restraints / parameters	7530/0/550
Final R indices [I>2σ(I)]	R1 =0.0529 wR2 = 0.1254
R indices (all data)	R1 = 0.0993 wR2 = 0.1512
GOF on F2	0.999

Crystal data and structure refinement for **Pd1**

Formula	C32H33O5PPdS2
Formula weight	699.07
Temperature[K]	298(2)
λ(Mo-Kα)[Å]	0.71073
Crystal system	Triclinic
Space group	P-1
a[Å]	10.0750(8)
b[Å]	11.6829(9)
c[Å]	14.3961(12)
α[°]	75.3070(10)
β[°]	72.5830(10)
γ[°]	84.033(2)
Volume[$Å^3$]	1563.2(2)
Z	2
D(calc)[$g \cdot cm^{-3}$]	1.485
μ[mm^{-1}]	0.817
F(000)	716
θ min-max (º)	2.592-23.712
h	-11-9
k	-13-11
l	-17-15
Reflections collected	7934
Reflections unique	5407
R(int)	0.0406
Data / restraints / parameters	5407/0/439
Final R indices [I>2σ(I)]	R1 = 0.0485 wR2 = 0.1087
R indices (all data)	R1 = 0.0707 wR2 = 0.1160
GOF on F^2	1.092

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