Electronic Supplementary Information (ESI)

Tunable branching and living character in ethylene polymerization

using "polyethylene glycol sandwich" α-diimine nickel catalysts

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1 Preparation of ligands and catalysts

N-(Naphthalen-1-yl)picolinamide. 1-Naphthylamine (7.2 g, 50 mmol) in pyridine (10 mL) was added dropwise in 15 min to a stirred solution of picolinic acid (6.2 g, 50 mmol) in pyridine (14 mL) at 50 °C. Triphenylphosphite (13 mL, 50 mmol) was added to the resulting mixture followed by stirring at 110 °C for 4 h. The mixture was cooled to room temperature followed by addition of distilled water (50 mL) and dichloromethane (50 mL). The mixture was placed in a 500 mL Erlenmeyer flask, and aqueous H₂SO₄ (150 mL; concentrated H₂SO₄/ water, 1/1 v/v) was added. The mixture was shaken, and the layers were separated. The organic layer was washed with aqueous H₂SO₄ (2 × 100 mL). The acidic aqueous layers were combined and neutralized with solid sodium bicarbonate. The tan solids formed were filtered and washed thoroughly with distilled water, then recrystallized from methanol to afford tan needles (10.9 g, 87%).

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 10.77 (s, 1H), 8.70 (d, 1H), 8.36 (d, 1H), 8.36 (d, 1H), 8.09 (d, 1H), 7.95-7.88 (m, 2H), 7.70 (d, 1H), 7.61-7.50 (m, 4H).

Standard procedure for the synthesis of substituted 4-iodobenzenes



General procedure: K_2CO_3 (18 mmol, 2.5 g) was suspended in 15 mL of DMF. The phenol (6.0 mmol) and the alkyl halide (6.6 mmol) were added subsequentially and the suspension was stirred overnight at 60 °C. The reaction mixture was diluted with 50 mL water and the resulting reaction mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (1 × 50 mL), dried over Na₂SO₄ and filtered. The solvent was evaporated under reduced pressure to give the product in a high purity.

Compound S1:

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 7.57-7.48 (m, 2H), 6.73-6.64 (m, 2H), 4.10-4.00 (m, 2H), 3.75-3.66 (m, 2H), 3.44 (s, 3H).

Compound S2:

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 7.57-7.50 (m, 2H), 6.72-6.65 (m, 2H), 4.12-4.07 (m, 2H), 3.87-3.81 (m, 2H), 3.73-3.67 (m, 2H), 3.59-3.54 (m, 2H), 3.39 (s, 3H).

Compound S3:

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 7.57-7.51 (m, 2H), 6.70-6.64 (m, 2H), 3.91 (t, 2H), 1.77 (m, 2H), 1.47-1.39 (m, 2H), 1.39-1.24 (m, 6H), 0.90 (t, 3H).

Standard procedure for the synthesis of 8-arylnaphthalen-1-amine



General procedure: A 50 mL flask was charged with *N*-(naphthalen-1-yl)picolinamide (2.2 g, 8.7 mmol), substituted 4-iodobenzenes (17.5 mmol), AgOAc (2.2 g, 13.1 mmol) and Pd(OAc)₂ (39 mg, 0.175 mmol). The resulting suspension was stirred at 140 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and filtered through a pad of Celite. Solids were thoroughly washed with dichloromethane (100 mL). The filtrate and washings were concentrated in vacuo. The residue was purified by flash column chromatography in EtOAc/*n*-hexane.

N-(8-Arylnaphthalen-1-yl)picolinamide (10 mmol) was refluxed for 24 h in a NaOH solution (4 g, NaOH in EtOH/H₂O, 10/1 v/v, 100 mL). The reaction mixture was cooled and diluted with 40 mL water. The product was extracted with dichloromethane (3×100 mL). The organic layers were combined, dried with MgSO₄ and concentrated to give the product.

Compound S4:

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 7.78-7.73 (m, 1H), 7.39-7.34 (m, 3H), 7.34-7.30 (m, 1H), 7.29-7.24 (m, 1H), 7.16-7.12 (m, 1H), 6.99-6.94 (m, 2H), 6.63-6.60 (m, 1H), 3.87 (s, 3H), 3.77 (s, 2H).

Compound S5:

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 7.79-7.74 (m,1H), 7.40-7.33 (m, 3H), 7.33-7.30 (m, 1H), 7.29-7.24 (m, 1H), 7.17-7.12 (m, 1H), 7.03-6.97 (m, 2H), 6.65-6.60 (m,1H), 4.22-4.16 (m, 2H), 3.84-3.71 (m, 4H), 3.49 (s, 3H).

Compound S6:

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 7.79-7.72 (m,1H), 7.40-7.33 (m, 3H), 7.33-7.29 (m, 1H), 7.29-7.24 (m, 1H), 7.15-7.11 (m, 1H), 7.01-6.96 (m, 2H), 6.64-6.60 (m, 1H), 4.24-4.18 (m, 2H), 3.94-3.88 (m, 2H), 3.83-3.72 (m, 4H), 3.64-3.58 (m, 2H), 3.41 (s, 3H).

Compound S7:

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 7.77-7.72 (m,1H), 7.39-7.33 (m, 3H), 7.33-7.29 (m, 1H), 7.28-7.23 (m, 1H), 7.16-7.11 (m, 1H), 6.98-6.93 (m, 2H), 6.64-6.59 (m, 1H), 4.02 (t, 2H), 3.80 (s, 2H), 1.88-1.77 (m, 2H), 1.53-1.44 (m, 2H), 1.43-1.28 (m, 6H), 0.91 (s, 3H).

Standard procedure for the synthesis of ligands.

General procedure: A 25 mL Schlenk flask was charged with a solution of 8-arylnaphthalen-1-amine (0.59 g, 2.53 mmol) in methanol (5 mL), and 2,3-butanedione (0.106 g, 1.23 mmol). Acetic acid (3-5 drops) was added to the reaction mixture followed by refluxing the solution for 2 days. The formed precipitate was filtered and washed with dry methanol (3-5 times) until the color of methanol

washings was pale. Then it was under vacuum to yield yellow diimine product.



Ligand L-O1: Compound S4 (780 mg, 3.13 mmol) was used, and the product was obtained as yellow solid (0.73 g, 82%).

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 7.88-7.81 (m, 2H), 7.71-7.64 (m, 2H), 7.52-7.40 (m, 4H), 7.24-7.18 (m, 2H), 7.12-7.04 (m, 4H), 6.83-6.76 (m, 4H), 6.47-6.41 (m, 2H), 3.84 (s, 6H, - OMe), 1.45 (s, 6H, N=CMe).

¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃, 77.16 ppm): δ 165.89 (N=*C*Me), 158.31, 148.25, 139.03, 137.22, 135.52, 130.21, 129.38, 128.19, 125.89, 125.22, 124.74, 124.05, 114.61, 112.79, 55.27 (OMe), 15.88 (N=*C*-Me).



Ligand L-O2: Compound S5 (735 mg, 2.50 mmol) was used, and the product was obtained as yellow solid (0.62 g, 78%).

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 7.88-7.81 (m, 2H), 7.71-7.64 (m, 2H), 7.52-7.40 (m, 4H), 7.24-7.18 (m, 2H), 7.12-7.04 (m, 4H), 6.83-6.76 (m, 4H), 6.47-6.41 (m, 2H), 4.15-4.08 (m, 4H), 3.85-3.78 (m, 4H), 3.50 (s, 6H, -OMe), 1.44 (s, 6H, N=C*Me*).

¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃, 77.16 ppm): δ 165.95 (N=*C*Me), 157.60, 148.20, 139.01, 137.45, 135.50, 130.21, 129.43, 128.17, 126.01, 125.20, 124.72, 124.01, 114.68, 113.39, 71.32, 67.39, 59.47, 15.87 (N=*C*-Me).



Ligand L-O3: Compound S6 (790 mg, 2.34 mmol) was used, and the product was obtained as yellow solid (0.68 g, 80%).

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): *δ* 7.88-7.81 (m, 2H), 7.71-7.64 (m, 2H), 7.52-7.40 (m, 4H), 7.24-7.18 (m, 2H), 7.12-7.04 (m, 4H), 6.83-6.76 (m, 4H), 6.47-6.41 (m, 2H), 4.17-4.10 (m, 4H), 3.96-3.89 (m, 4H), 3.80-3.73 (m, 4H), 3.64-3.57 (m, 4H), 3.42 (s, 3H, -OMe), 1.43 (s, 6H, N=CMe).

¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃, 77.16 ppm): δ 165.96 (N=CMe), 157.59, 148.22, 139.02, 137.40, 135.50, 130.20, 129.42, 128.17, 126.01, 125.21, 124.71, 123.98, 114.63, 113.44, 72.17, 71.04, 70.05, 67.51, 59.29, 15.87 (N=CMe).



Ligand L-C3: Compound S7 (750 mg, 2.25 mmol) was used, and the product was obtained as yellow solid (0.55 g, 68%).

¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): δ 7.86-7.81 (m, 2H), 7.69-7.64 (m, 2H), 7.48-7.41 (m, 4H), 7.24-7.18 (m, 2H), 7.09-7.02 (m, 4H), 6.81-6.76 (m, 4H), 6.47-6.41 (m, 2H), 3.94 (t, 4H), 1.90-1.82 (m, 4H), 1.52-1.45 (m, 4H), 1.44 (s, 6H, N=C*Me*), 1.43-1.30 (m,14H), 0.92 (t, 6H). ¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃, 77.16 ppm): δ 165.95 (N=CMe), 157.98, 148.27, 139.16, 136.97, 135.51, 130.16, 129.40, 128.11, 125.84, 125.21, 124.70, 124.08, 114.62, 113.30, 68.15, 31.96, 29.71, 29.34, 26.25, 22.80, 15.87 (N=CMe), 14.27.

Standard Procedure for the Synthesis of Catalysts.

Preparation of Ni catalysts: A mixture of ligand (0.31 mmol) and (DME)NiBr₂ (0.31 mmol) (DME = 1,2-dimethoxyethane) were stirred in 25 mL of dichloromethane overnight at room temperature. The solvent was evaporated under reduced pressure, the desired compound can be isolated from recrystallized from *n*-hexane and dichloromethane. The pure compound was obtained as brown solids.



Complex Ni-O1: brown solid (200 mg, 84%). Anal. Calcd for C₃₈H₃₂Br₂N₂NiO₂: C, 59.49; H, 4.20; N, 3.65. Found: C, 59.67; H, 4.28; N, 3.72.



Complex Ni-O2: brown solid (180 mg, 68%). Anal. Calcd for C₄₂H₄₀Br₂N₂NiO₄: C, 58.98; H, 4.71; N, 3.28. Found: C, 59.14; H, 4.79; N, 3.34.



Complex Ni-O3: brown solid (190 mg, 65%). Anal. Calcd for C₄₆H₄₈Br₂N₂NiO₆: C, 58.57; H, 5.13; N, 2.97. Found: C, 58.66; H, 5.20; N, 3.06.



Complex Ni-C3: brown solid (198 mg, 68%). Anal. Calcd for C₅₀H₅₆Br₂N₂NiO₂: C, 64.19; H, 6.03; N, 2.99. Found: C, 64.48; H, 6.11; N, 3.06.

Preparation of Pd catalysts: To a solution of ligand (0.31 mmol) in dry dichloromethane (25 mL) was added 1eq. of Pd(COD)MeCl. After stirring the mixture for 3 days at room temperature, the solvent was evaporated under reduced pressure, the desired compound can be isolated from recrystallized from diethyl ether and dichloromethane. The pure compound was obtained as orange solids.



Complex Pd-O1: orange solid (180 mg, 82%). ¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): 7.95-7.90 (m, 1H), 7.90-7.85 (m, 2H), 7.84-7.81 (m, 1H), 7.76-7.69 (m, 2H), 7.65-7.56 (m, 2H), 7.52-7.44 (m, 2H), 7.36-7.31 (m, 2H), 7.28-7.23 (m, 1H), 7.17-7.13 (m, 1H), 7.13-7.09 (m, 1H), 6.92-6.88 (m, 1H), 6.87-6.84 (m, 1H), 6.78-6.74 (m, 1H), 6.60-6.56 (m, 1H), 3.87 (s, 3H, -OMe), 3.80 (s, 3H, -OMe), 1.38 (s, 3H, N=C*Me*), 1.22 (s, 3H, N=C*Me*), 0.43 (s, 3H, Pd-Me) ppm.

¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃, 77.16 ppm): δ 172.25 (N=*C*Me), 167.27 (N=*C*Me), 158.82, 158.42, 143.89, 142.27, 137.66, 137.46, 135.60, 135.29, 135.10, 135.06, 134.96, 133.61, 131.31, 130.49, 129.07, 128.77, 128.33, 128.17, 127.71, 126.91, 125.84, 125.38, 125.08, 124.36, 121.54, 120.55, 115.15, 114.22, 112.99, 112.77, 55.34 (-OMe), 20.43 (N=C-*Me*), 19.45 (N=C-*Me*), 1.05 (Pd-Me) ppm.

Elemental analysis: Anal. Calcd for C₃₉H₃₅ClN₂O₂Pd: C, 66.39; H, 5.00; N, 3.97. Found: C, 66.54; H, 5.08; N, 4.04.



Complex Pd-O2: orange solid (196 mg, 80%). ¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): 7.94-7.90 (m, 1H), 7.89-7.84 (m, 2H), 7.84-7.80 (m, 1H), 7.77-7.72 (m, 1H), 7.73-7.69 (m, 1H), 7.68-7.62 (m, 2H), 7.52-7.44 (m, 2H), 7.36-7.30 (m, 2H), 7.28-7.22 (m, 1H), 7.16-7.12 (m, 1H), 7.12-7.08 (m, 1H), 6.92-6.88 (m, 1H), 6.88-6.84 (m, 1H), 6.83-6.79 (m, 1H), 6.66-6.62 (m, 1H), 4.29-4.19 (m, 2H), 4.10-4.04 (m, 1H), 4.02-3.97 (m, 1H), 3.88-3.80 (m, 2H), 3.80-3.70 (m, 2H), 3.53 (s, 3H, -OMe), 3.44 (s, 3H, -OMe), 1.36 (s, 3H, N=C*Me*), 1.22 (s, 3H, N=C*Me*), 0.44 (s, 3H, Pd-Me) ppm.

¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃, 77.16 ppm): δ 172.36 (N=*C*Me), 167.38 (N=*C*Me), 158.07, 157.75, 143.78, 142.26, 137.60, 137.43, 135.75, 135.30, 135.22, 135.02, 134.92, 133.57, 131.28, 130.51, 129.05, 128.75, 128.23, 128.08, 127.60, 126.91, 125.74, 125.43, 125.33, 125.21, 124.26, 124.22, 121588, 120.70, 115.50, 114.87, 113.76, 113.28, 71.34, 71.16, 67.54, 67.39, 59.49, 59.40, 20.41 (N=C-*Me*), 19.49 (N=C-*Me*), 1.11 (Pd-Me) ppm.

Elemental analysis: Anal. Calcd for C₄₃H₄₃ClN₂O₄Pd: C, 65.07; H, 5.46; N, 3.53. Found: C, 65.34; H, 5.52; N, 3.60.



Complex Pd-O3: orange solid (186 mg, 68%). ¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): 7.95-7.89 (m, 1H), 7.89-7.84 (m, 2H), 7.83-7.78 (m, 1H), 7.77-7.73 (m, 1H), 7.72-7.62 (m, 3H), 7.52-7.42 (m, 2H), 7.37-7.29 (m, 2H), 7.28-7.21 (m, 2H), 7.18-7.13 (m, 1H), 7.12-7.07 (m, 1H), 6.92-6.84 (m, 2H), 6.81-6.76 (m, 1H), 6.63-6.58 (m, 1H), 4.29-4.17 (m, 2H), 4.13-4.06 (m, 1H), 4.03-3.92 (m, 3H), 3.90-3.83 (m, 2H), 3.81-3.76 (m, 2H), 3.74-3.68 (m, 2H), 3.67-3.62 (m, 2H), 3.61-3.53 (m, 2H), 3.45 (s, 3H, -OMe), 1.36 (s, 3H, N=CMe), 1.21 (s, 3H, N=CMe), 0.43 (s, 3H, Pd-Me) ppm.

¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃, 77.16 ppm): δ 172.29 (N=*C*Me), 167.34 (N=*C*Me), 158.06, 157.73, 143.79, 142.25, 137.60. 137.43, 135.75, 135.28, 135.23, 135.02, 134.92, 133.58, 131.25, 130.52, 129.04, 128.76, 128.19, 128.06, 127.59, 126.90, 125.75, 125.50, 125.33, 125.25, 124.23, 121.59, 120.71, 115.86, 115.27, 113.42, 112.88, 72.17, 72.11, 71.06, 70.94, 70.06, 69.87, 67.58, 67.44, 59.31, 59.25, 20.39 (N=C-*Me*), 19.47 (N=C-*Me*), 1.11 (Pd-Me) ppm.

Elemental analysis: Anal. Calcd for C₄₇H₅₁ClN₂O₆Pd: C, 64.02; H, 5.83; N, 3.18. Found: C, 64.20; H, 5.91; N, 3.25.



Complex Pd-C3: orange solid (190 mg, 70%). ¹**H NMR** (500 MHz, 298 K, CDCl₃, 7.26 ppm): 7.94-7.89 (m, 1H), 7.89-7.84 (m, 2H), 7.83-7.80 (m, 1H), 7.75-7.70 (m, 2H), 7.64-7.54 (m, 2H), 7.53-7.43 (m, 2H), 7.35-7.29 (m, 2H), 7.28-7.22 (m, 2H), 7.21-7.17 (m, 1H), 7.12-7.08 (m, 1H), 6.91-6.86 (m, 2H), 6.77-6.73 (m, 1H), 6.58-6.55 (m, 1H), 4.09-3.98 (m, 2H), 3.94-3.87 (m, 1H), 3.84-3.77 (m, 1H), 1.93-1.86 (m, 2H), 1.81-1.74 (m, 2H), 1.55-1.46 (m, 2H), 1.45-1.39 (m, 4H), 1.38 (s, 3H, N=C*Me*), 1.37-1.26 (m, 12H), 1.21 (s, 3H, N=C*Me*), 0.96-0.88 (m, 6H), 0.42 (s, 3H, Pd-Me) ppm.

¹³C{¹H} NMR (125 MHz, 298 K, CDCl₃, 77.16 ppm): δ 172.35 (N=*C*Me), 167.32 (N=*C*Me), 158.45, 158.09, 143.91, 142.23, 137.77, 137.55, 135.36, 135.17, 135.03, 134.93, 134.88, 133.46, 131.33, 130.49, 129.01, 128.72, 127.61, 126.92, 125.79, 125.32, 125.08, 125.02, 124.29, 121.68, 120.63, 115.76, 114.89, 113.38, 112.91, 68.29, 68.10, 31.96, 31.93, 29.74, 29.55, 29.32, 29.26, 26.28, 26.20, 22.79, 22.77, 20.42 (N=C-*Me*), 19.44 (N=C-*Me*), 14.27, 0.96 (Pd-Me) ppm.

Elemental analysis: Anal. Calcd for C₅₁H₅₉ClN₂O₂Pd: C, 70.09; H, 6.81; N, 3.21. Found: C, 70.35; H, 6.91; N, 3.27.

2 Time-dependence studies of Ni-O1 toward ethylene polymerization



Figure S1. Time-dependence of polymer yield of Ni-O1 with the activation of MAO at 25 °C.



Figure S2. Time-dependence of molecular weight of Ni-O1 with the activation of MAO at 25 °C.



Figure S3. Time-dependence of polymer yield of Ni-O1 with the activation of MMAO at 25 °C.



Figure S4. Time-dependence of molecular weight of Ni-O1 with the activation of MMAO at 25 °C.



Figure S5. Time-dependence of polymer yield of Ni-O1 with the activation of AlEt₂Cl at 25 $^{\circ}$ C.



Figure S6. Time-dependence of molecular weight of Ni-O1 with the activation of AlEt₂Cl at 25 $^{\circ}$ C.

3 Possible intermediates by Al-O chelation



Figure S7. Two possibilities for the aluminum chelation with oxygen atoms in the PEG chains.

4 NMR figures of ligands and catalysts







Figure S9. ¹H NMR spectrum of S2 in CDCl₃



Figure S10. ¹H NMR spectrum of S3 in $CDCl_3$



Figure S11. ¹H NMR spectrum of S4 in CDCl₃



Figure S12. ¹H NMR spectrum of S5 in CDCl₃



Figure S13. ¹H NMR spectrum of S6 in CDCl₃



Figure S15. ¹H NMR spectrum of L-O1 in CDCl₃



Figure S17. ¹H NMR spectrum of L-O2 in CDCl₃



Figure S19. ¹H NMR spectrum of L-O3 in CDCl₃

1.99 3.81 3.99 1.95

2.01 2.00 4.12 4.01 4.07 4.06 5.78

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 fl(ppm)

6.00



Figure S21. ¹H NMR spectrum of L-C3 in CDCl₃



Figure S22. ¹³C NMR spectrum of L-C3 in CDCl₃

¹H, ¹³C, ¹H-¹H COSY, HSQC, HMBC NMR of Pd Complexes



Figure S23. ¹H NMR spectrum of Pd-O1 in CDCl₃





Figure S25. ¹H-¹H COSY NMR spectrum of Pd-O1 in CDCl₃.



Figure S26. ¹H-¹³C HSQC NMR spectrum of Pd-O1 in CDCl₃.



Figure S27. ¹H-¹³C HMBC NMR spectrum of Pd-O1 in CDCl₃.



Figure S28. ¹H NMR spectrum of Pd-O2 in CDCl₃



Figure S29. ¹³C NMR spectrum of Pd-O2 in CDCl₃



Figure S30. ¹H-¹H COSY NMR spectrum of Pd-O2 in CDCl₃.



Figure S31. ¹H-¹³C HSQC NMR spectrum of Pd-O2 in CDCl₃.



Figure S32. ¹H-¹³C HMBC NMR spectrum of Pd-O2 in CDCl₃.



Figure S33. ¹H NMR spectrum of Pd-O3 in CDCl₃



Figure S35. ¹H-¹H COSY NMR spectrum of Pd-O3 in CDCl₃.



Figure S36. ¹H-¹³C HSQC NMR spectrum of Pd-O3 in CDCl₃.



Figure S37. ¹H-¹³C HMBC NMR spectrum of Pd-O3 in CDCl₃.





Figure S39. ¹³C NMR spectrum of Pd-C3 in CDCl₃



Figure S40. ¹H-¹H COSY NMR spectrum of Pd-C3 in CDCl₃.



Figure S41. ¹H-¹³C HSQC NMR spectrum of Pd-C3 in CDCl₃.



Figure S42. ¹H-¹³C HMBC NMR spectrum of Pd-C3 in CDCl₃.

5 NMR figures of polyethylene



Figure S43. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O1 (MAO) from table 1, entry 1.



Figure S44. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O1 (MMAO) from table 1, entry 2.



Figure S45. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O1 (AlEt₂Cl) from table 1, entry 3.



Figure S46. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O2 (MAO) from table 1, entry 4.



Figure S47. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O2 (MMAO) from table 1, entry 5.



Figure S48. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O2 (AlEt₂Cl) from table 1, entry 6.



Figure S49. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O3 (MAO) from table 1, entry 7.



Figure S50. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O3 (MMAO) from table 1, entry 8.



Figure S51. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O3 (AlEt₂Cl) from table 1, entry 9.



Figure S52. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄, 110 °C) of the polyethylene generated by complex Ni-C3 (MAO) from table 1, entry 10.



Figure S53. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-C3 (MMAO) from table 1, entry 11.



Figure S54. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-C3 (AlEt₂Cl) from table 1, entry 12.



Figure S55. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O1 (MAO) from table 1, entry 13.



Figure S56. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄, 110 °C) of the polyethylene generated by complex Ni-O1 (MMAO) from table 1, entry 14.



Figure S57. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O1 (AlEt₂Cl) from table 1, entry 15.



Figure S58. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O2 (MAO) from table 1, entry 16.



Figure S59. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O2 (MMAO) from table 1, entry 17.



Figure S60. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O2 (AlEt₂Cl) from table 1, entry 18.



Figure S61. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O3 (MAO) from table 1, entry 19.



Figure S62. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄, 110 °C) of the polyethylene generated by complex Ni-O3 (MMAO) from table 1, entry 20.



Figure S63. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄, 110 °C) of the polyethylene generated by complex **Ni-O3** (**AlEt₂Cl**) from table 1, entry 21.



Figure S64. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-C3 (MAO) from table 1, entry 22.



Figure S65. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-C3 (MMAO) from table 1, entry 23.



Figure S66. ¹³C NMR spectrum (400 MHz, C₂D₂Cl₄, 110 °C) of the polyethylene generated by complex **Ni-C3 (MMAO)** from table 1, entry 23.



Figure S67. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-C3 (AlEt₂Cl) from table 1, entry 24.



Figure S68. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄, 110 °C) of the polyethylene generated by complex Ni-O2 (MAO) from table 1, entry 25.



Figure S69. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O2 (MAO) from table 1, entry 26.



Figure S70. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O1 (MMAO) from table 2, entry 1.



Figure S71. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O1 (MMAO) from table 2, entry 2.



Figure S72. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄, 110 °C) of the polyethylene generated by complex **Ni-O1 (MMAO)** from table 2, entry 3.



Figure S73. ¹H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O1 (MMAO) from table 2, entry 4.



Figure S74. Typical ¹³C NMR spectrum of a branched polyethylene (Table 1, entry 23).



Figure S75. ¹³C NMR spectrum (400 MHz, C₂D₂Cl₄, 110 °C) of the polyethylene generated by complex Ni-O2 (MMAO) from table 1, entry 5.



Figure S76. ¹³C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O3 (MAO) from table 1, entry 7.



Figure S77. ¹³C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O1 (AlEt₂Cl) from table 1, entry 15.



Figure S78. ¹³C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 °C) of the polyethylene generated by complex Ni-O3 (MAO) from table 1, entry 19.



Figure S79. ¹H NMR spectrum of the *in situ* reaction of ligand L-O2 with 2eq.Et₂AlCl in CDCl₃.

6 GPC traces of polyethylene



MW Averages

Peak No	Мр	Mn	Mw	Mz	Mz+1	Μv	PD
1	363183	339399	343923	348060	351885	344666	1.01333

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.77	18.08	21.10	-24.2101	0	1403.29	100
2	LS 15	16.65	18.07	20.45	60.1165	0	3260.25	100
3	LS 90	16.68	18.08	20.45	248.743	0	13329.4	100
4	Diff Pressure	16.60	18.07	20.57	296.758	0	17183	100

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



o an i to		(mins)	(mins)	(mins)	(mV)	,o noigin	(mV.secs)	,0 , 1 o a
1	Concentration	17.20	18.30	20.37	-32.7279	0	1835.62	100
2	LS 15	16.97	18.23	20.12	73.2666	0	3848.26	100
3	LS 90	16.93	18.25	20.18	309.561	0	16278.5	100
4	Diff Pressure	17.00	18.28	20.20	398.603	0	21489.7	100

Figure S81. GPC trace of the polymer from table 1, entry 2.



eak No	Мр	Mn	Mw	Mz	Mz+1	Mv	PD
1	292281	264846	275596	285230	294097	274377	1.04059

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.92	18.43	20.92	-35.9059	0	2183.34	100
2	LS 15	16.72	18.42	20.80	71.535	0	4035.27	100
3	LS 90	16.67	18.42	20.83	308.913	0	17440.4	100
4	Diff Pressure	16.73	18.45	20.75	427.656	0	24729.9	100

Figure S82. GPC trace of the polymer from table 1, entry 3.



Peak No	Мр	Mn	Mw	Mz	Mz+1	Μv	PD
1	668415	542088	609496	671110	731070	604233	1.12435

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.77	17.55	20.47	-15.2484	0	1148.52	100
2	LS 15	15.57	17.48	20.30	65.5079	0	4498	100
3	LS 90	15.57	17.52	20.32	232.968	0	15846.8	100
4	Diff Pressure	15.57	17.50	20.27	316.585	0	22479.5	100

Figure S83. GPC trace of the polymer from table 1, entry 4.





Peak No	Мр	Mn	Mw	Mz	Mz+1	Μv	PD
1	628197	459345	539701	610644	676245	535112	1.17493

Processed	Peaks
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Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.62	17.57	21.10	-17.9852	0	1692.77	100
2	LS 15	15.62	17.48	20.82	80.9933	0	6132.5	100
3	LS 90	15.52	17.48	20.92	281.791	0	21751.8	100
4	Diff Pressure	15.62	17.48	20.67	392.642	0	31028.8	100





MW Averages

Peak No	Мр	Mn	Mw	Mz	Mz+1	Μv	PD
1	298700	276428	280543	284336	287837	281510	1.01488

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.05	18.30	21.23	-41.6529	0	2974.97	100
2	LS 15	16.83	18.28	21.37	85.9428	0	5658.68	100
3	LS 90	16.88	18.28	21.37	364.795	0	23925.6	100
4	Diff Pressure	16.88	18.28	21.37	507.654	0	33916.2	100

Figure S85. GPC trace of the polymer from table 1, entry 6.



MW Averages

Peak No	Мр	Mn	Mw	Mz	Mz+1	Μv	PD
1	543628	376921	600637	892670	1264631	568068	1.59354

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Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.22	17.92	21.42	-16.6737	0	2124.41	100
2	LS 15	14.93	17.47	21.40	65.379	0	7975.64	100
3	LS 90	15.02	17.67	21.42	221.58	0	25824.1	100
4	Diff Pressure	15.22	17.60	21.42	336.947	0	40358.8	100





Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.22	17.85	21.27	-18.0719	0	2260.23	100
2	LS 15	15.12	17.40	21.27	76.6791	0	9281.94	100
3	LS 90	15.22	17.58	21.27	254.764	0	29460.6	100
4	Diff Pressure	15.22	17.53	21.10	393.378	0	46593.5	100

Figure S87. GPC trace of the polymer from table 1, entry 8.



Peak No	Мр	Mn	Mw	Mz	Mz+1	Μv	PD
1	219445	160278	238118	326922	419528	229480	1.48566

Processed	Peaks
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Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.52	18.75	21.95	-20.9924	0	2541.14	100
2	LS 15	16.43	18.20	21.95	36.331	0	3987.74	100
3	LS 90	16.40	18.35	21.95	151.984	0	16656.5	100
4	Diff Pressure	16.42	18.37	21.95	209.462	0	23660.3	100





Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.28	18.55	21.42	-32.2769	0	1946.04	100
2	LS 15	17.12	18.53	21.42	52.0254	0	2819.58	100
3	LS 90	17.15	18.55	21.42	229.696	0	12476.4	100
4	Diff Pressure	17.15	18.53	21.42	275.599	0	16004.9	100

Figure S89. GPC trace of the polymer from table 1, entry 10.





Peak No	Мр	Mn	Mw	Mz	Mz+1	Mv	PD
1	225412	205484	209921	213854	217362	210463	1.02159

Processed	Peaks
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Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.47	18.58	21.27	-34.0723	0	2114.37	100
2	LS 15	17.40	18.57	21.17	54.3615	0	2990.94	100
3	LS 90	17.42	18.58	21.20	240.652	0	13337.8	100
4	Diff Pressure	17.38	18.57	21.27	284.732	0	16852	100





Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.18	18.63	23.25	-34.5506	0	2167.86	100
2	LS 15	17.18	18.63	21.95	49.4526	0	2622.57	100
3	LS 90	17.18	18.63	21.83	220.113	0	11733.6	100
4	Diff Pressure	17.18	18.62	21.95	290.089	0	16618.1	100

Figure S91. GPC trace of the polymer from table 1, entry 12.



Processed	Processed Peaks												
Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area					
1	Concentration	16.60	18.18	21.50	-24.5032	0	1542.45	100					
2	LS 15	16.47	18.18	21.05	57.5677	0	3105.1	100					
3	LS 90	16.47	18.20	21.32	243.461	0	13109.4	100					
4	Diff Pressure	16.47	18.18	21.50	258.341	0	15154.1	100					





Peak No	Мр	Mn	Mw	Mz	Mz+1	Μv	PD
1	309200	247665	265772	280672	293035	266572	1.07311

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.12	18.22	21.32	-21.3652	0	1485.96	100
2	LS 15	16.78	18.22	21.32	49.171	0	2771.1	100
3	LS 90	16.78	18.20	21.32	208.402	0	11752.6	100
4	Diff Pressure	16.78	18.20	21.32	219.891	0	13615.8	100

Figure S93. GPC trace of the polymer from table 1, entry 14.



1	300146	247478	262176	274708	285409	263058	1.05939

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.02	18.25	21.17	-27.47	0	1963.32	100
2	LS 15	16.93	18.23	20.92	61.0472	0	3577.64	100
3	LS 90	16.95	18.23	20.92	258.9	0	15274.7	100
4	Diff Pressure	16.95	18.23	20.92	296.336	0	18890.9	100

Figure S94. GPC trace of the polymer from table 1, entry 15.



Figure S95. GPC trace of the polymer from table 1, entry 16.



1	400434	286416	380162	468127	546640	373229	1.32731

Pro	cess	ed	Pe	aks
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Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.27	18.13	21.65	-16.542	0	1901.91	100
2	LS 15	15.93	17.75	21.55	52.5666	0	4889.38	100
3	LS 90	15.98	17.83	21.58	199.19	0	18744.8	100
4	Diff Pressure	16.02	17.83	21.32	247.156	0	24011.2	100





Figure S97. GPC trace of the polymer from table 1, entry 18.



MW Averages

Peak No	Мр	Mn	Mw	Mz	Mz+1	Μv	PD
1	221289	163985	238915	321231	405897	231731	1.45693

Ρ	ro	се	ss	ed	Ρ	ea	ks
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Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.47	18.73	22.00	-18.3641	0	2215.34	100
2	LS 15	16.20	18.15	21.63	32.2933	0	3462.73	100
3	LS 90	16.20	18.25	21.72	132.074	0	14209.1	100
4	Diff Pressure	16.20	18.33	22.00	189.058	0	21040.2	100





Peak No	Mp	Mn	

277102 192258 290465 396046 501288 280244 1.51081 1

Processed Peaks

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eak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.38	18.47	21.90	-13.2712	0	1622.46	100
2	LS 15	16.20	17.93	21.23	29.5962	0	3097.48	100
3	LS 90	16.22	18.03	21.73	118.578	0	12413.4	100
4	Diff Pressure	16.13	18.07	21.60	162.9	0	17771.5	100

Figure S99. GPC trace of the polymer from table 1, entry 20.



1	112292	80808	121837	168670	219238	117468	1.50773

Processed	Peaks
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Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.10	19.42	22.67	-23.9071	0	2825.36	100
2	LS 15	16.93	18.93	22.17	21.7124	0	2294.67	100
3	LS 90	16.90	18.98	22.38	97.7916	0	10293.3	100
4	Diff Pressure	16.88	19.05	22.43	134.129	0	14588.7	100

Figure S100. GPC trace of the polymer from table 1, entry 21.



Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.37	18.50	21.23	-32.326	0	2068.26	100
2	LS 15	17.32	18.48	21.15	57.3081	0	3175.62	100
3	LS 90	17.32	18.50	21.23	251.672	0	13982.6	100
4	Diff Pressure	17.30	18.48	21.13	274.1	0	16352.9	100

Figure S101. GPC trace of the polymer from table 1, entry 22.



Processed Pe	aks
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Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.18	18.58	21.50	-40.3484	0	2876.93	100
2	LS 15	17.18	18.57	21.50	68.1524	0	4147.29	100
3	LS 90	17.13	18.57	21.50	301.417	0	18393.4	100
4	Diff Pressure	17.18	18.55	21.50	338.015	0	21760.4	100

Figure S102. GPC trace of the polymer from table 1, entry 23.



Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.42	18.70	22.35	-44.2092	0	2991.1	100
2	LS 15	17.42	18.70	21.67	63.3357	0	3714.84	100
3	LS 90	17.37	18.70	21.62	283.944	0	16706.8	100
4	Diff Pressure	17.42	18.68	21.67	347.144	0	21539	100

Figure S103. GPC trace of the polymer from table 1, entry 24.



Peak No	Мр	Mn	Mw	Mz	Mz+1	Mv	PD
1	638436	512728	709327	927122	1172357	678225	1.38344

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	15.57	17.67	20.55	-13.0971	0	1262.6	100
2	LS 15	15.33	17.33	19.92	60.8067	0	5667.8	100
3	LS 90	15.35	17.47	20.08	201.301	0	18232.9	100
4	Diff Pressure	15.42	17.45	20.13	304.483	0	28217.3	100

Figure S104. GPC trace of the polymer from table 1, entry 25.



		(mins)	(mins)	(mins)	(mV)	Ū.	(mV.secs)	
1	Concentration	15.53	17.65	20.33	-12.6115	0	1249.26	100
2	LS 15	15.43	17.27	20.05	63.7596	0	5709.78	100
3	LS 90	15.42	17.37	20.12	202.252	0	18301	100
4	Diff Pressure	15.48	17.35	20.12	315.971	0	28935.6	100

Figure S105. GPC trace of the polymer from table 1, entry 26.



Peak No	Мр	Mn	Mw	Mz	Mz+1	Μv	PD
1	620744	523237	560278	592262	619969	554790	1.07079

Ρ	ro	Ce	es	s	e	d	Ρ	е	а	k	s
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Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	16.60	17.77	20.27	-25.7012	0	1749.86	100
2	LS 15	16.48	17.72	20.08	101.564	0	6177.67	100
3	LS 90	16.40	17.72	20.10	378.787	0	23256.5	100
4	Diff Pressure	16.48	17.75	19.97	487.391	0	30393.4	100





Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
Concentration	16.85	18.05	20.55	-33.2557	0	2112.53	100
LS 15	16.60	17.98	20.17	97.49	0	5662.72	100
LS 90	16.63	17.98	20.23	392.017	0	22845	100
Diff Pressure	16.83	18.02	20.10	504.515	0	29754.2	100
	Name Concentration LS 15 LS 90 Diff Pressure	NameStart RT (mins)Concentration16.85LS 1516.60LS 9016.63Diff Pressure16.83	Name Start RT (mins) Max RT (mins) Concentration 16.85 18.05 LS 15 16.60 17.98 LS 90 16.63 17.98 Diff Pressure 16.83 18.02	Name Start RT (mins) Max RT (mins) End RT (mins) Concentration 16.85 18.05 20.55 LS 15 16.60 17.98 20.17 LS 90 16.63 17.98 20.23 Diff Pressure 16.83 18.02 20.10	Name Start RT (mins) Max RT (mins) End RT (mins) Pk Height (mV) Concentration 16.85 18.05 20.55 -33.2557 LS 15 16.60 17.98 20.17 97.49 LS 90 16.63 17.98 20.23 392.017 Diff Pressure 16.83 18.02 20.10 504.515	Name Start RT (mins) Max RT (mins) End RT (mins) Pk Height (mV) % Height (mV) Concentration 16.85 18.05 20.55 -33.2557 0 LS 15 16.60 17.98 20.17 97.49 0 LS 90 16.63 17.98 20.23 392.017 0 Diff Pressure 16.83 18.02 20.10 504.515 0	Name Start RT (mins) Max RT (mins) End RT (mins) Pk Height (mV) % Height (mV) Area (mV.secs) Concentration 16.85 18.05 20.55 -33.2557 0 2112.53 LS 15 16.60 17.98 20.17 97.49 0 5662.72 LS 90 16.63 17.98 20.23 392.017 0 22845 Diff Pressure 16.83 18.02 20.10 504.515 0 29754.2

Figure S107. GPC trace of the polymer from table 2, entry 2.



Processed Peal	ks
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Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.20	18.30	20.37	-32.7279	0	1835.62	100
2	LS 15	16.97	18.23	20.12	73.2666	0	3848.26	100
3	LS 90	16.93	18.25	20.18	309.561	0	16278.5	100
4	Diff Pressure	17.00	18.28	20.20	398.603	0	21489.7	100





Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1	Concentration	17.80	19.02	20.92	-47.4186	0	2347.86	100
2	LS 15	17.78	18.98	20.50	51.7163	0	2452.02	100
3	LS 90	17.77	18.98	20.58	236.214	0	11228.1	100
4	Diff Pressure	17.82	19.00	20.53	330.093	0	16073.2	100

Figure S109. GPC trace of the polymer from table 2, entry 4.

7 DSC of polymer



Figure S110. DSC data of the polymer from table 1, entry 4.



Figure S111. DSC data of the polymer from table 1, entry 7.



Figure S112. DSC data of the polymer from table 1, entry 8.



Figure S113. DSC data of the polymer from table 1, entry 19.



Figure S114. DSC data of the polymer from table 1, entry 20.



Figure S115. DSC data of the polymer from table 1, entry 25.



Figure S116. DSC data of the polymer from table 1, entry 26.

8 Crystallographic data for Pd-O2, Ni-O3 and Ni-C3.

	Pd-O2	Ni-O3	Ni-C3
Formula	C43H43ClN2O4Pd	C46H47Br2N2O6Ni	$C_{50}H_{56}Br_2N_2O_2Ni$
Formula weight	793.64	942.38	935.49
Crystal dimensions (mm ³)	$0.21 \times 0.22 \times 0.16$	$0.23 \times 0.11 \times 0.09$	$0.27\times 0.15\times 0.09$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P 21/c	P 21/n	P 21/c
a (Å)	11.7634(4)	8.8225(4)	24.6463(16)
b (Å)	19.4057(7)	23.3225(13)	40.129(3)
c (Å)	19.6256(7)	20.1979(10)	8.8579(5)
α()	90	90	90
β()	97.145(2)	90	97.615(2)
γ(9	90	90	90
Volume (Å ³)	4445.3(3)	4156.0(4)	8683.5(10)
Ζ	4	4	8
<i>T</i> (K)	173(2)	173(2)	173(2)
D_{calcd} (g cm ⁻³)	1.186	1.506	1.431
$\mu (\mathrm{mm}^{-1})$	4.220	3.339	3.118
F (000)	1640	1932	3872
No. of rflns. collected	18014	8004	44331
No. of indep. rflns. $/R_{int}$	6245 / 0.0512	3313 / 0.0315	12221 / 0.0417
No. of obsd. rflns. $[I_0 > 2\sigma(I_0)]$	5148	3015	6483
Data / restraints / parameters	6245 / 12 / 463	3313 / 0 / 514	12221 / 60 / 1028
$R_1 / wR_2 \left[I_0 > 2\sigma(I_0) \right]$	0.0829 / 0.1811	0.0651 / 0.1746	0.0989 / 0.2703
$R_1 / w R_2$ (all data)	0.0990 / 0.1936	0.0693 / 0.1789	0.1432 / 0.2996
GOF (on F^2)	0.943	1.001	1.133
Largest diff. peak and hole (e $Å^{-3}$)	1.172 / -1.204	0.798 / -0.734	1.125 / -0.640
CCDC No.	2049383	2046726	2046727