Supporting Information

Accessing Multiple Polyethylene Grades via a Single Redox-Active Olefin Polymerization Catalyst

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General Methods and Materials. All reactions were performed under an inert nitrogen atmosphere using an MBraun UniLab glovebox or using standard Schlenk techniques, unless otherwise noted. All solvents were dried using an Innovative Technologies PureSolv Solvent Purification System and degassed via three freeze-pump-thaw cycles. CD_2Cl_2 was dried over activated molecular sieves (4Å) and degassed by three freeze-pump-thaw cycles prior to use. MMAO-3A was received from Akzo-Nobel. All other reagents were purchased from commercial vendors and used without further purification. ^1H and ^{13}C NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz, Bruker 400 MHz or a Varian VNMRS 500 MHz narrow-bore broadband system. ^1H and ^{13}C NMR chemical shifts were referenced to the residual solvent. Polyethylene ^1H and ^{13}C NMR spectra were recorded at 120 °C on a Bruker 400 MHz NMR in $C_2D_2Cl_4$. All mass spectrometry analyses were performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with a DART (direct analysis in real time) ionization source. X-Ray diffraction measurements were performed on single crystals coated with Paratone oil, mounted on a loop, and frozen under a stream of N_2 while data was collected on a Bruker APEX diffractometer. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT 4.05. The structure was solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using the SHELXTL 5.0 software package. All of the solvent molecules were squeezed. EPR measurements were obtained on a Bruker EMX (X-band) EPR spectrometer. EPR spectra were quantified using SpinCount software referenced against CuEDTA standard. This software is available free from Carnegie Mellon University courtesy of the Hendrich group. Elemental microanalyses were carried out by Atlantic Microlab, Inc. (Norcross, GA). Gel permeation chromatography was performed at 140 °C in 1,2,4-trichlorobenzene at 1.0 mL/min on a Malvern Viscotek HT-GPC equipped with triple detection. Polymer melting transition temperatures (T_m) were measured on a TA Instruments Q2000 differential scanning calorimeter on the second heating cycle at a heating rate of 10 °C/min. Cyclic voltammetry measurements were performed on a CH Instruments potentiostat using 0.01 mmol compound in 5 ml DCM solution (0.002 M) with supporting electrolyte 0.2 M $(nBu)_4NPF_6$, using Ag/AgCl as the reference electrode, along with gold working and tungsten counter electrodes at a scan rate of 100 mVs^{-1}. 4-iodo-2,6-diisopropylaniline[1], ethynyl ferrocene[2], and bis(2,6-diisopropyl-4-iodophenyl)diazabutadiene[3] (**6**) were prepared according to a literature procedure. Polymer densities were measured using a Mettler-Toledo balance equipped with a density measurement kit following Archimedes Principle.

Quantitative ^{13}C NMR parameters. NMR measurements and calculations were performed following previous reports by Cotts[4] and Galland.[5,6] All spectra were obtained using a Varian 500 MHz NMR operating at 20 °C. ^{13}C NMR experiments were ran using inverse gated decoupling, a pulse width of 60°, an acquisition time of 1.2 s, and an acquisition delay of 3 s. Branching content was obtained using the formula $(CH_3/3)/[(CH + CH_2 + CH_3)/2] \times 1000$.[7]

Crystallographic data. Crystallographic data for the structural analysis of catalyst **1** has been deposited with the Cambridge Crystallographic Data Center (CCDC), CCDC # 1529504. Copies of this information may be obtained free of charge from the CCDC at https://www.ccdc.cam.ac.uk/.

Synthetic procedures.

General ethylene polymerization conditions. Catalyst (5 μmol) was dissolved in dichloromethane (2 mL) and added to a Fisher Porter bottle containing toluene (98 mL) and a magnetic stir bar. The bottle was sealed and placed in an oil bath at the desired temperature. The vessel was pressurized with ethylene (15 psi) and allowed to equilibrate under constant pressure for 10 minutes with stirring. MMAO-3A (2.5 mmol, 500 equiv) was injected to initiate polymerization and the reaction was stirred continuously for the desired time. The polymerization was quenched via the addition of MeOH (10 mL). The polymer was precipitated by adding excess acidic MeOH (5% HCl in MeOH), then dried in a vacuum oven to constant weight. Polymerizations using a redox reagent were performed using the same conditions except oxidant/reductant (5 μmol, 1 equiv for cobaltocene, or 10 μmol, 2 equiv for $AgBAr^F$) was added to the DCM solution with the catalyst prior to activation. A noticeable color change is observed upon combination of the redox reagent and catalyst.

Synthesis of (ArN=C(An)-C(An)=NAr) (Ar = 4-I-2,6-(*i*Pr)$_2$C$_6$H$_2$) (4). Acenaphthenequinone (1 eq.), 4-iodo-2,6-diisopropylaniline (2.1 eq.), and formic acid (4 eq.) were added to methanol and refluxed for 24 hours. The golden yellow precipitate was washed with methanol and dried under high vacuum. Yield: 89%. ^1H NMR (500 MHz, 25 °C, $CDCl_3$); δ, ppm:

0.94 (d, 12H), 1.19 (d, 12H), 2.92 (m, 4H), 6.77 (d, 2H), 7.44 (t, 2H), 7.55 (s, 4H), 7.93 (d, 2H). ^{13}C NMR (125 MHz, 25 °C, $CDCl_3$); δ, ppm: 23.02 ($CH(CH_3)_2$), 23.34 ($CH(CH_3)_2$), 28.79 ($CH(CH_3)_2$), 89.07 (aromatic C(I)), 123.60 (aromatic), 128.19 (aromatic), 129.22 (aromatic), 129.51 (aromatic), 132.96 (aromatic), 138.28 (aromatic), 141.03 (aromatic), 147.18 (aromatic), 161.22 (C=N). HRMS^{calc} $C_{38}H_{39}I_2N_2$ (H^+ adduct) = 753.12026 m/z; HRMS^{expt} $C_{38}H_{39}I_2N_2$ (H^+ adduct) = 753.11288 m/z.

Synthesis of (ArN=C(Me)-C(Me)=NAr) (Ar = 4-I-2,6-(*i*Pr)$_2$C$_6$H$_2$) (5). Butanedione (1 eq.), 4-iodo-2,6-diisopropylaniline (2 eq.), and formic acid (4 eq.) were added to methanol and refluxed for 24 hours. The off white precipitate was washed with methanol and dried under high vacuum. Yield: 87%. ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$); δ, ppm: 1.14 (d, 12H), 1.17 (d, 12H), 2.04 (s, 6H), 2.61 (m, 4H), 7.44 (s, 4H). ^{13}C NMR (125 MHz, 25 °C, $CDCl_3$); δ, ppm: 16.79 ($C(CH_3)$), 22.58 ($CH(CH_3)_2$), 22.95 ($CH(CH_3)_2$), 28.66 ($CH(CH_3)_2$), 88.44 (aromatic C(I)), 132.44 (aromatic), 137.88 (aromatic), 145.97 (aromatic), 168.64 (C=N). HRMS^{calc} $C_{28}H_{39}I_2N_2$ (H^+ adduct) = 657.12026 m/z; HRMS^{expt} $C_{28}H_{39}I_2N_2$ (H^+ adduct) = 657.11989 m/z.

Synthesis of (ArN=C(An)-C(An)=NAr) (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (7). To a degassed Schlenk flask was added (ArN=C(An)-C(An)=NAr) (Ar = 4-I-2,6-(*i*Pr)$_2$C$_6$H$_2$) (1.0 eq.) and ethynyl ferrocene (2.2 eq.). To a separate degassed flask was added CuI (0.2 eq.) and $PdCl_2(PPh_3)_2$ (0.1 eq.). THF was added to both vessels and the diimine/ethynyl ferrocene solution was transferred via cannula to the CuI/ $PdCl_2(PPh_3)_2$ suspension. Triethylamine (4.0 eq.) was added and the reaction was heated at 70 °C for 6 hr. The reaction mixture was filtered through celite and dried under reduced pressure. The resulting material was purified via column chromatography using 10% DCM/ 90% hexanes as eluent. The product was obtained as a burnt orange solid. Yield: 41%. ^{1}H NMR of ligand **1** (500 MHz, 25 °C, $CDCl_3$); δ, ppm: 1.00 (d, 12H), 1.25 (d, 12H), 3.00 (m, 4H), 4.27 (t, 4H), 4.31(s, 10H), 4.55 (t, 4H), 6.82 (d, 2H), 7.43 (m, 6H, aromatic), 7.92 (d, 2H). ^{13}C NMR (125 MHz, 25 °C, $CDCl_3$); δ, ppm: 23.13 ($CH(CH_3)_2$), 23.42 ($CH(CH_3)_2$), 28.80 ($CH(CH_3)_2$), 65.93 (Cp-C), 68.85 (Cp-C), 70.11 (Cp-C), 71.51 (Cp-C), 86.78 (alkyne C), 86.89 (alkyne C), 119.50 (aromatic), 123.70 (aromatic), 127.28 (aromatic), 128.16 (aromatic), 129.37 (aromatic), 131.30 (aromatic), 135.90 (aromatic), 141.02 (aromatic), 147.59 (aromatic), 161.05 (C=N). Analysis: Calculated for $C_{60}H_{56}Fe_2N_2$•0.5 DCM – C, 75.75; H, 5.99; N, 2.92. Found: C, 75.38; H, 6.10; N, 2.91.

Synthesis of (ArN=C(Me)-C(Me)=NAr) (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (8). Following the same procedure as **7**, compound **8** was synthesized using (ArN=C(Me)-C(Me)=NAr) (Ar = 4-I-2,6-(*i*Pr)$_2$C$_6$H$_2$). The product was obtained as a yellow-orange solid. Yield: 64%. ^{1}H NMR of ligand **2** (500 MHz, 25 °C, $CDCl_3$); δ, ppm: 1.20 (d, 12H), 1.23 (d, 12H), 2.08 (s, 6H), 2.70 (m, 4H), 4.25 (t, 4H), 4.28 (s, 10H), 4.53 (t, 4H), 7.32 (s, 4H). ^{13}C NMR (125 MHz, 25 °C, $CDCl_3$); δ, ppm: 16.83 ($C(CH_3)$), 22.68 ($CH(CH_3)_2$), 23.05 ($CH(CH_3)_2$), 28.68 ($CH(CH_3)_2$), 66.04 (Cp-C), 68.77 (Cp-C), 70.08 (Cp-C), 71.46 (Cp-C), 86.43 (alkyne C), 86.78 (alkyne C), 119.07 (aromatic), 126.71 (aromatic), 135.49 (aromatic), 146.21 (aromatic), 168.37 (C=N). Analysis: Calculated for $C_{52}H_{56}Fe_2N_2$•0.25 DCM – C, 74.54; H, 6.76; N, 3.33. Found: C, 74.52; H, 6.59; N, 3.25.

Synthesis of (ArN=C(H)-C(H)=NAr) (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (9). Followed the same procedure as **7**, compound **9** was synthesized using (ArN=C(H)-C(H)=NAr) (Ar = 4-I-2,6-(*i*Pr)$_2$C$_6$H$_2$). The product was obtained as a yellow solid. Yield: 55%. ^{1}H NMR of ligand **3** (500 MHz, 25 °C, $CDCl_3$); δ, ppm: 1.23 (d, 24H), 2.93 (m, 4H), 4.25 (t, 4H), 4.27 (s, 10H), 4.52 (t, 4H), 7.32 (s, 4H), 8.09 (s, 2H). ^{13}C NMR of ligand **3** (125 MHz, 25 °C, $CDCl_3$); δ, ppm: 23.44 ($CH(CH_3)_2$), 28.20 ($CH(CH_3)_2$), 65.76 (Cp-C), 68.88 (Cp-C), 70.11 (Cp-C), 71.52 (Cp-C), 86.42 (alkyne C), 87.22 (alkyne C), 120.67 (aromatic), 126.74 (aromatic), 137.19 (aromatic), 147.81 (aromatic), 163.08 (C=N). Analysis: Calculated for $C_{50}H_{52}Fe_2N_2$•0.25 DCM – C, 74.16; H, 6.50; N, 3.44. Found: C, 74.58; H, 6.52; N, 3.52.

Synthesis of (ArN=C(An)-C(An)=NAr)NiBr$_2$ (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (1). Under inert conditions, ligand **1** (1.0 eq.) and (DME)$NiBr_2$ (1.0 eq.) were added to a Schlenk flask. Dichloromethane was added and the reaction was stirred for 16 h. The reaction mixture was filtered and washed with hexanes (3x). Yield: 90%. ^{1}H NMR (paramagnetic)(500 MHz, 25 °C, CD_2Cl_2); δ, ppm: 0.88, 1.03, 1.12, 1.27, 1.55, 2.09, 4.30, 4.54, 4.73, 4.96, 5.84, 17.19, 23.72, 25.29. Analysis: Calculated for $C_{60}H_{56}Fe_2N_2Br_2Ni$•0.25 DCM – C, 62.57; H, 4.92; N, 2.42. Found: C, 62.56; H, 4.92; N, 2.61.

(ArN=C(Me)-C(Me)=NAr)NiBr$_2$ (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (2). Under inert conditions, ligand **2** (1.0 eq.) and (DME)NiBr$_2$ (1.0 eq.) were added to a Schlenk flask. Dichloromethane was added and the reaction was stirred for 16 h. The reaction mixture was filtered and washed with hexanes (3x). Yield: 88%. ^{1}H NMR (paramagnetic)(500 MHz, 25 °C, CD_2Cl_2); δ, ppm: -17.11, 2.58, 3.02, 4.26, 4.62, 4.78, 4.98, 7.35, 7.59, 24.95. Analysis: Calculated for $C_{52}H_{56}Fe_2N_2Br_2Ni$•0.5 DCM – C, 58.30; H, 5.31; N, 2.59. Found: C, 58.14; H, 5.18; N, 2.04.

(ArN=C(H)-C(H)=NAr)NiBr$_2$ (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (3). Under inert conditions, ligand **3** (1.0 eq.) and (DME)NiBr$_2$ (1.0 eq.) were added to a Schlenk flask. Dichloromethane was added and the reaction was stirred for 16 h. The reaction mixture was filtered and washed with hexanes (3x). Yield: 87%. ^{1}H NMR (paramagnetic)(500 MHz, 25 °C, CD_2Cl_2); δ, ppm: 1.21, 1.23, 2.94, 4.26, 4.40, 4.50, 4.70, 7.31, 8.09, 22.80. Analysis: Calculated for $C_{50}H_{52}Fe_2N_2Br_2Ni$ – C, 59.39; H, 5.18; N, 2.77. Found: C, 60.71; H, 5.45; N, 2.96.

Table S1 *Complete polymerization data using catalysts **1**, **2**, and **3**.*[a]

entry	catalyst	oxidant or reductant	yield (g)	M_n[b] (kg/mol)	M_w[b] (kg/mol)	Đ[b]	B[c]	T_m[d] (°C)
1	**1**	$AgBAr^F$	1.090	235	503	2.1	39	107
2	**1**	None	1.050	222	367	1.7	40	107
3	**1**	$CoCp_2$	0.662	264	553	2.1	9	119
4	**2**	$AgBAr^F$	0.632	179	314	1.8	28	102
5	**2**	None	0.623	199	398	2.0	25	105
6	**2**	$CoCp_2$	0.034	196	385	2.0	23	110
7	**3**	$AgBAr^F$	0.244	52	113	2.2	6	129
8	**3**	None	0.219	45	110	2.5	6	129
9	**3**	$CoCp_2$	0.057	45	96	2.1	5	130

[a]Polymerization conditions: catalyst loading = 5.0 µmol, 98 mL of toluene, 2 mL of dichloromethane, 20 °C, 15 psi ethylene, 15 min, and 500 equiv of MMAO. [b]Determined using triple detection gel permeation chromatography at 140 °C in 1,2,4-trichlorobenzene. [c]Determined by ^{1}H NMR. [d]Determined using differential scanning calorimetry (DSC).

Table S2 *Detailed polymerization data using catalysts **1**.*[a]

entry	catalyst	oxidant or reductant	yield (g)	M_n[b] (kg/mol)	M_w[b] (kg/mol)	Đ[b]	B[c,d]	T_m[e] (°C)
1	**1**	$AgBAr^F$	1.090	235	503	2.1	39 (±1.9)	107
2	**1**	None	1.050	222	367	1.7	40 (±1.4)	107
3	**1**	$CoCp_2$	0.662	264	553	2.1	9 (±2.4)	119

[a]Polymerization conditions: catalyst loading = 5.0 µmol, 98 mL of toluene, 2 mL of dichloromethane, 20 °C, 15 psi ethylene, 15 min, and 500 equiv of MMAO. [b]Determined using triple detection gel permeation chromatography at 140 °C in 1,2,4-trichlorobenzene. [c]Determined by ^{1}H NMR. [d] The average of three trials with standard deviation reported to ensure accuracy of results. [e]Determined using differential scanning calorimetry (DSC).

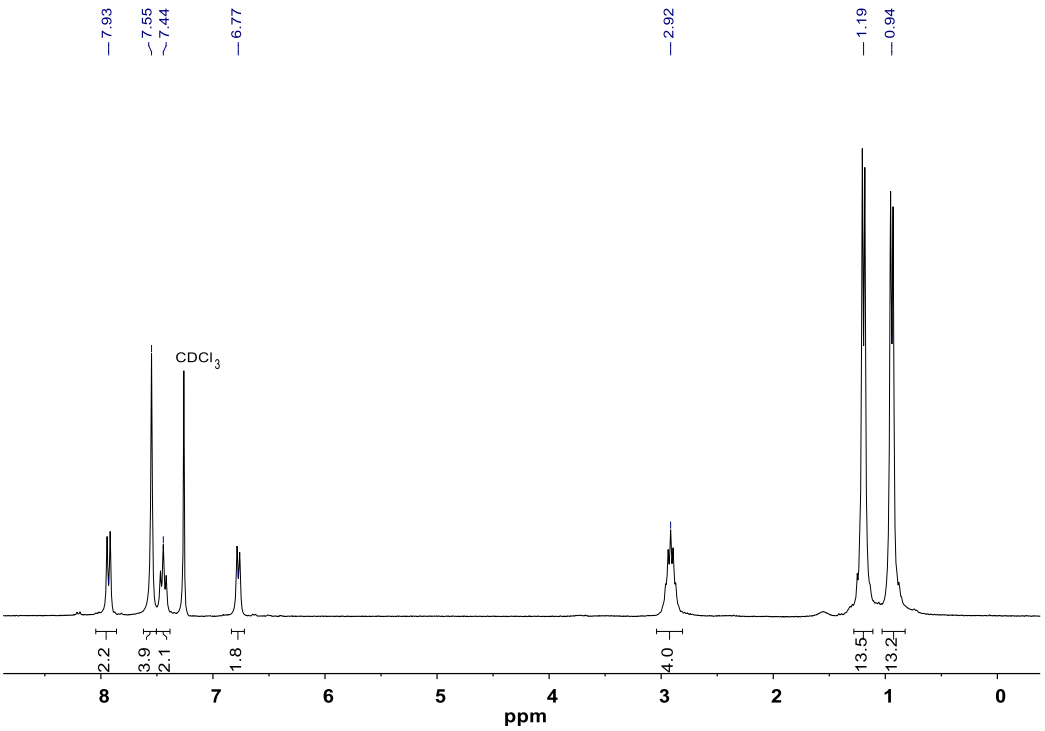


Figure S1. ^{1}H NMR of (ArN=C(An)-C(An)=NAr) (Ar = 4-I-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**4**).

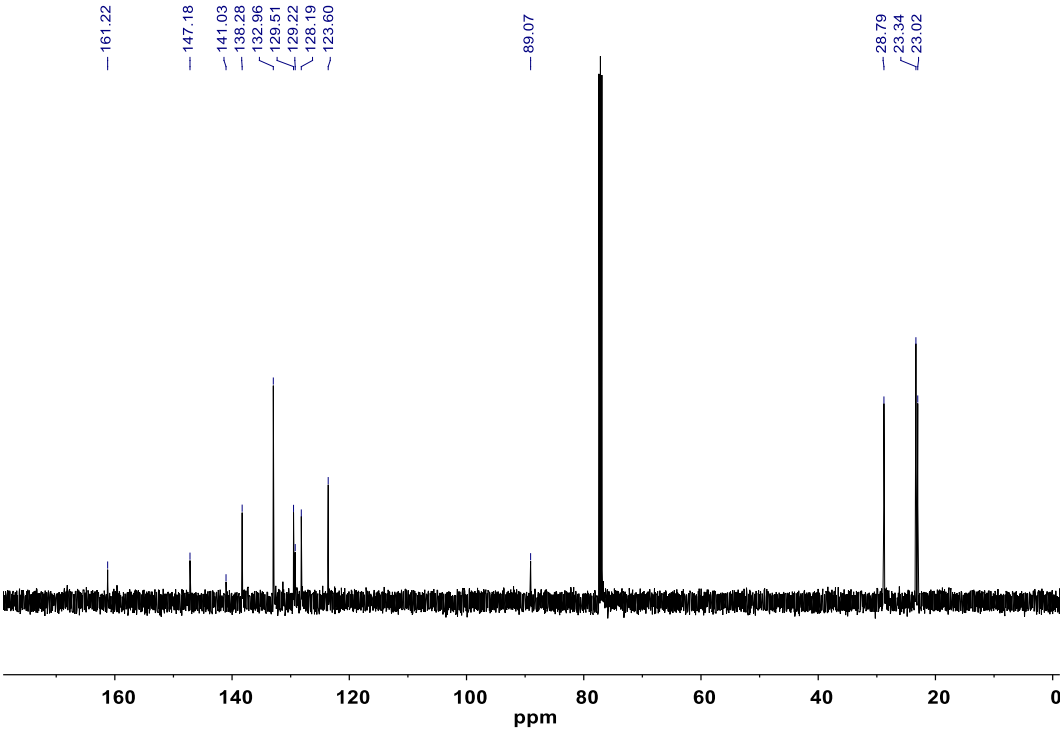


Figure S2. ^{13}C NMR of (ArN=C(An)-C(An)=NAr) (Ar = 4-I-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**4**).

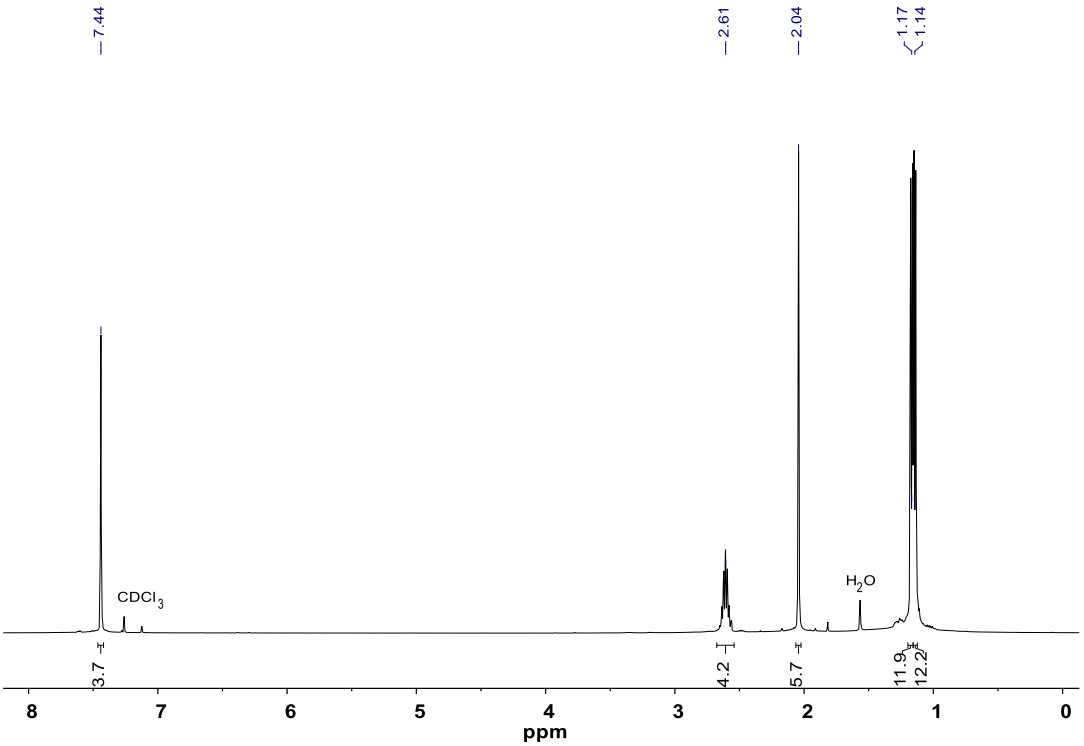


Figure S3. ^{1}H NMR of (ArN=C(Me)-C(Me)=NAr) (Ar = 4-I-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**5**).

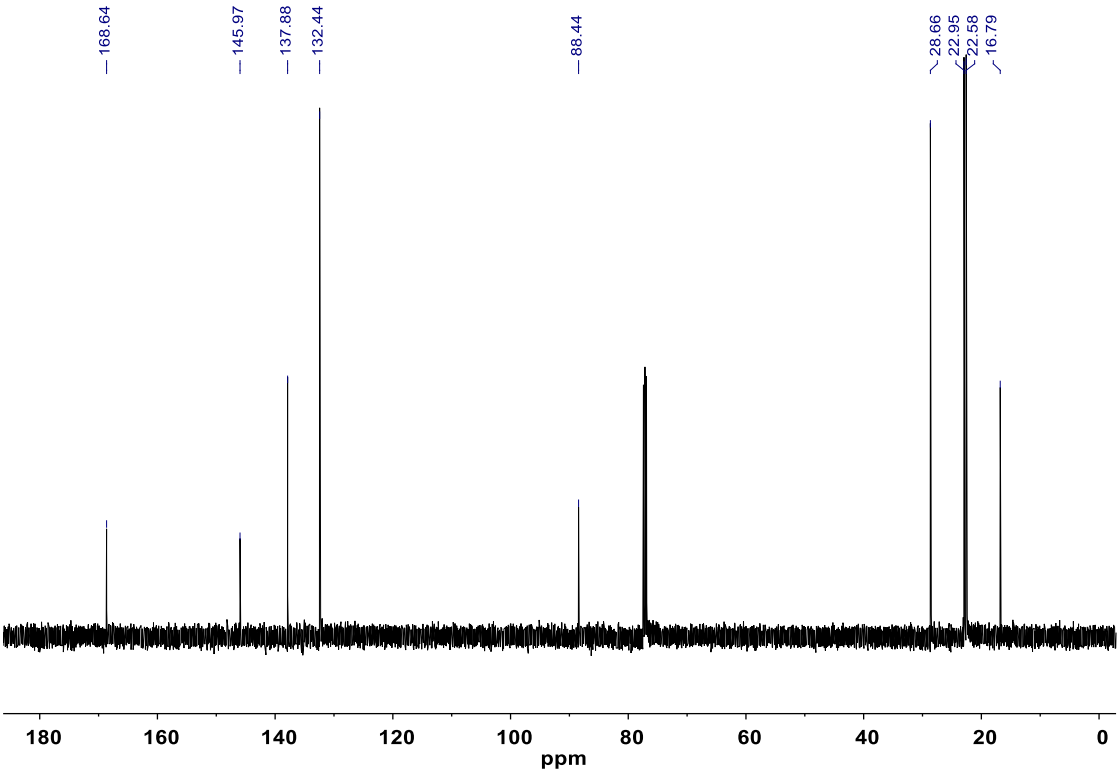


Figure S4. ^{13}C NMR of (ArN=C(Me)-C(Me)=NAr) (Ar = 4-I-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**5**).

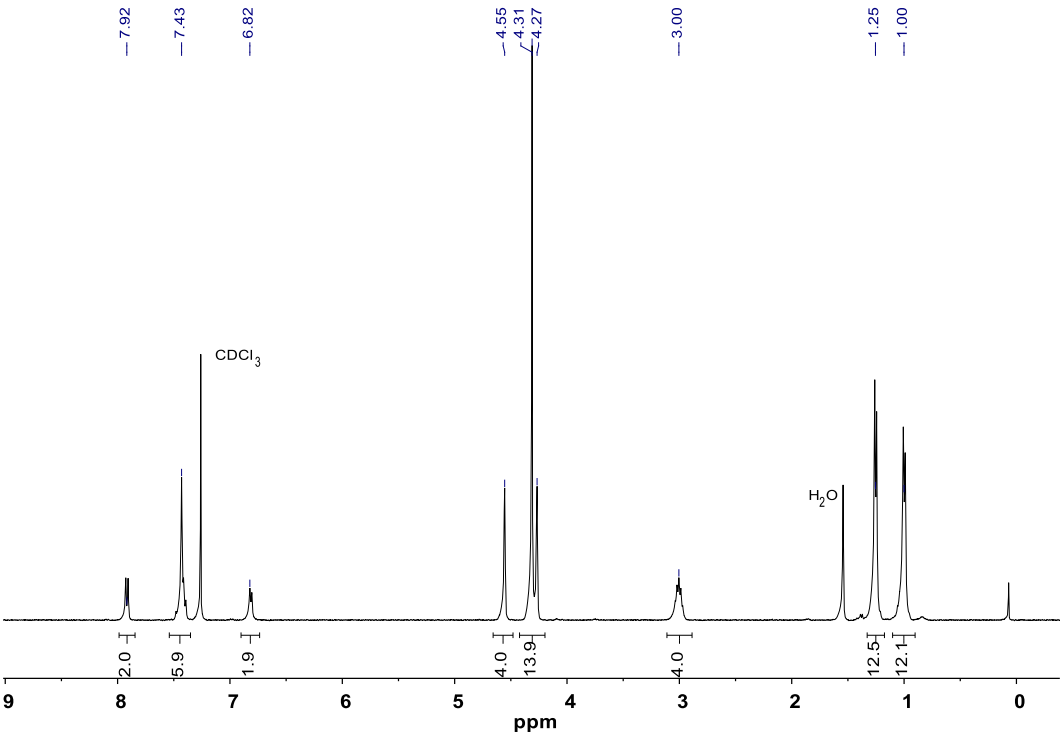


Figure S5. ^{1}H NMR of (ArN=C(An)-C(An)=NAr) (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**7**).

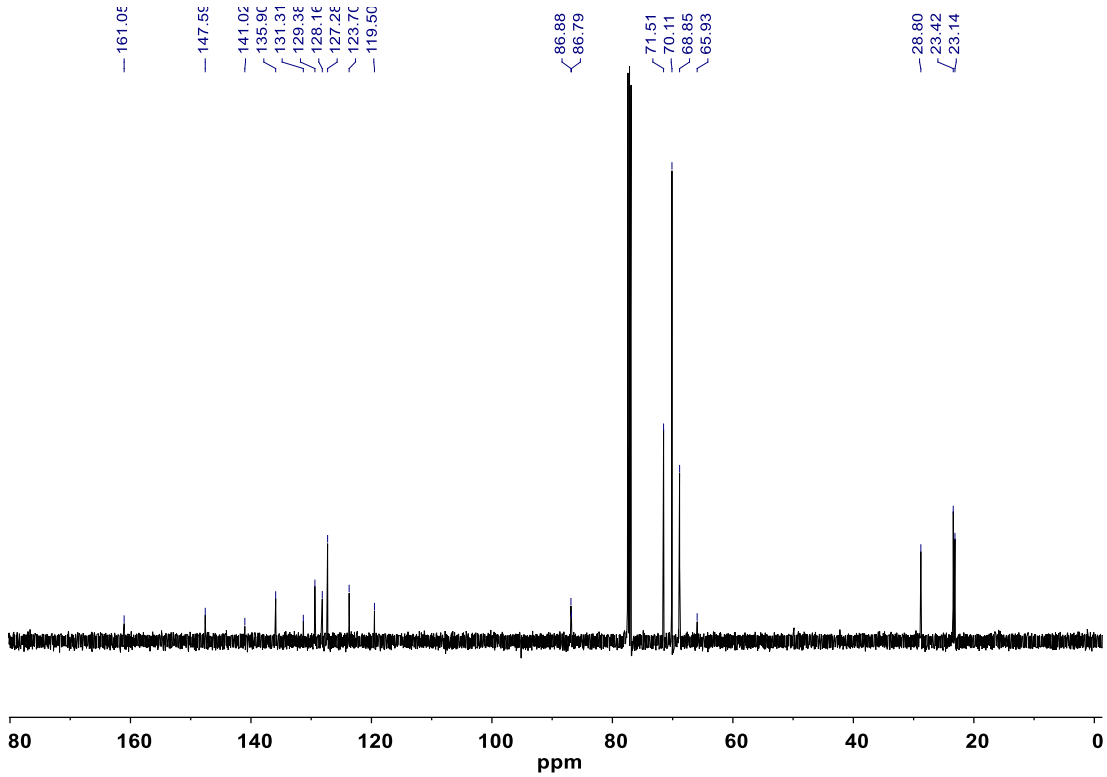


Figure S6. ^{13}C NMR of (ArN=C(An)-C(An)=NAr) (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**7**).

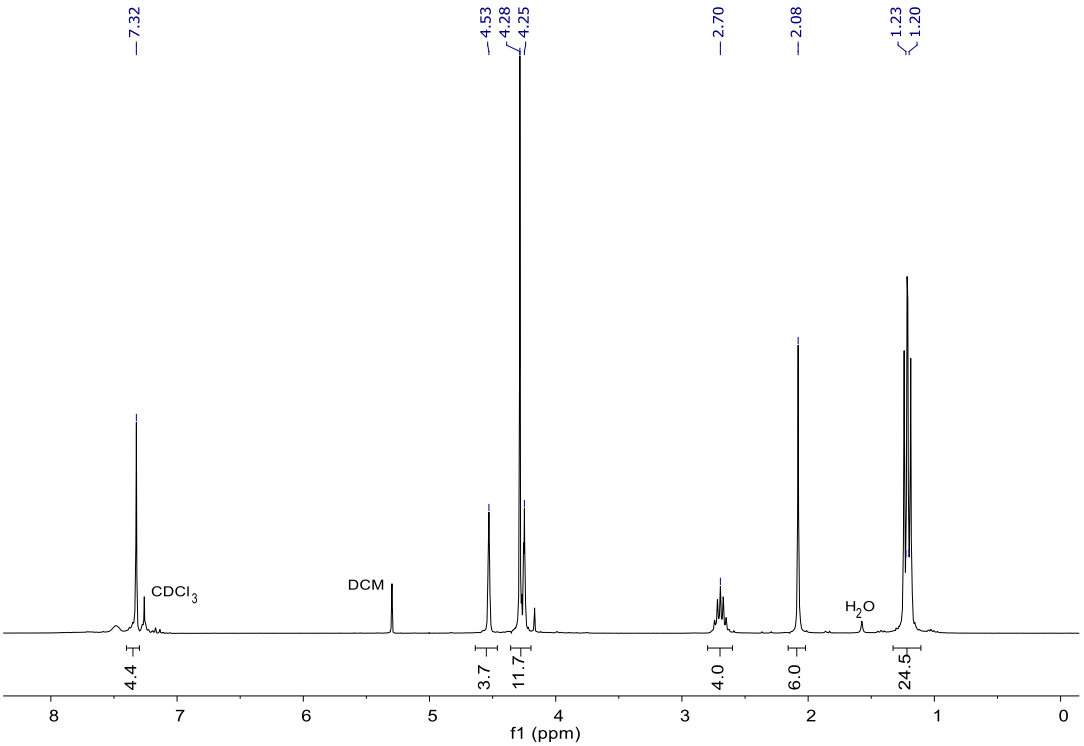


Figure S7. ^{1}H NMR of (ArN=C(Me)-C(Me)=NAr) (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**8**).

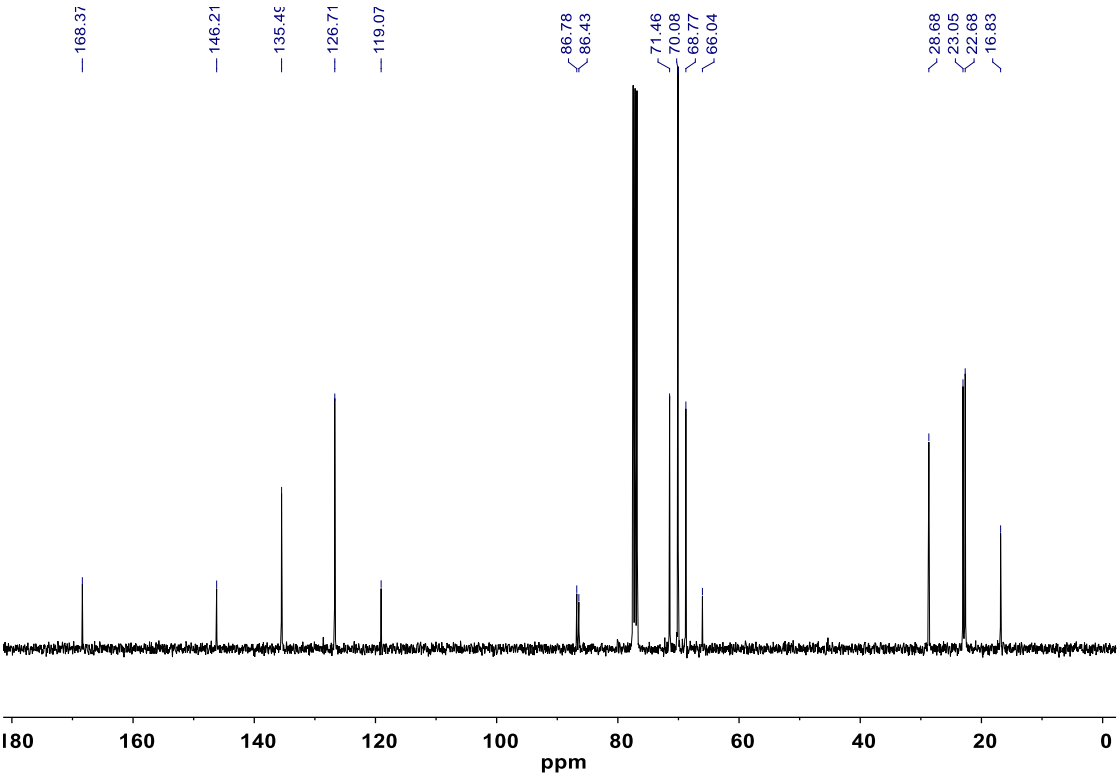


Figure S8. ^{13}C NMR of (ArN=C(Me)-C(Me)=NAr) (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**8**).

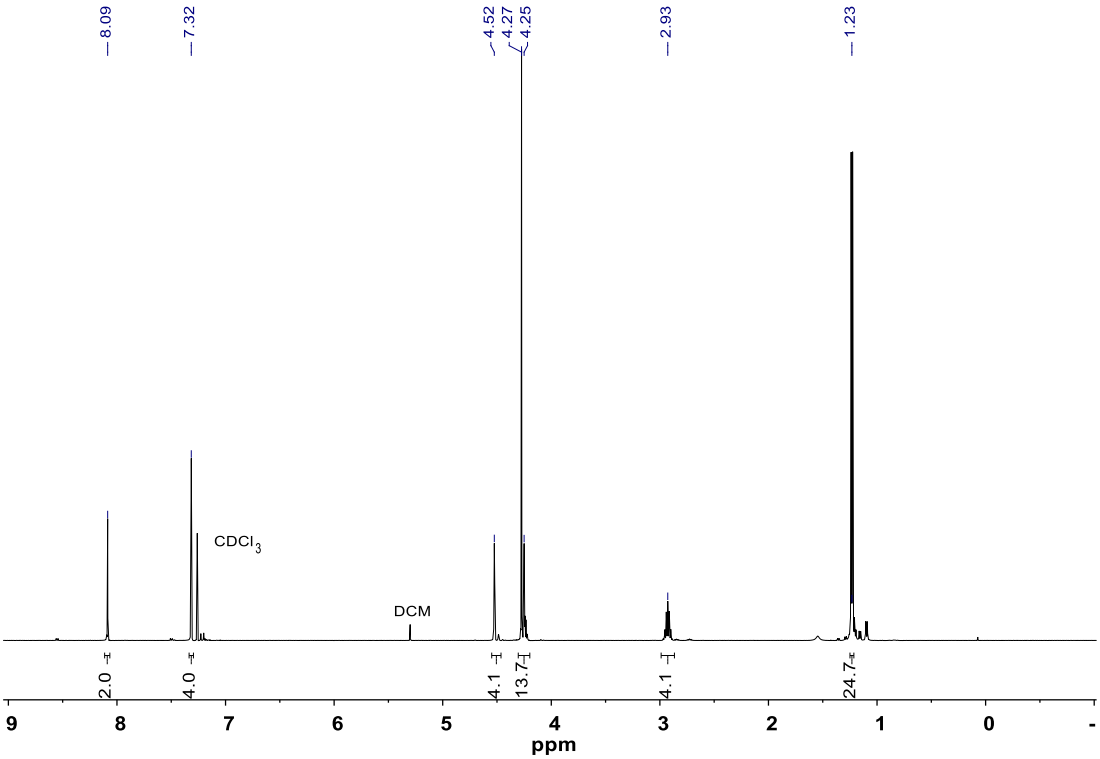


Figure S9. ^{1}H NMR of (ArN=C(H)-C(H)=NAr) (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**9**).

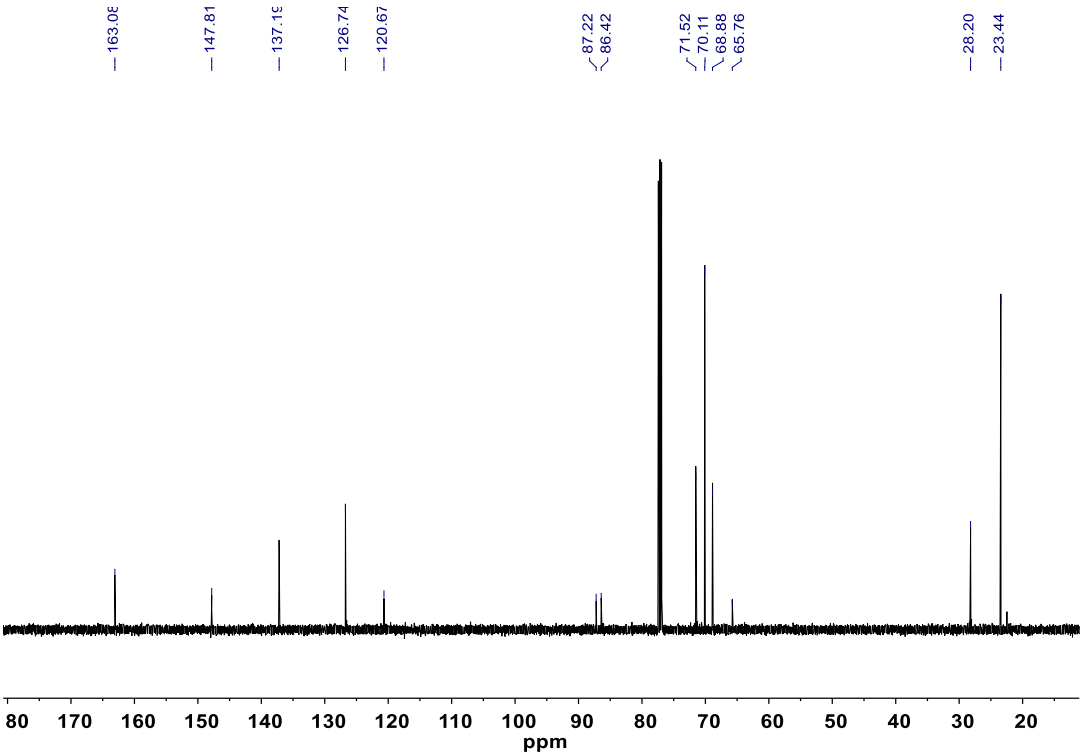


Figure S10. ^{13}C NMR of (ArN=C(H)-C(H)=NAr) (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**9**).

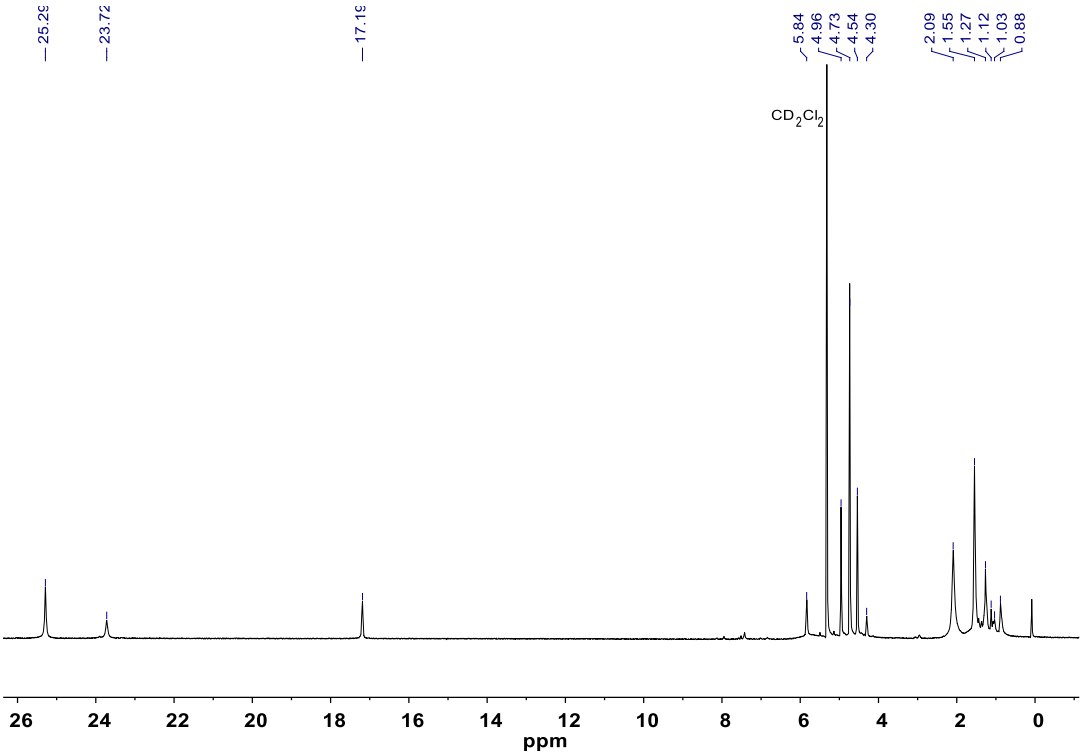


Figure S11. ^{1}H NMR of (ArN=C(An)-C(An)=NAr)$NiBr_2$ (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2C_6H_2$) (**1**).

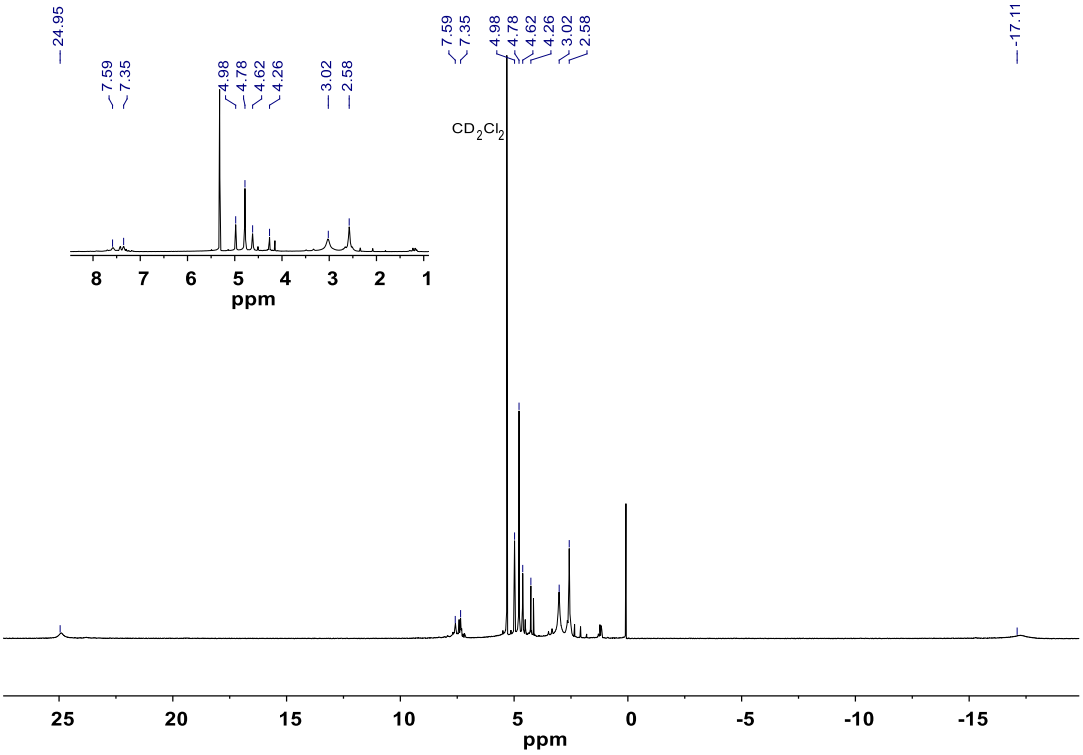


Figure S12. ^{1}H NMR of (ArN=C(Me)-C(Me)=NAr)$NiBr_2$ (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2C_6H_2$) (**2**).

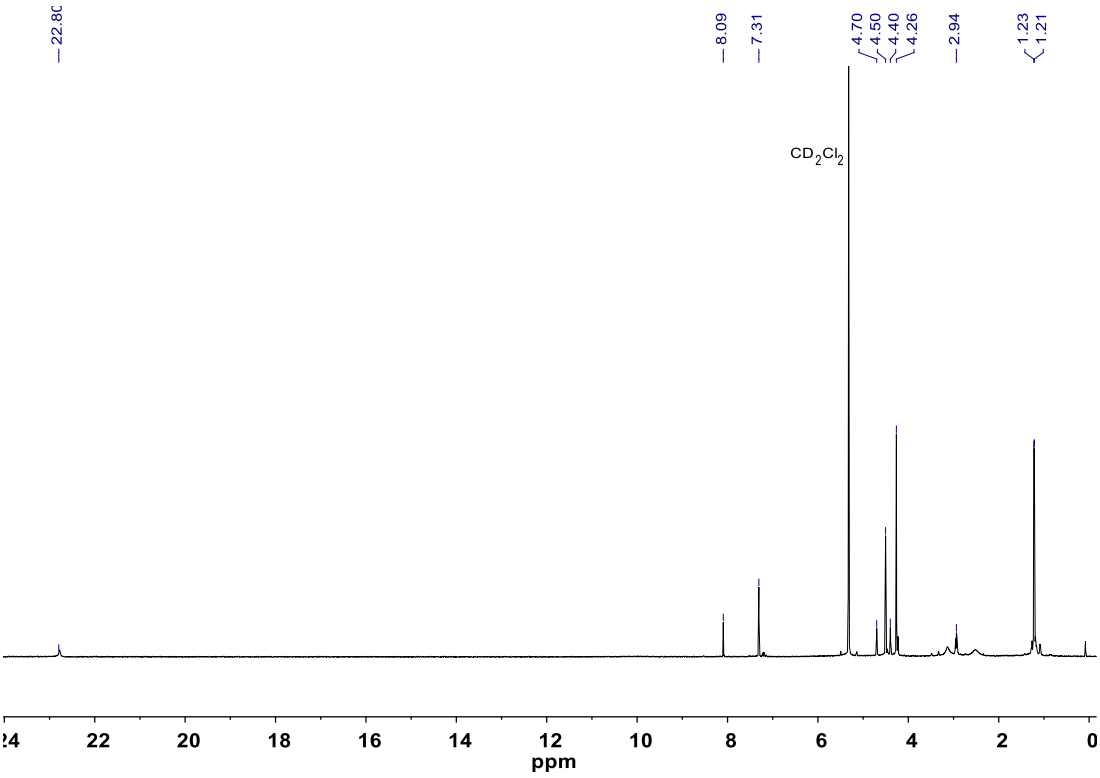


Figure S13. ^{1}H NMR of (ArN=C(H)-C(H)=NAr)$NiBr_2$ (Ar = 4-ethynylferrocene-2,6-(*i*Pr)$_2$C$_6$H$_2$) (**3**).

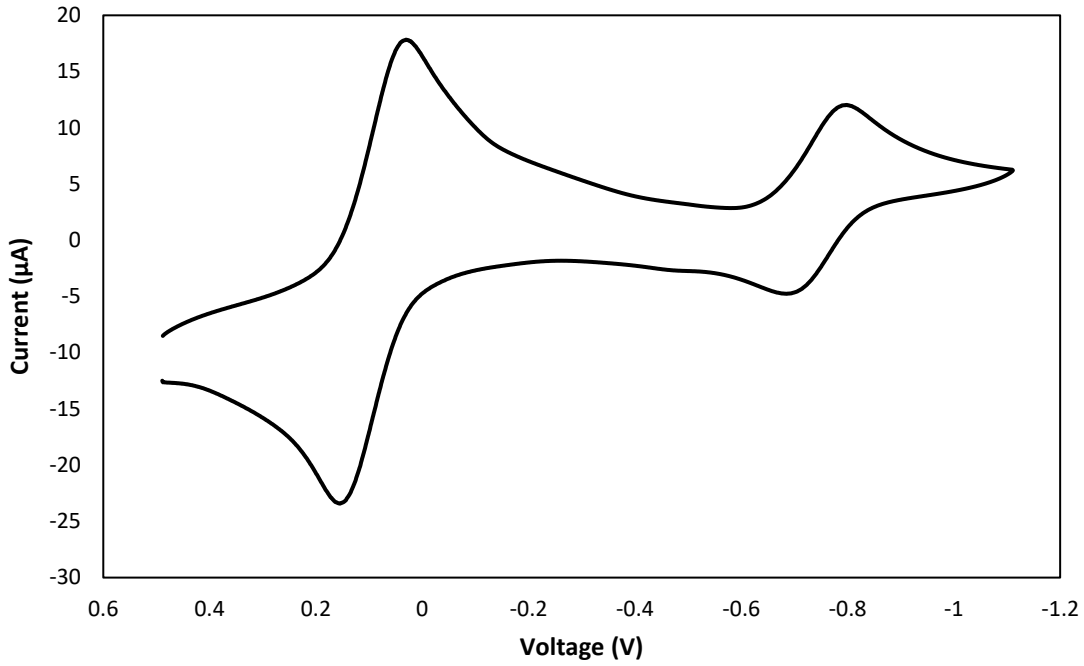


Figure S14. CV trace of catalyst **1**.

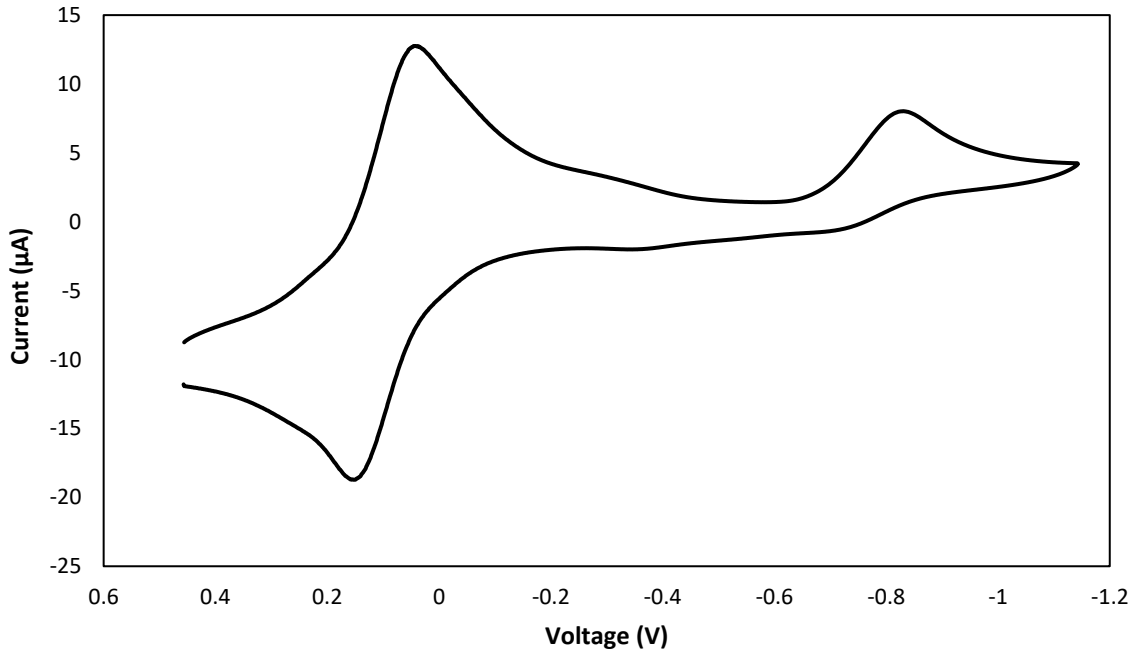


Figure S15. CV trace of catalyst **2**.

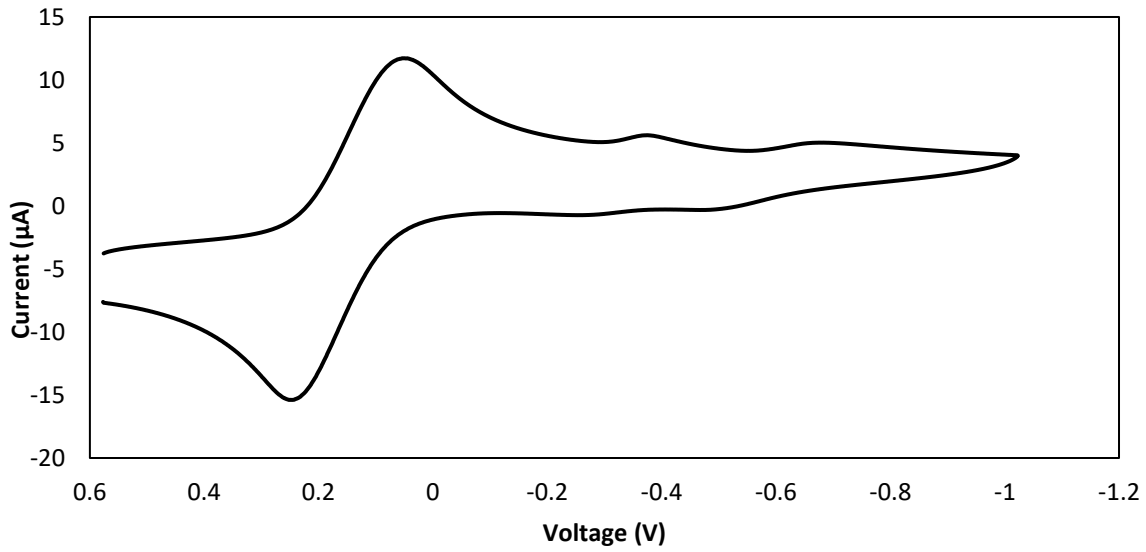


Figure S16. CV trace of catalyst **3**.

Table S3. Assignment of ^{13}C NMR peaks and integral ratios for polyethylene samples.

	Chemical Shift (ppm)			Integral Ratios		
Peak #	Previously reported values	Experimental	Assignment[a]	1_{ox} (S17)	1(S18)	1_{red} (S19)
1	20.04, 20.01, 19.90	20.13	$1B_1$	1	1	1
2	27.35, 27.3, 27.33, 27.20	27.26	βB_n	0.4	0.3	~0
3	27.45, 27.42	27.44	βB_1	1.4	1.4	1.5
4	30	30	$\delta B_{1\text{-}n}$ (Backbone CH_2)	32	30.2	81.6
5	30.38, 30.36	30.39	γB_1	1.7	2	2.1
6	30.50, 30.48	30.49	γB_n	0.5	0.5	0.3
7	33.26, 33.1, 33.14	33.24	brB_1	0.8	0.7	0.7
8	37.56, 37.47	37.55	αB_1	2.1	1.8	1.5

[a] xB_n = Branch. x = If greek, backbone carbon. If numbered, branch carbon. If br, branchpoint (methine carbon at branch). B_n = Branch of length n.

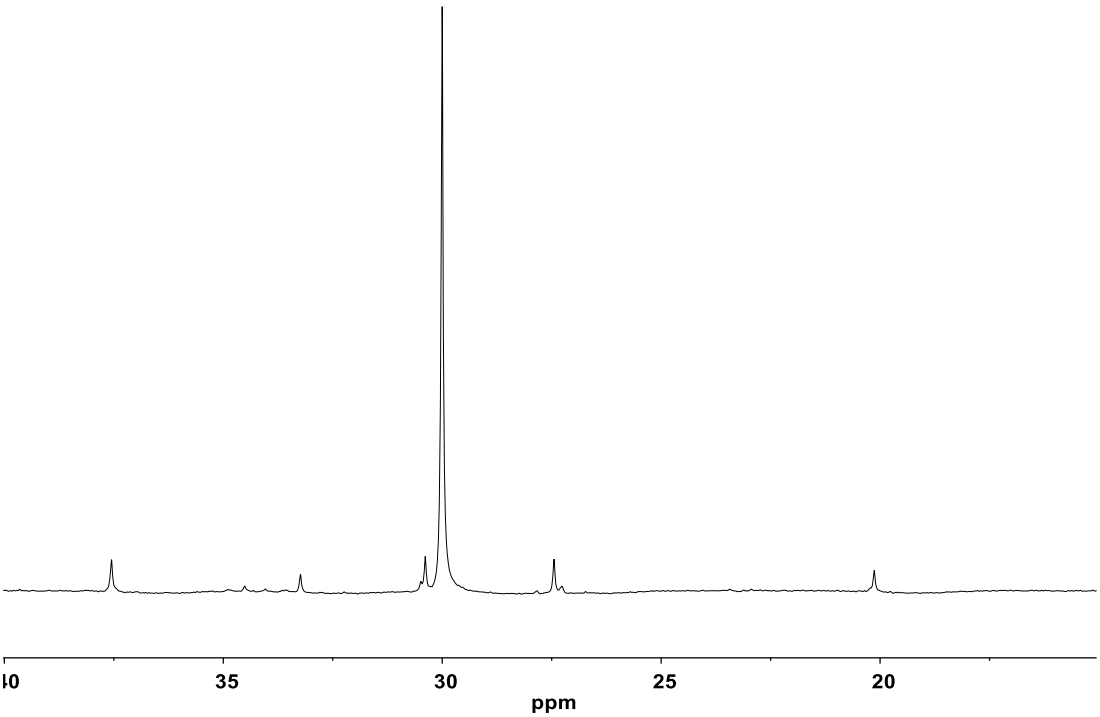


Figure S17. Representative ^{13}C NMR of polyethylene (Table 1, Entry 1) (catalyst **1** + oxidant)

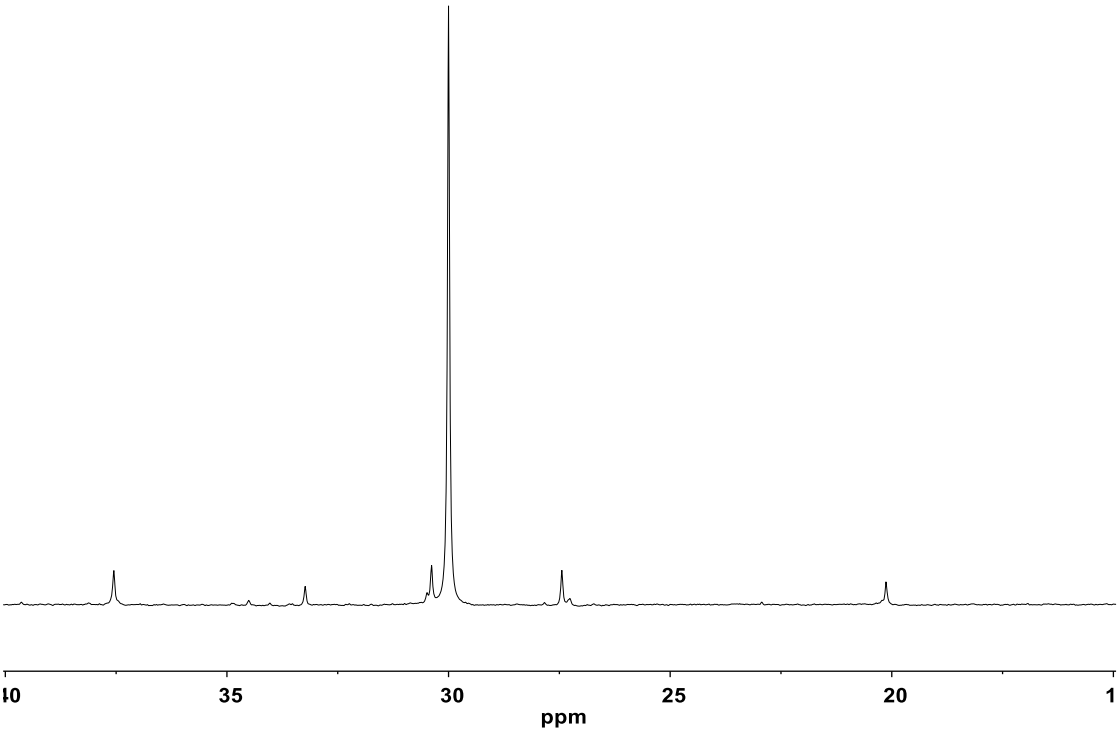


Figure S18. Representative ^{13}C NMR of polyethylene (Table 1, Entry 2) (catalyst **1**)

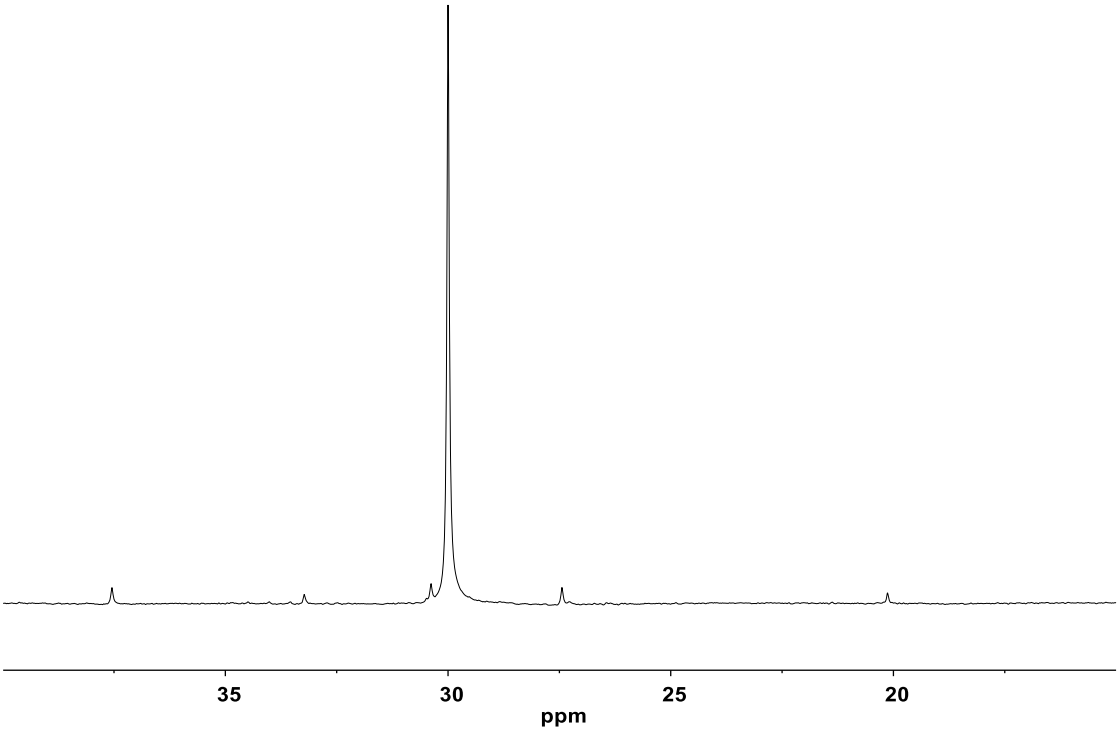


Figure S19. Representative ^{13}C NMR of polyethylene (Table 1, Entry 3) (catalyst **1** + reductant)

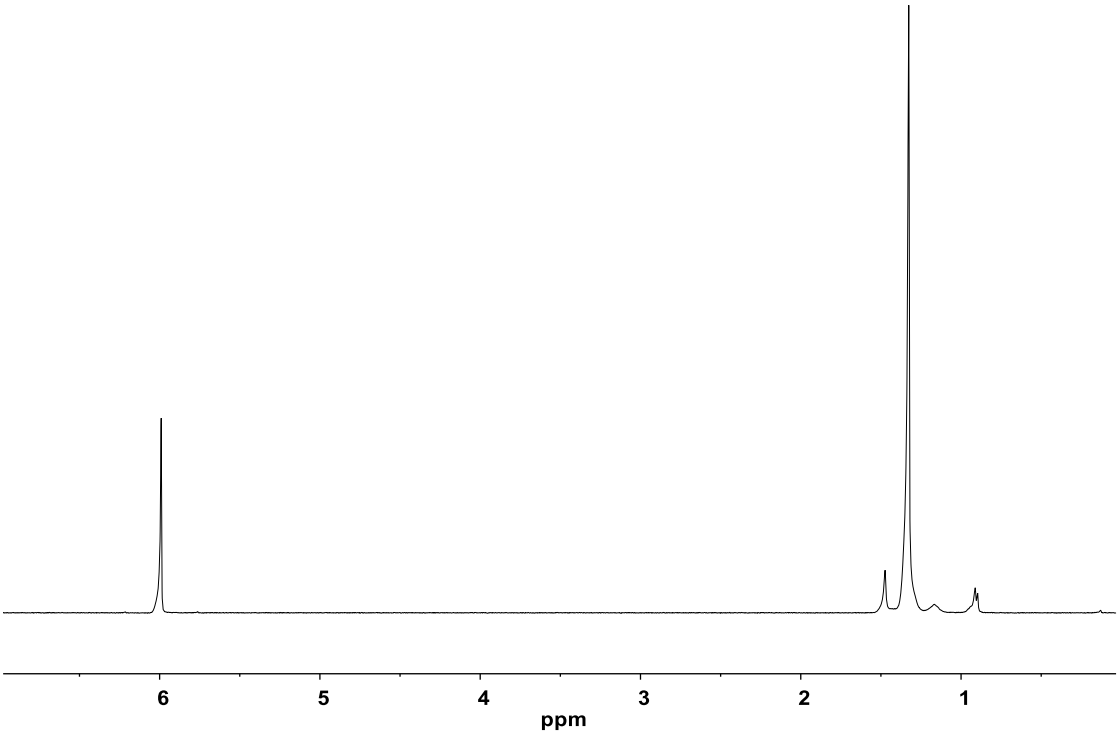


Figure S20. Representative ^{1}H NMR of polyethylene (Table 1, Entry 1) (catalyst **1** + oxidant)

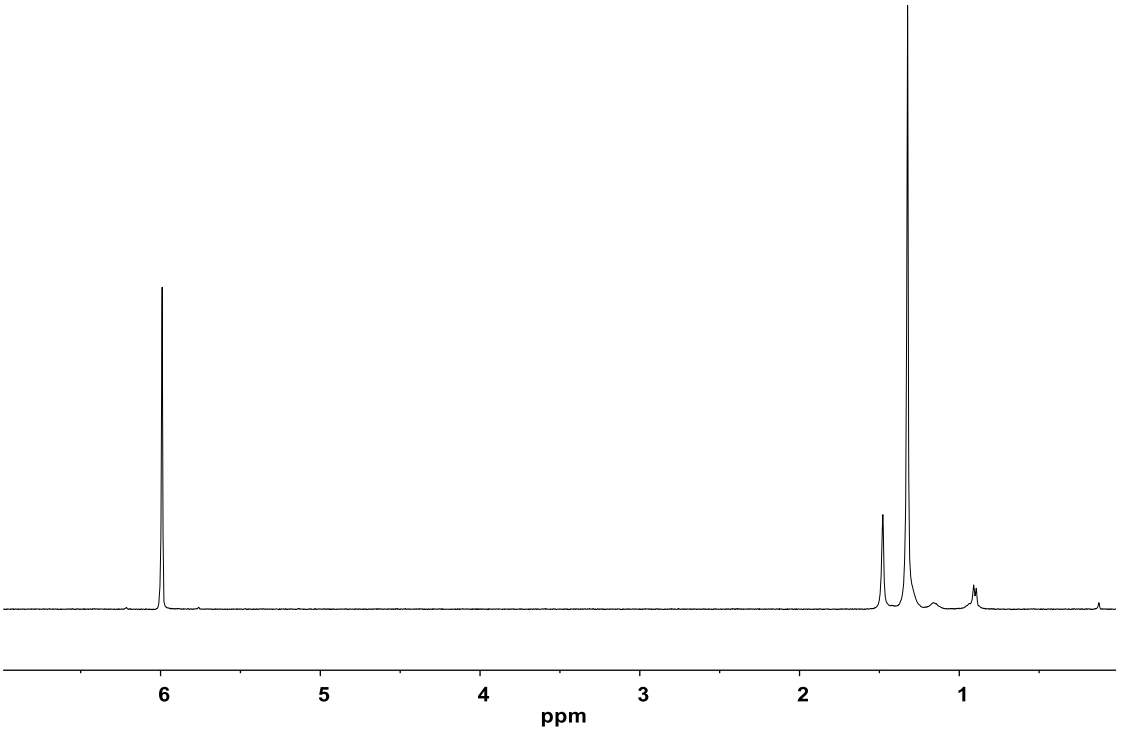


Figure S21. Representative ^{1}H NMR of polyethylene (Table 1, Entry 2) (catalyst **1**)

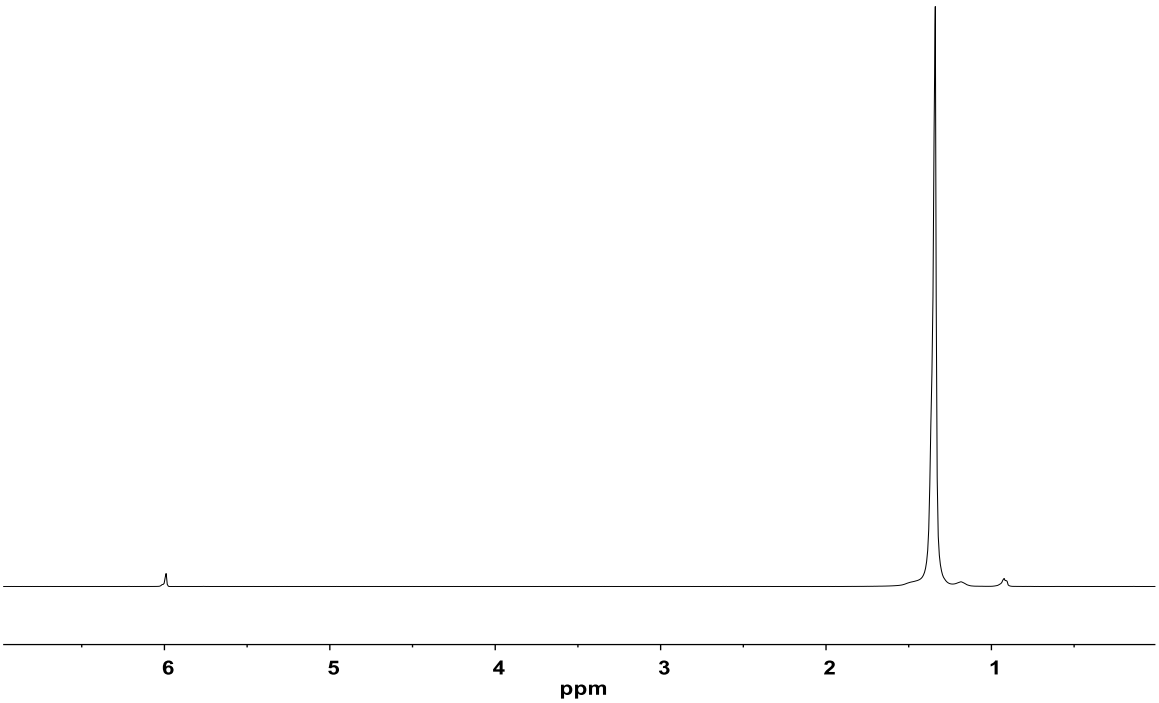


Figure S22. Representative ^{1}H NMR of polyethylene (Table 1, Entry 3) (catalyst **1** + reductant)

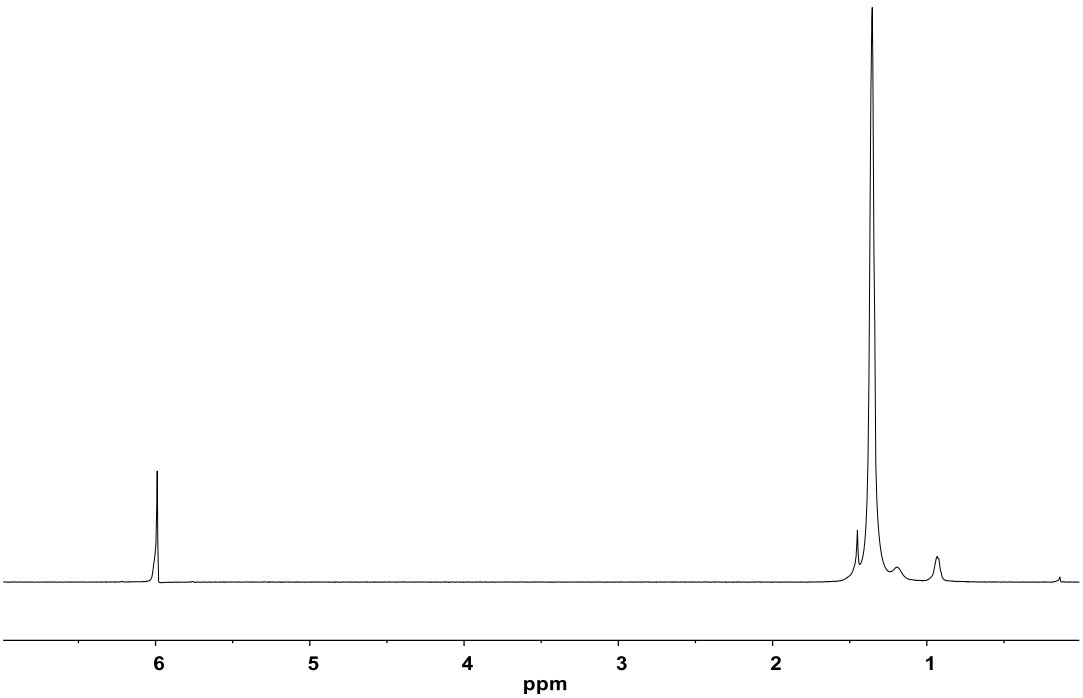


Figure S23. Representative ^{1}H NMR of polyethylene (Table 1, Entry 4) (catalyst **2** + oxidant)

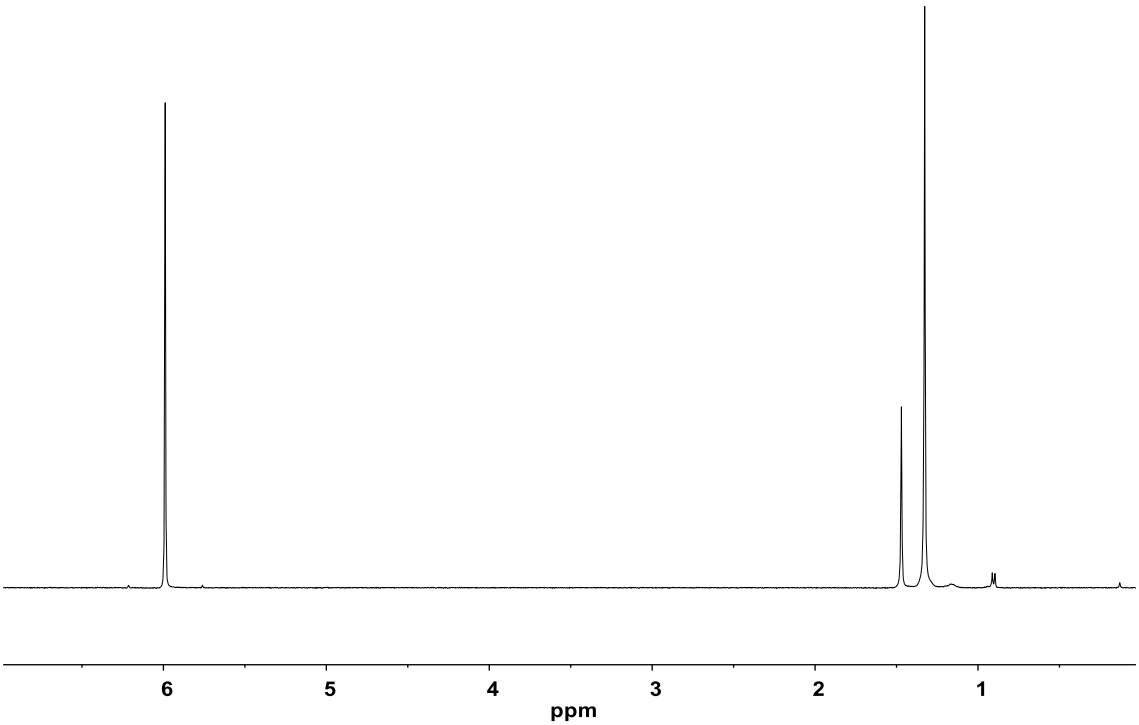


Figure S24. Representative ^{1}H NMR of polyethylene (Table 1, Entry 5) (Catalyst **2**)

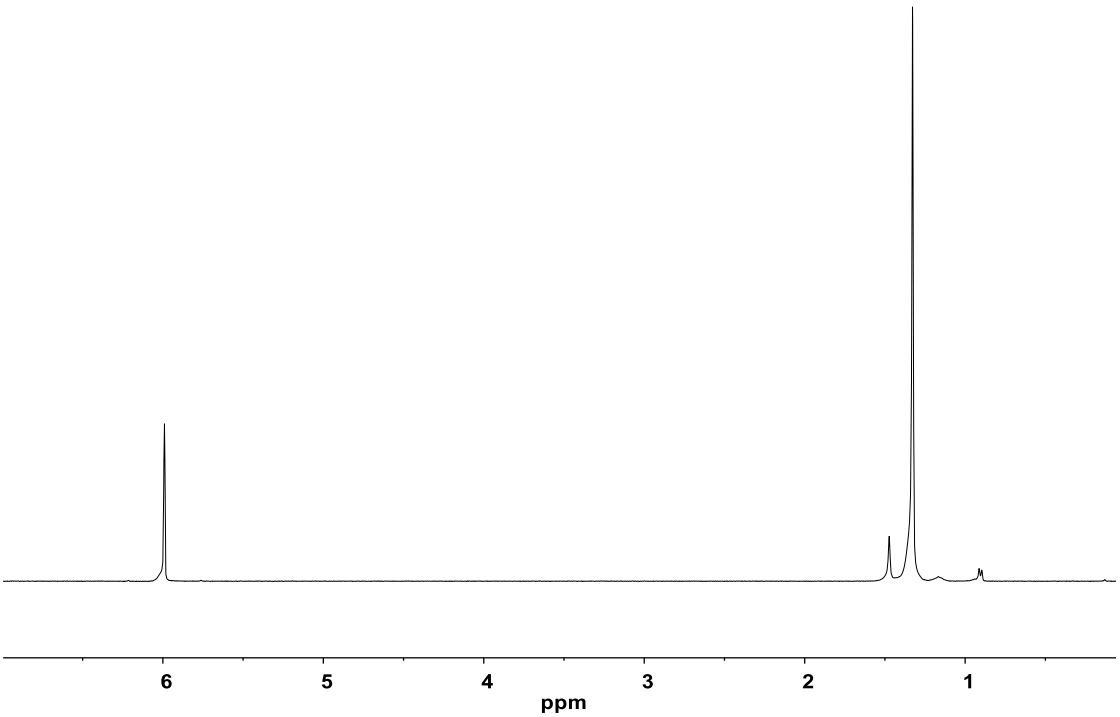


Figure S25. Representative ^{1}H NMR of polyethylene (Table 1, Entry 6) (catalyst **2** + reductant)

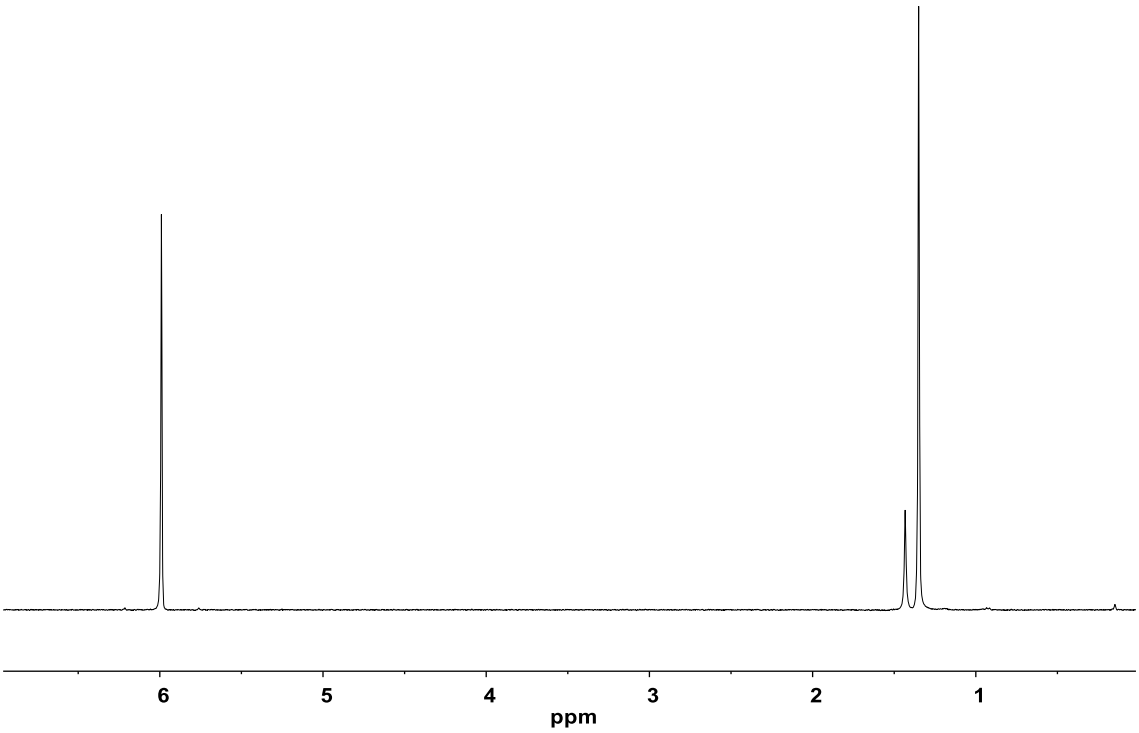


Figure S26. Representative ^{1}H NMR of polyethylene (Table 1, Entry 7) (catalyst **3** + oxidant)

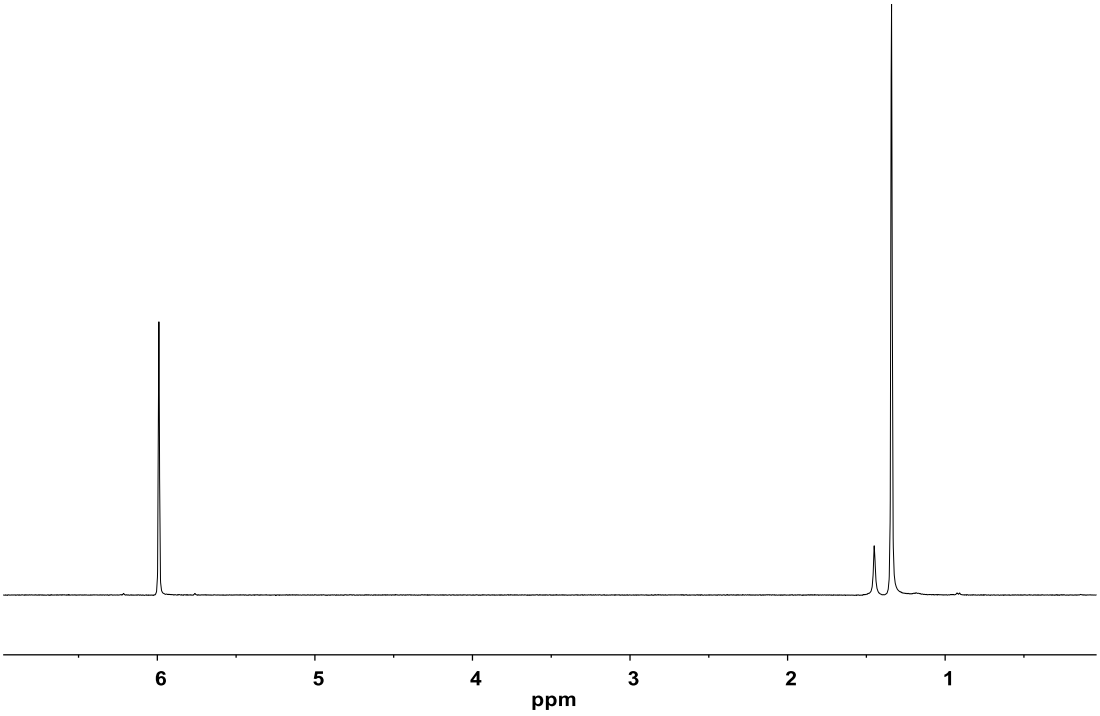


Figure S27. Representative ^{1}H NMR of polyethylene (Table 1, Entry 8) (catalyst **3**)

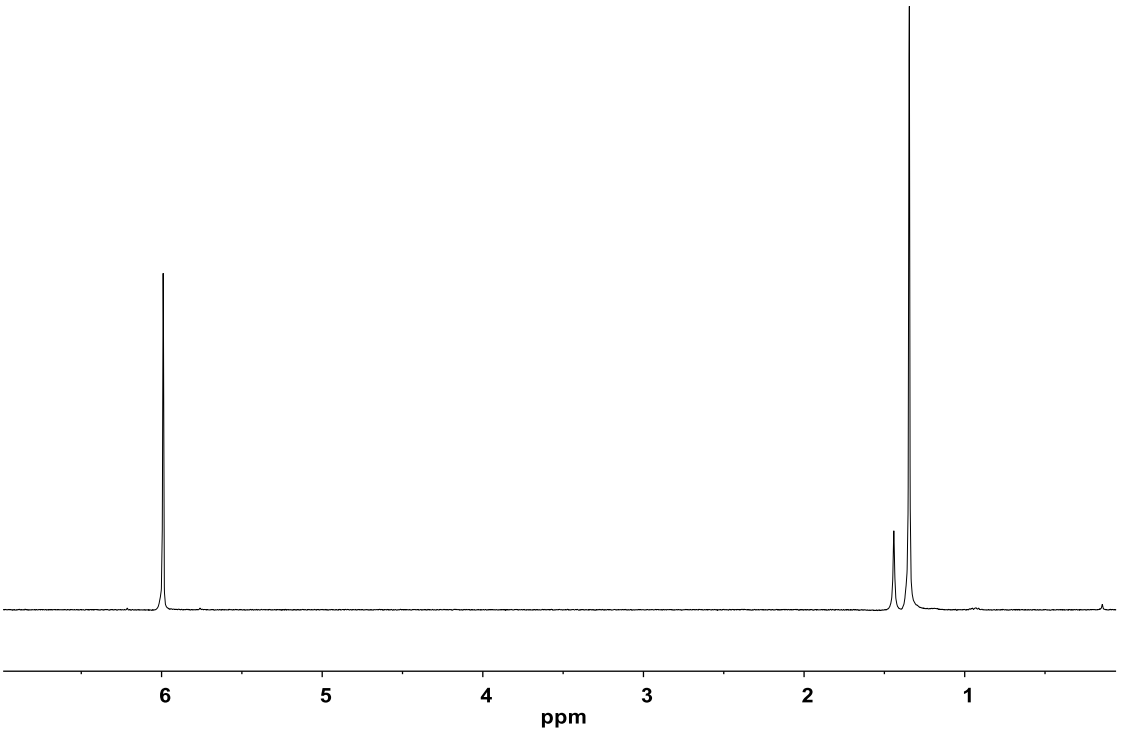


Figure S28. Representative ^{1}H NMR of polyethylene (Table 1, Entry 9) (catalyst **3** + reductant)

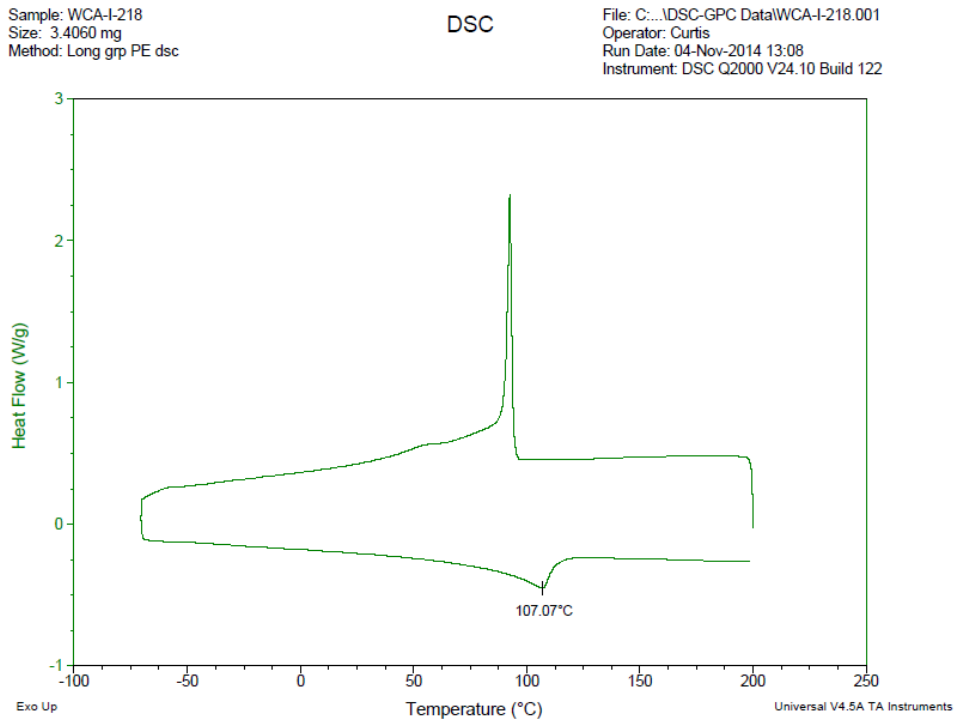


Figure S29. Representative DSC of polyethylene (Table 1, Entry 1) (catalyst **1** + oxidant)

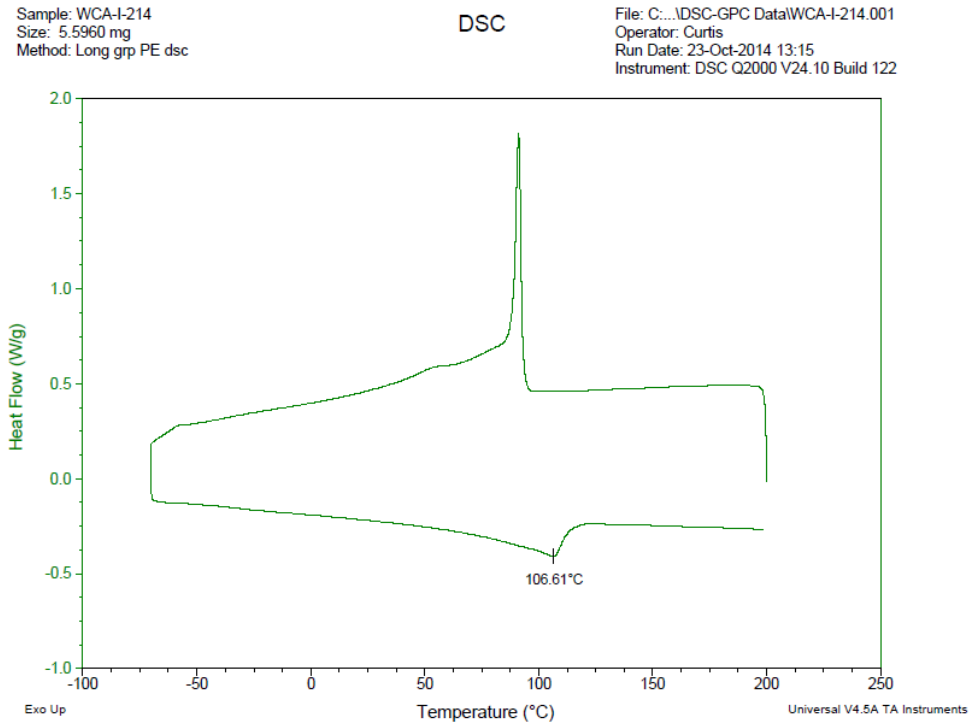


Figure 30. Representative DSC of polyethylene (Table 1, Entry 2) (catalyst **1**)

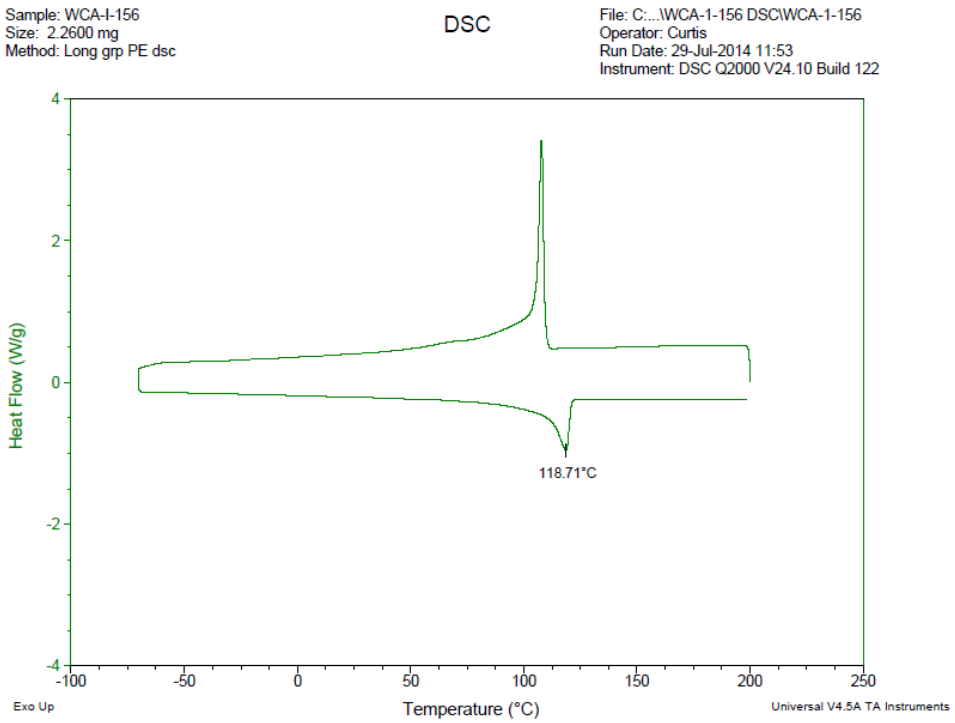


Figure 31. Representative DSC of polyethylene (Table 1, Entry 3) (catalyst **1** + reductant)

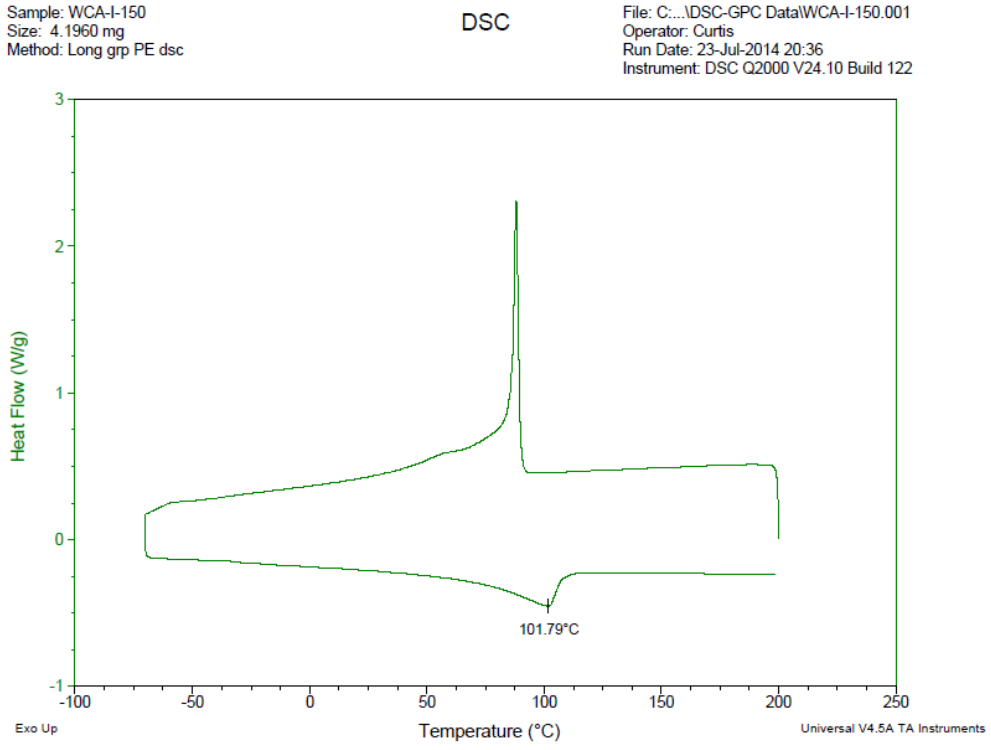


Figure S32. Representative DSC of polyethylene (Table 1, Entry 4) (catalyst **2** + oxidant)

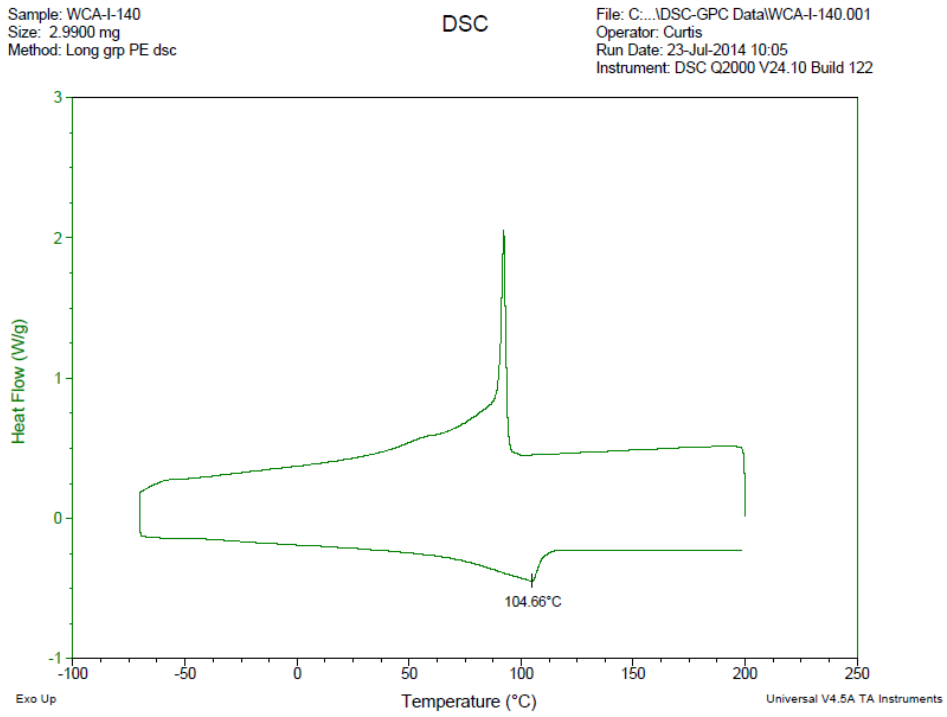


Figure S33. Representative DSC of polyethylene (Table 1, Entry 5) (catalyst **2**)

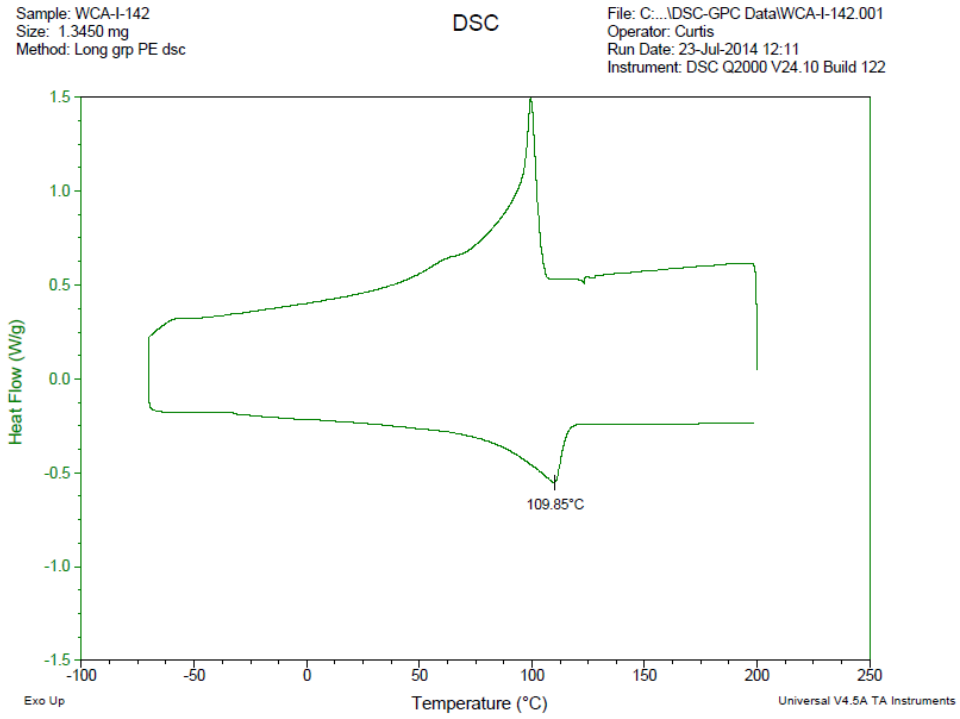


Figure S34. Representative DSC of polyethylene (Table 1, Entry 6) (catalyst **2** + reductant)

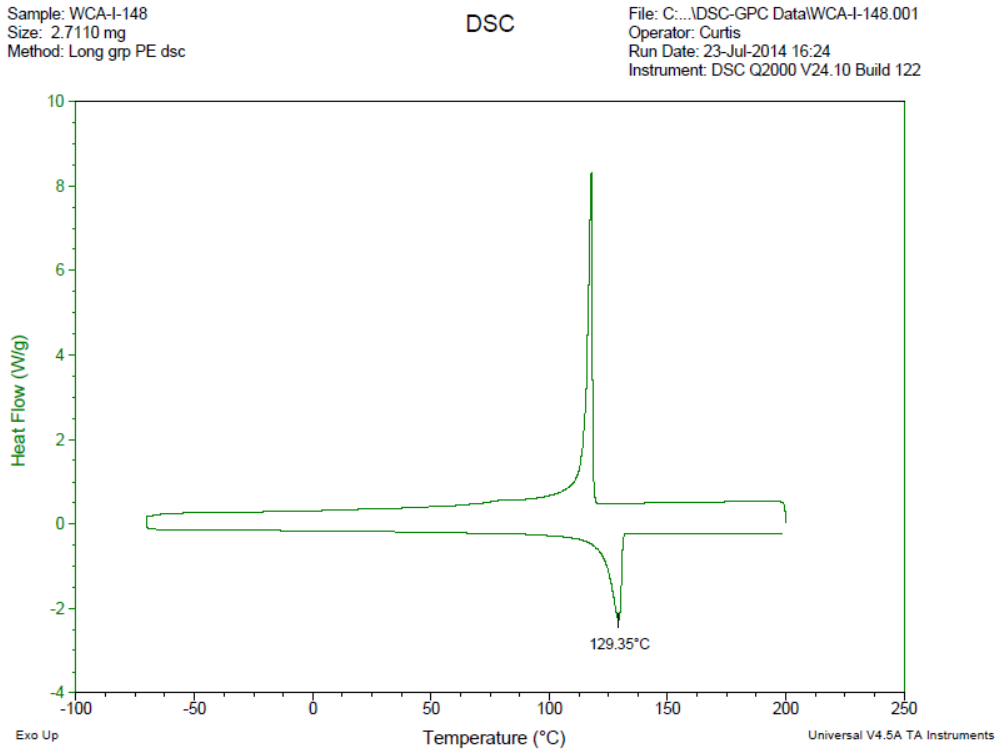


Figure S35. Representative DSC of polyethylene (Table 1, Entry 7) (catalyst **3** + oxidant)

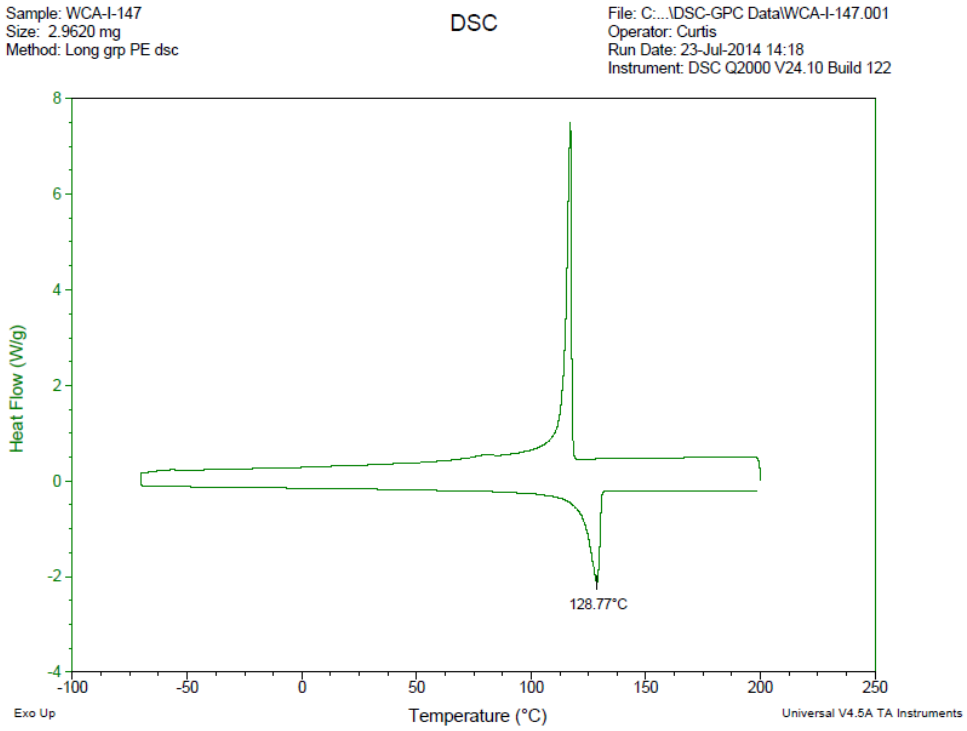


Figure S36. Representative DSC of polyethylene (Table 1, Entry 8) (catalyst **3**)

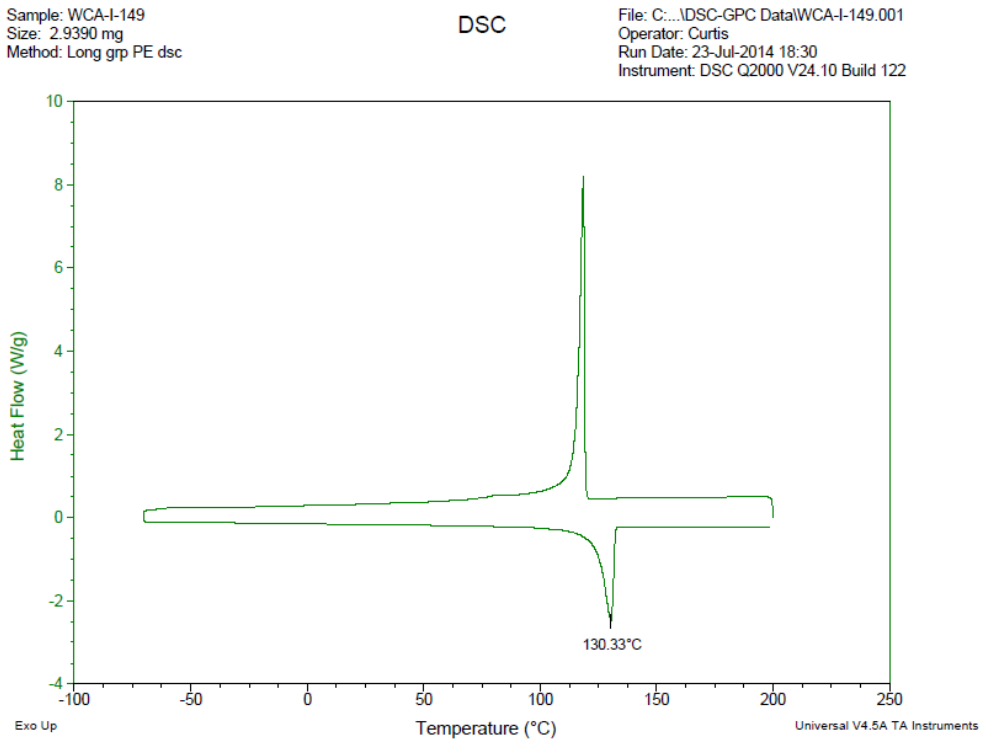


Figure S37. Representative DSC of polyethylene (Table 1, Entry 9) (catalyst **3** + reductant)

X-Ray Crystallographic Data

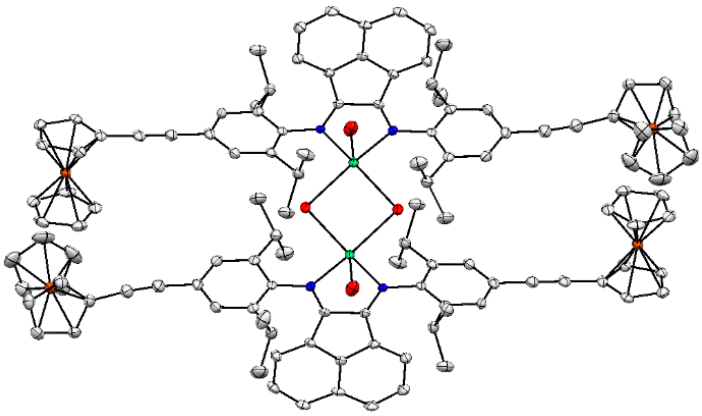
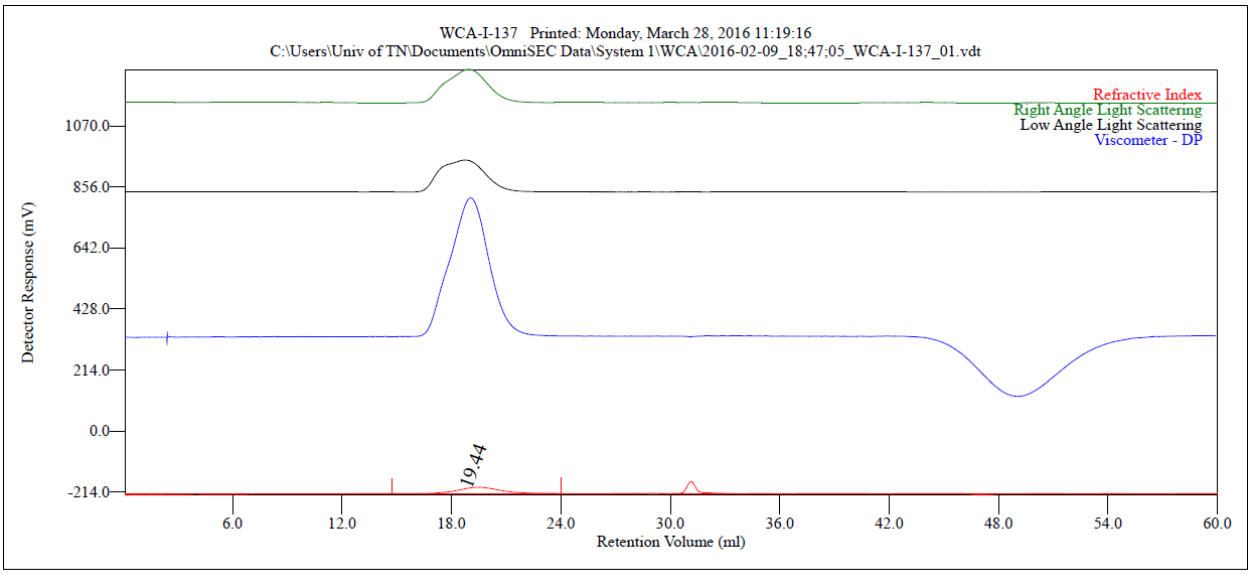


Figure S38. ORTEP representation of catalyst **1** with thermal ellipsoids drawn at 50% probability. Hydrogens were omitted for clarity. X-ray quality single crystals of complex **1** were grown overnight at ambient temperature using vapor diffusion of pentanes into a dichloromethane solution. Crystal data for $C_{120}H_{112}Br_4Fe_4N_4Ni_2 \cdot 2CH_2Cl_2$ (2438.77 g/mol); monoclinic; space group P-2_1/n; a = 13.5548(19) Å; b = 31.106(4) Å; c = 13.8370(19) Å; α = 90°; β = 91.823(2)°; γ = 90°; V = 5831.1(2) Å^3; Z = 2; T = 273(2) K; λ = 0.71073 Å; μ = 2.434 mm^{-1}; R_1 = 0.0455 (9913), wR_2 = 0.1817 (11922); GOF = 0.786.

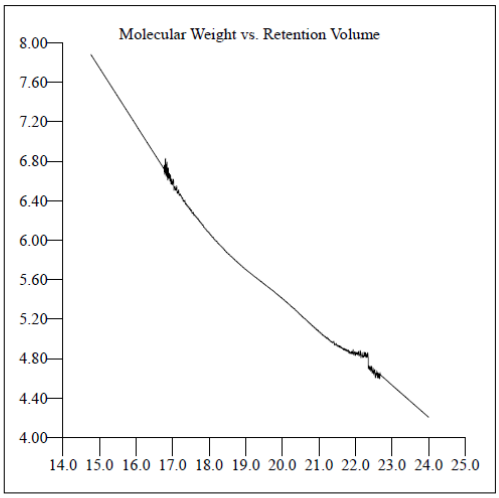


Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.440
Mn - (Daltons)	234,958
Mw - (Daltons)	502,890
Mz - (Daltons)	1.231 e 6
Mp - (Daltons)	374,596
Mw / Mn	2.140
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	4.0437
Rh(w) - (nm)	29.747
Rg(w) - (nm)	41.944
Wt Fr (Peak)	1.000
Mark-Houwink a	0.690
Mark-Houwink logK	-3.277
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	58.57
UV Area - (mvml)	0.00
RALS Area - (mvml)	309.03
LALS Area - (mvml)	322.71
IVDP Area - (mvml)	1210.35

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.990	0.000
Sample Recovery (%)	0.000	83.695
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 2-5-16-0013.vcm
Limits File	
Date Acquired	Feb 09, 2016 - 18:47:05
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	140.0
Column Temp. - (deg C)	140.0
OmniSEC Build Number	406



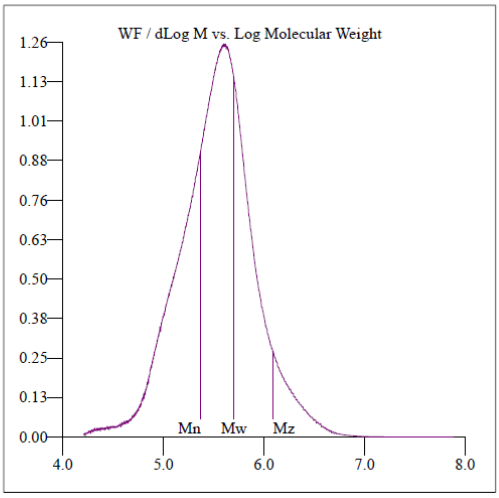
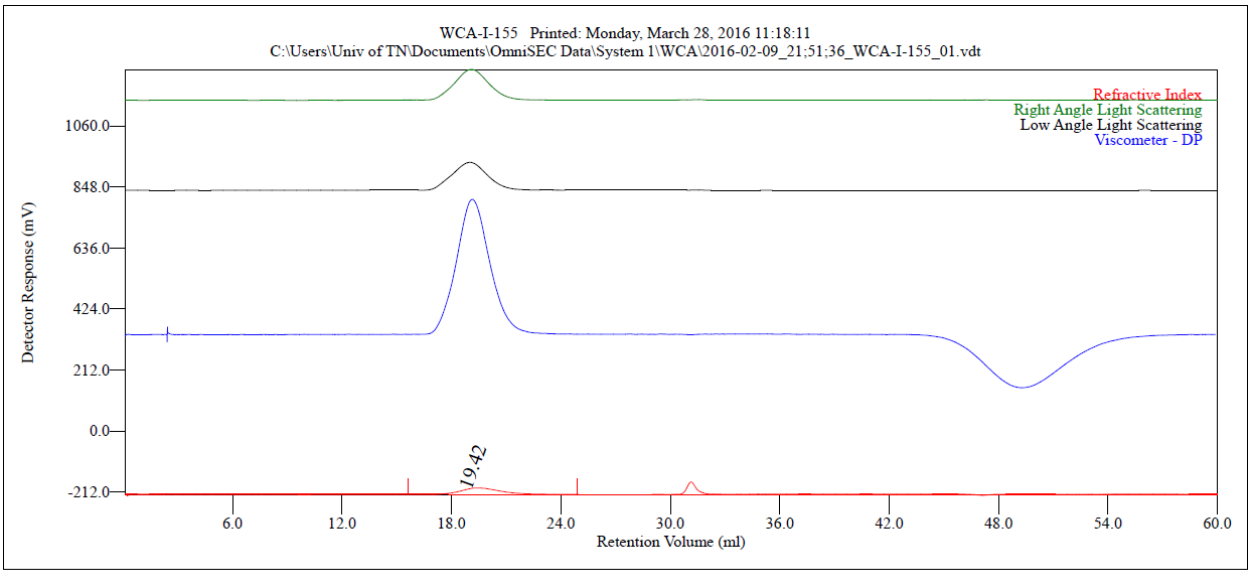


Figure S39. Representative GPC of polyethylene (Table 1, Entry 1) (catalyst **1** + oxidant)

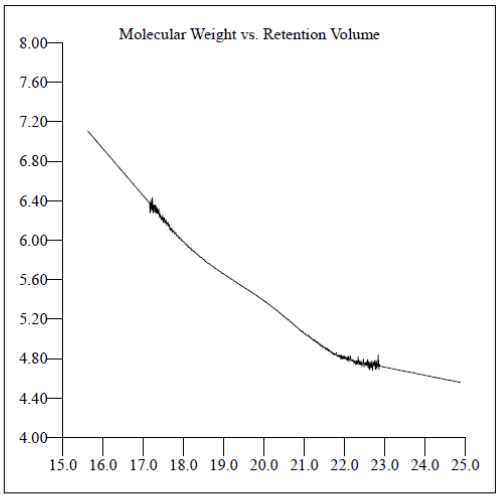


Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.420
Mn - (Daltons)	221,774
Mw - (Daltons)	367,169
Mz - (Daltons)	610,223
Mp - (Daltons)	349,405
Mw / Mn	1.656
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	3.6080
Rh(w) - (nm)	26.433
Rg(w) - (nm)	35.741
Wt Fr (Peak)	1.000
Mark-Houwink a	0.741
Mark-Houwink logK	-3.533
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	54.66
UV Area - (mvml)	0.00
RALS Area - (mvml)	236.75
LALS Area - (mvml)	218.14
IVDP Area - (mvml)	997.79

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.860	0.000
Sample Recovery (%)	0.000	83.575
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 2-5-16-0003.vcm
Limits File	
Date Acquired	Feb 09, 2016 - 21:51:36
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	140.0
Column Temp. - (deg C)	140.0
OmniSEC Build Number	406



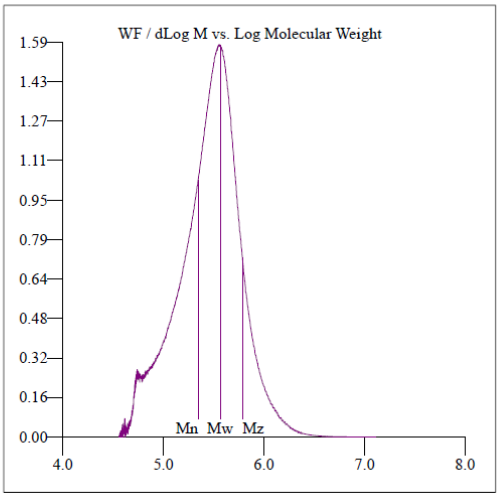
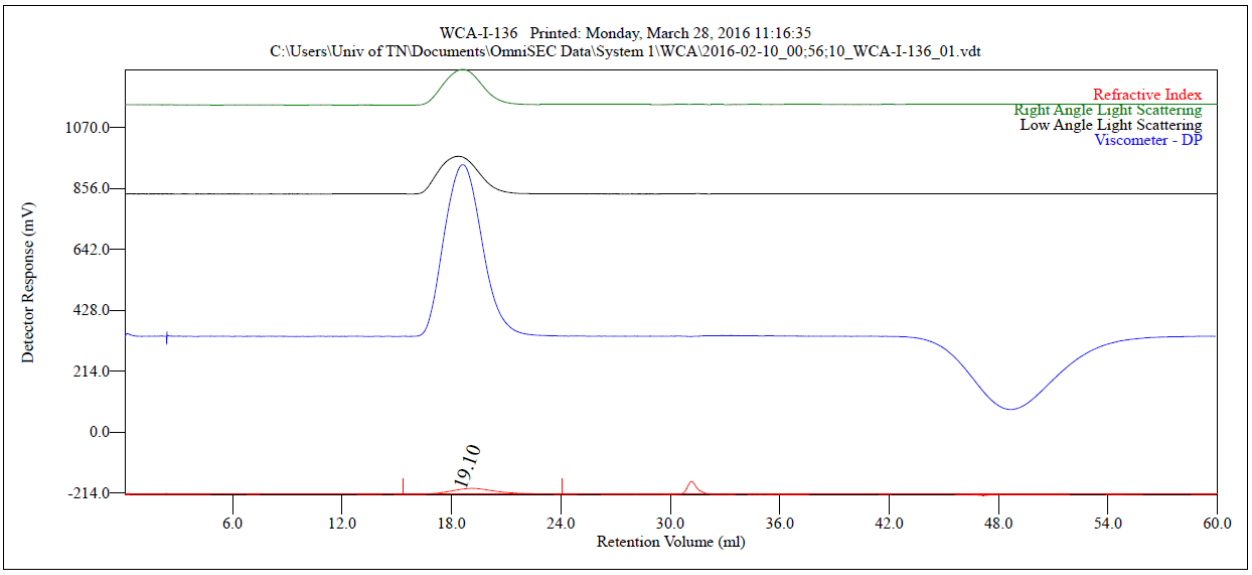


Figure S40. Representative GPC of polyethylene (Table 1, Entry 2) (catalyst **1**)

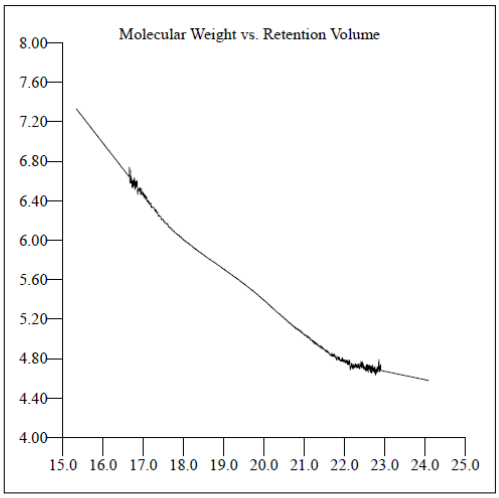


Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.103
Mn - (Daltons)	263,704
Mw - (Daltons)	552,824
Mz - (Daltons)	1.077 e 6
Mp - (Daltons)	474,241
Mw / Mn	2.096
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	5.0681
Rh(w) - (nm)	33.361
Rg(w) - (nm)	46.332
Wt Fr (Peak)	1.000
Mark-Houwink a	0.774
Mark-Houwink logK	-3.696
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	53.83
UV Area - (mvml)	0.00
RALS Area - (mvml)	305.51
LALS Area - (mvml)	338.31
IVDP Area - (mvml)	1453.20

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.910	0.000
Sample Recovery (%)	0.000	80.144
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 2-5-16-0011.vcm
Limits File	
Date Acquired	Feb 10, 2016 - 00:56:10
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	140.0
Column Temp. - (deg C)	140.0
OmniSEC Build Number	406



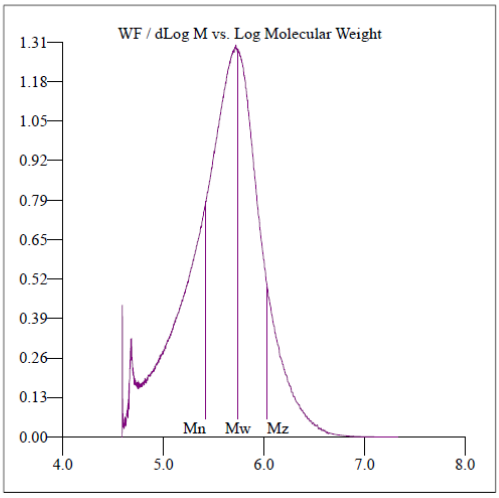
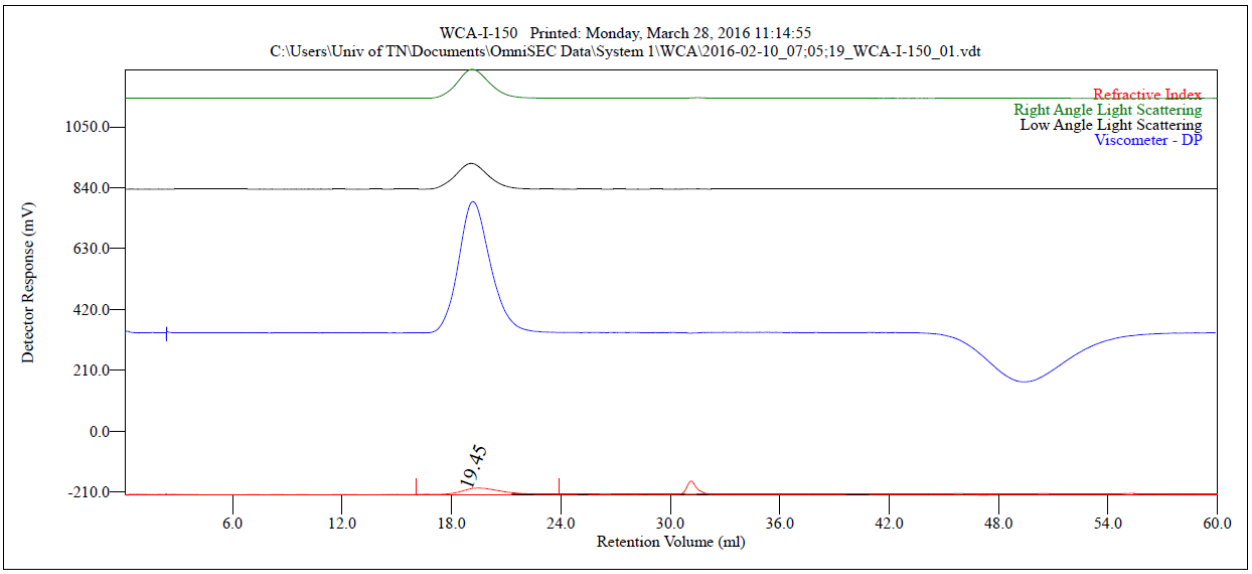


Figure S41. Representative GPC of polyethylene (Table 1, Entry 3) (catalyst **1** + reductant)

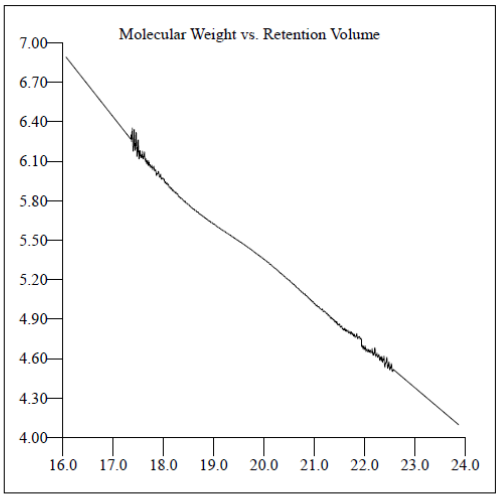


Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.450
Mn - (Daltons)	179,226
Mw - (Daltons)	313,578
Mz - (Daltons)	481,493
Mp - (Daltons)	321,210
Mw / Mn	1.750
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	3.3635
Rh(w) - (nm)	24.570
Rg(w) - (nm)	36.091
Wt Fr (Peak)	1.000
Mark-Houwink a	0.743
Mark-Houwink logK	-3.531
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	52.16
UV Area - (mvml)	0.00
RALS Area - (mvml)	203.77
LALS Area - (mvml)	184.84
IVDP Area - (mvml)	919.00

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.830	0.000
Sample Recovery (%)	0.000	81.048
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 2-5-16-0006.vcm
Limits File	
Date Acquired	Feb 10, 2016 - 07:05:19
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	140.0
Column Temp. - (deg C)	140.0
OmniSEC Build Number	406



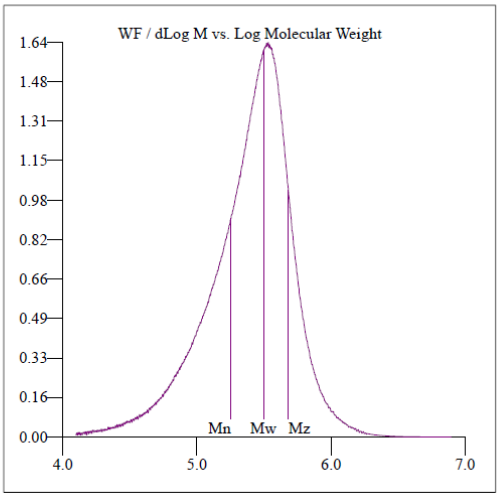
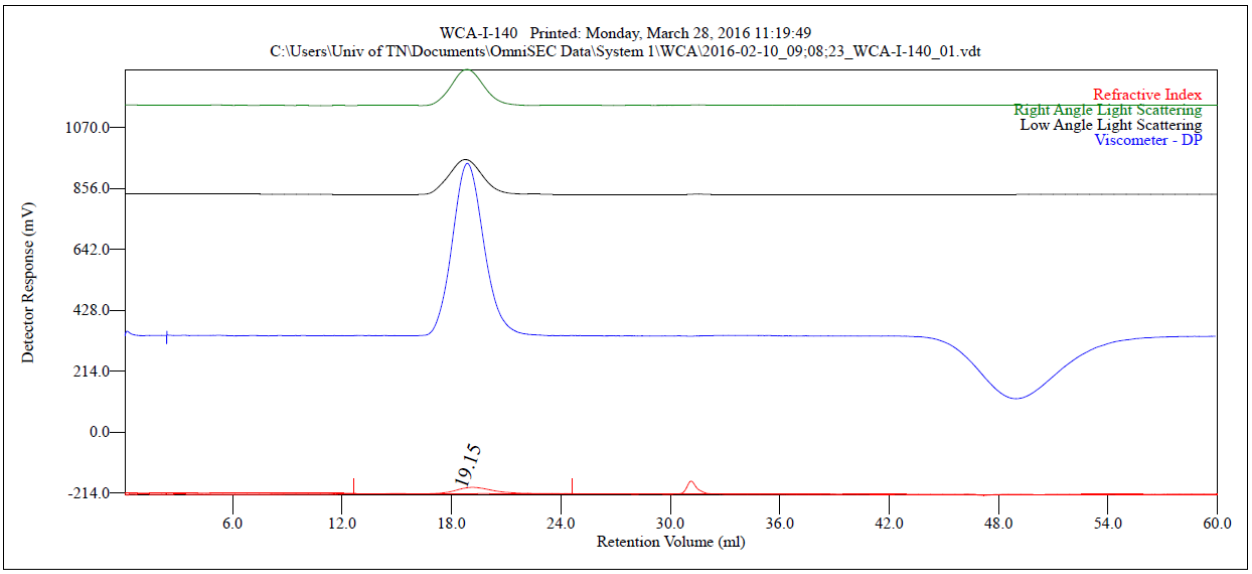


Figure S42. Representative GPC of polyethylene (Table 1, Entry 4) (catalyst **2** + oxidant)

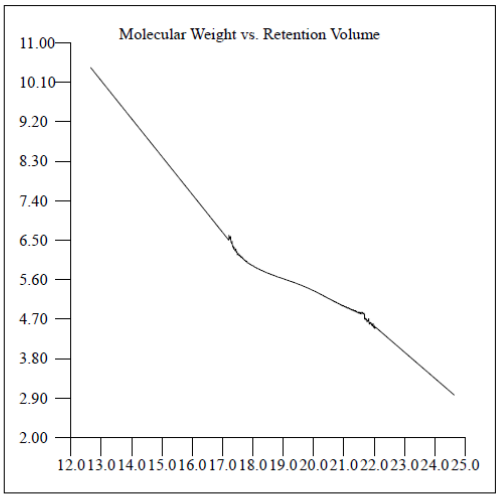


Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.153
Mn - (Daltons)	198,510
Mw - (Daltons)	397,860
Mz - (Daltons)	767,370
Mp - (Daltons)	382,832
Mw / Mn	2.004
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	4.0531
Rh(w) - (nm)	28.271
Rg(w) - (nm)	42.872
Wt Fr (Peak)	1.000
Mark-Houwink a	0.744
Mark-Houwink logK	-3.538
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	45.07
UV Area - (mvml)	0.00
RALS Area - (mvml)	261.33
LALS Area - (mvml)	257.76
IVDP Area - (mvml)	1227.78

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.830	0.000
Sample Recovery (%)	0.000	70.037
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 2-5-16-0016.vcm
Limits File	
Date Acquired	Feb 10, 2016 - 09:08:23
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	140.0
Column Temp. - (deg C)	140.0
OmniSEC Build Number	406



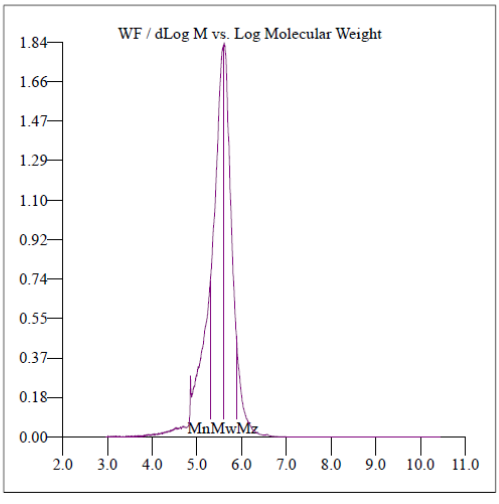
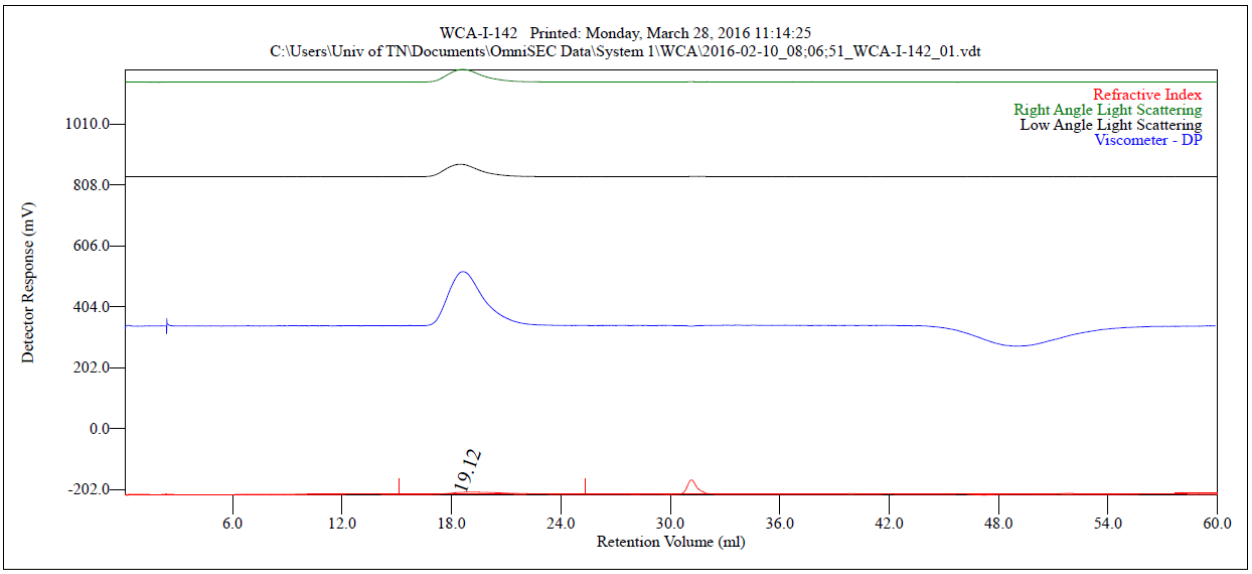


Figure S43. Representative GPC of polyethylene (Table 1, Entry 5) (catalyst **2**)

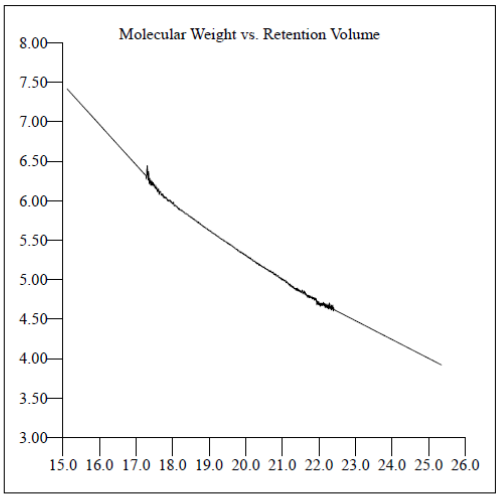


Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	19.117
Mn - (Daltons)	196,386
Mw - (Daltons)	384,557
Mz - (Daltons)	749,306
Mp - (Daltons)	387,585
Mw / Mn	1.958
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	3.7642
Rh(w) - (nm)	26.722
Rg(w) - (nm)	38.657
Wt Fr (Peak)	1.000
Mark-Houwink a	0.740
Mark-Houwink logK	-3.519
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	20.85
UV Area - (mvml)	0.00
RALS Area - (mvml)	92.48
LALS Area - (mvml)	90.19
IVDP Area - (mvml)	408.25

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	0.730	0.000
Sample Recovery (%)	0.000	81.227
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 2-5-16-0005.vcm
Limits File	
Date Acquired	Feb 10, 2016 - 08:06:51
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	140.0
Column Temp. - (deg C)	140.0
OmniSEC Build Number	406



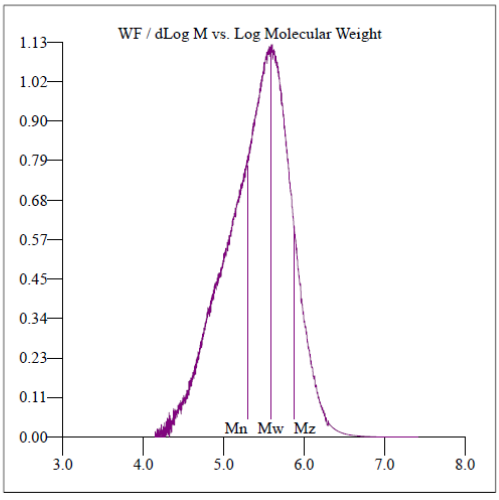
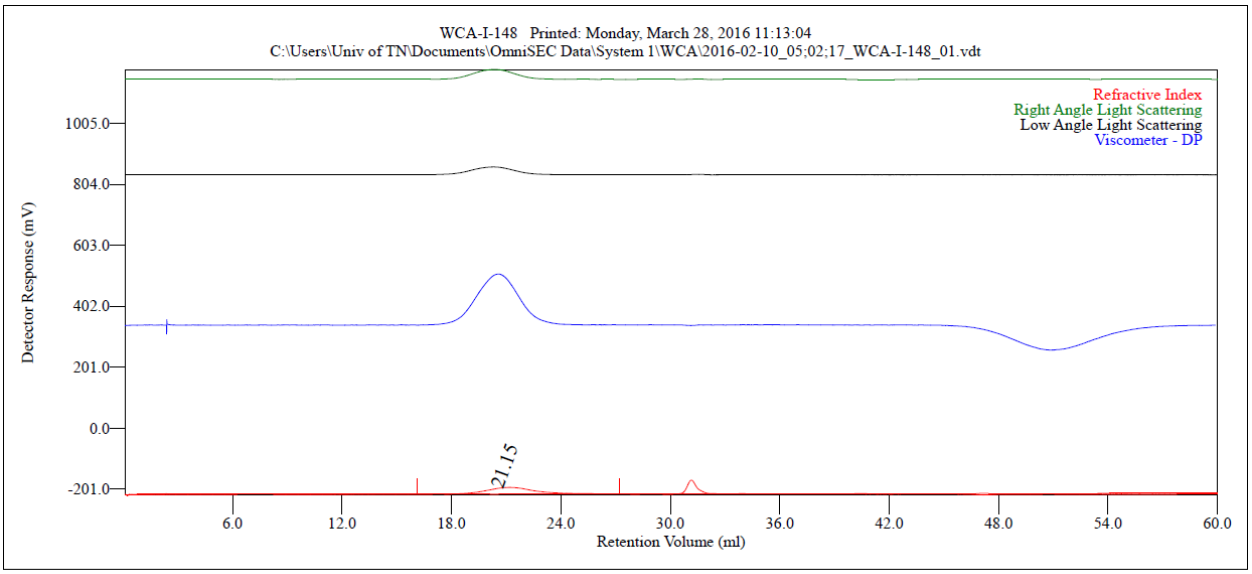


Figure S44. Representative GPC of polyethylene (Table 1, Entry 6) (catalyst **2** + reductant)

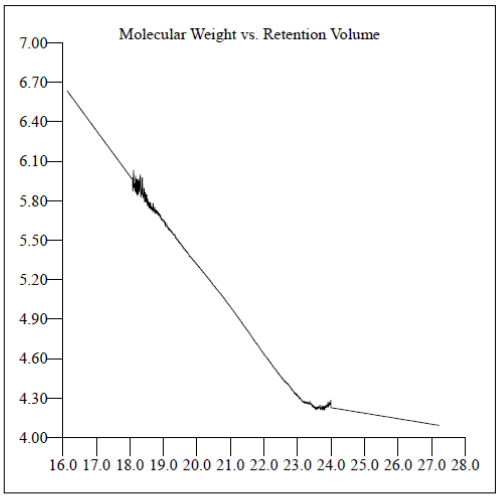


Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	21.153
Mn - (Daltons)	52,171
Mw - (Daltons)	113,307
Mz - (Daltons)	244,824
Mp - (Daltons)	86,888
Mw / Mn	2.172
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	1.5785
Rh(w) - (nm)	13.159
Rg(w) - (nm)	16.670
Wt Fr (Peak)	1.000
Mark-Houwink a	0.720
Mark-Houwink logK	-3.397
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	64.10
UV Area - (mvml)	0.00
RALS Area - (mvml)	89.31
LALS Area - (mvml)	69.90
IVDP Area - (mvml)	451.31

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.940	0.000
Sample Recovery (%)	0.000	93.964
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 2-5-16-0015.vcm
Limits File	
Date Acquired	Feb 10, 2016 - 05:02:17
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	140.0
Column Temp. - (deg C)	140.0
OmniSEC Build Number	406



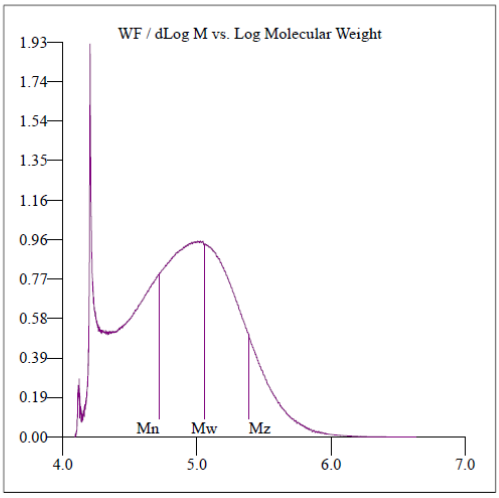
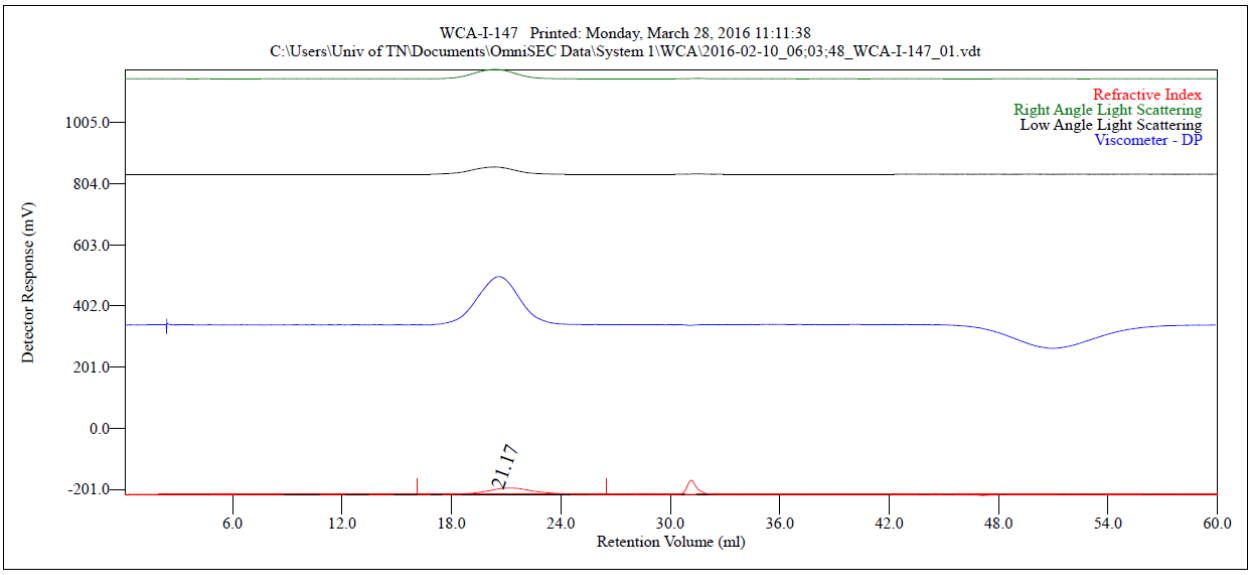


Figure S45. Representative GPC of polyethylene (Table 1, Entry 7) (catalyst **3** + oxidant)

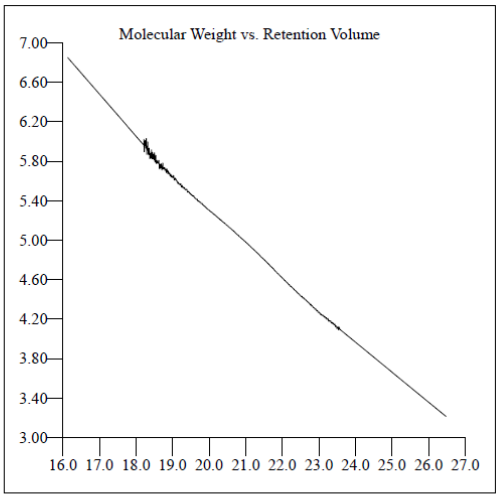


Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	21.167
Mn - (Daltons)	44,953
Mw - (Daltons)	110,173
Mz - (Daltons)	256,759
Mp - (Daltons)	83,299
Mw / Mn	2.451
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	1.5505
Rh(w) - (nm)	12.959
Rg(w) - (nm)	18.743
Wt Fr (Peak)	1.000
Mark-Houwink a	0.695
Mark-Houwink logK	-3.276
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	59.00
UV Area - (mvml)	0.00
RALS Area - (mvml)	82.90
LALS Area - (mvml)	66.06
IVDP Area - (mvml)	425.43

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.860	0.000
Sample Recovery (%)	0.000	90.211
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 2-5-16-0007.vcm
Limits File	
Date Acquired	Feb 10, 2016 - 06:03:48
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	140.0
Column Temp. - (deg C)	140.0
OmniSEC Build Number	406



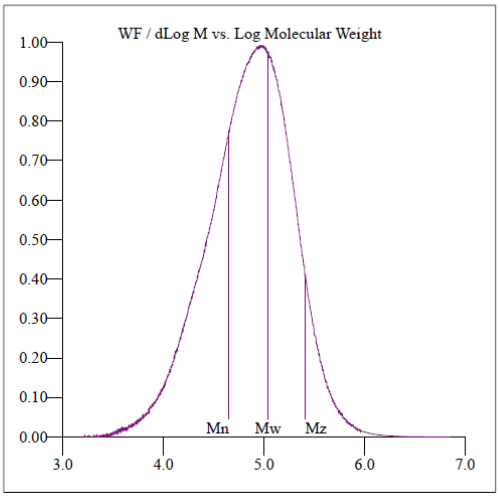
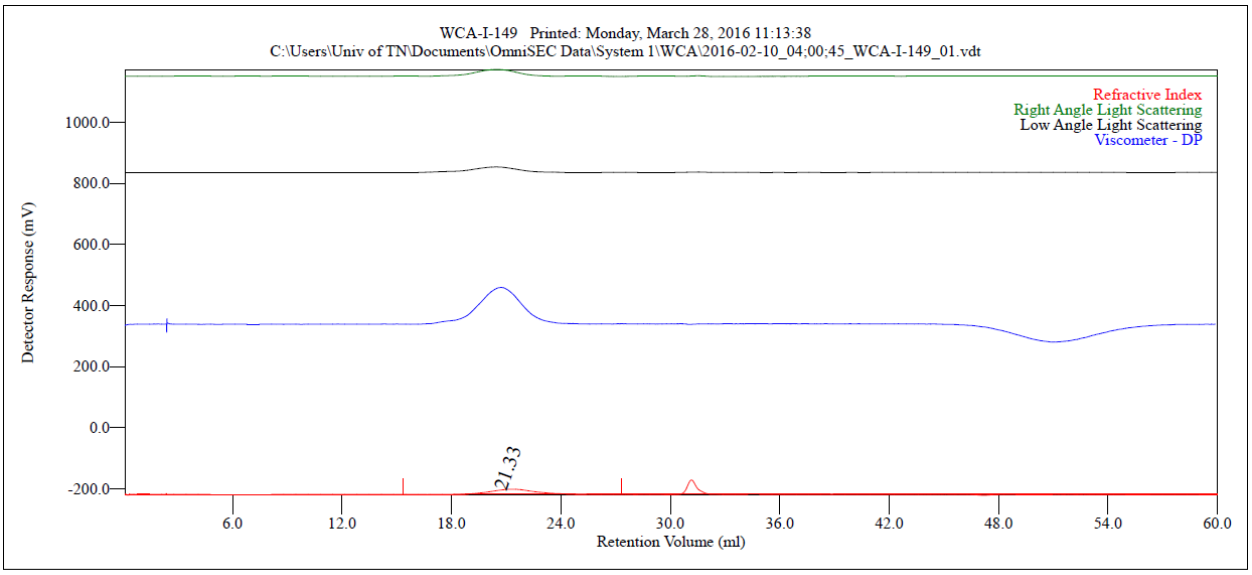


Figure S46. Representative GPC of polyethylene (Table 1, Entry 8) (catalyst **3**)

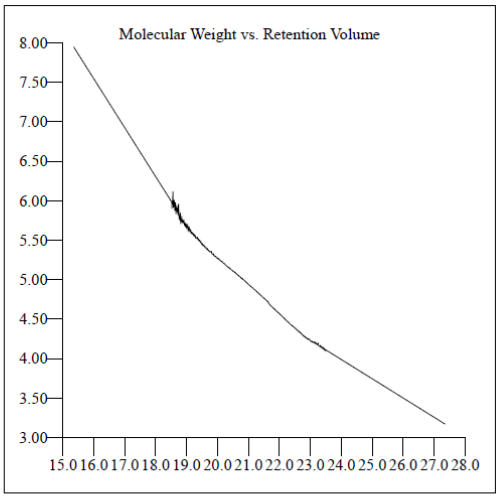


Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	21.333
Mn - (Daltons)	44,750
Mw - (Daltons)	95,893
Mz - (Daltons)	420,881
Mp - (Daltons)	66,211
Mw / Mn	2.143
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	1.3838
Rh(w) - (nm)	11.850
Rg(w) - (nm)	21.158
Wt Fr (Peak)	1.000
Mark-Houwink a	0.690
Mark-Houwink logK	-3.251
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	44.81
UV Area - (mvml)	0.00
RALS Area - (mvml)	61.66
LALS Area - (mvml)	50.64
IVDP Area - (mvml)	325.04

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.550	0.000
Sample Recovery (%)	0.000	82.216
dn/dc - (ml/g)	0.1040	0.0000
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	Long Group 2-5-16-0009.vcm
Limits File	
Date Acquired	Feb 10, 2016 - 04:00:45
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	CLM6210 - HT X 3
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	140.0
Column Temp. - (deg C)	140.0
OmniSEC Build Number	406



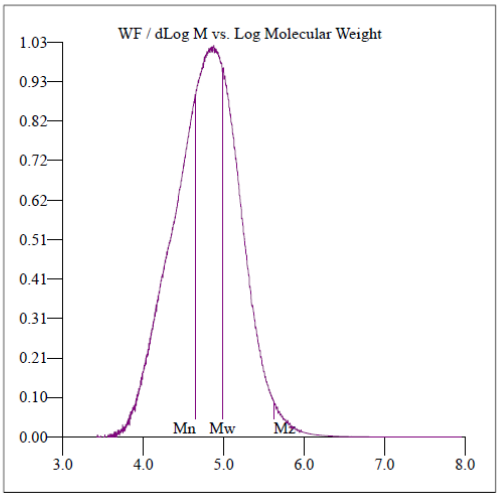


Figure S47. Representative GPC of polyethylene (Table 1, Entry 9) (catalyst **3** + reductant)

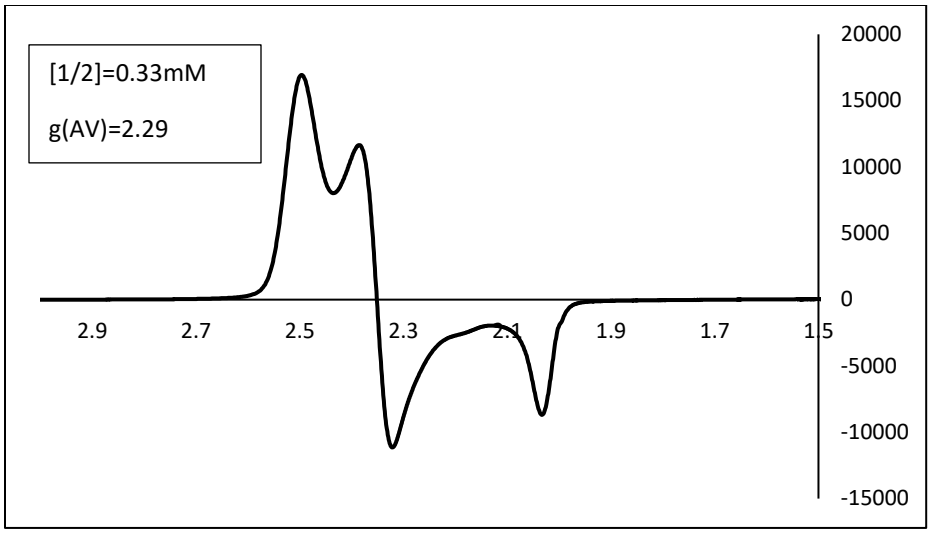


Figure S48. EPR spectrum of **1** in toluene at 120 K following addition of cobaltocene. (g_{xx}=2.49 G; g_{yy}=2.34 G; g_{zz}=2.03) Approximate quantified spin concentration obtained using SpinCount based on 0.5mM sample of **1** with 1 eq of Cobaltocene added.

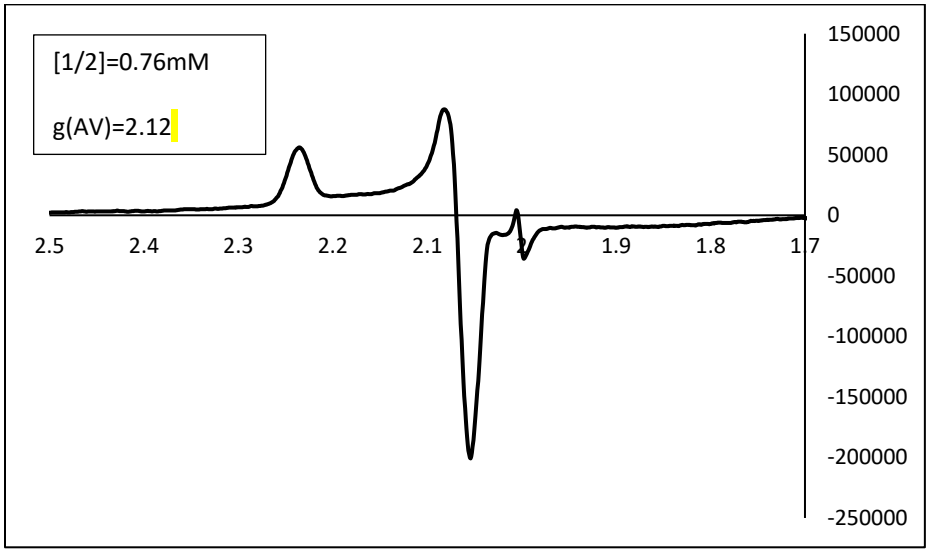


Figure S49. EPR spectrum of **1** in toluene at 120 K following addition of $AgBAr^F$. (g_{xx}=2.23 G; g_{yy}=2.07 G; g_{zz}=2.05) The peak at 2.0 corresponds to a small amount of Ag present after the solution was filtered. Approximate quantified spin concentration obtained using SpinCount software based on 0.5mM sample of **1** with 2 eq of $AgBAr^F$ added.

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