Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for:

Ethylene Polymerization Catalyzed by Bridging Ni/Zn Heterobimetallics

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Received January XXX, 2017. *E-mail: itonks@umn.edu*

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Synthesis and Characterization of Complexes 2 – 5.

General Materials, Considerations and Instrumentation

All air- and moisture-sensitive compounds were manipulated in a glovebox under a nitrogen atmosphere. All solvents were dried in a Glass Contour Solvent System (activated alumina) and liquid reagents were passed through activated basic alumina and titrated with a stock solution of Na/benzophenone where compatible to ensure dryness. Ultra high purity ethylene (99.9%) was purchased from Airgas, and oxygen and water were further removed by using a PUR-Gas In-Line Purifier System from Matheson. $NiBr_2 \cdot H_2O$ and $ZnBr_2$ were purchased from Sigma-Aldrich and dried at 260 and 180 ℃ respectively under high vacuum line for 24 hours. NaH (60 wt% dispersion in mineral oil) was purchased from Sigma-Aldrich and washed by hexanes in the glovebox to remove oil prior to use. 2,6-diformylphenol[1], $Ni(\eta^3\text{-}C_4H_8)_2$[2], (tmeda)Ni(o-tolyl)Cl[3], $(DME)NiBr_2$[4] were prepared according to literature procedure.

^1H and ^{13}C spectra of ligand and complexes were collected on Bruker Avance III HD NanoBay 400 MHz, Bruker Avance III HD 500 MHz, or Varian Inova 500 MHz spectrometers. ^{13}C spectra of polyethylene were collected at 100 ℃ in d_2-1,1,2,2-tetrachloroethane on Agilent/Varian VNMR 600 MHz spectrometer. X-ray crystallography was collected on Data collection was carried out on a Bruker APEX II CCD diffractometer with a 0.71073 Å Mo Kα source or on a Bruker-AXS D8 Venture diffractometer with a 1.54178 Å Cu Kα source. GPC analyses were carried out on an Agilent PL-GPC 220 high temperature GPC/SEC system at 135 ℃ in 1,2,4-trichlorobenzene calibrated with polystyrene standards.

Synthesis of 2,6-bis(((2,6-diisopropylphenyl)imino)methyl)phenol, $C_{32}H_{40}N_2O$, H(NON) (1).

To a stirring solution of 2,6-diformylphenol (950 mg 6.3 mmol, 1 equiv.) and formic acid (0.2 mL, 5.3 mmol, 0.84 equiv.) in methanol (100 mL), 2,6-diisopropylaniline (3.6 mL, 19 mmol, 3 equiv.) was added quickly at ambient temperature. After the mixture turned cloudy, the mixture was stirred for another 3 hours. The volatiles were removed in vacuo and the precipitate was collected via filtration and washed with minimal cold methanol at -78 ℃ to yield bright yellow powder of **1** (1.81 g, 61% yield). ^1H NMR ($CDCl_3$, 500 MHz): δ 13.63 (s, 1H), 8.73 (br, 1H), 8.40 (br, 2H), 7.55 (br, 1H), 7.21-7.09 (m, 7H), 3.03 (sep, 4H, J = 6.8 Hz), 1.21 (d, 24H, J = 6.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ166.74, 161.63, 157.47, 138.31, 135.40, 131.09, 125.53, 124.47, 123.15, 119.10, 28.07, 23.62 ppm. Anal. Calcd (%) for $C_{32}H_{40}N_2O$: C, 82.01; H, 8.60; N, 5.98. Found: C, 81.86; H, 8.53; N, 5.82.

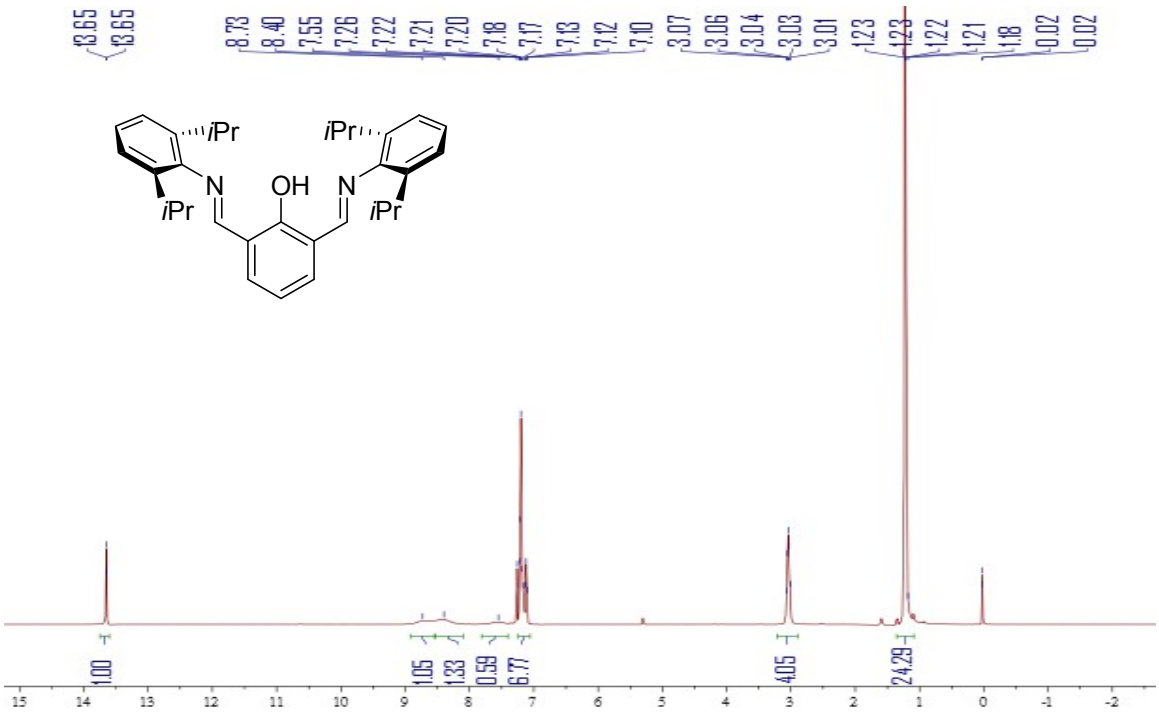

Figure S1: ^{1}H NMR spectrum of **1** in $CDCl_3$.

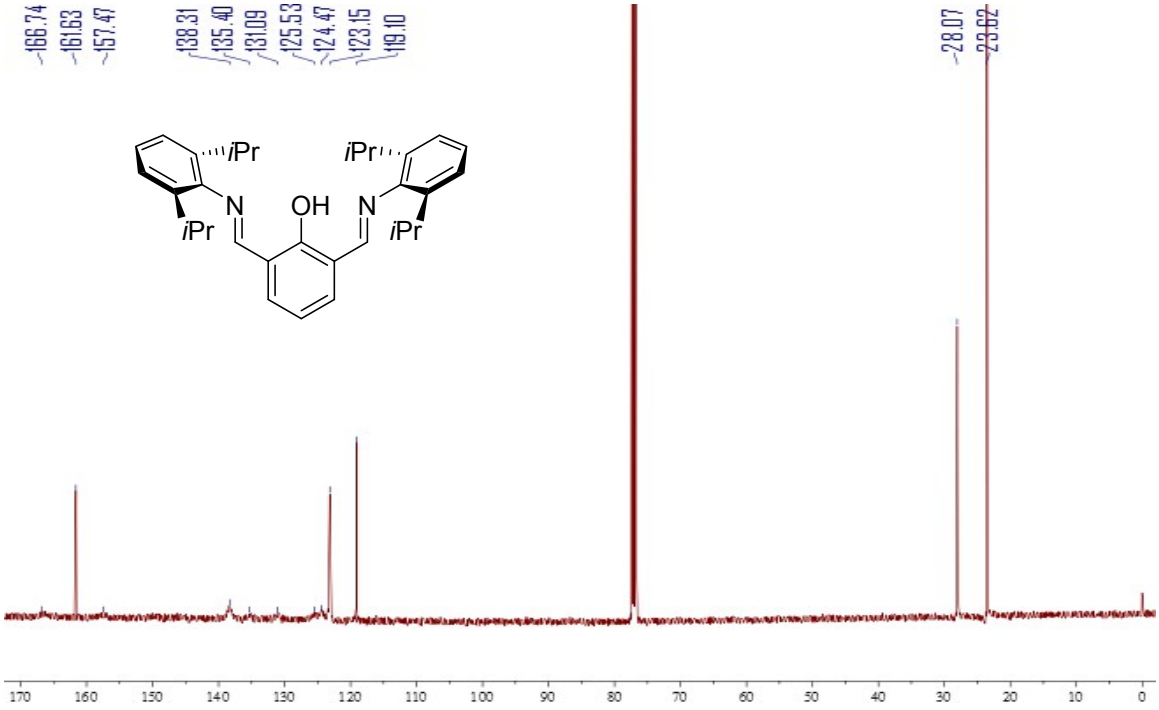

Figure S2: ^{13}C NMR spectrum of **1** in $CDCl_3$.

Synthesis of $C_{44}H_{51}N_3ONi$, (NON)Ni(*o*-tolyl)(py) (2)

In an inert atmosphere glovebox, a mixture of **1** (46.8 mg, 0.1 mmol, 1 equiv.) and NaH (10.3 mg, 0.43 mmol, , 4.3 equiv.) in THF (2 mL) was stirred at ambient temperature for 1 hour. The deprotonated ligand solution was then directly filtered into a solution of (tmeda)Ni(*o*-tolyl)Cl (30.6 mg, 0.1 mmol, 1 equiv.) and pyridine (30.0 ?L, 1.5 mmol, 15 equiv.) in THF (3 mL). After being stirred for another 2 hours, the mixture turned into a red orange solution, and NaCl precipitation was evident. Volatiles were removed *in vacuo*. The residue was then dissolved in minimal benzene and filtered to collect the filtrate. Volatiles of the filtrate were removed *in vacuo*. The crude product was washed with pentane to yield an orange solid (60.8 mg, 87% yield) Regioisomers (swapping position of tolyl and pyridine on Ni) were not separated (88:12). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.85 (s, 1H), 8.74 (dd, 1H, J = 7.5, 1.9 Hz), 8.61 (m, 2H), 7.60 (s, 1H), 7.13 (s, 1H), 7.08 (dd, 1H, J = 8.5, 6.7 Hz), 7.04 (dd, 1H, J = 7.7, 1.1 Hz), 7.02-6.99 (m, 3H), 6.95 (t, 1H, J = 7.7 Hz), 6.68 (dd, 1H, J = 7.7, 1.1 Hz), 6.59 (t, 1H, J = 7.5 Hz), 6.54 (m, 2H), 6.47 (m, 1H), 6.28 (tt, 1H, J = 7.6, 1.5 Hz), 6.02 (m, 2H), 4.78 (sep, 1H, J = 6.8 Hz), 3.29 (s, 3H), 3.22 (m, 3H), 1.72 (d, 3H, J = 6.9 Hz), 1.16 (d, 6H, J = 6.8 Hz), 1.02 (d, 6H, J = 6.8 Hz), 0.98 (d, 3H, J = 6.7 Hz), 0.94 (d, 3H, J = 6.7 Hz), 0.87 (d, 3H, J = 6.8 Hz) ppm. ^{13}C NMR (C_6D_6, 125 MHz): δ 167.51, 166.98, 159.28, 152.05, 151.41, 150.58, 149.35, 143.06, 141.41, 140.19, 138.09, 137.95, 136.45, 136.38, 133.56, 126.51, 126.19, 123.96, 123.43, 123.41, 123.16, 122.92, 122.79, 122.66, 122.15, 114.82, 29.33, 28.34, 28.09, 25.83, 25.56, 25.31, 23.75, 23.49, 23.09, 22.15 ppm. Anal. Calcd (%) for $C_{44}H_{51}N_3ONi$: C, 75.87; H, 7.38; N, 6.03. Found: C, 75.49; H, 7.52; N, 5.52.

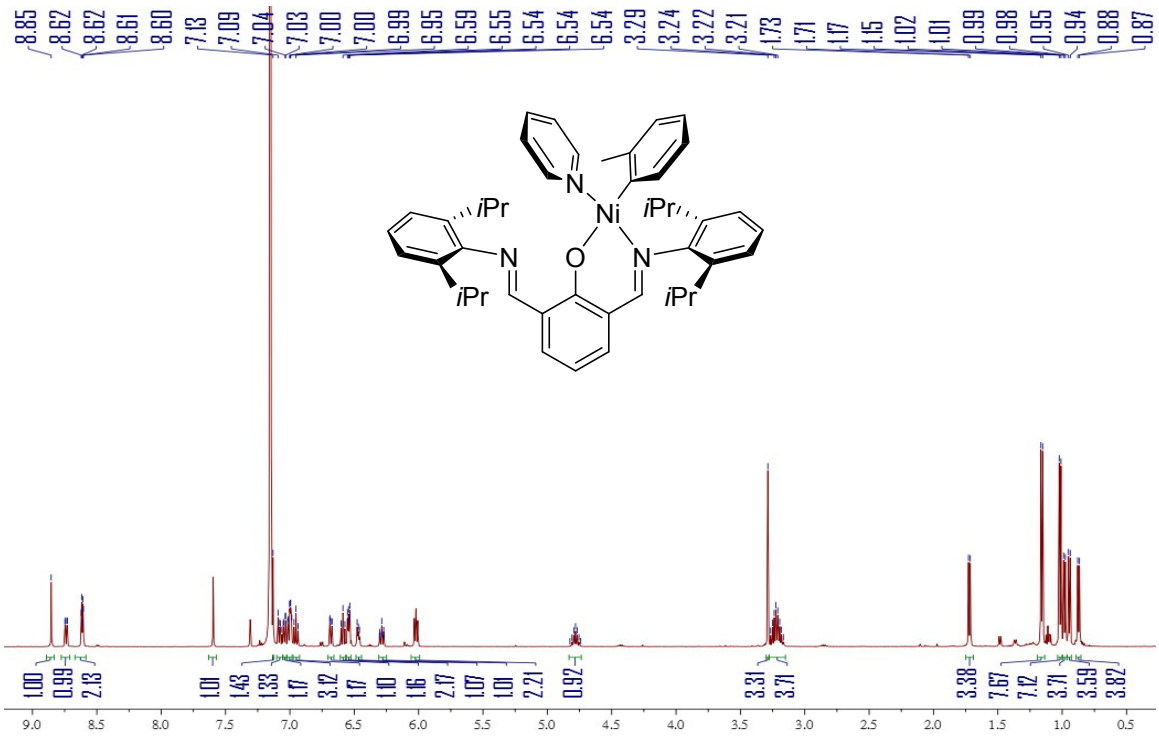

Figure S3: ^{1}H NMR spectrum of **2** in C_6D_6.

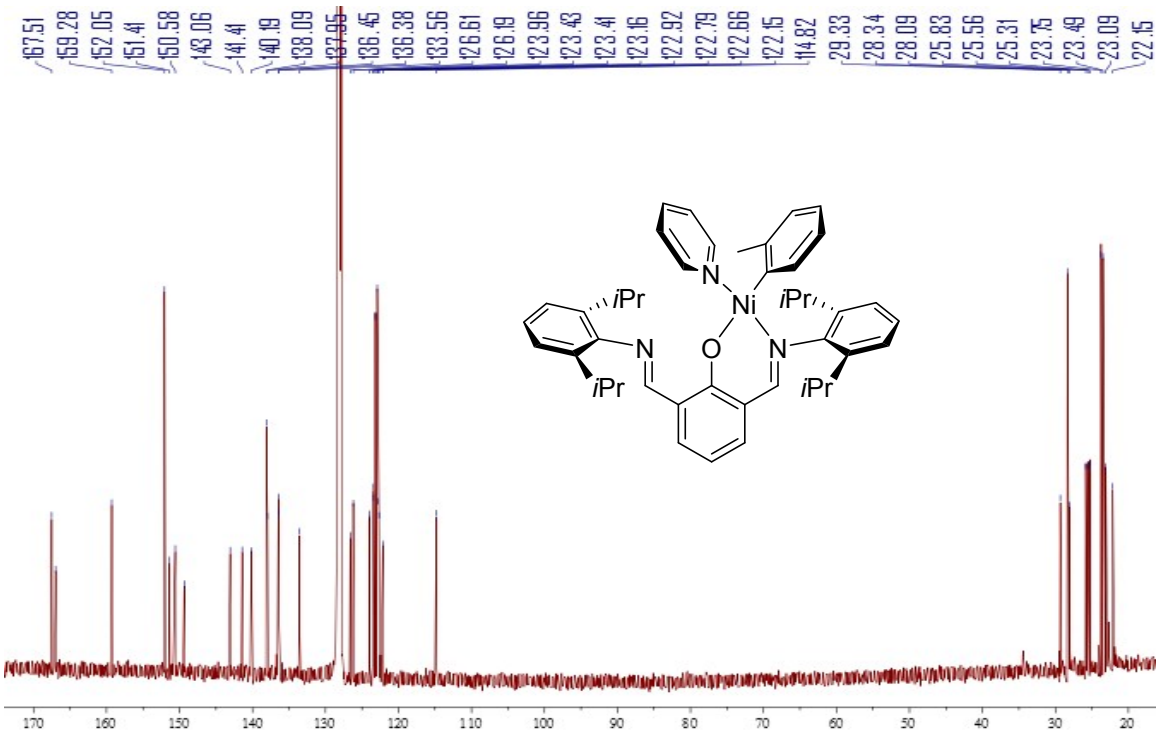

Figure S4: ^{13}C NMR spectrum of **2** in C_6D_6.

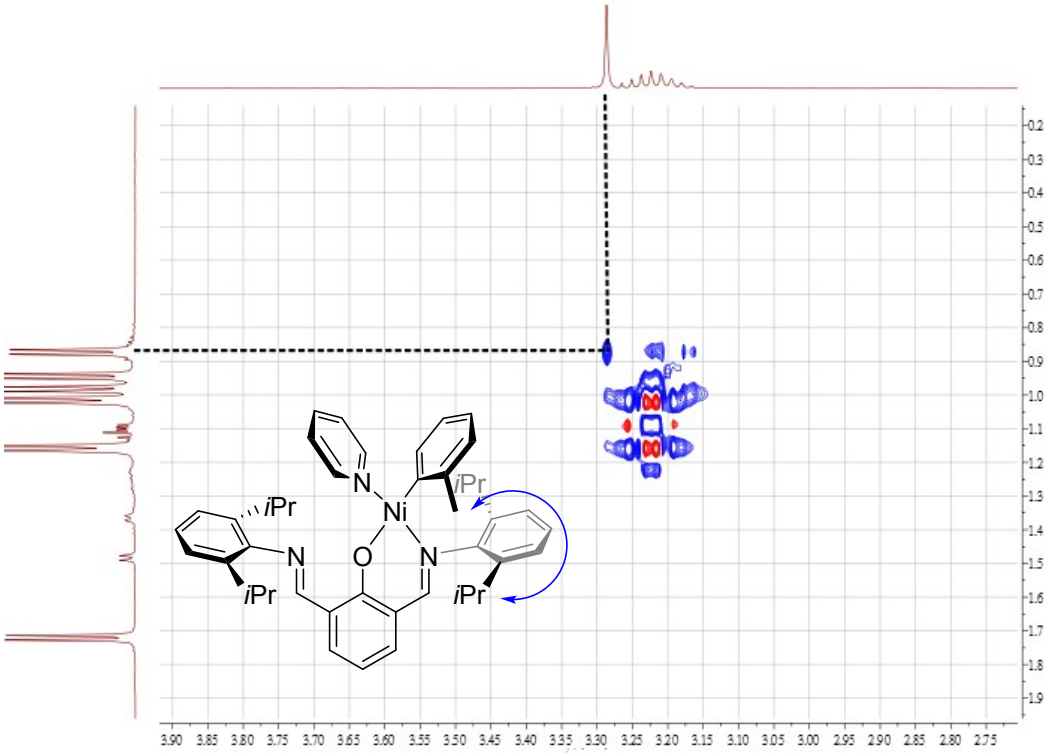

Figure S5: ^{1}H-^{1}H NOESY NMR spectrum of **2** in C_6D_6 showing the dominant regioisomer.

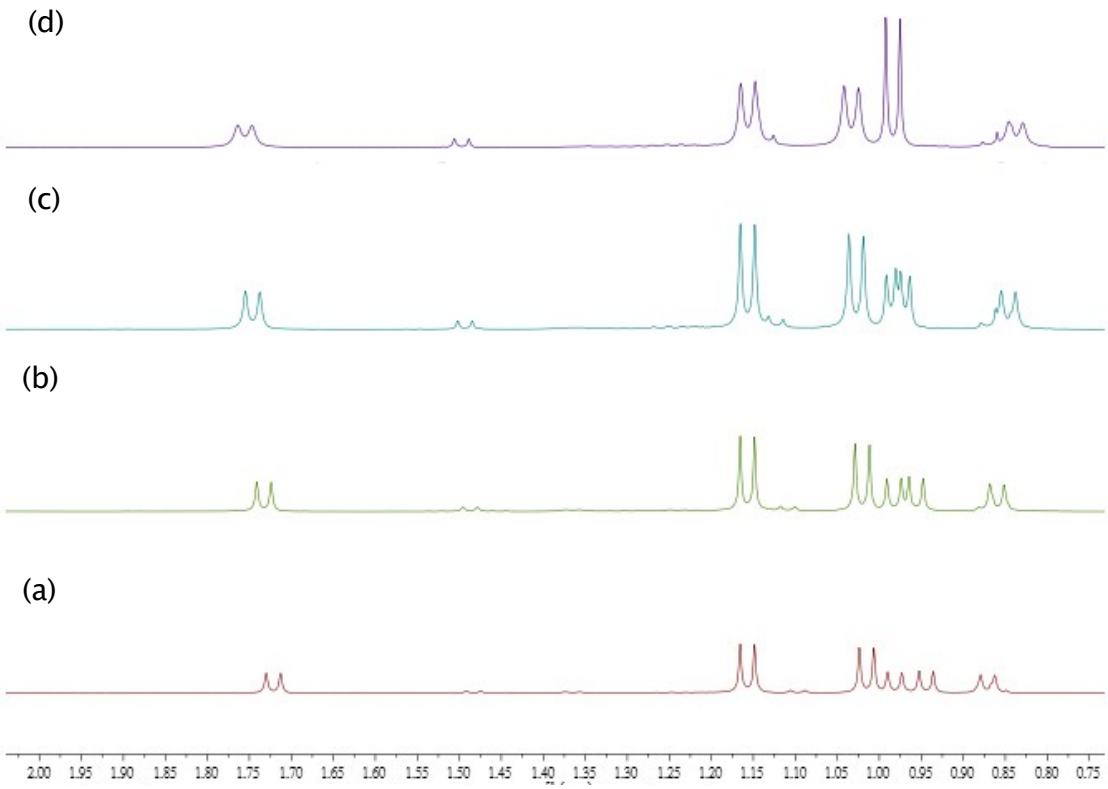

Figure S6: Variable temperature ^{1}H NMR spectra of **2** in C_6D_6 in the alkyl region: (a) RT, (b) 35 ℃, (c) 50 ℃, (d) 60 ℃.

This VT NMR shows that elevated temperature only results in the coalescence of two isopropyl peaks, which is same in the VT ^{1}H NMR of complex **5**.

Synthesis of $C_{36}H_{46}N_2ONi$, (NON)Ni(η^3-C_4H_7) (3).

1 (192 mg, 0.40 mmol, 1 equiv.) and Ni(η^3-methallyl)$_2$ (133.5 mg, 0.80 mmol, 2 equiv.) were dissolved in benzene (2 mL), and stirred at ambient temperature for 2 days. The volatiles were removed *in vacuo* and the residue triturated with hexanes (5 mL) to yield **3** as yellow powder that was collected by filtration. (150 mg, 64% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.80 (s, 1H), 8.30 (d, 1H, J = 7.3 Hz), 7.92 (s, 1H), 7.39-7.29 (m, 2H), 7.21-7.13 (m, 5H), 6.73 (t, 1H, J = 7.5 Hz), 3.91 (sep, 1H, J = 6.8 Hz), 3.36 (sep, 2H, J = 6.3 Hz), 3.13 (sep, 1H, J = 6.8 Hz), 2.99 (s, 1H), 2.62 (s, 1H), 2.30 (s, 3H), 1.46 (s, 1H), 1.37 (d, 6H, J = 4.3 Hz), 1.25-1.20 (m, 16H), 1.08 (d, 3H, J = 6.8 Hz) ppm. ^{13}C ($CDCl_3$, 125 MHz): δ 166.51, 165.04, 160.61, 152.03, 150.55, 140.05, 139.10, 138.38, 138.04, 132.46, 128.26, 126.88, 126.38, 123.79, 123.72, 123.41, 123.06, 120.41, 114.50, 60.73, 50.08, 28.37, 28.01, 25.51, 25.39, 23.92, 23.86, 23.07, 23.05, 22.67 ppm. Anal. Calcd (%) for $C_{36}H_{46}N_2ONi$: C, 74.36; H, 7.97; N, 4.82. Found: C, 74.29; H, 8.02; N, 4.68.

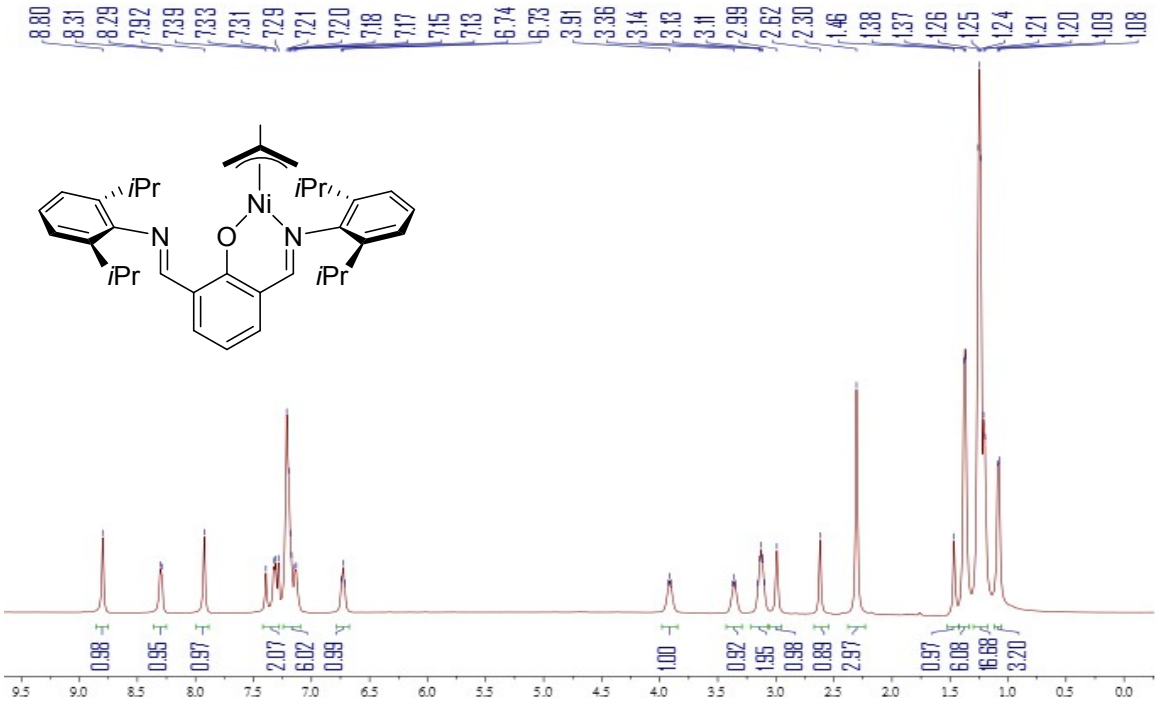

Figure S7: ^{1}H NMR spectrum of **3** in $CDCl_3$.

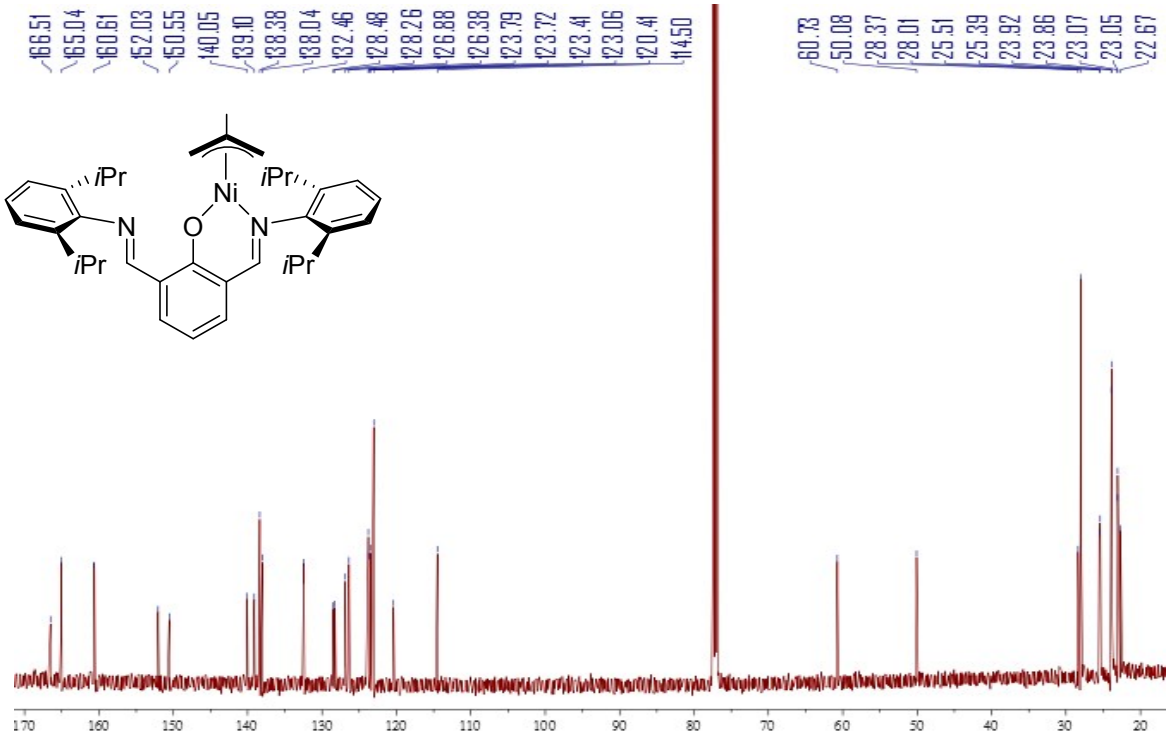

Figure S8: ^{13}C NMR spectrum of **3** in $CDCl_3$.

Synthesis of $C_{32}H_{40}N_2ONiBr_2$, H(NON)$NiBr_2$ (4)

THF (10 mL) was added to a mixture of solid $NiBr_2$ (63.1 mg, 0.29 mmol, 1 equiv.) and **1** (148 mg, 0.32 mmol, 1.1 equiv.) at ambient temperature. The mixture was stirred for three days and then the volatiles were removed *in vacuo*. The residue was then dissolved in minimal CH_2Cl_2 and filtered to collect the filtrate. Volatiles were removed *in vacuo* and the precipitate was washed with benzene (5 mL) to yield paramagnetic **4** as a dark brown yellow powder. (167 mg, 84% yield). X-ray quality brown flowery crystals were obtained by layering toluene on the top of CH_2Cl_2 solution at -30 ℃. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 44.38 (s), 35.66 (s), 25.86 (s), 18.26 (s), 14.94 (s), 13.77 (s), 12.50 (br), 11.05 (s), 10.04 (s) 6.38 (s), 6.17 (s), 2.62 (s), -0.05 (s), -7.64 (s) ppm. Anal. Calcd (%) for $C_{35}H_{44}N_2ONi$: C, 55.93; H, 5.87; N, 4.08. Found: C, 59.13; H, 6.06; N, 3.24.

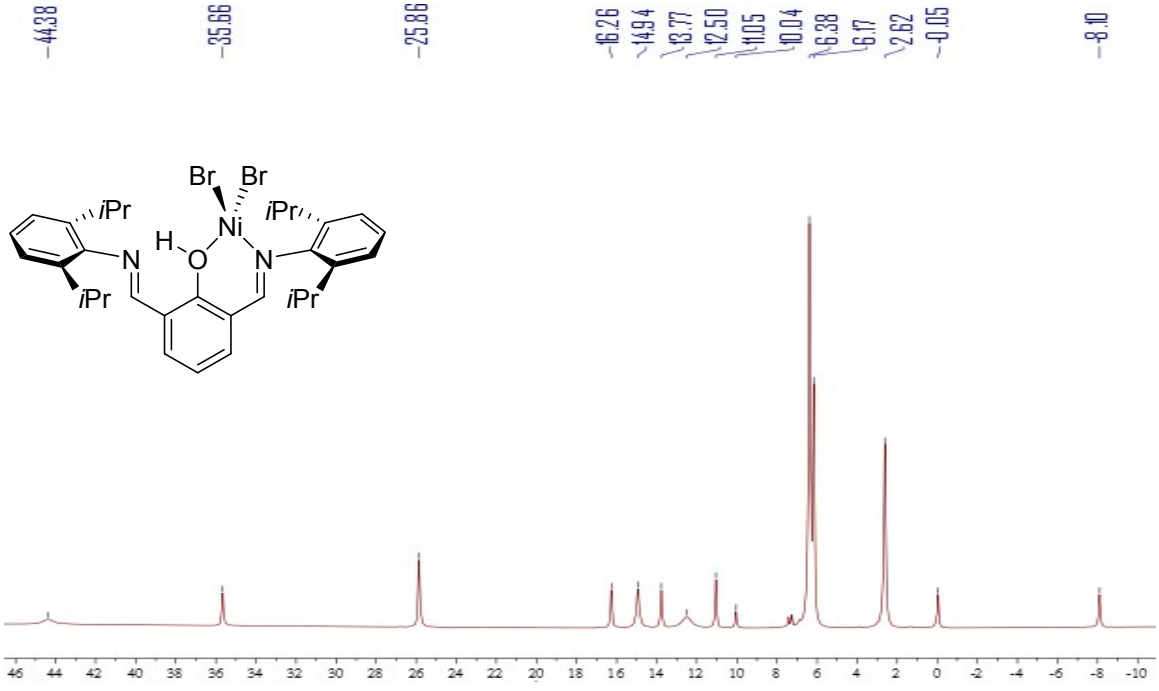

Figure S9: ^{1}H NMR spectrum of **4** in $CDCl_3$.

Synthesis of $C_{36}H_{46}N_2ONiZnBr_2$, (NON)Ni(η^3-C_4H_7)$ZnBr_2$ (5)

A mixture of **3** (46.8 mg, 0.81 mmol, 1 equiv.) and $ZnBr_2$ (20.8 mg, 0.92 mmol, 1.1 equiv.) in THF (2 mL) was stirred overnight at ambient temperature. Volatiles were then removed *in vacuo* and the residue was dissolved in minimal CH_2Cl_2 and filtered to collect the filtrate. Volatiles were removed *in vacuo.* The orange yellow crude product was recrystallized from slow vapor diffusion of pentane into THF to yield brown red crystals of **5** (57.8 mg, 89% yield) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.15 (s, 1H), 7.98 (s, 1H), 7.53 (t, 2H, J = 6.1 Hz), 7.29-7.19 (m, 6H), 7.08 (t, 1H, J = 7.6 Hz), 3.81 (s, 1H), 3.61 (sep, 1H, J = 6.7 Hz), 3.50 (sep, 1H, J = 6.7 Hz), 3.22 (sep, 1H, J = 6.9 Hz), 3.13 (sep, 1H, J = 6.9 Hz), 2.47 (s, 1H), 2.43 (s, 3H), 1.79 (s, 1H), 1.63 (s, 1H), 1.55 (d, 3H, J = 6.8 Hz), 1.36 (d, 3H, J = 6.8 Hz), 1.33 (d, 3H, J = 6.8 Hz), 1.29-1.27 (m, 6H), 1.16 (d, 3H, J = 6.8 Hz), 1.14 (d, 3H, J = 6.8 Hz), 1.10 (d, 3H, 6.9 Hz) ppm. ^{13}C ($CDCl_3$, 125 MHz): δ 169.63, 165.69, 164.10, 149.75, 144.62, 140.69, 140.10, 139.89, 139.78, 138.92, 130.39, 127.56, 127.32, 125.28, 124.70, 124.10, 123.90, 123.79, 118.86, 59.09, 53.44, 28.71, 28.60, 28.42, 28.40, 25.78, 25.33, 24.84, 24.11, 23.47, 23.37, 22.88, 22.52 ppm. Anal. Calcd (%) for $C_{36}H_{46}N_2ONiZnBr_2$: C, 53.60; H, 5.75; N, 3.47. Found: C, 54.40; H, 5.98; N, 2.77.

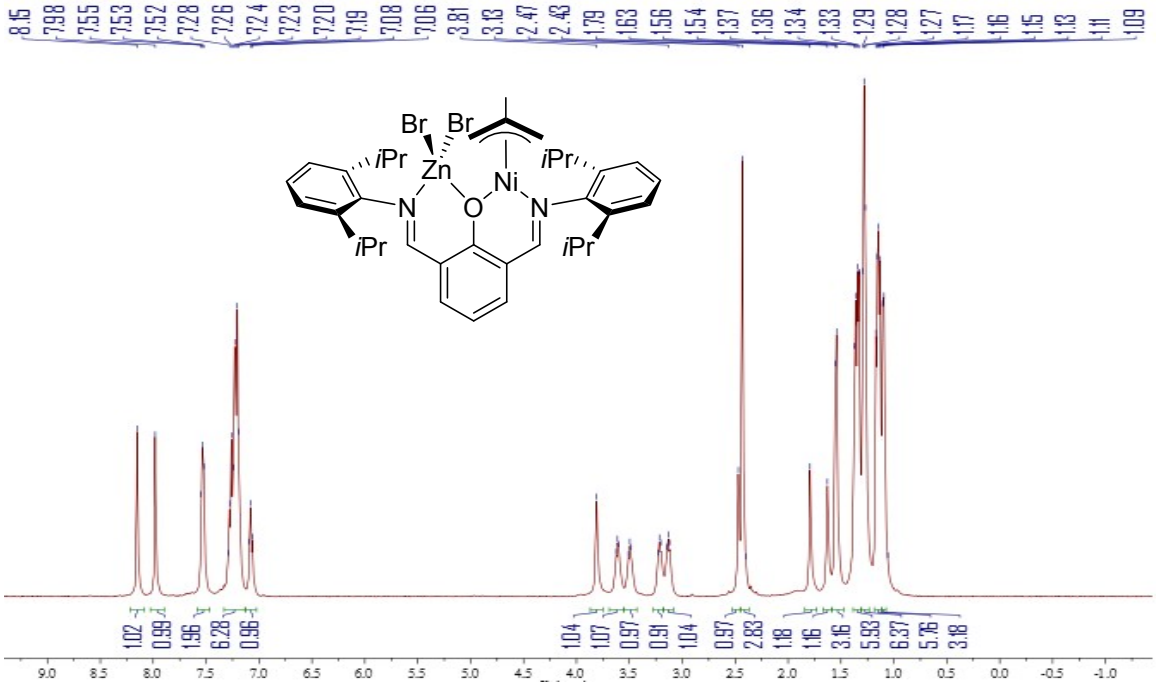

Figure S10: ^{1}H NMR spectrum of **5** in $CDCl_3$.

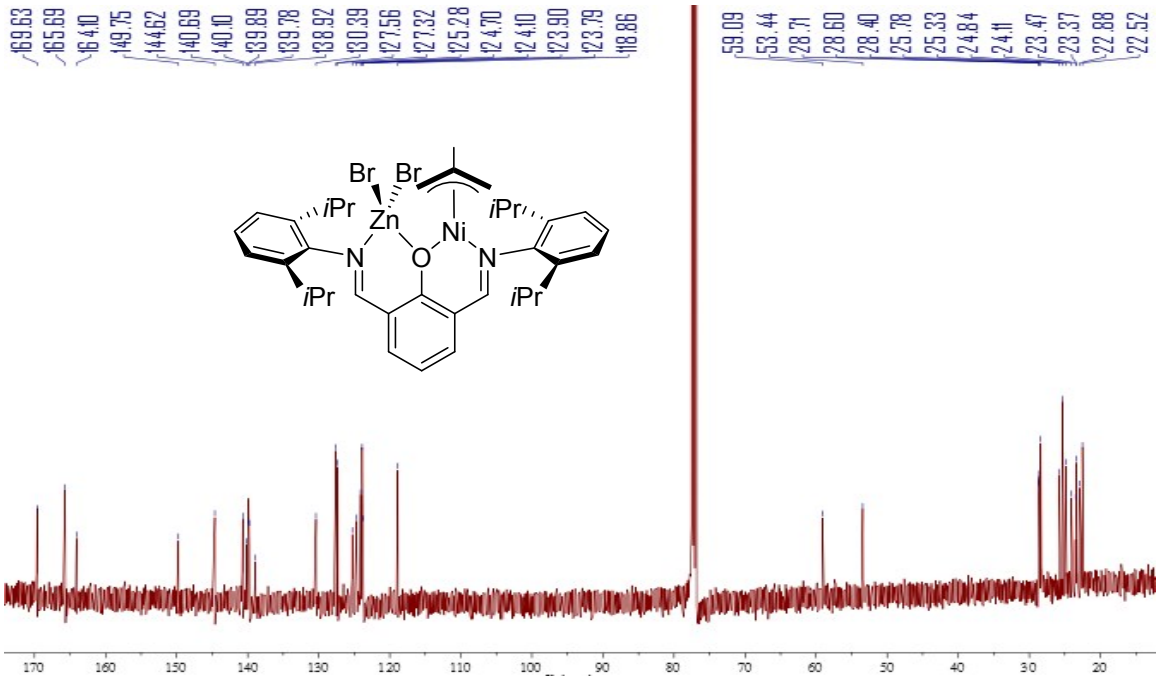

Figure S11: ^{13}C NMR spectrum of **5** in $CDCl_3$.

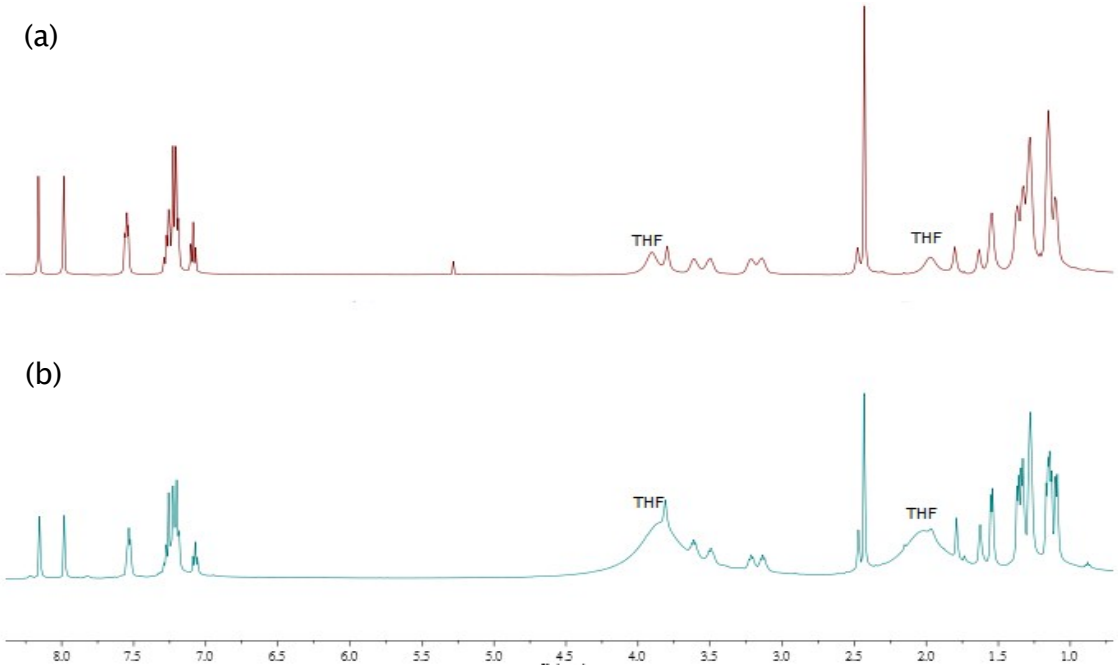

Figure S12: Stacked ^{1}H NMR spectrum of **5** in $CDCl_3$ (a) in the crude mixture with THF and (b) titrated with multiple equivalents of THF.

NMR reaction between complex 4 and $ZnEt_2$

To a solution of **4** (6.8 mg, 0.01 mmol, 1 equiv.) in CD_2Cl_2 (0.4 mL) in a NMR tube in a N_2-filled glovebox, $ZnEt_2$ (1.0 μL, 0.01 mmol, 1 equiv.) was added along the NMR tube wall. After being brought out of the glovebox, the NMR tube was cooled down in a LN_2 bath to prevent reaction. The NMR tube was warmed back up to ambient temperature and shaken to mix the reactants right before NMR data collection.

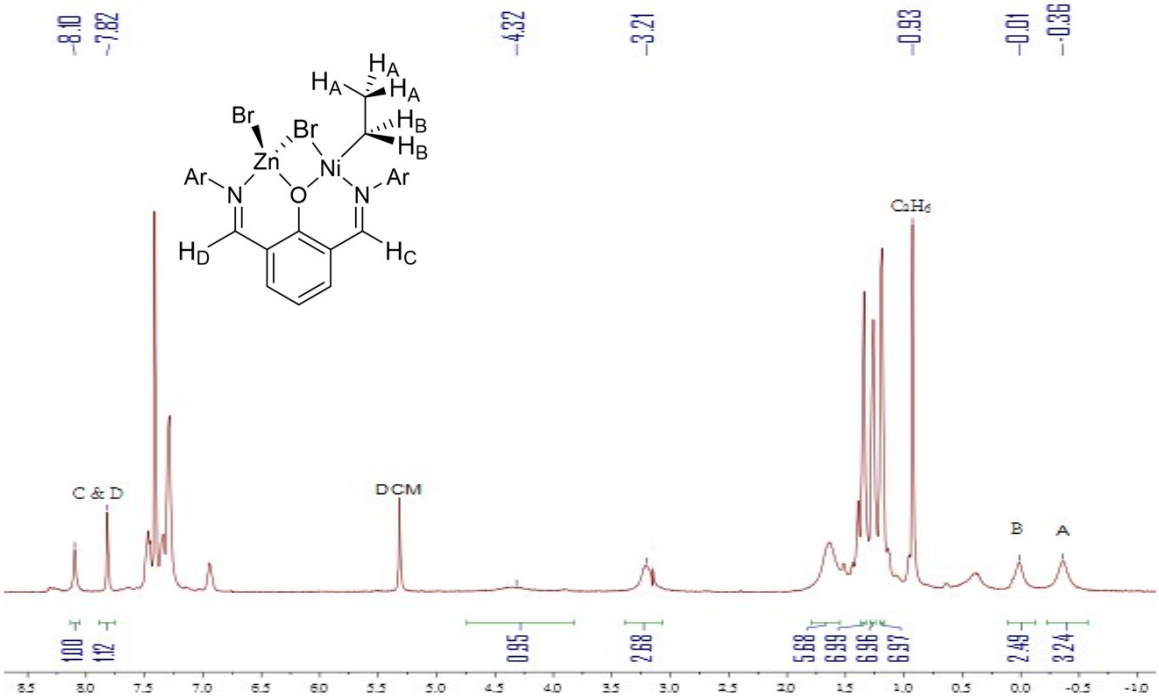

Figure S13: *In situ* ^{1}H NMR of stoichiometric mixture of **4** and $ZnEt_2$ in CD_2Cl_2.

X-ray Crystal Data: General Procedure

Crystals were removed quickly from a scintillation vial to a microscope slide coated with paraffin oil. Samples were selected and mounted on the tip of a 0.1 mm diameter glass capillary. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. All non-hydrogen atoms were refined anisotropically with the exception of the OH proton in **4** which was placed with residual electron density and found to be bound to the free imine. Additionally in **4**, the $NiBr_2$ moiety was modelled over the two positions in the ligand. In **5**, Br1 was modelled over two positions. A disordered pentane molecule in **4** was removed from the unit cell using Platon SQUEEZE12. Refined data details and cell parameters are available in Table S1.

Table S1: Crystal and refinement data for **4** and **5**.

	4	**5**
CCDC Number	1525489	1525490
Empirical Formula	$C_{32}H_{40}Br_2N_2NiO \cdot C_7H_8$	$C_{36}H_{46}Br_2N_2NiOZn$
Formula weight	779.28	806.65
T (K)	123	124
a, Å	14.2254(4)	47.250(3)
b, Å	15.6563(5)	10.7808(6)
c, Å	18.0121(5)	15.9557(10)
α, deg	90	90
β, deg	111.534(1)	107.470(2)
γ, deg	90	90
Volume, $Å^3$	3731.59(19)	7752.8(8)
Z	4	8
Crystal System	Monoclinic	Monoclinic
Space Group	P21/c	C2/c
d_{calc}, g/cm^3	1.387	1.382
ϑ Range, deg	2.599 - 28.25	2.276 - 3.489
μ, mm^{-1}	2.693	3.193
Abs. Correction	MULTI-SCAN	MULTI-SCAN
GOF	1.037	1.066
R_1,[a]	0.0444	0.0321
wR_2 [b] [I>2□(I)]	0.0940	0.0844

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

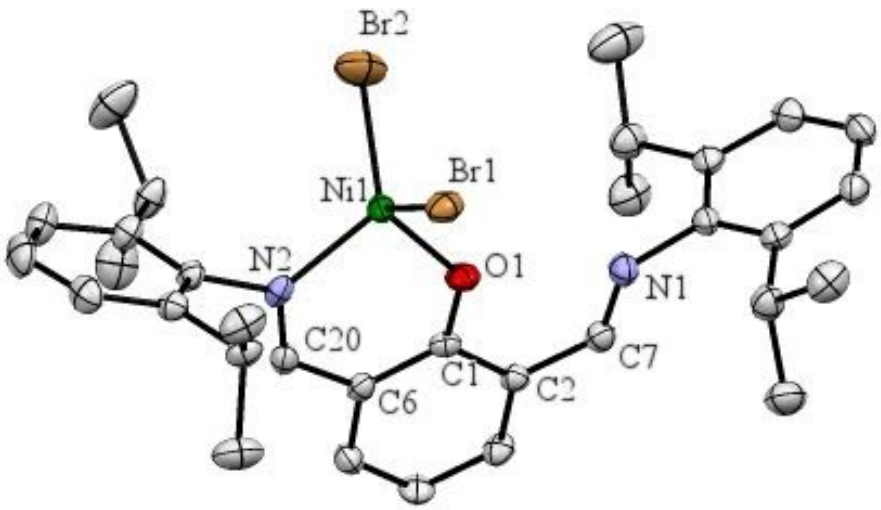

Figure S14: Thermal ellipsoid drawing of **4**. H atoms (other than on O1) and solvent removed for clarity

Polymerization Reactions and Polymer Characterizations

General Polymerization

All polymerization reactions were carried out in a Biotage Endeavor parallel pressure reactor with overhead stirring housed in a N_2 atmosphere glovebox. After $ZnBr_2$ was pre-weighed into the reaction vessels, the polymerization reactions were submitted in two batch methods (with or without metal alkyl activators) and then run under the desired conditions for three hours.

Method A with metal alkyls: Catalysts were dissolved in 1 mL of toluene in the reactor vessels. After the reactor was sealed, heated to desired temperature and pressurized to 100 psi of ethylene, 0.1-0.2 mL of $ZnEt_2$ or $AlEt_3$ stock solution (0.025M toluene solution) was injected through the ball valve ports followed by a toluene rinse to a total volume of 2 mL.

Method B without metal alkyls: Catalysts were dissolved in 2 mL of toluene in the reactor vessels. Afterwards, the reactor was sealed, heated to desired temperature and pressurized to 100 psi of ethylene.

Once the reactions were finished, the reactor was depressurized and purged with N_2 gas, and then the vessels were removed from the glovebox. Reactions were quenched by 1 mL of 1M HCl methanol solution. If polymers were yielded, 3 mL of acetone would be added to precipitate out the polymer, which were filtered to be collected and dried *in vacuo* prior to analysis by GPC and ^{1}H NMR.

Table S2. Supplementary Information of Ethylene Polymerization Experiment with **2 – 6**.[a]

entry	catalyst	additive (equiv.)	reaction temperature (℃)	Yield (mg)	Branches (1/1000C)
1	2	none	35	39	13
2	2	none	50	303	31
3	2	$ZnBr_2$ (11)	35	146	25
4	2	$ZnBr_2$ (11)	50	68	33
5	2	$ZnCl_2$(11)	35	55	23
6	2	$ZnCl_2$(11)	50	41	59
7	3	none	50	0	n.a.
8	3	$ZnBr_2$ (11)	35	5	33
9	3	$ZnBr_2$ (11)	50	13	38
10	4	none	35	0	n.a.
11	4	$ZnEt_2$ (1)	r.t.[e]	207	22
12	4	$ZnEt_2$ (1)	35	113	22
13	4	$ZnEt_2$ (1)	50	148	21
14	4	$ZnEt_2$ (2)	r.t.[e]	113	22
15	4	$ZnEt_2$ (1) $ZnBr_2$ (11)	r.t.[e]	244	24
16	4	$ZnEt_2$ (1) THF (20)	r.t.[e]	160	43
17	4	$ZnEt_2$ (1) $ZnBr_2$ (11) THF (20)	r.t.[e]	132	23
18	5	none	50	0	n.a.
19	5	$ZnBr_2$ (10)	35	6	21
20	5	$ZnBr_2$ (10)	50	9	32
21	6[d]	none	50	145	71
22	6[d]	$ZnBr_2$ (11)	35	607	37
23	6[d]	$ZnBr_2$ (11)	50	507	69

[a]Condition: [cat] = 1.25 mM in 2 mL of toluene, 100 psi of ethylene, 3 hours. All the data is triplicated and presented in the average. Bimodal distribution would be deconvoluted by LogNormal fiting. [b]$\mathbf{R_i}$ = (amplitude of lower M_n peak)/(amplitude of higher M_n peak). [c]Determined by ^{1}H NMR of polymers. [d]6 = (6-tBu-salicyl(2,6-diisopropylphenyl)iminato)Ni(o-tolyl)(py). [e]Without any thermal control.

Table S3: polymerization reactions with no ethylene consumption.

entry	catalyst	additive (equiv.)	reaction temperature (℃)
1	1	None	35
2	1	$ZnEt_2$(1)	35
3	2	$ZnEt_2$(1)	35
4	3	None	35
5	3	None	70
6	3	$ZnBr_2$ (1)	50
7	3	$ZnEt_2$(1)	50
8	4	None	35
9	4	$ZnEt_2$(10)	Not controlled
10	5	None	50

Ethylene Consumption Curves

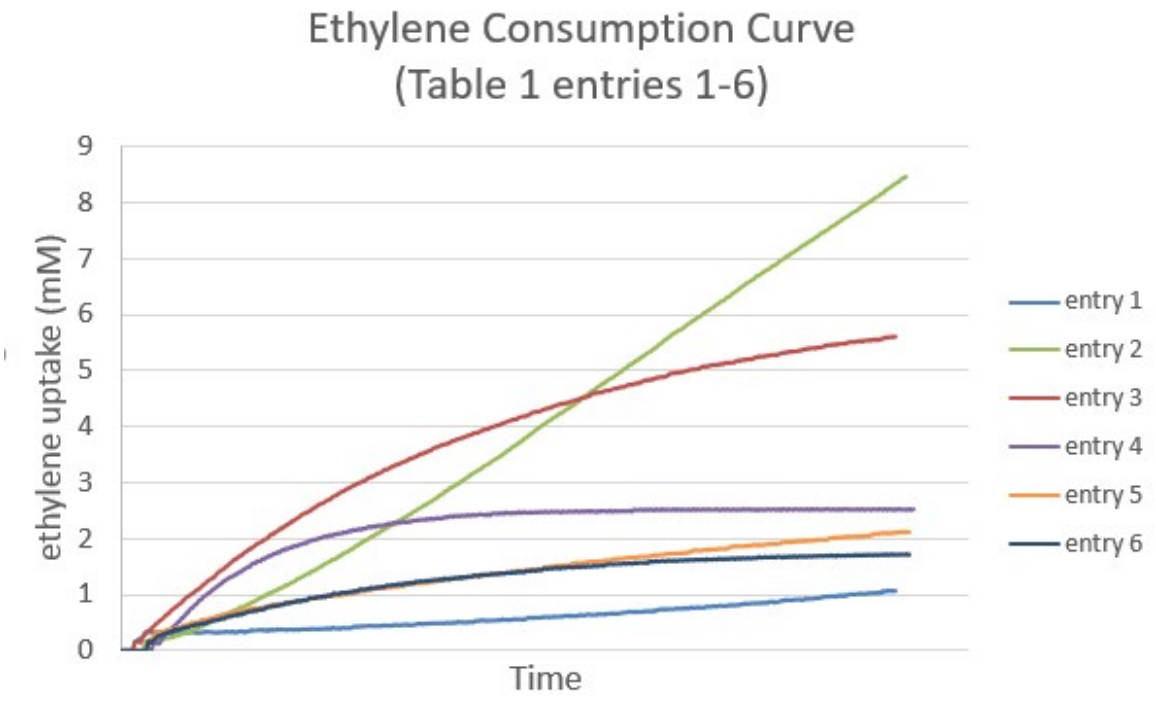

Figure S15: Ethylene consumption curves of **2** (Table 1, entries 1-7).

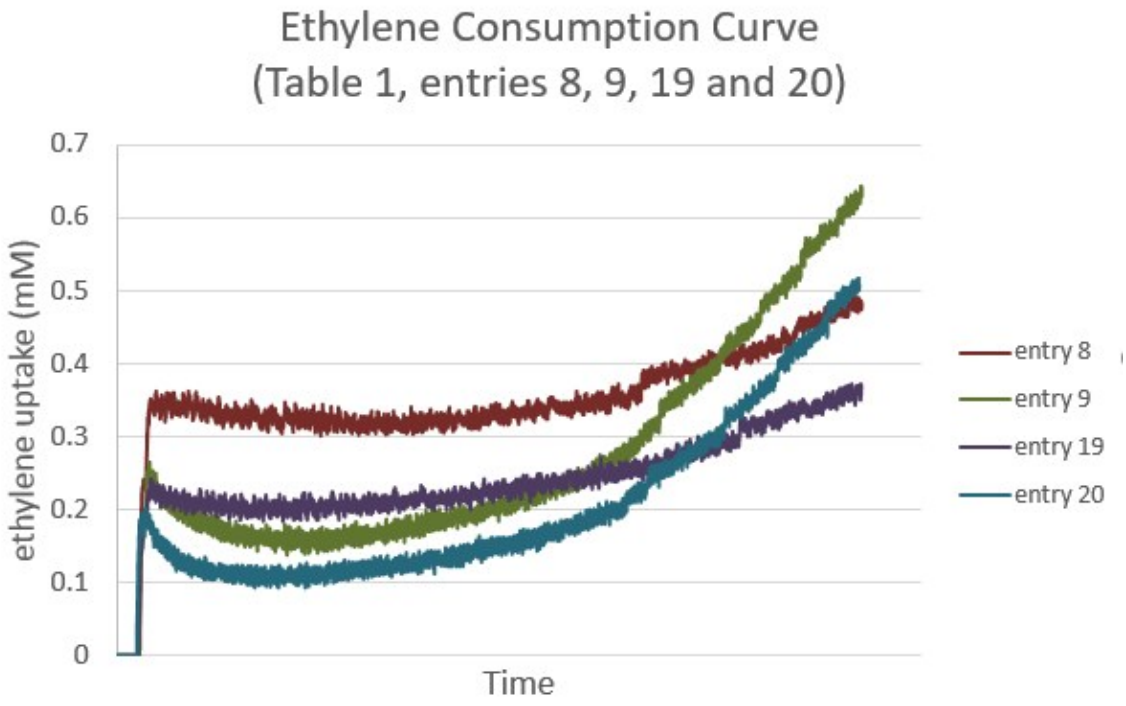

Figure S16: Ethylene consumption curves of **3** and **5** (Table 1, entries 9, 10, 20 and 21).

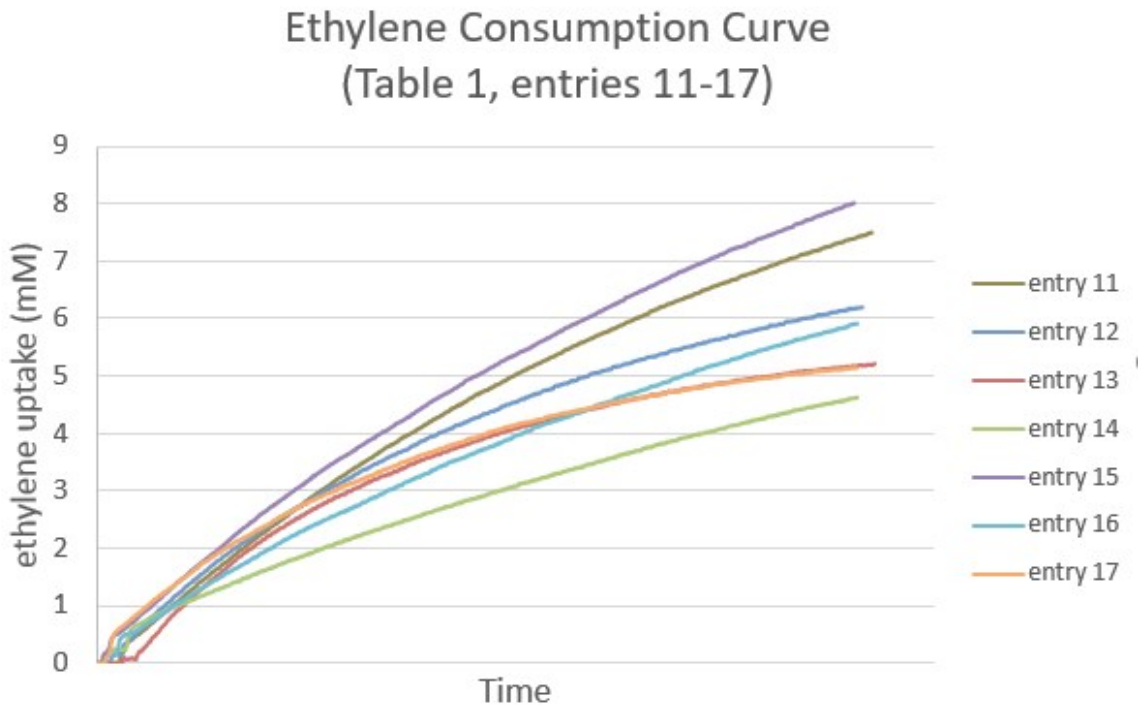

Figure S17: Ethylene consumption curves of **4** (Table 1, entries 12-18).

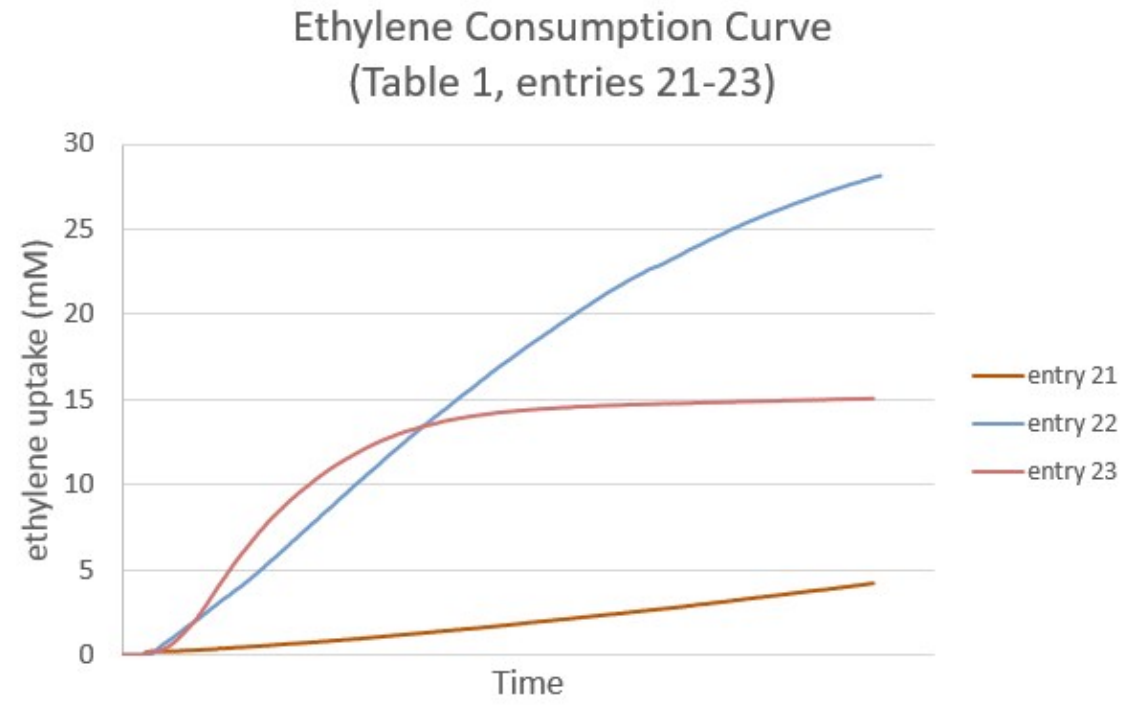

Figure S18: Ethylene consumption curves of **7** (Table 1, entries 20-22).

Polymer Characterization- GPC and ^{1}H NMR

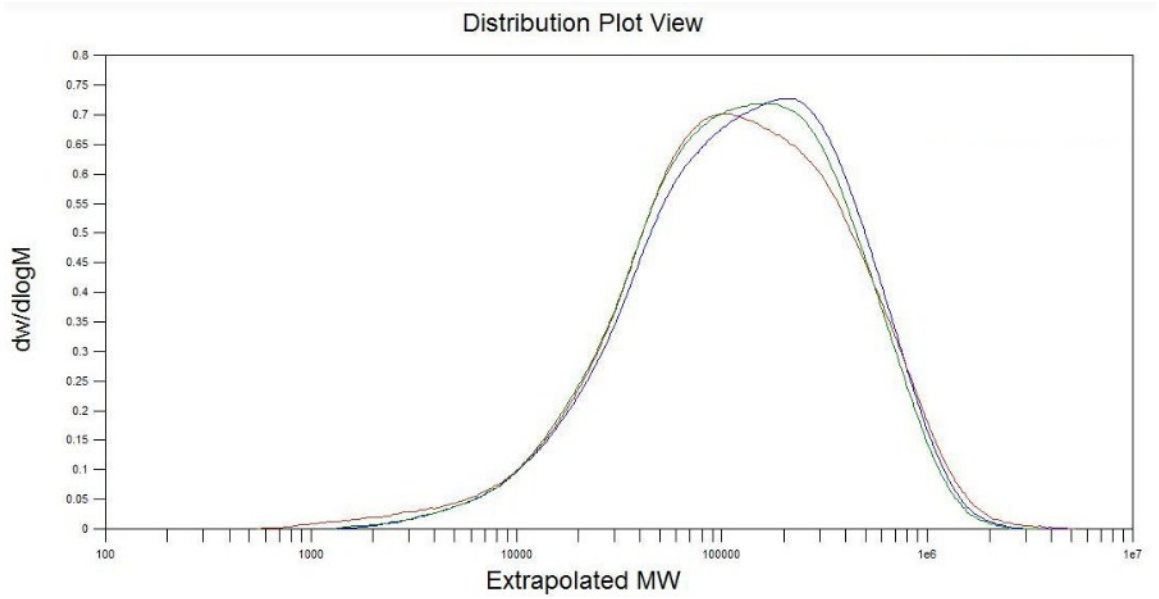

Figure S19: Overlapping molecular weight distribution of polyethylene made with **2** at 35 ℃ in three runs (Table 1, entry 1).

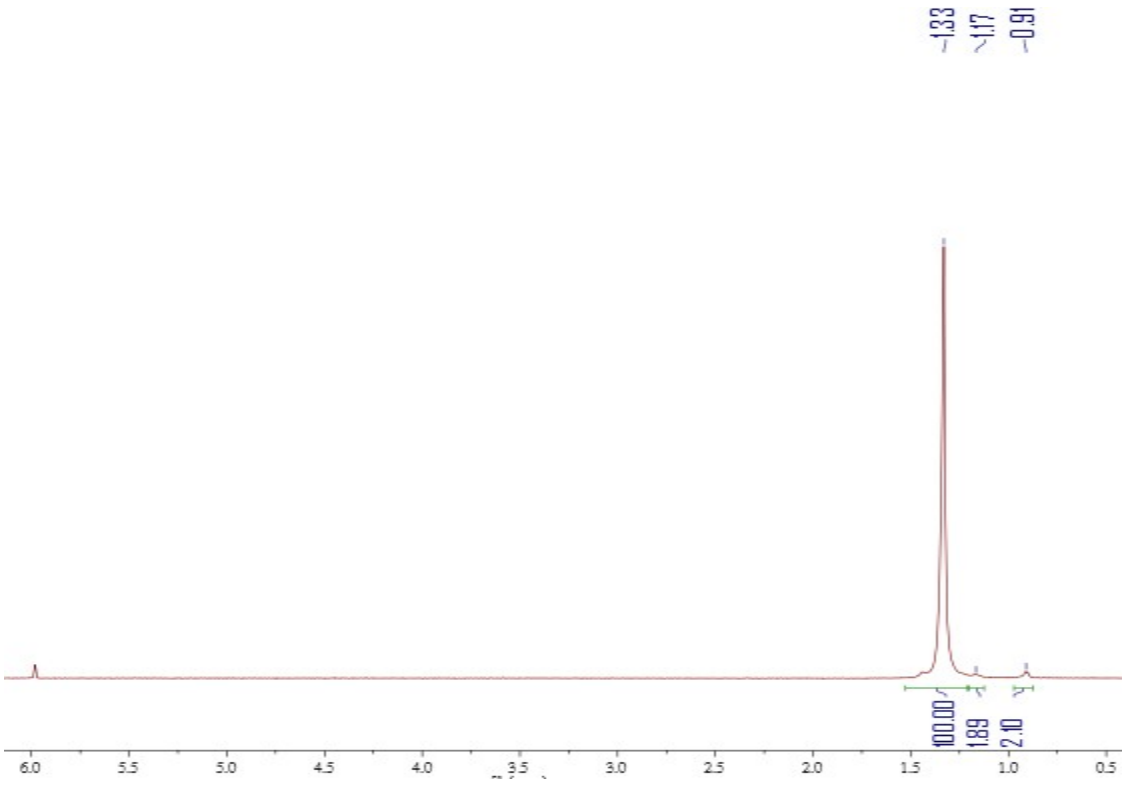

Figure S20: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **2** at 35 ℃ (Table 1, entry 1).

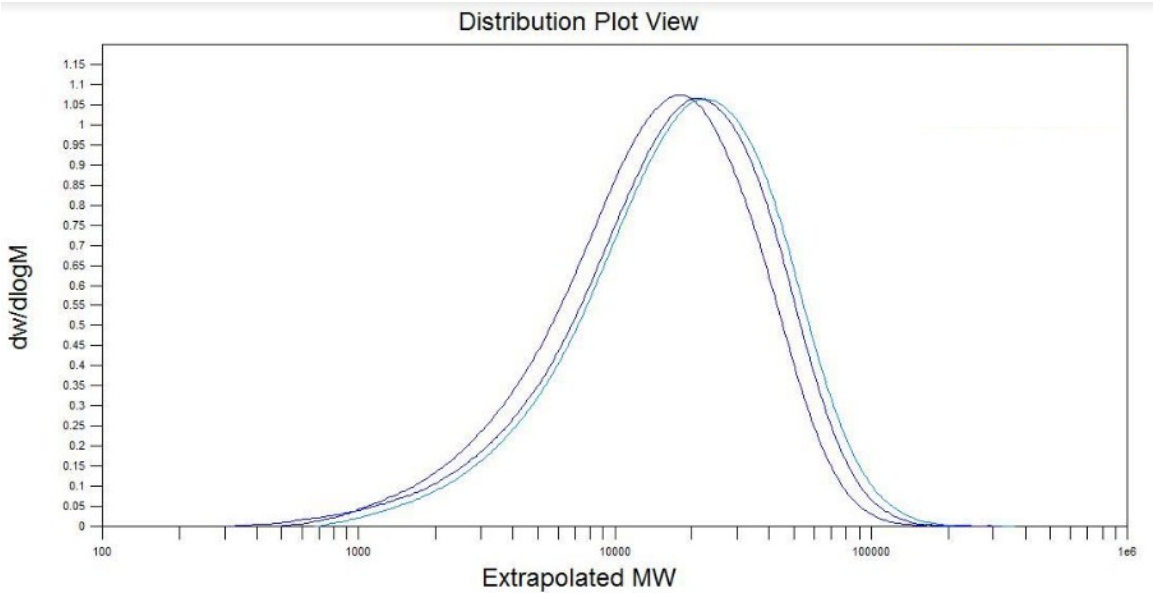

Figure S21: Overlapping molecular weight distribution of polyethylene made with **2** at 50 ℃ in three runs (Table 1, entry 2).

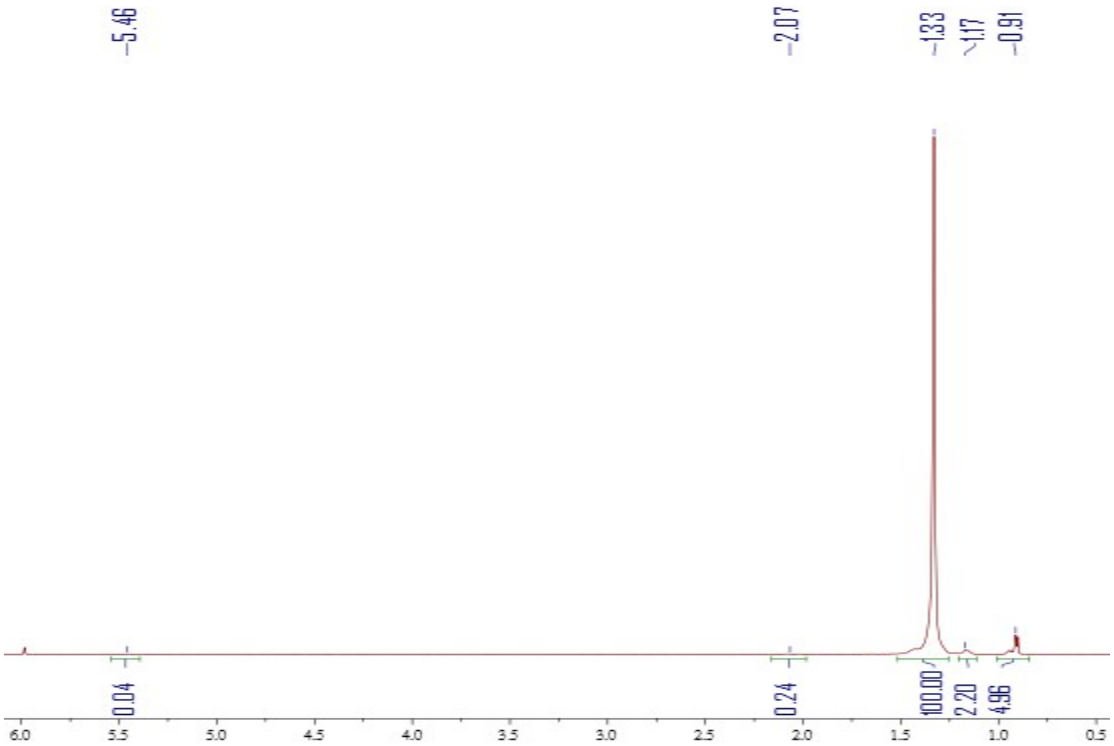

Figure S22: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **2** at 50 ℃ (Table 1, entry 2).

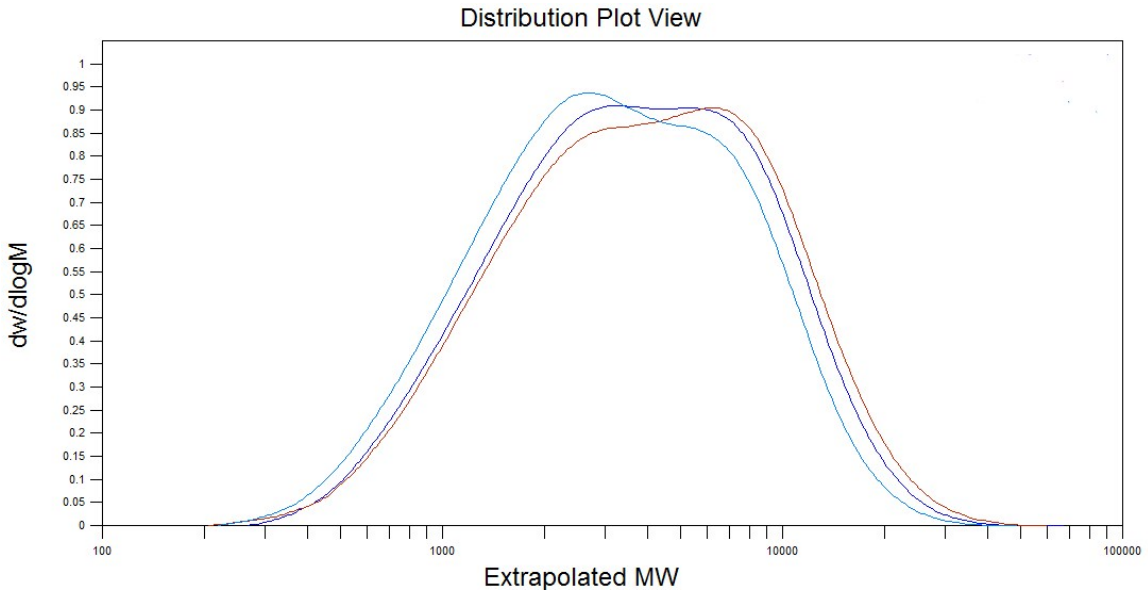

Figure S23: Overlapping molecular weight distribution of polyethylene made with **2** at 35 ℃ with 11 equiv. $ZnBr_2$ in three runs (Table 1, entry 3).

Table S4. GPC trace deconvolution of the polyethylene made with **2** at 35 ℃ with 11 equiv. $ZnBr_2$ in three runs (Table 1, entry 3).

	Peak label	**Location**	**Height**	**Area**	**FWHM**	**Fit function parameters**		
						Location	Width	Height
Trial 1	Low M_n	2680 ±10	0.937 ±0.002	8210 ±440	6630 ±350	2680 ±10	1.248 ±0.005	0.937 ±0.002
	High M_n	8100 ±20	0.318 ±0.005	2730 ±90	7740 ±260	8100 ±20	0.554 ±0.005	0.318 ±0.005
Trial 2	Low M_n	2620 ±20	0.791 ±0.003	5750 ±740	5720 ±740	2620 ±20	1.136 ±0.006	0.791 ±0.003
	High M_n	8500 ±30	0.554 ±0.007	6920 ±770	10920 ±1210	8500 ±30	0.726 ±0.004	0.554 ±0.007
Trial 3	Low M_n	3090 ±20	0.917 ±0.003	9880 ±970	8020 ±790	3090 ±20	1.294 ±0.006	0.917 ±0.003
	High M_n	8640 ±20	0.318 ±0.006	3050 ±100	8620 ±300	8640 ±20	0.577 ±0.006	0.318 ±0.006

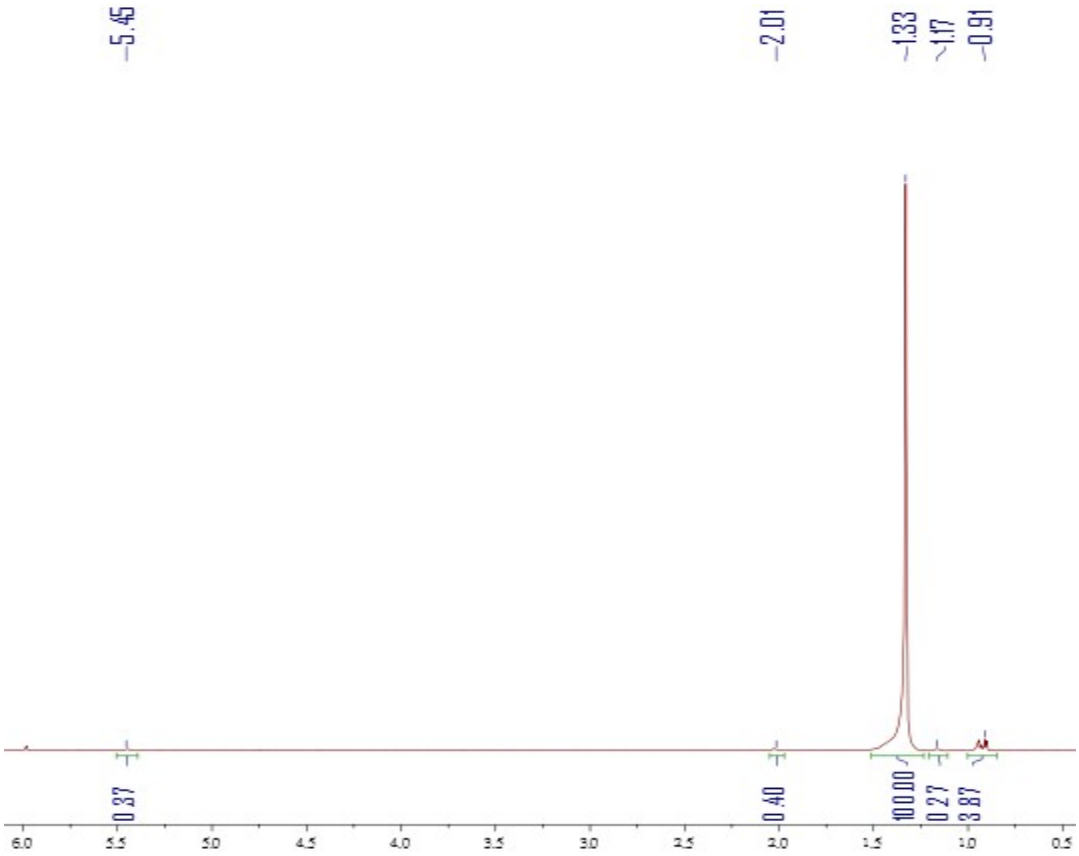

Figure S24: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **2** at 35 ℃ with 11 equiv. $ZnBr_2$ (Table 1, entry 3).

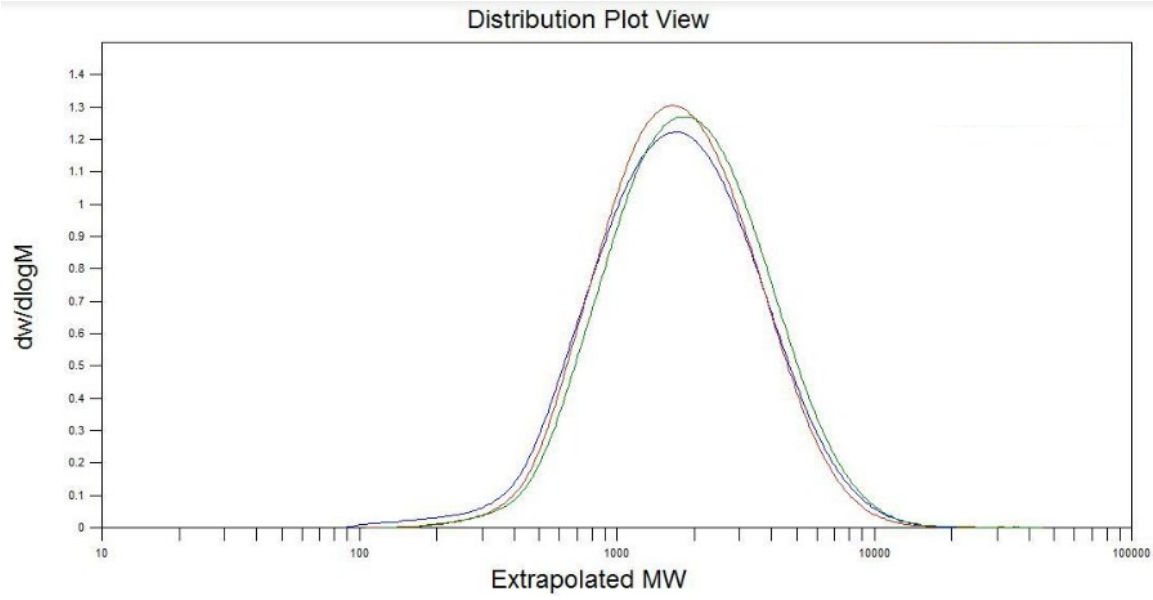

Figure S25: Overlapping molecular weight distribution of polyethylene made with **2** at 50 ℃ with 11 equiv. $ZnBr_2$ in three runs (Table 1, entry 4).

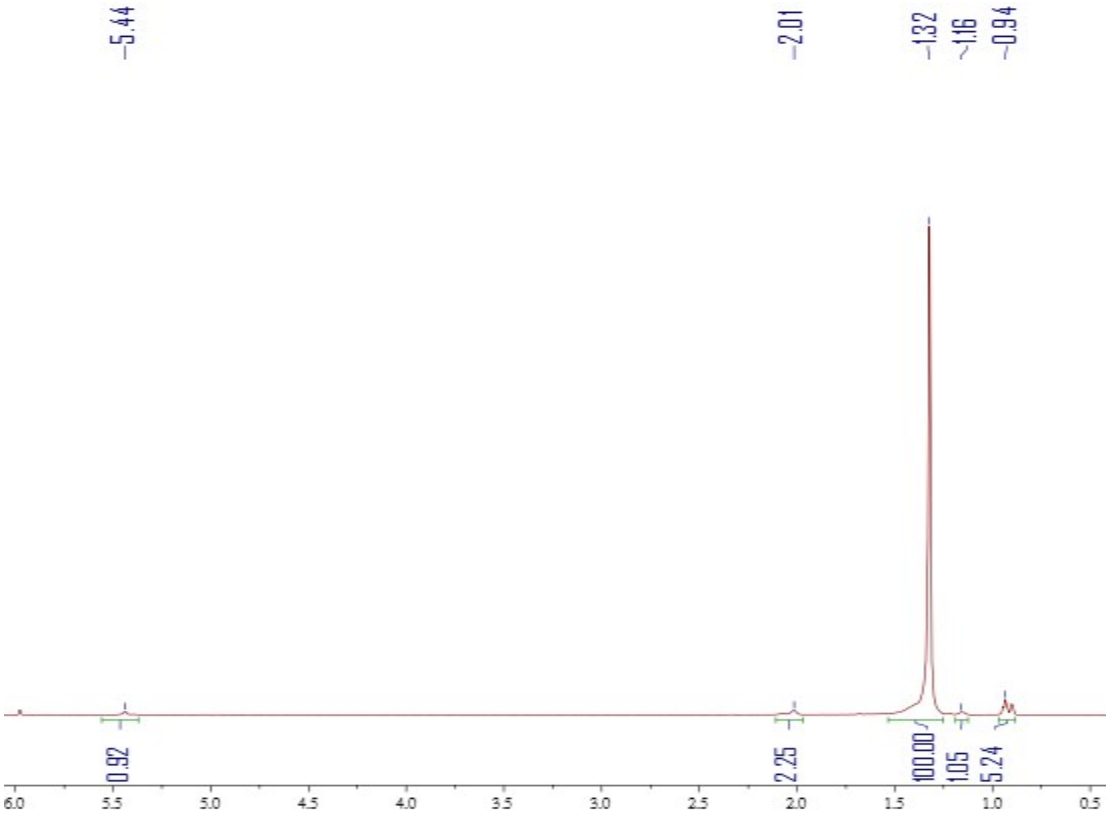

Figure S26: ^1H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **2** at 50 ℃ with 11 equiv. $ZnBr_2$ (Table 1, entry 4).

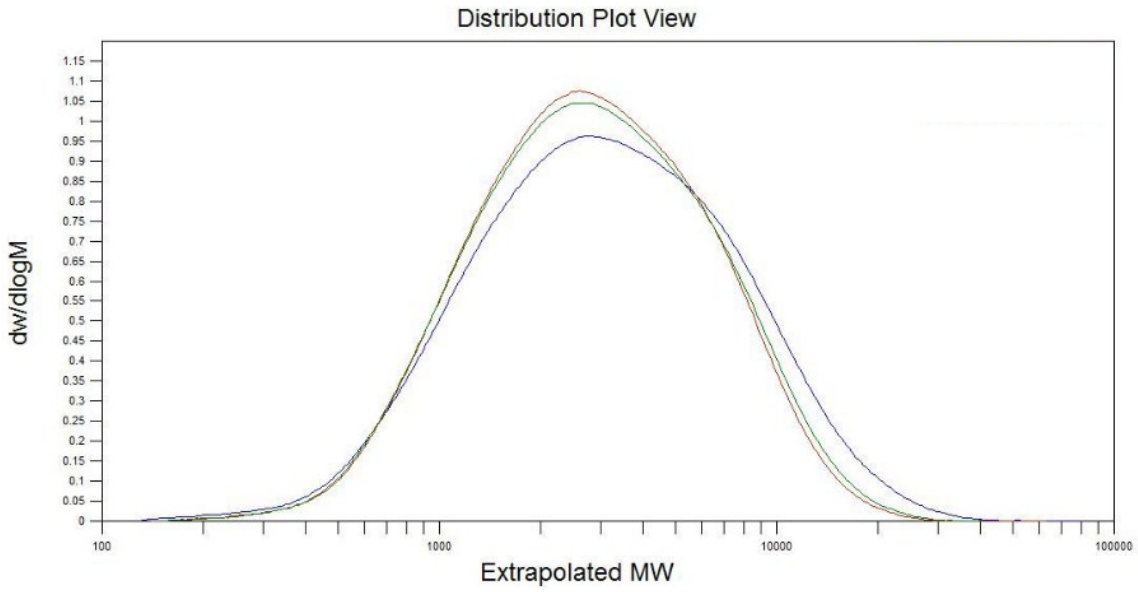

Figure S27: Overlapping molecular weight distribution of polyethylene made with **2** at 35 ℃ with 11 equiv. $ZnCl_2$ in three runs (Table 1, entry 5).

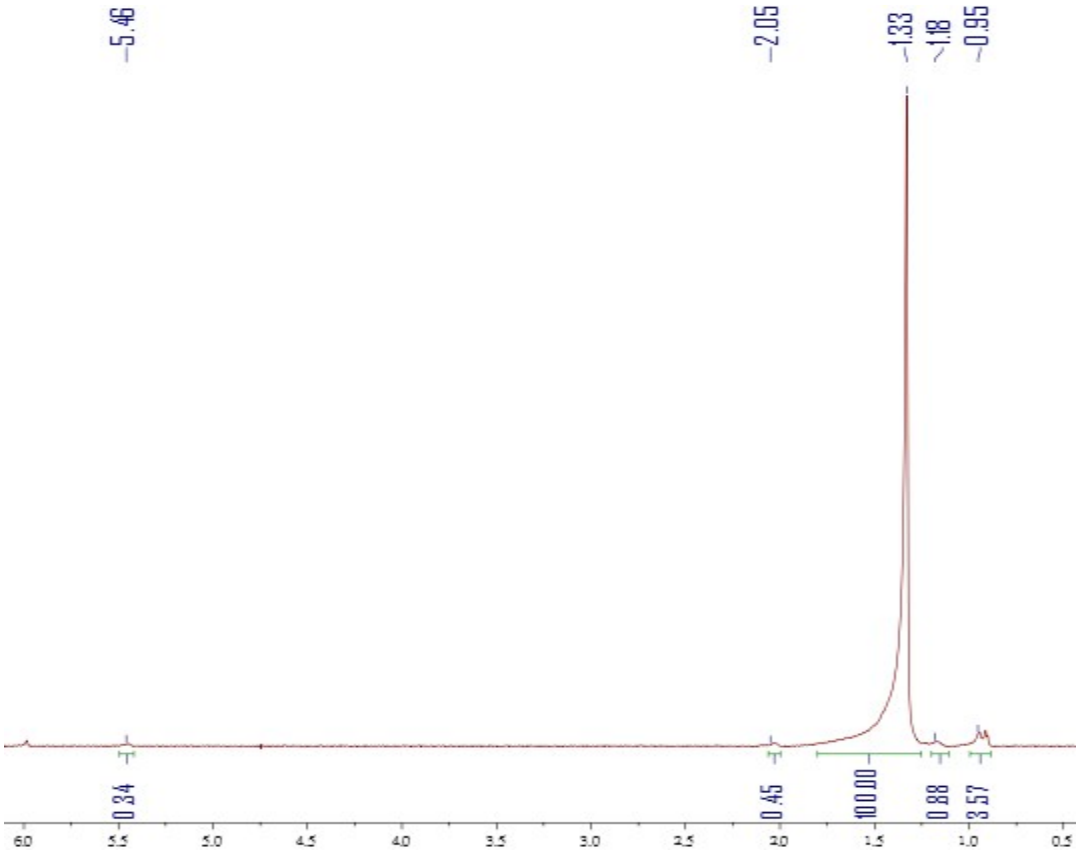

Figure S28: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **2** at 35 ℃ with 11 equiv. $ZnCl_2$ (Table 1, entry 5).

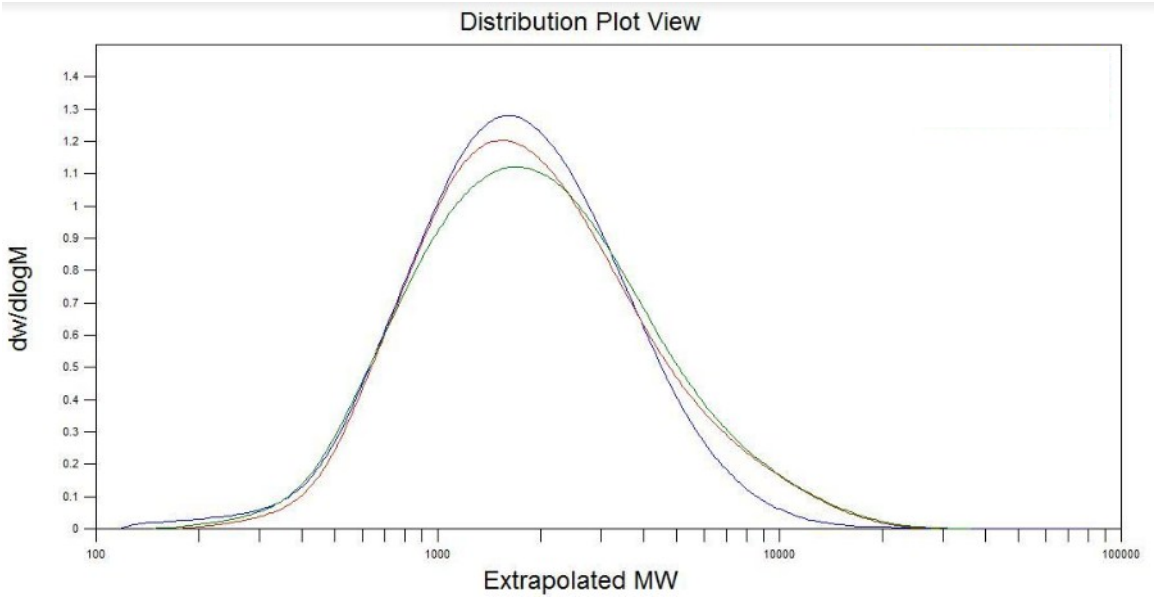

Figure S29: Overlapping molecular weight distribution of polyethylene made with **2** at 50 ℃ with 11 equiv. $ZnCl_2$ in three runs (Table 1, entry 6).

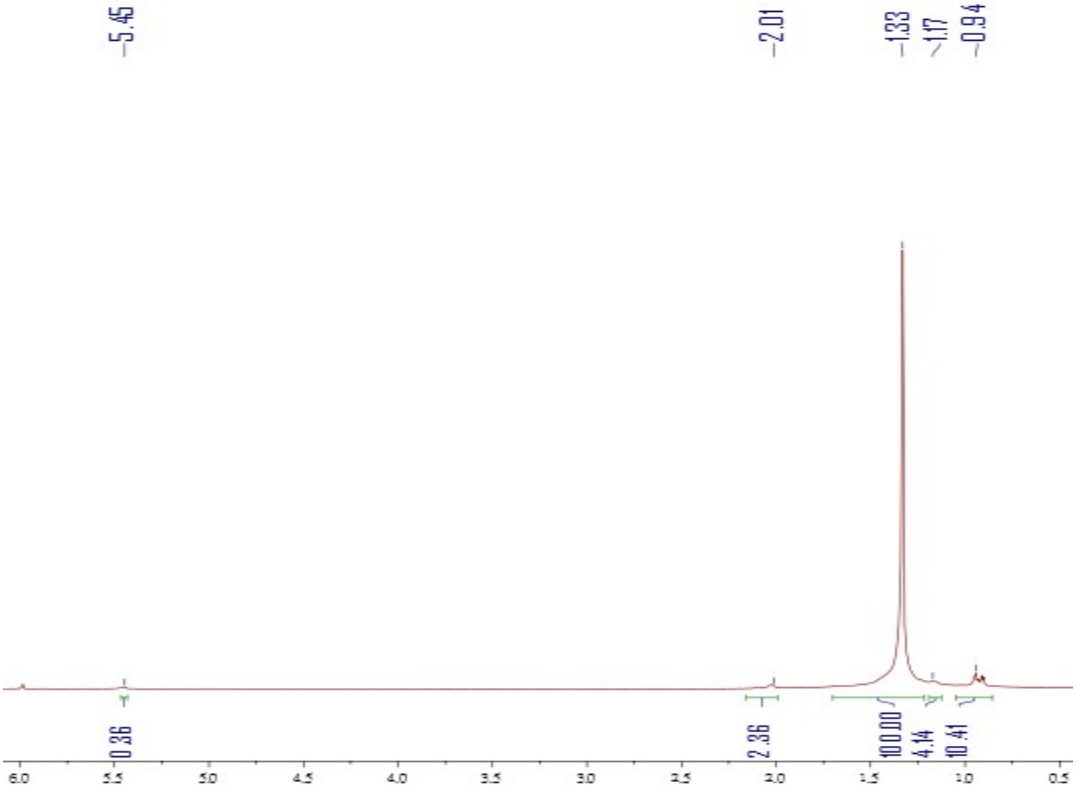

Figure S30: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **2** at 50 ℃ with 11 equiv. $ZnCl_2$ (Table 1, entry 6).

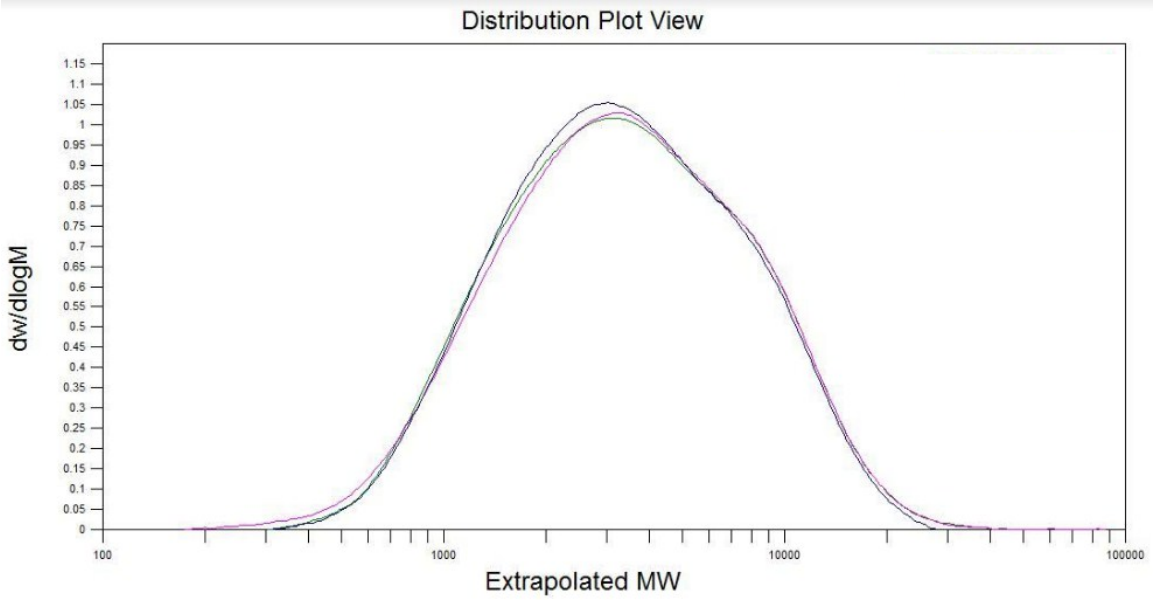

Figure S31: Overlapping molecular weight distribution of polyethylene made with **3** at 35 ℃ with 11 equiv. $ZnBr_2$ in three runs (Table 1, entry 8).

Table S5. GPC trace deconvolution of the polyethylene made with **3** at 35 ℃ with 11 equiv. $ZnBr_2$ in three runs (Table 1, entry 8).

	Peak label	**Location**	**Height**	**Area**	**FWHM**	**Fit function parameters**		
						Location	Width	Height
Trial 1	Low M_n	2450 ±30	0.971 ±0.008	5650 ±2380	4730 ±1990	2450 ±30	1.029 ±0.011	0.971 ±0.008
	High M_n	7910 ±110	0.485 ±0.017	5790 ±8360	10400 ±15020	7910 ±110	0.742 ±0.011	0.485 ±0.017
Trial 2	Low M_n	2670 ±20	1.072 ±0.004	7400 ±810	5520 ±600	2670 ±20	1.085 ±0.007	1.072 ±0.004
	High M_n	8720 ±60	0.369 ±0.009	4270 ±2040	10240 ±4890	8720 ±60	0.670 ±0.008	0.369 ±0.009
Trial 3	Low M_n	3000 ±10	1.033 ±0.002	8990 ±570	6780 ±430	3000 ±10	1.166 ±0.005	1.033 ±0.002
	High M_n	9120 ±40	0.244 ±0.006	2250 ±310	8360 ±1160	9120 ±40	0.533 ±0.009	0.244 ±0.006

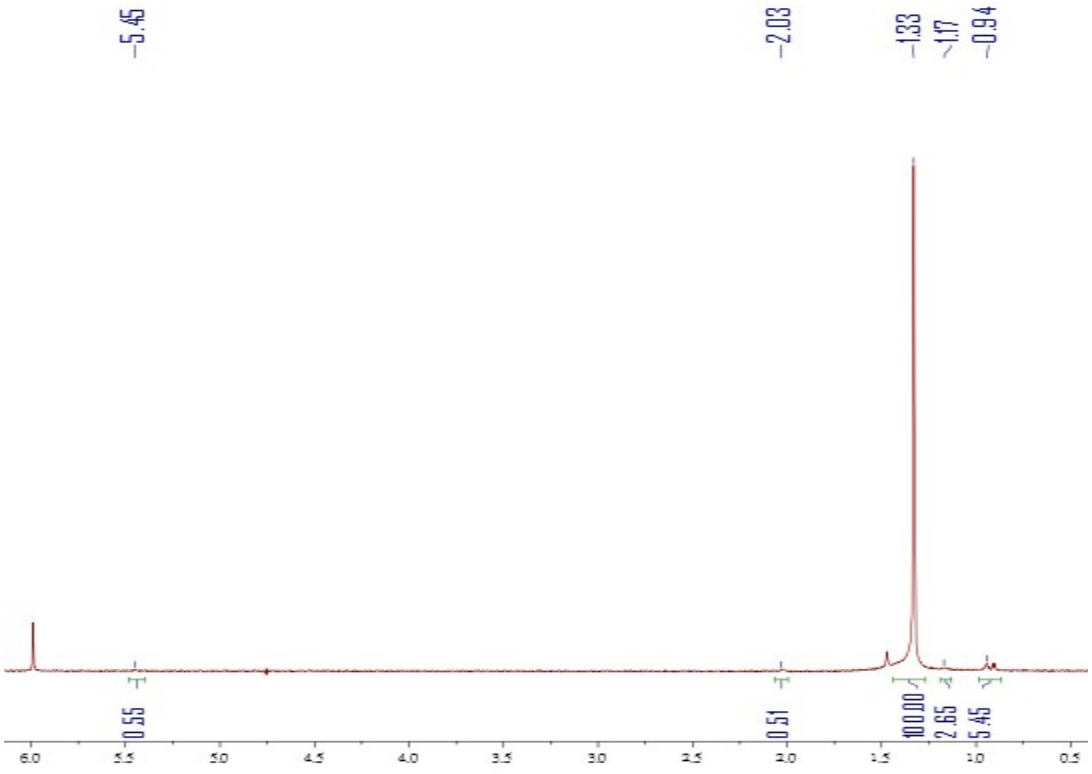

Figure S32: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **3** at 35 ℃ with 11 equiv. $ZnBr_2$ (Table 1, entry 8).

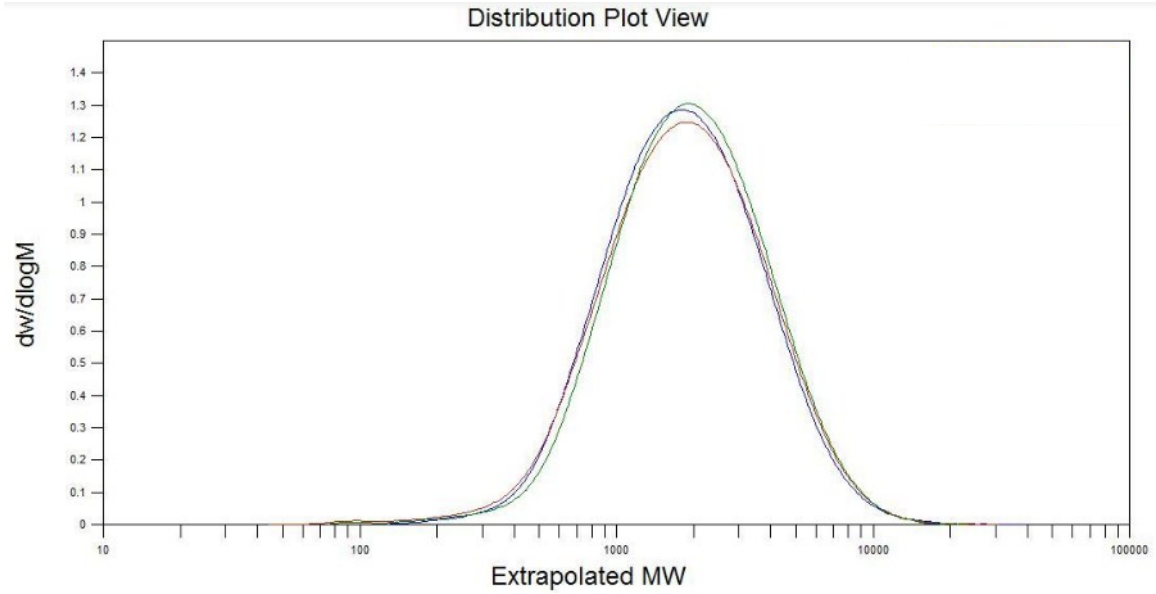

Figure S33: Overlapping molecular weight distribution of polyethylene made with **3** at 50 ℃ with 11 equiv. $ZnBr_2$ in three runs (Table 1, entry 9).

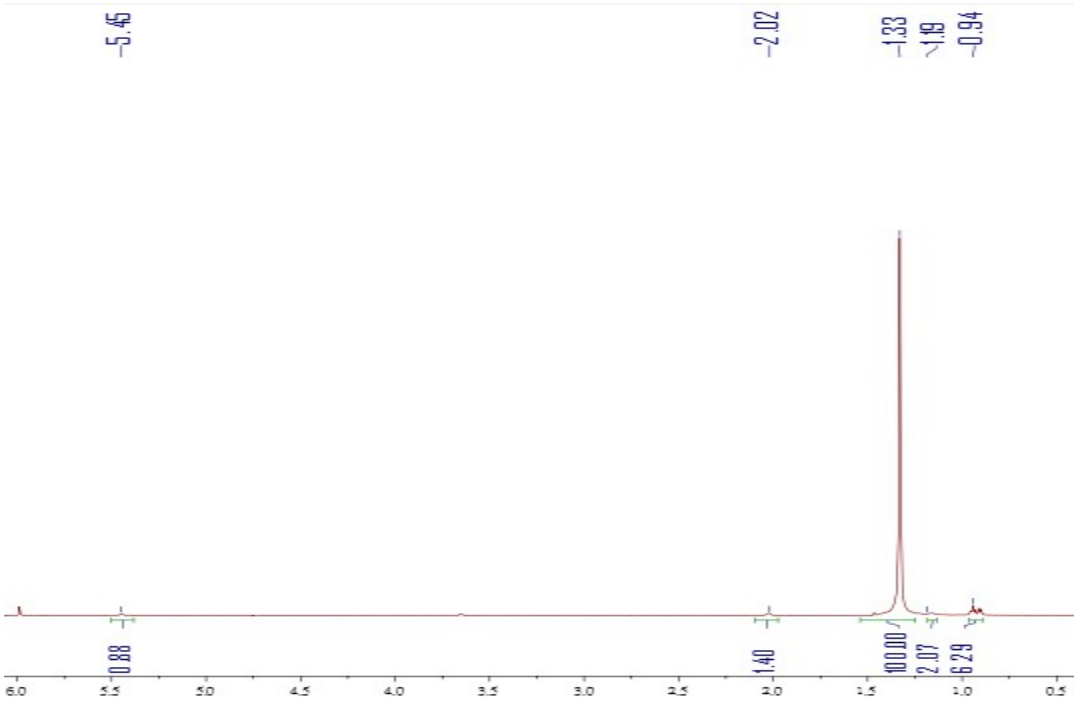

Figure S34: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **3** at 50 ℃ with 11 equiv. $ZnBr_2$ (Table 1, entry 9).

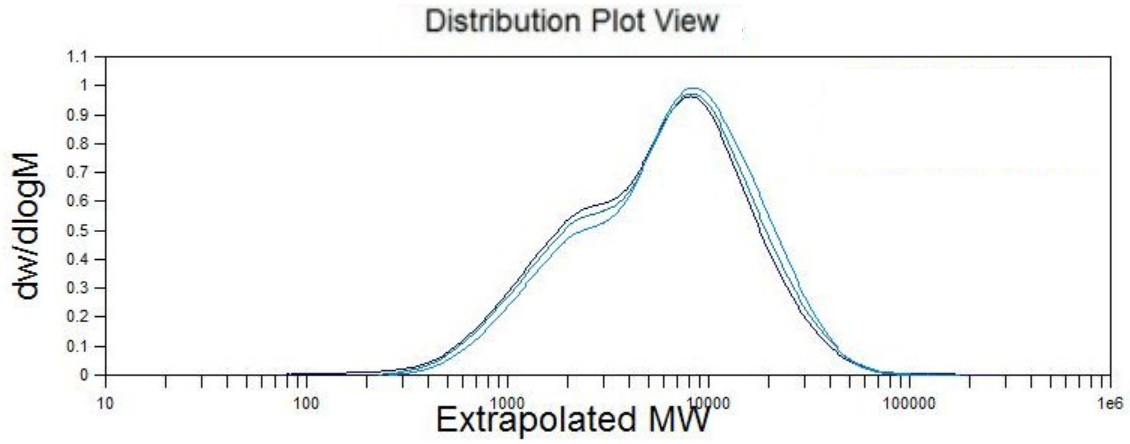

Figure S35: Overlapping molecular weight distribution of polyethylene made with **4** at the ambient temperature with 1 equiv. $ZnEt_2$ in three runs (Table 1, entry 11).

Table S6. GPC trace deconvolution of the polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$ in three runs (Table 1, entry 11).

	Peak label	**Location**	**Height**	**Area**	**FWHM**	**Fit function parameters**		
						Location	Width	Height

Trial 1	Low M_n	1690 ±30	0.382 ±0.005	1160 ±470	2580 ±1040	1690 ±30	0.845 ±0.017	0.382 ±0.005
	High M_n	8670 ±60	0.920 ±0.004	18580 ±7750	16470 ±6870	8670 ±60	1.015 ±0.008	0.920 ±0.004
Trial 2	Low M_n	1730 ±20	0.413 ±0.005	1330 ±470	2730 ±960	1730 ±20	0.869 ±0.014	0.413 ±0.005
	High M_n	8460 ±60	0.900 ±0.004	16740 ±6450	15340 ±5900	8460 ±60	0.977 ±0.007	0.900 ±0.004
Trial 3	Low M_n	1630 ±20	0.335 ±0.004	900 ±180	2310 ±470	1630 ±20	0.794 ±0.013	0.335 ±0.004
	High M_n	8900 ±40	0.964 ±0.003	21420 ±3540	17870 ±2960	8900 ±40	1.062 ±0.006	0.964 ±0.003

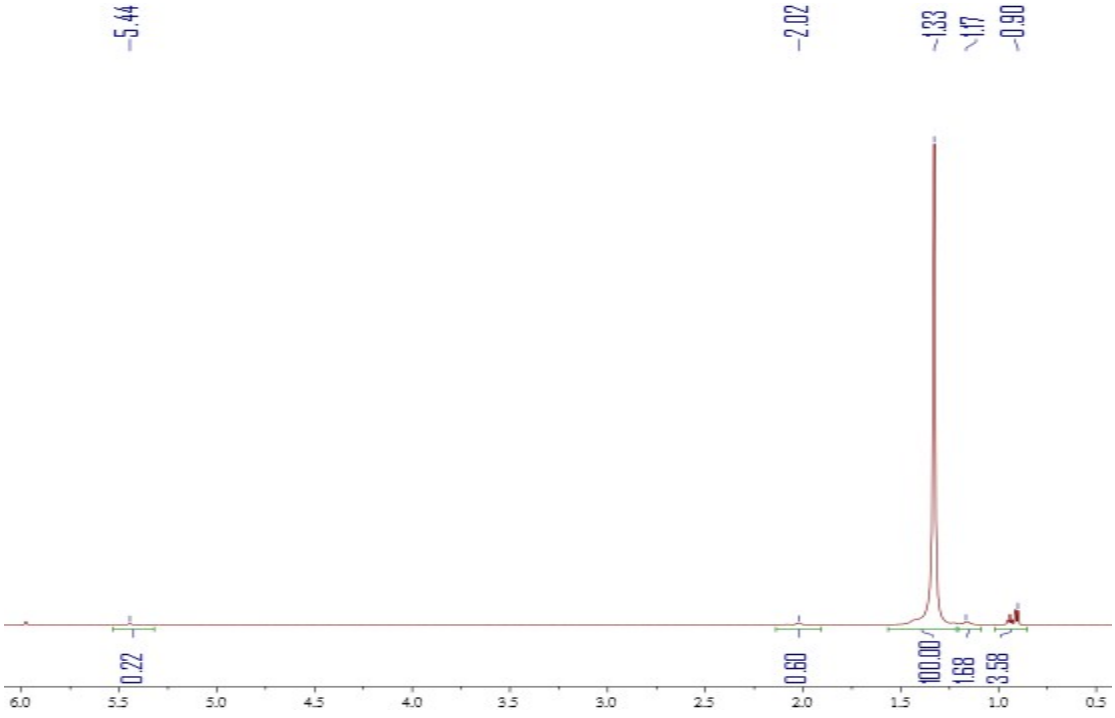

Figure S36: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$ (Table 1, entry 11).

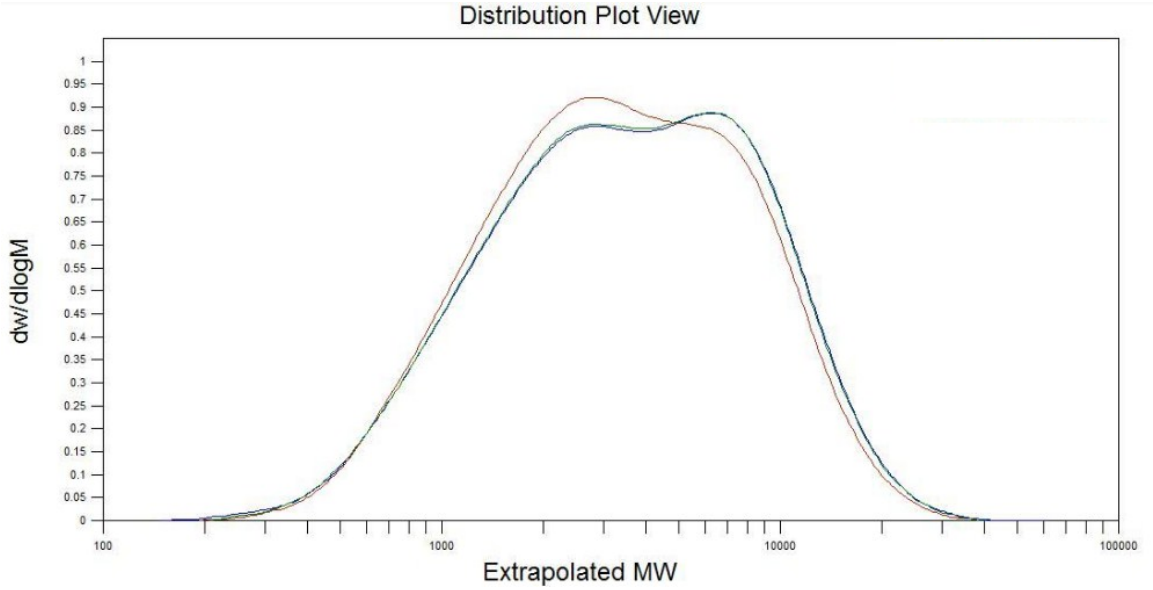

Figure S37: Overlapping molecular weight distribution of polyethylene made with **4** at 35 ℃ with 1 equiv. $ZnEt_2$ in three runs (Table 1, entry 12).

Table S7. GPC trace deconvolution of the polyethylene made with **4** at 35 ℃ with 1 equiv. $ZnEt_2$ in three runs (Table 1, entry 12).

	Peak label	**Location**	**Height**	**Area**	**FWHM**	**Fit function parameters**		
						Location	Width	Height
Trial 1	Low M_n	2750 ±20	0.862 ±0.004	8080 ±1530	7020 ±1330	2750 ±20	1.27 ±0.01	0.862 ±0.004
	High M_n	8420 ±20	0.419 ±0.009	4100 ±220	8750 ±470	8420 ±20	0.600 ±0.007	0.419 ±0.009
Trial 2	Low M_n	2700 ±20	0.923 ±0.003	8020 ±880	6610 ±720	2700 ±20	1.238 ±0.007	0.023 ±0.003
	High M_n	8370 ±20	0.360 ±0.008	3410 ±230	8490 ±580	8370 ±20	0.586 ±0.006	0.360 ±0.008
Trial 3	Low M_n	2620 ±20	0.833 ±0.003	6840 ±810	6280 ±750	2620 ±20	1.220 ±0.007	0.833 ±0.003
	High M_n	8350 ±20	0.476 ±0.007	4940 ±260	9230 ±490	8350 ±20	0.634 ±0.005	0.476 ±0.007

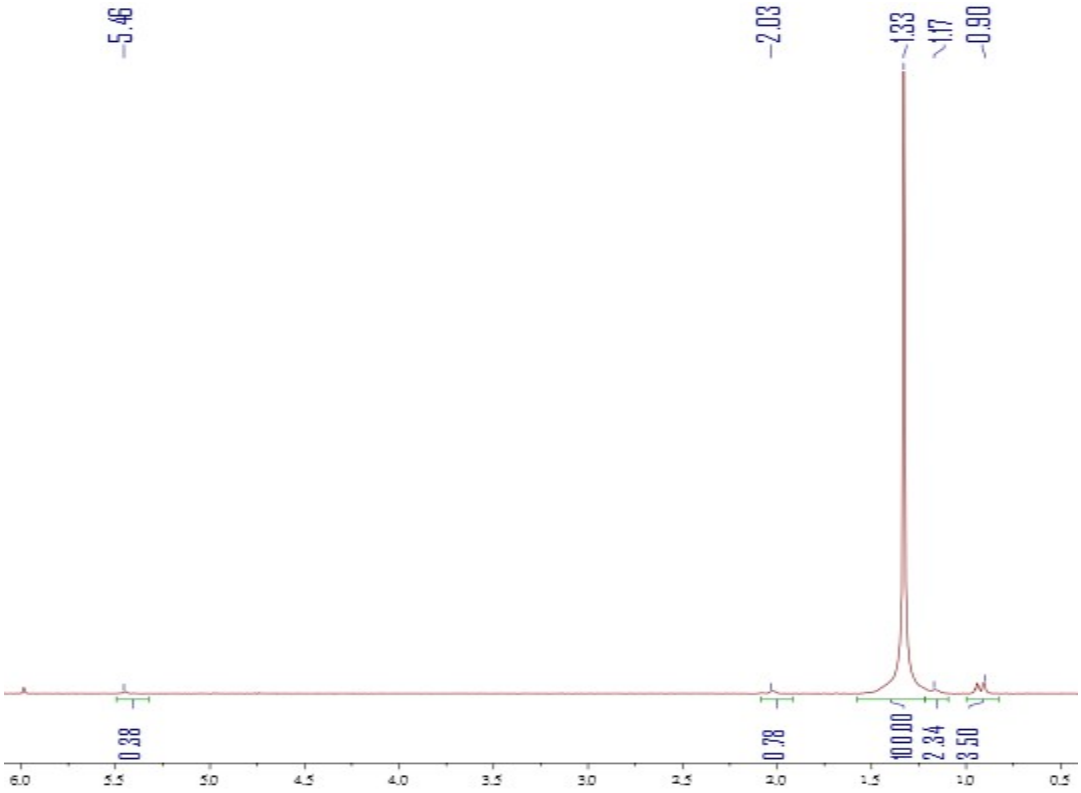

Figure S38: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **4** at 35 ℃ with 1 equiv. $ZnEt_2$ (Table 1, entry 12).

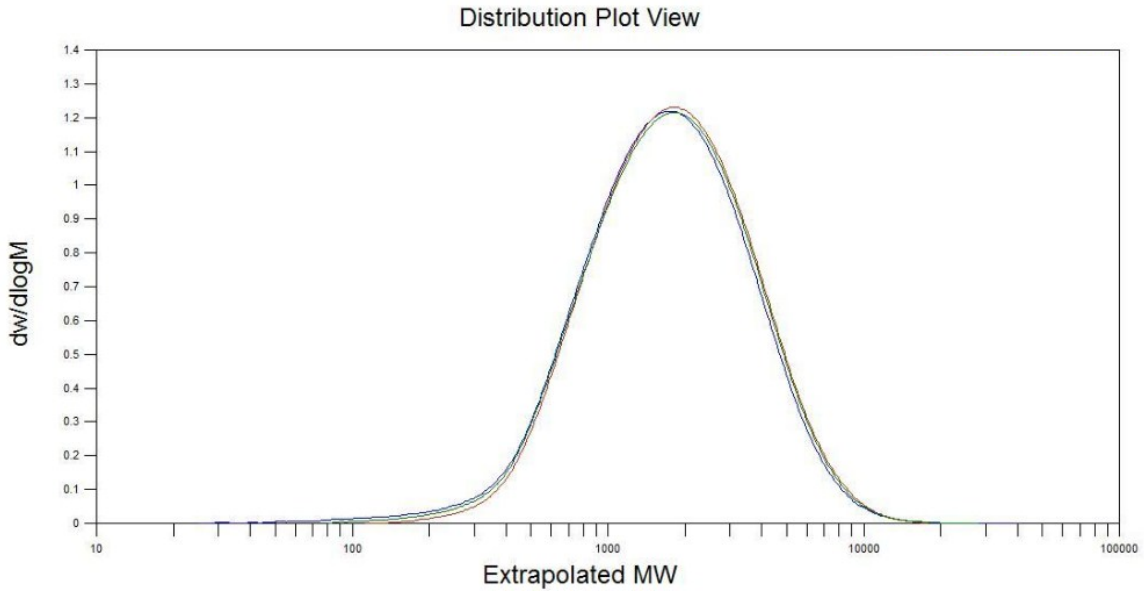

Figure S39: Overlapping molecular weight distribution of polyethylene made with **4** at 50 ℃ with 1 equiv. $ZnEt_2$ in three runs (Table 1, entry 13).

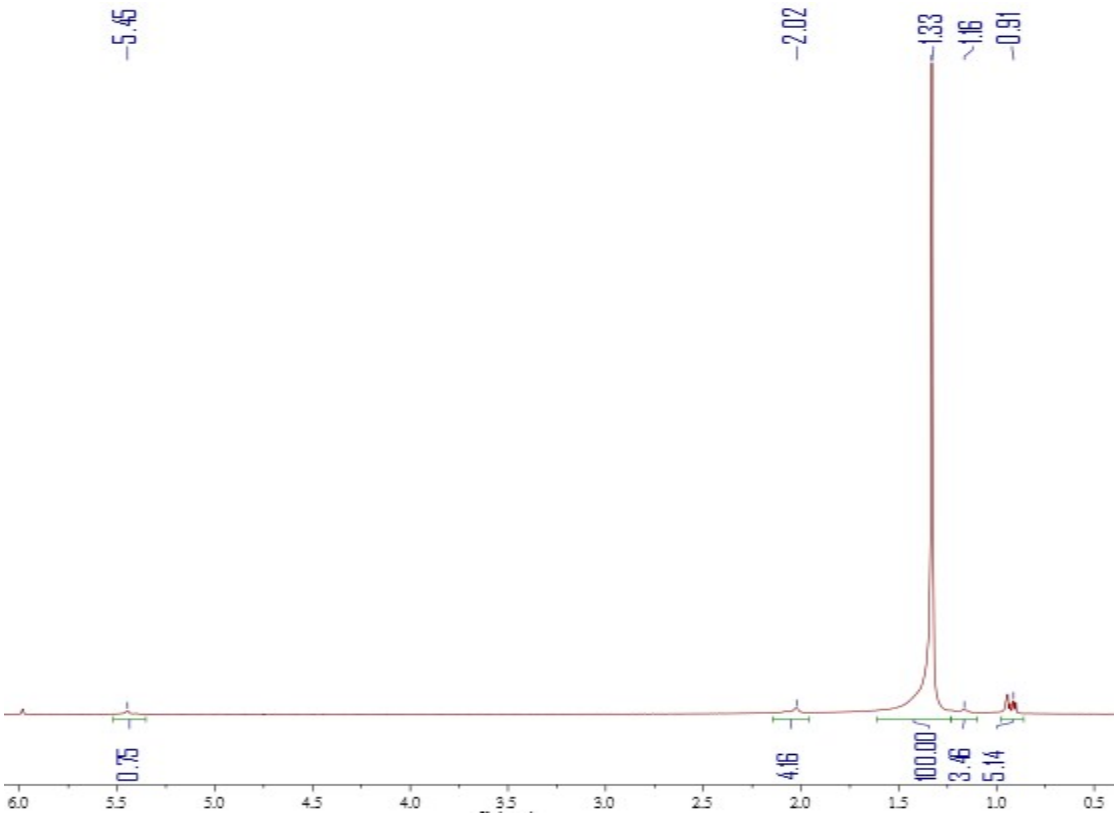

Figure S40: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **4** at 50 ℃ with 1 equiv. $ZnEt_2$ (Table 1, entry 13).

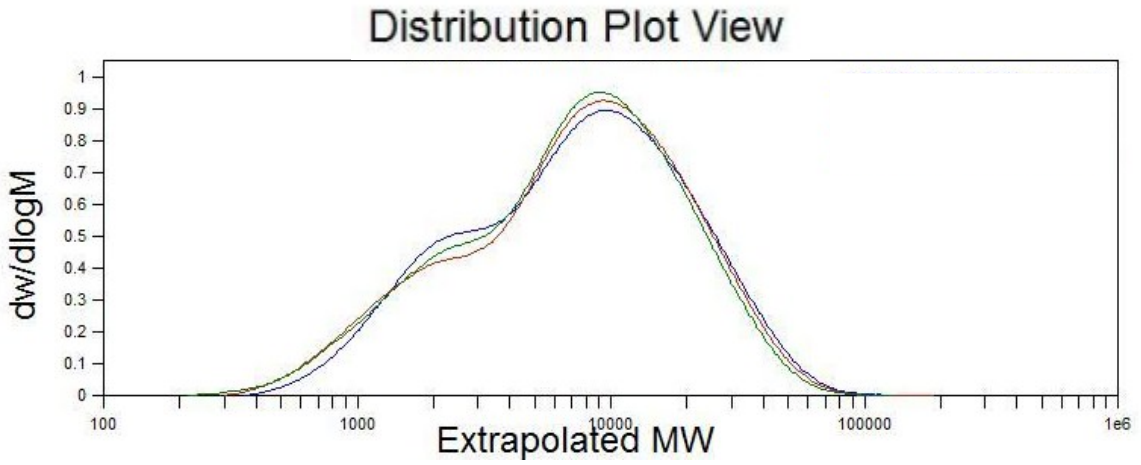

Figure S41: Overlapping molecular weight distribution of polyethylene made with **4** at ambient temperature with 2 equiv. $ZnEt_2$ in three runs (Table 1, entry 14).

Table S8. GPC trace deconvolution of the polyethylene made with **4** at ambient temperature with 2 equiv. $ZnEt_2$ in three runs (Table 1, entry 14).

	Peak label	Location	Height	Area	FWHM	Fit function parameters		
						Location	Width	Height
Trial 1	Low M_n	1650 ±20	0.315 ±0.003	970 ±260	2610 ±700	1650 ±20	0.874 ±0.014	0.315 ±0.003
	High M_n	9840 ±50	0.938 ±0.003	24830 ±5380	20960 ±4540	9840 ±50	1.113 ±0.006	0.938 ±0.003
Trial 2	Low M_n	1790 ±20	0.347 ±0.004	1030 ±150	2560 ±370	1790 ±20	0.798 ±0.010	0.347 ±0.004
	High M_n	10390 ±50	0.901 ±0.003	28370 ±5940	24290 ±5090	10390 ±50	1.196 ±0.006	0.901 ±0.003
Trial 3	Low M_n	1490 ±20	0.311 ±0.003	850 ±130	2330 ±350	1490 ±20	0.862 ±0.012	0.311 ±0.003
	High M_n	10110 ±40	0.945 ±0.003	27900 ±3370	22970 ±2780	10110 ±40	1.170 ±0.006	0.945 ±0.003

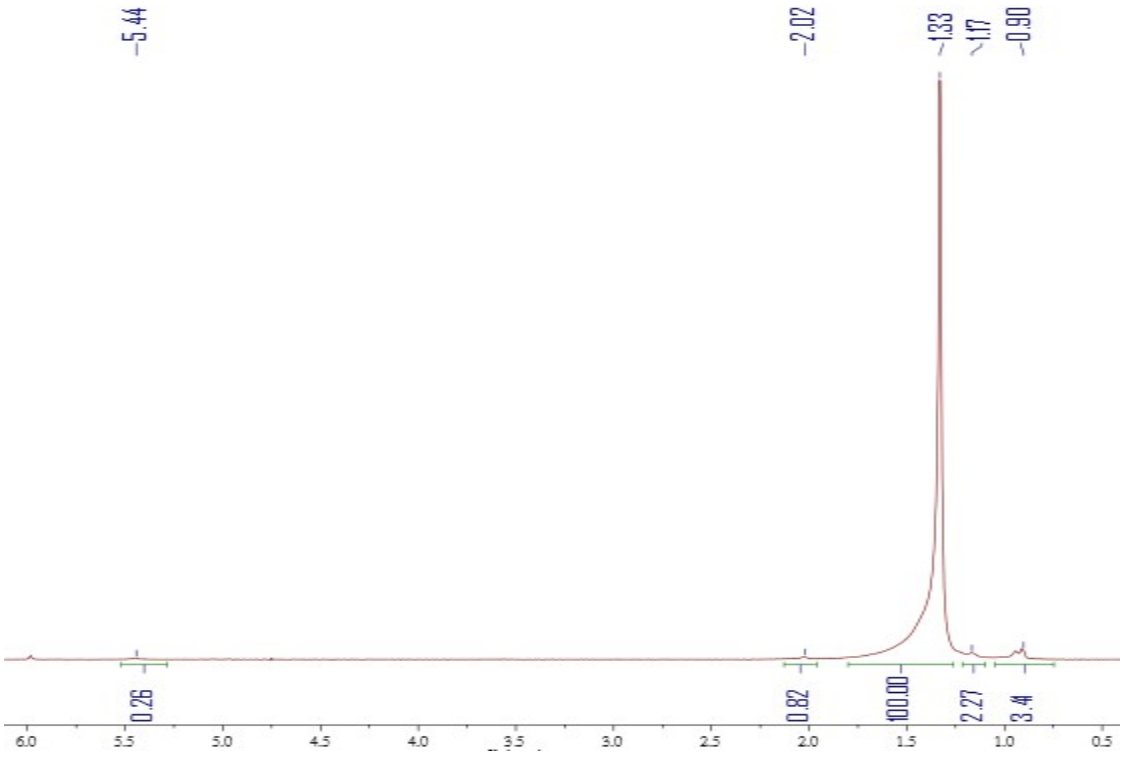

Figure S42: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **4** at ambient temperature with 2 equiv. $ZnEt_2$ (Table 1, entry 14).

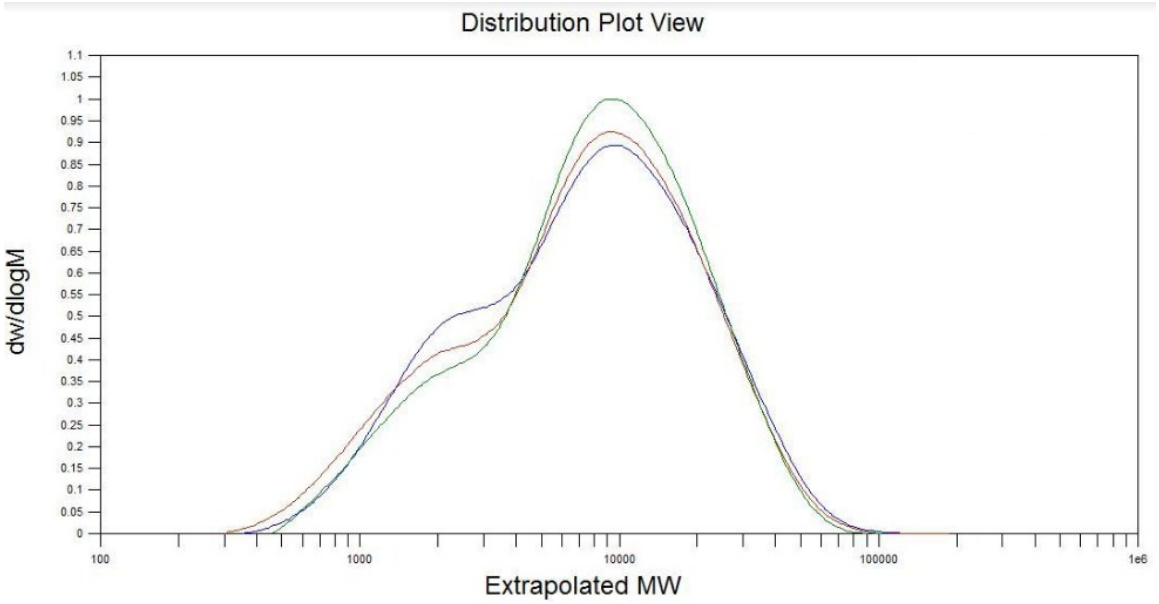

Figure S43: Overlapping molecular weight distribution of polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$ and 11 equiv. $ZnBr_2$ in three runs (Table 1, entry 15).

Table S9. GPC trace deconvolution of the polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$ and 11 equiv. $ZnBr_2$ in three runs (Table 1, entry 15).

	Peak label	**Location**	**Height**	**Area**	**FWHM**	**Fit function parameters**		
						Location	Width	Height
Trial 1	Low M_n	1580 ±20	0.279 ±0.004	720 ±170	2240 ±520	1580 ±20	0.794 ±0.015	0.279 ±0.004
	High M_n	9950 ±40	0.953 ±0.003	27020 ±4390	22170 ±3600	9950 ±40	1.153 ±0.006	0.953 ±0.003
Trial 2	Low M_n	1540 ±20	0.274 ±0.004	700 ±160	2210 ±510	1540 ±20	0.800 ±0.015	0.274 ±0.004
	High M_n	9820 ±40	0.935 ±0.003	26560 ±4450	22150 ±3710	9820 ±40	1.164 ±0.006	0.935 ±0.003
Trial 3	Low M_n	1720 ±20	0.336 ±0.004	900 ±170	2330 ±440	1720 ±20	0.761 ±0.012	0.336 ±0.004
	High M_n	9145 ±40	0.925 ±0.003	22030 ±4270	19000 ±3680	9145 ±40	1.091 ±0.006	0.925 ±0.003

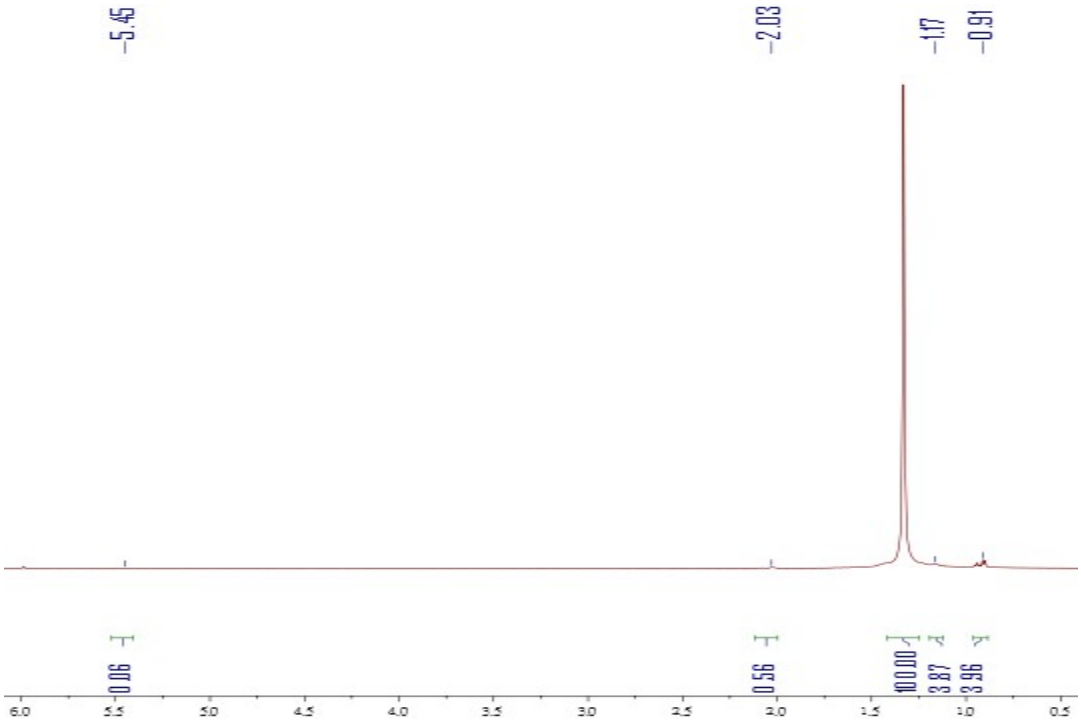

Figure S44: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$ and 11 equiv. $ZnBr_2$ (Table 1, entry 15).

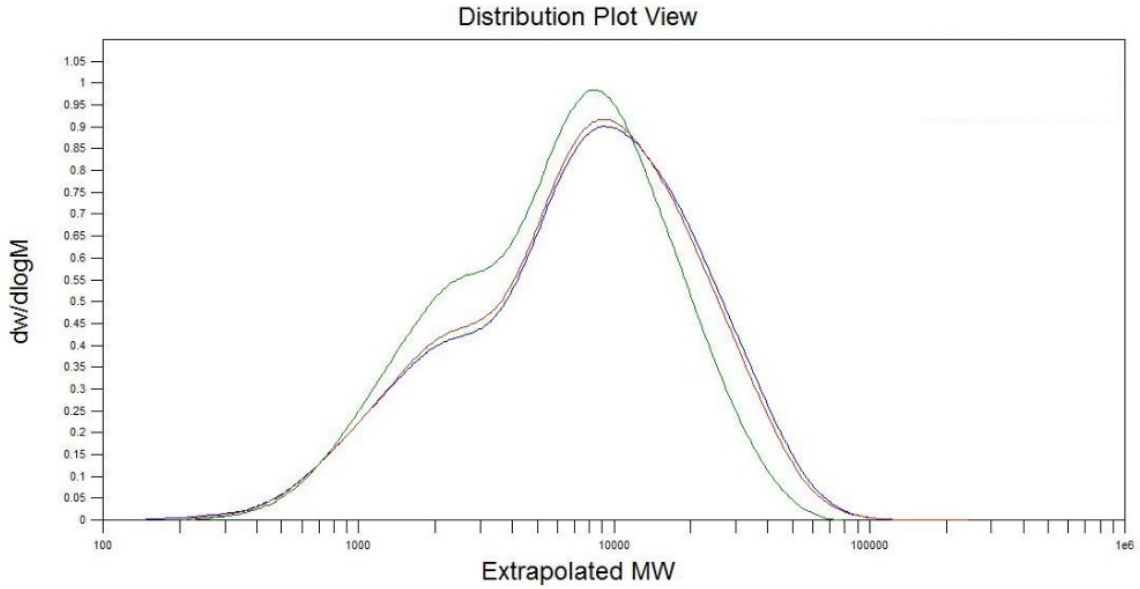

Figure S45: Overlapping molecular weight distribution of polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$ and 20 equiv. THF in three runs (Table 1, entry 16).

Table S10. GPC trace deconvolution of the polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$ and 20 equiv. THF in three runs (Table 1, entry 16).

	Peak label	Location	Height	Area	FWHM	Fit function parameters		
						Location	Width	Height
Trial 1	Low M_n	1460 ±20	0.269 ±0.004	690 ±200	2200 ±640	1460 ±20	0.836 ±0.017	0.269 ±0.004
	High M_n	10330 ±50	0.903 ±0.003	29020 ±6450	24620 ±5470	10330 ±50	1.214 ±0.007	0.903 ±0.003
Trial 2	Low M_n	1770 ±20	0.386 ±0.004	1180 ±240	2610 ±540	1770 ±20	0.821 ±0.011	0.386 ±0.004
	High M_n	8890 ±50	0.946 ±0.003	19700 ±4580	16960 ±3940	8890 ±50	1.019 ±0.006	0.946 0.003
Trial 3	Low M_n	1500 ±20	0.279 ±0.004	750 ±210	2300 ±630	1500 ±20	0.848 ±0.016	0.279 ±0.004
	High M_n	10050 ±50	0.911 ±0.003	27470 ±5980	23300 ±5070	10050 ±50	1.189 ±0.007	0.911 ±0.003

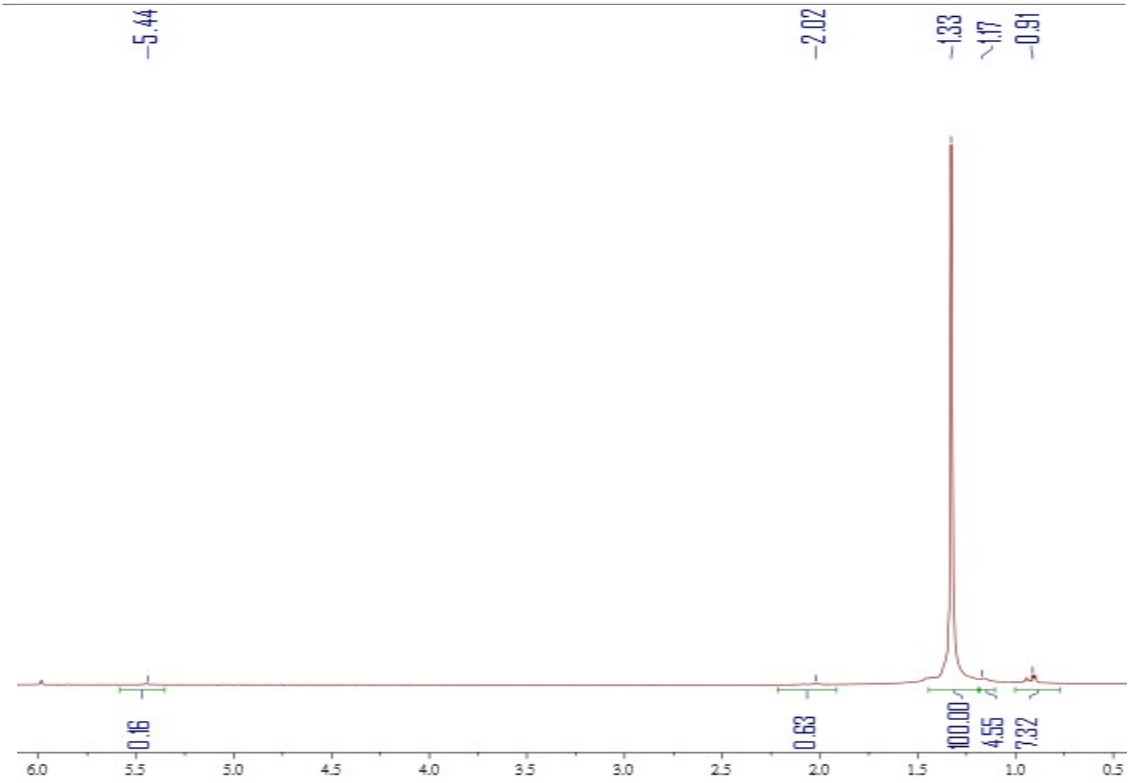

Figure S46: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$ and 20 equiv. THF (Table 1, entry 16).

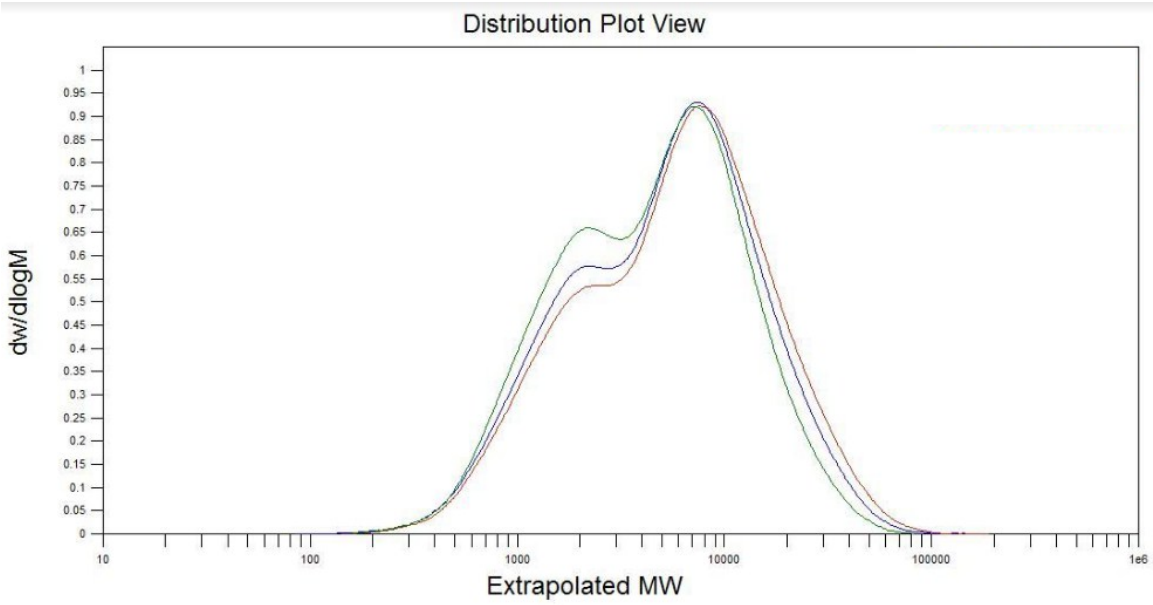

Figure S47: Overlapping molecular weight distribution of polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$ 11 equiv. $ZnBr_2$, and 20 equiv. THF in three runs (Table 1, entry 17).

Table S11. GPC trace deconvolution of the polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$, 11 equiv. $ZnBr_2$ and 20 equiv. THF in three runs (Table 1, entry 17).

	Peak label	**Location**	**Height**	**Area**	**FWHM**	**Fit function parameters**		
						Location	Width	Height
Trial 1	Low M_n	1470 ±20	0.406 ±0.006	970 ±270	2050 ±570	1470 ±20	0.780 ±0.015	0.406 ±0.006
	High M_n	7650 ±60	0.863 ±0.004	16260 ±6550	15200 ±6120	7650 ±60	1.053 ±0.009	0.863 ±0.004
Trial 2	Low M_n	1430 ±20	0.356 ±0.005	800 ±180	1960 ±430	1430 ±20	0.768 ±0.014	0.356 ±0.005
	High M_n	8050 ±50	0.866 ±0.003	19040 ±5710	17360 ±5200	8050 ±50	1.124 ±0.009	0.866 ±0.003
Trial 3	Low M_n	1630 ±20	0.529 ±0.005	1520 ±300	2460 ±490	1630 ±20	0.838 ±0.011	0.529 ±0.005
	High M_n	7600 ±50	0.849 ±0.004	13250 ±5270	13020 ±5180	7600 ±50	0.933 ±0.008	0.849 ±0.004

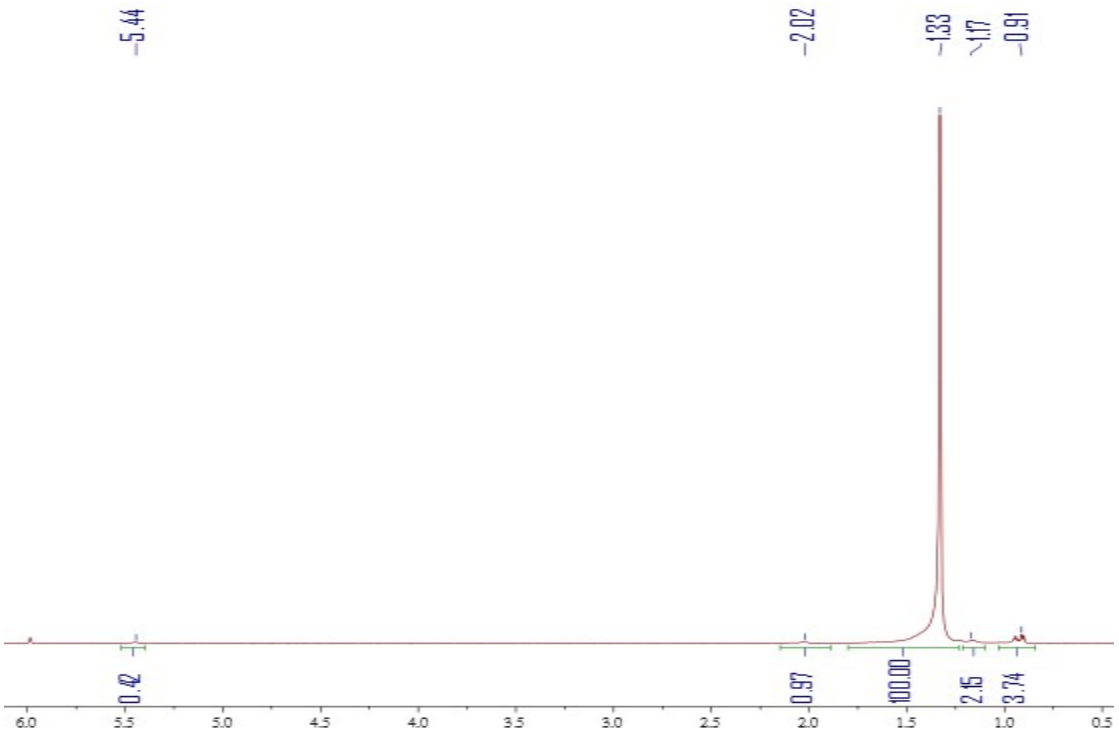

Figure S48: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **4** at ambient temperature with 1 equiv. $ZnEt_2$, 11 equiv. $ZnBr_2$ and 20 equiv. THF (Table 1, entry 17).

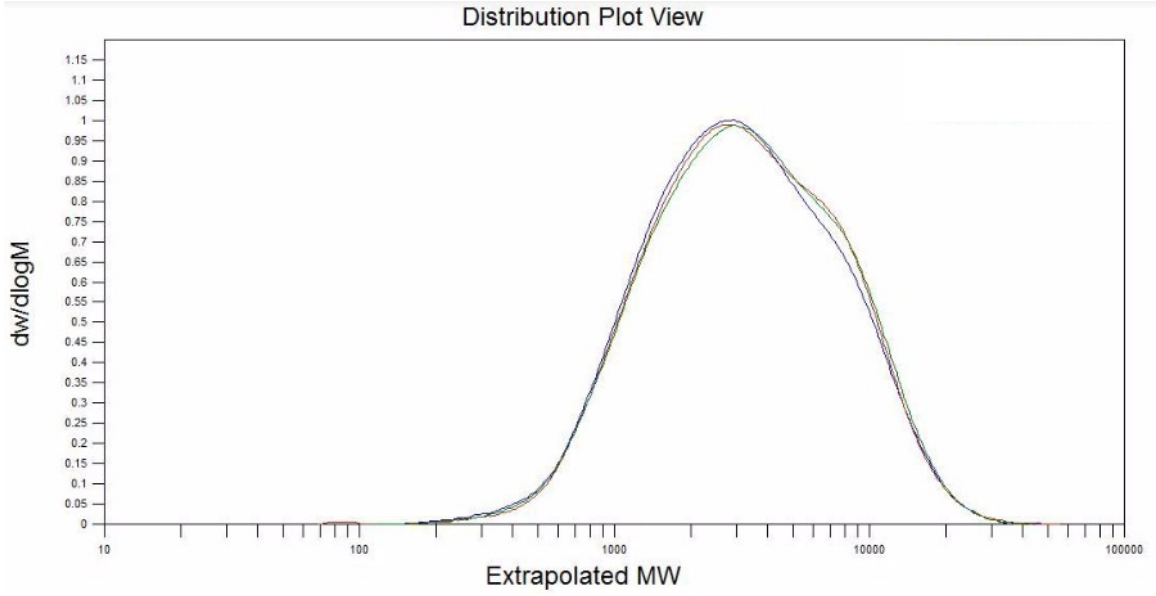

Figure S50: Overlapping molecular weight distribution of polyethylene made with **5** at 35 ℃ with 10 equiv. $ZnBr_2$ in three runs (Table 1, entry 19).

Table S12. GPC trace deconvolution of the polyethylene made with **5** at 35 ℃ with 10 equiv. $ZnBr_2$ in three runs (Table 1, entry 19).

	Peak label	Location	Height	Area	FWHM	Fit function parameters		
						Location	Width	Height
Trial 1	Low M_n	2450 ±10	0.965 ±0.003	5850 ±530	4890 ±440	2450 ±10	1.056 ±0.006	0.965 ±0.003
	High M_n	8070 ±50	0.440 ±0.008	4570 ±1190	9220 ±2400	8070 ±50	0.653 ±0.006	0.440 ±0.008
Trial 2	Low M_n	2430 ±20	0.985 ±0.004	5970 ±700	4880 ±570	2430 ±20	1.063 0.006	0.985 ±0.004
	High M_n	8220 ±70	0.383 ±0.009	4400 ±2450	10110 ±5610	8200 ±70	0.698 ±0.008	0.383 ±0.009
Trial 3	Low M_n	2620 ±20	0.977 ±0.003	7000 ±950	5650 ±770	2620 ±20	1.125 ±0.007	0.977 ±0.003
	High M_n	8630 ±60	0.360 ±0.009	3860 ±1370	9560 ±3390	8630 ±60	0.635 ±0.008	0.360 ±0.009

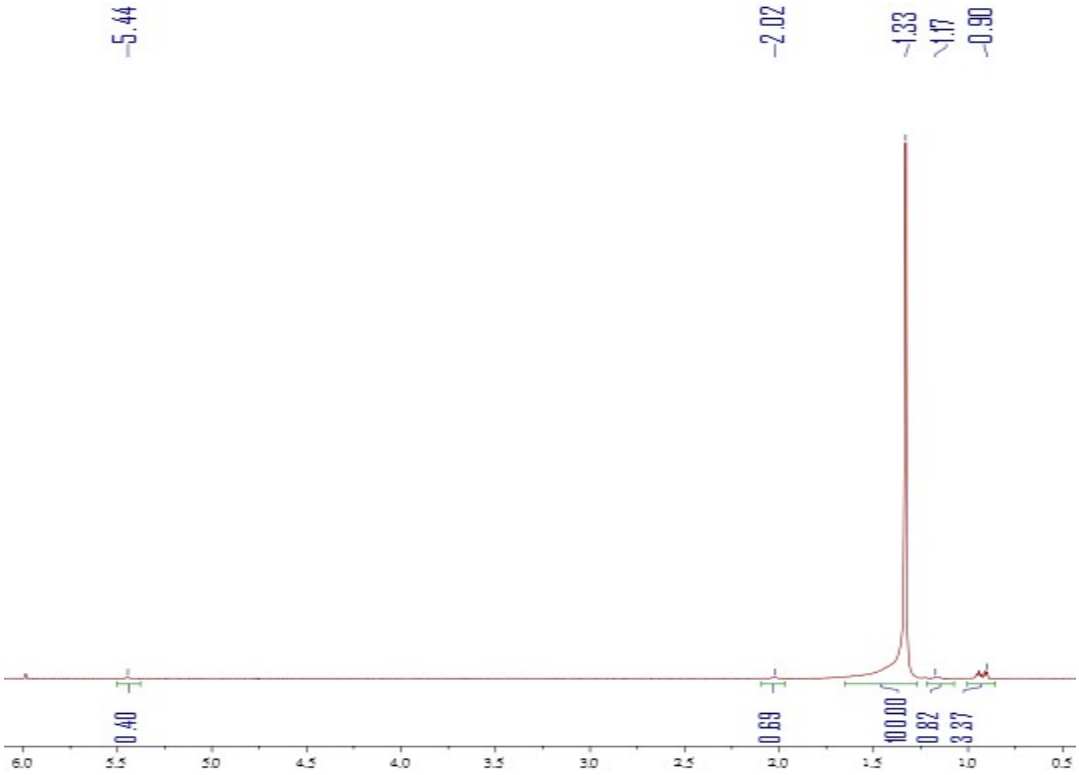

Figure S50: ^1H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **5** at 35 ℃ with 10 equiv. $ZnBr_2$ (Table 1, entry 19).

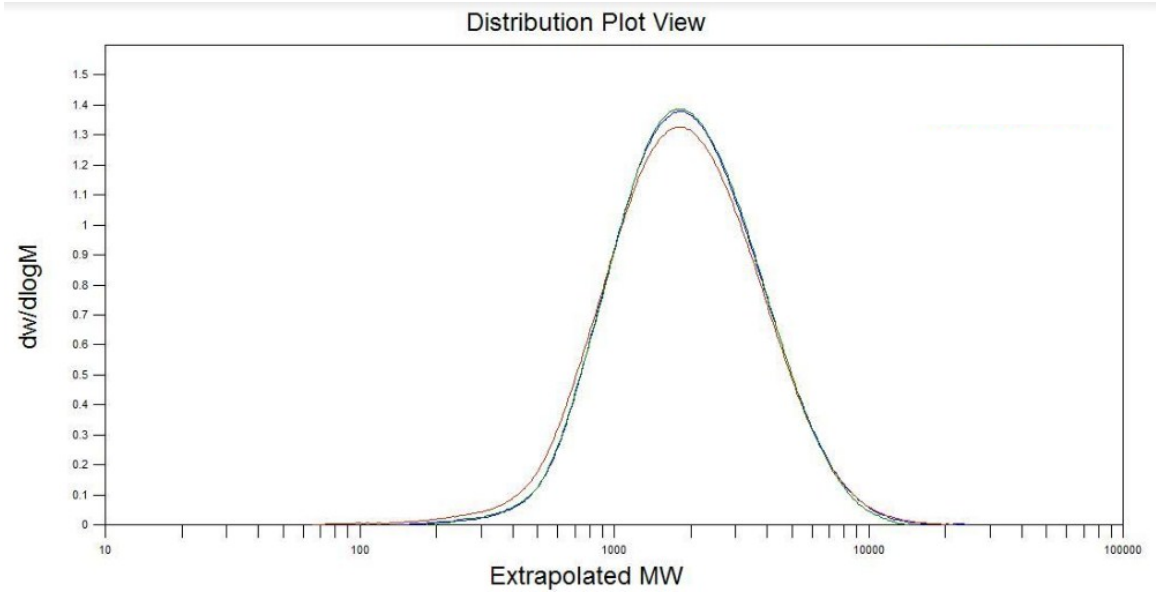

Figure S51: Overlapping molecular weight distribution of polyethylene made with **5** at 50 ℃ with 10 equiv. $ZnBr_2$ in three runs (Table 1, entry 20).

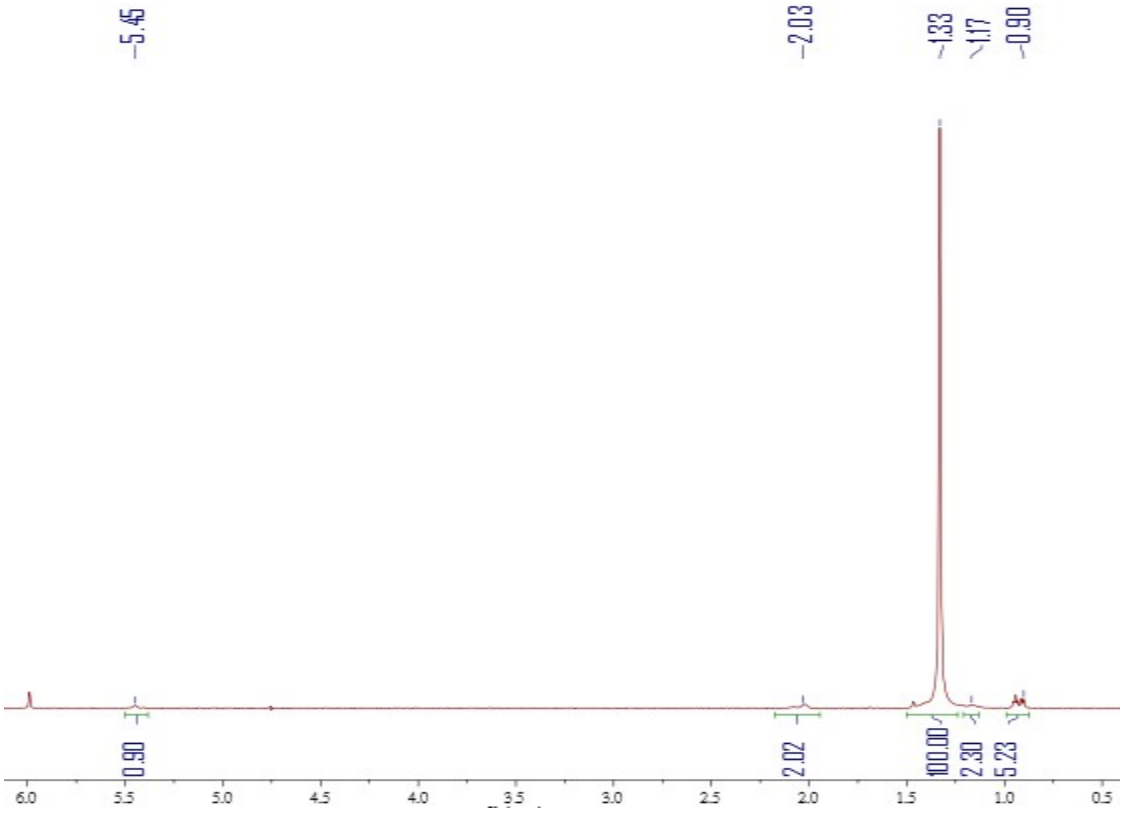

Figure S52: ^1H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **5** at 50 ℃ with 10 equiv. $ZnBr_2$ (Table 1, entry 20).

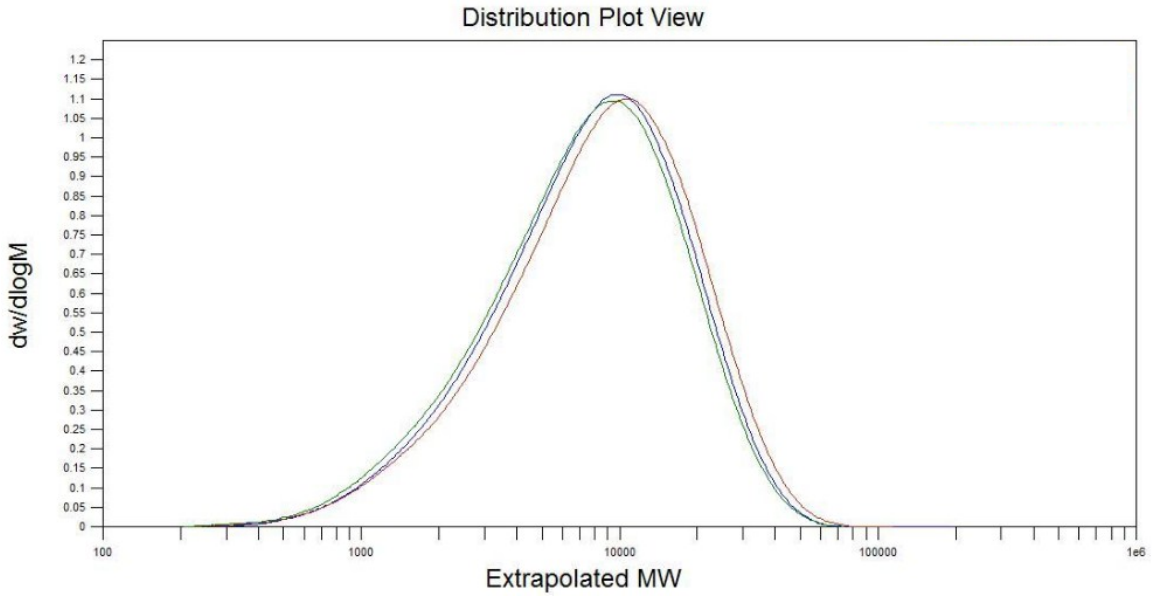

Figure S53: Overlapping molecular weight distribution of polyethylene made with **6** at 50℃ in three runs (Table 1, entry 21).

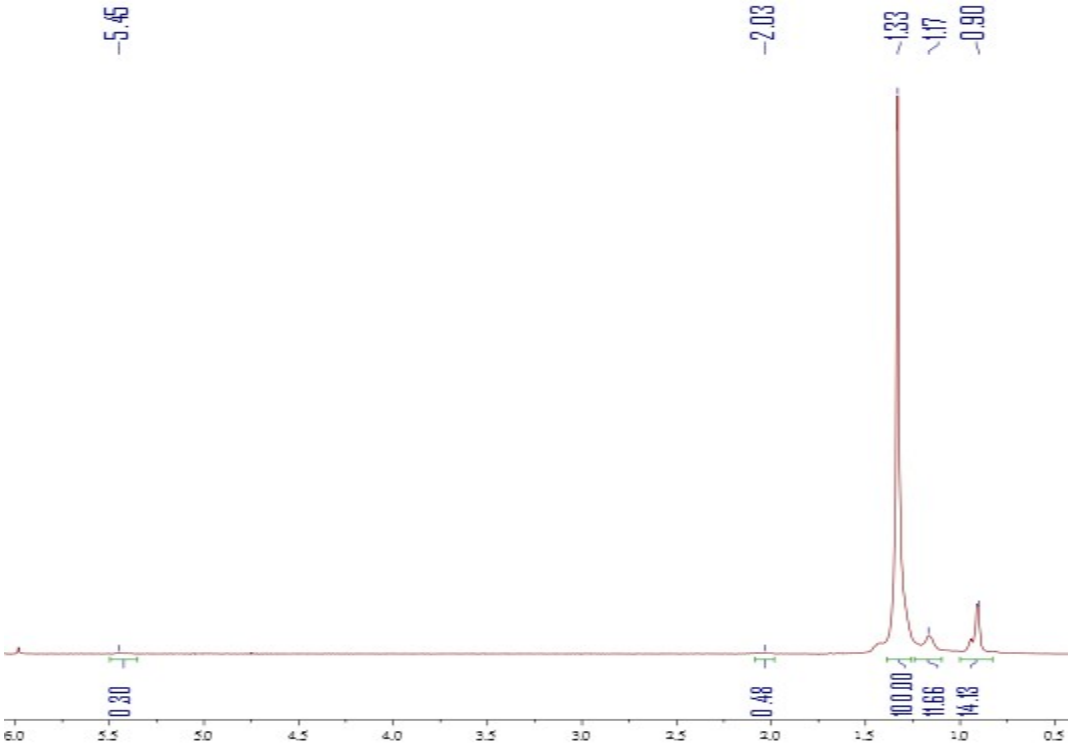

Figure S54: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **6** at 50 ℃ (Table 1, entry 21).

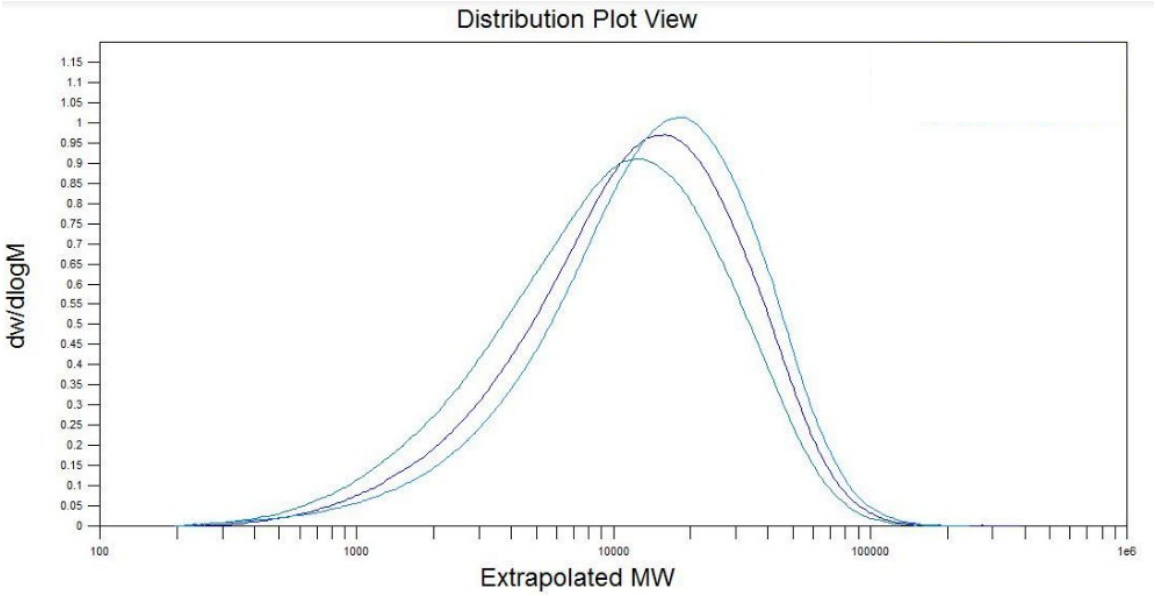

Figure S55: Overlapping molecular weight distribution of polyethylene made with **6** at 35 ℃ with 11 equiv. $ZnBr_2$in three runs (Table 1, entry 22).

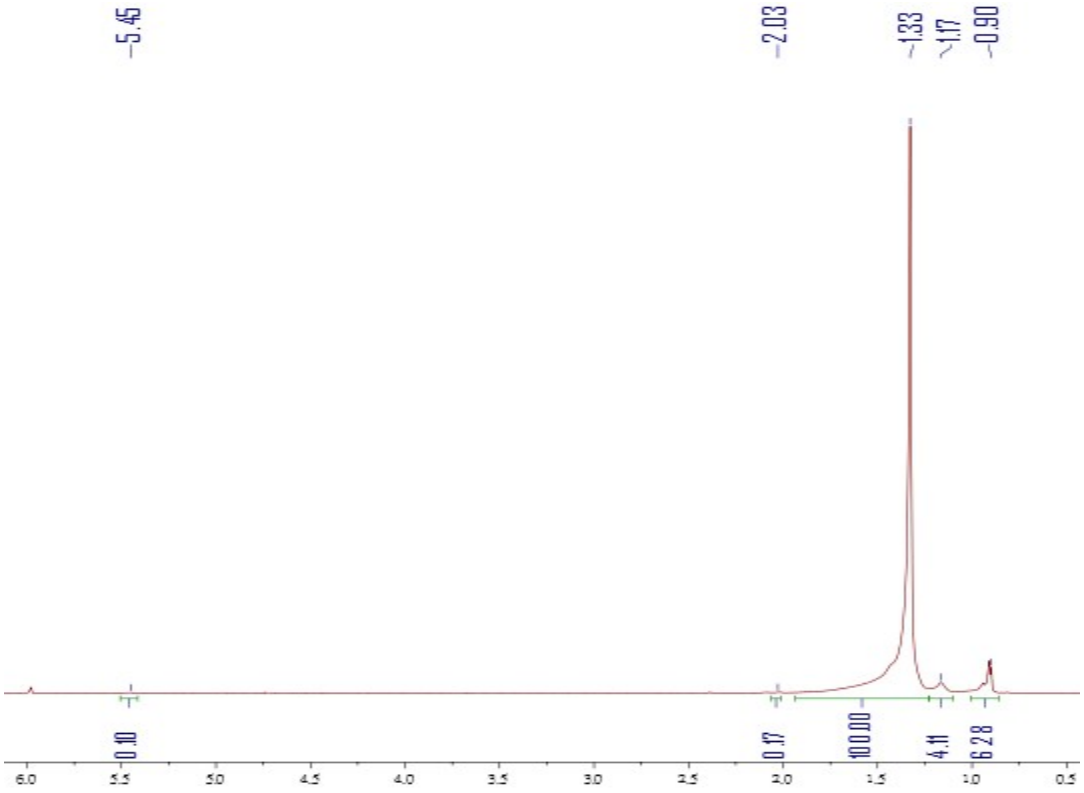

Figure S56: ^{1}H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **6** at 35 ℃ with 11 equiv. $ZnBr_2$ (Table 1, entry 22).

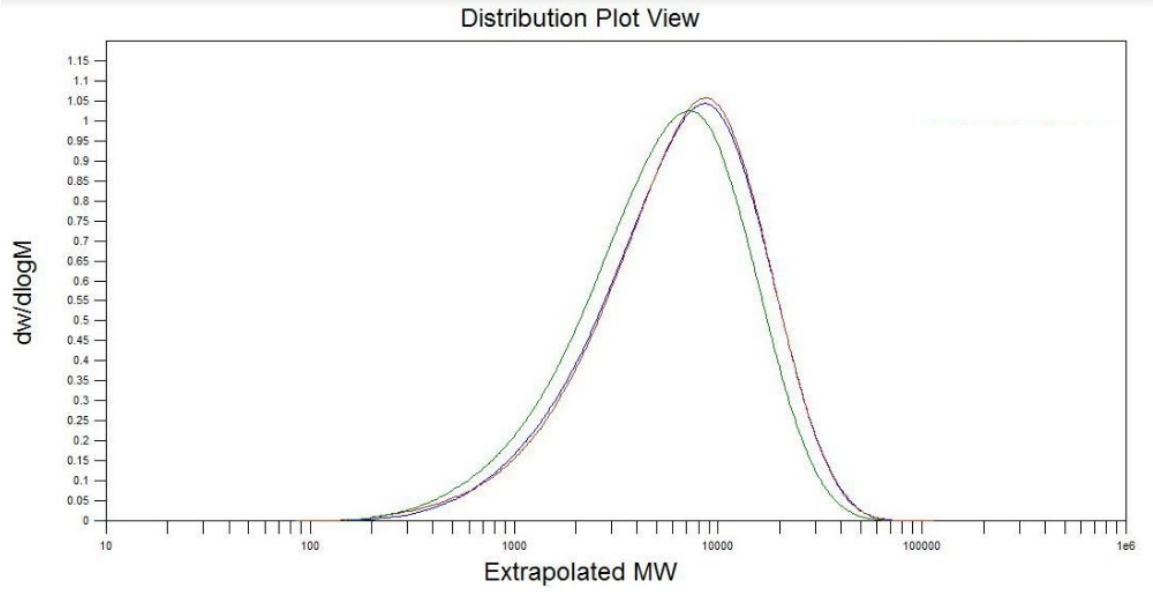

Figure S57: Overlapping molecular weight distribution of polyethylene made with **6** at 50 ℃ with 11 equiv. $ZnBr_2$in three runs (Table 1, entry 23).

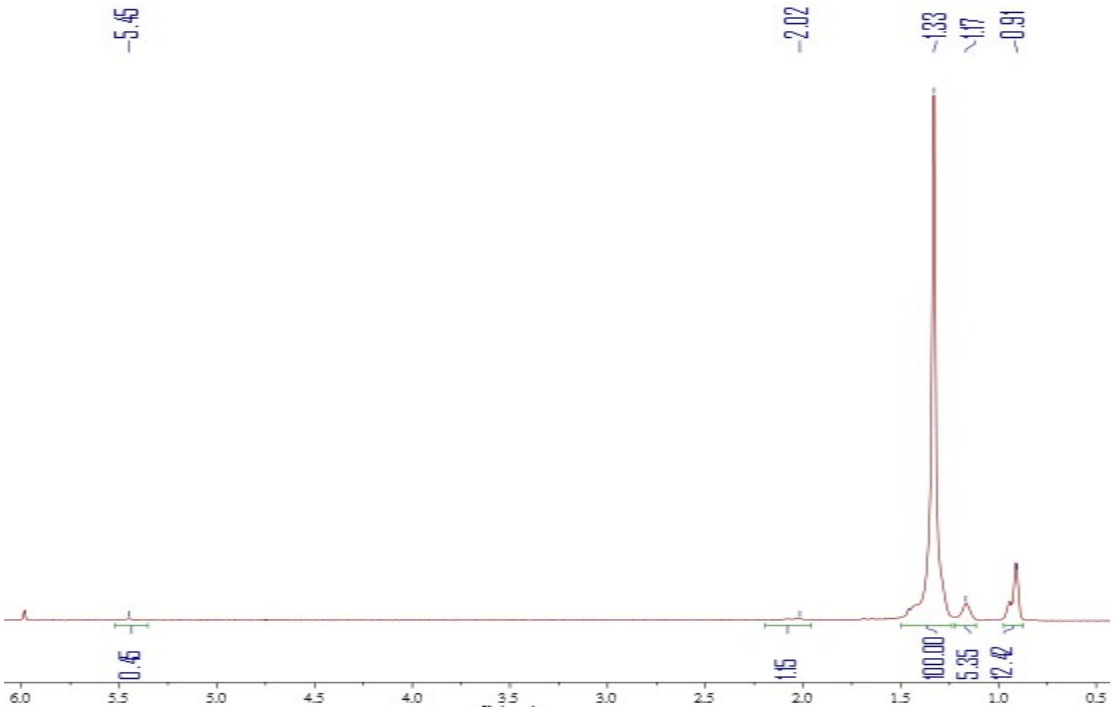

Figure S58: ^1H NMR spectrum of polyethylene in tetrachloroethane-D_2 at 100 ℃ of the polyethylene made with **6** at 50 ℃ with 11 equiv. $ZnBr_2$ (Table 1, entry 23).

Computational Results

Density functional theory calculations were perfomed using Gaussian 09 package (M06, 6-31g). All gometries were optimzed to obtain a stationary point with minimum energy representing their ground state energies. The calculations were performed at 50 °C using toluene as a solvent. The solvent effects on the complexes were calculated using SMD (Solvation Model based on Density). The optimized geometries and their respective cartesian coordinates are shown below. Images and cartesian coordinates of the optimized geometries were obtained using chemcraft.

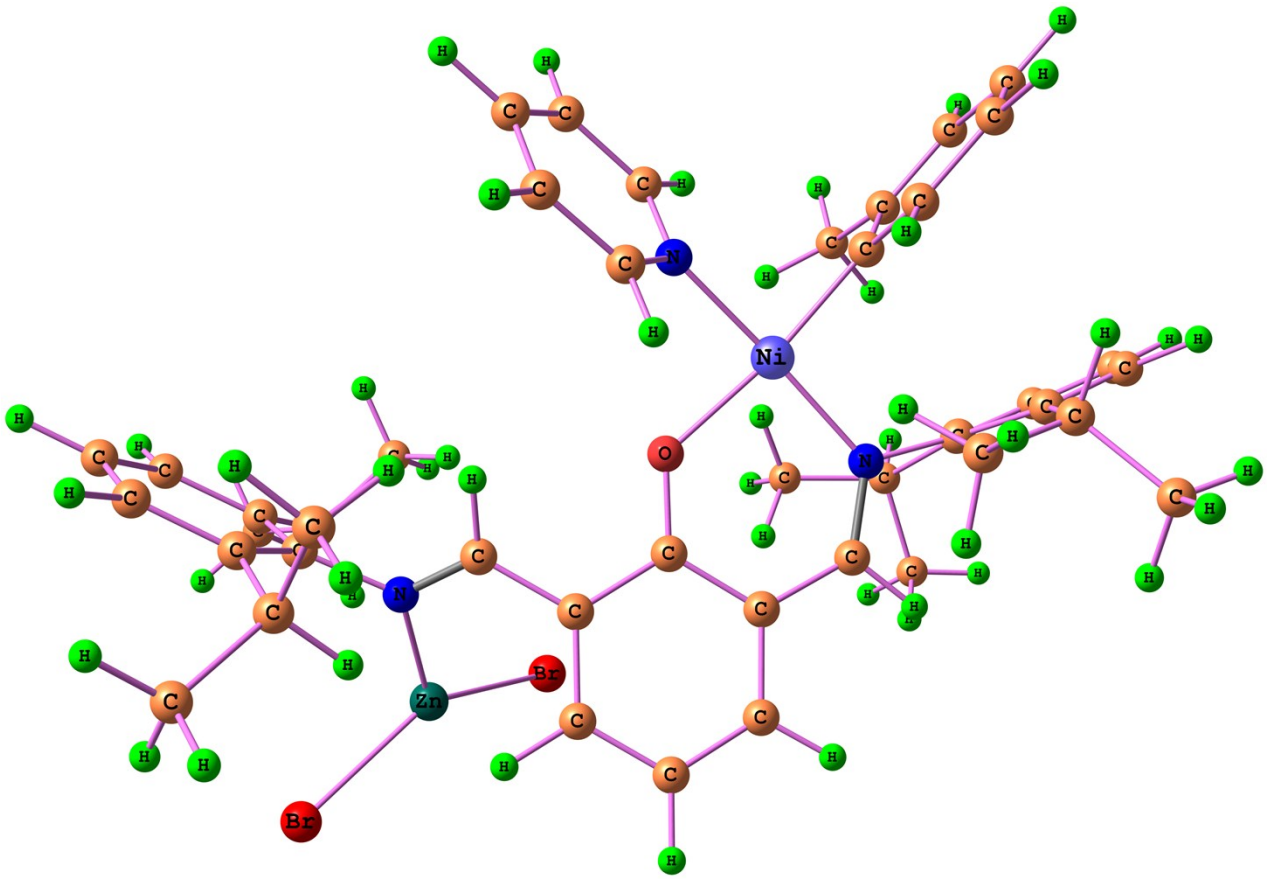

Figure S59: Optimized M06/6-31g/auto cartesian geometry for lowest energy of **7a.**

Table S13. Optimized M06/6-31g/auto cartesian coordinates (Å) for lowest energy of **7a**.

C	-2.048664000	0.538795000	0.632367000
C	-1.255054000	-0.519769000	1.198948000
C	-1.854707000	-1.563660000	1.916742000
H	-2.918982000	-1.507432000	2.157575000
C	-1.100464000	-2.620544000	2.426011000
H	-1.578978000	-3.414295000	2.988634000
C	0.266005000	-2.645473000	2.180383000
H	0.866201000	-3.482891000	2.532435000

C	0.909784000	-1.609537000	1.480452000
C	2.300154000	-1.743502000	1.175637000
C	0.157403000	-0.500141000	0.998664000
O	0.704337000	0.493088000	0.353608000
N	-3.252812000	0.310744000	0.193152000
H	-1.626666000	1.545900000	0.575190000
N	3.061394000	-0.901820000	0.525135000
H	2.762283000	-2.679824000	1.509172000
H	-5.639094000	4.091722000	1.277708000
C	-5.331828000	3.374895000	0.519686000
C	-4.524676000	2.290728000	0.887770000
C	-4.179336000	2.062482000	2.351518000
C	-4.129714000	1.397121000	-0.127278000
C	-4.639051000	1.486185000	-1.439122000
C	-4.291295000	0.426269000	-2.466168000
C	-5.447731000	2.578796000	-1.755130000
H	-5.840787000	2.681892000	-2.762634000
C	-5.770111000	3.532677000	-0.790242000
H	-6.393171000	4.382429000	-1.055945000
C	3.514385000	-2.796347000	-1.800558000
C	4.596128000	-2.155374000	-0.922193000
C	5.915183000	-2.463828000	-1.283908000
H	6.083695000	-3.044222000	-2.190006000
C	6.996114000	-2.038627000	-0.521874000
H	8.012225000	-2.253196000	-0.841533000

C	6.764691000	-1.360966000	0.667995000
H	7.607372000	-1.056661000	1.285801000
C	5.468221000	-1.050799000	1.103713000
C	5.391550000	-0.434575000	2.506413000
C	4.400038000	-1.386545000	0.246417000
C	5.945783000	-1.447834000	3.527514000
H	5.312973000	-2.347253000	3.544054000
H	5.941032000	-1.012109000	4.535539000
H	6.969790000	-1.762856000	3.299097000
C	4.051616000	0.068462000	3.054509000
H	3.406063000	-0.762095000	3.372849000
H	3.490545000	0.666849000	2.332115000
H	4.247170000	0.684651000	3.942307000
H	6.073867000	0.431181000	2.480875000
C	-5.325067000	0.288257000	-3.579832000
H	-5.318155000	1.157871000	-4.250862000
H	-6.336512000	0.166664000	-3.172681000
H	-5.093012000	-0.596045000	-4.185667000
C	-2.886854000	0.638515000	-3.045158000
H	-2.654940000	-0.142264000	-3.780596000
H	-2.112439000	0.602754000	-2.268490000
H	-2.832378000	1.615008000	-3.546177000
H	-4.285825000	-0.541753000	-1.937826000
C	-3.130255000	3.059692000	2.858359000
H	-2.192768000	2.993652000	2.289060000

H	−2.901665000	2.874916000	3.916066000
H	−3.503368000	4.089647000	2.769093000
C	−5.433391000	2.110020000	3.233558000
H	−5.180491000	1.816412000	4.260563000
H	−6.201263000	1.422558000	2.859351000
H	−5.864791000	3.118680000	3.276507000
H	−3.772099000	1.045475000	2.448090000
C	3.278984000	−4.244930000	−1.334669000
H	4.212692000	−4.819979000	−1.301181000
H	2.581223000	−4.754297000	−2.012612000
H	2.835168000	−4.257520000	−0.329066000
C	2.154615000	−2.111041000	−1.993464000
H	1.700397000	−2.487527000	−2.919634000
H	2.229235000	−1.022068000	−2.072329000
H	1.449574000	−2.341337000	−1.185663000
H	3.973123000	−2.856517000	−2.801204000
Ni	2.536982000	0.852721000	−0.020671000
Zn	−3.772324000	−1.564786000	−0.079030000
Br	−5.917044000	−1.794869000	0.788878000
Br	−2.343602000	−2.883340000	−1.335311000
H	2.601011000	2.702038000	−2.341169000
C	2.061717000	3.234525000	−1.567441000
C	1.542585000	4.503693000	−1.790168000
H	1.655928000	4.963887000	−2.765327000
C	0.894770000	5.166069000	−0.749685000

H	0.488836000	6.161966000	-0.896348000
C	0.780571000	4.528934000	0.485420000
H	0.290902000	5.012503000	1.323694000
C	1.303770000	3.251986000	0.637418000
H	1.219107000	2.711740000	1.573453000
N	1.935926000	2.612539000	-0.374931000
C	4.297944000	0.642322000	-2.806884000
C	4.949990000	1.327189000	-1.634877000
C	6.246598000	1.836481000	-1.807313000
H	6.738446000	1.702499000	-2.771345000
C	6.905928000	2.511514000	-0.782622000
H	7.911495000	2.896077000	-0.936473000
C	6.245748000	2.712730000	0.429479000
H	6.726639000	3.268362000	1.232579000
C	4.956415000	2.204952000	0.603721000
H	4.458258000	2.388488000	1.557397000
C	4.290921000	1.468855000	-0.393589000
H	4.582043000	1.114183000	-3.756966000
H	3.203797000	0.665314000	-2.726986000
H	4.590415000	-0.415299000	-2.871103000

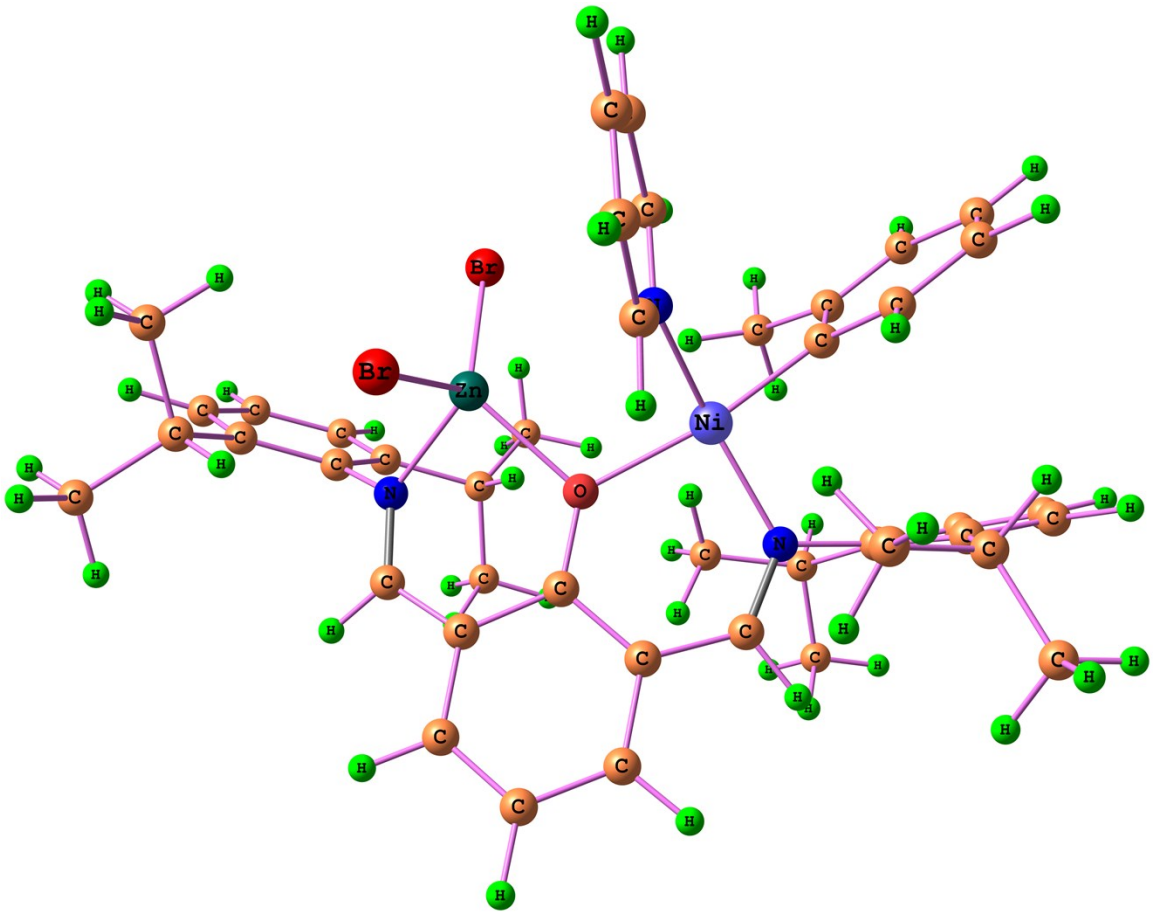

Figure S60: Optimized M06/6-31g/auto cartesian geometry for lowest energy of **7b.**

Table S14. Optimized M06/6-31g/auto cartesian coordinates (Å) for lowest energy of **7b**.

C	2.721303000	1.504098000	1.626643000
C	1.503828000	1.475601000	2.410190000
C	1.546645000	2.136450000	3.648074000
H	2.518633000	2.445390000	4.027563000
C	0.397721000	2.435250000	4.371327000
H	0.460987000	2.927759000	5.335157000
C	-0.830713000	2.173864000	3.782186000

H	-1.749489000	2.505844000	4.262602000
C	-0.928851000	1.511840000	2.546078000
C	-2.218473000	1.513067000	1.906839000
C	0.244060000	1.030602000	1.895829000
O	0.135996000	0.251955000	0.822904000
N	2.901763000	0.892520000	0.503683000
H	3.502792000	2.184592000	1.991940000
N	-2.565711000	0.917386000	0.803009000
H	-2.969960000	2.142193000	2.397465000
H	4.459474000	2.987928000	-3.228395000
C	4.681687000	2.359532000	-2.369255000
C	3.665521000	2.040715000	-1.467996000
C	2.251760000	2.575608000	-1.629169000
C	3.993935000	1.227187000	-0.364533000
C	5.278021000	0.697028000	-0.172614000
C	5.598623000	-0.273005000	0.948682000
C	6.264429000	1.043933000	-1.107000000
H	7.270064000	0.645977000	-0.988123000
C	5.974880000	1.868987000	-2.188229000
H	6.754403000	2.120556000	-2.902685000
C	-2.892607000	3.219128000	-1.145968000
C	-3.969137000	2.211304000	-0.736250000
C	-5.199610000	2.359405000	-1.388787000
H	-5.277031000	3.087590000	-2.194693000
C	-6.306899000	1.599394000	-1.032633000

H	-7.242614000	1.703586000	-1.574784000
C	-6.212700000	0.722785000	0.039492000
H	-7.084462000	0.145704000	0.343216000
C	-5.010937000	0.532586000	0.738140000
C	-5.119376000	-0.405918000	1.947125000
C	-3.880298000	1.242253000	0.286520000
C	-5.981996000	0.268192000	3.031475000
H	-5.478460000	1.166841000	3.415817000
H	-6.137380000	-0.418210000	3.874566000
H	-6.964553000	0.571805000	2.652695000
C	-3.859247000	-0.957998000	2.625767000
H	-3.412516000	-0.230765000	3.318623000
H	-3.084182000	-1.256374000	1.913573000
H	-4.139060000	-1.836891000	3.221522000
H	-5.683603000	-1.277768000	1.576460000
C	5.900175000	-1.663887000	0.374742000
H	6.825870000	-1.656093000	-0.218046000
H	5.080655000	-2.001673000	-0.271546000
H	6.013799000	-2.395537000	1.185020000
C	6.752693000	0.222632000	1.826096000
H	6.931338000	-0.480522000	2.649976000
H	6.536956000	1.209261000	2.258002000
H	7.685994000	0.305065000	1.252299000
H	4.710026000	-0.381963000	1.585701000
C	2.139253000	3.946147000	-0.945400000

H	2.363208000	3.881180000	0.129038000
H	1.130267000	4.363671000	-1.058299000
H	2.851715000	4.654037000	-1.392824000
C	1.804236000	2.652888000	-3.089047000
H	0.731494000	2.886262000	-3.141457000
H	1.965249000	1.692987000	-3.595422000
H	2.337090000	3.439172000	-3.641661000
H	1.569890000	1.878037000	-1.113651000
C	-3.227924000	4.582306000	-0.511570000
H	-4.237026000	4.920428000	-0.775882000
H	-2.509911000	5.345204000	-0.841501000
H	-3.170884000	4.514868000	0.584490000
C	-1.411869000	2.916350000	-0.891109000
H	-0.812693000	3.541802000	-1.566611000
H	-1.144039000	1.869921000	-1.062149000
H	-1.110925000	3.169793000	0.135059000
H	-3.008255000	3.335462000	-2.236230000
Ni	-1.518878000	-0.480296000	0.058582000
Zn	1.764941000	-0.667908000	0.025141000
Br	2.012930000	-1.129948000	-2.250846000
Br	2.370183000	-2.223894000	1.728106000
H	-0.548259000	-2.346973000	-2.139675000
C	-0.515757000	-2.907537000	-1.214561000
C	-0.254679000	-4.269245000	-1.192497000
H	-0.052640000	-4.788174000	-2.122468000

C	-0.272937000	-4.945406000	0.026461000
H	-0.087614000	-6.014205000	0.065503000
C	-0.521444000	-4.228823000	1.194941000
H	-0.518727000	-4.712547000	2.165039000
C	-0.724828000	-2.860064000	1.112039000
H	-0.862009000	-2.253719000	2.001780000
N	-0.739895000	-2.207379000	-0.077602000
C	-1.932107000	0.155491000	-3.009142000
C	-2.937656000	-0.791805000	-2.405602000
C	-3.932077000	-1.326385000	-3.240848000
H	-3.955790000	-1.020597000	-4.286930000
C	-4.867228000	-2.242472000	-2.765521000
H	-5.628667000	-2.643046000	-3.430587000
C	-4.791715000	-2.661677000	-1.437868000
H	-5.488614000	-3.404415000	-1.053935000
C	-3.806547000	-2.131399000	-0.602532000
H	-3.754842000	-2.495483000	0.423552000
C	-2.891768000	-1.162899000	-1.043766000
H	-1.782985000	-0.055458000	-4.075866000
H	-0.946513000	0.085454000	-2.524444000
H	-2.262176000	1.202116000	-2.934764000

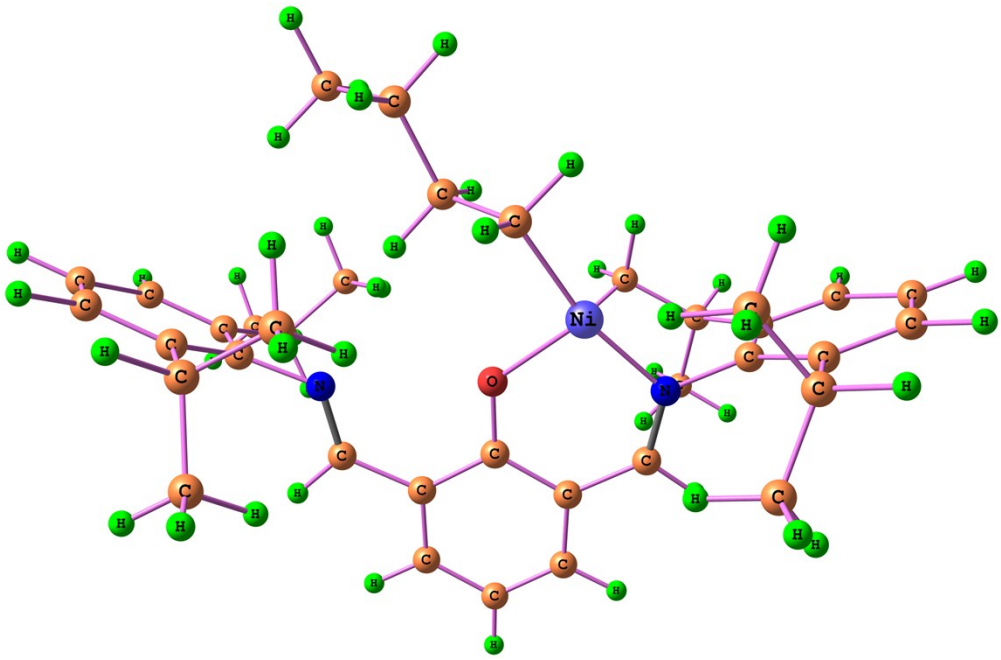

Figure S61: Optimized M06/6-31g/auto cartesian geometry for lowest energy of **INT1**.

Table S15. Optimized M06/6-31g/auto cartesian coordinates (Å) for lowest energy of **INT1**.

C	-2.401347000	1.511059000	-1.180856000
C	-1.052480000	1.990186000	-1.457146000
C	-0.966380000	3.207680000	-2.134420000
H	-1.896347000	3.694242000	-2.425563000
C	0.252330000	3.821841000	-2.438920000
H	0.276583000	4.770710000	-2.964139000
C	1.418237000	3.198808000	-2.040037000
H	2.384115000	3.660917000	-2.239471000
C	1.398206000	1.959946000	-1.364344000
C	2.655469000	1.437869000	-0.925252000
C	0.152553000	1.313167000	-1.067345000

O	0.068919000	0.154441000	-0.453517000
N	-2.725785000	0.439013000	-0.553734000
N	2.822970000	0.294281000	-0.319850000
H	-6.577113000	0.833697000	1.911366000
C	-6.041701000	0.341700000	1.103754000
C	-4.747586000	0.762988000	0.781682000
C	-4.044065000	1.845713000	1.588733000
C	-4.068686000	0.102246000	-0.275198000
C	-4.676120000	-0.964253000	-0.977203000
C	-3.990974000	-1.718964000	-2.105348000
C	-5.978301000	-1.332986000	-0.621512000
H	-6.455142000	-2.146510000	-1.166097000
C	-6.662459000	-0.692912000	0.407191000
H	-7.671382000	-1.000162000	0.669901000
C	3.635374000	1.476768000	2.313679000
C	4.512703000	0.577707000	1.446128000
C	5.798074000	0.290049000	1.926658000
H	6.118335000	0.748713000	2.859950000
C	6.655170000	-0.571231000	1.251204000
H	7.647148000	-0.775482000	1.644382000
C	6.221027000	-1.193485000	0.085722000
H	6.871814000	-1.897373000	-0.428960000
C	4.950763000	-0.940881000	-0.445278000
C	4.514082000	-1.748063000	-1.657018000
C	4.119101000	-0.017529000	0.225073000

C	4.056654000	-0.940196000	-2.878052000
H	3.043422000	-0.541064000	-2.751265000
H	4.044373000	-1.587753000	-3.764359000
H	4.735010000	-0.101950000	-3.082784000
C	3.447091000	-2.770769000	-1.249176000
H	2.515268000	-2.246631000	-0.971298000
H	3.768834000	-3.385704000	-0.399927000
H	3.181222000	-3.430962000	-2.083973000
H	5.403310000	-2.318604000	-1.967014000
C	-3.808769000	-0.864945000	-3.368456000
H	-3.057203000	-0.080674000	-3.214876000
H	-4.751161000	-0.387033000	-3.666247000
H	-3.465269000	-1.491975000	-4.202657000
C	-2.662894000	-2.363226000	-1.686649000
H	-2.279378000	-2.996109000	-2.499307000
H	-2.799257000	-2.993697000	-0.796826000
H	-1.910556000	-1.601148000	-1.447372000
H	-4.679431000	-2.537158000	-2.373672000
C	-4.988071000	2.692718000	2.442004000
H	-5.805409000	3.124114000	1.849935000
H	-4.429572000	3.518331000	2.901235000
H	-5.428205000	2.105119000	3.259553000
C	-2.954929000	1.223148000	2.477735000
H	-2.429489000	2.002337000	3.046914000
H	-2.217504000	0.672091000	1.879593000

H	-3.412082000	0.525171000	3.193819000
H	-3.544028000	2.531003000	0.887677000
C	3.523030000	2.924376000	1.810093000
H	4.499532000	3.318489000	1.499953000
H	3.137135000	3.565810000	2.613351000
H	2.827498000	3.014241000	0.966364000
C	2.249036000	0.902684000	2.635495000
H	1.777488000	1.501679000	3.425644000
H	2.319314000	-0.132528000	2.997970000
H	1.577739000	0.918129000	1.768255000
H	4.172762000	1.533261000	3.273755000
Ni	1.434171000	-0.952271000	-0.000755000
H	-3.189446000	2.180488000	-1.569990000
H	3.533487000	2.072153000	-1.094870000
C	0.325319000	-2.365005000	0.551935000
C	-0.842738000	-2.003268000	1.449524000
H	-0.502051000	-1.361507000	2.282759000
H	-1.558260000	-1.394239000	0.872723000
C	-1.566490000	-3.220145000	2.037936000
H	-1.869109000	-3.885513000	1.212248000
H	-0.861842000	-3.801639000	2.655355000
C	-2.789411000	-2.833092000	2.863500000
H	-2.506906000	-2.170852000	3.694323000
H	-3.520736000	-2.292992000	2.245058000
H	-3.293141000	-3.710072000	3.290501000

H	-0.025959000	-2.978741000	-0.295358000
H	1.068252000	-2.985844000	1.112786000

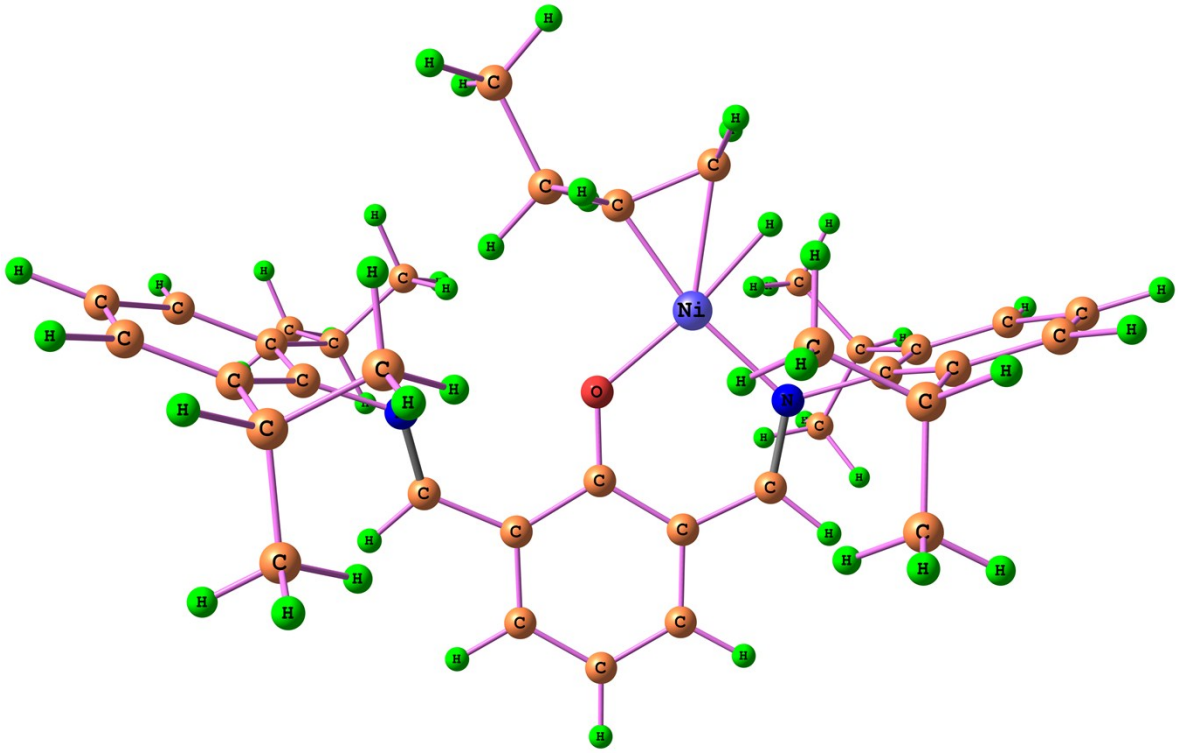

Figure S62: Optimized M06/6-31g/auto cartesian geometry for lowest energy of **INT2**.

Table S16. Optimized M06/6-31g/auto cartesian coordinates (Å) for lowest energy of **INT2**.

C	-2.602098000	1.213797000	1.329063000
C	-1.267784000	1.625741000	1.747847000
C	-1.201495000	2.675045000	2.664660000
H	-2.137639000	3.083806000	3.043701000
C	0.011133000	3.226658000	3.094410000
H	0.022189000	4.047134000	3.804228000
C	1.187469000	2.717185000	2.578730000

H	2.146191000	3.141846000	2.874149000
C	1.186595000	1.641354000	1.665514000
C	2.452766000	1.211130000	1.158666000
C	-0.050656000	1.048180000	1.250372000
O	-0.103205000	0.013204000	0.454146000
N	-2.889452000	0.446451000	0.339764000
N	2.669702000	0.216247000	0.336200000
H	-6.758624000	-2.005648000	0.624257000
C	-6.206883000	-1.200375000	0.146504000
C	-4.920356000	-0.889983000	0.597258000
C	-4.246814000	-1.694255000	1.698957000
C	-4.221562000	0.167359000	-0.037638000
C	-4.798490000	0.882790000	-1.112254000
C	-4.094197000	2.014128000	-1.847940000
C	-6.093154000	0.534553000	-1.515650000
H	-6.548067000	1.087077000	-2.336459000
C	-6.798462000	-0.493906000	-0.898615000
H	-7.801597000	-0.747832000	-1.231243000
C	4.488247000	-1.703020000	1.764795000
C	4.884402000	-0.861520000	0.556392000
C	6.182740000	-1.030074000	0.057173000
H	6.853253000	-1.715013000	0.572439000
C	6.624063000	-0.349586000	-1.072344000
H	7.635190000	-0.497738000	-1.441515000
C	5.759164000	0.519481000	-1.727213000

H	6.097804000	1.054915000	-2.612217000
C	4.448036000	0.730980000	-1.276825000
C	3.607458000	1.739794000	-2.057440000
C	4.025525000	0.031791000	-0.124180000
C	3.517589000	3.105007000	-1.356074000
H	2.835803000	3.078391000	-0.496565000
H	3.126951000	3.856768000	-2.054882000
H	4.502543000	3.441559000	-1.007813000
C	2.214426000	1.272925000	-2.496140000
H	1.513713000	1.200797000	-1.655103000
H	2.258462000	0.297638000	-2.998707000
H	1.797351000	1.995612000	-3.210467000
H	4.176473000	1.912097000	-2.985078000
C	-3.939191000	3.285496000	-0.999062000
H	-3.174731000	3.161710000	-0.221531000
H	-4.885056000	3.557797000	-0.512954000
H	-3.627066000	4.126218000	-1.633831000
C	-2.750245000	1.607501000	-2.467839000
H	-2.359967000	2.428835000	-3.084876000
H	-2.867439000	0.723788000	-3.108991000
H	-2.008093000	1.368255000	-1.695508000
H	-4.764016000	2.277560000	-2.683120000
C	-5.212599000	-2.547045000	2.520945000
H	-6.039596000	-1.954781000	2.933346000
H	-4.675785000	-3.008966000	3.359291000

H	-5.639309000	-3.362440000	1.920333000
C	-3.139338000	-2.581037000	1.105745000
H	-2.636978000	-3.153421000	1.897708000
H	-2.386948000	-1.972324000	0.588969000
H	-3.572372000	-3.293013000	0.388476000
H	-3.764675000	-0.988119000	2.392745000
C	3.961795000	-0.930618000	2.982404000
H	4.566572000	-0.038934000	3.192337000
H	4.002122000	-1.578455000	3.868034000
H	2.917340000	-0.622568000	2.855129000
C	3.507995000	-2.815553000	1.372215000
H	3.233560000	-3.420238000	2.245947000
H	3.941914000	-3.478712000	0.611853000
H	2.590210000	-2.375289000	0.958164000
H	5.419500000	-2.193050000	2.089950000
Ni	1.274596000	-0.919475000	-0.298404000
H	-3.414188000	1.681478000	1.914698000
H	3.319088000	1.793954000	1.494304000
C	1.530225000	-2.508047000	-1.655112000
C	0.179168000	-2.209421000	-1.101471000
H	2.356684000	-1.819549000	-1.180173000
H	-0.196876000	-2.960437000	-0.395797000
C	-0.893267000	-1.675353000	-2.016876000
H	-1.628679000	-1.126143000	-1.408135000
H	-0.456382000	-0.933223000	-2.707385000

C	-1.590074000	-2.773786000	-2.823082000
H	-0.875297000	-3.314283000	-3.460622000
H	-2.056854000	-3.507861000	-2.151376000
H	-2.377891000	-2.364086000	-3.468773000
H	1.639714000	-2.310625000	-2.726225000
H	1.923900000	-3.497581000	-1.405679000

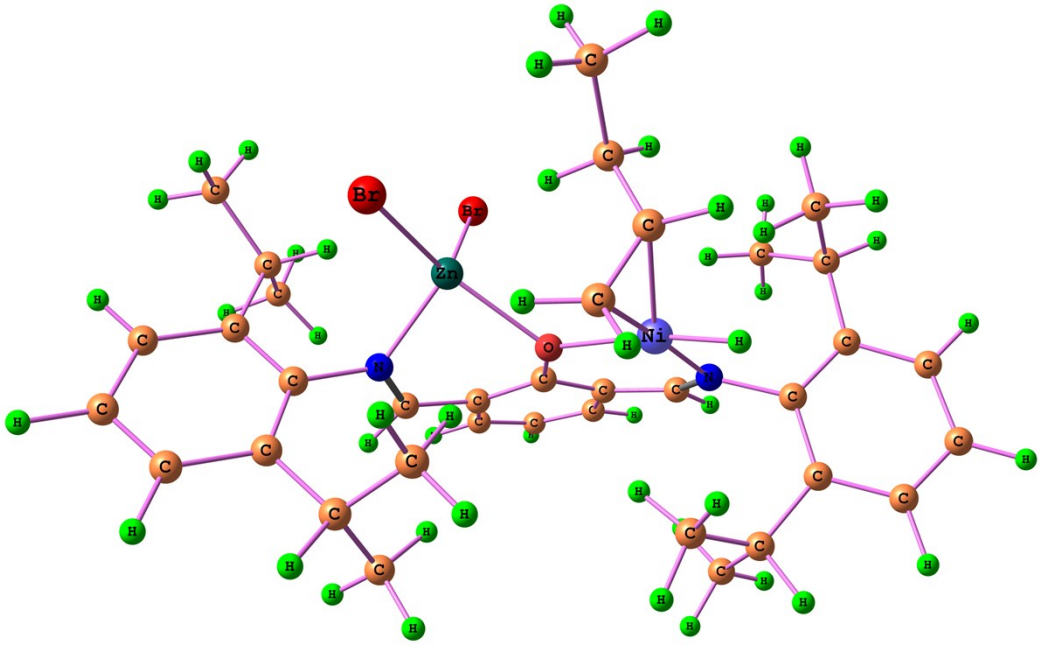

Figure S63: Optimized M06/6-31g/auto cartesian geometry for lowest energy of **INT2-$ZnBr_2$**.

Table S17. Optimized M06/6-31g/auto cartesian coordinates (Å) for lowest energy of **INT2-$ZnBr_2$**.

C	-1.961438000	1.698316000	1.266716000
C	-0.684959000	1.525075000	1.924875000
C	-0.587016000	2.130811000	3.184237000
H	-1.473192000	2.619539000	3.585214000

C	0.588629000	2.120839000	3.925125000
H	0.631397000	2.565167000	4.912826000
C	1.714986000	1.583047000	3.332026000
H	2.674581000	1.629272000	3.842714000
C	1.676677000	0.995771000	2.050168000
C	2.958631000	0.711574000	1.481362000
C	0.446317000	0.864998000	1.345721000
O	0.363455000	0.184851000	0.192923000
N	-2.426564000	0.955897000	0.318924000
N	3.223155000	0.286495000	0.279265000
H	-6.972830000	0.493853000	-0.008548000
C	-6.072874000	0.992425000	-0.360242000
C	-4.837065000	0.640946000	0.188752000
C	-4.701718000	-0.435775000	1.247128000
C	-3.689803000	1.304876000	-0.281841000
C	-3.737138000	2.240931000	-1.330481000
C	-2.510839000	2.884262000	-1.962846000
C	-5.000155000	2.555933000	-1.849348000
H	-5.064255000	3.278132000	-2.661046000
C	-6.157904000	1.954720000	-1.363637000
H	-7.124339000	2.218310000	-1.785049000
C	5.093149000	-2.058053000	0.717432000
C	5.504699000	-0.696301000	0.170305000
C	6.849982000	-0.532513000	-0.188000000
H	7.542582000	-1.347661000	0.012194000

C	7.307835000	0.632275000	-0.793174000
H	8.355990000	0.734697000	-1.060191000
C	6.413047000	1.662315000	-1.059648000
H	6.764527000	2.576355000	-1.534673000
C	5.056051000	1.559772000	-0.723811000
C	4.183601000	2.781159000	-1.007815000
C	4.623184000	0.369785000	-0.102286000
C	4.014683000	3.659152000	0.243151000
H	3.372000000	3.178334000	0.993234000
H	3.543624000	4.613921000	-0.026286000
H	4.983977000	3.875324000	0.710160000
C	2.827151000	2.541433000	-1.684292000
H	2.066902000	2.162373000	-0.987495000
H	2.909960000	1.837987000	-2.521797000
H	2.451270000	3.494778000	-2.079983000
H	4.772196000	3.377711000	-1.722671000
C	-1.822401000	3.938813000	-1.081744000
H	-1.206389000	3.475072000	-0.299381000
H	-2.550096000	4.606634000	-0.602830000
H	-1.149748000	4.553780000	-1.694672000
C	-1.491144000	1.850789000	-2.453984000
H	-0.658782000	2.352825000	-2.967257000
H	-1.949096000	1.133397000	-3.146526000
H	-1.077602000	1.283715000	-1.612333000
H	-2.889964000	3.416638000	-2.849124000

C	-4.778109000	0.137436000	2.668142000
H	-3.958738000	0.841185000	2.873785000
H	-4.704465000	-0.673407000	3.404723000
H	-5.730768000	0.663580000	2.824760000
C	-5.701888000	-1.577534000	1.075109000
H	-5.427173000	-2.405398000	1.741705000
H	-5.694668000	-1.955764000	0.045583000
H	-6.725961000	-1.271099000	1.331564000
H	-3.701141000	-0.870345000	1.128393000
C	4.281983000	-2.080778000	2.020262000
H	4.680383000	-1.385199000	2.770197000
H	4.322252000	-3.090026000	2.450051000
H	3.221891000	-1.850005000	1.852618000
C	4.350426000	-2.835537000	-0.376001000
H	4.032041000	-3.821363000	-0.012420000
H	4.976919000	-2.972995000	-1.266982000
H	3.465668000	-2.260740000	-0.670808000
H	6.037090000	-2.584063000	0.927101000
Ni	1.924587000	-0.337929000	-0.926529000
H	-2.563854000	2.545617000	1.618368000
H	3.811463000	0.972109000	2.117576000
C	0.747239000	-0.792024000	-2.473558000
C	1.356228000	-1.965563000	-2.045821000
C	0.711473000	-2.977334000	-1.148441000
H	1.424716000	-3.339755000	-0.393022000

H	-0.111108000	-2.518071000	-0.593002000
C	0.164896000	-4.153932000	-1.959933000
H	-0.574256000	-3.798628000	-2.688259000
H	0.966912000	-4.677722000	-2.496487000
H	-0.335069000	-4.868827000	-1.296333000
H	-0.290522000	-0.598609000	-2.219654000
H	2.226750000	-2.333192000	-2.591284000
H	3.038959000	-0.492449000	-1.819933000
Zn	-1.514260000	-0.794114000	0.030468000
Br	-2.729000000	-1.758130000	-1.747645000
Br	-1.305774000	-1.995903000	2.077993000
H	1.114168000	-0.276633000	-3.360521000

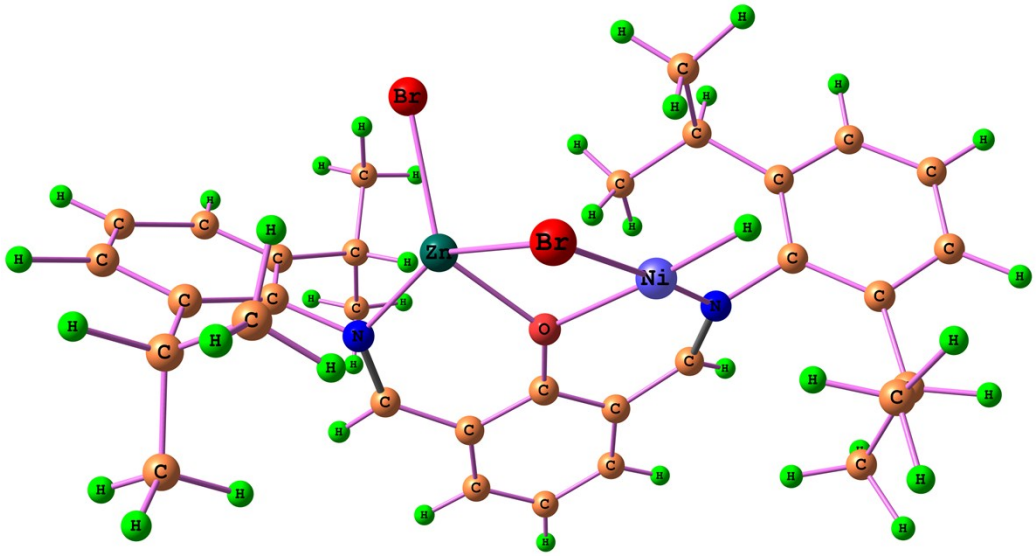

Figure S64: Optimized M06/6-31g/auto cartesian geometry for lowest energy of **INT3-$ZnBr_2$**.

Table S18. Optimized M06/6-31g/auto cartesian coordinates (Å) for lowest energy of **INT3-$ZnBr_2$**.

C	-2.189900000	2.145186000	-0.093428000
C	-0.867703000	2.710413000	0.004108000
C	-0.771515000	4.077200000	0.326857000
H	-1.682479000	4.673180000	0.331707000
C	0.442634000	4.661711000	0.663755000
H	0.495950000	5.716738000	0.908517000
C	1.581570000	3.862547000	0.733314000
H	2.528953000	4.289733000	1.057720000
C	1.541832000	2.501235000	0.400664000
C	2.723001000	1.695874000	0.602987000
C	0.316418000	1.926890000	-0.023143000
O	0.279865000	0.662280000	-0.406405000
N	-2.513442000	0.894196000	-0.270425000
N	2.933946000	0.487862000	0.158443000
H	-5.559301000	-0.104260000	2.999768000
C	-5.348761000	-0.022628000	1.936176000
C	-4.077304000	0.384621000	1.519132000
C	-2.986661000	0.654376000	2.549925000
C	-3.841706000	0.486826000	0.129997000
C	-4.803891000	0.110001000	-0.821964000
C	-4.575046000	0.141375000	-2.322385000
C	-6.059348000	-0.290286000	-0.349632000
H	-6.822537000	-0.571686000	-1.072392000
C	-6.338198000	-0.344594000	1.012606000
H	-7.319638000	-0.661418000	1.354670000

C	2.775111000	-1.670334000	2.232921000
C	4.065372000	-1.099003000	1.644285000
C	5.263250000	-1.656999000	2.112402000
H	5.213681000	-2.392521000	2.913445000
C	6.493935000	-1.301924000	1.573248000
H	7.408097000	-1.747551000	1.955846000
C	6.546238000	-0.386031000	0.527654000
H	7.504460000	-0.127669000	0.081697000
C	5.386525000	0.210459000	0.015496000
C	5.546548000	1.121353000	-1.201710000
C	4.156160000	-0.146267000	0.609937000
C	5.215829000	2.608218000	-0.989276000
H	4.137224000	2.802385000	-1.047727000
H	5.687454000	3.199128000	-1.785618000
H	5.593010000	2.980726000	-0.027620000
C	4.809414000	0.577102000	-2.431745000
H	3.739418000	0.443818000	-2.228418000
H	5.198496000	-0.407698000	-2.720393000
H	4.928254000	1.261241000	-3.282218000
H	6.622858000	1.085627000	-1.431977000
C	-4.647164000	1.570730000	-2.876924000
H	-3.829289000	2.187877000	-2.481596000
H	-5.597509000	2.051712000	-2.613547000
H	-4.557782000	1.561827000	-3.971203000
C	-3.290581000	-0.552150000	-2.791085000

H	-3.369829000	-0.816145000	-3.853533000
H	-3.099946000	-1.486770000	-2.243650000
H	-2.422883000	0.114719000	-2.708689000
H	-5.417348000	-0.417220000	-2.758261000
C	-3.153757000	2.038547000	3.192194000
H	-3.137820000	2.850628000	2.453097000
H	-2.353775000	2.225078000	3.920531000
H	-4.114943000	2.096564000	3.722371000
C	-2.938327000	-0.424609000	3.637943000
H	-2.061714000	-0.261884000	4.279145000
H	-2.852584000	-1.420931000	3.188650000
H	-3.826746000	-0.399212000	4.282803000
H	-2.011515000	0.615514000	2.037916000
C	1.610342000	-0.708620000	2.507242000
H	1.939333000	0.221190000	2.991222000
H	0.889559000	-1.202474000	3.172779000
H	1.073195000	-0.458255000	1.585881000
C	2.289434000	-2.845187000	1.365837000
H	1.384591000	-3.295008000	1.794216000
H	3.062823000	-3.618363000	1.274340000
H	2.042714000	-2.497026000	0.352979000
H	3.070456000	-2.086984000	3.208928000
Ni	1.781392000	-0.406393000	-0.927390000
H	-3.004484000	2.847327000	0.124251000
H	3.498399000	2.150806000	1.225972000

H	2.850591000	-1.314824000	-1.326816000
Zn	-1.252807000	-0.591593000	-0.585459000
Br	-1.756776000	-2.480167000	0.690233000
Br	0.255430000	-1.466975000	-2.418327000

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