

Supporting Information

α -Diimine Nickel Complexes Bearing Axially Bulky Terphenyl and Equatorially Bulky Dibenzobarrelene Groups: Synthesis, Characterization and Olefin Polymerization Studies

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1. Tables

Table S1. Ethylene polymerization results using **Ni2**/Et₂AlCl at 25°C.^a

entry	Time (min)	Yield (g)	Act. ^b	M _n ^c	M _w ^c	M _w /M _n ^c	B ^d
1	20	0.087	1.30	5.3	5.6	1.06	70.2
2	40	0.148	1.11	9.3	10.0	1.08	70.9
3	60	0.202	1.01	11.8	13.4	1.13	69.6
4	80	0.269	1.00	14.7	17.1	1.16	68.4
5	100	0.320	0.96	18.0	21.5	1.19	64.9

^a Polymerization conditions: 2.0 μmol of **Ni2**, 500 equiv of Et₂AlCl, 2 mL of CH₂Cl₂, solvent, toluene, total volume, 30 mL, 1 atm of ethylene, T = 25°C. ^b Activity (Act.) = 10⁵ g/(mol Ni•h).

^c M_n and M_w: 10⁴ g/mol, M_w and M_w/M_n were determined by GPC in trichlorobenzene at 150 °C using polystyrene standards. ^d B = branches per 1000 carbons, determined by ¹H NMR spectroscopy.

Table S2. Ethylene polymerization results using **Ni2** at 20 °C.^a

entry	Cocat.	Al/Ni	Yield (g)	Act. ^b	M _w ^c	M _w /M _n ^c	B ^d	T _m ^e (°C)
1	MAO	500	3.11	9.3	150.2	1.74	30.1	-
2	MAO	1000	4.12	12.3	163.4	1.46	31.6	90.0/128.8
3	MAO	2000	4.01	12.0	159.8	1.67	30.5	103.1
4	MAO	3000	3.87	11.6	152.1	1.68	36.4	97.2
5	MAO	4000	2.08	6.24	135.9	1.61	39.6	90.7
6	Et ₂ AlCl	200	1.74	5.22	131.1	1.40	35.0	85.8
7	Et ₂ AlCl	500	2.34	7.02	136.4	1.28	36.5	85.7
8	Et ₂ AlCl	800	2.03	6.09	115.3	1.49	34.2	86.2

^a Polymerization conditions: 2.0 μmol of **Ni2**, 2 mL of CH₂Cl₂, solvent, toluene, total volume, 60 mL, 10 atm of ethylene, time, 10 min, T = 20 °C. ^b Activity (Act.) = 10⁶ g/(mol Ni•h). ^c M_w: 10⁴ g/mol, M_w and M_w/M_n were determined by GPC in trichlorobenzene at 150 °C using polystyrene standards. ^d B = branches per 1000 carbons, determined by ¹H NMR spectroscopy. ^e T_m was determined by differential scanning calorimetry (DSC).

2. NMR Spectra of intermediates and ligands

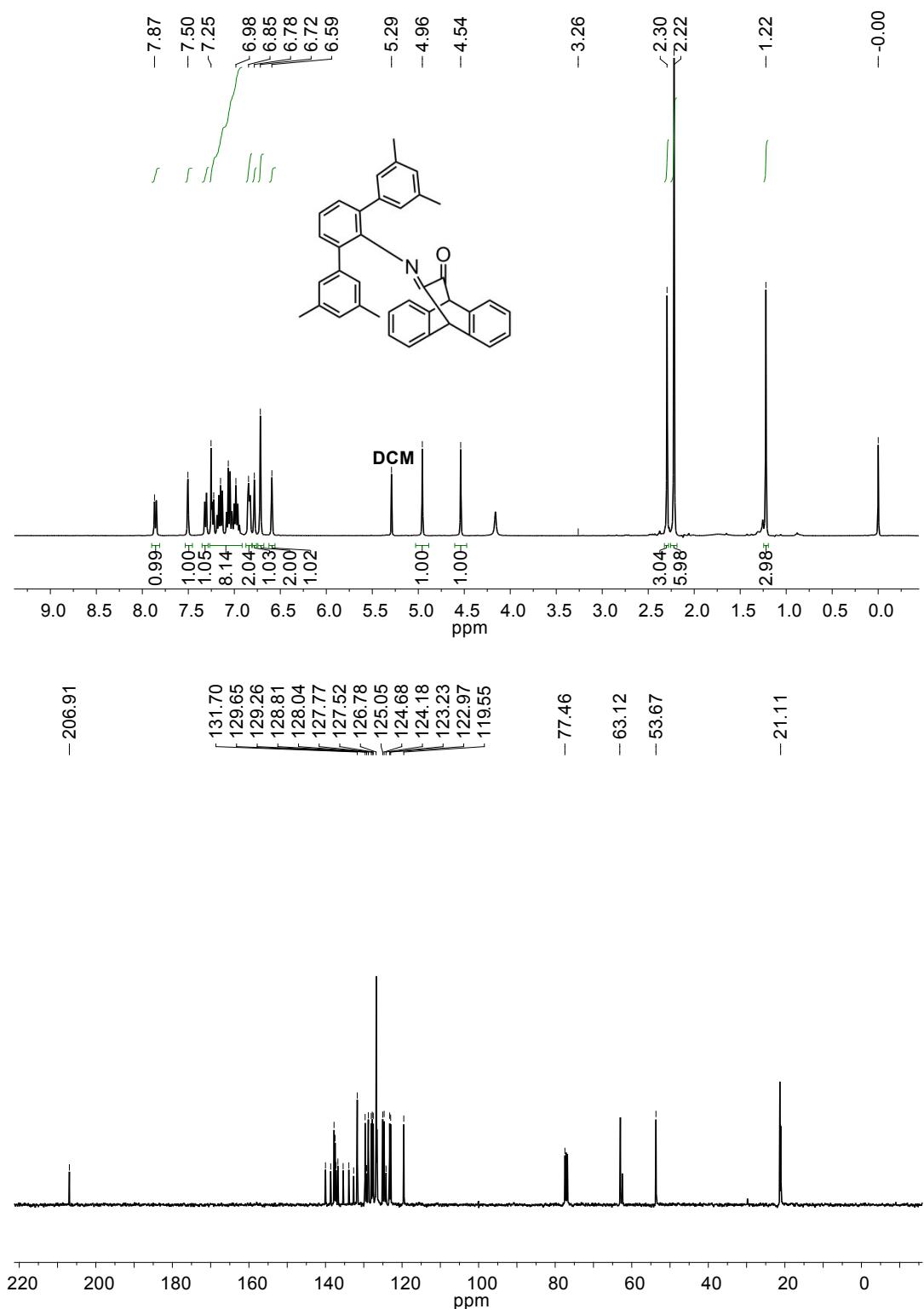
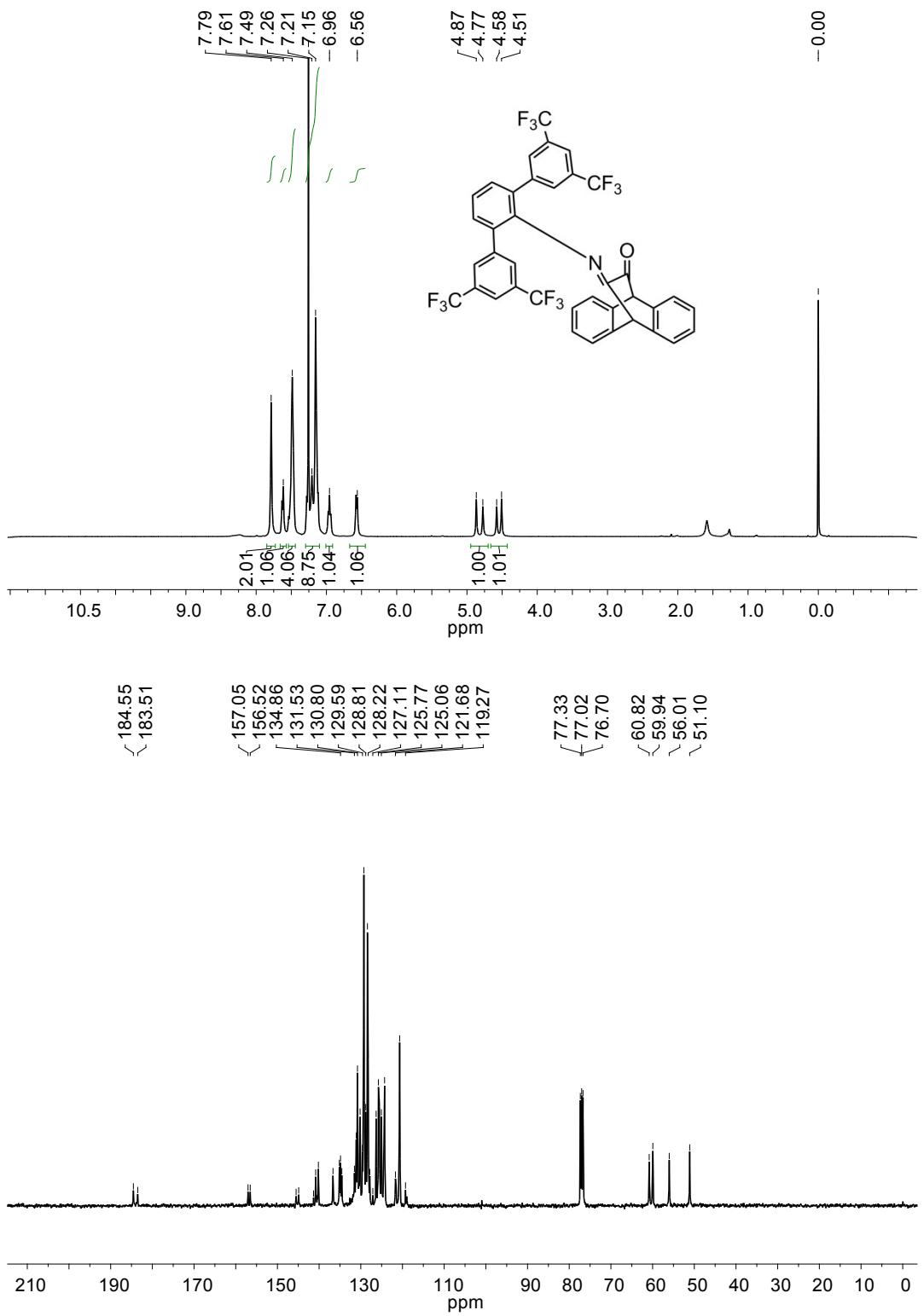


Figure S1. ¹H and ¹³C NMR spectrum of L0-CH₃.



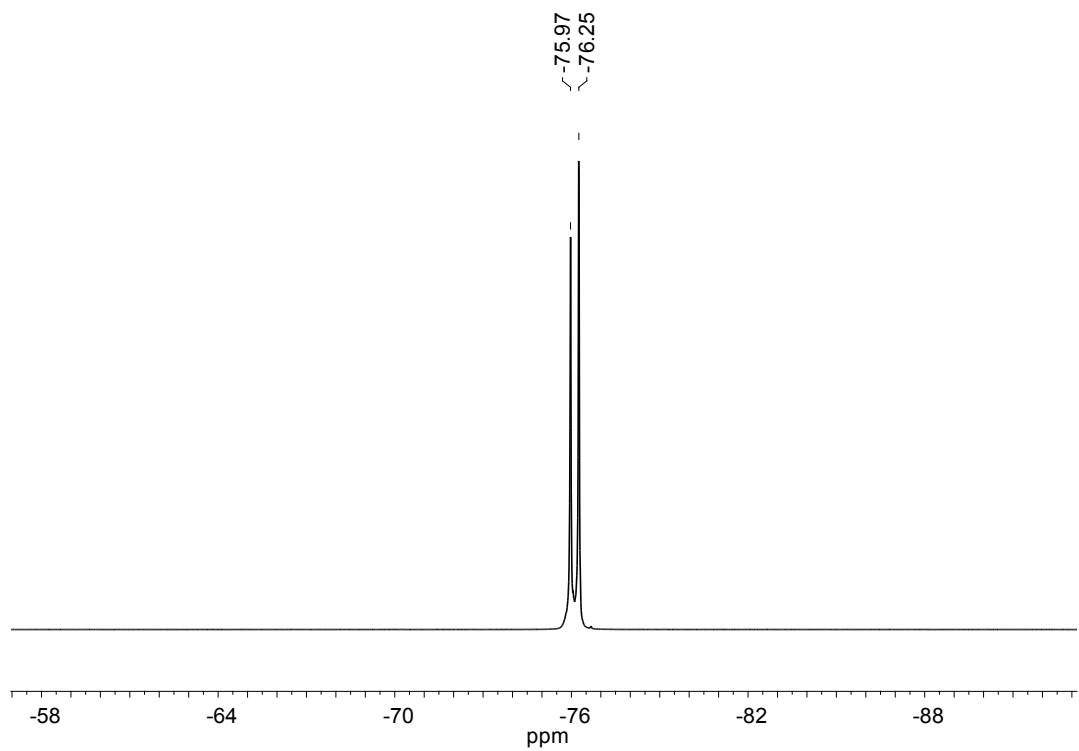
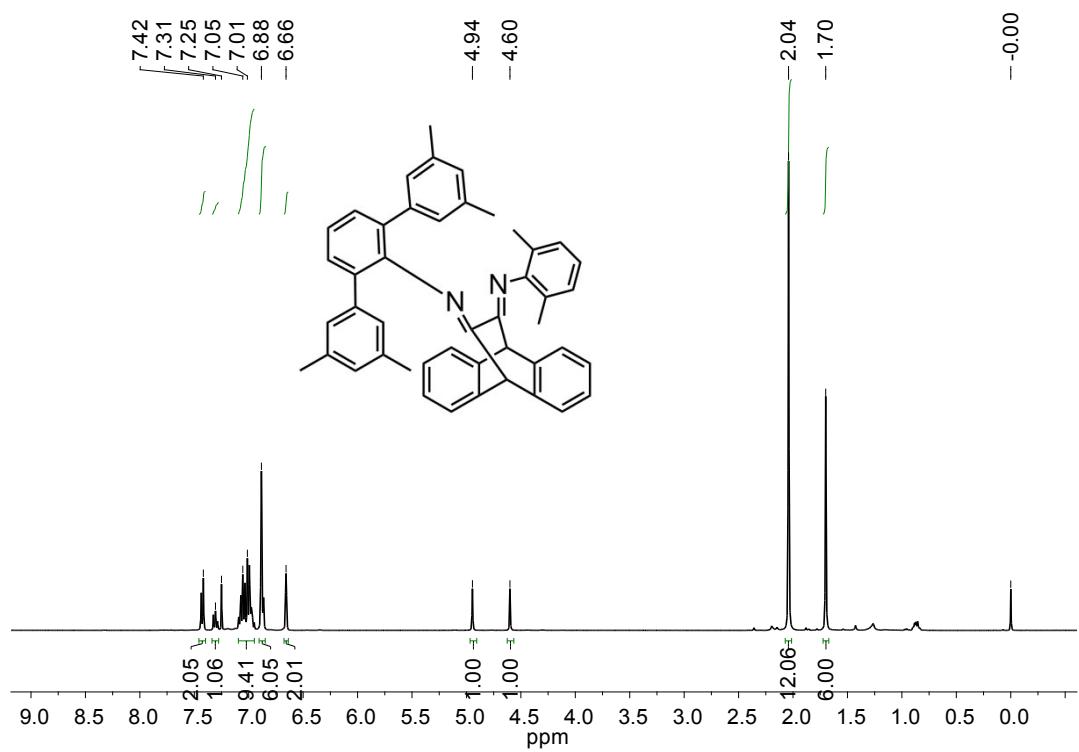


Figure S2. ^1H , ^{13}C NMR and ^{19}F NMR spectrum of **L0-CF₃**.



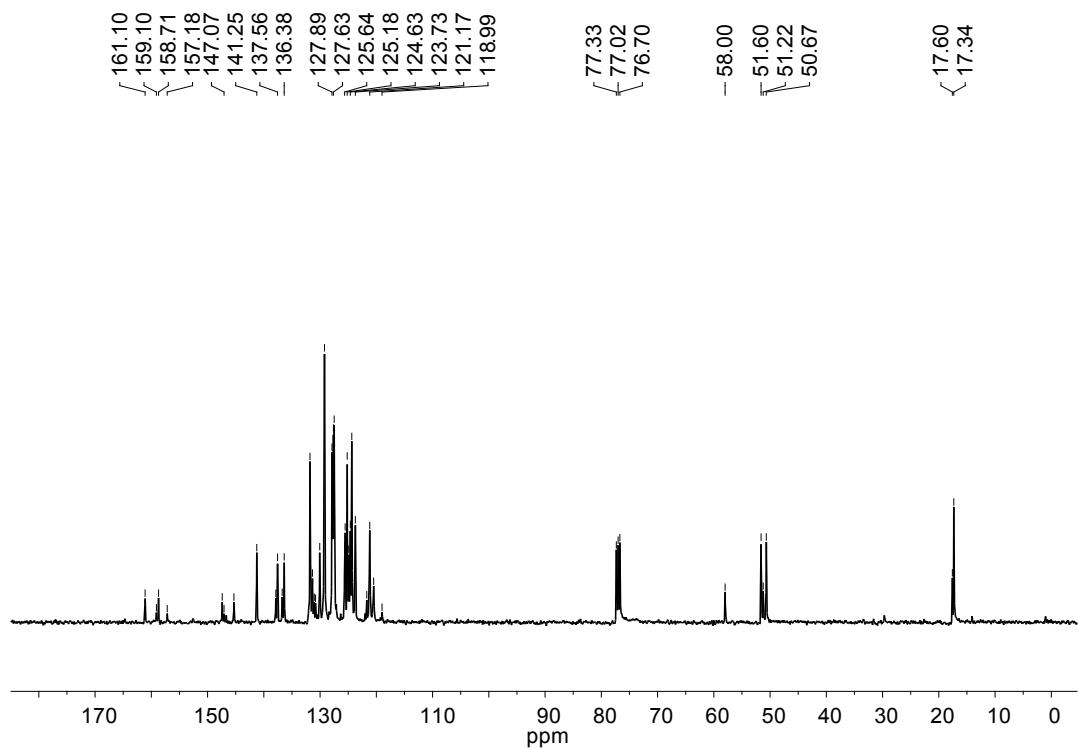
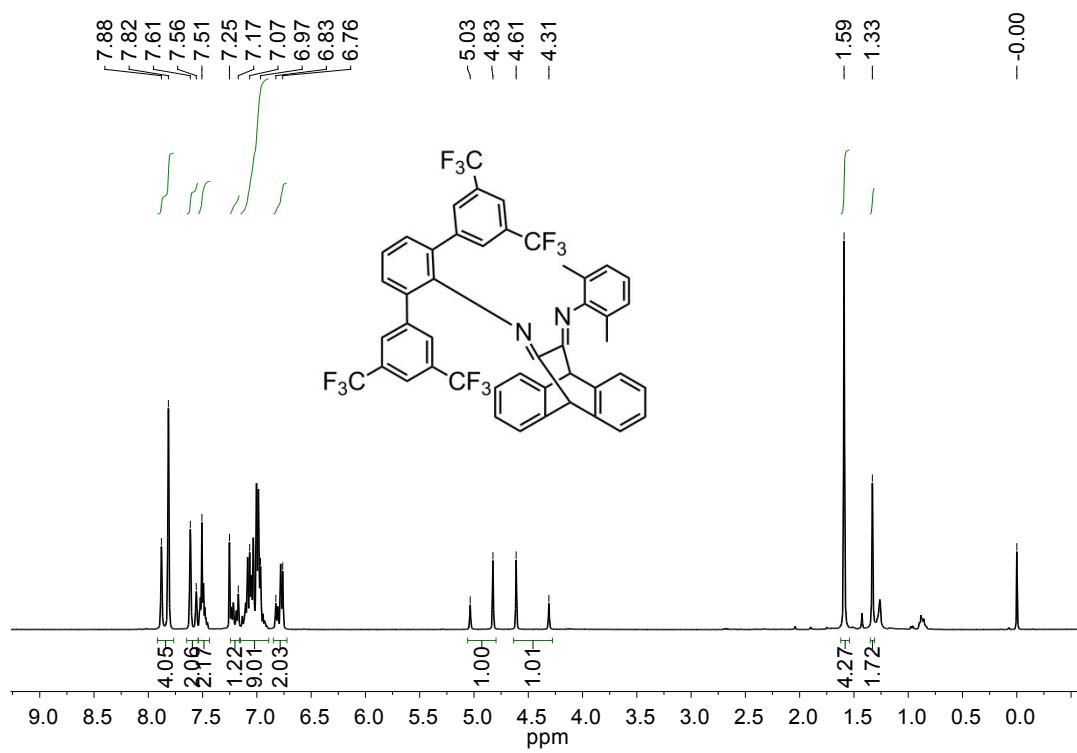


Figure S3. ^1H and ^{13}C NMR spectrum of **L1**.



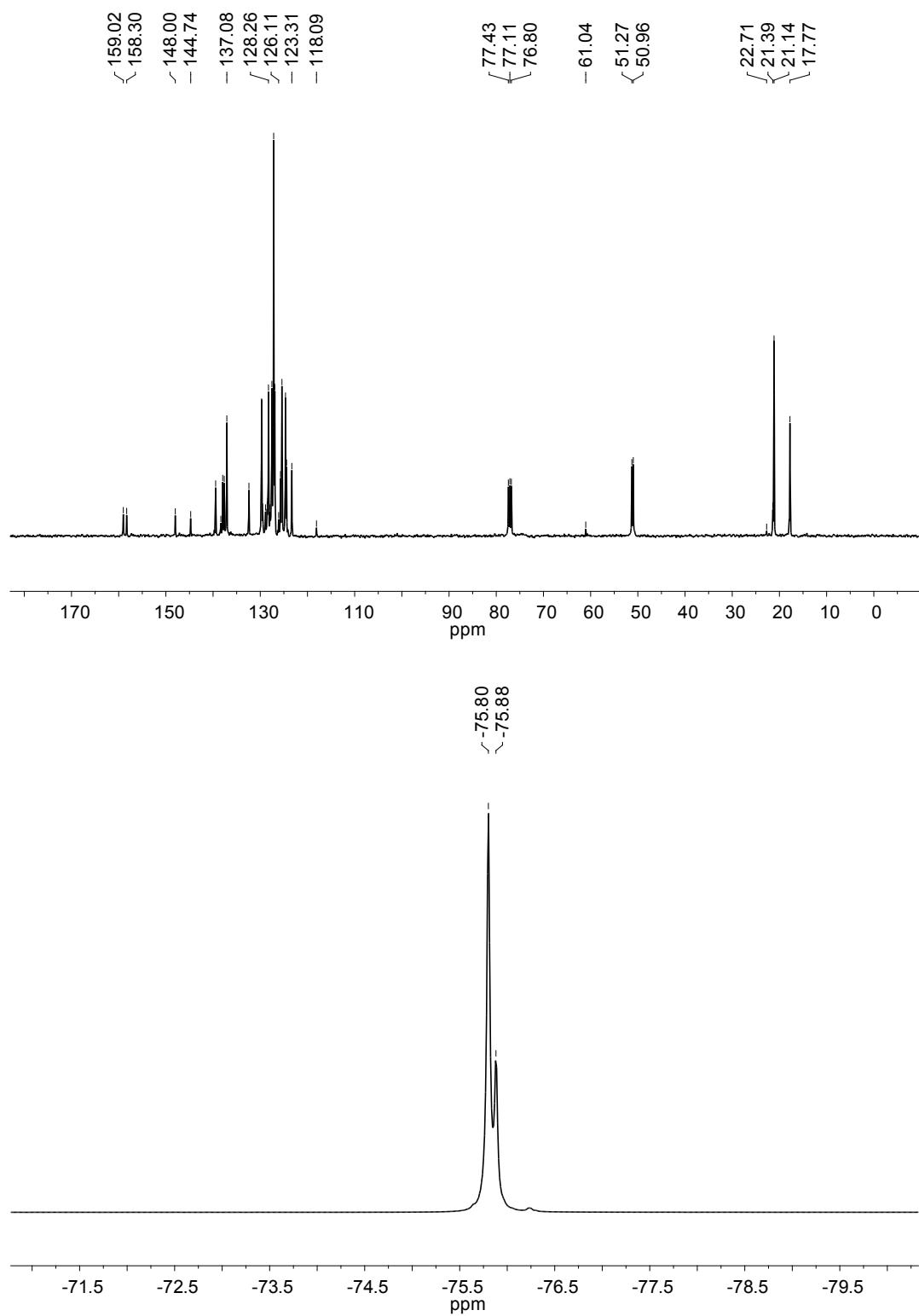
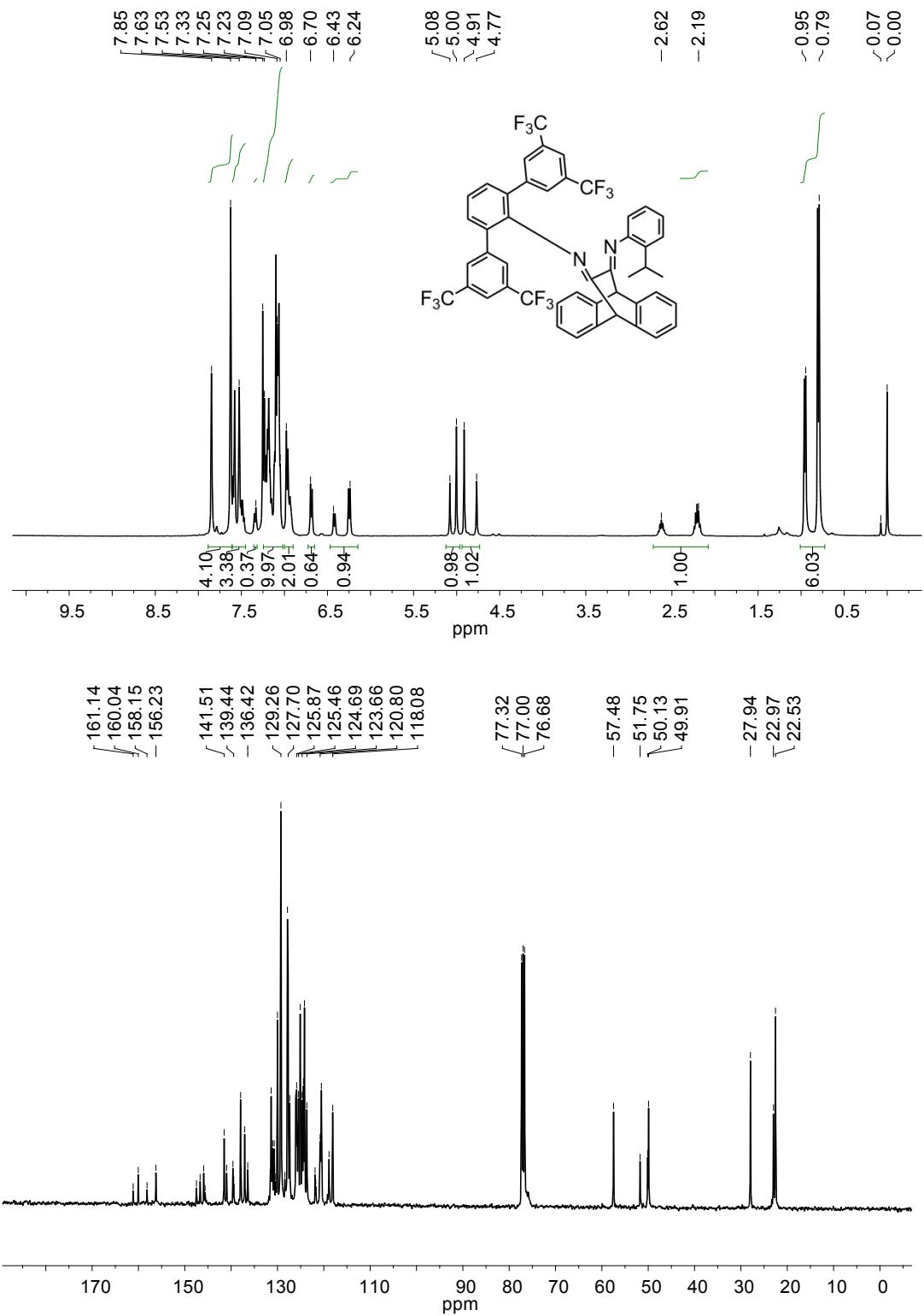


Figure S4. ^1H , ^{13}C NMR and ^{19}F NMR spectrum of **L2**.



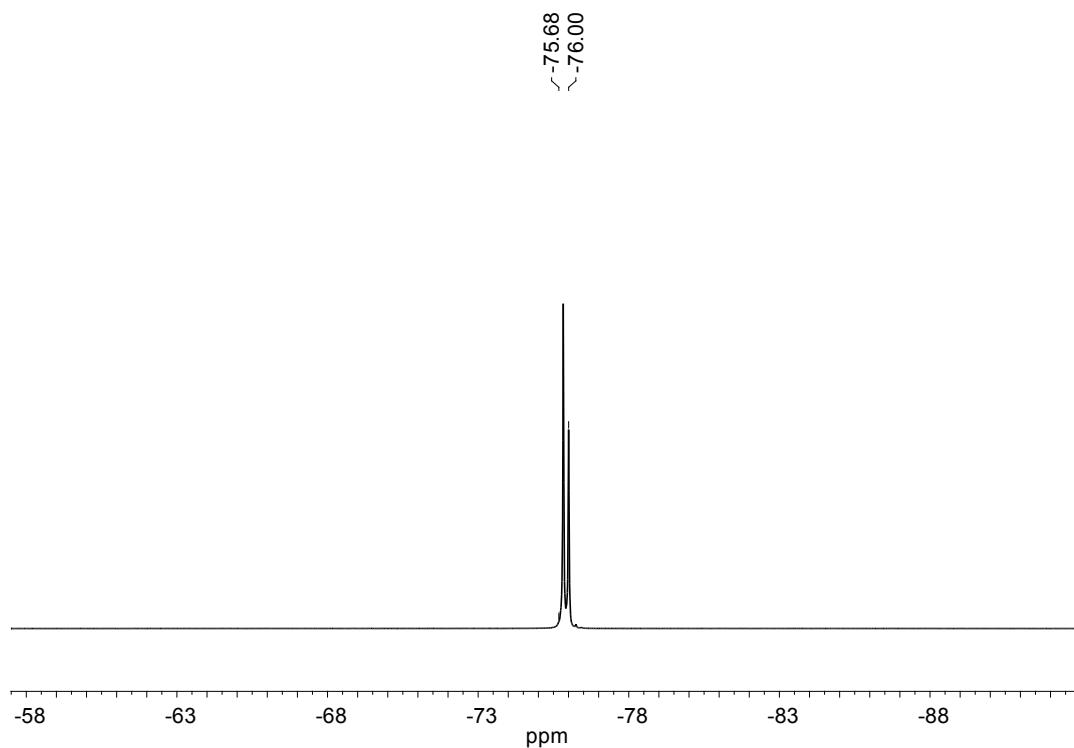
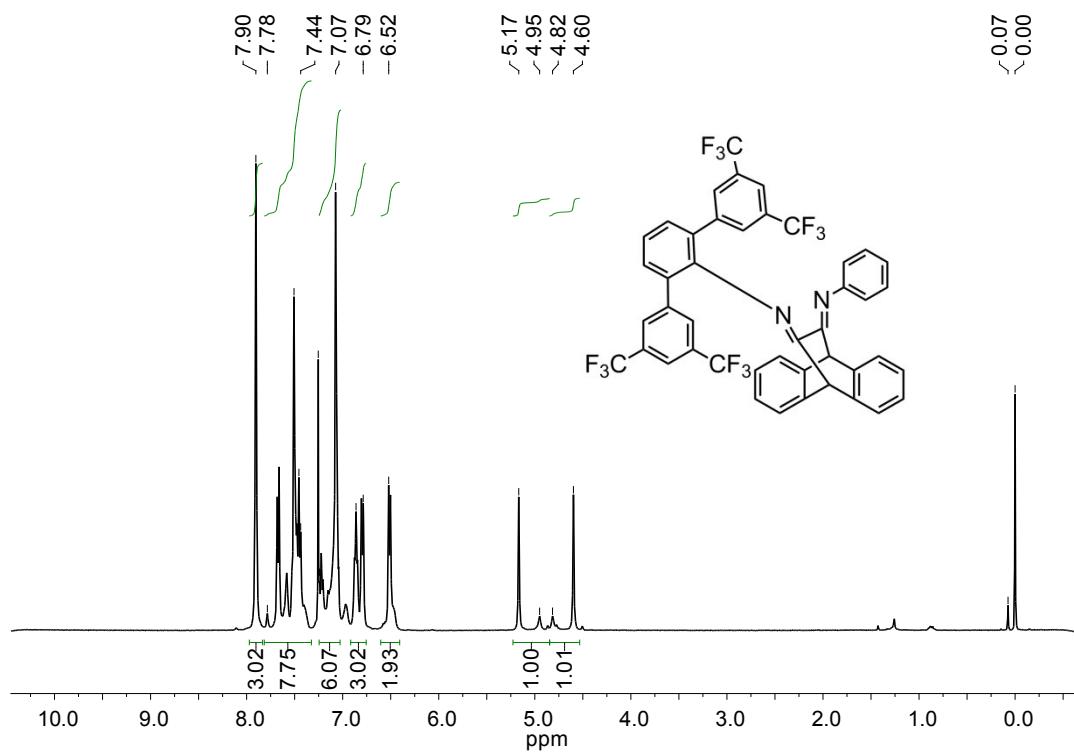


Figure S5. ^1H , ^{13}C NMR and ^{19}F NMR spectrum of **L3**.



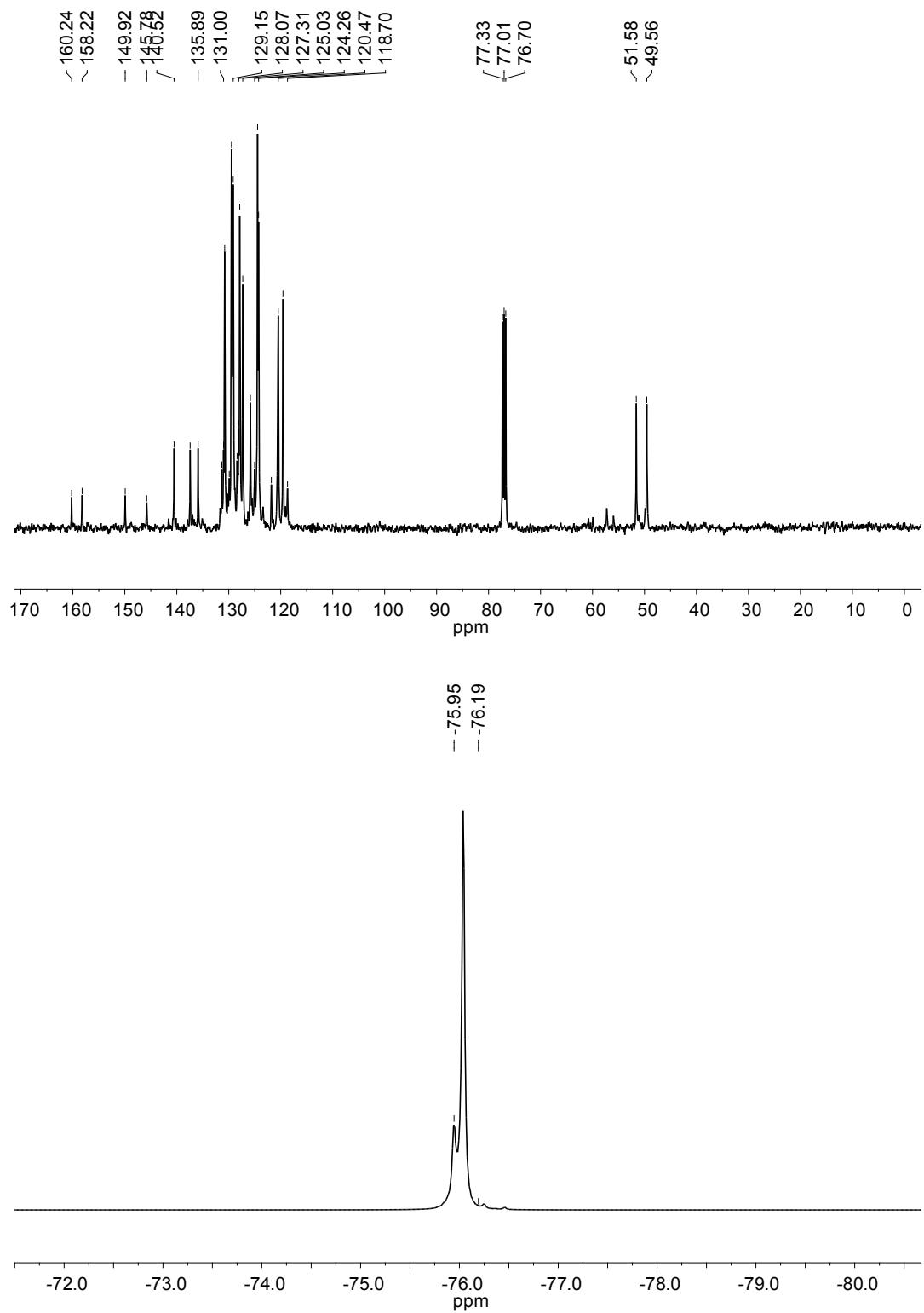
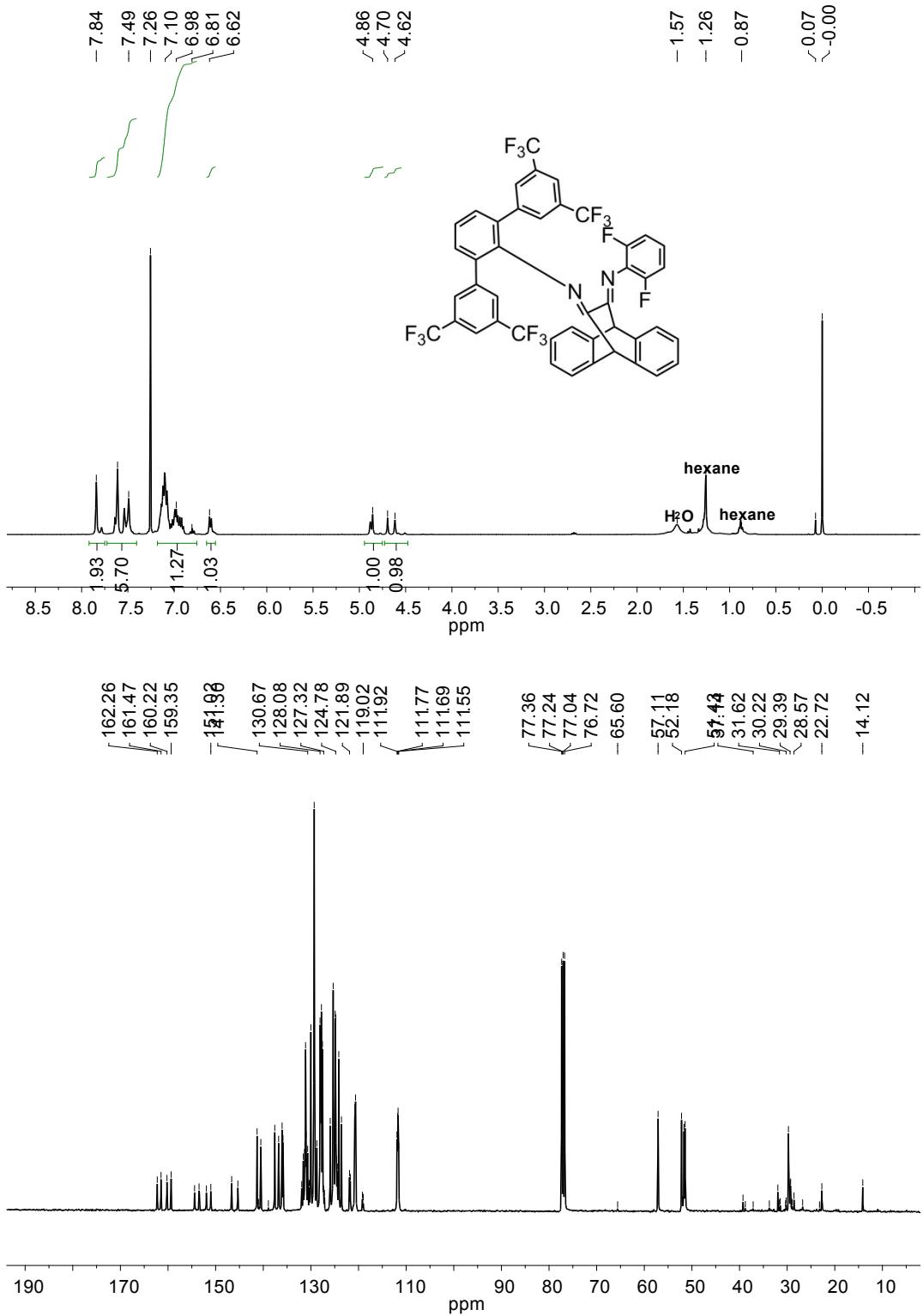


Figure S6. ¹H, ¹³C NMR and ¹⁹F NMR spectrum of L4.



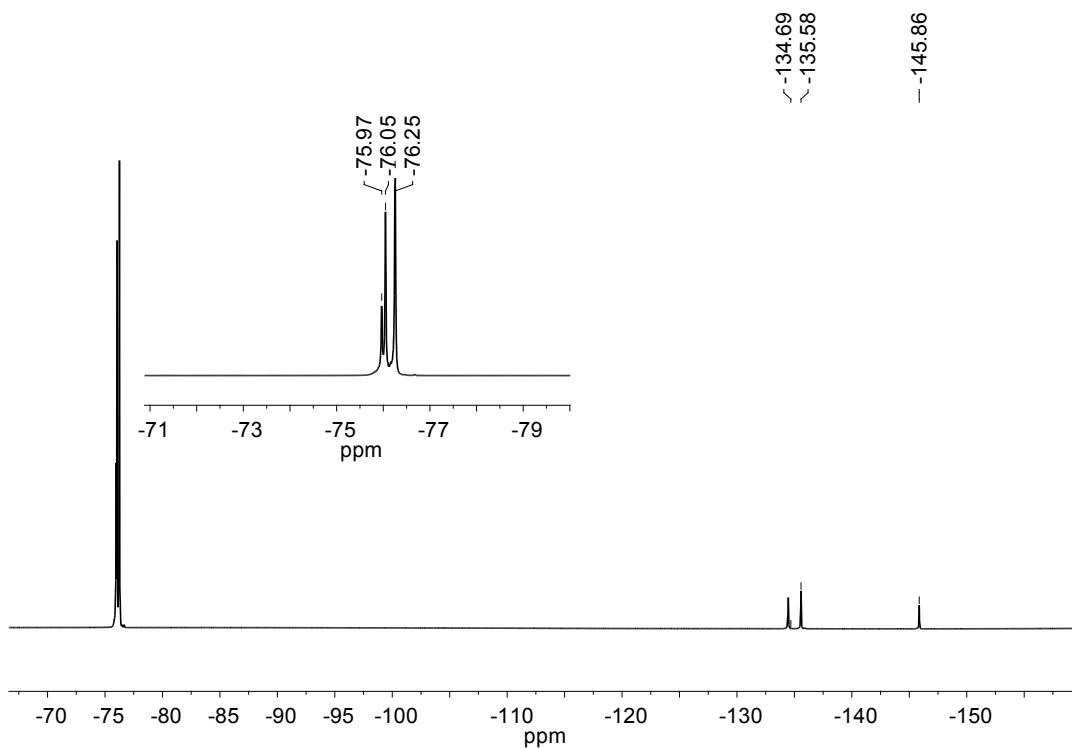


Figure S7. ^1H , ^{13}C NMR and ^{19}F NMR spectrum of **L5**.

3. NMR Spectra of polymers

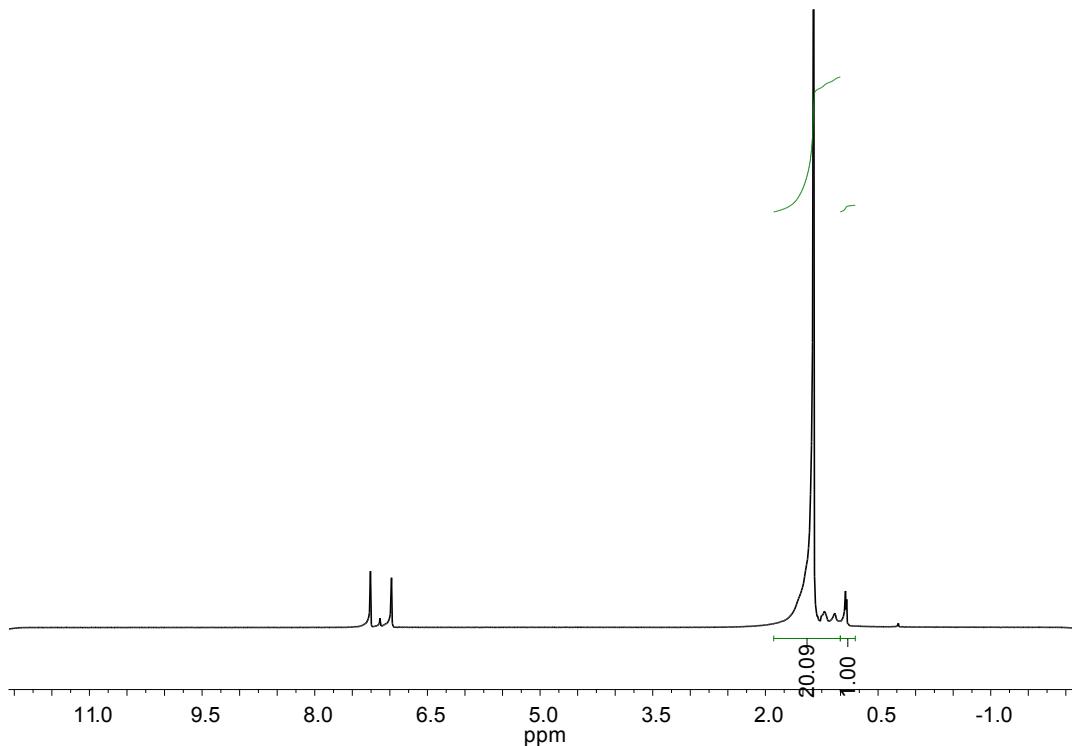


Figure S8. ^1H NMR spectrum of the polyethylene produced by **Ni2/MAO** from table 1, entry 1. (*o*-dichlorobenzene- d_4 , 120 °C).

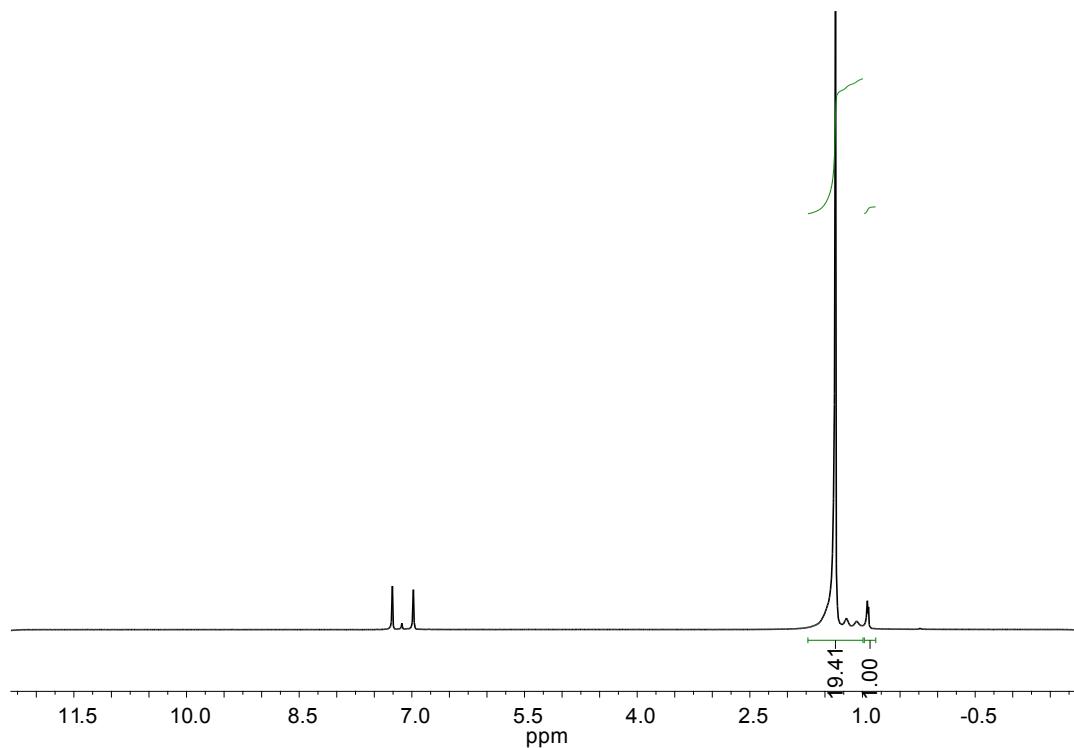


Figure S9. ¹H NMR spectrum of the polyethylene produced by **Ni2/MMAO** from table 1, entry 2. (*o*-dichlorobenzene-*d*₄, 120 °C).

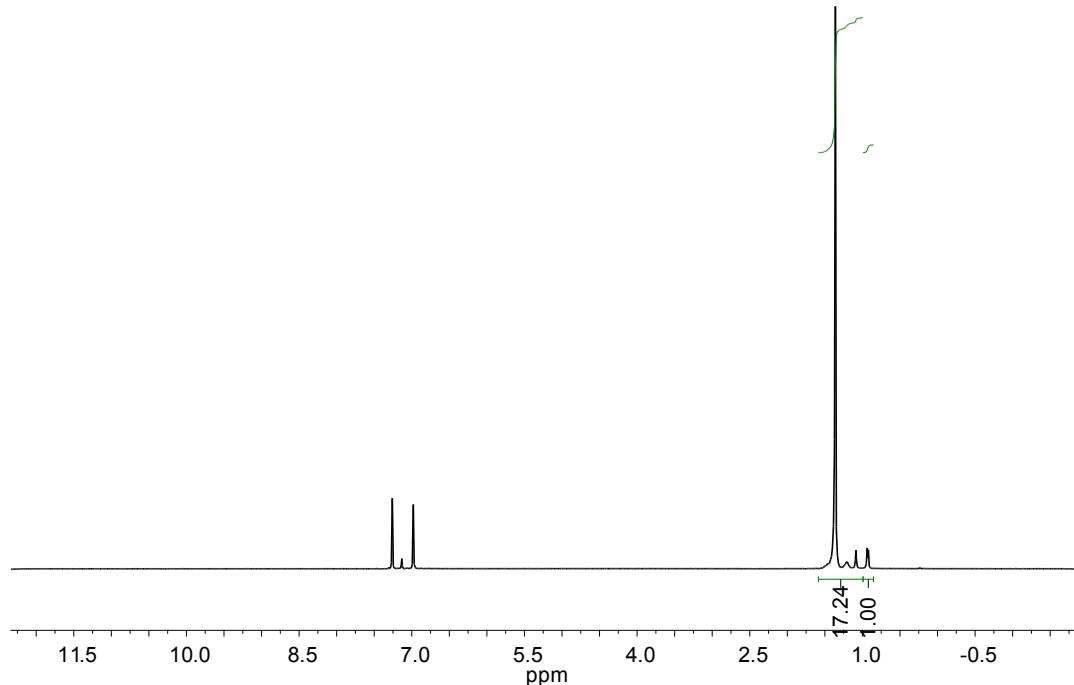


Figure S10. ¹H NMR spectrum of the polyethylene produced by **Ni2/Et₂AlCl** from table 1, entry 3. (*o*-dichlorobenzene-*d*₄, 120 °C).

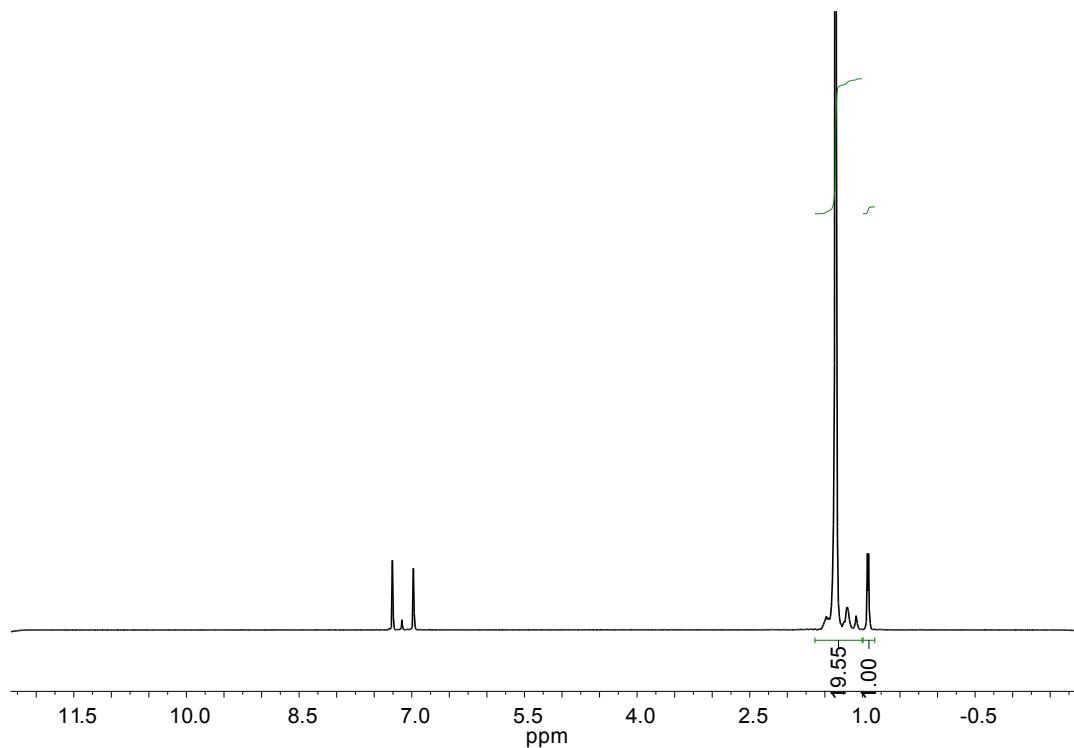


Figure S11. ¹H NMR spectrum of the polyethylene produced by **Ni2/EASC** from table 1, entry 4. (*o*-dichlorobenzene-*d*₄, 120 °C).

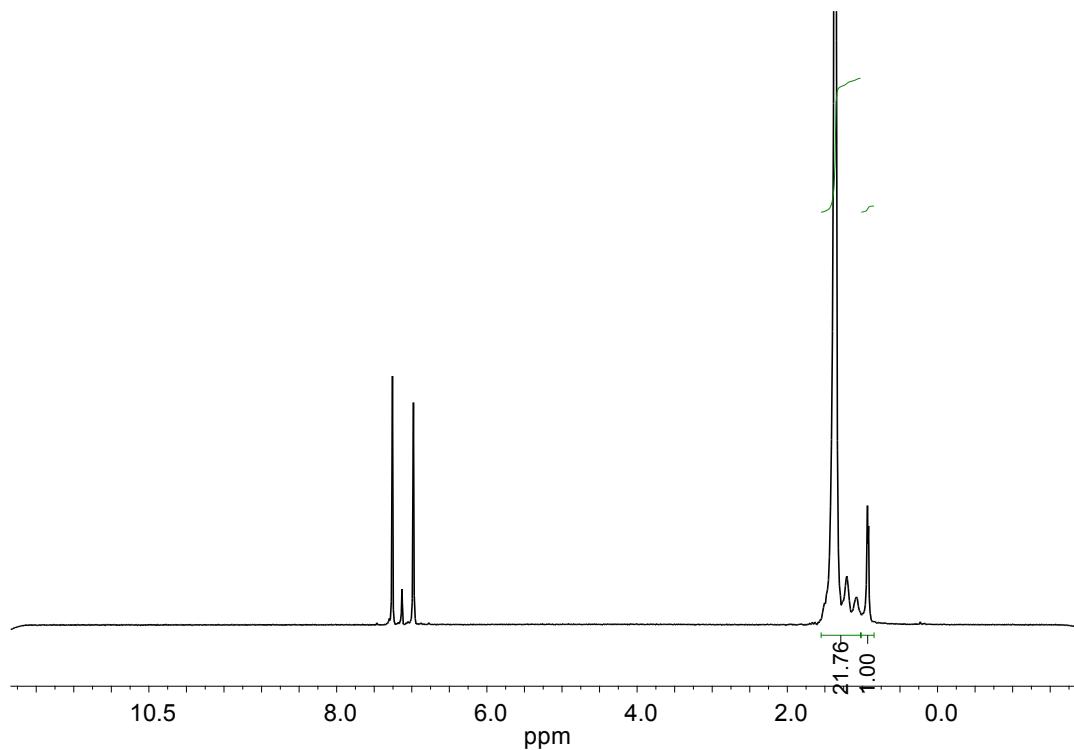


Figure S12. ¹H NMR spectrum of the polyethylene produced by **Ni1/MAO** from table 2, entry 1. (*o*-dichlorobenzene-*d*₄, 120 °C).

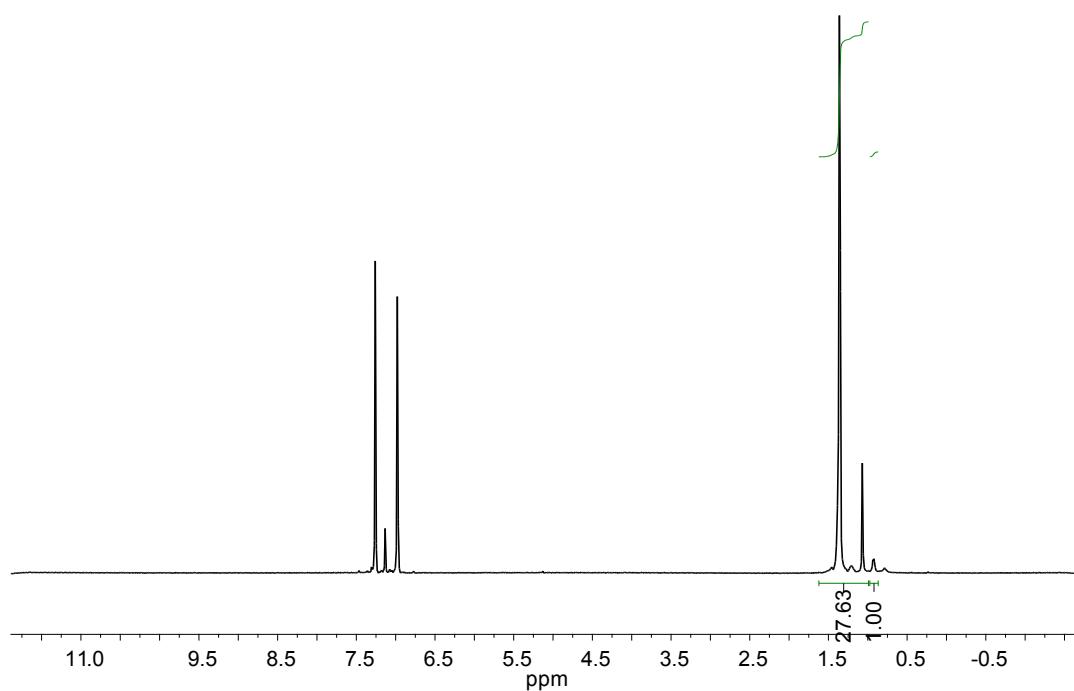


Figure S13. ¹H NMR spectrum of the polyethylene produced by **Ni3/MAO** from table 2, entry 3. (*o*-dichlorobenzene-*d*₄, 120 °C).

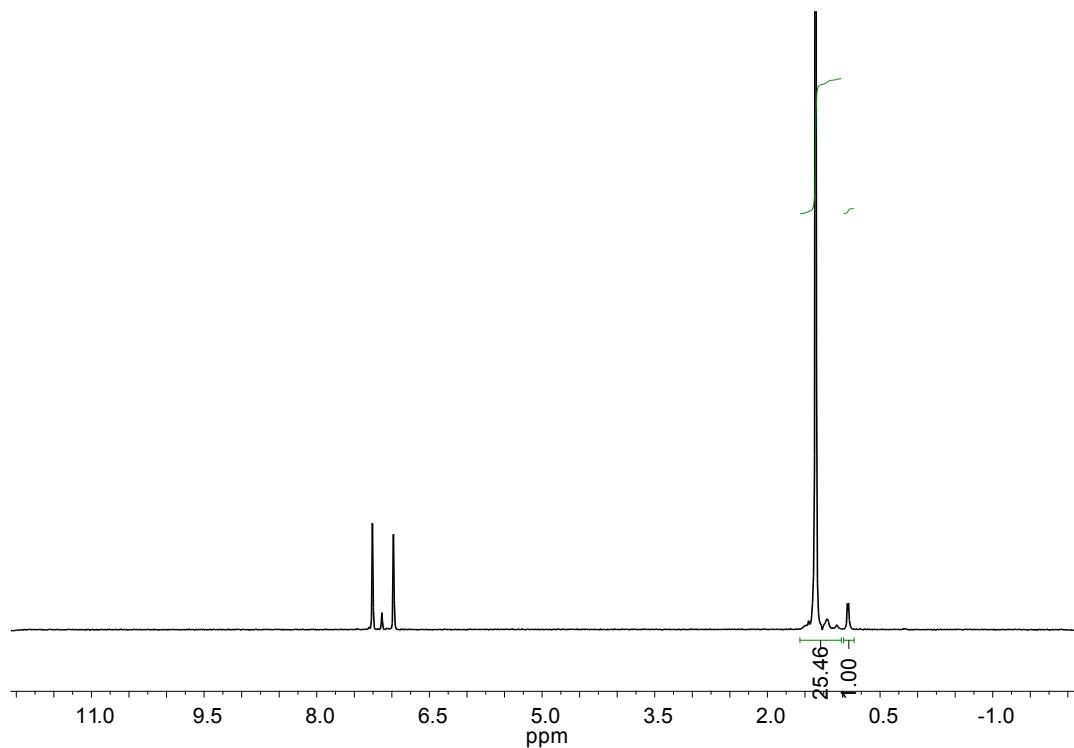


Figure S14. ¹H NMR spectrum of the polyethylene produced by **Ni4/MAO** from table 2, entry 4. (*o*-dichlorobenzene-*d*₄, 120 °C).

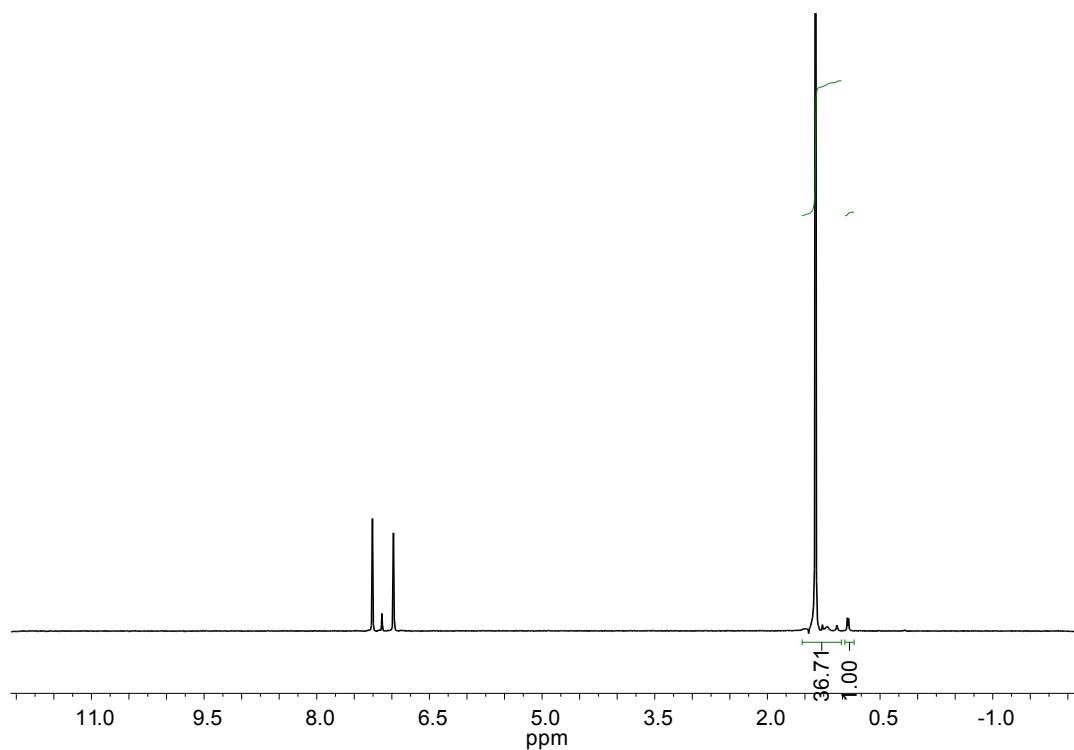


Figure S15. ¹H NMR spectrum of the polyethylene produced by **Ni5/MAO** from table 2, entry 5. (*o*-dichlorobenzene-*d*₄, 120 °C).

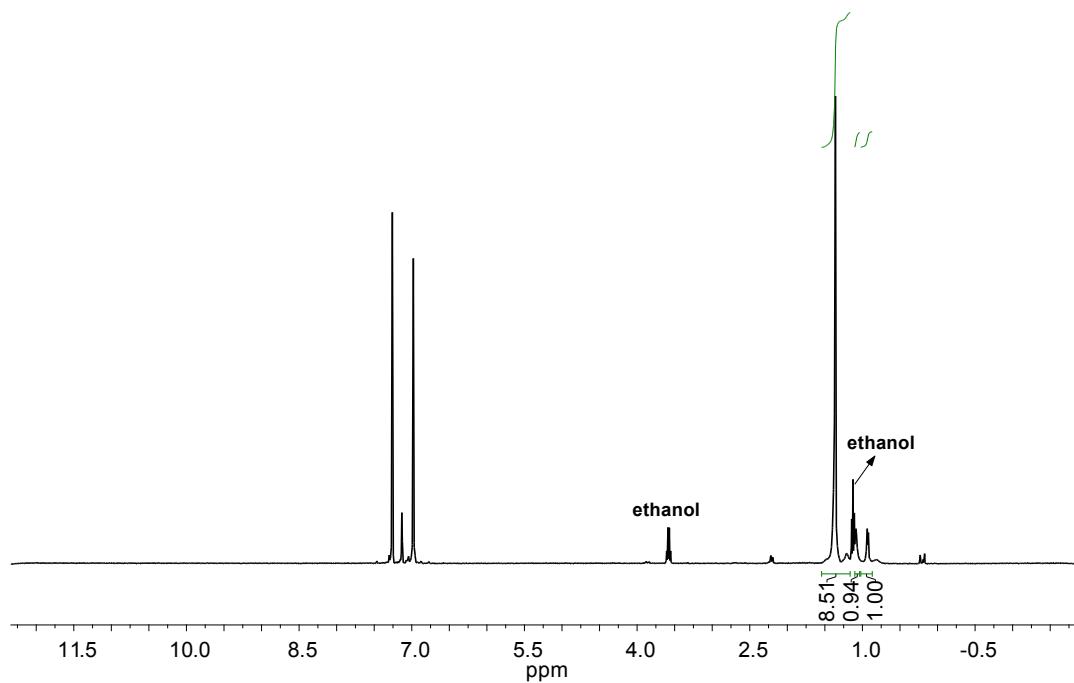


Figure S16. ¹H NMR spectrum of the polyethylene produced by **Ni1/MAO** from table 2, entry 6. (*o*-dichlorobenzene-*d*₄, 120 °C).

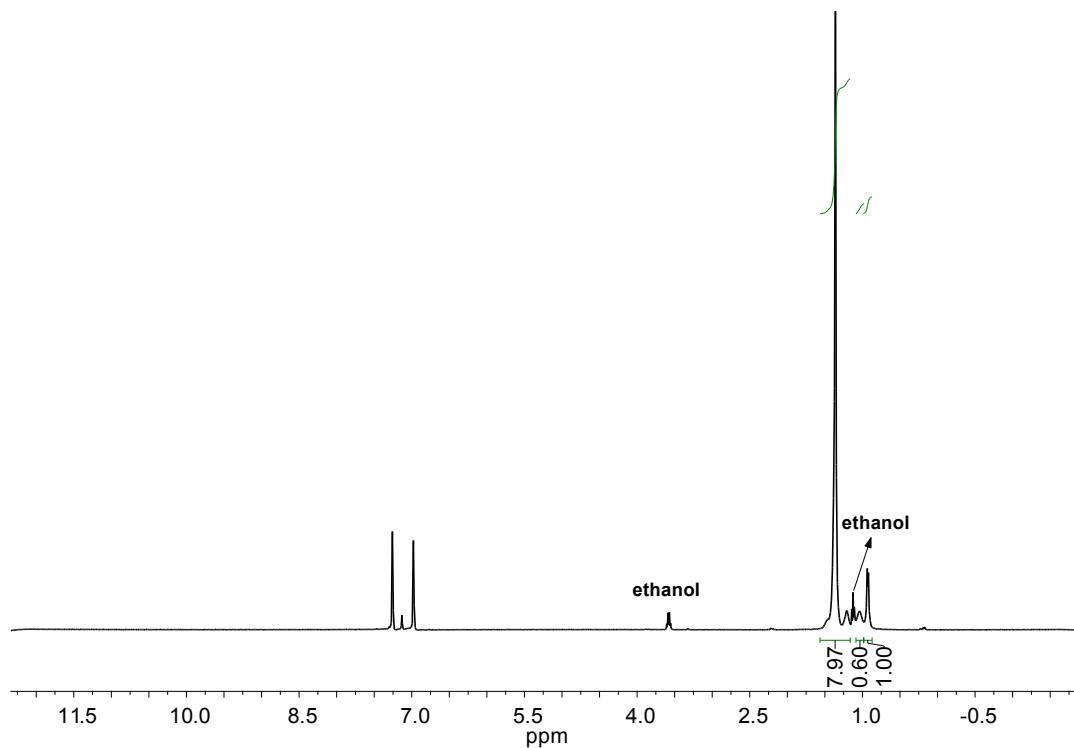


Figure S17. ¹H NMR spectrum of the polyethylene produced by **Ni1/MAO** from table 2, entry 7. (*o*-dichlorobenzene-*d*₄, 120 °C).

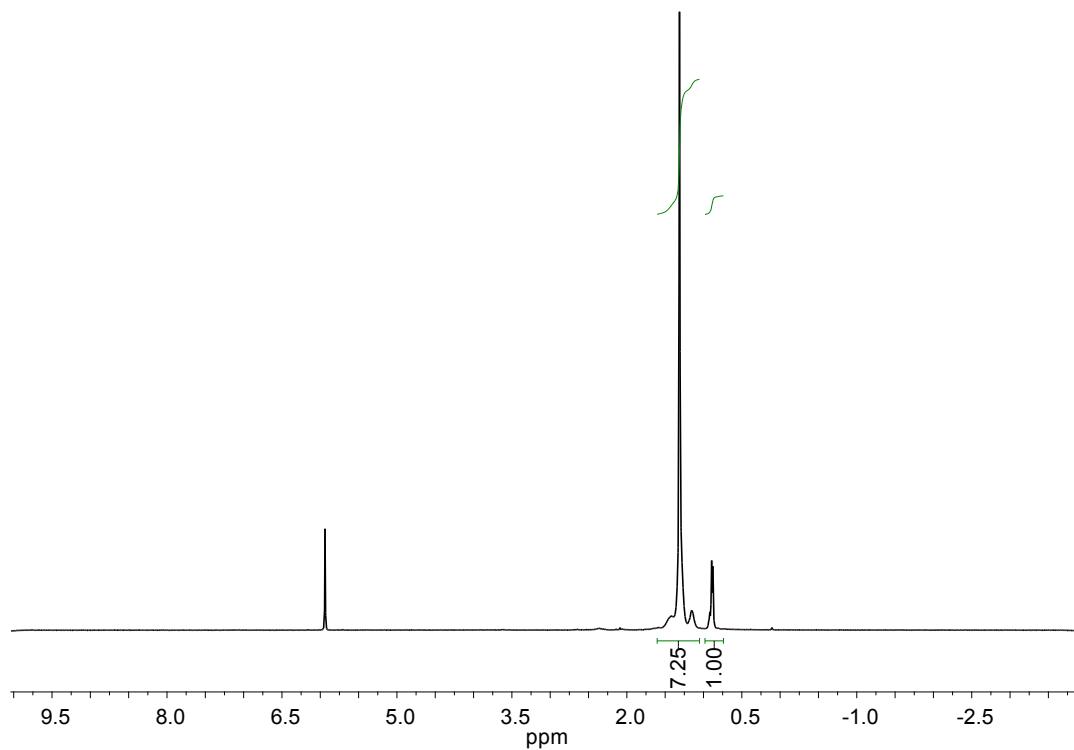


Figure S18. ¹H NMR spectrum of the polyethylene produced by **Ni1/MAO** from table 2, entry 8. (1,1,2,2-tetrachloroethane-*d*₂, 120 °C).

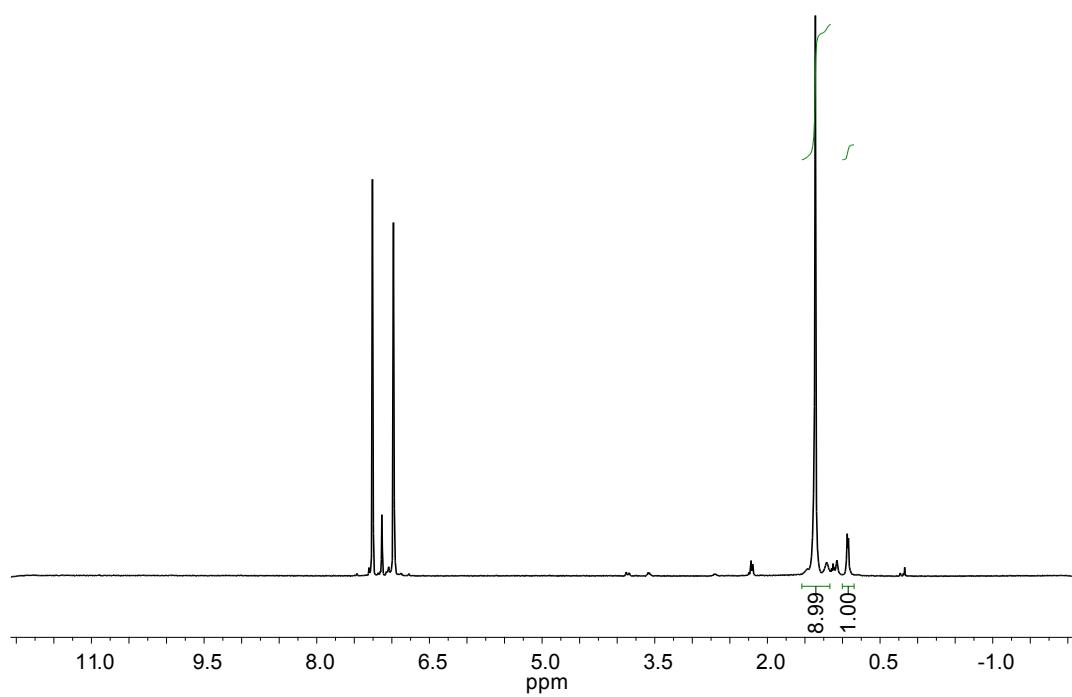


Figure S19. ¹H NMR spectrum of the polyethylene produced by **Ni2/MAO** from table 2, entry 9. (*o*-dichlorobenzene-*d*₄, 120 °C).

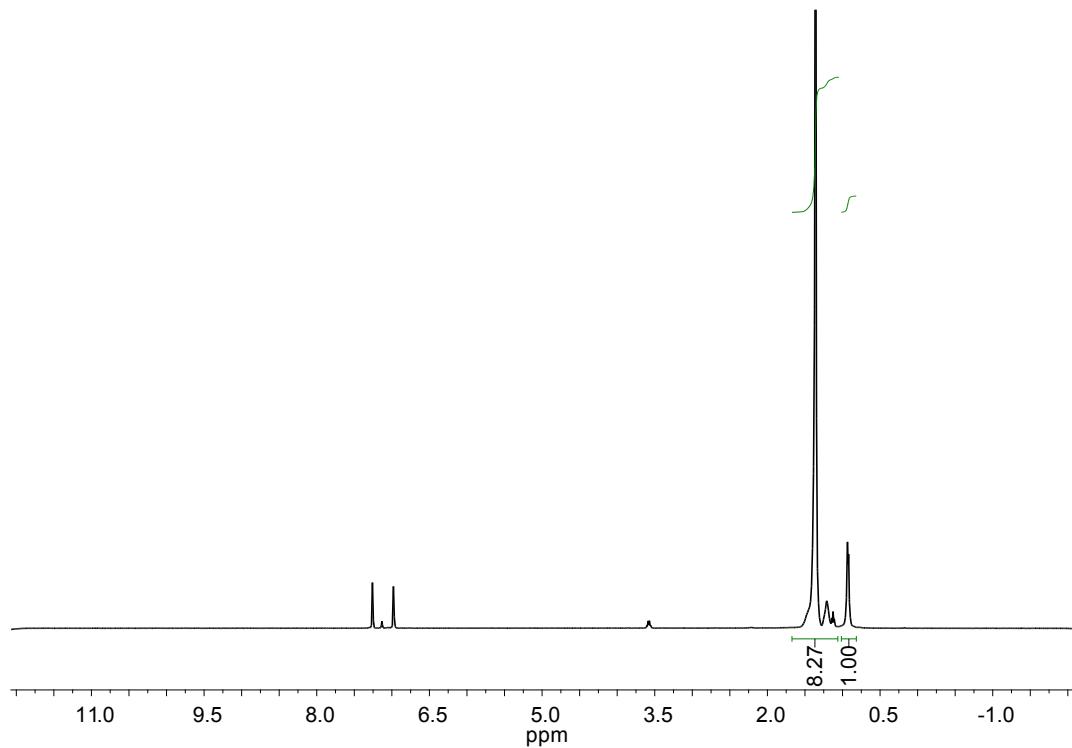


Figure S20. ¹H NMR spectrum of the polyethylene produced by **Ni2/MAO** from table 2, entry 10. (*o*-dichlorobenzene-*d*₄, 120 °C).

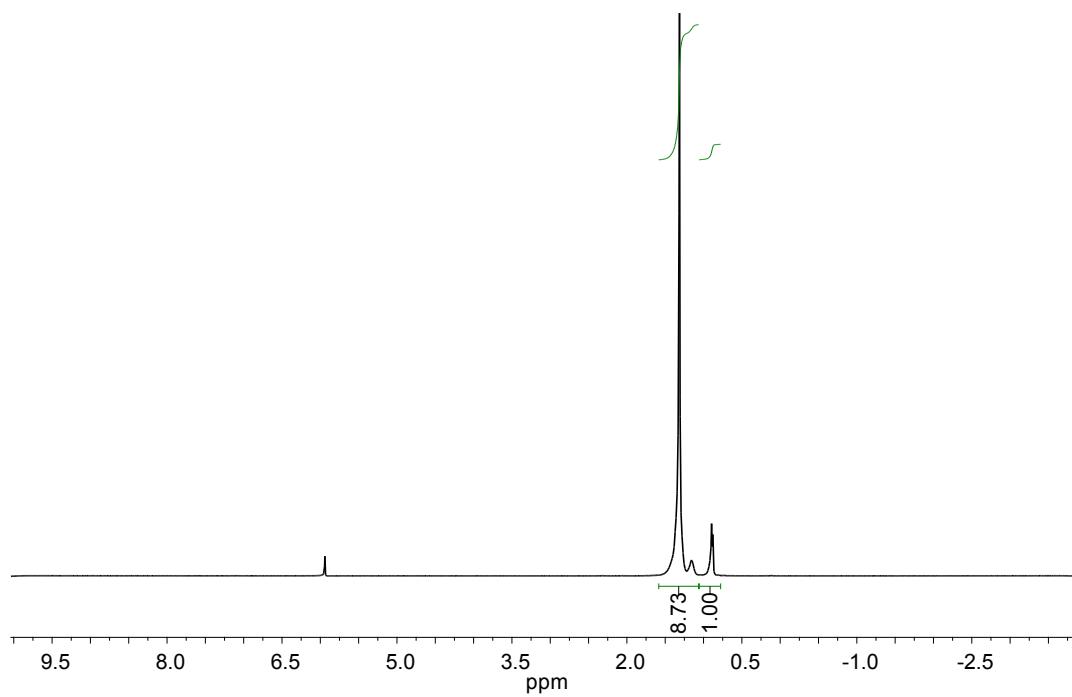


Figure S21. ¹H NMR spectrum of the polyethylene produced by **Ni2/MAO** from table 2, entry 11. (1,1,2,2-tetrachloroethane-*d*₂, 120 °C).

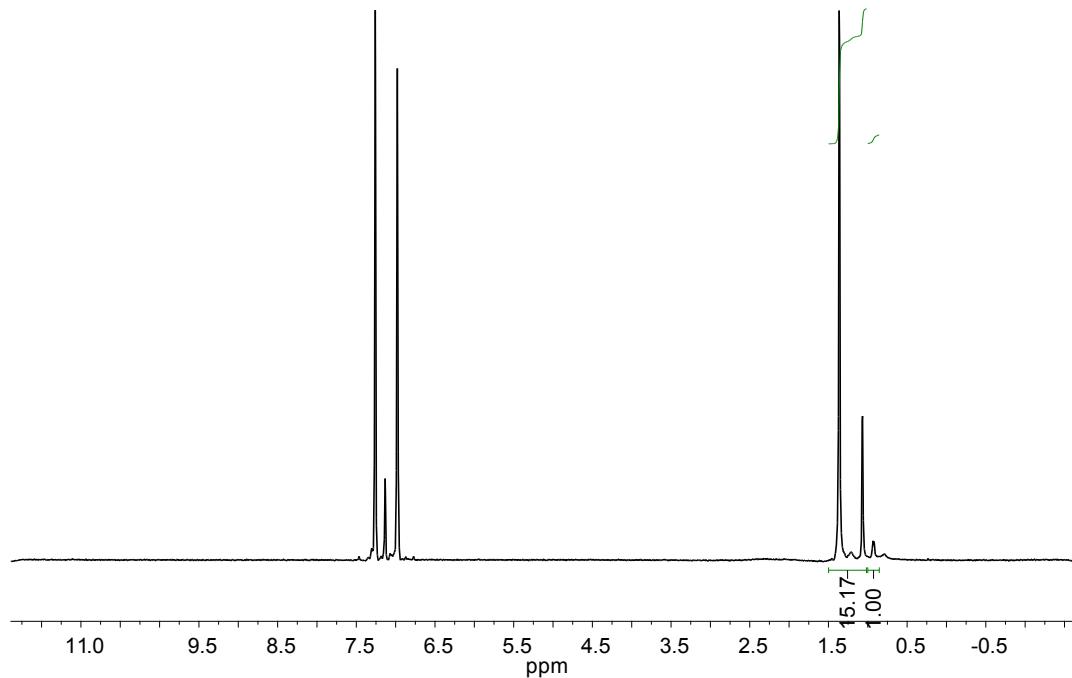


Figure S22. ¹H NMR spectrum of the polyethylene produced by **Ni3/MAO** from table 2, entry 12. (*o*-dichlorobenzene-*d*₄, 120 °C).

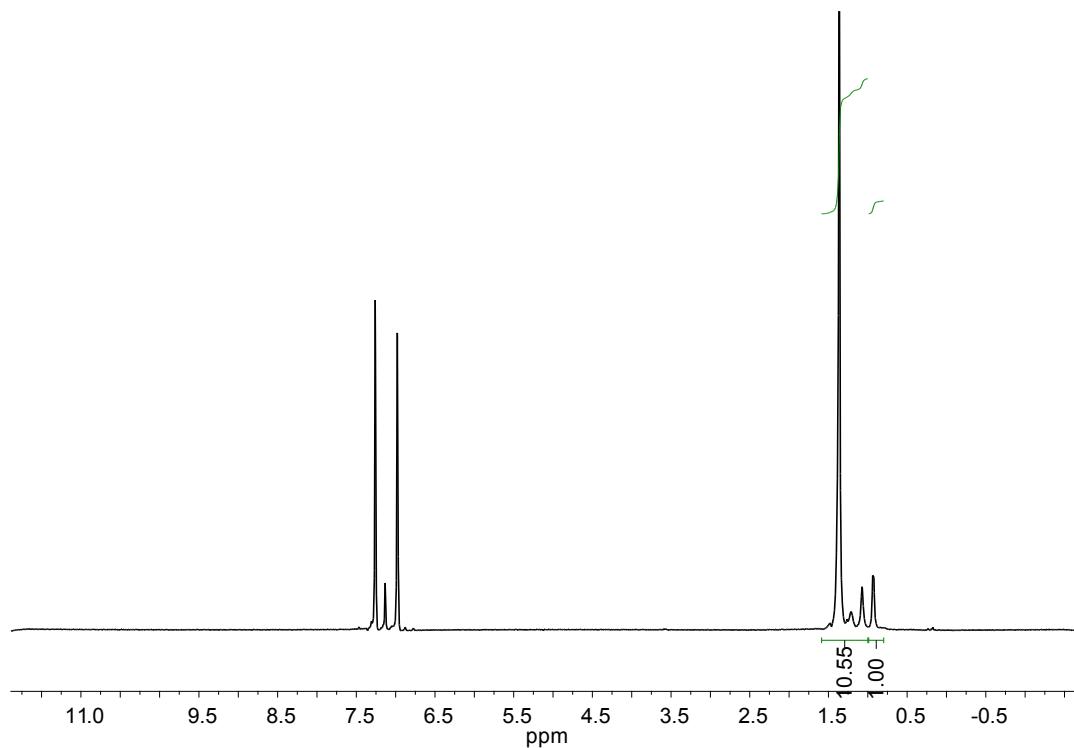


Figure S23. ¹H NMR spectrum of the polyethylene produced by **Ni3/MAO** from table 2, entry 13. (*o*-dichlorobenzene-*d*₄, 120 °C).

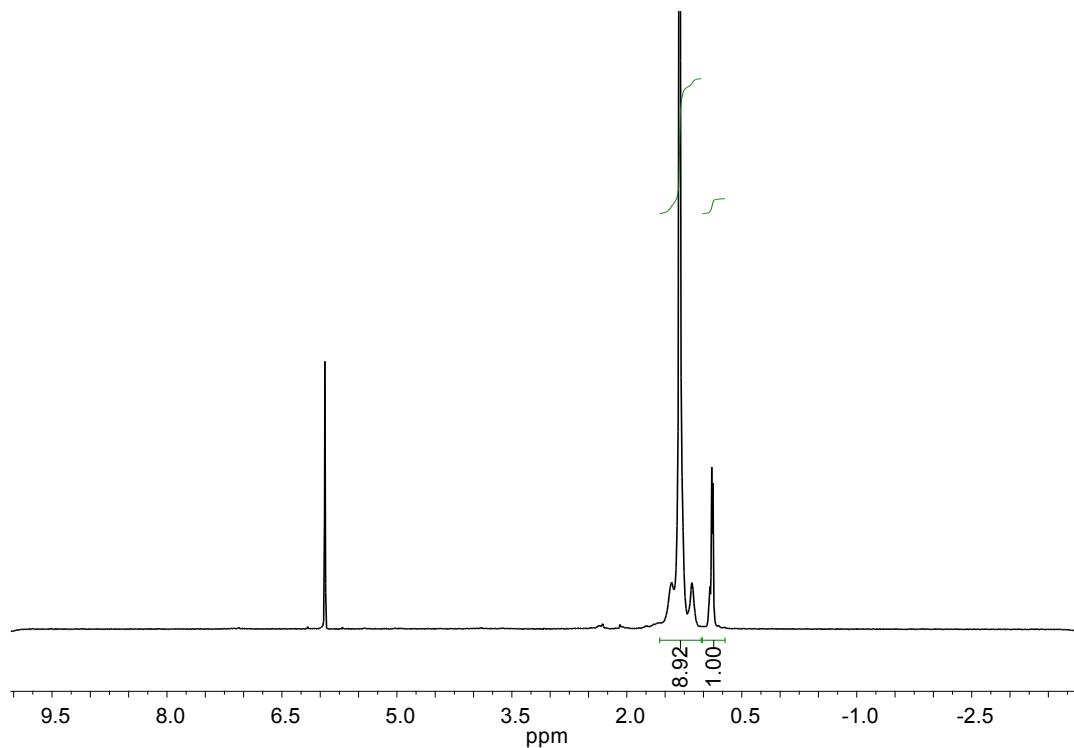


Figure S24. ¹H NMR spectrum of the polyethylene produced by **Ni3/MAO** from table 2, entry 14. (1,1,2,2-tetrachloroethane-*d*₂, 120 °C).

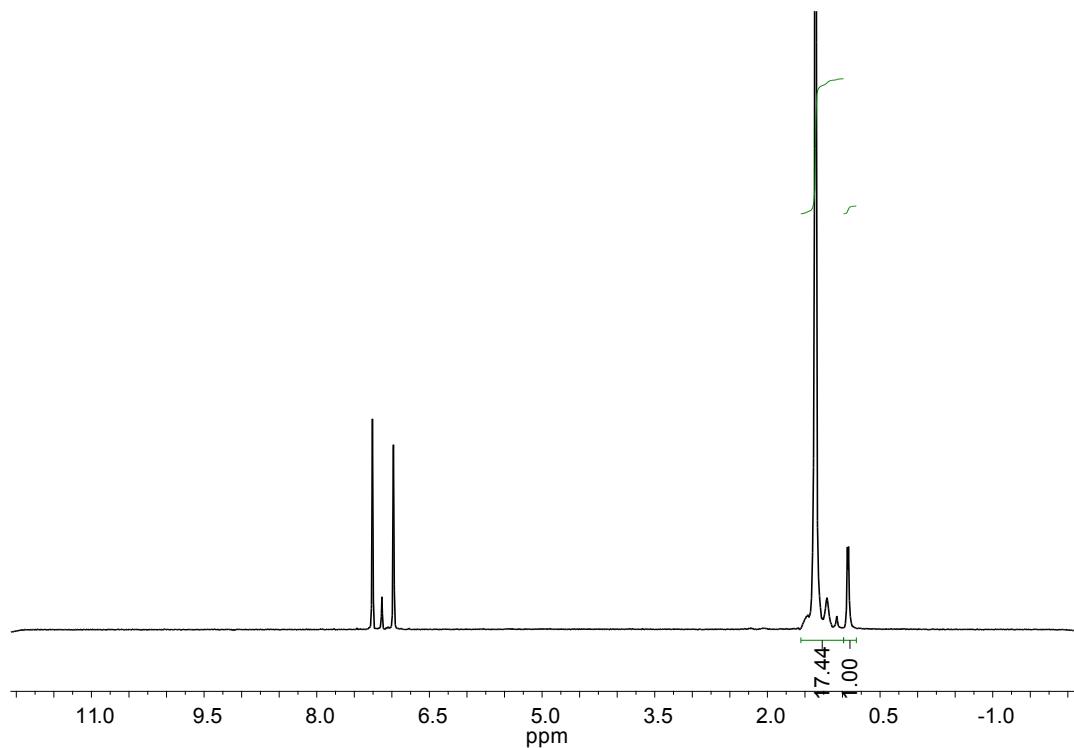


Figure S25. ¹H NMR spectrum of the polyethylene produced by **Ni4/MAO** from table 2, entry 15. (*o*-dichlorobenzene-*d*₄, 120 °C).

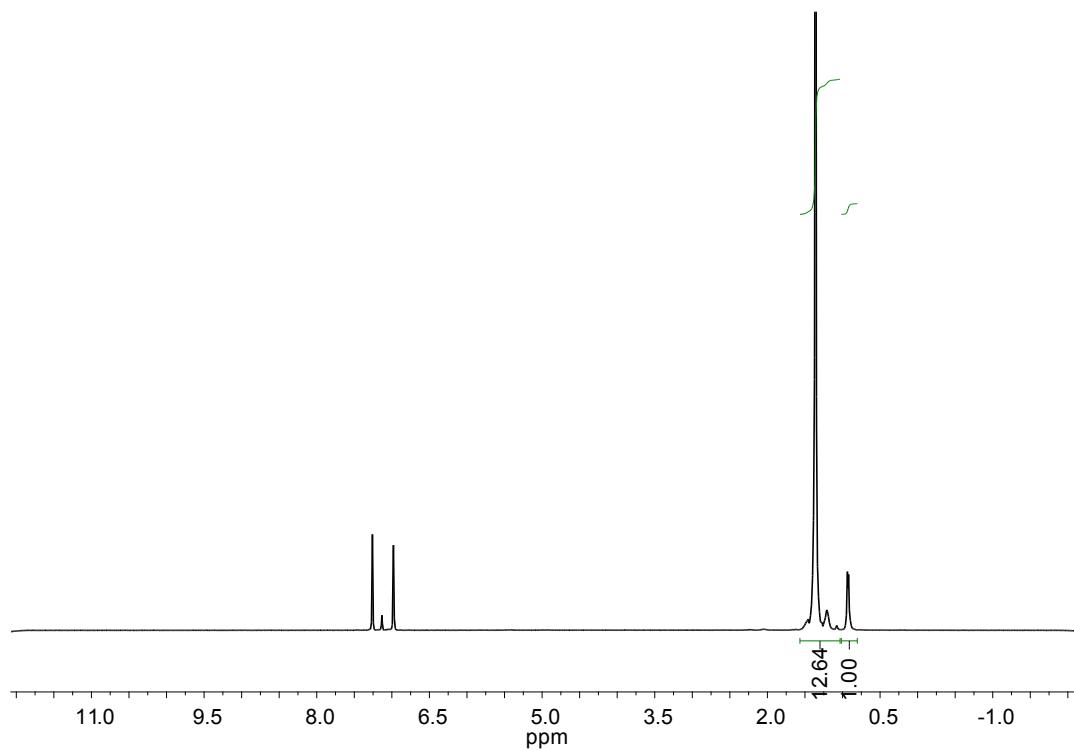


Figure S26. ¹H NMR spectrum of the polyethylene produced by **Ni4/MAO** from table 2, entry 16. (*o*-dichlorobenzene-*d*₄, 120 °C).

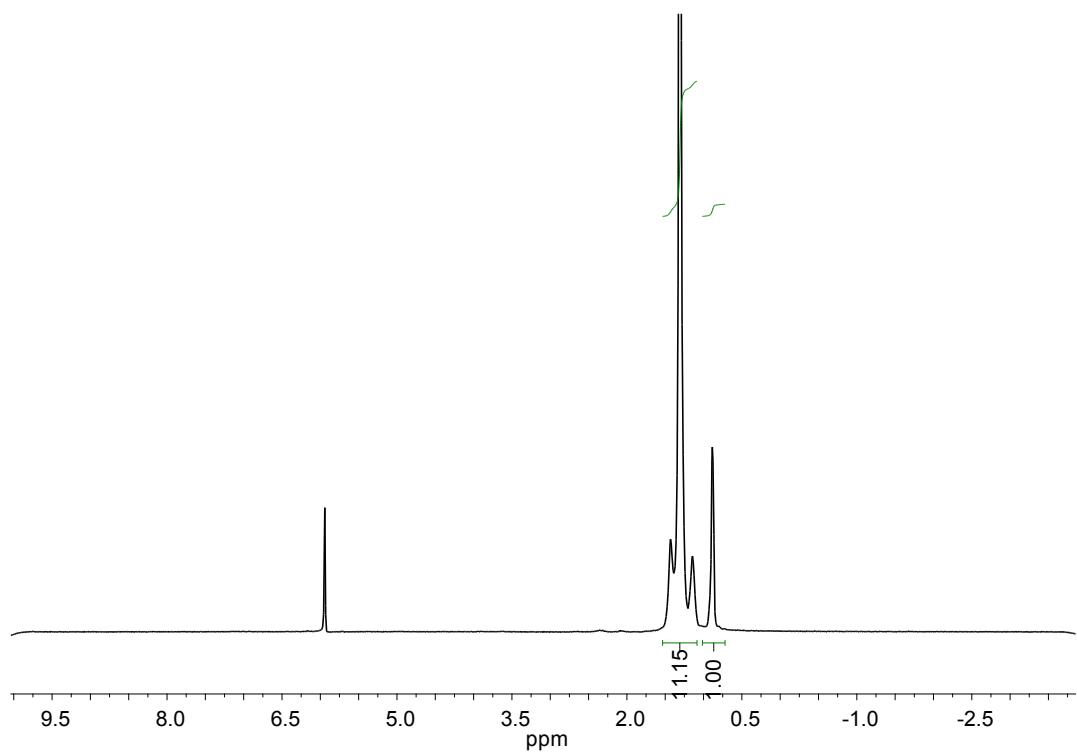


Figure S27. ¹H NMR spectrum of the polyethylene produced by **Ni4/MAO** from table 2, entry 17. (1,1,2,2-tetrachloroethane-*d*₂, 120 °C).

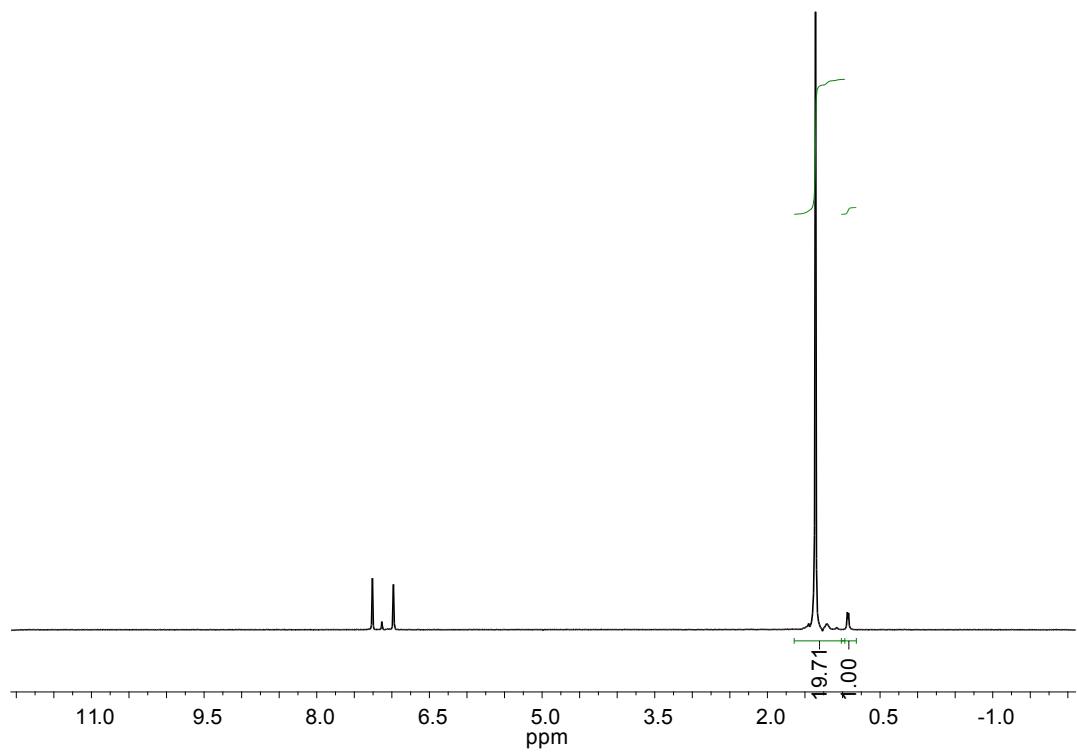


Figure S28. ¹H NMR spectrum of the polyethylene produced by **Ni5/MAO** from table 2, entry 18. (*o*-dichlorobenzene-*d*₄, 120 °C).

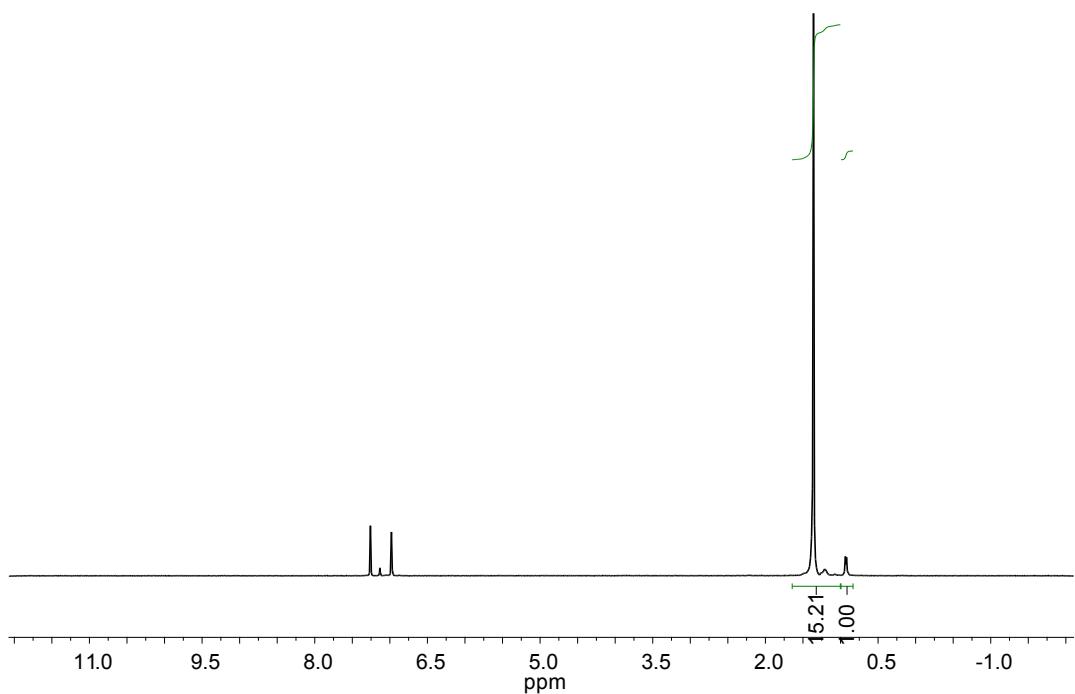


Figure S29. ¹H NMR spectrum of the polyethylene produced by **Ni5/MAO** from table 2, entry 19. (*o*-dichlorobenzene-*d*₄, 120 °C).

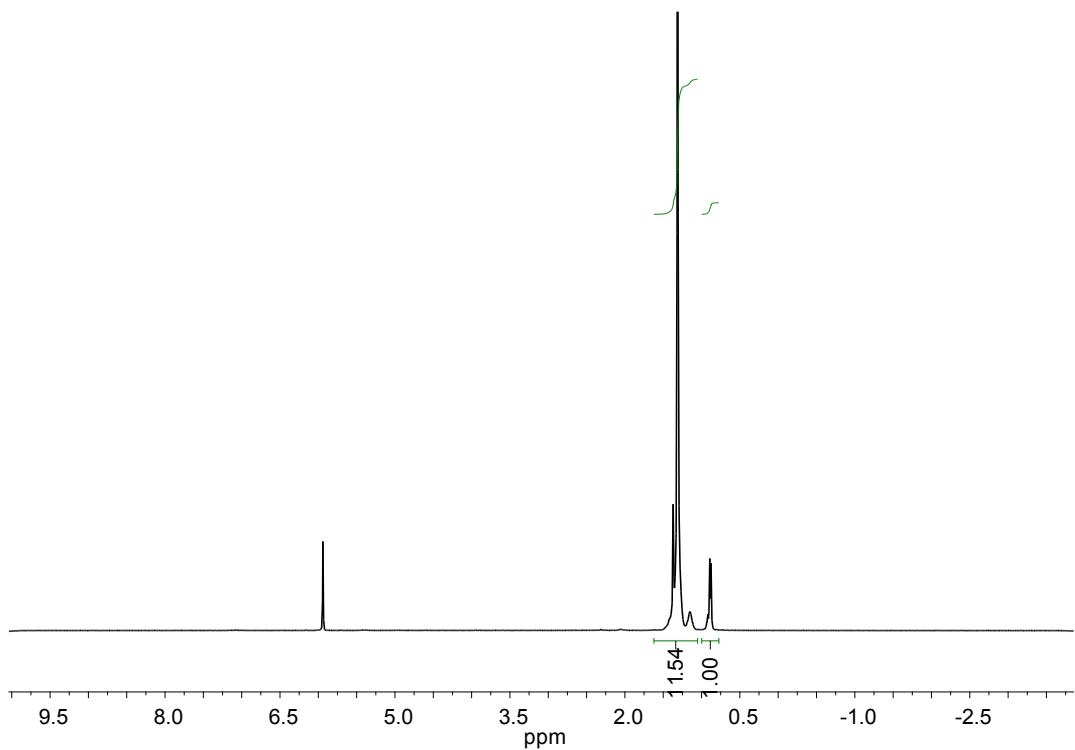


Figure S30. ¹H NMR spectrum of the polyethylene produced by **Ni5/MAO** from table 2, entry 20. (1,1,2,2-tetrachloroethane-*d*₂, 120 °C).

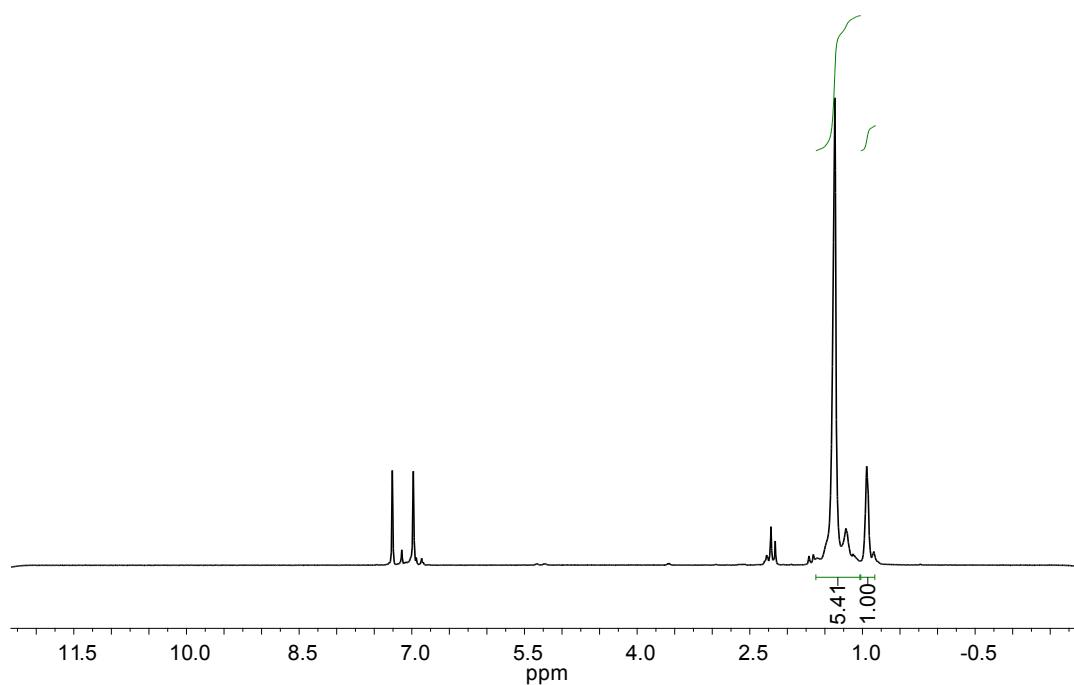


Figure S31. ¹H NMR spectrum of the poly(1-hexene) produced by **Ni1/EASC** from table 4, entry 1. (*o*-dichlorobenzene-*d*₄, 120 °C).

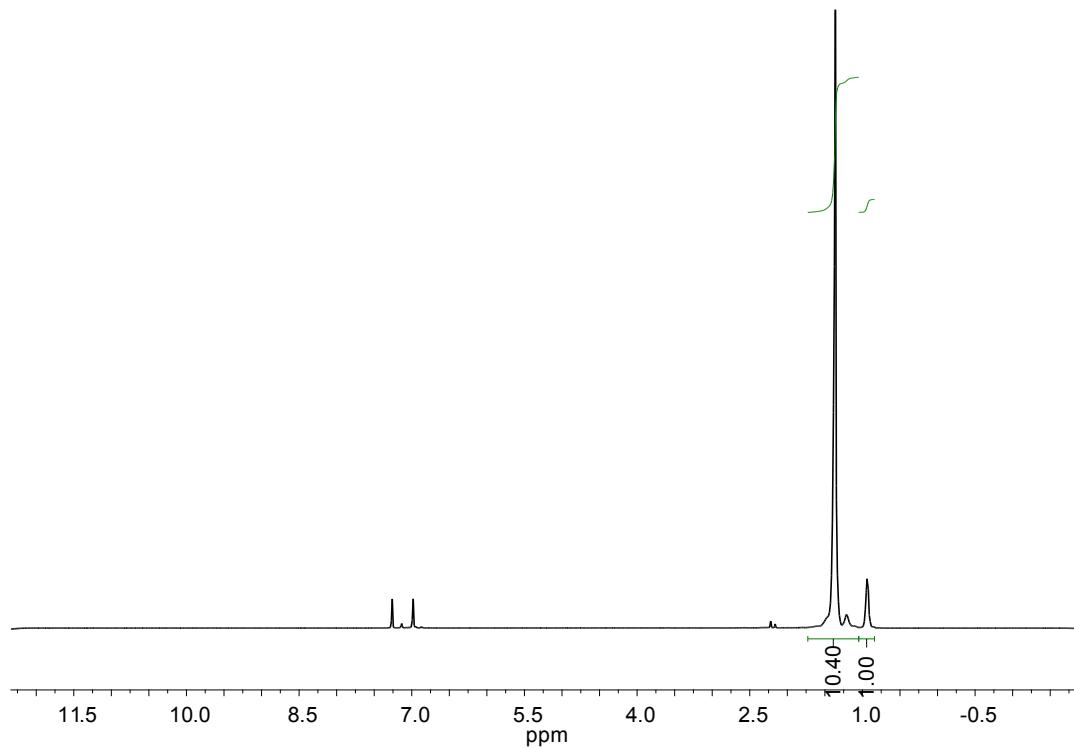


Figure S32. ¹H NMR spectrum of the poly(1-hexene) produced by **Ni2/EASC** from table 4, entry 2. (*o*-dichlorobenzene-*d*₄, 120 °C).

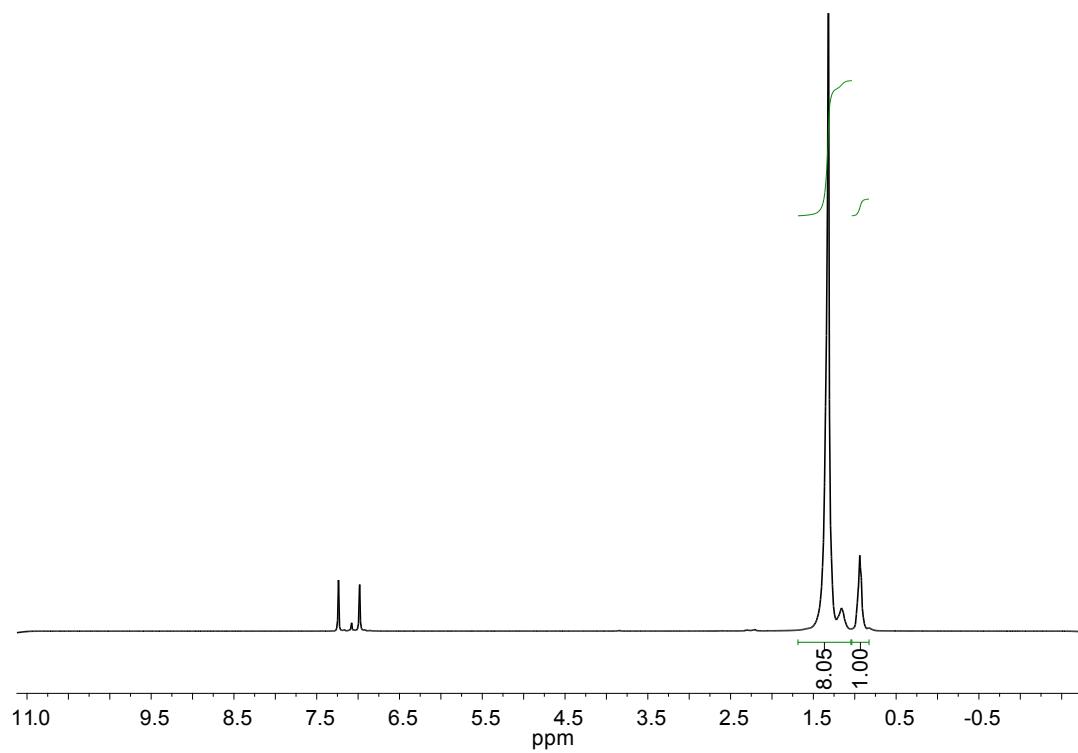


Figure S33. ¹H NMR spectrum of the poly(1-hexene) produced by Ni3/EASC from table 4, entry 3. (*o*-dichlorobenzene-*d*₄, 120 °C).

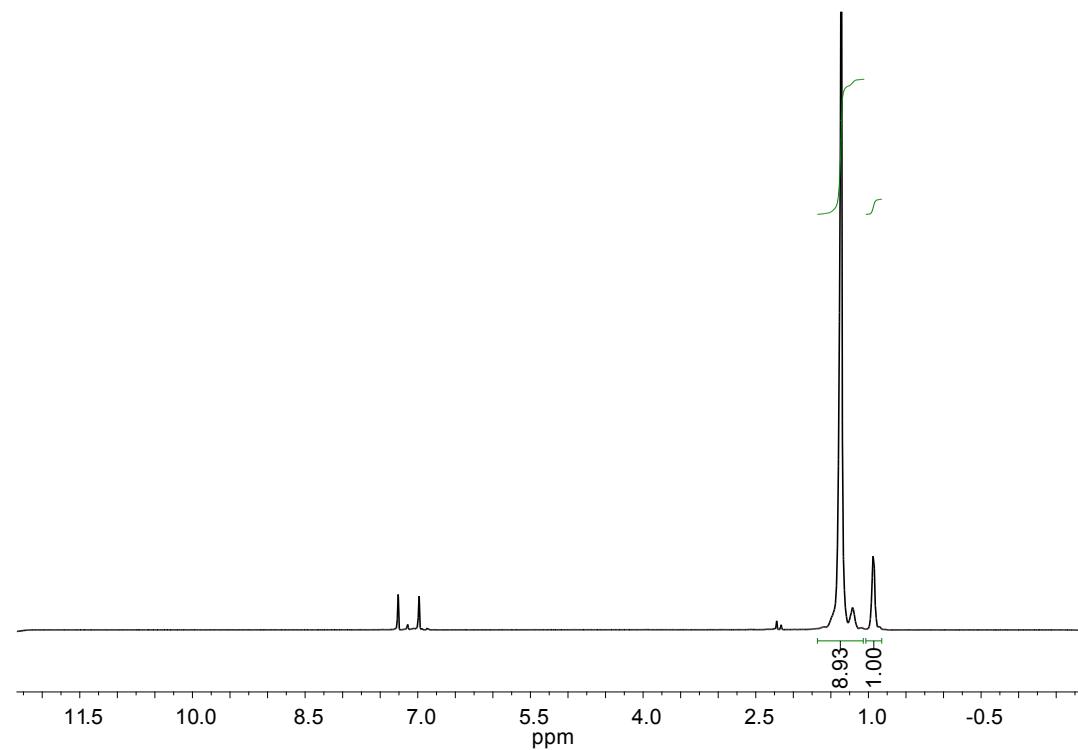


Figure S34. ¹H NMR spectrum of the poly(1-hexene) produced by Ni4/EASC from table 4, entry 4. (*o*-dichlorobenzene-*d*₄, 120 °C).

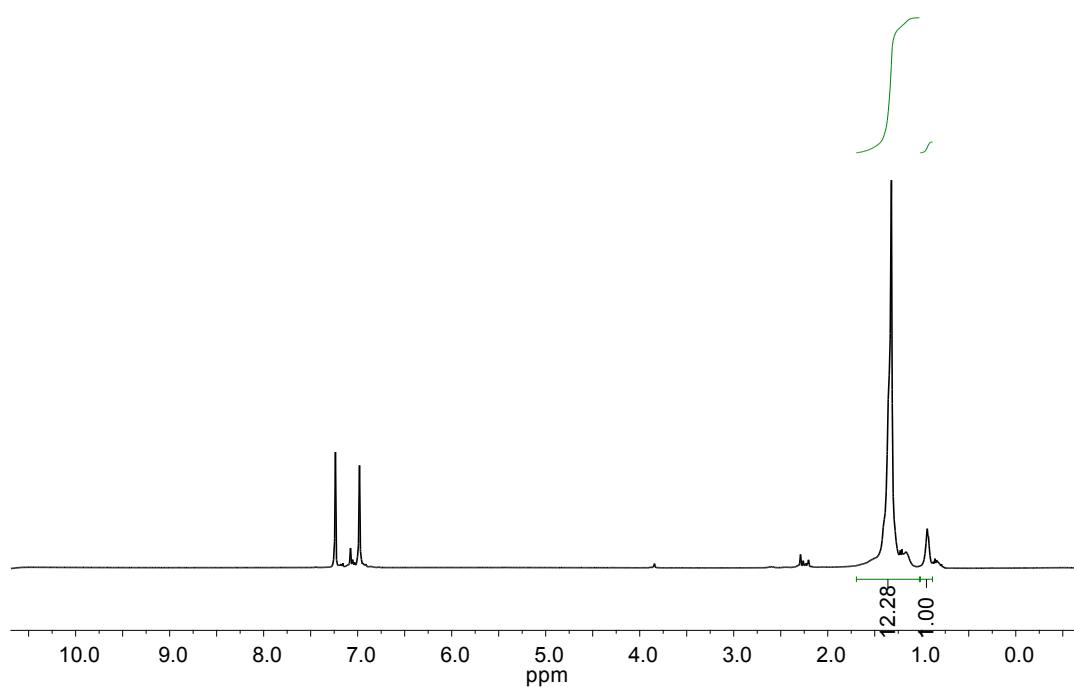


Figure S35. ¹H NMR spectrum of the poly(1-octene) produced by Ni2/EASC from table 4, entry 6. (*o*-dichlorobenzene-*d*₄, 120 °C).

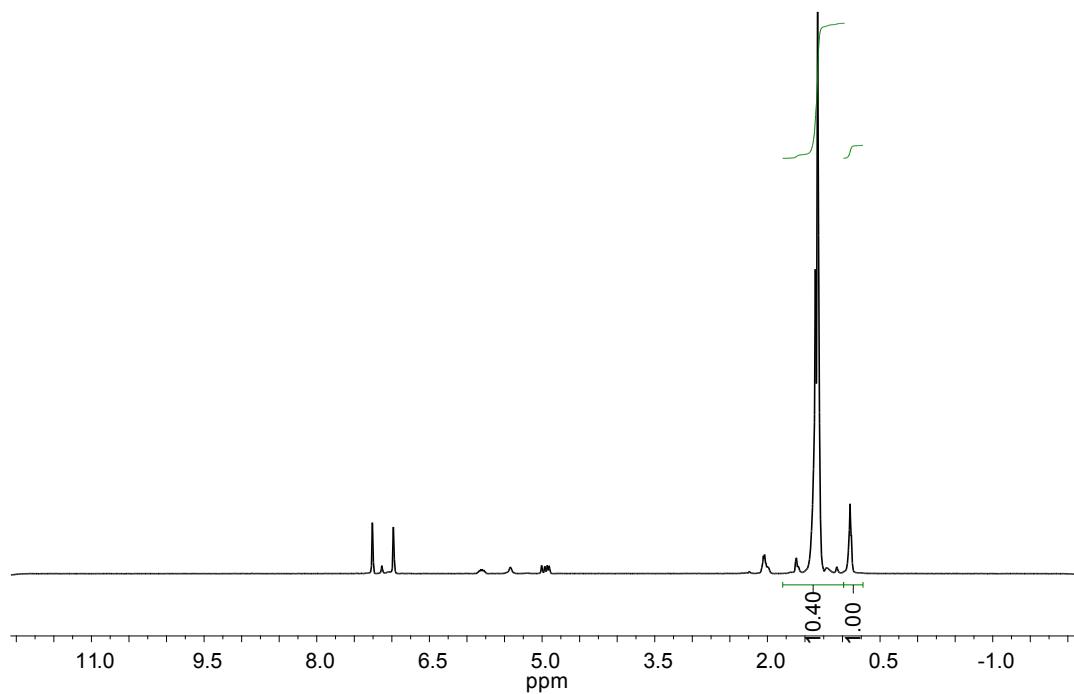


Figure S36. ¹H NMR spectrum of the poly(1-octadecene) produced by Ni2/EASC from table 4, entry 7. (*o*-dichlorobenzene-*d*₄, 120 °C).

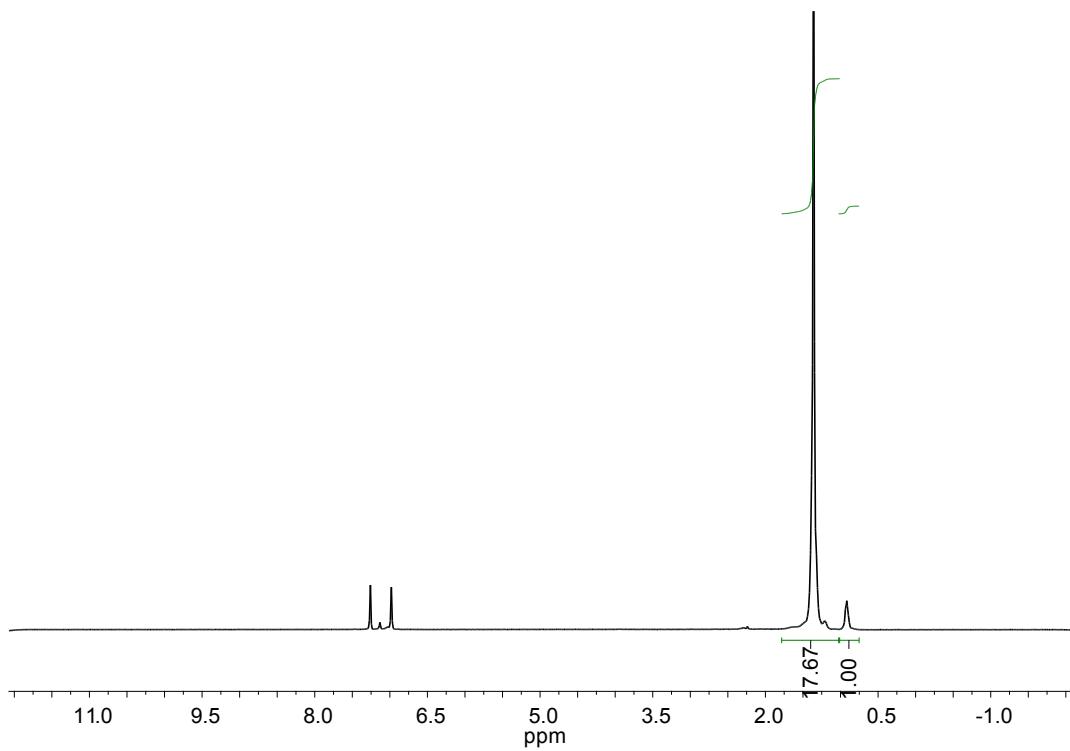
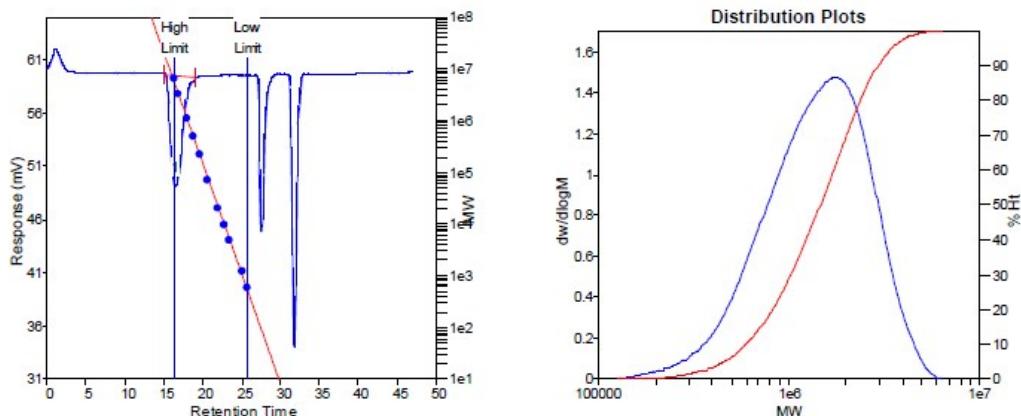


Figure S37. ¹H NMR spectrum of the poly(1-octadecene) produced by Ni2/EASC from table 4, entry 8. (*o*-dichlorobenzene-*d*₄, 120 °C).

4. GPC Spectra of polymers



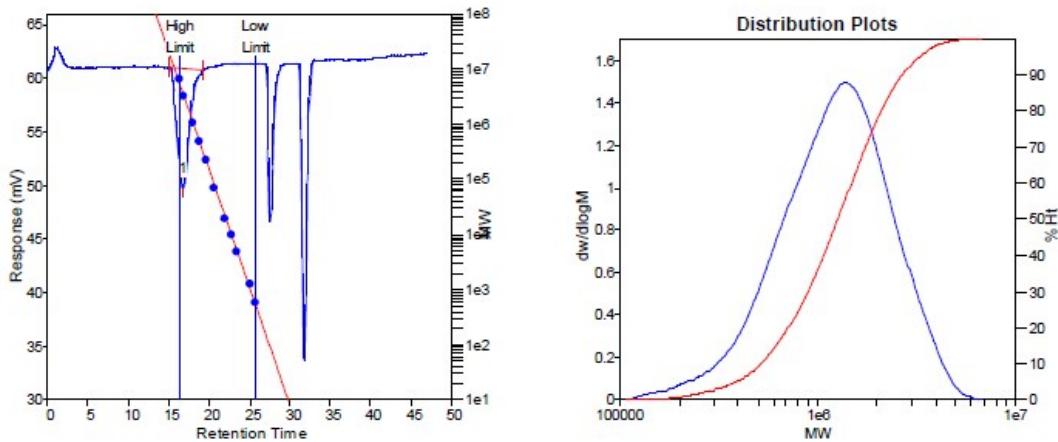
MW Averages

Peak No	M _p	M _n	M _w	M _z	M _{z+1}	M _v	PD
1	1811713	1112474	1634003	2170586	2671502	1563010	1.4688

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.07	16.38	19.17	-10.3895	100	1022.74	100

Figure S38. GPC of the polyethylene produced by Ni2/MAO from table 1, entry 1.



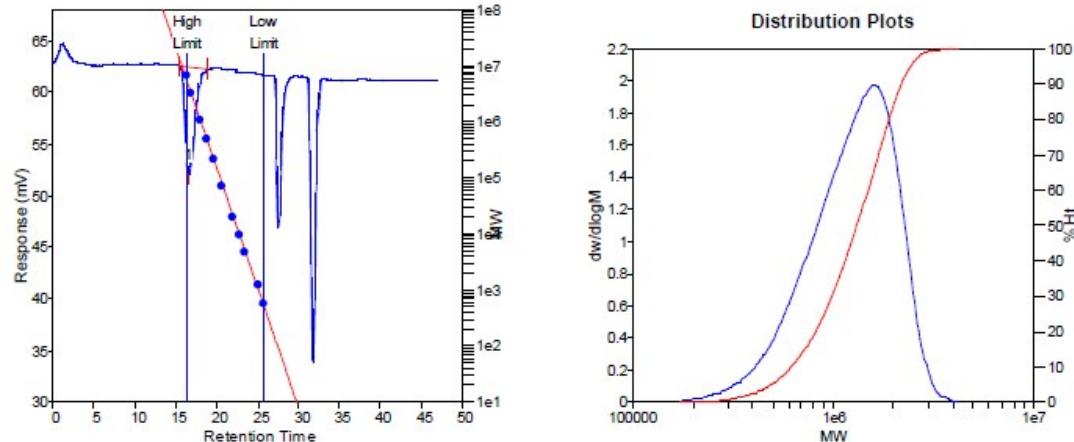
MW Averages

Peak No	M _p	M _n	M _w	M _z	M _{z+1}	M _v	PD
1	1405616	956321	1452994	1999232	2548868	1383491	1.51936

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.02	16.65	19.35	-11.2118	100	1090.56	100

Figure S39. GPC of the polyethylene produced by Ni2/MMAO from table 1, entry 2.



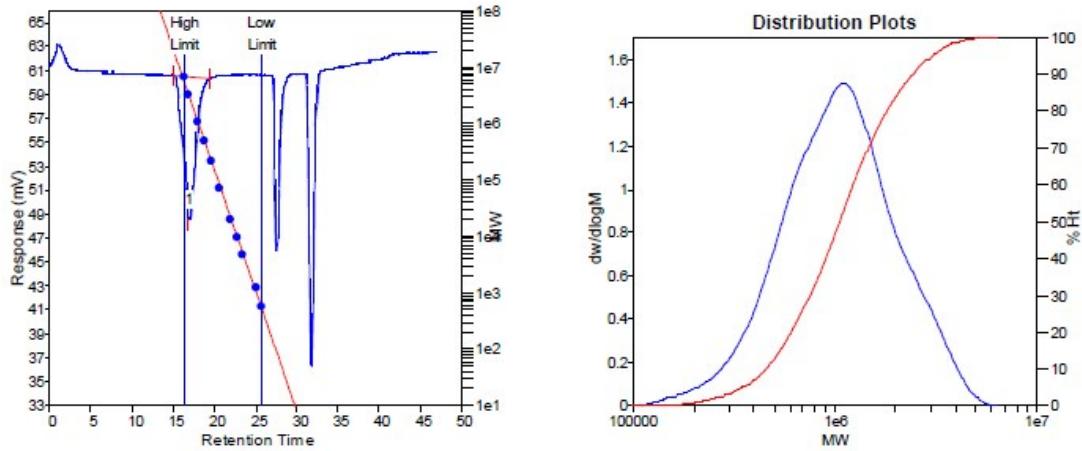
MW Averages

Peak No	M _p	M _n	M _w	M _z	M _{z+1}	M _v	PD
1	1595799	1065767	1364785	1631521	1859682	1327029	1.28057

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.48	16.52	18.85	-10.3618	0	762.51	100

Figure S40. GPC of the polyethylene produced by Ni2/Et₂AlCl from table 1, entry 3.



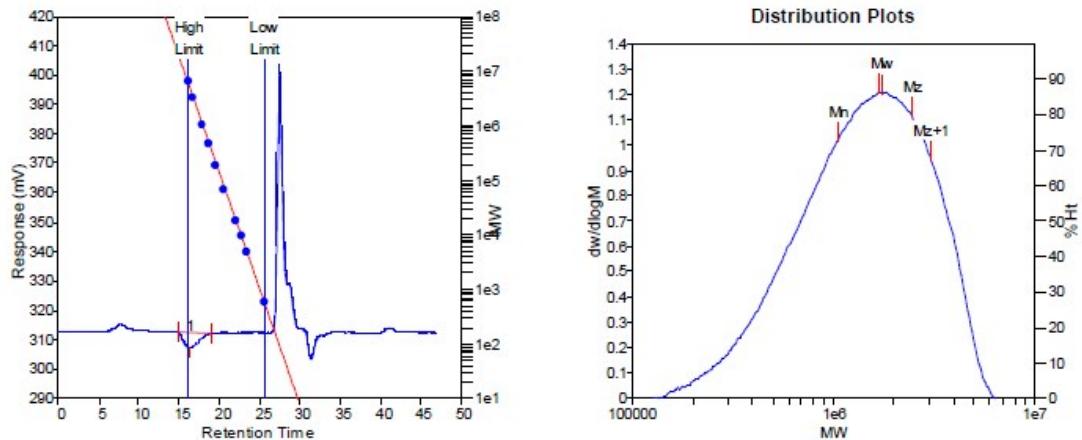
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1107983	834805	1265760	1813838	2408436	1200071	1.51623

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.07	16.90	19.45	-11.9259	100	1162.83	100

Figure S41. GPC of the polyethylene produced by Ni2/EASC from table 1, entry 4.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1670688	1050962	1747919	2478460	3087040	1650395	1.66316

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		14.92	16.33	19.05	-4.94002	0	596.105	100

Figure S42. GPC of the polyethylene produced by Ni1/MAO from table 2, entry 1.

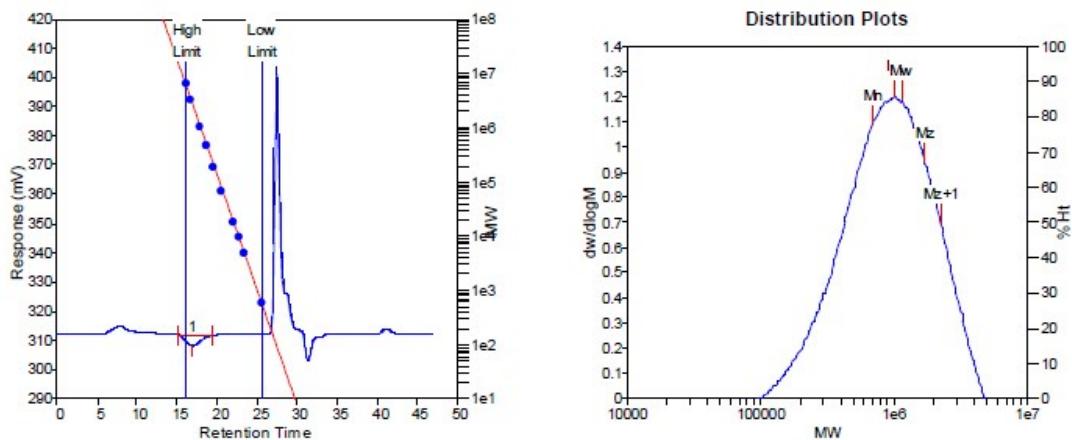


Figure S43. GPC of the polyethylene produced by **Ni3/MAO** from table 2, entry 3.

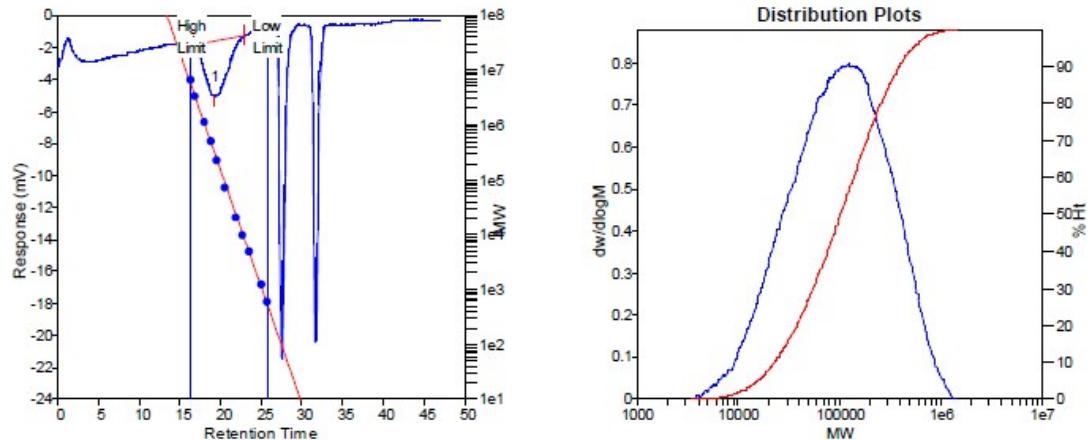
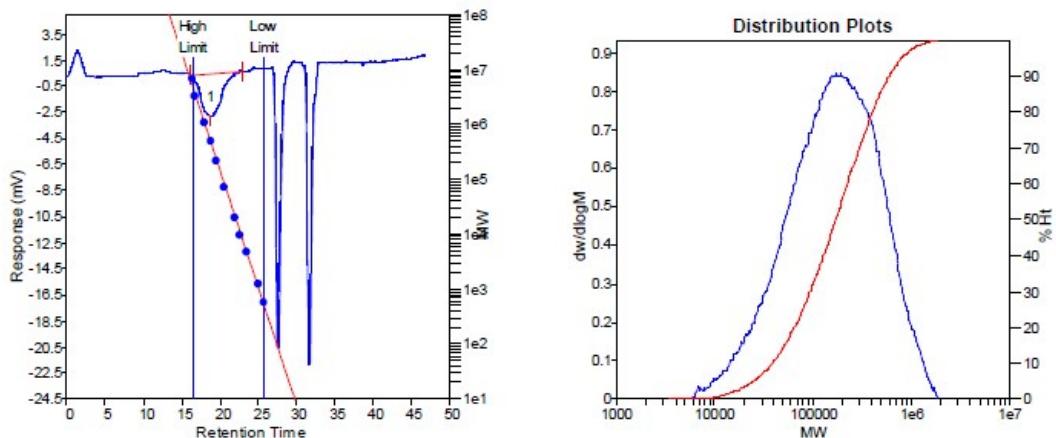


Figure S44. GPC of the polyethylene produced by **Ni4/MAO** from table 2, entry 4.



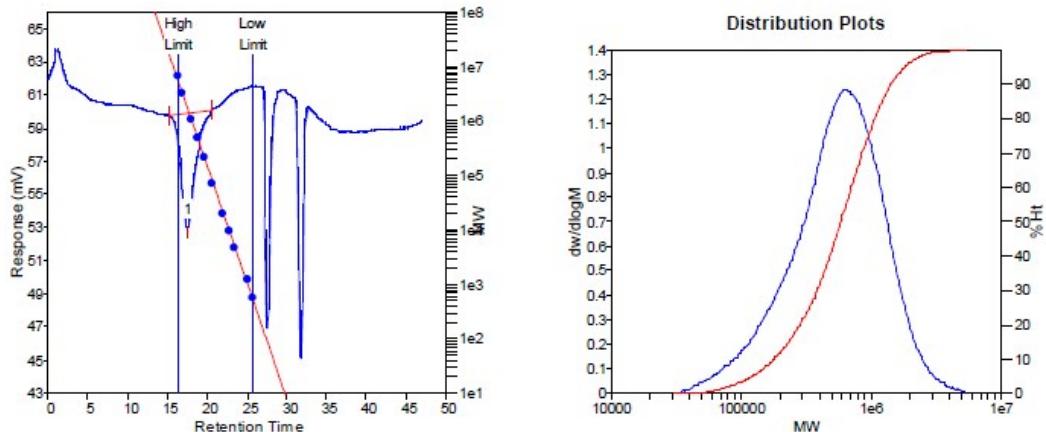
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	190486	87598	255068	513019	772124	226676	2.9118

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.33	18.75	22.97	-3.3169	100	570.006	100

Figure S45. GPC of the polyethylene produced by **Ni5/MAO** from table 2, entry 5.



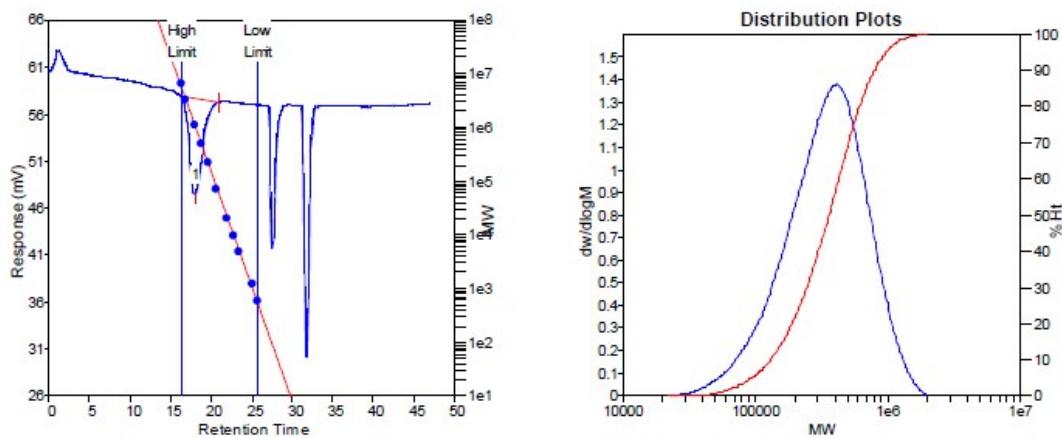
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	635948	373055	722588	1173880	1733411	670755	1.93695

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.25	17.48	20.68	-6.94794	100	816.1	100

Figure S46. GPC of the polyethylene produced by **Ni1/MAO** from table 2, entry 6.



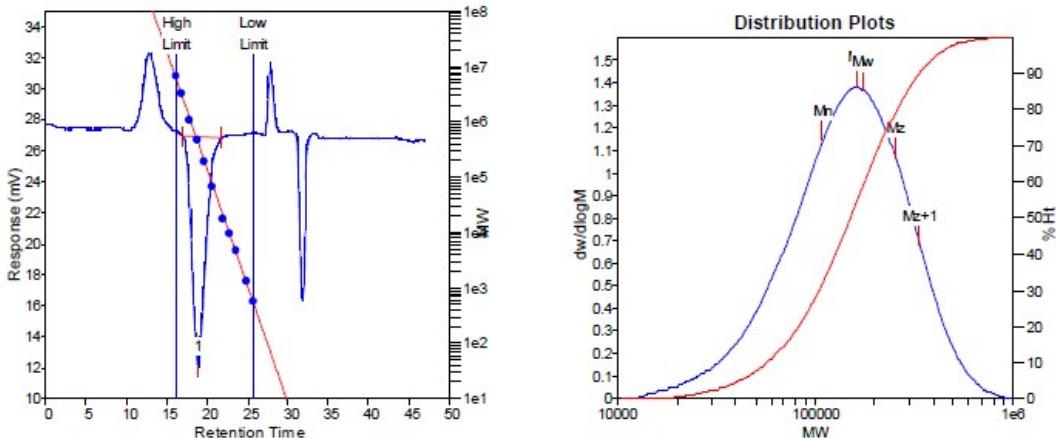
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	414401	255135	417932	599531	782715	395015	1.63808

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.27	17.93	21.02	-10.1848	100	1071.59	100

Figure S47. GPC of the polyethylene produced by Ni1/MAO from table 2, entry 7.



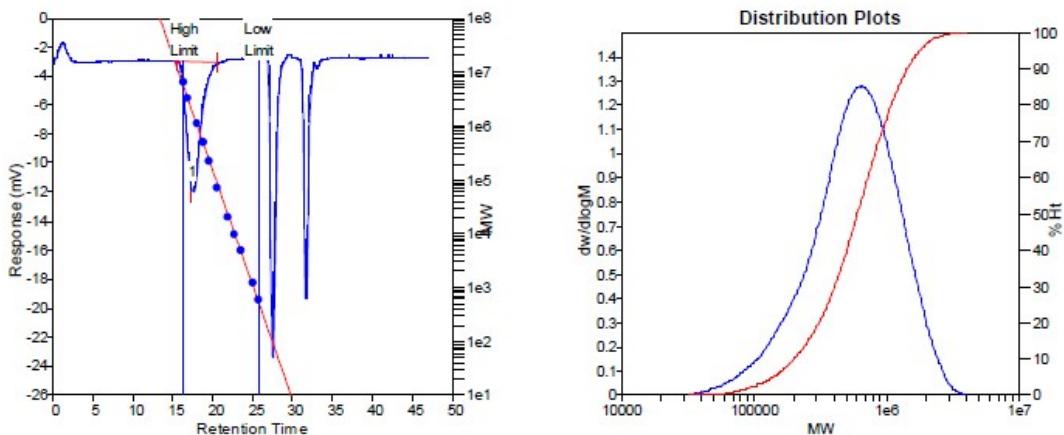
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	163434	109730	177227	255604	339892	167566	1.61512

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.93	18.83	21.73	-14.7701	100	1568.49	100

Figure S48. GPC of the polyethylene produced by Ni1/MAO from table 2, entry 8.



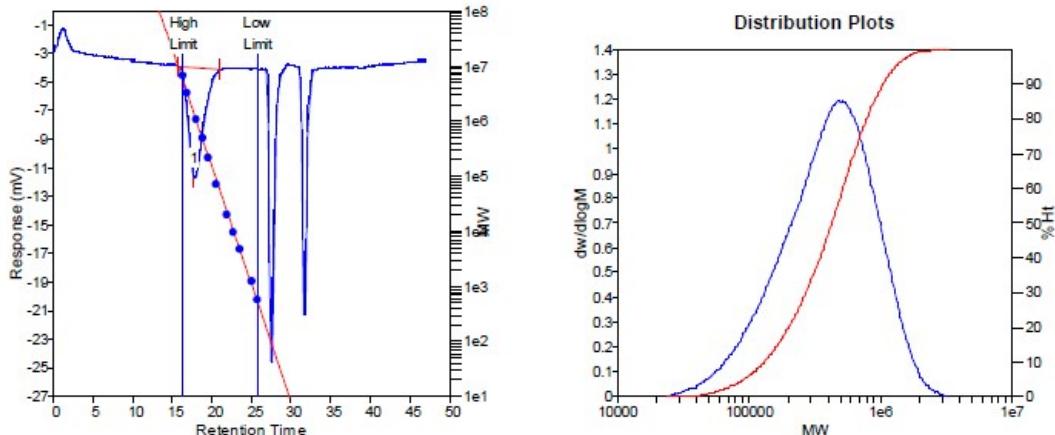
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	646116	404026	724327	1087145	1452518	679138	1.79277

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.53	17.47	20.63	-8.99406	100	1022.34	100

Figure S49. GPC of the polyethylene produced by **Ni2/MAO** from table 2, entry 9.



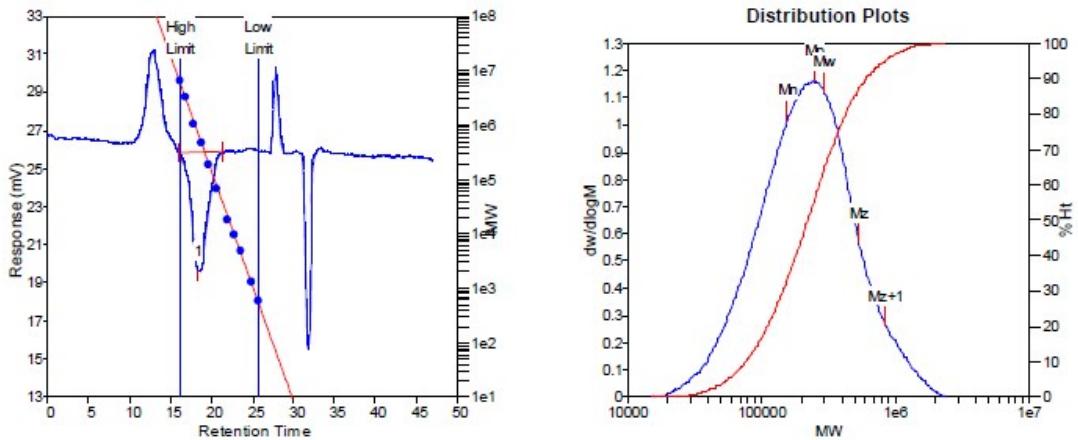
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	485635	274652	520552	814135	1116321	484611	1.89531

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.77	17.77	20.95	-7.73879	100	942.838	100

Figure S50. GPC of the polyethylene produced by **Ni2/MAO** from table 2, entry 10.



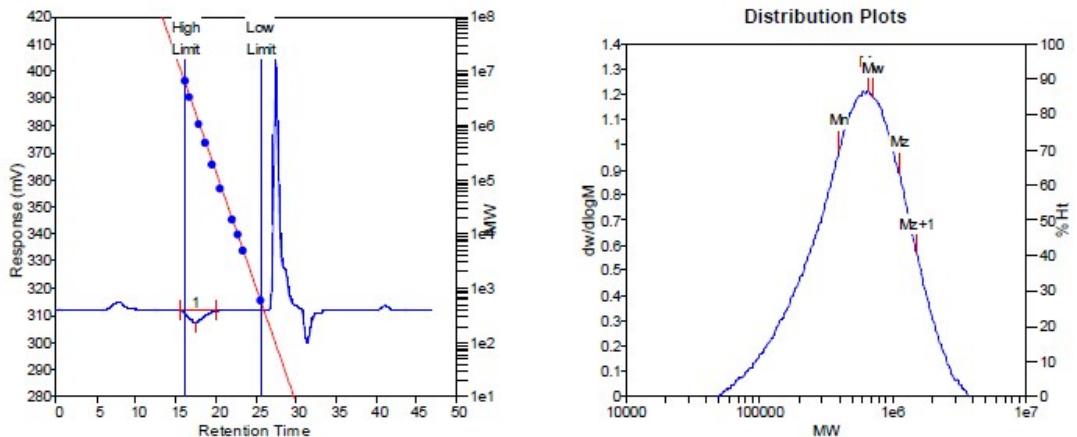
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	249696	156948	298112	536793	851520	273626	1.89943

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.00	18.38	21.37	-6.27879	100	793.843	100

Figure S51. GPC of the polyethylene produced by **Ni2/MAO** from table 2, entry 11.



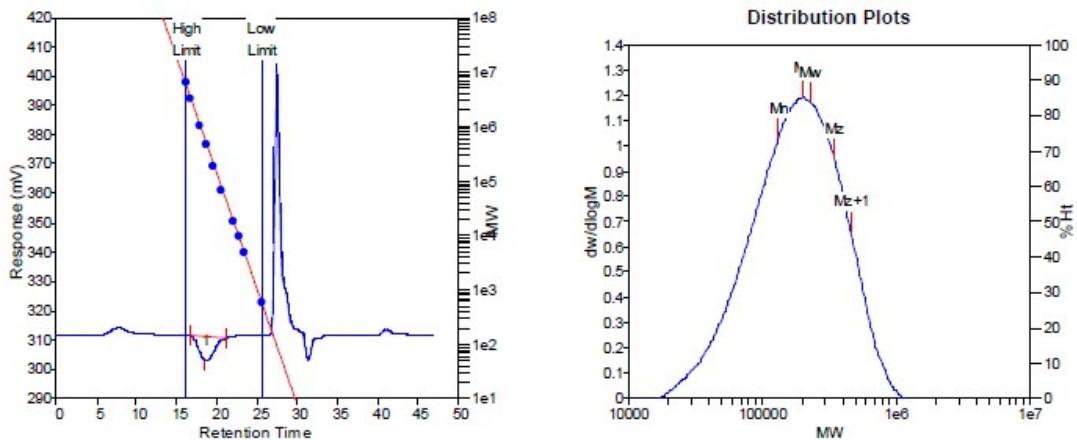
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	658835	398733	719576	1117235	1523680	671369	1.80466

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.48	17.32	20.07	-4.37125	100	526.051	100

Figure S52. GPC of the polyethylene produced by **Ni3/MAO** from table 2, entry 12.



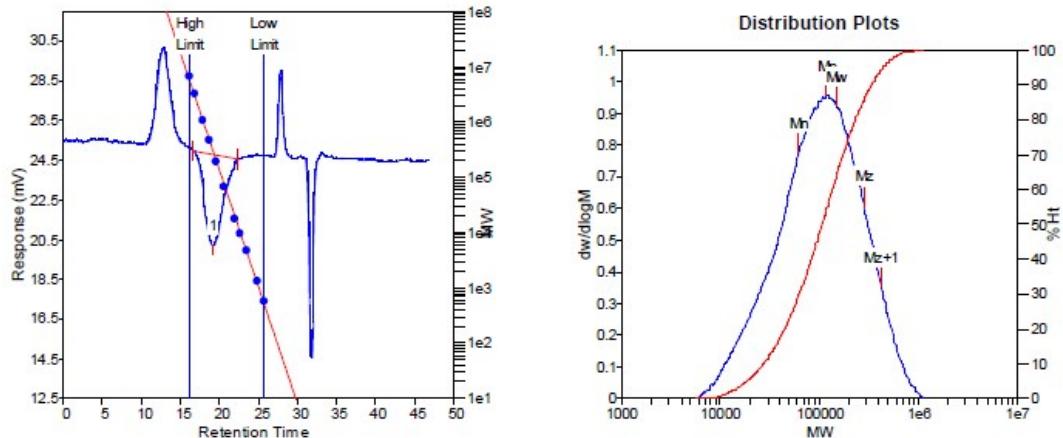
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	201867	132136	228382	345385	460394	213945	1.72839

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.73	18.57	21.18	-8.54767	100	1047.53	100

Figure S53. GPC of the polyethylene produced by **Ni3/MAO** from table 2, entry 13.



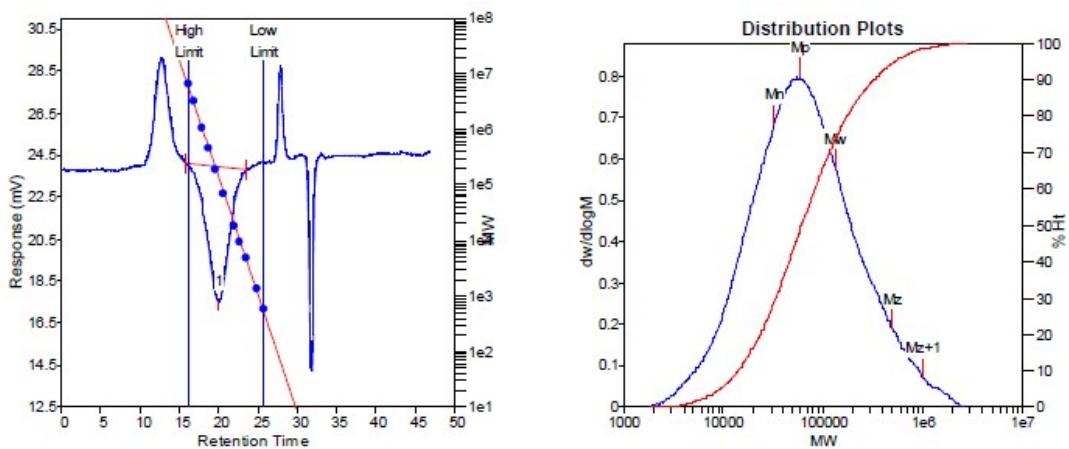
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	119398	62571	150230	282505	422792	135573	2.40095

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.77	19.17	22.42	-4.56855	100	699.215	100

Figure S54. GPC of the polyethylene produced by **Ni3/MAO** from table 2, entry 14.



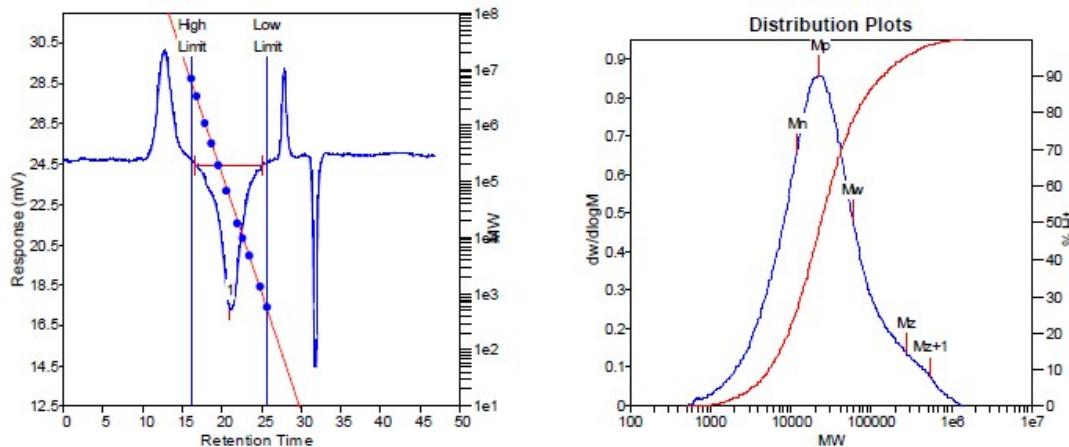
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	58914	32560	134227	492595	1005776	109408	4.12245

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.83	19.98	23.58	-6.40983	100	1179.24	100

Figure S55. GPC of the polyethylene produced by Ni4/MAO from table 2, entry 15.



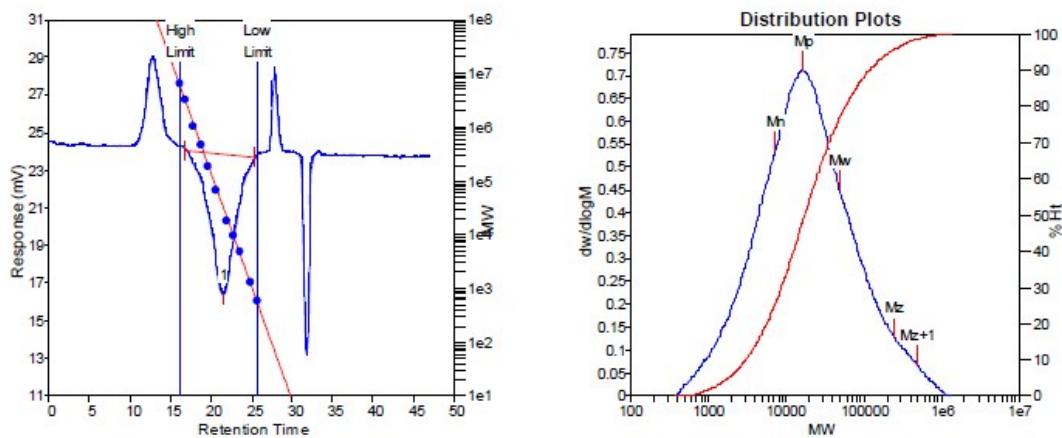
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	23070	11739	58842	270527	551671	45083	5.01252

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.77	21.07	25.07	-7.16128	0	1203.53	100

Figure S56. GPC of the polyethylene produced by Ni4/MAO from table 2, entry 16.



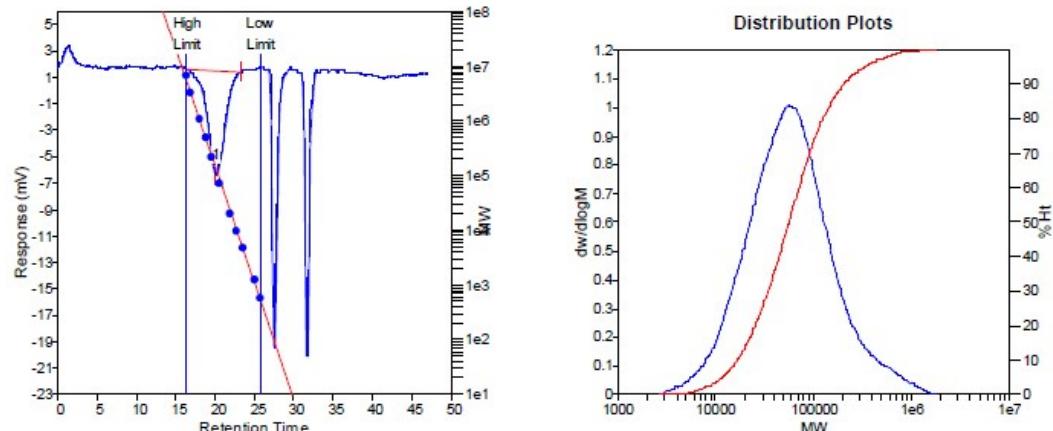
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	16511	7301	49084	243442	495055	36509	6.72291

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.83	21.42	25.35	-7.45979	100	1515.95	100

Figure S57. GPC of the polyethylene produced by Ni4/MAO from table 2, entry 17.



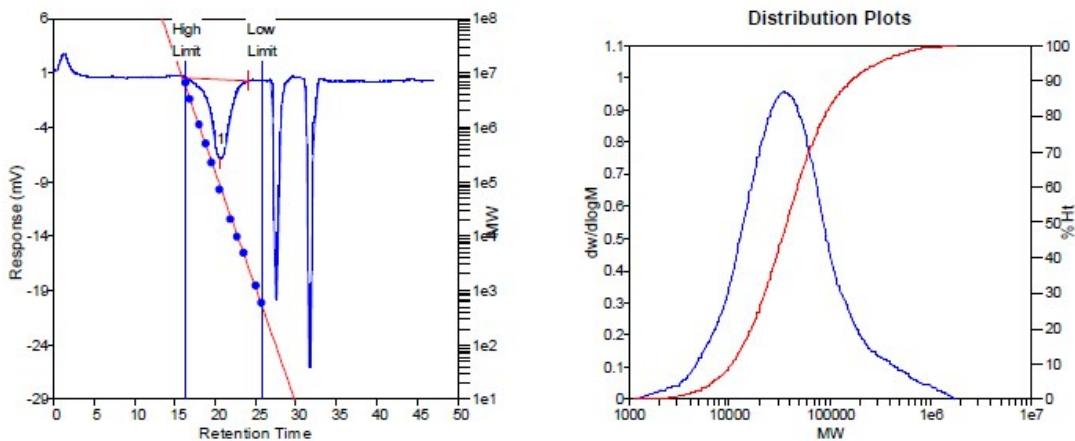
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	56158	35997	98272	300648	641970	84114	2.73001

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.37	20.03	23.22	-7.84957	100	1132.56	100

Figure S58. GPC of the polyethylene produced by Ni5/MAO from table 2, entry 18.



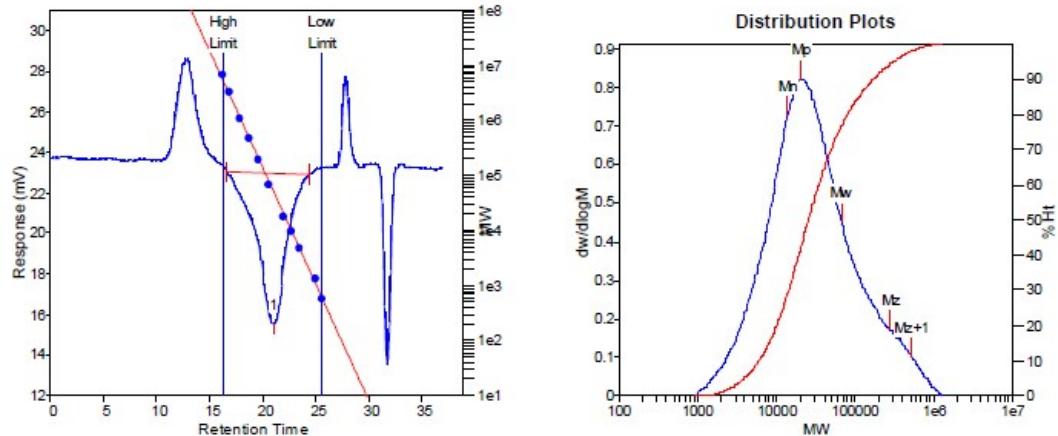
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	33804	22247	78526	337337	750662	63713	3.52973

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.42	20.57	24.15	-7.30727	100	1109.13	100

Figure S59. GPC of the polyethylene produced by Ni5/MAO from table 2, entry 19.



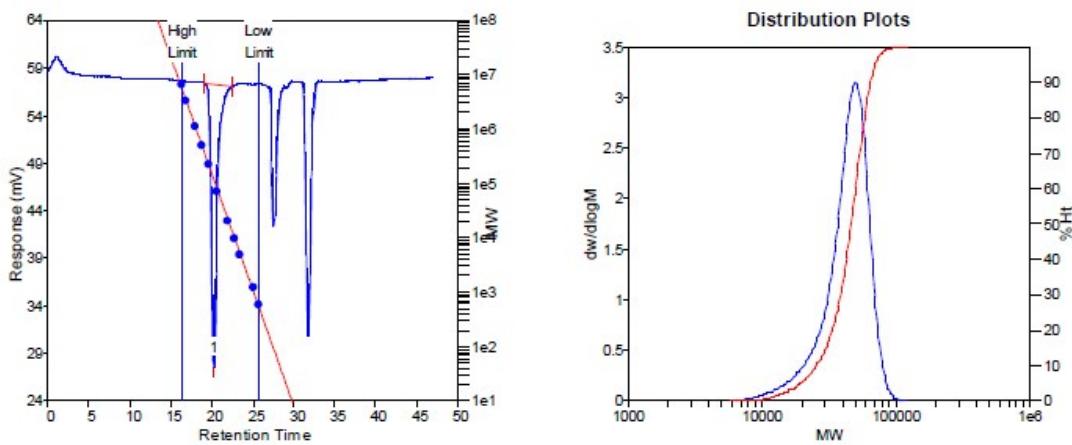
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	20260	13993	67394	284023	532154	52931	4.81627

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.67	21.05	24.35	-7.47258	100	1333.31	100

Figure S60. GPC of the polyethylene produced by Ni5/MAO from table 2, entry 20.



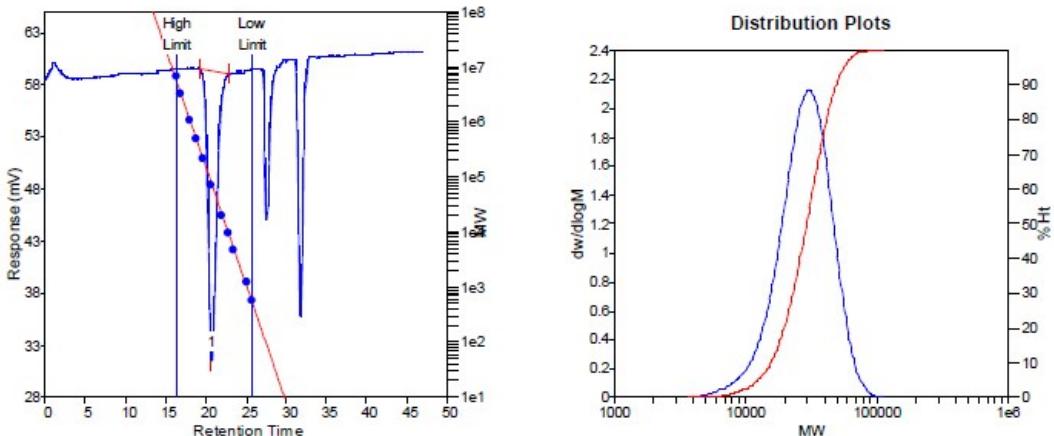
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	50257	38953	45659	50639	54687	44911	1.17216

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.22	20.15	22.40	-29.6714	0	1366.13	100

Figure S61. GPC of the poly(1-hexene) produced by Ni1/EASC from table 4, entry 1.



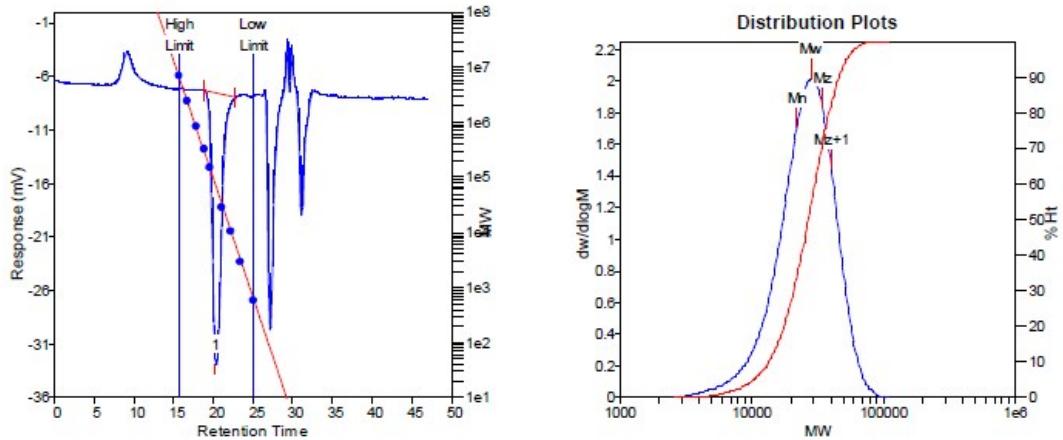
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	30251	24990	30919	36742	42556	30137	1.23725

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.32	20.68	22.90	-27.8387	100	1904.92	100

Figure S62. GPC of the poly(1-hexene) produced by Ni2/EASC from table 4, entry 2.



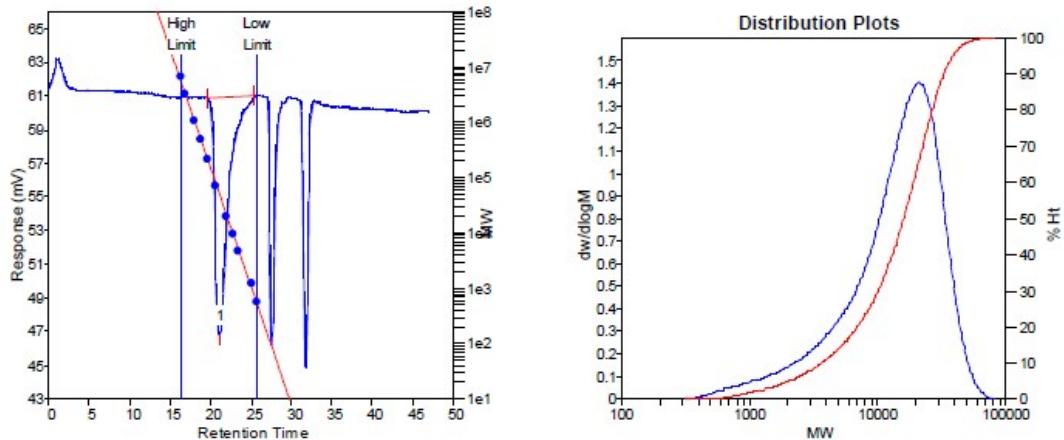
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	28504	22095	28521	34526	40391	27706	1.29084

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.87	20.27	22.75	-25.3371	100	1802.47	100

Figure S63. GPC of the poly(1-hexene) produced by Ni3/EASC from table 4, entry 3.



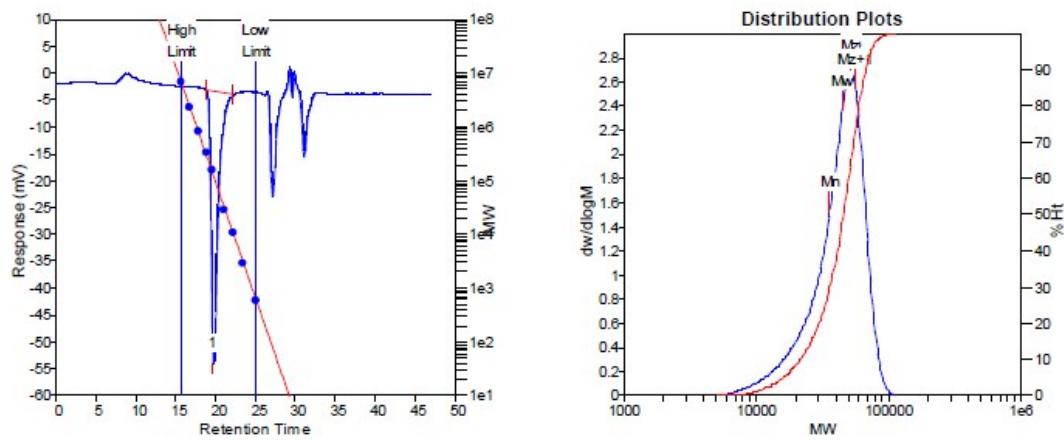
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	21004	7400	17393	24938	30850	16296	2.35041

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.63	21.07	25.48	-14.1266	100	1461.68	100

Figure S64. GPC of the poly(1-hexene) produced by Ni4/EASC from table 4, entry 4.



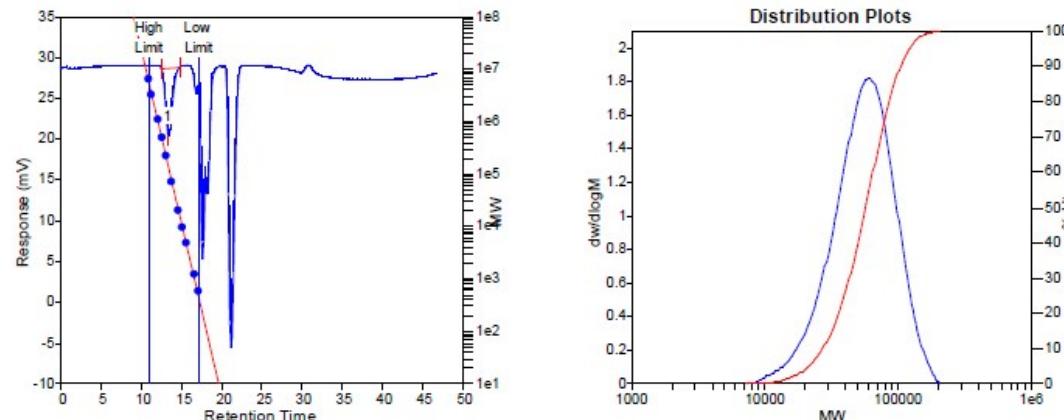
MW Averages

Peak No	M_p	M_n	M_w	M_z	M_{z+1}	M_v	PD
1	52447	36141	44989	51505	56518	44002	1.24482

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.83	19.63	22.07	-50.6238	0	2716.78	100

Figure S65. GPC of the poly(1-octene) produced by Ni2/EASC from table 4, entry 6.



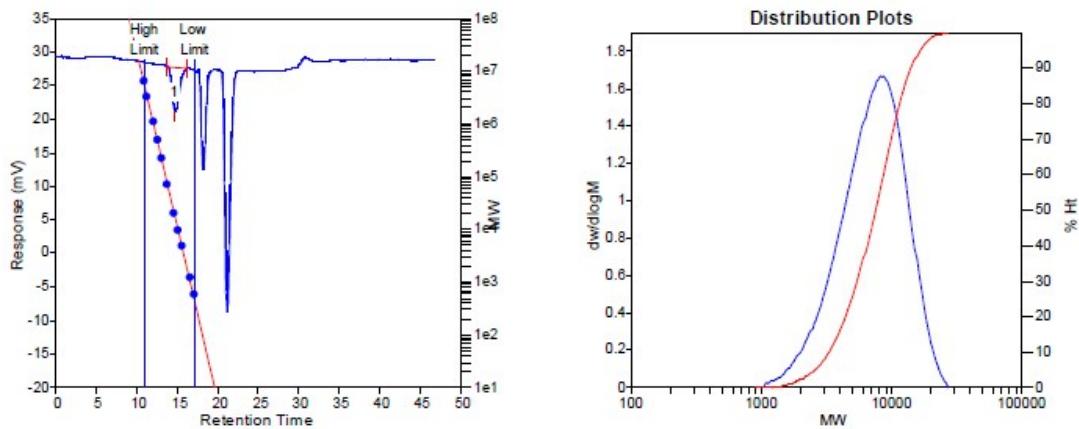
MW Averages

Peak No	M_p	M_n	M_w	M_z	M_{z+1}	M_v	PD
1	61876	46521	61356	76579	91544	59342	1.31889

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.55	13.37	14.82	-8.14968	100	418.152	100

Figure S66. GPC of the poly(1-octadecene) produced by Ni2/EASC from table 4, entry 7.



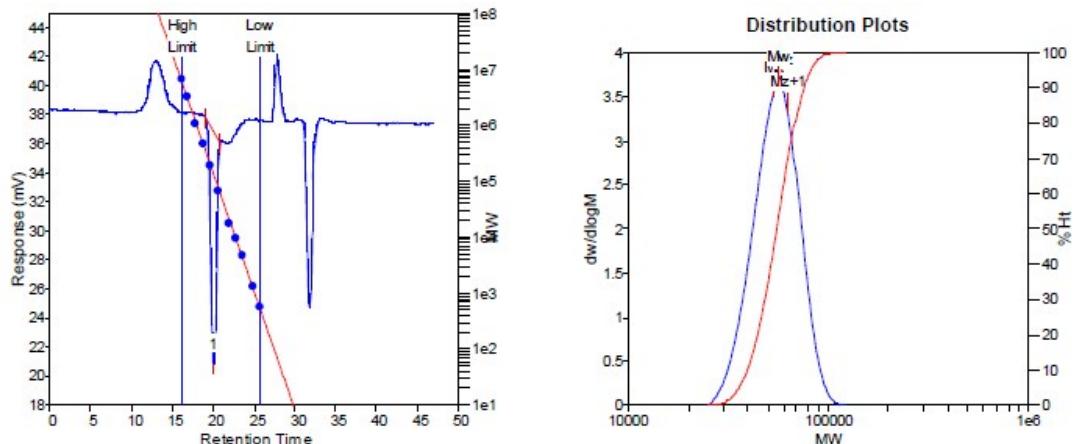
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8217	5925	8127	10352	12433	7829	1.37165

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.92	14.73	16.22	-6.53463	100	366.765	100

Figure S67. GPC of the poly(1-octadecene) produced by Ni2/EASC from table 4, entry 8.



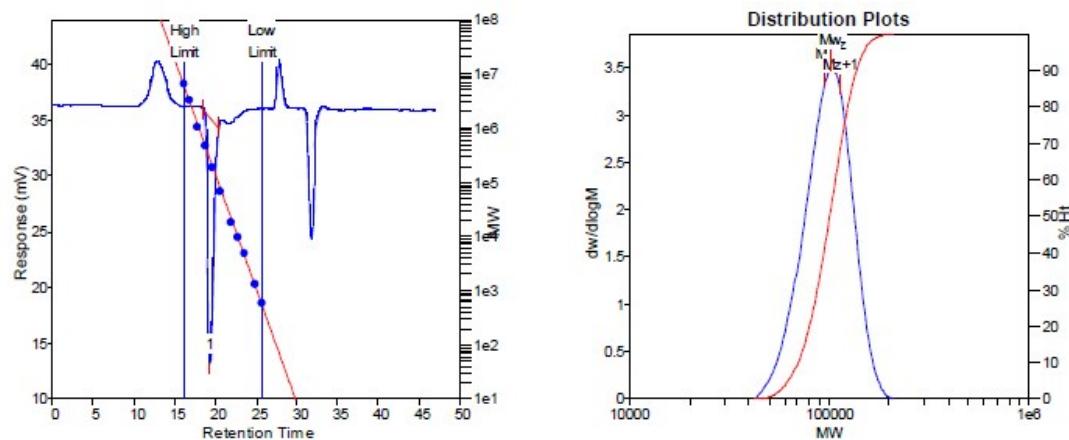
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	57093	53078	56431	59819	63187	55970	1.06317

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.15	19.95	20.82	-16.0973	0	650.556	100

Figure S68. GPC spectra of the polyethylene produced by **Ni2/Et₂AlCl** at 25 °C for 20 mim (table s1, entry 1).



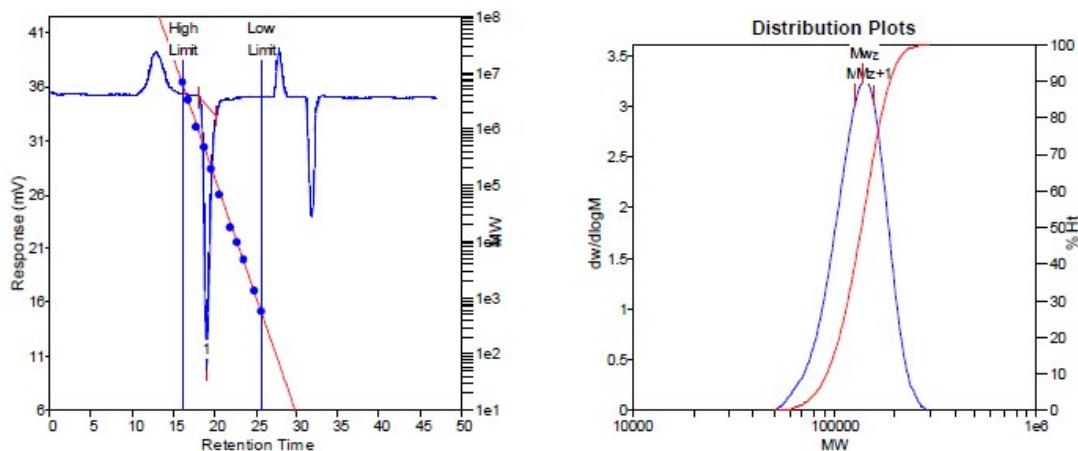
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	103667	95134	101763	108366	114835	100859	1.06968

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.55	19.32	20.27	-22.0008	100	923.526	100

Figure S69. GPC spectra of the polyethylene produced by **Ni2/Et₂AlCl** at 25 °C for 40 mim (table s1, entry 2).



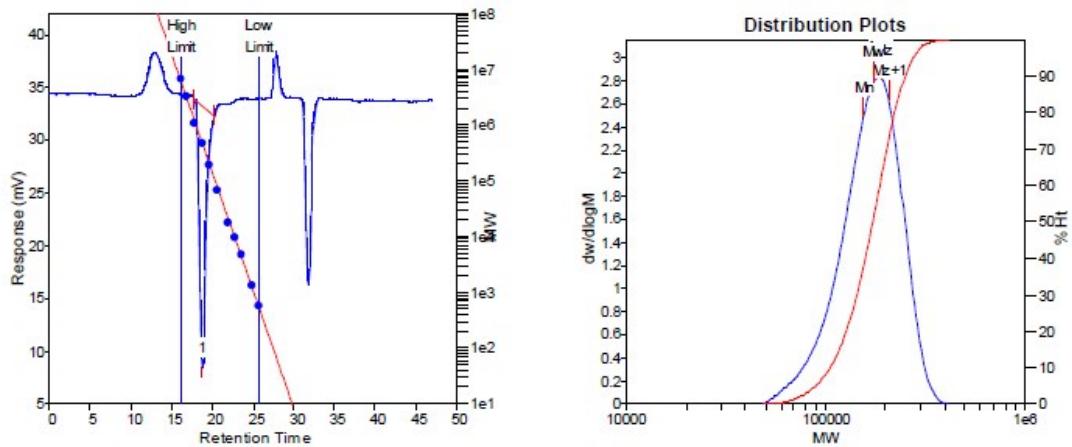
MW Averages

Peak No	M _p	M _n	M _w	M _z	M _{z+1}	M _v	PD
1	141902	127535	138155	148506	158427	136727	1.08327

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.22	18.98	20.07	-24.5334	100	1107.18	100

Figure S70. GPC spectra of the polyethylene produced by Ni₂/Et₂AlCl at 25 °C for 60 min (table s1, entry 3).



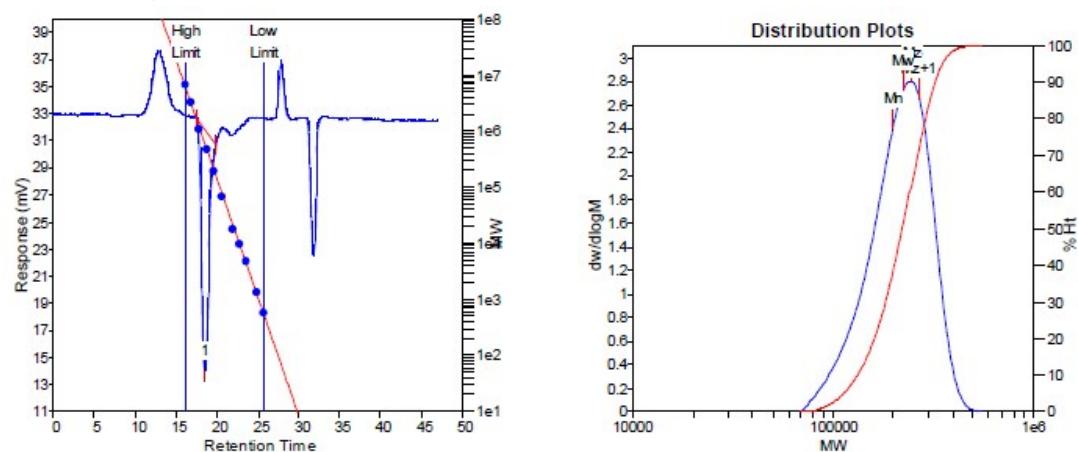
MW Averages

Peak No	M _p	M _n	M _w	M _z	M _{z+1}	M _v	PD
1	185303	156200	175259	192874	208974	172785	1.12202

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.85	18.70	20.12	-24.803	100	1284.14	100

Figure S71. GPC spectra of the polyethylene produced by **Ni2/Et₂AlCl** at 25 °C for 80 mim (table s1, entry 4).



MW Averages

Peak No	M _p	M _n	M _w	M _z	M _{z+1}	M _v	PD
1	245807	200052	224760	247706	268530	221536	1.12351

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.53	18.42	19.75	-17.9189	100	940.356	100

Figure S72. GPC spectra of the polyethylene produced by **Ni2/Et₂AlCl** at 25 °C for 100 mim (table s1, entry 5).

5. DSC Spectra of polymers

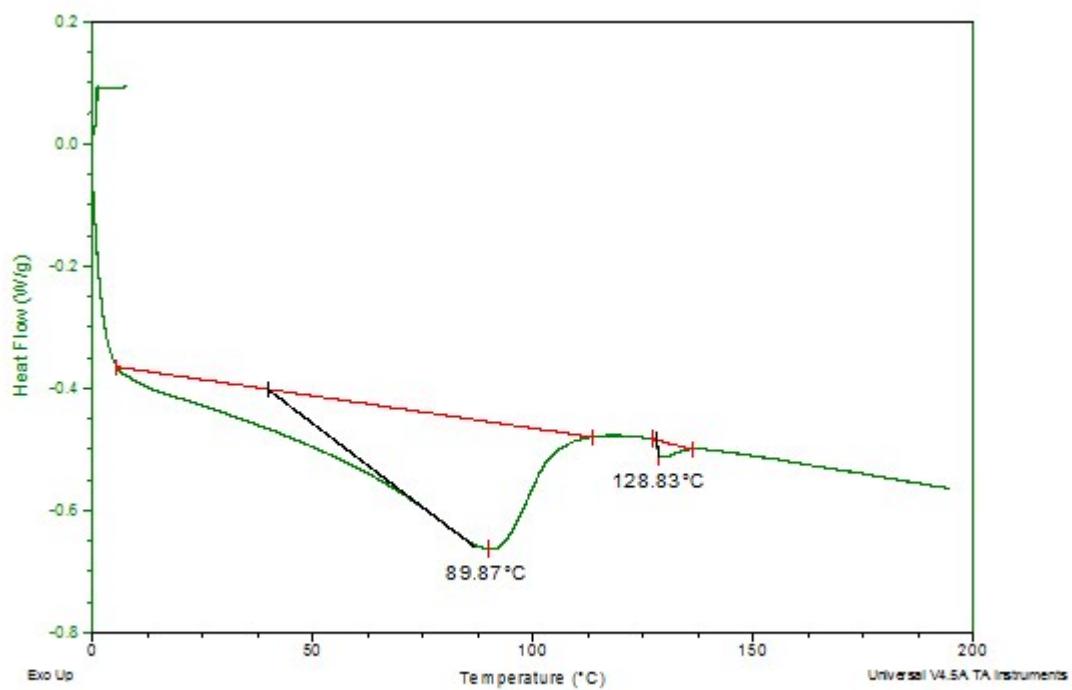


Figure S73. DSC spectra of the polyethylene produced by **Ni2/MAO** from table 1, entry 1.

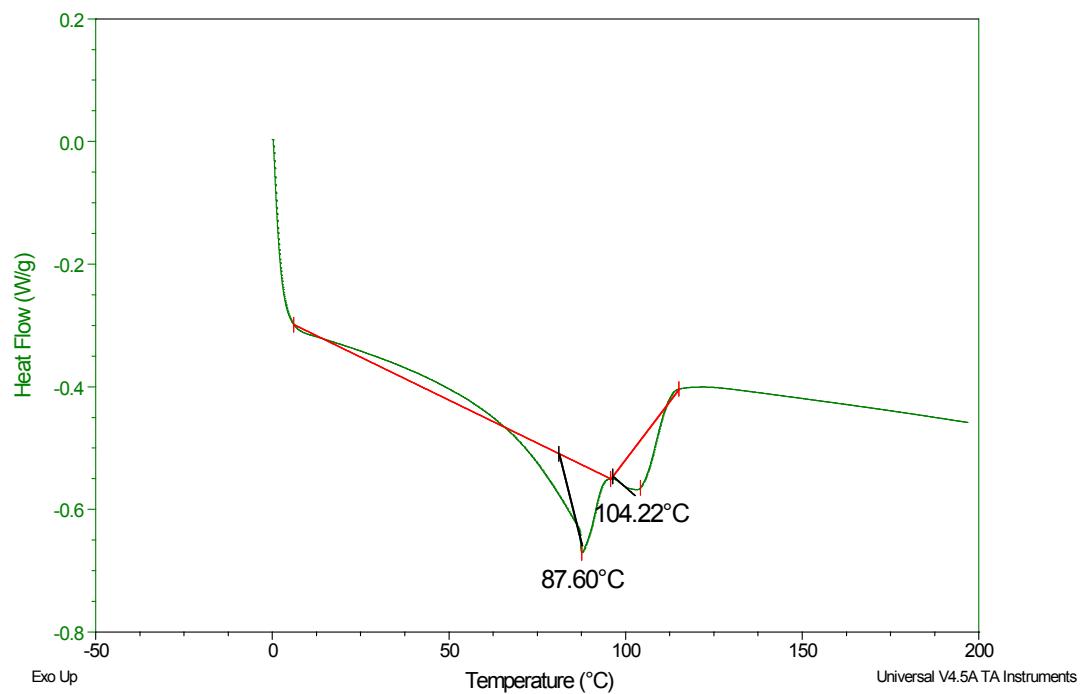


Figure S74. DSC spectra of the polyethylene produced by **Ni2/MMAO** from table 1, entry 2.

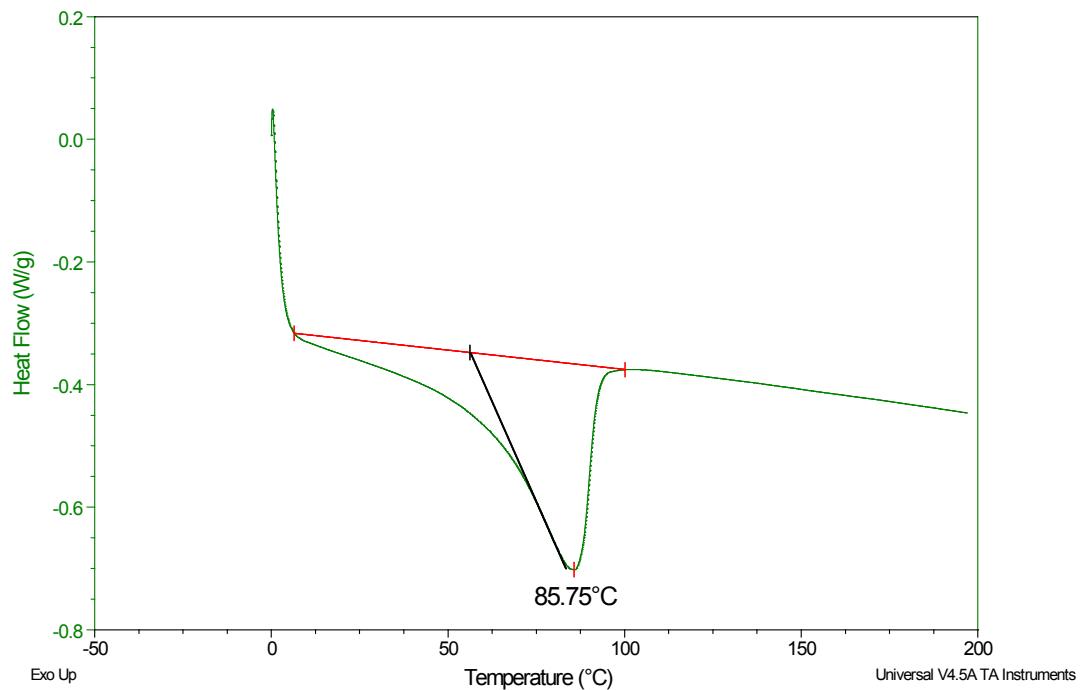


Figure S75. DSC spectra of the polyethylene produced by **Ni2/Et₂AlCl** from table 1, entry 3.

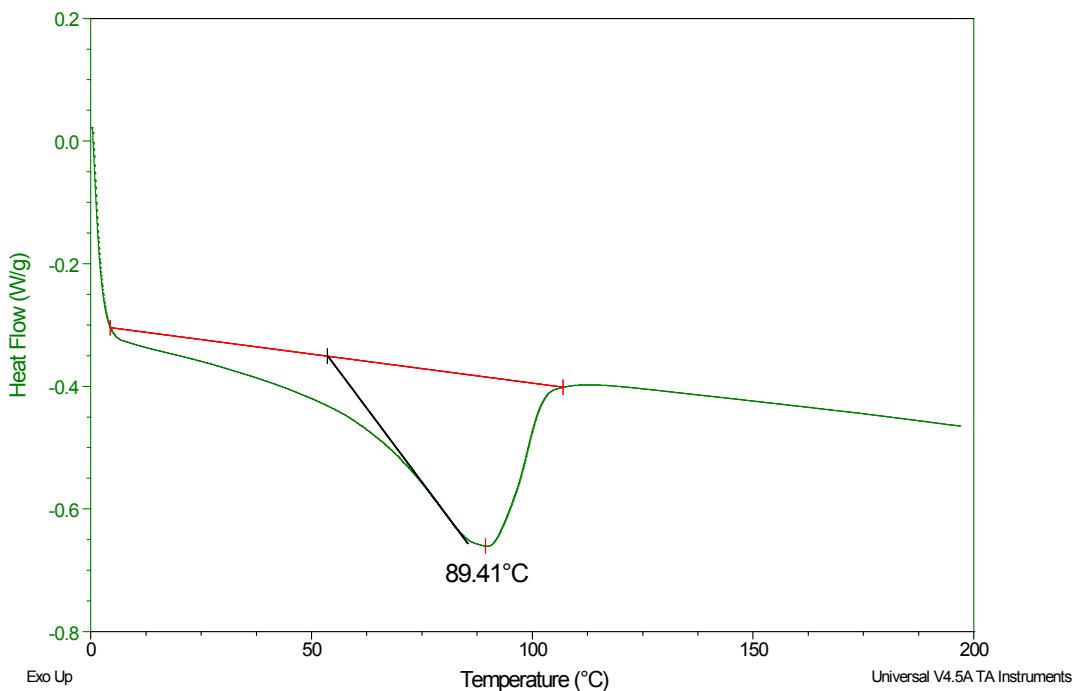


Figure S76. DSC spectra of the polyethylene produced by **Ni2/EASC** from table 1, entry 4.

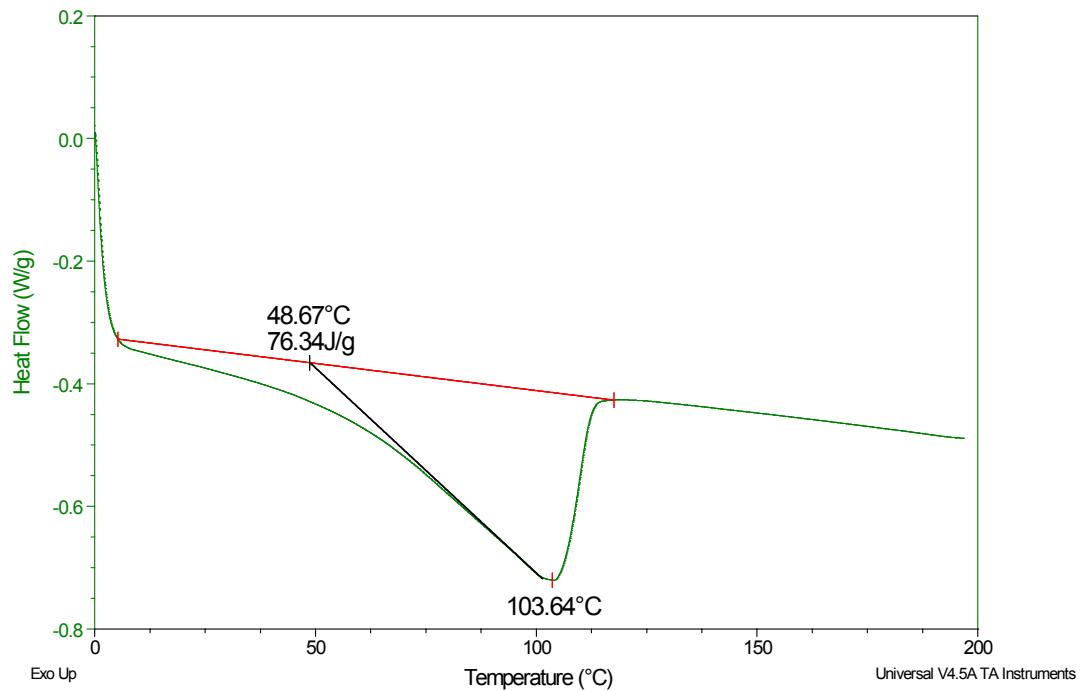


Figure S77. DSC spectra of the polyethylene produced by **Ni1/MAO** from table 2, entry 1.

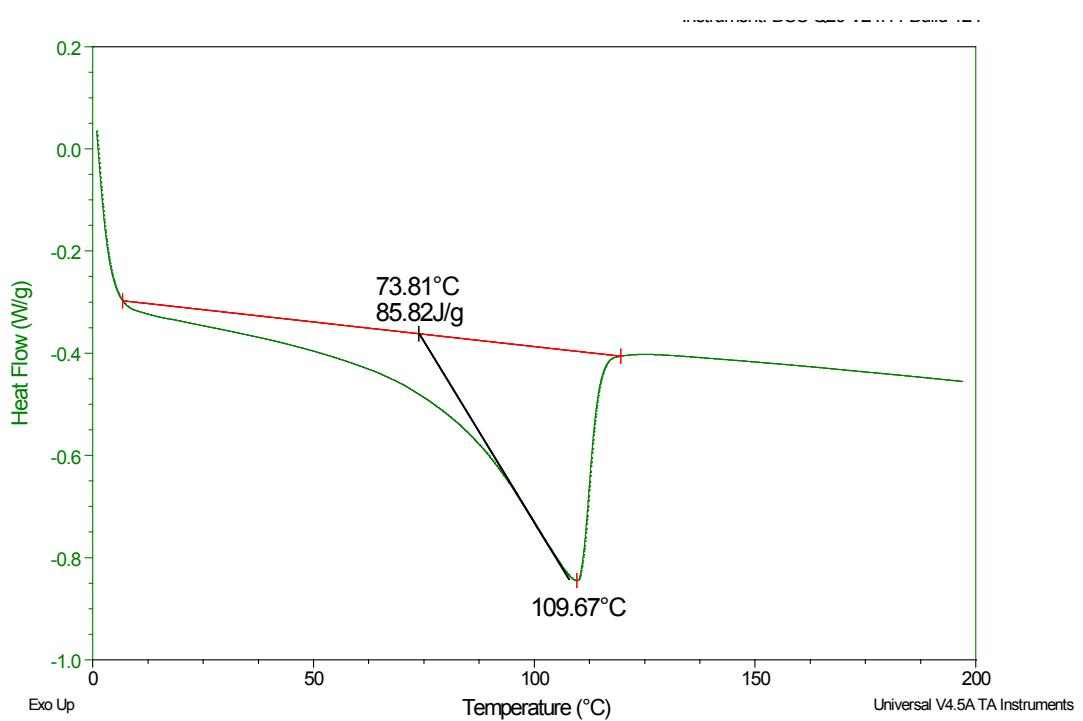


Figure S78. DSC spectra of the polyethylene produced by **Ni3/MAO** from table 2, entry 3.

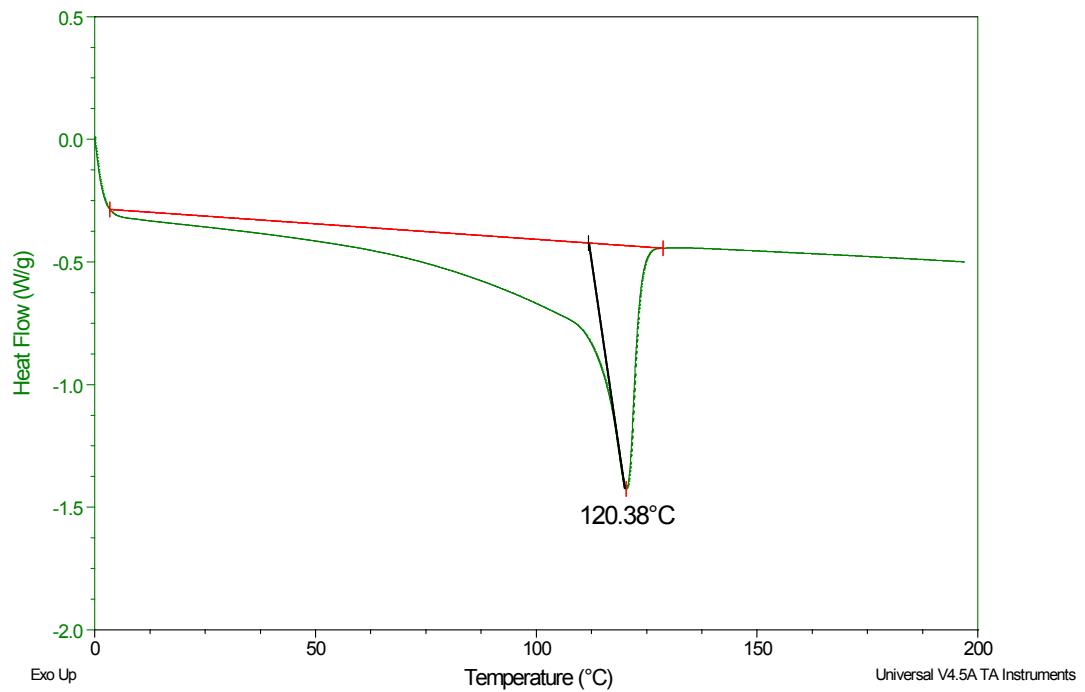


Figure S79. DSC spectra of the polyethylene produced by **Ni4/MAO** from table 2, entry 4.

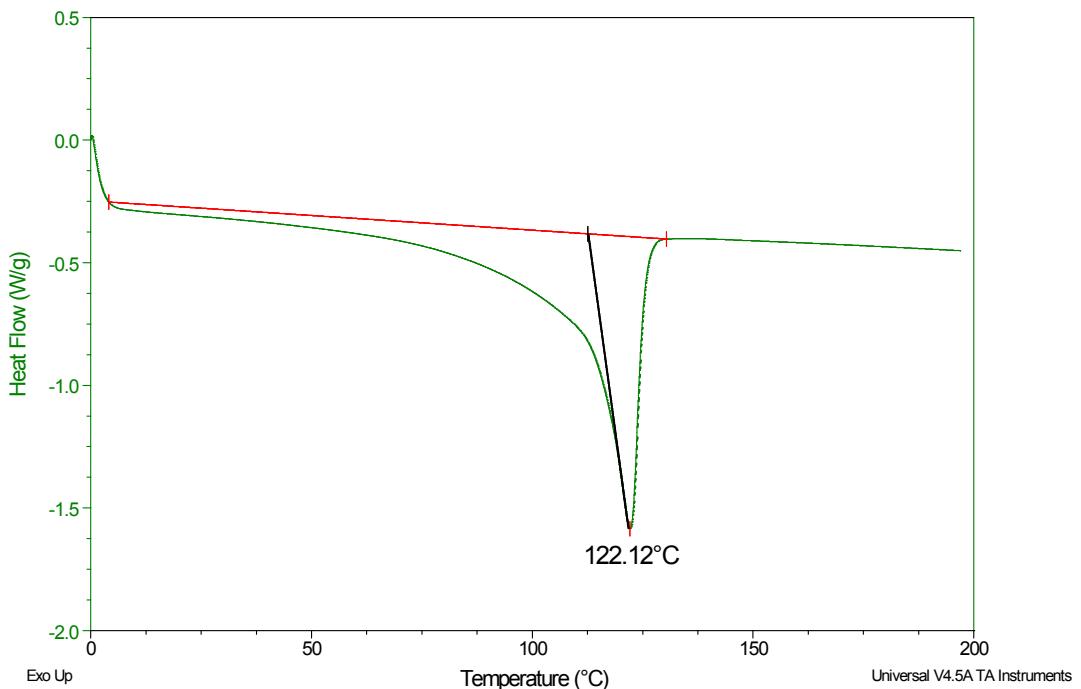


Figure S80. DSC spectra of the polyethylene produced by **Ni5/MAO** from table 2, entry 5.

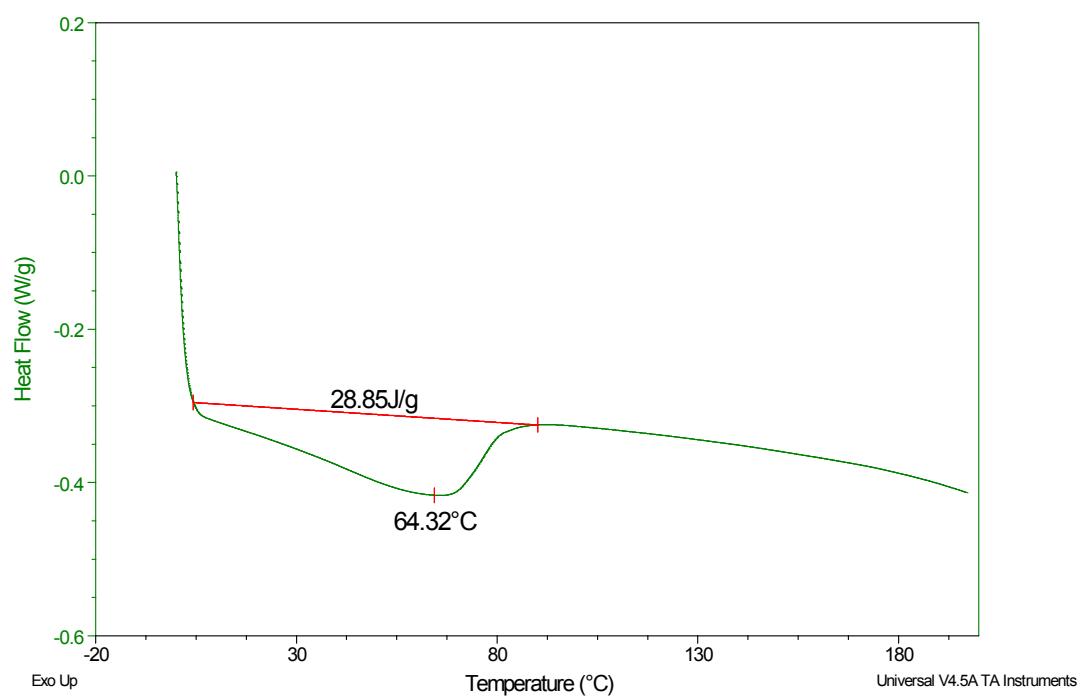


Figure S81. DSC spectra of the polyethylene produced by **Ni1/MAO** from table 2, entry 6.

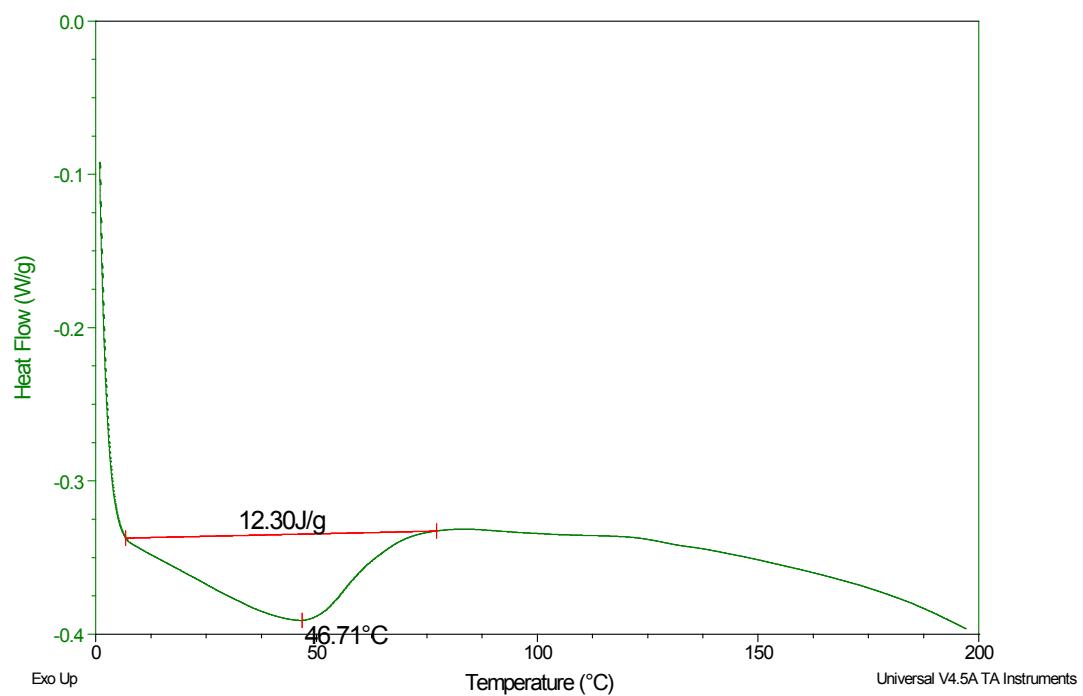


Figure S82. DSC spectra of the polyethylene produced by **Ni1/MAO** from table 2, entry 7.

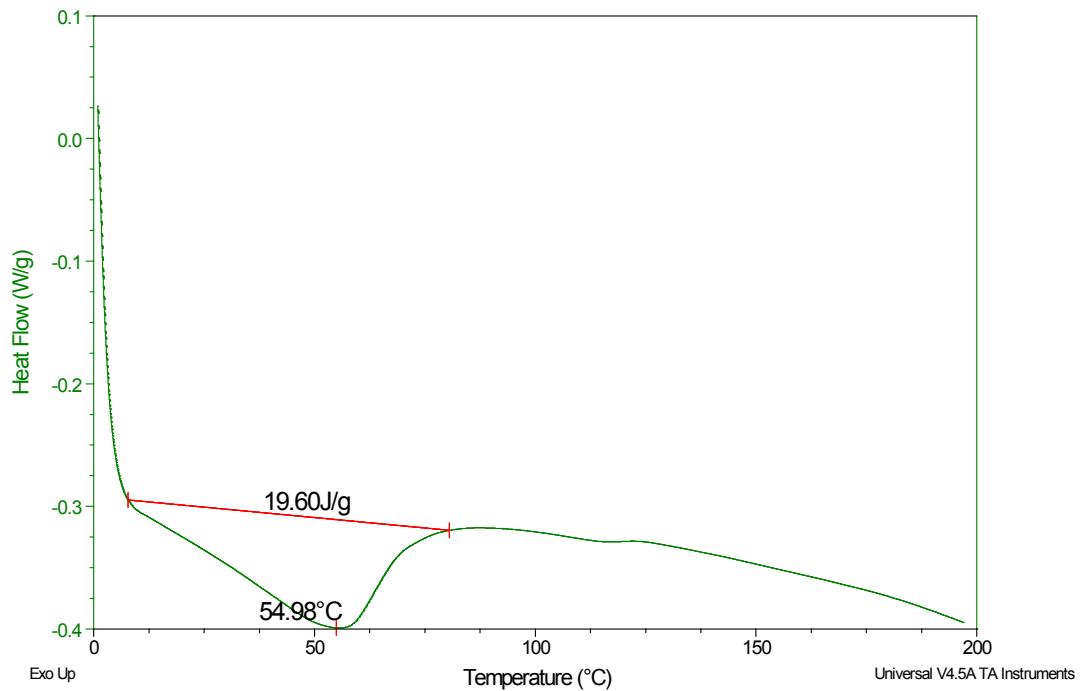


Figure S83. DSC spectra of the polyethylene produced by **Ni2/MAO** from table 2, entry 9.

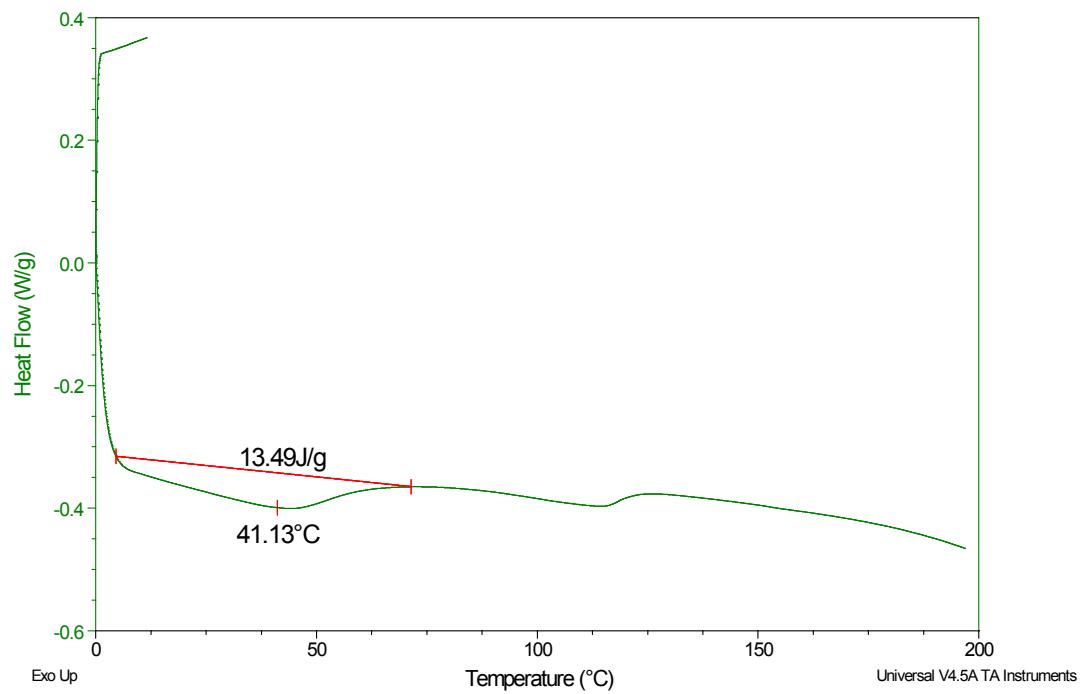


Figure S84. DSC spectra of the polyethylene produced by **Ni2/MAO** from table 2, entry 10.

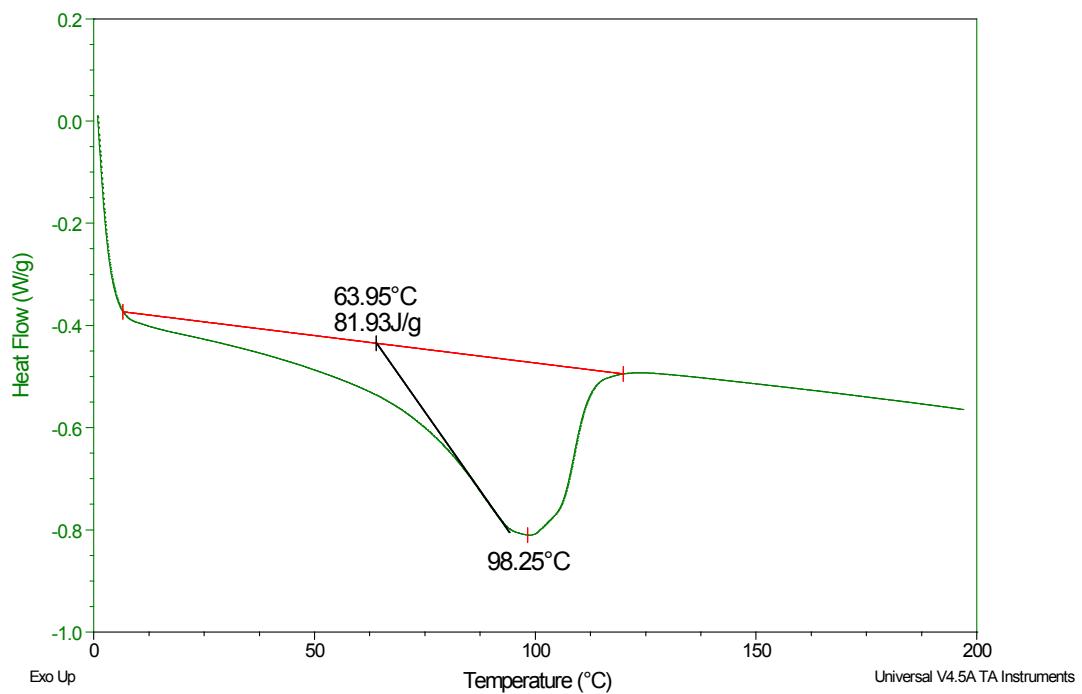


Figure S85. DSC spectra of the polyethylene produced by **Ni3/MAO** from table 2, entry 12.

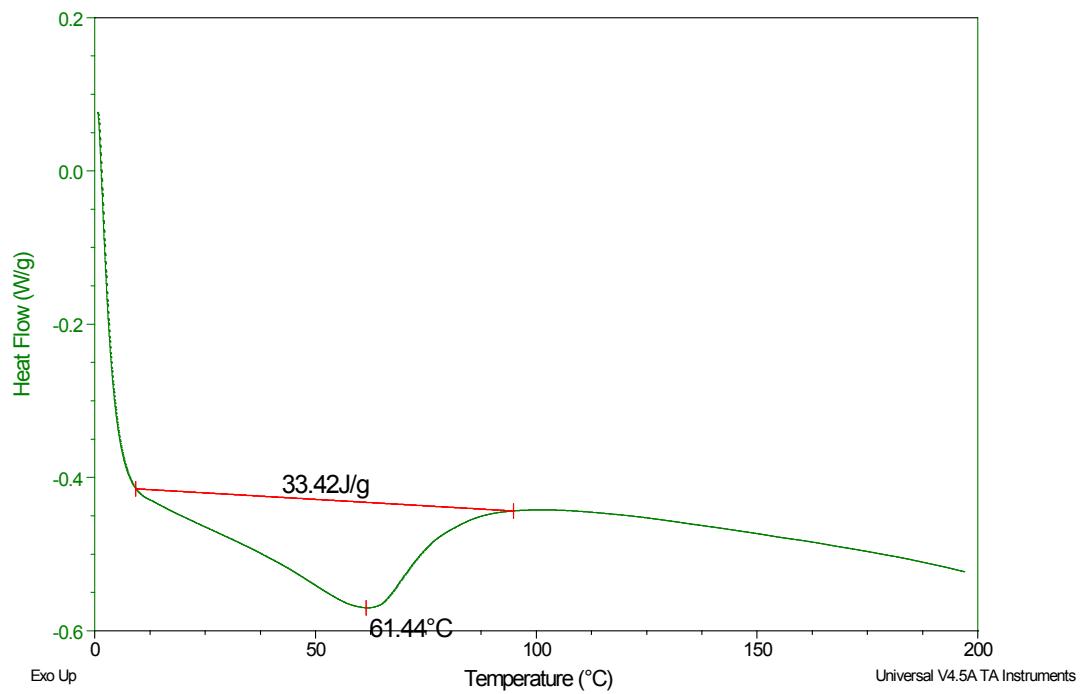


Figure S86. DSC spectra of the polyethylene produced by **Ni3/MAO** from table 2, entry 13.

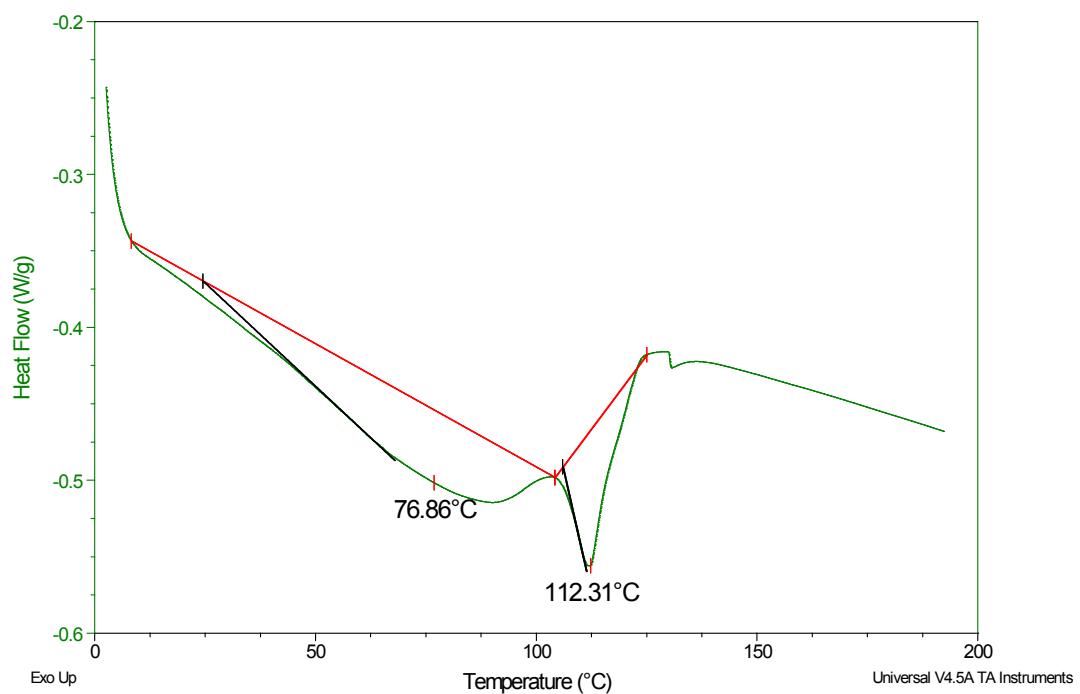


Figure S87. DSC spectra of the polyethylene produced by **Ni3/MAO** from table 2, entry 14.

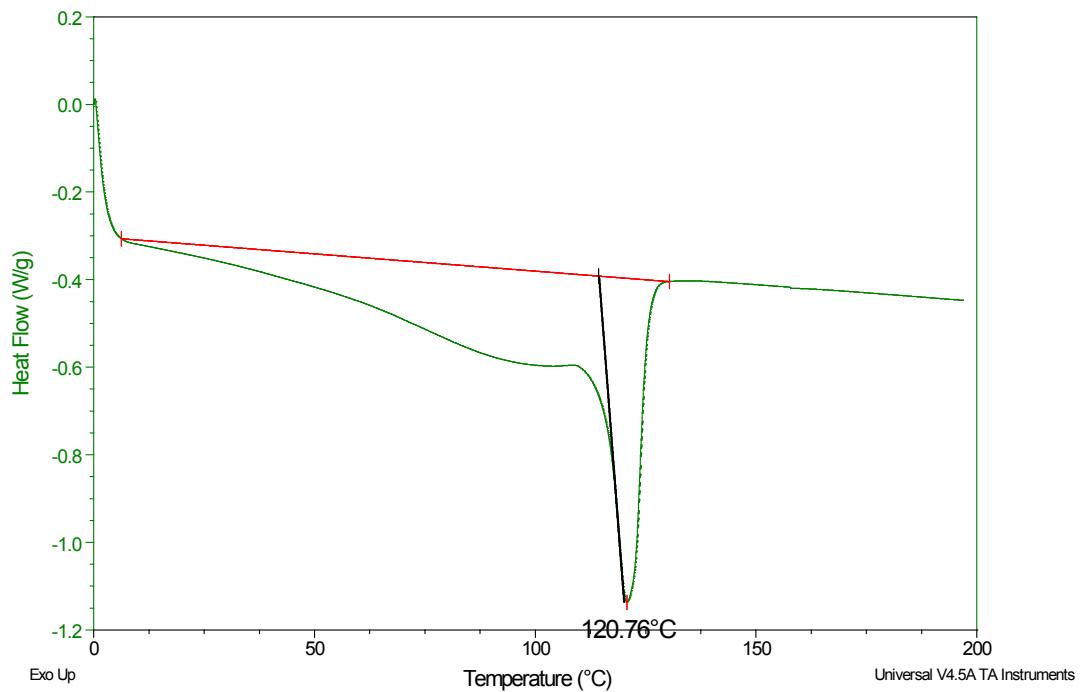


Figure S88. DSC spectra of the polyethylene produced by **Ni4/MAO** from table 2, entry 15.

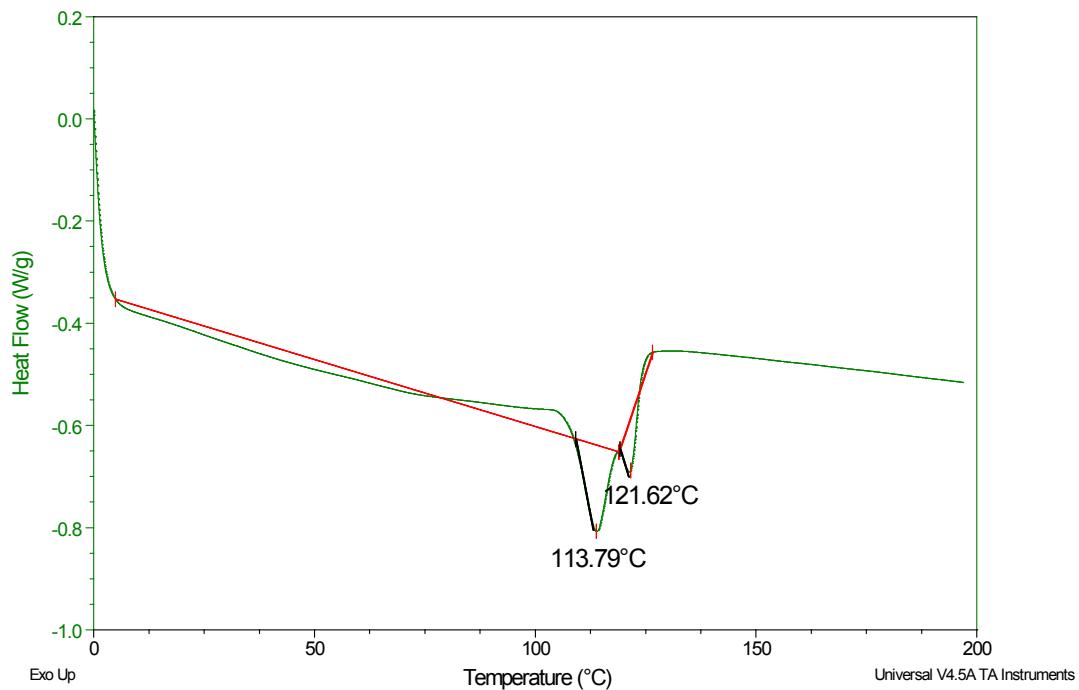


Figure S89. DSC spectra of the polyethylene produced by **Ni4/MAO** from table 2, entry 16.

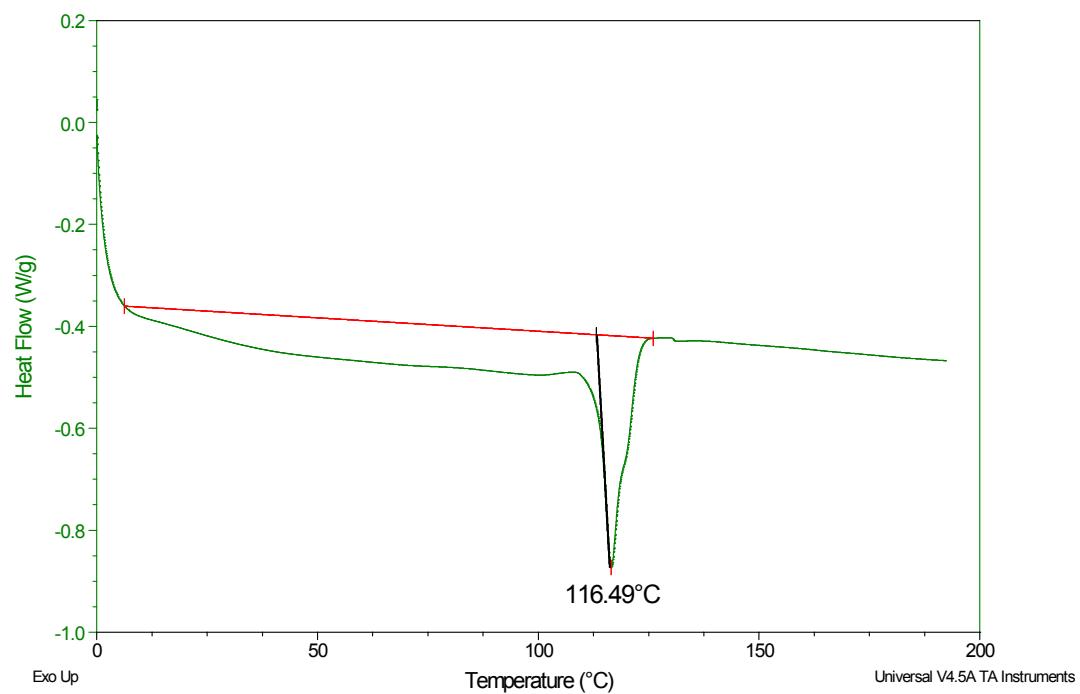


Figure S90. DSC spectra of the polyethylene produced by **Ni4/MAO** from table 2, entry 17.

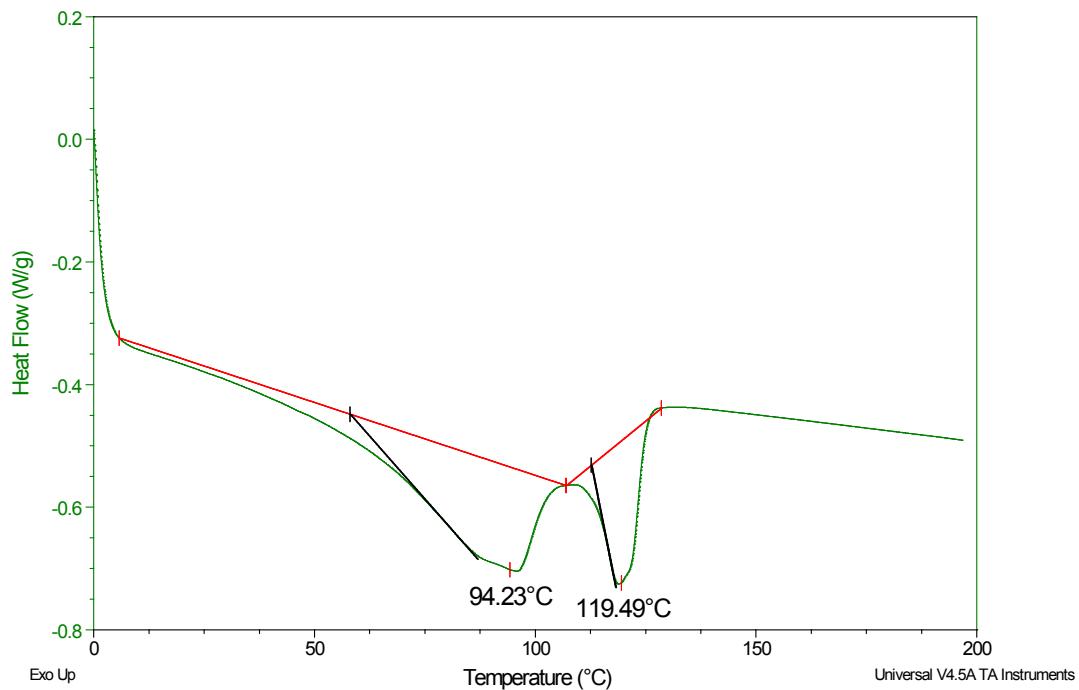


Figure S91. DSC spectra of the polyethylene produced by **Ni5/MAO** from table 2, entry 18.

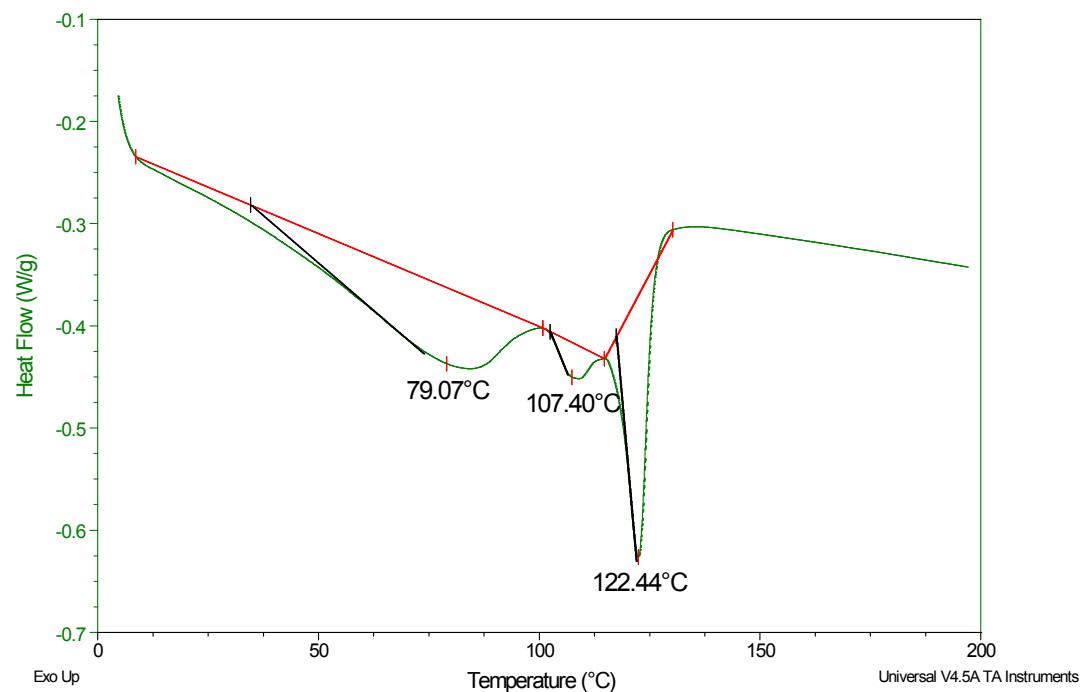


Figure S92. DSC spectra of the polyethylene produced by **Ni5/MAO** from table 2, entry 19.

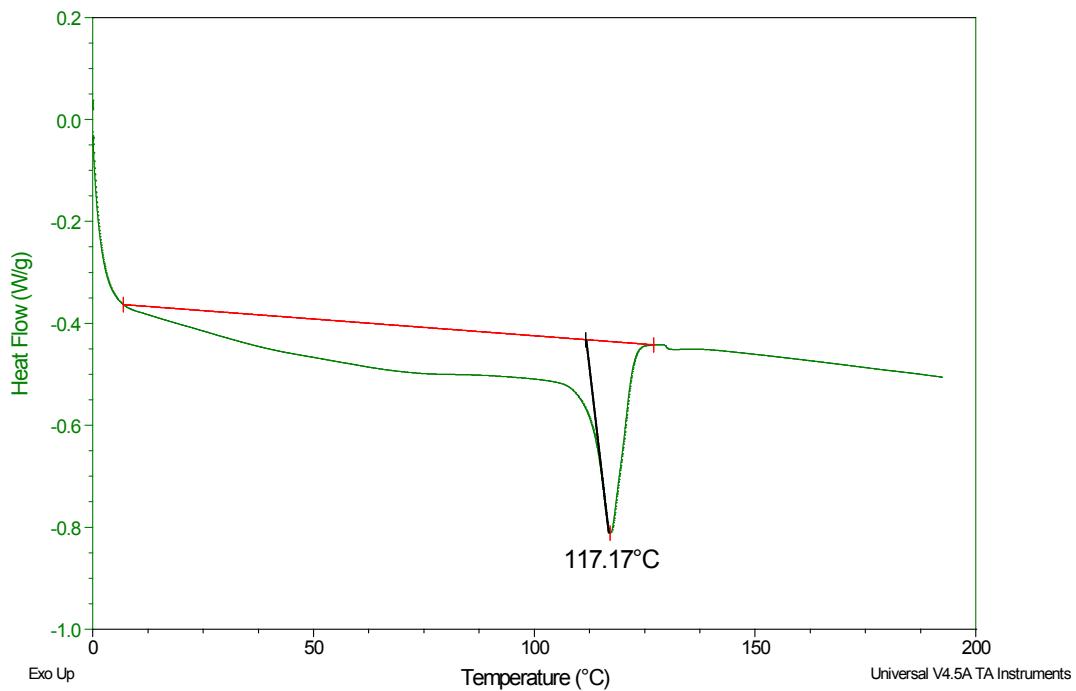


Figure S93. DSC spectra of the polyethylene produced by **Ni5/MAO** from table 2, entry 20.

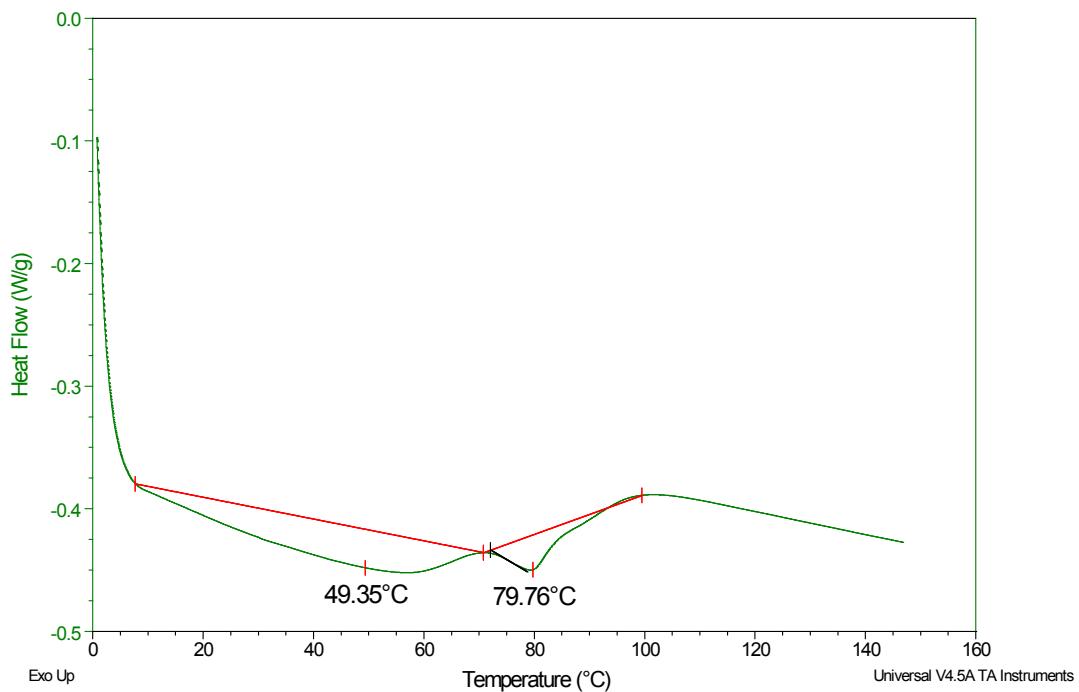


Figure S94. DSC spectra of the poly(1-hexene) produced by **Ni2/EASC** from table 4, entry 2.

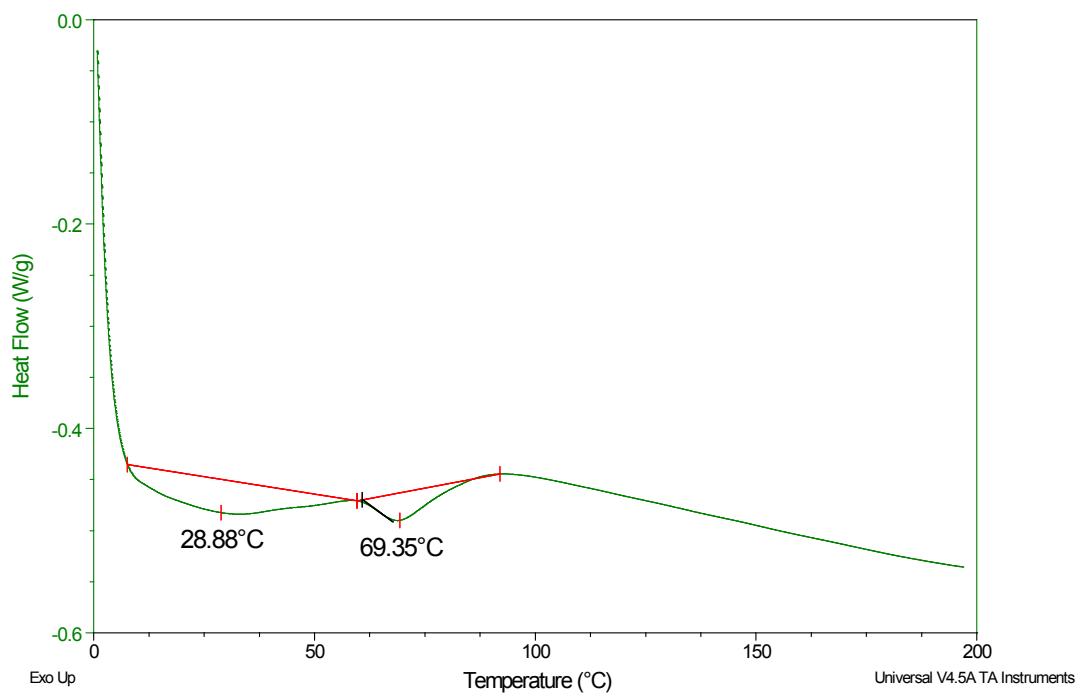


Figure S95. DSC spectra of the poly(1-hexene) produced by **Ni3/EASC** from table 4, entry 3.

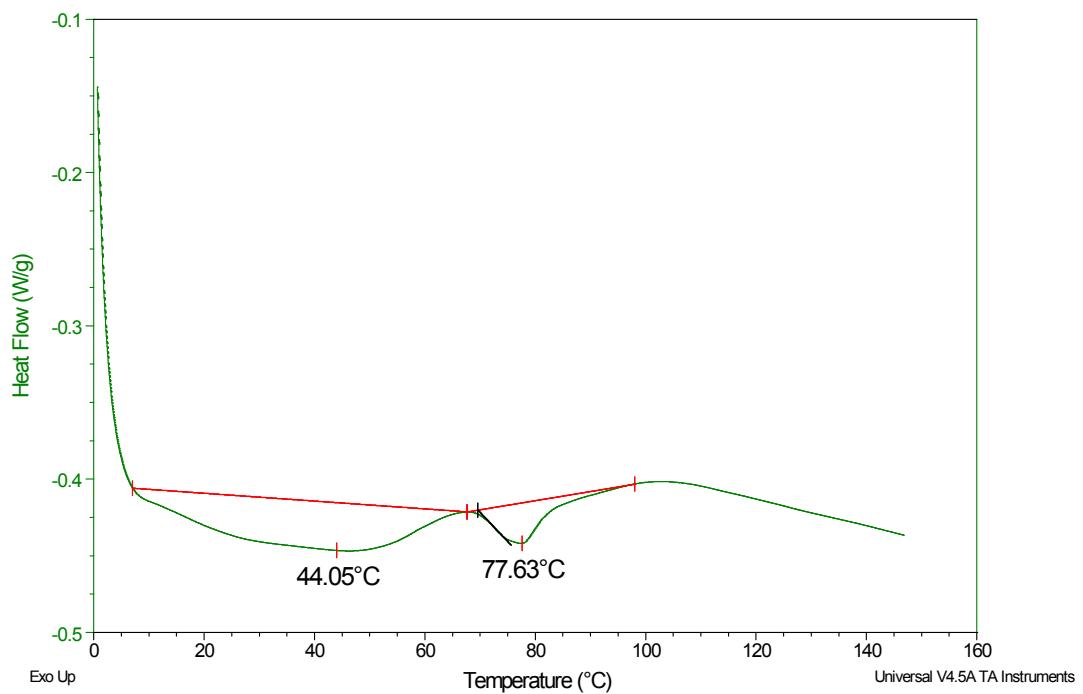


Figure S96. DSC spectra of the poly(1-hexene) produced by **Ni4/EASC** from table 4, entry 4.

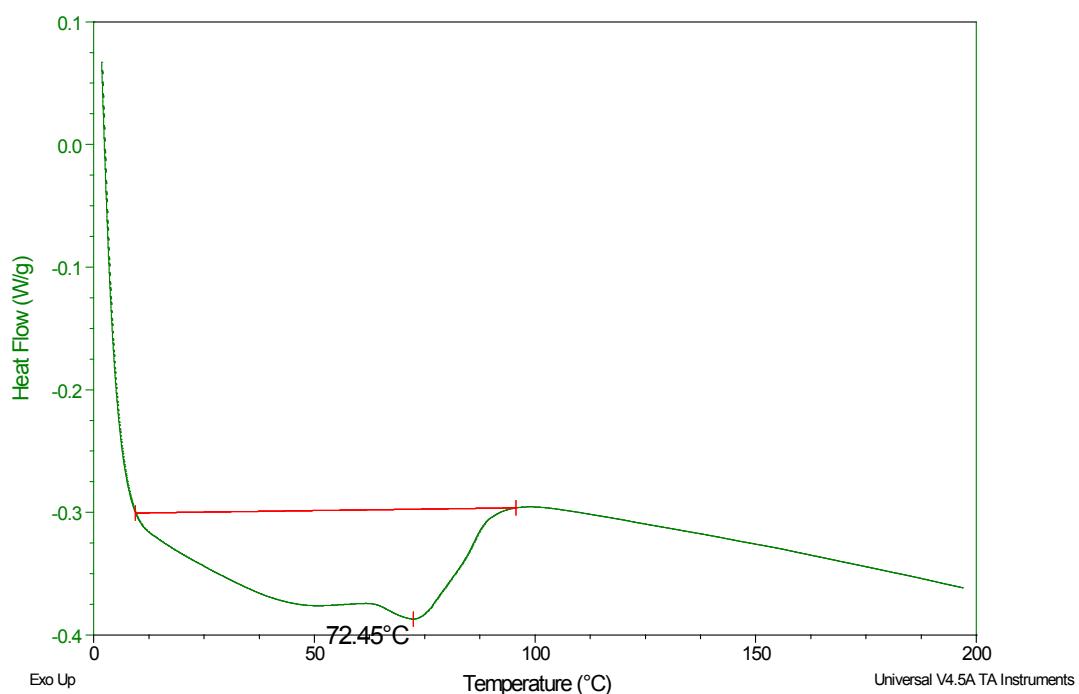


Figure S97. DSC spectra of the poly(1-octene) produced by Ni2/EASC from table 4, entry 6.

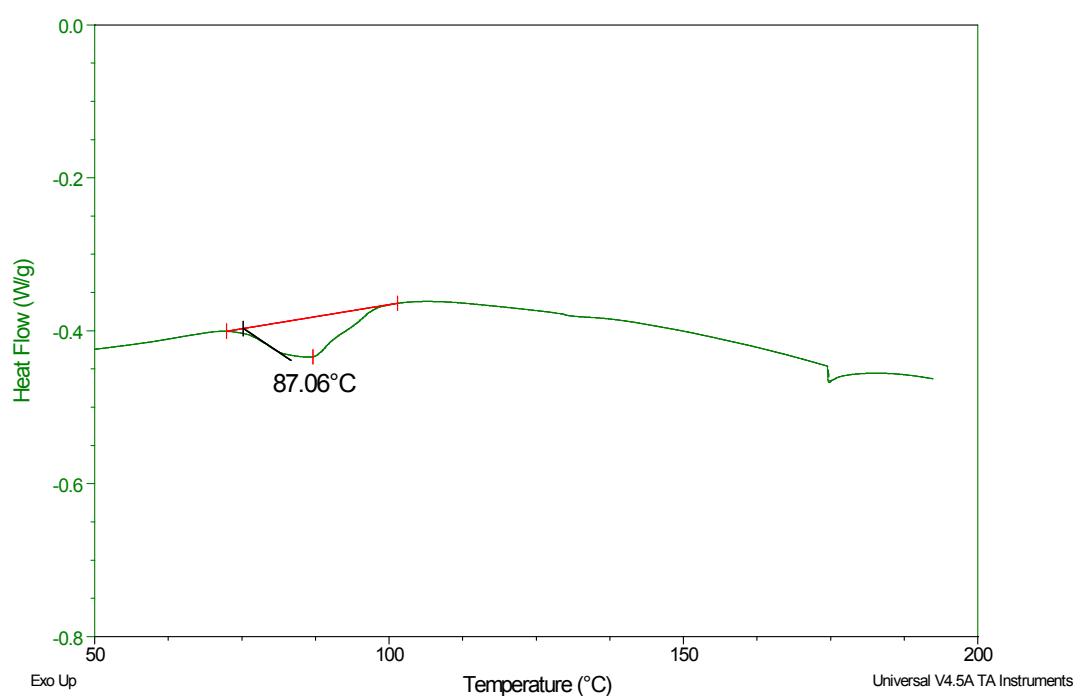


Figure S98. DSC spectra of the poly(1-octadecene) produced by Ni2/EASC from table 4, entry 7.

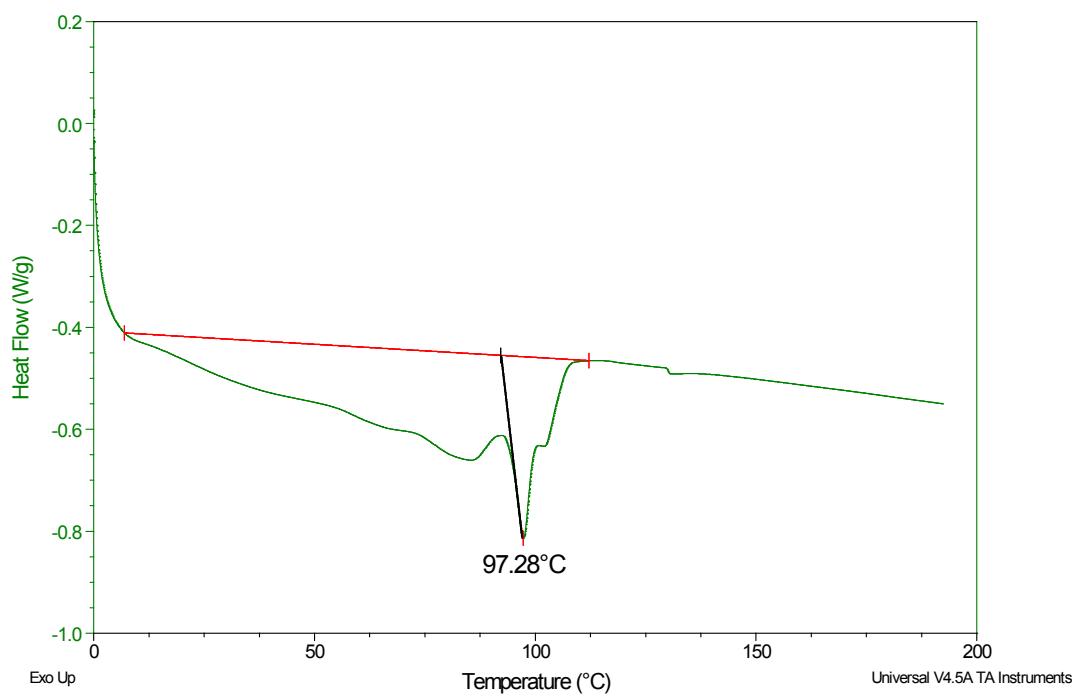


Figure S99. DSC spectra of the poly(1-octadecene) produced by **Ni2/EASC** from table 4, entry 8.

6. Crystallographic data for complexes Ni1 and Ni4.

Table S3. Crystallographic data for complexes Ni1 and Ni4.

	Ni1	Ni4
Formula	C ₄₆ H ₄₀ Br ₂ N ₂ Ni	C ₄₄ H ₂₄ Br ₂ F ₁₂ N ₂ Ni
Formula weight	839.33	1027.18
Temperature	210(2) K	191(2) K
Wavelength	1.54178 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
space group	P2(1)/c	P2(1)/c
a (Å)	11.2778(4)	14.785(2)
b (Å)	22.0014(7)	18.646(3)
c (Å)	17.4636(5)	17.519(2)
α (deg)	90	90
β (deg)	99.651(2)	107.516(3)
γ (deg)	90	90
Volume(Å ³)	4271.9(2)	4605.8(11)
Z	4	4
Calculated density (Mg/cm ³)	1.305	1.481
Absorption coefficient (mm ⁻¹)	3.078	2.236
F(000)	1712	2032
Crystal size (mm)	0.190 × 0.150 × 0.090	0.21 × 0.19 × 0.12
θ range (deg)	3.259 to 50.000 -11≤h≤11 -21≤k≤21 -17≤l≤17	1.44 to 26.41 -9≤h≤18 -23≤k≤23 -21≤l≤21
Limiting indices		
Reflections collected	34155	25862
Independent reflections	4351 [R(int) = 0.0929]	9363 [R(int) = 0.0700]
Max. and min. transmission	0.758 and 0.603	0.7752 and 0.6510
Data / restraints / parameters	4351 / 1996 / 460	9363 / 0 / 550
Goodness-of-fit on F ²	0.909	1.027
Final R indices [I>2sigma(I)]	R ₁ = 0.0559, wR ₂ = 0.1924	R ₁ = 0.0729, wR ₂ = 0.1956
R indices (all data)	R ₁ = 0.0674, wR ₂ = 0.2070	R ₁ = 0.1138, wR ₂ = 0.2168
Largest diff. peak and hole (e./Å ⁻³)	0.607 and -0.708	1.254 and -0.575