Supporting Information

A Tridentate Phenoxy-Phosphine (POP) Divalent Chromium Complex and Its Reactivities in Olefin Polymerizations

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1.NMR Characterization of L1

1.1 NMR spectra of ligands

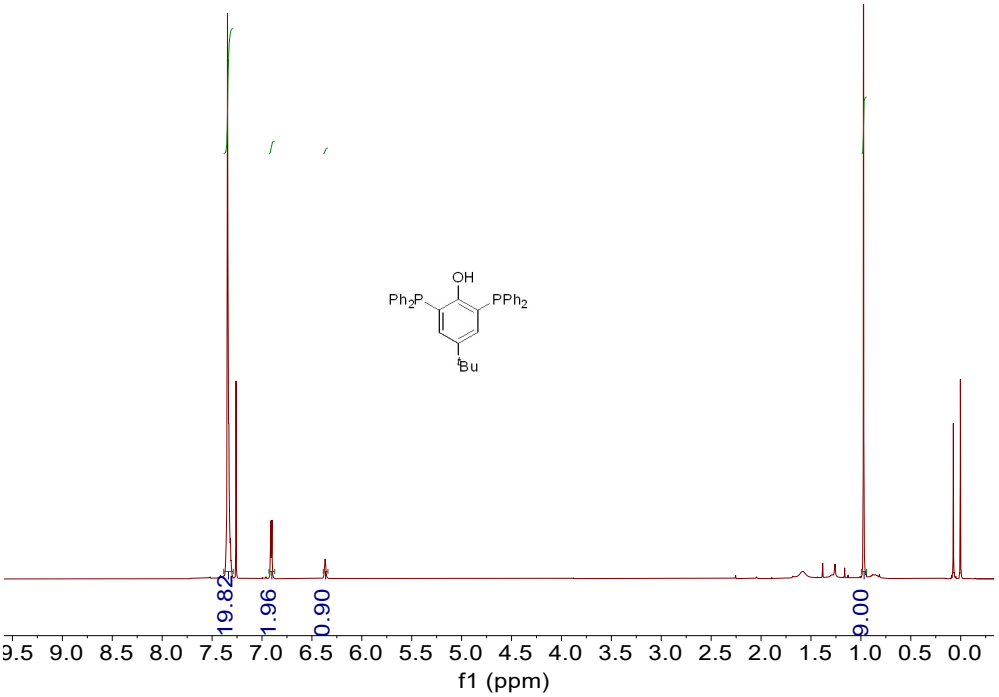


Figure S1.[1]H NMR spectrum of **L1** (400 MHz, $CDCl_3$)

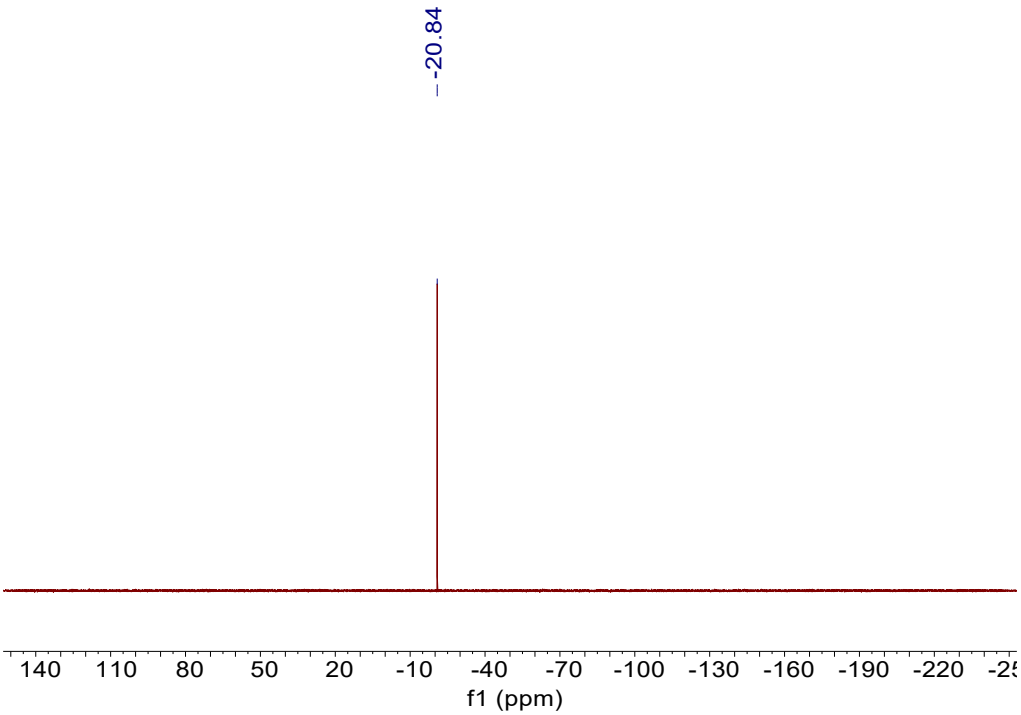


Figure S2.[31]P NMR spectrum of **L1** (161.9 MHz, $CDCl_3$)

2.Characterization of some representative polymers

2.1 NMR spectra of typical polymer samples

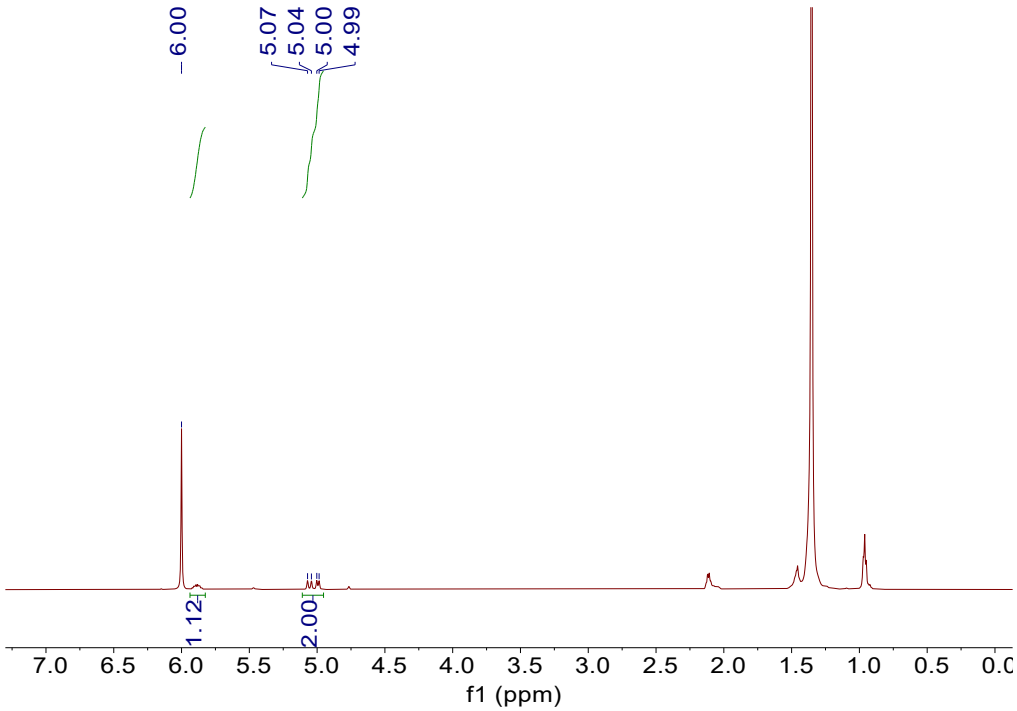


Figure S3. ^{1}H NMR spectrum of polyethylene in 1,1,2,2-tetrachloroethane-d_2 at 120 ^{o}C (Entry 5, Table 1).

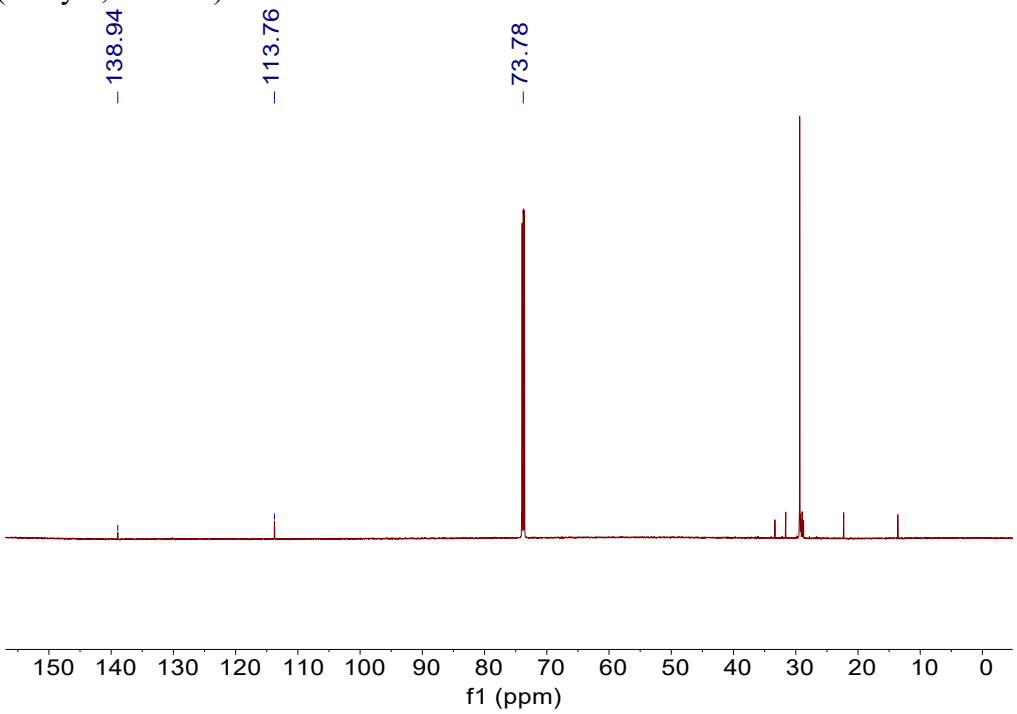


Figure S4. ^{13}C NMR spectrum of polyethylene in 1,1,2,2-tetrachloroethane-d_2 at 120 ^{o}C (Entry 5, Table 1).

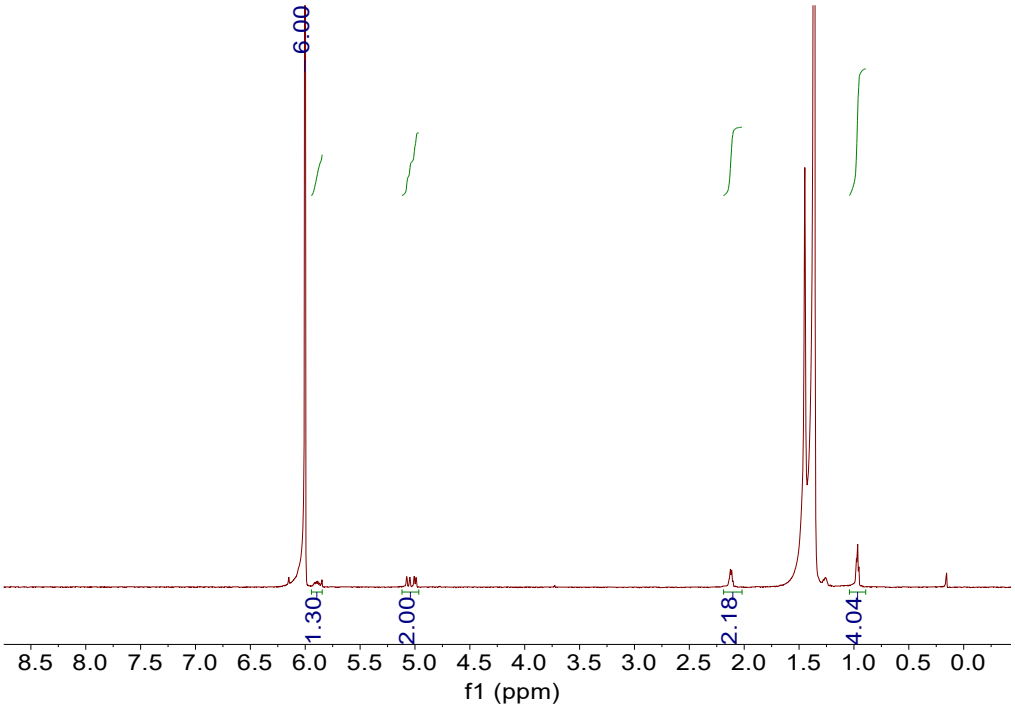


Figure S5. ^{1}H NMR spectrum of polyethylene in 1,1,2,2-tetrachloroethane-d_2 at 120 ^{o}C (Entry 10, Table 1).

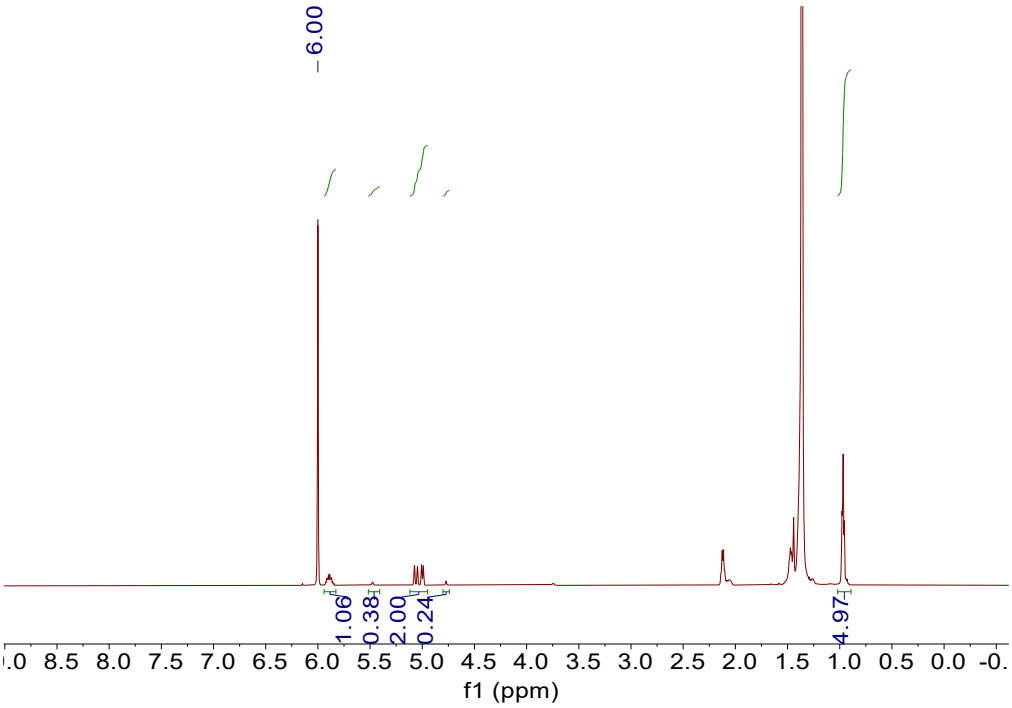


Figure S6. ^{1}H NMR spectrum of polyethylene in 1,1,2,2-tetrachloroethane-d_2 at 120 ^{o}C (Entry 12, Table 1).

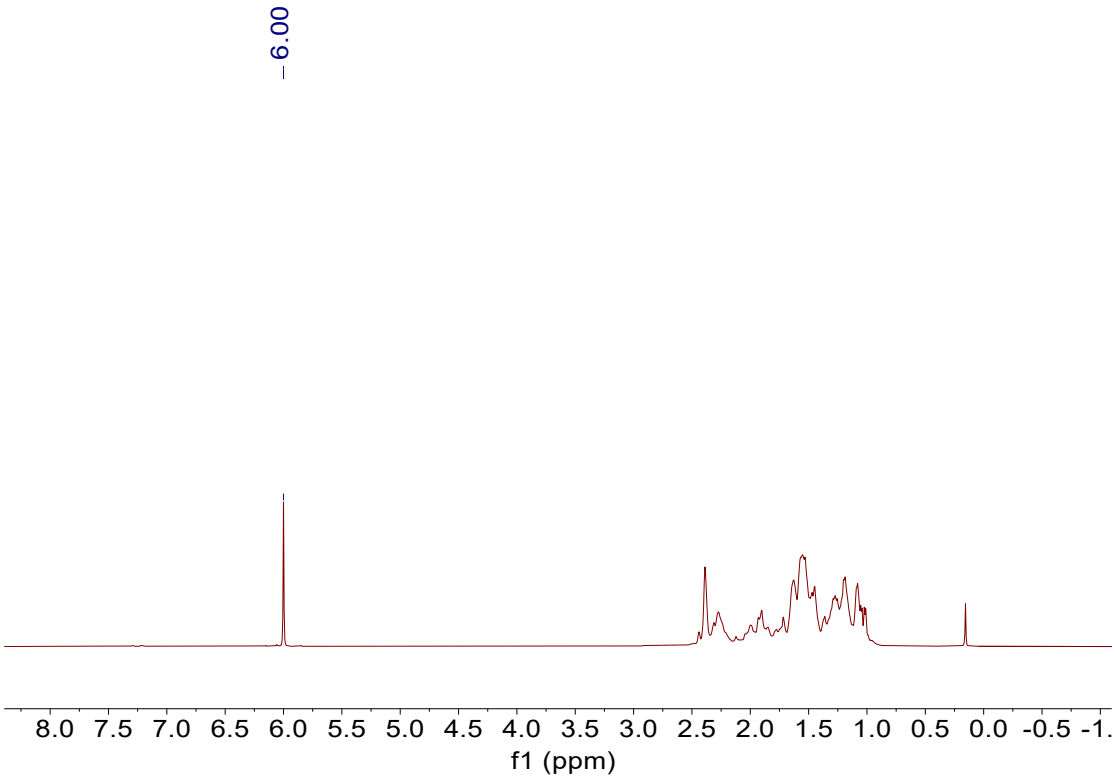


Figure S7. ^{1}H NMR spectrum of polynorbornene in 1,1,2,2-tetrachloroethane-d_2 at 120 ^{o}C (Entry 1, Table 2).

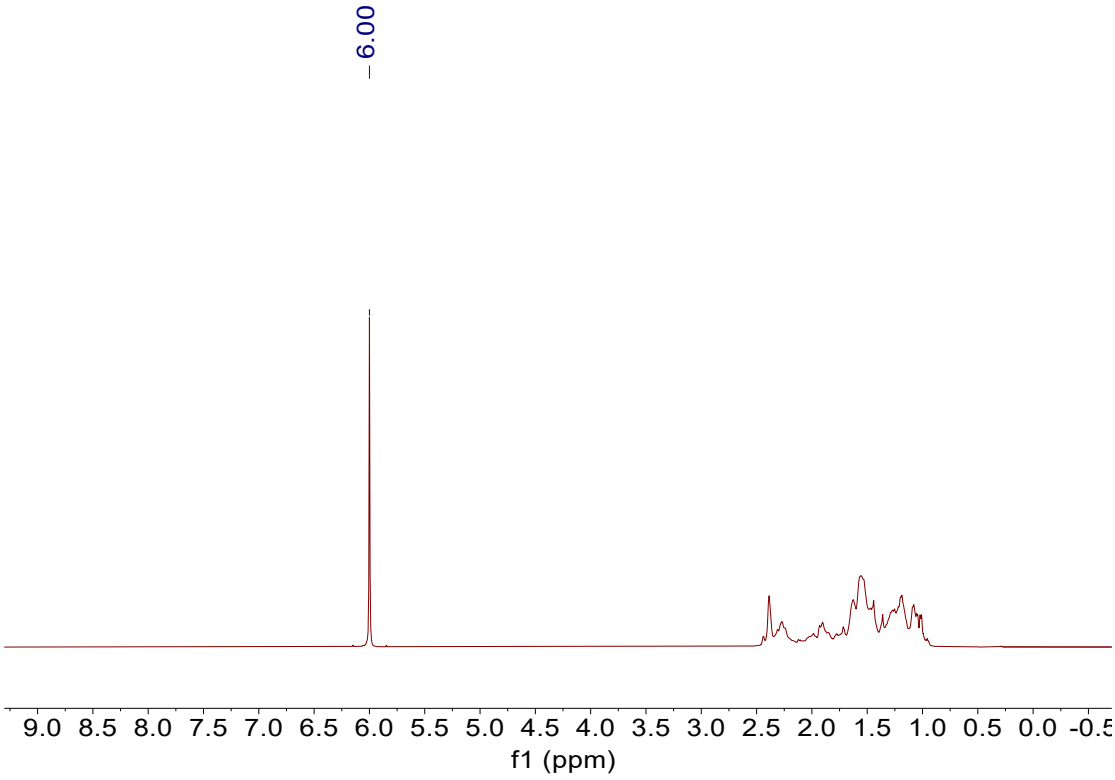


Figure S8. ^{1}H NMR spectrum of polynorbornene in 1,1,2,2-tetrachloroethane-d_2 at 110 ^{o}C (Entry 2, Table 2).

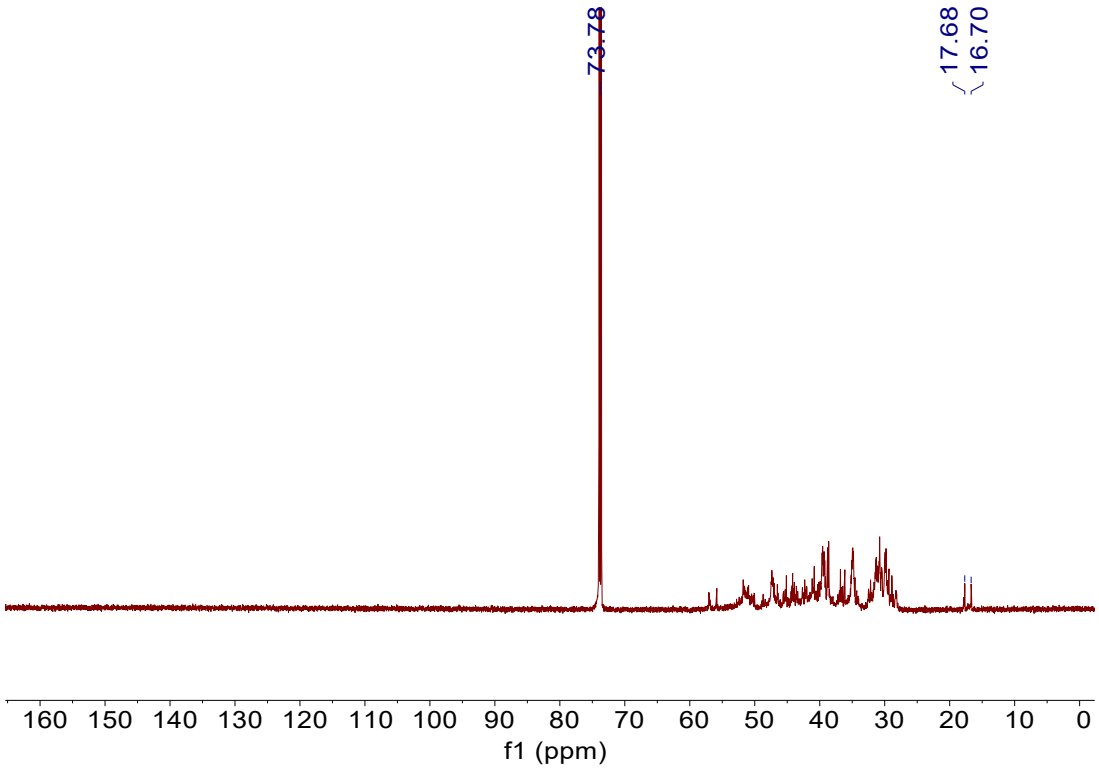


Figure S9. ^{13}C NMR spectrum of polynorbornene in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (Entry 2, Table 2).

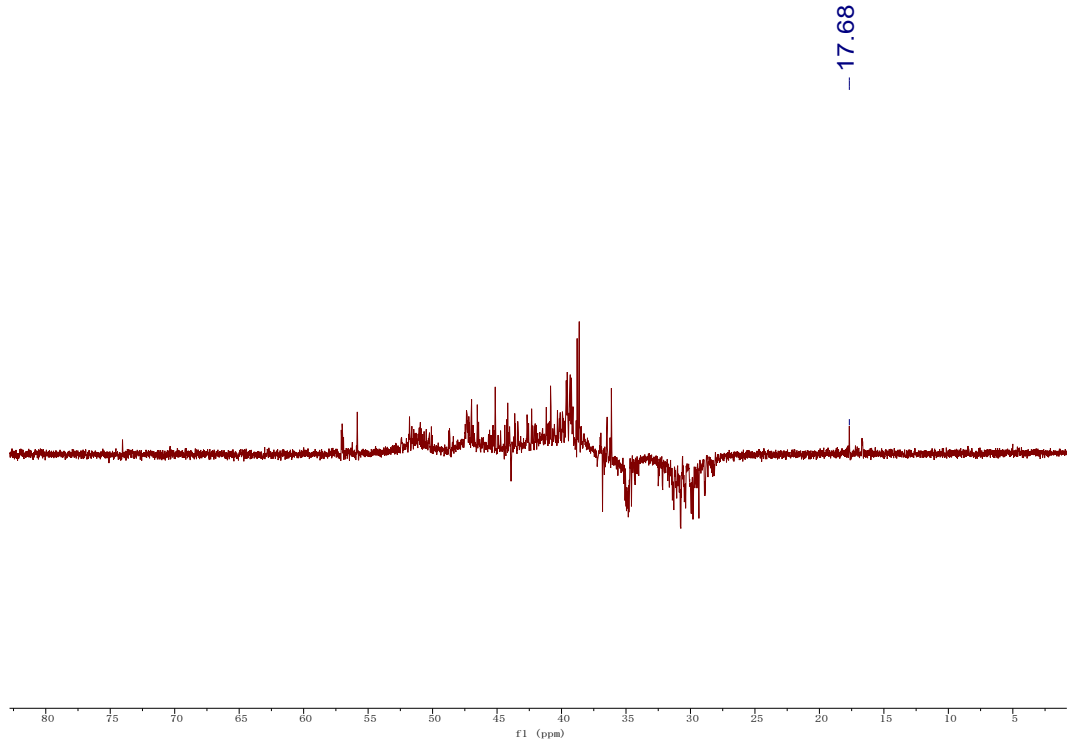
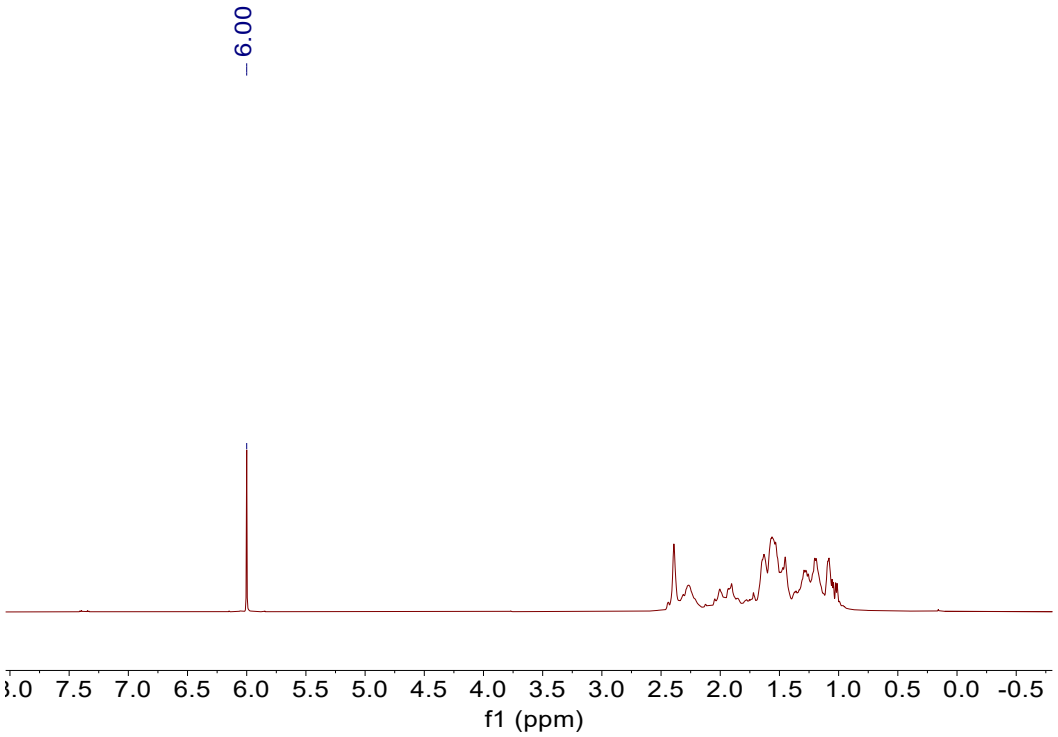


Figure S10. ^{13}C dept 135 NMR spectrum of polynorbornene in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (Entry 2, Table 2).



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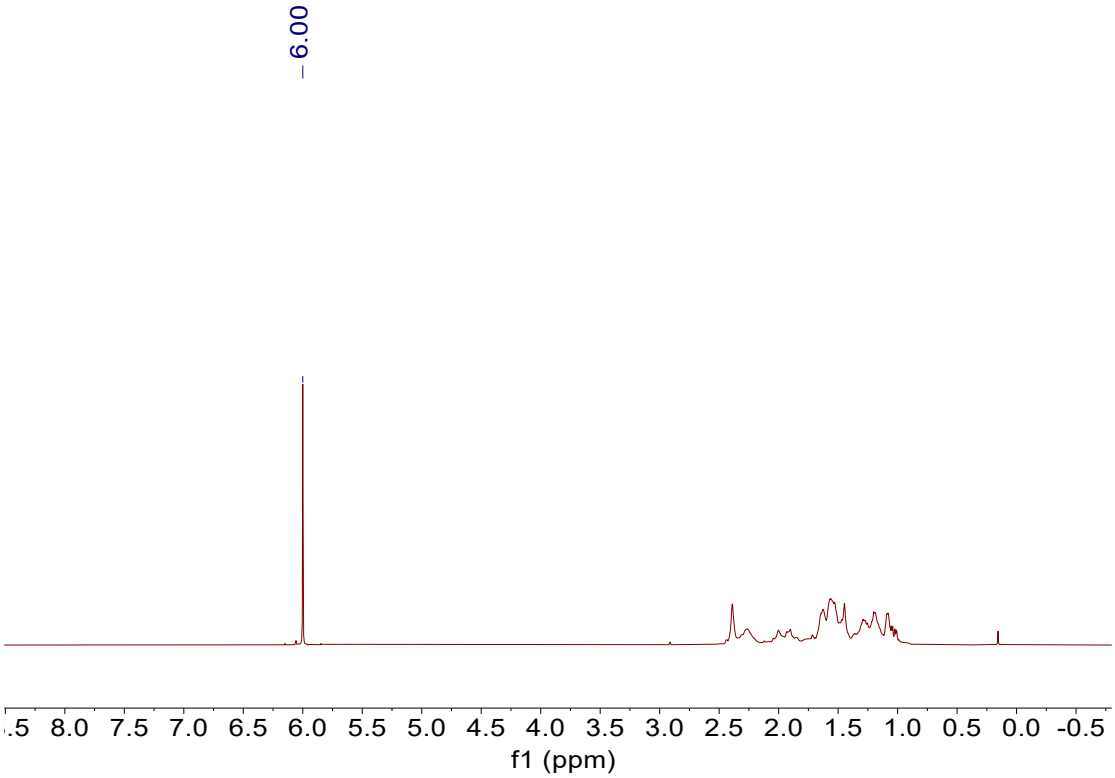


Figure S12. ^{1}H NMR spectrum of polynorbornene in 1,1,2,2-tetrachloroethane-d_2 at 110 ^{o}C (Entry 4, Table 2).

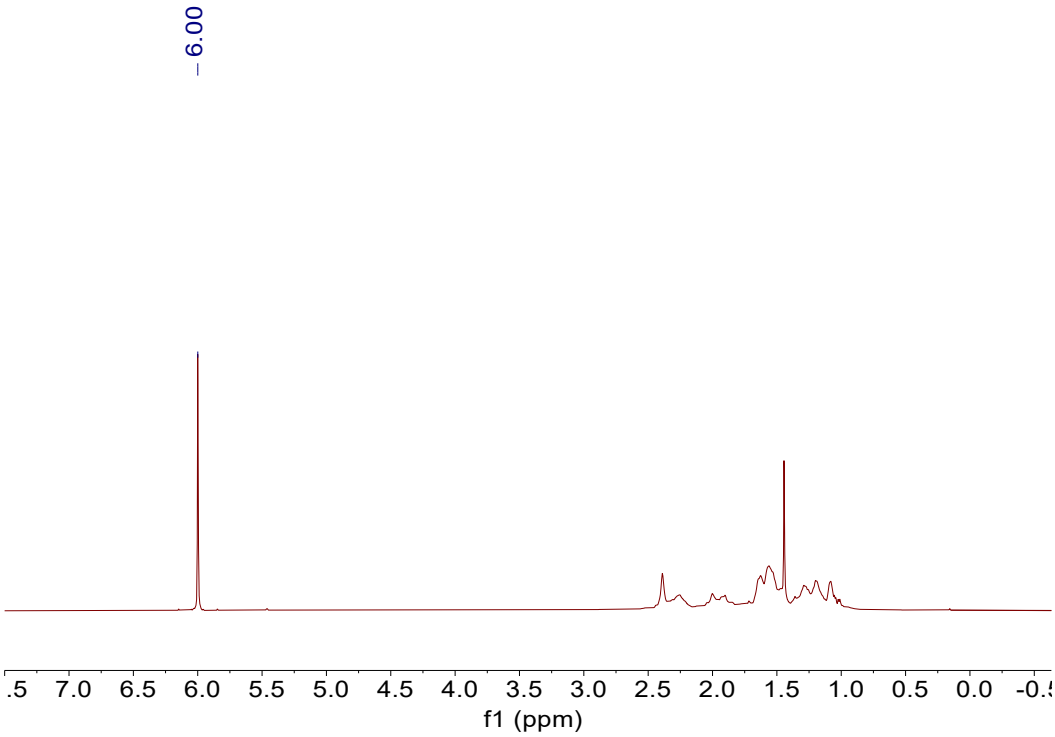


Figure S13. ^{1}H NMR spectrum of polynorbornene in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (Entry 5, Table 2).

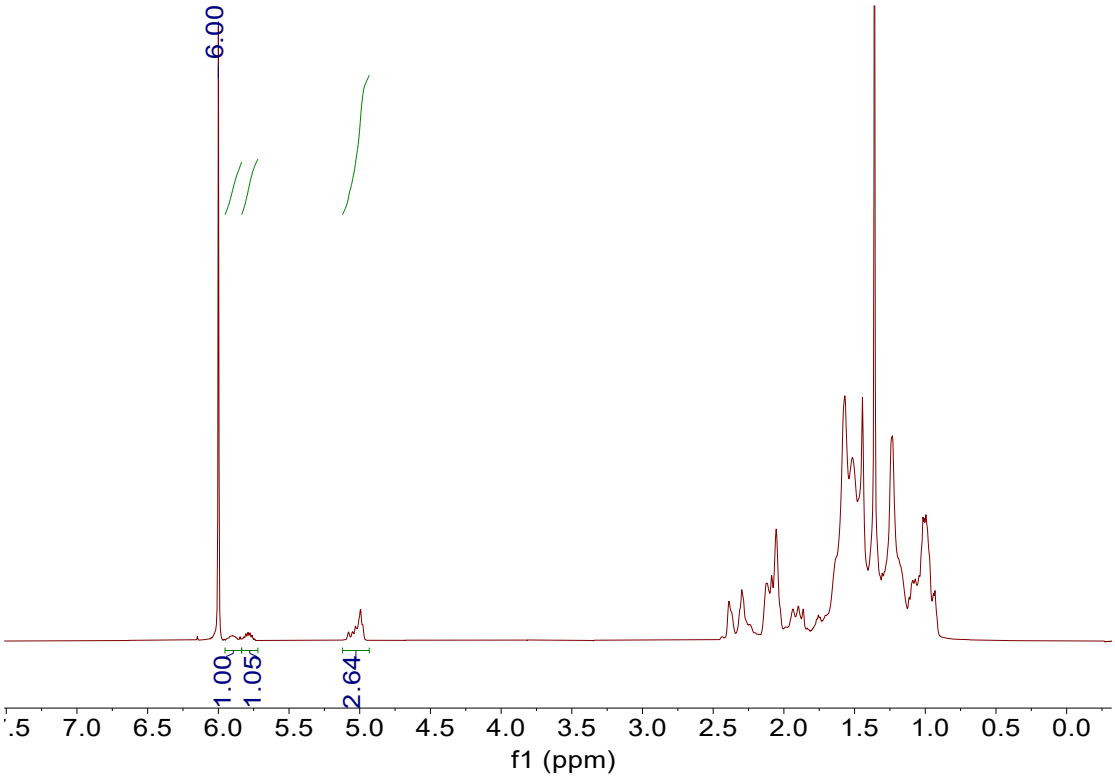
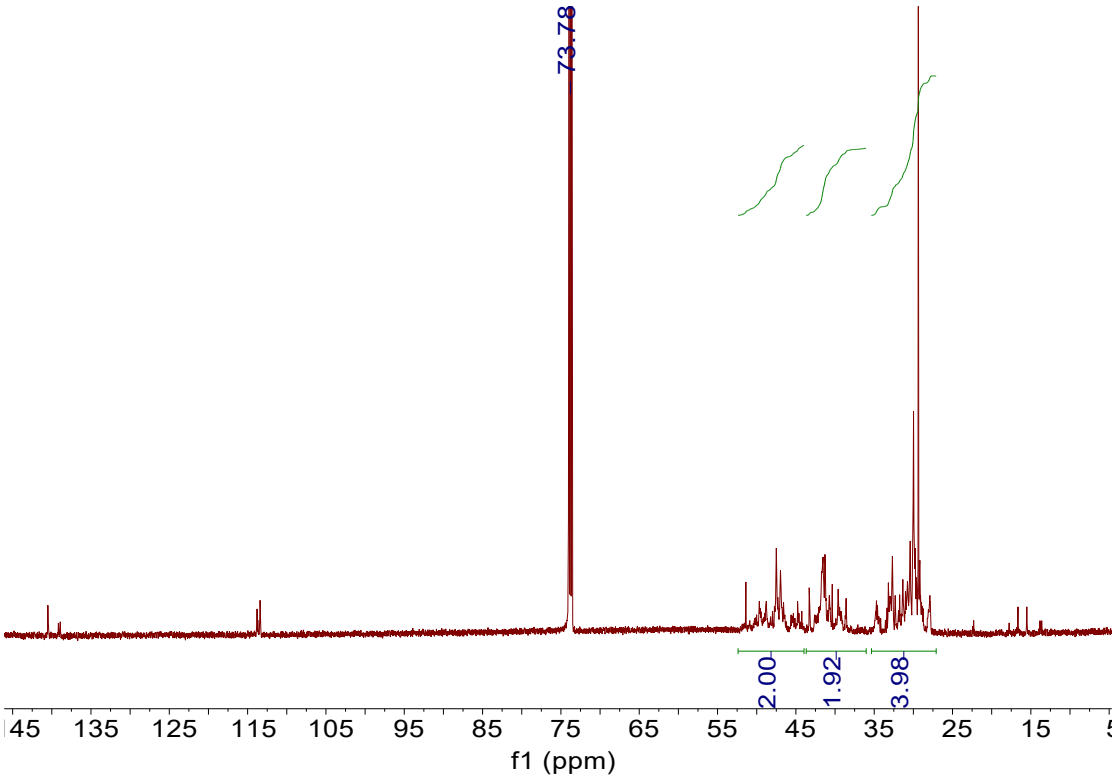


Figure S14. ^{1}H NMR spectrum of poly(ethylene-*co*-norbornene) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (Entry 7, Table 2).



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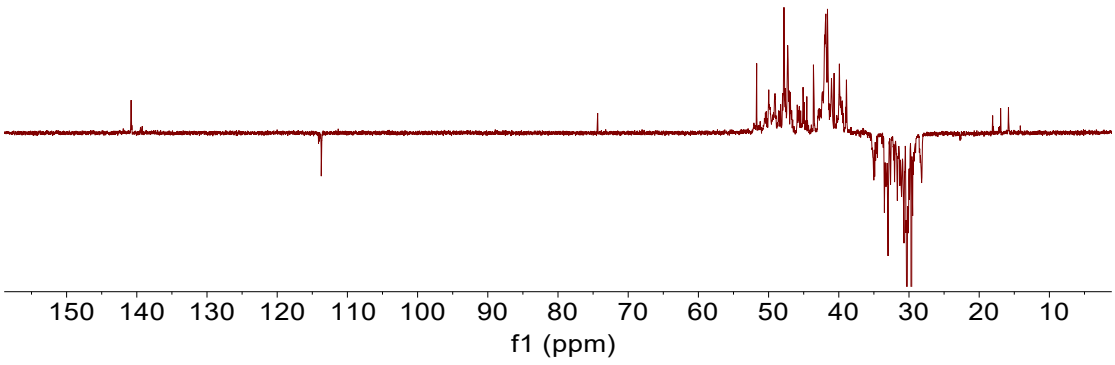
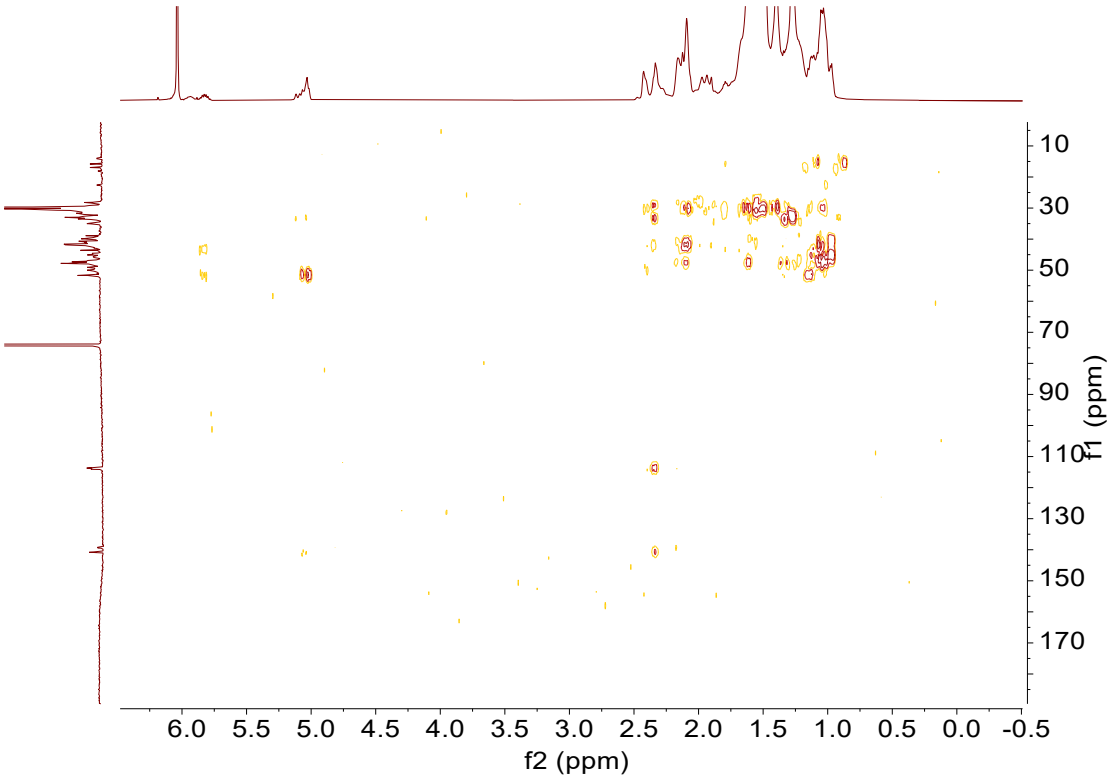


Figure S16. ^{13}C dept 135 NMR spectrum of poly(ethylene-*co*-norbornene) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C (Entry 7, Table 2).



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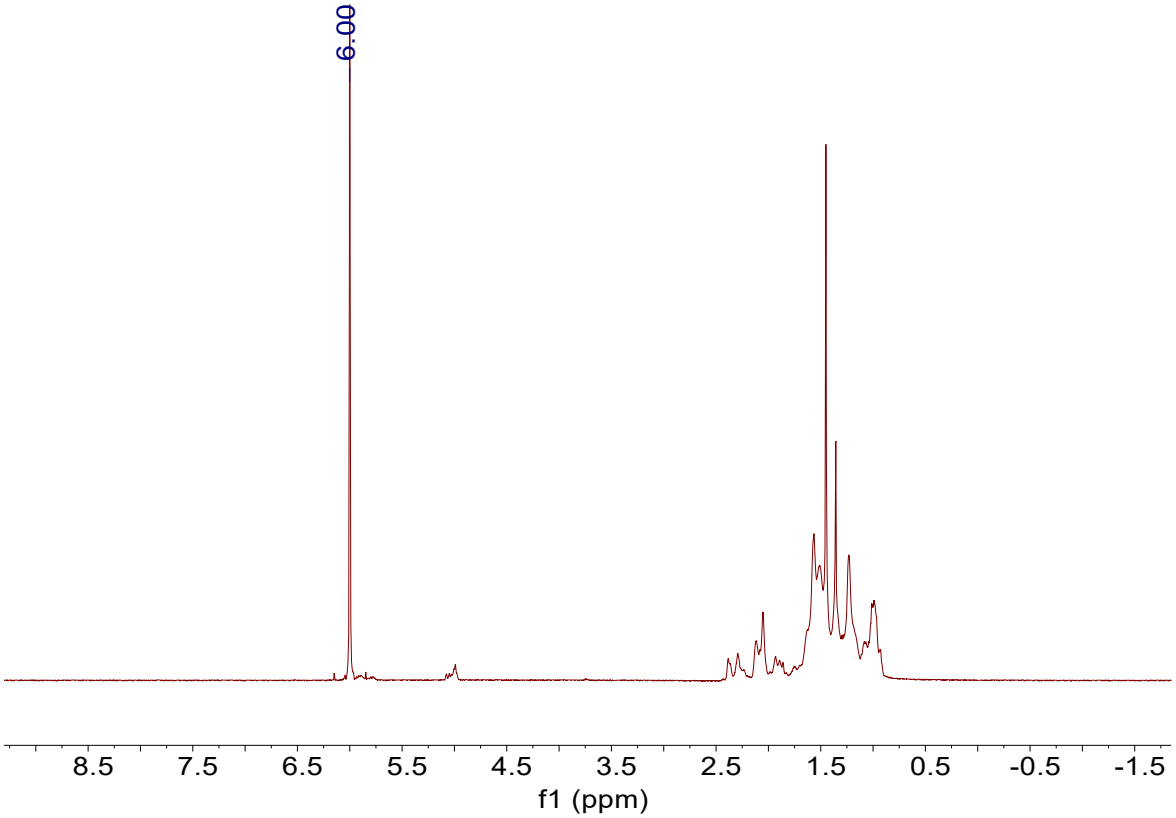


Figure S18. ^{1}H NMR spectrum of poly(ethylene-*co*-norbornene) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (Entry 8, Table 2).

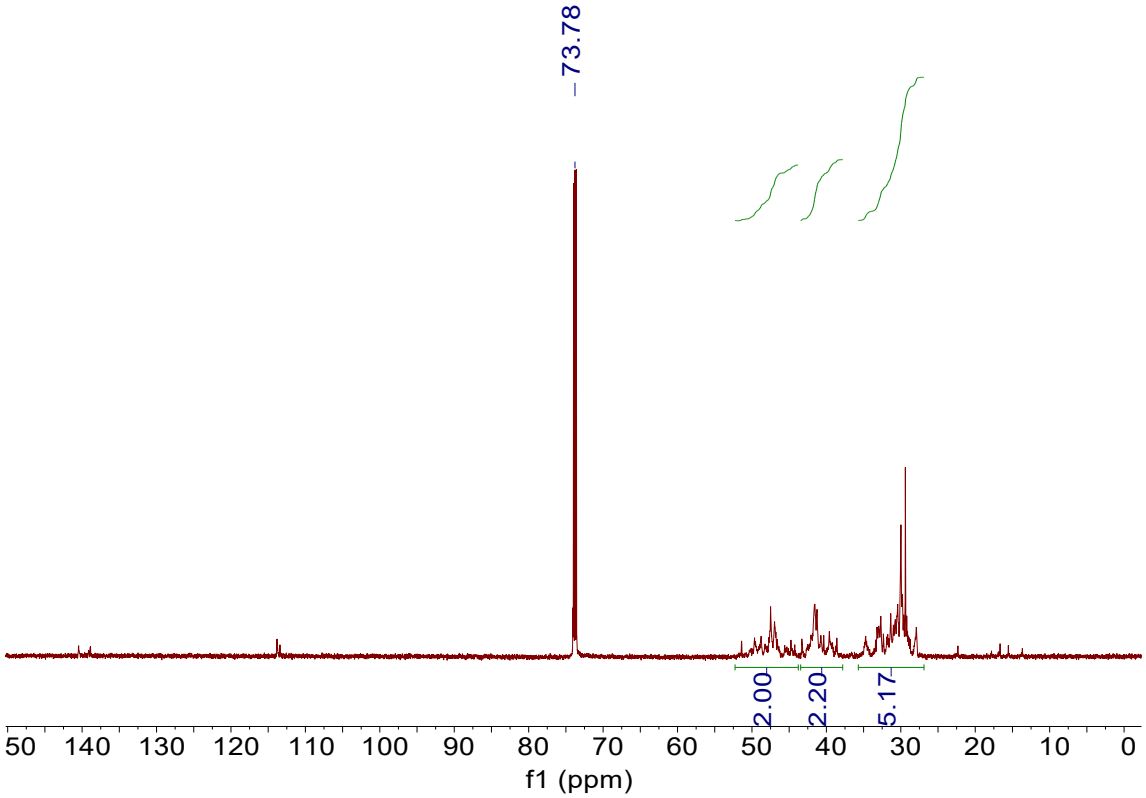


Figure S19. ^{13}C NMR spectrum of poly(ethylene-*co*-norbornene) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (Entry 8, Table 2).

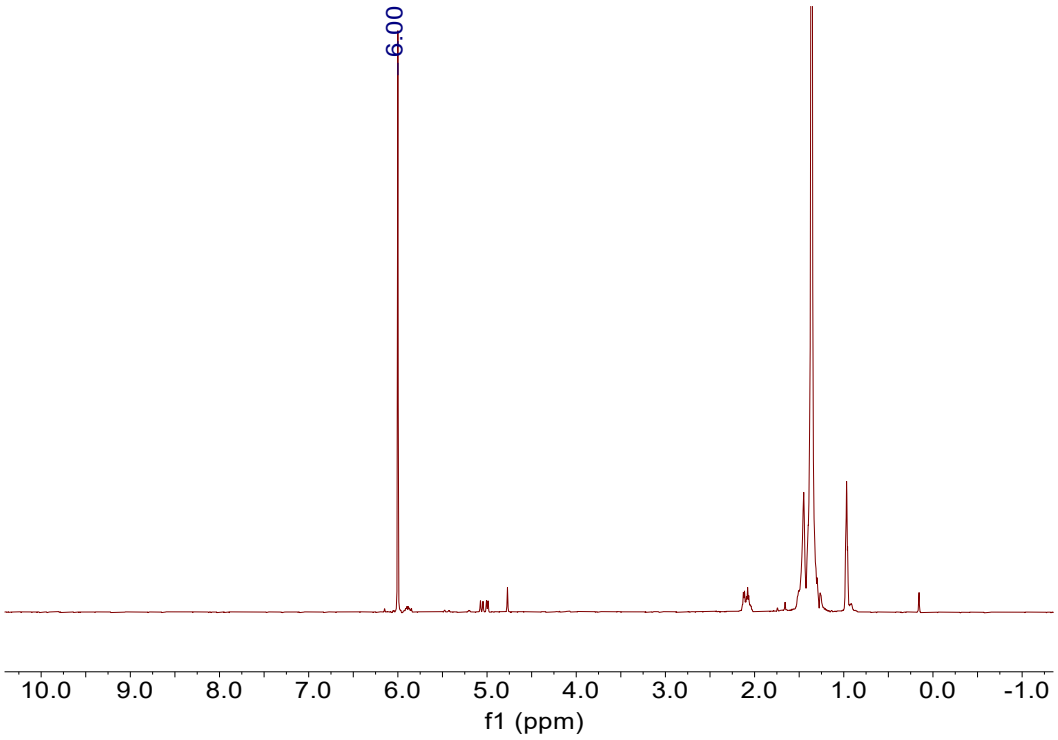


Figure S20. ^{1}H NMR spectrum of poly(ethylene-*co*-1-octene) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (Entry 9, Table 2).

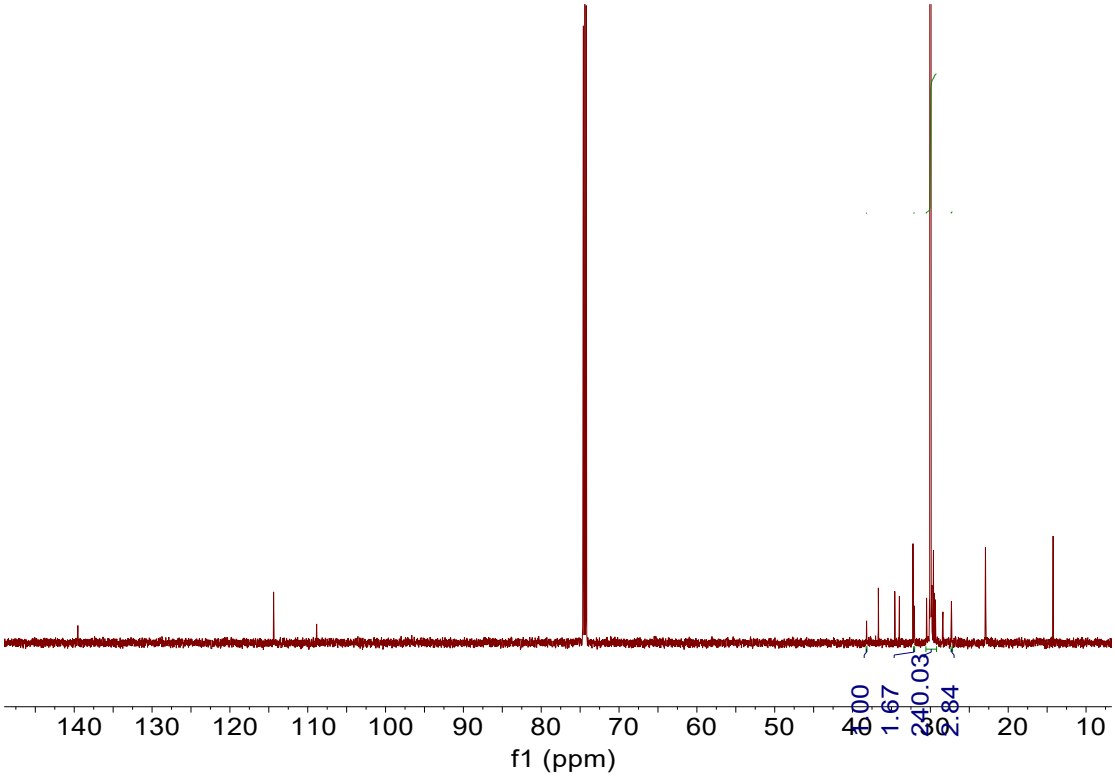


Figure S21. ^{13}C NMR spectrum of poly(ethylene-*co*-1-octene) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (Entry 9, Table 2).

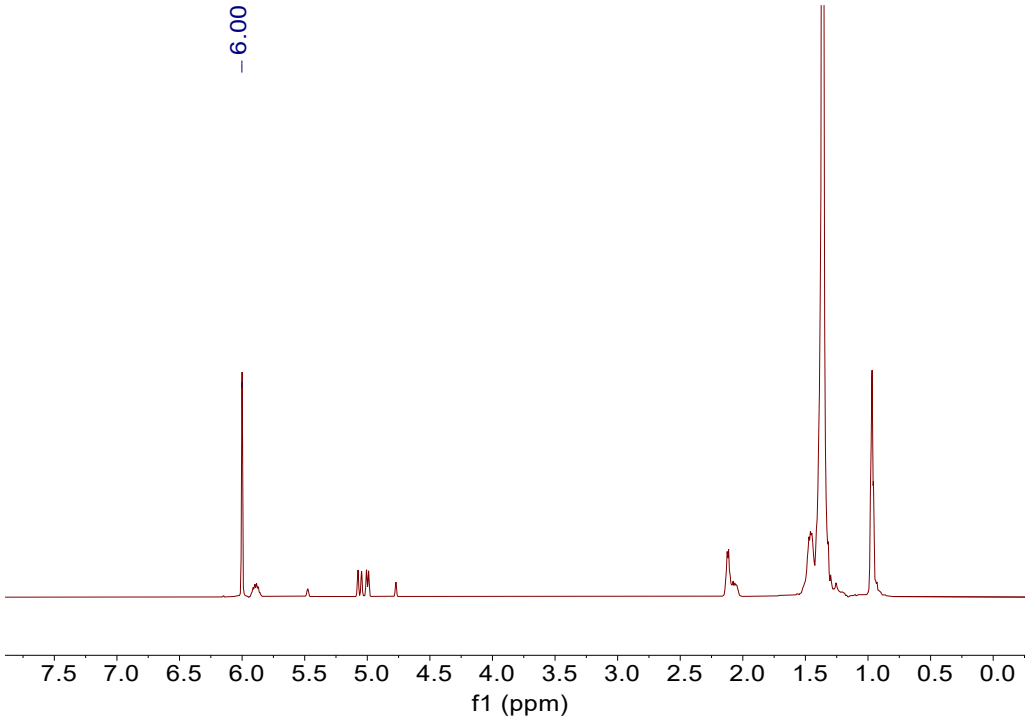


Figure S22. ^{1}H NMR spectrum of poly(ethylene-*co*-1-octene) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (Entry 10, Table 2).

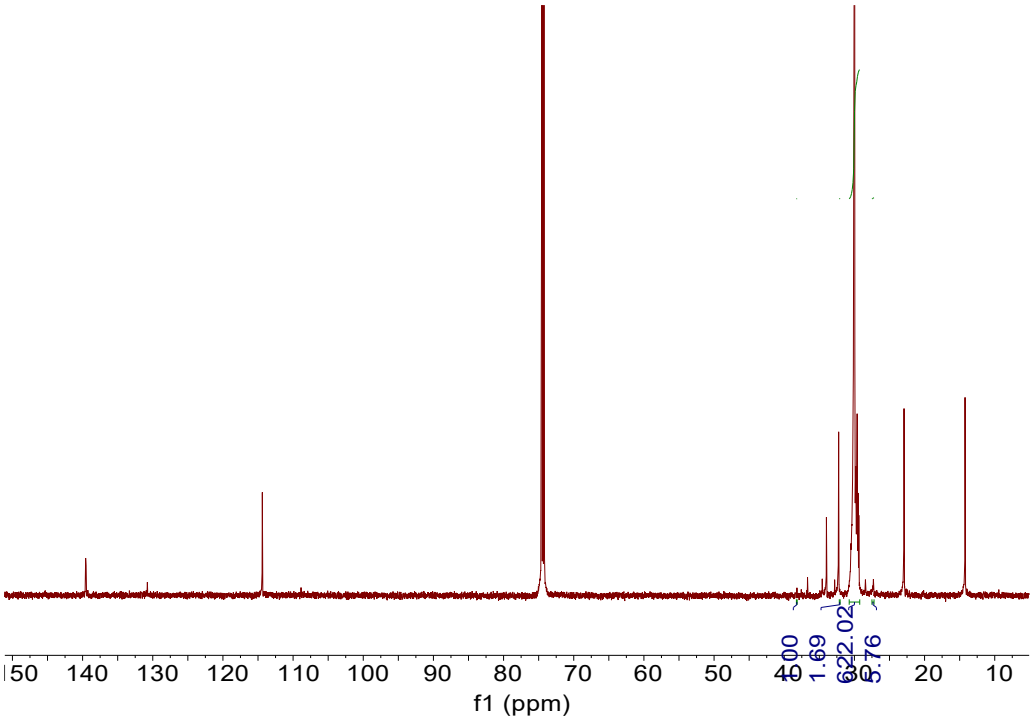


Figure S23. ^{13}C NMR spectrum of poly(ethylene-*co*-1-octene) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (Entry 10, Table 2).

2.2 GPC traces of typical polymer samples

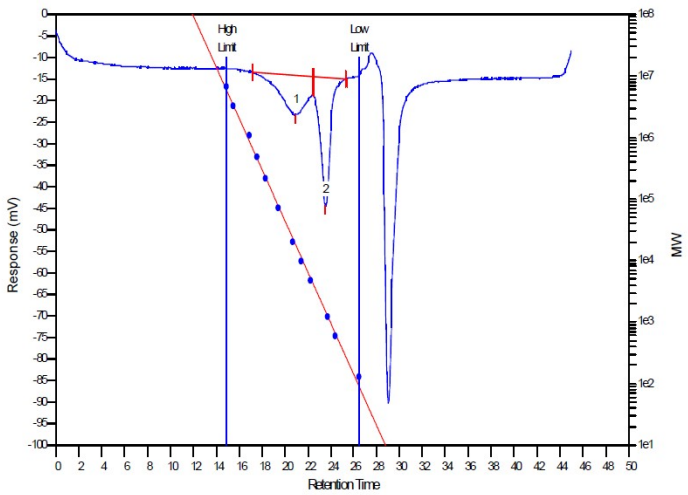


Figure S24. GPC trace of polyethylene (Entry 5, Table 1).

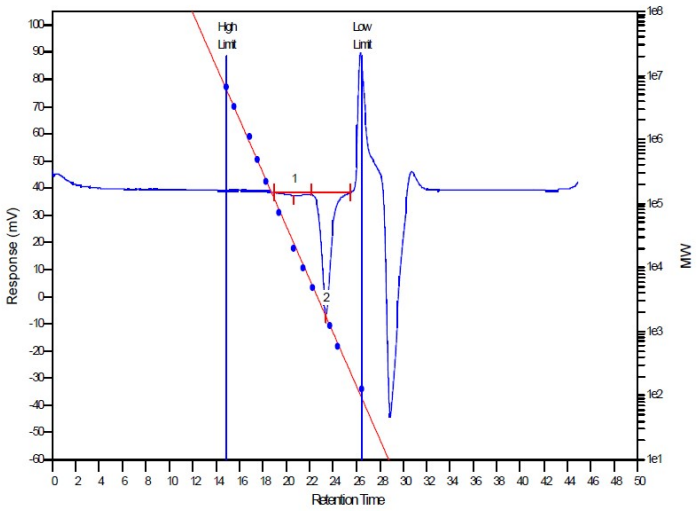


Figure S25. GPC trace of polyethylene (Entry 6, Table 1).

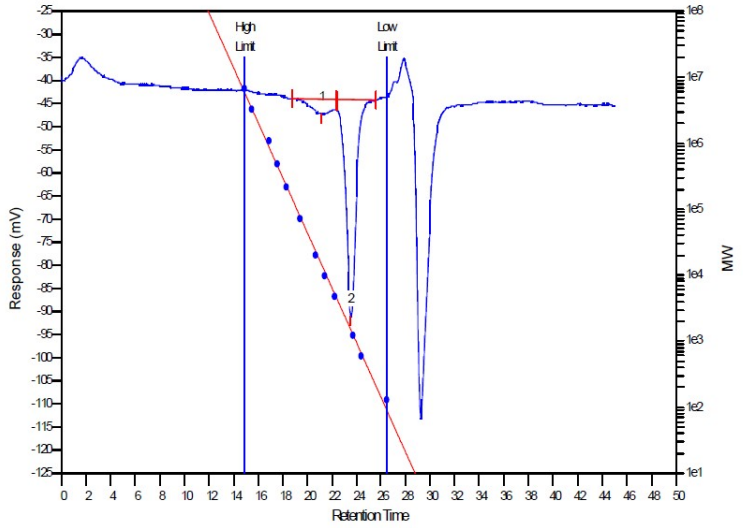


Figure S26. GPC trace of polyethylene (Entry 7, Table 1).

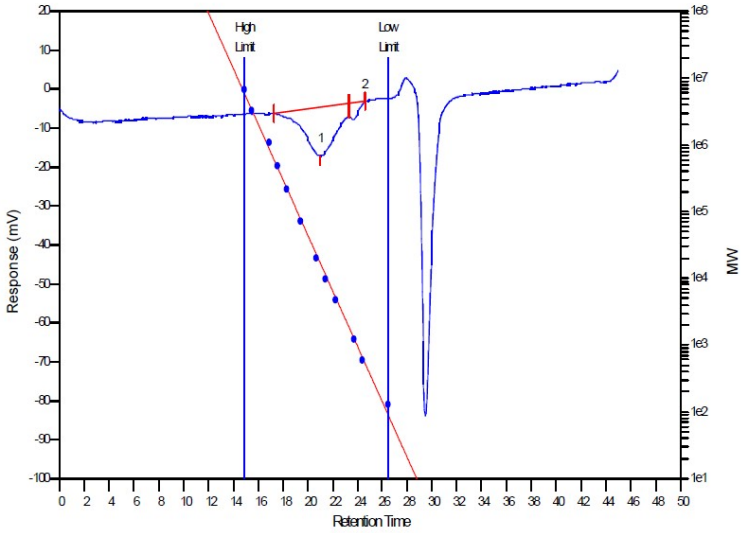


Figure S27. GPC trace of polyethylene (Entry 8, Table 1).

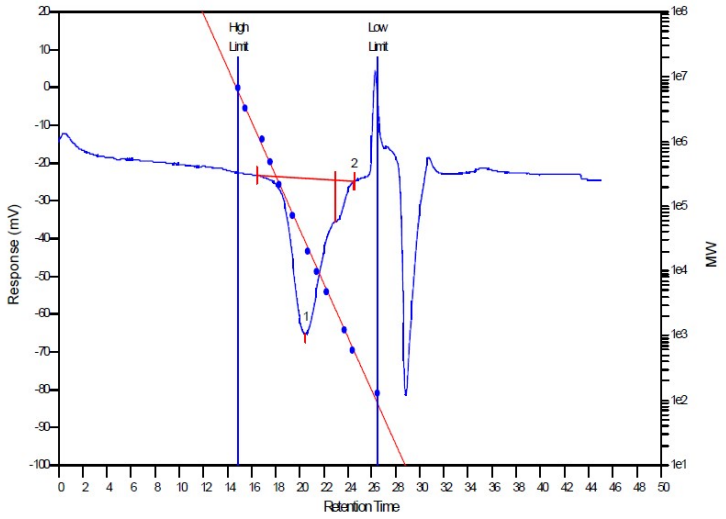


Figure S28. GPC trace of polyethylene (Entry 9, Table 1).

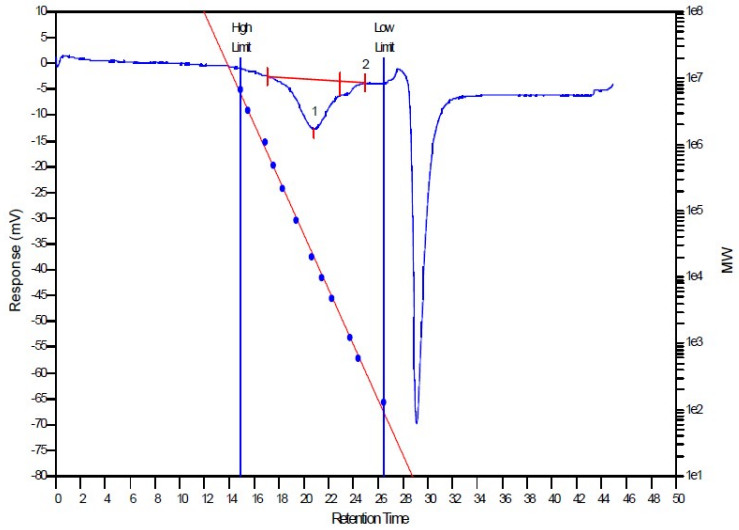


Figure S29. GPC trace of polyethylene (Entry 10, Table 1).

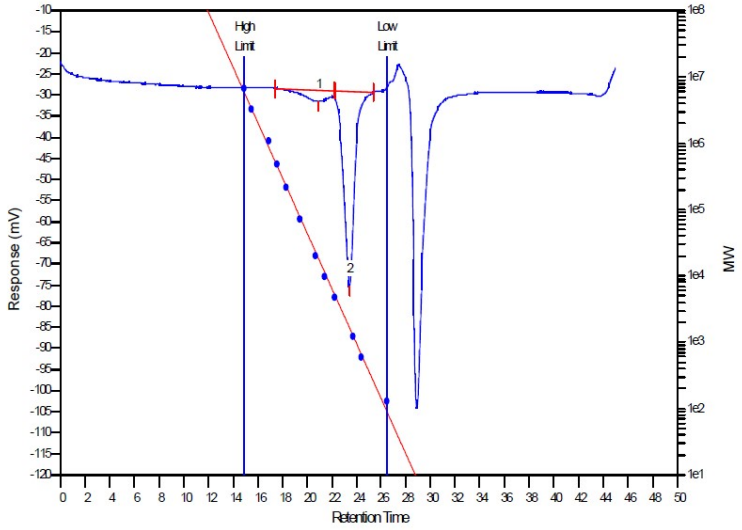


Figure S30. GPC trace for polyethylene (Entry 11, Table 1).

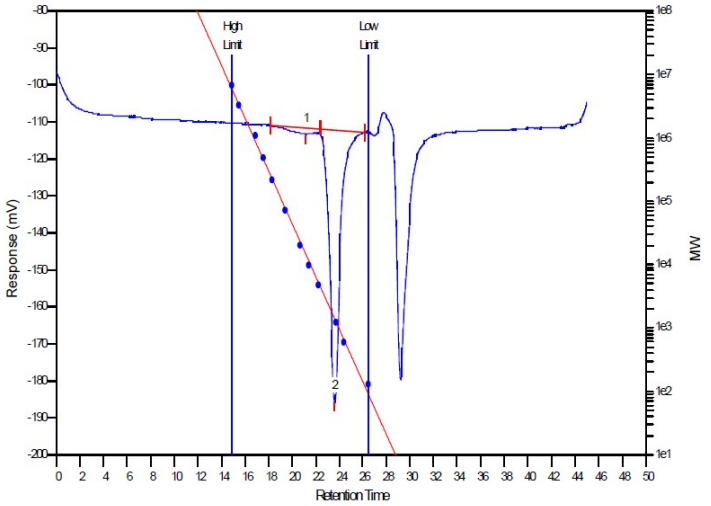


Figure S31. GPC trace for polyethylene (Entry 12, Table 1).

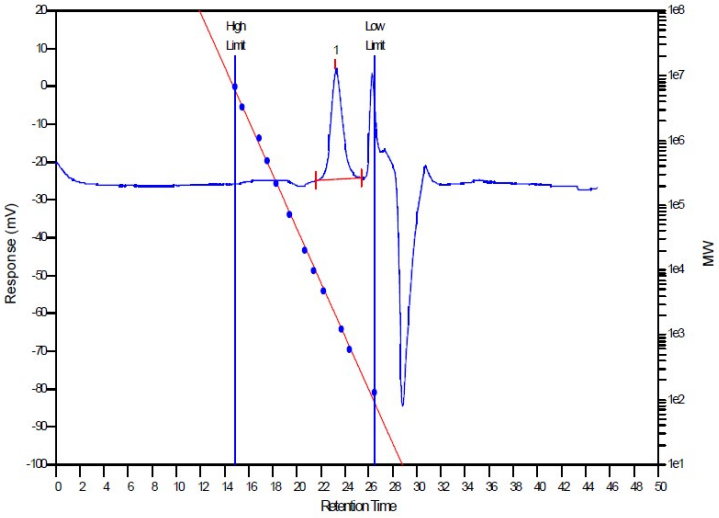


Figure S32. GPC trace for polynorbornene (Entry 1, Table 2).

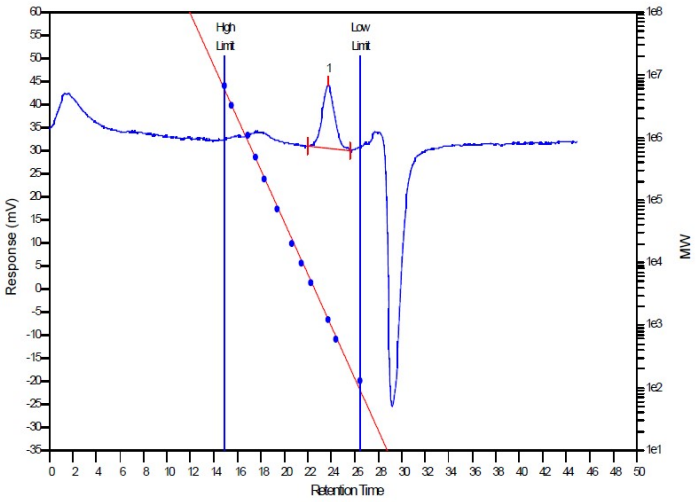


Figure S33. GPC trace for polynorbornene (Entry 2, Table 2).

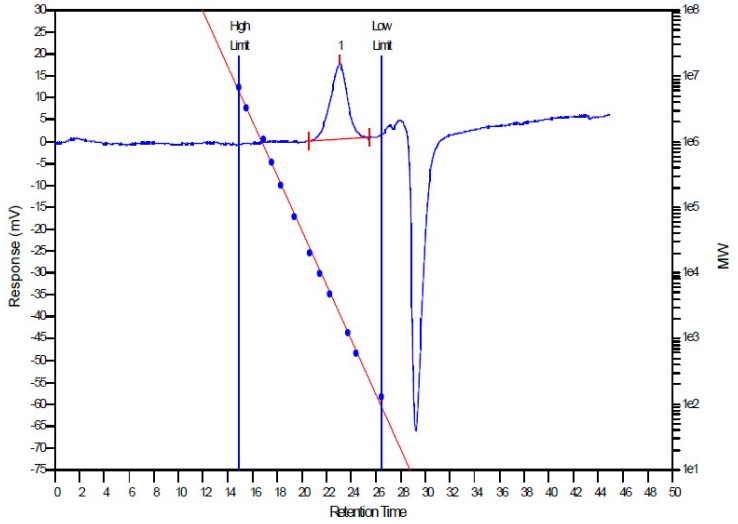


Figure S34. GPC trace for polynorbornene (Entry 3, Table 2).

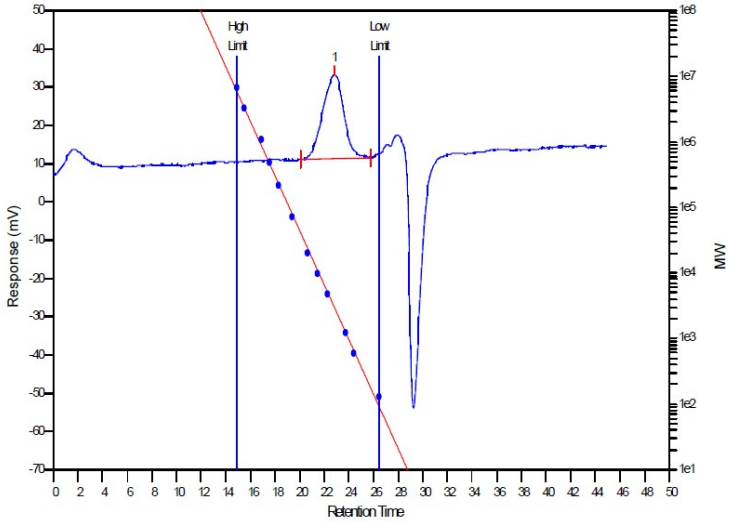


Figure S35. GPC trace for polynorbornene (Entry 4, Table 2).

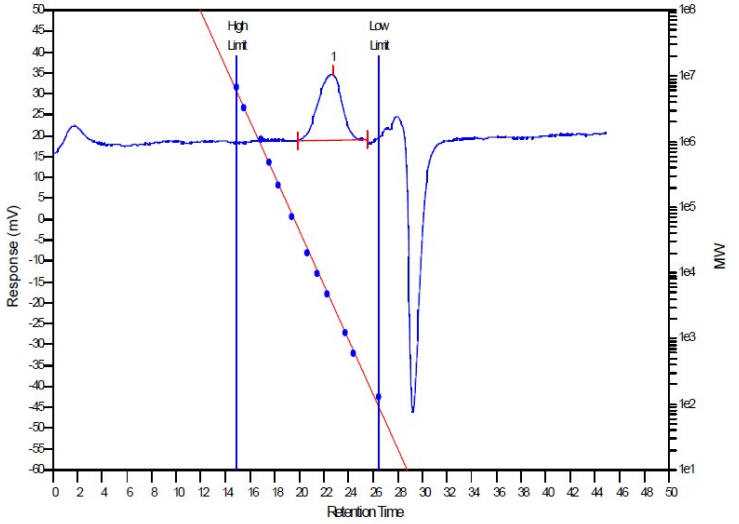
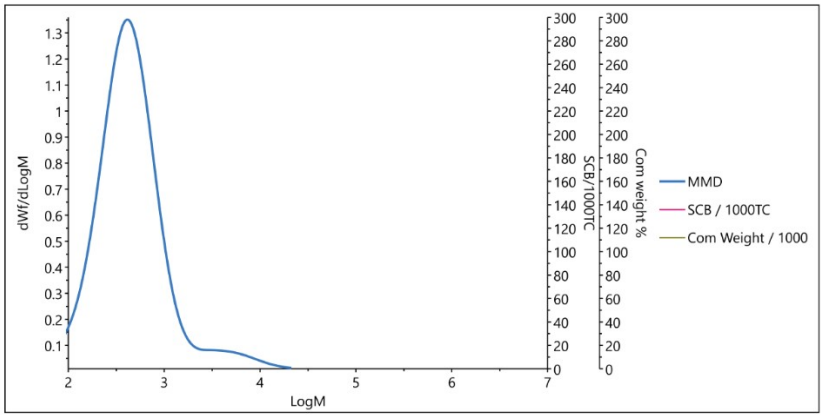


Figure S36. GPC trace of polynorbornene (Entry 5, Table 2).



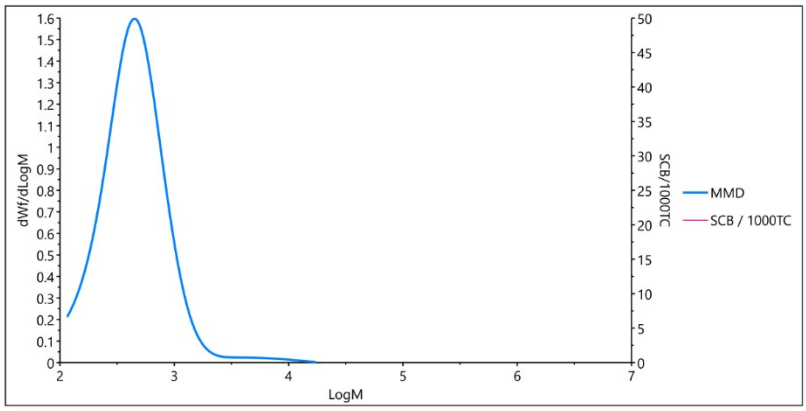
Results

Mw	800	g/mol
Mn	300	g/mol
Mw / Mn	2.4	

Calibrations

Flow Marker	27.53	mL
Mass constant	0.68	mL·V/mg

Figure S37. GPC trace of poly(ethylene-*co*-norbornene) (Entry 7, Table 2).



Results

Mw	600	g/mol
Mn	400	g/mol
Mw / Mn	1.6	

Calibrations

Flow Marker	27.53	mL
Mass constant	0.68	mL·V/mg

Figure S38. GPC trace of poly(ethylene-*co*-norbornene) (Entry 8, Table 2).

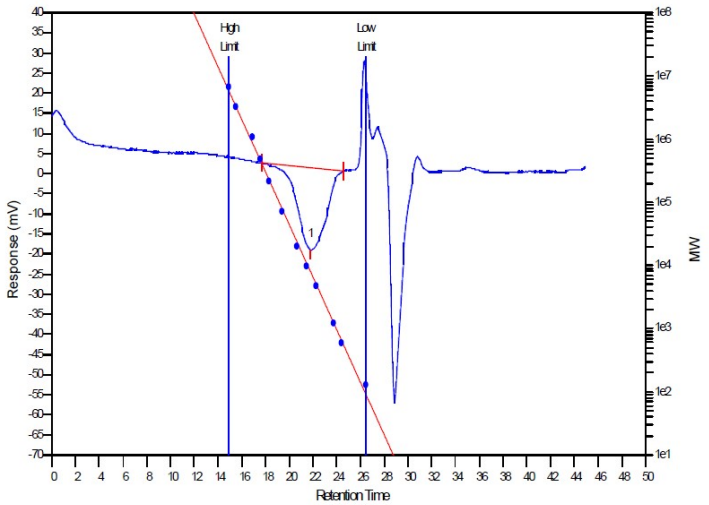


Figure S39. GPC trace of poly(ethylene-*co*-1-octene) (Entry 9, Table 2).

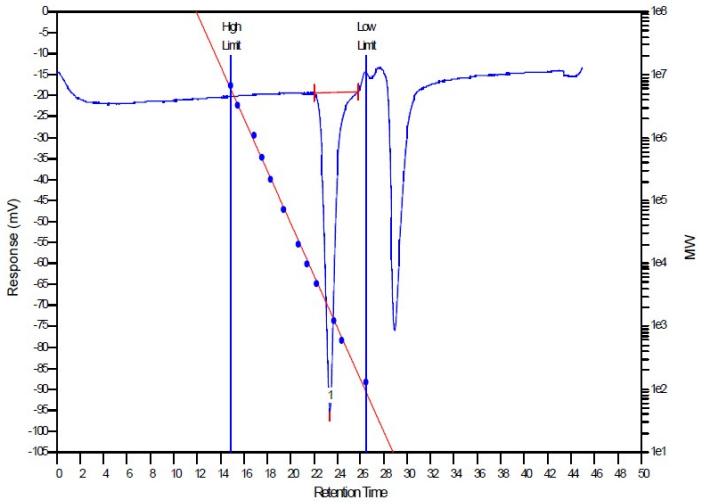


Figure S40. GPC trace of poly(ethylene-*co*-1-octene) (Entry 10, Table 2).

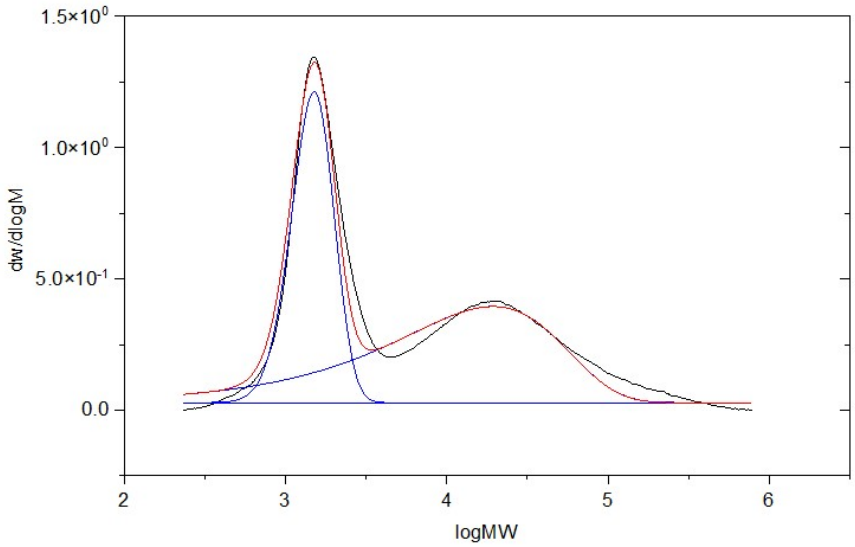


Figure S41. GPC trace of polyethylene (Entry 5, Table 1). The black trace is the experimental data whereas the blue trace and the red trace are the deconvolution distributions generated from Schulz-Flory fitting with $R^2 = 0.97$.

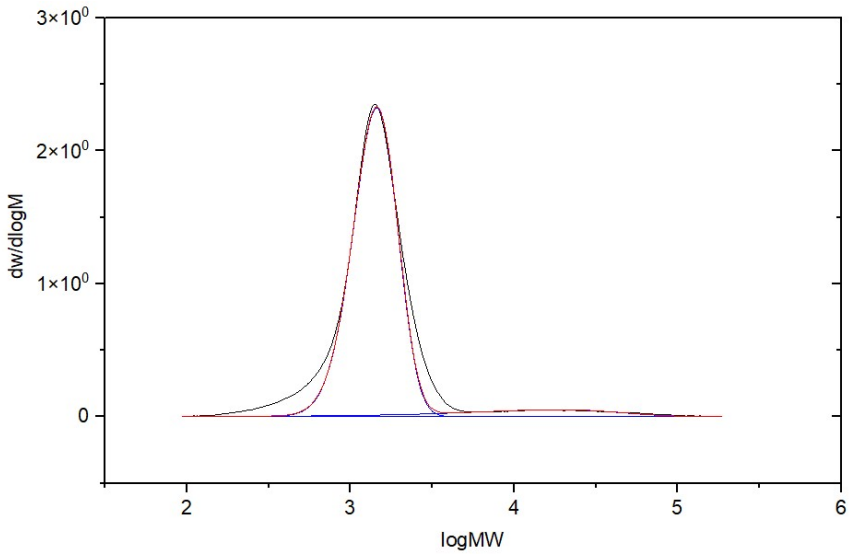


Figure S42. GPC trace of polyethylene (Entry 12, Table 1). The black trace is the experimental data whereas the blue trace and the red trace are the deconvolution distributions generated from Schulz-Flory fitting with $R^2 = 0.98$.

Table S1. GPC deconvolution of polyethylene from Entry 5 in Table 1.[a]

Peak Index	Peak Type	FWHM[b]	Max Height	Area IntgP
1	Schulz-Flory	0.30981	1.18294	43.53965
2	Schulz-Flory	1.2769	0.36602	56.46035

[a]See Figure S41. [b]Full width at half maximum.

Table S2. GPC deconvolution of polyethylene from Entry 12 in Table 1.[a]

Peak Index	Peak Type	FWHM[b]	Max Height	Area IntgP
1	Schulz-Flory	0.3209	2.32	92.54331
2	Schulz-Flory	1.1042	0.0525	7.45669

[a]See Figure S42. [b]Full width at half maximum.

3.UV-vis-NIR spectra of cat.1 at different reaction conditions

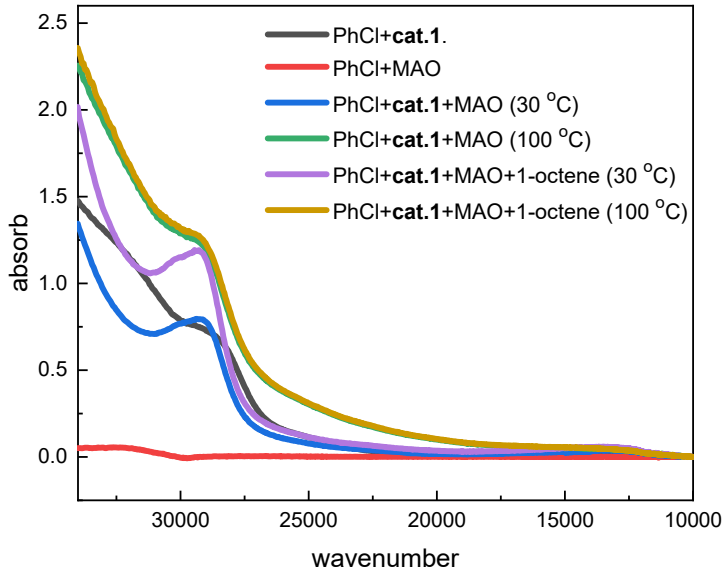


Figure S43. UV-vis-NIR spectra. MAO, 10 equiv./cat, 1-octene, 1000 equiv./cat.

4. Crystallographic data and figures of crystal structure

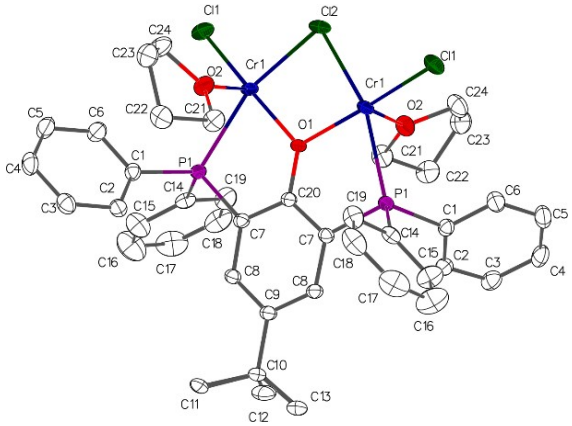


Figure S44. Crystal structure of complex cat.1

Table S3. Crystal data and structure refinement for final cat.1

Identification code	cxy3236_0m
Empirical formula	$C_{50}H_{63}Cl_3Cr_2O_5P_2$
Formula weight	1016.29
Temperature/K	100.0
Crystal system	monoclinic

Space group	C2/c
a/Å	21.5840(9)
b/Å	13.1523(5)
c/Å	17.7764(7)
α/°	90
β/°	91.481(2)
γ/°	90
Volume/Å^3	5044.7(3)
Z	4
ρ_{calc}g/cm^3	1.338
μ/mm^{-1}	5.958
F(000)	2128.0
Crystal size/mm^3	0.36 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.872 to 137.096
Index ranges	-25 ≤ h ≤ 25, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	53396
Independent reflections	4633 [R_{int} = 0.1106, R_{sigma} = 0.0360]
Data/restraints/parameters	4633/15/306
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0341, wR_2 = 0.0913
Final R indexes [all data]	R_1 = 0.0356, wR_2 = 0.0929
Largest diff. peak/hole / e Å^{-3}	0.66/-0.59

Table S4. Bond Lengths (Å) for cat.1

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cr1	Cl1	2.3074(5)	C8	C9	1.395(2)
Cr1	P1	2.4775(5)	C9	C10	1.537(3)
Cr1	Cl2	2.4203(5)	C10	C11	1.487(4)
Cr1	O1	2.0205(10)	C10	C12	1.632(4)
Cr1	O2	2.3088(12)	C10	C13	1.488(4)
P1	C1	1.8172(16)	C14	C15	1.391(3)
P1	C7	1.8114(17)	C14	C19	1.395(3)
P1	C14	1.8162(17)	C15	C16	1.388(3)
O1	C20	1.351(3)	C16	C17	1.385(3)
O2	C21	1.444(2)	C17	C18	1.377(3)
O2	C24	1.447(2)	C18	C19	1.383(3)
O3	C25	1.410(3)	C21	C22	1.531(6)
O3	C28	1.429(4)	C21	C22A	1.531(6)
C1	C2	1.388(2)	C22	C23	1.523(7)
C1	C6	1.397(3)	C23	C24	1.574(5)
C2	C3	1.397(2)	C24	C23A	1.492(5)

C3	C4	1.384(3)	C25	C26	1.495(4)
C4	C5	1.384(3)	C26	C27	1.493(4)
C5	C6	1.395(3)	C27	C28	1.495(4)
C7	C8	1.398(2)	C23A	C22A	1.521(8)
C7	C20	1.401(2)			

Table S5. Bond Angles (°) for cat.1

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Cr1	P1	97.677(18)	C20	C7	P1	115.61(13)
Cl1	Cr1	Cl2	98.284(17)	C9	C8	C7	122.17(16)
Cl1	Cr1	O2	104.89(4)	C8[1]	C9	C8	117.1(2)
Cl2	Cr1	P1	162.969(18)	C8	C9	C10	121.44(11)
O1	Cr1	Cl1	168.133(18)	C8[1]	C9	C10	121.44(11)
O1	Cr1	P1	79.73(4)	C9	C10	C12	106.34(16)
O1	Cr1	Cl2	83.44(4)	C11	C10	C9	110.27(17)
O1	Cr1	O2	86.67(3)	C11	C10	C12	106.3(2)
O2	Cr1	P1	88.33(4)	C11	C10	C13	113.1(2)
O2	Cr1	Cl2	93.28(4)	C13	C10	C9	114.30(17)
C1	P1	Cr1	110.25(6)	C13	C10	C12	105.9(2)
C7	P1	Cr1	98.28(6)	C15	C14	P1	122.66(13)
C7	P1	C1	108.15(8)	C15	C14	C19	119.30(17)
C7	P1	C14	104.03(7)	C19	C14	P1	118.03(14)
C14	P1	Cr1	129.54(6)	C16	C15	C14	120.10(19)
C14	P1	C1	104.81(8)	C17	C16	C15	119.9(2)
Cr1	Cl2	Cr1[1]	85.03(2)	C18	C17	C16	120.4(2)
Cr1	O1	Cr1[1]	108.09(7)	C17	C18	C19	119.99(19)
C20	O1	Cr1[1]	125.95(4)	C18	C19	C14	120.30(19)
C20	O1	Cr1	125.95(4)	O1	C20	C7	120.34(11)
C21	O2	Cr1	126.98(11)	O1	C20	C7[1]	120.34(11)
C21	O2	C24	109.71(13)	C7	C20	C7[1]	119.3(2)
C24	O2	Cr1	123.29(11)	O2	C21	C22	107.2(3)
C25	O3	C28	106.4(2)	O2	C21	C22A	103.8(3)
C2	C1	P1	124.04(13)	C23	C22	C21	98.7(4)
C2	C1	C6	120.00(15)	C22	C23	C24	103.7(4)
C6	C1	P1	115.90(13)	O2	C24	C23	103.6(2)
C1	C2	C3	119.59(16)	O2	C24	C23A	106.3(2)
C4	C3	C2	120.30(17)	O3	C25	C26	107.0(2)
C3	C4	C5	120.34(16)	C27	C26	C25	105.3(2)
C4	C5	C6	119.76(18)	C26	C27	C28	103.5(2)
C5	C6	C1	120.00(17)	O3	C28	C27	104.1(2)
C8	C7	P1	124.77(13)	C24	C23A	C22A	99.6(4)
C8	C7	C20	119.57(15)	C23A	C22A	C21	104.4(4)

Note: **cat.1** is C_2-symmetric, the coordinated atoms such as P, O and Cl are equivalent,

and prime marks were used in labelling the atoms in Figure 1 for the convenience of discussion.