Electronic Supplementary Information

for

SSynthesis of Cyclic Olefin Copolymers (COCs) by Ethylene Copolymerisations with Cyclooctene, Cycloheptene, and with Tricyclo[6.2.1.0(2,7)]undeca-4-ene: Effect of Cyclic Monomer Structures on Thermal Properties

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1. Additional results for ethylene copolymerisation with cyclooctene, cycloheptene, and with tricyclo[6.2.1.0(2,7)]undeca-4-ene.

Table S1. Copolymerization of ethylene (E) with cyclooctene (COE) by **1-9** - MAO catalysts.[a] Additional results (1).

run	cat. (μmol)	COE conc.[b]/ M	E / atm	temp. / ºC	yield / mg	activity[c]	M_n[d]	M_w/M_n[d]	cont.[e] / mol%	T_g (T_m)[f] / ºC
1	**1** (1.5)	2.5	2	25	78	312	59000	1.35	-	38 (129)
2	**1** (1.0)	5.0	2	25	42.5	255	35200	1.40	-	38 (127)
S1	**1** (1.0)	5.0	2	25	48.4	251	37100	1.53		28 (126)
3	**2** (1.5)	2.5	2	25	74.4	298	32600	1.36	-	40[j]
4	**2** (1.0)	2.5	4	25	124	742	48300	1.29	-	32[j]
S2	**2** (1.0)	2.5	4	25	123	736	52500	1.35	-	31[j]
5	**2** (1.5)	5.0	2	25	57.7	231	20700	1.62	43.7[h]	44[j]
6[g]	**2** (1.5)	5.0	2	25	81.5	326	10000	1.77	-	46 (115)
S3[g]	**2** (1.5)	5.0	2	25	82.0	328	9830	2.03		42 (115)
7	**3** (0.2)	5.0	4	25	146	4380	318000	1.47	22.5	6
26	**3** (0.05)	1.0	4	25	89.2	10700	1260000	2.05	7.0	(70)
27	**3** (0.2)	2.5	4	25	228	6850	863000	1.89	16.1	-15 (32)
S4	**3** (0.2)	2.5	4	25	245	7360	759000	1.37	16.7[i]	-17 (32)
28	**3** (0.2)	2.5	4	50	122	3660	423000	1.49	17.4[i]	-14 (32)
8	**3** (0.5)	5.0	2	25	138	1660	239000	1.57	28.0	32
9[g]	**3** (0.5)	5.0	2	25	202	2420	218000	2.21	-	13[j]
S5	**3** (0.5)	5.0	2	25	241	2890	374000	1.50	-	12[j]
10	**3** (0.5)	7.5	2	25	114	1360	141000	1.57	28.1	36
S6	**3** (0.5)	7.5	2	25	112	1340	131000	1.34	29.3[i]	38
11	**4** (1.0)	2.5	2	25	83.5	501	5600	1.24	-	14[j]
S7	**4** (1.0)	2.5	2	25	72.0	432	6310	1.30		17[j]
12	**4** (1.0)	5.0	2	25	100	602	5700	1.21	-	18[j]
S8	**4** (1.0)	5.0	2	25	90.3	542	4240	1.19		20[j]
13	**5** (0.01)	5.0	4	25	250	150000	1670000	1.72	-	(69)
S9	**5** (0.01)	5.0	4	25	215	129000	1360000	1.78		(70)
14	**5** (0.01)	5.0	2	25	127	76400	1650000	2.52	16.0[i]	-20 (48)
S10	**5** (0.01)	5.0	2	25	103	61900	2430000	2.40	16.0[i]	-20 (46)
15	**5** (0.03)	7.5	2	25	148	29700	1210000	2.30	20.2	-5
S11	**5** (0.03)	7.5	2	25	142	28400	1330000	2.22	20.2	-5.2
16	**6** (0.01)	5.0	4	25	290	174000	1470000	1.48	-	(71)
S12	**6** (0.01)	5.0	4	25	290	174000	1130000	2.06		(71)
17	**6** (0.01)	5.0	2	25	201	121000	3050000	2.15	16.3[i]	-19 (56)
18	**6** (0.02)	7.5	2	25	119	35800	2540000	2.15	20.4	-5.5
S13	**6** (0.02)	7.5	2	25	109	32600	1570000	2.08	20.4	-2.9

Table S1. Continued.

19	**7** (0.01)	5.0	4	25	139	83100	2270000	2.56	2.6	(105)
S14	**7** (0.01)	5.0	4	25	125	75200	2660000	2.48	2.6	(106)
20	**7** (0.01)	5.0	2	25	110	66100	1700000	3.09	-	(92)
S15	**7** (0.01)	5.0	2	25	124	74300	2010000	2.51		(92)
21	**7** (0.01)	7.5	2	25	98.9	59300	1050000	2.30	7.2	-17 (76)
22	**8** (1.0)	5.0	4	25	121	726	143000	1.73		(66)
S16	**8** (1.0)	5.0	4	25	135	810	148000	1.82		(67)
23	**8** (1.0)	2.5	2	25	94.4	566	161000	1.54		(77)[j]
24	**8** (1.0)	5.0	2	25	55.1	331	155000	1.36	9.9	(59)[j]
S17	**8** (1.0)	2.5	2	25	74.7	448	150000	1.56		(76)
25	**9** (0.5)	2.5	2	25	52.1	625	372000	1.24	-	(41)[j]
S18	**9** (0.5)	2.5	2	25	39.3	472	443000	1.25		44[j]
26	**9** (0.5)	5.0	2	25	133	1590	314000	1.39	-	(55)[j]
S19	**9** (0.5)	5.0	2	25	111	1340	371000	1.67		46[j]
27	**10** (0.05)	5.0	2	25	137	16500	290000	2.18	-	(133)
28	**11** (0.01)	2.5	2	25	105	63000	2500	4.12		(103,124)
29	**11** (0.02)	5.0	2	25	122	36600	1700	3.95		(108)
S20	**11** (0.02)	5.0	2	25	119	35700	1600	4.39		(110)
30	**11** (0.05)	7.5	2	25	96.2	11500	820	5.18		(98)
S21	**11** (0.05)	7.5	2	25	115	13800	1100	4.08		(99)

[a]Conditions: toluene + COE total 10 mL, d-MAO (prepared by removing toluene and $AlMe_3$ from the commercially available TMAO-S) 3.0 mmol. [b] Initial COE concentration (mol/L). [c]Activity = kg-polymer/mol-M·h (M = Ti or Zr). [d]GPC data in *o*-dichlorobenzene vs polystyrene standards. [e]COE content (mol%) estimated by ^{13}C NMR spectra. [f]By DSC thermograms. [g]Al^{i}Bu$_3$ (500 equiv) and $[Ph_3C][B(C_6F_5)_4]$ (1.5 equiv) were used instead of d-MAO. [h]COE content in the whole polymer estimated by the ^{13}C NMR spectrum. [i]Estimated on the basis of the plots of T_g and COE content. [j]Small T_m shoulder at ca.120 ºC was also observed on the DSC thermogram.

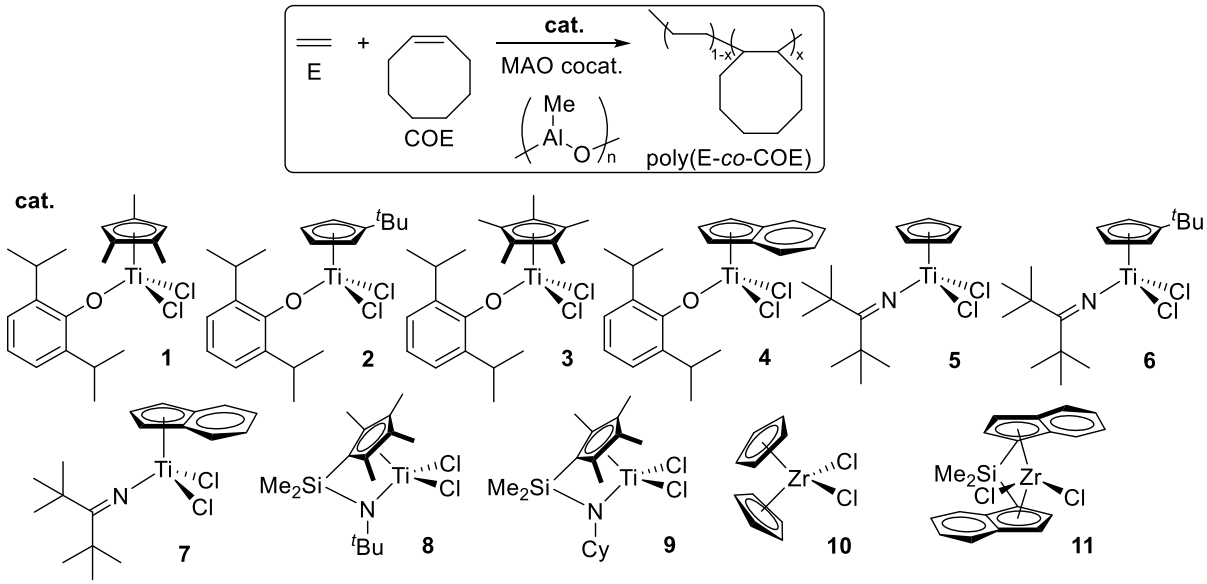


Table S2. Copolymerization of ethylene (E) with cyclooctene (COE) by Cp*$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**3**) - MAO catalyst (ethylene 4 atm, COE 5.0 M, 25 ºC).[a] Additional results (2).

run	**3** / μmol	MAO / mmol	time / min	yield / mg	activity[b]	M_n[c] ×10^{-4}	M_w/ M_n[c]	cont.[d] / mol%	T_g (T_m)[e] / ºC
35	0.5	1.0	10	87.4	1050	23.4	1.31	28.9[f]	36
S22	0.5	1.0	10	84.8	1020	22.5	1.32	28.7[f]	35
8	0.5	3.0	10	138	1660	23.9	1.57	28.0	32
36	0.5	5.0	10	171	2050	37.9	1.53	27.5[f]	30
S23	0.5	5.0	10	195	2340	19.9	1.63	24.5[f]	17
36	0.5	3.0	5	111	2670	31.9	1.34	27.7[f]	31
S24	0.5	3.0	5	114	2730	30.5	1.38	28.7[f]	35
8	0.5	3.0	10	138	1660	23.9	1.57	28.0	32
38	0.5	3.0	15	193	1550	31.9	1.41	27.5[f]	30
S25	0.5	3.0	15	222	1770	26.1	1.55	27.5[f]	30

[a]Conditions: toluene + COE total 10 mL, COE 5.0 M, d-MAO (prepared by removing toluene and $AlMe_3$ from the commercially available TMAO-S). [b]Activity = kg-polymer/mol-Ti·h. [c]GPC data in *o*-dichlorobenzene vs polystyrene standards. [e]COE content (mol%) estimated by ^{13}C NMR spectra. [e]By DSC thermograms. [f]Estimated on the basis of the plots of T_g and COE content.

Table S3. Copolymerization of ethylene (E) with cycloheptene (CHP) by Cp*$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**3**)–d-MAO catalyst.[a] Additional results.

run	cat. **3** / μmol	CHP conc.[b]/ M	E / atm	temp / ºC	yield / mg	activity[c]	M_n[d] ×10^{-4}	M_w/ M_n[d]	cont.[e] / mol%	T_g (T_m)[f] / ºC
43	0.001	1.0	4	25	77.7	466000	244	1.36	10.3	-67
44	0.01	2.5	2	25	69.6	41800	132	1.77	32.3	-5
S26	0.01	2.5	2	25	68.4	41000	164	1.58	31.7[g]	-10
45	0.01	5.0	2	25	63.3	38000	174	1.54	35.7	9
S27	0.01	5.0	2	25	62.4	37400	201	1.58	35.2[g]	9
46	0.01	5.0	4	50	161	96500	308	1.34	32.8[g]	-4
47	0.02	7.5	2	25	92.6	27800	178	1.54	37.1	17

[a]Conditions: toluene + CHP total 10 mL, d-MAO 3.0 mmol, 10 min. [b]Initial CHP concentration (mol/L). [c]Activity= kg-polymer/mol-Ti·h. [d]GPC data in *o*-dichlorobenzene vs polystyrene standards. [e]CHP content (mol%) estimated by ^{13}C NMR spectra. [f]By DSC thermograms. [g]Estimated on the basis of the plots of T_g and CHP content.

Table S4. Copolymerization of ethylene (E) and tricyclo[6.2.1.0(2,7)]undeca-4-ene (TCUE) by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) (**1**)–d-MAO catalyst.[a] Additional results.

run	cat. **1** / μmol	TCUE conc.[b]/ M	E / atm	yield / mg	activity[c]	M_n[d] $\times 10^{-4}$	M_w/M_n[d]	cont.[e] / mol %	T_g (T_m)[f] / ºC
48	0.02	1.0	4	74.8	22400	20.4	1.53	19.5	43
49	0.1	1.0	2	98.7	5920	6.16	1.52	26.5	64
50	0.5	2.5	2	155	1860	2.34	1.68	35.1	116
S28	0.5	2.5	2	140	1670	2.08	2.04	34.6[g]	111
51	0.8	5.0	2	204	1530	1.38	2.10	38.8	130
S29	0.8	5.0	2	231	1730	1.65	1.81	39.4[g]	134
52	0.5	5.0	2	222	1640	1.59	2.02	40.0[g]	137

[a]Conditions: toluene + TCUE total 10 mL, 25 ºC, 10 min, d-MAO (prepared by removing toluene and $AlMe_3$ from the commercially available TMAO-212) 3.0 mmol. [b]Initial TCUE concentration (mol/L). [c]Activity= kg-polymer/mol-Ti·h. [d]GPC data in *o*-dichlorobenzene vs polystyrene standards. [e]TCUE content (mol%) estimated by ^{13}C NMR spectra. [f]By DSC thermograms. [g]Estimated on the basis of the plots of T_g and TCUE content. [h]d-MAO 2.0 mmol. [i]d-MAO 1.0 mmol.

2. Selected ^{13}C NMR spectra for resultant copolymers including assignment of resonances and estimation of comonomer contents.

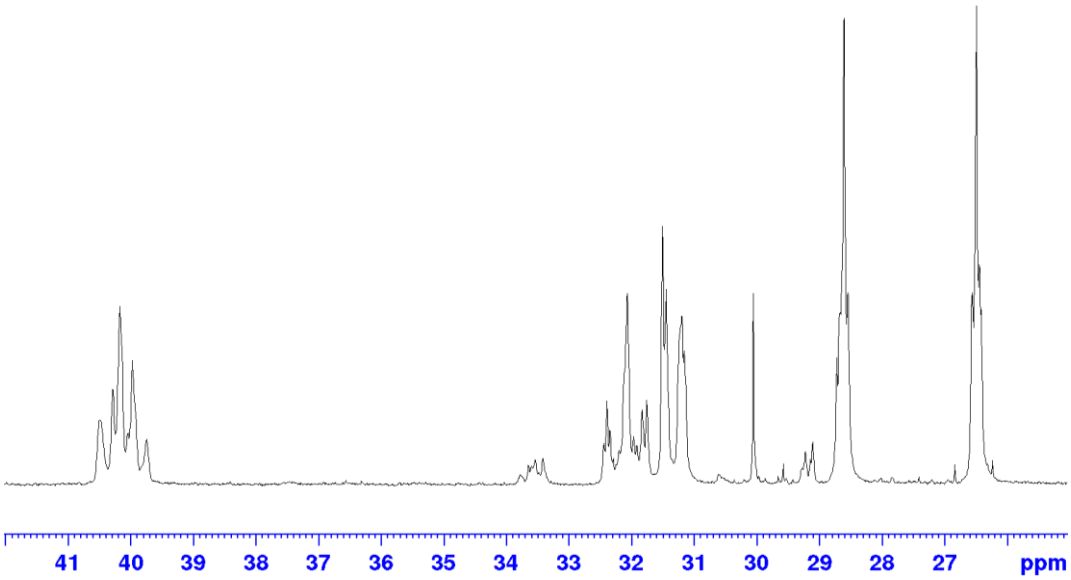


Figure S1. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-COE) prepared by (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-Cl$_2$C$_6$H$_3$) (**2**) - MAO catalyst [run 5, Table 1, COE 43.7 mol% (COE content in the whole polymer)].

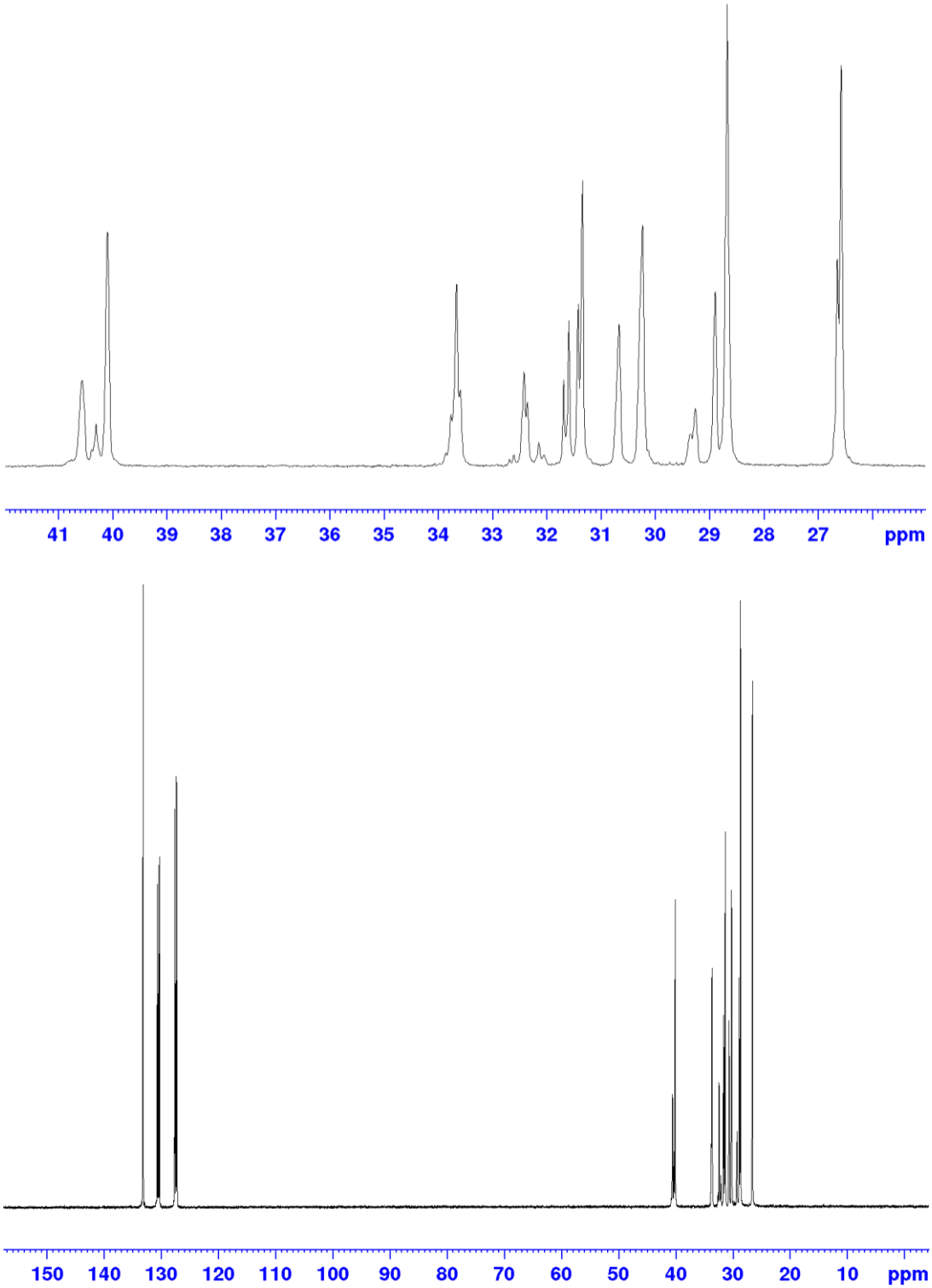


Figure S2. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4 at 130 ºC) for poly(ethylene-*co*-COE) prepared by Cp*$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**3**) - MAO catalyst (run 7, Table 1, COE 22.5 mol%).

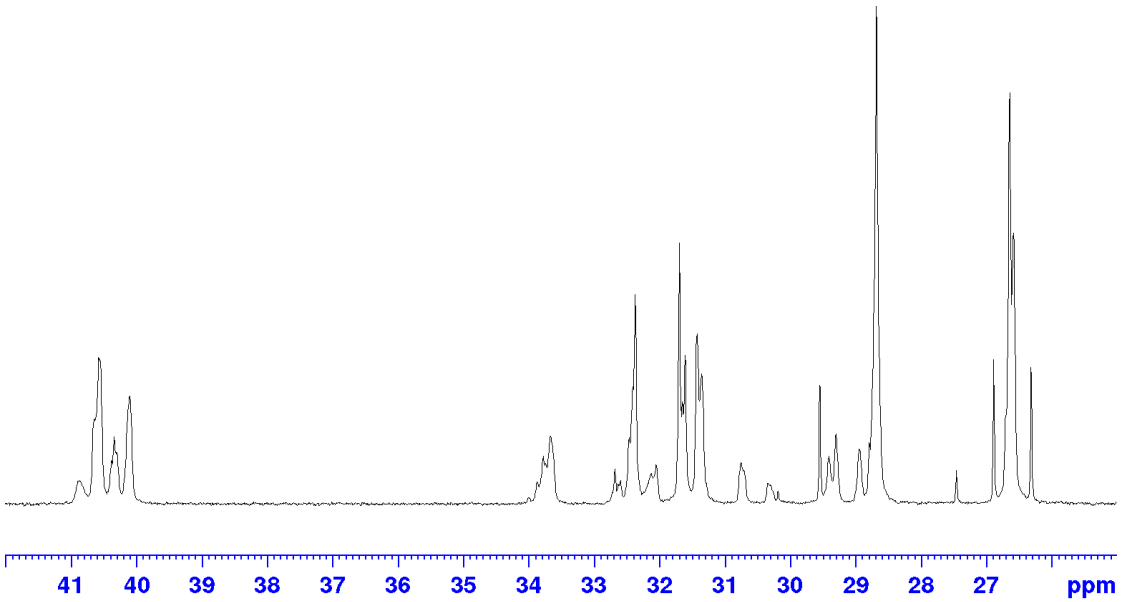


Figure S3. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4 at 130 ºC) for poly(ethylene-*co*-COE) prepared by Cp*$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**3**) - MAO catalyst (run 8, Table 1, COE 28.0 mol%).

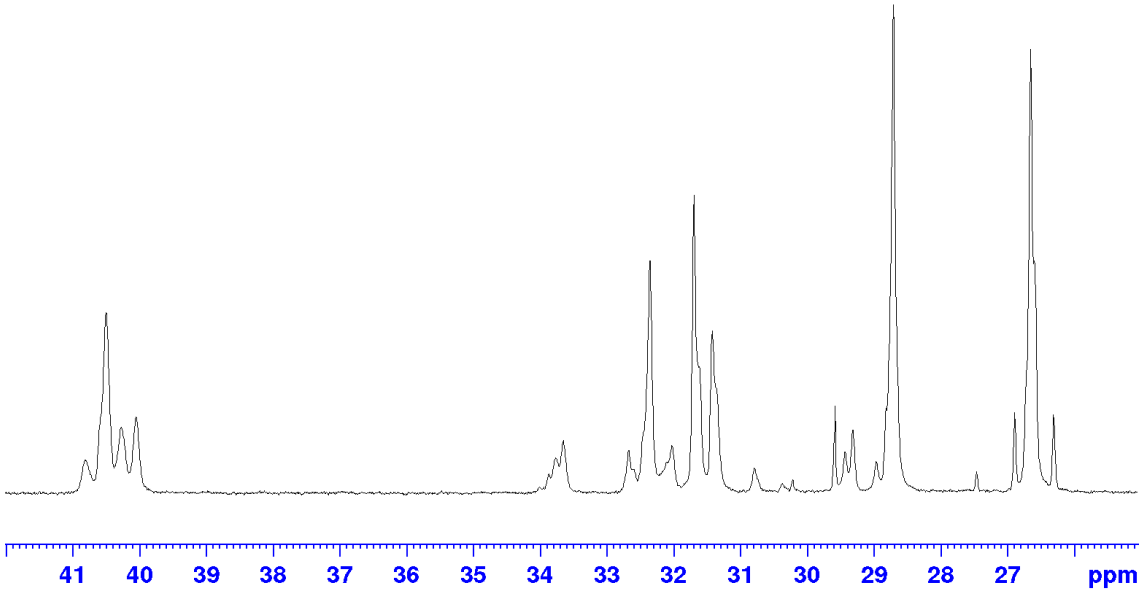


Figure S4. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4 at 130 ºC) for poly(ethylene-*co*-COE) prepared by Cp*$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**3**) - MAO catalyst (run 10, Table 1, COE 28.1 mol%).

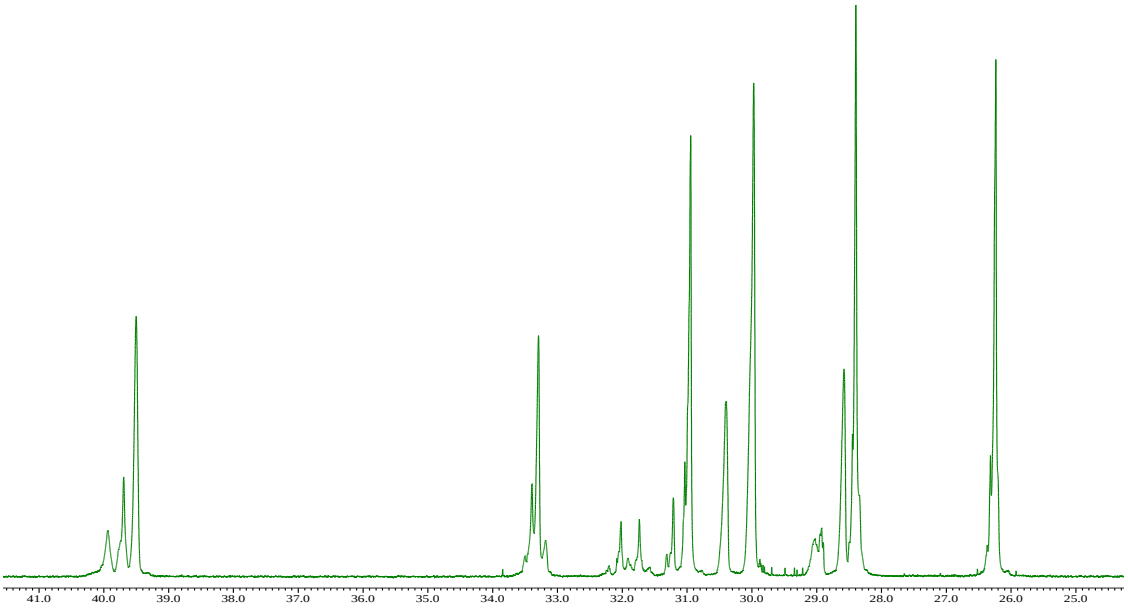


Figure S5. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4/bromobenzene-d_5 at 150 ºC) for poly(ethylene-*co*-COE) prepared by $CpTiCl_2(N{=}C^tBu_2)$ (**5**) - MAO catalyst (run 15, Table 1, COE 20.2 mol%).

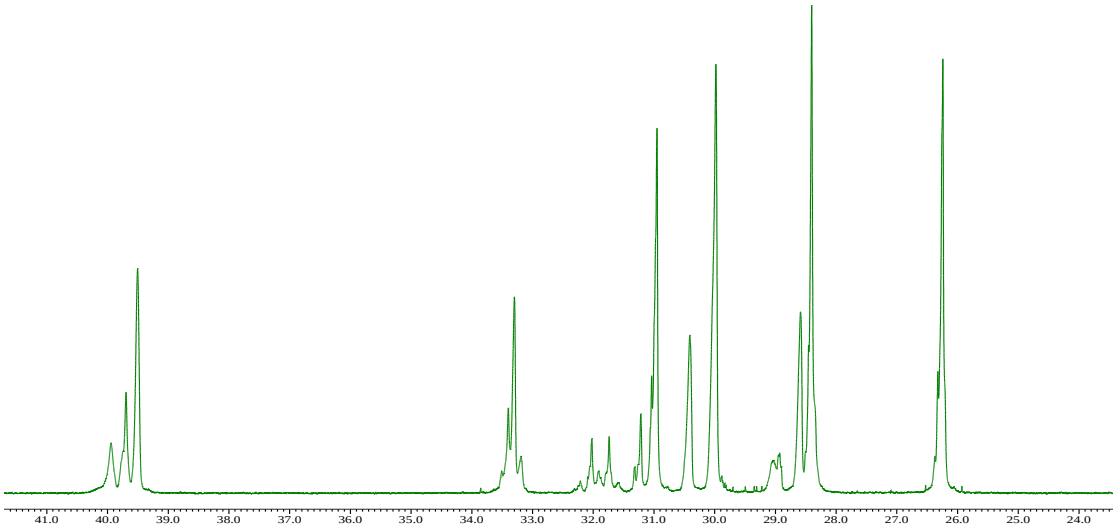


Figure S6. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4/bromobenzene-d_5 at 150 ºC) for poly(ethylene-*co*-COE) prepared by $(^tBuC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**6**) - MAO catalyst (run 18, Table 1, COE 20.4 mol%).

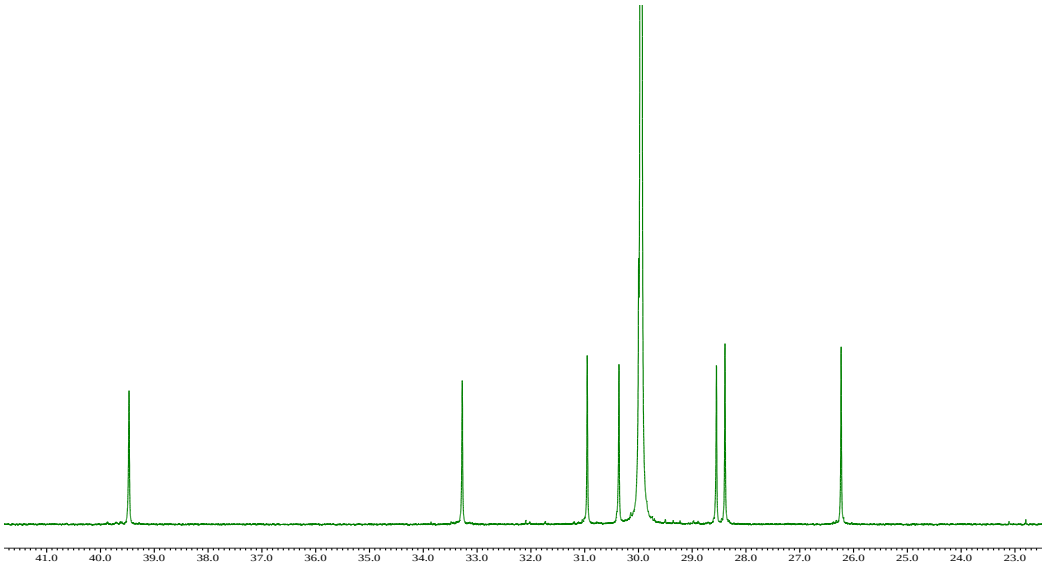


Figure S7. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4/bromobenzene-d_5 at 150 ºC) for poly(ethylene-*co*-COE) prepared by (indenyl)$TiCl_2$(N=C^{t}Bu$_2$) (**7**) - MAO catalyst (run 19, Table 1, COE 2.6 mol%).

Figure S8. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4/bromobenzene-d_5 at 150 ºC) for poly(ethylene-*co*-COE) prepared by (indenyl)$TiCl_2$(N=C^{t}Bu$_2$) (**7**) - MAO catalyst (run 21, Table 1, COE 7.2 mol%).

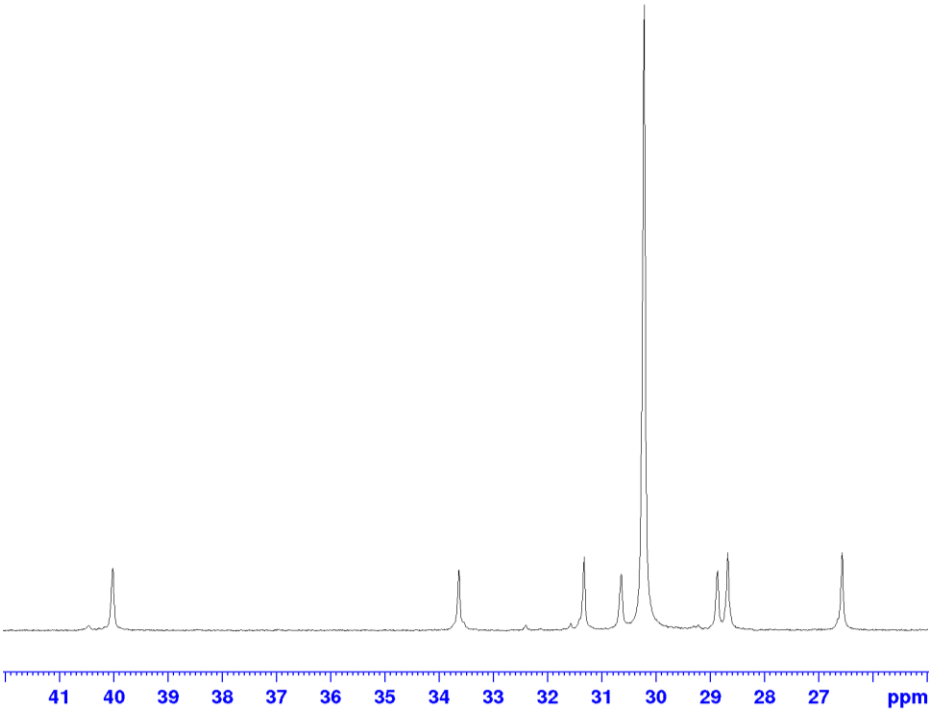


Figure S9. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4 at 130 ºC) for poly(ethylene-*co*-COE) prepared by Cp*$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**3**) - MAO catalyst (run 31, Table 2, COE 7.0 mol%).

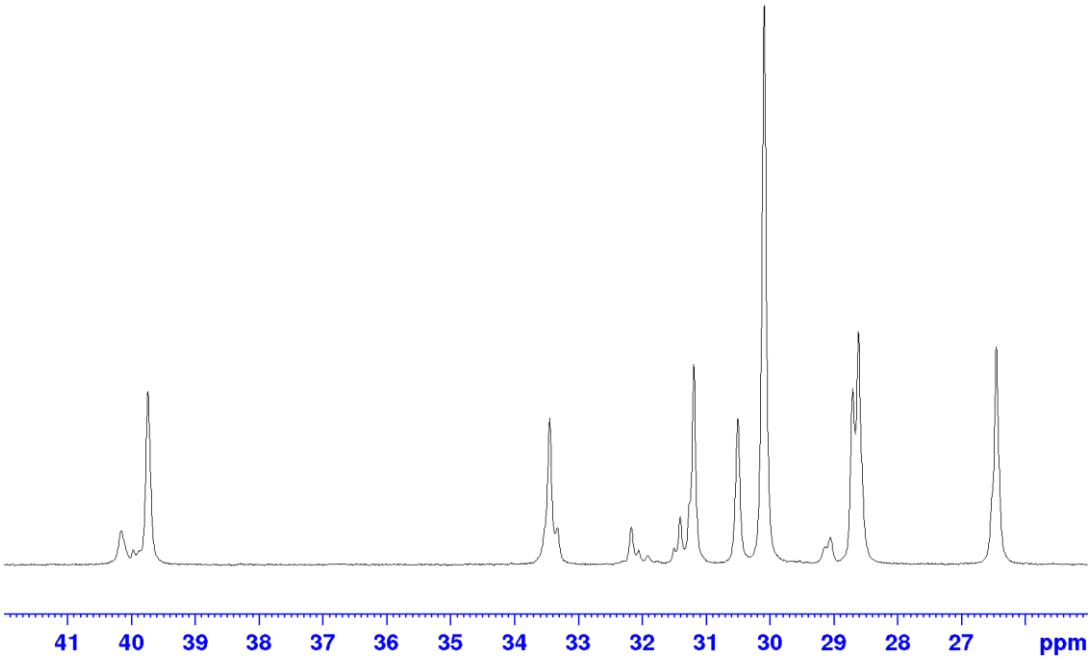


Figure S10. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-COE) prepared by Cp*$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**3**) - MAO catalyst (run 32, Table 2, COE 16.1 mol%).

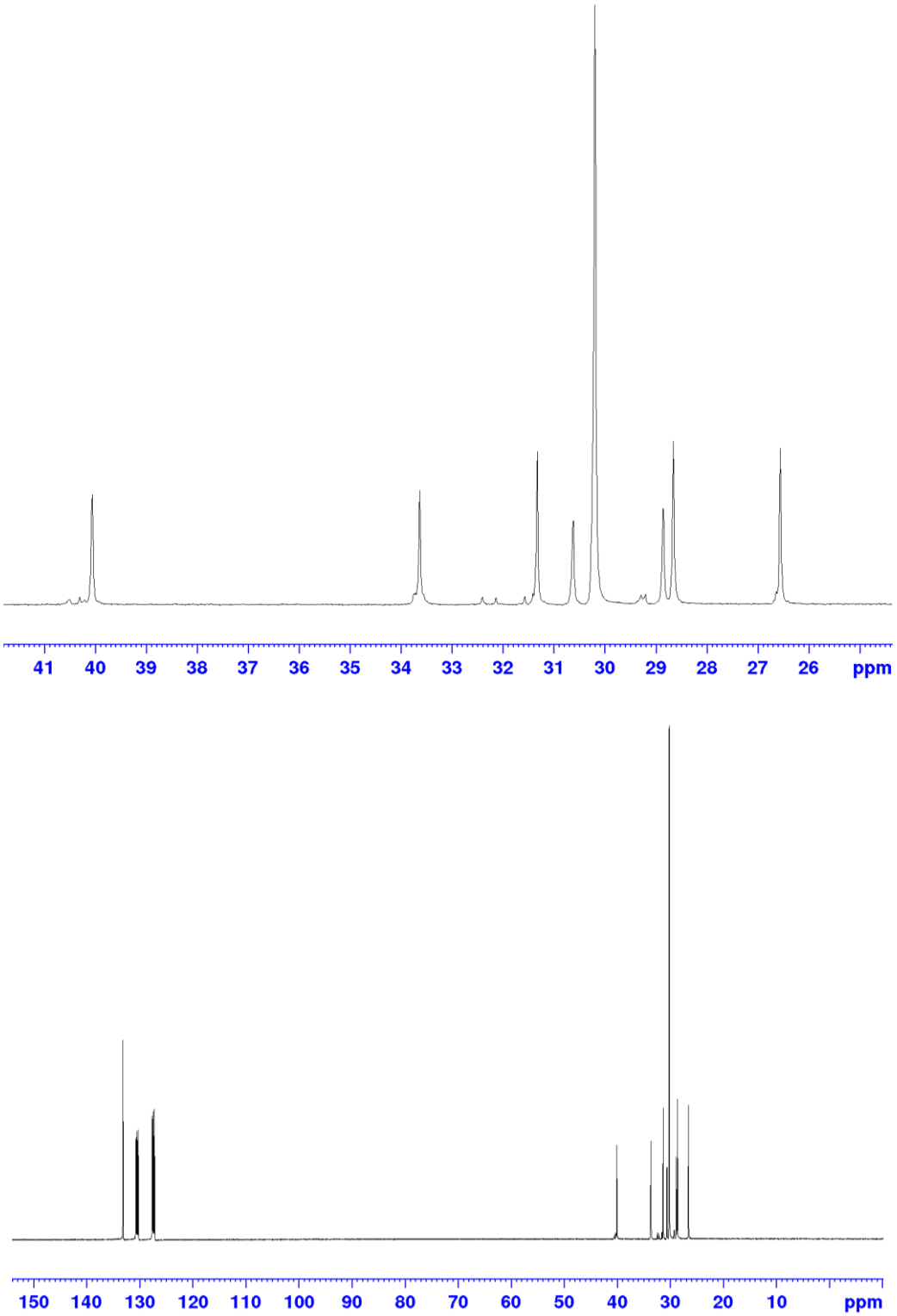


Figure S11. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4 at 130 ºC) for poly(ethylene-*co*-COE) prepared by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**8**) - MAO catalyst (run 24, Table 1, COE 9.9 mol%).

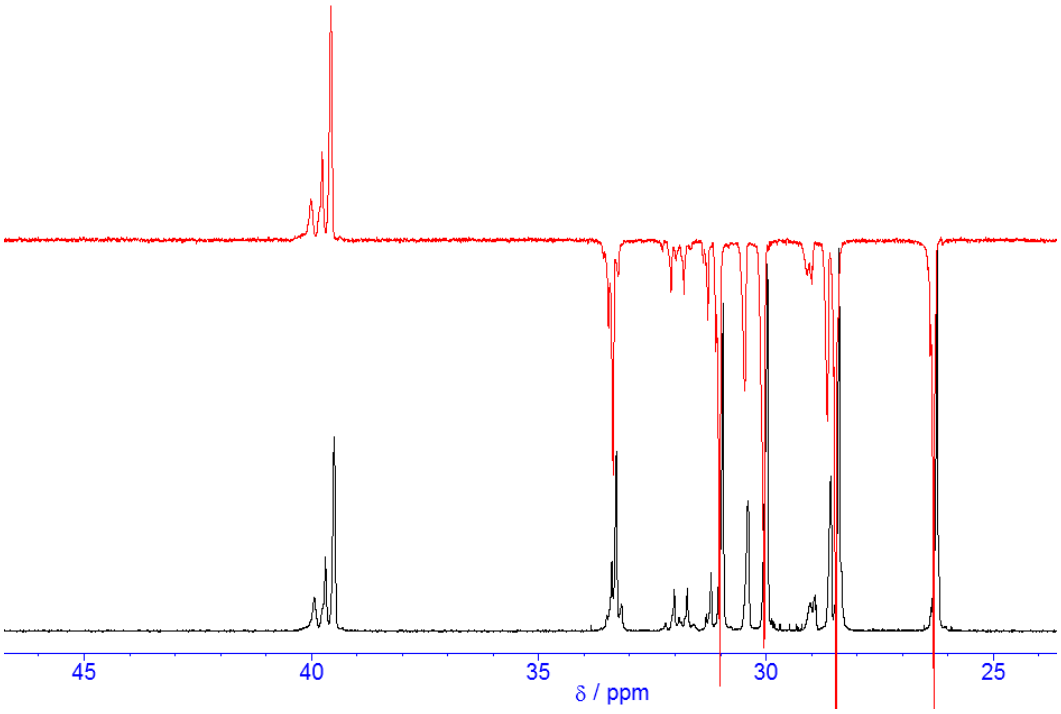
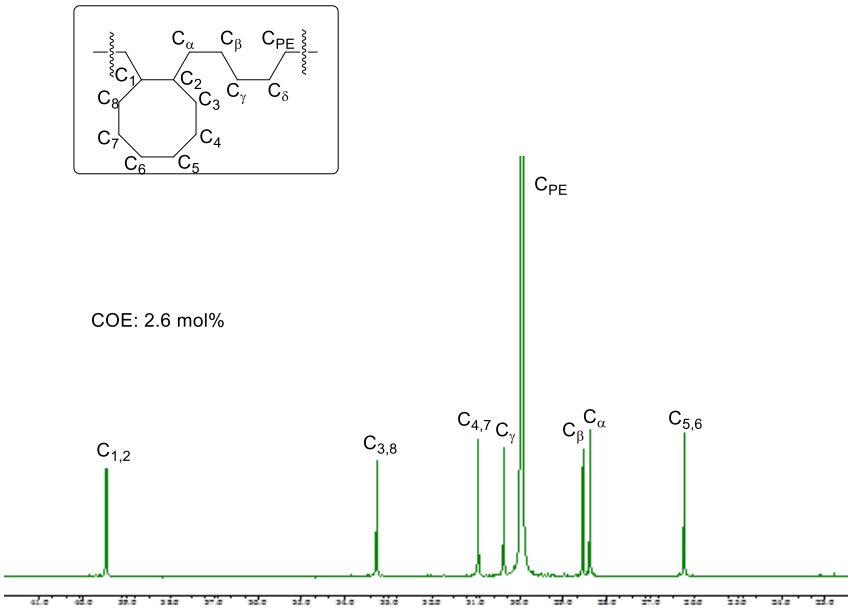


Figure S12. ^{13}C NMR and the dept spectrum (in *o*-dichlorobenzene-d_4/bromobenzene-d_5 at 150 ºC) for poly(ethylene-*co*-COE) prepared by $CpTiCl_2(N{=}C^tBu_2)$ (**5**) - MAO catalyst (run 15, Table 1, COE 20.2 mol%).



(spectrum, run 19, Table 1)

$$\text{COE (mol\%)} = \frac{(C_{1,2} + C_{3,8} + C_{4,7} + C_{5,6})/8}{(C_{1,2} + C_{3,8} + C_{4,7} + C_{5,6})/8 + (C_\alpha + C_\beta + C_\gamma + C_{PE})/2} \times 100$$

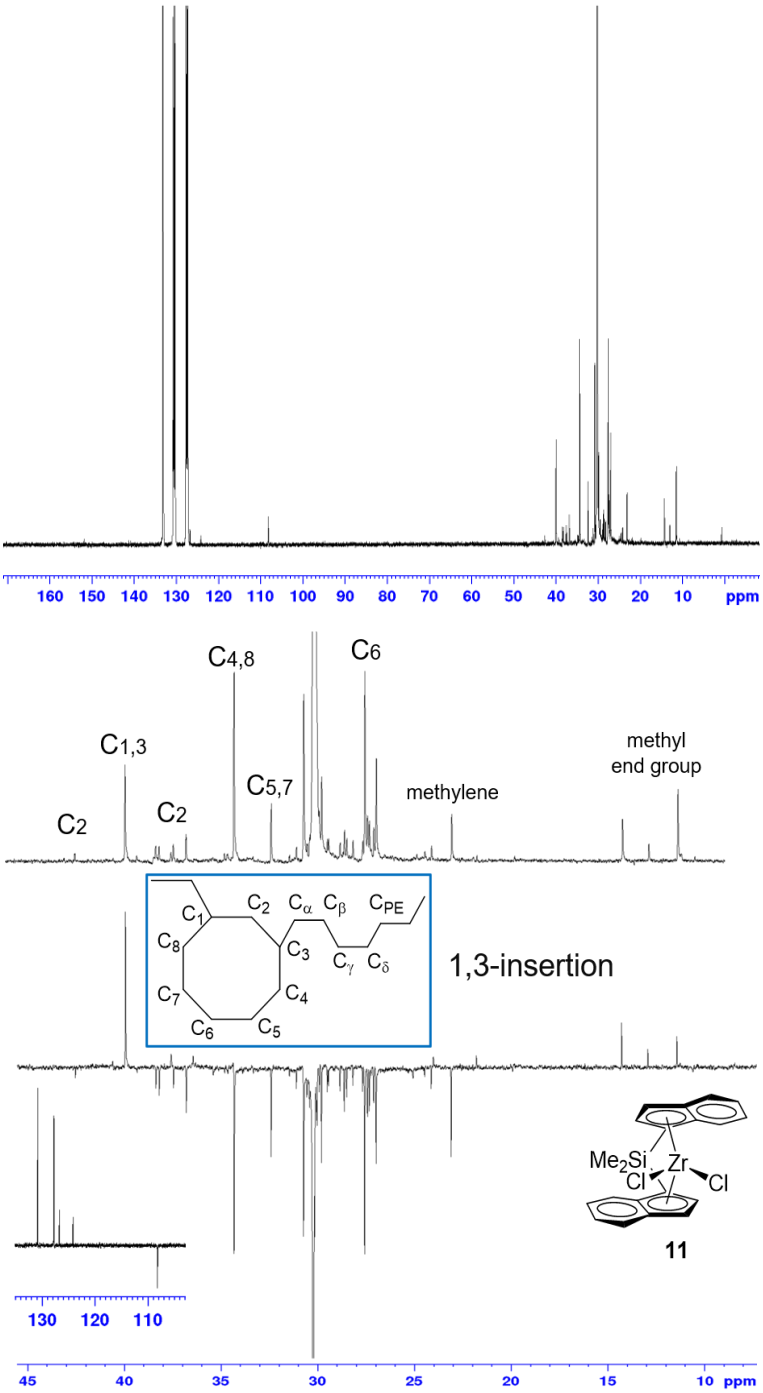


Figure S13. ^{13}C NMR and the dept spectrum (in *o*-dichlorobenzene-d_4 at 110 ºC) for poly(ethylene-*co*-COE) prepared by $[Me_2Si(Ind)_2]ZrCl_2$ (**11**) - MAO catalyst (run 28, Table 1).

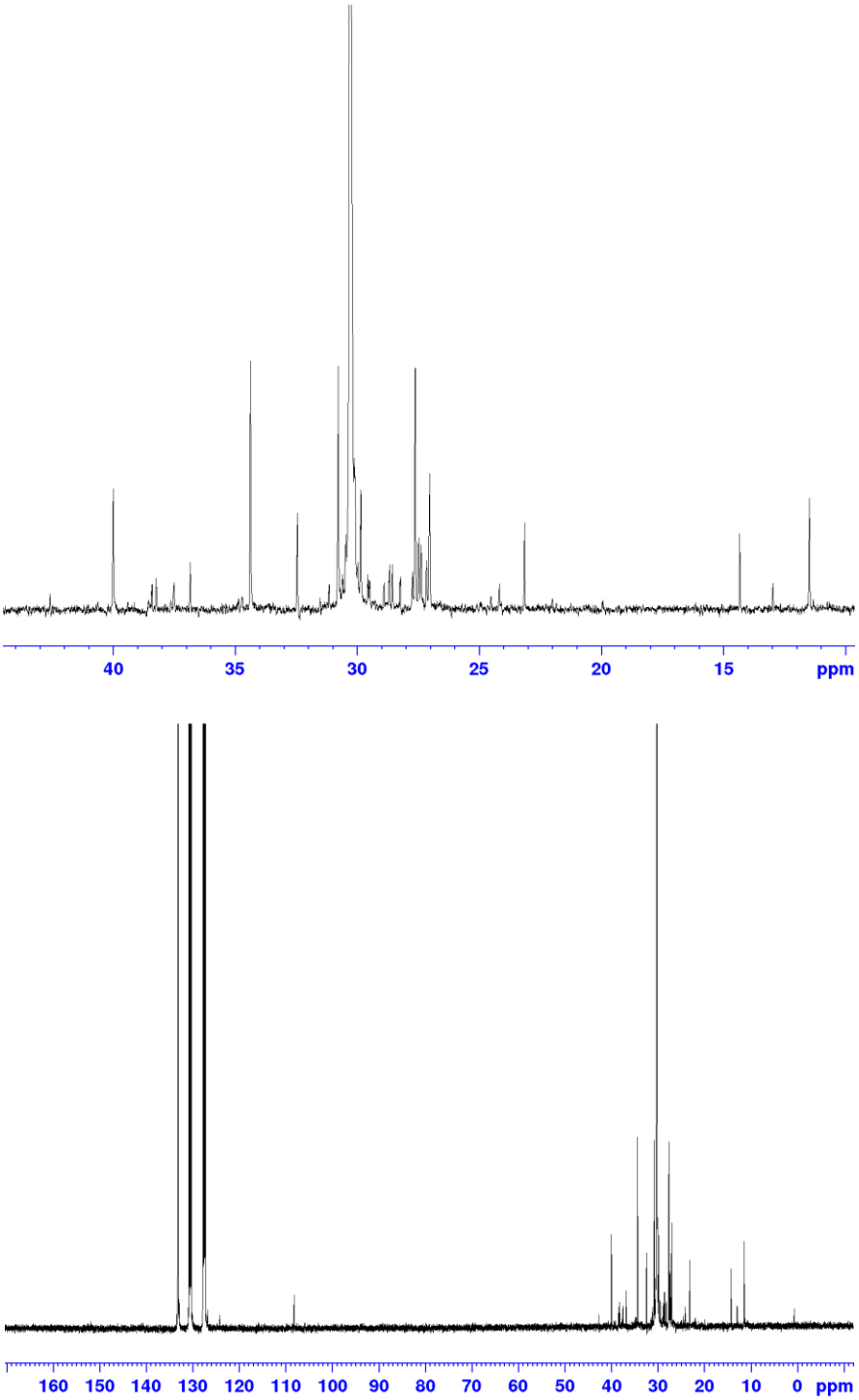


Figure S14. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4 at 110 ºC) for poly(ethylene-*co*-COE) prepared by $[Me_2Si(Ind)_2]ZrCl_2$ (**11**) - MAO catalyst (run 29, Table 1).

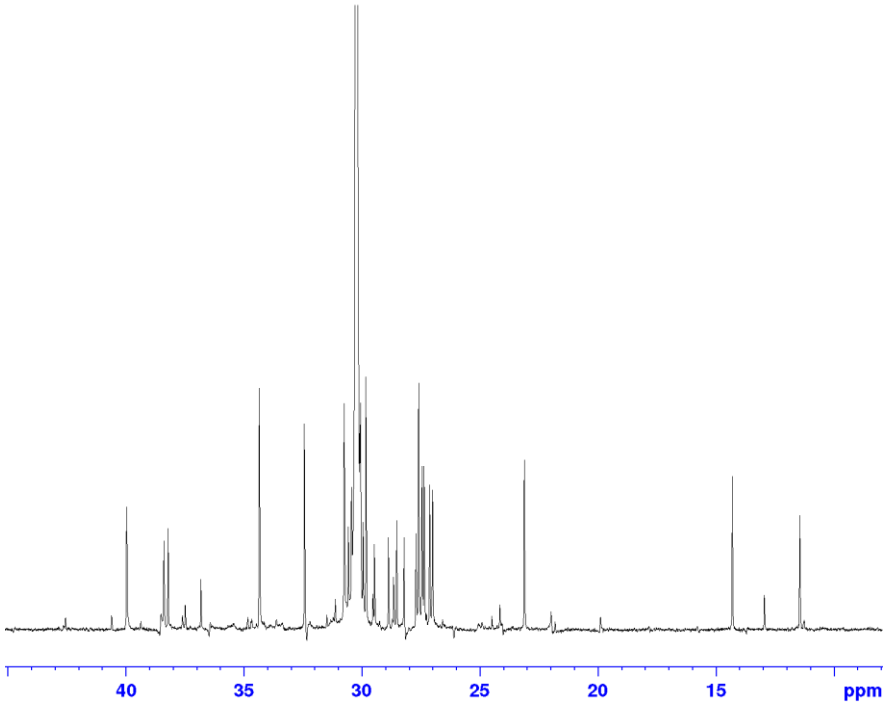


Figure S15. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4 at 110 ºC) for poly(ethylene-*co*-COE) prepared by $[Me_2Si(Ind)_2]ZrCl_2$ (**11**) - MAO catalyst (run S21).

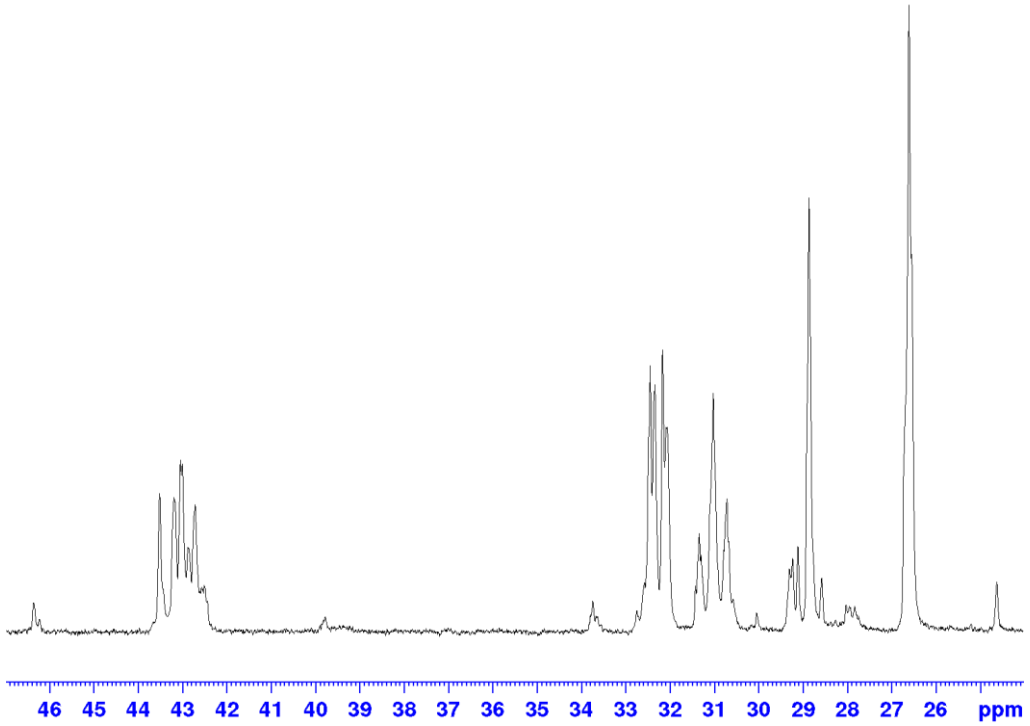


Figure S16. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-CHP) prepared by ($^{t}BuC_5H_4$)$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**2**) - MAO catalyst (run 40, Table 3, CHP 38.6 mol%).

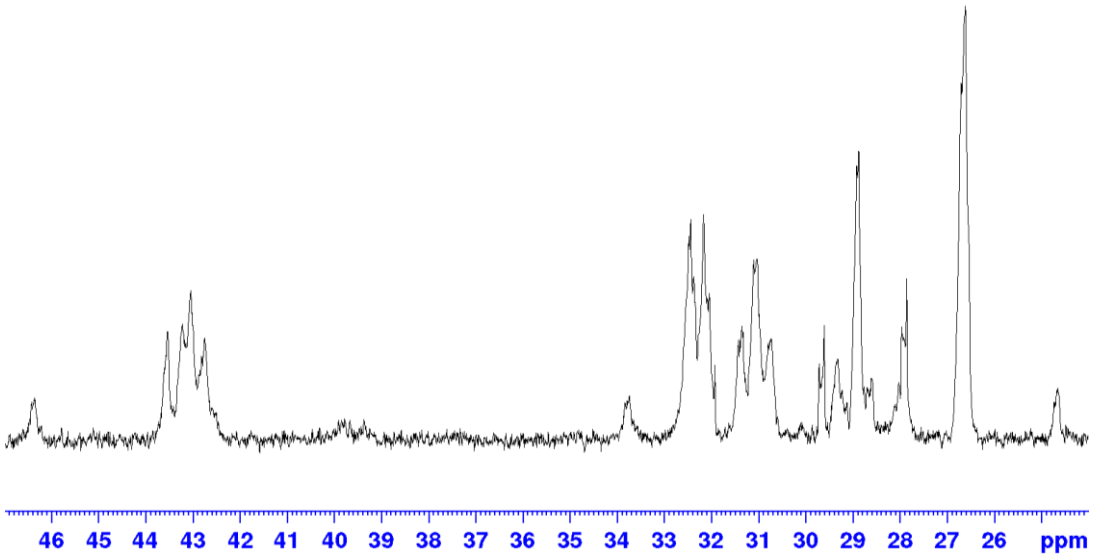


Figure S17. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-CHP) prepared by ($^{t}BuC_5H_4$)$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**2**) - MAO catalyst (run 42, Table 3, CHP 40.8 mol%).

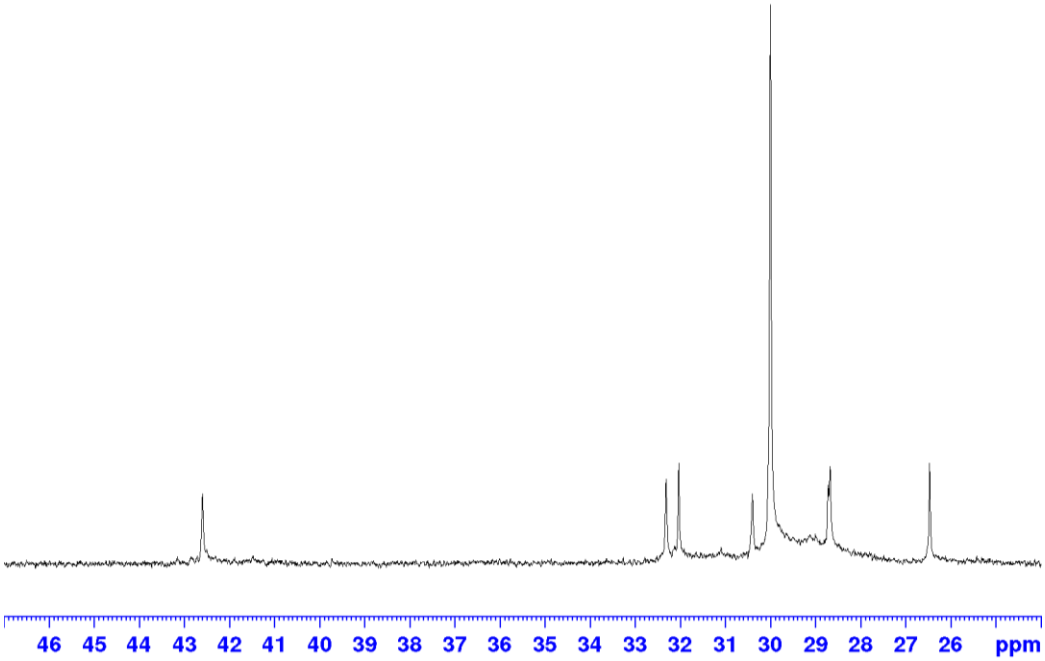


Figure S18. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4 at 130 ºC) for poly(ethylene-*co*-CHP) prepared by Cp*$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**3**) - MAO catalyst (run 43, Table 3, CHP 10.3 mol%).

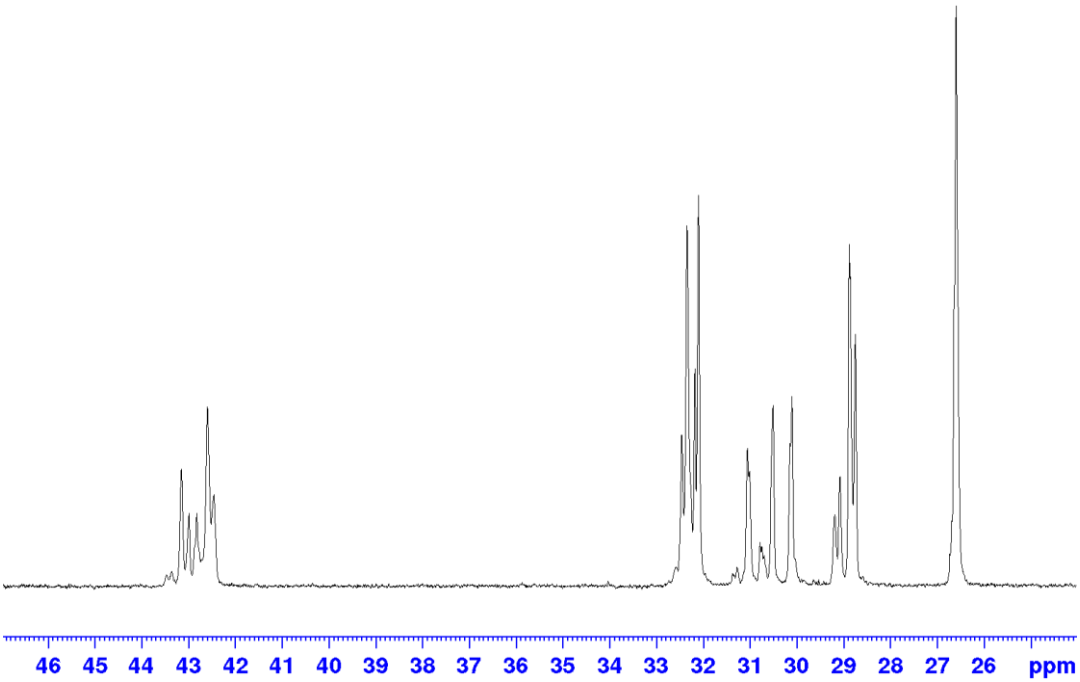


Figure S19. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-CHP) prepared by Cp*$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**3**) - MAO catalyst (run 44, Table 3, CHP 32.3 mol%).

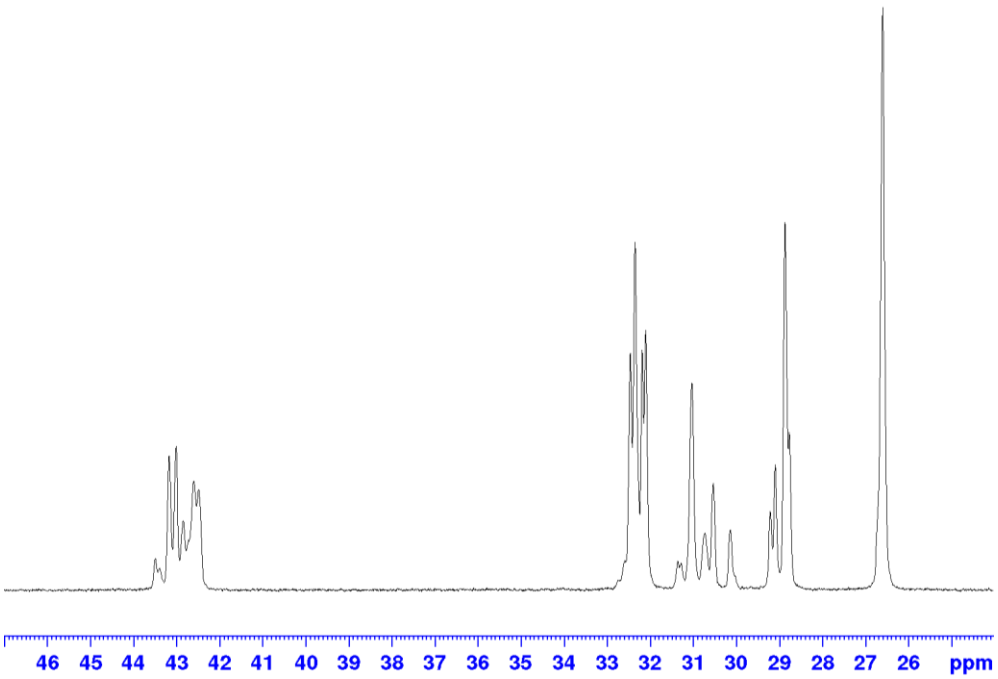


Figure S20. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-CHP) prepared by Cp*$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**3**) - MAO catalyst (run 45, Table 3, CHP 35.7 mol%).

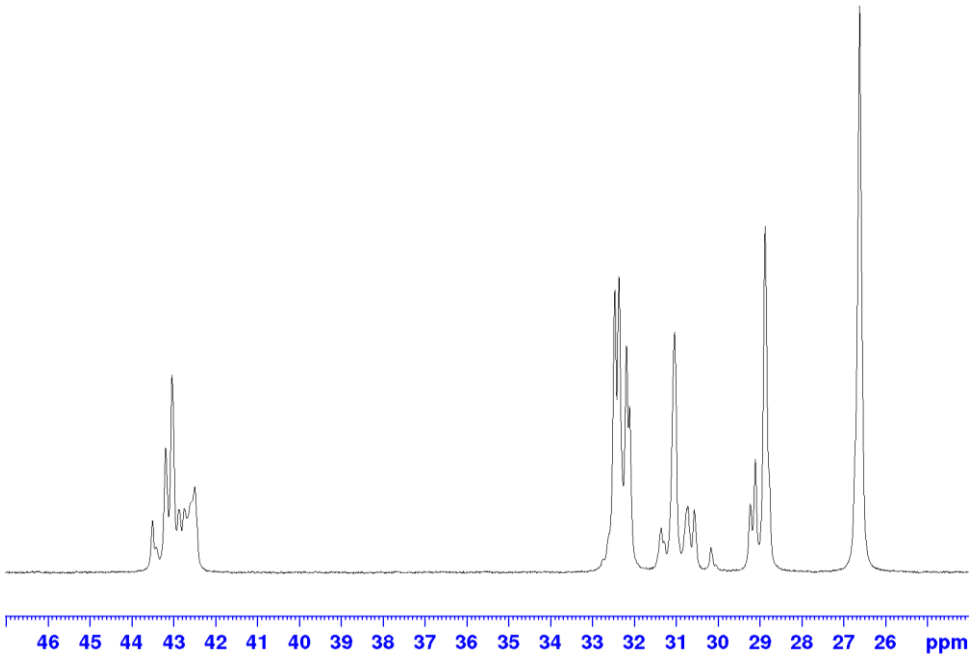


Figure S21. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-CHP) prepared by Cp*$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**3**) - MAO catalyst (run 47, Table 3, CHP 37.1 mol%).

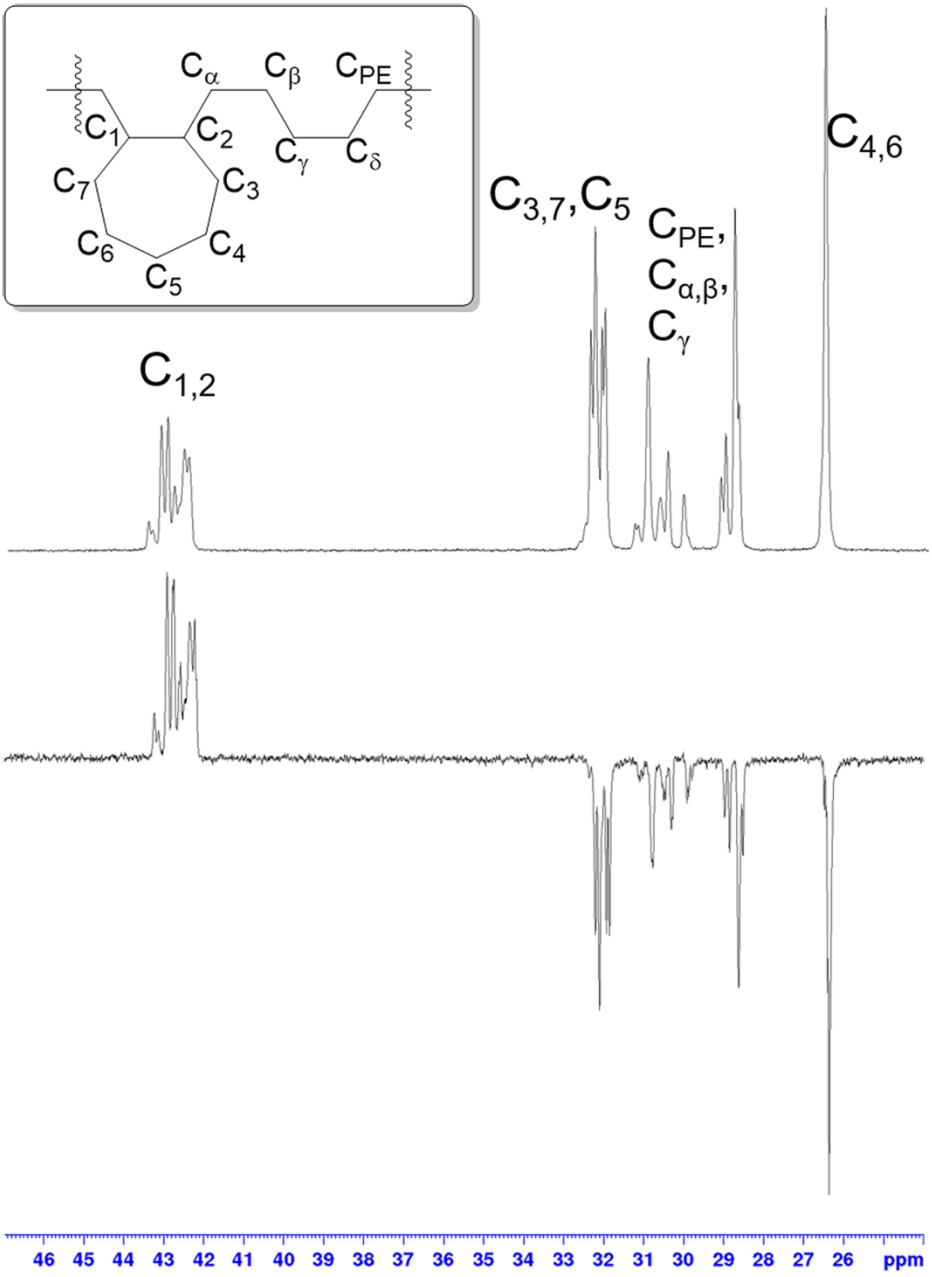


Figure S22. ^{13}C NMR and the dept spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-CHP) prepared by Cp*TiCl$_2$(O-2,6-Cl$_2$C$_6$H$_3$) (**3**) - MAO catalyst (run 45, Table 3, CHP 35.7 mol%).

$$\text{CHP (mol\%)} = \frac{(C_{1,2} + C_{7,3} + C_{4,6} + C_5)/7}{(C_{1,2} + C_{7,3} + C_{4,6} + C_5)/7 + (C_{\alpha,\beta} + C_\gamma + C_{PE})/2} \times 100$$

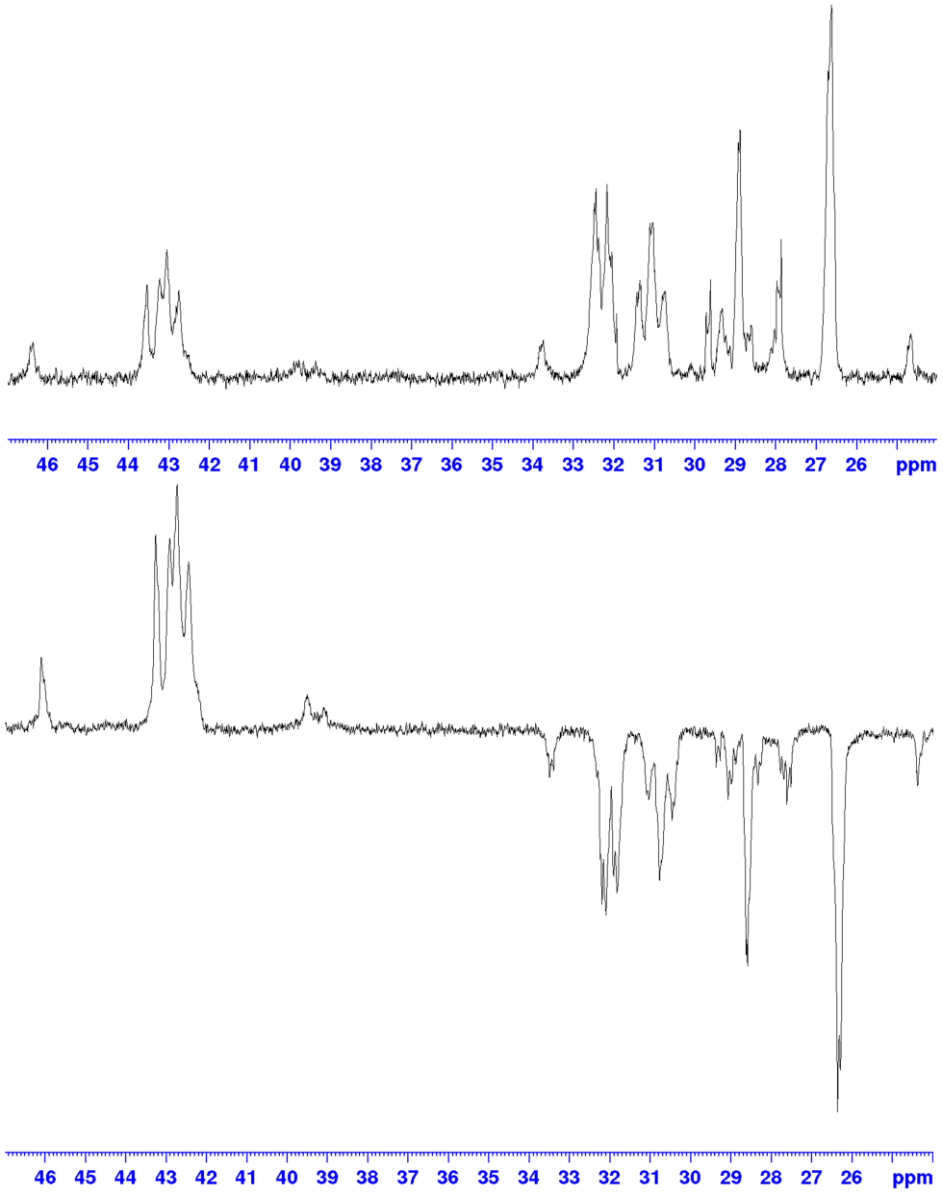


Figure S23. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) and the dept spectrum for poly(ethylene-*co*-CHP) prepared by ($^{t}BuC_5H_4$)$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**2**) - MAO catalyst (run 42, Table 3, CHP 40.8 mol%).

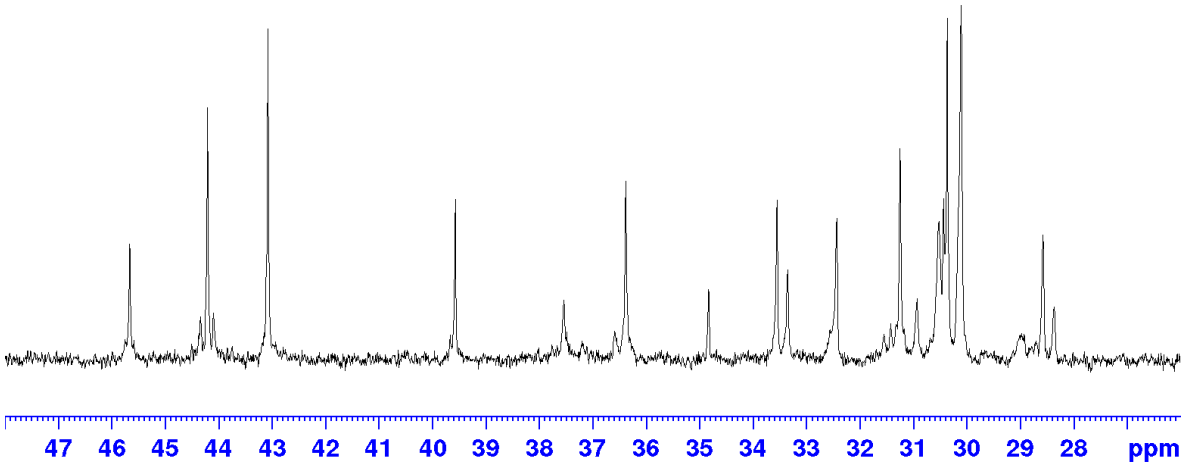


Figure S24. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-TCUE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**1**) - MAO catalyst (run 48, Table 4, TCUE 19.5 mol%).

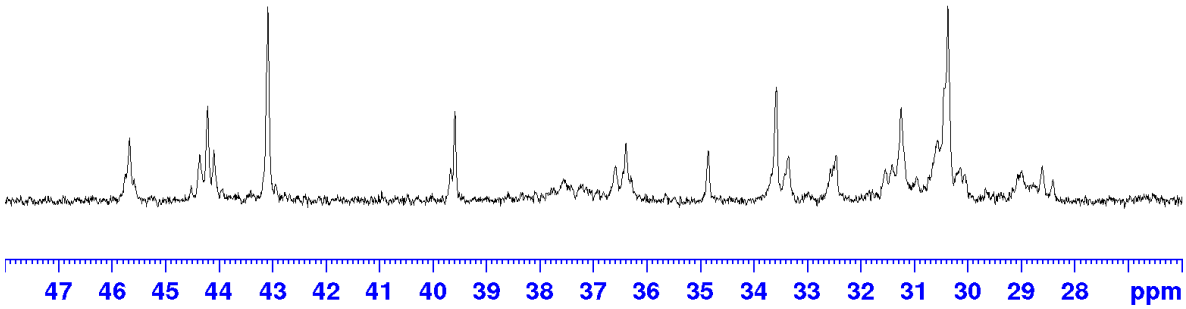


Figure S25. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-TCUE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**1**) - MAO catalyst (run 49, Table 4, TCUE 26.5 mol%).

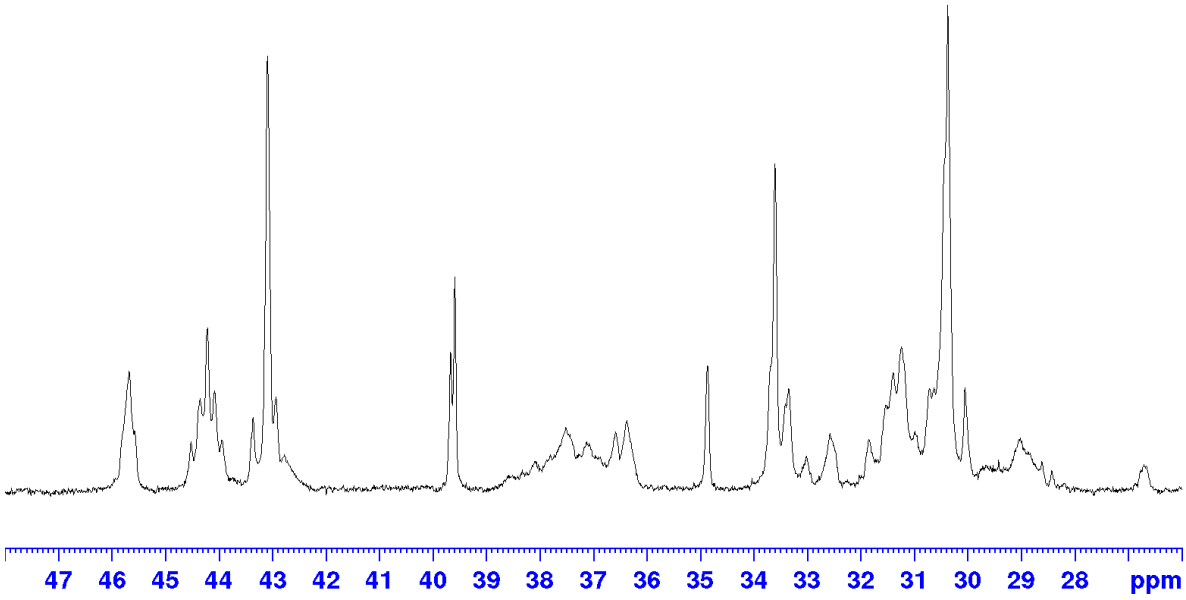


Figure S26. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-TCUE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**1**) - MAO catalyst (run 50, Table 4, TCUE 35.1 mol%).

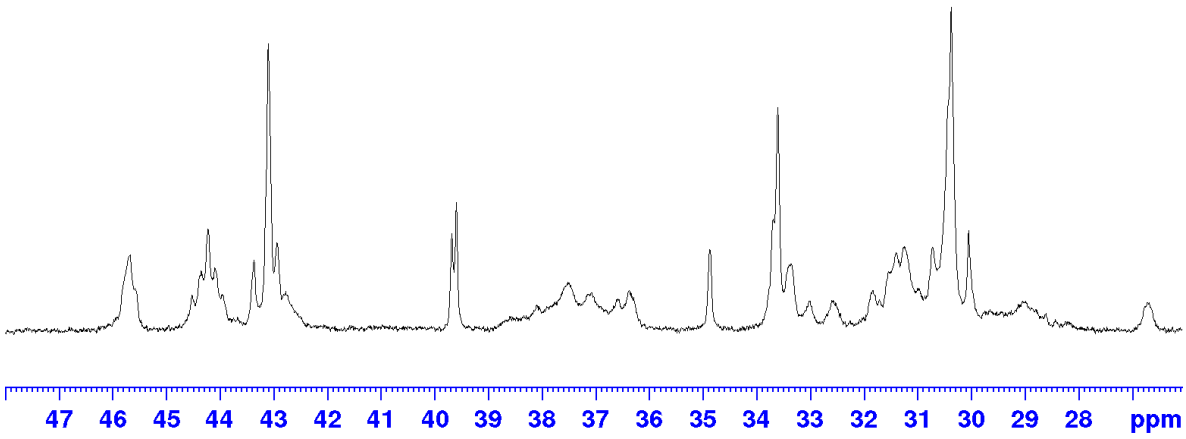


Figure S27. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-TCUE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**1**) - MAO catalyst (run 51, Table 4, TCUE 38.8 mol%).

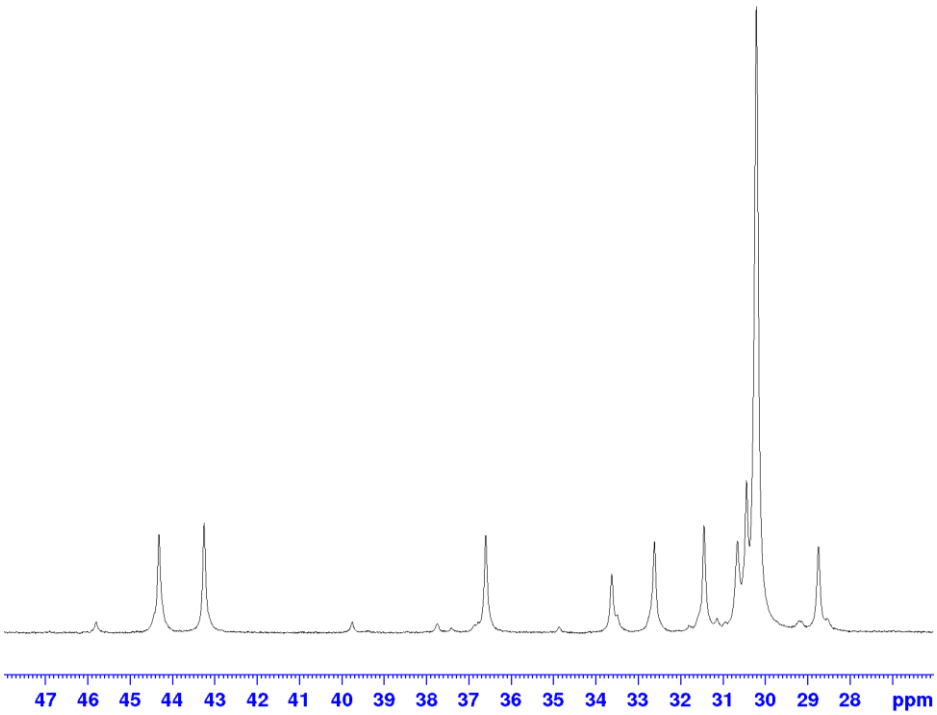


Figure S28. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4 at 130 ºC) for poly(ethylene-*co*-TCUE) prepared by $CpTiCl_2(N{=}C^tBu_2)$ (**5**) - MAO catalyst (run 56, Table 4, TCUE 9.4 mol%).

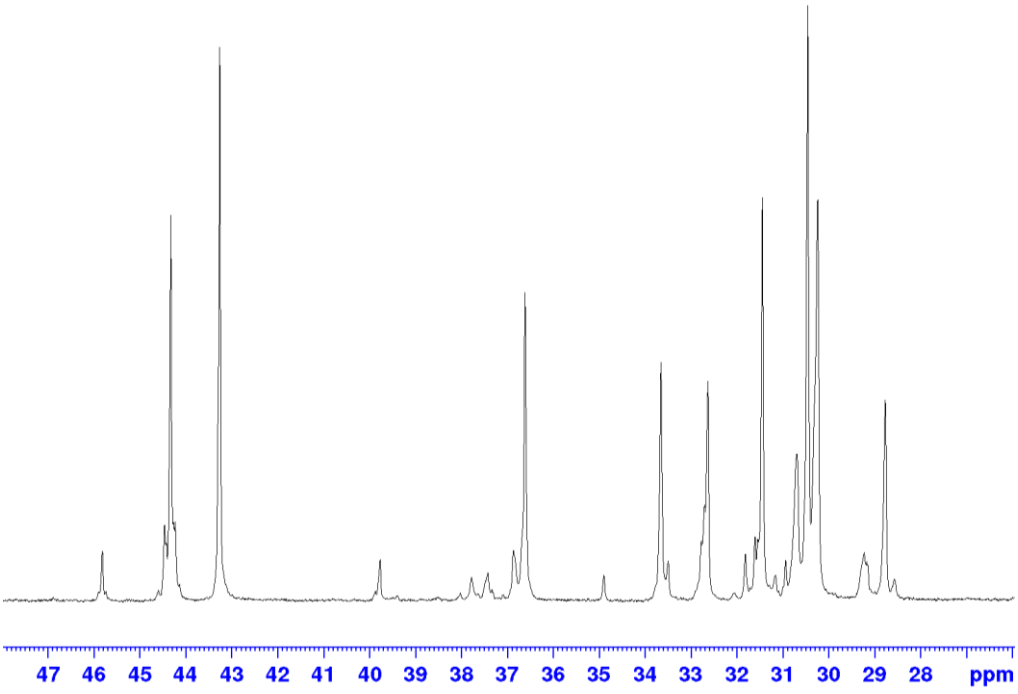


Figure S29. ^{13}C NMR spectrum (in *o*-dichlorobenzene-d_4 at 130 ºC) for poly(ethylene-*co*-TCUE) prepared by $CpTiCl_2(N{=}C^tBu_2)$ (**5**) - MAO catalyst (run 57, Table 4, TCUE 20.7 mol%).

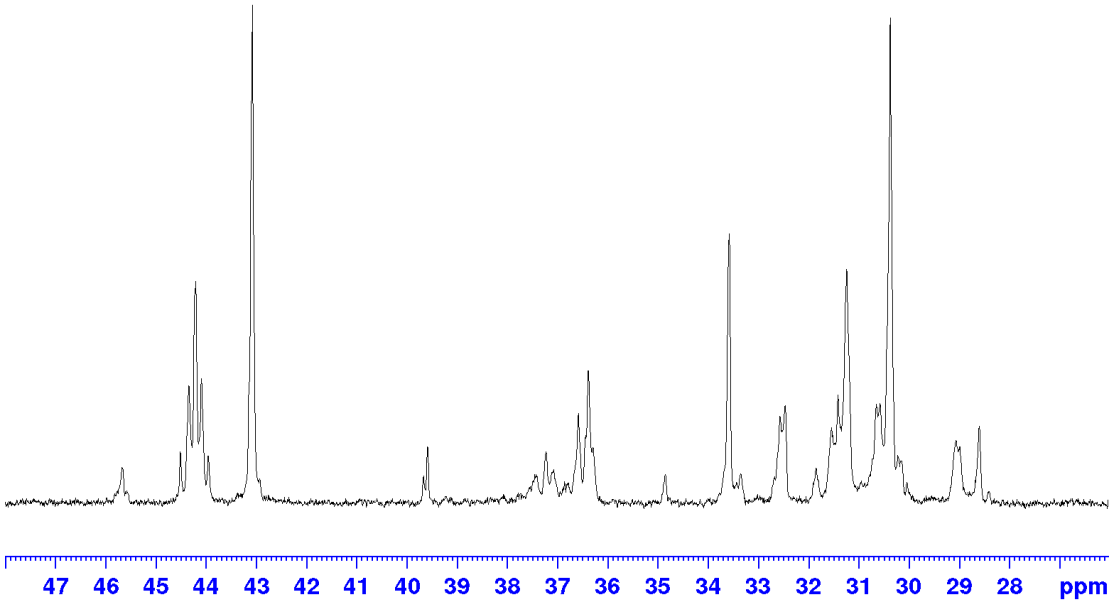


Figure S30. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-TCUE) prepared by $CpTiCl_2(N{=}C^tBu_2)$ (**5**) - MAO catalyst (run 58, Table 4, TCUE 31.7 mol%).

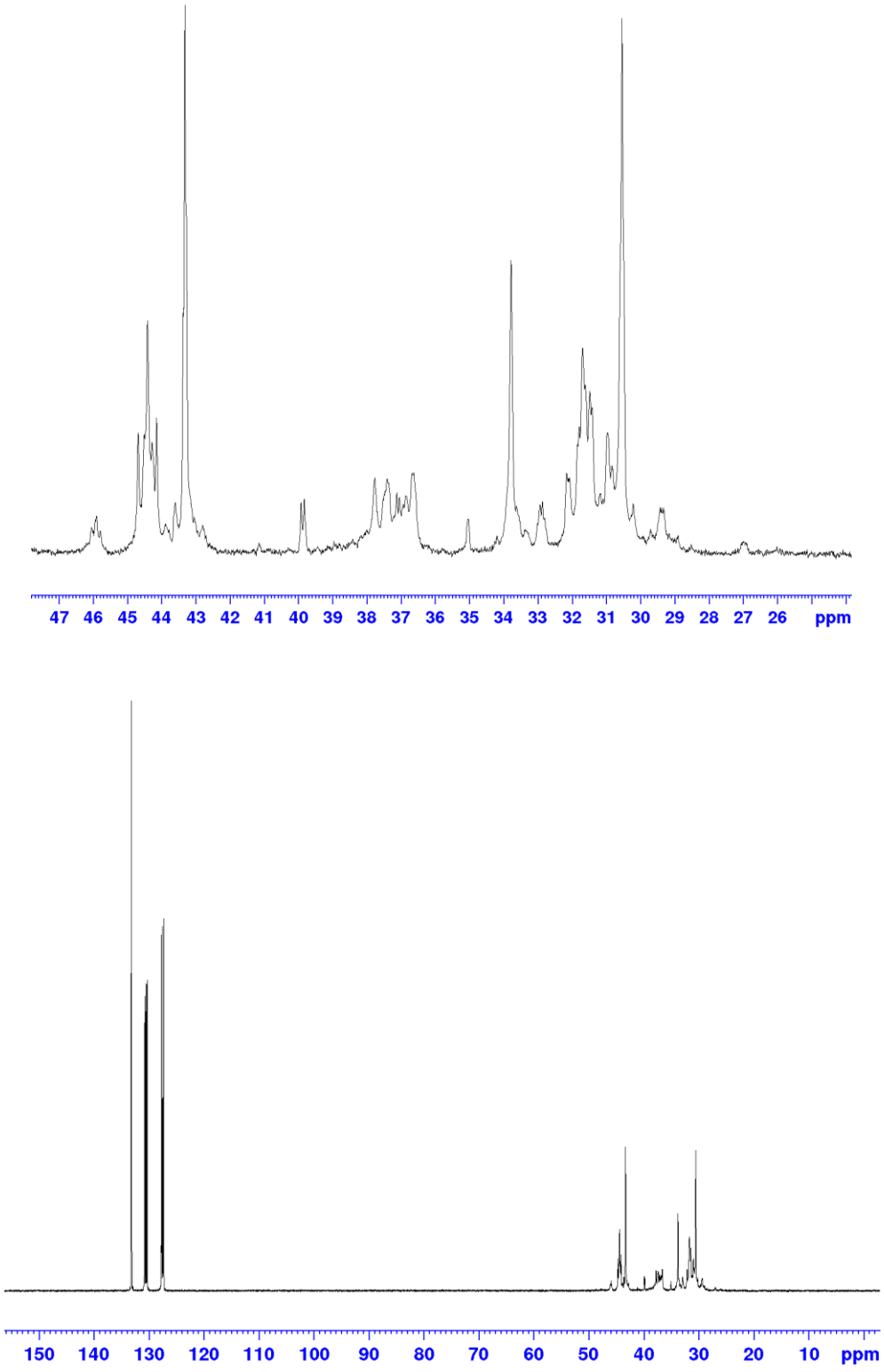


Figure S31. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-TCUE) prepared by $CpTiCl_2(N{=}C^tBu_2)$ (**5**) - MAO catalyst (run 62, Table 4, TCUE 40.7 mol%).

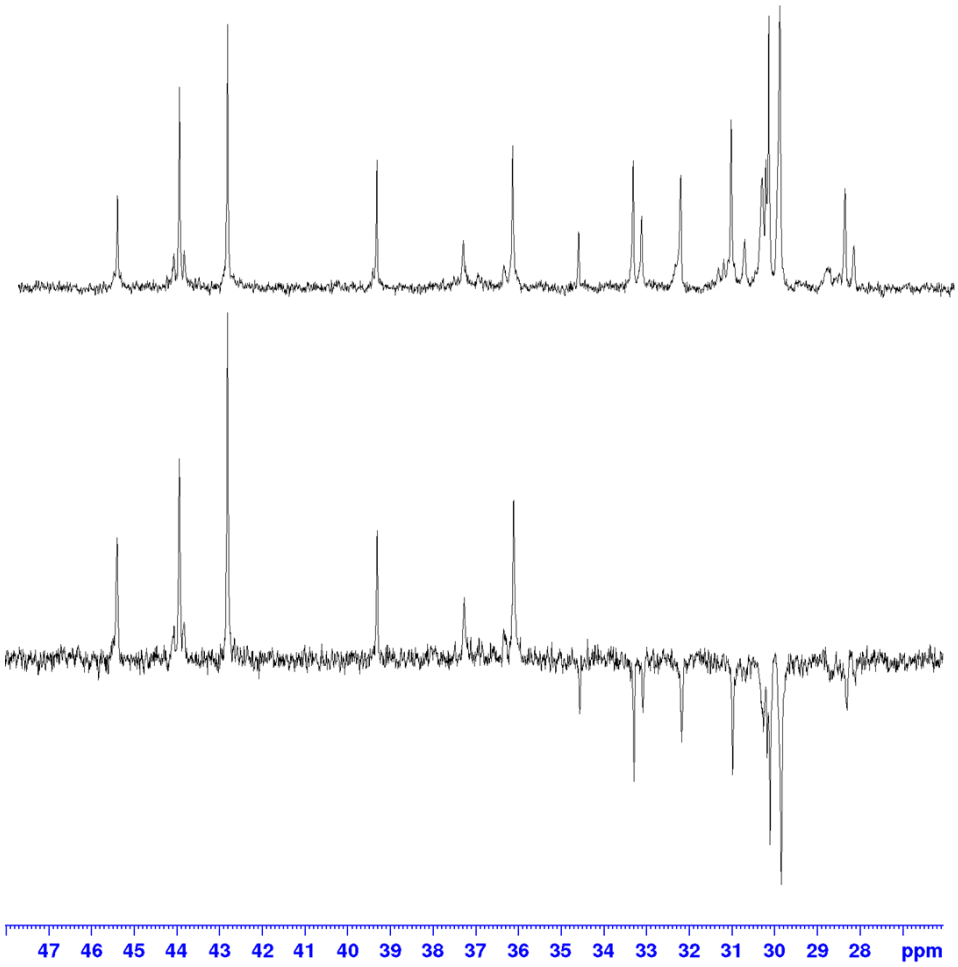
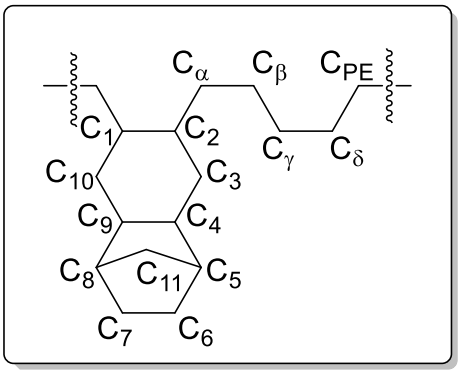
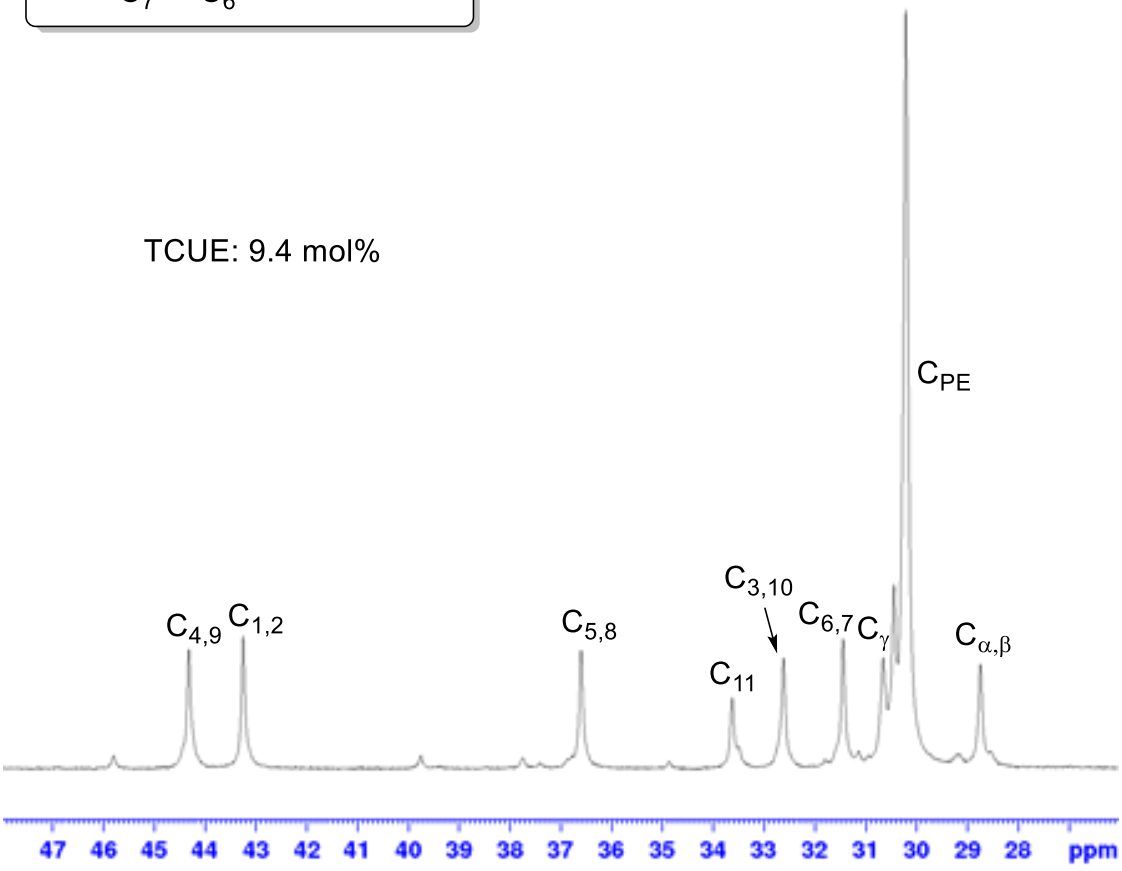


Figure S32. ^{13}C NMR and the dept spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) for poly(ethylene-*co*-TCUE) prepared by (1,2,4-$Me_3C_5H_2$)$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**1**) - MAO catalyst (run 48, Table 4, TCUE 19.5 mol%).



TCUE: 9.4 mol%



$$\text{TCUE (mol\%)} = \frac{(C_{1,2} + C_{3,10} + C_{4,9} + C_{5,8} + C_{6,7} + C_{11})/11}{(C_{1,2} + C_{3,10} + C_{4,9} + C_{5,8} + C_{6,7} + C_{11})/11 + (C_{\alpha,\beta} + C_{\gamma} + C_{PE})/2} \times 100$$

3. DSC thermograms in the copolymers.

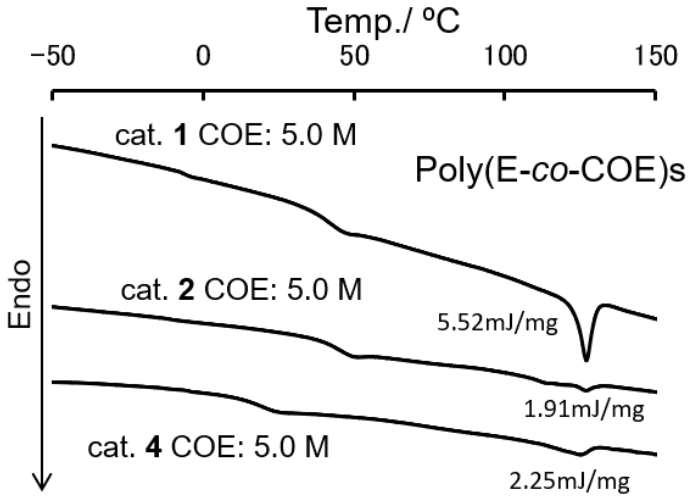


Figure S33. DSC thermograms of polymers prepared by **1**, **2**, **4** - MAO catalysts in ethylene polymerization in the presence of COE. Detailed results are shown in Table 1 (runs 2, 5, 12).

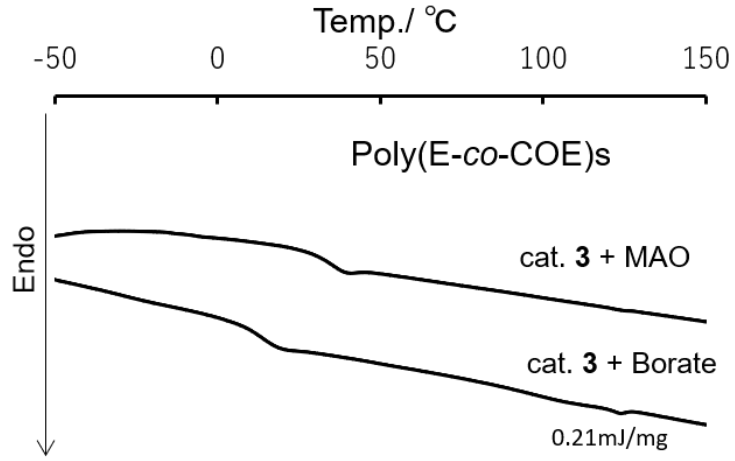


Figure S34. DSC thermograms of poly(ethylene-*co*-COE)s prepared by Cp*$TiCl_2$(O-2,6-$Cl_2C_6H_3$) (**3**) - MAO or borate catalysts. Detailed results are shown in Table 1 (runs 8, 9).

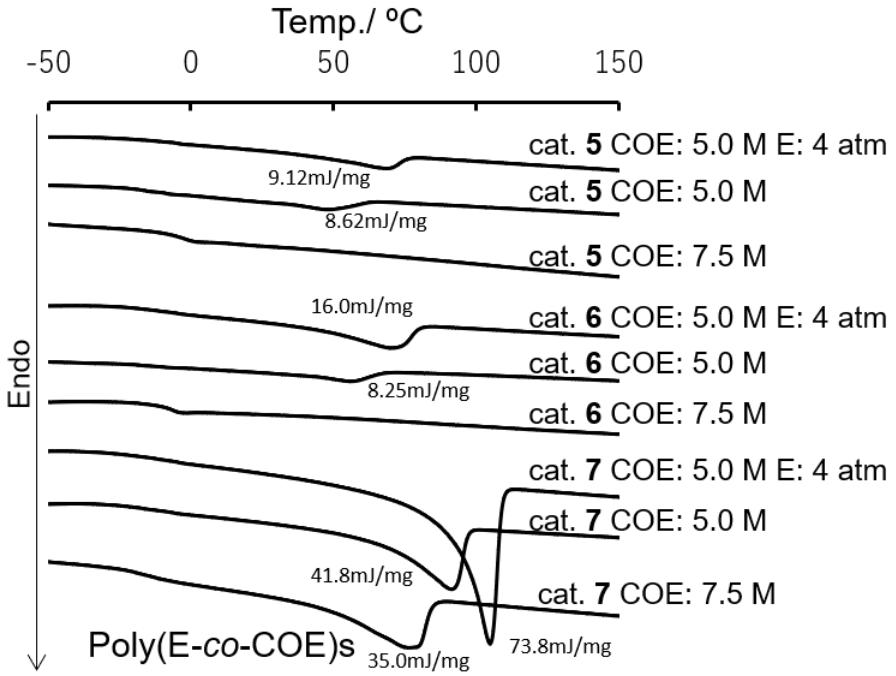


Figure S35. Detailed results are shown in Table 1 (runs 13-21).

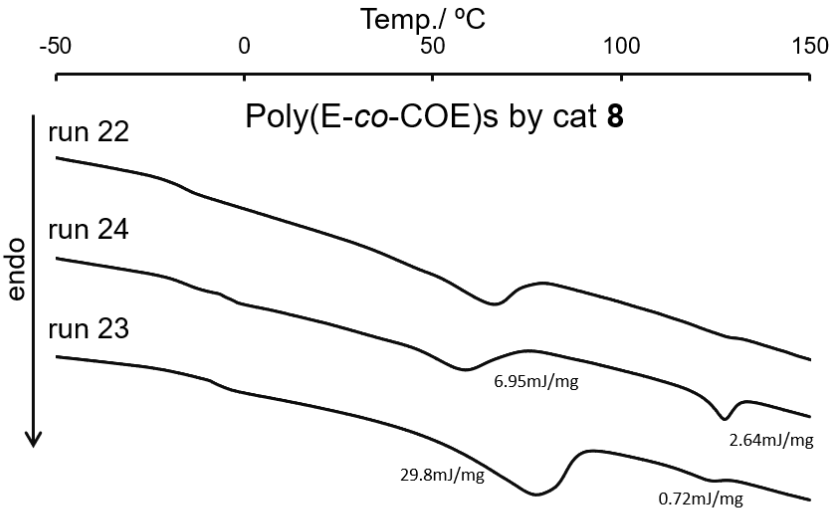


Figure S36. DSC thermograms of polymers prepared by **8** - MAO catalysts in ethylene polymerization in the presence of COE. Detailed results are shown in Table 1 (runs 22-24).

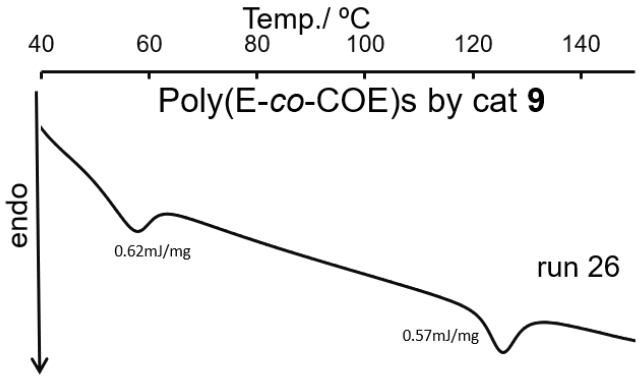


Figure S37. DSC thermograms of polymers prepared by **9** - MAO catalysts in ethylene polymerization in the presence of COE. Detailed results are shown in Table 1 (run 26).

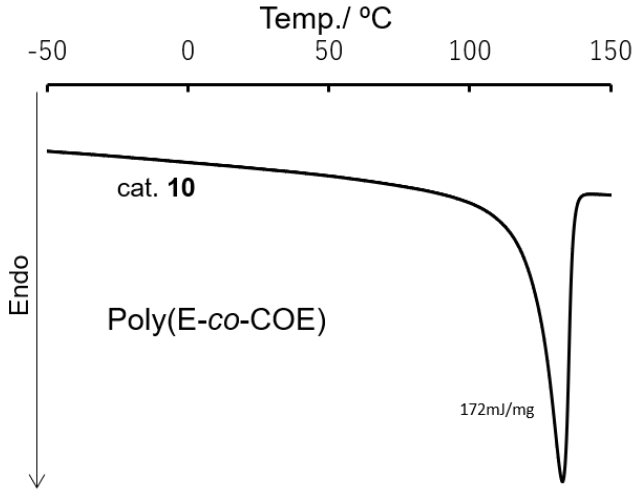


Figure S38. DSC thermograms of polymers prepared by **10** - MAO catalyst in ethylene polymerization in the presence of COE. Detailed results are shown in Table 1 (run 27).

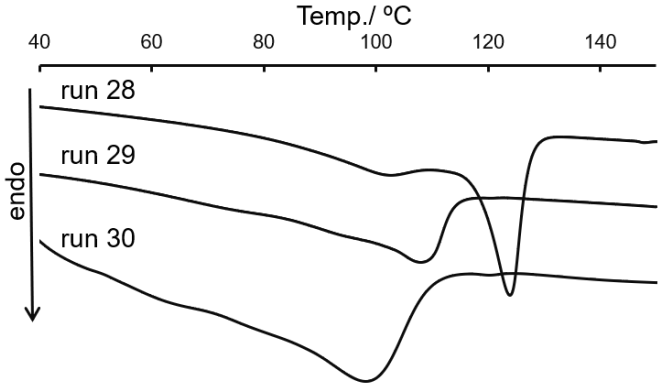


Figure S39. DSC thermograms of polymers prepared by **11** - MAO catalyst in ethylene polymerization in the presence of COE. Detailed results are shown in Table 1 (runs 28-30).

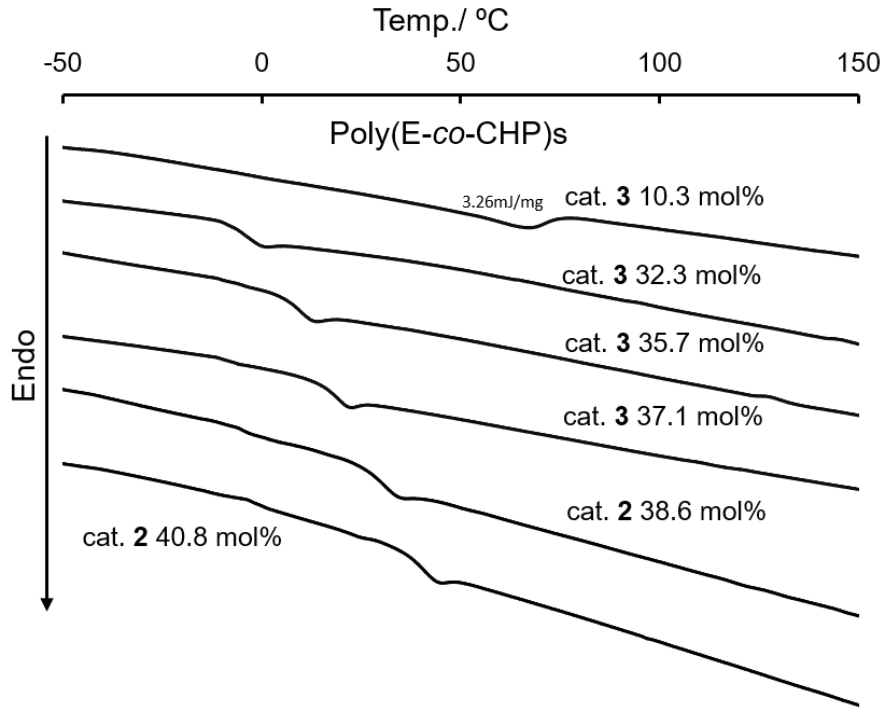


Figure S40. DSC thermograms for poly(ethylene-*co*-CHP)s prepared by Cp'$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) [Cp' = $^t BuC_5H_4$ (**2**), Cp* (**3**)] – d-MAO catalysts. CHP content: 10.3 mol% (run 43, Table 3), 32.3 mol % (run 44), 35.7 mol% (run 45), 37.1 mol% (run 47), 38.6 mol% (run 40), and 40.8 mol% (run 42).

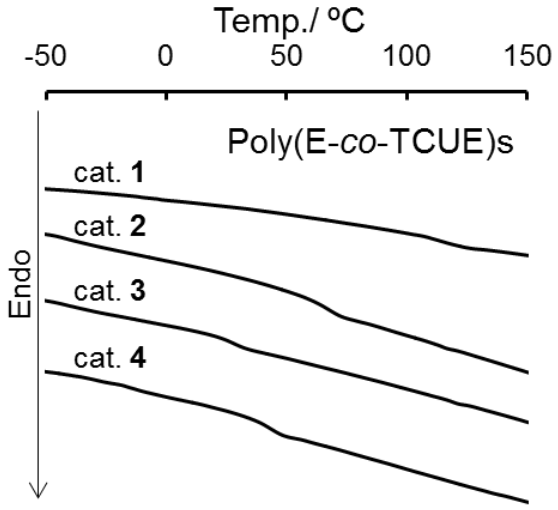


Figure S41. DSC thermograms of polymers prepared by **1-4** - MAO catalysts in ethylene polymerization in the presence of TCUE. Detailed results are shown in Table 4 (runs S28,53-55).

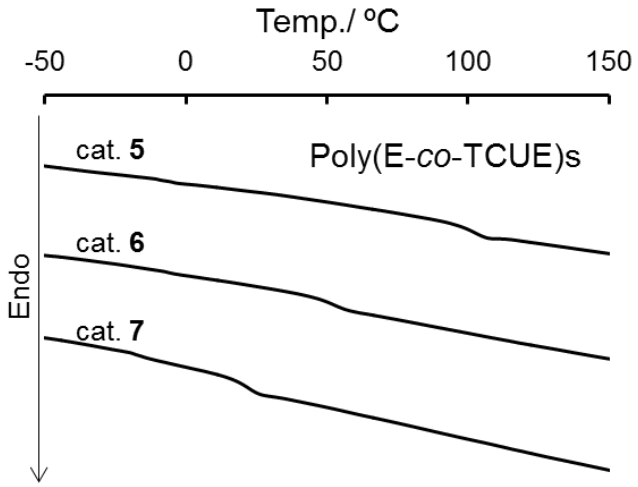


Figure S42. DSC thermograms of polymers prepared by **5-7** - MAO catalysts in ethylene polymerization in the presence of TCUE. Detailed results are shown in Table 4 (runs 62-64).

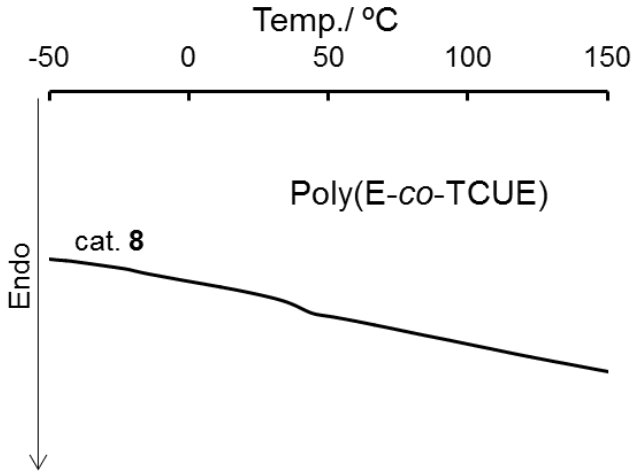


Figure S43. DSC thermograms of polymers prepared by **8** - MAO catalysts in ethylene polymerization in the presence of TCUE. Detailed results are shown in Table 4 (runs 65).

4. Plots of glass transition temperature (T_g) vs comonomer content (mol%) in ethylene copolymers with norbornene (NBE), tetracyclododecene (TCD), and with tricyclo[6.2.1.0(2,7)]undeca-4-ene (TCUE).

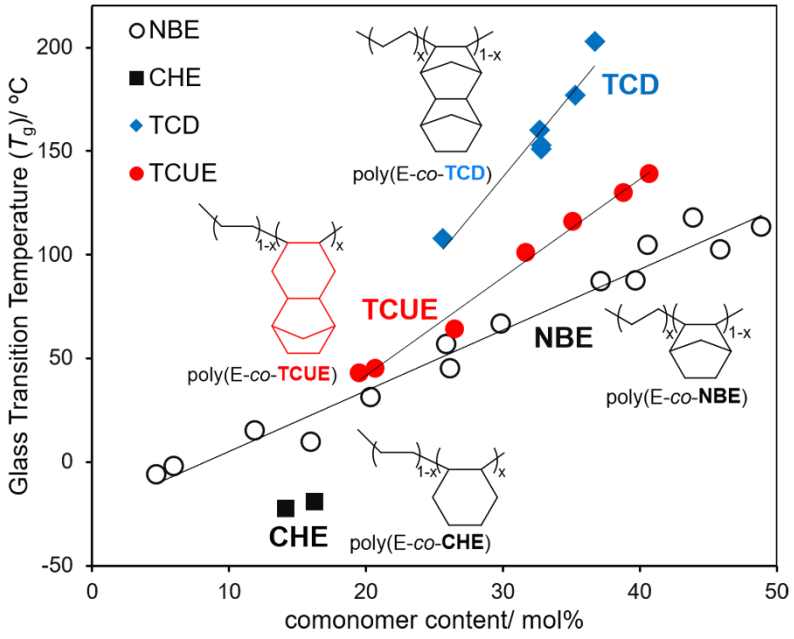


Figure S44. Plots of glass transition temperature (T_g) vs comonomer content (mol%) in ethylene copolymers with norbornene (NBE, cited from: K. Nomura, *Chin. J. Polym. Sci.*, 2008, **26**, 513-523.), tetracyclododecene (TCD, cited from: W. Apisuk, H. Ito, and K. Nomura, *J. Polym. Sci. Part A: Polym. Chem.*, 2016, **54**, 2662-2667.), and with tricyclo[6.2.1.0(2,7)]-undeca-4-ene (TCUE).