

Electronic Supplementary Information (ESI)

Synthesis of Ethylene Copolymers with 2-Allylphenol by Half-Titanocene
Catalysts Containing SiEt₃-, SiⁱPr₃-Substituted Phenoxide ligands, Cp*TiCl₂(O-
2,6-ⁱPr₂-4-SiR₃-C₆H₂) (R = Et, ⁱPr)

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1. Additional results in ethylene copolymerization with 2-Allylphenol (AP)

Table S1. Ethylene Copolymerization with 2-Allylphenol (AP) by Cp*TiCl₂(O-2,6-*i*-Pr₂-4-RC₆H₂) [R = H (**1**), SiEt₃ (**2**), Si(*i*-Pr)₃ (**3**)]-MAO catalyst systems (in toluene at 50 °C).^a

run	cat.	ethylene	AP ^b	TIBA ^c	yield ^d	activity ^e	M_n^f	M_w	$T_m/(T_g)^g$	AP ^h
	(μ mol)	/ atm	/ M	/ equiv.	/ mg		$\times 10^{-4}$	$/M_n^f$	/ °C	/ mol%
1 ⁱ	1 (5.0)	2	0.25	1.1	88.5	110	2.42	2.38	110.6	4.1
S1 ⁱ	1 (5.0)	2	0.25	1.1	85.4	100	3.16	2.08	111.6	
2 ⁱ	1 (5.0)	2	0.51	1.1	34.5	40	1.07	1.73	95.3, 129.7	(7.8) ^k
S2 ^j	1 (5.0)	2	0.51	1.1	71.3	90	11.7	1.55	98.5,131.4	
3 ⁱ	1 (5.0)	2	0.76	1.1	28.5	30	0.71	2.47	83.8,130.2(2.6)	(10.5) ^k
4	1 (0.5)	4	0.25	1.1	169.2	2030	3.82	2.03	125.5	0.9
S3	1 (0.5)	4	0.25	1.1	165.8	1990	3.60	2.15	125.7	
8	2 (0.5)	4	0.25	1.2	183.5	2200	6.23	2.24	122.3	1.2
S4	2 (0.5)	4	0.25	1.2	211.3	2540	6.19	2.53	122.4	
S5 ⁱ	2 (0.5)	4	0.38	1.2	147.5	1770	8.38	1.94	121.8	
10	2 (0.5)	4	0.76	1.2	107.2	1290	3.86	1.87	108.1,123.1,126.5	(4.1) ^k
11	2 (0.5)	6	0.25	1.0	156.3	1880	11.3	2.23	121.5	1.6
S6	2 (2.0)	4	0.25	1.2	373.1	1120	6.00	2.56	119.1	
12	2 (1.0)	6	0.25	1.0	323.9	1940	9.19	2.30	121.7	1.5
S7	2 (1.0)	6	0.25	1.0	319.0	1910	6.03	2.02		
13	2 (1.0)	6	0.25	1.2	306.4	1840	6.81	2.21	121.6	1.7
S8	2 (1.0)	6	0.25	1.2	311.8	1870	4.87	2.05		
17 ⁱ	3 (1.0)	6	0.38	1.2	395.1	2370	4.57	1.86	123.6	1.0
18 ⁱ	3 (1.0)	6	0.51	1.2	344.5	2070	3.8	1.91	122.5	1.2

^aConditions: Toluene and 2-allylphenol (AP) total 30.0 mL, d-MAO 3.0 mmol, 50 °C, 10 min.

^bInitial AP concentration in mmol/mL (M). ^cMolar ratio of TIBA/AP, TIBA = Al(*i*-Bu)₃.

^dIsolated yield. ^eActivity in kg-polymer/mol-Ti·h. ^fGPC data (g/mol) in *o*-dichlorobenzene vs

polystyrene standards. ^gBy DSC thermograms. ^hEstimated by ¹H NMR spectra in C₂D₂Cl₄ at

110 °C. ⁱMAO 4.0 mmol. ^jMAO 10.0 mmol. ^kEstimated AP content as whole polymer.

Table S2. Ethylene Copolymerization with 2-Allylphenol (AP) by Cp*TiCl₂(O-2,6-*i*-Pr₂-4-RC₆H₂) [R = H (**1**), SiEt₃ (**2**), Si(*i*-Pr)₃ (**3**)], 1,2,4-Me₃CpTiCl₂(O-2,6-*i*-Pr₂-4-C₆H₃) (**4**), ^tBuCpTiCl₂(O-2,6-*i*-Pr₂-4-C₆H₃) (**5**)–MAO catalyst systems (in toluene at 50 °C).^a

run	cat.	ethylene	AP ^b	yield ^c	activity ^d	M _n ^e	M _w	T _m /(T _g) ^f	AP ^g
	(μmol)	/ atm	/ M	/ mg		×10 ⁻⁴	/M _n ^e	/ °C	/ mol%
31	1 (5.0)	2	0.25	222.7	270	1.98	1.71	106.6	4.7
S9	1 (5.0)	2	0.25	223.5	270	3.51	1.72	107.0	
32	1 (5.0)	2	0.51	89.2	110	1.49	1.66	102.9	6.0
33 ^h	1 (5.0)	2	0.51	120.9	150	1.29	1.60	102.1	6.2
35 ^h	2 (5.0)	2	0.25	202.2	240	1.43	1.57	110.8	4.1
S10 ^h	2 (5.0)	2	0.25	196.8	240	2.82	1.76	106.7	
36	2 (5.0)	2	0.51	74.4	90	3.25	1.65	99.0(5.4)	7.2
37 ^h	2 (5.0)	2	0.51	117.2	140	0.95	2.19	92.8(2.6)	8.0
22	2 (0.5)	4	0.25	272.5	3270	17.0	2.05	119.6	1.9
S11	2 (0.5)	4	0.25	265.1	3180	14.7	1.86		
23	2 (0.5)	4	0.51	125.3	1500	9.68	1.84		
24	2 (0.5)	4	0.76	41.0	480	4.42	1.86	114.5	3.0
39	3 (5.0)	2	0.25	248.8	300	4.32	1.81	108.3	4.2
S12	3 (5.0)	2	0.25	217.5	260	1.68	1.65	107.4	
40	3 (5.0)	2	0.51	77.2	90	1.12	1.73	102.9	6.0
S13	3 (5.0)	2	0.51	71.1	90	0.73	1.86		
41 ^h	3 (5.0)	2	0.51	89.2	110	0.95	1.58	95.9(4.0)	8.2
42 ^h	3 (5.0)	2	0.76	77.9	90	1.06	1.57	91.8(2.5)	9.0
25	3 (1.0)	4	0.25	225.9	1360	7.01	1.71	117.9	2.2
S14	3 (1.0)	4	0.25	250.8	1540	5.22	2.00	118.2	
26	3 (1.0)	4	0.51	201.0	1200	6.10	2.01	117.0	2.4
S15	3 (1.0)	4	0.51	183.9	1130	6.64	1.93		
27	3 (1.0)	4	0.76	55.8	330	2.91	1.95	111.0	3.8
S16	3 (1.0)	4	0.76	52.4	320	2.98	1.85	115.2	
29	4 (5.0)	2	0.25	54.9	70	1.48	2.03	111.8	3.6
S17	4 (5.0)	2	0.25	55.2	70	1.31	1.73	111.5	
S18 ^h	4 (5.0)	2	0.25	77.3	90	1.50	1.37	111.8	
S19 ^h	4 (5.0)	2	0.51	42.3	50	0.91	1.70	103.4	
28	4 (1.0)	4	0.25	173.5	1050	10.9	2.97	121.3	
S20	4 (1.0)	4	0.25	174.7	1050	11.4	2.95		
S21 ^h	5 (5.0)	2	0.25	54.2	70	1.64	1.45	118.8	2.6
30	5 (1.0)	4	0.25	84.0	510	6.10	2.19	126.1	
S22	5 (1.0)	4	0.25	69.0	410	7.28	2.57		

^aConditions: toluene and 2-allylphenol (AP) total 30.0 mL, d-MAO 4.0 mmol (10.0 mmol), 1.1 equiv of TIBA and 2,6-di-*tert*-butylphenol [based on mole ratio of -OH group (AP), TIBA = Al(*i*-Bu)₃], 50 °C, 10 min. ^bInitial AP concentration in mmol/mL(M). ^cIsolated yield. ^dActivity in kg-polymer/mol-Ti·h. ^eGPC data (g/mol) in *o*-dichlorobenzene vs polystyrene standards. ^fBy DSC thermograms. ^gEstimated by ¹H NMR spectra in C₂D₂Cl₄ at 110 °C. ^hMAO 10.0 mmol.

2. Selected NMR spectra in the copolymers

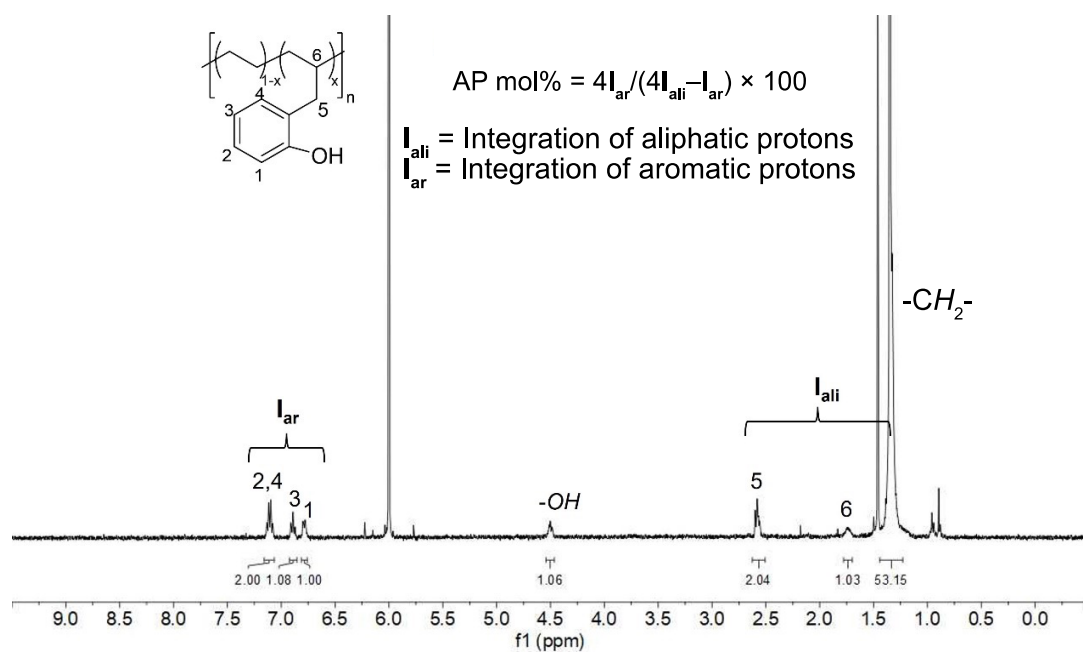


Figure S1. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 1-MAO catalyst system at 50 °C, AP 0.51 M, ethylene 2 atm (Table 1, run 2, AP 7.8 mol%).

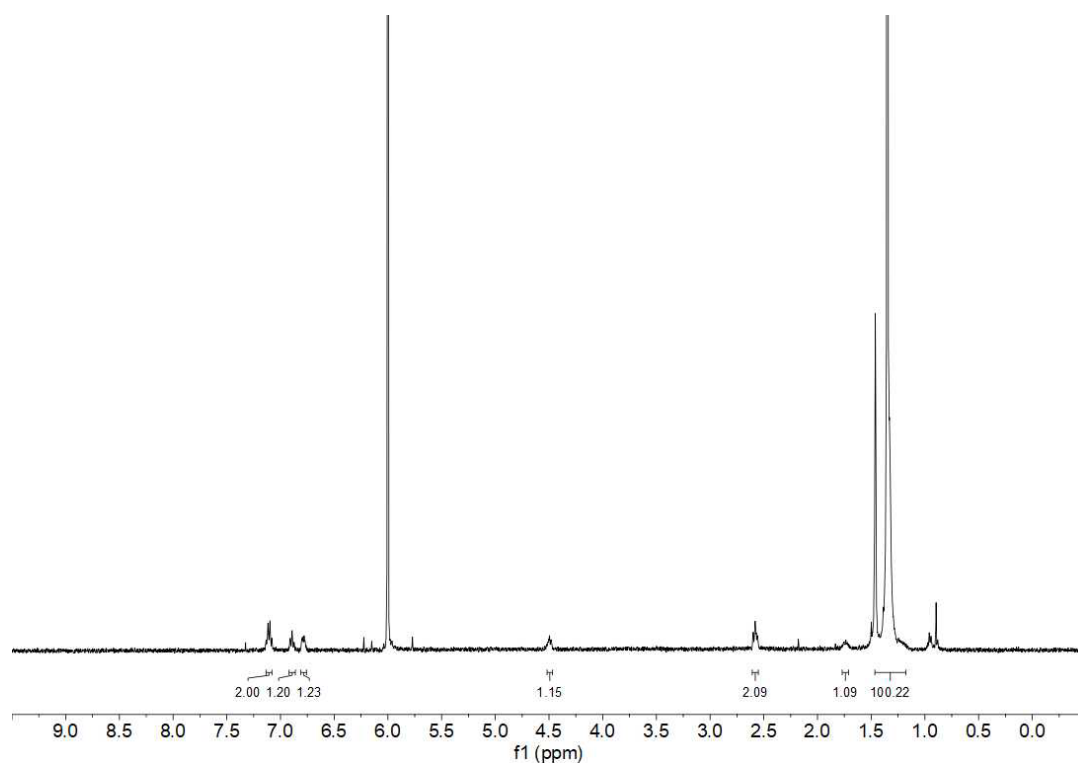


Figure S2. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 1-MAO catalyst system at 50 °C, AP 0.25 M, ethylene 2 atm (Table 1, run 1, AP 4.1 mol%).

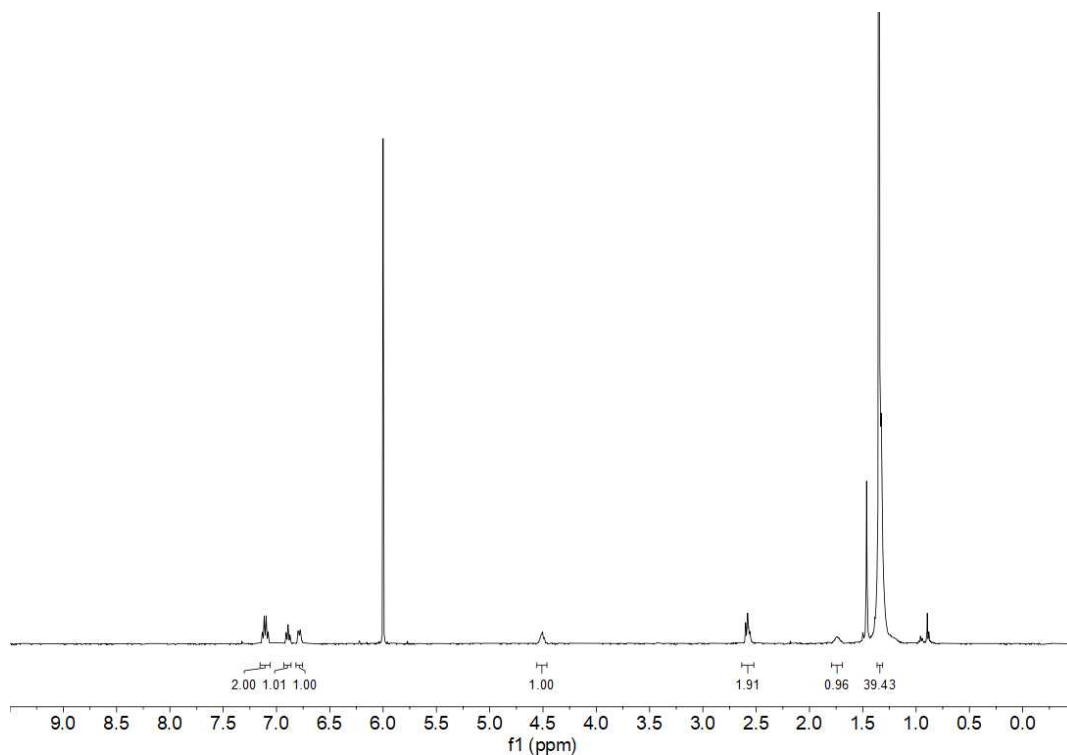


Figure S3. ^1H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 $^\circ\text{C}$) for poly(ethylene-*co*-AP) prepared by 1-MAO catalyst system at 50 $^\circ\text{C}$, AP 0.76 M, ethylene 2 atm (Table 1, run 3, AP 10.5 mol%).

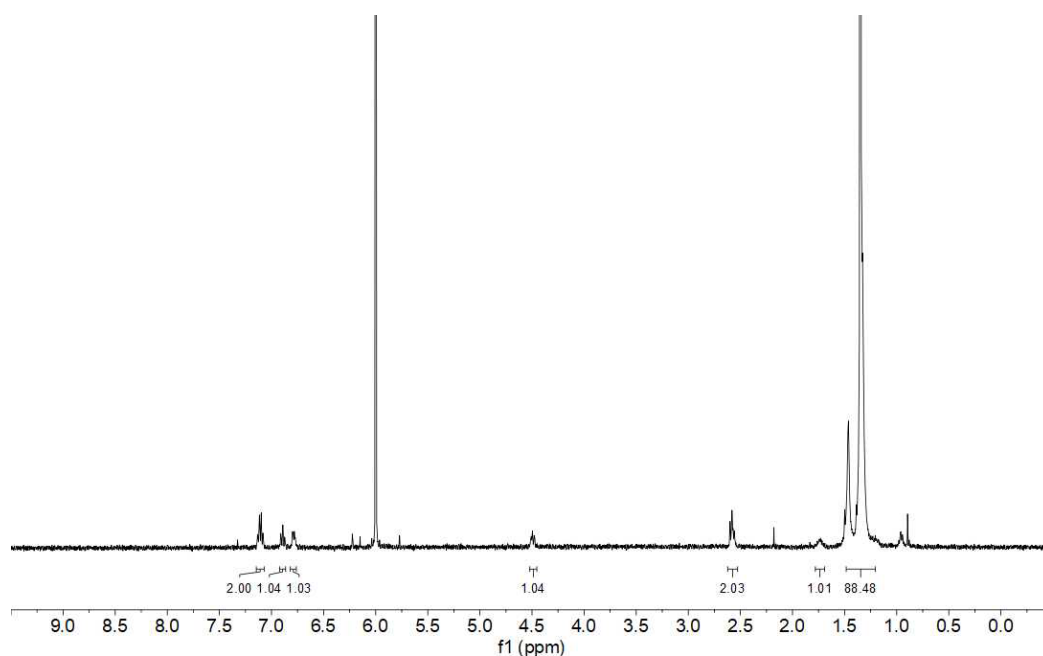


Figure S4. ^1H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 $^\circ\text{C}$) for poly(ethylene-*co*-AP) prepared by 2-MAO catalyst system at 50 $^\circ\text{C}$, AP 0.25 M, ethylene 2 atm (Table 1, run 5, AP 4.5 mol%).

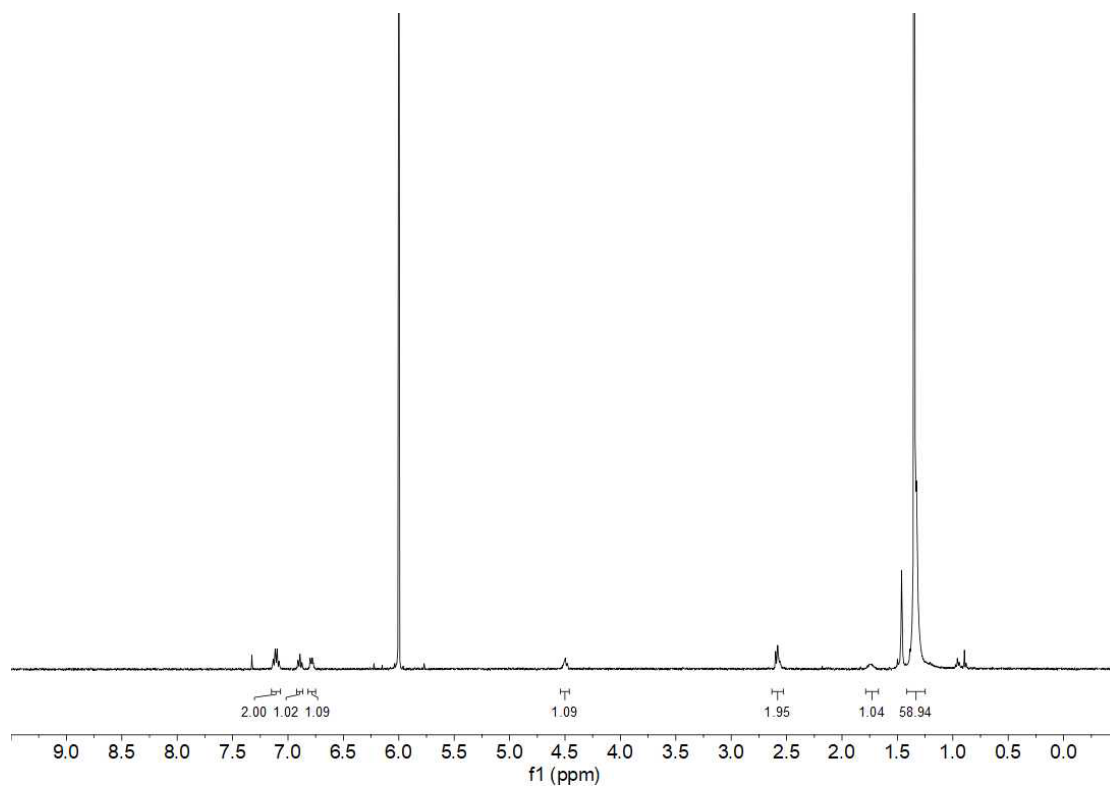


Figure S5. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 2-MAO catalyst system at 50 °C, AP 0.51 M, ethylene 2 atm (Table 1, run 6, AP 7.1 mol%).

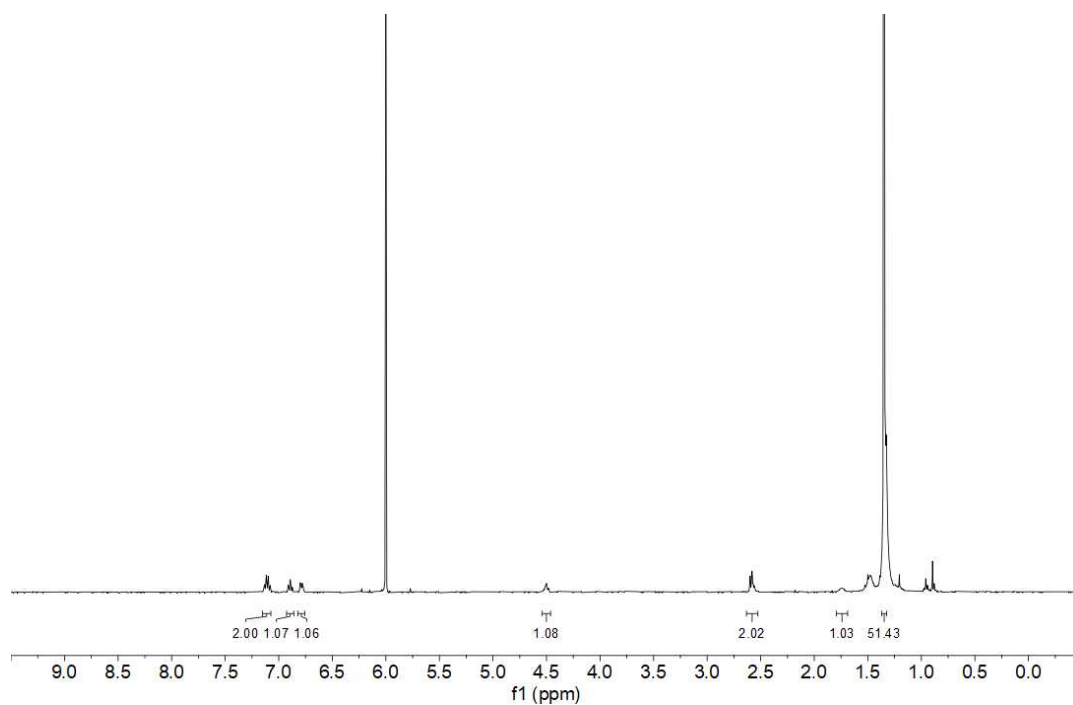


Figure S6. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 2-MAO catalyst system at 50 °C, AP 0.76 M, ethylene 2 atm (Table 1, run 7, AP 8.2 mol%).

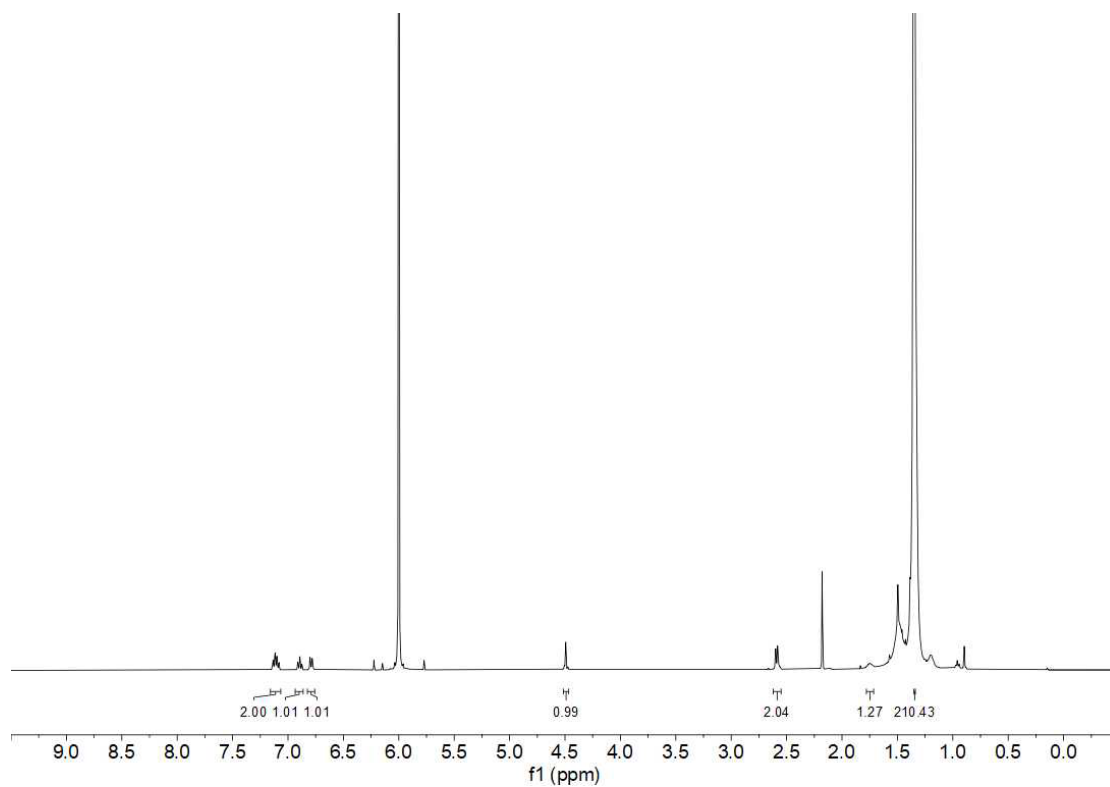


Figure S7. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 2-MAO catalyst system at 50 °C, AP 0.51 M, ethylene 4 atm (Table 1, run 9, AP 1.9 mol%).

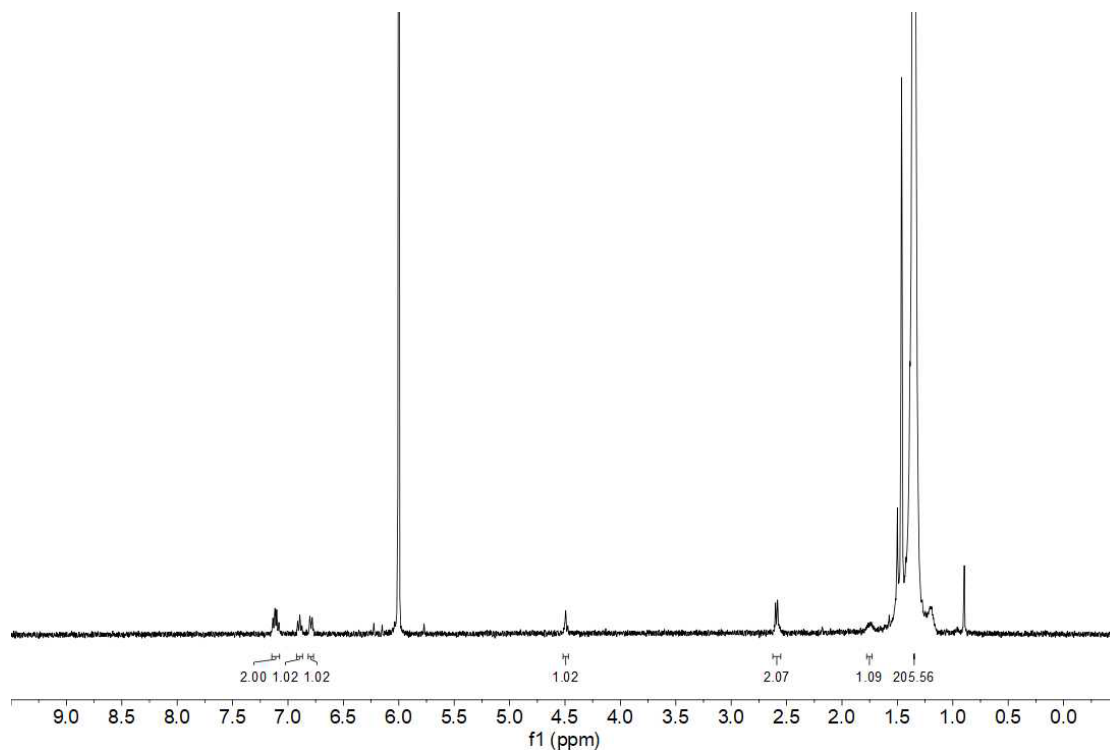


Figure S8. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 2-MAO catalyst system at 50 °C, AP 0.25 M, ethylene 4 atm (Table 2, run 22, AP 1.9 mol%).

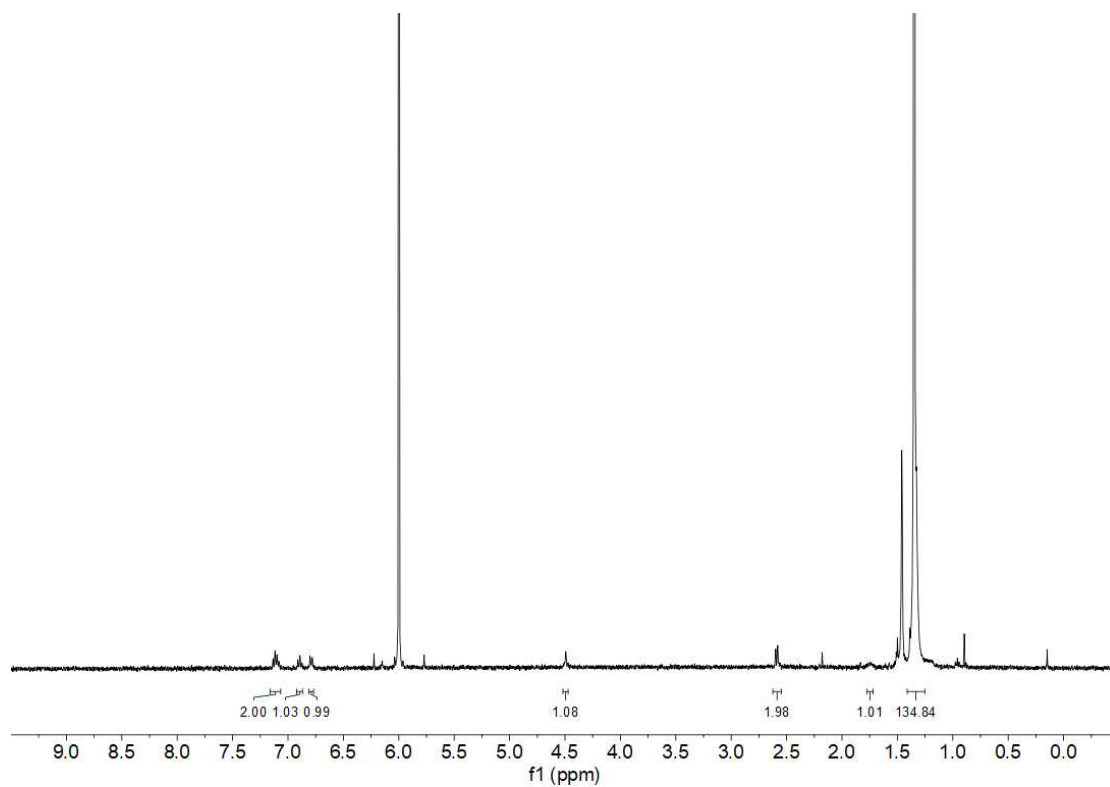


Figure S9. ^1H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 $^\circ\text{C}$) for poly(ethylene-*co*-AP) prepared by 2-MAO catalyst system at 50 $^\circ\text{C}$, AP 0.76 M, ethylene 4 atm (Table 2, run 24, AP 3.0 mol%).

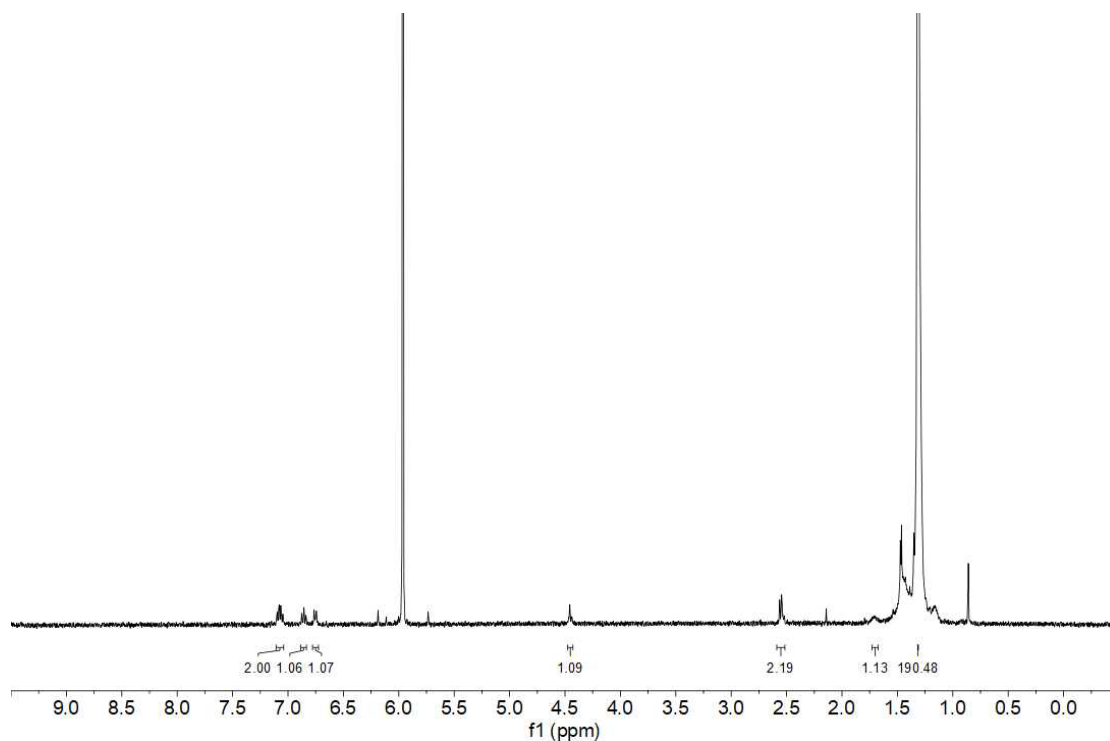


Figure S10. ^1H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 $^\circ\text{C}$) for poly(ethylene-*co*-AP) prepared by 3-MAO catalyst system at 50 $^\circ\text{C}$, AP 0.76 M, ethylene 4 atm (Table 2, run 25, AP 2.2 mol%).

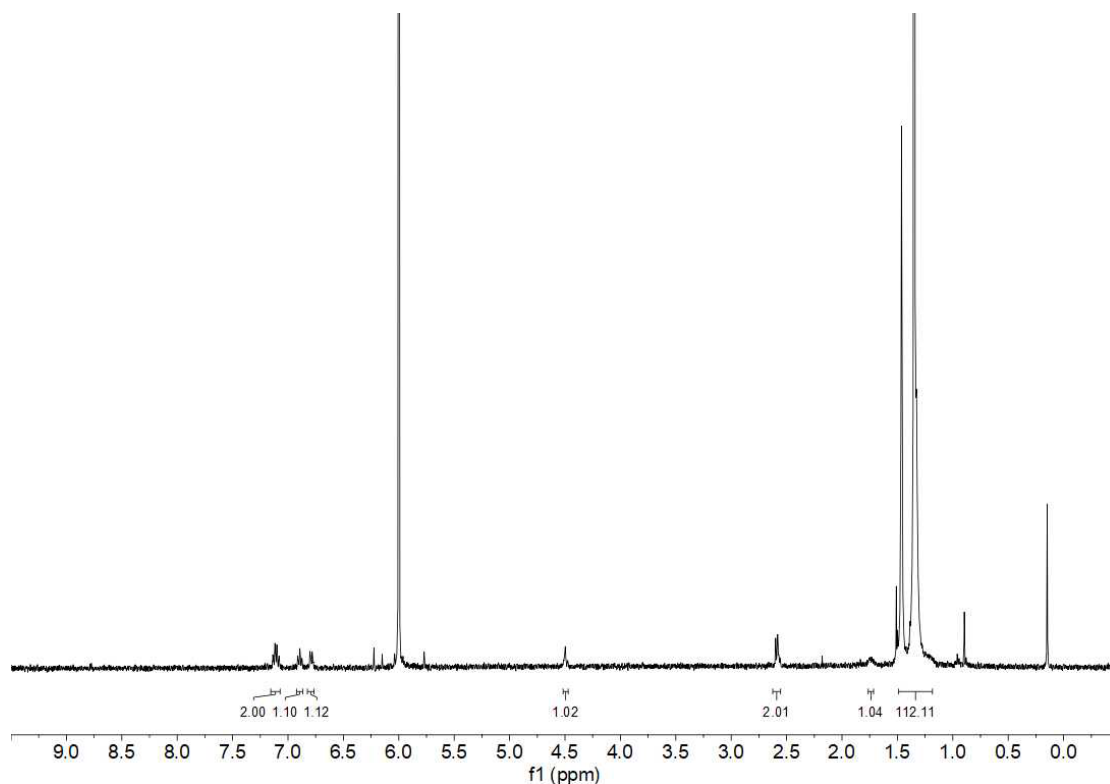


Figure S11. ^1H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 $^\circ\text{C}$) for poly(ethylene-*co*-AP) prepared by 3-MAO catalyst system at 50 $^\circ\text{C}$, AP 0.76 M, ethylene 4 atm (Table 2, run 27, AP 3.8 mol%).

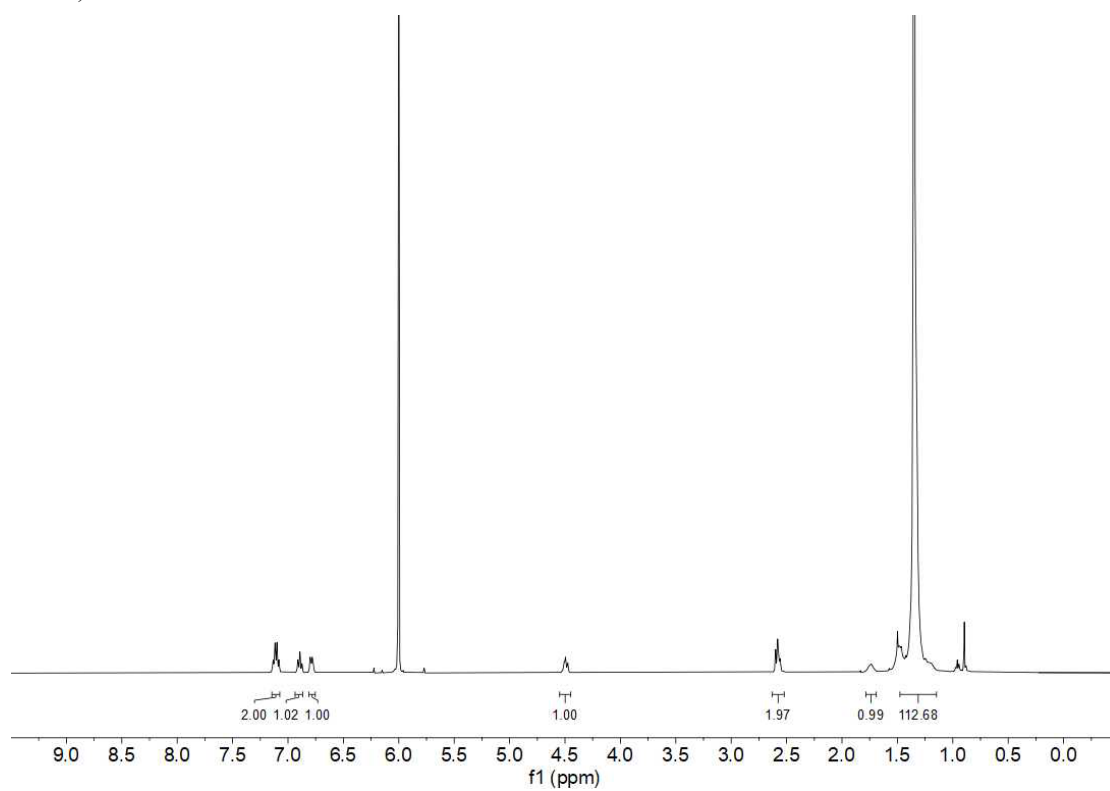


Figure S12. ^1H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 $^\circ\text{C}$) for poly(ethylene-*co*-AP) prepared by 4-MAO catalyst system at 50 $^\circ\text{C}$, AP 0.25 M, ethylene 2 atm (Table 2, run 29, AP 3.6 mol%).

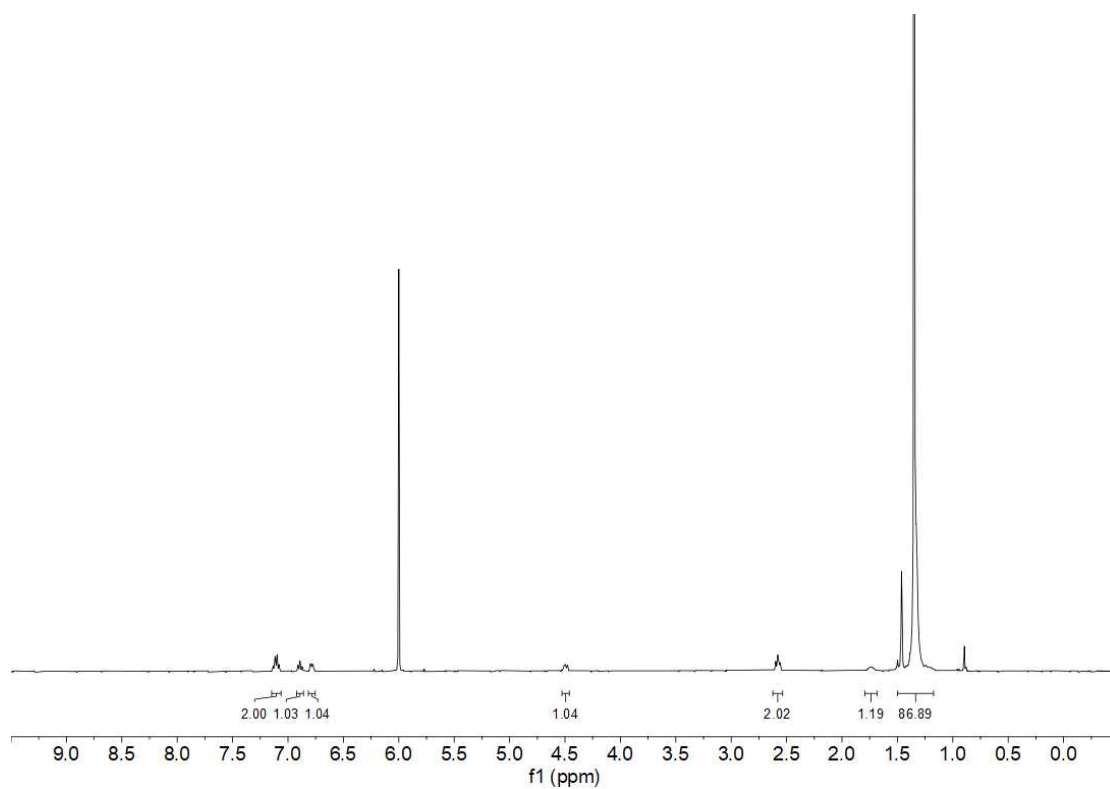


Figure S13. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 1-MAO catalyst system at 50 °C, AP 0.25M, ethylene 2 atm (Table 3, run 31, AP 4.7 mol%).

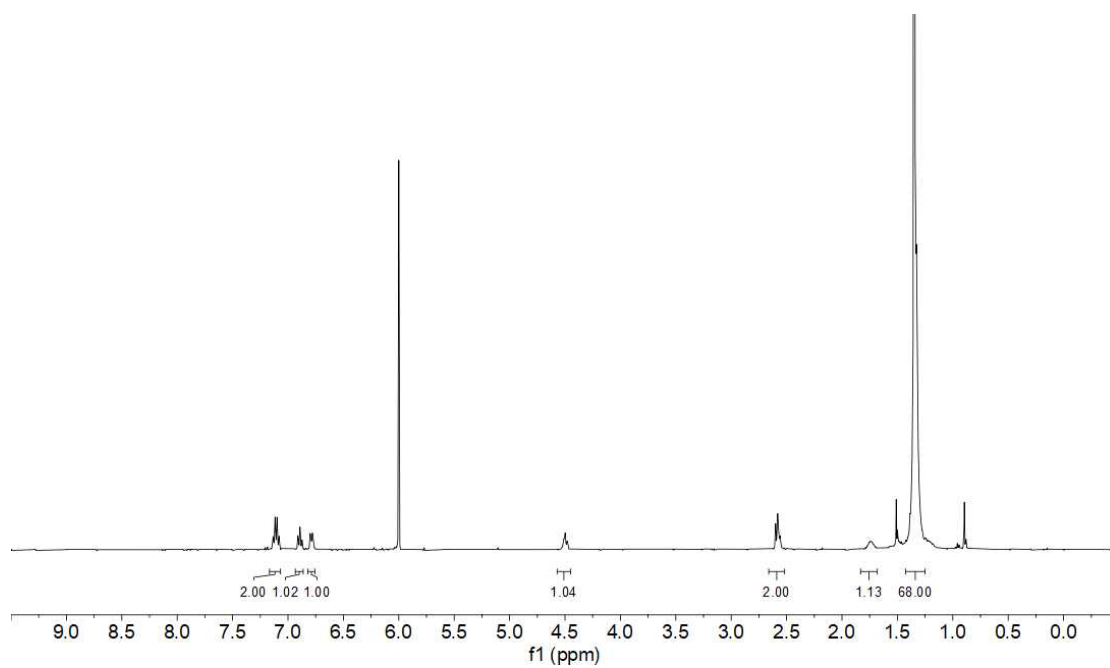


Figure S14. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 1-MAO catalyst system at 50 °C, AP 0.51M, ethylene 2 atm. (Table 3, run 32, AP 6.0 mol%).

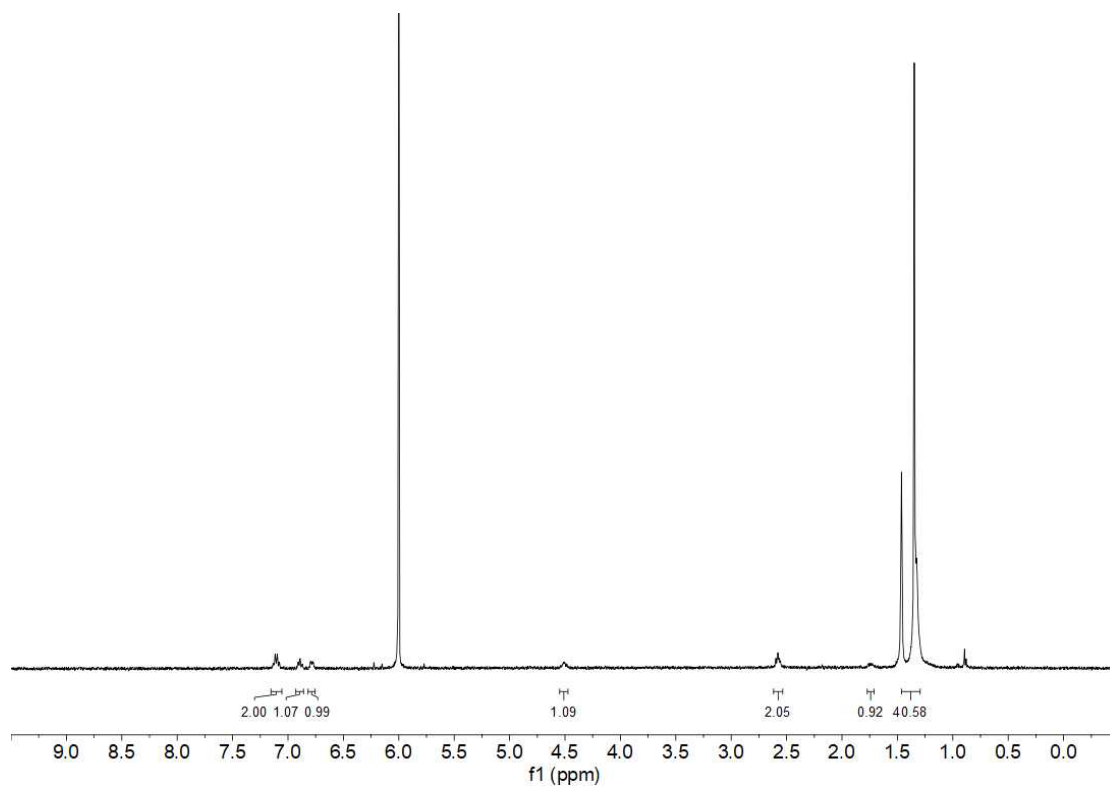


Figure S15. ^1H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co*-AP) prepared by 1-MAO catalyst system at 50 °C, AP 0.76 M, ethylene 2 atm (Table 3, run 34, AP 10.3 mol%).

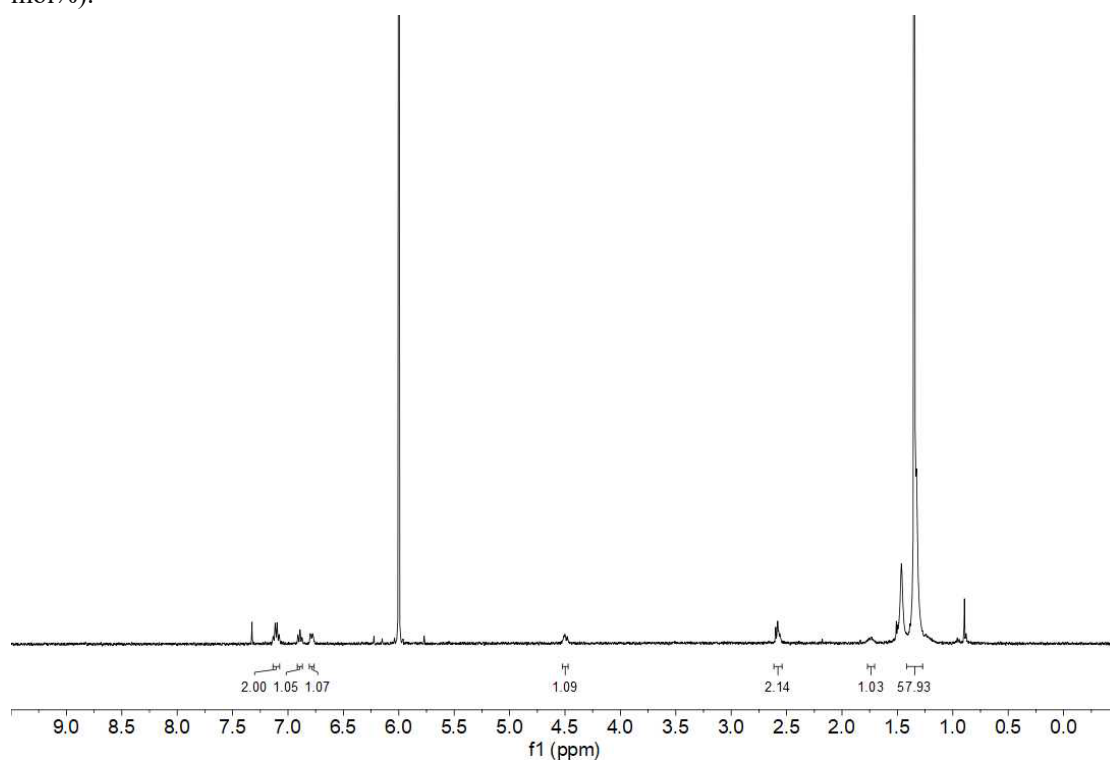


Figure S16. ^1H NMR spectrum (1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co*-AP) prepared by 2-MAO catalyst system at 50 °C, AP 0.51 M, ethylene 2 atm (Table 3, run 36, AP 7.2 mol%).

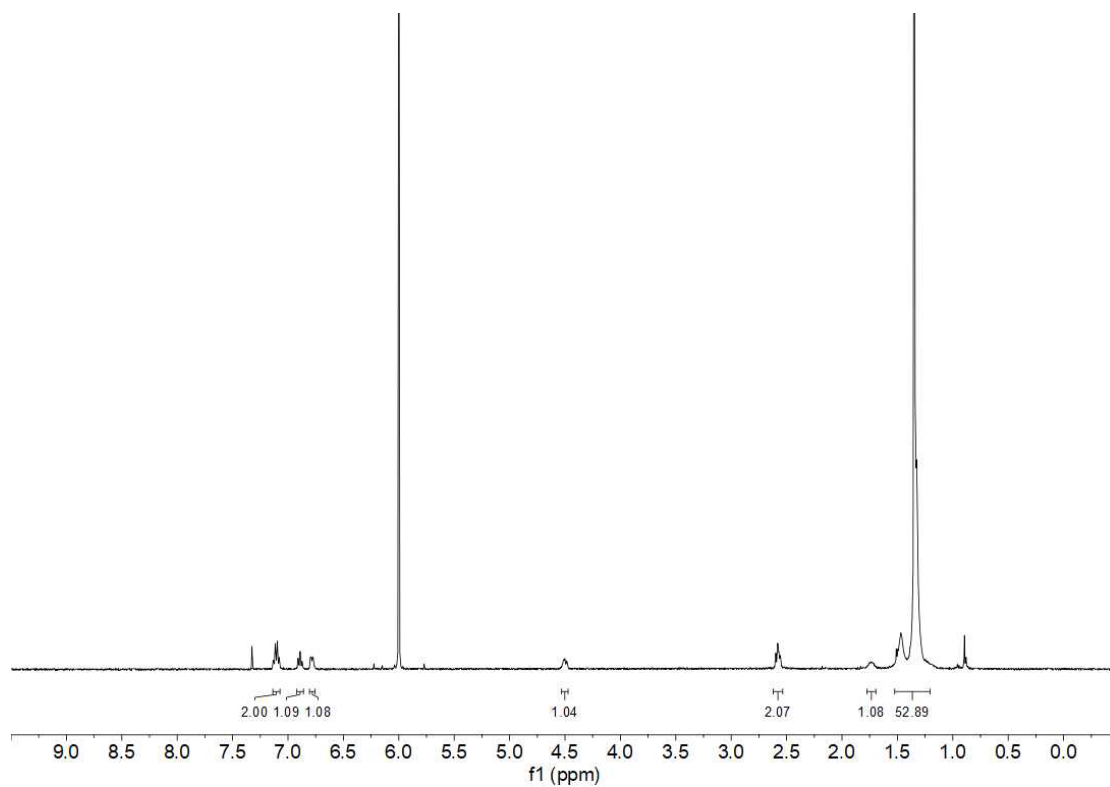


Figure S17. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 2-MAO catalyst system at 50 °C, AP 0.51 M, ethylene 2 atm (Table 3, run 37, AP 8.0 mol%).

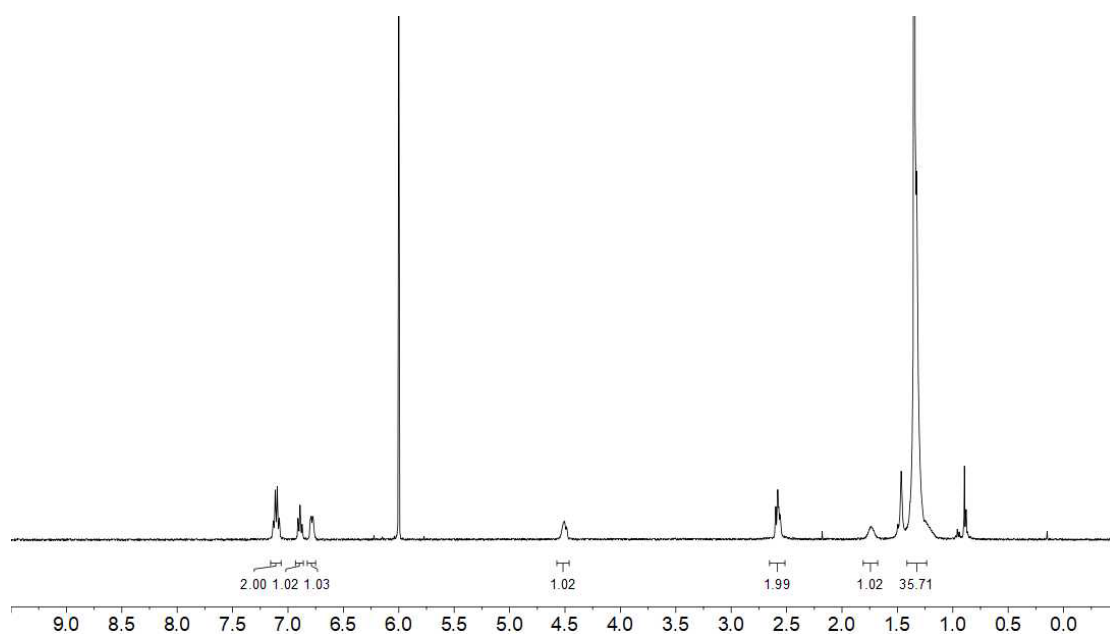


Figure S18. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 2-MAO catalyst system at 50 °C, AP 0.76 M, ethylene 2 atm (Table 3, run 38, AP 11.7 mol%).

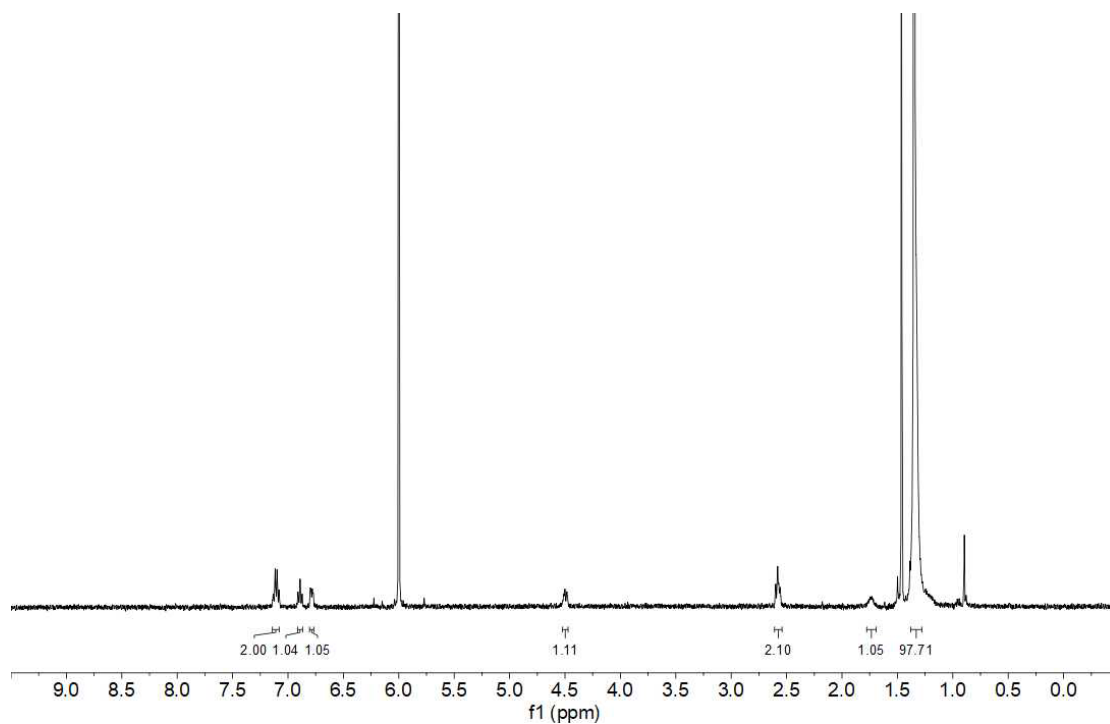


Figure S19. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 3-MAO catalyst system at 50 °C, AP 0.25 M, ethylene 2 atm (Table 3, run 39, AP 4.2 mol%).

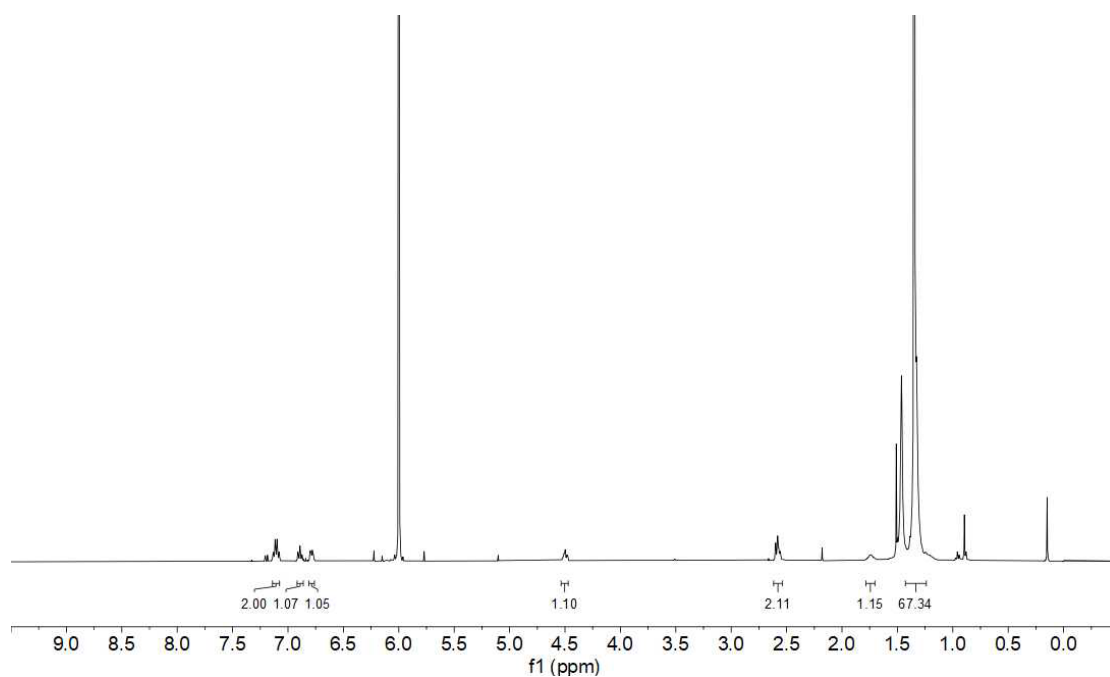


Figure S20. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 3-MAO catalyst system at 50 °C, AP 0.51 M, ethylene 2 atm (Table 3, run 40, AP 6.0 mol%).

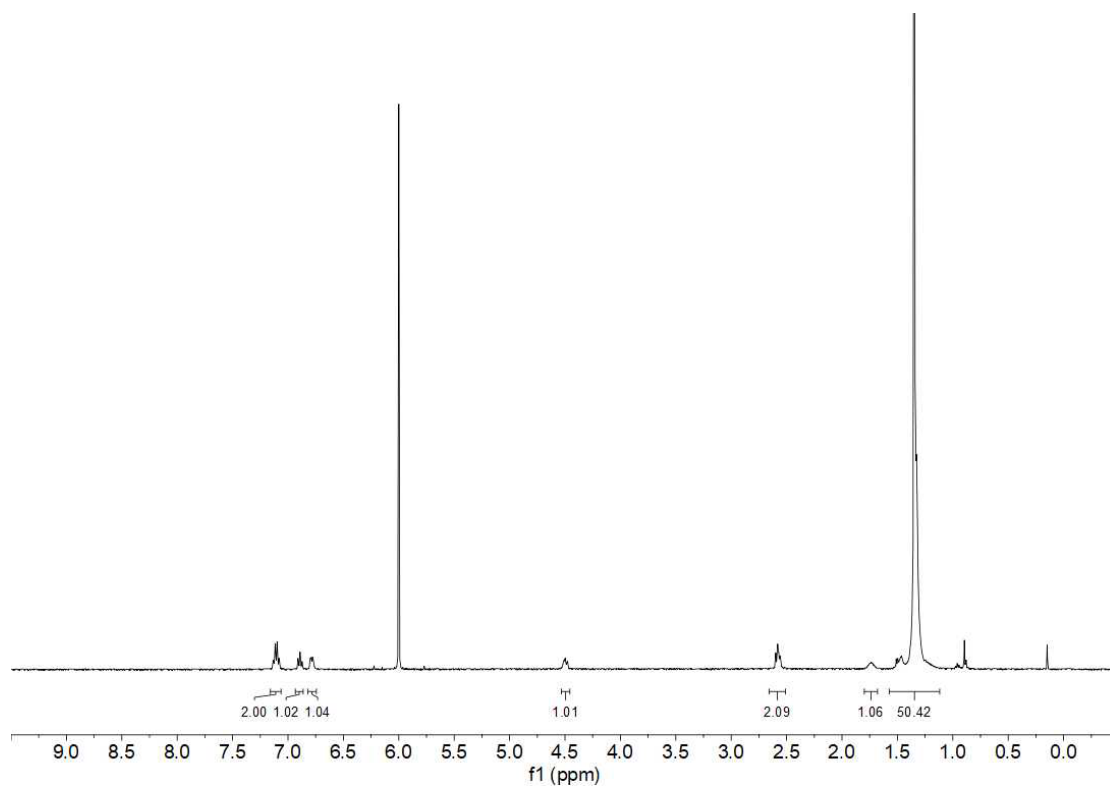


Figure S21. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 3-MAO catalyst system at 50 °C, AP 0.51 M, ethylene 2 atm (Table 3, run 41, AP 8.2 mol%).

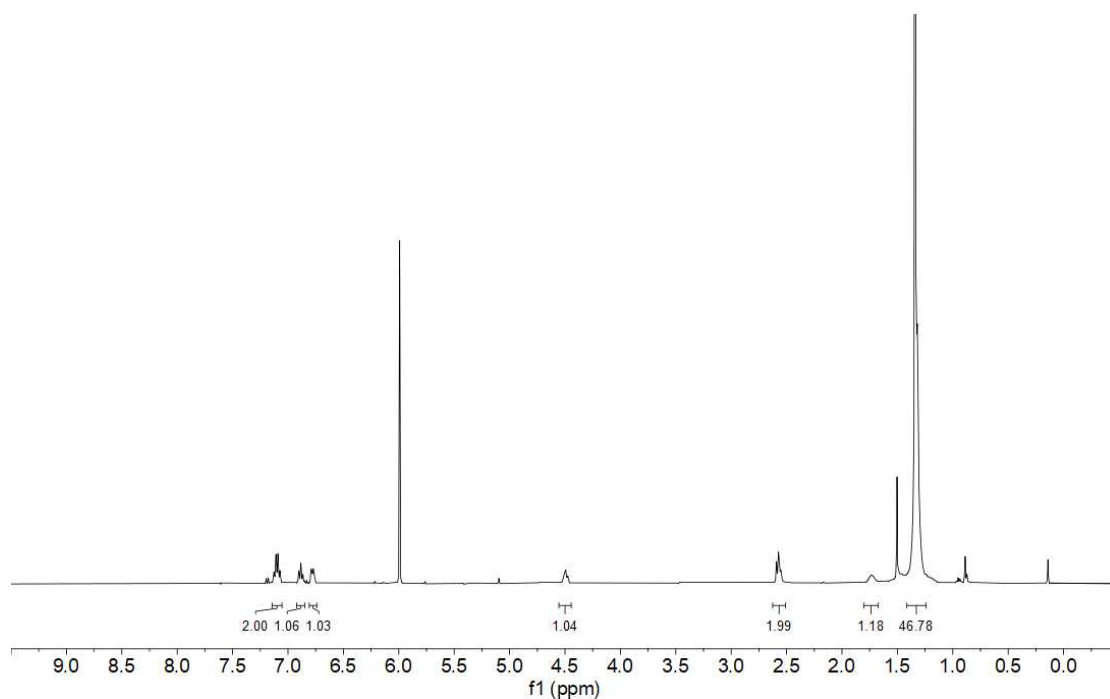


Figure S22. ¹H NMR spectrum (1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for poly(ethylene-*co*-AP) prepared by 3-MAO catalyst system at 50 °C, AP 0.76 M, ethylene 2 atm (Table 3, run 42, AP 9.0 mol%).

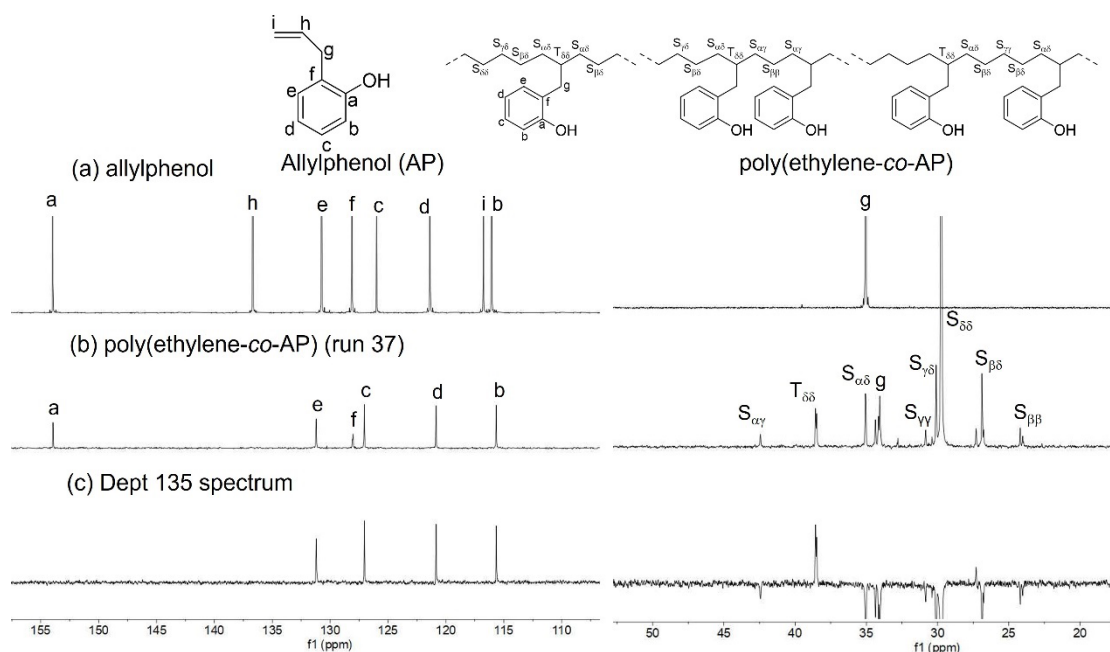
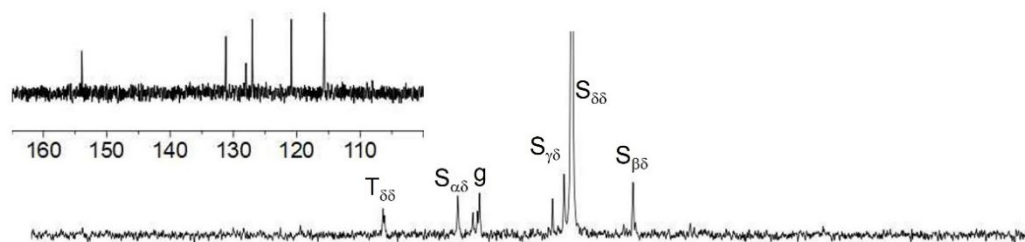


Figure S23. (a,b) ^{13}C NMR spectra and (c) dept spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 $^{\circ}\text{C}$) for (a) allylphenol (AP) and (b,c) poly(ethylene-co-AP) (Table 3, run 37, AP 8.0 mol%).

(a) ^{13}C NMR spectrum of the sample run 35 (by cat.2)



(b) Dept 135 spectrum

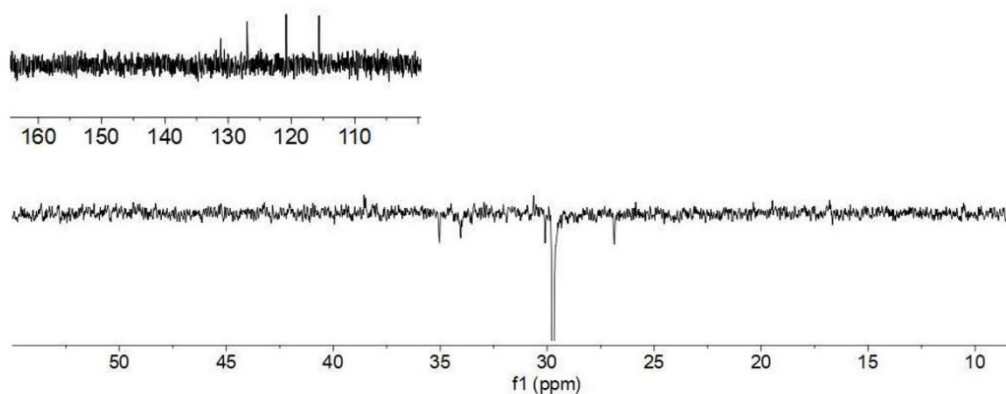


Figure S24. (a) ^{13}C NMR and (b) dept spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 $^{\circ}\text{C}$) for poly(ethylene-co-AP) (Table 3, run 35, AP 4.1 mol%).

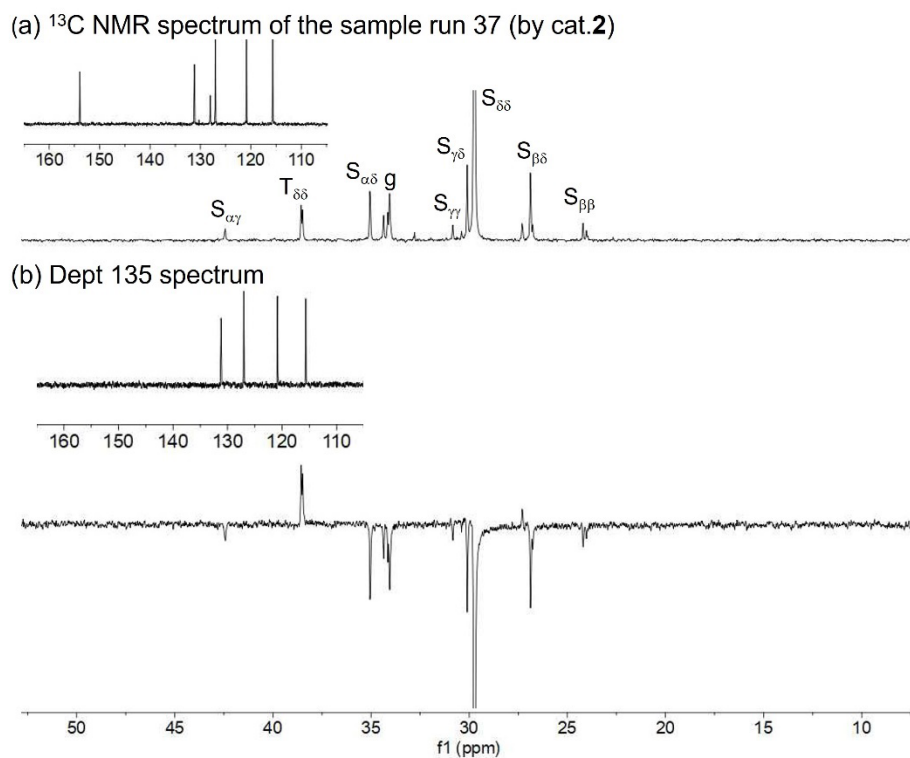


Figure S25. (a) ^{13}C NMR and (b) dept spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 $^{\circ}\text{C}$) for poly(ethylene-*co*-AP) (Table 3, run 37, AP 8.0 mol%).

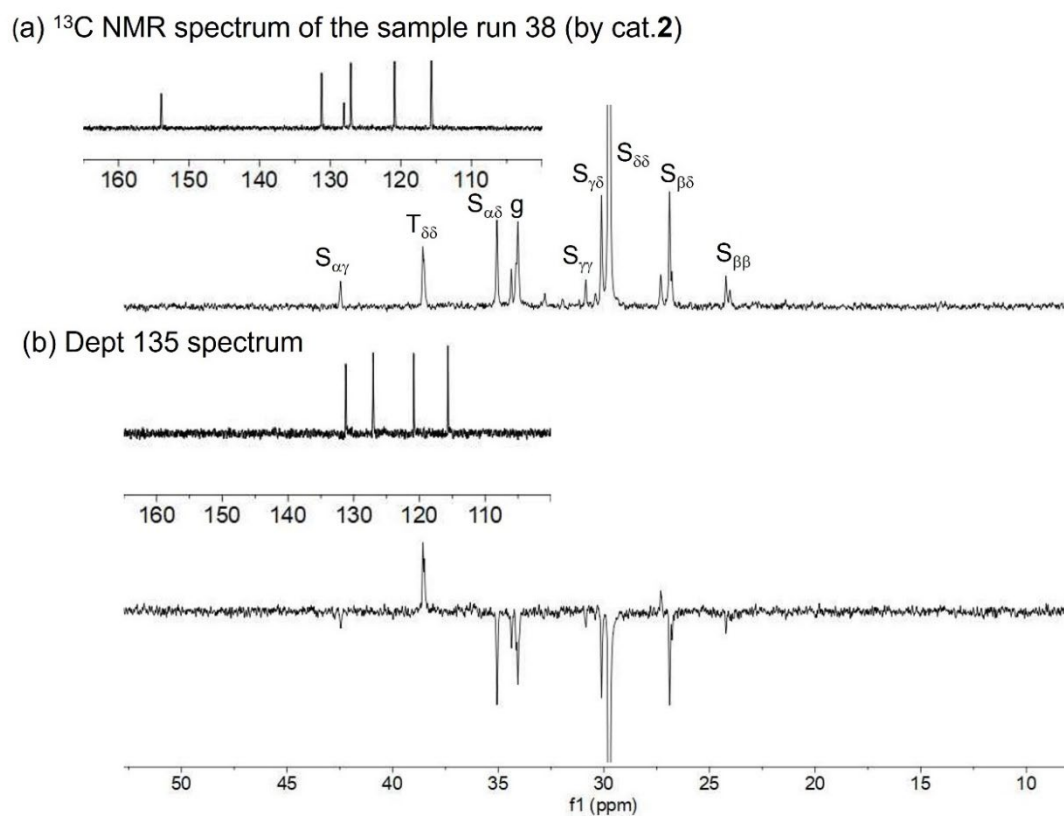


Figure S26. (a) ^{13}C NMR and (b) dept spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 $^{\circ}\text{C}$) for poly(ethylene-*co*-AP) (Table 3, run 38, AP 11.7 mol%).

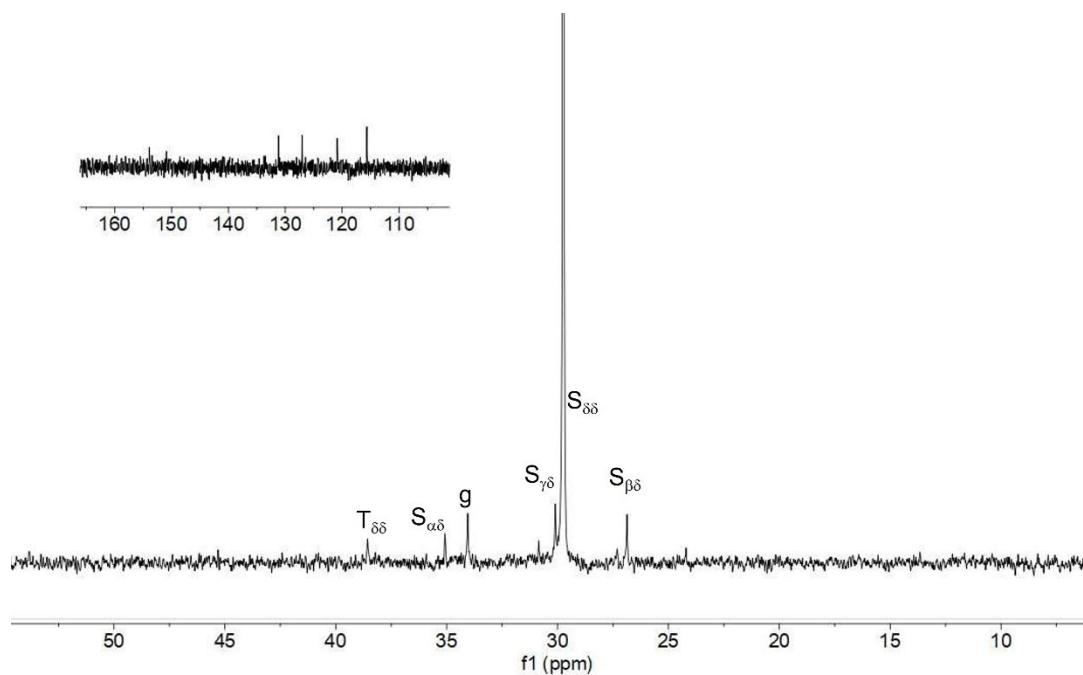
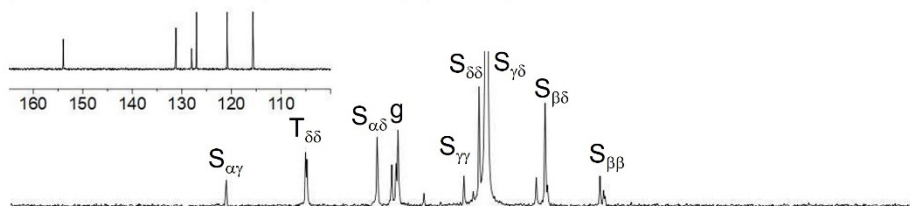


Figure S27. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 $^\circ\text{C}$) for poly(ethylene-*co*-AP) (Table 2, run 24, AP 3.0 mol%).

(a) ^{13}C NMR spectrum of the sample run 31 (by cat.1)



(b) Dept 135 spectrum

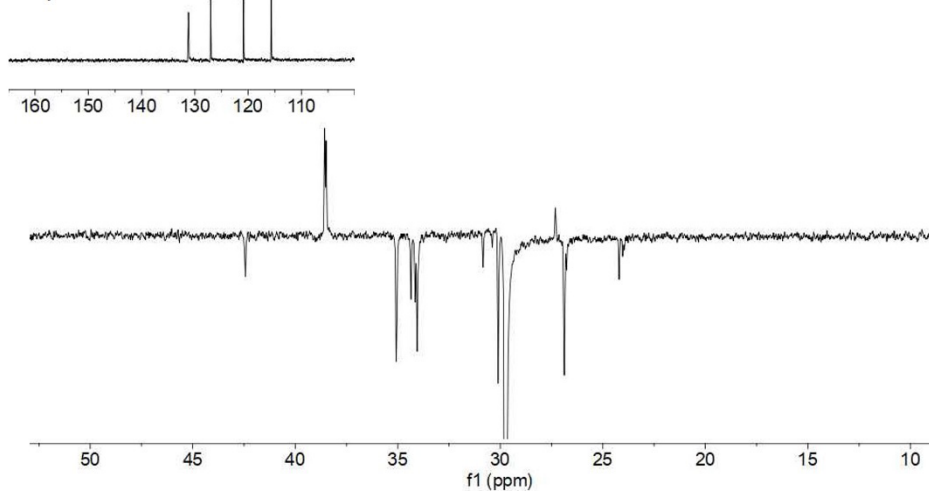


Figure S28. (a) ^{13}C NMR and (b) dept spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 $^\circ\text{C}$) for poly(ethylene-*co*-AP) (Table 3, run 31, AP 4.7 mol%).

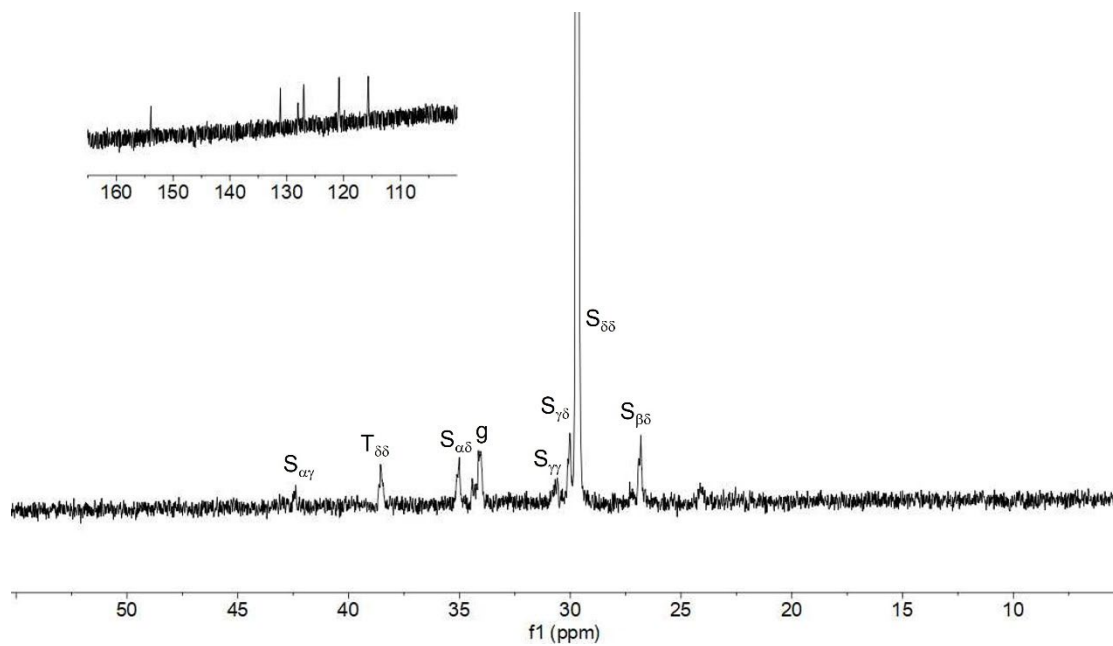


Figure S29. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co*-AP) (Table 3, run 32, AP 6.0 mol%).

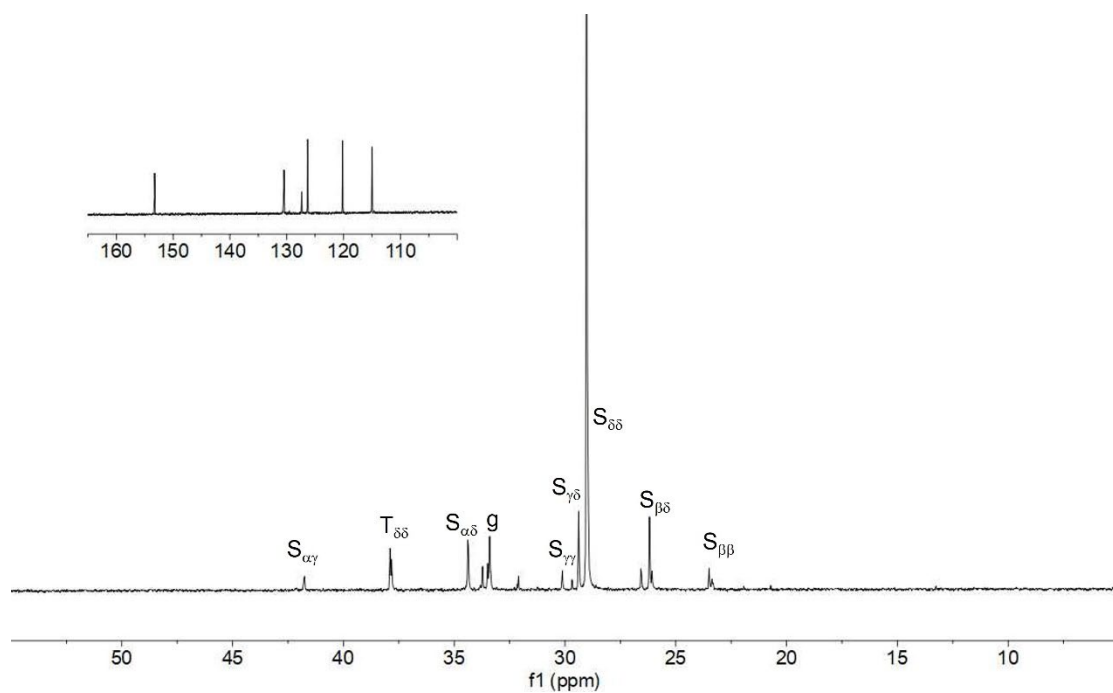
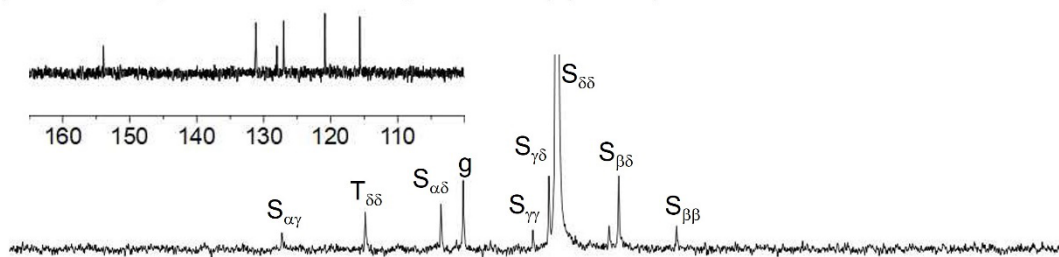


Figure S30. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co*-AP) (Table 3, run 34, AP 10.3 mol%).

(a) ^{13}C NMR spectrum of the sample run 21 (by cat.1)



(b) Dept 135 spectrum

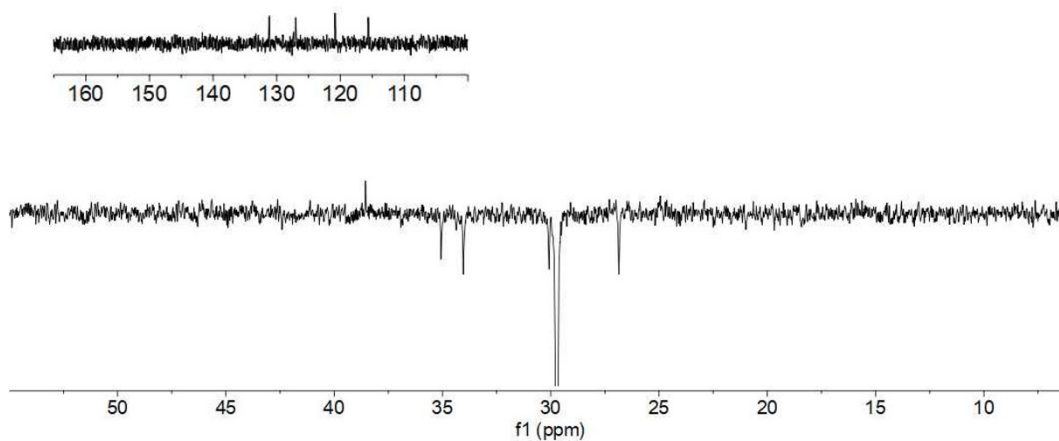


Figure S31. (a) ^{13}C NMR and (b) dept spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co*-AP) (Table 2, run 21, AP 3.0 mol%).

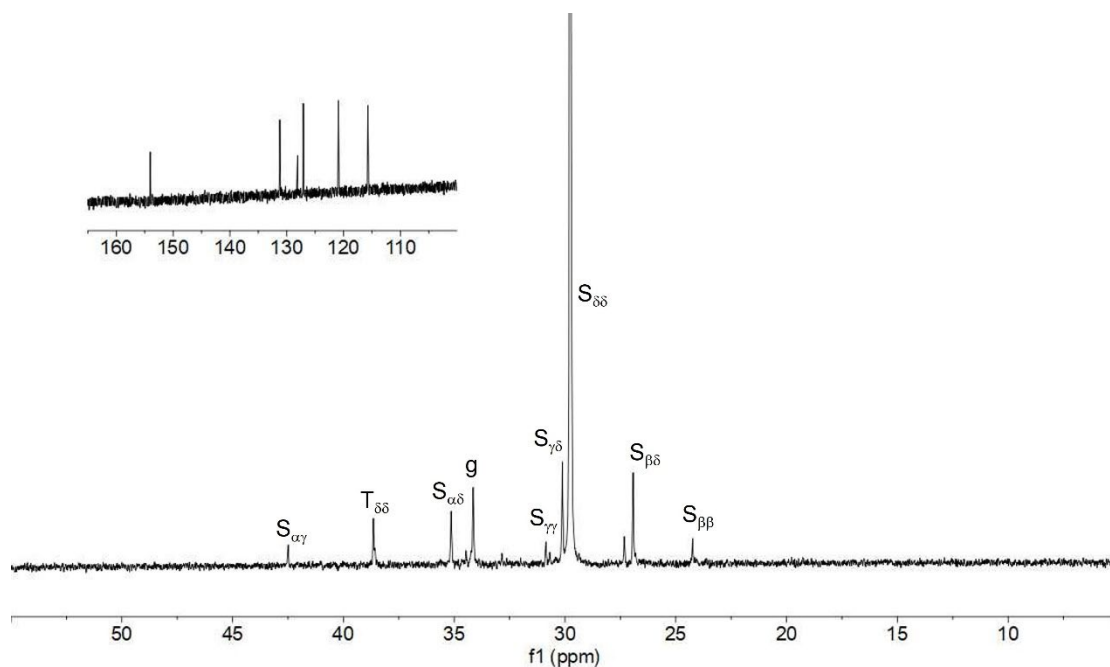


Figure S32. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co*-AP) (Table 2, run 27, AP 3.8 mol%).

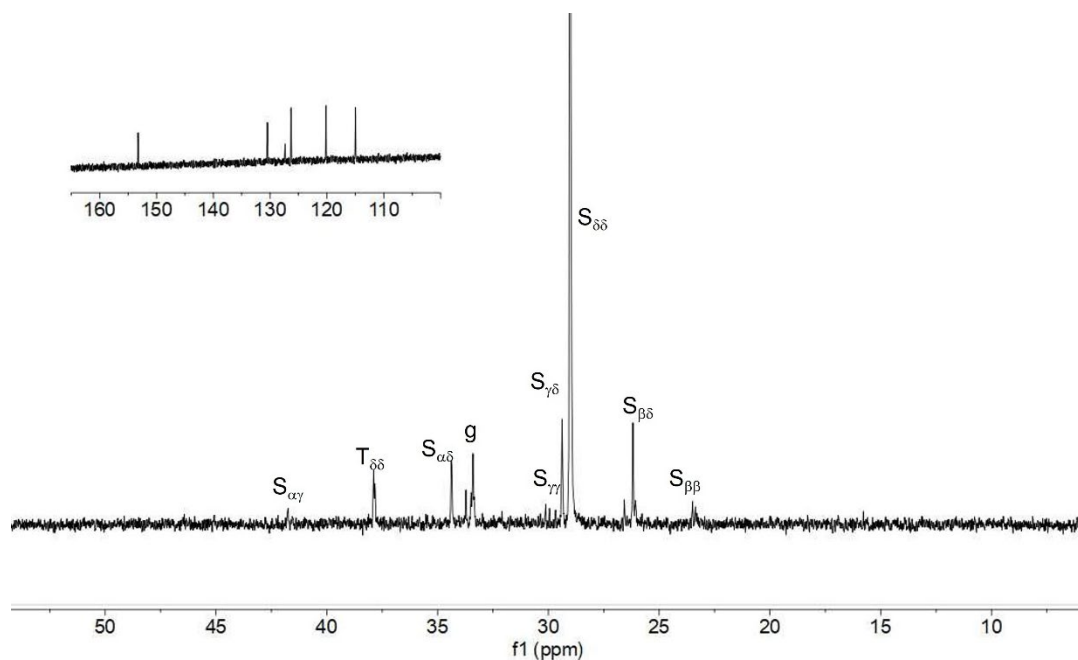
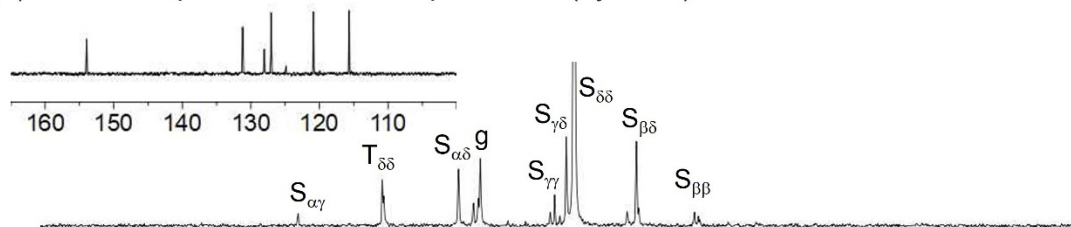


Figure S33. ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co*-AP) (Table 3, run 41, AP 8.2 mol%).

(a) ^{13}C NMR spectrum of the sample run 42 (by cat. 3)



(b) Dept 135 spectrum

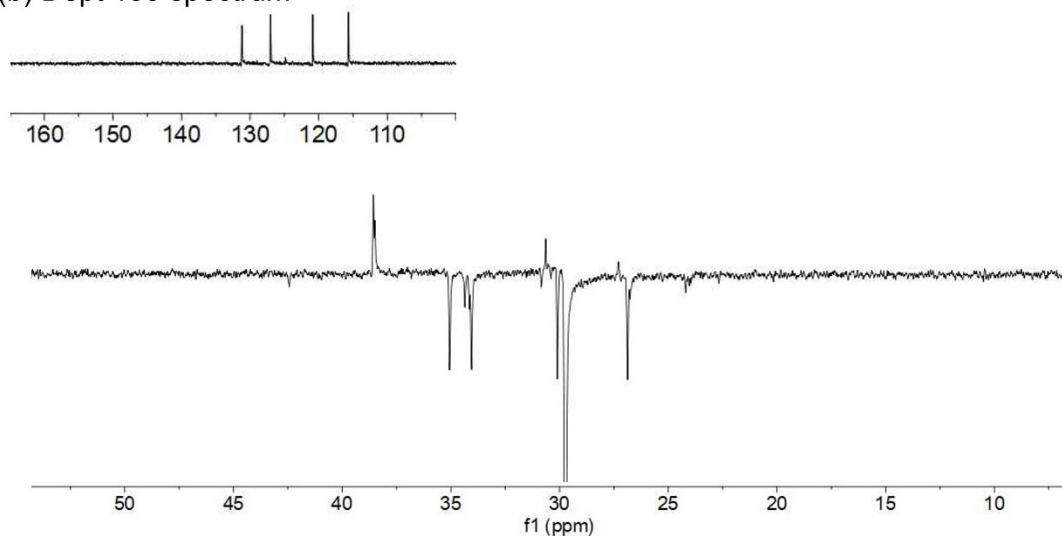


Figure S34. (a) ^{13}C NMR and (b) dept spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C) for poly(ethylene-*co*-AP) (Table 3, run 42, AP 9.0 mol%).

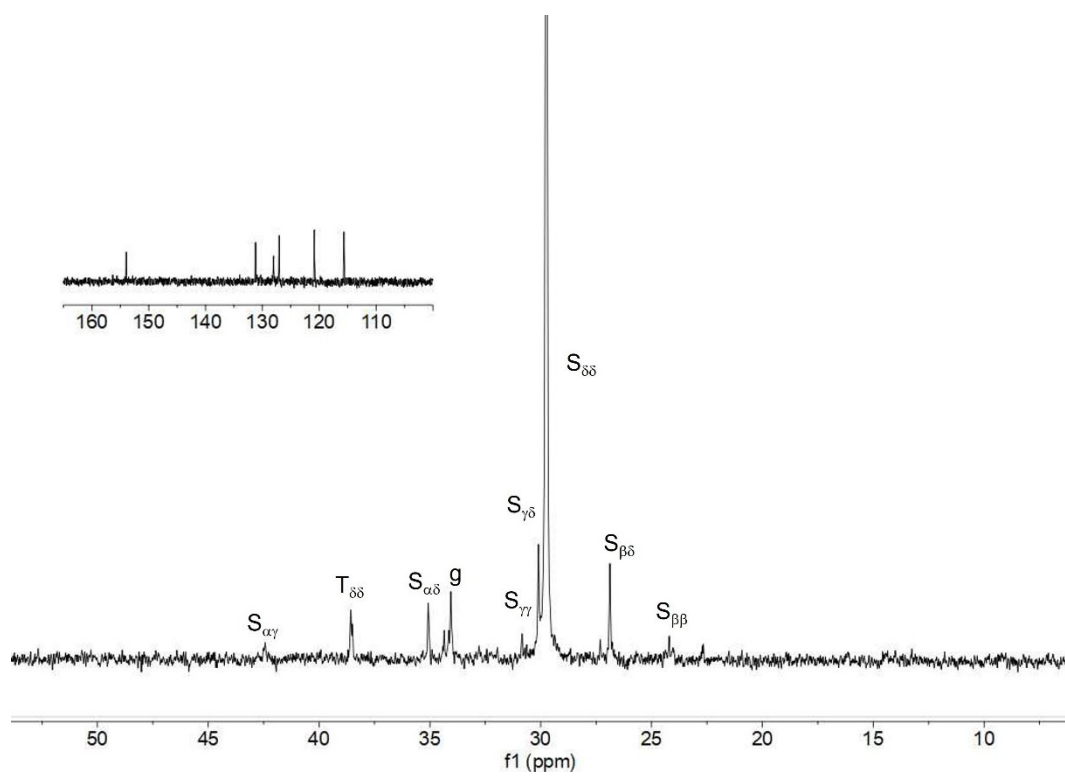


Figure S35. ^{13}C NMR spectrum (in $1,1,2,2\text{-tetrachloroethane-}d_2$ at $110\text{ }^\circ\text{C}$) for poly(ethylene-co-AP) (Table 2, run 29, AP 3.6 mol%).

3. Selected DSC thermograms in the copolymers.

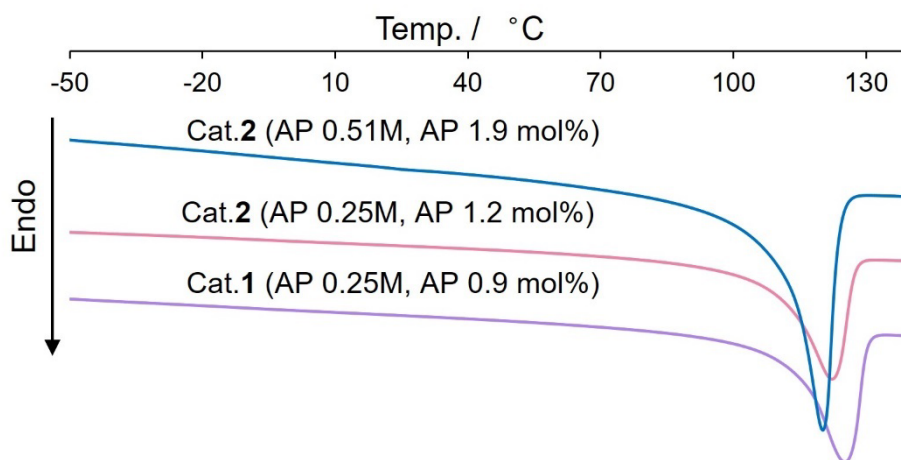


Figure S36. DSC thermograms for resultant polymers in ethylene copolymerization of allylphenol (AP) by 1,2-MAO catalyst systems, ethylene 4 atm. The detailed data are shown in Table 1.

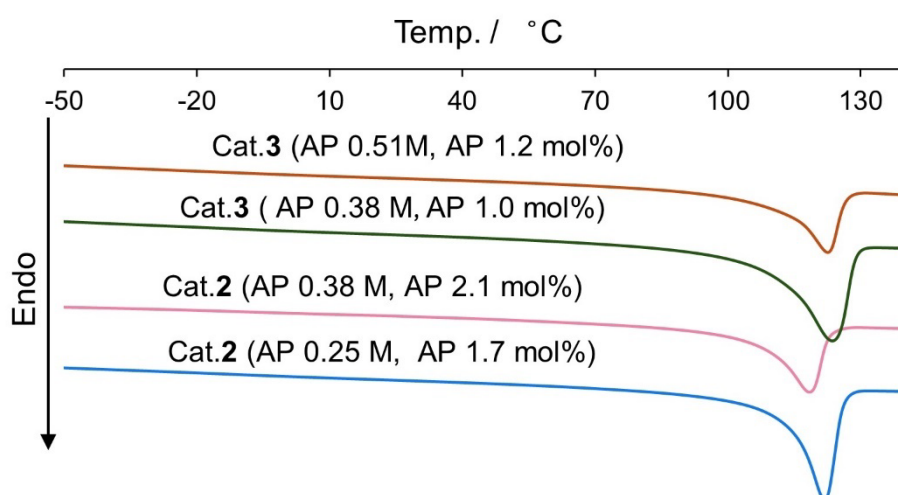


Figure S37. DSC thermograms for resultant polymers in ethylene copolymerization of allylphenol (AP) by 2,3-MAO catalyst systems, ethylene 6 atm. The detailed data are shown in Table 1.

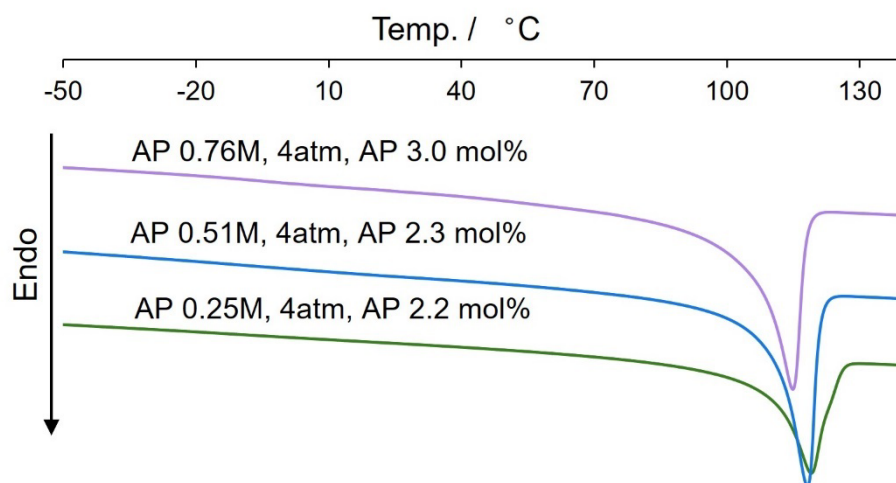


Figure S38. DSC thermograms for resultant polymers in ethylene copolymerization of allylphenol (AP) by 1-MAO catalyst system with pretreatment of AP with Al^iBu_3 and 2,6- $t\text{Bu}_2\text{C}_6\text{H}_4\text{OH}$, ethylene 4 atm. The detailed data are shown in Table 2 (runs 19-21).

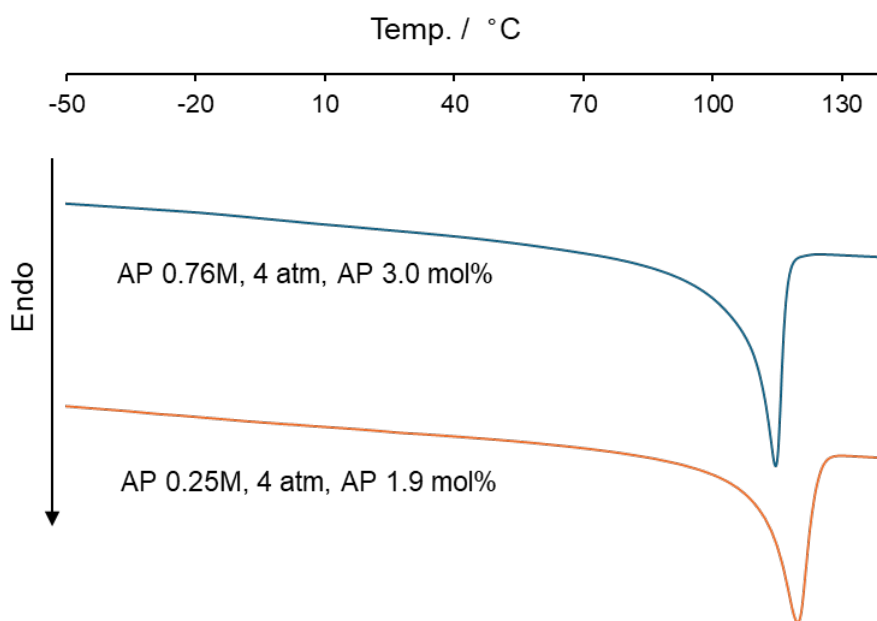


Figure S39. DSC thermograms for resultant polymers in ethylene copolymerization of allylphenol (AP) by 2-MAO catalyst system with pretreatment of AP with Al^iBu_3 and 2,6- $t\text{Bu}_2\text{C}_6\text{H}_4\text{OH}$, ethylene 4 atm. The detailed data are shown in Table 2 (runs 22-24).

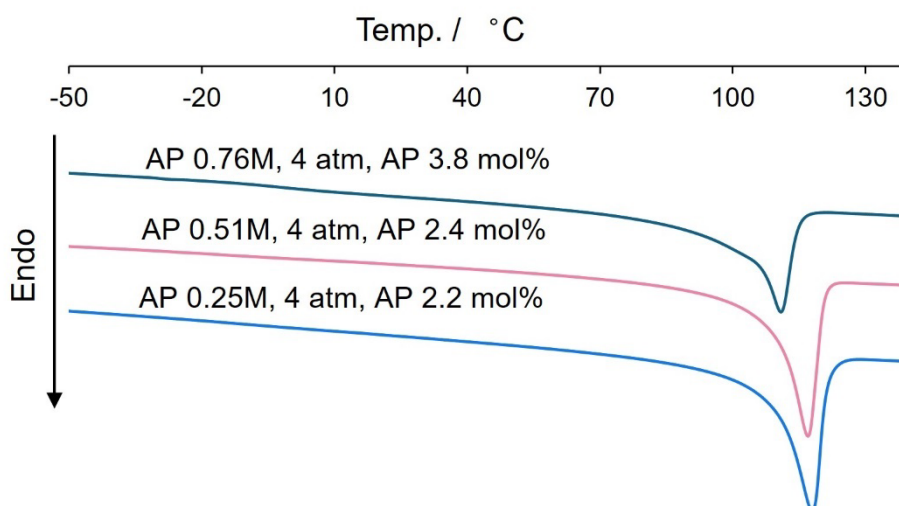


Figure S40. DSC thermograms for resultant polymers in ethylene copolymerization of allylphenol (AP) by 3-MAO catalyst system with pretreatment of AP with Al^tBu_3 and 2,6- $t\text{Bu}_2\text{C}_6\text{H}_4\text{OH}$, ethylene 4 atm. The detailed data are shown in Table 2 (runs 25-27).

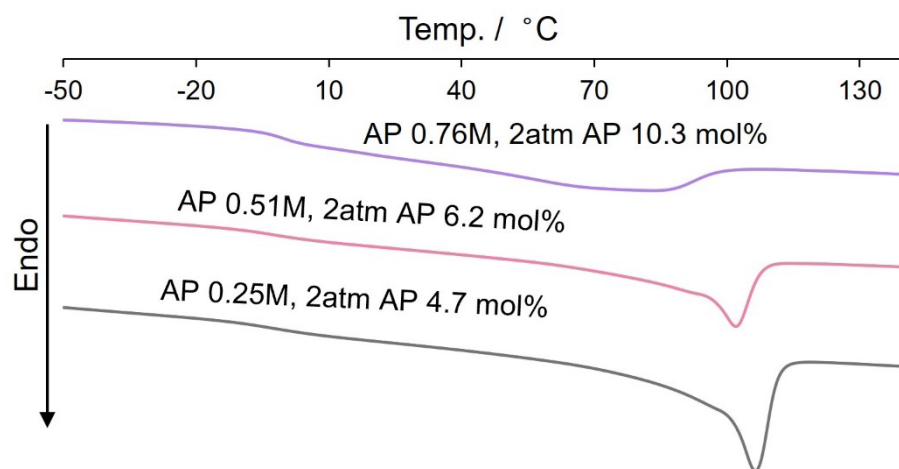


Figure S41. DSC thermograms for resultant polymers in ethylene copolymerization of allylphenol (AP) by 1-MAO catalyst system with pretreatment of AP with Al^tBu_3 and 2,6- $t\text{Bu}_2\text{C}_6\text{H}_4\text{OH}$, ethylene 2 atm. The detailed data are shown in Table 3 (runs 31,33,34).

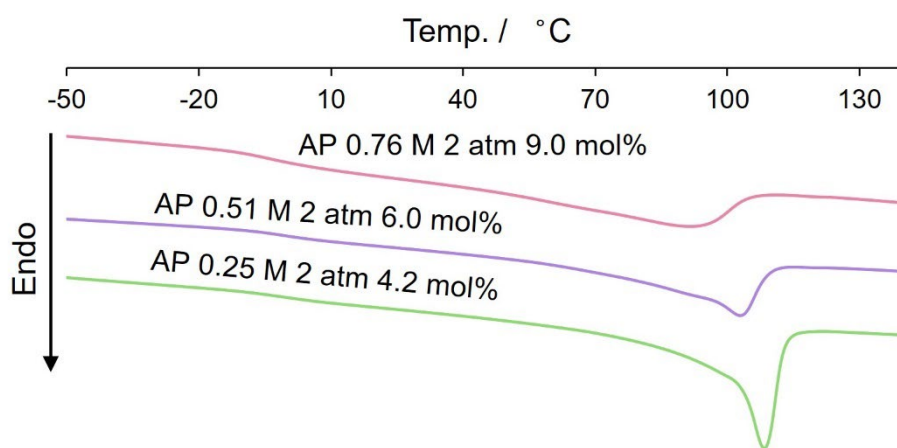


Figure S42. DSC thermograms for resultant polymers in ethylene copolymerization of allylphenol (AP) by 3-MAO catalyst system. The detailed data are shown in Table 3 (runs 39,40,42).