Supporting Information

for

Synthesis of Bio-Based Long Chain Polyesters by Acyclic Diene Metathesis (ADMET) Polymerization and Tandem Hydrogenation, and Depolymerization with Ethylene

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Contents

1. Additional polymerization results

Table S1. Synthesis of saturated polyesters by tandem ADMET polymerization and hydrogenation using ruthenium-carbene catalysts.[a]

run	monomer (mmol)	cat.	H_2 / MPa	time / h	temp. / ºC	yield [b] / %	M_n x10^{-4} [c] before	M_n x10^{-4} [c] after	M_w/M_n [c] before	M_w/M_n [c] after
31	ME1 (0.71)	HG2	1.0	3	50	88	1.28	1.38	1.41	1.45
S1	ME1 (0.71)	G2	1.0	3	25	93	1.16	1.28	1.43	1.42
S2	ME1 (0.71)	HG2	1.0	1	50	91	1.11	1.29	1.39	1.38
S3	ME1 (0.71)	G2	1.0	1	50	88	1.02	1.19	1.44	1.49
S4	ME1 (0.71)	G2	0.5	3	50	90	1.06	1.21	1.43	1.45
S5	ME1 (0.71)	HG2	0.5	3	50	93	1.20	1.34	1.47	1.39
33	ME1 (2.36)	HG2	1.0	3	25	94	1.23	1.32	1.46	1.48
32	ME1 (2.36)	HG2	1.0	3	50	90	1.64	1.66	1.51	1.48
34	ME2 (0.65)	HG2	1.0	3	50	87	1.40	1.59	1.42	1.44
35	ME2 (0.65)	G2	1.0	3	50	85	1.19	1.31	1.38	1.28
36	ME2 (0.65)	HG2	2.0	3	50	90	1.32	1.60	1.45	1.49
37	ME2 (2.08)	HG2	1.0	3	50	93	1.37	1.58	1.48	1.53
38	ME3 (0.65)	G2	1.0	3	50	93	0.95	1.04	1.41	1.42
39	ME3 (0.65)	HG2	1.0	3	50	92	1.02	1.11	1.38	1.39
40	ME3 (0.65)	HG2	0.5	3	50	90	0.97	1.09	1.37	1.34
41	ME3 (0.65)	HG2	2.0	3	50	91	1.07	1.18	1.34	1.32
S6	ME3 (0.65)	HG2	1.0	3	25	88	1.07	1.16	1.39	1.37
S7	ME3 (0.65)	HG2	1.0	1	50	91	1.01	1.13	1.32	1.35
S8	ME3 (0.65)	G2	1.0	3[d]	50	90	0.78	0.83	1.32	1.35
S9	ME3 (0.65)	HG2	1.0	3[d]	50	91	0.91	0.96	1.38	1.32
42	ME3 (2.08)	HG2	1.0	3	50	92	1.09	1.10	1.46	1.53
43	ME4 (2.09)	HG2	1.0	3	50	92	0.86	0.92	1.48	1.51

[a]Conditions: Ru cat. 2.0 mol%, monomer 300 mg in $CHCl_3$ 0.14 mL or monomer 1000 mg in $CHCl_3$ 0.34 mL (run 32, 0.38 mL), 50 ºC. ADMET polymerization 24 h, and hydrogenation 3 h after addition of Al_2O_3. Al_2O_3 5 mg (1.7 wt %, monomer 300 mg scale) or 10 mg (1.0 wt%, monomer 1000 mg scale). [b]Isolated yeld as MeOH insoluble fraction. [c]GPC data in THF vs polystyrene standards. [d]Attempted tandem hydrogenation without adding Al_2O_3.

2. Selected NMR spectra

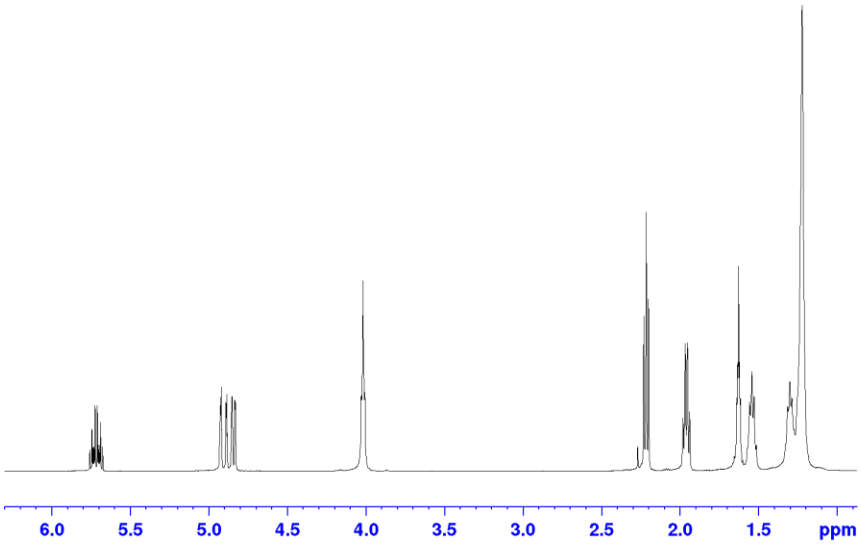


Figure S1. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for ME1.

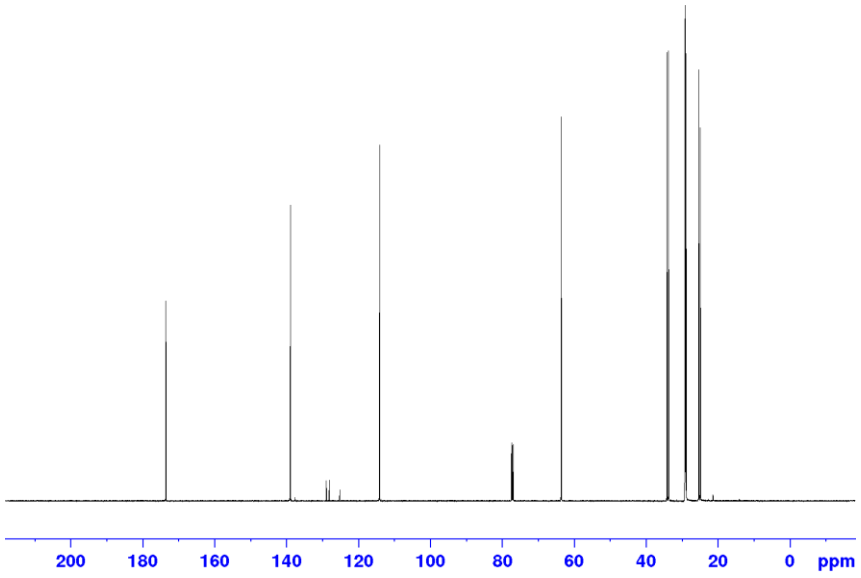


Figure S2. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for ME1.

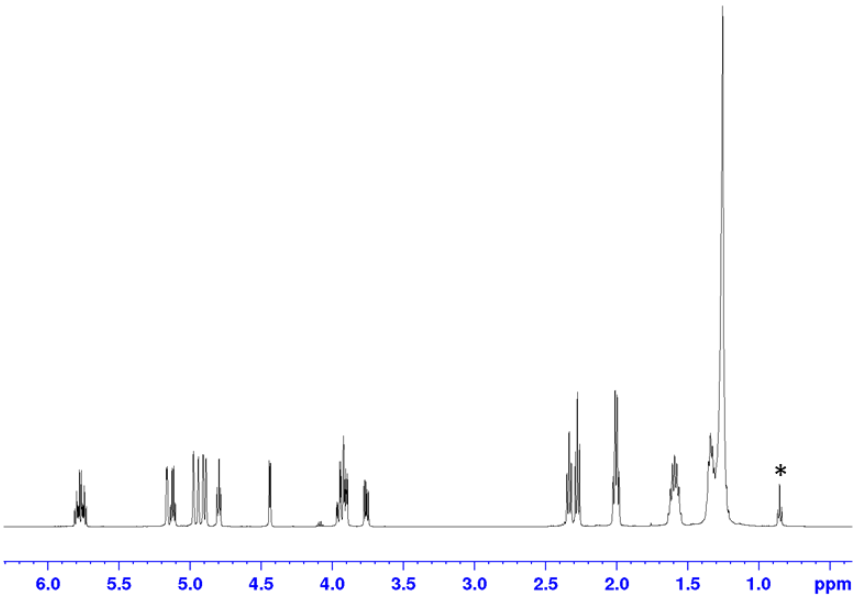


Figure S3. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for ME2. *impurity

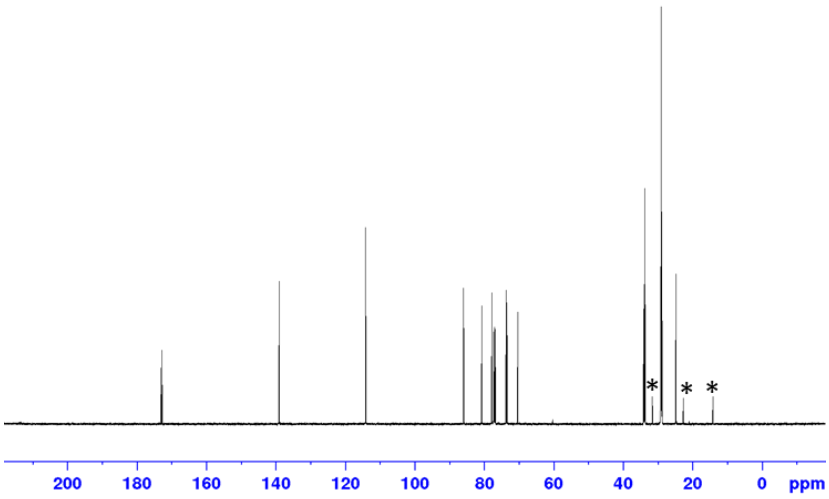


Figure S4. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for ME2. *impurity

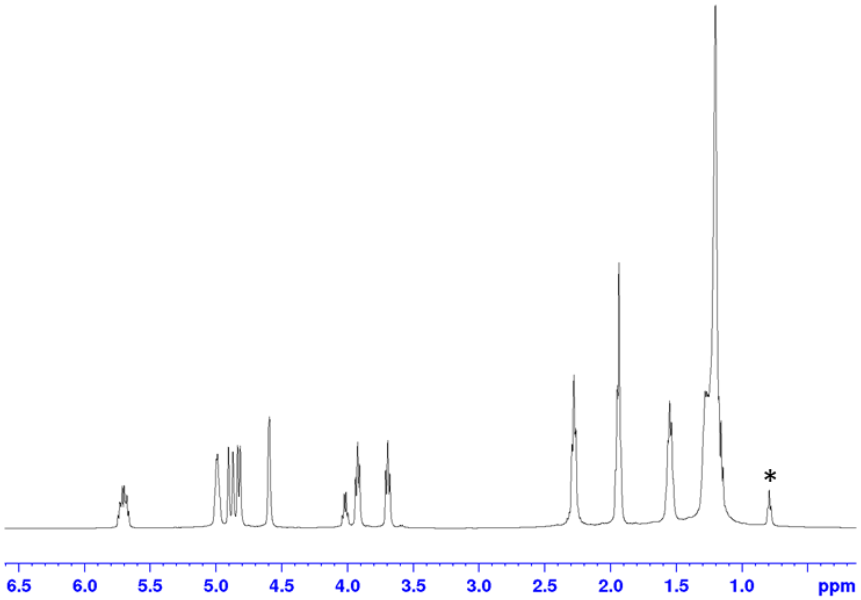


Figure S5. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for ME3. *impurity

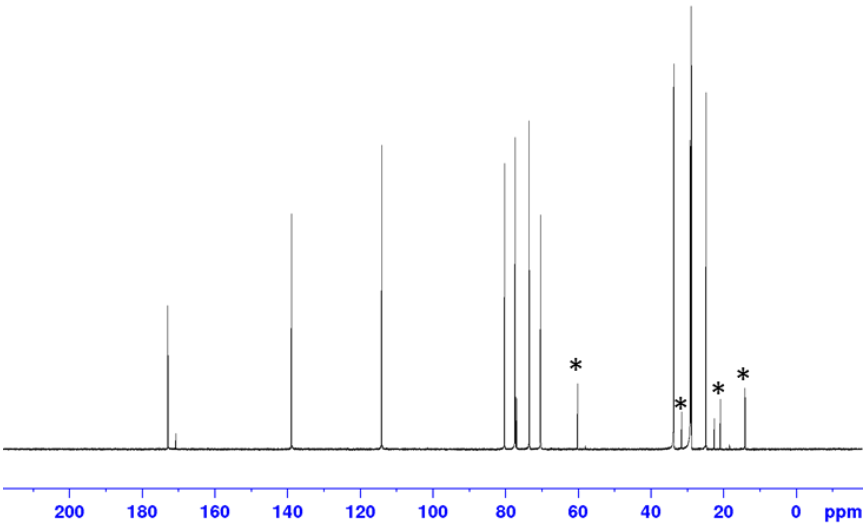


Figure S6. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for ME3. *impurity

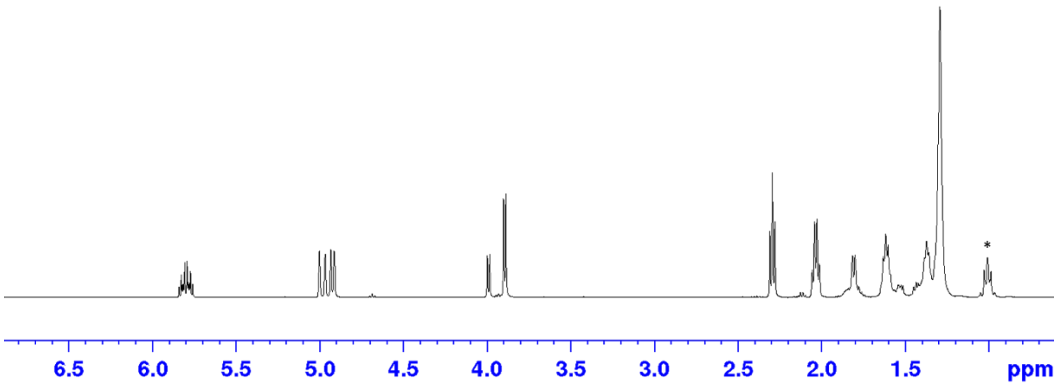


Figure S7. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for ME4. *impurity

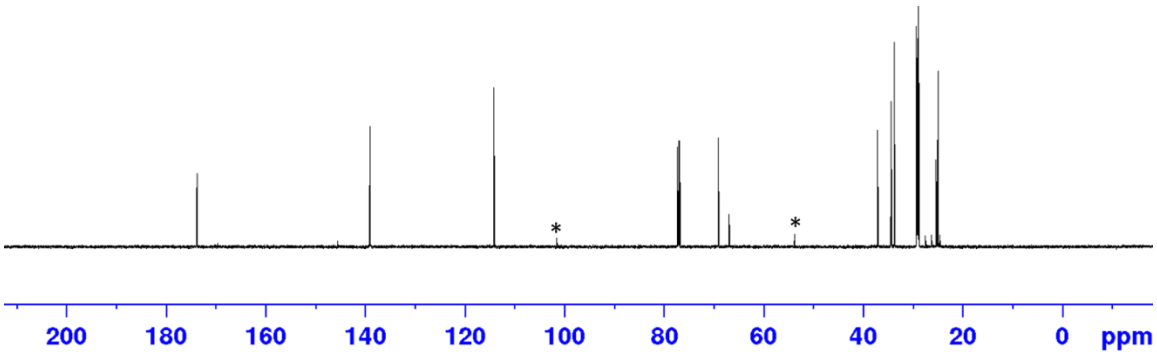


Figure S8. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for ME4. *impurity

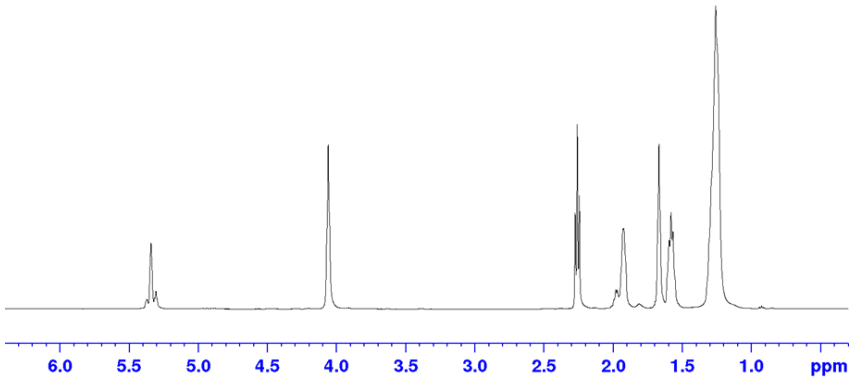


Figure S9. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for PE1 (run 3, Table 1).

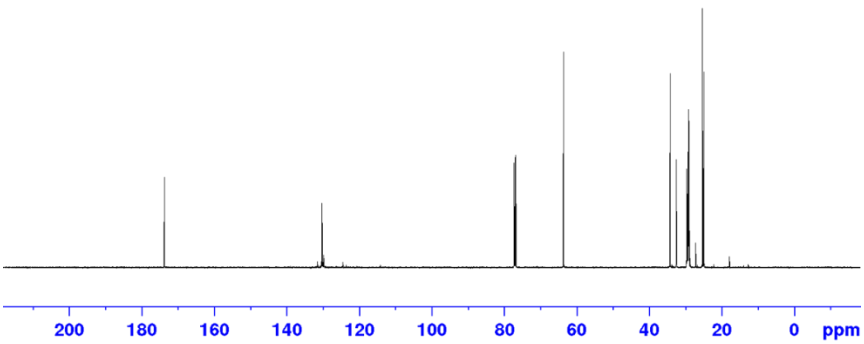


Figure S10. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for PE1 (run 3, Table 1).

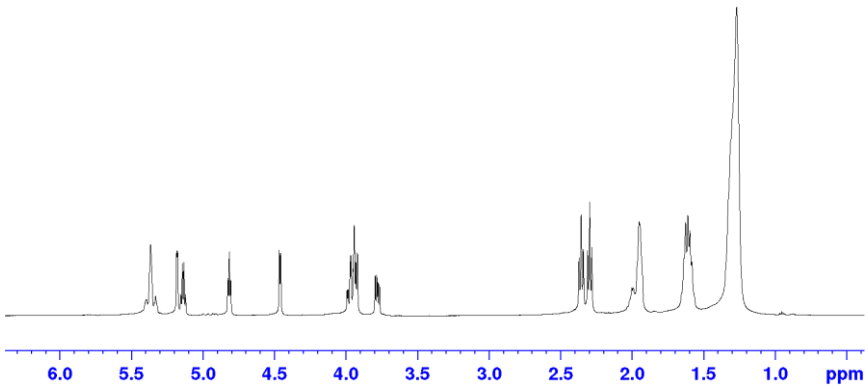


Figure S11. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for PE2 (run 15, Table 1).

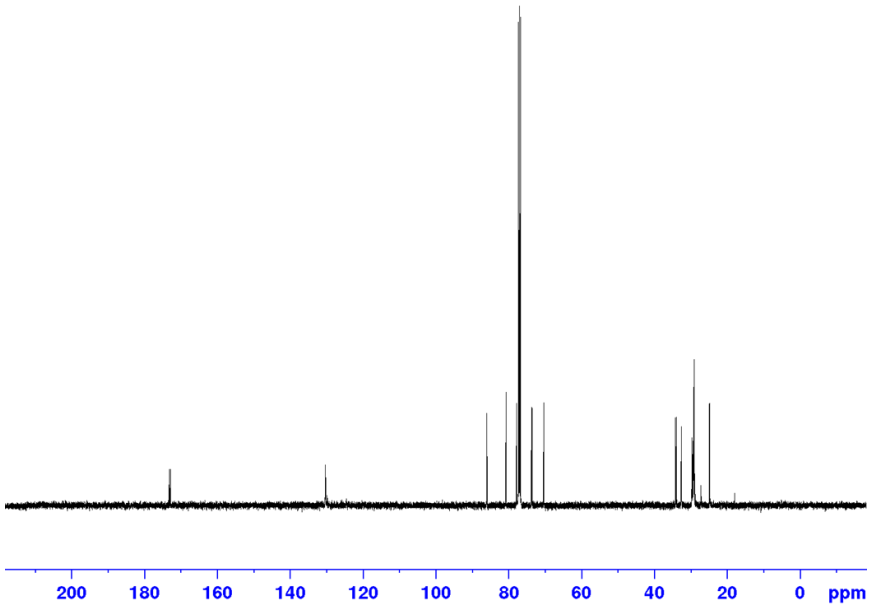


Figure S12. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for PE2 (run 15, Table 1).

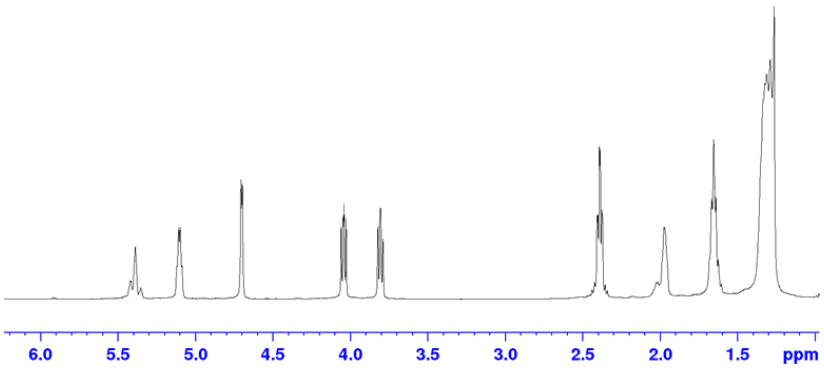


Figure S13. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for PE3 (run 23, Table 1).

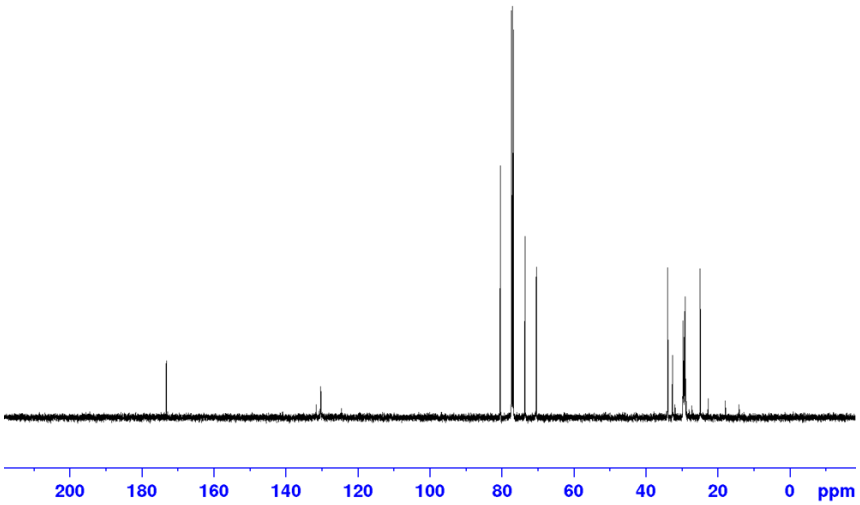


Figure S14. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for PE3 (run 23, Table 1).

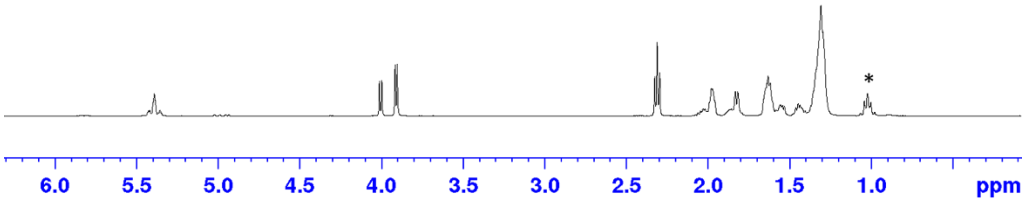


Figure S15. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for PE4 (run 29, Table 1). *impurity

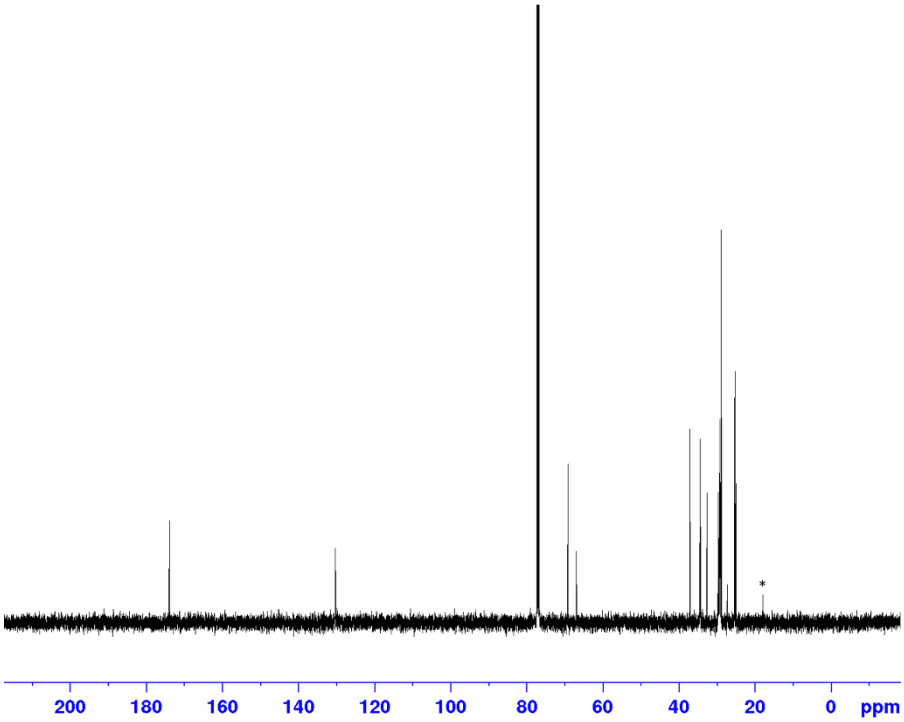


Figure S16. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for PE4 (run 29, Table 1). *impurity

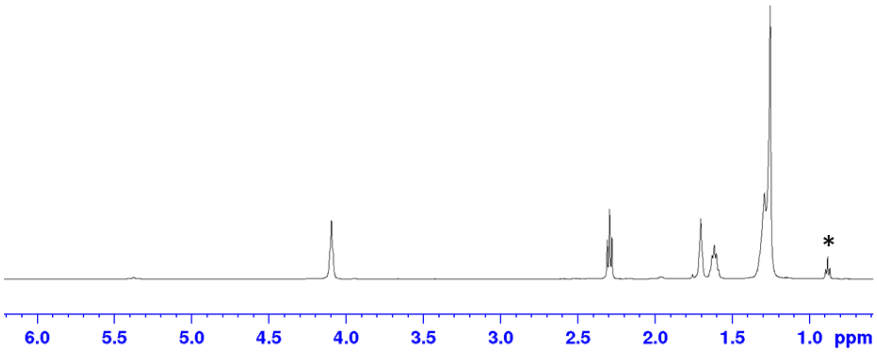


Figure S17. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for HPE1 (run 33, Table 2). *impurity

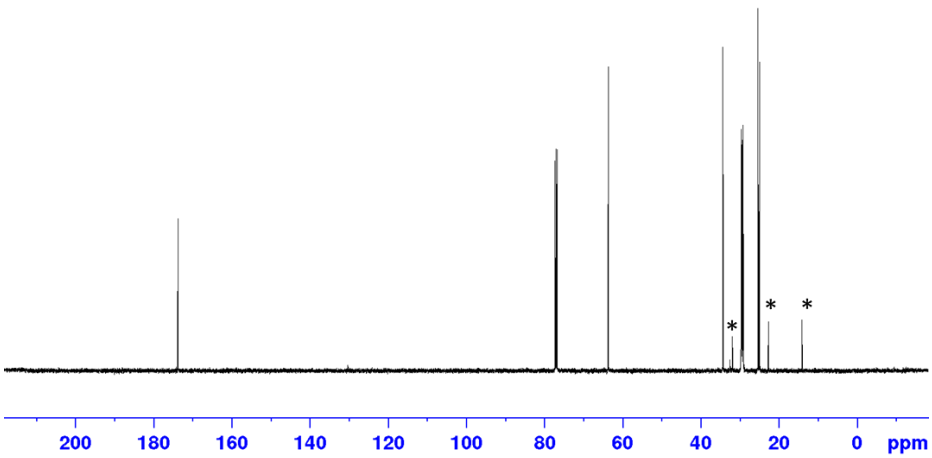


Figure S18. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for HPE1 (run 33, Table 2). *impurity

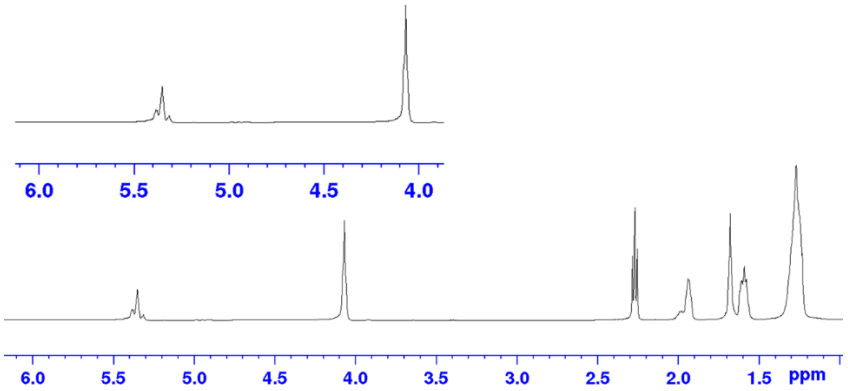


Figure S19. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for HPE1 (run S2, Table S1-1). Incomplete hydrogenation

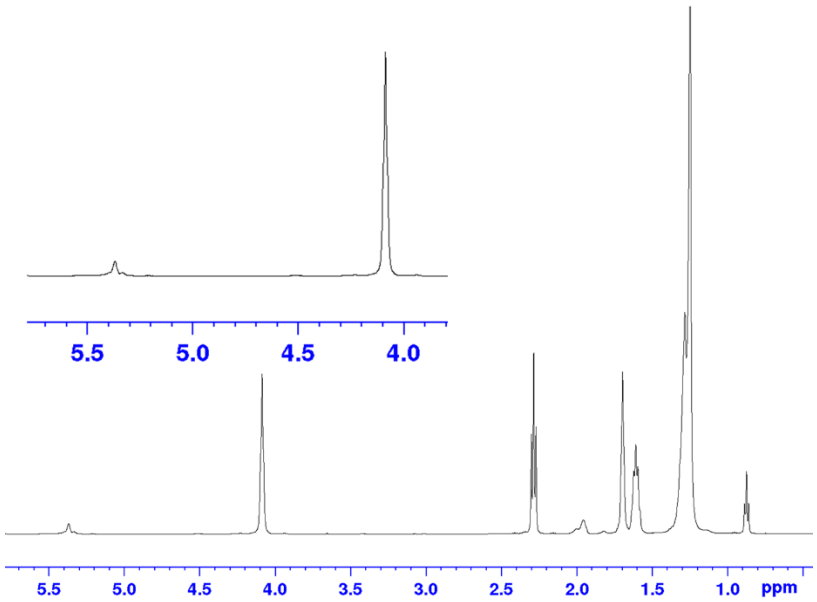


Figure S20. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for HPE1 (run S4, Table S1-1). Incomplete hydrogenation

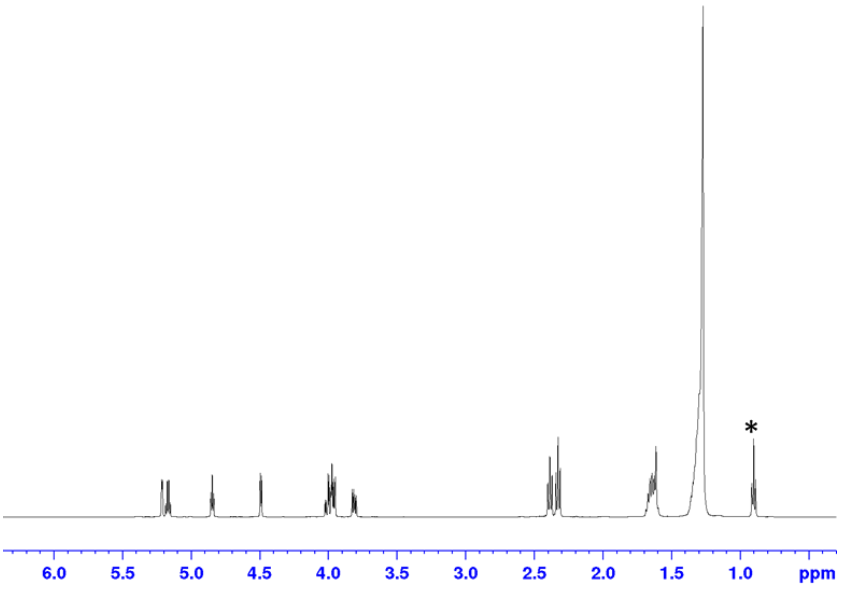


Figure S21. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for HPE2 (run 37, Table 2). *impurity

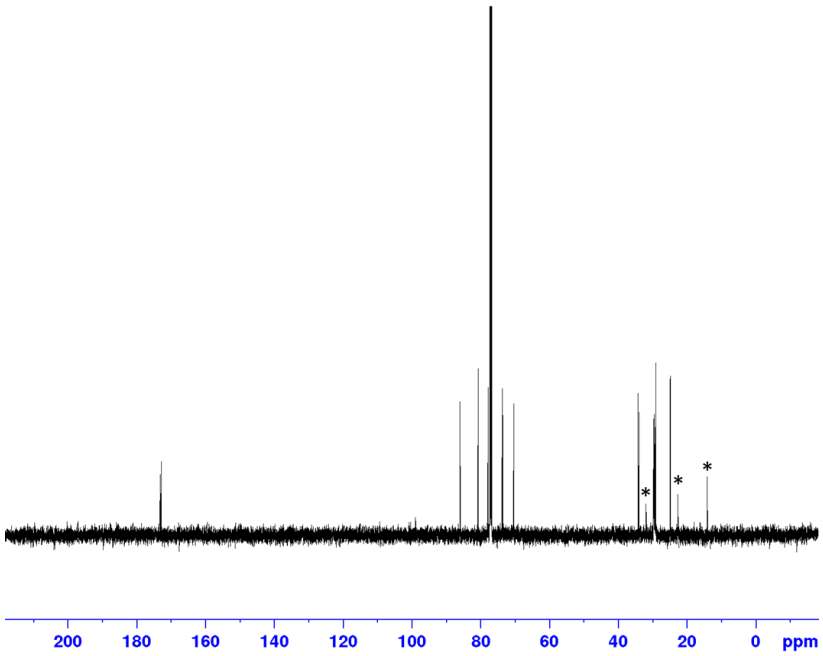


Figure S22. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for HPE2 (run 37, Table 2). *impurity

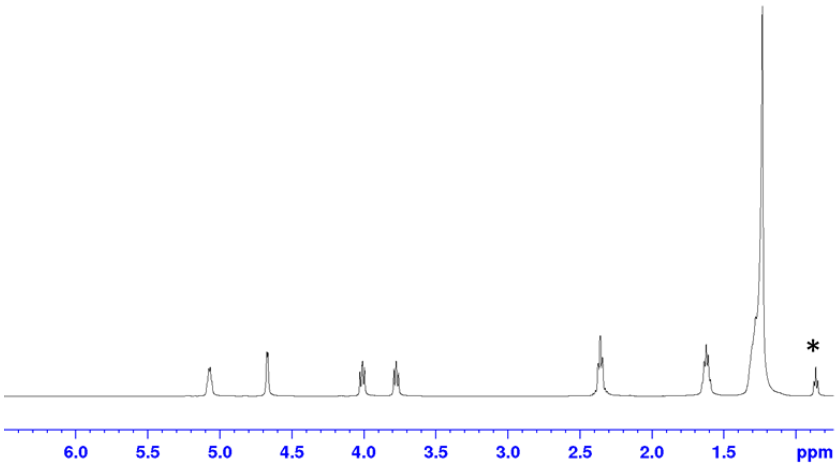


Figure S23. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for HPE3 (under 2.0 MPa H_2, run 41, Table 2). *impurity

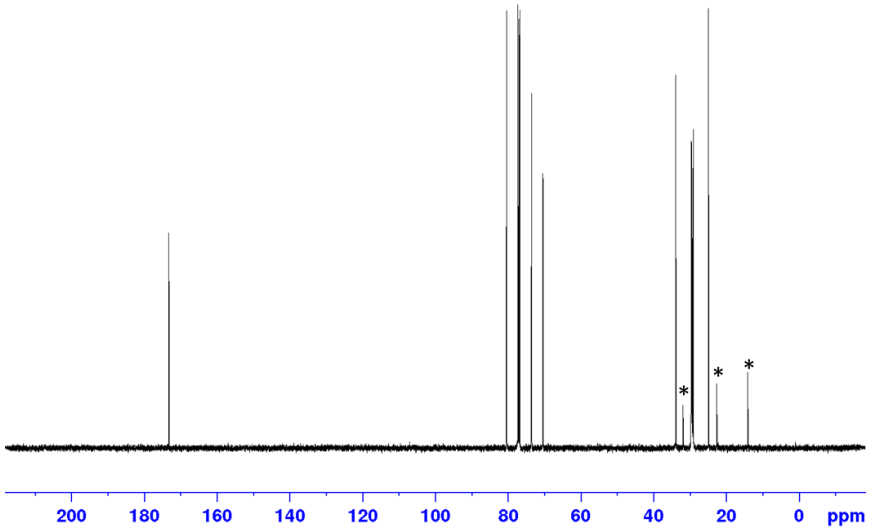


Figure S24. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for HPE3 (under 2.0 MPa H_2, run 41, Table 2). *impurity

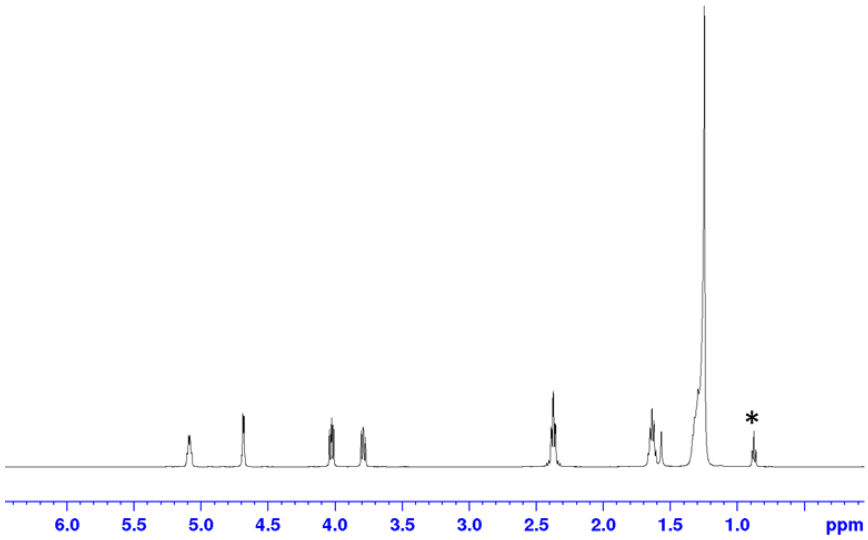


Figure S25. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for HPE3 (under 1.0 MPa H_2, run 39, Table 2). *impurity

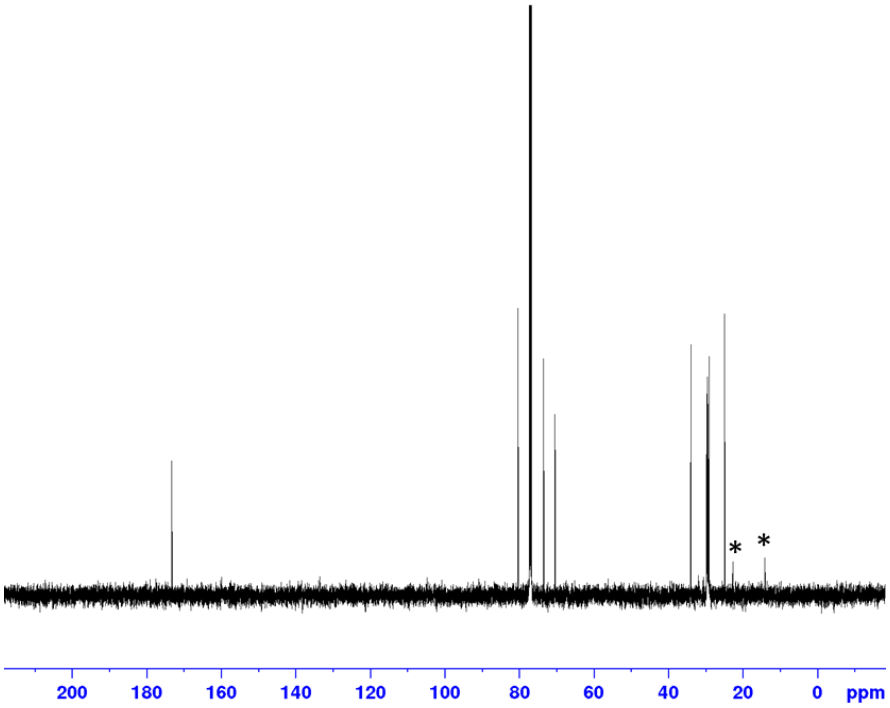


Figure S26. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for HPE3 (under 1.0 MPa H_2, run 39, Table 2). *impurity

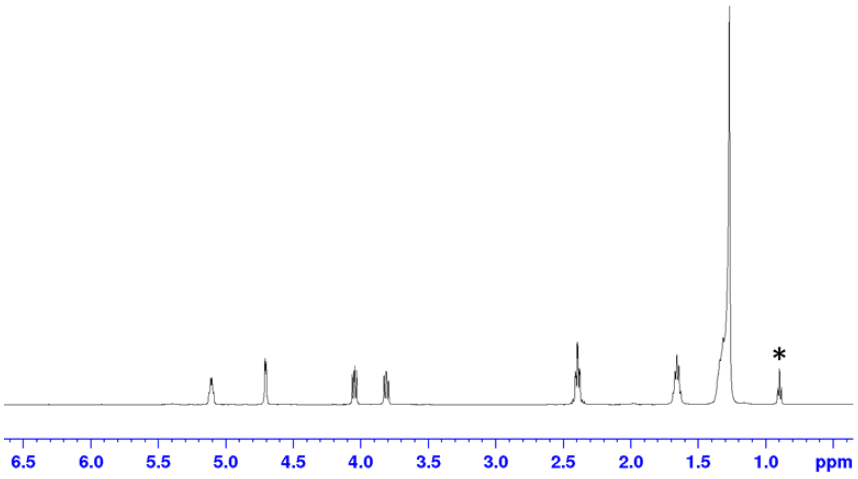


Figure S27. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for HPE3 (under 0.5 MPa H_2, run 40, Table 2). *impurity

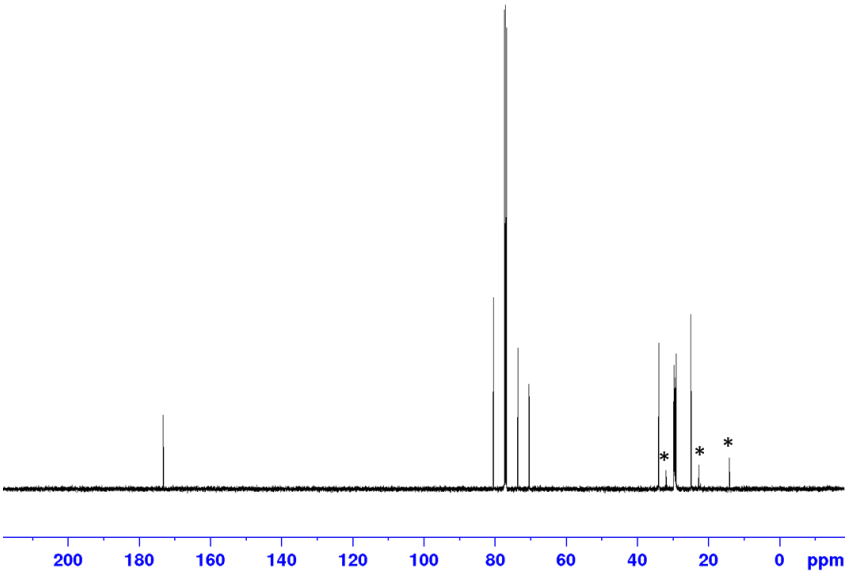


Figure S28. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for HPE3 (under 0.5 MPa H_2 run 40, Table 2). *impurity

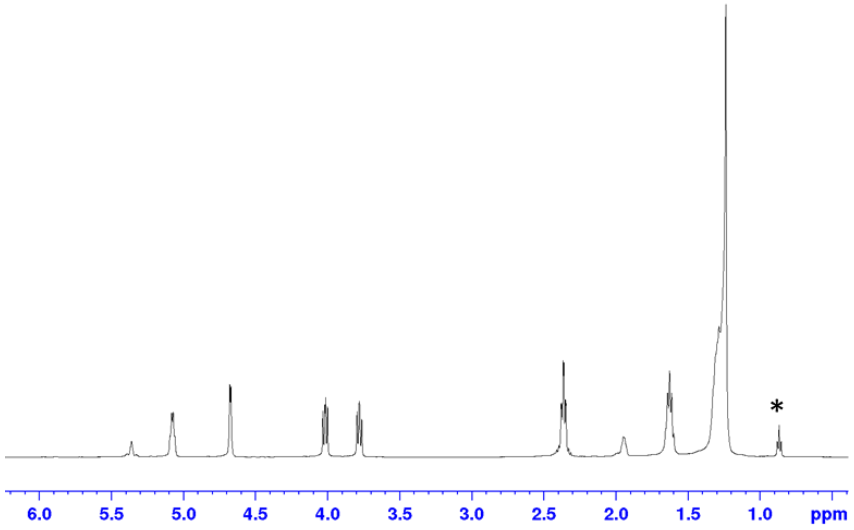


Figure S29. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for attempted tandem hydrogenation of PE3 (under 1.0 MPa H_2 without Al_2O_3, run S9, Table S1-1). *impurity

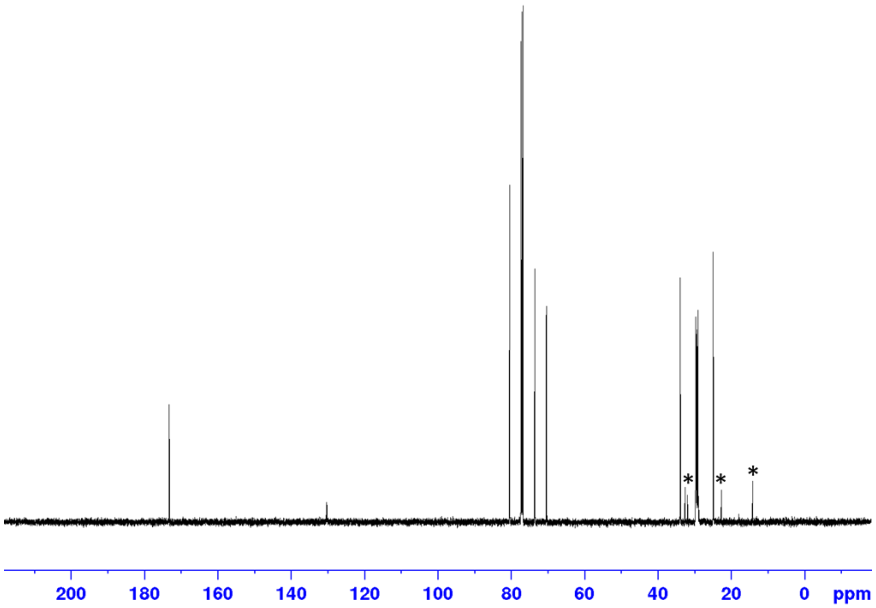


Figure S30. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for attempted tandem hydrogenation of PE3 (under 1.0 MPa H_2 without Al_2O_3, run S9, Table S1-1). *impurity

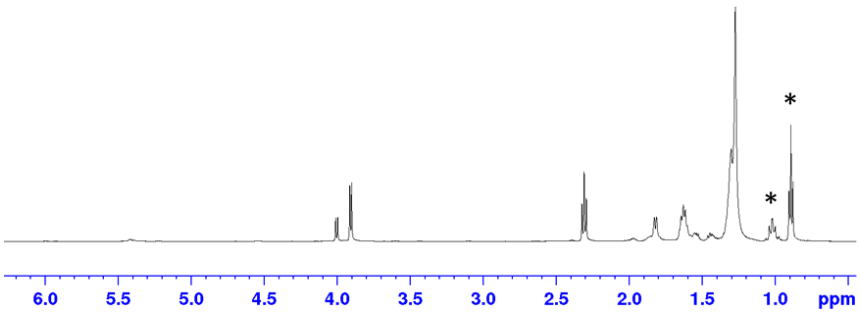


Figure S31. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for HPE4 (run 43, Table 2). *impurity

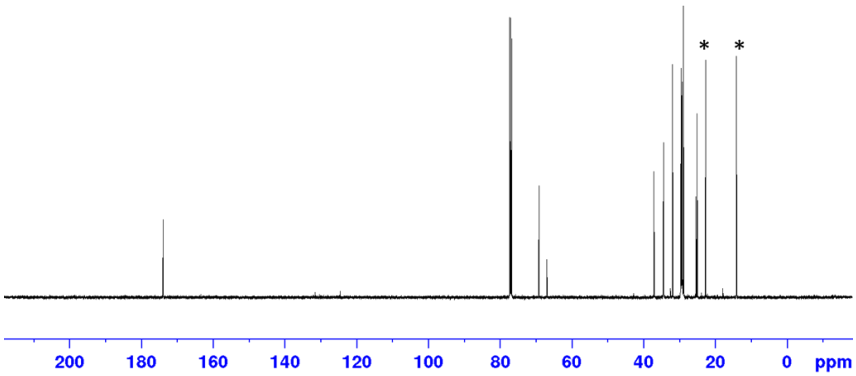


Figure S32. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for HPE4 (run 43, Table 2). *impurity

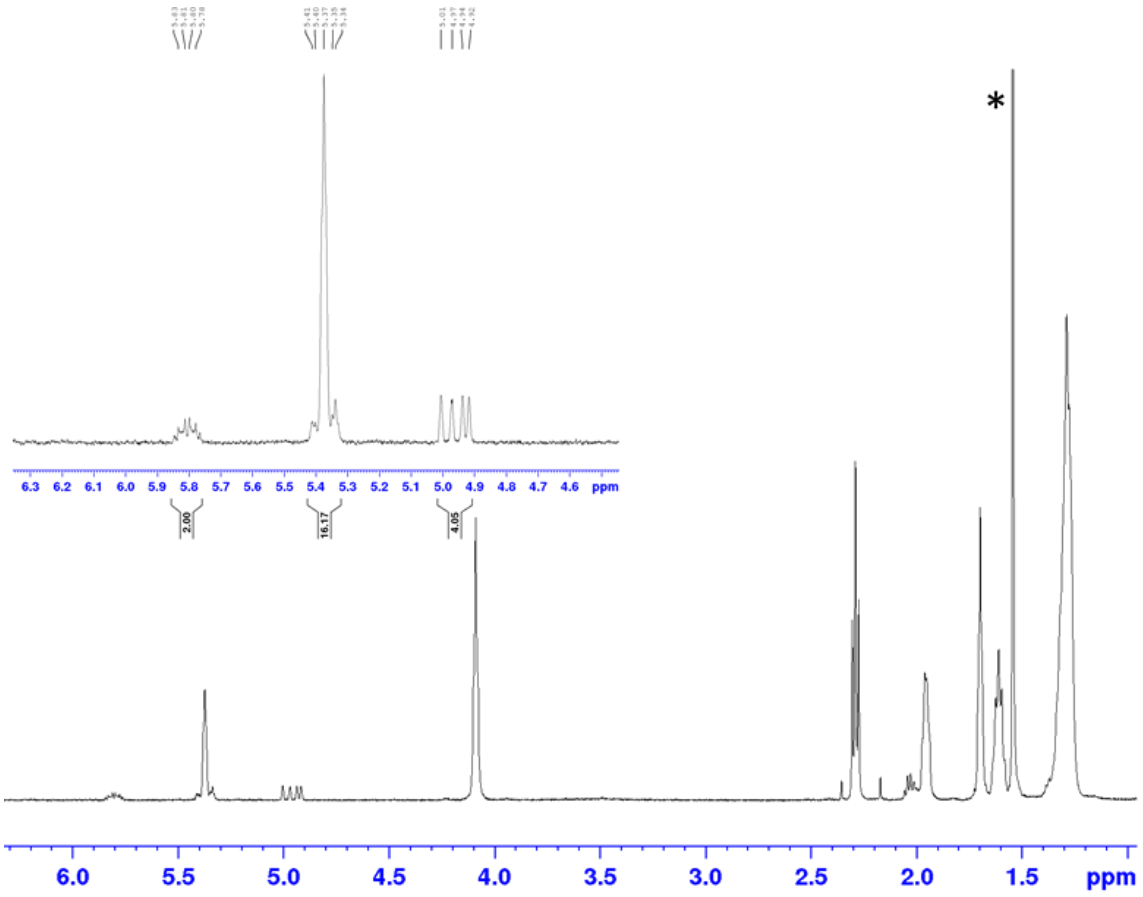


Figure S33. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for DPE1. *impurity

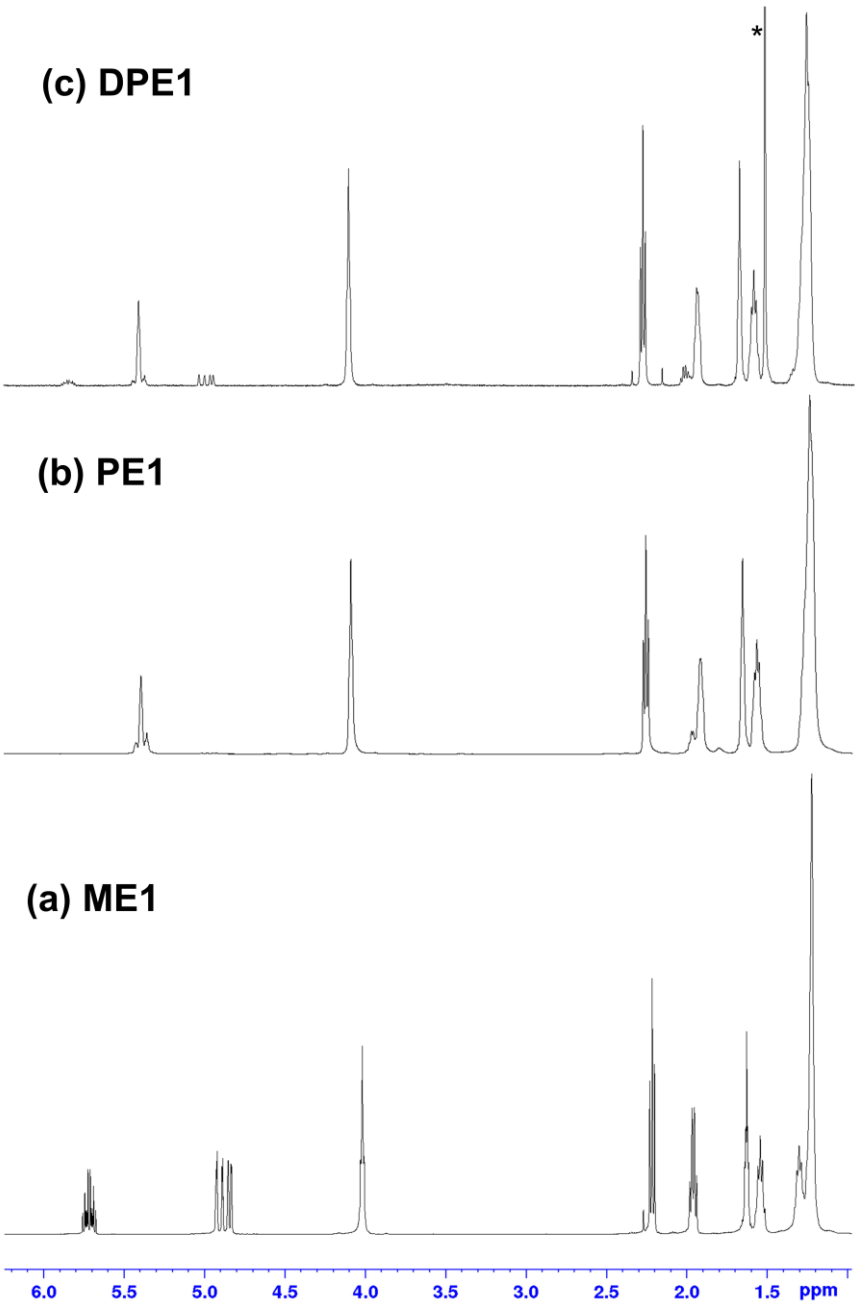


Figure S34. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) for (a) ME1, (b) PE1 (run3), and (c) DPE1. *impurity

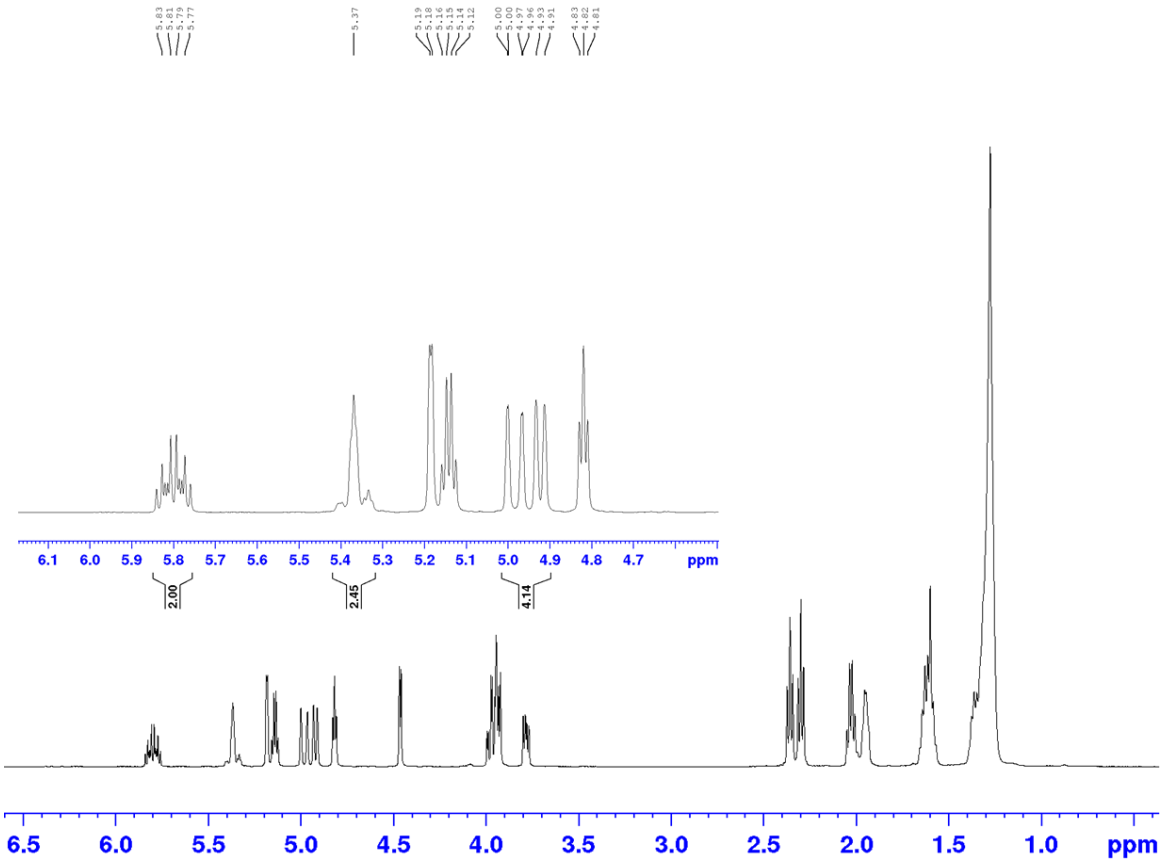


Figure S35. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for DPE2. *impurity

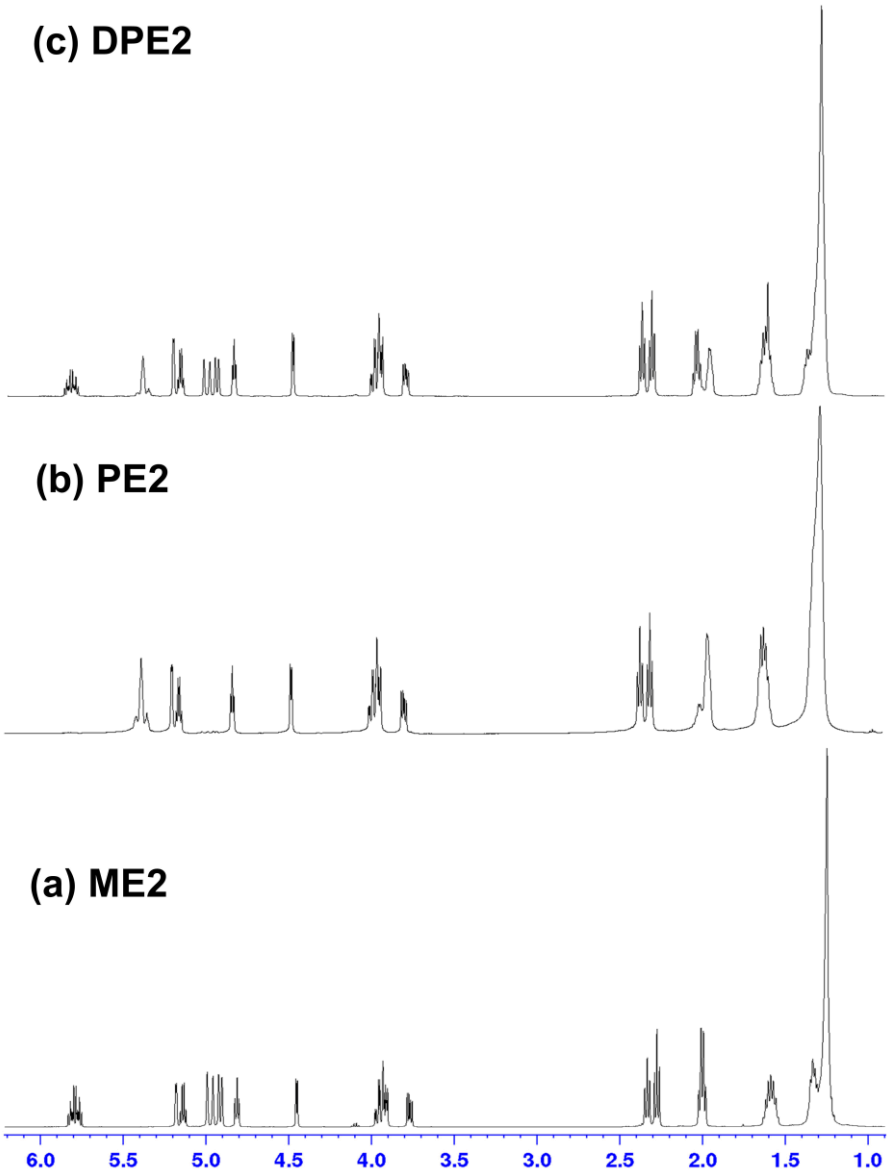


Figure S36. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) for (a) ME2, (b) PE2 (run15), and (c) DPE2.

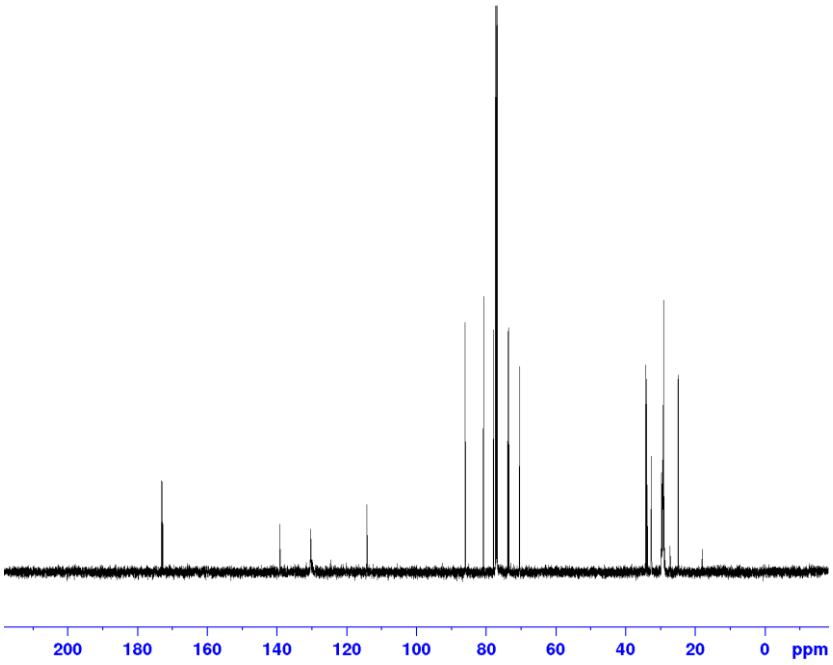


Figure S37. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) for DPE2. *impurity

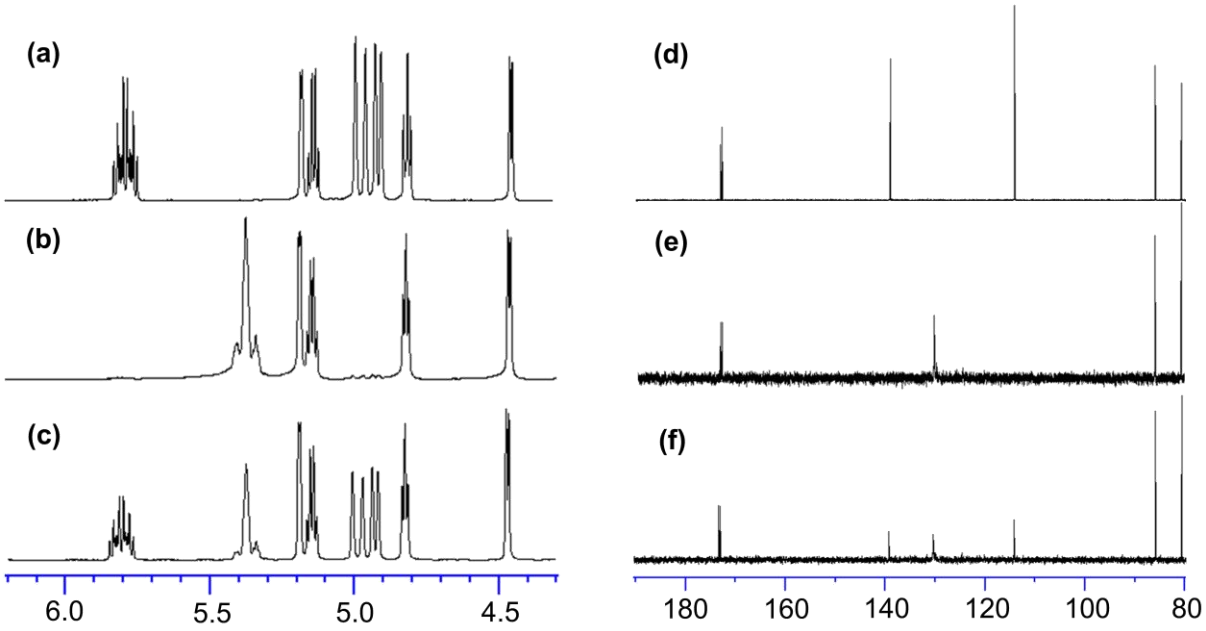


Figure S38. (left) ^{1}H NMR spectra (in $CDCl_3$ at 25 °C, expanded) for (a) ME2, (b) PE2 (run 15), and (c) DPE2. (right) ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C, expanded) for (d) ME2, (e) PE2 (run15), and (f) DPE2.

3. Selected additional DSC thermograms

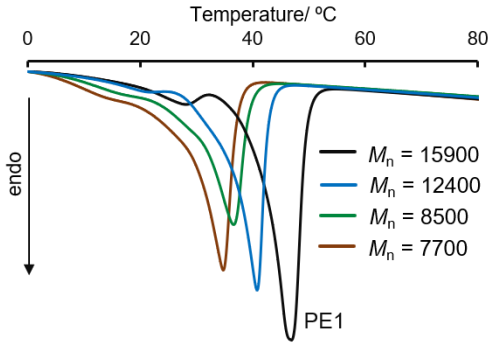


Figure S39. DSC thermograms for PE1s with different molecular weights by HG2. M_n = 15900 (run 3, 24 h, HG 2.0 mol%, T_m = 46.9 ºC), 12400 (run 6, 24 h, HG 1.0 mol%, T_m = 40.9 ºC), 8500 (run 2, 12 h, HG 2.0 mol%, , T_m = 36.6 ºC), 7700 (run 1, 6 h, HG 2.0 mol%, T_m = 34.8 ºC).

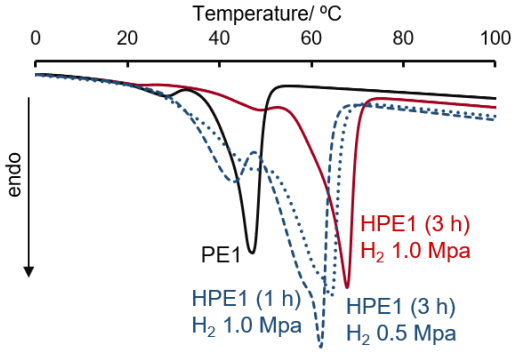


Figure S40. DSC thermograms for PE1 (run 3), HPE1 (run 32, prepared under H_2 at 1.0 MPa for 3 h) by HG2, and samples with incomplete hydrogenation HPE1 (run S2, prepared under H_2 at 1.0 MPa for 1 h; run S4 by G2, prepared under H_2 at 0.5 MPa for 3 h) by HG2.

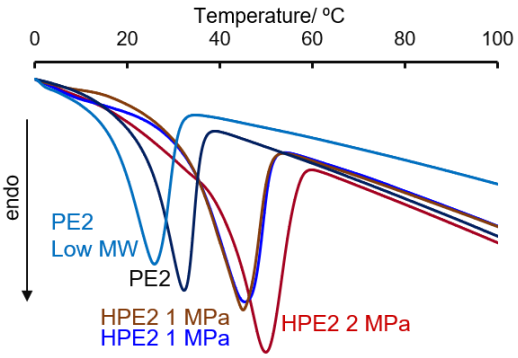
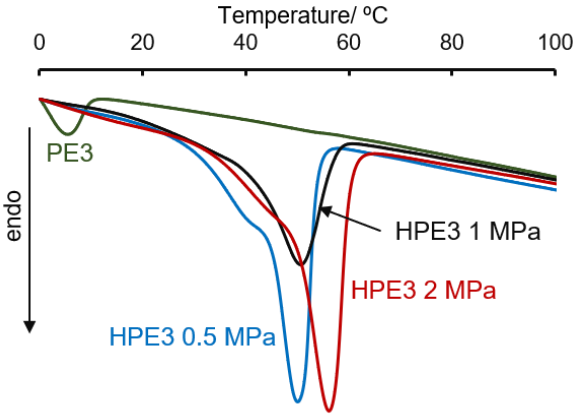


Figure S41. DSC thermograms for samples: PE2 LowMW (run 14), PE2 (run 15), HPE2 1 MPa (plotted in blue, run 34, prepared under H_2 at 1.0 MPa) by HG2, HPE2 1 MPa (plotted in brown, run 35, prepared under H_2 at 1.0 MPa) by G2, HPE2 2.0 MPa (run 36) prepared under H_2 at 2.0 MPa by HG2.



S2-1,

Figure S42. DSC thermograms for PE3 (run 23), HPE3 (run 40, prepared under H_2 at 0.5 MPa) by HG2, HPE3 (run 39, prepared under H_2 at 1.0 MPa) by HG2, HPE3 (run 41, prepared under H_2 at 2.0 MPa) by HG2.

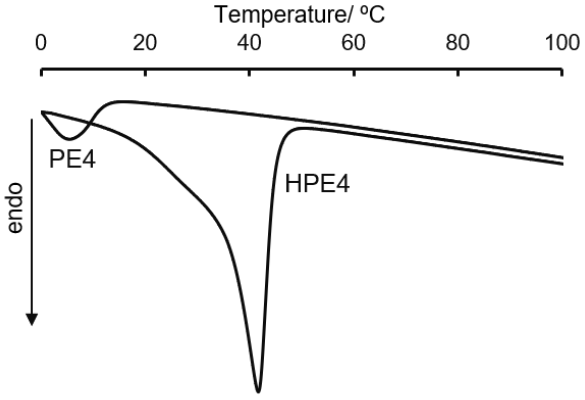


Figure S43. DSC thermograms for PE4 (run 30), and HPE4 (run 43, prepared under H_2 at 1.0 MPa) by HG2.

4. Selected GPC traces before/after depolymerization.

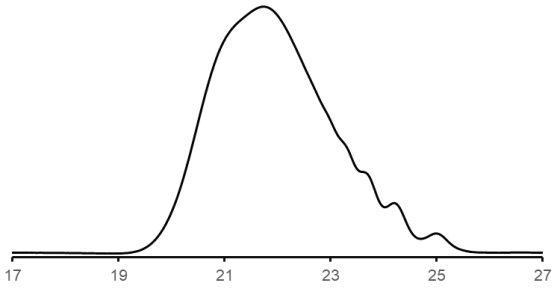


Figure S44. GPC trace for PE1 (run 46). M_n = 8400, M_w/M_n = 1.62.

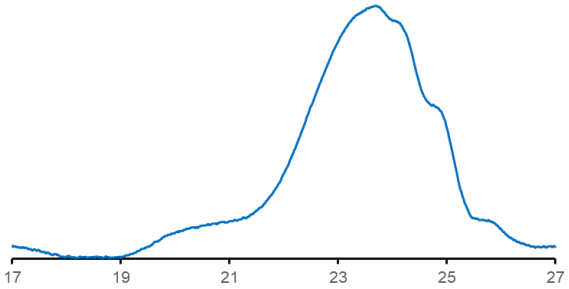


Figure S45. GPC trace for DPE1 (run 46). M_n = 1500, M_w/M_n = 1.54.

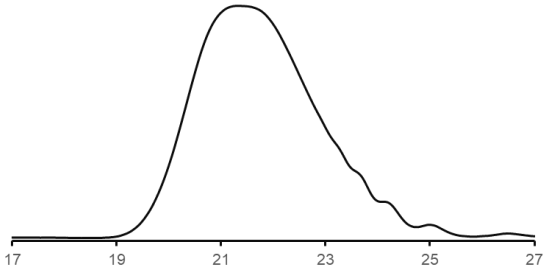


Figure S46. GPC trace for PE2 (run 49). M_n = 8500, M_w/M_n = 1.54.

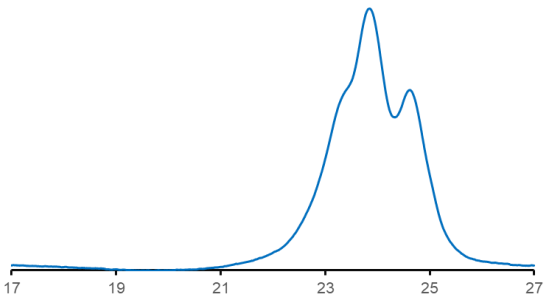


Figure S47. GPC trace for DPE2 (run 49). M_n = 1400, M_w/M_n = 1.48.