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Electronic Supplementary Information

A cascade strategy towards the direct synthesis of green polyesters with versatile functional groups

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Reagents

Ethylene brassylate (EB) was purchased (Adamas, ≥ 98%) and distilled under reduced pressure. 1,10-Decanediol (DD, Aladdin, 98%), 2-butene-1,4-diol (BD, Energy Chemical, ≥ 98%, mixture of cis- and trans- isomers), 2-butyne-1,4-diol (ByD, Energy Chemical, ≥ 98%), 4,4'-bis(hydroxymethyl)biphenyl (BPDM, Energy Chemical, 98%), 2,6-pyridinedimethanol (PyDM, Energy Chemical, ≥ 98%), 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (HFPD, Aladdin, ≥ 98%), 2,2-bis(bromomethyl)-1,3-propanediol (BBMP, Energy Chemical, ≥ 98%), tetraglycol (TEG, Aldrich, ≥ 99%), isosorbide (IS, Adamas, ≥ 98%), dimethyl terephthalate (Aladdin, 99%), ethylene glycol (Aladdin, ≥ 99%), zinc acetate (Sigma-Aldrich, 97.5%), thionyl chloride ($SOCl_2$, Alfa Aesar, AR), *N*,*N*-dimethylformamide (DMF, Alfa Aesar, ≥ 99.8%), 9-anthracene acid (Energy Chemical, ≥ 98%), hydrochloric acid (Qiangsheng Chemical of Suzhou, GR), sodium bicarbonate (Sigma-Aldrich, ≥ 99.7%), sodium sulfate (Alfa Aesar, 99%), dihydroxyl-terminated PTHF (PTMO, M_n = 2900 Da, Sigma-Aldrich), poly(ethylene glycol) (PEO, M_n = 2000 Da, Sigma-Aldrich, 99%), tetrahydrofuran (THF) (Qiangsheng Chemical of Suzhou, AR), chloroform ($CHCl_3$) (Qiangsheng Chemical of Suzhou, AR), benzophenone (Sigma-Aldrich, ≥ 99%), titanium tetrabutoxide (Ti $(n\text{-}C_4H_9O)_4$, Alfa Aesar, 98%), Amano Lipase PS® (Sigma-Aldrich, ≥ 30,000 U/g) were all used as received.

Methods

Nuclear magnetic resonance (NMR) ^1H spectra were recorded on Agilent Direct-Drive II 600 MHz spectrometer equipped with four broad-band rf channels and a 5 mm ^1H-^{19}F/^{15}N-^{31}P pulse field gradient (PFG) probe. Chemical shifts are reported in δ (ppm) relative to the residual solvent peak ($CDCl_3$: 7.26 for ^1H NMR). The ^1H quantitative NMR spectrum was collected with a 1.50 s acquisition time, 20 s relaxation delay, 9.6 kHz spectral window, 32 transients, and 8.4 μs 90° pulse width.

Gel permeation chromatography (GPC) was measured on a TOSOH HLC-8320 gel permeation chromatography (GPC) with three TSKgel SuperMultipore HZ-M columns at 40 °C, in which THF with a flow rate of 0.35 mL min^{-1} was used as the eluent and polystyrene (PS) homopolymers with low dispersity acted as standard samples.

Fourier transform infrared (FT-IR) spectra were collected on a Nicolet 6700 FT-IR spectrometer with 32 scans for each sample.

Tensile testing was taken on a universal material testing machine (MTS CMT-4104) with a tensile rate of 10 mm min^{-1}.

Synthetic Procedures and Characterization Data

Synthesis of bis(hydroxyethyl) terephthalate (BHET). BHET was synthesized by dimethyl terephthalate, glycol and zinc acetate using the similar procedure as literature.[1,2] Yield: 70%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (s, 4H), 4.58-4.61 (t, 4H), 4.14-4.17 (t, 4H).

Synthesis of *N*,*N*-bis(2-hydroxyethyl)anthracene-9-carboxamide) (BHAC). A mixture of 9-anthroic acid (10 g, 0.032 mol), *N*,*N*-dimethylformamide (DMF) (3 drops) and $SOCl_2$ (20 mL) was heated to reflux at 80 ºC for 6 h. The excess $SOCl_2$ was removed by rotation evaporation under reduced pressure. The product was dissolved with CH_2Cl_2 (50 mL), and added dropwise to a mixture of diethanolamine (10 mL, 0.087 mmol), triethylamine (10 mL) and CH_2Cl_2 (20 mL), and reacted for 12 h. Then the solution was diluted with CH_2Cl_2 and washed successively with hydrochloric acid, sodium bicarbonate solution and deionized water. The obtained organic layer was dried over sodium sulfate, and concentrated via rotary evaporation. The crude product was recrystallized from toluene to afford yellow crystals (9.62 g, yield: 59%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.01 (d, 2H), 7.91 (d, 2H), 7.50 (m, 4H), 4.21 (t, 2H), 4.03 (t, 2H), 3.32 (t, 2H), 3.19 (t, 2H).

Calculations

(1) Measurement of monomer conversion (*Conv*)

The monomer conversion (*Conv*) was calculated by equation (S1):

$$Conv = \frac{\frac{I_{\mathrm{c}}}{4} - \frac{I_{\mathrm{f'}}}{4}}{\frac{I_{\mathrm{c}}}{4}} \times 100\% \tag{S1}$$

where I_{c}, $I_{\mathrm{f'}}$ are the integration values for corresponding carboxy-connected methylene peaks of brassylate (OOCCH_2(c)CH$_2$, δ = 2.32 ppm, from monomer and polymers) and ester-connected ethylene peaks from residue EB monomer (OCH_2(f')CH_2(f')O, δ = 4.31 ppm), respectively.

(2) Measurement of molecular weight of polyesters (M_{n})

For the polymerization systems using small molecular diols as initiators (entries 1-16), the number-average molecular weights (M_{n}s) of polyesters were determined by ^{1}H quantitative NMR spectra, according to the following equations (S2-S4):

$$\frac{I_{\mathrm{a}}}{4} = \frac{I_{\mathrm{FG}}}{n_{\mathrm{FG}} \times N_{\mathrm{FG}}} \tag{S2}$$

$$\frac{I_{\mathrm{a}}}{4} = \frac{I_{\mathrm{c}} \times Conv}{4N_{\mathrm{B}}} \tag{S3}$$

$$M_{\mathrm{n}} = N_{\mathrm{FG}} \times FW_{\mathrm{I}} + N_{\mathrm{B}} \times 270 - 62N_{\mathrm{FG}} \tag{S4}$$

where I_{a}, I_{FG} are the corresponding integration values for peaks of hydroxymethylene chain-ends (CH_2(a)OH) and the functional group moiety in copolyesters (please refer to Table S1), n_{FG} is the corresponding number of protons of the functional group moiety, *Conv* is the EB monomer conversion, N_{FG}, N_{B} are the average total repeating units of functional group moiety and brassylate in polymer, respectively. FW_{I} is the corresponding formula weight of initiator.

For polyether diol systems (entries 17-19), with the multiblock copolymer structure formed, their number-average molecular weights were determined according to equations (S5):

$$M_{\mathrm{n}} = N_{FG} \times FW_{M} + N_{B} \times 270 - 62 \times \left(\frac{N_{FG} \times FW_{M}}{M_{I}} - 1\right) \tag{S5}$$

where FW_{M} is the corresponding formula weight of repeating unit (monomer) in polyether diols, M_{I} is the number-average molecular weight of polyether diol initiator.

(3) Measurement of functional group content (α_{FG})

When small molecular diols were used as initiators (entries 1-16), functional group content (α_{FG}) of copolyesters was calculated by the molar ratio of functional groups to brassylate in polyesters from the quantitative ^{1}H NMR spectra, according to equation (S6):

$$\alpha_{\mathrm{FG}} = \frac{\frac{I_{\mathrm{FG}}}{n_{\mathrm{FG}}}}{\frac{I_{\mathrm{c}}}{4} \times Conv} \times 100\% \tag{S6}$$

When polyether diols were used as initiators (entries 17-19), poly(ether ester) multiblock copolymers are obtained. The molar ratio cannot represent the structure of copolymers. Thus functional group content (α_{FG}) of copolyesters was calculated by the weight ratio of functional polyethers in polyesters from the quantitative ^{1}H NMR spectra, according to equation (S7):

$$\alpha_{\mathrm{FG}} = \frac{N_{\mathrm{FG}} \times FW_{\mathrm{M}}}{N_{\mathrm{FG}} \times FW_{\mathrm{M}} + N_{\mathrm{B}} \times 270} \times 100\% \tag{S7}$$

Supporting Tables

Table S1. Peak integration from ^{1}H NMR spectra for copolyesters from entries 1-19. Solvent: $CDCl_3$.

Entry	I_a (δ ppm)	I_c (δ ppm)	$I_{\mathrm{f'}}$ (δ ppm)	I_FG (δ ppm)
1	4.00 (3.84-3.82)	221.99 (2.34-2.27)	1.27 (4.31)	109.43 (g, 4.04-4.06)
2	4.00 (3.84-3.82)	238.45 (2.36-2.27)	24.47 (4.31)	20.65 (g, 4.04-4.06)
3	4.00 (3.84-3.82)	558.55 (2.36-2.29)	3.70 (4.31)	209.76 (g, 4.68-4.67)
4	4.00 (3.84-3.82)	426.74 (2.36-2.29)	3.65 (4.31)	175.72 (g, 4.68-4.67)
5	4.00 (3.84-3.82)	102.76 (2.36-2.29)	7.70 (4.31)	13.52 (g, 4.68-4.67)
6	4.00 (3.84-3.82)	433.91 (2.36-2.29)	3.02 (4.31)	58.37 (g, 4.68-4.67)
7	4.00 (3.84-3.82)	105.88 (2.36-2.29)	17.56 (4.31)	12.64 (g, 4.68-4.67)
8	4.00 (3.84-3.82)	400.81 (2.31-2.35)	4.67 (4.31)	53.83 (g, 4.71)
9	4.00 (3.84-3.82)	311.97 (2.38-2.30)	114.95 (4.31)	27.16 (g, 5.15)
10	4.00 (3.84-3.82)	321.27 (2.42-2.31)	2.50 (4.31)	35.30 (g, 5.22)
11	4.00 (3.84-3.82)	256.82 (2.42-2.31)	1.00 (4.31)	46.53 (g, 4.59-4.54)
12	4.00 (3.84-3.82)	252.59 (2.36-2.31)	92.08 (4.31)	11.76 (g, 4.15)
13	4.00 (3.84-3.82)	321.03 (2.36-2.31)	1.38 (4.31)	156.44 (h, 3.70-3.68)
14	4.00 (3.84-3.82)	382.08 (2.38-2.29)	9.75 (4.31)	7.97 (k, 4.47)
15	4.00 (3.84-3.82)	461.48 (2.37-2.30)	191.11 (4.31)	25.29 (i, 8.11)
16	0.45 (3.84-3.82)	36.10 (2.44-2.00)	0.24 (4.31)	1.84 (l, 8.49)
17	4.00 (3.84-3.82)	111.57 (2.35-2.27)	6.77 (4.31)	1622.51 (i, 3.42-3.40)
18	4.00 (3.84-3.82)	209.34 (2.35-2.27)	45.39 (4.31)	2847.17 (i, 3.42-3.40)
19	4.00 (3.84-3.82)	160.22 (2.35-2.30)	22.61 (4.31)	3487.51 (i, 3.64)

Table S2. Peak integration from ^{1}H NMR spectra for copolyesters from entry 15 with different reaction time. Solvent: $CDCl_3$. Polymerization conditions: 220 ºC under N_2 purge, 0.2 *wt*% $Ti(n\text{-}C_4H_9O)_4$ as catalyst.

Reaction Time (min)	I_a (δ 3.84-3.82 ppm)	I_c (δ 2.36-2.31 ppm)	$I_{f'}$ (δ 4.31 ppm)	I_i (δ 8.11 ppm)
15	4.00	113.47	86.85	5.99
30	4.00	135.75	89.54	7.33
45	4.00	169.19	101.00	9.13
60	4.00	200.7	111.01	10.85
75	4.00	237.58	123.83	12.6
90	4.00	267.46	134.03	14.67
105	4.00	307.39	150.17	15.99
120	4.00	342.17	160.78	18.65
135	4.00	379.05	170.95	20.33
150	4.00	407.78	176.15	22.26
165	4.00	422.49	177.50	23.39
180	4.00	461.48	191.11	25.29

Supporting Figures

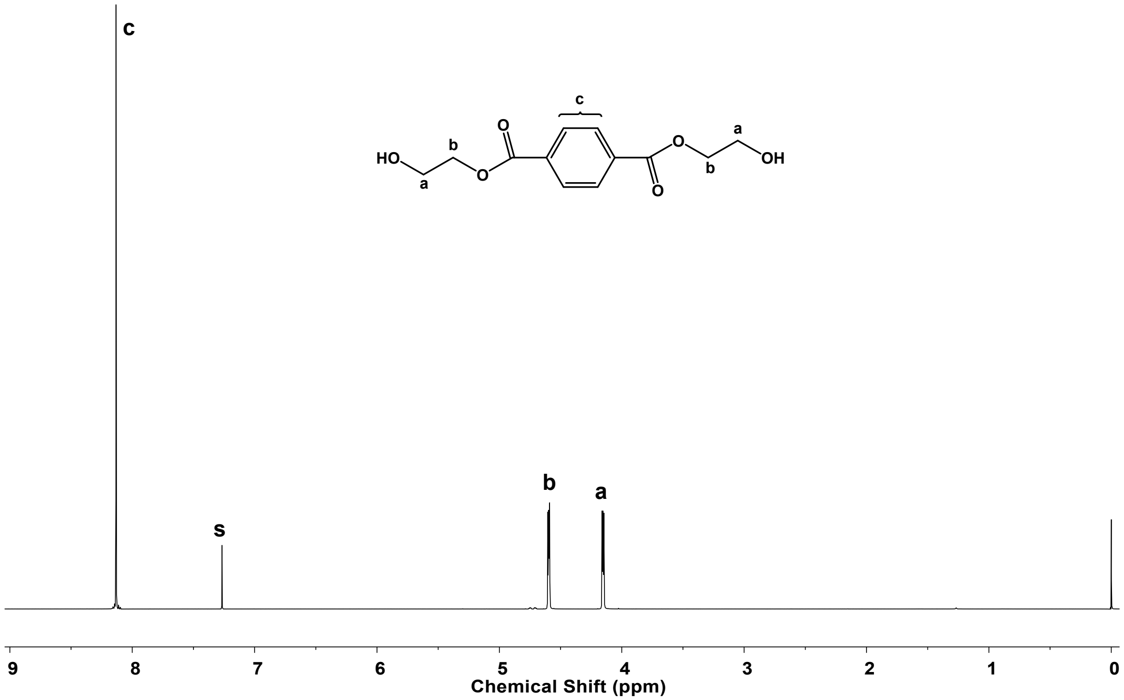

Figure S1. ^{1}H NMR spectrum of BHET. S: solvent.

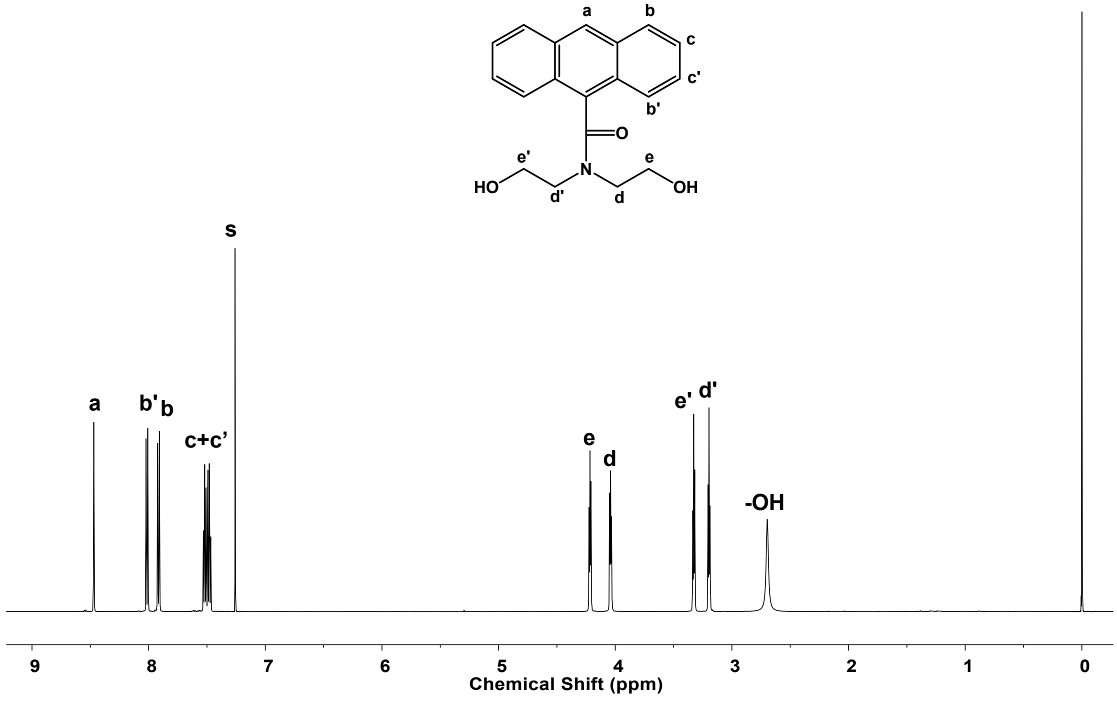

Figure S2. ^{1}H NMR spectrum of BHAC. S: solvent.

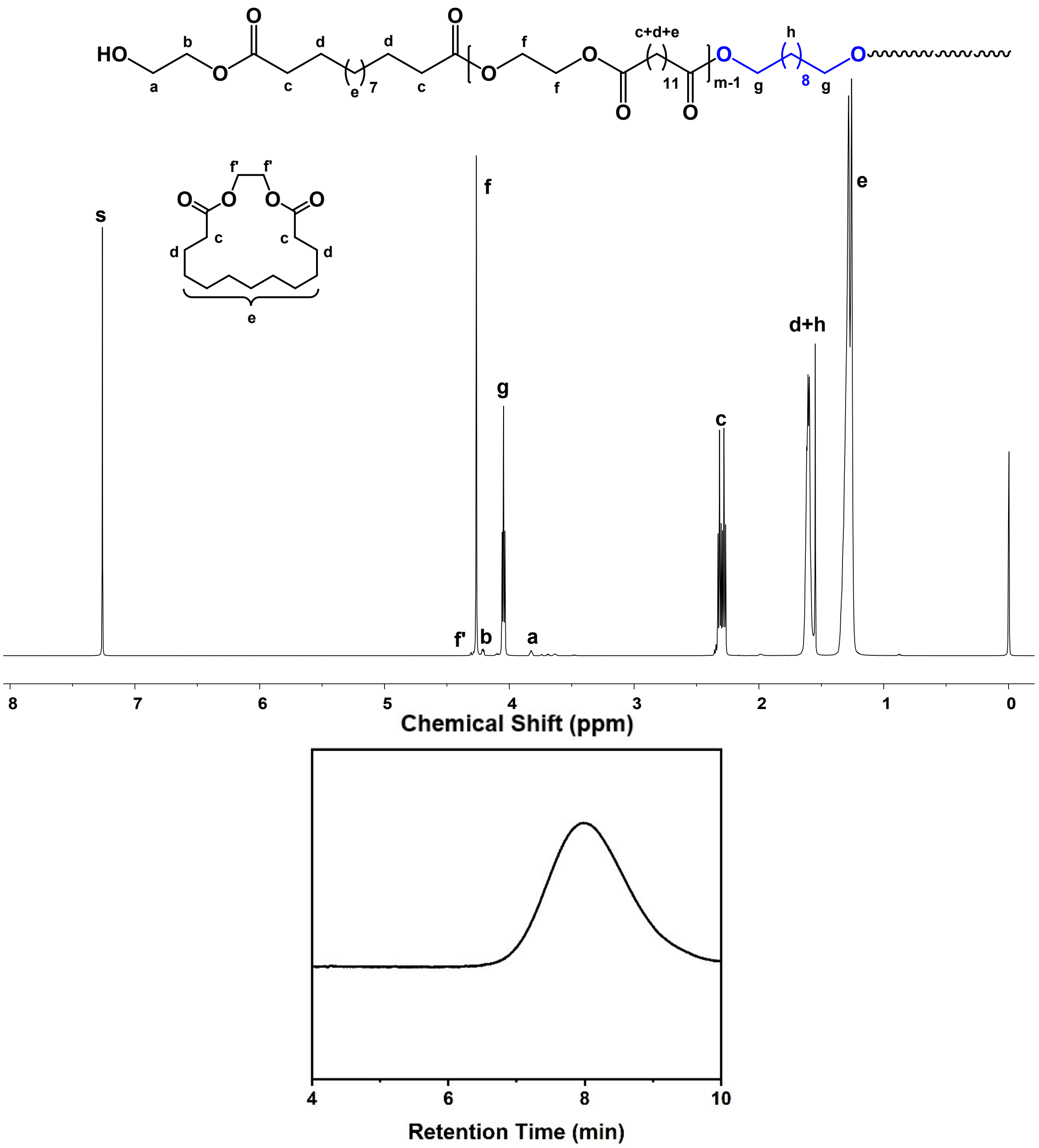

Figure S3. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 1 ($n_{FG} = n_g = 4$). S: solvent.

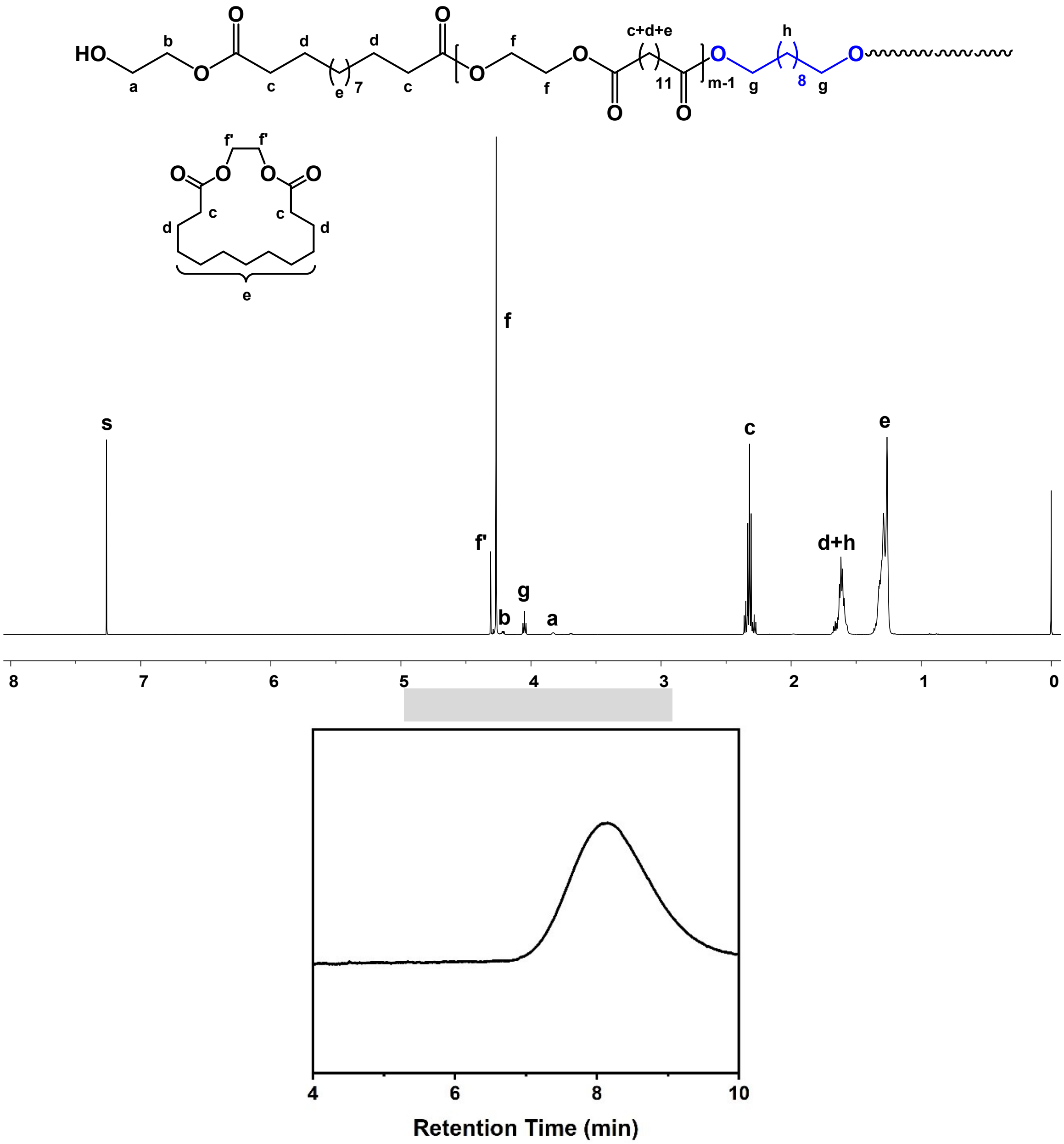

Figure S4. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 2 (n_{FG} = n_g = 4). S: solvent.

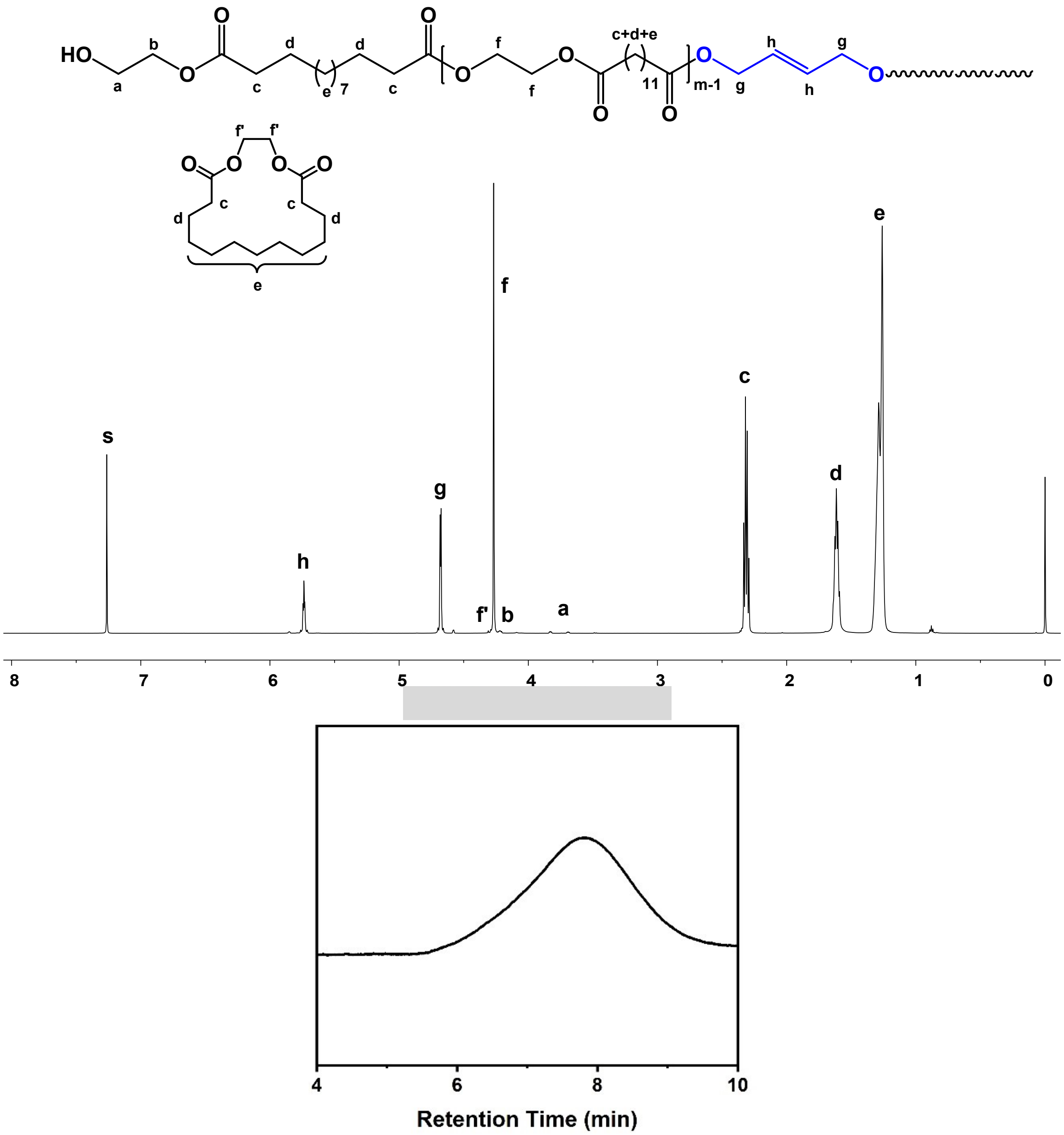

Figure S5. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 3 (n_{FG} = n_g = 4). S: solvent.

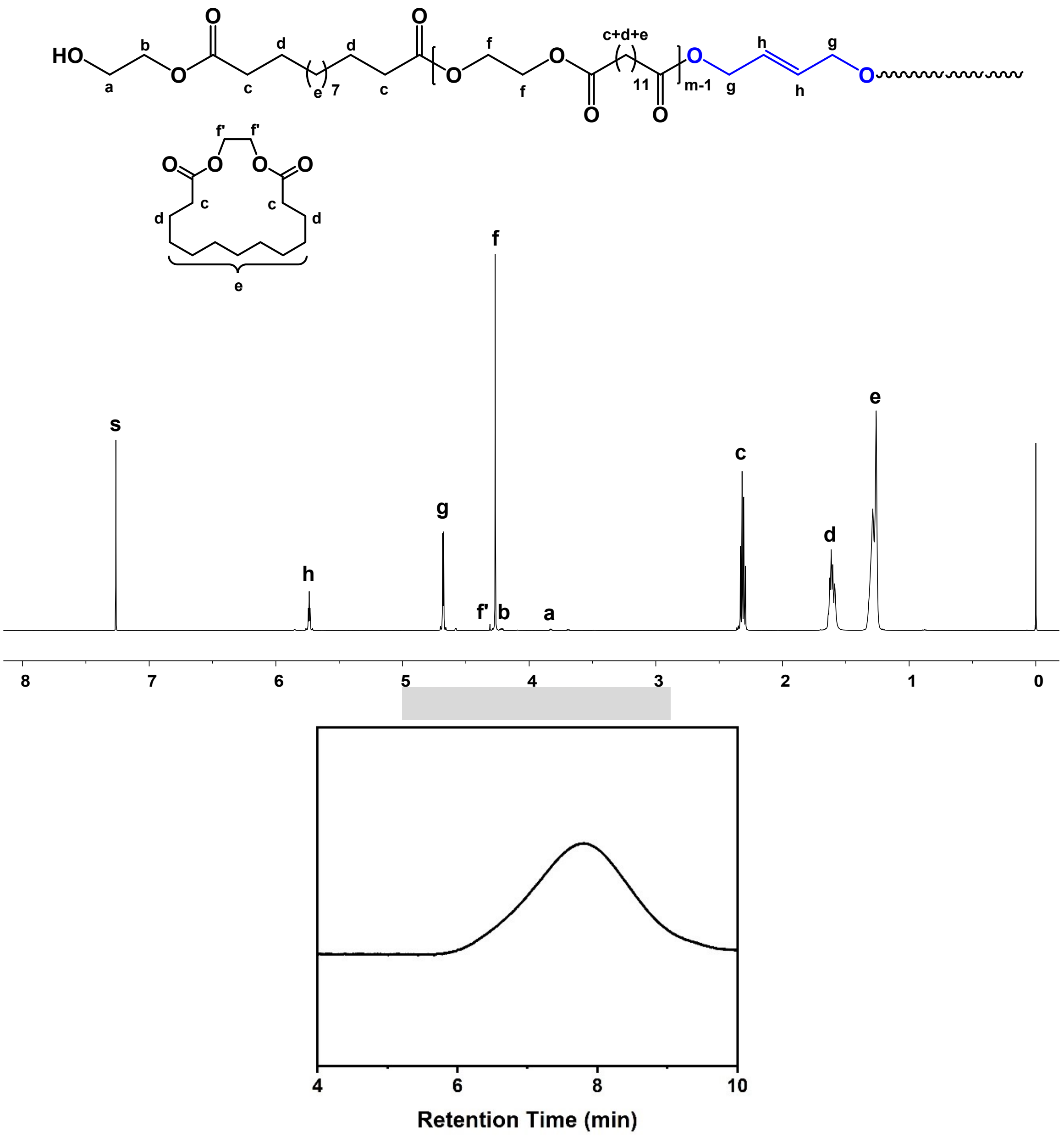

Figure S6. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 4 ($n_{FG} = n_g = 4$). S: solvent.

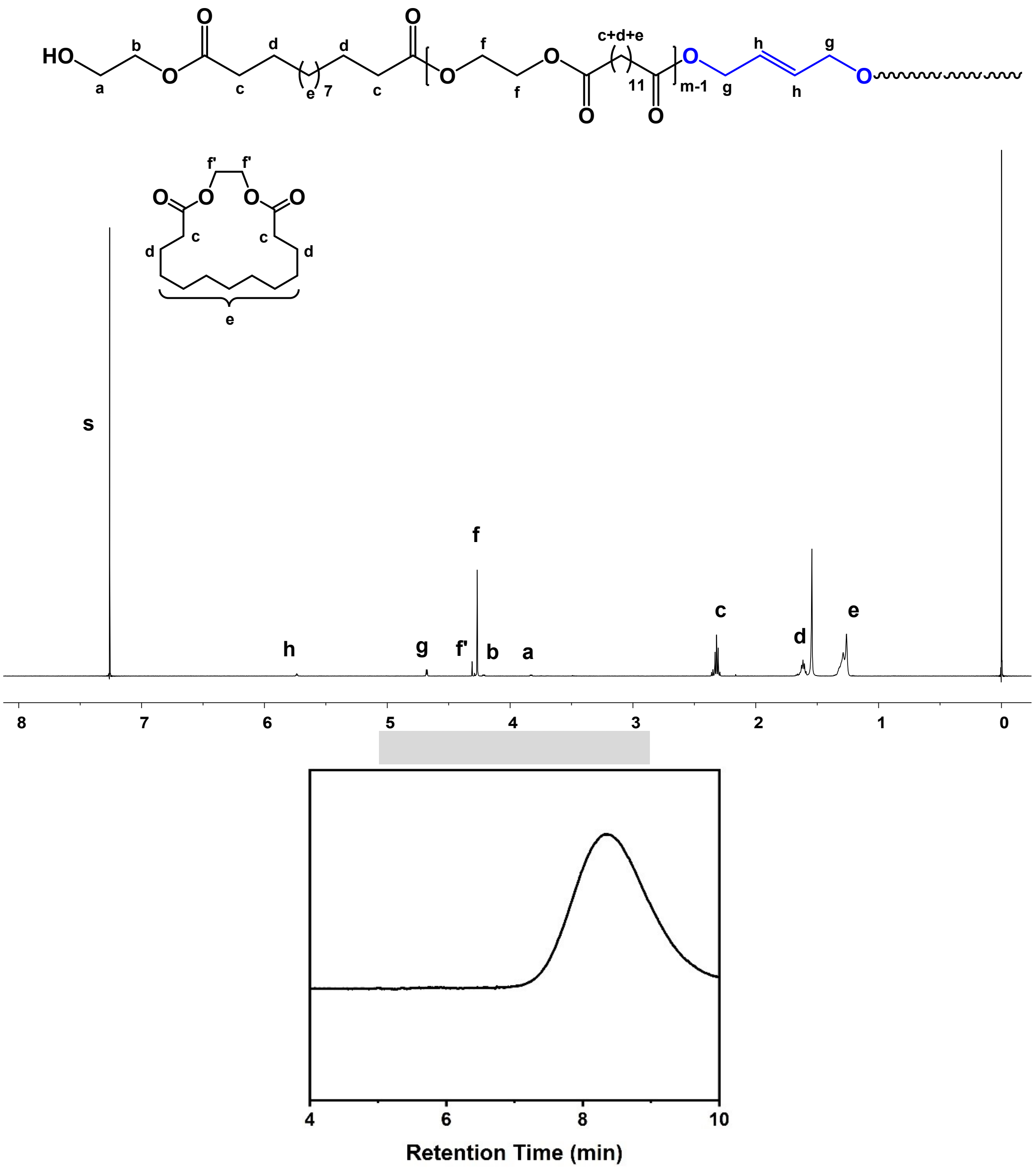

Figure S7. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 5 (n_{FG} = n_g = 4). S: solvent.

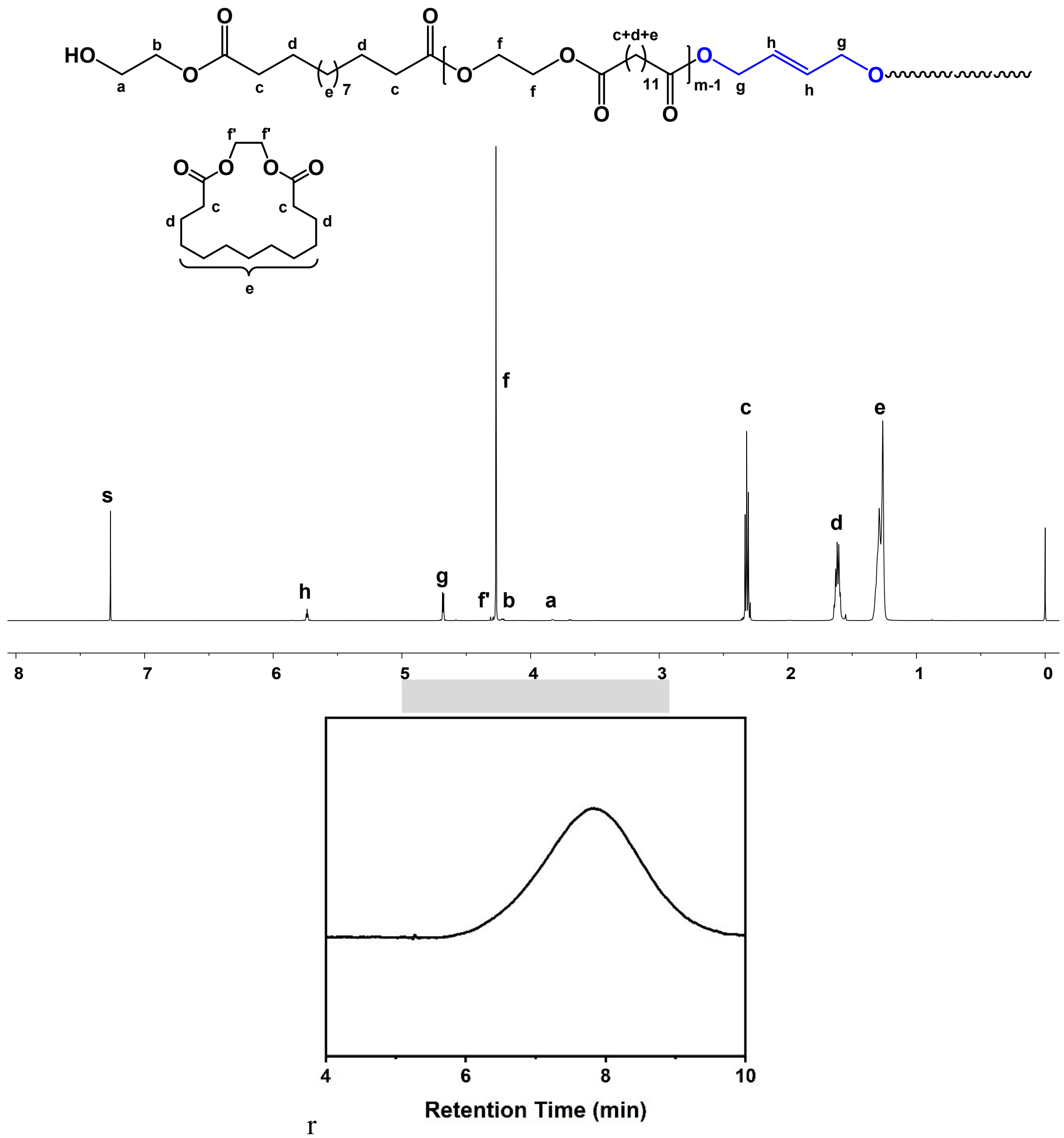

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Figure S8. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 6 (n_{FG} = n_g = 4). S: solvent.

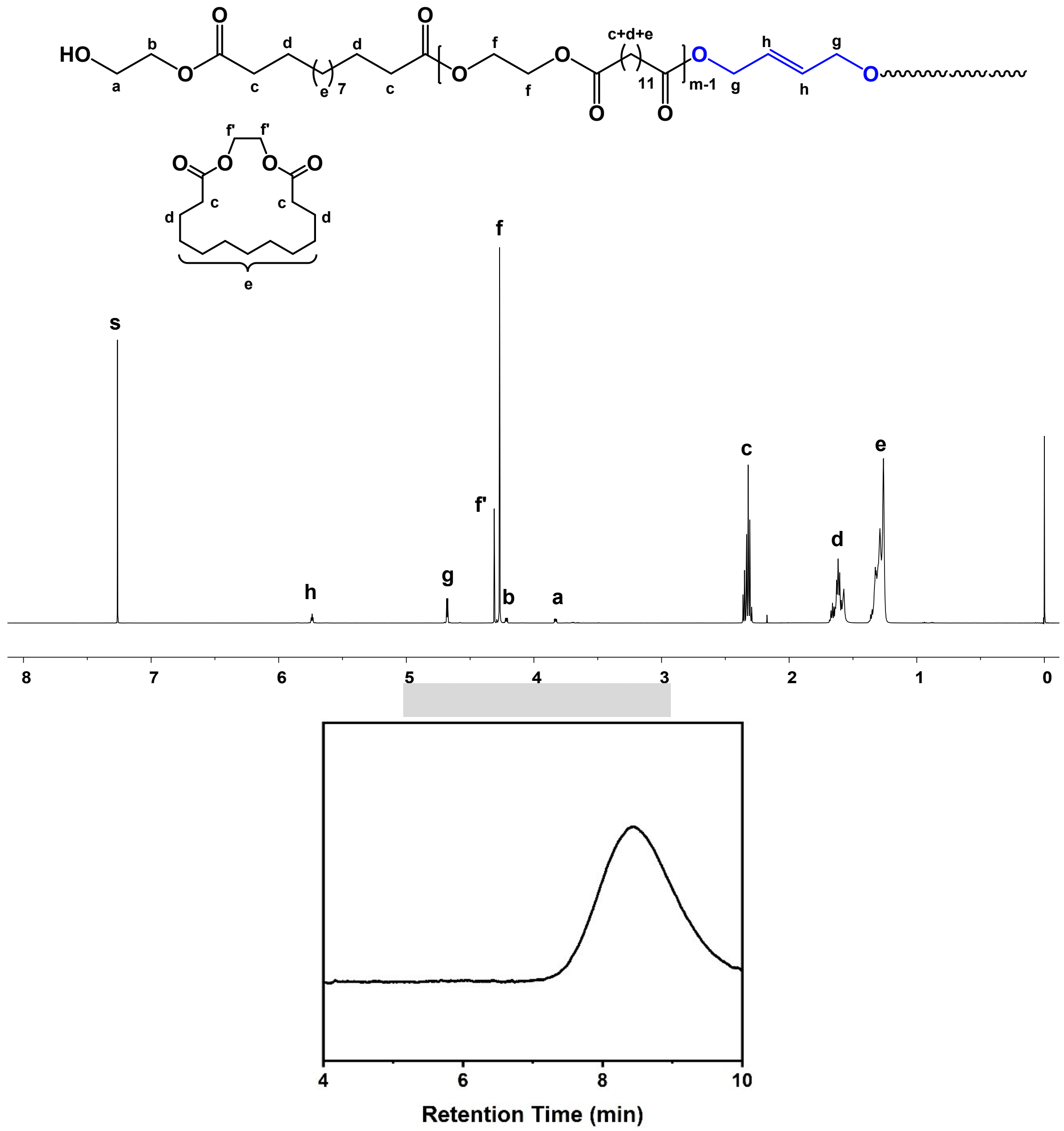

Figure S9. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 7 (n_{FG} = n_g = 4). S: solvent.

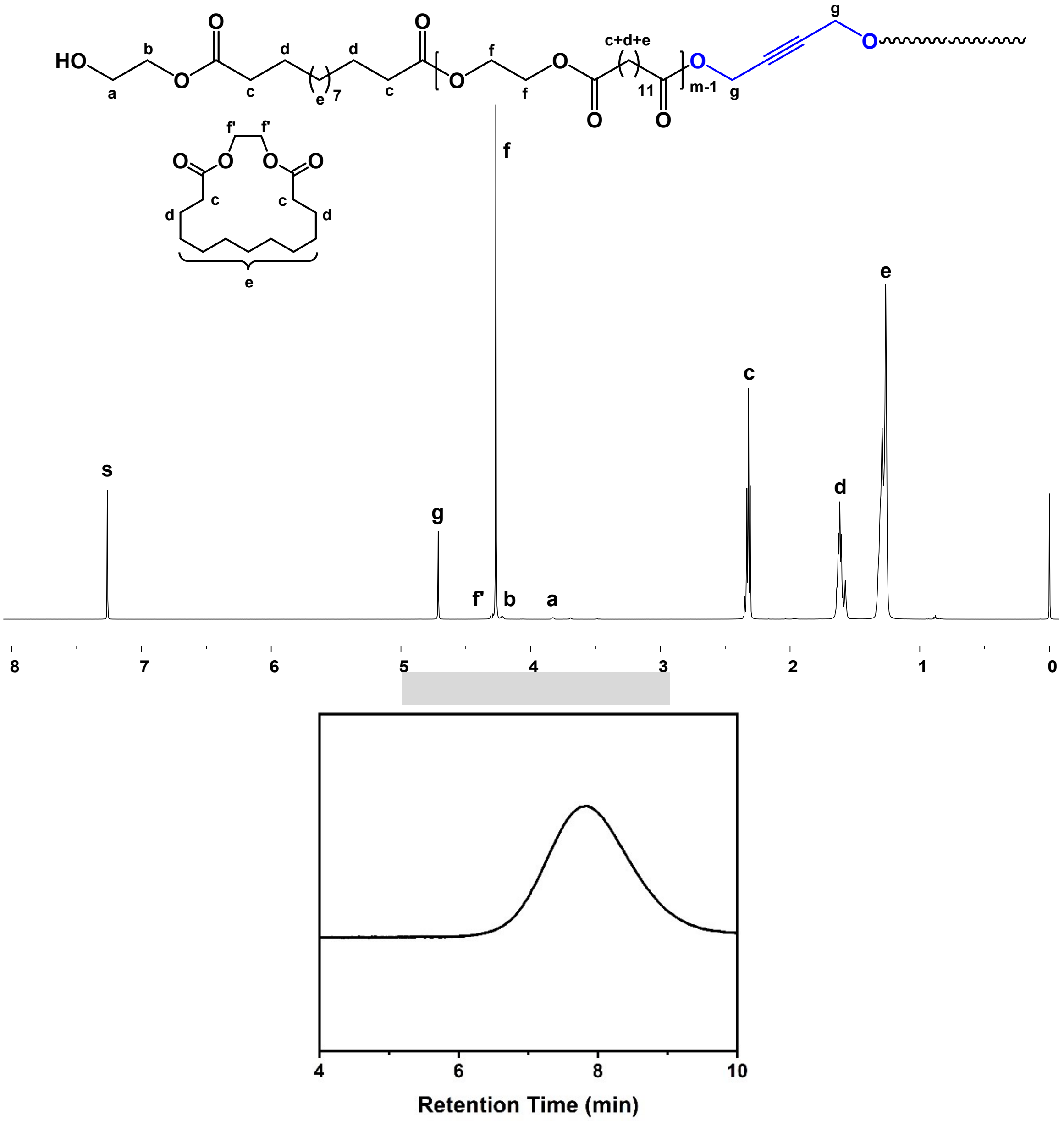

Figure S10. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 8 ($n_{FG} = n_g = 4$). S: solvent.

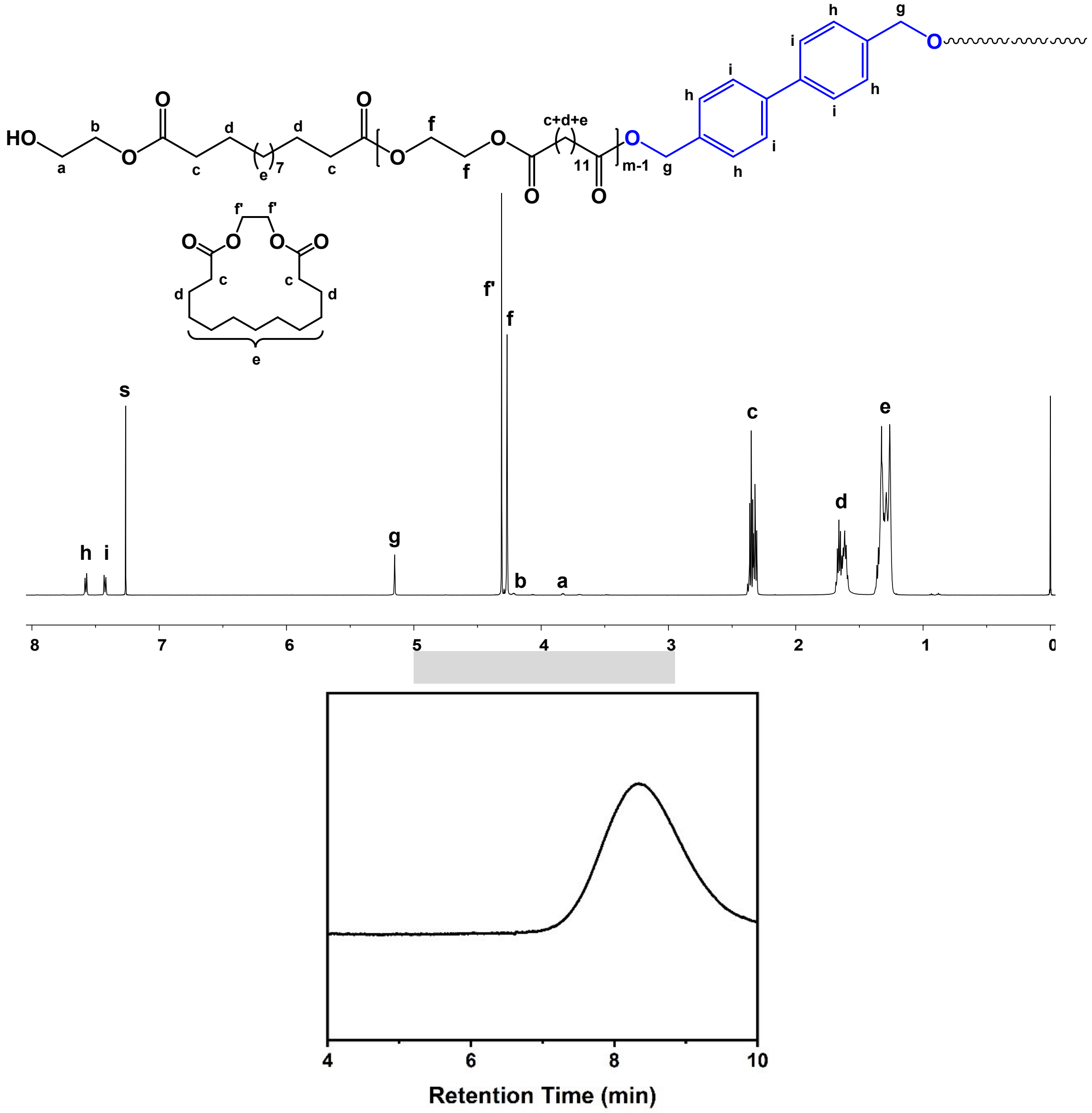

Figure S11. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 9 (n_{FG} = n_g = 4). S: solvent.

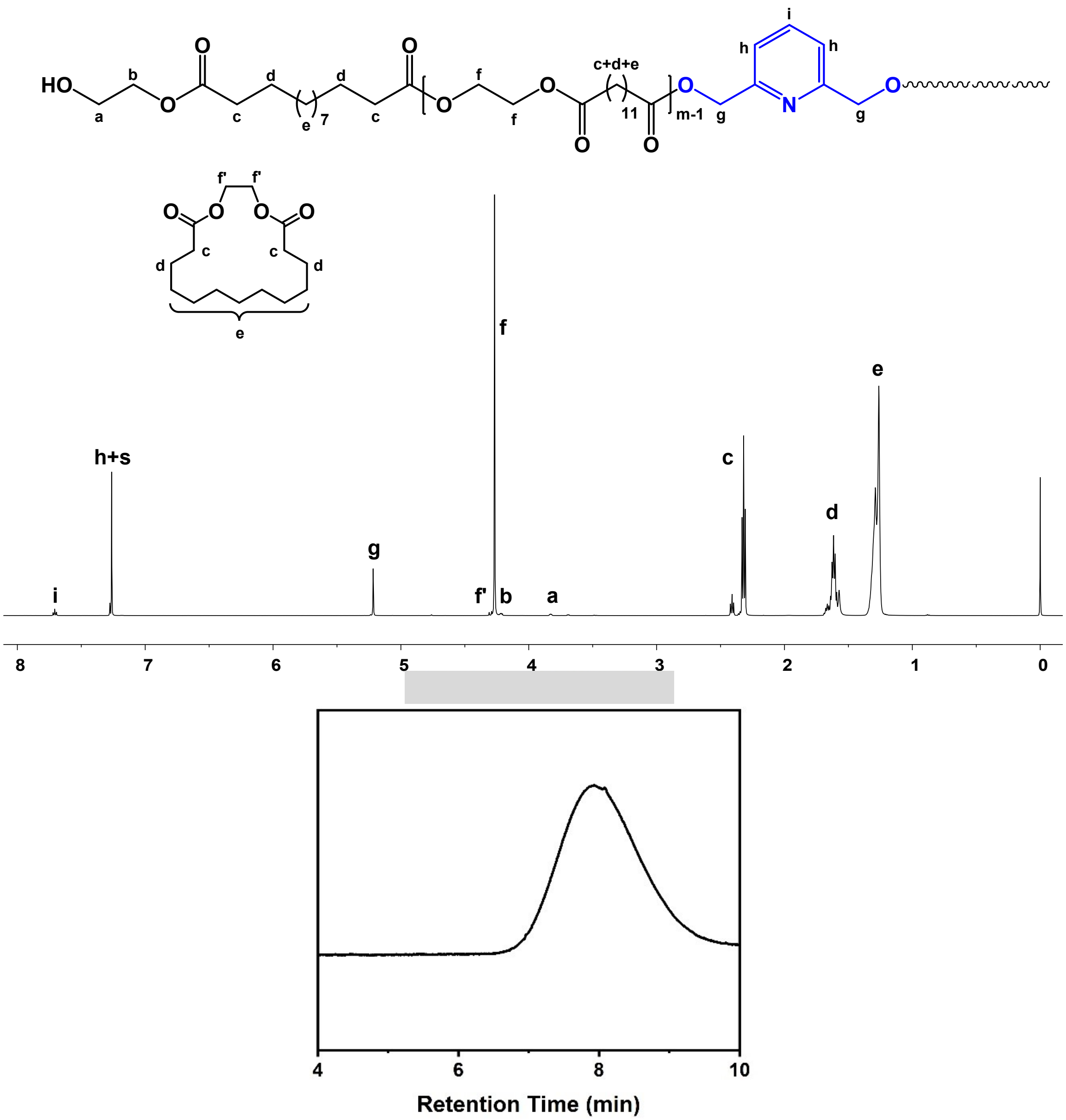

Figure S12. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 10 ($n_{FG} = n_g = 4$). S: solvent.

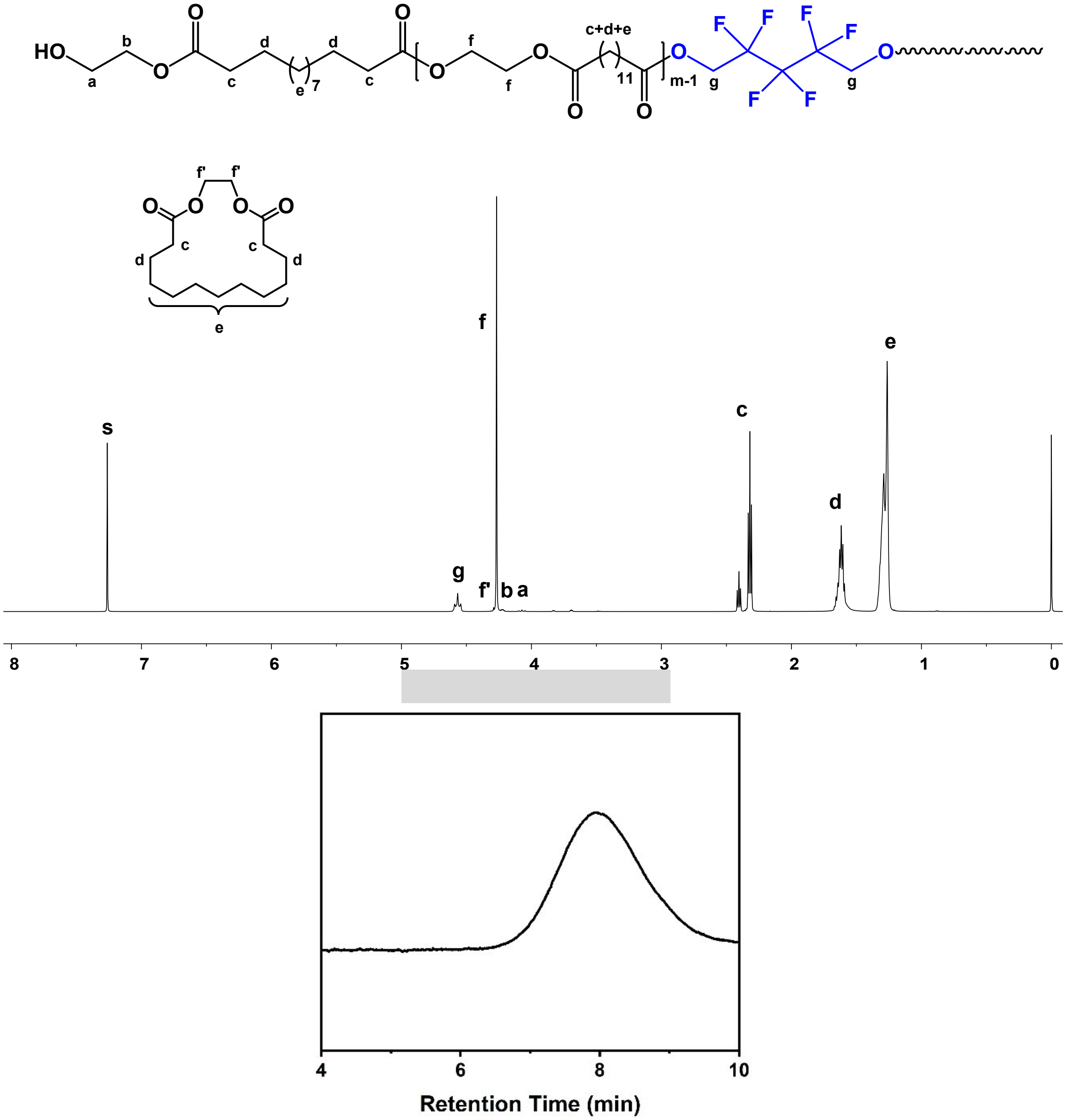

Figure S13. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 11 ($n_{FG} = n_g = 4$). S: solvent.

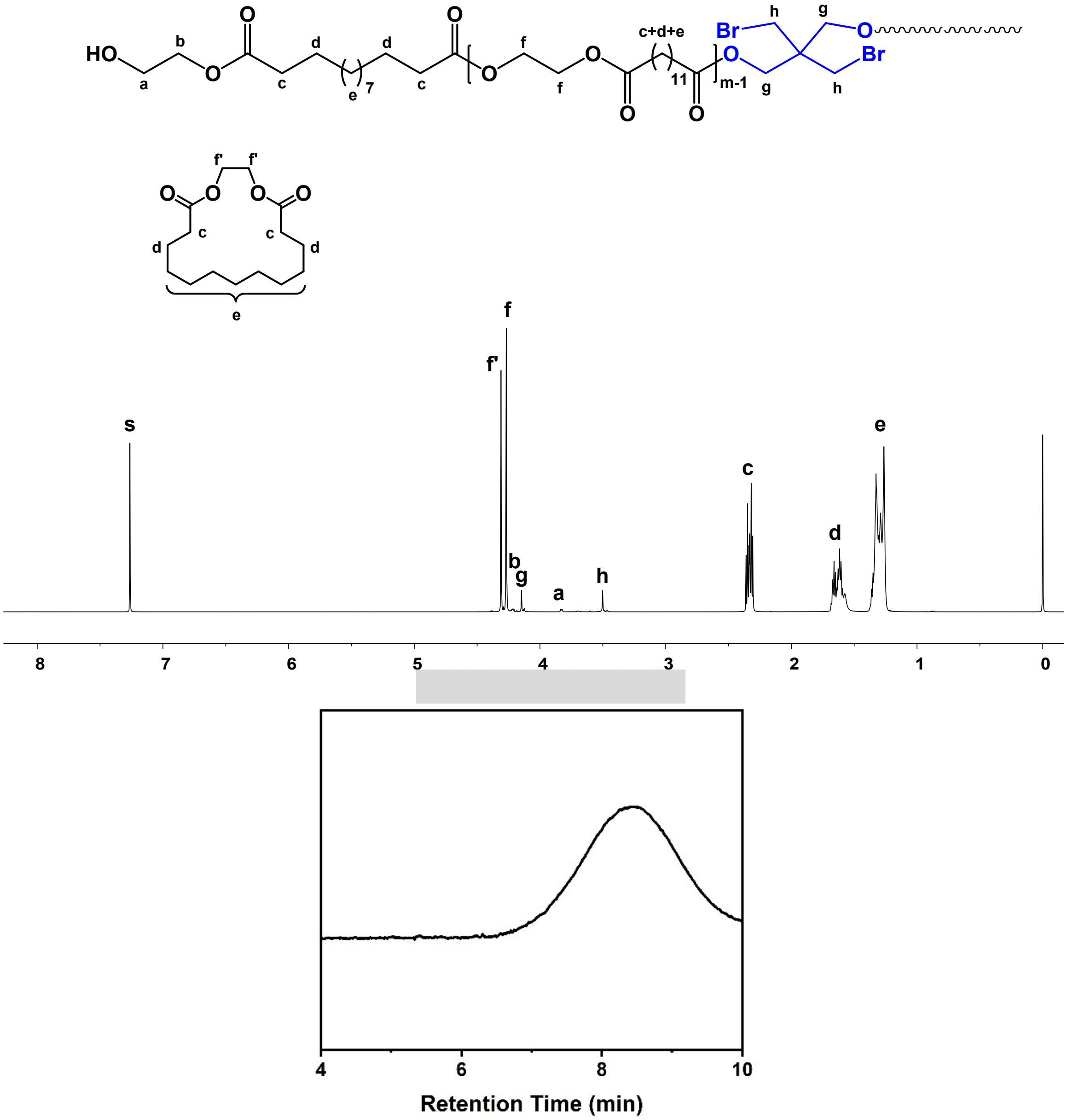

Figure S14. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 12 ($n_{\mathrm{FG}} = n_{\mathrm{g}} = 4$). S: solvent.

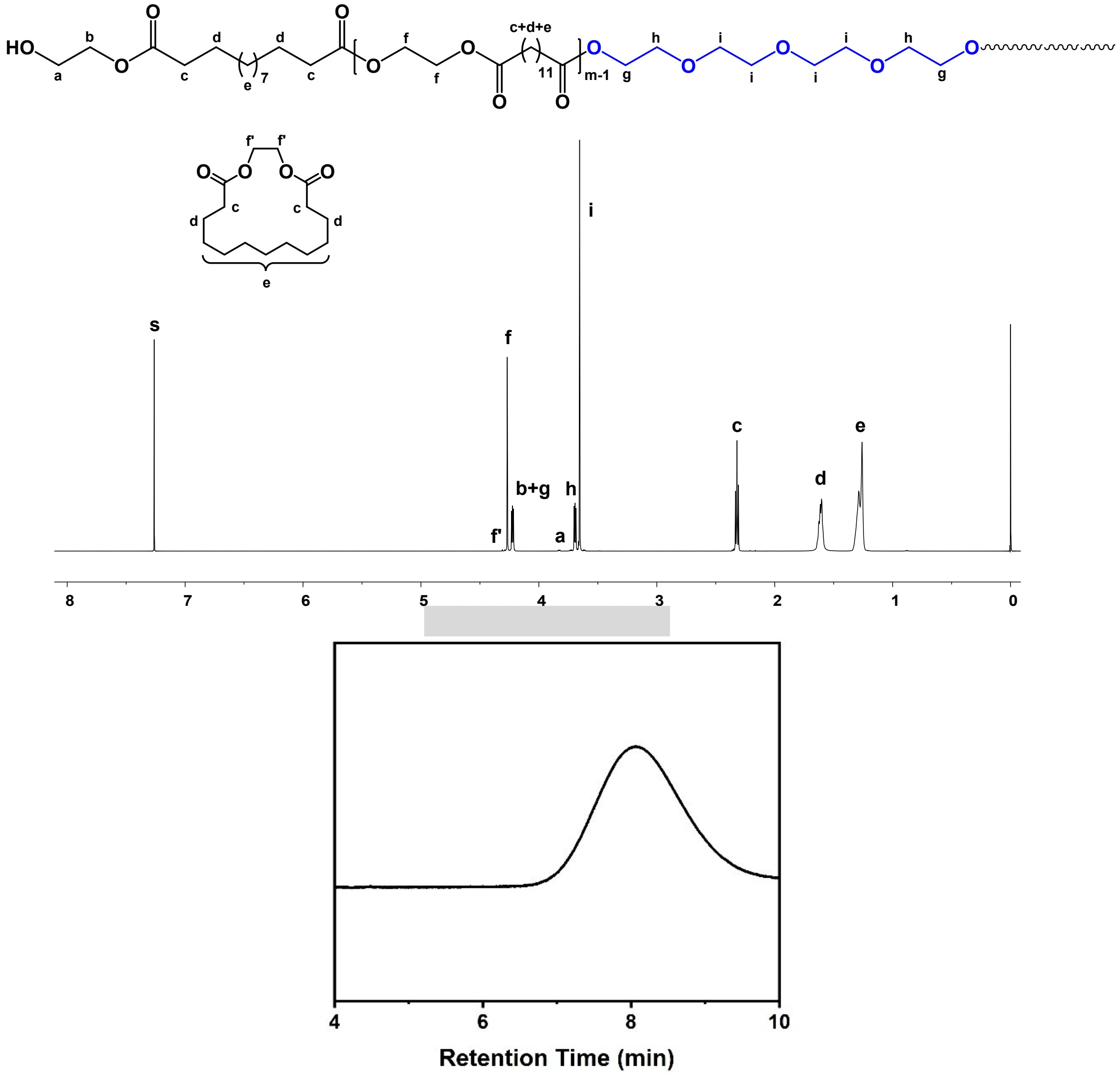

Figure S15. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 13 ($n_{FG} = n_h = 4$). S: solvent.

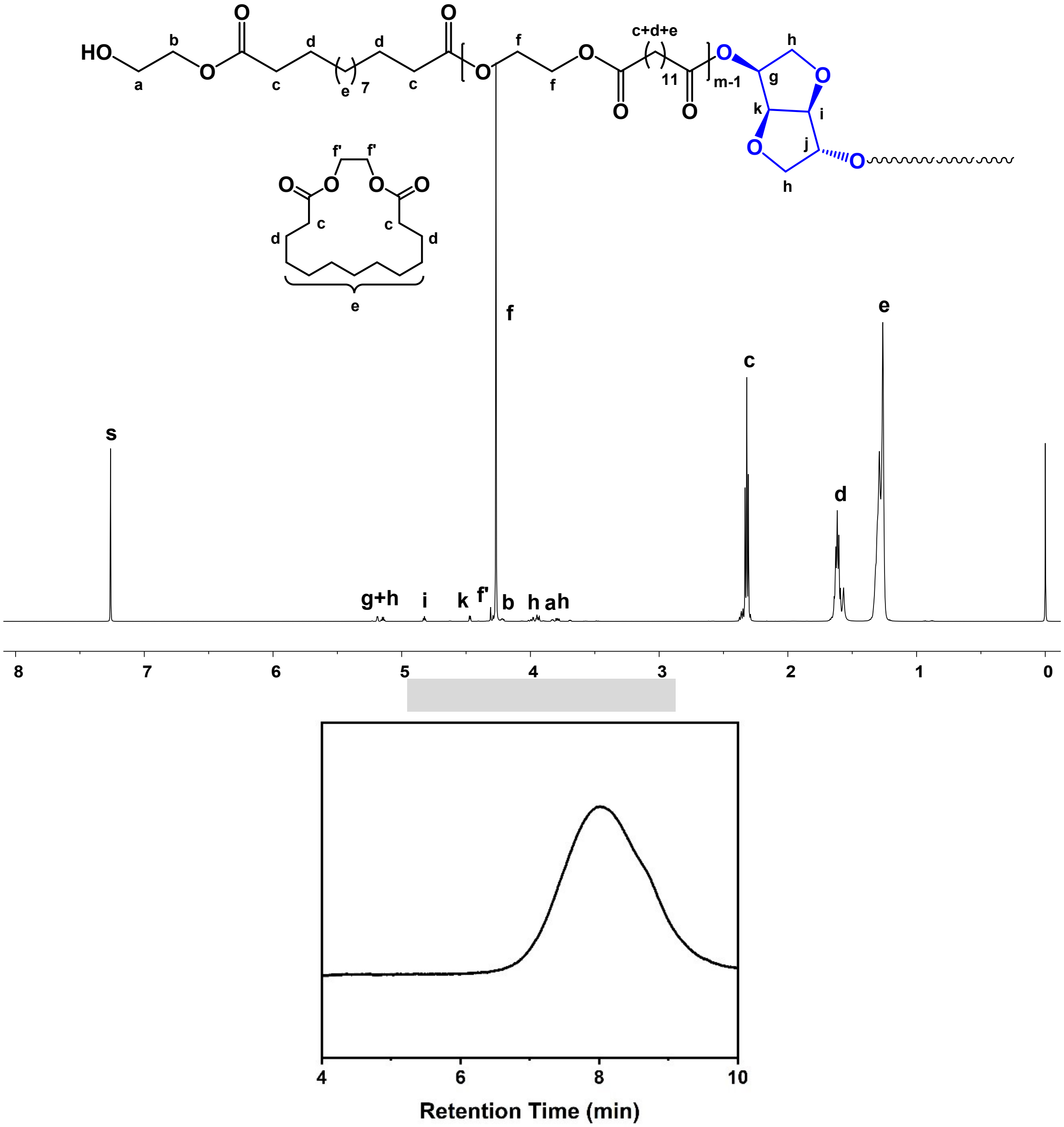

Figure S16. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 14 ($n_{\mathrm{FG}} = n_{\mathrm{k}} = 1$). S: solvent.

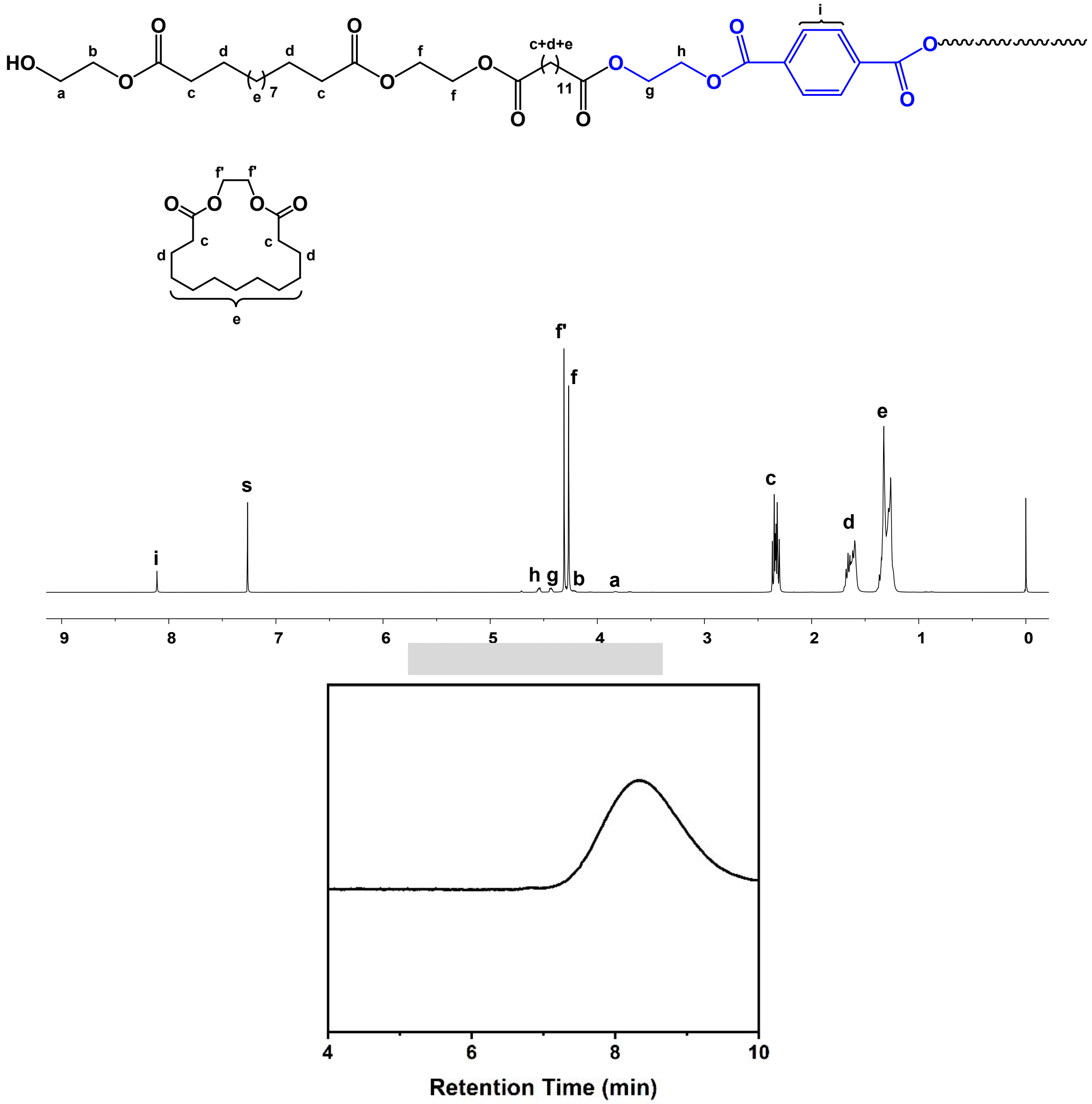

Figure S17. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 15 ($n_{FG} = n_i = 4$). S: solvent.

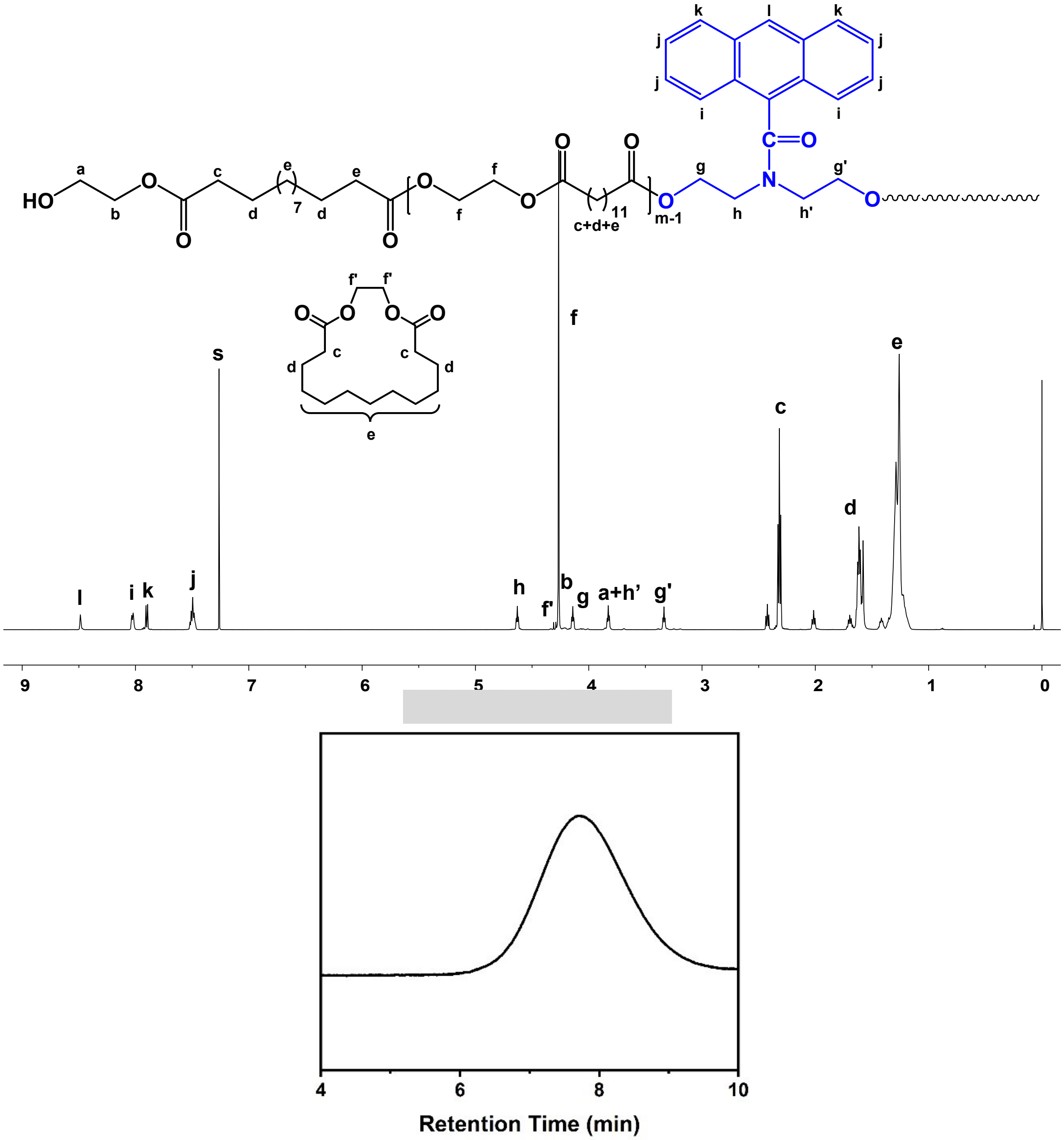

Figure S18. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 16 ($n_{\mathrm{FG}} = n_{\mathrm{l}} = 1$). S: solvent.

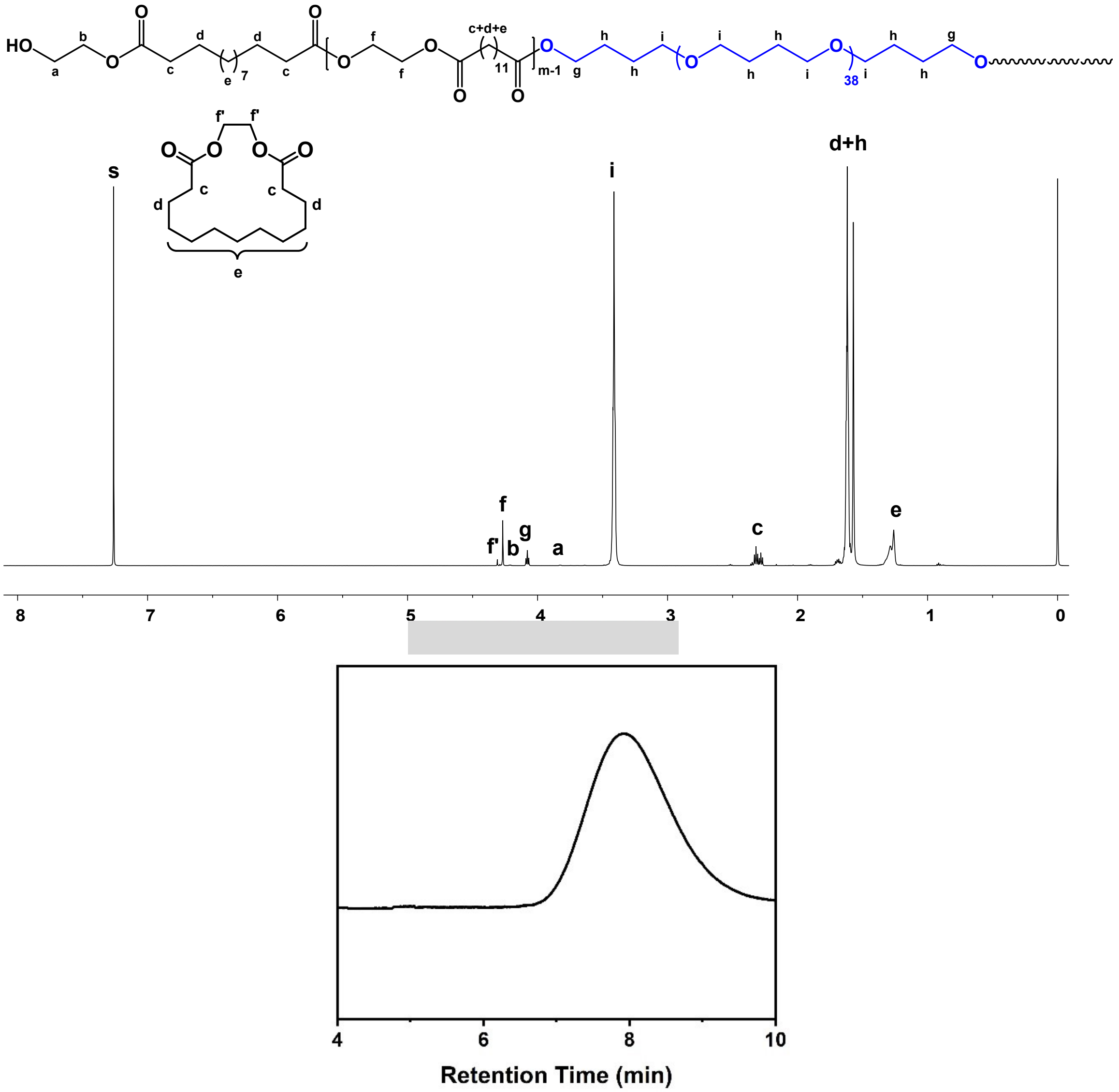

Figure S19. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 17 ($n_{FG} = n_i = 4$). S: solvent.

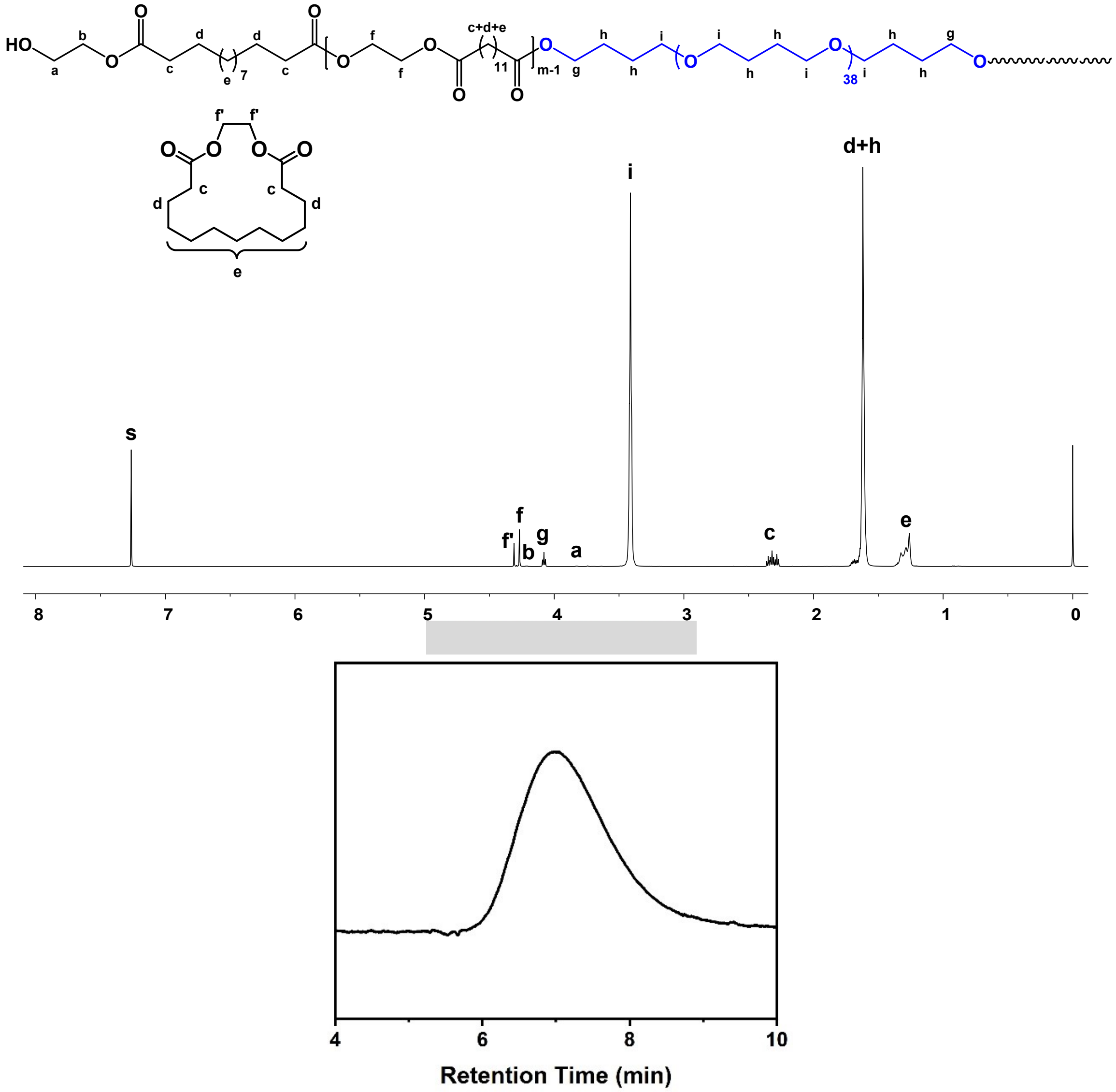

Figure S20. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 18 ($n_{FG} = n_i = 4$). S: solvent.

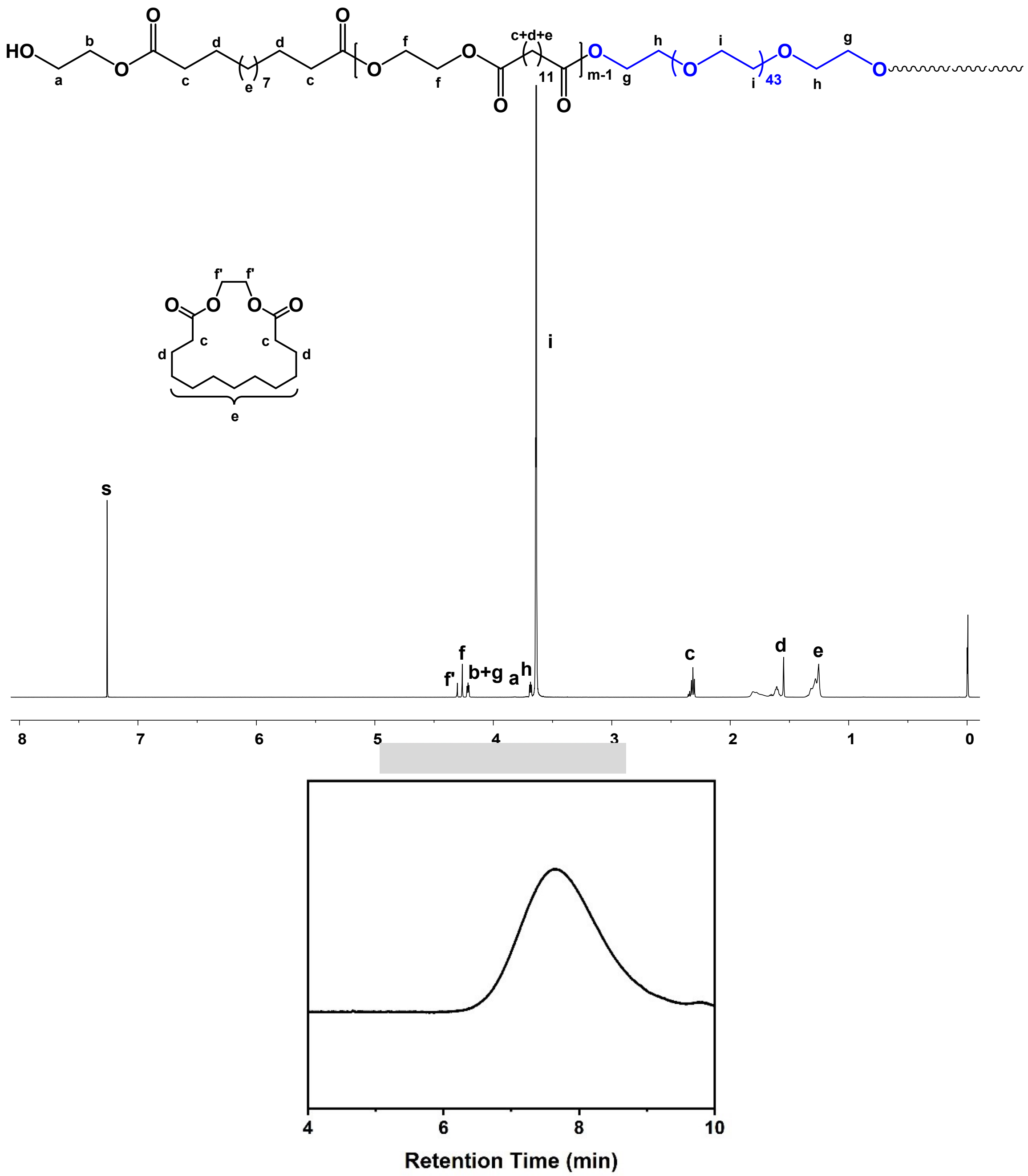

Figure S21. ^{1}H NMR spectrum (top) and GPC curve (bottom) of sample from entry 19 ($n_{FG} = n_i = 4$). S: solvent.

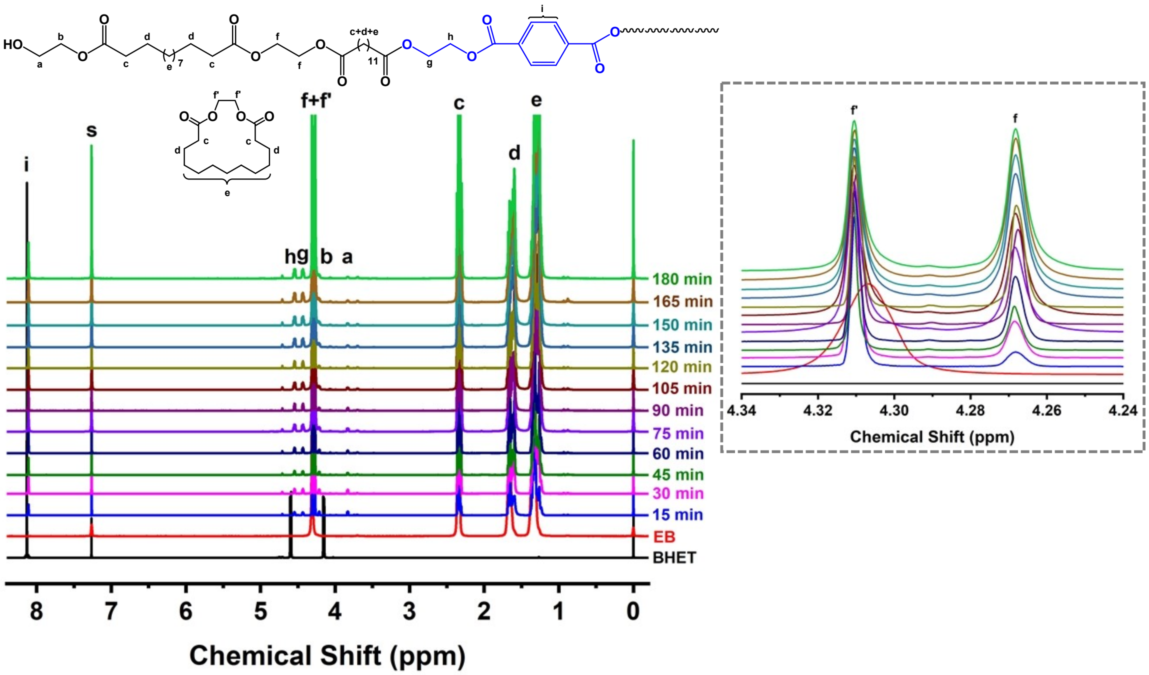

Figure S22. ^{1}H NMR spectra of PETB copolyesters with different reaction times. Polymerization condition: 220 ºC under N_2 purge, 0.2 *wt*% Ti(n-C_4H_9O)$_4$ as catalyst. Solvent: $CDCl_3$. Concentration: 10 mg/mL.

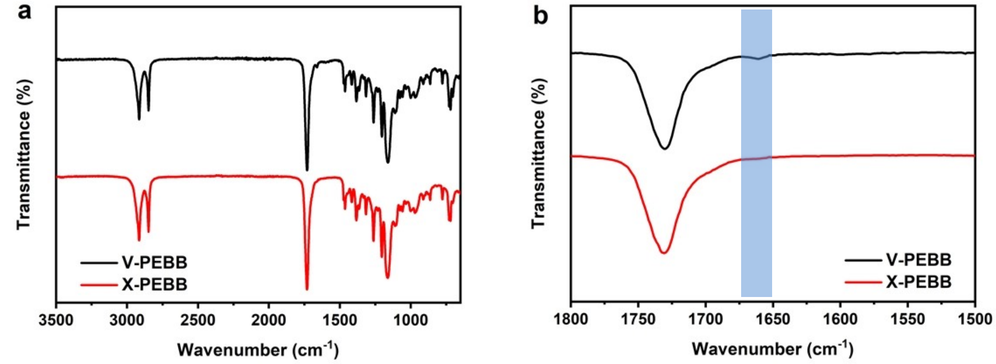

Figure S23. FT-IR full spectra of virgin PEBB (V-PEBB) and crosslinked PEBB (X-PEBB) (a), and their enlarged spectra at interested region (b).

References

(1) Besnoin, J. -M.; Lei, G. D.; Choi, K. Y. Melt Transesterfication of Dimethyl Terephthalate with Ethylene Glycol. *AIChE J.* **1989**, *35*, 1445-1456.

(2) Jadhav, A. L.; Malkar, R. S.; Yadav, G. D. Zn- and Ti-Modified Hydrotalcites for Transesterification of Dimethyl Terephthalate with Ethylene Glycol: Effect of the Metal Oxide and Catalyst Synthesis Method. *ACS Omega* **2020**, *5*, 2088-2096.