Supporting Information

Introducing the Tishchenko Reaction into Sustainable Polymers Chemistry

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Affiliations

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1. Materials and Instruments

1.1. Materials

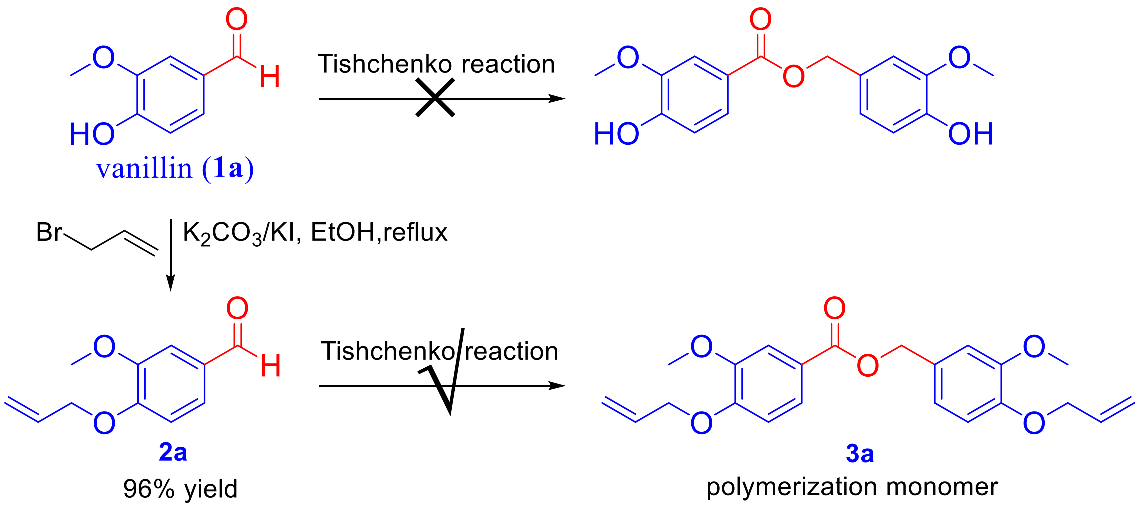
Vanillin (**1a**), 4-hydroxybenzaldehyde (**1d**), syringaldehyde (**1e**), 3-fluoro-4-hydroxybenzaldehyde (**1f**), 3-bromo-4-hydroxybenzaldehyde (**1g**), 4-hydroxy-3-methylbenzaldehyde (**1h**), allyl bromide, 6-bromo-1-hexene, 10-bromodec-1-ene, 2,2-dimethoxy-2-phenylacetophenone (DMPA), 1,2-ethanedithiol (**4a**), 1,3-propanedithiol (**4b**), 1,6-hexanedithiol (**4c**), 1,10-decanedithiol (**4d**), the second generation Hoveyda-Grubbs catalyst (HG-II), p-benzoquinone, ethyl vinyl ether, p-toluenesulfonyl hydrazide, triethylamine (TEA), pyridine, sodium hydride (60% dispersion in mineral oil) and hydrogen peroxide solution (30 wt.% in H_2O) were purchased from Aladdin (Shanghai) Inc. Potassium carbonate, potassium iodide, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methanol, ethanol, petroleum ether and ethyl acetate were obtained from Kermel Chemical Reagent (Tianjin) Inc. Tetrahydrofuran (THF) and dichloromethane were distilled over calcium hydride under a nitrogen atmosphere.

1.2. Instruments

NMR spectra were recorded on a JOEL ECX500 spectrometer (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR and 376 MHz for ^{19}F) or AVANCE III Bruker NMR spectrometer (600 MHz for ^{1}H NMR and 151 MHz for ^{13}C NMR), referenced to $CDCl_3$ or DMSO-d_6. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 instrument at a heating rate of 10 ^{o}C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analyses were performed on a TA Instruments Q2000 using hermetically-sealed T-zero aluminum pans. The glass transition temperature (T_g) and melting point were taken from the second heating cycle at a rate of 10 ^{o}C/min under a nitrogen atmosphere. Polymer molecular weights were measured by gel permeation chromatography (GPC) with DMF containing 0.01 M LiBr as the eluent, at 40 ^{o}C against polystyrene (PS) calibration standards. GPC was performed on a Shimadzu Prominence-i LC-2030C 3D equipped with both a refractive index (RI) and a photo-diode array (PDA) detector and using a Shodex GPC KD-804 column. X-ray scattering was performed using a PANalytical X PertPowder Cu Kα X-ray source, where the wavelength λ is 0.1542 nm, the scattering angle is 2θ. Fourier-transform infrared (FTIR) spectra were collected on a Thermoscientic (Nicolet iS50) at room temperature in the range of 500–4000 cm^{-1}.

2. Monomer synthesis

2.1. Optimization of the Tishchenko Reaction



Scheme S1. Feasibility Study of the Tishchenko Reaction.

The Tishchenko reaction did not occur using vanillin (**1a**) as substrate catalyzed by t-BuOK, CaH_2 or NaH, all of which have been reported as highly efficient catalysts.[1-3] Williamson allylation of vanillin gave compound **2a** and removed the detrimental effect of the weakly acidic phenolic groups on the Tishchenko reaction.

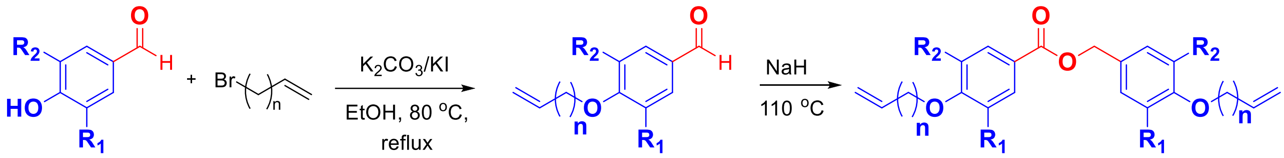
Table S1. Optimized conditions of the Tishchenko reaction.

Entry	Cat.(10 mol%)	Solvent	Temp. (°C)	Yield (%)
1	t-BuOK	toluene	80	57
2	CaH_2	toluene	80	15
4	NaH	toluene	80	65
5[b]	NaH	toluene	80	78
6	NaH	THF	65	64
7	NaH	DCM	40	trace
8	NaH	DMSO	80	0
9	NaH	CCl_4	78	trace
10	NaH	hexane	80	59
11	NaH	solvent-free	80	83
12	NaH	solvent-free	23	16
13	NaH	solvent-free	110	94
14	NaH	solvent-free	130	90

Reaction condition: vanillin (1 mmol, 0.154 g), cat. (10 mol%), 3 ml solvent, 24 h, yield determined by HPLC.

The optimized Tishchenko reaction was catalyzed by NaH under solvent-free conditions at 110 °C. When 4-(allyloxy)-3-methoxybenzaldehyde **2a** was employed as substrate, 4-(allyloxy)-3-methoxybenzyl 4-(allyloxy)-3-methoxybenzoate **3a** was obtained in 94% yield.

2.2. Preparation of α,ω-diene monomers



1 **2** **3**

	Yields	Yields
2a: R_1 = H, R_2 = OCH_3, n = 1	96%	**3a**:94%
2b: R_1 = H, R_2 = OCH_3, n = 4	95%	**3b**:89%
2c: R_1 = H, R_2 = OCH_3, n = 8	92%	**3c**:85%
2d: R1 = H, R_2= H, n = 1	94%	**3d**:86%
2e: R_1 = OCH_3, R_2 = OCH_3, n = 1	95%	**3e**:89%
2f: R_1 = H, R_2 = F, n = 1	91%	**3f**: 92%
2g: R_1 = H, R_2 = Br, n = 1	91%	**3g**:94%
2h: R_1 = H, R_2 = CH_3, n = 1	90%	**3h**:84%

Scheme 2. Synthesis route to α,ω-diene monomers.

General procedure for Williamson etherification. To a stirring solution of aromatic aldehyde (100 mmol, 1.0 equiv.) in anhydrous ethanol (100 ml) was gradually added K_2CO_3 (20.94 g, 150 mmol, 1.5 equiv.) and KI (3.32 g, 20 mmol, 0.2 equiv.) at room temperature under a nitrogen atmosphere. After 20 min., an ω-bromo alkene (200 mmol, 2.0 equiv.) was added dropwise. Then the mixture was refluxed at 80 °C for 48 to 72 hours. After cooling to room temperature, the precipitate was filtered off and the filtrate was concentrated in vacuo. The residue was diluted with 100 ml of deionized water and extracted with ethyl acetate (EtOAc, 3 x 150 ml). The combined organic was washed with brine (2 x 150 ml), dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatograph (ethyl acetate /petroleum ether = 1/20 to 1/4) to afford ethers **2a-h** in 90-96% yield.

General procedure for the Tishchenko reaction. Sodium hydride (60% dispersion in mineral oil, 3 mmol, 0.12 g, 10 mol%) was added to a melted ether **2a-h** (30 mmol) in a Schlenk-flask at 110 °C. The mixture was stirred under reduced pressure (20 mbar) for 4 h., then charged with nitrogen and further stirred for 24 to 48 h at 110 °C. After the reaction, the mixture was diluted with CH_2Cl_2 (30 ml) and 10 wt.% HCl and the aqueous phase was extracted with CH_2Cl_2 (3 x 30 ml). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatograph (ethyl acetate /petroleum ether = 1/20 to 1/6) to afford α,ω-diene esters **3a-h** in 84-94% yield (determined by HPLC).

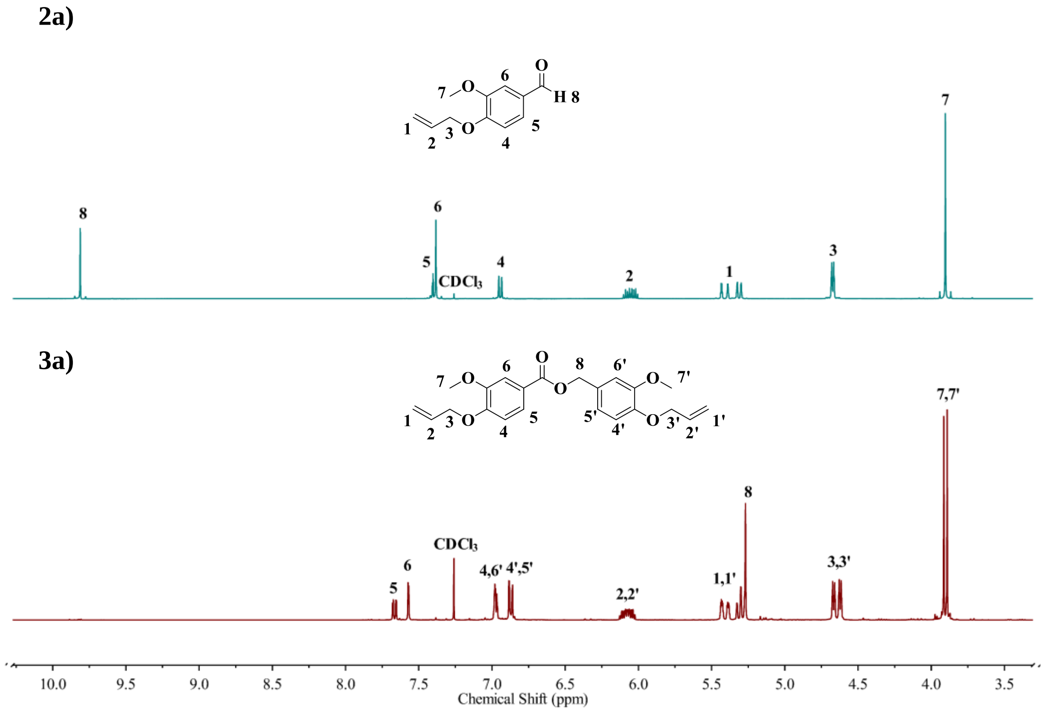


Figure S1. Comparative ^{1}H NMR spectra of 2a and 3a.

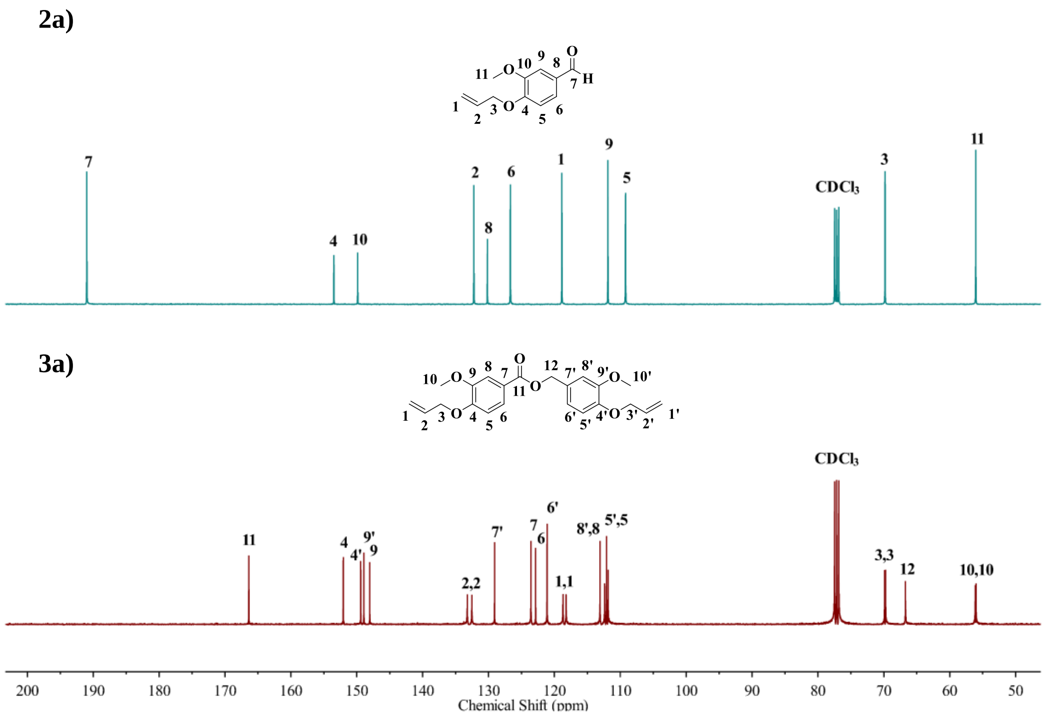
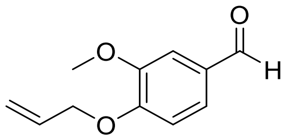


Figure S2. Comparative ^{13}C NMR spectra of 2a and 3a.

In the ^{1}H NMR spectrum the signal at 5.27 ppm is attributed to the newly formed methylene and the signal of the formyl group at 9.81 ppm completely disappeared (Figure S1). Meanwhile in the ^{13}C NMR spectrum the signal of the newly formed methylene appeared at 66.7 ppm and the signal of the

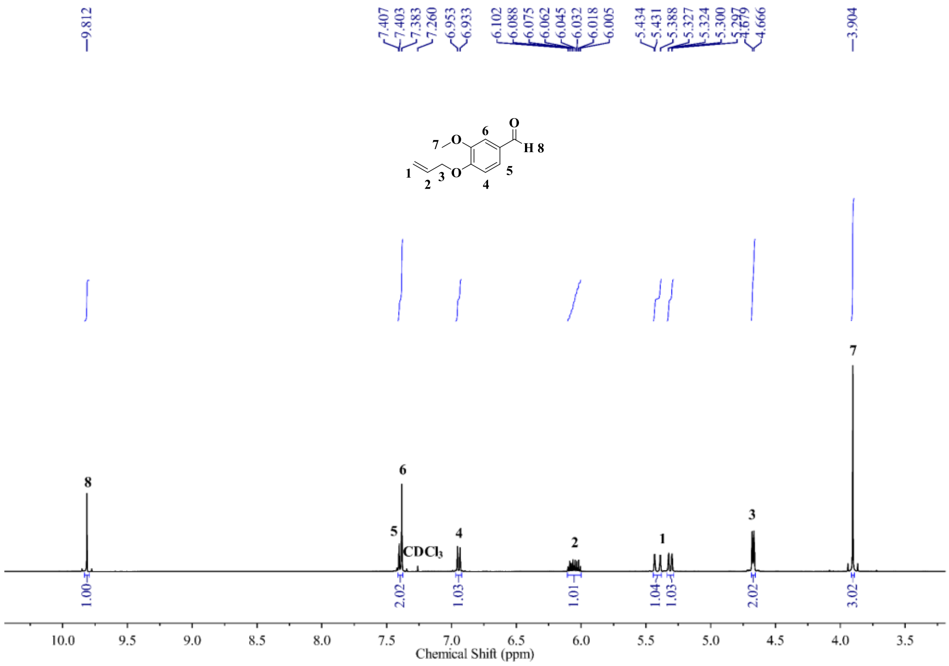
C=O group shifted from 190.9 ppm to 166.4 ppm (Figure S2).

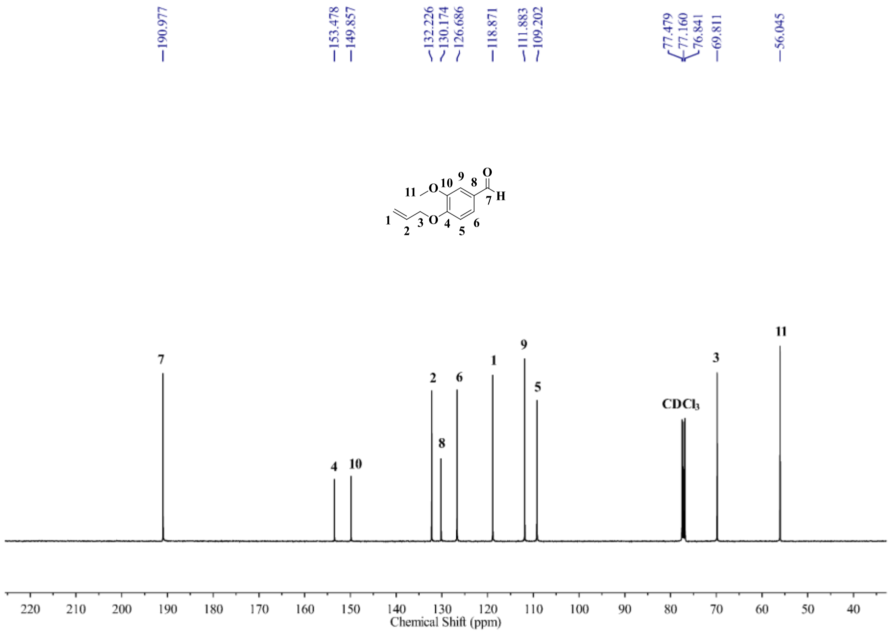
2.2.1. 4-(allyloxy)-3-methoxybenzaldehyde (2a)



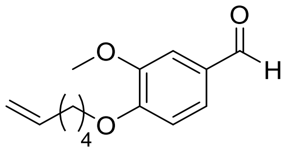
2a

Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.81 (s, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.38 (s, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.10 - 6.01 (m, 1H), 5.41 (ddd, J = 13.9 Hz, 11.7 Hz, 1.3 Hz, 2H), 4.67 (dt, J = 5.2, 1.2 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.01, 153.51, 149.89, 132.26, 130.20, 126.72, 118.90, 111.91, 109.23, 77.51, 77.19, 76.87, 69.84, 56.07. FTIR (KBr), cm^{-1}: 1683 (C=O), 1650 (C=C), 1268 (C-O).



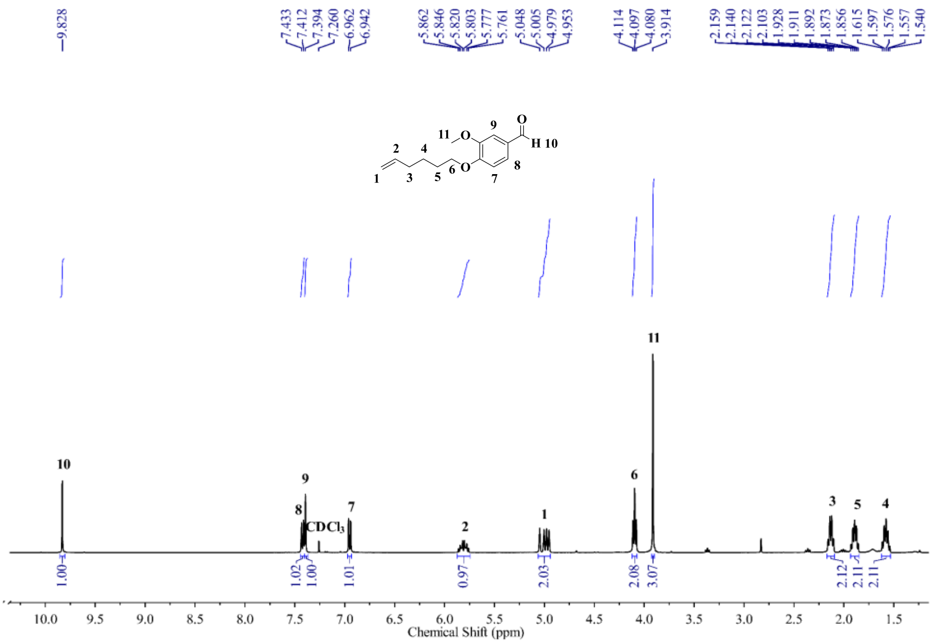


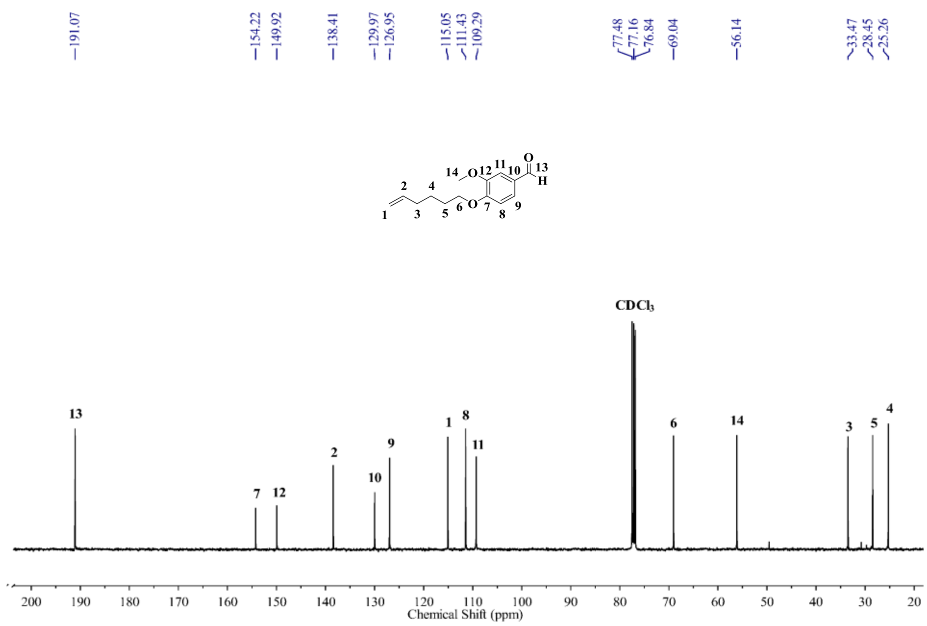
2.2.2. 4-(hex-5-en-1-yloxy)-3-methoxybenzaldehyde (2b)



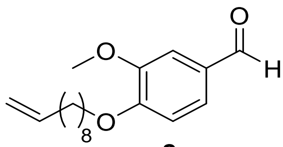
2b

Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.83 (s, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.39 (s, 1H), 6.95 (d, J = 8.0 Hz), 5.81 (m, 1H), 5.00 (dd, J = 24.2, 13.8 Hz, 2H), 4.10 (t, J = 6.8 Hz, 2H), 3.91 (s, 3H), 2.13 (m, 2H), 1.93-1.86 (m, 2H), 1.62-1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.07, 154.22, 149.92, 138.41, 129.97, 126.95, 115.05, 111.43, 109.29, 69.04, 56.14, 33.47, 28.45, 25.26. FTIR (KBr), cm^{-1}: 1770 (C=O), 1654 (C=C), 1241 (C-O).



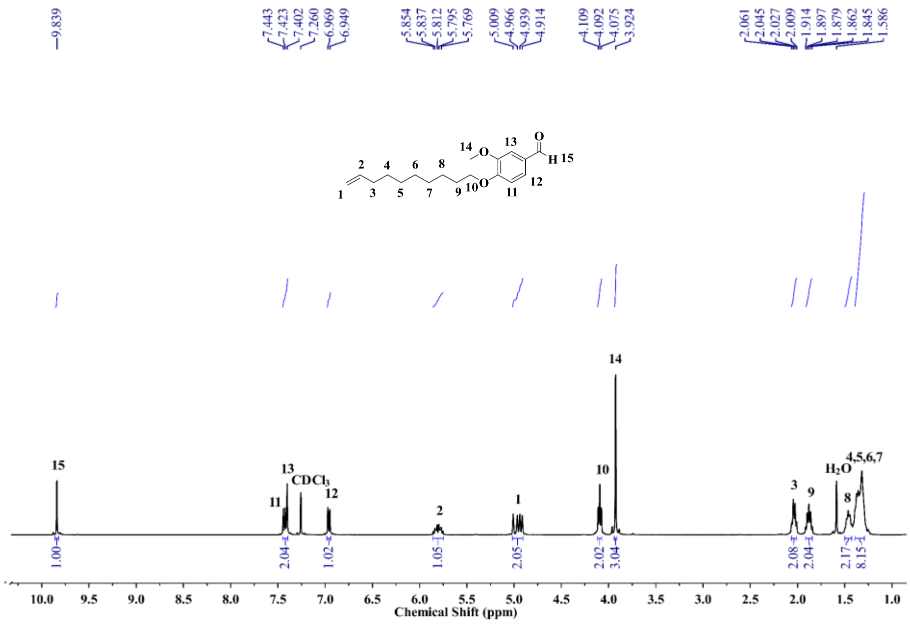


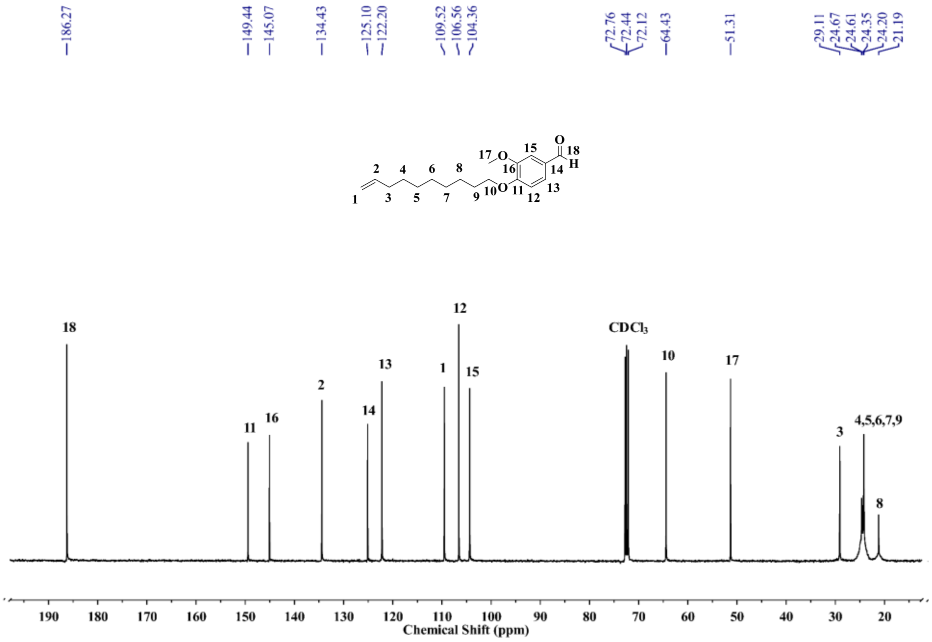
2.2.3. 4-(dec-9-en-1-yloxy)-3-methoxybenzaldehyde (2c)



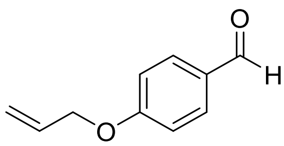
2c

Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.84 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.40 (s, 1H), 6.96 (d, J = 8.0 Hz, 1H), 5.88-5.77 (m, 1H), 4.96 (dd, J = 24.5, 13.6 Hz, 2H), 4.09 (t, J = 6.8 Hz, 2H), 3.92 (s, 3H), 2.06-2.01 (m, 2H), 1.91-1.85 (m, 2H), 1.50-1.43 (m, 2H), 1.39-1.32 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 186.27, 149.44, 145.07, 134.43, 125.10, 122.20, 109.52, 106.56, 104.36, 64.43, 51.31, 29.11, 24.67, 24.61, 24.35, 24.20, 21.19. FTIR (KBr), cm^{-1}: 1686 (C=O), 1640 (C-O), 1268 (C-O).



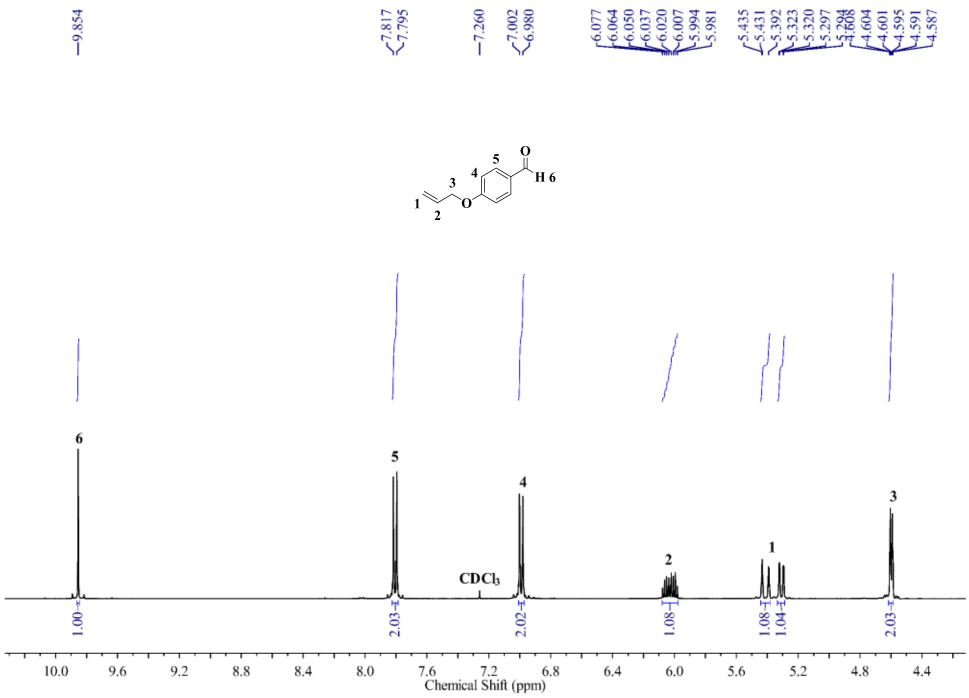


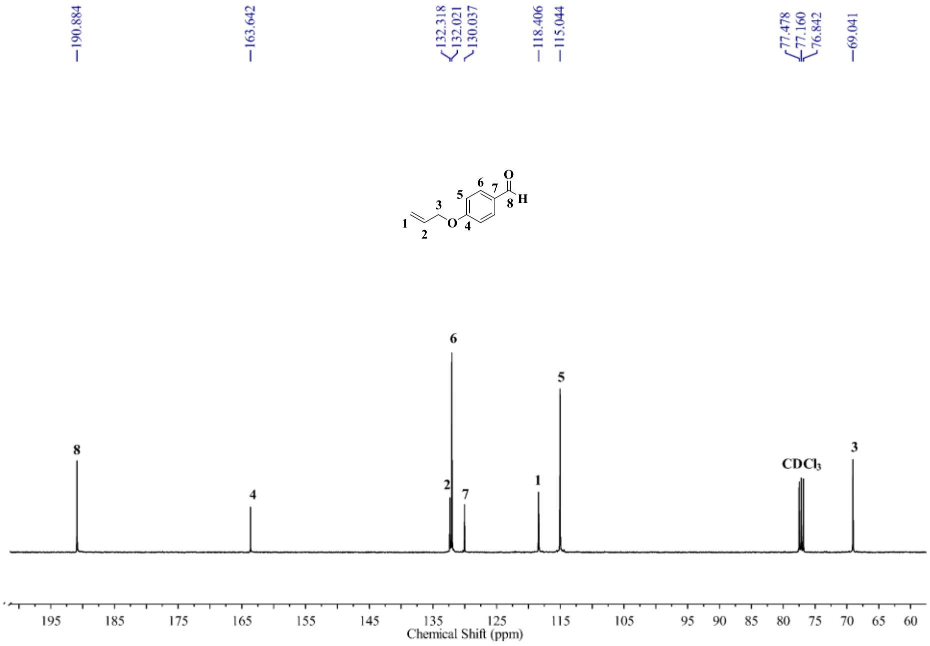
2.2.4. 4-(allyloxy)benzaldehyde (2d)



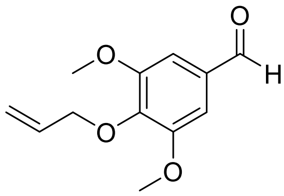
2d

Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.85 (s, 1H), 7.81 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 6.08-5.98 (m, 1H), 5.41 (dd, J = 17.2, 1.5 Hz, 1H), 5.31 (dd, J = 10.6, 1.3 Hz, 1H), 4.60 (dt, J = 5.4, 1.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.88, 163.64, 132.32, 132.02, 130.04, 118.41, 115.04, 69.04. FTIR (KBr), cm^{-1}: 1691 (C=O), 1651 (C=C), 1259 (C-O).



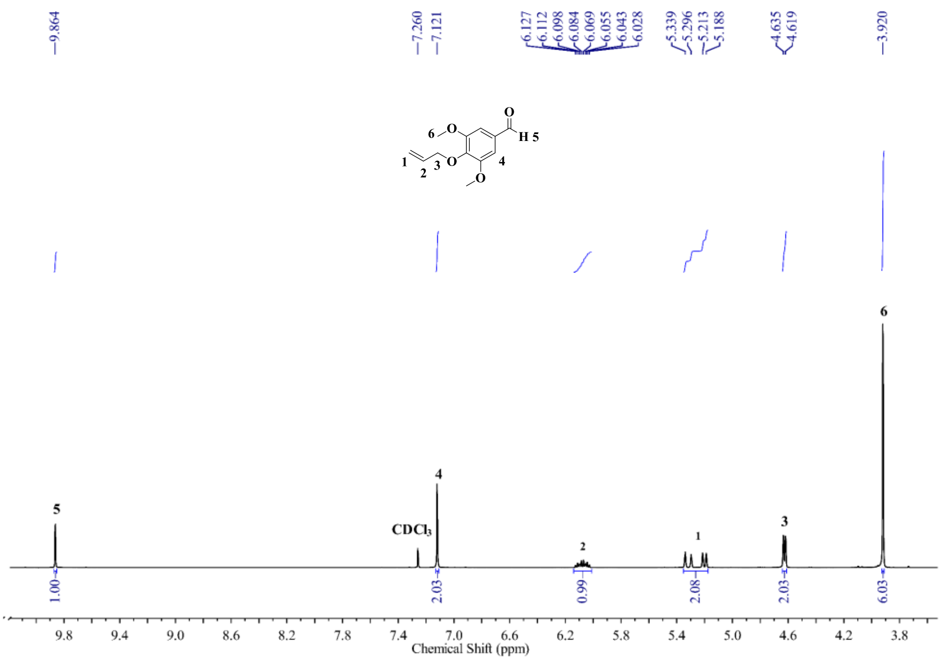


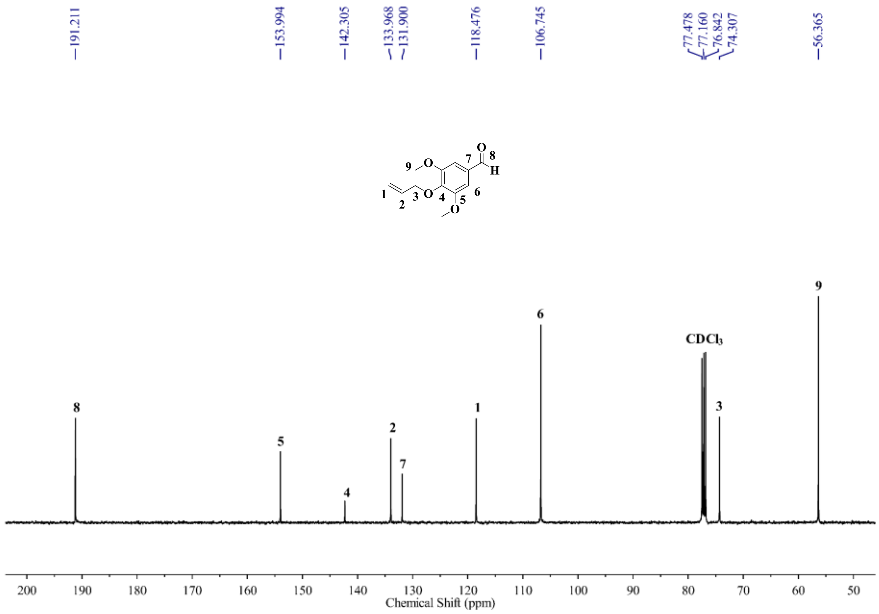
2.2.5. 4-(allyloxy)-3,5-dimethoxybenzaldehyde (2e)



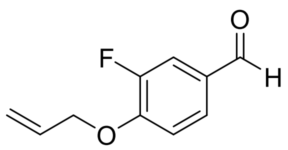
2e

Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.86 (s, 1H), 7.12 (s, 2H), 6.13-6.02 (m, 1H), 5.32 (d, J = 17.2 Hz, 1H), 5.20 (d, J = 10.0 Hz, 1H), 4.63 (d, J = 6.2 Hz, 2H), 3.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.21, 153.99, 142.31, 133.97, 131.90, 118.48, 106.74 , 74.31, 56.36. FTIR (KBr), cm^{-1}: 1683 (C=O), 1647 (C=C), 1329 (C-O).



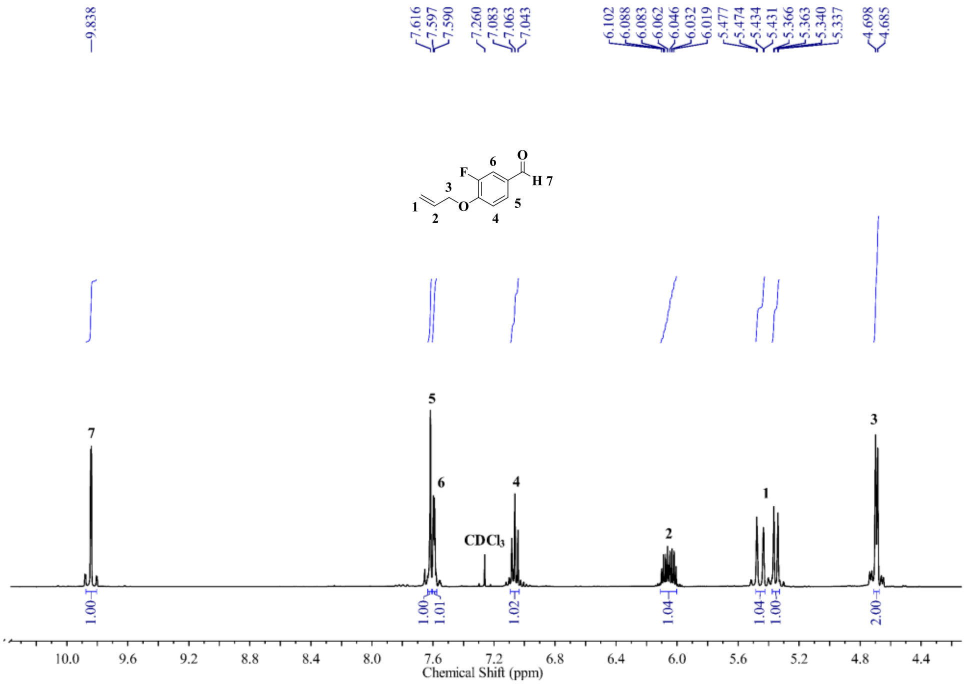


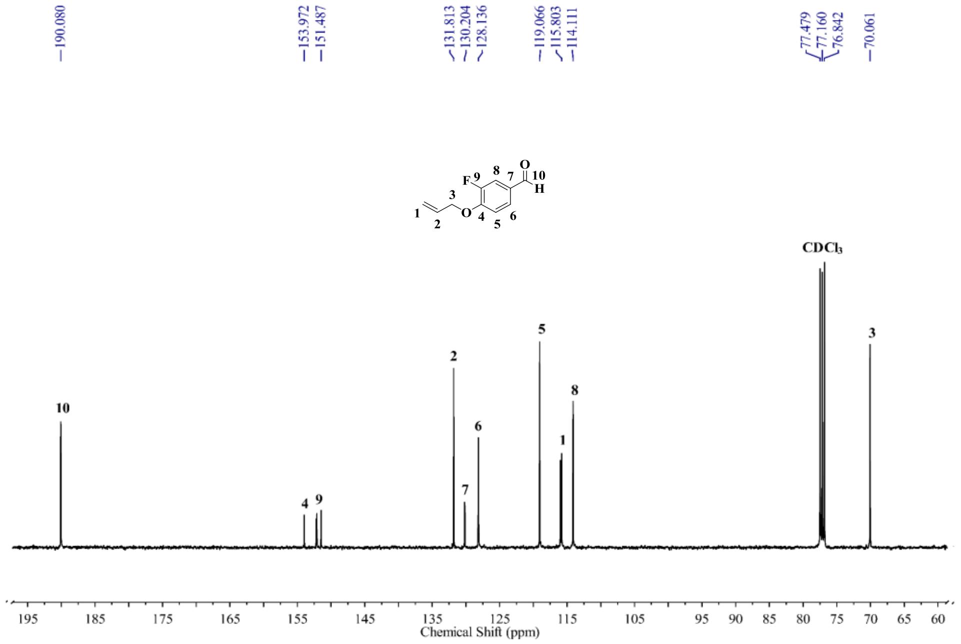
2.2.6. 4-(allyloxy)-3-fluorobenzaldehyde (2f)



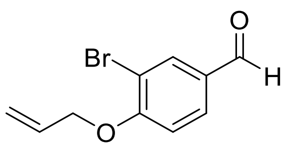
2f

Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.84 (s, 1H), 7.62 (s, 1H), 7.59 (d, J = 2.8 Hz, 1H), 7.06 (t, J = 8.1 Hz, 1H), 6.11-6.00 (m, 1H), 5.45 (dd, J = 17.2, 1.2 Hz, 1H), 5.35 (dd, J = 10.5, 1.2 Hz, 1H), 4.69 (d, J = 5.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.08, 153.97, 151.49, 131.81, 130.20, 128.14, 119.07, 115.80, 114.11, 70.06. FTIR (KBr), cm^{-1}: 1693 (C=O), 1650 (C=C), 1281 (C-O).



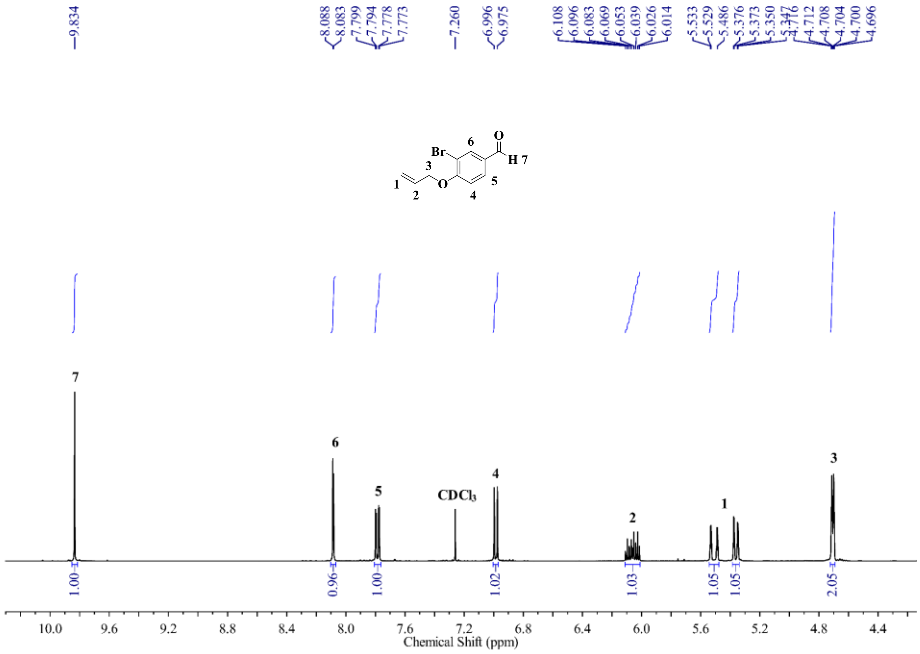


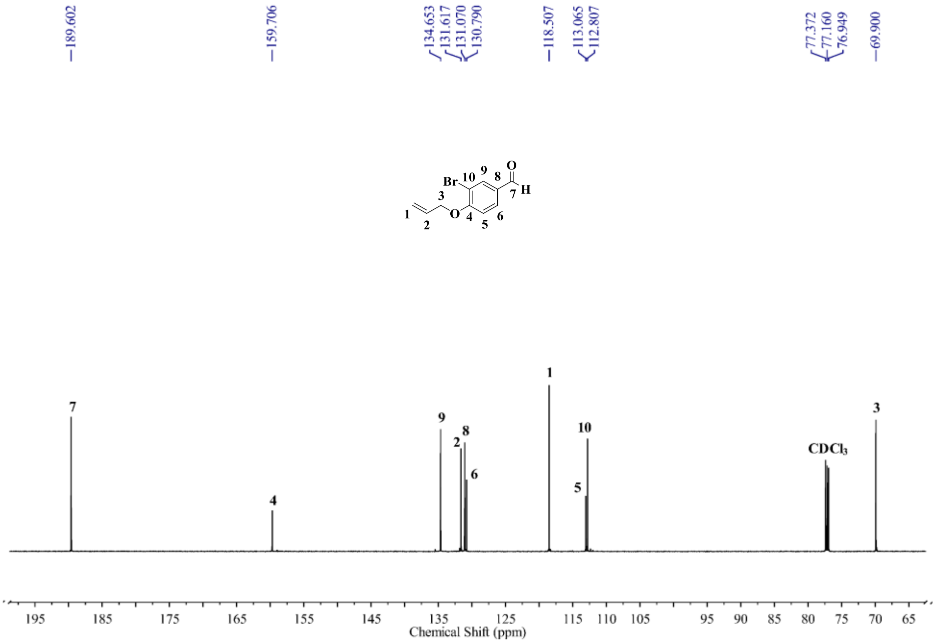
2.2.7. 4-(allyloxy)-3-bromobenzaldehyde (2g)



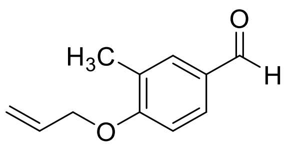
2g

Yield: 91%. [1]H NMR (400 MHz, $CDCl_3$) δ: 9.83 (s, 1H), 8.09 (d, J = 2.1 Hz, 1H), 7.79 (dd, J = 8.5, 2.0 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 6.11-6.01 (m, 1H), 5.51 (dd, J = 17.3, 1.4 Hz, 1H), 5.36 (dd, J = 10.6, 1.4 Hz, 1H), 4.71 (dt, J = 5.0, 1.6 Hz, 2H). [13]C NMR (151 MHz, $CDCl_3$) δ: 189.60, 159.71, 134.65, 131.62, 131.07, 130.79, 118.51, 113.07, 112.81, 69.90. FTIR (KBr), cm^{-1}: 1693 (C=O), 1649 (C=C), 1271 (C-O).



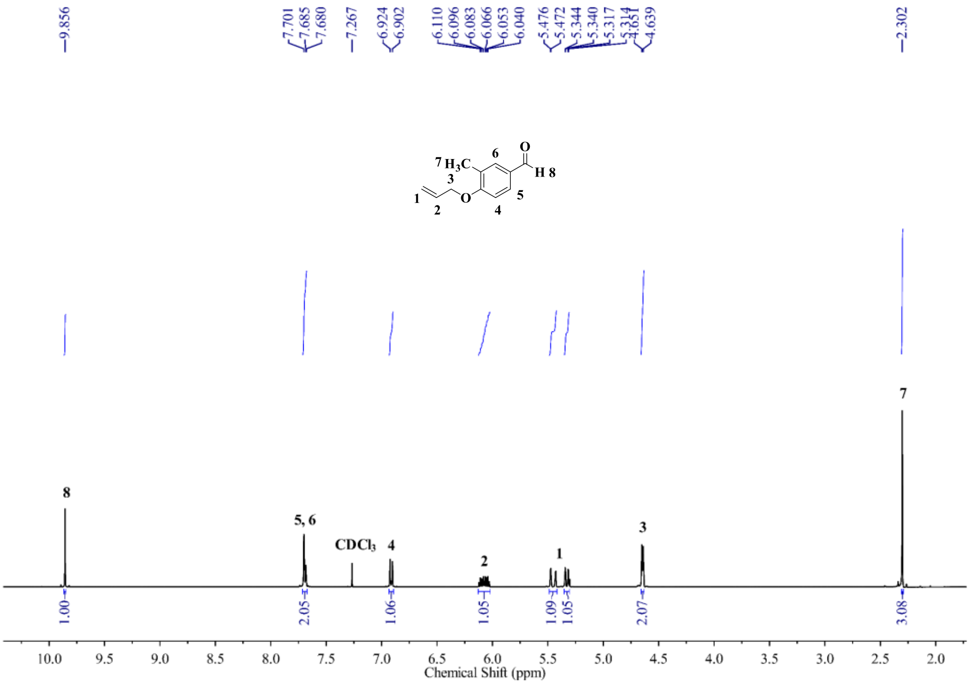


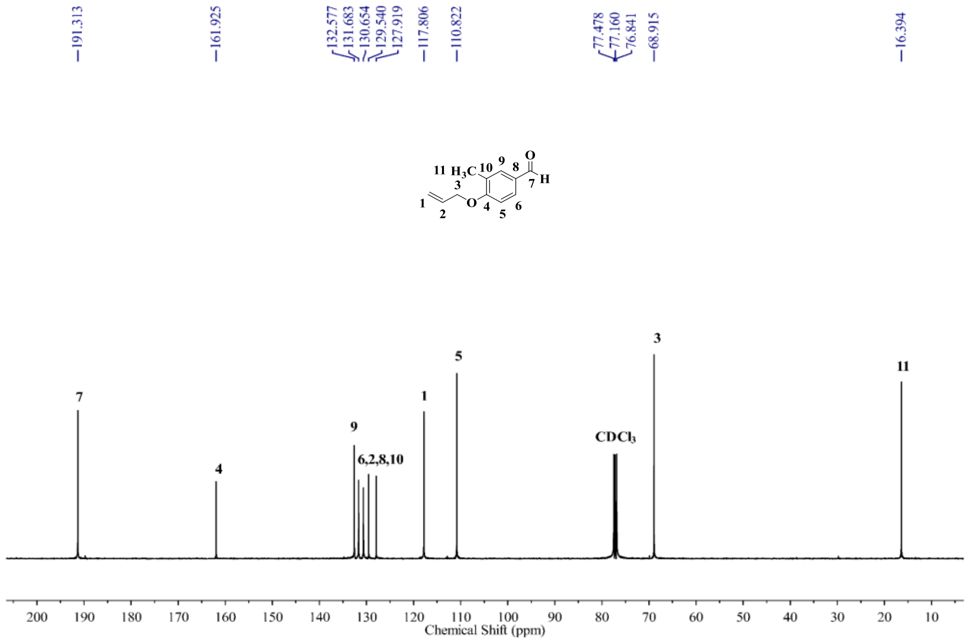
2.2.8. 4-(allyloxy)-3-methylbenzaldehyde (2h)



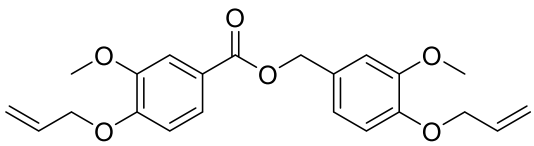
2h

Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.86 (s, 1H), 7.70-7.68 (m, 2H), 6.91 (d, J = 8.8 Hz, 1H), 6.12-6.02 (m, 1H), 5.45 (dd, J = 17.0, 1.4 Hz, 1H), 5.33 (dd, J = 10.6, 1.4 Hz, 1H), 4.64 (J = 4.8 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.31, 161.93, 132.58, 131.68, 130.65, 129.54, 127.92, 117.81, 110.82, 68.91, 16.39. FTIR (KBr), cm^{-1}: 1689 (C=O), 1640 (C=C), 1269 (C-O).



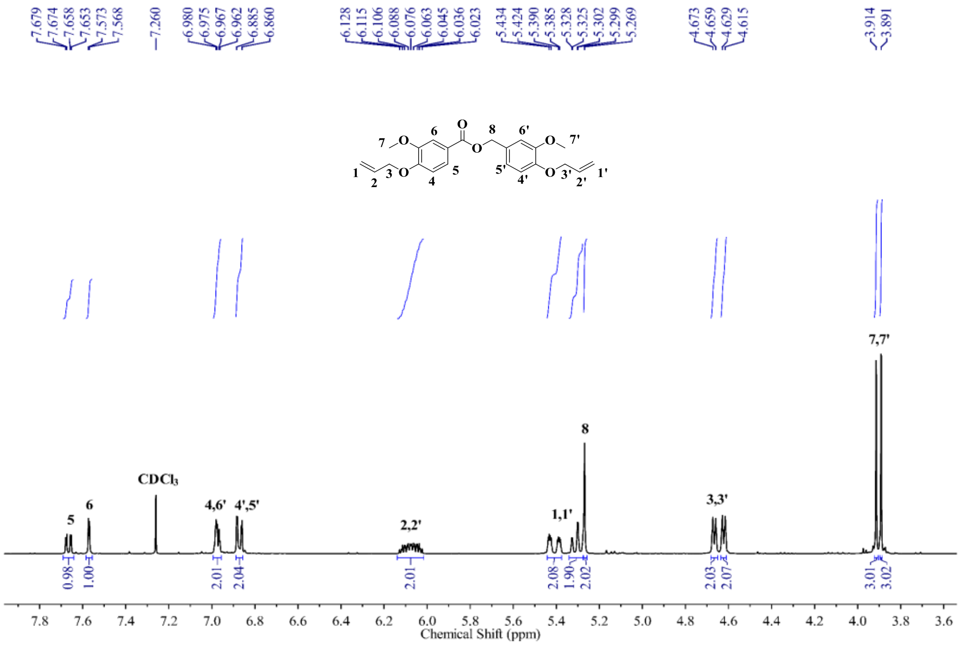


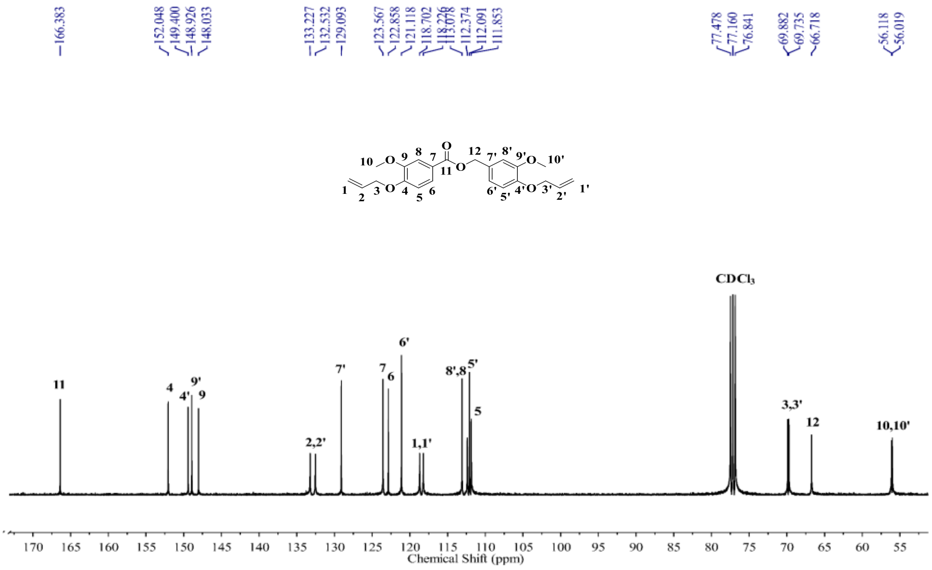
2.2.9. 4-(allyloxy)-3-methoxybenzyl 4-(allyloxy)-3-methoxybenzoate (3a)



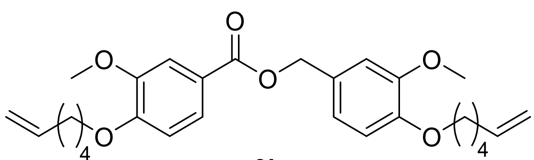
3a

Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.00 – 6.96 (m, 2H), 6.88 (d, J = 1.2 Hz, 1H), 6.86 (d, J = 1.2 Hz, 1H), 6.13 – 6.02 (m, 2H), 5.43 (dd, J = 3.8 Hz, 1.6 Hz, 1H), 5.39 (dd, J = 3.8 Hz, 1.6 Hz, 1H), 5.31 (d, J = 10.4, 2H), 5.27 (s, 2H), 4.67 (d, J = 5.6 Hz, 2H), 4.62 (d, J = 5.6 Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.33, 152.05, 149.41, 148.93, 148.03, 133.23, 132.54, 129.11, 123.54, 122.86, 121.09, 118.63, 118.15, 113.12, 112.39, 112.11, 111.88, 77.48, 77.16, 76.84, 69.87, 66.68, 56.00. FTIR (KBr), cm^{-1}: 1710 (C=O), 1650 (C=C), 1269 (C-O).



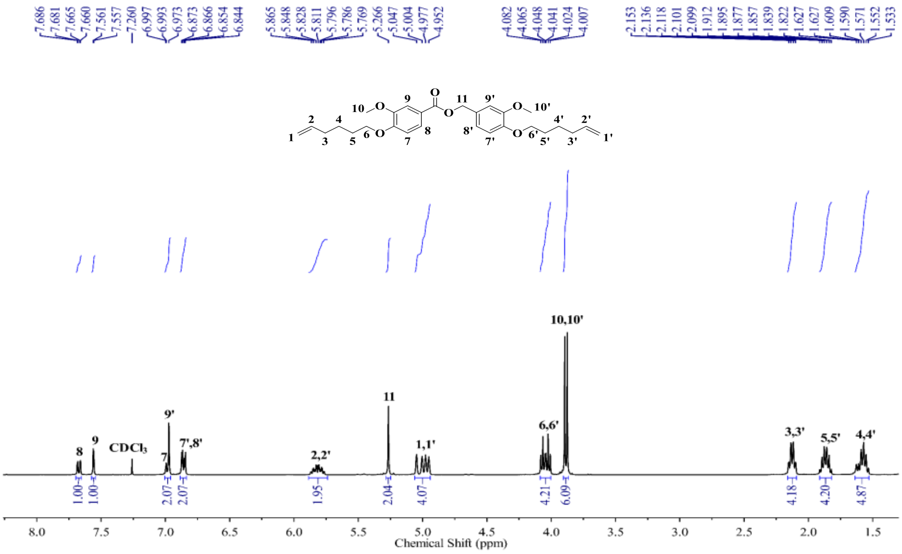


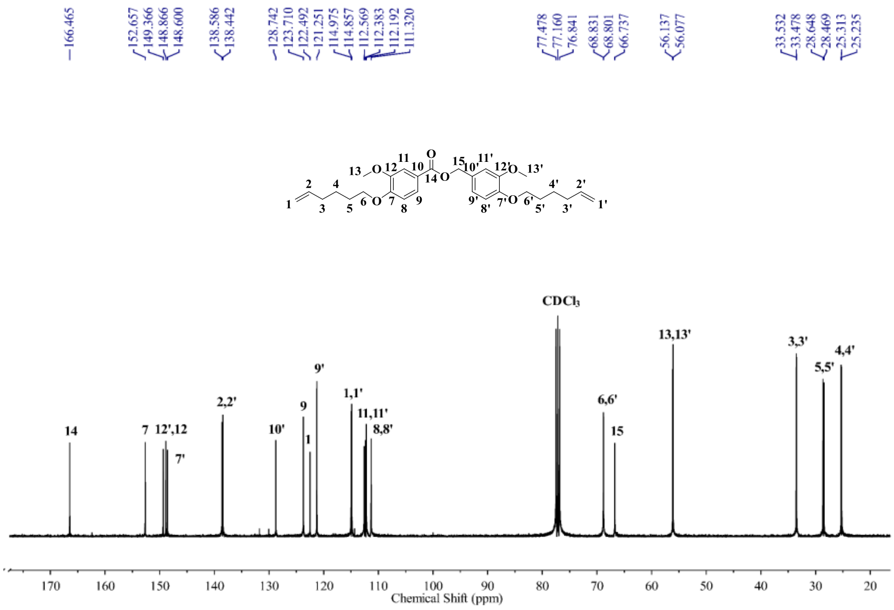
2.2.10. 4-(hex-5-en-1-yloxy)-3-methoxybenzyl 4-(hex-5-en-1-yloxy)-3-methoxybenzoate (3b)



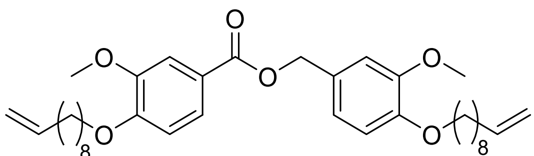
3b

Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, J = 8.4, 1.9 Hz, 1H), 7.56 (d, J = 1.9 Hz, 1H), 7.01-6.96 (m, 2H), 6.86 (dd, J = 8.2, 3.3 Hz, 2H), 5.89-5.74 (m, 2H), 5.27 (s, 2H), 5.00 (dd, J = 24.4, 13.6 Hz, 4H), 4.04 (dt, J = 16.3, 6.8 Hz, 4H), 3.89 (d, J = 8.0 Hz, 6H), 2.16-2.09 (m, 4H), 1.91-1.82 (m, 4H), 1.63-1.53 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.46, 152.66, 149.37, 148.87, 148.60, 138.59, 138.44, 128.74, 123.71, 122.49, 121.25, 114.98, 114.86, 112.57, 112.38, 112.19, 111.32, 68.83, 68.80, 66.74, 56.14, 56.08, 33.53, 33.48, 28.65, 28.47, 25.31, 25.23. FTIR (KBr), cm^{-1}: 1712 (C=O), 1639 (C=C), 1273 (C-O).





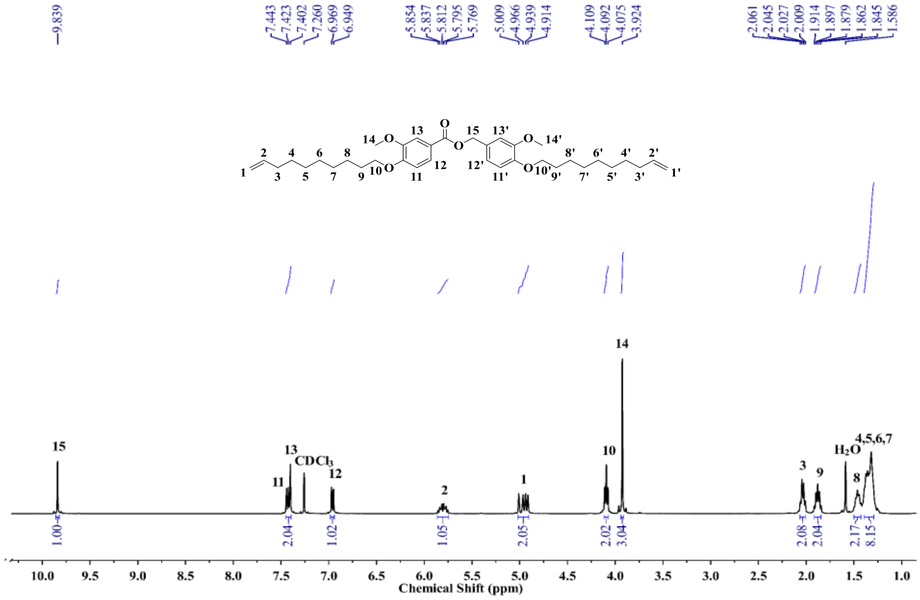
2.2.11. 4-(dec-9-en-1-yloxy)-3-methoxybenzyl 4-(dec-9-en-1-yloxy)-3-methoxybenzoate (3c)

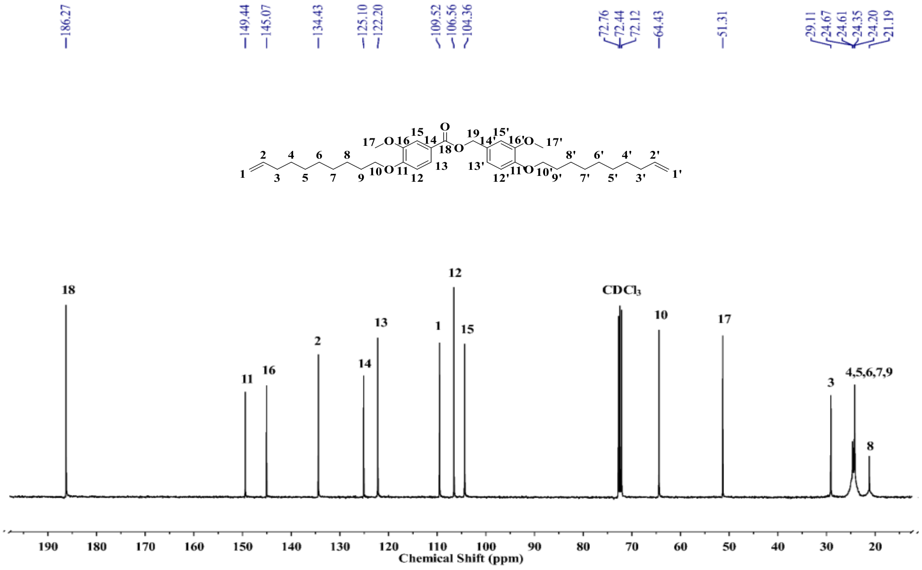


3c

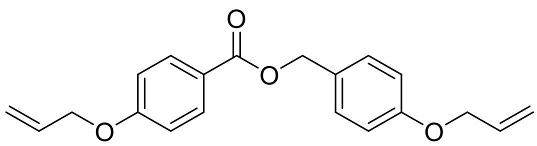
Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, J = 8.4, 1.9 Hz, 1H), 7.55 (d, J = 1.9 Hz, 1H), 7.00-6.95 (m, 2H), 6.86 (dd, J = 8.2, 3.1 Hz, 2H), 5.85-5.74 (m, 2H), 5.26 (s, 2H), 4.98 (dd, J = 17.1, 1.7 Hz, 2H), 4.92 (dd, J = 10.2, 1.9 Hz, 2H), 4.07-3.98 (m, 6H), 3.88 (d, J = 7.8 Hz, 6H), 2.06-1.99 (m, 4H), 1.87-1.79 (m, 5H), 1.47-1.42 (m, 4H), 1.39-

1.28 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.50, 152.82, 149.50, 148.99, 148.77, 139.26, 128.81, 123.77, 122.56, 121.29, 114.27, 112.78, 112.57, 112.36, 111.47, 69.16, 69.11, 66.75, 56.16, 33.90, 31.57, 29.81, 29.46, 29.25, 29.15, 29.08, 29.01, 26.00. FTIR (KBr), cm^{-1}: 1714 (C=O), 1640 (C=C), 1270 (C-O).



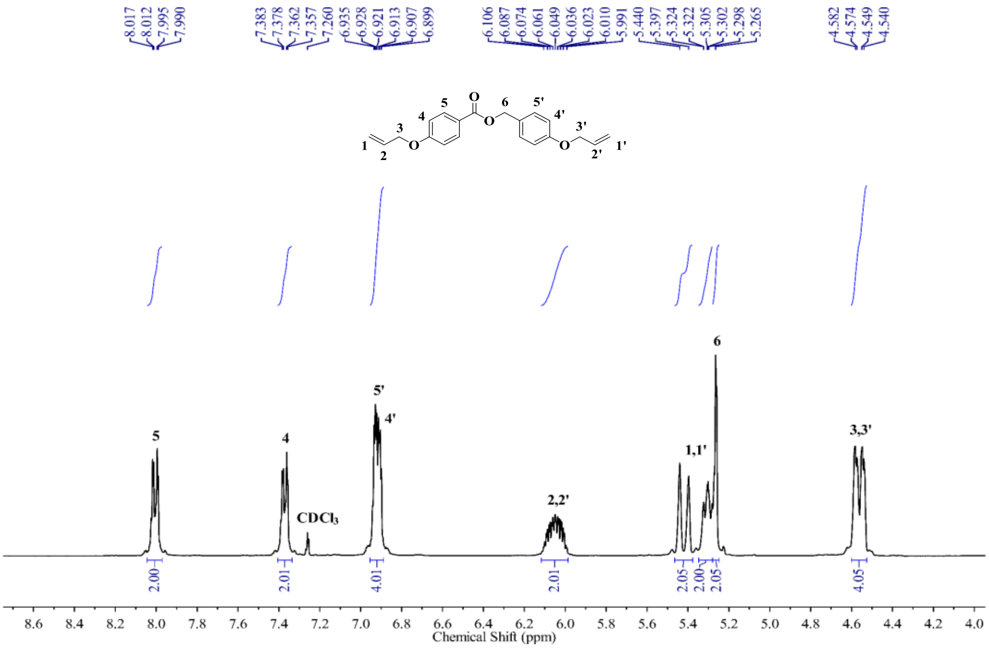


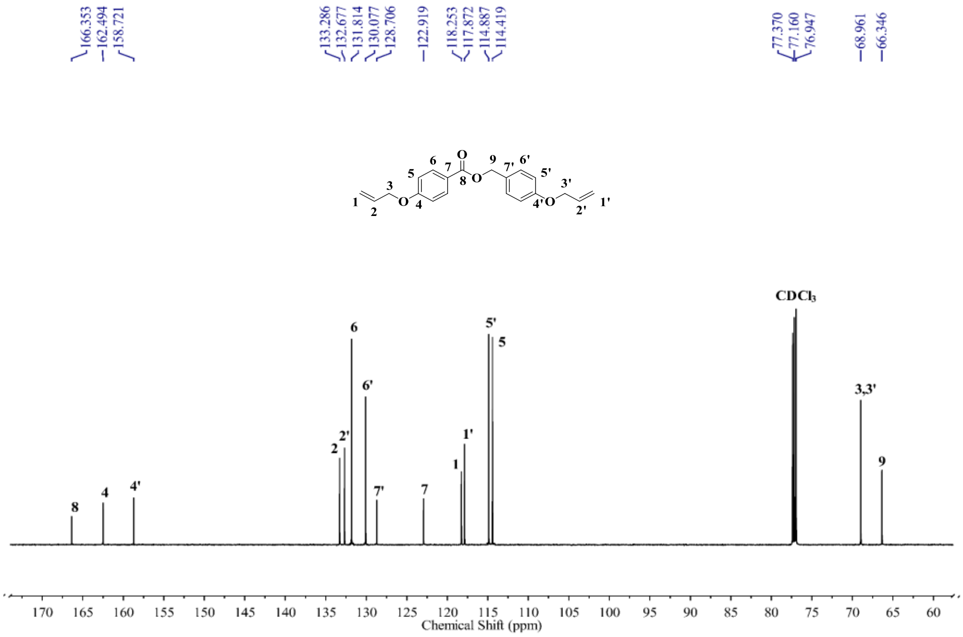
2.2.12. 4-(allyloxy)benzyl 4-(allyloxy)benzoate (3d)



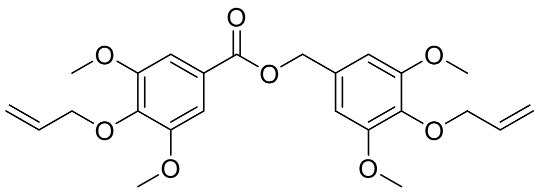
3d

Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (dd, J = 8.9, 2.2 Hz, 2H), 7.37 (dd, J = 8.6, 2.1 Hz, 2H), 6.95-6.89 (m, 4H), 6.12-5.99 (m, 2H), 5.42 (d, J = 17.3 Hz, 2H), 5.35-5.28 (m, 2H), 5.27 (s, 2H), 4.56 (dd, J = 13.4, 3.7 Hz, 4H). ^{13}C NMR (101 MHz, CDCl3) δ: 166.35, 162.49, 158.72, 133.29, 132.68, 131.81, 130.08, 128.71, 122.92, 118.25, 117.87, 114.89, 114.42, 68.96, 66.35. FTIR (KBr), cm^{-1}: 1711 (C=O), 1652 (C=C), 1249 (C-O).





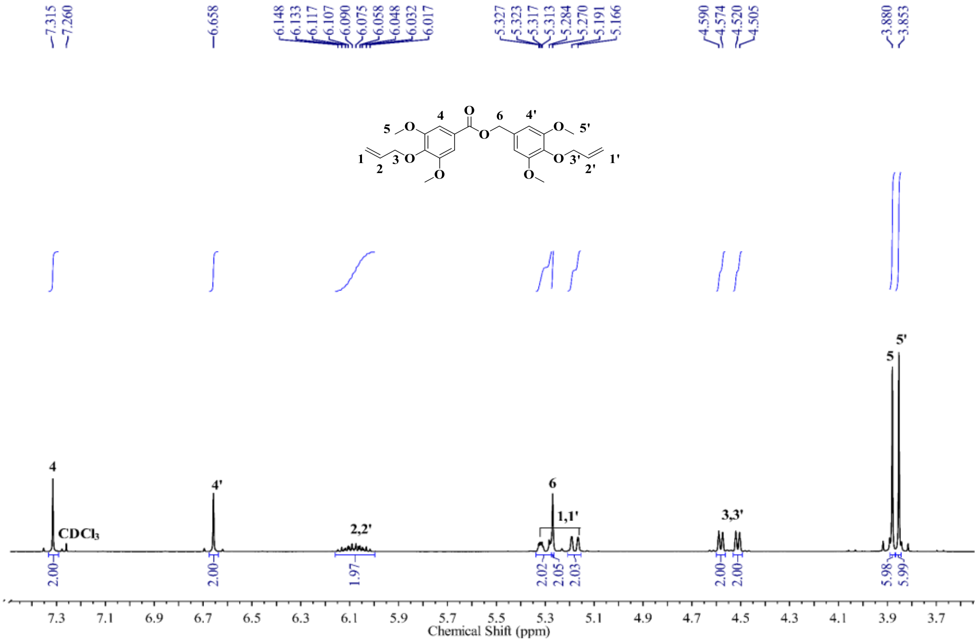
2.2.13. 4-(allyloxy)-3,5-dimethoxybenzyl 4-(allyloxy)-3,5-dimethoxybenzoate (3e)

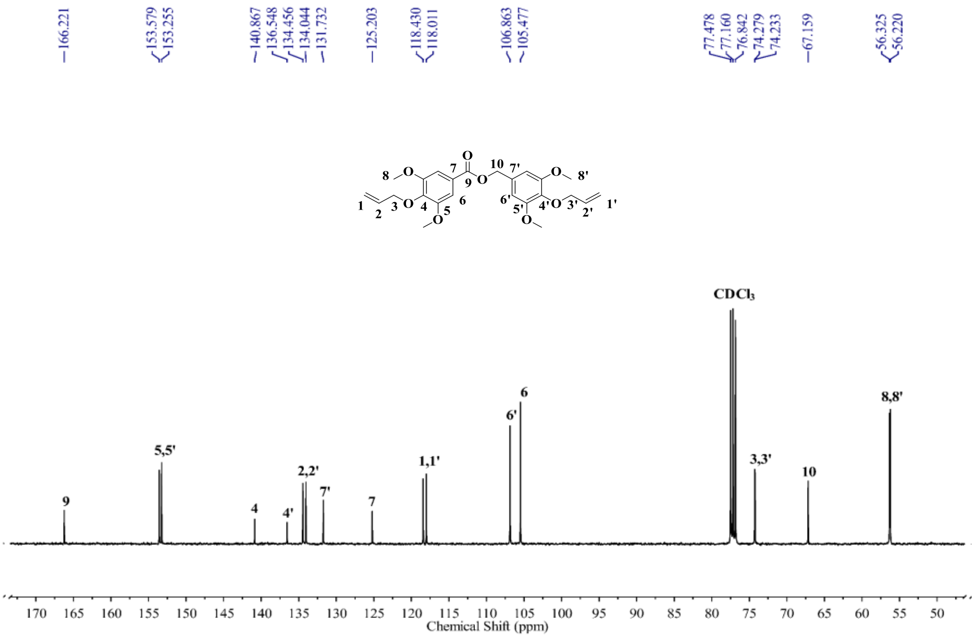


3e

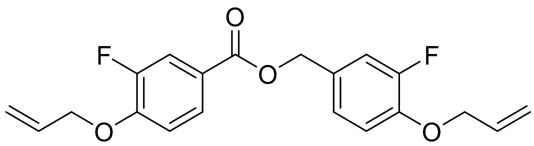
Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (s, 2H), 6.66 (s, 2H), 6.15-6.01 (m, 2H), 5.34-5.28 (m, 2H), 5.27 (s, 2H), 5.18 (d, J = 9.8 Hz, 2H), 4.58 (d, J

= 6.2 Hz, 2H), 4.51 (d, J = 6.1 Hz, 2H), 3.88 (s, 6H), 3.85 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.22, 153.58, 153.26, 140.87, 136.55, 134.46, 134.04, 131.73, 125.20, 118.43, 118.01, 106.86, 105.48, 74.28, 74.23, 67.16, 56.32, 56.22. FTIR (KBr), cm^{-1}: 1712 (C=O), 1649 (C=C), 1248 (C-O).



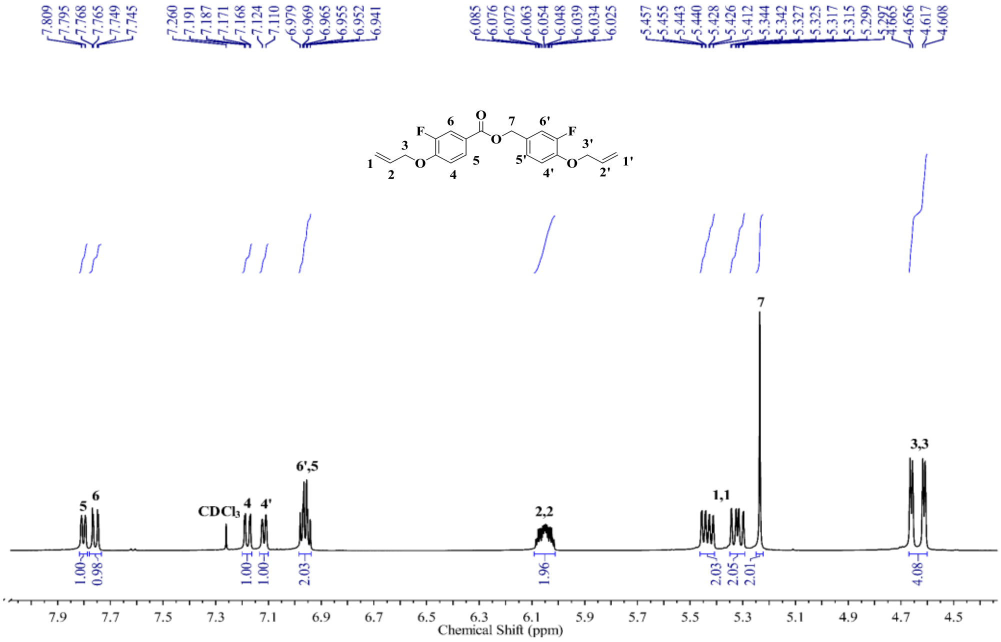


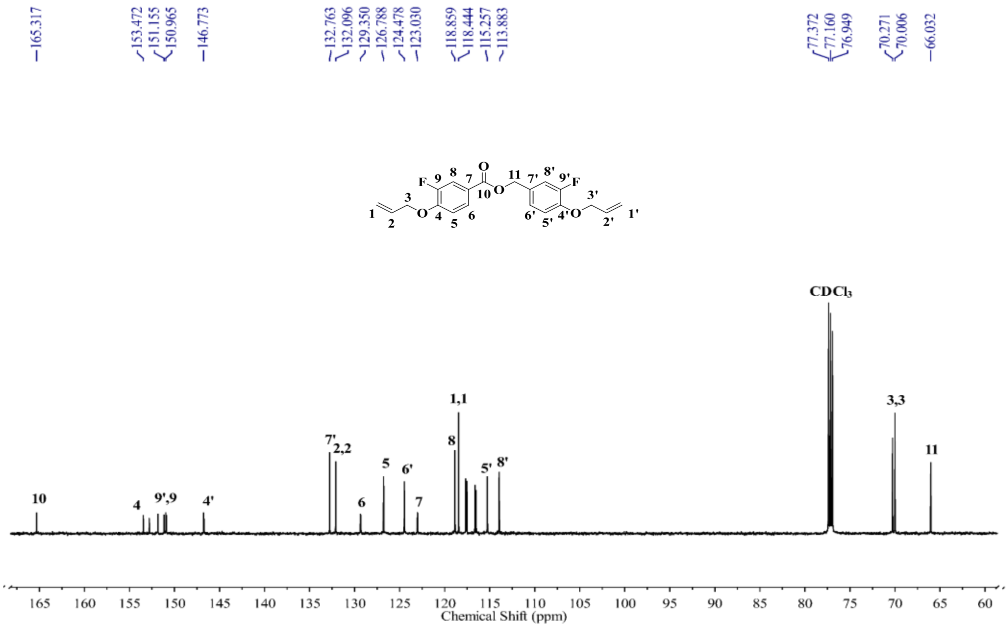
2.2.14. 4-(allyloxy)-3-fluorobenzyl 4-(allyloxy)-3-fluorobenzoate (3f)



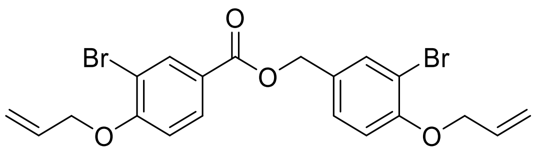
3f

Yield: 92%. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.80 (d, J = 8.6 Hz, 1H), 7.76 (dd, J = 11.6, 2.0 Hz, 1H), 7.18 (dd, J = 11.7, 2.0 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 6.98-6.94 (m, 2H), 6.09-6.01 (m, 2H), 5.43 (ddd, J = 17.3, 8.6, 1.4 Hz, 2H), 5.32 (ddd, J = 16.6, 10.5, 1.2 Hz, 2H), 5.24 (s, 2H), 4.64 (dd, J = 28.9, 5.3 Hz, 4H). [13]C NMR (151 MHz, $CDCl_3$) δ: 165.32, 153.47, 151.16, 150.97, 146.77, 132.76, 132.10, 129.35, 126.79, 124.48, 123.03, 118.86, 118.44, 115.26, 113.88, 70.27, 70.01, 66.03. FTIR (KBr), cm^{-1}: 1715 (C=O), 1648 (C=C), 1277 (C-O).





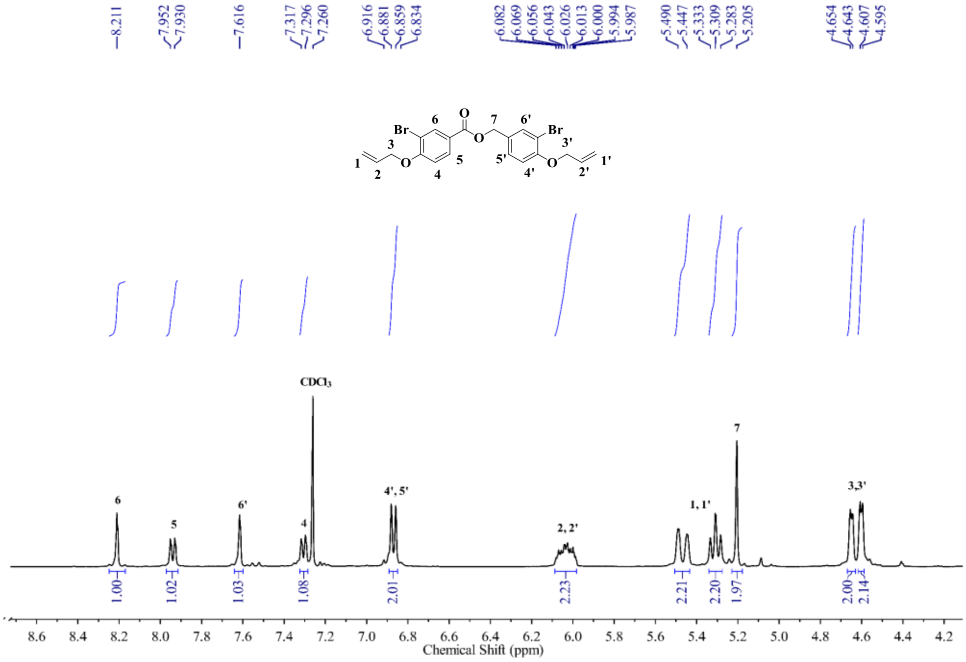
2.2.15. 4-(allyloxy)-3-bromobenzyl 4-(allyloxy)-3-bromobenzoate (3g)

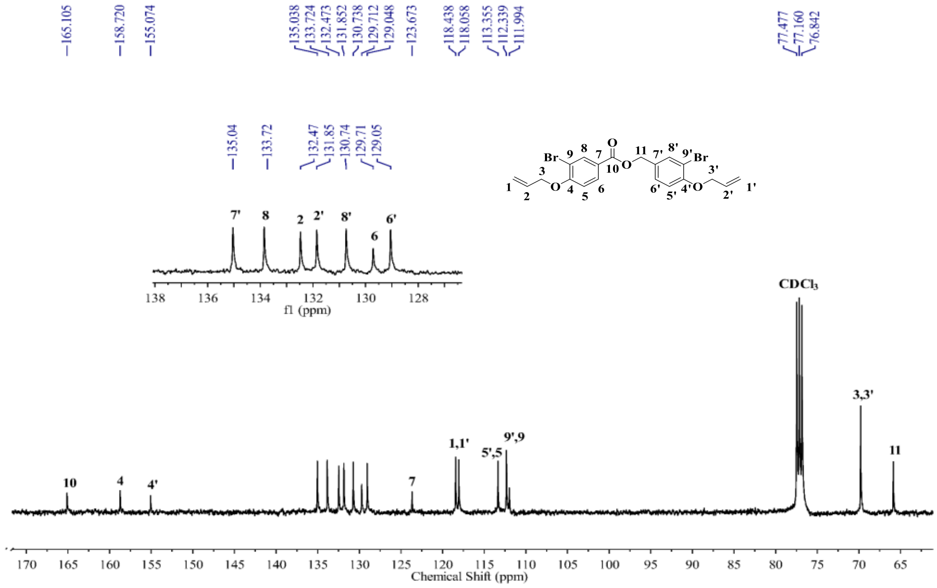


3g

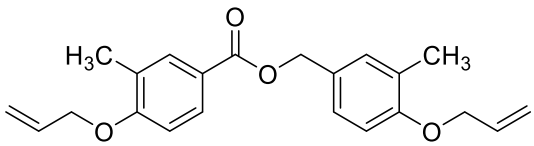
Yield: 94%. [1]H NMR (400 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.62 (s, 1H), 7.31 (d, J = 8.2 Hz, 1H), 6.87 (d, J = 8.6 Hz, 2H), 6.09-5.98 (m, 2H), 5.47 (d, J = 17.2 Hz, 2H), 5.31 (t, J = 10.0 Hz, 2H), 5.20 (s, 2H), 4.65 (d, J = 3.6 Hz, 2H), 4.60

(d, J = 3.6 Hz, 2H). [13]C NMR (101 MHz, $CDCl_3$) δ: 165.11, 158.72, 155.07, 135.04, 133.72, 132.47, 131.85, 130.74, 129.71, 129.05, 123.67, 118.44, 118.06, 113.36, 112.34, 111.99, 69.80, 65.87. FTIR (KBr), cm^{-1}: 1716 (C=O), 1648 (C=C), 1265 (C-O).





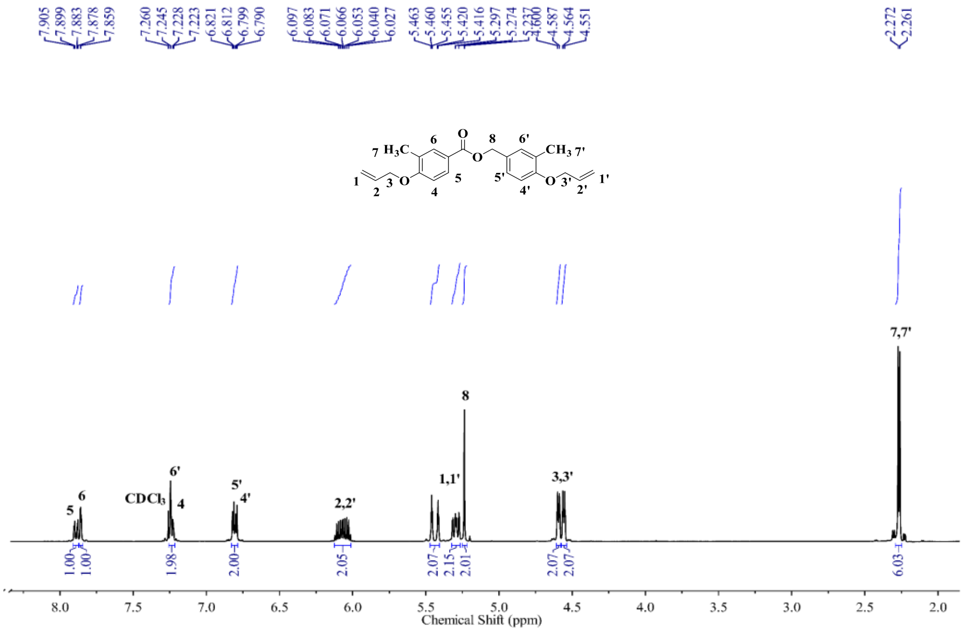
2.2.16. 4-(allyloxy)-3-methylbenzyl 4-(allyloxy)-3-methylbenzoate (3h)

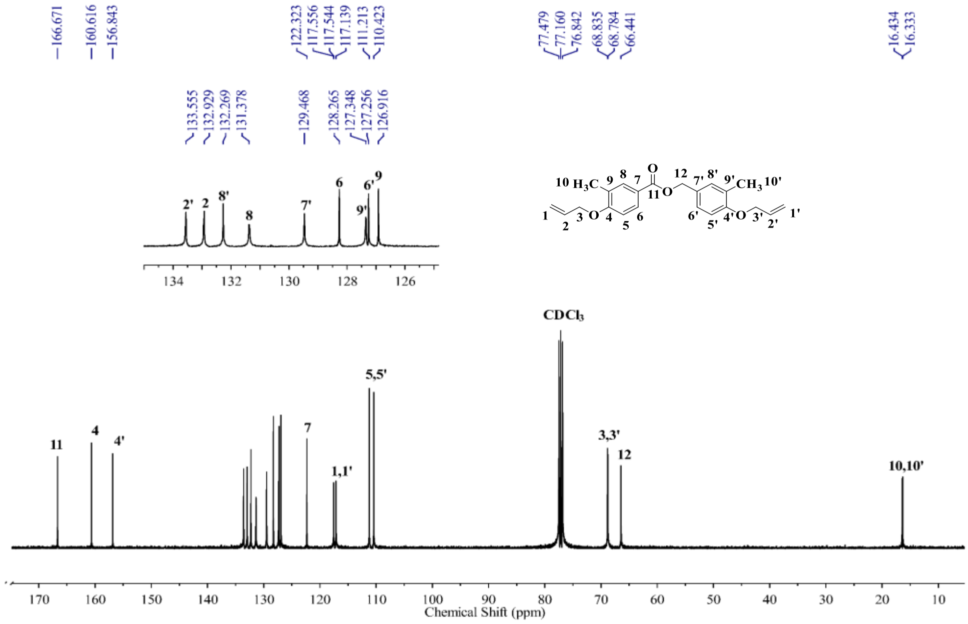


3h

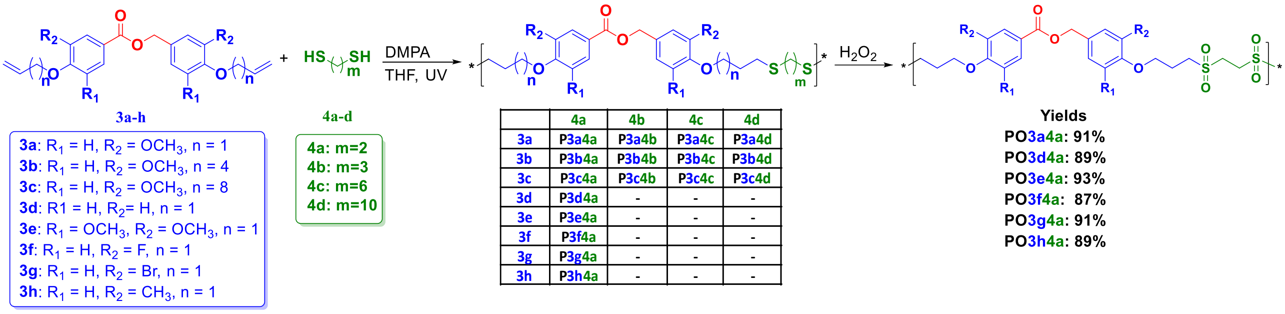
Yield: 84%. [1]H NMR (400 MHz, $CDCl_3$) δ: 7.89 (dd, J = 8.6, 2.2 Hz, 1H), 7.86 (s, 1H), 7.24-7.22 (m, 2H), 6.81 (dd, J = 8.8, 3.6 Hz, 2H), 6.12-6.01 (m, 2H), 5.44 (dt, J = 17.2, 1.5 Hz, 2H), 5.32-5.26 (m, 2H), 5.24 (s, 2H), 4.59 (d, J = 5.0 Hz, 2H), 4.56 (d, J =

5.0 Hz, 2H), 2.27 (d, J = 4.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.67, 160.62, 156.84, 122.32, 117.56, 117.54, 117.14, 111.21, 110.42, 68.83, 68.78, 66.44, 16.43, 16.33. FTIR (KBr), cm^{-1}: 1712 (C=O), 1649 (C=C), 1261 (C-O).





3. Thiol-ene polymerizations and post-polymerization oxidization



Scheme S3. Novel aromatic polyesters obtained via thiol-ene polymerization and poly(sulfone ether esters) obtained by oxidation.

General procedure for Thiol-ene polymerizations. α,ω-diene ester (3 mmol), dithiol (3 mmol) and DMPA (5 mol%, 0.15 mmol, 38. 83 mg) were added to a quartz reactor, then THF (10 ml) was added. The quartz reactor was placed under the UV light (365 nm) and irradiated for 4 h. After irradiation, the mixture was poured into cold methanol to precipitate. The resulting poly(thioether esters) were isolated by centrifuging, purified by three dissolving-precipitation cycles, and dried under vacuum at 50 ^{o}C for 24 h.

General procedure for post-oxidization. The oxidation reactions were carried out according to literature.[4] The poly(thioether ester) (1 mmol) was added to a 10 mL vial then 30% hydrogen peroxide (3 ml, 29.4 mmol) were added. The mixture was stirred for two days at room temperature. The resulting poly(thioether esters) were isolated by centrifuging, purified by three dissolving-precipitation cycles, and dried under vacuum at 50 ^{o}C for 24 h.

Poly(thioether esters) and poly(sulfone ether esters) were successfully synthesized as confirmed by ^{1}H and ^{13}C NMR spectra. As a representative example, Figure S3 displays the ^{1}H NMR spectrum of **P3a4a** revealing the disappearance of the terminal double bond and the formation of multiple peaks of methylene groups at 2.06-2.13 ppm and 2.73 ppm. After post-polymerization oxidization, new peaks corresponding to protons adjacent to sulfones appear and peaks belonging to the thioether vanished completely in the ^{1}H NMR spectrum of **PO3a4a**. In addition, The corresponding ^{13}C NMR spectrum comparison also successfully confirmed thiol-ene polymerization and post-polymerization oxidization (Figure S4).

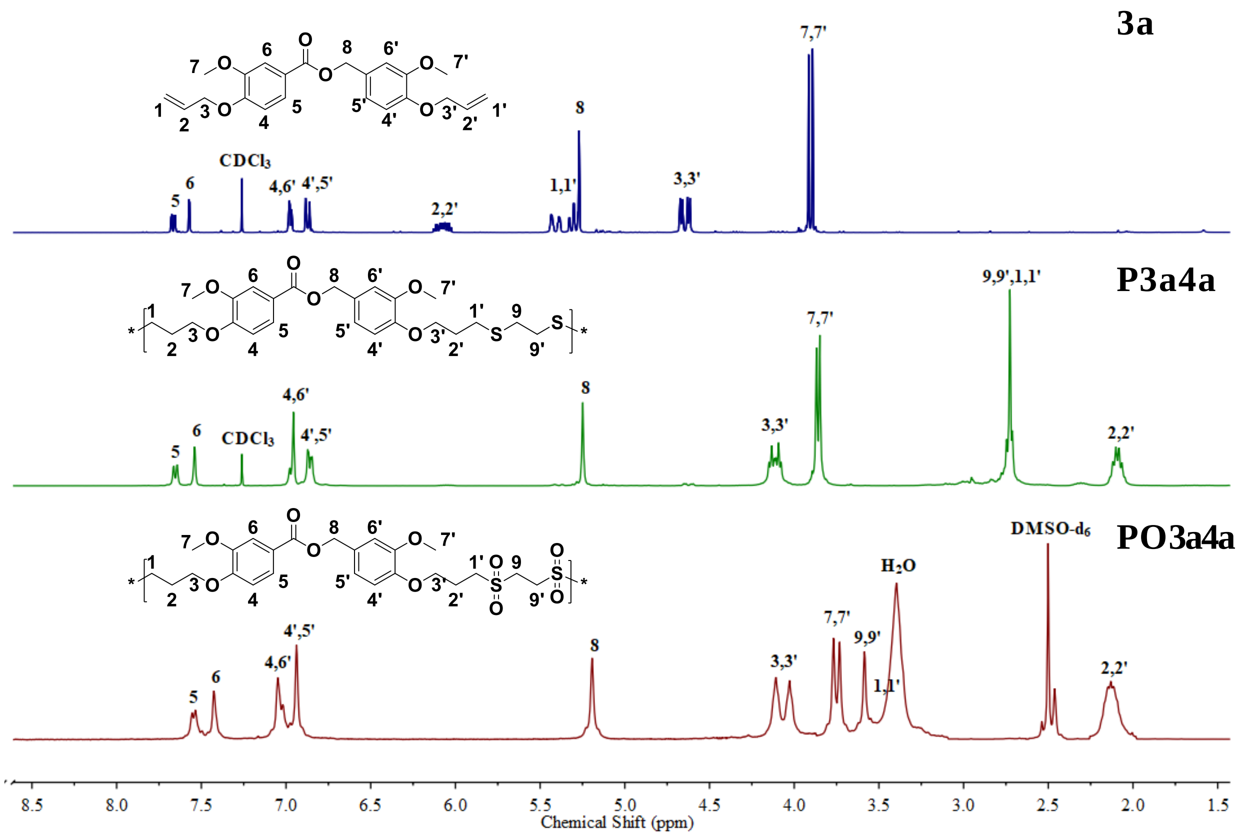


Figure S3. Comparative ^{1}H NMR spectra of **3a**, **P3a4a** and **PO3a4a**.

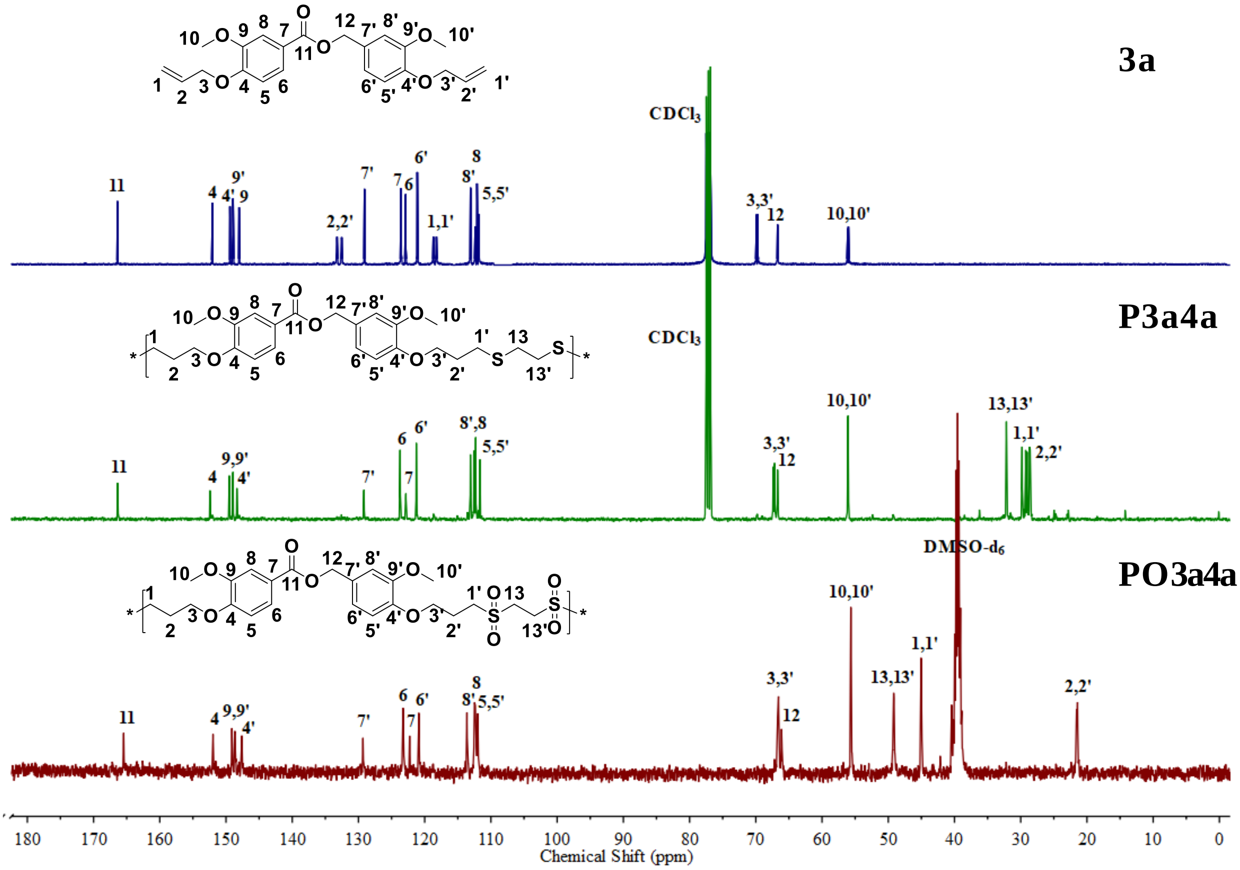
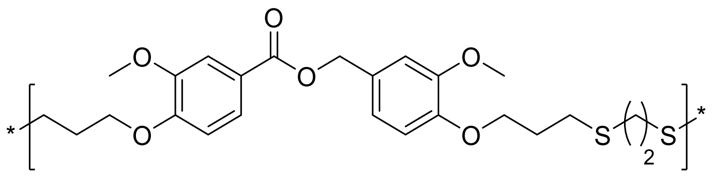


Figure S4. Comparative ^{13}C NMR spectra of **3a**, **P3a4a** and **PO3a4a**.

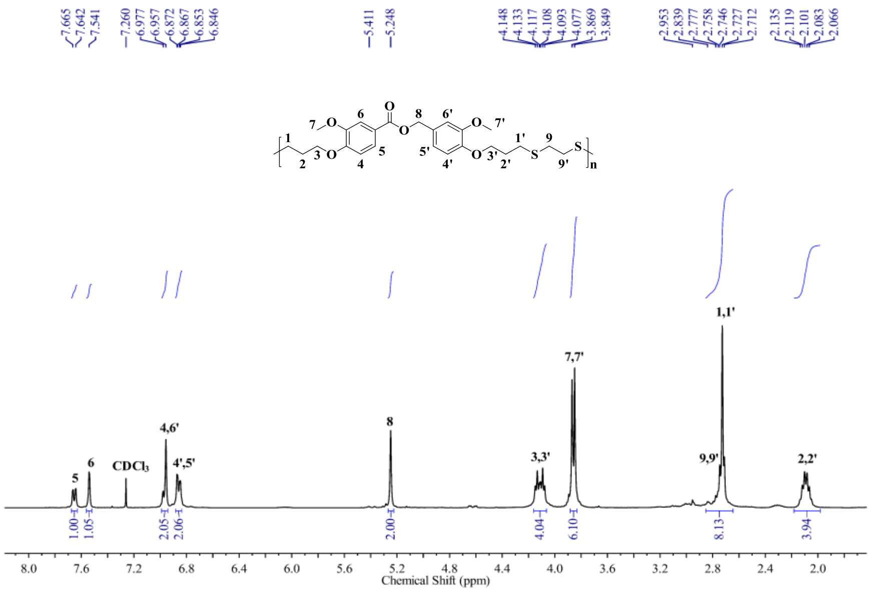
3.1. Representative ^{1}H NMR and ^{13}C NMR spectra for poly(thioether esters)

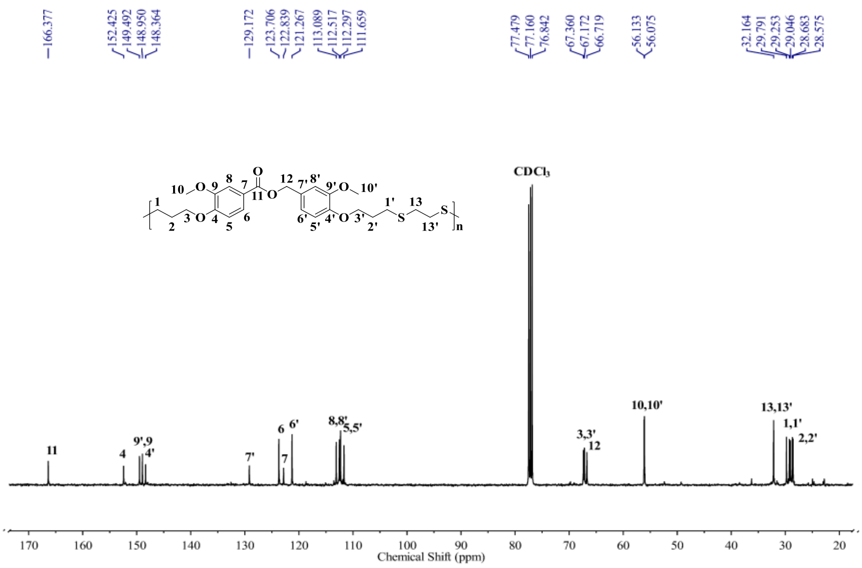
3.1.1. Poly(thioether ester) P3a4a derived from α,ω-diene ester (3a) and 1,2-ethanedithiol (4a)



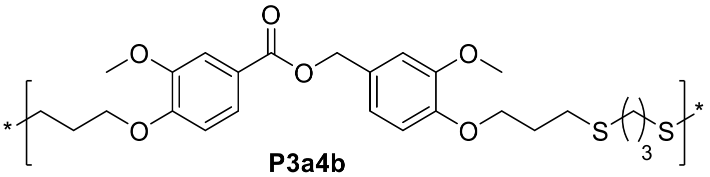
P3a4a

Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, J = 9.4 Hz, 1H), 7.54 (s, 1H), 6.97 (d, J = 8.3 Hz, 2H), 6.86 (dd, J = 8.1, 2.4 Hz, 2H), 5.25 (s, 2H), 4.11 (dt, J = 15.8, 6.1 Hz, 4H), 3.86 (d, J = 7.8 Hz, 6H), 2.85 -2.64 (m, 8H), 2.18-1.98 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.38, 152.43, 149.49, 148.95, 148.36, 129.17, 123.71, 122.84, 121.27, 113.09, 112.52, 112.30, 111.66, 67.36, 67.17, 66.72, 56.13, 56.08, 32.16, 29.79, 29.25, 29.05, 28.68, 28.58.



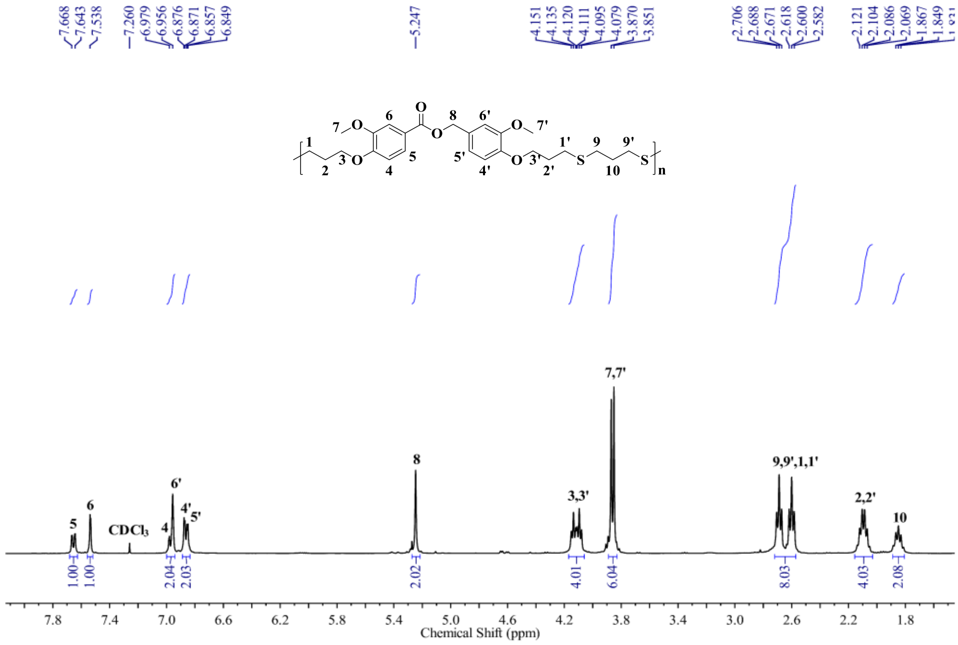


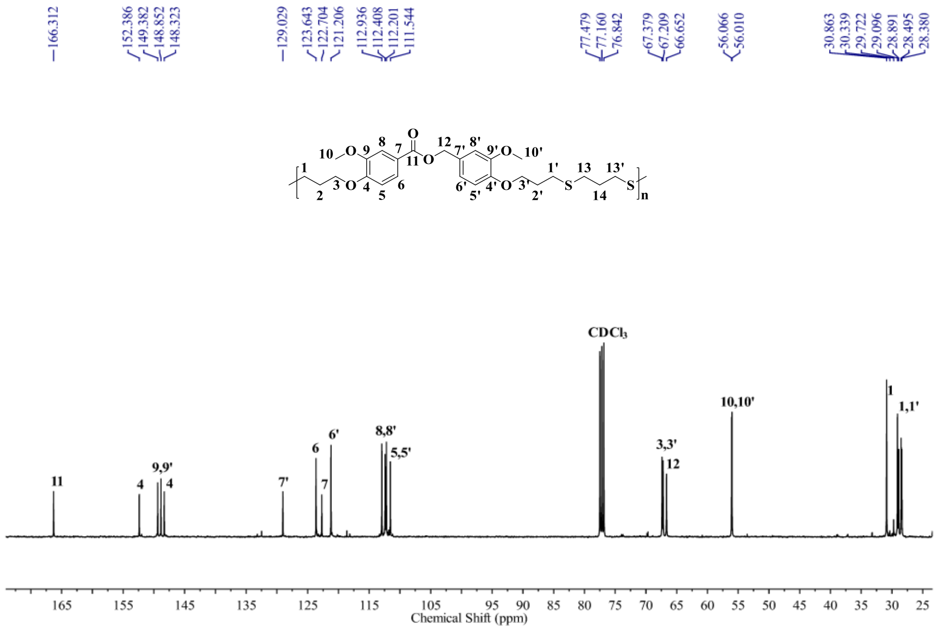
3.1.2. Poly(thioether ester) P3a4b derived from α,ω-diene ester (3a) and 1,3-propanedithiol (4b)



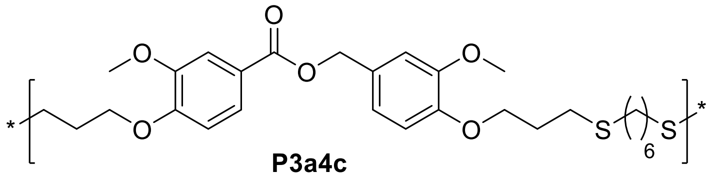
P3a4b

Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, J = 10.0 Hz, 1H), 7.54 (s, 1H), 6.97 (d, J = 9.3 Hz, 2H), 6.86 (dd, J = 8.2, 2.6 Hz, 2H), 5.25 (s, 2H), 4.12 (dt, J = 16.0, 6.1 Hz, 4H), 3.86 (d, J = 7.7 Hz, 6H), 2.64 (dt, J = 35.5, 7.1 Hz, 8H), 2.13-2.05 (m, 4H), 1.89-1.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.31, 152.39, 149.38, 148.85, 148.32, 129.03, 123.64, 122.70, 121.21, 112.94, 112.41, 112.20, 111.54, 67.38, 67.21, 66.65, 56.07, 56.01, 30.86, 30.34, 29.72, 29.10, 28.89, 28.50, 28.38.



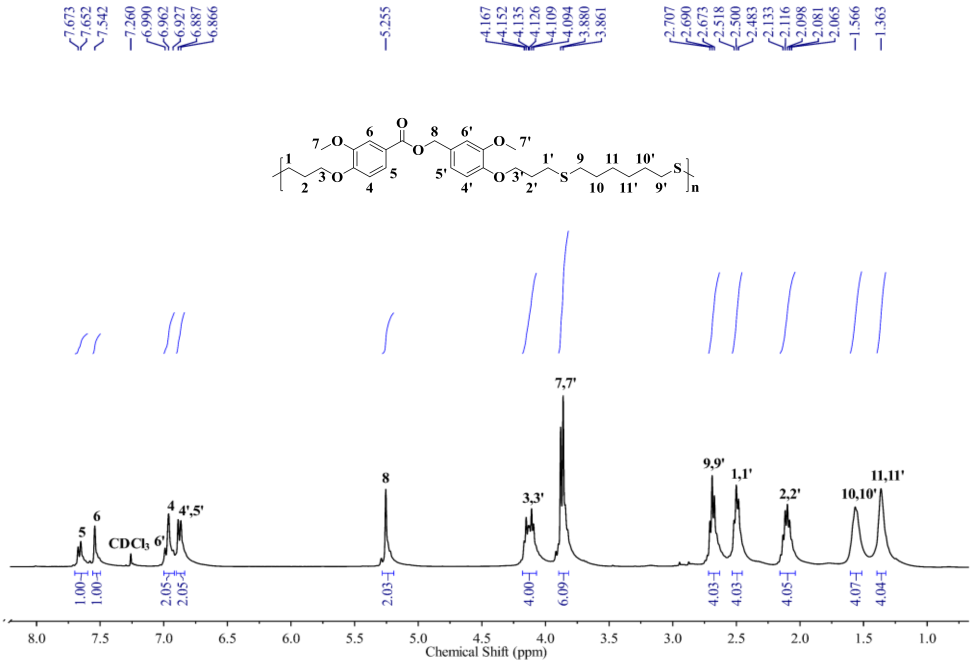


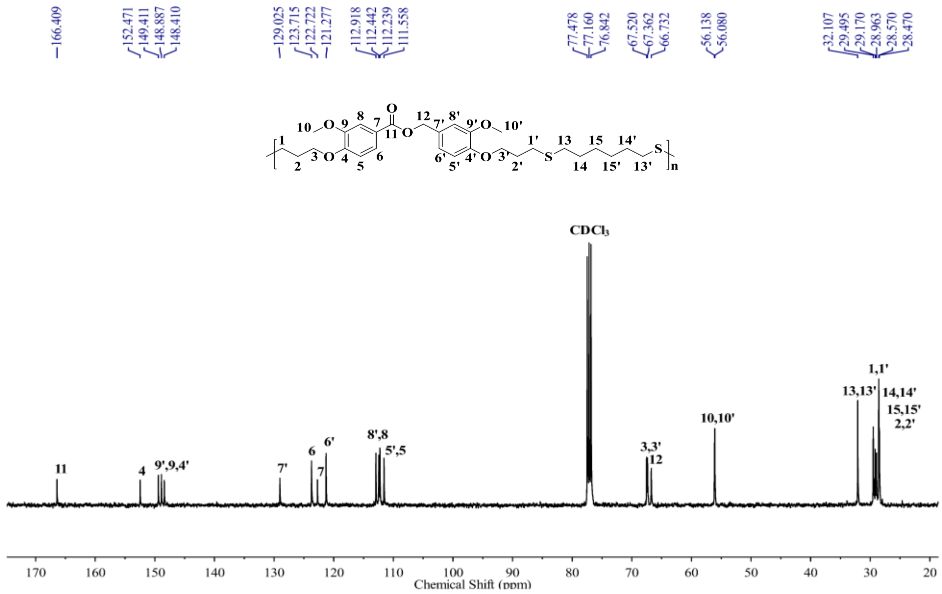
3.1.3. Poly(thioether ester) P3a4c derived from α,ω-diene ester (3a) and 1,6-hexanedithiol (4c)



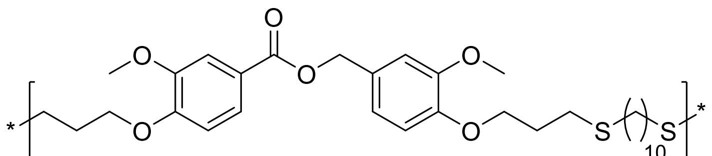
P3a4c

Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, J = 8.3 Hz, 1H), 7.54 (s, 1H), 7.00-6.92 (m, 2H), 6.88 (d, J = 8.3 Hz, 2H), 5.25 (s, 2H), 4.13 (dt, J = 12.8, 6.1 Hz, 4H), 3.87 (d, J = 7.7 Hz, 6H), 2.69 (t, J = 7.0 Hz, 4H), 2.53-2.45 (m, 4H), 2.14-2.06 (m, 4H), 1.57 (s, 4H), 1.36 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.41, 152.47, 149.41, 148.89, 148.41, 129.03, 123.72, 122.72, 121.28, 112.92, 112.44, 112.24, 111.56, 67.52, 67.36, 66.73, 56.14, 56.08, 32.11, 29.49, 29.17, 28.96, 28.57, 28.47.



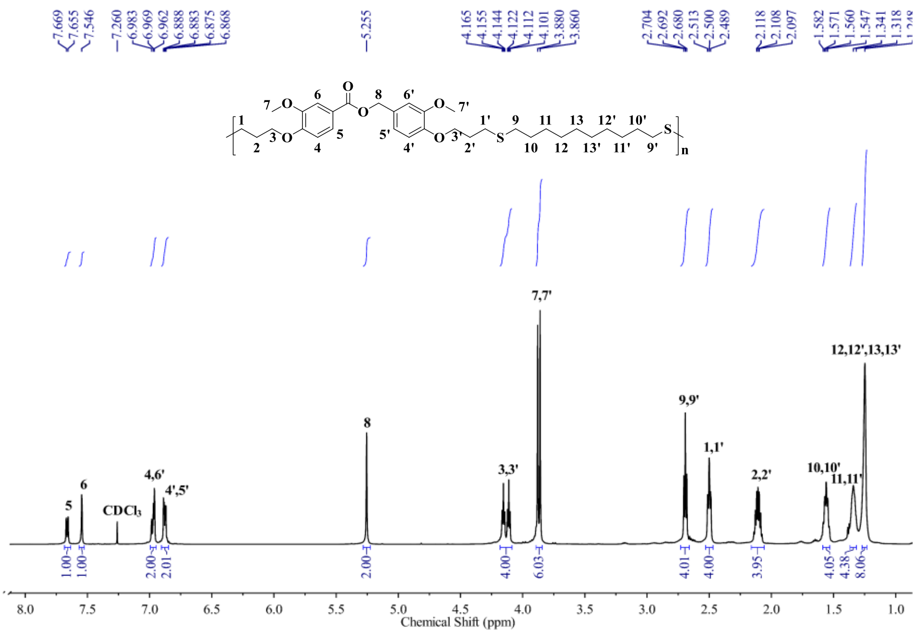


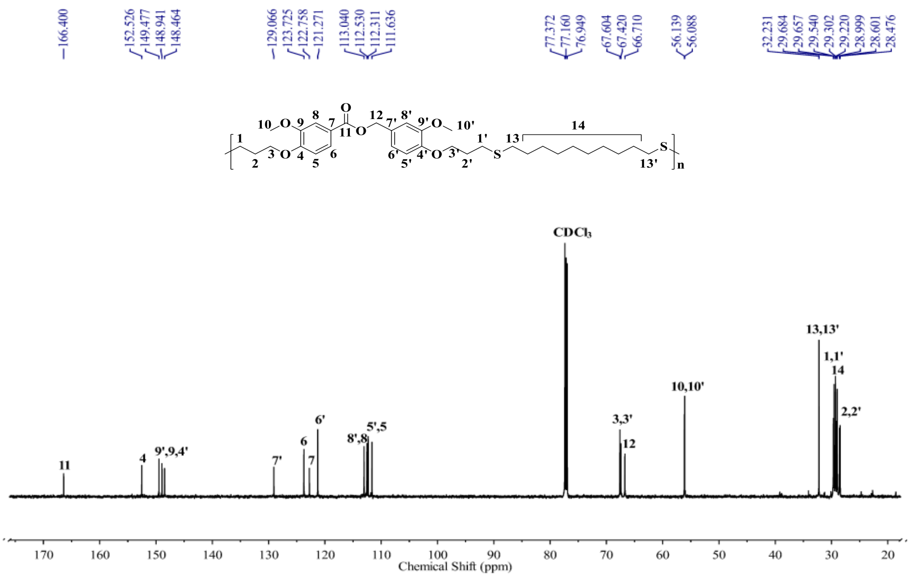
3.1.4. Poly(thioether ester) P3a4d derived from α,ω-diene ester (3a) and 1,10-decanedithiol (4d)



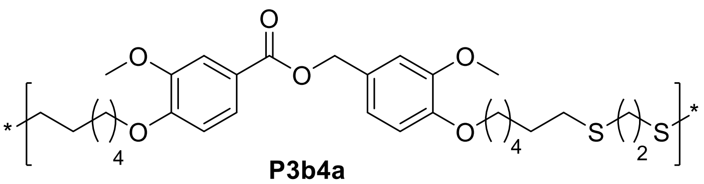
P3a4d

Yield: 93%. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.66 (d, J = 8.5 Hz, 1H), 7.55 (s, 1H), 6.99-6.95 (m, 2H), 6.88 (dd, J = 8.3, 3.5 Hz, 2H), 5.25 (s, 2H), 4.13 (dt, J = 25.9, 6.3 Hz, 4H), 3.87 (d, J = 11.8 Hz, 6H), 2.69 (t, J = 7.1 Hz, 4H), 2.50 (t, J = 7.4 Hz, 4H), 2.11 (dt, J = 13.1, 6.6 Hz, 4H), 1.59-1.53 (m, 4H), 1.39-1.33 (m, 4H), 1.25 (s, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 166.40, 152.53, 149.48, 148.94, 148.46, 129.07, 123.72, 122.76, 121.27, 113.04, 112.53, 112.31, 111.64, 67.60, 67.42, 66.71, 56.14, 56.09, 32.23, 29.68, 29.66, 29.54, 29.30, 29.22, 29.00, 28.60, 28.48.



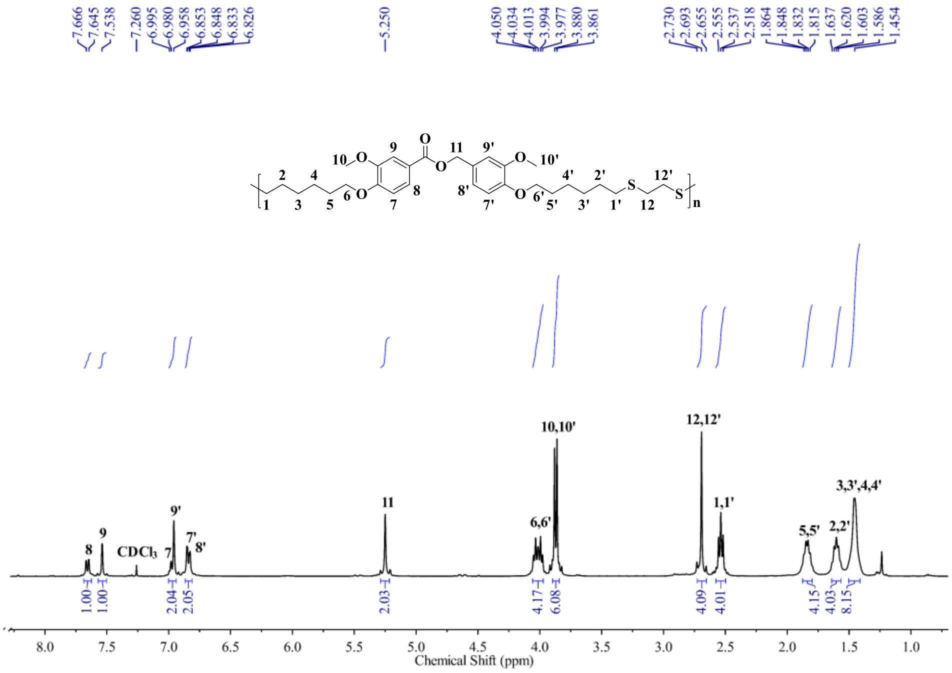


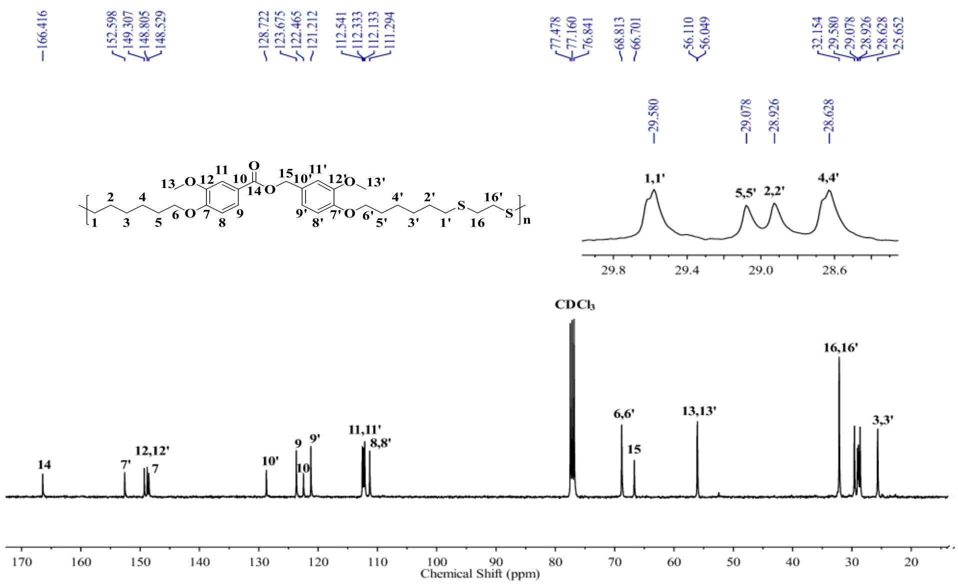
3.1.5. Poly(thioether ester) P3b4a derived from α,ω-diene ester (3b) and 1,2-ethanedithiol (4a)



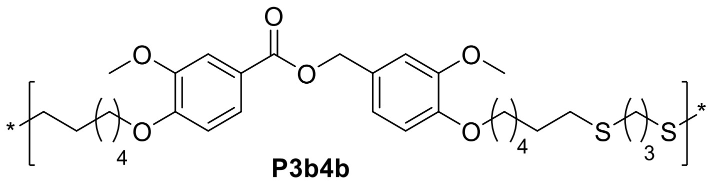
P3b4a

Yield: 88%. [1]H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, J = 8.4 Hz, 1H), 7.54 (s, 1H), 7.00-6.94 (m, 2H), 6.84 (dd, J = 8.3, 2.3 Hz, 2H), 5.25 (s, 2H), 4.06-3.97 (m, 4H), 3.87 (d, J = 7.8 Hz, 6H), 2.74-2.65 (m, 4H), 2.54 (t, J = 7.3 Hz, 4H), 1.87-1.80 (m, 4H), 1.64-1.58 (m, 4H), 1.45 (s, 8H). [13]C NMR (101 MHz, $CDCl_3$) δ: 166.42, 152.60, 149.31, 148.81, 148.53, 128.72, 123.68, 122.46, 121.21, 112.54, 112.33, 112.13, 111.29, 77.48, 77.16, 76.84, 68.81, 66.70, 56.11, 56.05, 32.15, 29.58, 29.08, 28.93, 28.63, 25.65.



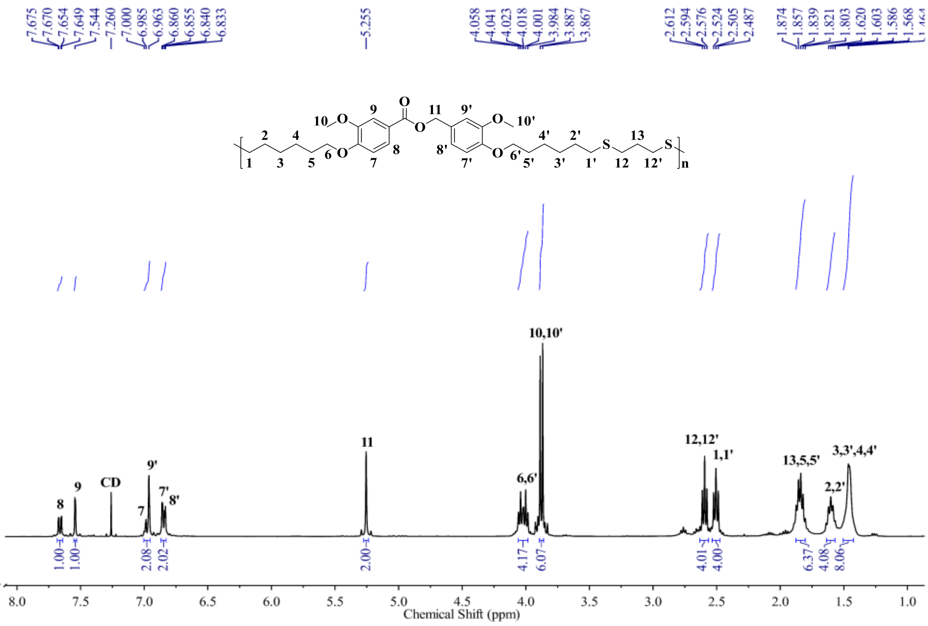


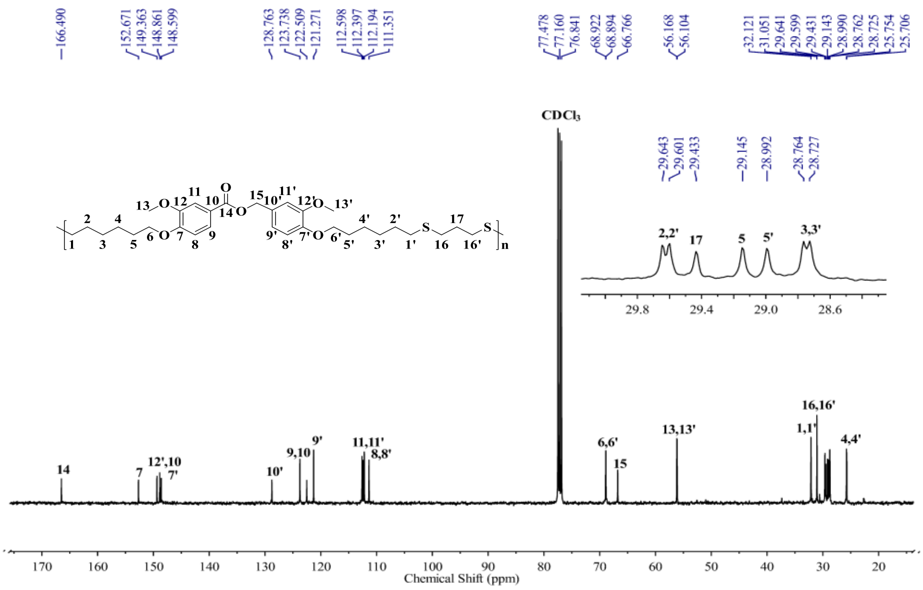
3.1.6. Poly(thioether ester) P3b4b derived from α,ω-diene ester (3b) and 1,3-propanedithiol (4b)



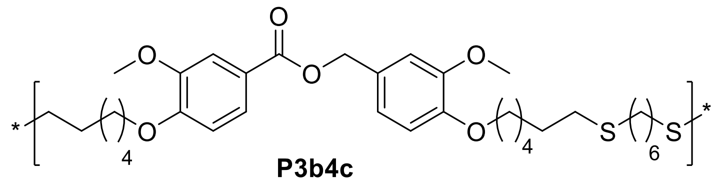
P3b4b

Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (dd, J = 8.5, 1.8 Hz, 1H), 7.54 (d, J = 1.7 Hz, 1H), 7.00-6.95 (m, 2H), 6.85 (dd, J = 8.3, 2.6 Hz, 2H), 5.26 (s, 2H), 4.02 (dt, J = 15.8, 6.7 Hz, 4H), 3.88 (d, J = 7.9 Hz, 6H), 2.59 (t, J = 7.2 Hz, 4H), 2.51 (t, J = 7.3 Hz, 4H), 1.88-1.80 (m, 6H), 1.64-1.56 (m, 4H), 1.46 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.49, 152.67, 149.36, 148.86, 148.60, 128.76, 123.74, 122.51, 121.27, 112.60, 112.40, 112.19, 111.35, 68.92, 68.89, 66.77, 56.17, 56.10, 32.12, 31.05, 29.64, 29.60, 29.43, 29.14, 28.99, 28.76, 28.73, 25.75, 25.71.



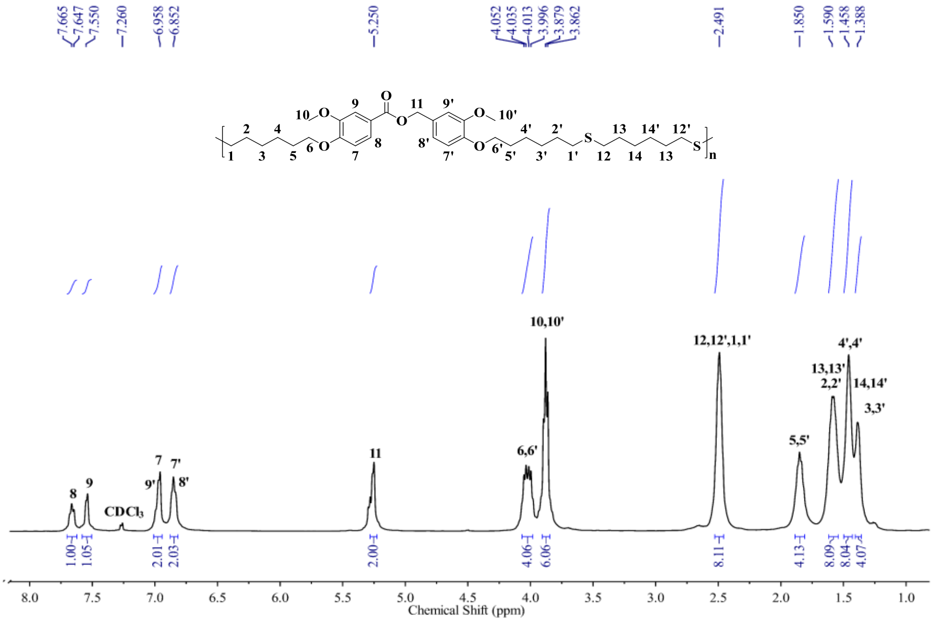


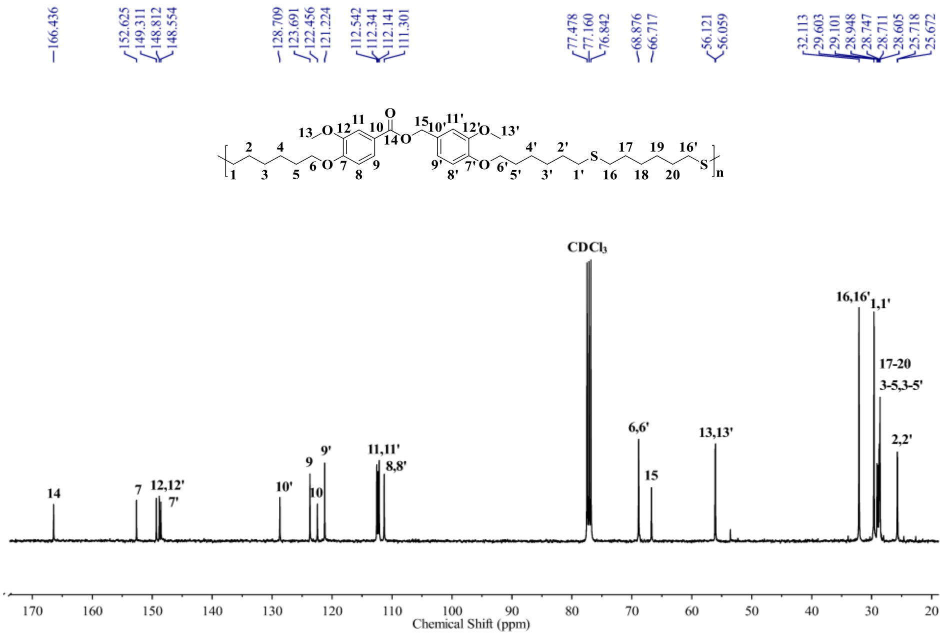
3.1.7. Poly(thioether ester) P3b4c derived from α,ω-diene ester (3b) and 1,6-hexanedithiol (4c)



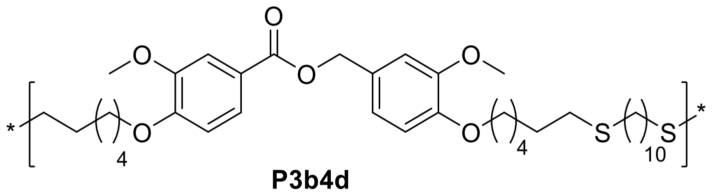
P3b4c

Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, J = 7.2 Hz, 1H), 7.55 (s, 1H), 6.96 (s, 2H), 6.85 (s, 2H), 5.25 (s, 2H), 4.02 (dd, J = 15.5, 6.7 Hz, 4H), 3.87 (d, J = 6.9 Hz, 6H), 2.49 (s, 8H), 1.85 (s, 4H), 1.59 (s, 8H), 1.46 (s, 8H), 1.39 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.44, 152.62, 149.31, 148.81, 148.55, 128.71, 123.69, 122.46, 121.22, 112.54, 112.34, 112.14, 111.30, 68.88, 66.72, 56.12, 56.06, 32.11, 29.60, 29.10, 28.95, 28.75, 28.71, 28.60, 25.72, 25.67.

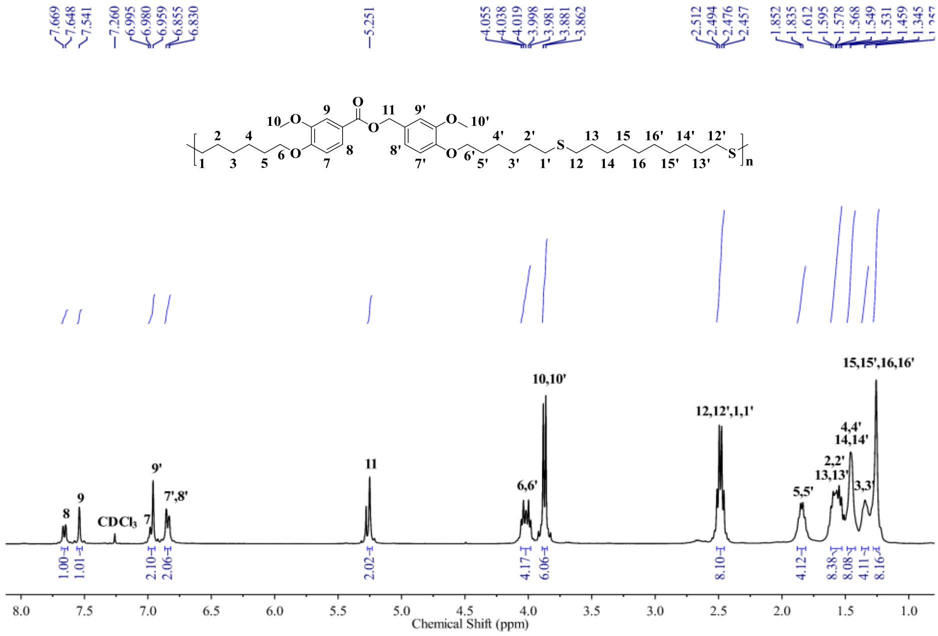


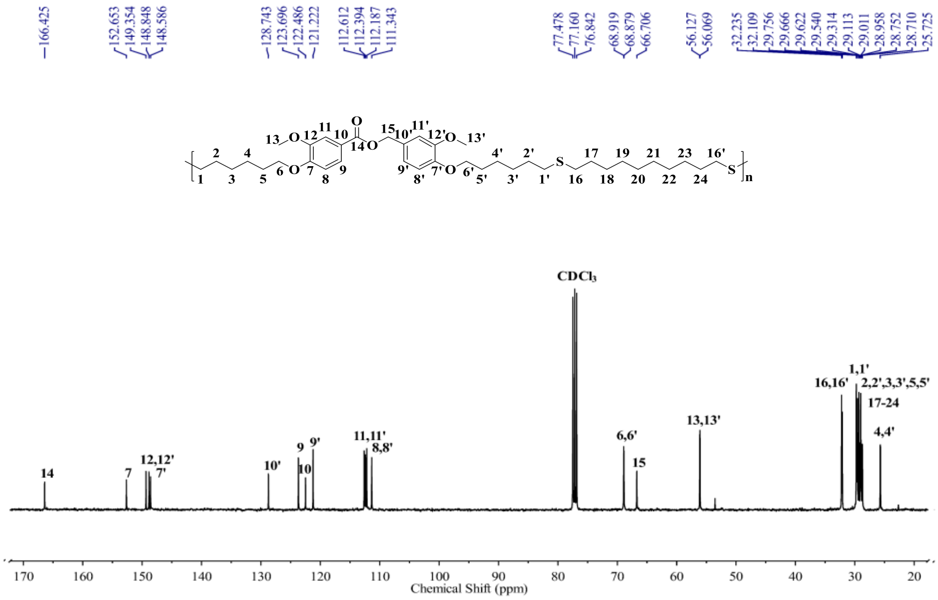


3.1.8. Poly(thioether ester) P3b4d derived from α,ω-diene ester (3b) and 1,10-decanedithiol (4d)

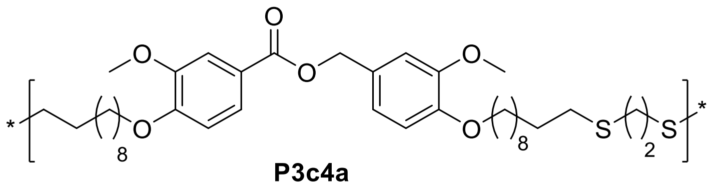


Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, J = 8.3 Hz, 1H), 7.54 (s, 1H), 7.00-6.94 (m, 2H), 6.84 (d, J = 10.1 Hz, 2H), 5.25 (s, 2H), 4.06-3.97 (m, 4H), 3.87 (d, J = 7.8 Hz, 6H), 2.53-2.44 (m, 8H), 1.88-1.81 (m, 4H), 1.61-1.53 (m, 8H), 1.46 (s, 8H), 1.34 (s, 4H), 1.26 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.42, 152.65, 149.35, 148.85, 148.59, 128.74, 123.70, 122.49, 121.22, 112.61, 112.39, 112.19, 111.34, 68.92, 68.88, 66.71, 56.13, 56.07, 32.23, 32.11, 29.76, 29.67, 29.62, 29.54, 29.31, 29.11, 29.01, 28.96, 28.75, 28.71, 25.73, 25.67.



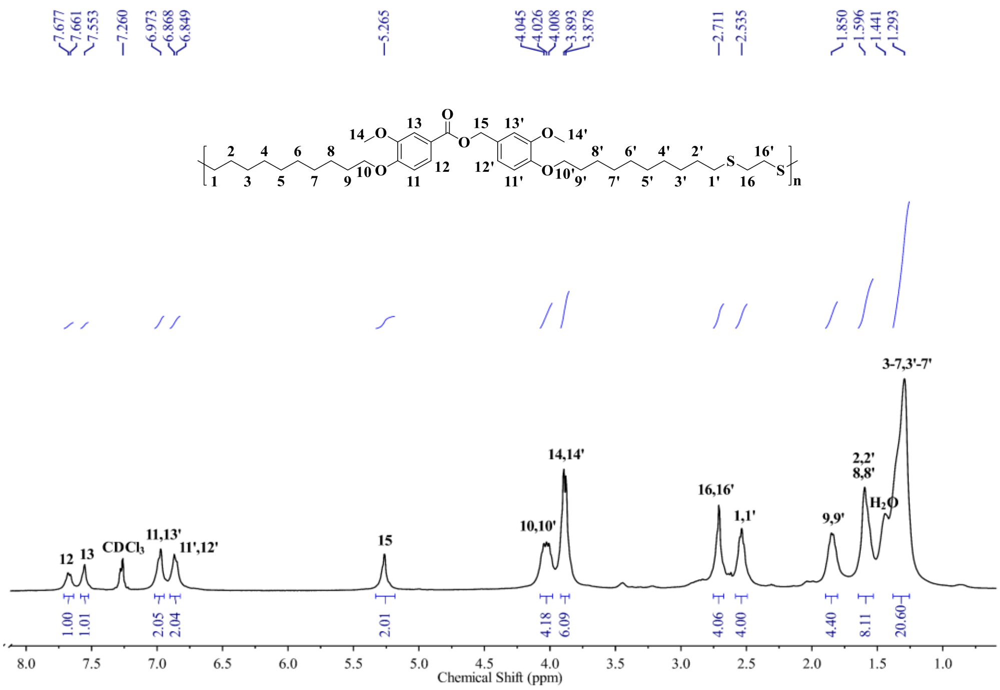


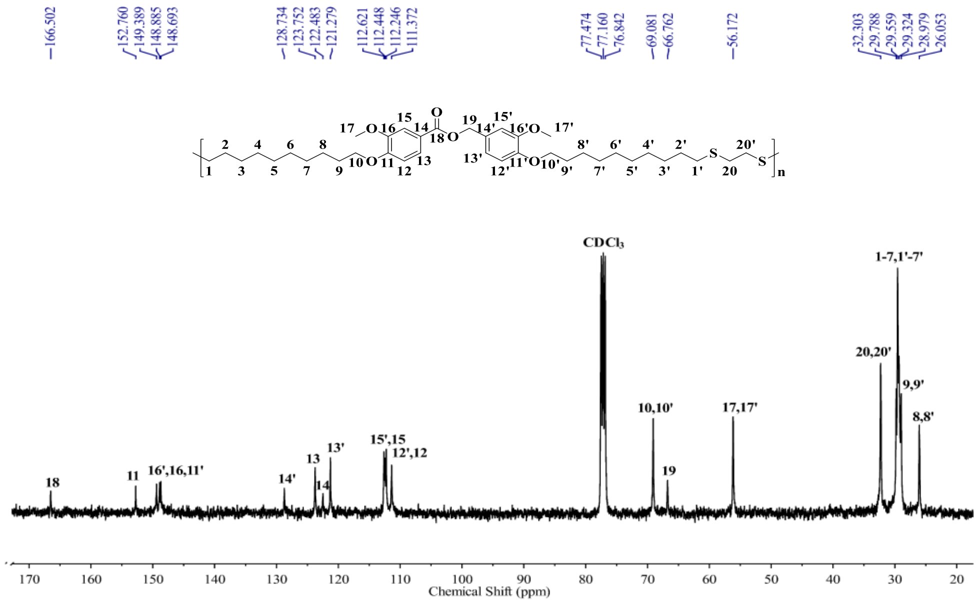
3.1.9. Poly(thioether ester) P3c4a derived from α,ω-diene ester (3c) and 1,2-ethanedithiol (4a)



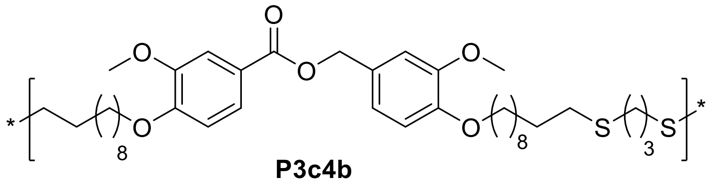
P3c4a

Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, J = 6.6 Hz, 1H), 7.55 (s, 1H), 6.97 (s, 2H), 6.86 (d, J = 7.8 Hz, 2H), 5.26 (s, 2H), 4.07-3.98 (m, 4H), 3.89 (d, J = 5.9 Hz, 6H), 2.71 (s, 4H), 2.53 (s, 4H), 1.85 (s, 4H), 1.60 (s, 8H), 1.29 (s, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.50, 152.76, 149.39, 148.89, 148.69, 128.73, 123.75, 122.48, 121.28, 112.62, 112.45, 112.25, 111.37, 69.08, 66.76, 56.17, 32.30, 29.79, 29.56, 29.32, 28.98, 26.05.

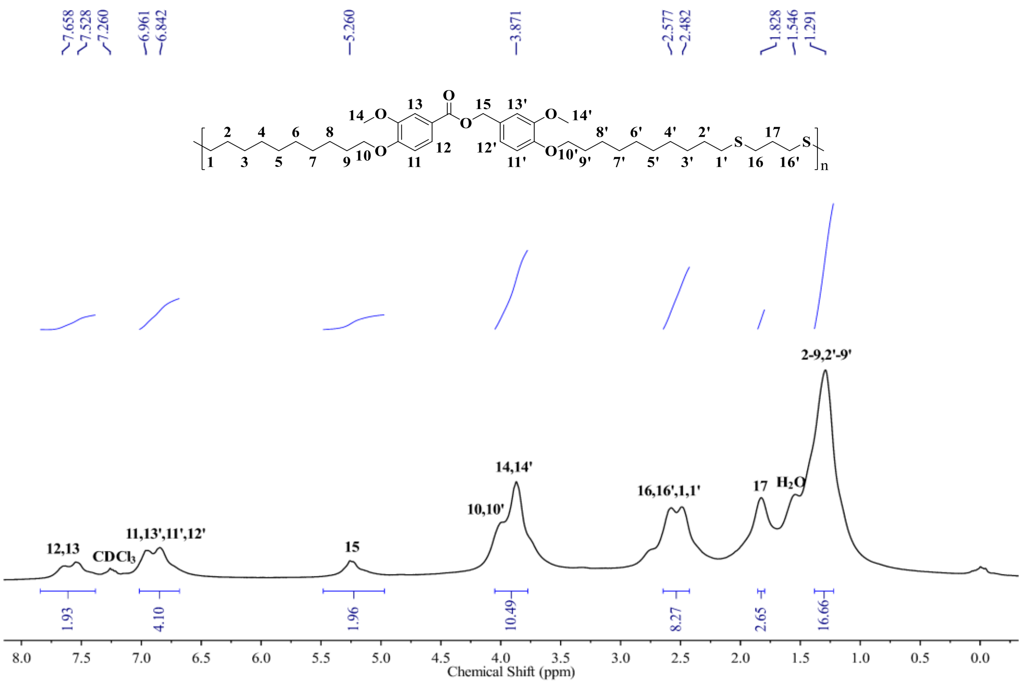


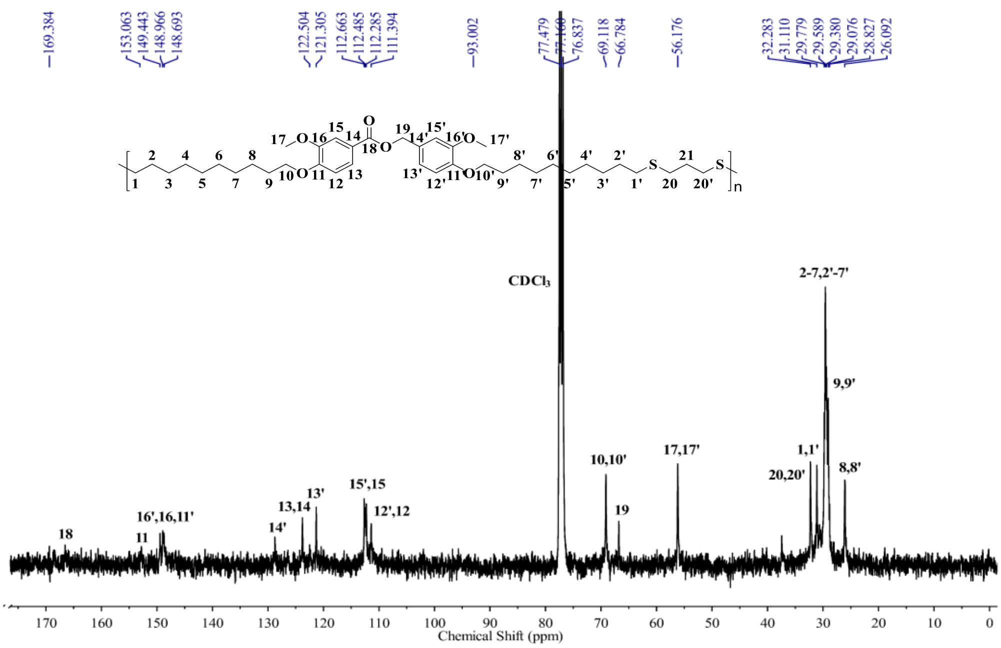


3.1.10. Poly(thioether ester) P3c4a derived from α,ω-diene ester (3c) and 1,3-propanedithiol (4b)

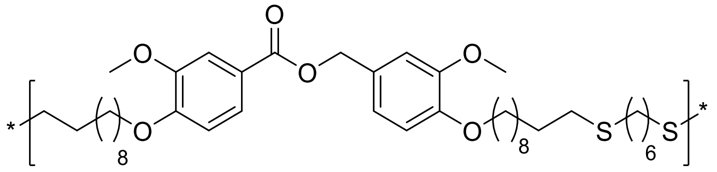


Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, J = 51.9 Hz, 2H), 6.90 (d, J = 47.4 Hz, 4H), 5.26 (s, 2H), 3.87 (s, 10H), 2.53 (d, J = 38.0 Hz, 8H), 1.83 (s, 3H), 1.29 (s, 17H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.38, 153.06, 149.44, 148.97, 148.69, 122.50, 121.31, 112.66, 112.49, 112.29, 111.39, 93.00, 69.12, 66.78, 56.18, 32.28, 31.11, 29.78, 29.59, 29.38, 29.08, 28.83, 26.09.



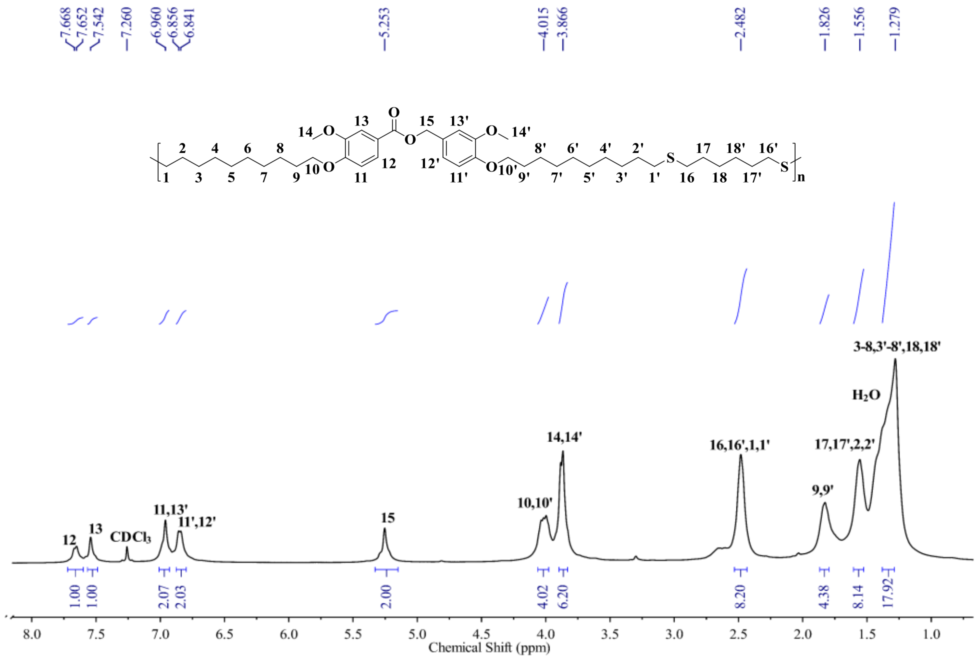


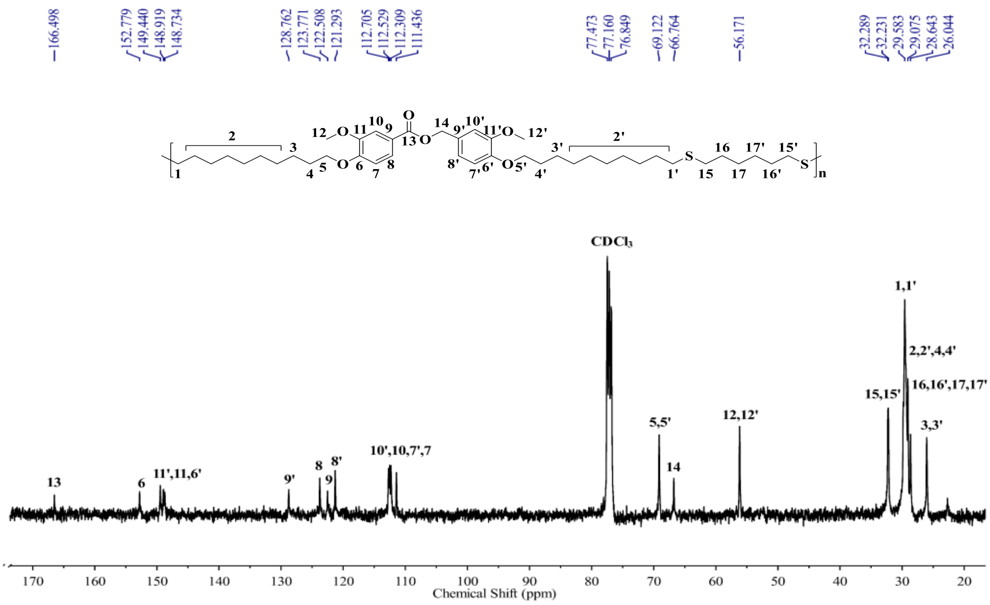
3.1.11. Poly(thioether ester) P3c4c derived from α,ω-diene ester (3c) and 1,6-hexanedithiol (4c)



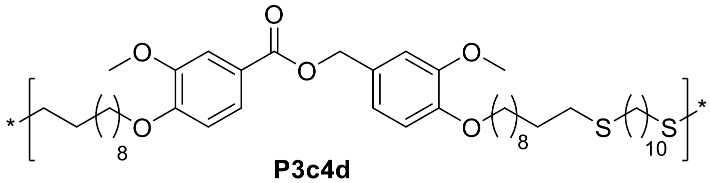
P3c4c

Yield: 90%. [1]H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, J = 6.4 Hz, 1H), 7.54 (s, 1H), 6.96 (s, 2H), 6.85 (d, J = 6.1 Hz, 2H), 5.25 (s, 2H), 4.02 (s, 4H), 3.87 (s, 6H), 2.48 (s, 8H), 1.83 (s, 4H), 1.56 (s, 8H), 1.29 (s, 16H). [13]C NMR (101 MHz, $CDCl_3$) δ: 166.50, 152.78, 149.44, 148.92, 148.73, 128.76, 123.77, 122.51, 121.29, 112.70, 112.53, 112.31, 111.44, 69.12, 66.76, 56.17, 32.29, 32.23, 29.58, 29.08, 28.64, 26.04.



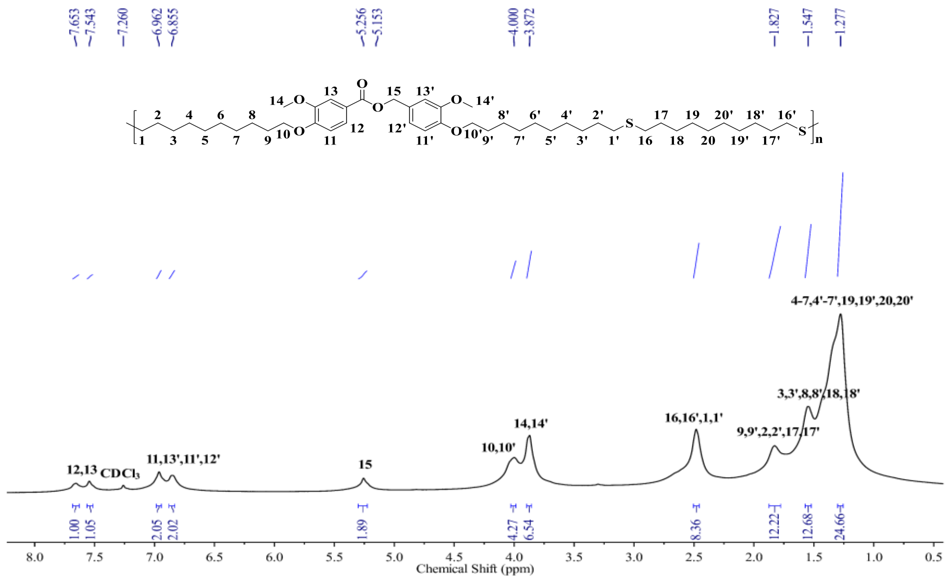


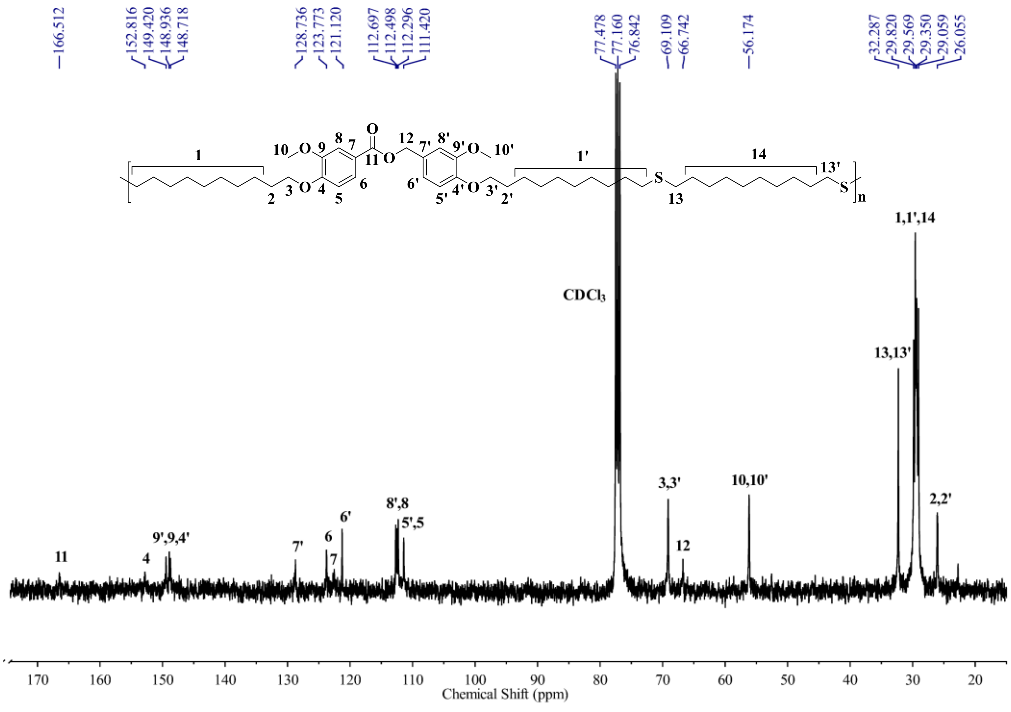
3.1.12. Poly(thioether ester) P3c4d derived from α,ω-diene ester (3c) and 1,10-decanedithiol (4d)



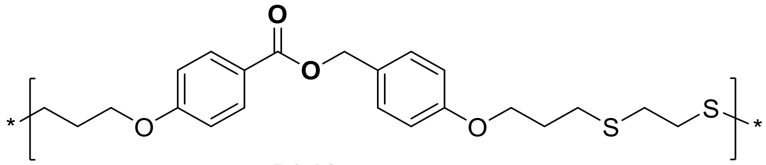
P3c4d

Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (s, 1H), 7.54 (s, 1H), 6.96 (s, 2H), 6.86 (s, 2H), 5.26 (s, 2H), 4.00 (s, 4H), 3.87 (s, 6H), 2.48 (s, 8H), 1.83 (s, 12H), 1.55 (s, 12H), 1.28 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.51, 152.82, 149.42, 148.94, 148.72, 128.74, 123.77, 121.12, 112.70, 112.50, 112.30, 111.42, 69.11, 66.74, 56.17, 32.29, 29.82, 29.57, 29.35, 29.06, 26.06.



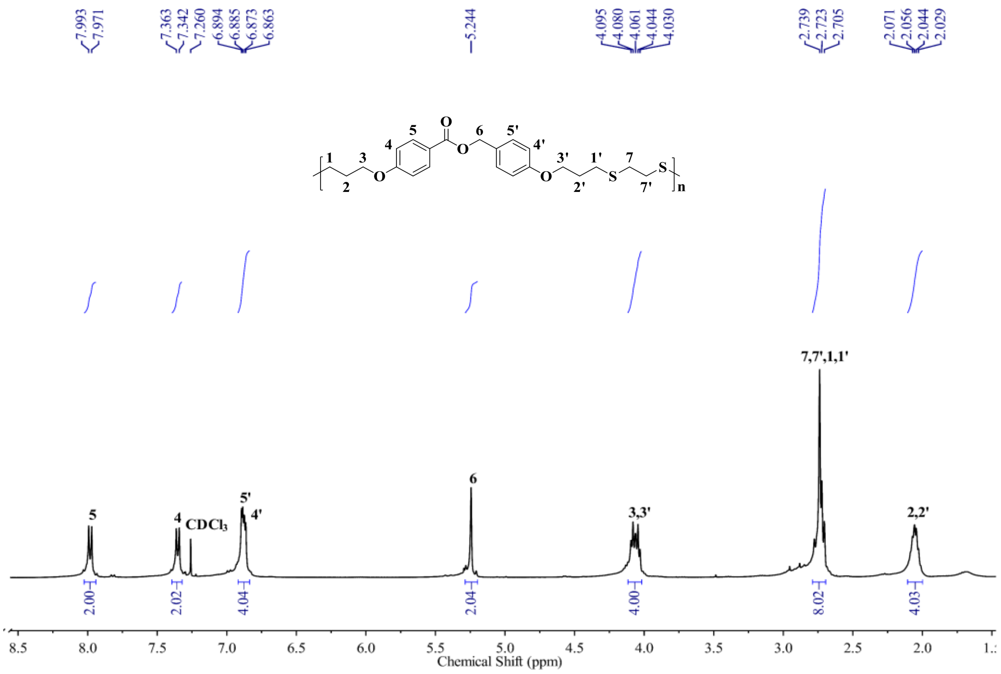


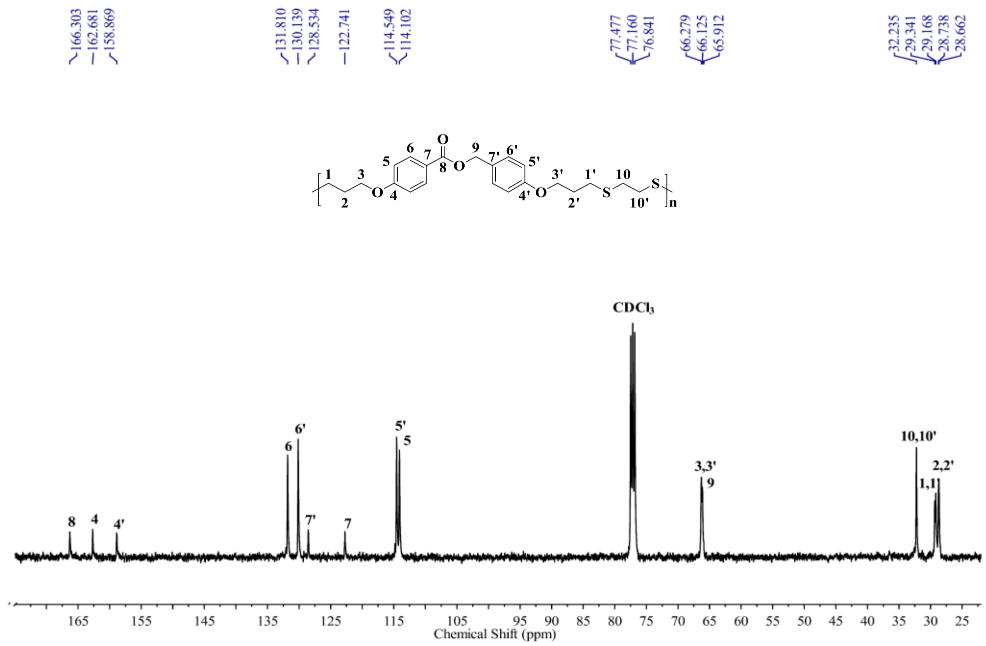
3.1.13. Poly(thioether ester) P3d4a derived from α,ω-diene ester (3d) and 1,2-ethanedithiol (4a)



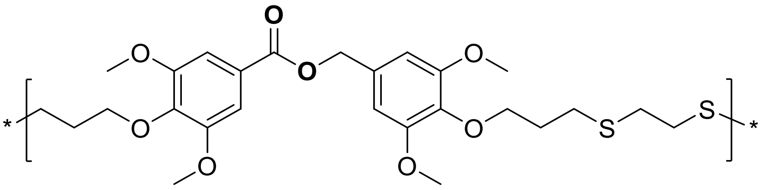
P3d4a

Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.90-6.86 (m, 2H), 5.24 (s, 2H), 4.12-4.02 (m, 4H), 2.79-2.69 (m, 8H), 2.09-2.01 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.30, 162.68, 158.87, 131.81, 130.14, 128.53, 122.74, 114.55, 114.10, 66.28, 66.12, 65.91, 32.24, 29.34, 29.17, 28.74, 28.66.



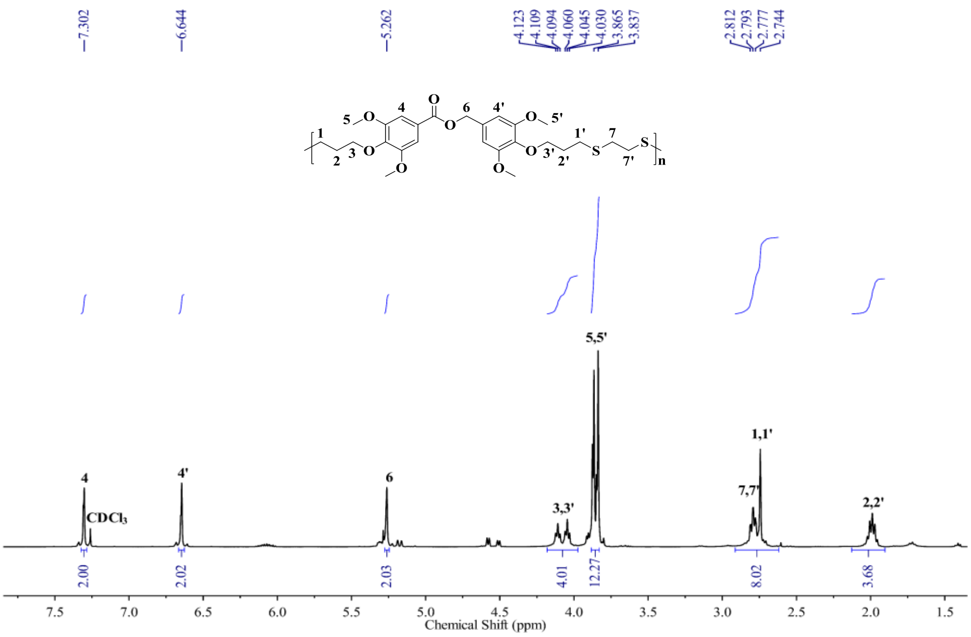


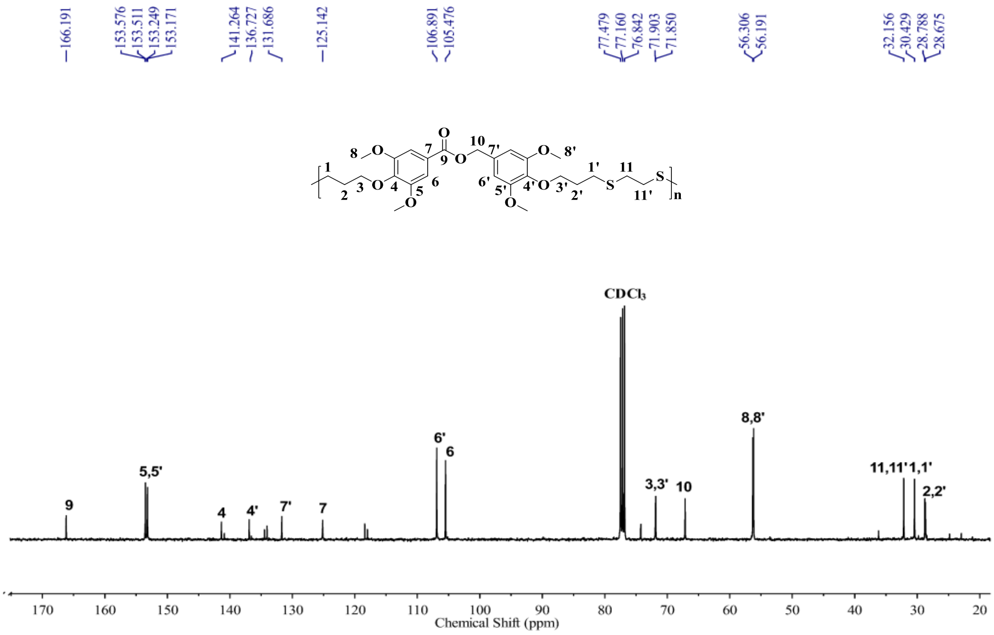
3.1.14. Poly(thioether ester) P3e4a derived from α,ω-diene ester (3e) and 1,2-ethanedithiol (4a)



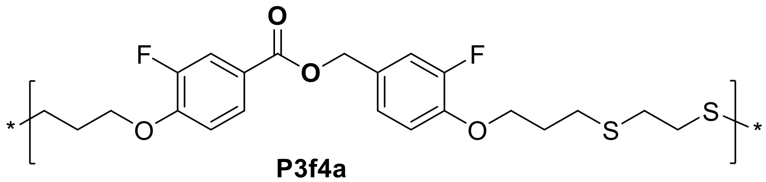
P3e4a

Yield: 89%. [1]H NMR (400 MHz, $CDCl_3$) δ: 7.30 (s, 2H), 6.64 (s, 2H), 5.26 (s, 2H), 4.08 (dt, J = 11.9, 5.7 Hz, 4H), 3.85 (d, J = 11.2 Hz, 12H), 2.84-2.69 (m, 8H), 2.05-1.93 (m, 4H). [13]C NMR (101 MHz, $CDCl_3$) δ: 166.19, 153.58, 153.51, 153.25, 153.17, 141.26, 136.73, 131.69, 125.14, 106.89, 105.48, 71.90, 71.85, 56.31, 56.19, 32.16, 30.43, 28.79, 28.67.



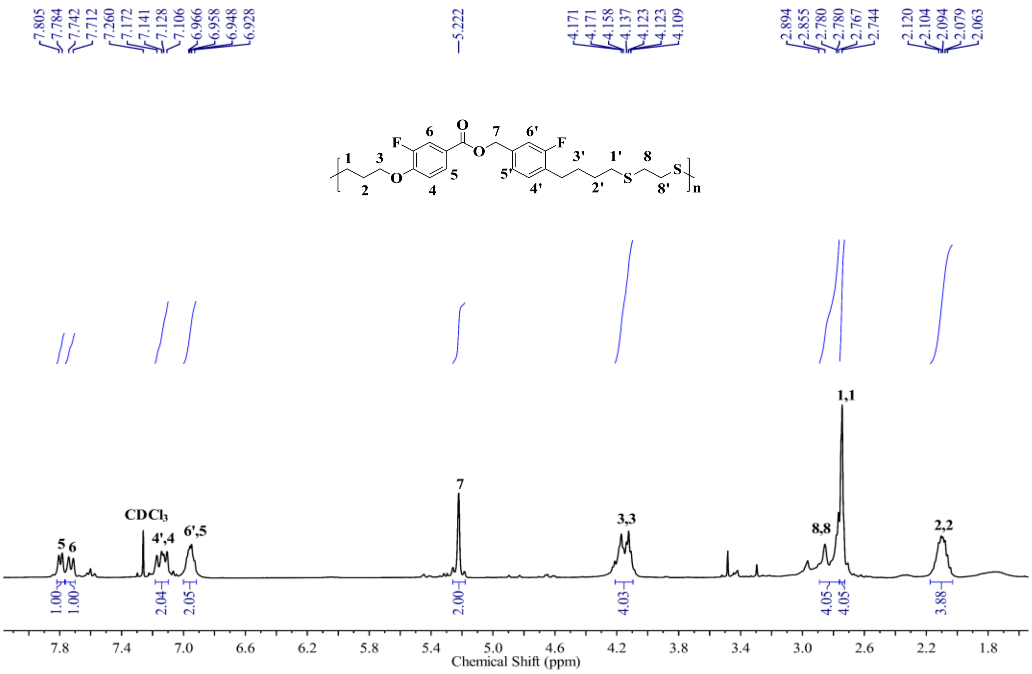


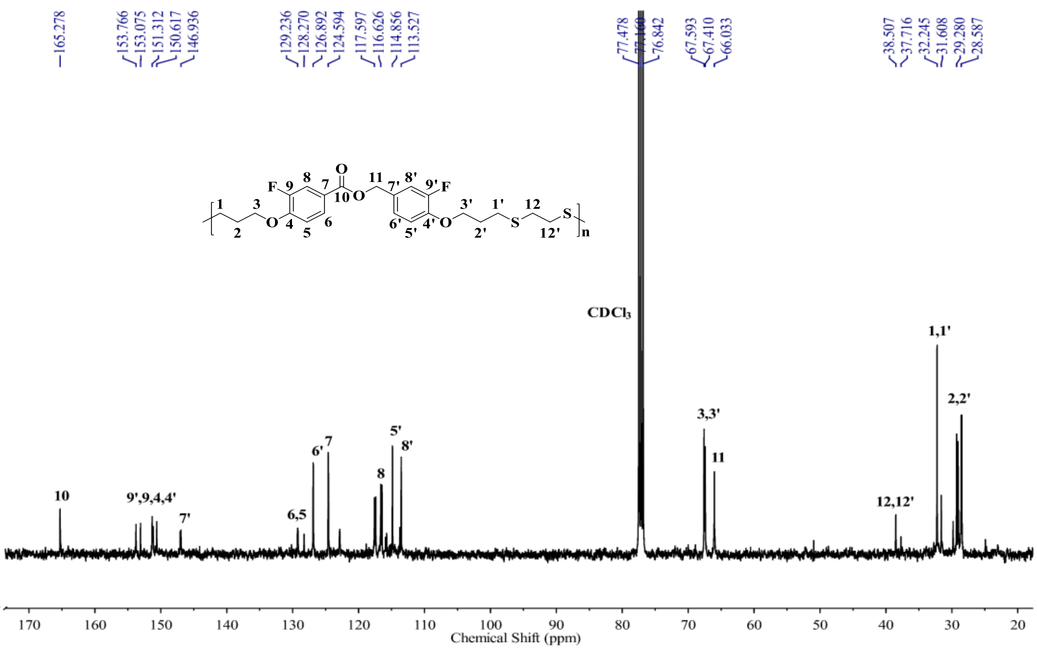
3.1.15. Poly(thioether ester) P3f4a derived from α,ω-diene ester (3f) and 1,2-ethanedithiol (4a)



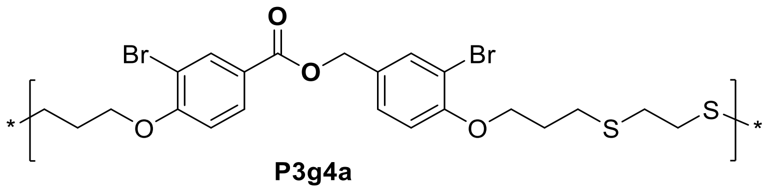
P3f4a

Yield: 89%. [1]H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 11.8 Hz, 1H), 7.19-7.10 (m, 2H), 7.00-6.92 (m, 2H), 5.22 (s, 2H), 4.21-4.10 (m, 4H), 2.89-2.76 (m, 4H), 2.74 (s, 4H), 2.17- 2.03 (m, 4H). [13]C NMR (101 MHz, $CDCl_3$) δ: 165.28, 153.77, 153.08, 151.31, 150.62, 146.94, 129.24, 128.27, 126.89, 124.59, 117.60, 116.63, 114.86, 113.53, 77.48, 67.59, 67.41, 66.03, 38.51, 37.72, 32.24, 31.61, 29.28, 28.59.

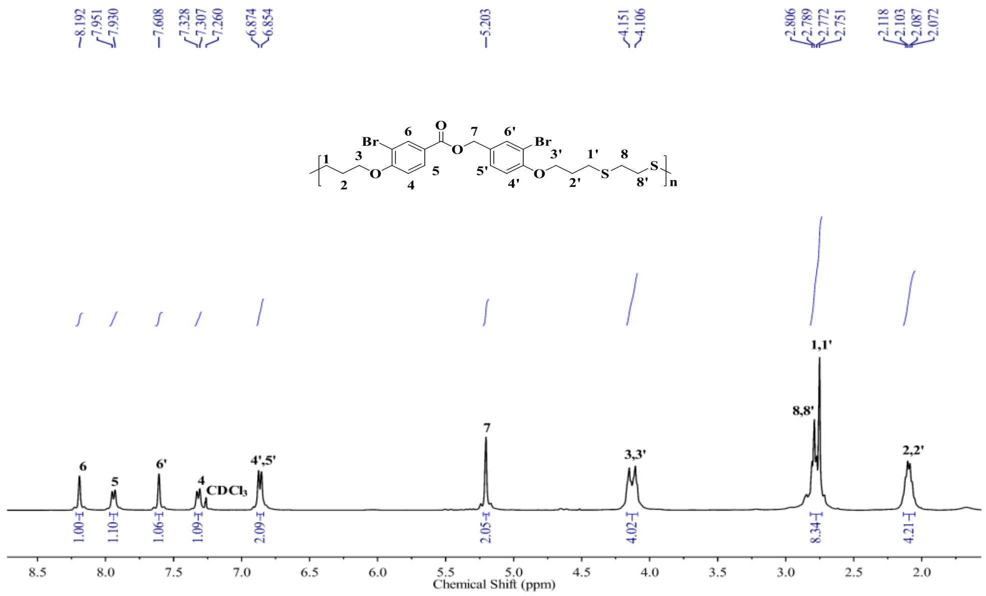


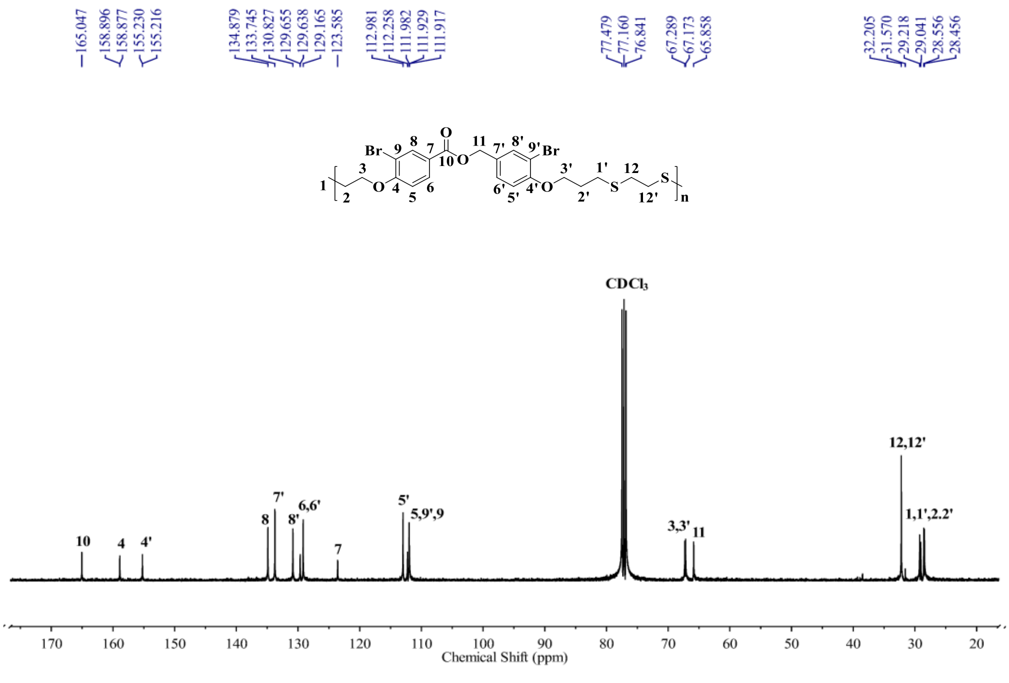


3.1.16. Poly(thioether ester) P3g4a derived from α,ω-diene ester (3g) and 1,2-ethanedithiol (4a)

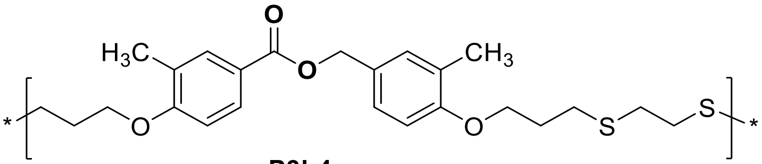


Yield: 93%. [1]H NMR (400 MHz, $CDCl_3$) δ: 8.19 (s, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.61 (s, 1H), 7.32 (d, J = 8.3 Hz, 1H), 6.86 (d, J = 8.3 Hz, 2H), 5.20 (s, 2H), 4.13 (dt, J = 11.0, 5.3 Hz, 4H), 2.81-2.74 (m, 8H), 2.12-2.05 (m, 4H). [13]C NMR (101 MHz, $CDCl_3$) δ: 165.05, 158.90, 158.88, 155.23, 155.22, 134.88, 133.75, 130.83, 129.65, 129.64, 129.16, 123.58, 112.98, 112.26, 111.98, 111.93, 111.92, 67.29, 67.17, 65.86, 32.20, 31.57, 29.22, 29.04, 28.56, 28.46.



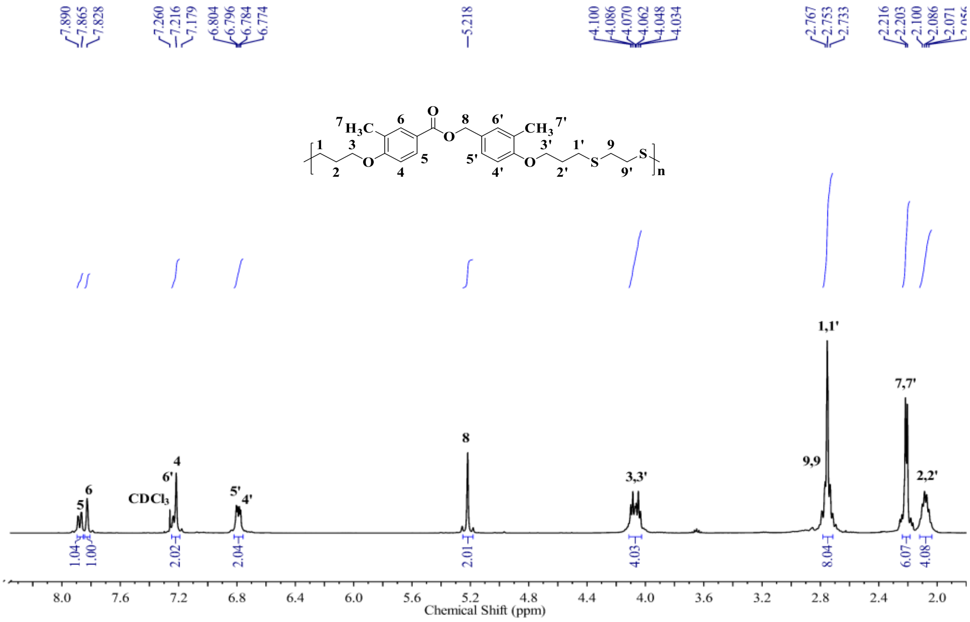


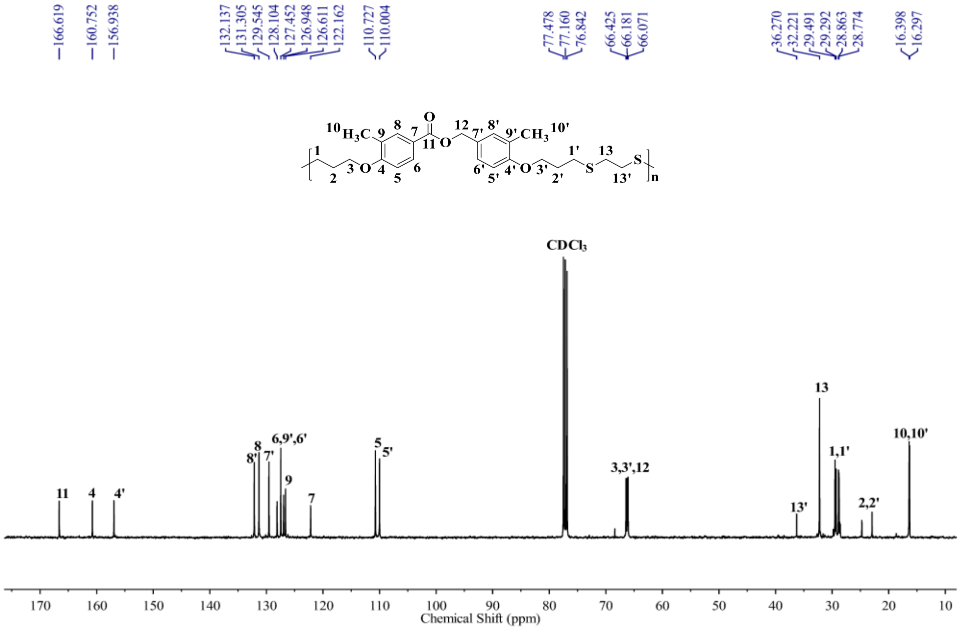
3.1.17. Poly(thioether ester) P3h4a derived from α,ω-diene ester (3h) and 1,2-ethanedithiol (4a)



P3h4a

Yield: 98%. [1]H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J = 9.9 Hz, 1H), 7.83 (s, 1H), 7.20 (d, J = 15.0 Hz, 2H), 6.79 (dd, J = 8.3, 3.4 Hz, 2H), 5.22 (s, 2H), 4.07 (dt, J = 14.5, 5.8 Hz, 4H), 2.78- 2.72 (m, 8H), 2.21 (d, J = 5.2 Hz, 6H), 2.12-2.05 (m, 4H). [13]C NMR (101 MHz, $CDCl_3$) δ: 166.62, 160.75, 156.94, 132.14, 131.31, 129.55, 128.10, 127.45, 126.95, 126.61, 122.16, 110.73, 110.00, 66.43, 66.18, 66.07, 36.27, 32.22, 29.49, 29.29, 28.86, 28.77, 16.40, 16.30.





3.2. Thermal properties and XRD spectra of poly(thioether esters)

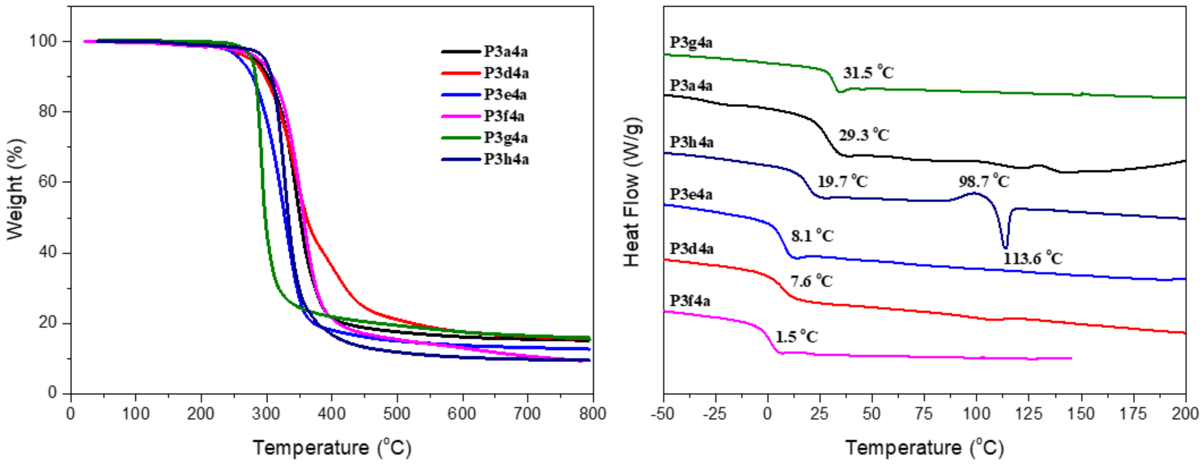


Figure S5. TGA and DSC thermograms of poly(thioether esters) with different substituent groups on the aromatic ring.

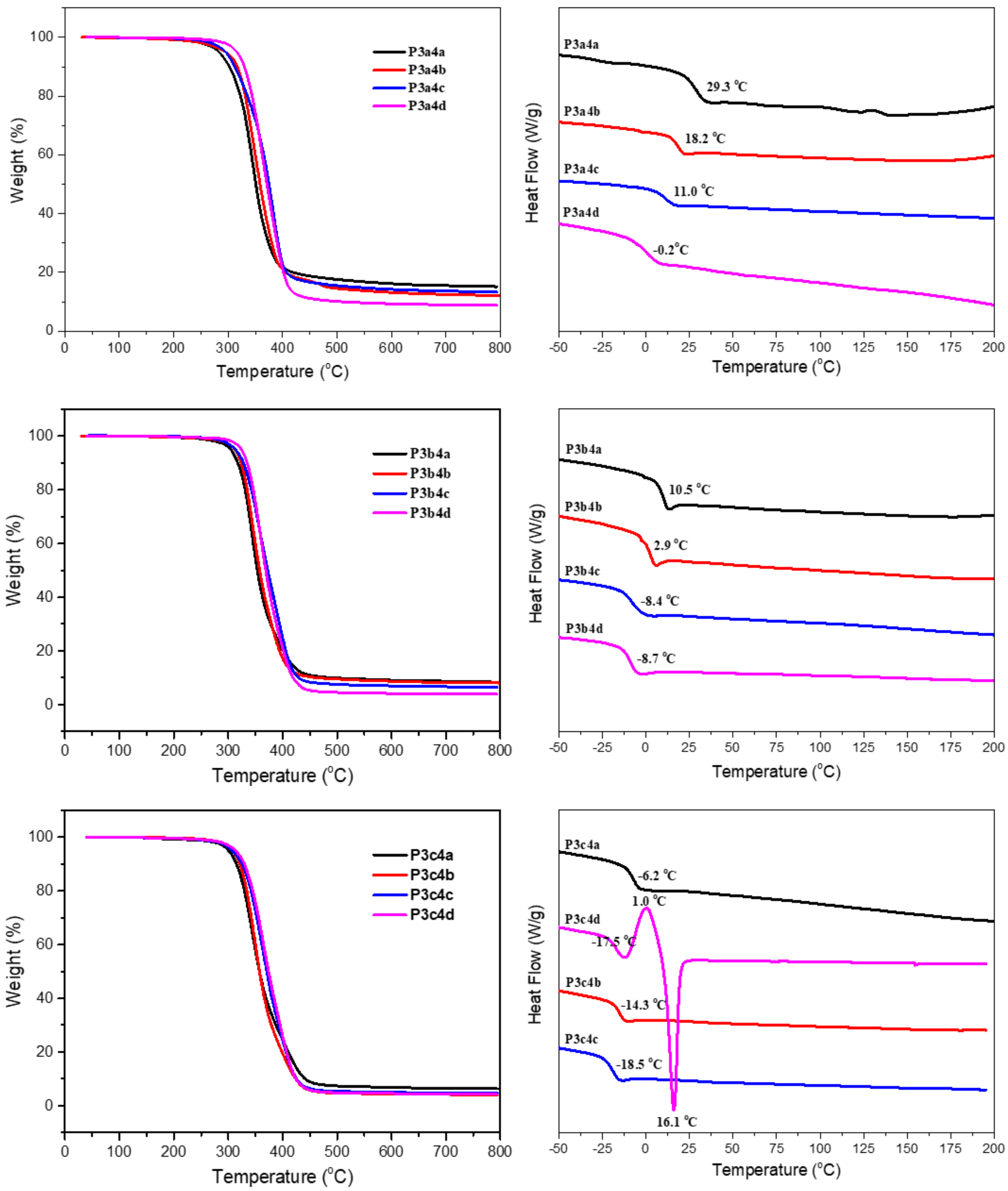


Figure S6. TGA and DSC thermograms of vanillin-derived poly(thioether esters) with different length methylene spacers.

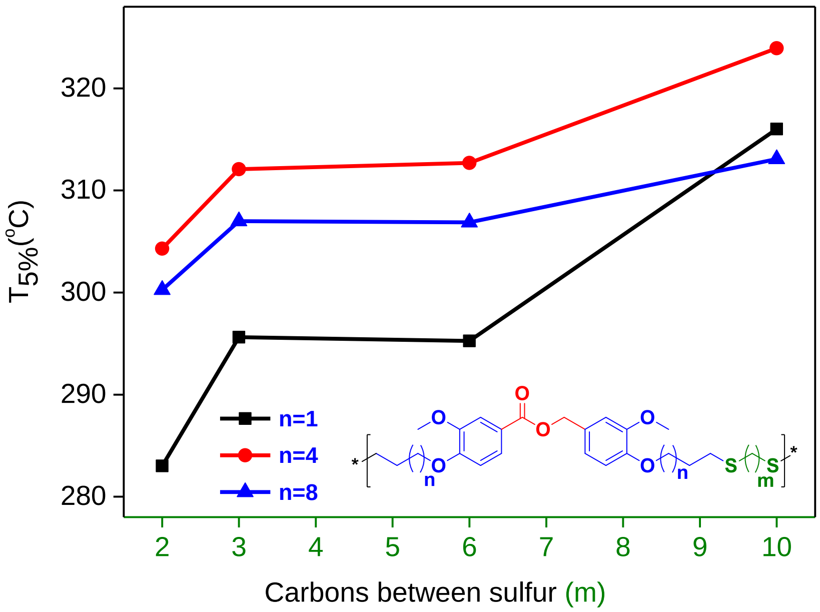


Figure S7. Plot of $T_{5\%}$ (°C) of **P3a4(a-d)**, **P3a4(a-d)** and **P3a4(a-d)**.

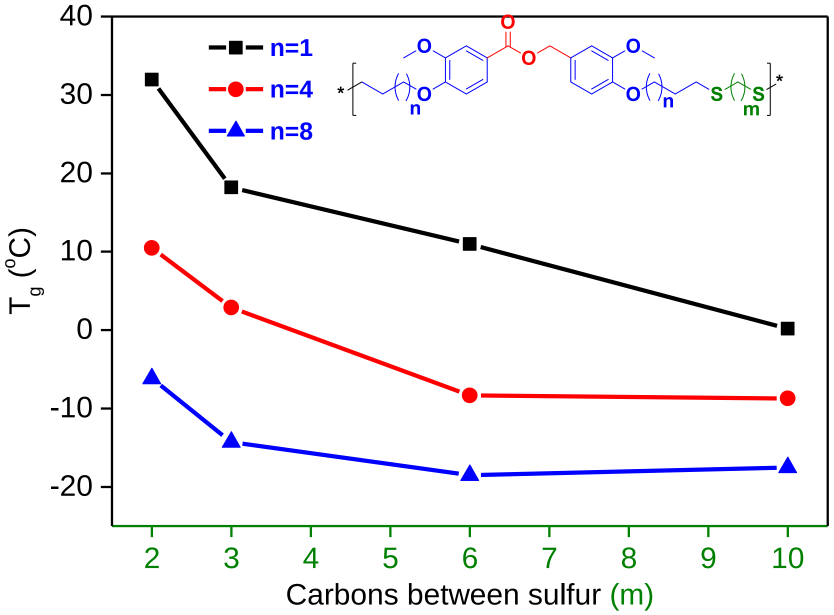


Figure S8. Plot of T_g (°C) of **P3a4(a-d)**, **P3a4(a-d)** and **P3a4(a-d)**.

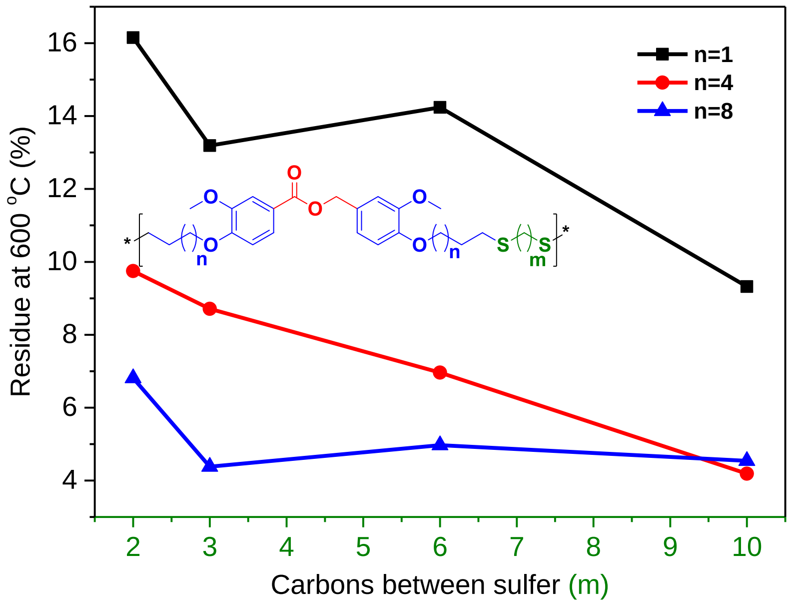


Figure S9. Plot of residue at 600 °C of **P3a4(a-d)**, **P3a4(a-d)** and **P3a4(a-d)**.

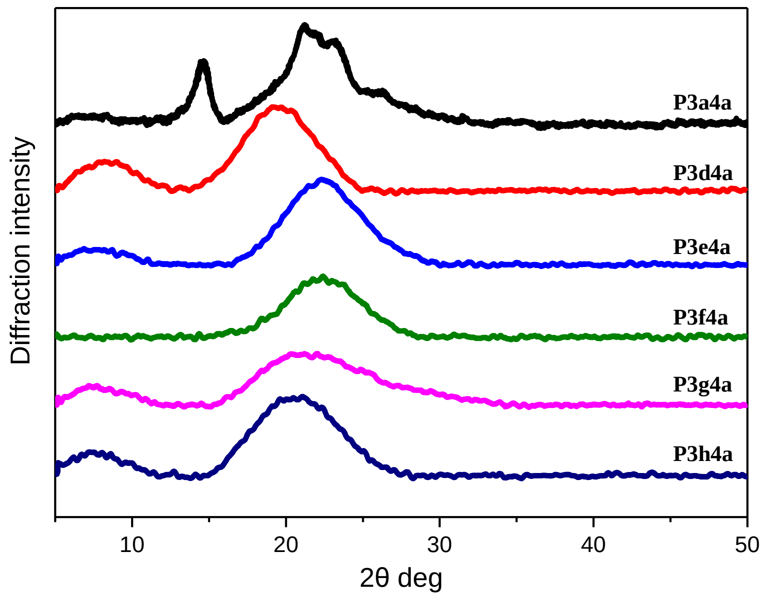


Figure S10. Wide-angle X-ray diffraction of poly(thioether ester)s with different substituent groups on the aromatic ring.

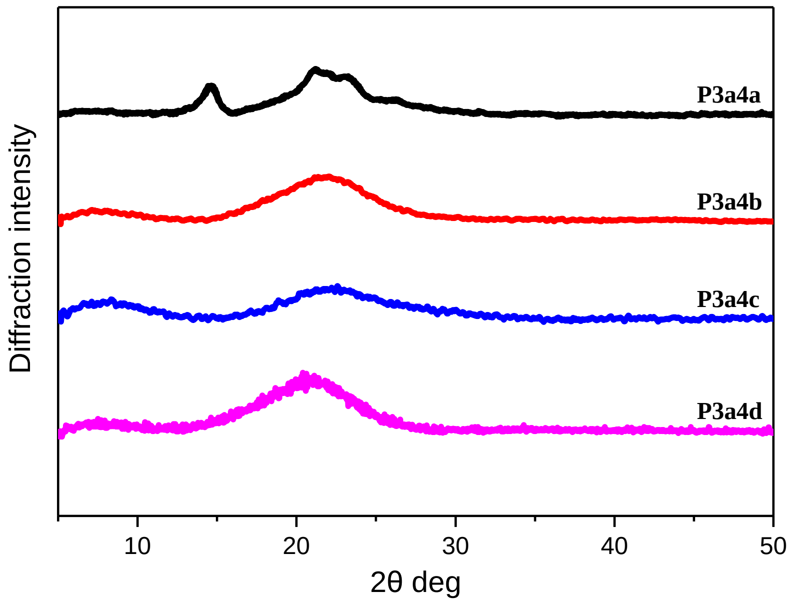


Figure S11. Wide-angle X-ray diffraction of **P3a4a-P3a4d**.

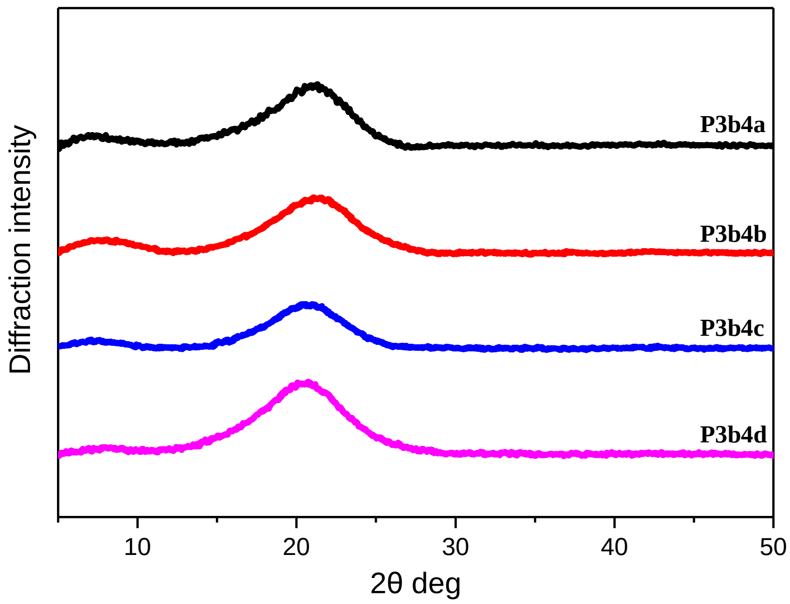


Figure S12. Wide-angle X-ray diffraction of **P3b4a-P3b4d**.

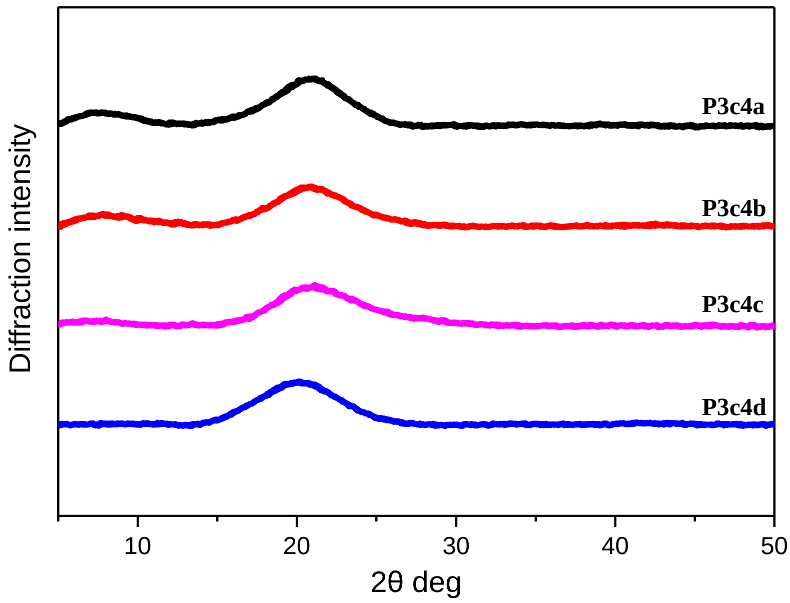
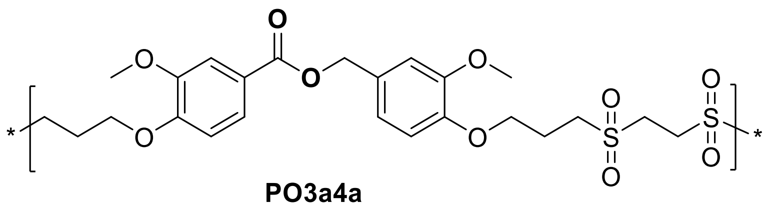


Figure S13. Wide-angle X-ray diffraction of **P3c4a-P3c4d**.

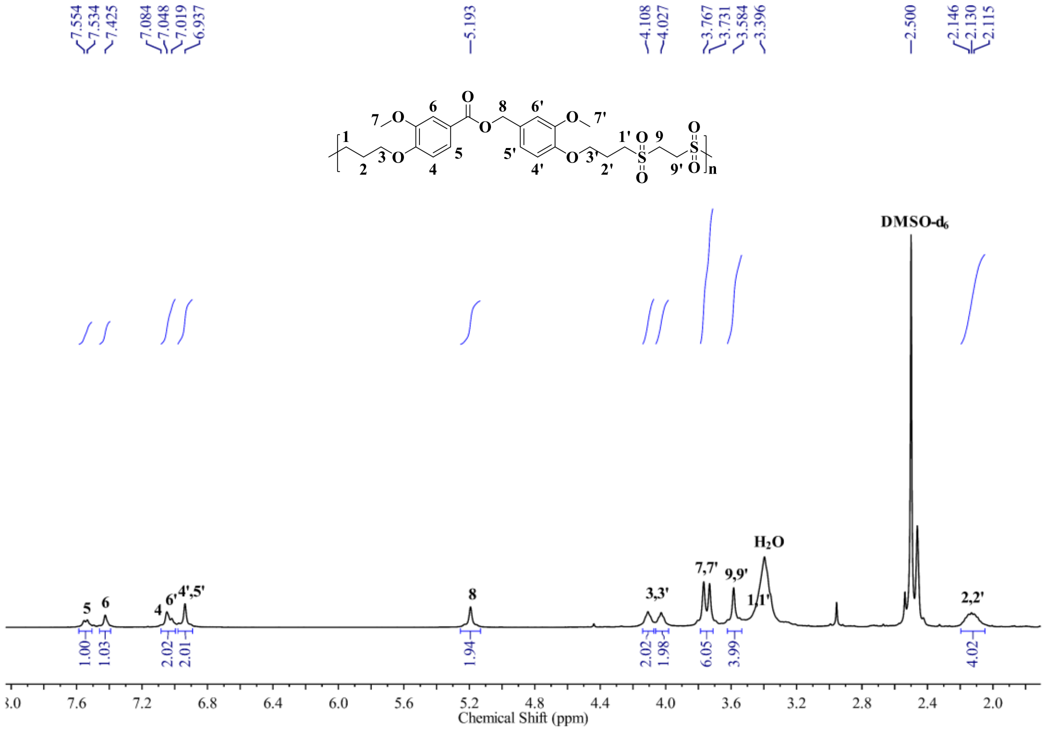
3.3. Representative ^{1}H NMR and ^{13}C NMR spectra for poly(sulfone esters)

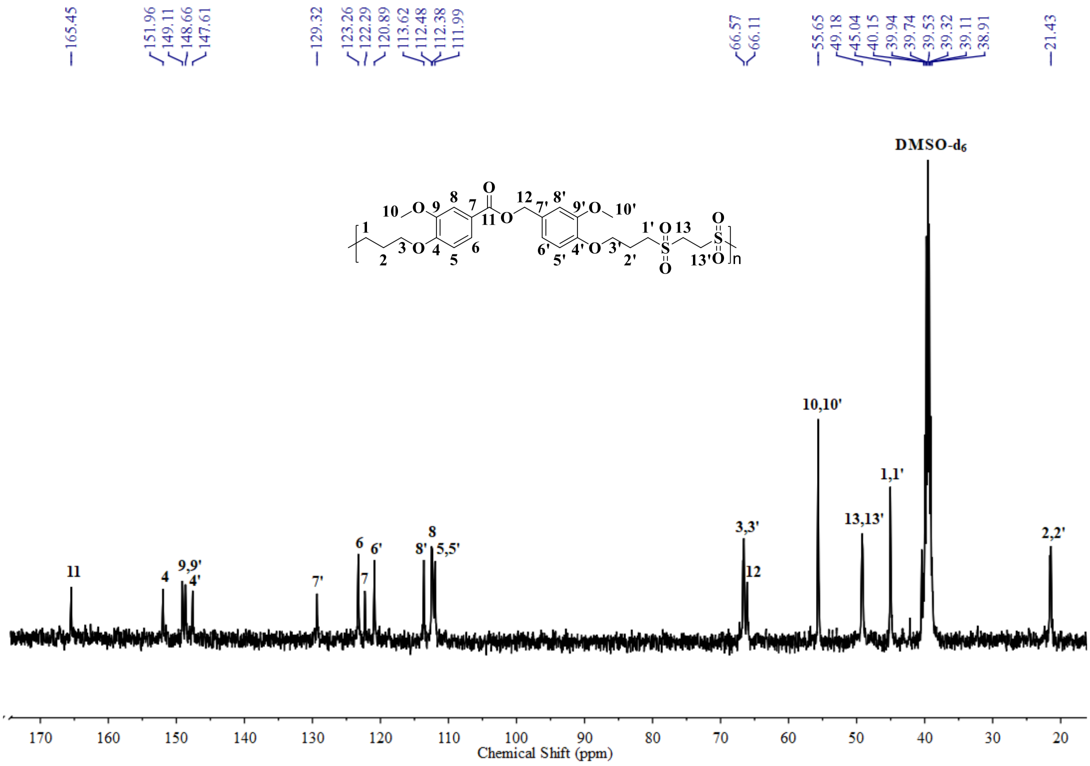
3.3.1. poly(sulfone ester) PO3a4a



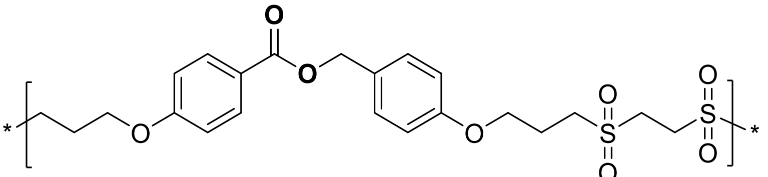
PO3a4a

Yield: 91%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.54 (d, J = 8.0 Hz, 1H), 7.43 (s, 1H), 7.03 (d, J = 11.9 Hz, 2H), 6.94 (s, 2H), 5.19 (s, 2H), 4.11 (s, 2H), 4.03 (s, 2H) 3.75 (d, J = 14.2 Hz, 6H), 3.58 (s, 4H), 3.39 (s, 4H), 2.20-2.05 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 165.45, 151.96, 149.11, 148.66, 147.61, 129.32, 123.26, 122.29, 120.89, 113.62, 112.48, 112.38, 111.99, 66.57, 66.11, 55.65, 49.18, 45.04, 40.15, 39.94, 39.74, 39.53, 39.32, 39.11, 38.91, 21.43.


7.554
7.534
7.425
7.084
7.048
7.019
6.937
5.193
4.108
4.027
3.767
3.731
3.584
3.396
2.500
2.146
2.130
2.115
DMSO-d6
H2O
7,7'
9,9'
1,1'
3,3'
8
5
6
4
6'
4',5'
2,2'
1.00
1.03
2.02
2.01
1.94
2.02
1.98
6.05
3.99
4.02
Chemical Shift (ppm)

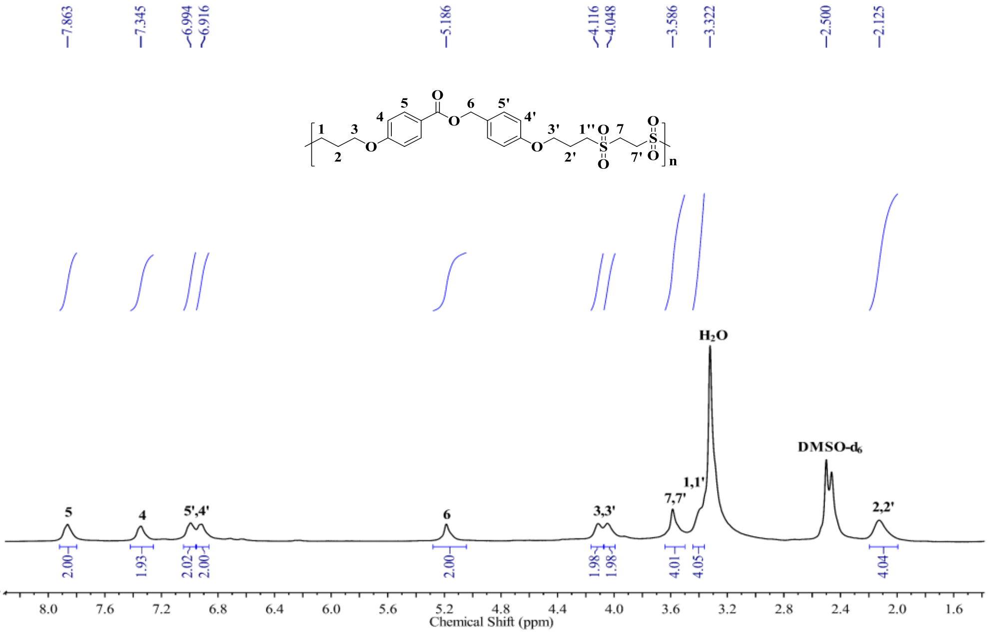

165.45
151.96
149.11
148.66
147.61
129.32
123.26
122.29
120.89
113.62
112.48
112.38
111.99
66.57
66.11
55.65
49.18
45.04
40.15
39.94
39.74
39.53
39.32
39.11
38.91
21.43
DMSO-d6
10,10'
1,1'
13,13'
3,3'
12
2,2'
11
4
9,9'
4'
7'
6
7
6'
8
8'
5,5'
Chemical Shift (ppm)

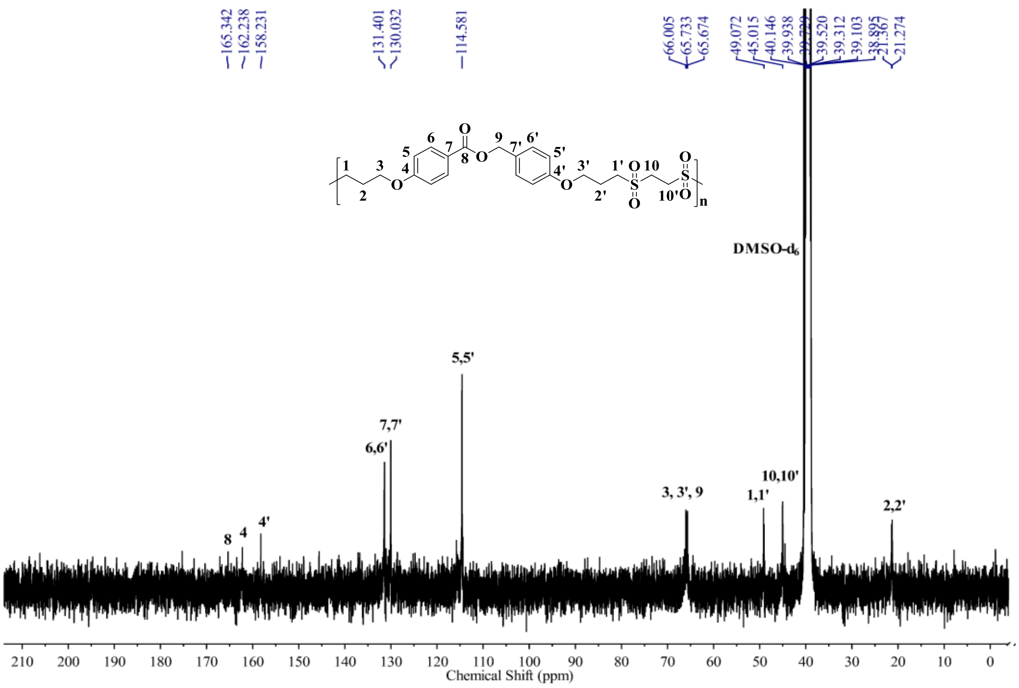
3.3.2. poly(sulfone ester) PO3d4a



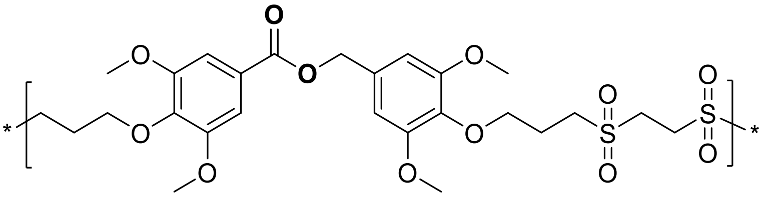
PO3d4a

Yield: 89%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.86 (s, 2H), 7.34 (s, 2H), 6.99 (s, 2H), 6.92 (s, 2H), 5.19 (s, 2H), 4.12 (s, 2H), 4.05 (s, 2H), 3.59 (s, 4H), 3.36 (s, 4H), 2.13 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 165.34, 162.24, 158.23, 131.40, 130.03, 114.58, 66.01, 65.73, 65.67, 49.14, 49.07, 45.02, 44.96, 21.37, 21.27.



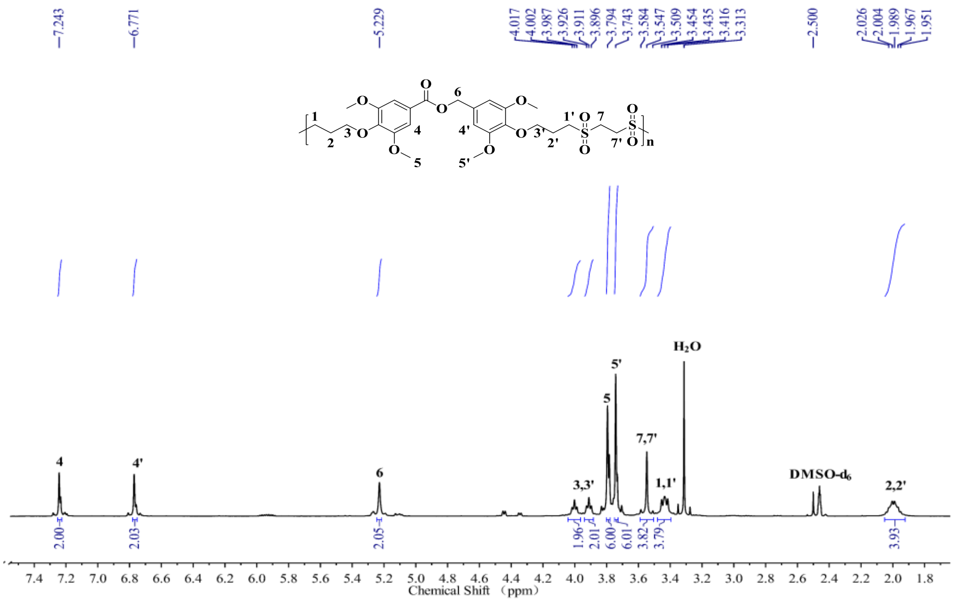


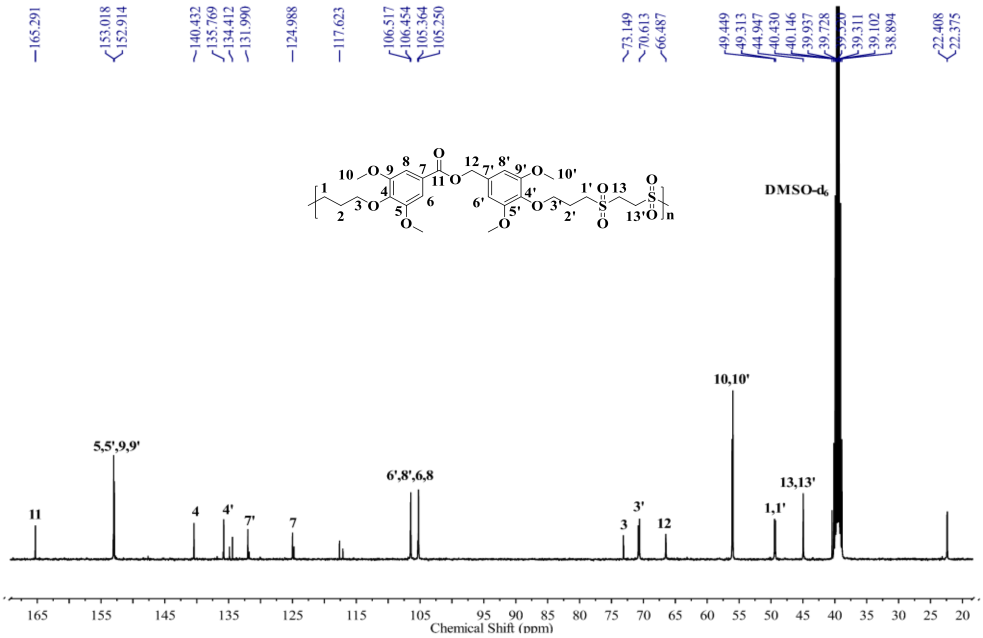
3.3.3. poly(sulfone ester) PO3e4a



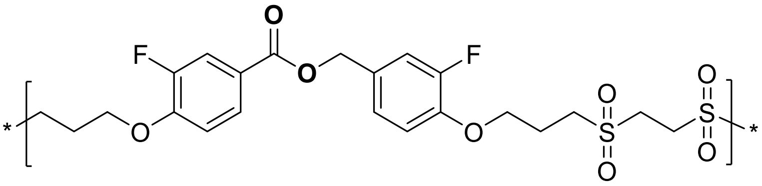
PO3e4a

Yield: 93%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.24 (s, 2H), 6.77 (s, 2H), 5.23 (s, 2H), 4.00 (t, J = 5.9 Hz, 2H), 3.91 (t, J = 5.9 Hz, 2H), 3.79 (s, 6H), 3.74 (s, 6H), 3.59-3.50 (m, 4H), 3.48-3.40 (m, 4H), 2.03-1.95 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 165.29, 153.02, 152.91, 140.43, 135.77, 134.41, 131.99, 124.99, 117.62, 106.52, 106.45, 105.36, 105.25, 73.15, 70.61, 66.49, 49.45, 49.31, 44.95, 40.43, 22.41, 22.38.



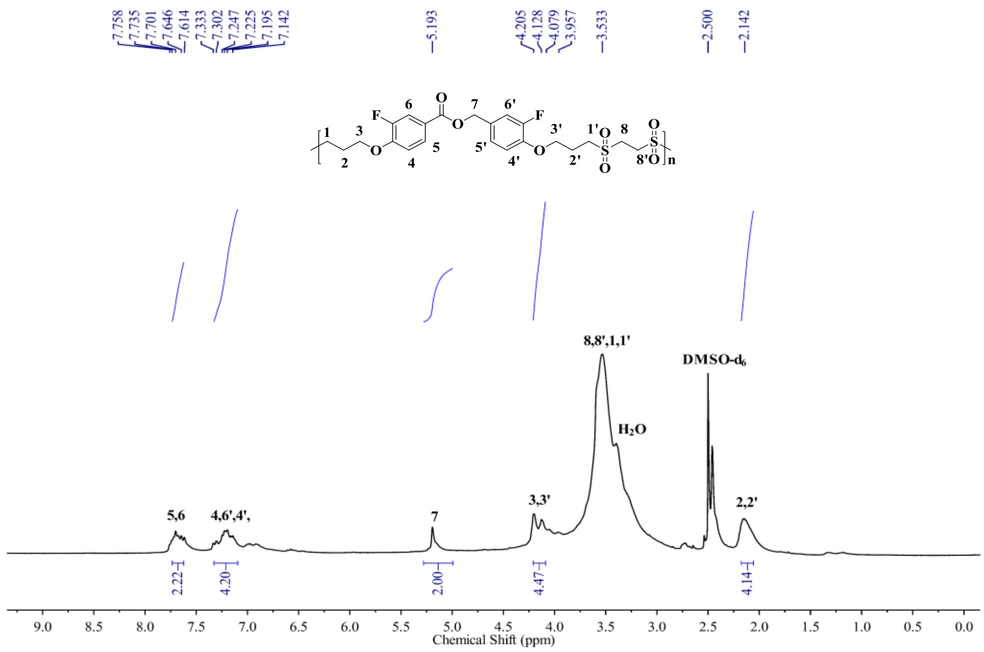


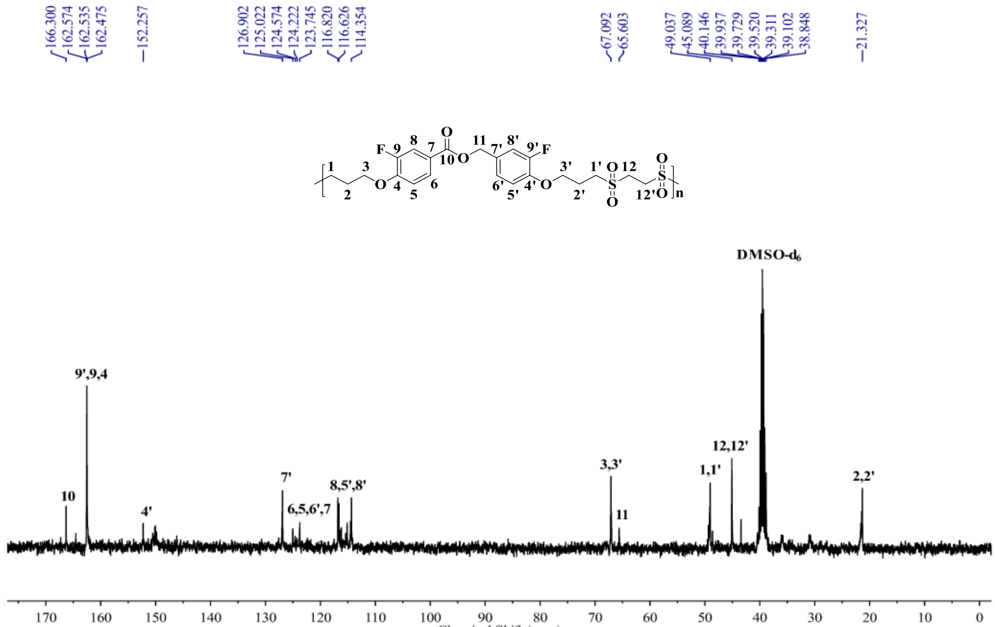
3.3.4. poly(sulfone ester) PO3f4a



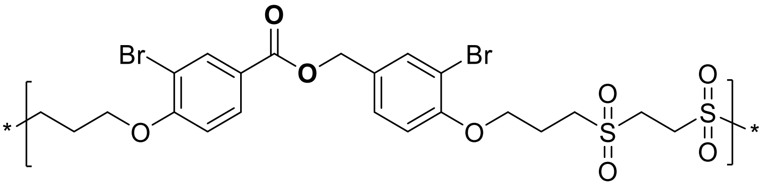
PO3f4a

Yield: 87%. [1]H NMR (400 MHz, DMSO-d6) δ: 7.73-7.62 (m, 2H), 7.33-7.09 (m, 4H), 5.19 (s, 2H), 4.22-4.08 (m, 7 Hz, 4H), 3.53 (s, 8H), 2.14 (s, 4H). [13]C NMR (101 MHz, DMSO-d6) δ: 166.30, 162.57, 162.54, 162.47, 152.26, 126.90, 125.02, 124.57, 124.22, 123.75, 116.82, 116.63, 114.35, 67.09, 65.60, 49.04, 45.09, 21.33.



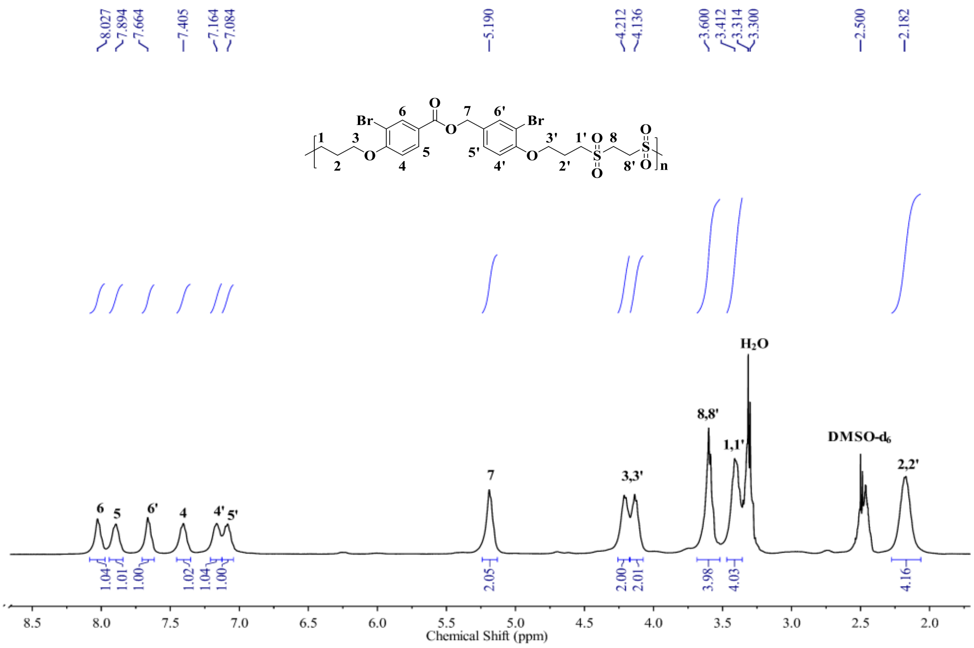


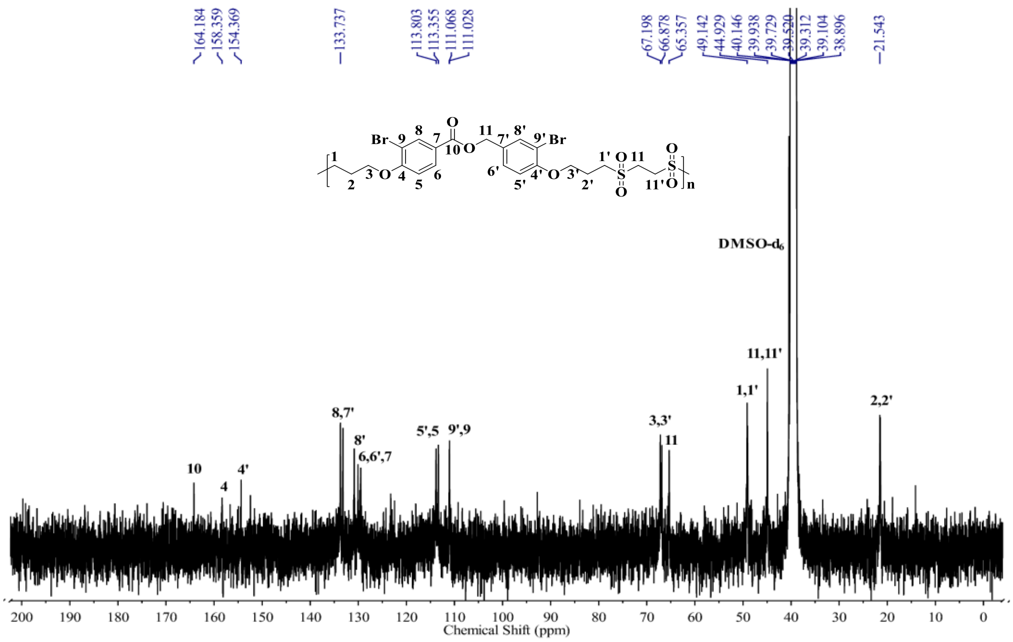
3.3.5. poly(sulfone ester) PO3g4a



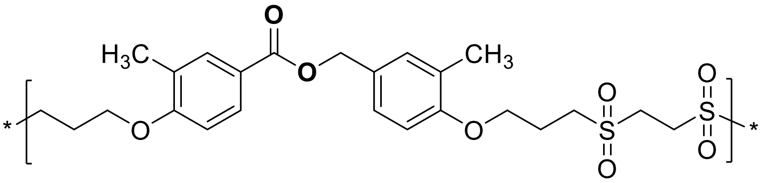
PO3g4a

Yield: 91%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.03 (s, 1H), 7.89 (s, 1H), 7.66 (s, 1H), 7.40 (s, 1H), 7.16 (s, 1H), 7.08 (s, 1H), 5.19 (s, 2H), 4.21 (s, 2H), 4.14 (s, 2H), 3.60 (s, 4H), 3.41 (s, 4H), 2.18 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 164.18, 158.36, 154.37, 133.74, 113.80, 113.35, 111.07, 111.03, 67.20, 66.88, 65.36, 49.14, 44.93, 21.54.



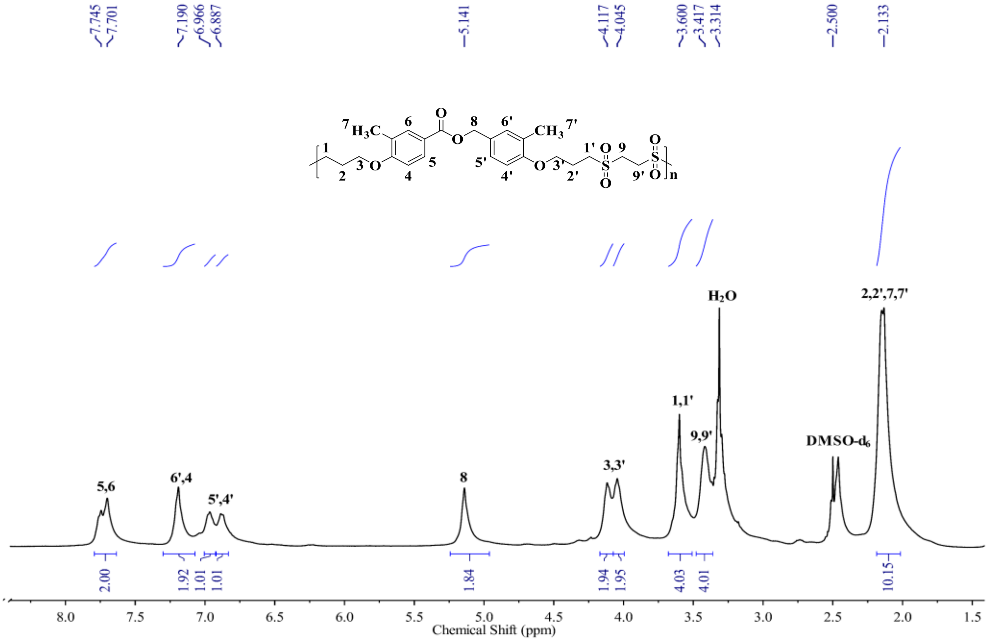


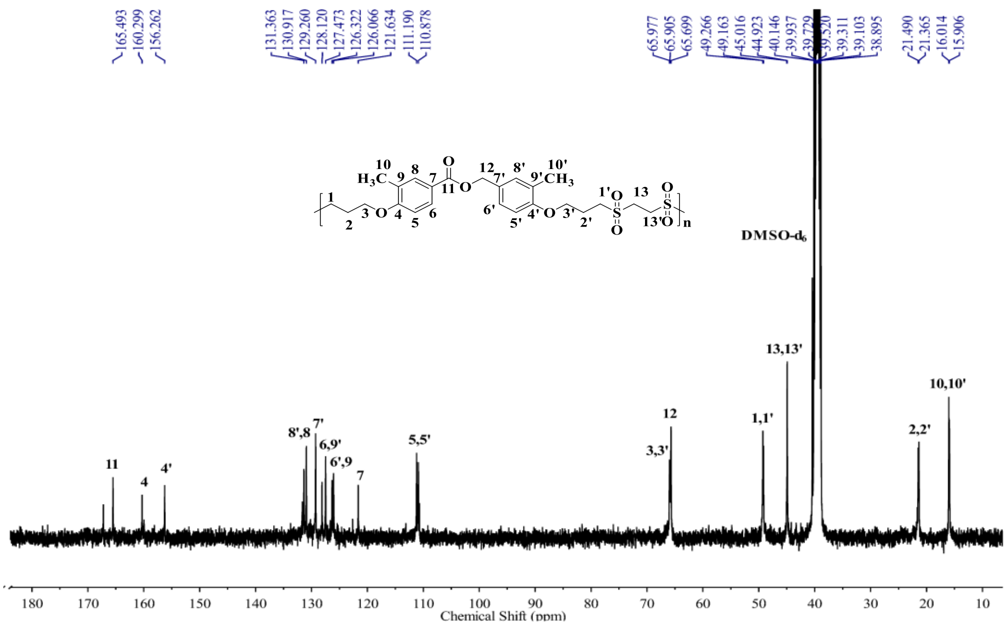
3.3.6. poly(sulfone ester) PO3h4a



PO3h4a

Yield: 89%. [1]H NMR (400 MHz, DMSO-d6) δ: 7.72 (d, J = 17.5 Hz, 2H), 7.19 (s, 2H), 6.97 (s, 1H), 6.89 (s, 1H), 5.14 (s, 2H), 4.12 (s, 2H), 4.05 (s, 2H), 3.60 (s, 4H), 3.42 (s, 4H), 2.13 (s, 10H). [13]C NMR (101 MHz, DMSO-d6) δ: 165.49, 160.30, 156.26, 131.36, 130.92, 129.26, 128.12, 127.47, 126.32, 126.07, 121.63, 111.19, 110.88, 65.98, 65.91, 65.70, 49.27, 49.16, 45.02, 44.92, 21.49, 21.37, 16.01, 15.91.





3.4. Thermal properties and XRD spectra of poly(sulfone esters)

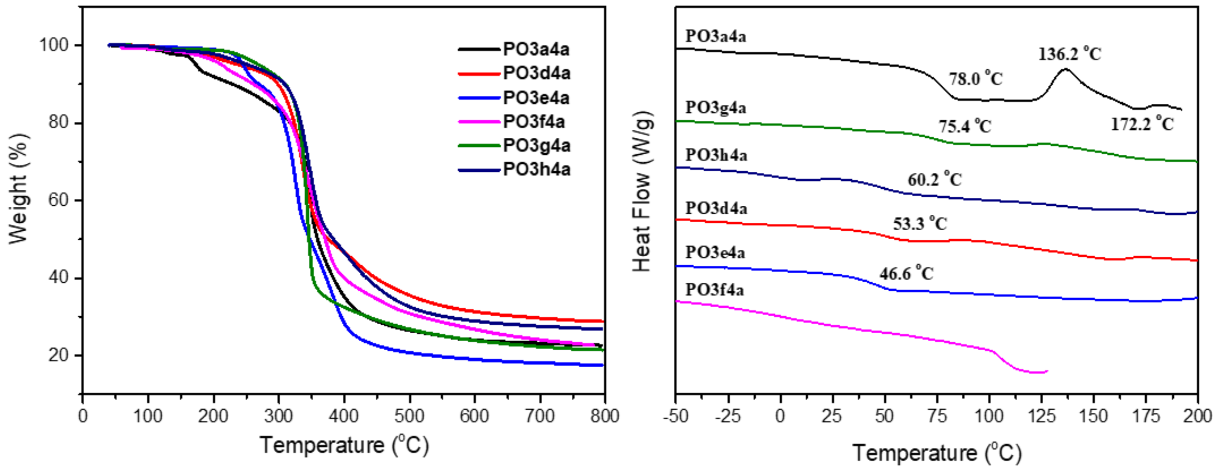


Figure S14. TGA and DSC thermograms of poly(sulfone esters).

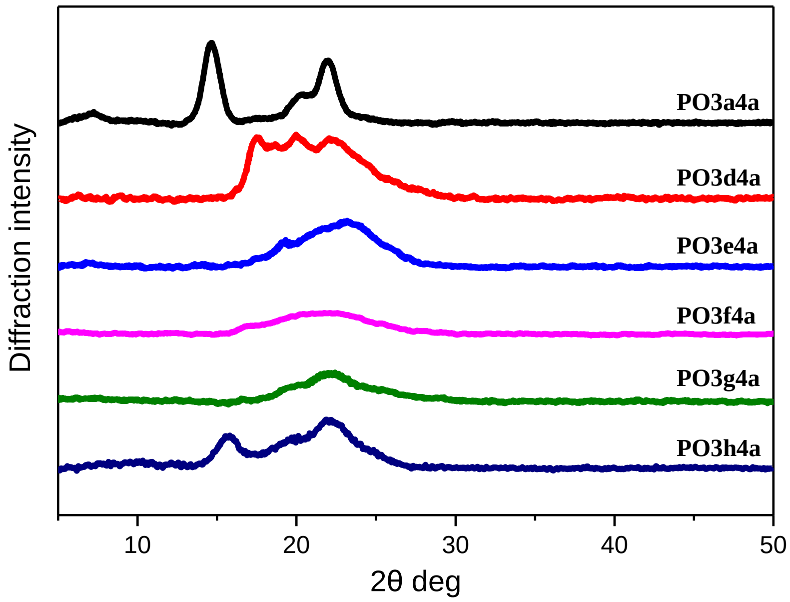
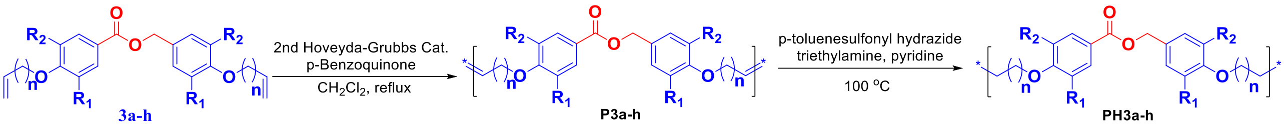


Figure S15. Wide-angle X-ray diffraction of poly(sulfone esters).

4. ADMET polymerization and post-hydrogenation



Scheme S4. The preparation of unsaturated polyesters via ADMET polymerization and their hydrogenation to saturated polyesters.

General procedure for ADMET polymerizations. α,ω-diene ester (3 mmol), p-benzoquinone (6.55 mg, 0.06 mmol, 2 mol%) and Hoveyda-Grubbs Catalyst 2nd Generation (19.38 mg, 0.03 mmol, 1 mol%) were dissolved in CH_2Cl_2 in a 25 ml Schlenk-flask. The solution was degassed by freeze-pump-thawing three times. Then, the reaction was refluxed at 40 ^oC whilst blowing nitrogen through the flask. After 48 h., the mixture was quenched with ethyl vinyl ether (5 ml) and precipitated in cold methanol. The resulting poly(ethylene ether esters) were purified by three dissolving-precipitation cycles, and dried under vacuum at 50 ^oC for 24 h.

General procedure for post-polymerization hydrogenation. Poly(ethylene ether ester) (1 mmol), p-toluenesulfonyl hydrazide[5] (3 mmol, 0.57 g), triethylamine (3 mmol, 0.306 g) and pyridine (5 ml) were added to a 25 ml Schlenk-flask and stirred at 100 ^oC for 10 h. The mixture was then precipitated in cold methanol. The resulting polymers were isolated by centrifuging, purified by three dissolving-precipitation cycles, and dried under vacuum at 50 ^oC for 24 h.

The unsaturated polyesters synthesized by ADMET polymerization and saturated polyesters obtained by post-polymerization hydrogenation were characterized by ^1H NMR and ^{13}C NMR spectroscopy. As a representative example, Figure S16 displays the ^1H NMR spectrum of **P3a** revealing the disappearance of the terminal double bond and the formation of internal double bonds at 6.09 ppm. The methylene group next to the ester bond can be assigned to the singlet at 5.25 ppm. The methylene groups next to double bond can be identified as multiplets at 4.60-4.70 ppm. The methoxy adjacent to the benzene ring can be identified as singlet at 3.87 ppm. After post-polymerization hydrogenation, the internal double bond peaks at 6.09 ppm had disappeared and a new single peak at 2.05 ppm was identified as the methylene obtained by post-polymerization hydrogenation, which were also confirmed by ^{13}C NMR spectra comparison (Figure S17).

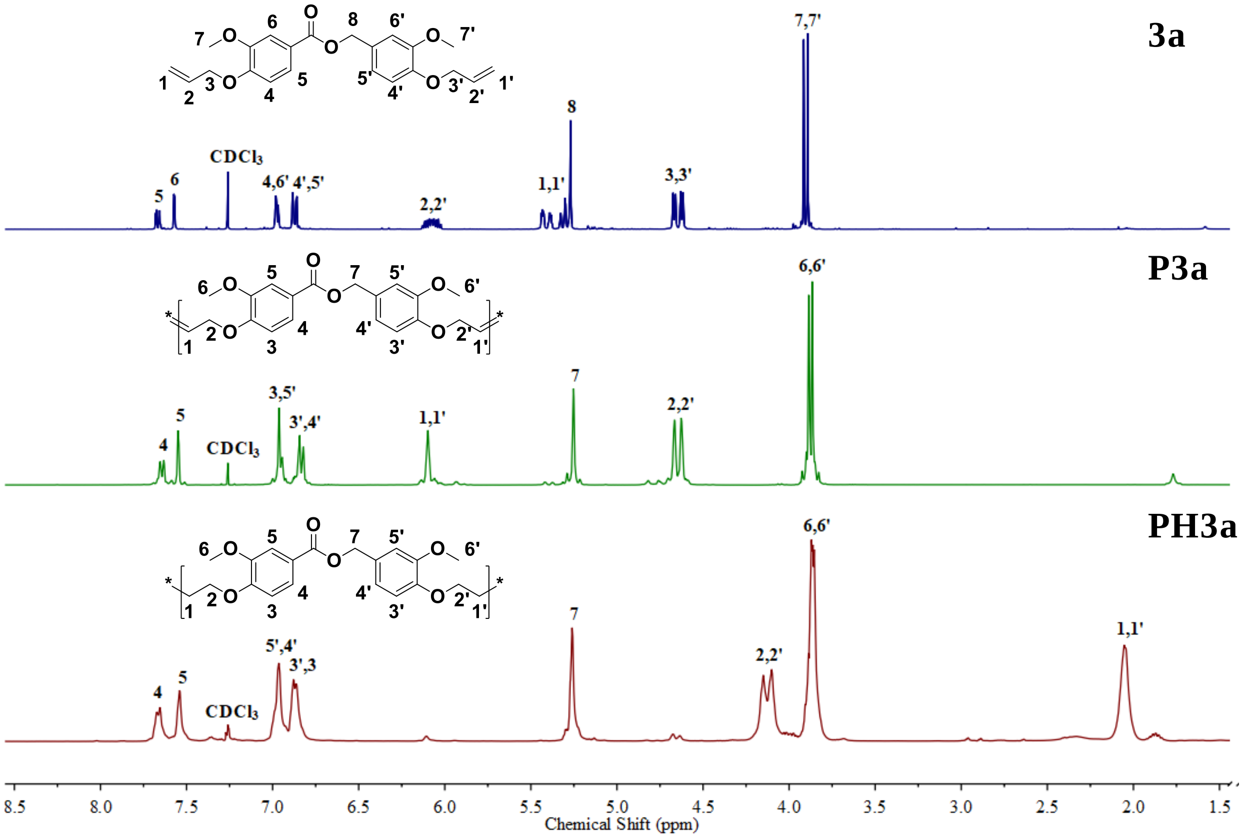


Figure S16. Comparative ^{1}H NMR spectra of **3a**, **P3a** and **PH3a**.

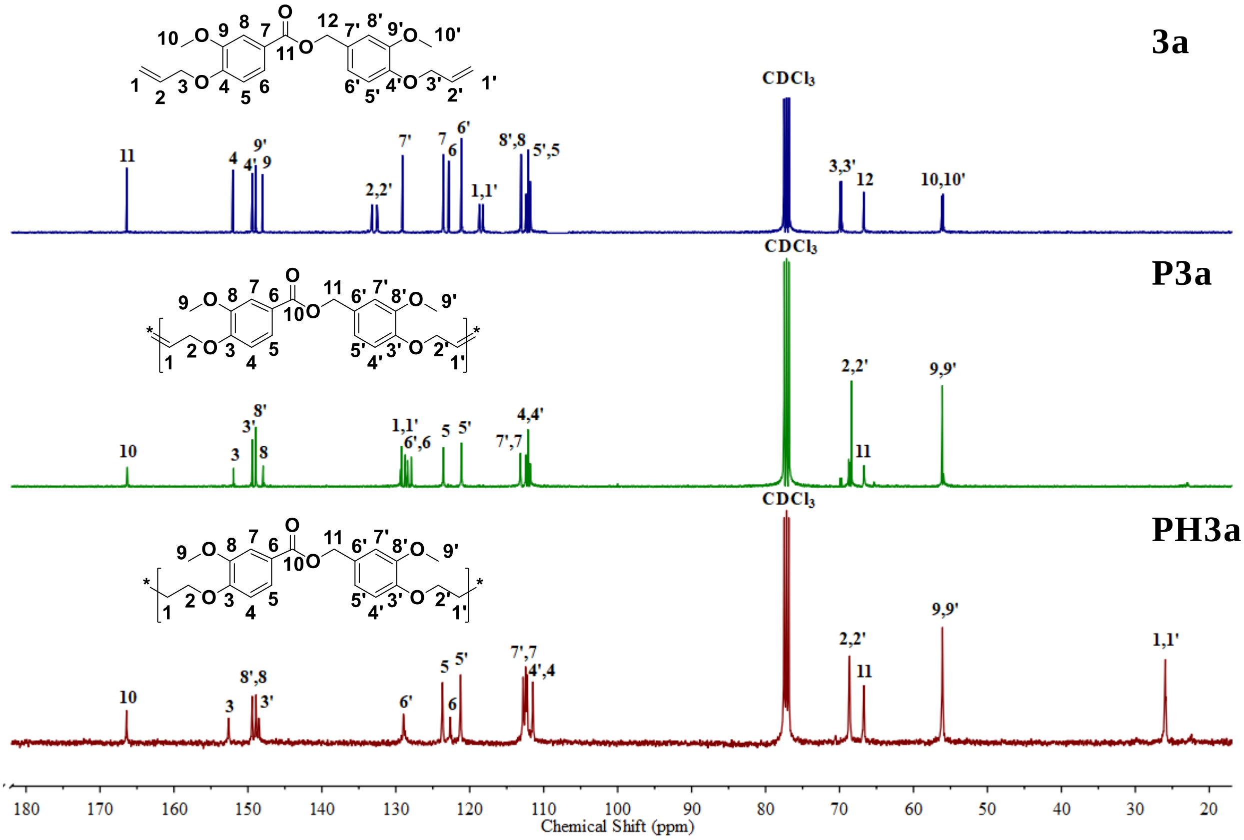
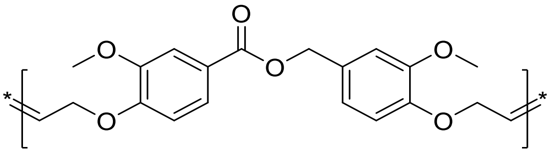


Figure S17. Comparative ^{13}C NMR spectra of **3a**, **P3a** and **PH3a**.

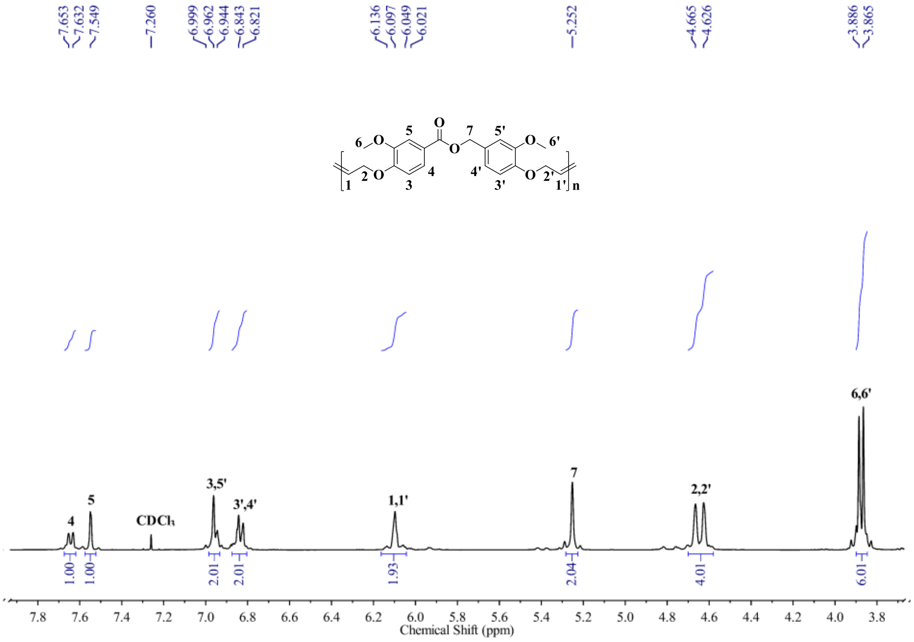
4.1. Representative ^{1}H NMR and ^{13}C NMR spectra of ADMET polymers

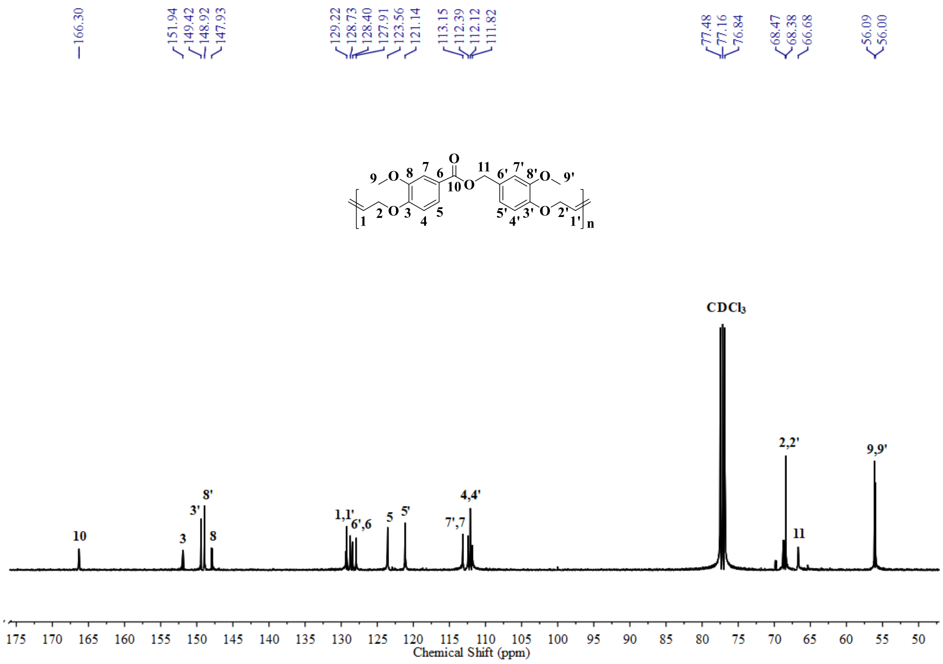
4.1.1. ADMET polymer P3a



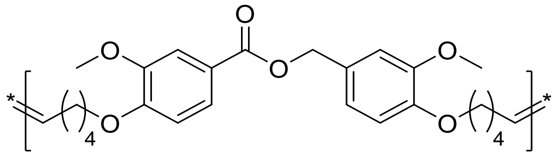
P3a

Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 8.5 Hz, 1H), 7.55 (s, 1H), 7.00-6.94 (m, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.16-6.04 (m, 2H), 5.25 (s, 2H), 4.65 (d, J = 15.5 Hz, 4H), 3.88 (d, J = 8.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.30, 151.94, 149.42, 148.92, 147.93, 129.22, 128.73, 128.40, 127.91, 123.56, 121.14, 113.15, 112.39, 112.12, 111.82, 77.48, 77.16, 76.84, 68.47, 68.38, 66.68, 56.09, 56.00.



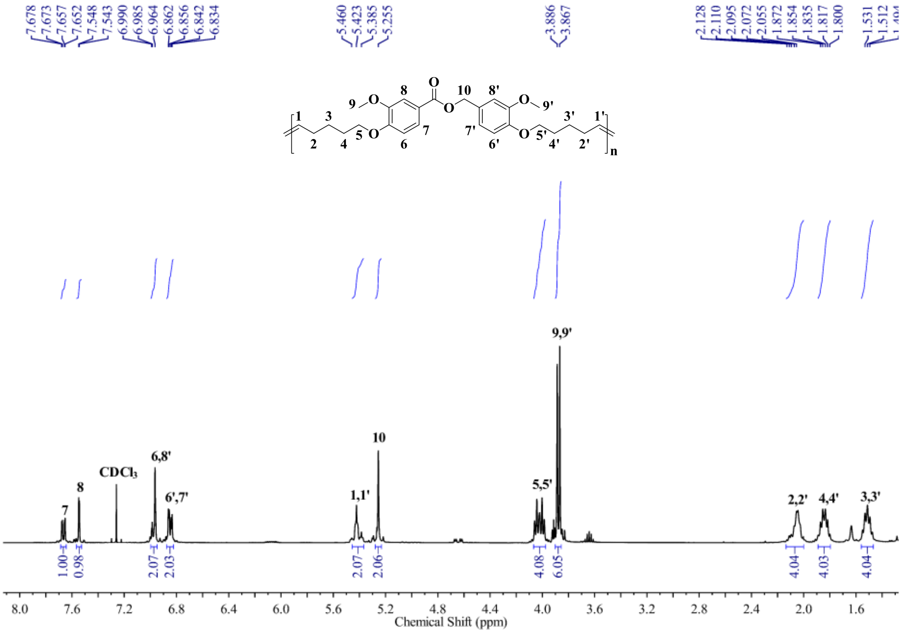


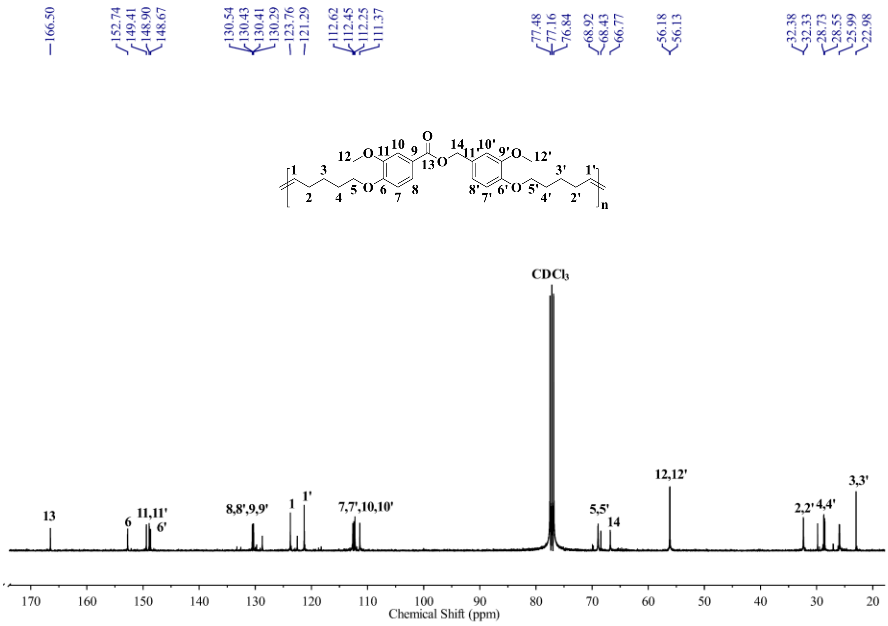
4.1.2. ADMET polymer P3b



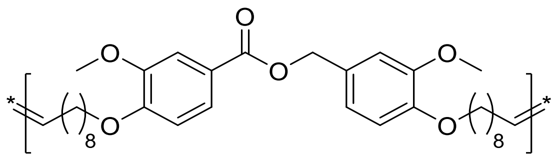
P3b

Yield: 95%. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, J = 8.4, 1.9 Hz, 1H), 7.55 (d, J = 1.9 Hz, 1H), 7.00-6.95 (m, 2H), 6.85 (dd, J = 8.3, 2.9 Hz, 2H), 5.46-5.37 (m, 2H), 5.26 (s, 2H), 4.07-3.97 (m, 4H), 3.88 (d, J = 7.8 Hz, 6H), 2.14-2.00 (m, 4H), 1.90-1.80 (m, 4H), 1.55-1.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.50, 152.74, 149.41, 148.90, 148.67, 130.54, 130.43, 130.41, 130.29, 123.76, 121.29, 112.62, 112.45, 112.25, 111.37, 68.92, 68.43, 66.77, 56.18, 56.13, 32.38, 32.33, 28.73, 28.55, 25.99, 22.98.



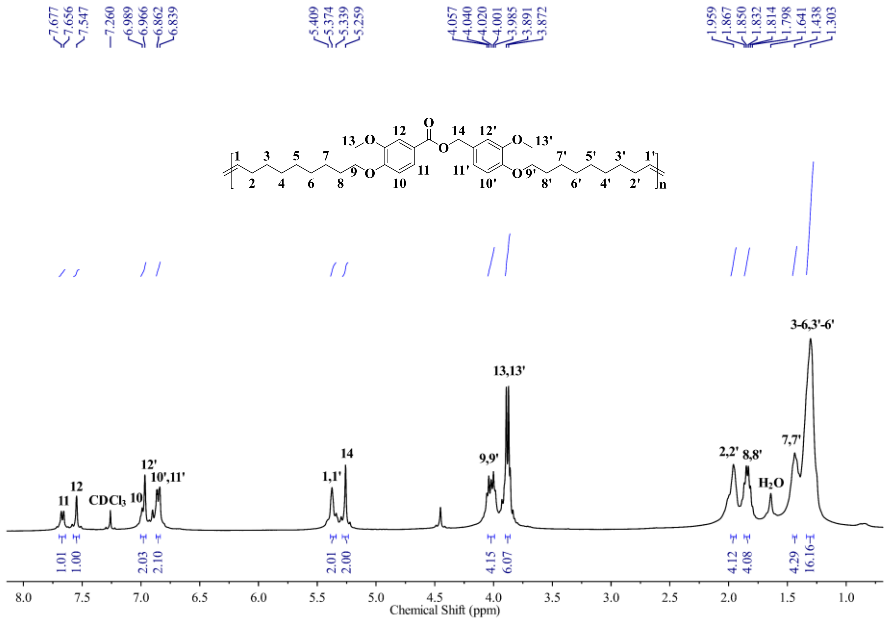


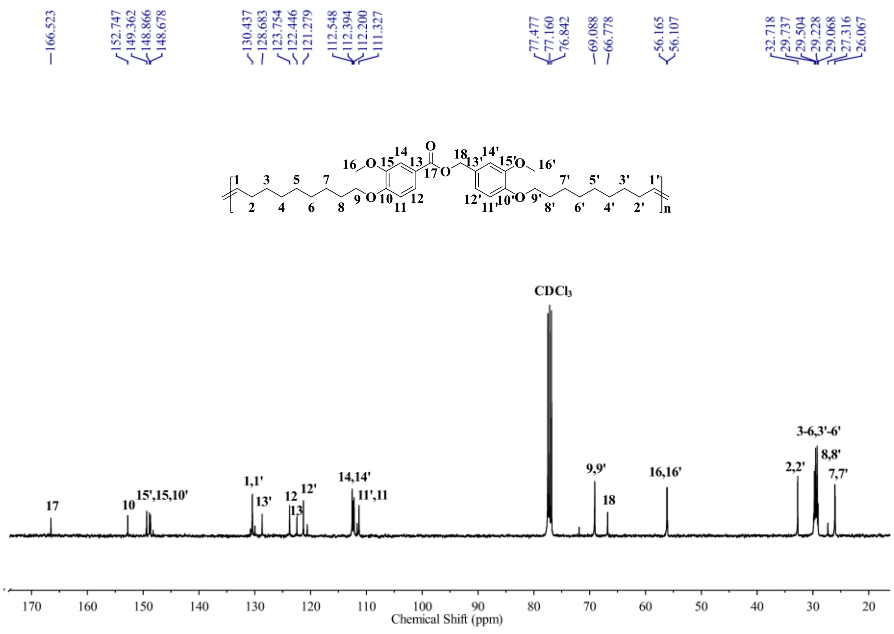
4.1.3. ADMET polymer P3c



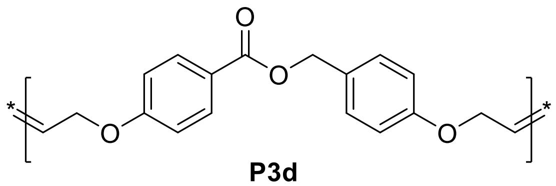
P3c

Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, J = 8.3 Hz, 1H), 7.55 (s, 1H), 7.02-6.96 (m, 2H), 6.85 (d, J = 9.1 Hz, 2H), 5.41-5.33 (m, 2H), 5.26 (s, 2H), 4.06-3.98 (m, 4H), 3.88 (d, J = 7.7 Hz, 6H), 1.96 (s, 4H), 1.87-1.79 (m, 4H), 1.44 (s, 4H), 1.30 (s, 16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.52, 152.75, 149.36, 148.87, 148.68, 130.44, 128.68, 123.75, 122.45, 121.28, 112.55, 112.39, 112.20, 111.33, 69.09, 66.78, 56.17, 56.11, 32.72, 29.74, 29.50, 29.23, 29.07, 27.32, 26.07.



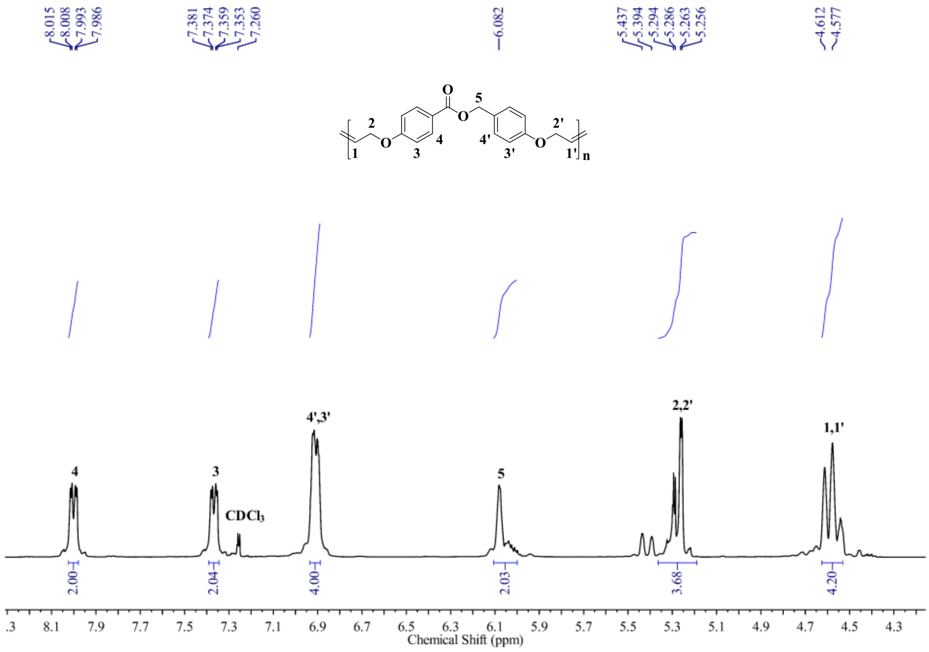


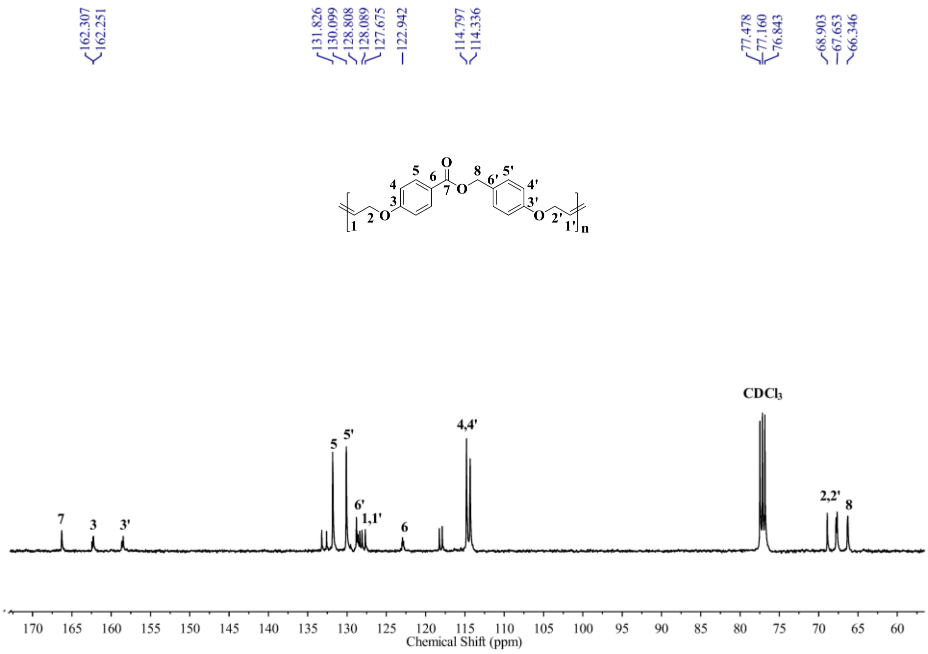
4.1.4. ADMET polymer P3d



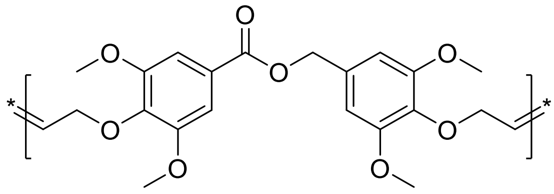
P3d

Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (dd, J = 8.8, 2.8 Hz, 2H), 7.37 (dd, J = 8.6, 2.8 Hz, 2H), 6.94-6.88 (m, 4H), 6.08 (s, 2H), 5.30-5.23 (m, 4H), 4.65-4.54 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.31, 162.25, 131.83, 130.10, 128.81, 128.09, 127.67, 122.94, 114.80, 114.34, 68.90, 67.65, 66.35.



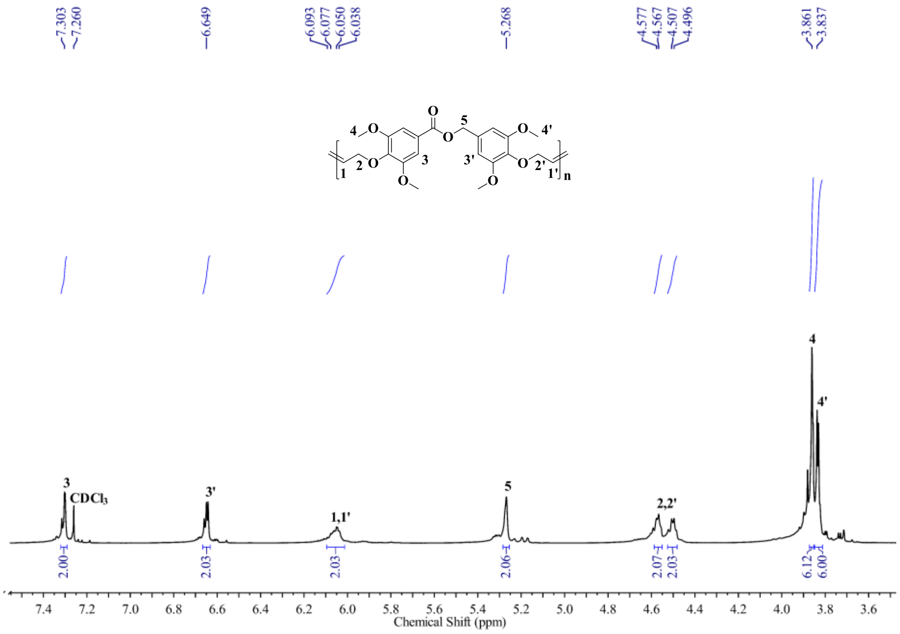


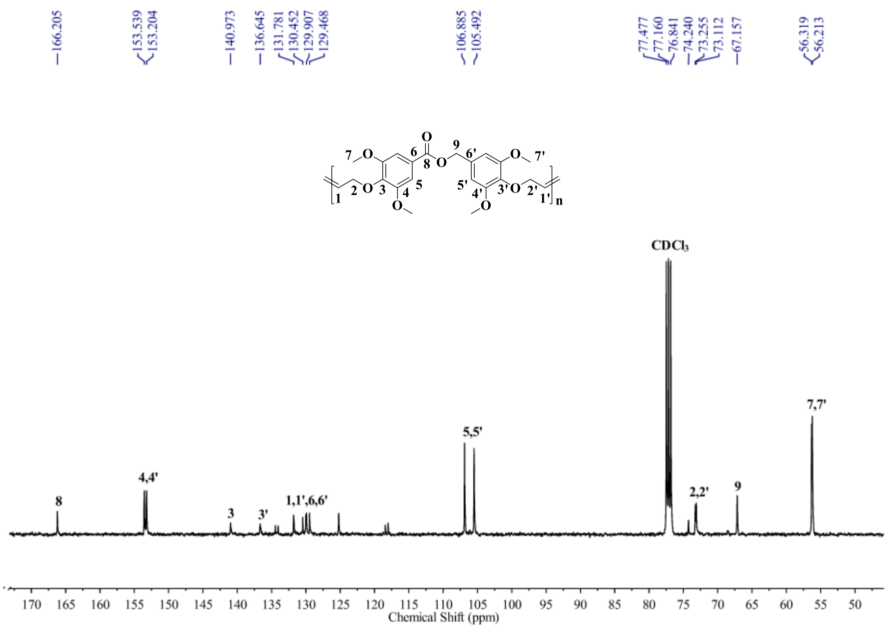
4.1.5. ADMET polymer P3e



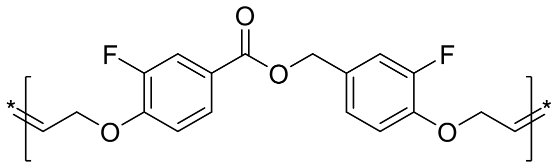
P3e

Yield: 96%. [1]H NMR (400 MHz, $CDCl_3$) δ: 7.30 (s, 2H), 6.65 (s, 2H), 6.09-6.01 (m, 2H), 5.27 (s, 2H), 4.57 (d, J = 3.9 Hz, 2H), 4.50 (d, J = 4.4 Hz, 2H), 3.86 (s, 6H), 3.84 (s, 6H). [13]C NMR (101 MHz, $CDCl_3$) δ: 166.21, 153.54, 153.20, 140.97, 136.64, 131.78, 130.45, 129.91, 129.47, 106.88, 105.49, 74.24, 73.26, 73.11, 67.16, 56.32, 56.21.

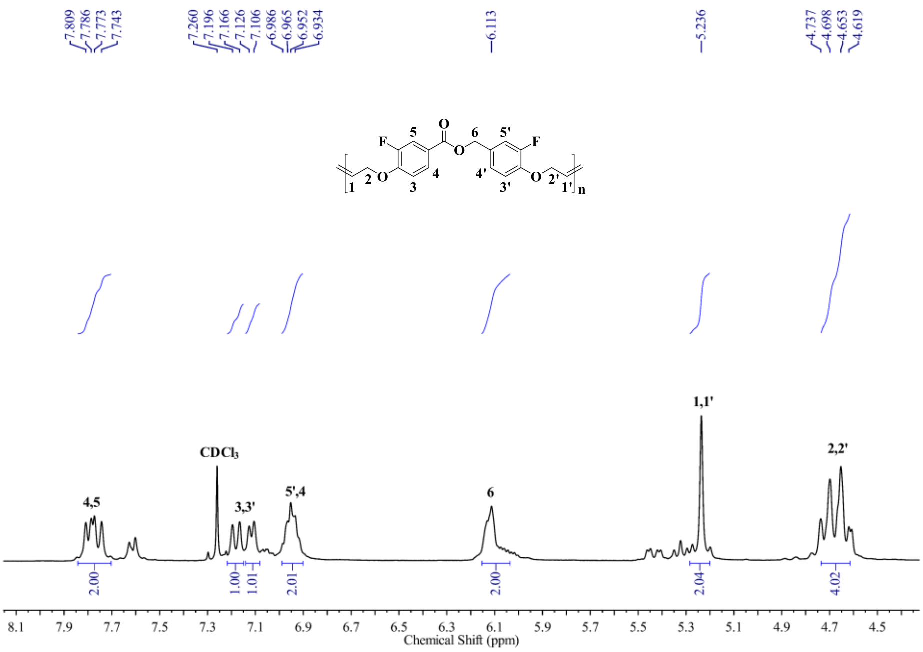


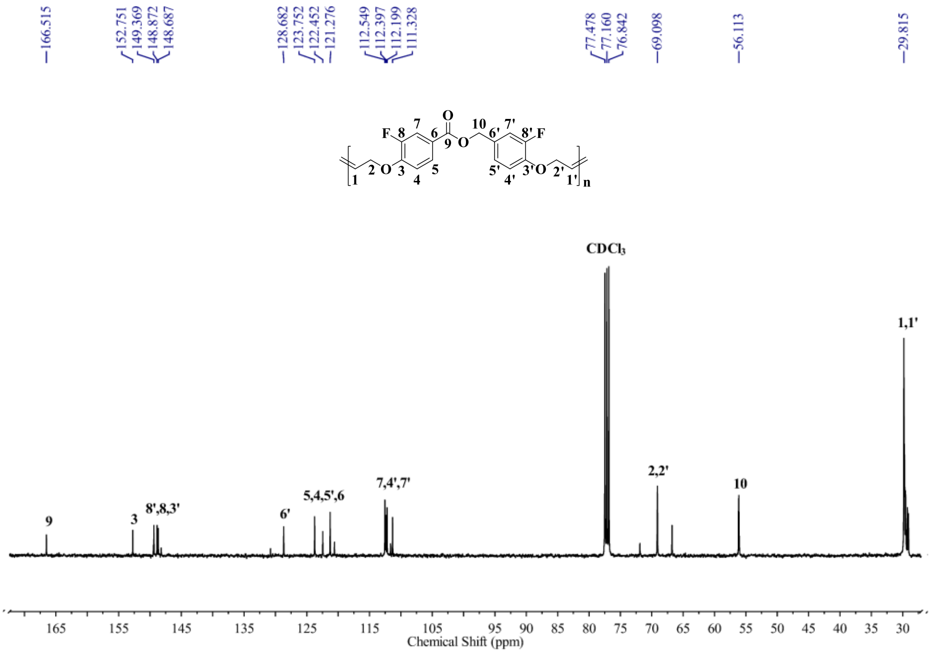


4.1.6. ADMET polymer P3f

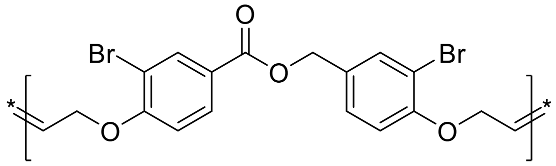


Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (dd, J = 15.7, 10.5 Hz, 2H), 7.18 (d, J = 12.0 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 6.99-6.93 (m, 2H), 6.11 (s, 2H), 5.24 (s, 2H), 4.74-4.61 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.51, 152.75, 149.37, 148.87, 148.69, 128.68, 123.75, 122.45, 121.28, 112.55, 112.40, 112.20, 111.33, 69.10, 56.11, 29.81.



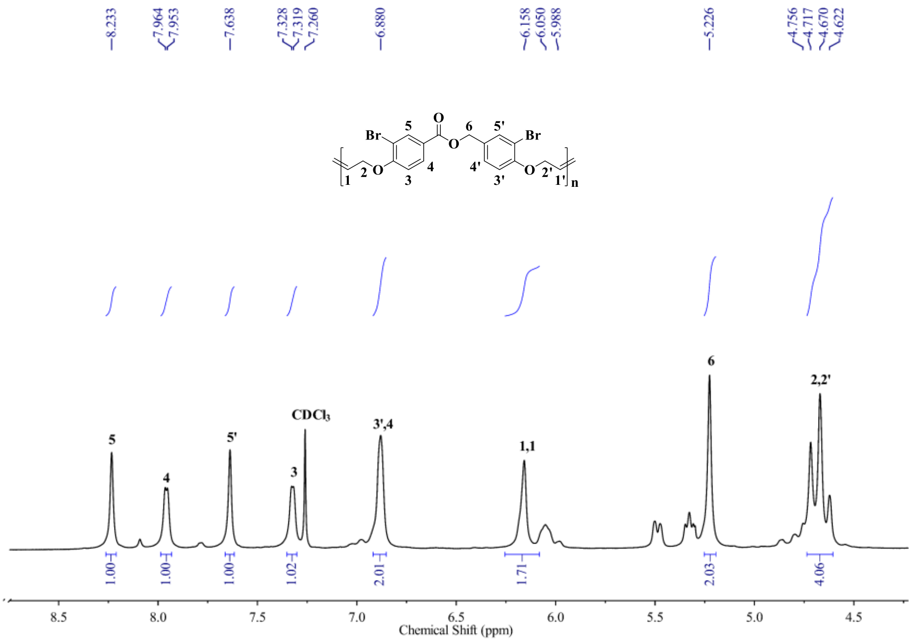


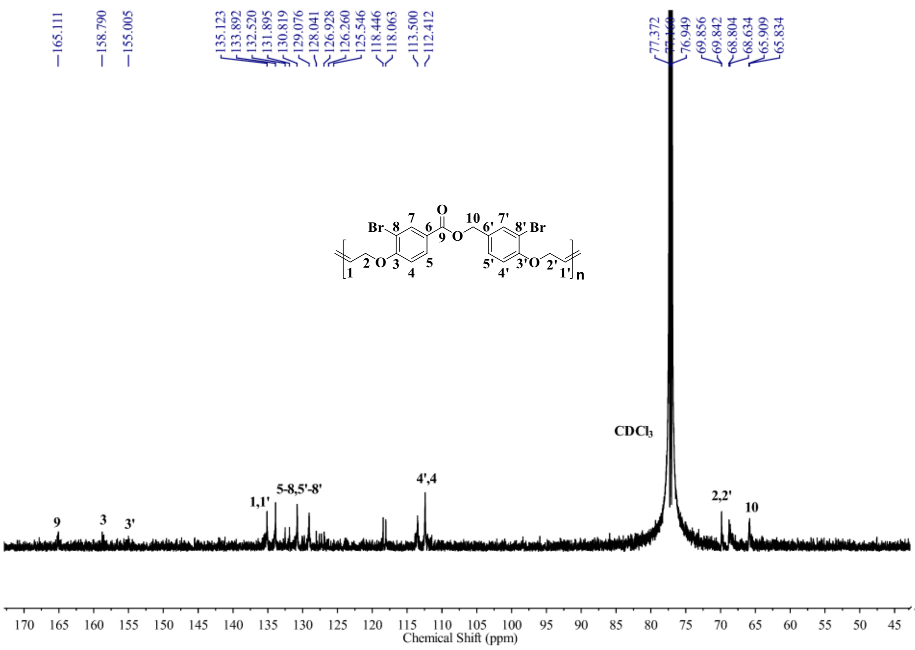
4.1.7. ADMET polymer P3g



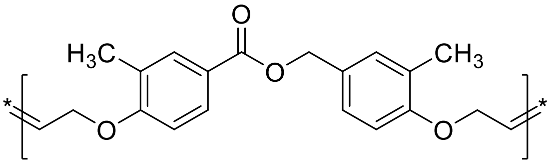
P3g

Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 7.96 (d, J = 6.4 Hz, 1H), 7.64 (s, 1H), 7.32 (d, J = 5.4 Hz, 1H), 6.88 (s, 2H), 6.16 (s, 2H), 5.23 (s, 2H), 4.76-4.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.11, 158.79, 155.00, 135.12, 133.89, 132.52, 131.89, 130.82, 129.08, 128.04, 126.93, 126.26, 125.55, 118.45, 118.06, 113.50, 112.41, 69.86, 69.84, 68.80, 68.63, 65.91, 65.83.



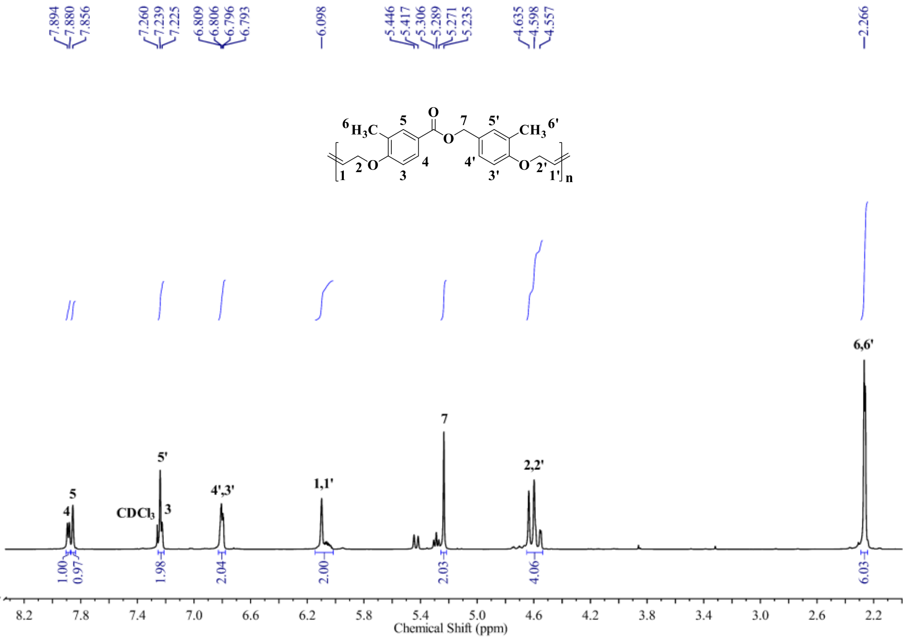


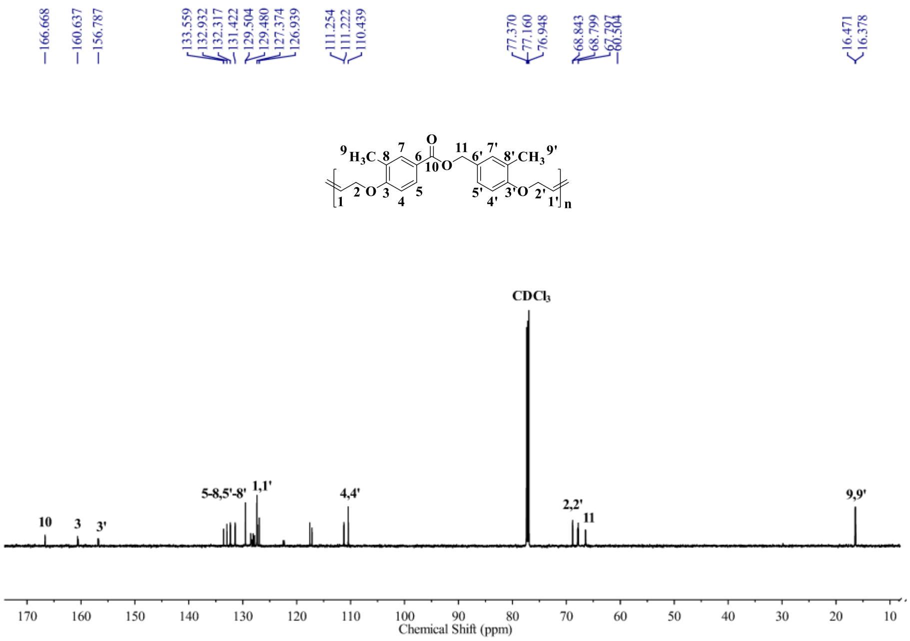
4.1.8. ADMET polymer P3h



P3h

Yield: 92%. [1]H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J = 8.5 Hz, 1H), 7.86 (s, 1H), 7.23 (d, J = 8.1 Hz, 2H), 6.80 (dd, J = 8.0, 2.1 Hz, 2H), 6.10 (s, 2H), 5.24 (s, 2H), 4.64-4.55 (m, 4H), 2.27 (s, 6H). [13]C NMR (101 MHz, $CDCl_3$) δ: 166.67, 160.64, 156.79, 133.56, 132.93, 132.32, 131.42, 129.50, 129.48, 127.37, 126.94, 111.25, 111.22, 110.44, 68.84, 68.80, 67.88, 67.80, 66.48, 60.50, 16.47, 16.38.





4.2. Thermal properties and XRD spectra of ADMET polymers

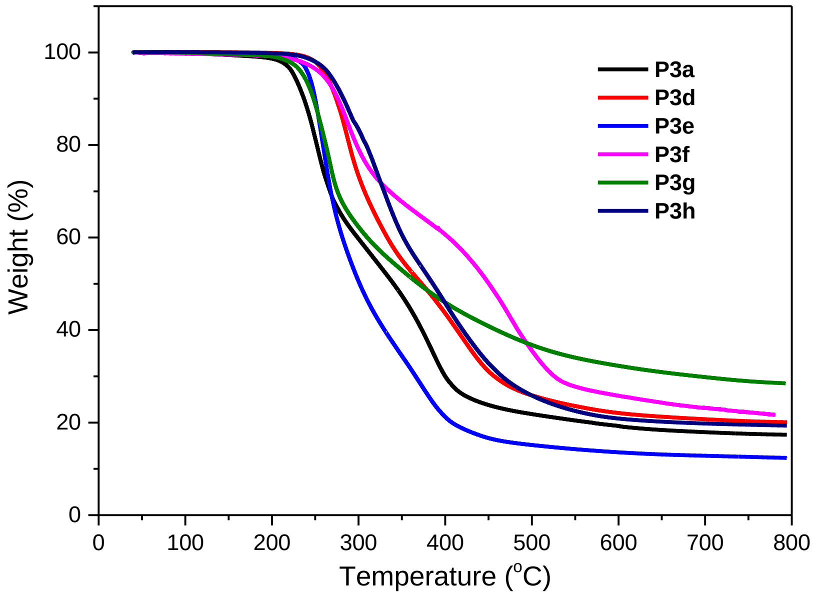


Figure S18. TGA thermograms of **P3a**, **P3d-P3h**.

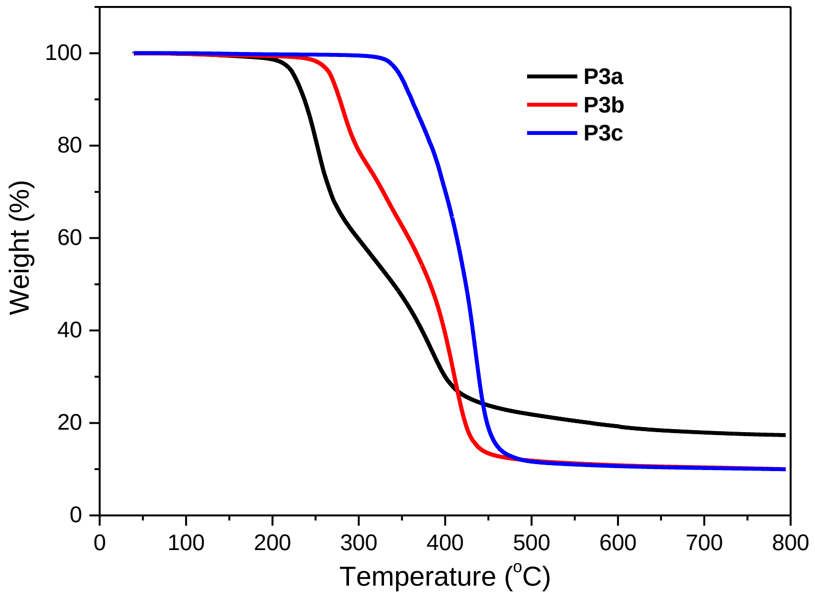


Figure S19. TGA thermograms of **P3a**, **P3b** and **P3c**.

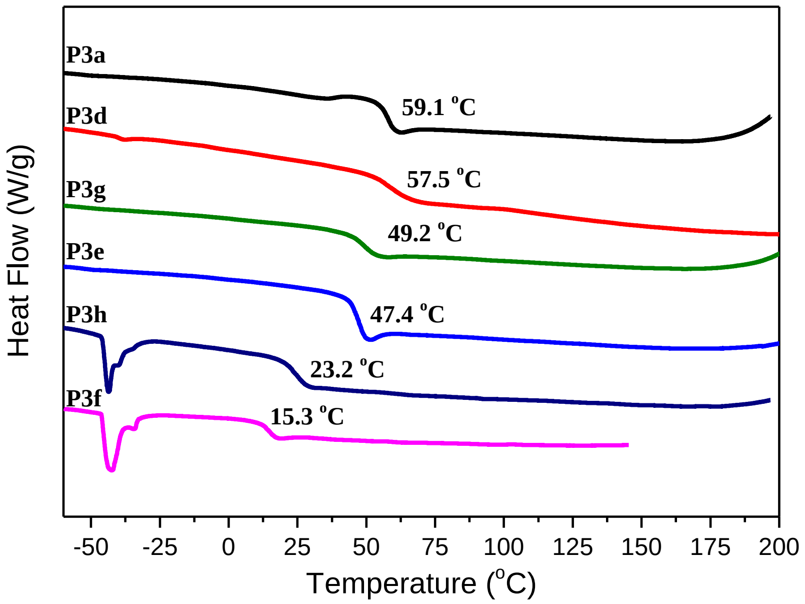


Figure S20. DSC thermograms of **P3a**, **P3d-P3h**.

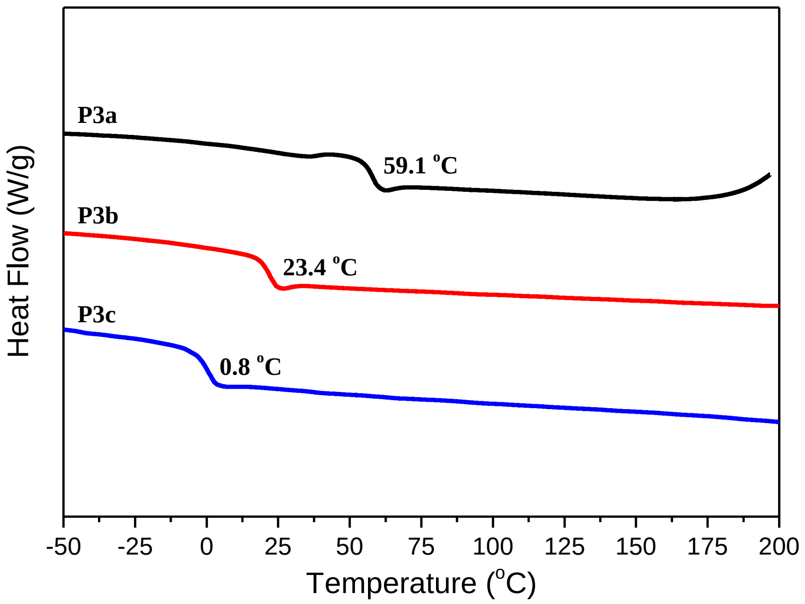


Figure S21. DSC thermograms of **P3a**, **P3b** and **P3c**.

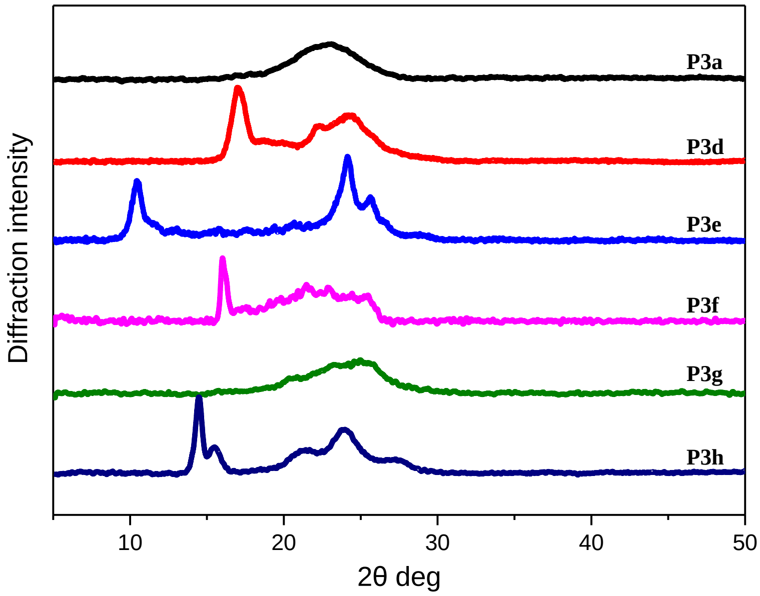


Figure S22. Wide-angle X-ray diffraction of **P3a**, **P3d-P3h**.

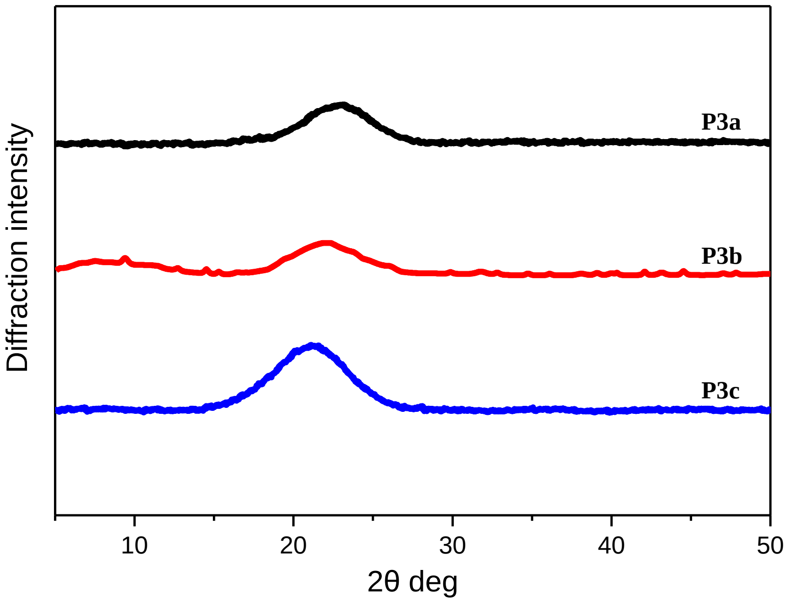
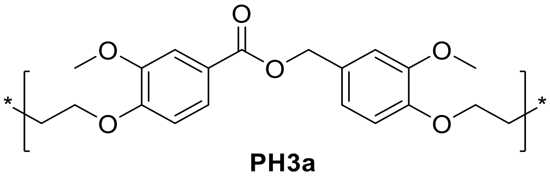


Figure S23. Wide-angle X-ray diffraction of **P3a**, **P3b** and **P3c**.

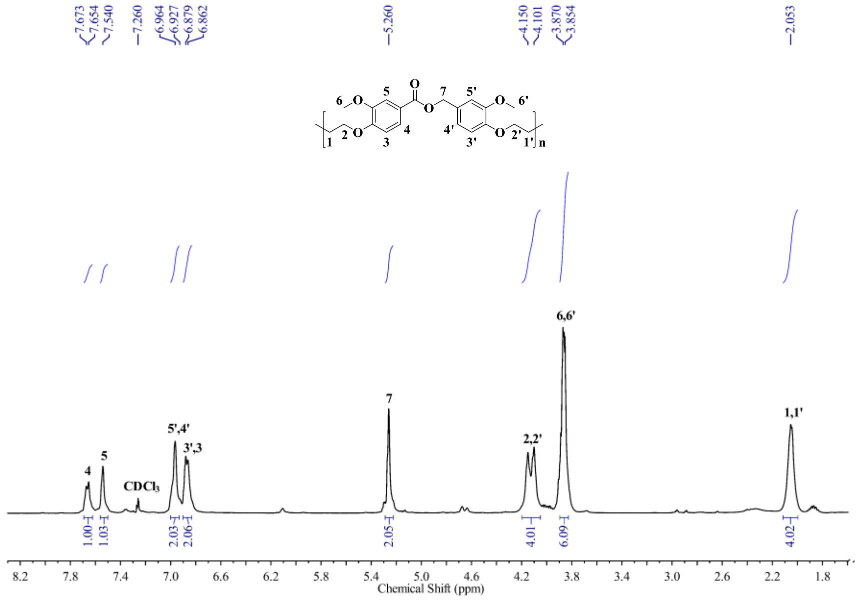
4.3. Representative ^{1}H NMR and ^{13}C NMR spectra of hydrogenated ADMET polymers

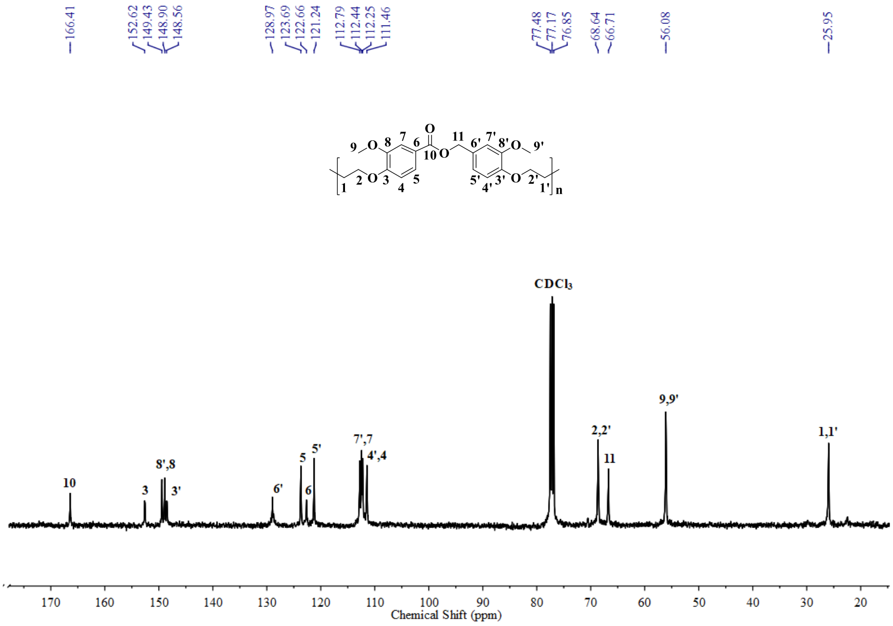
4.3.1. Hydrogenated ADMET polymer PH3a



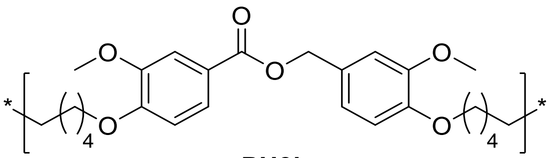
PH3a

Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, J = 7.5 Hz, 1H), 7.54 (s, 1H), 6.96 (s, 2H), 6.87 (d, J = 7.1 Hz, 2H), 5.26 (s, 2H), 4.13 (d, J = 19.6 Hz, 4H), 3.86 (d, J = 6.3 Hz, 6H), 2.05 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.41, 152.62, 149.43, 148.90, 148.56, 128.97, 123.69, 122.66, 121.24, 112.79, 112.44, 112.25, 111.46, 77.48, 77.17, 76.85, 68.64, 66.71, 56.08, 25.95.



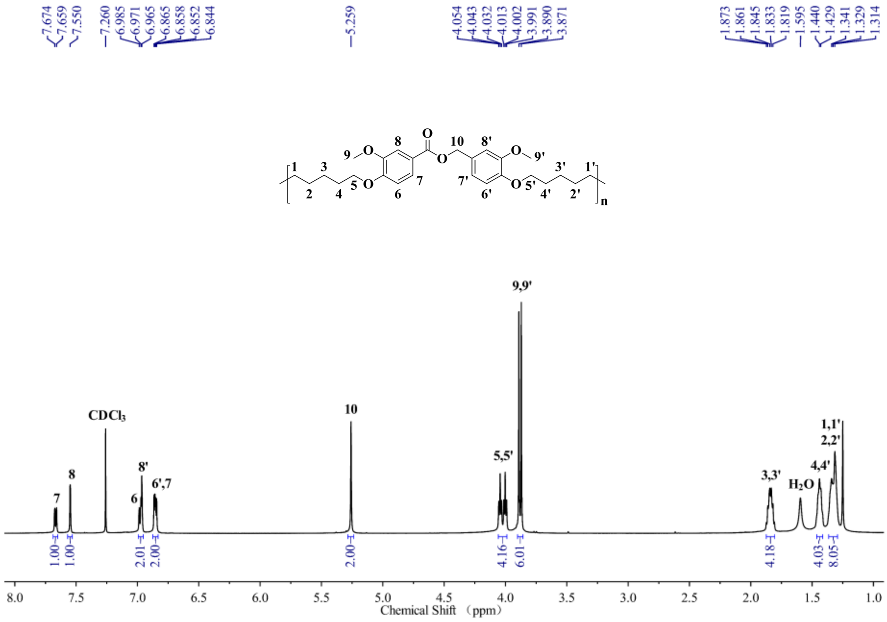


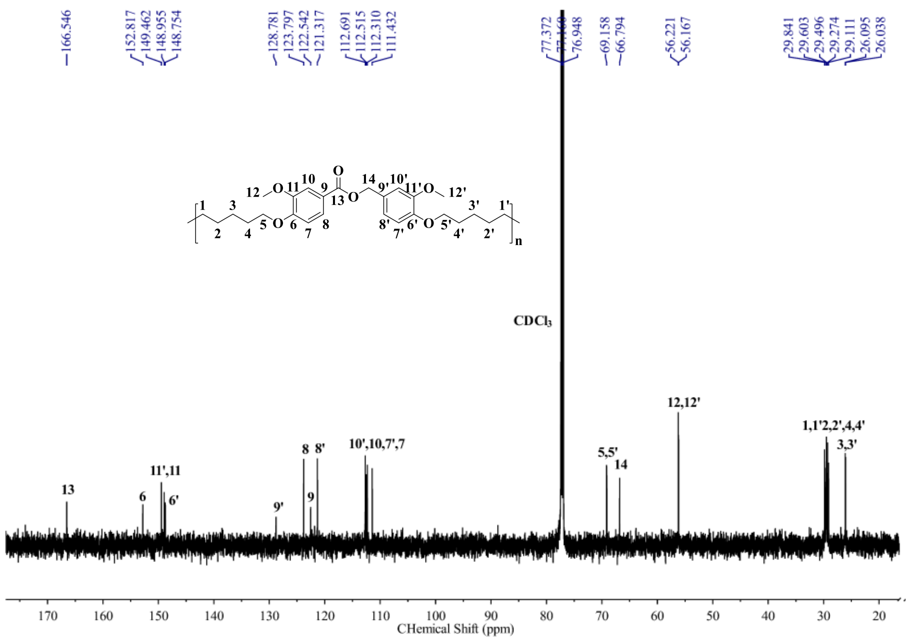
4.3.2. Hydrogenated ADMET polymer PH3b



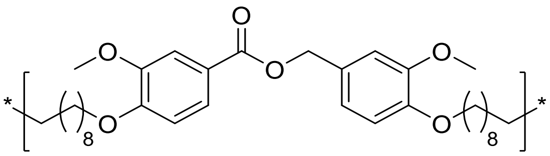
PH3b

Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, J = 8.5 Hz, 1H), 7.55 (s, 1H), 6.99-6.95 (m, 2H), 6.85 (dd, J = 8.2, 4.5 Hz, 2H), 5.26 (s, 2H), 4.02 (dt, J = 24.6, 6.8 Hz, 4H), 3.88 (d, J = 11.8 Hz, 6H), 1.87-1.82 (m, 4H), 1.46-1.40 (m, 4H), 1.37-1.29 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.55, 152.82, 149.46, 148.95, 148.75, 128.78, 123.80, 122.54, 121.32, 112.69, 112.52, 112.31, 111.43, 69.16, 66.79, 56.22, 56.17, 29.84, 29.60, 29.50, 29.27, 29.11, 26.10, 26.04.



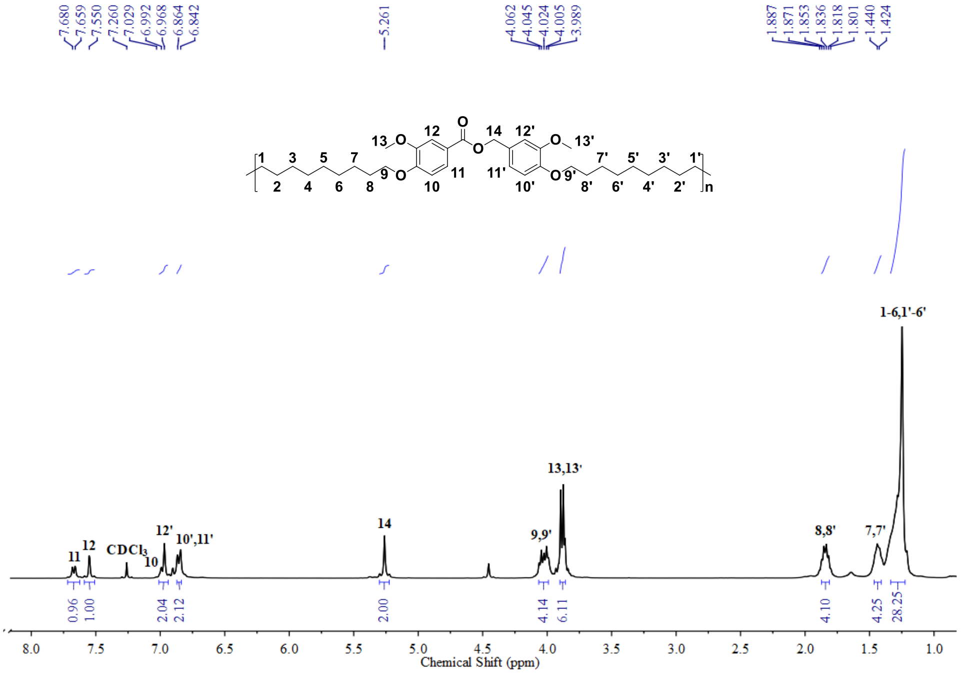


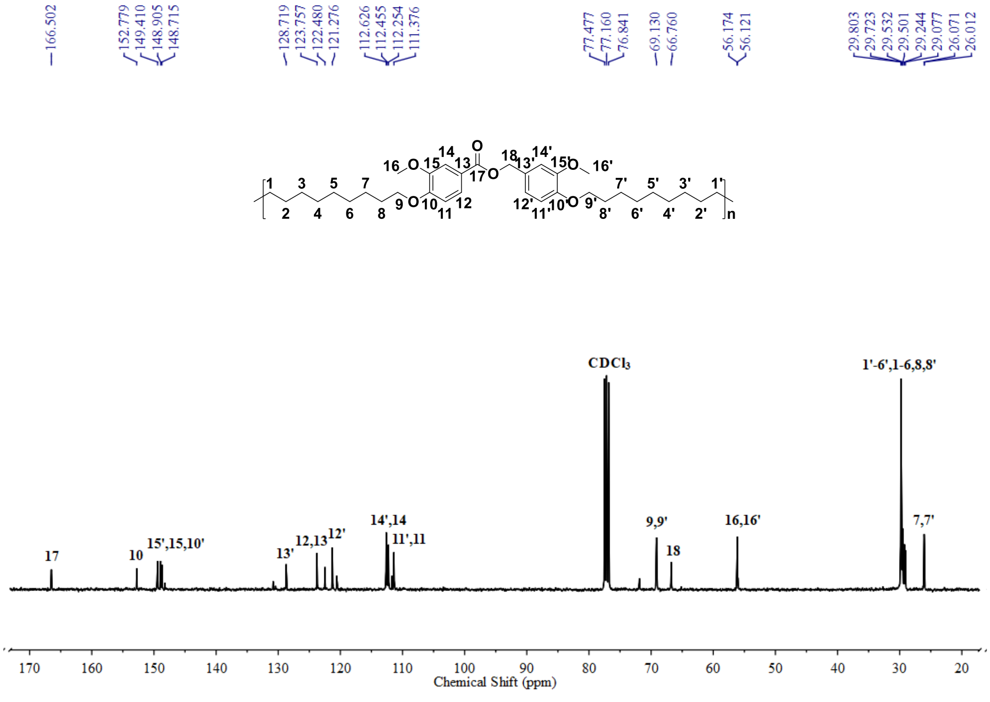
4.3.3. Hydrogenated ADMET polymer PH3c



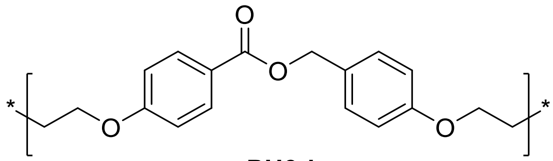
PH3c

Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, J = 8.3 Hz, 1H), 7.55 (s, 1H), 6.98 (d, J = 9.3 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 5.26 (s, 2H), 4.06-3.98 (m, 4H), 3.88 (d, J = 7.8 Hz, 6H), 1.89-1.80 (m, 4H), 1.44 (s, 4H), 1.25 (s, 28H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.50, 152.78, 149.41, 148.91, 148.71, 128.72, 123.76, 122.48, 121.28, 112.63, 112.46, 112.25, 111.38, 69.13, 66.76, 56.17, 56.12, 29.80, 29.72, 29.53, 29.50, 29.24, 29.08, 26.07, 26.01.



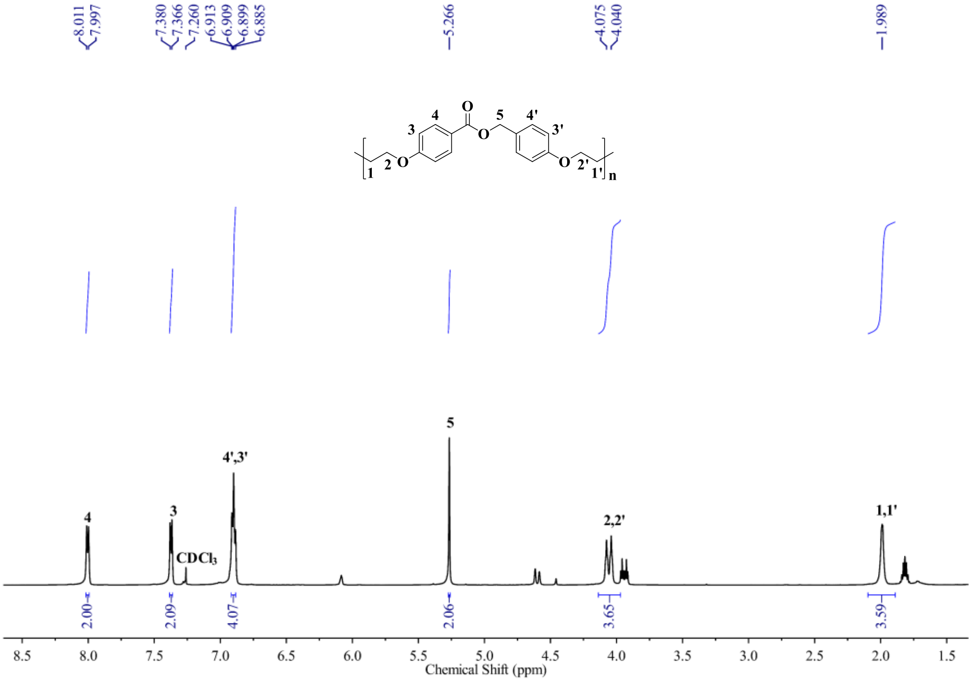


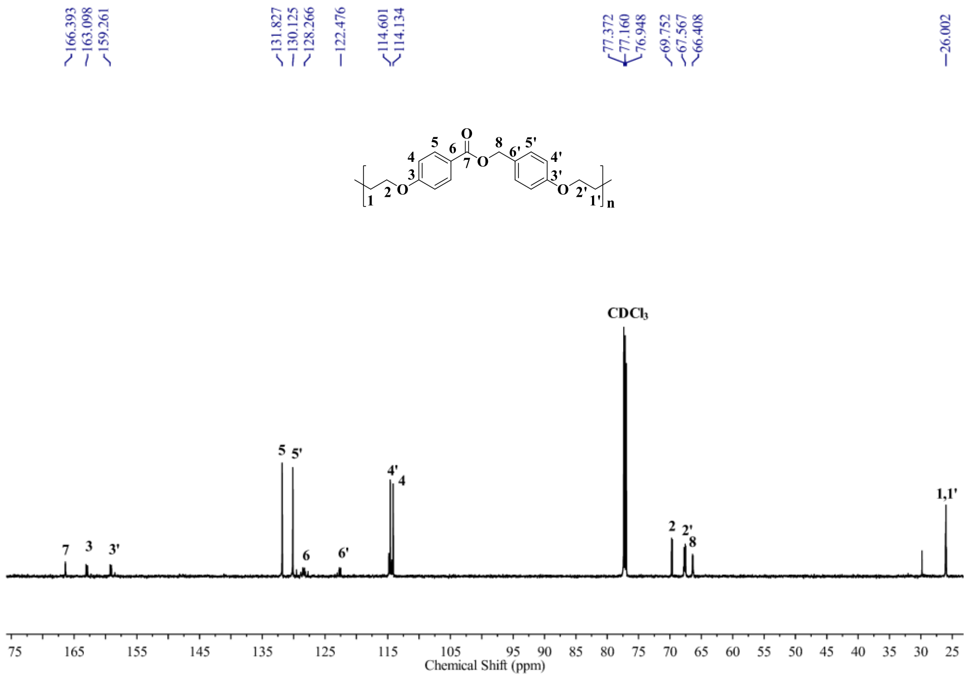
4.3.4. Hydrogenated ADMET polymer PH3d



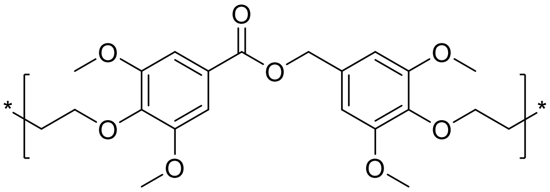
PH3d

Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 6.90 (dd, J = 11.5, 5.1 Hz, 4H), 5.27 (s, 2H), 4.12-3.89 (m, 4H), 1.99 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.39, 163.10, 159.26, 131.83, 130.13, 128.27, 122.48, 114.60, 114.13, 69.75, 67.57, 66.41, 26.00.



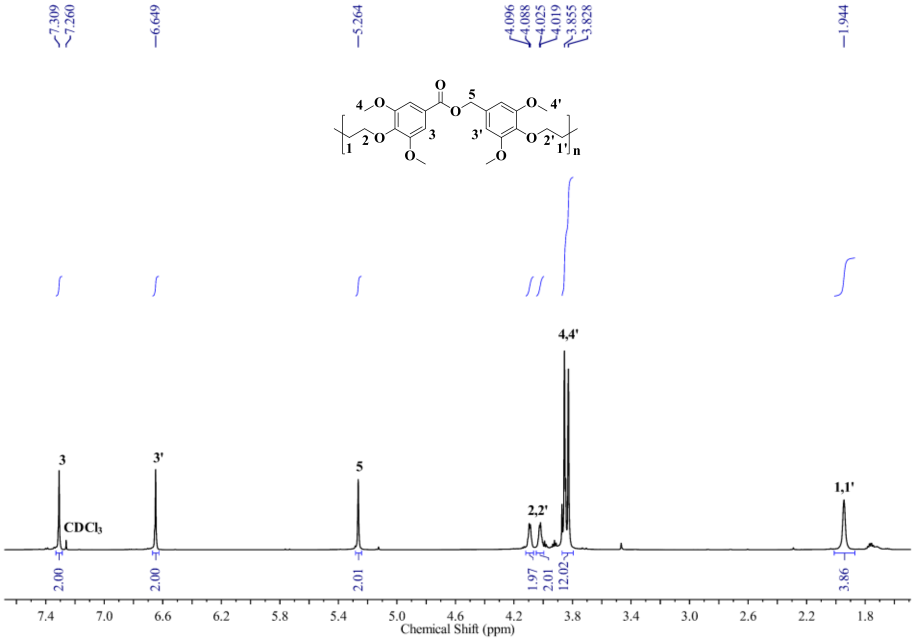


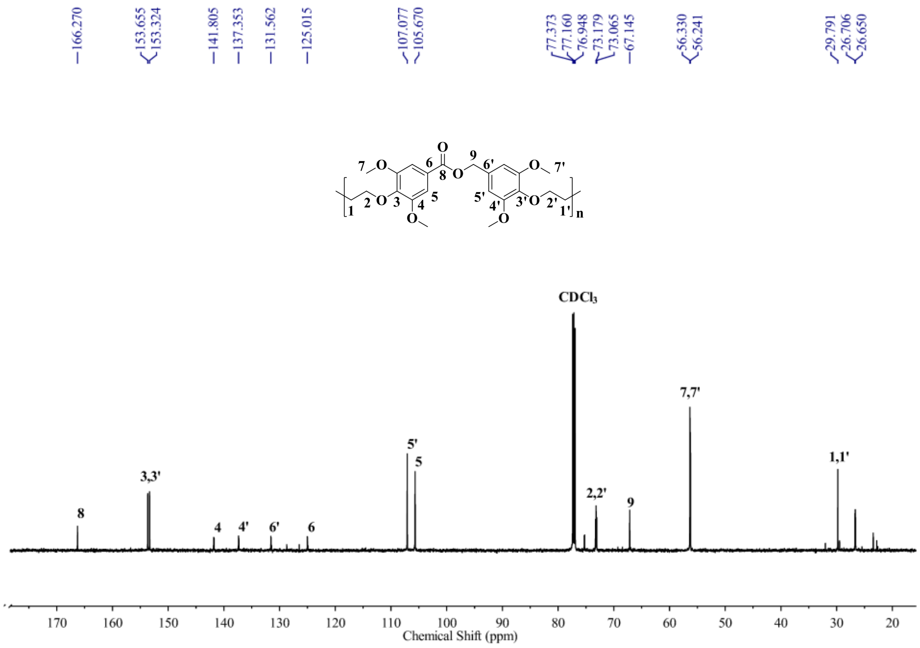
4.3.5. Hydrogenated ADMET polymer PH3e



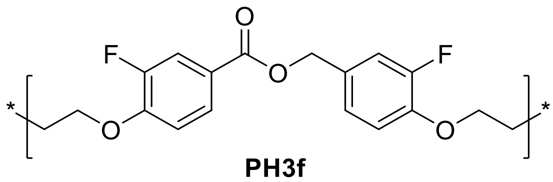
PH3e

Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (s, 2H), 6.65 (s, 2H), 5.26 (s, 2H), 4.09 (d, J = 4.7 Hz, 2H), 4.02 (d, J = 4.0 Hz, 2H), 3.84 (d, J = 16.4 Hz, 12H), 1.94 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.27, 153.66, 153.32, 141.81, 137.35, 131.56, 125.02, 107.08, 105.67, 73.18, 73.06, 67.15, 56.33, 56.24, 29.79, 26.71, 26.65.



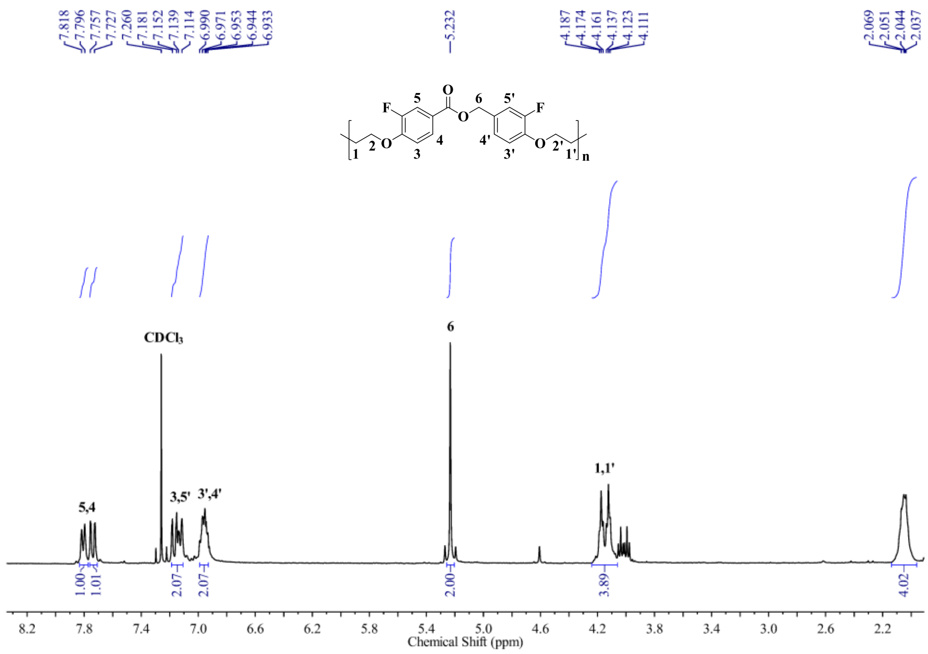


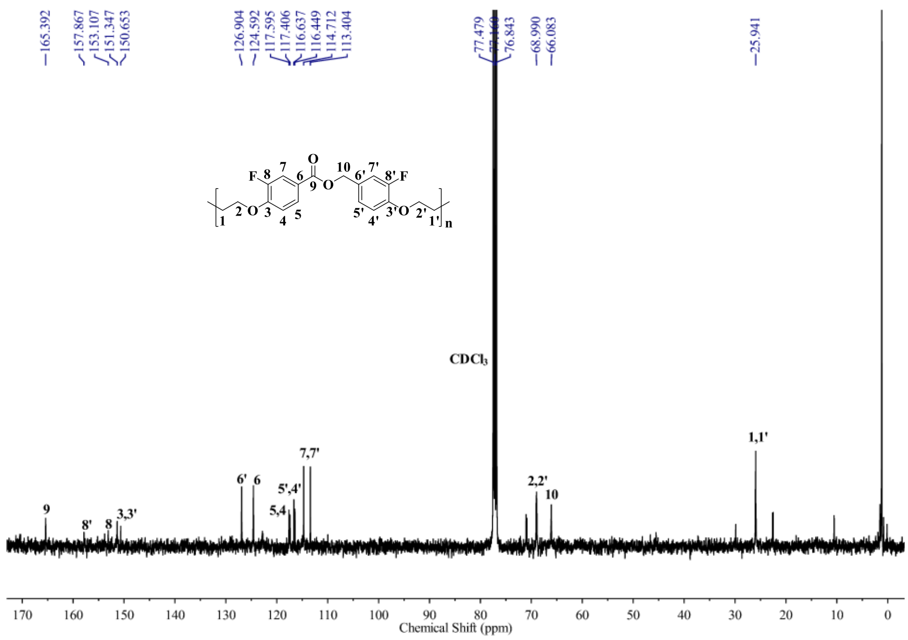
4.3.6. Hydrogenated ADMET polymer PH3f



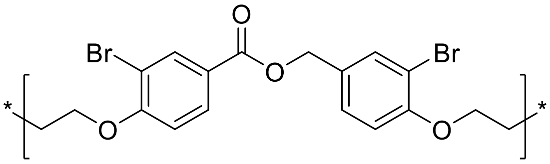
PH3f

Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J = 8.7 Hz, 1H), 7.74 (d, J = 11.6 Hz, 1H), 7.15 (dd, J = 16.0, 10.7 Hz, 2H), 7.00-6.91 (m, 2H), 5.23 (s, 2H), 4.15 (dt, J = 19.8, 4.9 Hz, 4H), 2.10-2.01 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.39, 157.87, 153.11, 151.35, 150.65, 126.90, 124.59, 117.59, 117.41, 116.64, 116.45, 114.71, 113.40, 68.99, 66.08, 25.94.



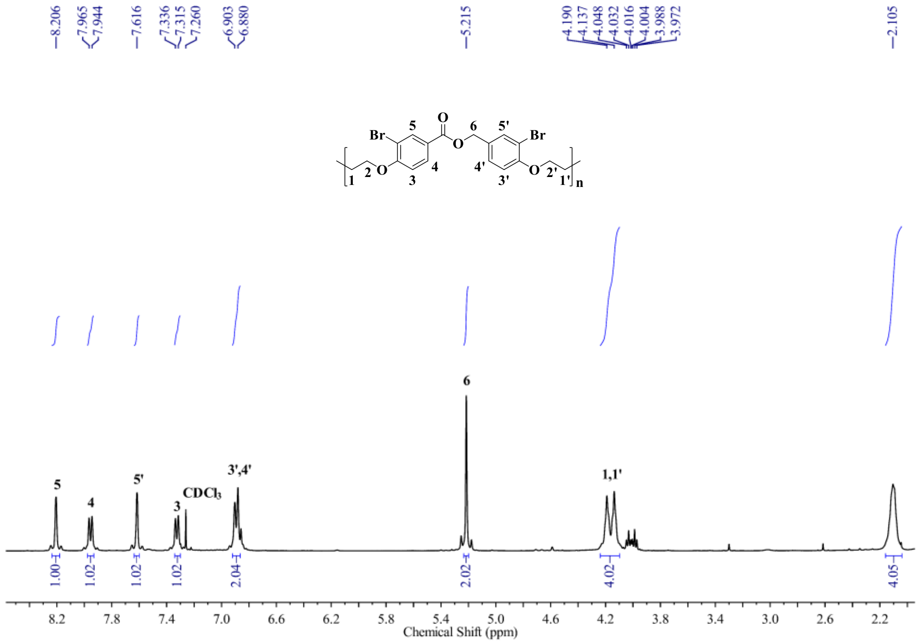


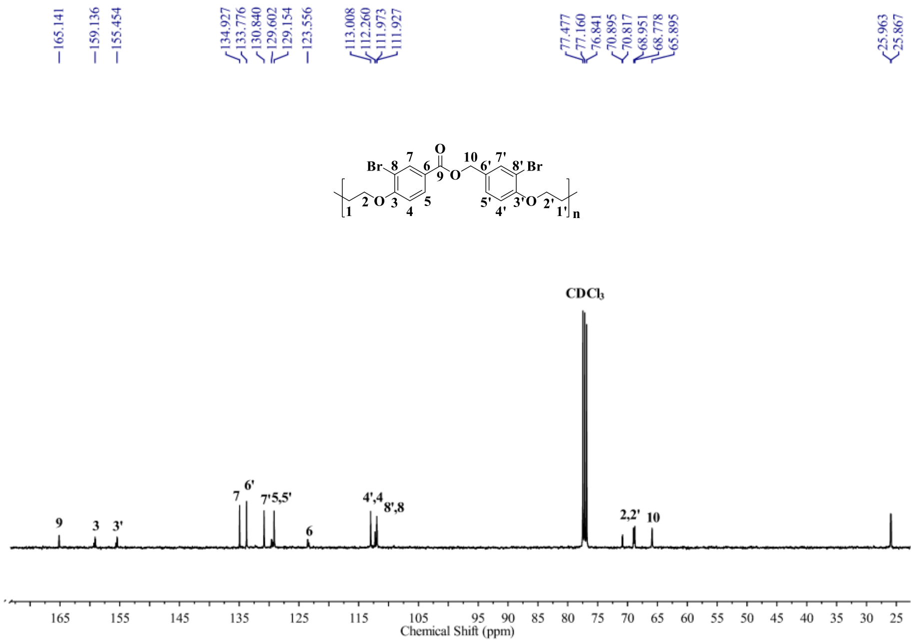
4.3.7. Hydrogenated ADMET polymer PH3g



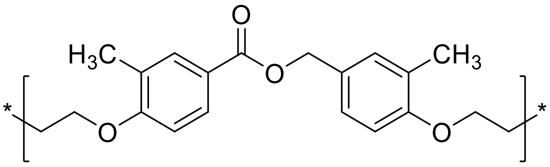
PH3g

Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.62 (s, 1H), 7.33 (d, J = 8.3 Hz, 1H), 6.89 (d, J = 9.2 Hz, 2H), 5.22 (s, 2H), 4.16 (d, J = 21.3 Hz, 4H), 2.10 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.14, 159.14, 155.45, 134.93, 133.78, 130.84, 129.60, 129.15, 123.56, 113.01, 112.26, 111.97, 111.93, 70.89, 70.82, 68.95, 68.78, 65.90, 25.96, 25.87, 22.58, 22.47, 10.68, 10.62.



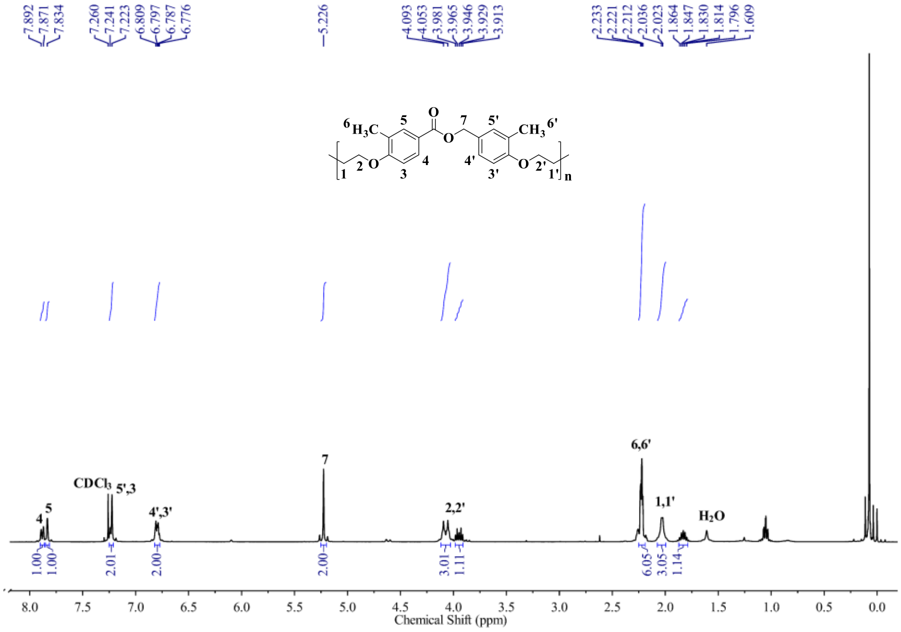


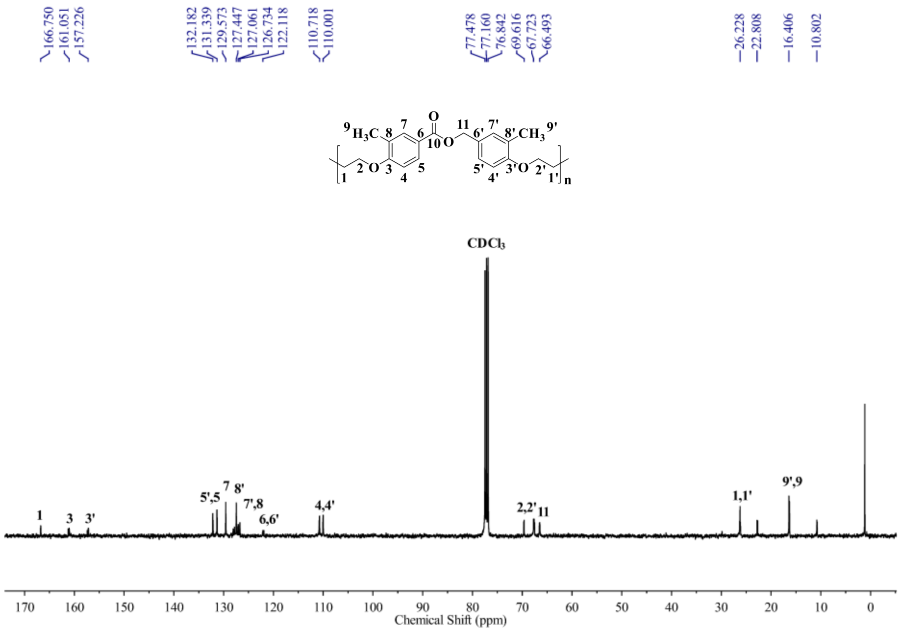
4.3.8. Hydrogenated ADMET polymer PH3h



PH3h

Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J = 8.5 Hz, 1H), 7.83 (s, 1H), 7.23 (d, J = 7.1 Hz, 2H), 6.79 (dd, J = 8.4, 4.7 Hz, 2H), 5.23 (s, 2H), 4.11 – 3.91 (m, 4H), 2.22 (t, J = 4.2 Hz, 6H), 2.03 (d, J = 5.3 Hz, 3H), 1.83 (dt, J = 13.6, 6.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.75, 161.05, 157.23, 132.18, 131.34, 129.57, 127.45, 127.06, 126.73, 122.12, 110.72, 110.00, 69.62, 67.72, 66.49, 26.23, 22.81, 16.41, 10.80.





4.4. Thermal properties and XRD spectra of hydrogenated ADMET polymers

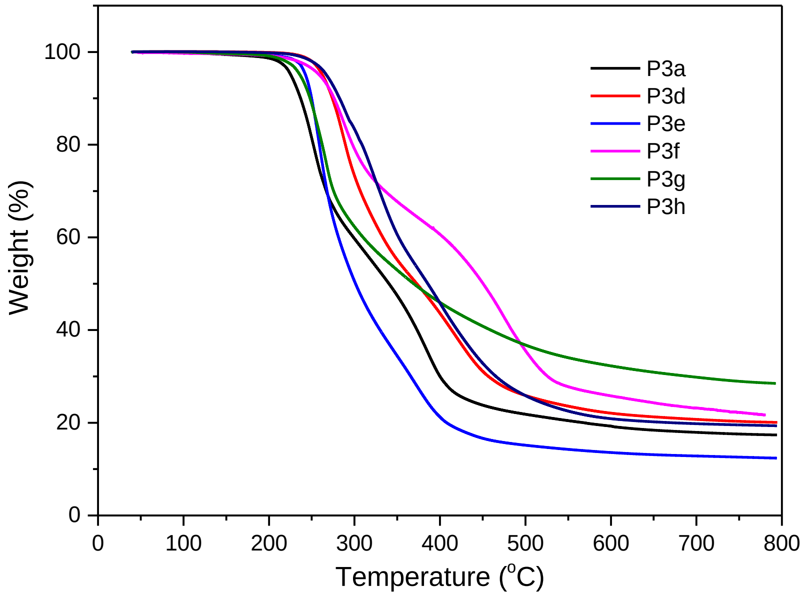


Figure S24. TGA thermograms of **PH3a**, **PH3d-PH3h**.

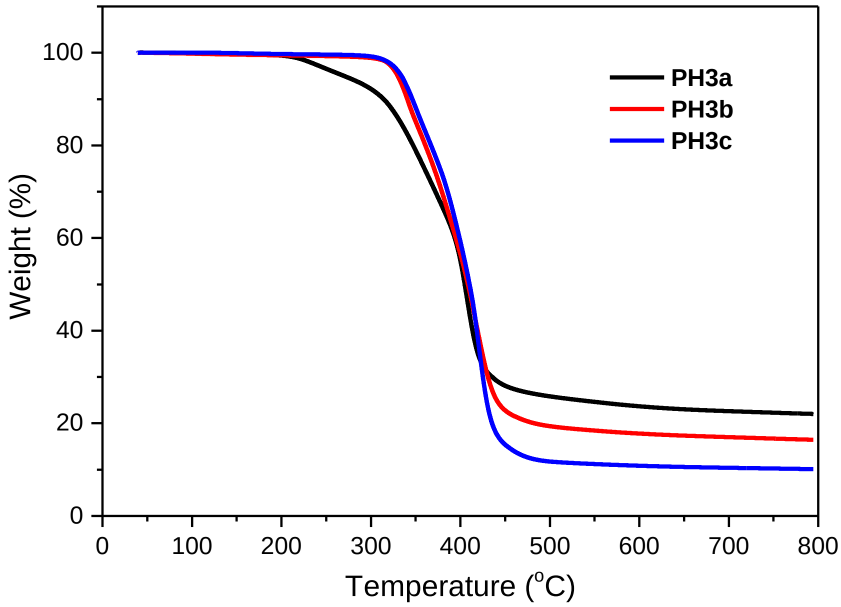


Figure S25. TGA thermograms of **PH3a**, **PH3b** and **PH3c**.

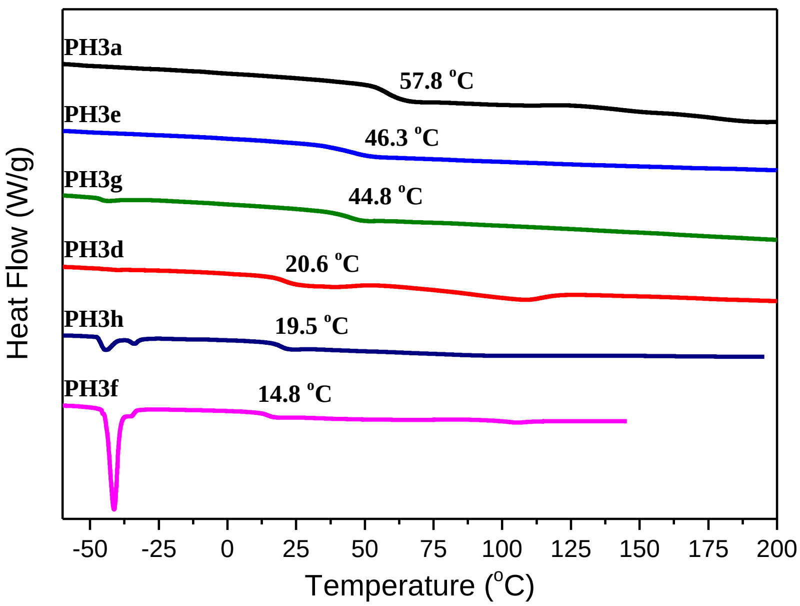


Figure S26. DSC thermograms of **PH3a**, **PH3d-PH3h**.

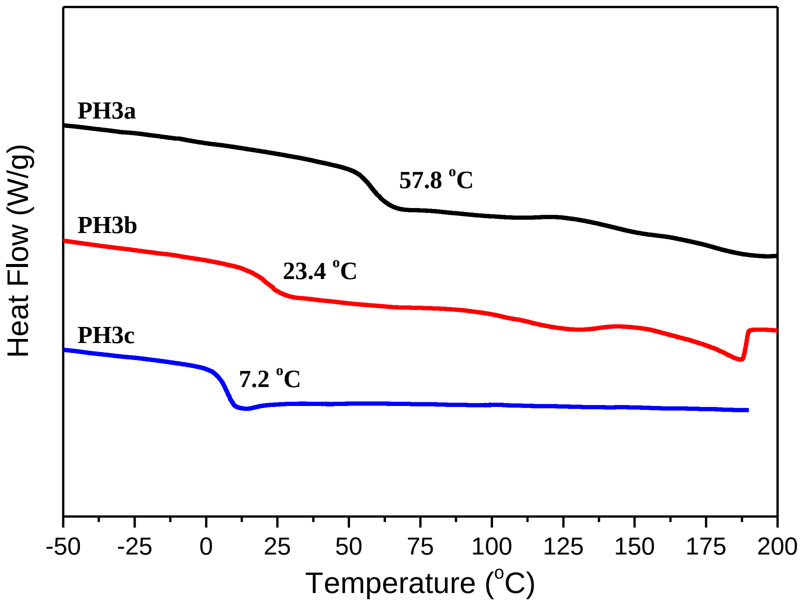


Figure S27. DSC thermograms of **PH3a**, **PH3b** and **PH3c**.

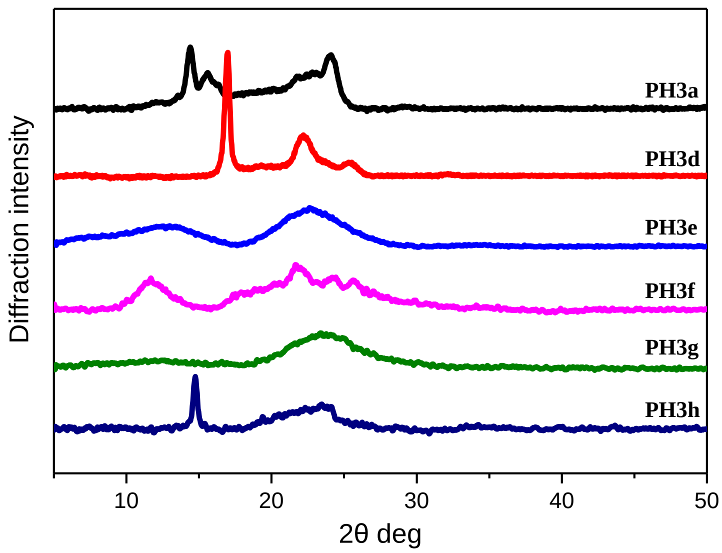


Figure S28. Wide-angle X-ray diffraction of **PH3a**, **PH3d-PH3h**.

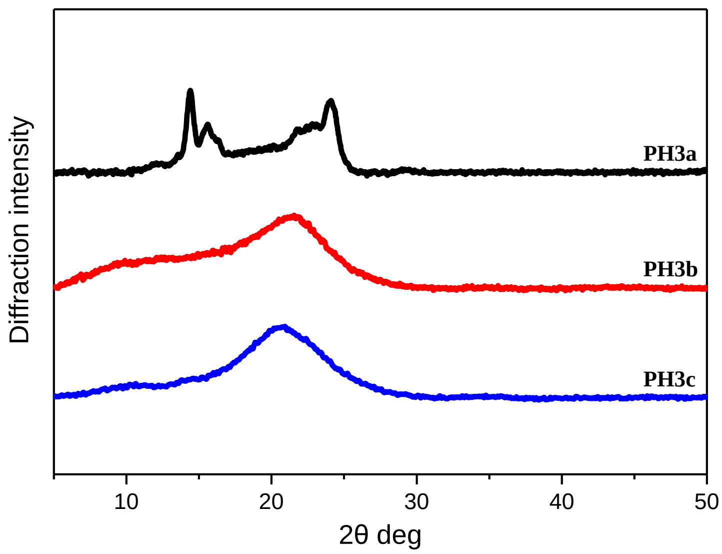


Figure S29. Wide-angle X-ray diffraction of **PH3a**, **PH3b** and **PH3c**.

5. Representative ^{19}F spectra

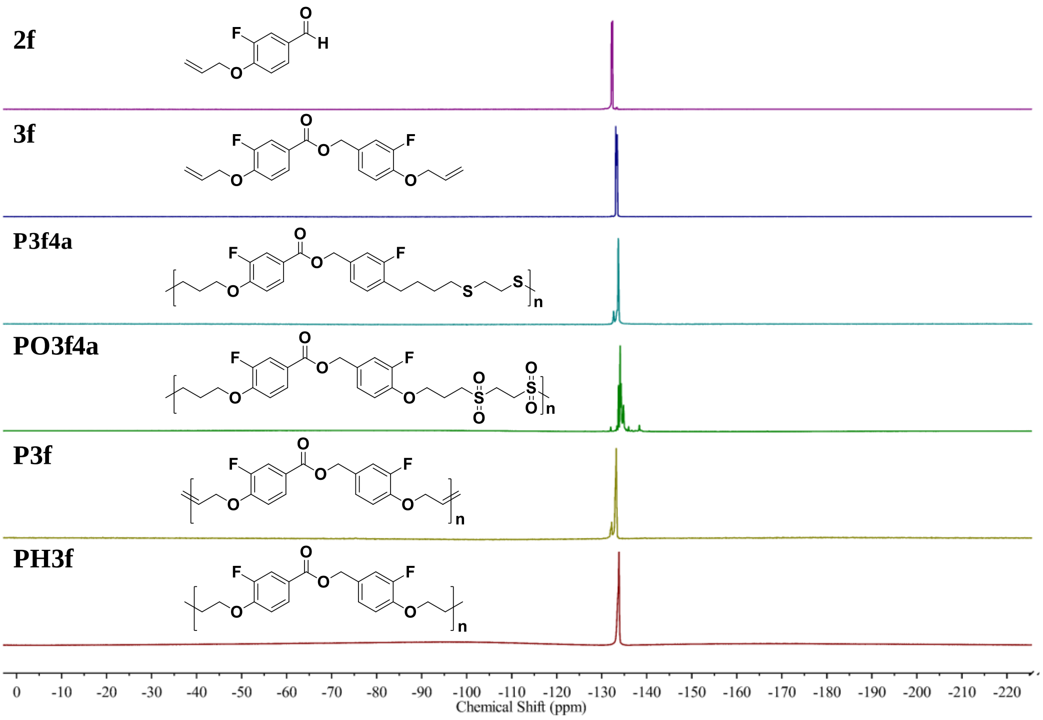


Figure S30. Comparative ^{19}F NMR spectra of containing fluorine products.

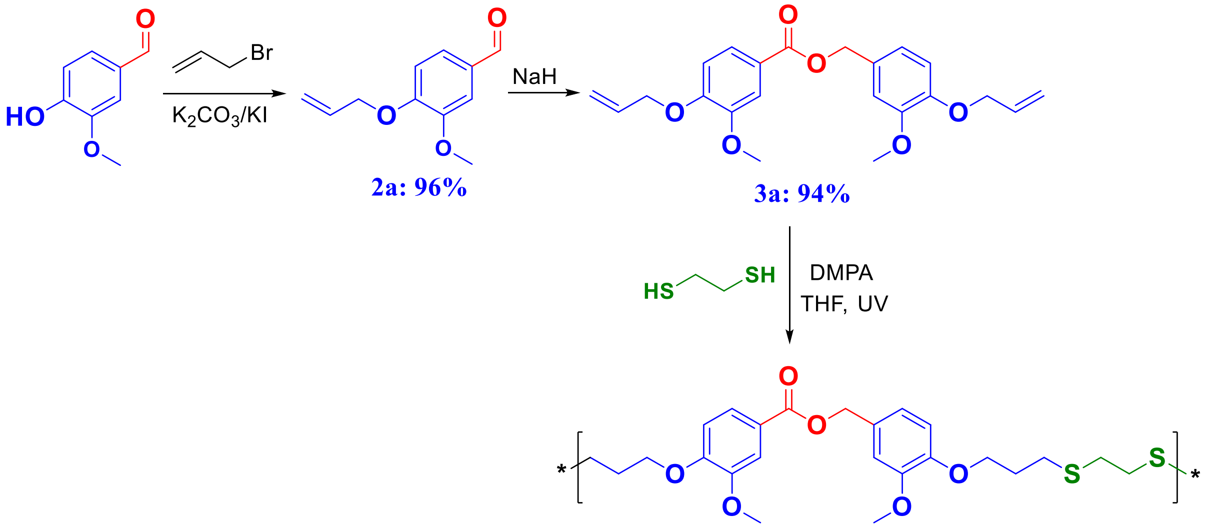
6. E-factor analysis of the process toward bio-based polyesters

R. A. Sheldon has proposed the environment impact factor (*E*-factor) to quantify the sustainability of a process.[6-8] The *E*-factor is calculated by kilograms of waste generated including 10% of solvent losses divided by kilograms of desired product.

$$\text{E-factor} = \frac{\sum m\,(rawmaterials) + \sum m\,(reagents) + \sum m\,(solvents) \times 10\% - m\,(product)}{m\,(product)}$$

Herein we provide details of our *E*-factor anaylsis of the bio-based polyesters (Tables S2-S19). The overall process *E*-factor of vanillin-based polymer **P3a4a, P3a4b, P3a4c, P3a4d, PO3a4a, P3a, P3b, P3c and PH3a** were determined as 3.3, 3.4, 2.9, 2.8, 3.9, 6.1, 5.7, 5.1 and 10.8 kg/kg, respectively, which are in accordance with Sheldon's analysis of bulk and fine chemicals that have an *E*-factor of 4-50.[6-8]

Table S2. Material input-output table for the process toward **P3a4a**.



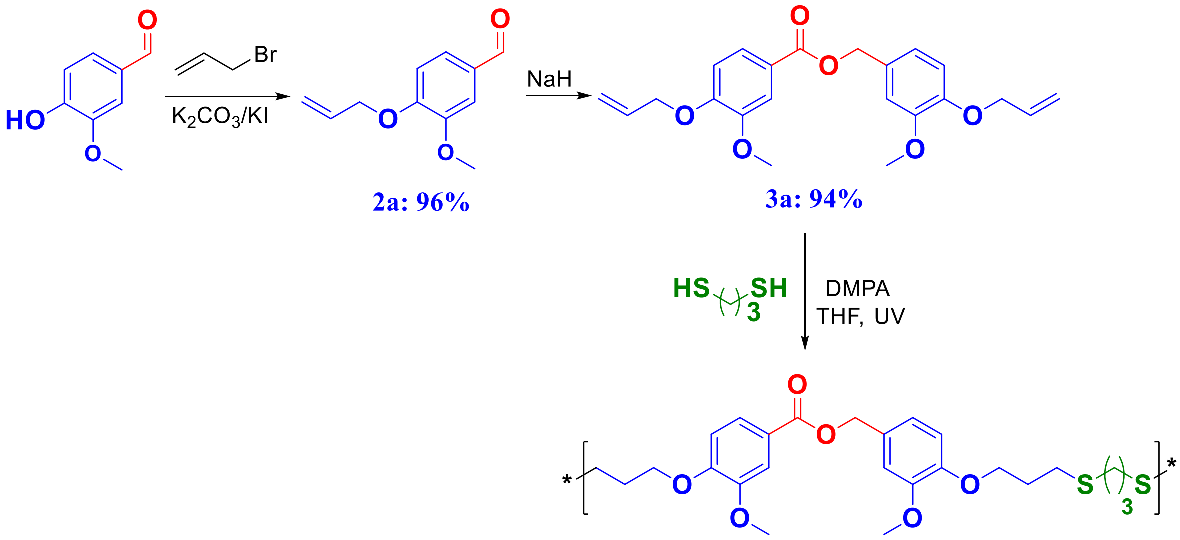
P3a4a: 96%

Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Input volume (L)	Output weight (kg)	Output mol	Yield
1	vanillin	raw material		152.15		1	4.838	0.736				
	allyl bromide	raw material		120.98	1.398	2	9.677	1.171				
	K_2CO_3	reagent		138.21		1.5	7.258	1.003				
	KI	reagent		166.01		0.2	0.968	0.161				
	ethanol	solvent		46.07	0.79			3.822	4.838			96%
			2a	192.21						0.893	4.645	
2	**2a**	intermediate		192.21		1	4.645	0.893				
	NaH	reagent		24		0.1	0.464	0.011				
			3a	384.42						0.893	4.645	94%
3	**3a**	intermediate		384.42		1	2.174	0.836				
	1,2-						2.174	0.205				
	Ethanedithiol	raw material		94.2	1.12	1						
	DMPA	reagent		256.3		0.05	0.109	0.028				
	THF	solvent		72.11	0.889			6.377	7.173			
			P3a4a	478.62						1.000	2.089	96%

Table S3. E-factor analysis of the process toward **P3a4a**.

Step	Raw	Reagen	Solven	Produc	Step E-Factor	E-Factor
1	1.90	1.164	3.822	0.893	2.867	2.560
2	0.89	0.011	0.000	0.836	0.082	0.068
3	1.04	0.028	6.377	1.000	0.706	0.706
Tota	2.11	1.203	10.20	1.000		3.334

Table S4. Material input-output table for the process toward **P3a4b**.



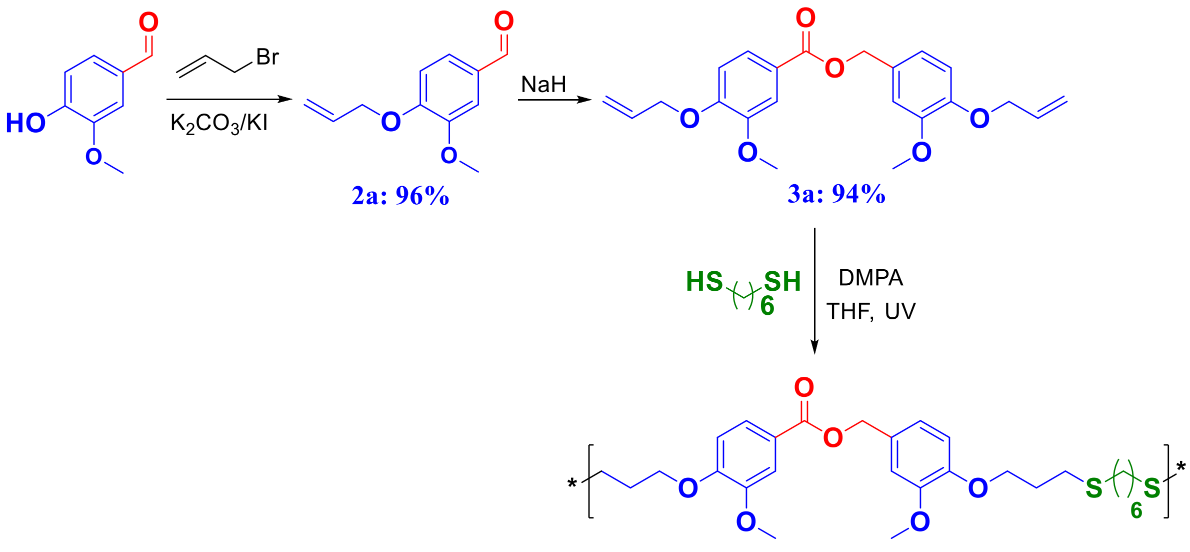
P3a4b: 93%

Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Input volume (L)	Output weight (kg)	Output mol	Yield
1	vanillin	raw material		152.15		1	4.884	0.743				
	allyl bromide	raw material		120.98	1.398	2	9.769	1.182				
	K_2CO_3	reagent		138.21		1.5	7.326	1.013				
	KI	reagent		166.01		0.2	0.977	0.162				
	ethanol	solvent		46.07	0.79			3.859	4.884			96%
			2a	192.21						0.901	4.689	
2	**2a**	intermediate		192.21		1	4.689	0.901				
	NaH	reagent		24		0.1	0.469	0.011				
			3a	384.42						0.844	2.194	94%
3	**3a**	intermediate		384.42		1	2.194	0.844				
	1,3-propanedithiol	raw material		108.22	1.12	1	2.194	0.237				
	DMPA	reagent		256.3		0.05	0.110	0.028				
	THF	solvent		72.11	0.889			6.438	7.242			
			P3a4b	492.65						1	2.030	93%

Table S5. E-factor analysis of the process toward **P3a4b**.

Step number	Raw material (kg)	Reagent (kg)	Solvent	Product (kg)	Step E-Factor	E-Factor
1	1.925	1.175	3.859	0.901	2.867	2.584
2	0.901	0.011	0.000	0.844	0.082	0.069
3	1.081	0.028	6.438	1.000	0.753	0.753
Total	2.162	1.214	10.30	1.000		3.406

Table S6. Material input-output table for the process toward **P3a4c**.

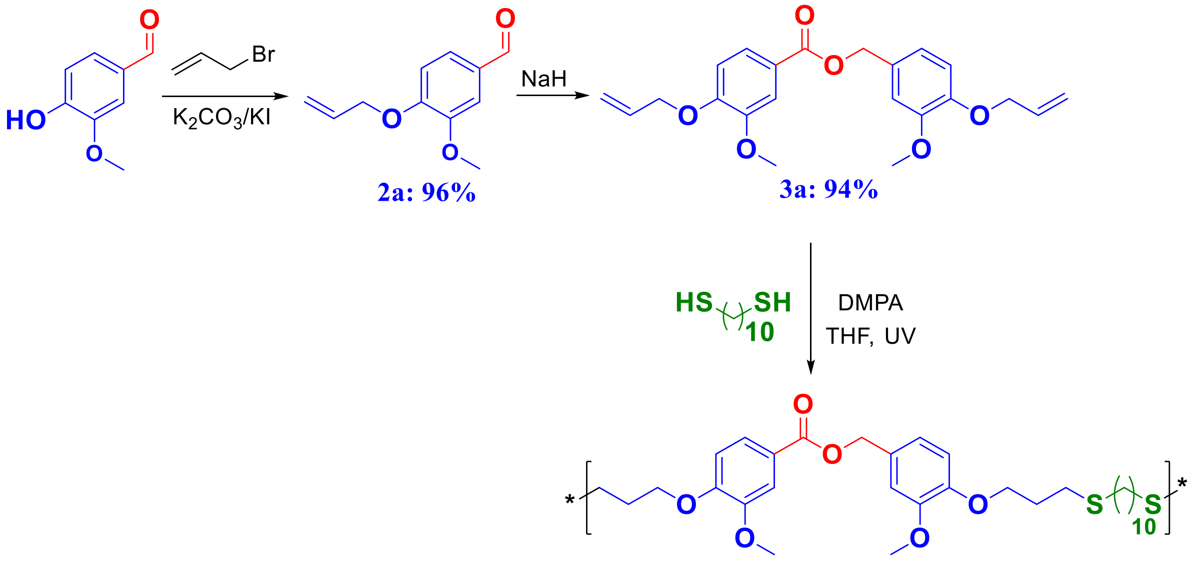


Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Input volume (L)	Output weight (kg)	Output mol	Yield
1	vanillin	raw material		152.15		1	4.282	0.652				
	allyl bromide	raw material		120.98	1.398	2	8.565	1.036				
	K_2CO_3	reagent		138.21		1.5	6.424	0.888				
	KI	reagent		166.01		0.2	0.856	0.142				
	ethanol	solvent		46.07	0.79			3.383	4.282			96%
			2a	192.21						0.790	4.111	
2	**2a**	intermediate		192.21		1	4.111	0.790				
	NaH	reagent		24		0.1	0.411	0.010				
			3a	384.42						0.740	1.924	94%
3	**3a**	intermediate		384.42		1	1.924	0.740				
	1,6-Hexanedithiol	raw material		150.3	1.12	1	1.924	0.289				
	DMPA	reagent		256.3		0.05	0.096	0.025				
	THF	solvent		72.11	0.889			5.644	6.349			
			P3a4c	534.73						1	1.870	97%

Table S7. E-factor analysis of the process toward **P3a4c**.

Step number	Raw material (kg)	Reagent (kg)	Solvent	Product (kg)	Step E-Factor	E-Factor
1	1.688	1.030	3.383	0.790	2.867	2.266
2	0.790	0.010	0.000	0.740	0.082	0.060
3	1.029	0.025	5.644	1.000	0.618	0.618
Total	1.977	1.065	9.03	1.000		2.944

Table S8. Material input-output table for the process toward **P3a4d**.



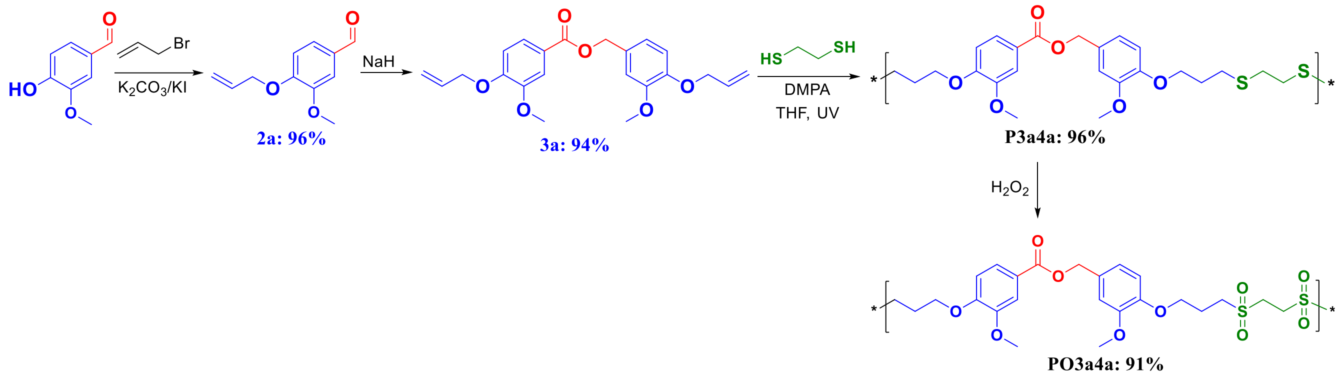
P3a4d: 93%

Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Input volume (L)	Output weight (kg)	Output mol	Yield
1	vanillin	raw material		152.15		1	4.033	0.614				
	allyl bromide	raw material		120.98	1.398	2	8.067	0.976				
	K_2CO_3	reagent		138.21		1.5	6.050	0.836				
	KI	reagent		166.01		0.2	0.807	0.134				
	ethanol	solvent		46.07	0.79			3.186	4.033			96%
			2a	192.21						0.744	3.872	
2	**2a**	intermediate		192.21		1	3.872	0.744				
	NaH	reagent		24		0.1	0.387	0.009				
			3a	384.42						0.697	1.812	94%
3	**3a**	intermediate		384.42		1	1.812	0.697				
	1,10-Decanedithiol	raw material		206.41	1.12	1	1.812	0.374				
	DMPA	reagent		256.3		0.05	0.091	0.023				
	THF	solvent		72.11	0.889			5.316	5.980			
			P3a4d	590.83						1	1.693	93%

Table S9. E-factor analysis of the process toward **P3a4d**.

Step number	Raw material (kg)	Reagent (kg)	Solvent	Product (kg)	Step E-Factor	E-Factor
1	1.590	0.970	3.186	0.744	2.867	2.134
2	0.744	0.009	0.000	0.697	0.082	0.057
3	1.071	0.023	5.316	1.000	0.626	0.626
Total	1.964	1.003	8.50	1.000		2.817

Table S10. Material input-output table for the process toward **PO3a4d**.

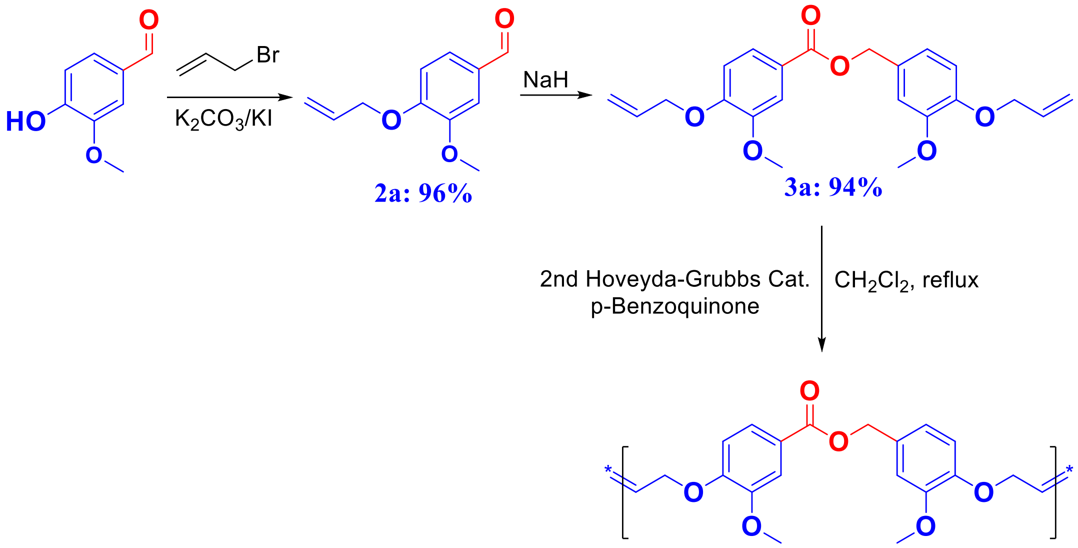


Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Input volume (L)	Output weight (kg)	Output mol	Yield
1	vanillin	raw material		152.15		1	4.700	0.715				
	allyl bromide	raw material		120.98	1.398	2	9.400	1.137				
	K_2CO_3	reagent		138.21		1.5	7.050	0.974				
	KI	reagent		166.01		0.2	0.940	0.156				
	ethanol	solvent		46.07	0.79			3.713	4.700			96%
			2a	192.21						0.867	4.512	
2	**2a**	intermediate		192.21		1	4.512	0.867				
	NaH	reagent		24		0.1	0.451	0.011				
			3a	384.42						0.812	2.112	94%
3	**3a**	intermediate		384.42		1	2.112	0.812				
	1,2-Ethanedithiol	raw material		94.2	1.12	1	2.112	0.199				
	DMPA	reagent		256.3		0.05	0.106	0.027				
	THF	solvent		72.11	0.889			6.195	6.968			
			P3a4a	478.62						0.971	2.029	96%
4	**P3a4a**	intermediate		478.62		1	2.029	0.971				
	H_2O_2	solvent		43.01	1.11			6.757	6.088			
			PO3a4a	542.13						1	1.845	91%

Table S11. E-factor analysis of the process toward **PO3a4d**.

Step number	Raw material	Reagent (kg)	Solvent	Product (kg)	Step E-Factor	E-Factor
1	1.852	1.130	3.713	0.867	2.867	2.487
2	0.867	0.011	0.000	0.812	0.082	0.066
3	1.011	0.027	6.195	0.971	0.706	0.686
4	0.971	0.000	6.757	1.000	0.647	0.647
Total	2.051	1.168	16.67	1.000		3.886

Table S12. Material input-output table for the process toward **P3a**.

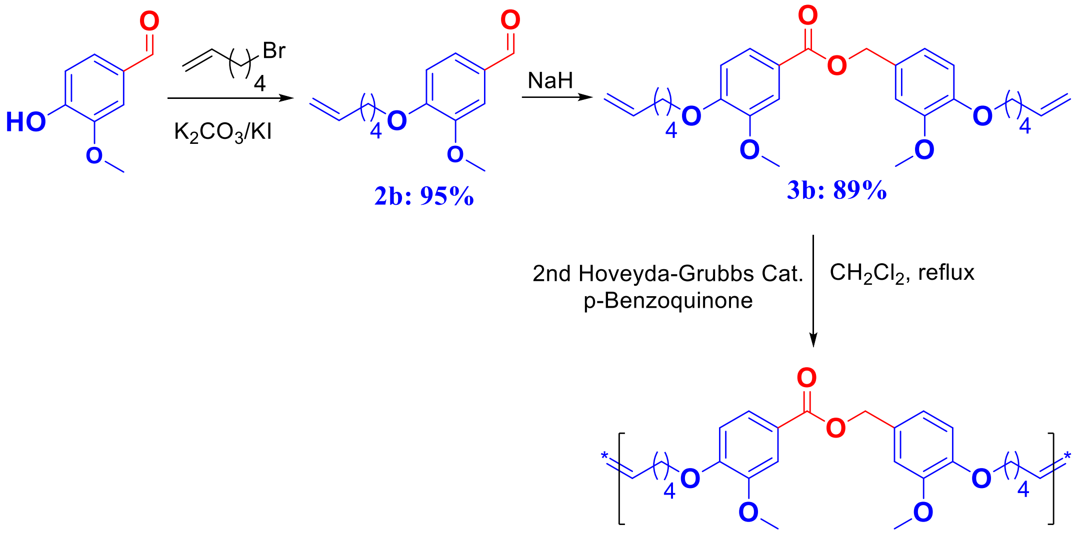


Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Input volume (L)	Output weight (kg)	Output mol	Yield
1	vanillin	raw material		152.15		1	5.976	0.909				
	allyl bromide	raw material		120.98	1.398	2	11.952	1.446				
	K_2CO_3	reagent		138.21		1.5	8.964	1.239				
	KI	reagent		166.01		0.2	1.195	0.198				
	ethanol	solvent		46.07	0.79			4.721	5.976			96%
			2a	192.21						1.103	5.737	
2	**2a**	intermediate		192.21		1	5.737	1.103				
	NaH	reagent		24		0.1	0.574	0.014				
			3a	384.42						1.032	2.685	94%
3	**3a**	intermediate		384.42		1	2.685	1.032				
	p-benzoquinone	reagent		108.09		0.02	0.054	0.006				
	2-HG	reagent		626.62		0.01	0.027	0.017				
	dichloromethane	solvent		84.93	1.325			28.459	21.478			
			P3a	478.62						1	2.615	97%

Table S13. E-factor analysis of the process toward **P3a**.

Step number	Raw material (kg)	Reagent (kg)	Solvent	Product (kg)	Step E-Factor	E-Factor
1	2.355	1.437	4.721	1.103	2.867	3.162
2	1.103	0.014	0.000	1.032	0.082	0.084
3	1.032	0.023	28.459	1.000	2.901	2.901
Total	2.355	1.474	33.18	1.000		6.147

Table S14. Material input-output table for the process toward **P3b**.

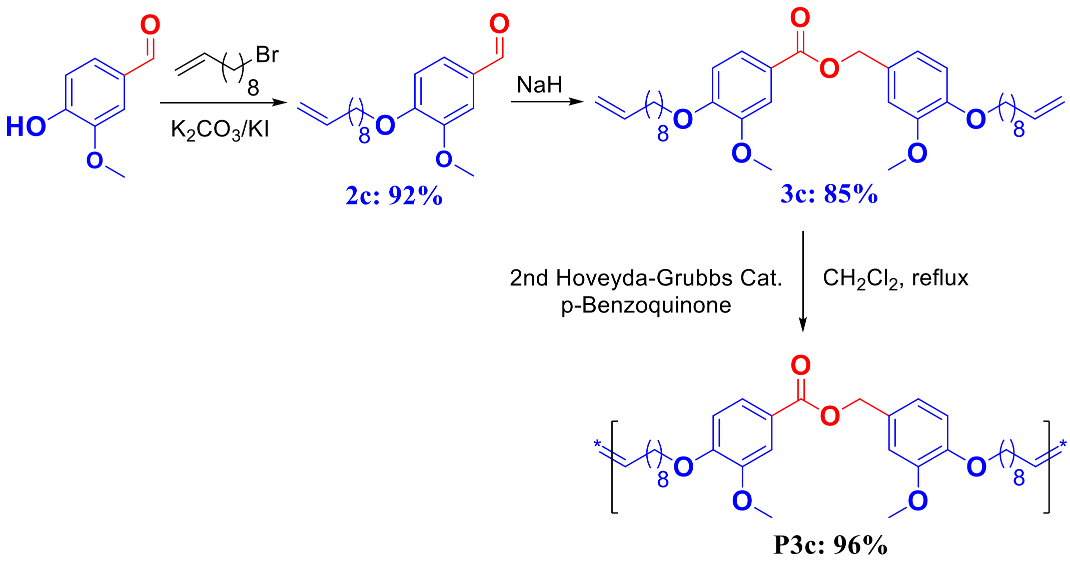


Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Input volume (L)	Output weight (kg)	Output mol	Yield
1	vanillin	raw material		152.15		1	5.319	0.809				
	6-Bromo-1-hexene	raw material		163.06	1.398	2	10.638	1.735				
	K_2CO_3	reagent		138.21		1.5	7.978	1.103				
	KI	reagent		166.01		0.2	1.064	0.177				
	ethanol	solvent		46.07	0.79			4.202	5.319			
			2b	234.3						1.183	5.048	95%
2	**2b**	intermediate		234.3		1	5.048	1.183				
	NaH	reagent		24		0.1	0.505	0.012				
			3b	468.59						1.056	2.254	89%
3	3b	intermediate		468.59		1	2.254	1.056				
	p-benzoquinone	reagent		108.09		0.02	0.045	0.005				
	2-HG	reagent		626.62		0.01	0.023	0.014				
	dichloromethane	solvent		84.93	1.325			23.890	18.030			
			P3b	466.57						1	2.143	95%

Table S15. E-factor analysis of the process toward **P3b**.

Step number	Raw material (kg)	Reagent (kg)	Solvent	Product (kg)	Step E-Factor	E-Factor
1	2.544	1.279	4.202	1.183	2.588	3.061
2	1.183	0.012	0.000	1.056	0.131	0.139
3	1.056	0.019	23.890	1.000	2.464	2.464
Total	2.544	1.310	28.09	1		5.663

Table S16. Material input-output table for the process toward **P3c**.

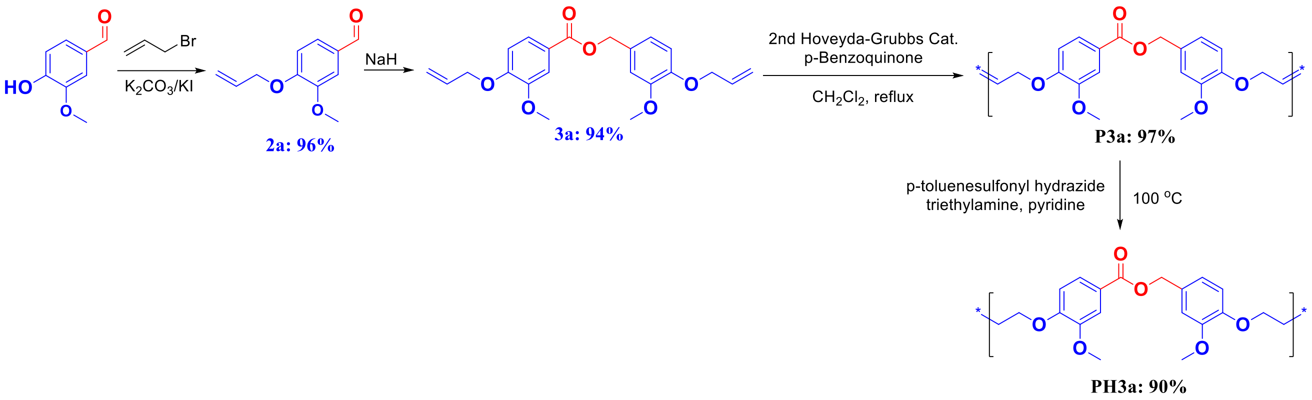


Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Input volume (L)	Output weight (kg)	Output mol	Yield
1	vanillin	raw material		152.15		1	4.602	0.700				
	10-Bromo-1-Decene	raw material		219.16	1.398	2	9.204	2.017				
	K_2CO_3	reagent		138.21		1.5	6.903	0.954				
	KI	reagent		166.01		0.2	0.920	0.153				
	ethanol	solvent		46.07	0.79			3.636	4.602			
			2c	290.4						1.231	4.239	92%
2	2c	intermediate		290.4		1	4.239	1.231				
	NaH	reagent		24		0.1	0.424	0.010				
			3c	580.81						1.047	1.803	85%
3	3c	intermediate		580.81		1	1.803	1.047				
	p-benzoquinone	reagent		108.09		0.02	0.036	0.004				
	2-HG	reagent		626.62		0.01	0.018	0.011				
	dichloromethane	solvent		84.93	1.325			19.117	14.428			
			P3c	578.79						1	1.728	95%

Table S17. E-factor analysis of the process toward **P3c**.

Step number	Raw material (kg)	Reagent (kg)	Solvent	Product (kg)	Step E-Factor	E-Factor
1	2.717	1.107	3.636	1.231	2.402	2.957
2	1.231	0.010	0.000	1.047	0.185	0.194
3	1.047	0.015	19.117	1.000	1.974	1.974
Total	2.717	1.132	22.75	1.000		5.125

Table S18. Material input-output table for the process toward **PH3a**.



Step	Input material	Input type	Output material	MW (g/mol)	Density (g/mL)	Equiv.	Input mol	Input weight (kg)	Output weight (kg)	Input volume (L)	Output mol	Yield
1	vanillin	raw material		152.15		1	6.600	1.004				
	allyl bromide	raw material		120.98	1.398	2	13.200	1.597				
	K_2CO_3	reagent		138.21		1.5	9.900	1.368				
	KI	reagent		166.01		0.2	1.320	0.219				
	ethanol	solvent		46.07	0.79			5.214		6.600		96%
			2a	192.21					1.218		6.336	
2	**2a**	intermediate		192.21		1	6.336	1.218				
	NaH	reagent		24		0.1	0.634	0.015				
			3a	384.42					1.140		2.965	94%
3	**3a**	intermediate		384.42		1	2.965	1.140				
	p-benzoquinone	reagent		108.09		0.02	0.059	0.006				
	2-HG	reagent		626.62		0.01	0.030	0.019				
	dichloromethane	solvent		84.93	1.325			31.431		23.721		
			P3a	382.41					1.104		2.888	97%
4	**P3a**	intermediate		382.41		1	2.888	1.104				
	p-toluenesulfonyl hydrazide	reagent		186.23		3	8.664	1.614				
	triethylamine	reagent		101.19		3	8.664	0.877				
	pyridine	solvent		79.1	0.978			14.123		14.440		
			PH3a	386.44					1		2.588	90%

Table S19. E-factor analysis of the process toward **PH3a**.

Step number	Raw material (kg)	Reagent (kg)	Solvent	Product (kg)	Step E-Factor	E-Factor
1	2.601	1.587	5.214	1.218	2.867	3.492
2	1.218	0.015	0.000	1.140	0.082	0.093
3	1.146	0.019	31.431	1.104	2.901	3.204
4	1.104	2.490	14.123	1.000	4.007	4.007

Total	2.601	4.118	50.77	1.000			10.796

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