Supporting Information

Nickel-Catalyzed Reductive Cross-Coupling Polymerization of Dithiosulfonates and Dibromides for the Synthesis of Polythioethers

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1. General information

Unless otherwise stated, all reactions were magnetically stirred and conducted in anhydrous solvents under N_2, applying standard Schlenk techniques. Solvents and liquid reagents, as well as solutions of solid or liquid reagents were added via syringes, stainless steel cannulas through rubber septa or through a weak N_2 counter–flow. Solid reagents were first added to the reactor or Schlenk Reaction Tube for refilling N_2 for three times. Heated oil baths were used for reactions requiring elevated temperatures. Solvents were removed under reduced pressure at 30°C using a rotary evaporator, and unless otherwise stated, the remaining compound was dried in high vacuum at ambient temperature.

Chemicals

Chemicals were purchased from commercial suppliers (including Energy Chemical, Bidepharm, Aladdin, Meryer, SCR) and used without further purification unless otherwise stated.

Solvents

Solvents (*n*-hexane) were dried by distillation from an appropriate drying agent. In addition, DMF and more solvents were purchased from commercial suppliers.

Gas

Dry N_2 were purchased from Hangzhou Jingong Materials with > 99.9% purity.

Column Chromatography

Column chromatography (CC) was carried out using Nuotai silica gel (90 Å, 100–200 mesh) using technical grade solvents. Elution was accelerated using compressed air. All reported yields, unless otherwise specified, refer to spectroscopically and chromatographically pure compounds.

Nuclear Magnetic Resonance Spectroscopy

^{1}H, ^{13}C, ^{29}Si, nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV–500, AV–400 spectrometer in a suitable deuterated solvent. The solvent employed and respective measuring frequency are indicated for each experiment. Chemical shifts are reported with tetramethylsilane (TMS) serving as a universal reference of all nuclides and with two or one digits after the comma. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and bs (broad singlet). All spectra were recorded at 298 K unless otherwise noted, processed with program MestReNova 14.0, and coupling constants are reported as observed. The residual deuterated solvent signal relative to tetramethylsilane (TMS) was used as the internal reference in ^{1}H NMR spectra ($CDCl_3$ δ 7.26), and are reported as follows: chemical shift δ in ppm (multiplicity, coupling constant J in Hz, number of protons). ^{13}C NMR spectra reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ δ 77.16). All spectra are broadband decoupled unless otherwise noted.

High resolution Mass Spectrometry

Electrospray ionization (ESI) mass spectrometry was conducted on a Bruker micro QII–ESI–TOF. The ionization method and mode of detection employed is indicated for the respective experiment and all masses are reported in atomic units per elementary charge (m/z) with an intensity normalized to the most intense peak.

Gel permeation chromatography

GPC traces were determined by MALLS using THF as the eluent with Waters 1515.

Thermogravimertric analysis

The thermal stability of the polymers was analyzed by thermosgravimetric analysis (TGA) using a TG209 instrument. Experiments were carried out from 25°C to 800°C at a heating rate of 10°C /min in a nitrogen atmosphere.

Differential scanning calorimetry

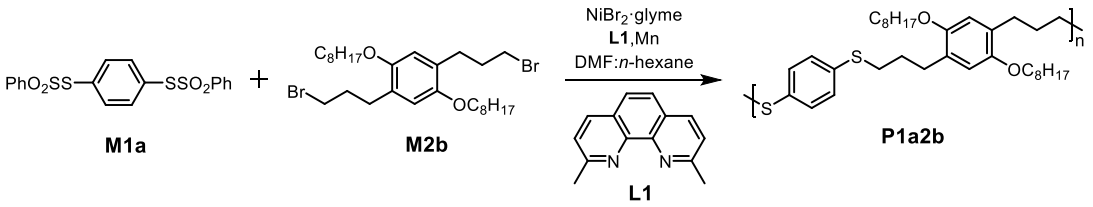
Differential scanning calorimetry (DSC) experiments were conducted using a DSC 204 instrument, operating under nitrogen flow. Samples were subjected to a cycle of –30°C to 250°C at a rate of 10°C /min.

Infrared spectroscopy

IR spectra were obtained using a Bruker vertex 70 equipped with PIKE MIRacle attenuated total reflection (MIR–ATR) attachment.

2. Reaction optimization

Table S1. Screening of reaction optimization

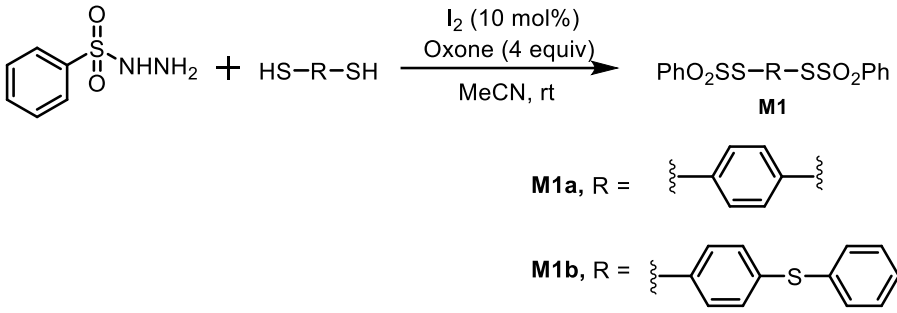


Entry	[Ni] (mol%)	L1 (mol%)	Mn (eq)	T (°C)	DMF:*n*-hexane	Yield (%)	M_n (kDa)	M_w (kDa)	*Mw/Mn*
1	5	7.5	2	30	4:1	39	2.9	3.9	1.32
2	5	7.5	3	30	4:1	84	7.0	9.2	1.31
3	5	7.5	5	30	4:1	86	5.2	7.5	1.45
4	10	15	3	30	4:1	77	6.0	6.6	1.10
5	20	30	3	30	4:1	74	4.3	4.8	1.12
6	5	7.5	3	10	4:1	n.d	n.d	n.d	n.d
7	5	7.5	3	50	4:1	87	6.4	10.4	1.62
8	5	7.5	3	30	1:1	68	5.6	7.9	1.41
9	5	7.5	3	30	7:1	76	6.1	8.9	1.46

Reactions were performed with $NiBr_2$·glyme (5 mol %, 0.0025 mmol), neocuproine (**L1**, 7.5 mol %, 0.00375 mmol), Mn powder, *S*–phenyl benzenethiosulfonate (0.05 mmol) and alkyl bromide (0.05 mmol) in the mixed solution (0.5 mL) of DMF and *n*-hexane; yields are for the isolated compounds. M_n, M_w and *Đ* were measured by MALLS using THF as the eluent.

3. Monomer synthesis

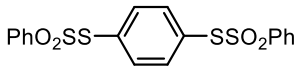
S-Phenyl benzenesulfonothioate (**2**)[1], 1,4-bis(3-bromopropyl)benzene (**M2a**)[2], 1,2-Bis(2-bromoethoxy)ethane (**M2g**)[3] were synthesized according to the literatures.



Scheme S1. Synthetic route of monomer **M1**

General procedures for synthesis of **M1**: Put potassium peroxymonosulfonate (8.6 g, 14 mmol, 4 equiv.), diiodo (177.7 g, 0.7 mmol, 10 mol%), benzenesulfonyl hydrazide (3.02 g, 17.6 mmol, 5 equiv.), 1,4-thiols (3.5 mmol, 1 equiv.) in a double necked flask with a magnet and dissolve it in MeCN (30 mL) under N_2 protection. Stir the mixture at room temperature for 12 h. At the end of the reaction, the solvent was removed by rotation evaporation, the mixture was poured into water and extracted with EtOAc. The organic phases were dried and filtered through Na_2SO_4. Solvent was removed in *vacuo* to provide a crude mixture. Then the crude product was purified by a silica column with PEE: EtOAc = 3:1 as the eluent to obtain both **M1a** and **M1b** with 21% yields, respectively.

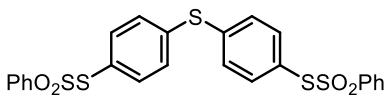
***O, O'*-diphenyl-1,4-sulfonothioate (M1a)**



M1a

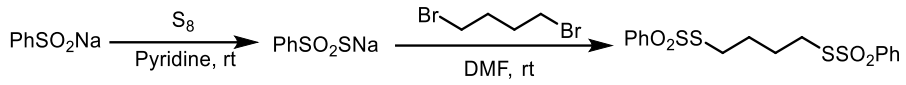
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.54 (m, 6H), 7.47 (t, *J*=8.0, 4H), 7.34 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 136.1, 133.2, 130.9, 128.2, 126.6.
HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{18}H_{14}O_4S_4Na$: 444.9667, found: 444.9671.

***O, O*'-diphenyl-4,4'-thiodibenzenesulfonothioate (M1b)**



M1b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.57 (m, 6H), 7.46 (t, *J* = 7.4 Hz, 4H), 7.31 (d, *J* = 8.4 Hz, 4H), 7.29–7.24 (m,4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 139.5, 137.4, 134.0, 131.5, 129.1, 127.7, 127.1.
HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{24}H_{18}O_4S_5Na$: 552.9701, found: 552.9701.

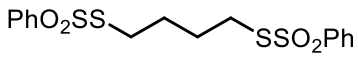


M1c

Scheme S2. Synthetic route of monomer **M1c**

Procedures for synthesis of **M1c**: $PhSO_2Na$ (4.92 g, 30 mmol) and sulfur were weighted into a 250 mL round-bottom flask. Pyridine (30 mL) was then added, and the mixture was stirred at room temperature for 10 h. The mixture was filtered, and the reside was washed with Et_2O three times. $PhSO_2SNa$ (5.3 g, 90% yield) was obtained as a white solid. To a solution of $PhSO_2SNa$ (3g, 15.31 mmol) in DMF was added 1,4-dibromobutane (1.1 g, 5.1 mmol) and the reaction mixture was stirred at room temperature. After the completion of the reaction, the reaction mixture was diluted with EtOAc and washed with water. The organic phase was separated and dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography to provide the **M1c** (1.5g, 73%).

***O, O*-diphenyl butane-1,4-bis(sulfonothioate) (M1c)**

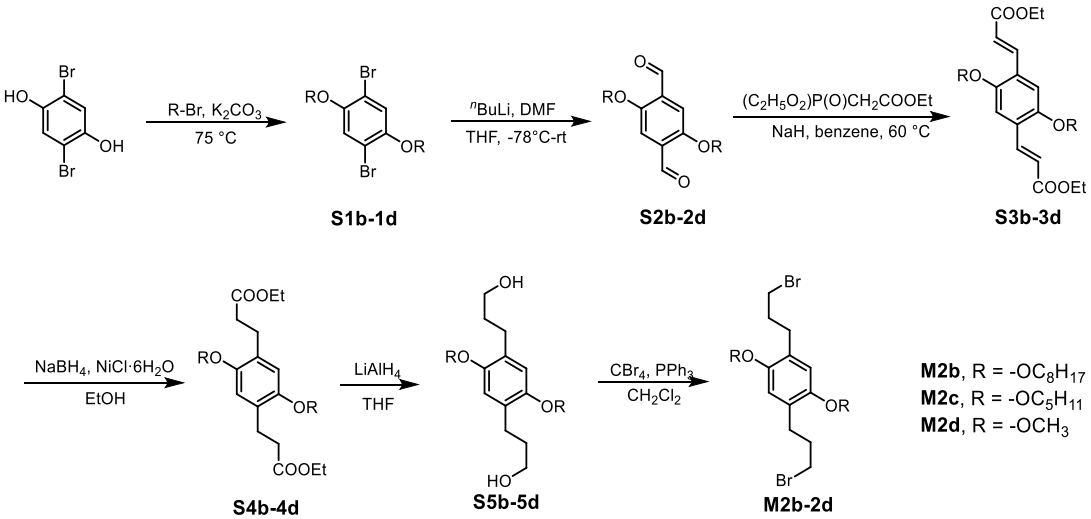


M1c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 4H), 7.63 (t, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 8.0, 4H), 2.89 (p, *J* = 6.4 Hz, 4H), 1.61 (p, *J* = 6.8 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 133.9, 129.5, 127.0, 35.3, 27.6.

HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{16}H_{18}O_4S_4Na$: 424.998, found: 424.9983.

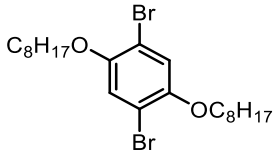


Scheme S3. Synthetic route of **M2**

General procedures for the synthesis of **S1:** Potassium carbonate (10.32 g, 74.65 mmol, 4 equiv.), aryl bormide (4 equiv.) were added to a solution of phenol (5 g, 1 equiv.) in DMF under N_2 protection. The mixture was refluxed at 75°C for 12 h. Cool the reaction mixture to room temperature. The mixture was poured into water and extracted with

DCM. Dry the organic phase over anhydrous Na_2SO_4. The solvent was removed in the *vacuo* to obtain a crude mixture. The crude product was then purified with a silica gel column and PEE: EtOAc = 20: 1 was used as the eluent to obtain **S1** with yields of 86%–95%.

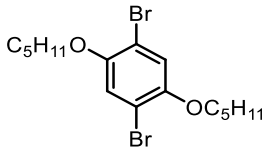
1,4-dibromo-2,5-bis(octyloxy)benzene (S1b)



S1b

The structure was confirmed by comparison of the NMR spectra with the literature.[4]

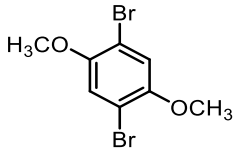
1,4-dibromo-2,5-bis(pentyloxy)benzene (S1c)



S1c

The structure was confirmed by comparison of the NMR spectra with the literature.[5]

1,4-dibromo-2,5-dimethoxybenzene (S1d)



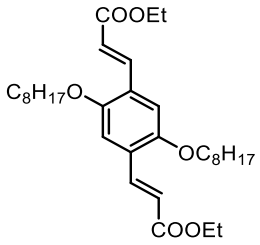
S1d

The structure was confirmed by comparison of the NMR spectra with the literature.[4]

General procedures for synthesis of **S2:** Put **S1** (1 equiv.) in a double necked flask with a magnet and dissolved it in THF under N_2 protection. 2.5 M *n*–butyllithium (2.5 equiv.) was added into the mixture at -78°C, the reaction mixture was stirred for 1h, then *N,N*–dimethylformamide (6 equiv.) was added, the mixture was stirred at room temperature for 5h. The mixture was poured into water and extracted with DCM. Dry the organic phase over anhydrous Na_2SO_4. The solvent was removed in the *vacuo* to obtain a crude mixture. The crude product was then purified with a silica gel column and PEE: EtOAc = 70:1 was used as the eluent to obtain **S2** with a yield of 76%–80%.
General procedures for synthesis of **S3:** Place sodium hydride (2.4 equiv.) in a double necked flask with a magnet and dissolved it in toluene under N_2 protection. added $(EtO)_2P(O)CH_2CO_2Et$ (2 equiv) at 30–35 °C. After stirred for 1 h, the solution of **S2** (1 equiv.) in anhydrous toluene was added at 20–30°C. The reaction mixture was then

stirred at 60°C for 12h, The mixture was poured into water and extracted with DCM. Dry the organic phase over anhydrous Na_2SO_4. The solvent was removed in the *vacuo* to obtain a crude mixture. The crude product was then purified with a silica gel column and PEE: EtOAc = 50:1 was used as the eluent to obtain **S3** with the yields of 55%–70%.

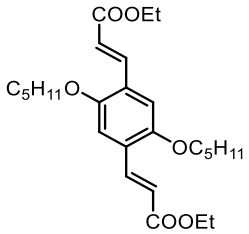
Diethyl 3,3'-(2,5-bis(octyloxy)-1,4-phenylene) diacrylate (S3b)



S3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 14.6 Hz, 2H), 7.02 (s, 2H), 6.54 (d, *J* = 16.0 Hz, 2H), 4.27 (q, *J* = 7.0 Hz, 4H), 3.99 (t, *J* = 6.6 Hz, 4H), 1.84 (p, *J* = 6.6 Hz, 4H), 1.52–1.43 (m, 4H), 1.41–1.21 (m, 22H), 0.89 (t, *J* = 7.2 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 152.1, 139.4, 126.3, 119.8, 112.3, 69.4, 60.6, 31.9, 29.5, 29.4, 29.4, 26.3, 22.8, 14.5, 14.3.
HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{32}H_{50}O_6Na$: 553.3500, found: 553.3479.

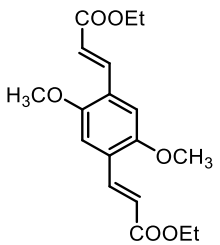
Diethyl 3,3'-(2,5-bis(pentyloxy)-1,4-phenylene) diacrylate (S3c)



S3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 15.2 Hz, 2H), 7.02 (s, 2H), 6.53 (d, *J* = 16.8 Hz, 2H), 4.26 (q, *J* = 7.0 Hz, 4H), 3.99 (t, *J* = 6.6 Hz, 4H), 1.90–1.76 (m, 4H), 1.52–1.36 (m, 10H), 1.34 (t, *J* = 6.2 Hz, 4H), 0.94 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 152.0, 139.4, 126.2, 119.7, 112.2, 69.4, 60.6, 29.0, 28.4, 22.6, 14.5, 14.2.
HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{26}H_{38}O_6Na$: 469.2561, found: 469.2562.

Diethyl 3,3'-(2,5-dimethoxy-1,4-phenylene) diacrylate (S3d)

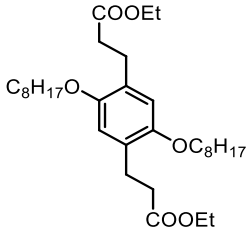


S3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 15.6 Hz, 2H), 7.02 (s, 2H), 6.54 (d, *J* = 16.4 Hz, 2H), 4.27 (q, *J* = 7.0 Hz, 4H), 3.87 (s, 6H), 1.34 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 152.6, 139.2, 126.0, 119.9, 111.1, 60.7, 56.1, 14.5.
HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{18}H_{22}O_6Na$: 357.1309, found: 357.1490.

General procedures for synthesis of **S4:** Put $NiBr_2$·glyme (0.41 equiv.) and $NaBH_4$ (8.1 equiv.) in a double necked flask with a magnet and protected by N_2. Add the ethanol solution of **S3** (1 euqiv.) to the flask. The reaction mixture was stirred at room temperature for 12 h. The mixture was poured into water and extracted with anhydrous ether. Dry the organic phase on anhydrous Na_2SO_4. The solvent is removed in the *vacuo* to obtain a crude mixture. Then the crude product was purified with a silica gel column, and PEE: EtOAc =10:1 was used as the eluent to obtain **S4** in the yields of 73%–81%.

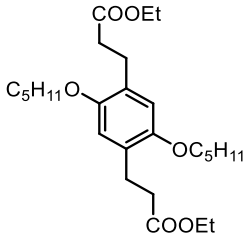
Diethyl 3,3'-(2,5-bis(octyloxy)-1,4-phenylene) dipropionate (S4b)



S4b

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 2H), 4.03 (q, *J* = 7.2 Hz, 4H), 3.80 (t, *J* = 6.4 Hz, 4H), 2.80 (t, *J* = 7.8 Hz, 4H), 2.50 (t, *J* = 7.0 Hz, 4H), 1.77–1.55 (m, 4H), 1.36 (q, *J* = 7.0 Hz, 4H), 1.32–1.04 (m, 22H), 0.80 (t, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 149.5, 126.5, 112.8, 67.5, 59.1, 33.5, 30.8, 28.5, 28.4, 28.3, 25.3, 25.2, 21.7, 13.2, 13.1.
HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{32}H_{54}O_6Na$: 557.3813, found: 557.3821.

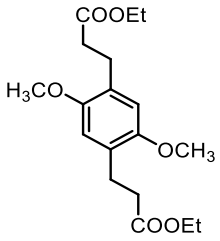
Diethyl 3,3'-(2,5-bis(pentyloxy)-1,4-phenylene) dipropionate (S4c)



S4c

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 4H), 3.88 (t, *J* = 6.6 Hz, 4H), 2.88 (t, *J* = 7.8 Hz, 4H), 2.58 (t, *J* = 8.6 Hz, 4H), 1.81–1.70 (m, 4H), 1.47–1.32 (m, 10H), 1.24 (t, *J* = 7.2 Hz, 4H), 0.92 (t, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 150.6, 127.7, 113.9, 68.7, 60.4, 34.7, 29.3, 28.46, 26.4, 22.6, 14.4, 14.2.
HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{26}H_{42}O_6Na$: 473.2874, found: 473.2875.

Diethyl 3,3'-(2,5-dimethoxy-1,4-phenylene) dipropionate (S4d)

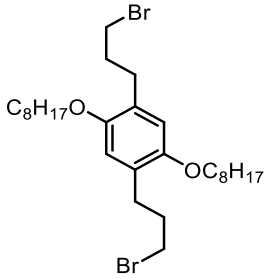


S4d

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 2H), 4.09 (q, *J* = 7.0, 4H), 3.74 (s, 6H), 2.87 (t, *J* = 7.8 Hz, 4H), 2.56 (t, *J* = 8.2 Hz, 4H), 1.21 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 151.2, 127.4, 112.9, 60.3, 55.9, 34.51, 26.2, 14.3.
HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{27}O_6$: 339.1802, found: 339.1805.

General procedures for synthesis of **S5:** To a suspension of lithium aluminum hydride (4 equiv.) in anhydrous THF was added the THF solution of **S4** (1 equiv.) at 0°C under N_2. The reaction mixture was stirred at room temperature for 6 h and was then added to water at 0°C, followed by extraction with Et_2O. The extracts were washed with water three times, then dried with anhydrous Na_2SO_4, and the solvent was removed by evaporation. Then the crude product was purified with a silica gel column, and PEE: EtOAc=3:1 was used as the eluent to obtain **S5** in the yields of 70%–90%.
General procedures for synthesis of **M2:** Put CBr_4 (2.1 equiv.) and PPh_3(2.1 equiv.) in a double necked flask with a magnet and protected by N_2. DCM solution (1 equiv.) of **S5** was added. Stir the reaction mixture for 2h at room temperature. The mixture was poured into water and the organic phase was dried on anhydrous Na_2SO_4. The solvent was removed in the *vacuo* to obtain a crude mixture. Then the crude product was purified with a silica gel column, and **M2** was obtained by PEE with the yields of 70%–81%.

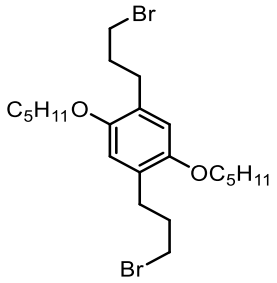
1,4-bis(3-bromopropyl)-2,5-bis(octyloxy)benzene (M2b)



M2b

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 2H), 3.89 (t, *J* = 6.4 Hz, 4H), 3.41 (t, *J* = 6.7 Hz, 4H), 2.72 (t, *J* = 7.2 Hz, 4H), 2.17–2.10 (m, 4H), 1.85–1.68 (m, 4H), 1.53–1.18 (m, 20H), 0.89 (t, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 127.6, 114.3, 68.8, 34.1, 33.1, 31.9, 29.7, 29.5, 29.4, 29.2, 26.4, 22.8, 14.3.
HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{28}H_{48}Br_2O_2Na$: 597.1913, found: 597.1899.

1,4-bis(3-bromopropyl)-2,5-bis(pentyloxy)benzene (M2c)



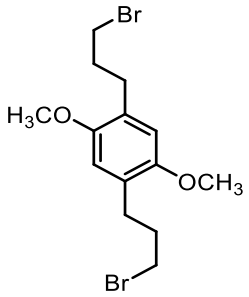
M2c

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 2H), 3.89 (t, *J* = 6.4 Hz, 4H), 3.41 (t, *J* =6.7 Hz, 4H), 2.72 (t, *J* = 7.2 Hz, 4H), 2.17–2.10 (m, 4H), 1.80–1.73 (m, 4H), 1.52–1.30 (m, 8H), 0.93 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 127.6, 114.3, 68.8, 34.1, 33.0, 29.4, 29.2, 28.5, 22.6, 14.3.

HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{22}H_{36}Br_2O_2Na$: 513.0974, found: 513.2335.

1,4-bis(3-bromopropyl)-2,5-dimethoxybenzene (M2d)



M2d

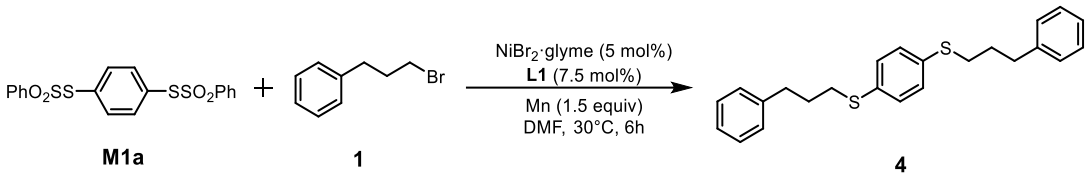
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (s, 2H), 3.69 (s, 6H), 3.32 (t, *J* = 6.8 Hz, 4H), 2.65 (t, *J* = 7.0 Hz, 4H), 2.08–2.02 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 127.4, 113.3, 56.0, 33.9, 32.9, 29.0.

HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{14}H_{20}Br_2O_2Na$: 400.9722, found: 400.9716.

4. Model reactions

1,4-bis((3-phenylpropyl)thio)benzene (4)



Scheme S4. Synthetic route of **4**

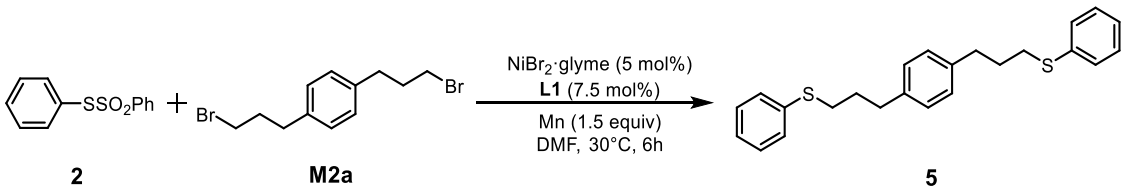
In glovebox, an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $NiBr_2$·glyme (5 mol%, 1.5 mg, 0.005 mmol), neocuproine (**L1**, 1.6 mg, 0.075 mmol) and Mn powder (8.2 mg, 0.15 mmol). DMF (0.2 mL) was added and the mixture was stirred at 30 °C for 1 h. The DMF (0.8 mL) solution of **M1a** (42.2 mg, 0.1 mmol) and **1** (39.8 mg, 0.2 mmol) was added via syringe, the resulting solution was stirred for 23 h at 30 °C. After this time, the crude reaction mixture was diluted with DCM and washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified with a silica gel column, and PEE: EtOAc=15:1 was used as the eluent to obtain **4** in 90% yield (34 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.17 (m, 4H), 7.16–7.06 (m, 10H), 2.81 (t, *J* = 7.2 Hz, 4H), 2.67 (t, *J* = 7.4 Hz, 4H), 1.87 (p, *J* = 7.4 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 134.2, 129.9, 128.6, 128.6, 126.1, 34.8, 33.3, 30.7.

HRMS (ESI) (m/z): $[M+Na]^+$ calculated for $C_{24}H_{26}S_2Na$: 401.1368, found: 401.1361.

1,4-bis(3-(phenylthio)propyl)benzene (5)

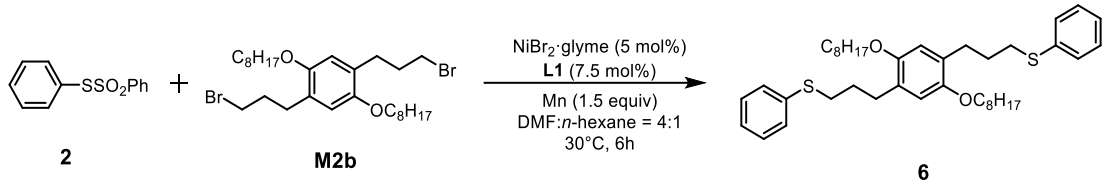


Scheme S5. Synthetic route of **5**

In glovebox, an oven-dried 10mL Schlenk tube equipped with a magnetic stir bar was charged with $NiBr_2$·glyme (5 mol%, 1.5 mg, 0.005 mmol), neocuproine (**L1**, 1.6 mg, 0.075 mmol) and Mn powder (8.2 mg, 0.15 mmol). DMF (0.2 mL) was added and the mixture was stirred at 30 °C for 1 h. The DMF (0.8mL) solution of **M2a** (32 mg, 0.1 mmol) and **2** (50 mg, 0.2 mmol) was added via syringe, The resulting solution was stirred for 23 h at 30 °C. After this time, the crude reaction mixture was diluted with DCM and washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified with a silica gel column, and PEE: EtOAc=15:1 was used as the eluent to obtain **5** in 89% yield (33.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.13 (m, 8H), 7.07 (t, *J* = 6.4 Hz, 2H), 7.00 (s, 4H), 2.83 (t, *J* = 7.2 Hz, 4H), 2.64 (t, *J* = 7.4 Hz, 4H), 1.86 (p, *J* = 7.4 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 136.7, 129.2, 128.9, 128.6, 125.9, 34.4, 32.9, 30.8.
HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{24}H_{26}S_2Na$: 401.1368, found: 401.1426.

((2,5-bis(octyloxy)-1,4-phenylene)bis(propane-3,1-diyl))bis(phenylsulfane) (6)

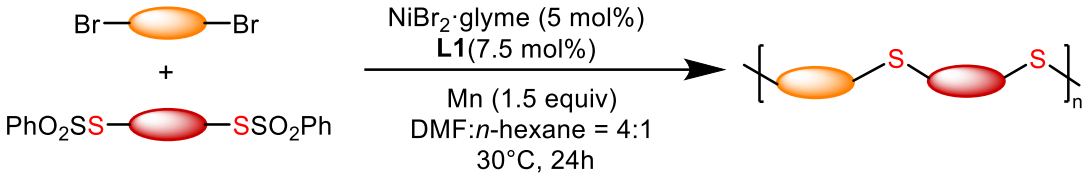


2 **M2b** **6**

Scheme S6. Synthetic route of **6**

In glovebox, an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $NiBr_2$·glyme (5 mol%, 1.5 mg, 0.005 mmol), neocuproine (**L1**, 1.6 mg, 0.075 mmol) and Mn powder (8.2 mg, 0.15 mmol). DMF (0.2 mL) was added and the mixture was stirred at 30 °C for 1 h. The mixed solution of DMF (0.8 mL) and *n*-hexane (0.2 mL) of **2** (50 mg, 0.2 mmol) and **M2b** (42.2 mg, 0.1 mmol) was added via syringe, The resulting solution was stirred for 23 h at 30 °C. After this time, the crude reaction mixture was diluted with DCM and washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified with a silica gel column, and PEE: EtOAc=15:1 was used as the eluent to obtain **6** in 87% yield (55.2 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.19 (m, 8H), 7.14(t, *J* = 2H), 6.61 (s, 2H), 3.83 (t, *J* = 6.4 Hz, 4H), 2.92 (t, *J* = 7.2 Hz, 4H), 2.71 (t, *J* = 7.4 Hz, 4H), 1.96–1.89(m, 4H), 1.82–1.63 (m, 4H), 1.53–1.16 (m, 20H), 0.89 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 137.1, 128.9, 128.8, 128.2, 125.7, 114.2, 68.8, 33.1, 32.0, 29.7, 29.6, 29.5, 29.5, 26.3, 22.8, 14.3, 1.2.
HRMS (ESI) (m/z): [M+Na] $^+$ calculated for $C_{40}H_{58}O_2S_2Na$: 657.3770, found: 657.3709.

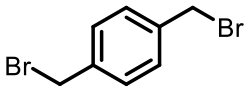
5. General procedure of reductive cross-coupling polymerization



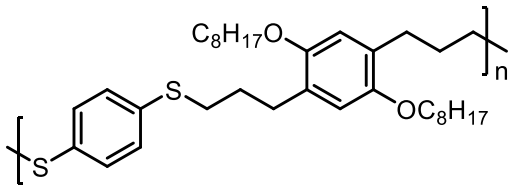
Scheme S7. Synthetic route of **P1a2a-P1b2g**

General procedure: In glovebox, an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with $NiBr_2$·glyme (5 mol%, 0.0025 mmol), neocuproine (**L1**, 0.00375 mmol) and Mn powder (0.15 mmol). DMF (0.2 mL) was added and the mixture was stirred for 1 h. The mixed solution of DMF (0.2 mL) and *n*-hexane (0.1 mL) of *S*–phenyl benzenethiosulfonate (0.05 mmol) and alkyl bromide (0.05 mmol) (**P1a2b, P1a2c, P1a2d, P1b2b** was added via syringe; while pure DMF (0.3 mL) was used in the preparation of **P1a2a, P1a2e, P1a2f, P1a2g** and **P1b2g**). The resulting solution was stirred for 23 h at 30 °C. After this time, the crude reaction mixture was diluted with DCM and precipitated and solution was collected. The solvent was removed by rotation evaporation. Then the crude product was dissolved in a small amount of DCM and poured into vigorously stirred MeOH and precipitated polymer was collected by centrifugation. The centrifugation was repeated for 3 times. After drying under *vacuum*, the collected polymers were characterized with ^{1}H NMR, ^{13}C NMR, FT-IR, SEC, DSC and TGA measurements.

The limitation of the monomer was showed as following, none of the targeting polymer was found:



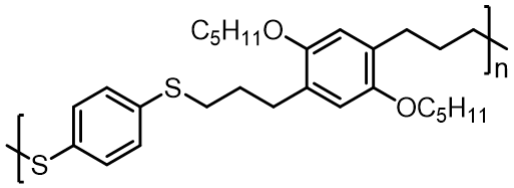
P1a2b



84% yield; **TGA** T_d = 349 °C.
GPC M_n = 7.0 kDa, M_w = 9.2 kDa, $Đ$ = 1.31.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (ws, 4H), 6.59 (ws, 2H), 3.83 (ws, 4H), 2.88 (ws, 4H), 2.69 (ws, 4H), 1.90 (ws, 4H), 1.71 (ws, 4H), 1.55–1.08 (w, 20H), 0.87 (ws, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 134.4, 129.6, 128.2, 114.2, 68.8, 33.6, 31.9, 29.7, 29.5, 29.5, 26.4, 22.8, 14.3, 1.2.

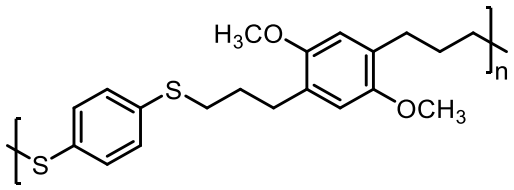
IR (KBr, cm^{-1}) n 2853, 2919, 1206, 803.

P1a2c



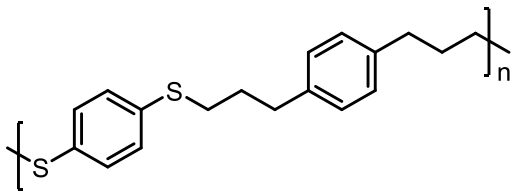
82% yield; **TGA** T_d = 330 °C; **DSC** T_g = -18 °C.
GPC M_n = 9.3 kDa, M_w = 15.3 kDa, $Đ$ = 1.64.
1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.10 (m, 4H), 6.60 (s, 2H), 3.84 (t, *J* = 6.4 Hz, 4H), 2.88 (t, *J* = 7.4 Hz, 4H), 2.69 (t, *J* = 7.4 Hz, 4H), 1.94–1.87 (m, 4H), 1.76–1.69 (m, 4H), 1.45–1.31 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 6H).
13C NMR (101 MHz, $CDCl_3$) δ 150.7, 134.4, 129.6, 128.2, 114.2, 68.8, 33.6, 29.6, 29.4, 28.5, 22.6, 14.3, 1.2.
IR (KBr, cm^{-1}) n 2858, 2925, 1204, 807.

P1a2d



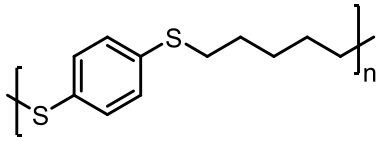
76% yield; **TGA** T_d = 292 °C; **DSC** T_g = 19 °C.
GPC M_n = 5.8 kDa, M_w = 7.5 kDa, $Đ$ = 1.29.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (ws, 4H), 6.61 (ws, 2H), 3.71 (ws, 6H), 2.89 (ws, 4H), 2.69 (ws, 4H), 1.89 (ws, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 134.4, 129.8, 128.1, 113.2, 56.1, 33.6, 29.5, 29.4.
IR (KBr, cm^{-1}) *n* 2923, 1206, 1040, 802.

P1a2a



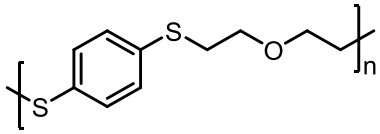
95% yield; **TGA** T_d = 253 °C;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.13 (m, 4H), 7.12–7.03 (m, 4H), 2.87 (t, *J* = 8.0 Hz, 4H), 2.70 (t, *J* = 7.4 Hz, 4H), 2.03–1.86 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 134.1, 129.9, 128.6, 34.3, 33.3, 30.8.
IR (KBr, cm^{-1}) n 3370, 2918, 1513, 1106, 1006, 798.

P1a2e



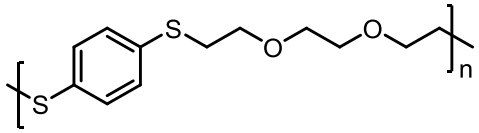
93% yield; **TGA** T_d = 349 °C.
GPC M_n = 4.6 kDa, M_w = 5.9 kDa, $Đ$ = 1.29.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (w, 4H), 2.82 (w, 4H), 1.53 (w, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 129.9, 33.9, 28.7, 27.9.
IR (KBr, cm^{-1}) n 3379, 2922, 1477, 1105, 1008, 803.

P1a2f



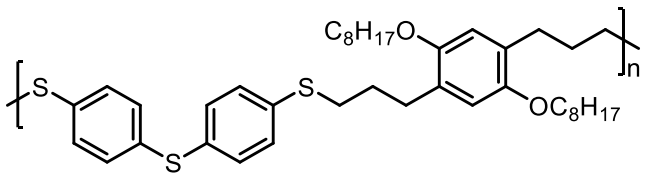
61% yield; **TGA** T_d = 299 °C; **DSC** T_g = -20 °C.
GPC M_n = 5.2 kDa, M_w = 6.3 kDa, $Đ$ = 1.20.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (w, 4H), 3.66–3.56 (m, 4H), 3.08–3.03 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 130.2, 69.7, 33.5.
IR (KBr, cm^{-1}) n 2922, 1477, 1260, 1098, 1007, 802.

P1a2g



61% yield; **TGA** T_d = 270 °C.
GPC M_n = 4.8 kDa, M_w = 5.4 kDa, $Đ$ = 1.11.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 4H), 3.77–3.39 (m, 8H), 3.08 (ws, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 130.2, 70.5, 70.1, 33.4.
IR (KBr, cm^{-1}) n 2874, 1479, 1287, 1101, 1006, 801.

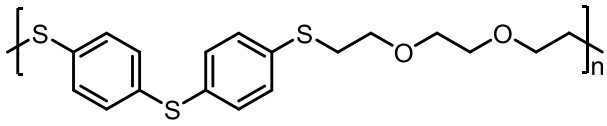
P1b2b



62% yield; **TGA** T_d = 317 °C; **DSC** T_g = -13 °C.
GPC M_n = 5.8 kDa, M_w = 8.7 kDa, $Đ$ = 1.52.

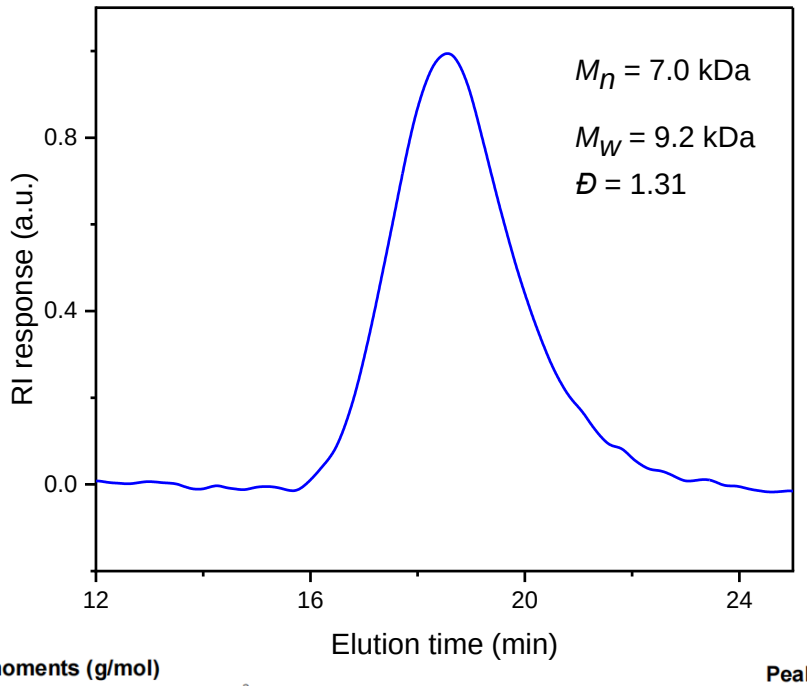
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (w, 8H), 6.60 (ws, 2H), 3.83 (ws, 4H), 2.90 (ws, 4H), 2.69 (ws, 4H), 1.92 (ws, 4H), 1.70 (ws, 4H), 1.48–1.16 (w, 20H), 0.87 (ws, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 132.7, 131.5, 129.2, 114.2, 68.8, 33.0, 31.9, 29.7, 29.6, 29.5, 29.5, 26.4, 22.8, 14.3, 1.2.
IR (KBr, cm^{-1}) n 2962, 1258, 1011, 794.

P1b2g



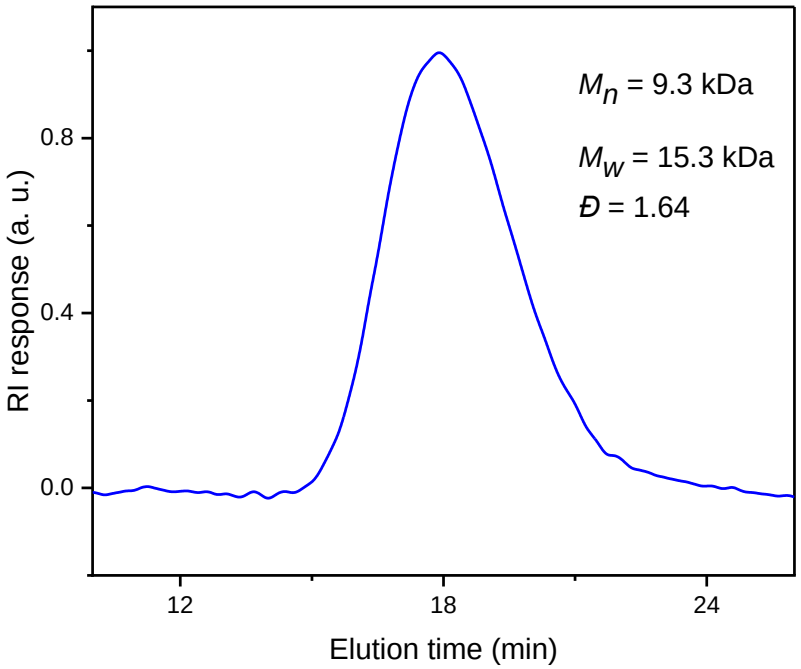
77% yield; **TGA** T_d = 264 °C; **DSC** T_g = -9 °C.
GPC M_n = 7.6 kDa, M_w = 8.6 kDa, $Đ$ = 1.13.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.15 (m, 8H), 3.65 (t, J = 7.2 Hz, 4H), 3.59 (s, 4H), 3.09 (t, J = 6.8 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 133.4, 131.6, 129.9, 70.5, 70.0, 33.1.
IR (KBr, cm^{-1}) n 2897, 1474, 1095, 1007, 803.

6. GPC traces



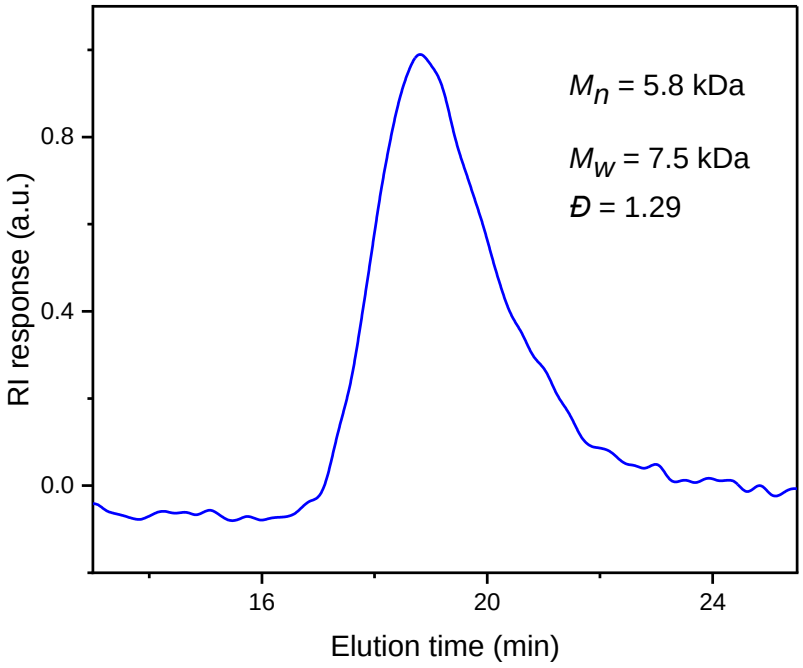
Molar mass moments (g/mol)			Peak 1
Mn	6.988×10^3 (±4.331%)	Polydispersity Mw/Mn	1.314 (±5.499%)
Mw	9.179×10^3 (±3.387%)		

Figure S1. GPC trace of **P1a2b**



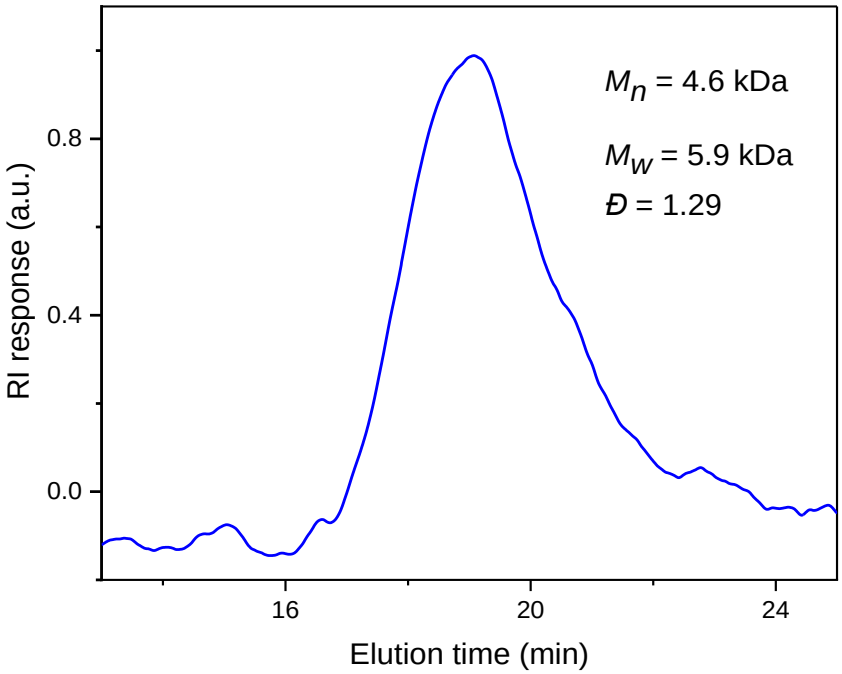
Molar mass moments (g/mol)			Peak 1
Mn	9.290×10^3 (±4.953%)	Polydispersity Mw/Mn	1.641 (±7.042%)
Mw	1.525×10^4 (±5.006%)		

Figure S2. GPC trace of **P1a2c**



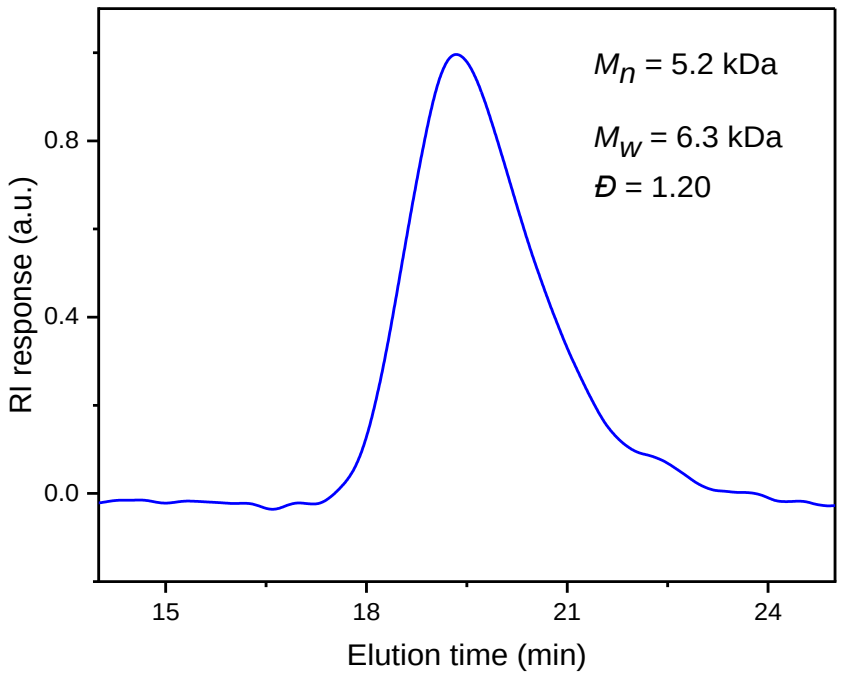
Molar mass moments (g/mol)			Peak 1
Mn	5.840×10^3 (±4.476%)	**Polydispersity**	
Mw	7.516×10^3 (±4.227%)	**Mw/Mn**	1.287 (±6.156%)

Figure S3. GPC trace of **P1a2d**



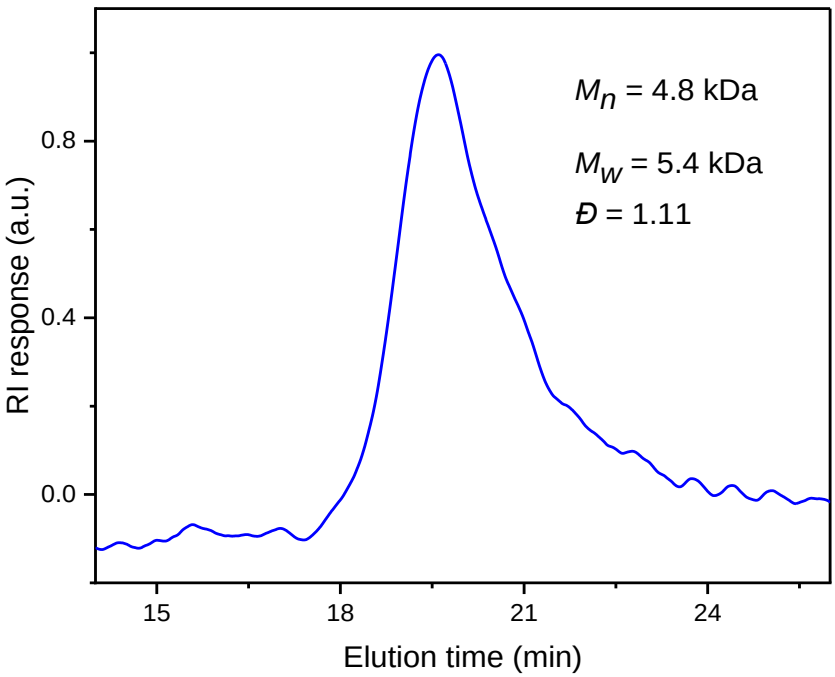
Molar mass moments (g/mol)			Peak 1
Mn	4.584×10^3 (±9.648%)	**Polydispersity**	
Mw	5.931×10^3 (±8.371%)	**Mw/Mn**	1.294 (±12.773%)

Figure S4. GPC trace of **P1a2e**



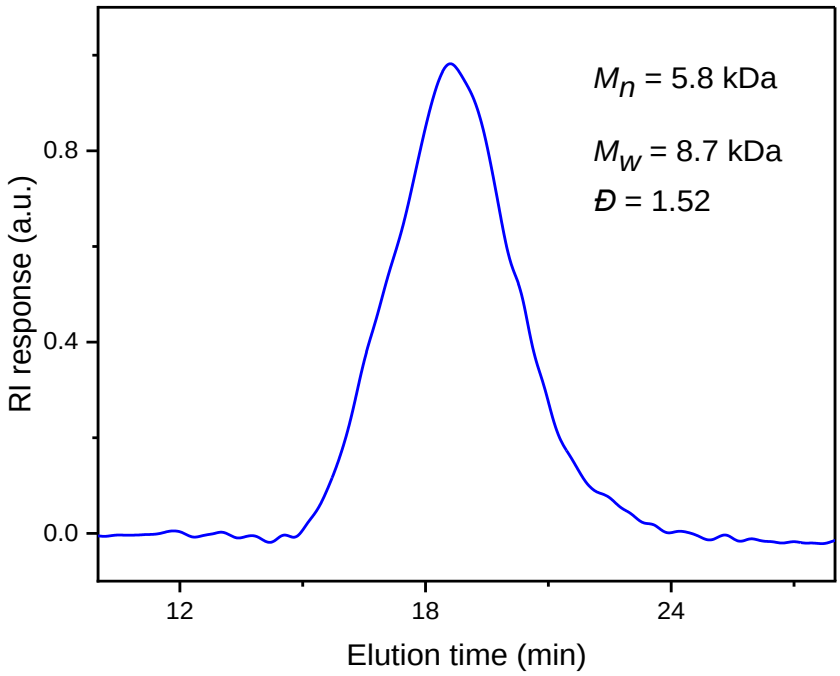
Molar mass moments (g/mol)			Peak 1
Mn	5.247×10^3 (±3.476%)	Polydispersity	
Mw	6.287×10^3 (±3.203%)	Mw/Mn	1.198 (±4.727%)

Figure S5. GPC trace of **P1a2f**



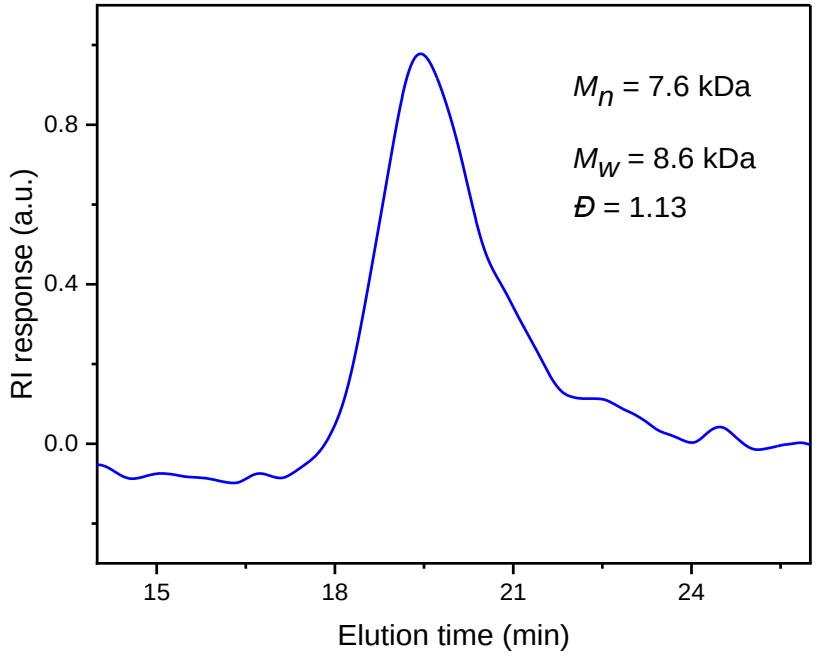
Molar mass moments (g/mol)			Peak 1
Mn	4.828×10^3 (±5.954%)	Polydispersity	
Mw	5.357×10^3 (±5.707%)	Mw/Mn	1.110 (±8.248%)

Figure S6. GPC trace of **P1a2g**



Molar mass moments (g/mol)			Peak 1
Mn	5.752×10^3 (±7.521%)	Polydispersity	
Mw	8.740×10^3 (±6.020%)	Mw/Mn	1.520 (±9.633%)

Figure S7. GPC trace of **P1b2b**



Molar mass moments (g/mol)			Peak 1
Mn	7.626×10^3 (±5.541%)	Polydispersity	
Mw	8.639×10^3 (±5.254%)	Mw/Mn	1.133 (±7.636%)

Figure S8. GPC trace of **P1b2g**

7. FT–IR traces

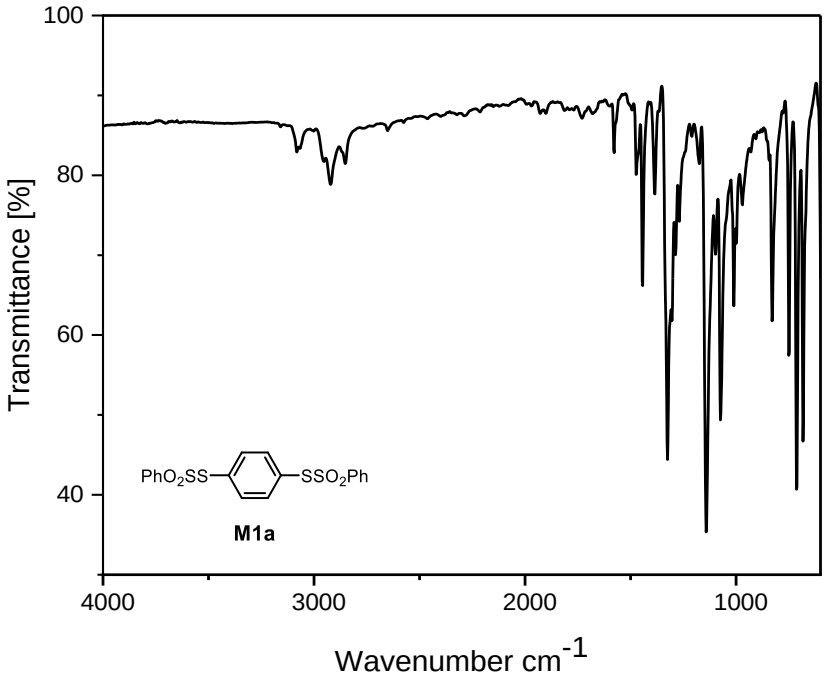


Figure S9. FT–IR of **M1a**

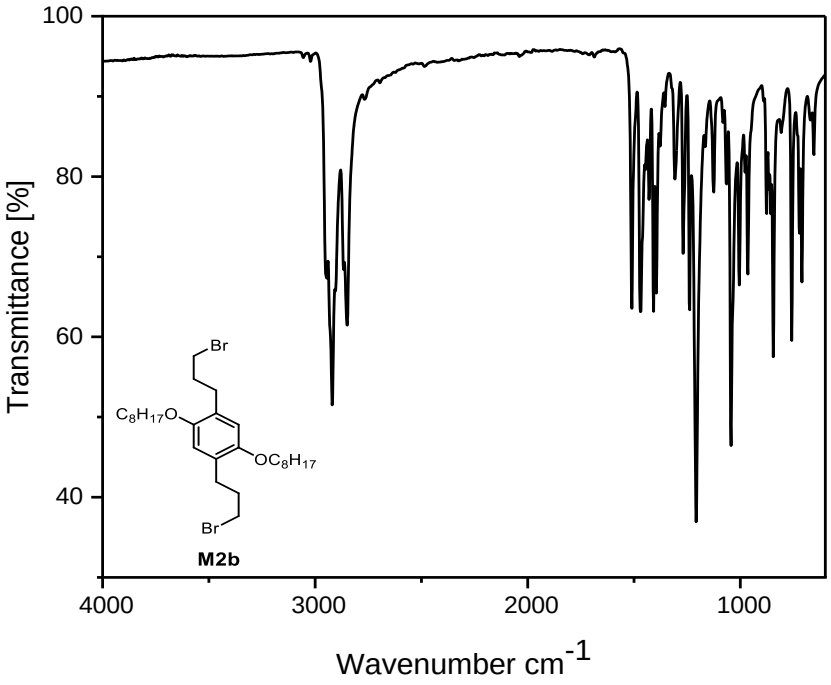


Figure S10. FT–IR of **M2b**

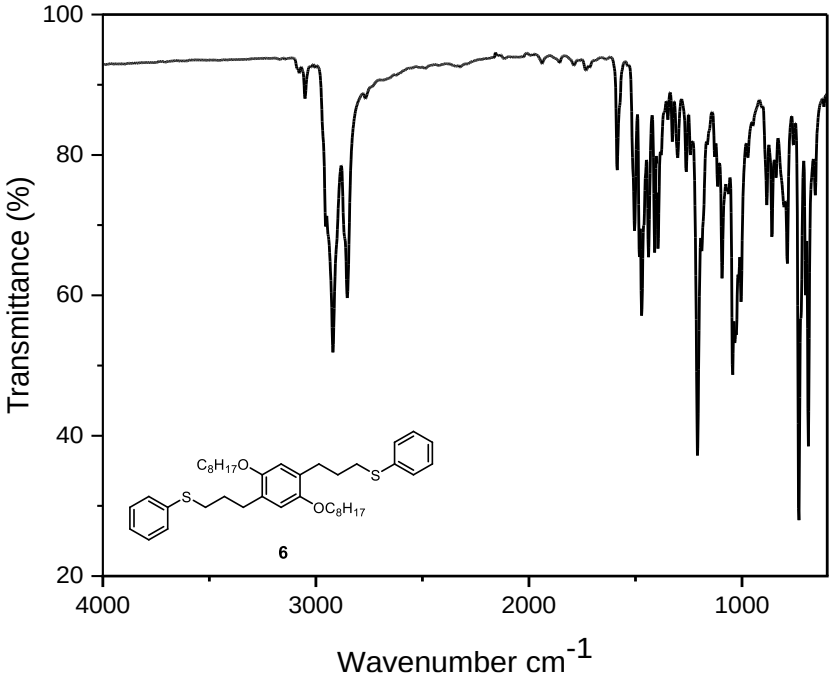


Figure S11. FT–IR of **6**

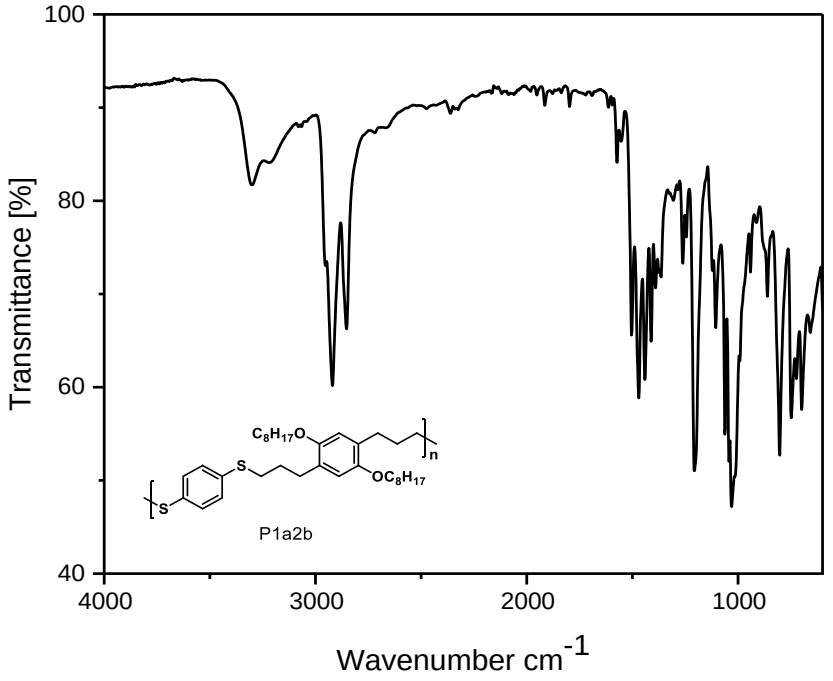


Figure S12. FT–IR of **P1a2b**

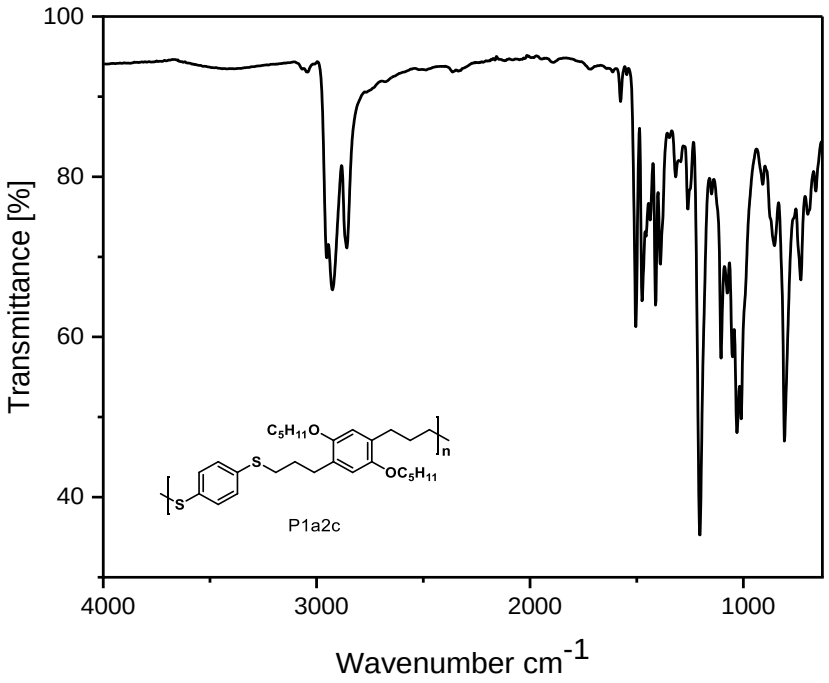


Figure S13. FT–IR of **P1a2c**

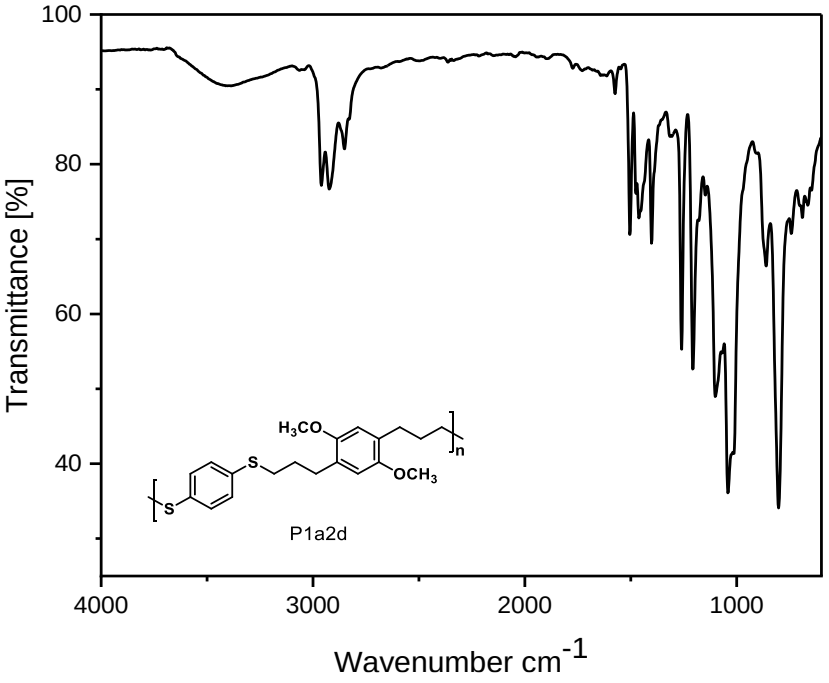


Figure S14. FT–IR of **P1a2d**

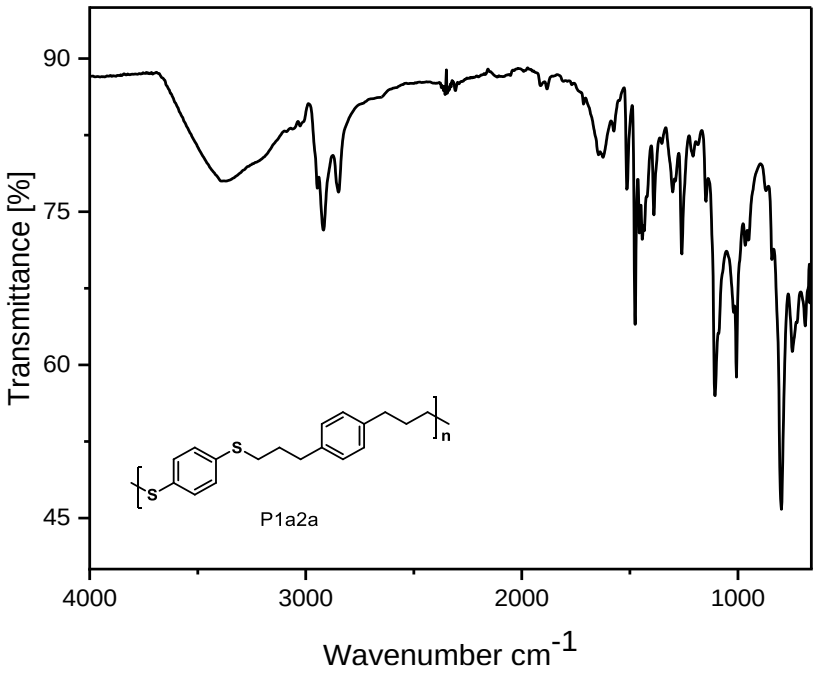


Figure S15. FT–IR of **P1a2a**

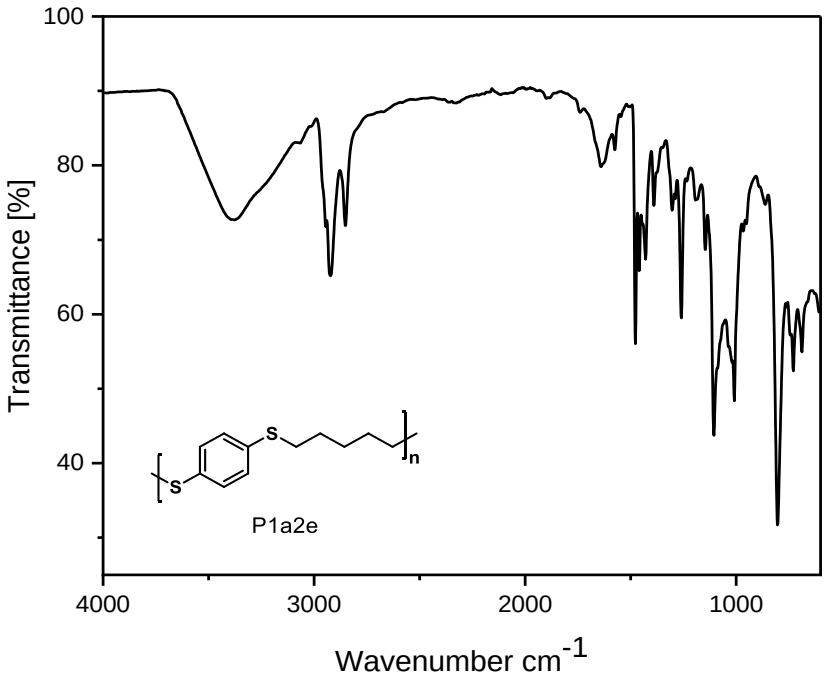


Figure S16. FT–IR of **P1a2e**

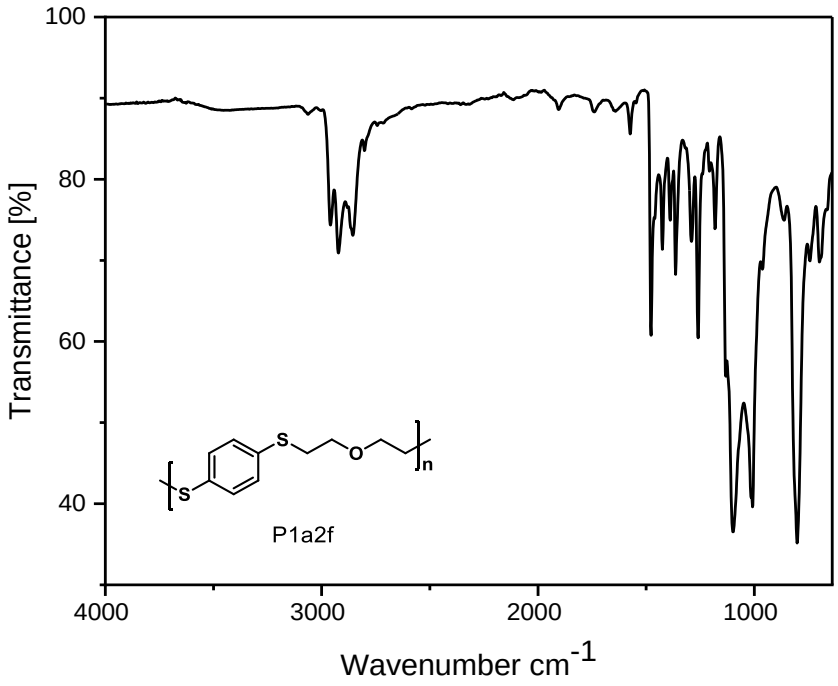


Figure S17. FT–IR **of P1a2f**

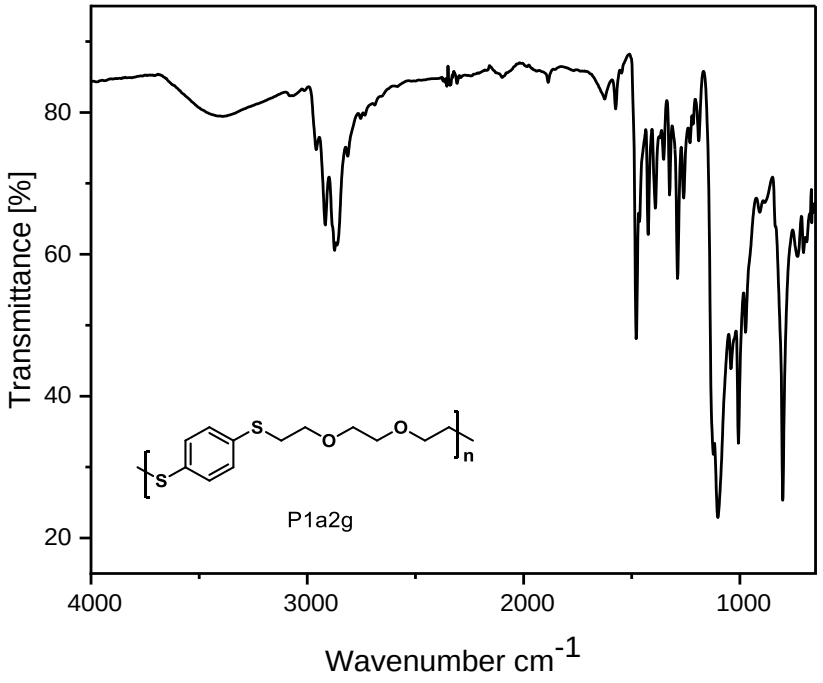


Figure S18. FT–IR **of P1a2g**

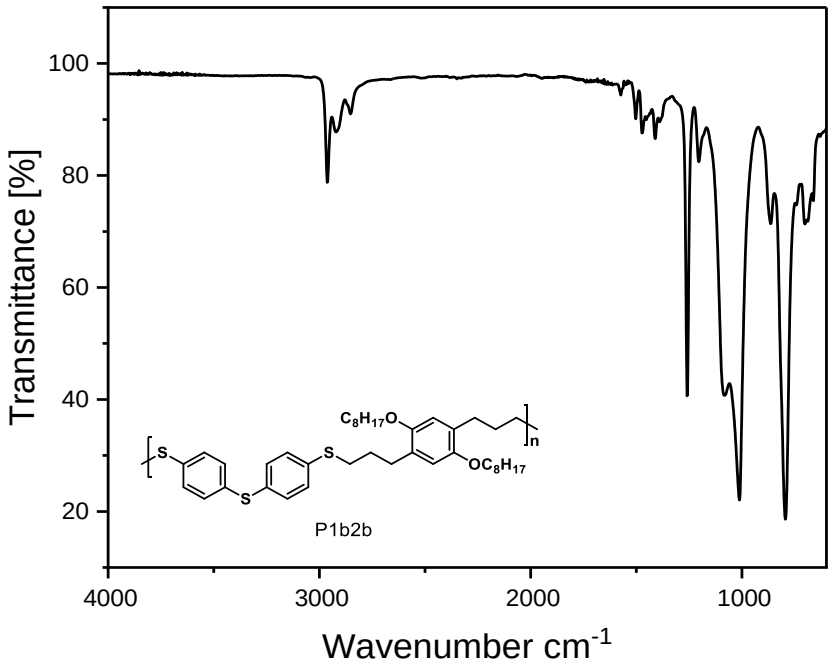


Figure S19. FT–IR of **P1b2b**

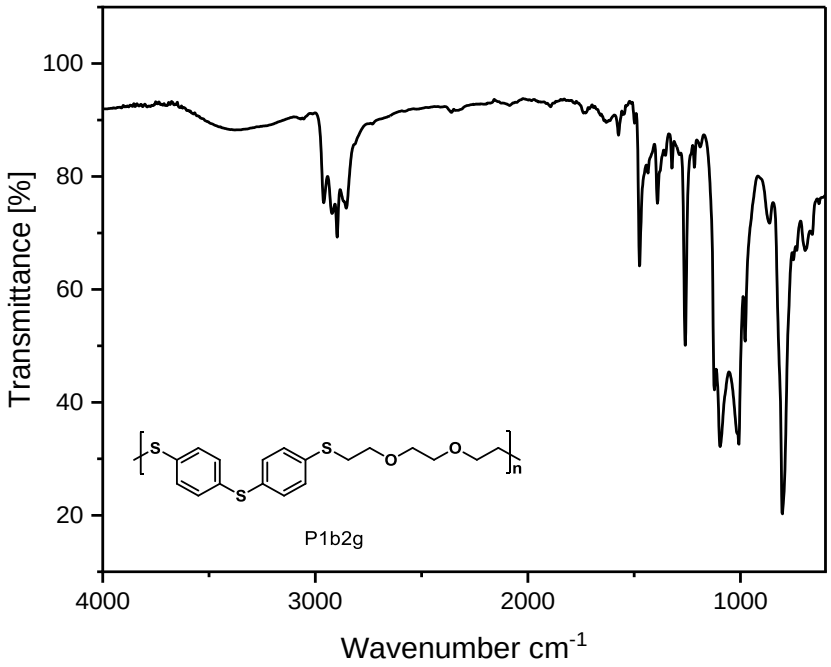


Figure S20. FT–IR of **P1b2g**

8. Raman traces

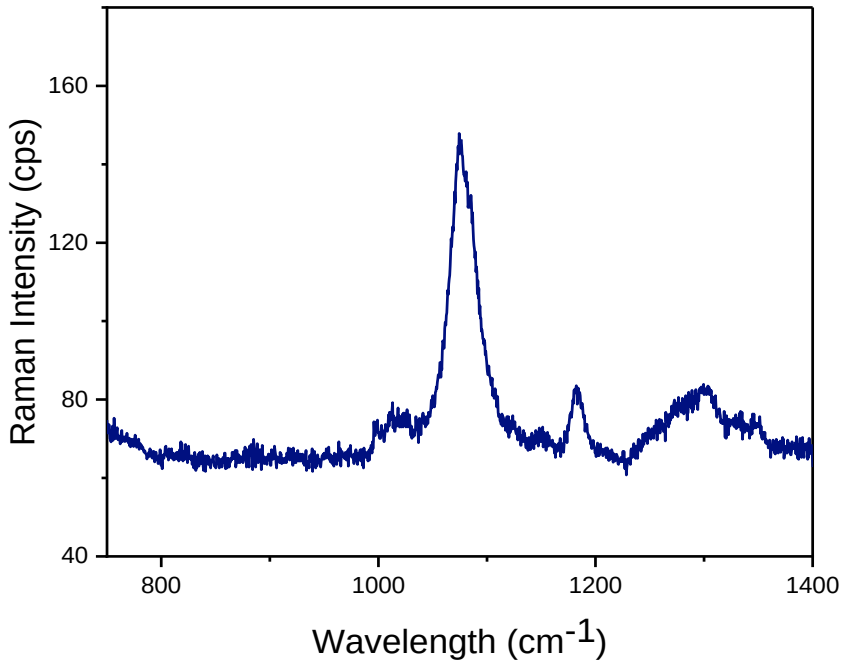


Figure S21. Raman traces of **P1a2b**

9. Refractive index

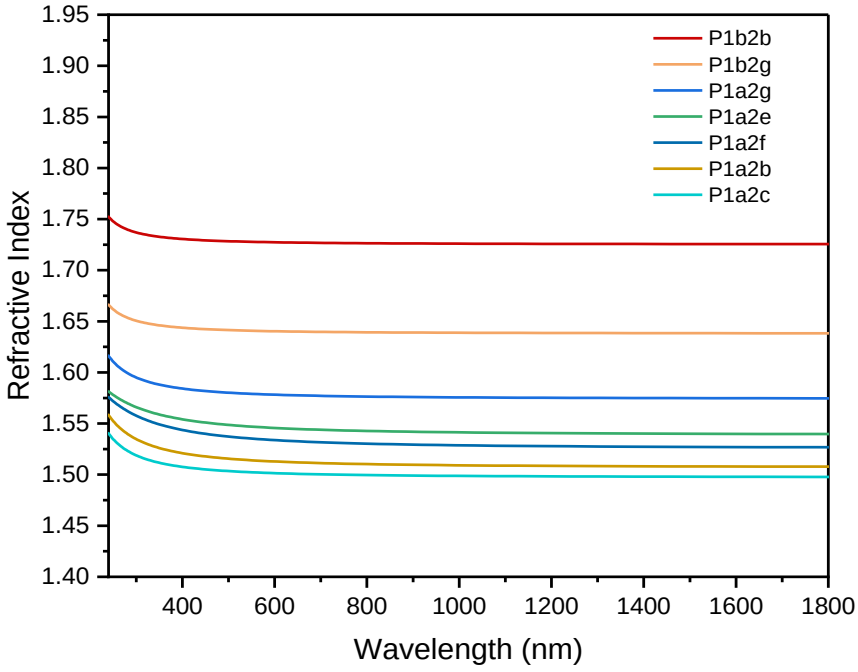


Figure S22. Refractive index of Polymers

10. TGA traces

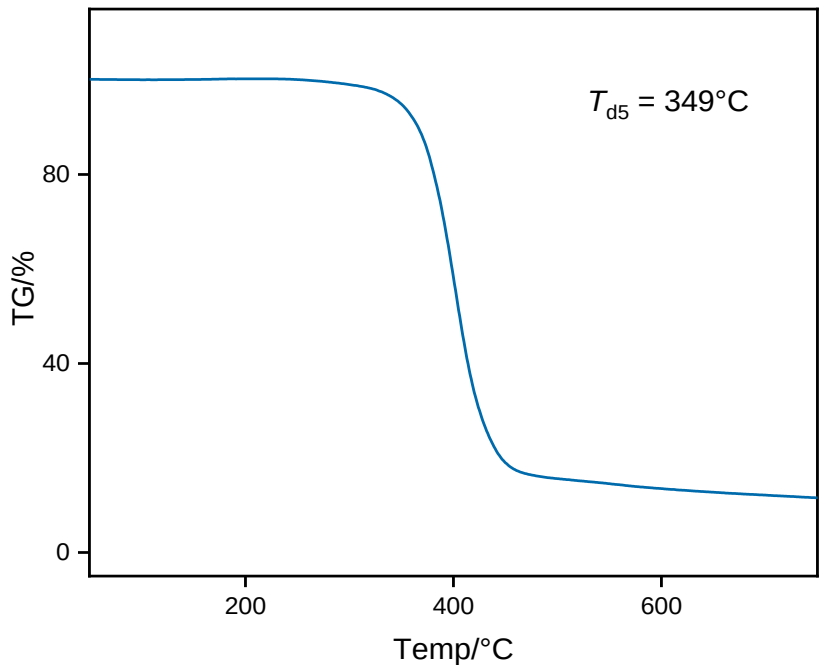


Figure S23. TGA of **P1a2b**

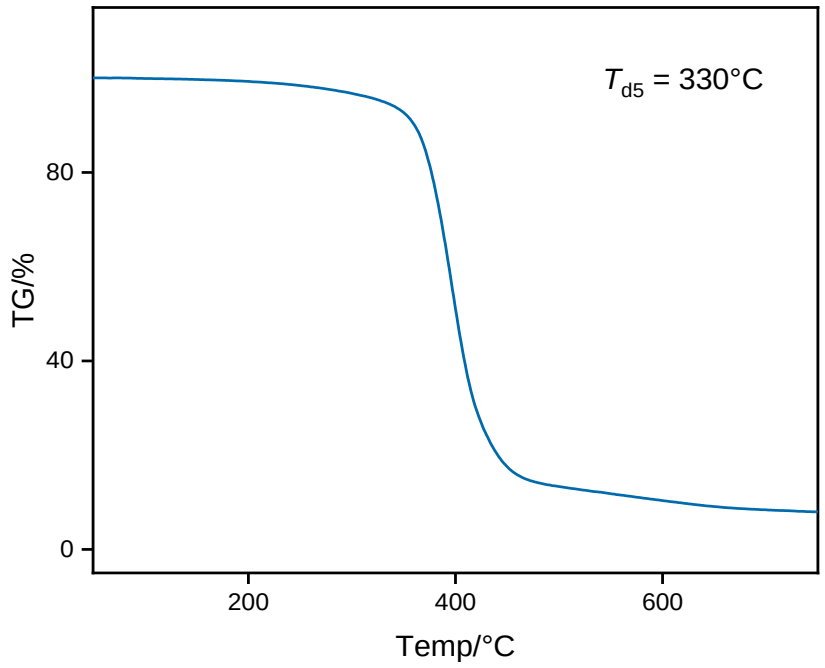


Figure S24. TGA of **P1a2c**

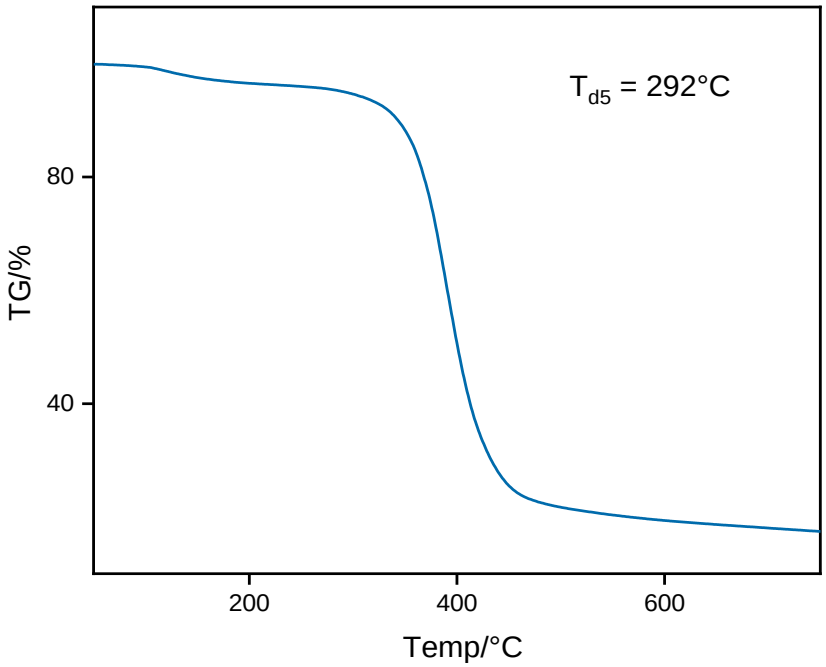


Figure S25. TGA of **P1a2d**

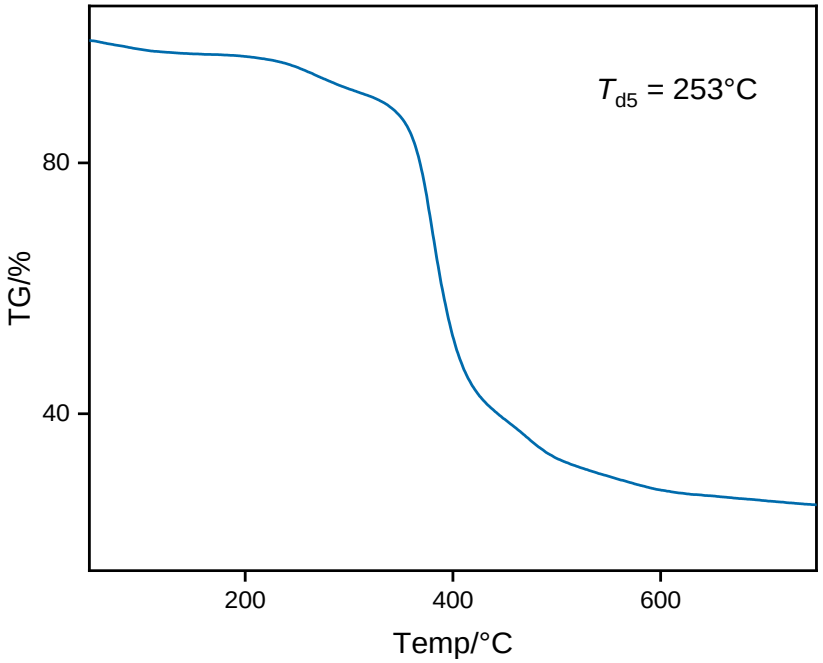


Figure S26. TGA of **P1a2a**

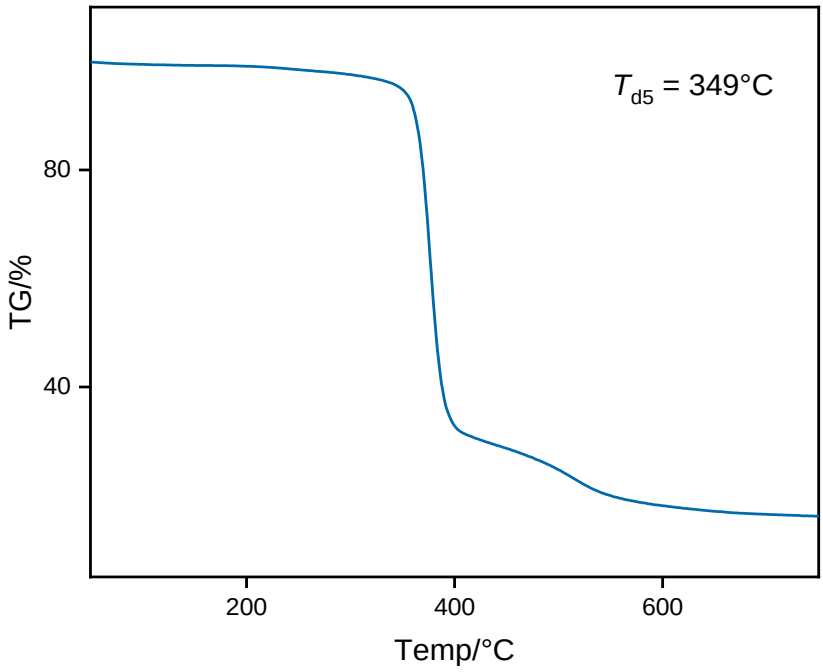


Figure S27. TGA of **P1a2e**

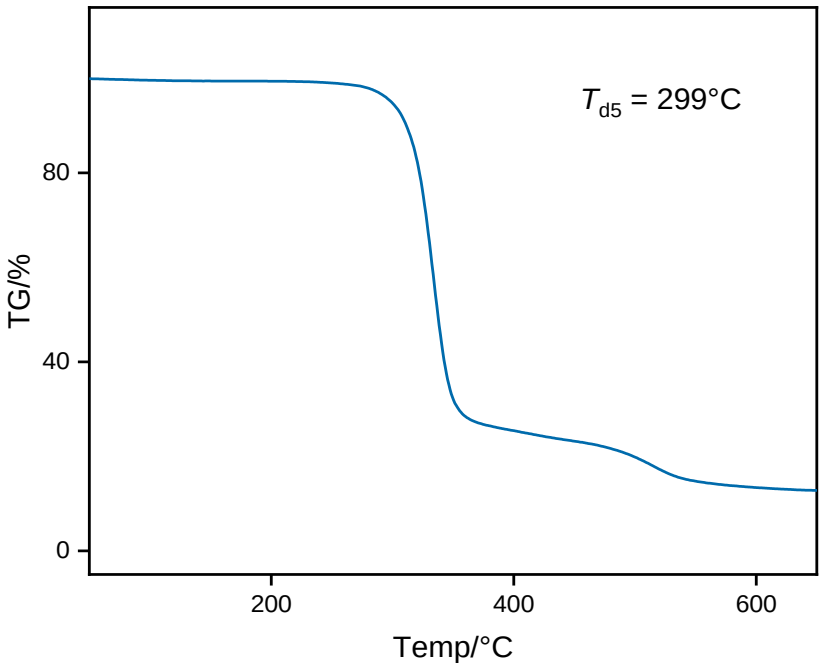


Figure S28. TGA of **P1a2f**

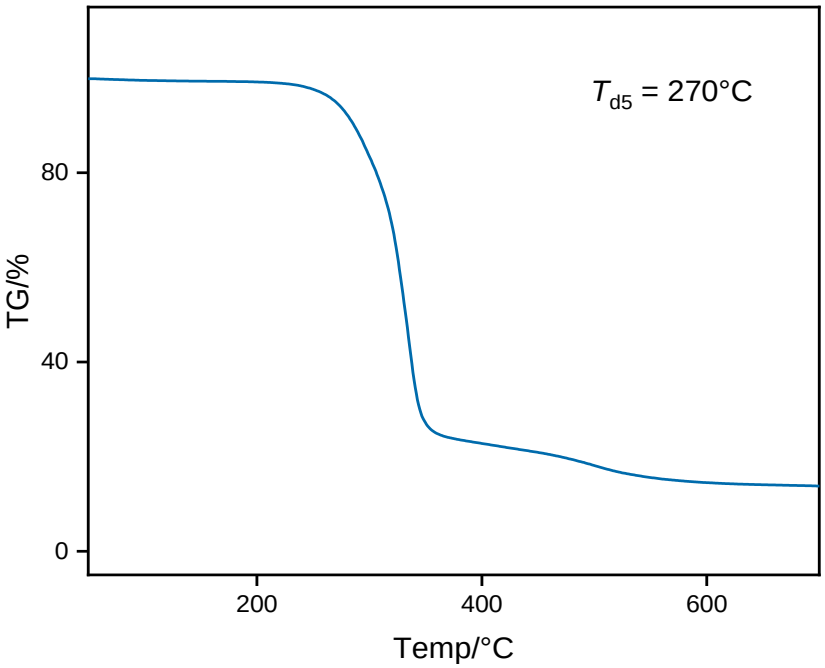


Figure S29. TGA of **P1a2g**

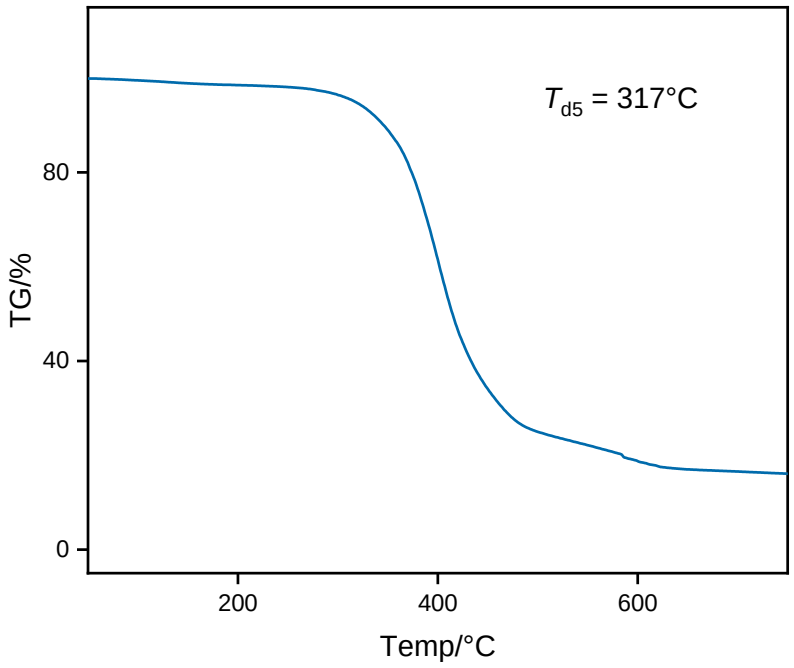


Figure S30. TGA of **P1b2b**

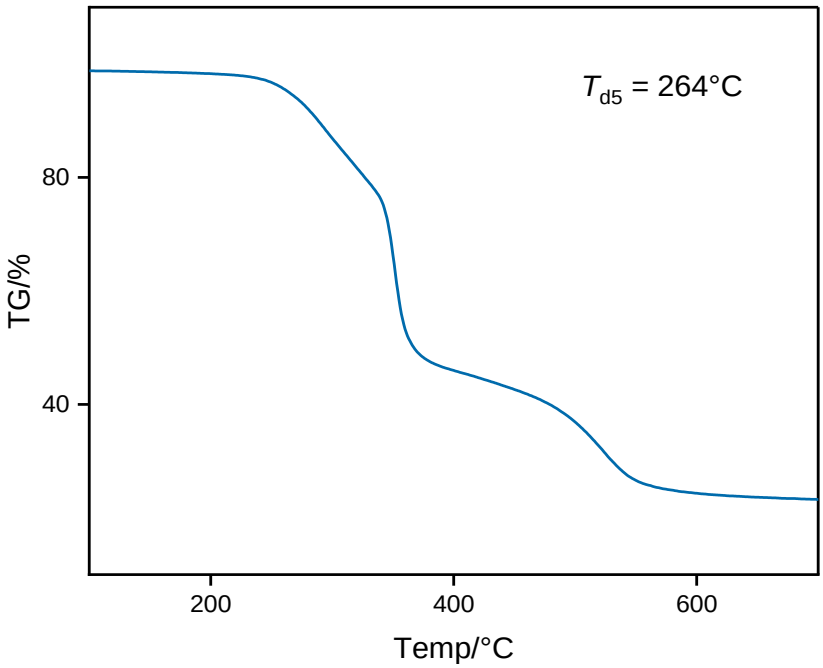


Figure S31. TGA of **P1b2g**

11. DSC traces

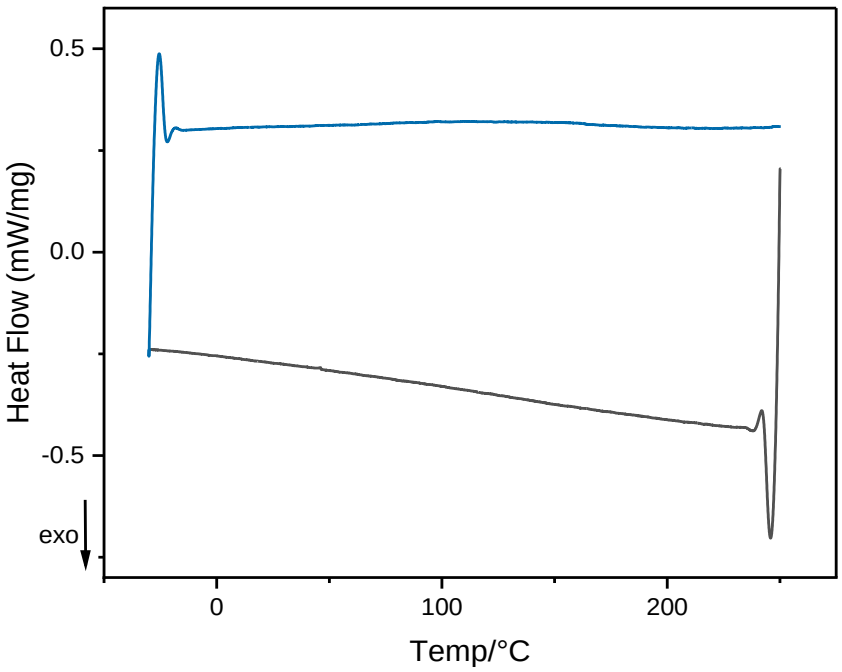


Figure S32. DSC of **P1a2b**

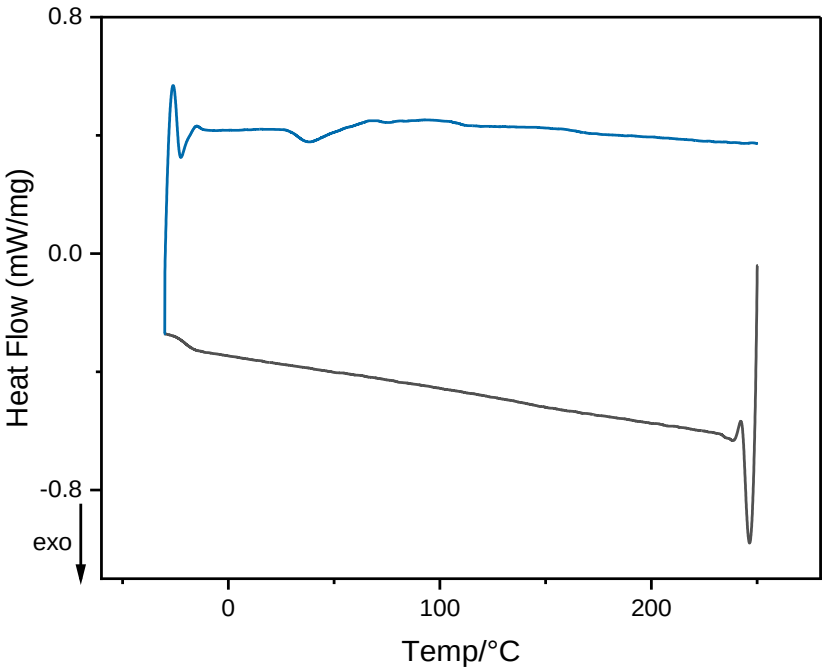


Figure S33. DSC of **P1a2c**

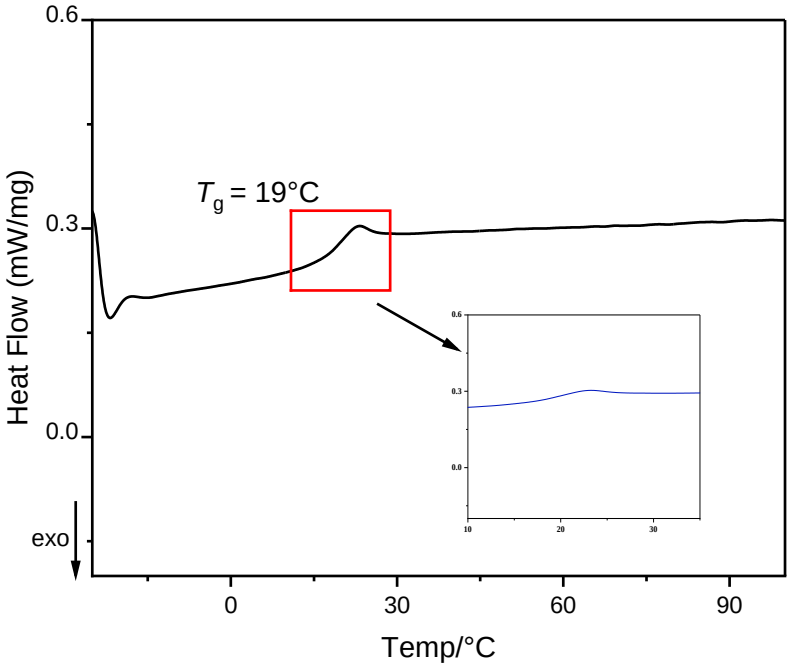


Figure S34. DSC of P1a2d

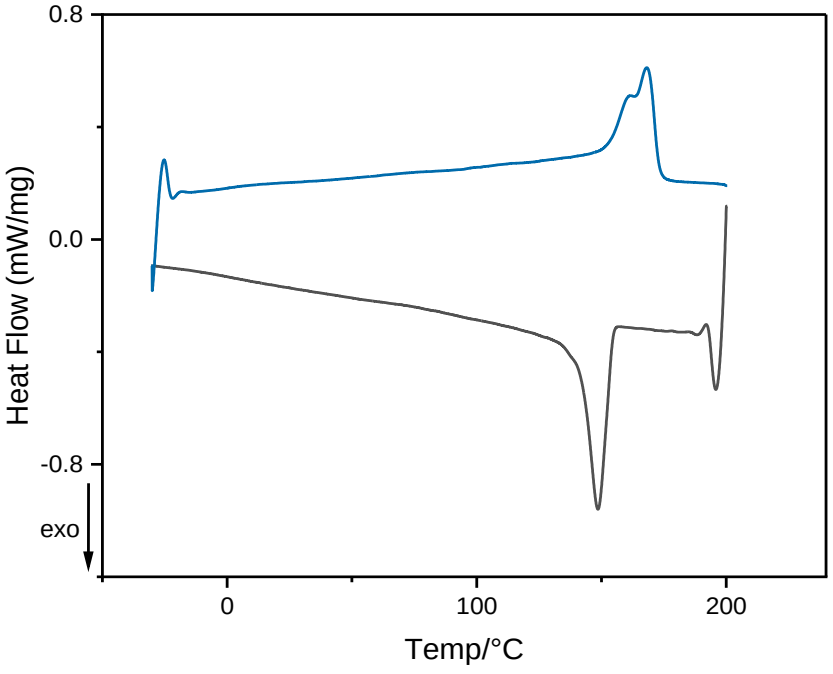


Figure S35. DSC of **P1a2a**

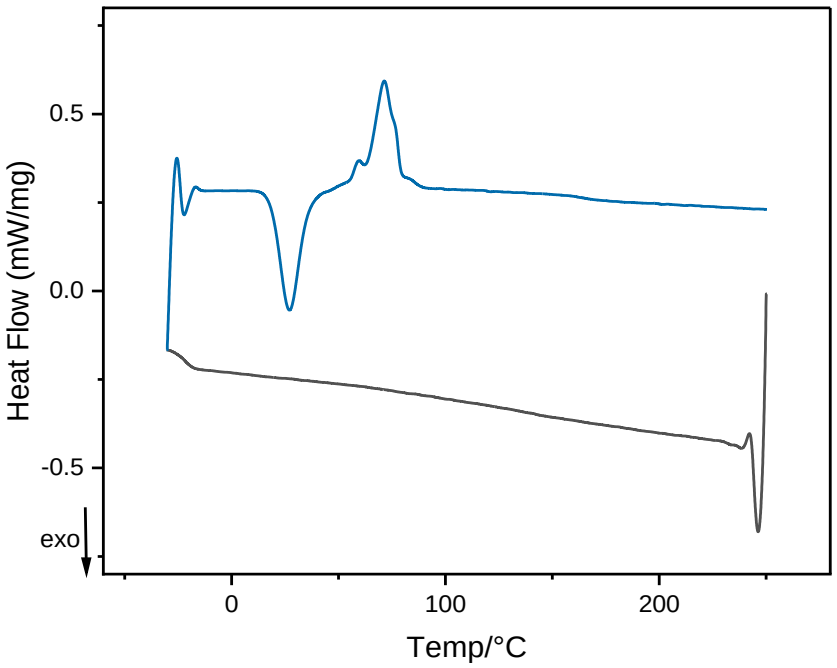


Figure S36. DSC of **P1a2e**

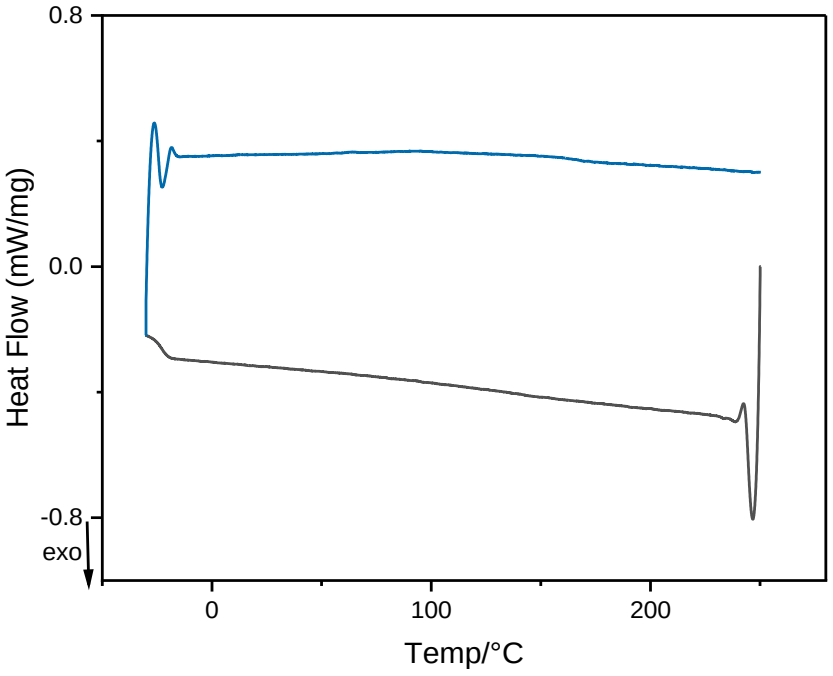


Figure S37. DSC of **P1a2f**

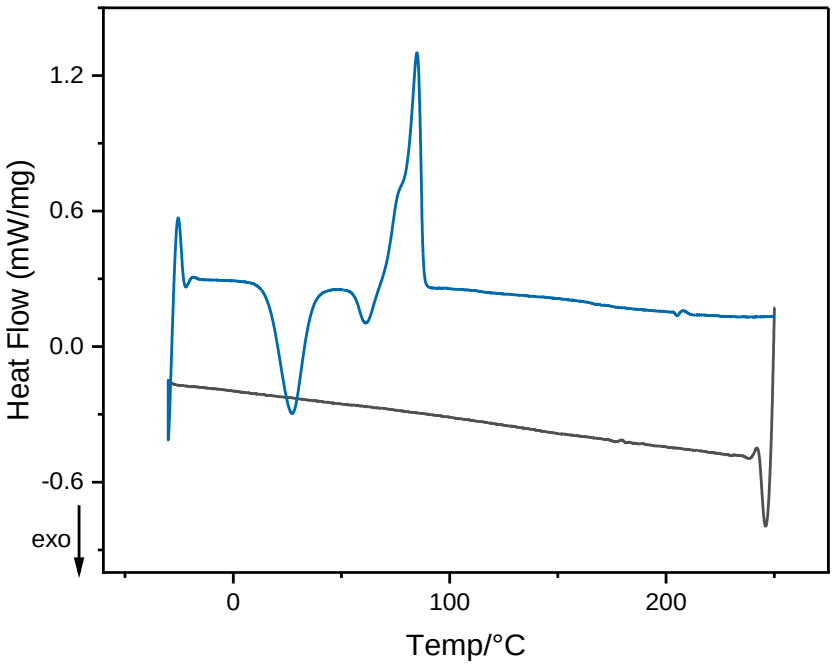


Figure S38. DSC of **P1a2g**

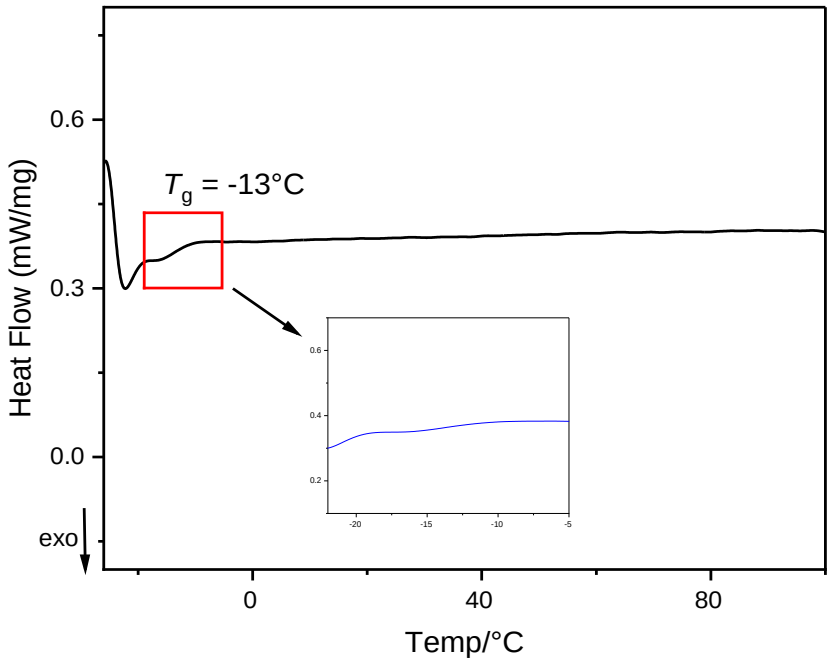


Figure S39. DSC of **P1b2b**

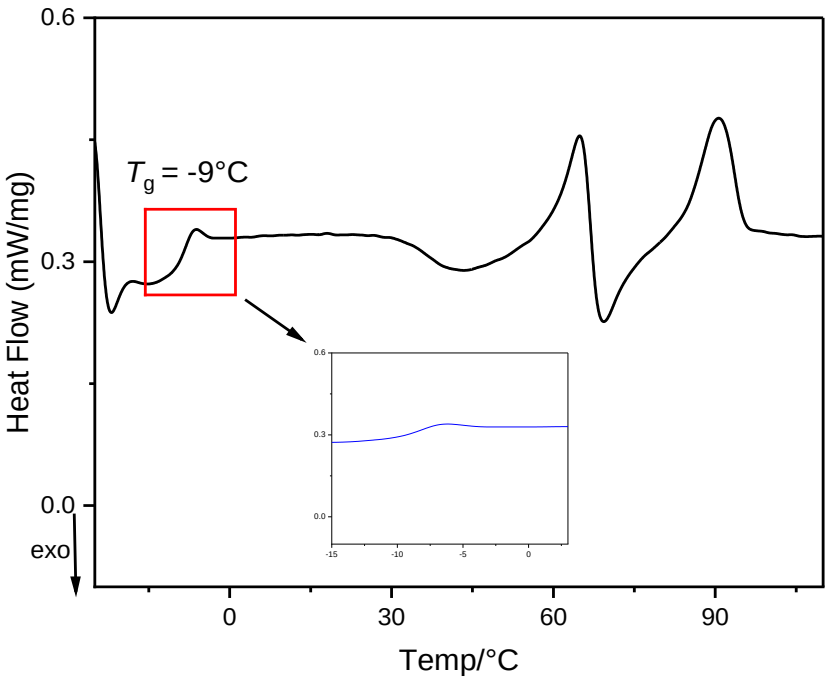
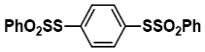
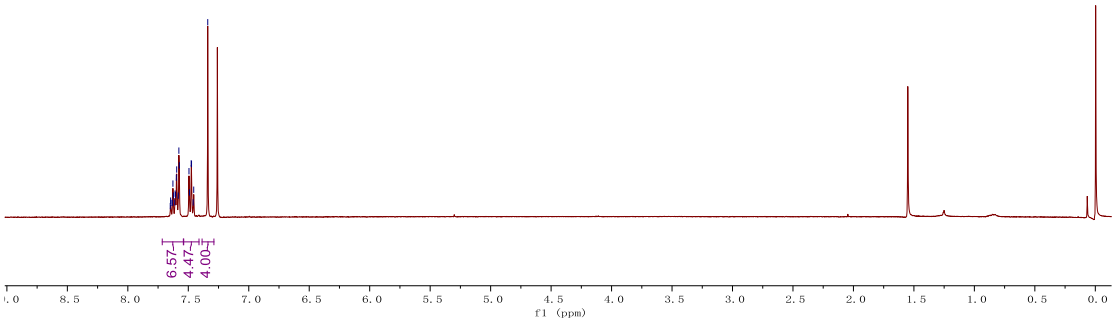


Figure S40. DSC of **P1b2g**

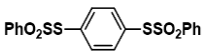
12. NMR spectra



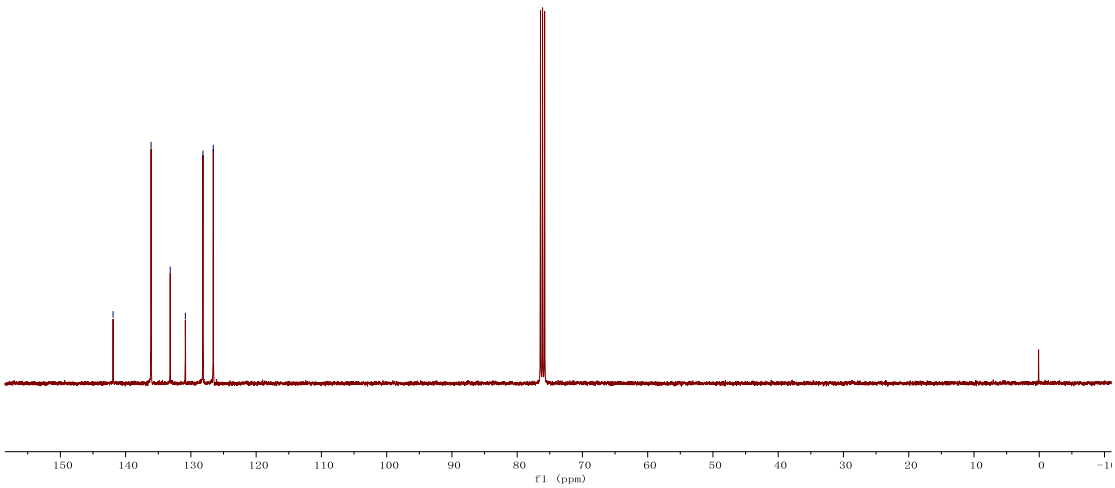
M1a



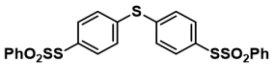
^{1}H NMR, $CDCl_3$, 400 MHz



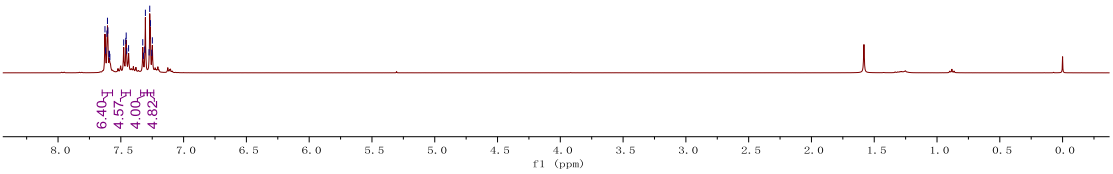
M1a



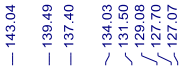
^{13}C NMR, $CDCl_3$, 101 MHz

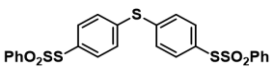


M1b

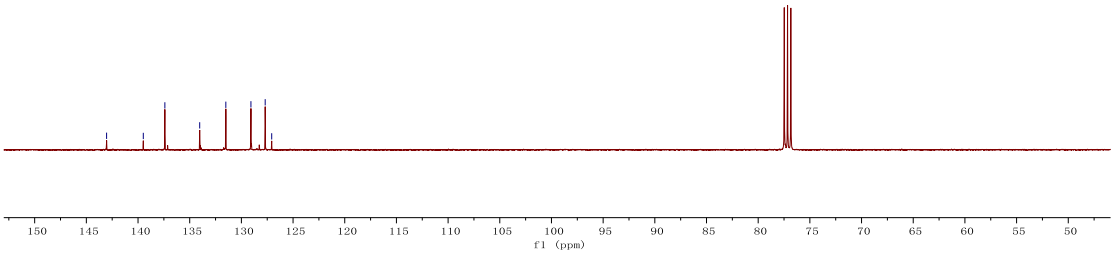


^{1}H NMR, $CDCl_3$, 400 MHz

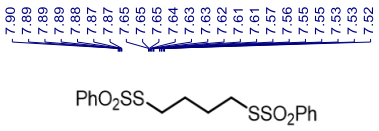




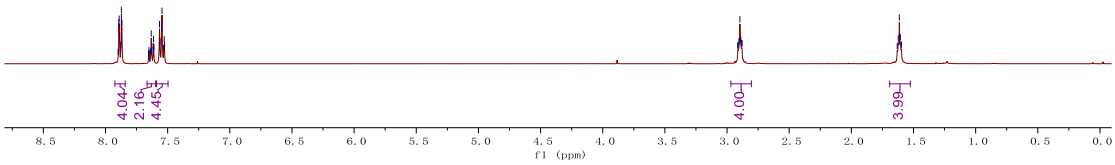
M1b



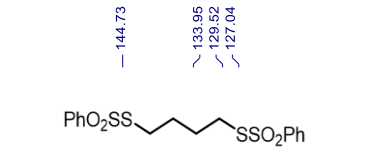
^{13}C NMR, $CDCl_3$, 101 MHz



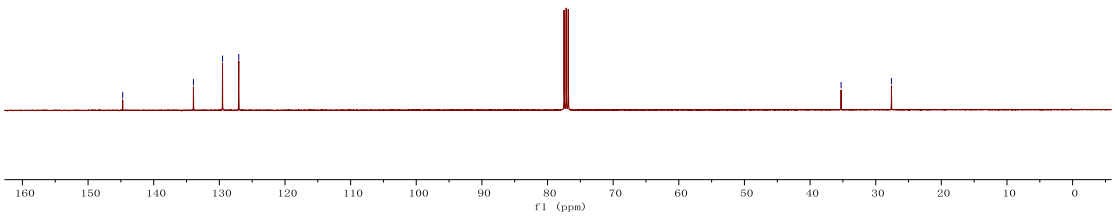
M1c



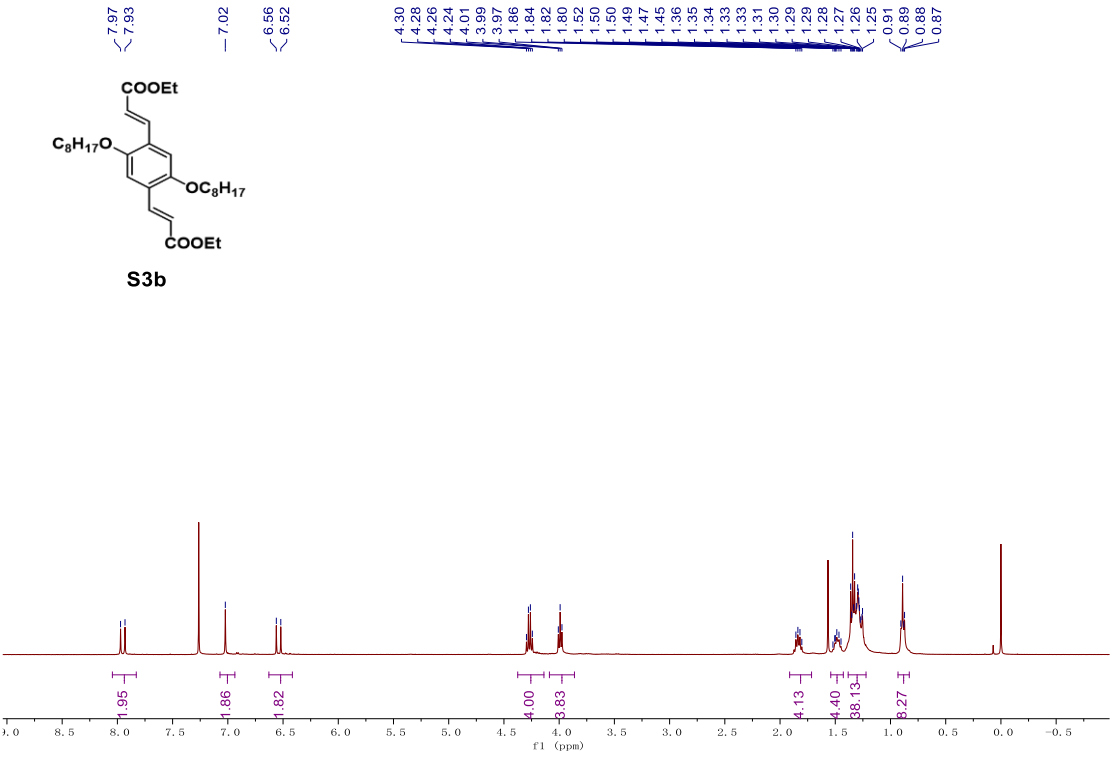
^{1}H NMR, $CDCl_3$, 400 MHz



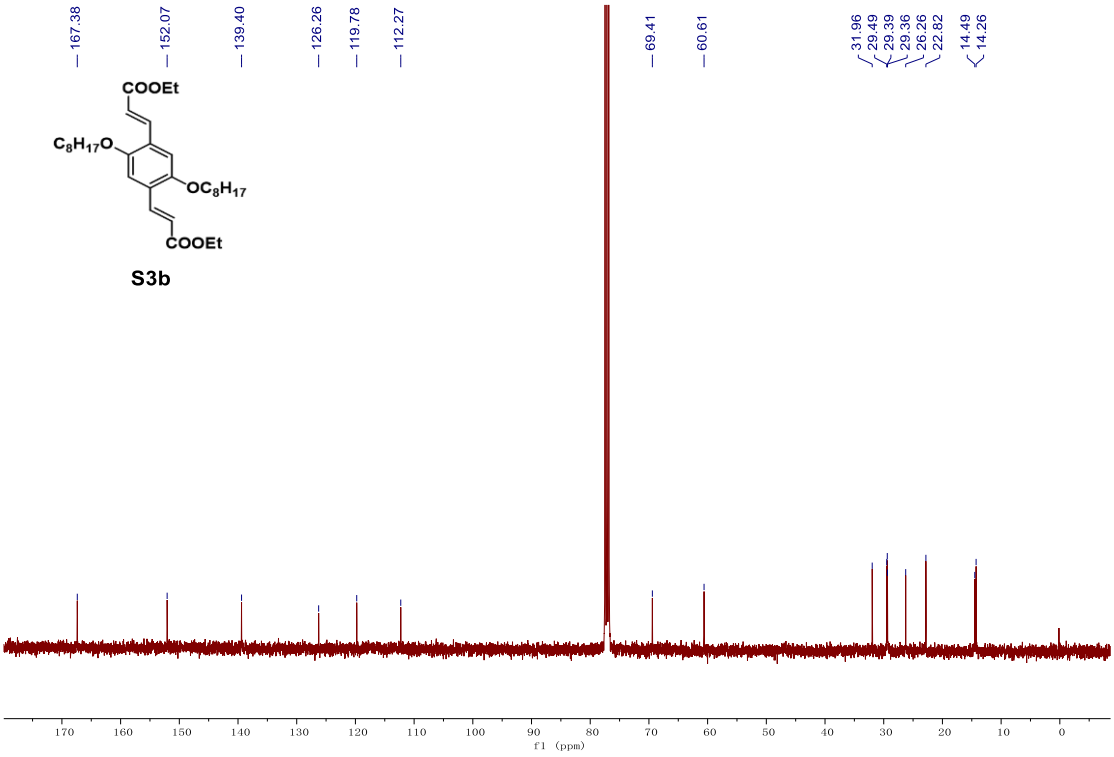
M1c



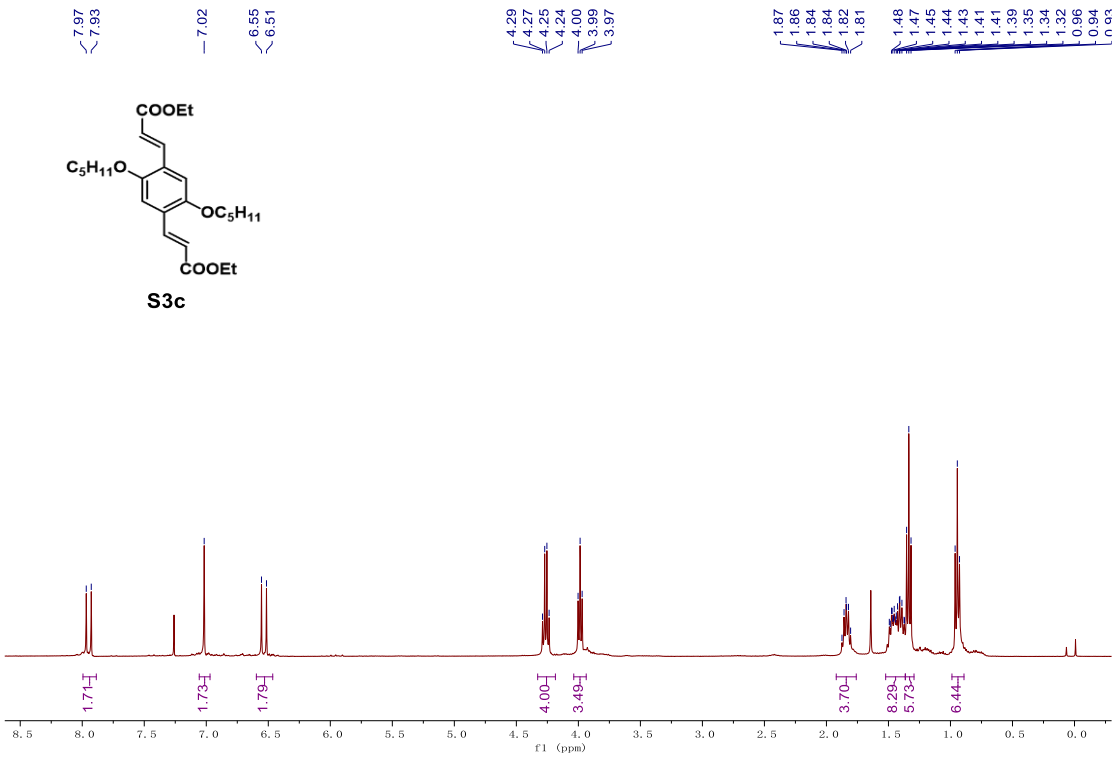
^{13}C NMR, $CDCl_3$, 101 MHz



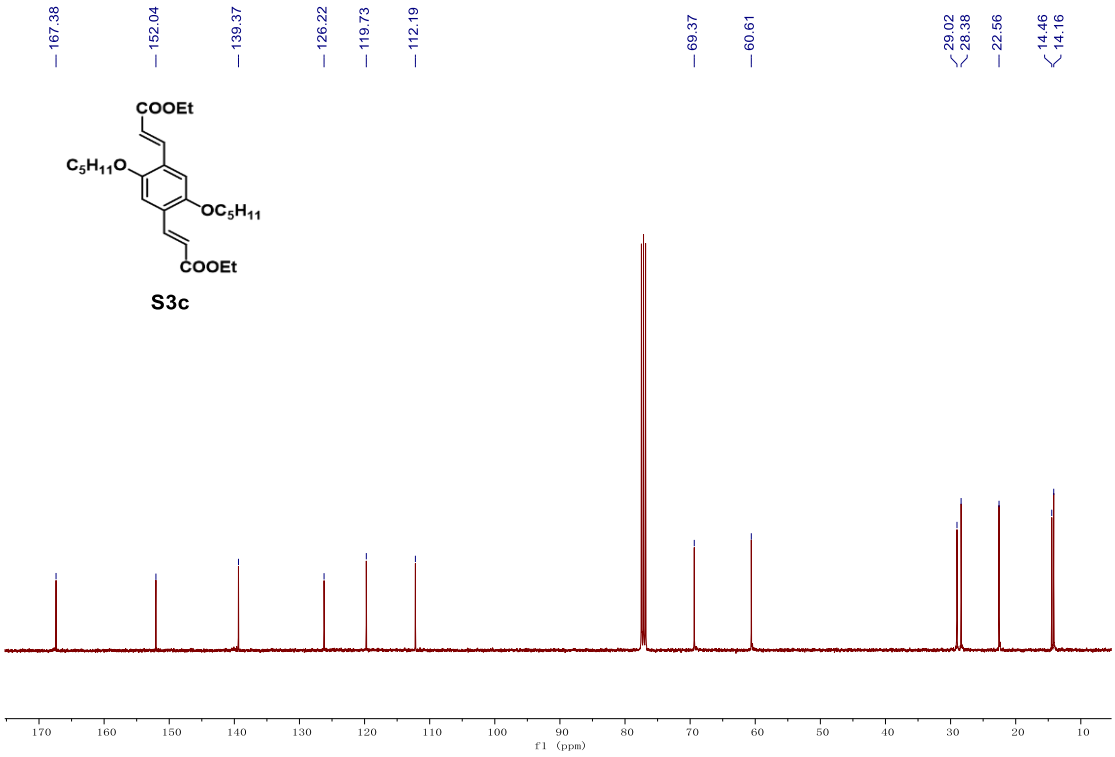
^{1}H NMR, $CDCl_3$, 400 MHz



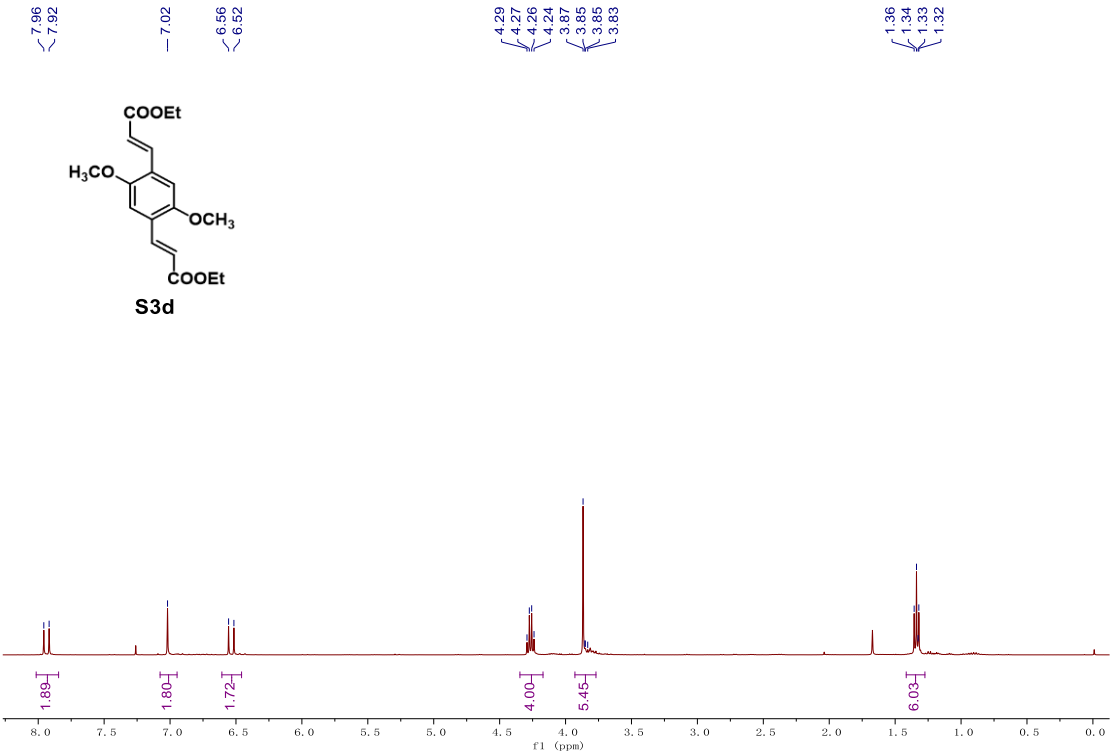
^{13}C NMR, $CDCl_3$, 101 MHz



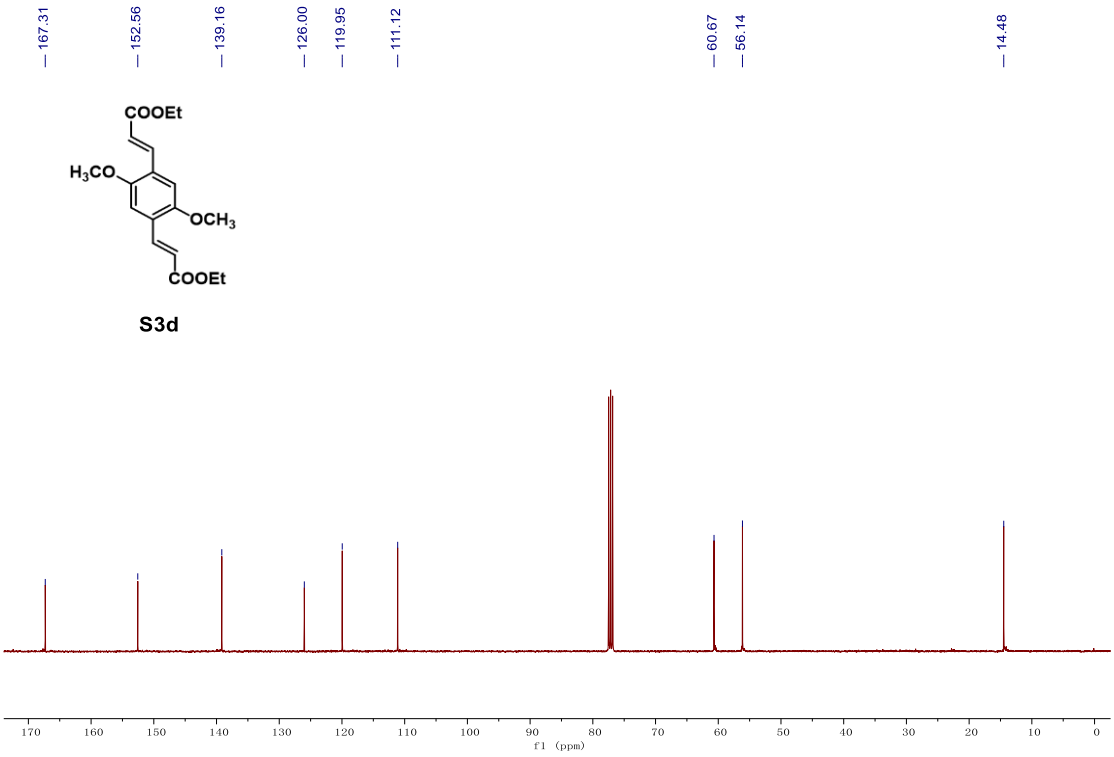
^{1}H NMR, CDCl3, 400 MHz



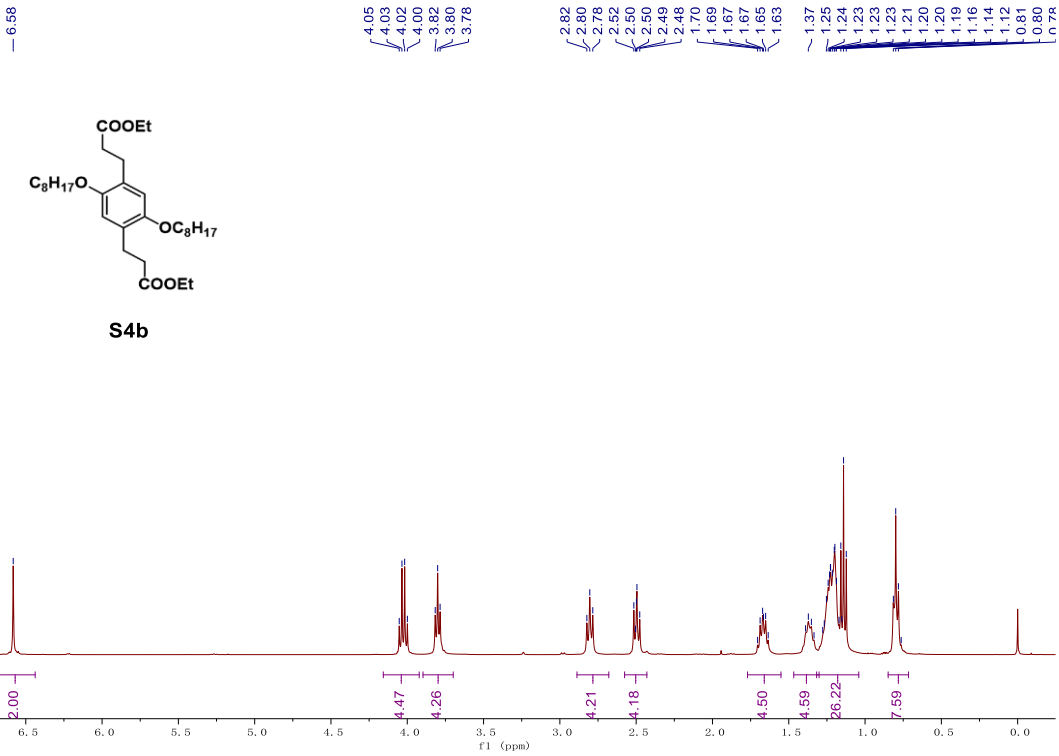
^{13}C NMR, CDCl$_3$, 101 MHz



^{1}H NMR, $CDCl_3$, 400 MHz

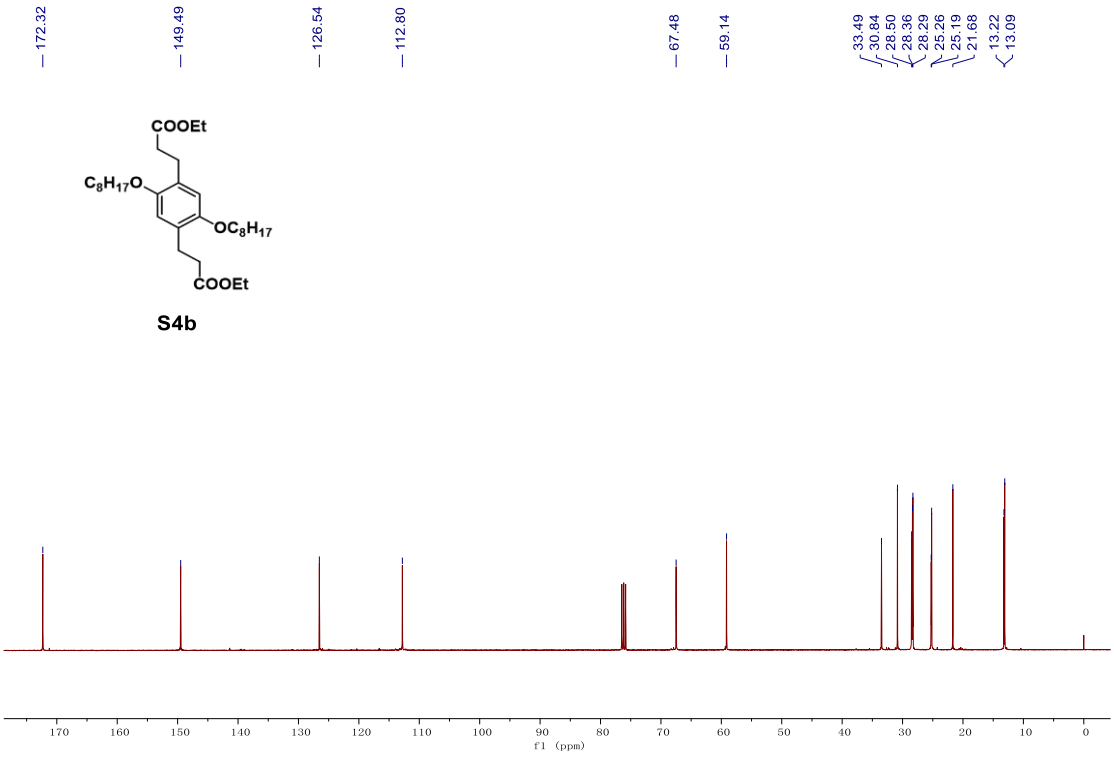


^{13}C NMR, $CDCl_3$, 101 MHz



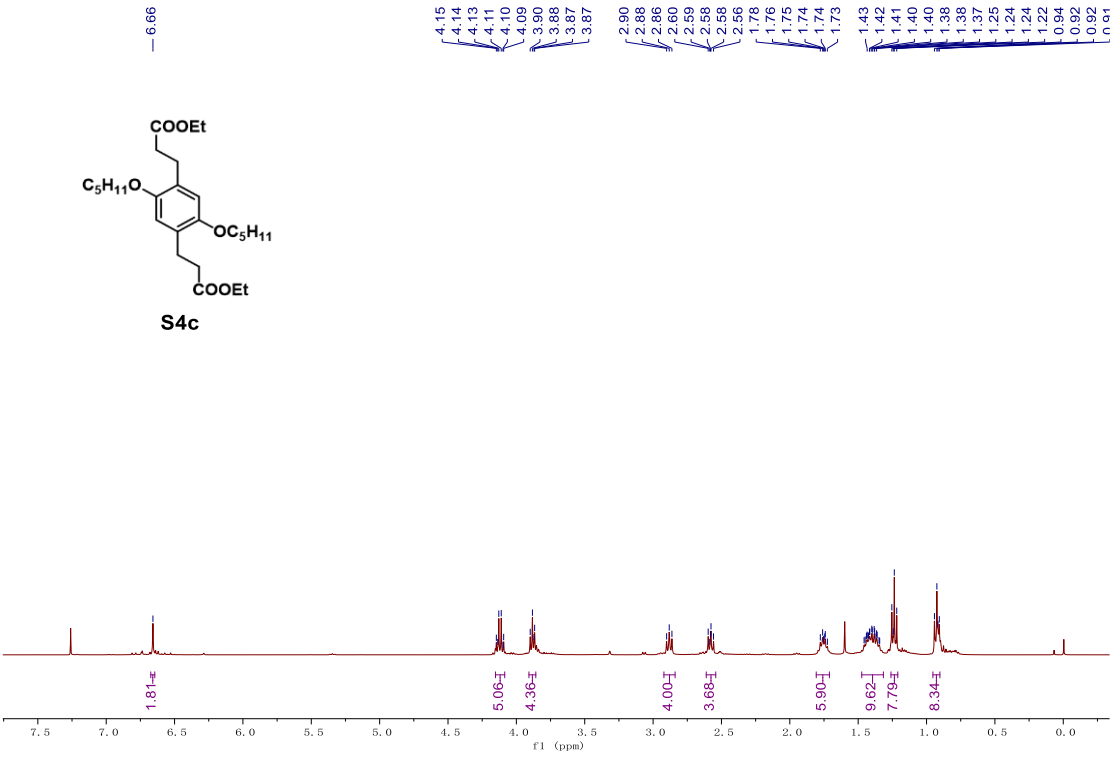
S4b

^{1}H NMR, $CDCl_3$, 400 MHz

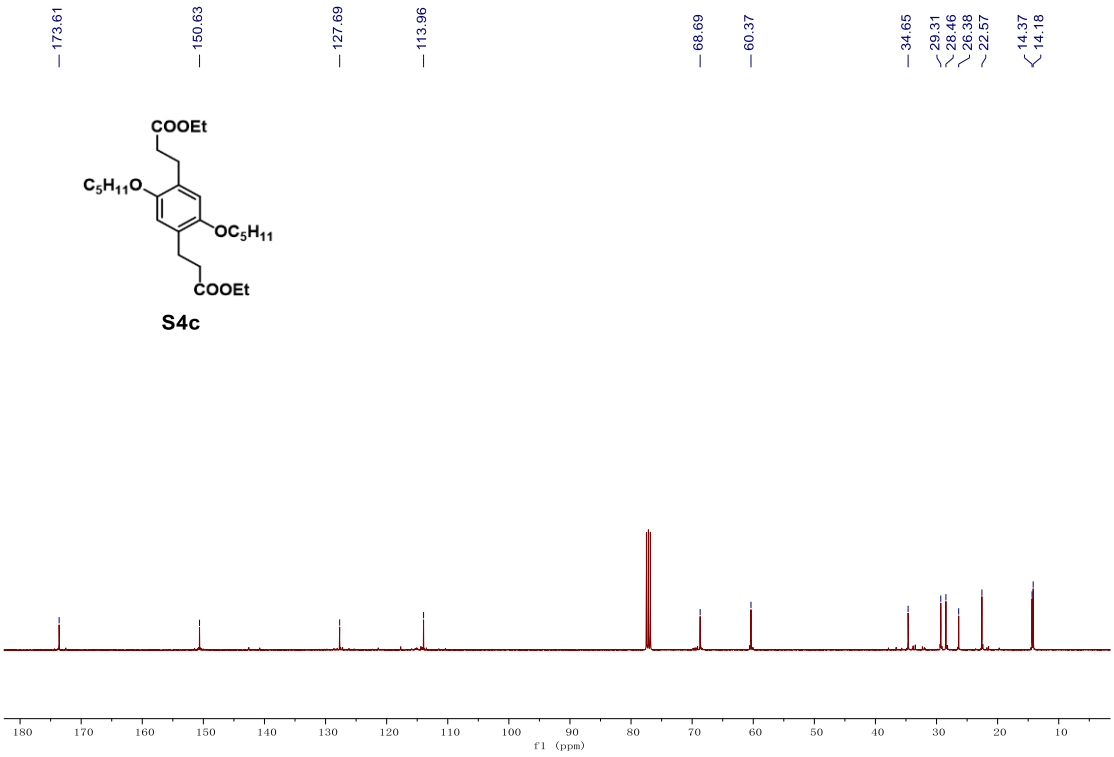


S4b

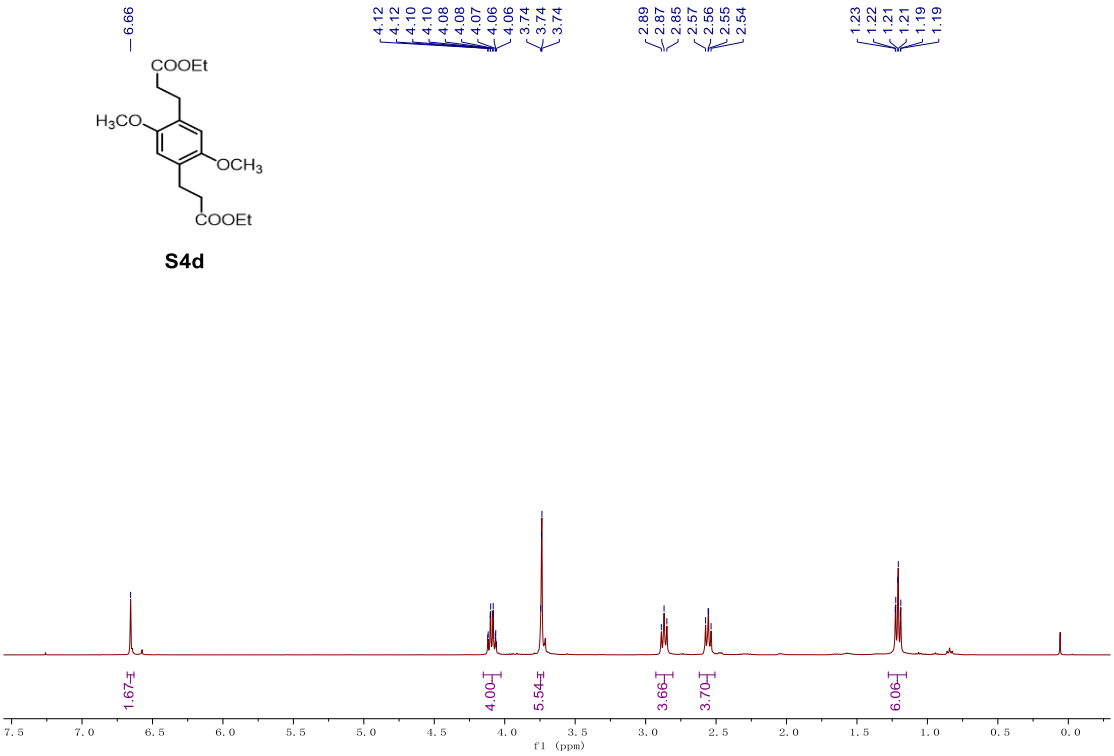
^{13}C NMR, $CDCl_3$, 101 MHz



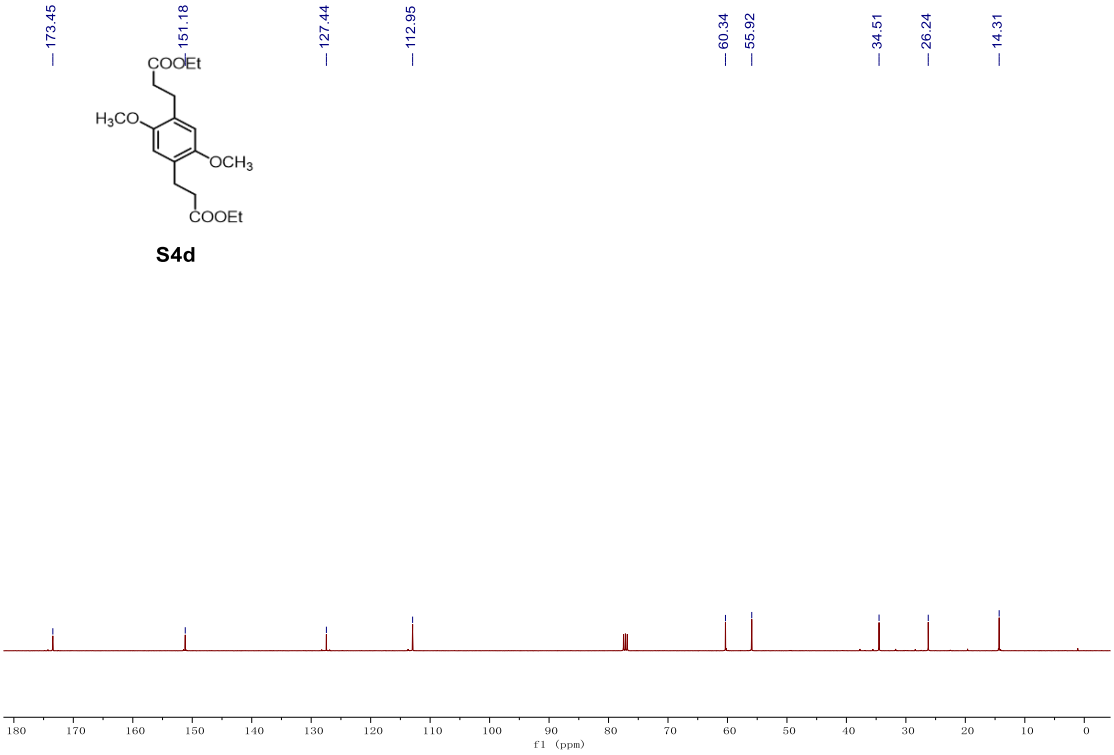
^{1}H NMR, $CDCl_3$, 400 MHz



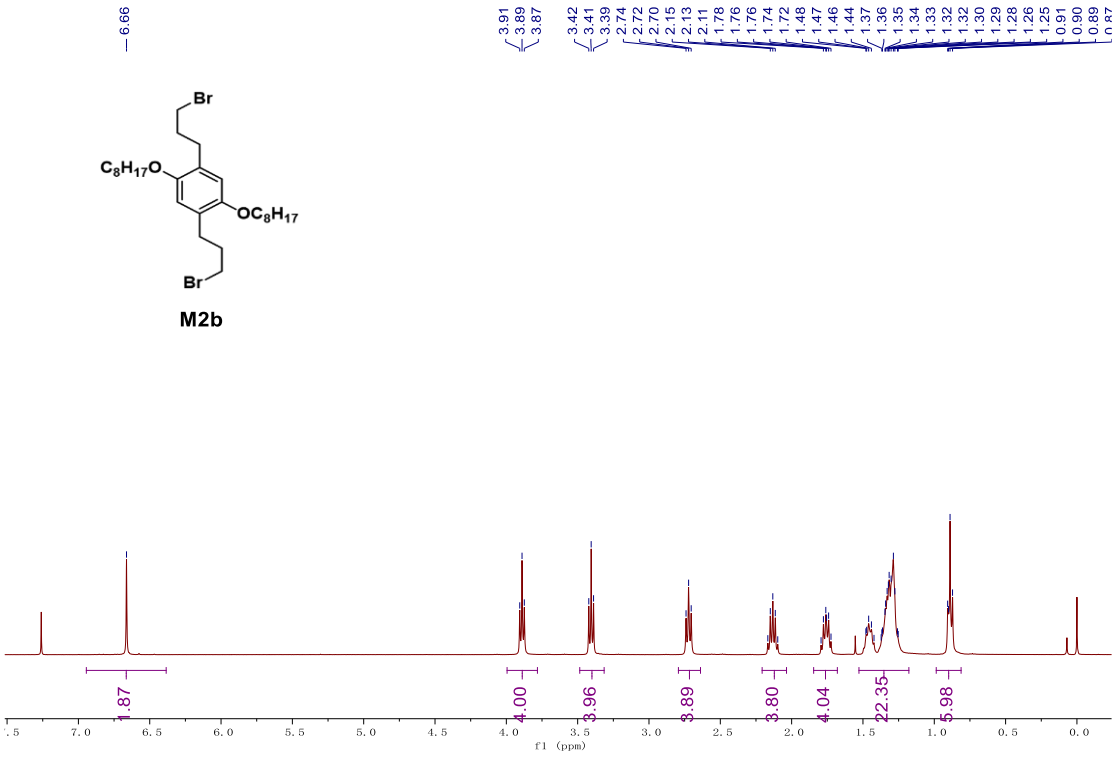
^{13}C NMR, $CDCl_3$, 101 MHz



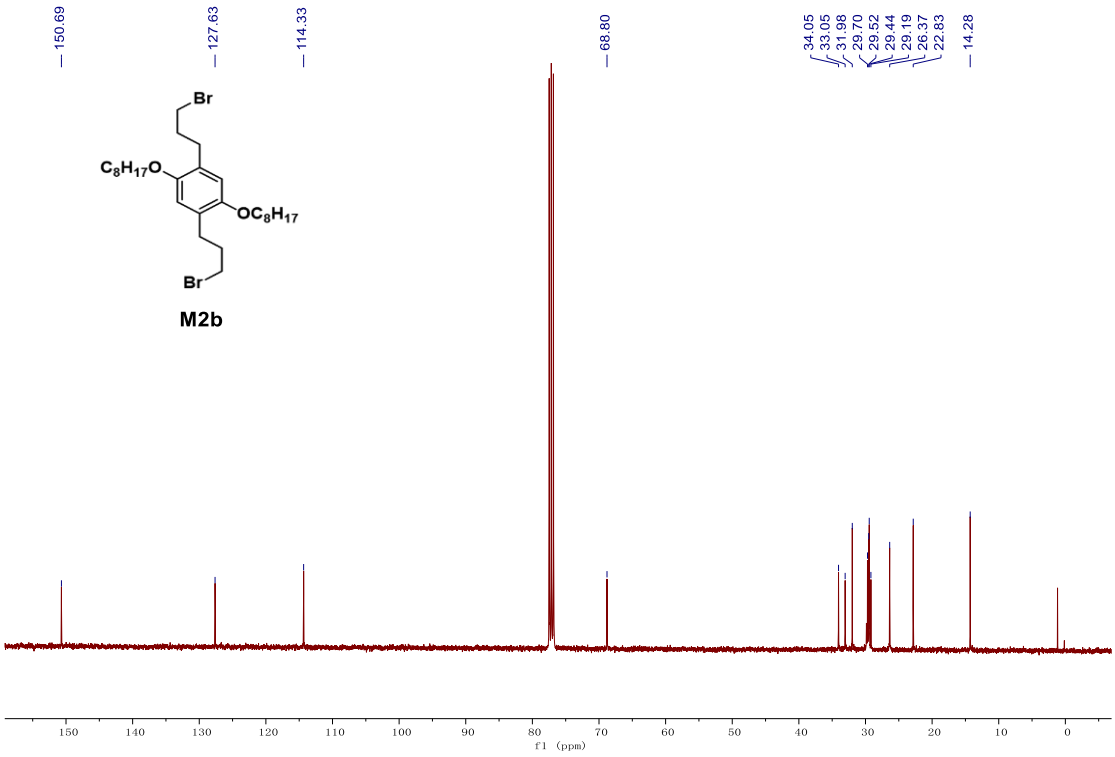
^{1}H NMR, $CDCl_3$, 400 MHz



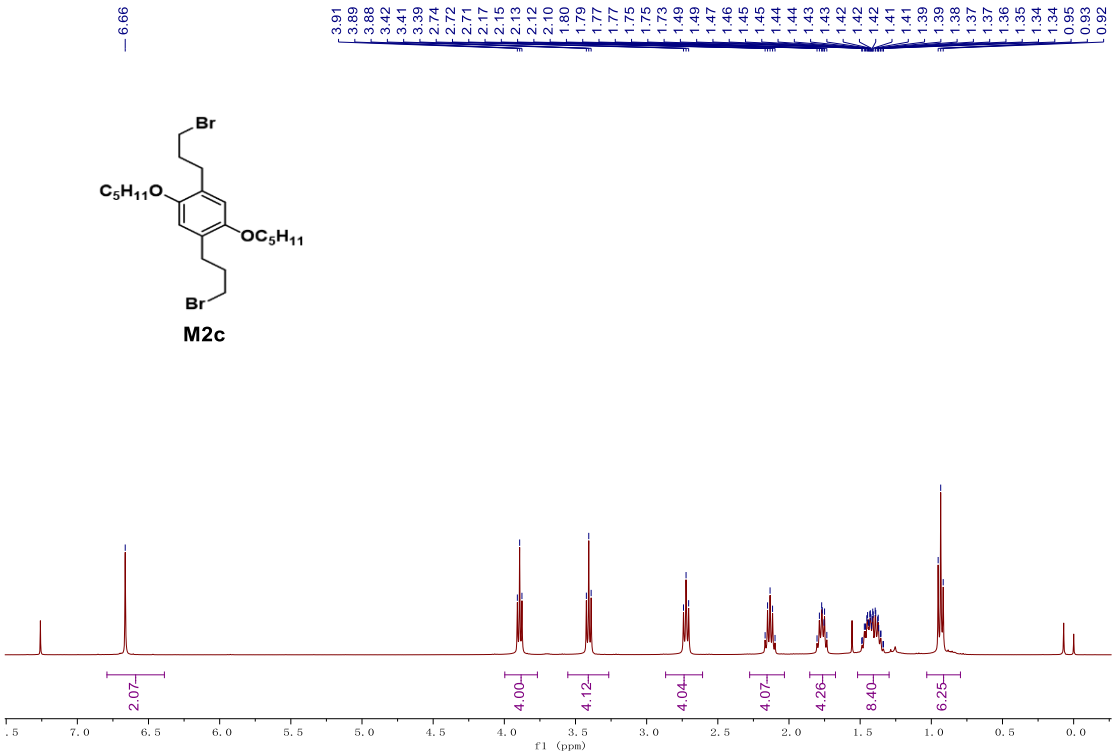
^{13}C NMR, $CDCl_3$, 101 MHz



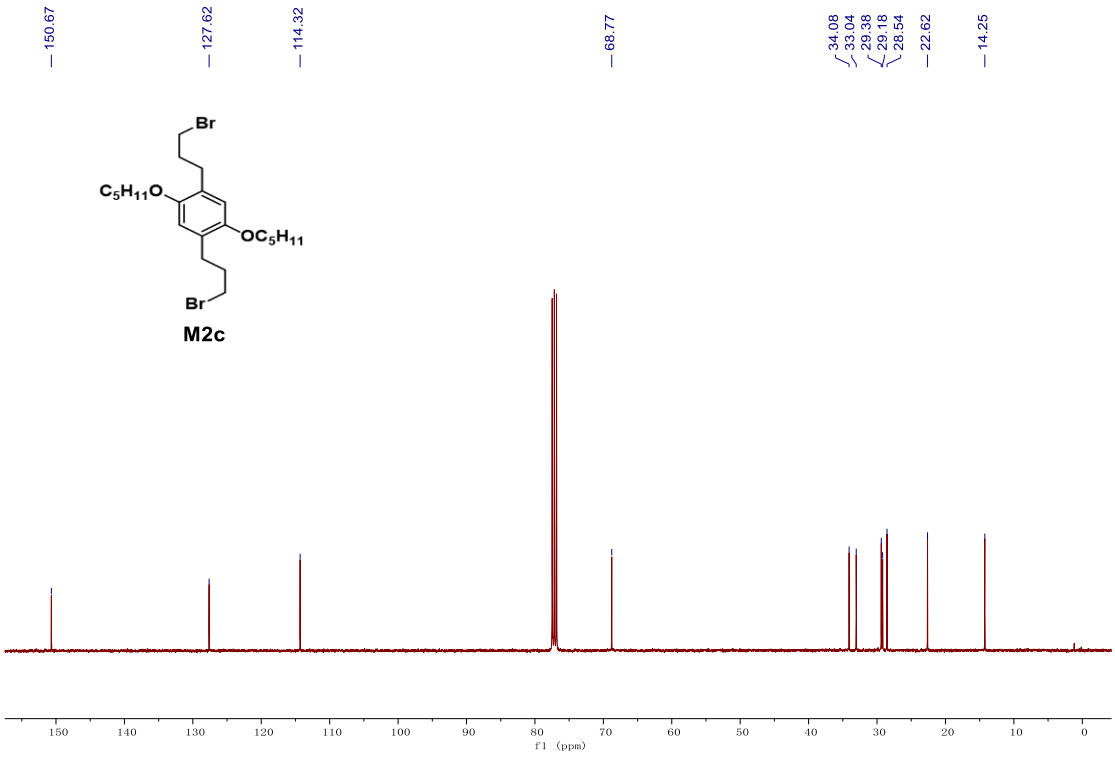
^{1}H NMR, $CDCl_3$, 400 MHz



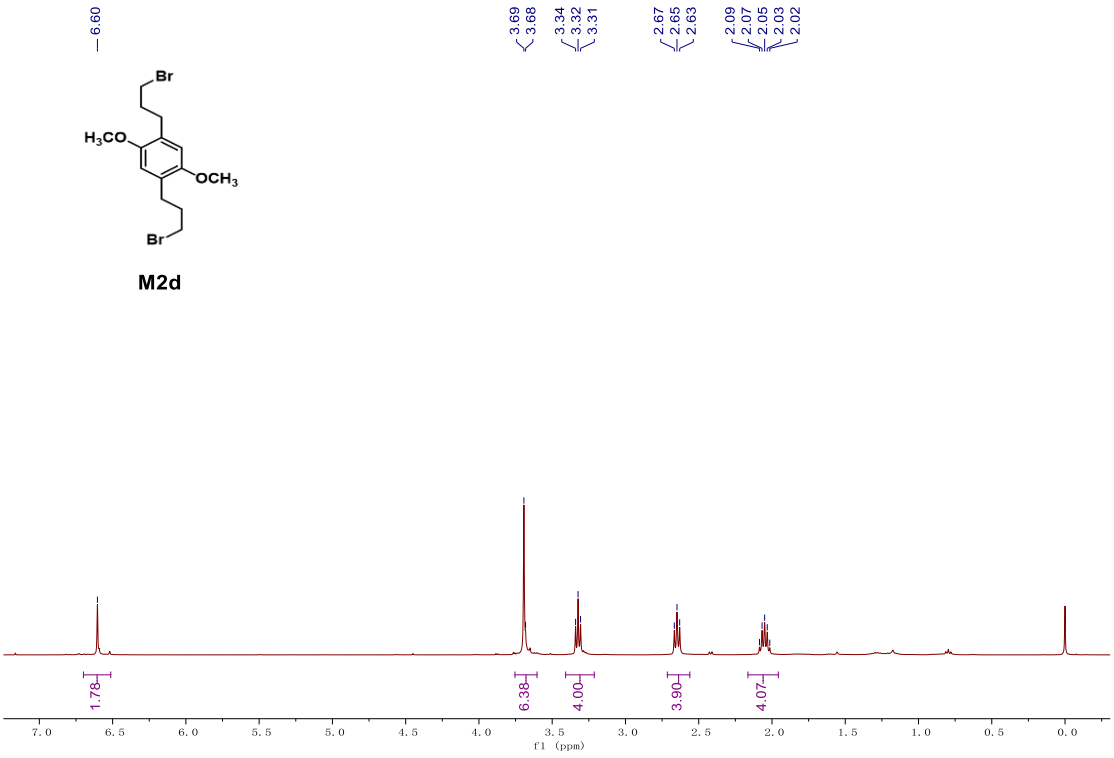
^{13}C NMR, $CDCl_3$, 101 MHz



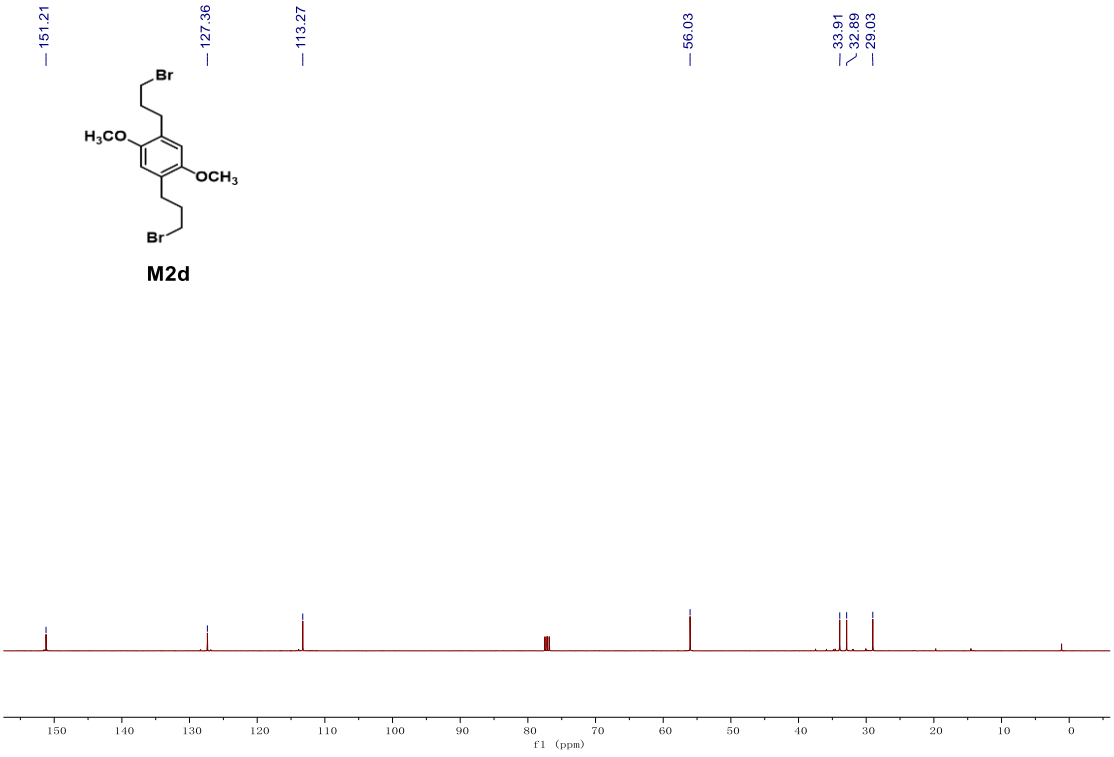
^{1}H NMR, $CDCl_3$, 400 MHz



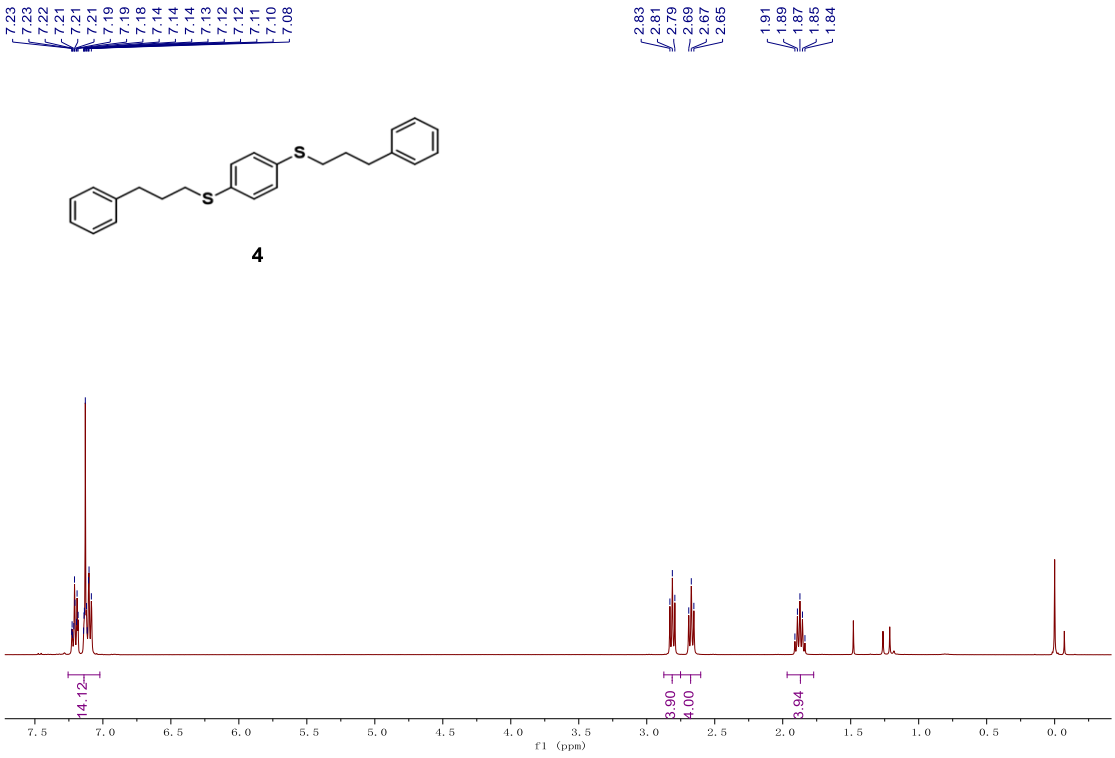
^{13}C NMR, $CDCl_3$, 101 MHz



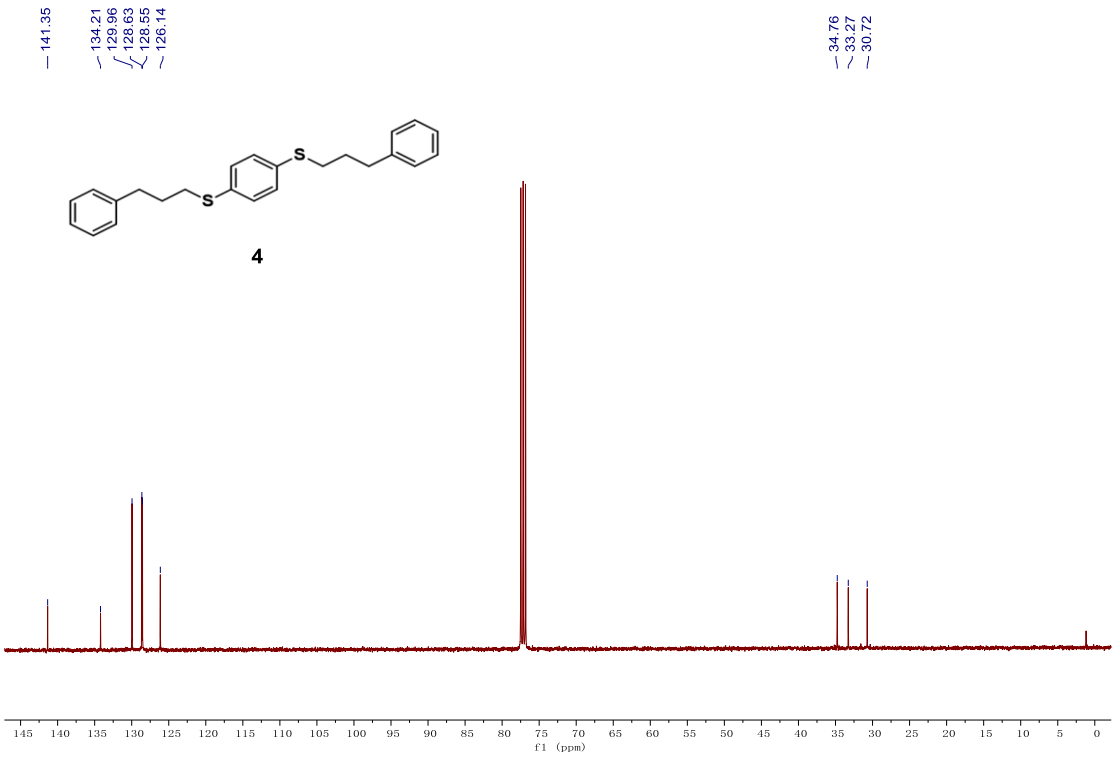
^{1}H NMR, $CDCl_3$, 400 MHz



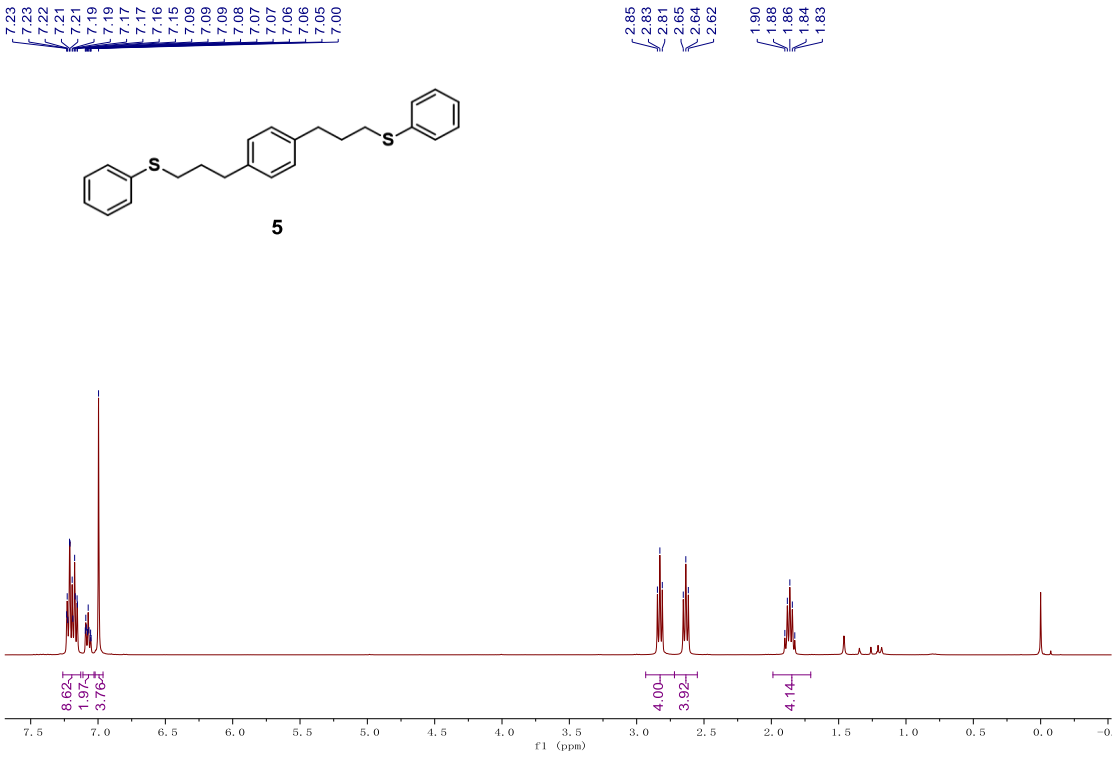
^{13}C NMR, $CDCl_3$, 101 MHz



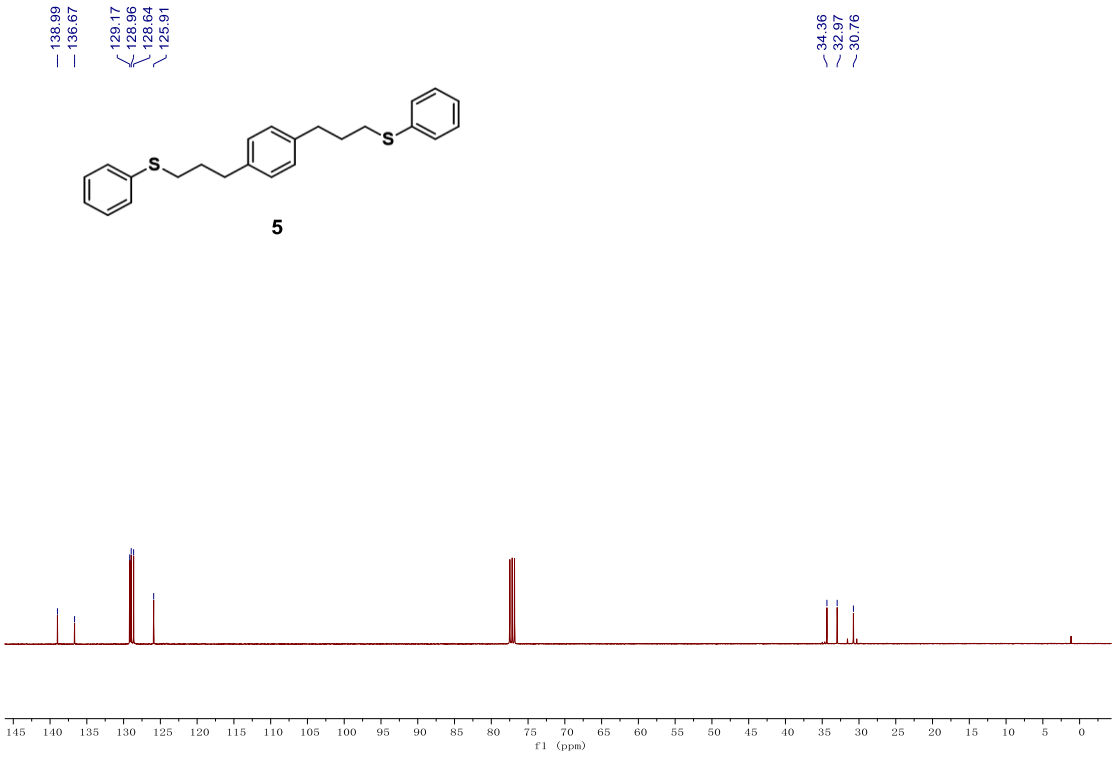
^{1}H NMR, $CDCl_3$, 400 MHz



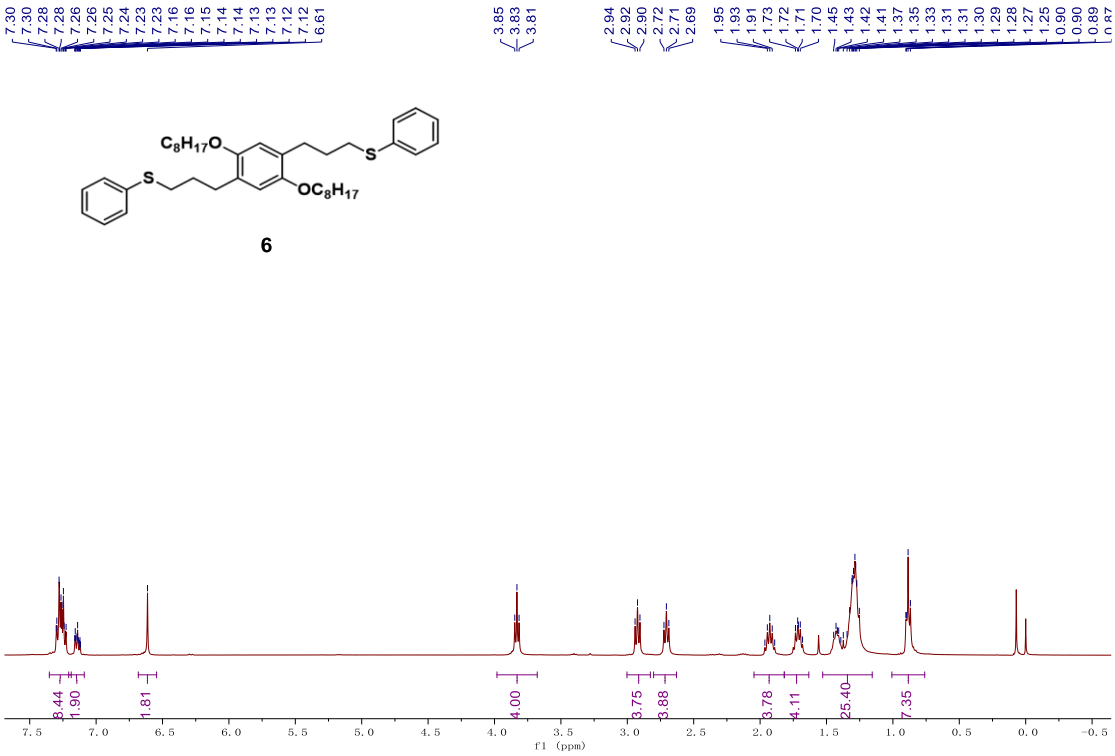
^{13}C NMR, $CDCl_3$, 101 MHz



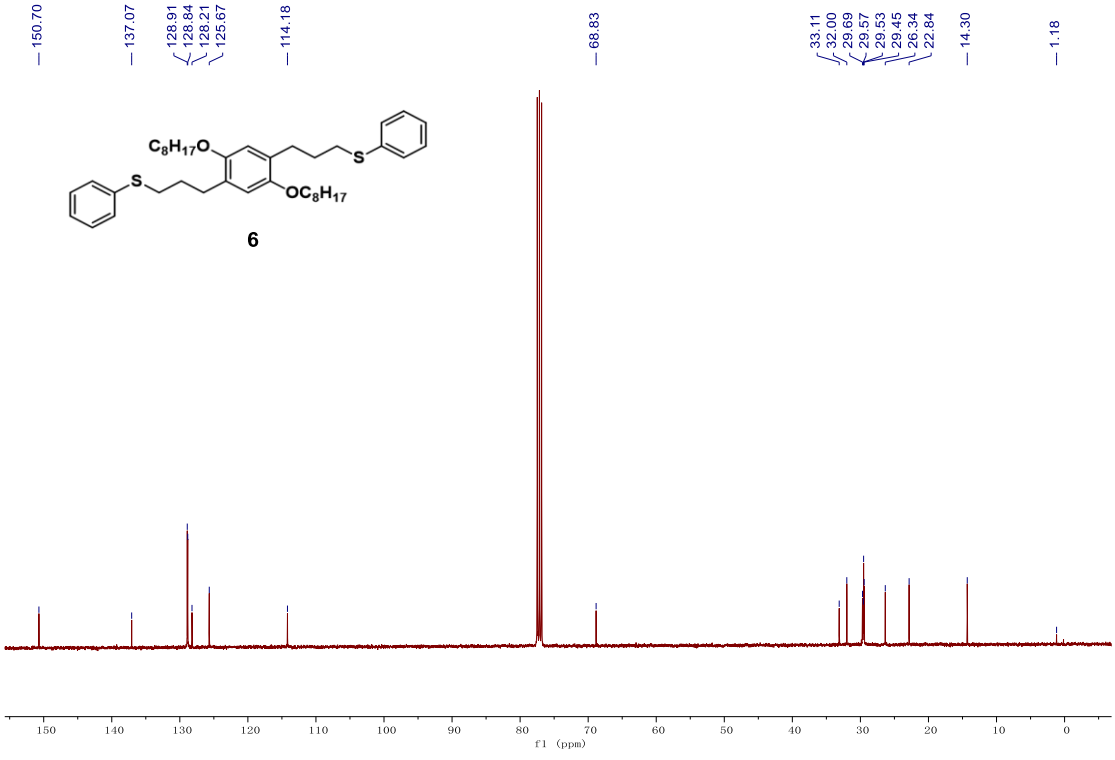
^{1}H NMR, $CDCl_3$, 400 MHz



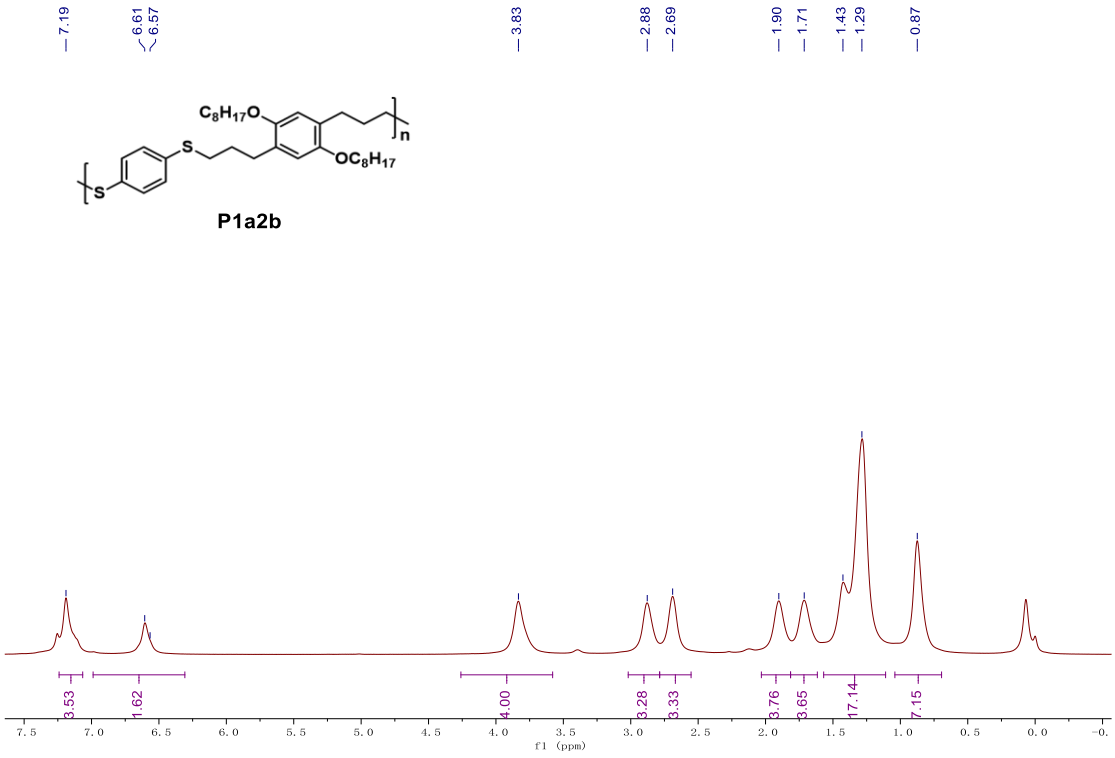
^{13}C NMR, $CDCl_3$, 101 MHz



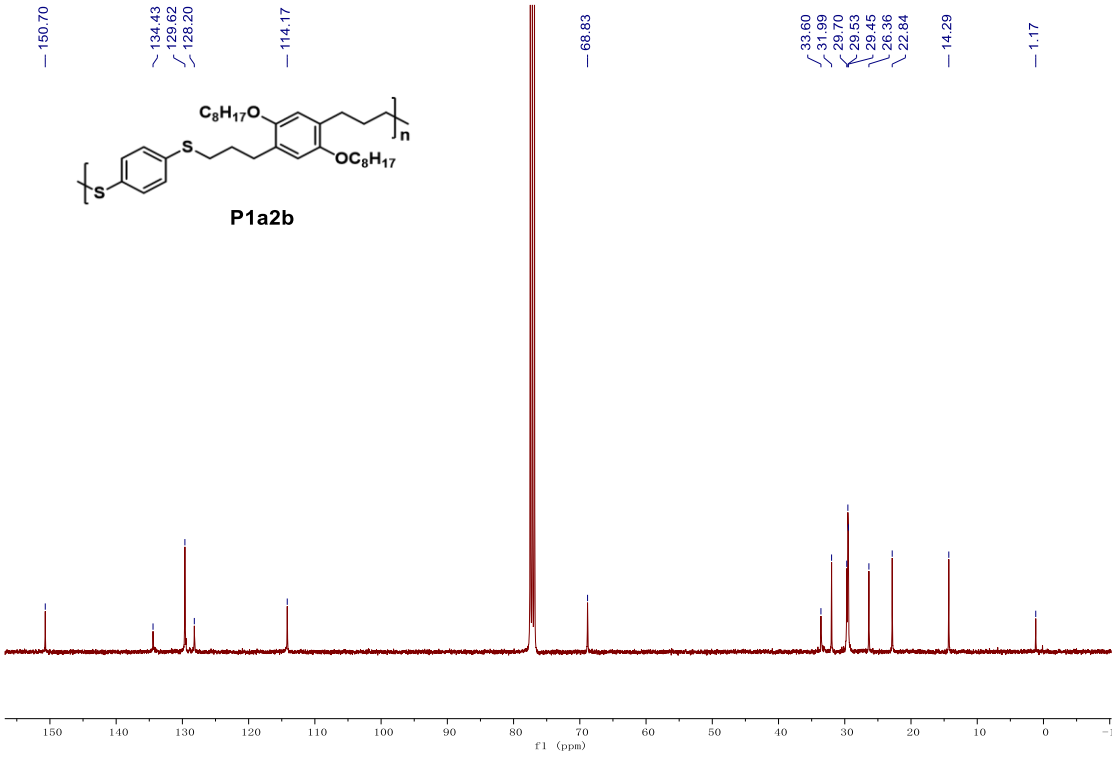
^{1}H NMR, $CDCl_3$, 400 MHz



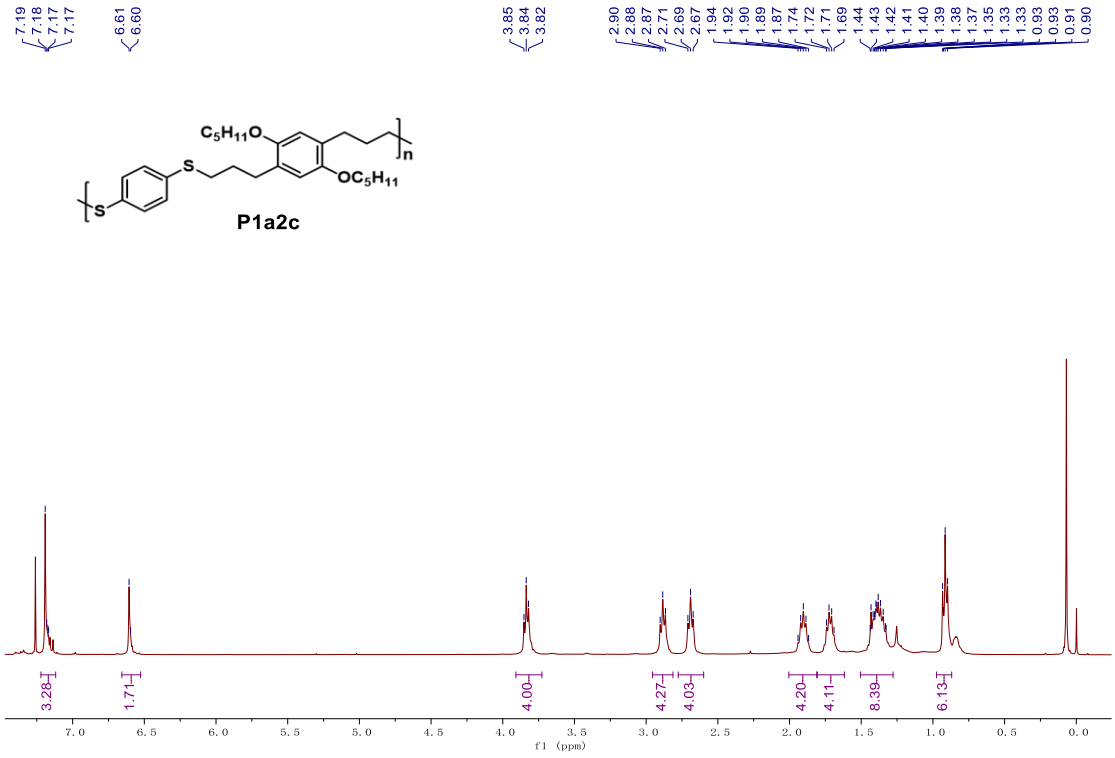
^{13}C NMR, $CDCl_3$, 101 MHz



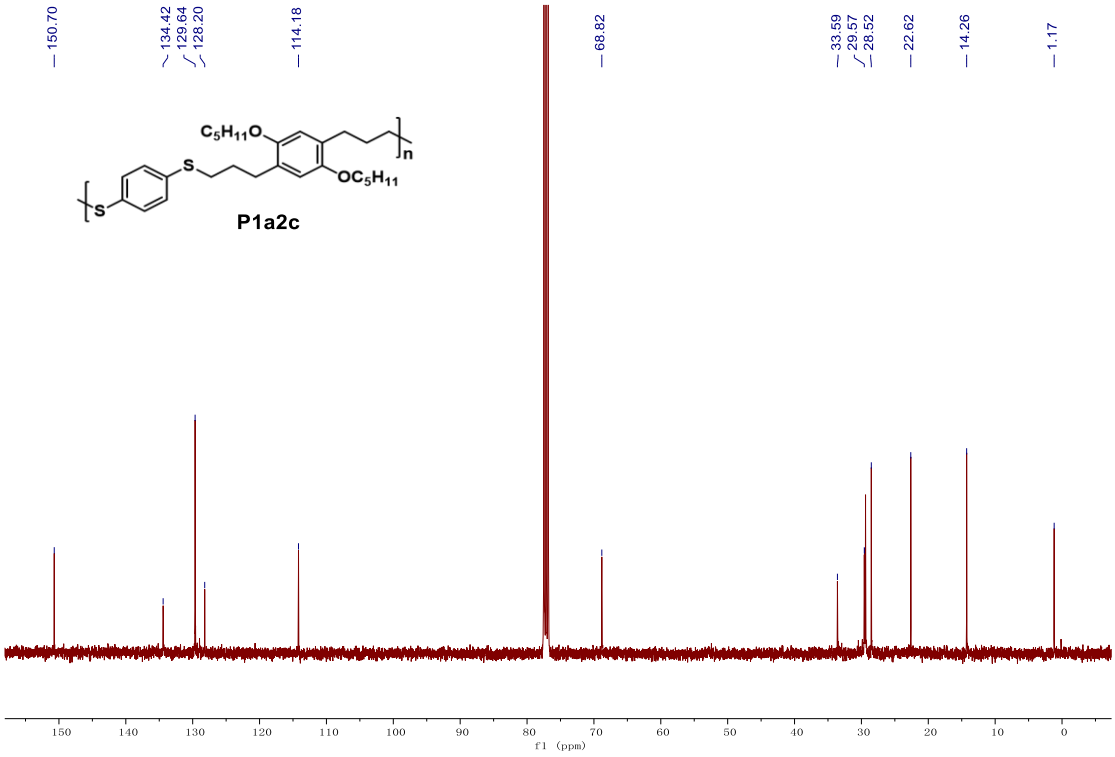
^{1}H NMR, $CDCl_3$, 400 MHz



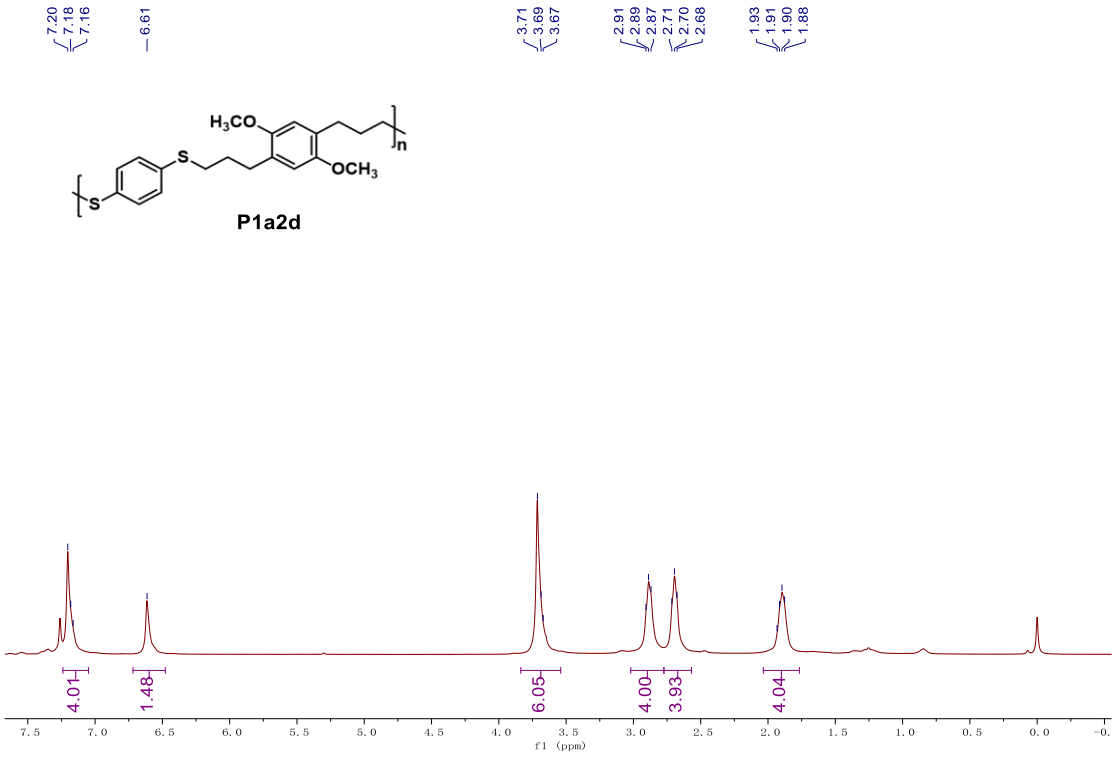
^{13}C NMR, $CDCl_3$, 101 MHz



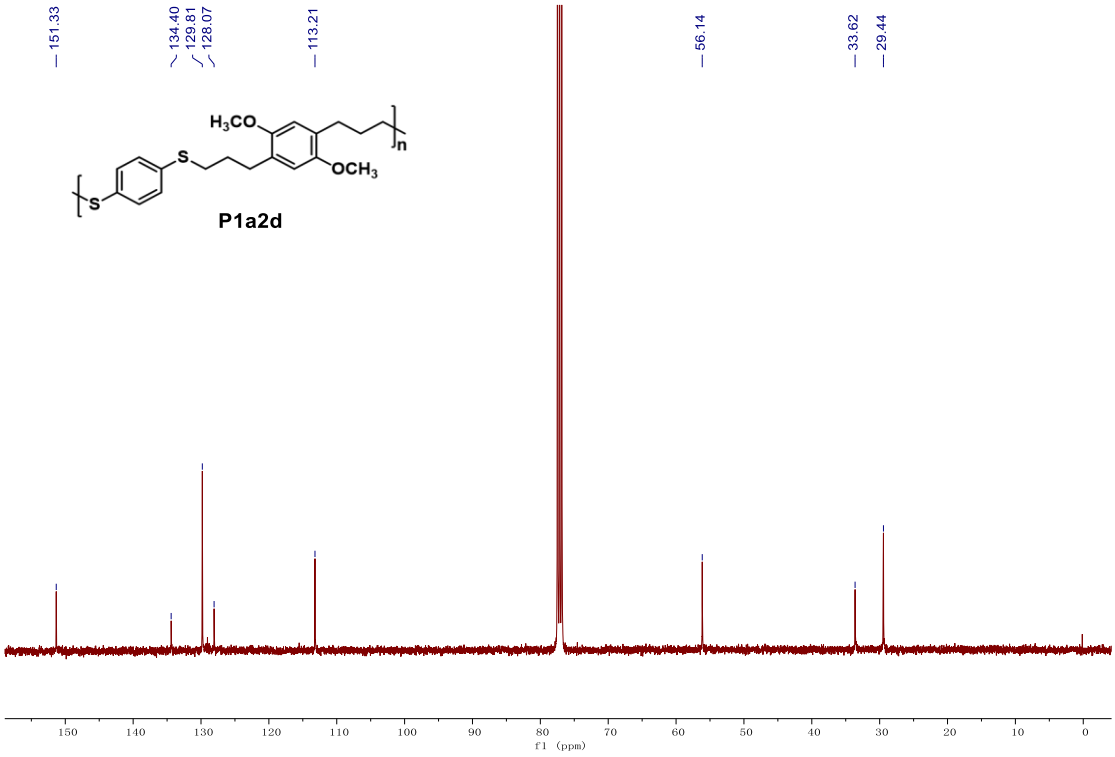
^{1}H NMR, $CDCl_3$, 400 MHz



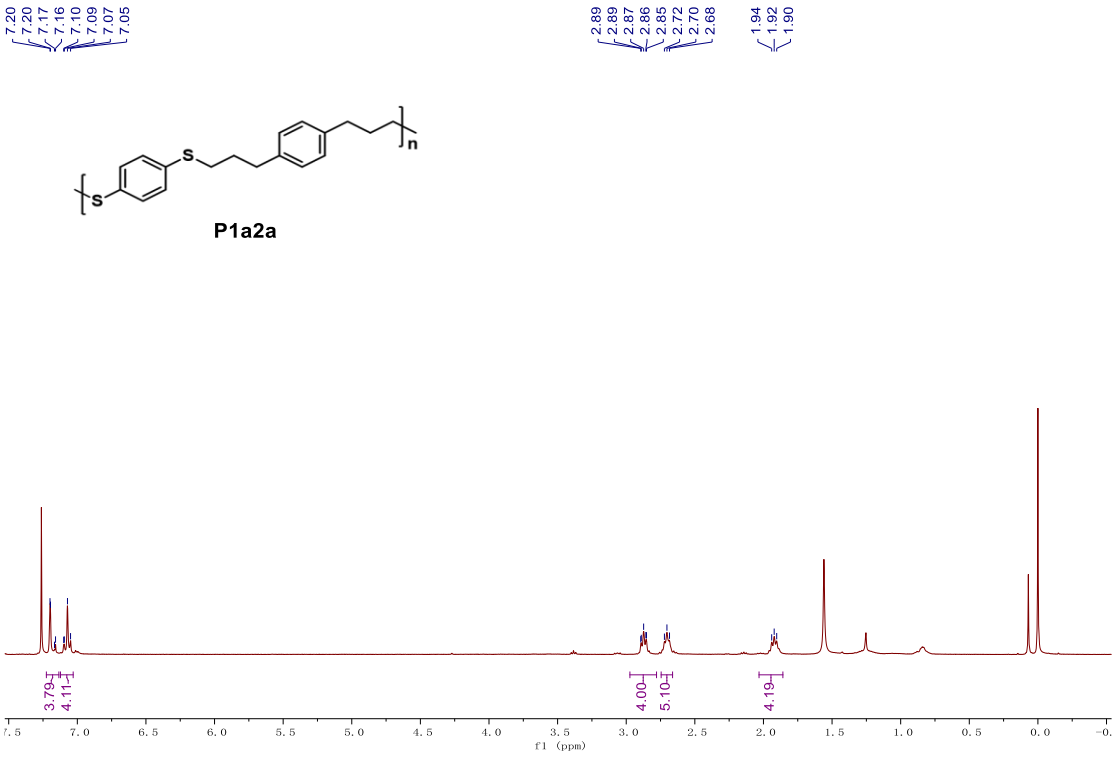
^{13}C NMR, $CDCl_3$, 101 MHz



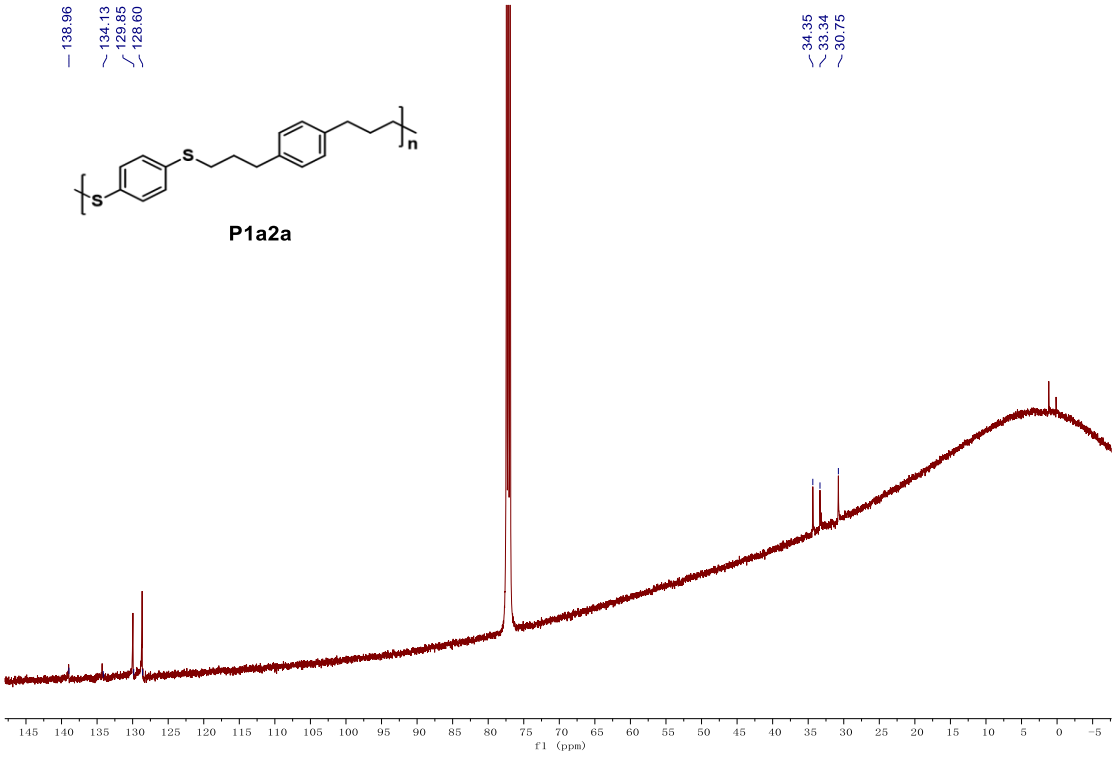
^{1}H NMR, $CDCl_3$, 400 MHz



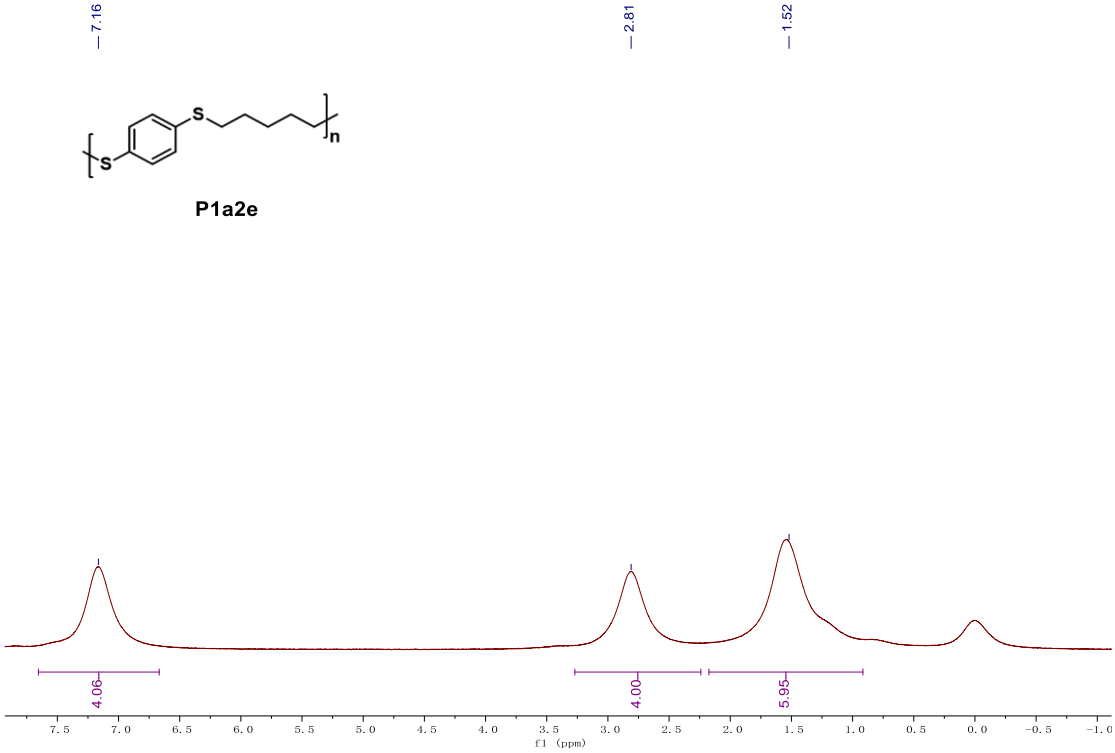
^{13}C NMR, $CDCl_3$, 101 MHz



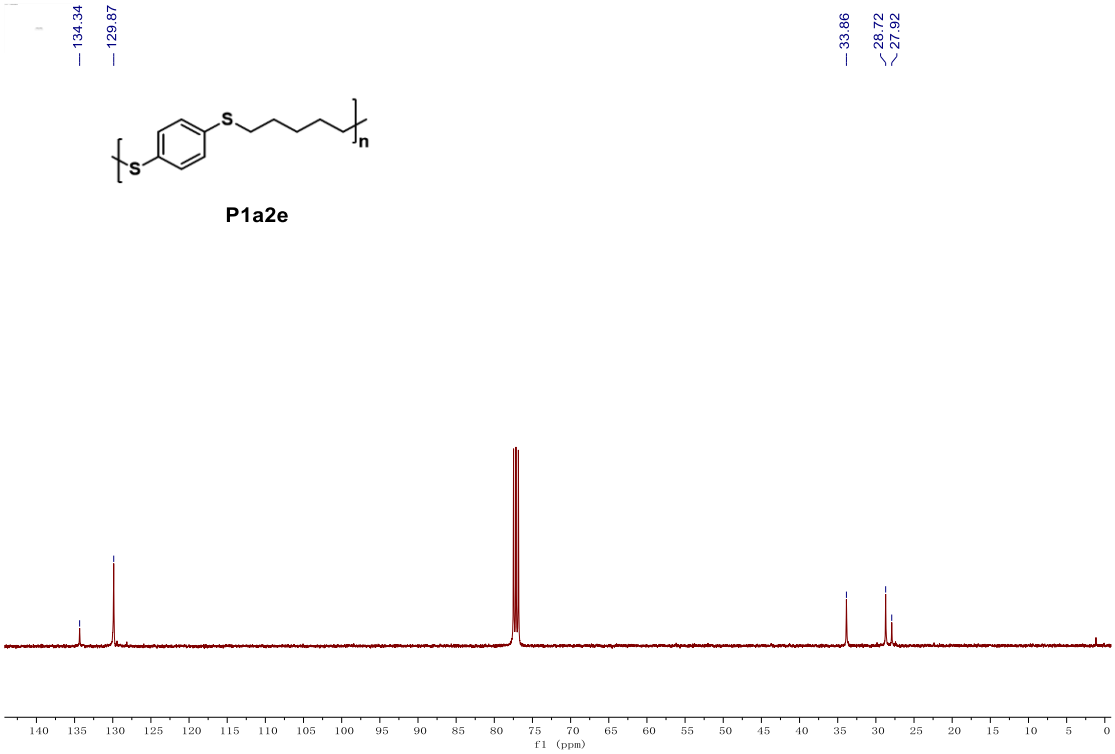
^{1}H NMR, $CDCl_3$, 400 MHz



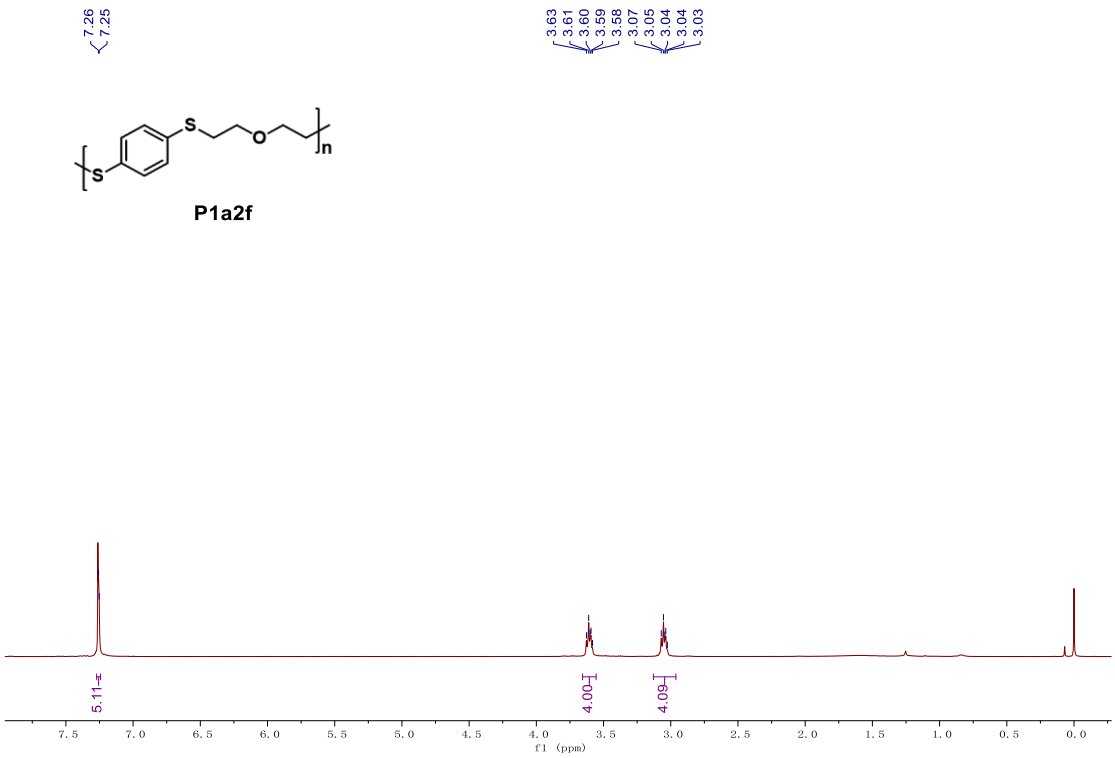
^{13}C NMR, $CDCl_3$, 126 MHz



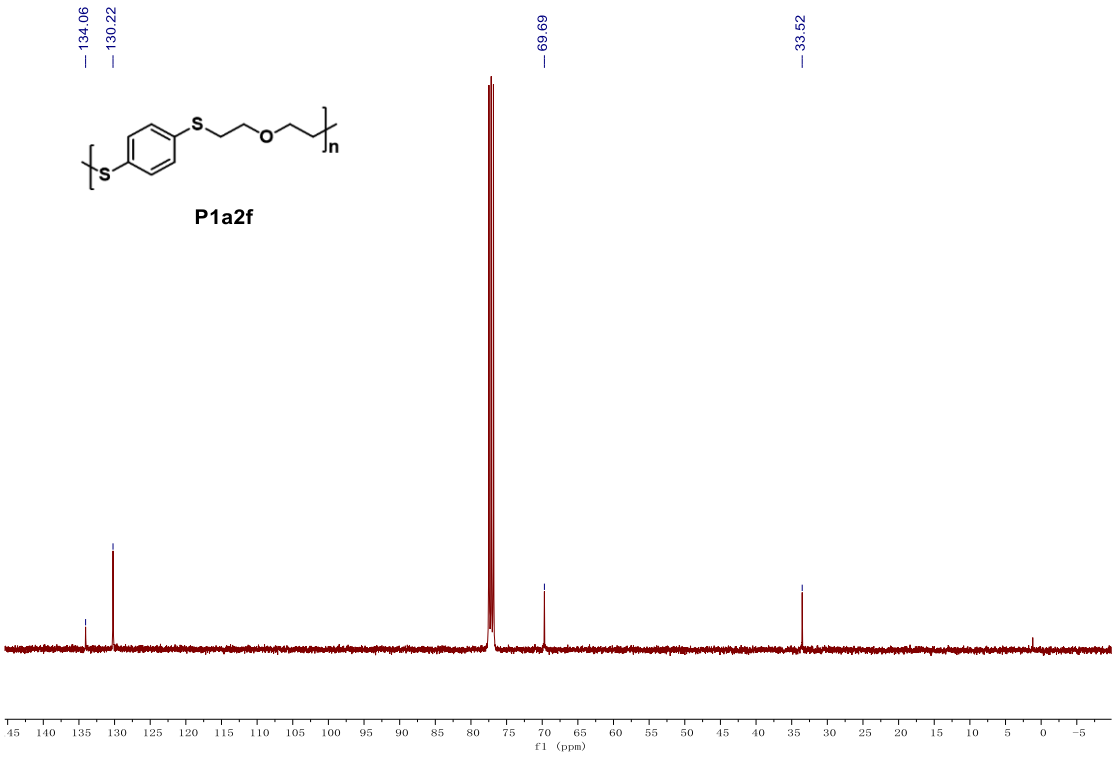
^{1}H NMR, $CDCl_3$, 400 MHz



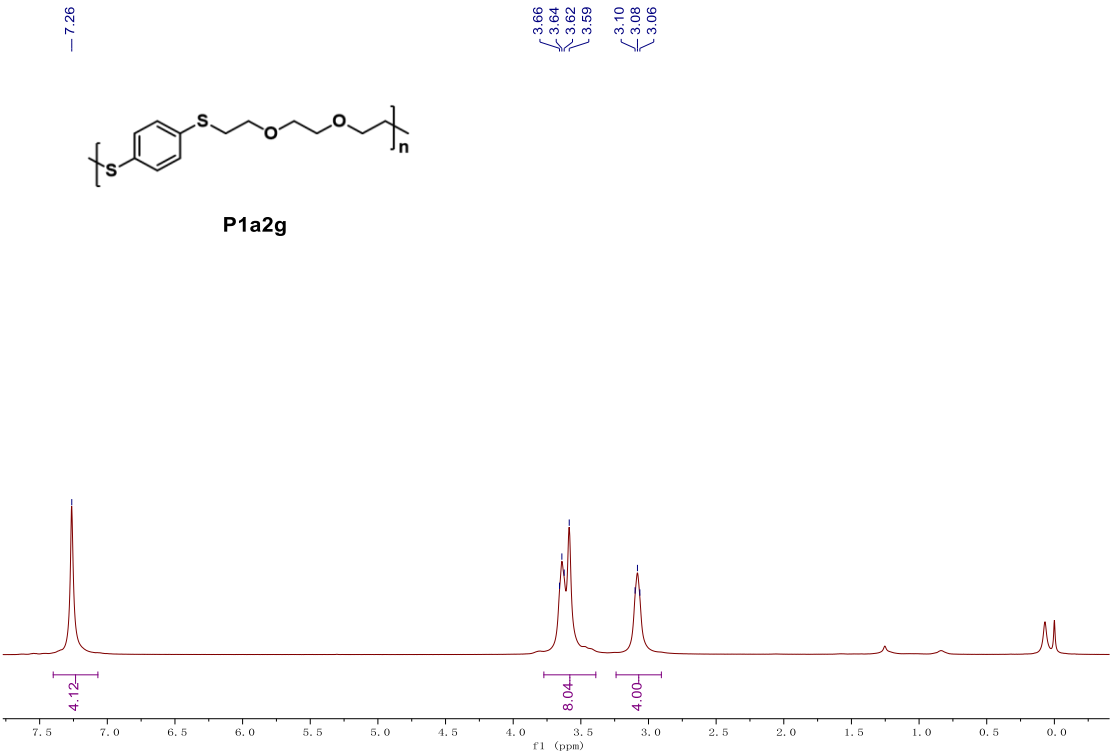
^{13}C NMR, $CDCl_3$, 101 MHz



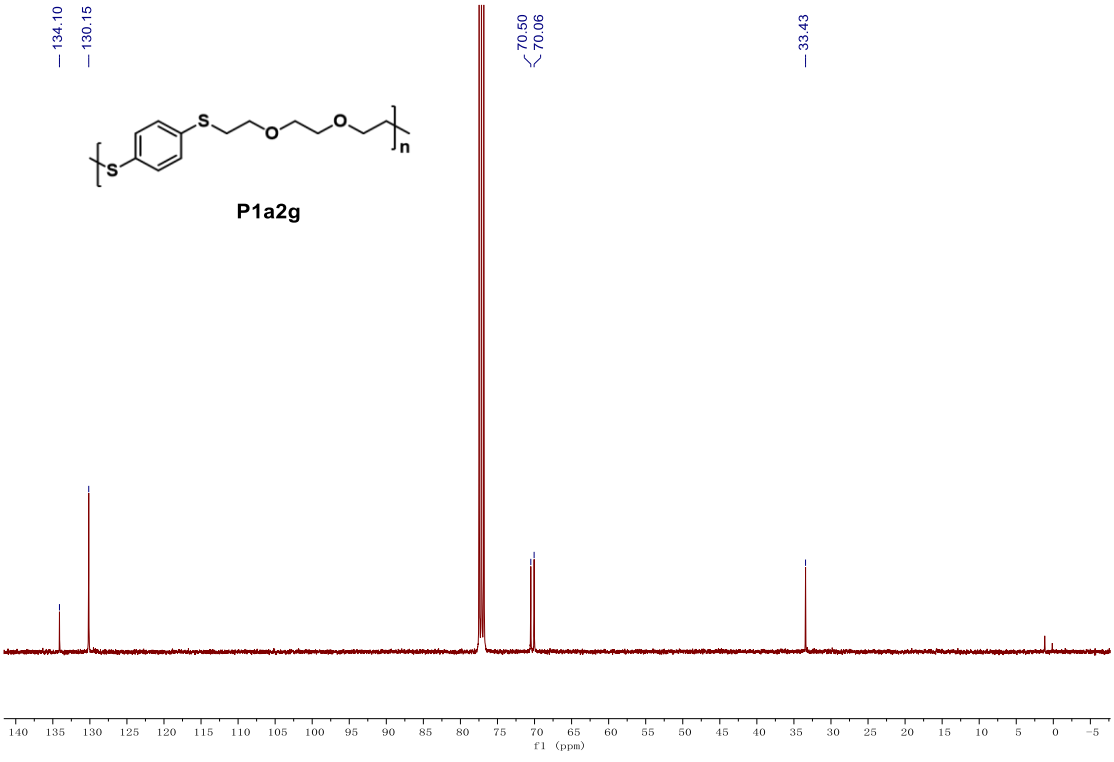
^{1}H NMR, $CDCl_3$, 400 MHz



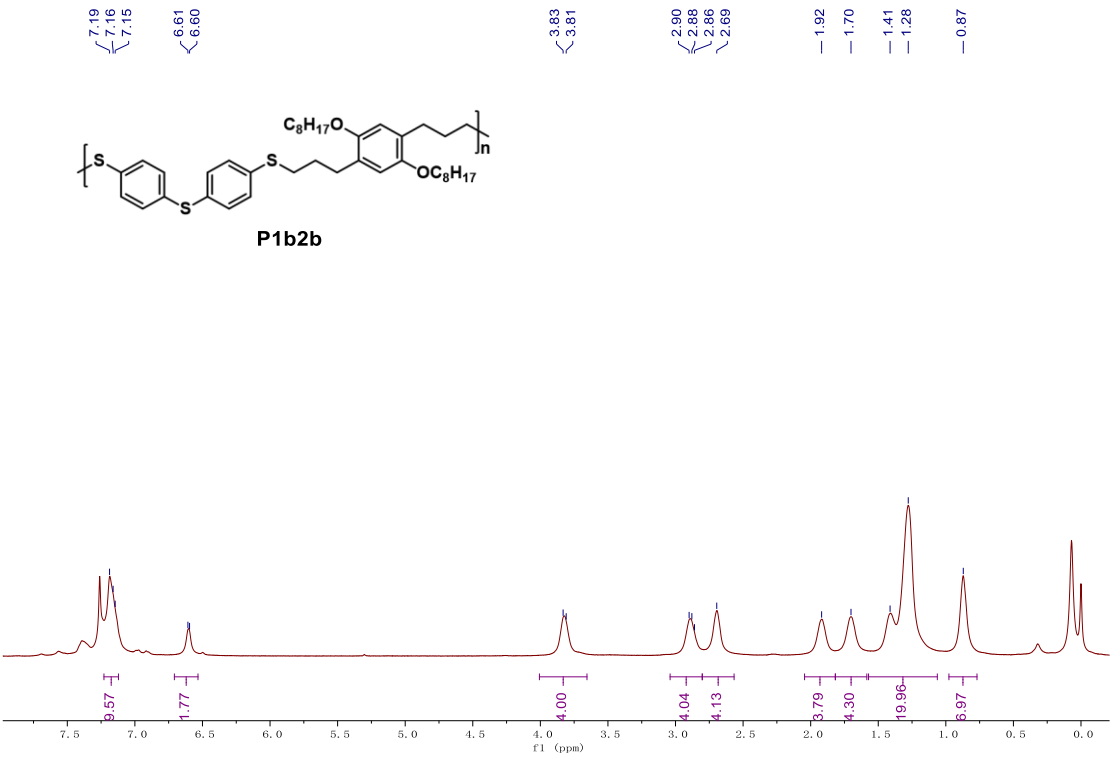
^{13}C NMR, $CDCl_3$, 101 MHz



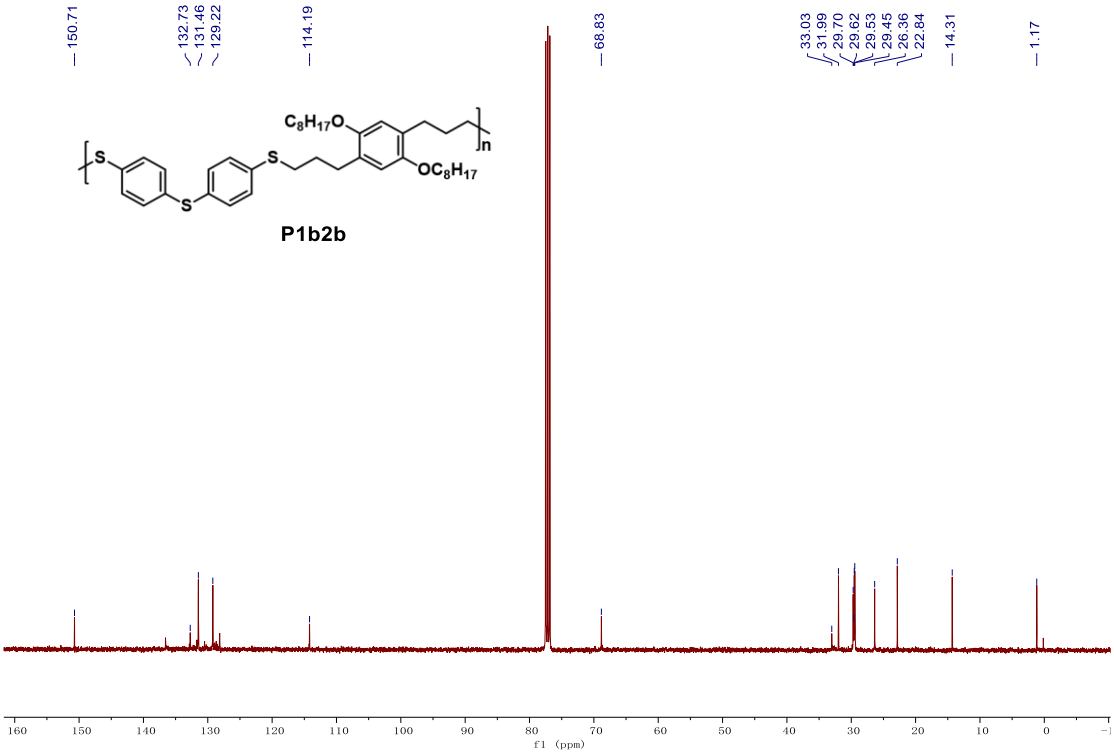
^{1}H NMR, $CDCl_3$, 400 MHz



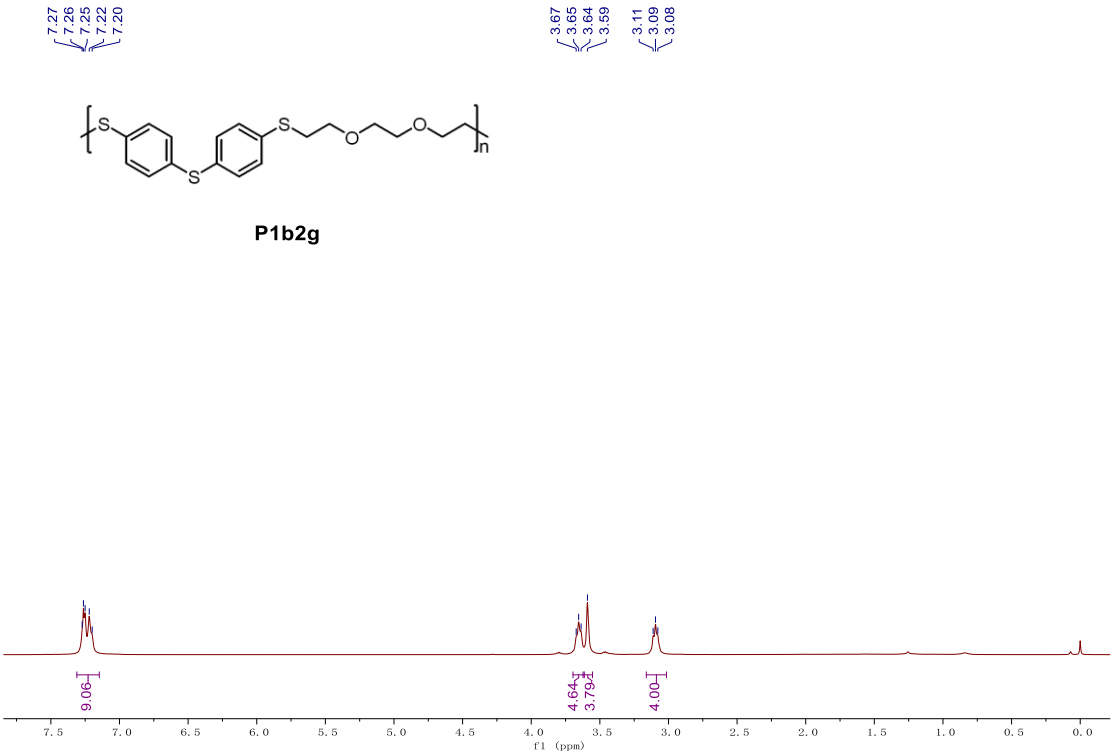
^{13}C NMR, $CDCl_3$, 101 MHz



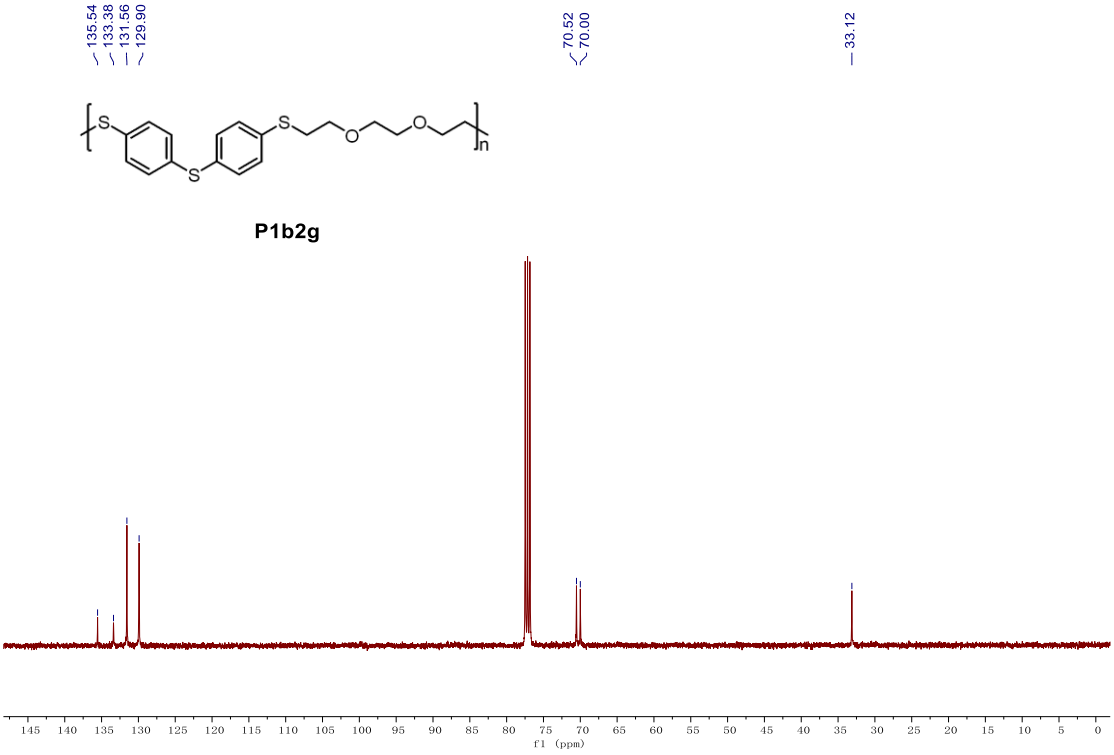
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

13. Reference

1. Liang, G. G.; Liu, M. C.; Chen, J. X.; Ding, J. C.; Gao, W. X.; Wu, H. Y. NBS-Promoted Sulfenylation of Sulfinates with Disulfides Leading to Unsymmetrical or Symmetrical Thiosulfonates. *Chin. J. Chem.* **2012**, *30*, 1611-1616.
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