

Supporting Information

New Classes of Functionalized Parylenes and Poly(phenylene vinylene)s via Coupling of Dihaloxyl Diesters

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General Information: Unless otherwise specified, all reagents were purchased from commercial sources and used without further purification. Solvents were dried and degassed using a solvent purification system. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 (^1H : 7.26 ppm; ^{13}C : 77.16 ppm) or $\text{DMSO}-d_6$ (^1H : 2.50 ppm; ^{13}C : 39.52 ppm) or CD_3OD (^1H : 3.31 ppm; ^{13}C : 49.00 ppm) or CD_2Cl_2 (^1H : 5.32 ppm) using Bruker 400 and 100 MHz spectrometers, respectively. Coupling constants (J) are expressed in hertz (Hz). Infrared (FT-IR) spectra were recorded on a PerkinElmer frontier FT-IR spectrometer. Size exclusion chromatography (SEC) was performed on a Malvern GPCmax system. THF was used as the eluent at a flow rate of 0.8 mL min^{-1} . UV-vis spectroscopy data were recorded on an Agilent Cary 100 UV-vis spectrometer in 10 mm quartz cuvettes. Thermogravimetric analysis (TGA) data were recorded under nitrogen at a flow rate of 60 mL min^{-1} on a TA Instruments TGA Q500 module at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ and using a platinum sample pan. Differential scanning calorimetry (DSC) data were recorded under nitrogen at a flow rate of 50 mL min^{-1} on a TA Instruments DSC Q2000 module at a heating and cooling rate of 10 or $20\text{ }^\circ\text{C min}^{-1}$ and using a Tzero aluminium sample pan and lid. High-resolution mass spectra (HRMS) were recorded in electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) mode on a Waters Xevo G2-XS QToF mass spectrometer. Polarized optical microscopy (POM) images were recorded using an Olympus BX53-P system that was equipped with a rotatable graduated sample platform, an Instec HCS402 dual heater temperature stage and a QImaging Retiga 2000R CCD camera. X-ray diffraction (XRD) data were recorded on a Rigaku D/MAX2500V/PC equipped with a Cu-rotating anode X-ray system. Melting points were performed on a MPA 100 Optimelt Automated Melting point system and are uncorrected.

General Procedure A: An oven-dried 150 mL pressure tube was charged with 1,4-phenylenediacetic acid (15 mmol) and an alcohol (30 mL). H_2SO_4 (2 mL) was added dropwise to the solution. The reaction mixture was stirred at $80\text{ }^\circ\text{C}$ for 20 h, and then cooled to room temperature. The residual alcohol was removed under reduced pressure. An aqueous solution saturated with NaHCO_3 (50 mL) was added to the solution until a pH of 7 was measured and then extracted with CH_2Cl_2 ($3 \times 30\text{ mL}$). The organic layers were combined, dried over anhydrous MgSO_4 and concentrated under reduced pressure to afford the corresponding ester.

General Procedure B: An oven-dried, 100 mL Schlenk flask was charged with dialkyl 2,2'-(1,4-phenylene)diacetate (10.00 mmol) and 25 mL of CHCl_3 . After the addition of NBS (24.00 mmol) and AIBN (0.20 mmol), the resulting mixture was stirred at $60\text{ }^\circ\text{C}$ for 24 h. After cooling

solution to room temperature, a solid precipitate formed and was removed by filtration. The filtrate was washed with an aqueous solution saturated with NaHCO₃ (30 mL). The aqueous layer was extracted with CH₂Cl₂ (3 × 20 mL). The organic layers were combined, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude product was further purified by column chromatography.

General Procedure C: An oven-dried, 200 mL 2-neck flask was charged with an alcohol (6.30 mmol) and 60 mL of CH₂Cl₂. After adding dicyclohexyl carbodiimide (DCC) (6.60 mmol), DMAP (0.30 mmol), and **7** (see below) (3.00 mmol) at 0 °C, the resulting mixture was stirred at room temperature for 20 h. Solids that precipitated were removed by filtration and the filtrate was washed with an aqueous solution saturated with NaHCO₃ (60 mL), water (60 mL) and brine (60 mL). The organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude product was further purified by column chromatography.

Dimethyl 2,2'-(1,4-phenylene)diacetate (1a): General Procedure A was used to prepare 3.11 g (93% yield) of the desired product as a white solid. m.p. 57-59 °C (Lit.¹: 58-59 °C); ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.24 (s, 4H), 3.69 (s, 6H), 3.61 (s, 4H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 172.03, 132.97, 129.61, 52.17, 40.94. Spectral data matched with literature values.¹

Diethyl 2,2'-(1,4-phenylene)diacetate (1b): General Procedure A was used to prepare 3.64 g (97% yield) of the desired product as a white solid. m.p. 58-60 °C (Lit.²: 59 °C); ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.24 (s, 4H), 4.14 (q, *J* = 7.2 Hz, 4H), 3.59 (s, 4H), 1.25 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 171.64, 133.03, 129.53, 60.97, 41.16, 14.28. Spectral data matched with literature values.³

Dibutyl 2,2'-(1,4-phenylene)diacetate (1c): General Procedure A was used to prepare 4.04 g (88% yield) of the desired product as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.24 (s, 4H), 4.08 (t, *J* = 6.8 Hz, 4H), 3.59 (s, 4H), 1.66 – 1.51 (m, 4H), 1.42 – 1.25 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 171.73, 133.08, 129.53, 64.90, 41.21, 30.73, 19.21, 13.80.

Dimethyl 2,2'-(1,4-phenylene)bis(2-bromoacetate) (2a): General Procedure B was used to prepare 3.50 g (92% yield) of the desired product as a white solid. m.p. 76-78 °C; ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.55 (s, 4H), 5.34 (s, 2H), 3.79 (s, 6H); ¹³C NMR (100 MHz, CDCl₃,

ppm): δ 168.61, 136.93, 129.33, 53.64, 45.70, 45.67; HRMS (ESI): $[M-H]^+$ calcd for $C_{12}H_{11}Br_2O_4$: 378.8998; Found: 378.8999.

Diethyl 2,2'-(1,4-phenylene)bis(2-bromoacetate) (2b): General Procedure B was used to prepare 3.75 g (92% yield) of the desired product as a white solid. m.p. 65-67 °C; 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.55 (s, 4H), 5.31 (s, 2H), 4.24 (ddd, J = 10.0, 7.1, 0.6 Hz, 4H), 1.29 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.13, 136.98, 129.29, 62.82, 46.04, 46.01, 14.06; HRMS (ESI): $[M-H]^+$ calcd for $C_{14}H_{15}Br_2O_4$: 406.9311; Found: 406.9315.

Dibutyl 2,2'-(1,4-phenylene)bis(2-bromoacetate) (2c): General Procedure B was used to prepare 3.34 g (72% yield) of the desired product as a yellow oil. 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (s, 4H), 5.32 (s, 2H), 4.18 (q, J = 6.6 Hz, 4H), 1.69 – 1.55 (m, 4H), 1.42 – 1.27 (m, 4H), 0.91 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.18, 137.01, 129.25, 66.61, 46.11, 46.08, 30.50, 19.10, 13.74; HRMS (APCI): $[M-H]^+$ calcd for $C_{18}H_{23}Br_2O_4$: 462.9937; Found: 462.9963.

Di(pent-4-en-1-yl) 2,2'-(1,4-phenylene)bis(2-bromoacetate) (2d): General Procedure C was used to prepare 1.03 g (70% yield) of the desired product as a colorless oil. 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.55 (s, 4H), 5.76 (ddt, J = 16.9, 10.2, 6.7 Hz, 2H), 5.32 (s, 2H), 5.07 – 4.92 (m, 4H), 4.27 – 4.11 (m, 4H), 2.10 (q, J = 7.0 Hz, 4H), 1.82 – 1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.11, 137.15, 129.27, 115.77, 66.07, 46.03, 46.00, 29.93, 27.62; HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{24}Br_2O_4$: 488.0021; Found: 489.0099.

Di(but-3-yn-1-yl) 2,2'-(1,4-phenylene)bis(2-bromoacetate) (2e): General Procedure C was used to prepare 1.05 g (77% yield) of the desired product as a pale yellow solid. m.p. 67-69 °C; 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.56 (s, 4H), 5.35 (s, 2H), 4.36 – 4.20 (m, 4H), 2.55 (td, J = 6.7, 2.7 Hz, 4H), 1.97 (t, J = 2.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.91, 136.77, 129.35, 79.37, 70.50, 64.11, 45.59, 18.87; HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{16}Br_2O_4$: 455.9395; Found: 456.9492.

Dibenzyl 2,2'-(1,4-phenylene)bis(2-bromoacetate) (2f): General Procedure C was used to prepare 1.09 g (68% yield) of the desired product as a white solid. m.p. 83-85 °C; 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.53 (s, 4H), 7.34 (qd, J = 7.6, 6.6, 3.2 Hz, 10H), 5.37 (s, 2H), 5.28 – 5.14 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.93, 136.82, 134.93, 129.33, 128.77,

128.72, 128.35, 68.34, 45.81; HRMS (ESI): $[M+Na]^+$ calcd for $C_{24}H_{20}Br_2O_4$: 531.9708; Found: 554.9605.

Bis(2-cholesteryl ethyl ether) 2,2'-(1,4-phenylene)bis(2-bromoacetate) (2g): General Procedure C was used to prepare 2.31 g (64% yield) of the desired product as yellow crystals. m.p. 118-120 °C; 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.55 (s, 4H), 5.38 – 5.30 (m, 2H) 5.36 (s, 2H), 4.39 – 4.22 (m, 4H), 3.68 (t, J = 3.9 Hz, 4H), 3.15 (tt, J = 11.2, 4.3 Hz, 2H), 2.42 – 1.74 (m, 16H), 1.62 – 0.77 (m, 68H), 0.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.18, 140.77, 136.84, 129.34, 121.96, 79.73, 66.08, 65.52, 56.91, 56.31, 50.31, 45.78, 45.75, 42.47, 39.92, 39.66, 39.09, 37.30, 36.98, 36.34, 35.94, 32.09, 32.03, 28.44, 28.42, 28.38, 28.16, 24.44, 23.98, 22.97, 22.71, 21.22, 19.53, 18.87, 12.02; HRMS (APCI): $[M+H]^+$ calcd for $C_{70}H_{108}Br_2O_6$: 1204.6492; Found: 1205.6566.

Bis(2-cholesteryl hexyl ether) 2,2'-(1,4-phenylene)bis(2-bromoacetate) (2h): General Procedure C was used to prepare 2.45 g (62% yield) of the desired product as yellow crystals. m.p. 58-60 °C; 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (s, 4H), 5.39 – 5.28 (m, 2H), 5.31 (s, 2H), 4.23 – 4.09 (m, 4H), 3.51 – 3.33 (m, 4H), 2.48 – 1.74 (m, 16H), 1.71 – 0.78 (m, 86H), 0.67(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.19, 141.22, 136.96, 129.27, 121.60, 79.15, 67.97, 66.79, 56.92, 56.30, 54.93, 50.35, 50.10, 46.03, 45.52, 43.23, 42.46, 39.93, 39.65, 39.33, 38.80, 37.43, 37.05, 36.33, 35.92, 35.85, 32.10, 32.04, 30.15, 28.69, 28.62, 28.43, 28.38, 28.15, 28.13, 25.94, 25.73, 24.43, 23.96, 22.96, 22.70, 21.21, 19.53, 19.01, 18.86, 17.41, 12.11, 12.00; HRMS (ESI): $[M+Cl]^-$ calcd for $C_{78}H_{124}Br_2O_6$: 1316.7744; Found: 1351.7465.

Bis(6-(4-(phenyldiazenyl)phenoxy)hexyl) 2,2'-(1,4-phenylene)bis(2-bromoacetate) (2i): General Procedure C was used to prepare 2.45 g (62% yield) of the desired product as a brown solid. m.p. 156-158 °C; 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.90 (ddd, J = 15.7, 7.5, 1.6 Hz, 8H), 7.55 (s, 4H), 7.54 – 7.38 (m, 6H), 7.05 – 6.95 (m, 4H), 5.32 (s, 2H), 4.29 – 4.12 (m, 4H), 4.03 (td, J = 6.7, 3.6 Hz, 4H), 1.96 – 1.30 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.18, 161.71, 152.89, 147.02, 136.97, 130.46, 129.29, 129.16, 124.90, 122.67, 114.81, 68.17, 66.66, 46.02, 45.99, 29.16, 28.41, 25.75, 25.64; HRMS (APCI): $[M+H]^+$ calcd for $C_{46}H_{48}Br_2N_4O_6$: 912.1920; Found: 913.2035.

Cholesteryl p-toluenesulfonate (3): An oven-dried, 250 mL flask was charged with cholesterol (15.00 g, 38.79 mmol) and chloroform (40 mL). After cooling to 0 °C, p-

toluenesulfonyl chloride (11.15 g, 58.48 mmol), pyridine (20 mL) and a catalytic amount of DMAP was added to the reaction mixture and stirred at room temperature for 14 h. The solution was diluted with chloroform (40 mL) and washed with an aqueous solution of HCl (1 N, 2 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was recrystallized from CH₂Cl₂ / CH₃OH to afford the desired product as a white solid (18.95 g, 88%). m.p. 118-120 °C (Lit⁴: 133 °C); ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.29 (m, 2H), 5.30 (dd, *J* = 4.9, 2.4 Hz, 1H), 4.38 – 4.26 (m, 1H), 2.44 (s, 3H), 2.27 (ddd, *J* = 13.3, 5.3, 2.1 Hz, 1H), 2.04 – 1.20 (m, 18H) 1.18 – 0.78 (m, 24H), 0.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 144.53, 139.01, 134.85, 129.88, 127.78, 123.67, 82.55, 56.80, 56.25, 50.06, 42.44, 39.80, 39.66, 39.02, 37.04, 36.50, 36.31, 35.91, 32.00, 31.90, 28.78, 28.34, 28.16, 24.40, 23.96, 22.97, 22.71, 21.79, 21.14, 19.30, 18.85, 11.99.

Cholesteryl ethylene glycol ether (4a): An oven-dried, 250 mL flask was charged with **6** (see below) (6.00 g, 10.81 mmol) and anhydrous 1,4-dioxane (50 mL). After adding ethylene glycol (8 mL, 143.06 mmol), the reaction vessel was equipped with a condenser and heated to reflux at 120 °C for 14 h. After cooling the vessel to room temperature, the solvent was removed from the reaction mixture under reduced pressure. The residue was dissolved in CH₂Cl₂ (50 mL) and washed with an aqueous solution saturated with NaHCO₃ (50 mL), water (50 mL) and brine (50 mL). The organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude product was further purified by column chromatography (10% ethyl acetate in n-hexane as eluent) to afford the desired product as a white solid (3.50 g, 73%). m.p. 106-108 °C (Lit⁴: 99-100 °C); ¹H NMR (400 MHz, CDCl₃, ppm): δ 5.39 – 5.31 (m, 1H), 3.75 – 3.66 (m, 2H), 3.58 (ddd, *J* = 4.6, 3.6, 1.7 Hz, 2H), 3.26 – 3.14 (m, 1H), 2.37 (ddd, *J* = 13.2, 4.8, 2.3 Hz, 1H), 2.21 (ddt, *J* = 13.5, 10.1, 2.6 Hz, 1H), 2.06 – 1.75 (m, 7H), 1.63 – 0.81 (m, 34H), 0.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 140.87, 121.91, 79.60, 69.08, 62.26, 56.92, 56.31, 50.33, 42.48, 39.93, 39.67, 39.26, 37.33, 37.02, 36.34, 35.94, 32.10, 32.04, 28.58, 28.39, 28.17, 24.45, 23.98, 22.98, 22.72, 21.23, 19.53, 18.87, 12.02.

Cholesteryl hexylene glycol ether (4b): An oven-dried, 250 mL flask was charged with **6** (see below) (6.00 g, 10.81 mmol) and anhydrous 1,4-dioxane (50 mL). After adding 1,6-hexanediol (13.19 g, 111.61 mmol), the vessel was equipped with a condenser and heated to 120 °C for 20 h. After cooling the vessel to room temperature, the solvent was removed from the reaction mixture under reduced pressure. The residue was dissolved in CH₂Cl₂ (50 mL) and washed

with an aqueous solution of saturated with NaHCO_3 (50 mL), water (50 mL) and brine (50 mL). The organic layer was dried over anhydrous MgSO_4 and concentrated under reduced pressure. The crude product was further purified by column chromatography (15% ethyl acetate in n-hexane as eluent) to afford the desired product as a white solid (4.11 g, 76%). m.p. 101-103 °C; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 5.33 (dt, J = 5.5, 1.9 Hz, 1H), 3.63 (t, J = 6.5 Hz, 2H), 3.45 (td, J = 6.7, 1.6 Hz, 2H), 3.12 (tt, J = 11.3, 4.4 Hz, 1H), 2.35 (ddd, J = 13.3, 4.8, 2.2 Hz, 1H), 2.18 (ddt, J = 13.7, 10.4, 2.6 Hz, 1H), 2.07 – 1.74 (m, 5H), 1.66 – 0.76 (m, 44H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 141.26, 121.57, 79.14, 68.12, 63.09, 56.93, 56.31, 50.36, 42.47, 39.94, 39.66, 39.34, 37.44, 37.05, 36.34, 35.93, 32.86, 32.10, 32.04, 30.29, 28.63, 28.38, 28.16, 26.19, 25.75, 24.44, 23.97, 22.97, 22.71, 21.21, 19.54, 18.86, 12.00.

4-Hydroxyazobenzene (5): An oven-dried, 500 mL flask was charged with aqueous HCl (30 mL) and water (20 mL). After cooling to 0 °C, aniline (10.01 g, 107.48 mmol) was added dropwise. A solution of NaNO_2 (8.00 g, 115.95 mmol) dissolved in 50 mL of water was added slowly to resultant solution and stirred for 30 min. Phenol (10.08 g, 107.11 mmol) was added to a 10 wt. % aqueous solution of NaOH (100 mL), and then added slowly to the diazonium salt solution. The resulting mixture was stirred for 1 h at 0 °C. The solids that precipitated were filtered, washed with water, and recrystallized from a mixture of ethanol and water to afford the desired product as a brown powder (17.50 g, 82%). m.p. 150-152 °C (Lit⁵: 154-155 °C); ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.92 – 7.83 (m, 4H), 7.54 – 7.40 (m, 3H), 6.98 – 6.91 (m, 2H), 5.47 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 158.60, 152.67, 147.19, 130.62, 129.21, 125.25, 122.69, 116.00.

6-(4-(Phenyldiazenyl)phenoxy)hexan-1-ol (6): An oven-dried, 500 mL flask was charged with **5** (8.00 g, 40.36 mmol) and DMF (150 mL). K_2CO_3 (8.37 g, 60.56 mmol) was added, and the resultant mixture was stirred for 30 min. Next, 6-chloro-1-hexanol (8.26 g, 60.46 mmol) and a catalytic amount of KI were added, and the resulting mixture was heated to 90 °C. After 14 h, the mixture was cooled to room temperature, poured into a deionized water, and extracted with chloroform (3 × 150 mL). The organic layers were combined, dried over anhydrous MgSO_4 and concentrated under reduced pressure. The crude product was further purified by column chromatography (30% ethyl acetate in n-hexane as eluent) to afford the desired product as an orange solid (11.37 g, 94%). m.p. 80-82 °C; ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.98 – 7.80 (m, 4H), 7.58 – 7.35 (m, 3H), 7.09 – 6.91 (m, 2H), 4.04 (t, J = 6.5 Hz, 2H), 3.66 (t, J = 6.5 Hz, 2H), 1.83 (dt, J = 7.8, 6.4 Hz, 2H), 1.69 – 1.33 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3 ,

ppm): δ 161.80, 152.84, 146.95, 130.45, 129.15, 124.91, 122.65, 114.82, 68.32, 62.97, 32.78, 29.29, 25.99, 25.67.

2,2'-(1,4-Phenylene)bis(2-bromoacetic acid) (7): An oven-dried pressure tube was charged with 1,4-phenylenediacetic acid (4.46 g, 22.97 mmol) and acetonitrile (60 mL). After adding of NBS (10.00 g, 56.19 mmol) and AIBN (0.20 g, 1.22 mmol), the solution was stirred at 80 °C for 18 h. After cooling solution to room temperature, the mixture was concentrated under reduced pressure. The residue was diluted with a mixture of 1 : 9 v/v ethyl acetate : CH₂Cl₂ (100 mL) and filtered. The filtrate was concentrated under reduced pressure and further purified by column chromatography (50% ethyl acetate in n-hexane as eluent) to afford the desired product as a pale-yellow solid (6.71g, 83%). m.p. 186-188 °C (Lit⁶: 201-202 °C); ¹H NMR (400 MHz, DMSO-d₆, ppm): δ 7.55 (s, 4H), 5.78 (s, 2H); ¹³C NMR (100 MHz, DMSO-d₆, ppm): δ 169.17, 137.63, 129.04, 47.50, 47.46.

Dimerization of EBPA: diethyl 2,3-diphenylsuccinate: An oven-dried, 15 mL Schlenk flask was charged with ethyl α -bromo phenyl acetate (60.3 mg, 0.25 mmol) and 1 mL of DMF. A solution of tetrakis(dimethylamino)ethylene (200.5 mg, 1.00 mmol) in 1 mL of DMF was added dropwise. The reaction mixture was stirred for 18 h and then diluted with CH₂Cl₂ (5 mL). The mixture was then filtered to remove the precipitate. The filtrate was washed with water, an aqueous solution saturated with NaHCO₃ (5 mL) and brine (5 mL). The organic layer was separated, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude product was further purified by column chromatography (10% ethyl acetate in n-hexane as eluent). Yield: 81% (32.6 mg, *dl* : *meso* = 6:4). ¹H NMR (400 MHz, CDCl₃, ppm): *dl* isomer: δ 7.53 – 7.49 (m, 4H), 7.37 – 7.25 (m, 6H), 4.37 (s, 2H), 3.86 (m, 4H), 0.93 (t, 6H, *J* = 7.2 Hz); *meso* isomer: δ 7.16 – 7.09 (m, 6H), 7.05 – 7.00 (m, 4H), 4.22 (s, 2H), 4.15 (m, 4H), 1.21 (t, 6H, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃, ppm): *dl* isomer: δ 171.53, 136.62, 128.72, 128.67, 127.98, 60.89, 55.40, 13.91. *meso* isomer: δ 173.20, 136.04, 128.53, 128.51, 127.47, 61.28, 55.15, 14.17.

Dimerization of EBPA: diethyl 2-bromo-2,3-diphenylsuccinate: An oven-dried, 15 mL Schlenk flask was charged with ethyl α -bromo phenyl acetate (100 mg, 0.41 mmol) and 2 mL of DMF. After the addition of NaOH (8.23 mg, 0.21 mmol), the reaction mixture was stirred for 6 h. The solution was then diluted with CH₂Cl₂ (10 mL) and filtered to remove the excess reagent. The filtrate was washed with water and the organic layer was separated, dried over

anhydrous MgSO₄ and concentrated under reduced pressure. The crude product was further purified by column chromatography (10% ethyl acetate in n-hexane as eluent). Yield: 58% (48.4 mg). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.47 – 6.80 (m, 8H), 4.87, 4.59 (s, 1H), 4.44 – 3.95 (m, 4H), 1.37 – 0.88 (m, 6H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 170.91, 170.72, 170.69, 170.64, 136.85, 135.03, 133.45, 133.37, 131.32, 131.15, 131.00, 128.94, 128.81, 128.79, 128.60, 128.53, 128.48, 128.45, 128.34, 128.15, 128.00, 127.84, 127.58, 127.51, 126.61, 68.48, 63.15, 62.86, 61.43, 61.20, 61.14, 60.43, 14.16, 14.06, 13.90, 13.75. HRMS (ESI): [M+H]⁺ calcd for C₂₀H₂₁BrO₄: 404.0623; Found: 405.0698 (⁷⁹Br), 407.0681 (⁸¹Br).

Dimerization of EBPA: diethyl 2,3-diphenylbut-2-enedioate: An oven-dried, 15 mL Schlenk flask was charged with ethyl α-bromo phenyl acetate (61.6 mg, 0.25 mmol) and 1 mL of DMF. After the addition of NaOH (108.8 mg, 2.72 mmol), the reaction mixture was stirred for 18 h. The solution was then diluted with CH₂Cl₂ (5 mL) and filtered to remove excess reagent. The filtrate was washed with water and the organic layer was separated, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude product was further purified by column chromatography (10% ethyl acetate in n-hexane as eluent). Yield: 83% (34.3 mg). ¹H NMR (400 MHz, CDCl₃, ppm): *cis*⁷: δ 7.22 – 7.14 (m, 6H), 7.13 – 7.07 (m, 4H), 4.30 (q, 4H, *J* = 7.2 Hz), 1.30 (t, 6H, *J* = 7.2 Hz); *trans*: δ 7.45 – 7.41 (m, 4H), 7.39 – 7.33 (m, 6H), 4.00 (q, 4H, *J* = 7.2 Hz), 0.94 (t, 6H, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃, ppm): *cis*⁷: δ 168.05, 138.80, 134.84, 129.87, 128.30, 128.18, 61.79, 14.16; *trans*: δ 168.16, 137.84, 135.76, 128.79, 128.48, 128.35, 61.45, 13.76.

General procedure used to synthesize the PPXs: An oven dried, Schlenk flask was charged with **2** (0.50 mmol) and dry DMF (0.25 mL). Tetrakis(dimethylamino)ethylene (2.00 mmol) in a solution of DMF (see Table 1) was added dropwise and the resultant solution was stirred for 24 h. The precipitated TDAE salt was filtered, and the filtrate was poured into methanol. The resultant precipitated solid was filtered, washed with CH₃OH and dried to afford the corresponding polymer.

General procedure used to synthesize the BrPPXs: An oven-dried Schlenk flask was charged with **2** (0.50 mmol) and dry DMF. After cooling the solution in an ice-bath, TEA (1.03 mmol) was added dropwise, and the resulting mixture stirred for 18 or 24 h. The solution was poured into CH₃OH and resulting precipitate was filtered, washed with CH₃OH and dried to afford the corresponding polymer. See Table S1 for additional data.

Table S1. Summary of data recorded for the BrPPXs.

Polymer	Conc. (M)	Time (h)	Yield (%) ^a	M_n (kDa) ^b	\bar{D}	T_g (°C) ^c
BrPPX-2a	0.30	18	70	64.3	2.43	106
BrPPX-2b	0.30	18	60	39.1	2.17	62
BrPPX-2c	0.30	18	57	39.1	2.50	46
BrPPX-2d	0.48	24	48	59.2	2.55	16
BrPPX-2e	0.48	24	49	31.0	2.43	70
BrPPX-2f	0.12	24	56	38.5	2.57	81
BrPPX-2g ^e	0.12	24	81	52.9	2.06	105
BrPPX-2h ^e	0.12	24	80	24.3	1.86	37
BrPPX-2i ^e	0.48	24	86	3.0	2.26	46

^a Isolated yield. ^b Determined by SEC relative to polystyrene standards in THF. ^c The glass transition temperatures (T_g) were measured by DSC (heating rate: 20 °C/min). ^e The polymerization reaction was conducted in THF.

General procedure used to synthesize the PPVs: An oven dried Schlenk flask was charged with a BrPPX (0.50 mmol based on the repeat unit) and dry DMF (see Table 2). Excess TEA was added and then the resultant solution was stirred at 60 °C for 18 or 24 h. After cooling the mixture to room temperature, the solution was poured into CH₃OH and resulting precipitate was filtered, washed with CH₃OH and dried to afford the corresponding polymer.

NMR Spectra Recorded During the EBPA Dimerization Experiments

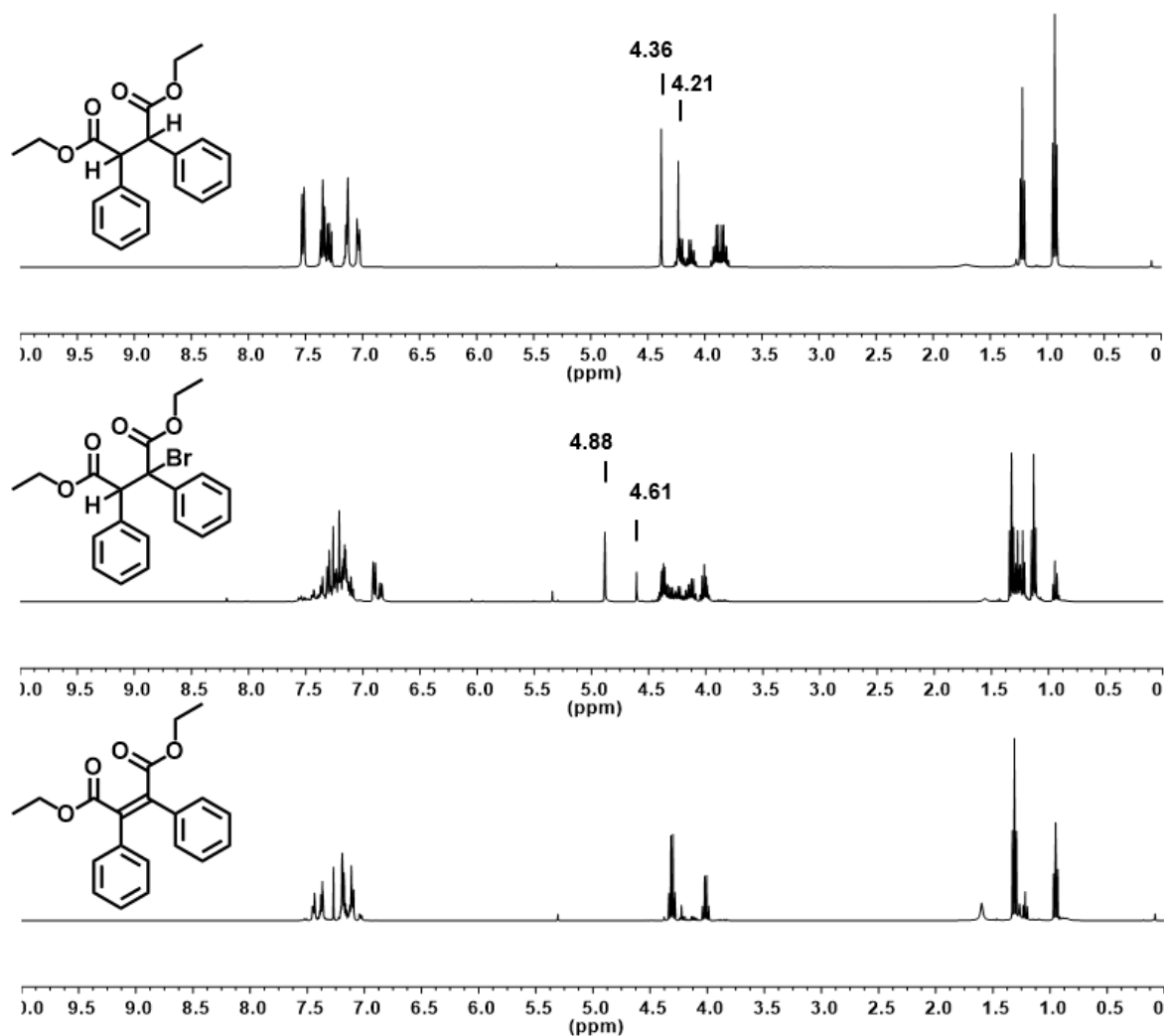


Figure S1. ^1H NMR spectra (CDCl_3) recorded for products obtained from the dimerization of EBPA.

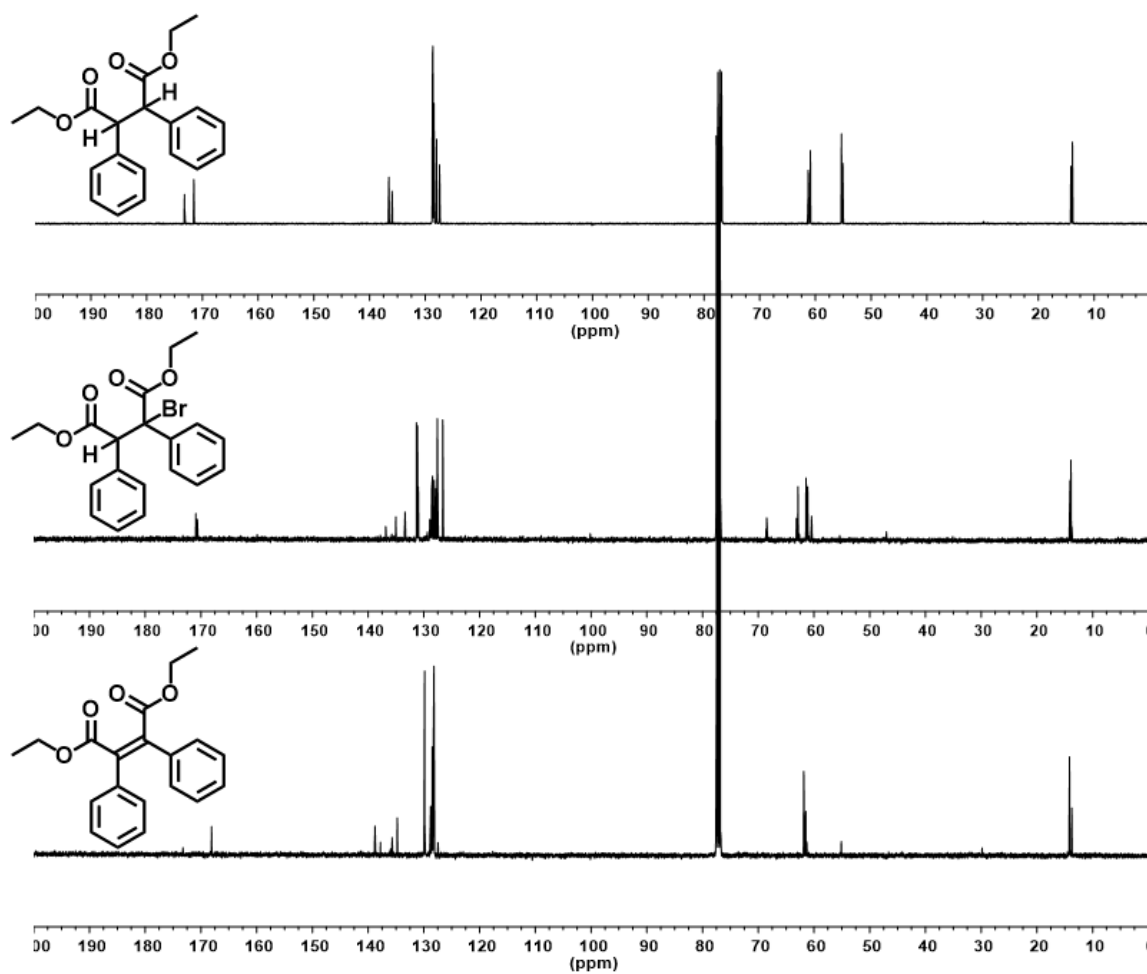


Figure S2. ^{13}C NMR spectra (CDCl_3) recorded for products obtained from the dimerization of EBPA.

NMR Spectra Recorded for PPX-2a, BrPPX-2a and PPV-2a

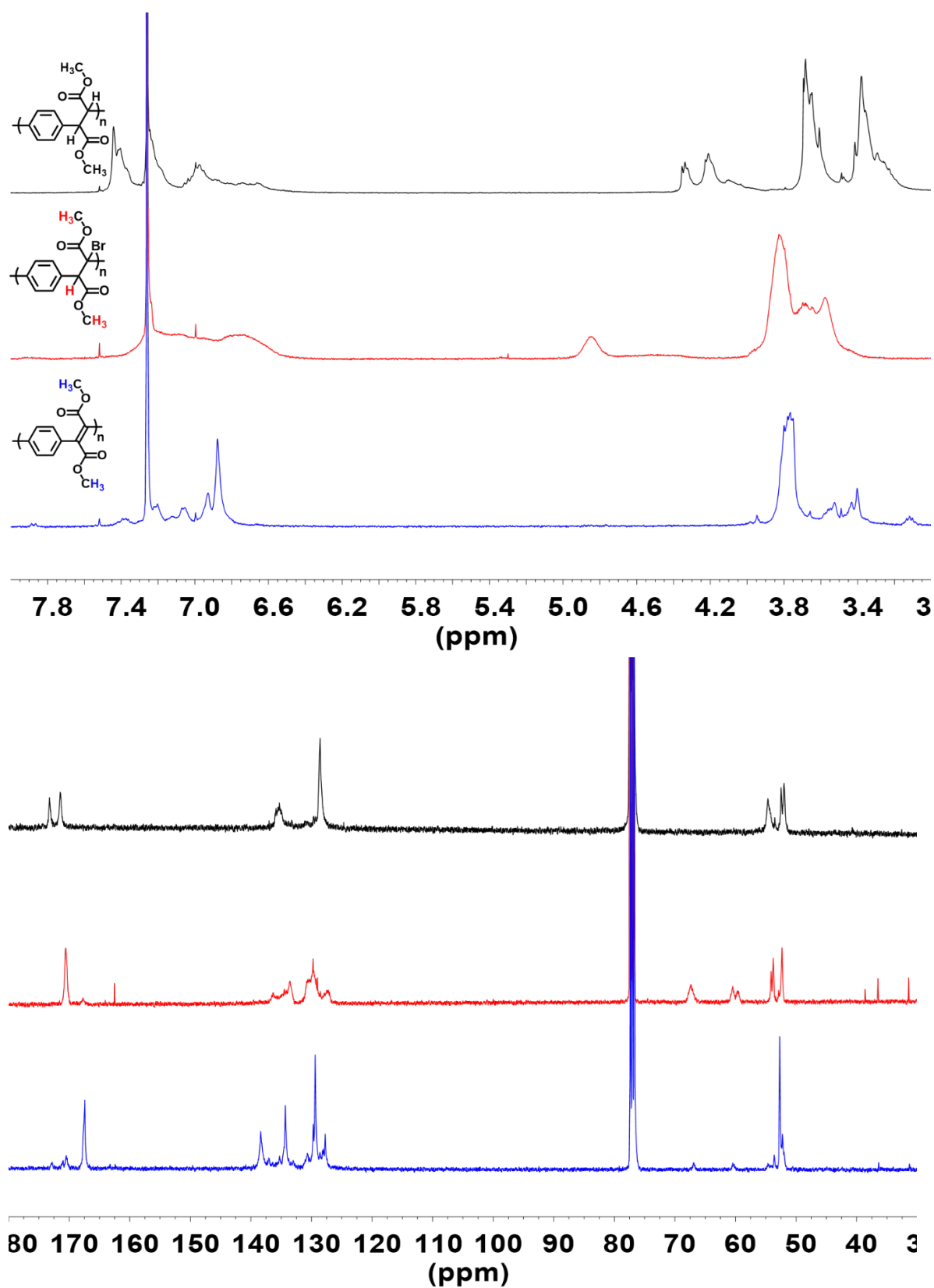


Figure S3. ¹H NMR and ¹³C NMR spectra recorded for **PPX-2a** (black), **BrPPX-2a** (red), **PPV-2a** (blue) in CDCl₃. Comparison of the NMR data indicated that approximately 85% of **BrPPX-2a** underwent elimination.

IR Spectra Recorded for PPX-2a, BrPPX-2a and PPV-2a

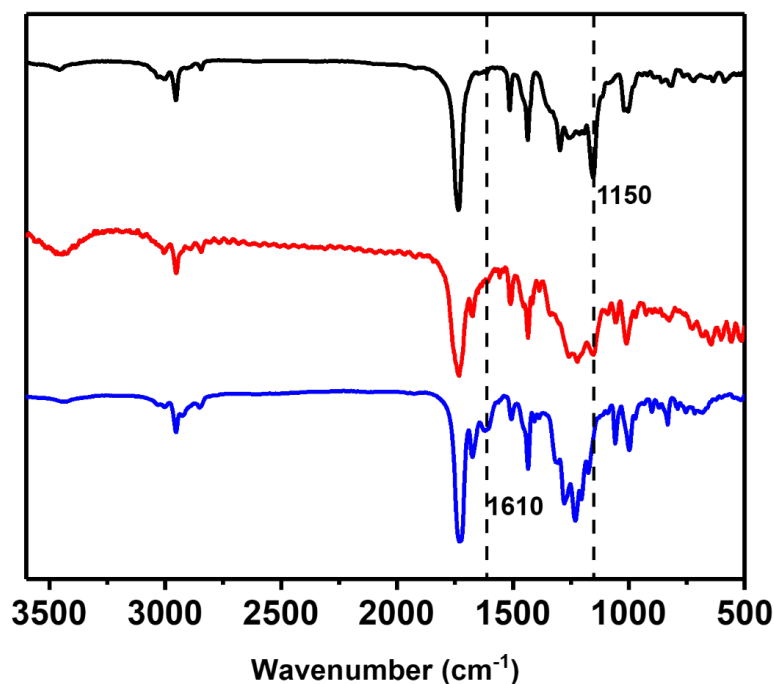


Figure S4. FT-IR spectra recorded as KBr pellets for **PPX-2a** (black), **BrPPX-2a** (red), **PPV-2a** (blue).

TGA Data Recorded for PPXs and PPVs

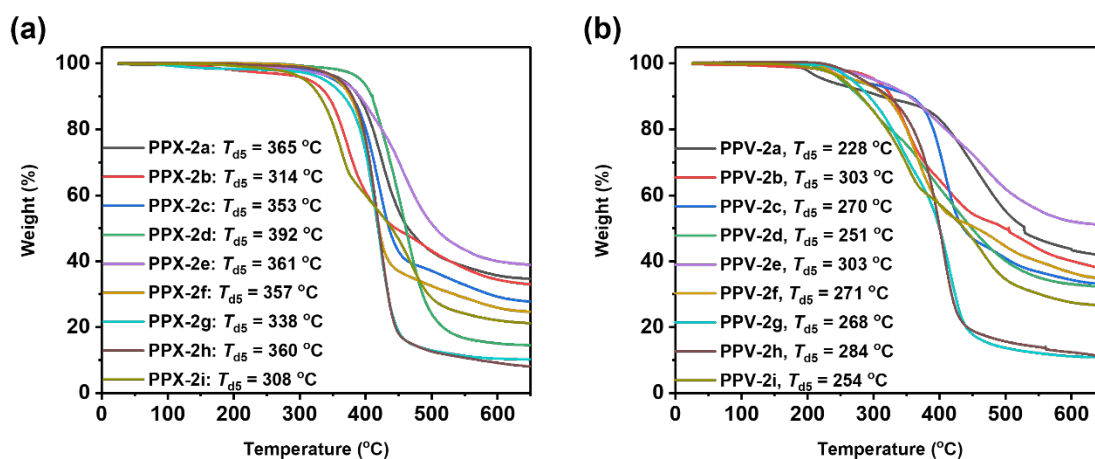


Figure S5. TGA data recorded for various polymers (indicated). Conditions: N₂: 60 mL / min, Ramp rate: 10 °C / min.

Additional Data Recorded for the Dehydrohalogenation of BrPPX-2a

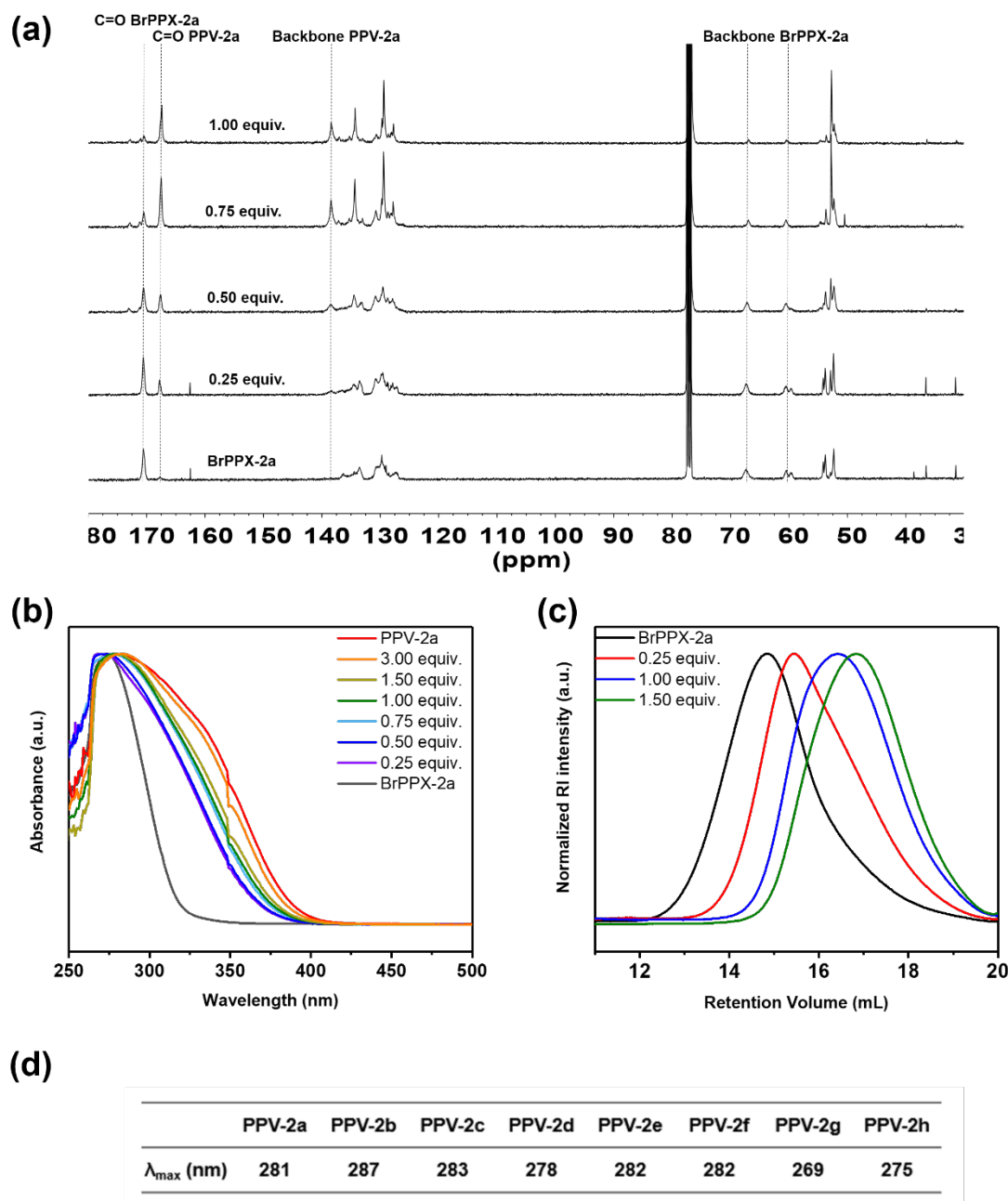


Figure S6. (a) ¹³C NMR spectra recorded after BrPPX-2a was treated with TEA to effect dehydrohalogenation (CDCl₃, with decoupling, no NOE, relaxation time = 10 s). (b) UV-vis spectra recorded in DMF as BrPPX-2a was converted to PPV-2a in a stepwise manner. (c) Size exclusion chromatography data recorded for BrPPX-2a (black) and after treatment with 0.25 equiv. (red), 1.00 equiv. (blue), or 1.50 equiv. (green) of TEA. (d) Summary of the λ_{max} values that were measured for various PPVs in CH₂Cl₂.

Additional Data Recorded for the Post-Polymerization Modification

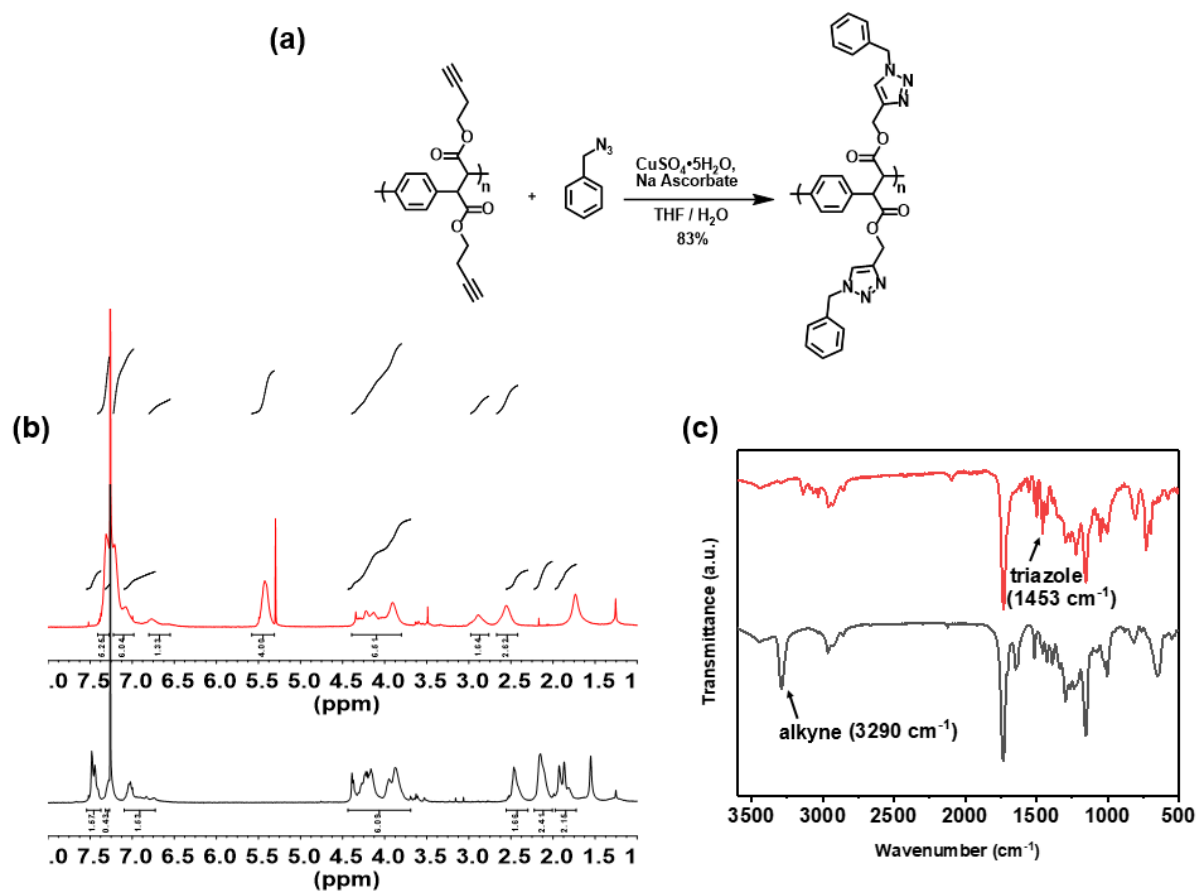


Figure S7. (a) Illustration of an alkyne-azide cycloaddition reaction. (b) ^1H NMR spectra recorded for **PPX-2e** before (black) and after the cycloaddition reaction (red) (c) FT-IR recorded for **PPX-2e** before (black) and after the cycloaddition reaction.

Additional NMR Spectra

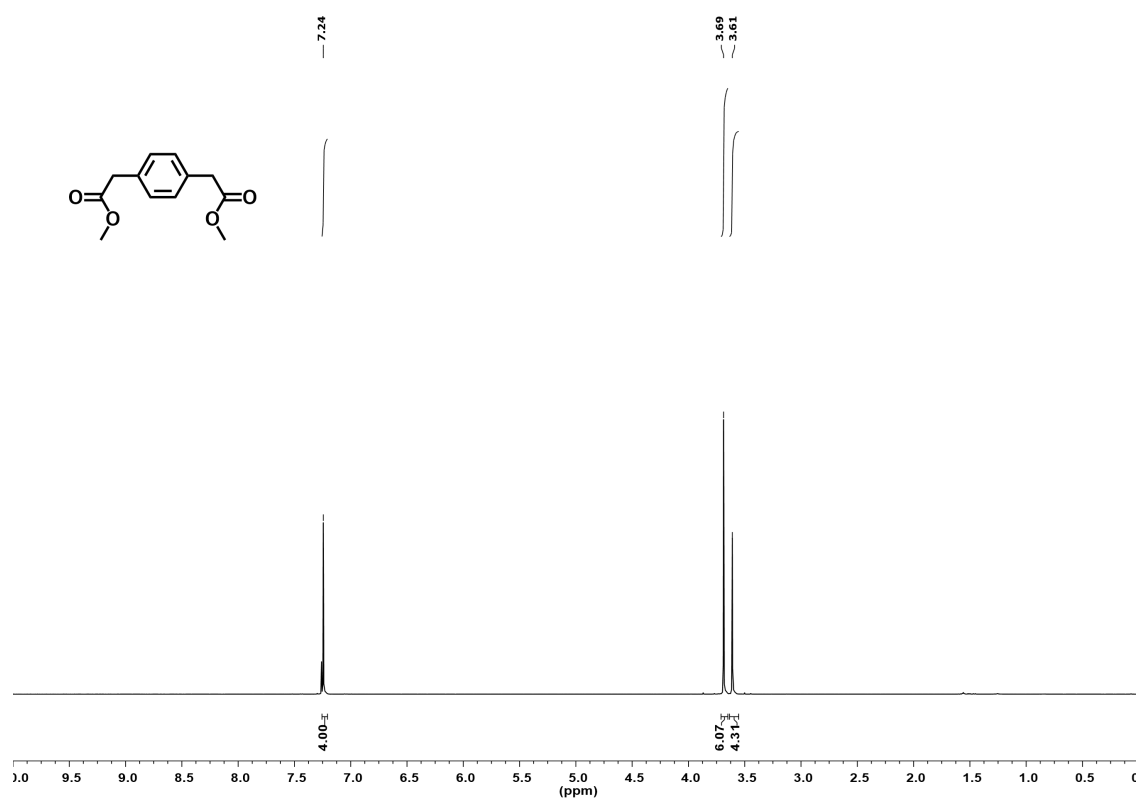


Figure S8. ¹H NMR spectrum recorded for **1a** in CDCl₃.

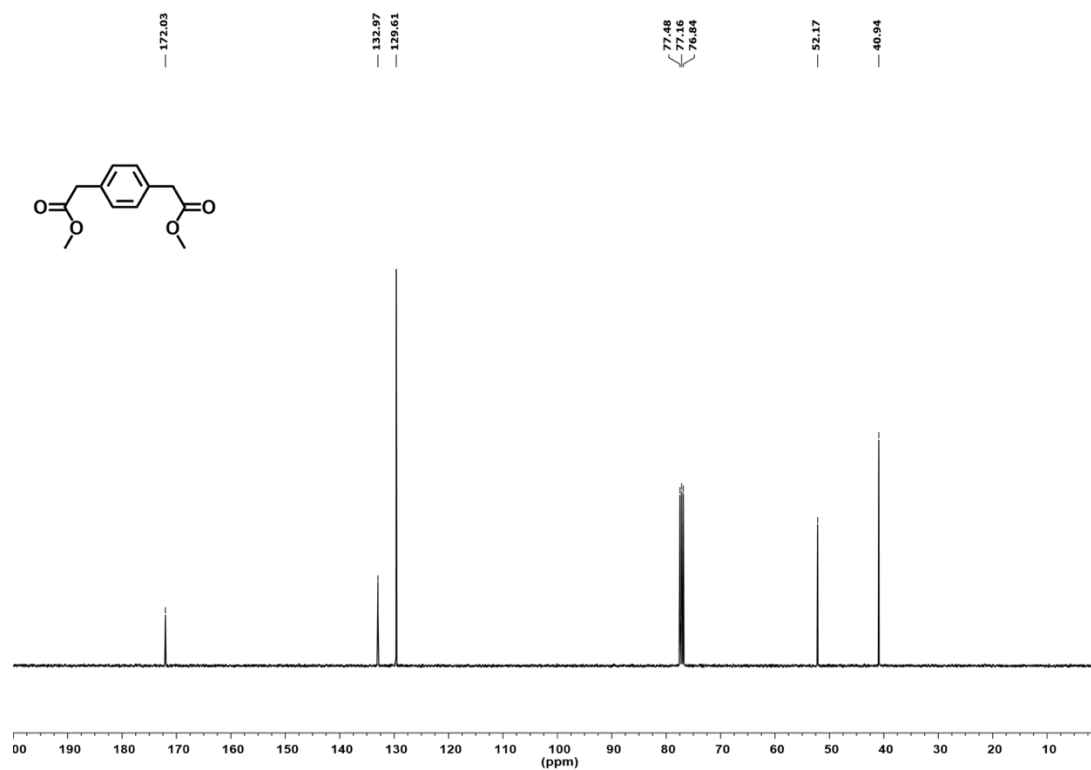


Figure S9. ¹³C NMR spectrum recorded for **1a** in CDCl₃.

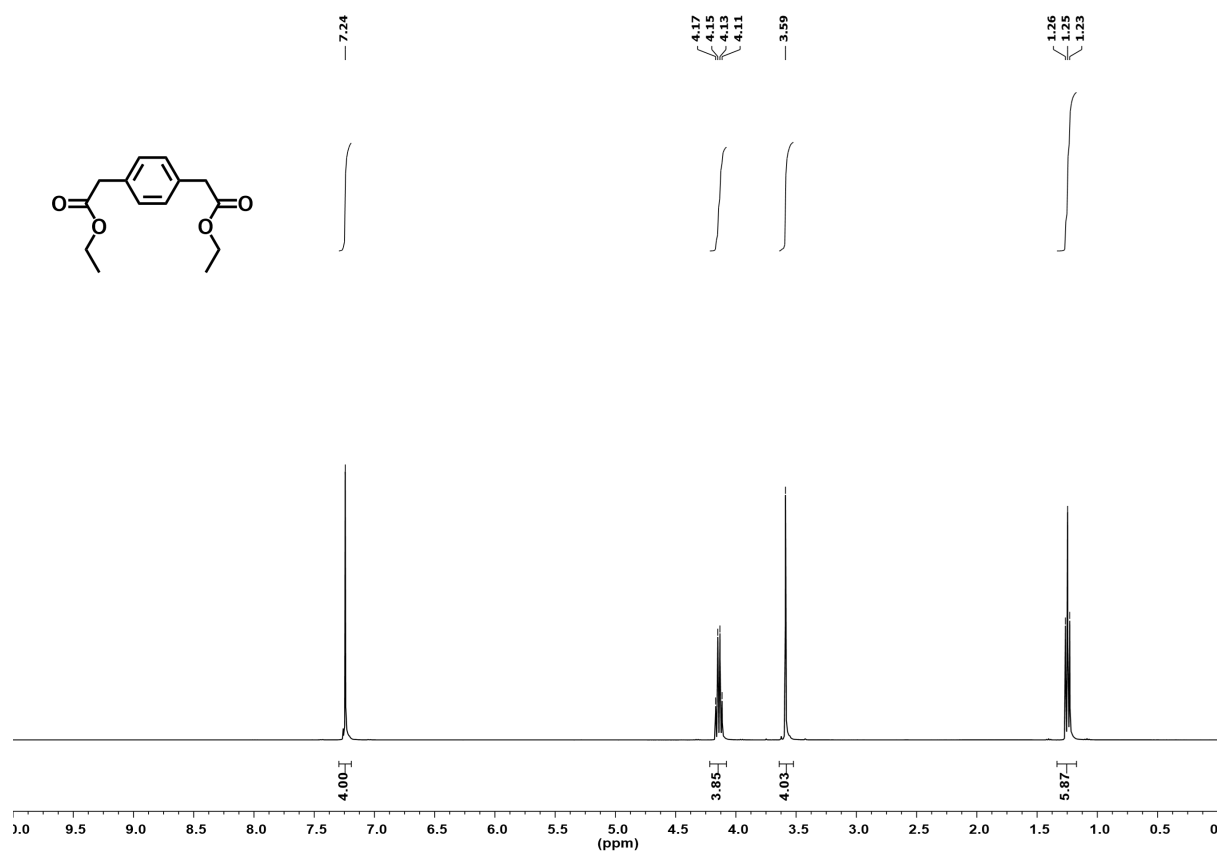


Figure S10. ¹H NMR spectrum recorded for **1b** in CDCl₃.

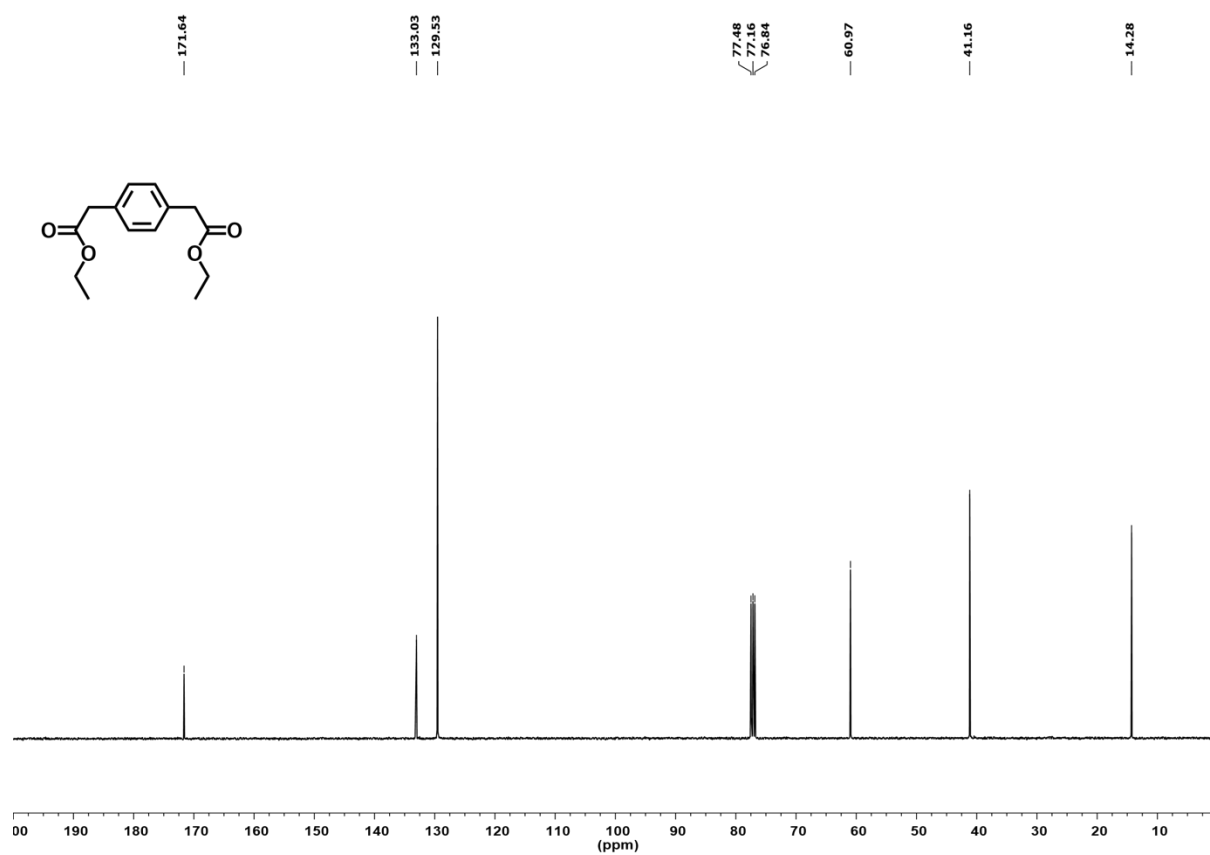


Figure S11. ¹³C NMR spectrum recorded for **1b** in CDCl₃.

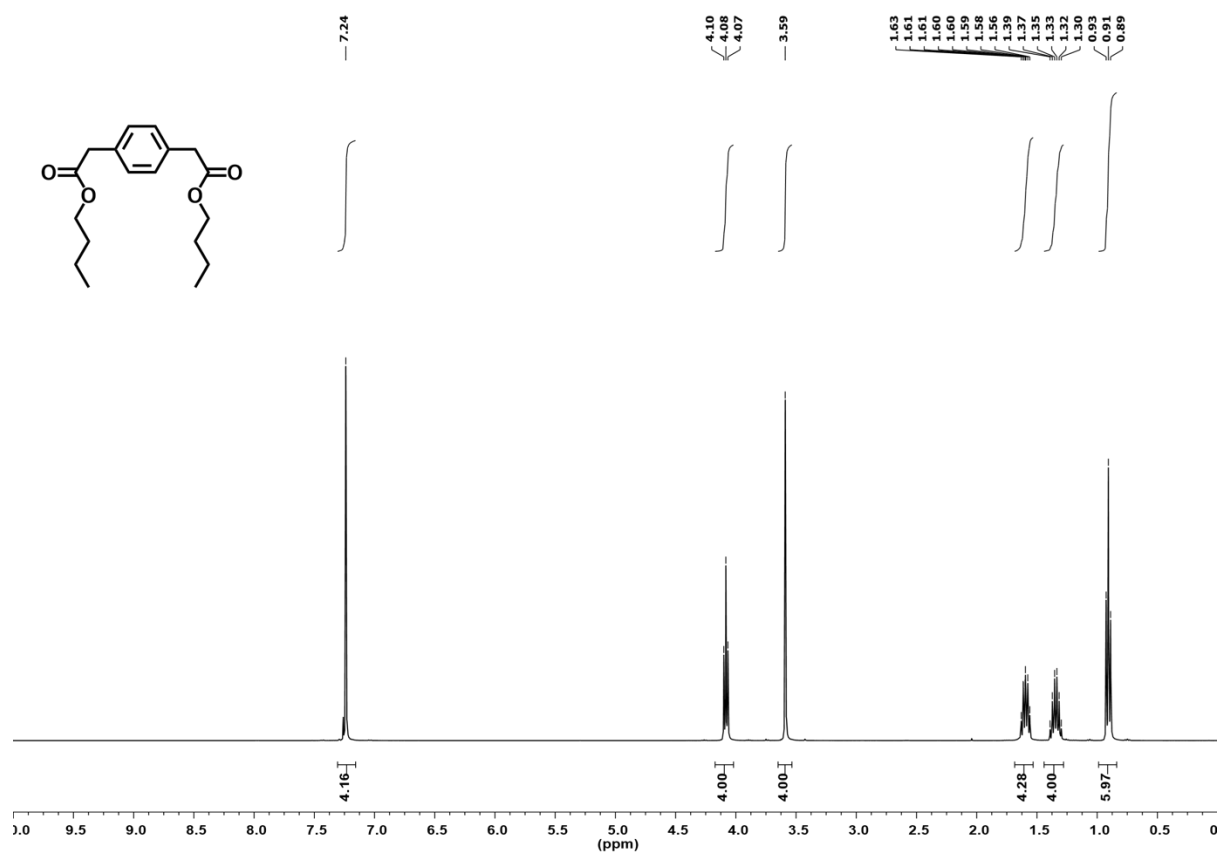


Figure S12. ¹H NMR spectrum recorded for **1c** in CDCl₃.

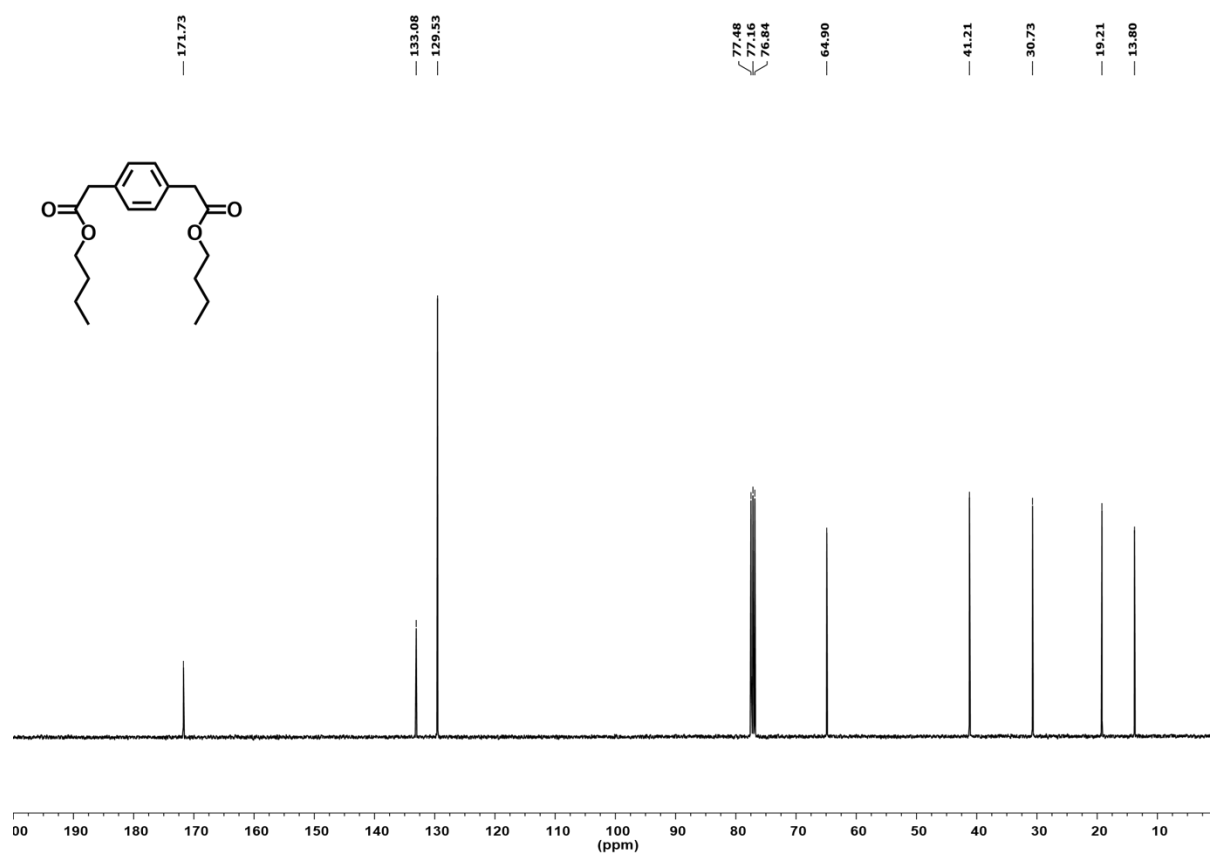


Figure S13. ¹³C NMR spectrum recorded for **1c** in CDCl₃.

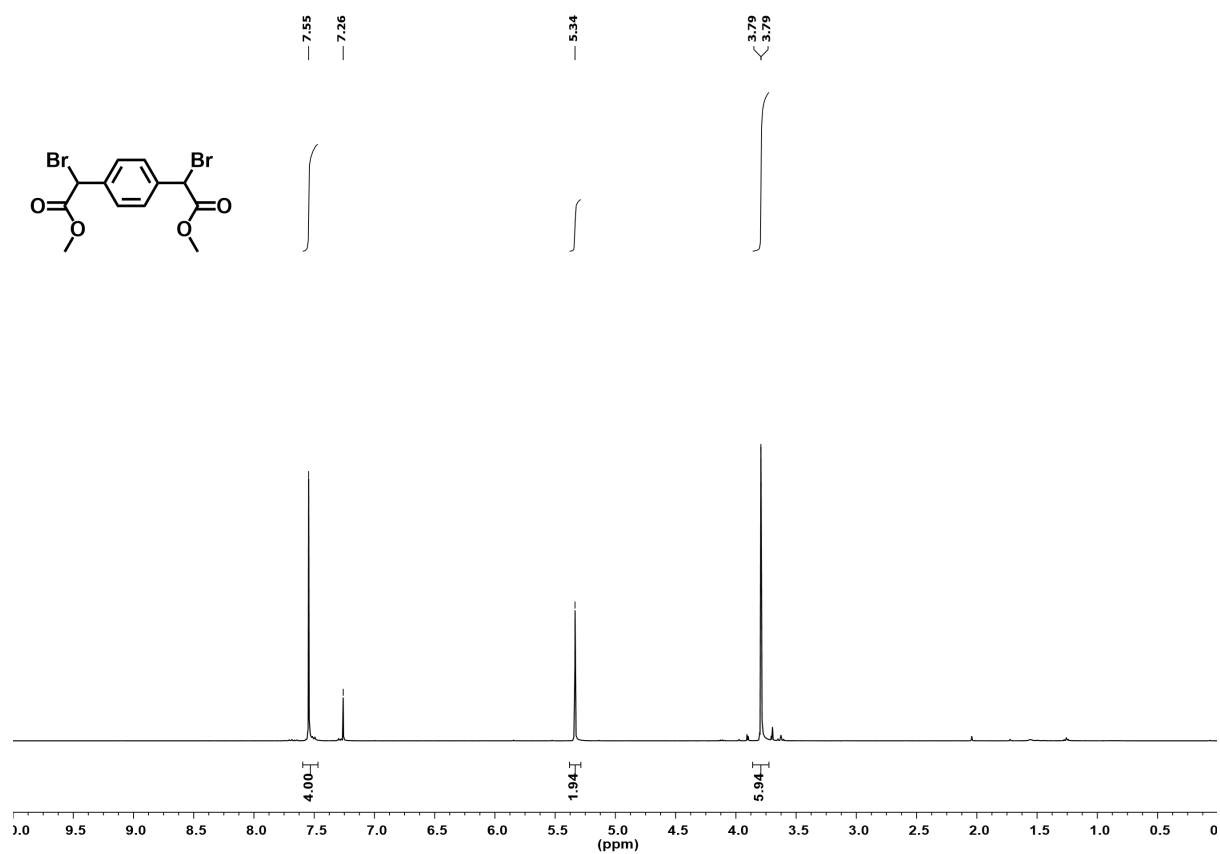


Figure S14. ¹H NMR spectrum recorded for **2a** in CDCl₃.

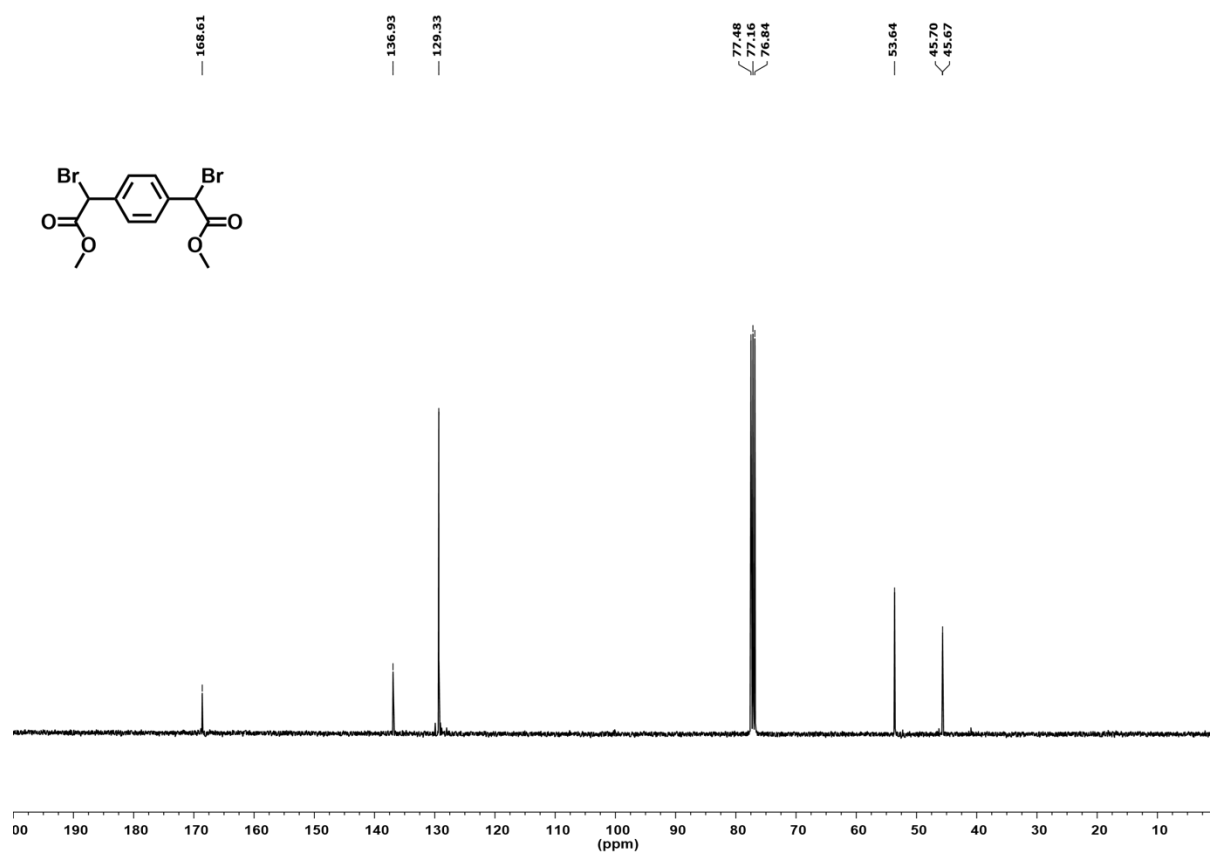


Figure S15. ¹³C NMR spectrum recorded for **2a** in CDCl₃.

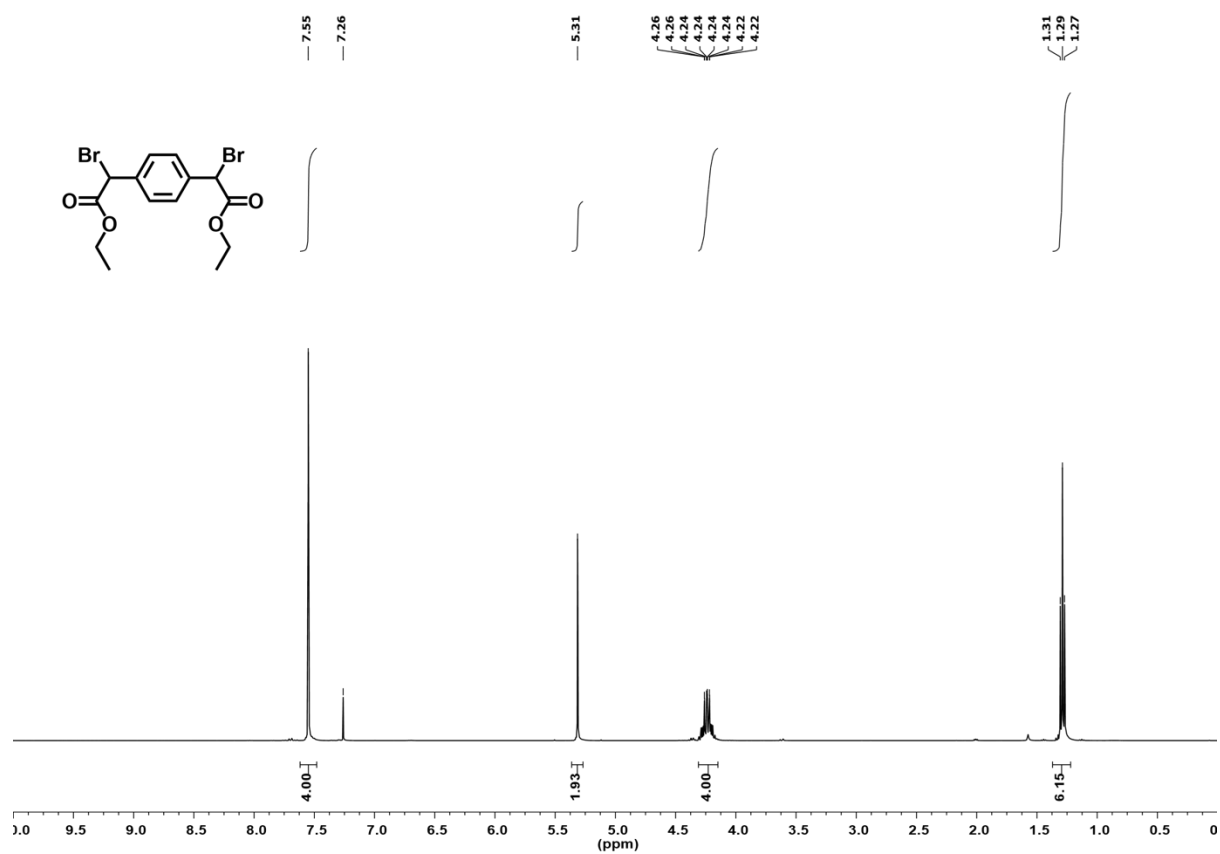


Figure S16. ¹H NMR spectrum recorded for **2b** in CDCl₃.

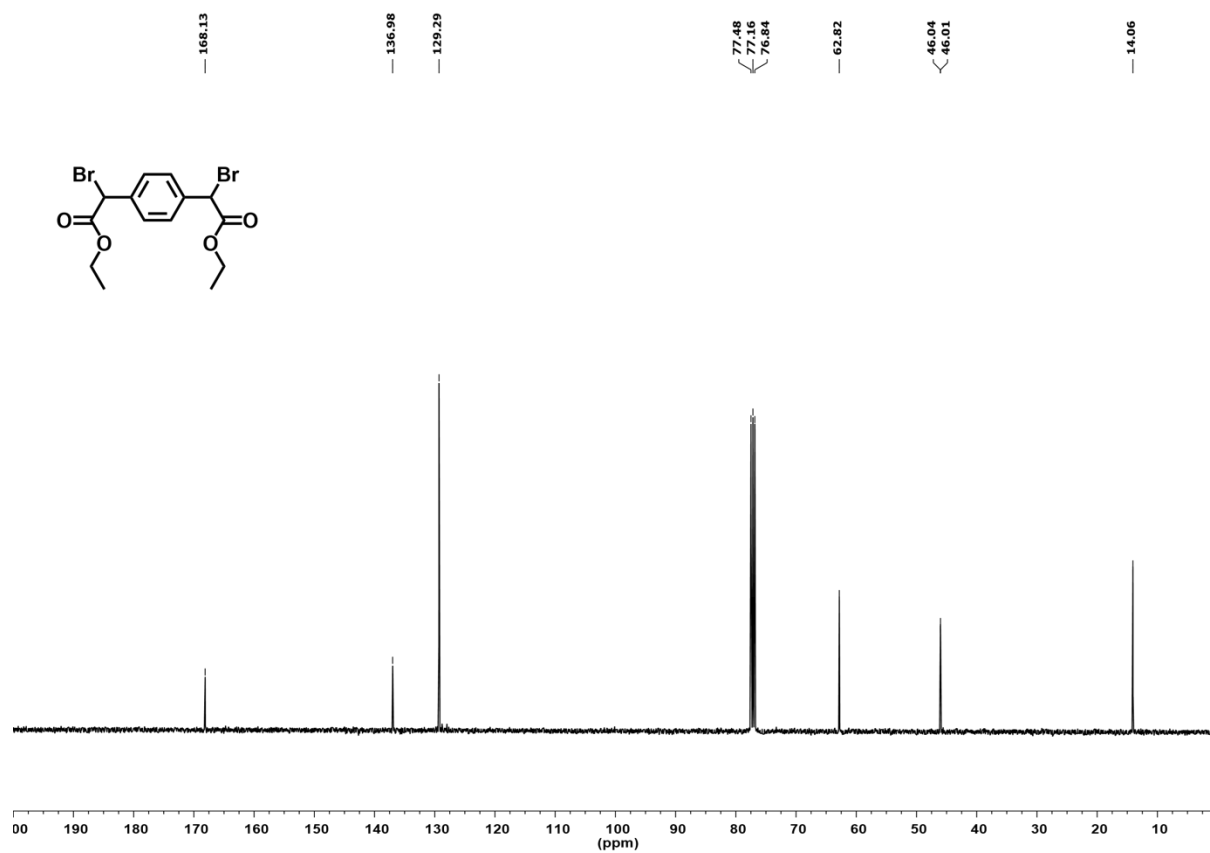


Figure S17. ¹³C NMR spectrum recorded for **2b** in CDCl₃.

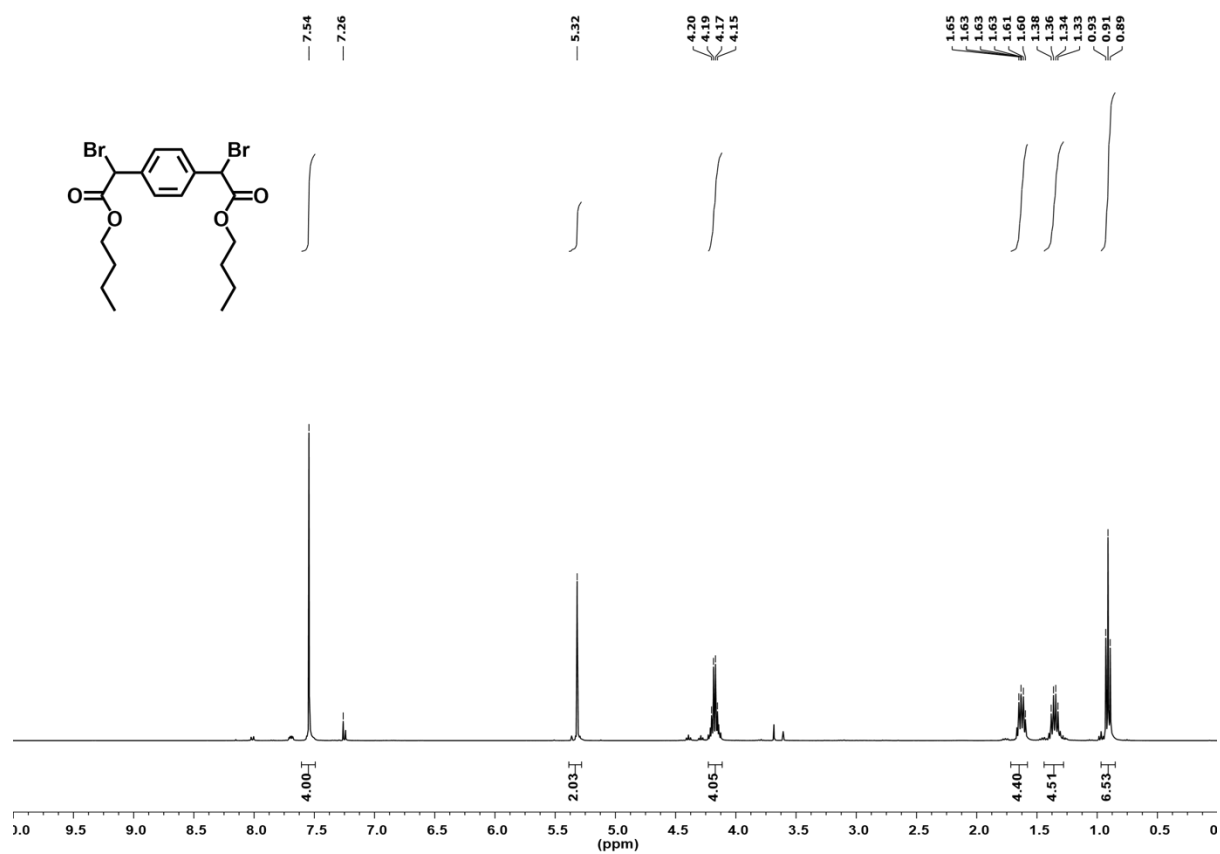


Figure S18. ¹H NMR spectrum recorded for **2c** in CDCl₃.

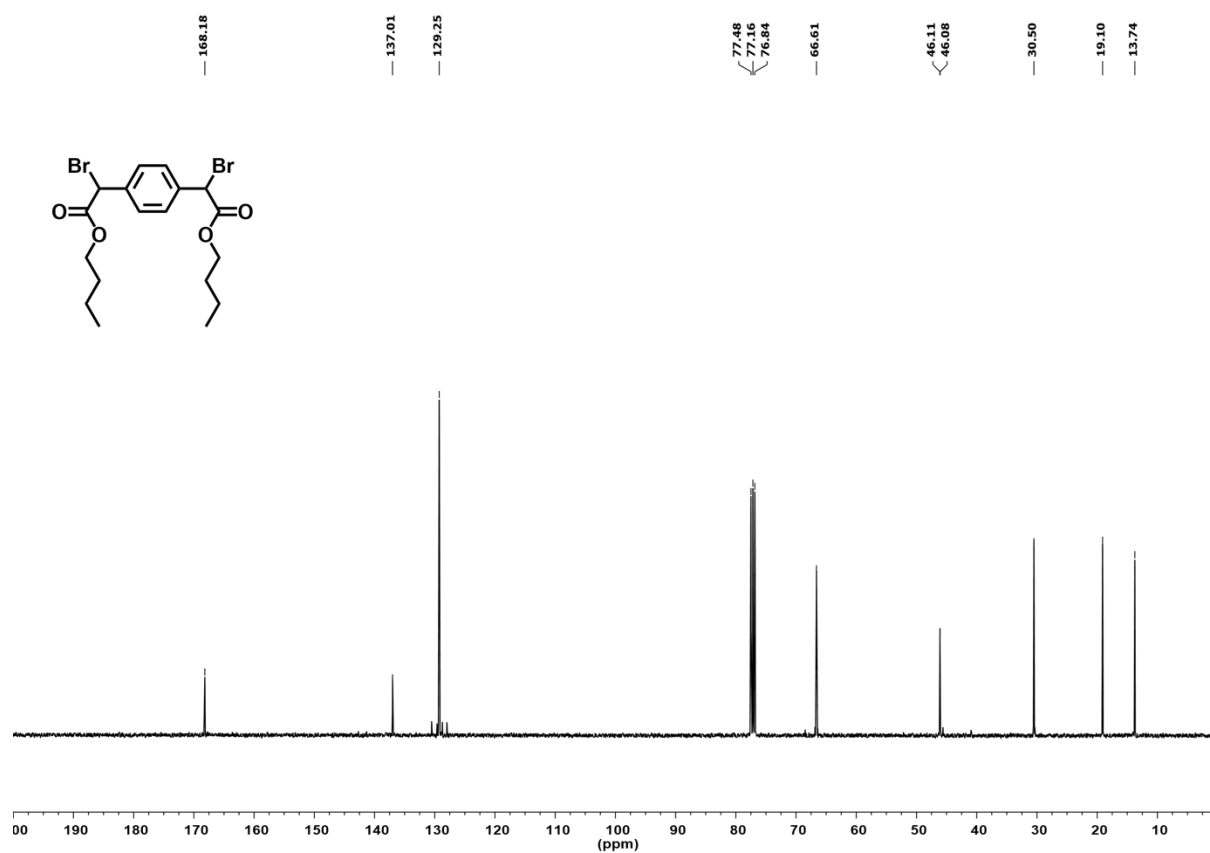


Figure S19. ¹³C NMR spectrum recorded for **2c** in CDCl₃.

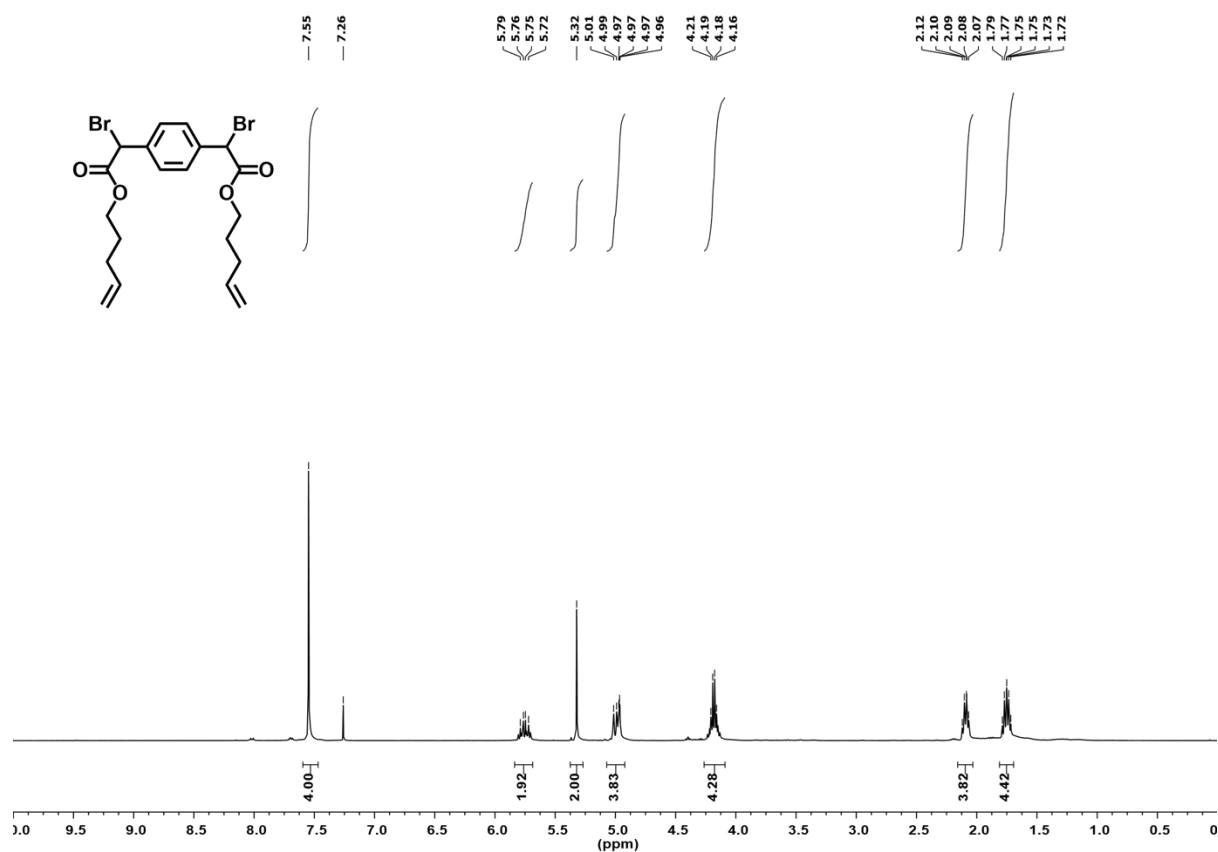


Figure S20. ¹H NMR spectrum recorded for **2d** in CDCl₃.

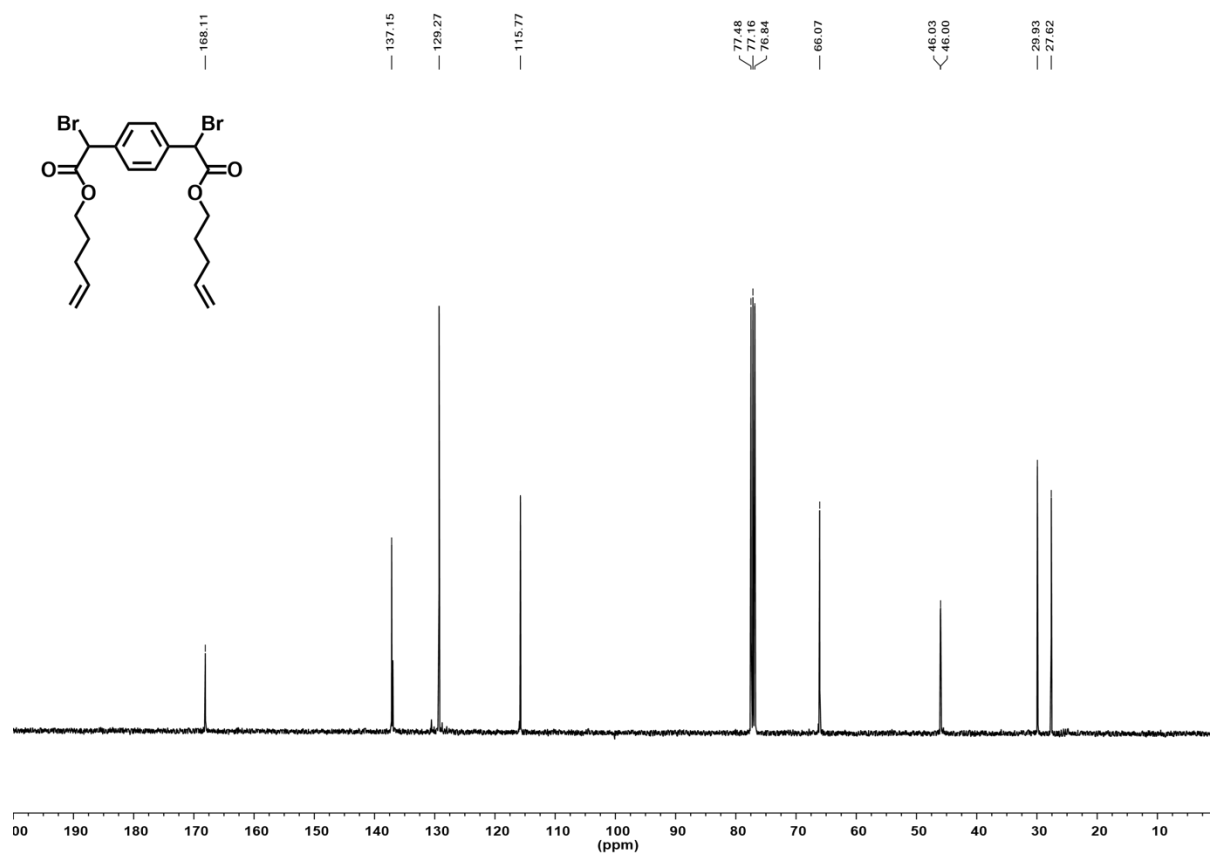


Figure S21. ¹³C NMR spectrum recorded for **2d** in CDCl₃.

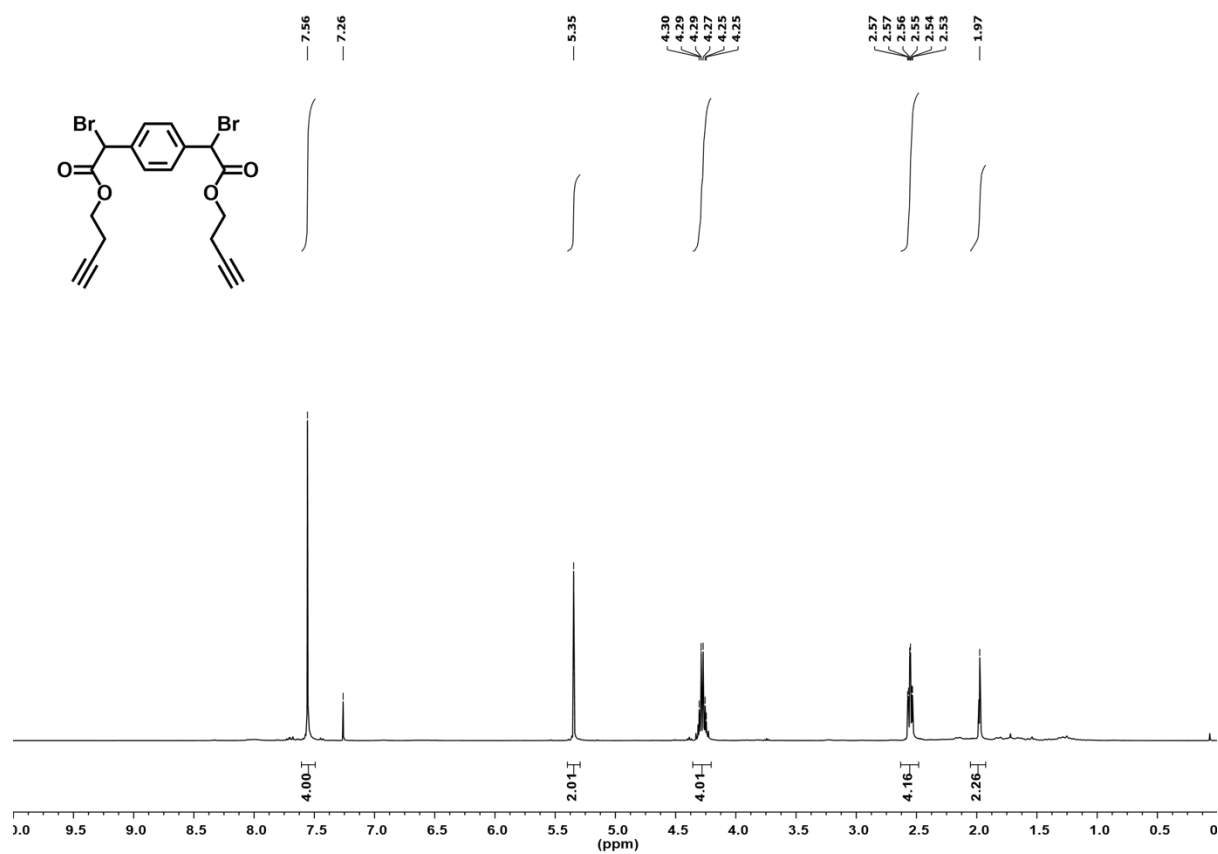


Figure S22. ¹H NMR spectrum recorded for **2e** in CDCl₃.

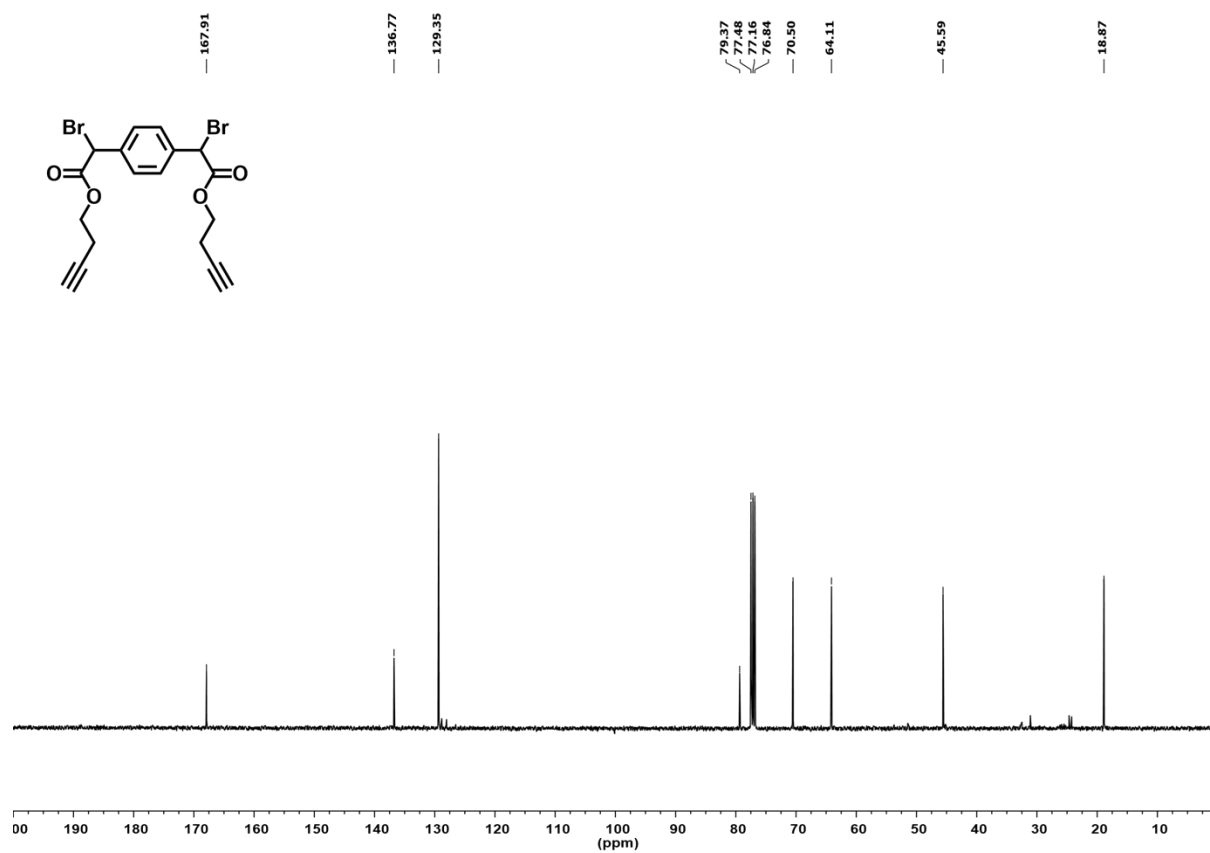


Figure S23. ¹³C NMR spectrum recorded for **2e** in CDCl₃.

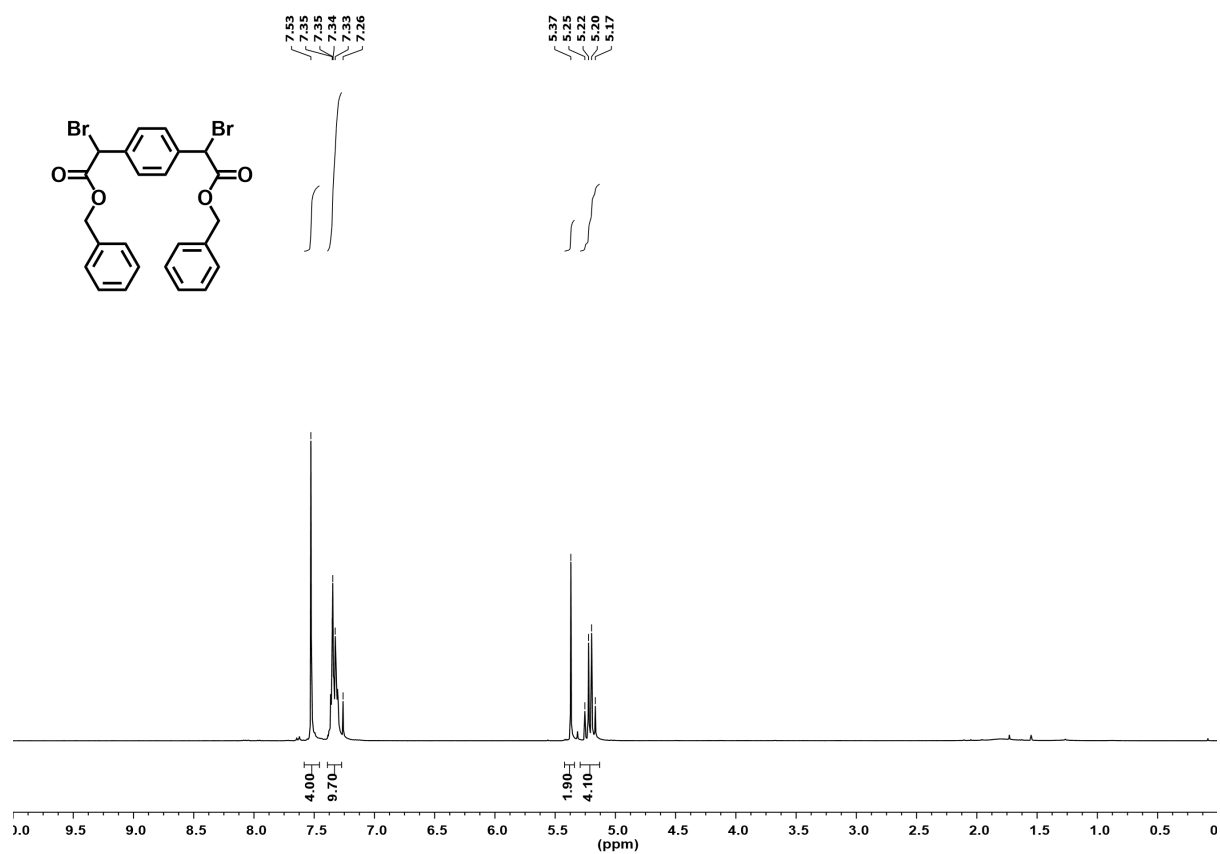


Figure S24. ¹H NMR spectrum recorded for **2f** in CDCl₃.

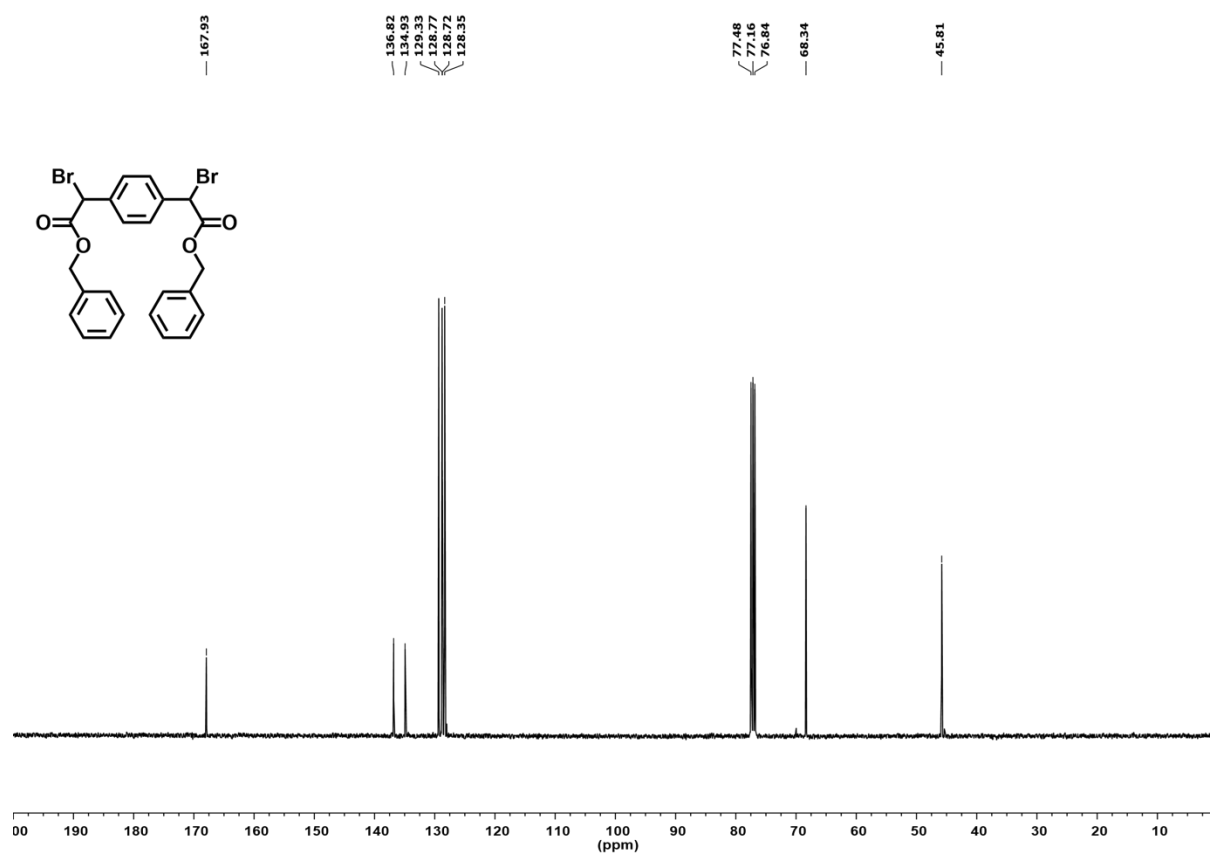


Figure S25. ¹³C NMR spectrum recorded for **2f** in CDCl₃.

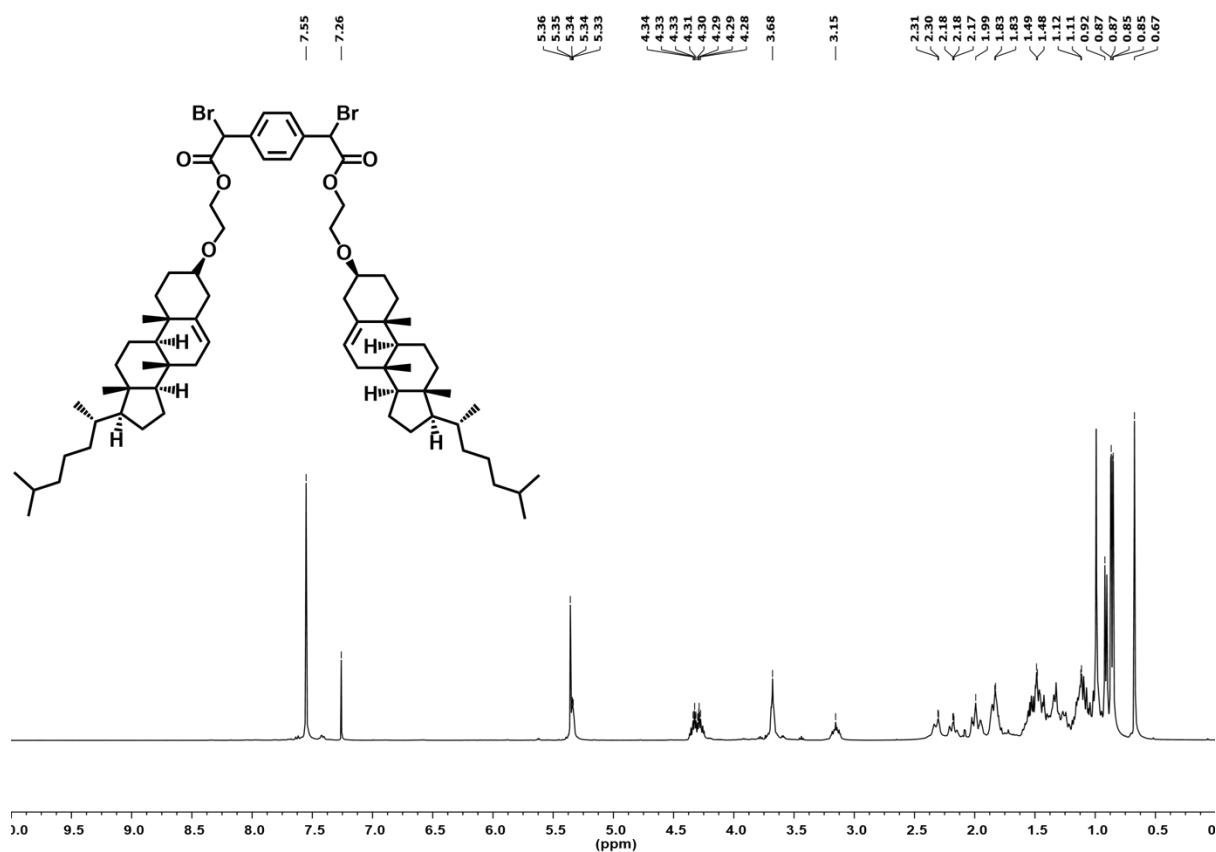


Figure S26. ^1H NMR spectrum recorded for **2g** in CDCl_3 .

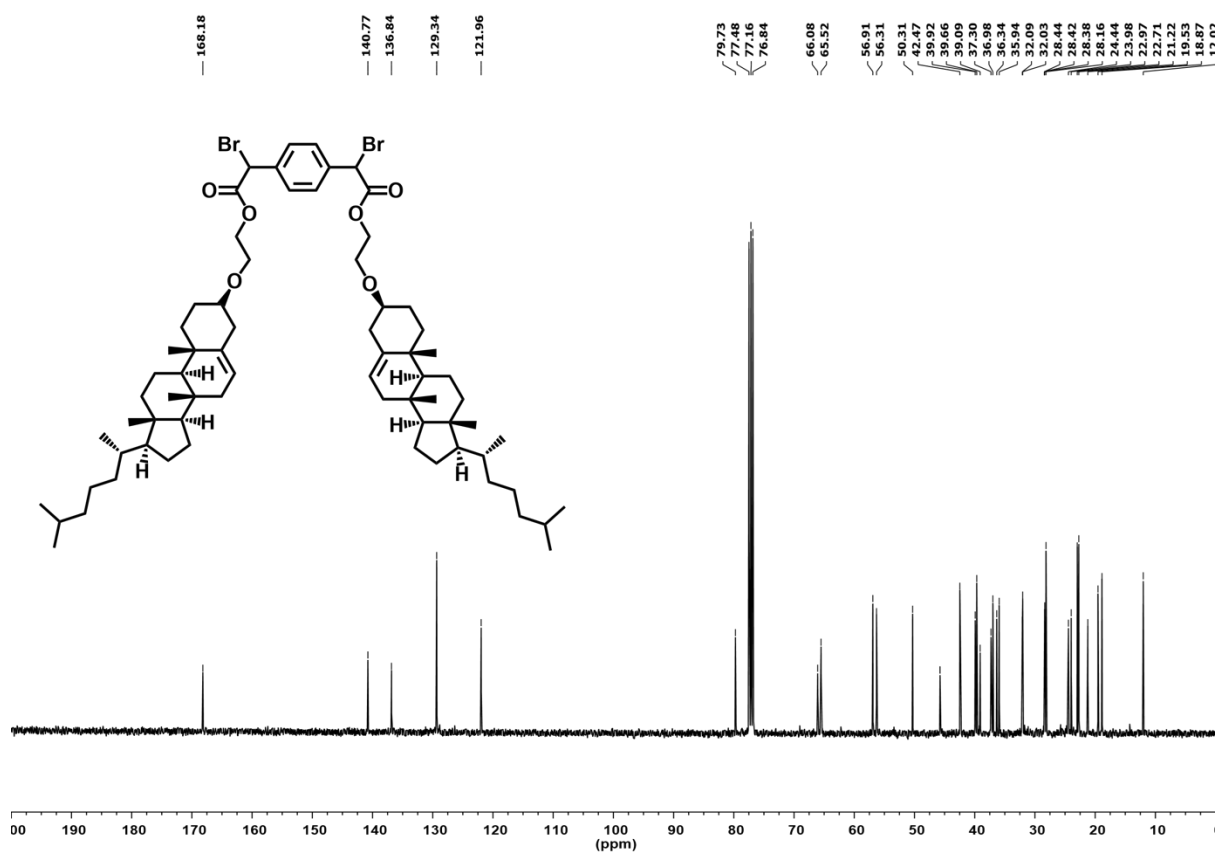
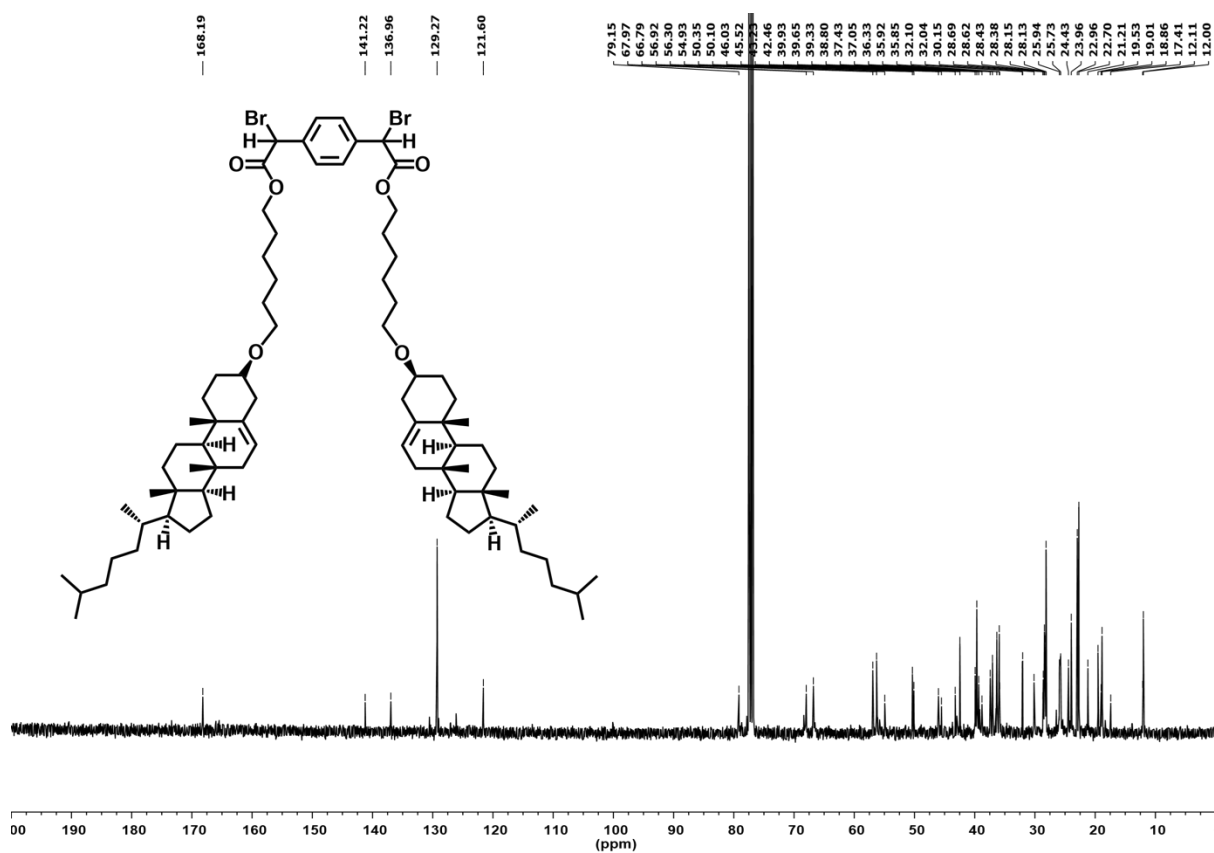
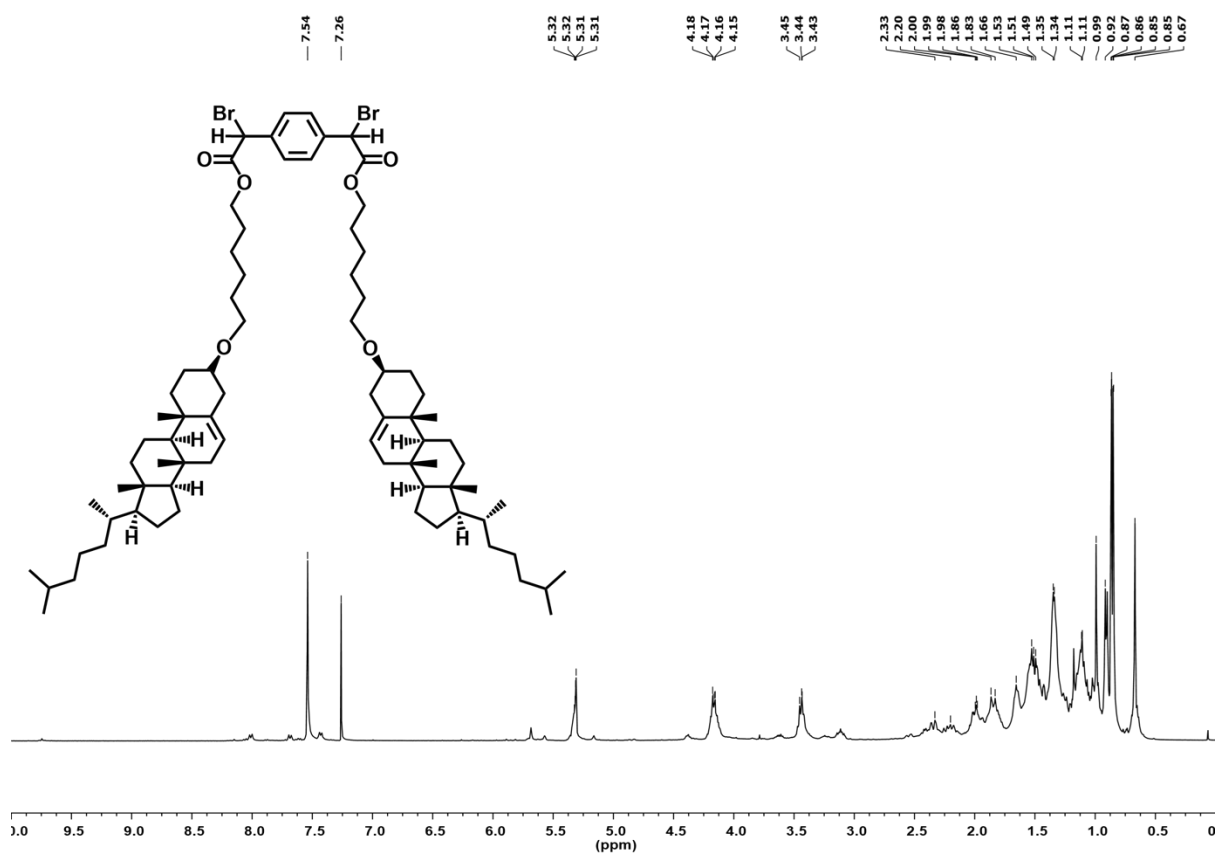


Figure S27. ^{13}C NMR spectrum recorded for **2g** in CDCl_3 .



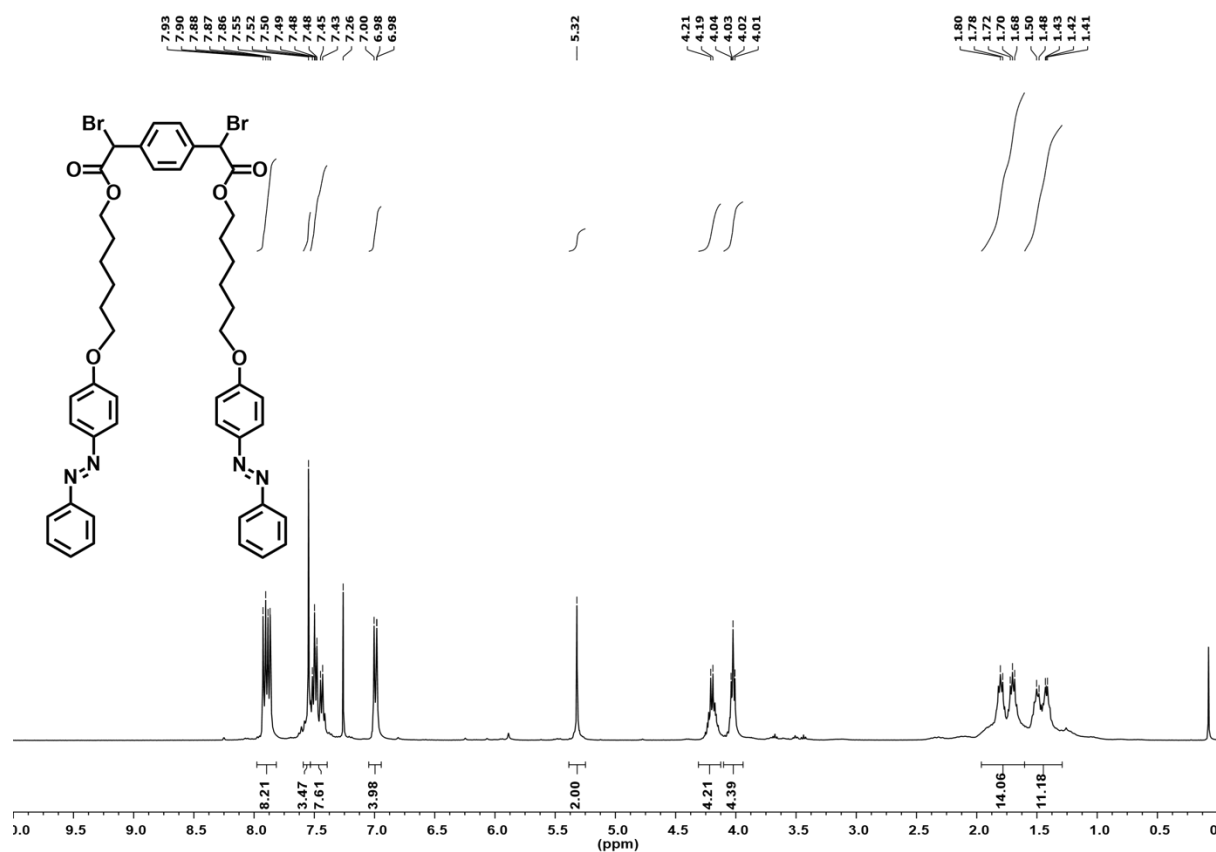


Figure S30. ¹H NMR spectrum recorded for **2i** in CDCl₃.

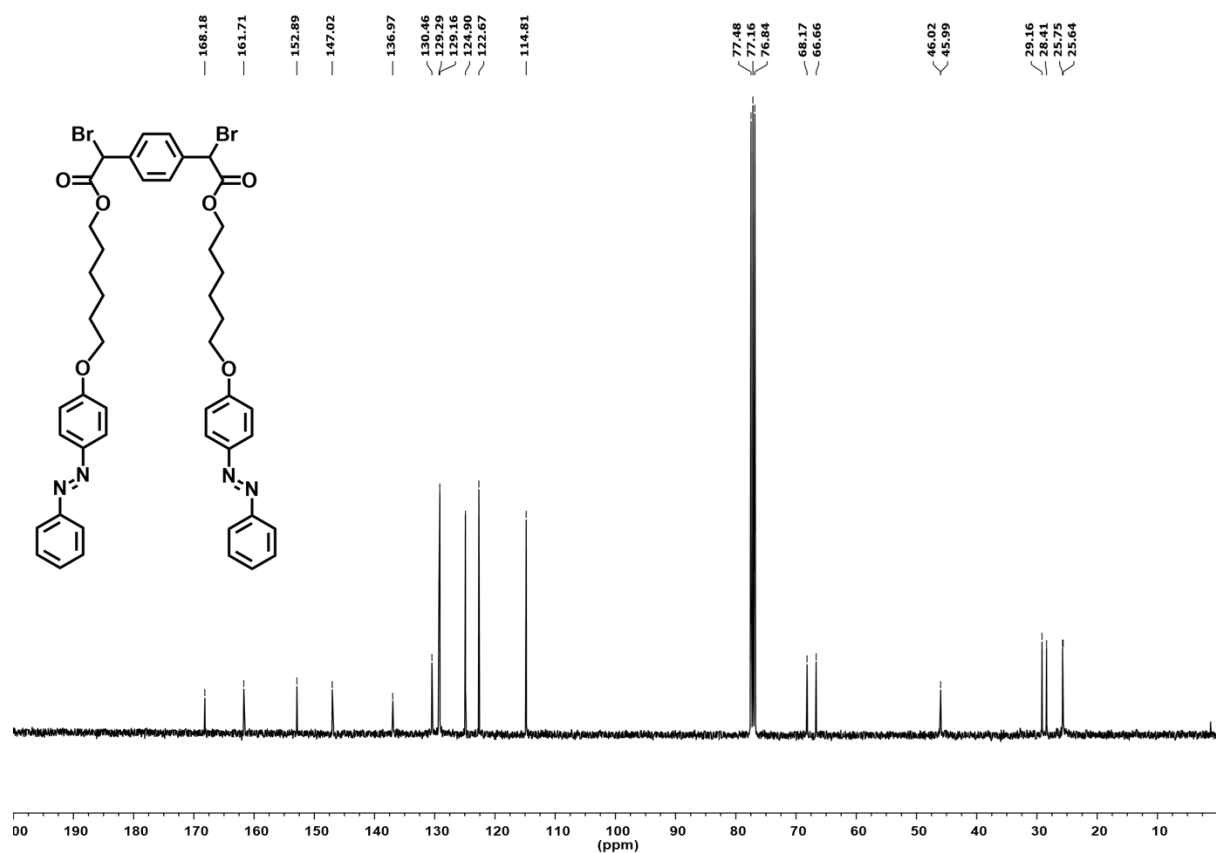


Figure S31. ¹³C NMR spectrum recorded for **2i** in CDCl₃.

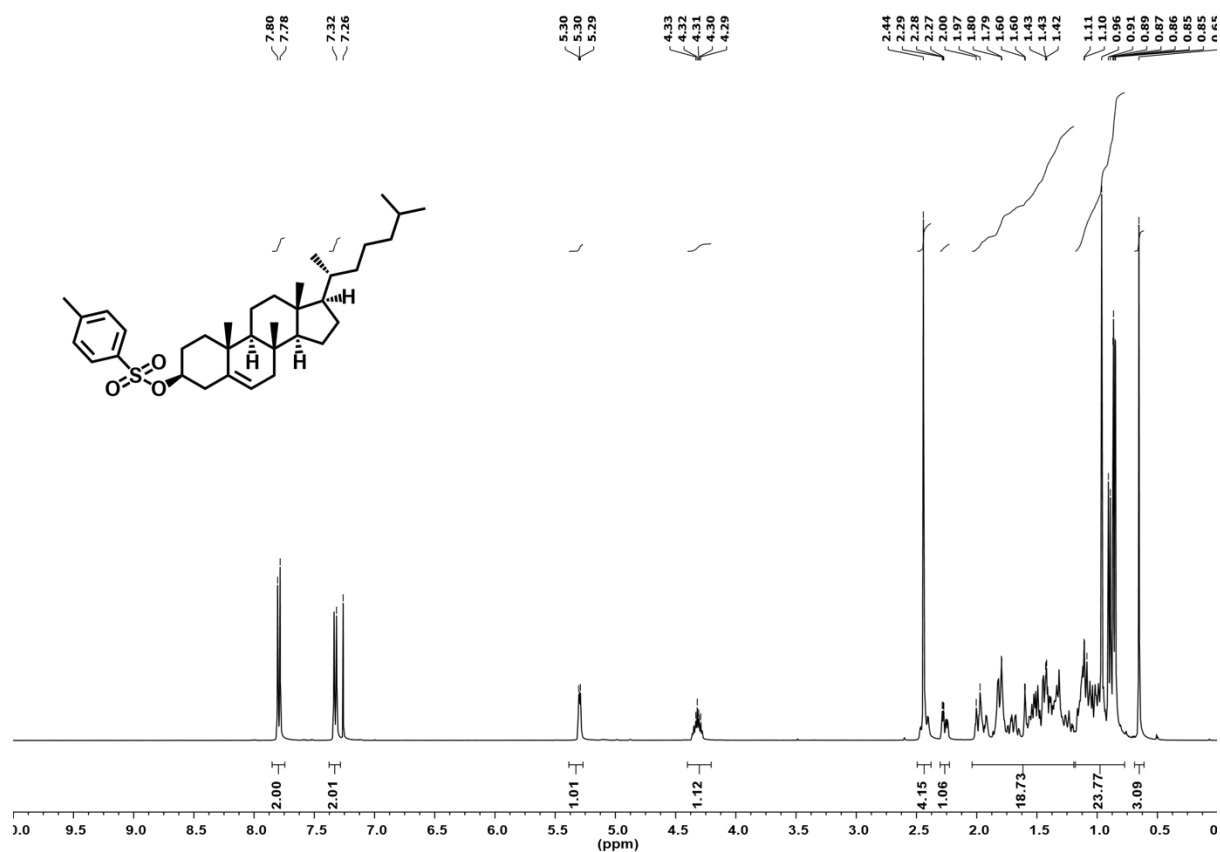


Figure S32. ^1H NMR spectrum recorded for **3** in CDCl_3 .

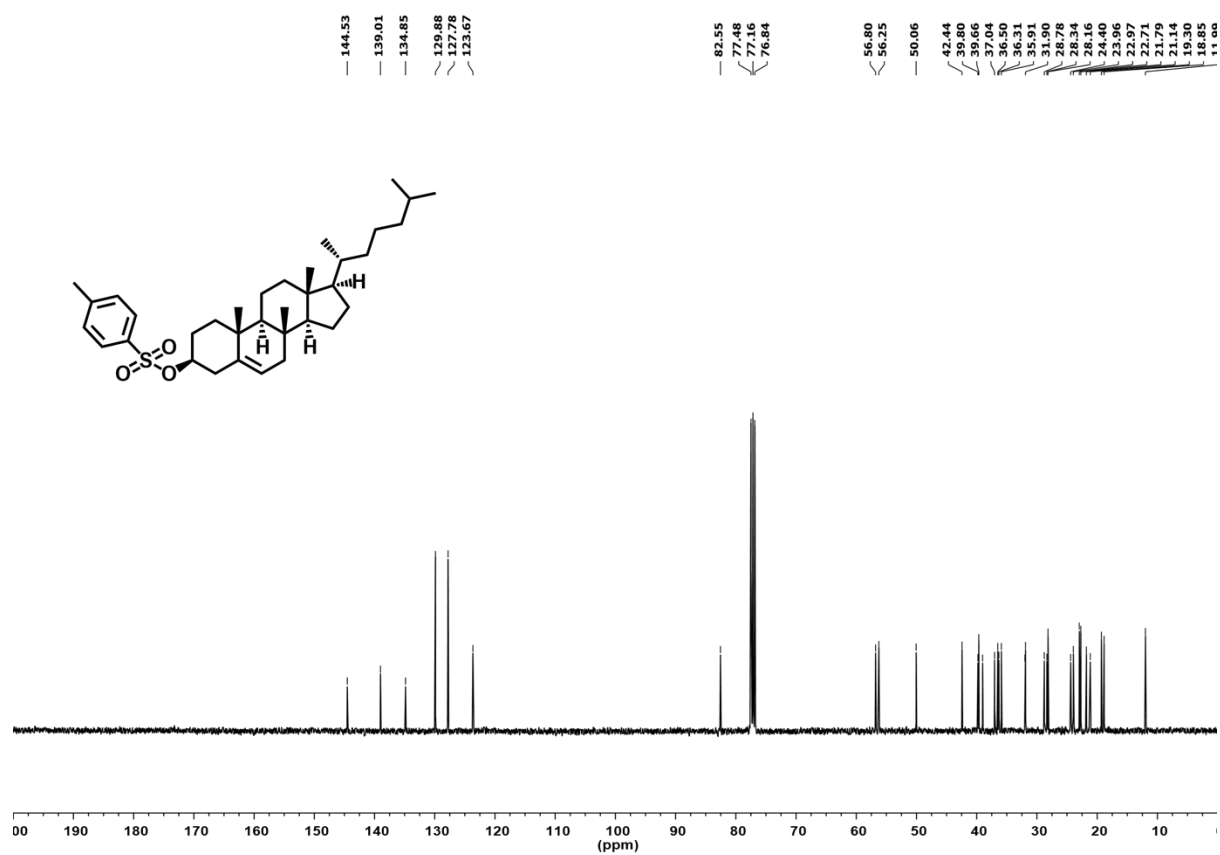


Figure S33. ^{13}C NMR spectrum recorded for **3** in CDCl_3 .

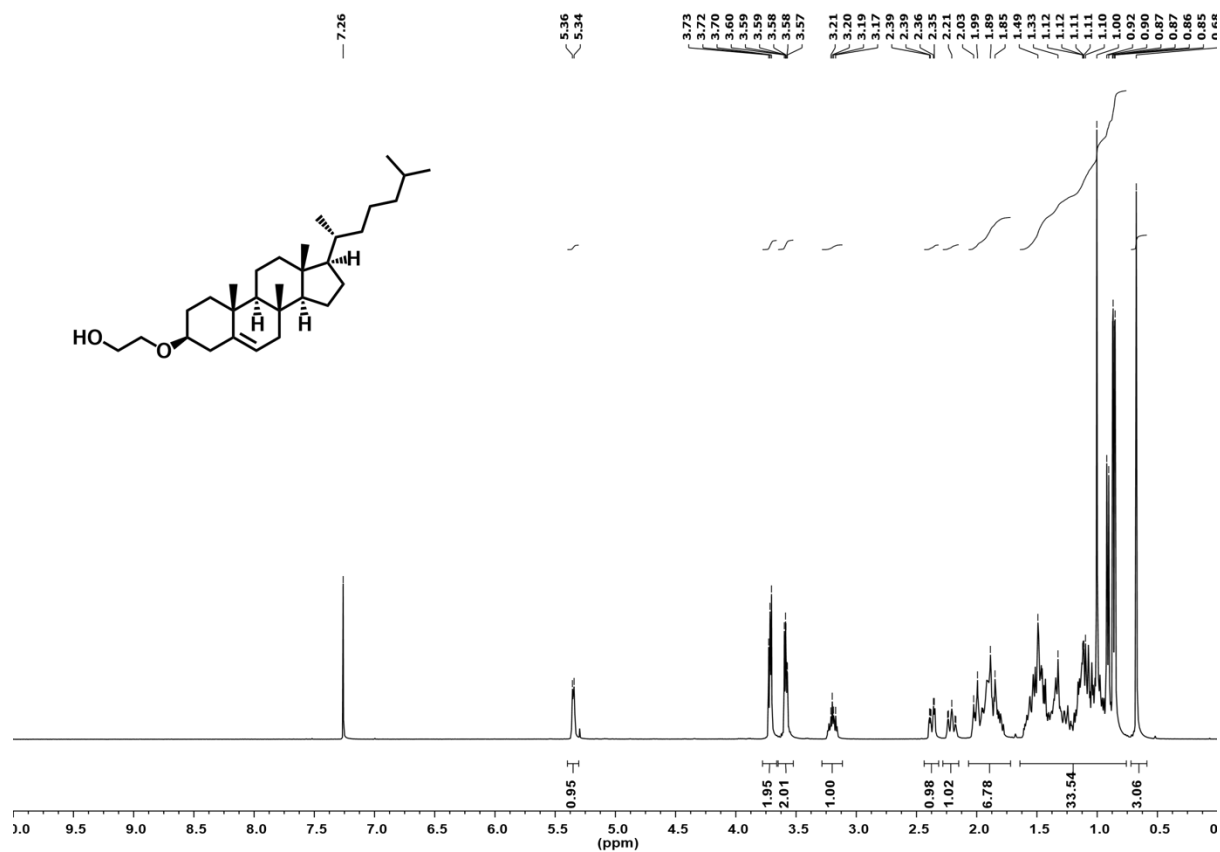


Figure S34. ¹H NMR spectrum recorded for **4a** in CDCl₃.

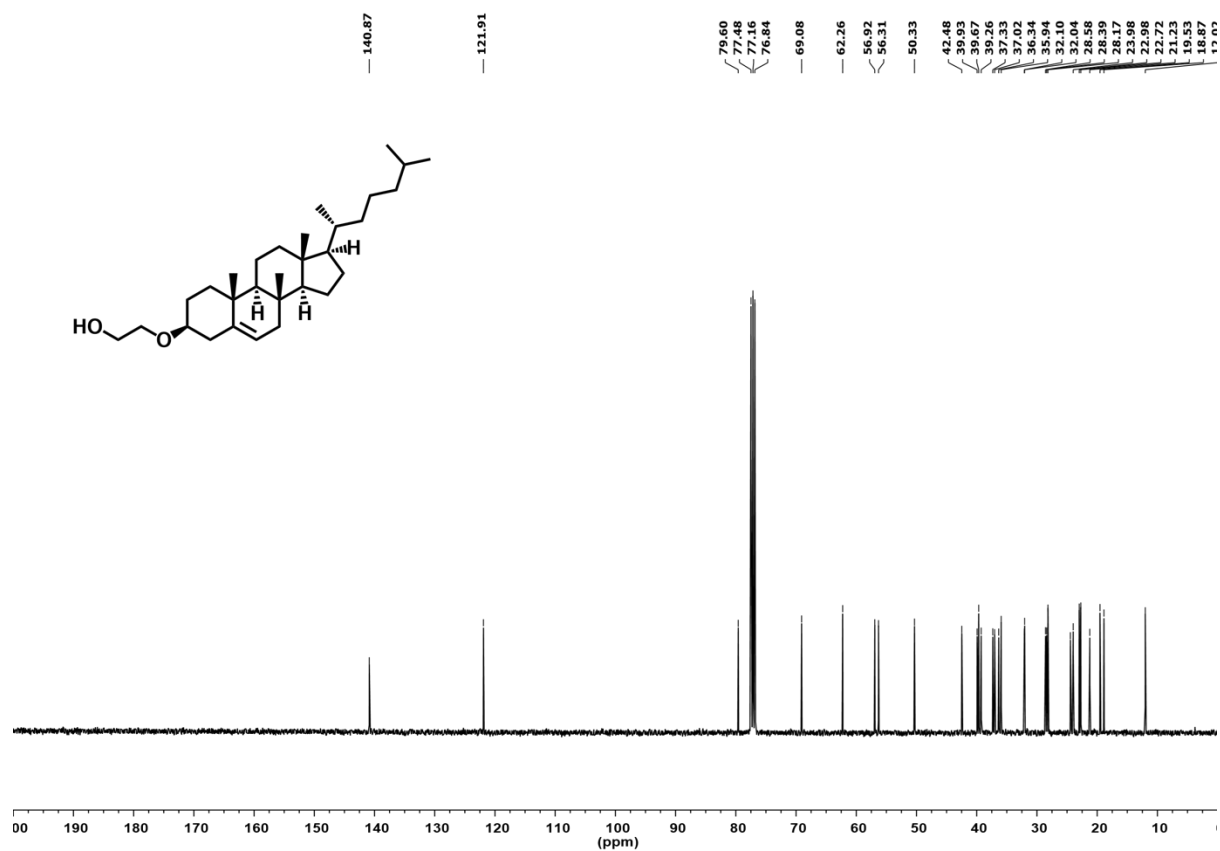


Figure S35. ¹³C NMR spectrum recorded for **4a** in CDCl₃.

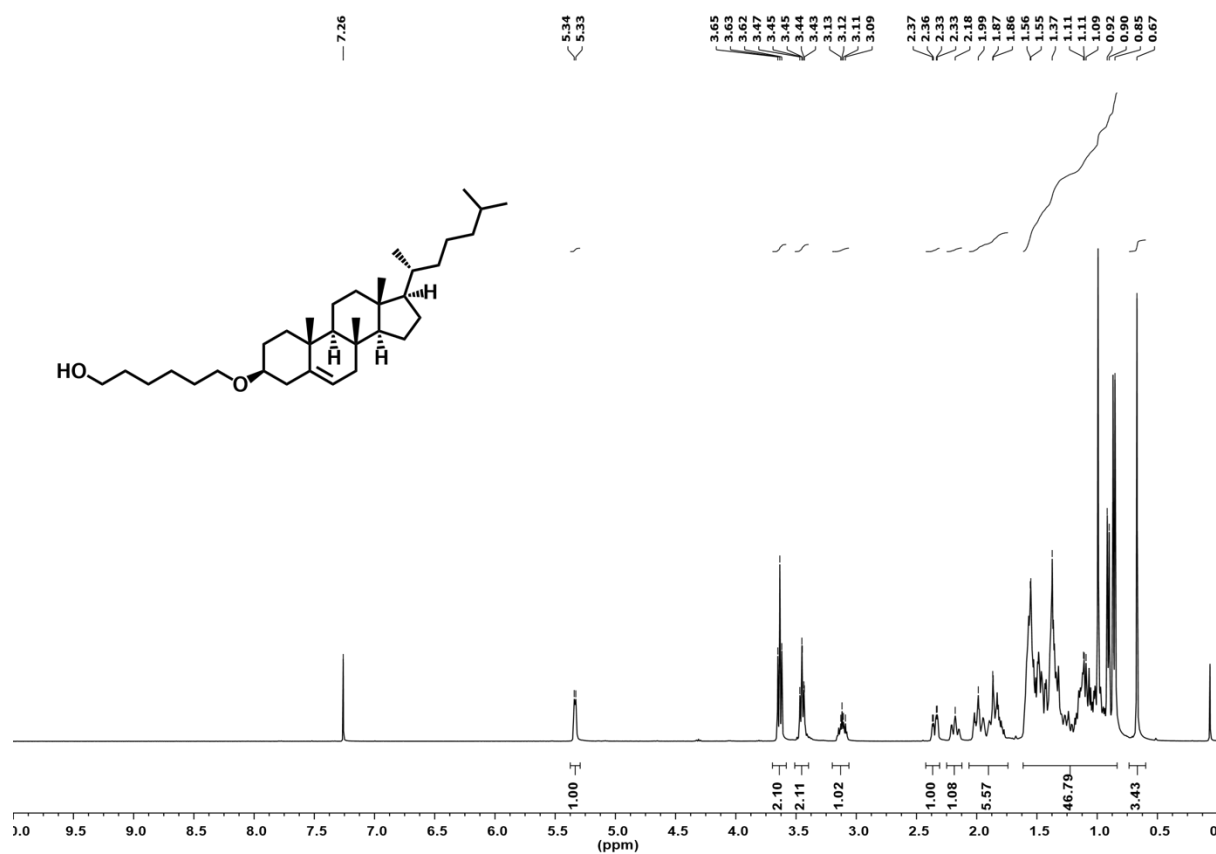


Figure S36. ^1H NMR spectrum recorded for **4b** in CDCl_3 .

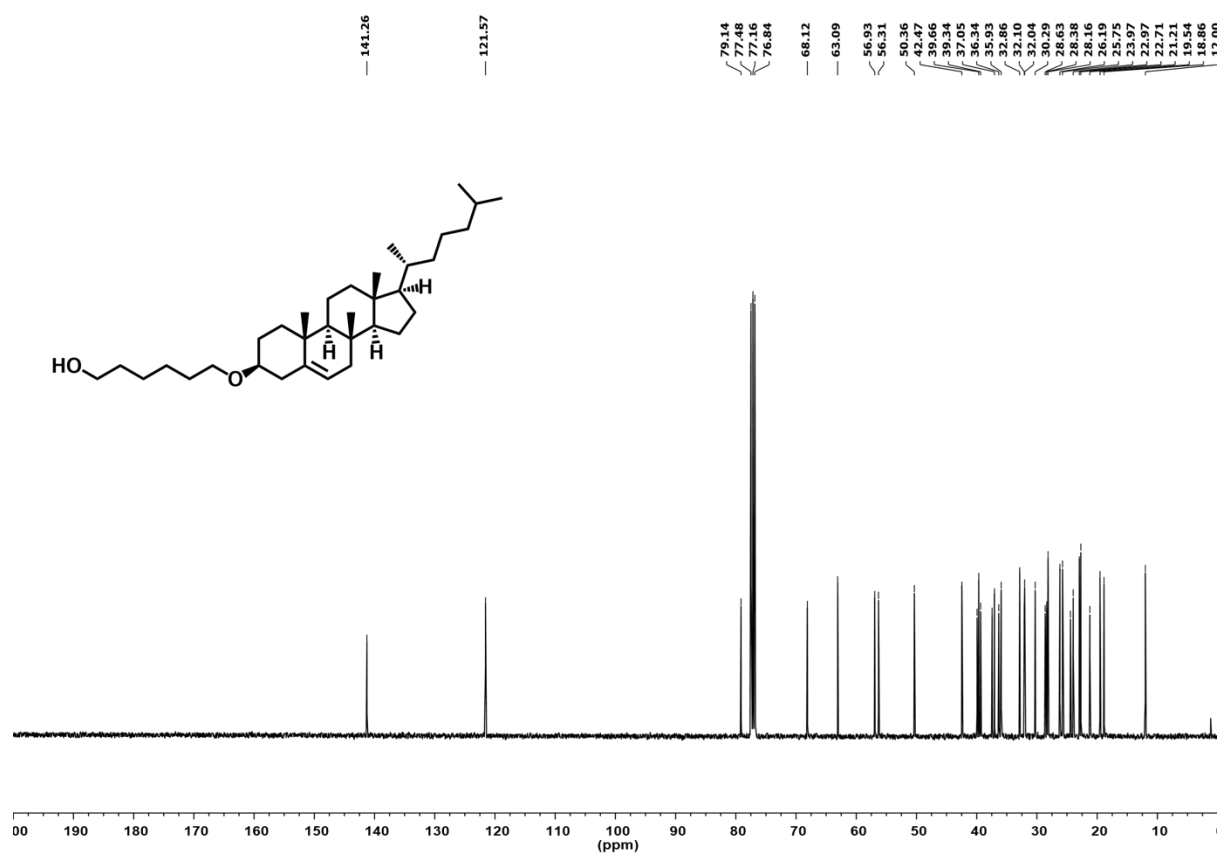


Figure S37. ^{13}C NMR spectrum recorded for **4b** in CDCl_3 .

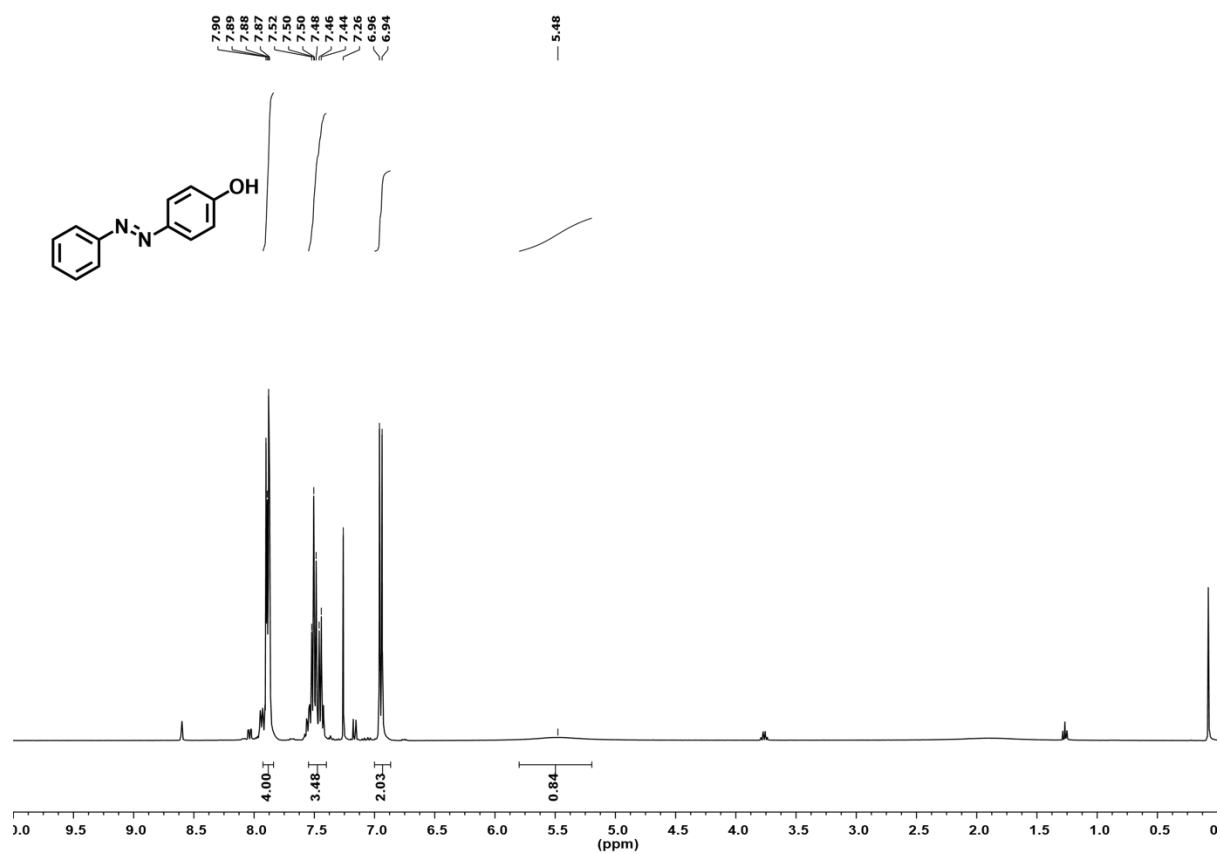


Figure S38. ¹H NMR spectrum recorded for **5** in CDCl₃.

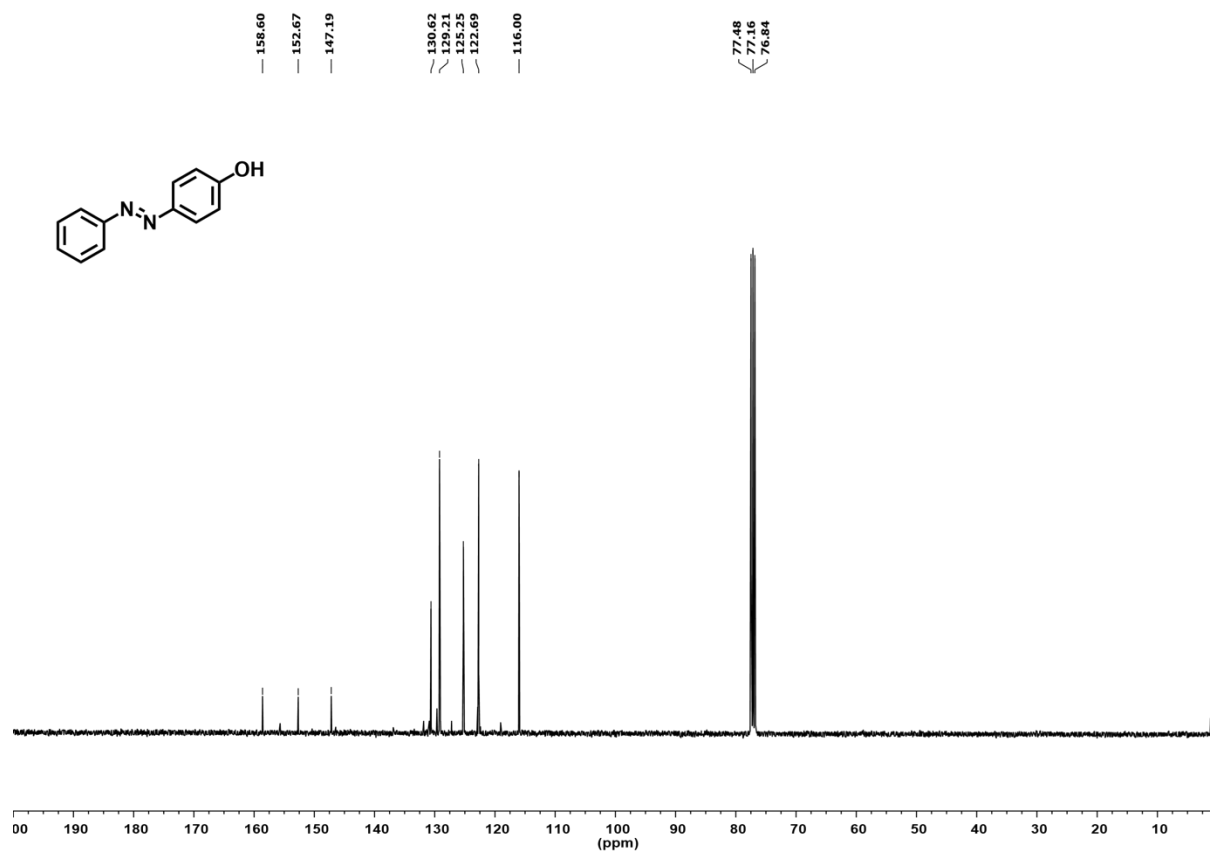


Figure S39. ¹³C NMR spectrum recorded for **5** in CDCl₃.

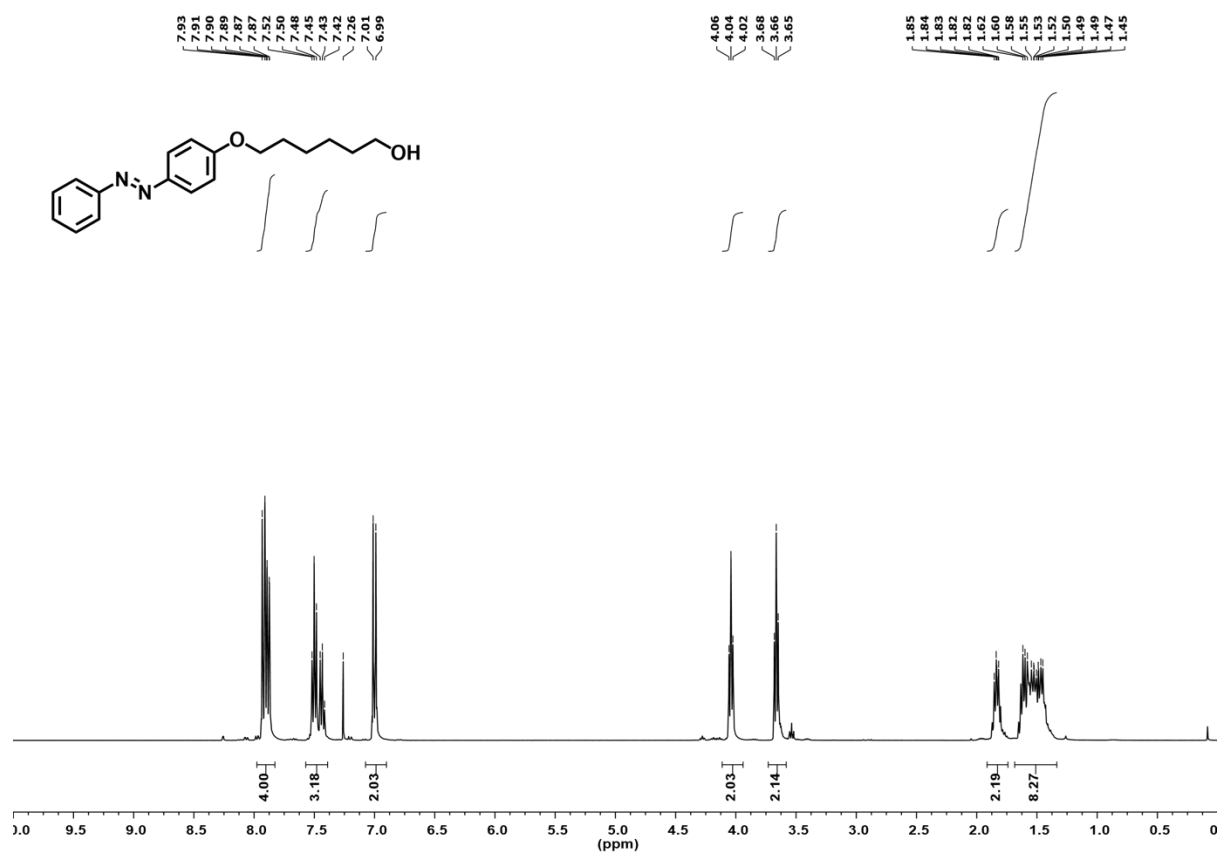


Figure S40. ¹H NMR spectrum recorded for **6** in CDCl₃.

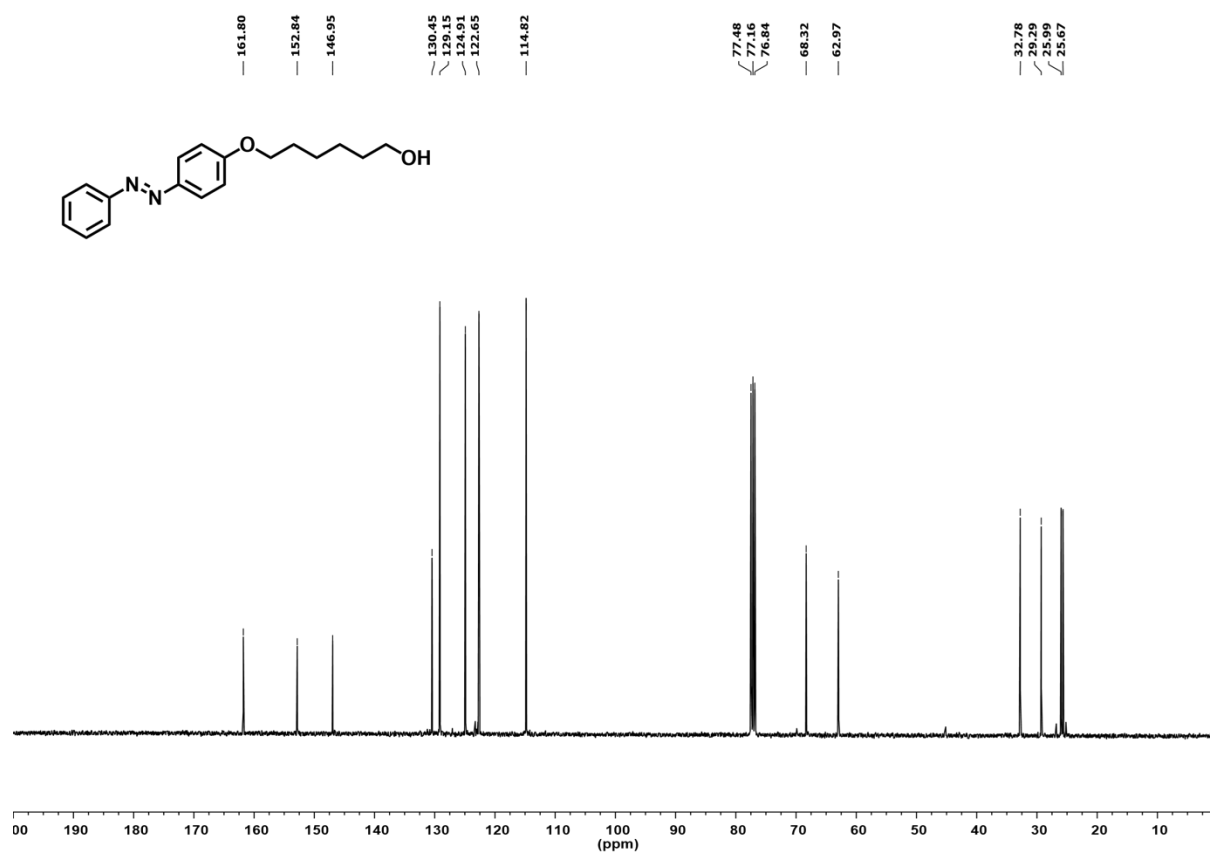


Figure S41. ¹³C NMR spectrum recorded for **6** in CDCl₃.

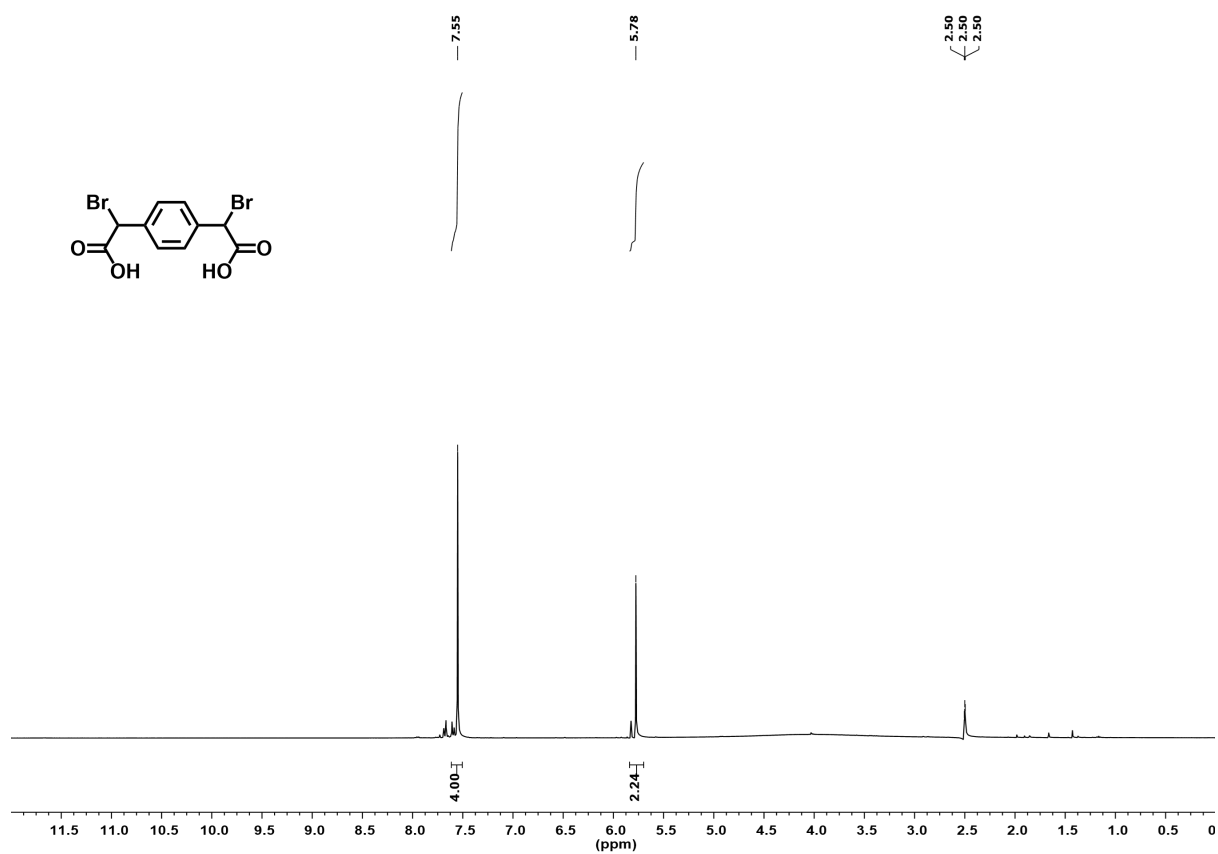


Figure S42. ¹H NMR spectrum recorded for 7 in DMSO-*d*₆.

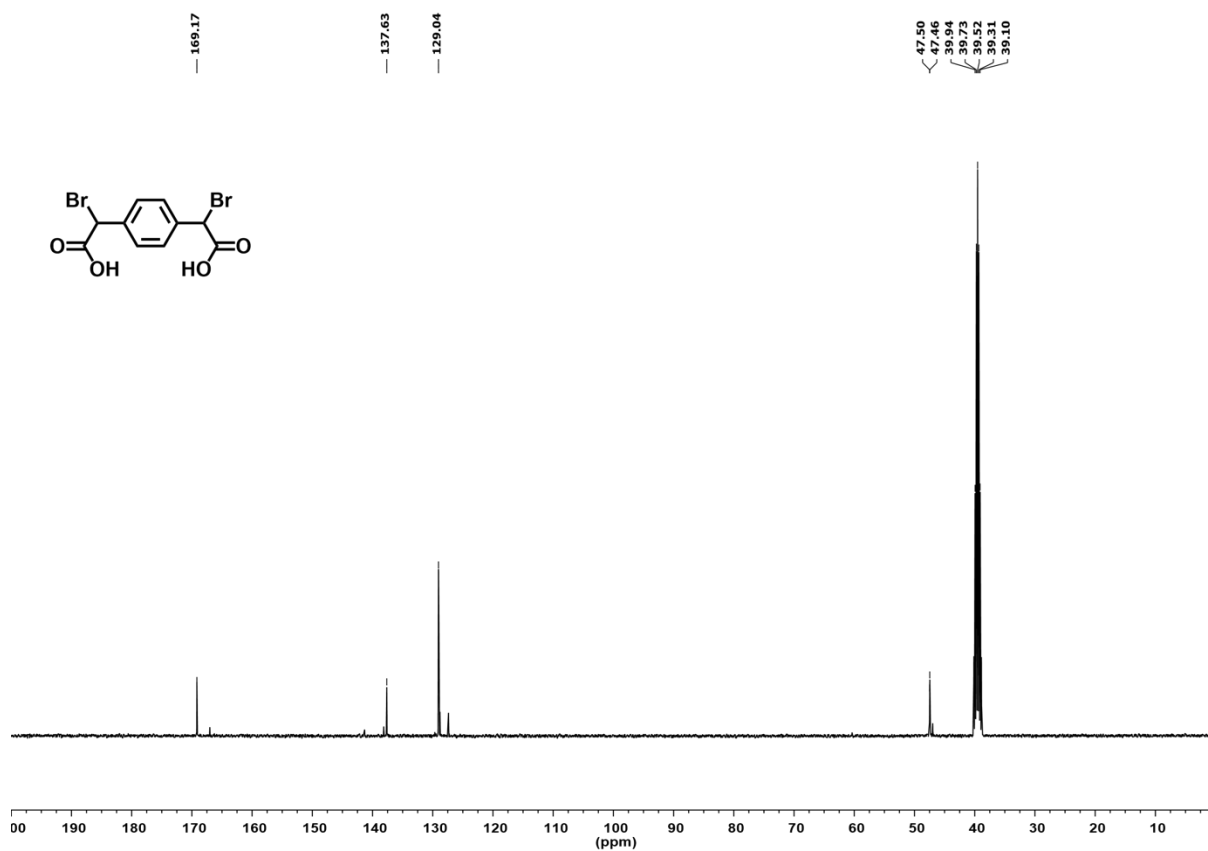


Figure S43. ¹³C NMR spectrum recorded for 7 in DMSO-*d*₆.

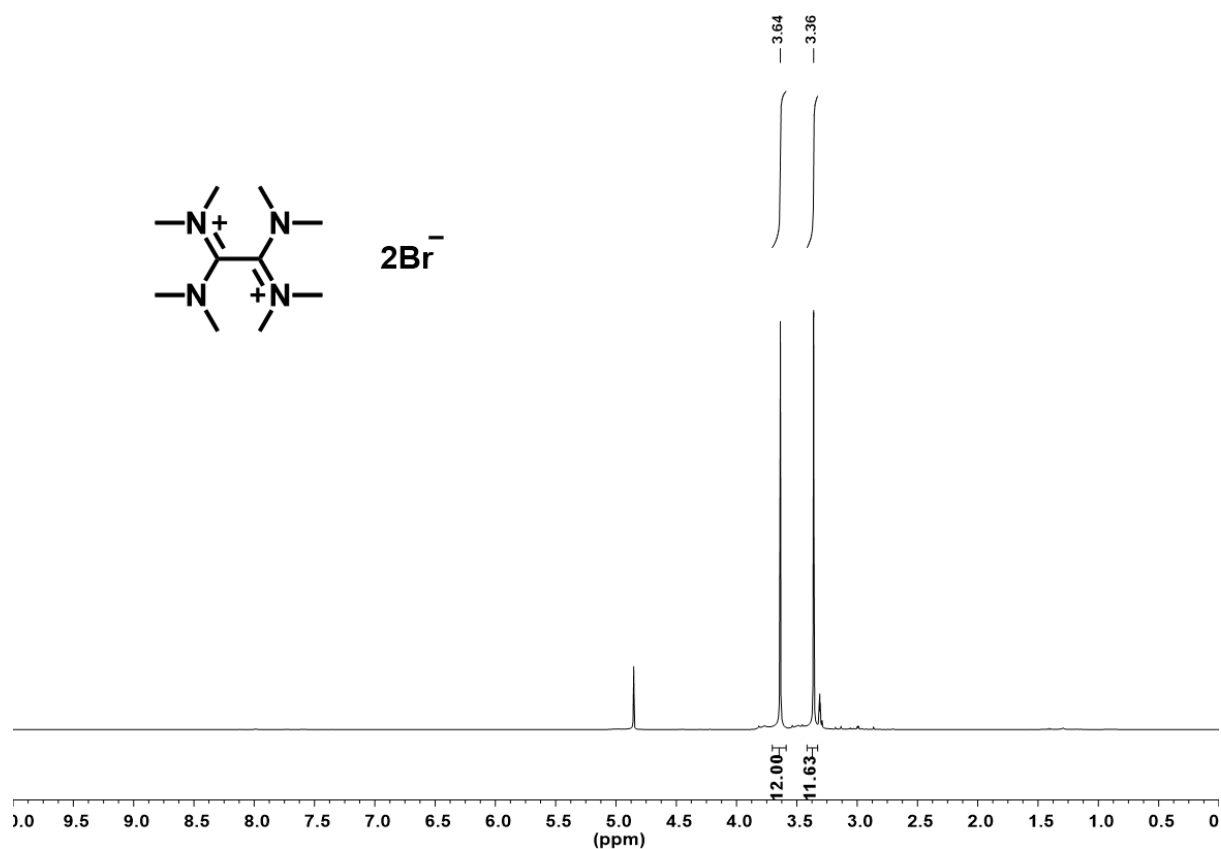


Figure S44. ¹H NMR spectrum recorded for TDAE⁺Br⁻ salts in CD₃OD.

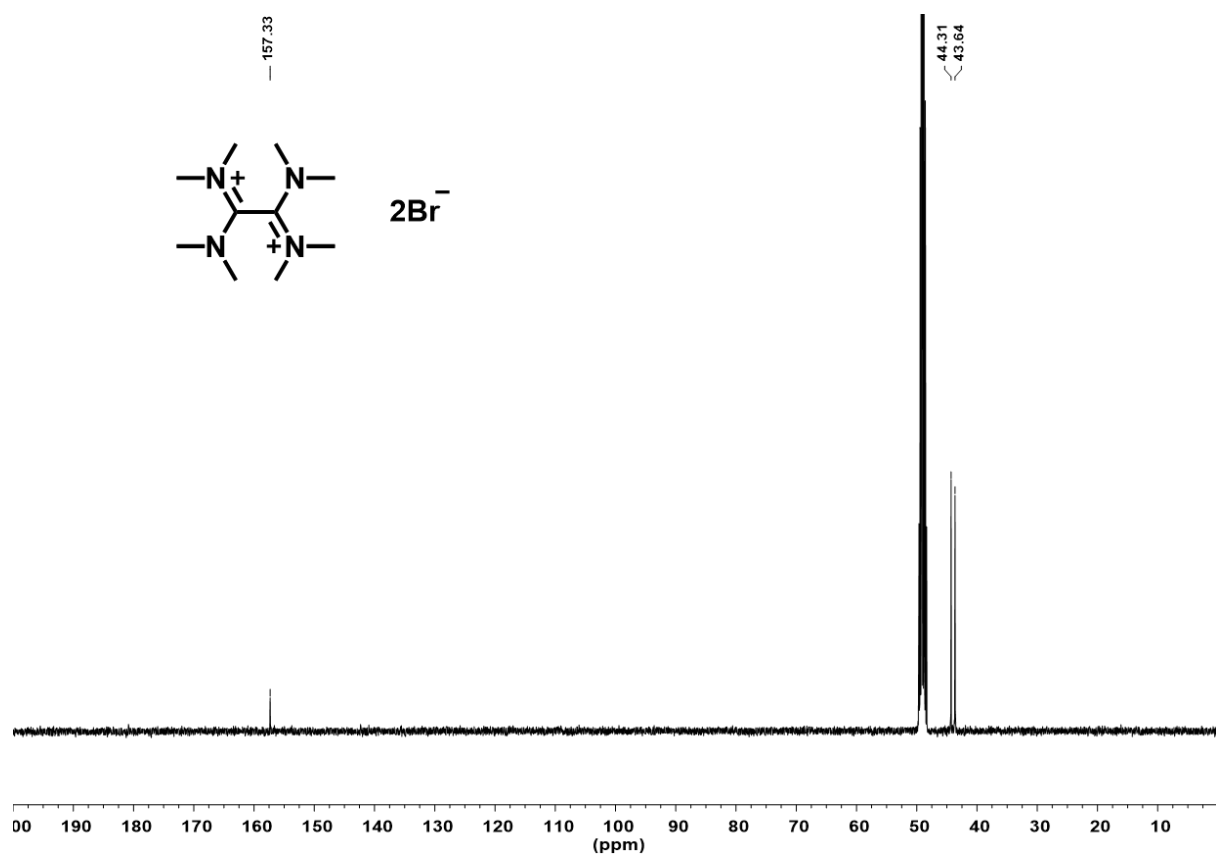


Figure S45. ¹³C NMR spectrum recorded for TDAE⁺Br⁻ salts in CD₃OD.

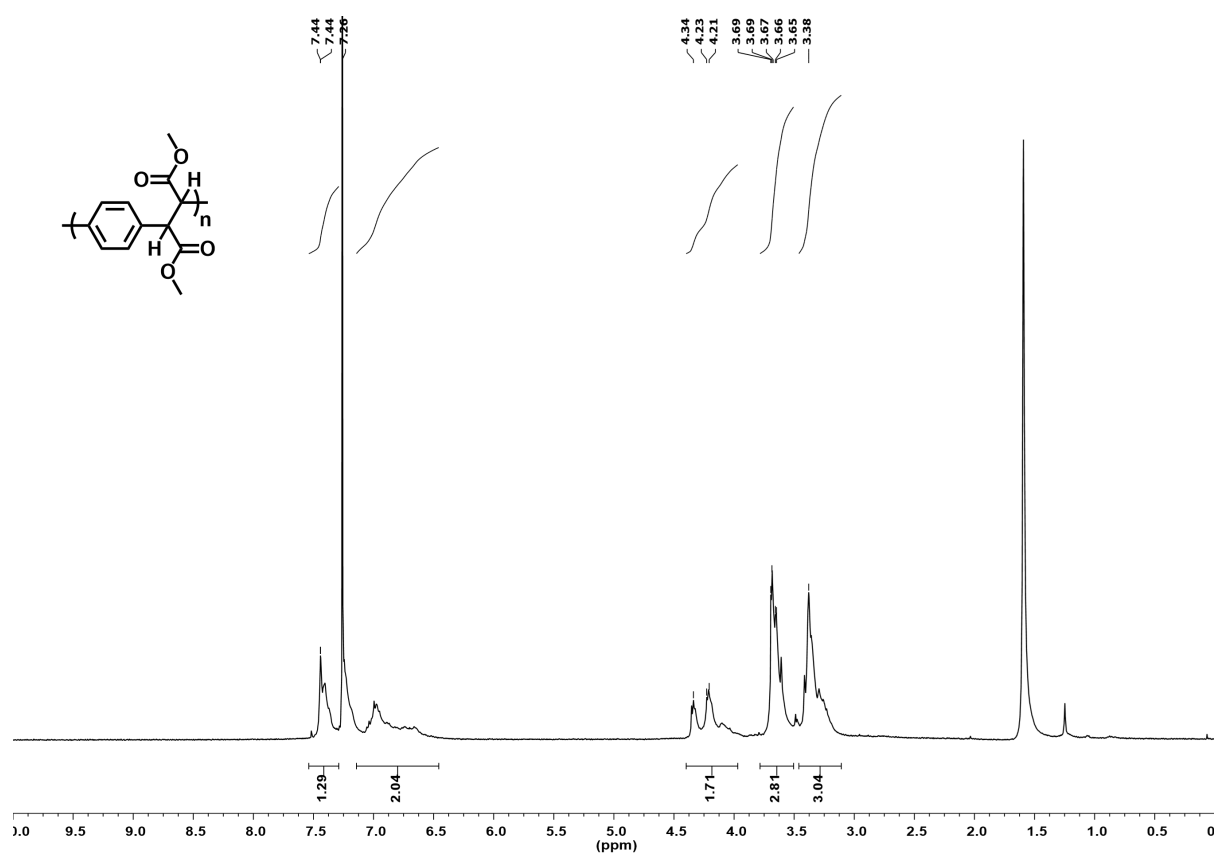


Figure S46. ^1H NMR spectrum recorded for **PPX-2a** in CDCl₃.

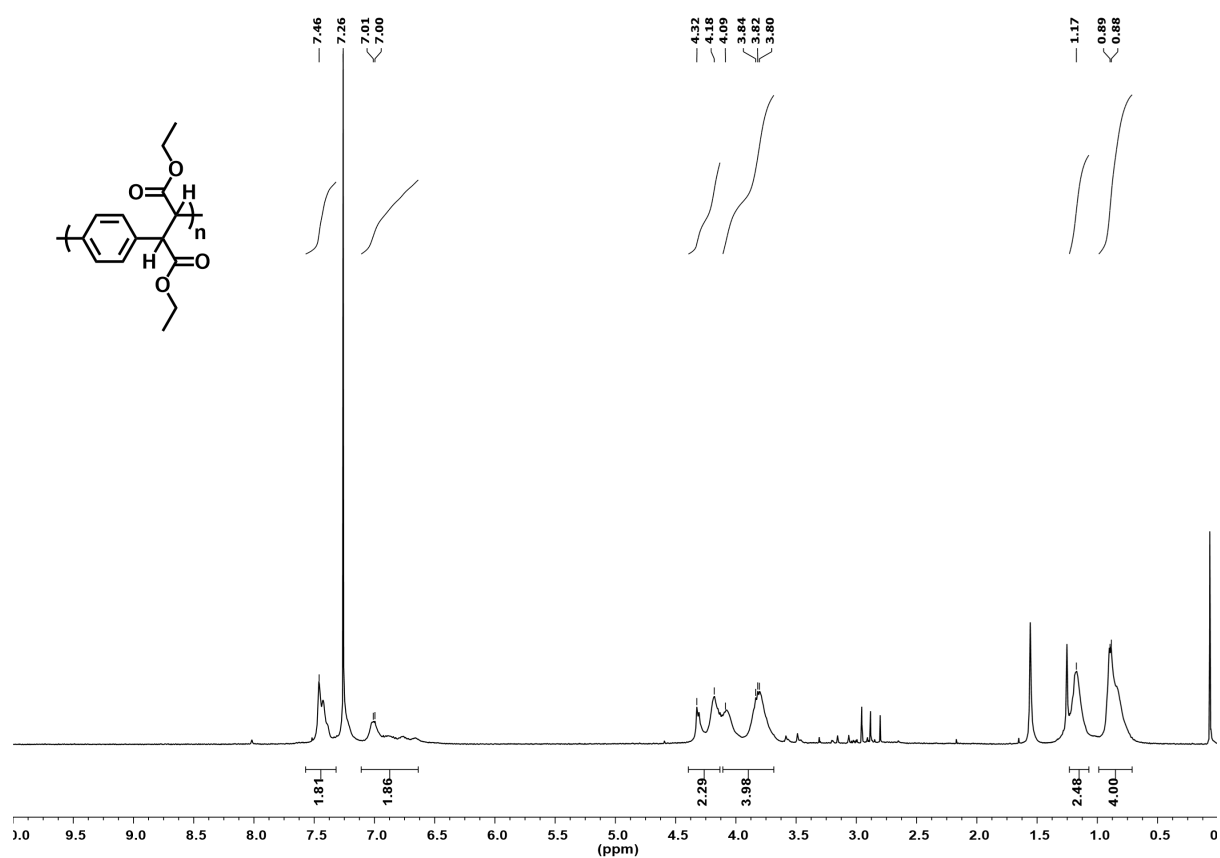


Figure S47. ^1H NMR spectrum recorded for **PPX-2b** in CDCl₃.

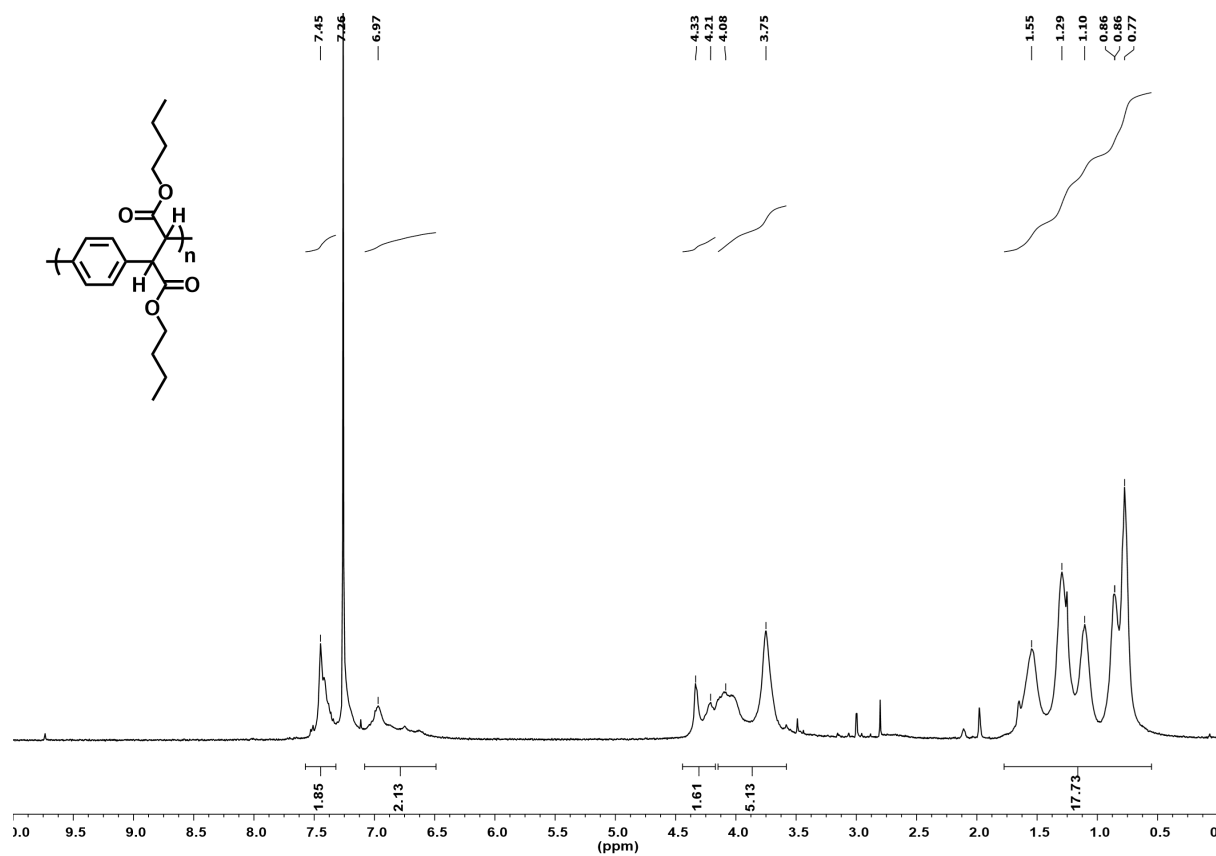


Figure S48. ^1H NMR spectrum recorded for **PPX-2c** in CDCl₃.

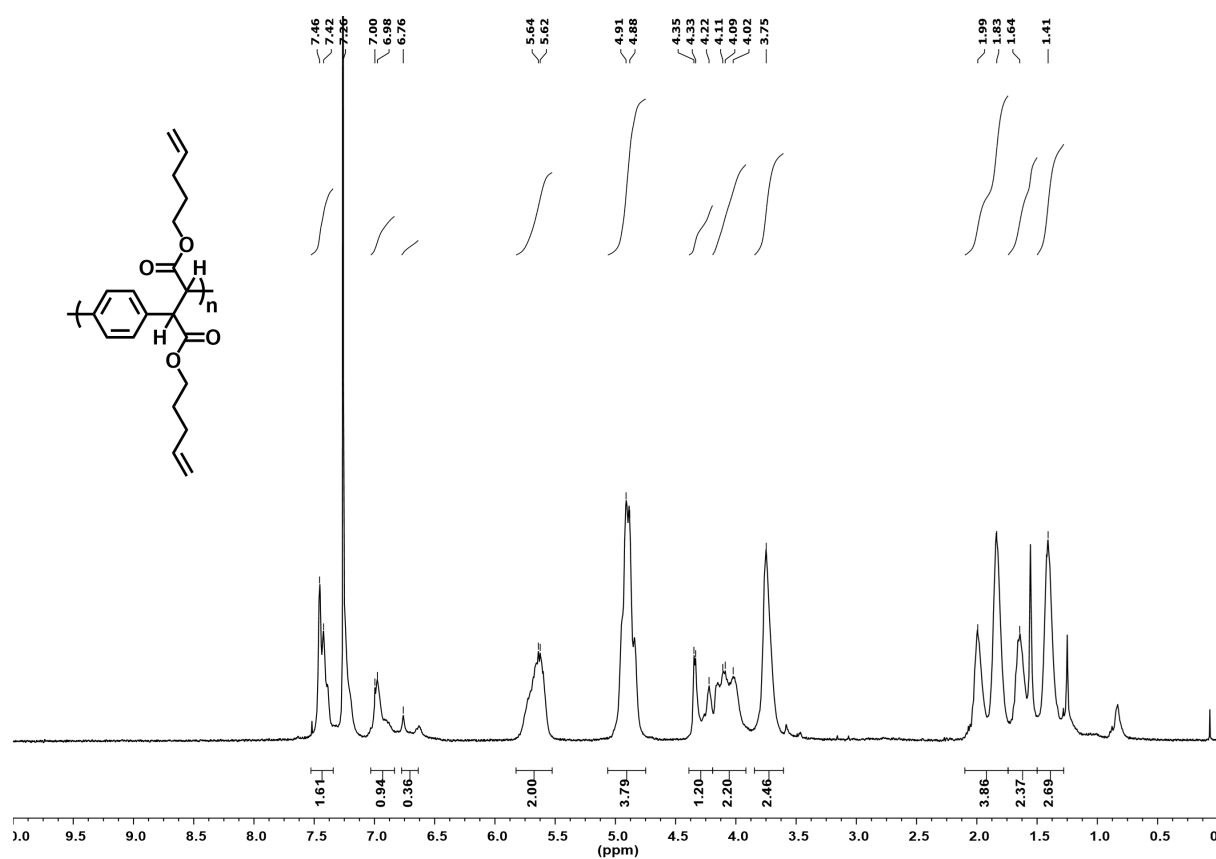


Figure S49. ^1H NMR spectrum recorded for **PPX-2d** in CDCl₃.

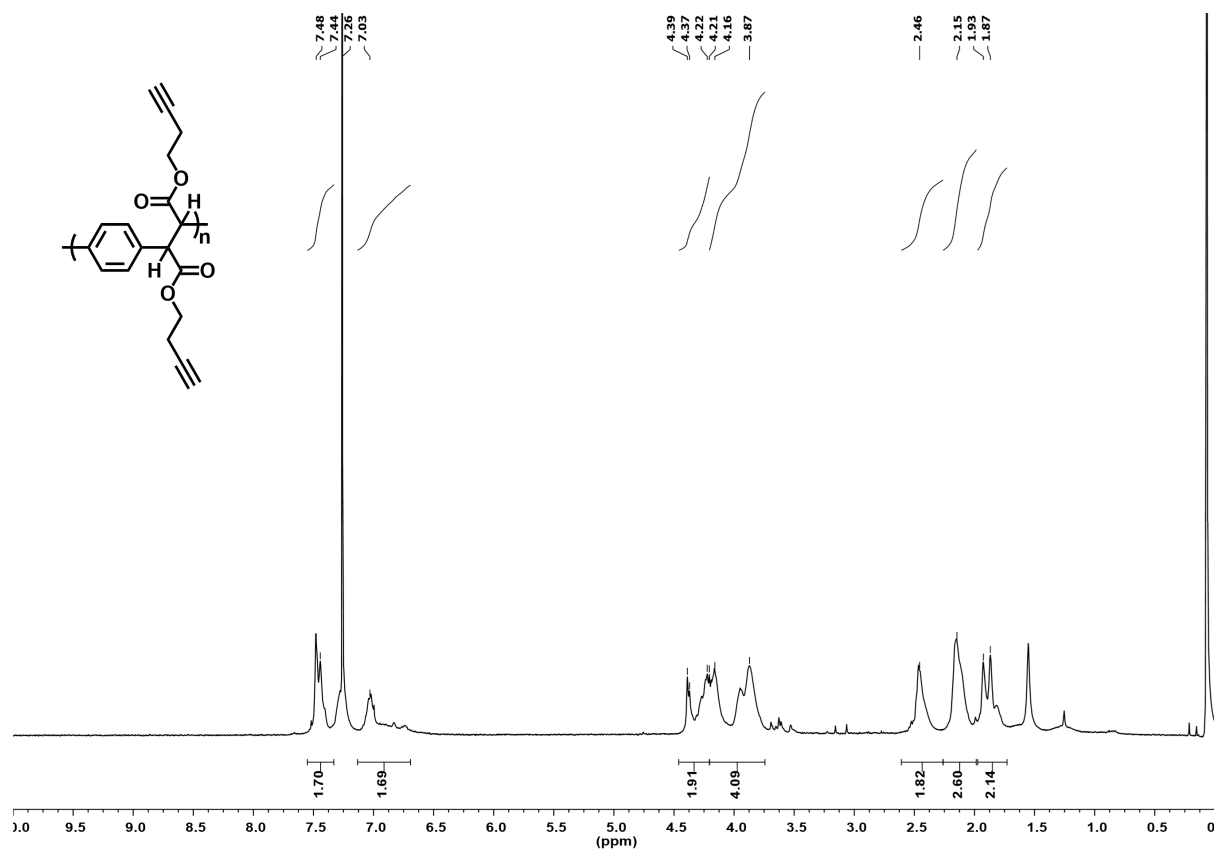


Figure S50. ¹H NMR spectrum recorded for **PPX-2e** in CDCl₃.

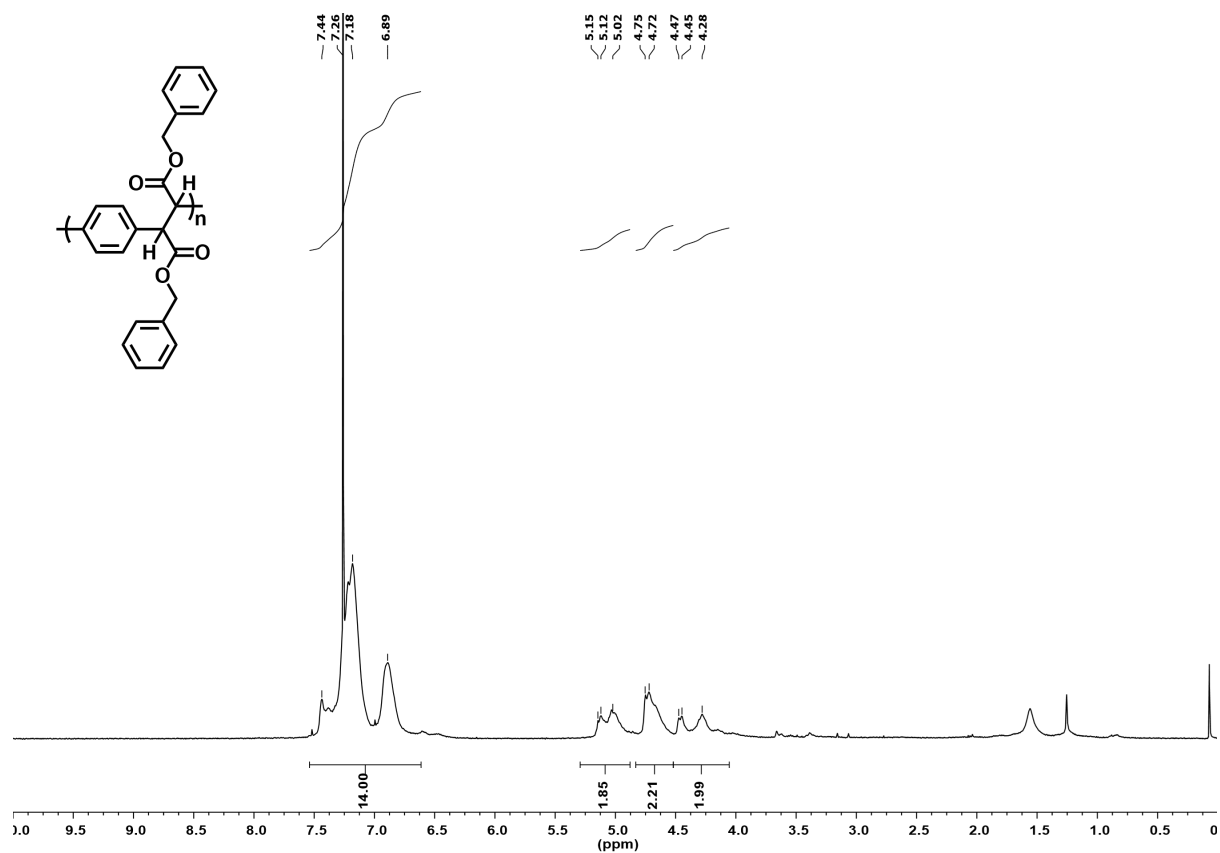


Figure S51. ¹H NMR spectrum recorded for **PPX-2f** in CDCl₃.

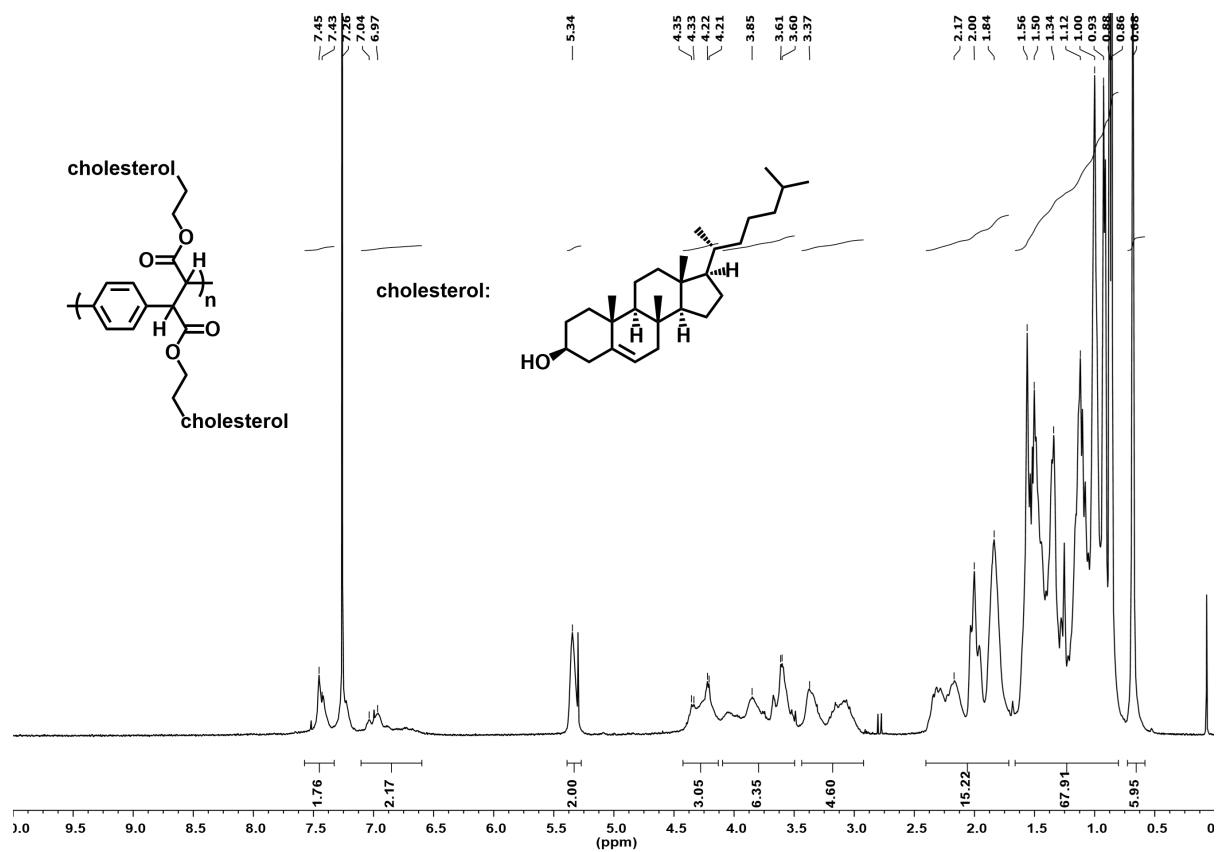


Figure S52. ^1H NMR spectrum recorded for **PPX-2g** in CDCl_3 .

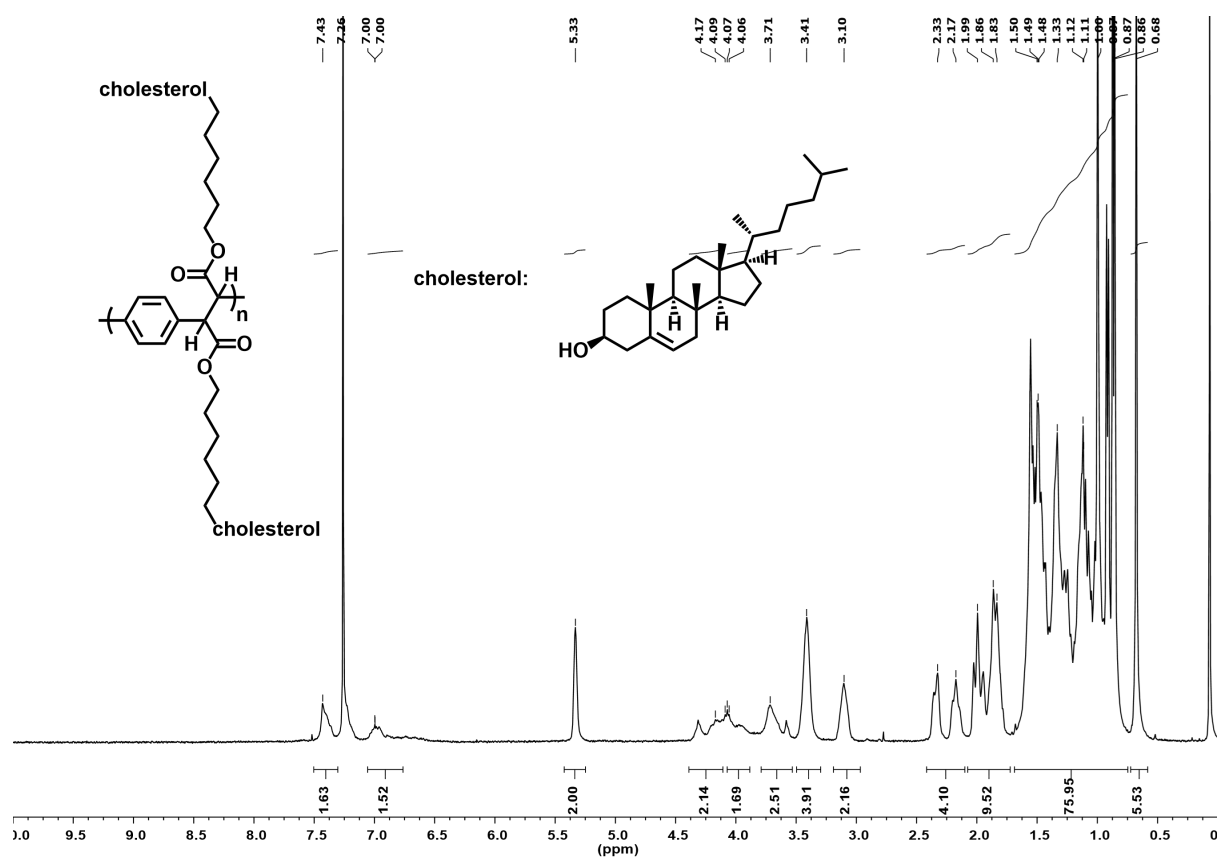


Figure S53. ^1H NMR spectrum recorded for **PPX-2h** in CDCl_3 .

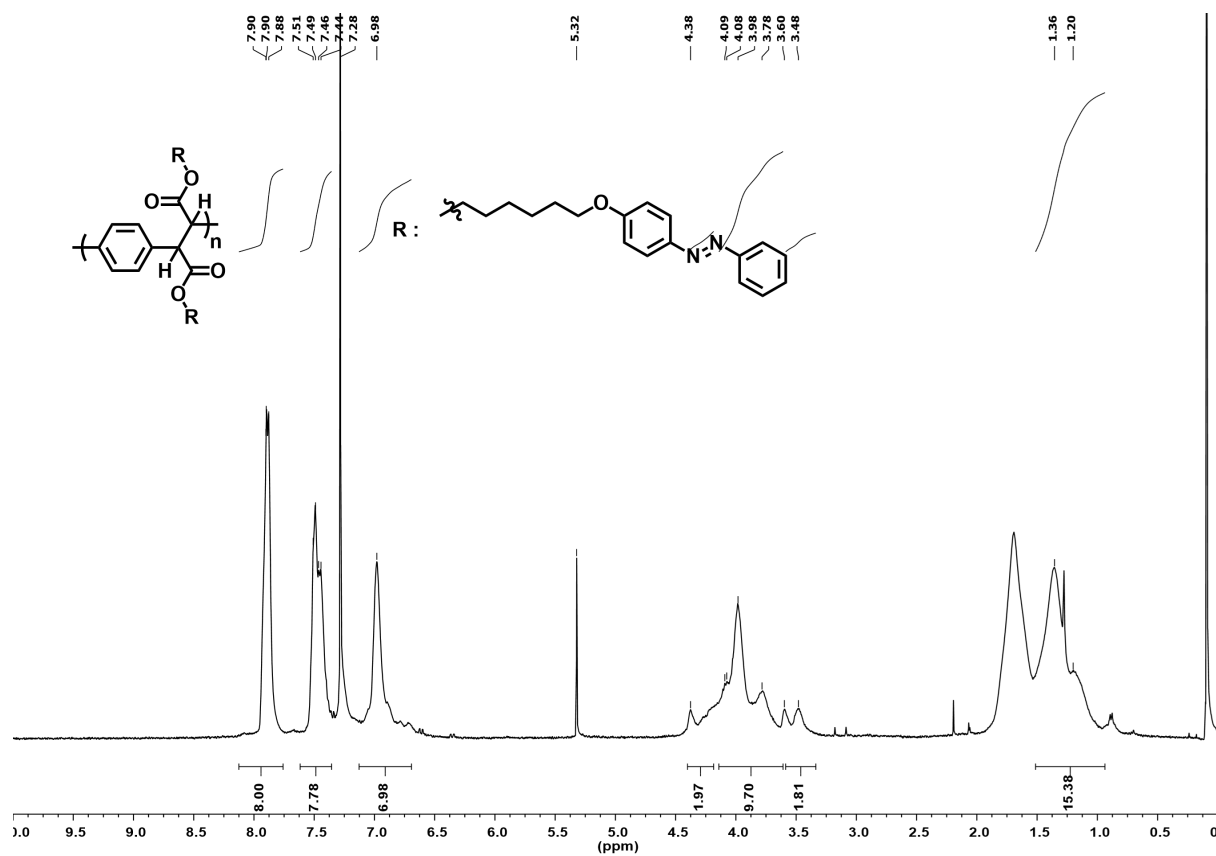


Figure S54. ^1H NMR spectrum recorded for **PPX-2i** in CDCl₃.

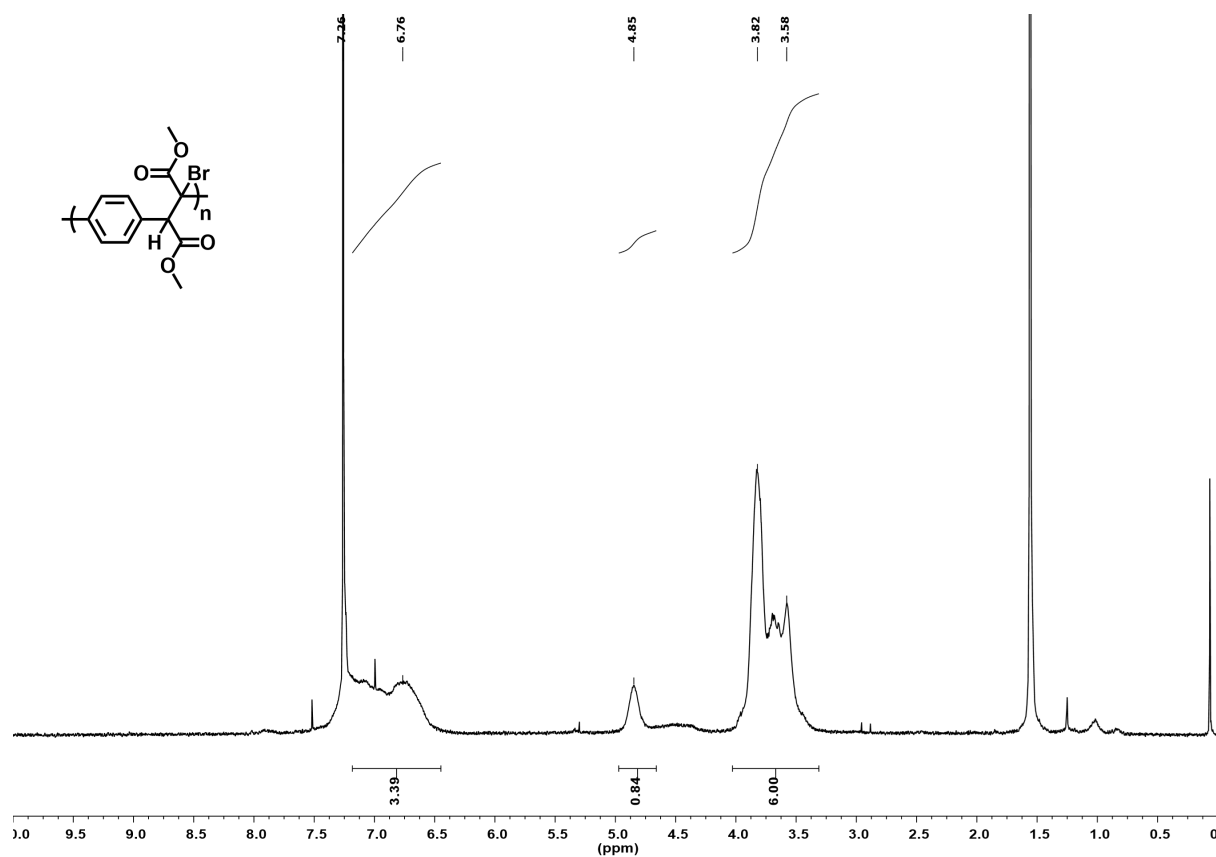


Figure S55. ^1H NMR spectrum recorded for **BrPPX-2a** in CDCl₃.

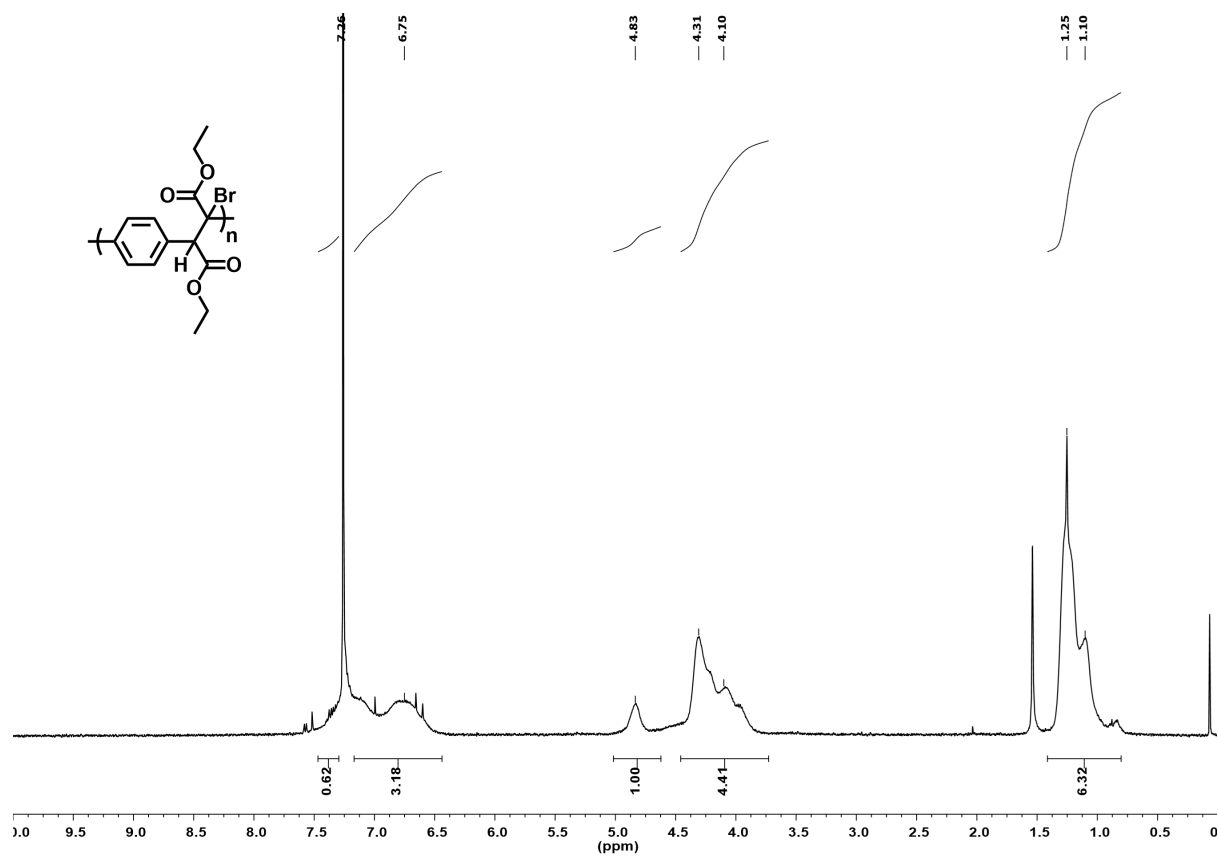


Figure S56. ^1H NMR spectrum recorded for **BrPPX-2b** in CDCl₃.

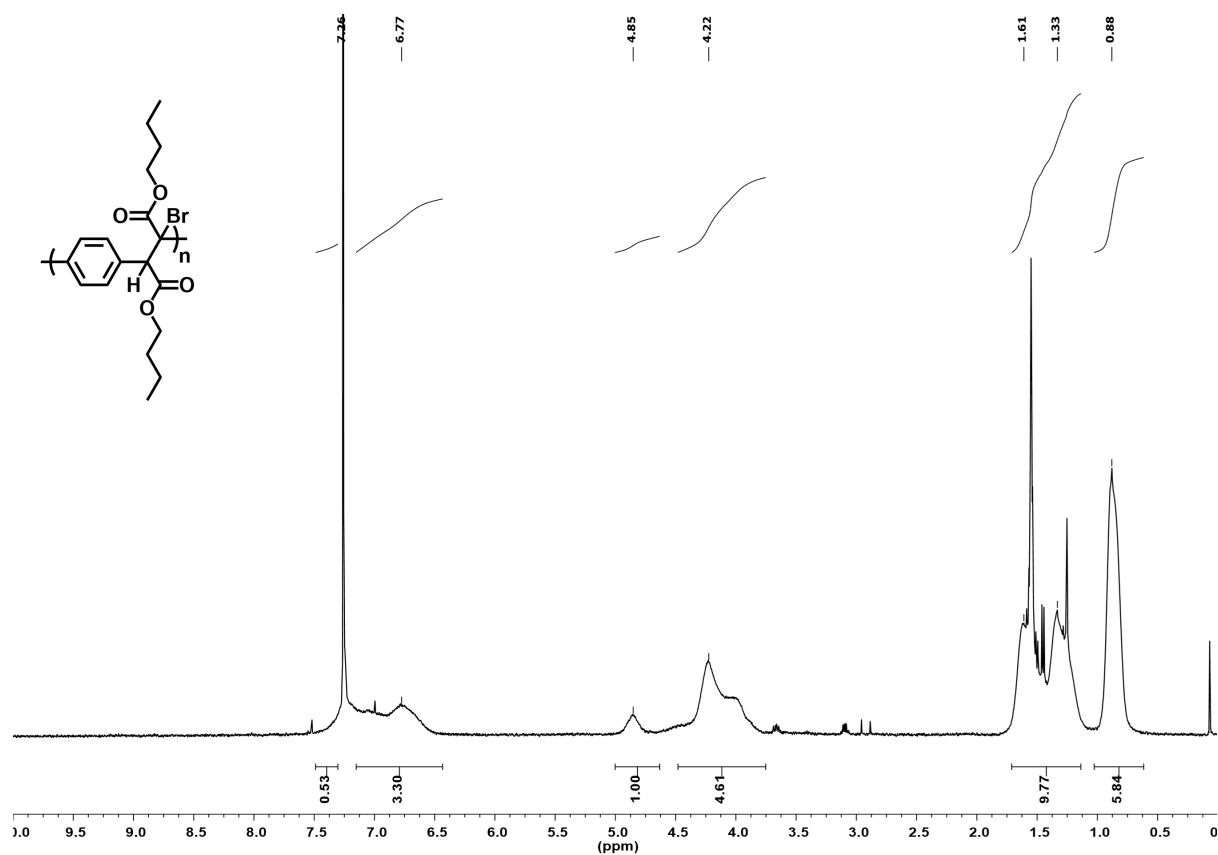


Figure S57. ^1H NMR spectrum recorded for **BrPPX-2c** in CDCl₃.

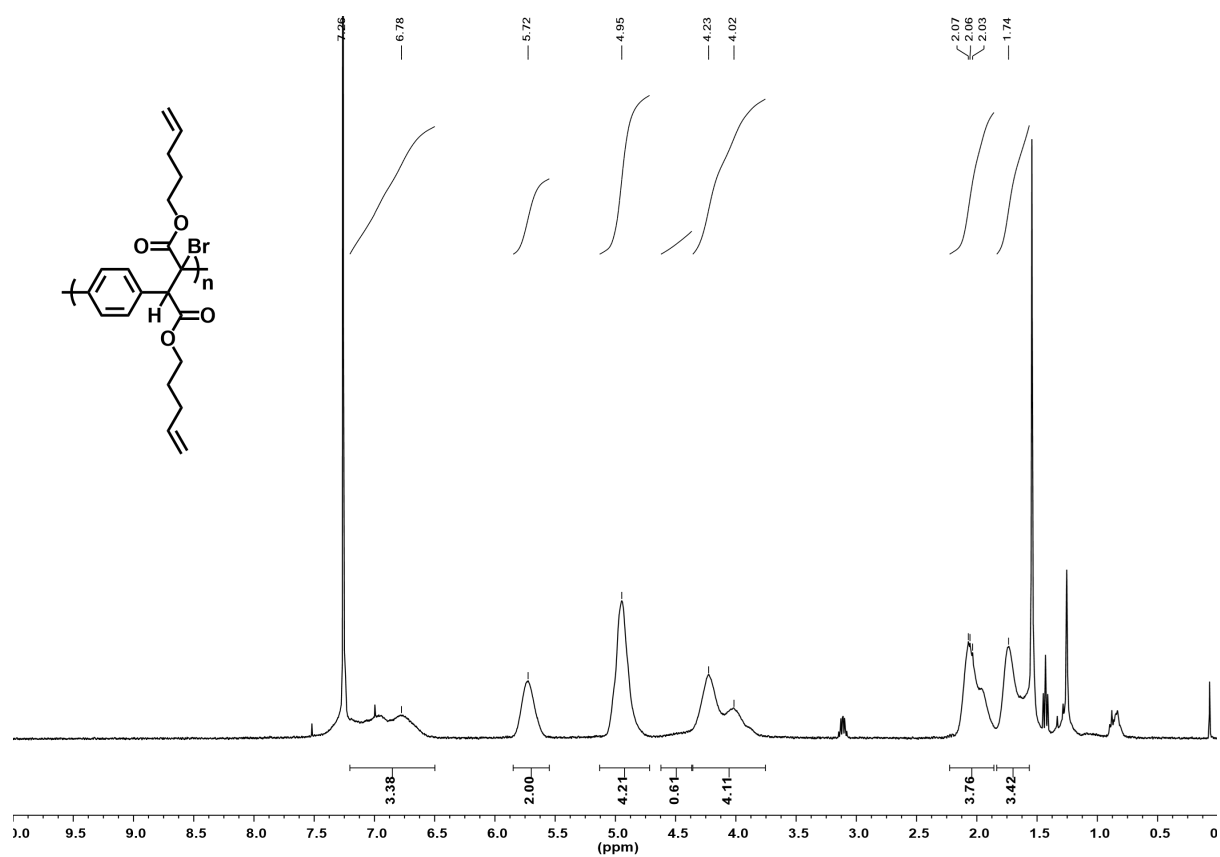


Figure S58. ^1H NMR spectrum recorded for **BrPPX-2d** in CDCl₃.

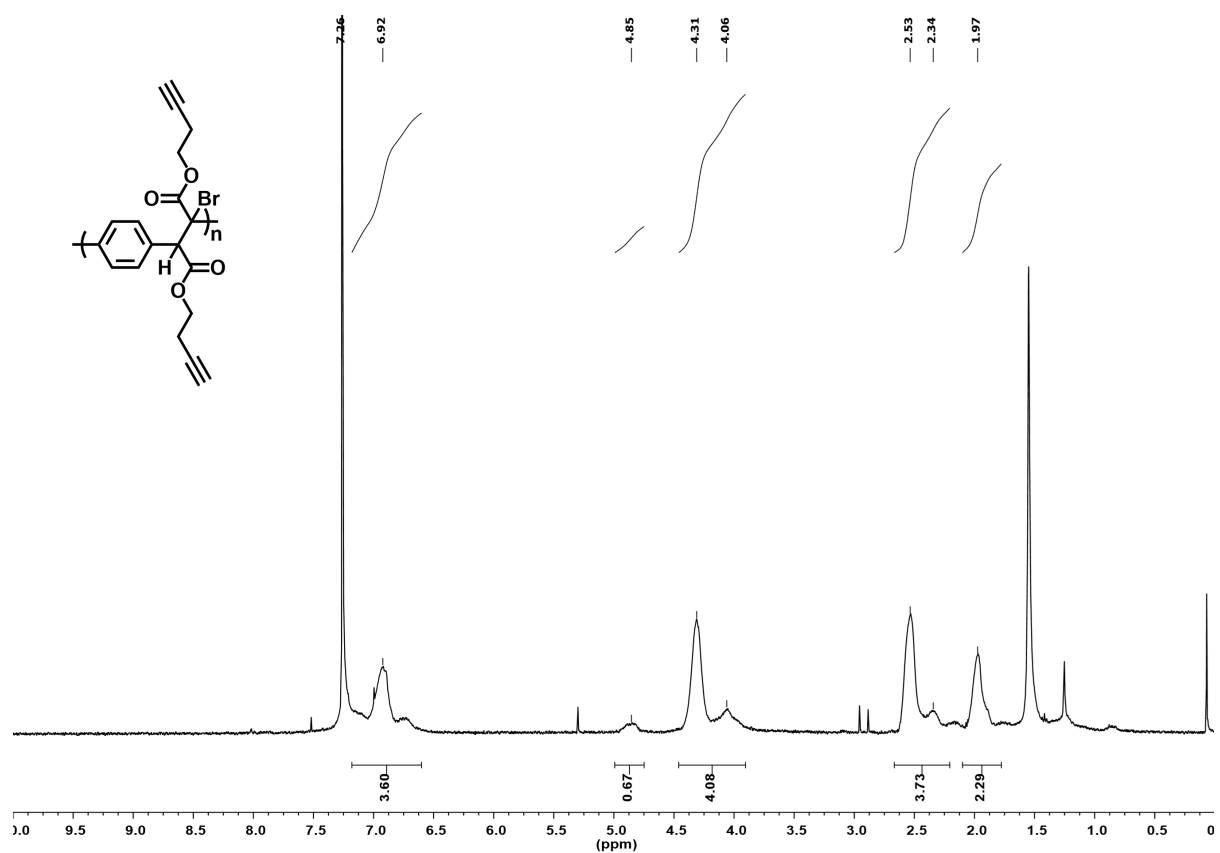


Figure S59. ^1H NMR spectrum recorded for **BrPPX-2e** in CDCl₃.

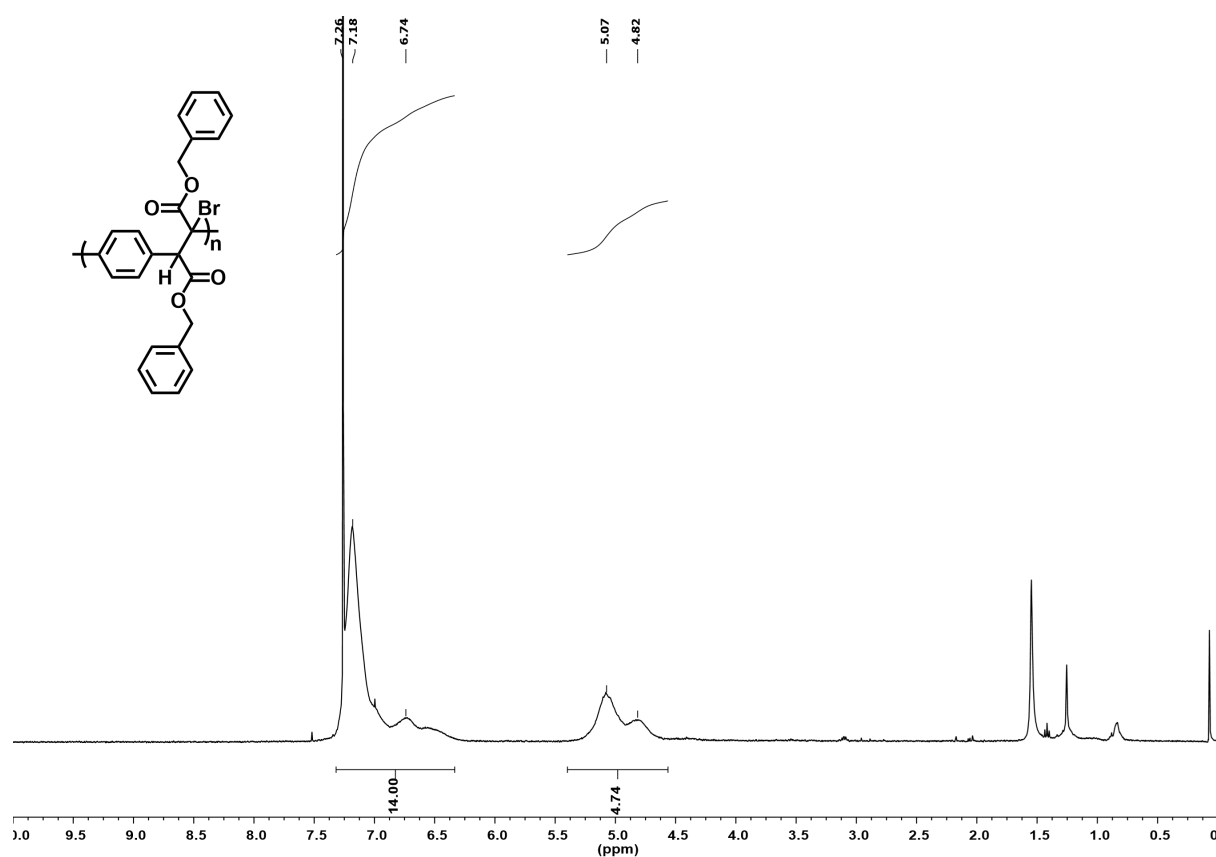


Figure S60. ^1H NMR spectrum recorded for **BrPPX-2f** in CDCl_3 .

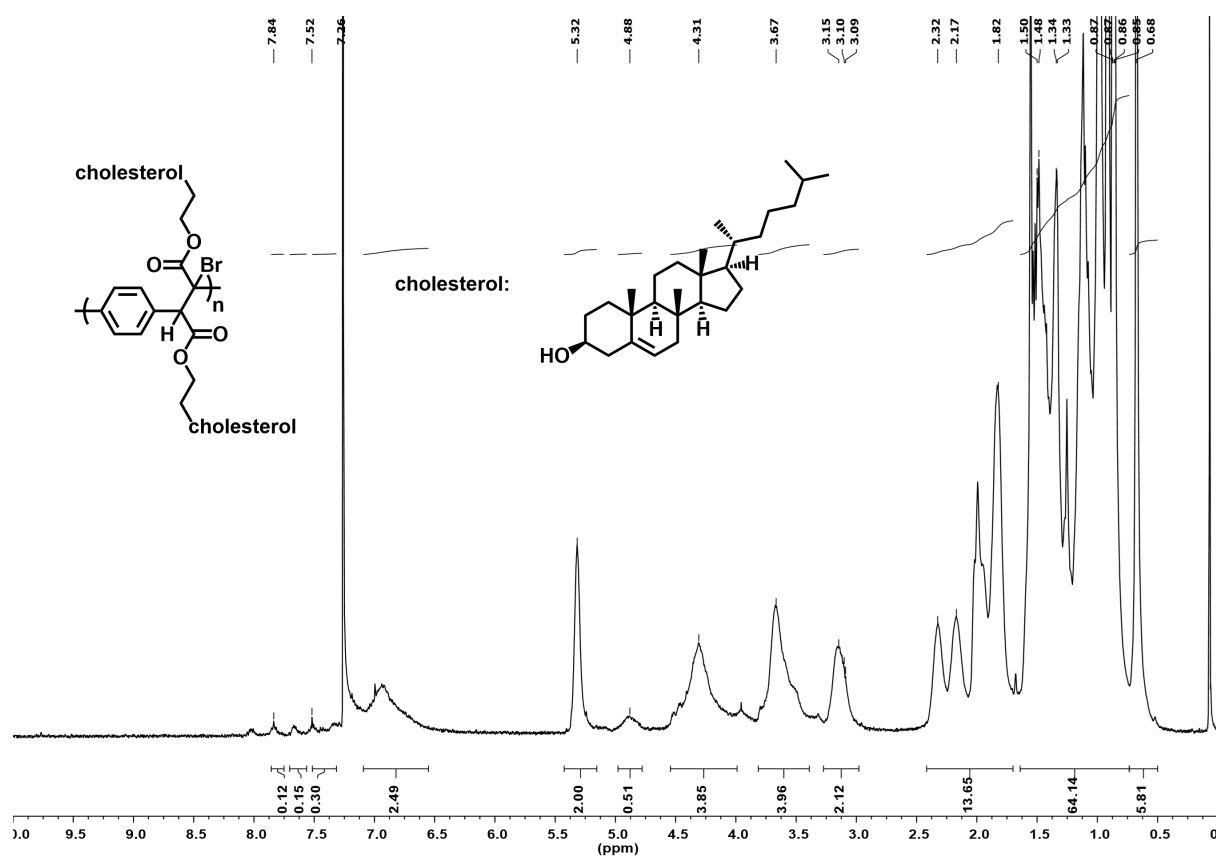


Figure S61. ^1H NMR spectrum recorded for **BrPPX-2g** in CDCl_3 .

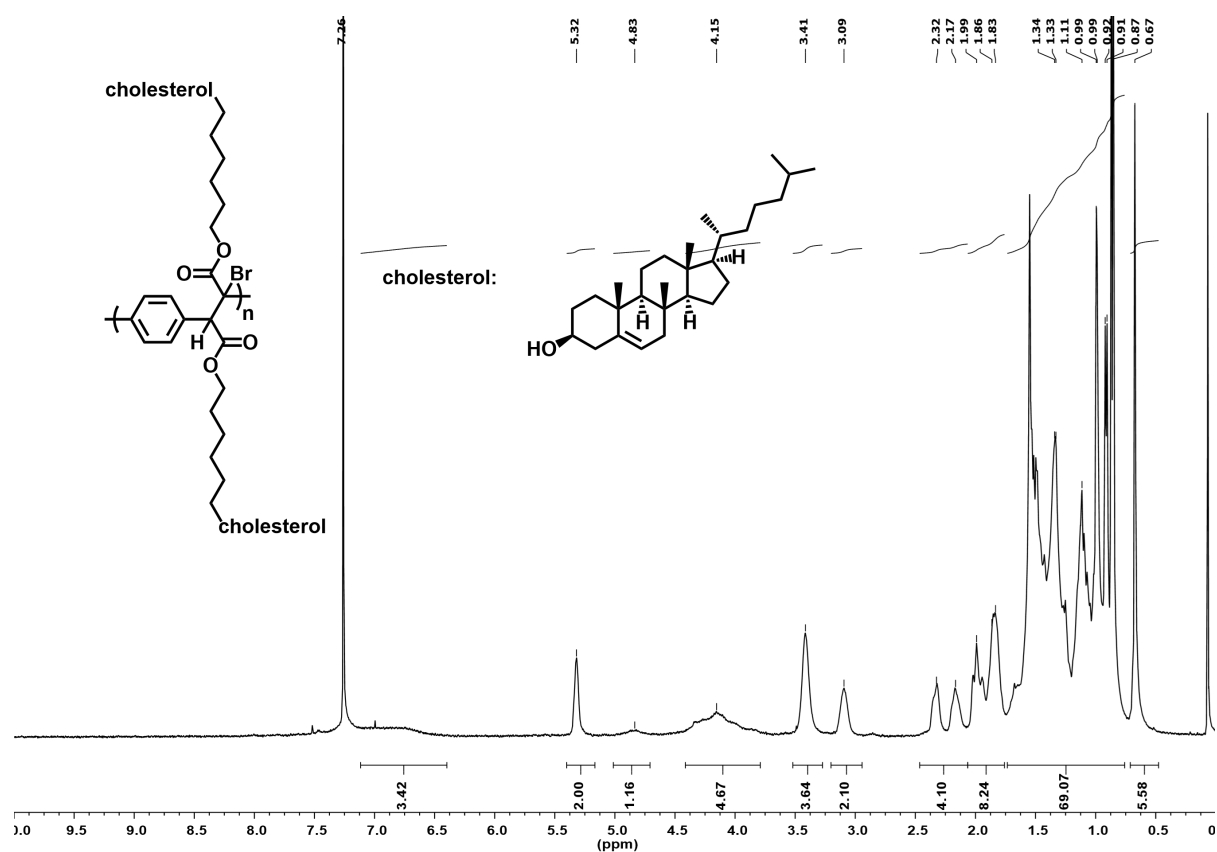


Figure S62. ¹H NMR spectrum recorded for BrPPX-2h in CDCl₃.

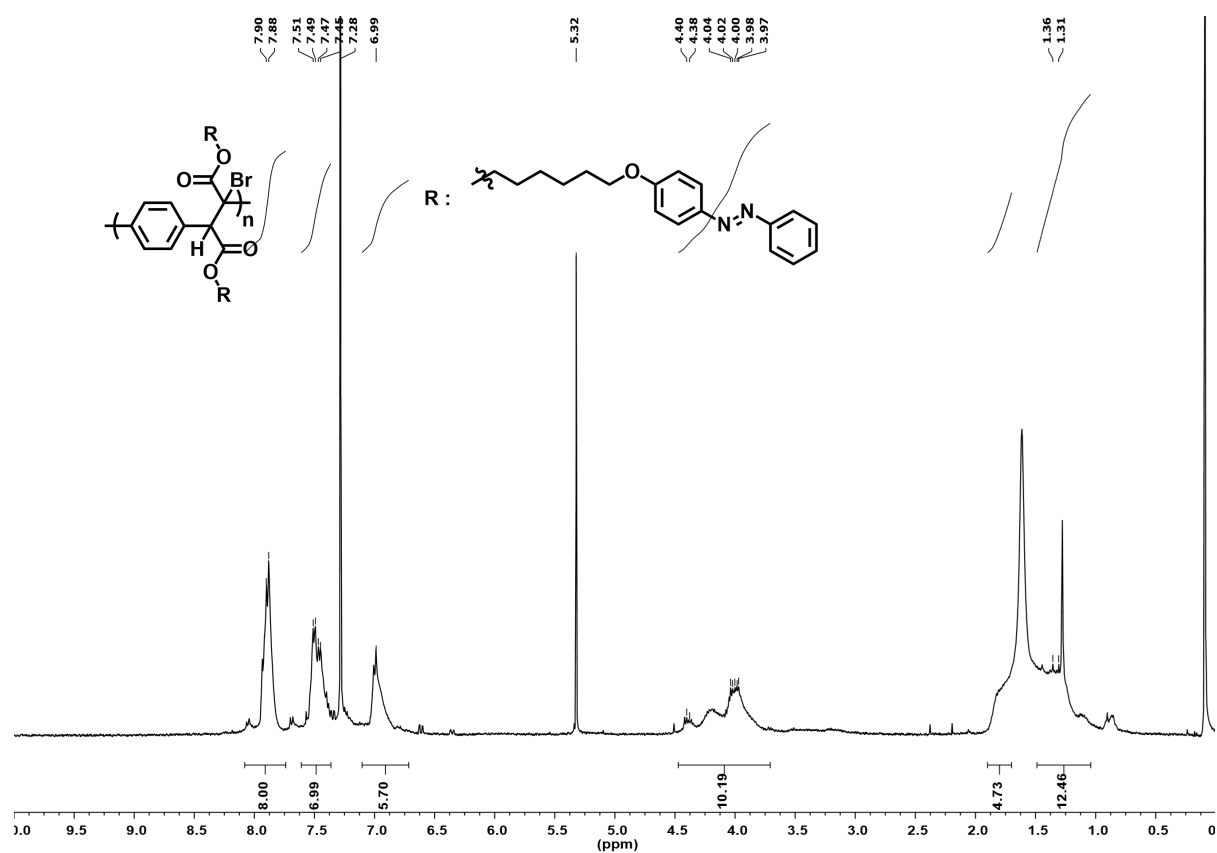


Figure S63. ¹H NMR spectrum recorded for BrPPX-2i in CDCl₃.

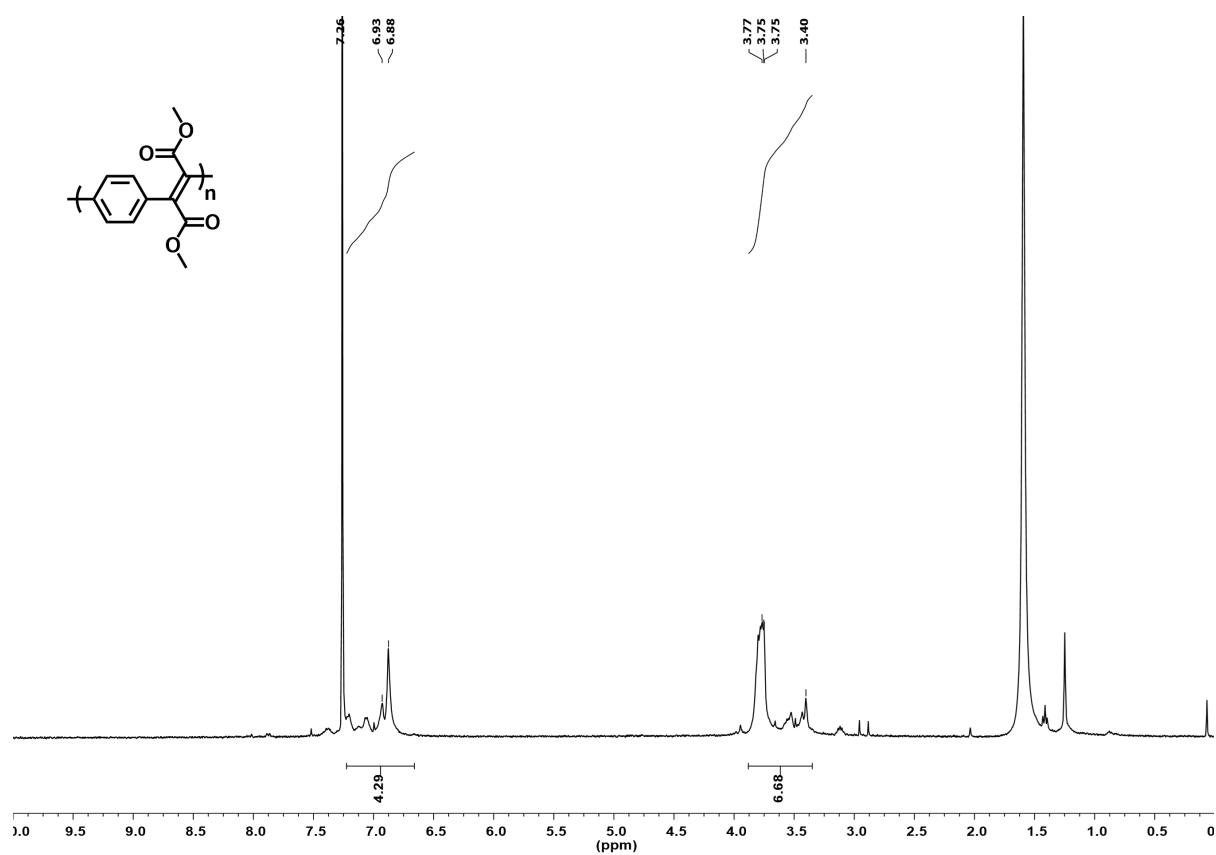


Figure S64. ¹H NMR spectrum recorded for **PPV-2a** in CDCl₃.

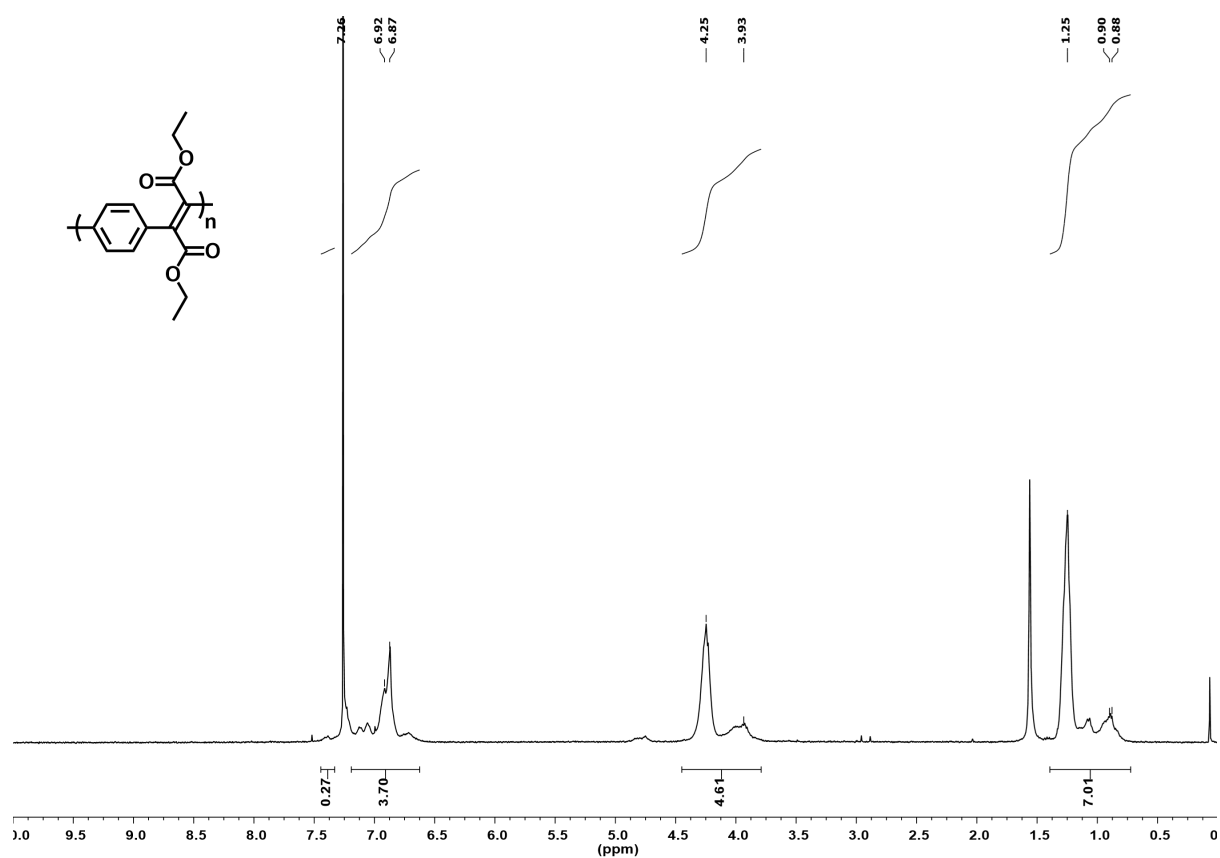


Figure S65. ¹H NMR spectrum recorded for **PPV-2b** in CDCl₃.

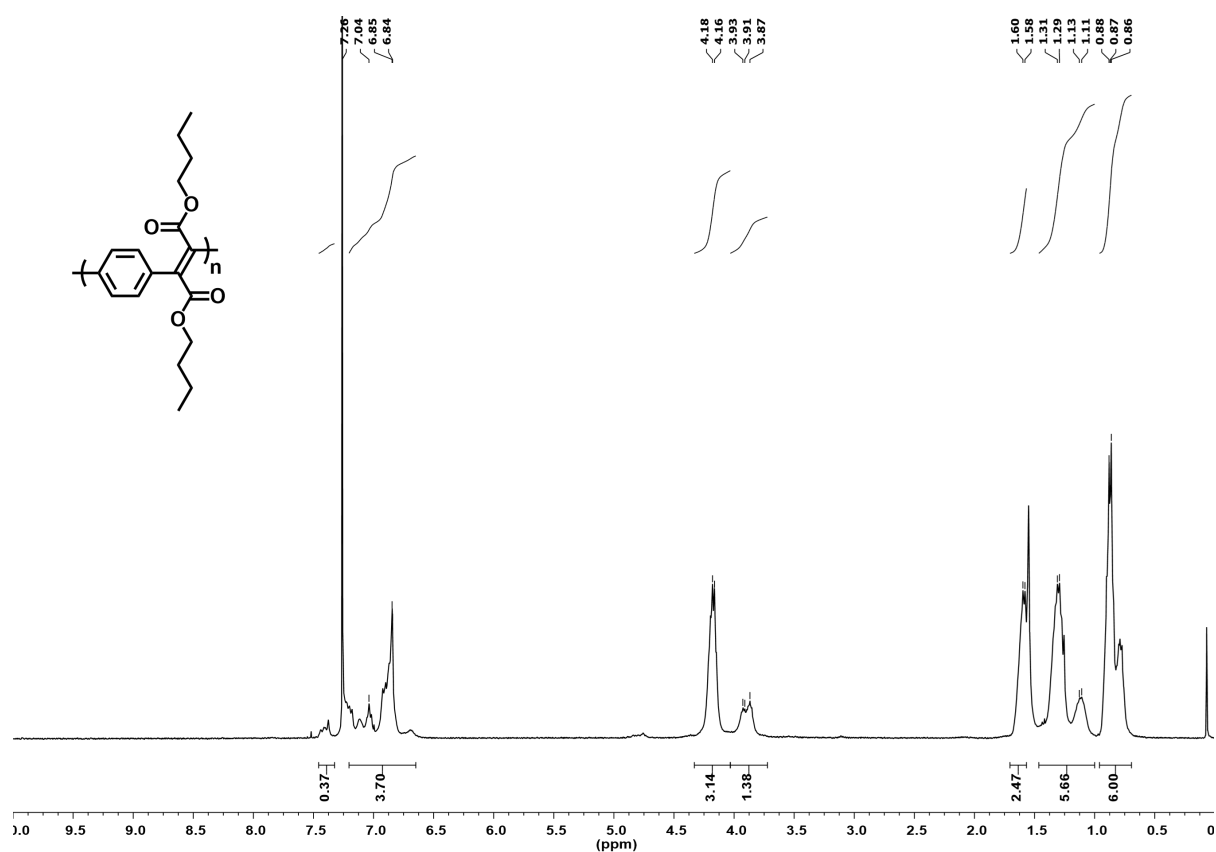


Figure S66. ¹H NMR spectrum recorded for **PPV-2c** in CDCl₃.

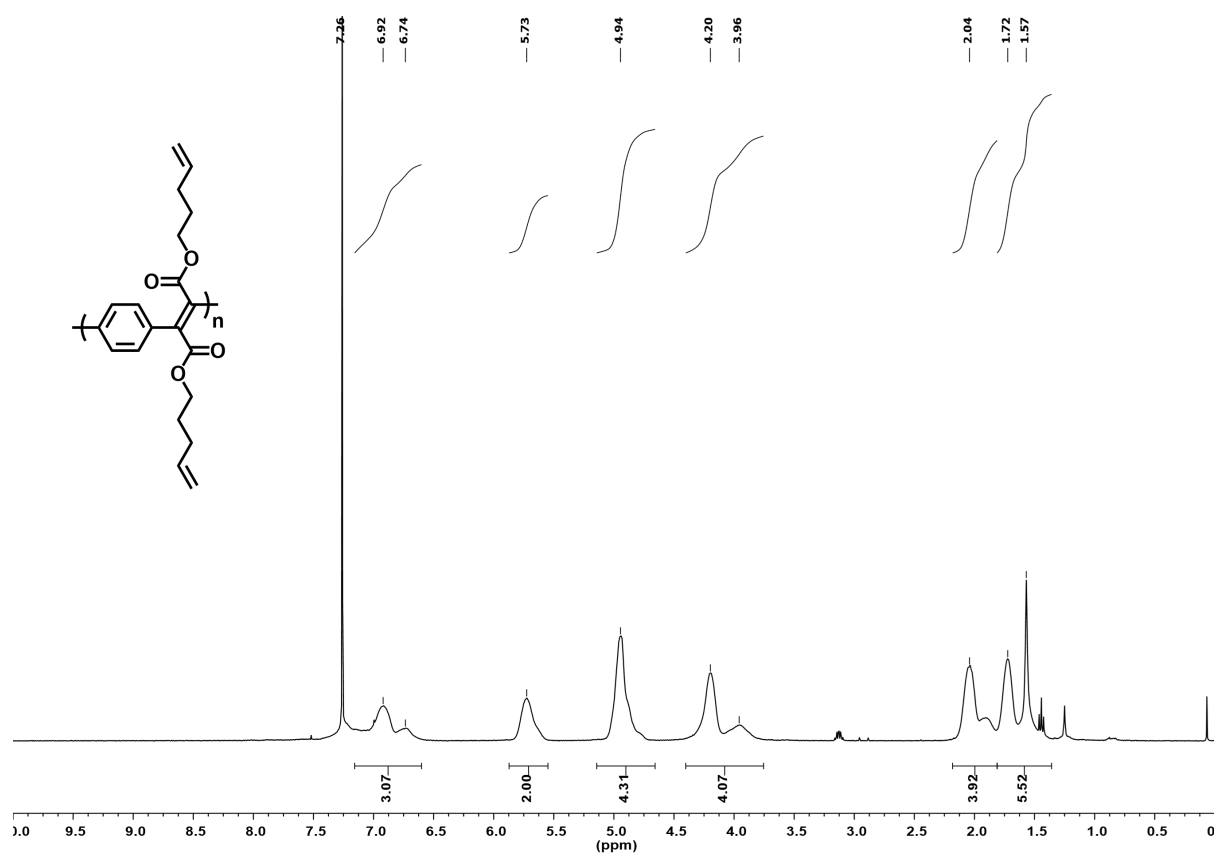


Figure S67. ¹H NMR spectrum recorded for **PPV-2d** in CDCl₃.

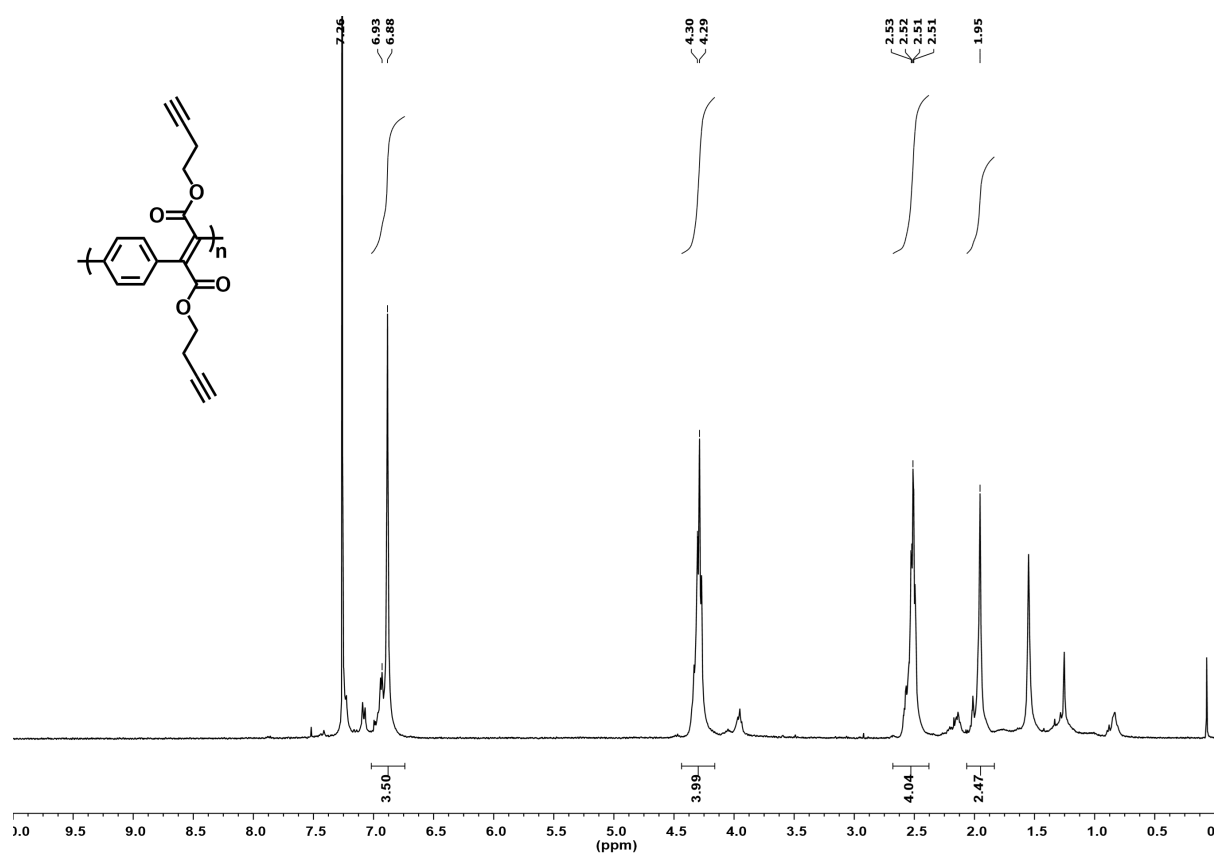


Figure S68. ¹H NMR spectrum recorded for **PPV-2e** in CDCl₃.

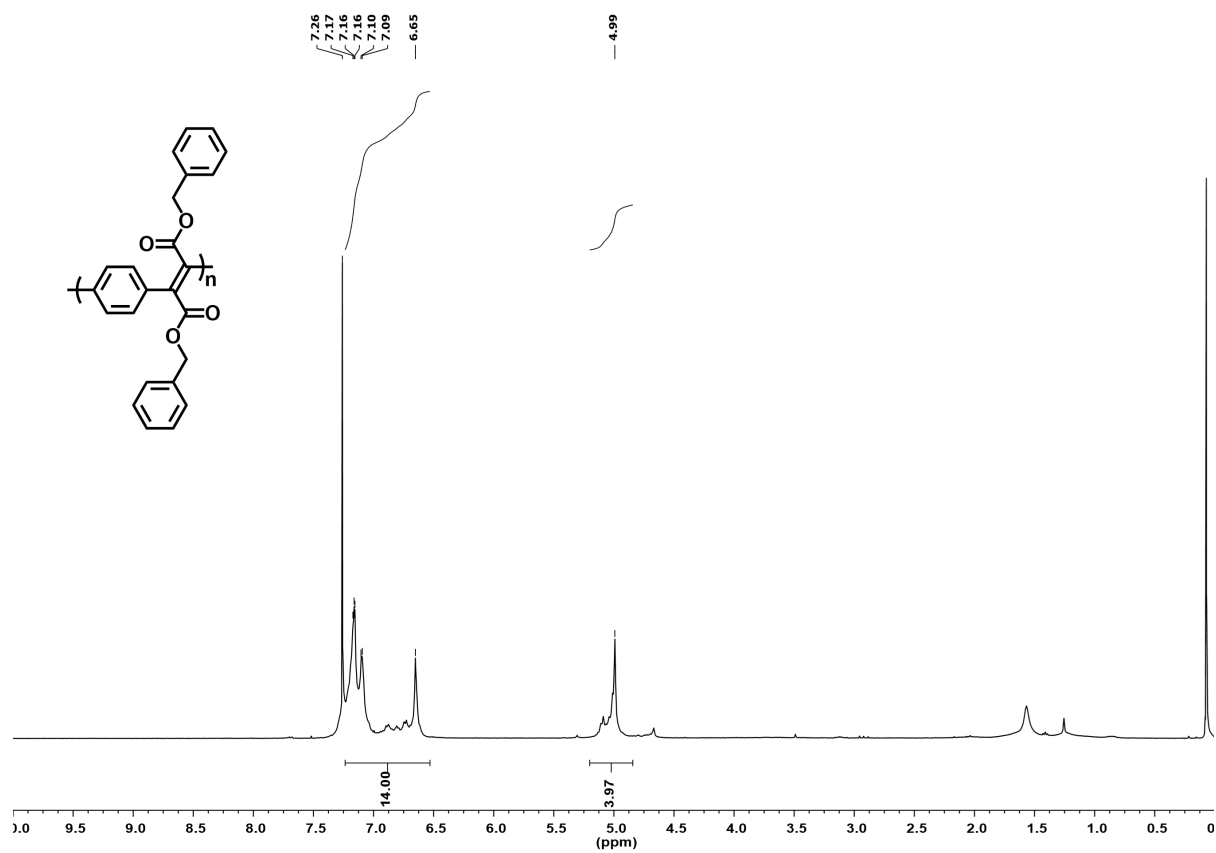


Figure S69. ¹H NMR spectrum recorded for **PPV-2f** in CDCl₃.

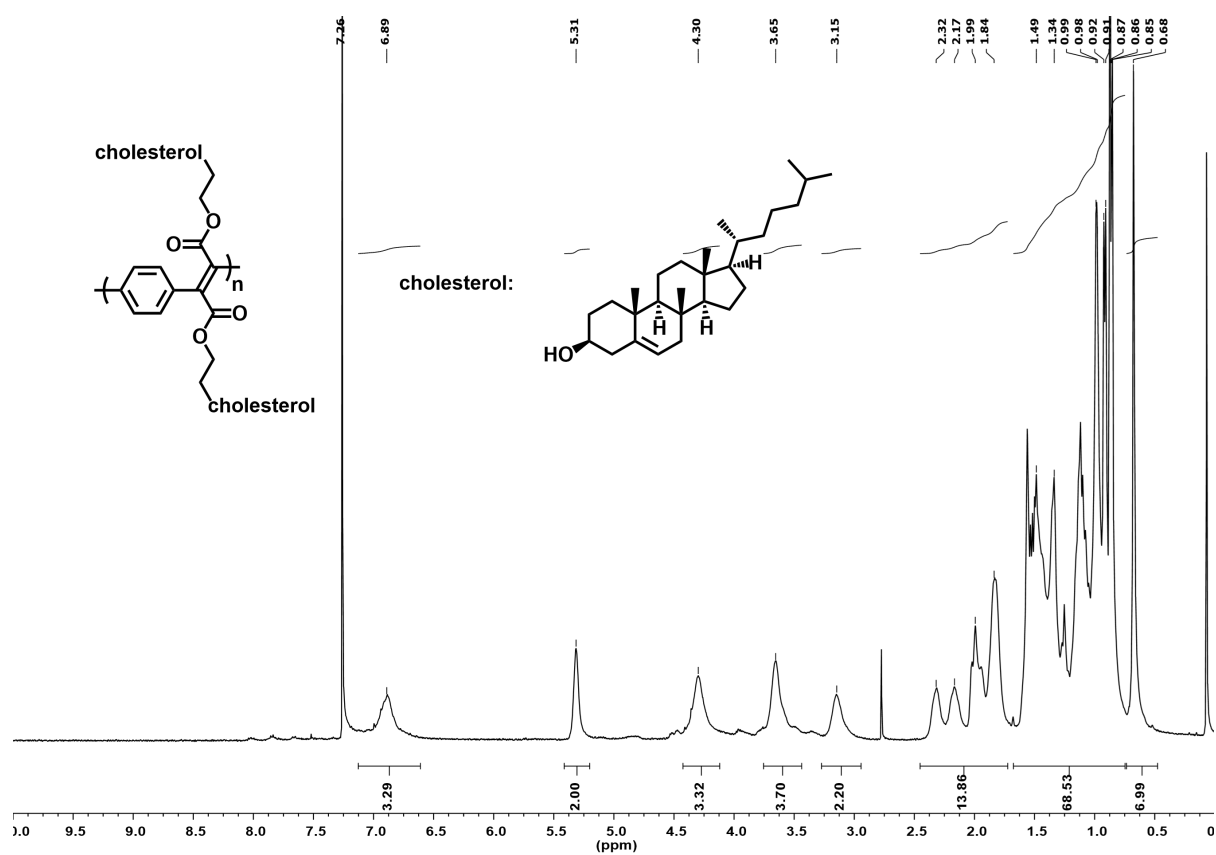


Figure S70. ^1H NMR spectrum a recorded for **PPV-2g** in CDCl_3 .

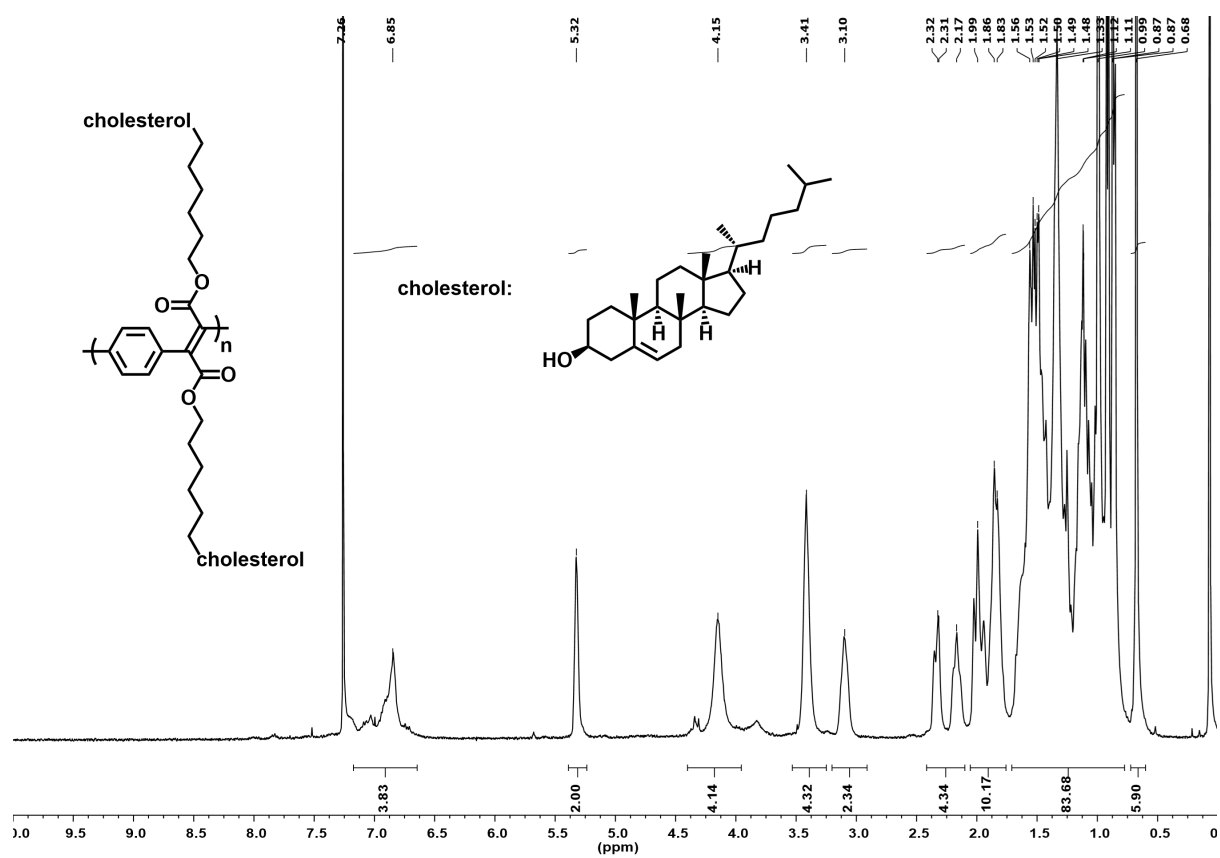


Figure S71. ^1H NMR spectrum recorded for **PPV-2h** in CDCl_3 .

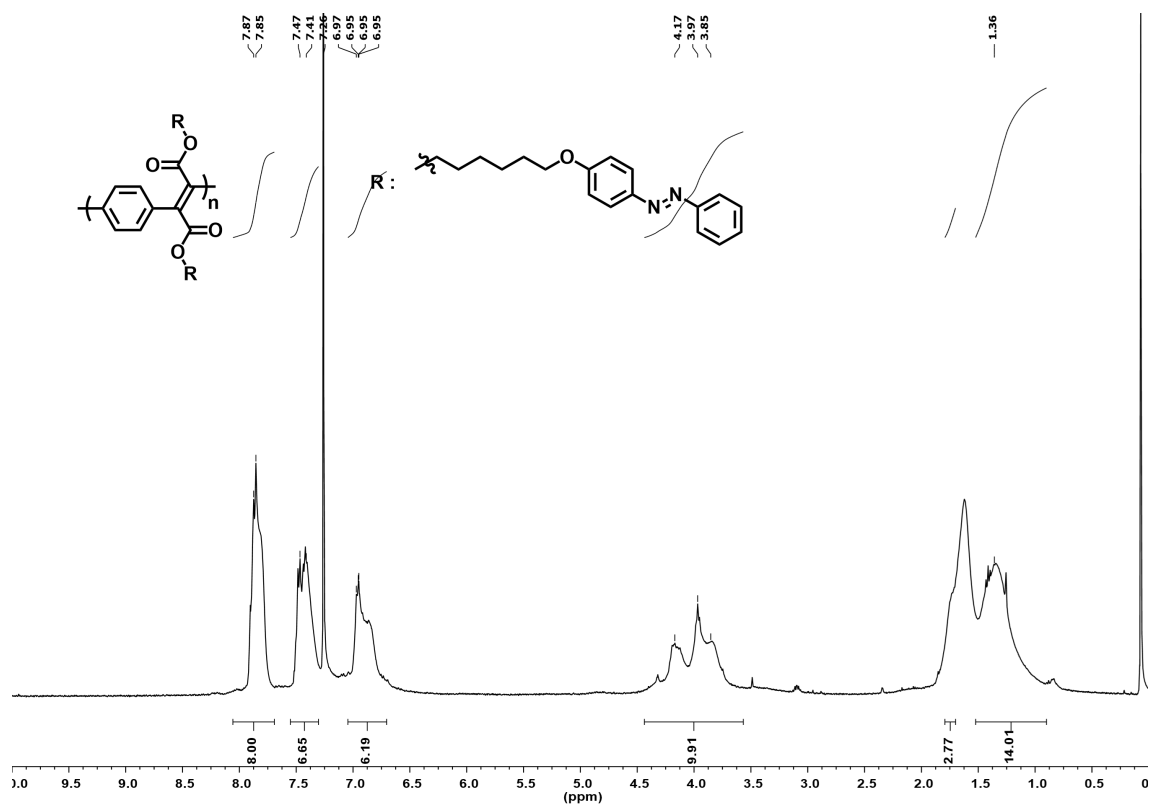


Figure S72. ^1H NMR spectrum recorded for **PPV-2i** in CDCl_3 .

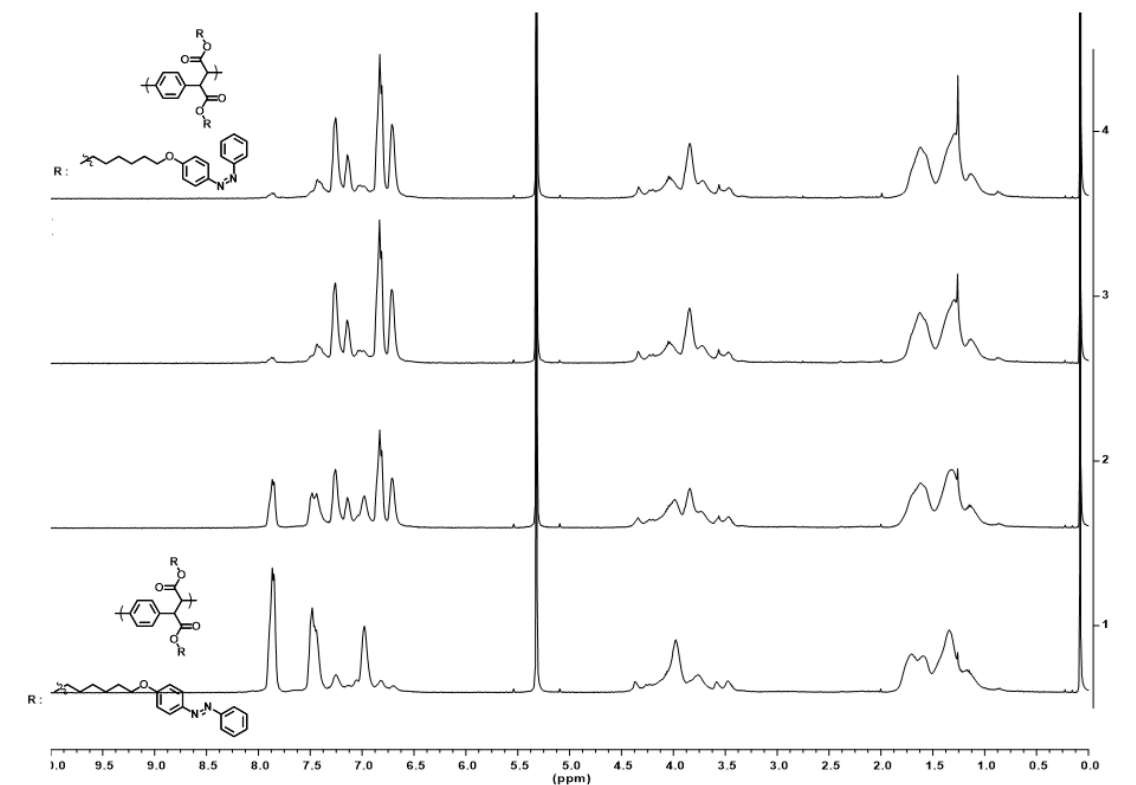


Figure S73. ^1H NMR spectra recorded after **PPX-2i** was irradiated at 365 nm (*trans*, 1, bottom). Photoisomerization of *trans* to *cis* (30 min, 2, 54% *cis*; 60 min, 3, 94% *cis*; 120 min, 4, 95% *cis* contents, in CD_2Cl_2).

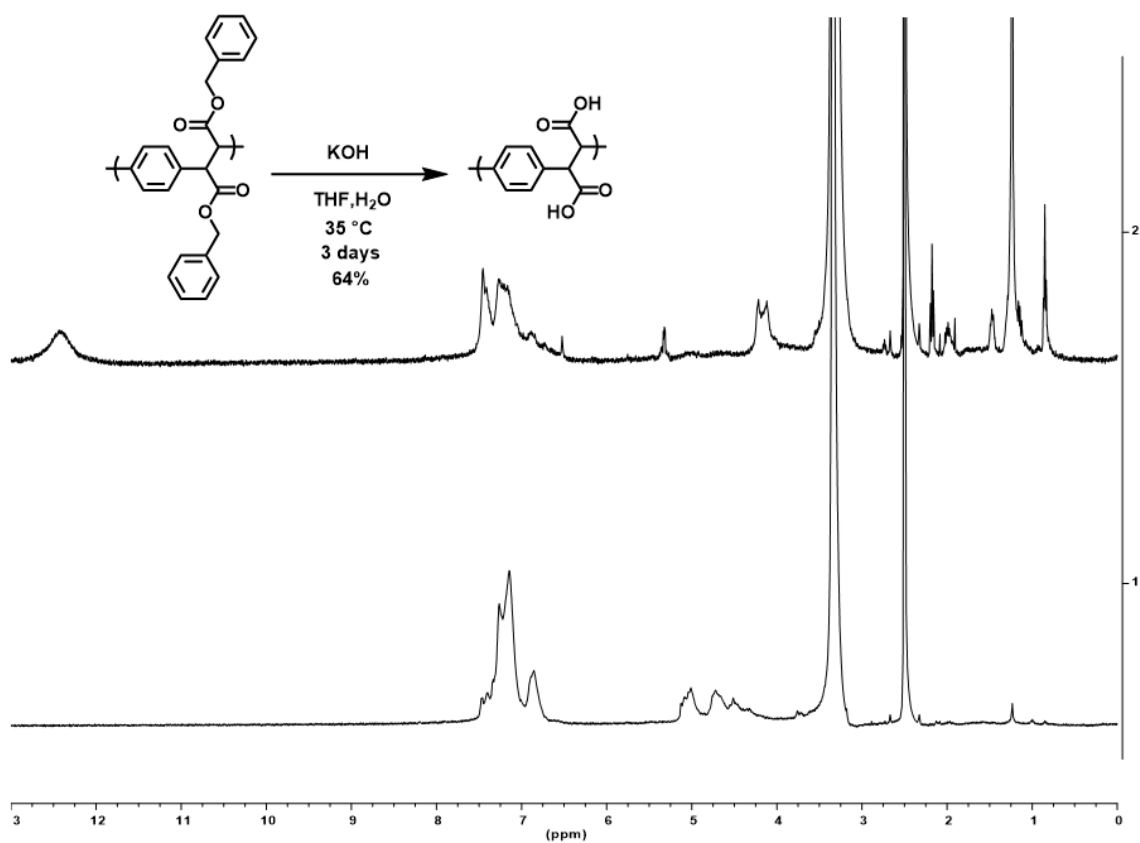


Figure S74. ^1H NMR spectrum recorded in $\text{DMSO}-d_6$ for **PPX-2f** before (bottom) and after treatment with potassium hydroxide in THF and H_2O solution for 3 days (top).

Jihong2-NMR_924.tif
JL-7-164-2

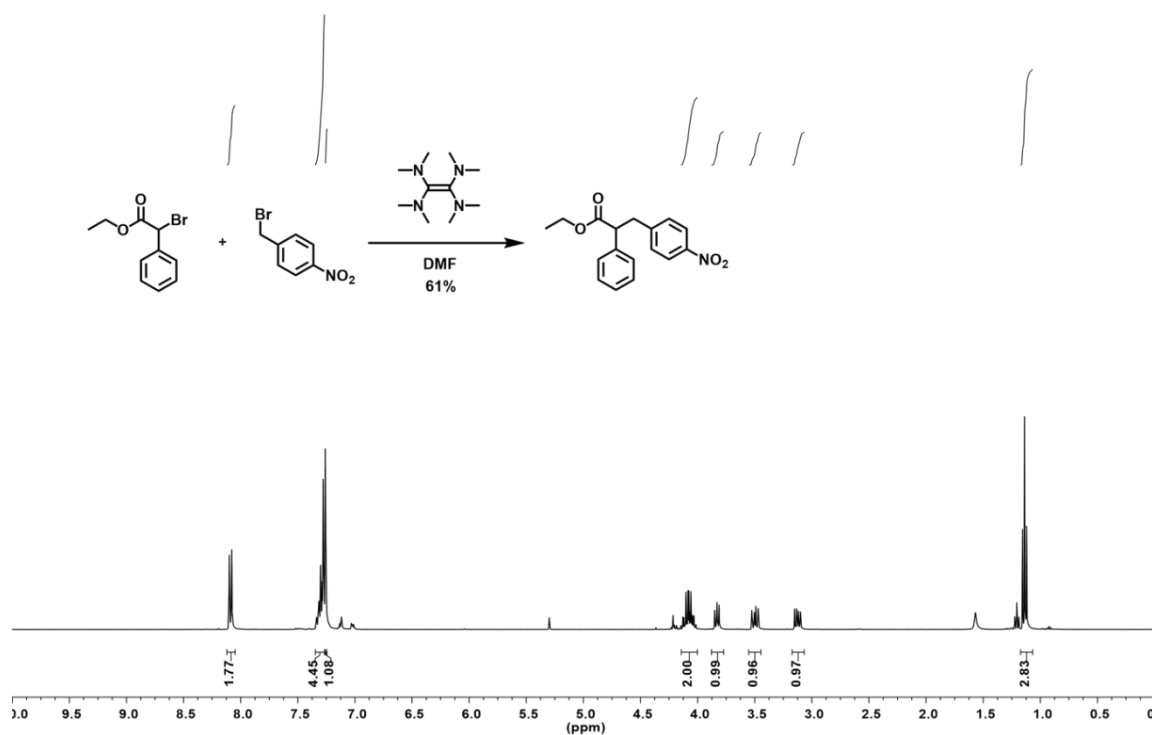


Figure S75. ^1H NMR spectrum recorded in CDCl_3 for the product (ethyl 3-(4-nitrophenyl)-2-phenylpropanoate) obtained from EBPA, 4-nitrobenzyl bromide and TDAE.

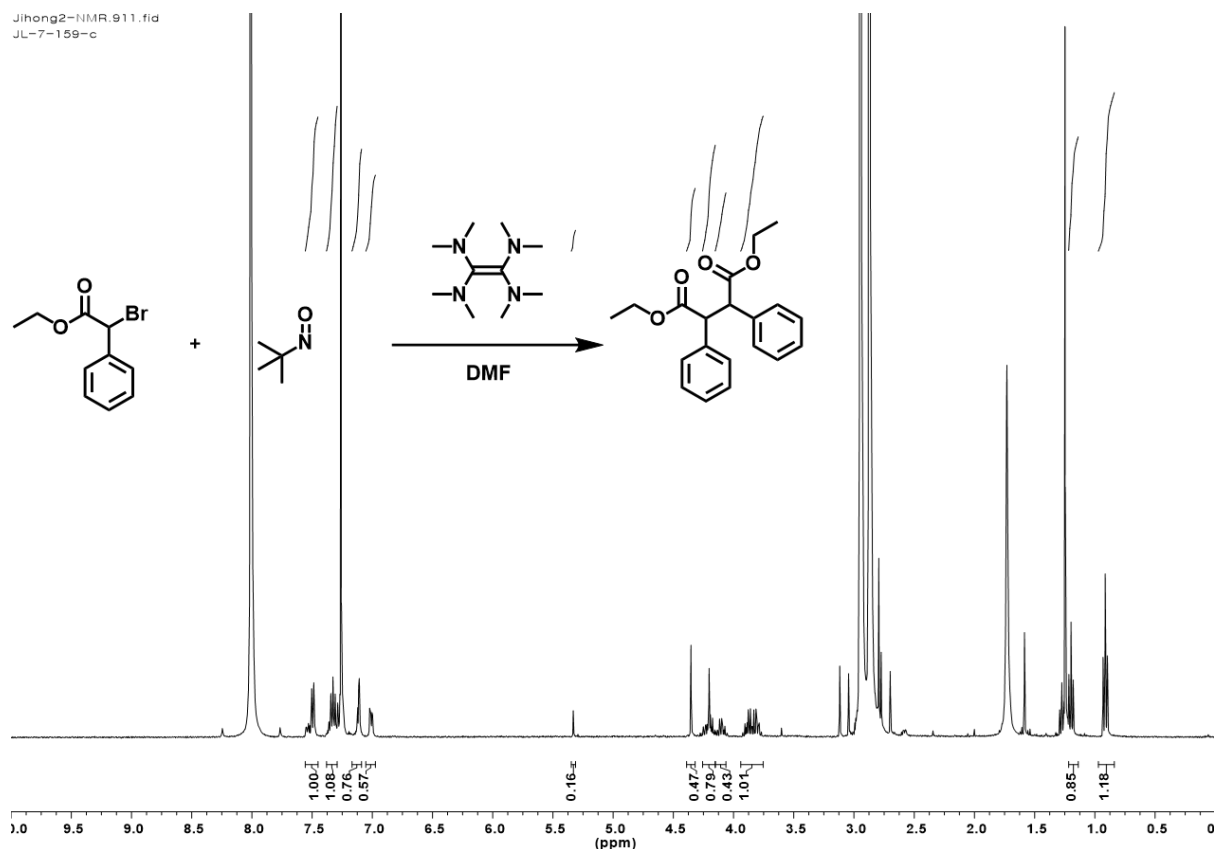


Figure S76. ¹H NMR spectrum recorded in CDCl₃ after a dimerization reaction was conducted in the presence of 2-methyl-2-nitrosopropane.

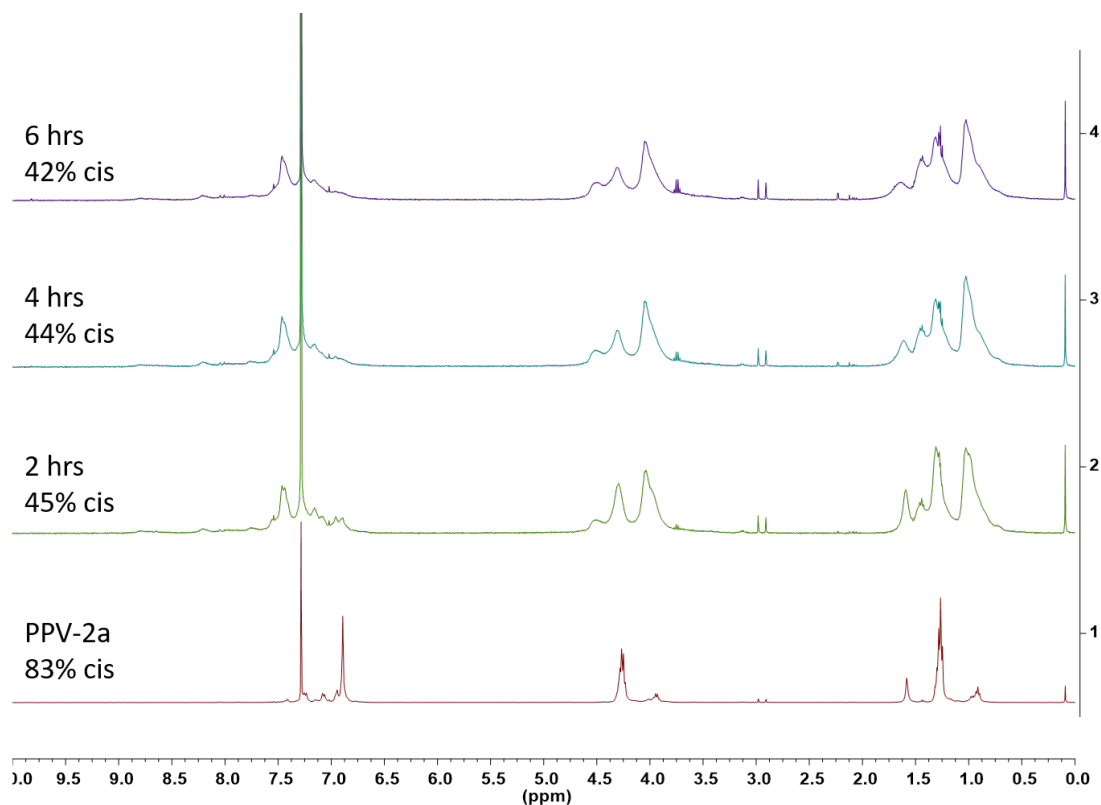


Figure S77. ¹H NMR spectra that were recorded in CDCl₃ after PPV-2a was irradiated at 350 nm for various periods of time (indicated).

Additional IR Spectra

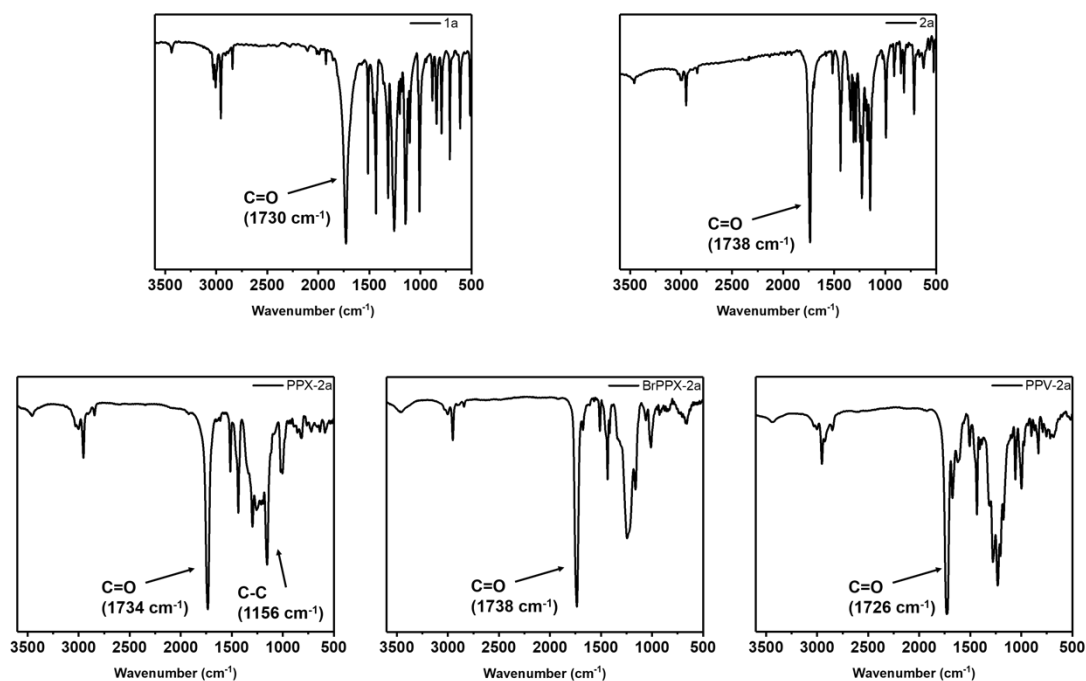


Figure S78. FT-IR spectra recorded for methyl derivatives of **1a**, **2a**, **PPX-2a**, **BrPPX-2a** and **PPV-2a** (indicated) (KBr).

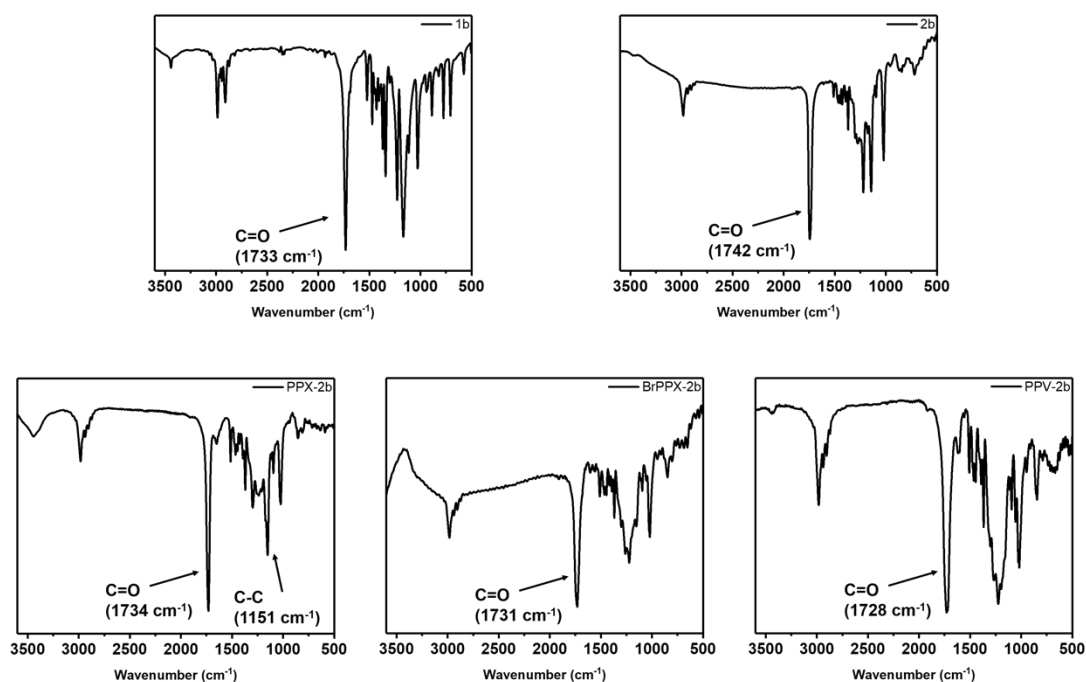


Figure S79. FT-IR spectra recorded for ethyl derivatives of **1b**, **2b**, **PPX-2b**, **BrPPX-2b** and **PPV-2b** (indicated) (KBr).

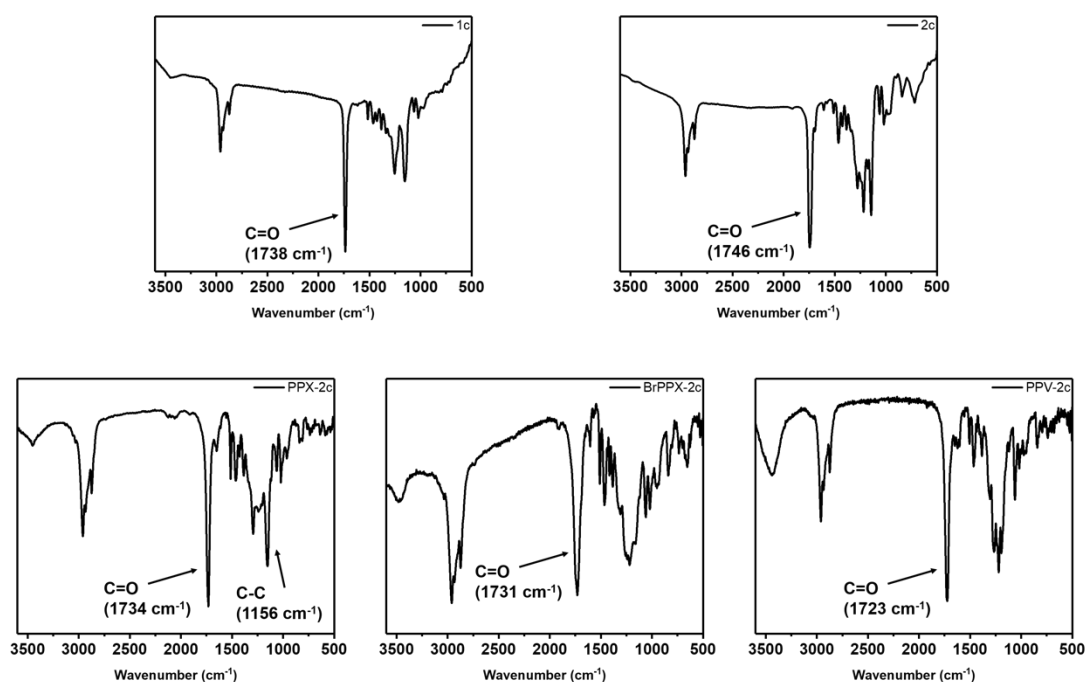


Figure S80. FT-IR spectra recorded for n-butyl derivatives of **1c**, **2c**, **PPX-2c**, **BrPPX-2c** and **PPV-2c** (indicated) (KBr).

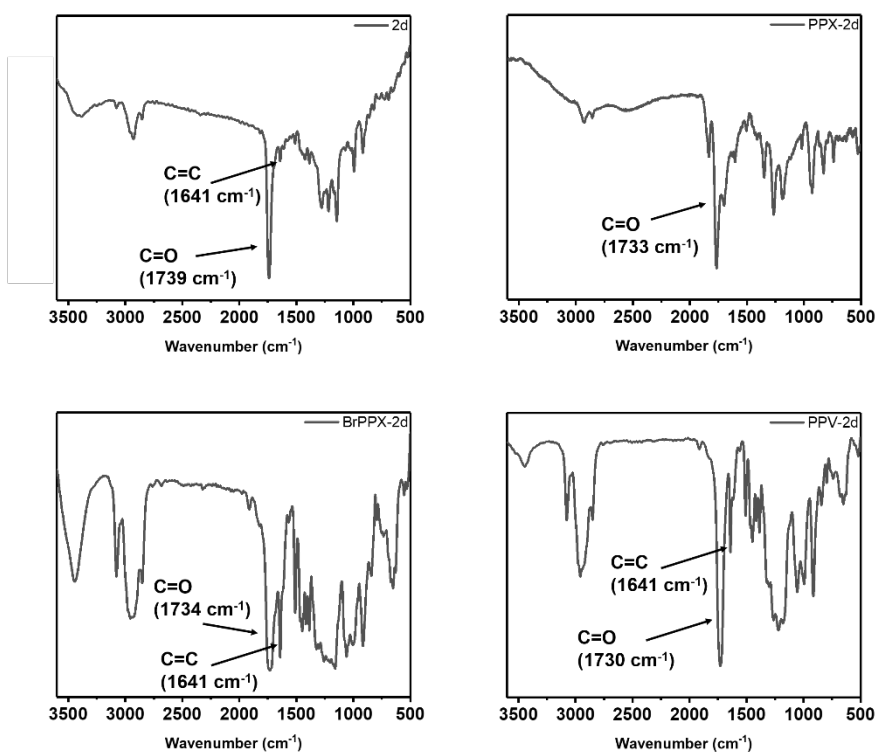


Figure S81. FT-IR spectra recorded for alkenyl derivatives of **2d**, **PPX-2d**, **BrPPX-2d** and **PPV-2d** (indicated) (KBr).

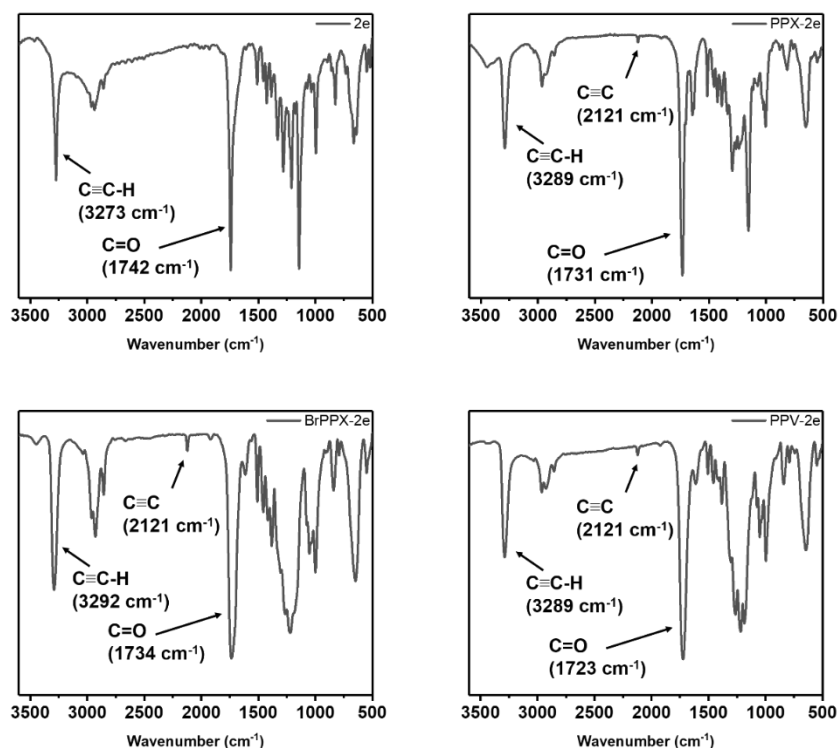


Figure S82. FT-IR spectra recorded for alkynyl derivatives of **2e**, **PPX-2e**, **BrPPX-2e** and **PPV-2e** (indicated) (KBr).

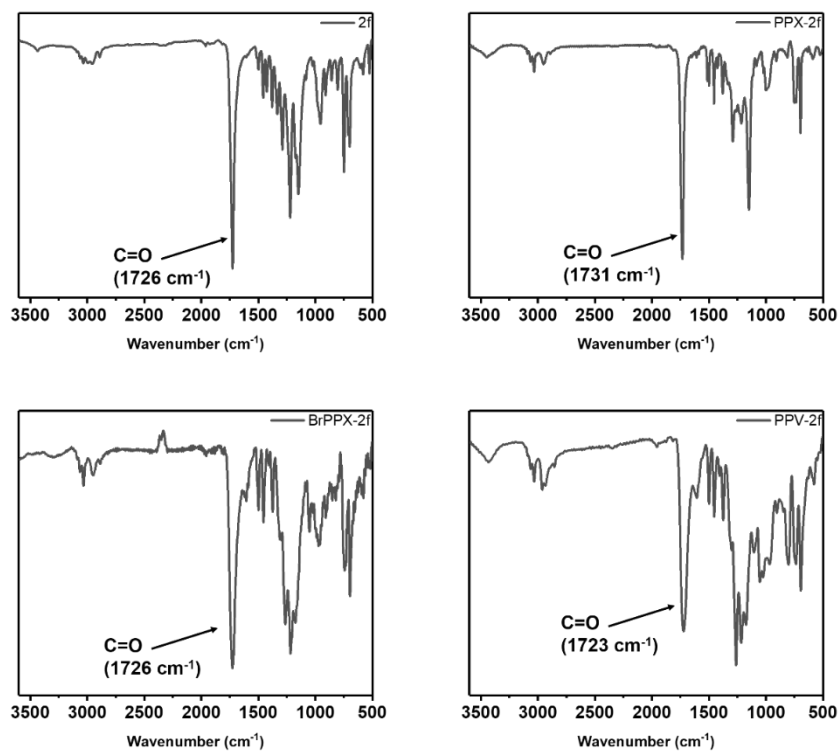


Figure S83. FT-IR spectra recorded for benzyl derivatives of **2f**, **PPX-2f**, **BrPPX-2f** and **PPV-2f** (indicated) (KBr).

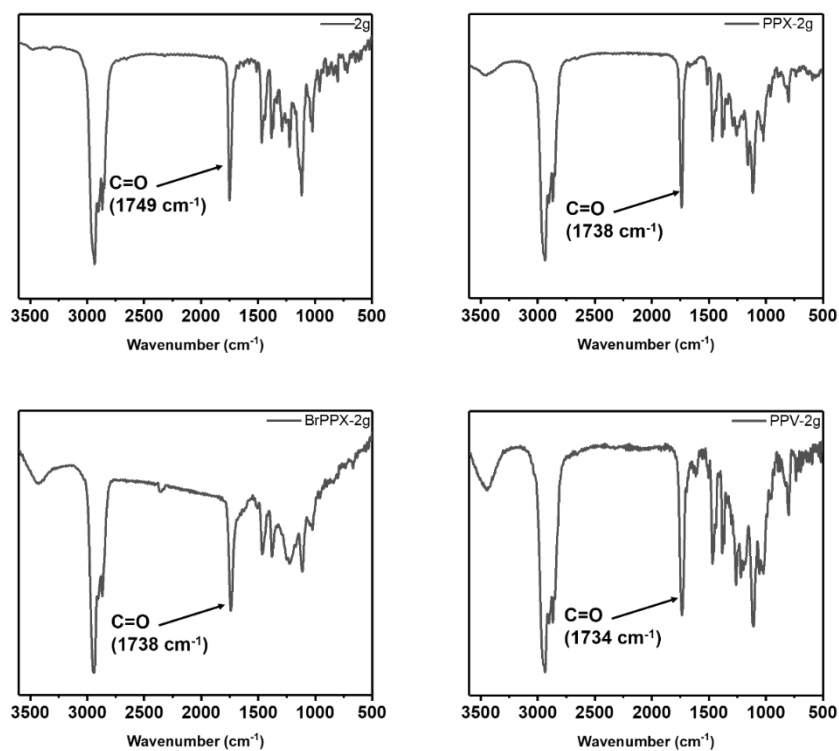


Figure S84. FT-IR spectra recorded for cholesterol derivatives of **2g**, **PPX-2g**, **BrPPX-2g** and **PPV-2g** (indicated) (KBr).

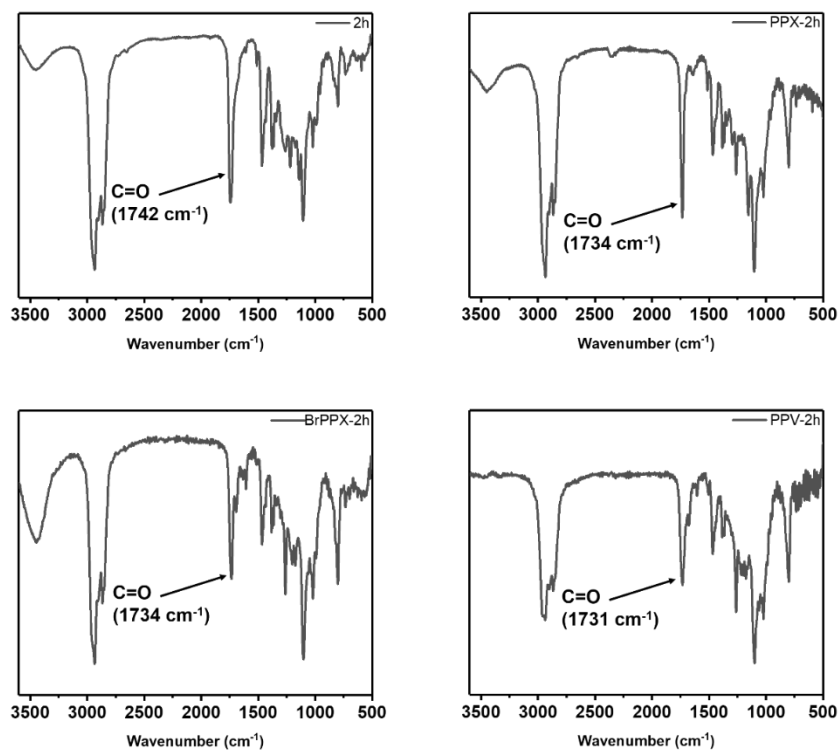


Figure S85. FT-IR spectra recorded for cholesterol derivatives of **2h**, **PPX-2h**, **BrPPX-2h** and **PPV-2h** (indicated) (KBr).

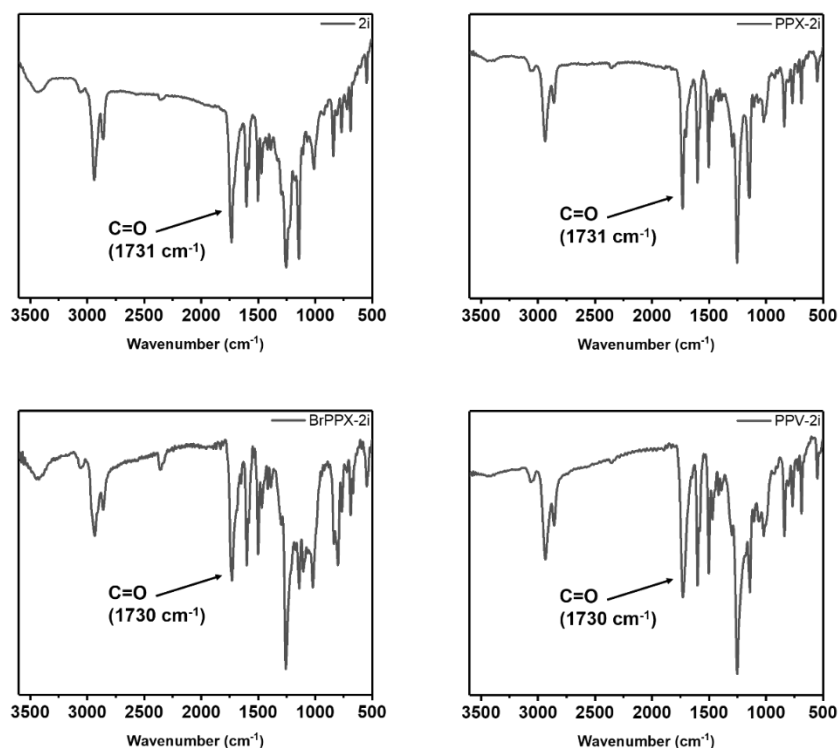


Figure S86. FT-IR spectra recorded for azobenzene derivatives of **2i**, **PPX-2i**, **BrPPX-2i** and **PPV-2i** (indicated) (KBr).

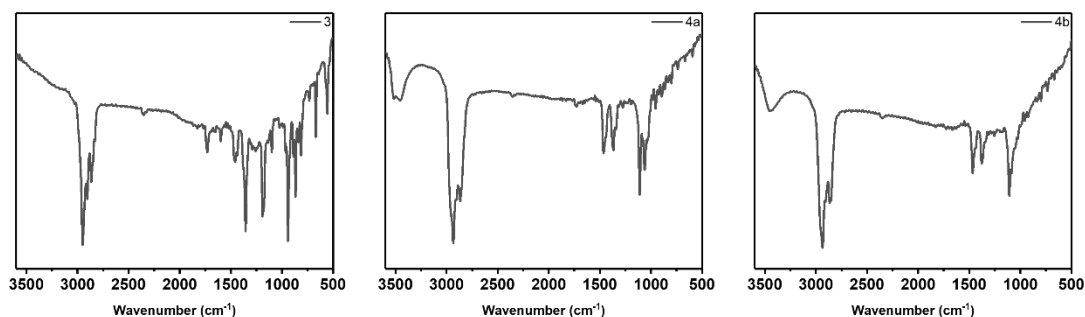


Figure S87. FT-IR spectra recorded for cholesteryl tosylate (**3**) and its corresponding alcohols (**4a** and **4b**) (KBr).

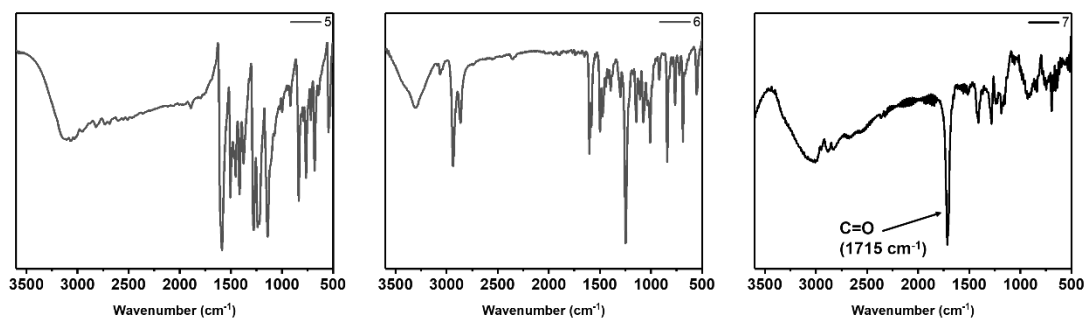


Figure S88. FT-IR spectra recorded for 4-hydroxyazobenzene (**5**) and its corresponding alcohol (**6**) as well as 2,2'-(1,4-phenylene)bis(2-bromoacetic acid) (**7**) (KBr).

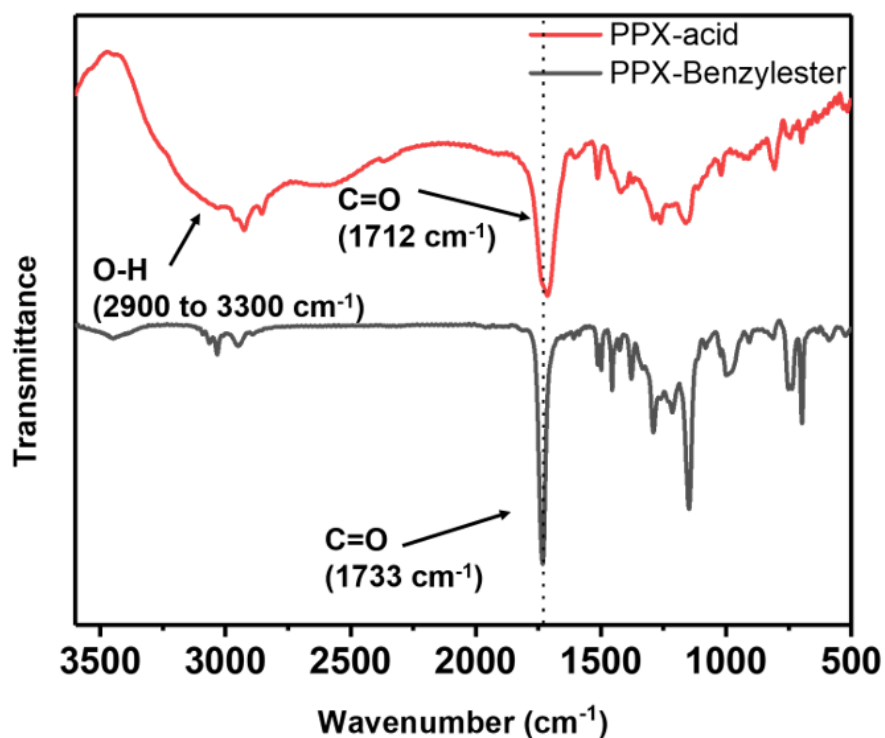


Figure S89. FT-IR spectra recorded for **PPX-2f** before (black) and after treatment with potassium hydroxide in a solution of THF and H_2O for three days to obtain the corresponding carboxylic acid derivative, **PPX-acid** (red).

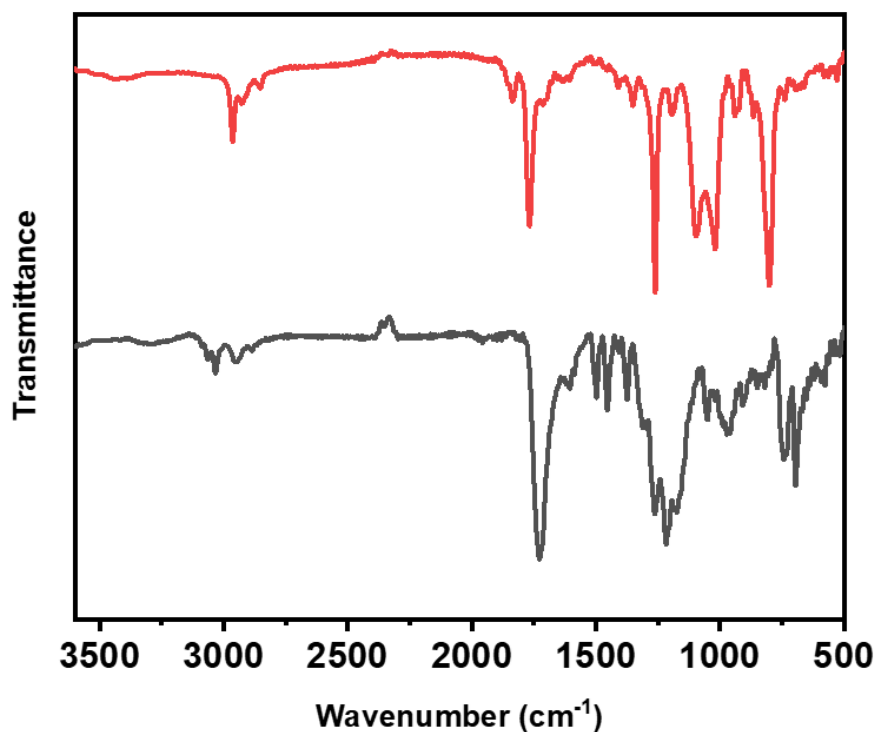


Figure S90. FT-IR spectra recorded for **PPV-2f** before (black) and after treatment with potassium hydroxide in a solution of THF and H_2O followed by treatment with an aqueous solution of HCl; the product was tentatively identified as an anhydride derivative (red).

Additional Thermal Data

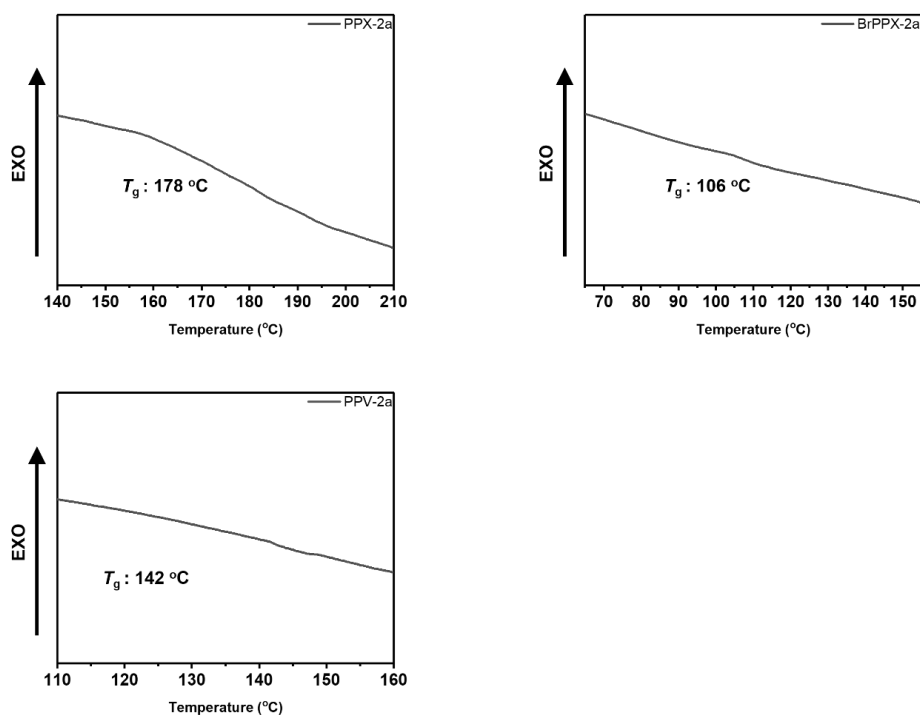


Figure S91. DSC data recorded for methyl derivatives of **PPX-2a**, **BrPPX-2a** and **PPV-2a** at a heating rate of 20 °C min^{-1} under an atmosphere of N_2 .

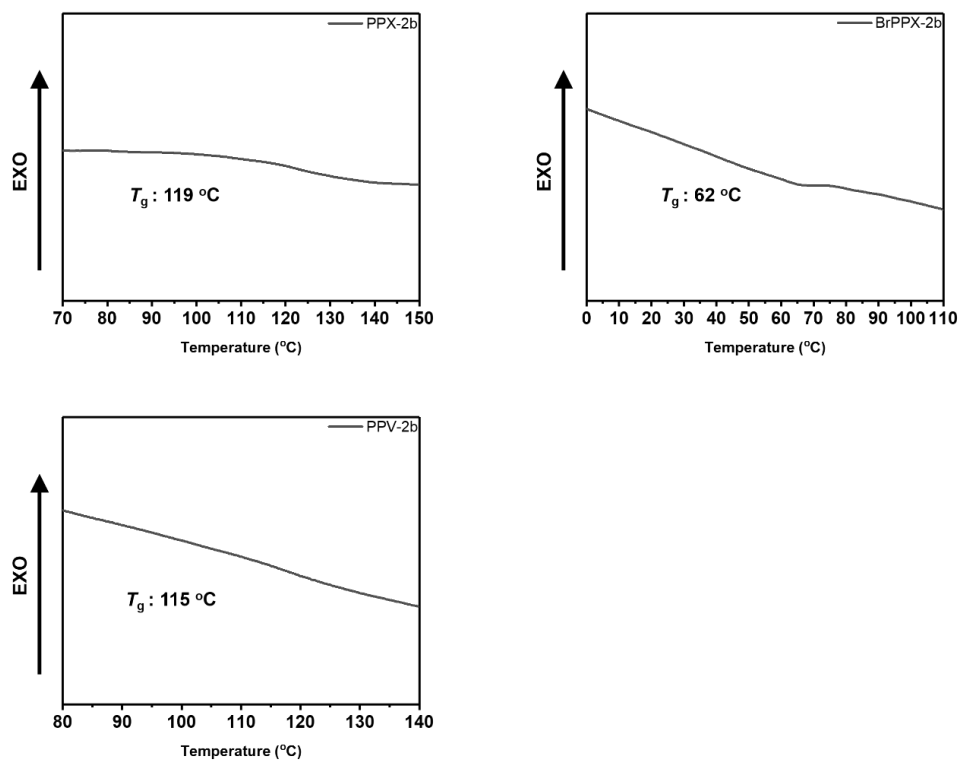


Figure S92. DSC data recorded for ethyl derivatives of **PPX-2b**, **BrPPX-2b** and **PPV-2b** at a heating rate of 20 °C min^{-1} under an atmosphere of N_2 .

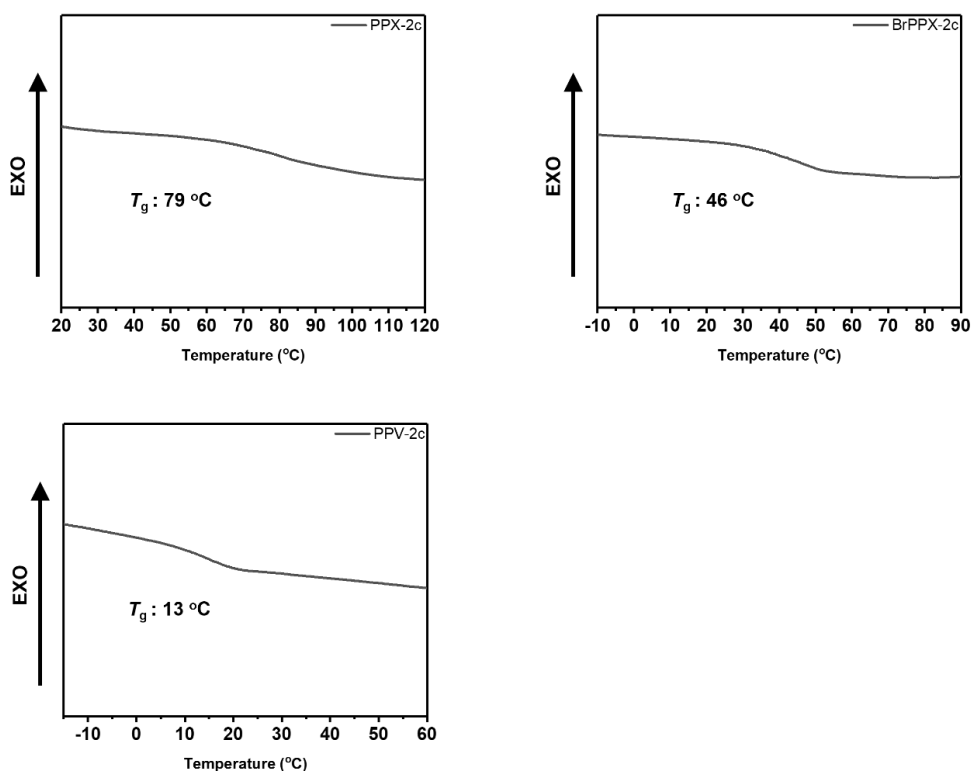


Figure S93. DSC data recorded for n-butyl derivatives of **PPX-2c**, **BrPPX-2c** and **PPV-2c** at a heating rate of 20 °C min^{-1} under an atmosphere of N_2 .

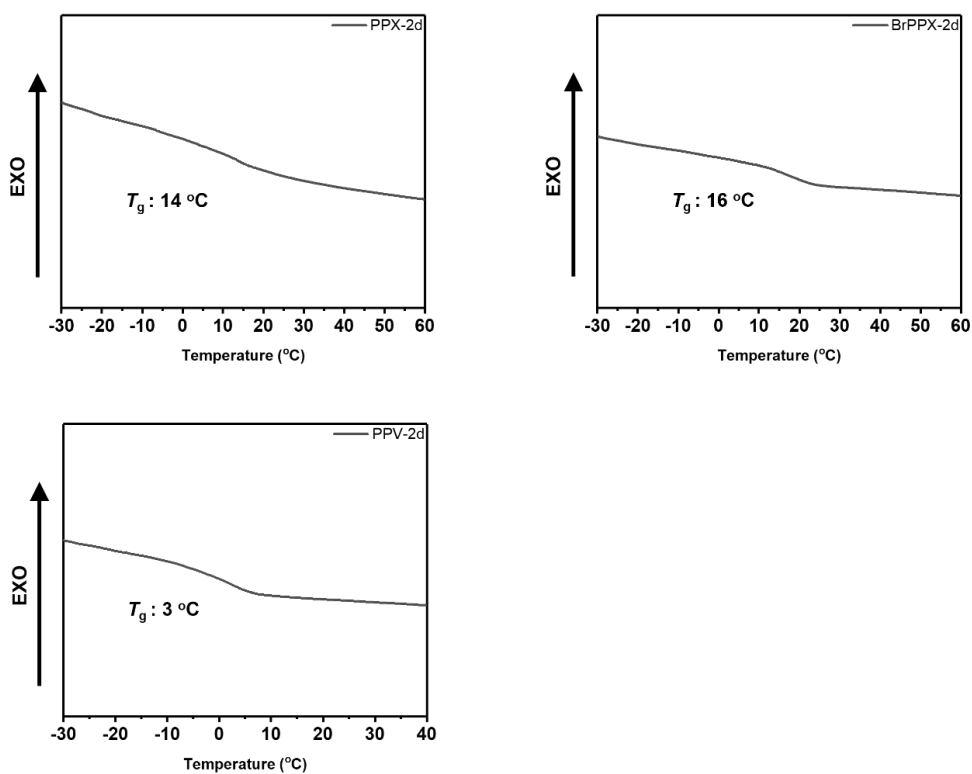


Figure S94. DSC data recorded for alkenyl derivatives of **PPX-2d**, **BrPPX-2d** and **PPV-2d** at a heating rate of 20 °C min^{-1} under an atmosphere of N_2 .

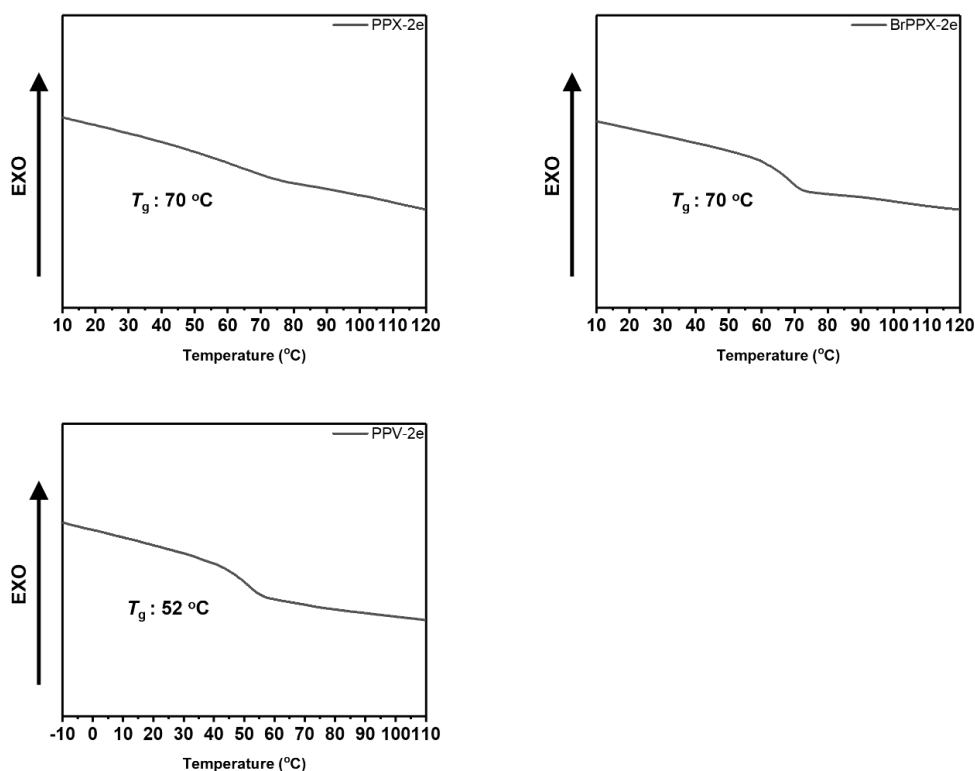


Figure S95. DSC data recorded for alkynyl derivatives of **PPX-2e**, **BrPPX-2e** and **PPV-2e** at a heating rate of 20 °C min⁻¹ under an atmosphere of N₂.

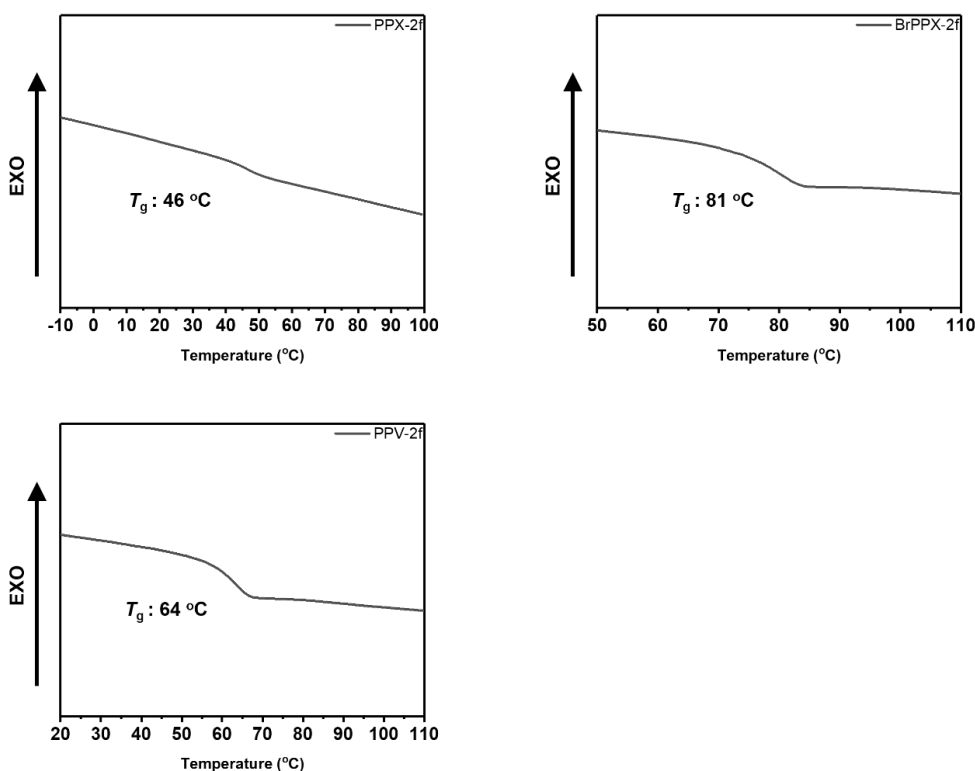


Figure S96. DSC data recorded for benzyl derivatives of **PPX-2f**, **BrPPX-2f** and **PPV-2f** at a heating rate of 20 °C min⁻¹ under an atmosphere of N₂.

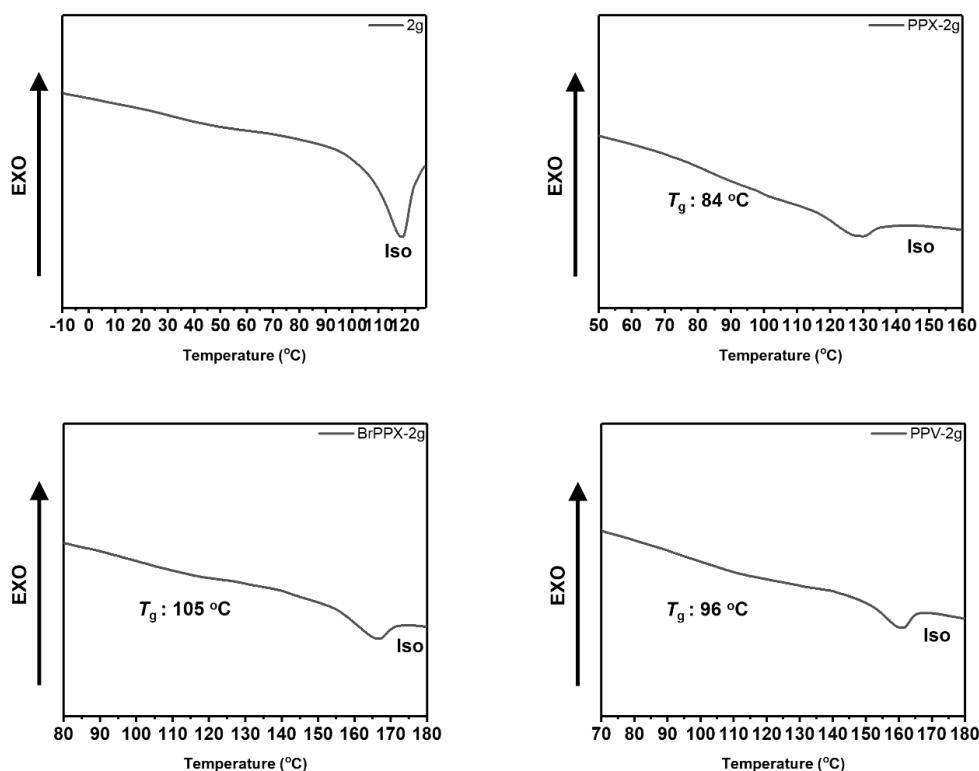


Figure S97. DSC data recorded for cholesterol derivatives of **2g**, **PPX-2g**, **BrPPX-2g** and **PPV-2g** at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under an atmosphere of N_2 .

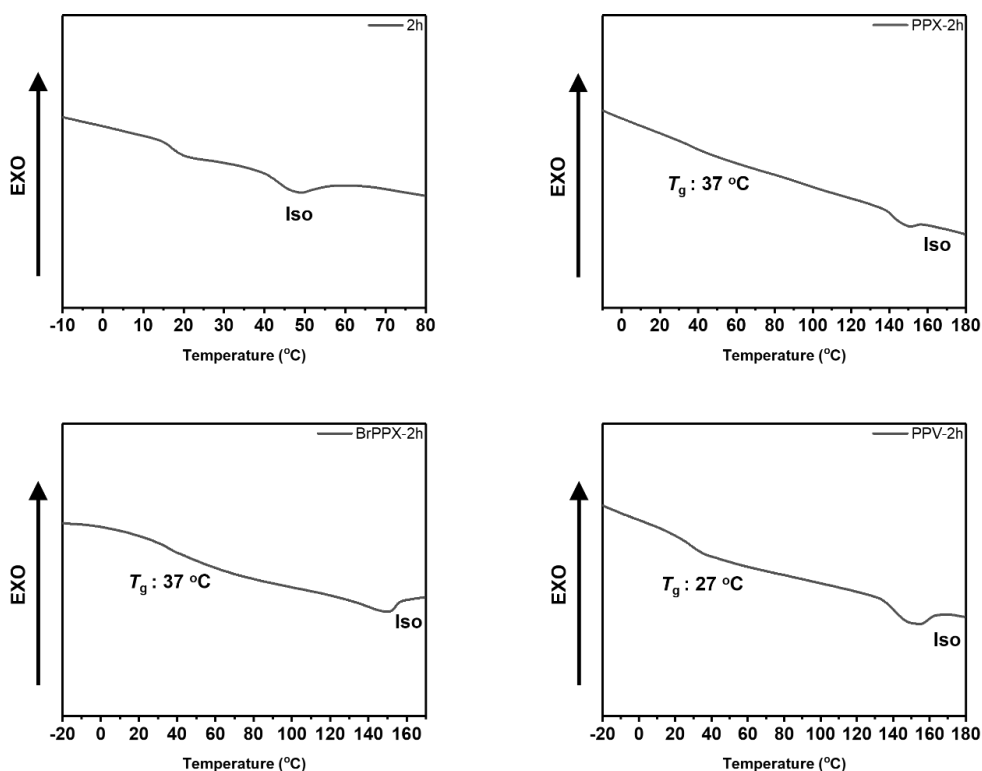


Figure S98. DSC data recorded for cholesterol derivatives of **2h**, **PPX-2h**, **BrPPX-2h** and **PPV-2h** at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under an atmosphere of N_2 .

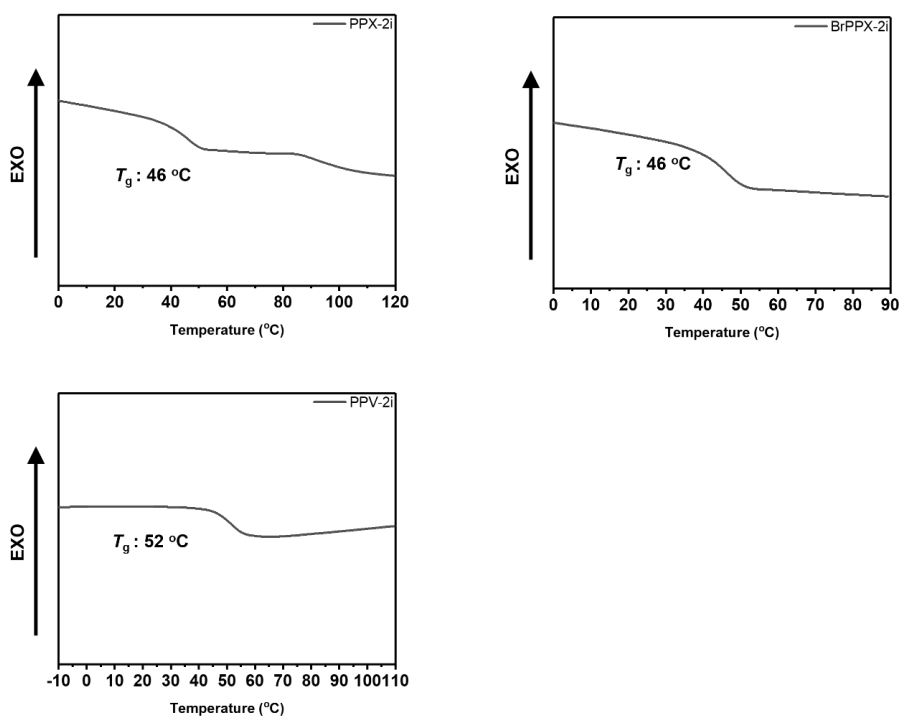


Figure S99. DSC data recorded for azobenzene derivatives of **PPX-2i**, **BrPPX-2i** and **PPV-2i** at a heating rate of 20 °C min⁻¹ under an atmosphere of N₂.

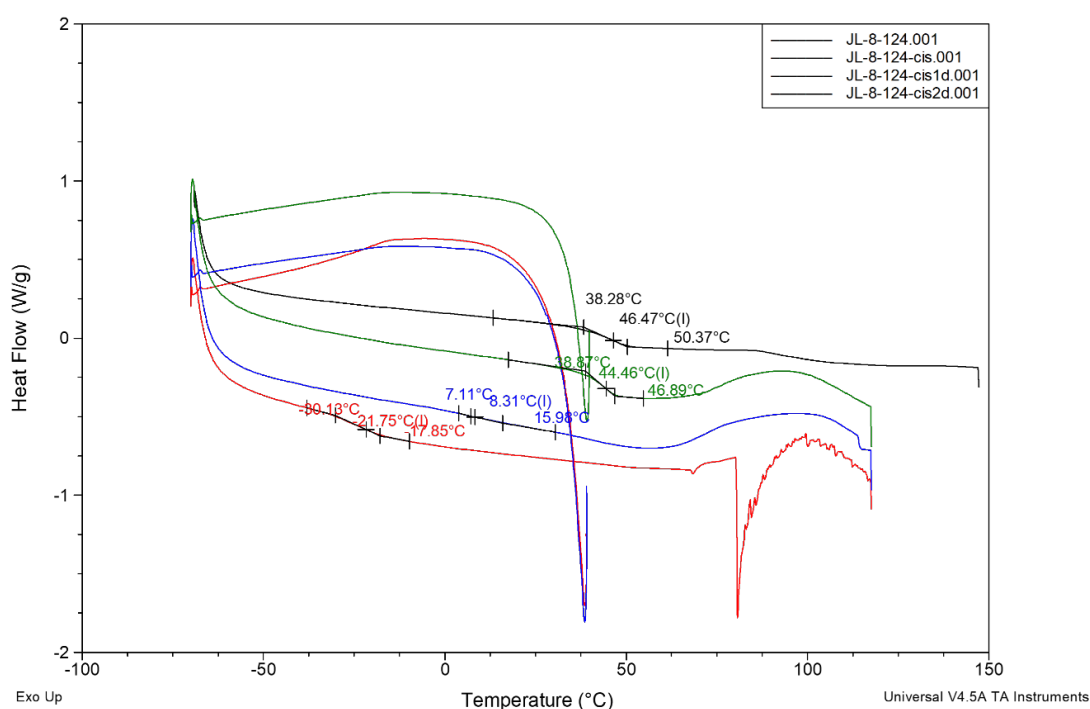


Figure S100. DSC data recorded for **PPX-2i** before (black) and after irradiation at 365 nm for 4 h to facilitate the photoisomerization of *trans* to *cis* (red, 92% *cis* by ¹H NMR). The *cis* isomer was kept in the dark and checked via DSC after 1 d (blue, 47% *cis* by ¹H NMR) and 2 d (green, 30% *cis* by ¹H NMR). The broad exothermic signals recorded at 70 °C were assigned to the thermal isomerization of *cis* to *trans*. All measurements are performed at a heating rate of 20 °C min⁻¹ and under an atmosphere of N₂.

Polarized Optical Microscopy Data

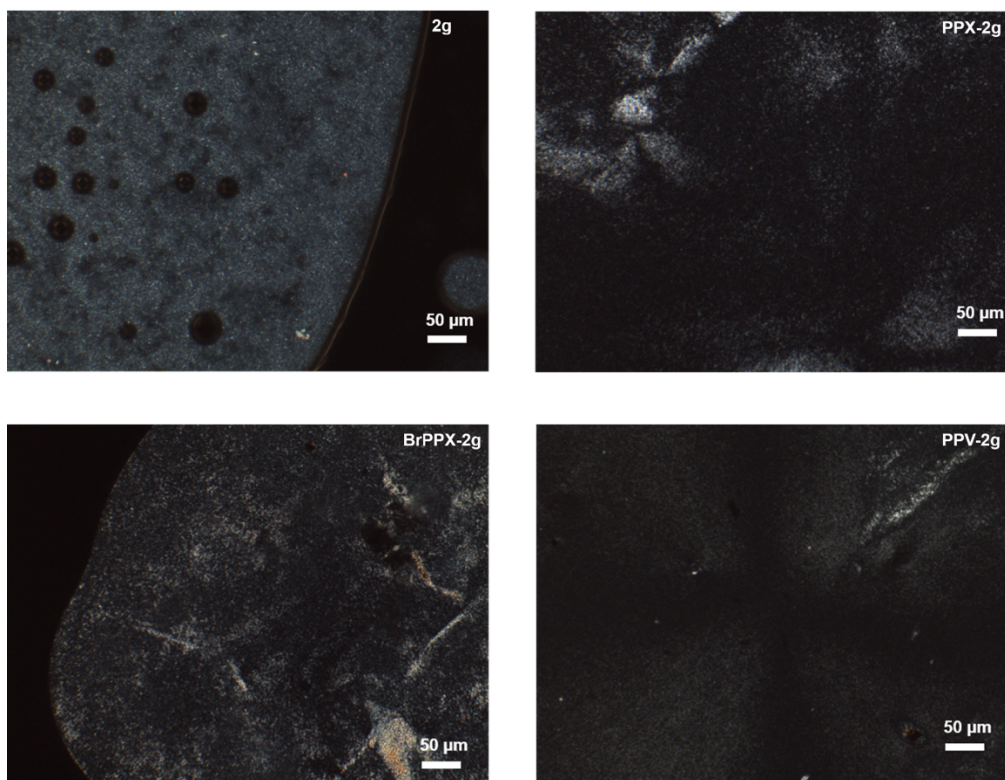


Figure S101. POM images recorded for the cholesterol derivatives of **2g** at 70 °C, **PPX-2g** at 120 °C, **BrPPX-2g** at 160 °C and **PPV-2g** at 120 °C.

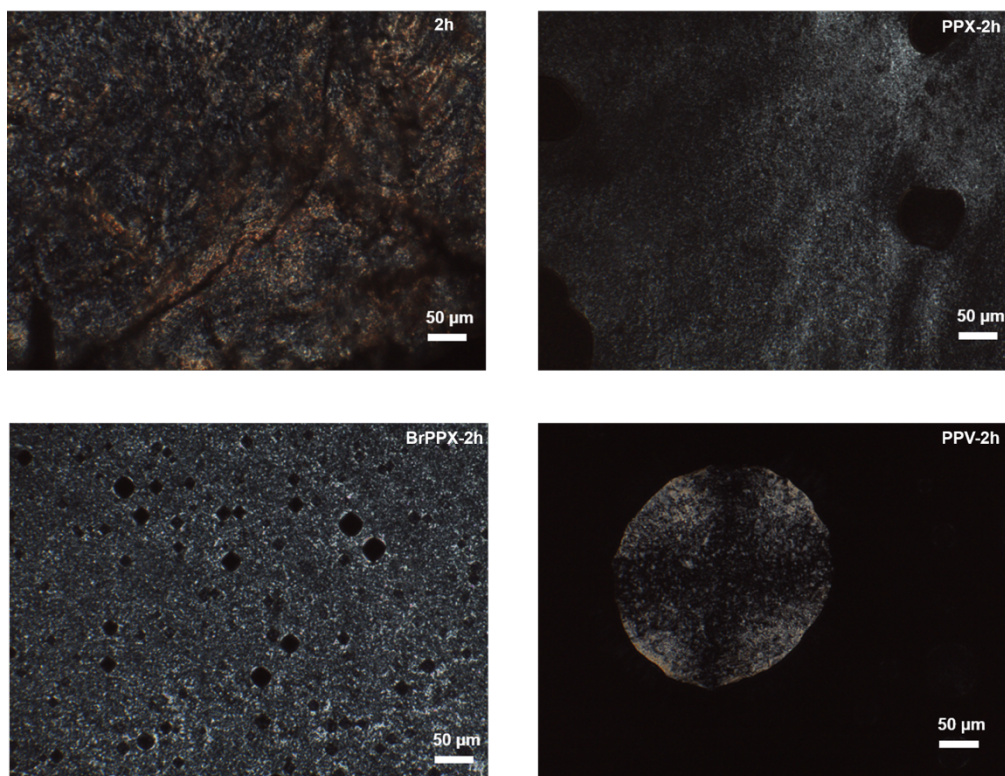


Figure S102. POM images recorded the cholesterol derivatives of **2h** at 25 °C, **PPX-2h** at 130 °C, **BrPPX-2h** at 110 °C and **PPV-2h** at 120 °C.

X-Ray Diffraction Data

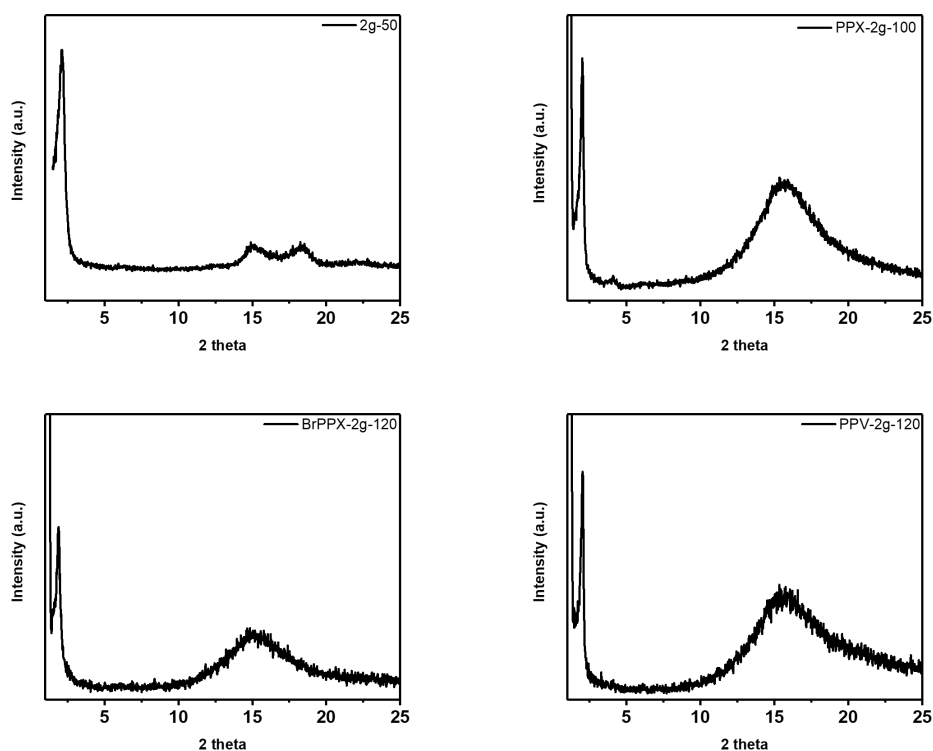


Figure S103. XRD data recorded for the cholesterol derivatives of **2g** at 50 °C, **PPX-2g** at 100 °C, **BrPPX-2g** at 120 °C and **PPV-2g** at 120 °C.

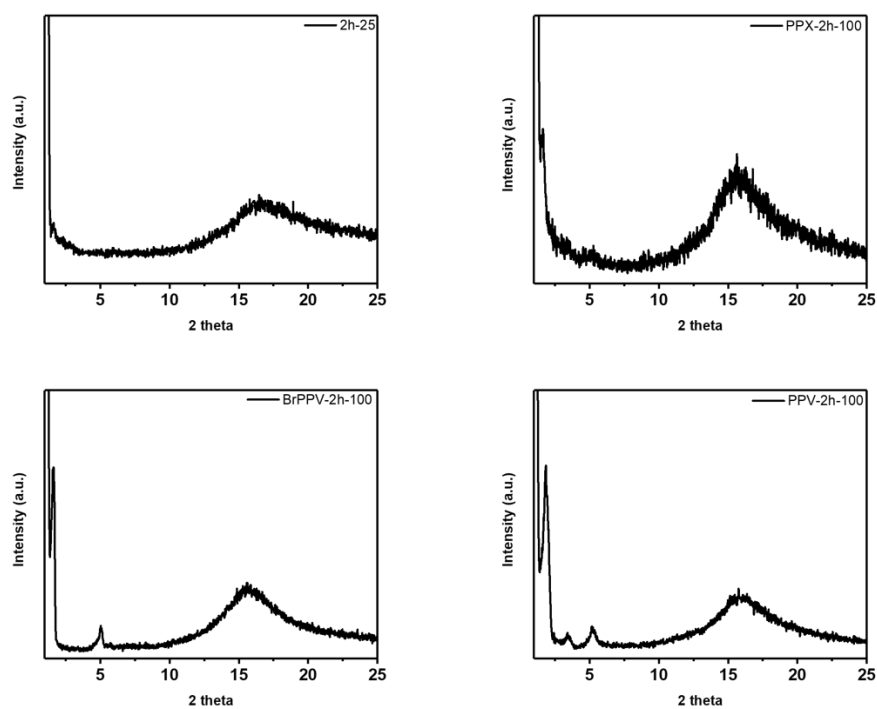


Figure S104. XRD data recorded for the cholesterol derivatives of **2h** at 25 °C, **PPX-2h** at 100 °C, **BrPPX-2h** at 100 °C and **PPV-2h** at 100 °C.

Additional UV-vis Spectroscopy Data

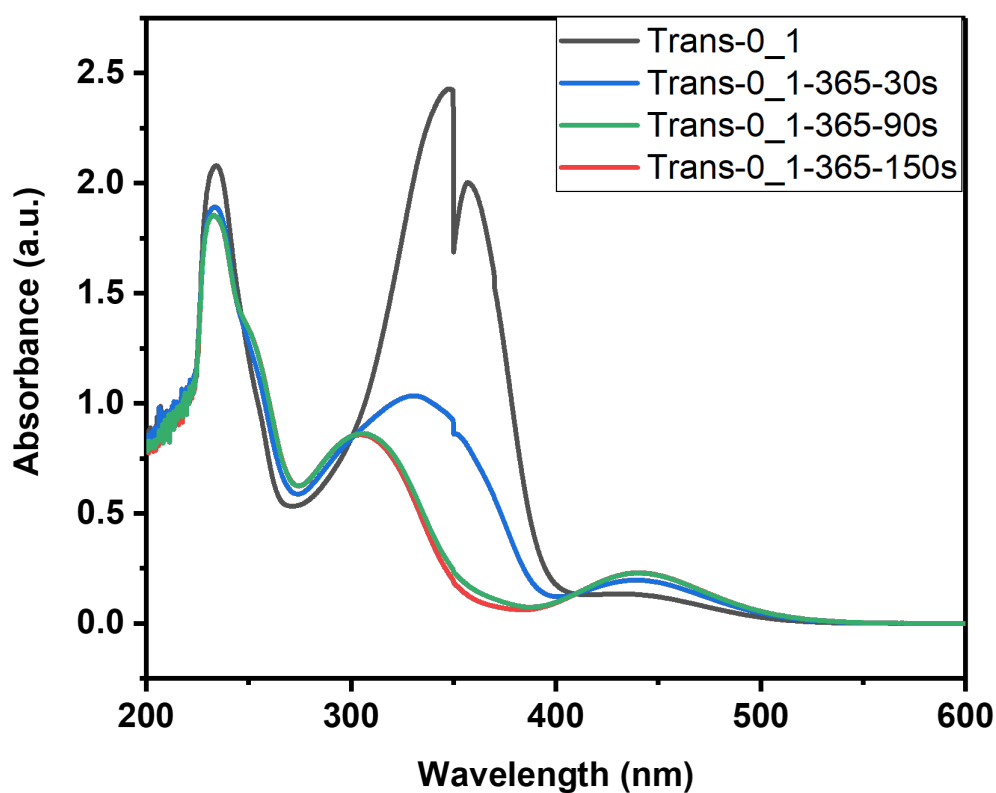


Figure S105. UV-vis spectra recorded for a solution of **PPX-2i** in CH₂Cl₂ (concentration: 4.2×10^{-5} M) to ascertain the photostationary state of *cis* formation over time. Note: 96% *cis* was measured after 150 s of irradiation (red) using the following equation: $([cis]/[trans]_0) = (1 - A/A_0)(1 - \epsilon_{cis}/\epsilon_{trans})$, where $[cis]$ = concentration of the *cis* fraction, $[trans]_0$ = initial concentration of the *trans* fraction, A = absorbance at λ_{max} (348 nm) and $\epsilon_{cis}/\epsilon_{trans} = 0.050$ (from the literature)⁸. UV source: Hg lamp, 300 W, 8 cm distance.

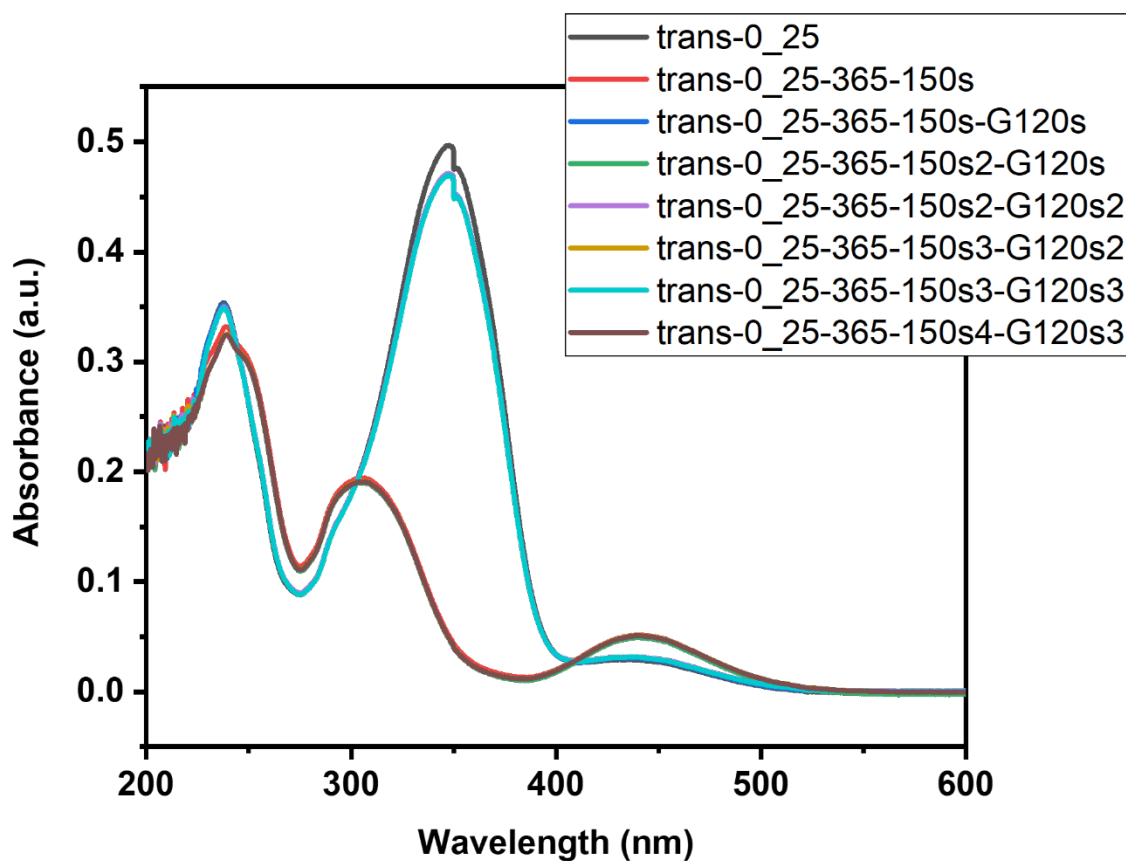


Figure S106. UV-vis spectra recorded for a solution of **PPX-2i** in CH₂Cl₂ (concentration: 1.1×10^{-5} M) and used to assess photofatigue. UV source: Hg lamp, 300 W, 8 cm distance. Visible light source: green LED (520 nm).

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