Supporting Information

for

Side Chain Liquid Crystalline Polymers Bearing Achiral Mesognes and an Optically Active Polynorbornene Backbone

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General considerations. Hoveyda-Grubbs 2nd generation catalyst and D-pantolactone were purchased from Aldrich Inc. 4-Butyloxybenzoic acid was purchased from TCI Inc. Acryloyl chloride, cyclopentadiene, $TiCl_4$ (1 M) in petroleum ether solution, 2,5-dihydroxybenzoic acid, benzyl bromide, 3-bromo-1-propanol, 6-bromo-1-propanol, dicyclohexylcarbodiimide (DCC), and dimethylaminopyridine (DMAP) were purchased from Aladdin Inc. Liquid crystal cells were purchased from Instec Inc. THF was distilled from sodium benzophenone ketyl under nitrogen. Other chemical reagents were used without further purification. All non-aqueous reactions were conducted in oven-dried glasswares, under a dry nitrogen atmosphere. A Sigma 2K 15 centrifuge was used for isolation of polymers after precipitation. All flash chromatography were performed using Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm).

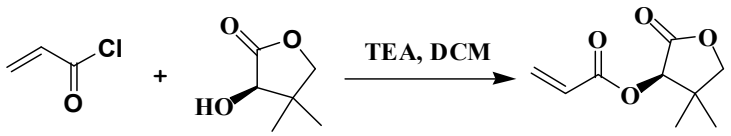
All ^1H and ^{13}C NMR spectra were obtained using either a Bruker HW500MHz

spectrometer (AVANCE AV-500) or a Bruker HW300 MHz spectrometer (AVANCE AV-300), using $CDCl_3$ as the solvent and tetramethylsilane as the interior reference. High-resolution mass spectrometry to obtain accurate mass was obtained with a Waters micromass Q-TOF micro system mass spectrometer in positive ion mode. Gel permeation chromatography (GPC) was performed on an HP 1100 high pressure liquid chromatography (HPLC), equipped with an HP 1047A refractive index detector and a Plgel MIXED-C 300−7.5 mm column (packed with 5 μm particles). The column packing allowed the separation of polymers over a wide molecular weight range of 200−3000000. THF was used as the eluent at a low flow rate of 1 mL/min at 45 °C. Polystyrene standards were used as the references. Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) under nitrogen purge at a heating rate of 10 °C/min from −50 to +150 °C. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA7.

Polarized optical microscopy (POM) observations of the liquid crystalline textures of the monomers, polymers were performed on an Olympus BX53P microscope with a Mettler PF82HT hot stage. The images were captured using a Microvision MV-DC200 digital camera with Phenix Phmias2008 Cs Ver2.2 software. X-ray scattering experiments were performed with a high-flux small angle X-ray scattering instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system and a temperature control unit (Anton Paar TCS300). At each single steady temperature, both small angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were simultaneously recorded on an imaging-plate (IP) which extended to high-angle range (the q range covered by the IP was from 0.06 to 29 nm^{-1}, $q = 4\pi(\sin\theta)/\lambda$, where the wavelength λ is 0.1542 nm of Cu Kα radiation and 2θ is the scattering angle) at 40 kV and 40 mA for 30 min.

CD and UV-vis spectra were recorded on a Applied Photophysics Chirascan. The sample solution was thermostated at 25 °C. The light path length of the quartz cell used was 1 cm. The concentration was 9.36×10^{-6} and the solvent was THF.

Synthesis and ^{1}H NMR spectra of (-)-(1S,2S)-5-norbornene-2-carboxylic acid.



1 **2** **3**

Pantolactone acrylate (3). Under nitrogen atmosphere, acryloyl chloride (8.7 g, 96.1 mmol) was added slowly to a stirred cold solution(-10 °C) of D-pantolactone (13.0 g, 99.9 mmol) and NEt_3(15.2 g, 150.2 mmol) in dry CH_2Cl_2 (150 mL). The reaction mixture was stirred at -10 °C for 6 h, and then washed with 1 M HCl, saturated aq. $NaHCO_3$ and water. The organic solution was dried over anhydrous magnesium sulfate and then concentrated by rotary evaporation. The crude compound was directly subjected to purification by column chromatography (petroleum ether : ethyl acetate = 12 : 1) to give the desired product **3** (16.1 g, Yield : 87.1%) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) ： δ 6.53 (d, 1H, J = 17.3 Hz), 6.23 (dd, 1H, J = 17.3, 10.5 Hz), 5.98 (d, 1H, J = 10.5 Hz), 5.45 (s, 1H), 4.07 (s, 2H), 1.23 (s, 3H), 1.14 (s, 3H).

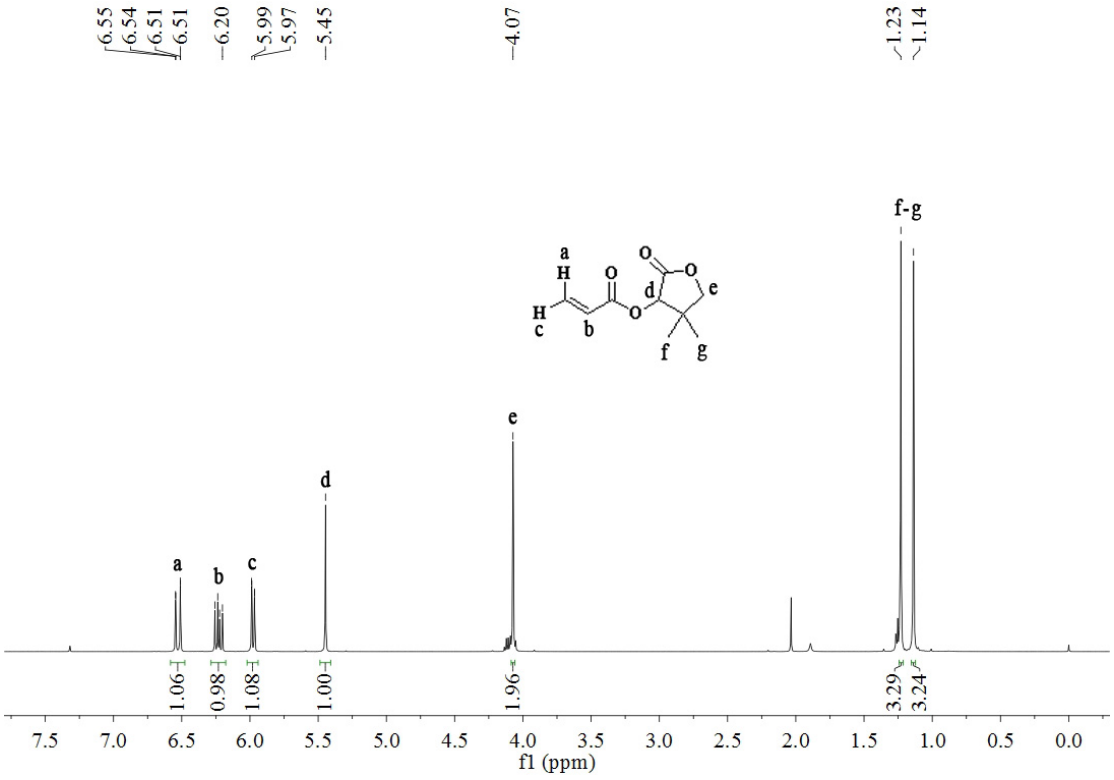
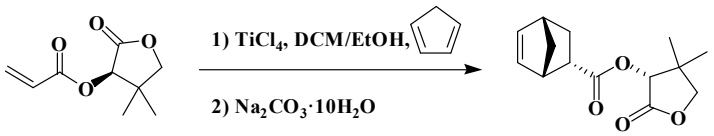


Fig S1. ^{1}H NMR spectrum of Compound **3**.



3 4

Diels–Alder adduct (4). Under nitrogen atmosphere, 1 M $TiCl_4$ (8.7 mL) in petroleum ether was added slowly into a solution of pantolactone acrylate **3** (16.0 g, 87.0 mmol) in dry CH_2Cl_2/petroleum ether (7/1, 160 mL) at -10 °C. After the reaction mixture has been stirred for 30 minutes, freshly distilled cyclopentadiene (7.2 g, 105.9 mmol) was added. After stirring for another 3 h at -10 °C, the reaction was quenched by addition of finely pulverized $Na_2CO_3 \cdot 10H_2O$. The mixture was cooled to r.t., the newly formed precipitate was then filtered off. The filtrate was concentrated and the resulting crude compound was purified by two recrystallizations in n-hexane/AcOEt (5/3) solvent to give the desired product (14.8 g, Yield: 68.1 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.26 (m, 1H), 5.91 (m, 1H), 5.33 (s, 1H), 4.03 (d, 2H, J = 9.0 Hz), 3.27 (s, 1H), 3.20 – 3.11 (m, 1H), 2.95 (s, 1H), 1.95 (m, 1H), 1.52 – 1.44 (m, 2H), 1.33 (m, 1H), 1.18 (s, 3H), 1.15 (s, 3H).

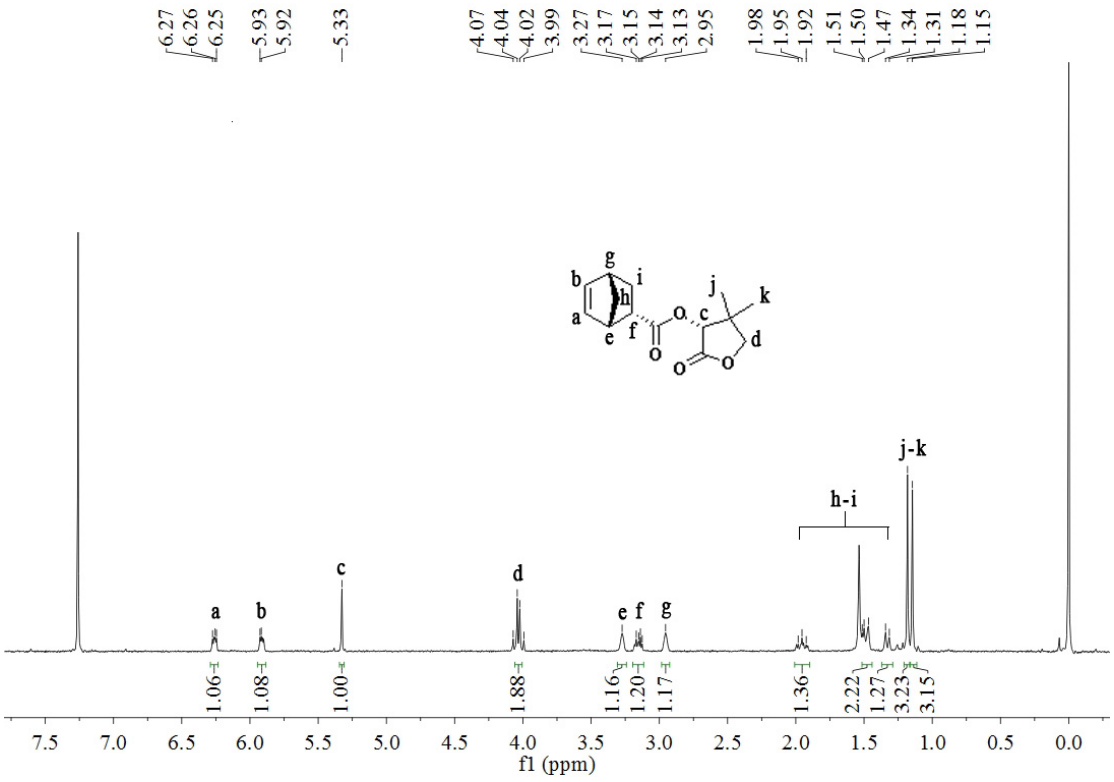
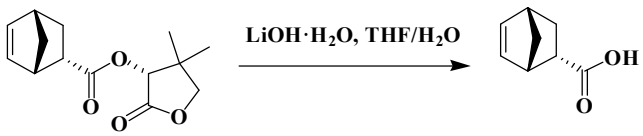


Fig S2. ^{1}H NMR spectrum of Compound **4**.



4 5

(-)-(1S,2S)-5-norbornene-2-carboxylic acid (5). A mixture of compound **4** (6.2 g, 24.8 mmol) and $LiOH·H_2O$ (4.4 g, 104.9 mmol) in THF/water (5/4, 125 mL) was vigorously stirred at r.t. for 26 h. THF was then evaporated in vacuo, the aqueous solution was acidified and extracted with n-pentane/CH_2Cl_2 (98/2). The organic phases were dried over anhydrous sodium sulfate. After evaporation of the solvents, faint yellow solid (2.5 g, Yield: 72.8 %) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.61 (s, 1H), 6.21 (dd, 1H, J = 7.05, 3.85 Hz), 6.00 (dd, 1H, J = 7.05, 3.5 Hz), 3.24 (s, 1H), 3.00 (m, 1H), 2.92 (s, 1H), 1.96 – 1.88 (m, 1H), 1.45 (m, 1H), 1.43 – 1.37 (m, 1H), 1.29 (m, 1H).

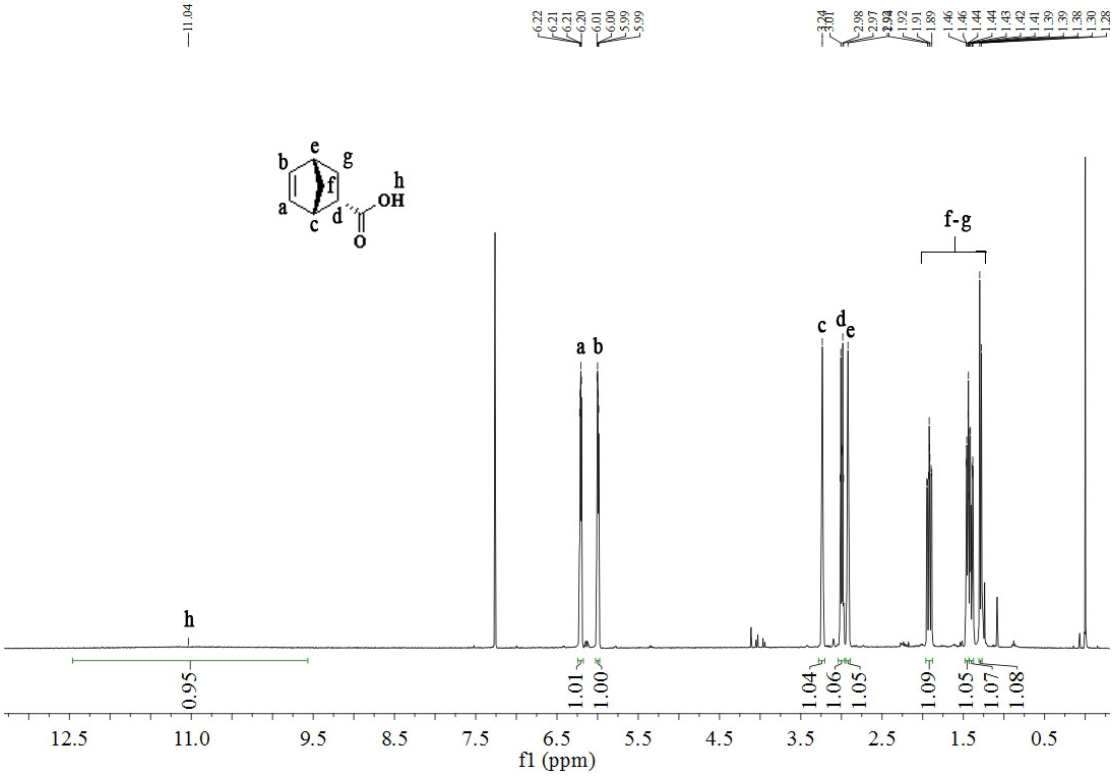
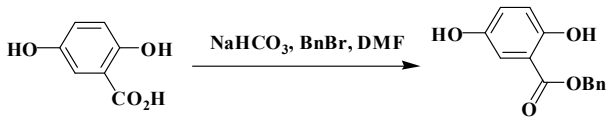


Fig S3. ^{1}H NMR spectrum of Compound **5**.

Synthesis of Side-on Mesogens.



6 **7**

Benzyl 2,5-Dihydroxybenzoate (7). 2,5-Dihydroxybenzoic acid **6** (6.16 g, 40.0 mmol) was dissolved in dry DMF (60 mL). $NaHCO_3$ (9.9 g, 117.8 mmol) was added and the reaction mixture was stirred at 70 °C for 1 h. Benzyl bromide (6.84 g, 40.0 mmol) were then added slowly and the mixture was stirred at 70 °C for additional 7 h. After cooling to room temperature, the reaction mixture was diluted with 200 mL water and extracted twice with n-hexane/ethyl acetate (1/1, 100 mL). The organic layer was washed twice with water, followed by drying over anhydrous magnesium sulfate. Then, the filtrate was concentrated under reduced pressure to give crude products. The final purification was carried out by column chromatography to give the product **7** (7.6 g, Yield: 77.7 %) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 - 7.34 (m, 5H), 7.31 (d, 1H, J = 3.05 Hz), 7.04 - 6.81 (m, 2H), 5.36 (s, 2H), 4.52 (s, 2H).

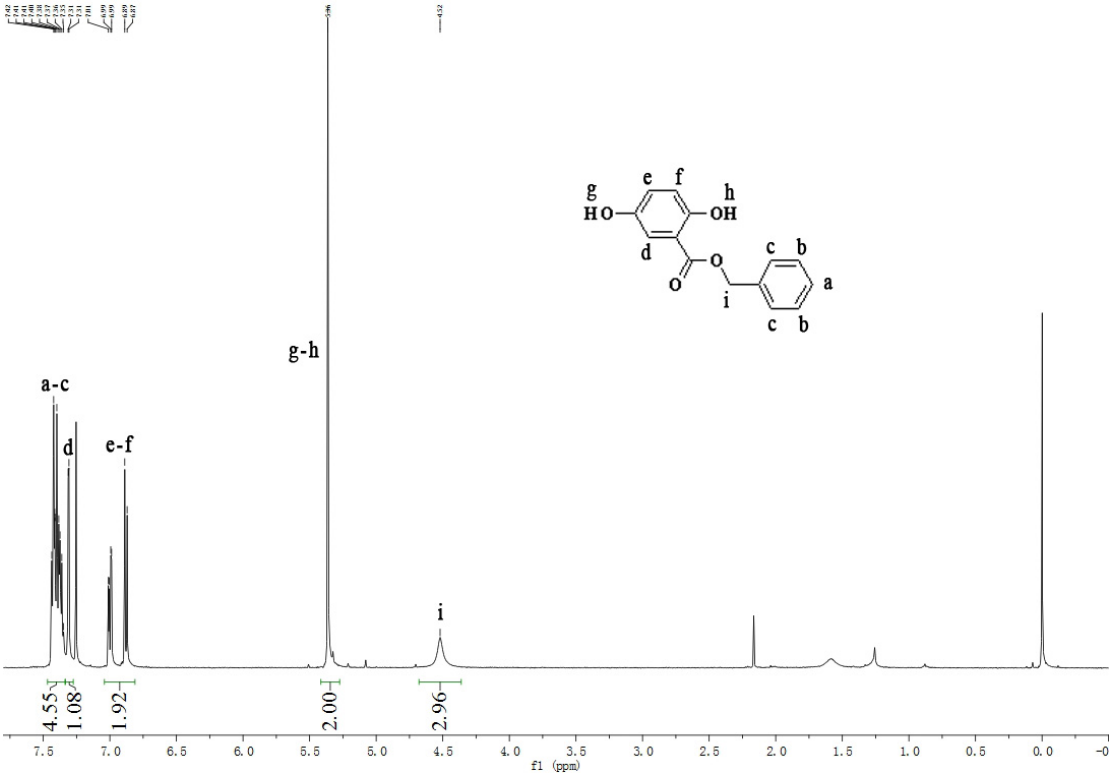
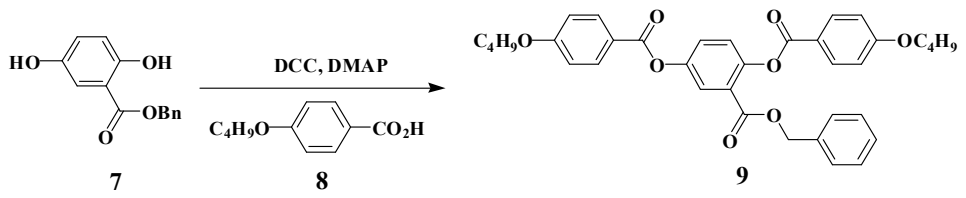


Fig S4. ^{1}H NMR spectrum of Compound **7**.



Benzyl 2,5-Di(4'-butyloxybenzoyloxy)benzoate (9). 4-Butyloxybenzoic acid (**8**) (10.5 g, 54.0 mmol), compound **7** (6.0 g, 24.6 mmol), DMAP (0.8 g, 5.4 mmol) and dry CH_2Cl_2 (150 mL) were added into a 250 mL round-bottom flask. Under a nitrogen atmosphere, DCC (11.1 g, 54.0 mmol) was added into the above flask in one portion at r.t. The reaction mixture was stirred at r.t. for 12 h. After filtering off the solids, the reaction solution was then concentrated by rotary evaporation and the resulting crude solid was recrystallized in methanol to give the desired product (12.3 g, Yield: 84%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 - 8.01 (m, 4H), 7.9 (d, 1H, J = 2.85 Hz), 7.26 - 7.24 (m, 7H), 7.04 – 6.86 (m, 4H), 5.19 (s, 2H), 4.06 (t, 4H, J = 6.45 Hz), 1.8 (m, 4H), 1.5 (m, 4H), 1.0 (t, 6H, J = 7.25 Hz).

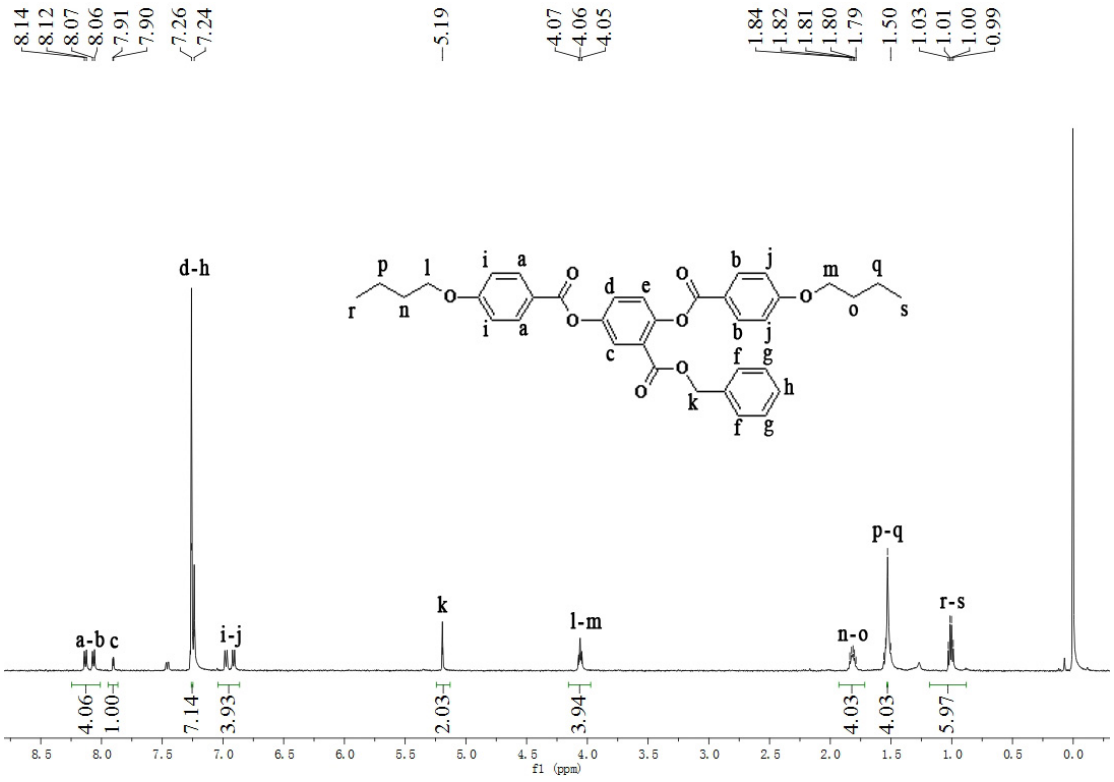
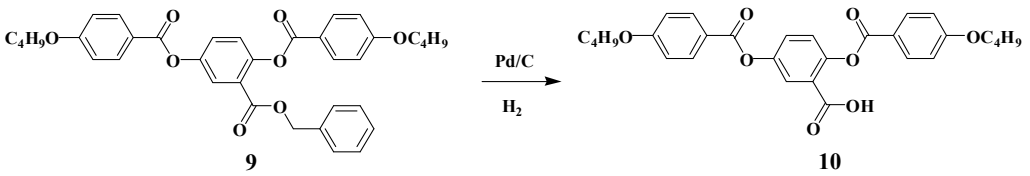


Fig S5. ^{1}H NMR spectrum of Compound **9**.



2,5-Di(4'-butyloxybenzoyloxy)benzoic Acid (10). Hydrogen was allowed to bubble through a stirred suspension of 10 % Pd/C (3.0 g) in 200 mL of dichloromethane for 15 minutes. Benzyl ether **9** (12.3 g, 20.6 mmol) was added, and the reaction mixture was stirred at r.t. for 10 h. After filtering through a celite pad, the filtrate was concentrated, and the product (9.6 g, 92 %) was further dried under vacuum. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23-8.07 (m, 4H), 7.9 (d, 1H, J = 2.85 Hz), 7.69-7.38 (dd, 2H, J = 8.7, 2.9 Hz), 7.04 - 6.92 (m, 4H), 4.06 (t, 4H, J = 3.5 Hz), 1.83 (m, 4H), 1.52 (m, 4H), 1.00 (m, 6H).

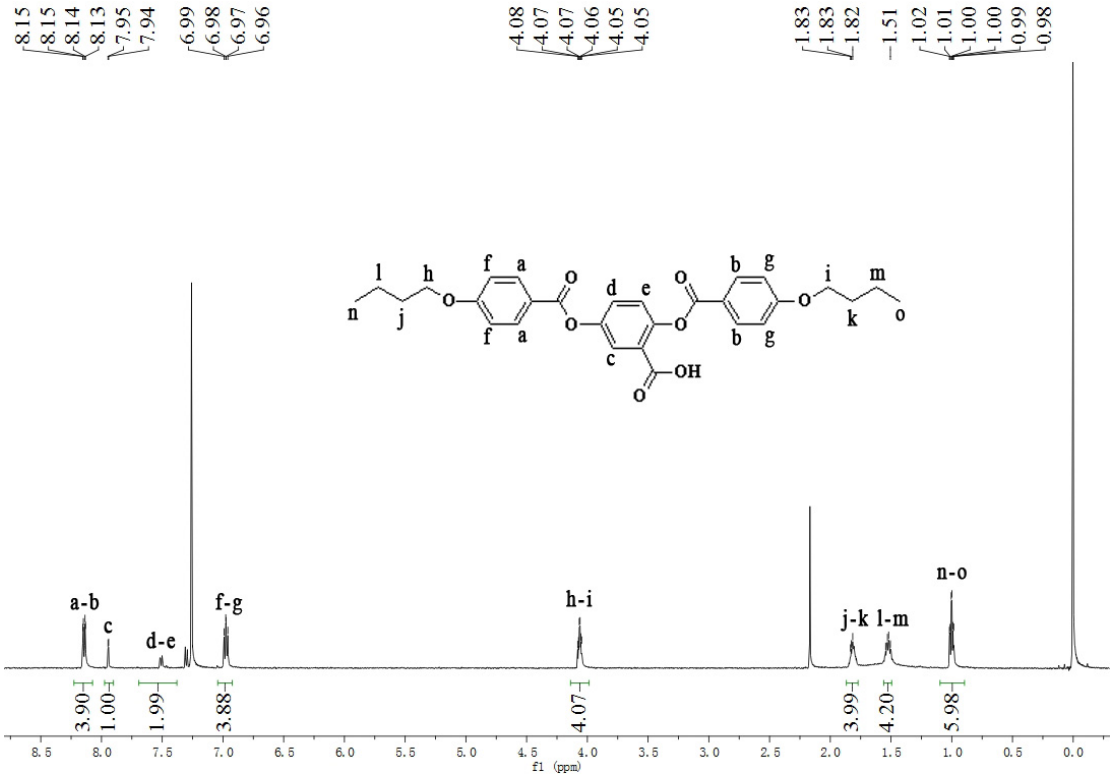
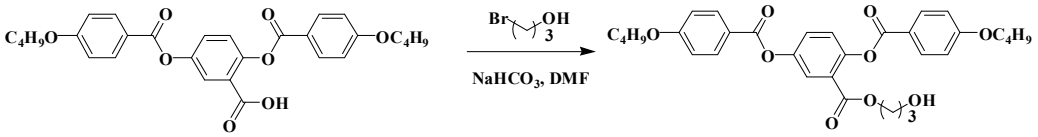


Fig S6. ^{1}H NMR spectrum of Compound **10**.



2,5-Bis-(4-butoxy-benzoyloxy)-benzoic acid 3-hydroxy-propyl ester (11a). To a stirred solution of compound **10** (2.00 g, 3.9 mmol) in DMF (15 mL) was added solid $NaHCO_3$ (1.00 g, 11.8 mmol). The mixture was heated and stirred at 70 °C for 1 h. 3-Bromo-1-propanol (0.7 mL, 7.74 mmol) was added, and the mixture was heated at 70 °C for 7 h. The reaction mixture was cooled to r.t., diluted with water (100 mL), and extracted three times with 100 mL of a hexane/ethyl acetate (1/1) mixture. The organic layer was washed with water (100 mL) and dried over Na_2SO_4. After evaporation of the solvents, the residue was recrystallized twice in ethanol to give the desired product (1.40 g, Yield: 62.8 %) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (m, 4H), 7.89 (d, 1H, J = 2.9 Hz), 7.45 (dd, 1H, J = 8.7, 2.9 Hz), 7.26 (d, 1H, J = 1.6 Hz), 6.98 (d, 4H, J = 8.1 Hz), 4.31 (t, 2H, J = 6.1 Hz), 4.05 (t, 4H, J = 3.5 Hz), 3.57 (m, 2H), 1.87 – 1.77 (m, 4H), 1.77 – 1.70 (m, 2H), 1.53 (m, 4H), 1.00 (t, 6H, J = 7.4 Hz).

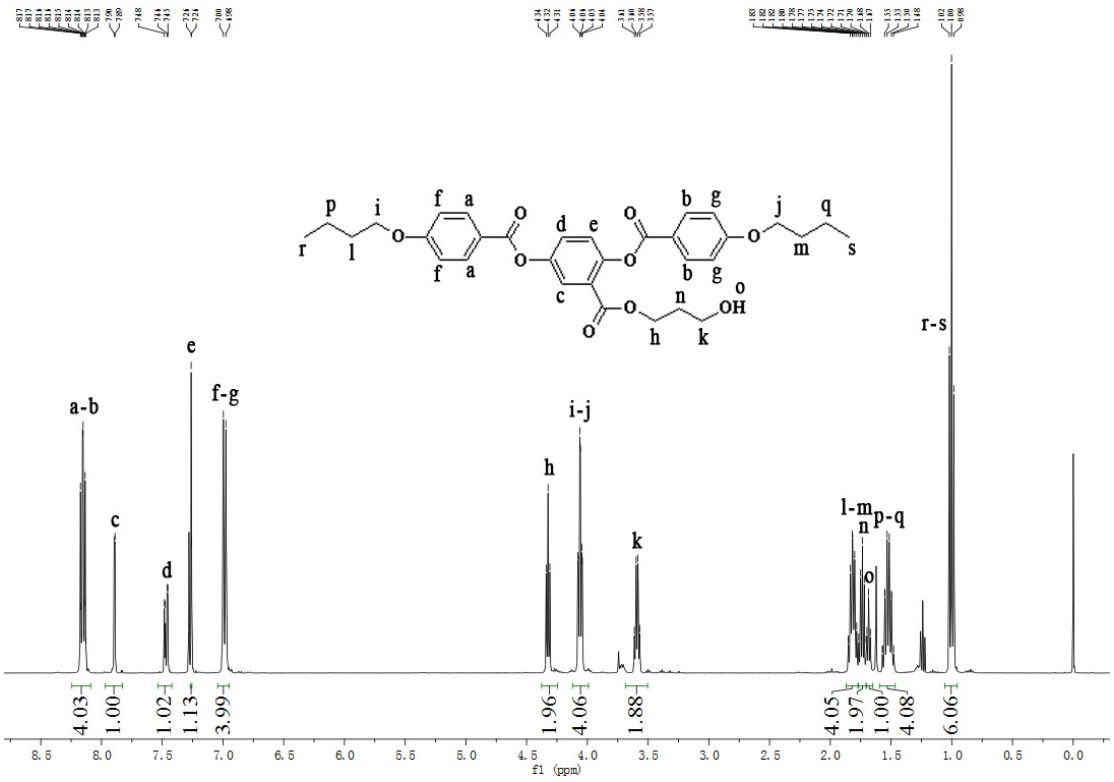
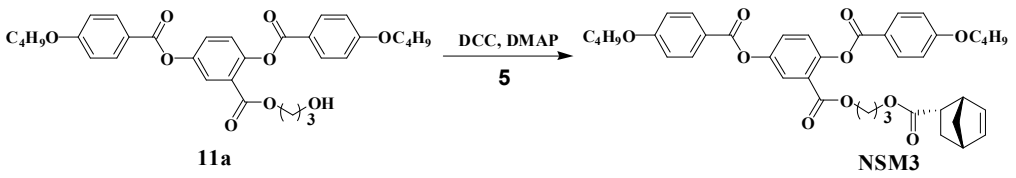


Fig S7. ^{1}H NMR spectrum of Compound **11a**.



Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 3-[2,5-bis-(4-butoxy-benzoyloxy)-benzoyloxy]-propyl ester (NSM3). Compound **11a** (2.48 g, 4.4 mmol), (-)-(1S,2S)-5-norbornene-2-carboxylic acid (**5**) (0.5 g, 3.67 mmol), DMAP (0.09 g, 0.72 mmol) and dry CH_2Cl_2 (25 mL) were added into a 100 mL round-bottom flask. Under a nitrogen atmosphere, DCC (0.91 g, 4.41 mmol) was added into the above flask in one portion at r.t. The reaction mixture was stirred at r.t. for 18 h. After filtering off the solids, the filtrate was then concentrated by rotary evaporation and the resulting crude solid was purified by flash chromatography (5:1 petroleum ether/ethyl acetate) to give the desired product **NSM3** (2.04 g, Yield: 81.3 %) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (m, 4H), 7.89 (d, 1H, J = 2.9 Hz), 7.47 (dd, 1H, J = 8.7, 2.9 Hz), 7.26 (d, 1H, J = 2.5 Hz), 6.98 (d, 4H, J = 8.7 Hz), 6.15 (dd, 1H, J = 5.6, 3.0 Hz), 5.86 (dd, 1H, J = 5.6, 2.8 Hz), 4.25 (t, 2H, J = 4.1 Hz), 4.06 (t, 4H, J = 6.2 Hz), 3.99 (t, 2H, J = 6.2 Hz), 3.13 (s, 1H), 2.89 (m, 2H), 1.90 – 1.75 (m, 7H), 1.56 – 1.48 (m, 4H), 1.45 – 1.32 (m, 2H), 1.24 (m, 1H), 1.00 (t, 6H, J = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.63, 148.34, 148.14, 137.73, 132.26, 124.94, 120.98, 114.37 68.02, 67.99, 60.60 49.58, 45.66, 43.22, 42.47, 31.30, 29.16, 27.84, 19.16, 13.78. ESI-MS m/z: 707.5 $[M + Na]^+$, calculated for **NSM3**, 684.3.

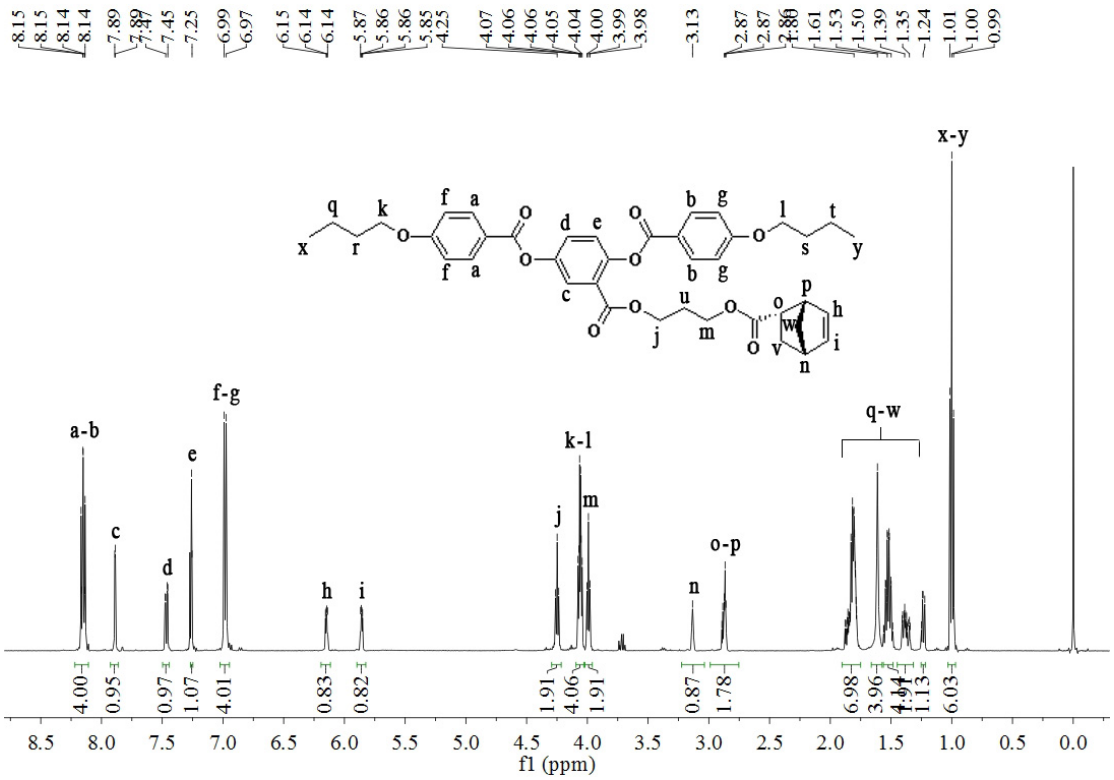


Fig S8. ^{1}H NMR spectrum of monomer **NSM3**.

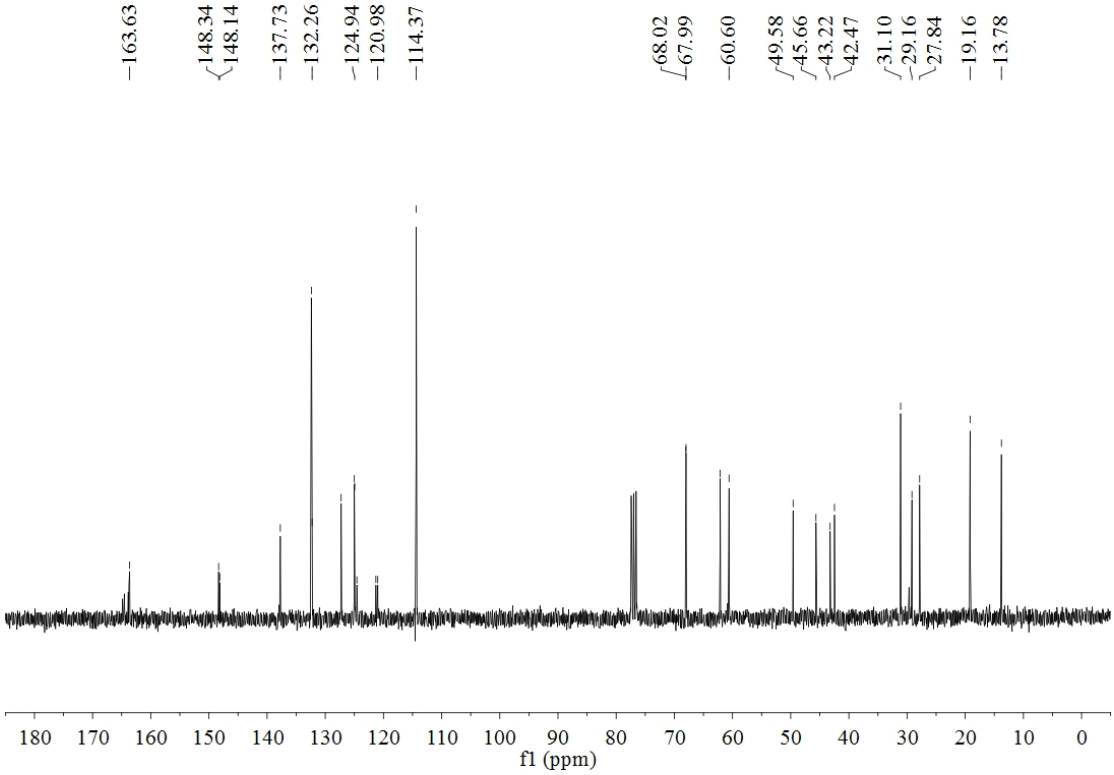


Fig S9. ^{13}C NMR spectrum of monomer **NSM3**.

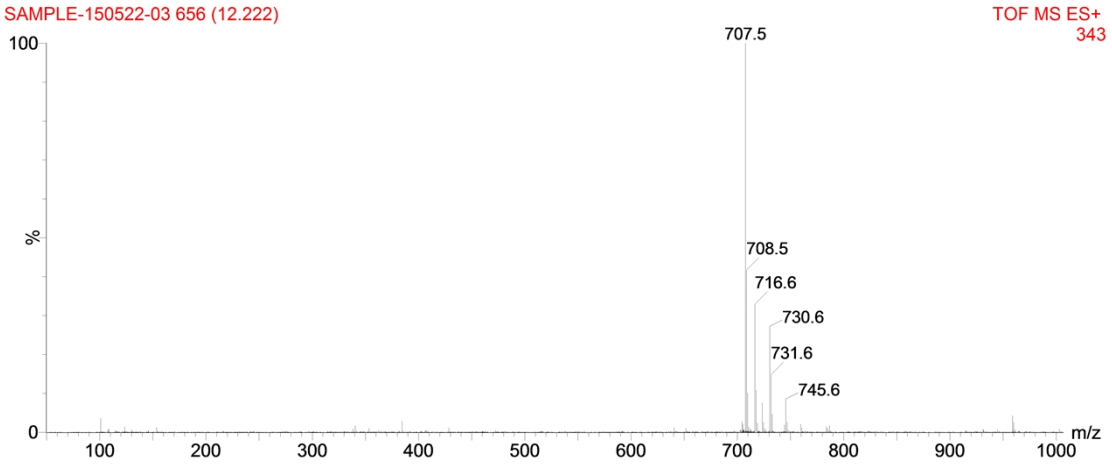


Fig S10. ESI-MS spectrum of **NSM3**.

2,5-Bis-(4-butoxy-benzoyloxy)-benzoic acid 6-hydroxy-hexyl ester (11b). **11b** was prepared following the above described procedure. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (m, 4H), 7.89 (d, 1H, J = 2.9 Hz), 7.45 (dd, 1H, J = 8.7, 2.9 Hz), 7.26 (d, 1H, J = 2.9 Hz), 7.03 – 6.91 (m, 4H), 4.31 (t, 2H, J = 6.6 Hz), 4.05 (t, 4H, J = 6.2 Hz), 3.58 (t, 2H, J = 6.5 Hz), 1.98 – 1.71 (m, 4H), 1.61 – 1.42(m, 2H), 1.27 - 1.20 (m, 4H), 1.00 (t, 6H. J = 7.4 Hz).

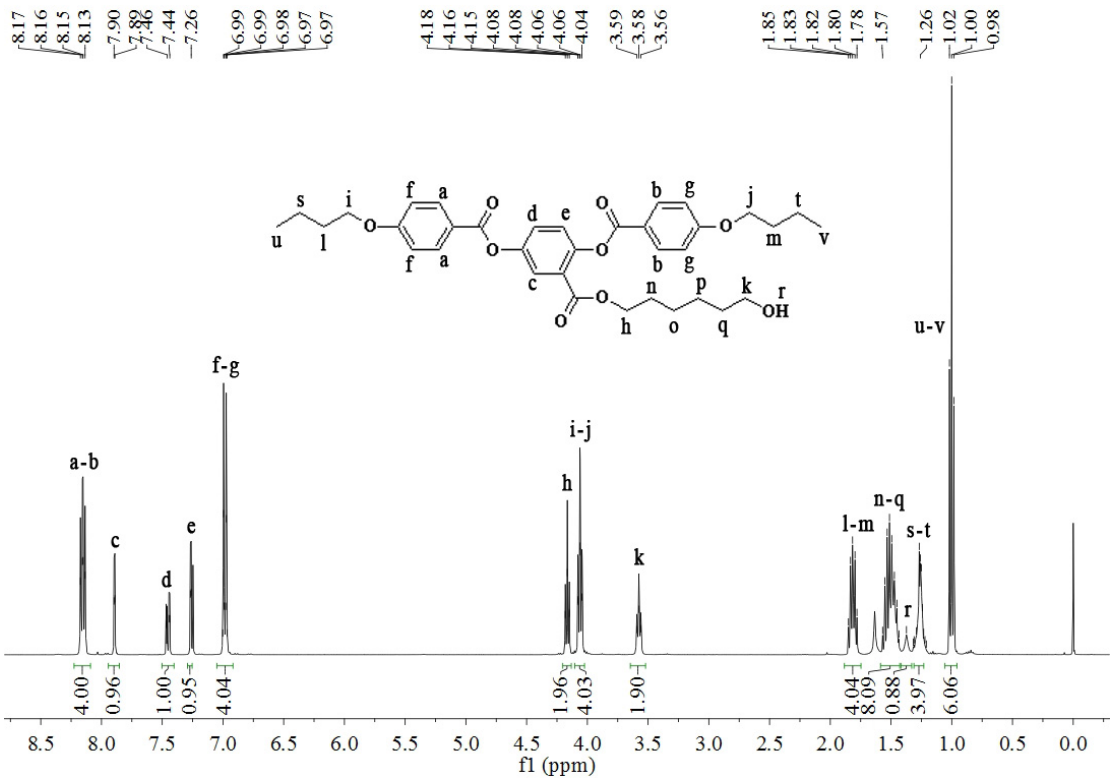


Fig S11. ^{1}H NMR spectrum of Compound **11b**.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 6-[2,5-bis-(4-butoxy-benzoyloxy)-benzoyloxy]-hexyl ester (NSM6). **NSM6** was prepared from **11b** using the same procedure as with **NSM3**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (m, 4H), 7.89 (d, 1H, J = 2.8 Hz), 7.45 (dd, 1H, J = 8.7, 2.9 Hz), 7.26 (d, 1H, J = 2.5 Hz), 6.98 (d, 4H, J = 8.7 Hz), 6.17 (dd, 1H, J = 5.6, 3.0 Hz), 5.90 (dd, 1H, J = 5.6, 2.7 Hz), 4.16 (t, 2H, J = 6.7 Hz), 4.06 (t, 4H, J = 6.5 Hz), 4.01 – 3.90 (m, 2H), 3.18 (s, 1H), 2.95 – 2.84 (m, 2H), 1.91 – 1.85 (m, 1H), 1.86 – 1.73 (m, 4H), 1.58 – 1.45 (m, 8H), 1.44 – 1.37 (m, 2H), 1.32 – 1.39 (m, 5H), 1.00 (t, 6H, J = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.60, 148.32, 148.07, 137.68, 132.35, 124.92, 121.02, 114.37, 114.30, 68.02, 65.34, 64.05, 49.58, 45.67, 43.31, 42.50, 31.10, 28.30, 25.47, 19.16, 13.78. ESI-MS m/z: 749.6 [M + Na]$^{+}$, calculated for **NSM6**, 726.3.

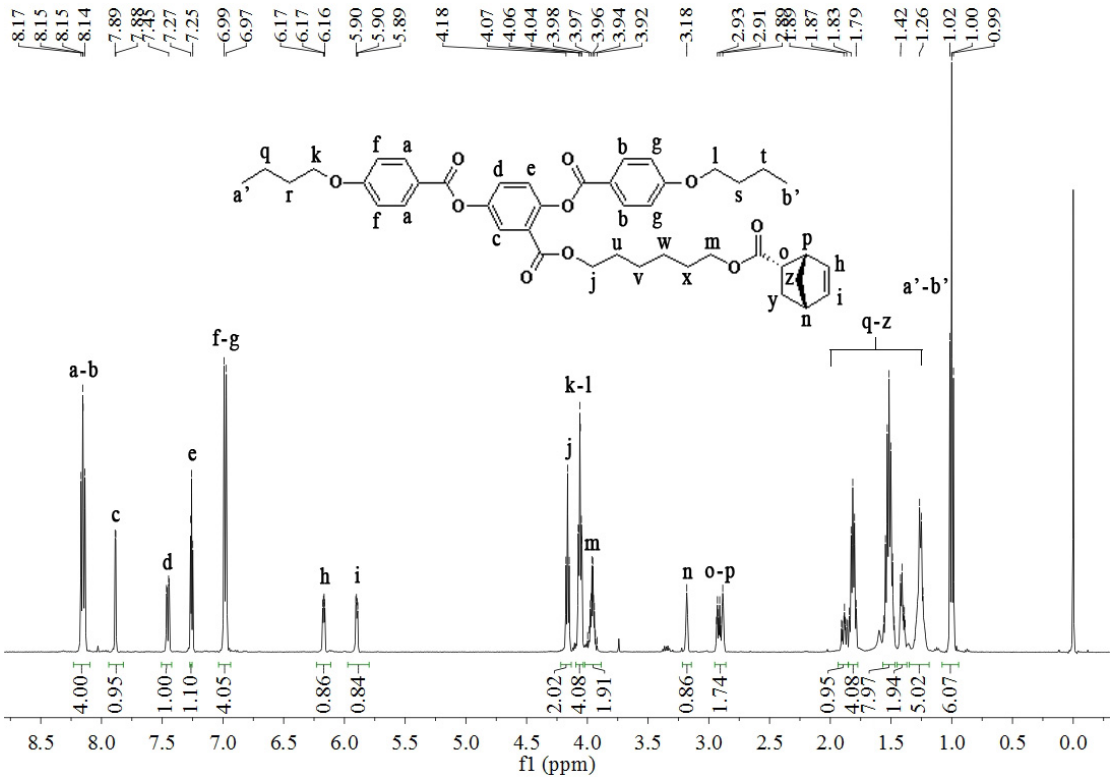


Fig S12. ^{1}H NMR spectrum of monomer **NSM6**.

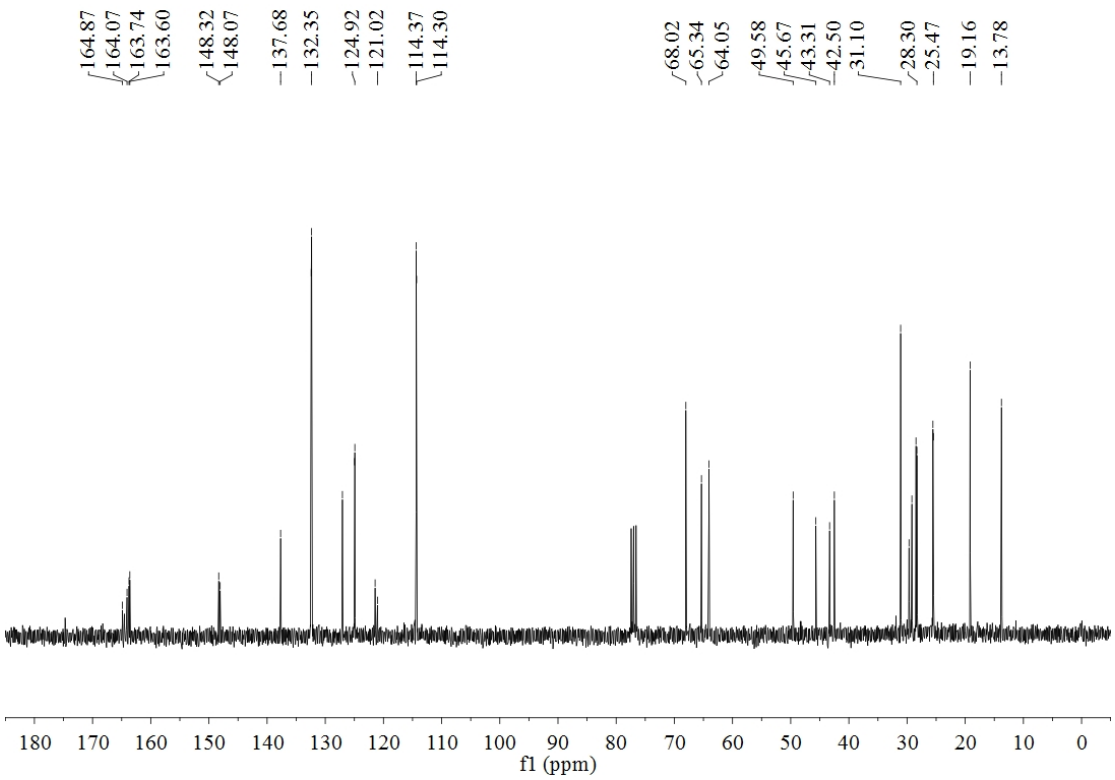


Fig S13. ^{13}C NMR spectrum of monomer **NSM6**.

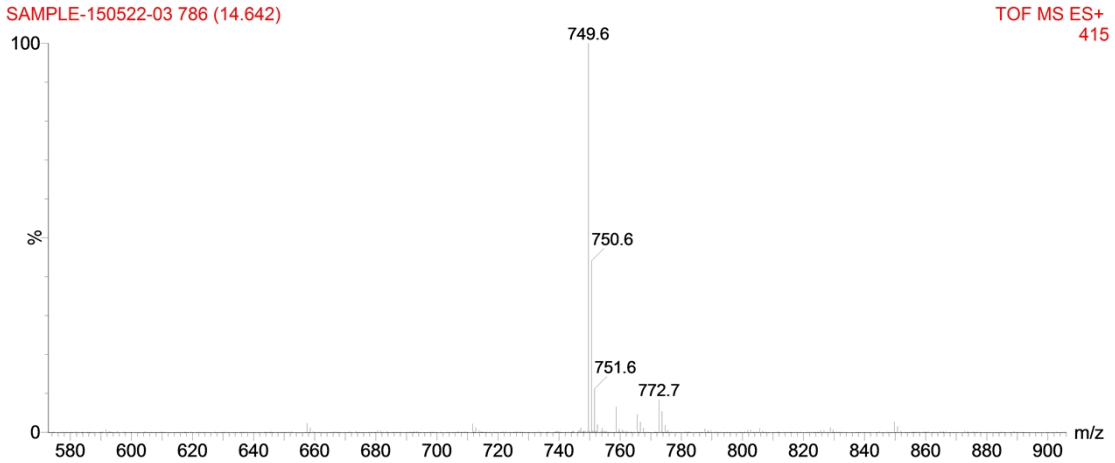
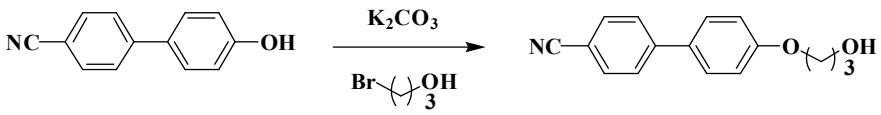


Fig S14. ESI-MS spectrum of **NSM6**.

Synthesis of End-on Mesogens.



13 **14a**

4-cyano-4'-[(3-hydroxypropyl)oxy]biphenyl (14a). 4-cyano-4'-hydroxybiphenyl (2.04 g, 10.5 mmol), 3-bromo-1-propanol (1.62 g, 11.62 mmol), potassium carbonate (2.98 g, 21.55 mmol) and 100 mL acetone were added to a 250 mL round-bottomed flask equipped with a condenser tube, the reaction mixture was stirred at 64 °C for 48 h. After completion of the reaction, the solvent was concentrated under reduced pressure to give a yellow solid. Thereafter, this solid and 70 mL water were mixed together, to which diethyl ether (3 X 50 mL) was added for extraction. The separated organic phase was dried over anhydrous magnesium sulfate and filtered, followed by distilling off the solvent under reduced pressure to provide a yellow solid. This solid was purified by recrystallization from a mixed solvent of hexane/ethyl acetate (2/1) to give the desired product as a white solid (2.46 g, Yield: 92.5%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (m, 4H), 7.55 (d, 2H, J = 8.5 Hz), 7.03 (d, 2H, J = 8.5 Hz), 4.21 (t, 2H, J = 5.9 Hz), 3.91 (t, 2H, J = 5.9 Hz), 2.19 (s, 1H), 2.11 (m, 2H).

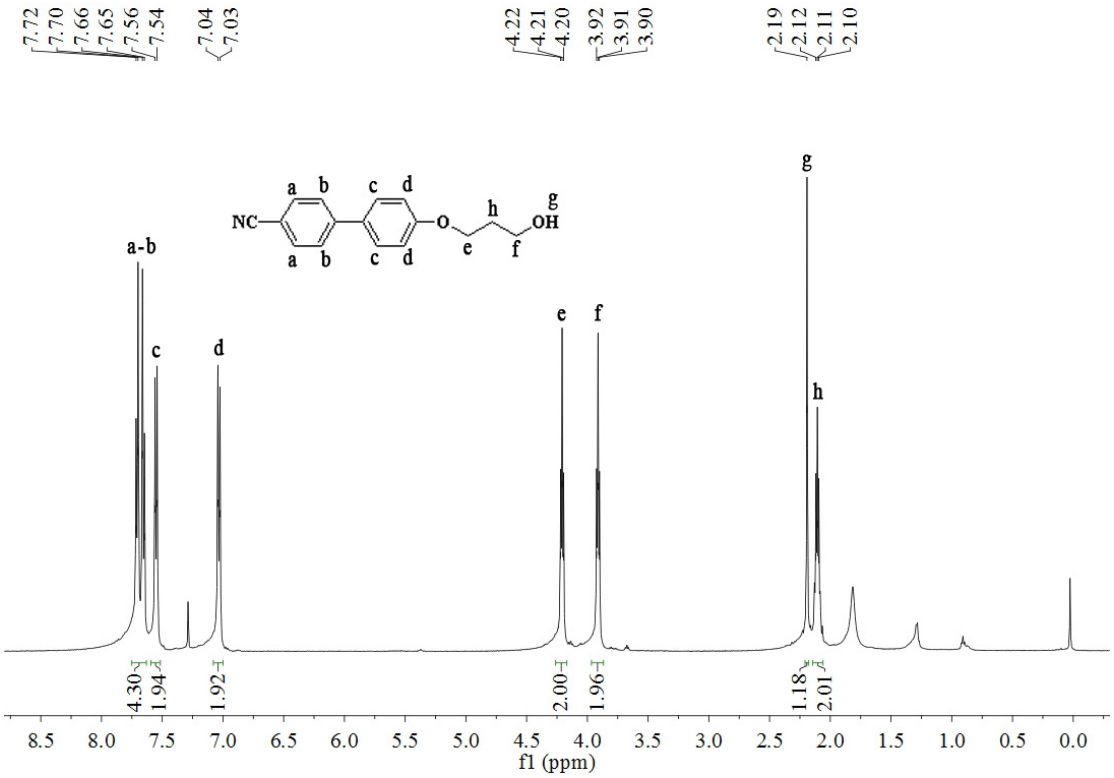


Fig S15. ^{1}H NMR spectrum of Compound **14a**.

14a **NEM3**

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 3-(4'-cyano-biphenyl-4-yloxy)-propyl ester (NEM3). Compound **14** (0.99 g, 3.93 mmol), compound **5** (0.43 g, 3.14 mmol), DMAP (0.04 g, 0.31 mmol) and dry CH_2Cl_2 (20 mL) were added into a 100 mL round-bottom flask. Under a nitrogen atmosphere, DCC (0.81 g, 3.95 mmol) was added into the above flask in one portion at r.t. The reaction mixture was stirred at r.t. for 20 h. After filtering off the solids, the reaction solution was then concentrated by rotary evaporation and the resulting crude solid was purified by flash chromatography (10 : 1 petroleum ether – ethyl acetate) to give the desired product (0.98 g, Yield: 83.8 %) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.88 – 7.59 (m, 4H), 7.54 (d, 2H, J = 8.6 Hz), 7.00 (d, 2H, J = 8.6 Hz), 6.27 – 6.10 (dd, 1H, J = 8.55, 4.95 Hz), 5.95 – 5.82 (dd, 1H, J = 8.65, 4.25 Hz), 4.24 (t, 2H, J = 6.2 Hz), 4.10 (t, 2H, J = 6.1 Hz), 3.21 (s, 1H), 3.08 – 2.87 (m, 2H), 2.14 (m, 2H), 1.90 (m, 1H), 1.57 (s, 1H), 1.44 (d, 1H, J = 9.6 Hz), 1.28 (d, 1H, J = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.65, 159.43, 145.16, 137.84, 132.54, 127.09, 115.07, 114.57, 110.13, 64.57, 60.87, 49.63, 45.74, 43.33, 42.51, 29.20, 28.66. ESI-MS m/z: 396.3 $[M + Na]^+$, calculated for **NEM3**, 373.2.

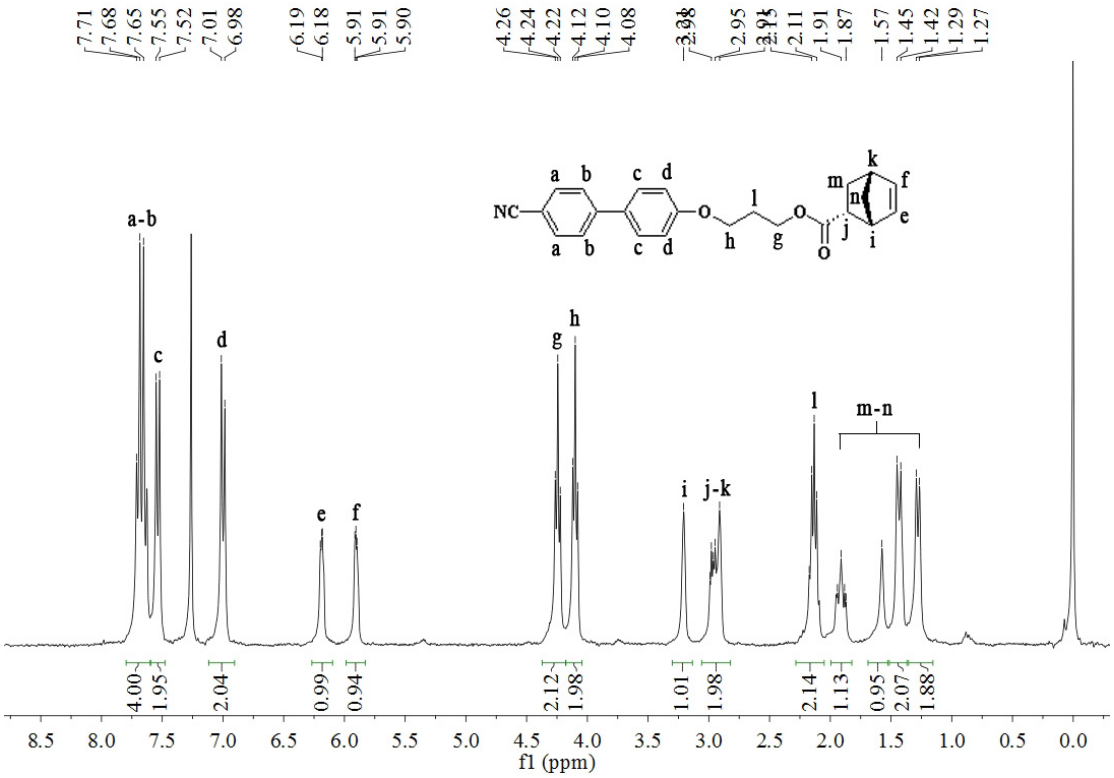


Fig S16. ^{1}H NMR spectrum of monomer **NEM3**.

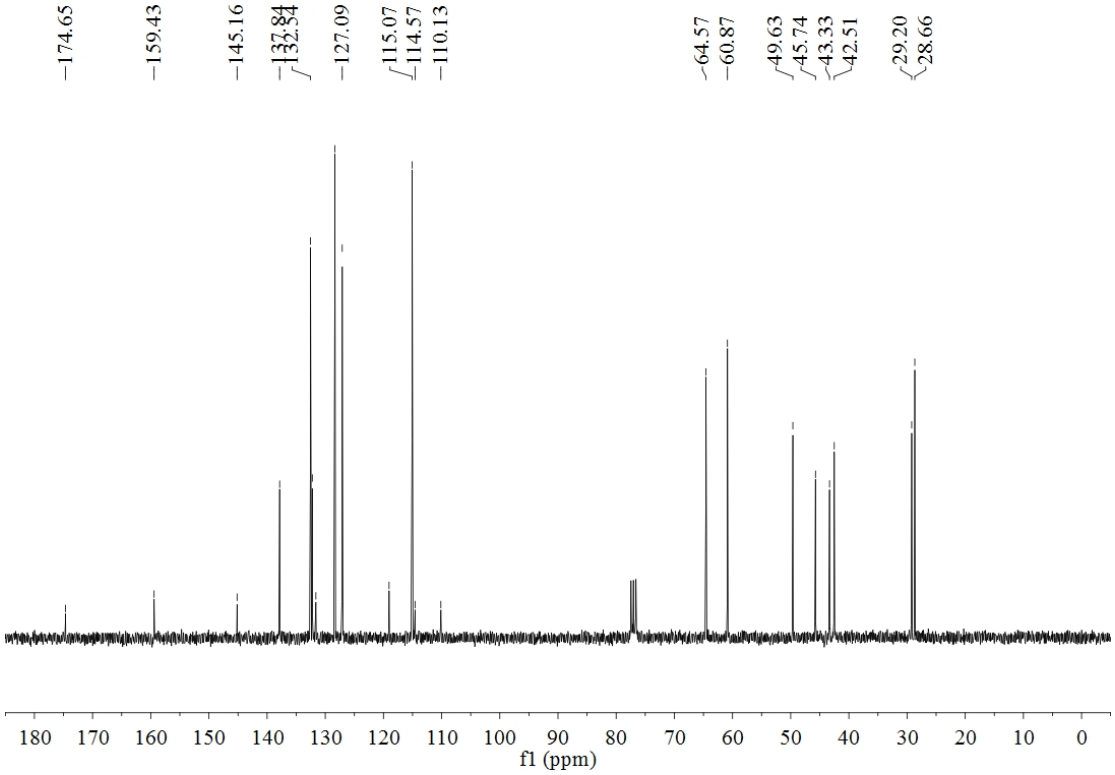


Fig S17. ^{13}C NMR spectrum of monomer **NEM3**.

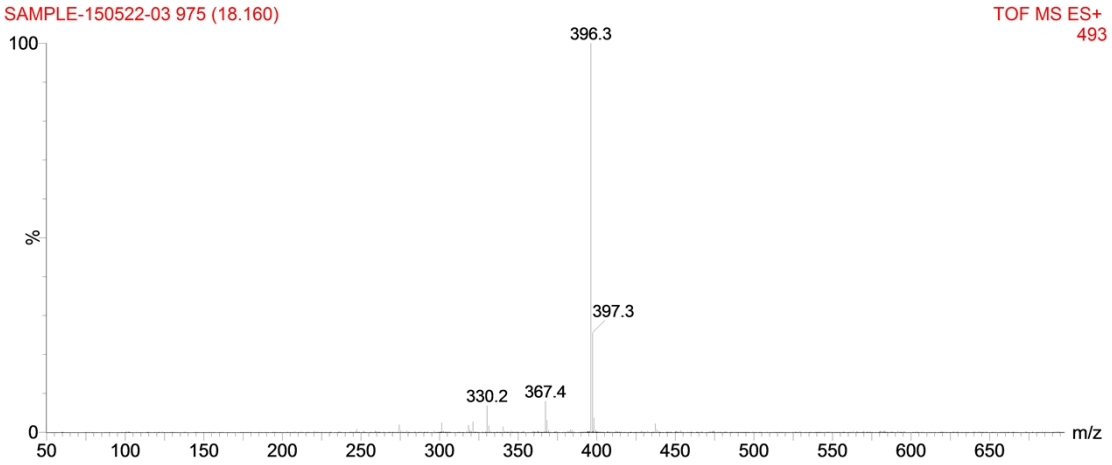


Fig S18. ESI-MS spectrum of **NEM3**.

4-cyano-4'-[(3-hydroxyhexyl)oxy]biphenyl (14b). **14b** was prepared by the same procedure as **14a** by substituting 6-bromo-hexanol for 3-bromo-1-propanol. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (m, 4H), 7.53 (d, 2H, J = 8.6 Hz), 6.99 (d, 2H, J = 8.6 Hz), 4.02 (t, 2H, J = 6.4 Hz), 3.68 (t, 2H, J = 6.4 Hz), 1.70 – 1.59 (m, 2H), 1.49 (m, 6H).

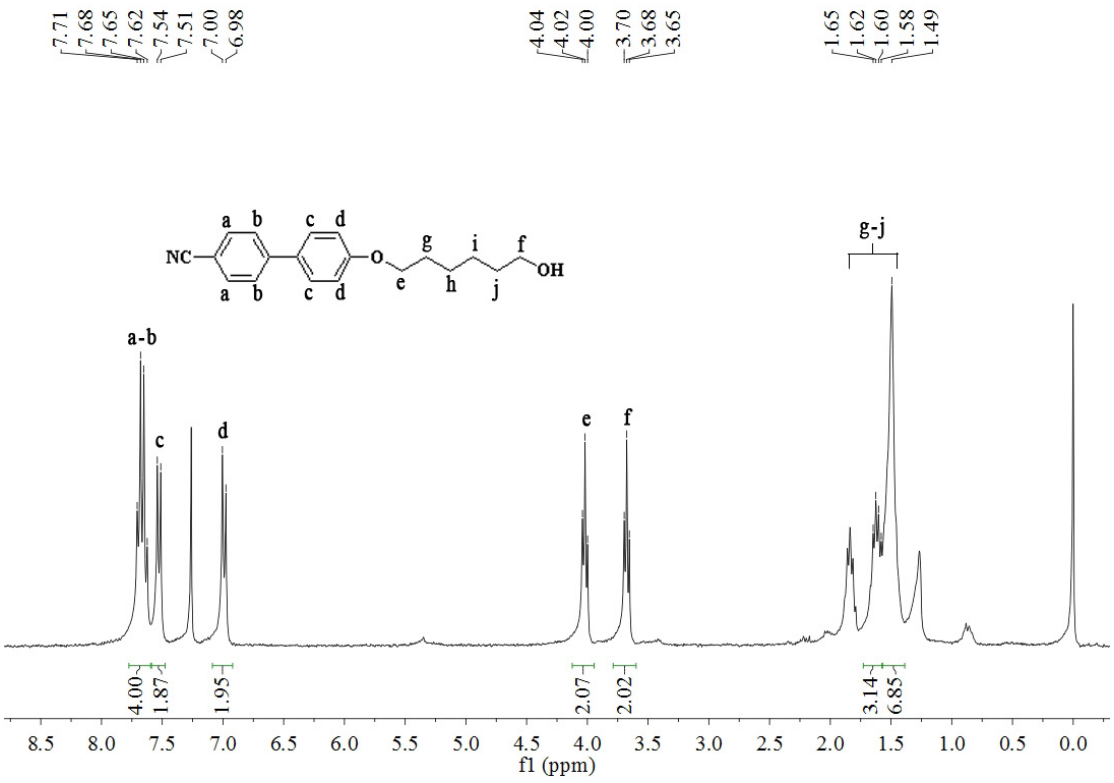


Fig S19. ^{1}H NMR spectrum of Compound **14b**.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 6-(4'-cyano-biphenyl-4-yloxy)-hexyl ester (NEM6). **NEM6** was prepared from **14b** using the same procedure as with **NEM3**. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.66 (m, 4H), 7.53 (d, 2H, J = 8.7 Hz), 6.99 (d, 2H, J = 8.8 Hz), 6.19 (dd, 1H, J = 5.6, 3.1 Hz), 5.92 (dd, 1H, J = 5.6, 2.8 Hz), 4.04 (m, 4H), 3.20 (s, 1H), 3.01 – 2.83 (m, 2H), 1.96 – 1.76 (m, 3H), 1.74 – 1.37 (m, 9H), 1.32 – 1.24 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.77, 159.72, 145.23, 137.72, 132.31, 127.04, 115.06, 110.04, 67.92, 64.07, 49.60, 45.70, 43.34, 42.51, 29.66, 29.17, 29.09, 28.59, 25.72, 25.68. ESI-MS m/z: 438.4 $[M + Na]^+$, calculated for **NEM6**, 415.2.

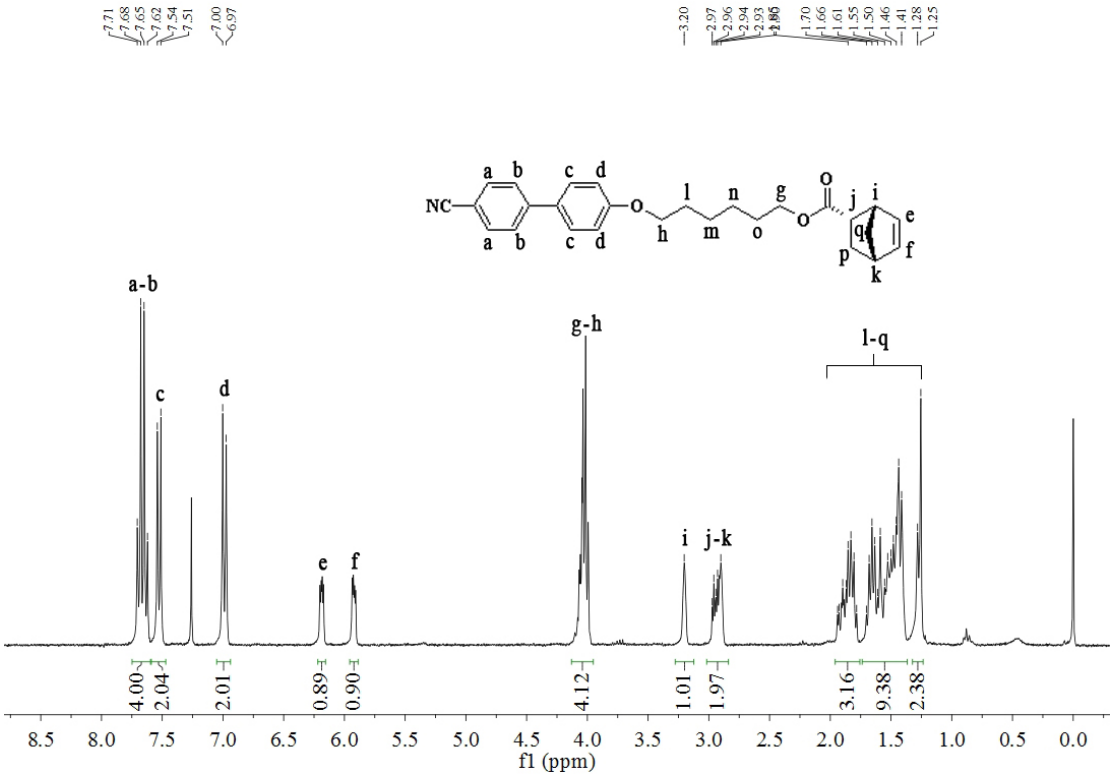


Fig S20. ^{1}H NMR spectrum of monomer **NEM6**.

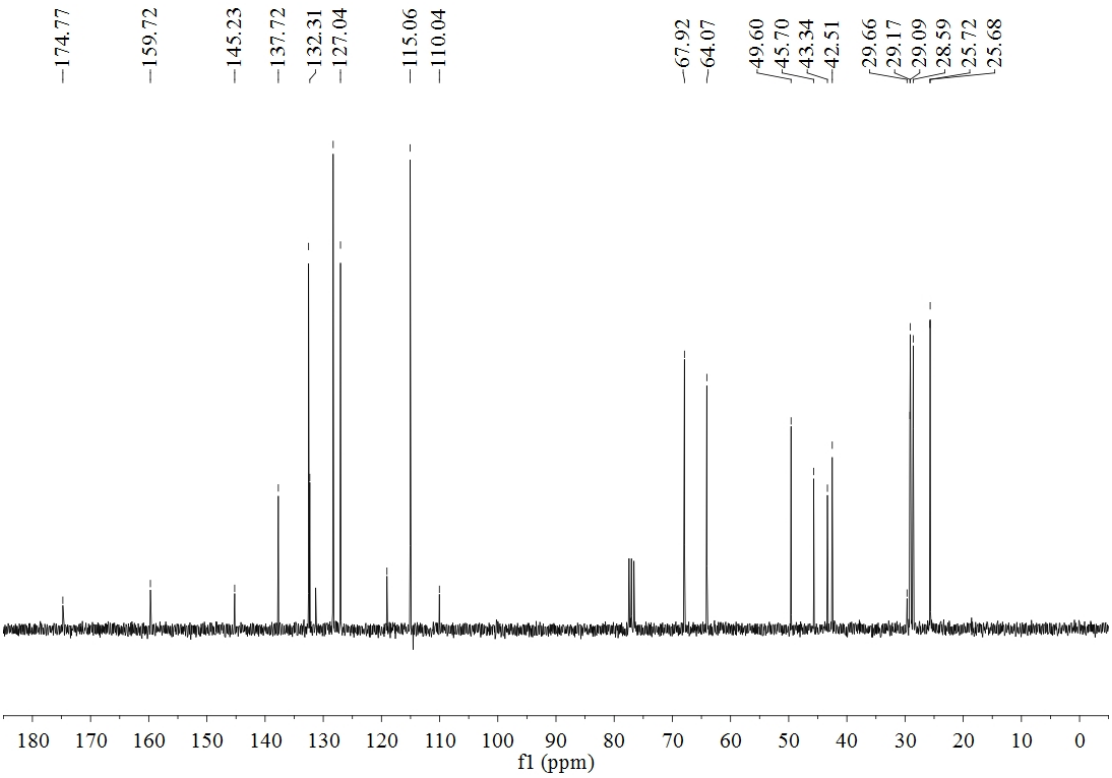


Fig S21. ^{13}C NMR spectrum of monomer **NEM6**.

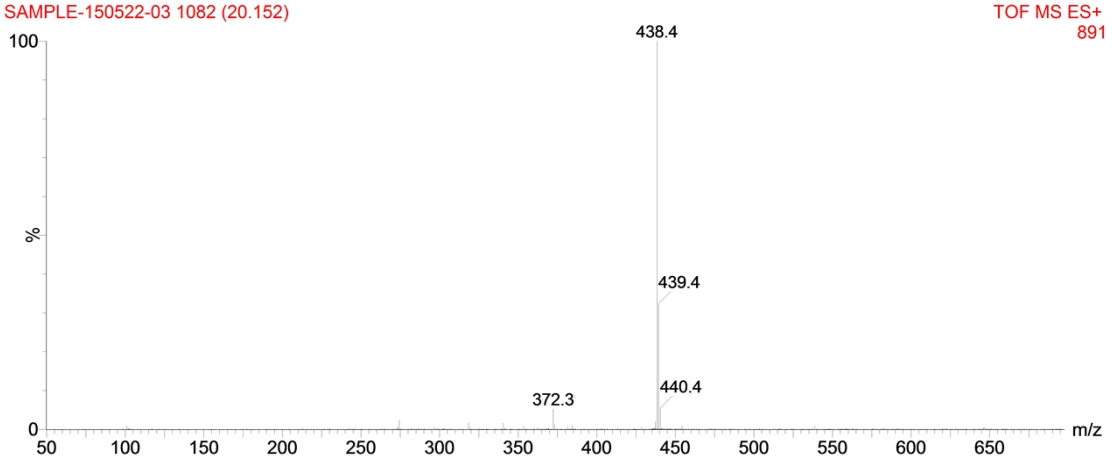


Fig S22. ESI-MS spectrum of **NEM6**.

Synthesis of Liquid Crystalline Polymers and ^{1}H NMR spectra.

PNSM3. **NSM3** (100 mg, 0.15 mmol), Hoveyda-Grubbs 2nd generation catalyst (1.83 mg, 0.003 mmol), and 1,2-dichloroethane (1.5 mL) were added into a Schlenk-type flask. The flask was degassed and exchanged with nitrogen. The reaction mixture was stirred at 50 °C for 2 h. The reaction mixture was then poured into methanol to precipitate the polymer. The resulting brownish polymer was further purified by dissolving in THF, reprecipitating from methanol several times, and drying in vacuo, which gave the desired polymer (80 mg, Yield: 80 %) as a brownish solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (s, 4H), 7.84 (s, 1H), 7.40 (s, 1H), 7.22 (s, 1H), 6.94 (s, 4H), 5.36 – 5.03 (m, 2H), 4.16 (s, 2H), 4.00 (s, 4H), 3.73 (s, 2H), 3.05 (s, 1H), 2.77 (s, 2H), 1.80 – 1.50 (m, 7H), 1.56 – 1.43 (s, 4H), 1.32 – 1.22 (s, 2H), 1.21 – 1.06 (s, 1H), 0.97 (s, 6H).

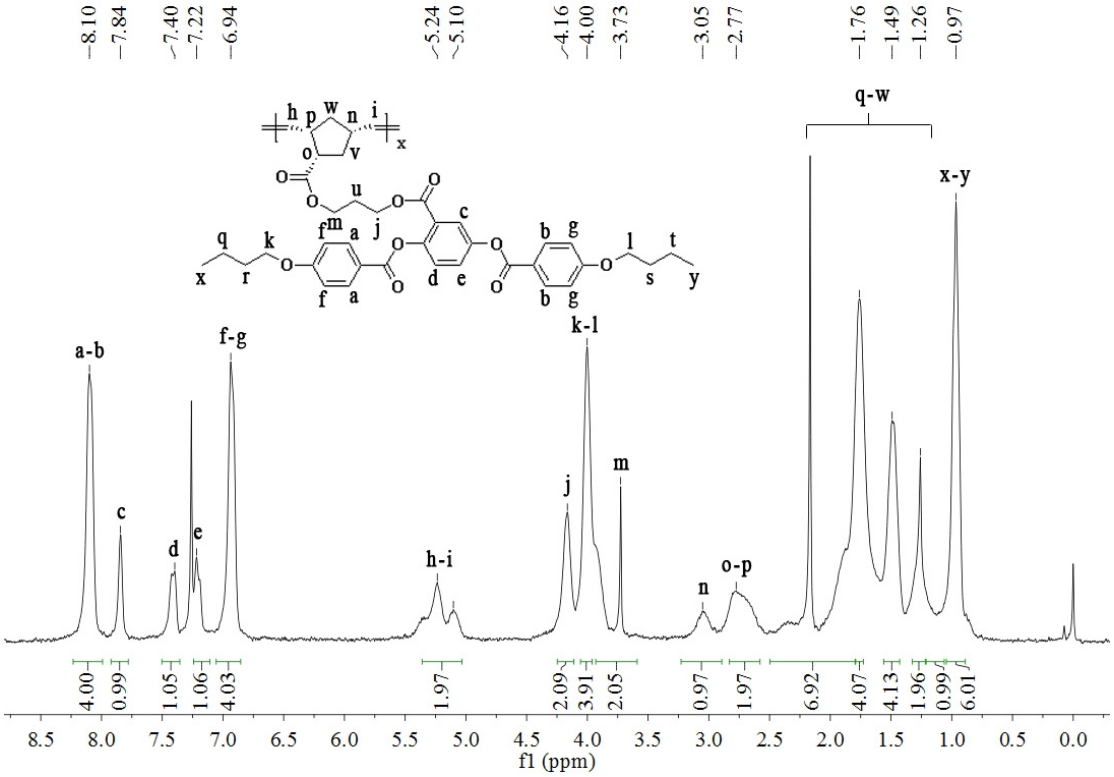


Fig S23. ^{1}H NMR spectrum of polymer **PNSM3**.

P**NSM6**. P**NSM6** was prepared from **NSM6** using the same procedure as with P**NSM3**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (s, 4H), 7.87 (s, 1H), 7.44 (s, 1H), 7.24 (s, 1H), 6.96 (s, 4H), 5.55 – 5.03 (m, 2H), 4.13 (s, 2H), 4.04 (s, 4H), 3.99 – 3.76 (s, 2H), 3.10 (s, 1H), 2.95 – 2.57 (d, 2H, J = 51.8 Hz), 1.96 (s, 2H), 1.79 (s, 5H), 1.49 (m, 9H), 1.28 (s, 2H), 1.22 (s, 4H), 0.99 (s, 6H).

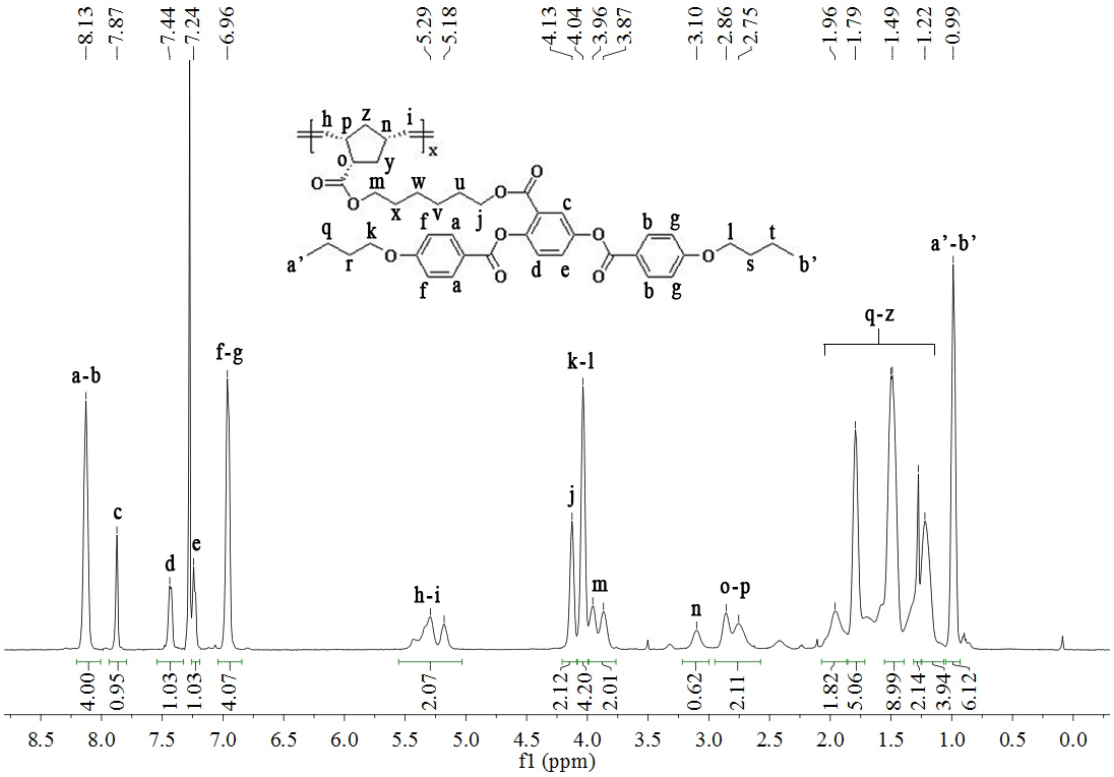


Fig S24. ^{1}H NMR spectrum of polymer **PNSM6**.

P**NEM3**. P**NEM3** was prepared from **NEM3** using the same procedure as with P**NSM3**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 – 6.79 (m, 4H), 7.49 (s, 2H), 6.95 (s, 2H), 5.54– 5.05 (m, 2H), 4.49 – 3.90 (m, 1H), 3.12 (s, 1H), 2.97 – 2.57 (m, 2H), 2.08 (s, 2H), 1.85 (s, 1H), 1.75 (s, 1H), 1.60 (s, 1H), 1.28 (m, 2H).

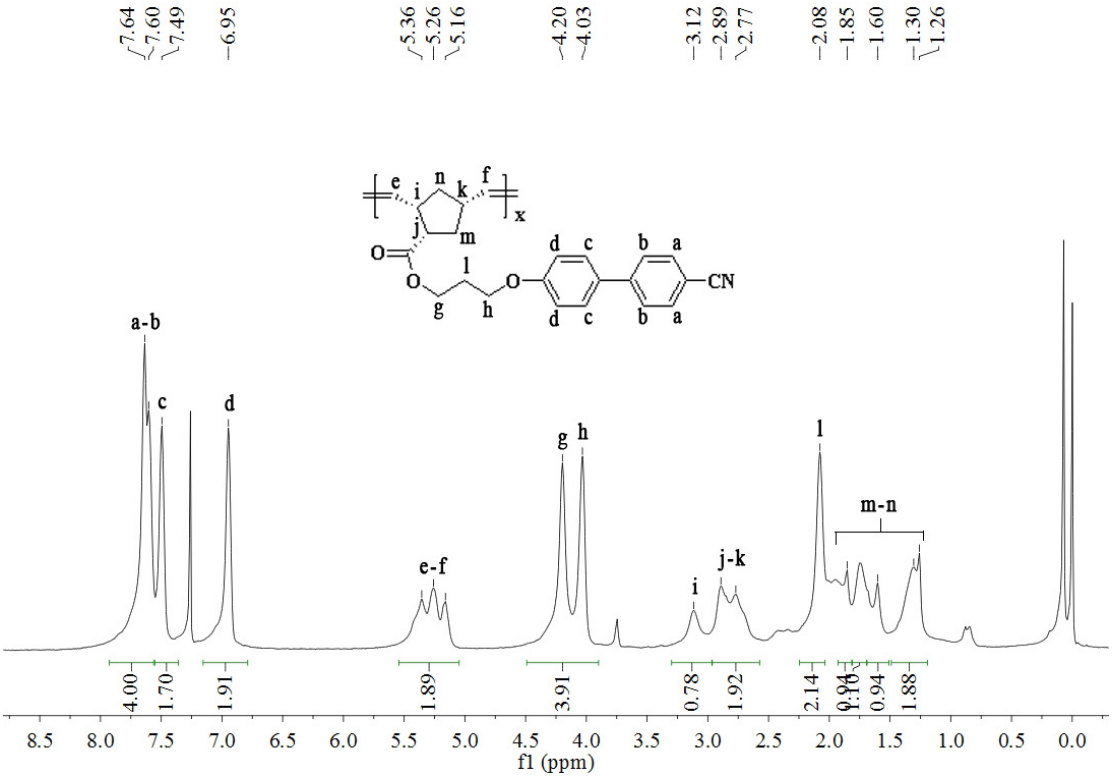


Fig S25. ^{1}H NMR spectrum of polymer **PNEM3**.

P**NEM6**. P**NEM6** was prepared from **NEM6** using the same procedure as with P**NSM3**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 – 7.56 (m, 4H), 7.50 (d, 2H, J = 6.2 Hz), 6.97 (s, 2H), 5.50 – 5.12 (m, 2H), 3.98 (s, 4H), 3.14 (s, 1H), 2.85 (m, 2H), 2.03 (s, 2H), 1.79 (s, 3H), 1.63 (s, 7H), 1.52 (m, 2H), 1.42 (s, 1H), 1.28 (s, 1H)..

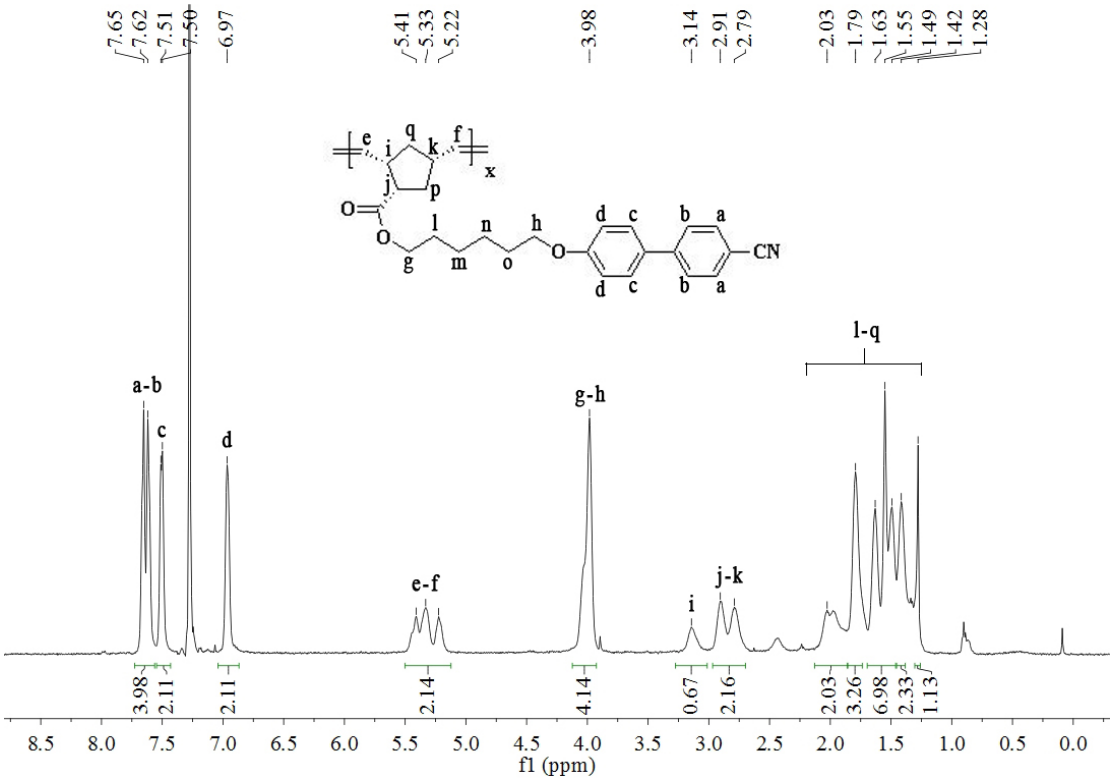


Fig S26. ^{1}H NMR spectrum of polymer **PNEM6**.