Electronic Supplementary Material (ESI) for ChemComm.

Construction of Supramolecular Organogels and Hydrogels from Crown Ether Based Unsymmetric Bolaamphiphiles

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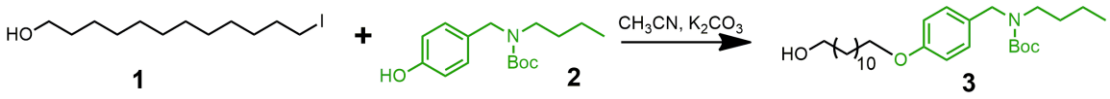
Electronic Supplementary Information (35 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Benzo[21]crown-7 carboxylic acid **C7-COOH**, dibenzo[24]crown-8 carboxylic acid **C8-COOH**, compound **1**, compound **2**, compound **13** and compound **15** were prepared according to the literature procedure.[S1] ^{1}H NMR spectra were collected on a temperature-controlled 400 MHz or 500 MHz spectrometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent or TMS and coupling constants were recorded in Hertz (Hz). ^{13}C NMR spectra were recorded on a Bruker Avance-400or AVANCE DMX-500 spectrometer. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker Daltonics, Inc. APEXⅢ 7.0 TESLA FTMS or Waters GCT Premier GC-TOFMA. Rheological data were obtained by using an ARES G2 rheometer (TA Instruments) with 8 mm parallel plate geometry. Linear dynamic oscillatory frequency sweep was performed from 0.1 to 200 rad/s with strain in the linear rheological range. Rheological experiments were performed at 10 ℃.

*2. Synthesis of compound **3***



A mixture of **2** (3.21 g, 11.5 mmol), 12-iododododecan-1-ol **1** (3.59 g, 11.5 mmol) and K_2CO_3 (3.17 g, 23.0 mmol) in acetonitrile (200 mL) was stirred at 85 ℃ under nitrogen protection for 4 days. Then the solution was filtered through celite and the solvent was removed to give the crude product, which was purified by column chromatography on silica gel (ethyl acetate (EA) : petroleum ether (PE) = 1 : 30, *v/v*) to afford **3** as a yellowish oil (3.83 g, 72%). The proton NMR spectrum of **3** is shown in Figure S1. ^{1}H NMR (400 MHz, acetone-d_6, room temperature) δ (ppm): 7.20 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 4.37 (s, 2H), 3.98 (t, J = 6.5 Hz, 2H), 3.52 (t, J = 6.6 Hz, 2H), 3.15 (br, 2H), 1.76 (m, 2H), 1.56–1.42 (m, 15H), 1.40–1.22 (m, 16H), 0.88 (t, J = 7.4 Hz, 3H). The ^{13}C NMR spectrum of **3** is shown in Figure S2. ^{13}C NMR (125 MHz, acetone-d_6, room temperature) δ (ppm): 159.35, 131.75, 129.82, 115.18, 79.40, 68.51, 62.48, 62.35, 50.07, 49.61, 46.60, 33.80, 33.75, 30.42, 30.34, 30.32, 30.11, 30.04, 28.62, 26.78, 26.70, 20.62, 14.12. HRESIMS: *m/z* calcd for $[M]^+$ $C_{28}H_{49}NO_4$, 463.3662; found 463.3679, error 3.7 ppm.

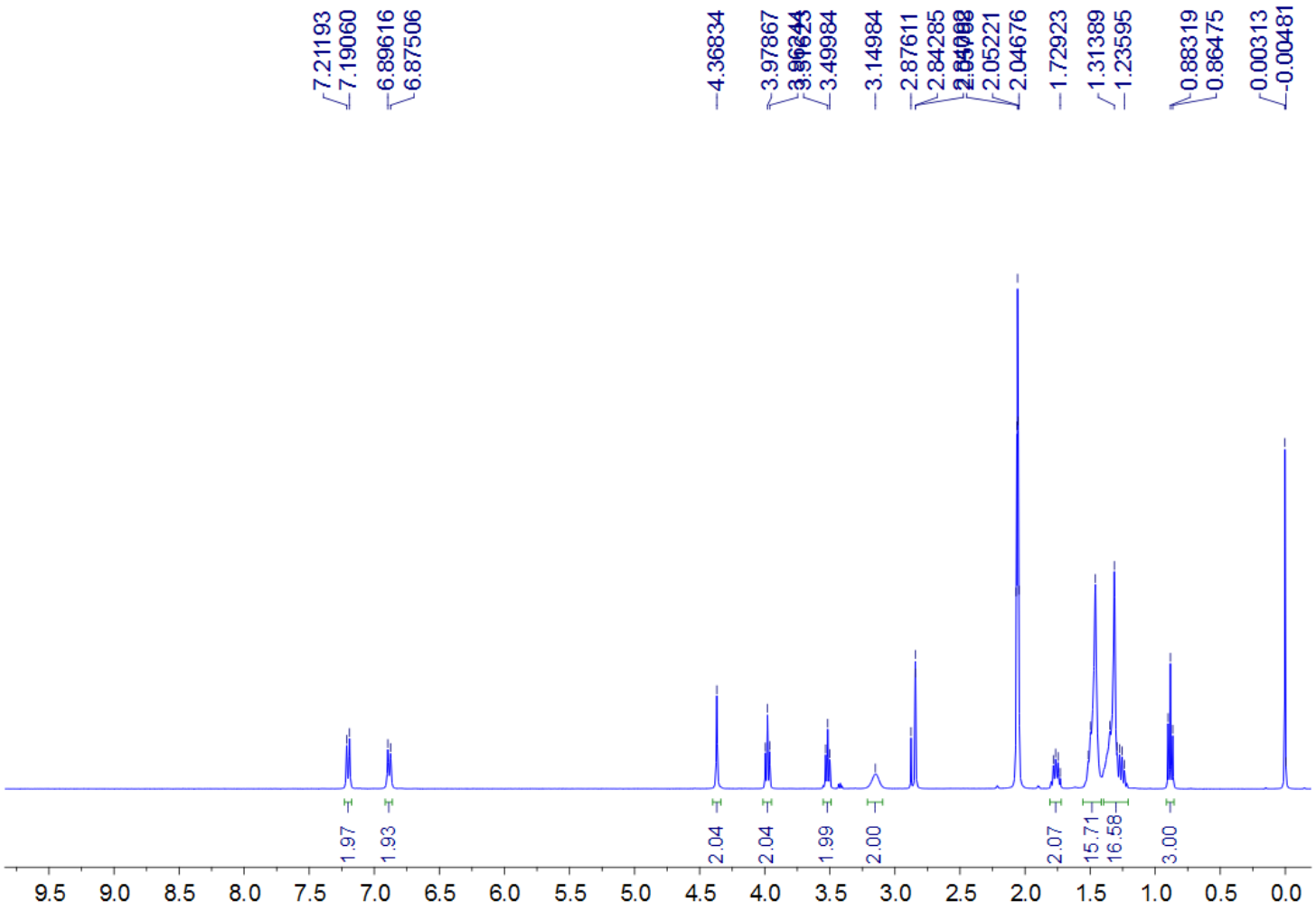


Figure S1. ^{1}H NMR spectrum (400 MHz, acetone-d_6, room temperature) of **3**.

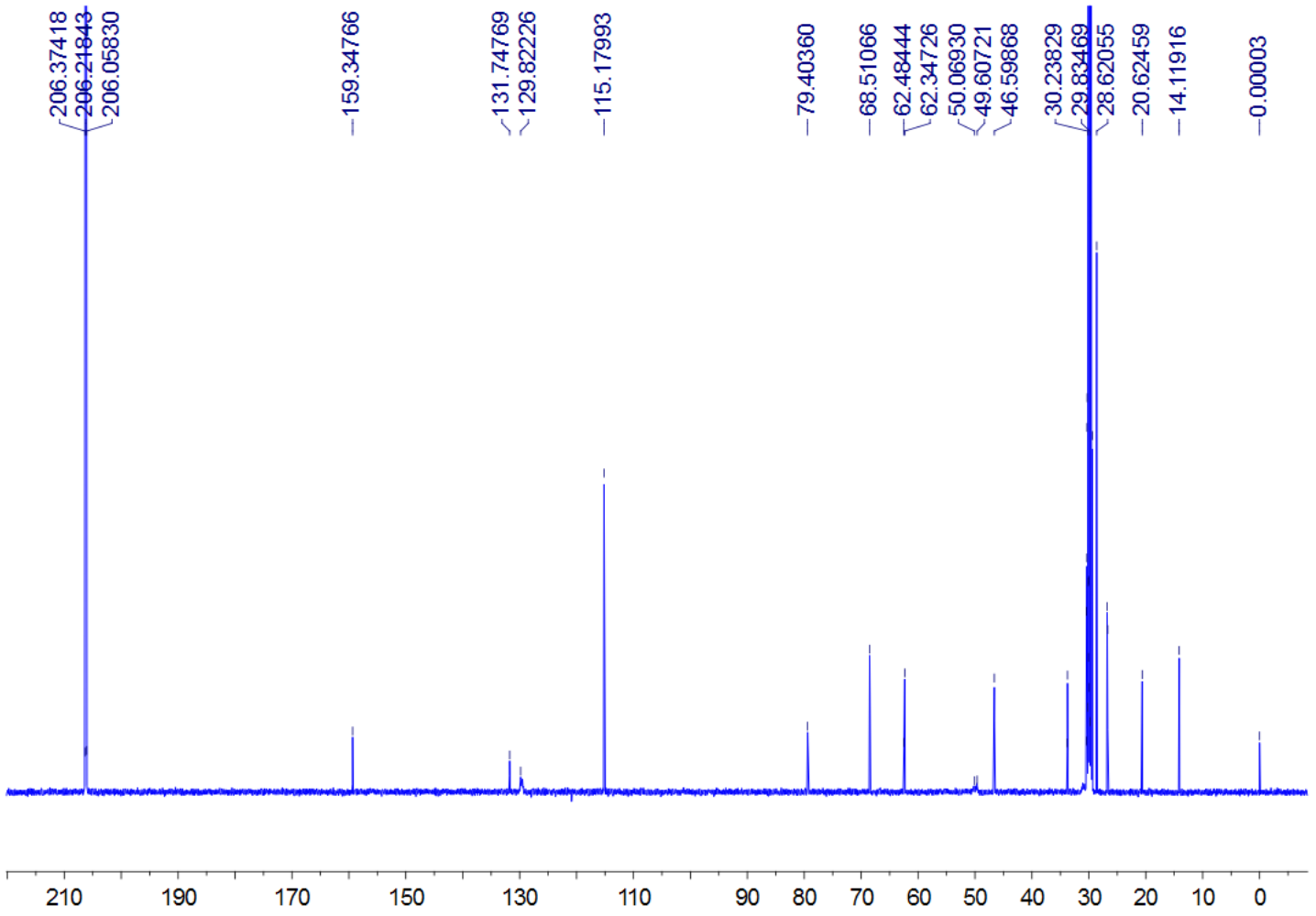
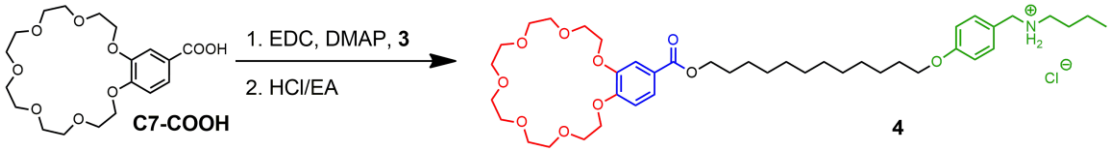


Figure S2. ^{13}C NMR spectrum (125 MHz, acetone-d_6, room temperature) of **3**.

*3. Synthesis of compound **4***



A solution of **C7-COOH** (1.90 g, 4.10 mmol), **3** (1.60 g, 4.10 mmol), EDC (790 mg, 4.10 mmol) and 4-dimethylaminopyridine (DMAP) (500 mg, 4.10 mmol) in dichloromethane (30 mL) was stirred for 24 h at room temperature. The solvent was removed to give the crude product. It was purified by column chromatography on silica gel (EA : PE = 4 : 1, *v/v*). The oil was dissolved in 10% HCl/ethyl acetate (25 mL) and stirred overnight. The white solid was filtered and washed with ethyl acetate thoroughly to afford monomer **4** as a yellowish solid (1.50 g, 36%), mp 104.3−104.7 ℃. The proton NMR spectrum of **4** is shown in Figure S3. ^{1}H NMR (500 MHz, DMSO-d_6, room temperature) δ (ppm): 9.13 (s, 2H), 7.56 (dd, J = 8.5, 1.9 Hz, 1H), 7.45 (d, J = 8.6, 2H), 7.43 (d, J = 1.8, 1H), 7.07 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 4.22 (t, J = 6.6 Hz, 2H), 4.19–4.15 (m, 2H), 4.14–4.10 (m, 2H), 4.02 (t, J = 5.5 Hz, 2H), 3.96 (t, J = 6.5 Hz, 2H), 3.81–3.74 (m, 4H), 3.64–3.59 (m, 4H), 3.58–3.54 (m, 4H), 3.51 (s, 8H), 2.81 (br, 2H), 1.73–1.65 (m, 4H), 1.65–1.58 (m, 2H), 1.43 – 1.22 (m, 18H), 0.87 (t, J = 7.4 Hz, 3H). The ^{13}C NMR spectrum of **4** is shown in Figure S4. ^{13}C NMR (125 MHz, DMSO-d_6, room temperature) δ (ppm): 165.92, 159.67, 152.83, 148.16, 131.90, 123.68, 122.64, 115.02, 113.71, 112.76, 70.81, 70.72, 70.66, 70.60, 70.34, 69.30, 69.18, 68.01, 64.85, 50.05, 46.52, 29.38, 29.22, 29.08, 28.64 27.86, 25.92, 19.72, 13.90. HRESIMS: m/z calcd for $[M - Cl]^+$ $C_{42}H_{68}NO_{10}$, 746.4838; found 746.4824, error -1.9 ppm.

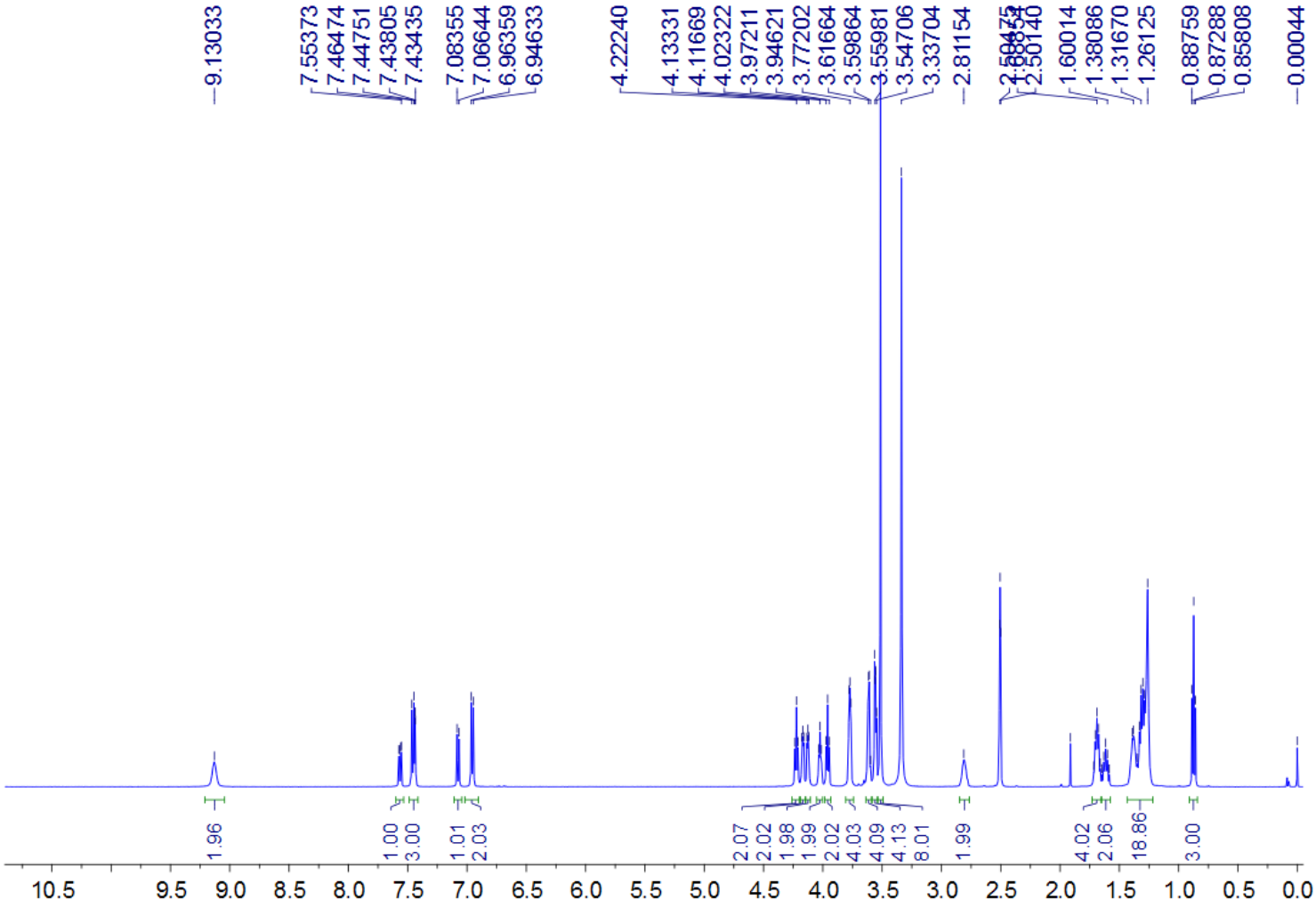


Figure S3. ^{1}H NMR spectrum (500 MHz, DMSO-d_6, room temperature) of **4**.

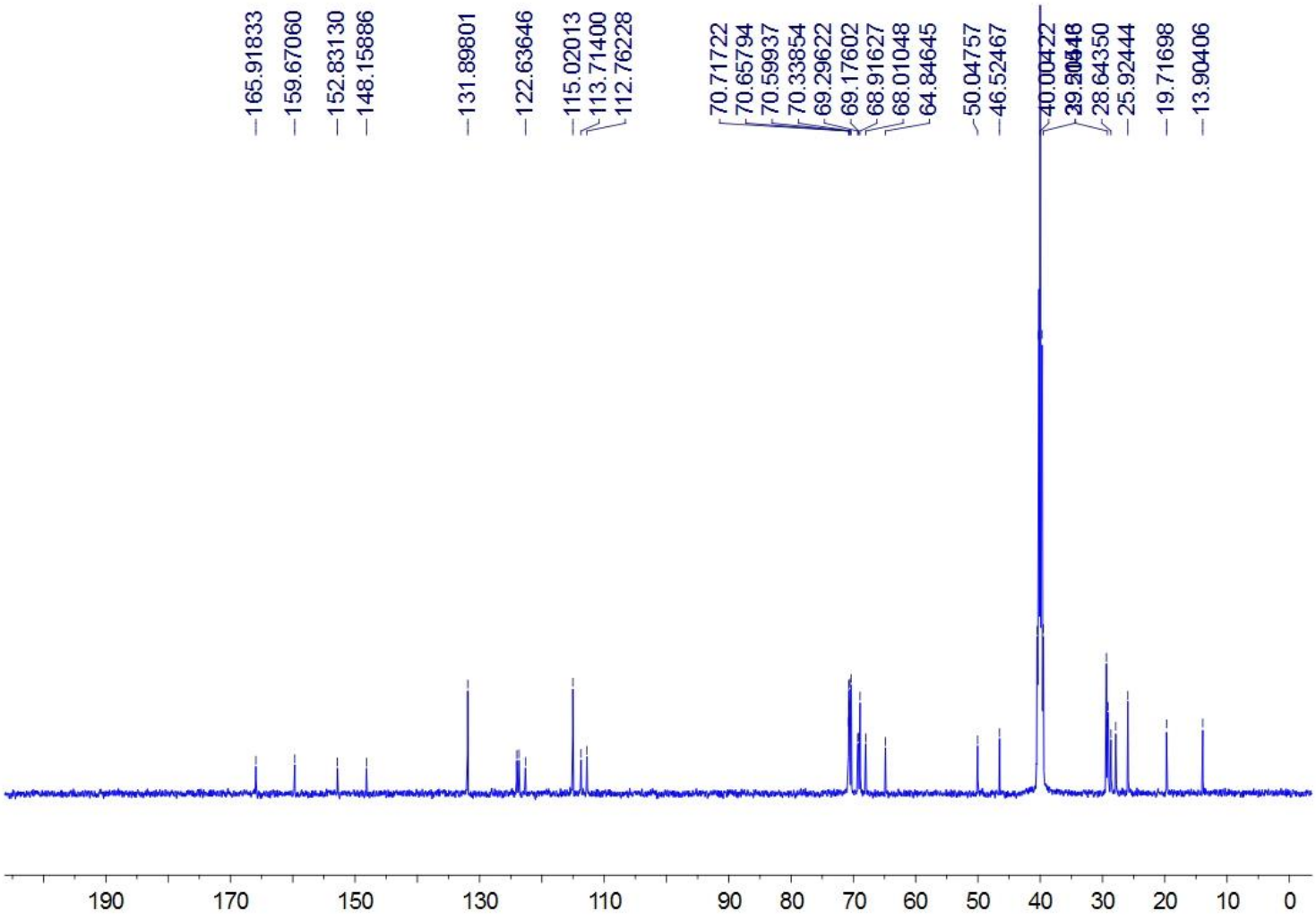
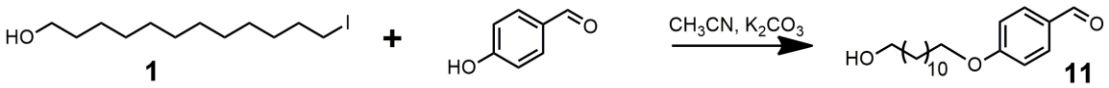


Figure S4. ^{13}C NMR spectrum (125 MHz, DMSO-d_6, room temperature) of **4**.

*4. Synthesis of compound **11***



A mixture of 4-hydroxybenzaldehyde (0.80 g, 6.50 mmol), **1** (2.04 g, 6.53 mmol) and K_2CO_3 (1.35 g, 9.80 mmol) in acetonitrile (120 mL) was stirred at 85 ℃ under nitrogen protection for 2 days. Then the solution was filtered through celite and the solvent was removed to give the crude product, which was purified by column chromatography on silica gel (EA : PE = 1 : 20, *v/v*) to afford **11** as a white solid (1.30 g, 65%).[S2] The proton NMR spectrum of **11** is shown in Figure S5. ^{1}H NMR (400 MHz, acetone-d_6, room temperature) δ (ppm): 9.88 (s, 1H), 7.83 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 4.04 (t, J = 6.5 Hz, 2H), 3.64 (q, J = 6.2 Hz, 2H), 1.86–1.75 (m, 2H), 1.61–1.52 (m, 2H), 1.51–1.41 (m, 2H), 1.40–1.25 (br, 14H).

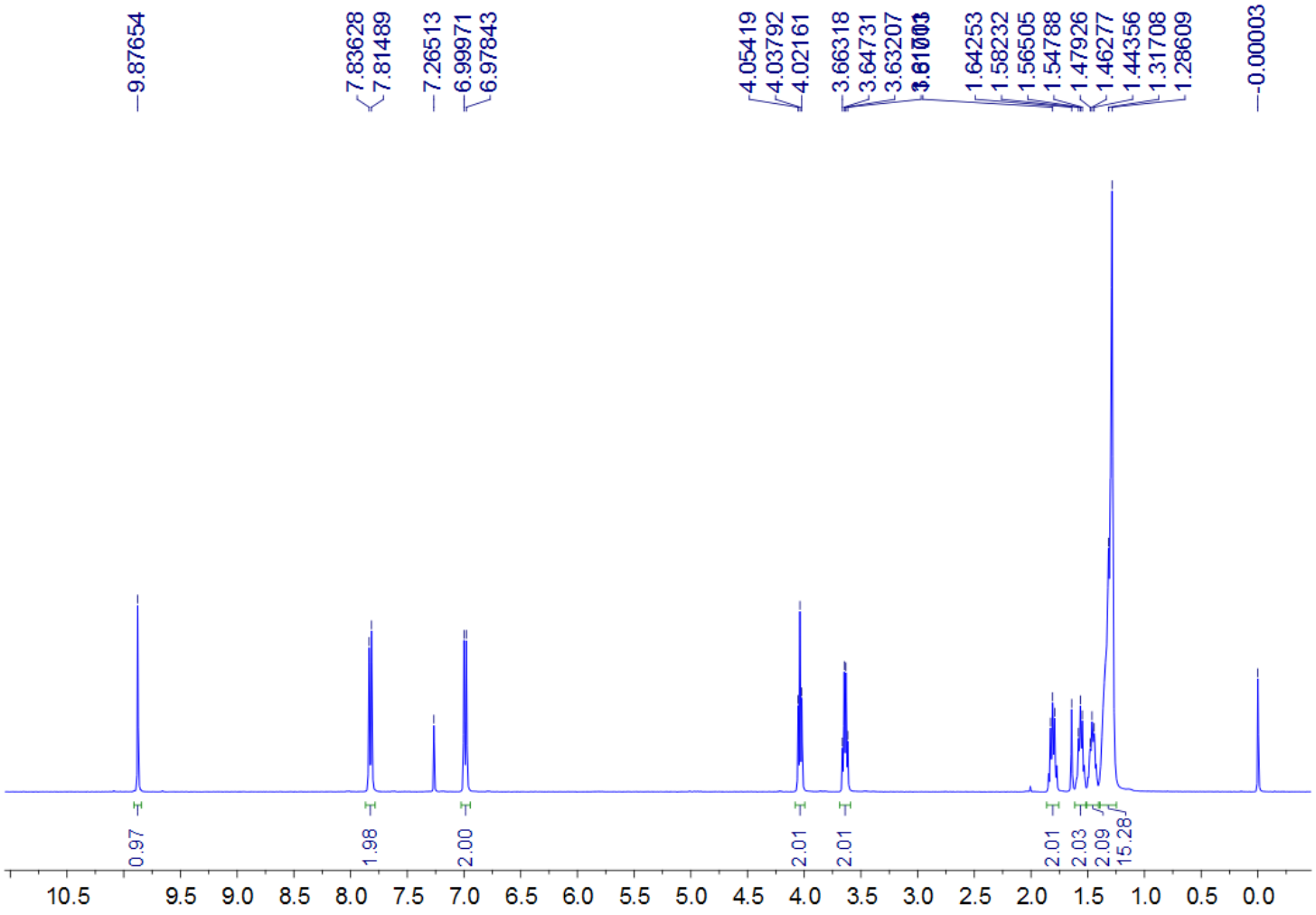
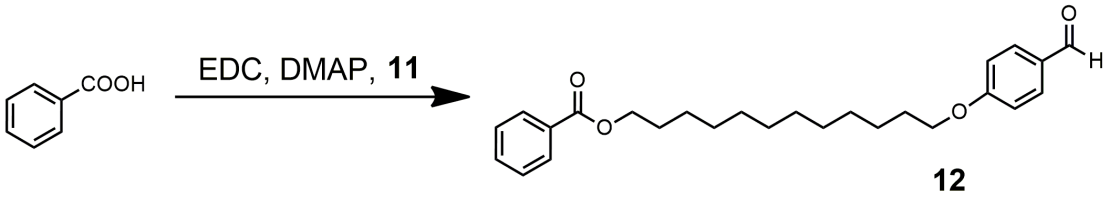


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$-*d*, room temperature) of **11**.

*5. Synthesis of compound **12***



12

A solution of benzoic acid (244 mg, 2.00 mmol), **11** (613 mg, 2.00 mmol), EDC (392 mg, 2.00 mmol) and DMAP (247 mg, 2.00 mmol) in dichloromethane (20 mL) was stirred for 24 h at room temperature. The solvent was removed to give the crude product. It was purified by column chromatography on silica gel (EA : PE = 1 : 50, *v/v*) to afford **12** as a white solid (700 mg, 86%), mp 40.1−41.5 ℃. The proton NMR spectrum of **12** is shown in Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$-*d*, room temperature) δ (ppm): 9.88 (s, 1H), 8.04 (d, *J* = 5.2 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 1.85–1.72 (m, 4H), 1.51–1.40 (m, 4H), 1.39–1.24 (m, 12H). The ^{13}C NMR spectrum of **12** is shown in Figure S7. ^{13}C NMR (100 MHz, $CDCl_3$-*d*, room temperature) δ (ppm): 190.81, 166.70, 164.28, 132.80, 131.99, 130.55, 129.76, 129.53, 128.32, 114.76, 68.43, 65.12, 29.52, 29.33, 29.26, 29.06, 28.72, 26.03, 25.96. HRESIMS: *m*/*z* calcd for $[M]^+$ $C_{26}H_{34}O_4$, 410.2457; found 410.2455, error -0.5 ppm.

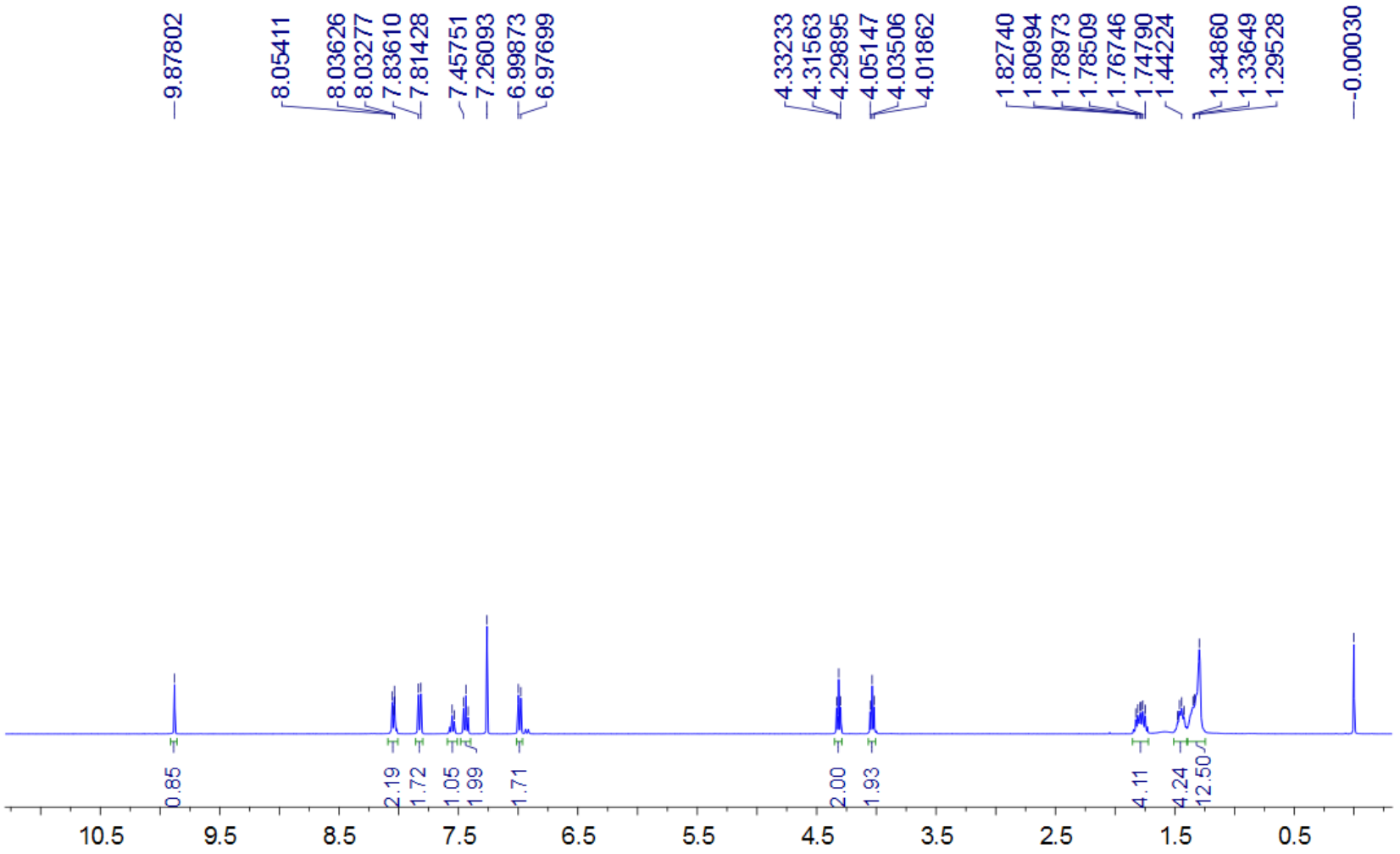


Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$-*d*, room temperature) of **12**.

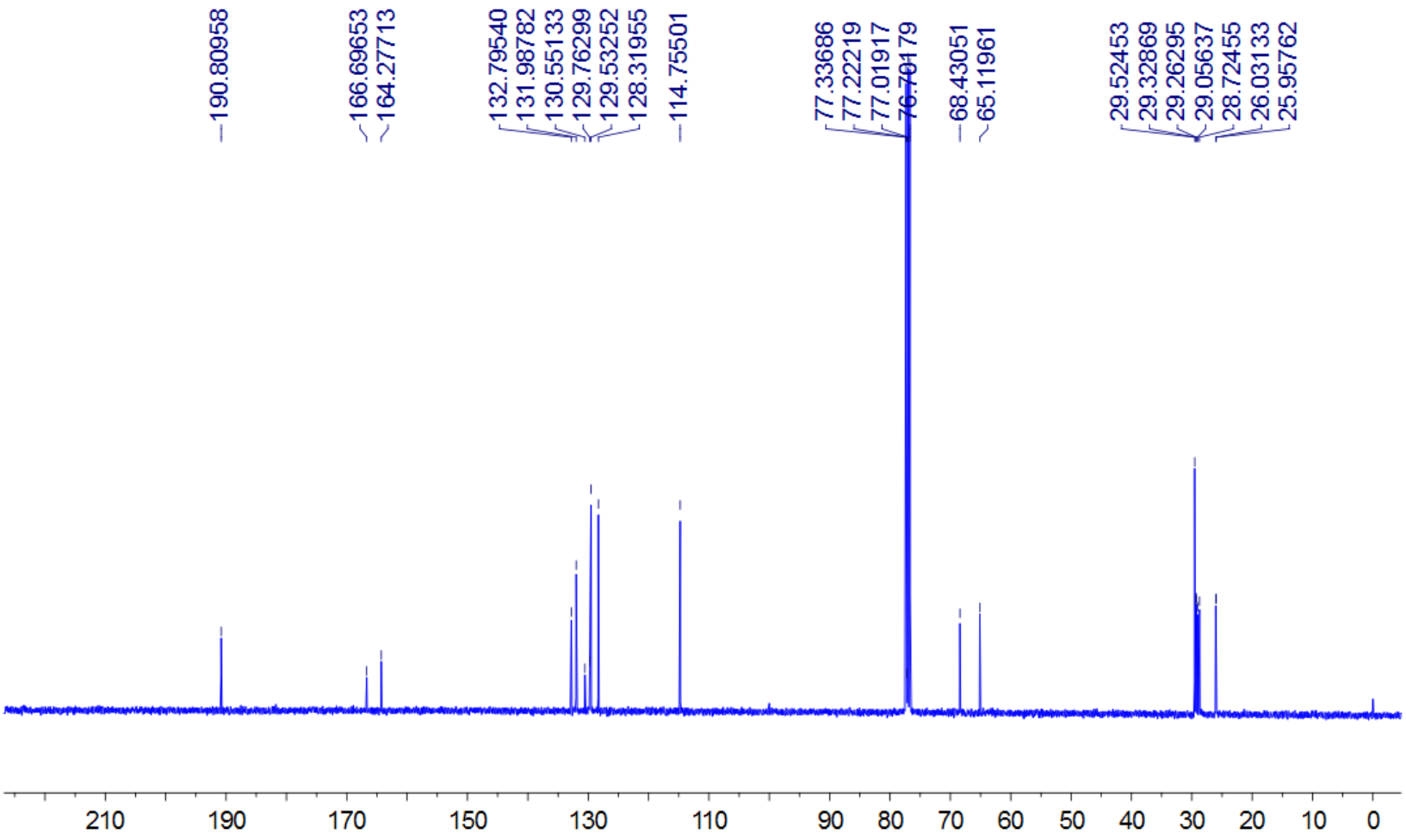
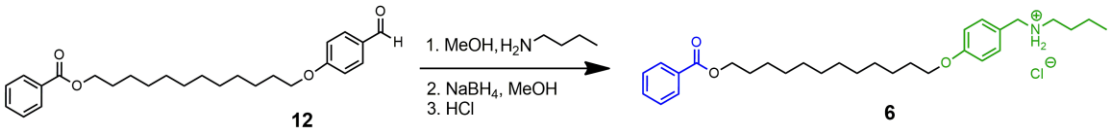


Figure S7. ^{13}C NMR spectrum (100 MHz, $CDCl_3$-*d*, room temperature) of **12**.

6. Synthesis of compound ***6***



A solution of **12** (700 mg, 1.70 mmol) and butan-1-amine (120 mg, 1.70 mmol) in MeOH (15 mL) was stirred at room temperature overnight. Then $NaBH_4$ (87 mg, 2.30 mmol) was added. The reaction was quenched by addition of water. The solvent was removed and ethyl acetate was added. The resulting solution was extracted with water. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford a crude product. The crude product was dissolved in ethyl acetate (25 mL) and concentrated HCl was added dropwise. The white solid was filtered, washed with ethyl acetate thoroughly to afford **6** as a white solid (685 mg, 80%), mp 127.5−131.1 ℃. The proton NMR spectrum of **6** is shown in Figure S8. ^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ (ppm): 9.10 (s, 2H), 7.96 (d, J = 5.8 Hz, 2H), 7.66 (s, 1H), 7.59–7.38 (m, 4H), 6.96 (d, J = 6.7 Hz, 2H), 4.27 (s, 2H), 4.08–3.88 (m, 4H), 2.81 (s, 2H), 1.80–1.53 (m, 6H), 1.45–1.20(m, 18H), 0.87 (t, J = 5.1 Hz, 3H). The ^{13}C NMR spectrum of **6** is shown in Figure S9. ^{13}C NMR (100 MHz, acetone-d_6, room temperature) δ (ppm): 166.11, 159.56, 133.62, 131.95, 130.34, 129.42, 129.23, 124.04, 114.80, 67.86, 65.02, 49.67, 46.16, 29.29, 29.12, 28.98, 28.49, 27.67, 25.85, 19.72, 13.86. HRESIMS: m/z calcd for $[M - Cl]^+$ $C_{30}H_{46}NO_3$, 468.3472; found 468.3475, error 0.6 ppm.

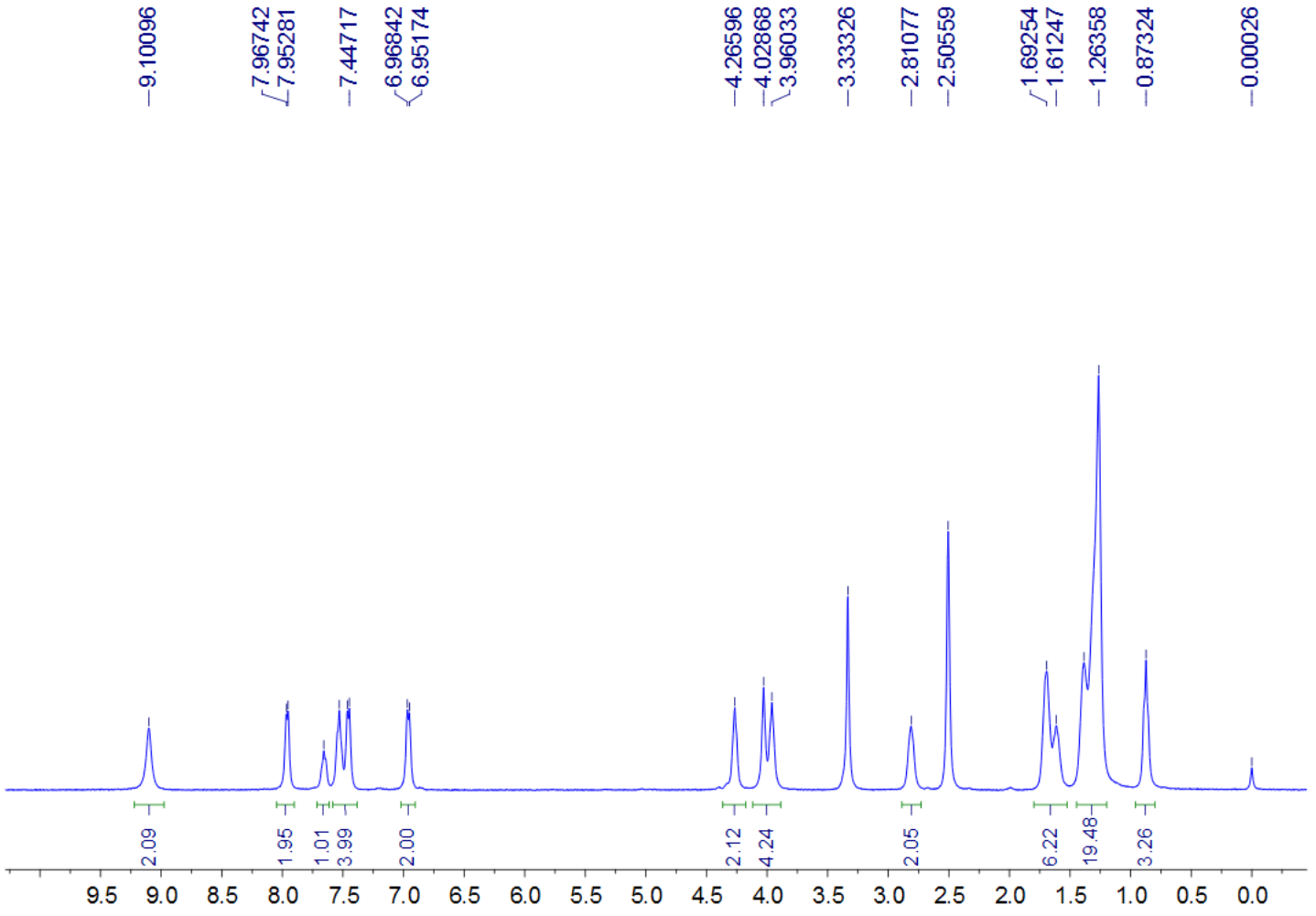


Figure S8. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, room temperature) of **6**.

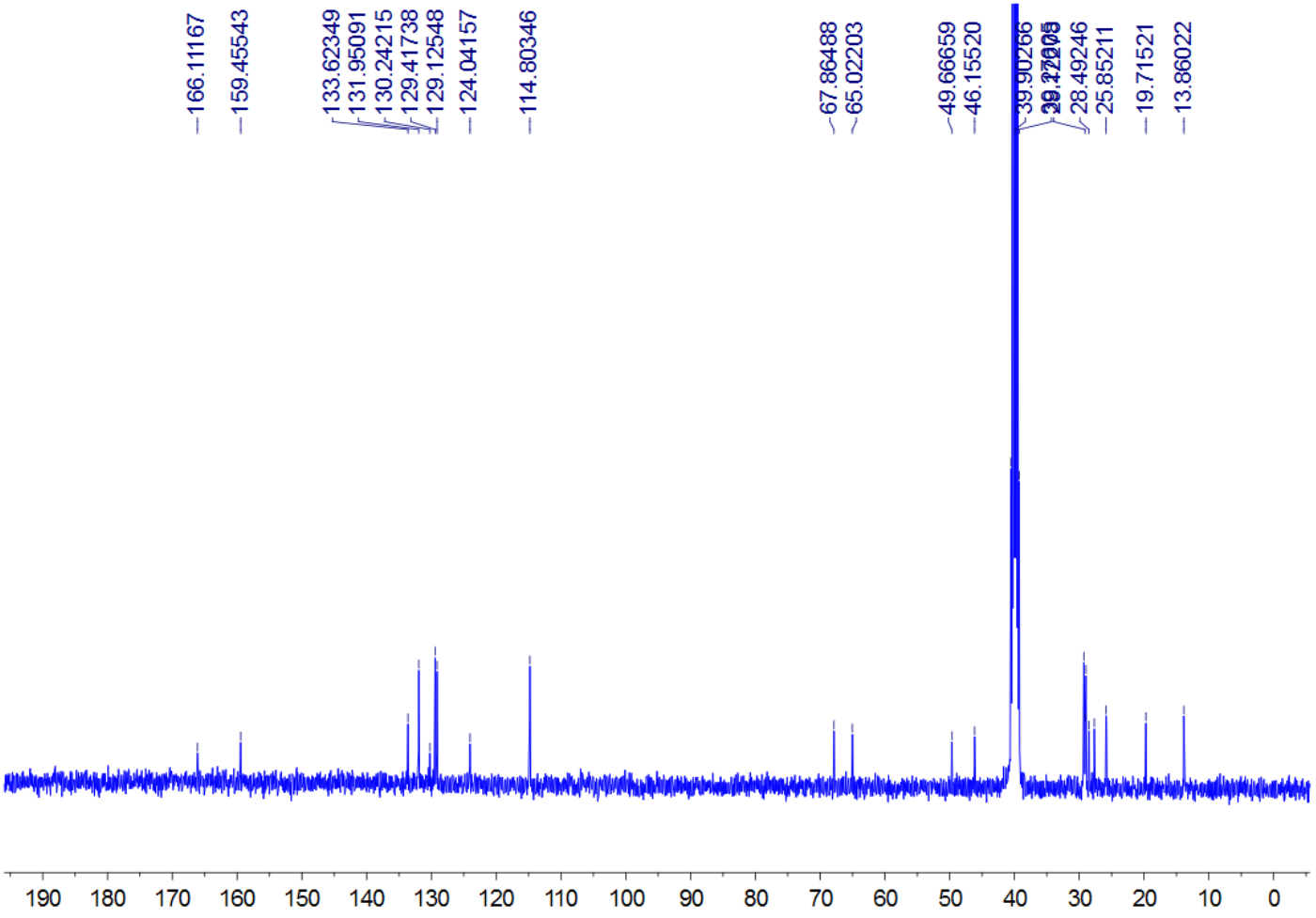
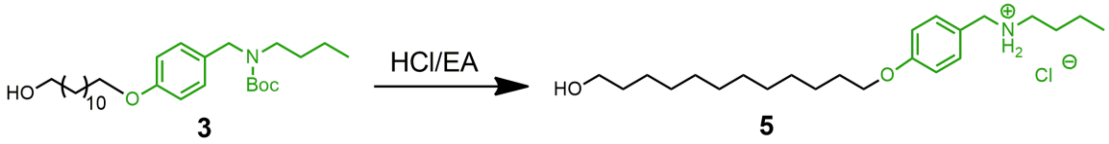


Figure S9. ^{13}C NMR spectrum (100 MHz, acetone-d_6, room temperature) of **6**.

7. Synthesis of compound ***5***



3 **5**

3 was dissolved in 10% HCl/ethyl acetate (10 mL) and stirred overnight. The white solid was filtered and washed with ethyl acetate thoroughly to afford monomer **5** as a yellowish solid quantitatively, mp 133.7−135.2 ℃. The proton NMR spectrum of **5** is shown in Figure S10. ^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ (ppm): 9.40–8.50 (br, 2H), 7.43 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.3 Hz, 2H), 4.05–3.91 (m, 6H), 2.84–2.75 (m, 2H), 1.75–1.66 (m, 2H), 1.65–1.50 (m, 4H), 1.45–1.20 (m, 18H), 0.88 (t, J = 7.3 Hz, 3H). The ^{13}C NMR spectrum of **5** is shown in Figure S11. ^{13}C NMR (100 MHz, $CDCl_3$-d_6, room temperature) δ (ppm): 171.27, 159.92, 131.82, 121.90, 114.90, 68.02, 64.66, 50.04, 45.54, 29.54, 29.38, 29.24, 29.17, 28.59, 27.82, 26.01, 25.90, 21.02, 20.06, 13.48. HRESIMS: m/z calcd for $[M - Cl]^+$ $C_{23}H_{42}NO_2$, 364.2310; found 364.2326, error 4.4 ppm.

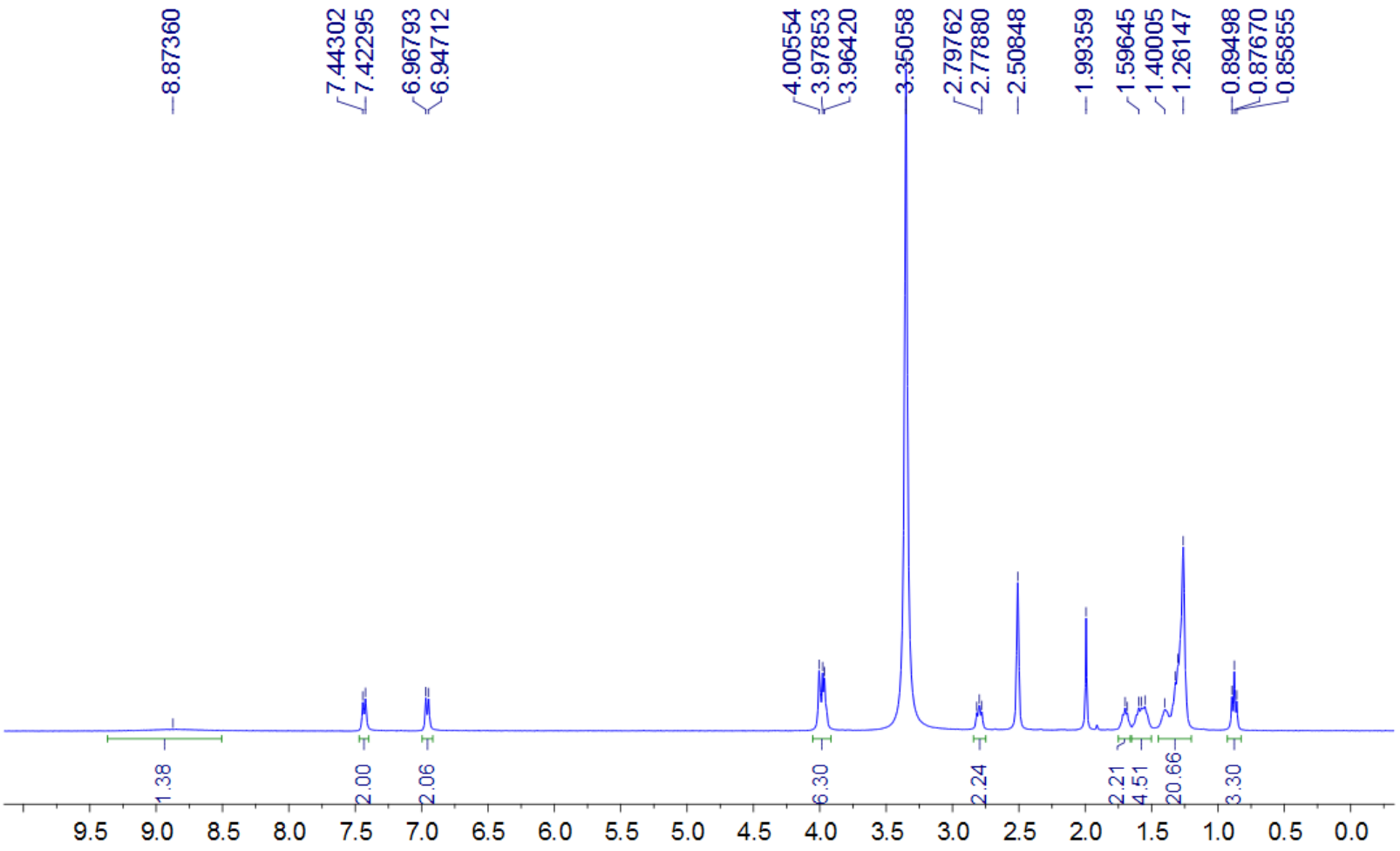


Figure S10. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, room temperature) of **5**.

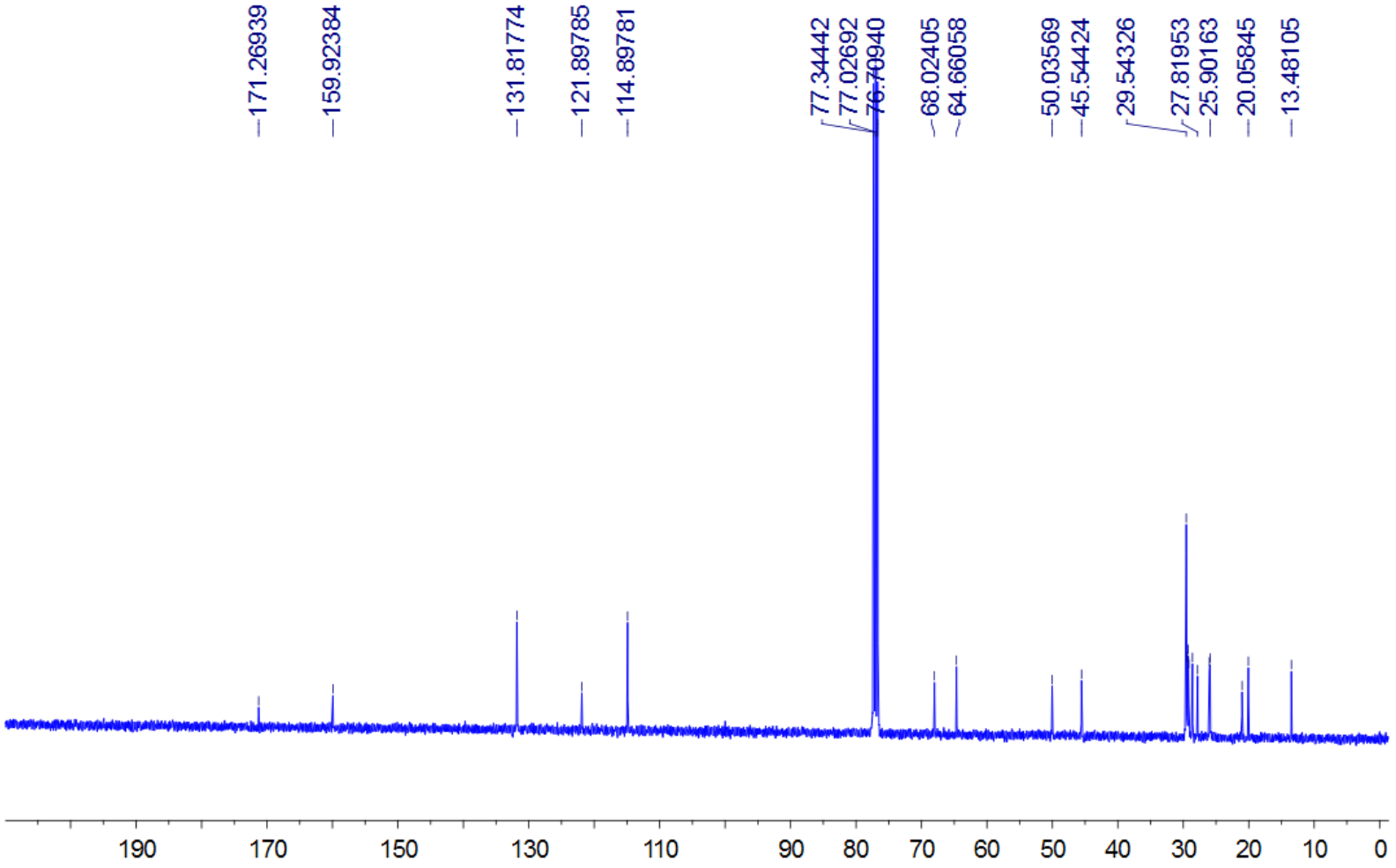


Figure S11. ^{13}C NMR spectrum (100 MHz, $CDCl_3$-*d*, room temperature) of **5**.

*8. Synthesis of compound **7***

A solution of **C7-COOH** (950 mg, 2.40 mmol), 6-bromohexan-1-ol (430 mg, 2.40 mmol), EDC (650 mg, 3.40 mmol) and DMAP (410 mg, 3.40 mmol) in dichloromethane (25 mL) was stirred for 24 h at room temperature. The solvent was removed to give the crude product. After removal of most of unreacted substrates by column chromatography on silica gel (EA : PE = 1 : 1, *v/v*), the residue was dissolved in acetonitrile (20 mL) and **2** (250 mg, 0.90 mmol) and K_2CO_3 (300 mg, 2.20 mmol) were added. The resultant solution was stirred at 85 ℃ under nitrogen protection for 4 days. Then the solution was filtered through celite and the solvent was removed to give the crude product. It was purified by column chromatography on silica gel (EA : PE = 4 : 1, *v/v*). The oil was dissolved in 10% HCl/ethyl acetate (10 mL) and stirred overnight. The solvent was removed to afford monomer **7** as a yellowish oil (440 mg, 26%). The proton NMR spectrum of **7** is shown in Figure S12. ^{1}H NMR (500 MHz, DMSO-d_6, room temperature) δ (ppm): 8.95 (s, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.45–7.41 (br, 3H), 7.07 (d, J = 8.5 Hz, 1H), 6.96 (d, J = 8.3 Hz, 2H), 4.24 (t, J = 6.4 Hz, 2H), 4.20–4.10 (m, 4H), 4.03 (s, 2H), 3.98 (t, J = 6.3 Hz, 1H), 3.80–3.73 (m, 4H), 3.64–3.59 (m, 4H), 3.58–3.54 (m, 4H), 3.51 (s, 8H), 2.82 (s, 2H), 1.77–1.68 (m, 4H), 1.64–1.56 (m, 2H), 1.51–1.43 (m, 4H), 1.35–1.28 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). The ^{13}C NMR spectrum of **7** is shown in Figure S13. ^{13}C NMR (100 MHz, $CDCl_3$-*d*, room temperature) δ (ppm): 166.39, 159.80, 152.81, 148.20, 131.85, 123.85, 122.05, 114.86, 114.56, 112.23, 71.22, 71.11, 70.95, 70.80, 70.53, 69.62, 69.48, 69.20, 69.00, 67.79, 64.76, 50.02, 45.54, 29.67, 29.07, 28.68, 27.73, 25.90, 25.82, 25.74, 20.00, 13.48. HRESIMS: *m/z* calcd for $[M - Cl]^+$ $C_{36}H_{56}O_{10}$, 662.3899; found 662.3918, error 2.8 ppm.

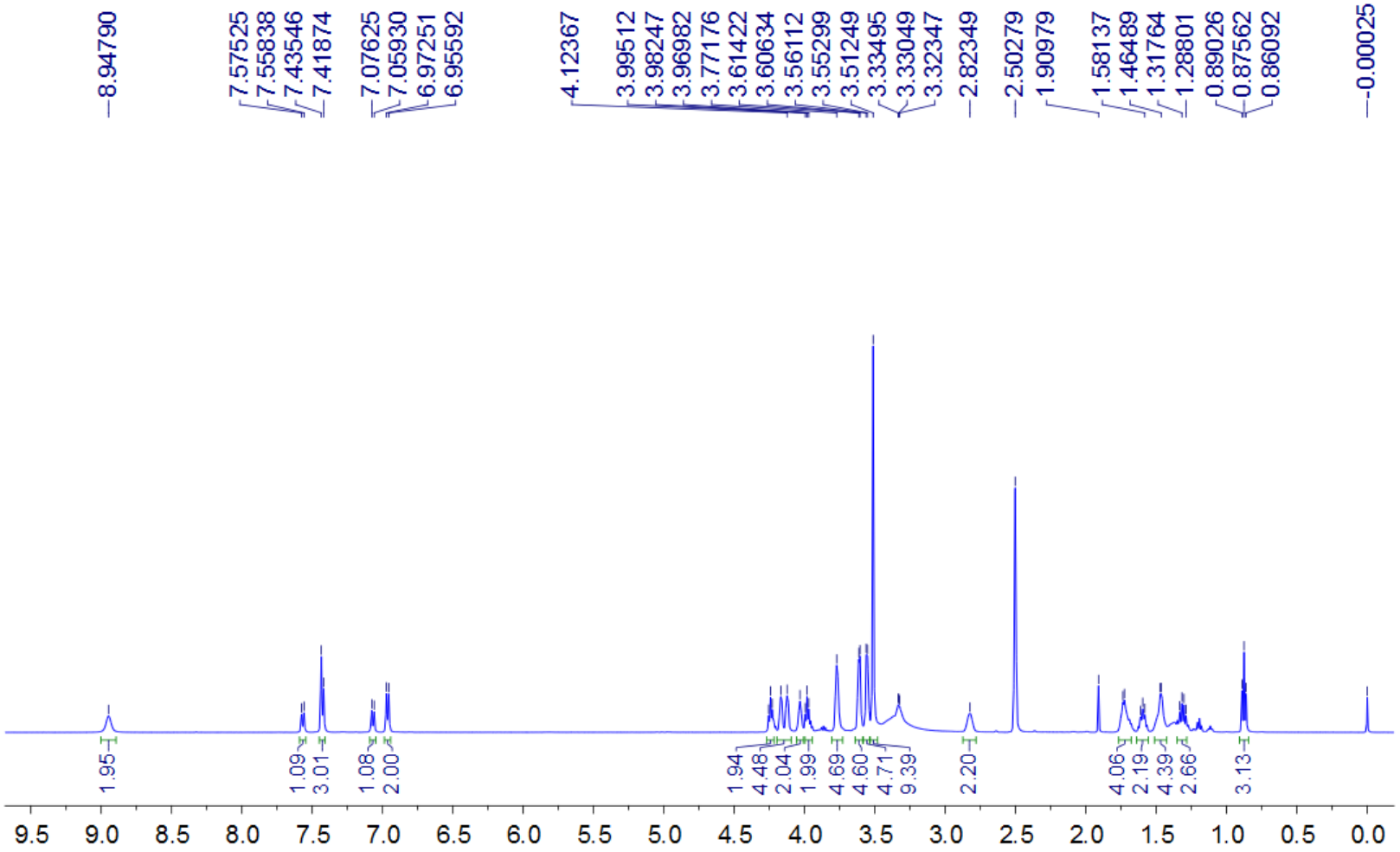


Figure S12. ^{1}H NMR spectrum (500 MHz, DMSO-d_6, room temperature) of **7**.

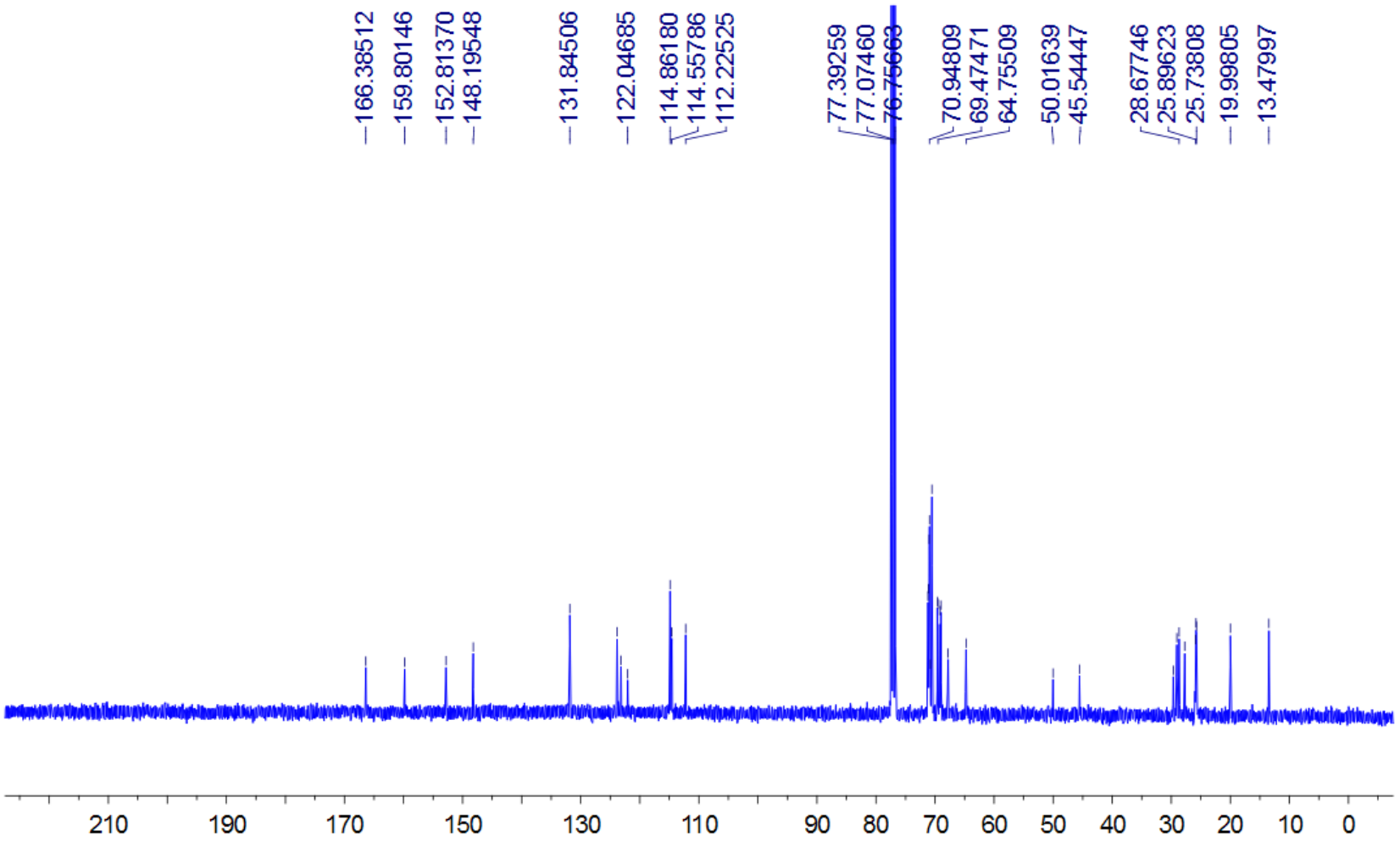
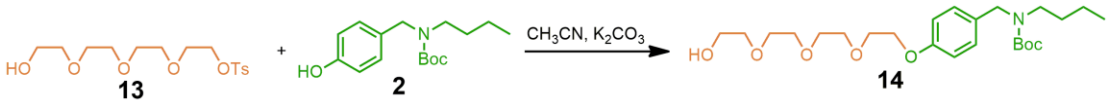


Figure S13. ^{13}C NMR spectrum (100 MHz, $CDCl_3$-*d*, room temperature) of **7**.

*9. Synthesis of compound **14***



A solution of **2** (1.33 g, 4.80 mmol), **13** (1.66 g, 4.80 mmol) and K_2CO_3 (1.99 mg, 14.4 mmol) in acetonitrile (30 mL) was stirred at 85 ℃ under nitrogen protection for 24 h. Then the solution was filtered through celite and the solvent was removed to give the crude product, which was purified by column chromatography on silica gel (EA : PE = 1 : 10, *v/v*) to afford **14** as a yellow oil (1.60 g, 73%). The proton NMR spectrum of **14** is shown in Figure S14. ^{1}H NMR (400 MHz, acetone-d_6, room temperature) δ (ppm): 7.21 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 4.37 (s, 2H), 4.13 (t, J = 4.9 Hz, 2H), 3.81 (t, J = 4.6 Hz, 2H), 3.68–3.64 (m, 2H), 3.64–3.57 (m, 8H), 3.52 (t, J = 5.0 Hz, 2H), 3.15 (s, 2H), 1.52–1.40 (m, 11H), 1.32–1.19 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). The ^{13}C NMR spectrum of **14** is shown in Figure S15. ^{13}C NMR (100 MHz, acetone-d_6, room temperature) δ (ppm): 159.08, 131.98, 129.72, 115.24, 79.37, 73.51, 71.25, 71.23, 71.09, 70.32, 68.29, 61.96, 50.22, 49.55, 46.58, 28.60, 20.59, 14.11. HRESIMS: *m/z* calcd for $[M + Na]^+$ $C_{24}H_{41}NNaO_7$, 478.2775; found 478.2765, error -2.1 ppm.

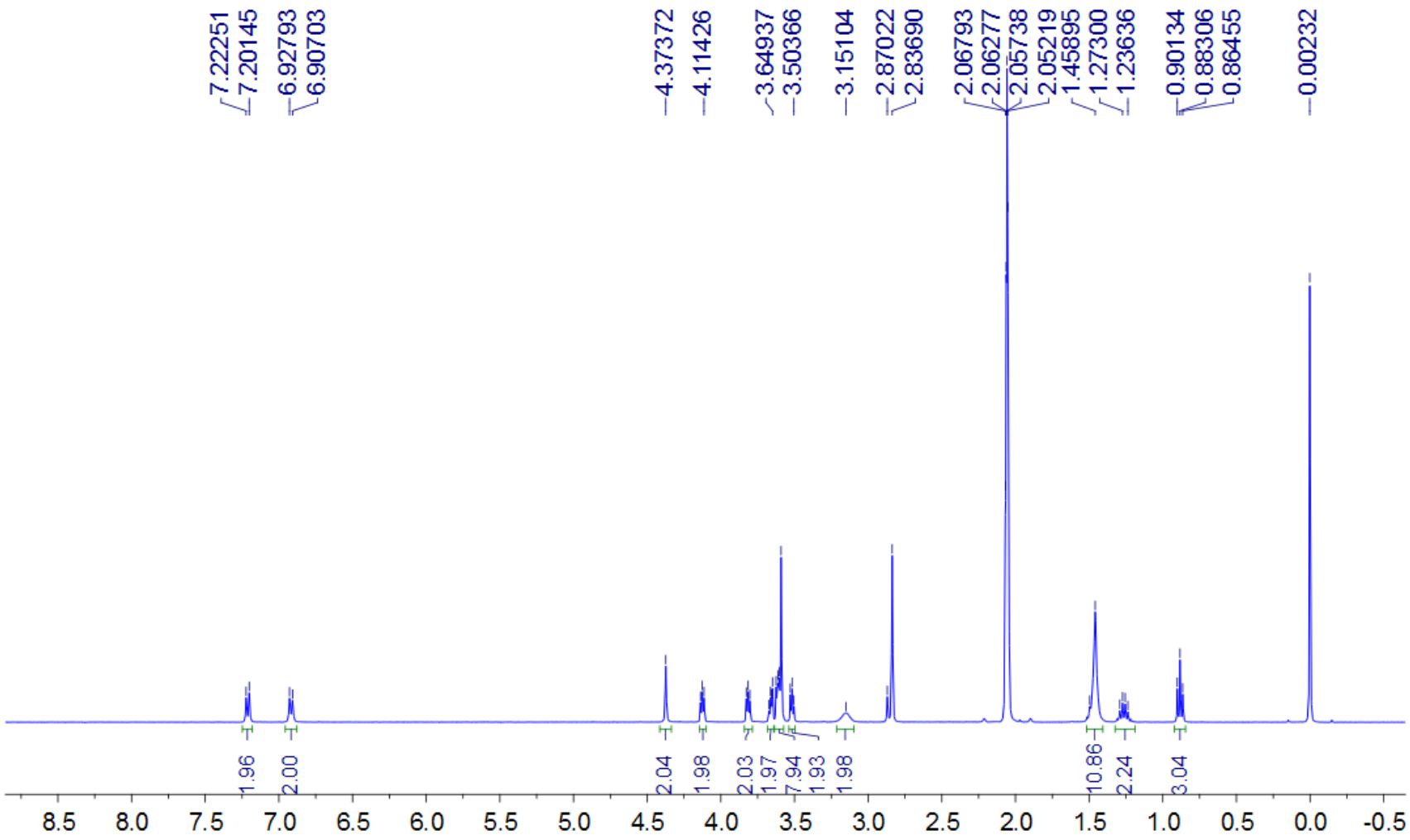


Figure S14. ^{1}H NMR spectrum (400 MHz, acetone-d_6, room temperature) of **14**.

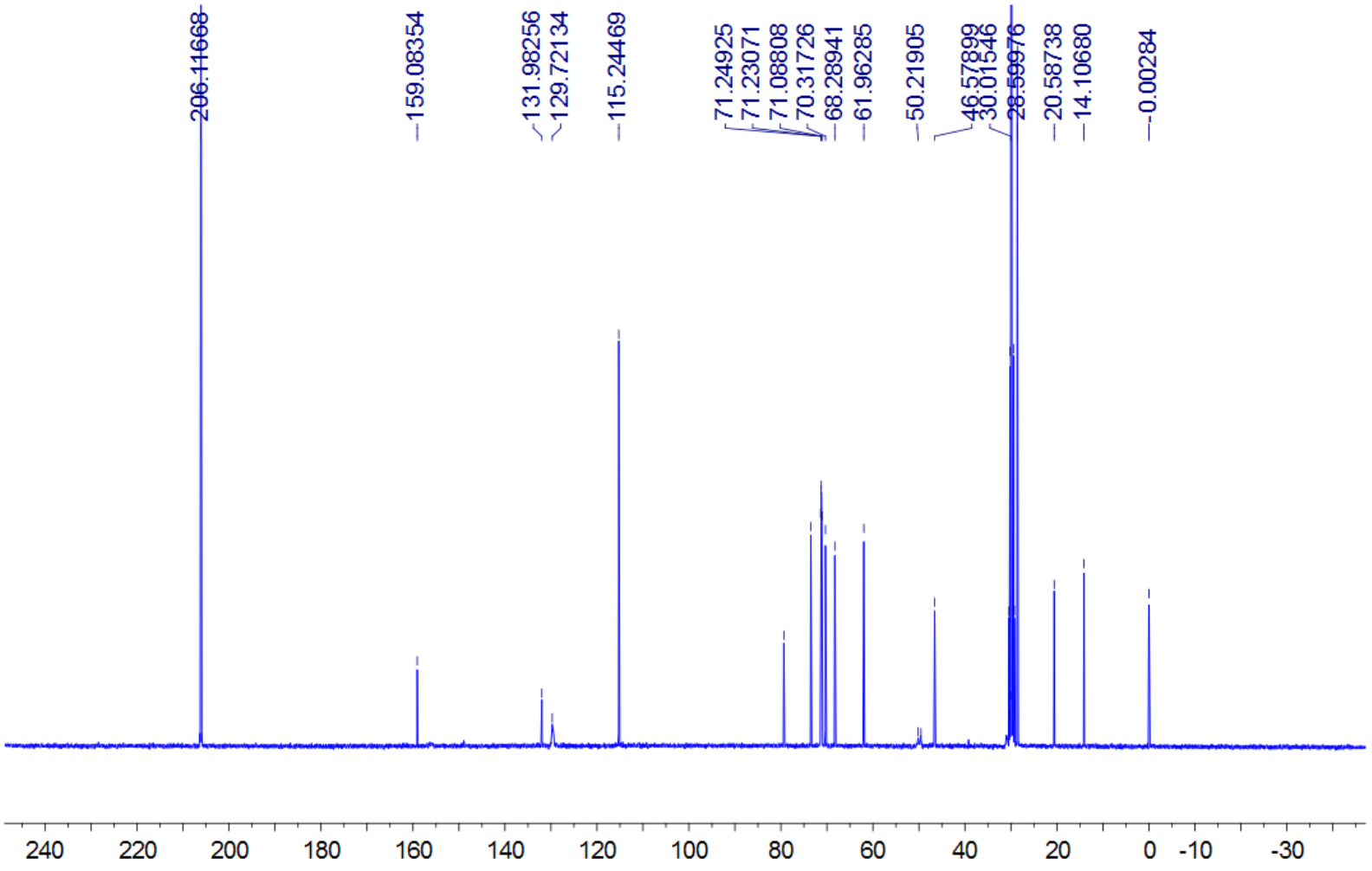
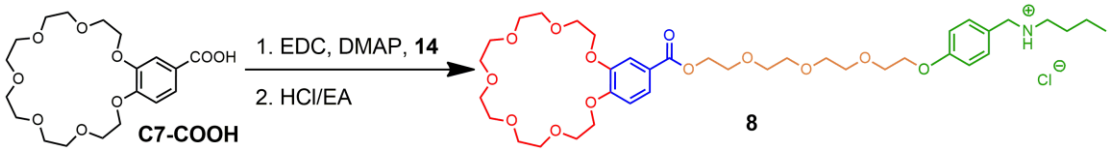


Figure S15. ^{13}C NMR spectrum (100 MHz, acetone-d_6, room temperature) of **14**.

*10. Synthesis of compound **8***



A solution of **C7-COOH** (1.27 g, 3.20 mmol), **14** (1.44 g, 3.20 mmol), EDC (610 mg, 3.20 mmol) and DMAP (390 mg, 3.20 mmol) in dichloromethane (30 mL) was stirred over night at room temperature. The solvent was removed to give the crude product. It was purified by column chromatography on silica gel (EA : PE = 2 : 1, *v/v*). The oil was dissolved in 10% HCl/ethyl acetate (25 mL) and stirred over night. The solvent was removed. It was dissolved in dichloromethane and washed with aqueous solution of Na_2CO_3. The organic layers were combined and the solvent was removed. Then, it was dissolved in water and concentrated HCl was added to afford monomer **8** as a yellow oil (1.40 g, 56%). The proton NMR spectrum of **8** is shown in Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$-*d*, room temperature) δ (ppm): 9.65 (s, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.59–7.46 (m, 3H), 6.96–6.83 (m, 3H), 4.46–4.41 (m, 1H), 4.20 (s, 4H), 4.08–4.03 (m, 1H), 4.03–3.91 (m, 8H), 3.86–3.57 (m, 31H), 2.75 (s, 2H), 1.81 (s, 2H), 1.40–1.28 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H). The ^{13}C NMR spectrum of **8** is shown in Figure S17. ^{13}C NMR (100 MHz, $CDCl_3$-*d*, room temperature) δ (ppm): 166.26, 159.53, 152.91, 148.18, 131.92, 131.86, 124.09, 122.81, 122.30, 115.03, 114.59, 112.17, 71.24, 71.13, 71.02, 70.96, 70.79, 70.73, 70.65, 70.53, 69.62, 69.57, 69.48, 69.29, 69.23, 69.02, 67.39, 61.58, 49.98, 45.73, 45.55, 27.79, 20.04, 13.49. HRESIMS: *m/z* calcd for $[M - Cl]^+$ $C_{38}H_{59}NO_{13}$, 737.3986; found 737.4007, error 2.8 ppm.

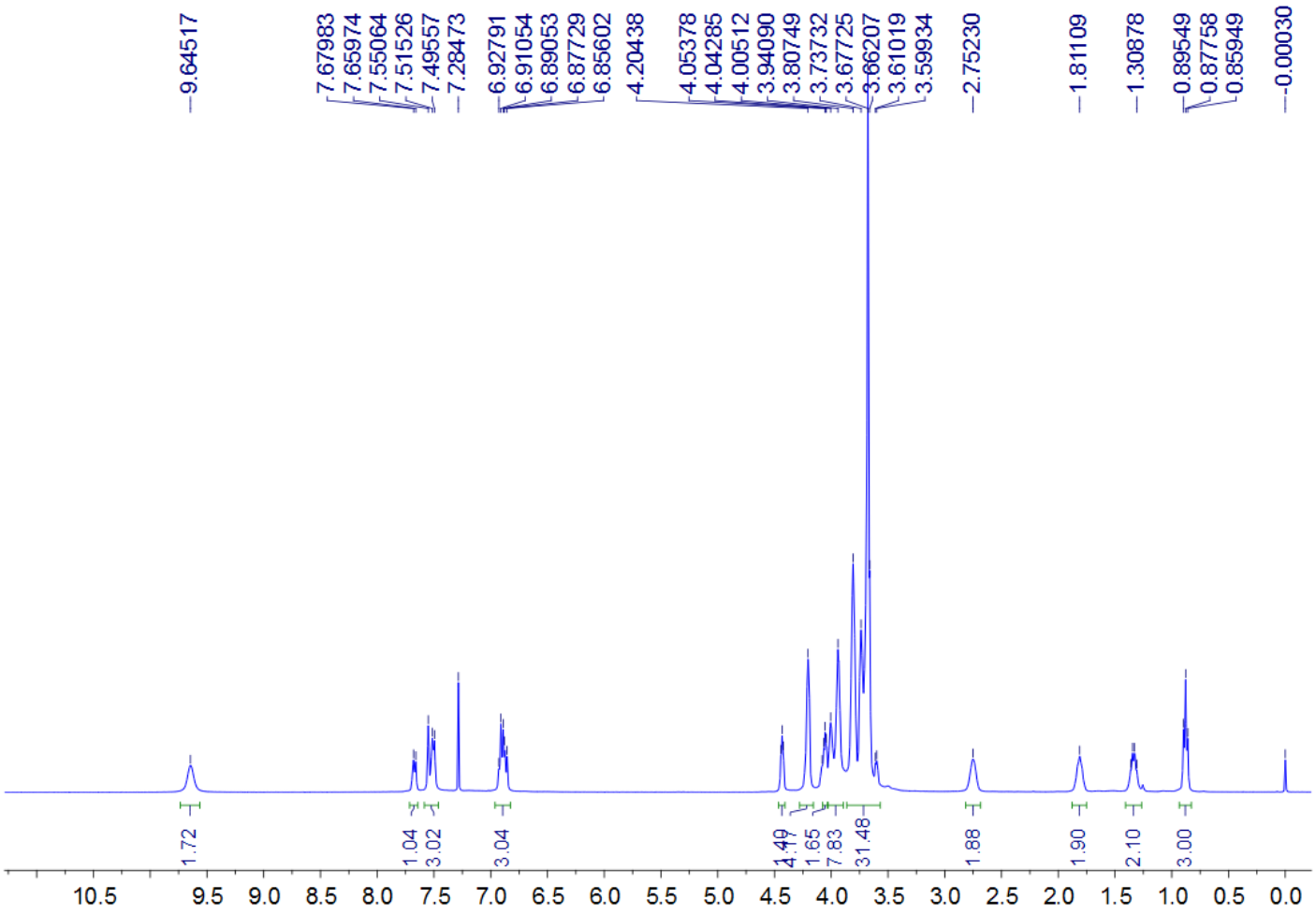


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$-*d*, room temperature) of **8**.

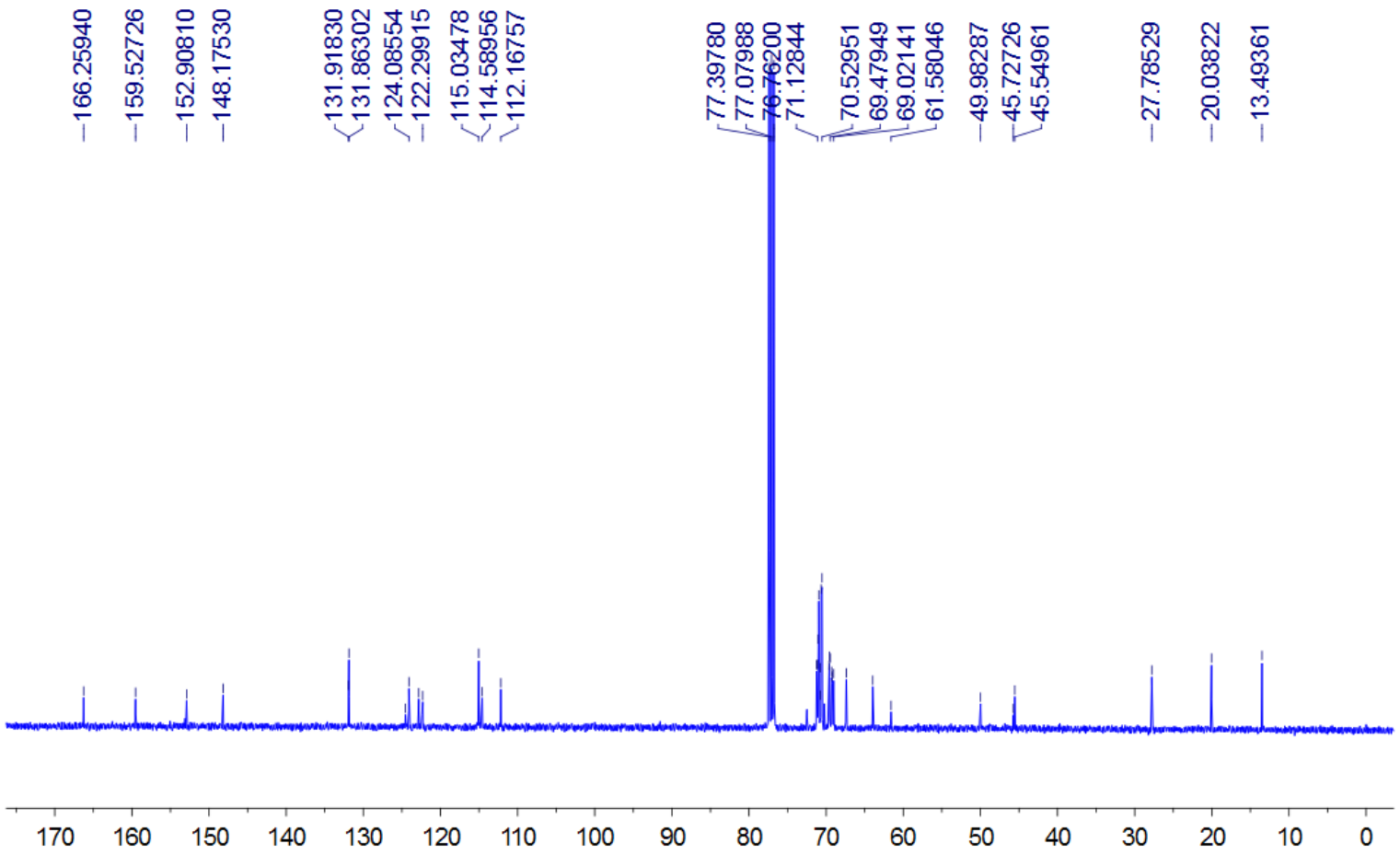
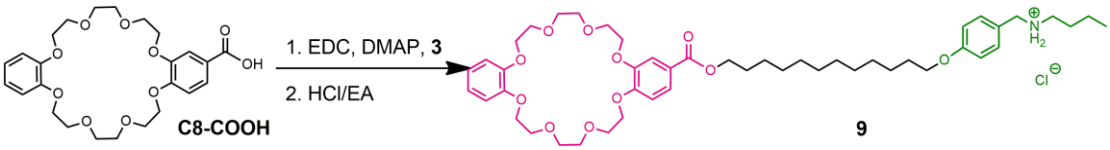


Figure S17. ^{13}C NMR spectrum (100 MHz, $CDCl_3$-*d*, room temperature) of **8**.

11. Synthesis of compound ***9***



A solution of **C8-COOH** (956 mg, 1.94 mmol), **3** (900 mg, 1.94 mmol), EDC (726 mg, 3.80 mmol) and DMAP (61 mg, 0.50 mmol) in dichloromethane (15 mL) was stirred for 24 h at room temperature. The solvent was removed to give the crude product. It was purified by column chromatography on silica gel (EA : PE=2:1, *v/v*). The oil was dissolved in 10% HCl/ethyl acetate (10 mL) and stirred overnight. The white solid was filtered and washed with ethyl acetate thoroughly to afford monomer **9** as a white solid (200 mg, 11%), mp 118.6−120.1 ℃. The proton NMR spectrum of **9** is shown in Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$-*d*, room temperature) δ (ppm): 9.78–9.60 (br, 2H), 7.63 (d, J = 8.3 Hz, 1H), 7.53–7.44 (m, 3H), 6.90–6.80 (m, 7H), 4.25 (t, J = 6.6 Hz, 2H), 4.22–4.08 (m, 8H), 4.00–3.78 (m, 20H), 2.71 (s, 2H), 1.85–1.66 (m, 6H), 1.48–1.20 (m, 18H), 0.87 (t, J = 7.3 Hz, 3H). The ^{13}C NMR spectrum of **9** is shown in Figure S19. ^{13}C NMR (100 MHz, $CDCl_3$-*d*, room temperature) δ (ppm): 166.62, 160.15, 153.01, 149.12, 148.44, 132.04, 124.03, 123.48, 122.06, 121.63, 115.12, 114.61, 114.25, 112.23, 71.66, 71.56, 71.48, 70.16, 70.00, 69.85, 69.71, 69.61, 69.56, 69.49, 68.24, 65.20, 50.25, 45.78, 29.79, 29.61, 29.52, 29.39, 28.98, 28.03, 26.25, 26.22, 20.28, 13.70. HRESIMS: *m/z* calcd for [M − Cl] $C_{48}H_{71}NO_{11}$, 837.5027; found 837.5023, error -0.5 ppm.

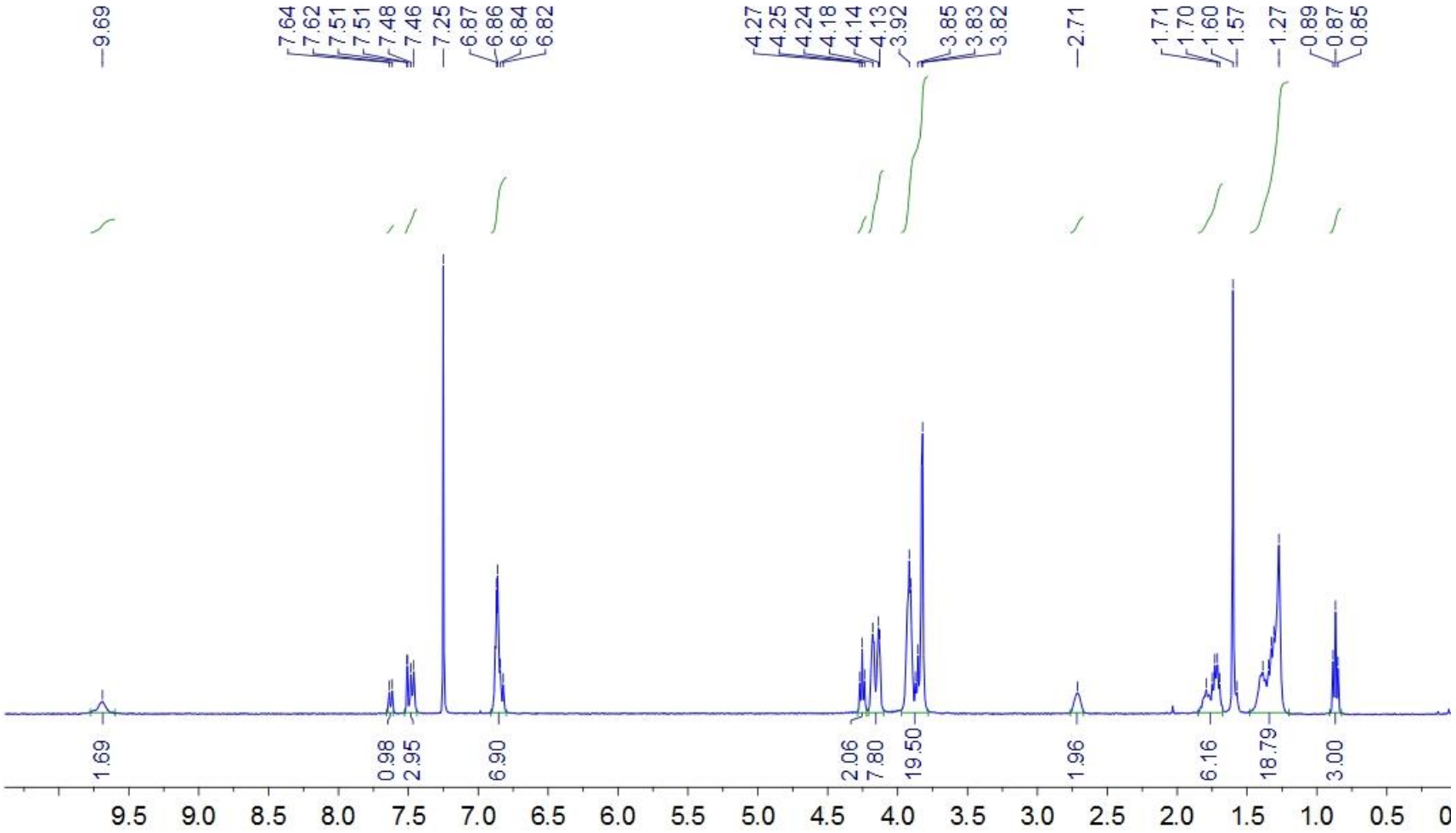


Figure S18. ^{1}H NMR spectrum (400 MHz, $CDCl_3$-*d*, room temperature) of **9**.

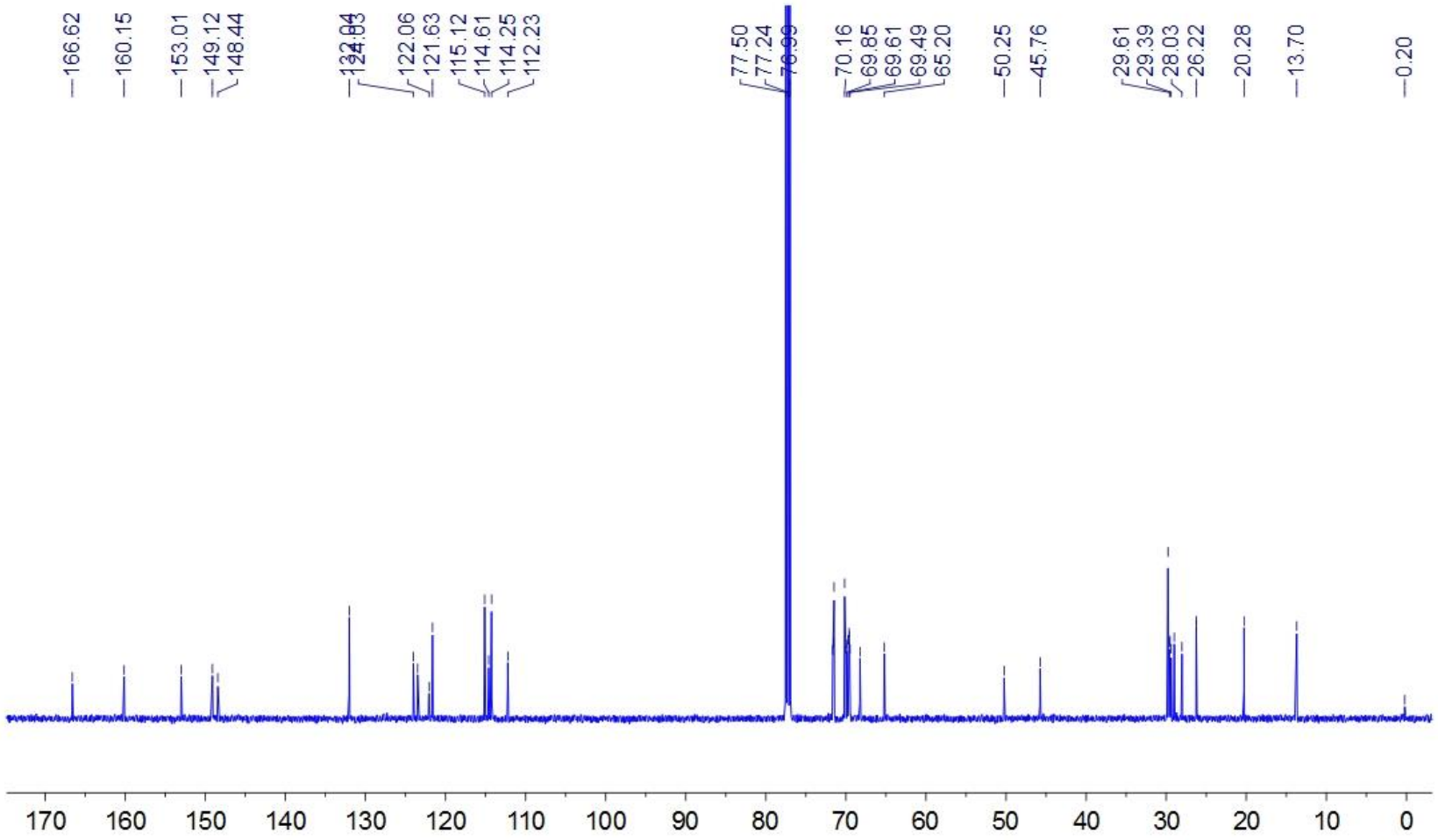
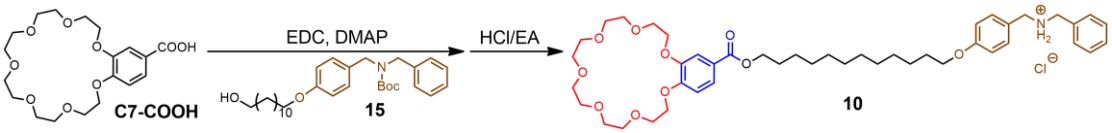


Figure S19. ^{13}C NMR spectrum (100 MHz, $CDCl_3$-*d*, room temperature) of **9**.

*12. Synthesis of compound **10***



A solution of **C7-COOH** (426 mg, 1.07 mmol), **15** (530 mg, 1.07 mmol), EDC (306 mg, 1.50 mmol) and DMAP (24 mg, 0.20 mmol) in dichloromethane (10 mL) was stirred for 24 h at room temperature. The solvent was removed to give the crude product. It was purified by column chromatography on silica gel (EA : PE=2:1, *v/v*). The oil was dissolved in 10% HCl/ethyl acetate (10 mL) and stirred overnight. The white solid was filtered and washed with ethyl acetate thoroughly to afford monomer **10** as a white solid (400 mg, 46%), mp 140−141.3 ℃. The proton NMR spectrum of **10** is shown in Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$-*d*, room temperature) δ (ppm): 10.24–10.04 (br, 2H), 7.65 (d, J = 8.3 Hz, 1H), 7.57–7.48 (m, 3H), 7.43–7.30 (m, 5H), 6.90–6.81 (m, 3H), 4.27 (t, J = 6.7 Hz, 2H), 4.23–4.17 (m, 4H), 3.98–3.90 (m, 4H), 3.87–3.61 (m, 22H), 1.80–1.66 (m, 5H), 1.47–1.23 (m, 18H). The ^{13}C NMR spectrum of **10** is shown in Figure S21. ^{13}C NMR (100 MHz, $CDCl_3$-*d*, room temperature) δ (ppm): 166.63, 160.11, 153.02, 148.45, 132.10, 130.55, 130.41, 129.49, 129.29, 124.05, 123.53, 121.61, 115.10, 114.83, 112.47, 71.53, 71.42, 72.31, 71.23, 70.78, 69.88, 69.73, 69.51, 69.31, 66.20, 65.20, 48.66, 48.44, 29.79, 29.52, 29.38, 28.99, 26.25, 26.21. HRESIMS: *m*/*z* calcd for [M − Cl] $C_{45}H_{65}NO_{10}$, 779.4608; found 779.4612, error 0.5 ppm.

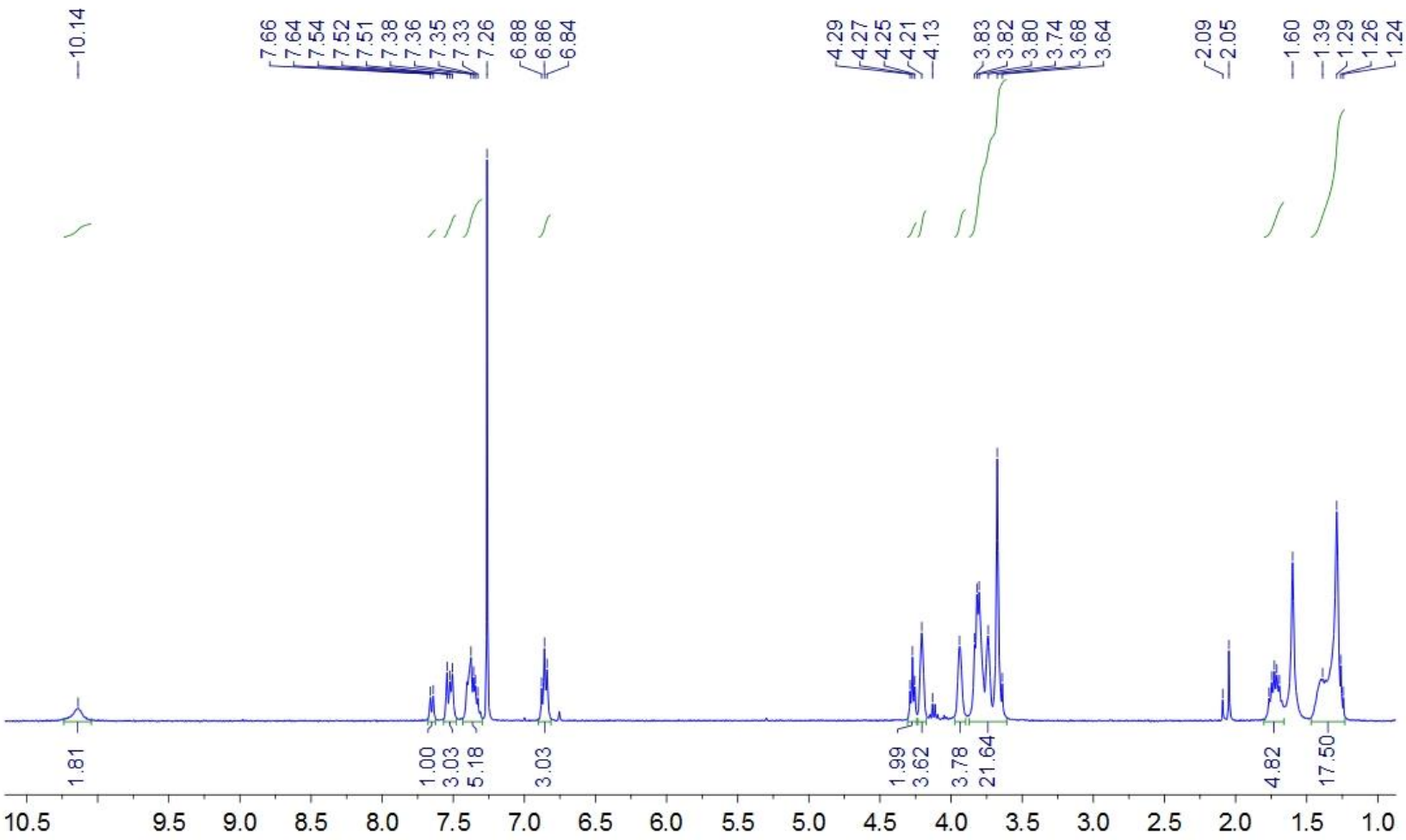


Figure S20. ^{1}H NMR spectrum (400 MHz, $CDCl_3$-*d*, room temperature) of **10**.

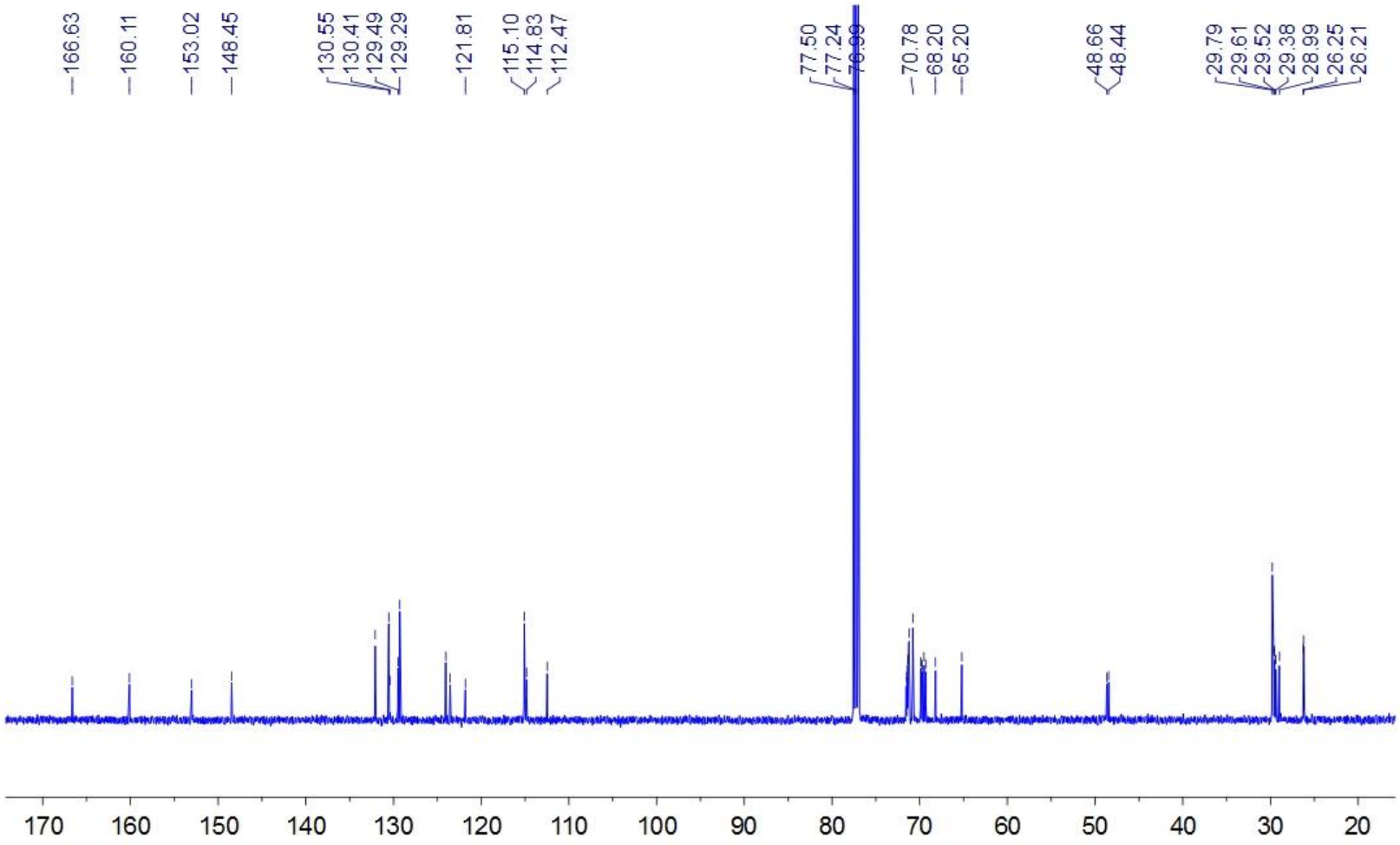


Figure S21. ^{13}C NMR spectrum (100 MHz, $CDCl_3$-*d*, room temperature) of **10**.

13. Rheological results

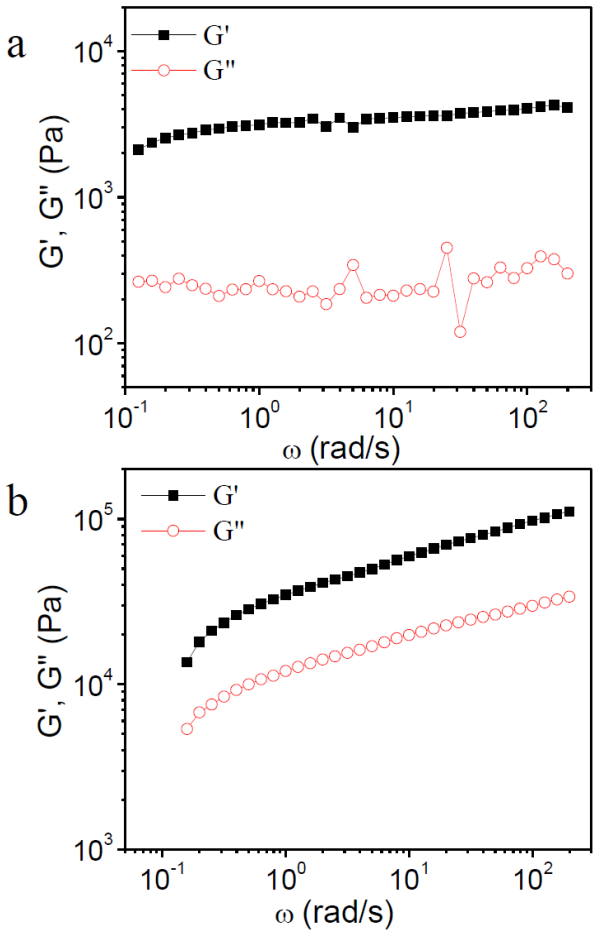


Figure S22. Storage modulus (G') and loss modulus (G") versus frequency (ω) for gels prepared from **4** in water (a) and in acetonitrile (b).

References:

S1. (a) D.-J. Feng, X.-Q. Li, X.-Z. Wang, X.-K. Jiang and Z.-T. Li, *Tetrahedron*, 2004, **60**, 613; (b) K. Kishimoto, T. Suzawa, T. Yokota, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2005, **127**, 15618; (c) L. Wu, Y.-M. He and Q.-H. Fan, *Adv. Synth. Catal.*, 2011, **353**, 2915; (d) S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao and F. Huang, *Angew. Chem., Int. Ed.*, 2011, **50**, 1905; (e) B. Zheng, M. Zhang, S. Dong, J. Liu and F. Huang, *Org. Lett.*, 2012, **14**, 306..

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