

Supporting Information

Synthesis of diamido-bridged bis-pillar[5]arenes and tris-pillar[5]arenes for construction of unique [1]rotaxanes and bis-[1]rotaxanes

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Experimental procedures and characterization data

Materials and methods

All reactions were performed in open atmosphere unless otherwise stated. All reagents, unless otherwise indicated, were obtained from commercial sources. Melting points (m.p.) were determined using a Focus X-4 apparatus and were not corrected. All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 400 MHz or 600 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. 2D NOESY experiments were performed on a Bruker DPX 600 MHz spectrometer. High-resolution ionization mass spectra (HR-ESI-MS) were recorded on Trace DSQ XaMis LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. The starting materials mono-(ω -bromoalkyl)pillar[5]arenes **1a–c** [1], amido-functionalized pillar[5]arenes **4a–d** [2], and di-(ω -bromobutyl)pillar[5]arenes **6** [1] were prepared according to the published methods.

[1] Huo, G. F.; Han, Y.; Sun, J.; Yan, C. G. *J Incl Phenom Macrocycl Chem* **2016**, 86, 231-240.

[2] Han, Y.; Huo, G. F.; Sun, J.; Xie, J.; Yan, C. G.; Zhao, Y.; Wu, X.; Lin, C.; Wang, L. Y. *Sci. Reports* **2016**, 6, 28748.

1. General procedure for the synthesis of pillar[5]arene mono-oxyalkoxybenzoates

2a–f: A mixture of mono-(ω -bromoalkyl)pillar[5]arene **1a–c** (1.0 mmol), methyl or ethyl 4-hydroxybenzoate (1.2 mmol), potassium iodide (0.5 g) and potassium carbonate (40.0 mmol, 5.50 g) in dry acetonitrile (50.0 mL) was refluxed for one day. After cooling, the solid was removed by filtration and the solvent was removed by evaporation at reduced pressure. The resulting crude product was recrystallized from ethanol to give the pure product.

2a: White solid, 80%, m.p. 88-90 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.98 (d, J = 4.4 Hz, 2H, ArH), 6.88 (d, J = 4.8 Hz, 2H, ArH), 6.80-6.77 (m, 10H, ArH), 4.01-4.00 (m, 2H, CH_2), 3.92-3.91 (m, 2H, CH_2), 3.89 (s, 3H, OCH_3), 3.84 (t, J = 6.4 Hz, 2H, CH_2), 3.77-3.76 (m, 10H, CH_2), 3.68-3.64 (m, 24H, OCH_3), 1.96 (brs, 4H, CH_2), 1.78-1.72 (m, 2H, CH_2), 1.54-1.47 (m, 2H, CH_2), 0.95 (t, J = 7.2 Hz, 3H, CH_3), ^{13}C NMR (100 MHz, CDCl_3) δ : 166.8, 162.7, 150.7, 150.7, 150.7, 150.7, 150.6, 150.1, 149.7, 131.5, 128.3, 128.3, 128.1, 122.4, 114.9, 114.1, 114.0, 114.0, 114.0, 113.9, 113.9, 68.1, 67.8, 67.6, 60.5, 55.8, 55.7, 55.7, 55.7, 55.7, 55.6, 51.8, 31.8, 29.7, 29.6, 29.5,

26.2, 26.0, 19.4, 13.9, IR (KBr) ν : 3579, 3414, 3052, 2944, 2862, 2835, 2750, 1928, 1713, 1660, 1610, 1503, 1460, 1400, 1260, 1211, 1177, 1105, 1045, 983, 931, 849, 772, 770 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{59}\text{H}_{69}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 985.4738, found: 985.4749.

2b: White solid, 78%, m.p. 90-92 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.98 (d, $J = 8.8$ Hz, 2H, ArH), 6.88 (d, $J = 8.8$ Hz, 2H, ArH), 6.78-6.75 (m, 10H, ArH), 4.37-4.32 (m, 2H, CH_2), 4.01-4.00 (m, 2H, CH_2), 3.89 (t, $J = 5.2$ Hz, 2H, CH_2), 3.83 (t, $J = 6.4$ Hz, 2H, CH_2), 3.77-3.76 (m, 10H, CH_2), 3.65-3.60 (m, 24H, OCH_3), 1.94 (brs, 4H, CH_2), 1.77-1.70 (m, 2H, CH_2), 1.52-1.47 (m, 2H, CH_2), 1.38 (t, $J = 7.2$ Hz, 3H, CH_3), 0.94 (t, $J = 7.6$ Hz, 3H, CH_3), ^{13}C NMR (100 MHz, CDCl_3) δ : 166.4, 162.7, 150.7, 150.6, 150.6, 150.6, 150.6, 150.1, 149.6, 131.5, 128.4, 128.4, 128.3, 128.3, 128.2, 122.7, 114.8, 114.0, 113.9, 113.8, 113.8, 68.1, 67.9, 67.6, 60.6, 55.8, 55.8, 55.7, 55.7, 55.6, 31.8, 29.6, 29.6, 29.5, 29.5, 26.3, 19.4, 14.3, 13.9, IR (KBr) ν : 3462, 3051, 2944, 2863, 2835, 2750, 1934, 1708, 1607, 1503, 1461, 1400, 1361, 1211, 1177, 1104, 1044, 931, 850, 772, 701 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{60}\text{H}_{71}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 999.4895, found: 999.4910.

2c: White solid, 81%, m.p. 99-101 $^{\circ}\text{C}$; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.90 (d, $J = 8.4$ Hz, 2H, ArH), 7.01 (d, $J = 8.4$ Hz, 2H, ArH), 6.77-6.75 (m, 10H, ArH), 4.04 (brs, 2H, CH_2), 3.86-3.81 (m, 7H, CH_2OCH_3), 3.65-3.61 (m, 34H, CH_2 , OCH_3), 1.77 (brs, 4H, CH_2), 1.69-1.59 (m, 4H, CH_2), 1.48-1.42 (m, 2H, CH_2), 0.90 (t, $J = 7.6$ Hz, 3H, CH_3), ^{13}C NMR (100 MHz, CDCl_3) δ : 166.8, 162.8, 150.7, 150.6, 150.6, 150.6, 150.0, 149.7, 131.4, 128.3, 128.1, 115.0, 114.8, 114.0, 68.1, 55.7, 51.8, 31.8, 29.6, 29.5, 29.4, 29.4, 19.4, 13.9, IR (KBr) ν : 3845, 3579, 3408, 3072, 2943, 2864, 2835, 2742, 1927, 1714, 1606, 1504, 1462, 1399, 1257, 1211, 1107, 1045, 930, 870, 850, 773, 701 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{60}\text{H}_{71}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 999.4895, found: 999.4907

2d: White solid, 76%, m.p. 96-98 $^{\circ}\text{C}$; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.90 (d, $J = 8.8$ Hz, 2H, ArH), 7.01 (d, $J = 8.8$ Hz, 2H, ArH), 6.77-6.75 (m, 10H, ArH), 4.29-4.24 (m, 2H, CH_2), 4.05 (brs, 2H, CH_2), 3.85-3.80 (m, 4H, CH_2), 3.65-3.61 (m, 34H, CH_2 , OCH_3), 1.78 (brs, 4H, CH_2), 1.69-1.64 (m, 4H, CH_2), 1.47-1.42 (m, 2H, CH_2), 1.29 (t, $J = 7.2$ Hz, 3H, CH_3), 0.90 (t, $J = 7.6$ Hz, 3H, CH_3), ^{13}C NMR (100 MHz, CDCl_3) δ : 166.4, 162.8, 162.8, 150.5, 150.4, 150.4, 149.9, 149.6, 131.4, 128.5, 128.4, 128.3, 116.6, 114.6, 114.0, 113.7, 113.7, 113.6, 113.5, 68.1, 67.9, 60.6, 57.8, 55.7, 55.7, 31.9, 29.5, 19.5, 17.5, 14.3, 14.0, IR (KBr) ν : 3578, 3051, 2942, 2865, 2835, 1708, 1606, 1503, 1462, 1399, 1310, 1259, 1211, 1172, 1105, 1045, 930, 870, 773, 702 cm^{-1} , MS (m/z):

HRMS (ESI) Calcd. for C₆₁H₇₃O₁₃ ([M+H]⁺): 1013.5051, found: 1013.5056.

2e: White solid, 79%, m.p. 111-113 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.98 (d, *J* = 8.4 Hz, 2H, ArH), 6.85 (d, *J* = 8.4 Hz, 2H, ArH), 6.78-6.76 (m, 10H, ArH), 3.89 (s, 3H, OCH₃), 3.82 (brs, 6H, CH₂), 3.76 (brs, 10H, CH₂), 3.64-3.60 (m, 24H, OCH₃), 1.74 (brs, 4H, CH₂), 1.48-1.46 (m, 4H, CH₂), 1.38 (t, *J* = 7.2 Hz, 2H, CH₂), 1.25-1.24 (m, 2H, CH₂), 0.93 (t, *J* = 6.8 Hz, 3H, CH₃), ¹³C NMR (100 MHz, CDCl₃) δ: 167.0, 163.1, 150.7, 150.7, 150.6, 150.6, 150.6, 150.1, 131.4, 128.2, 128.2, 113.9, 68.1, 60.6, 55.9, 55.8, 55.7, 51.8, 31.8, 29.7, 19.3, 14.4, 13.9, IR (KBr) ν: 3656, 2942, 2862, 2836, 1714, 1606, 1503, 1462, 1399, 1261, 1211, 1174, 1104, 1044, 929, 850, 773, 701 cm⁻¹, MS (m/z): HRMS (ESI) Calcd. for C₆₁H₇₃O₁₃ ([M+H]⁺): 1013.5051, found: 1013.5060.

2f: White solid, 78%, m.p. 96-98 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.98 (d, *J* = 8.8 Hz, 2H, ArH), 6.86 (d, *J* = 8.8 Hz, 2H, ArH), 6.79-6.73 (m, 10H, ArH), 4.37-4.32 (m, 2H, CH₂), 3.85-3.81 (m, 8H, CH₂), 3.77-3.76 (m, 10H, CH₂), 3.65-3.59 (m, 24H, OCH₃), 1.76-1.71 (m, 4H, CH₂), 1.62 (brs, 2H, CH₂), 1.50-1.47 (m, 4H, CH₂), 1.38 (t, *J* = 6.8 Hz, 3H, CH₃), 0.94 (t, *J* = 7.2 Hz, 3H, CH₃), ¹³C NMR (100 MHz, CDCl₃) δ: 166.5, 163.3, 162.9, 150.7, 150.7, 150.7, 150.7, 150.1, 149.8, 131.3, 128.2, 114.9, 113.9, 68.2, 60.6, 55.8, 55.7, 31.8, 29.7, 19.3, 14.4, 13.9, IR (KBr) ν: 3657, 2942, 2862, 2835, 1708, 1607, 1502, 1462, 1398, 1263, 1211, 1173, 1100, 928, 850, 773, 702 cm⁻¹, MS (m/z): HRMS (ESI) Calcd. for C₆₂H₇₅O₁₃ ([M+H]⁺): 1027.5208, found: 1027.5216.

2. General procedure for the synthesis of pillar[5]arene oxyalkoxybenzoic acids (**3a–c**):

A mixture of pillar[5]arene oxyalkoxybenzoates **2a–f** (0.5 mmol) and potassium hydroxide (10.0 mmol, 0.56 g) in 95% ethanol was refluxed overnight. After cooling, the solution was neutralized with dilute hydrochloric acid to give white precipitates, which were washed with water to give the pure products **3a–c**.

3a: White solid, 81%, m.p. 100-102 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ: 12.65 (s, 1H, COOH), 7.88 (d, *J* = 8.8 Hz, 2H, ArH), 7.00 (d, *J* = 8.8 Hz, 2H, ArH), 6.79-6.75 (m, 10H, ArH), 4.12 (t, *J* = 6.0 Hz, 2H, CH₂), 3.90 (t, *J* = 6.0 Hz, 2H, CH₂), 3.82 (t, *J* = 6.4 Hz, 2H, CH₂), 3.65-3.64 (m, 34H, CH₂ OCH₃), 1.96-1.90 (m, 4H, CH₂), 1.71-1.64 (m, 2H, CH₂), 1.48-1.42 (m, 2H, CH₂), 0.90 (t, *J* = 7.2 Hz, 3H, CH₃), ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 167.6, 162.5, 150.3, 150.3, 150.2, 149.6, 149.4, 131.7, 128.1, 127.9, 127.9, 127.9, 127.9, 127.8, 114.5, 113.7, 113.7, 113.6, 67.9, 55.8, 55.7, 31.6, 29.5, 29.4, 26.2, 25.9, 19.3, 14.1, IR (KBr) ν: 3834, 3577, 3427, 2941, 2862, 2835, 2659, 1926, 1685, 1605, 1504, 1461, 1398, 1309, 1252, 1232, 1187, 1101, 1043, 931, 851, 775 cm⁻¹, MS

(m/z):HRMS (ESI) Calcd. for $C_{58}H_{67}O_{13}$ ($[M+H]^+$): 971.4582, found: 971.4587.

3b: White solid, 78%, m.p. 106-108 °C; 1H NMR (400 MHz, DMSO- d_6) δ : 12.61 (s, 1H, COOH), 7.88 (d, J = 8.8 Hz, 2H, ArH), 7.00 (d, J = 8.8 Hz, 2H, ArH), 6.77-6.76 (m, 10H, ArH), 4.05 (t, J = 6.0 Hz, 2H, CH₂), 3.87-3.80 (m, 4H, CH₂), 3.65-3.64 (m, 34H, CH₂, OCH₃), 3.82 (t, J = 6.4 Hz, 2H, CH₂), 3.65-3.61 (m, 34H, CH₂, OCH₃), 1.79 (t, J = 6.4 Hz, 4H, CH₂), 1.69-1.63 (m, 4H, CH₂), 1.48-1.42 (m, 2H, CH₂), 0.90 (t, J = 7.2 Hz, 3H, CH₃), ^{13}C NMR (100 MHz, DMSO- d_6) δ : 167.4, 162.6, 150.3, 150.3, 150.2, 150.2, 149.6, 131.7, 128.0, 128.0, 127.9, 127.8, 127.8, 114.5, 113.7, 113.7, 113.6, 113.6, 68.1, 68.0, 67.8, 55.8, 55.7, 55.7, 31.6, 29.3, 22.7, 19.3, 14.2, δ : IR (KBr) ν : 3656, 2940, 2862, 2835, 1685, 1605, 1503, 1462, 1399, 1255, 1211, 1171, 1100, 1044, 930, 850, 775, 701 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $C_{59}H_{69}O_{13}$ ($[M+H]^+$): 985.4738, found: 985.4743.

3c: White solid, 79%, m.p. 110-112 °C; 1H NMR (400 MHz, DMSO- d_6) δ : 12.61 (s, 1H, COOH), 7.87 (d, J = 8.8 Hz, 2H, ArH), 6.97 (d, J = 8.8 Hz, 2H, ArH), 6.77-6.76 (m, 10H, ArH), 4.00 (t, J = 6.4 Hz, 2H, CH₂), 3.85-3.80 (m, 4H, CH₂), 3.65-3.64 (m, 34H, CH₂, OCH₃), 3.82 (t, J = 6.4 Hz, 2H, CH₂), 3.65-3.61 (m, 34H, CH₂, OCH₃), 1.78-1.64 (m, 6H, CH₂), 1.53-1.40 (m, 6H, CH₂), 0.90 (t, J = 7.2 Hz, 3H, CH₃), ^{13}C NMR (100 MHz, DMSO- d_6) δ : 167.5, 162.5, 150.4, 150.3, 150.3, 150.3, 149.5, 149.5, 131.6, 128.0, 127.9, 127.9, 114.5, 113.8, 113.7, 113.7, 68.1, 68.0, 67.8, 55.8, 31.6, 28.8, 25.8, 25.7, 19.3, 14.1, IR (KBr) ν : 3634, 2940, 2860, 2836, 2661, 1686, 1605, 1503, 1462, 1399, 1304, 1254, 1211, 1171, 1100, 1043, 930, 850, 775, 703 cm^{-1} , MS (m/z):HRMS (ESI) Calcd. for $C_{60}H_{71}O_{13}$ ($[M+H]^+$): 999.4895, found: 999.4903.

3. General procedure for the preparation of diamido-bridged bispillar[5]arenes 5a–d: A mixture of pillar[5]arene oxybutoxybenzoic acid **3a** (0.6 mmol, 0.58g), amido-functionalized pillar[5]arenes **4a–d** (0.6 mmol), HOBt (1.0 mmol, 0.14g) and EDCI (1.0 mmol, 0.19 g) in dry CHCl₃ (10.0 mL) was stirred at room temperature for twelve hours. The solvent was removed under reduced pressure. The residue was subjected to column chromatography with methylene dichloride/methanol (v/v = 30:1–10:1) as eluent to give the pure product **5a–d** for analysis.

5a: White solid, 29%, m.p. 126-128 °C; 1H NMR (600 MHz, CDCl₃) δ : 7.51 (d, J = 7.2 Hz, 2H, ArH), 6.99-6.87 (m, 6H, ArH), 6.83-6.67 (m, 16H, ArH), 6.43 (brs, 1H, NH), 4.32 (s, 2H, CH₂), 4.10 (t, J = 6.0 Hz, 2H, CH₂), 4.00 (brs, 1H, NH), 3.93 (t, J = 6.0 Hz, 2H, CH₂), 3.86-3.63 (m, 68H, 10CH₂, 16OCH₃), 3.36 (brs, 2H, CH₂), 2.09-2.04 (m, 2H, CH₂), 2.02-1.97 (m, 2H, CH₂),

1.85-1.81 (m, 2H, CH₂), 1.75-1.70 (m, 2H, CH₂), 1.62 (s, 4H, CH₂), 1.58-1.54 (m, 2H, CH₂), 1.51-1.47 (m, 2H, CH₂), 1.28-1.22 (m, 2H, CH₂), 0.99 (t, $J = 7.2$ Hz, 3H, CH₃), 0.94 (t, $J = 7.2$ Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ : 161.2, 151.5, 150.9, 150.8, 150.7, 150.6, 150.5, 150.3, 150.2, 150.1, 149.7, 148.9, 129.0, 128.7, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.0, 115.0, 114.9, 114.8, 114.6, 114.5, 114.2, 114.1, 114.0, 113.9, 113.8, 113.2, 112.9, 112.8, 68.1, 67.9, 67.7, 66.5, 56.1, 55.9, 55.8, 55.7, 55.4, 55.3, 52.4, 38.1, 31.9, 31.8, 29.7, 29.6, 29.4, 26.5, 26.4, 22.6, 19.4, 14.0, 13.9; IR (KBr) ν : 3397, 2933, 2837, 1667, 1610, 1501, 1460, 1397, 1309, 1210, 1101, 1042, 928, 871, 770 cm⁻¹; MS (m/z): HRMS (ESI) Calcd. for C₁₀₉H₁₂₇N₂O₂₃ ([M+H]⁺): 1832.8863, found: 1832.8849.

5b: White solid, 44%, m.p. 136-138 °C; ¹H NMR (600 MHz, CDCl₃) δ : 7.71 (d, $J = 8.4$ Hz, 2H, ArH), 6.97-6.75 (m, 22H, ArH), 6.51 (brs, 1H, NH), 4.43 (brs, 1H, NH), 4.11 (t, $J = 6.0$ Hz, 2H, CH₂), 3.98-3.92 (m, 4H, CH₂), 3.89 (brs, 2H, CH₂), 3.84-3.64 (m, 68H, 10CH₂, 16OCH₃), 3.57 (brs, 2H, CH₂), 3.32 (brs, 2H, CH₂), 2.09-2.06 (m, 2H, CH₂), 2.01-1.99 (m, 2H, CH₂), 1.81-1.79 (m, 2H, CH₂), 1.79-1.72 (m, 2H, CH₂), 1.57 (s, 4H, CH₂), 1.55-1.48 (m, 4H, CH₂), 0.98 (t, $J = 7.2$ Hz, 3H, CH₃), 0.95 (t, $J = 7.2$ Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ : 161.0, 150.8, 150.7, 150.6, 150.5, 150.4, 150.3, 150.2, 149.7, 148.4, 128.8, 128.6, 128.3, 128.2, 128.1, 128.0, 114.9, 114.8, 114.1, 114.0, 113.9, 68.1, 67.9, 67.7, 55.8, 55.7, 55.6, 36.0, 35.1, 31.9, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 26.4, 26.3, 22.6, 19.4, 14.1, 14.0, 13.9; IR (KBr) ν : 3401, 2931, 2857, 1663, 1611, 1501, 1460, 1396, 1307, 1210, 1042, 928, 873, 770 cm⁻¹; MS (m/z): HRMS (ESI) Calcd. for C₁₁₀H₁₂₉N₂O₂₃ ([M+H]⁺): 1846.9020, found: 1846.9072.

5c: White solid, 16%, m.p. 130-132 °C; ¹H NMR (600 MHz, CDCl₃) δ : 7.85 (d, $J = 8.4$ Hz, 2H, ArH), 7.02-6.96 (m, 8H, ArH), 6.90 (s, 1H, ArH), 6.84-6.75 (m, 12H, ArH), 6.61 (s, 1H, ArH), 5.25 (brs, 1H, NH), 4.62 (brs, 1H, NH), 4.54 (d, $J = 5.4$ Hz, 2H, CH₂), 4.14 (t, $J = 6.0$ Hz, 2H, CH₂), 3.94 (t, $J = 6.0$ Hz, 2H, CH₂), 3.87-3.63 (m, 68H, 10CH₂, 16OCH₃), 3.53 (s, 2H, CH₂), 2.10-2.08 (m, 2H, CH₂), 2.02-2.00 (m, 2H, CH₂), 1.74-1.72 (m, 2H, CH₂), 1.59 (s, 6H, CH₂), 1.51-1.49 (m, 2H, CH₂), 1.47-1.43 (m, 2H, CH₂), 1.24 (m, 2H, CH₂), 0.95-0.91 (m, 6H, CH₃), -1.88- -2.14 (m, 4H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ : 166.5, 161.2, 150.8, 150.7, 150.6, 150.5, 150.4, 150.2, 150.1, 150.0, 149.8, 149.7, 148.4, 131.9, 129.8, 129.0, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.5, 127.4, 126.6, 117.8, 117.0, 114.8, 114.1, 114.0, 113.9, 113.7, 113.1, 113.0, 112.6, 112.4, 68.1, 67.9, 67.8, 66.0, 57.7, 55.8, 55.7, 55.6, 55.4, 55.3, 39.8, 37.2,

31.8, 31.4, 29.7, 29.6, 29.5, 29.4, 28.7, 28.5, 27.4, 26.5, 26.4, 22.8, 22.6, 19.4, 14.0, 13.9; IR (KBr) ν : 3408, 2937, 1670, 1610, 1501, 1460, 1397, 1306, 1210, 1102, 1042, 928, 873, 771, 703 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{111}\text{H}_{131}\text{N}_2\text{O}_{23}$ ($[\text{M}+\text{H}]^+$): 1860.9176, found: 1860.9220.

5d: White solid, 28%, m.p. 129-131 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ : 7.85 (d, J = 8.4 Hz, 2H, ArH), 7.01-6.74 (m, 22H, ArH), 6.13 (brs, 1H, NH), 5.28 (brs, 1H, NH), 4.59 (d, J = 5.4 Hz, 2H, CH_2), 4.12 (t, J = 6.0 Hz, 2H, CH_2), 3.92 (t, J = 6.0 Hz, 2H, CH_2), 3.83-3.73 (m, 48H, 16 OCH_3), 3.66-3.60 (m, 20H, 10 CH_2), 3.52 (s, 2H, CH_2), 2.09-2.04 (m, 2H, CH_2), 1.99-1.97 (m, 2H, CH_2), 1.74-1.70 (m, 2H, CH_2), 1.62-1.58 (m, 8H, CH_2), 1.51-1.45 (m, 4H, CH_2), 1.24-1.23 (m, 6H, CH_2), 0.95-0.89 (m, 6H, CH_3), 0.07 (s, 2H, CH_2), -0.28 (s, 2H, CH_2), -0.72- -0.97 (m, 2H, CH_2), -1.58- -1.66 (m, 2H, CH_2), -2.07 (s, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ : 167.6, 166.5, 161.4, 150.9, 150.8, 150.7, 150.6, 150.5, 150.4, 150.3, 150.2, 150.1, 149.7, 147.2, 129.6, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.1, 115.8, 115.2, 115.0, 114.9, 114.8, 114.3, 114.1, 114.0, 113.9, 112.8, 112.7, 112.2, 68.9, 68.1, 67.9, 67.8, 67.7, 65.9, 57.0, 56.3, 55.9, 55.8, 55.7, 55.6, 55.5, 55.4, 55.3, 55.1, 40.0, 37.9, 31.9, 31.8, 30.1, 29.7, 29.6, 29.5, 29.4, 28.9, 28.8, 28.6, 28.5, 26.4, 26.3, 26.2, 25.9, 24.2, 24.1, 23.4, 22.6, 19.4, 14.1, 13.9; IR (KBr) ν : 3411, 2934, 2858, 1668, 1609, 1501, 1460, 1397, 1306, 1210, 1100, 1043, 929, 872, 770, 704 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{113}\text{H}_{135}\text{N}_2\text{O}_{23}$ ($[\text{M}+\text{H}]^+$): 1888.9489, found: 1888.9523.

4. General procedure for the synthesis of pillar[5]arene di-oxyalkoxybenzoic acid 8: A mixture of di-(ω -bromobutyl)pillar[5]arene **6** (1.0 mmol, 0.990 g), methyl 4-hydroxybenzoate (2.4 mmol, 0.365 g), potassium iodide (2.4 mmol, 0.40 g) and potassium carbonate (40.0 mmol, 5.50 g) in dry acetonitrile (50.0 mL) was refluxed for one day. After cooling, the solid was removed by filtration and the solvent was removed by evaporation at reduced pressure. The residue was subjected to column chromatography with light petroleum and ethyl acetate (v/v = 3:1) to give the product. It was recrystallized from ethanol to give pure product **7**. Then, the product **7** was poured into potassium hydroxide (10.0 mmol, 0.56 g) in 95% ethanol and was refluxed overnight. After cooling, the solution was neutralized with dilute hydrochloric acid to give white precipitate, which was washed with water to give the pure product **8**.

7: White solid, 40%, m.p. 84.5-86.3 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.87 (d, J = 4 Hz, 4H, ArH), 6.87 (d, J = 4 Hz, 4H, ArH), 6.77-6.72 (m, 10H, ArH), 4.99 (t, J = 6 Hz, 4H, OCH_2),

3.89-3.88 (m, 10H, 4OCH₂, 6OCH₃), 3.77-3.75 (m, 10H, CH₂), 3.64-3.57 (m, 24H, OCH₃), 1.94-1.88 (m, 8H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ: 166.8, 162.7, 150.7, 150.7, 150.7, 150.6, 149.8, 131.5, 128.3, 128.3, 128.3, 128.2, 128.1, 122.3, 114.9, 114.1, 114.1, 114.0, 114.0, 113.8, 113.8, 67.9, 67.6, 60.4, 55.8, 55.8, 55.7, 52.6, 51.8, 29.6, 29.5, 26.2, 25.9, 21.0, 14.1; IR (KBr) ν: 3435, 2936, 2829, 1715, 1606, 1580, 1501, 1466, 1436, 1399, 1281, 1256, 1212, 1168, 1103, 1046, 1010, 975, 930, 880, 849, 772, 732 cm⁻¹; MS (m/z): HRMS (ESI) Calcd. for C₆₇H₇₄O₁₆ ([M+Na]⁺): 1157.4875, found: 1157.4856.

8: White solid, 85%, m.p. 216.6-218.2 °C; ¹H NMR (400 MHz, CDCl₃) δ: 12.62(s, 2H, COOH), 7.87 (d, *J* = 4Hz, 4H, ArH), 6.98 (d, *J* = 4Hz, 4H, ArH), 6.78-6.73 (m, 10H, ArH), 4.09 (s, 4H, CH₂), 3.92-3.57 (m, 36H, 12CH₂, 24OCH₃), 3.34 (s, 2H, CH₂), 1.93-1.90 (m, 8H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ: 167.4, 162.6, 150.3, 150.2, 149.5, 131.7, 128.0, 127.9, 127.9, 127.8, 123.2, 114.5, 114.5, 114.4, 113.7, 113.7, 113.6, 67.9, 67.7, 55.7, 29.4, 29.2, 29.1, 26.1, 25.9; IR (KBr) ν: 3436, 2931, 1682, 1605, 1579, 1501, 1466, 1427, 1400, 1255, 1212, 1168, 1105, 1047, 929, 849, 774, 698 cm⁻¹; MS (m/z): HRMS (ESI) Calcd. for C₆₅H₇₀O₁₆Na ([M+Na]⁺): 1129.4592, found: 1129.4540.

5. General procedure for the preparation of diamido-bridged tris-pillar[5]arenes 9a-9d: To a solution of amido-functionalized pillar[5]arenes **4a-4d** (0.22mmol), pillar[5]arene di-oxybutoxybenzoic acid **8** (0.1 mmol, 0.11g) in dry CHCl₃ (20.0 mL) was added HOBt (0.25 mmol, 0.033g) and EDCI (0.25 mmol, 0.048 g). The mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure. The residue was subjected to column chromatography with methylene dichloride/methanol (v/v = 12:1) as eluent to give the pure product **9a-d** for analysis.

9a: White solid, 26%, m.p. 129-131 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.50 (d, *J* = 8 Hz, 4H, ArH), 6.96-6.65 (m, 34H, ArH), 6.40 (s, 2H, NH), 5.05 (s, 2H, NH), 4.29 (s, 4H, CH₂), 4.09-3.62 (m, 114H, 42CH₂, 72OCH₃), 3.35 (s, 4H, CH₂), 3.14 (brs, 4H, CH₂), 2.06-1.97 (m, 8H, CH₂), 1.84-1.77 (m, 4H, CH₂), 1.58-1.51 (m, 4H, CH₂), 0.97 (t, *J* = 7.4Hz, 6H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 165.3, 161.2, 151.5, 150.8, 150.8, 150.8, 150.7, 150.7, 150.6, 150.6, 150.5, 150.3, 150.3, 150.3, 150.2, 150.1, 150.0, 148.8, 130.1, 129.0, 128.7, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.7, 127.6, 127.5, 127.0, 114.9, 114.6, 114.2, 114.2, 114.1, 114.0, 114.0, 113.9, 113.9, 113.7, 113.7, 113.5, 113.4, 113.4, 113.4, 113.3, 113.2, 113.2, 113.2,

113.1, 112.9, 112.8, 68.0, 67.6, 66.4, 56.1, 55.8, 55.8, 55.8, 55.8, 55.7, 55.6, 55.6, 55.5, 55.4, 55.3, 55.3, 55.2, 38.1, 31.9, 29.7, 29.6, 29.1, 27.5, 27.5, 27.5, 26.4, 26.4, 26.3, 19.4, 13.9; IR (KBr) ν : 3397, 2935, 2829, 1662, 1608, 1501, 1463, 1400, 1309, 1250, 1045, 928, 878, 848, 771, 700 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{167}\text{H}_{190}\text{N}_4\text{O}_{36}\text{Na}$ ($[\text{M}+\text{Na}]^+$): 2851.3091, found: 2851.3060.

9b: White solid, 22%, m.p. 136-138°C; ^1H NMR (400 MHz, CDCl_3) δ : 7.72 (d, $J = 8$ Hz, 4H, ArH), 7.01-6.77 (m, 34H, ArH), 6.53 (s, 2H, NH), 4.95 (s, 2H, NH), 4.44 (s, 4H, CH_2), 4.14-3.58 (m, 118H, 46 CH_2 , 72 OCH_3), 3.35 (s, 4H, CH_2), 2.10-2.00 (m, 8H, CH_2), 1.84-1.77 (m, 4H, CH_2), 1.59-1.49 (m, 4H, CH_2), 0.99 (t, $J = 8$ Hz, 6H, CH_3), -1.80 (brs, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ : 161.0, 150.9, 150.8, 150.8, 150.7, 150.6, 150.6, 150.4, 150.3, 150.0, 148.4, 129.1, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 114.9, 114.2, 114.0, 114.0, 113.9, 68.0, 67.7, 55.8, 55.8, 55.7, 55.3, 36.0, 35.1, 31.9, 29.7, 29.6, 26.5, 26.4, 19.4, 14.0; IR (KBr) ν : 3340, 2935, 2830, 1664, 1608, 1501, 1400, 1309, 1249, 1211, 1044, 828, 878, 849, 771 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{169}\text{H}_{194}\text{N}_4\text{O}_{36}\text{Na}$ ($[\text{M}+\text{Na}]^+$): 2879.3404, found: 2879.3399.

9c: White solid, 19%, m.p. 146-148°C; ^1H NMR (400 MHz, CDCl_3) δ : 7.86 (d, $J = 6$ Hz, 4H, ArH), 7.03-6.77 (m, 34H, ArH), 6.62 (s, 2H, NH), 5.25 (s, 2H, NH), 4.54 (s, 4H, CH_2), 4.15 (t, $J = 6$ Hz, 4H, CH_2), 3.95-3.53 (m, 118H, 46 CH_2 , 72 OCH_3), 2.10-2.01 (m, 10H, CH_2), 1.47-1.41 (m, 6H, CH_2), 0.93 (t, $J = 8$ Hz, 6H, CH_3), -2.00 (m, 8H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ : 166.6, 166.4, 161.2, 151.4, 150.9, 150.8, 150.8, 150.7, 150.6, 150.5, 150.5, 150.2, 150.1, 150.0, 149.8, 148.4, 131.9, 129.9, 129.0, 128.7, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.5, 127.4, 126.6, 117.8, 117.0, 114.9, 114.3, 114.1, 114.0, 113.9, 113.7, 113.1, 113.1, 113.1, 113.0, 112.9, 112.6, 112.5, 112.4, 70.7, 68.0, 67.7, 66.0, 57.6, 55.8, 55.8, 55.8, 55.7, 55.4, 55.3, 39.8, 37.2, 31.8, 31.3, 29.7, 29.7, 29.6, 28.7, 28.5, 27.4, 26.4, 26.4, 22.9, 22.7, 19.3, 13.9; IR (KBr) ν : 3399, 2935, 2829, 1664, 1608, 1501, 1463, 1400, 1308, 1249, 1211, 1044, 928, 879, 771, 701 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{171}\text{H}_{198}\text{N}_4\text{O}_{36}\text{Na}$ ($[\text{M}+\text{Na}]^+$): 2907.3717, found: 2907.3667.

9d: White solid, 17%, m.p. 140-142°C; ^1H NMR (400 MHz, CDCl_3) δ : 7.84 (d, $J = 4$ Hz, 4H, ArH), 7.01-6.74 (m, 34H, ArH), 6.14 (s, 2H, NH), 5.28 (s, 2H, NH), 4.58 (s, 4H, CH_2), 4.11 (t, $J = 4$ Hz, 4H, CH_2), 3.91-3.62 (m, 118H, 46 CH_2 , 72 OCH_3), 2.70 (brs, 2H, CH_2), 2.51 (brs, 2H, CH_2), 2.08-1.95 (m, 8H, CH_2), 1.48-1.42 (m, 4H, CH_2), 0.89 (t, $J = 4$ Hz, 6H, CH_3), -0.29 (brs, 4H, CH_2), -0.74 (brs, 2H, CH_2), -0.97 (brs, 2H, CH_2), -1.62 (brs, 4H, CH_2), -2.08 (brs, 4H, CH_2); ^{13}C NMR

(100 MHz, CDCl₃) δ : 167.6, 166.4, 161.4, 150.9, 150.9, 150.8, 150.8, 150.7, 150.7, 150.6, 150.6, 150.5, 150.4, 150.3, 150.3, 150.2, 150.1, 149.9, 147.2, 129.6, 129.3, 128.8, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.1, 115.8, 115.1, 115.1, 115.0, 114.8, 114.3, 114.3, 114.1, 114.1, 114.0, 113.9, 113.9, 112.8, 112.7, 112.7, 112.2, 112.2, 112.1, 109.9, 68.8, 67.9, 67.7, 65.8, 57.0, 56.2, 55.9, 55.8, 55.8, 55.7, 55.5, 55.5, 55.4, 55.3, 55.0, 53.1, 40.0, 37.9, 31.8, 30.1, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 28.8, 28.6, 28.5, 26.4, 26.3, 26.2, 26.1, 24.1, 23.4, 23.3, 19.4, 13.9; IR (KBr) ν : 3409, 2935, 2856, 1673, 1608, 1500, 1464, 1400, 1307, 1249, 1210, 1100, 1045, 928, 879, 850, 771, 702 cm⁻¹; MS (m/z): HRMS (ESI) Calcd. for C₁₇₅H₂₀₆N₄O₃₆Na ([M+Na]⁺): 2963.4343, found: 2963.4339.

Figures of single crystal structures S1-S3

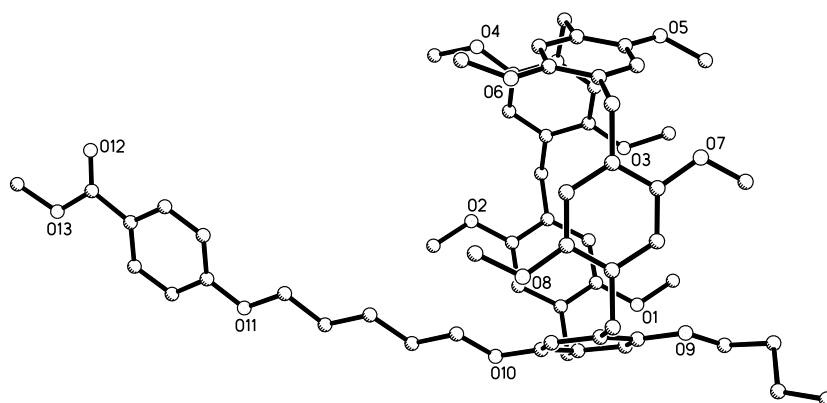


Figure S1: Single crystal structure of pillar[5]arene **2c**.

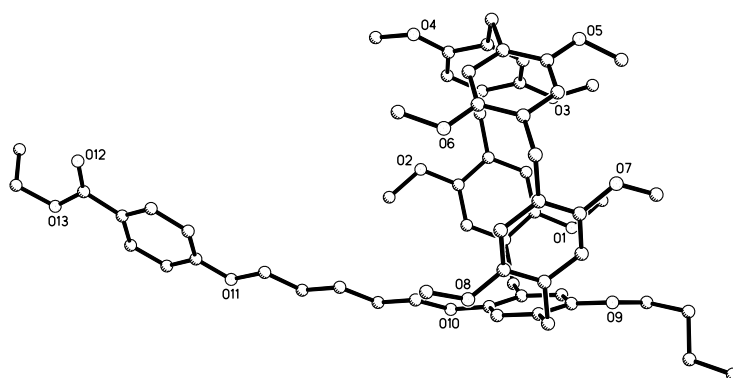


Figure S2: Single crystal structure of pillar[5]arene **2d**.

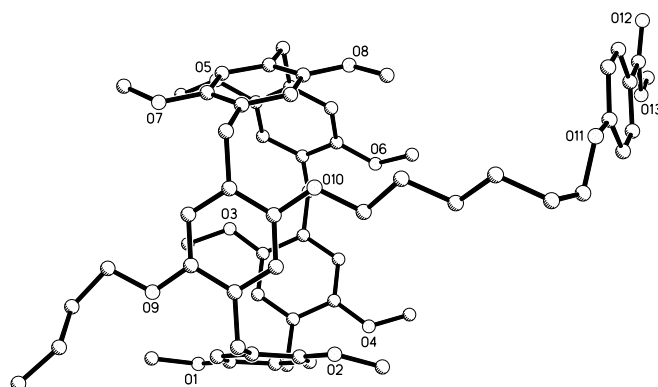


Figure S3: Single crystal structure of pillar[5]arene **2e**.

2D NOESY spectra

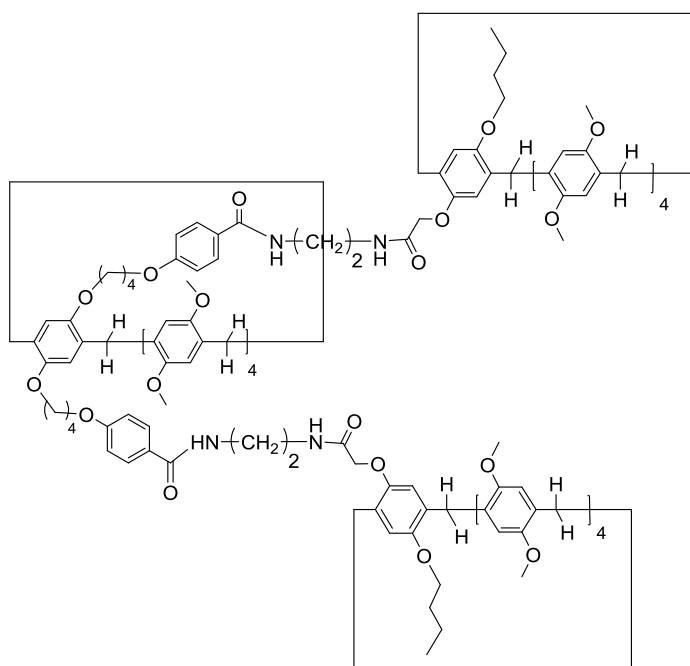
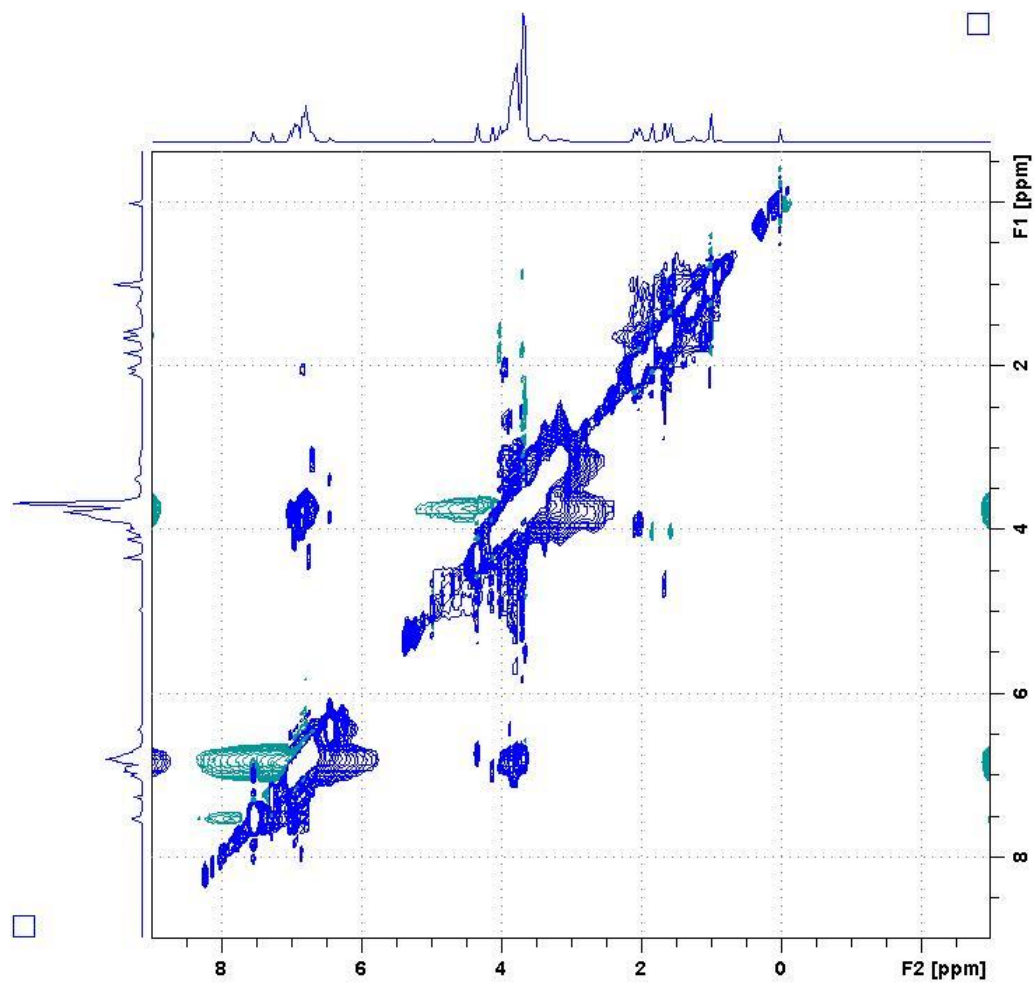


Figure S4: 2D NOESY spectra of the tris-pillar[5]arene **9a**.

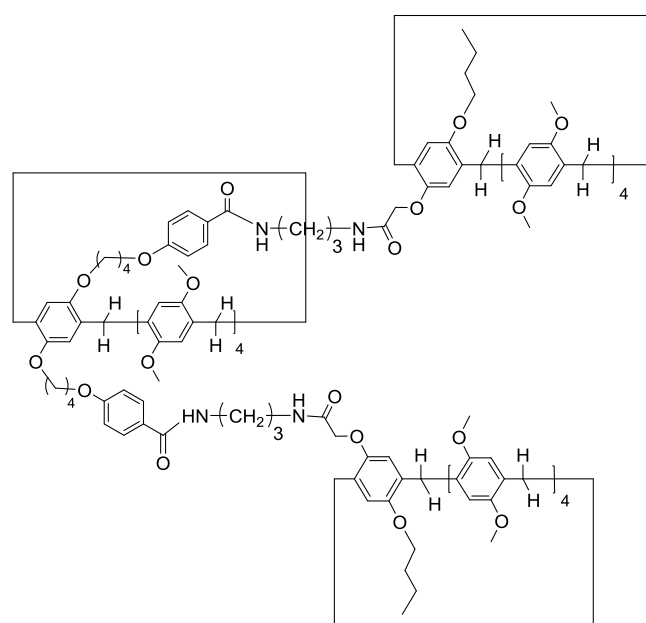
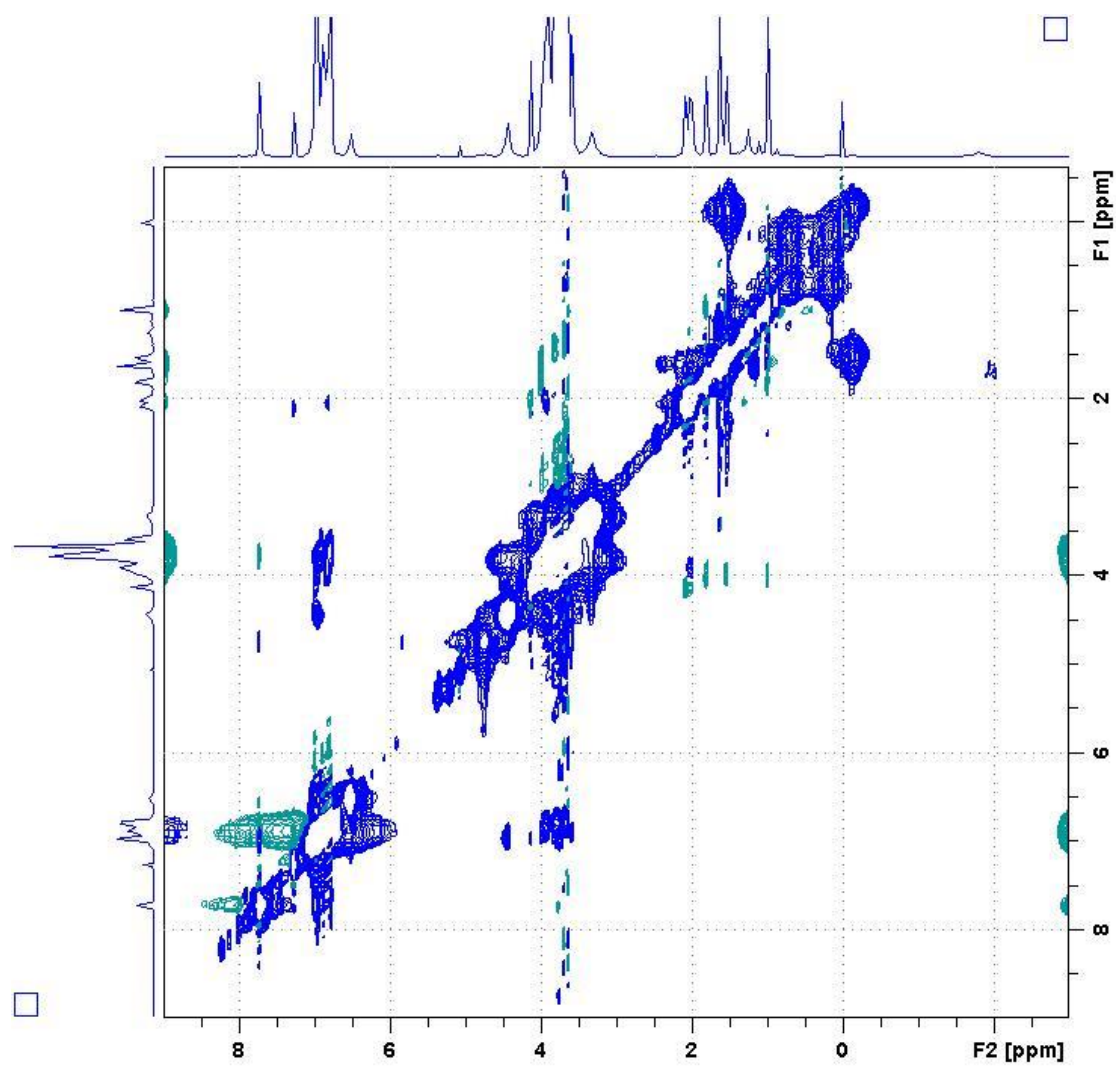


Figure S5: 2D NOESY spectra of the tris-pillar[5]arene **9b**.

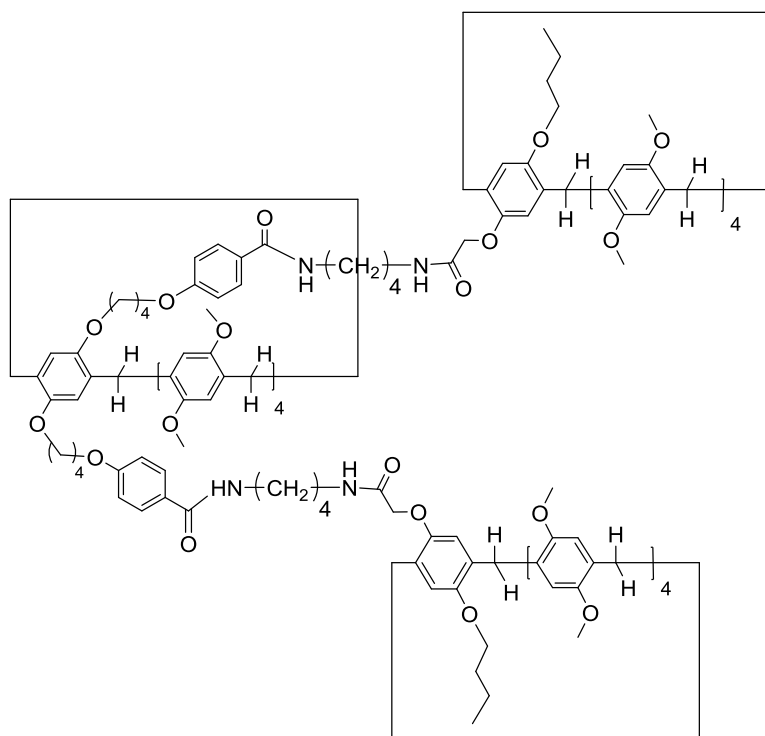
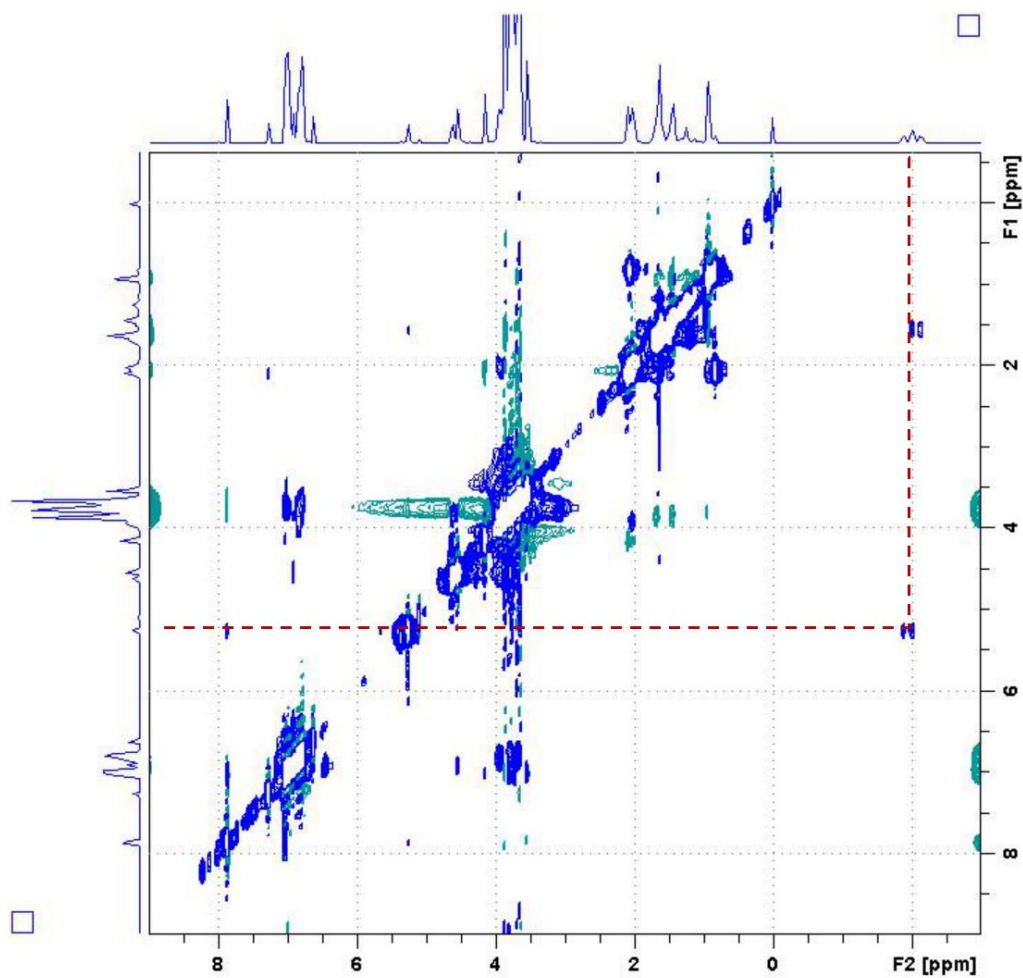
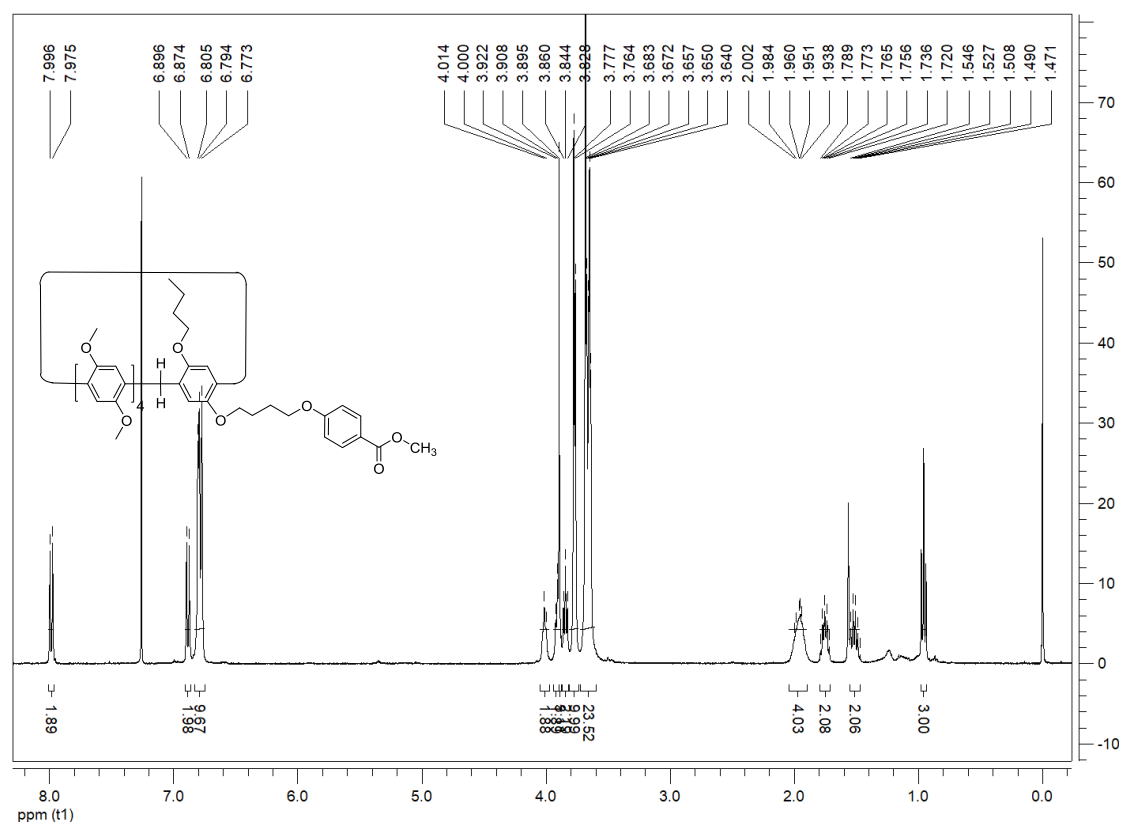
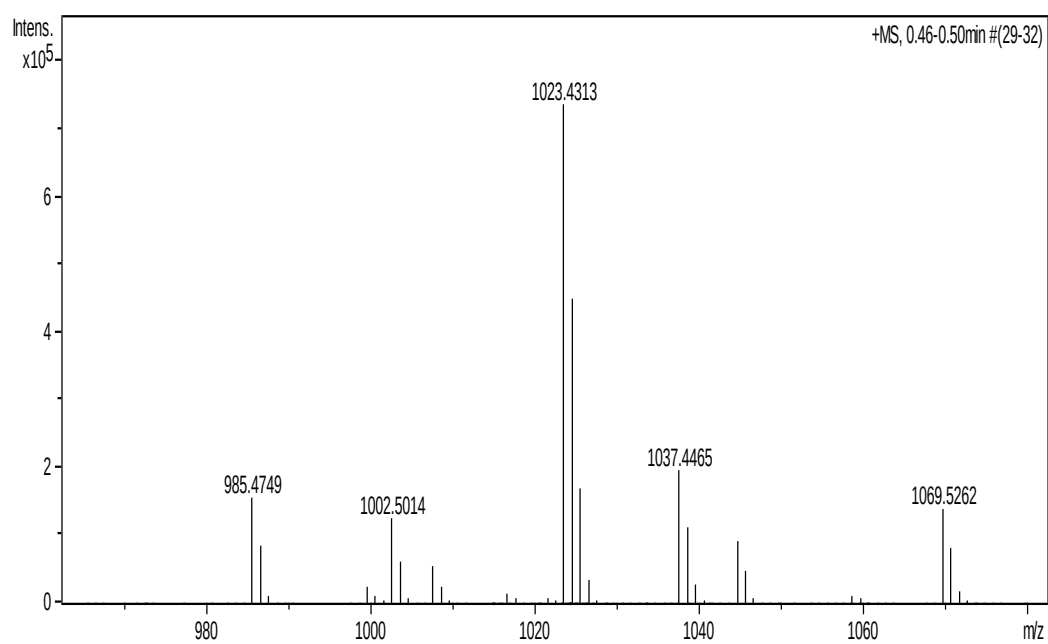
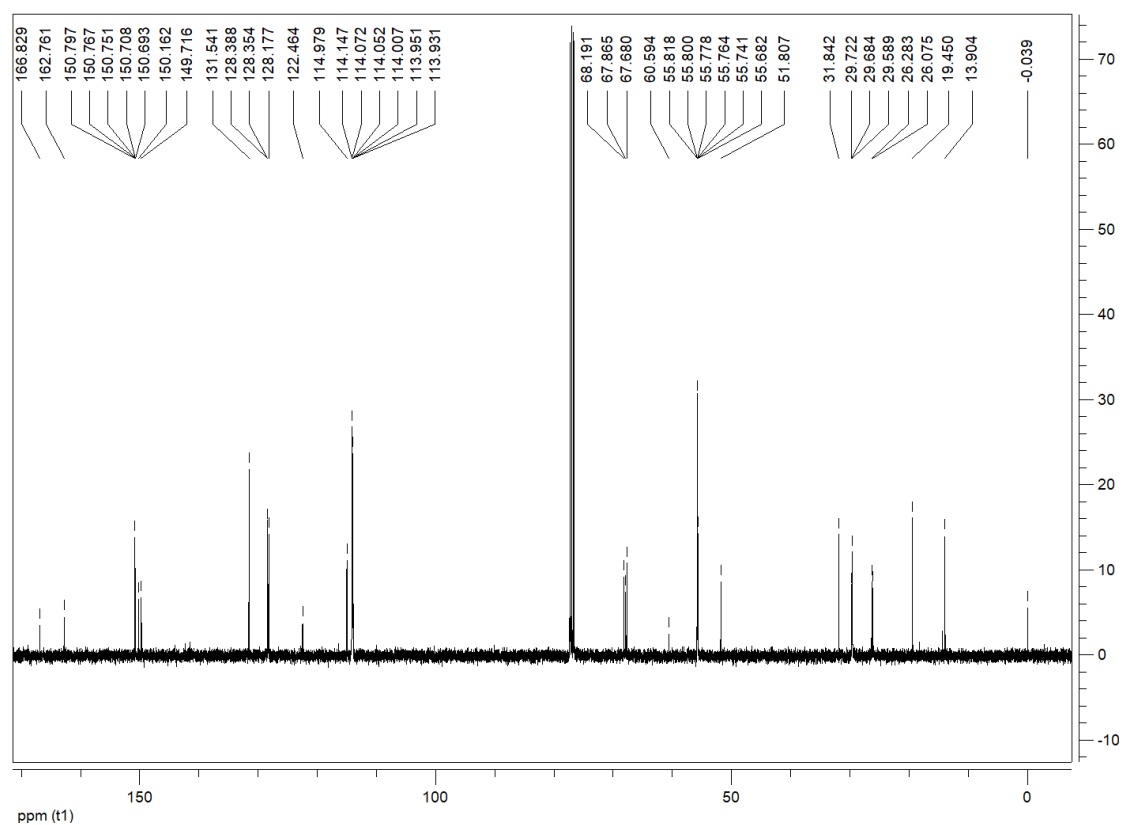


Figure S6: 2D NOESY spectra of the tris-pillar[5]arene **9c**.

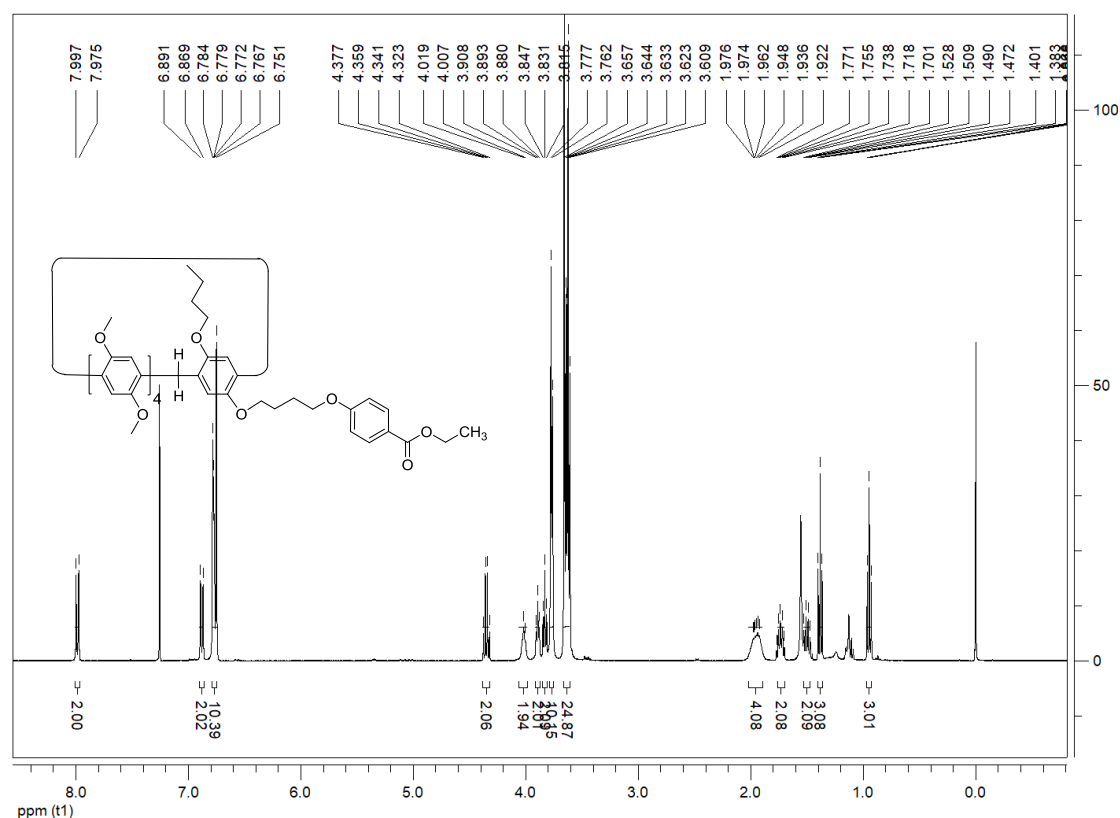
Characterization data and ^1H NMR, ^{13}C NMR, HRMS spectra

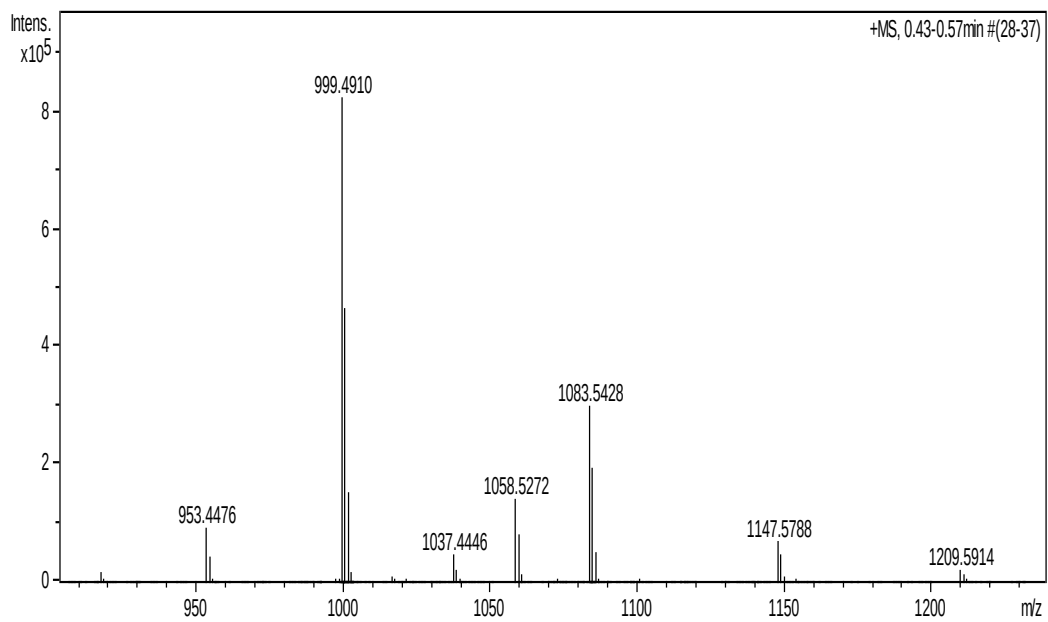
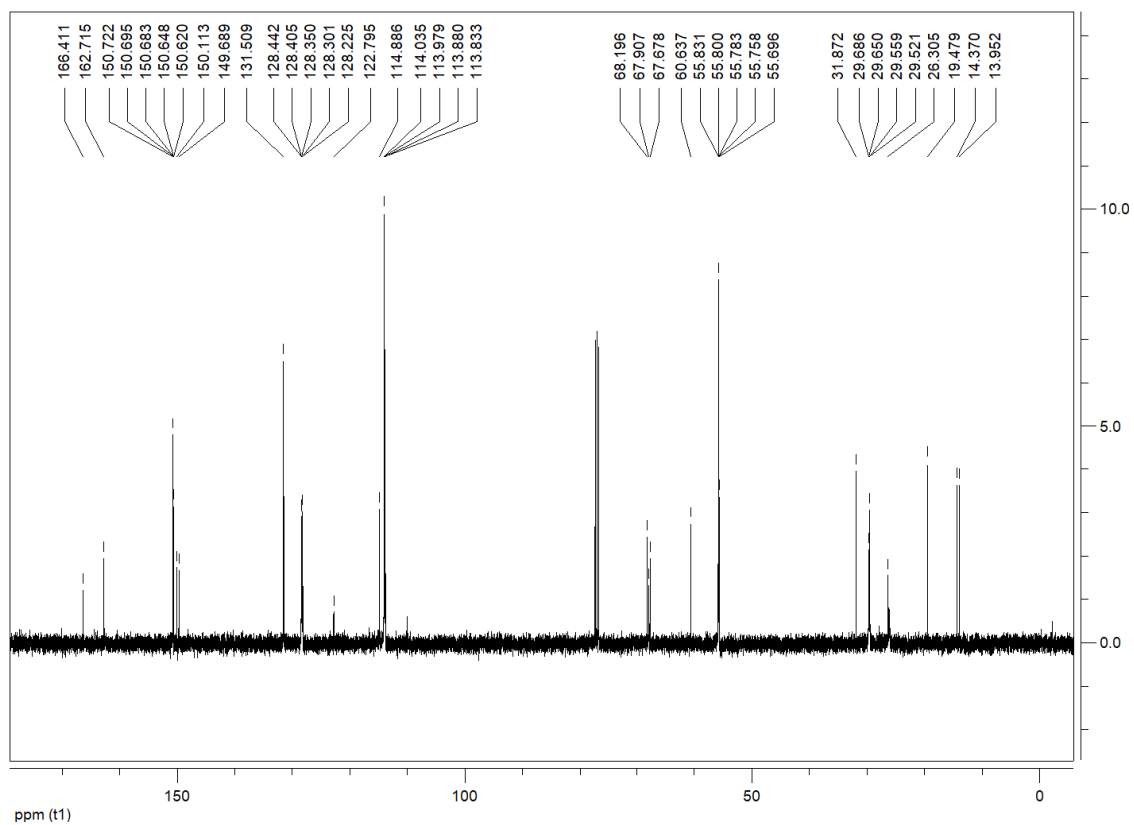
2a: White solid, 80%, m.p. 88-90 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.98 (d, J = 4.4 Hz, 2H, ArH), 6.88 (d, J = 4.8 Hz, 2H, ArH), 6.80-6.77 (m, 10H, ArH), 4.01-4.00 (m, 2H, CH_2), 3.92-3.91 (m, 2H, CH_2), 3.89 (s, 3H, OCH_3), 3.84 (t, J = 6.4 Hz, 2H, CH_2), 3.77-3.76 (m, 10H, CH_2), 3.68-3.64 (m, 24H, OCH_3), 1.96 (brs, 4H, CH_2), 1.78-1.72 (m, 2H, CH_2), 1.54-1.47 (m, 2H, CH_2), 0.95 (t, J = 7.2 Hz, 3H, CH_3), ^{13}C NMR (100 MHz, CDCl_3) δ : 166.8, 162.7, 150.7, 150.7, 150.7, 150.7, 150.6, 150.1, 149.7, 131.5, 128.3, 128.3, 128.1, 122.4, 114.9, 114.1, 114.0, 114.0, 114.0, 113.9, 113.9, 68.1, 67.8, 67.6, 60.5, 55.8, 55.7, 55.7, 55.7, 55.7, 55.6, 51.8, 31.8, 29.7, 29.6, 29.5, 26.2, 26.0, 19.4, 13.9, IR (KBr) ν : 3579, 3414, 3052, 2944, 2862, 2835, 2750, 1928, 1713, 1660, 1610, 1503, 1460, 1400, 1260, 1211, 1177, 1105, 1045, 983, 931, 849, 772, 770 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{59}\text{H}_{69}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 985.4738, found: 985.4749.



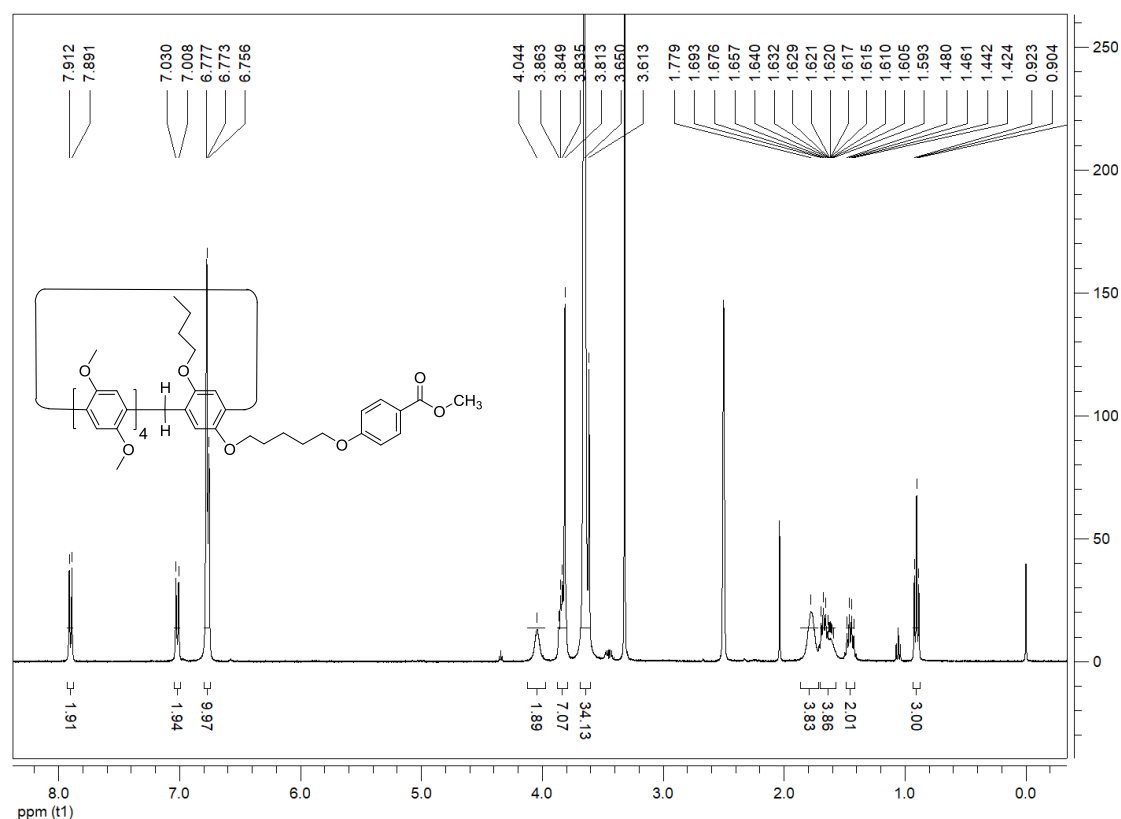


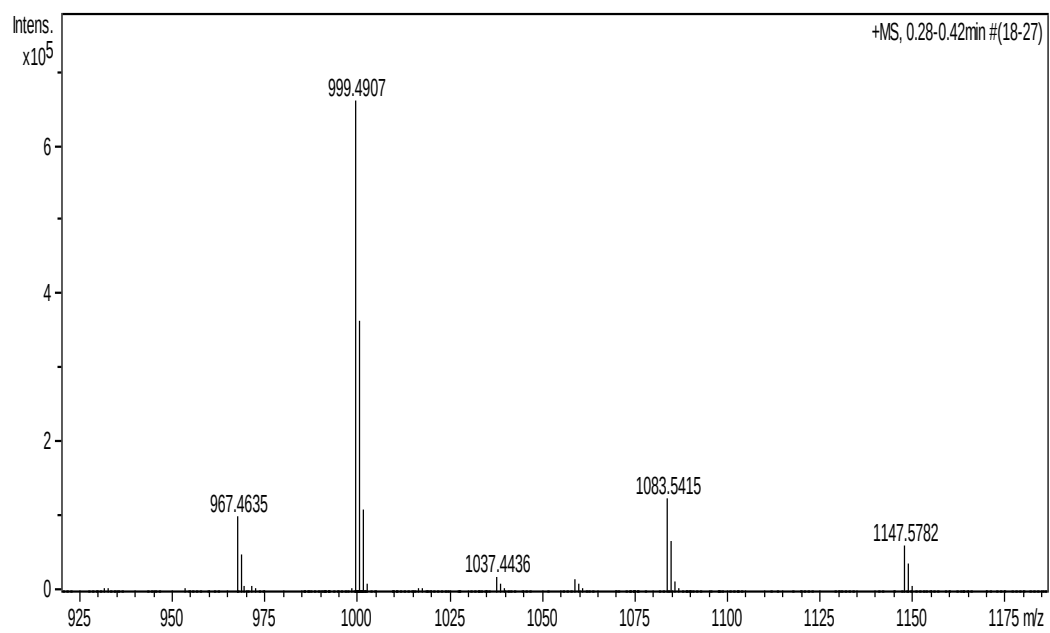
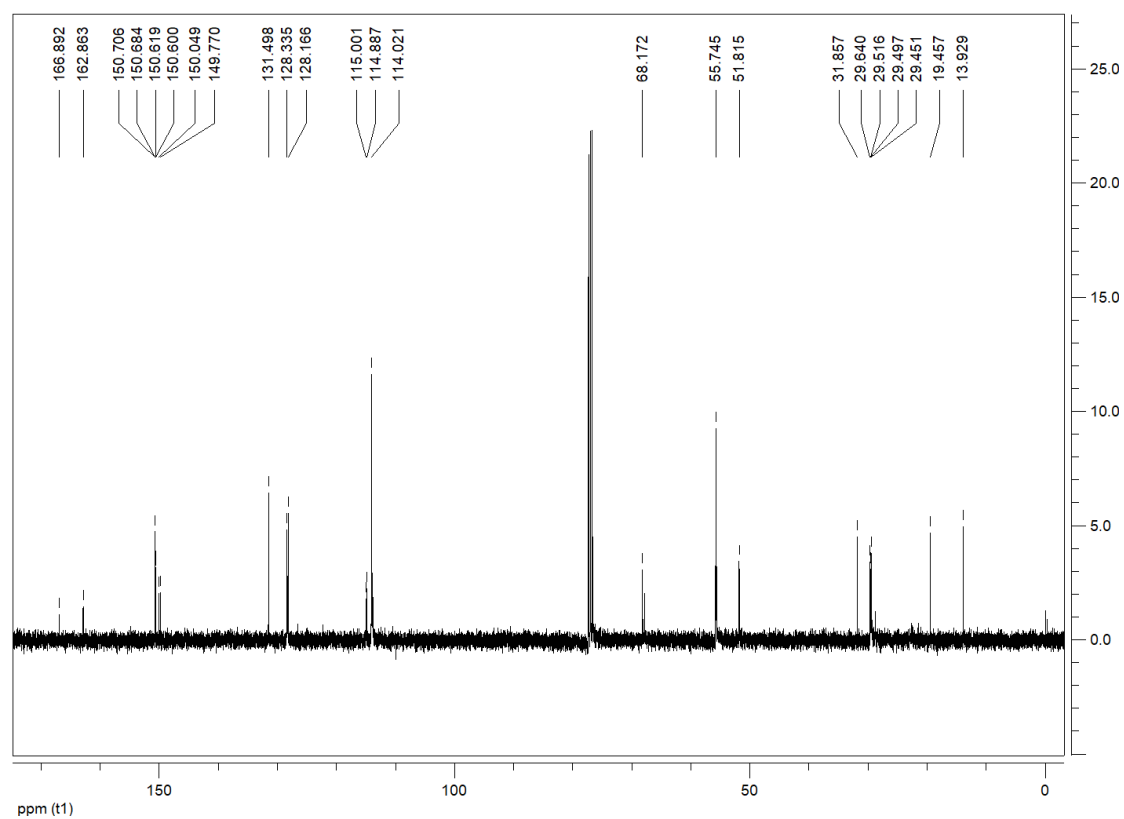
2b: White solid, 78%, m.p. 90-92 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.98 (d, $J = 8.8$ Hz, 2H, ArH), 6.88 (d, $J = 8.8$ Hz, 2H, ArH), 6.78-6.75 (m, 10H, ArH), 4.37-4.32 (m, 2H, CH_2), 4.01-4.00 (m, 2H, CH_2), 3.89 (t, $J = 5.2$ Hz, 2H, CH_2), 3.83 (t, $J = 6.4$ Hz, 2H, CH_2), 3.77-3.76 (m, 10H, CH_2), 3.65-3.60 (m, 24H, OCH_3), 1.94 (brs, 4H, CH_2), 1.77-1.70 (m, 2H, CH_2), 1.52-1.47 (m, 2H, CH_2), 1.38 (t, $J = 7.2$ Hz, 3H, CH_3), 0.94 (t, $J = 7.6$ Hz, 3H, CH_3), ^{13}C NMR (100 MHz, CDCl_3) δ : 166.4, 162.7, 150.7, 150.6, 150.6, 150.6, 150.6, 150.1, 149.6, 131.5, 128.4, 128.4, 128.3, 128.3, 128.2, 122.7, 114.8, 114.0, 113.9, 113.8, 113.8, 68.1, 67.9, 67.6, 60.6, 55.8, 55.8, 55.7, 55.7, 55.6, 31.8, 29.6, 29.6, 29.5, 29.5, 26.3, 19.4, 14.3, 13.9, IR (KBr) ν : 3462, 3051, 2944, 2863, 2835, 2750, 1934, 1708, 1607, 1503, 1461, 1400, 1361, 1211, 1177, 1104, 1044, 931, 850, 772, 701 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{60}\text{H}_{71}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 999.4895, found: 999.4910.



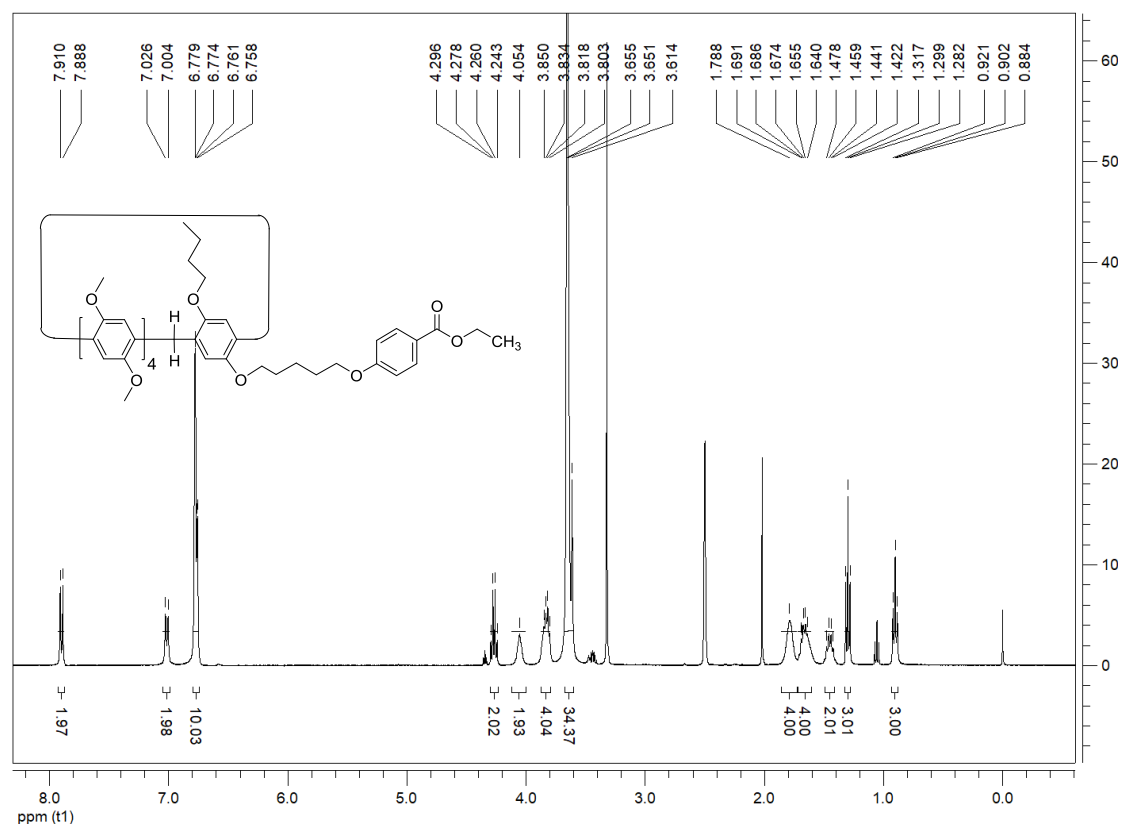


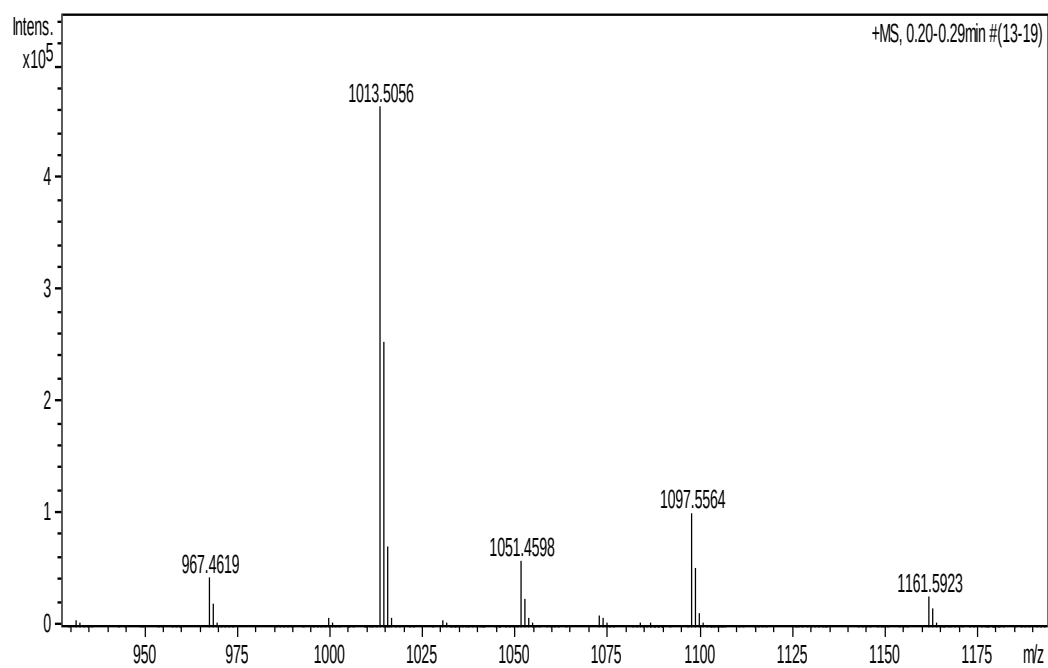
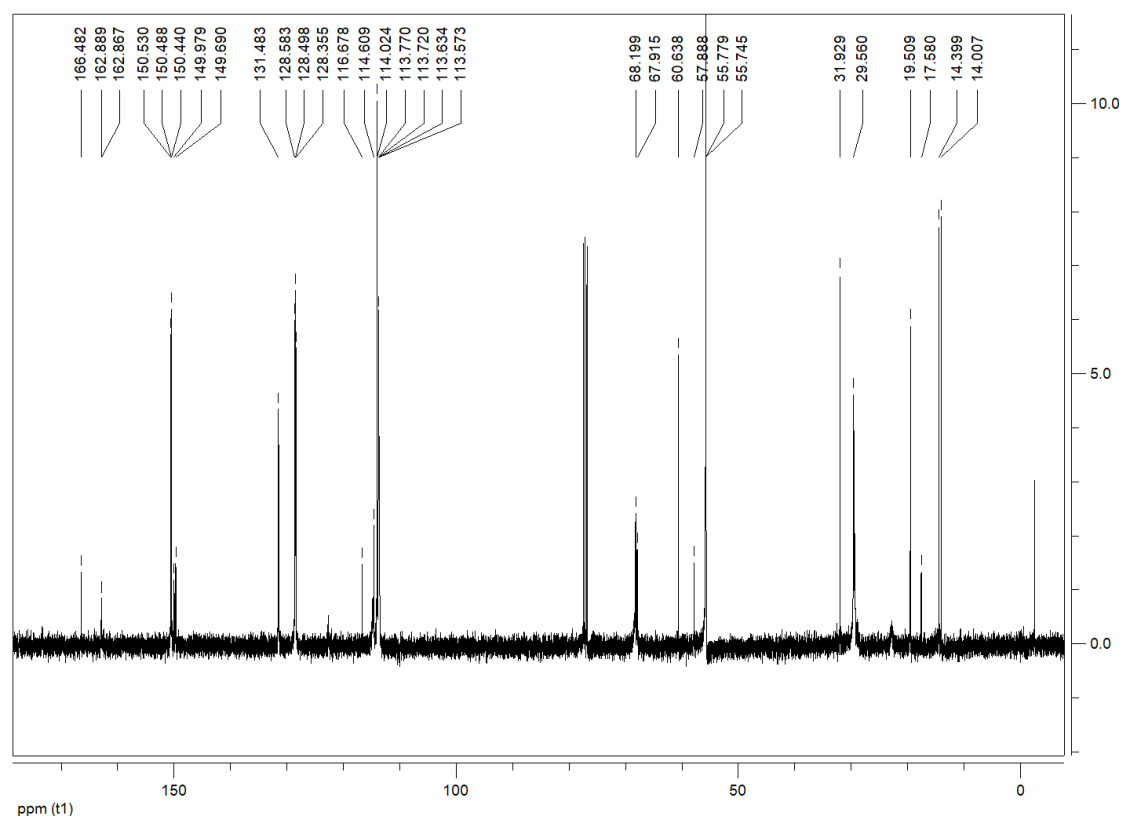
2c: White solid, 81%, m.p. 99-101 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.90 (d, $J = 8.4$ Hz, 2H, ArH), 7.01 (d, $J = 8.4$ Hz, 2H, ArH), 6.77-6.75 (m, 10H, ArH), 4.04 (brs, 2H, CH_2), 3.86-3.81 (m, 7H, CH_2OCH_3), 3.65-3.61 (m, 34H, CH_2 , OCH_3), 1.77 (brs, 4H, CH_2), 1.69-1.59 (m, 4H, CH_2), 1.48-1.42 (m, 2H, CH_2), 0.90 (t, $J = 7.6$ Hz, 3H, CH_3), ^{13}C NMR (100 MHz, CDCl_3) δ : 166.8, 162.8, 150.7, 150.6, 150.6, 150.6, 150.0, 149.7, 131.4, 128.3, 128.1, 115.0, 114.8, 114.0, 68.1, 55.7, 51.8, 31.8, 29.6, 29.5, 29.4, 29.4, 19.4, 13.9, IR (KBr) ν : 3845, 3579, 3408, 3072, 2943, 2864, 2835, 2742, 1927, 1714, 1606, 1504, 1462, 1399, 1257, 1211, 1107, 1045, 930, 870, 850, 773, 701 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{60}\text{H}_{71}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 999.4895, found: 999.4907.



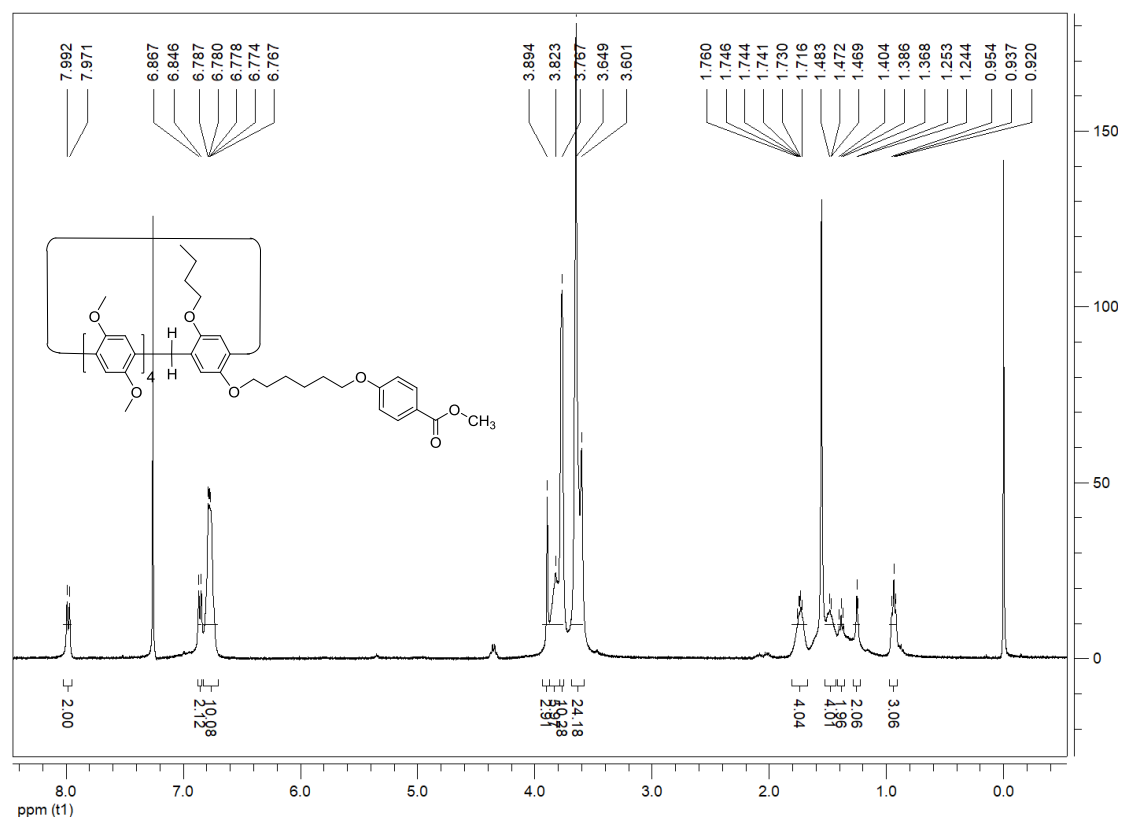


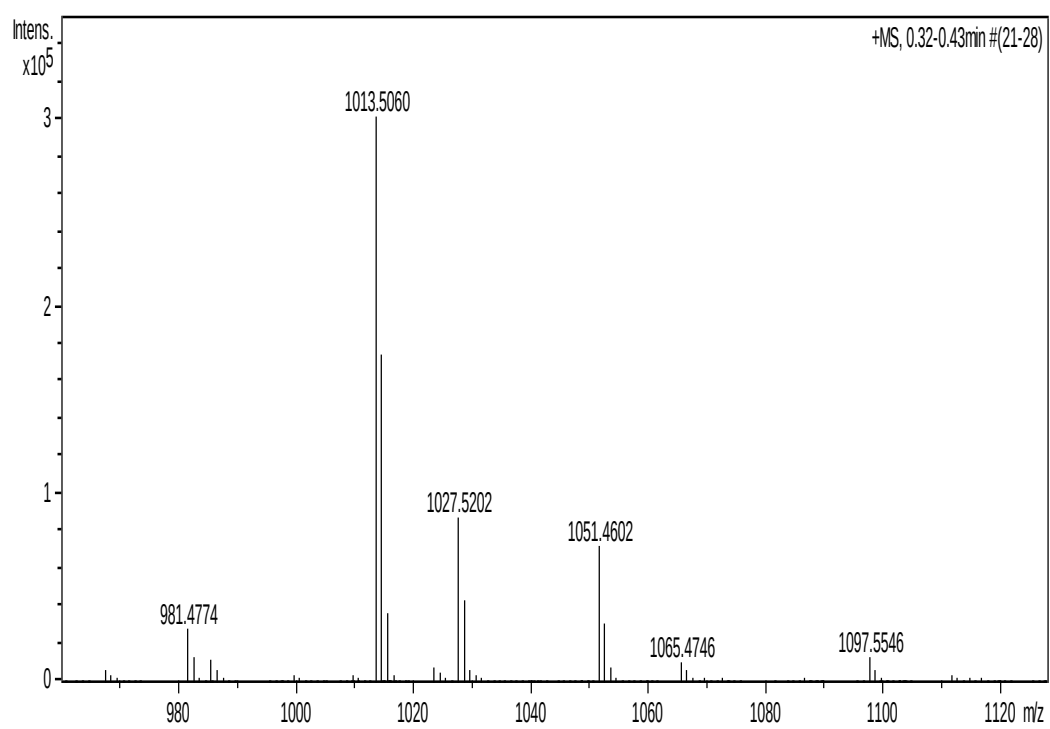
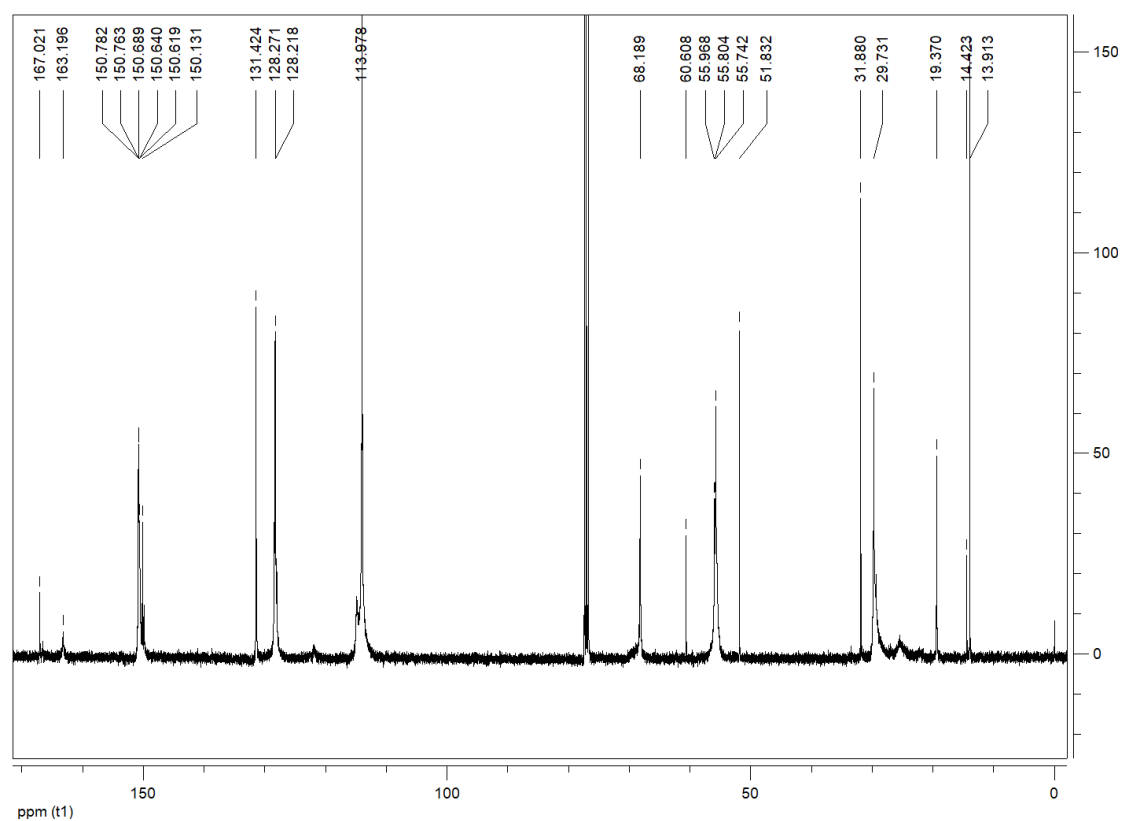
2d: White solid, 76%, m.p. 96-98 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.90 (d, $J = 8.8$ Hz, 2H, ArH), 7.01 (d, $J = 8.8$ Hz, 2H, ArH), 6.77-6.75 (m, 10H, ArH), 4.29-4.24 (m, 2H, CH_2), 4.05 (brs, 2H, CH_2), 3.85-3.80 (m, 4H, CH_2), 3.65-3.61 (m, 34H, CH_2 , OCH_3), 1.78 (brs, 4H, CH_2), 1.69-1.64 (m, 4H, CH_2), 1.47-1.42 (m, 2H, CH_2), 1.29 (t, $J = 7.2$ Hz, 3H, CH_3), 0.90 (t, $J = 7.6$ Hz, 3H, CH_3), ^{13}C NMR (100 MHz, CDCl_3) δ : 166.4, 162.8, 162.8, 150.5, 150.4, 150.4, 149.9, 149.6, 131.4, 128.5, 128.4, 128.3, 116.6, 114.6, 114.0, 113.7, 113.7, 113.6, 113.5, 68.1, 67.9, 60.6, 57.8, 55.7, 55.7, 31.9, 29.5, 19.5, 17.5, 14.3, 14.0, IR (KBr) ν : 3578, 3051, 2942, 2865, 2835, 1708, 1606, 1503, 1462, 1399, 1310, 1259, 1211, 1172, 1105, 1045, 930, 870, 773, 702 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{61}\text{H}_{73}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 1013.5051, found: 1013.5056.



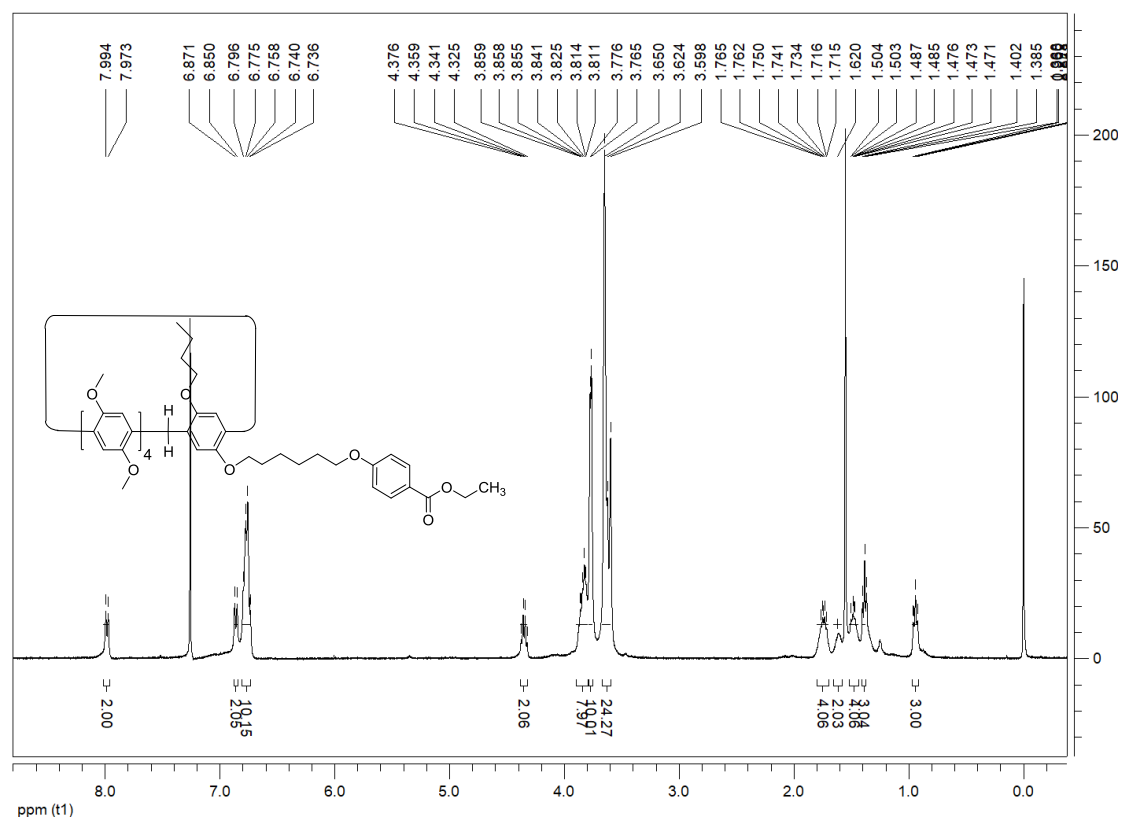


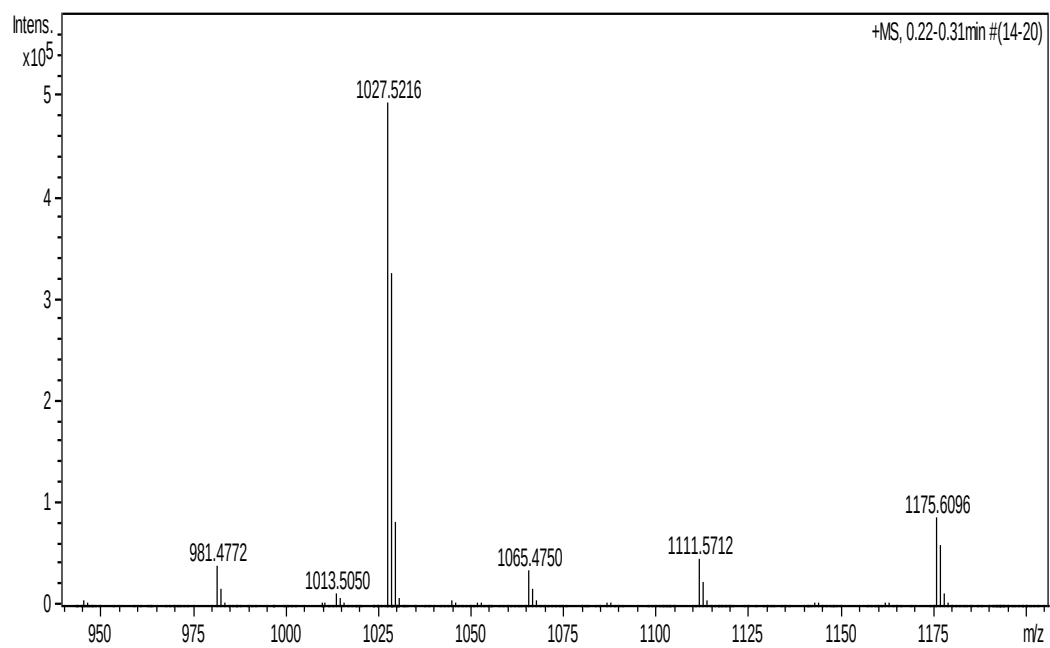
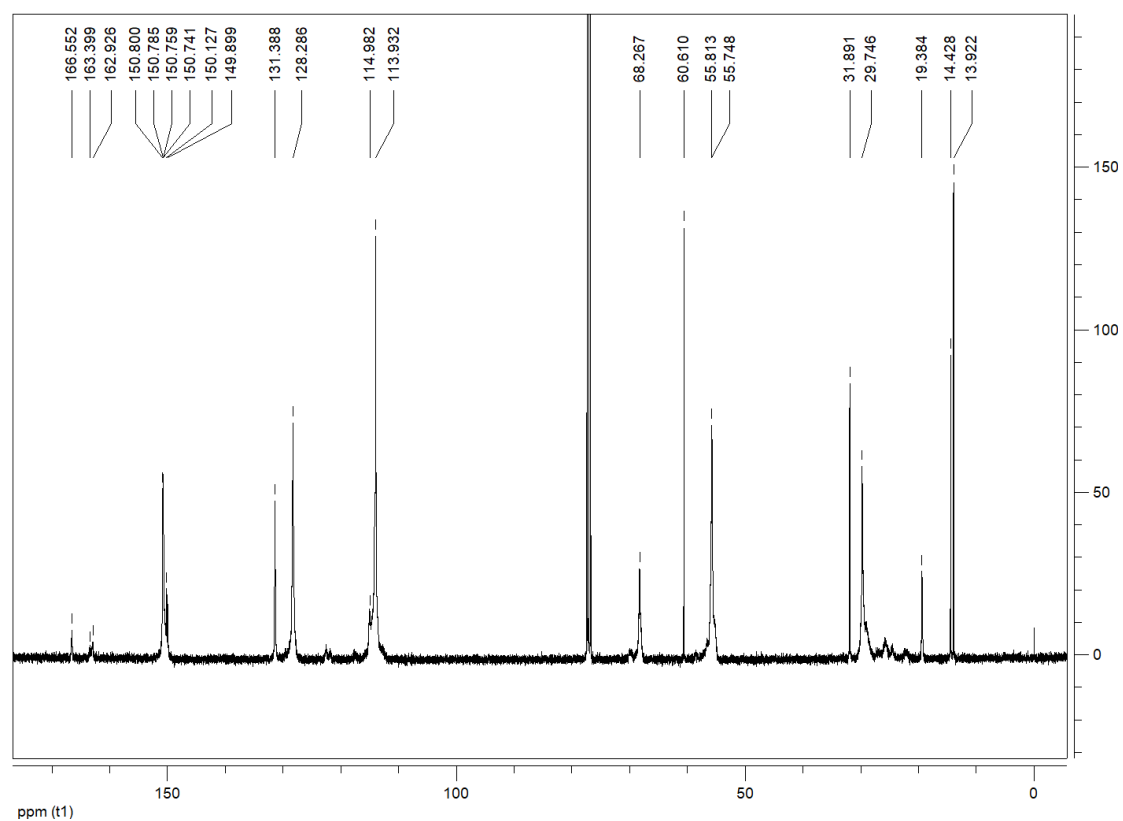
2e: White solid, 79%, m.p. 111-113 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.98 (d, $J = 8.4$ Hz, 2H, ArH), 6.85 (d, $J = 8.4$ Hz, 2H, ArH), 6.78-6.76 (m, 10H, ArH), 3.89 (s, 3H, OCH_3), 3.82 (brs, 6H, CH_2), 3.76 (brs, 10H, CH_2), 3.64-3.60 (m, 24H, OCH_3), 1.74 (brs, 4H, CH_2), 1.48-1.46 (m, 4H, CH_2), 1.38 (t, $J = 7.2$ Hz, 2H, CH_2), 1.25-1.24 (m, 2H, CH_2), 0.93 (t, $J = 6.8$ Hz, 3H, CH_3), ^{13}C NMR (100 MHz, CDCl_3) δ : 167.0, 163.1, 150.7, 150.7, 150.6, 150.6, 150.6, 150.1, 131.4, 128.2, 128.2, 113.9, 68.1, 60.6, 55.9, 55.8, 55.7, 51.8, 31.8, 29.7, 19.3, 14.4, 13.9, IR (KBr) ν : 3656, 2942, 2862, 2836, 1714, 1606, 1503, 1462, 1399, 1261, 1211, 1174, 1104, 1044, 929, 850, 773, 701 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{61}\text{H}_{73}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 1013.5051, found: 1013.5060.



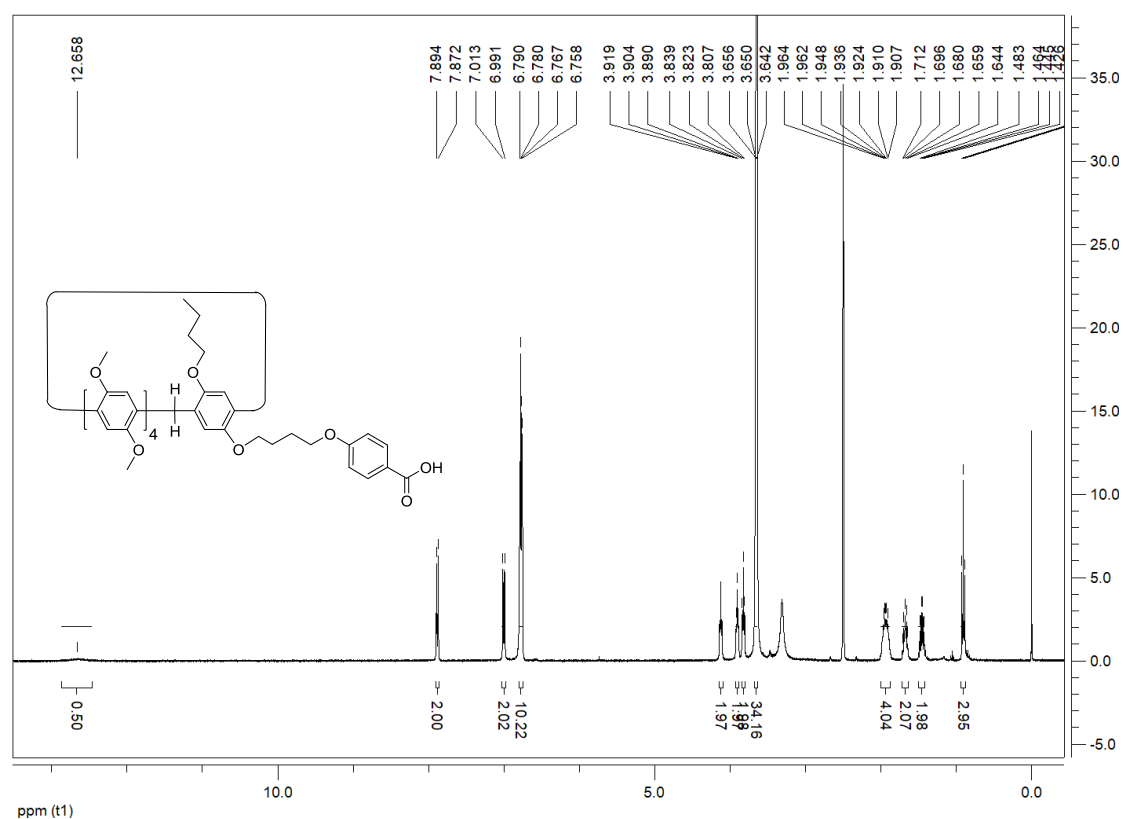


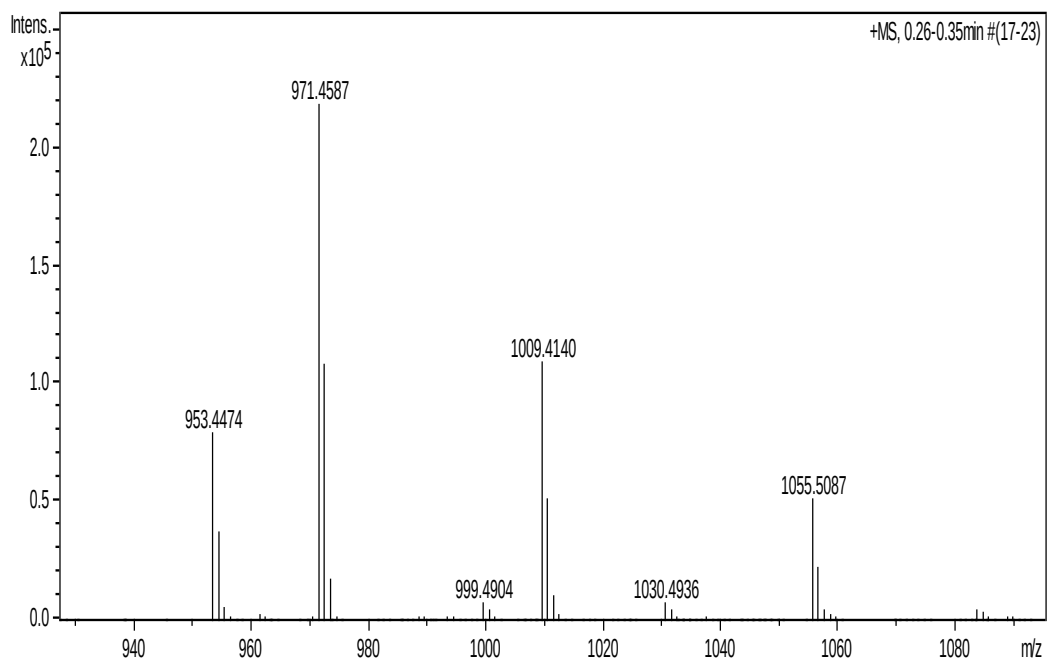
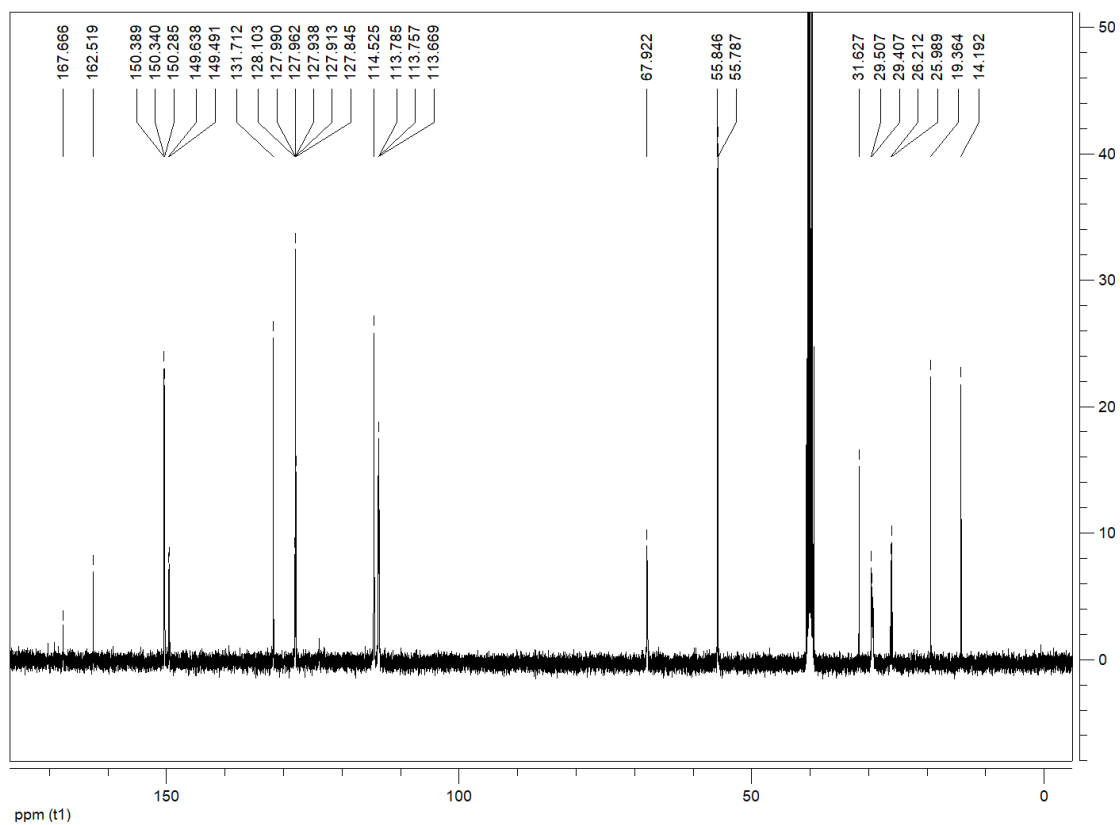
2f: White solid, 78%, m.p. 96-98 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.98 (d, J = 8.8 Hz, 2H, ArH), 6.86 (d, J = 8.8 Hz, 2H, ArH), 6.79-6.73 (m, 10H, ArH), 4.37-4.32 (m, 2H, CH_2), 3.85-3.81 (m, 8H, CH_2), 3.77-3.76 (m, 10H, CH_2), 3.65-3.59 (m, 24H, OCH_3), 1.76-1.71 (m, 4H, CH_2), 1.62 (brs, 2H, CH_2), 1.50-1.47 (m, 4H, CH_2), 1.38 (t, J = 6.8 Hz, 3H, CH_3), 0.94 (t, J = 7.2 Hz, 3H, CH_3), ^{13}C NMR (100 MHz, CDCl_3) δ : 166.5, 163.3, 162.9, 150.7, 150.7, 150.7, 150.7, 150.1, 149.8, 131.3, 128.2, 114.9, 113.9, 68.2, 60.6, 55.8, 55.7, 31.8, 29.7, 19.3, 14.4, 13.9, IR (KBr) ν : 3657, 2942, 2862, 2835, 1708, 1607, 1502, 1462, 1398, 1263, 1211, 1173, 1100, 928, 850, 773, 702 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{62}\text{H}_{75}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 1027.5208, found: 1027.5216.



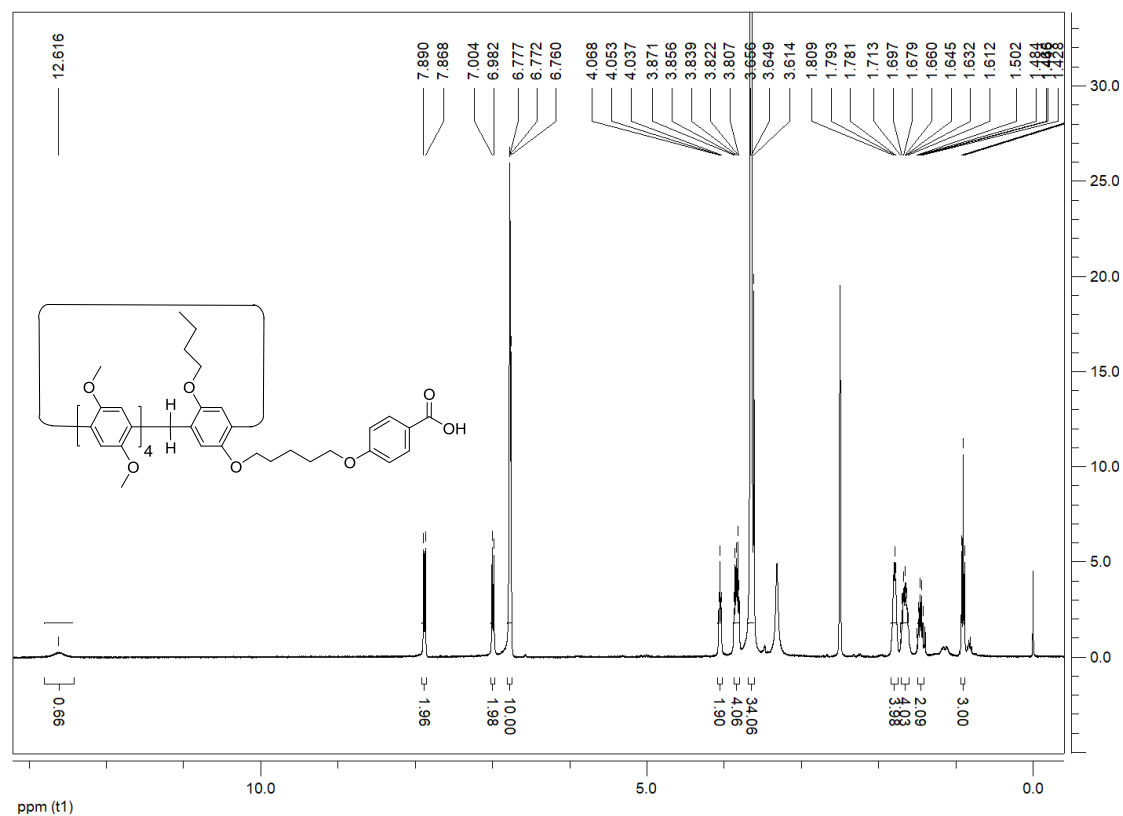


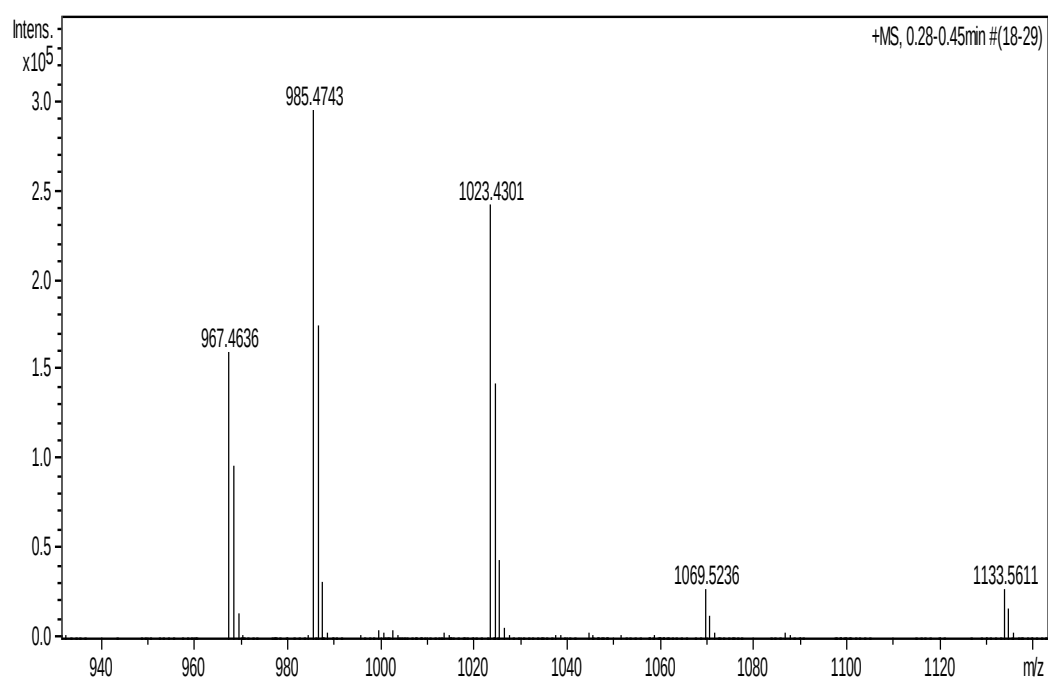
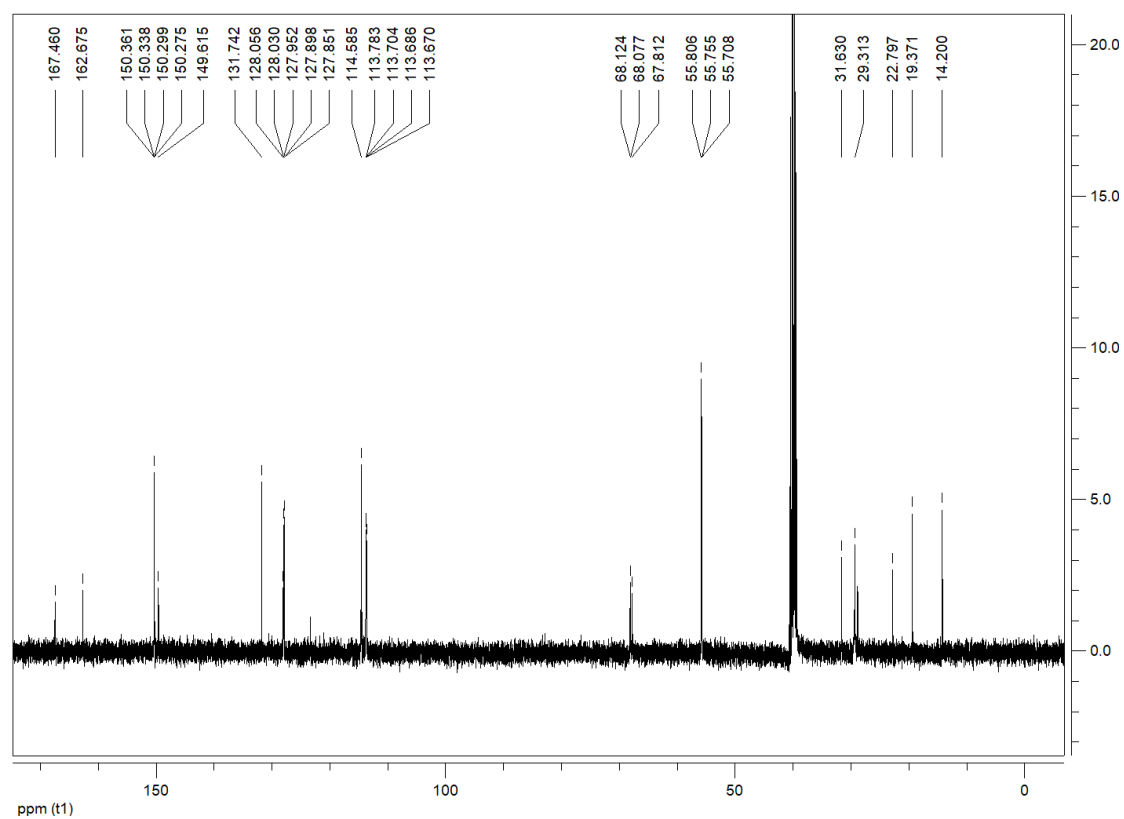
3a: White solid, 81%, m.p. 100-102 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 12.65 (s, 1H, COOH), 7.88 (d, $J = 8.8$ Hz, 2H, ArH), 7.00 (d, $J = 8.8$ Hz, 2H, ArH), 6.79-6.75 (m, 10H, ArH), 4.12 (t, $J = 6.0$ Hz, 2H, CH_2), 3.90 (t, $J = 6.0$ Hz, 2H, CH_2), 3.82 (t, $J = 6.4$ Hz, 2H, CH_2), 3.65-3.64 (m, 34H, CH_2 , OCH_3), 1.96-1.90 (m, 4H, CH_2), 1.71-1.64 (m, 2H, CH_2), 1.48-1.42 (m, 2H, CH_2), 0.90 (t, $J = 7.2$ Hz, 3H, CH_3), ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 167.6, 162.5, 150.3, 150.3, 150.2, 149.6, 149.4, 131.7, 128.1, 127.9, 127.9, 127.9, 127.9, 127.8, 114.5, 113.7, 113.7, 113.6, 67.9, 55.8, 55.7, 31.6, 29.5, 29.4, 26.2, 25.9, 19.3, 14.1, IR (KBr) ν : 3834, 3577, 3427, 2941, 2862, 2835, 2659, 1926, 1685, 1605, 1504, 1461, 1398, 1309, 1252, 1232, 1187, 1101, 1043, 931, 851, 775, 699 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{58}\text{H}_{67}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 971.4582, found: 971.4587.



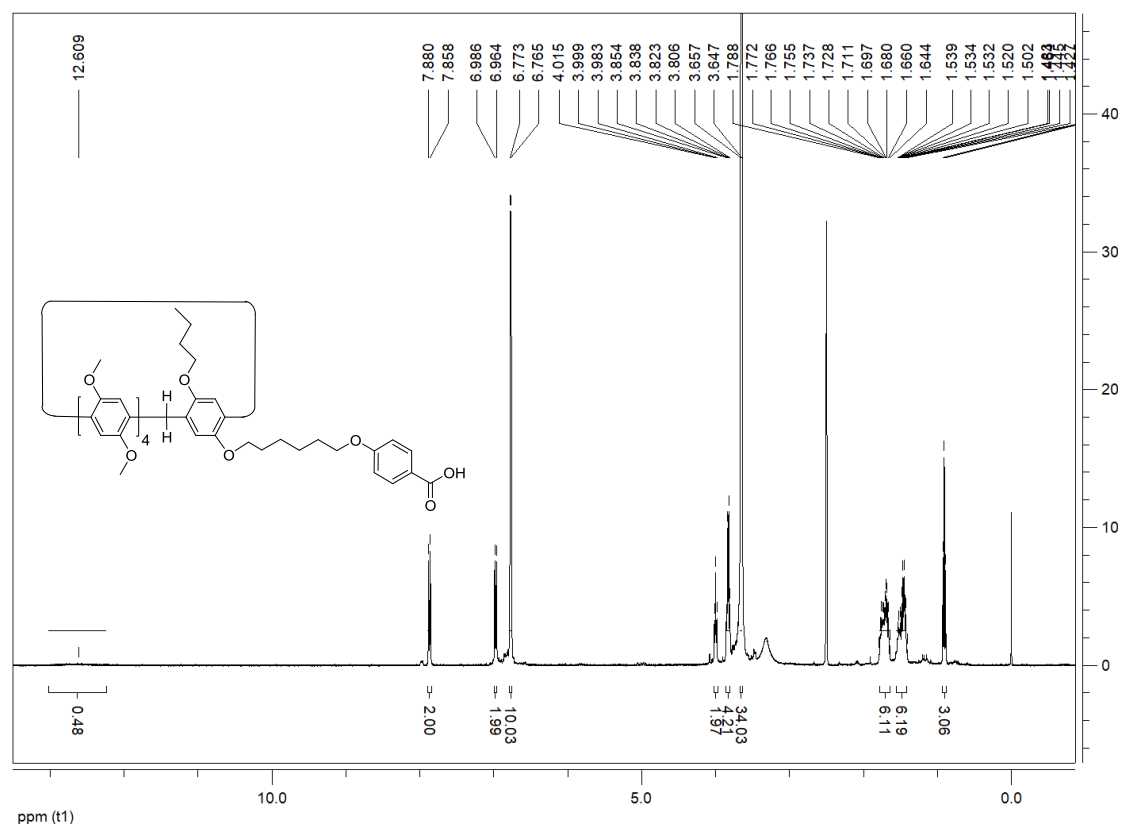


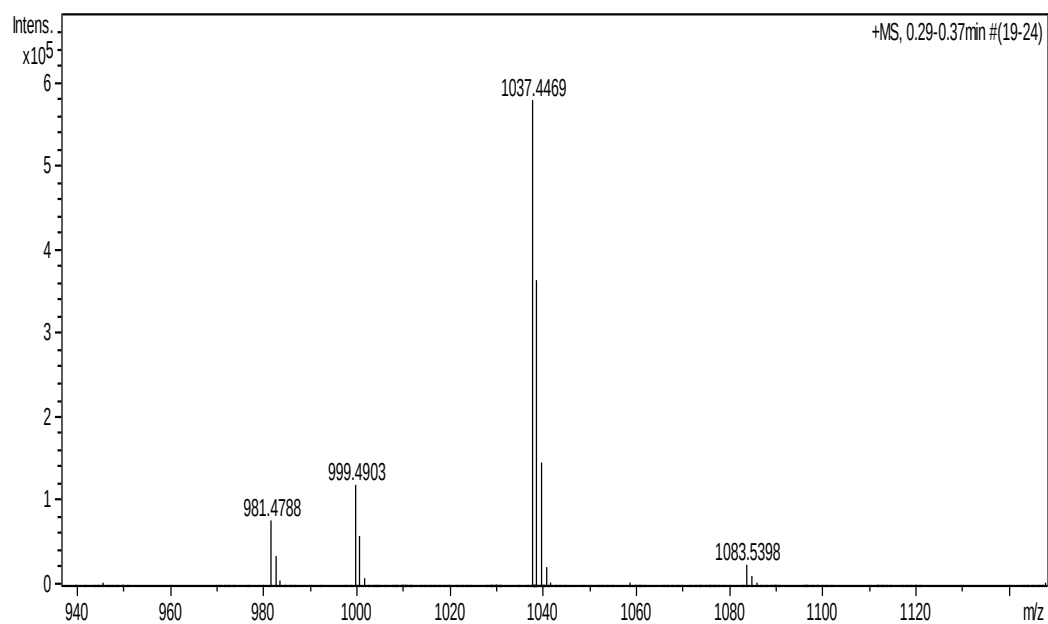
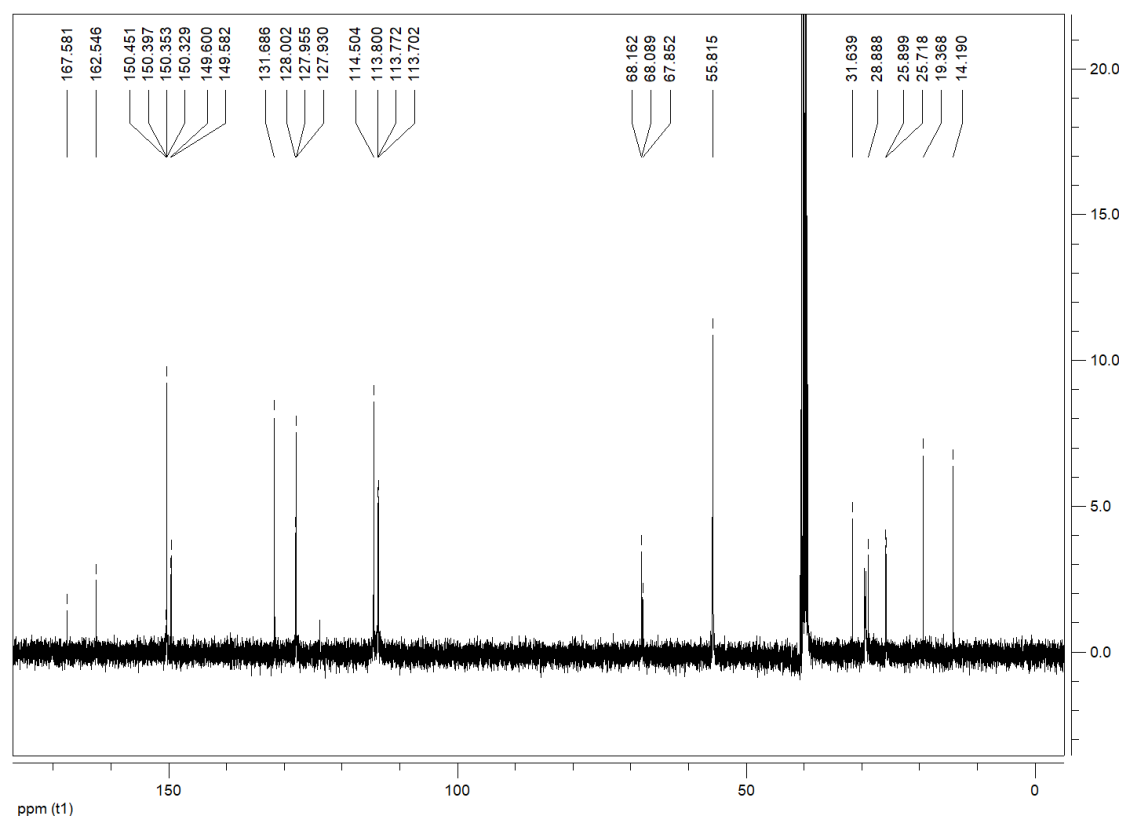
3b: White solid, 78%, m.p. 106-108 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 12.61 (s, 1H, COOH), 7.88 (d, $J = 8.8$ Hz, 2H, ArH), 7.00 (d, $J = 8.8$ Hz, 2H, ArH), 6.77-6.76 (m, 10H, ArH), 4.05 (t, $J = 6.0$ Hz, 2H, CH_2), 3.87-3.80 (m, 4H, CH_2), 3.65-3.64 (m, 34H, CH_2OCH_3), 3.82 (t, $J = 6.4$ Hz, 2H, CH_2), 3.65-3.61 (m, 34H, CH_2OCH_3), 1.79 (t, $J = 6.4$ Hz, 4H, CH_2), 1.69-1.63 (m, 4H, CH_2), 1.48-1.42 (m, 2H, CH_2), 0.90 (t, $J = 7.2$ Hz, 3H, CH_3), ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 167.4, 162.6, 150.3, 150.3, 150.2, 150.2, 149.6, 131.7, 128.0, 128.0, 127.9, 127.8, 127.8, 114.5, 113.7, 113.7, 113.6, 113.6, 68.1, 68.0, 67.8, 55.8, 55.7, 55.7, 31.6, 29.3, 22.7, 19.3, 14.2, IR (KBr) ν : 3656, 2940, 2862, 2835, 1685, 1605, 1503, 1462, 1399, 1255, 1211, 1171, 1100, 1044, 930, 850, 775, 701 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{59}\text{H}_{69}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 985.4738, found: 985.4743.



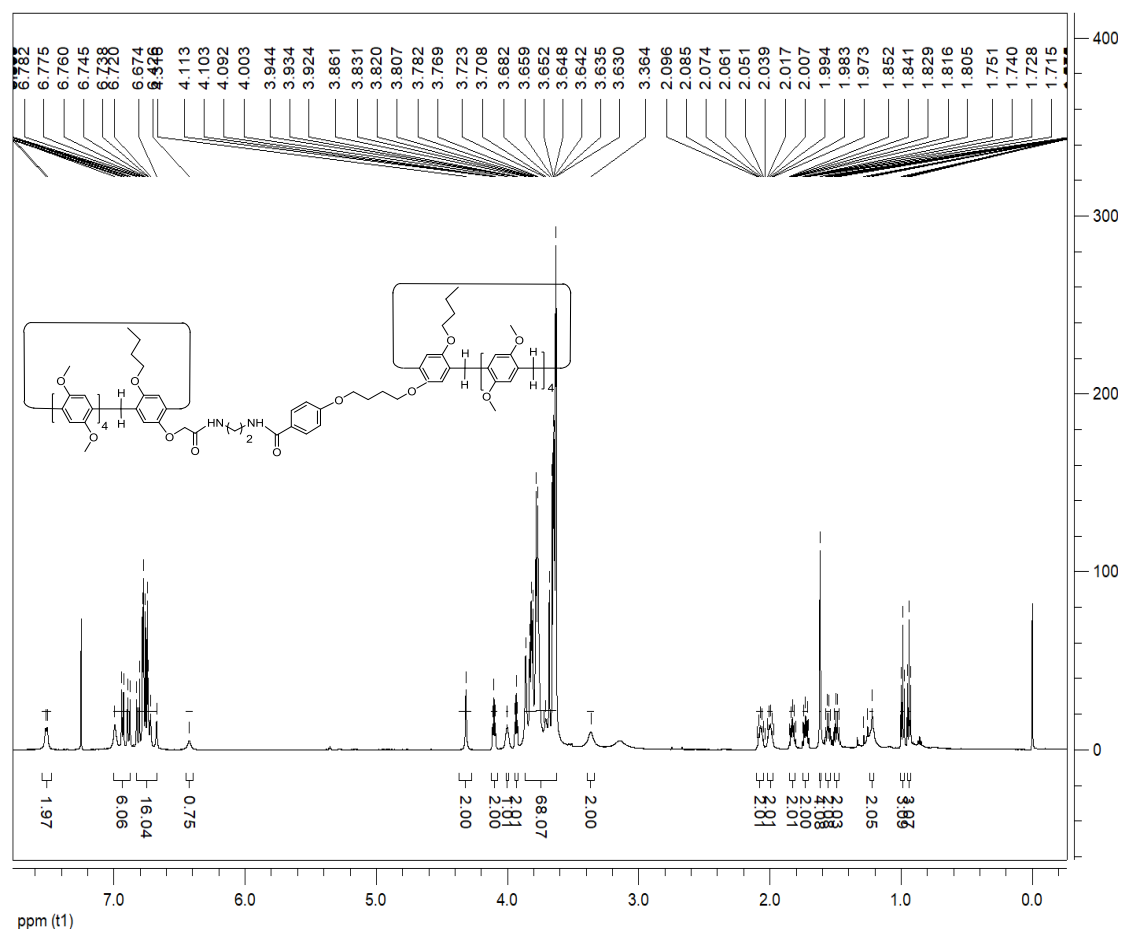


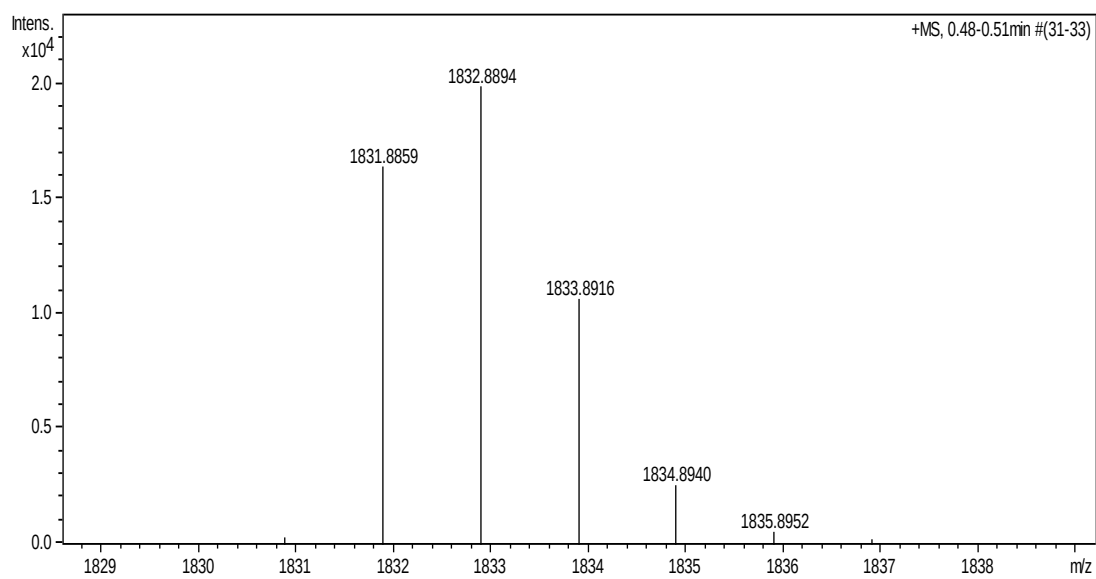
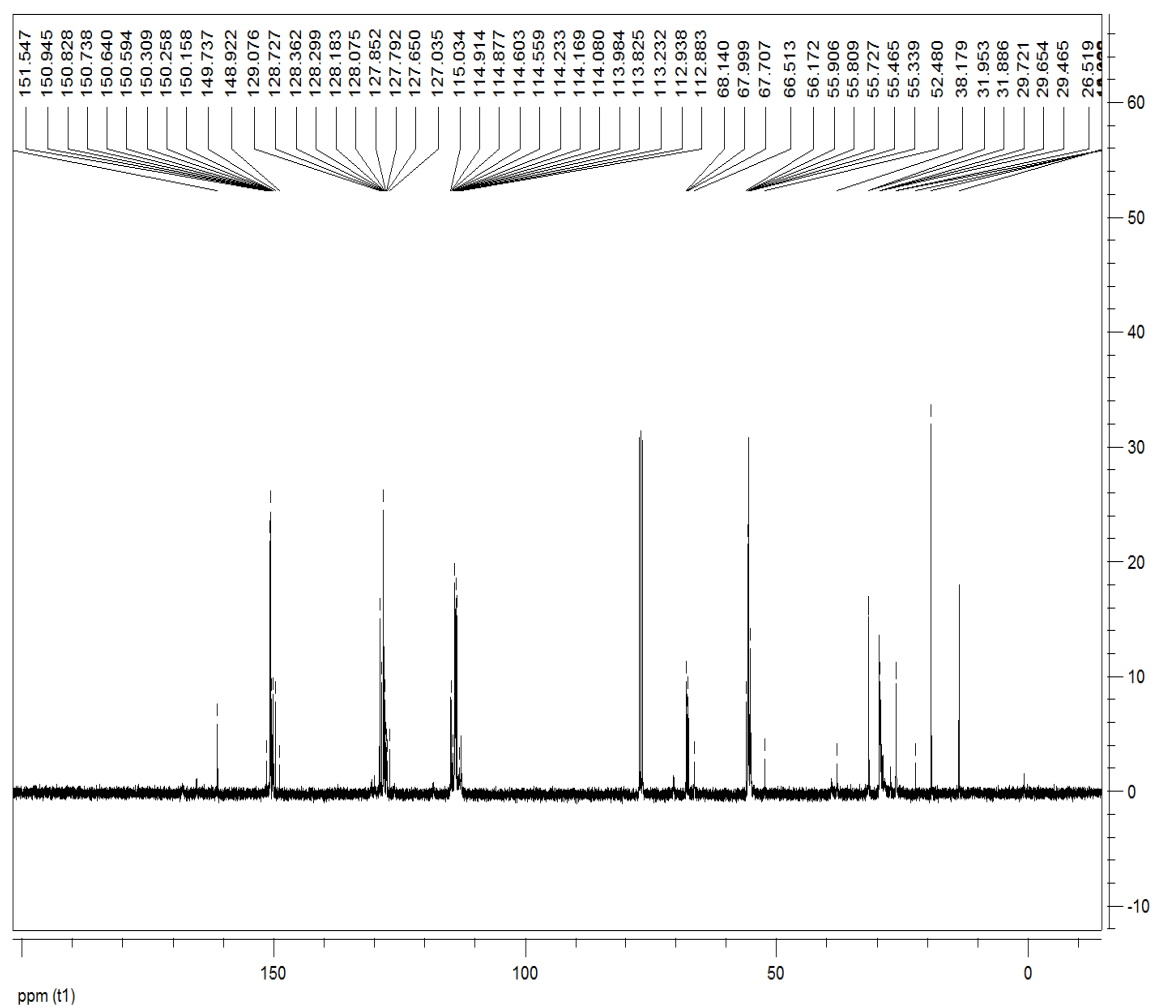
3c: White solid, 79%, m.p. 110-112 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 12.61 (s, 1H, COOH), 7.87 (d, J = 8.8 Hz, 2H, ArH), 6.97 (d, J = 8.8 Hz, 2H, ArH), 6.77-6.76 (m, 10H, ArH), 4.00 (t, J = 6.4 Hz, 2H, CH_2), 3.85-3.80 (m, 4H, CH_2), 3.65-3.64 (m, 34H, CH_2 , OCH_3), 3.82 (t, J = 6.4 Hz, 2H, CH_2), 3.65-3.61 (m, 34H, CH_2 , OCH_3), 1.78-1.64 (m, 6H, CH_2), 1.53-1.40 (m, 6H, CH_2), 0.90 (t, J = 7.2 Hz, 3H, CH_3), ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 167.5, 162.5, 150.4, 150.3, 150.3, 150.3, 149.5, 149.5, 131.6, 128.0, 127.9, 127.9, 114.5, 113.8, 113.7, 113.7, 68.1, 68.0, 67.8, 55.8, 31.6, 28.8, 25.8, 25.7, 19.3, 14.1, IR (KBr) ν : 3634, 2940, 2860, 2836, 2661, 1686, 1605, 1503, 1462, 1399, 1304, 1254, 1211, 1171, 1100, 1043, 930, 850, 775, 703 cm^{-1} , MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{60}\text{H}_{71}\text{O}_{13}$ ($[\text{M}+\text{H}]^+$): 999.4895, found: 999.4903.



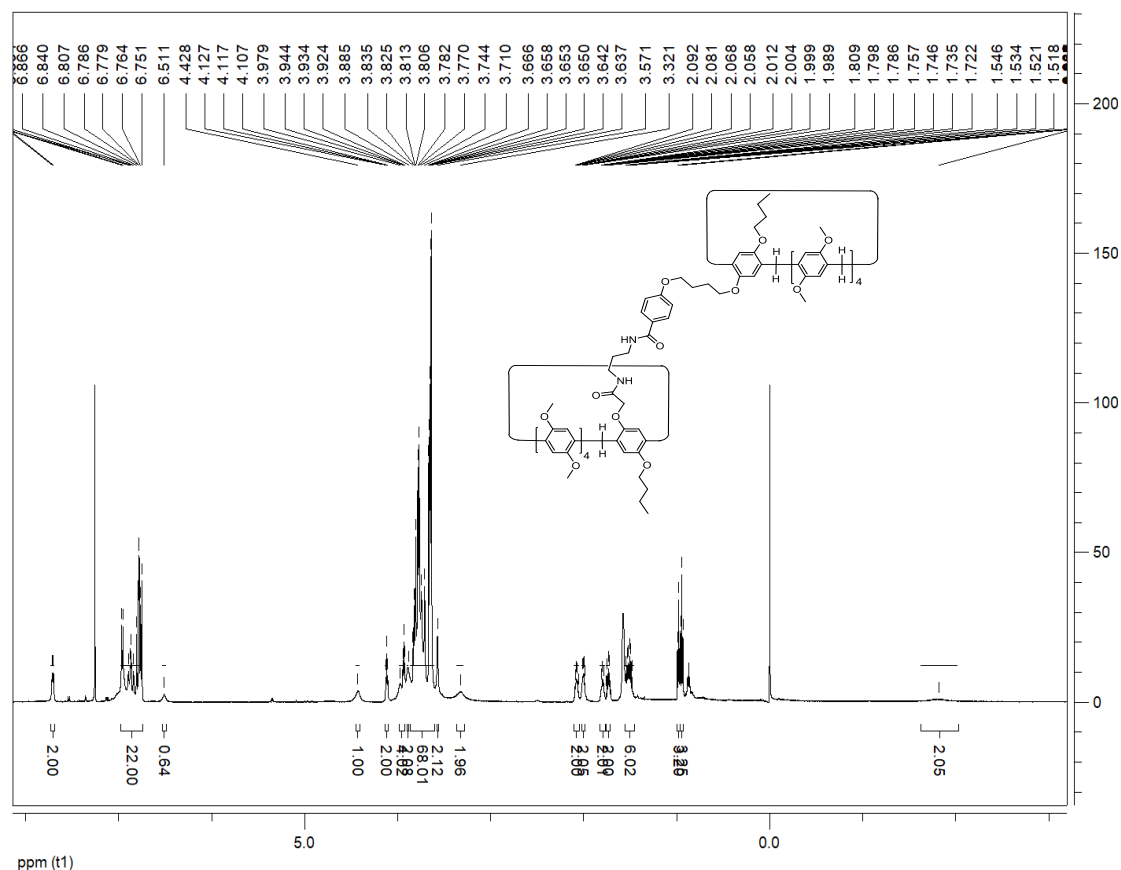


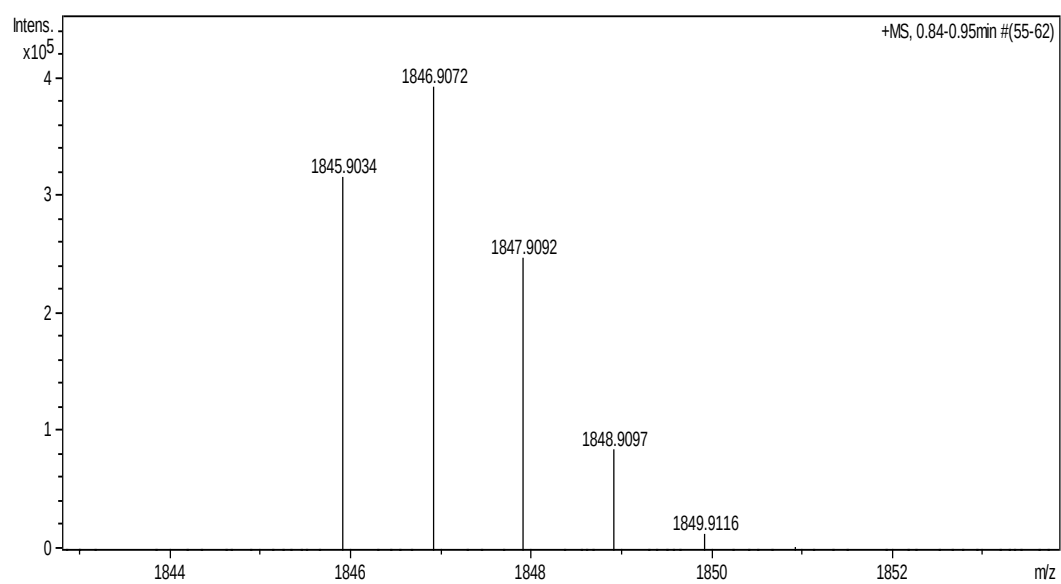
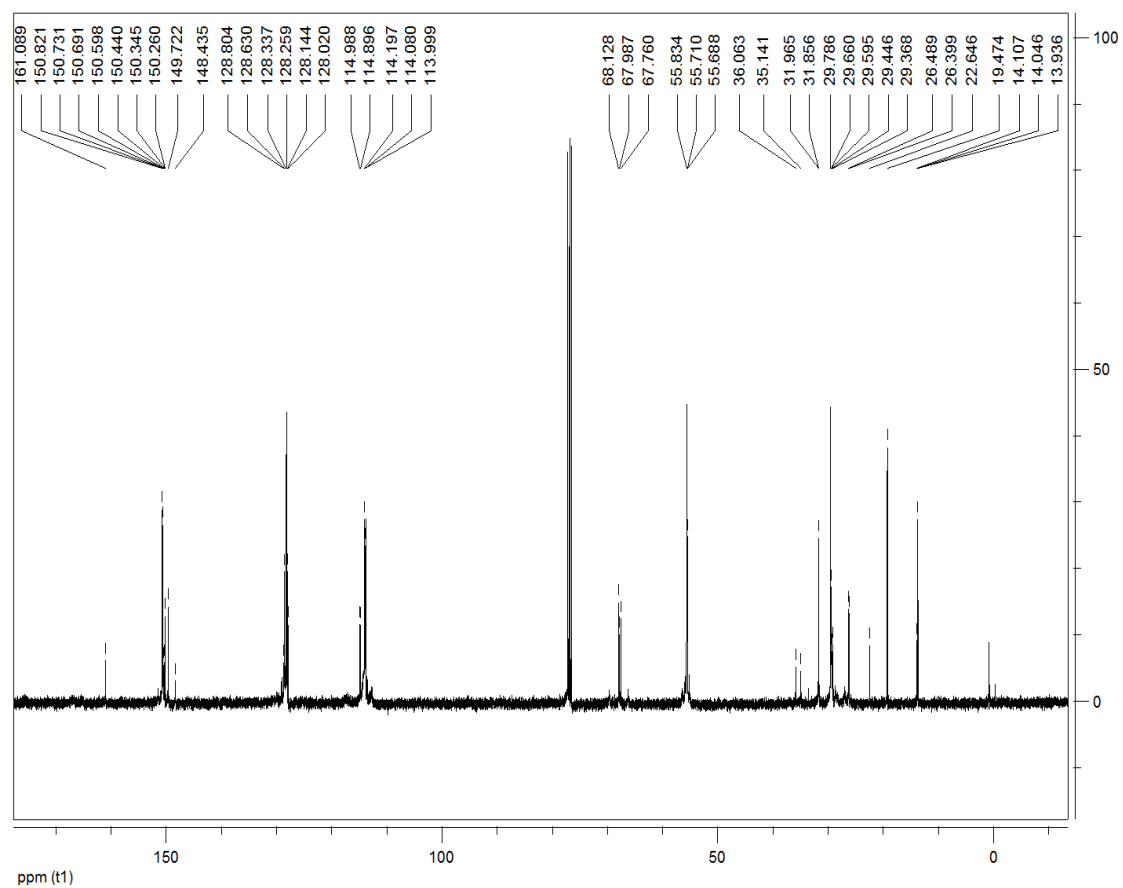
5a: White solid, 29%, m.p. 126-128 °C; ^1H NMR (600 MHz, CDCl_3) δ : 7.51 (d, $J = 7.2$ Hz, 2H, ArH), 6.99-6.87 (m, 6H, ArH), 6.83-6.67 (m, 16H, ArH), 6.43 (brs, 1H, NH), 4.32 (s, 2H, CH_2), 4.10 (t, $J = 6.0$ Hz, 2H, CH_2), 4.00 (brs, 1H, NH), 3.93 (t, $J = 6.0$ Hz, 2H, CH_2), 3.86-3.63 (m, 68H, 10CH_2 , 16OCH_3), 3.36 (brs, 2H, CH_2), 2.09-2.04 (m, 2H, CH_2), 2.02-1.97 (m, 2H, CH_2), 1.85-1.81 (m, 2H, CH_2), 1.75-1.70 (m, 2H, CH_2), 1.62 (s, 4H, CH_2), 1.58-1.54 (m, 2H, CH_2), 1.51-1.47 (m, 2H, CH_2), 1.28-1.22 (m, 2H, CH_2), 0.99 (t, $J = 7.2$ Hz, 3H, CH_3), 0.94 (t, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ : 161.2, 151.5, 150.9, 150.8, 150.7, 150.6, 150.5, 150.3, 150.2, 150.1, 149.7, 148.9, 129.0, 128.7, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.0, 115.0, 114.9, 114.8, 114.6, 114.5, 114.2, 114.1, 114.0, 113.9, 113.8, 113.2, 112.9, 112.8, 68.1, 67.9, 67.7, 66.5, 56.1, 55.9, 55.8, 55.7, 55.4, 55.3, 52.4, 38.1, 31.9, 31.8, 29.7, 29.6, 29.4, 26.5, 26.4, 22.6, 19.4, 14.0, 13.9; IR (KBr) ν : 3397, 2933, 2837, 1667, 1610, 1501, 1460, 1397, 1309, 1210, 1101, 1042, 928, 871, 770, 696 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{109}\text{H}_{127}\text{N}_2\text{O}_{23}$ ($[\text{M}+\text{H}]^+$): 1832.8863, found: 1832.8894.



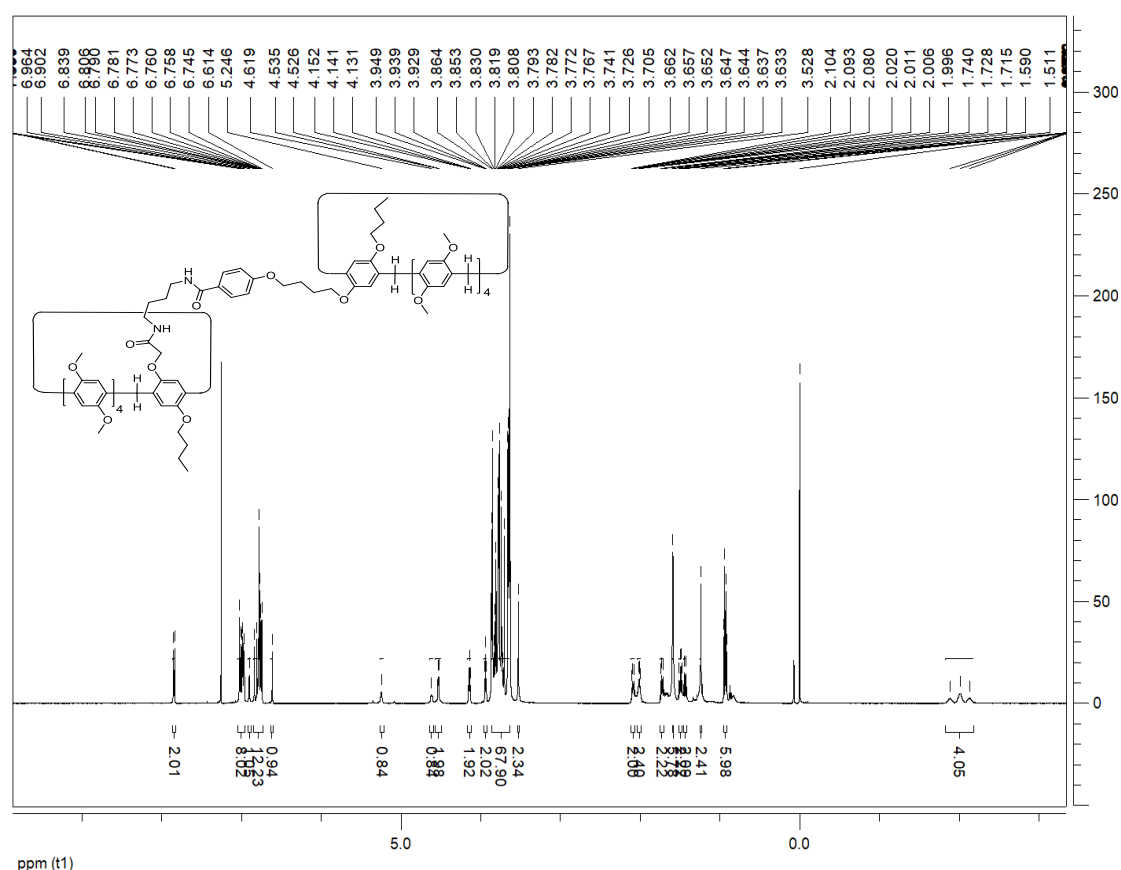


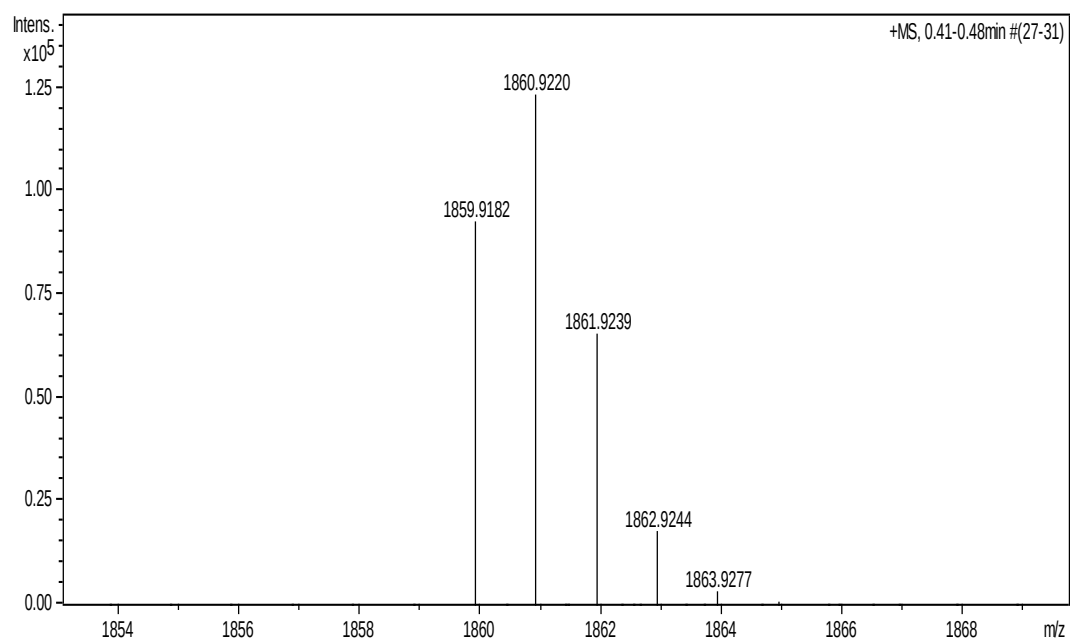
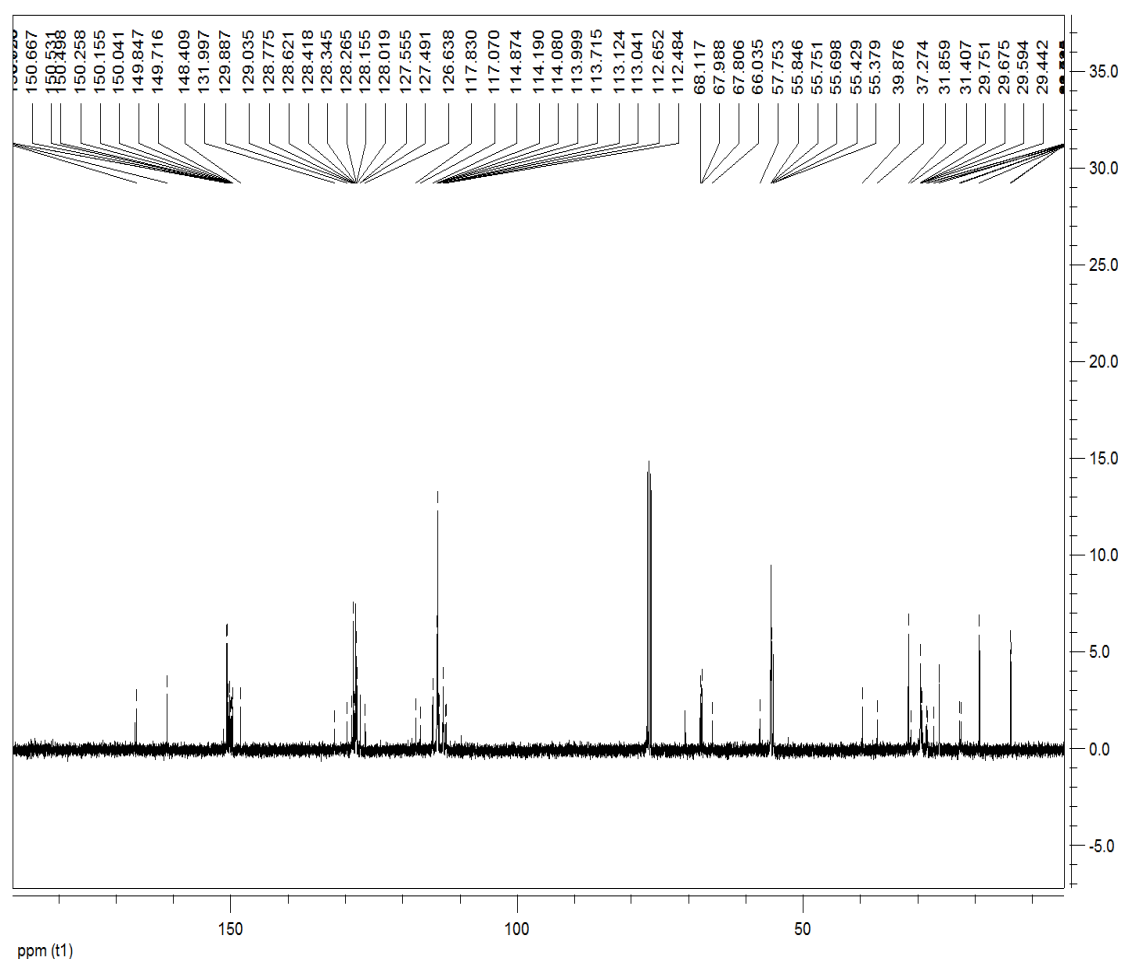
5b: White solid, 44%, m.p. 136-138 °C; ^1H NMR (600 MHz, CDCl_3) δ : 7.71 (d, $J = 8.4$ Hz, 2H, ArH), 6.97-6.75 (m, 22H, ArH), 6.51 (brs, 1H, NH), 4.43 (brs, 1H, NH), 4.11 (t, $J = 6.0$ Hz, 2H, CH_2), 3.98-3.92 (m, 4H, CH_2), 3.89 (brs, 2H, CH_2), 3.84-3.64 (m, 68H, 10 CH_2 , 16 OCH_3), 3.57 (brs, 2H, CH_2), 3.32 (brs, 2H, CH_2), 2.09-2.06 (m, 2H, CH_2), 2.01-1.99 (m, 2H, CH_2), 1.81-1.79 (m, 2H, CH_2), 1.79-1.72 (m, 2H, CH_2), 1.55-1.48 (m, 6H, CH_2), 0.98 (t, $J = 7.2$ Hz, 3H, CH_3), 0.95 (t, $J = 7.2$ Hz, 3H, CH_3), -1.82 (brs, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ : 161.0, 150.8, 150.7, 150.6, 150.5, 150.4, 150.3, 150.2, 149.7, 148.4, 128.8, 128.6, 128.3, 128.2, 128.1, 128.0, 114.9, 114.8, 114.1, 114.0, 113.9, 68.1, 67.9, 67.7, 55.8, 55.7, 55.6, 36.0, 35.1, 31.9, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 26.4, 26.3, 22.6, 19.4, 14.1, 14.0, 13.9; IR (KBr) ν : 3401, 2931, 2857, 1663, 1611, 1501, 1460, 1396, 1307, 1210, 1042, 928, 873, 770 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{110}\text{H}_{129}\text{N}_2\text{O}_{23}$ ($[\text{M}+\text{H}]^+$): 1846.9020, found: 1846.9072.



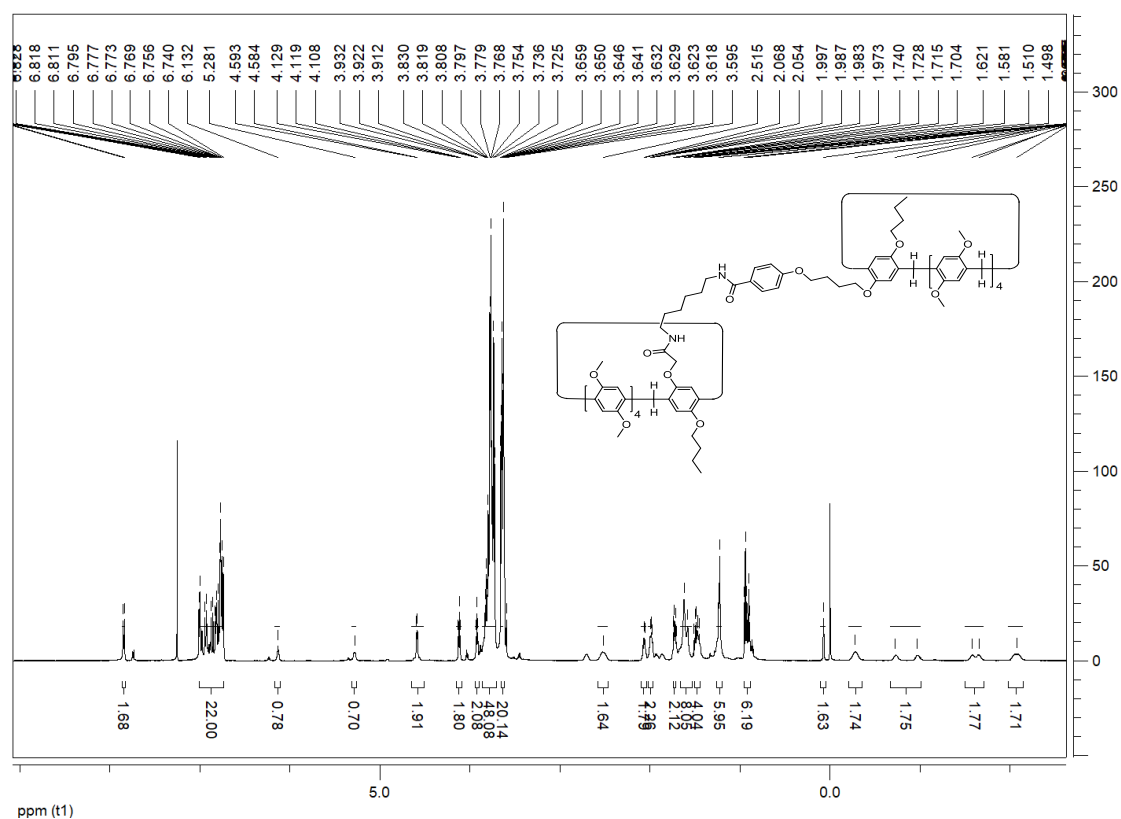


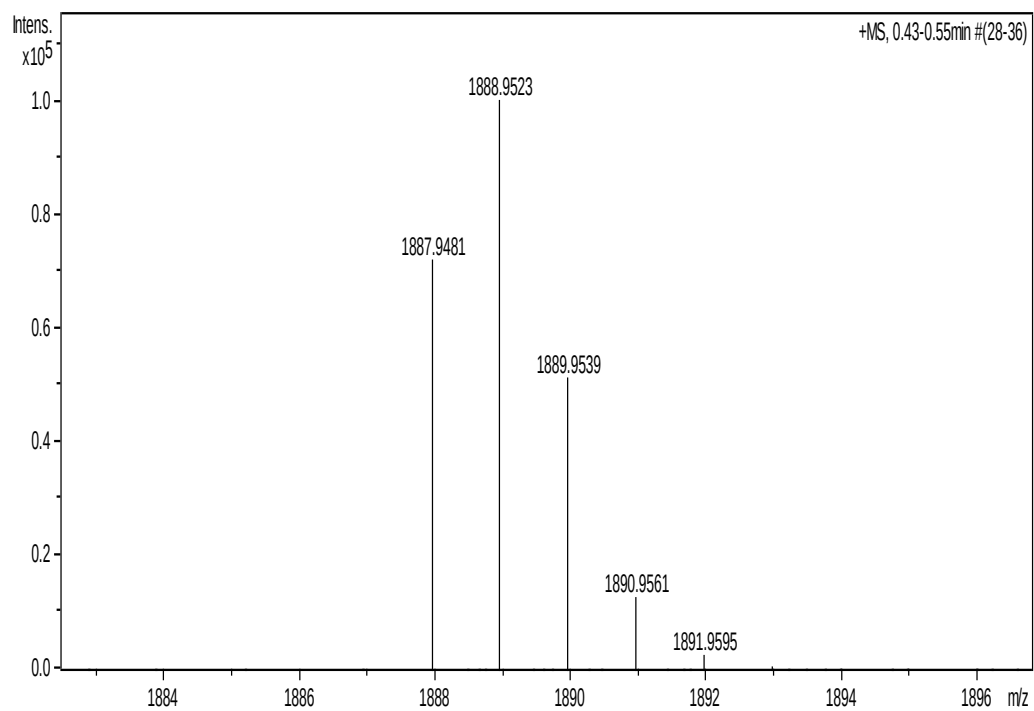
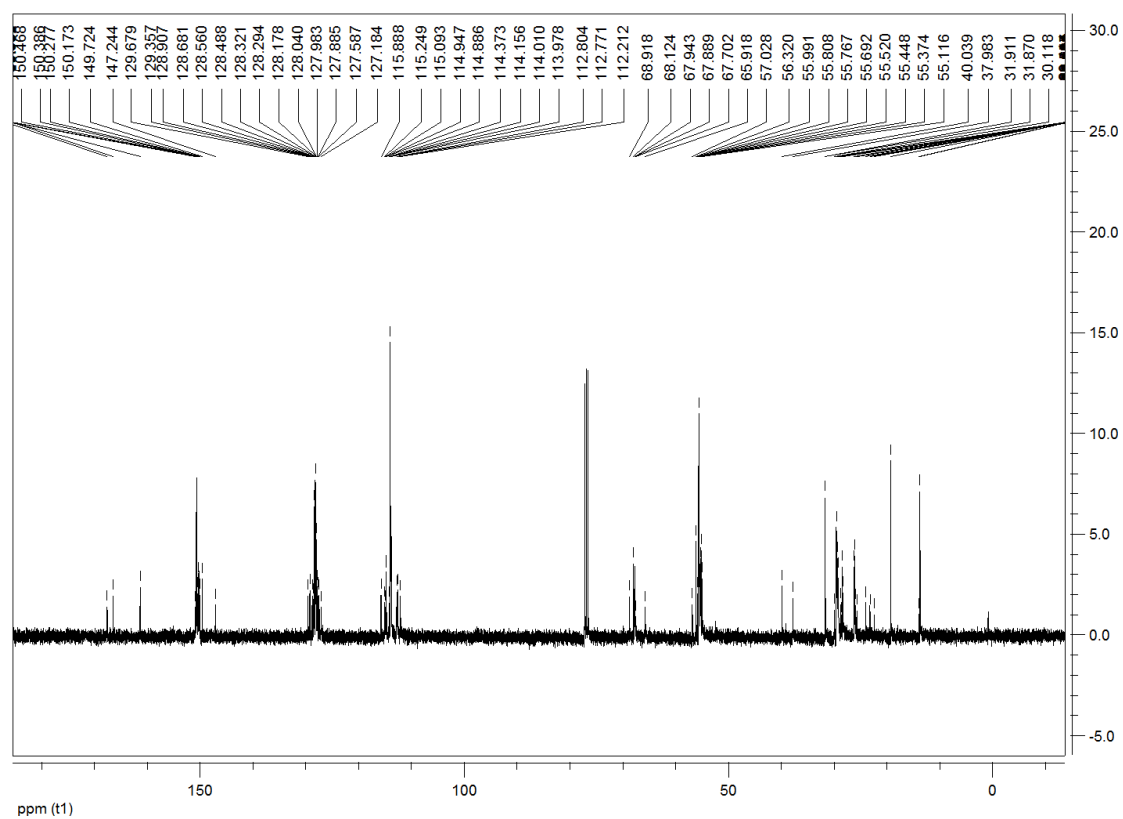
5c: White solid, 16%, m.p. 130-132 °C; ^1H NMR (600 MHz, CDCl_3) δ : 7.85 (d, J = 8.4 Hz, 2H, ArH), 7.02-6.96 (m, 8H, ArH), 6.90 (s, 1H, ArH), 6.84-6.75 (m, 12H, ArH), 6.61 (s, 1H, ArH), 5.25 (brs, 1H, NH), 4.62 (brs, 1H, NH), 4.54 (d, J = 5.4 Hz, 2H, CH_2), 4.14 (t, J = 6.0 Hz, 2H, CH_2), 3.94 (t, J = 6.0 Hz, 2H, CH_2), 3.87-3.63 (m, 68H, 10 CH_2 , 16 OCH_3), 3.53 (s, 2H, CH_2), 2.10-2.08 (m, 2H, CH_2), 2.02-2.00 (m, 2H, CH_2), 1.74-1.72 (m, 2H, CH_2), 1.59 (s, 6H, CH_2), 1.51-1.49 (m, 2H, CH_2), 1.47-1.43 (m, 2H, CH_2), 1.24 (m, 2H, CH_2), 0.95-0.91 (m, 6H, CH_3), -1.88- -2.14 (m, 4H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ : 166.5, 161.2, 150.8, 150.7, 150.6, 150.5, 150.4, 150.2, 150.1, 150.0, 149.8, 149.7, 148.4, 131.9, 129.8, 129.0, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.5, 127.4, 126.6, 117.8, 117.0, 114.8, 114.1, 114.0, 113.9, 113.7, 113.1, 113.0, 112.6, 112.4, 68.1, 67.9, 67.8, 66.0, 57.7, 55.8, 55.7, 55.6, 55.4, 55.3, 39.8, 37.2, 31.8, 31.4, 29.7, 29.6, 29.5, 29.4, 28.7, 28.5, 27.4, 26.5, 26.4, 22.8, 22.6, 19.4, 14.0, 13.9; IR (KBr) ν : 3408, 2937, 1670, 1610, 1501, 1460, 1397, 1306, 1210, 1102, 1042, 928, 873, 771, 703 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{111}\text{H}_{131}\text{N}_2\text{O}_{23}$ ($[\text{M}+\text{H}]^+$): 1860.9176, found: 1860.9220.



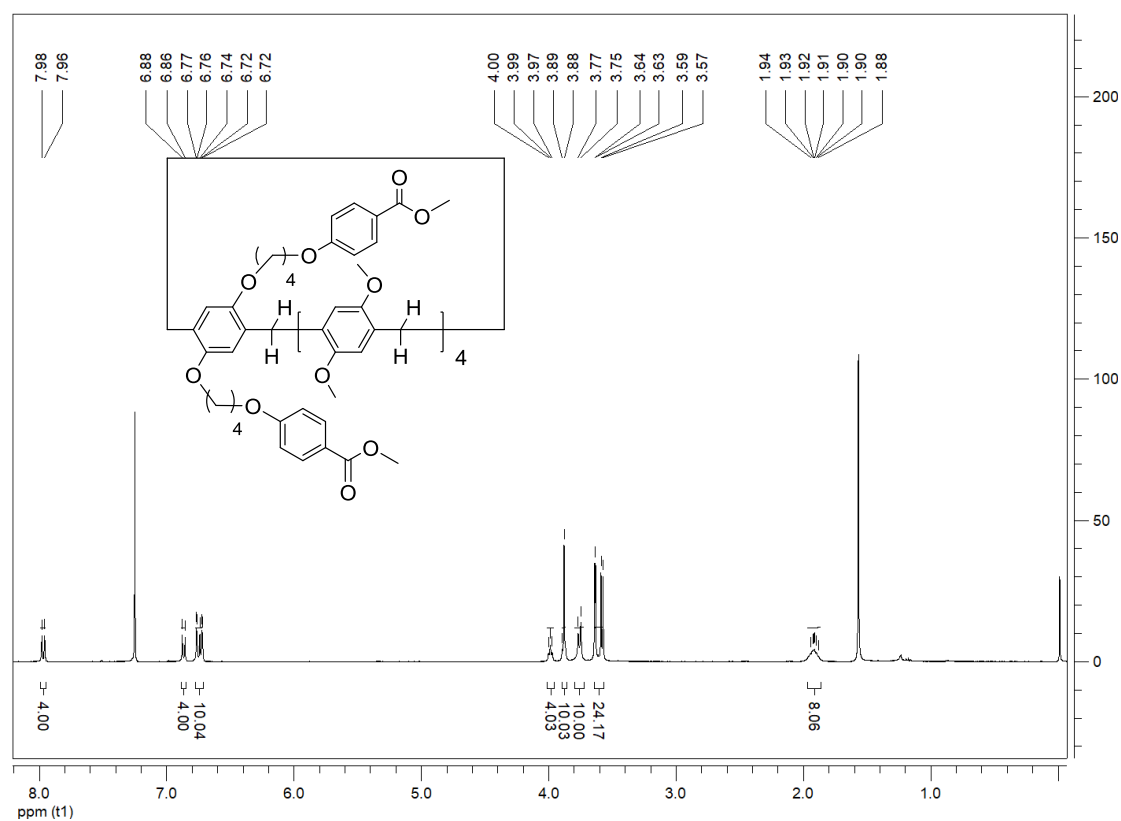


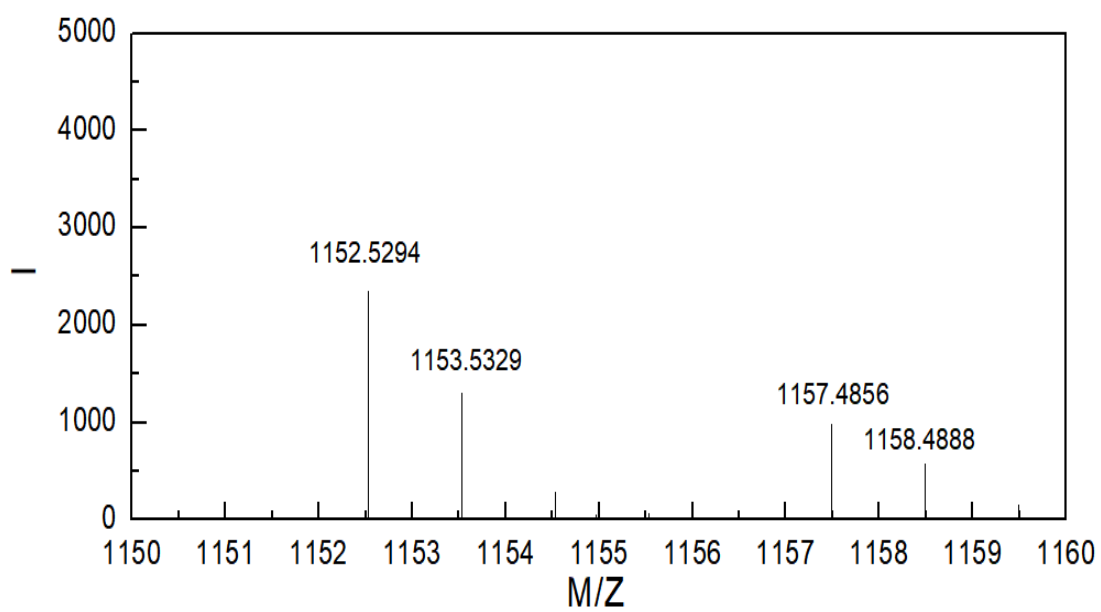
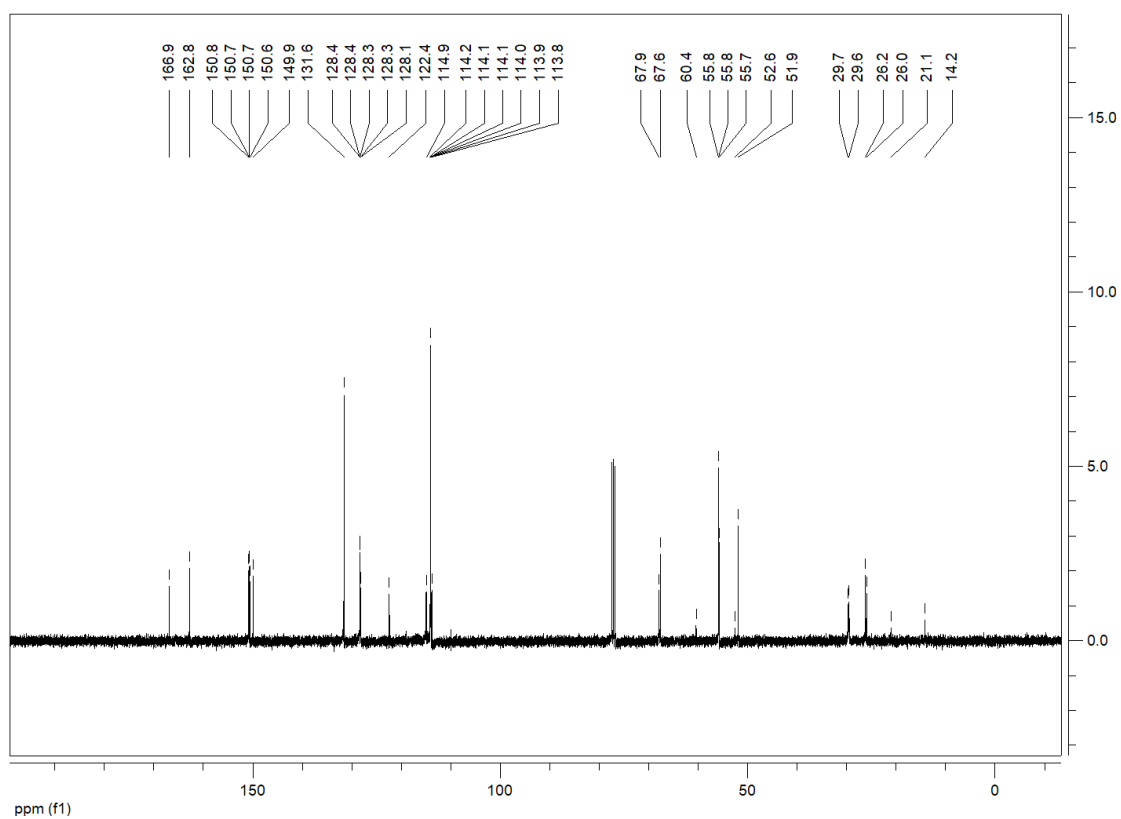
5d: White solid, 8%, m.p. 129-131 °C; White solid, 16%, m.p. 130-132 °C; ^1H NMR (600 MHz, CDCl_3) δ : 7.85 (d, J = 8.4 Hz, 2H, ArH), 7.01-6.74 (m, 22H, ArH), 6.13 (brs, 1H, NH), 5.28 (brs, 1H, NH), 4.59 (d, J = 5.4 Hz, 2H, CH_2), 4.12 (t, J = 6.0 Hz, 2H, CH_2), 3.92 (t, J = 6.0 Hz, 2H, CH_2), 3.83-3.73 (m, 48H, 16OCH_3), 3.66-3.60 (m, 20H, 10CH_2), 3.52 (s, 2H, CH_2), 2.09-2.04 (m, 2H, CH_2), 1.99-1.97 (m, 2H, CH_2), 1.74-1.70 (m, 2H, CH_2), 1.62-1.58 (m, 8H, CH_2), 1.51-1.45 (m, 4H, CH_2), 1.24-1.23 (m, 6H, CH_2), 0.95-0.89 (m, 6H, CH_3), 0.07 (s, 2H, CH_2), -0.28 (s, 2H, CH_2), -0.72- -0.97 (m, 2H, CH_2), -1.58- -1.66 (m, 2H, CH_2), -2.07 (s, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ : 167.6, 166.5, 161.4, 150.9, 150.8, 150.7, 150.6, 150.5, 150.4, 150.3, 150.2, 150.1, 149.7, 147.2, 129.6, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.1, 115.8, 115.2, 115.0, 114.9, 114.8, 114.3, 114.1, 114.0, 113.9, 112.8, 112.7, 112.2, 68.9, 68.1, 67.9, 67.8, 67.7, 65.9, 57.0, 56.3, 55.9, 55.8, 55.7, 55.6, 55.5, 55.4, 55.3, 55.1, 40.0, 37.9, 31.9, 31.8, 30.1, 29.7, 29.6, 29.5, 29.4, 28.9, 28.8, 28.6, 28.5, 26.4, 26.3, 26.2, 25.9, 24.2, 24.1, 23.4, 22.6, 19.4, 14.1, 13.9; IR (KBr) ν : 3411, 2934, 2858, 1668, 1609, 1501, 1460, 1397, 1306, 1210, 1100, 1043, 929, 872, 770, 704 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{113}\text{H}_{135}\text{N}_2\text{O}_{23}$ ($[\text{M}+\text{H}]^+$): 1888.9489, found: 1888.9523.



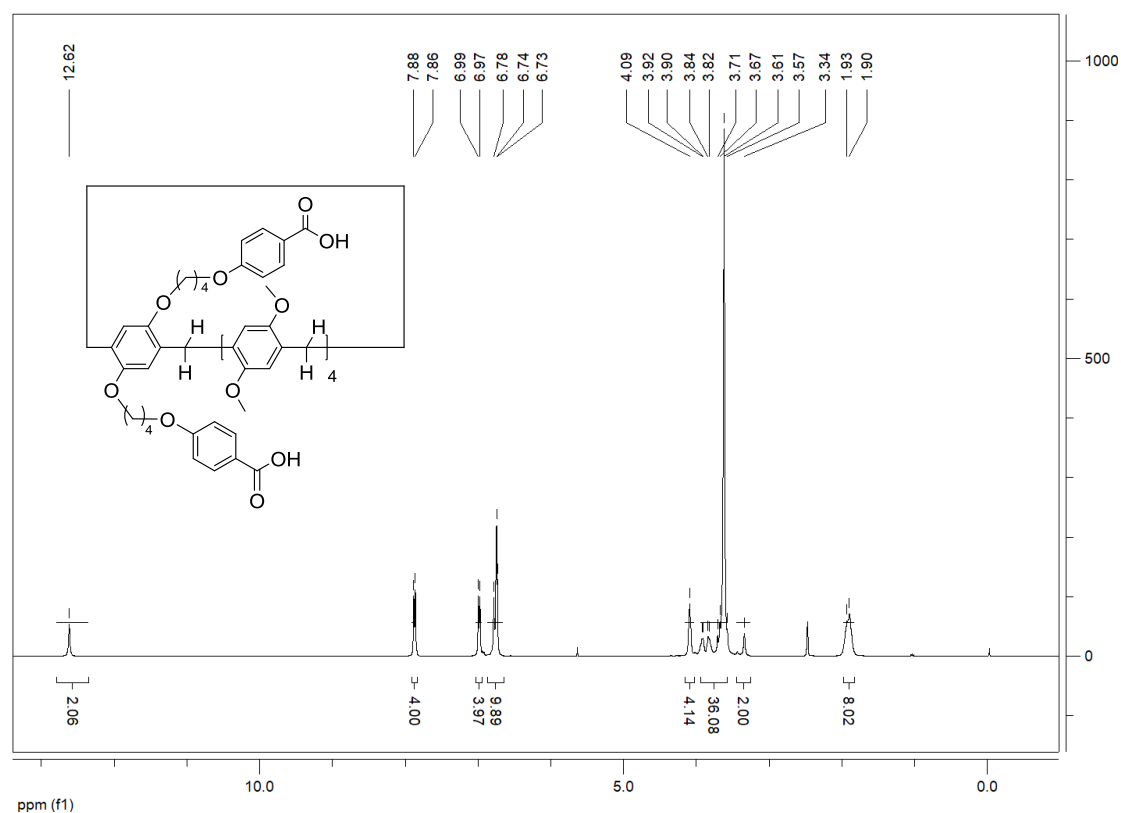


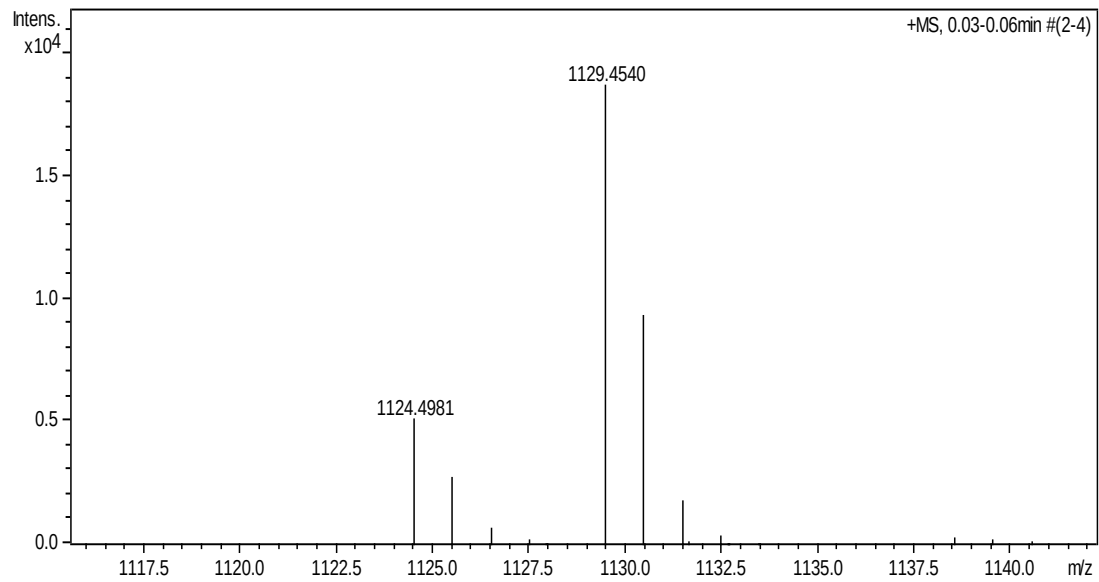
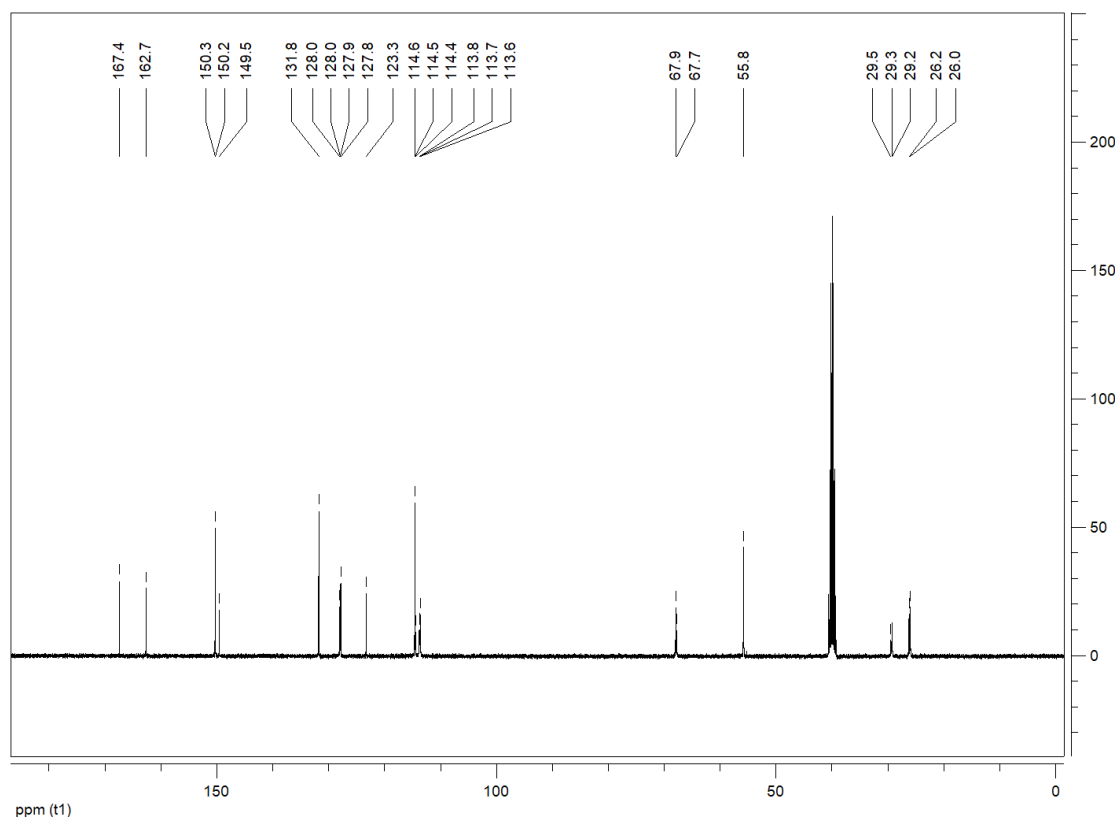
7: White solid, 20%, m.p. 84.5-86.3 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.87 (d, J = 4 Hz, 4H, ArH), 6.87 (d, J = 4 Hz, 4H, ArH), 6.77-6.72 (m, 10H, ArH), 4.99 (t, J = 6 Hz, 4H, OCH_2), 3.89-3.88 (m, 10H, 4OCH_2 , 6OCH_3), 3.77-3.75 (m, 10H, CH_2), 3.64-3.57 (m, 24H, OCH_3), 1.94-1.88 (m, 8H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ : 166.8, 162.7, 150.7, 150.7, 150.7, 150.6, 149.8, 131.5, 128.3, 128.3, 128.3, 128.2, 128.1, 122.3, 114.9, 114.1, 114.1, 114.0, 114.0, 113.8, 113.8, 67.9, 67.6, 60.4, 55.8, 55.8, 55.7, 52.6, 51.8, 29.6, 29.5, 26.2, 25.9, 21.0, 14.1; IR (KBr) ν : 3435, 2936, 2829, 1715, 1606, 1580, 1501, 1466, 1436, 1399, 1281, 1256, 1212, 1168, 1103, 1046, 1010, 975, 930, 880, 849, 772, 732 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{67}\text{H}_{74}\text{O}_{16}\text{Na}$ ($[\text{M}+\text{Na}]^+$): 1157.4875, found: 1157.4856.



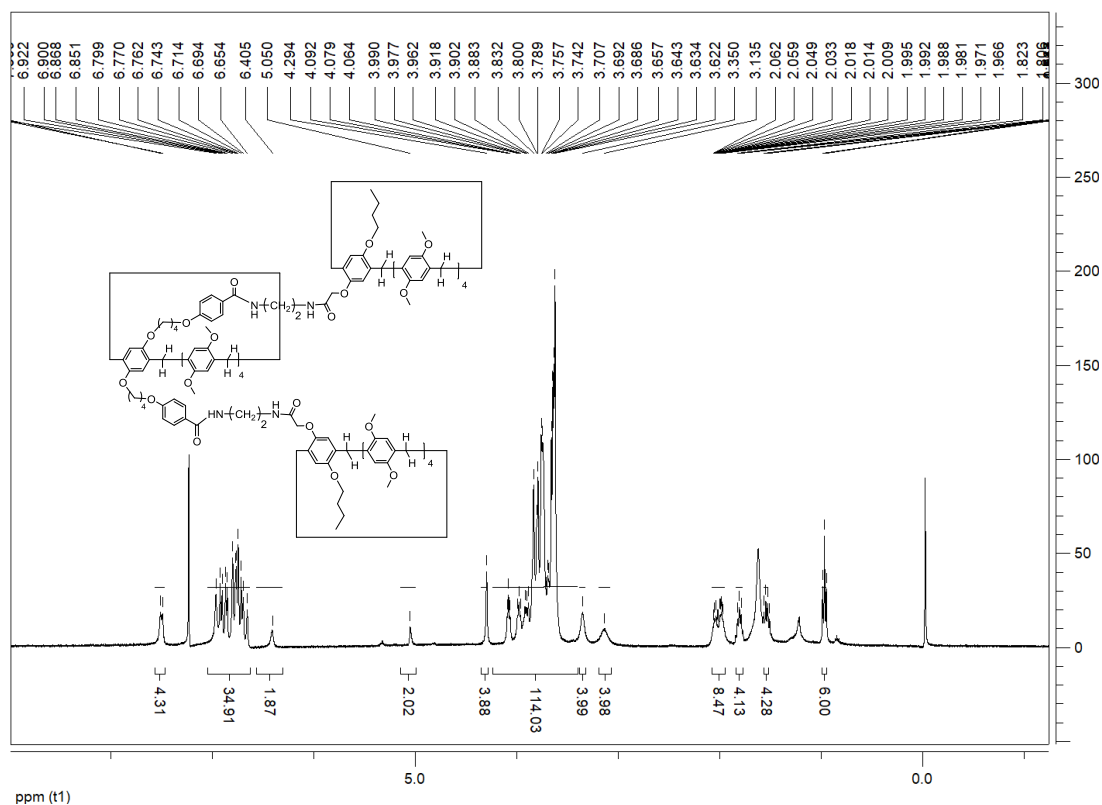


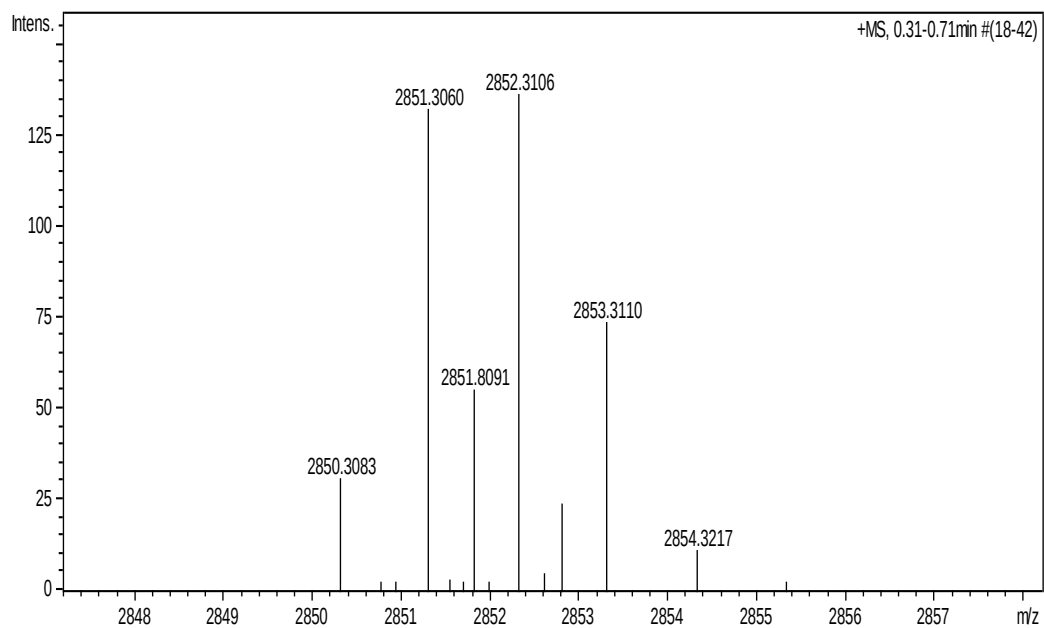
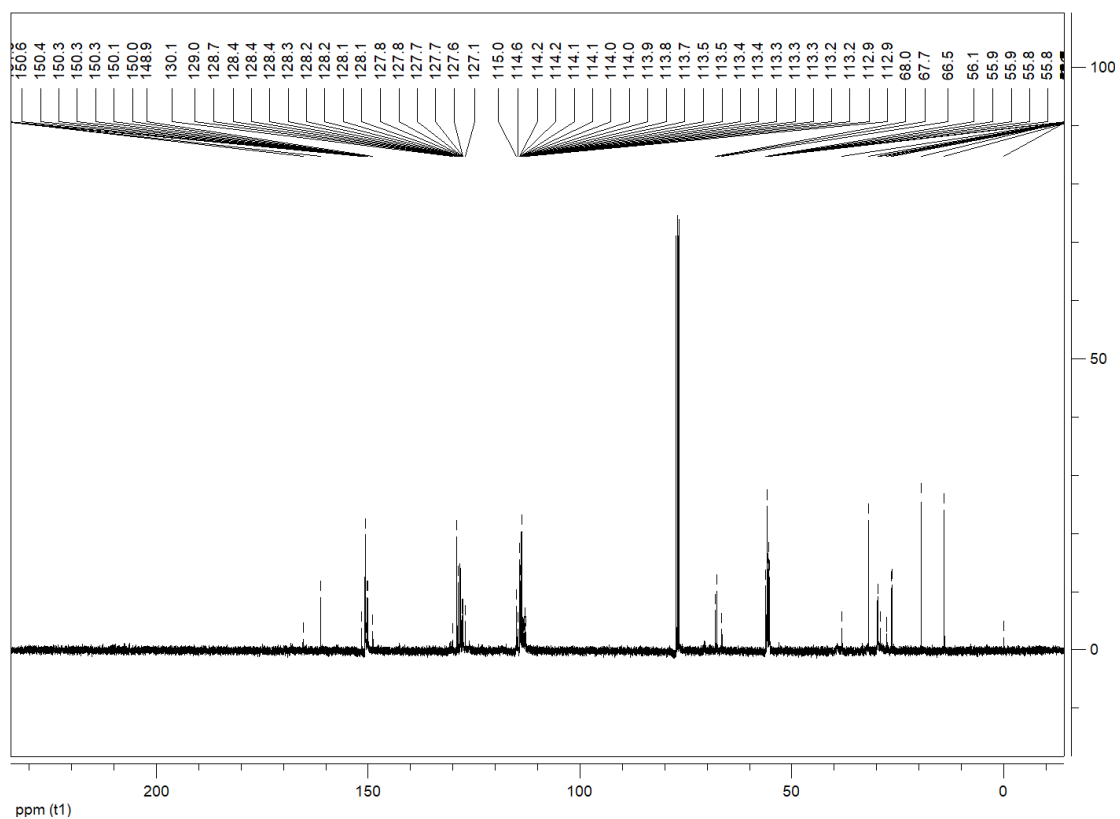
8: White solid, 85%, m.p. 216.6-218.2 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 12.62(s, 2H, COOH), 7.87 (d, $J = 4\text{Hz}$, 4H, ArH), 6.98(d, $J = 4\text{Hz}$, 4H, ArH), 6.78-6.73 (m, 10H, ArH), 4.09 (s, 4H, CH_2), 3.92-3.57 (m, 36H, 12CH_2 , 24OCH_3), 3.34 (s, 2H, CH_2), 1.93-1.90 (m, 8H, CH_2); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ : 167.4, 162.6, 150.3, 150.2, 149.5, 131.7, 128.0, 127.9, 127.9, 127.8, 123.2, 114.5, 114.5, 114.4, 113.7, 113.7, 113.6, 67.9, 67.7, 55.7, 29.4, 29.2, 29.1, 26.1, 25.9; IR (KBr) ν : 3436, 2931, 1682, 1605, 1579, 1501, 1466, 1427, 1400, 1255, 1212, 1168, 1105, 1047, 929, 849, 774 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{65}\text{H}_{70}\text{O}_{16}\text{Na}$ ($[\text{M}+\text{Na}]^+$): 1129.4562, found: 1129.4540.



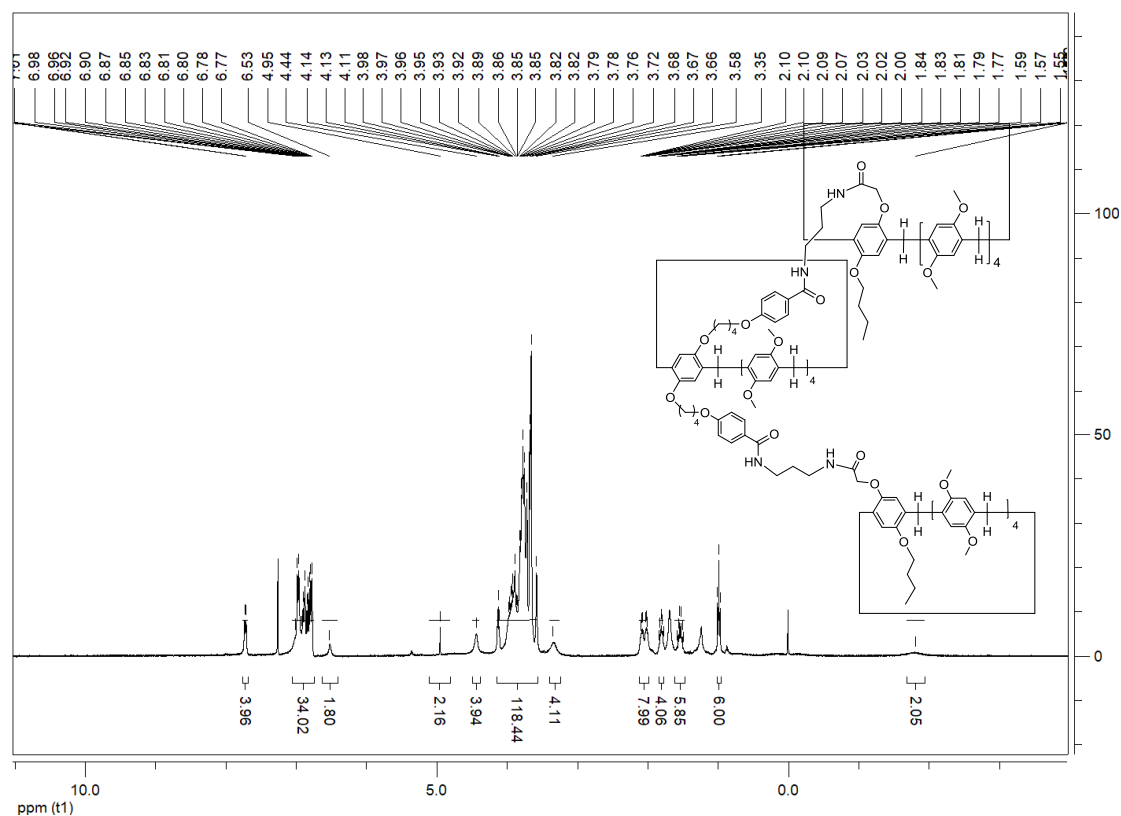


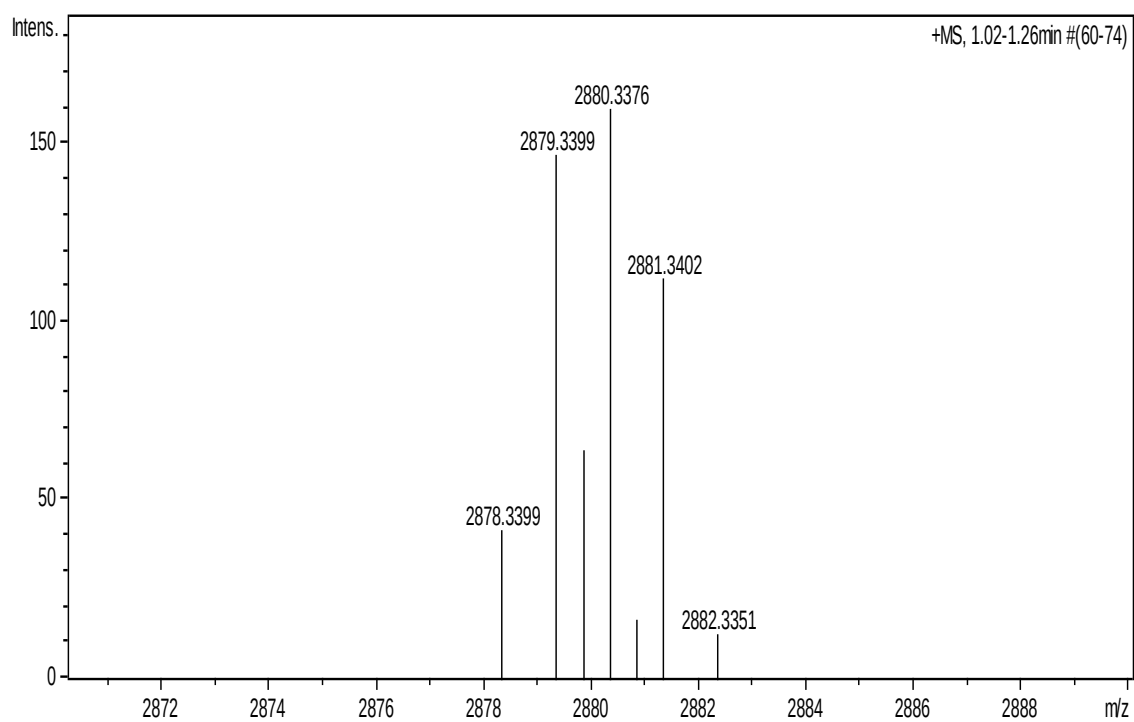
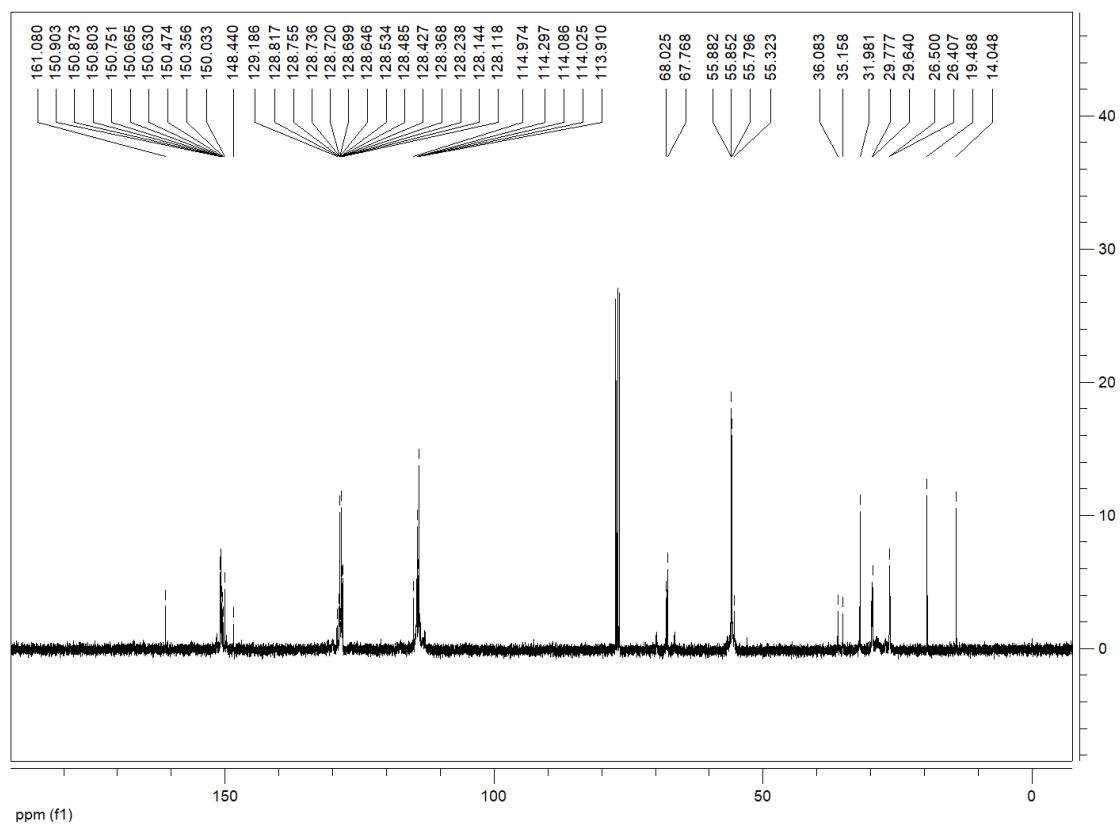
9a: White solid, 26%, m.p. 129-131 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.50 (d, J = 8 Hz, 4H, ArH), 6.96-6.65 (m, 34H, ArH), 6.40 (s, 2H, NH), 5.05 (s, 2H, NH), 4.29 (s, 4H, CH_2), 4.09-3.62 (m, 114H, 42 CH_2 , 72 OCH_3), 3.35 (s, 4H, CH_2), 3.14 (brs, 4H, CH_2), 2.06-1.97 (m, 8H, CH_2), 1.84-1.77 (m, 4H, CH_2), 1.58-1.51 (m, 4H, CH_2), 0.97 (t, J = 7.4Hz, 6H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ : 165.3, 161.2, 151.5, 150.8, 150.8, 150.8, 150.7, 150.7, 150.6, 150.6, 150.5, 150.3, 150.3, 150.3, 150.2, 150.1, 150.0, 148.8, 130.1, 129.0, 128.7, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.7, 127.6, 127.5, 127.0, 114.9, 114.6, 114.2, 114.2, 114.1, 114.0, 114.0, 113.9, 113.9, 113.7, 113.7, 113.5, 113.4, 113.4, 113.4, 113.3, 113.2, 113.2, 113.2, 113.1, 112.9, 112.8, 68.0, 67.6, 66.4, 56.1, 55.8, 55.8, 55.8, 55.8, 55.7, 55.6, 55.6, 55.5, 55.4, 55.3, 55.3, 55.2, 38.1, 31.9, 29.7, 29.6, 29.1, 27.5, 27.5, 27.5, 26.4, 26.4, 26.3, 19.4, 13.9; IR (KBr) ν : 3397, 2935, 2829, 1662, 1608, 1501, 1463, 1400, 1309, 1250, 1045, 928, 878, 848, 771, 700 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{167}\text{H}_{190}\text{N}_4\text{O}_{36}\text{Na}$ ($[\text{M}+\text{Na}]^+$): 2851.3091, found: 2851.3060.



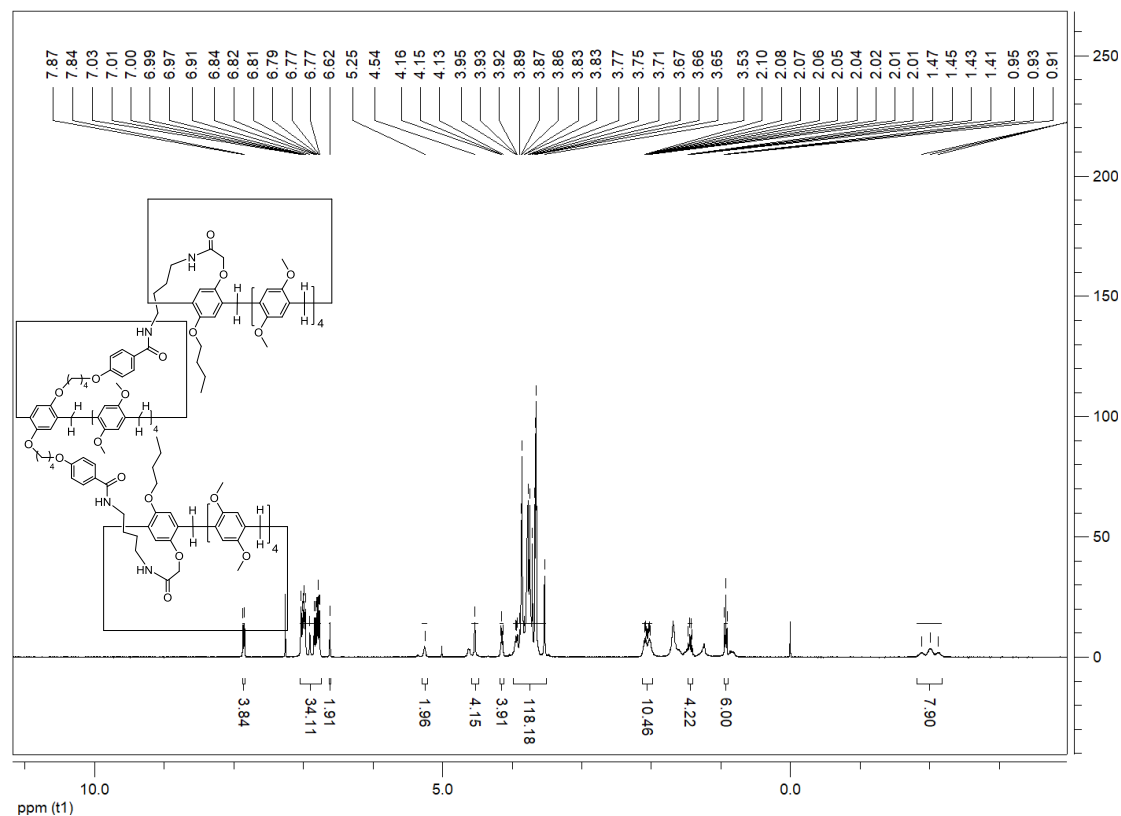


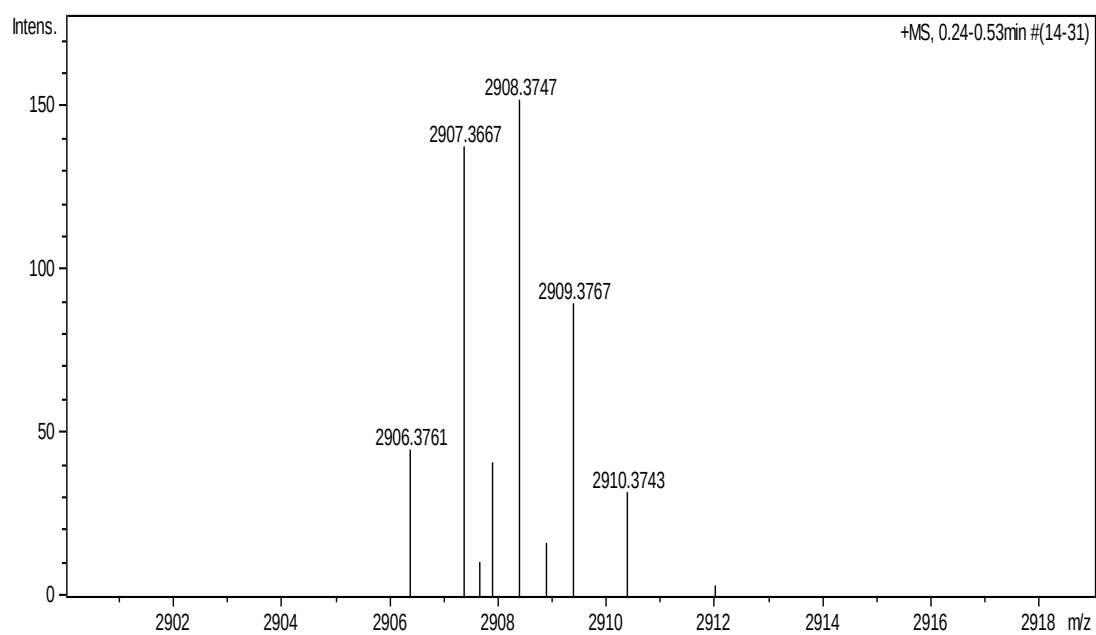
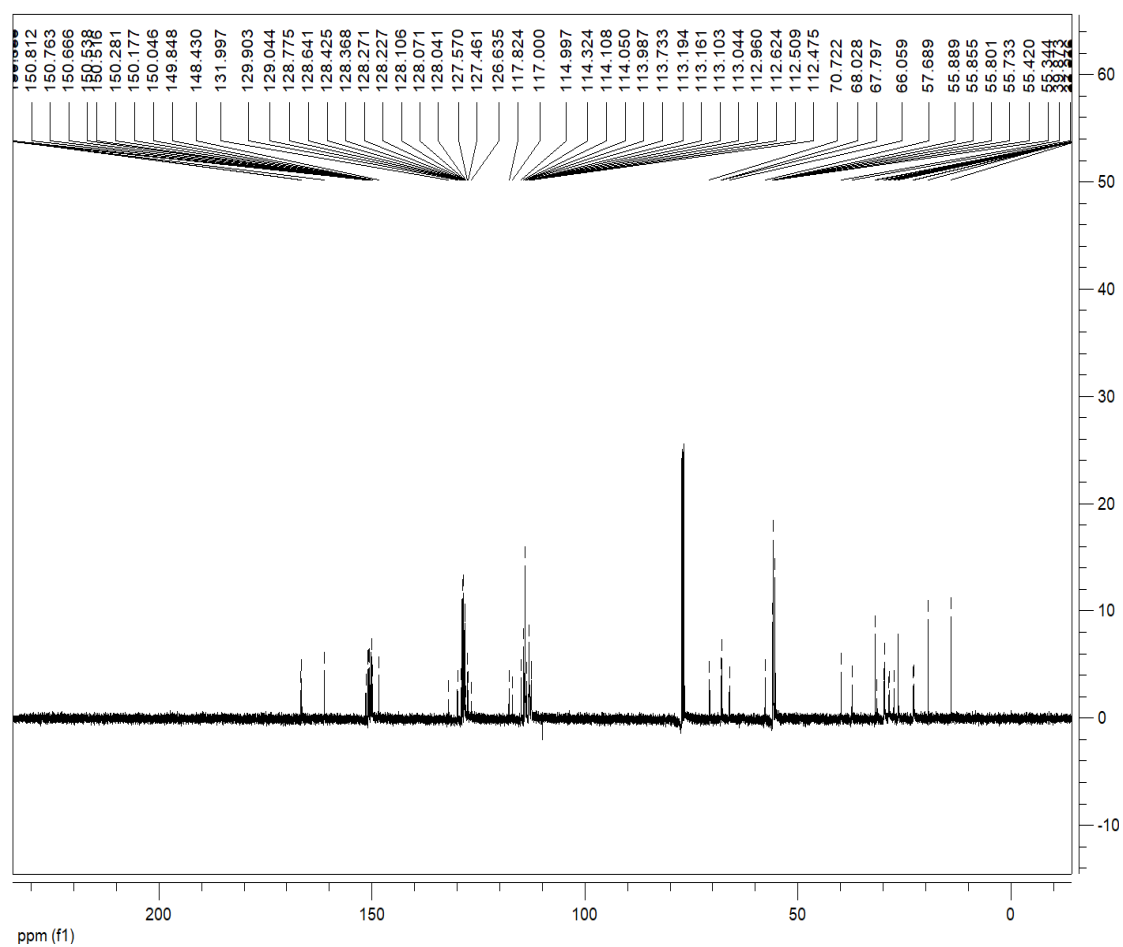
9b: White solid, 22%, m.p. 136-138 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.72 (d, J = 8 Hz, 4H, ArH), 7.01-6.77 (m, 34H, ArH), 6.53 (s, 2H, NH), 4.95 (s, 2H, NH), 4.44 (s, 4H, CH_2), 4.14-3.58 (m, 118H, 46CH_2 , 72OCH_3), 3.35(s, 4H, CH_2), 2.10-2.00 (m, 8H, CH_2), 1.84-1.77 (m, 4H, CH_2), 1.59-1.49 (m, 4H, CH_2), 0.99 (t, J = 8 Hz, 6H, CH_3), -1.80 (brs, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ : 161.0, 150.9, 150.8, 150.8, 150.7, 150.6, 150.6, 150.4, 150.3, 150.0, 148.4, 129.1, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 114.9, 114.2, 114.0, 114.0, 113.9, 68.0, 67.7, 55.8, 55.8, 55.7, 55.3, 36.0, 35.1, 31.9, 29.7, 29.6, 26.5, 26.4, 19.4, 14.0; IR (KBr) ν : 3340, 2935, 2830, 1664, 1608, 1501, 1400, 1309, 1249, 1211, 1044, 828, 878, 849, 771 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{169}\text{H}_{194}\text{N}_4\text{O}_{36}\text{Na}$ ($[\text{M}+\text{Na}]^+$): 2879.3404, found: 2879.3399.





9c: White solid, 19%, m.p. 146-148 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.86(d, J = 6 Hz, 4H, ArH), 7.03-6.77 (m, 34H, ArH), 6.62 (s, 2H, NH), 5.25(s, 2H, NH), 4.54 (s, 4H, CH_2), 4.15(t, J = 6 Hz, 4H, CH_2), 3.95-3.53 (m, 118H, 46 CH_2 , 72 OCH_3), 2.10-2.01 (m, 10H, CH_2), 1.47-1.41 (m, 6H, CH_2), 0.93 (t, J = 8 Hz, 6H, CH_3), -2.00 (m, 8H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ : 166.6, 166.4, 161.2, 151.4, 150.9, 150.8, 150.8, 150.7, 150.6, 150.5, 150.5, 150.2, 150.1, 150.0, 149.8, 148.4, 131.9, 129.9, 129.0, 128.7, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.5, 127.4, 126.6, 117.8, 117.0, 114.9, 114.3, 114.1, 114.0, 113.9, 113.7, 113.1, 113.1, 113.1, 113.0, 112.9, 112.6, 112.5, 112.4, 70.7, 68.0, 67.7, 66.0, 57.6, 55.8, 55.8, 55.8, 55.7, 55.4, 55.3, 39.8, 37.2, 31.8, 31.3, 29.7, 29.7, 29.6, 28.7, 28.5, 27.4, 26.4, 26.4, 22.9, 22.7, 19.3, 13.9; IR (KBr) ν : 3399, 2935, 2829, 1664, 1608, 1501, 1463, 1400, 1308, 1249, 1211, 1044, 928, 879, 771, 701 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{171}\text{H}_{198}\text{N}_4\text{O}_{36}\text{Na}$ ($[\text{M}+\text{Na}]^+$): 2907.3717, found: 2907.3667.





9d: White solid, 17%, m.p. 140-142 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.84 (d, J = 4 Hz, 4H, ArH), 7.01-6.74 (m, 34H, ArH), 6.14 (s, 2H, NH), 5.28 (s, 2H, NH), 4.58 (s, 4H, CH_2), 4.11 (t, J = 4 Hz, 4H, CH_2), 3.91-3.62 (m, 118H, 46 CH_2 , 72 OCH_3), 2.70 (brs, 2H, CH_2), 2.51 (brs, 2H, CH_2), 2.08-1.95 (m, 8H, CH_2), 1.48-1.42 (m, 4H, CH_2), 0.89 (t, J = 4 Hz, 6H, CH_3), -0.29 (brs, 4H, CH_2), -0.74 (brs, 2H, CH_2), -0.97 (brs, 2H, CH_2), -1.62 (brs, 4H, CH_2), -2.08 (brs, 4H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ : 167.6, 166.4, 161.4, 150.9, 150.9, 150.8, 150.8, 150.7, 150.7, 150.6, 150.6, 150.5, 150.4, 150.3, 150.3, 150.2, 150.1, 149.9, 147.2, 129.6, 129.3, 128.8, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.1, 115.8, 115.1, 115.1, 115.0, 114.8, 114.3, 114.3, 114.1, 114.1, 114.0, 113.9, 113.9, 112.8, 112.7, 112.7, 112.2, 112.2, 112.1, 109.9, 68.8, 67.9, 67.7, 65.8, 57.0, 56.2, 55.9, 55.8, 55.8, 55.7, 55.5, 55.5, 55.4, 55.3, 55.0, 53.1, 40.0, 37.9, 31.8, 30.1, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 28.8, 28.6, 28.5, 26.4, 26.3, 26.2, 26.1, 24.1, 23.4, 23.3, 19.4, 13.9; IR (KBr) ν : 3409, 2935, 2856, 1673, 1608, 1500, 1464, 1400, 1307, 1249, 1210, 1100, 1045, 928, 879, 850, 771, 702, 647, 454 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{175}\text{H}_{206}\text{N}_4\text{O}_{36}\text{Na}$ ($[\text{M}+\text{Na}]^+$): 2963.4343, found: 2963.4339.

