Bis- and mono(m-benzoic acid)-functionalized pillar[5]arenes

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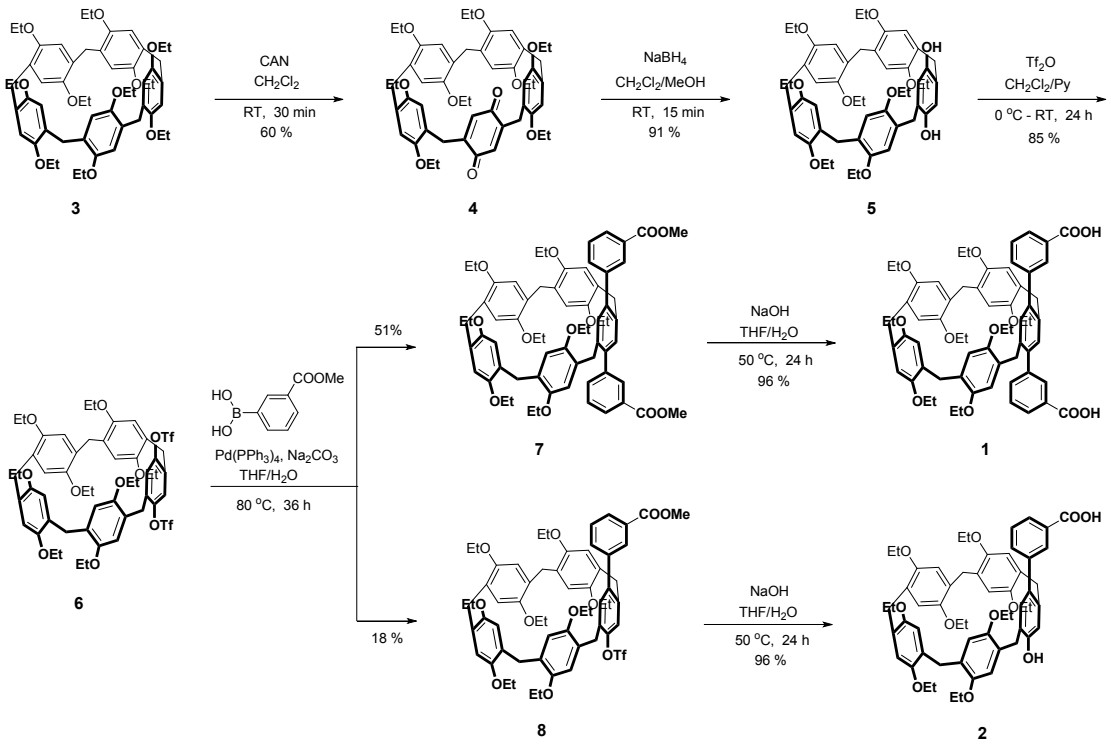
General Methods: Unless otherwise noted, all commercial reagents and solvents were used without purification. Separation by flash column chromatography was performed on Merck silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Bruker **NMR** spectrometers (400 MHz, 500 MHz or 600 MHz) with TMS as internal reference. Mass spectra (ESI) were recorded on an Esquire 6000 spectrometer (LC/MS). Single crystal X-ray diffraction data were collected on BL17B beamline of National Center for Protein Sciences Shanghai (NCPSS) at Shanghai Synchrotron Radiation Facility. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added at their geometrically ideal positions and refined isotropically.

Scheme S1. Synthesis of Pillar[5]arenes 1 and 2：



Pillar[5]arenes **3, 4, 5** and **6** (Scheme S1) were prepared according to reported procedures.[S1-3]

Bis- and mono(methyl *m*-benzoate)-functionalized pillar[5]arenes 7 and 8. A mixture of pillar[5]arene **6** (1.10 g, 1.0 mmol), methyl 3-boronobenzoate (900.0 mg, 5.0 mmol), Na_2CO_3 (650.0 mg，5.0 mmol) and $Pd(PPh_3)_4$ (300.0 mg, 0.26 mmol) in a mixed solvent of THF and H_2O (60 ml, 5:1, *v/v*) was heated under N_2 at 80 ºC for 36 h, then poured into water (100 mL),

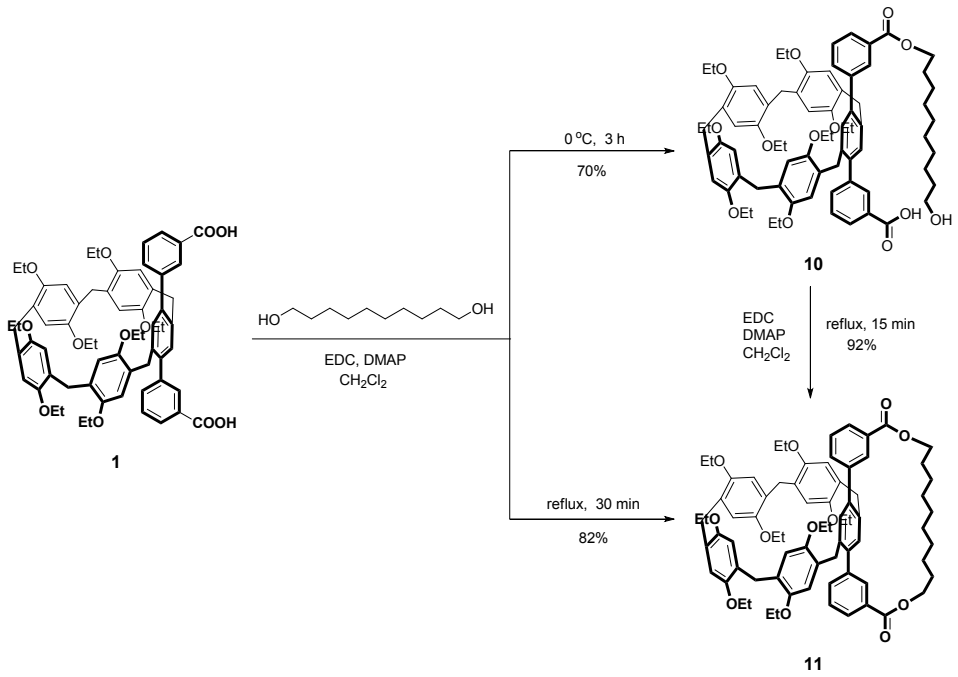
and extracted with ethyl acetate (3 × 100 mL). The combined organic phases were concentrated to result in a residue which was subjected to column chromatography (petroleum ether/EtOAc, 50:1, *v/v*) to afford **7** as a pink solid (0.55 g, 51%) and **8** as a pale yellow solid (0.20 g, 18%). **7**: mp 167.2-168.2 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.79 (s, 2H), 7.46 (d, *J* = 36.0 Hz, 4H), 7.20 (s, 2H), 6.76 (s, 2H), 6.66 (s, 2H), 6.60 (s, 2H), 5.73 (s, 2H), 3.90-3.62 (m, 27H), 3.55 (d, *J* = 13.1 Hz, 2H), 3.41 (dd, *J* = 15.3, 7.2 Hz, 3H), 1.22 (s, 6H), 1.18 (s, 6H), 1.09 (s, 6H), 0.96 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.6, 149.6, 149.5, 149.3, 149.1, 142.4, 139.5, 136.8, 134.60, 132.5, 130.2, 130.2,129.1, 128.5, 128.2, 128.2, 128.0, 127.2, 115.0, 114.6, 113.7, 79.7, 63.6, 63.5, 63.2, 63.2, 52.6, 32.2, 29.4, 15.2, 15.0, 14.7; HRMS (ESI): calcd for $C_{65}H_{78}NO_{12}$ *m/z* 1088.5519 [M+NH_4^+], found 1088.5515. **8**: mp 156.2-157.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.96 (s, 1H), 7.39 (s, 1H), 7.23 (d, *J* = 11.0 Hz, 3H), 6.80 – 6.68 (m, 6H), 6.61 (s, 1H), 5.83 (s, 1H), 3.93 (s, 4H), 3.92-3.78 (m, 18H), 3.71 (s, 5H), 3.56 (d, *J* = 6.6 Hz, 2H), 1.37-1.28 (m, 9H), 1.23 (d, *J* = 7.0 Hz, 9H), 1.10 (d, *J* = 20.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ166.8, 150.0, 150.0, 149.9, 149.8, 149.8, 149.2, 147.7, 141.3, 139.9, 134.1, 134.0, 131.0, 130.5, 130.2, 129.7, 129.3, 129.0, 128.8, 128.6, 128.3, 128.1, 126.8, 125.0, 122.8, 115.4, 115.0, 114.7, 114.5, 114.0, 64.0, 63.9, 63.8, 63.8, 63.7, 63.5, 63.2, 52.2, 32.5, 31.6, 30.0, 29.7, 29.5, 15.2, 15.1, 15.0, 15.0, 14.7, 14.5; HRMS (ESI) calcd for $C_{60}H_{71}F_3NO_{13}S$ *m/z* 1102.4593 [M+NH_4^+], found 1102.4652.

Bis(*m*-benzoic acid)-functionalized pillar[5]arene 1: A mixture of pillar[5]arene **7** (1.07 g, 1.0 mmol) and NaOH (4.0 g, 100.0 mmol) in a mixed solvent of THF and H_2O (200 ml, 1:1, *v/v*) was heated at 50 ºC for 24 h, poured into an aqueous HCl solution (1.0 M, 300 mL), and extracted with dichloromethane (3 × 100 mL). The combined extracts were dried over anhydrous Na_2SO_4 and concentrated to result in a residue which was subjected to column chromatography (CH_3OH/CH_2Cl_2, 1:10, *v/v*) to afford **1** as a bright yellow solid (1.0 g, 96%). mp 223.1-224.1 °C; ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.09 (d, *J* = 7.7 Hz, 2H), 8.03 (s, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.33 (s, 2H), 6.90 (s, 2H), 6.80 (s, 2H), 6.71 (s, 2H), 5.77 (s, 2H), 3.99-3.89 (m, 10H), 3.87-3.78 (m, 8H), 3.72 (d, *J* = 12.9 Hz, 2H), 3.63 (d, *J* = 12.9 Hz, 2H), 3.57-3.52 (m, 2H), 3.49-3.44 (m, 2H), 1.41 (t, *J* = 7.0 Hz, 6H), 1.33 (d, *J* = 6.9 Hz, 6H), 1.23 (t, *J* = 6.9 Hz, 6H), 1.15 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6)

δ 149.6, 149.5, 149.4, 149.1, 142.1, 139.7, 136.7, 133.6, 132.6, 130.5, 128.4, 128.3, 128.1, 127.4, 115.0, 114.6, 113.7, 79.74, 63.6, 63.5, 63.3, 63.2, 32.2, 29.4, 15.2, 15.1, 15.1, 14.8; HRMS (ESI): calcd for $C_{65}H_{70}O_{12}Na$ *m/z* 1065.4759 [M+Na^+], found 1065.4758.

Mono(*m*-benzoic acid)-functionalized pillar[5]arene 2: A mixture of pillar[5]arene **8** (1.08 g, 1.0 mmol) and NaOH (4.0 g, 100.0 mmol) in a mixed solvent of THF and H_2O (200 ml, 1:1, *v/v*) was heated at 50 ºC for 24 h, poured into an aqueous HCl solution (1.0 M, 300 mL), and extracted with dichloromethane (3 × 100 mL). The combined extracts were dried over anhydrous Na_2SO_4 and concentrated to result in a residue which was subjected to column chromatography (CH_3OH/CH_2Cl_2, 1:10, *v/v*) to afford **2** as a bright yellow solid (0.9 g, 96%). mp 195.9-196.7 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.94 (s, 2H), 7.49 (s, 2H), 7.06 (s, 1H), 6.95-6.61 (m, 9H), 6.09 (s, 1H), 3.94-3.83 (m, 12H), 3.68 (t, J = 20.9 Hz, 15H), 1.38-1.29 (m, 15H), 1.22 (d, *J* = 7.0 Hz, 6H), 1.10 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.6, 149.8, 149.7, 149.6, 149.6, 149.3, 149.3, 149.2, 149.0, 142.5, 137.8, 132.7, 131.1, 128.9, 128.6, 128.3, 128.1, 128.0, 128.0, 127.6, 126.0, 117.7, 115.7, 115.1, 115.0, 114.6, 114.4, 114.2, 113.9, 64.0, 63.7, 63.6, 63.6, 63.5, 31.4, 31.3, 29.7, 29.5, 29.1, 15.6, 15.5, 15.4, 15.3, 15.3, 15.2, 15.0; HRMS (ESI): calcd for $C_{58}H_{70}NO_{11}$ *m/z* 956.4943 [M+NH_4^+], found 956.4941.

Scheme S2. Synthesis of monoester 10 and diester 11 from esterification of 1 with decane-1,10-diol (11)



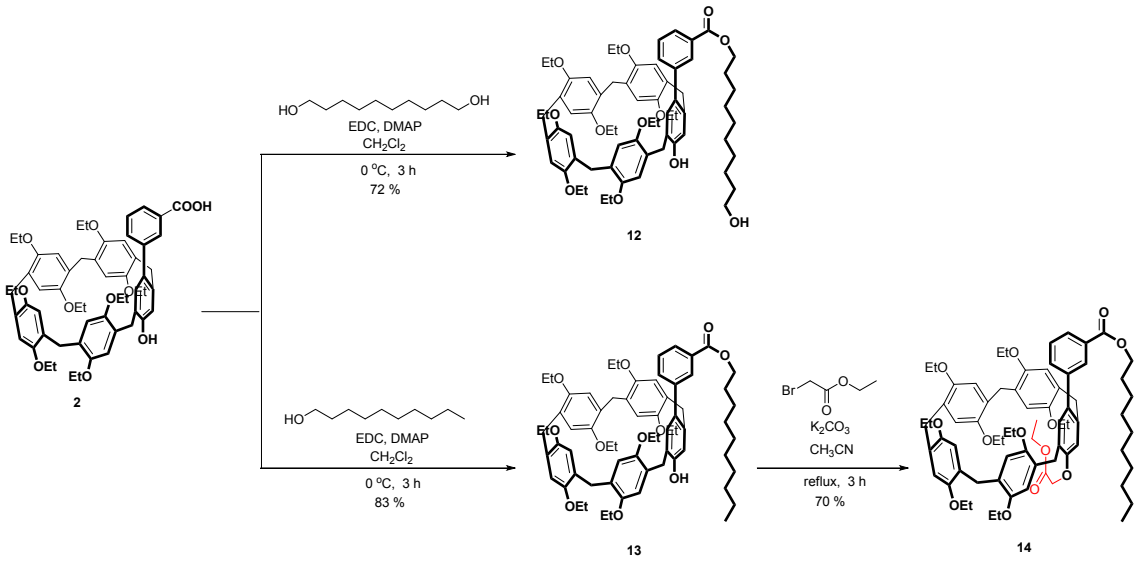
A1[(10-Hydroxydecyl *m*-benzoate)]/A2[(*m*-benzoic acid)]-functionalized pillar[5]arene 10: A mixture of pillar[5]arene **1** (1.04 g, 1.0 mmol), decane-1,10-diol **9** (174 mg, 1.0 mmol), EDC.HCl (1.92 g, 10.0 mmol), and DMAP (3.6 mg, 0.03 mmol) in CH_2Cl_2 (500 ml) was stirred at 0 ºC for 3 h, washed with an aqueous HCl solution (1.0 M, 300 mL), dried over anhydrous Na_2SO_4 and concentrated. The resulting residue was subjected to column chromatography (CH_3OH/CH_2Cl_2, 1:100, *v/v*) to afford **10** as a yellow solid (839 mg, 70%). mp 226.3-227.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (s, 2H), 7.95 (s, 2H), 7.20 (d, *J* = 11.2 Hz, 4H), 6.89-6.81 (m, 4H), 6.78 (s, 2H), 6.68 (s, 2H), 6.45 (s, 2H), 5.83 (s, 2H), 3.89- 3.46 (m, 30H), 1.50 (s, 3H), 1.37 (s, 6H), 1.30 (s, 1H), 1.26 (s, 1H), 1.20 (d, *J* = 16.3 Hz, 16H), 1.10 (s, 6H), 0.86 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.7, 150.1, 150.0, 149.7, 149.6, 142.8, 139.6, 137.0, 134.9, 132.0, 130.3, 129.6, 129.4, 129.1, 128.8, 128.2, 127.1, 115.3, 115.3, 115.2, 114.8, 64.1, 63.4, 33.6, 29.9, 29.7, 15.3, 15.1, 14.9, 14.6; HRMS (ESI): calcd for $C_{75}H_{94}NO_{13}$ *m/z* 1216.6720 [M+NH_4^+], found 1216.6718.

Pillar[5]arene 1 and decane-1,10-diol 9 derived cyclic bi-ester 11: A mixture of pillar[5]arene **1** (1.04 g, 1.0 mmol), decane-1,10-diol **9** (174.0 mg, 1.0 mmol), EDC.HCl (1.92

g, 10 mmol), and DMAP (3.6 mg, 0.03 mmol) in CH_2Cl_2 (20 ml) was heated at 50 ºC for 30 min, washed with an aqueous HCl solution (1.0 M, 50 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was subjected to column chromatography (CH_3OH/CH_2Cl_2, 1:200, *v/v*) to afford **11** as a yellow solid (968 mg, 82%). mp 188.8−189.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97-7.86 (m, 4H), 7.16 (d, *J* = 14.9 Hz, 2H), 6.93 (d, *J* = 31.0 Hz, 4H), 6.75 (s, 2H), 6.62 (s, 2H), 6.47 (s, 2H), 5.79 (s, 2H), 3.86 (s, 4H), 3.82-3.76 (m, 9H), 3.70 (dd, *J* = 18.2, 13.8 Hz, 6H), 3.60 (dd, *J* = 17.8, 11.2 Hz, 4H), 3.55-3.47 (m, 4H), 3.43 (dd, *J* = 6.9, 4.2 Hz, 3H), 1.37 (s, 2H), 1.28 (t, *J* = 6.9 Hz, 8H), 1.22-1.13 (m, 18H), 1.04 (t, *J* = 6.9 Hz, 6H), 0.90 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 150.0, 149.6, 149.5, 142.4, 139.6, 136.9, 134.1, 132.2, 130.3, 129.7, 129.2, 128.8, 128.8, 128.1, 127.6, 127.5, 115.4, 115.0, 114.8, 114.6, 64.1, 64.0, 63.8, 63.4, 63.1, 52.1, 32.9, 32.8, 30.0, 29.9, 29.7, 29.6, 29.5, 25.7, 15.2, 15.1, 14.8, 14.5; HRMS (ESI): calcd for $C_{75}H_{92}NO_{12}$ *m/z* 1198.6614 [M+NH_4^+], found 1198.6339.

Synthesis of 11 from Intramolecular Esterification of 10: A mixture of pillar[5]arene **10** (1.20 g, 1.0 mmol), EDC.HCl (1.92 g, 10.0 mmol), and DMAP (3.6 mg, 0.03 mmol) in CH_2Cl_2 (20 mL) was heated at 50 ºC for 15 min, washed with an aqueous HCl solution (1.0 M, 30 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was subjected to column chromatography (CH_3OH/CH_2Cl_2, 1:200 *v/v*) to afford **11** as a yellow solid (1.08 g, 92 %).

Scheme S3. Synthesis of monoesters 12, 13 and 14



Mono(10-hydroxydecyl *m*-benzoate) functionalized pillar[5]arene 12: A mixture of pillar[n]arene **2** (938 mg, 1.0 mmol), decane-1,10-diol **9** (5.22 g, 30.0 mmol), EDC.HCl (1.92 g, 10.0 mmol), and DMAP (3.6 mg, 0.03 mmol) in CH_2Cl_2 (20 mL) was stirred at 0 ºC for 3 h, washed with an aqueous HCl solution (1.0 M, 30 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (CH_3OH/CH_2Cl_2, 1:100, *v/v*) to afford **12** as a white solid (787 mg, 72 %). mp 137.1-137.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.94 (s, 1H), 7.50 (d, *J* = 23.6 Hz, 3H), 7.34 (s, 1H), 7.00 (d, *J* = 27.7 Hz, 2H), 6.85 (d, *J* = 14.1 Hz, 5H), 6.70 (s, 2H), 4.38 (s, 2H), 4.08 – 3.68 (m, 27H), 3.03 (s, 1H), 1.81 (s, 2H), 1.49 – 1.40 (m, 16H), 1.31 (dd, *J* = 32.3, 25.3 Hz, 21H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 153.9, 149.9, 149.8, 149.5, 142.9, 134.9, 130.8, 130.5, 128.7, 128.2, 127.8, 127.6, 126.3, 118.0, 114.8, 114.5, 114.0, 63.8, 63.6, 63.5, 63.3, 32.1, 32.0, 30.8, 30.0, 29.8, 29.6, 29.2, 27.7, 24.8, 15.3, 15.3, 15.2, 15.0; HRMS (ESI): calcd for $C_{68}H_{90}NO_{12}$ *m/z* 1112.6458 [M+NH_4^+], found 1112.6457.

Mono(decyl *m*-benzoate) functionalized pillar[5]arene 13: A mixture of pillar[5]arene **2** (938 mg, 1.0 mmol), 1-decanol (4.75 g, 30.0 mmol), EDC.HCl (1.92 g, 10.0 mmol), and DMAP (3.6 mg, 0.03 mmol) in CH_2Cl_2 (20 mL) was stirred at 0 ºC for 3 h, washed with an aqueous HCl solution (1.0 M, 30 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (CH_3OH/CH_2Cl_2, 1:300, *v/v*) to afford **13** as a yellow solid (895 mg, 83 %). mp 173.3-173.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-7.98 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.45 (s, 1H), 7.32 (s, 1H), 7.01 (d, *J* = 5.5 Hz, 2H), 6.76 (s, 3H), 6.60 (d, *J* = 9.9 Hz, 2H), 6.52 (s, 1H), 6.29 (d, *J* = 9.3 Hz, 2H), 4.09 (d, *J* = 7.0 Hz, 2H), 3.96-3.68 (m, 30H), 3.37 (d, *J* = 6.9 Hz, 2H), 1.50- 1.40 (m, 7H), 1.39-1.22 (m, 15H), 1.20-1.09 (m, 12H), 0.89 (s, 1H), 0.59 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 153.8, 151.1, 150.3, 150.2, 149.9, 149.7, 149.6, 149.5, 147.2, 142.5, 139.4, 134.6, 131.1, 130.9, 130.1, 129.9, 129.2, 128.7, 128.5, 128.4, 128.2, 127.9, 127.4, 126.3, 125.1, 117.7, 115.8, 115.5, 115.3, 115.1, 114.3, 113.6, 65.1, 64.4, 64.3, 63.9, 63.8, 63.8, 63.7, 63.6, 63.1, 52.1, 32.8, 31.0, 30.7, 29.8, 29.5, 29.1, 15.2, 15.2, 15.1, 15.0, 14.9, 14.8, 14.7, 14.2, 14.0; HRMS (ESI): calcd for $C_{68}H_{90}NO_{11}$ *m/z* 1096.6508 [M+NH_4]$^+$, found 1096.6512

Mono(decyl *m*-benzoate), ethyl 2-phenoxyacetate-functionalized pillar[5]arene 14: A mixture of pillar[5]arene **13** (1.08 g, 1.0 mmol), ethyl bromoacetate (0.5 g, 3.0 mmol) and K_2CO_3(1.38 g, 10.0 mmol) in CH_3CN (50 mL) was refluxed for 3 h, poured into water (100 mL), extracted with EtOAc (3 × 30 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by (CH_3OH/CH_2Cl_2, 1:100, *v/v*) to afford **14** as a white solid (815 mg, 70 %). mp 177.1-177.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ8.01 (d, J = 14.7 Hz, 2H), 7.49 (d, J = 4.9 Hz, 2H), 7.19 (s, 1H), 6.93 (s, 1H), 6.88 (d, J = 6.7 Hz, 3H), 6.84 (s, 1H), 6.80 (d, J = 13.1 Hz, 2H), 6.71 (s, 1H), 5.87 (s, 1H), 4.53 (s, 2H), 4.09 – 3.75 (m, 24H), 3.69 (d, J = 22.3 Hz, 4H), 3.59 (d, J = 6.9 Hz, 2H), 2.01 (s, 2H), 1.52 – 1.37 (m, 20H), 1.28 (dd, J = 15.7, 9.3 Hz, 18H), 0.88 (s, 3H), -1.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.1, 155.4, 150.5, 150.1, 149.9, 149.5, 149.4, 149.0, 148.8, 148.5, 142.8, 139.1, 134.8, 132.8, 131.5, 131.1, 130.0, 129.2, 128.9, 128.8, 128.5, 128.1, 127.9, 127.7, 127.2, 126.5, 126.4, 116.2, 115.4, 115.1, 114.7, 113.8, 113.8, 113.0, 113.0, 111.2, 64.1, 63.9, 63.8, 63.7, 63.5, 63.4, 63.0, 60.9, 52.1, 32.2, 30.9, 30.6, 29.7, 29.0, 28.7, 15.4, 15.4, 15.4, 15.3, 15.1, 15.1, 10.5, 1.1; HRMS (ESI): calcd for $C_{72}H_{96}NO_{13}$ *m/z* 1182.6876 [M+NH_4^+], found 1182.6872.

Crystallographic Data of 1: [$C_{166}H_{205}N_8O_{26}F_{30}P_5$]; *Mr* = 3453.22; T = 173(2) K; T = 173(2) K; triclinic; space group $P\bar{1}$; a = 20.5486(17); b = 21.3959(19); c = 24.984(2) Å; α = 65.6220(10); β = 74.3130(10); γ = 66.014(2); V = 9071.2(13) Å^3; Z = 2; ρ_{calcd} = 1.264 g/cm^3; crystal size = 0.300 x 0.250 x 0.100 mm; μ = 0.146 mm^{-1}; reflections collected 63342; unique reflections 38333; data/restraints/parameters 38333/91/2071; *GOF* on F^2 1.027; R_{int} for independent data 0.0356; final R_1 = 0.1115, wR_2 = 0.3021; R indices (all data) R_1 = 0.1918, wR_2 = 0.3579; largest diff. peak and hole: 0.776 and -0.530 eÅ^{-3}.

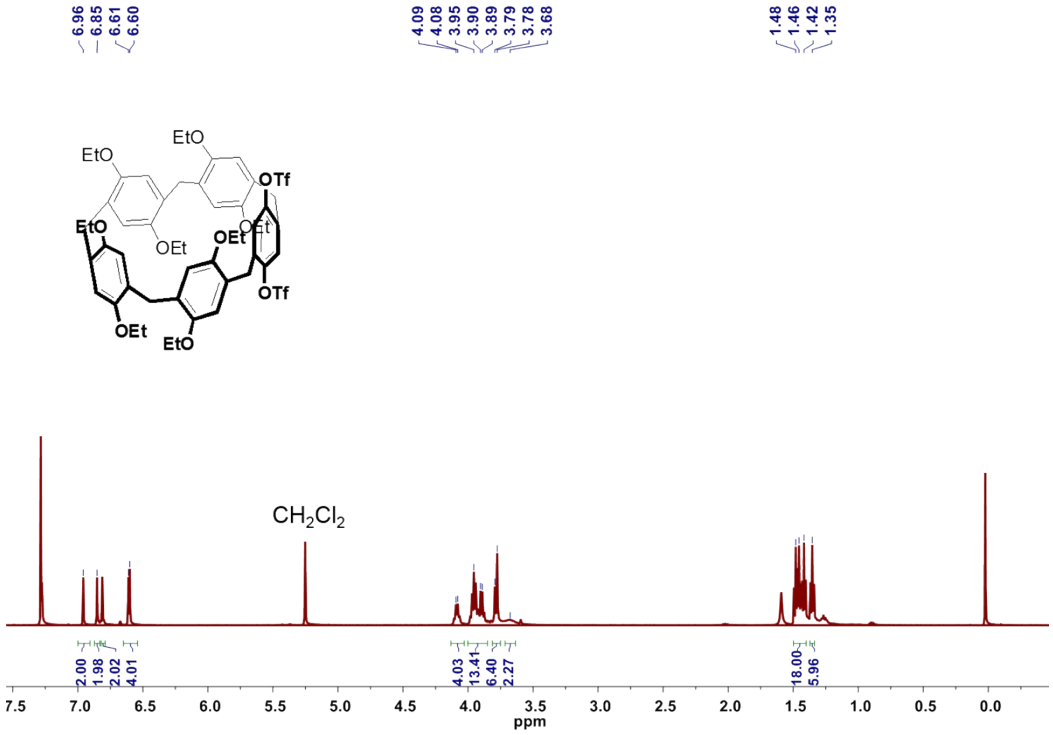


Fig. S1 ^{1}H NMR spectrum (500 MHz) of **6** in $CDCl_3$.

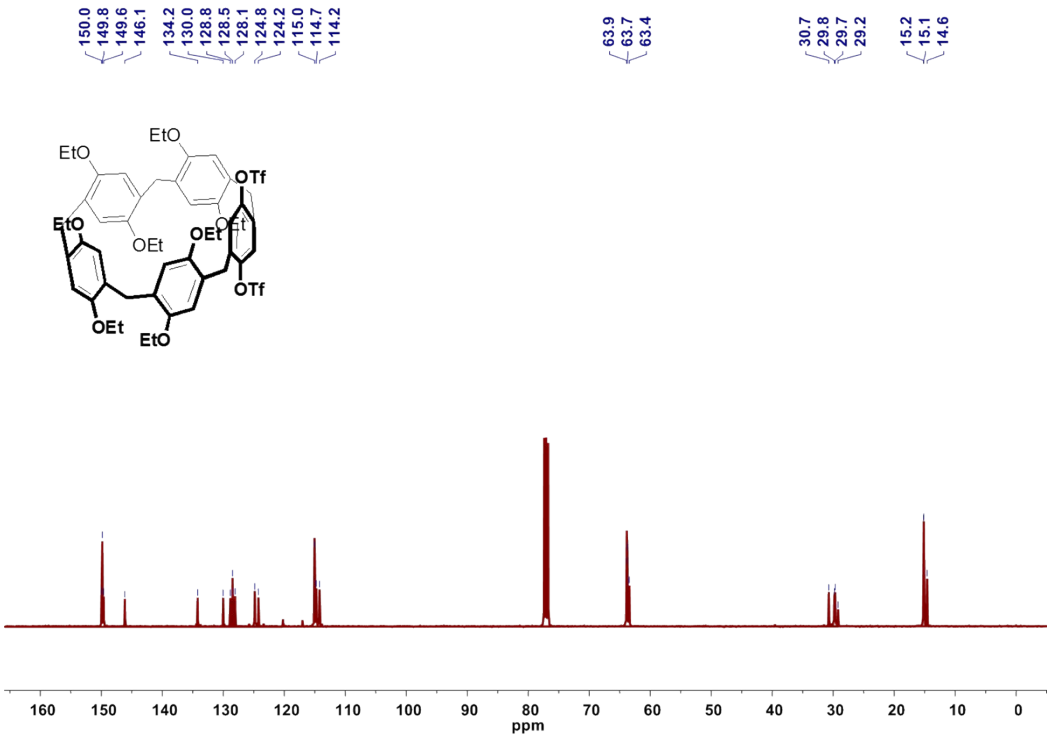


Fig. S2 ^{13}C NMR spectrum (126 MHz) of **6** in $CDCl_3$.

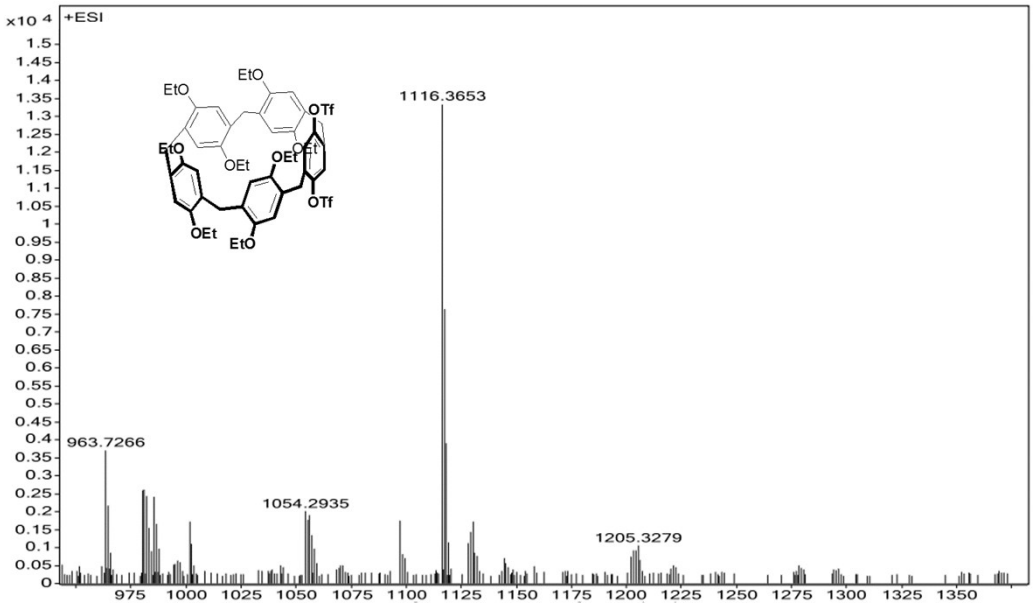


Fig. S3 HRMS (ESI) of **6**.HRMS (ESI): calcd for $[M+Na^+]$ $C_{53}H_{60}F_6O_{14}S_2Na^+$ 1116.3667, found 1116.3665.

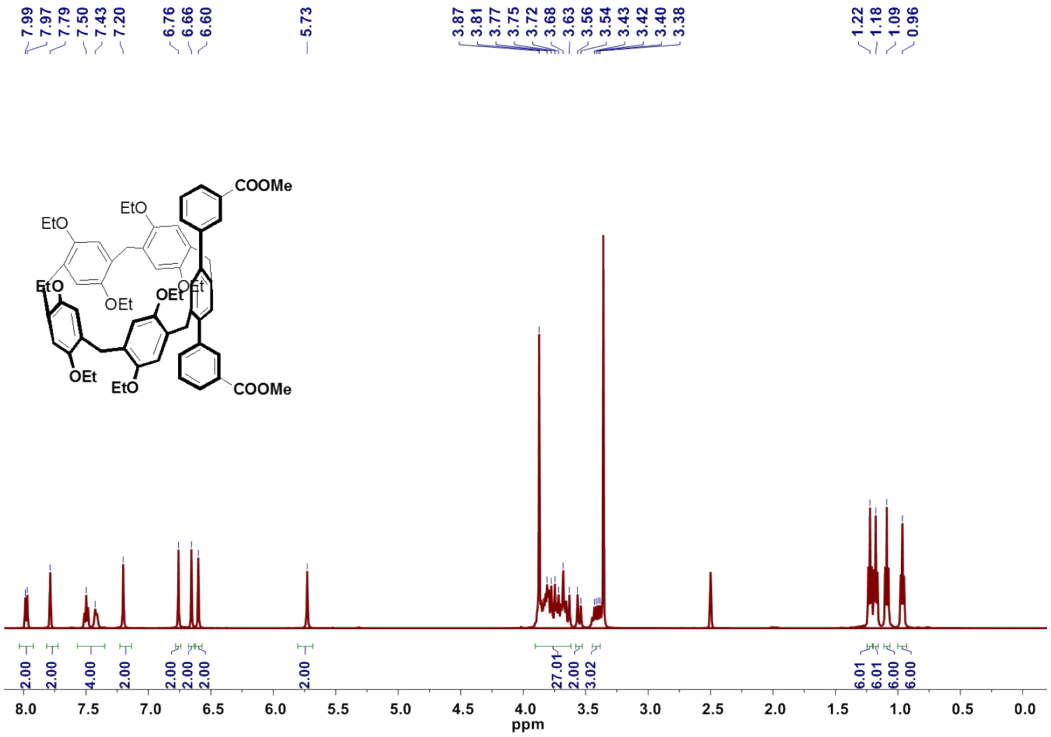


Fig. S4 ^{1}H NMR spectrum (500 MHz) of **7** in DMSO-d_6.

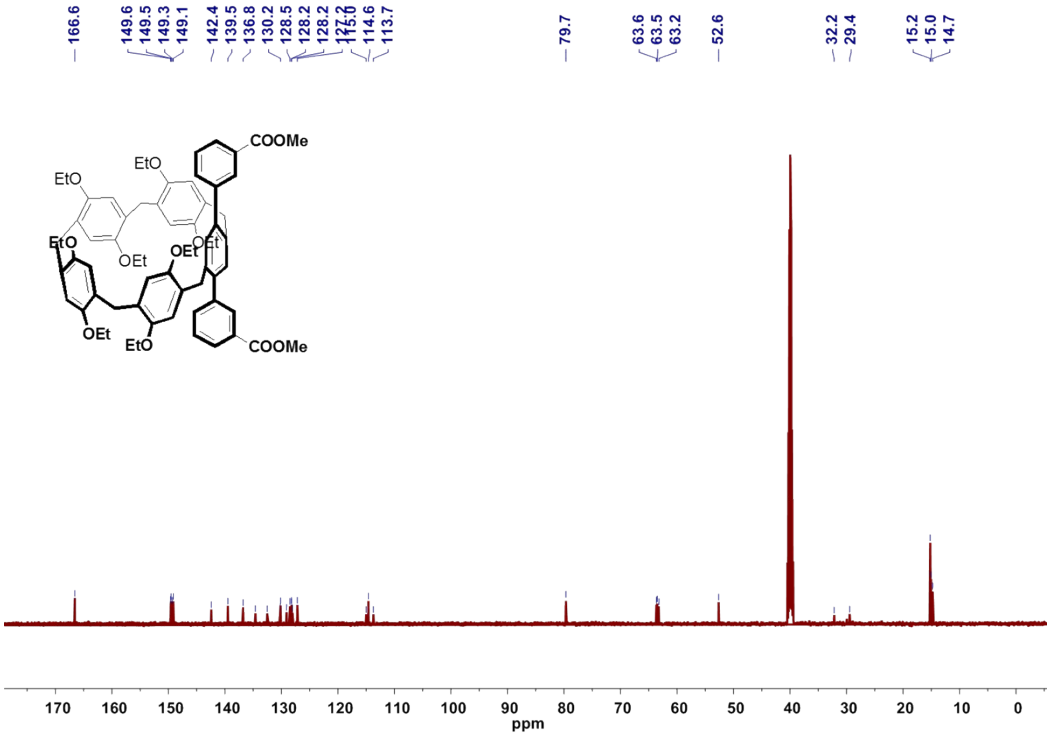


Fig. S5. ^{13}C NMR spectrum (126 MHz) of **7** in DMSO-d_6.

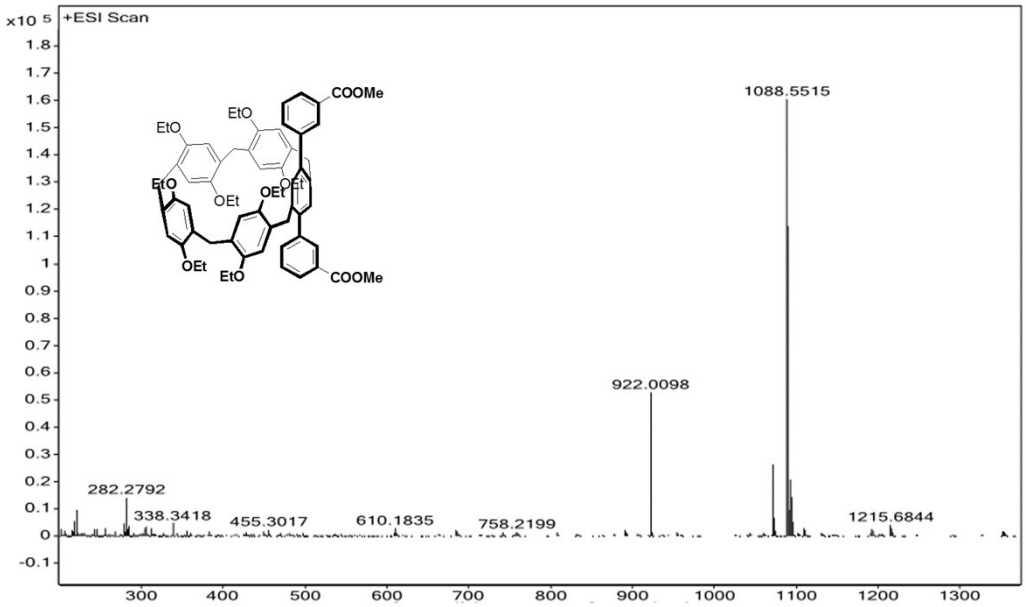


Fig. S6 HRMS (ESI) of **7**.HRMS (ESI): calcd for $[M+NH_4^+]$ $C_{65}H_{78}NO_{12}^+$ 1088.5519, found 1088.5515.

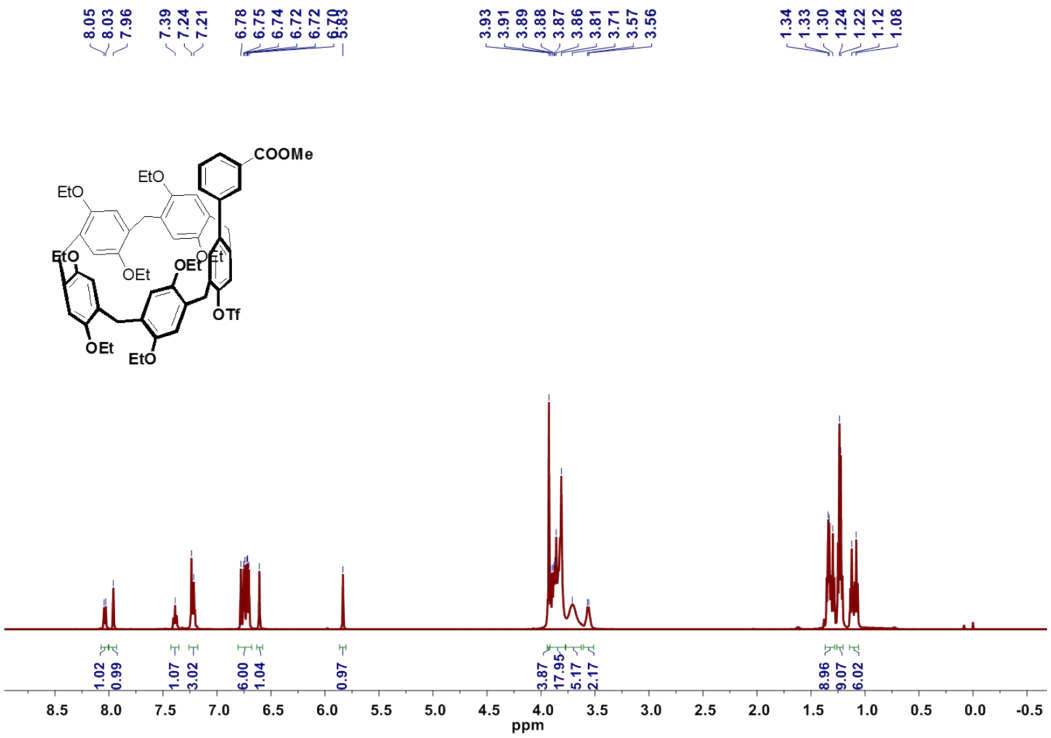


Fig. S7. ^{1}H NMR spectrum (500 MHz) of **8** in $CDCl_3$.

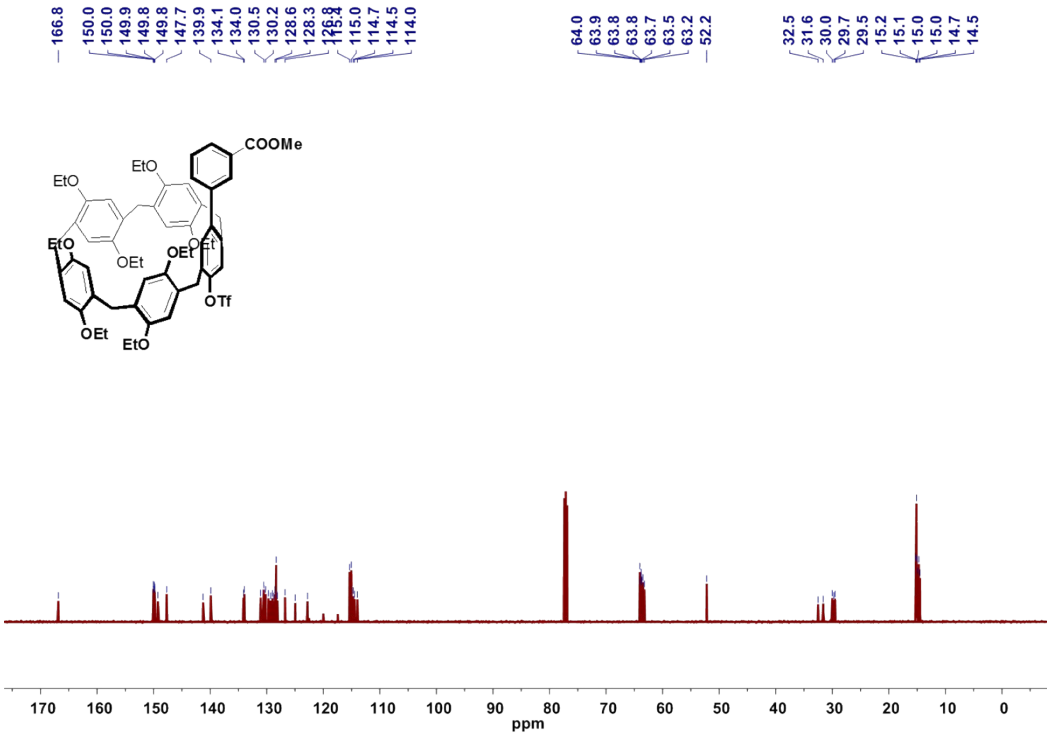


Fig. S8 ^{13}C NMR spectrum (126 MHz) of **8** in $CDCl_3$.

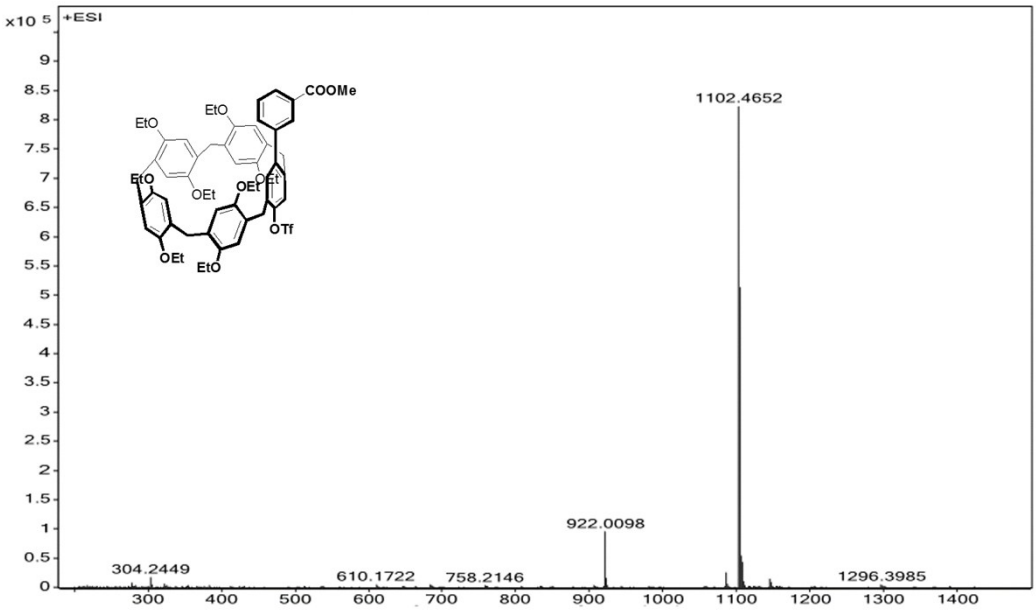


Fig. S9 HRMS (ESI) of **8**.HRMS (ESI): calcd for $[M+NH_4^+]$ $C_{60}H_{71}F_3NO_{13}S$ 1102.4593, found 1102.4652.

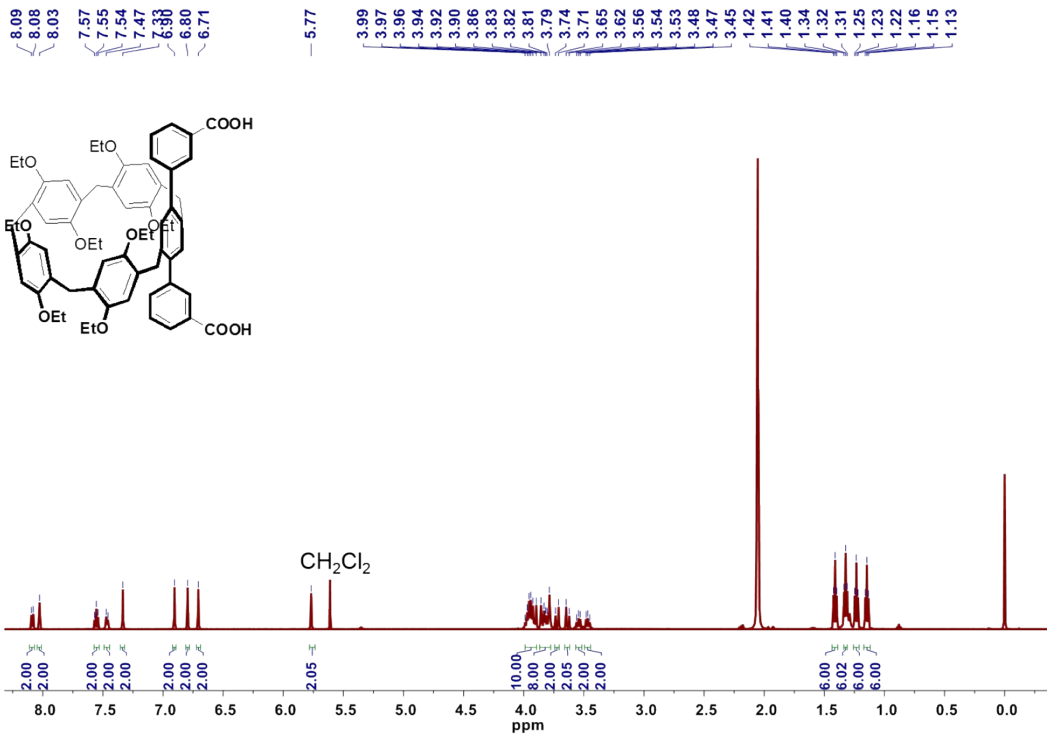


Fig. S10 ^{1}H NMR spectrum (500 MHz) of **1** in $(CD_3)_2O$.

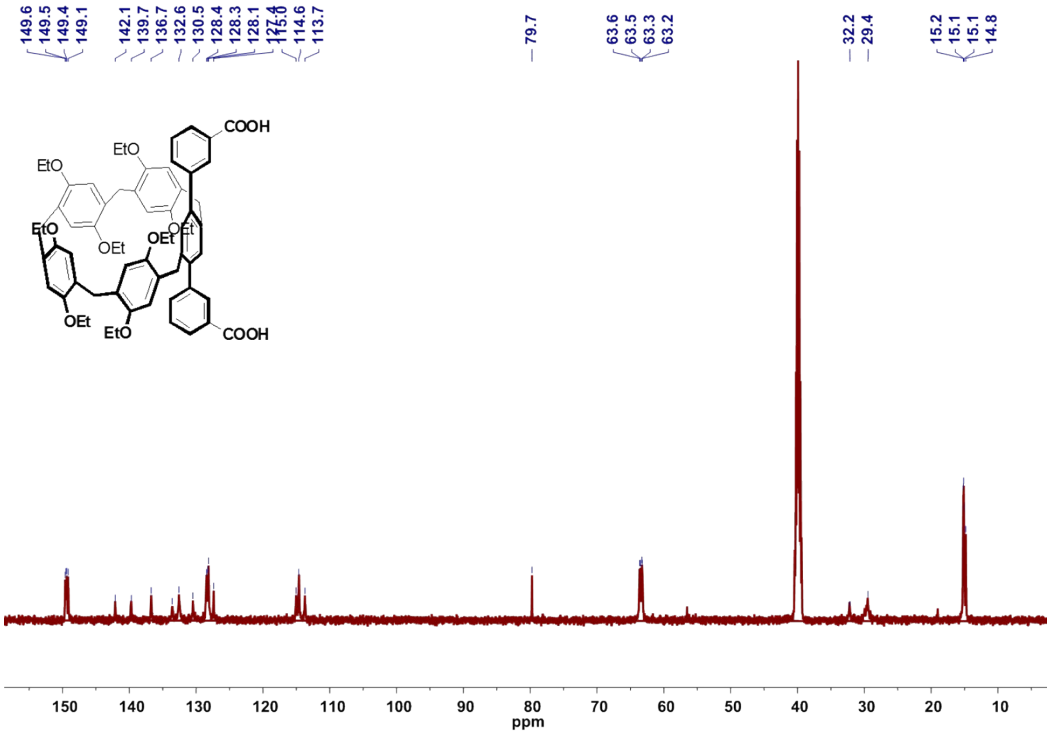


Fig. S11. ^{13}C NMR spectrum (126 MHz) of **1** in DMSO-d_6.

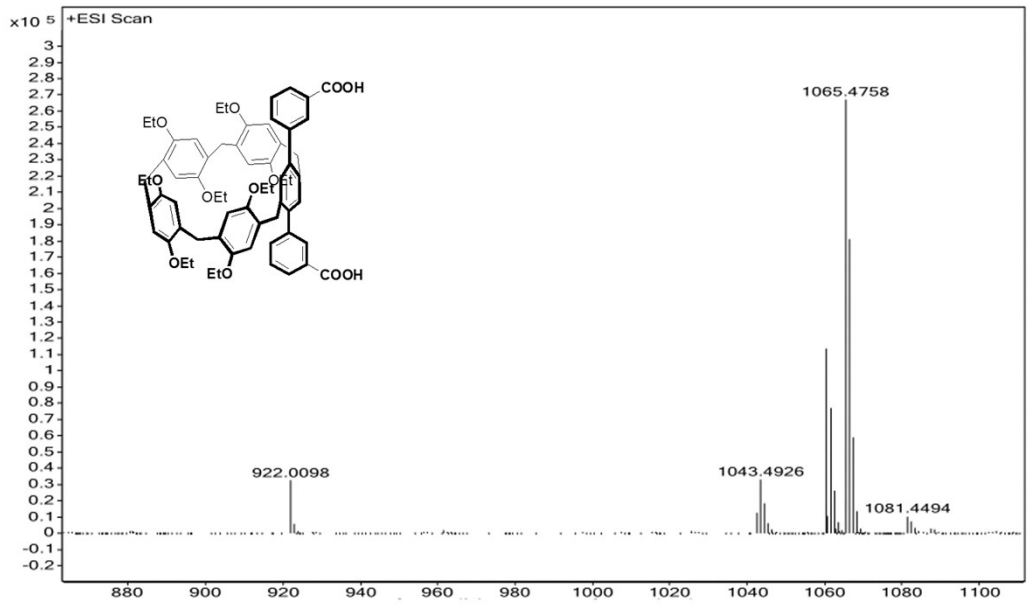


Fig. S12 HRMS (ESI) of **1**: calcd for $[M+Na^+]$ $C_{65}H_{70}O_{12}Na^+$ 1065.4759, found 1065.4758.

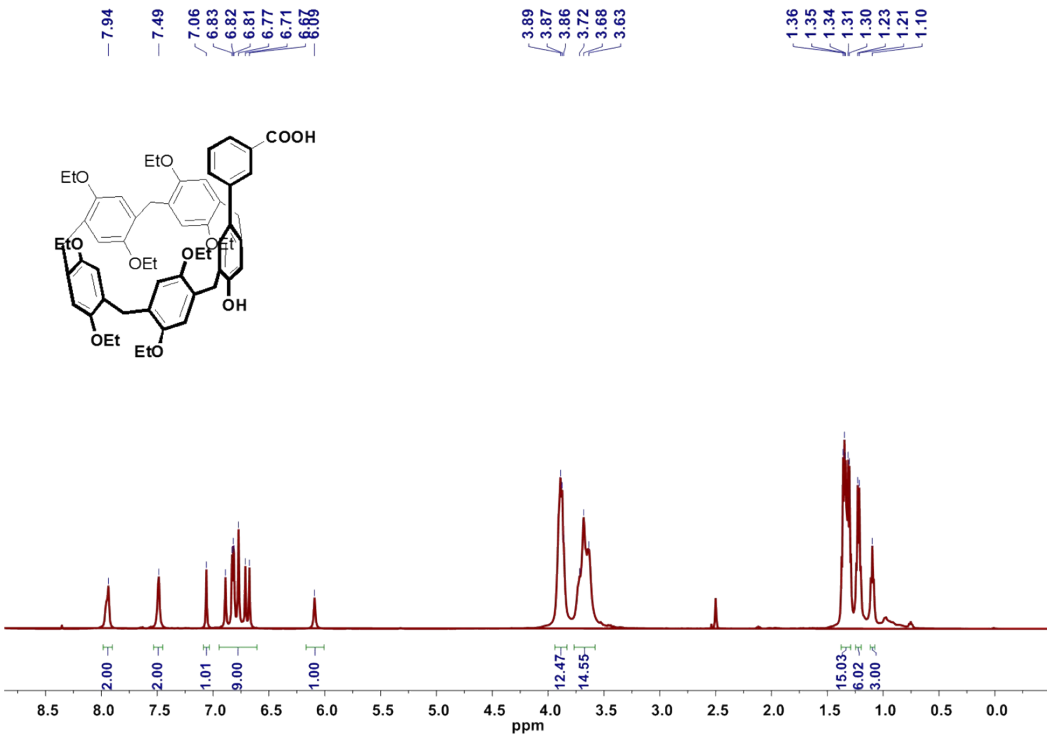


Fig. S13 [1]H NMR spectrum (500 MHz) of **2** in DMSO-d_6.

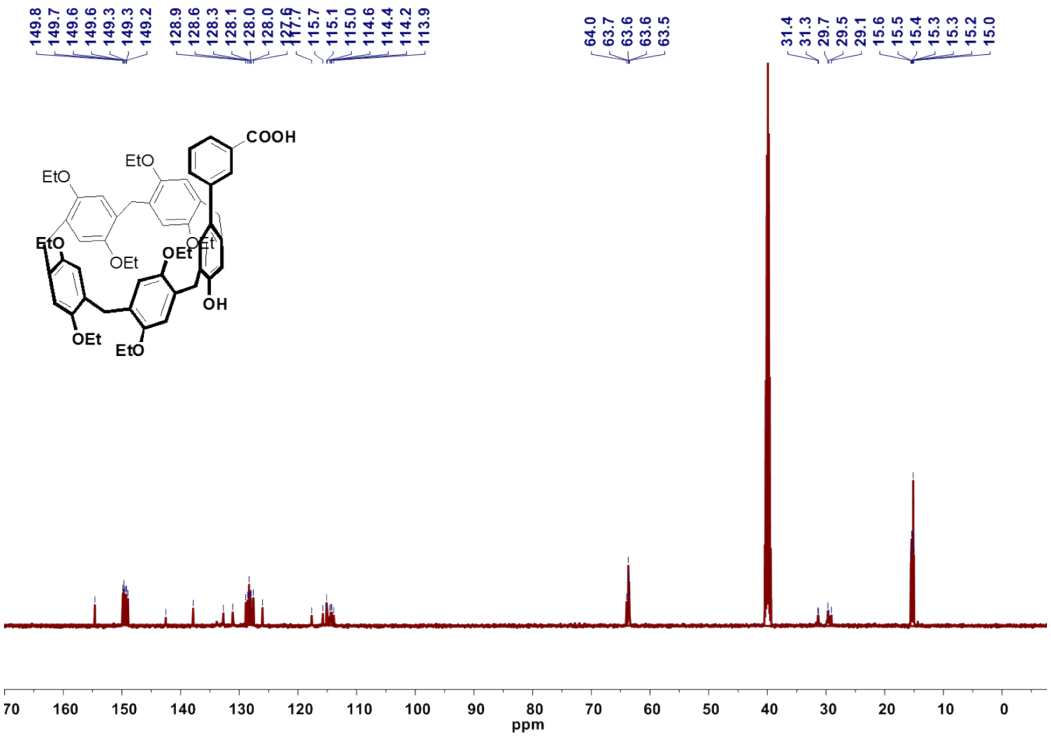


Fig. S14 [13]C NMR spectrum (126 MHz) of **2** in DMSO-d_6.

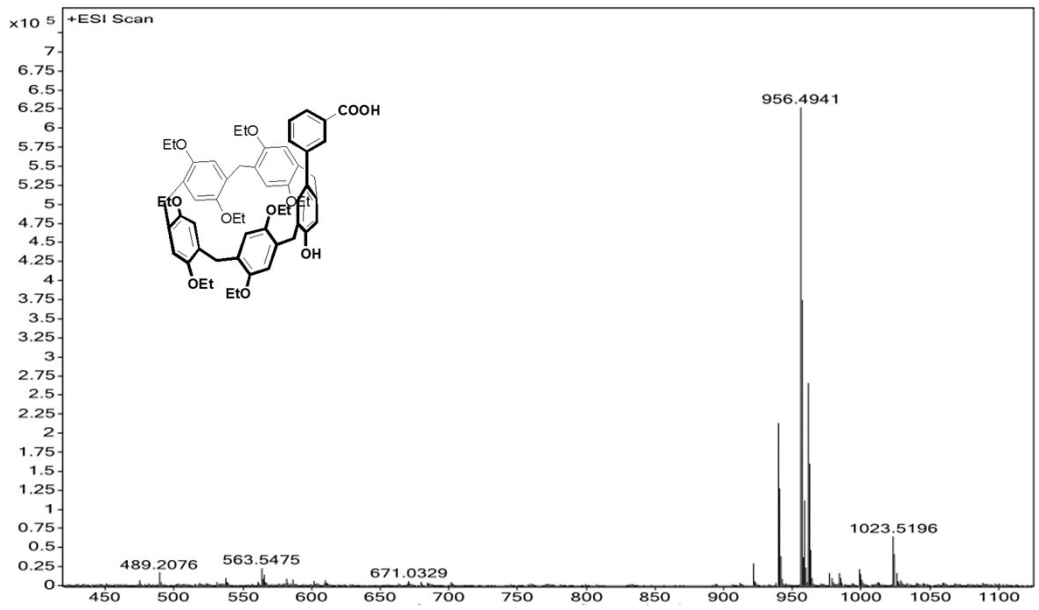


Fig. S15 HRMS (ESI) of **2**: calcd for $[M+NH_4^+]$ $C_{58}H70NO11^+$ 956.4943, found 956.4941.

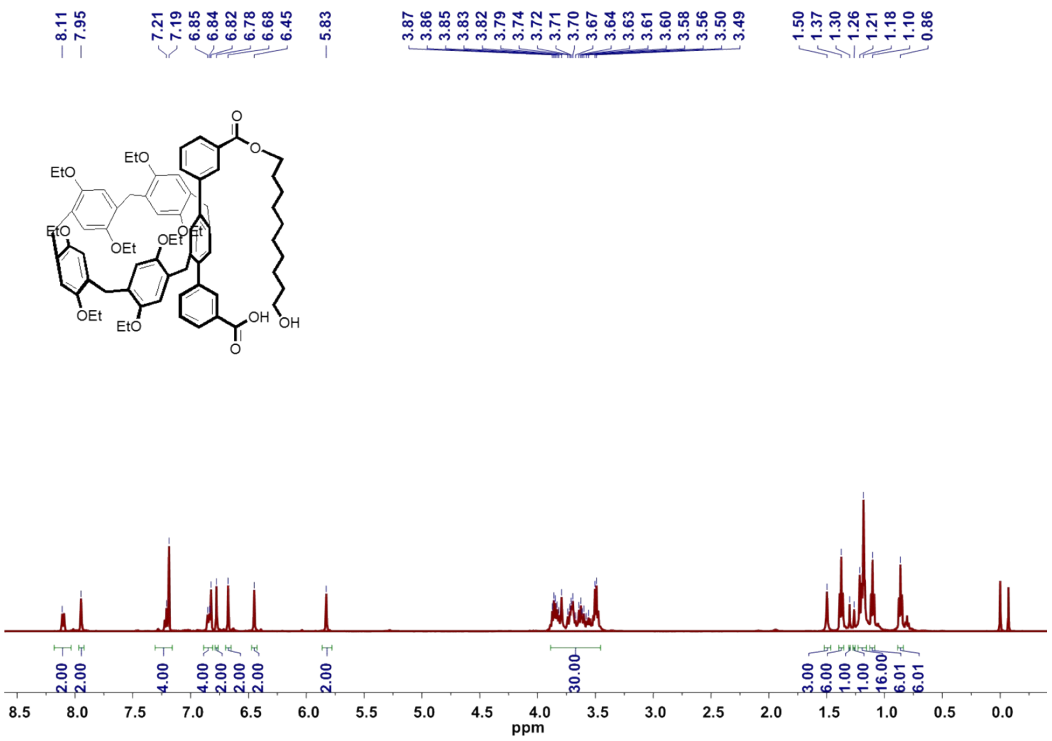


Fig. S16 ^{1}H NMR spectrum (500 MHz) of **10** in $CDCl_3$.

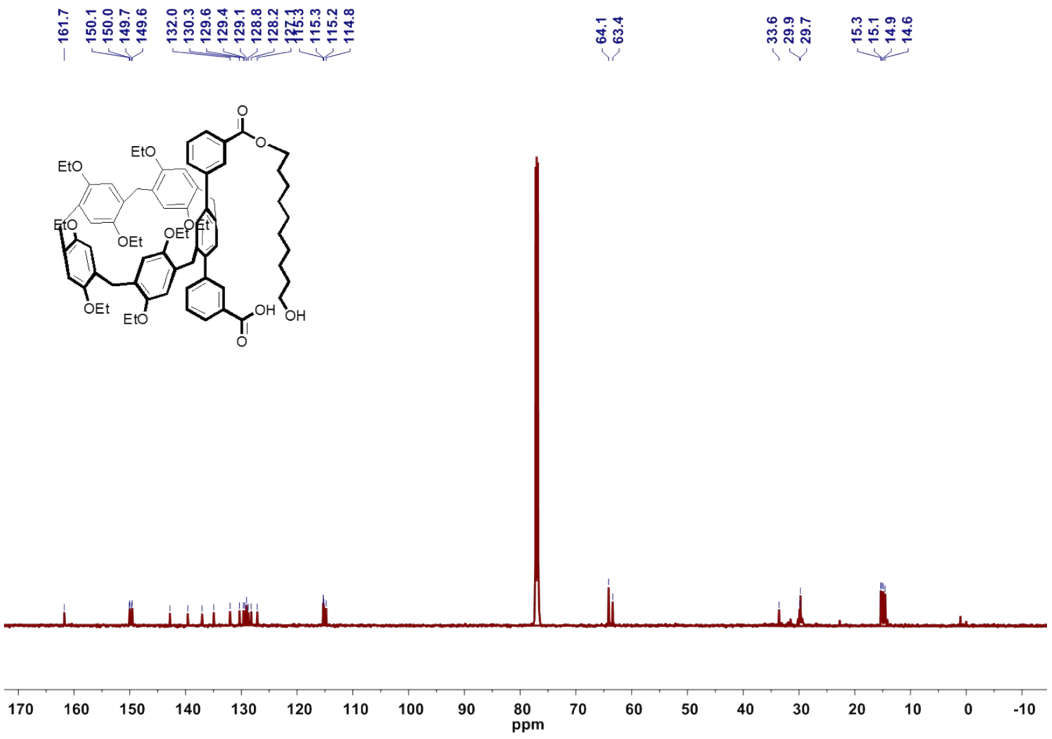


Fig. S17 ^{13}C NMR spectrum (126 MHz) of **10** in $CDCl_3$.

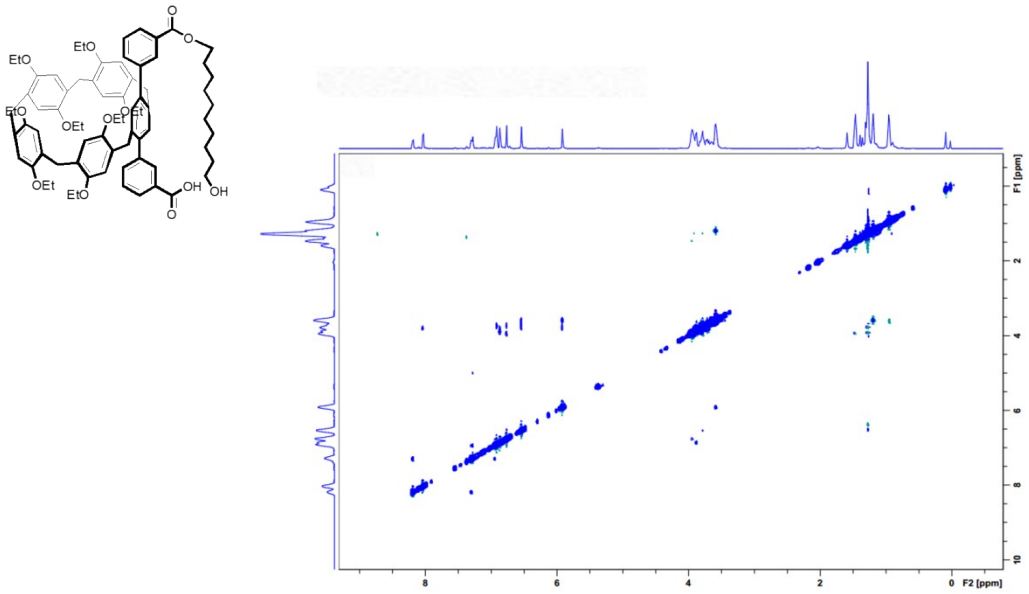


Fig. S18 Partial 2D NOESY spectrum of **10** in $CDCl_3$.

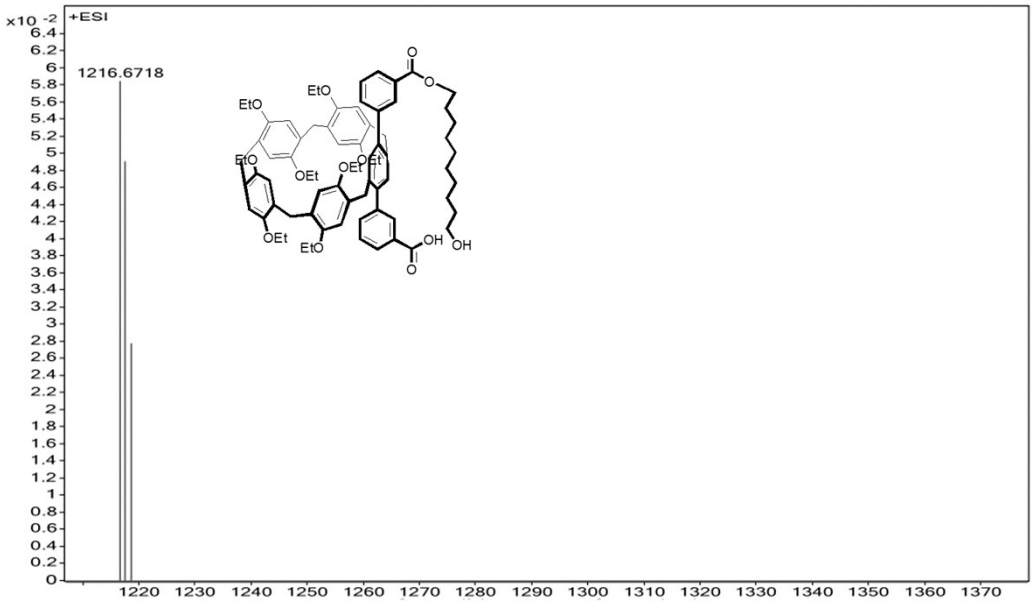


Fig. S19. HRMS (ESI) of **10**: calcd for $[M+NH_4^+]$ $C_{75}H_{94}NO_{13}^+$ 1216.6720, found 1216.6718.

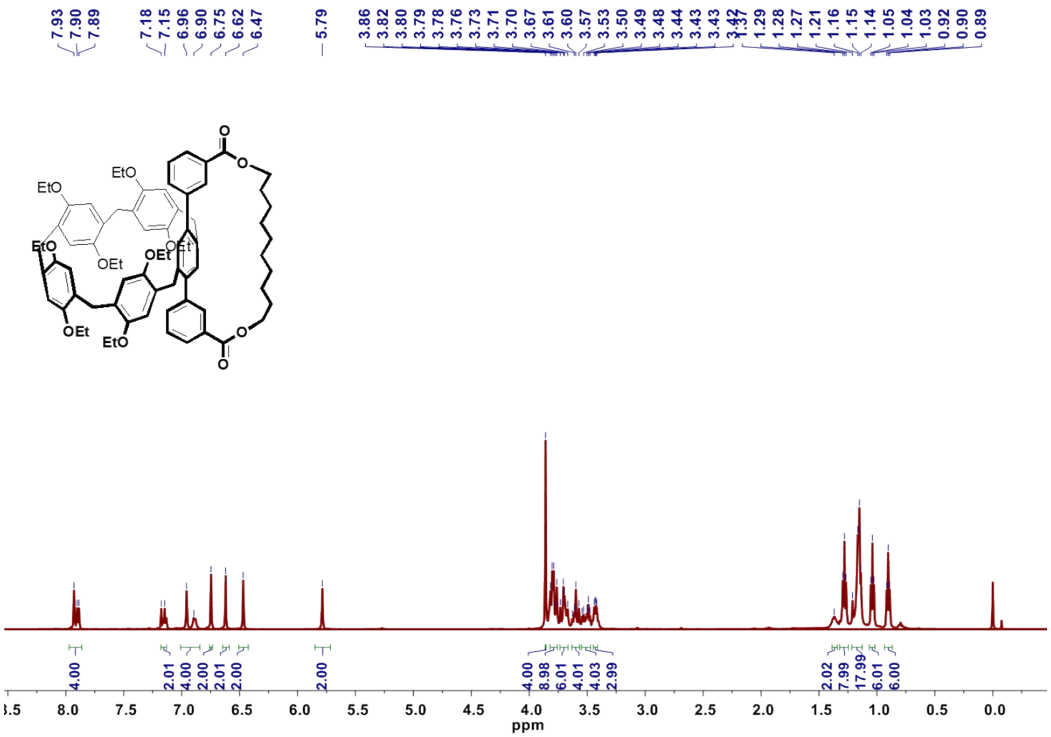


Fig. S20 ^{1}H NMR spectrum (500 MHz) of **11** in $CDCl_3$.

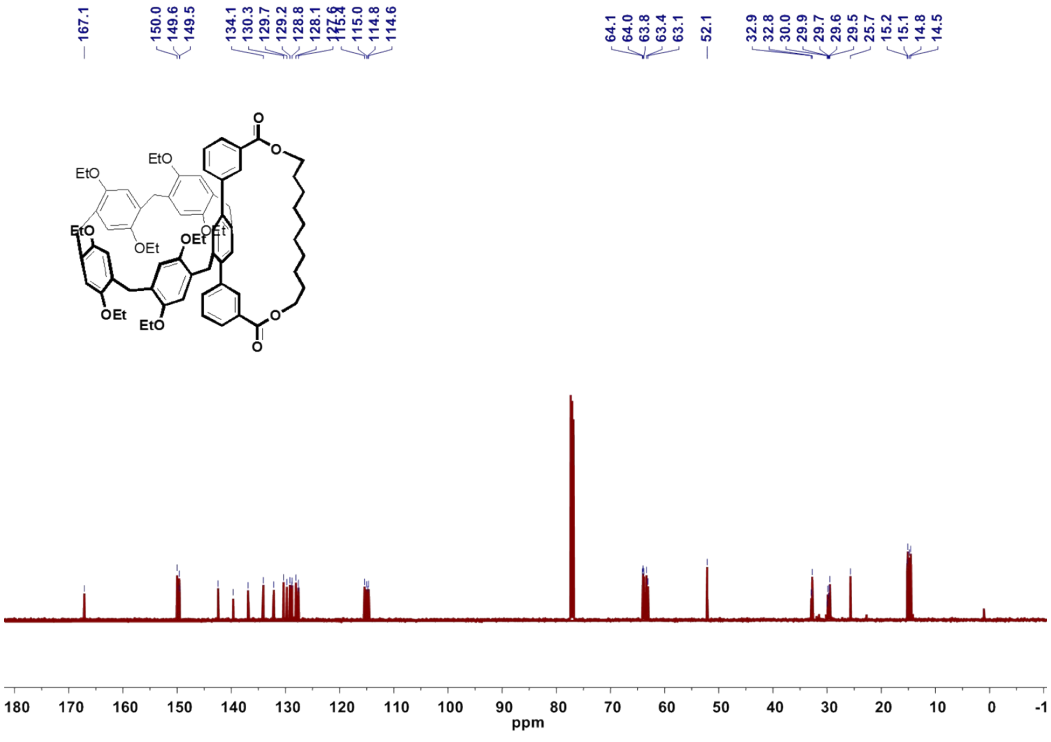


Fig. S21 ^{13}C NMR spectrum (126 MHz) of **11** in $CDCl_3$.

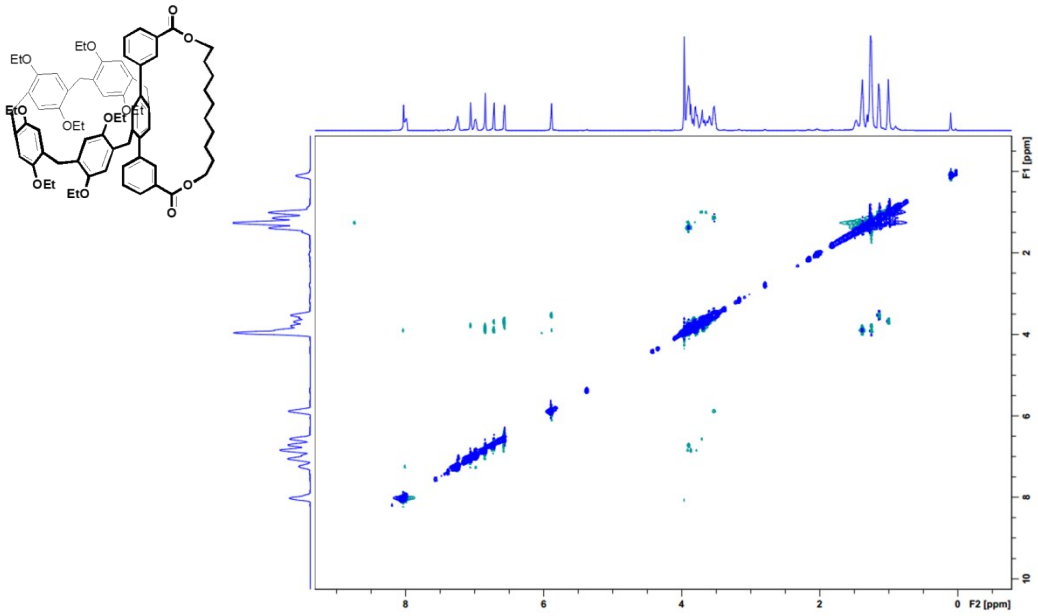


Fig.S22 Partial 2D NOESY spectrum of **11** in $CDCl_3$.

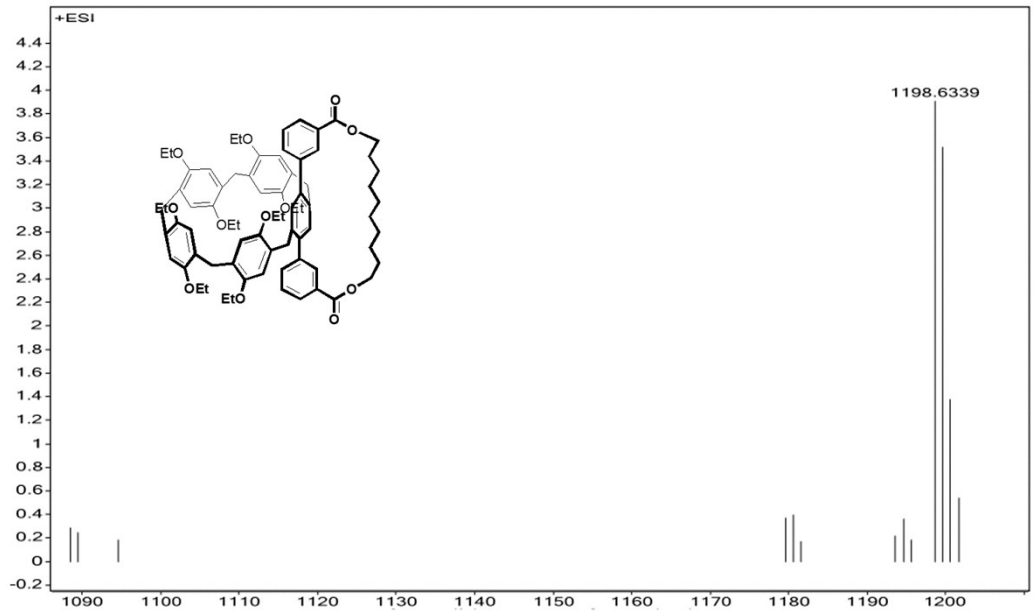


Fig. S23 HRMS (ESI) of **11**: calcd for $[M+NH_4^+]$ $C_{75}H_{92}NO_{12}^+$ 1198.6614, found 1198.6339.

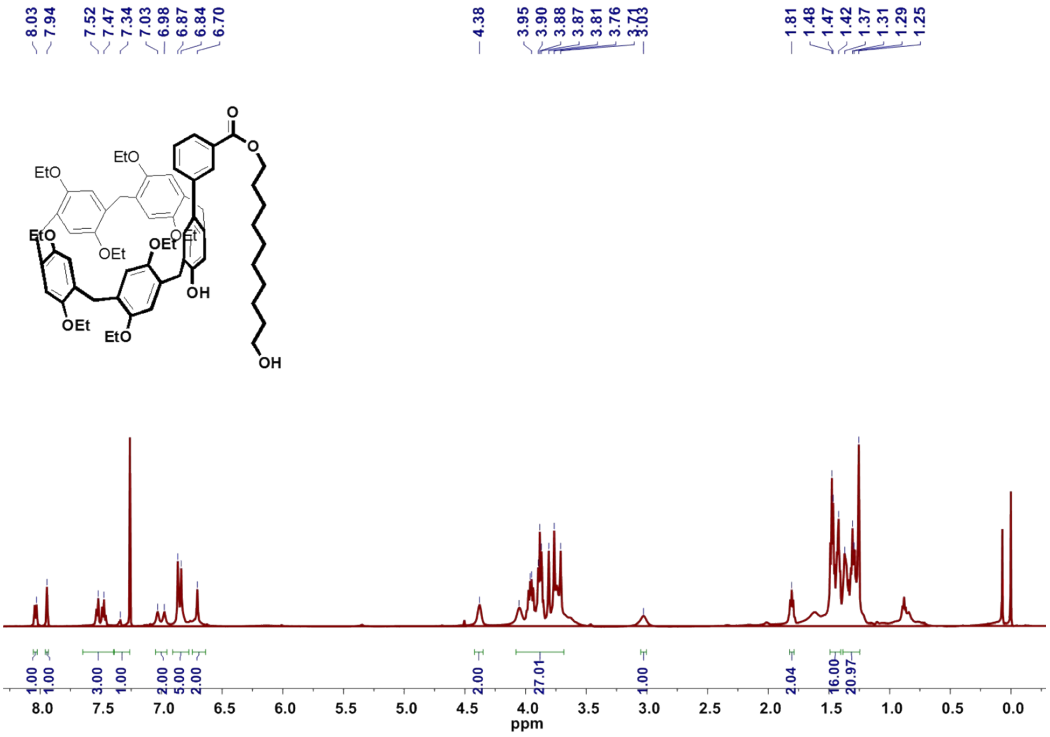


Fig. S24 ^{1}H NMR spectrum (500 MHz) of **12** in $CDCl_3$.

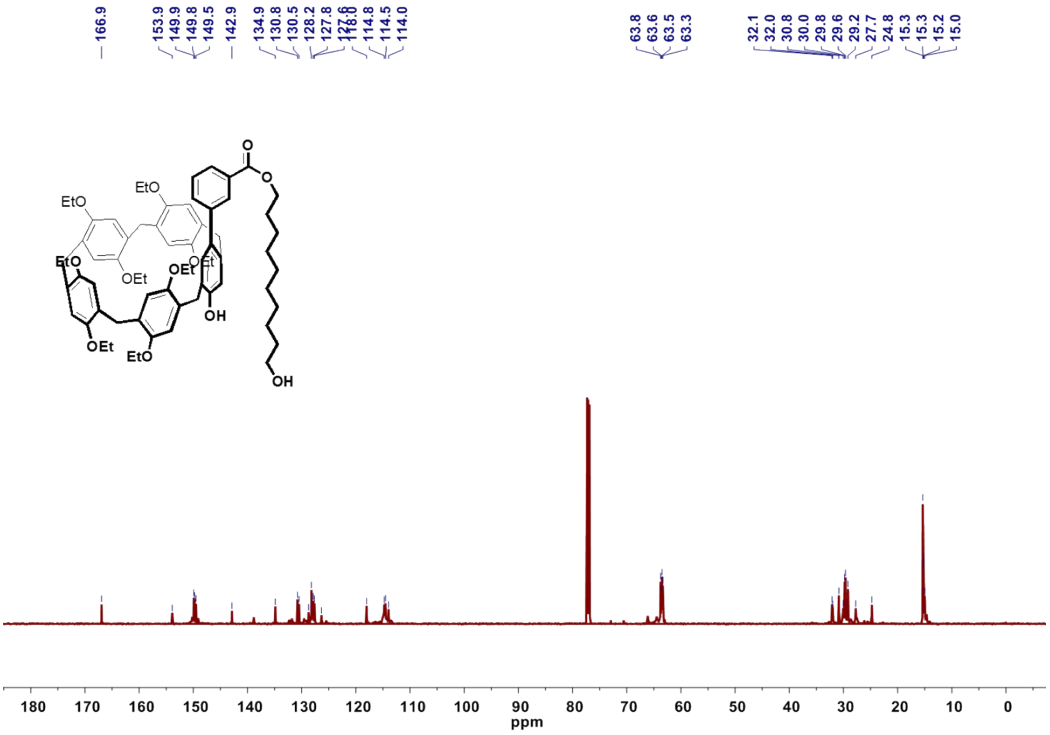


Fig. S25 ^{13}C NMR spectrum (126 MHz) of **12** in $CDCl_3$.

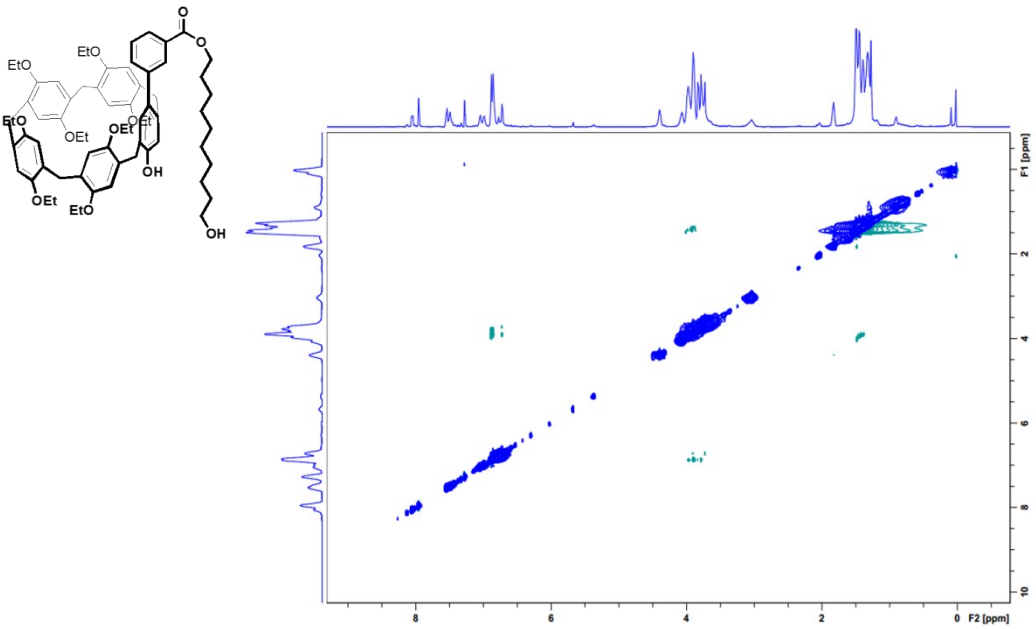


Fig. S26 Partial 2D NOESY spectrum of **12** in $CDCl_3$.

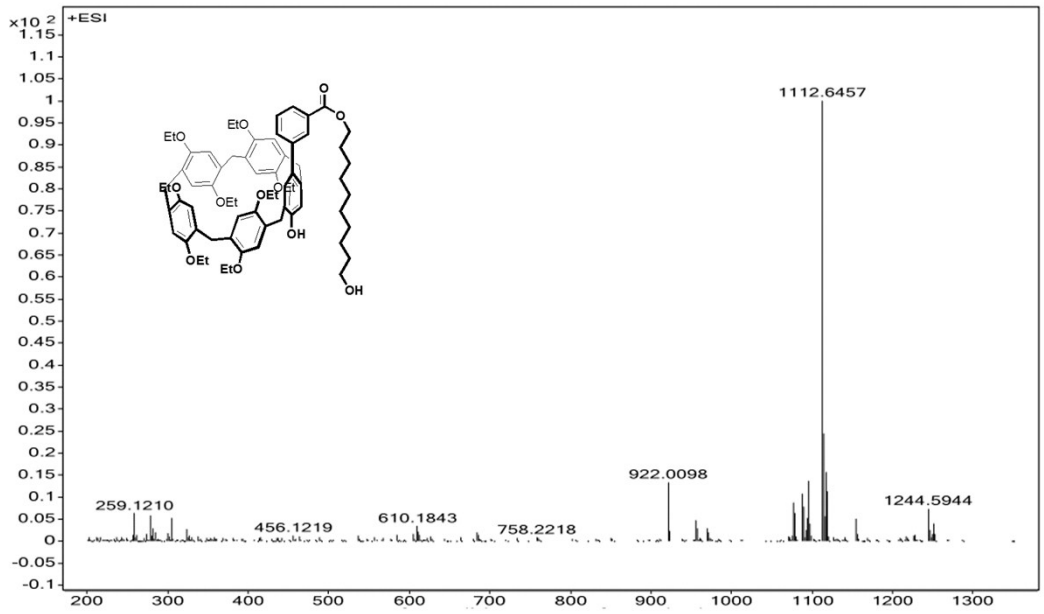


Fig.S27 HRMS (ESI) of **12**: calcd for $[M+NH_4^+]$ $C_{68}H_{90}NO_{12}$ 1112.6458, found 1112.6457.

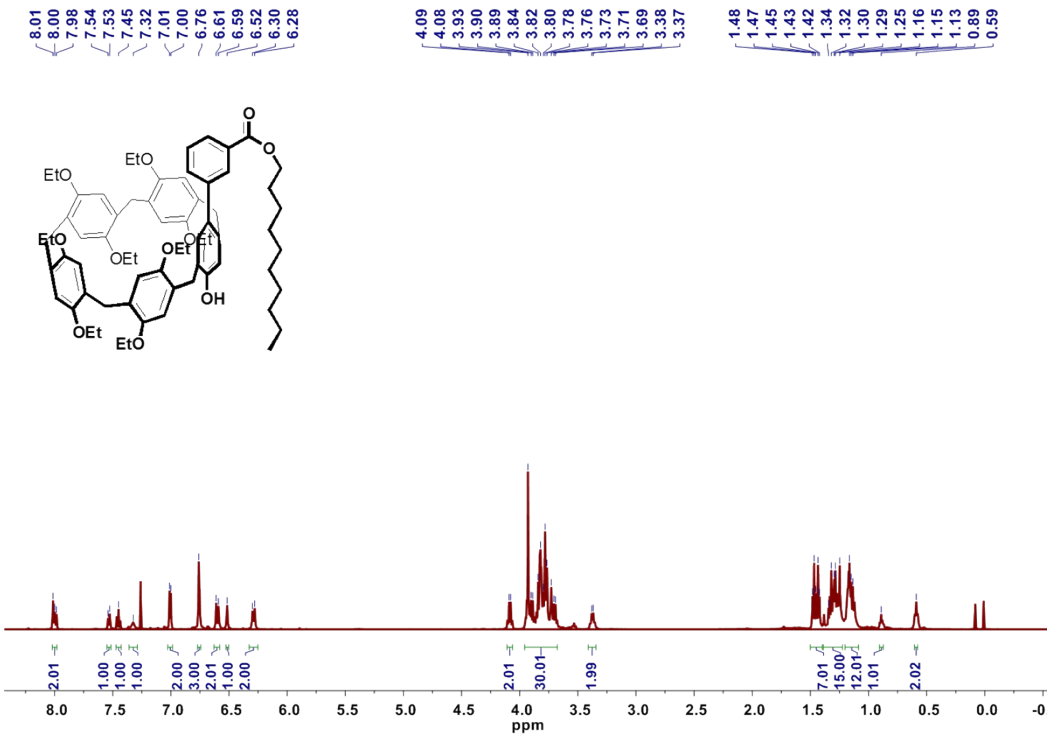


Fig. S28 ^{1}H NMR spectrum (500 MHz) of **13** in $CDCl_3$.

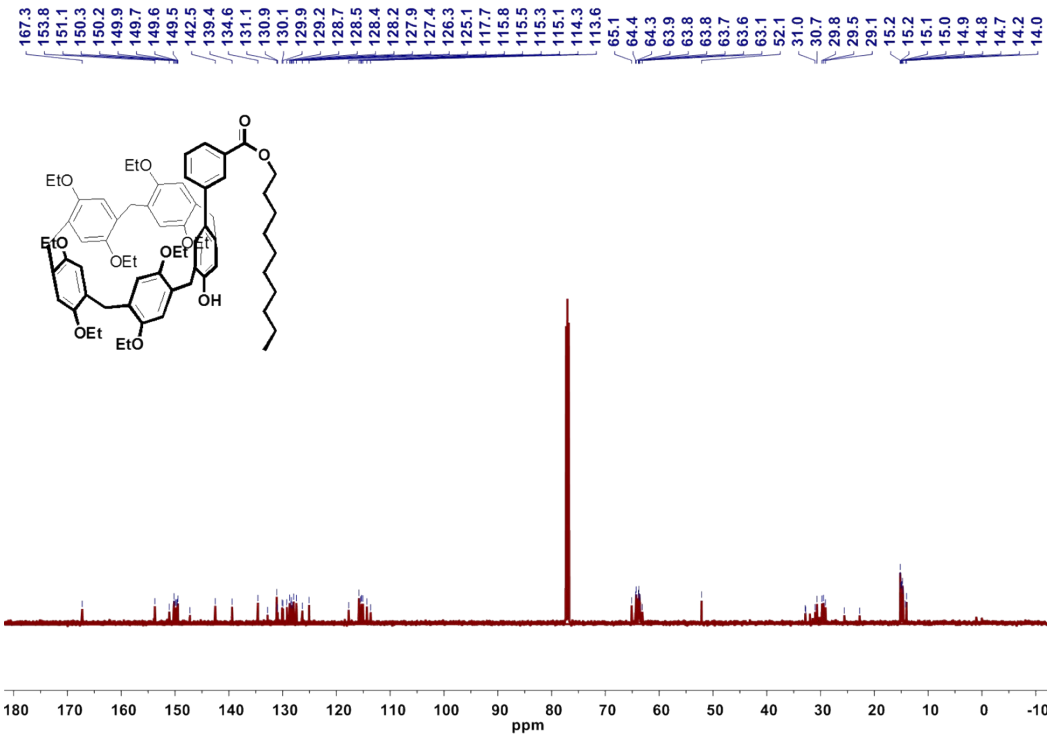


Fig. S29 ^{13}C NMR spectrum (126 MHz) of **13** in $CDCl_3$.

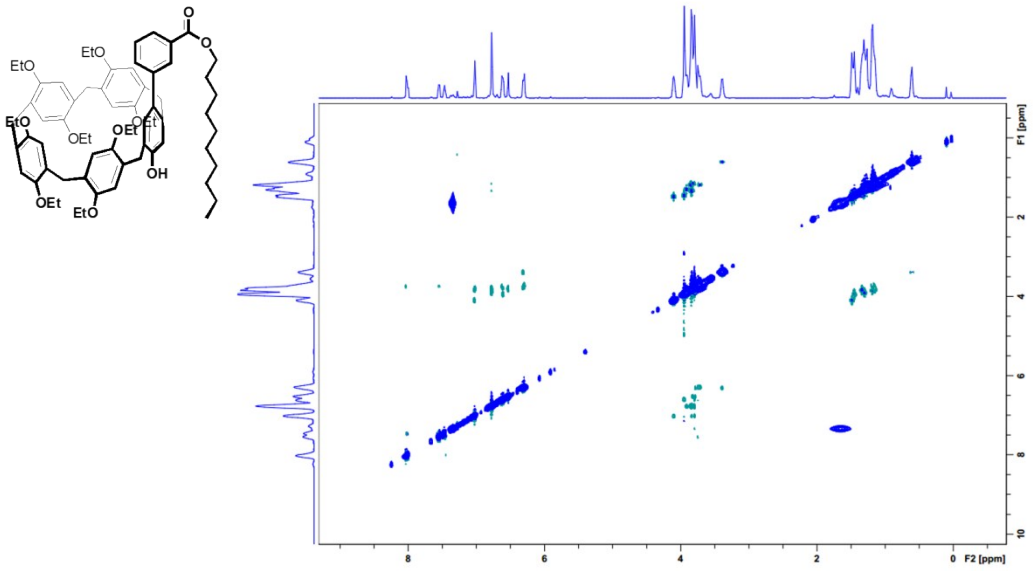


Fig.S30 Partial 2D NOESY spectrum of **13** in $CDCl_3$.

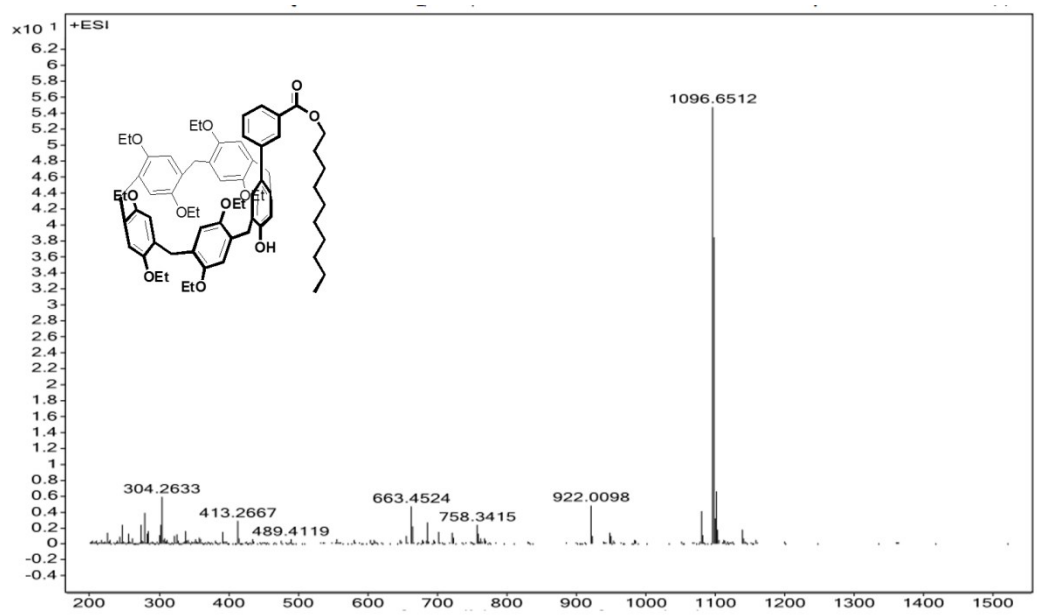


Fig.S31 HRMS (ESI) of **13**: calcd for $[M+NH_4^+]$ $C_{68}H_{90}NO_{11}^+$ 1096.6508, found 1096.6512.

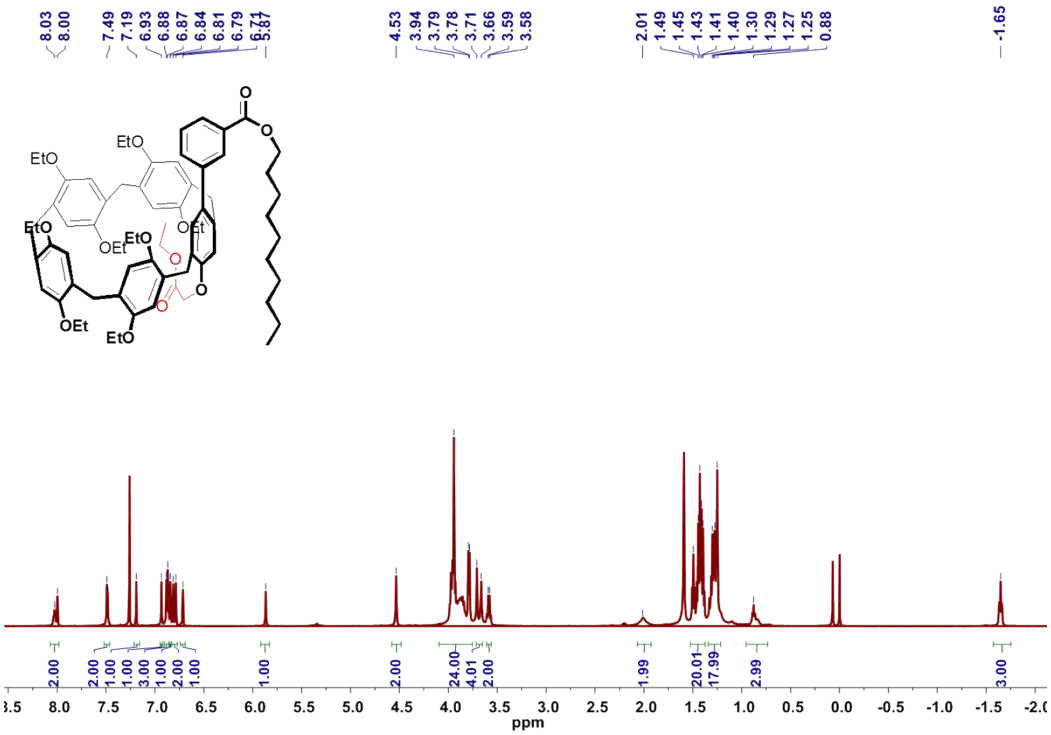


Fig.S32. ^{1}H NMR spectrum (500 MHz) of **14** in $CDCl_3$.

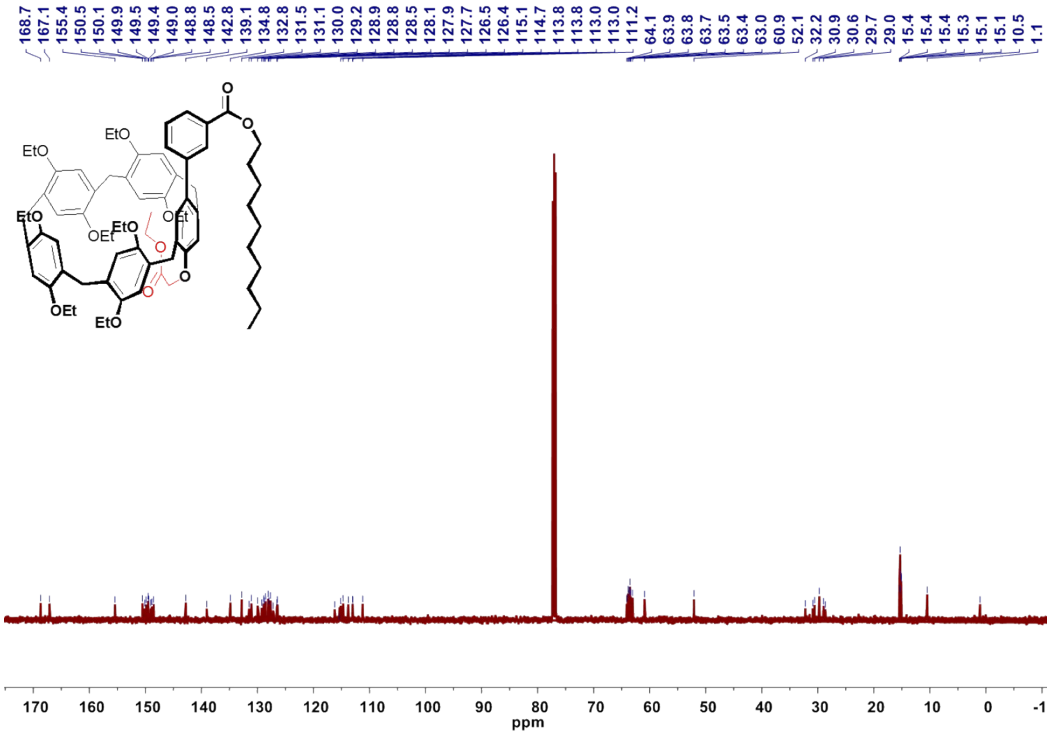


Fig. S33 ^{13}C NMR spectrum (126 MHz) of **14** in $CDCl_3$.

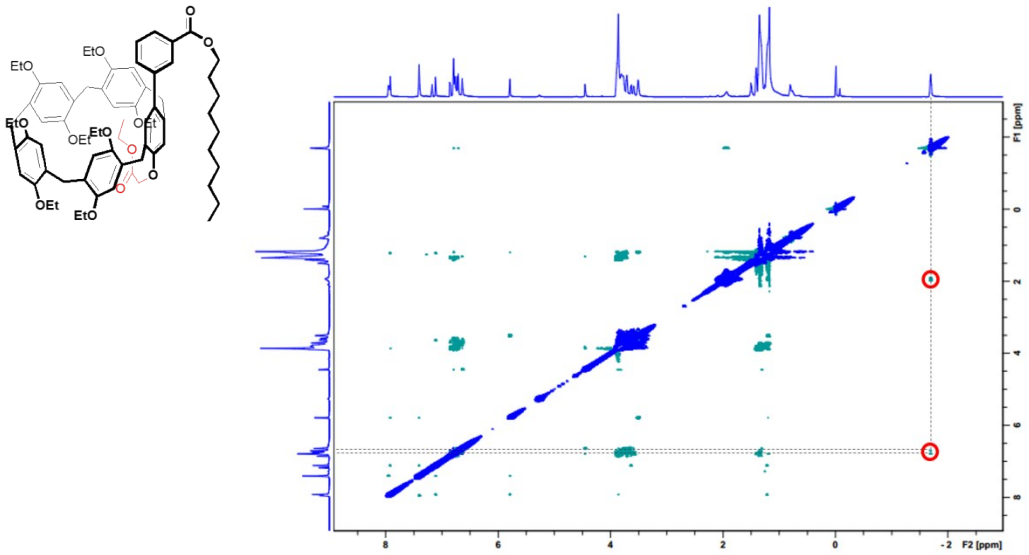


Fig. S34 Partial 2D NOESY spectrum of **14**.

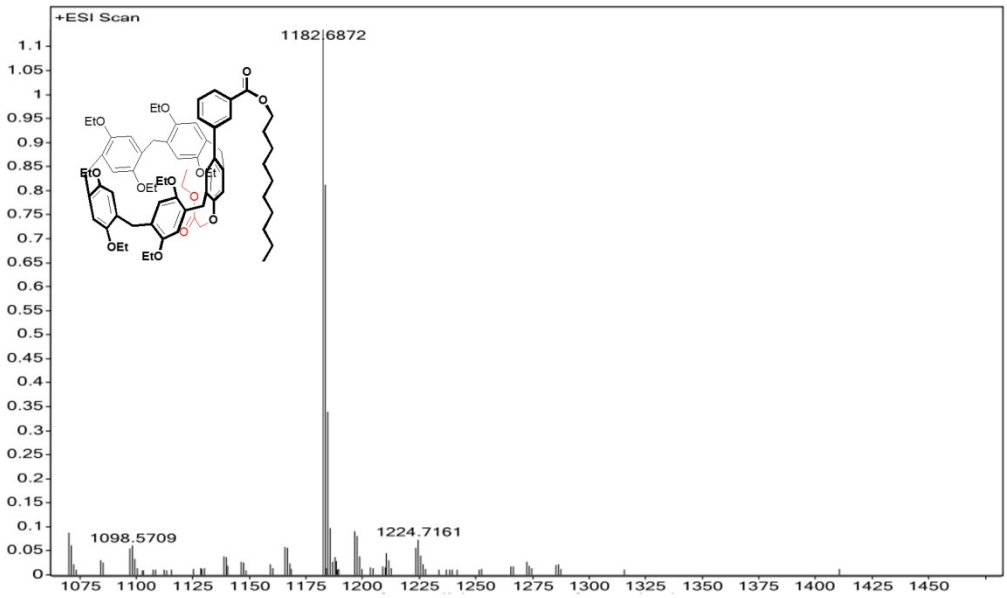


Fig. S35 HRMS (ESI) of **14**: calcd for $[M+NH_4^+]$ $C_{72}H_{96}NO_{13}^+$ 1182.6876, found 1182.6872.

References:

S1. H. Tao, D. Cao, L. Liu, Y. Kou, L. Wang and H. Meier, *Sci.China, Ser. B Chem*., 2012, **55**, 223-228.
S2. C. Xie, W. Hu, W. Hu, Y. A. Liu, J. Huo, J. Li, B. Jiang and K. Wen, *Chin. J. Chem.,* 2015, **33**, 379-383.
S3. W.-B. Hu, W.-J. Hu, X.-L. Zhao, Y. A. Liu, J.-S. Li, B. Jiang and K. Wen, *J. Org. Chem.,* 2016, **81**, 3877-3881.