Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Enriching calixarene functionality with 1,3-diketone groups

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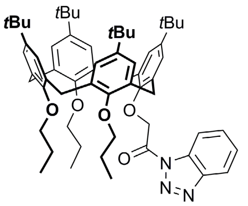
Supplementary Information

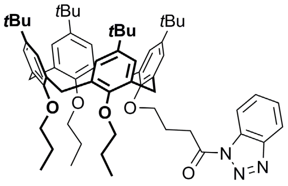
Contents

Synthesis and characterization of novel compounds

General experimental methods: ^{1}H and ^{13}C NMR spectra were acquired on Bruker Avance 400 and Avance 600 instruments at 20 ºC and chemical shifts are reported as ppm referenced to solvent signals. ESI mass spectra were obtained from Sciex TripleTOF 5600+ and Thermo Scientific LTQ Orbitrap spectrometers. Chemicals received from commercial sources were used without further purification. Compounds **1**,[S1] **2**,[S2] **3**,[S3] **4**,[S4] **9**,[S5] **11**,[S6] **15**,[S5] **19**,[S7] **26**,[S8] **27**,[S9] **46**[S10] and **47**[S11] were prepared according to the published procedures, the procedure for the preparation of known calixarene **20**[S12] was improved.

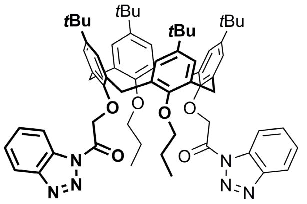


Calixarene 1-acylbenzotriazole **5**. A solution of acid **1** (0.252 g, 0.303 mmol), 1,2,3-benzotriazole (0.216 g, 1.82 mmol) and N,N'-diisopropylcarbodiimide (DIC, 0.281 mL, 1.82 mmol) in dry dichloromethane (3 mL) was stirred at room temperature for 24 h. Aqueous HCl (2 M) was added at vigorous stirring, the organic layer was separated, the aqueous layer was washed with dichloromethane. The combined organic phase was washed with water, and the solvent was evaporated under reduced pressure. Methanol was added to the residue and the mixture was cooled to –18 °C. The solid formed was filtered, washed with cold methanol and dried. Yield 0.207 g (73%), white solid. M.p. 213–215 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39–8.35 (m, 1H; ArH_{Bt}), 8.17–8.14 (m, 1H; ArH_{Bt}), 7.70–7.64 (m, 1H; ArH_{Bt}), 7.56–7.50 (m, 1H; ArH_{Bt}), 7.03 (s, 2H; ArH), 6.99 (s, 2H; ArH), 6.60 (d, 2H, ^{4}J = 2.4 Hz; ArH), 6.58 (d, 2H, ^{4}J = 2.4 Hz; ArH), 6.11 (s, 2H; CH_2CO), 4.87 (d, 2H, ^{2}J = 12.9 Hz; $ArCH_2Ar$), 4.41 (d, 2H, ^{2}J = 12.5 Hz; $ArCH_2Ar$), 3.86–3.66 (m, 2H; OCH_2), 3.28 (d, 2H, ^{2}J = 12.9 Hz; $ArCH_2Ar$), 3.12 (d, 2H, ^{2}J = 12.5 Hz; $ArCH_2Ar$), 2.12–2.00 (m, 2H; $OCH_2C\underline{H}_2$), 1.99–1.86 (m, 4H; $OCH_2C\underline{H}_2$), 1.24 (s, 9H; $C(CH_3)_3$), 1.23 (s, 9H; $C(CH_3)_3$), 0.94 (t, 6H, ^{3}J = 7.4 Hz; CH_3), 0.93 (s, 18H; $C(CH_3)_3$), 0.69 (t, 3H, ^{3}J = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.66 (C=O), 154.17, 153.45, 153.19, 145.81, 145.27, 144.65, 144.18, 135.06, 134.48, 132.74, 132.33, 131.11 (C_{Ar}), 130.31, 126.07, 125.85, 125.23, 124.76, 124.60, 120.14, 114.21 (CH_{Ar}), 77.45, 76.77, 71.69 (OCH_2), 33.98, 33.95, 33.66 ($\underline{C}(CH_3)_3$), 31.88 ($ArCH_2Ar$), 31.63, 31.56, 31.27 ($C(\underline{C}H_3)_3$), 30.96 ($ArCH_2Ar$), 23.32, 23.30 ($OCH_2\underline{C}H_2$), 10.51, 9.73 (CH_3) ppm. ESI-MS *m*/*z*: 951.6360 $[M+NH_4]^+$ for $C_{61}H_{83}N_4O_5$ (951.6358).

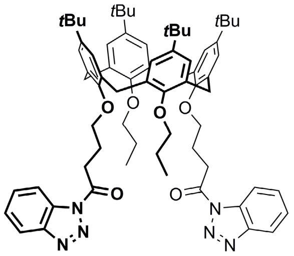


Calixarene 1-acylbenzotriazole **6** was prepared as described for compound **5** from acid **2** (0.688 g, 0.80 mmol), 1,2,3-benzotriazole (0.190 g, 1.60 mmol) and DIC (0.247 mL, 1.60 mmol) in dry dichloromethane (40 mL). Yield 0.637 g (83%), white solid. M.p. 122–

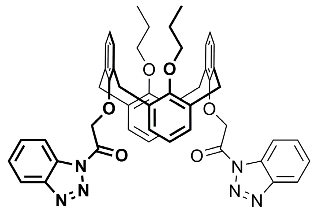
124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36–8.32 (m, 1H; ArH_{Bt}), 8.16–8.12 (m, 1H; ArH_{Bt}), 7.70–7.64 (m, 1H; ArH_{Bt}), 7.55–7.49 (m, 1H; ArH_{Bt}), 6.87 (s, 2H; ArH), 6.86 (s, 2H; ArH), 6.68 (d, 2H, ^4J = 2.4 Hz; ArH), 6.67 (d, 2H, ^4J = 2.4 Hz; ArH), 4.41 (d, 4H, ^2J = 12.4 Hz; $ArCH_2Ar$), 4.12–4.06 (m, 2H; OCH_2), 3.90–3.83 (m, 2H; OCH_2), 3.81–3.72 (m, 4H; OCH_2), 3.64–3.58 (m, 2H; CH_2CO), 3.14 (d, 2H, ^2J = 12.4 Hz; $ArCH_2Ar$), 3.10 (d, 2H, ^2J = 12.4 Hz; $ArCH_2Ar$), 2.70–2.63 (m, 2H; $OCH_2C\underline{H}_2CH_2$), 2.06–1.88 (m, 6H; $OCH_2C\underline{H}_2CH_3$), 1.15 (s, 9H; $C(CH_3)_3$), 1.14 (s, 9H; $C(CH_3)_3$), 0.99 (s, 18H; $C(CH_3)_3$), 0.93 (t, 6H, ^3J = 7.5 Hz; CH_3), 0.92 (m, 3H, ^3J = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.24 (C=O), 153.93, 153.59, 153.29, 146.24, 144.72, 144.26, 144.11, 134.35, 134.32, 133.30, 133.13, 131.17 (C_{Ar}), 130.33, 126.07, 125.17, 125.00, 124.83, 124.69, 120.15, 114.47 (CH_{Ar}), 77.16, 76.85, 73.73 (OCH_2), 33.89, 33.86, 33.72 ($\underline{C}(CH_3)_3$), 32.52 ($\underline{C}H_2CO$), 31.55, 31.52, 31.37 ($C(\underline{C}H_3)_3$), 31.14, 31.06 ($ArCH_2Ar$), 25.04 ($OCH_2\underline{C}H_2CH_2$), 23.37, 23.22 ($OCH_2\underline{C}H_2$), 10.33, 10.16 ($CH_3$) ppm. ESI-MS *m*/*z*: 1000.5963 $[M+K]^+$ for $C_{63}H_{83}KN_3O_5$ (1000.5964).



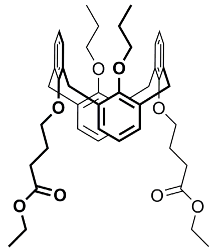
Calixarene bis(1-acylbenzotriazole) **7** was prepared as described for compound **5** from bis(acid) **3** (2.54 g, 3.00 mmol), 1,2,3-benzotriazole (4.28 g, 36.0 mmol) and DIC (5.57 mL, 36.0 mmol) in dry dichloromethane (30 mL). The product was additionally purified by crystallization from dichloromethane/hexane. Yield 2.17 g (69%), white solid. M.p. 233–235 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.14 (m, 2H; ArH_{Bt}), 7.92–7.89 (m , 2H; ArH_{Bt}), 7.58–7.53 (m, 2H; ArH_{Bt}), 7.48–7.43 (m, 2H; ArH_{Bt}), 7.11 (s, 4H; ArH), 6.55 (s, 4H; ArH), 6.14 (s, 4H; OCH_2CO), 4.89 (d, 4H, ^2J = 13.0 Hz; $ArCH_2Ar$), 3.77–3.71 (m, 4H; $OC\underline{H}_2CH_2$), 3.29 (d, 4H, ^2J = 13.0 Hz; $ArCH_2Ar$), 1.86–1.75 (m, 4H; $OCH_2C\underline{H}_2$), 1.30 (s, 18H; $C(CH_3)_3$), 0.90 (s, 18H; $C(CH_3)_3$), 0.81 (t, 6H, ^3J = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.54 (C=O), 153.70, 153.22, 145.63, 145.52, 144.39, 134.81, 132.00, 131.10 (C_{Ar}), 130.06, 126.04, 125.77, 124.64, 119.91, 114.06 (CH_{Ar}), 77.61, 71.78 (OCH_2), 34.04, 33.63 ($\underline{C}(CH_3)_3$), 31.86 ($ArCH_2Ar$), 31.61, 31.20 ($C(\underline{C}H_3)_3$), 23.12 ($OCH_2\underline{C}H_2$), 10.43 (CH_3) ppm. ESI-MS *m*/*z*: 1073.5886 $[M+Na]^+$ for $C_{66}H_{78}NaN_6O_6$ (1073.5875).



Calixarene bis(1-acylbenzotriazole) **8** was prepared as described for compound **5** from bis(acid) **4** (3.62 g, 4.00 mmol), 1,2,3-benzotriazole (1.90 g, 16.0 mmol) and DIC (2.47 mL, 16.0 mmol) in dry dichloromethane (200 mL). Yield 4.03 g (91%), white solid. M.p. 267–269 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15–8.11 (m, 2H; ArH_{Bt}), 8.04–8.00 (m, 2H; ArH_{Bt}), 7.51–7.45 (m, 2H; ArH_{Bt}), 7.42–7.36 (m, 2H; ArH_{Bt}), 7.02 (s, 4H; ArH), 6.56 (s, 4H; ArH), 4.43 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 4.23–4.17 (m, 4H; OCH_2), 3.74–3.69 (m, 4H; OCH_2), 3.63–3.57 (m, 4H; CH_2CO), 3.15 (d, 4H, $^2J = 12.5$ Hz; $ArCH_2Ar$), 2.78–2.67 (m, 4H; $OCH_2C\underline{H_2}$), 1.94–1.83 (m, 4H; $OCH_2C\underline{H_2}$), 1.25 (s, 18H; $C(CH_3)_3$), 0.89 (s, 18H; $C(CH_3)_3$), 0.89 (t, 6H, $^3J = 7.5$ Hz; $CH_2CH_2C\underline{H_3}$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.24 (C=O), 153.99, 152.73, 146.03, 144.90, 144.02, 135.11, 132.41, 130.98 (C_{Ar}), 130.15, 125.85, 125.35, 124.57, 119.94, 114.20 (CH_{Ar}), 77.46, 73.74 (OCH_2), 33.98, 33.61 ($\underline{C}(CH_3)_3$), 32.14 ($ArCH_2Ar$), 31.62, 31.21 ($C(\underline{C}H_3)_3$), 31.08, 24.60 ($OCH_2\underline{C}H_2\underline{C}H_2$), 23.41 ($OCH_2\underline{C}H_2$), 10.41 ($CH_3$) ppm. ESI-MS *m*/*z*: 1124.6951 $[M+NH_4]^+$ for $C_{70}H_{90}N_7O_6$ (1124.6947).

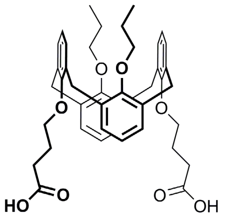


Calixarene bis(1-acylbenzotriazole) **10** was prepared as described for compound **5** from bis(acid) **9** (0.765 g, 1.23 mmol), 1,2,3-benzotriazole (0.584 g, 4.90 mmol) and DIC (0.758 mL, 4.90 mmol) in dry dichloromethane (60 mL). Yield 0.760 g (75%), white solid. M.p. 151–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34–8.30 (m, 2H; ArH_{Bt}), 7.82–7.79 (m, 2H; ArH_{Bt}), 7.68–7.63 (m, 2H; ArH_{Bt}), 7.49–7.43 (m, 2H; ArH_{Bt}), 7.15 (d, 4H, $^3J = 7.5$ Hz; ArH), 7.10 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.80 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.36 (t, 2H, $^3J = 7.5$ Hz; ArH), 4.81 (s, 4H; CH_2CO), 4.12 (d, 4H, $^2J = 15.0$ Hz; $ArCH_2Ar$), 3.80 (d, 4H, $^2J = 15.0$ Hz; $ArCH_2Ar$), 3.60–3.55 (m, 4H; OCH_2), 1.58–1.47 (m, 4H; $OCH_2C\underline{H_2}$), 0.88 (t, 6H, $^3J = 7.6$ Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.83 (C=O), 157.24, 155.54, 145.47, 134.69, 133.65, 131.10 (C_{Ar}), 130.56, 130.24, 130.20, 125.94, 122.44, 122.24, 119.90, 114.18 (CH_{Ar}), 73.08, 71.12 (OCH_2), 37.11 ($ArCH_2Ar$), 22.68 ($OCH_2\underline{C}H_2$), 10.12 (CH_3) ppm. ESI-MS *m*/*z*: 844.3825 $[M+NH_4]^+$ for $C_{50}H_{50}N_7O_6$ (844.3817).

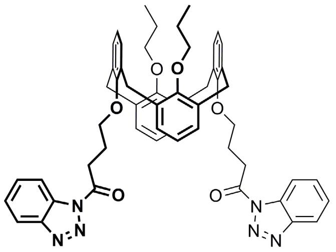


Calixarene bis(ester) **12**. A mixture of calixarene **11** (0.652 g, 1.00 mmol) and anhydrous Cs_2CO_3 (1.30 g, 4.00 mmol) in dry DMF (25 mL) was stirred at room temperature for 1 h. 1-Iodopropane (0.485 mL, 5.00 mmol) was added and the mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the residue was parted between dichloromethane and aqueous HCl (2 M). The organic layer was separated, washed with water, and the solvent was evaporated. The product was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 100:1) followed by crystallization from a dichloromethane/methanol mixture. Yield 0.435 g (59%), white solid. M.p. 115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.99 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.72 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.71 (t, 2H, $^3J = 7.5$ Hz; ArH), 4.16 (q, 4H, $^3J = 7.2$ Hz; $OC\underline{H_2}CH_3$), 3.69 (d, 4H, $^2J = 15.0$ Hz; $ArCH_2Ar$), 3.64 (d, 4H, $^2J = 15.0$ Hz; $ArCH_2Ar$), 3.57–3.52 (m, 4H; OCH_2), 3.47–3.42 (m, 4H; OCH_2), 2.24 (t, 4H, $^3J = 7.3$ Hz; CH_2CO), 1.85–1.75 (m, 4H; $OCH_2C\underline{H_2}$), 1.51–1.40 (m, 4H; $OCH_2C\underline{H_2}$), 1.29 (t, 6H, $^3J = 7.2$ Hz; $OCH_2C\underline{H_3}$), 0.81 (t, 6H, $^3J = 7.5$ Hz; CH_3)

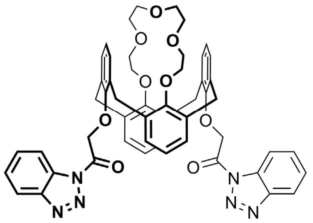
ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.54 (C=O), 156.62, 156.35, 133.83, 133.64 (C_{Ar}), 129.72, 129.56, 121.81, 121.67 (CH_{Ar}), 72.82, 69.92 (OCH_2), 60.22 ($O\underline{C}H_2CH_3$), 37.06 ($ArCH_2Ar$), 30.58 ($\underline{C}H_2CO$), 25.28, 23.03 ($OCH_2\underline{C}H_2$), 14.27 ($OCH_2\underline{C}H_3$), 10.23 (CH_3) ppm. ESI-MS *m*/*z*: 754.4313 $[M+NH_4]^+$ for $C_{46}H_{60}NO_8$ (754.4313).



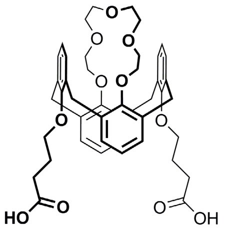
Calixarene bis(acid) ***13***. To a stirred solution of calixarene **12** (0.368 g, 0.50 mmol) in a mixture of methanol (15 mL) and THF (10 mL) a solution of K_2CO_3 (0.414 g, 3.00 mmol) in water (5 mL) was added. The mixture was stirred at reflux for 6 h, cooled and the solvents were evaporated under reduced pressure. The residue was parted between dichloromethane and aqueous HCl (2 M). The organic layer was separated, washed with water, dried, and the solvent was evaporated. Yield 0.324 g (95%), white solid. M.p. 208–210 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, 4H, $^3J = 7.5$ Hz; ArH), 7.03 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.90–6.85 (m, 2H; ArH), 6.80 (t, 2H, $^3J = 7.5$ Hz; ArH), 3.82 (d, 4H, $^2J = 16.1$ Hz; $ArCH_2Ar$), 3.78 (d, 4H, $^2J = 16.1$ Hz; $ArCH_2Ar$), 3.52–3.46 (m, 4H; OCH_2), 3.40–3.34 (m, 4H; OCH_2), 2.12–2.03 (m, 4H; CH_2CO), 1.76–1.67 (m, 4H; $OCH_2C\underline{H}_2$), 1.32–1.18 (m, 4H; $OCH_2C\underline{H}_2$), 0.71 (t, 6H, $^3J = 7.5$ Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.79 (C=O), 156.85, 156.61, 134.15, 133.87 (C_{Ar}), 129.74, 129.59, 122.25, 122.14 (CH_{Ar}), 71.85, 69.02 (OCH_2), 38.17 ($ArCH_2Ar$), 30.95 ($\underline{C}H_2CO$), 25.15, 22.42 ($OCH_2\underline{C}H_2$), 9.97 (CH_3) ppm. ESI-MS *m*/*z*: 698.3687 $[M+NH_4]^+$ for $C_{42}H_{52}NO_8$ (698.3687).



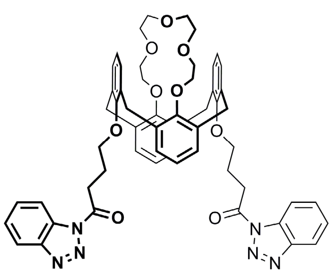
Calixarene bis(1-acylbenzotriazole) ***14*** was prepared as described for compound **5** from bis(acid) **13** (0.270 g, 0.40 mmol), 1,2,3-benzotriazole (0.190 g, 1.60 mmol) and DIC (0.247 mL, 1.60 mmol) in dry dichloromethane (20 mL). Yield 0.290 g (82%), white solid. M.p. 221–223 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15–8.10 (m, 2H; ArH_{Bt}), 8.00–7.96 (m, 2H; ArH_{Bt}), 7.55–7.49 (m, 2H; ArH_{Bt}), 7.41–7.36 (m, 2H; ArH_{Bt}), 7.08 (d, 4H, $^3J = 7.5$ Hz; ArH), 7.03 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.77 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.74 (t, 2H, $^3J = 7.5$ Hz; ArH), 3.80 (d, 4H, $^2J = 15.6$ Hz; $ArCH_2Ar$), 3.76 (d, 4H, $^2J = 15.6$ Hz; $ArCH_2Ar$), 3.60–3.55 (m, 4H; OCH_2), 3.44–3.38 (m, 4H; OCH_2), 3.25–3.19 (m, 4H; CH_2CO), 1.94–1.85 (m, 4H; $OCH_2C\underline{H}_2$), 1.37–1.26 (m, 4H; $OCH_2C\underline{H}_2$), 0.74 (t, 6H, $^3J = 7.5$ Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.27 (C=O), 156.81, 156.34, 145.92, 134.07, 133.83, 130.90 (C_{Ar}), 130.05, 129.70, 129.50, 125.79, 122.17, 122.11, 119.86, 114.24 (CH_{Ar}), 72.21, 69.13 (OCH_2), 37.77 ($ArCH_2Ar$), 31.99 ($\underline{C}H_2CO$), 24.26, 22.68 ($OCH_2\underline{C}H_2$), 10.09 (CH_3) ppm. ESI-MS *m*/*z*: 900.4444 $[M+NH_4]^+$ for $C_{54}H_{58}N_7O_6$ (900.4443).



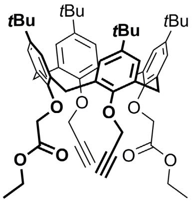
Crowned calixarene bis(1-acylbenzotriazole) ***16*** was prepared as described for compound **5** from bis(acid) **15** (0.279 g, 0.40 mmol), 1,2,3-benzotriazole (0.190 g, 1.60 mmol) and DIC (0.247 mL, 1.60 mmol) in dry dichloromethane (20 mL). Yield 0.223 g (62%), white solid. M.p. 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28–8.24 (m, 4H; ArH_{Bt}), 7.70–7.67 (m, 4H; ArH_{Bt}), 7.66–7.60 (m, 4H; ArH_{Bt}), 7.46–7.40 (m, 4H; ArH_{Bt}), 7.21 (d, 4H, $^3J = 7.5$ Hz; ArH), 7.12 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.94 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.32 (t, 2H, $^3J = 7.5$ Hz; ArH), 4.65 (s, 4H; OCH_2CO), 4.30 (d, 4H, $^2J = 16.1$ Hz; $ArCH_2Ar$), 3.91 (d, 4H, $^2J = 16.1$ Hz; $ArCH_2Ar$), 3.74–3.69 (m, 4H; OCH_2), 3.67–3.61 (m, 8H; OCH_2), 3.28–3.22 (m, 4H; OCH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.03 (C=O), 156.51, 155.71, 145.31, 135.07, 133.91, 131.10 (C_{Ar}), 130.31, 130.09, 130.06, 125.79, 123.04, 122.77, 119.77, 114.12 (CH_{Ar}), 73.21, 70.97, 70.96, 69.44, 68.10 (OCH_2), 37.88 ($ArCH_2Ar$) ppm. ESI-MS *m*/*z*: 918.3859 $[M+NH_4]^+$ for $C_{52}H_{52}N_7O_9$ (918.3821).



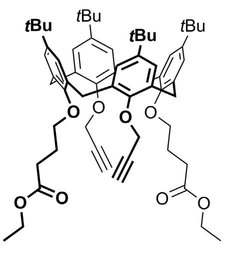
Crowned calixarene bis(acid) ***17***. A mixture of calixarene **11** (1.30 g, 2.00 mmol), anhydrous Cs_2CO_3 (1.96 g, 6.00 mmol) and tetraethylene glycol ditosylate (1.10 g, 2.20 mmol) in dry acetonitrile (120 mL) was stirred at 75 °C for 24 h. The solvent was removed under reduced pressure and the residue was parted between dichloromethane and aqueous HCl (2 M). The organic layer was separated, washed with water, and the solvent was evaporated. The product was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 100:1) to obtain a fraction (0.824 g) containing the desired crowned bis(ester). A solution of KOH (90%, 0.56 g, 9.00 mmol) in ethanol (30 mL) was added to the sample and the mixture was stirred at reflux for 6 h. After cooling, the solvent was evaporated under reduced pressure and aqueous HCl (2 M) was added to the residue. The sticky solid formed was separated, washed with water and THF (rapidly), dried and then dissolved in ethanol. Diethyl ether was added and the solid formed was separated, washed with diethyl ether and dried. Yield 0.535 g (36%), white solid. M.p. 263–265 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.09 (bs, 2H; CO_2H), 7.31 (d, 4H, $^3J = 7.5$ Hz; ArH), 7.18 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.94 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.82 (t, 4H, $^3J = 7.5$ Hz; ArH), 3.99–3.92 (m, 4H; OCH_2), 3.81 (d, 4H, $^2J = 15.2$ Hz; $ArCH_2Ar$), 3.76–3.70 (m, 4H; OCH_2), 3.74 (d, 4H, $^2J = 15.2$ Hz; $ArCH_2Ar$), 3.66–3.58 (m, 12H, OCH_2), 2.20–2.13 (m, 4H; CH_2CO), 1.78–1.68 (m, 4H; $CH_2C\underline{H}_2CH_2$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 174.53 (C=O), 156.94, 154.77, 135.92, 133.48 (C_{Ar}), 130.77, 130.42, 123.03, 121.86 (CH_{Ar}), 70.63, 70.15, 69.73, 69.57, 69.46 (OCH_2), 36.13 ($ArCH_2Ar$), 29.47 ($CH_2\underline{C}O$), 24.46 ($CH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m*/*z*: 772.3689 $[M+NH_4]^+$ for $C_{44}H_{54}NO_{11}$ (772.3691).



Crowned calixarene bis(1-acylbenzotriazole) ***18*** was prepared as described for compound **5** from bis(acid) **17** (0.490 g, 0.65 mmol), 1,2,3-benzotriazole (0.309 g, 2.60 mmol) and DIC (0.402 mL, 2.60 mmol) in dry dichloromethane (40 mL). Yield 0.432 g (70%), white solid. M.p. 77–79 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.10–8.06 (m, 2H; ArH$_{\mathrm{Bt}}$), 7.98–7.94 (m, 2H; ArH$_{\mathrm{Bt}}$), 7.51–7.45 (m, 2H; ArH$_{\mathrm{Bt}}$), 7.38–7.33 (m, 2H; ArH$_{\mathrm{Bt}}$), 7.11 (d, 4H, ^3J = 7.5 Hz; ArH), 7.09 (d, 4H, ^3J = 7.5 Hz; ArH), 6.89 (t, 2H, ^3J = 7.5 Hz; ArH), 6.76 (t, 4H, ^3J = 7.5 Hz; ArH), 3.88 (bs, 8H, ArCH$_2$Ar), 3.64–3.53 (m, 12H, OCH$_2$), 3.47–3.41 (m, 4H; OCH$_2$), 3.15–3.05 (m, 8H; OCH$_2$+CH$_2$CO), 1.77–1.68 (m, 4H; CH$_2$C$\underline{\mathrm{H}}_2$CH$_2$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 172.24 (C=O), 156.56, 156.07, 145.91, 134.11, 134.03, 130.89 (C$_{\mathrm{Ar}}$), 130.02, 129.27, 129.26, 125.76, 122.83, 122.72, 119.85, 114.22 (CH$_{\mathrm{Ar}}$), 72.82, 70.68, 69.69, 68.75, 68.01 (OCH$_2$), 38.16 (ArCH$_2$Ar), 31.87 (CH$_2\underline{\mathrm{C}}$O), 23.98 (CH$_2\underline{\mathrm{C}}$H$_2$CH$_2$) ppm. ESI-MS *m*/*z*: 974.4484 [M+NH$_4$]$^+$ for C$_{56}$H$_{60}$N$_7$O$_9$ (974.4447).

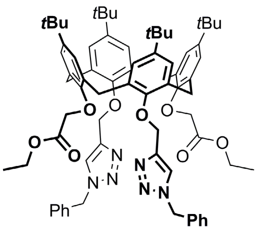


Propargylated calixarene bis(ester) ***20***. To a stirred suspension of dipropargyl ether **19** (1.15 g, 1.59 mmol) in dry THF (114 mL) NaH (60%, 0.380 g, 9.51 mmol) was added. The mixture was stirred at room temperature for 30 min, ethyl bromoacetate (0.879 mL, 7.93 mmol) was added and the mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction was quenched with several drops of aqueous HCl (2 M) and the solvent was removed under reduced pressure. The residue was parted between dichloromethane and aqueous HCl (2 M). The organic layer was separated, washed with water, dried, and the solvent was evaporated to almost dryness. Methanol was added and the solid formed was separated, washed with methanol and dried. Yield 1.03 g (72%), white solid. The analytical data for the obtained compounds were similar to those reported previously.[S12]

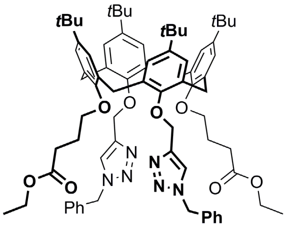


Propargylated calixarene bis(ester) ***21***. To a stirred suspension of dipropargyl ether **19** (2.17 g, 3.00 mmol) in dry DMF (90 mL) NaH (60%, 0.720 g, 18.0 mmol) was added. The mixture was stirred at room temperature for 30 min, ethyl 4-bromobutyrate (2.15 mL, 15.0 mmol) was added and the mixture was stirred at room temperature for 48 h. The reaction was quenched with several drops of aqueous HCl (2 M) and the solvent was removed under reduced pressure. The residue was parted between dichloromethane and aqueous HCl (2 M). The organic layer was separated, washed with water, dried, and the solvent was evaporated to almost dryness. Methanol was added and the solid formed was separated, washed with methanol and dried. Yield 2.67 g (93%), white solid. M.p. 128–130 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.07 (s, 4H; ArH), 6.45

(s, 4H; ArH), 4.96 (d, 4H, ${}^4J = 2.4$ Hz; $C\underline{H}_2C{\equiv}CH$), 4.48 (d, 4H, ${}^2J = 12.8$ Hz; $ArCH_2Ar$), 4.15 (q, 4H, ${}^3J = 7.1$ Hz; $OC\underline{H}_2CH_3$), 3.80–3.73 (m, 4H; $OC\underline{H}_2CH_2$), 3.14 (d, 4H, ${}^2J = 12.8$ Hz; $ArCH_2Ar$), 2.63–2.57 (m, 4H; CH_2CO), 2.45 (t, 2H, ${}^4J = 2.4$ Hz; $CH_2C{\equiv}C\underline{H}$), 2.33–2.23 (m, 4H; $OCH_2C\underline{H}_2$), 1.30 (s, 18H; $C(CH_3)_3$), 1.26 (t, 6H, ${}^3J = 7.1$ Hz; CH_3), 0.82 (s, 18H; $C(CH_3)_3$) ppm; ${}^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 173.44 (C=O), 152.83, 151.13, 145.81, 144.35, 136.15, 131.86 (C_{Ar}), 125.41, 124.43 (CH_{Ar}), 81.39 ($CH_2\underline{C}{\equiv}CH$), 74.64, 74.53 ($CH_2C{\equiv}\underline{C}H$, $O\underline{C}H_2CH_2$), 60.33, 59.76 ($\underline{C}H_2C{\equiv}CH$, $O\underline{C}H_2CH_3$), 34.09, 33.55 ($\underline{C}(CH_3)_3$), 31.68 ($ArCH_2Ar$ or $OCH_2\underline{C}H_2$), 31.62 ($C(\underline{C}H_3)_3$), 31.36 ($\underline{C}H_2CO$ or $ArCH_2Ar$), 31.09 ($C(\underline{C}H_3)_3$), 25.76 ($OCH_2\underline{C}H_2$), 14.27 (CH_3) ppm. ESI-MS *m*/*z*: 953.5924 $[M+H]^+$ for $C_{62}H_{81}O_8$ (953.5926).

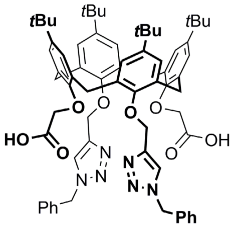


Triazolated calixarene bis(ester) **22**. Under argon, a freshly prepared solution of CuI (0.078 g, 0.41 mmol) and triethylamine (1.14 mL, 8.2 mmol) in toluene (10 mL) was added to a stirred solution of calixarene **20** (1.22 g, 1.36 mmol) in toluene (50 mL). Benzyl azide (0.435 g, 3.27 mmol) was added and the mixture was stirred at 60 °C for 24 h. After cooling, the solvent was removed under reduced pressure, the residue was suspended in dichloromethane, aqueous $Na_2S_2O_3$ (10%) was added and the heterogeneous mixture was intensively stirred for at least 2 h. The organic phase was separated, the aqueous phase was extracted with dichloromethane. The combined organic fractions were washed with water, dried and the solvent was evaporated. The product was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 20:1). Yield 1.13 g (71%), white solid. M.p. 102–104 °C. ${}^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 2H; ArH_{Trz}), 7.35–7.30 (m, 6H; ArH_{Ph}), 7.25–7.21 (m, 4H; ArH_{Ph}), 6.85 (s, 4H; ArH), 6.50 (s, 4H; ArH), 5.49 (s, 4H; NCH_2), 5.21 (s, 4H; OCH_2Trz), 4.45 (s, 4H; CH_2CO), 4.30 (d, 4H, ${}^2J = 12.9$ Hz; $ArCH_2Ar$), 4.11 (q, 4H, ${}^3J = 7.2$ Hz; $OC\underline{H}_2CH_3$) 2.94 (d, 4H, ${}^2J = 12.9$ Hz; $ArCH_2Ar$), 1.19 (t, 6H, ${}^3J = 7.2$ Hz; CH_3), 1.18 (s, 18H; $C(CH_3)_3$), 0.88 (s, 18H; $C(CH_3)_3$) ppm; ${}^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 170.38 (C=O), 152.90, 152.39, 145.33, 145.05, 144.62, 135.36, 135.14, 132.17 (C_{Ar}), 128.85, 128.33, 127.83, 125.20, 124.84, 124.46 (CH_{Ar}), 71.79 ($\underline{C}H_2CO$), 65.91 (OCH_2Trz), 60.50 ($O\underline{C}H_2CH_3$), 53.72 (NCH_2), 33.89, 33.59 ($\underline{C}(CH_3)_3$), 31.70 ($ArCH_2Ar$), 31.52, 31.12 ($C(\underline{C}H_3)_3$), 14.14 (CH_3) ppm. ESI-MS *m*/*z*: 1185.6400 $[M+Na]^+$ for $C_{72}H_{86}NaN_6O_8$ (1185.6399).

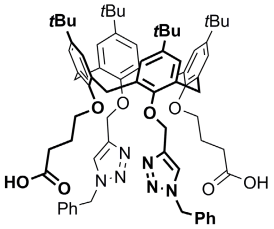


Triazolated calixarene bis(ester) **23** was prepared as described for compound **22** from calixarene **21** (1.91 g, 2.01 mmol), benzyl azide (0.639 g, 4.80 mmol), CuI (0.114 g, 0.60 mmol) and triethylamine (1.67 mL, 12.0 mmol) in toluene (60 mL). Yield 2.21 g (90%), white solid. M.p. 109–111 °C. ${}^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.59 (s, 2H;

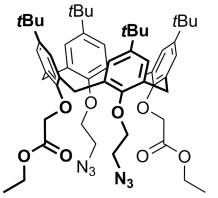
ArH_{Trz}), 7.39–7.29 (m, 10H; ArH_{Ph}), 6.82 (s, 4H; ArH), 6.53 (s, 4H; ArH), 5.56 (s, 4H; NCH_2), 4.96 (s, 4H; OCH_2Trz), 4.19 (d, 4H, $^2J = 12.6$ Hz; $ArCH_2Ar$), 4.12 (q, 4H, $^3J = 7.1$ Hz; $OC\underline{H}_2CH_3$), 3.78–3.71 (m, 4H; $OC\underline{H}_2CH_2$), 2.88 (d, 4H, $^2J = 12.6$ Hz; $ArCH_2Ar$), 2.22–2.16 (m, 4H; CH_2CO), 2.09–2.00 (m, 4H; $OCH_2C\underline{H}_2$), 1.25 (t, 6H, $^3J = 7.1$ Hz; CH_3), 1.16 (s, 18H; $C(CH_3)_3$), 0.92 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 173.72$ (C=O), 153.71, 151.44, 144.81, 144.69, 144.58, 135.34, 134.36, 133.25 (C_{Ar}), 128.94, 128.48, 128.08, 125.08, 124.70, 123.78 (CH_{Ar}), 73.80 ($O\underline{C}H_2CH_2$), 67.31 (OCH_2Trz), 60.15 ($O\underline{C}H_2CH_3$), 53.81 (NCH_2), 33.87, 33.66 ($\underline{C}(CH_3)_3$), 31.52, 31.22 ($C(\underline{C}H_3)_3$), 31.12 ($ArCH_2Ar$), 30.68 ($\underline{C}H_2CO$), 25.14 ($OCH_2\underline{C}H_2$), 14.28 ($CH_2\underline{C}H_3$) ppm. ESI-MS *m/z*: 1219.7203 $[M+H]^+$ for $C_{76}H_{95}N_6O_8$ (1219.7206).



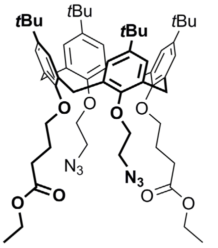
Triazolated calixarene bis(acid) ***24***. To a stirred solution of calixarene **22** (2.65 g, 2.28 mmol) in ethanol (100 mL) a solution of KOH (90%, 5.11 g, 82.1 mmol) in ethanol (30 mL) was added. The mixture was stirred at reflux for 6 h and cooled to room temperature. The solvent was removed under reduced pressure, auqeous HCl (2 M) was added and the product was extracted with dichloromethane. The solution was wahsed with water, brine, dried and the solvent was evaporated. Yield 2.52 g (100%), white solid. M.p. 147–149 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.67$ (s, 2H; ArH_{Trz}), 7.40–7.31 (m, 10H; ArH_{Ph}), 7.06 (s, 4H; ArH), 6.52 (s, 4H; ArH), 5.59 (s, 4H; NCH_2), 4.96 (s, 4H; OCH_2Trz), 4.29 (s, 4H; CH_2CO), 4.10 (d, 4H, $^2J = 13.0$ Hz; $ArCH_2Ar$), 3.09 (d, 4H, $^2J = 13.0$ Hz; $ArCH_2Ar$), 1.30 (s, 18H; $C(CH_3)_3$), 0.82 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.11$ (C=O), 152.58, 149.57, 147.16, 146.19, 142.80, 134.59, 134.41, 132.24 (C_{Ar}), 129.06, 128.66, 128.39, 125.88, 125.29, 124.92 (CH_{Ar}), 71.66 ($\underline{C}H_2CO$), 68.54 (OCH_2Trz), 54.38 (NCH_2), 34.12, 33.68 ($\underline{C}(CH_3)_3$), 31.51 ($C(\underline{C}H_3)_3$), 31.17 ($ArCH_2Ar$), 30.89 ($C(\underline{C}H_3)_3$) ppm. ESI-MS *m/z*: 1107.5952 $[M+H]^+$ for $C_{68}H_{79}N_6O_8$ (1107.5954).



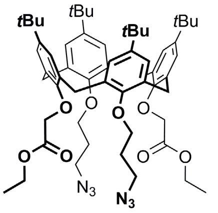
Triazolated calixarene bis(acid) ***25*** was prepared as described for compound **24** from calixarene **23** (2.21 g, 1.81 mmol) and KOH (90%, 4.06 g, 65.3 mmol) in ethanol (100 mL). Yield 2.00 g (95%), white solid. M.p. 147–149 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.45$ (s, 2H; ArH_{Trz}), 7.34–7.27 (m, 10H; ArH_{Ph}), 6.95 (s, 4H; ArH), 6.41 (s, 4H; ArH), 5.54 (s, 4H; NCH_2), 4.88 (s, 4H; OCH_2Trz), 4.17 (d, 4H, $^2J = 12.5$ Hz; $ArCH_2Ar$), 3.84–3.76 (m, 4H; $OC\underline{H}_2CH_2$), 2.85 (d, 4H, $^2J = 12.5$ Hz; $ArCH_2Ar$), 2.41–2.32 (m, 4H; $C\underline{H}_2CO$), 2.12–2.02 (m, 4H; $OCH_2C\underline{H}_2$), 1.28 (s, 18H; $C(CH_3)_3$), 0.81 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 178.08$ (C=O), 154.10, 150.99, 144,81, 144.64, 144.24, 135.12, 134.98, 132.47 (C_{Ar}), 128.97, 128.58, 128.37, 125.29, 124.56, 123.83 (CH_{Ar}), 73.84 ($O\underline{C}H_2CH_2$), 67.21 (OCH_2Trz), 54.11 (NCH_2), 34.00, 33.57 ($\underline{C}(CH_3)_3$), 31.67 ($C(\underline{C}H_3)_3$), 31.30 ($ArCH_2Ar$, $\underline{C}H_2CO$), 31.07 ($C(\underline{C}H_3)_3$), 25.14 ($OCH_2\underline{C}H_2$) ppm. ESI-MS *m*/*z*: 1163.6587 $[M+H]^+$ for $C_{72}H_{87}N_6O_8$ (1163.6580).



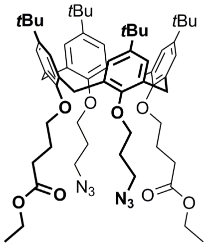
2-Azidoethylated calixarene bis(ester) ***28*** was prepared as described for compound **21** from bis(azide) **26** (1.10 g, 1.40 mmol), ethyl bromoacetate (0.78 mL, 7.0 mmol) and NaH (60%, 0.336 g, 8.4 mmol) in DMF (42 mL). Yield 0.910 g (68%), white solid. M.p. 196–198 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.03 (s, 4H; ArH), 6.53 (s, 4H; ArH), 4.44 (s, 4H; OCH_2CO), 4.43 (4H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 4.30 (q, 4H, $^3J = 7.1$ Hz; $OC\underline{H}_2CH_3$), 4.27–4.22 (m, 4H; $OC\underline{H}_2CH_2$), 4.10–4.03 (m, 4H; CH_2N_3), 3.17 (4H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 1.32 (t, 6H, $^3J = 7.1$ Hz; $C\underline{H}_3$), 1.27 (s, 18H; $C(CH_3)_3$), 0.86 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.44 (C=O), 153.85, 151.54, 145.43, 145.18, 134.67, 131.94 (C_{Ar}), 125.57, 125.01 (CH_{Ar}), 72.00, 71.70 (OCH_2), 60.91 ($O\underline{C}H_2CH_3$), 50.84 (CH_2N_3), 34.03, 33.65 ($\underline{C}(CH_3)_3$), 31.59, 31.08 ($C(\underline{C}H_3)_3$), 30.99 ($ArCH_2Ar$), 14.23 (CH_3) ppm. ESI-MS *m*/*z*: 976.5915 $[M+NH_4]^+$ for $C_{56}H_{78}N_7O_8$ (976.5906).



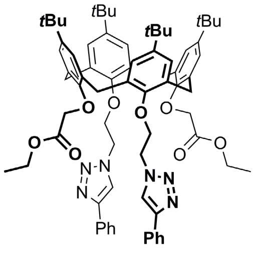
2-Azidoethylated calixarene bis(ester) ***29*** was prepared as described for compound **21** from bis(azide) **26** (1.37 g, 1.74 mmol), ethyl 4-bromobutyrate (1.25 mL, 8.7 mmol) and NaH (60%, 0.418 g, 10.4 mmol) in DMF (53 mL). Yield 0.818 g (46%), white solid. M.p. 105–107 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.89 (s, 4H; ArH), 6.65 (s, 4H; ArH), 4.32 (d, 4H, $^2J = 12.6$ Hz; $ArCH_2Ar$), 4.15 (q, 4H, $^3J = 7.2$ Hz; $OC\underline{H}_2CH_3$), 4.10–4.05 (m, 4H; $OC\underline{H}_2CH_2N_3$), 3.92–3.87 (m, 4H; $C\underline{H}_2N_3$), 3.87–3.82 (m, 4H; $OC\underline{H}_2CH_2CH_2$), 3.16 (d, 4H, $^2J = 12.6$ Hz; $ArCH_2Ar$), 2.52–2.46 (m, 4H; CH_2CO), 2.33–2.24 (m, 4H; $OCH_2C\underline{H}_2CH_2$), 1.26 (t, 6H, $^3J = 7.2$ Hz; $C\underline{H}_3$), 1.15 (s, 18H; $C(CH_3)_3$), 0.97 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.16 (C=O), 152.74, 152.62, 145.34, 144.67, 134.09, 132.85 (C_{Ar}), 125.35, 124.92 (CH_{Ar}), 74.50, 71.57 (OCH_2), 60.40 ($O\underline{C}H_2CH_3$), 50.68 (CH_2N_3), 33.92, 33.77 ($\underline{C}(CH_3)_3$), 31.45, 31.27 ($C(\underline{C}H_3)_3$), 30.94, 30.85 ($ArCH_2Ar$, $\underline{C}H_2CO$), 25.50 ($OCH_2\underline{C}H_2CH_2$), 14.22 ($\underline{C}H_3$) ppm. ESI-MS *m*/*z*: 1032.6540 $[M+NH_4]^+$ for $C_{60}H_{86}N_7O_8$ (1032.6532).



3-Azidopropylated calixarene bis(ester) ***30*** was prepared as described for compound **21** from bis(azide) **27** (1.14 g, 1.40 mmol), ethyl bromoacetate (0.78 mL, 7.0 mmol) and NaH (60%, 0.336 g, 8.4 mmol) in DMF (42 mL). Yield 0.914 g (66%), white solid. M.p. 189–191 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.93 (s, 4H; ArH), 6.63 (s, 4H; ArH), 4.53 (s, 4H; OCH_2CO), 4.48 (d, 4H, ${}^2J$ = 12.7 Hz; $ArCH_2Ar$), 4.24 (q, 4H, ${}^3J$ = 7.1 Hz; $OC\underline{H}_2CH_3$), 4.09–4.03 (m, 4H; $OC\underline{H}_2CH_2CH_2$), 3.57–3.49 (m, 4H, $C\underline{H}_2N_3$), 3.17 (d, 4H, ${}^2J$ = 12.7 Hz; $ArCH_2Ar$), 2.41–2.31 (m, 4H; $OCH_2C\underline{H}_2CH_2$), 1.29 (t, 6H, ${}^3J$ = 7.1 Hz; CH_3), 1.19 (s, 18H; $C(CH_3)_3$), 0.94 (s, 18H; $C(CH_3)_3$) ppm; ${}^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 169.62 (C=O), 153.85, 152.19, 145.01, 144.99, 134.29, 132.52 (C_{Ar}), 125.36, 125.12 (CH_{Ar}), 72.10, 71.60 (OCH_2), 60.63 ($O\underline{C}H_2CH_3$), 49.09 (CH_2N_3), 33.92, 33.71 ($\underline{C}(CH_3)_3$), 31.53 ($C(\underline{C}H_3)_3$), 31.26 ($ArCH_2Ar$), 31.20 ($C(\underline{C}H_3)_3$), 29.42 ($OCH_2\underline{C}H_2CH_2$), 14.21 ($OCH_2\underline{C}H_3$) ppm. ESI-MS *m*/*z*: 1004.6228 $[M+NH_4]^+$ for $C_{58}H_{82}N_7O_8$ (1004.6219).

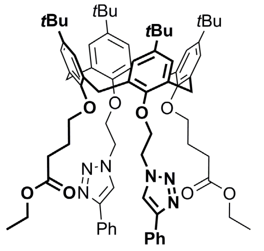


3-Azidopropylated calixarene bis(ester) ***31*** was prepared as described for compound **21** from bis(azide) **27** (2.12 g, 2.60 mmol), ethyl 4-bromobutyrate (1.86 mL, 13.0 mmol) and NaH (60%, 0.624 g, 15.6 mmol) in DMF (42 mL). Yield 2.07 g (76%), white solid. M.p. 82–84 °C. ${}^1H$ NMR (400 MHz, $CDCl_3$): δ = 6.88 (s, 4H; ArH), 6.65 (s, 4H; ArH), 4.31 (d, 4H, ${}^2J$ = 12.6 Hz; $ArCH_2Ar$), 4.15 (q, 4H, ${}^3J$ = 7.1 Hz; $OC\underline{H}_2CH_3$), 4.02–3.96 (m, 4H, OCH_2), 3.86–3.79 (m, 4H; OCH_2), 3.56–3.49 (m, 4H; CH_2N_3), 3.14 (d, 4H, ${}^2J$ = 12.6 Hz; $ArCH_2Ar$), 2.52–2.46 (m, 4H; CH_2CO), 2.35–2.20 (m, 8H; $OCH_2C\underline{H}_2CH_2$), 1.26 (t, 6H, ${}^3J$ = 7.1 Hz; CH_3), 1.15 (s, 18H; $C(CH_3)_3$), 0.98 (s, 18H; $C(CH_3)_3$) ppm; ${}^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 173.12 (C=O), 153.32, 152.71, 144.93, 144.57, 134.13, 132.93 (C_{Ar}), 125.28, 124.91 (CH_{Ar}), 74.40, 71.99 (OCH_2), 60.39 ($O\underline{C}H_2CH_3$), 48.91 (CH_2N_3), 33.90, 33.73 ($\underline{C}(CH_3)_3$), 31.49, 31.30 ($C(\underline{C}H_3)_3$), 31.05, 30.97 ($ArCH_2Ar$, $\underline{C}H_2CO$), 29.65, 25.57 ($OCH_2\underline{C}H_2CH_2$), 14.25 ($CH_3$) ppm. ESI-MS *m*/*z*: 1060.6855 $[M+NH_4]^+$ for $C_{62}H_{90}N_7O_8$ (1060.6845).

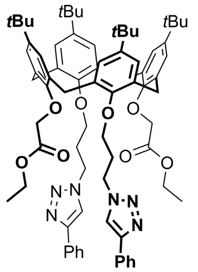


Triazolated calixarene bis(ester) ***32***. A solution of calixarene **28** (0.900 g, 0.94 mmol), phenylacetylene (0.248 mL, 2.26 mmol) and CuI (0.054 g, 0.28 mmol) in the mixture of toluene (56 mL) and triethylamine (14 mL) was stirred at room temperature for 72 h. The solvens were removed under reduced pressure, and the residue was suspended in dichloromethane. Aqueous HCl (2 M) was added and the heterogeneous mixture was intensively stirred for at least 2 h. The organic phase was separated, the aqueous phase was extracted with dichloromethane. The combined organic fractions were washed with aqueous Na_2SO_3 (5%), water, dried and the solvent was evaporated to almost dryness. Methanol was added, and the solid formed was separated, washed with methanol and dried. Yield 0.525 g (48%), yellowish solid. M.p. 253–255 °C. ${}^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 2H; ArH_{Trz}), 7.77–7.73 (m, 4H; ArH_{Ph}), 7.31–7.21 (m, 6H; ArH_{Ph}), 7.15 (s, 4H; ArH), 6.50 (s, 4H; ArH), 5.45–5.37 (m, 4H; NCH_2), 4.67–4.60 (m, 4H; $OC\underline{H}_2CH_2$), 4.43 (s, 4H; CH_2CO), 4.39 (d, 4H, ${}^2J$ = 12.7 Hz; $ArCH_2Ar$), 4.16 (q, 4H,

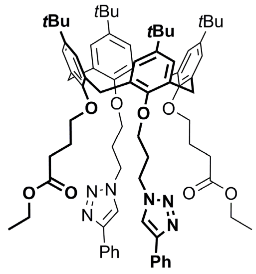
^3J = 7.2 Hz; $OC\underline{H}_2CH_3$), 3.22 (d, 4H, ^2J = 12.7 Hz; $ArCH_2Ar$), 1.34 (s, 18H; $C(CH_3)_3$), 1.18 (t, 6H, ^3J = 7.2 Hz; CH_3), 0.82 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.53 (C=O), 153.71, 151.05, 147.44, 146.17, 145.45, 135.08, 131.54, 130.80 (C_{Ar}), 128.65, 127.73, 125.83, 125.52, 125.06, 120.68 (CH_{Ar}), 72.24, 72.03 (OCH_2), 61.11 ($O\underline{C}H_2CH_3$), 49.17 (NCH_2), 34.16, 33.63 ($\underline{C}(CH_3)_3$), 31.65 ($C(\underline{C}H_3)_3$), 30.98 ($C(\underline{C}H_3)_3$, $ArCH_2Ar$), 14.05 (CH_3) ppm. ESI-MS *m*/*z*: 1163.6584 $[M+H]^+$ for $C_{72}H_{87}N_6O_8$ (1163.6580).



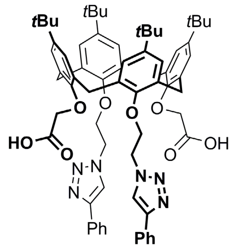
Triazolated calixarene bis(ester) **33** was prepared as described for compound **32** from calixarene **29** (1.207 g, 1.19 mmol), phenylacetylene (0.313 mL, 2.86 mmol) and CuI (0.068 g, 0.36 mmol) in the mixture of toluene (80 mL) and triethylamine (20 mL). Instead of crystallization from methanol, the product was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 20:1). Yield 0.958 g (66%), white solid. M.p. 101–103 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 2H; ArH_{Trz}), 7.93–7.88 (m, 4H; ArH_{Ph}), 7.40–7.34 (m, 4H; ArH_{Ph}), 7.33–7.27 (m, 2H; ArH_{Ph}), 7.11 (s, 4H; ArH), 6.51 (4H; ArH), 5.26–5.19 (m, 4H; NCH_2), 4.62–4.55 (m, 4H; $OC\underline{H}_2CH_2N$), 4.31 (d, 4H, ^2J = 12.7 Hz; $ArCH_2Ar$), 4.00 (q, 4H, ^3J = 7.1 Hz; $OC\underline{H}_2CH_3$), 3.80–3.74 (m, 4H; $OC\underline{H}_2CH_2CH_2$), 3.22 (d, 4H, ^2J = 12.7 Hz; $ArCH_2Ar$), 2.43–2.37 (m, 4H; CH_2CO), 2.24–2.15 (m, 4H; $OCH_2C\underline{H}_2CH_2$), 1.31 (s, 18H; $C(CH_3)_3$), 1.10 (t, 6H, ^3J = 7.1 Hz; CH_3), 0.85 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.93 (C=O), 153.12, 151.89, 147.89, 146.20, 144.79, 134.98, 131.75, 130.69 (C_{Ar}), 128.70, 127.94, 125.84, 125.72, 124.80, 120.46 (CH_{Ar}), 74.85, 71.62 (OCH_2), 60.44 ($O\underline{C}H_2CH_3$), 49.41 (NCH_2), 34.13, 33.64 ($\underline{C}(CH_3)_3$), 31.60, 31.09 ($C(\underline{C}H_3)_3$), 31.02, 30.75 ($\underline{C}H_2CO$, $ArCH_2Ar$), 25.62 ($CH_2\underline{C}H_2CH_2$), 14.09 (CH_3) ppm. ESI-MS *m*/*z*: 1219.7206 $[M+H]^+$ for $C_{76}H_{95}N_6O_8$ (1219.7206).



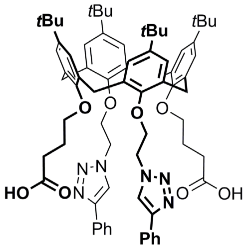
Triazolated calixarene bis(ester) **34** was prepared as described for compound **33** from calixarene **30** (0.858 g, 0.87 mmol), phenylacetylene (0.229 mL, 2.09 mmol) and CuI (0.050 g, 0.26 mmol) in the mixture of toluene (56 mL) and triethylamine (14 mL). Yield 0.607 g (59%), yellowish solid. M.p. 106–108 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 2H; ArH_{Trz}), 7.84–7.80 (m, 4H; ArH_{Ph}), 7.40–7.34 (m, 4H; ArH_{Ph}), 7.31–7.26 (m, 2H; ArH_{Ph}), 7.07 (s, 4H; ArH), 6.51 (s, 4H; ArH), 4.56–4.50 (m, 4H; NCH_2), 4.43 (d, 4H, ^2J = 12.7 Hz; $ArCH_2Ar$), 4.39 (s, 4H; CH_2CO), 4.18–4.13 (m, 4H; $OC\underline{H}_2CH_2$), 4.12 (q, 4H, ^3J = 7.2 Hz; $OC\underline{H}_2CH_3$), 3.16 (d, 4H, ^2J = 12.7 Hz; $ArCH_2Ar$), 2.81–2.71 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.29 (s, 18H; $C(CH_3)_3$), 1.17 (t, 6H, ^3J = 7.2 Hz; CH_3), 0.85 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.46 (C=O), 154.06, 151.56, 147.39, 145.33, 145.10, 134.98, 131.80, 130.94 (C_{Ar}), 128.74, 127.86, 125.66, 125.53, 124.96, 120.33 (CH_{Ar}), 71.97, 71.65 (OCH_2), 60.74 ($O\underline{C}H_2CH_3$), 48.01 (NCH_2), 34.04, 33.63 ($\underline{C}(CH_3)_3$), 31.63 ($C(\underline{C}H_3)_3$), 31.06 ($C(\underline{C}H_3)_3$, $ArCH_2Ar$), 30.67 ($CH_2\underline{C}H_2CH_2$), 14.06 (CH_3) ppm. ESI-MS *m*/*z*: 1191.6894 $[M+H]^+$ for $C_{74}H_{91}N_6O_8$ (1191.6893).



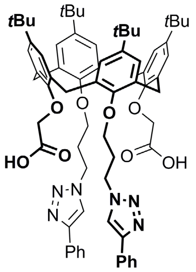
Triazolated calixarene bis(ester) **35** was prepared as described for compound **33** from calixarene **31** (2.19 g, 2.10 mmol), phenylacetylene (0.553 mL, 5.04 mmol) and CuI (0.120 g, 0.63 mmol) in the mixture of toluene (140 mL) and triethylamine (35 mL). The product was additionally purified by crystallization from hexane. Yield 1.32 g (50%), yellowish solid. M.p. 84–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 2H; ArH_{Trz}), 7.84–7.79 (m, 4H; ArH_{Ph}), 7.41–7.34 (m, 4H; ArH_{Ph}), 7.32–7.26 (m, 2H; ArH_{Ph}), 6.95 (s, 4H; ArH), 6.58 (s, 4H; ArH), 4.53–4.46 (m, 4H; NCH_2), 4.30 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 4.06 (q, 4H, ^3J = 7.1 Hz; $OC\underline{H}_2CH_3$), 4.04–3.97 (m, 4H; $C\underline{H}_2CH_2CH_2N$), 3.80–3.73 (m, 4H, $OC\underline{H}_2CH_2CH_2CO$), 3.14 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 2.71–2.60 (m, 4H; $C\underline{H}_2CH_2N$), 2.47–2.41 (m, 4H; $C\underline{H}_2CO$), 2.27–2.16 (m, 4H; $C\underline{H}_2CH_2CO$), 1.20 (s, 18H; $C(CH_3)_3$), 1.18 (t, 6H, ^3J = 7.1 Hz; CH_3), 0.91 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.24 (C=O), 153.31, 152.34, 147.48, 145.24, 144.57, 134.52, 132.47, 130.74 (C_{Ar}), 128.75, 127.94, 125.55, 125.43, 124.81, 120.37 (CH_{Ar}), 74.48, 71.44 (OCH_2), 60.41 ($O\underline{C}H_2CH_3$), 47.67 (NCH_2), 33.95, 33.66 ($\underline{C}(CH_3)_3$), 31.52, 31.19 ($C(\underline{C}H_3)_3$), 31.03, 30.94, 30.76 ($CH_2\underline{C}H_2CH_2$, $ArCH_2Ar$, CH_2CO), 25.61 ($CH_2\underline{C}H_2CH_2$), 14.17 (CH_3) ppm. ESI-MS *m*/*z*: 1247.7518 $[M+H]^+$ for $C_{78}H_{99}N_6O_8$ (1247.7519).



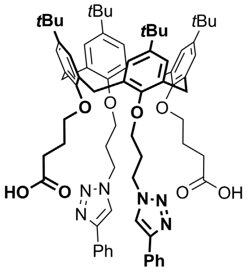
Triazolated calixarene bis(acid) **36** was prepared as described for compound **13** from calixarene **32** (0.541 g, 0.47 mmol) and K_2CO_3 (0.773 g, 5.60 mmol) in the mixture of methanol (36 mL), THF (9.3 mL) and water (3.6 mL). The product was additionally purified by crystallization from a dichloromethane solution upon addition of methanol. Yield 0.488 g (95%), white solid. M.p. 208–210 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.55 (s, 2H; ArH_{Trz}), 7.87–7.82 (m, 4H; ArH_{Ph}), 7.44–7.38 (m, 4H; ArH_{Ph}), 7.36–7.30 (m, 2H; ArH_{Ph}) 7.21 (s, 4H; ArH), 6.55 (s, 4H; ArH), 5.44–5.37 (m, 4H, NCH_2), 4.61–4.54 (m, 4H; $OC\underline{H}_2CH_2$), 4.36 (d, 4H, ^2J = 12.8 Hz; $ArCH_2Ar$), 4.35 (s, 4H; CH_2CO), 3.24 (d, 4H, ^2J = 12.8 Hz; $ArCH_2Ar$), 1.28 (s, 18H; $C(CH_3)_3$), 0.83 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.83 (C=O), 153.68, 151.11, 146.08, 145.25, 144.22, 134.82, 131.63, 130.90 (C_{Ar}), 128.86, 127.78, 125.57, 125.16, 124.68, 121.74 (CH_{Ar}), 71.97, 71.89 (OCH_2), 48.64 (NCH_2), 33.87, 33.34 ($\underline{C}(CH_3)_3$), 31.42, 30.80 ($C(\underline{C}H_3)_3$), 30.27 ($ArCH_2Ar$) ppm. ESI-MS *m*/*z*: 1107.5957 $[M+H]^+$ for $C_{68}H_{79}N_6O_8$ (1107.5954).



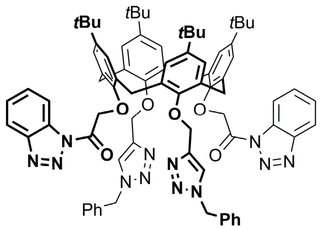
Triazolated calixarene bis(acid) ***37*** was prepared as described for compound **13** from calixarene **33** (0.455 g, 0.37 mmol) and K_2CO_3 (0.63 g, 4.57 mmol) in the mixture of methanol (29 mL), THF (7.6 mL) and water (2.9 mL). To the residue obtained after concentration of the reaction mixture, aqueous HCl (2 M) was added, and the suspension was stirred at room temperature for 24 h. The solid was filtered, washed with water and dried. Yield 0.391 g (90%), white solid. M.p. 272–274 °C. ^1H NMR (400 MHz, DMSO-d_6): $\delta = 8.63$ (s, 2H; ArH_{Trz}), 7.90–7.83 (m, 4H; ArH_{Ph}), 7.47–7.40 (m, 4H; ArH_{Ph}), 7.36–7.30 (m, 2H; ArH_{Ph}), 6.95 (s, 4H; ArH), 6.68 (s, 4H; ArH), 5.11–5.02 (m, 4H; NCH_2), 4.50–4.42 (m, 4H; $OC\underline{H}_2CH_2N$), 4.22 (d, 4H, $^2J = 12.5$ Hz; $ArCH_2Ar$), 3.75–3.66 (m, 4H; $OC\underline{H}_2CH_2CH_2$), 3.16 (d, 4H, $^2J = 12.5$ Hz; $ArCH_2Ar$), 2.37–2.30 (m, 4H; CH_2CO), 2.15–2.05 (m, 4H; $OCH_2C\underline{H}_2CH_2$), 1.12 (s, 18H; $C(CH_3)_3$), 0.95 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 174.30$ (C=O), 152.68, 152.46, 146.44, 144.71, 143.78, 133.76, 132.58, 130.81 (C_{Ar}), 128.88, 127.84, 125.21, 125.17, 124.68, 121.50 (CH_{Ar}), 74.38, 71.67 (OCH_2), 49.30 (NCH_2), 33.66, 33.43 ($\underline{C}(CH_3)_3$), 31.23, 31.02 ($C(\underline{C}H_3)_3$), 30.29, 30.24 ($ArCH_2Ar$, CH_2CO), 25.09 ($CH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m*/*z*: 1163.6585 $[M+H]^+$ for $C_{72}H_{87}N_6O_8$ (1163.6580).



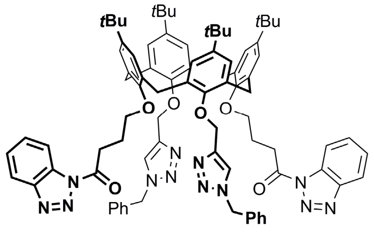
Triazolated calixarene bis(acid) ***38*** was prepared as described for compound **13** from calixarene **34** (1.55 g, 1.30 mmol) and K_2CO_3 (2.14 g, 15.5 mmol) in the mixture of methanol (103 mL), THF (26.3 mL) and water (10.3 mL). The product was additionally purified by crystallization from a dichloromethane solution upon addition of hexane. Yield 1.17 g (79%), white solid. M.p. 181–183 °C. ^1H NMR (400 MHz, DMSO-d_6): $\delta = 12.2$ (bs, 2H; CO_2H), 8.53 (s, 2H; ArH_{Trz}), 7.86–7.81 (m, 4H; ArH_{Ph}), 7.46–7.40 (m, 4H; ArH_{Ph}), 7.35–7.29 (m, 2H; ArH_{Ph}), 6.97 (s, 4H; ArH), 6.73 (s, 4H; ArH), 4.66–4.59 (m, 4H; NCH_2), 4.61 (s, 4H; CH_2CO), 4.46 (d, 4H, $^2J = 12.6$ Hz; $ArCH_2Ar$), 3.87–3.80 (m, 4H; $OC\underline{H}_2CH_2$), 3.19 (d, 4H, $^2J = 12.6$ Hz; $ArCH_2Ar$), 2.59–2.50 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.13 (s, 18H; $C(CH_3)_3$), 0.95 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 170.89$ (C=O), 152.30, 151.97, 146.36, 144.94, 144.30, 133.64, 132.82, 130.83 (C_{Ar}), 128.89, 127.80, 125.29, 125.17, 124.95, 121.22 (CH_{Ar}), 72.33, 71.50 (OCH_2), 47.16 (NCH_2), 33.66, 33.48 ($\underline{C}(CH_3)_3$), 31.19, 30.97 ($C(\underline{C}H_3)_3$), 30.27 ($ArCH_2Ar$), 22.09 ($CH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m*/*z*: 1135.6266 $[M+H]^+$ for $C_{70}H_{83}N_6O_8$ (1135.6267).



Triazolated calixarene bis(acid) ***39*** was prepared as described for compound **37** from calixarene **35** (0.947 g, 0.76 mmol) and K_2CO_3 (1.26 g, 9.13 mmol) in the mixture of methanol (60 mL), THF (16 mL) and water (6 mL). Yield 0.890 g (98%), white solid. M.p. 288–290 °C. ^1H NMR (400 MHz, DMSO-d_6): $\delta = 12.1$ (bs, 2H; CO_2H), 8.52 (s, 2H; ArH_{Trz}), 7.88–7.82 (m, 4H; ArH_{Ph}), 7.46–7.39 (m, 4H; ArH_{Ph}), 7.35–7.29 (m, 2H; ArH_{Ph}), 6.86 (s, 4H; ArH), 6.72 (s, 4H; ArH), 4.66–4.58 (m, 4H; NCH_2), 4.26 (d, 4H, ^{2}J = 12.5 Hz; $ArCH_2Ar$), 3.90–3.83 (m, 4H; $C\underline{H}_2CH_2CH_2N$), 3.82–3.74 (m, 4H; $OC\underline{H}_2CH_2CH_2CO$), 3.12 (d, 4H, ^{2}J = 12.5 Hz; $ArCH_2Ar$), 2.61–2.52 (m, 4H; $C\underline{H}_2CH_2N$), 2.41–2.34 (m, 4H; $C\underline{H}_2CO$), 2.17–2.08 (m, 4H; $C\underline{H}_2CH_2CO$), 1.07 (s, 18H; $C(CH_3)_3$), 0.98 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 174.34 (C=O), 152.98, 152.68, 146.42, 144.07, 143.67, 133.54, 132.92, 130.75 (C_{Ar}), 128.86, 127.82, 125.15, 124.90, 124.65, 121.19 (CH_{Ar}), 74.10, 71.61 (OCH_2), 47.03 (NCH_2), 33.54, 33.43 ($\underline{C}(CH_3)_3$), 31.17, 31.06 ($C(\underline{C}H_3)_3$), 30.50, 30.31, 30.22 ($CH_2\underline{C}H_2CH_2$, $ArCH_2Ar$, $\underline{C}H_2CO$), 25.12 ($CH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m*/*z*: 1191.6892 $[M+H]^+$ for $C_{74}H_{91}N_6O_8$ (1191.6893).

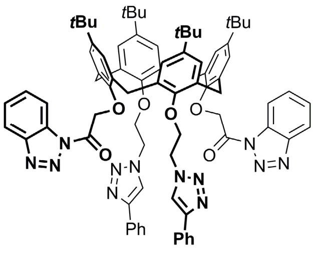


Triazolated calixarene bis(1-acylbenzotriazole) ***40***. To a stirred solution of 1,2,3-benzotriazole (0.410 g, 3.45 mmol) in dry dichloromethane (3 mL) $SOCl_2$ (0.094 mL, 1.29 mmol) was added. The mixture was stirred at room temperature for 20 min and then transferred to a stirred solution of bis(acid) **24** (0.477 g, 0.431 mmol) in dry dichloromethane (5.5 mL) and the mixture was stirred at room temperature for 24 h. Aqueous HCl (2 M, 8 mL) was added and the mixture was intensively stirred for 10 min. The organic layer was separated, the aqueous layer was washed with dichloromethane. The combined organic phase was washed twice with aqueous HCl (2 M), water, brine, dried, and then evaporated to dryness under reduced pressure. Yield 0.482 g (85%), white solid. M.p. 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16–8.10 (m, 2H; ArH_{Bt}), 7.99–7.94 (m, 2H; ArH_{Bt}), 7.74 (s, 2H; ArH_{Trz}), 7.59–7.47 (m, 4H; ArH_{Bt}), 7.22–7.14 (m, 6H; ArH_{Ph}), 7.13–7.05 (m, 4H; ArH_{Ph}), 7.00 (s, 4H; ArH), 6.59 (s, 4H; ArH), 5.81 (s, 4H; CH_2CO), 5.11 (s, 4H; NCH_2), 5.00 (s, 4H; OCH_2Trz), 4.79 (d, 4H, ^{2}J = 13.0 Hz; $ArCH_2Ar$), 3.18 (d, 4H, ^{2}J = 13.0 Hz; $ArCH_2Ar$), 1.24 (s, 18H; $C(CH_3)_3$), 0.95 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.31 (C=O), 153.58, 152.34, 145.63, 145.57, 145.13, 144.90, 135.40, 134.27, 132.68, 131.07 (C_{Ar}), 130.34, 125.67, 128.16, 127.71, 125.99, 125.88, 124.91, 123.61, 119.78, 114.29 (CH_{Ar}), 71.98 ($\underline{C}H_2CO$), 67.94 (OCH_2Trz), 53.45 (NCH_2), 33.98, 33.71 ($\underline{C}(CH_3)_3$), 31.92 ($ArCH_2Ar$), 31.50, 31.21 ($C(\underline{C}H_3)_3$) ppm. ESI-MS *m*/*z*: 1309.6716 $[M+H]^+$ for $C_{80}H_{85}N_{12}O_6$ (1309.6710).

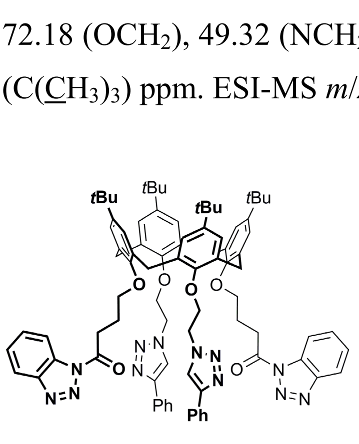


Triazolated calixarene bis(1-acylbenzotriazole) ***41*** was prepared as described for compound **5** from bis(acid) **25** (2.00 g, 1.72 mmol), 1,2,3-benzotriazole (0.818 g, 6.87 mmol) and DIC (1.06 mL, 6.87 mmol) in dry dichloromethane (85 mL). Methanol was replaced with ethanol at the purification step. Yield 2.04 g

(87%), white solid. M.p. 225–227 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09–8.00 (m, 4H; ArH_{Bt}), 7.63 (s, 2H; ArH_{Trz}), 7.43–7.38 (m, 4H; ArH_{Bt}), 7.26–7.22 (m, 6H; ArH_{Ph}), 7.17–7.11 (m, 4H; ArH_{Ph}), 6.98 (s, 4H; ArH), 6.50 (s, 4H; ArH), 5.36 (s, 4H; NCH_2), 4.93 (s, 4H; OCH_2Trz), 4.33 (d, 4H, ^2J = 12.6 Hz; $ArCH_2Ar$), 4.02–3.96 (m, 4H; $OC\underline{H}_2CH_2$), 3.42–3.35 (m, 4H; $C\underline{H}_2CO$), 2.98 (d, 4H, ^2J = 12.6 Hz; $ArCH_2Ar$), 2.44–2.34 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.26 (s, 18H; $C(CH_3)_3$), 0.87 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.70 (C=O), 154.01, 151.30, 146.07, 144.94, 144.79, 144.68, 135.14, 135.00, 132.72, 130.98 (C_{Ar}), 130.15, 128.85, 128.38, 127.80, 125.92, 125.29, 124.68, 123.54, 120.12, 114.01 (CH_{Ar}), 73.65 ($O\underline{C}H_2CH_2$), 67.58 (OCH_2Trz), 53.74 (NCH_2), 33.99, 33.62 ($\underline{C}(CH_3)_3$), 32.11 ($ArCH_2Ar$), 31.63 ($C(\underline{C}H_3)_3$), 31.13 ($C(\underline{C}H_3)_3$, $\underline{C}H_2CO$), 24.00 ($CH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m*/*z*: 1365.7333 $[M+H]^+$ for $C_{84}H_{93}N_{12}O_6$ (1365.7336).

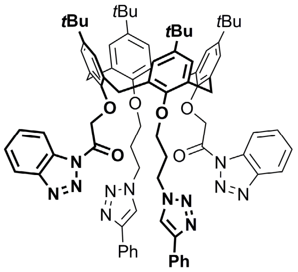


Triazolated calixarene bis(1-acylbenzotriazole) ***42*** was prepared as described for compound **5** from bis(acid) **36** (0.488 g, 0.44 mmol), 1,2,3-benzotriazole (0.210 g, 1.76 mmol) and DIC (0.272 mL, 1.76 mmol) in dry dichloromethane (21 mL). Yield 0.268 g (46%), white solid. M.p. 292–294 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 2H; ArH_{Trz}), 8.07–8.00 (m, 4H; ArH_{Bt}), 7.79–7.73 (m, 4H; ArH_{Ph}), 7.46–7.40 (m, 2H; ArH_{Bt}), 7.37–7.30 (m, 2H; ArH_{Bt}), 7.30–7.22 (m, 6H; ArH_{Ph}), 7.18 (s, 4H; ArH), 6.60 (s, 4H; ArH), 5.58 (s, 4H; CH_2CO), 5.54–5.47 (m, 4H; NCH_2), 4.81–4.74 (m, 4H; OCH_2), 4.52 (d, 4H, ^2J = 12.8 Hz; $ArCH_2Ar$), 3.34 (d, 4H, ^2J = 12.8 Hz; $ArCH_2Ar$), 1.34 (s, 18H; $C(CH_3)_3$), 0.89 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.02 (C=O), 153.62, 151.08, 147.44, 146.35, 146.01, 145.82, 134.83, 131.71, 130.85 (C_{Ar}), 130.82 (CH_{Ar}), 130.76 (C_{Ar}), 128.68, 127.76, 126.41, 125.99, 125.51, 125.36, 120.68, 120.18, 114.09 (CH_{Ar}), 73.56, 72.18 (OCH_2), 49.32 (NCH_2), 34.18, 33.75 ($\underline{C}(CH_3)_3$), 31.63 ($C(\underline{C}H_3)_3$), 31.10 ($ArCH_2Ar$), 31.03 ($C(\underline{C}H_3)_3$) ppm. ESI-MS *m*/*z*: 1309.6712 $[M+H]^+$ for $C_{80}H_{85}N_{12}O_6$ (1309.6710).

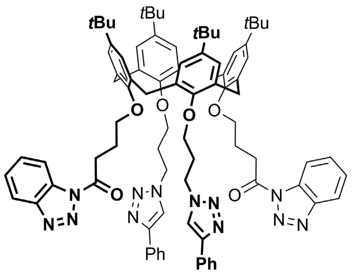


Triazolated calixarene bis(1-acylbenzotriazole) ***43*** was prepared as described for compound **5** from bis(acid) **37** (0.355 g, 0.306 mmol), 1,2,3-benzotriazole (0.145 g, 1.22 mmol) and DIC (0.190 mL, 1.22 mmol) in dry dichloromethane (15 mL). Yield 0.358 g (86%), white solid. M.p. 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 2H; ArH_{Trz}), 8.12–8.09 (m, 2H; ArH_{Bt}), 7.94–7.90 (m, 2H; ArH_{Bt}), 7.65–7.61 (m, 4H; ArH_{Ph}), 7.53–7.48 (m, 2H; ArH_{Bt}), 7.40–7.34 (m, 2H; ArH_{Bt}), 7.15–7.04 (m, 6H; ArH_{Ph}), 7.10 (s, 4H; ArH), 6.57 (s, 4H; ArH), 5.24–5.17 (m, 4H; NCH_2), 4.71–4.64 (m, 4H; $OC\underline{H}_2CH_2N$), 4.39 (d, 4H, ^2J = 12.8 Hz; $ArCH_2Ar$), 3.93–3.87 (m, 4H; $OC\underline{H}_2CH_2CH_2$), 3.63–3.57 (m, 4H; CH_2CO), 3.26

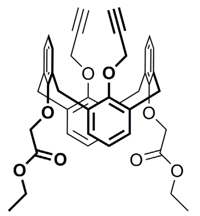
(d, 4H, ^2J = 12.8 Hz; $ArCH_2Ar$), 2.52–2.42 (m, 4H; $OCH_2C\underline{H}_2CH_2$), 1.30 (s, 18H; $C(CH_3)_3$), 0.89 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.69 (C=O), 152.67, 151.88, 147.67, 146.13, 145.91, 144.91, 134.89, 131.94, 130.96, 130.41 (C_{Ar}), 130.17, 128.40, 127.54, 125.87, 125.86, 125.46, 124.86, 120.35, 119.88, 114.37 (CH_{Ar}), 74.66, 71.66 (OCH_2), 49.48 (NCH_2), 34.10, 33.67 ($\underline{C}(CH_3)_3$), 32.43 ($ArCH_2Ar$), 31.58, 31.12 ($C(\underline{C}H_3)_3$), 30.89 ($\underline{C}H_2CO$), 24.80 ($CH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m/z*: 1365.7340 $[M+H]^+$ for $C_{84}H_{93}N_{12}O_6$ (1365.7336).



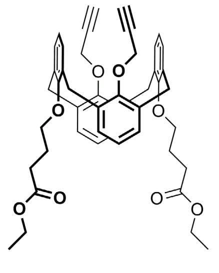
Triazolated calixarene bis(1-acylbenzotriazole) ***44*** was prepared as described for compound **5** from bis(acid) **38** (1.57 g, 1.38 mmol), 1,2,3-benzotriazole (0.657 g, 5.52 mmol) and DIC (0.853 mL, 5.52 mmol) in dry dichloromethane (68 mL). Yield 1.11 g (60%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07–8.02 (m, 2H; ArH_{Bt}), 7.91 (s, 2H; ArH_{Trz}), 7.78–7.71 (m, 6H; ArH_{Bt}+ArH_{Ph}), 7.41–7.27 (m, 10H, ArH_{Bt}+ArH_{Ph}), 7.04 (s, 4H; ArH), 6.67 (s, 4H; ArH), 6.03 (s, 4H; CH_2CO), 4.85 (d, 4H, ^2J = 13.0 Hz; $ArCH_2Ar$), 4.66–4.59 (m, 4H; NCH_2), 4.04–3.96 (m, 4H; $OC\underline{H}_2CH_2$), 3.35 (d, 4H, ^2J = 13.0 Hz; $ArCH_2Ar$), 2.71–2.58 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.24 (s, 18H; $C(CH_3)_3$), 0.99 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.27 (C=O), 153.18, 152.93, 147.48, 145.96, 145.44, 145.34, 133.91, 132.28 (C_{Ar}), 130.92 (CH_{Ar}), 130.85, 130.73 (C_{Ar}), 128.56, 127.79, 126.37, 126.21, 125.63, 125.17, 120.12, 119.65, 113.60 (CH_{Ar}), 72.47, 72.15 (OCH_2), 47.88 (NCH_2), 34.02, 33.78 ($\underline{C}(CH_3)_3$), 31.69 ($ArCH_2Ar$), 31.48, 31.25 ($C(\underline{C}H_3)_3$), 30.84 ($CH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m/z*: 1337.7024 $[M+H]^+$ for $C_{82}H_{89}N_{12}O_6$ (1337.7023).



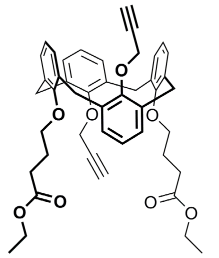
Triazolated calixarene bis(1-acylbenzotriazole) ***45*** was prepared as described for compound **5** from bis(acid) **39** (0.848 g, 0.713 mmol), 1,2,3-benzotriazole (0.339 g, 2.85 mmol) and DIC (0.441 mL, 2.85 mmol) in dry dichloromethane (37 mL). Yield 0.778 g (78%), white solid. M.p. 236–238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10–8.06 (m, 2H; ArH_{Bt}), 8.03–7.99 (m, 2H; ArH_{Bt}), 7.91 (s, 2H; ArH_{Trz}), 7.58–7.54 (m, 4H; ArH_{Ph}), 7.46–7.41 (m, 2H; ArH_{Bt}), 7.40–7.35 (m, 2H; ArH_{Bt}), 7.20–7.09 (m, 6H; ArH_{Ph}), 6.91 (s, 4H; ArH), 6.69 (s, 4H; ArH), 4.60–4.52 (m, 4H; NCH_2), 4.39 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 4.13–4.07 (m, 4H; $C\underline{H}_2CH_2CH_2N$), 4.02–3.96 (m, 4H; $OC\underline{H}_2CH_2CH_2CO$), 3.65–3.30 (m, 4H; $C\underline{H}_2CO$), 3.19 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 2.79–2.69 (m, 4H; $CH_2C\underline{H}_2CH_2$), 2.59–2.49 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.16 (s, 18H; $C(CH_3)_3$), 0.98 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.09 (C=O), 152.18, 152.64, 147.28, 146.00, 145.16, 144.79, 134.12, 132.87, 130.96, 130.48 (C_{Ar}), 130.26, 128.53, 127.67, 125.92, 125.38, 125.31, 125.01, 120.19, 119.92, 114.20 (CH_{Ar}), 74.35, 71.78 (OCH_2), 47.68 (NCH_2), 33.92, 33.74 ($\underline{C}(CH_3)_3$), 32.45 ($ArCH_2Ar$), 31.47, 31.27 ($C(\underline{C}H_3)_3$), 31.03, 31.01 (CH_2CO, $CH_2\underline{C}H_2CH_2$), 24.63 ($CH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m*/*z*: 1393.7654 $[M+H]^+$ for $C_{86}H_{97}N_{12}O_6$ (1393.7649).



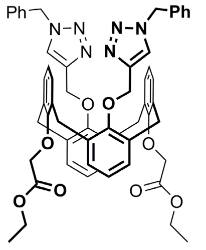
Propargylated calixarene bis(ester) ***48***. A mixture of dipropargyl ether **47** (1.20 g, 2.40 mmol), Cs_2CO_3 (3.91 g, 12.0 mmol) and dry acetone (50 mL) was stirred at room temperature for 24 h. Ethyl bromoacetate (1.60 mL, 14.4 mmol) was added and the mixture was stirred at room temperature for 48 h. The mixture was filtered, the solid was washed with acetone and the filtrate was concentrated under reduced pressure without heating. The residue was dissolved in dichloromethane, the solution was washed with aqueous HCl (2 M) and water, dried and then concentrated under reduced pressure (10^{-2} mm Hg) at 30 °C. The residue was dissolved in minimum amount of dichloromethane, methanol was added, and the solution was stored at –18 °C overnight. The crystals formed were collected, washed with cold methanol and dried to give a crude product, which was purified by column chromatography (silica, gradient from hexane to hexane/ethyl acetate 5:1). Yield 0.668 g (41%), white solid. M.p. 128–130 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.13 (d, 4H, ^3J = 7.5 Hz; ArH), 7.12 (d, 4H, ^3J = 7.5 Hz; ArH), 6.78 (t, 2H, ^3J = 7.5 Hz; ArH), 6.75 (t, 2H, ^3J = 7.5 Hz; ArH), 4.26 (d, 4H, ^4J = 2.4 Hz; $C\underline{H}_2CCH$), 4.16 (q, 4H, ^3J = 7.2 Hz; $C\underline{H}_2CH_3$), 3.88 (d, 4H, ^2J = 14.7 Hz; $ArCH_2Ar$), 3.80 (d, 4H, ^2J = 14.7 Hz; $ArCH_2Ar$), 3.60 (s, 4H, CH_2CO), 2.44 (t, 2H, ^4J = 2.4 Hz; CCH), 1.27 (t, 6H, ^3J = 7.2 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.81 (C=O), 155.72, 155.09, 134.77, 133.33 (C_{Ar}), 130.59, 130.12, 123.24, 122.67 (CH_{Ar}), 80.15 ($OCH_2\underline{C}$), 74.73 (CH), 68.97 ($O\underline{C}H_2CO$), 60.43 ($\underline{C}H_2CH_3$), 58.84 ($\underline{C}H_2CCH$), 36.73 ($ArCH_2Ar$), 14.12 (CH_3) ppm. ESI-MS *m*/*z*: 690.3083 $[M+NH_4]^+$ for $C_{42}H_{44}NO_8$ (690.3061).



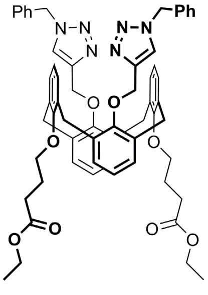
Propargylated calixarene bis(ester) ***49***. *Method A:* A mixture of dipropargyl ether **47** (1.20 g, 2.40 mmol), Cs_2CO_3 (2.40 g, 7.36 mmol) and dry acetone (50 mL) was stirred at room temperature for 24 h. Ethyl 4-bromobutyrate (2.10 mL, 14.7 mmol) was added and the mixture was stirred at 50 °C for 24 h. After cooling to room temperature, the mixture was filtered, the solid was washed with acetone and the filtrate was concentrated under reduced pressure without heating. The residue was dissolved in dichloromethane, the solution was washed with aqueous HCl (2 M) and water, dried and then concentrated under reduced pressure. The residue was purified by column chromatography (silica, gradient from hexane to hexane/ethyl acetate 5:1). Yield 0.285 g (16%), white solid. *Method B:* A mixture of bis(ester) **11** (1.30 g, 2.00 mmol), Cs_2CO_3 (2.61 g, 8.00 mmol) and dry DMF (60 mL) was stirred at room temperature for 30 min. Propargyl bromide (80% in toluene, 1.12 mL, 10.00 mmol) was added and the mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure at a moderate heating (< 45 °C). The residue was parted between dichloromethane and aqueous HCl (2 M), the organic phase was separated, washed with water, dried and then concentrated under reduced pressure. The residue was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 50:1), the obtained sample was dissolved in a minimum amount of dichloromethane, methanol was added, and the solid formed was collected, washed with methanol and dried. Yield 0.680 g (47%), white solid. M.p. 133–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (d, 4H, $^3J = 7.5$ Hz; ArH), 7.03 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.79 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.77 (t, 2H, $^3J = 7.5$ Hz; ArH), 4.17 (q, 4H, $^3J = 7.1$ Hz; $C\underline{H}_2CH_3$), 3.95 (d, 4H, $^4J = 2.3$ Hz; $C\underline{H}_2CCH$), 3.82 (d, 4H, $^2J = 14.8$ Hz; $ArCH_2Ar$), 3.66 (d, 4H, $^2J = 14.8$ Hz; $ArCH_2Ar$), 3.57–3.51 (m, 4H; $OC\underline{H}_2CH_2$), 2.39 (t, 2H, $^4J = 2.3$ Hz; CCH), 2.27–2.22 (m, 4H; CH_2CO), 1.88–1.80 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.30 (t, 6H, $^3J = 7.1$ Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.46 (C=O), 155.25, 155.27, 134.49, 133.66 (C_{Ar}), 130.26, 129.94, 122.57 (CH_{Ar}), 80.43 ($OCH_2\underline{C}$), 74.43 (CH), 70.04 ($O\underline{C}H_2CH_2$), 60.26 ($\underline{C}H_2CH_3$), 58.59 ($\underline{C}H_2CCH$), 37.21 ($ArCH_2Ar$), 30.47 ($\underline{C}H_2CO$), 25.31 ($CH_2\underline{C}H_2CH_2$), 14.27 (CH_3) ppm. ESI-MS *m*/*z*: 746.3710 $[M+NH_4]^+$ for $C_{46}H_{52}NO_8$ (746.3687).



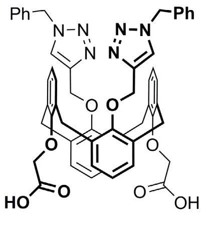
Propargylated calixarene bis(ester) ***50*** was obtained as a less polar product during the column purification of calixarene **49** (Method B). The separated product was dissolved in a minimum amount of dichloromethane, methanol was added, and the solid formed was collected, washed with methanol and dried. Yield 0.539 g (37%), white solid. M.p. 109–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, 2H, $^3J = 7.5$ Hz; ArH), 7.08 (d, 2H, $^3J = 7.5$ Hz; ArH), 7.03 (dd, 2H, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz; ArH), 6.97 (t, 1H, $^3J = 7.5$ Hz; ArH), 6.95–6.90 (m, 1H; ArH), 6.48 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.29 (dd, 2H, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz; ArH), 4.50 (d, 2H, $^4J = 2.4$ Hz; $C\underline{H}_2CCH$), 4.19 (d, 2H, $^2J = 13.8$ Hz; $ArCH_2Ar$), 4.17 (q, 4H, $^3J = 7.1$ Hz; $C\underline{H}_2CH_3$), 4.00 (d, 2H, $^4J = 2.4$ Hz; $C\underline{H}_2CCH$), 3.89–3.82 (m, 2H; $OC\underline{H}_2CH_2$), 3.77 (d, 2H, $^2J = 13.2$ Hz; $ArCH_2Ar$), 3.69–3.61 (m, 2H; $OC\underline{H}_2CH_2$), 3.66 (d, 2H, $^2J = 13.2$ Hz; $ArCH_2Ar$), 3.10 (d, 2H, $^2J = 13.8$ Hz; $ArCH_2Ar$), 2.66–2.48 (m, 4H; $CH_2C\underline{H}_2CH_2$), 2.55 (t, 1H, $^4J = 2.4$ Hz; CCH), 2.25–2.17 (m, 4H; CH_2CO), 2.18 (t, 1H, $^4J = 2.4$ Hz; CCH), 1.27 (t, 6H, $^3J = 7.1$ Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.26 (C=O), 156.30, 155.72, 153.78, 137.85, 134.32, 133.17, 131.54 (C_{Ar}), 130.52, 130.49, 129.22, 128.80, 128.36, 123.01, 122.09 (CH_{Ar}), 80.54, 80.53 ($OCH_2\underline{C}$), 74.86, 74.49 (CH), 73.11 ($O\underline{C}H_2CH_2$), 60.41, 59.61 ($\underline{C}H_2CCH$), 57.35 ($\underline{C}H_2CH_3$), 35.79, 31.37 ($ArCH_2Ar$), 31.00 ($\underline{C}H_2CO$), 25.80 ($CH_2\underline{C}H_2CH_2$), 14.23 (CH_3) ppm. ESI-MS *m*/*z*: 729.3437 $[M+H]^+$ for $C_{46}H_{49}O_8$ (729.3422).



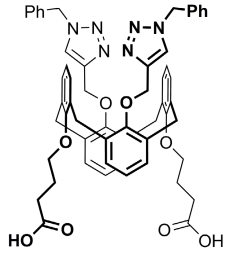
Triazolated calixarene bis(ester) **51**. Under argon, a freshly prepared solution of CuI (0.048 g, 0.25 mmol) and triethylamine (0.70 mL, 5.0 mmol) in toluene (6 mL) was added to a stirred solution of calixarene **48** (0.420 g, 0.625 mmol) in toluene (34 mL). Benzyl azide (0.200 g, 1.50 mmol) was added and the mixture was stirred at room temperature for 72 h. The solvent was removed under reduced pressure, the residue was suspended in dichloromethane, aqueous HCl (2 M) was added and the heterogeneous mixture was intensively stirred for at least 2 h. The organic phase was separated, the aqueous phase was extracted with dichloromethane. The combined organic fractions were washed with water, dried and the solvent was evaporated. The residue was dissolved in a minimum amount of dichloromethane, hexane was added, and the solid formed was separated, washed with hexane and dried. Yield 0.508 g (87%), white solid. M.p. 83–85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.33 (m, 6H; ArH_{Ph}), 7.31–7.26 (m, 4H; ArH_{Ph}), 7.05 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.78 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.68 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.43 (s, 2H; ArH_{Trz}), 6.08 (t, 2H, $^3J = 7.5$ Hz; ArH), 5.61 (s, 4H; NCH_2), 4.74 (s, 4H; OCH_2Trz), 4.03 (q, 4H, $^3J = 7.1$ Hz; $C\underline{H}_2CH_3$), 3.91 (d, 4H, $^2J = 15.9$ Hz; $ArCH_2Ar$), 3.44 (d, 4H, $^2J = 15.9$ Hz; $ArCH_2Ar$), 3.15 (s, 4H; CH_2CO), 1.16 (t, 6H, $^3J = 7.1$ Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.93 (C=O), 155.85, 154.78, 144.31, 135.27, 133.48 (C_{Ar}), 130.17, 130.15 (CH_{Ar}), 128.90 (C_{Ar}), 128.50, 127.73, 123.55, 123.47, 122.55 (CH_{Ar}), 68.11 ($\underline{C}H_2CO$), 64.32 (OCH_2Trz), 60.14 ($\underline{C}H_2CH_3$), 53.71 (NCH_2), 37.61 ($ArCH_2Ar$), 14.02 (CH_3) ppm. ESI-MS *m*/*z*: 939.4084 $[M+H]^+$ for $C_{56}H_{55}N_6O_8$ (939.4076).



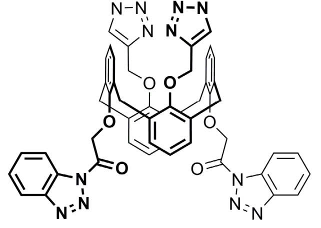
Triazolated calixarene bis(ester) **52** was prepared as described for compound **51** from calixarene **49** (0.524 g, 0.72 mmol), benzyl azide (0.230 g, 1.73 mmol), CuI (0.055 g, 0.29 mmol) and triethylamine (0.83 mL, 6.0 mmol) in toluene (50 mL). At the purification step, a dichloromethane/hexane solution was decanted from the product appeared as a viscous oil, which was then dried under reduced pressure. Yield 0.704 g (98%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.32 (m, 6H; ArH_{Ph}), 7.29–7.25 (m, 4H; ArH_{Ph}), 6.98 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.83–6.78 (m, 2H; ArH), 6.64 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.45 (s, 2H; ArH_{Trz}), 6.08 (t, 2H, $^3J = 7.5$ Hz; ArH), 5.58 (s, 4H; NCH_2), 4.68 (s, 4H; OCH_2Trz), 4.12 (q, 4H, $^3J = 7.1$ Hz; $C\underline{H}_2CH_3$), 3.62 (d, 4H, $^2J = 15.8$ Hz; $ArCH_2Ar$), 3.43 (d, 4H, $^2J = 15.8$ Hz; $ArCH_2Ar$), 3.40–3.35 (m, 4H; $OC\underline{H}_2CH_2$), 2.05–1.99 (m, 4H; CH_2CO), 1.62–1.53 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.27 (t, 6H, $^3J = 7.1$ Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.52 (C=O), 156.16, 155.16, 144.59, 135.33, 134.38, 133.43 (C_{Ar}), 129.47, 129.32, 128.81, 128.38, 127.65, 123.42, 122.80, 122.08 (CH_{Ar}), 68.86 ($OCH_2\underline{C}H_2$), 63.64 (OCH_2Trz), 60.09 ($\underline{C}H_2CH_3$), 53.57 (NCH_2), 37.70 ($ArCH_2Ar$), 30.28 ($\underline{C}H_2CO$), 24.94 ($CH_2\underline{C}H_2CH_2$), 14.24 (CH_3) ppm. ESI-MS *m*/*z*: 995.4704 $[M+H]^+$ for $C_{60}H_{63}N_6O_8$ (995.4702).



Triazolated calixarene bis(acid) **53** was prepared as described for compound **13** from calixarene **51** (0.508 g, 0.54 mmol) and K_2CO_3 (0.447 g, 3.24 mmol) in the mixture of methanol (40 mL), THF (8 mL) and water (4 mL). Yield 0.420 g (88%), white solid. M.p. 233–235 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.33 (m, 6H; ArH_{Ph}), 7.28–7.22 (m, 4H; ArH_{Ph}), 6.98–6.94 (m, 4H; ArH), 6.90–6.85 (m, 2H; ArH), 6.72 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.43 (s, 2H; ArH_{Trz}), 6.27 (t, 2H, $^3J = 7.5$ Hz; ArH), 5.58 (s, 4H; NCH_2), 4.71 (s, 4H; OCH_2Trz), 3.99 (s, 4H; CH_2CO), 3.63 (d, 4H, $^2J = 16.3$ Hz; $ArCH_2Ar$), 3.56 (d, 4H, $^2J = 16.2$ Hz; $ArCH_2Ar$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ = 170.44 (C=O), 154.77, 153.57, 144.06, 134.87, 134.06 (C_{Ar}), 133.11, 129.42 (CH_{Ar}), 129.23 (C_{Ar}), 128.69, 128.35, 127.43, 124.05, 123.30, 123.19 (CH_{Ar}), 66.59 ($O\underline{C}H_2CO$), 63.27 (OCH_2Trz), 53.48 (NCH_2), 37.17 ($ArCH_2Ar$) ppm. ESI-MS *m/z*: 883.3453 $[M+H]^+$ for $C_{52}H_{47}N_6O_8$ (883.3450).

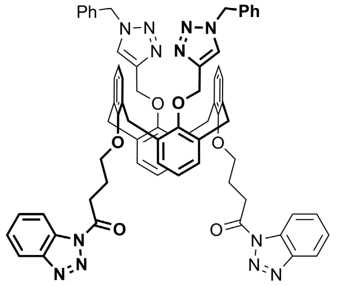


Triazolated calixarene bis(acid) **54** was prepared as described for compound **13** from calixarene **52** (0.700 g, 0.70 mmol) and K_2CO_3 (0.583 g, 4.23 mmol) in the mixture of methanol (25 mL), THF (15 mL) and water (5 mL). Yield 0.620 g (94%), white solid. M.p. 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.34 (m, 6H; ArH_{Ph}), 7.30–7.26 (m, 4H; ArH_{Ph}), 7.00–6.97 (m, 4H; ArH), 6.89–6.84 (m, 2H; ArH), 6.65 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.40 (s, 2H; ArH_{Trz}), 6.08 (t, 2H, $^3J = 7.5$ Hz; ArH), 5.60 (s, 4H; NCH_2), 4.69 (s, 4H; OCH_2Trz), 3.63 (d, 4H, $^2J = 16.0$ Hz; $ArCH_2Ar$), 3.45 (d, 4H, $^2J = 16.0$ Hz; $ArCH_2Ar$), 3.45–3.41 (m, 4H; $OC\underline{H_2}CH_2$), 2.02–1.95 (m, 4H; CH_2CO), 1.73–1.63 (m, 4H; $CH_2C\underline{H_2}CH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.86 (C=O), 156.19, 155.12, 144.46, 135.28, 134.43, 133.44 (C_{Ar}), 129.56, 129.36, 128.85, 128.44, 127.69, 123.57, 123.15, 122.31 (CH_{Ar}), 68.84 ($O\underline{C}H_2CH_2$), 63.48 (OCH_2Trz), 53.63 (NCH_2), 37.85 ($ArCH_2Ar$), 30.79 ($\underline{C}H_2CO$), 25.17 ($CH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m/z*: 939.4082 $[M+H]^+$ for $C_{56}H_{55}N_6O_8$ (939.4076).

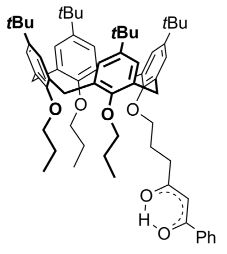


Triazolated calixarene bis(1-acylbenzotriazole) **55** was prepared as described for compound **40** from calixarene **53** (0.330 g, 0.374 mmol), 1,2,3-benzotriazole (0.440 g, 3.70 mmol) and $SOCl_2$ (0.109 mL, 1.50 mmol) in dry dichloromethane (35 mL). Yield 0.368 g (91%), white solid. M.p. 180–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28–8.23 (m, 2H; ArH_{Bt}), 7.71–7.67 (m, 2H; ArH_{Bt}), 7.66–7.61 (m, 2H; ArH_{Bt}), 7.47–7.31 (m, 12H; ArH_{Ph}+ArH_{Bt}), 7.07 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.75 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.48 (s, 2H; ArH_{Trz}), 6.27 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.08 (t, 2H, $^3J = 7.5$ Hz; ArH), 5.64 (s, 4H; NCH_2), 4.82 (s, 4H; CH_2CO), 4.54 (s, 4H; OCH_2Trz), 4.09 (d, 4H, $^2J = 15.8$ Hz; $ArCH_2Ar$), 3.51 (d, 4H, $^2J = 15.8$ Hz;

$ArCH_2Ar$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.94 (C=O), 156.02, 155.37, 145.39, 144.30, 135.54, 135.27, 133.55, 131.11 (C_{Ar}), 130.47, 130.39, 130.17, 129.00, 128.63, 127.87, 125.92, 123.72, 123.14, 122.73, 119.87, 114.12 (CH_{Ar}), 70.92, 64.34 (OCH_2), 53.85 (NCH_2), 37.56 ($ArCH_2Ar$) ppm. ESI-MS *m*/*z*: 1085.4207 $[M+H]^+$ for $C_{64}H_{53}N_{12}O_6$ (1085.4206).

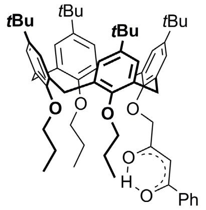


Triazolated calixarene bis(1-acylbenzotriazole) **56** was prepared as described for compound **40** from calixarene **54** (0.523 g, 0.558 mmol), 1,2,3-benzotriazole (0.664 g, 5.58 mmol) and $SOCl_2$ (0.163 mL, 2.23 mmol) in dry dichloromethane (60 mL). The product was additionally purified by rapid washing the sample with cold methanol. Yield 0.449 g (71%), white solid. M.p. 221–223 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.09–8.05 (m, 2H; ArH_{Bt}), 7.97–7.94 (m, 2H; ArH_{Bt}), 7.52–7.47 (m, 42; ArH_{Bt}), 7.42–7.33 (m, 8H; $ArH_{Ph}+ArH_{Bt}$), 7.29–7.25 (m, 4H; ArH_{Ph}), 7.04 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.78 (d, 4H, $^3J = 7.5$ Hz; ArH), 6.67 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.42 (s, 2H; ArH_{Trz}), 6.11 (t, 2H, $^3J = 7.5$ Hz; ArH), 5.59 (s, 4H; NCH_2), 4.70 (s, 4H; OCH_2Trz), 3.68 (d, 4H, $^2J = 16.0$ Hz; $ArCH_2Ar$), 3.48–3.43 (m, 4H; $OC\underline{H}_2CH_2$), 3.47 (d, 4H, $^2J = 16.0$ Hz; $ArCH_2Ar$), 3.11–3.06 (m, 4H; CH_2CO), 1.83–1.74 (m, 4H, $CH_2C\underline{H}_2CH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.25 (C=O), 156.07, 155.23, 145.92, 144.58, 135.38, 134.58, 133.57, 130.88 (C_{Ar}), 130.07, 129.53, 129.43, 128.87, 128.44, 127.72, 125.83, 123.48, 123.27, 122.38, 119.88, 114.21 (CH_{Ar}), 68.67, 63.66 (OCH_2), 53.64 (NCH_2), 37.89 ($ArCH_2Ar$), 31.92 ($\underline{C}H_2CO$), 24.26 ($CH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m*/*z*: 1141.4829 $[M+H]^+$ for $C_{68}H_{61}N_{12}O_6$ (1141.4832).

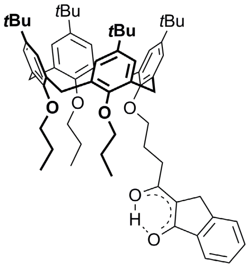


Calixarene 1,3-diketone **57**. At stirring or sonication, to a suspension of $MgBr_2 \cdot Et_2O$ (0.181 g, 0.70 mmol) in dry dichloromethane (4 mL) acetophenone (0.093 mL, 0.80 mmol) was added followed by DIPEA (0.122 mL, 0.70 mmol). The gel-like suspension formed was transferred to a stirred solution of calixarene **5** (0.192, 0.20 mmol) in dry dichloromethane (2 mL), and the mixture was stirred at room temperature for 2 h. Aqueous HCl (2 M) was added, and the mixture was intensively stirred. The organic phase was separated, the aqueous phase was extracted with dichloromethane. The combined organic phase was washed with water, brine, dried, and the solvent was evaporated under reduced pressure. To the resultant oil, a small portion of methanol was added, the mixture was cooled down to –18 °C and the solid formed was rapidly separated, washed with cold methanol and dried. The product was finally purified by column chromatography (silica, hexane/chloroform 1:1). Yield 0.130 g (68%), white solid. M.p. 115–117 °C. ^1H NMR (400 MHz, $CDCl_3$, only signals of enol form (92%) are presented): δ = 16.24 (bs, 1H; OH), 7.91–7.87 (m, 2H; ArH_{Ph}), 7.55–7.50 (m, 1H; ArH_{Ph}), 7.48–7.42 (m, 2H;

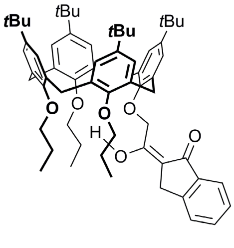
ArH_{Ph}), 6.84 (s, 2H; ArH), 6.84 (s, 2H; ArH), 6.70 (d, 2H, ^4J = 2.4 Hz; ArH), 6.68 (d, 2H, ^4J = 2.4 Hz; ArH), 6.22 (s, 1H; CH), 4.40 (d, 2H, ^2J = 12.4 Hz; $ArCH_2Ar$), 4.39 (d, 2H, ^2J = 12.4 Hz; $ArCH_2Ar$), 4.00–3.93 (m, 2H; OCH_2), 3.87–3.81 (m, 2H; OCH_2), 3.81–3.74 (m, 4H; OCH_2), 3.12 (d, 2H, ^2J = 12.4 Hz; $ArCH_2Ar$), 3.10 (d, 2H, ^2J = 12.4 Hz; $ArCH_2Ar$), 2.60–2.54 (m, 2H; $OCH_2C\underline{H}_2CH_2$), 2.48–2.38 (m, 2H; CH_2CO), 2.07–1.93 (m, 6H; $C\underline{H}_2CH_3$), 1.12 (s, 9H; $C(CH_3)_3$), 1.12 (s, 9H; $C(CH_3)_3$), 1.01 (s, 18H; $C(CH_3)_3$), 0.98 (t, 6H, ^3J = 7.5 Hz; CH_3), 0.95 (t, 3H, ^3J = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of enol form are presented): δ = 195.91 (C=O), 183.97 (CH=$\underline{C}$–OH), 153.86, 153.64, 153.40, 144.57, 144.24, 144.13, 135.18, 134.20, 134.15, 133.43, 133.24 (C_{Ar}), 132.23, 128.59, 126.98, 125.09, 124.97, 124.85, 124.73 (CH_{Ar}), 95.98 ($\underline{C}$H=C–OH), 77.12, 76.86, 74.16 (OCH_2), 36.02 ($\underline{C}H_2CO$), 33.86, 33.84, 33.74 ($\underline{C}(CH_3)_3$), 31.52, 31.51, 31.39 ($C(\underline{C}H_3)_3$), 31.13, 31.07 ($ArCH_2Ar$), 26.48 ($OCH_2\underline{C}H_2CH_2$), 23.41, 23.24 ($\underline{C}H_2CH_3$), 10.42, 10.20 ($CH_3$) ppm. ESI-MS *m*/*z*: 980.6778 $[M+NH_4]^+$ for $C_{65}H_{90}NO_6$ (980.6763).



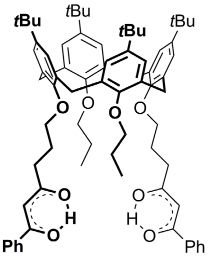
Calixarene 1,3-diketone ***58*** was prepared as described for compound **57** from calixarene **5** (0.075 g, 0.080 mmol), acetophenone (0.037 mL, 0.32 mmol), $MgBr_2·Et_2O$ (0.072 g, 0.28 mmol) and DIPEA (0.049 mL, 0.28 mmol) in dichloromethane (3 mL). At the final purification step, a gradient from dichloromethane to dichloromethane/ethanol 140:1 was used. Yield 0.044 g (59%), white solid. M.p. 77–79 °C. ^1H NMR (400 MHz, $CDCl_3$, only signals of enol form (90%) are presented): δ = 15.96 (bs, 1H; OH), 7.94–7.89 (m, 2H; ArH_{Ph}), 7.57–7.52 (m, 1H; ArH_{Ph}), 7.50–7.44 (m, 2H; ArH_{Ph}), 6.82 (s, 4H; ArH), 6.77 (bs, 2H; ArH), 6.76 (bs, 2H; ArH), 6.52 (s, 1H; CH), 4.72 (s, 2H; OCH_2CO), 4.55 (d, 2H, ^2J = 12.6 Hz; $ArCH_2Ar$), 4.41 (d, 2H, ^2J = 12.6 Hz; $ArCH_2Ar$), 3.88–3.83 (m, 4H; OCH_2), 3.79–3.74 (m, 2H; OCH_2), 3.20 (d, 2H, ^2J = 12.6 Hz; $ArCH_2Ar$), 3.12 (d, 2H, ^2J = 12.6 Hz; $ArCH_2Ar$), 2.12–1.92 (m, 6H; $C\underline{H}_2CH_3$), 1.11 (s, 18H; $C(CH_3)_3$), 1.07 (s, 18H; $C(CH_3)_3$), 1.02 (t, 3H, ^3J = 7.5 Hz; CH_3), 0.88 (t, 6H, ^3J = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of enol form are presented): δ = 191.44 (C=O), 184.81 (CH=$\underline{C}$–OH), 153.63, 153.48, 153.03, 144.77, 144.33, 144.28, 135.13, 134.06, 133.671, 133.669, 133.01 (C_{Ar}), 132.46, 128.63, 127.14, 125.29, 125.13, 124.87, 124.82 (CH_{Ar}), 95.53 ($\underline{C}$H=C–OH), 76.97, 76.88, 76.04 (OCH_2), 33.82, 33.80, 33.79 ($\underline{C}(CH_3)_3$), 31.47, 31.42, 31.38 ($C(\underline{C}H_3)_3$), 31.33, 31.09 ($ArCH_2Ar$), 23.46, 23.20 ($\underline{C}H_2CH_3$), 10.35, 10.19 (CH_3) ppm. ESI-MS *m*/*z*: 935.6182 $[M+H]^+$ for $C_{63}H_{83}O_6$ (935.6184).



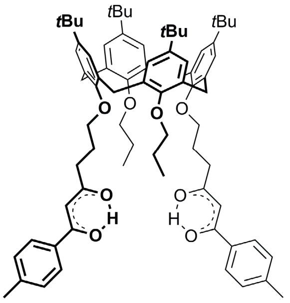
Calixarene 1,3-diketone ***59*** was prepared as described for compound **57** from calixarene **6** (0.048 g, 0.050 mmol), 1-indanone (0.026 g, 0.20 mmol), $MgBr_2\cdot Et_2O$ (0.045 g, 0.175 mmol) and DIPEA (0.030 mL, 0.175 mmol) in dichloromethane (2 mL). Repeated washing with methanol was sufficient to purify the product. Yield 0.038 g (78%), white solid. M.p. 188–190 °C. ^1H NMR (600 MHz, $CDCl_3$, only signals of enol form (79%) are presented): δ = 13.91 (bs, 1H; OH), 7.86–7.83 (m, 1H; ArH_{Ind}), 7.58–7.54 (m, 1H; ArH_{Ind}), 7.52–7.50 (m, 1H; ArH_{Ind}), 7.44–7.41 (m, 1H; ArH_{Ind}), 6.90 (s, 2H; ArH), 6.90 (s, 2H; ArH), 6.68 (d, 2H, $^4J = 2.3$ Hz; ArH), 6.65 (d, 2H, $^4J = 2.3$ Hz; ArH), 4.42 (d, 2H, $^2J = 12.4$ Hz; $ArCH_2Ar$), 4.41 (d, 2H, $^2J = 12.4$ Hz; $ArCH_2Ar$), 4.06–4.02 (m, 2H; OCH_2), 3.90–3.86 (m, 2H; OCH_2), 3.80–3.72 (m, 4H; OCH_2), 3.62 (s, 2H; $CH_{2\,Ind}$), 3.14 (d, 2H, $^2J = 12.4$ Hz; $ArCH_2Ar$), 3.12 (d, 2H, $^2J = 12.4$ Hz; $ArCH_2Ar$), 2.58–2.47 (m, 4H; $OCH_2C\underline{H_2}CH_2+CH_2CO$), 2.08–1.91 (m, 6H; $C\underline{H_2}CH_3$), 1.18 (s, 9H; $C(CH_3)_3$), 1.18 (s, 9H; $C(CH_3)_3$), 0.99 (s, 18H; $C(CH_3)_3$), 0.98 (t, 6H, $^3J = 7.5$ Hz; CH_3), 0.96 (t, 3H, $^3J = 7.5$ Hz; CH_3) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, only signals of enol form are presented): δ = 191.97 (C=O), 179.99 (C=$\underline{C}$–OH), 154.01, 153.76, 153.26, 147.49, 144.63, 144.28, 144.08, 138.40, 134.43, 134.42, 133.18, 132.98 (C_{Ar}), 132.77, 127.34, 125.69, 125.15, 125.03, 124.78, 124.64, 123.19 (CH_{Ar}), 109.85 ($\underline{C}$=C–OH), 77.19, 76.81, 74.18 (OCH_2), 33.90, 33.87, 33.70 ($\underline{C}(CH_3)_3$), 31.55, 31.54 ($C(\underline{C}H_3)_3$), 31.44 ($\underline{C}H_2CO$), 31.34 ($C(\underline{C}H_3)_3$), 31.15, 31.05 ($ArCH_2Ar$), 30.05 ($CH_{2\,Ind}$), 26.36 ($OCH_2\underline{C}H_2CH_2$), 23.42, 23.23 ($\underline{C}H_2CH_3$), 10.43, 10.14 ($CH_3$) ppm. ESI-MS *m*/*z*: 992.6772 $[M+NH_4]^+$ for $C_{66}H_{90}NO_6$ (992.6763).



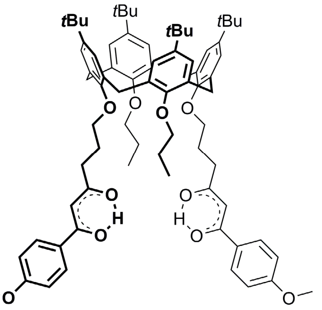
Calixarene 1,3-diketone ***60*** was prepared as described for compound **57** from calixarene **5** (0.033 g, 0.035 mmol), 1-indanone (0.019 g, 0.14 mmol), $MgBr_2\cdot Et_2O$ (0.032 g, 0.123 mmol) and DIPEA (0.021 mL, 0.123 mmol) in dichloromethane (1.3 mL). At the final purification step, a gradient from dichloromethane to dichloromethane/ethanol 100:1 was used for the column chromatography. Yield 0.018 g (54%), white solid. M.p. 216–218 °C. ^1H NMR (400 MHz, $CDCl_3$, only signals of non-canonical enol form (88%) are presented): δ = 9.75 (s, 1H; OH), 7.82–7.78 (m, 1H; ArH_{Ind}), 7.56–7.53 (m, 2H; ArH_{Ind}), 7.41–7.35 (m, 1H; ArH_{Ind}), 7.14 (s, 2H; ArH), 7.13 (s, 2H; ArH), 6.55 (d, 2H, $^4J = 2.4$ Hz; ArH), 6.51 (d, 2H, $^4J = 2.4$ Hz; ArH), 5.42 (bs, 2H; OCH_2CO), 4.46 (d, 2H, $^2J = 12.4$ Hz; $ArCH_2Ar$), 4.29 (d, 2H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 4.15–4.09 (m, 2H; OCH_2), 3.83 (s, 2H; $CH_{2\,Ind}$), 3.72–3.58 (m, 4H; OCH_2), 3.20 (d, 2H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 3.13 (d, 2H, $^2J = 12.4$ Hz; $ArCH_2Ar$), 2.07–1.94 (m, 2H; $C\underline{H_2}CH_3$), 1.85–1.70 (m, 4H; $C\underline{H_2}CH_3$), 1.34 (s, 9H; $C(CH_3)_3$), 1.33 (s, 9H; $C(CH_3)_3$), 0.95 (t, 3H, $^3J = 7.5$ Hz; CH_3), 0.82 (t, 6H, $^3J = 7.5$ Hz; CH_3), 0.82 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of non-canonical enol form are presented): δ = 193.58 (C=O), 164.13 (C=$\underline{C}$–OH), 154.49, 152.26, 151.21, 147.97, 146.57, 144.88, 144.62, 141.02, 135.48, 135.39 (C_{Ar}), 132.54 (CH_{Ar}), 132.36, 132.05 (C_{Ar}), 126.79, 125.84, 125.71, 125.31, 124.80, 124.71, 123.03 (CH_{Ar}), 108.30 ($\underline{C}$=C–OH), 78.11, 77.70, 70.94 (OCH_2), 34.16, 34.05, 33.61 ($\underline{C}(CH_3)_3$), 31.75, 31.65, 31.06 ($C(\underline{C}H_3)_3$), 30.95, 29.67 ($ArCH_2Ar$, $CH_{2\,Ind}$), 23.02, 22.69 ($\underline{C}H_2CH_3$), 10.37, 9.95 (CH_3) ppm. ESI-MS *m*/*z*: 947.6184 $[M+H]^+$ for $C_{64}H_{83}O_6$ (947.6184).



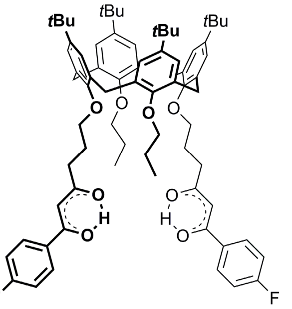
Calixarene bis(1,3-diketone) ***61*** was prepared as described for compound **57** from calixarene **8** (0.553 g, 0.50 mmol), acetophenone (0.466 mL, 4.00 mmol), $MgBr_2·Et_2O$ (0.903 g, 3.50 mmol) and DIPEA (0.608 mL, 3.50 mmol) in dichloromethane (40 mL). Repeated washing with cold methanol was sufficient to purify the product. Yield 0.415 g (75%), white solid. M.p. 158–160 °C. ^1H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (86%) are presented): δ = 16.26 (bs, 2H; OH), 7.88–7.84 (m, 4H; ArH_{Ph}), 7.52–7.47 (m, 2H; ArH_{Ph}), 7.44–7.38 (m, 4H; ArH_{Ph}), 6.93 (s, 4H; ArH), 6.61 (s, 4H; ArH), 6.23 (s, 2H; CH), 4.39 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 4.05–3.98 (m, 4H; OCH_2), 3.77–3.70 (m, 4H; OCH_2), 3.13 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 2.58–2.51 (m, 4H; CH_2CO), 2.49–2.39 (m, 4H; $OCH_2C\underline{H_2}CH_2$), 2.04–1.92 (m, 4H; $C\underline{H_2}CH_3$), 1.19 (s, 18H; $C(CH_3)_3$), 0.96 (t, 6H, ^3J = 7.5 Hz; CH_3), 0.94 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 195.25 (C=O), 183.66 (CH=$\underline{C}$–OH), 153.82, 153.06, 144.71, 144.13, 135.05, 134.64, 132.80 (C_{Ar}), 132.20, 128.56, 126.98, 125.23, 124.70 (CH_{Ar}), 96.07 ($\underline{C}$H=C–OH), 77.32, 74.11 (OCH_2), 35.92 ($\underline{C}H_2CO$), 33.93, 33.68 ($\underline{C}(CH_3)_3$), 31.57, 31.30 ($C(\underline{C}H_3)_3$), 31.13 ($ArCH_2Ar$), 26.37 ($OCH_2\underline{C}H_2CH_2$), 23.51 ($\underline{C}H_2CH_3$), 10.53 ($CH_3$) ppm. ESI-MS *m*/*z*: 1131.6688 $[M+Na]^+$ for $C_{74}H_{92}NaO_8$ (1131.6684).



Calixarene bis(1,3-diketone) ***62*** was prepared as described for compound **57** from calixarene **8** (0.553 g, 0.50 mmol), 4'-methylacetophenone (0.536 mL, 4.00 mmol), $MgBr_2·Et_2O$ (0.903 g, 3.50 mmol) and DIPEA (0.608 mL, 3.50 mmol) in dichloromethane (40 mL). Repeated washing with cold methanol was sufficient to purify the product. Yield 0.406 g (71%), white solid. M.p. 126–128 °C. ^1H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (82%) are presented): δ = 16.31 (bs, 2H; OH), 7.79–7.74 (m, 4H; ArH_{Tol}), 7.23–7.18 (m, 4H; ArH_{Tol}), 6.92 (s, 4H; ArH), 6.61 (s, 4H; ArH), 6.19 (s, 2H; CH), 4.39 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 4.03–3.97 (m, 4H; OCH_2), 3.77–3.71 (m, 4H; OCH_2), 3.12 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 2.55–2.49 (m, 4H; CH_2CO), 2.47–2.36 (m, 4H; $OCH_2C\underline{H_2}CH_2$), 2.38 (s, 6H; $PhCH_3$); 2.03–1.92 (m, 4H; $C\underline{H_2}CH_3$), 1.18 (s, 18H; $C(CH_3)_3$), 0.97 (t, 6H, ^3J = 7.5 Hz; CH_3), 0.94 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 195.45 (C=O), 184.11 (CH=$\underline{C}$–OH), 153.79, 153.04, 144.66, 144.09, 142.93, 134.61, 132.82, 132.33 (C$_{Ar}$), 129.28, 127.03, 125.19, 124.67 (CH$_{Ar}$), 95.66 ($\underline{C}$H=C–OH), 77.32, 74.12 (OCH$_2$), 35.71 ($\underline{C}$H$_2$CO), 33.91, 33.67 ($\underline{C}$(CH$_3$)$_3$), 31.56, 31.28 (C($\underline{C}$H$_3$)$_3$), 31.09 (ArCH$_2$Ar), 26.43 (OCH$_2\underline{C}$H$_2$CH$_2$), 23.50 ($\underline{C}$H$_2$CH$_3$), 21.57 (PhCH$_3$), 10.53 (CH$_3$) ppm. ESI-MS *m*/*z*: 1154.7432 [M+NH$_4$]$^+$ for $C_{76}H_{100}NO_8$ (1154.7443).

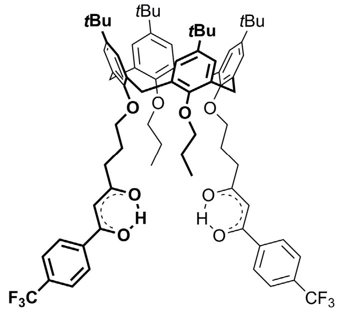


Calixarene bis(1,3-diketone) ***63*** was prepared as described for compound **57** from calixarene **8** (0.221 g, 0.20 mmol), 4'-methoxyacetophenone (0.240 mL, 1.60 mmol), MgBr$_2$·Et$_2$O (0.361 g, 1.40 mmol) and DIPEA (0.243 mL, 1.40 mmol) in dichloromethane (10 mL). Repeated washing with cold methanol was sufficient to purify the product. Yield 0.100 g (43%), white solid. M.p. 110–112 °C. ^{1}H NMR (400 MHz, CDCl$_3$, only signals of bis(enol) (73%) are presented): δ = 16.41 (bs, 2H; OH), 7.87–7.82 (m, 4H; ArH$_{PhOMe}$), 6.92 (s, 4H; ArH), 6.91–6.87 (m, 4H; ArH$_{PhOMe}$), 6.60 (s, 4H; ArH), 6.16 (s, 2H; CH), 4.39 (d, 4H, ^2J = 12.5 Hz; ArCH$_2$Ar), 4.03–3.98 (m, 4H; OCH$_2$), 3.83 (s, 6H; OCH$_3$), 3.76–3.70 (m, 4H; OCH$_2$), 3.12 (d, 4H, ^2J = 12.5 Hz; ArCH$_2$Ar), 2.53–2.47 (m, 4H; CH$_2$CO), 2.47–2.37 (m, 4H; OCH$_2$C$\underline{H}_2$CH$_2$), 2.03–1.91 (m, 4H; C$\underline{H}_2$CH$_3$), 1.19 (s, 18H; C(CH$_3$)$_3$), 0.97 (t, 6H, ^3J = 7.5 Hz; CH$_3$), 0.94 (s, 18H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 194.01 (C=O), 184.54 (CH=$\underline{C}$–OH), 162.98, 153.83, 153.02, 144.66, 144.07, 134.65, 132.77 (C$_{Ar}$), 129.08 (CH$_{Ar}$), 127.71 (C$_{Ar}$), 125.20, 124.65, 113.84 (CH$_{Ar}$), 95.14 ($\underline{C}$H=C–OH), 77.32, 74.14 (OCH$_2$), 55.37 (OCH$_3$), 35.38 ($\underline{C}$H$_2$CO), 33.92, 33.66 ($\underline{C}$(CH$_3$)$_3$), 31.56, 31.27 (C($\underline{C}$H$_3$)$_3$), 31.08 (ArCH$_2$Ar), 26.55 (OCH$_2\underline{C}$H$_2$CH$_2$), 23.50 ($\underline{C}$H$_2$CH$_3$), 10.55 (CH$_3$) ppm. ESI-MS *m*/*z*: 1191.6901 [M+Na]$^+$ for $C_{76}H_{96}NaO_{10}$ (1191.6896).

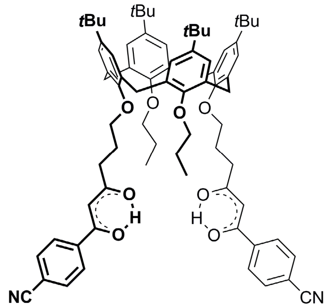


Calixarene bis(1,3-diketone) ***64*** was prepared as described for compound **57** from calixarene **8** (0.221 g, 0.20 mmol), 4'-fluoroacetophenone (0.194 mL, 1.60 mmol), MgBr$_2$·Et$_2$O (0.361 g, 1.40 mmol) and DIPEA (0.243 mL, 1.40 mmol) in dichloromethane (10 mL). Repeated washing with cold methanol was sufficient to purify the product. Yield 0.174 g (76%), white solid. M.p. 120–122 °C. ^{1}H NMR (400 MHz, CDCl$_3$, only signals of bis(enol) (85%) are presented): δ = 16.26 (bs, 2H; OH), 7.90–7.84 (m, 4H; ArH$_{PhF}$), 7.12–7.06 (m, 4H; ArH$_{PhF}$), 6.94 (s, 4H; ArH), 6.59 (s, 4H; ArH), 6.16 (s, 2H; CH), 4.38 (d, 4H, ^2J = 12.5 Hz; ArCH$_2$Ar), 4.04–3.98 (m, 4H; OCH$_2$), 3.76–3.70 (m, 4H; OCH$_2$), 3.12 (d, 4H, ^2J = 12.5 Hz; ArCH$_2$Ar), 2.55–2.49 (m, 4H; CH$_2$CO), 2.49–2.39 (m, 4H; OCH$_2$C$\underline{H}_2$CH$_2$), 2.02–1.90 (m, 4H; C$\underline{H}_2$CH$_3$), 1.20 (s, 18H; C(CH$_3$)$_3$), 0.96 (t, 6H,

^{3}J = 7.5 Hz; CH$_3$), 0.93 (s, 18H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 195.42 (C=O), 183.24 (CH=$\underline{\mathrm{C}}$–OH), 165.21 (d, $^{1}J_{\mathrm{C,F}}$ = 253.6 Hz; C$_{\mathrm{Ar}}$), 153.84, 152.95, 144.76, 144.14, 134.69, 132.69 (C$_{\mathrm{Ar}}$), 131.36 (d, $^{4}J_{\mathrm{C,F}}$ = 3.1 Hz; C$_{\mathrm{Ar}}$), 129.39 (d, $^{3}J_{\mathrm{C,F}}$ = 9.1 Hz; CH$_{\mathrm{Ar}}$), 125.24, 124.66 (CH$_{\mathrm{Ar}}$), 115.71 (d, $^{2}J_{\mathrm{C,F}}$ = 21.8 Hz; CH$_{\mathrm{Ar}}$), 95.73 ($\underline{\mathrm{C}}$H=C–OH), 77.32, 74.08 (OCH$_2$), 35.62 ($\underline{\mathrm{C}}$H$_2$CO), 33.94, 33.66 ($\underline{\mathrm{C}}$(CH$_3$)$_3$), 31.57, 31.26 (C($\underline{\mathrm{C}}$H$_3$)$_3$), 31.08 (ArCH$_2$Ar), 26.40 (OCH$_2\underline{\mathrm{C}}$H$_2$CH$_2$), 23.50 ($\underline{\mathrm{C}}$H$_2$CH$_3$), 10.55 (CH$_3$) ppm; ^{19}F NMR (376 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = –107.74 ppm. ESI-MS *m*/*z*: 1162.6941 [M+NH$_4$]$^+$ for $C_{74}H_{94}F_2NO_8$ (1162.6942).

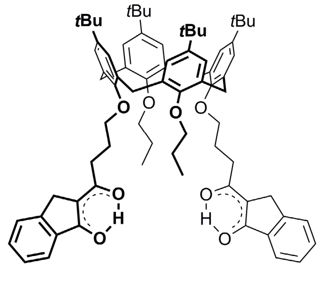


Calixarene bis(1,3-diketone) ***65*** was prepared as described for compound **57** from calixarene **8** (0.553 g, 0.50 mmol), 4'-(trifluoromethyl)acetophenone (0.752 mL, 4.00 mmol), MgBr$_2$·Et$_2$O (0.903 g, 3.50 mmol) and DIPEA (0.608 mL, 3.50 mmol) in dichloromethane (40 mL). Repeated washing with cold methanol was sufficient to purify the product. Yield 0.323 g (52%), white solid. M.p. 120–122 °C. ^{1}H NMR (400 MHz, CDCl$_3$, only signals of bis(enol) (95%) are presented): δ = 16.10 (bs, 2H; OH), 7.95–7.91 (m, 4H; ArH$_{\mathrm{PhCF3}}$), 7.68–7.63 (m, 4H; ArH$_{\mathrm{PhCF3}}$), 6.95 (s, 4H; ArH), 6.59 (s, 4H; ArH), 6.23 (s, 2H; CH), 4.38 (d, 4H, ^{2}J = 12.5 Hz; ArCH$_2$Ar), 4.05–3.99 (m, 4H; OCH$_2$), 3.76–3.70 (m, 4H; OCH$_2$), 3.13 (d, 4H, ^{2}J = 12.5 Hz; ArCH$_2$Ar), 2.61–2.54 (m, 4H; CH$_2$CO), 2.51–2.40 (m, 4H; OCH$_2$C$\underline{\mathrm{H}}_2$CH$_2$), 2.02–1.90 (m, 4H; C$\underline{\mathrm{H}}_2$CH$_3$), 1.21 (s, 18H; C(CH$_3$)$_3$), 0.97 (t, 6H, ^{3}J = 7.5 Hz; CH$_3$), 0.92 (s, 18H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 197.85 (C=O), 181.00 (CH=$\underline{\mathrm{C}}$–OH), 153.83, 152.88, 144.83, 144.16, 138.04, 134.70 (C$_{\mathrm{Ar}}$), 133.53 (q, $^{2}J_{\mathrm{C,F}}$ = 32.7 Hz; C$_{\mathrm{Ar}}$), 132.30 (C$_{\mathrm{Ar}}$), 127.17 (CH$_{\mathrm{Ar}}$), 125.53 (q, $^{3}J_{\mathrm{C,F}}$ = 3.7 Hz; CH$_{\mathrm{Ar}}$), 125.26, 124.65 (CH$_{\mathrm{Ar}}$), 123.59 (q, $^{1}J_{\mathrm{C,F}}$ = 272.7 Hz; CF$_3$), 96.74 ($\underline{\mathrm{C}}$H=C–OH), 77.32, 74.01 (OCH$_2$), 36.19 ($\underline{\mathrm{C}}$H$_2$CO), 33.92, 33.64 ($\underline{\mathrm{C}}$(CH$_3$)$_3$), 31.54, 31.22 (C($\underline{\mathrm{C}}$H$_3$)$_3$), 31.06 (ArCH$_2$Ar), 26.12 (OCH$_2\underline{\mathrm{C}}$H$_2$CH$_2$), 23.49 ($\underline{\mathrm{C}}$H$_2$CH$_3$), 10.54 (CH$_3$) ppm; ^{19}F NMR (376 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = –63.04 ppm. ESI-MS *m*/*z*: 1262.6876 [M+NH$_4$]$^+$ for $C_{76}H_{94}F_6NO_8$ (1262.6878).

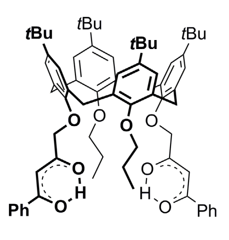


Calixarene bis(1,3-diketone) ***66*** was prepared as described for compound **57** from calixarene **8** (0.277 g, 0.25 mmol), 4'-cyanoacetophenone (0.290 g, 2.00 mmol), MgBr$_2$·Et$_2$O (0.452 g, 1.75 mmol) and DIPEA (0.304 mL, 1.75 mmol) in dichloromethane (20 mL), due to solubility issues, dry THF (1 mL) was added at the magnesium enolate preparation step. Repeated washing with cold methanol was sufficient to purify the product. Yield 0.143 g (49%), white solid. M.p. 111–

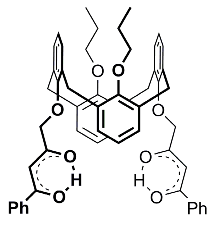
113 °C. ^{1}H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (95%) are presented): δ = 16.02 (bs, 2H; OH), 7.96–7.91 (m, 4H; ArH_{PhCN}), 7.74–7.69 (m, 4H; ArH_{PhCN}), 6.95 (s, 4H; ArH), 6.59 (s, 4H; ArH), 6.23 (s, 2H; CH), 4.37 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 4.04–3.98 (m, 4H; OCH_2), 3.76–3.69 (m, 4H; OCH_2), 3.13 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 2.61–2.55 (m, 4H; CH_2CO), 2.49–2.40 (m, 4H; $OCH_2C\underline{H}_2CH_2$), 2.01–1.90 (m, 4H; $C\underline{H}_2CH_3$), 1.20 (s, 18H; $C(CH_3)_3$), 0.96 (t, 6H, ^3J = 7.5 Hz; CH_3), 0.93 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 198.47 (C=O), 179.82 (CH=$\underline{C}$–OH), 153.79, 152.87, 144.87, 144.22, 138.69, 134.64, 132.61 (C_{Ar}), 132.36, 127.30, 125.27, 124.68 (CH_{Ar}), 118.02 (CN), 115.35 (C_{Ar}), 97.06 ($\underline{C}$H=C–OH), 77.29, 73.97 (OCH_2), 36.40 ($\underline{C}H_2CO$), 33.94, 33.66 ($\underline{C}(CH_3)_3$), 31.55, 31.24 ($C(\underline{C}H_3)_3$), 31.06 ($ArCH_2Ar$), 26.10 ($OCH_2\underline{C}H_2CH_2$), 23.49 ($\underline{C}H_2CH_3$), 10.56 ($CH_3$) ppm. ESI-MS *m*/*z*: 1176.7029 $[M+NH_4]^+$ for $C_{76}H_{94}N_3O_8$ (1176.7035).



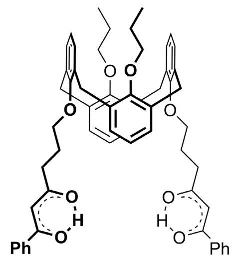
Calixarene bis(1,3-diketone) **67** was prepared as described for compound **57** from calixarene **8** (0.111 g, 0.10 mmol), 1-indanone (0.106 g, 0.80 mmol), $MgBr_2 \cdot Et_2O$ (0.181 g, 0.70 mmol) and DIPEA (0.122 mL, 0.70 mmol) in dichloromethane (7 mL). Repeated washing with cold methanol was sufficient to purify the product. Yield 0.080 g (70%), white solid. M.p. 239–241 °C. ^{1}H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (67%) are presented): δ = 13.88 (bs, 2H; OH), 7.77–7.74 (m, 2H; ArH_{Ind}), 7.55–7.51 (m, 2H; ArH_{Ind}), 7.49–7.46 (m, 2H; ArH_{Ind}), 7.37–7.33 (m, 2H; ArH_{Ind}), 7.02 (s, 4H; ArH), 6.58 (s, 4H; ArH), 4.42 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 4.12–4.07 (m, 4H; OCH_2), 3.75–3.71 (m, 4H; OCH_2), 3.58 (s, 4H; $CH_{2\,Ind}$), 3.15 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 2.58–2.48 (m, 8H; $OCH_2C\underline{H}_2CH_2$+$CH_2CO$), 2.01–1.92 (m, 4H; $C\underline{H}_2CH_3$), 1.26 (s, 18H; $C(CH_3)_3$), 0.98 (t, 6H, ^3J = 7.5 Hz; CH_3), 0.92 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, only signals of enol form are presented): δ = 191.63 (C=O), 180.19 (C=$\underline{C}$–OH), 154.03, 152.86, 147.49, 144.79, 144.04, 138.26, 134.98, 132.71 (C_{Ar}), 132.45, 127.23, 125.68, 125.31, 124.58, 123.00 (CH_{Ar}), 109.96 ($\underline{C}$=C–OH), 77.42, 74.11 (OCH_2), 33.96, 33.62 ($\underline{C}(CH_3)_3$), 31.62, 31.23 ($C(\underline{C}H_3)_3$), 31.13 ($ArCH_2Ar$, $\underline{C}H_2CO$), 30.02 ($CH_{2\,Ind}$), 26.18 ($OCH_2\underline{C}H_2CH_2$), 23.51 ($\underline{C}H_2CH_3$), 10.54 ($CH_3$) ppm. ESI-MS *m*/*z*: 1155.6678 $[M+Na]^+$ for $C_{76}H_{92}NaO_8$ (1155.6684).



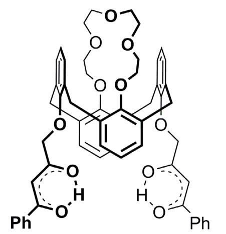
Calixarene bis(1,3-diketone) **68** was prepared as described for compound **57** from calixarene **7** (0.525 g, 0.50 mmol), acetophenone (0.466 mL, 4.00 mmol), $MgBr_2 \cdot Et_2O$ (0.903 g, 3.50 mmol) and DIPEA (0.608 mL, 3.50 mmol) in dichloromethane (40 mL), another portion of DIPEA (0.174 mL, 1.00 mmol) was added to the calixarene solution before addition of the prepared magnesium enolate of acetophenone. During the product purification, the sample obtained after extraction step was crystallized three times from a dichloromethane/methanol mixture. The obtained sample was passed though a layer of silica using dichloromethane/ethanol (20:1) mixture as an eluent. The solid colleted after removal of the solvents was dissolved in dichloromethane, and the solution was washed continuously with aqueous HCl (2 M) and water, dried, and the solvent was evaporated. The residue was crystallized from a dichloromethane/hexane mixture. Yield 0.154 g (29%), white solid. M.p. 185–187 °C. ^{1}H NMR (400 MHz, $CDCl_3$, only signals of canonical bis(enol) (76%) are presented): δ = 15.97 (bs, 2H; OH), 7.92–7.88 (m, 4H; ArH_{Ph}), 7.55–7.49 (m, 2H; ArH_{Ph}), 7.46–7.41 (m, 4H; ArH_{Ph}), 6.83 (s, 4H; ArH), 6.75 (s, 4H; ArH), 6.55 (s, 2H; CH), 4.69 (s, 4H; CH_2CO), 4.51 (d, 4H, ^{2}J = 12.7 Hz; $ArCH_2Ar$), 3.91–3.85 (m, 4H; OCH_2), 3.18 (d, 4H, ^{2}J = 12.7 Hz; $ArCH_2Ar$), 1.97–1.86 (m, 4H; $C\underline{H}_2CH_3$), 1.12 (s, 18H; $C(CH_3)_3$), 1.05 (s, 18H; $C(CH_3)_3$), 0.74 (t, 6H, ^{3}J = 7.4 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 190.76 (C=O), 185.19 (CH=$\underline{C}$–OH), 153.68, 152.90, 144.93, 144.52, 135.04, 133.85, 132.99 (C_{Ar}), 132.54, 128.65, 127.19, 125.27, 125.12 (CH_{Ar}), 95.77 ($\underline{C}$H=C–OH), 76.79, 76.07 (OCH_2), 33.85, 33.81 ($\underline{C}(CH_3)_3$), 31.48, 31.34 ($C(\underline{C}H_3)_3$), 31.12 ($ArCH_2Ar$), 23.10 ($\underline{C}H_2CH_3$), 10.10 (CH_3) ppm. ESI-MS *m*/*z*: 1053.6235 $[M+H]^+$ for $C_{70}H_{85}O_8$ (1053.6239).



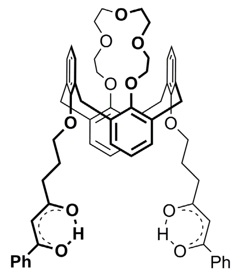
Calixarene bis(1,3-diketone) ***70*** was prepared as described for compound **57** from calixarene **10** (0.087 g, 0.105 mmol), acetophenone (0.098 mL, 0.84 mmol), $MgBr_2 \cdot Et_2O$ (0.190 g, 0.735 mmol) and DIPEA (0.128 mL, 0.735 mmol) in dichloromethane (10 mL), another portion of DIPEA (0.037 mL, 0.21 mmol) was added to the calixarene solution before addition of the prepared magnesium enolate of acetophenone. Repeated washing with cold methanol was sufficient to purify the product. Yield 0.067 g (77%), white solid. M.p. 213–215 °C. ^{1}H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (89%) are presented): δ = 16.06 (bs, 2H; OH), 7.95–7.90 (m, 4H; ArH_{Ph}), 7.50–7.39 (m, 6H; ArH_{Ph}), 7.07 (d, 4H, ^{3}J = 7.5 Hz; ArH), 7.03 (d, 4H, ^{3}J = 7.5 Hz; ArH), 6.76 (t, 2H, ^{3}J = 7.5 Hz; ArH), 6.49 (t, 2H, ^{3}J = 7.5 Hz; ArH), 6.44 (s, 2H; CH), 4.31 (s, 4H; CH_2CO), 3.66 (d, 4H, ^{2}J = 14.3 Hz; $ArCH_2Ar$), 3.61 (d, 4H, ^{2}J = 14.3 Hz; $ArCH_2Ar$), 3.62–3.56 (m, 4H; OCH_2), 1.82–1.71 (m, 4H; $OCH_2C\underline{H}_2$), 0.97 (t, 6H, ^{3}J = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 191.74 (C=O), 183.84 (CH=$\underline{C}$–OH), 156.77, 155.04, 134.37, 133.67, 133.23 (C_{Ar}), 132.72, 130.81, 130.41, 128.64, 127.35, 122.24, 121.65 (CH_{Ar}), 95.02 ($\underline{C}$H=C–OH), 73.82, 73.06 (OCH_2), 36.34 ($ArCH_2Ar$), 23.65 ($\underline{C}H_2CH_3$), 10.38 (CH_3) ppm. ESI-MS *m*/*z*: 846.4000 $[M+NH_4]^+$ for $C_{54}H_{56}NO_8$ (846.4000).



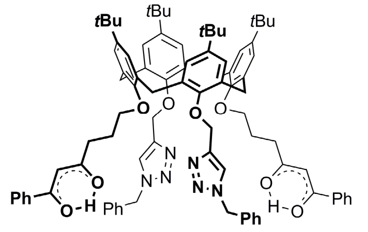
Calixarene bis(1,3-diketone) ***71*** was prepared as described for compound **57** from calixarene **14** (0.093 g, 0.105 mmol), acetophenone (0.098 mL, 0.84 mmol), MgBr$_2$·Et$_2$O (0.190 g, 0.735 mmol) and DIPEA (0.128 mL, 0.735 mmol) in dichloromethane (10 mL), another portion of DIPEA (0.037 mL, 0.21 mmol) was added to the calixarene solution before addition of the prepared magnesium enolate of acetophenone. At the final purification step, a gradient from dichloromethane to dichloromethane/ethanol 200:1 was used for the column chromatography. Yield 0.036 g (39%), white solid. M.p. 59–61 °C. ^{1}H NMR (400 MHz, CDCl$_3$, only signals of bis(enol) (60%) are presented): δ = 16.17 (bs, 2H; OH), 7.89–7.84 (m, 4H; ArH$_{Ph}$), 7.52–7.40 (m, 6H; ArH$_{Ph}$), 7.05 (d, 4H, ^3J = 7.5 Hz; ArH), 7.00 (d, 4H, ^3J = 7.5 Hz; ArH), 6.78 (t, 2H, ^3J = 7.5 Hz; ArH), 6.74 (t, 2H, ^3J = 7.5 Hz; ArH), 6.11 (s, 2H; CH), 3.74 (d, 4H, ^2J = 15.8 Hz; ArCH$_2$Ar), 3.71 (d, 4H, ^2J = 15.8 Hz; ArCH$_2$Ar), 3.59–3.54 (m, 4H; OCH$_2$), 3.45–3.40 (m, 4H; OCH$_2$), 2.31–2.26 (m, 4H; CH$_2$CO), 1.83–1.73 (m, 4H; OCH$_2$C$\underline{H_2}$), 1.43–1.30 (m, 4H; OCH$_2$C$\underline{H_2}$), 0.77 (t, 6H, ^3J = 7.5 Hz; CH$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 197.08 (C=O), 182.70 (CH=$\underline{C}$–OH), 156.79, 156.40, 134.81, 133.99, 133.68 (C$_{Ar}$), 132.19, 129.63, 129.47, 128.58, 126.89, 121.97, 121.74 (CH$_{Ar}$), 96.01 ($\underline{C}$H=C–OH), 72.56, 69.86 (OCH$_2$), 37.38 (ArCH$_2$Ar), 35.65 ($\underline{C}$H$_2$CO), 25.80 (CH$_2\underline{C}$H$_2$CH$_2$), 22.87 ($\underline{C}$H$_2$CH$_3$), 10.18 (CH$_3$) ppm. ESI-MS *m*/*z*: 902.4624 [M+NH$_4$]$^+$ for C$_{58}$H$_{64}$NO$_8$ (902.4626).



Calixarene bis(1,3-diketone) ***72*** was prepared as described for compound **57** from calixarene **16** (0.100 g, 0.111 mmol), acetophenone (0.104 mL, 0.89 mmol), MgBr$_2$·Et$_2$O (0.201 g, 0.78 mmol) and DIPEA (0.136 mL, 0.78 mmol) in dichloromethane (9 mL). The column purification using a gradient from dichloromethane to dichloromethane/ethanol 50:1 was applied first and the sample obtained was then crystallized from methanol. Yield 0.062 g (62%), white solid. M.p. 82–84 °C. ^{1}H NMR (600 MHz, CDCl$_3$, only signals of bis(enol) (73%) are presented): δ = 15.97 (bs, 2H; OH), 7.73–7.70 (m, 4H; ArH$_{Ph}$), 7.51–7.47 (m, 2H; ArH$_{Ph}$), 7.44–7.40 (m, 4H; ArH$_{Ph}$), 7.17 (d, 4H, ^3J = 7.5 Hz; ArH), 7.01 (d, 4H, ^3J = 7.5 Hz; ArH), 6.93 (t, 2H, ^3J = 7.5 Hz; ArH), 6.55 (t, 2H, ^3J = 7.5 Hz; ArH), 5.93 (s, 2H; CH), 4.07 (s, 4H; CH$_2$CO), 3.90 (d, 4H, ^2J = 15.7 Hz; ArCH$_2$Ar), 3.82 (d, 4H, ^2J = 15.7 Hz; ArCH$_2$Ar), 3.65–3.56 (m, 8H; OCH$_2$), 3.45–3.41 (m, 4H; OCH$_2$), 3.35–3.32 (m, 4H; OCH$_2$) ppm; ^{13}C NMR (150 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 192.18 (C=O), 183.35 (CH=$\underline{C}$–OH), 156.13, 155.96, 134.33, 134.28, 134.02 (C$_{Ar}$), 132.55, 130.37, 130.22, 128.45, 127.42, 123.23, 123.12 (CH$_{Ar}$), 95.12 ($\underline{C}$H=C–OH), 72.70 ($\underline{C}$H$_2$CO), 72.39, 70.64, 70.17, 69.15 (OCH$_2$), 37.89 (ArCH$_2$Ar) ppm. ESI-MS *m*/*z*: 920.4026 [M+NH$_4$]$^+$ for C$_{56}$H$_{58}$NO$_{11}$ (920.4004).

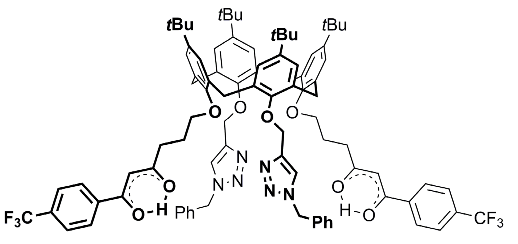


Calixarene bis(1,3-diketone) ***73*** was prepared as described for compound **57** from calixarene **18** (0.154 g, 0.161 mmol), acetophenone (0.150 mL, 1.29 mmol), MgBr$_2$·Et$_2$O (0.291 g, 1.13 mmol) and DIPEA (0.196 mL, 1.13 mmol) in dichloromethane (14 mL), another portion of DIPEA (0.056 mL, 0.32 mmol) was added to the calixarene solution before addition of the prepared magnesium enolate of acetophenone. At the final purification step, a gradient from dichloromethane to dichloromethane/ethanol 50:1 was used for the column chromatography. Yield 0.086 g (56%), yellow oil. ^{1}H NMR (600 MHz, CDCl$_3$, only signals of bis(enol) (71%) are presented): δ = 16.15 (bs, 2H; OH), 7.87–7.84 (m, 4H; ArH$_{\mathrm{Ph}}$), 7.51–7.47 (m, 2H; ArH$_{\mathrm{Ph}}$), 7.45–7.41 (m, 4H; ArH$_{\mathrm{Ph}}$), 7.10 (d, 4H, ^3J = 7.5 Hz; ArH), 7.08 (d, 4H, ^3J = 7.5 Hz; ArH), 6.89 (t, 2H, ^3J = 7.5 Hz; ArH), 6.88 (t, 2H, ^3J = 7.5 Hz; ArH), 6.04 (s, 2H; CH), 3.87 (d, 4H, ^2J = 16.2 Hz; ArCH$_2$Ar), 3.86 (d, 4H, ^2J = 16.2 Hz; ArCH$_2$Ar), 3.62–3.59 (m, 4H; OCH$_2$), 3.58–3.54 (m, 4H; OCH$_2$), 3.53–3.49 (m, 4H; OCH$_2$), 3.45–3.41 (m, 4H; OCH$_2$), 3.11–3.08 (m, 4H; OCH$_2$), 2.10–2.07 (m, 4H; CH$_2$CO), 1.57–1.50 (m, 4H; OCH$_2$C$\underline{\mathrm{H}}_2$) ppm; ^{13}C NMR (150 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 197.25 (C=O), 182.57 (CH=$\underline{\mathrm{C}}$–OH), 156.67, 156.19, 134.84, 134.15, 133.94 (C$_{\mathrm{Ar}}$), 132.15, 129.22, 129.18, 128.57, 126.84, 122.64, 122.50 (CH$_{\mathrm{Ar}}$), 95.94 ($\underline{\mathrm{C}}$H=C–OH), 72.81, 70.68, 69.68, 69.04, 67.98 (OCH$_2$), 38.17 (ArCH$_2$Ar), 35.50 ($\underline{\mathrm{C}}$H$_2$CO), 25.38 (CH$_2\underline{\mathrm{C}}$H$_2$CH$_2$) ppm. ESI-MS *m*/*z*: 976.4655 [M+NH$_4$]$^+$ for C$_{60}$H$_{66}$NO$_{11}$ (976.4630).

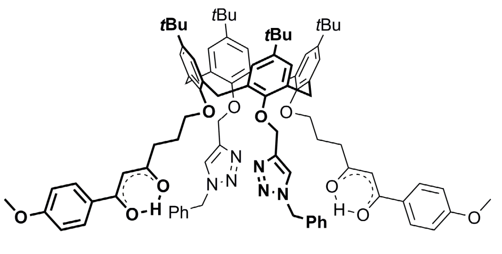


Calixarene bis(1,3-diketone) ***74*** was prepared as described for compound **57** from calixarene **41** (0.561 g, 0.411 mmol), acetophenone (0.383 mL, 3.29 mmol), MgBr$_2$·Et$_2$O (0.743 g, 2.88 mmol) and DIPEA (0.500 mL, 2.88 mmol) in dichloromethane (33 mL). Due to high solubility of the product in methanol, the crystallization step was skipped and the product was purified only by the column chromatography (gradient from dichloromethane to dichloromethane/ethanol 20:1). The obtained sample was dissolved in dichloromethane, and the solution was washed with aqueous HCl (2 M), water, dried, and the solvent was evaporated. Yield 0.264 g (47%), white solid. M.p. 102–104 °C. ^{1}H NMR (400 MHz, CDCl$_3$, only signals of bis(enol) (80%) are presented): δ = 16.29 (bs, 2H; OH), 7.94–7.89 (m, 4H; ArH$_{\mathrm{Ph}}$), 7.56 (s, 2H; ArH$_{\mathrm{Trz}}$), 7.52–7.46 (m, 2H; ArH$_{\mathrm{Ph}}$), 7.44–7.38 (m, 4H; ArH$_{\mathrm{Ph}}$), 7.34–7.28 (m, 6H; ArH$_{\mathrm{Ph}}$), 7.24–7.19 (m, 4H; ArH$_{\mathrm{Ph}}$), 6.85 (s, 4H; ArH), 6.54 (s, 4H; ArH), 6.29 (s, 2H; CH), 5.49 (s, 4H; NCH$_2$), 4.97 (s, 4H; OCH$_2$Trz), 4.24 (d, 4H, ^2J = 12.5 Hz; ArCH$_2$Ar), 3.84–3.78 (m, 4H; OCH$_2$), 2.92 (d, 4H, ^2J = 12.5 Hz; ArCH$_2$Ar), 2.35–2.28 (m, 4H; CH$_2$CO), 2.17–2.07 (m, 4H; OCH$_2$C$\underline{\mathrm{H}}_2$), 1.17 (s, 18H; C(CH$_3$)$_3$), 0.92 (s, 18H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 198.03 (C=O), 182.22

(CH=$\underline{\text{C}}$–OH), 153.75, 151.46, 144.79, 144.74, 144.66, 135.17, 134.66, 134.47, 133.23 (C$_{\text{Ar}}$), 132.18, 128.94, 128.58, 128.47, 127.93, 127.05, 125.12, 124.74, 123.73 (CH$_{\text{Ar}}$), 96.54 ($\underline{\text{C}}$H=C–OH), 73.97 (O$\underline{\text{C}}$H$_2$CH$_2$), 67.30 (OCH$_2$Trz), 53.81 (NCH$_2$), 35.97 ($\underline{\text{C}}$H$_2$CO), 33.90, 33.67 ($\underline{\text{C}}$(CH$_3$)$_3$), 31.54, 31.21 (C($\underline{\text{C}}$H$_3$)$_3$), 31.17 (ArCH$_2$Ar), 25.66 (OCH$_2$$\underline{\text{C}}H_2$) ppm. ESI-MS *m*/*z*: 1367.7526 [M+H]$^+$ for $C_{88}H_{99}N_6O_8$ (1367.7519).

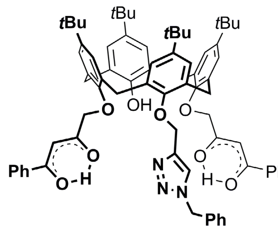


Calixarene bis(1,3-diketone) **75** was prepared as described for compound **57** from calixarene **41** (0.818 g, 0.600 mmol), 4'-(trifluoromethyl)-acetophenone (0.902 g, 4.80 mmol), $MgBr_2\cdot Et_2O$ (1.08 g, 4.20 mmol) and DIPEA (0.730 mL, 4.20 mmol) in dichloromethane (48 mL). Due to high solubility of the product in methanol, the crystallization step was skipped and the product was purified only by the column chromatography (gradient from dichloromethane to dichloromethane/ethanol 20:1). The obtained sample was dissolved in dichloromethane, and the solution was washed with aqueous HCl (2 M), water, dried, and the solvent was evaporated. Yield 0.495 g (55%), white solid. M.p. 180–182 °C. ^{1}H NMR (400 MHz, CDCl$_3$, only signals of bis(enol) (88%) are presented): δ = 16.08 (bs, 2H; OH), 8.05–8.00 (m, 4H; ArH$_{\text{PhCF3}}$), 7.66–7.61 (m, 4H; ArH$_{\text{PhCF3}}$), 7.46 (s, 2H; ArH$_{\text{Trz}}$), 7.37–7.31 (m, 6H; ArH$_{\text{Ph}}$), 7.27–7.21 (m, 4H; ArH$_{\text{Ph}}$), 6.84 (s, 4H; ArH), 6.56 (s, 4H; ArH), 6.41 (s, 2H; CH), 5.52 (s, 4H; NCH$_2$), 5.02 (s, 4H; OCH$_2$Trz), 4.21 (d, 4H, $^2J = 12.5$ Hz; ArCH$_2$Ar), 3.85–3.78 (m, 4H; OCH$_2$), 2.90 (d, 4H, $^2J = 12.5$ Hz; ArCH$_2$Ar), 2.45–2.39 (m, 4H; CH$_2$CO), 2.21–2.11 (m, 4H; OCH$_2$C$\underline{\text{H}}_2$), 1.17 (s, 18H; C(CH$_3$)$_3$), 0.94 (s, 18H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 199.32 (C=O), 179.73 (CH=$\underline{\text{C}}$–OH), 153.67, 151.32, 144.88, 144.75, 144.71, 137.87, 135.08, 134.30 (C$_{\text{Ar}}$), 133.37 (q, $^2J_{\text{C,F}} = 32.7$ Hz; C$_{\text{Ar}}$), 133.36 (C$_{\text{Ar}}$), 129.00, 128.59, 127.94, 127.37 (CH$_{\text{Ar}}$), 125.50 (q, $^3J_{\text{C,F}} = 3.8$ Hz; CH$_{\text{Ar}}$), 125.12, 124.78, 123.70 (CH$_{\text{Ar}}$), 123.67 (q, $^1J_{\text{C,F}} = 272.6$ Hz; CF$_3$), 97.30 ($\underline{\text{C}}$H=C–OH), 74.01 (O$\underline{\text{C}}$H$_2$CH$_2$), 67.12 (OCH$_2$Trz), 53.90 (NCH$_2$), 36.43 ($\underline{\text{C}}$H$_2$CO), 33.90, 33.70 ($\underline{\text{C}}$(CH$_3$)$_3$), 31.51, 31.22 (C($\underline{\text{C}}$H$_3$)$_3$), 31.19 (ArCH$_2$Ar), 25.58 (OCH$_2$$\underline{\text{C}}H_2$) ppm; ^{19}F NMR (376 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = –62.96 ppm. ESI-MS *m*/*z*: 1503.7275 [M+H]$^+$ for $C_{90}H_{97}F_6N_6O_8$ (1503.7267).

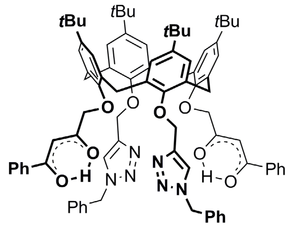


Calixarene bis(1,3-diketone) **76** was prepared as described for compound **57** from calixarene **41** (0.818 g, 0.600 mmol), 4'-methoxyacetophenone (0.720 g, 4.80 mmol), $MgBr_2\cdot Et_2O$ (1.08 g, 4.20 mmol) and DIPEA (0.730 mL, 4.20 mmol) in dichloromethane

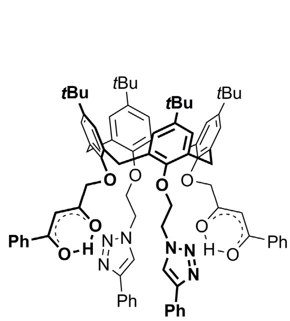
(48 mL). Due to high solubility of the product in methanol, the crystallization step was skipped and the product was purified only by the column chromatography (gradient from dichloromethane to dichloromethane/ethanol 20:1). The obtained sample was dissolved in dichloromethane, and the solution was washed with aqueous HCl (2 M), water, dried, and the solvent was evaporated. Yield 0.143 g (17%), white solid. M.p. 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (66%) are presented): δ = 16.47 (bs, 2H; OH), 7.93–7.88 (m, 4H; ArH_{PhOMe}), 7.59 (s, 2H; ArH_{Trz}), 7.34–7.27 (m, 6H; ArH_{Ph}), 7.25–7.19 (m, 4H; ArH_{Ph}), 6.93–6.88 (m, 4H; ArH_{PhOMe}), 6.86 (s, 4H; ArH), 6.54 (s, 4H; ArH), 6.21 (s, 2H; CH), 5.49 (s, 4H; NCH_2), 4.96 (s, 4H; OCH_2Trz), 4.25 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 3.84 (s, 6H; OCH_3), 3.83–3.78 (m, 4H; OCH_2), 2.93 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 2.30–2.23 (m, 4H; $C\underline{H}_2CO$), 2.16–2.06 (m, 4H; $OCH_2C\underline{H}_2$), 1.18 (s, 18H; $C(CH_3)_3$), 0.92 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 195.69 (C=O), 183.32 (CH=$\underline{C}$–OH), 162.99, 153.79, 151.50, 144.79, 144.71, 144.63, 135.18, 134.49, 133.18 (C_{Ar}), 129.19, 128.92, 128.45, 127.38, 125.12, 124.73, 123.75, 113.89 (CH_{Ar}), 95.55 ($\underline{C}$H=C–OH), 74.00 ($O\underline{C}H_2CH_2$), 67.33 (OCH_2Trz), 55.38 (OCH_3), 53.81 (NCH_2), 35.43 ($\underline{C}H_2CO$), 33.89, 33.66 ($\underline{C}(CH_3)_3$), 31.54, 31.20 ($C(\underline{C}H_3)_3$), 31.12 ($ArCH_2Ar$), 25.90 ($OCH_2\underline{C}H_2$) ppm. ESI-MS *m/z*: 1427.7734 $[M+H]^+$ for $C_{90}H_{103}N_6O_{10}$ (1427.7730).



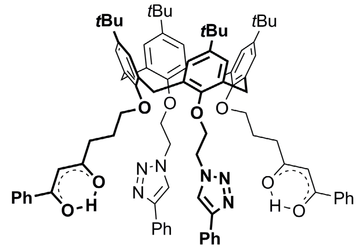
Calixarene bis(1,3-diketone) ***77*** was prepared as described for compound **57** from calixarene **40** (0.589 g, 0.450 mmol), acetophenone (0.419 mL, 3.60 mmol), $MgBr_2 \cdot Et_2O$ (0.813 g, 3.15 mmol) and DIPEA (0.548 mL, 3.15 mmol) in dichloromethane (32 mL). The reaction was conducted for 24 h. The crystallization step was skipped and the product was purified by the column chromatography (gradient from dichloromethane to dichloromethane/ethanol 20:1). The obtained sample was dissolved in dichloromethane, and the solution was washed with aqueous HCl (2 M), water, dried, and the solvent was evaporated. Yield 0.116 g (23%), white solid. M.p. 132–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (82%) are presented): δ = 15.67 (bs, 2H; CHC–O$\underline{H}$), 8.40 (s, 1H; ArH_{Trz}), 7.72–7.66 (m, 4H; ArH_{Ph}), 7.48–7.41 (m, 2H; ArH_{Ph}), 7.38–7.31 (m, 4H; ArH_{Ph}), 7.24–7.19 (m, 5H; ArH_{Ph}), 7.13 (s, 2H; ArH), 7.10 (s, 2H; ArH), 6.53 (d, 2H, ^4J = 2.8 Hz; ArH), 6.52 (d, 2H, ^4J = 2.8 Hz; ArH), 6.44 (s, 2H; CH), 6.34 (s, 1H; OH), 5.42 (s, 2H; NCH_2), 5.27 (s, 2H; OCH_2Trz), 4.42 (d, 2H, ^2J = 15.6 Hz; CH_2CO), 4.39 (d, 2H, ^2J = 13.2 Hz; $ArCH_2Ar$), 4.25 (d, 2H, ^2J = 12.9 Hz; $ArCH_2Ar$), 4.22 (d, 2H, ^2J = 15.6 Hz; CH_2CO), 3.27 (d, 2H, ^2J = 13.2 Hz; $ArCH_2Ar$), 3.17 (d, 2H, ^2J = 12.9 Hz; $ArCH_2Ar$), 1.34 (s, 9H; $C(CH_3)_3$), 1.32 (s, 9H; $C(CH_3)_3$), 0.80 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 191.71 (C=O), 183.00 (CH=$\underline{C}$–OH), 152.38, 151.18, 150.62, 146.59, 146.05, 145.06, 141.51, 135.76, 134.75, 134.10 (C_{Ar}), 132.45 (CH_{Ar}), 131.79, 131.73 (C_{Ar}), 128.83, 128.69, 128.57 (CH_{Ar}), 128.53 (C_{Ar}), 128.51, 128.46, 127.02, 125.83, 125.37, 125.23, 125.17 (CH_{Ar}), 94.21 ($\underline{C}H{=}C{-}OH$), 76.52 ($\underline{C}H_2CO$), 67.65 (OCH_2Trz), 54.20 (NCH_2), 34.16, 33.85, 33.66 ($\underline{C}(CH_3)_3$), 31.74, 31.61 ($C(\underline{C}H_3)_3$), 31.36, 31.19 ($ArCH_2Ar$), 30.91 ($C(\underline{C}H_3)_3$) ppm. ESI-MS *m*/*z*: 1140.6099 $[M+H]^+$ for $C_{74}H_{82}N_3O_8$ (1140.6096).



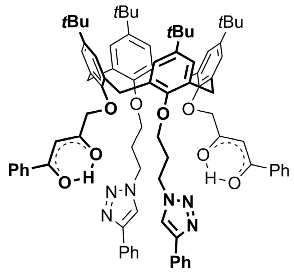
Calixarene bis(1,3-diketone) **78** was prepared as described for compound **57** from calixarene **40** (0.392 g, 0.300 mmol), acetophenone (0.280 mL, 2.40 mmol), $MgBr_2·Et_2O$ (0.542 g, 2.10 mmol) and DIPEA (0.365 mL, 2.10 mmol) in dichloromethane (24 mL), another portion of DIPEA (0.104 mL, 0.600 mmol) was added to the calixarene solution before addition of the prepared magnesium enolate of acetophenone. The reaction was conducted for 30 min. Due to instability of the product, no column separation was applied, and the sample obtained after the extraction step was washed with cold ethanol and then crystallized twice from a hexane/diethyl ether mixture. Yield 0.119 g (30%), white solid. M.p. 147–149 °C. ^1H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 15.73 (bs, 2H; OH), 7.88–7.83 (m, 4H; ArH_{Ph}), 7.59 (s, 2H; ArH_{Trz}), 7.47–7.41 (m, 2H; ArH_{Ph}), 7.36–7.30 (m, 4H; ArH_{Ph}), 7.30–7.23 (m, 6H; ArH_{Ph}), 7.19–7.14 (m, 4H; ArH_{Ph}), 6.74 (s, 4H; ArH), 6.67 (s, 4H; ArH), 6.32 (s, 2H; CH), 5.36 (s, 4H; NCH_2), 5.17 (s, 4H; OCH_2Trz), 4.64 (s, 4H; OCH_2CO), 4.40 (d, 4H, ^2J = 12.8 Hz; $ArCH_2Ar$), 3.01 (d, 4H, ^2J = 12.8 Hz; $ArCH_2Ar$), 1.08 (s, 18H; $C(CH_3)_3$), 1.02 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 192.68 (C=O), 183.01 ($CH{=}\underline{C}{-}OH$), 153.16, 152.15, 145.11, 145.04, 144.81, 135.10, 134.58, 134.19, 132.85 (C_{Ar}), 132.35, 128.89, 128.57, 128.41, 127.87, 127.83, 127.16, 125.15, 123.93 (CH_{Ar}), 95.38 ($\underline{C}H{=}C{-}OH$), 75.92 (CH_2CO), 66.46 (OCH_2Trz), 53.75 (NCH_2), 33.82, 33.75 ($\underline{C}(CH_3)_3$), 31.76 ($ArCH_2Ar$), 31.39, 31.29 ($C(CH_3)_3$) ppm. ESI-MS *m*/*z*: 1311.6895 $[M+H]^+$ for $C_{84}H_{91}N_6O_8$ (1311.6893).



Calixarene bis(1,3-diketone) **79** was prepared as described for compound **57** from calixarene **42** (0.392 g, 0.300 mmol), acetophenone (0.280 mL, 2.40 mmol), $MgBr_2·Et_2O$ (0.542 g, 2.10 mmol) and DIPEA (0.365 mL, 2.10 mmol) in dichloromethane (24 mL), another portion of DIPEA (0.104 mL, 0.600 mmol) was added to the calixarene solution before addition of the prepared magnesium enolate of acetophenone. Washing with cold methanol followed by crystallization from a diethyl ether/hexane mixture was sufficient to purify the product. Yield 0.225 g (57%), white solid. M.p. 149–151 °C. ^1H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (71%) are presented): δ = 15.62 (bs, 2H; OH), 7.87 (s, 2H; ArH_{Trz}), 7.77–7.70 (m, 8H; ArH$_{Ph}$), 7.43–7.36 (m, 2H; ArH$_{Ph}$), 7.33–7.22 (m, 10H; ArH$_{Ph}$), 7.12 (s, 4H; ArH), 6.54 (s, 4H; ArH), 6.26 (s, 2H; CH), 5.36–5.30 (m, 4H; NCH$_2$), 4.66–4.59 (m, 4H; $OC\underline{H}_2CH_2$), 4.57 (s, 4H; CH$_2$CO), 4.43 (d, 4H, $^2J = 12.8$ Hz; ArCH$_2$Ar), 3.23 (d, 4H, $^2J = 12.8$ Hz; ArCH$_2$Ar), 1.32 (s, 18H; C(CH$_3$)$_3$), 0.86 (s, 18H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 190.51 (C=O), 183.50 ($CH{=}\underline{C}$–OH), 153.48, 151.61, 147.69, 146.16, 145.39, 134.94, 133.99, 132.60, 131.84, 130.66 (C$_{Ar}$), 128.58, 128.55, 127.03, 125.79, 125.68, 125.63, 125.07, 120.29 (CH$_{Ar}$), 95.40 ($\underline{C}H{=}C$–OH), 77.21, 71.94 (OCH$_2$), 49.40 (NCH$_2$), 34.13, 33.67 ($\underline{C}(CH_3)_3$), 31.61, 31.03 (C(CH$_3$)$_3$), 30.70 (ArCH$_2$Ar) ppm. ESI-MS *m*/*z*: 1311.6897 [M+H]$^+$ for $C_{84}H_{91}N_6O_8$ (1311.6893).

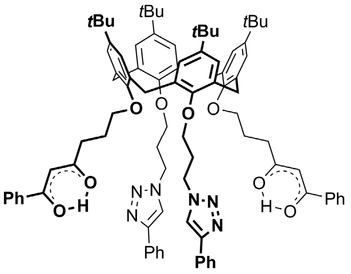


Calixarene bis(1,3-diketone) **80** was prepared as described for compound **57** from calixarene **43** (0.352 g, 0.258 mmol), acetophenone (0.240 mL, 2.06 mmol), MgBr$_2$·Et$_2$O (0.467 g, 1.81 mmol) and DIPEA (0.315 mL, 1.81 mmol) in dichloromethane (20 mL), another portion of DIPEA (0.090 mL, 0.516 mmol) was added to the calixarene solution before addition of the prepared magnesium enolate of acetophenone. Repeated washing with cold methanol was sufficient to purify the product. Yield 0.152 g (43%), white solid. M.p. 102–104 °C. ^{1}H NMR (400 MHz, CDCl$_3$, only signals of bis(enol) (73%) are presented): δ = 16.10 (bs, 2H; OH), 8.67 (s, 2H; ArH$_{Trz}$), 7.86–7.77 (m, 8H; ArH$_{Ph}$), 7.48–7.42 (m, 2H; ArH$_{Ph}$), 7.39–7.25 (m, 10H; ArH$_{Ph}$), 7.03 (s, 4H; ArH), 6.58 (s, 4H; ArH), 6.10 (s, 2H; CH), 5.22–5.16 (m, 4H; NCH$_2$), 4.64–4.57 (m, 4H; $OC\underline{H}_2CH_2N$), 4.32 (d, 4H, $^2J = 12.8$ Hz; ArCH$_2$Ar), 3.84–3.78 (m, 4H; $OC\underline{H}_2CH_2CH_2$), 3.22 (d, 4H, $^2J = 12.8$ Hz; ArCH$_2$Ar), 2.54–2.48 (m, 4H; CH$_2$CO), 2.33–2.23 (m, 4H; $C\underline{H}_2CH_2CO$), 1.25 (s, 18H; C(CH$_3$)$_3$), 0.91 (s, 18H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, only signals of bis(enol) are presented): δ = 197.07 (C=O), 182.08 ($CH{=}\underline{C}$–OH), 152.91, 152.25, 147.95, 146.05, 144.84, 134.59, 134.40 (C$_{Ar}$), 132.19 (CH$_{Ar}$), 132.17, 130.54 (C$_{Ar}$), 128.76, 128.52, 127.98, 126.97, 125.72, 125.69, 124.92, 120.38 (CH$_{Ar}$), 96.25 ($\underline{C}H{=}C$–OH), 74.95, 71.71 (OCH$_2$), 49.62 (NCH$_2$), 36.00 ($\underline{C}H_2CO$), 34.08, 33.70 ($\underline{C}(CH_3)_3$), 31.55, 31.17 (C(CH$_3$)$_3$), 31.08 (ArCH$_2$Ar), 26.06 ($OCH_2\underline{C}H_2CH_2$) ppm. ESI-MS *m*/*z*: 1367.7521 [M+H]$^+$ for $C_{88}H_{99}N_6O_8$ (1367.7519).

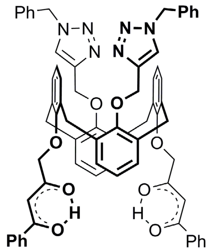


Calixarene bis(1,3-diketone) **81** was prepared as described for compound **57** from calixarene **44** (0.324 g, 0.243 mmol), acetophenone (0.226 mL, 1.94 mmol), MgBr$_2$·Et$_2$O (0.439 g, 1.70 mmol) and DIPEA (0.296 mL, 1.70 mmol) in dichloromethane (20 mL), another portion of DIPEA (0.084 mL, 0.486 mmol) was added to the calixarene solution before addition of the prepared magnesium enolate of acetophenone.

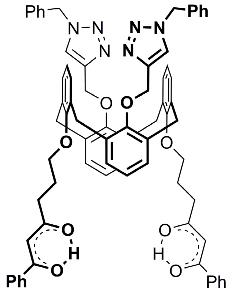
Washing with cold methanol followed by crystallization from a diethyl ether/hexane mixture was sufficient to purify the product. Yield 0.214 g (66%), white solid. M.p. 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 15.85 (bs, 2H; OH), 7.80–7.77 (m, 4H; ArH_{Ph}), 7.66 (s, 2H; ArH_{Trz}), 7.66–7.62 (m, 4H; ArH_{Ph}), 7.49–7.43 (m, 2H; ArH_{Ph}), 7.37–7.31 (m, 4H; ArH_{Ph}), 7.25–7.20 (m, 6H; ArH_{Ph}), 7.07 (s, 4H; ArH), 6.55 (s, 4H; ArH), 6.21 (s, 2H; CH), 4.56 (s, 4H; CH_2CO), 4.49 (d, 4H, ^2J = 12.7 Hz; $ArCH_2Ar$), 4.43–4.37 (m, 4H; NCH_2), 4.15–4.08 (m, 8H; OCH_2), 3.19 (d, 4H, ^2J = 12.7 Hz; $ArCH_2Ar$), 2.71–2.62 (m, 4H; $OCH_2C\underline{H}_2$), 1.28 (s, 18H; $C(CH_3)_3$), 0.87 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 190.60 (C=O), 183.82 (CH=$\underline{C}$–OH), 153.80, 151.87, 147.33, 145.38, 145.08, 135.01, 134.22 (C_{Ar}), 132.61 (CH_{Ar}), 132.05, 130.60 (C_{Ar}), 128.64, 127.75, 127.10, 125.63, 125.51, 125.47, 125.00, 120.13 (CH_{Ar}), 95.33 ($\underline{C}$H=C–OH), 76.85, 71.54 (OCH_2), 47.93 (NCH_2), 34.04, 33.66 ($\underline{C}(CH_3)_3$), 31.62, 31.09 ($C(CH_3)_3$), 31.06 ($ArCH_2Ar$), 30.84 ($OCH_2\underline{C}H_2$) ppm. ESI-MS *m*/*z*: 1339.7211 $[M+H]^+$ for $C_{86}H_{95}N_6O_8$ (1339.7206).



Calixarene bis(1,3-diketone) ***82*** was prepared as described for compound **57** from calixarene **45** (0.336 g, 0.241 mmol), acetophenone (0.225 mL, 1.93 mmol), $MgBr_2 \cdot Et_2O$ (0.436 g, 1.69 mmol) and DIPEA (0.294 mL, 1.69 mmol) in dichloromethane (16 mL), another portion of DIPEA (0.084 mL, 0.482 mmol) was added to the calixarene solution before addition of the prepared magnesium enolate of acetophenone. Repeated washing with cold methanol was sufficient to purify the product. Yield 0.219 g (65%), white solid. M.p. 185–187 °C. ^{1}H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (74%) are presented): δ = 16.21 (bs, 2H; OH), 7.84 (s, 2H; ArH_{Trz}), 7.83–7.79 (m, 4H; ArH_{Ph}), 7.77–7.73 (m, 4H; ArH_{Ph}), 7.48–7.43 (m, 2H; ArH_{Ph}), 7.38–7.22 (m, 10H; ArH_{Ph}), 6.89 (s, 4H; ArH), 6.65 (s, 4H; ArH), 6.21 (s, 2H; CH), 4.55–4.50 (m, 4H; NCH_2), 4.35 (d, 4H, ^2J = 12.7 Hz; $ArCH_2Ar$), 4.04–3.99 (m, 4H; OCH_2), 3.90–3.85 (m, 4H; OCH_2), 3.16 (d, 4H, ^2J = 12.7 Hz; $ArCH_2Ar$), 2.70–2.62 (m, 4H; $OCH_2C\underline{H}_2$), 2.60–2.54 (m, 4H; CH_2CO), 2.37–2.27 (m, 4H; $OCH_2C\underline{H}_2$), 1.16 (s, 18H; $C(CH_3)_3$), 0.97 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, only signals of bis(enol) are presented): δ = 197.26 (C=O), 182.35 (CH=$\underline{C}$–OH), 153.24, 152.67, 147.60, 145.19, 144.68, 134.47, 134.20, 132.89 (C_{Ar}), 132.26 (CH_{Ar}), 130.62 (C_{Ar}), 128.80, 128.57, 127.97, 127.00, 125.56, 125.38, 124.97, 120.14 (CH_{Ar}), 96.35 ($\underline{C}$H=C–OH), 74.61, 71.60 (OCH_2), 47.81 (NCH_2), 35.98 ($\underline{C}H_2CO$), 33.94, 33.75 ($\underline{C}(CH_3)_3$), 31.50, 31.29 ($C(CH_3)_3$, $ArCH_2Ar$), 31.07, 26.10 ($OCH_2\underline{C}H_2$) ppm. ESI-MS *m*/*z*: 1396.7865 $[M+H]^+$ for $C_{90}H_{103}N_6O_8$ (1396.7865).



Calixarene bis(1,3-diketone) ***83*** was prepared as described for compound **57** from calixarene **55** (0.467 g, 0.431 mmol), acetophenone (0.402 mL, 3.45 mmol), $MgBr_2 \cdot Et_2O$ (0.778 g, 3.02 mmol) and DIPEA (0.525 mL, 3.02 mmol) in dichloromethane (16 mL). Repeated washing with cold methanol was sufficient to purify the product. Yield 0.280 g (60%), white solid. M.p. 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (69%) are presented): δ = 15.98 (bs, 2H; OH), 7.80–7.73 (m, 4H; ArH_{Ph}), 7.51–7.27 (m, 16H; ArH_{Ph}), 6.94 (d, 4H, ^3J = 7.5 Hz; ArH), 6.72 (d, 4H, ^3J = 7.5 Hz; ArH), 6.68 (s, 2H; ArH_{Trz}), 6.51 (t, 2H, ^3J = 7.5 Hz; ArH), 6.08 (t, 2H, ^3J = 7.5 Hz; ArH), 6.05 (s, 2H; CH), 5.57 (s, 4H; NCH_2), 4.82 (s, 4H; OCH_2Trz), 4.02 (s, 4H; CH_2CO), 3.64 (d, 4H, ^2J = 15.2 Hz; $ArCH_2Ar$), 3.44 (d, 4H, ^2J = 15.2 Hz; $ArCH_2Ar$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.80 (C=O), 183.50 (CH=$\underline{C}$–OH), 155.30, 155.27, 144.66, 135.10, 134.41, 134.19, 133.31 (C_{Ar}), 132.65, 130.53, 130.23, 129.04, 128.68, 128.51, 127.92, 127.35, 123.44, 123.17, 122.39 (CH_{Ar}), 94.96 ($\underline{C}$H=C–OH), 72.65, 64.33 (OCH_2), 53.91 (NCH_2), 37.14 ($ArCH_2Ar$) ppm. ESI-MS *m*/*z*: 1087.4382 $[M+H]^+$ for $C_{68}H_{59}N_6O_8$ (1087.4389).



Calixarene bis(1,3-diketone) ***84*** was prepared as described for compound **57** from calixarene **56** (0.365 g, 0.320 mmol), acetophenone (0.298 mL, 2.56 mmol), $MgBr_2 \cdot Et_2O$ (0.578 g, 2.24 mmol) and DIPEA (0.389 mL, 2.24 mmol) in dichloromethane (25 mL), another portion of DIPEA (0.111 mL, 0.640 mmol) was added to the calixarene solution before addition of the prepared magnesium enolate of acetophenone. Due to instability of the product, no column separation was applied, and the sample obtained after the extraction step was washed with cold hexane, cold methanol and then with cold diethyl ether. Yield 0.231 g (71%), white solid. M.p. 67–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$, only signals of bis(enol) (68%) are presented): δ = 16.17 (bs, 2H; OH), 7.87–7.83 (m, 4H; ArH_{Ph}), 7.53–7.26 (m, 16H; ArH_{Ph}), 7.00 (d, 4H, ^3J = 7.5 Hz; ArH), 6.87–6.82 (m, 4H; ArH), 6.65 (t, 2H, ^3J = 7.5 Hz; ArH), 6.42 (s, 2H; ArH_{Trz}), 6.10 (t, 2H, ^3J = 7.5 Hz; ArH), 6.04 (s, 2H; CH), 5.59 (s, 4H; NCH_2), 4.67 (s, 4H; OCH_2Trz), 3.64 (d, 4H, ^2J = 16.0 Hz; $ArCH_2Ar$), 3.45–3.40 (m, 4H; $OC\underline{H_2}CH_2$), 3.44 (d, 4H, ^2J = 16.0 Hz; $ArCH_2Ar$), 2.13–2.08 (m, 4H; CH_2CO), 1.66–1.56 (m, 4H, $OCH_2C\underline{H_2}$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.22 (C=O), 182.50 (CH=$\underline{C}$–OH), 156.13, 155.23, 144.55, 135.34, 134.71, 134.50, 133.42 (C_{Ar}), 132.21, 129.42, 129.26, 128.83, 128.58, 128.40, 127.65, 126.82, 123.43, 122.84, 122.24 (CH_{Ar}), 95.94 ($\underline{C}$H=C–OH), 68.88, 63.57 (OCH_2), 53.59 (NCH_2), 37.80 ($ArCH_2Ar$), 35.39 ($\underline{C}H_2CO$), 25.51 ($OCH_2\underline{C}H_2$) ppm. ESI-MS *m*/*z*: 1143.5015 $[M+H]^+$ for $C_{72}H_{67}N_6O_8$ (1143.5015).

NMR spectra of novel compounds

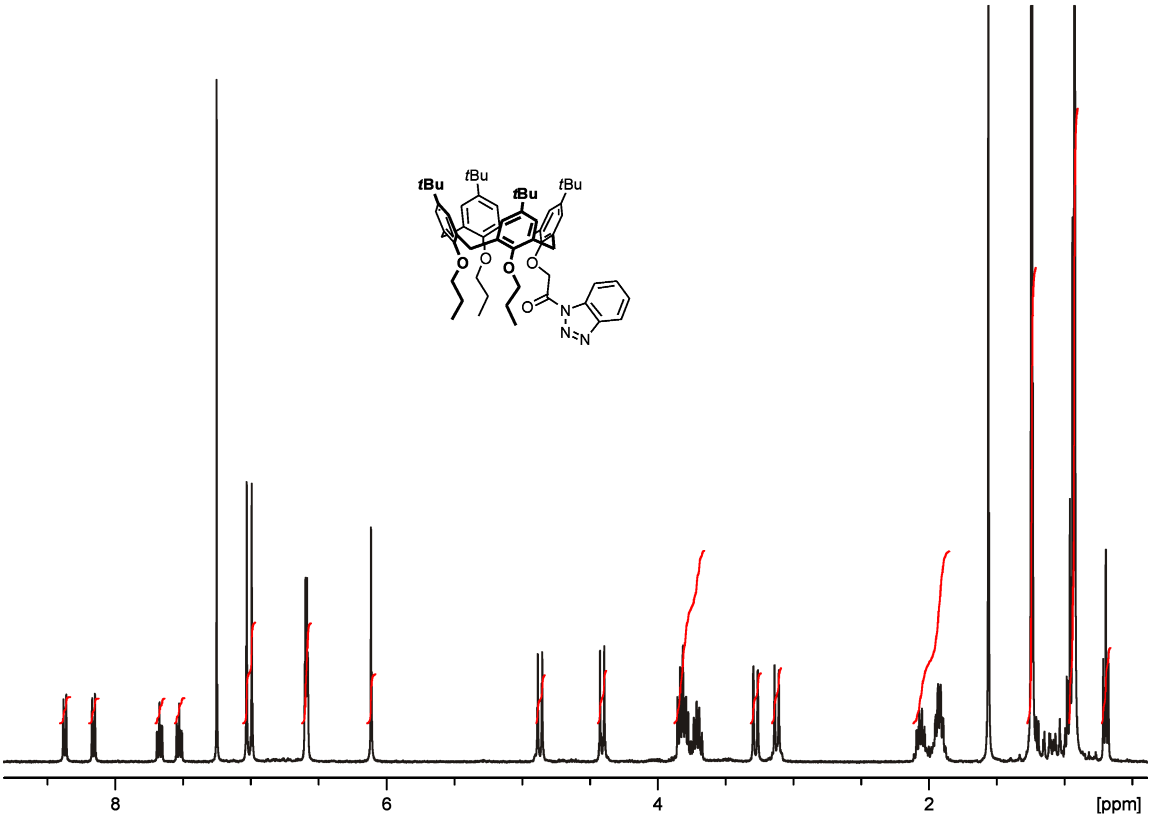


Figure S1. ^{1}H NMR spectrum of 1-acylbenzotriazole **5** (400 MHz, $CDCl_3$).

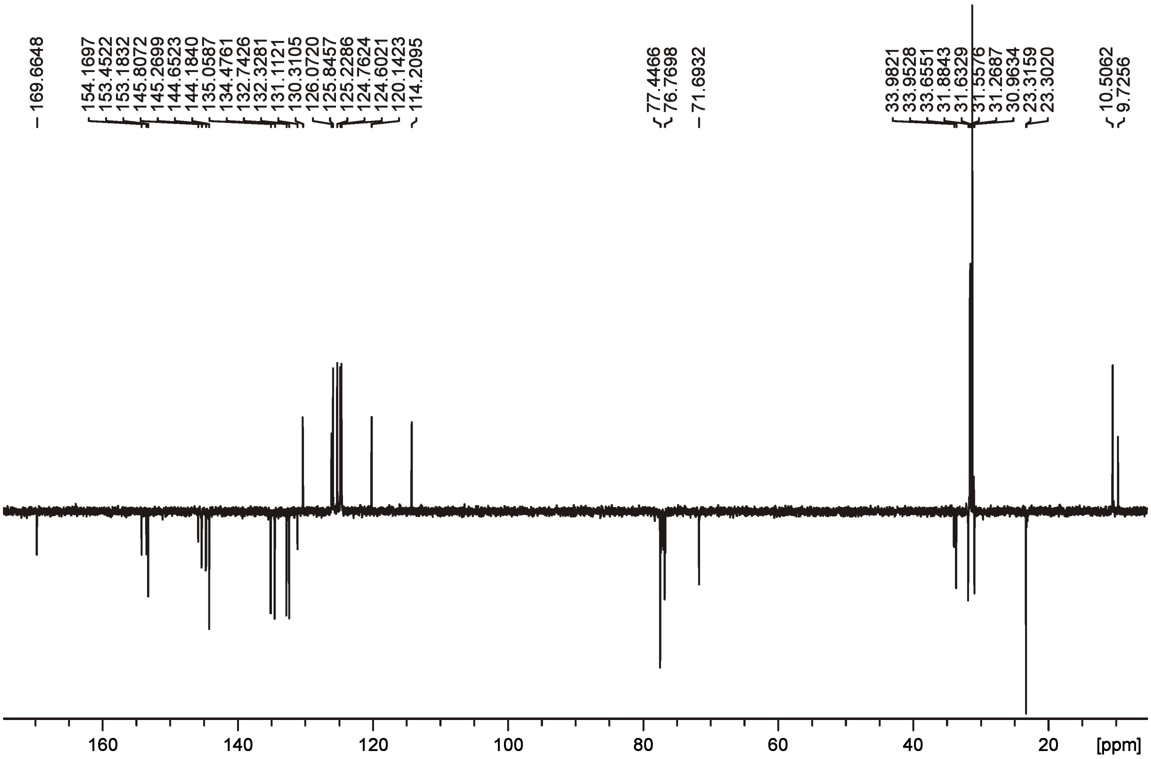


Figure S2. ^{13}C NMR spectrum (APT) of 1-acylbenzotriazole **5** (100 MHz, $CDCl_3$).

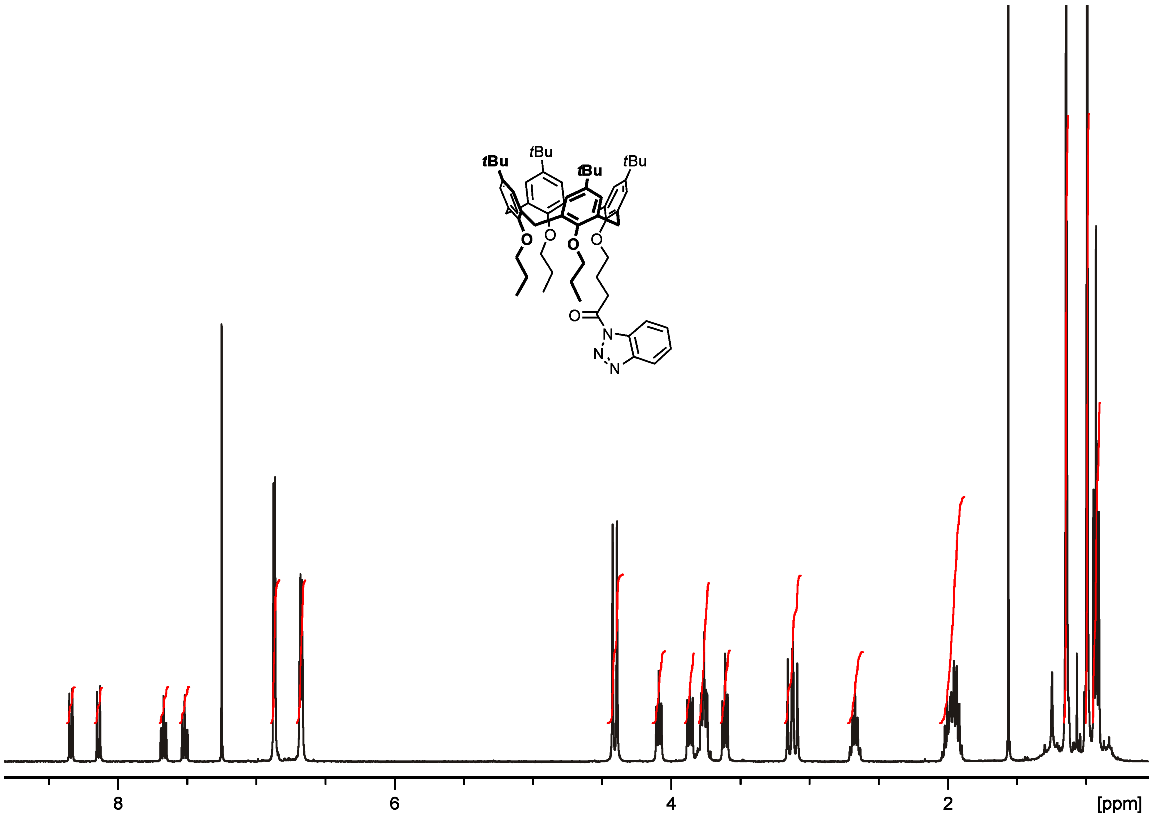


Figure S3. ^{1}H NMR spectrum of 1-acylbenzotriazole **6** (400 MHz, $CDCl_3$).

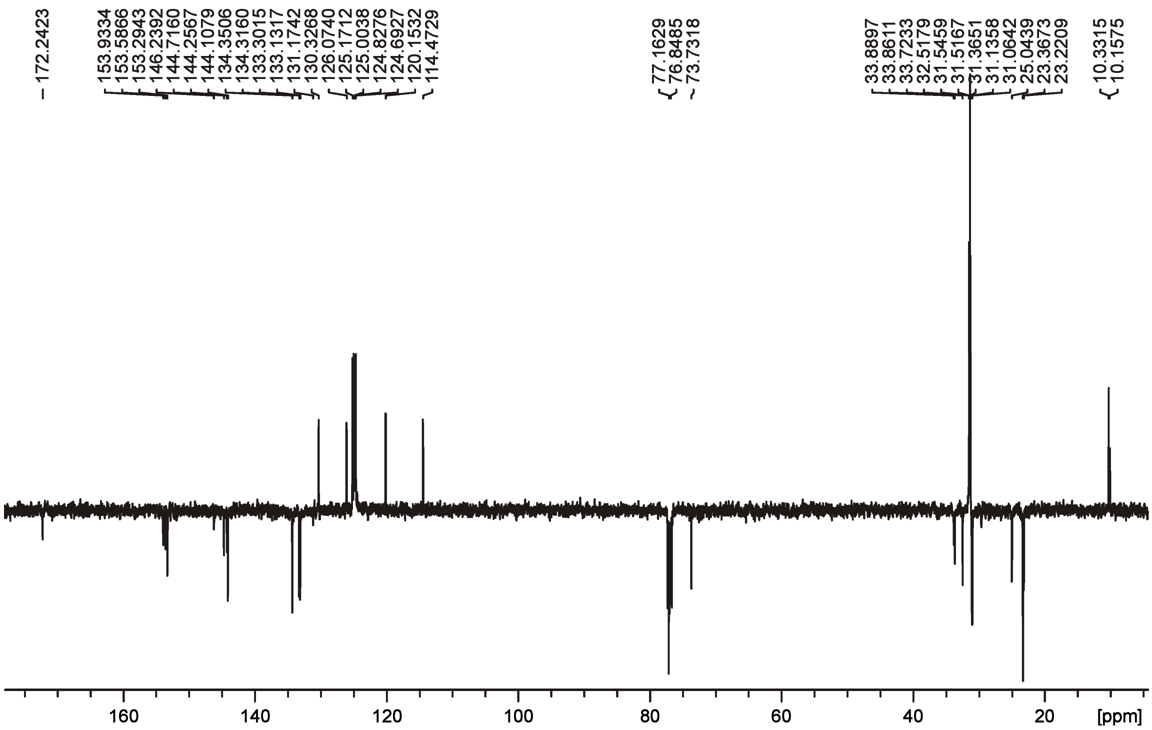


Figure S4. ^{13}C NMR spectrum (APT) of 1-acylbenzotriazole **6** (100 MHz, $CDCl_3$).

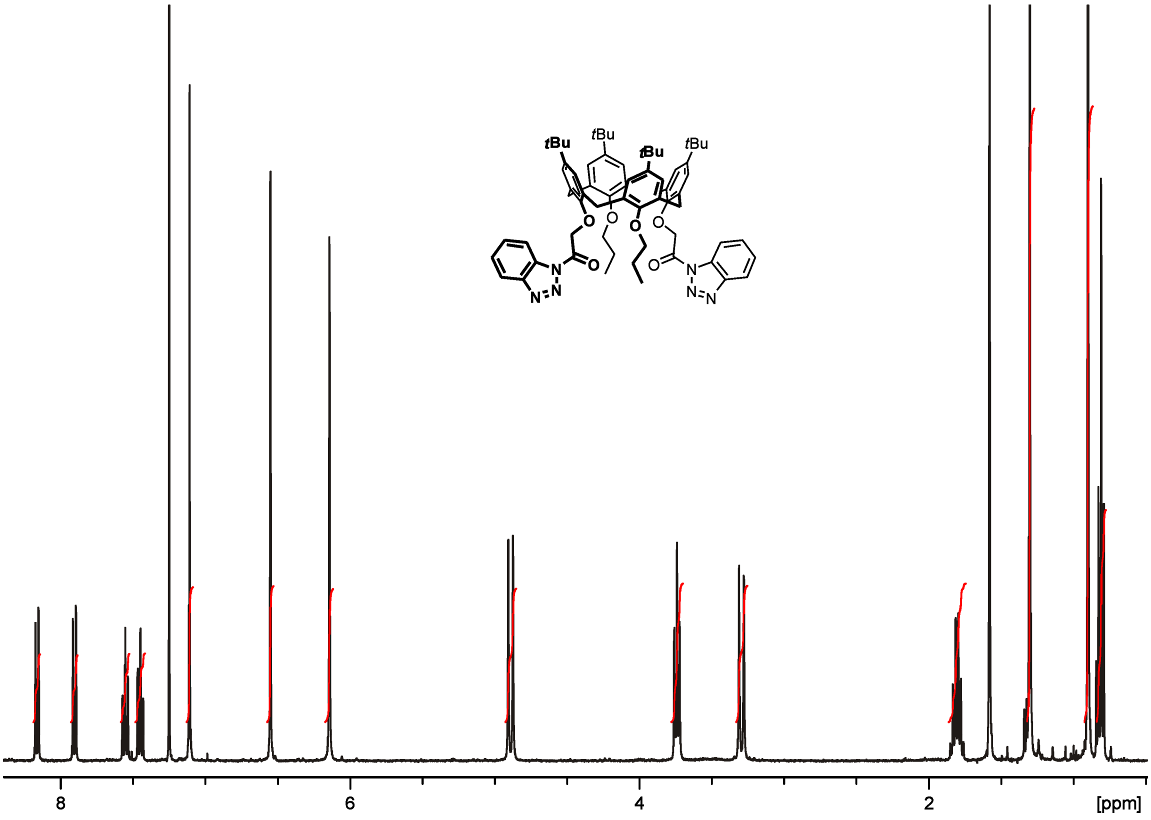


Figure S5. ^{1}H NMR spectrum of bis(1-acylbenzotriazole) **7** (400 MHz, $CDCl_3$).

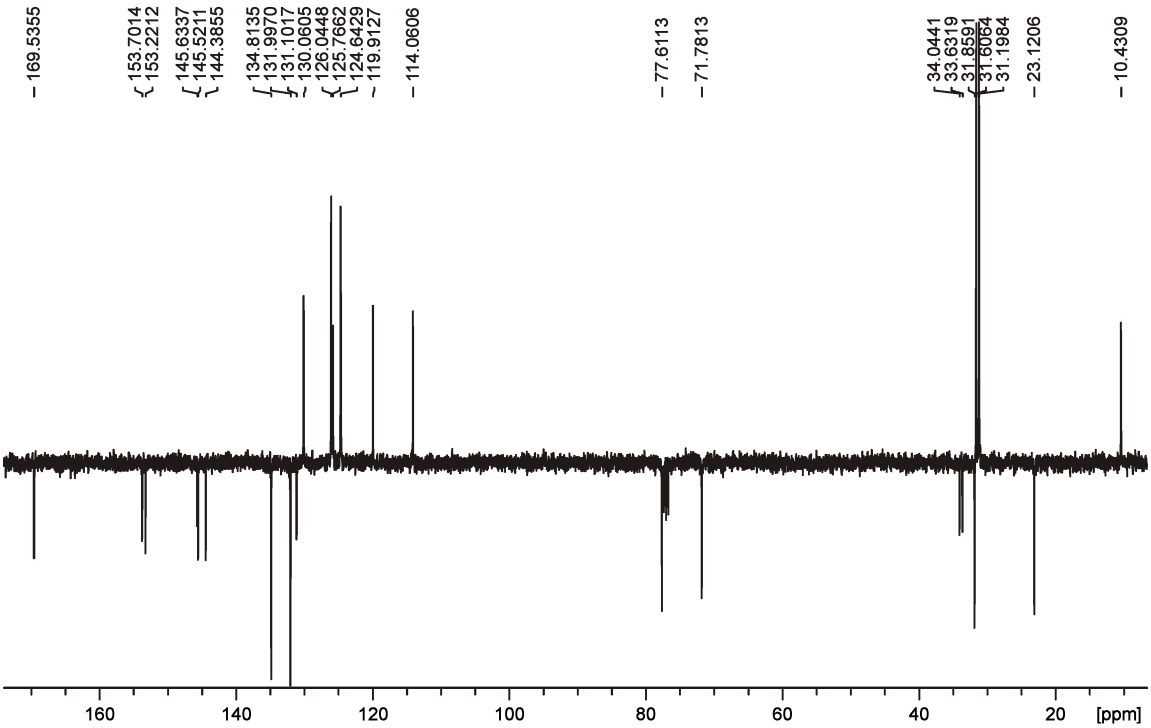


Figure S6. ^{13}C NMR spectrum (APT) of bis(1-acylbenzotriazole) **7** (100 MHz, $CDCl_3$).

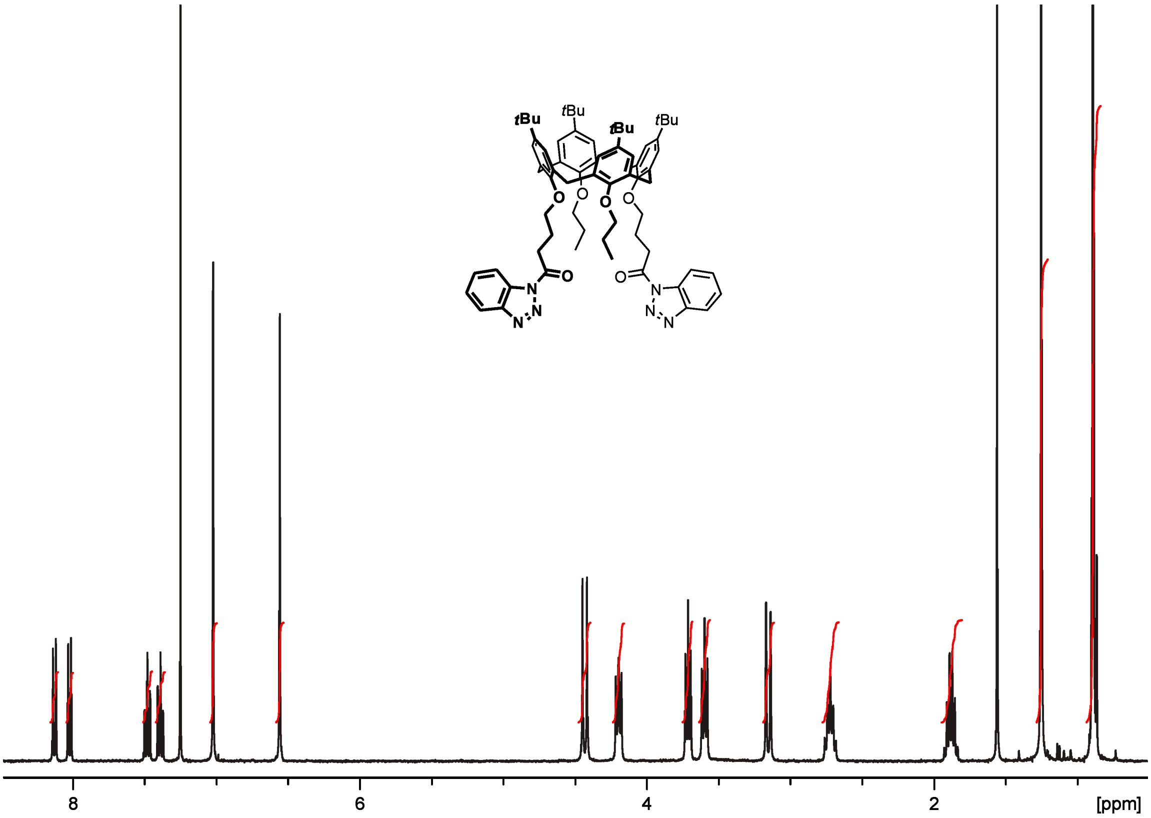


Figure S7. ^{1}H NMR spectrum of bis(1-acylbenzotriazole) **8** (400 MHz, $CDCl_3$).

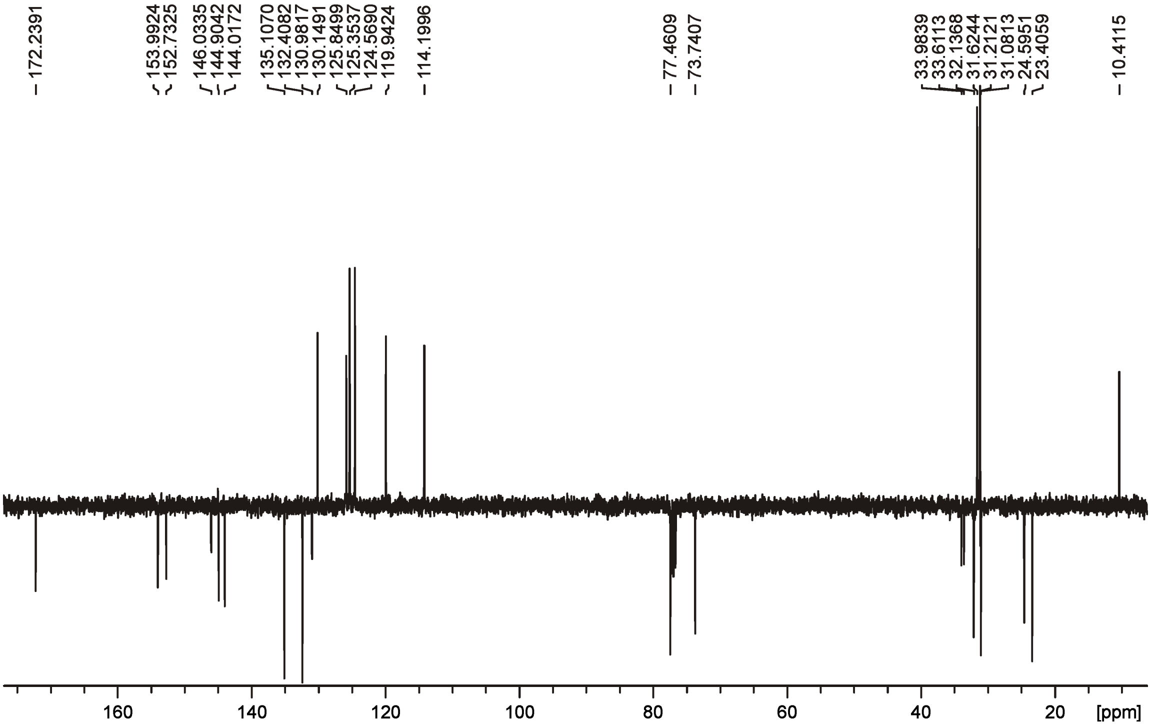


Figure S8. ^{13}C NMR spectrum (APT) of bis(1-acylbenzotriazole) **8** (100 MHz, $CDCl_3$).

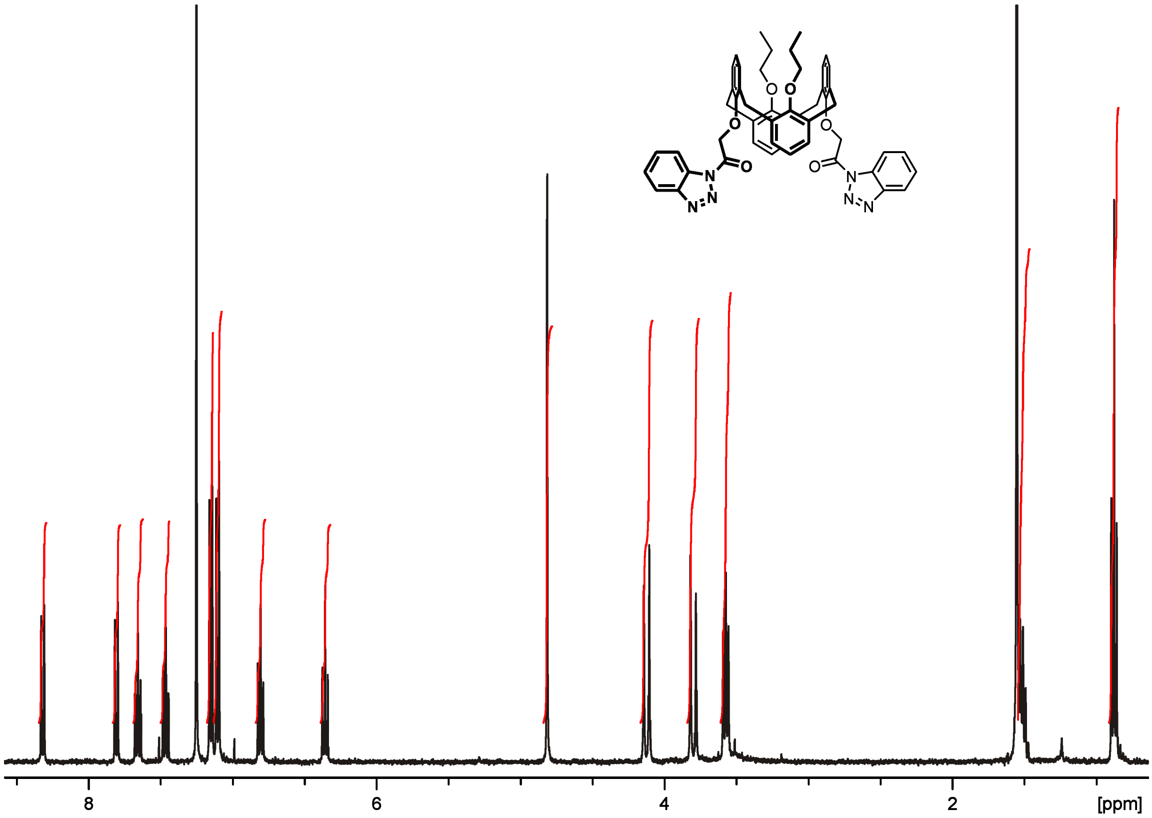


Figure S9. ^{1}H NMR spectrum of bis(1-acylbenzotriazole) **10** (400 MHz, $CDCl_3$).

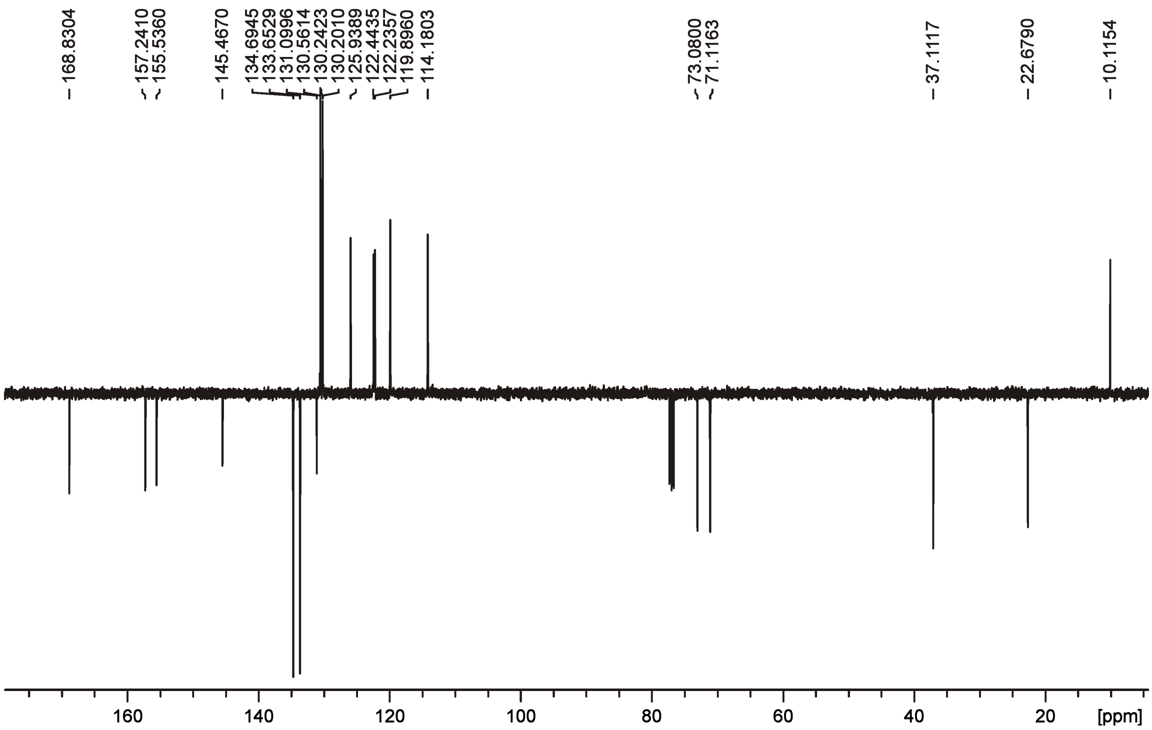


Figure S10. ^{13}C NMR spectrum (APT) of bis(1-acylbenzotriazole) **10** (100 MHz, $CDCl_3$).

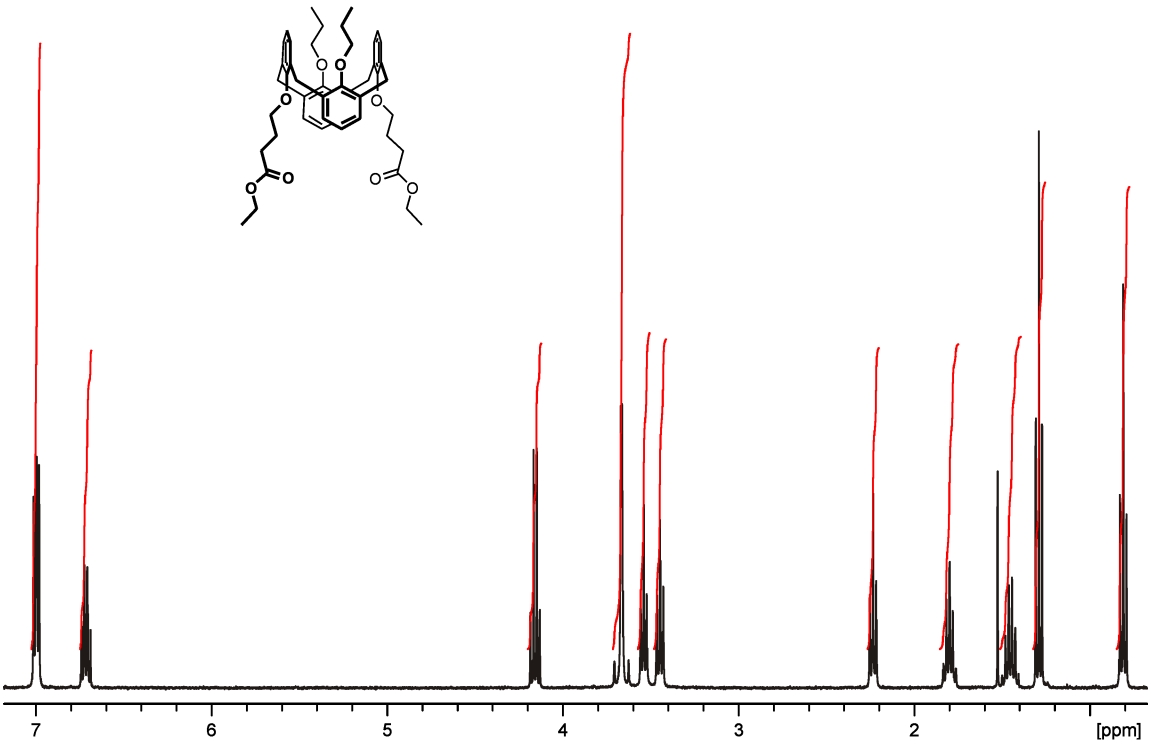


Figure S11. ^{1}H NMR spectrum of bis(ester) **12** (400 MHz, $CDCl_3$).

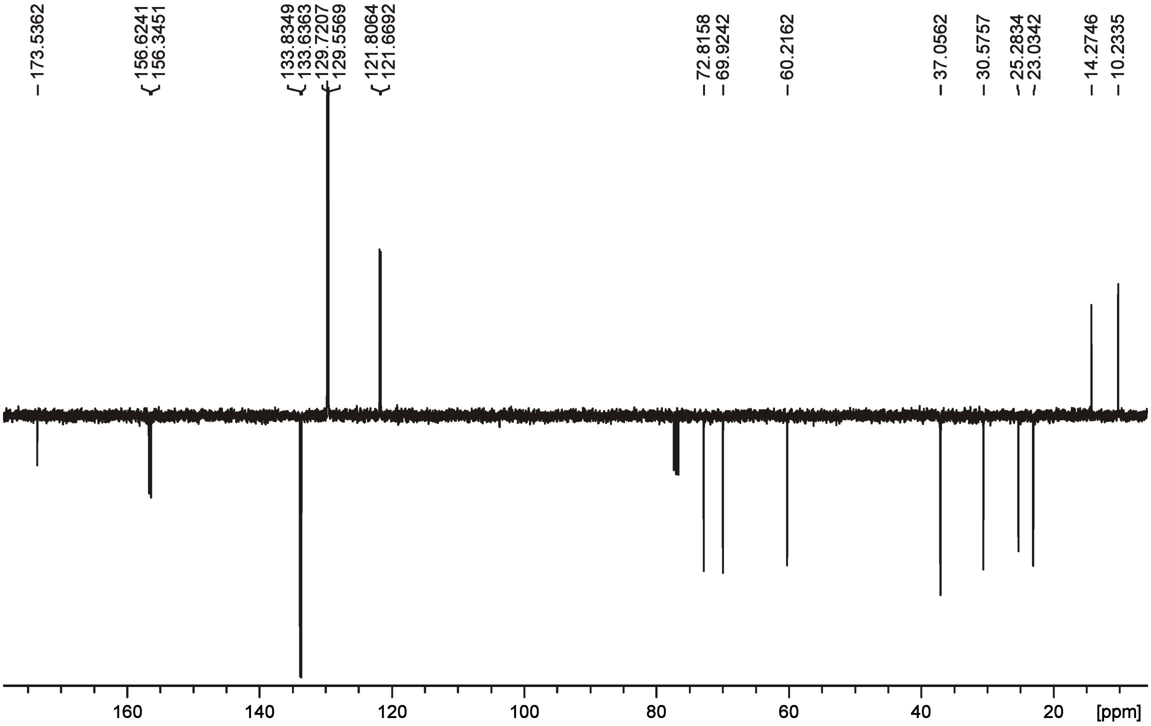


Figure S12. ^{13}C NMR spectrum (APT) of bis(ester) **12** (100 MHz, $CDCl_3$).

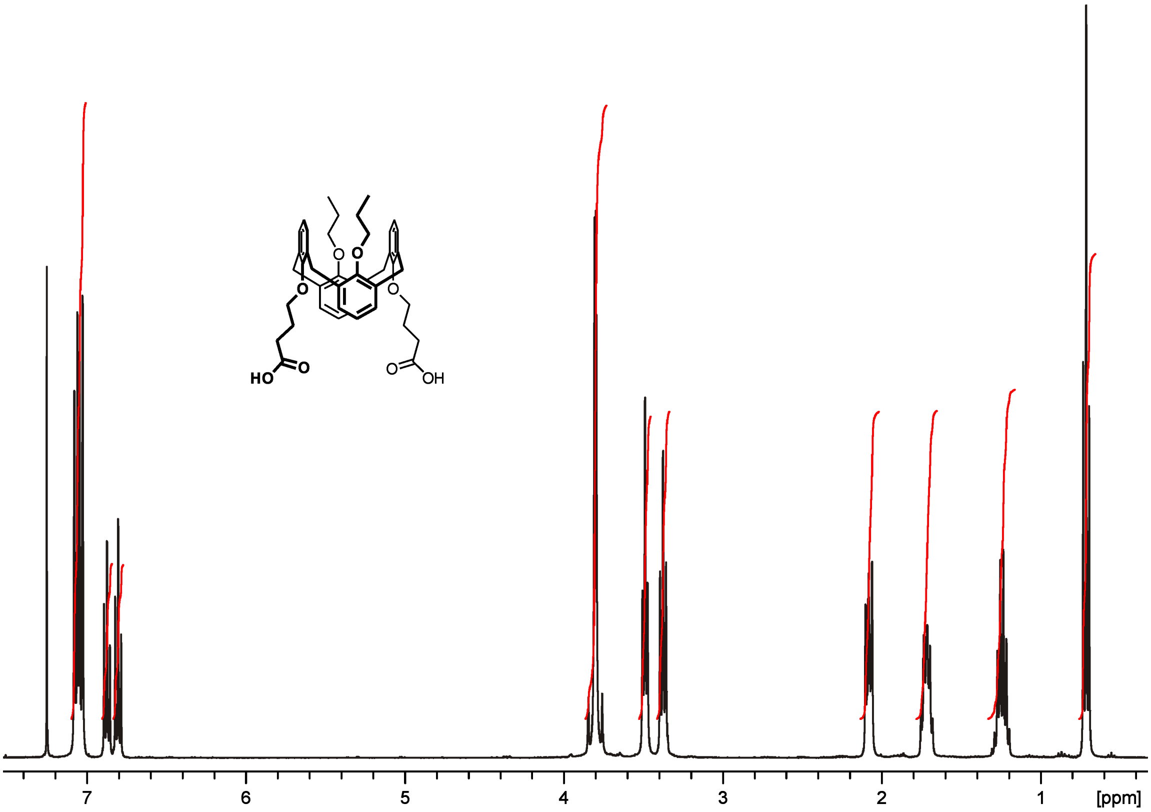


Figure S13. ^{1}H NMR spectrum of bis(acid) **13** (400 MHz, $CDCl_3$).

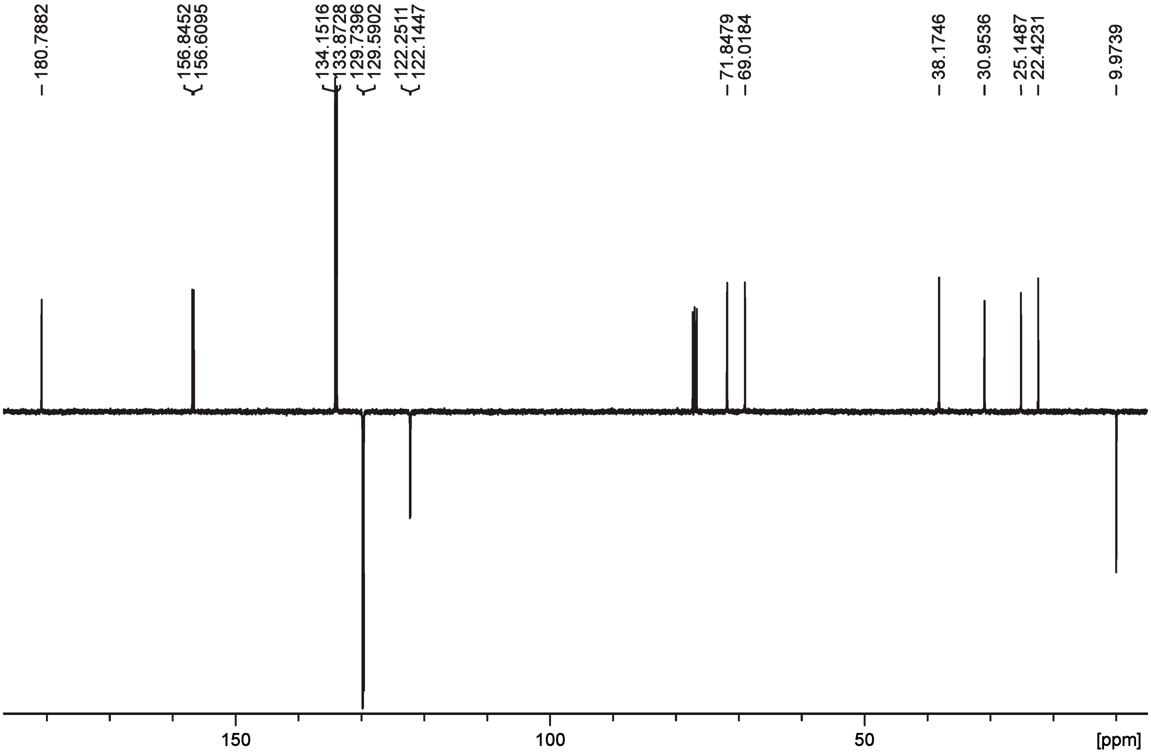


Figure S14. ^{13}C NMR spectrum (APT) of bis(acid) **13** (100 MHz, $CDCl_3$).

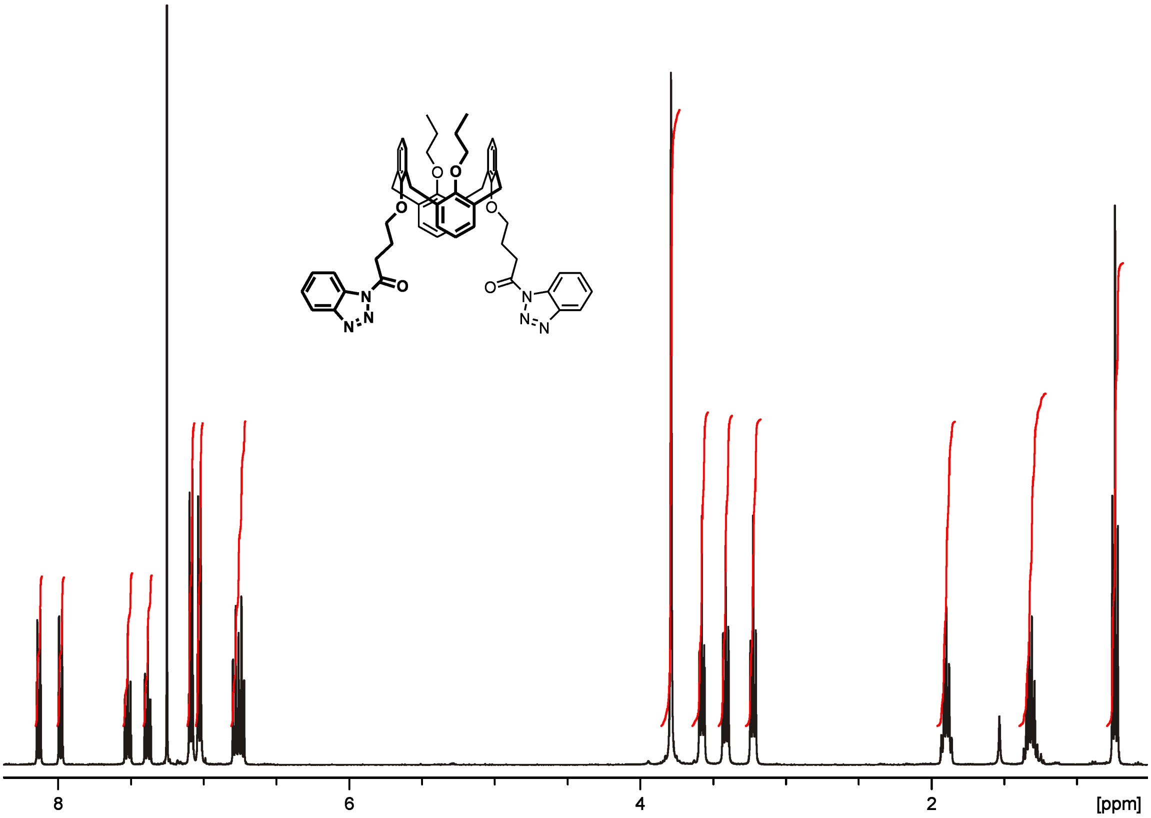


Figure S15. ^{1}H NMR spectrum of bis(1-acylbenzotriazole) **14** (400 MHz, $CDCl_3$).

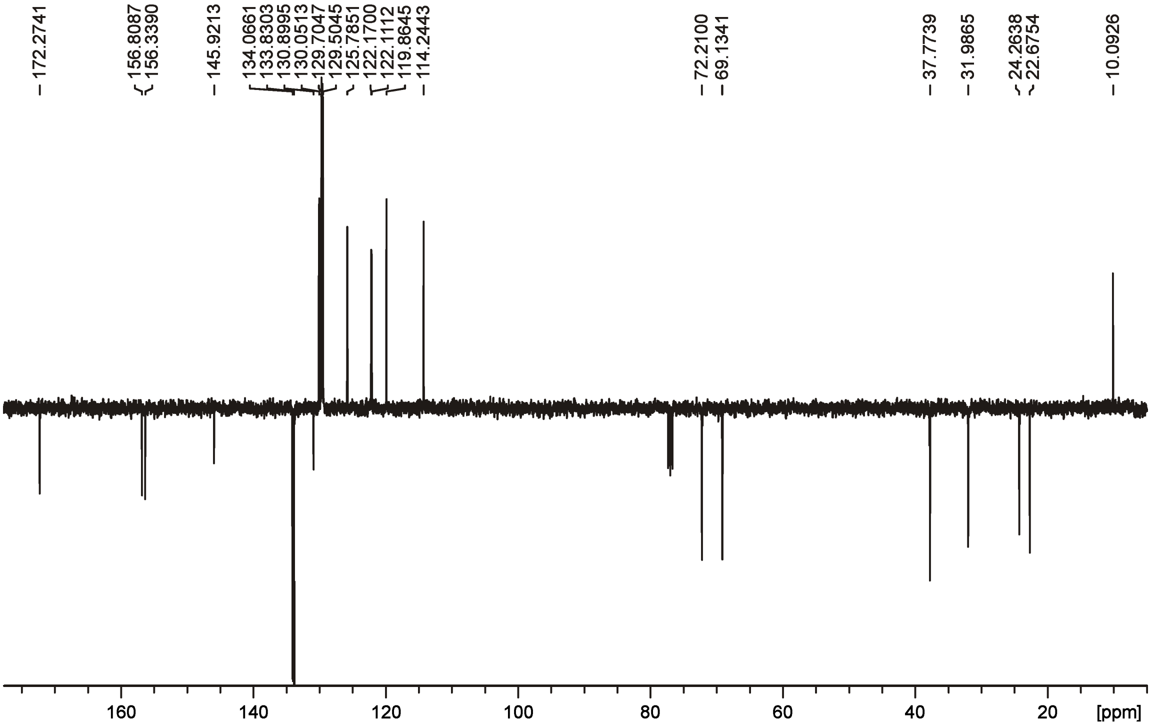


Figure S16. ^{13}C NMR spectrum (APT) of bis(1-acylbenzotriazole) **14** (100 MHz, $CDCl_3$).

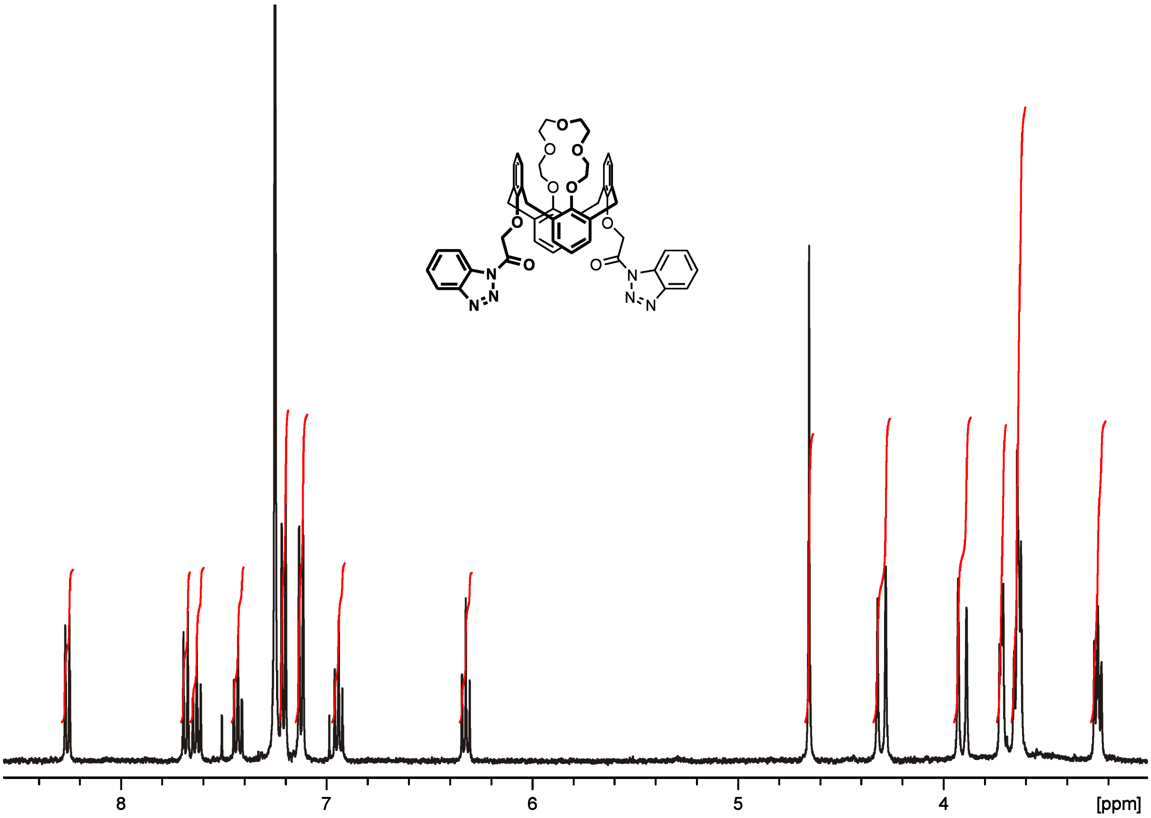


Figure S17. ^{1}H NMR spectrum of bis(1-acylbenzotriazole) **16** (400 MHz, $CDCl_3$).

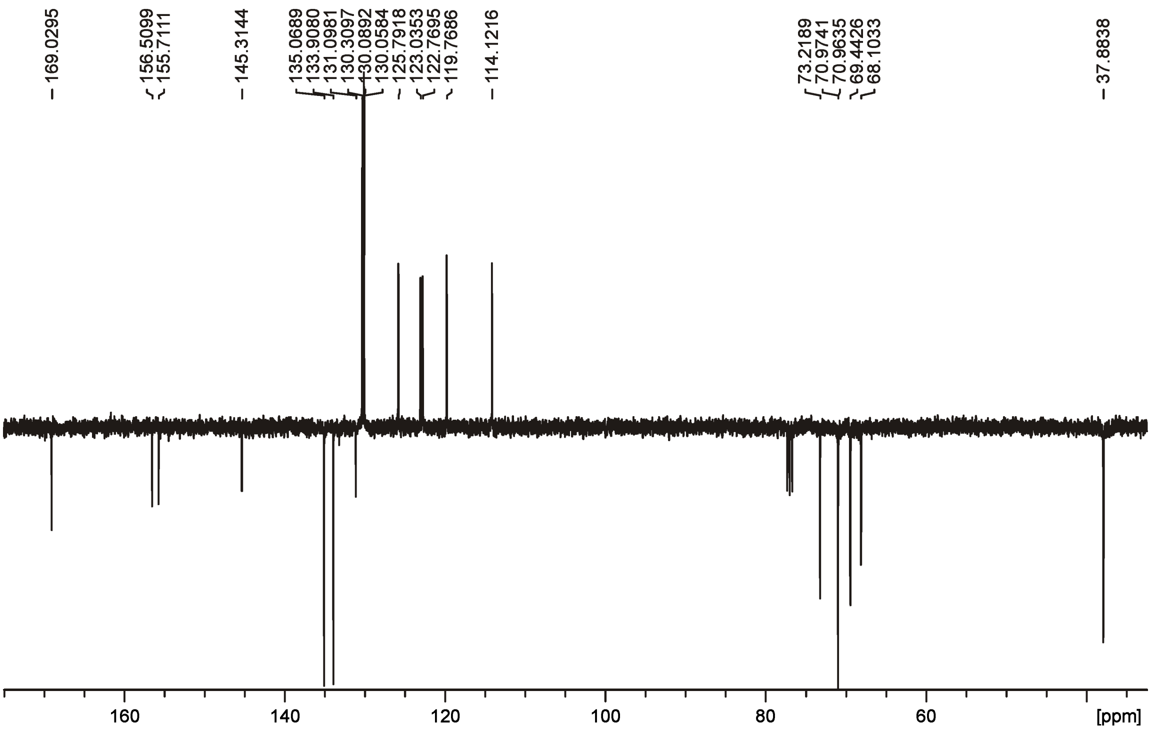


Figure S18. ^{13}C NMR spectrum (APT) of bis(1-acylbenzotriazole) **16** (100 MHz, $CDCl_3$).

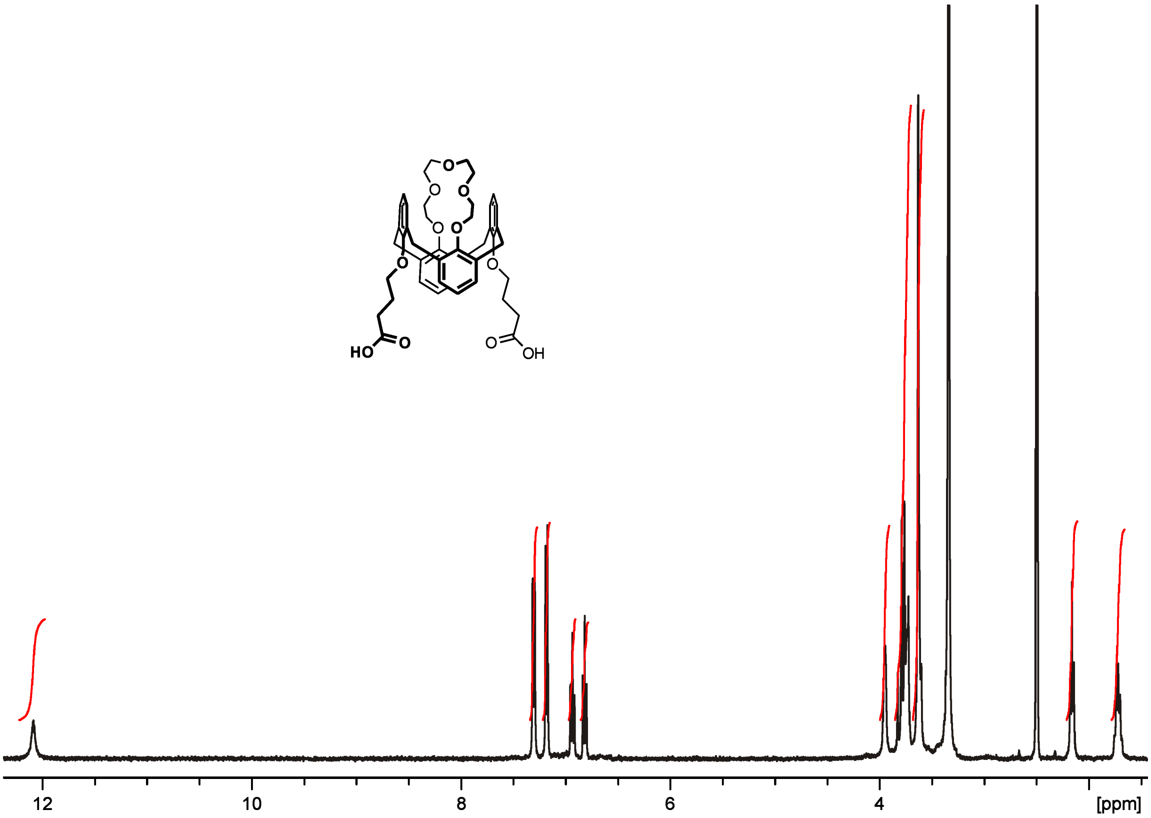


Figure S19. ^{1}H NMR spectrum of bis(acid) **17** (400 MHz, DMSO-d_6).

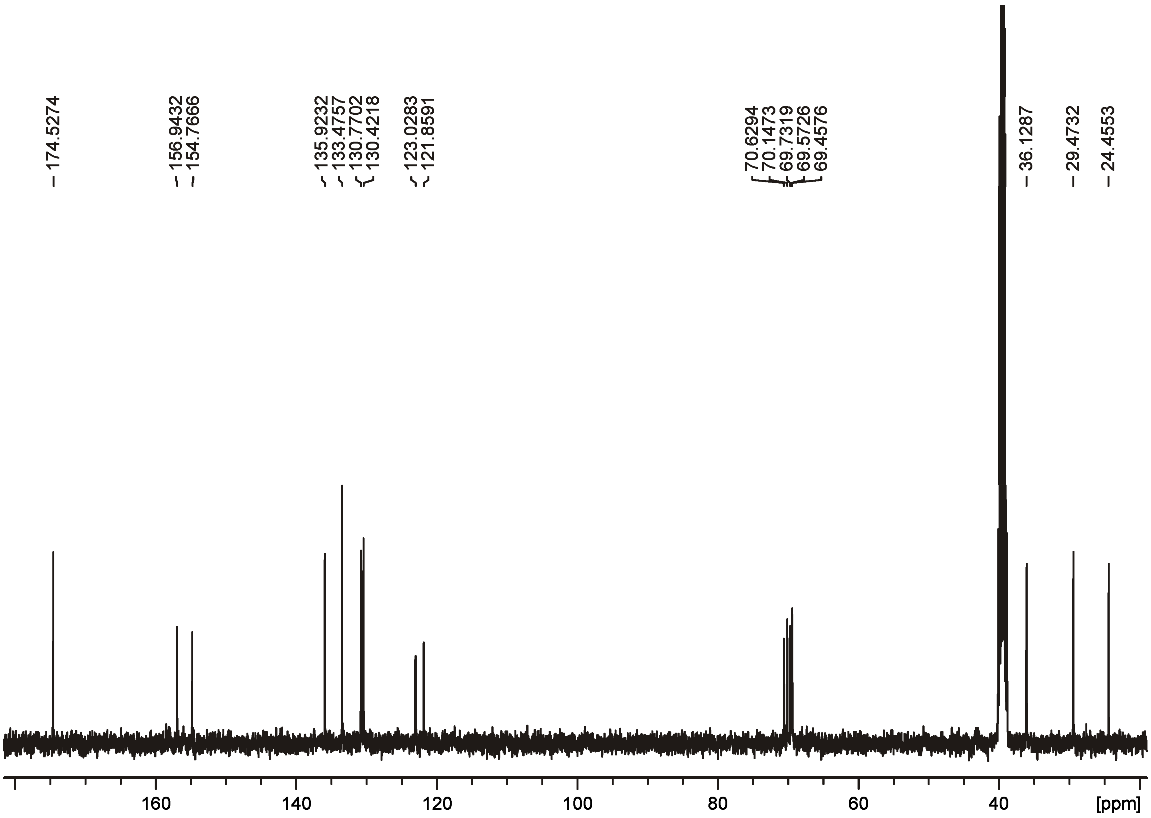


Figure S20. ^{13}C NMR spectrum of bis(acid) **17** (100 MHz, DMSO-d_6).

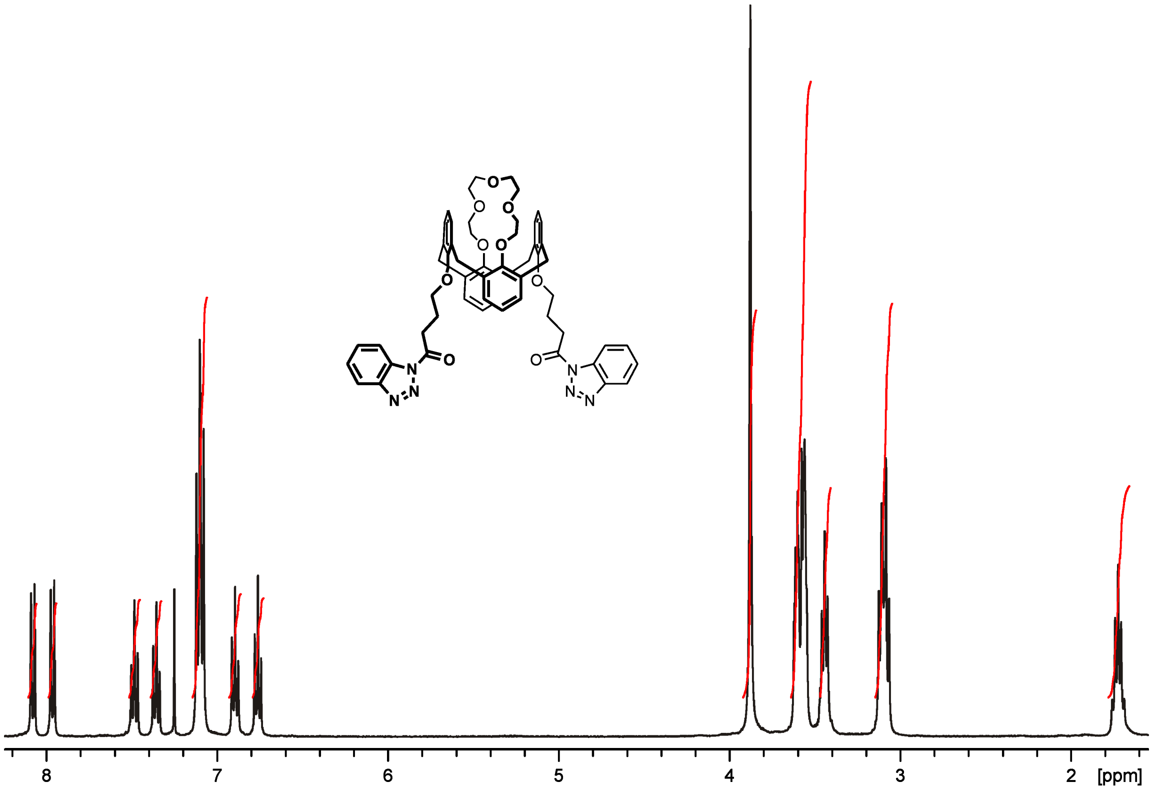


Figure S21. ^{1}H NMR spectrum of bis(1-acylbenzotriazole) **18** (400 MHz, $CDCl_3$).

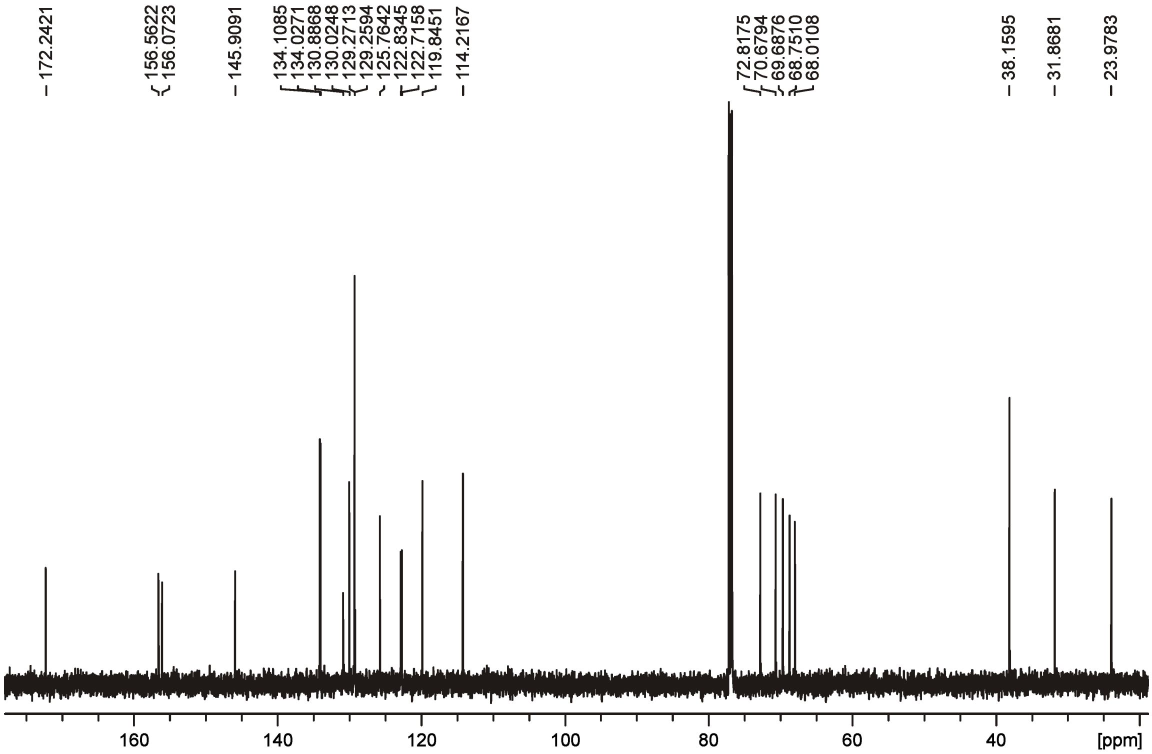


Figure S22. ^{13}C NMR spectrum of bis(1-acylbenzotriazole) **18** (100 MHz, $CDCl_3$).

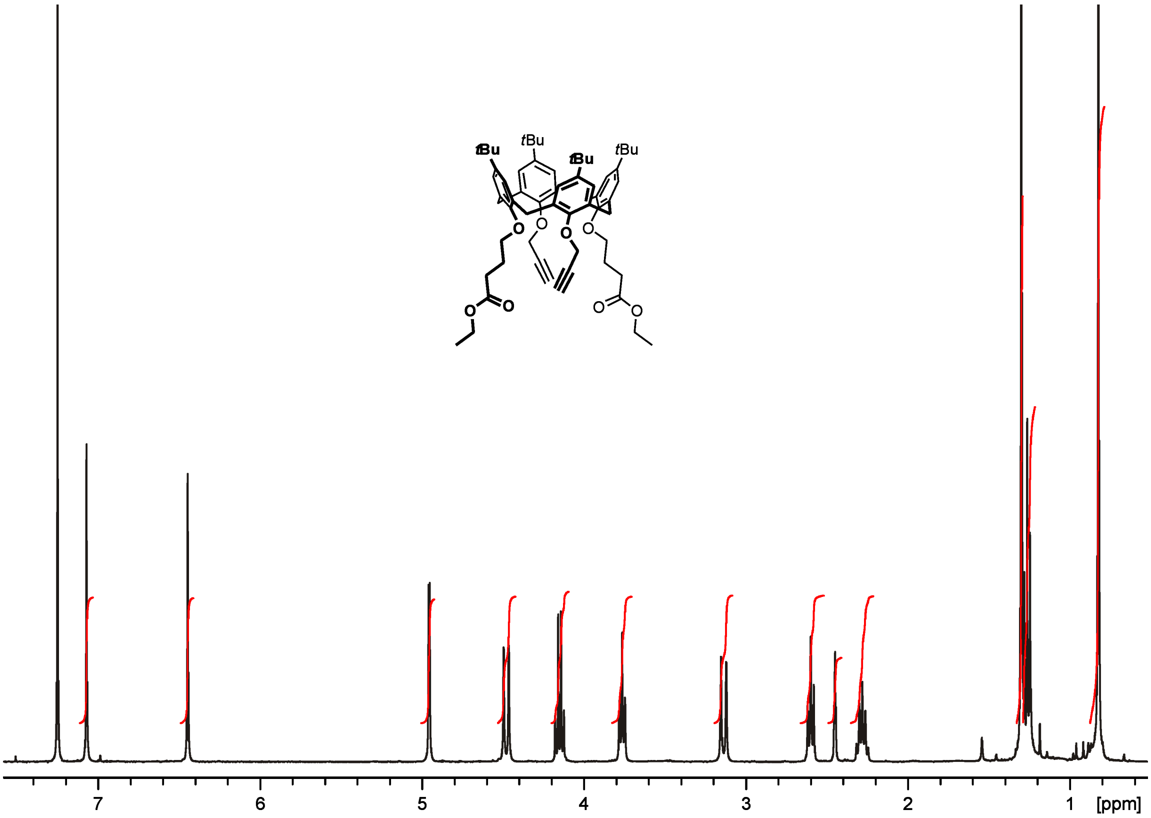


Figure S23. ^{1}H NMR spectrum of propargylated bis(ester) **21** (400 MHz, CDCl$_3$).

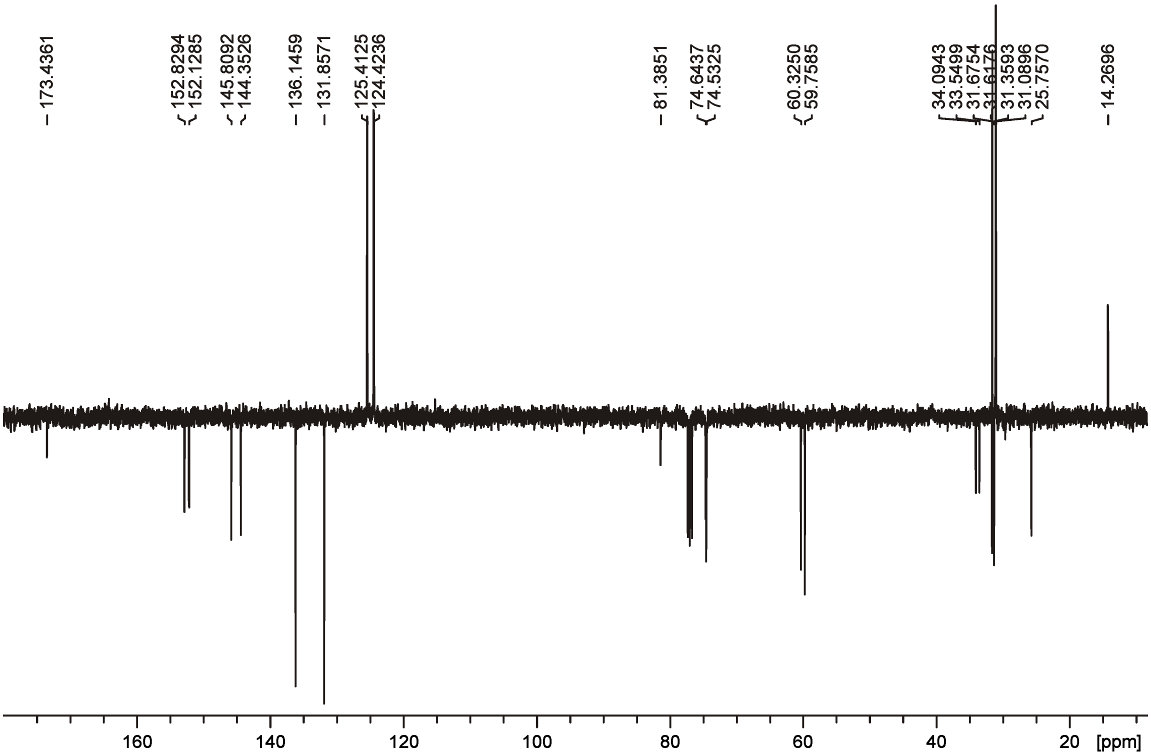


Figure S24. ^{13}C NMR spectrum (APT) of propargylated bis(ester) **21** (100 MHz, CDCl$_3$).

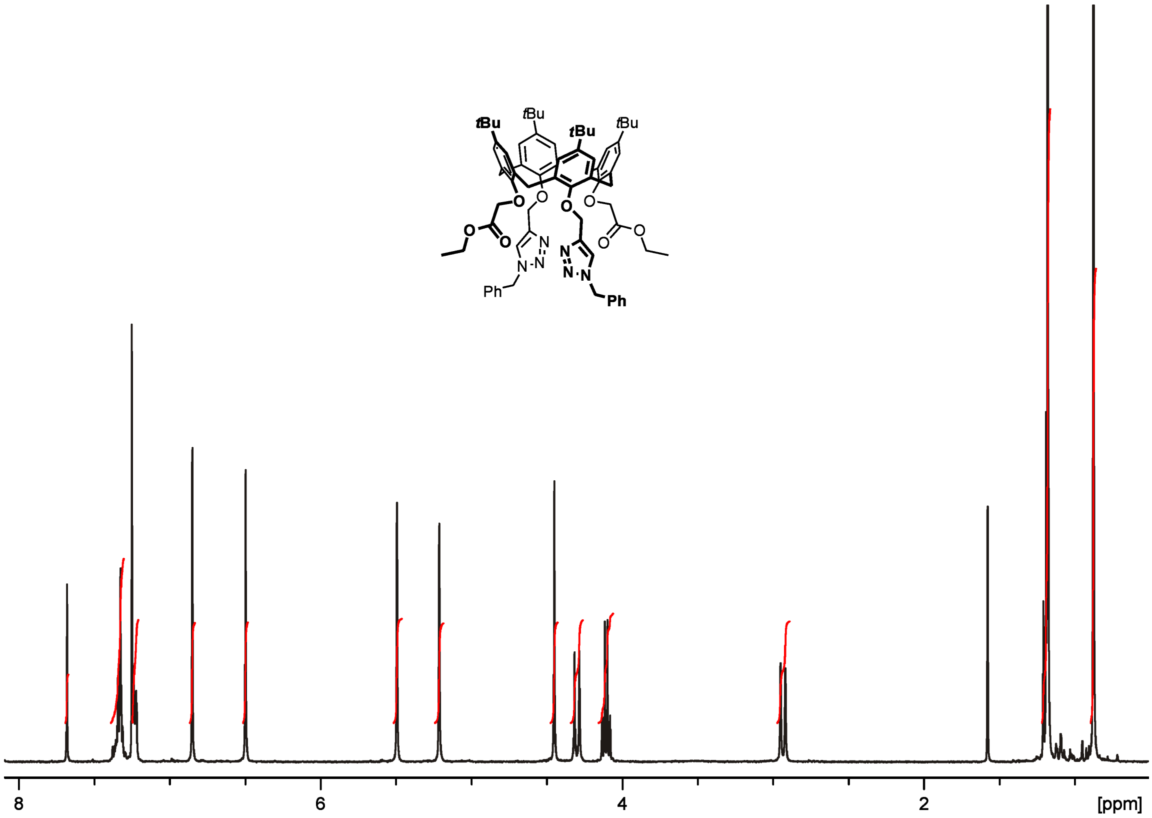


Figure S25. ^{1}H NMR spectrum of triazolated bis(ester) **22** (400 MHz, CDCl$_3$).

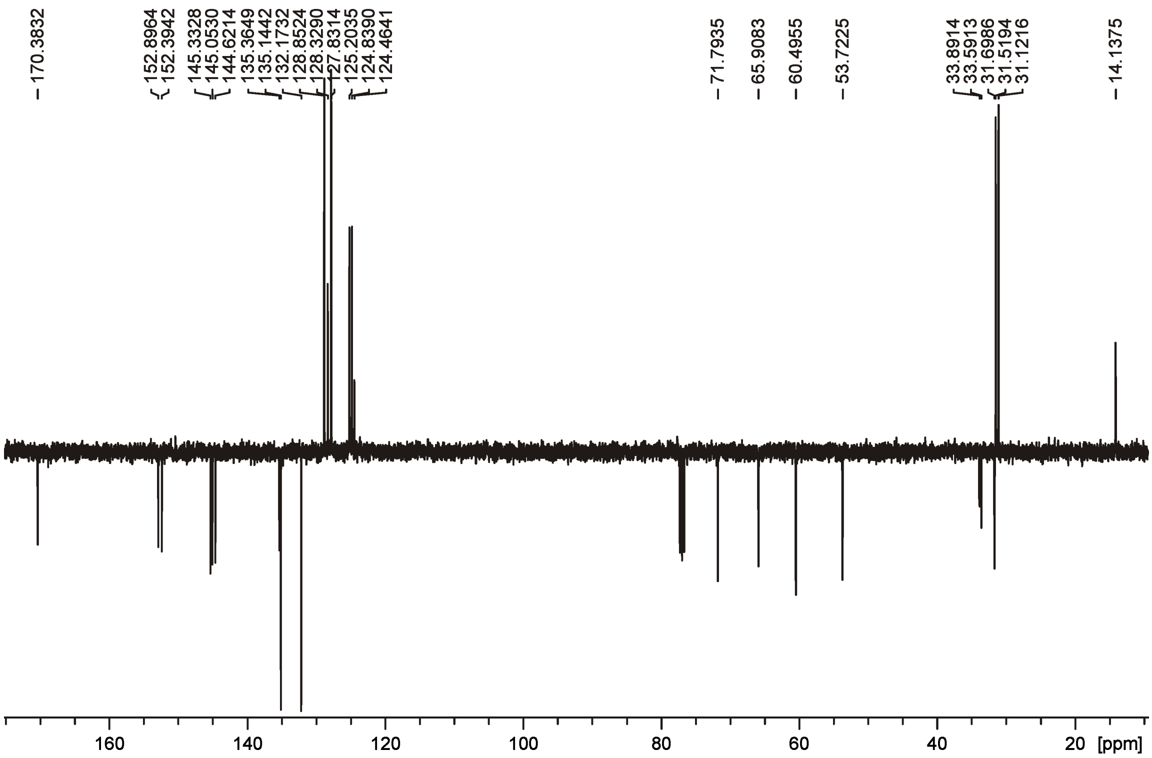


Figure S26. ^{13}C NMR spectrum (APT) of triazolated bis(ester) **22** (100 MHz, CDCl$_3$).

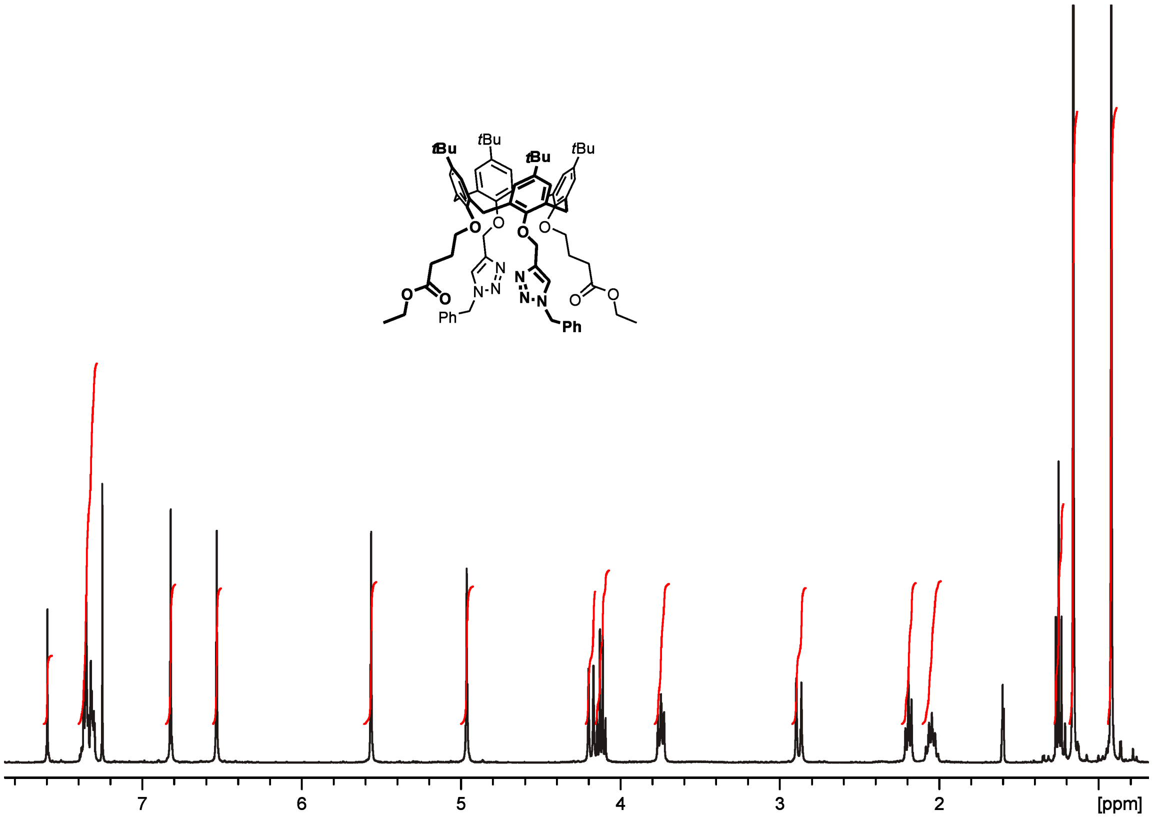


Figure S27. ^{1}H NMR spectrum of triazolated bis(ester) **23** (400 MHz, CDCl$_3$).

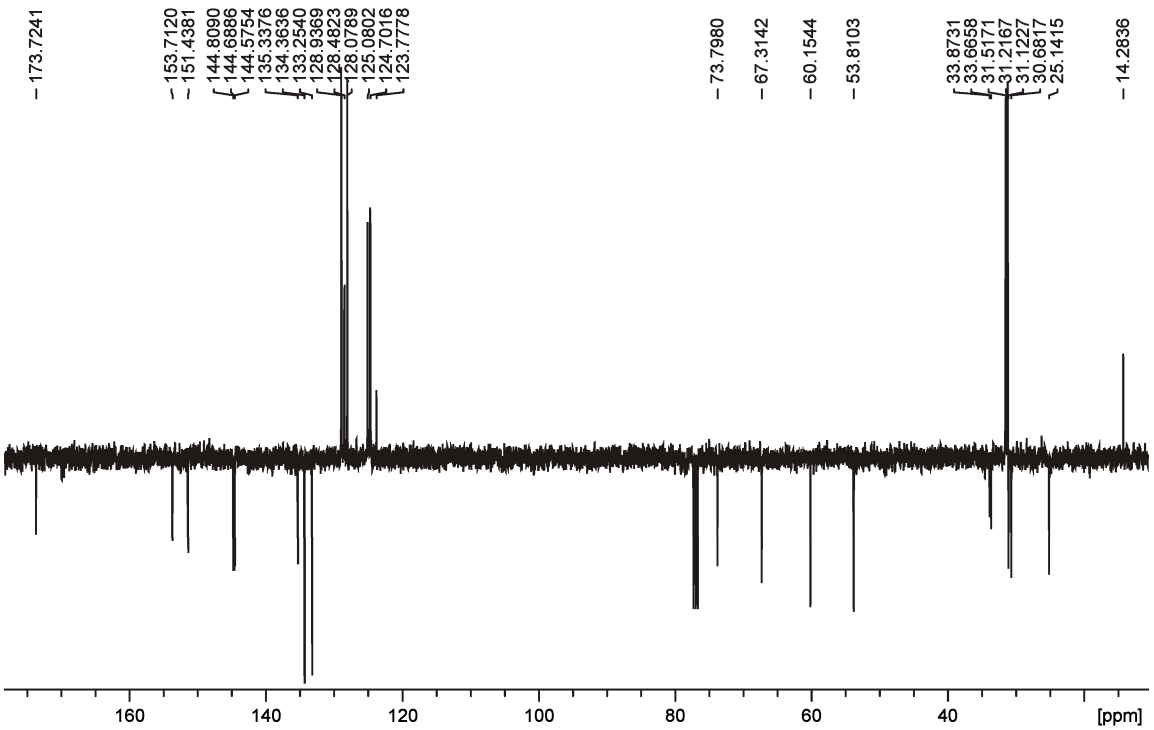


Figure S28. ^{13}C NMR spectrum (APT) of triazolated bis(ester) **23** (100 MHz, CDCl$_3$).

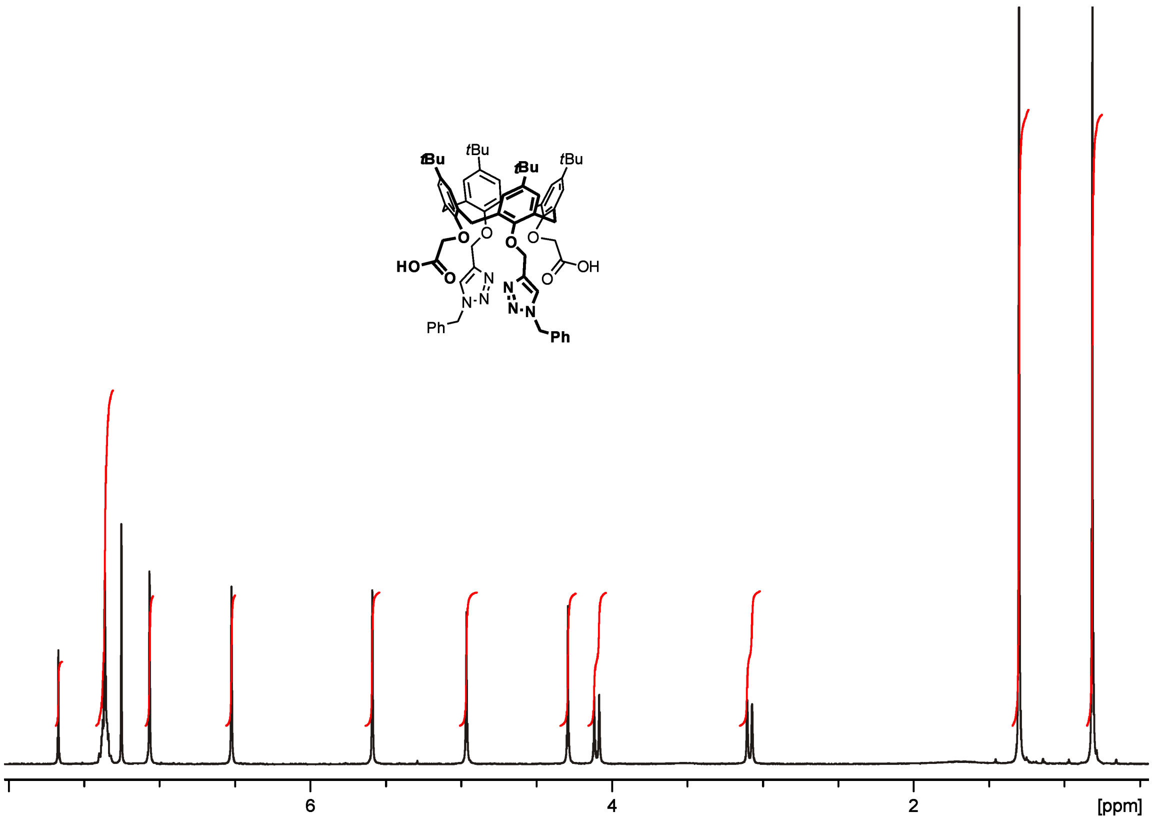


Figure S29. ^{1}H NMR spectrum of triazolated bis(acid) **24** (400 MHz, $CDCl_3$).

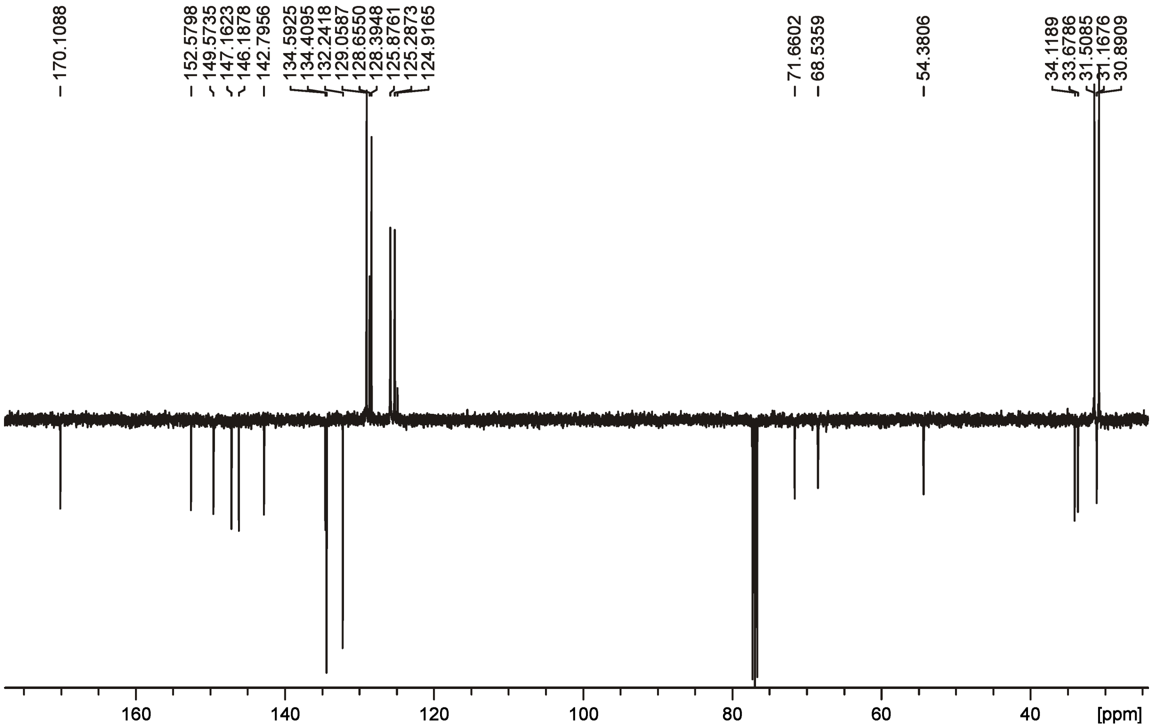


Figure S30. ^{13}C NMR spectrum (APT) of triazolated bis(acid) **24** (100 MHz, $CDCl_3$).

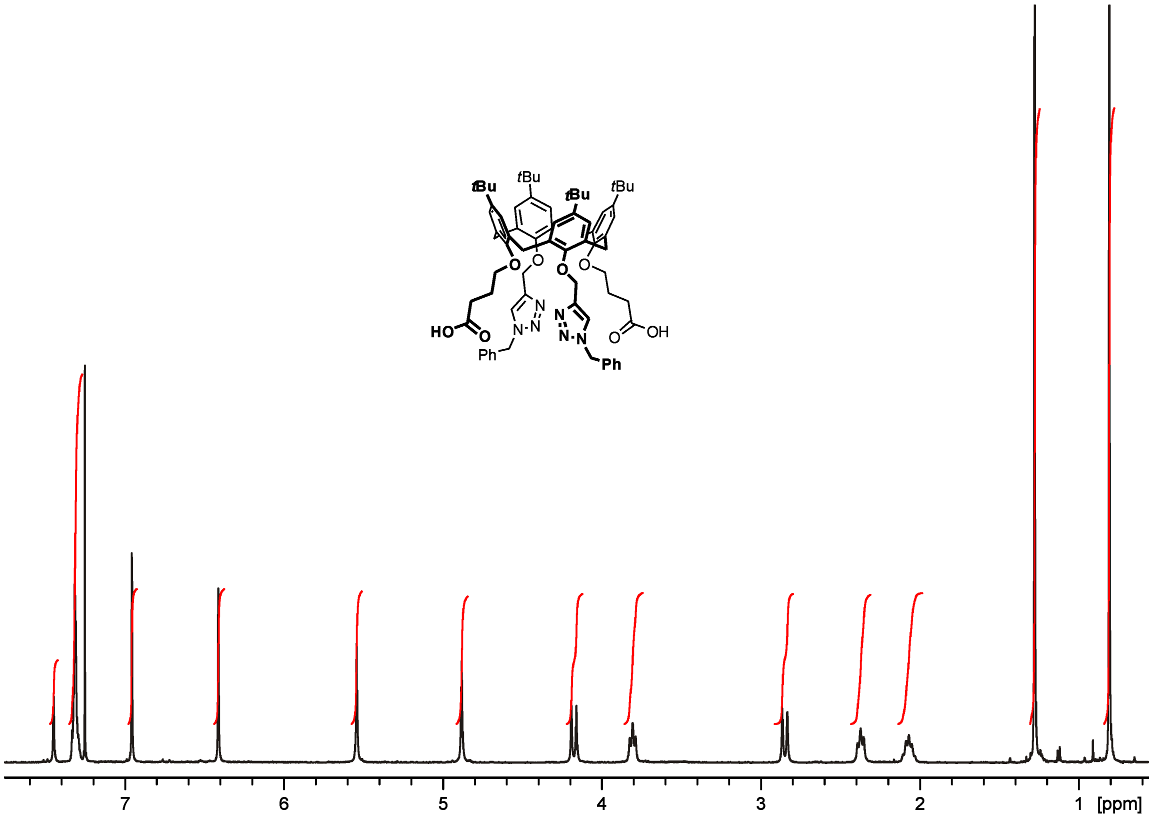


Figure S31. ^{1}H NMR spectrum of triazolated bis(acid) **25** (400 MHz, $CDCl_3$).

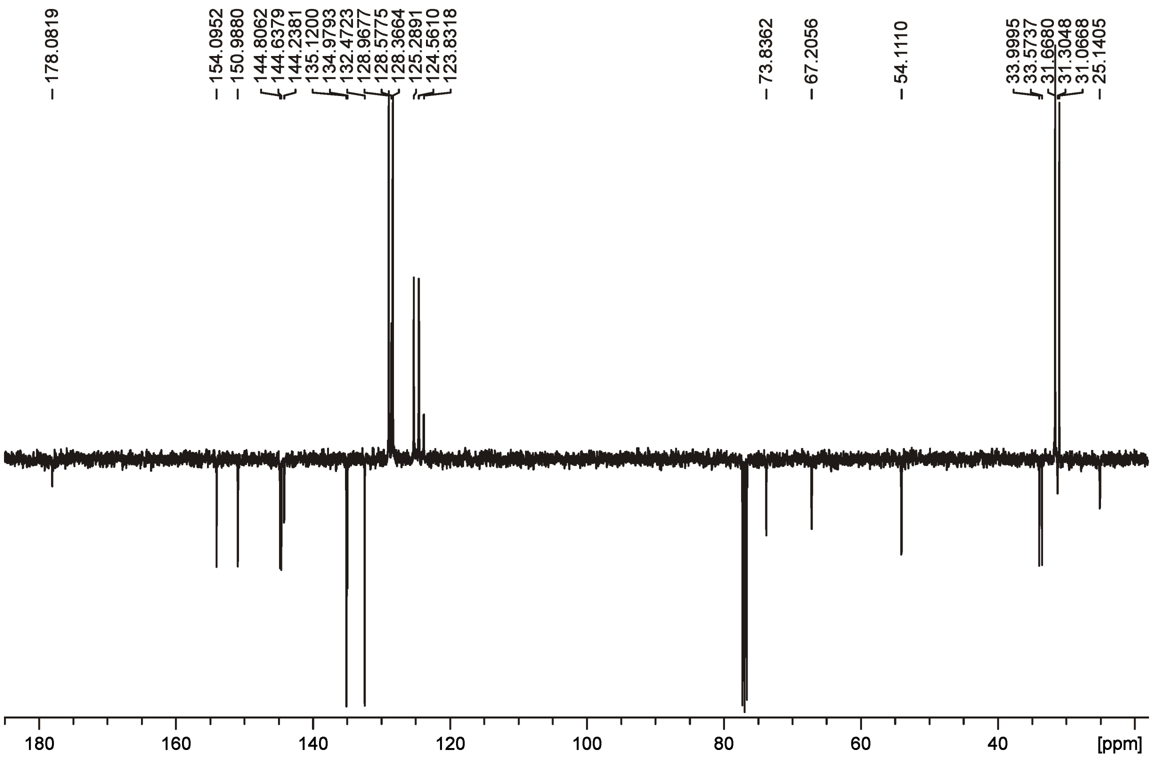


Figure S32. ^{13}C NMR spectrum (APT) of triazolated bis(acid) **25** (100 MHz, $CDCl_3$).

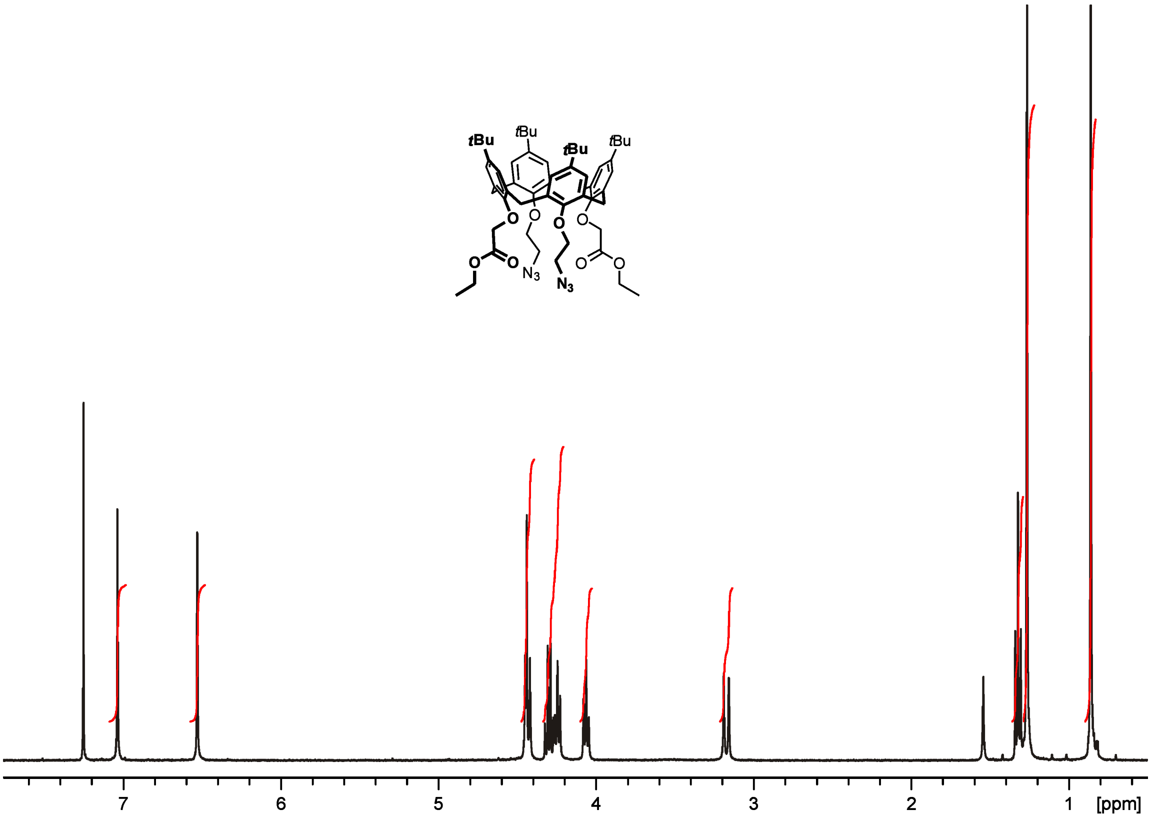


Figure S33. ^{1}H NMR spectrum of 2-azidoethylated bis(ester) **28** (400 MHz, $CDCl_3$).

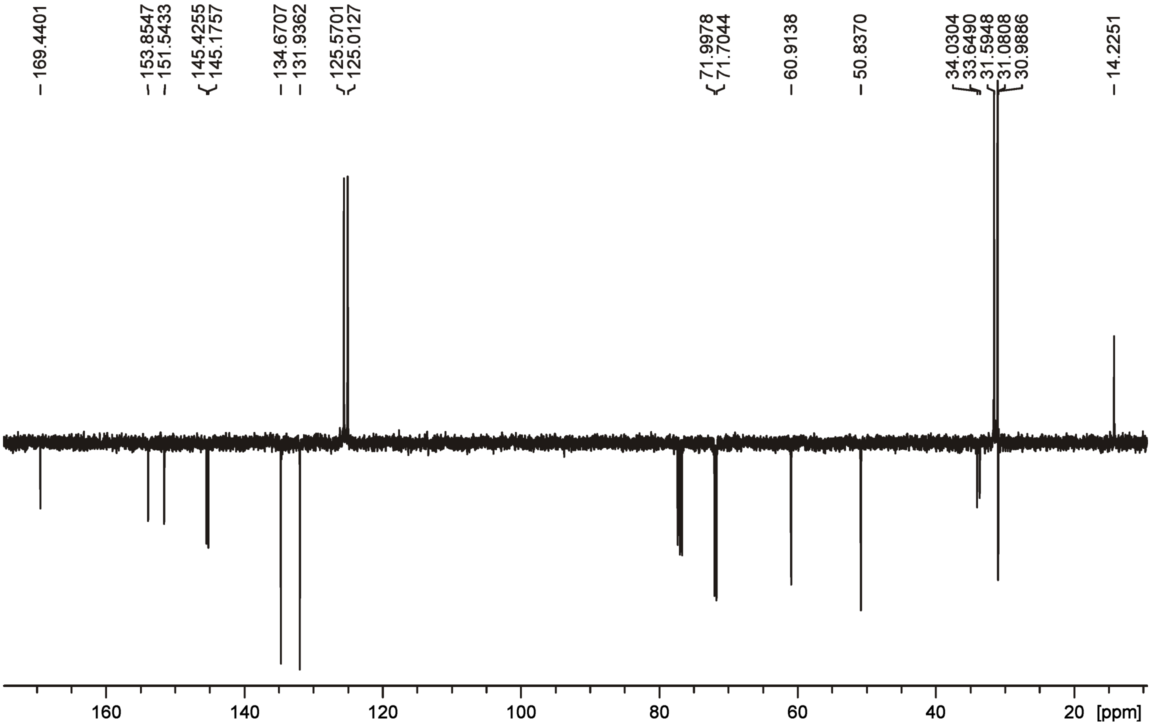


Figure S34. ^{13}C NMR spectrum (APT) of 2-azidoethylated bis(ester) **28** (100 MHz, $CDCl_3$).

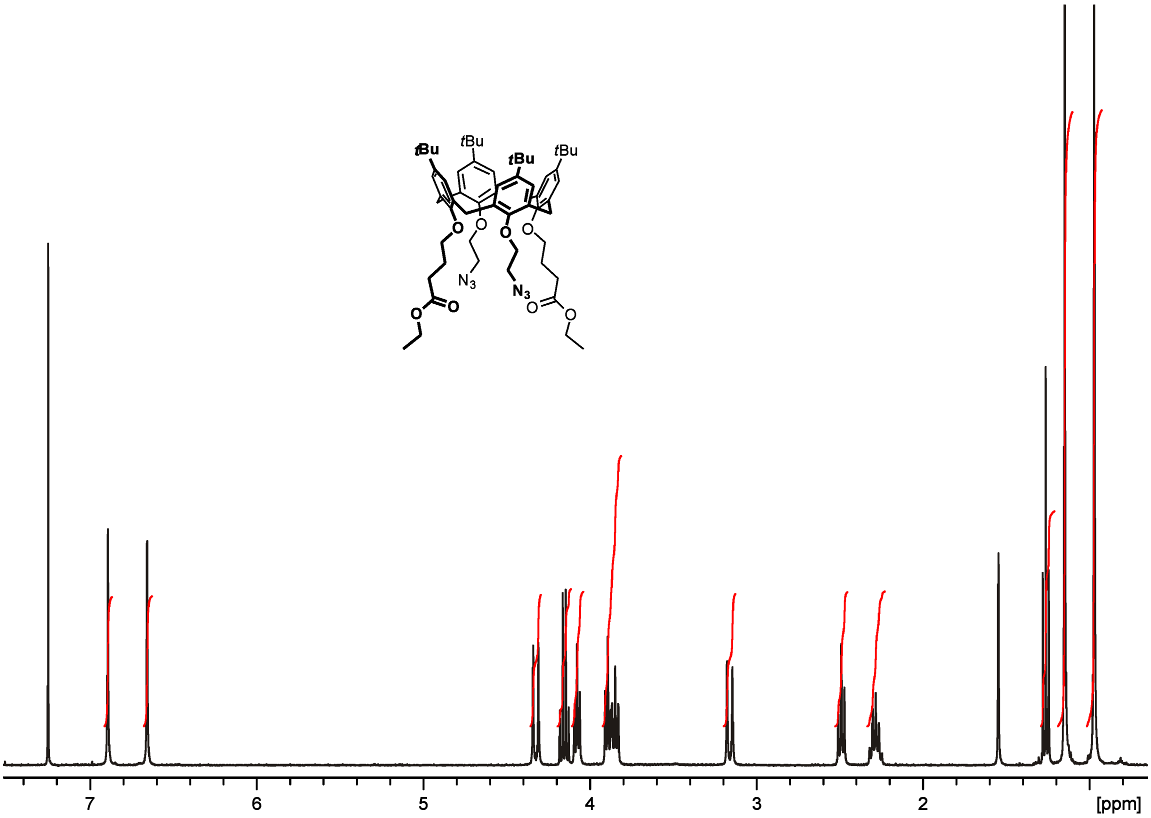


Figure S35. ^{1}H NMR spectrum of 2-azidoethylated bis(ester) **29** (400 MHz, $CDCl_3$).

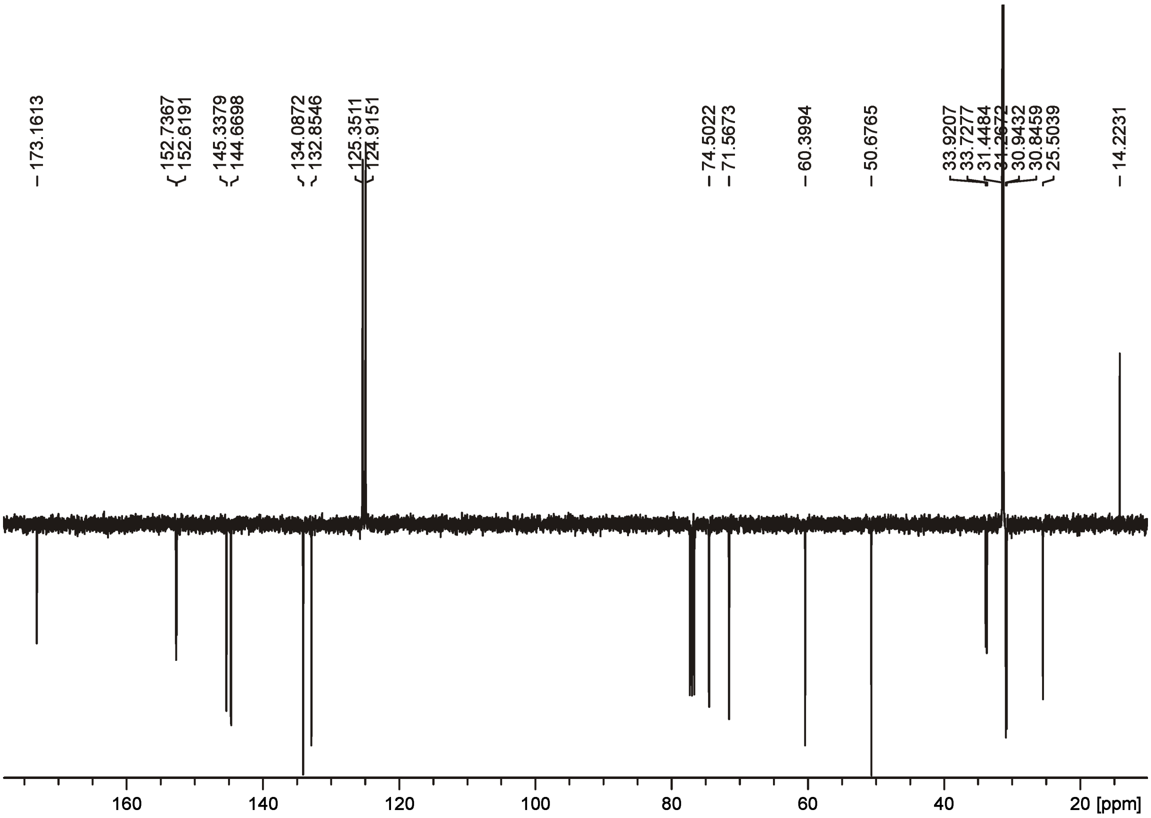


Figure S36. ^{13}C NMR spectrum (APT) of 2-azidoethylated bis(ester) **29** (100 MHz, $CDCl_3$).

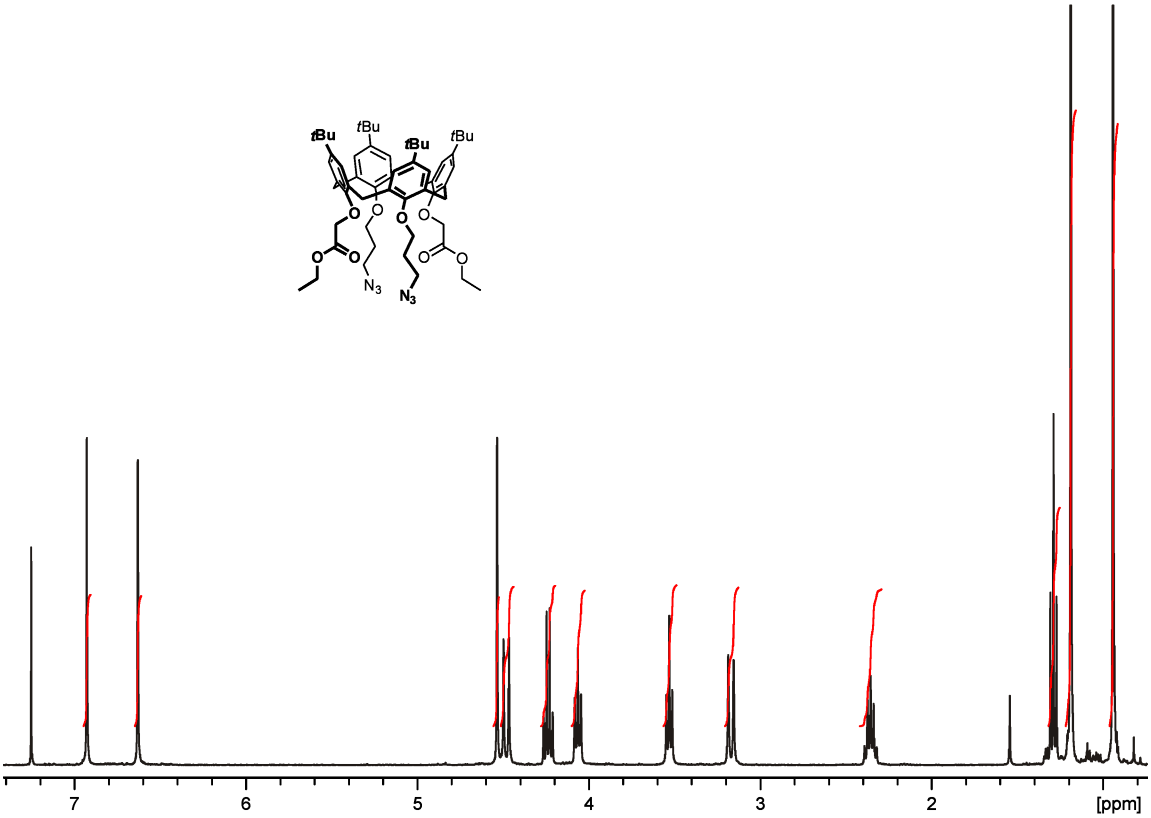


Figure S37. ^{1}H NMR spectrum of 3-azidopropylated bis(ester) **30** (400 MHz, $CDCl_3$).

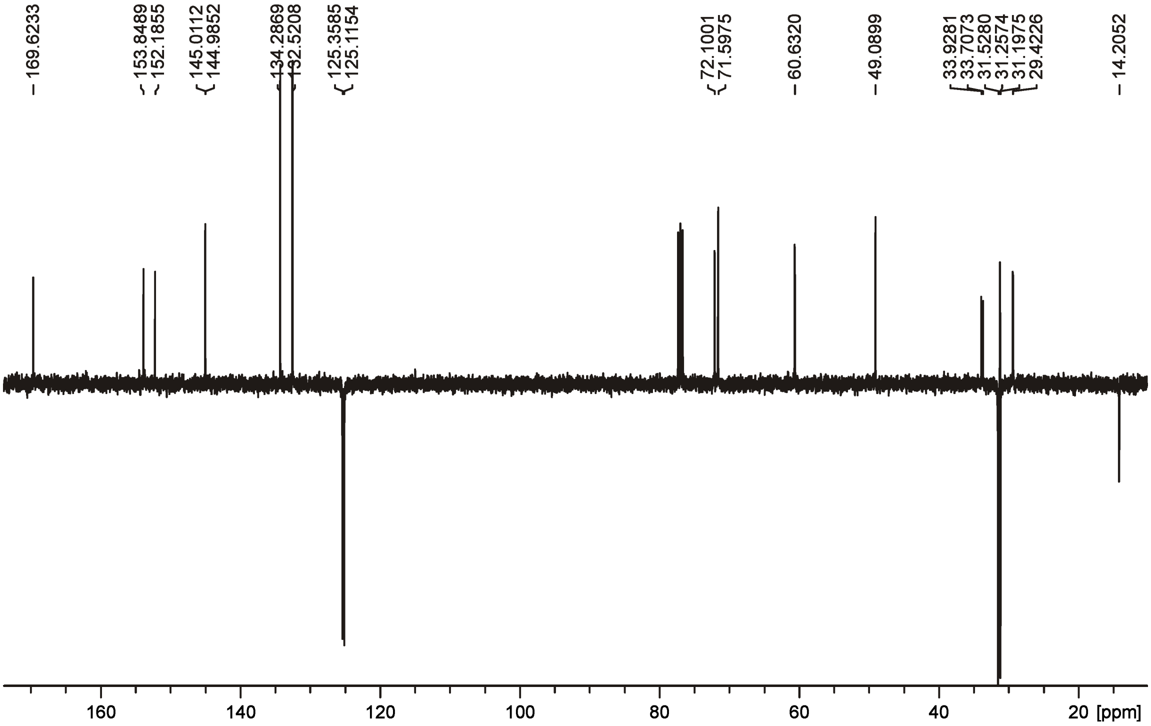


Figure S38. ^{13}C NMR spectrum (APT) of 3-azidopropylated bis(ester) **30** (100 MHz, $CDCl_3$).

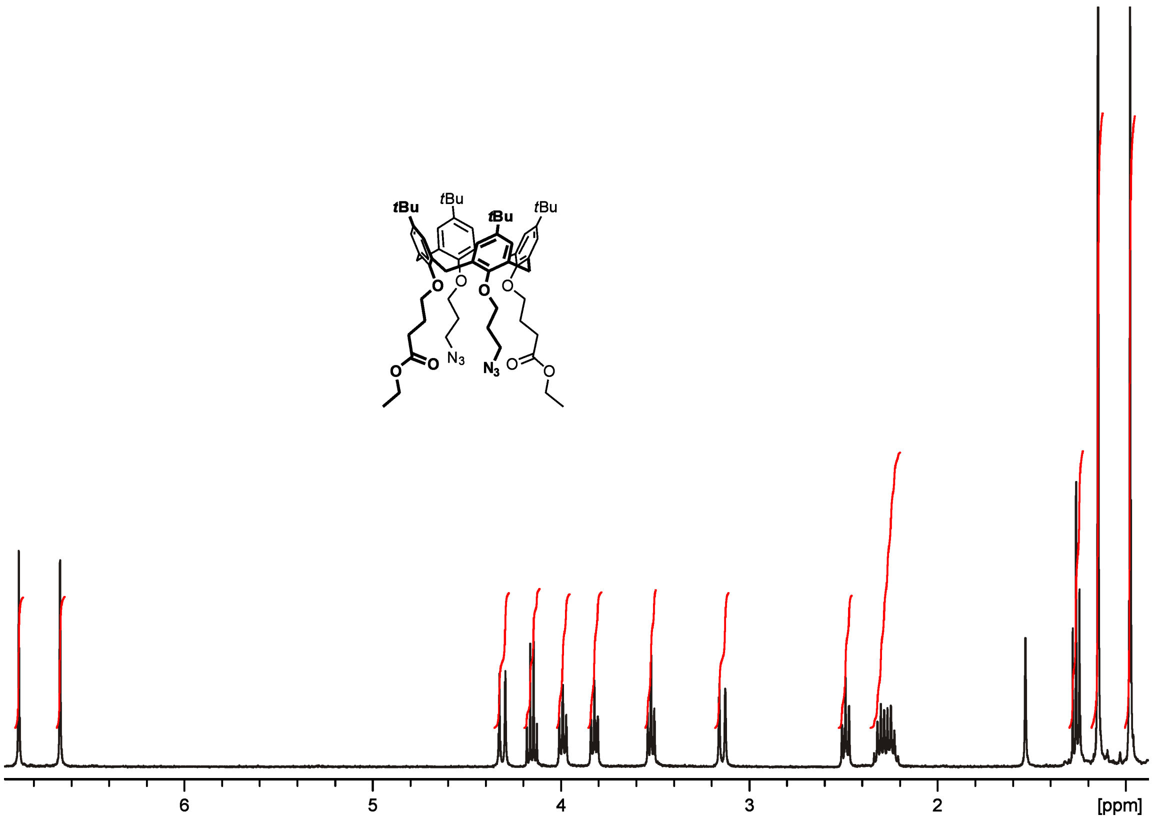


Figure S39. ^{1}H NMR spectrum of 3-azidopropylated bis(ester) **31** (400 MHz, CDCl$_3$).

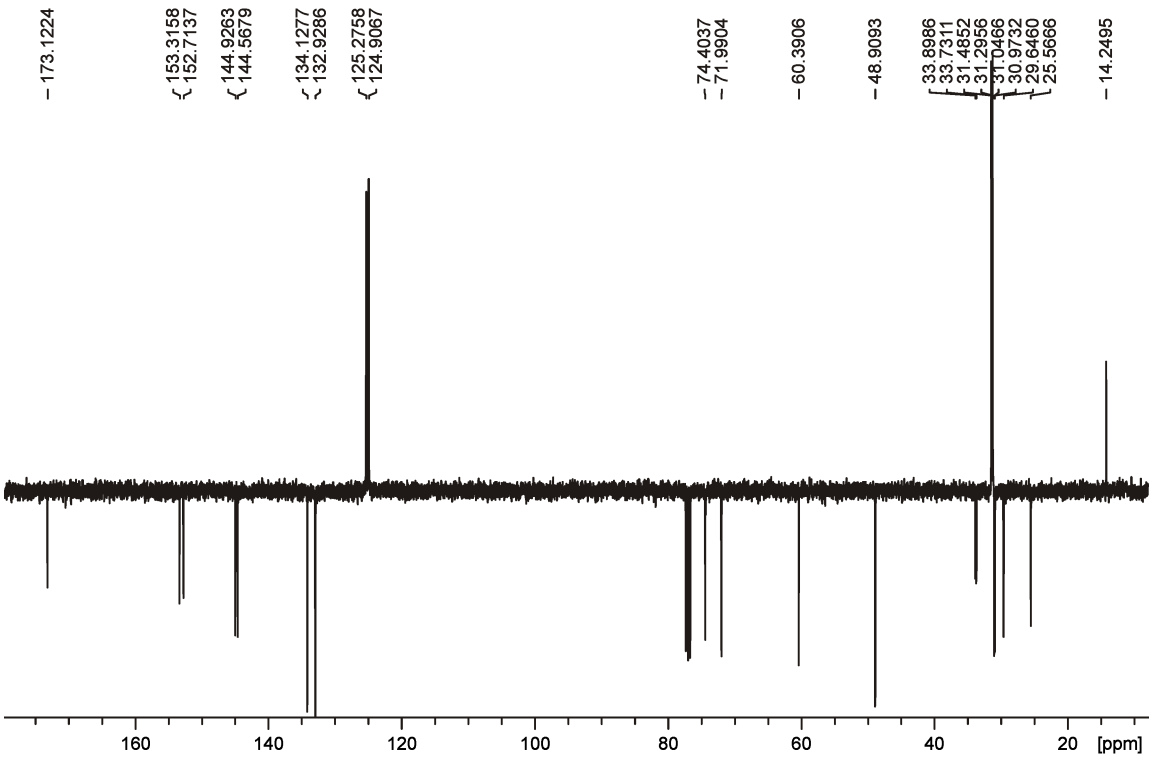


Figure S40. ^{13}C NMR spectrum (APT) of 3-azidopropylated bis(ester) **31** (100 MHz, CDCl$_3$).

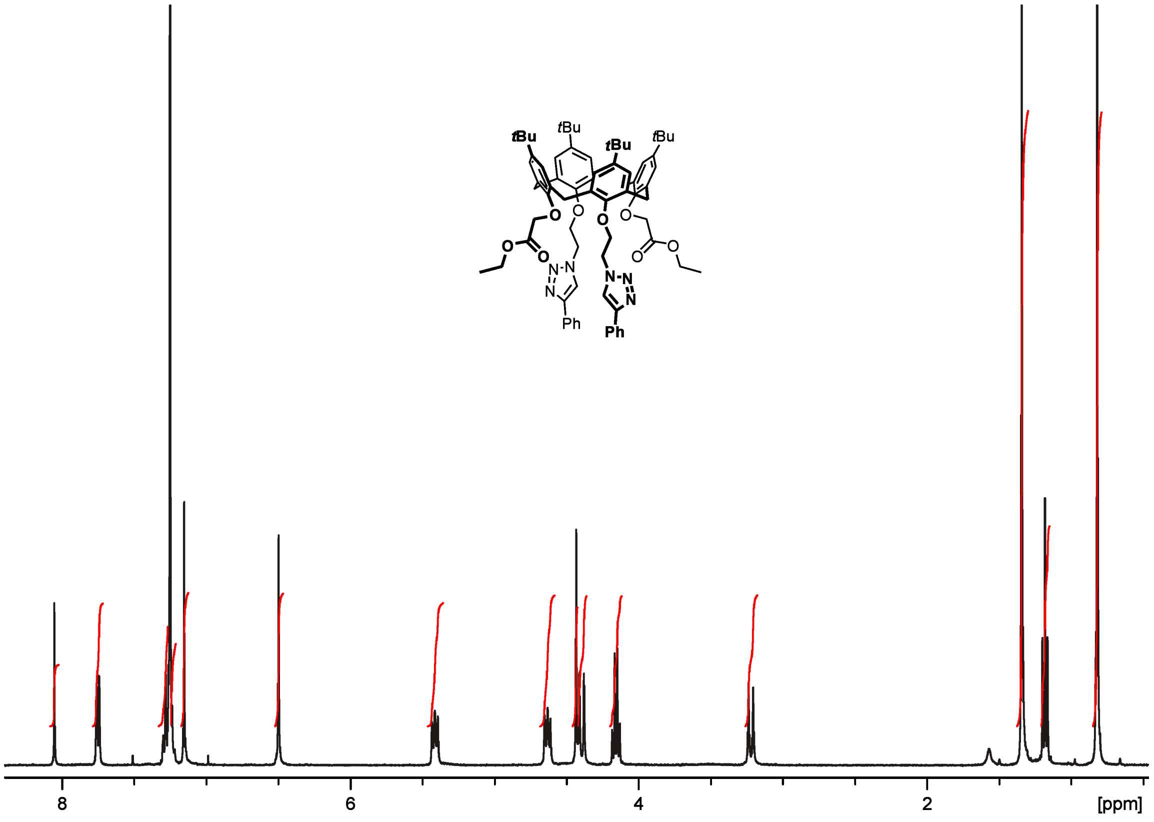


Figure S41. ^{1}H NMR spectrum of triazolated bis(ester) **32** (400 MHz, $CDCl_3$).

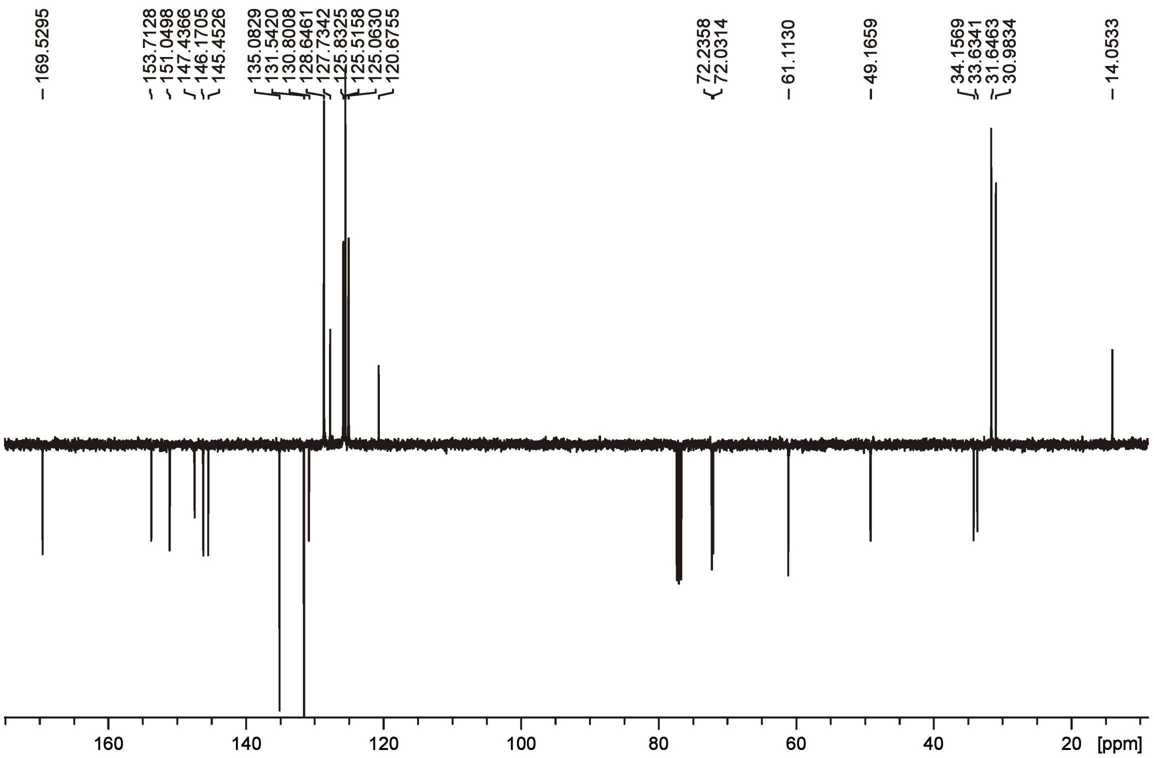


Figure S42. ^{13}C NMR spectrum (APT) of triazolated bis(ester) **32** (100 MHz, $CDCl_3$).

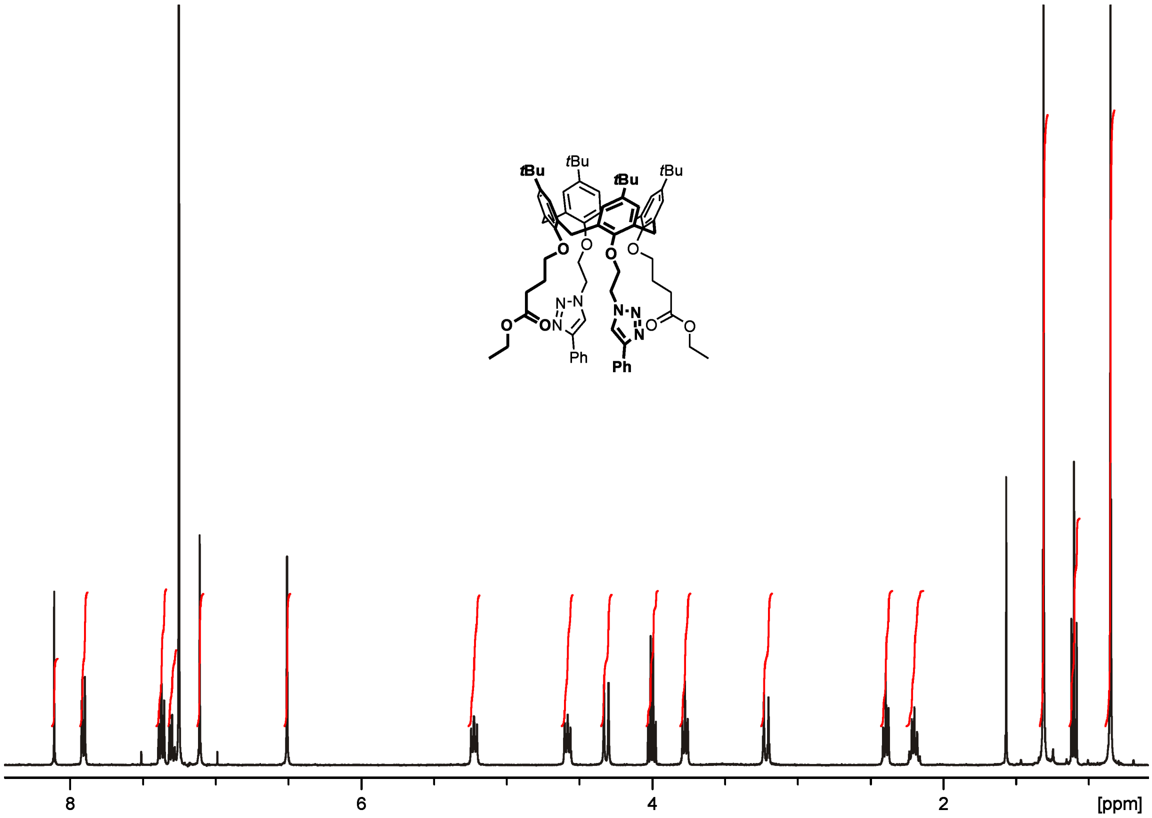


Figure S43. ^{1}H NMR spectrum of triazolated bis(ester) **33** (400 MHz, CDCl$_3$).

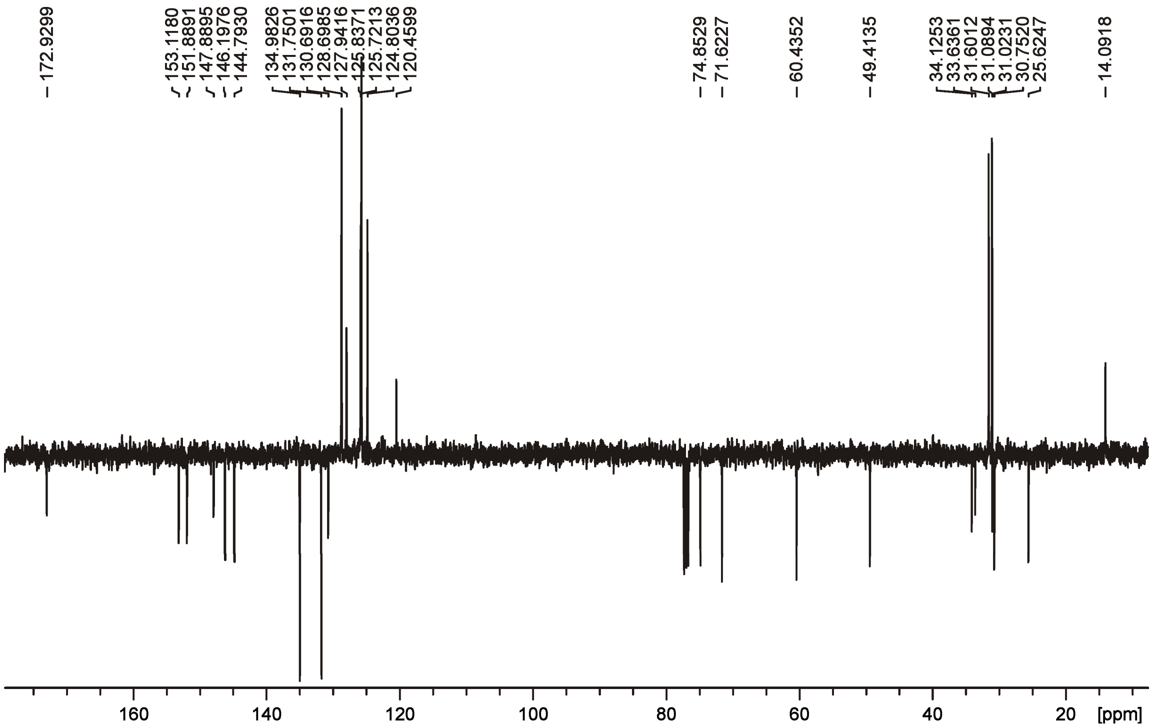


Figure S44. ^{13}C NMR spectrum (APT) of triazolated bis(ester) **33** (100 MHz, CDCl$_3$).

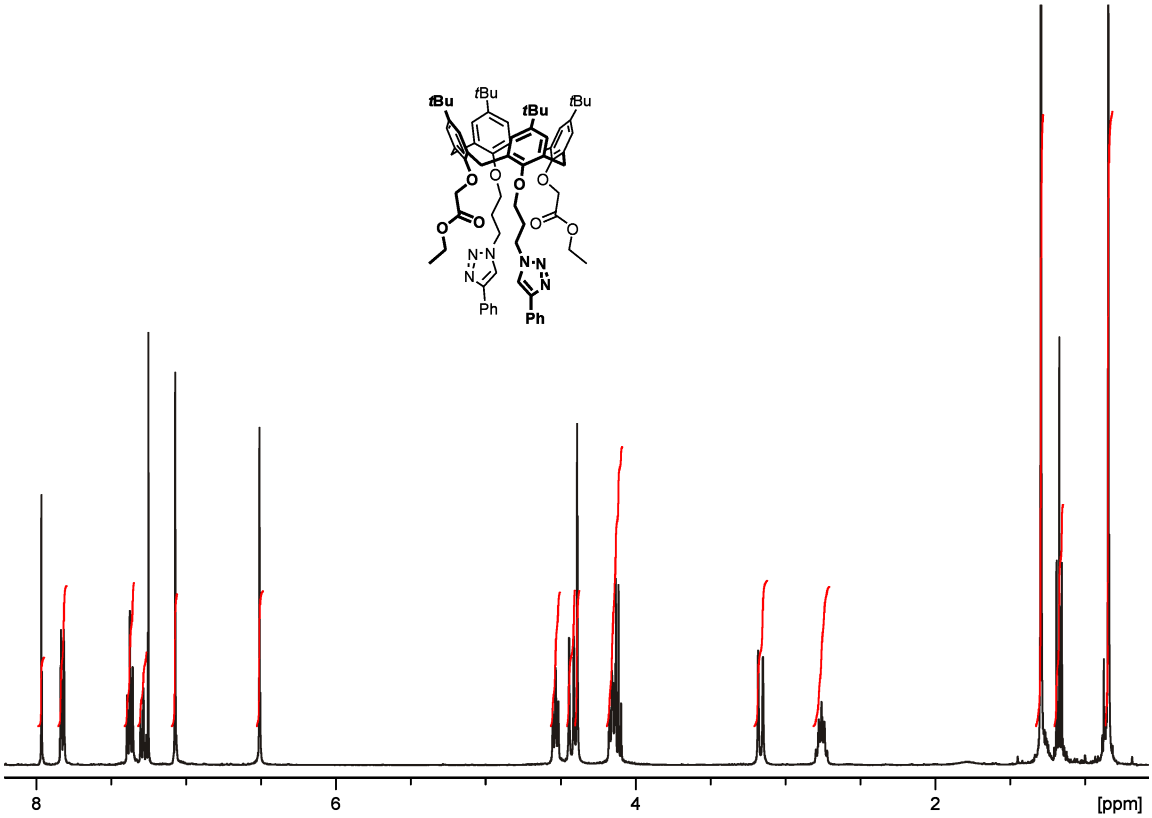


Figure S45. ^{1}H NMR spectrum of triazolated bis(ester) **34** (400 MHz, $CDCl_3$).

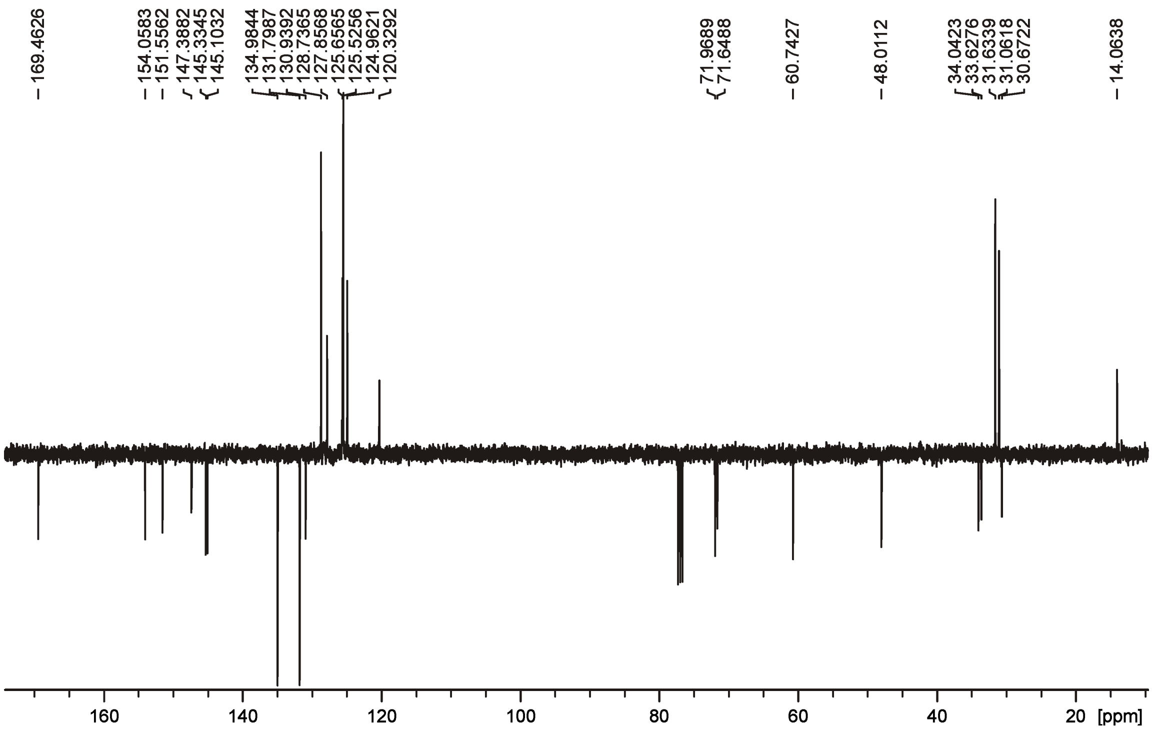


Figure S46. ^{13}C NMR spectrum (APT) of triazolated bis(ester) **34** (100 MHz, $CDCl_3$).

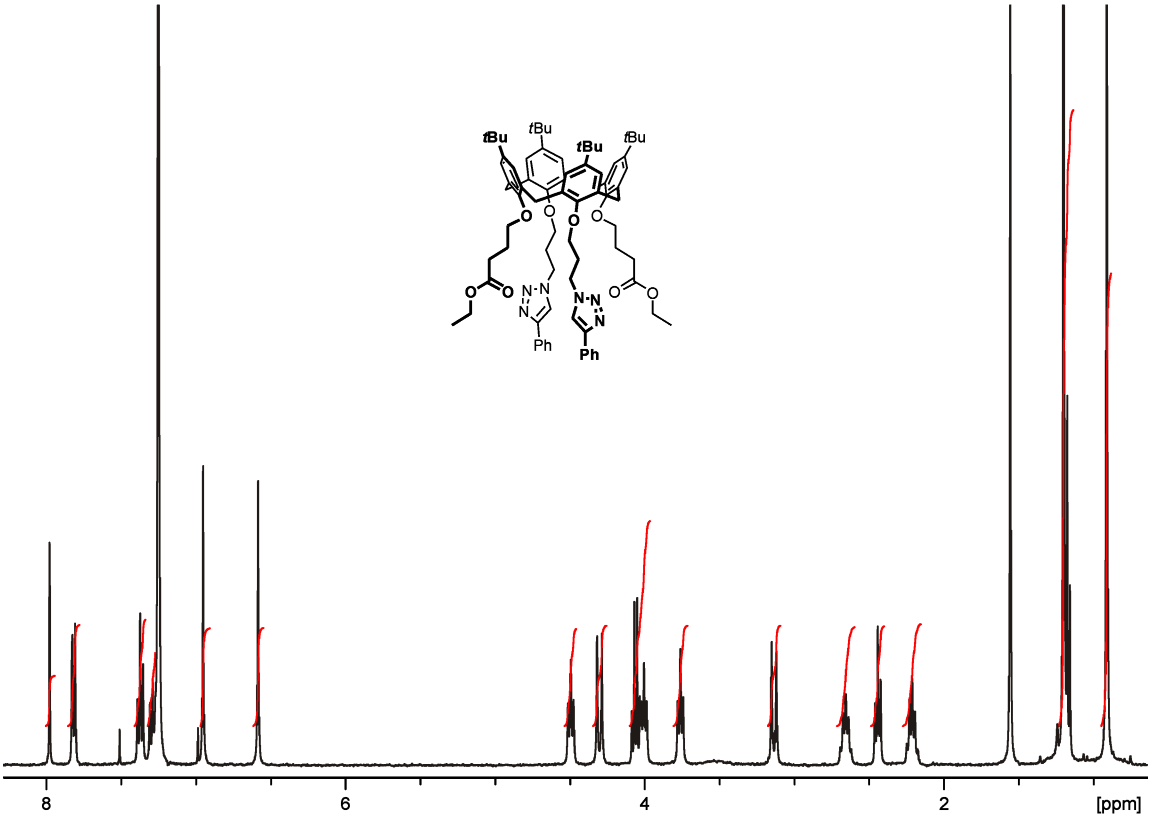


Figure S47. ^{1}H NMR spectrum of triazolated bis(ester) **35** (400 MHz, $CDCl_3$).

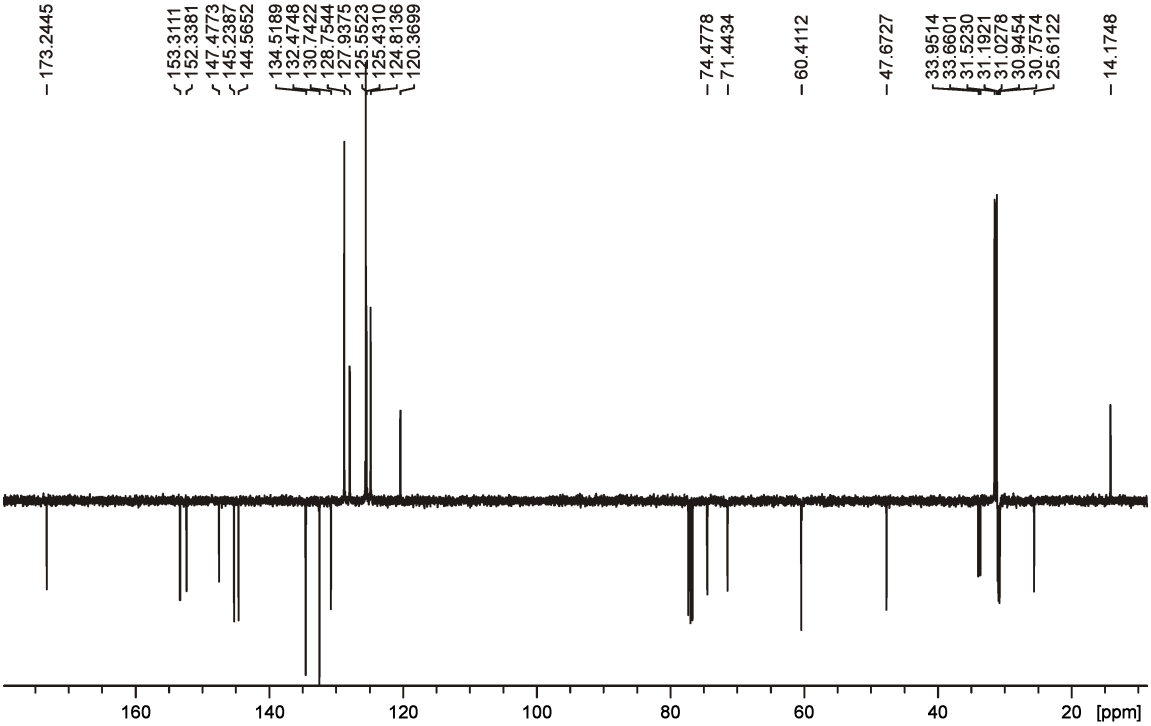


Figure S48. ^{13}C NMR spectrum (APT) of triazolated bis(ester) **35** (100 MHz, $CDCl_3$).

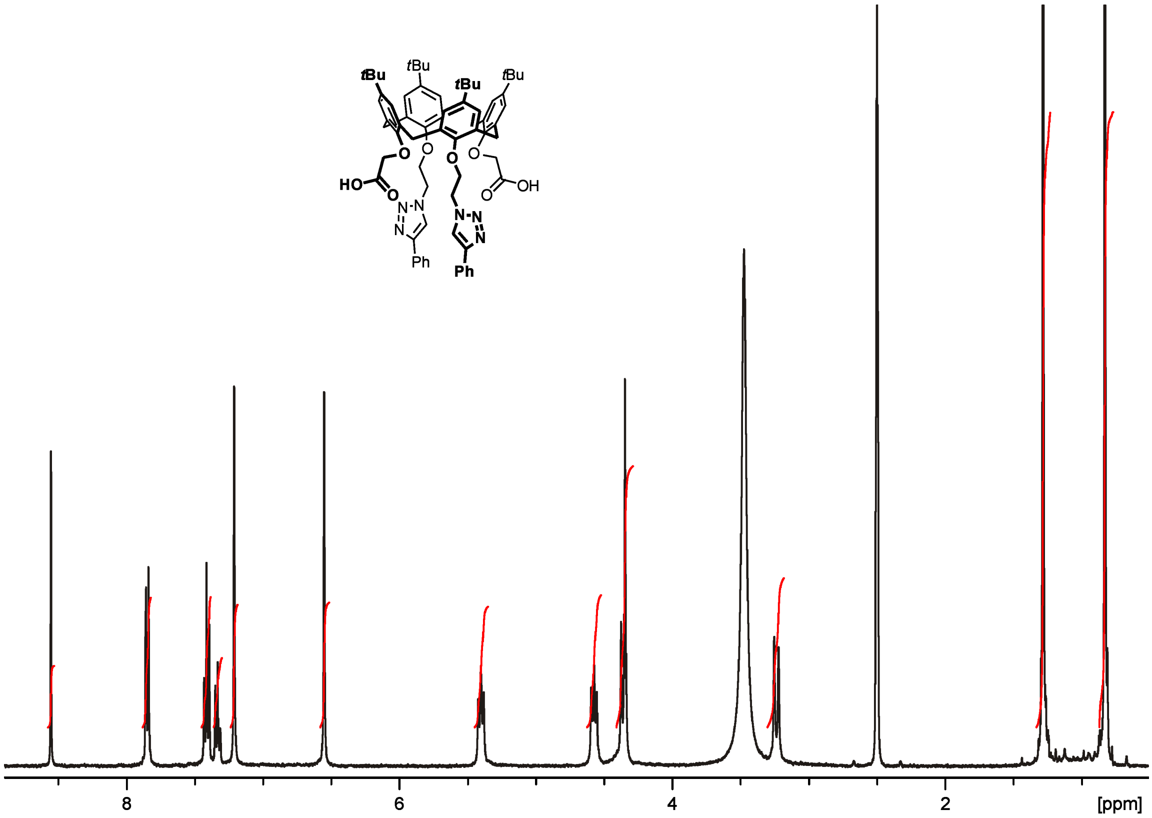


Figure S49. ^{1}H NMR spectrum of triazolated bis(acid) **36** (400 MHz, DMSO-d_6).

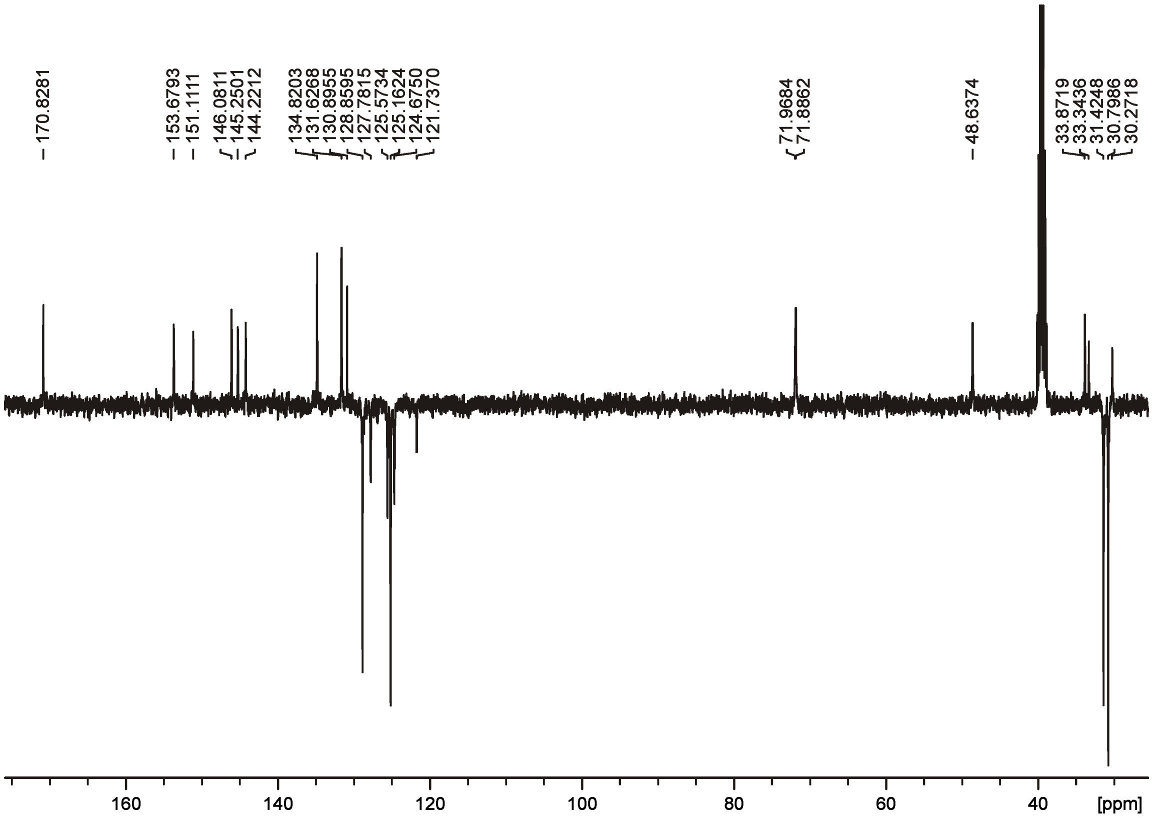


Figure S50. ^{13}C NMR spectrum (APT) of triazolated bis(acid) **36** (100 MHz, DMSO-d_6).

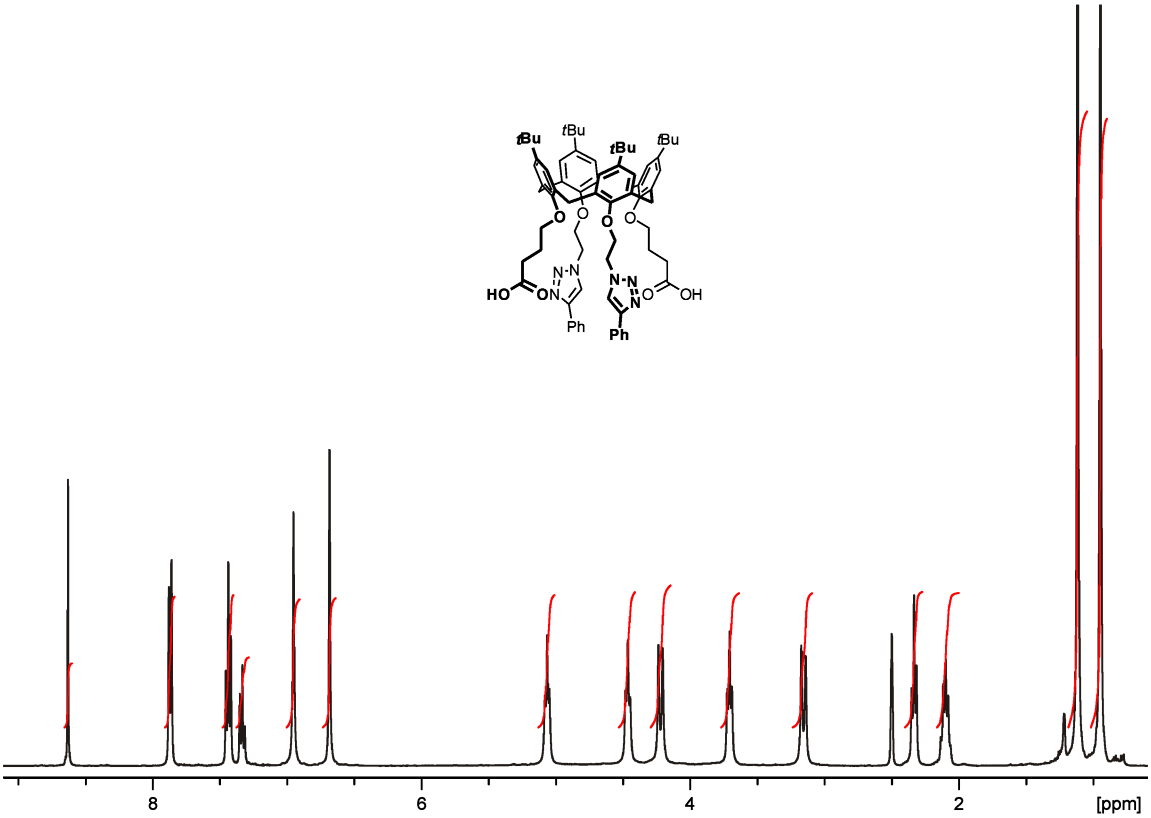


Figure S51. ^{1}H NMR spectrum of triazolated bis(acid) **37** (400 MHz, DMSO-d_6).

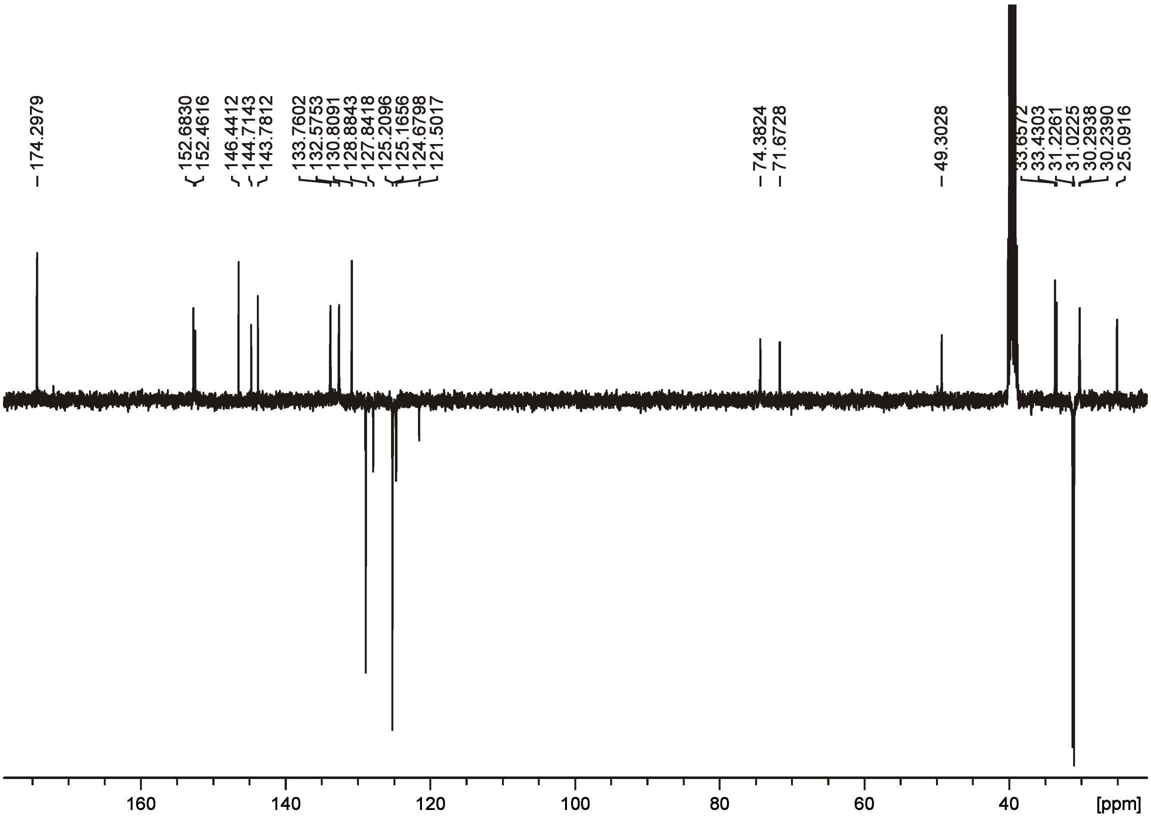


Figure S52. ^{13}C NMR spectrum (APT) of triazolated bis(acid) **37** (100 MHz, DMSO-d_6).

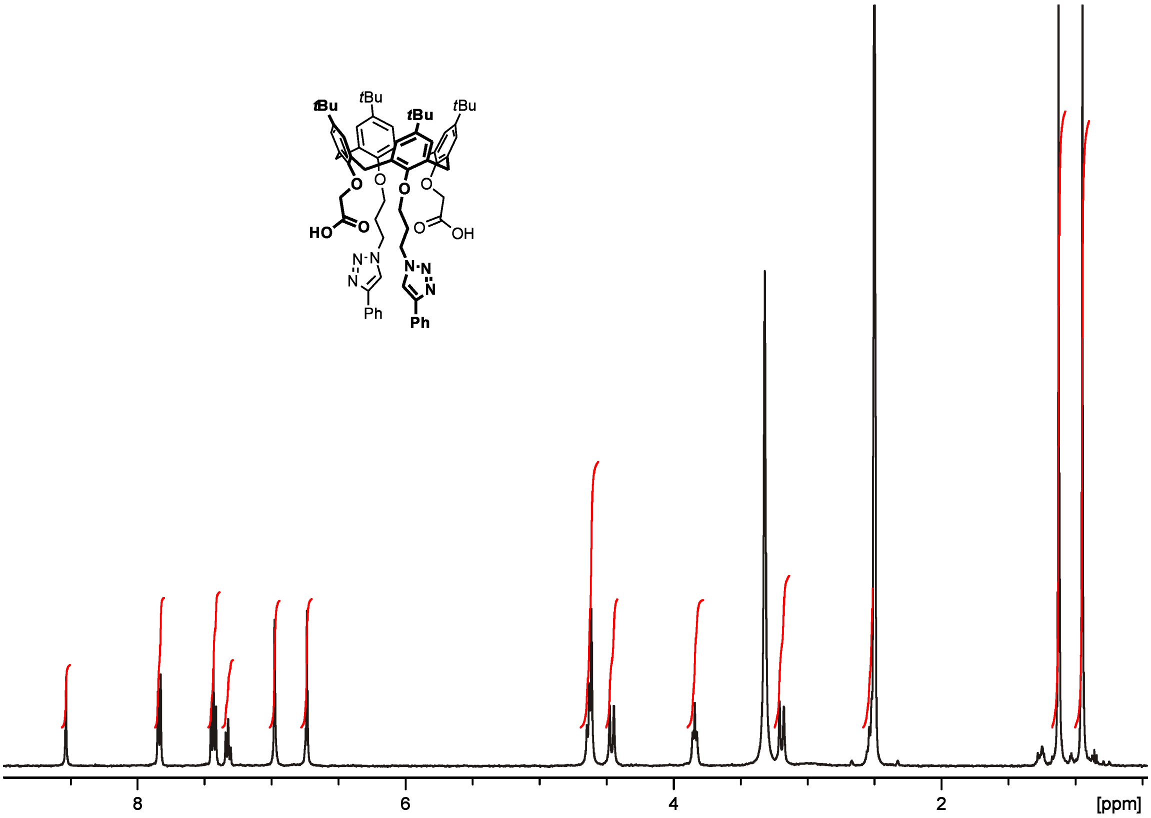


Figure S53. ^{1}H NMR spectrum of triazolated bis(acid) **38** (400 MHz, DMSO-d_6).

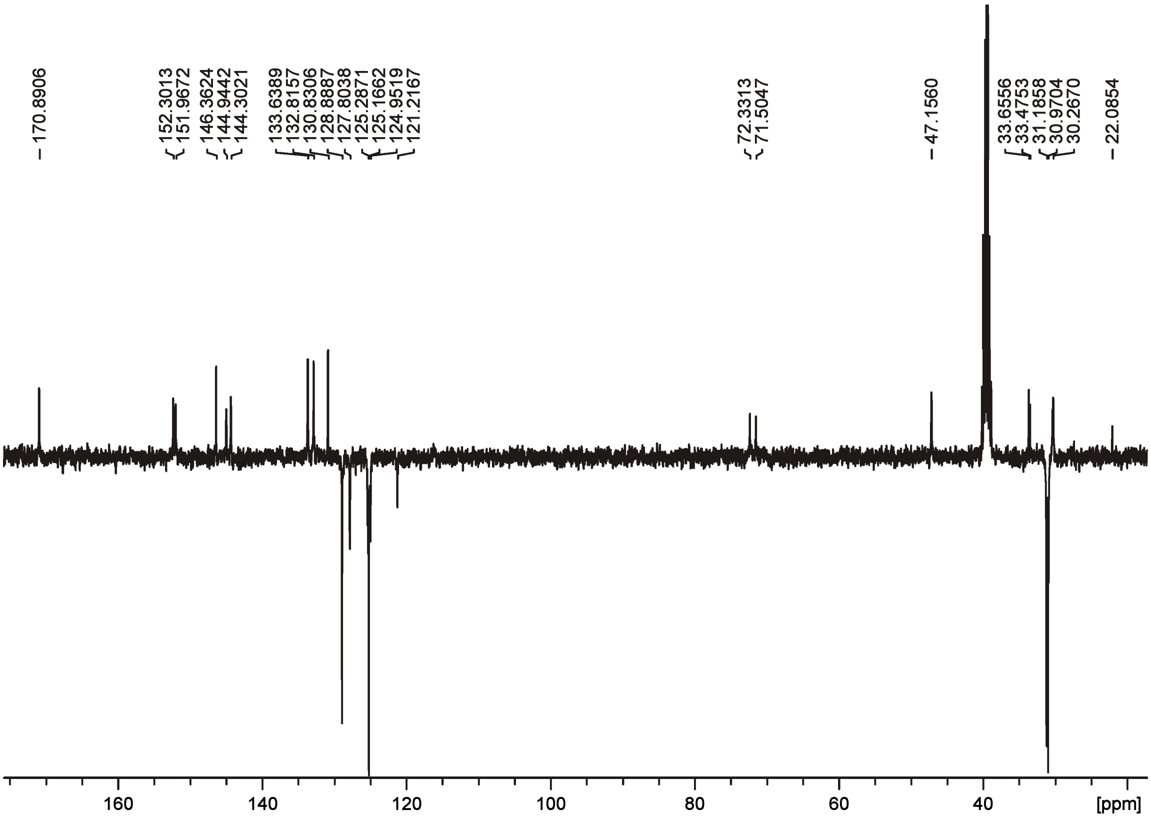


Figure S54. ^{13}C NMR spectrum (APT) of triazolated bis(acid) **38** (100 MHz, DMSO-d_6).

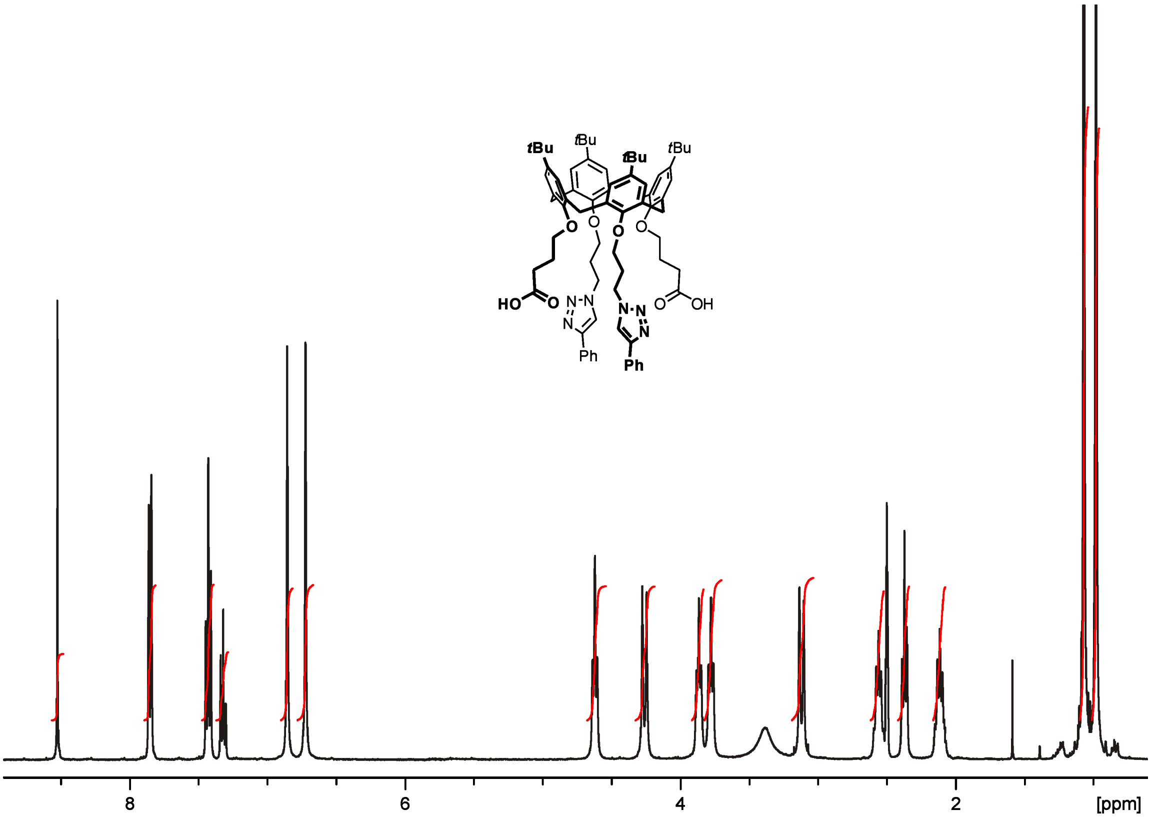


Figure S55. ^{1}H NMR spectrum of triazolated bis(acid) **39** (400 MHz, DMSO-d_6).

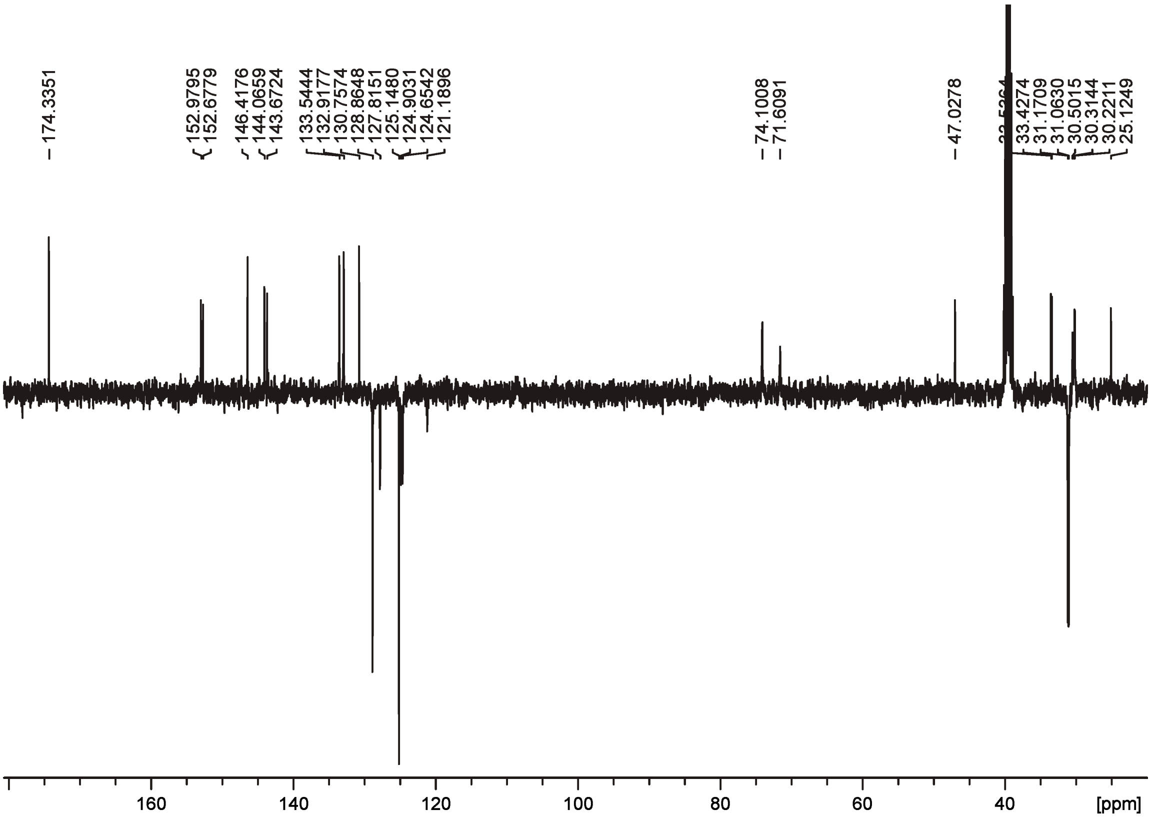


Figure S56. ^{13}C NMR spectrum (APT) of triazolated bis(acid) **39** (100 MHz, DMSO-d_6).

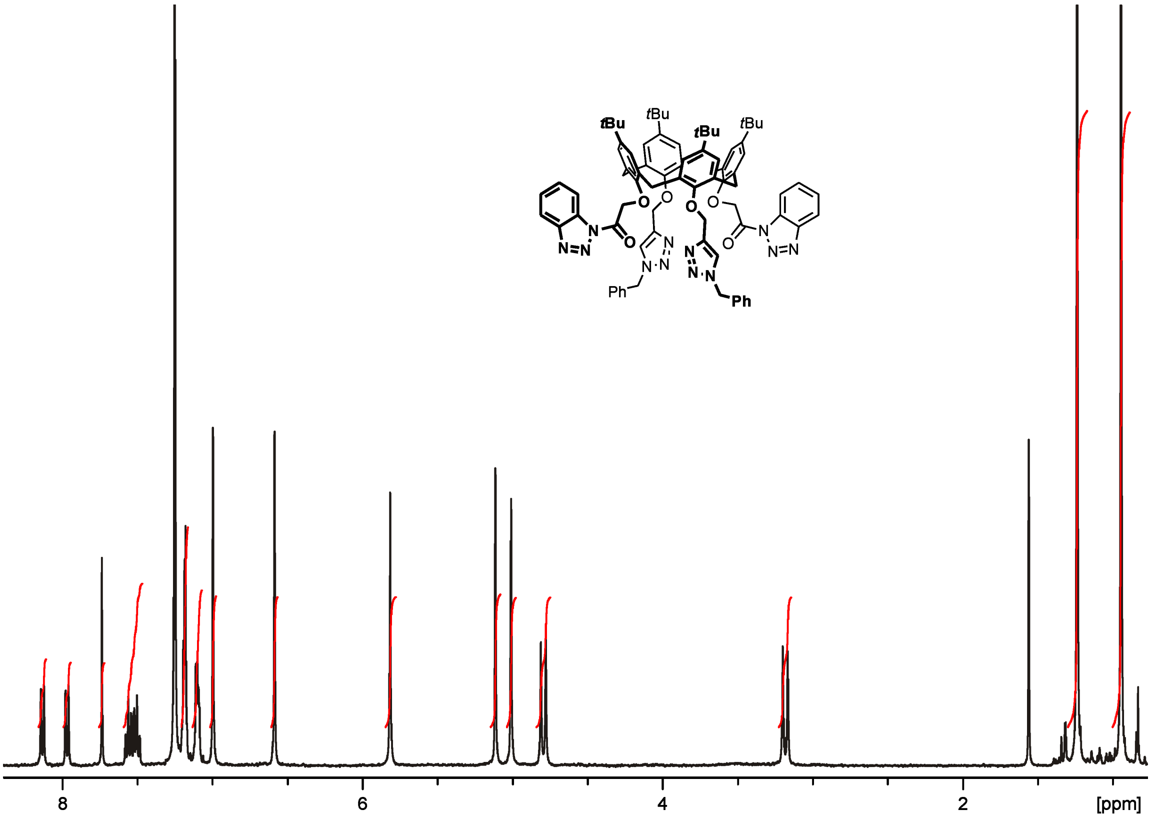


Figure S57. ^{1}H NMR spectrum of triazolated bis(1-acylbenzotriazole) **40** (400 MHz, CDCl$_3$).

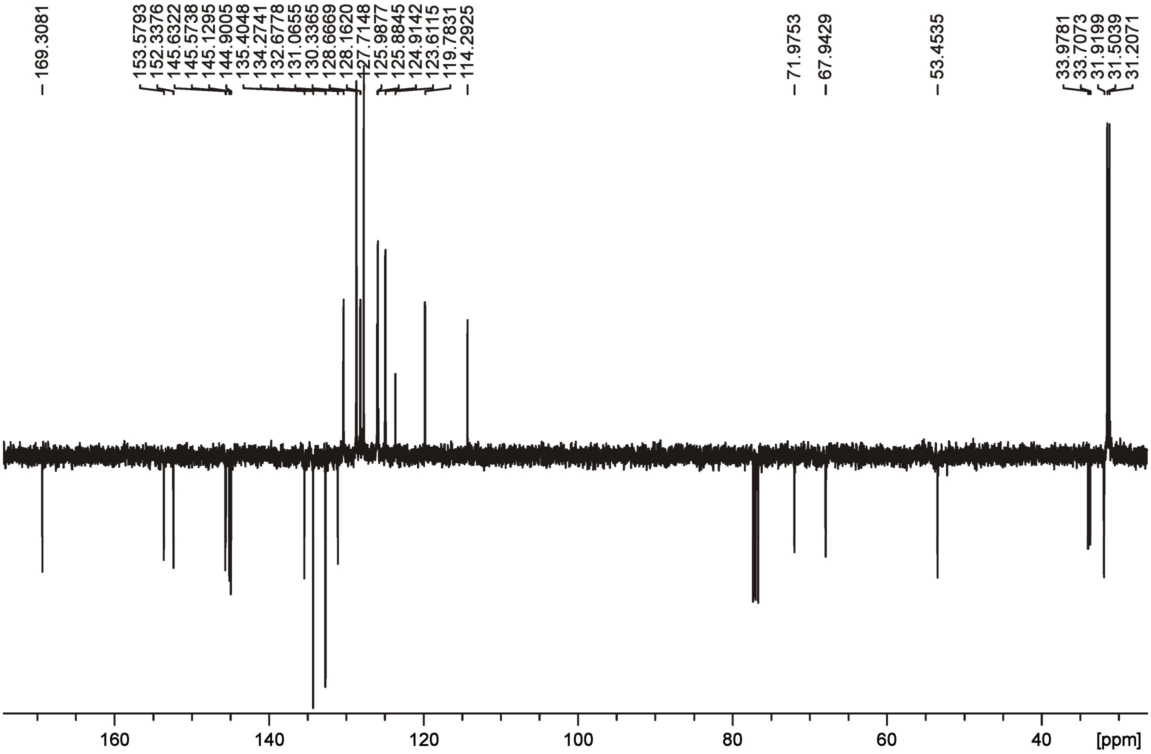


Figure S58. ^{13}C NMR spectrum (APT) of triazolated bis(1-acylbenzotriazole) **40** (100 MHz, CDCl$_3$).

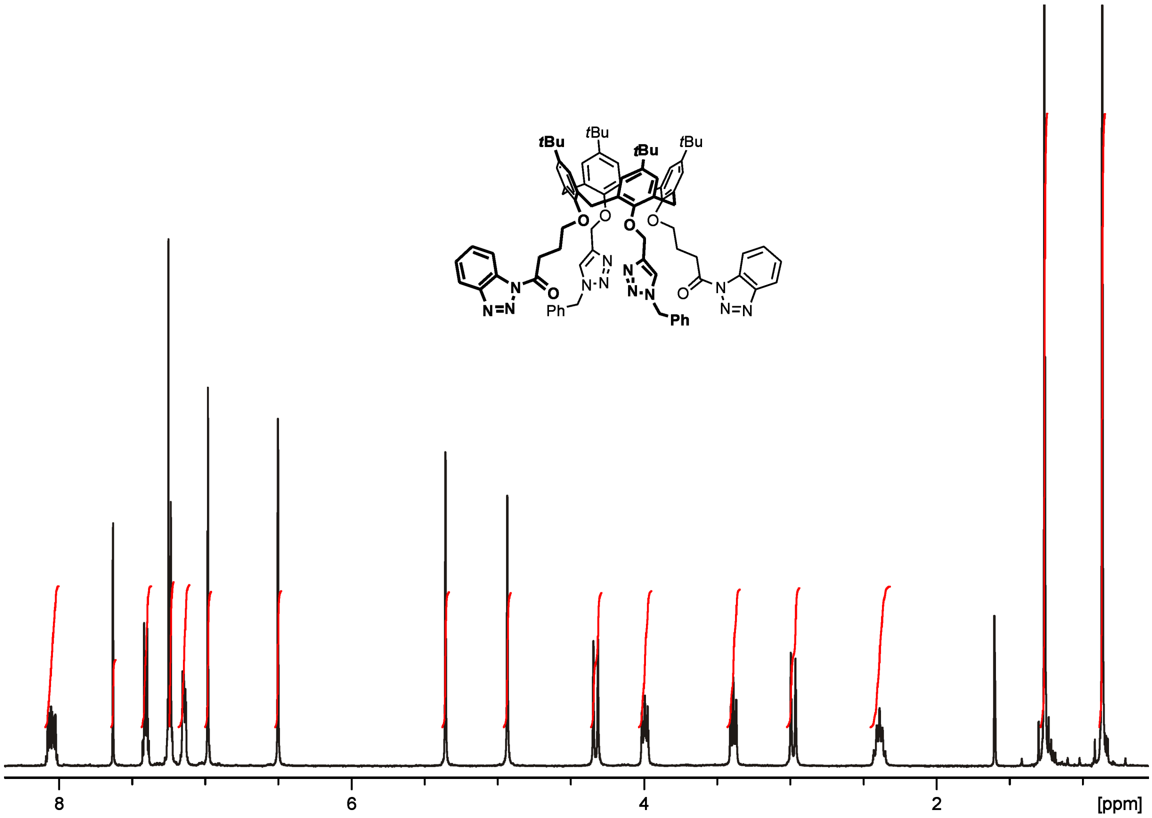


Figure S59. ^{1}H NMR spectrum of triazolated bis(1-acylbenzotriazole) **41** (400 MHz, $CDCl_3$).

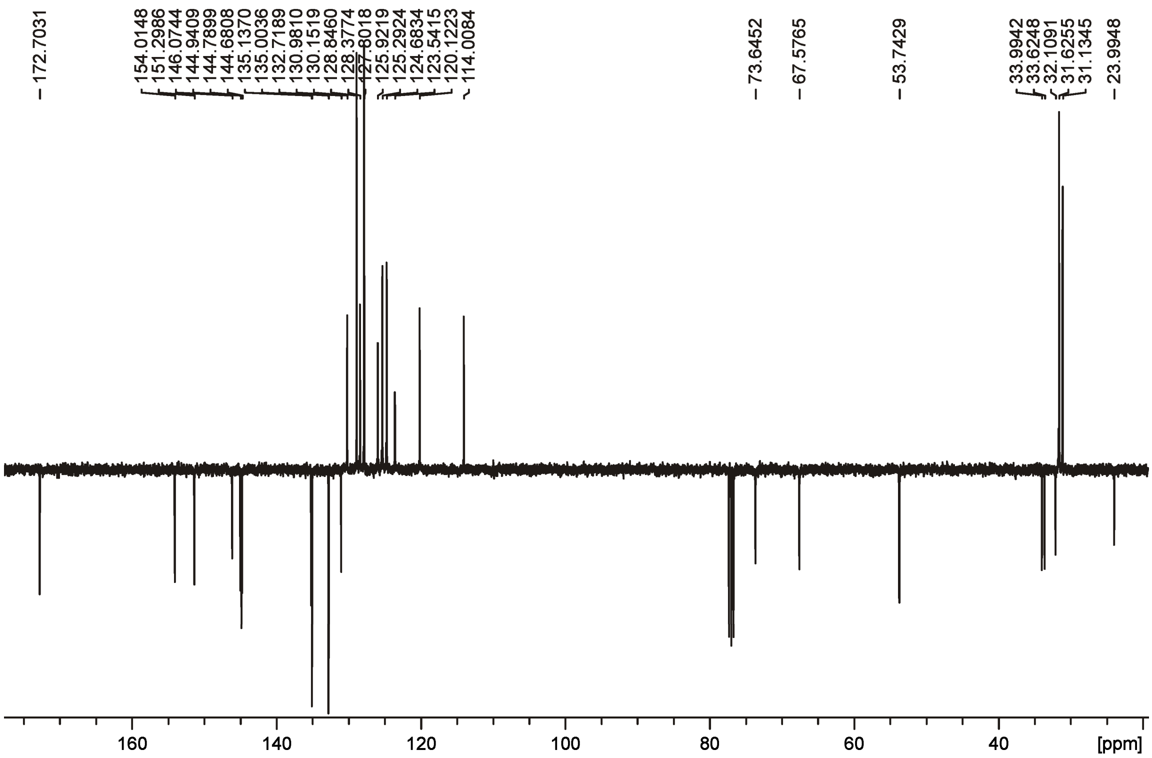


Figure S60. ^{13}C NMR spectrum (APT) of triazolated bis(1-acylbenzotriazole) **41** (100 MHz, $CDCl_3$).

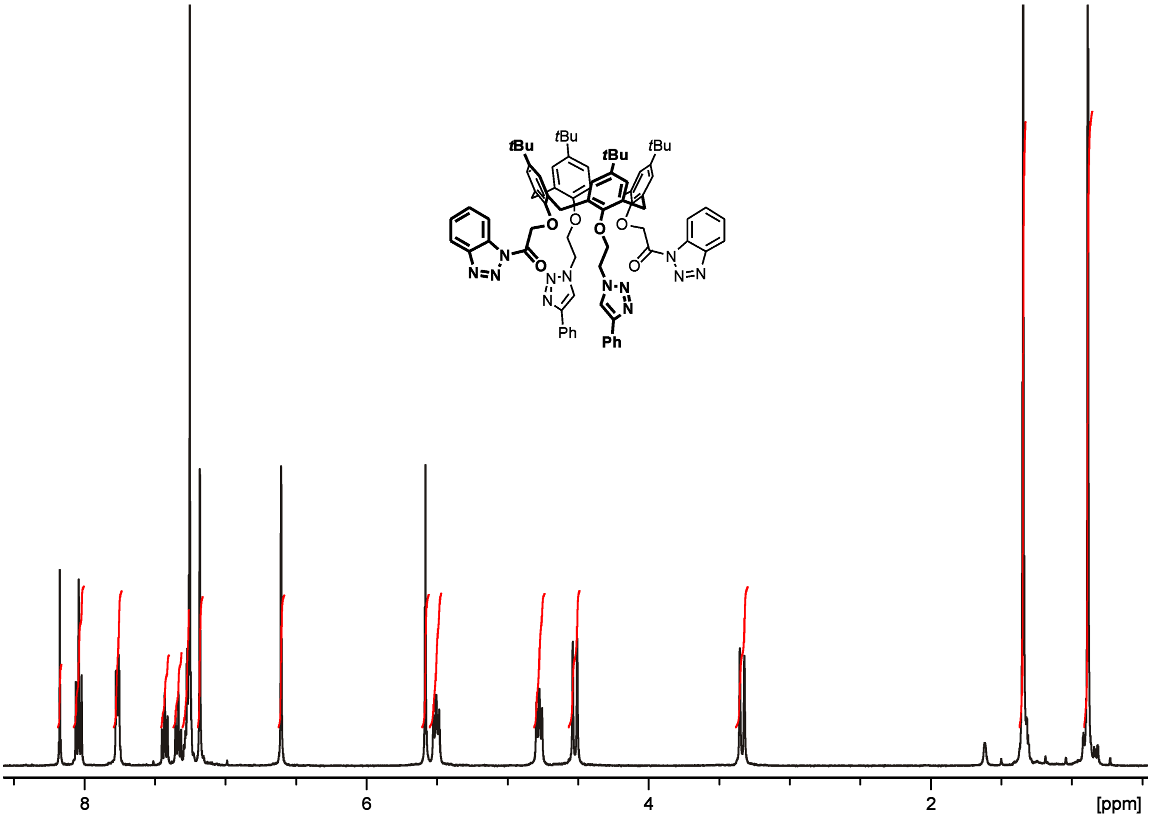


Figure S61. ^{1}H NMR spectrum of triazolated bis(1-acylbenzotriazole) **42** (400 MHz, CDCl$_3$).

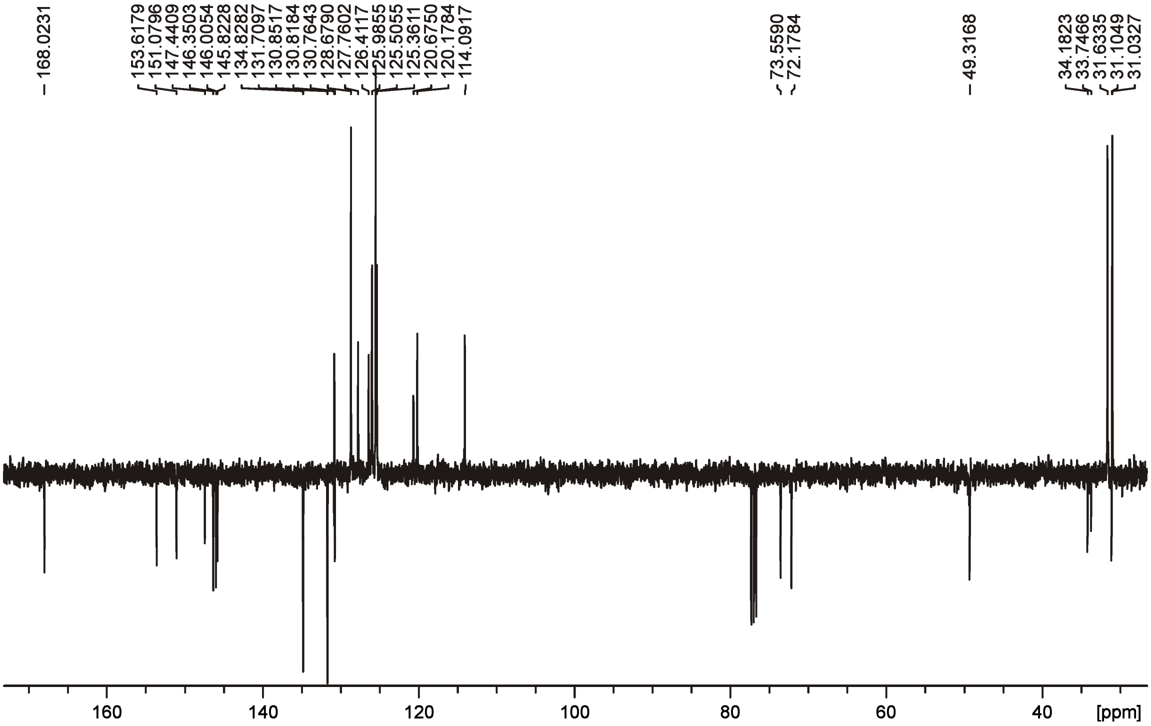


Figure S62. ^{13}C NMR spectrum (APT) of triazolated bis(1-acylbenzotriazole) **42** (100 MHz, CDCl$_3$).

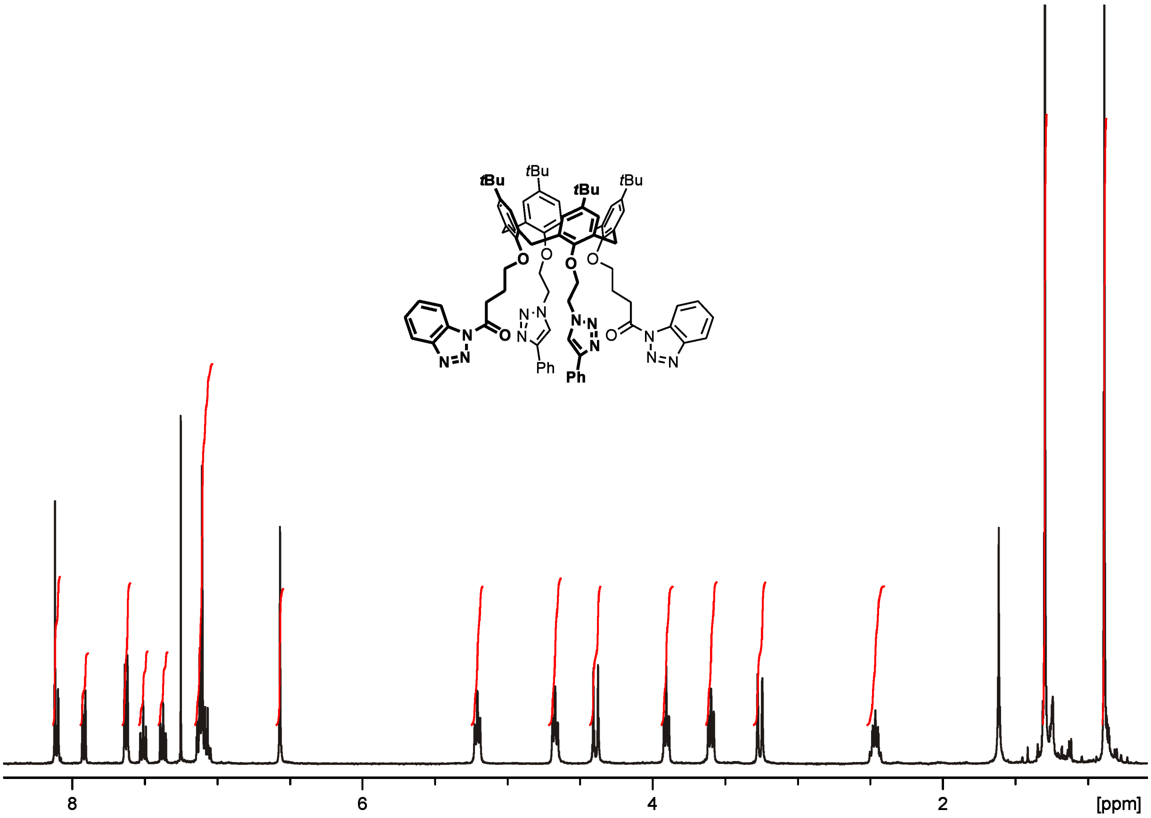


Figure S63. ^{1}H NMR spectrum of triazolated bis(1-acylbenzotriazole) **43** (400 MHz, $CDCl_3$).

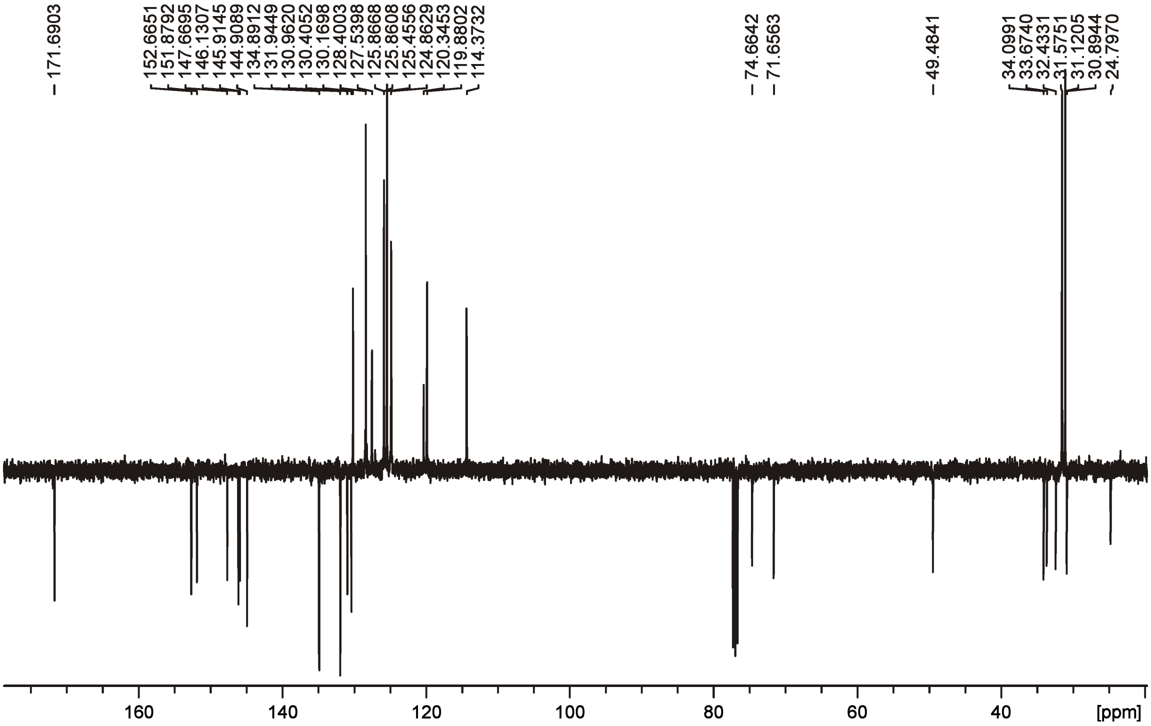


Figure S64. ^{13}C NMR spectrum (APT) of triazolated bis(1-acylbenzotriazole) **43** (100 MHz, $CDCl_3$).

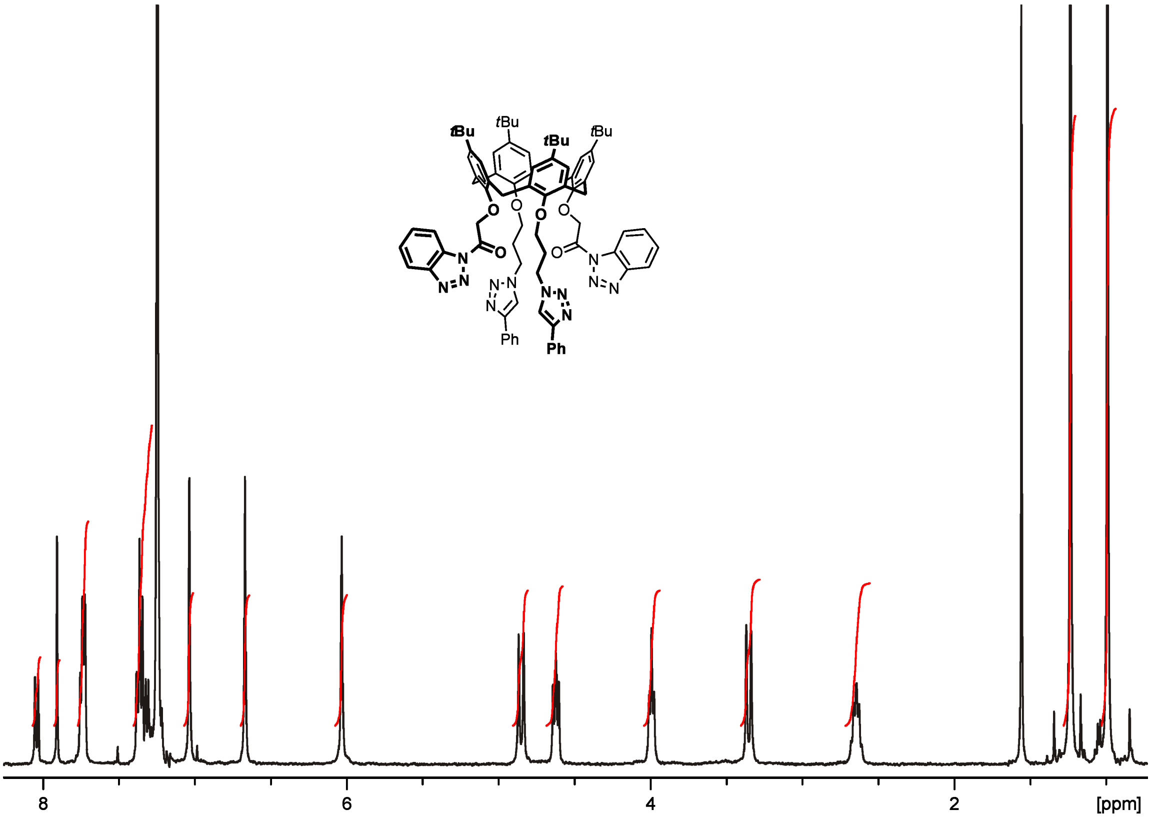


Figure S65. ^{1}H NMR spectrum of triazolated bis(1-acylbenzotriazole) **44** (400 MHz, $CDCl_3$).

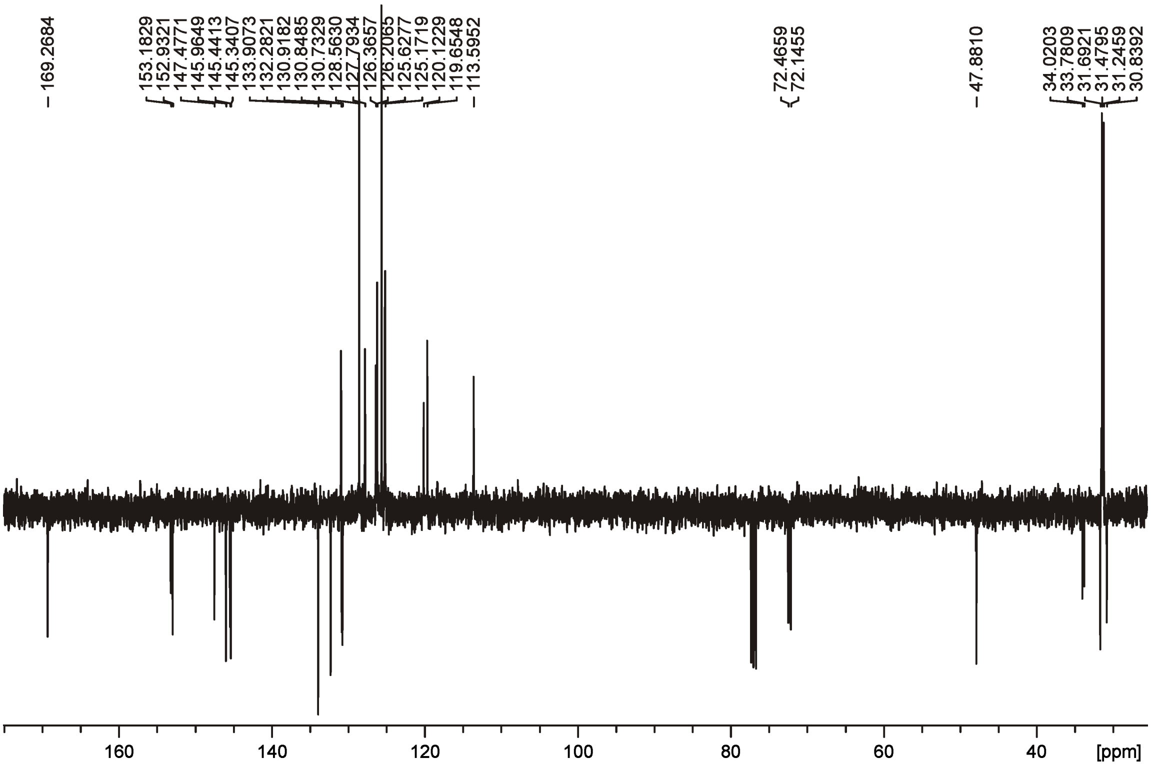


Figure S66. ^{13}C NMR spectrum (APT) of triazolated bis(1-acylbenzotriazole) **44** (100 MHz, $CDCl_3$).

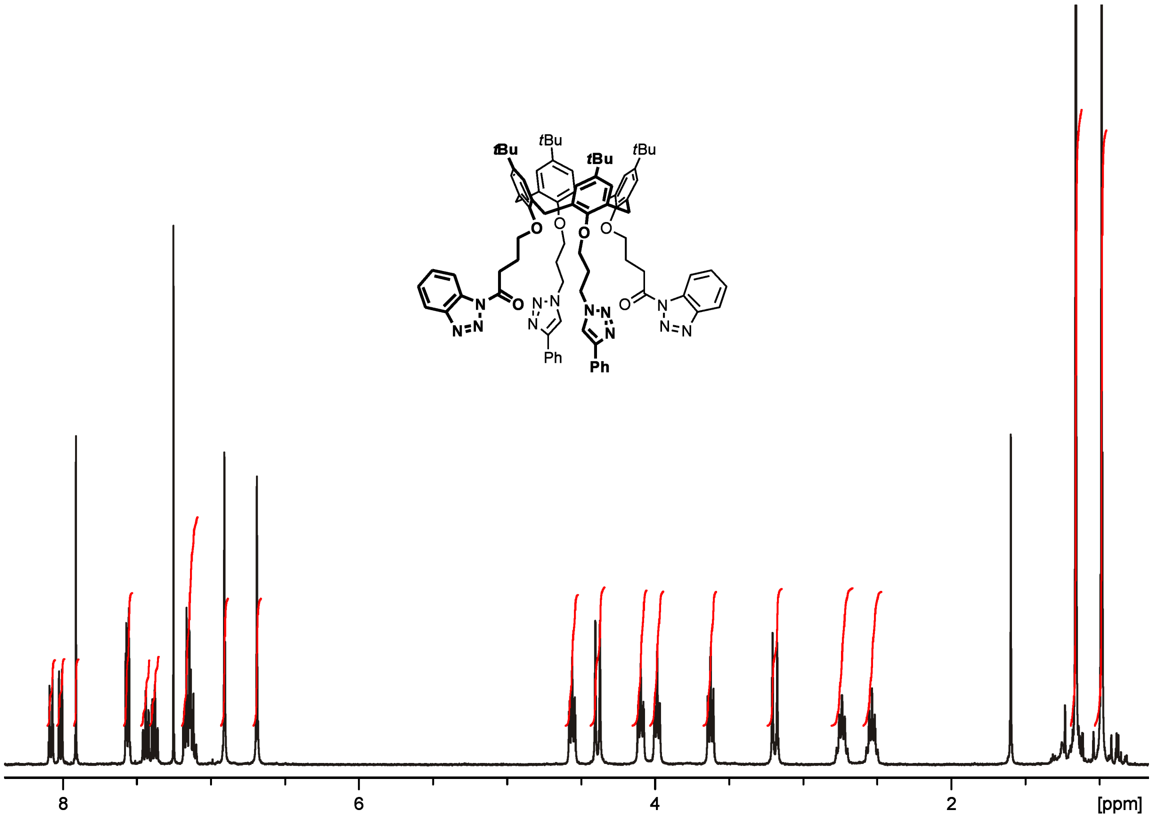


Figure S67. ^{1}H NMR spectrum of triazolated bis(1-acylbenzotriazole) **45** (400 MHz, CDCl$_3$).

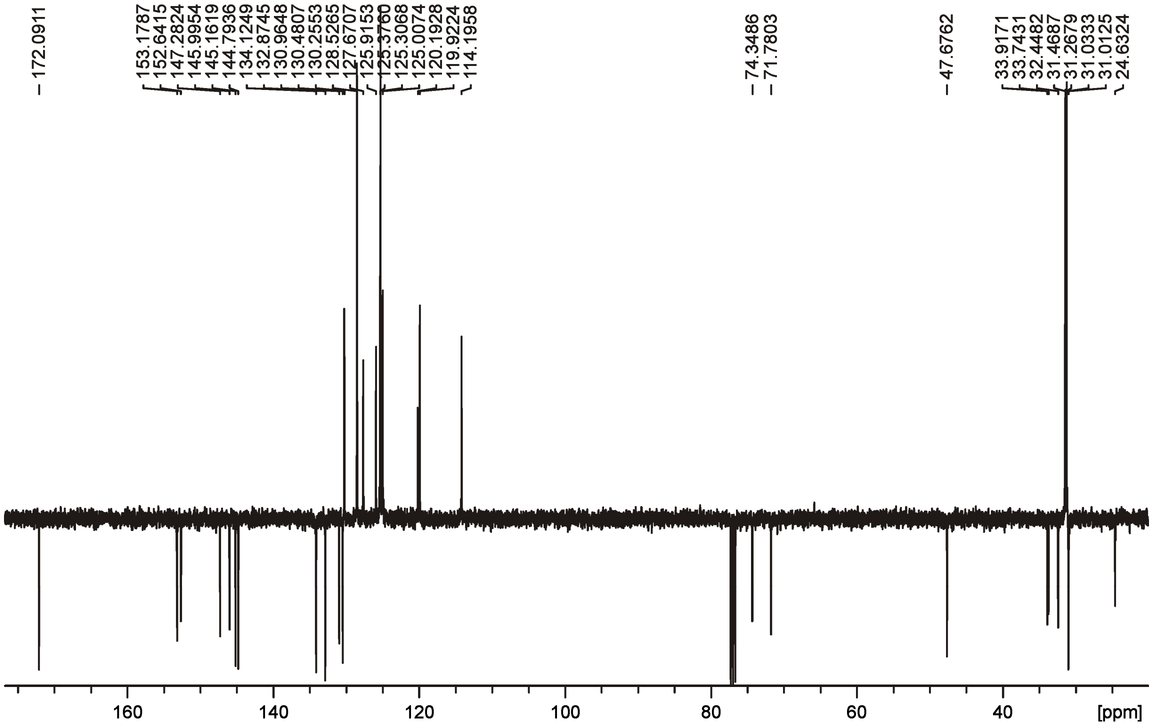


Figure S68. ^{13}C NMR spectrum (APT) of triazolated bis(1-acylbenzotriazole) **45** (100 MHz, CDCl$_3$).

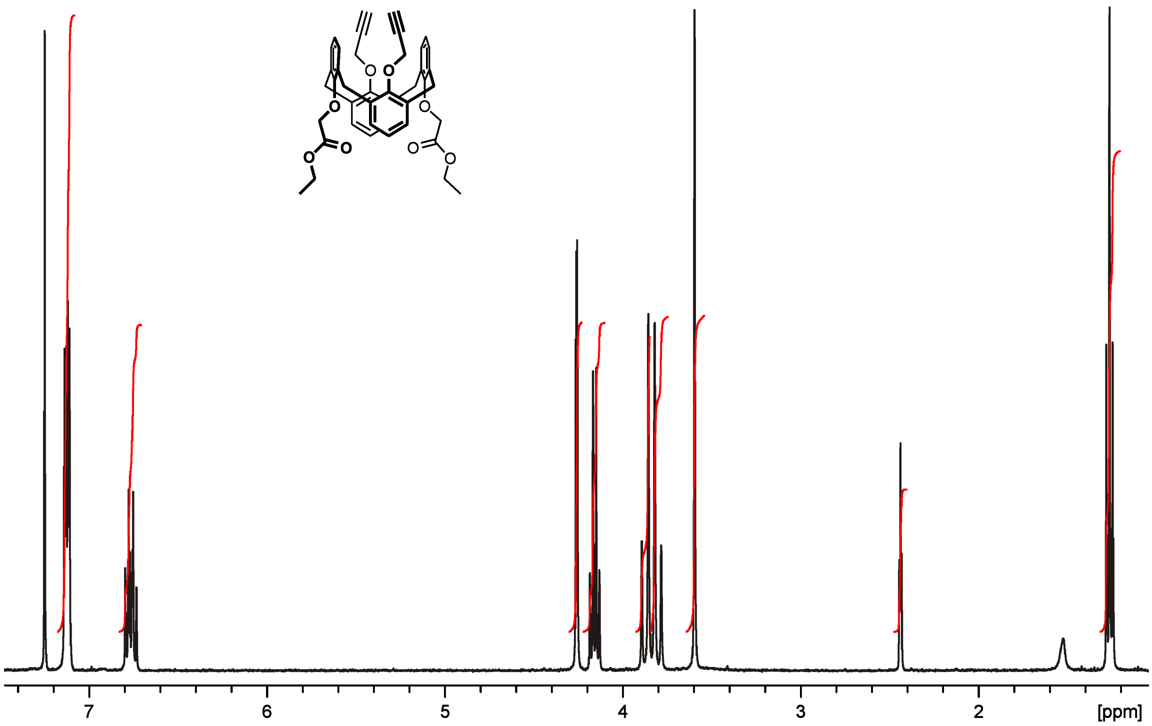


Figure S69. ^{1}H NMR spectrum of propargylated bis(ester) **48** (400 MHz, $CDCl_3$).

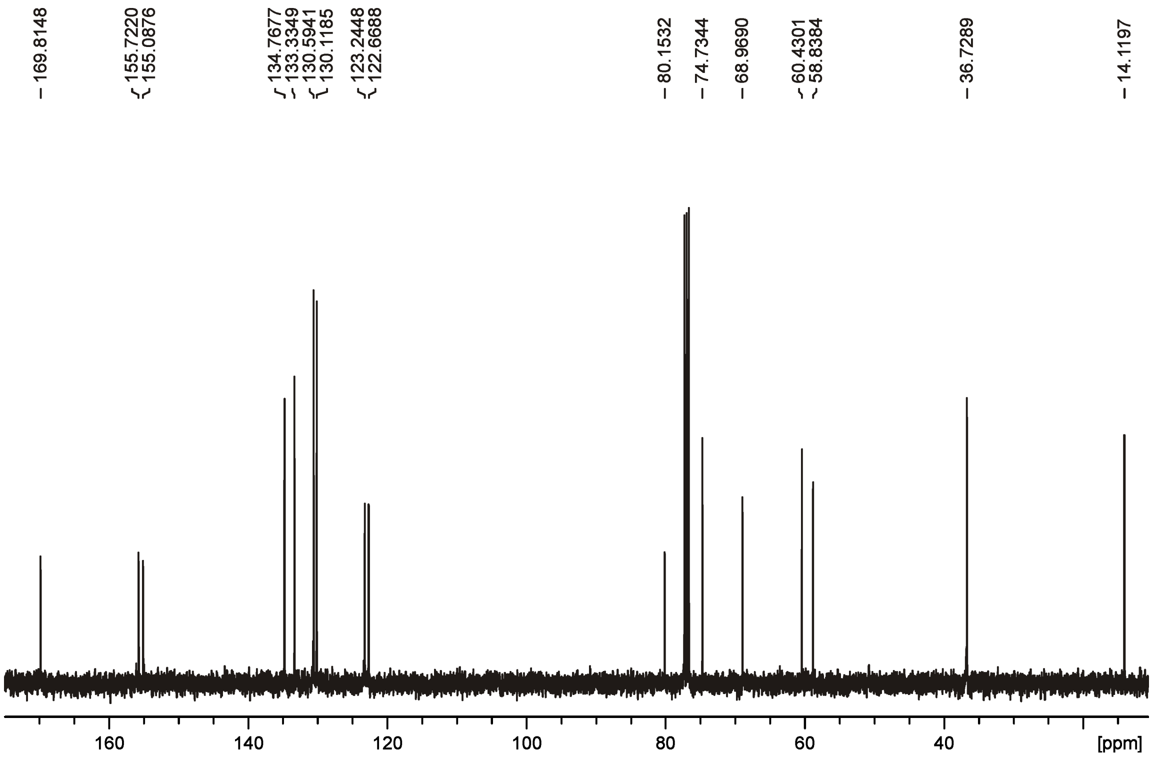


Figure S70. ^{13}C NMR spectrum of propargylated bis(ester) **48** (100 MHz, $CDCl_3$).

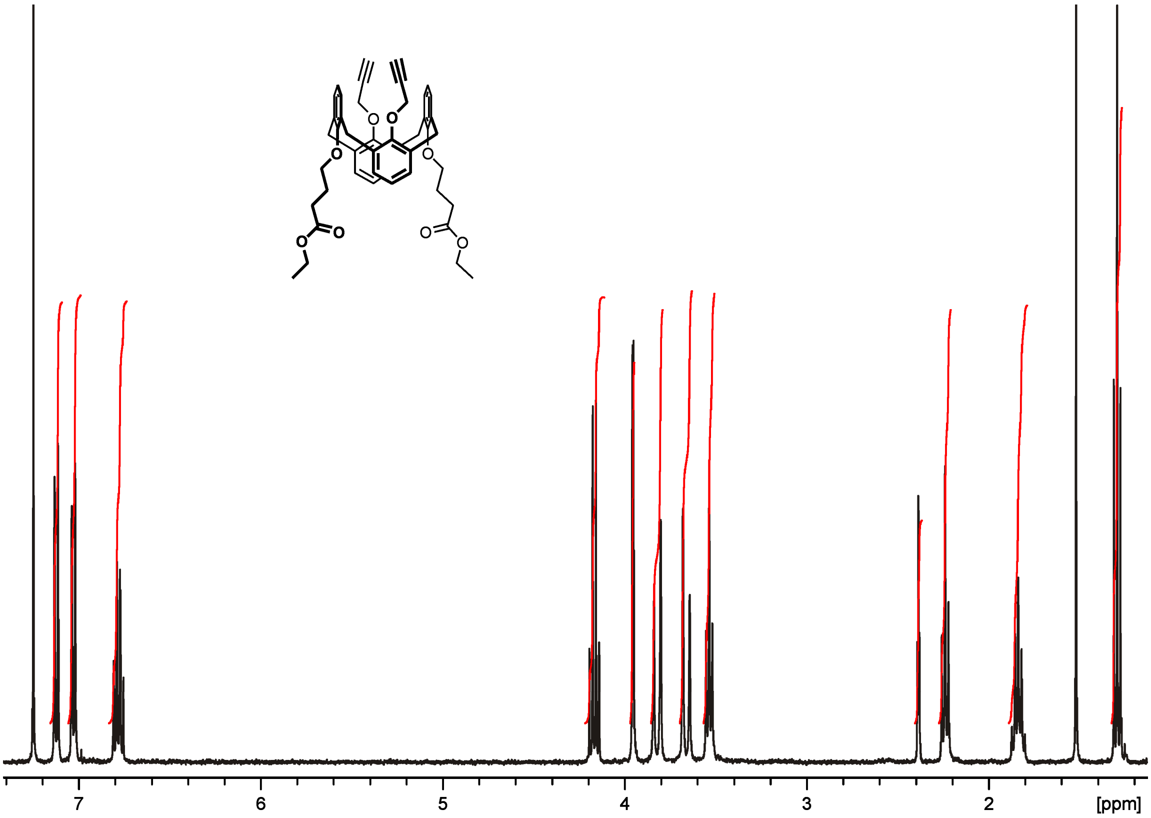


Figure S71. ^{1}H NMR spectrum of propargylated bis(ester) **49** (400 MHz, $CDCl_3$).

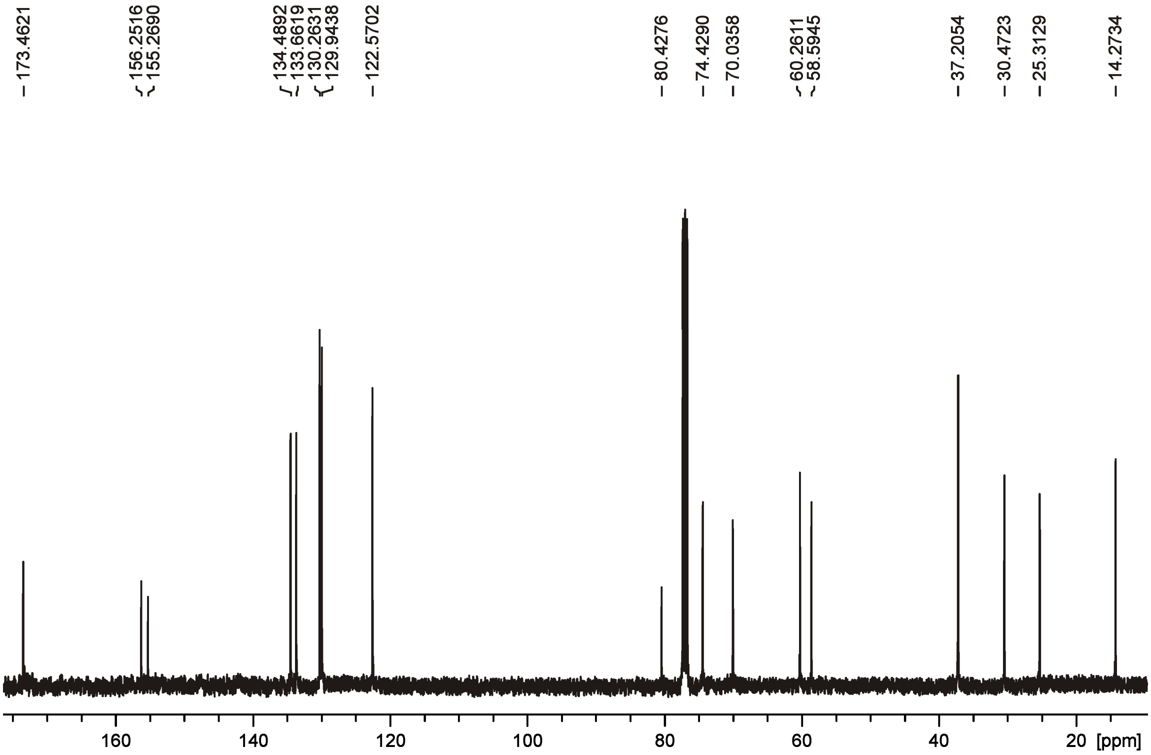


Figure S72. ^{13}C NMR spectrum of propargylated bis(ester) **49** (100 MHz, $CDCl_3$).

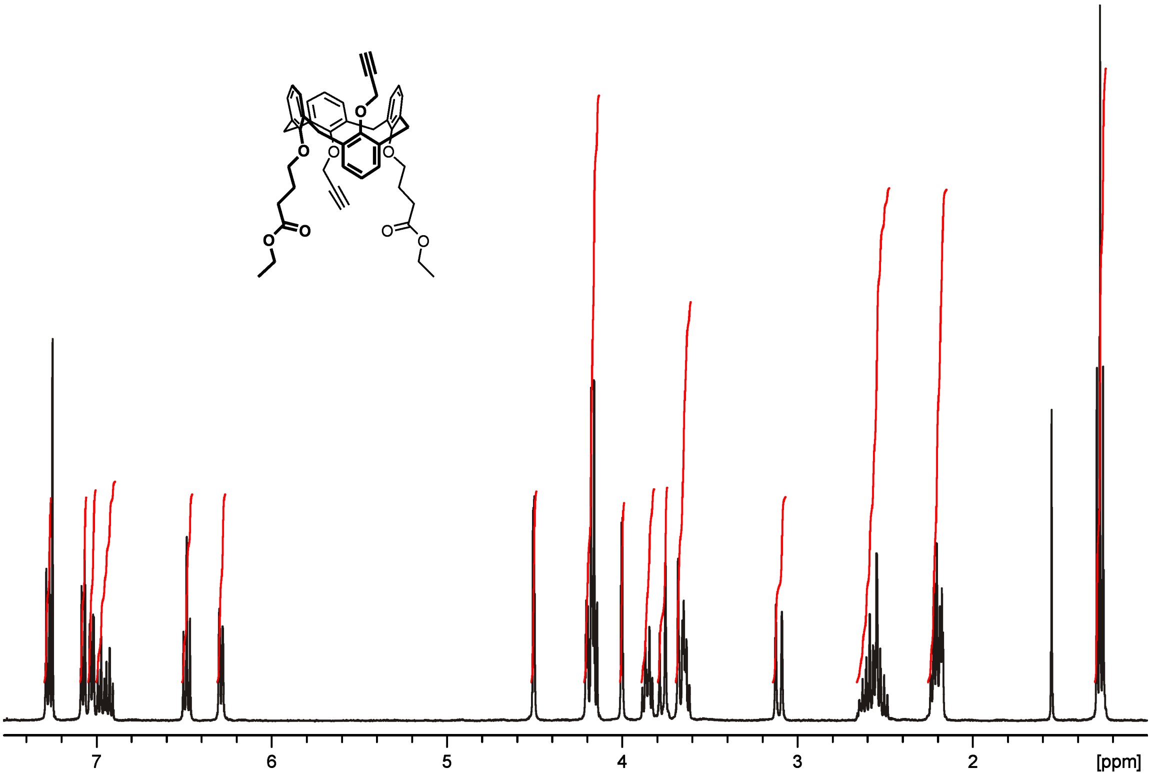


Figure S73. ^{1}H NMR spectrum of propargylated bis(ester) **50** (400 MHz, $CDCl_3$).

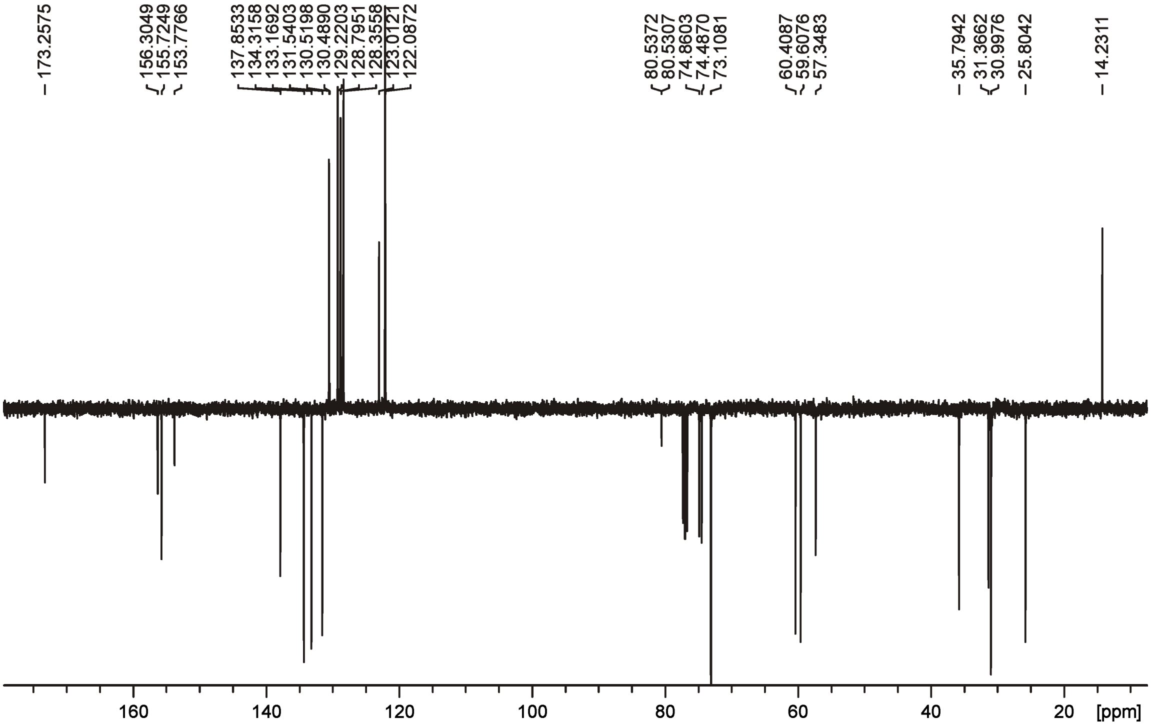


Figure S74. ^{13}C NMR spectrum (APT) of propargylated bis(ester) **50** (100 MHz, $CDCl_3$).

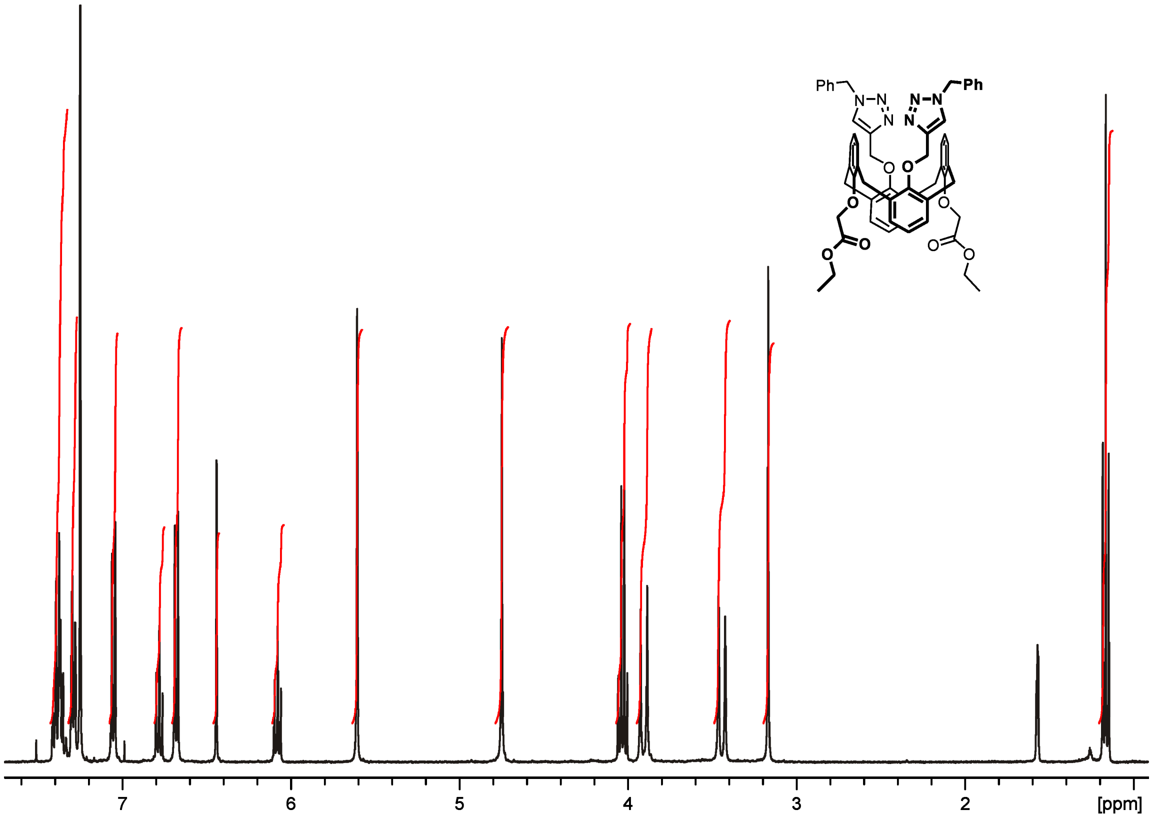


Figure S75. ^{1}H NMR spectrum of triazolated bis(ester) **51** (400 MHz, $CDCl_3$).

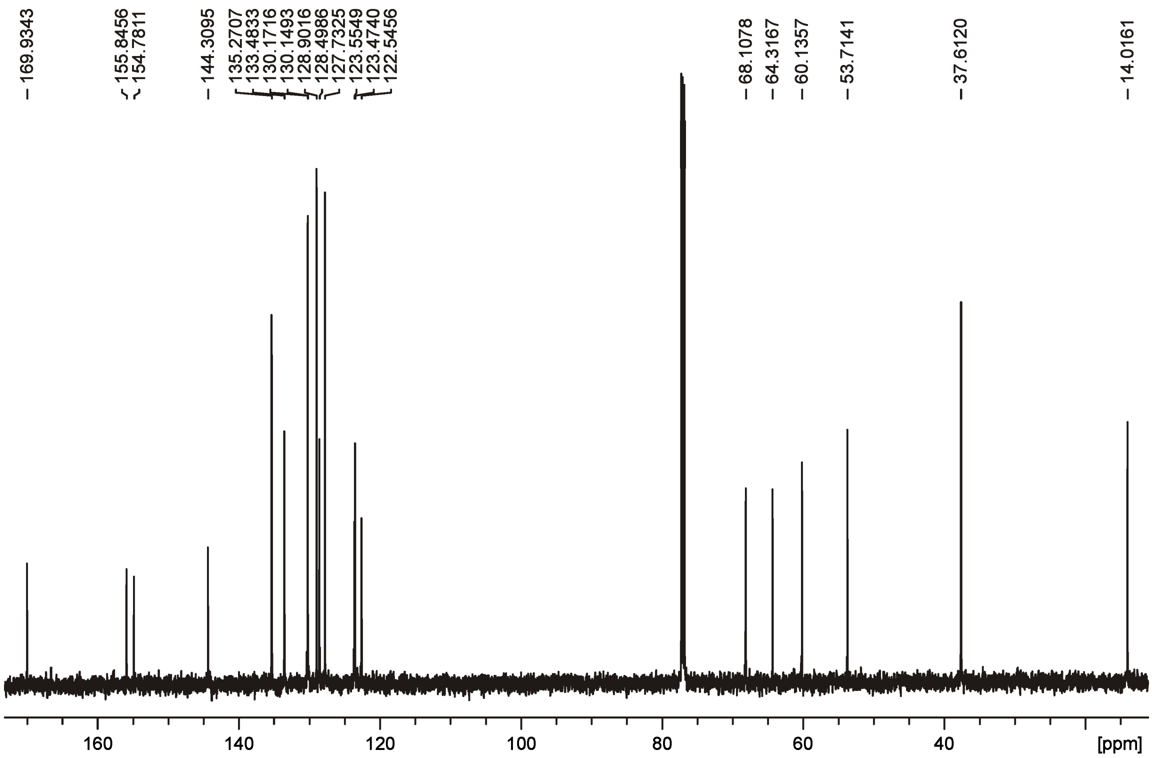


Figure S76. ^{13}C NMR spectrum of triazolated bis(ester) **51** (100 MHz, $CDCl_3$).

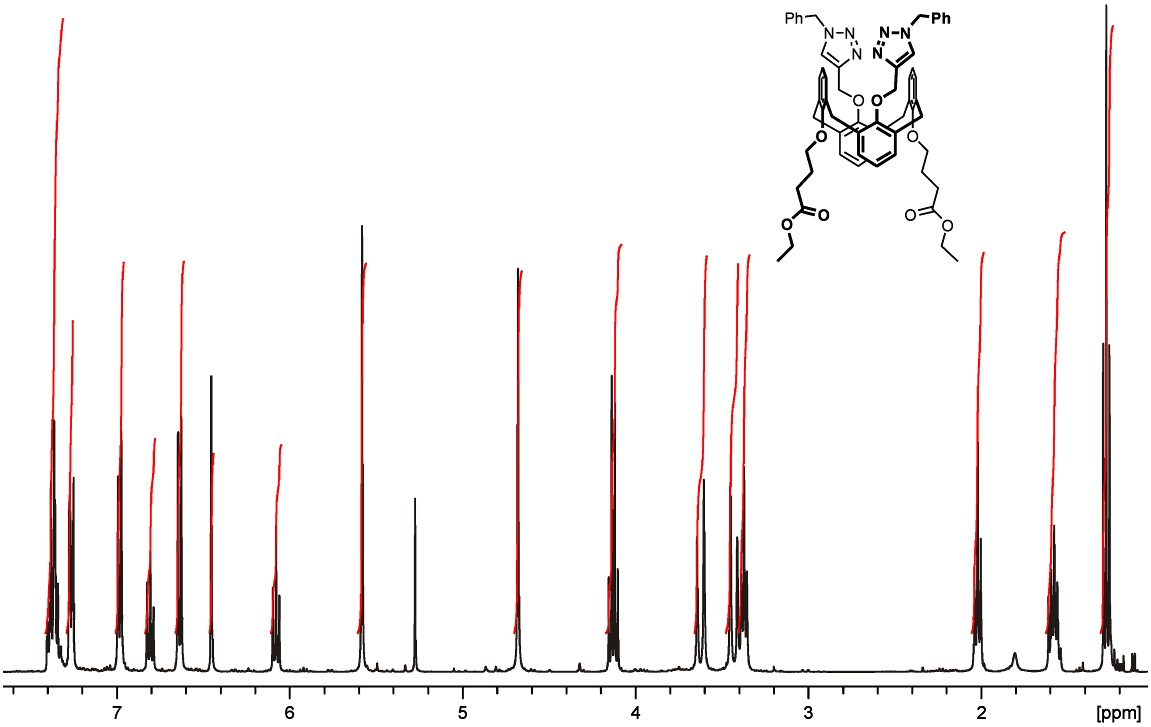


Figure S77. ^{1}H NMR spectrum of triazolated bis(ester) **52** (400 MHz, $CDCl_3$).

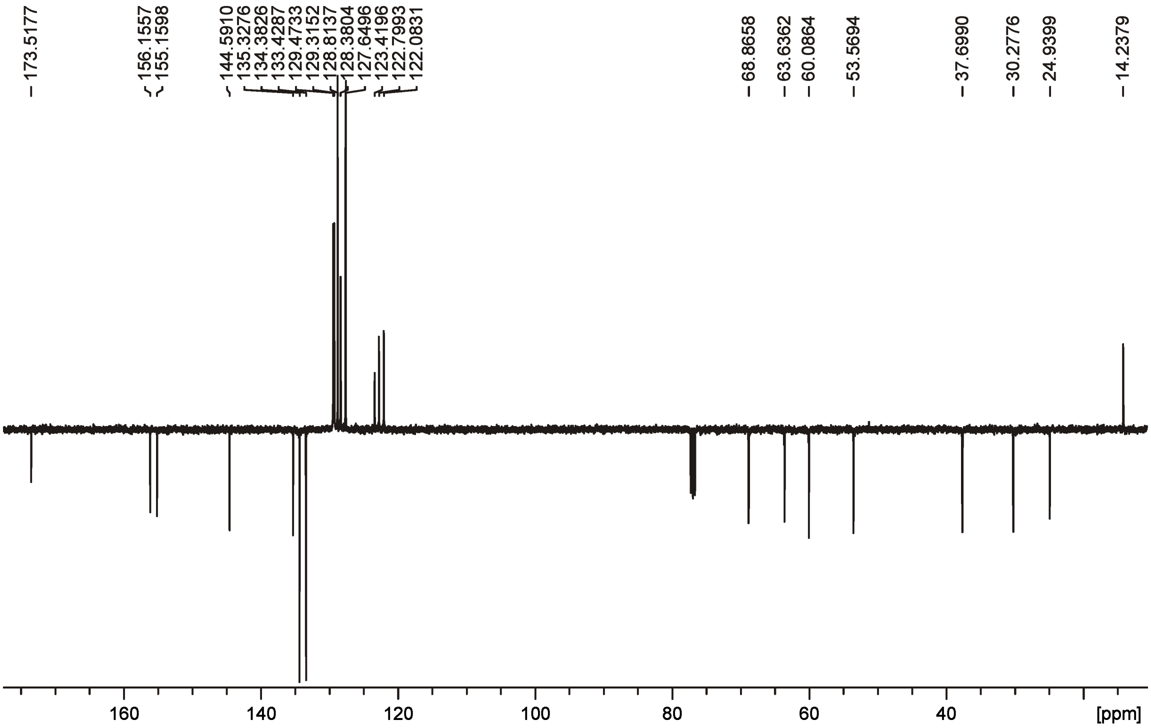


Figure S78. ^{13}C NMR spectrum (APT) of triazolated bis(ester) **52** (100 MHz, $CDCl_3$).

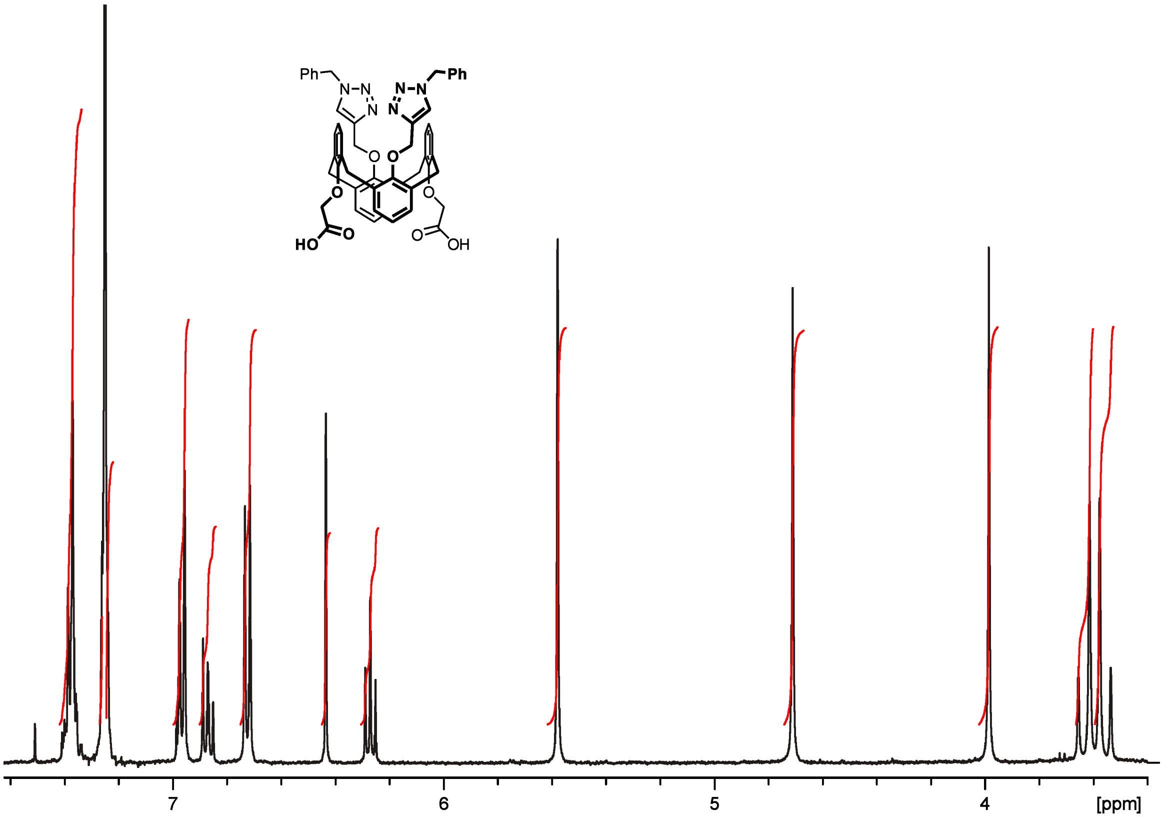


Figure S79. ^{1}H NMR spectrum of triazolated bis(acid) **53** (400 MHz, $CDCl_3$).

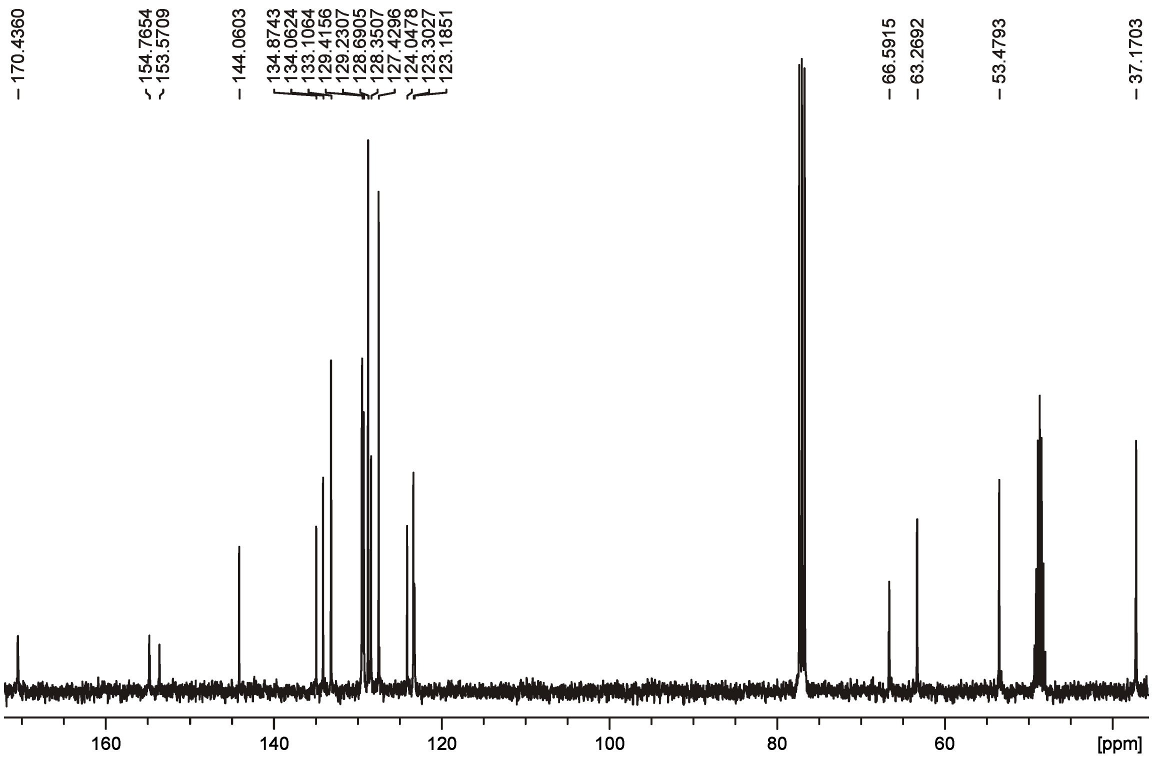


Figure S80. ^{13}C NMR spectrum of triazolated bis(acid) **53** (100 MHz, $CDCl_3$+CD_3OD).

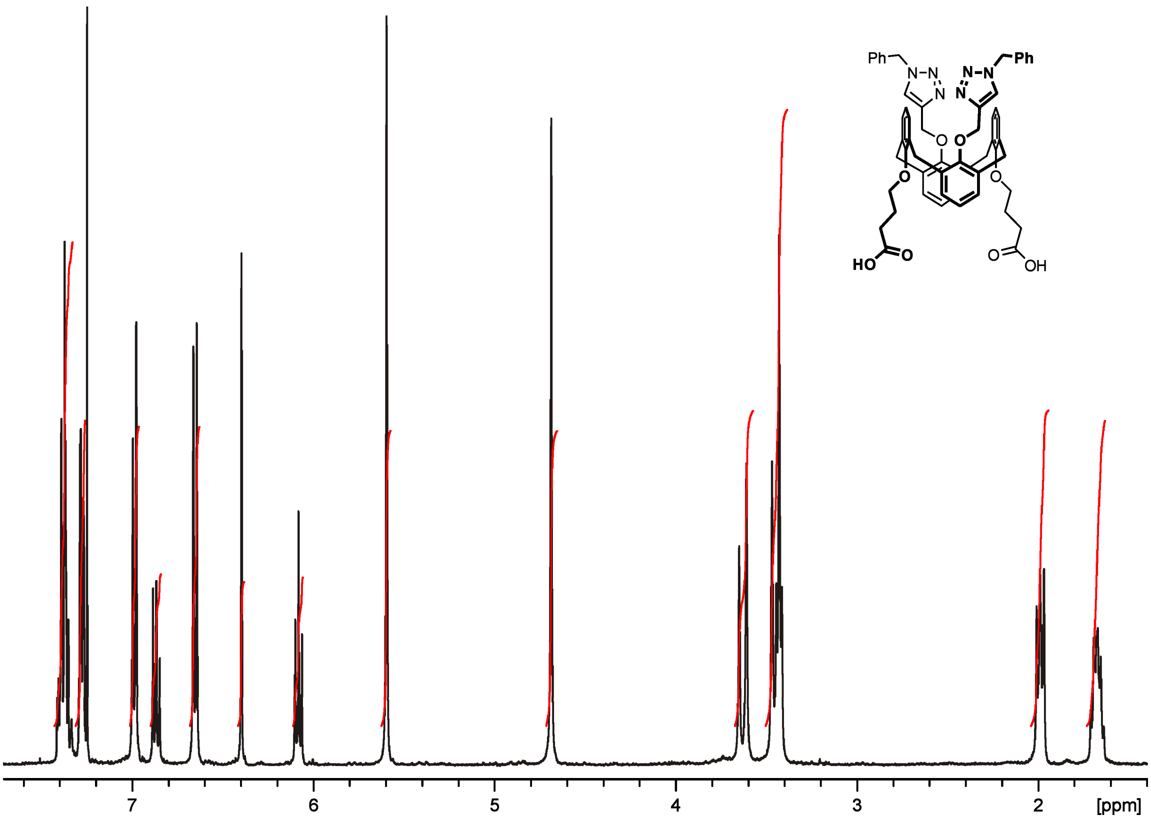


Figure S81. ^{1}H NMR spectrum of triazolated bis(acid) **54** (400 MHz, CDCl$_3$).

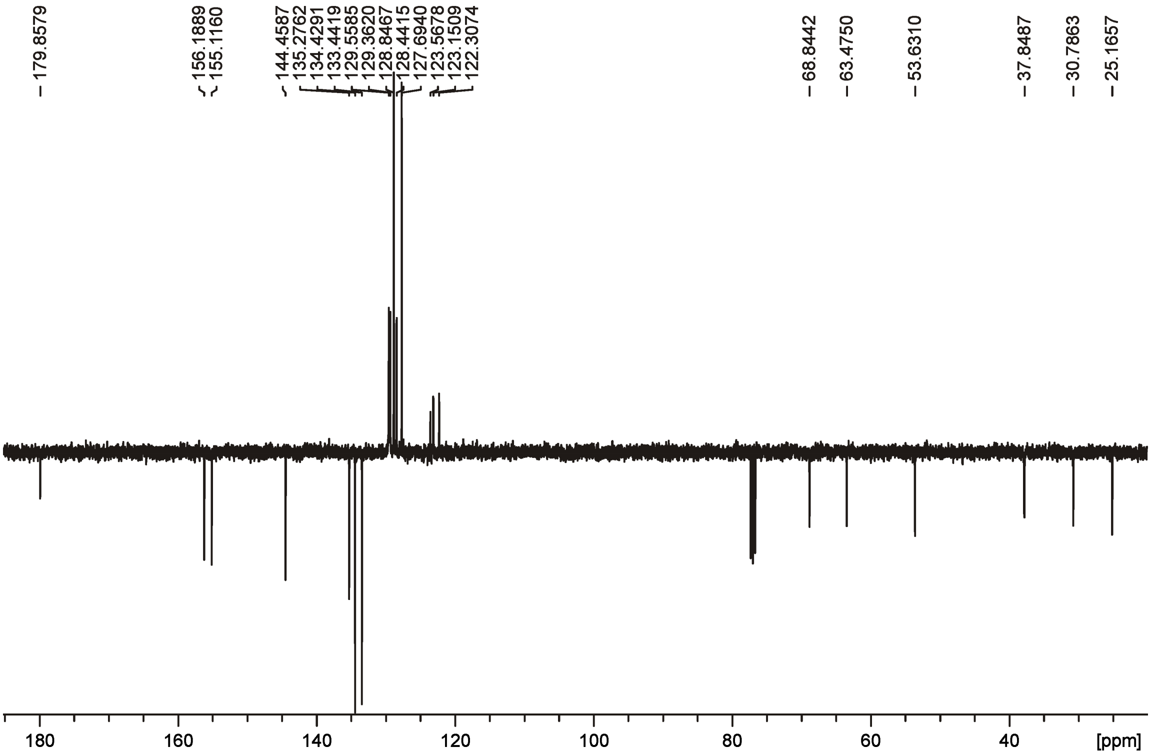


Figure S82. ^{13}C NMR spectrum (APT) of triazolated bis(acid) **54** (100 MHz, CDCl$_3$).

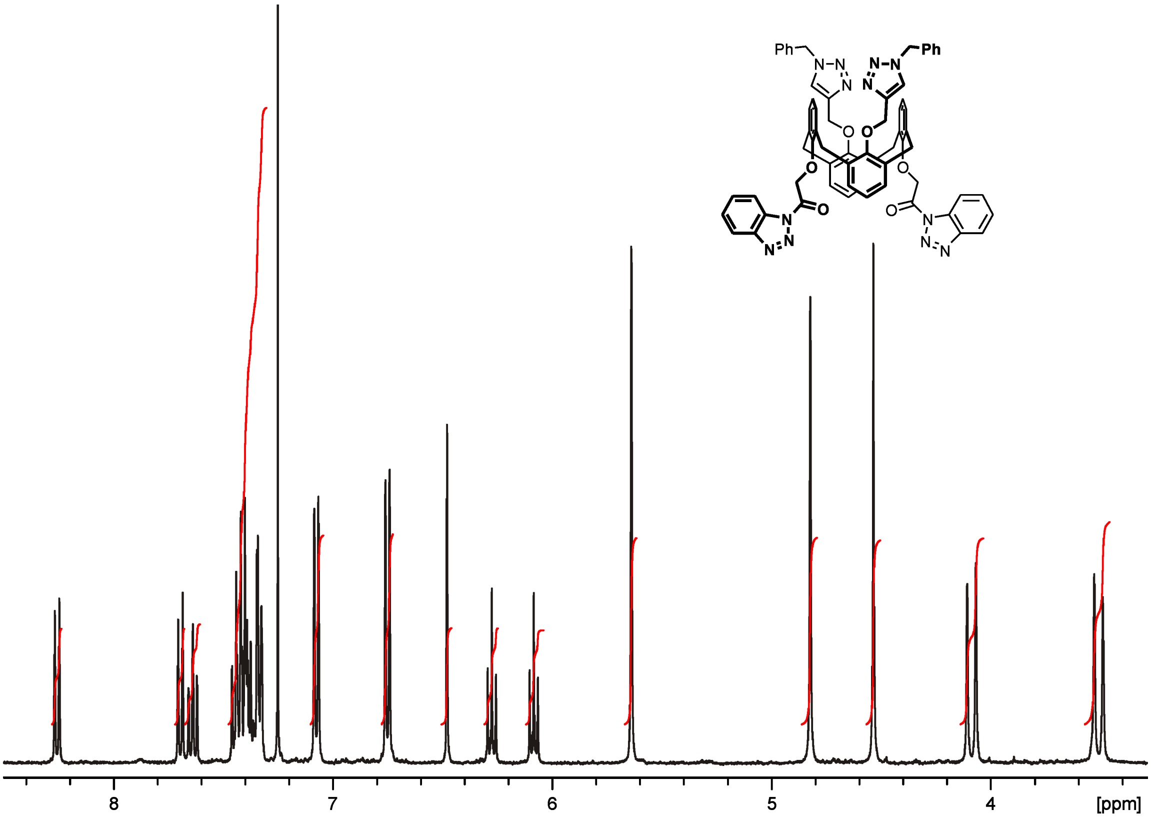


Figure S83. ^{1}H NMR spectrum of triazolated bis(1-acylbenzotriazole) **55** (400 MHz, $CDCl_3$).

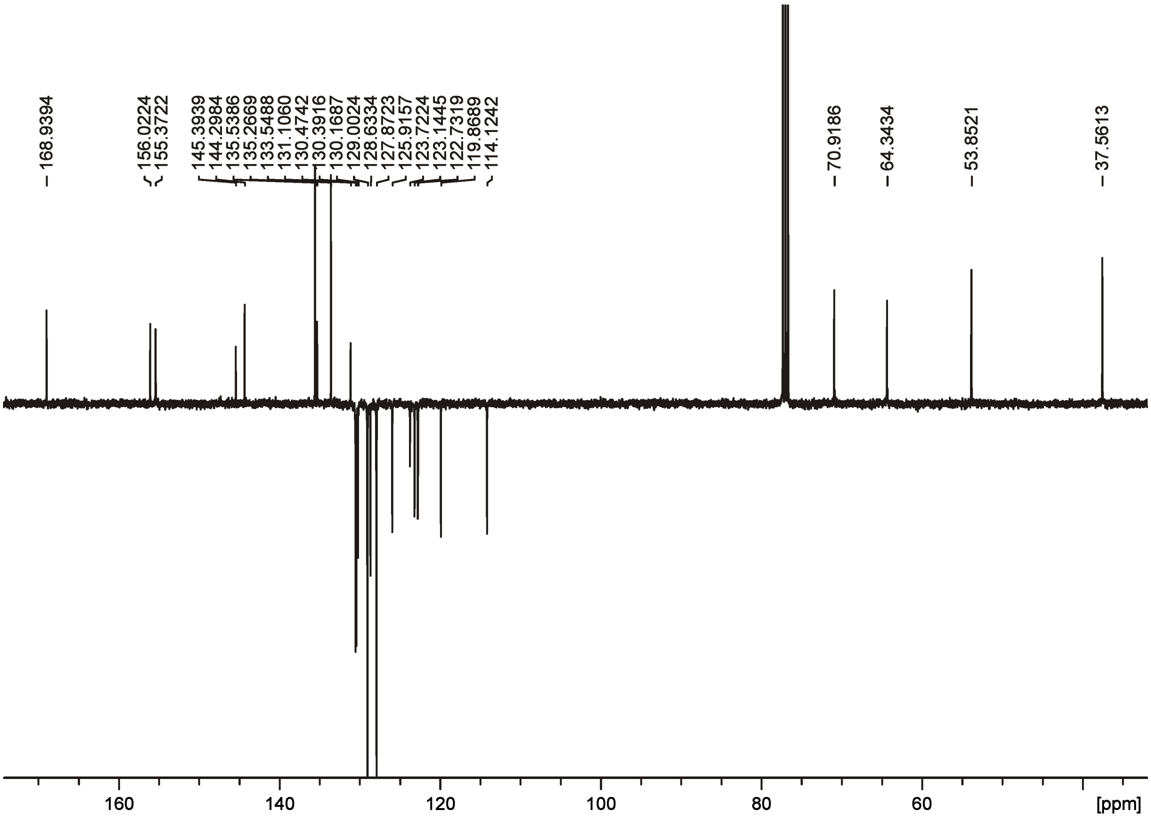


Figure S84. ^{13}C NMR spectrum (APT) of triazolated bis(1-acylbenzotriazole) **55** (100 MHz, $CDCl_3$).

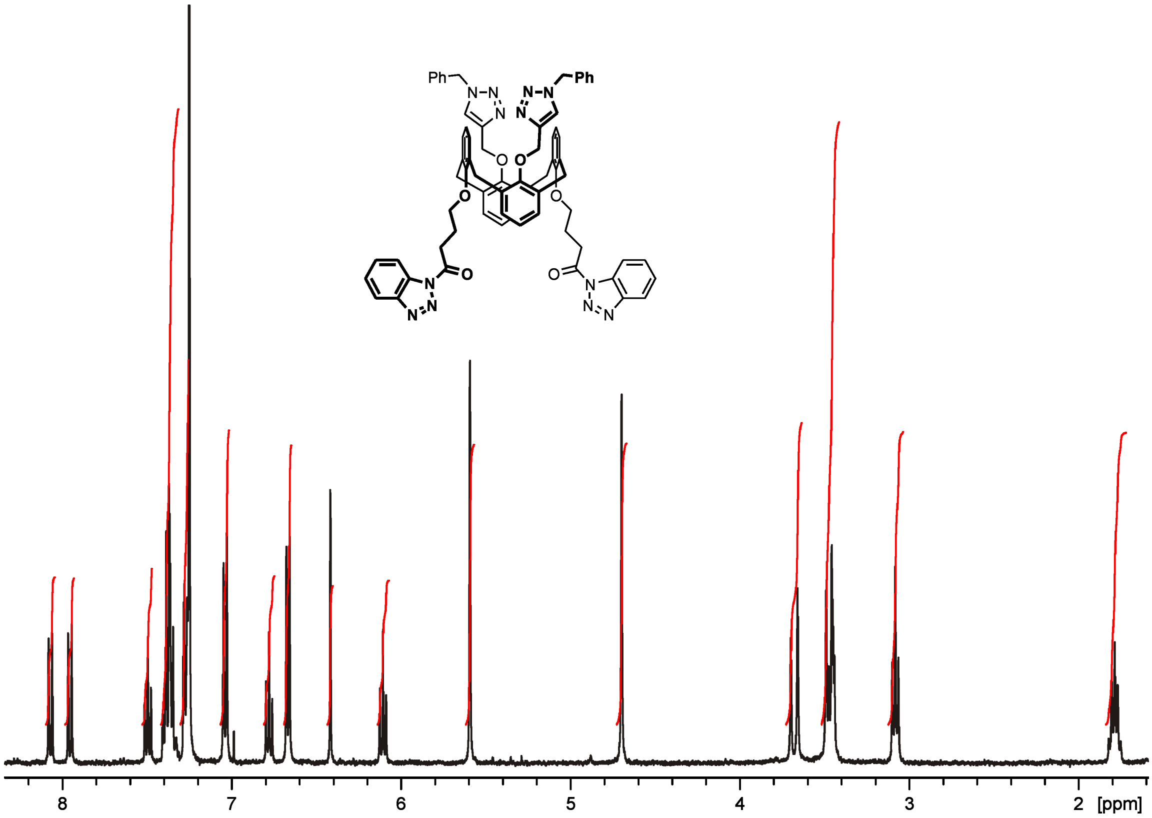


Figure S85. ^{1}H NMR spectrum of triazolated bis(1-acylbenzotriazole) **56** (400 MHz, $CDCl_3$).

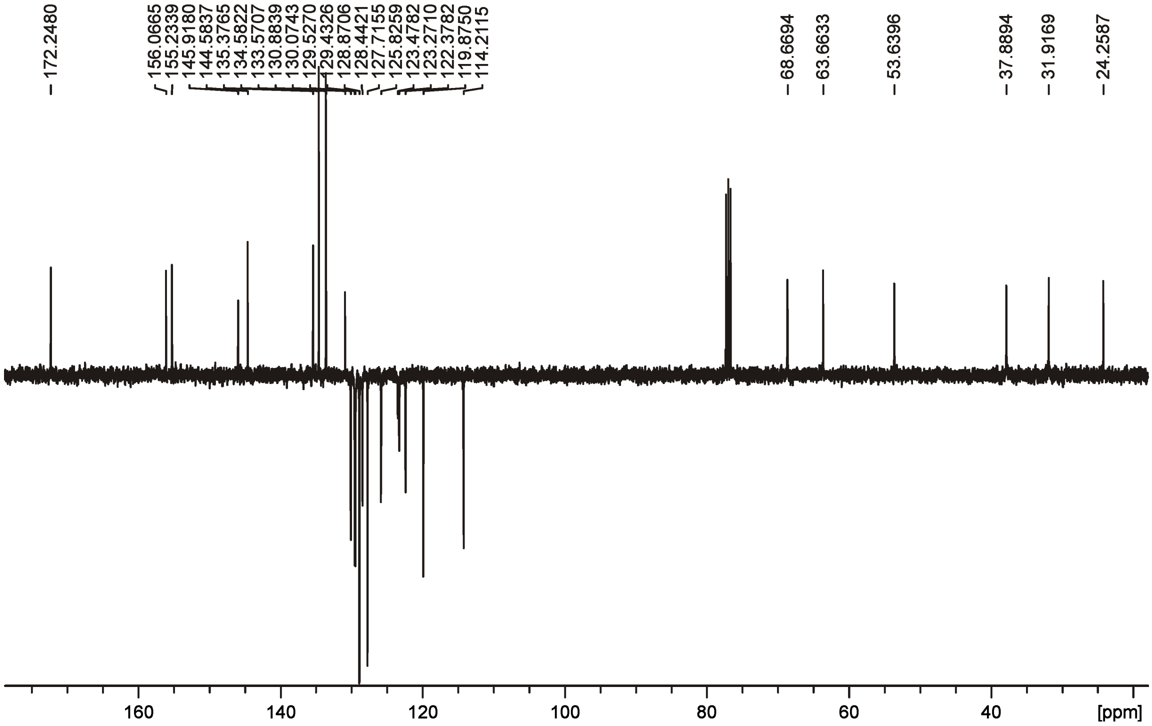


Figure S86. ^{13}C NMR spectrum (APT) of triazolated bis(1-acylbenzotriazole) **56** (100 MHz, $CDCl_3$).

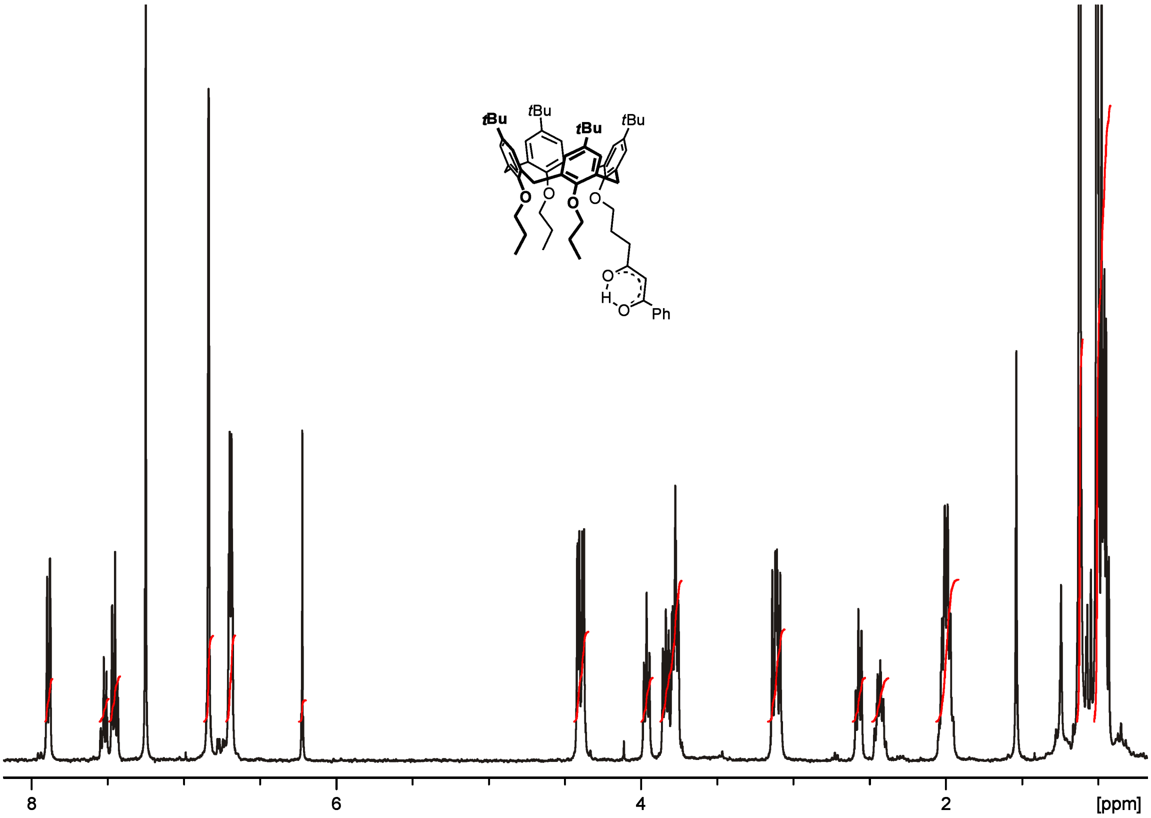


Figure S87. ^{1}H NMR spectrum of calixarene 1,3-diketone **57** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

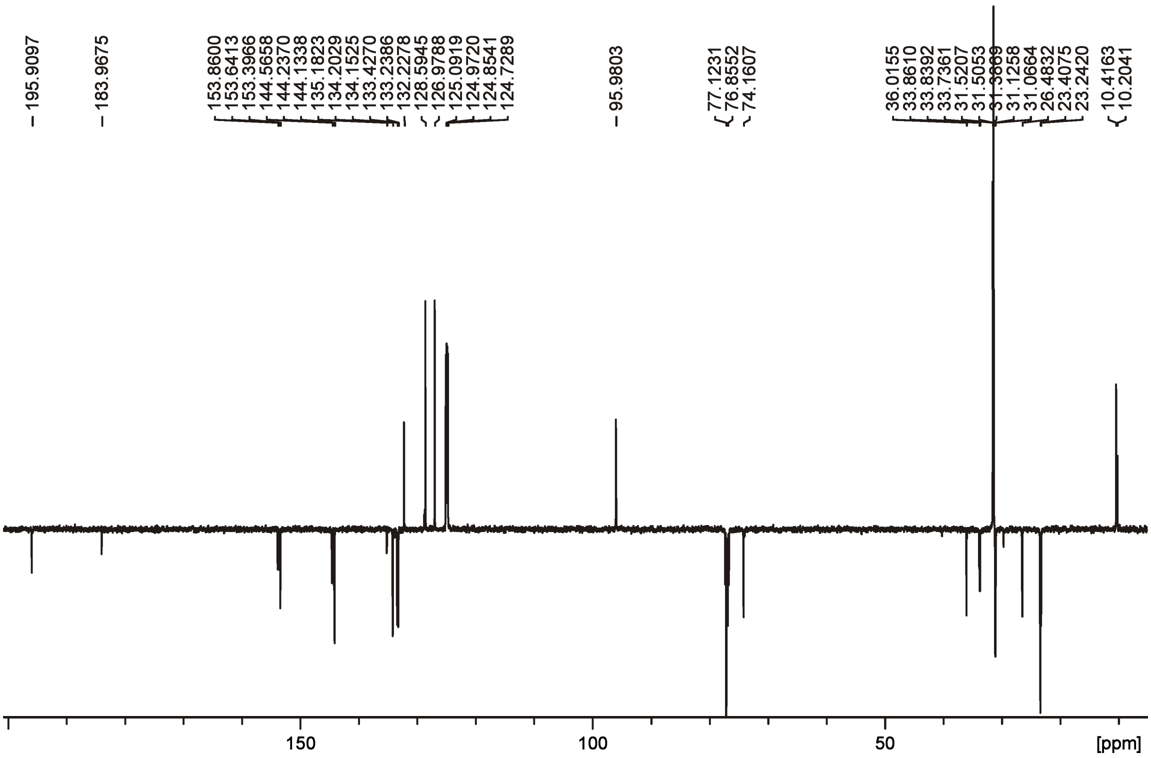


Figure S88. ^{13}C NMR spectrum (APT) of calixarene 1,3-diketone **57** (100 MHz, $CDCl_3$).

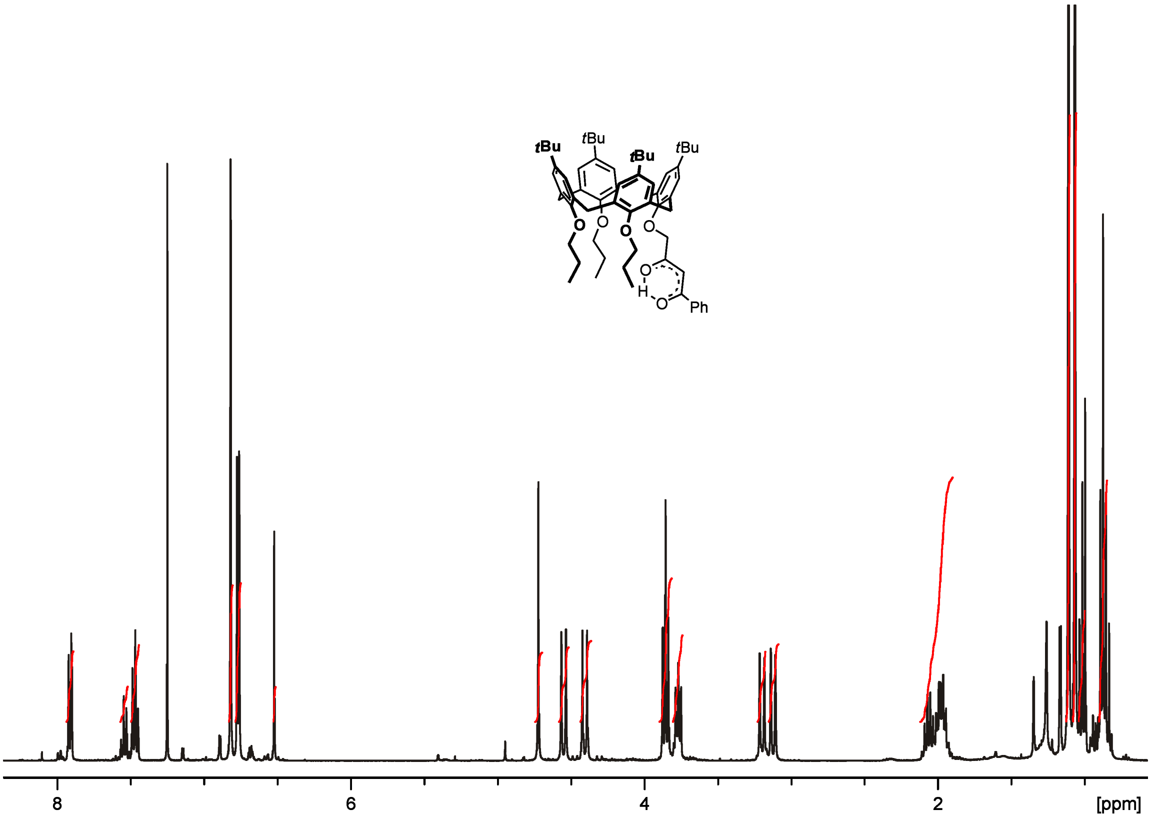


Figure S89. ^{1}H NMR spectrum of calixarene 1,3-diketone **58** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

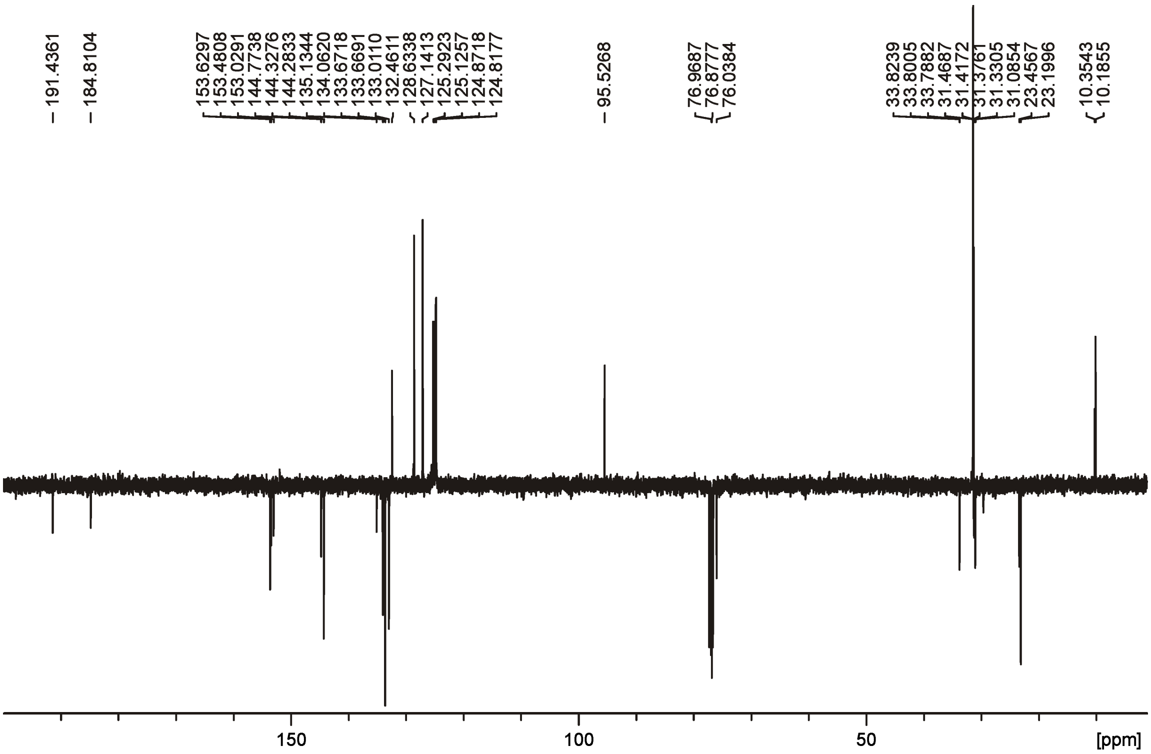


Figure S90. ^{13}C NMR spectrum (APT) of calixarene 1,3-diketone **58** (100 MHz, $CDCl_3$).

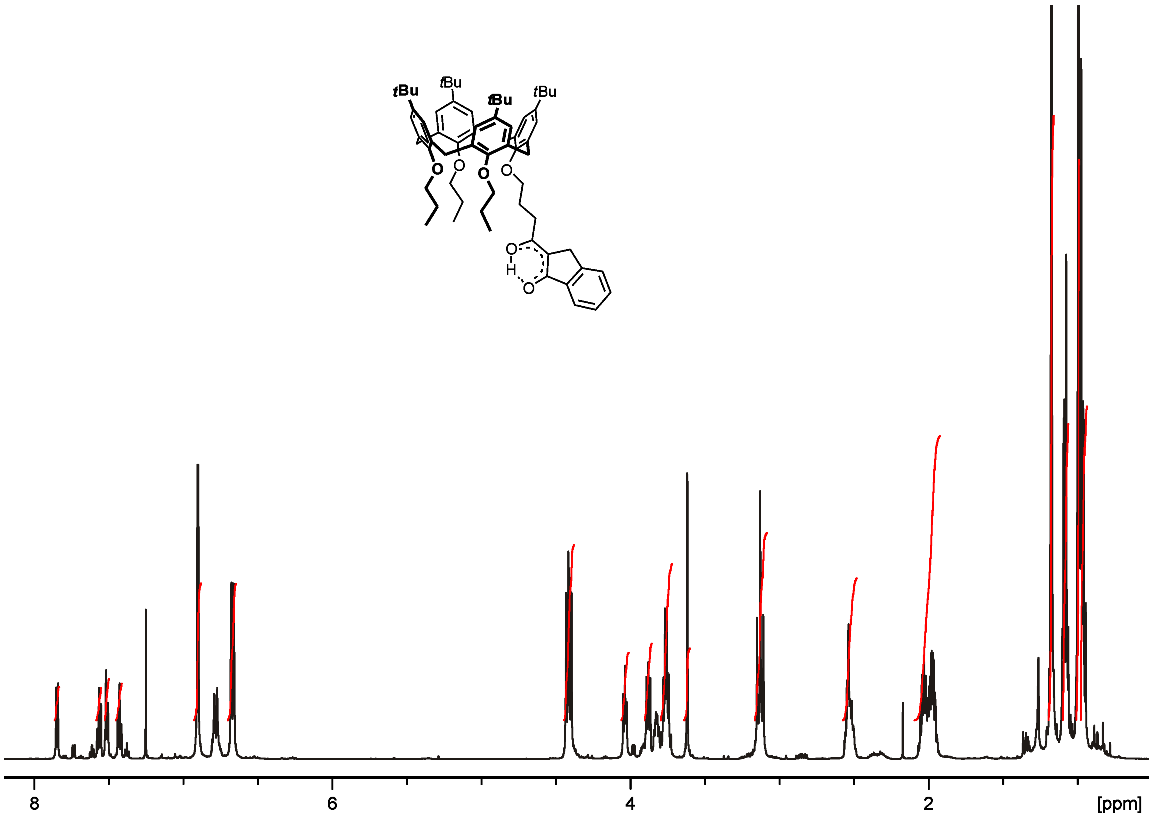


Figure S91. ^{1}H NMR spectrum of calixarene 1,3-diketone **59** (600 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

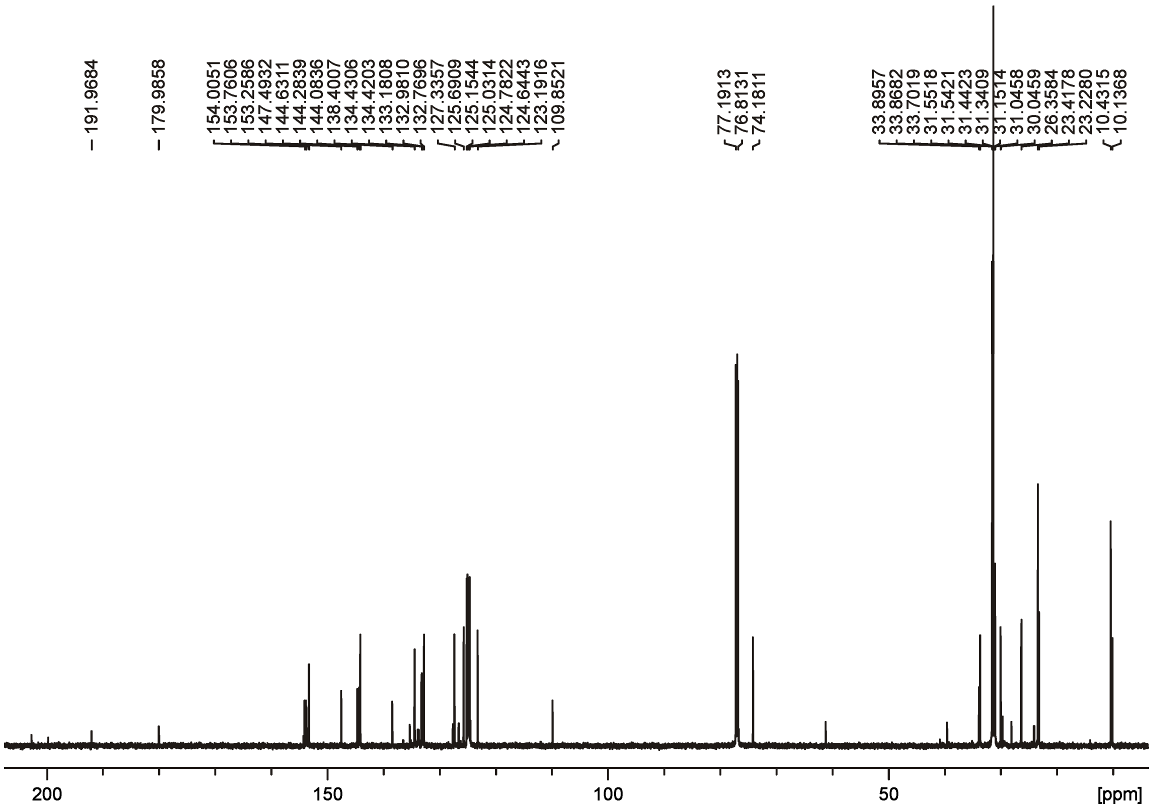


Figure S92. ^{13}C NMR spectrum of calixarene 1,3-diketone **59** (150 MHz, $CDCl_3$).

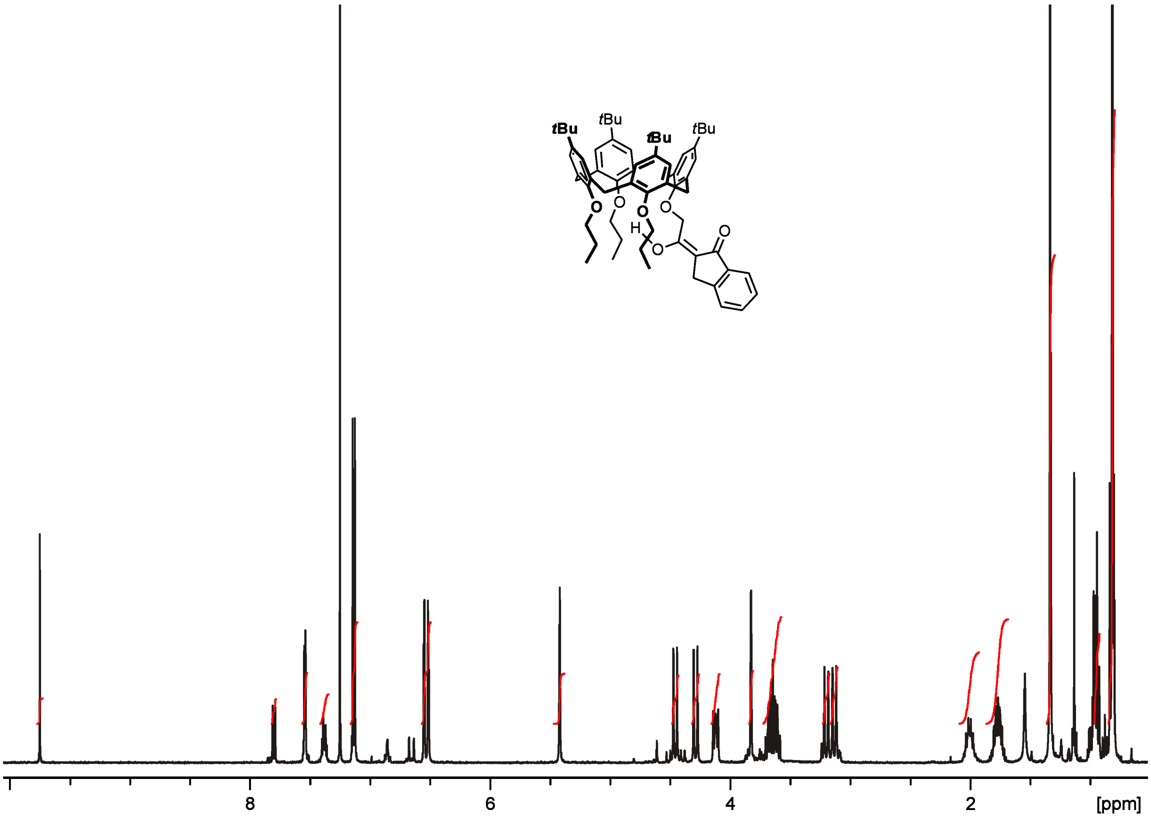


Figure S93. ^{1}H NMR spectrum of calixarene 1,3-diketone **60** (400 MHz, CDCl$_3$).

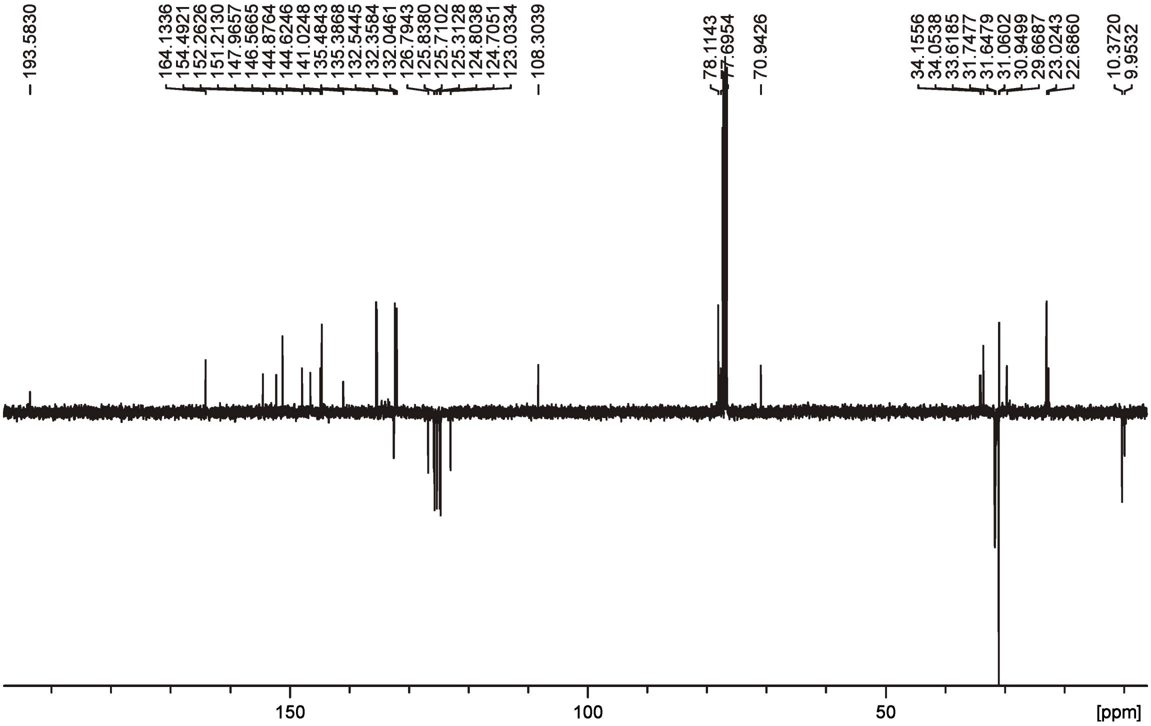


Figure S94. ^{13}C NMR spectrum (APT) of calixarene 1,3-diketone **60** (100 MHz, CDCl$_3$).

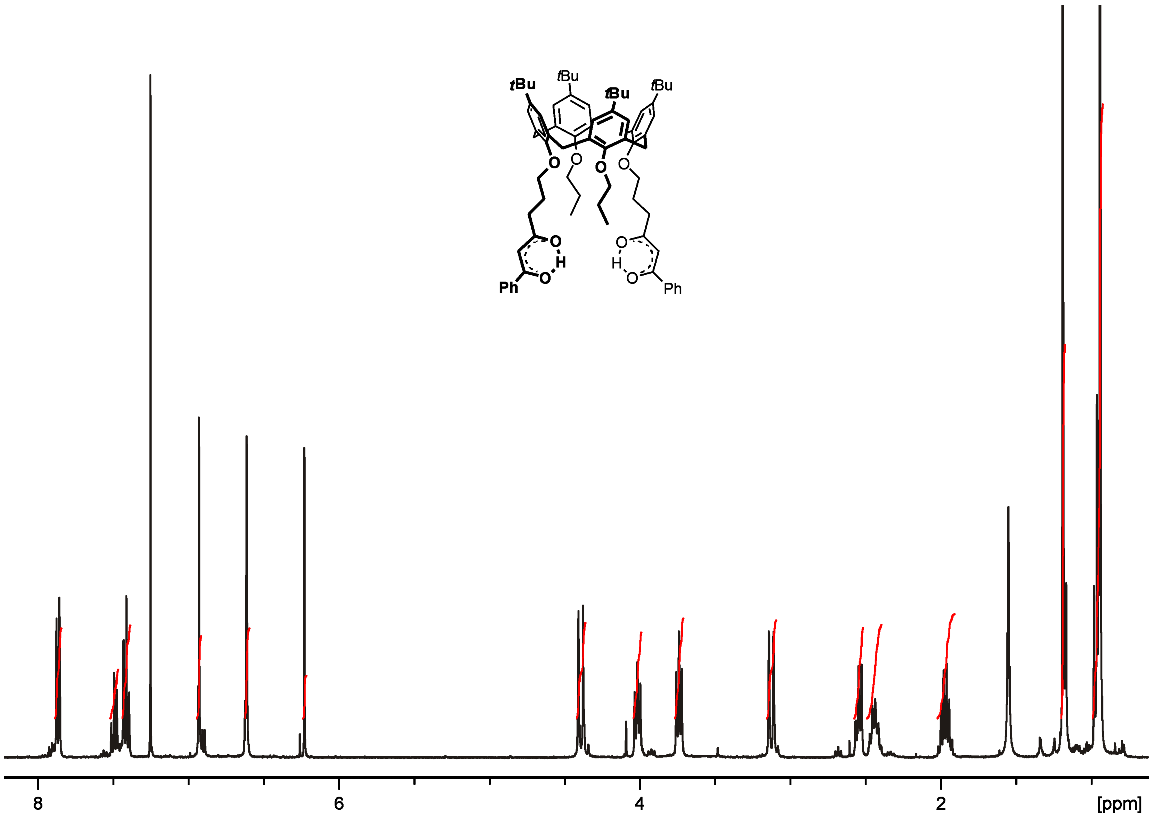


Figure S95. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **61** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

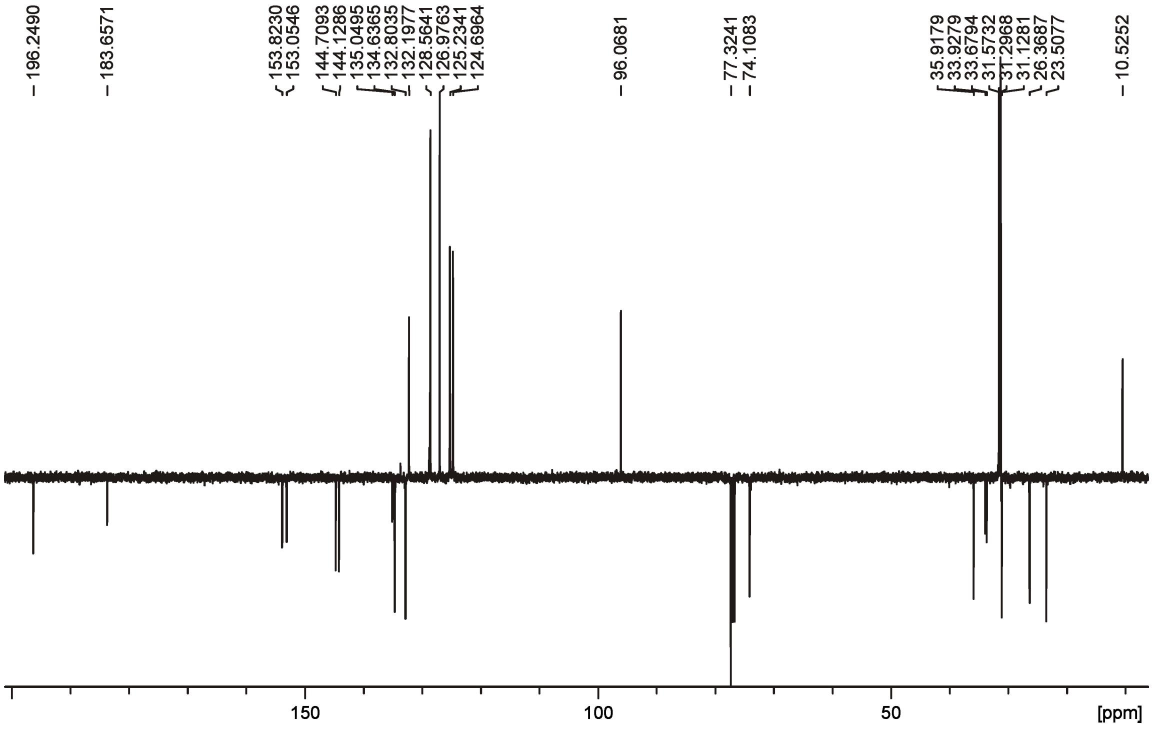


Figure S96. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **61** (100 MHz, $CDCl_3$).

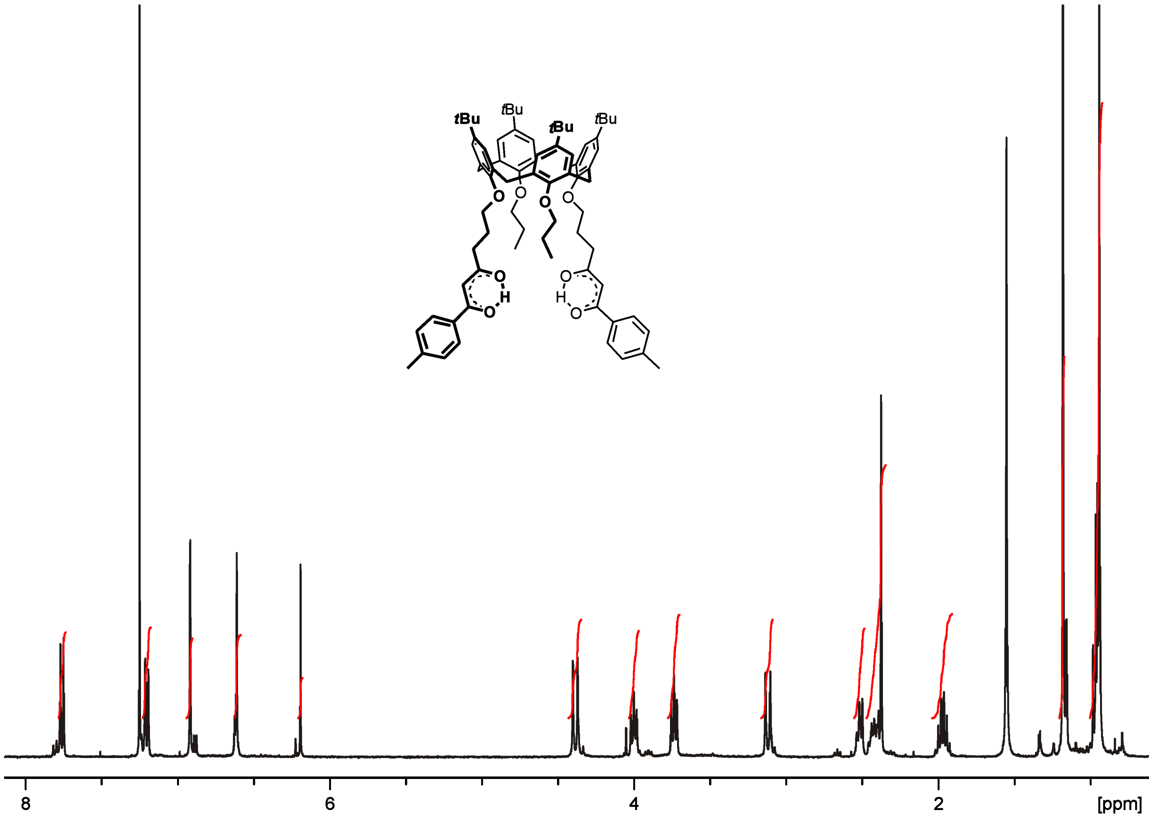


Figure S97. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **62** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

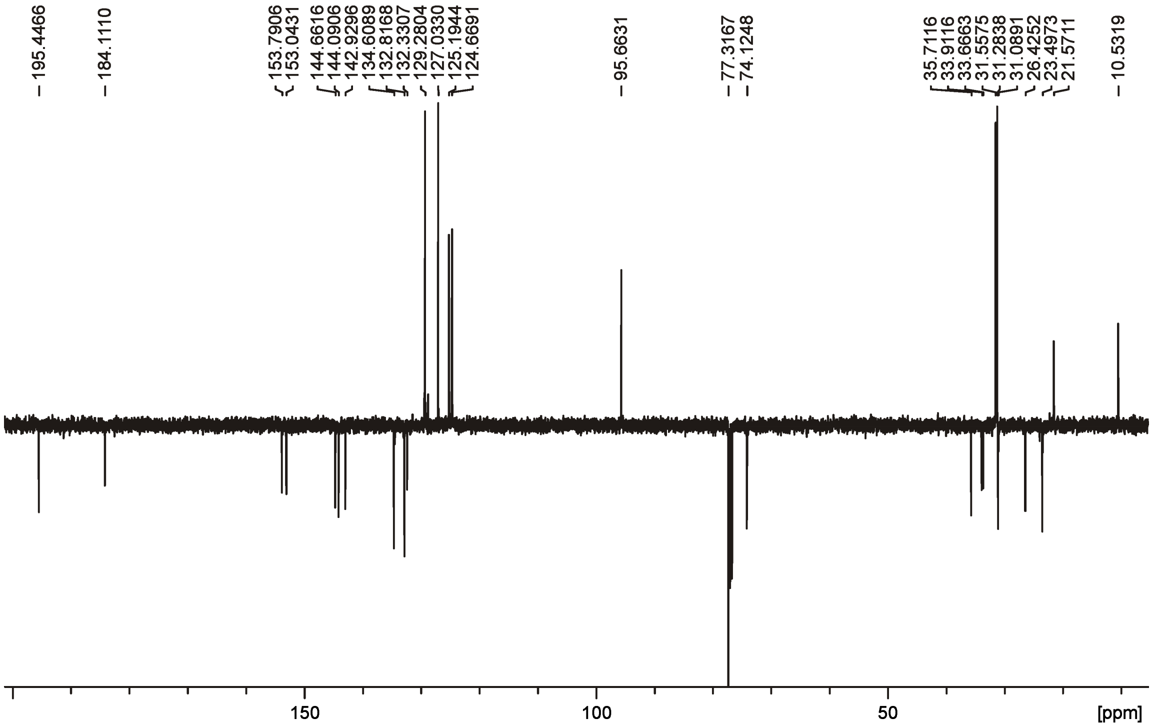


Figure S98. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **62** (100 MHz, $CDCl_3$).

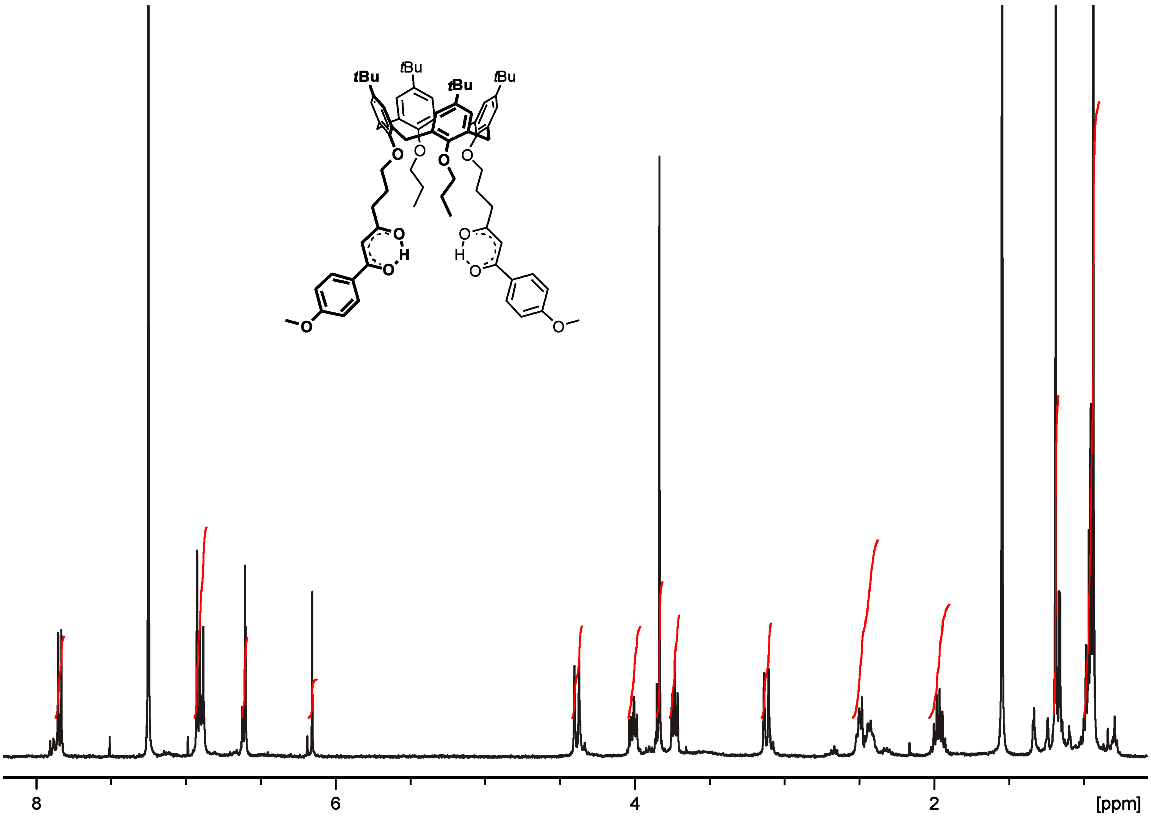


Figure S99. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **63** (400 MHz, CDCl$_3$, the downfield-shifted resonance from the enol OH is not shown).

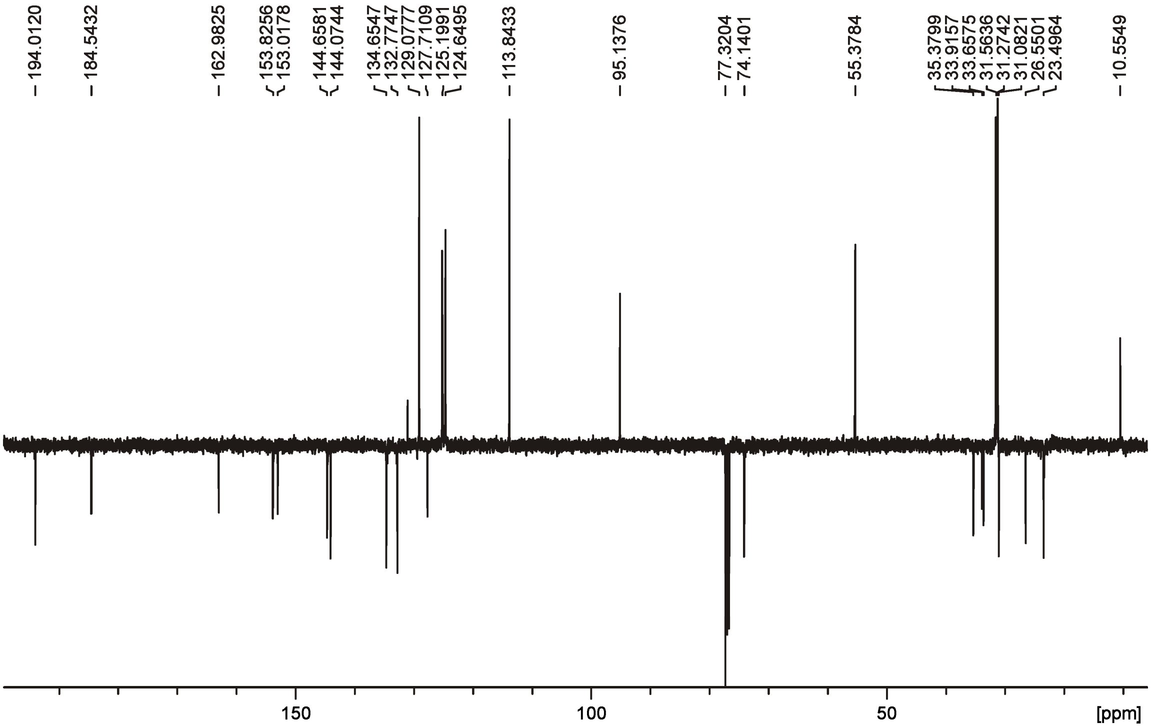


Figure S100. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **63** (100 MHz, CDCl$_3$).

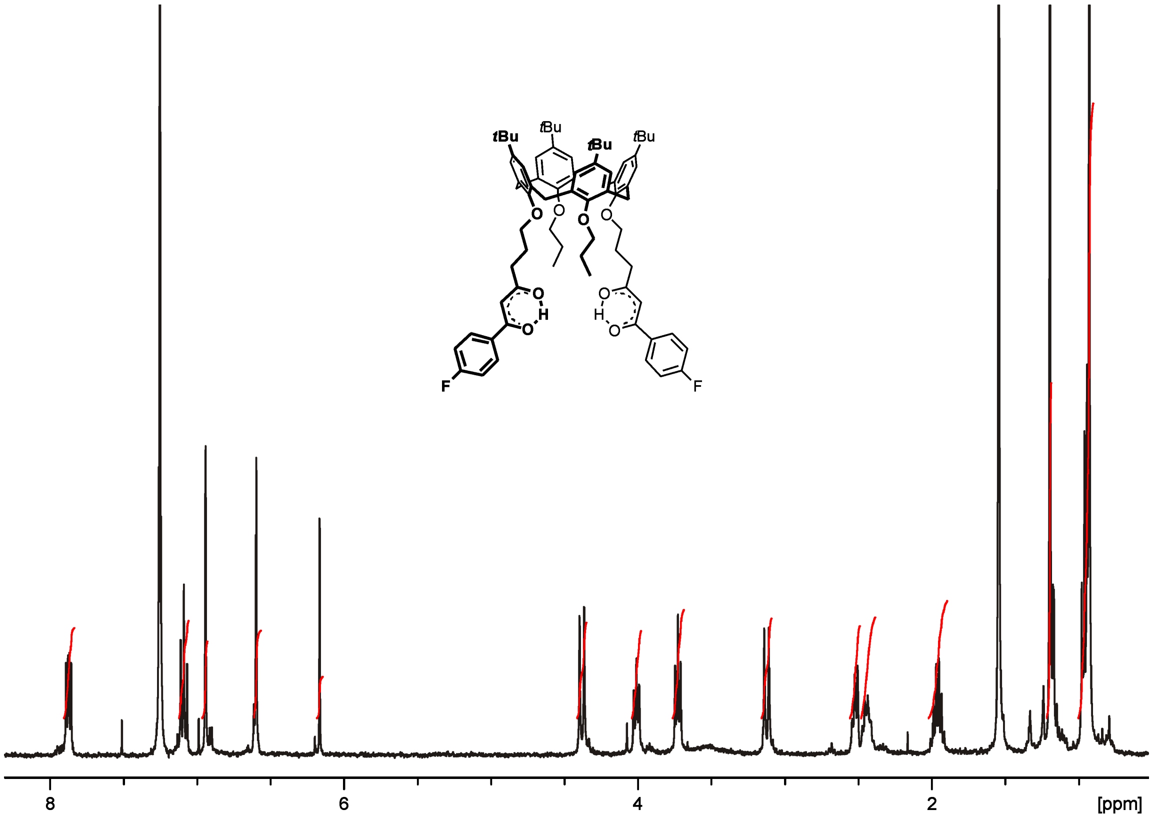


Figure S101. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **64** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

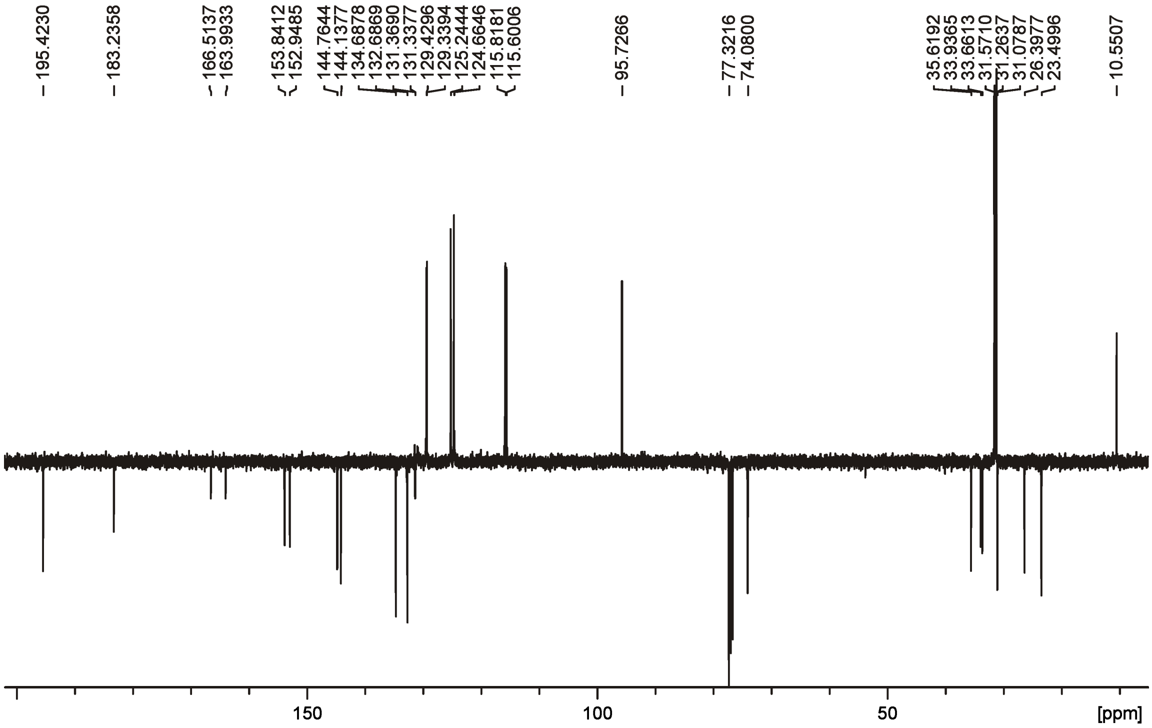


Figure S102. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **64** (100 MHz, $CDCl_3$).

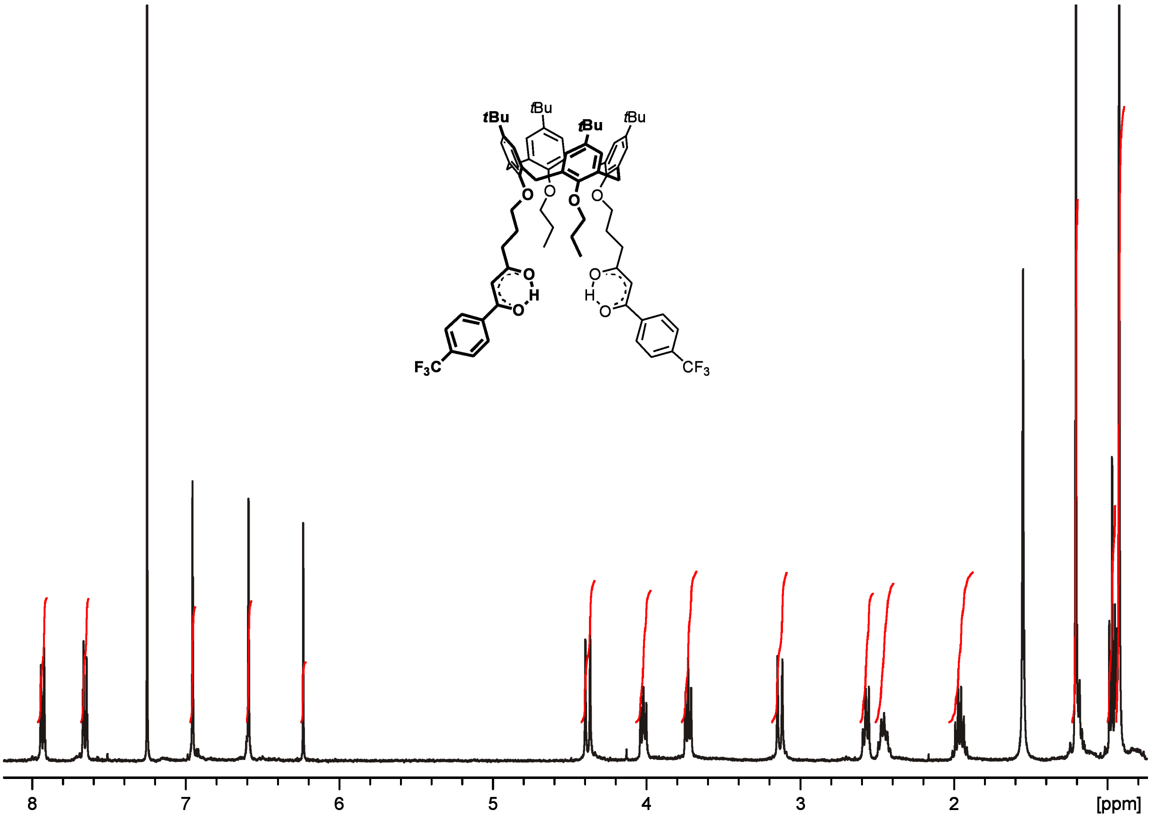


Figure S103. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **65** (400 MHz, CDCl$_3$, the downfield-shifted resonance from the enol OH is not shown).

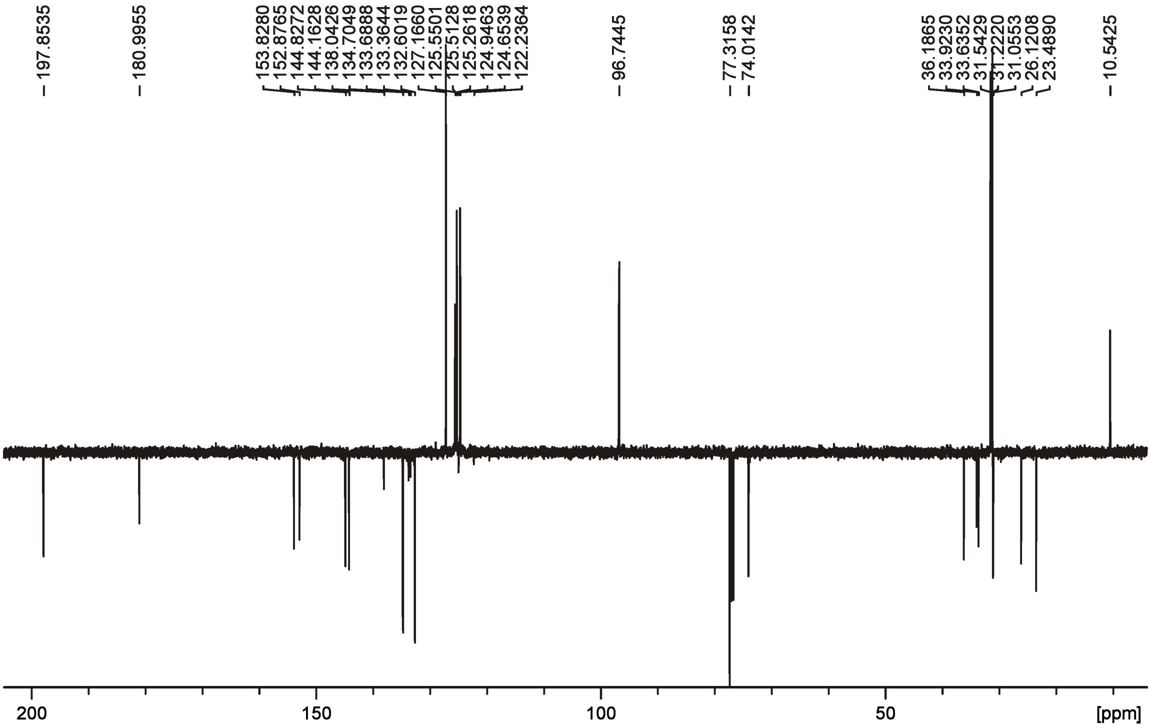


Figure S104. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **65** (100 MHz, CDCl$_3$).

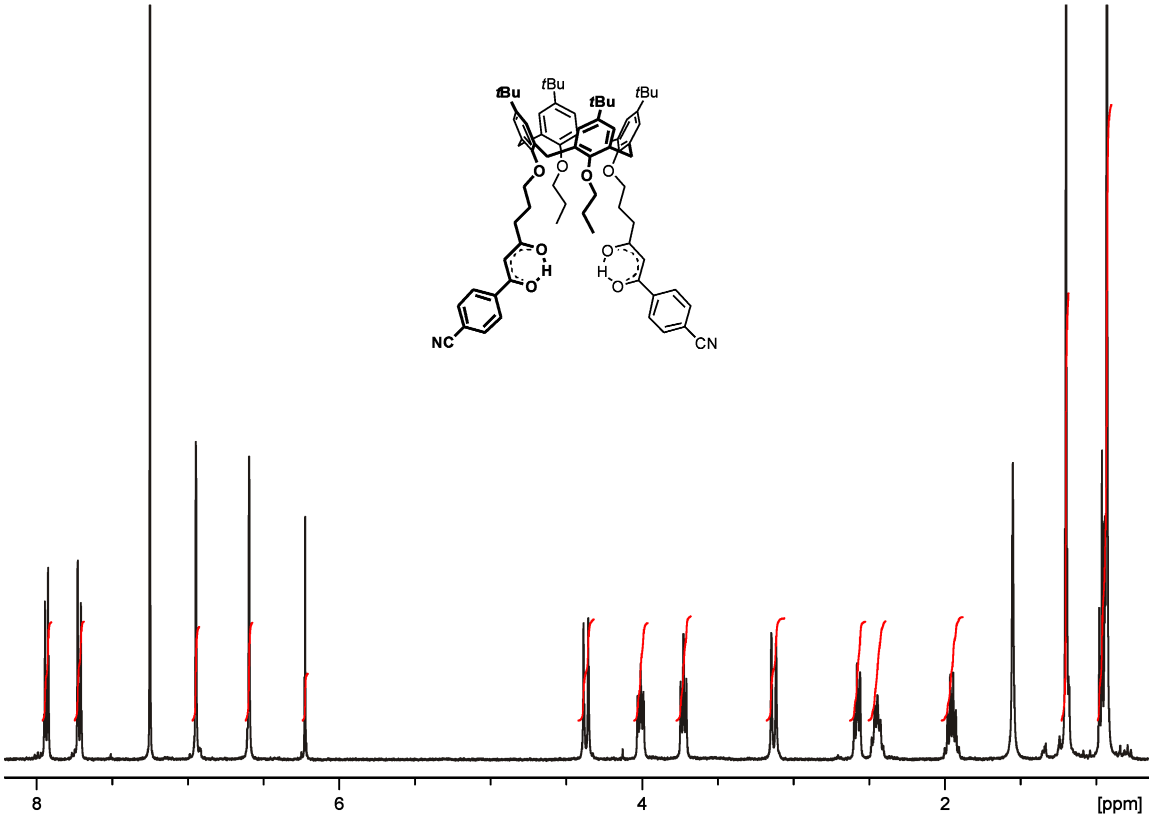


Figure S105. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **66** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

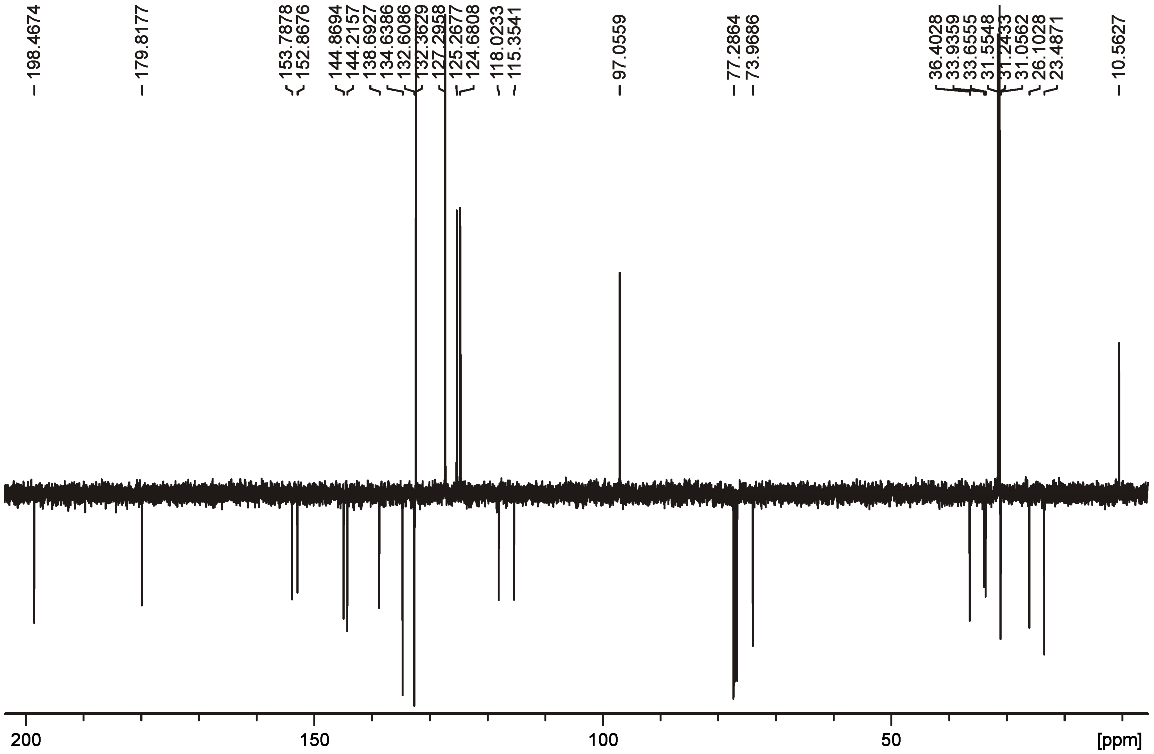


Figure S106. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **66** (100 MHz, $CDCl_3$).

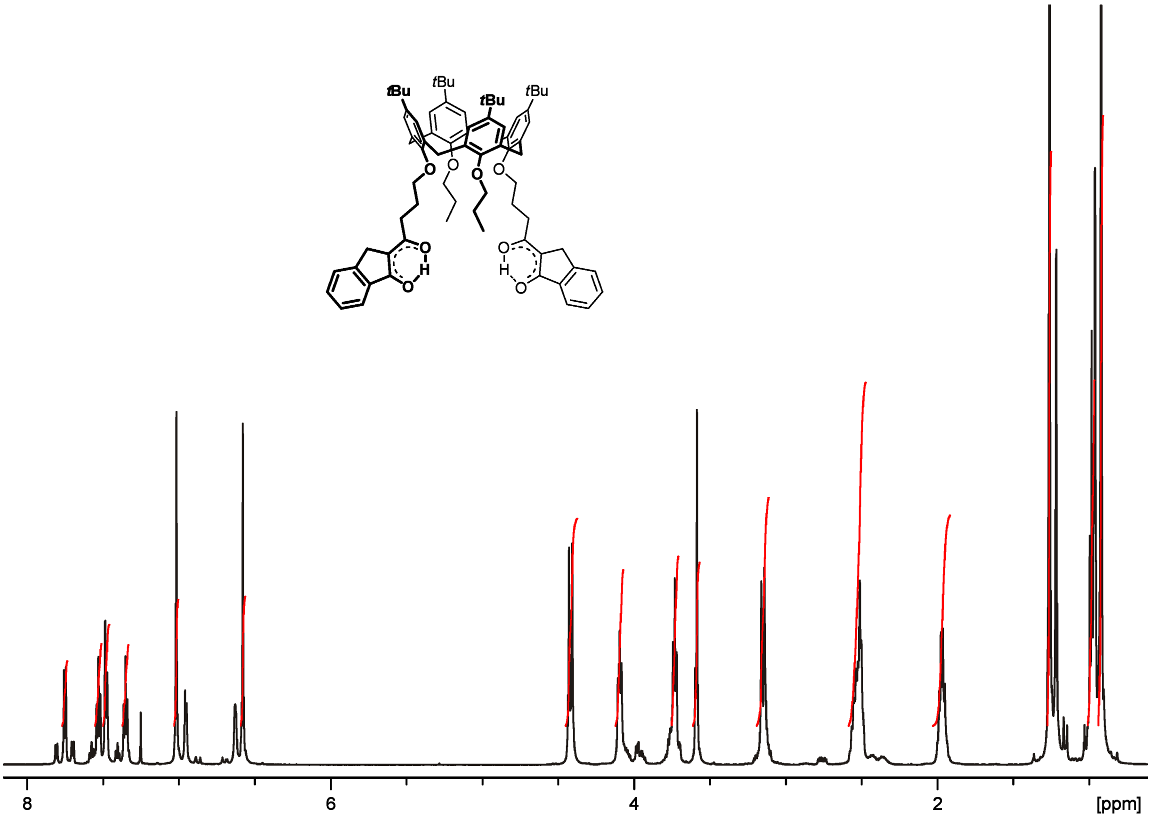


Figure S107. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **67** (600 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

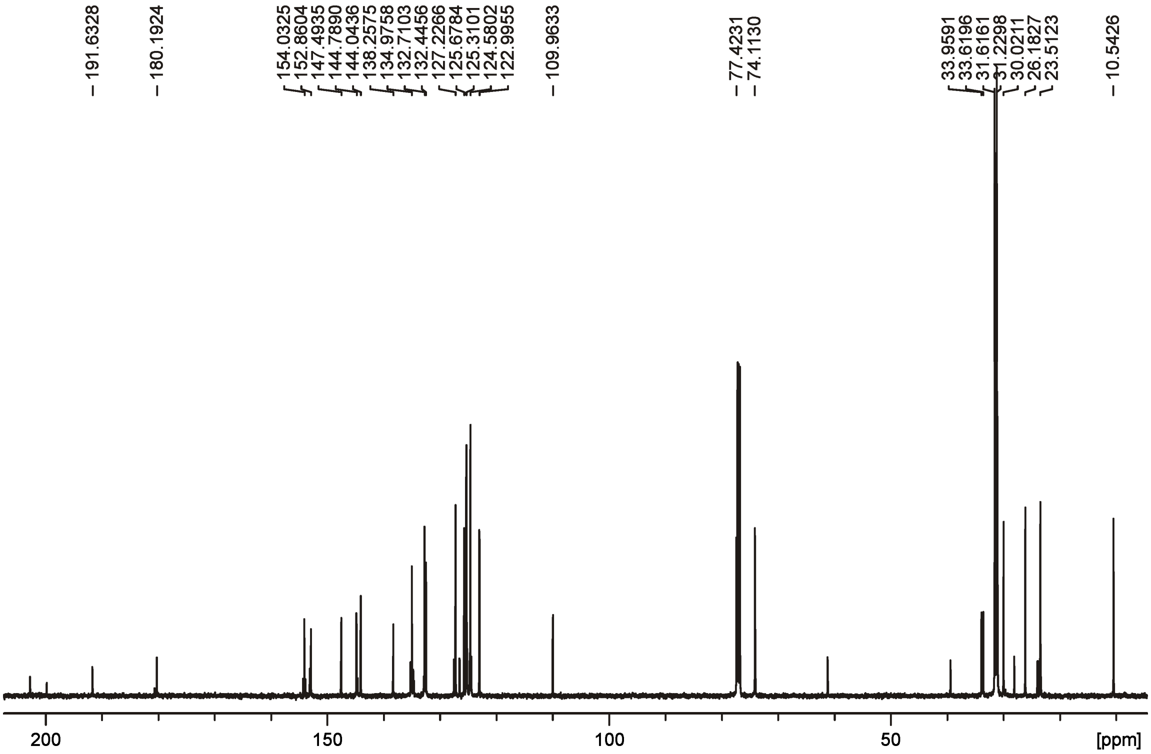


Figure S108. ^{13}C NMR spectrum of calixarene bis(1,3-diketone) **67** (150 MHz, $CDCl_3$).

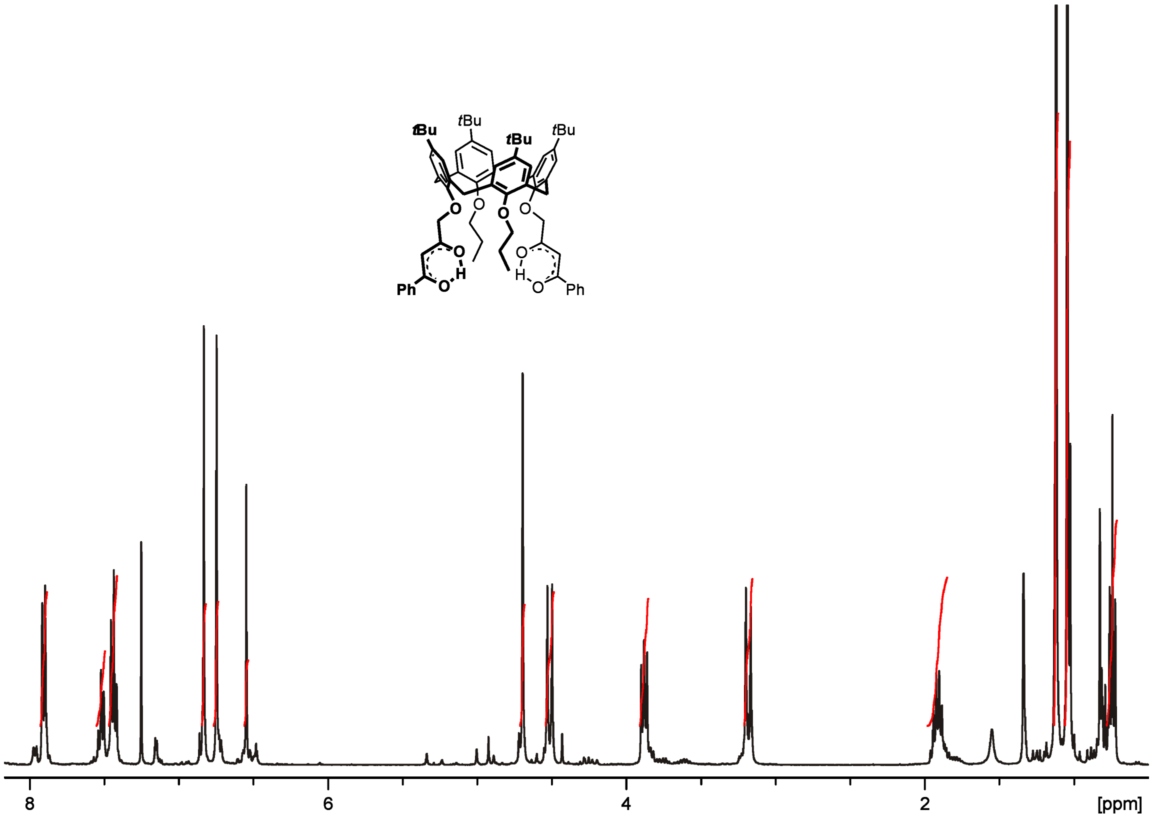


Figure S109. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **68** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

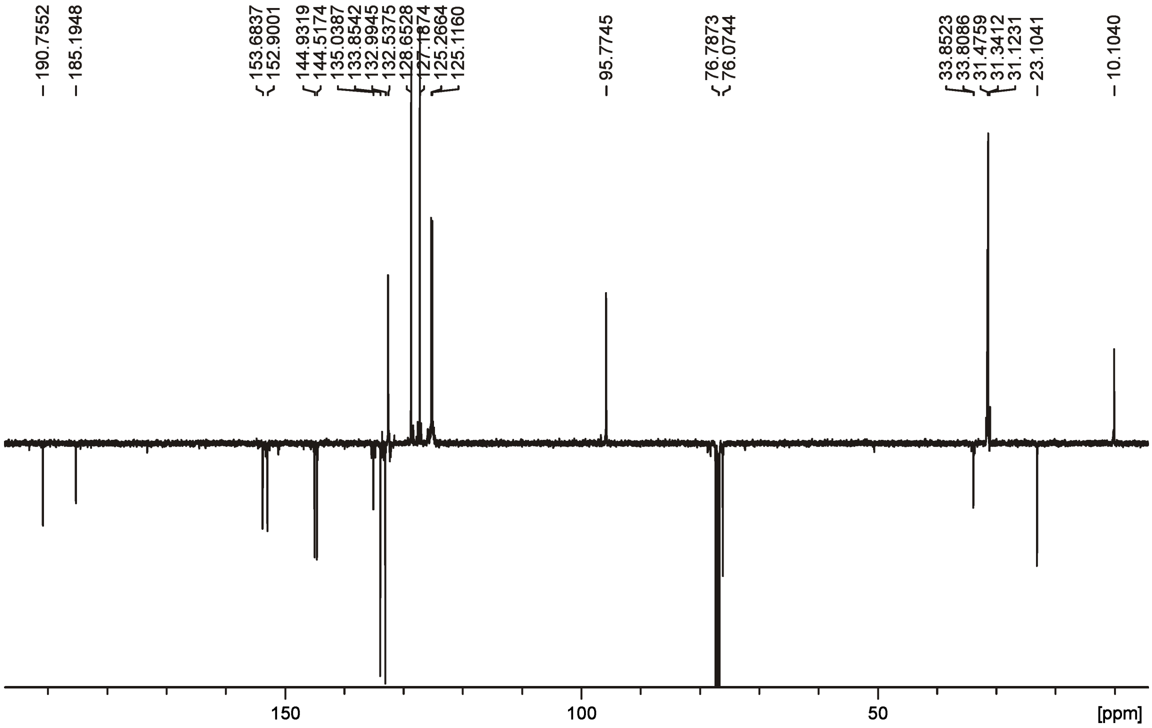


Figure S110. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **68** (100 MHz, $CDCl_3$).

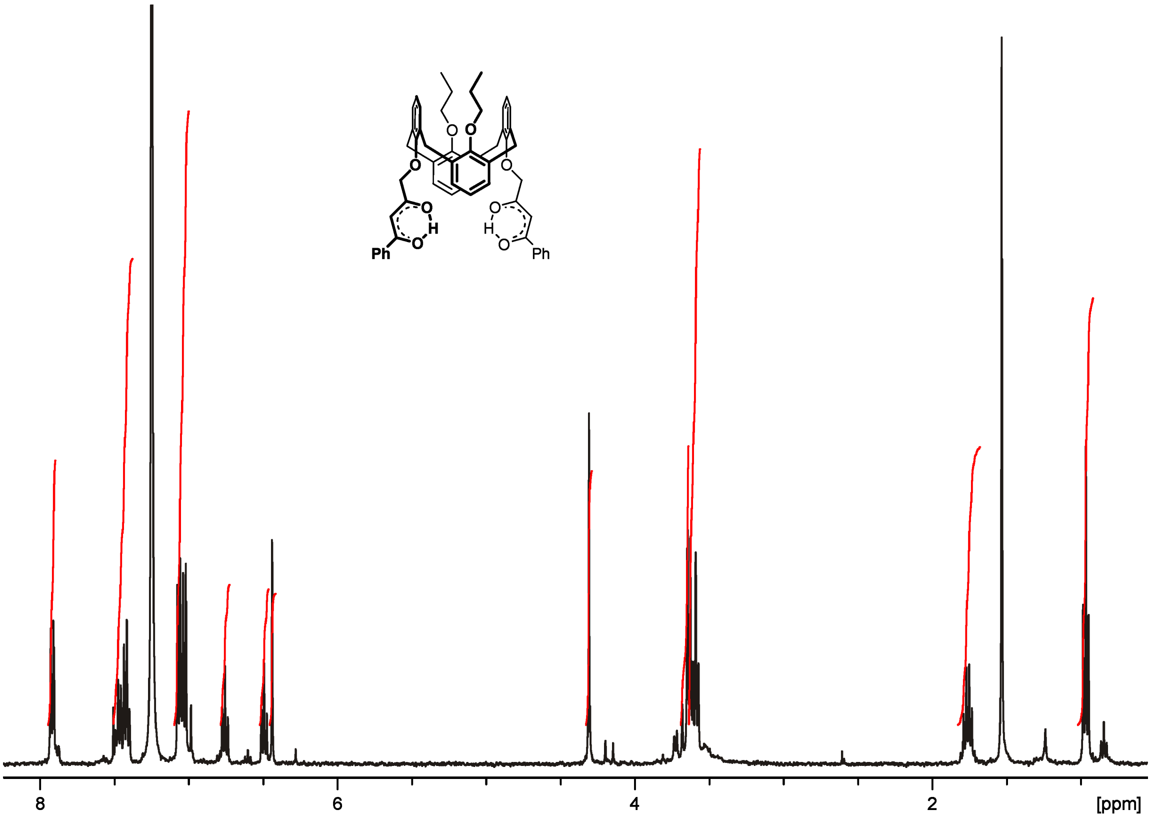


Figure S111. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **70** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

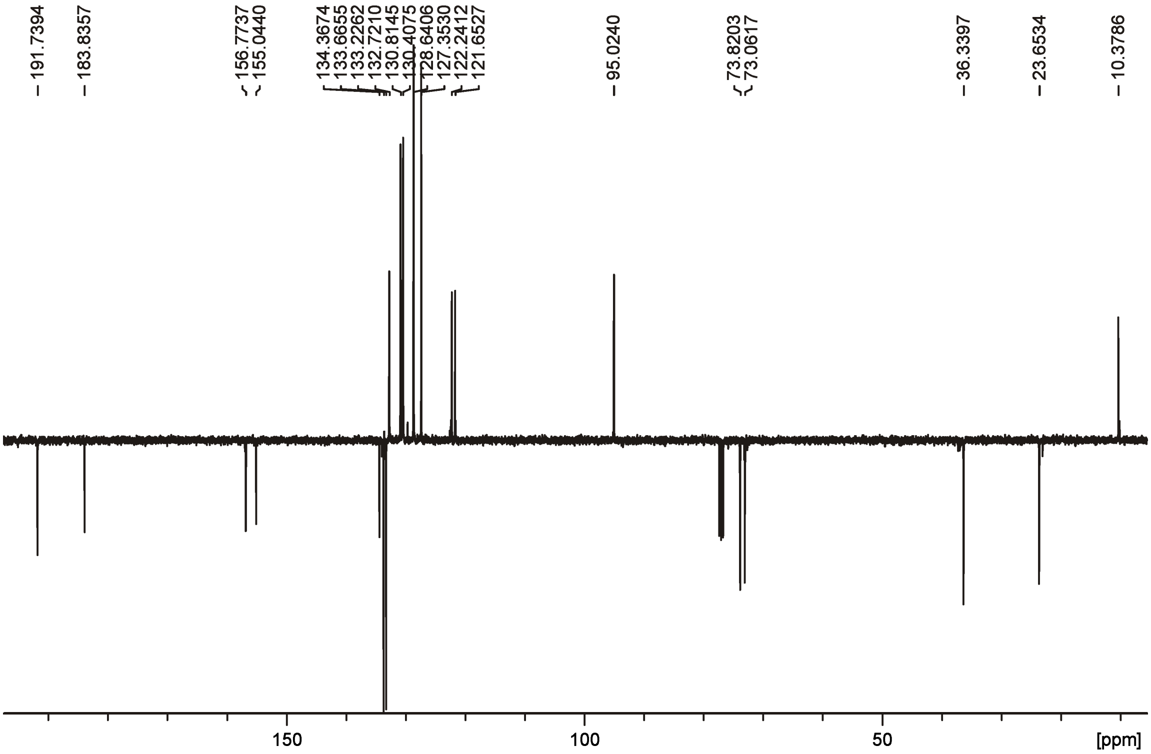


Figure S112. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **70** (100 MHz, $CDCl_3$).

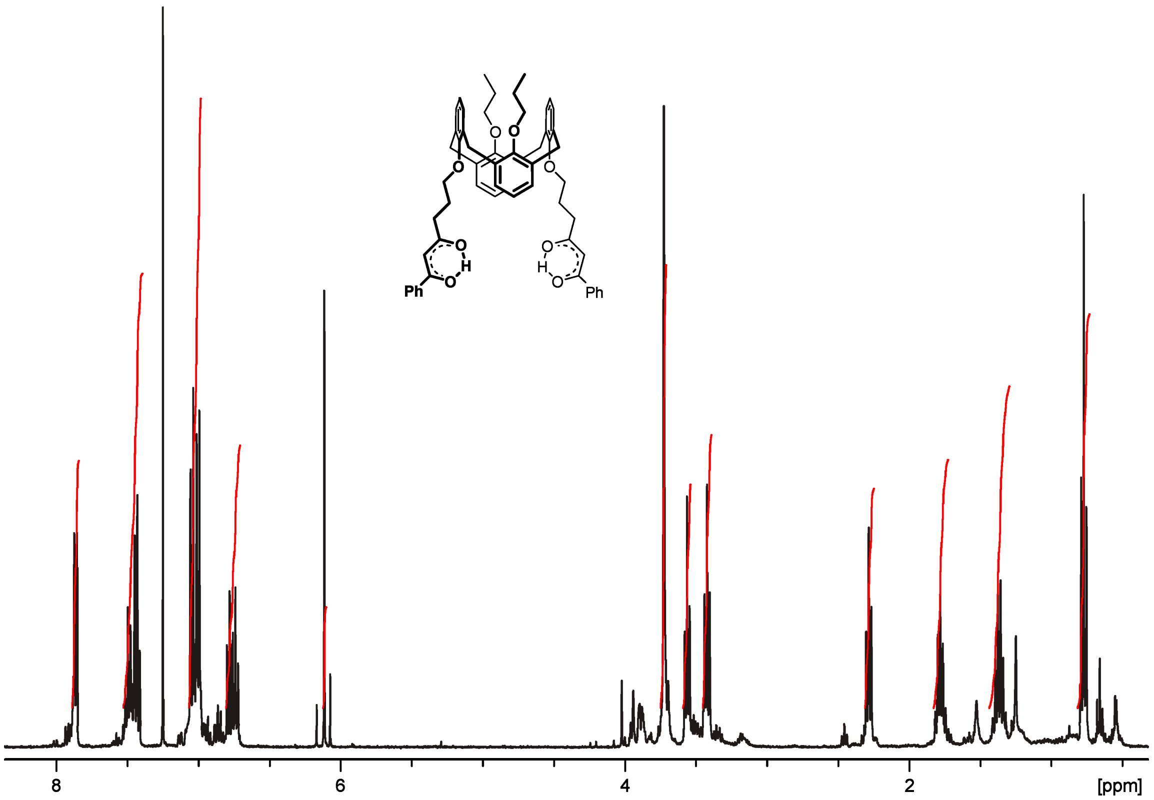


Figure S113. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **71** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

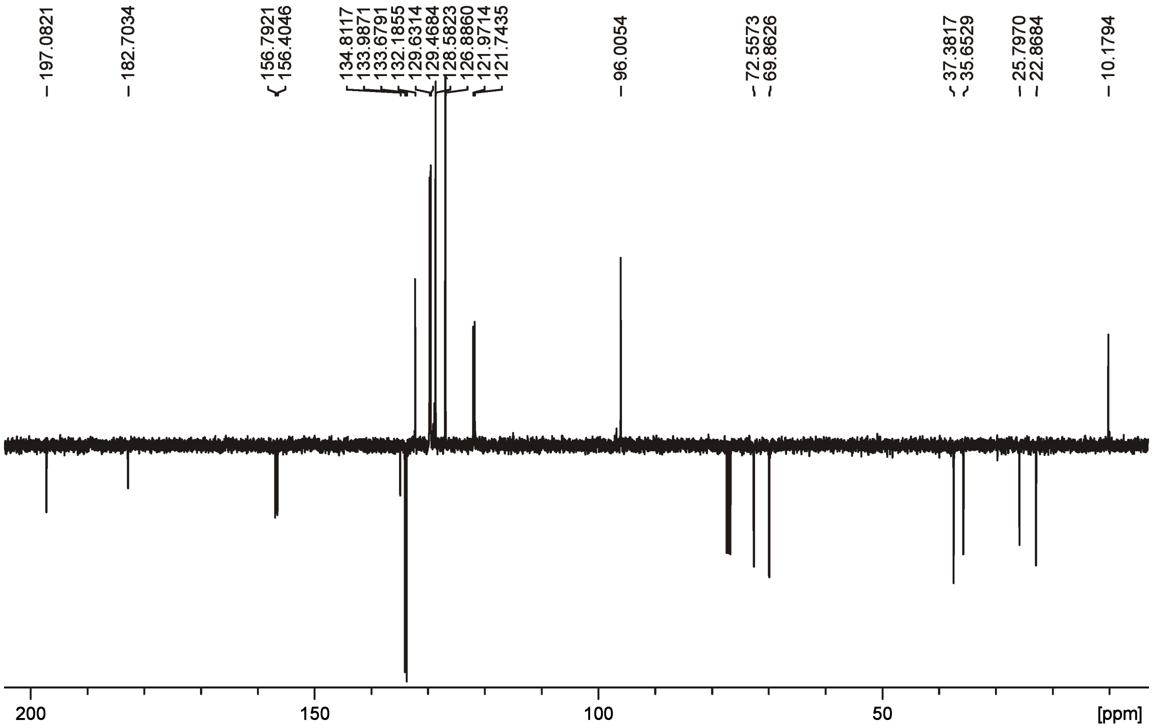


Figure S114. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **71** (100 MHz, $CDCl_3$).

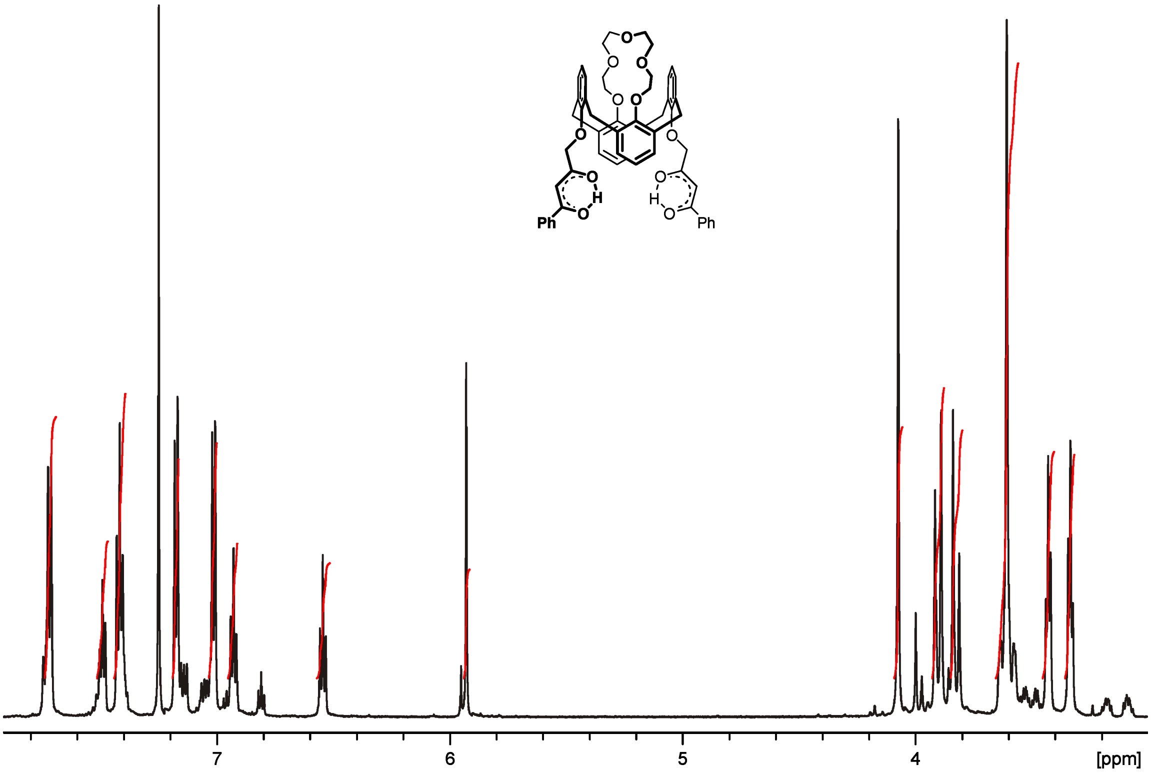


Figure S115. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **72** (600 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

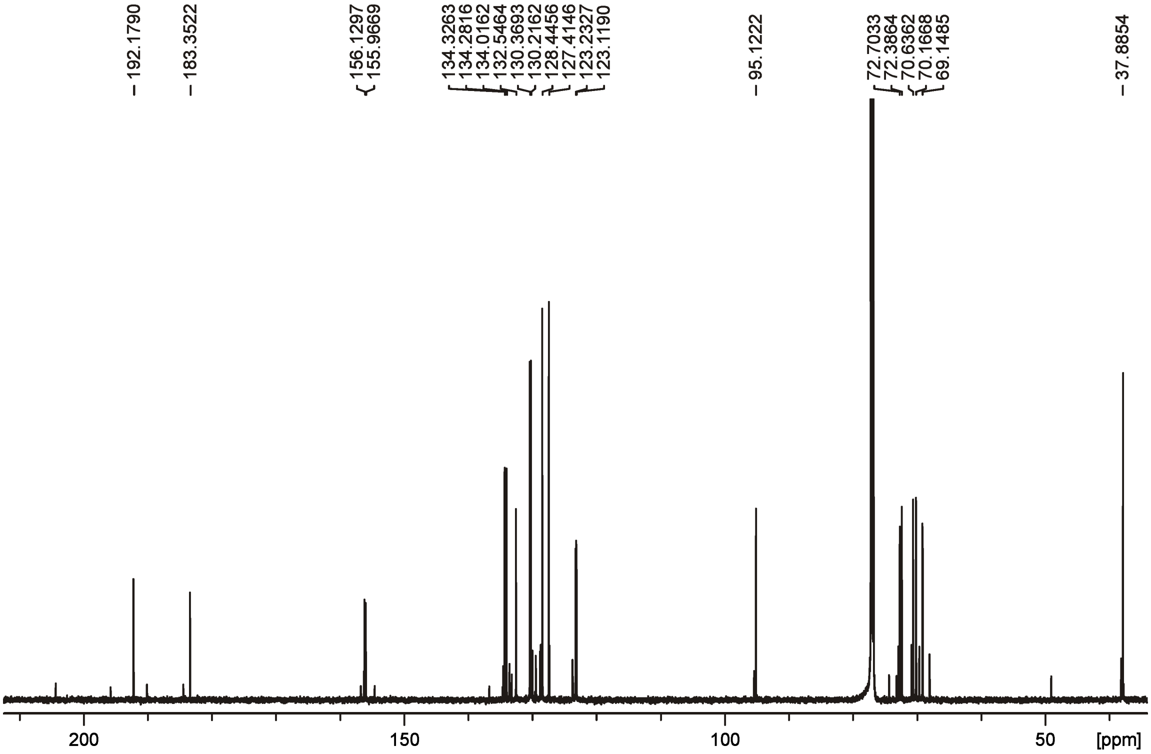


Figure S116. ^{13}C NMR spectrum of calixarene bis(1,3-diketone) **72** (150 MHz, $CDCl_3$).

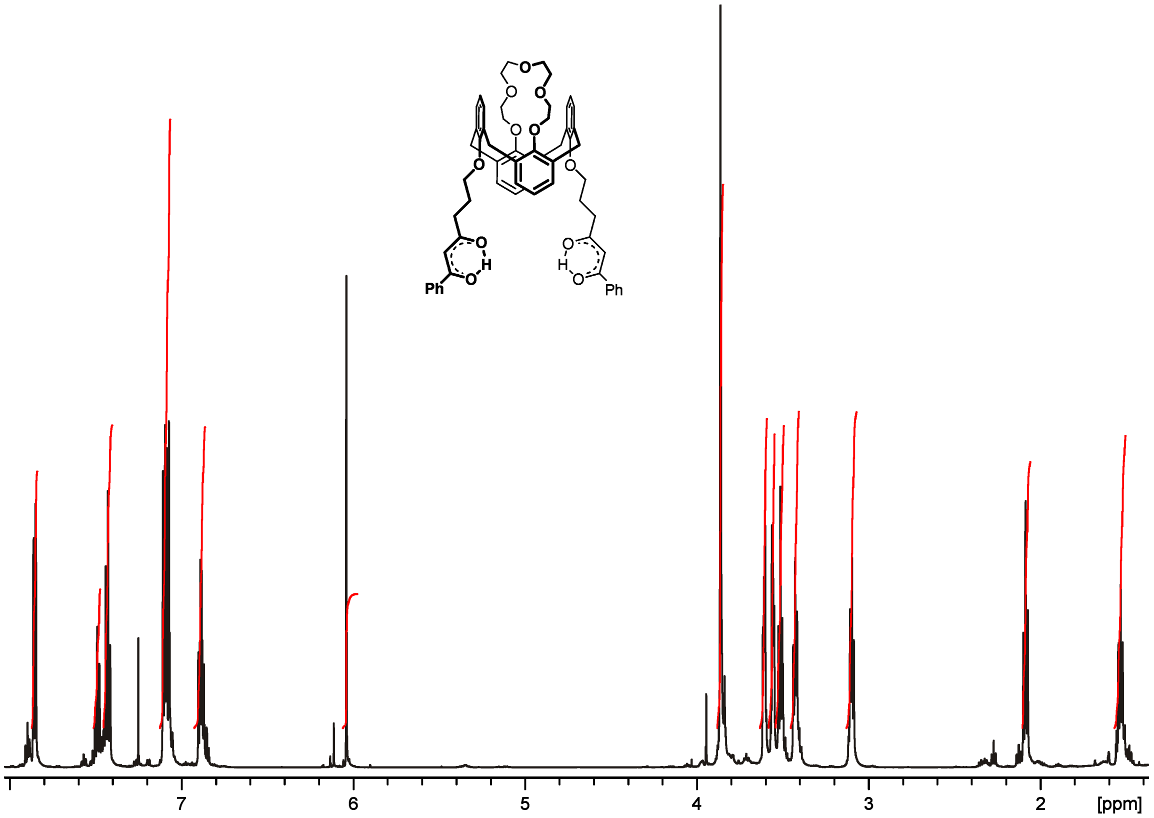


Figure S117. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **73** (600 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

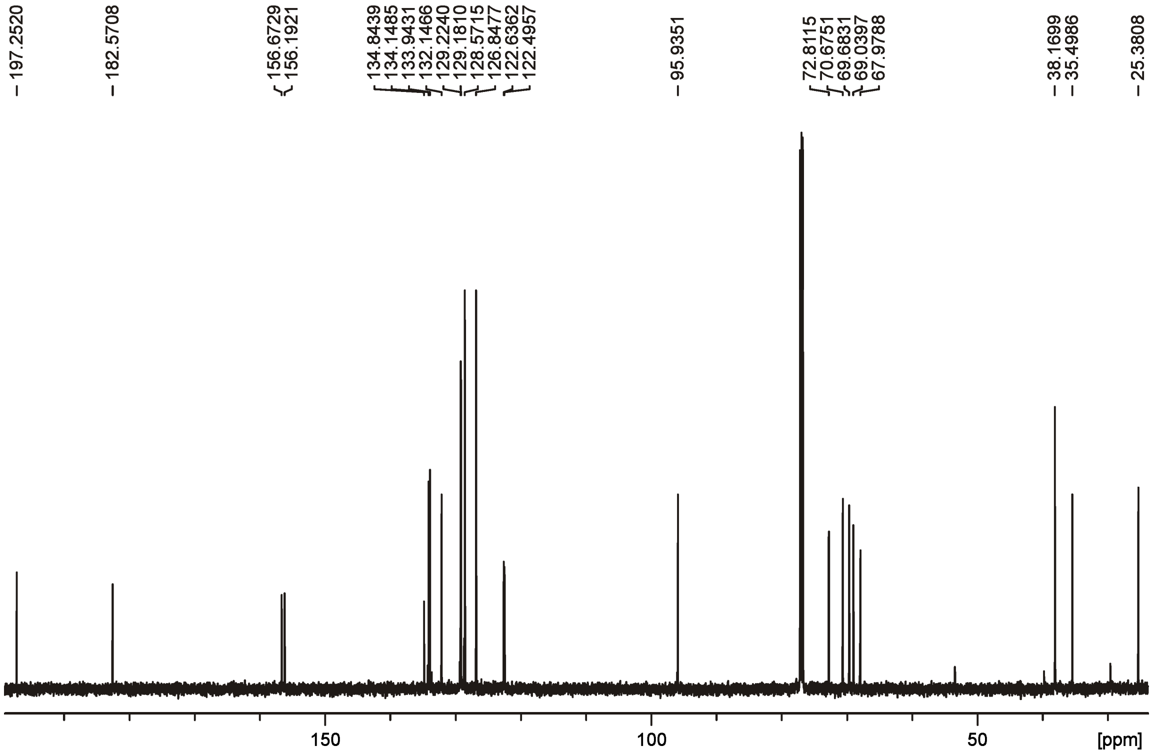


Figure S118. ^{13}C NMR spectrum of calixarene bis(1,3-diketone) **73** (150 MHz, $CDCl_3$).

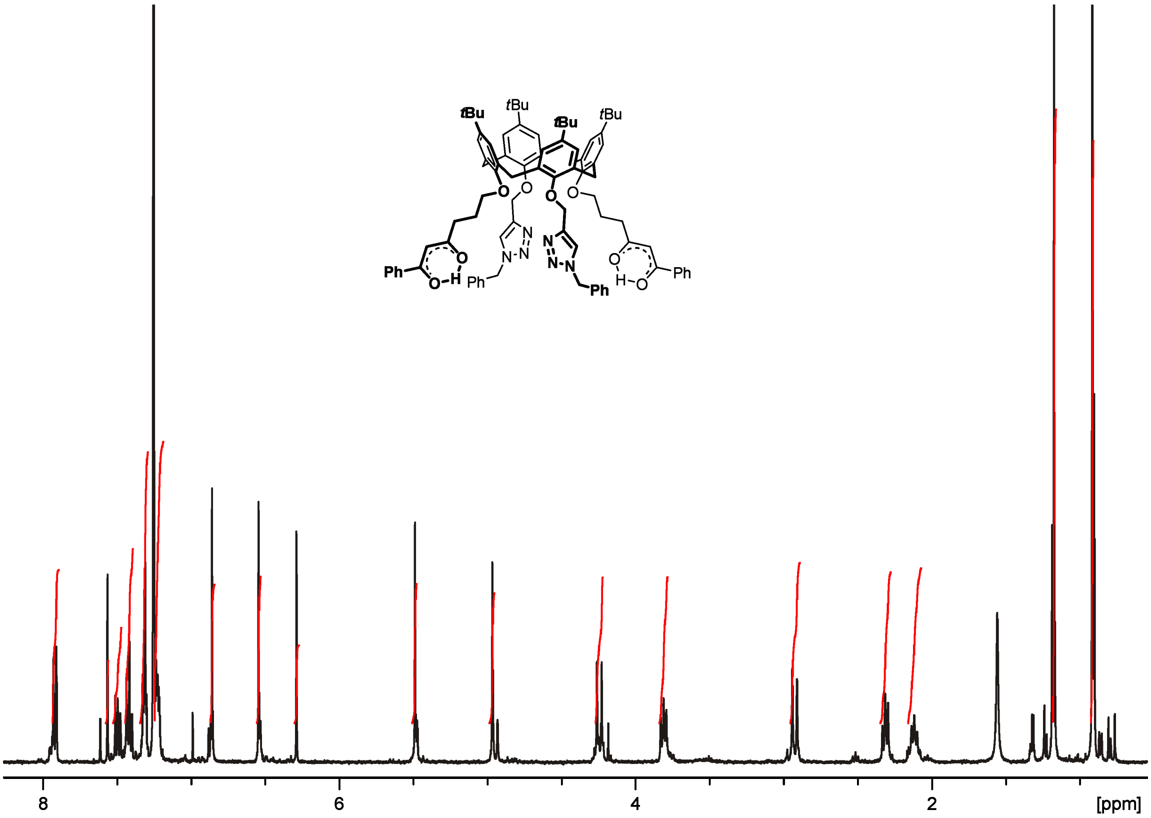


Figure S119. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **74** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

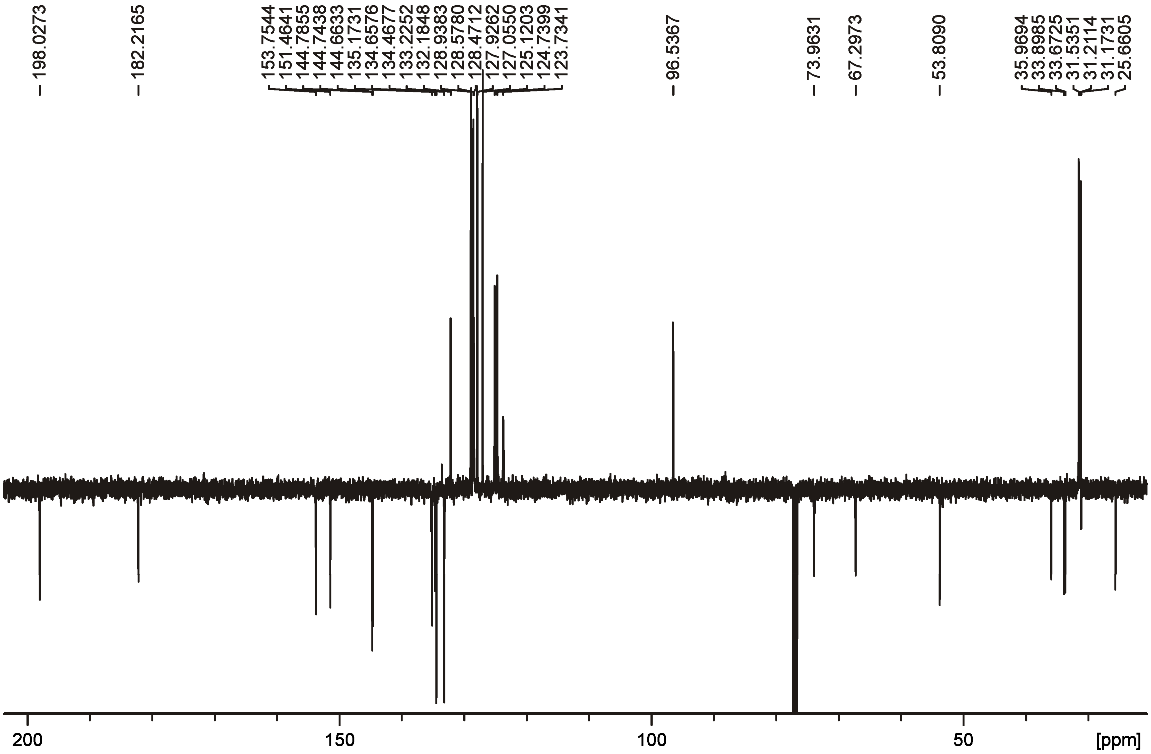


Figure S120. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **74** (100 MHz, $CDCl_3$).

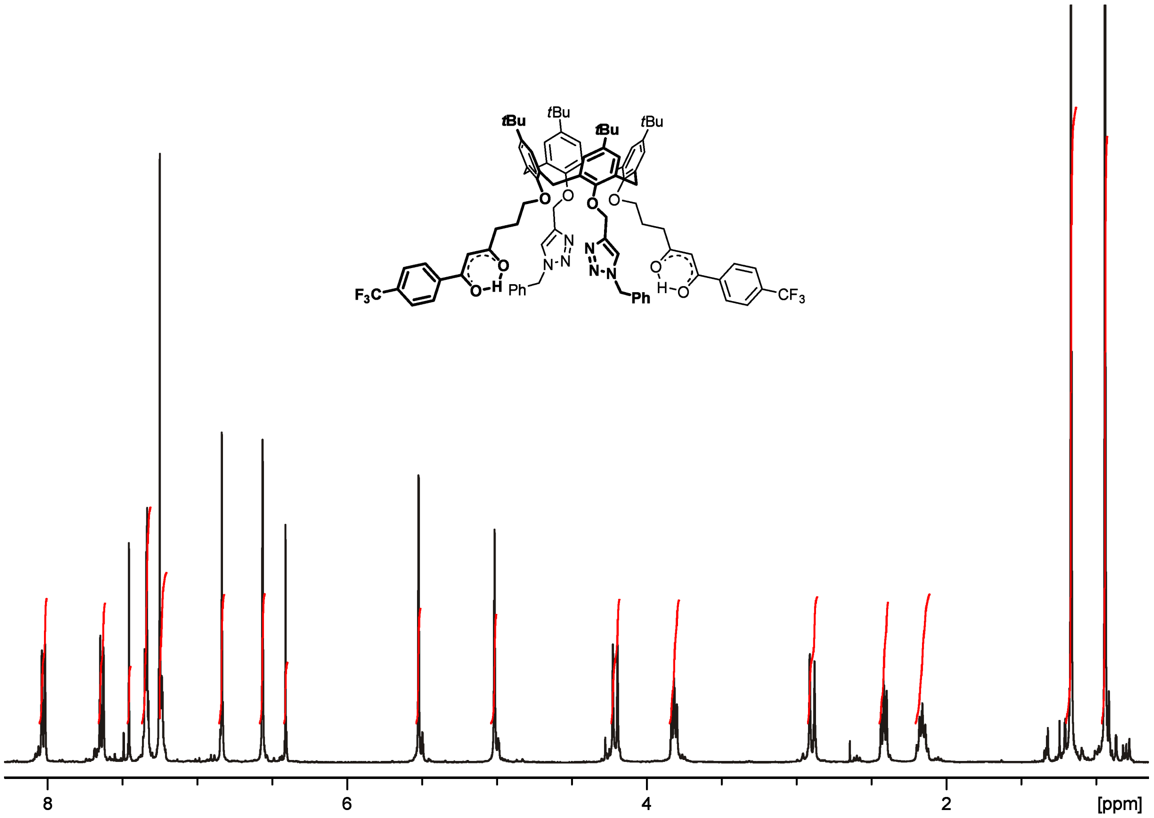


Figure S121. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **75** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

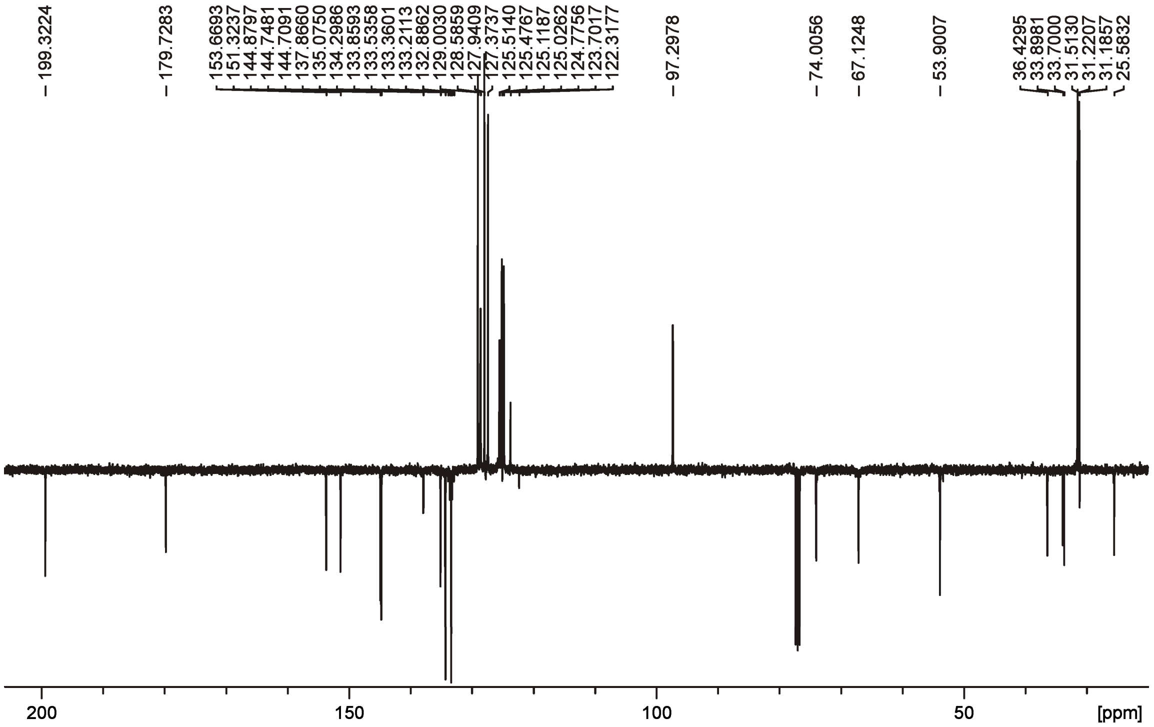


Figure S122. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **75** (100 MHz, $CDCl_3$).

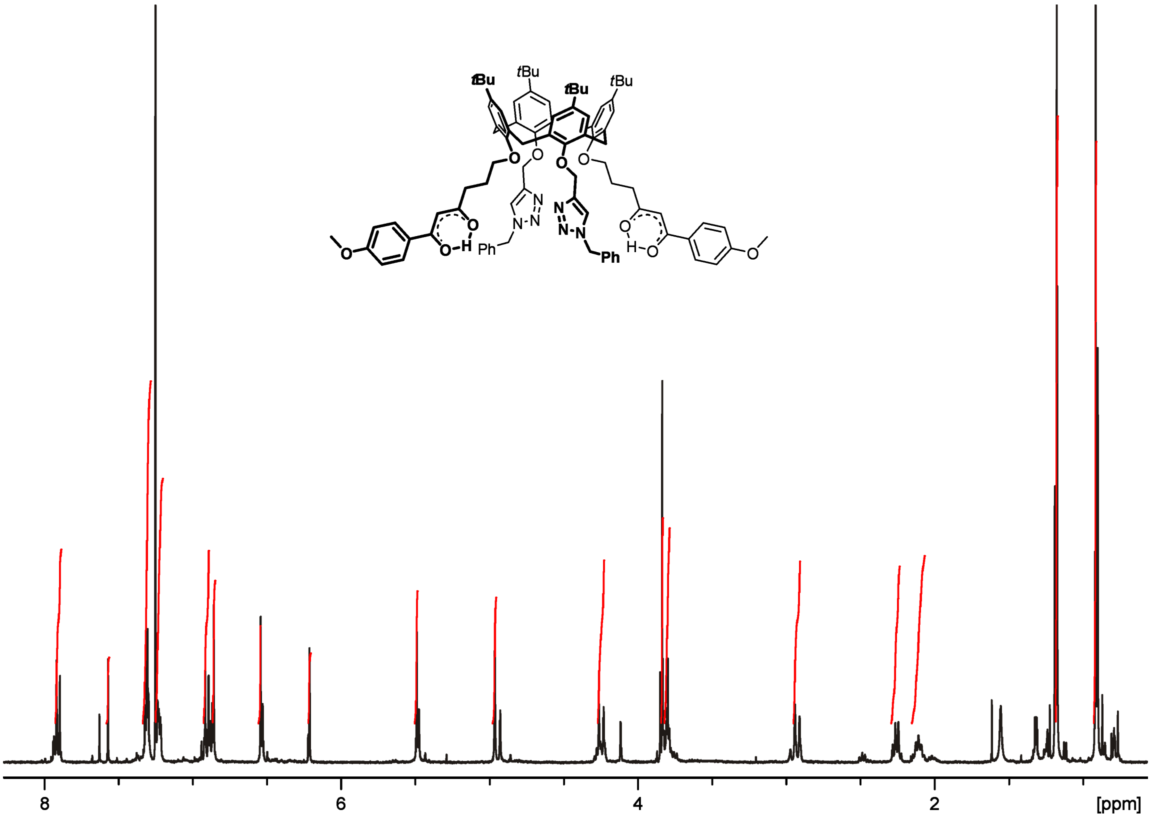


Figure S123. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **76** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

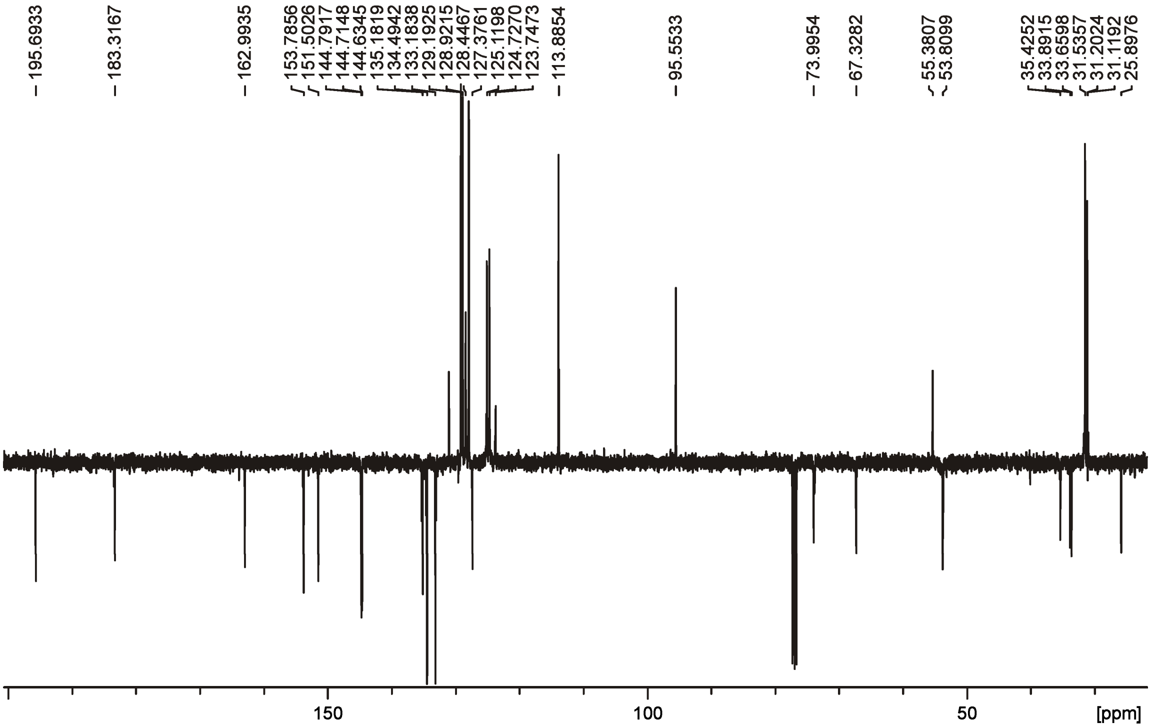


Figure S124. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **76** (100 MHz, $CDCl_3$).

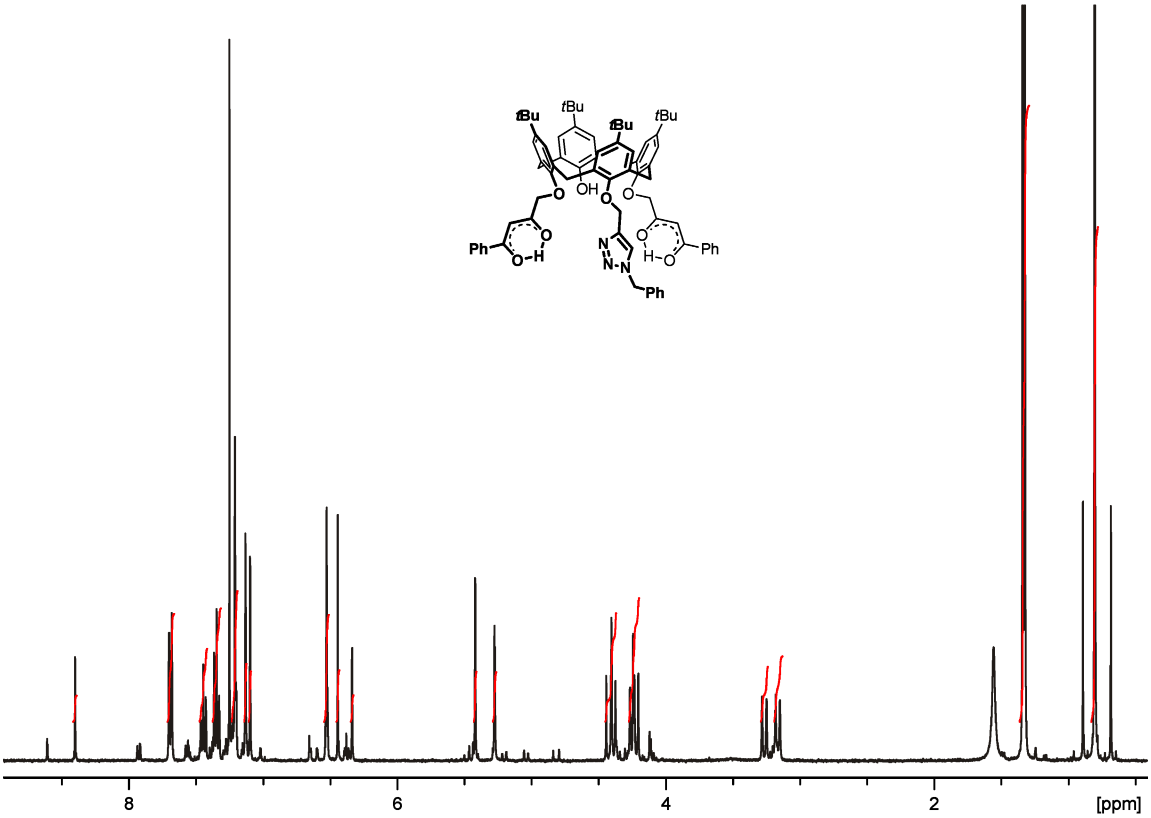


Figure S125. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **77** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

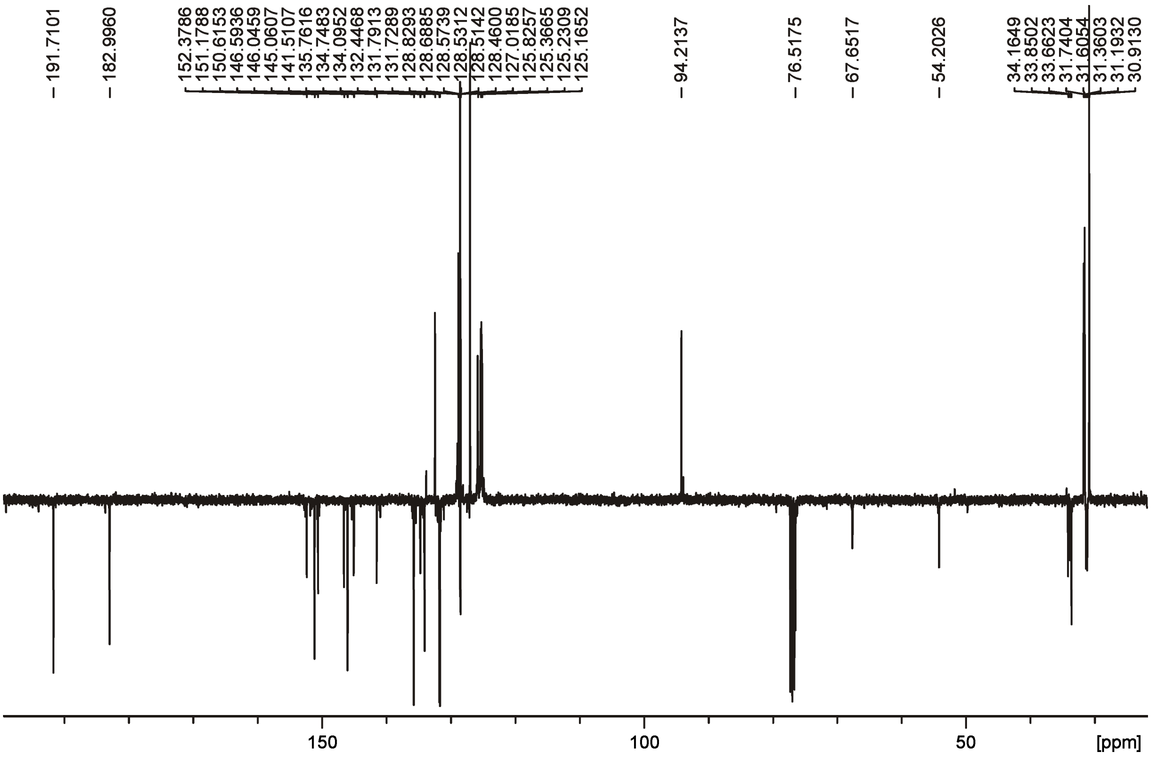


Figure S126. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **77** (100 MHz, $CDCl_3$).

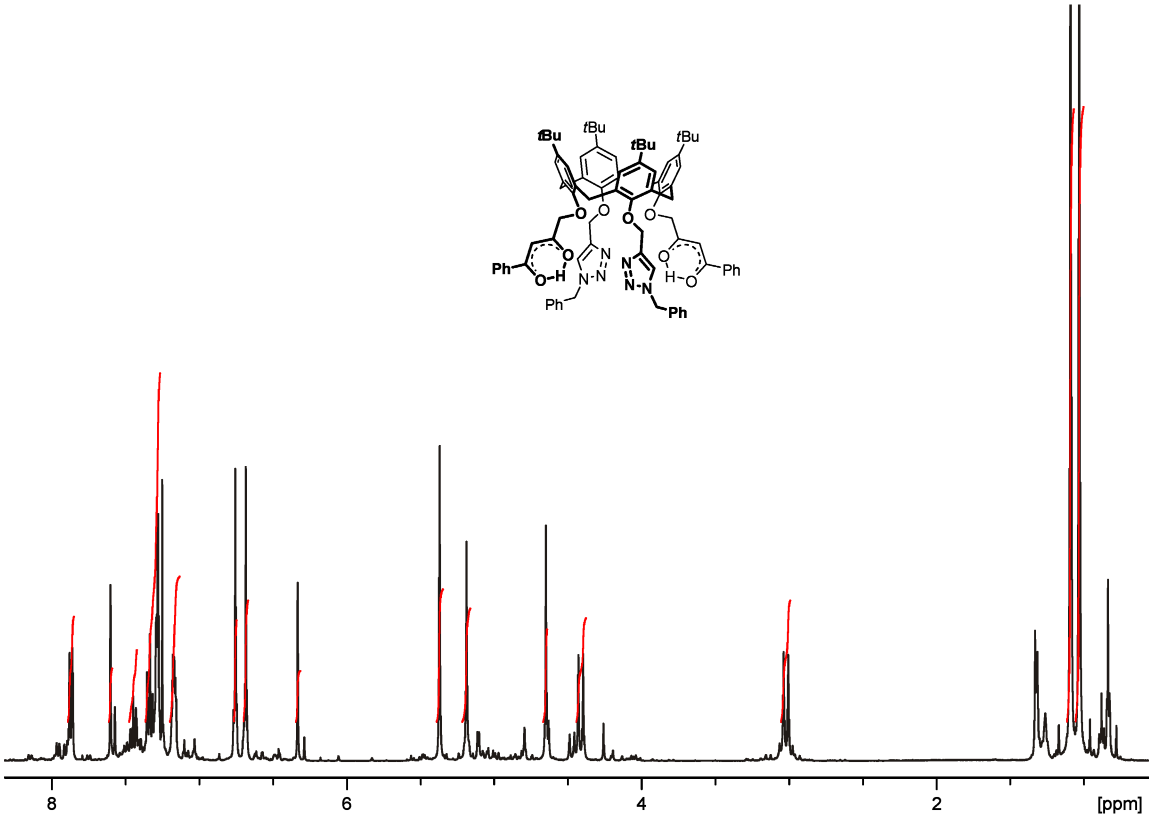


Figure S127. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **78** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

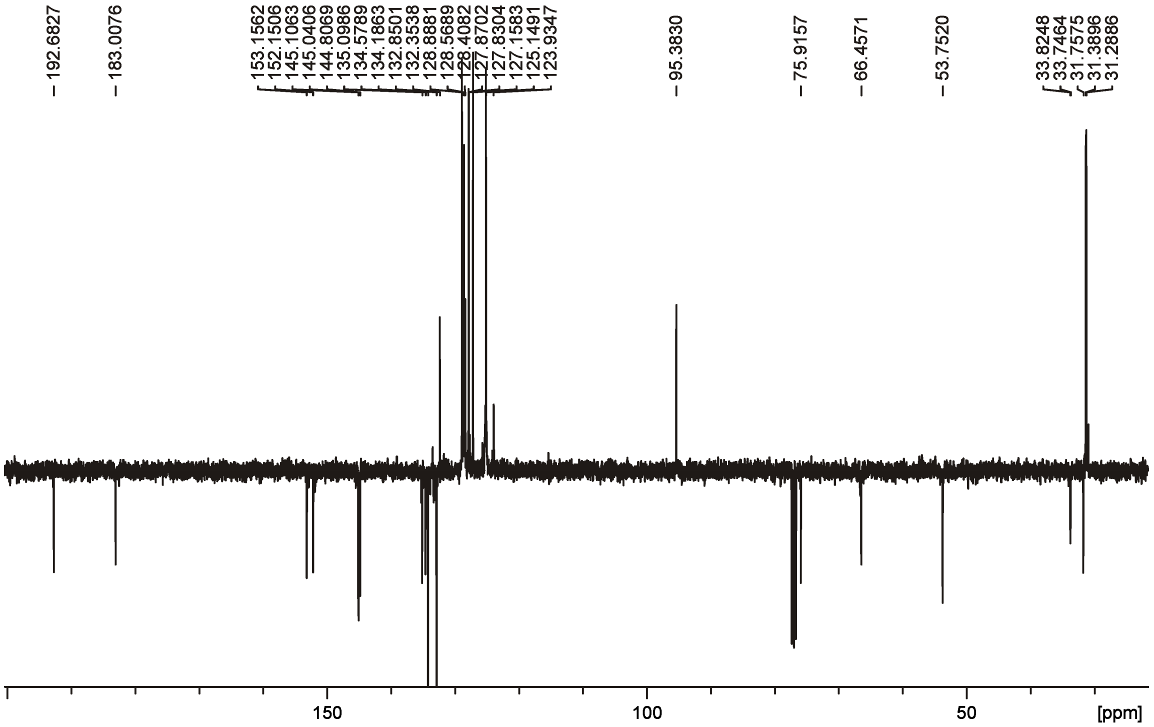


Figure S128. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **78** (100 MHz, $CDCl_3$).

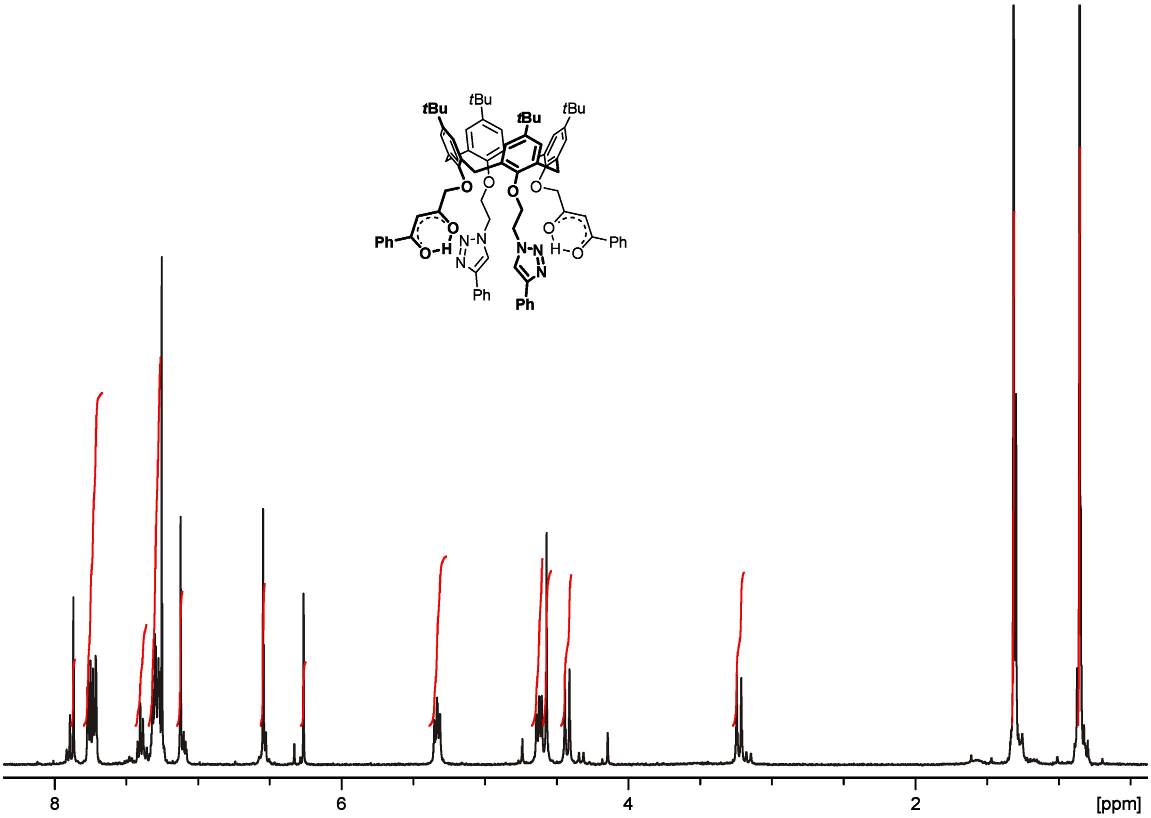


Figure S129. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **79** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

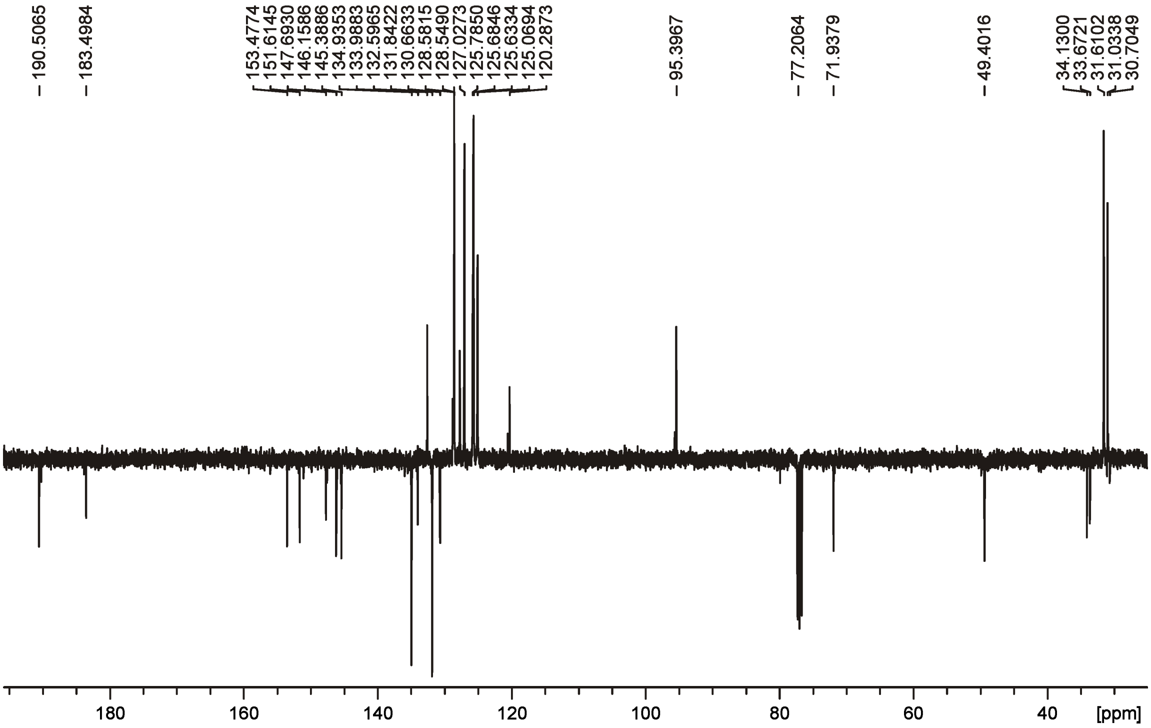


Figure S130. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **79** (100 MHz, $CDCl_3$).

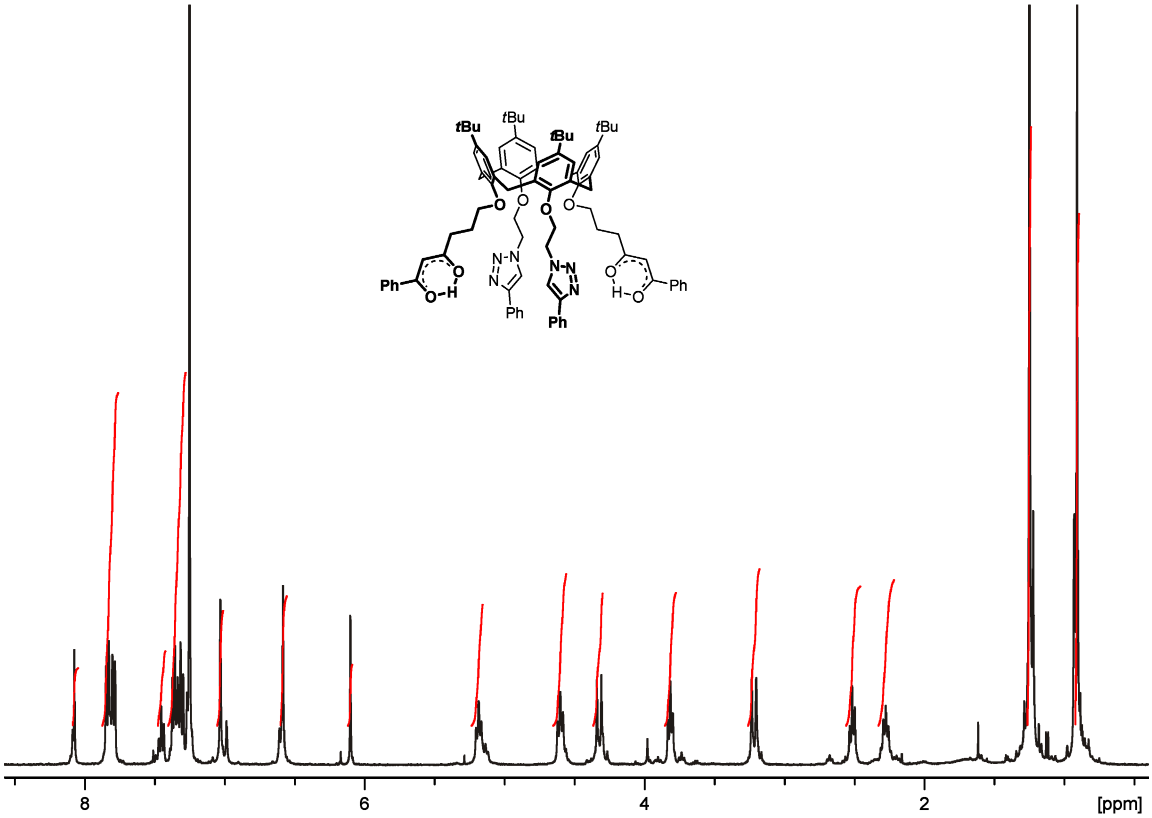


Figure S131. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **80** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

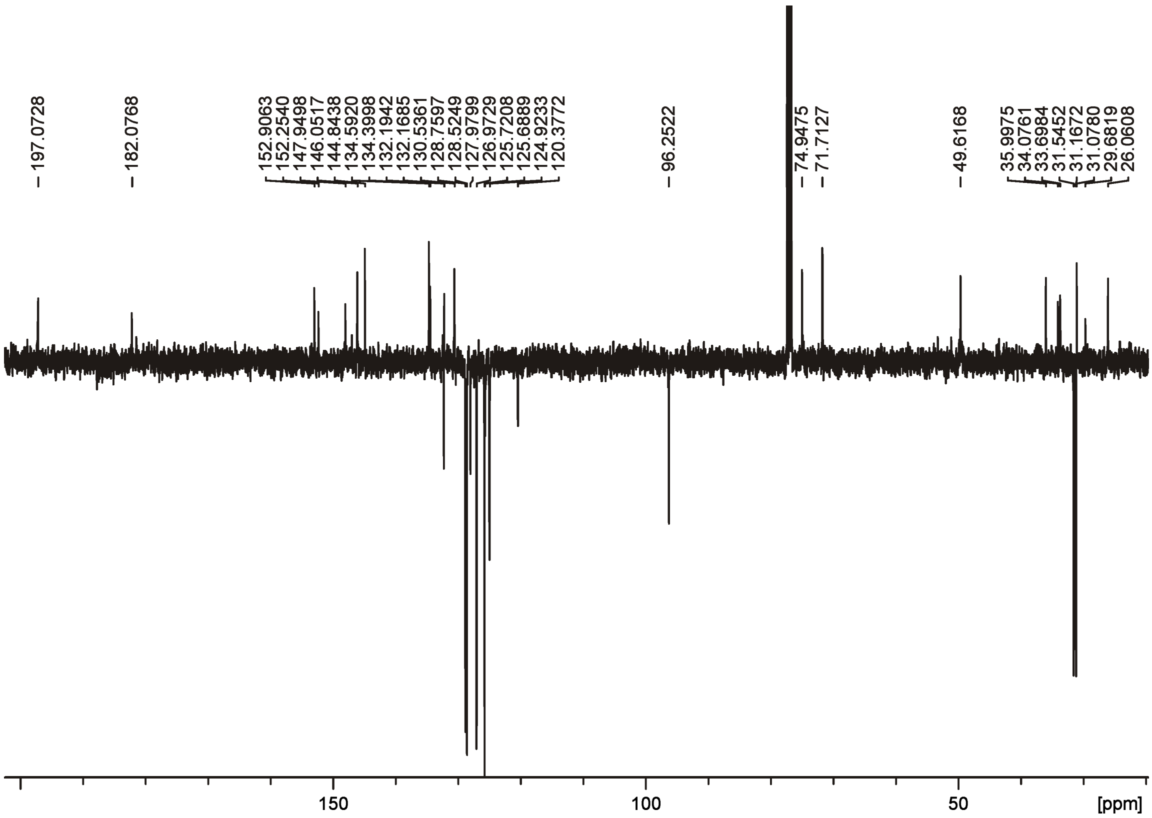


Figure S132. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **80** (100 MHz, $CDCl_3$).

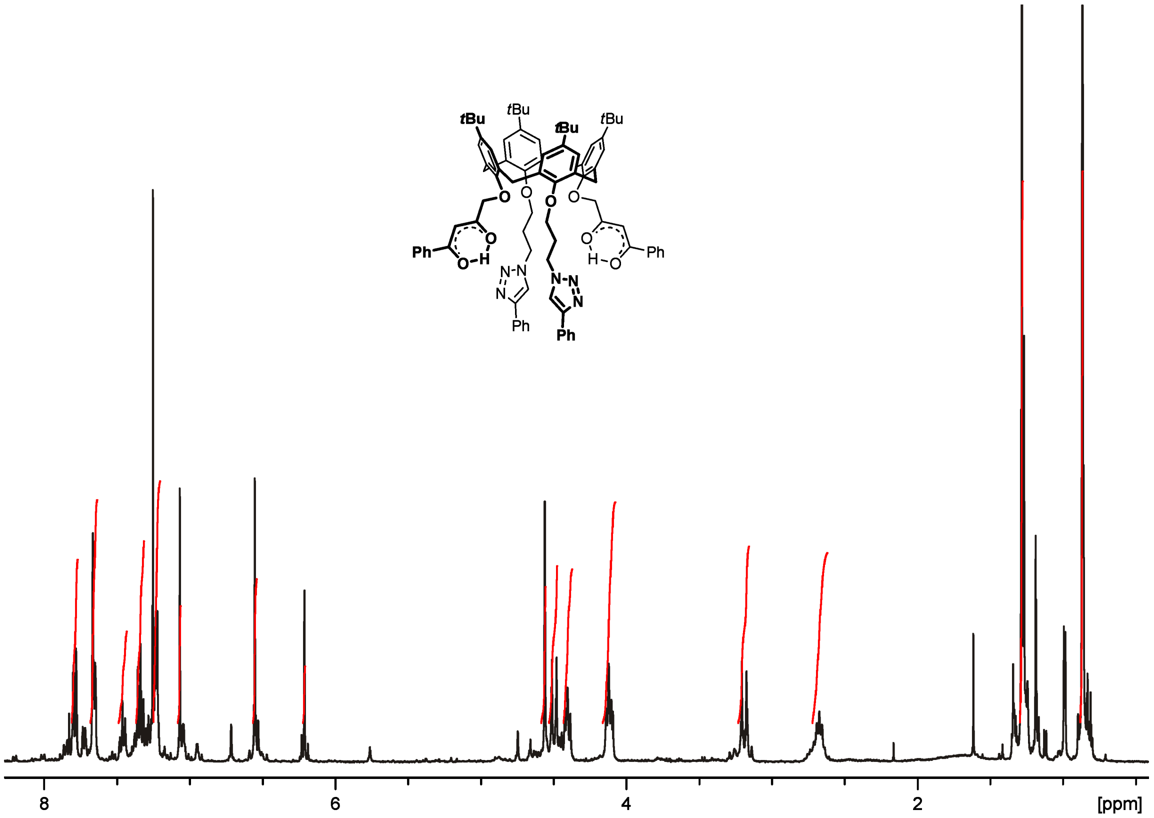


Figure S133. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **81** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

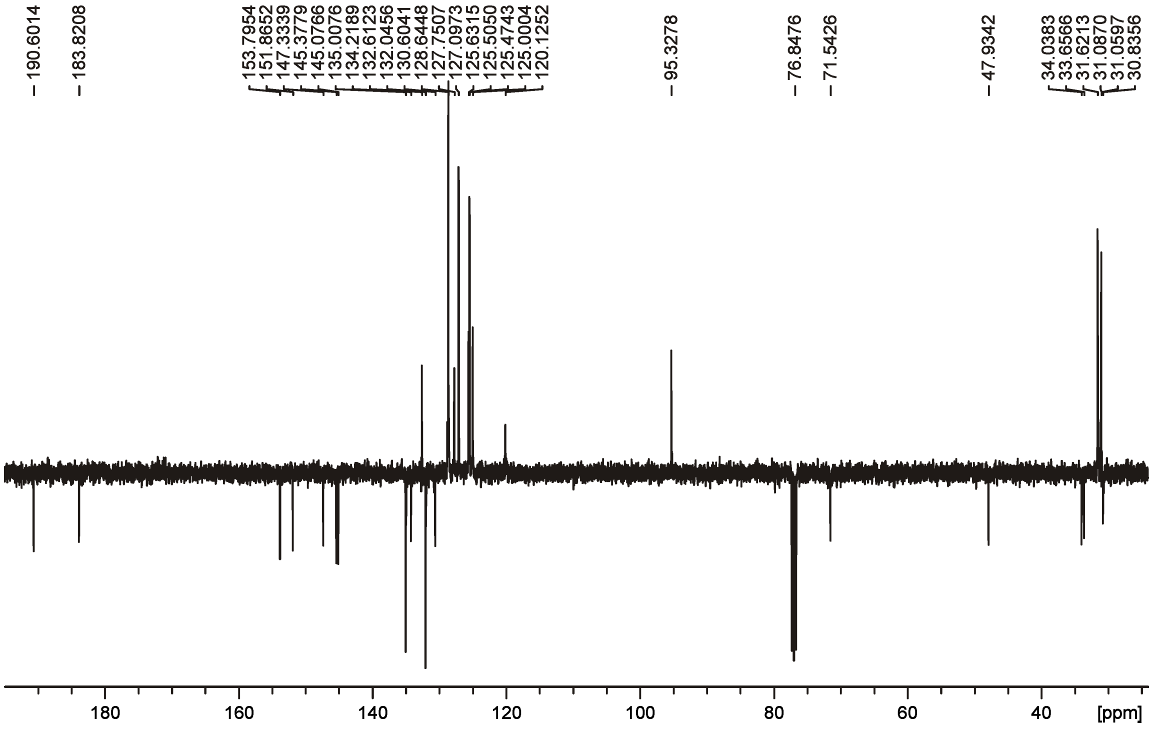


Figure S134. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **81** (100 MHz, $CDCl_3$).

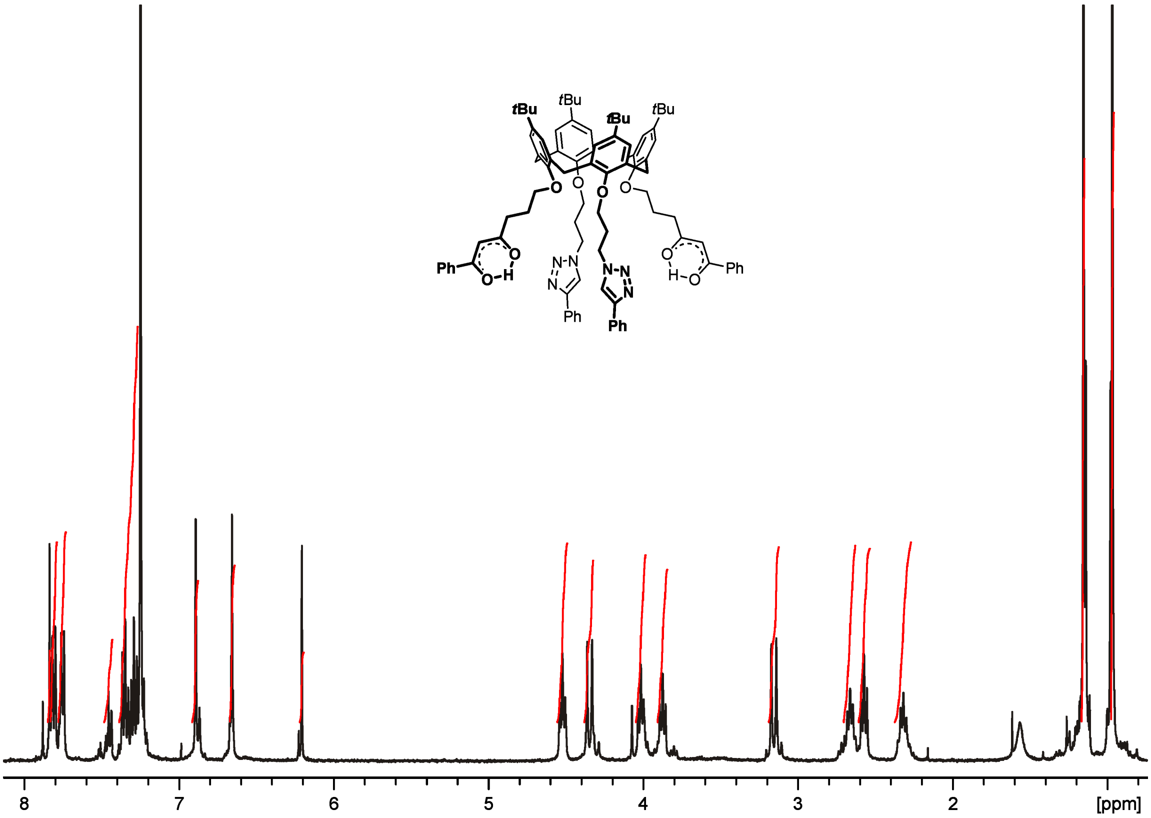


Figure S135. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **82** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

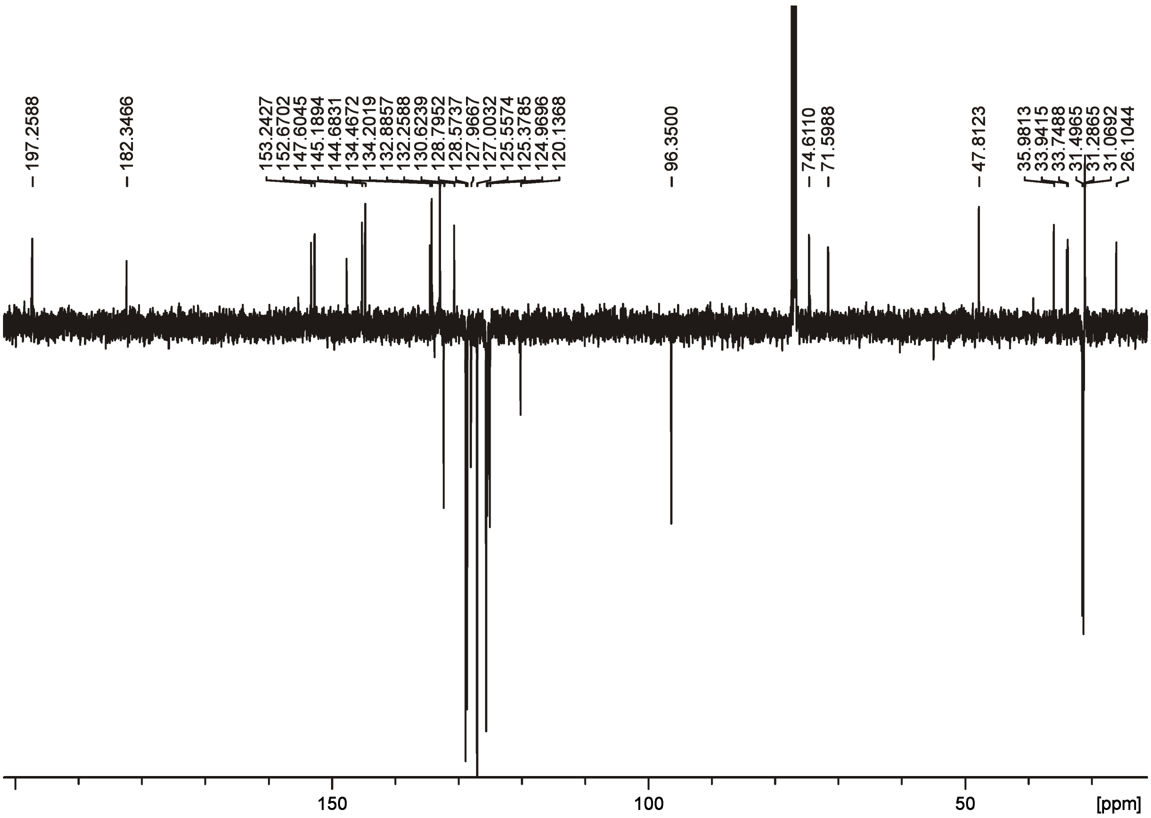


Figure S136. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **82** (100 MHz, $CDCl_3$).

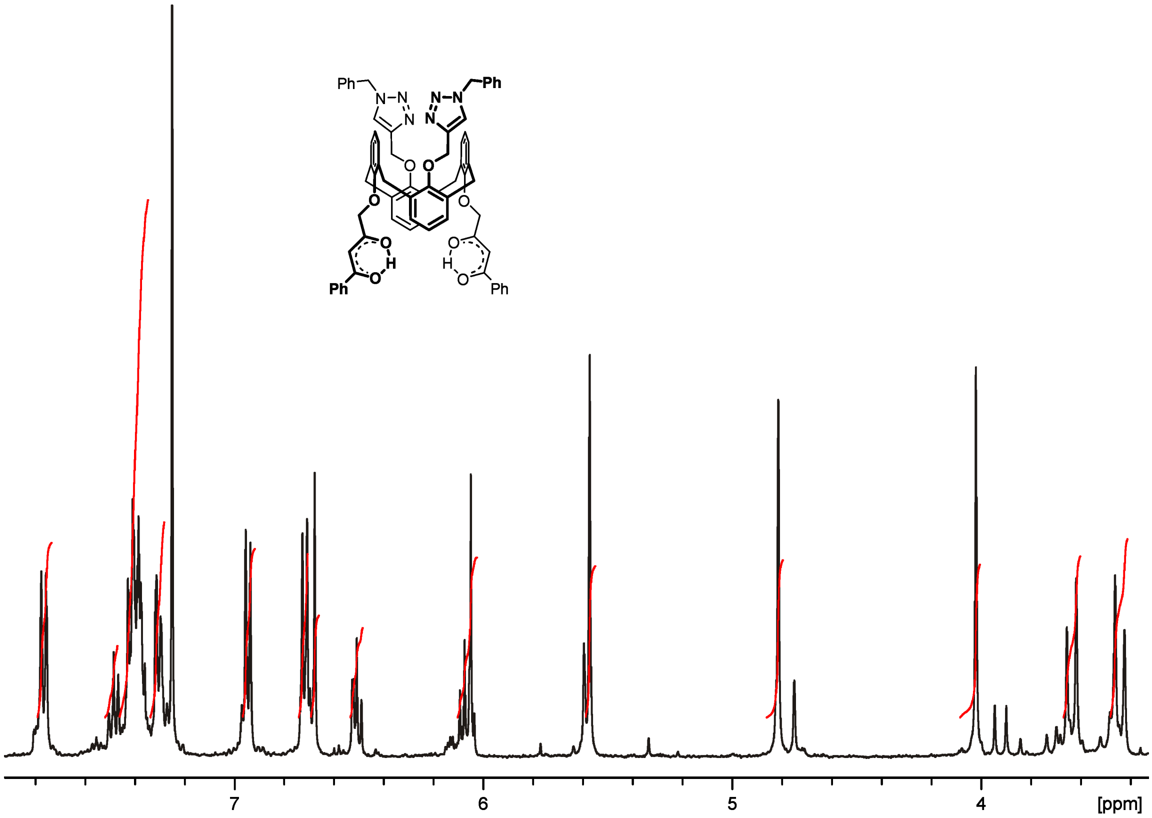


Figure S137. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **83** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

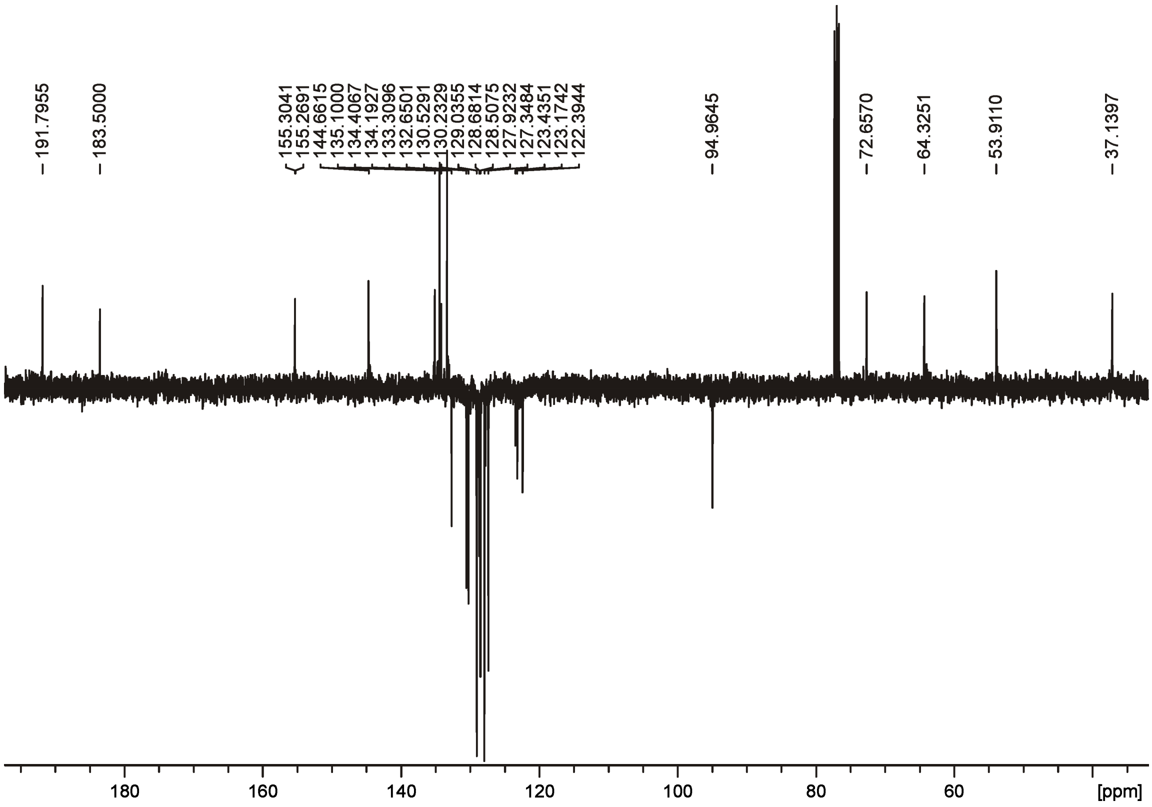


Figure S138. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **83** (100 MHz, $CDCl_3$).

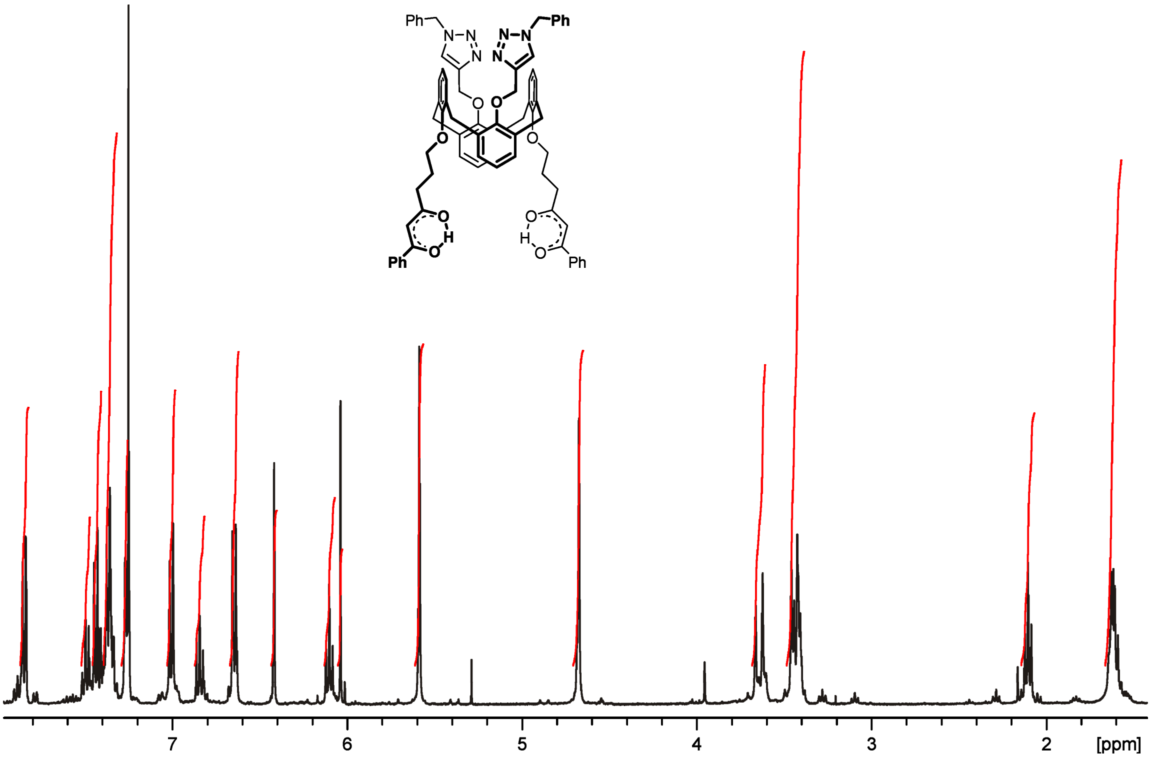


Figure S139. ^{1}H NMR spectrum of calixarene bis(1,3-diketone) **84** (400 MHz, $CDCl_3$, the downfield-shifted resonance from the enol OH is not shown).

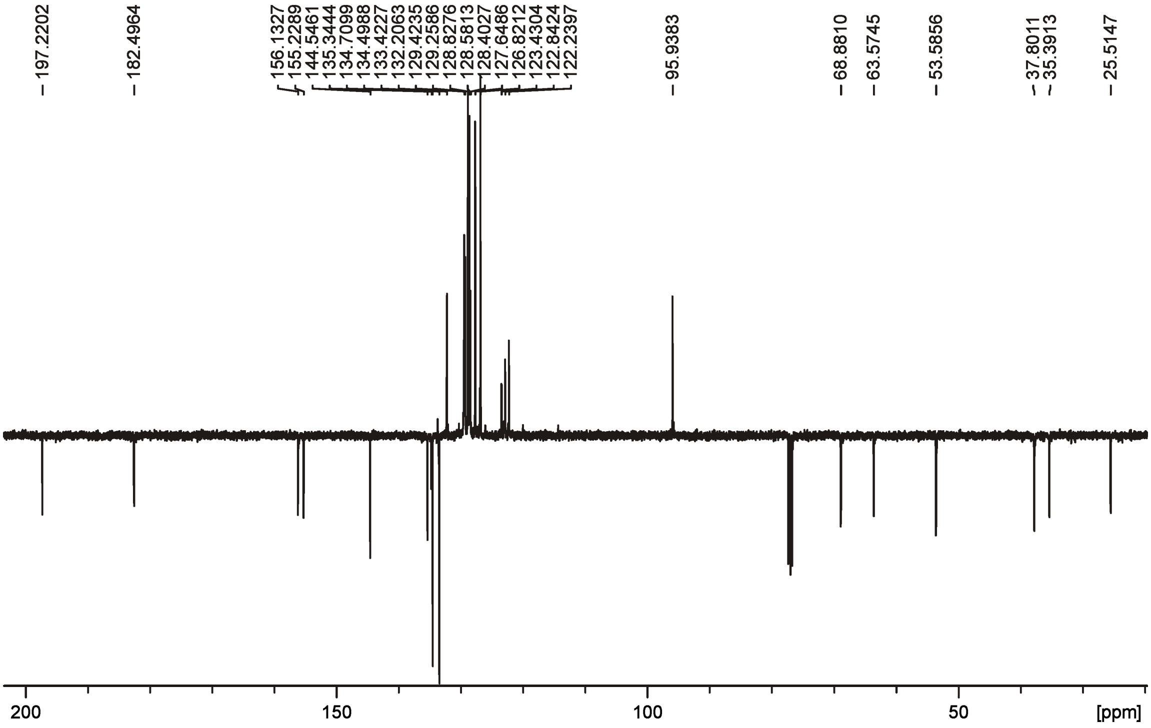


Figure S140. ^{13}C NMR spectrum (APT) of calixarene bis(1,3-diketone) **84** (100 MHz, $CDCl_3$).

Details of X-ray diffraction measurements

Crystallographic data were collected on a Bruker D8 Venture diffractometer using graphite monochromatized Mo–Kα radiation (λ = 0.71073 Å) using a ω-scan mode. Absorption correction based on measurements of equivalent reflections was applied.[S13] The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using Olex2 package.[S14] Hydrogen atoms were placed in calculated positions and refined using a riding model. In the structure **70**, the enol H004 atom was found from the difference Fourier map and refined freely. In the structure **61**, the enol H005 and H007 atoms were found from the difference Fourier map and refined freely. In the structure of the copper(II) complex of deprotonated bis(1,3-diketone) **61**, several highly disordered solvent methanol molecules were not located and their contribution was suppressed by the SQUEEZE procedure.[S15] Crystallographic details are presented in Table S1–S3.

Table S1. Details of the X-ray crystal data collection and structure refinement for compounds **21**, **23**, **36** and **41**.

Compound	**21**	**23**	**36**	**41**
Formula	$C_{62}H_{80}O_8$	$C_{76}H_{94}N_6O_8$	$C_{68}H_{78}N_6O_8\cdot2.8CH_3OH$	$C_{84}H_{92}N_{12}O_6$
M_w	953.26	1219.57	1197.72	1365.69
Temperature (K)	100(2)	150(2)	230(2)	150(2)
Size (mm)	0.05 × 0.08 × 0.14	0.02 × 0.08 × 0.10	0.12 × 0.20 × 0.30	0.03 × 0.09 × 0.11
Cryst. system	triclinic	orthorhombic	triclinic	monoclinic
Space group	P-1	Pbca	P-1	C2/c
a (Å)	11.7935(11)	23.9383(15)	13.6183(7)	69.434(4)
b (Å)	13.6631(12)	16.3679(10)	17.5853(10)	9.8951(7)
c (Å)	18.6769(18)	35.5184(18)	18.1084(10)	23.4704(15)
α (°)	87.204(3)	90	116.217(2)	90
β (°)	73.312(3)	90	98.958(2)	109.282(2)
γ (°)	79.156(3)	90	99.748(2)	90
V (Å^3)	2831.2(5)	13916.8(14)	3701.7(4)	15221.0(17)
Z	2	8	2	8
θ range (deg)	$1.83 < \theta < 25.05$	$1.90 < \theta < 25.03$	$1.76 < \theta < 25.05$	$1.86 < \theta < 25.05$
collected/ /unique rflns	68758 / 10033	52572 / 12298	51521 / 13063	73255 / 13436
Completeness to θ (%)	100.0	99.9	99.6	99.7
data/ /restraints/ /params	10033/64/741	12298/21/825	13063/45/793	13436/30/912
Goodness of fit on F^2	1.030	1.011	1.034	1.038
Final R indices ($I > 2\sigma(I)$)	R1 = 0.0698 wR2 = 0.1727	R1 = 0.0794 wR2 = 0.1778	R1 = 0.0852 wR2 = 0.2495	R1 = 0.0764 wR2 = 0.1902
Largest diff peak/hole (e/Å^3)	0.72 / −0.94	1.52 / −0.48	1.68 / −0.60	0.74 / −0.47

Table S2. Details of the X-ray crystal data collection and structure refinement for compounds **48**, **49**, **50** and **60**.

Compound	**48**	**49**	**50**	**60**
Formula	$C_{43}H_{44}O_9$	$C_{46}H_{48}O_8$	$C_{46}H_{48}O_8$	$C_{64}H_{82}O_6$
M_w	704.78	728.84	728.84	947.29
Temperature (K)	150(2)	150(2)	150(2)	100(2)
Size (mm)	0.03 × 0.08 × 0.40	0.03 × 0.10 × 0.13	0.11 × 0.12 × 0.16	0.15 × 0.18 × 0.35
Cryst. system	monoclinic	triclinic	monoclinic	orthorhombic
Space group	C2/c	P-1	$P2_1/n$	$P2_12_12_1$
a (Å)	31.322(4)	7.6834(4)	9.0719(3)	14.1107(5)
b (Å)	7.5748(9)	15.2752(7)	38.9659(14)	15.5336(5)
c (Å)	19.293(2)	16.8833(8)	12.0650(5)	25.4103(8)
α (°)	90	99.401(2)	90	90
β (°)	126.657(2)	101.168(2)	111.9300(10)	90
γ (°)	90	93.4820(10)	90	90
V (Å^3)	3672.0(8)	1909.13(16)	3956.3(3)	5569.7(3)
Z	4	2	4	4
θ range (deg)	$2.11 < \theta < 26.00$	$2.00 < \theta < 26.41$	$2.09 < \theta < 27.00$	$1.95 < \theta < 28.05$
collected/ /unique rflns	9958 / 3541	31397 / 7802	56379 / 8600	228083 / 13527
Completeness to θ (%)	97.9	99.4	99.4	100.0
data/ /restraints/ /params	3541/1/244	7802/4/484	8600/3/505	13527/17/647
Goodness of fit on F^2	1.092	1.051	1.043	1.118
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0519 wR2 = 0.1274	R1 = 0.0575 wR2 = 0.1427	R1 = 0.0407 wR2 = 0.0930	R1 = 0.0592 wR2 = 0.1488
Largest diff peak/hole (e/Å^3)	0.65 / −0.43	0.40 / −0.61	0.22 / −0.21	0.63 / −0.44

Table S3. Details of the X-ray crystal data collection and structure refinement for compounds **61**, **70**, **81** and for the copper(II) complex of deprotonated bis(1,3-diketone) **61**.

Compound	**61**	**70**	**81**	**Copper(II) complex**
Formula	$C_{74}H_{92}O_8$	$C_{54}H_{52}O_8$	$C_{86}H_{94}N_6O_8$	$C_{74}H_{90}O_8Cu$
M_w	1109.47	828.96	1339.67	2342.03
Temperature (K)	100(2)	230(2)	150(2)	100(2)
Size (mm)	0.19 × 0.22 × 0.24	0.01 × 0.04 × 0.13	0.05 × 0.05 × 0.24	0.02 × 0.08 × 0.10
Cryst. system	monoclinic	orthorhombic	trigonal	triclinic
Space group	$P2_1/c$	Pbcn	R-3	P-1
a (Å)	23.3701(19)	18.8623(12)	61.4200(19)	12.242(2)
b (Å)	13.8905(11)	7.7799(5)	61.4200(19)	14.810(2)
c (Å)	21.460(2)	29.4405(18)	10.6481(3)	22.121(4)
α (°)	90	90	90	97.483(5)
β (°)	112.992(3)	90	90	98.817(5)
γ (°)	90	90	120	109.567(5)
V (Å^3)	6413.1(10)	4320.3(5)	34787(2)	3662.7(11)
Z	4	4	18	2
θ range (deg)	$1.79 < \theta < 26.40$	$2.16 < \theta < 25.05$	$1.95 < \theta < 25.05$	$1.88 < \theta < 25.10$
collected/ /unique rflns	103894 / 13122	37920 / 3830	179997 / 13683	36892 / 12964
Completeness to θ (%)	99.9	99.9	99.8	99.2
data/ /restraints/ /params	13122/27/774	3830/13/257	13683/31/892	12964/64/756
Goodness of fit on F^2	1.037	1.085	1.034	0.930
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0720 wR2 = 0.1827	R1 = 0.1243 wR2 = 0.2381	R1 = 0.0901 wR2 = 0.2369	R1 = 0.0876 wR2 = 0.1847
Largest diff peak/hole (e/Å^3)	0.78 / −0.46	0.27 / −0.45	0.68 / −0.56	0.49 / −0.44

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