Electronic Supplementary Information

Triptycene-derived calix[6]arenes: synthesis, structure and tubular assemblies in the solid state

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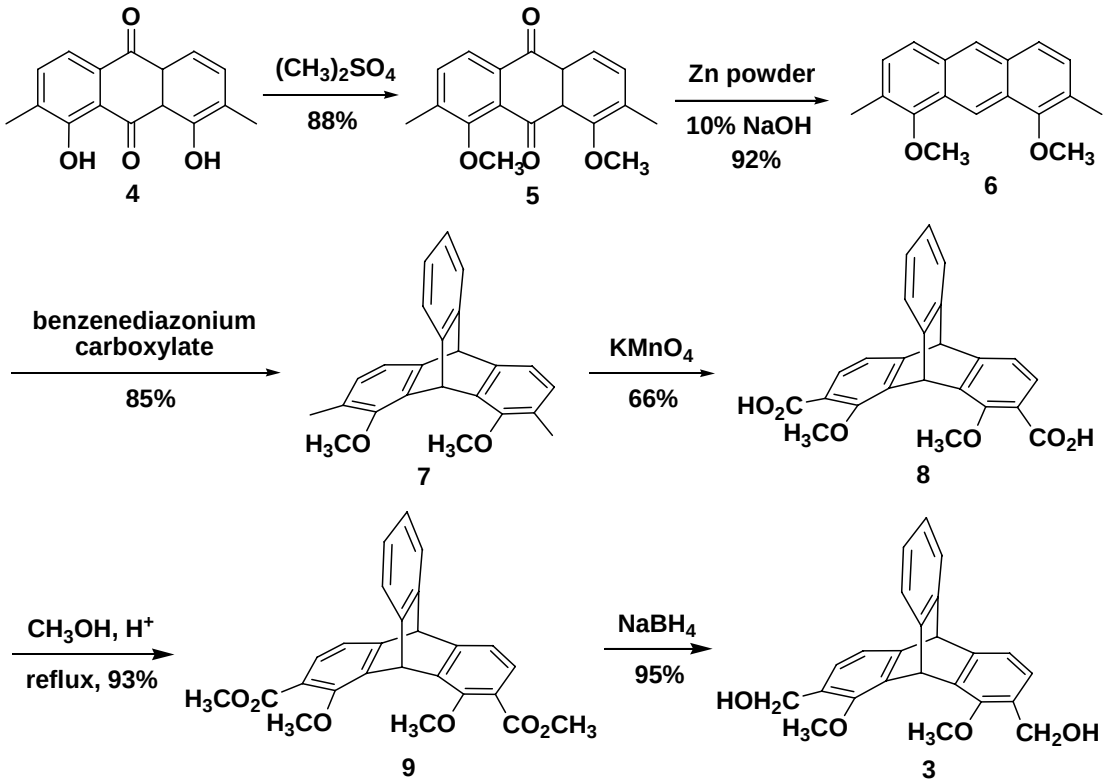
Content

1. Synthesis and characterization data of macrocycles 1 and 2



2, 7-Dimethyl-1, 8-dimethoxy-9, 10-anthracenedione (5). To a vigorously stirred mixture of 2, 7-dimethyl-1, 8- dihydroxy-9, 10-anthracenedione **4**[S1] (3.0 g, 11.1 mmol) and K_2CO_3 (12.3 g, 89.1 mmol) in acetone (100 mL) was added dimethylsulfate (8.4 mL, 88.8 mmol). The reaction mixture was refluxed for 24 h. The solvent was evaporated under reduced pressure, and then concentrated ammonia solution was added. The solution was stirred for 3 h at r.t. and filtered. The residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (4:1) as eluent to afford **5** (2.9 g, 88 %) as a yellow solid. Mp: 160-162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 6H), 3.95 (s, 6H), 7.53 (d, J = 7.8 Hz, 2H), 7.94 (d, J = 7.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.7, 61.6, 122.5, 127.7, 133.1, 135.6, 140.4, 158.4, 183.0, 183.6. EI-MS: 321 $[M+Na]^+$. Anal. calcd. for $C_{18}H_{16}O_4$: C 72.96, H 5.44; found: C 72.64, H 5.56.

2, 7-Dimethyl-1, 8-dimethoxyanthracene (6). To a 10% NaOH solution (150 mL) of compound **5** (2.9 g, 9.7 mmol) was added zinc powder (3.3 g, 49.8 mmol). The mixture was stirred for 4 h at 120 °C, cooled to room temperature and then filtered.

The filtered cake was washed with CH_2Cl_2. The organic solution was concentrated, and the residue was subjected to chromatography on silica gel with petroleum ether/ CH_2Cl_2 (4:1) as eluent to give compound **6** (2.4 g, 92 %) as a light-yellow crystals. Mp: 152-153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 6H), 4.01 (s, 6H), 7.26 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 8.34 (s, 1H), 8.85 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 61.1, 114.3, 123.9, 124.6, 126.4, 126.9, 129.2, 131.8, 153.3. EI-MS: 267 $[M+H]^+$, 289 $[M+Na]^+$. Anal. calcd. for $C_{18}H_{18}O_2$: C 81.17, H 6.81; found: C 81.12, H 6.87.

2, 7-Dimethyl-1, 8-dimethoxytriptycene (7). To a refluxing solution of compound **6** (2.4 g, 9.0 mmol) in 1,2-dichloroethane (100 mL) and 1, 2-epoxypropane (10 mL) was added portionwise benzenediazonium carboxylate (5.4 g, 36.0 mmol) over 24 h. The reaction mixture was concentrated under reduced pressure and then purified by column chromatography (petroleum ether/CH_2Cl_2 4:1) to give **7** (2.6 g, 85 %) as a white solid. Mp: 156-158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.18 (s, 6H), 3.87 (s, 6H), 5.33 (s, 1H), 6.15 (s, 1H), 6.78 (d, J = 7.4 Hz, 2H), 6.98 (m, 2H), 7.04 (d, J = 7.4 Hz, 2H), 7.30– 7.73 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$): δ 15.7, 42.3, 53.8, 61.4, 119.2, 123.5, 123.6, 125.1, 127.4, 127.9, 137.0, 144.8, 145.8, 146.4, 153.7. EI-MS: 365 $[M+Na]^+$. Anal. calcd. for $C_{24}H_{22}O_2$: C 84.18, H 6.48; found: C 83.97, H 6.55.

1, 8-Dimethoxytriptycene-2, 7-dicarboxylic acid (8). To a refluxing solution of compound **7** (2.6 g, 7.7 mmol) in pyridine (60 mL) and H_2O (20 mL) was added portionwise $KMnO_4$ (21.9 g, 138.6 mmol, 9 equiv per CH_3 group) over 24 h. After cooling to r.t., the reaction mixture was filtered and washed with 1 % NaOH solution. The filtrate was evaporated, and then acidified to pH 1 with 6 N HCl. The suspension was filtered, dried and further purified by recrystallization from methanol to afford **8** (2.1 g, 66 %) as a white solid. Mp: 254-256 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 6H), 5.86 (s, 1H), 6.26 (s, 1H), 7.07 (m, 2H), 7.35 (d, J = 7.6 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.50 (m, 1H), 7.61 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.7, 62.6, 119.6, 123.1, 123.8, 124.2, 125.5, 125.7, 128.6, 137.9, 143.7, 144.2, 150.8, 154.1, 166.8. EI-MS: 401 $[M-H]^+$. Anal. calcd. for $C_{24}H_{22}O_2$: C 71.64, H 4.51; found: C

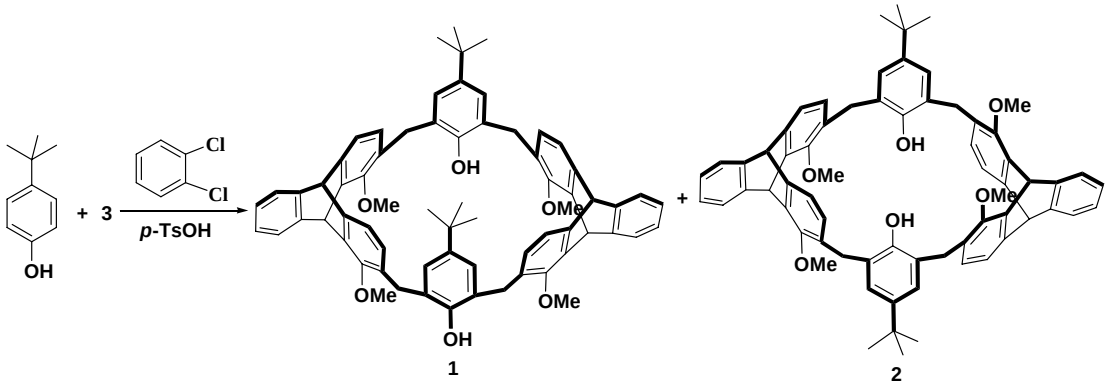
71.86, H 4.68.

1, 8-Dimethoxytriptycene-2, 7-dicarboxylic acid dimethyl ester (9). To a refluxing solution of compound **8** (2.1 g, 5.2 mmol) in methanol (40 mL) was added $SOCl_2$ (5.0 mL) dropwise. The mixture was refluxed for another 8 h. After the mixture was cooled, the suspension was filtered to afford **9** (2.1 g, 93 %) as a white solid. Mp: 200-202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 6H), 3.99 (s, 6H), 5.49 (s, 1H), 6.33 (s, 1H), 7.03 (m, 2H), 7.20 (d, J = 7.7 Hz, 2H), 7.38–7.47 (m, 2H), 7.55 (d, J = 7.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.7, 52.0, 54.4, 63.1, 119.5, 122.0, 124.0, 124.1, 125.7, 125.9, 129.4, 138.6, 143.8, 144.2, 151.5, 155.2, 166.2. EI-MS: *m/z* 431 $[M+H]^+$, 453 $[M+Na]^+$. Anal. calcd. for $C_{26}H_{22}O_6$: C 72.55, H 5.15; found: C 72. 21, H 5.21.

2, 6-Dihydroxymethyl-1, 8-dimethoxytriptycene (3). To a solution of **9** (2.1 g, 4.9mmol) in THF was added sodium borohydride (1.9 g, 49mmol). The mixture was stirred for 15 min at refluxing temperature. Methanol (8 mL) was then added dropwise. The mixture was refluxed for another 3 h. After cooling to r.t., 3 N HCl was added to quench the reaction and extracted with CH_2Cl_2. The organic phase was dried and concentrated to give pure alcohol **3** (1.7 g, 95 %) as a white solid**.** Mp: 170-171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92 (s, 2H), 3.96 (s, 6H), 4.61 (s, 4H), 5.41 (s, 1H), 6.15 (s, 1H), 6.97 (d, J = 7.4 Hz, 2H), 7.02 (m, 2H), 7.14 (d, J = 7.4 Hz, 2H), 7.30–7.52 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.2, 54.0, 61.3, 62.7, 119.7, 123.5, 123.9, 125.5, 126.1, 131.1, 137.0, 144.0, 145.6, 147.7, 153.5. EI-MS: *m/z* 397 $[M+Na]^+$. Anal. calcd. for $C_{24}H_{22}O_4$: C 76.99, H 5.92; found: C 76.64, H 5.94.

Reference:

S1. C. Marschalk, F. Koenig, N. Ouroussoff, *Bull. Soc. Chim. Fr.*, 1936, **5**, 1545–1568.



1 and 2. To a solution of catalytic amount of TsOH in *o*-dichlorobenzene (60 mL) was slowly added at 100 °C a solution of **3** (0.374 g, 1 mmol) and *p-tert*-butylphenol (0.15 g, 1 mmol) in *o*-dichlorobenzene (120 mL) under argon atmosphere. After 24 h an additional quantity of *p-tert*-butylphenol (0.15g, 1 mmol) was added and the mixture heated for an additional 24 h. The dark resolution was evaporated in vacuum, and then the mixture was separated by column chromatography over silica gel (eluent: 1:10 ethyl acetate/petroleum ether) to afford **1** (0.19 g, 19%) and **2** (0.17 g, 17%). **1** and **2** could be further crystallized from CH_2Cl_2/petroleum ether. **1.** Mp: 300 > °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (s, 18H), 3.35 (d, J = 15.3 Hz, 4H), 3.91 (s, 12H), 4.25 (d, J = 15.3 Hz, 4H), 5.24 (s, 2H), 5.97 (s, 2H), 6.09 (s, 2H), 6.64 (d, J = 7.6 Hz, 4H), 6.88–6.97 (m, 8H), 7.08 (s, 4H), 7.28–7.40 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.9, 31.7, 33.9, 42.6, 53.7, 62.5, 119.9, 123.4, 123.6, 125.1, 125.2, 125.4, 126.5, 127.2, 130.0, 136.7, 141.9, 144.9, 145.8, 146.6, 150.2, 152.6. MALDI-TOF MS: *m/z* 999 $[M+Na]^+$, 1015 $[M+K]^+$. Anal. Calcd for $C_{68}H_{64}O_6 \cdot 1.5CH_2Cl_2 \cdot 0.5H_2O$: C 74.96, H 6.15; found: C 74.97, H 6.21. **2.** Mp: > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (s, 18H), 3.20 (s, 12H), 3.68 (d, J = 14.5 Hz, 4H), 3.87 (d, J = 14.5 Hz, 4H), 5.34 (s, 2H), 5.86 (s, 2H), 6.00 (s, 2H), 6.97 (m, 8H), 7.16–7.02 (m, 8H), 7.30–7.40 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.6, 32.6, 34.0, 42.5, 53.9, 61.9, 119.4, 123.4, 125.1, 125.3, 126.1, 127.3, 128.0, 130.9, 136.8, 143.0, 144.6, 146.3, 146.5, 150.5, 153.2. MALDI-TOF MS: *m/z* 999 $[M+Na]^+$, 1015 $[M+K]^+$. Anal. Calcd for $C_{68}H_{64}O_6 \cdot 0.5H_2O$: C 74.66, H 6.12; found: C 74.84, H 6.36.

2. Copies of ^{1}H NMR and ^{13}C NMR spectra of new compounds

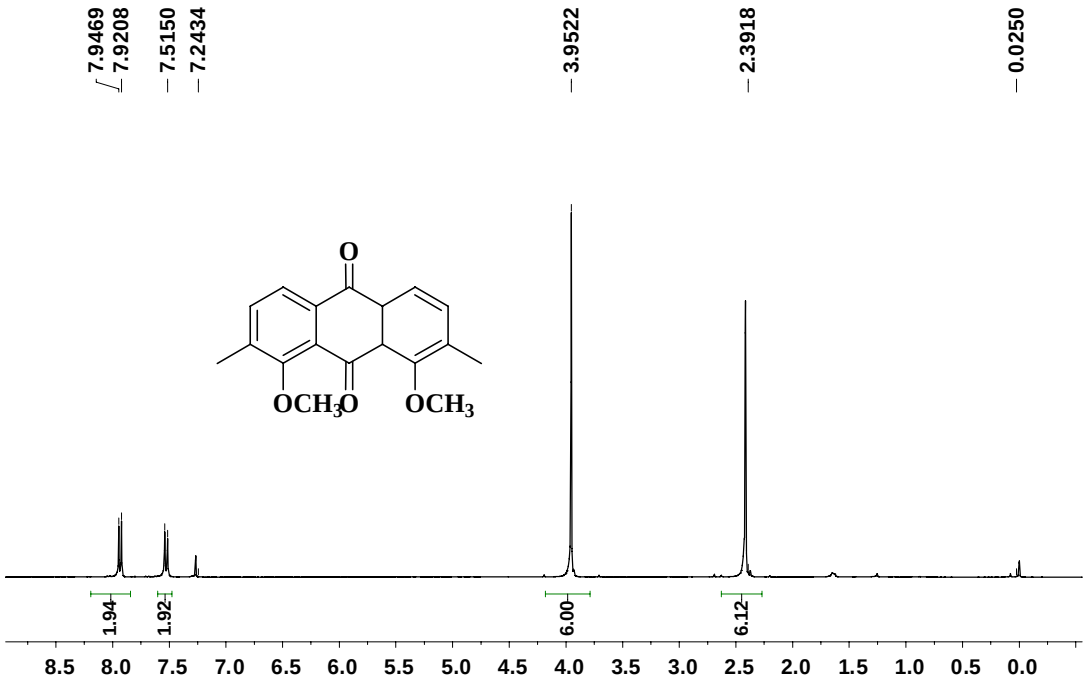


Figure S1. ^{1}H NMR spectrum ($CDCl_3$) of **5**.

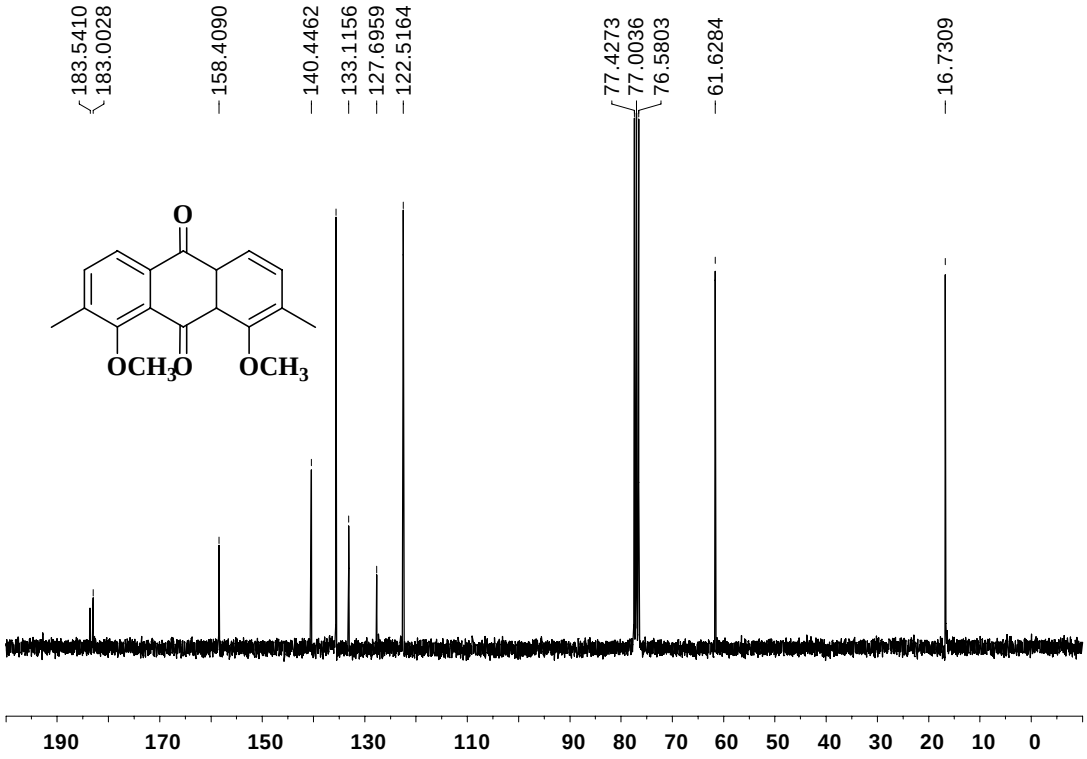


Figure S2. ^{13}C NMR spectrum ($CDCl_3$) of **5**.

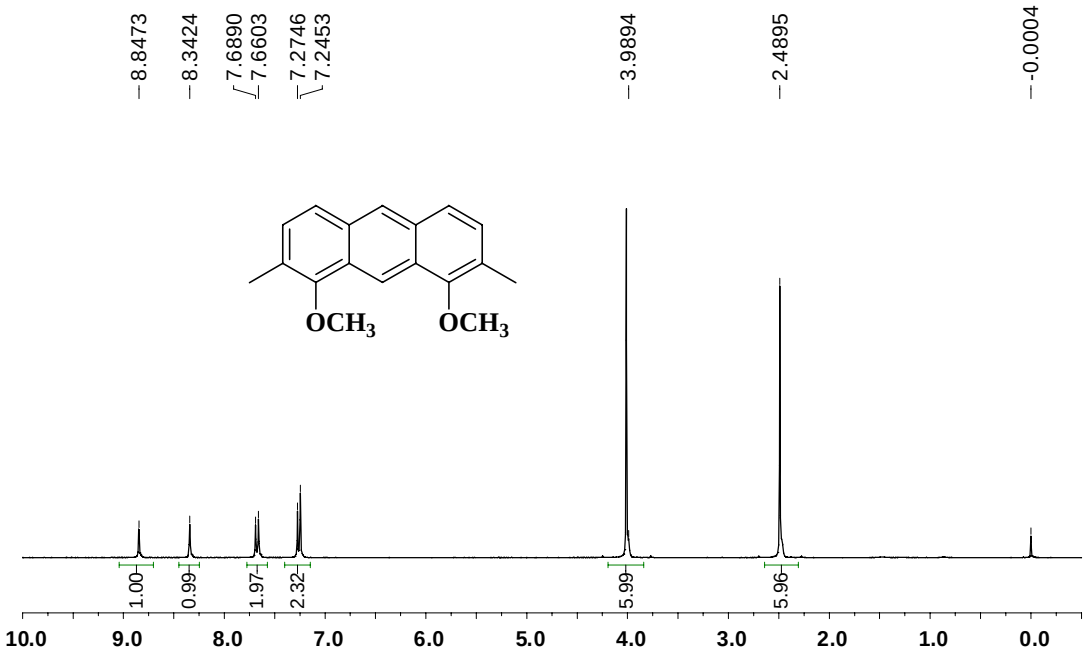


Figure S3. ^{1}H NMR spectrum ($CDCl_3$) of **6**.

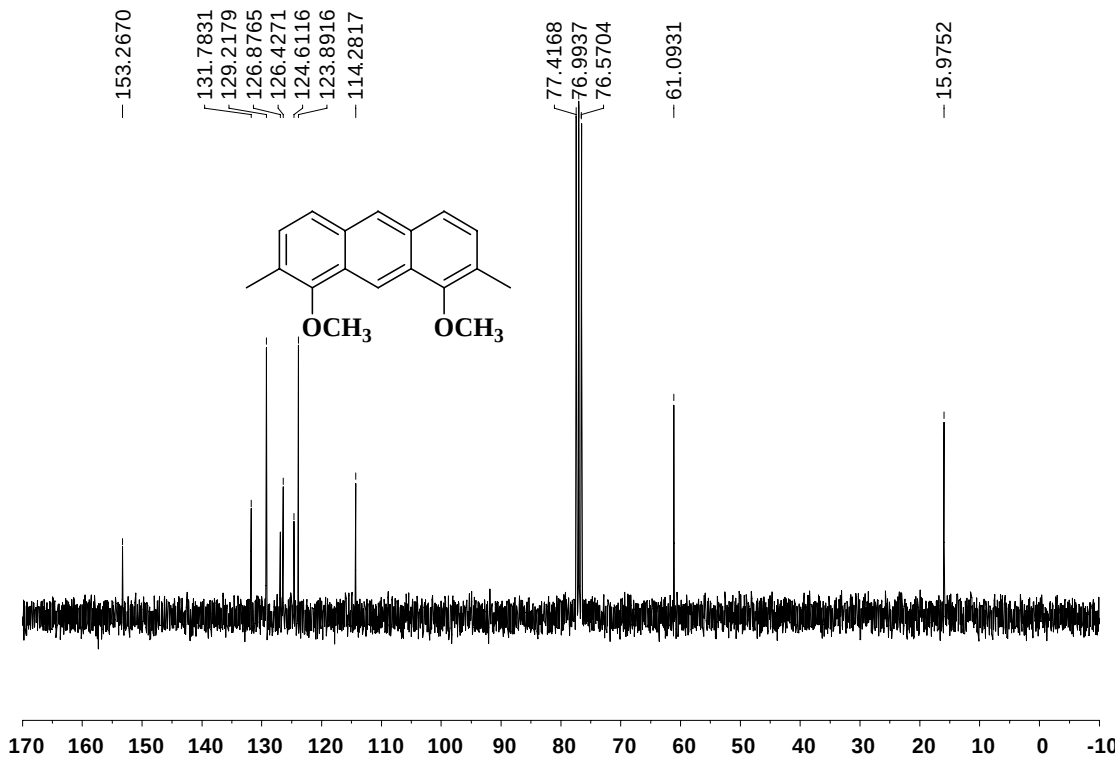


Figure S4. ^{13}C NMR spectrum ($CDCl_3$) of **6**.

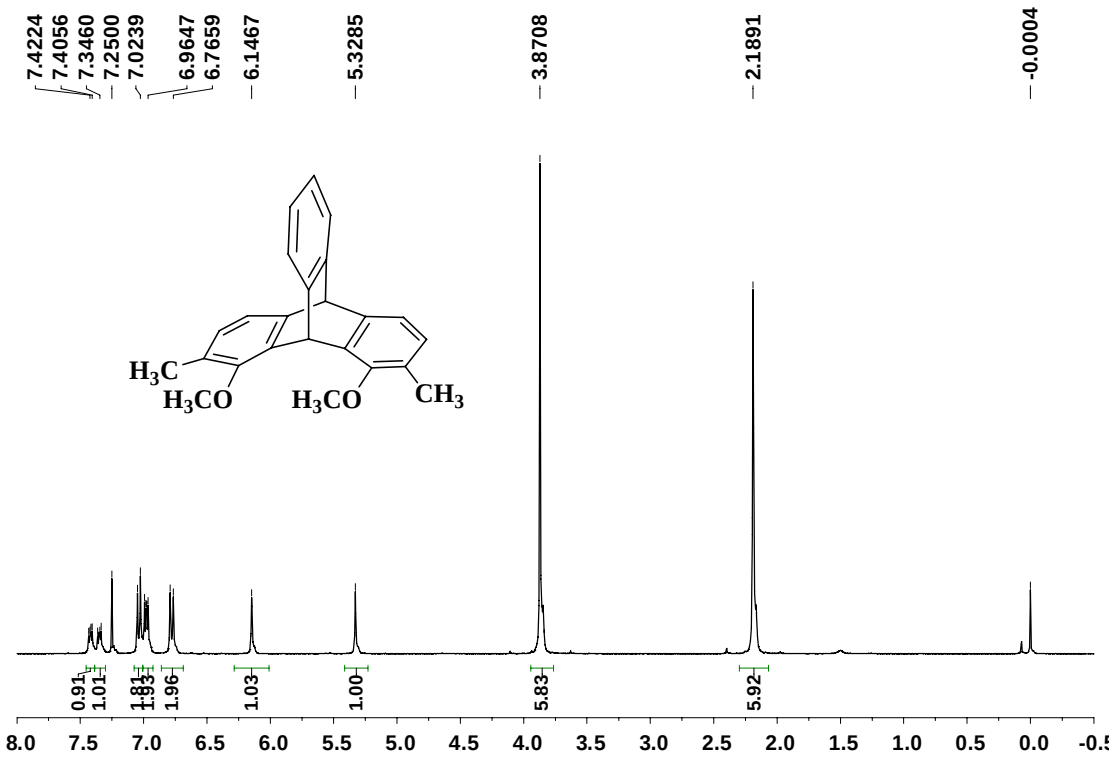


Figure S5. ^{1}H NMR spectrum ($CDCl_3$) of **7**.

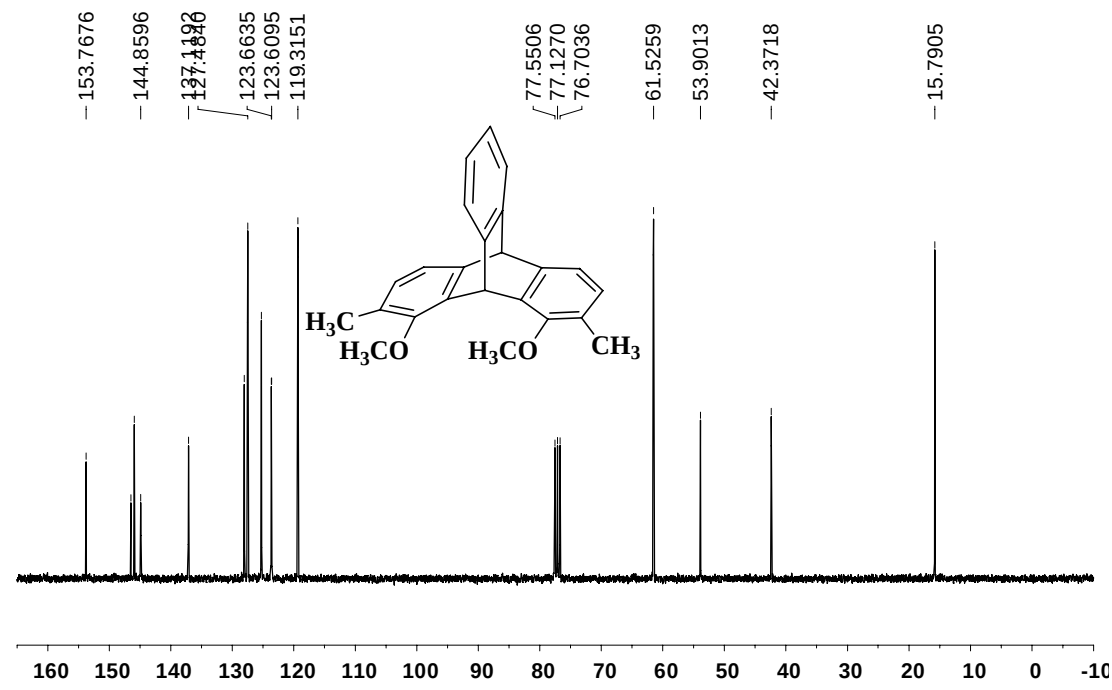


Figure S6. ^{13}C NMR spectrum ($CDCl_3$) of **7**.

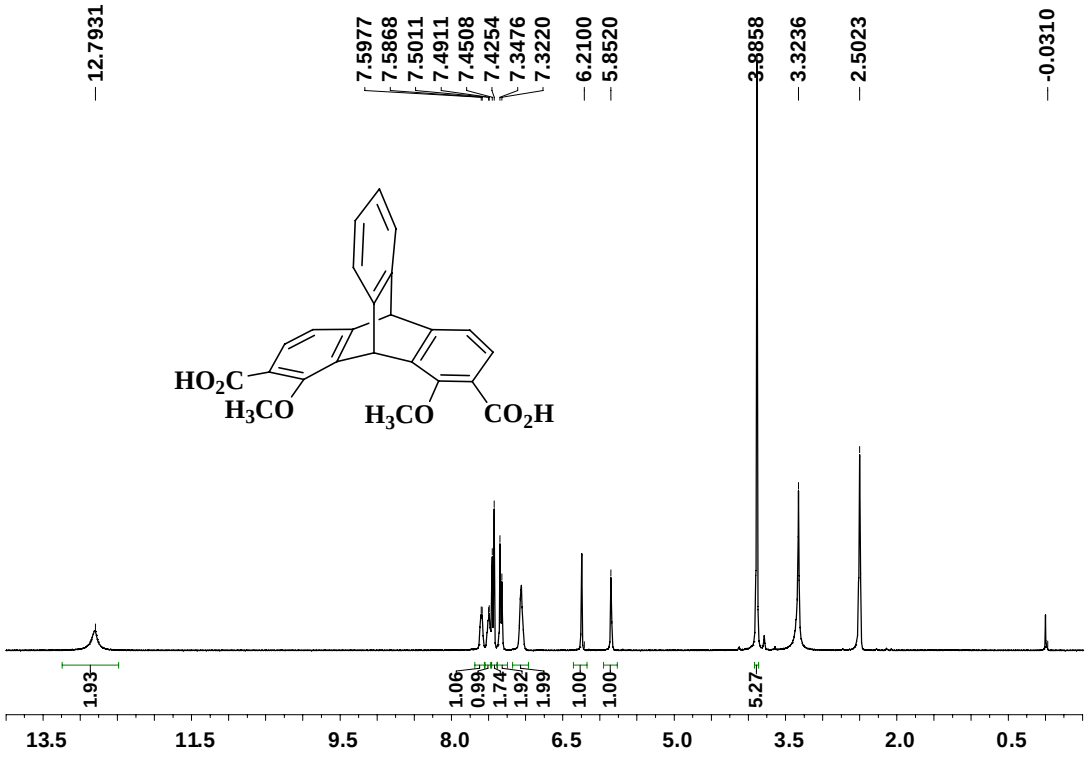


Figure S7. ^{1}H NMR spectrum ($CDCl_3$) of **8**.

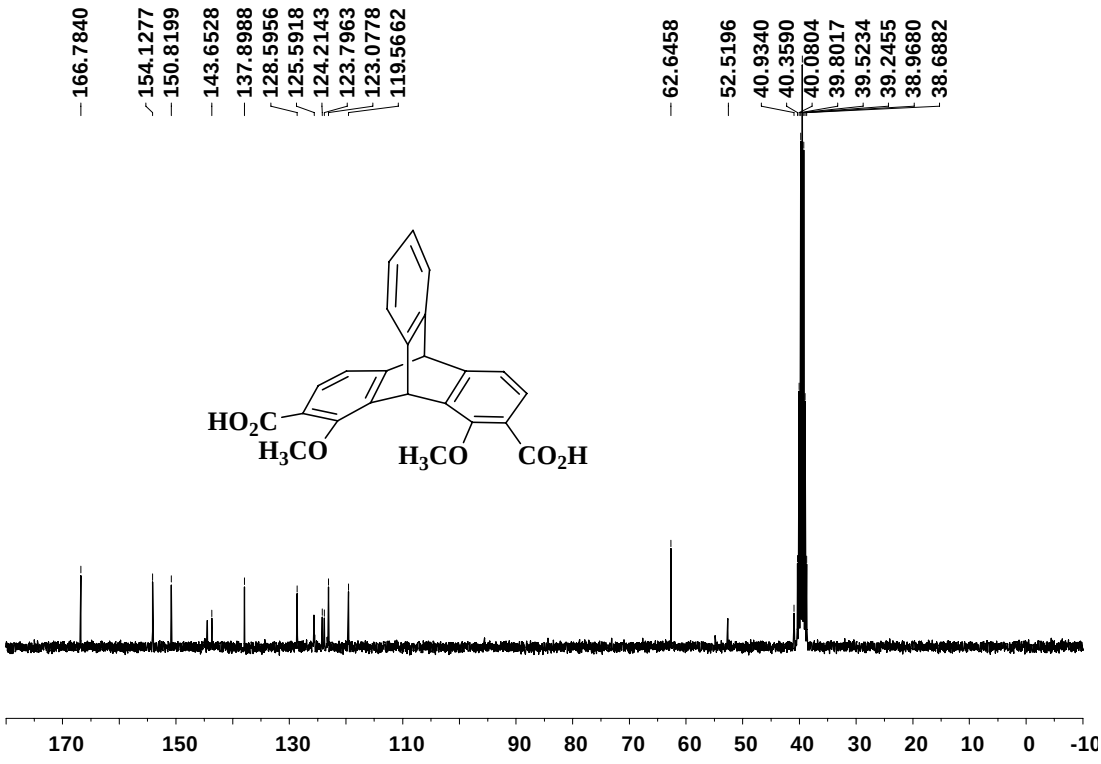


Figure S8. ^{1}H NMR spectrum ($CDCl_3$) of **8**.

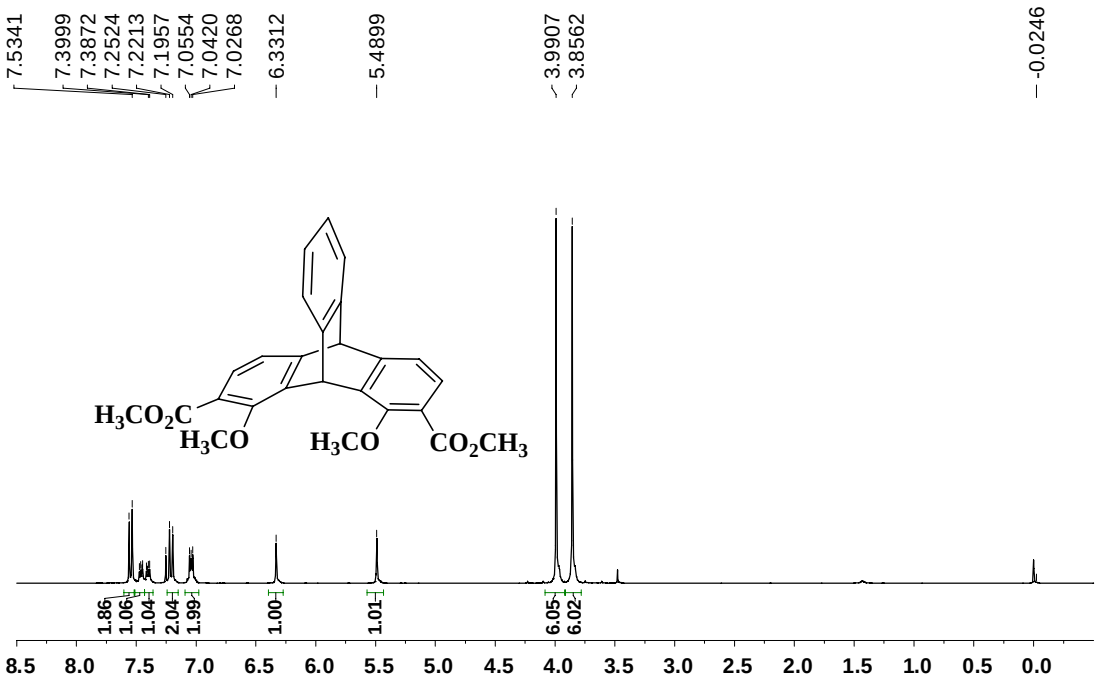


Figure S9. ^{13}C NMR spectrum ($CDCl_3$) of **9**.

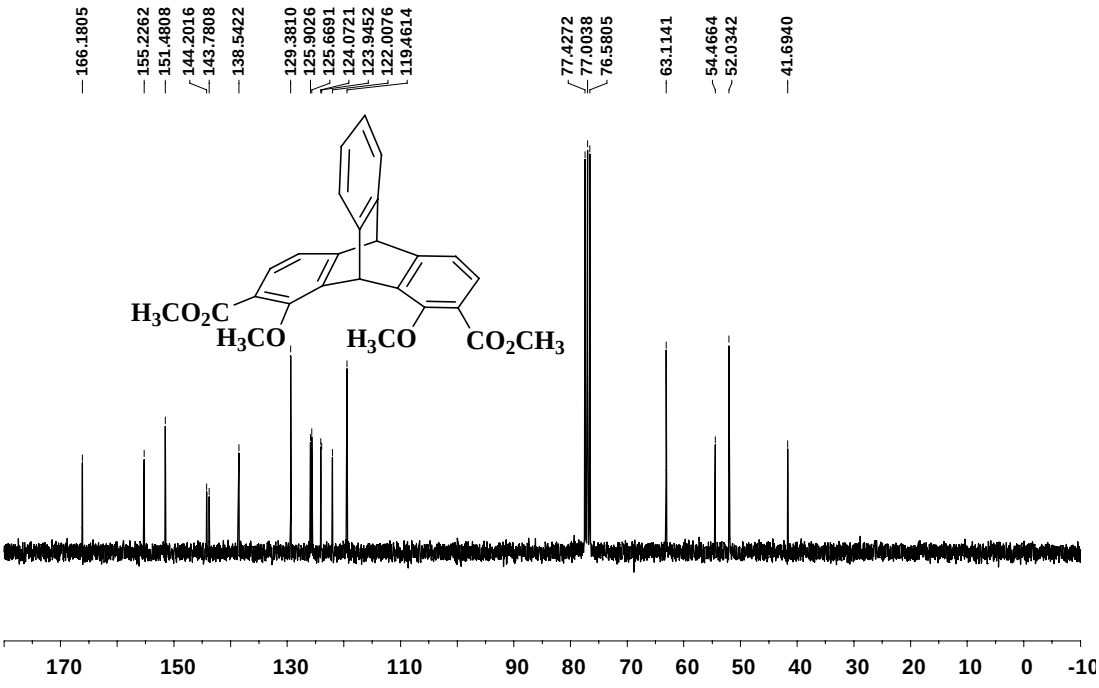


Figure S10. ^{13}C NMR spectrum ($CDCl_3$) of **9**.

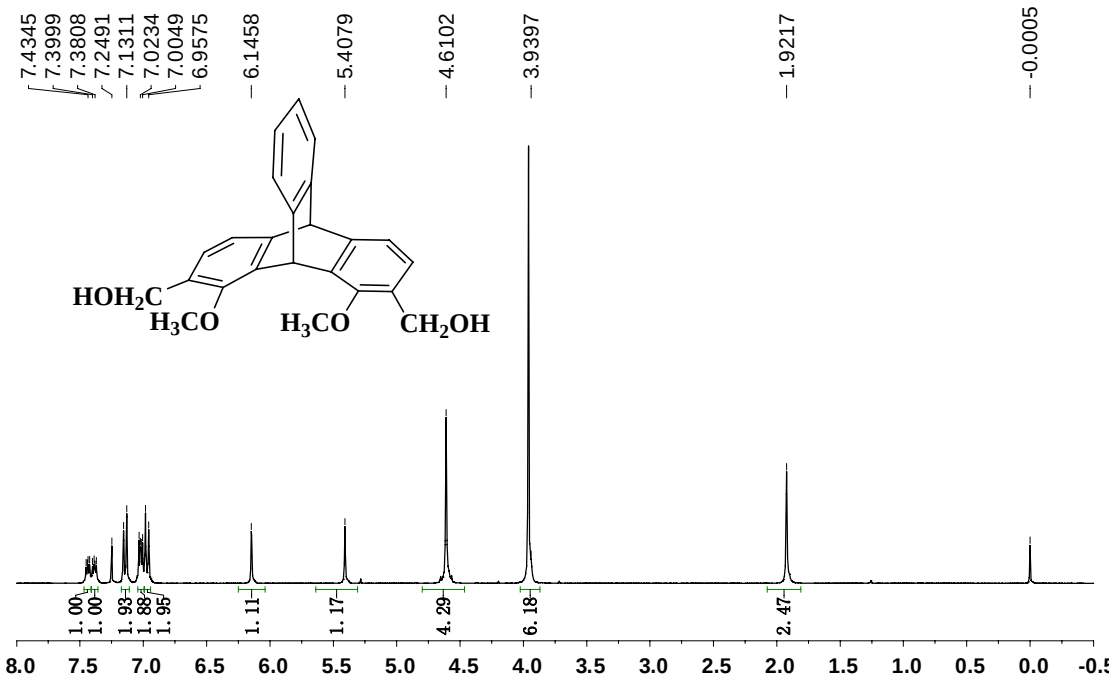


Figure S11. ^{1}H NMR spectrum ($CDCl_3$) of **3**

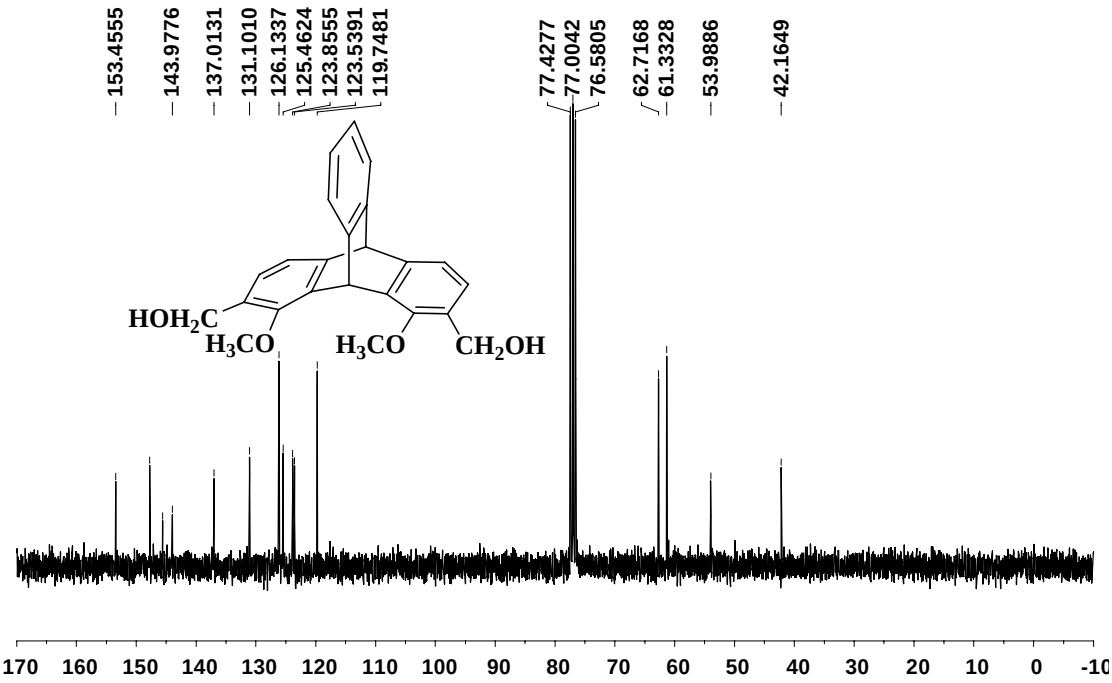


Figure S12. ^{13}C NMR spectrum ($CDCl_3$) of **3**

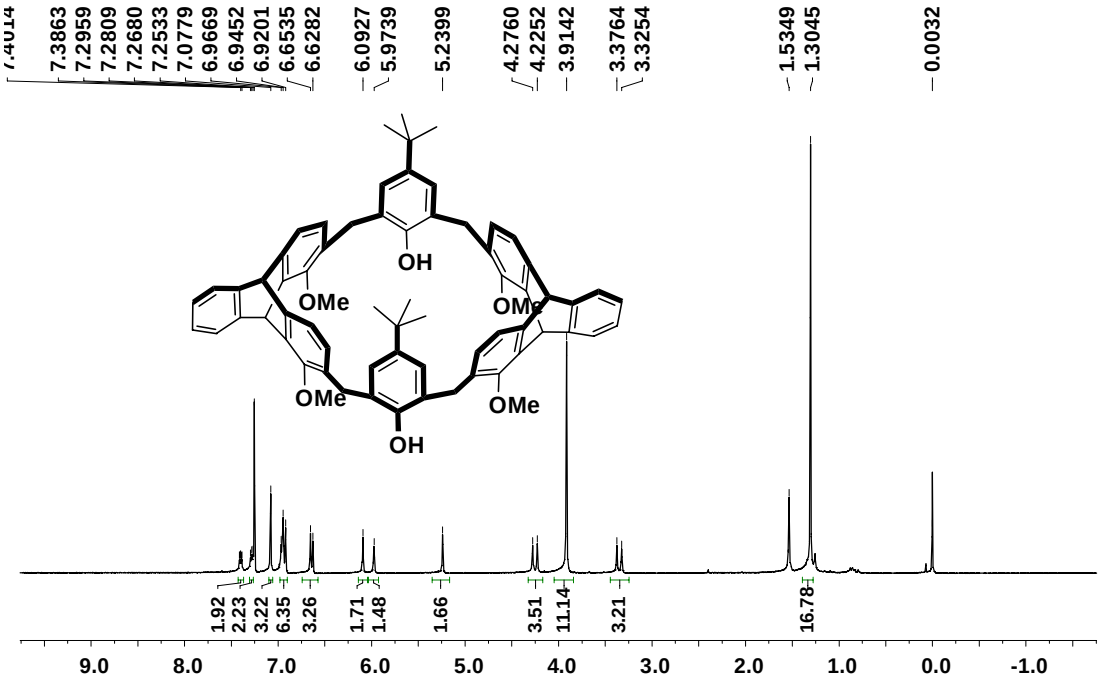


Figure S3. ^{1}H NMR spectrum ($CDCl_3$) of **1**

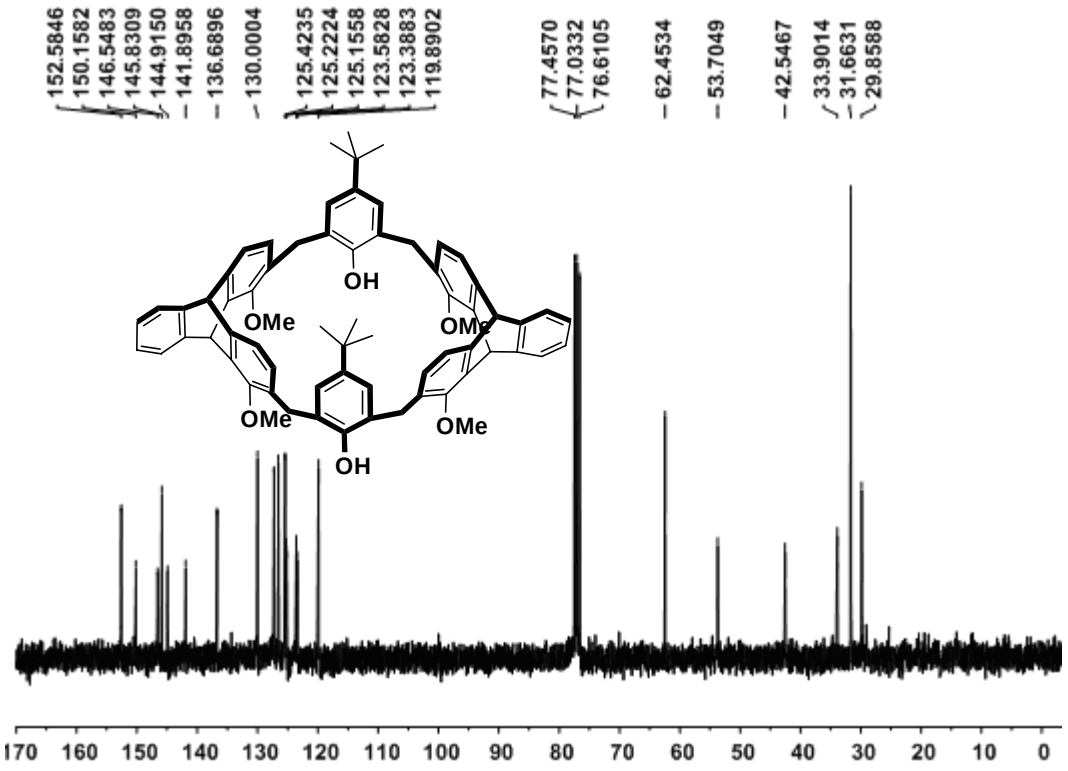


Figure S14. ^{13}C NMR spectrum ($CDCl_3$) of **1**.

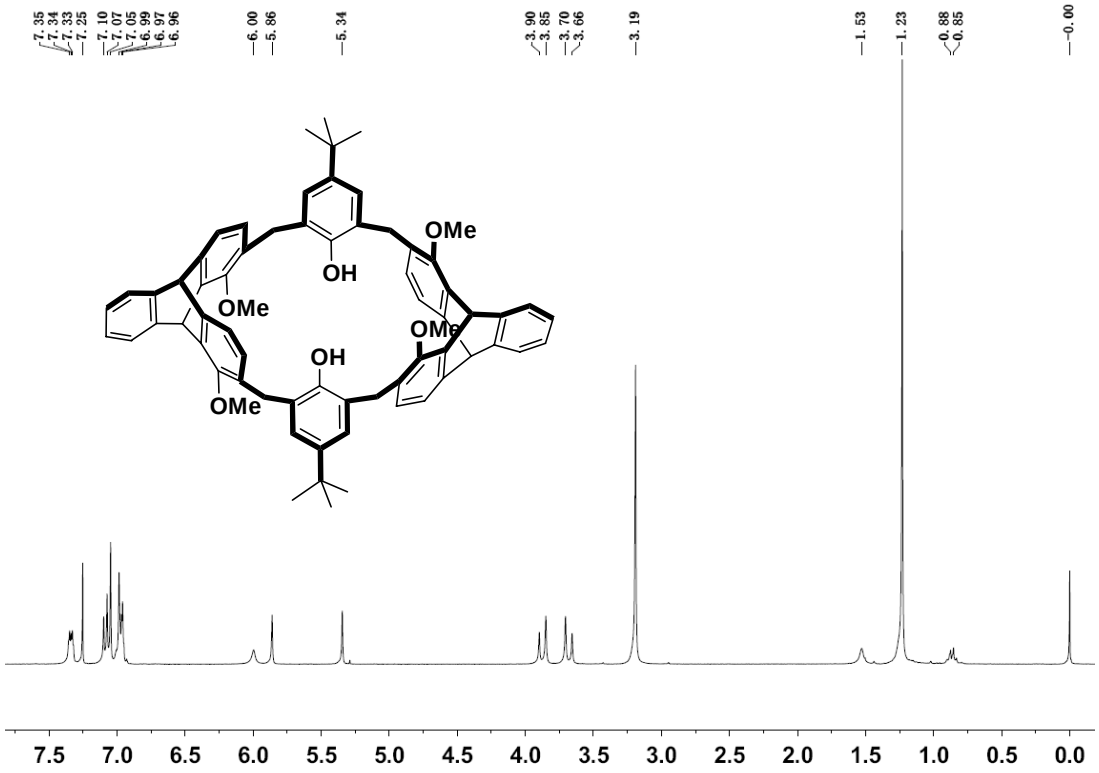


Figure S15. ^{1}H NMR spectrum ($CDCl_3$) of **2**

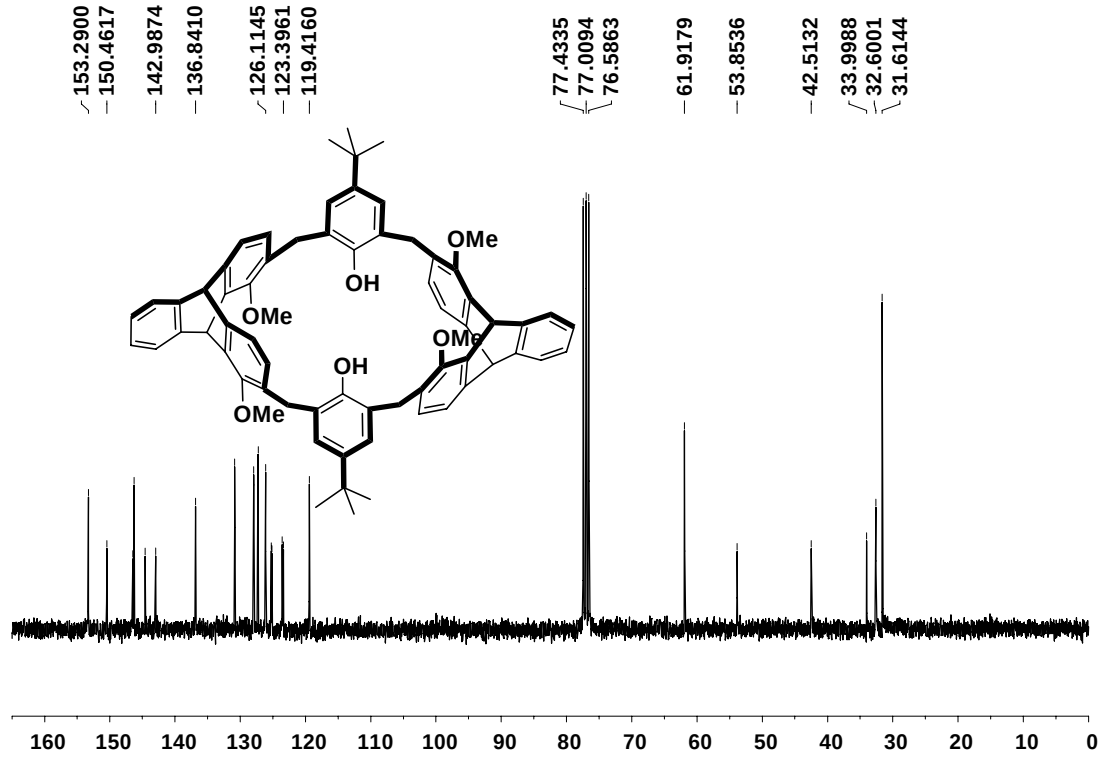


Figure S16. ^{13}C NMR spectrum ($CDCl_3$) of **2**.

3. ^{1}H-^{1}H COSY and ^{13}C-^{1}H COSY 2D NMR spectra of 1 and 2

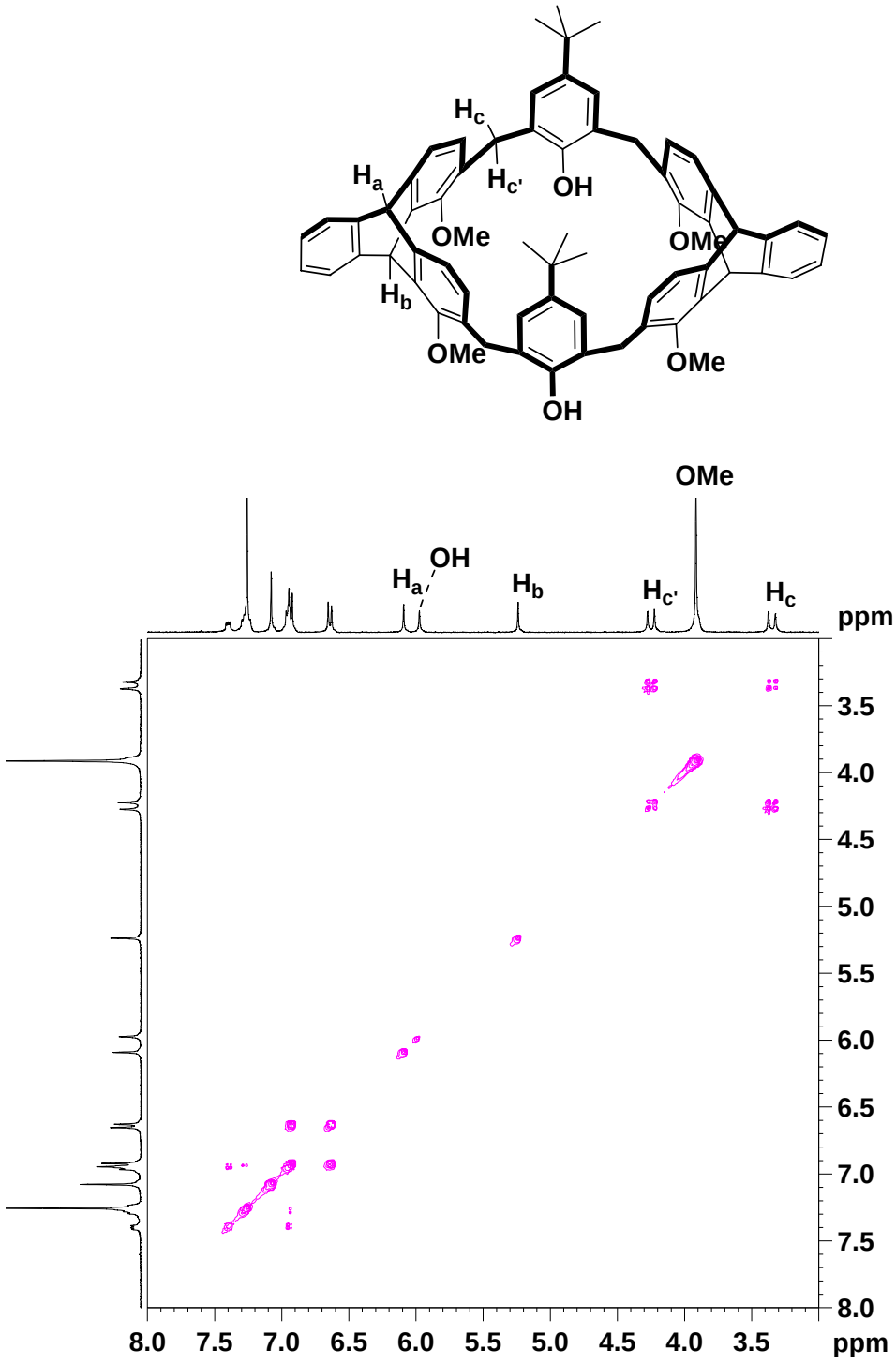


Figure S17. ^{1}H-^{1}H COSY spectrum of **1**.

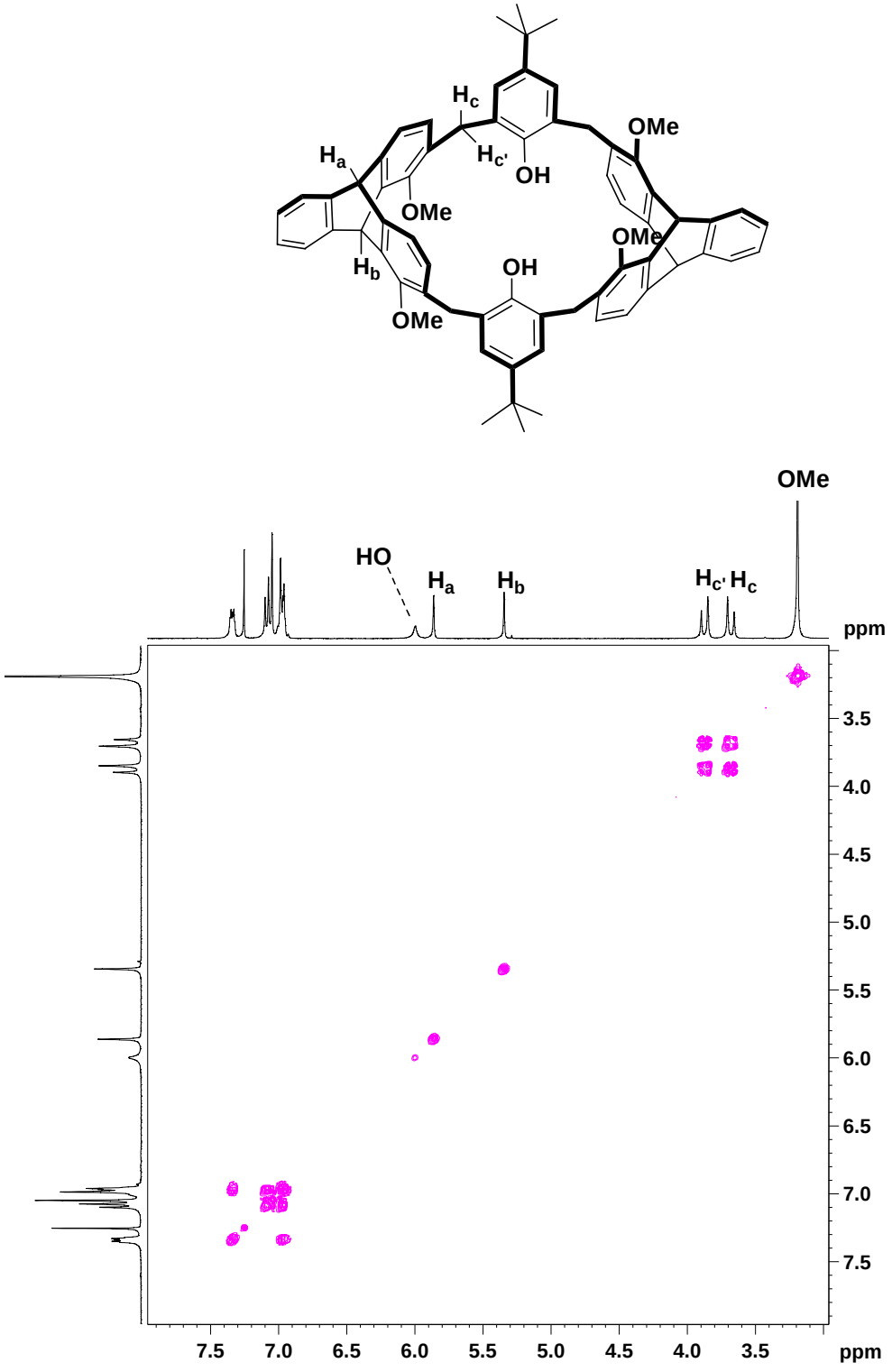


Figure S18. ^{1}H-^{1}H COSY spectrum of **2**.

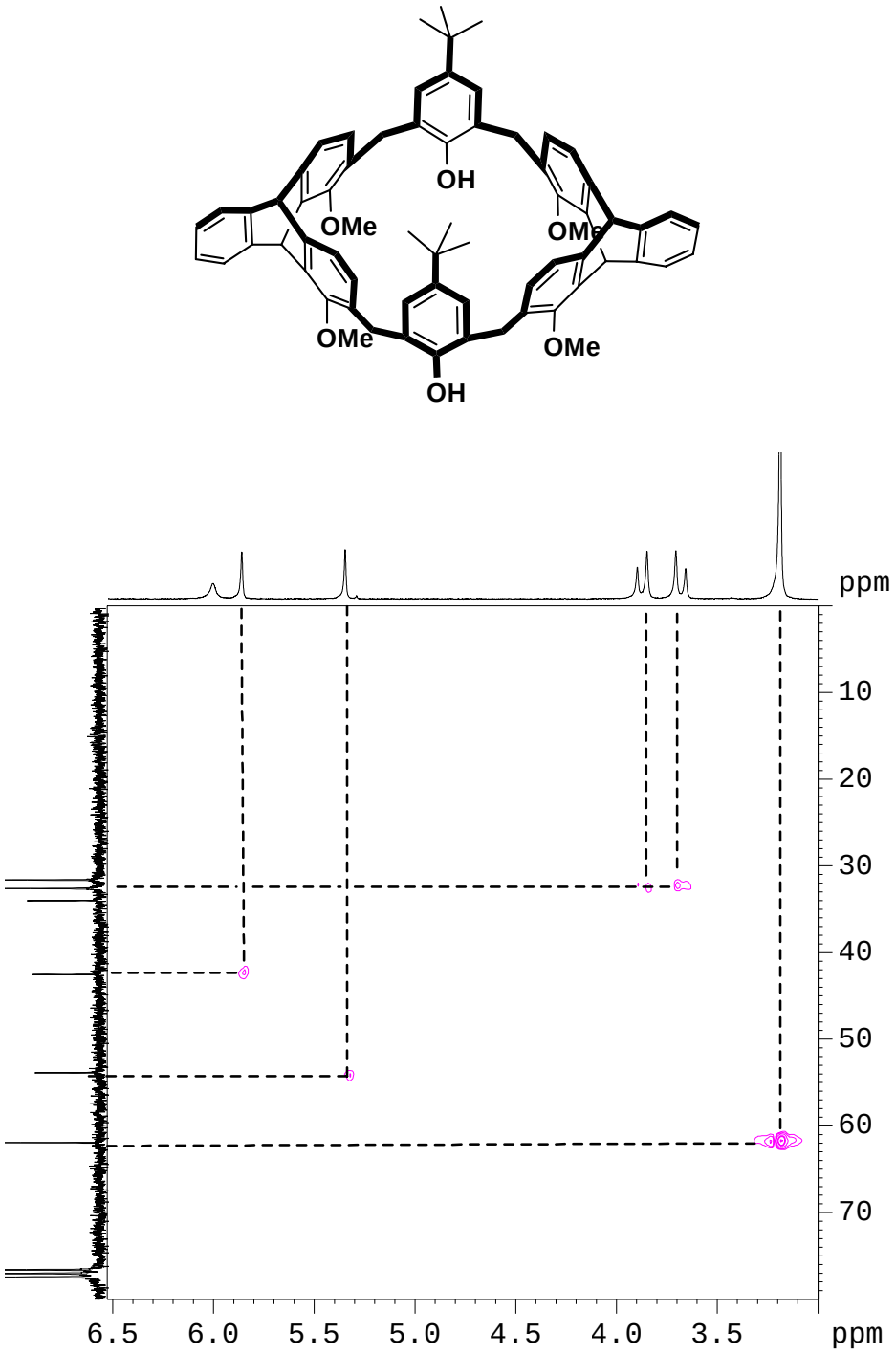


Figure S19. ^{13}C-^{1}H COSY spectrum of **1**.

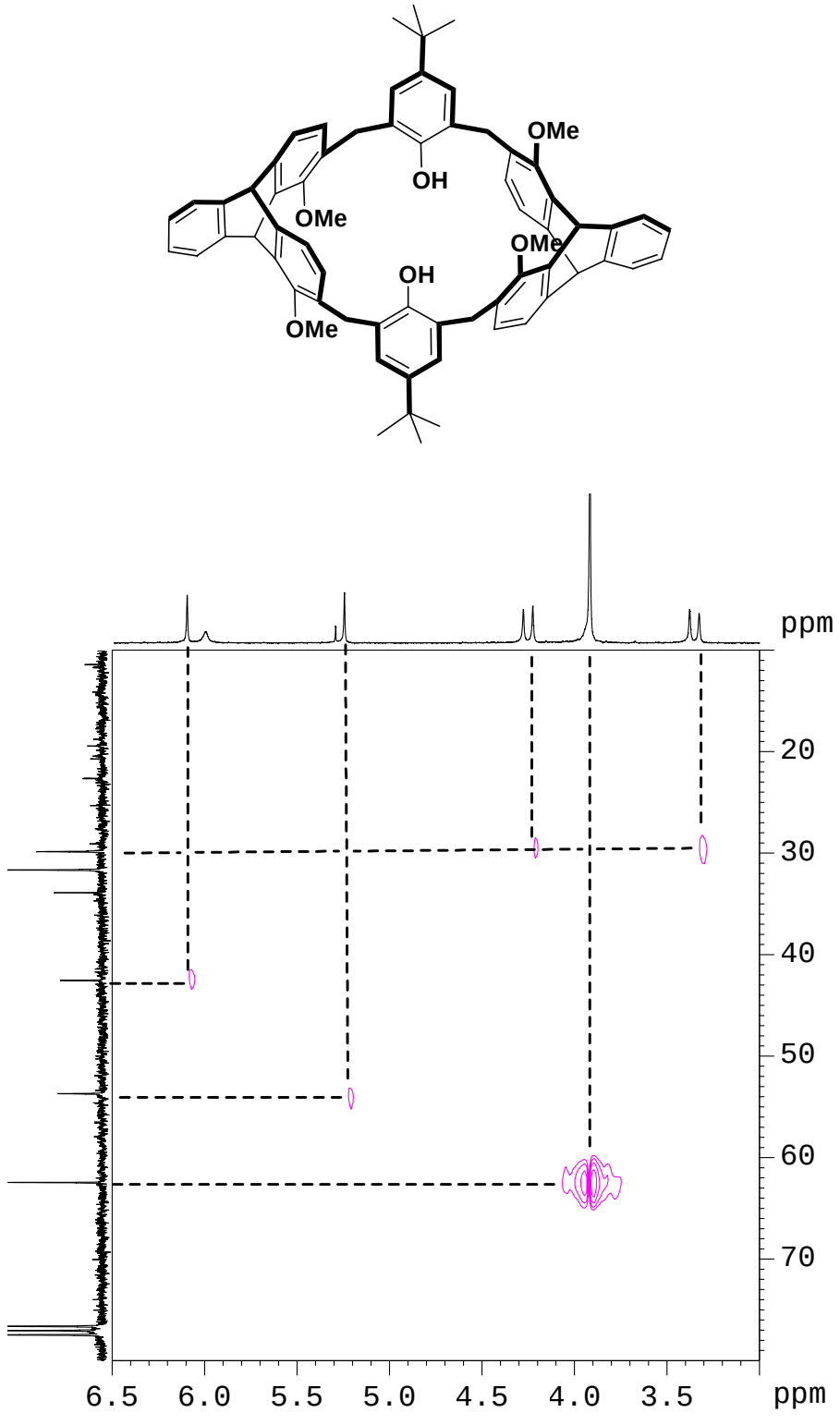


Figure S20. ^{13}C-^{1}H COSY spectrum of **2**.

4. X-ray crystal structures and packing of 1 and 2

The X-ray measurements were carried on a Saturn724+ CCD diffractometer with graphite-monochromator Mo-Kα radiation (λ = 0.71073 Å) at 173 K. Intensities were collected using CrystalClear (Rigaku Inc., 2008) technique and absorption effects were collected using the multi-scan technique. The structure of **1** was solved by direct methods and refined by a full matrix least squares technique based on F^2 using SHELXL 97 program. The structure of **2** was solved using SHELXS-97 (Sheldrick, 1990) program and refined by a full matrix least squares technique based on F^2 using SHELXL 97 program. Application of the restraints is for confining the thermal vibration parameters of the disordered solvent molecules, which can make them be isotropic. Because highly disordered solvent molecules were difficult to be determined, they were deleted with SQUEEZE program in the crystal structure of **1**. For **2**, the high *R*-factor and weighted *R*-factor might be mainly due to the solvent molecules which haven't been treated with SQUEEZE program.

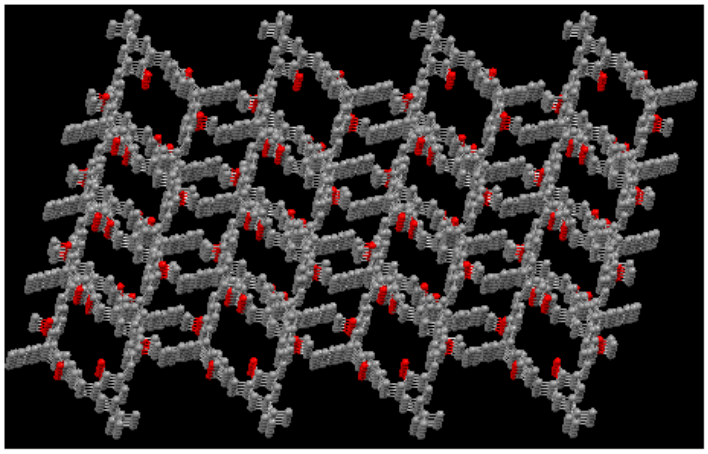


Figure S21. A 3D microporous structure of **1** viewed along the *b*-axis. Solvent molecules and hydrogen atoms were omitted for clarity.

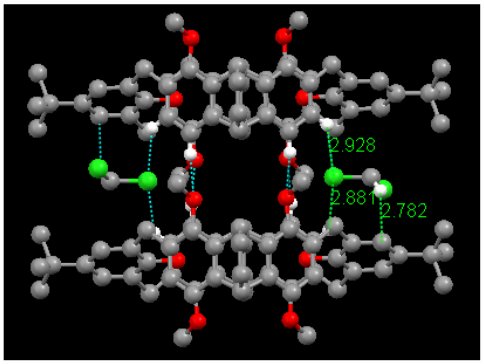


Figure S22. View of the non-covalent interactions between CH_2Cl_2 molecules and macrocycle **2** during the formation of the organic tube. Other solvent molecules and hydrogen atoms not involved in the interactions are omitted for clarity.

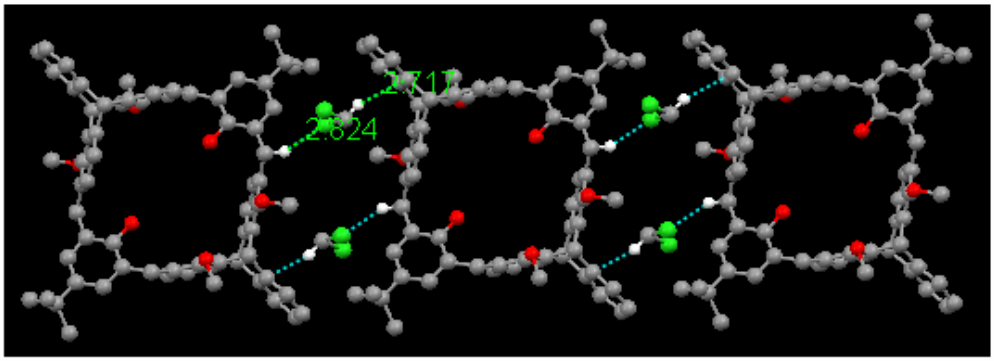


Figure S23. Packing of **2**. View of a 2D layer structure. Dashed lines denote the non-covalent interactions between the CH_2Cl_2 molecule and its adjacent macrocycles.

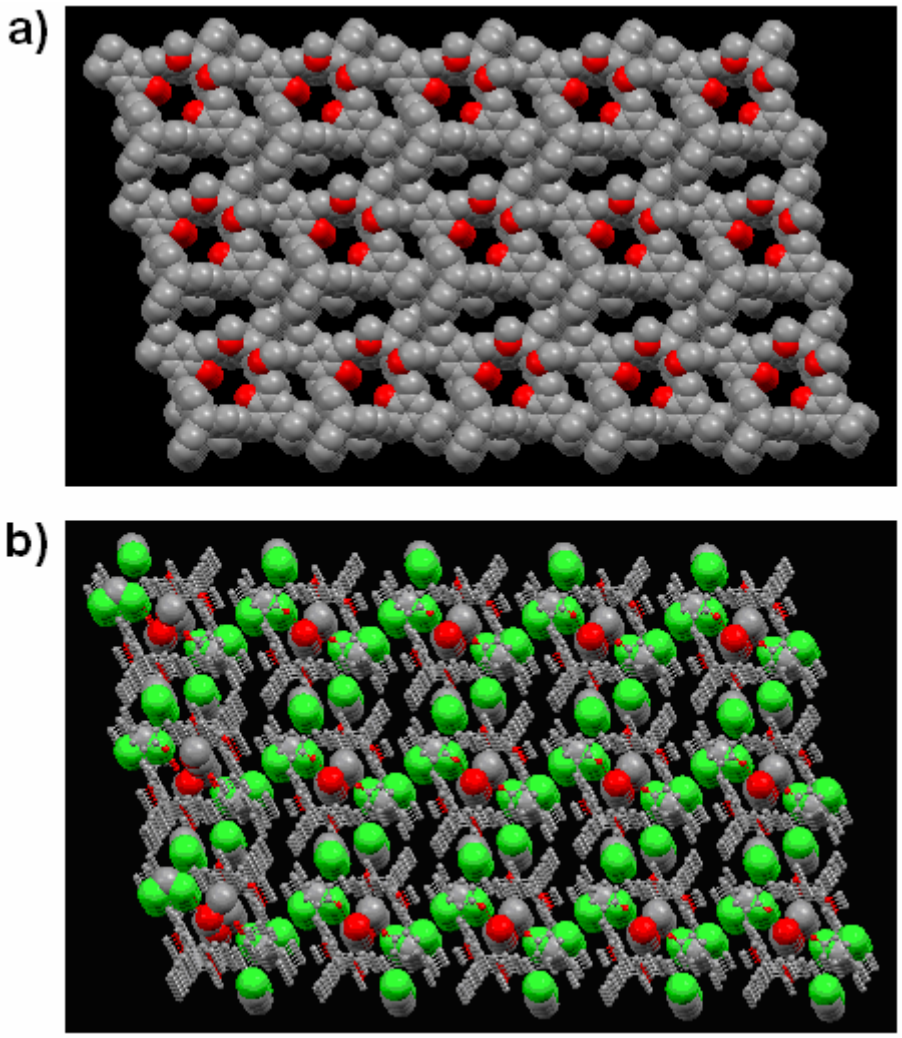


Figure S24. Packing of **2**. View of the 3D microporous structure (a) without the solvents, and (b) with the solvents situated in the different channels along the *a*-axis. Hydrogen atoms are omitted for clarity.