Electronic Supplementary Material (ESI) for ChemComm.

SUPPLEMENTARY INFORMATION

Rigid Tetraarylene-Bridged Cavitands from Reduced-Symmetry Resorcin[4]arene Derivatives

Jordan N. Smith and Nigel T. Lucas

MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Chemistry, University of Otago, Union Place, Dunedin 9016, New Zealand

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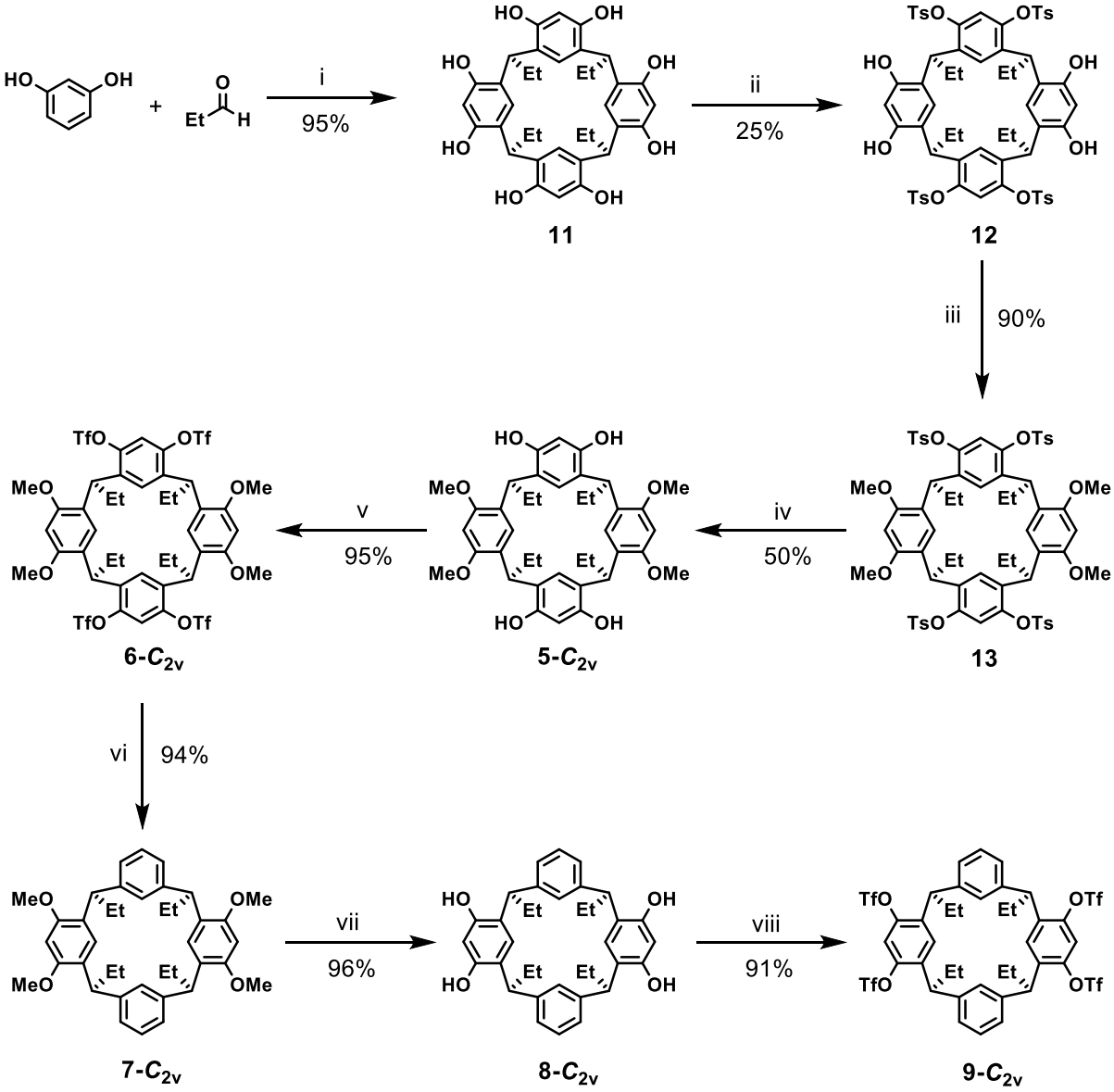
1. General

All commercially purchased starting materials were used as received unless otherwise noted. Solvents listed as "dry" were dried using a Pure-Solv MD-6 solvent purification system. All other solvents were LR grade unless otherwise noted. "Petrol" refers to the petroleum fraction boiling in the range 40–60 °C. Solvents were removed under "reduced pressure" by rotary evaporation. Standard Schlenk techniques were employed where an inert atmosphere of argon or nitrogen was required. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in 5 mm diameter tubes at 25 °C on a Varian 400 MR spectrometer (400, 100 and 376 MHz, respectively) or a Varian 500 AR spectrometer (500, 126 and 470 MHz, respectively). ^{1}H and ^{13}C NMR signals were referenced against residual non-perdeuterated solvents where applicable. All reported coupling constants (*J*) are in Hz. 2-Dimensional NMR spectra (COSY, NOESY, HSQC, HMBC) were recorded for all new compounds to assist in assignments. HR MS (ESI) mass spectra were recorded on a Bruker MicrOTOF-Q electrospray ionisation mass spectrometer. Elemental composition was measured on a Carlo Erba 1108 CHNS combustion analyser at the Campbell Microanalytical Laboratory, University of Otago, Dunedin with an absolute uncertainty of ±0.3%. UV-visible absorption and emission spectra were recorded on an Edinburgh Instruments FS5 spectrofluorometer in 10 mm quartz cells.

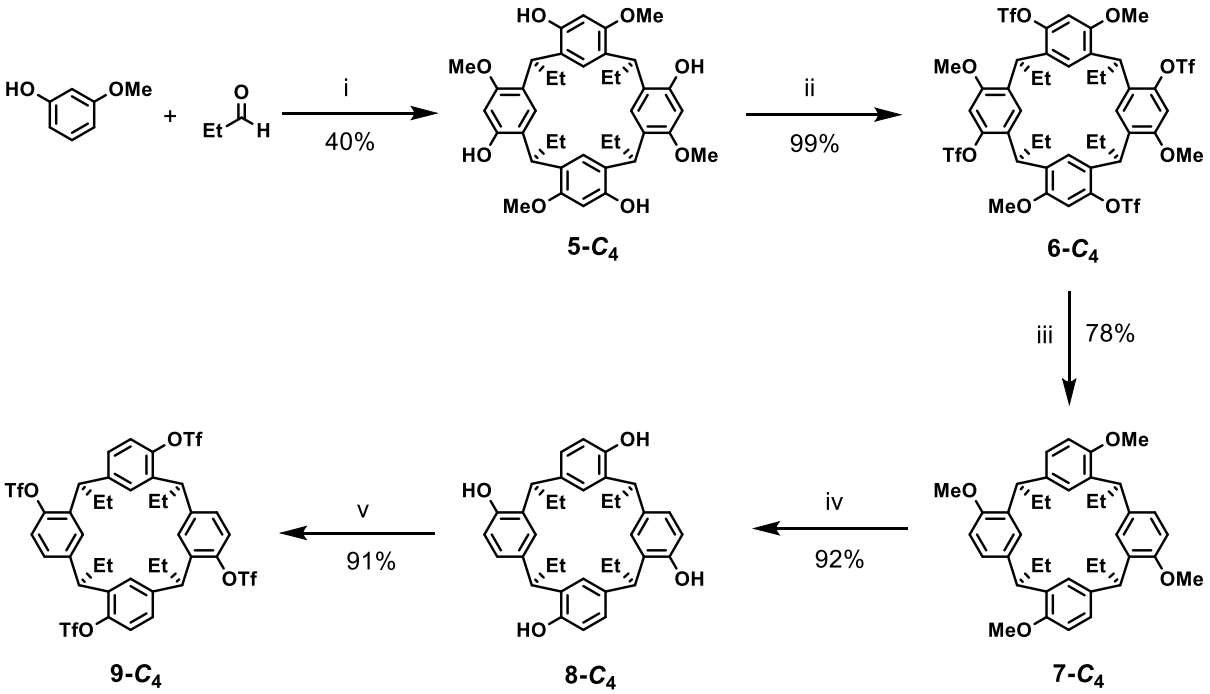
2. Synthesis

2.1 Precursor Synthesis

C_{2v}-symmetric compounds **11**, **12**, **13** and **5-C_{2v}** were prepared following literature procedures and were consistent with characterisation data as reported.[1] **5-C_4** was prepared via a modified literature procedure[2] and was consistent with characterisation data reported.[3]



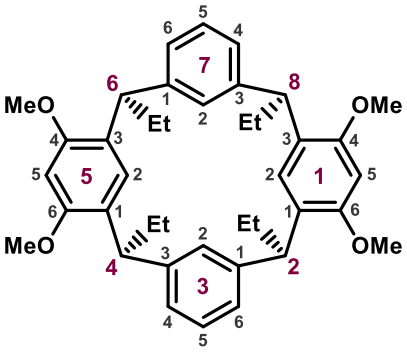
Scheme S1. Synthesis of **9-C_{2v}**. Reaction conditions: i. HCl, EtOH, 80 °C, 19 h; ii. TsCl, NEt_3, MeCN, 15 h, rt; iii. K_2CO_3, MeI, acetone, 70 °C, 19 h; iv. KOH, *n*-propanol, reflux, 21 h; v. Tf_2O, pyridine, CH_2Cl_2, 0 °C–rt, 16 h; vi. $Pd_2(dba)_3$, (±)-BINAP, NEt_3, formic acid, toluene, reflux, 48 h; vii. BBr_3, CH_2Cl_2, 0 °C–rt, 18 h; viii. Tf_2O, pyridine, CH_2Cl_2, 0 °C–rt, 16 h.



Scheme S2. Synthesis of **9-*C*$_4$**. Compounds **5-*C*$_4$**–**9-*C*$_4$** were prepared as racemates; one enantiomer is shown for clarity. Reaction conditions: i. $BF_3.Et_2O$, CH_2Cl_2, 2h, rt; ii. Tf_2O, pyridine, CH_2Cl_2, 0 °C–rt, 16 h; iii. $Pd_2(dba)_3$, (±)-BINAP, NEt_3, formic acid, toluene, reflux, 48 h; iv. BBr_3, CH_2Cl_2, 0 °C–rt, 18 h; v. Tf_2O, pyridine, CH_2Cl_2, 0 °C–rt, 16 h.

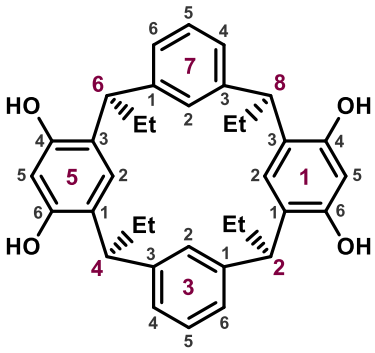
2.2 Synthetic Methods and Characterisation

2.2.1 2,4,6,8-Tetraethyl-*1⁴,1⁶,5⁴,5⁶*-tetramethoxy-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (**7-*C*$_{2v}$**)



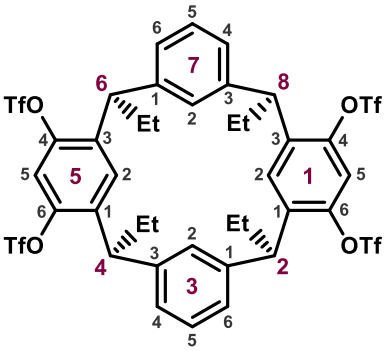
Tetratriflate **6-*C*$_{2v}$** (1.20 g, 1.01 mmol) was dissolved in toluene (20 mL) and deoxygenated with argon bubbling for 10 mins. Triethylamine (1.70 mL, 1.22 g, 12.0 mmol), tris(dibenzylideneacetone)palladium(0) (90 mg, 0.10 mmol), (±)-BINAP (125 mg, 0.2 mmol) and formic acid (0.45 mL, 550 mg, 12.0 mmol) were added and the mixture heated at reflux for 48 h. After cooling, the dark brown mixture was diluted with CH_2Cl_2, the organic phase washed with H_2O, dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The dark solid was purified by column chromatography (SiO_2, 50% CH_2Cl_2/petrol) affording **7-*C*$_{2v}$** as a white solid (555 mg, 0.94 mmol, 94%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.19–7.14 (m, 6H, Ar-*H*-3^4,3^5,3^6,7^4,7^5,7^6), 6.78 (s, 2H, Ar-*H*-1^2,5^2), 6.71 (s, 2H, Ar-*H*-3^2,7^2), 6.26 (s, 2H, Ar-*H*-1^5,5^5), 4.06 (t, *J* = 7.2 Hz, 4H, -C*H*), 3.70 (s, 12H, -OC*H*$_3$), 1.96–1.90 (m, 8H, -C*H*$_2$), 0.85 (t, *J* = 7.3 Hz, 12H, -C*H*$_3$). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 155.62 (Ar-*C*-1^4,1^6,5^4,5^6), 144.59 (Ar-*C*-3^1,3^3,7^1,7^3), 127.07 (Ar-*C*-3^5,7^5), 126.75 (Ar-*C*-3^2,7^2), 126.54 (Ar-*C*-3^4,3^6,7^4,7^6), 125.97 (Ar-*C*-1^1,1^3,5^1,5^3), 125.67 (Ar-*C*-1^2,5^2), 95.43 (Ar-*C*-1^5,5^5), 55.75 (-O*C*H$_3$), 44.62 (-*C*H), 28.04 (-*C*H$_2$-), 12.95 (-*C*H$_3$). HR-ESI-MS: calcd [M+Na]$^+$ ($C_{40}H_{48}O_4Na$) *m/z* 615.345; found 615.345. Anal. calcd [$C_{40}H_{48}O_4$·0.5H_2O·0.25$CHCl_3$]: C 77.59, H 8.01; found C 77.43, H 8.06.

2.2.2 2,4,6,8-Tetraethyl-*1⁴,1⁶,5⁴,5⁶*-tetrahydroxy-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (**8-*C*$_{2v}$**)



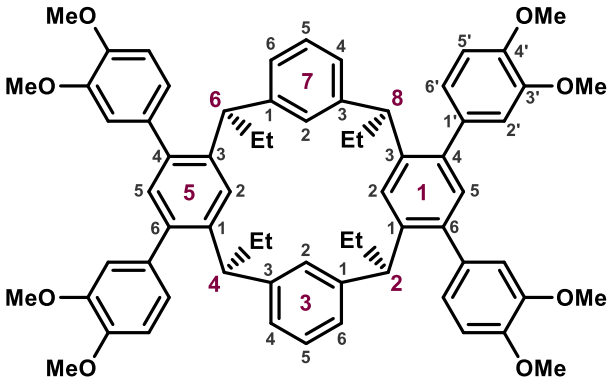
Tetramethoxy **7-*C*$_{2v}$** (555 mg, 0.94 mmol) was dissolved in dry CH_2Cl_2 (30 mL) under argon and the solution cooled in an ice-water bath. Boron tribromide (0.90 mL, 2.36 g, 9.40 mmol) was added dropwise and the resulting brown solution stirred cold for 30 min before allowing to warm to rt over 17 h. The reaction was quenched by the dropwise addition of methanol (5 mL) and diluted with CH_2Cl_2. The organic phase was washed with H_2O, aqueous NaCl (sat), dried over $MgSO_4$, filtered, and the solvents removed under reduced pressure affording **8-*C*$_{2v}$** as a white solid (485 mg, 0.90 mmol, 96%). ^{1}H-NMR (500 MHz, d_6-acetone): δ 7.74 (br s, 4H, -O*H*), 7.16 (d, *J* = 7.8 Hz, 4H, Ar-*H*-3^4,3^6,7^4,7^6), 7.08 (t, *J* = 7.8 Hz, 2H, Ar-*H*-3^5,7^5), 7.02 (m, 4H, Ar-*H*-1^2,3^2,5^2,7^2), 6.16 (s, 2H, Ar-*H*-1^5,5^5), 4.10 (t, *J* = 7.90 Hz, 4H, -C*H*), 2.02 (m, 8H, -C*H*$_2$-), 0.85 (t, *J* = 7.3 Hz, 12H, -C*H*$_3$). ^{13}C-NMR (126 MHz, d_6-acetone): δ 153.76 (Ar-*C*-1^4,1^6,5^4,5^6), 146.40 (Ar-*C*-3^1,3^3,7^1,7^3), 127.49 (Ar-*C*-3^4,3^6,7^4,7^6), 127.46 (Ar-*C*-3^5,7^5), 126.59 (Ar-*C*-3^2,7^2), 126.03 (Ar-*C*-1^2,5^2), 123.90 (Ar-*C*-1^1,1^3,5^1,5^3), 102.90 (Ar-*C*-1^5,5^5), 45.62 (-*C*H), 28.74 (-*C*H$_2$-), 13.19 (-*C*H$_3$). HR-ESI-MS: calcd [M+Na]$^+$ ($C_{36}H_{40}O_4Na$) *m/z* 559.282; found 559.281. Anal. calcd [$C_{36}H_{40}O_4$·Et$_2$O·0.5H_2O]: C 77.51, H 8.29; found C 77.40, H 8.10.

2.2.3 2,4,6,8-Tetraethyl-$1^4,1^6,5^4,5^6$-tetra(triflyloxy)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (**9-C_{2v}**)



Tetrol **8-C_{2v}** (440 mg, 0.82 mmol) was suspended in dry CH_2Cl_2 (20 mL) and the mixture cooled in an ice water bath under an argon atmosphere. Pyridine (1.59 mL, 19.7 mmol) was added before the dropwise addition of triflic anhydride (0.83 mL, 1.40 g, 4.92 mmol). The resulting yellow solution was stirred cold for 30 min before allowing to warm to rt over 18 h. The reaction was quenched with HCl (5 M, 15 mL) with vigorous stirring, washed with water and then brine. The organic phase was dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, 25% CH_2Cl_2/petrol) affording **9-C_{2v}** as a white solid (798 mg, 91%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.36–7.33 (m, 2H, Ar-*H*-3^5,7^5), 7.26–7.24 (m, 4H, Ar-*H*-3^4,3^6,7^4,7^6), 7.07 (s, 2H, Ar-*H*-1^5,5^5), 6.91 (s, 2H, Ar-*H*-1^2,5^2), 6.28 (s, 2H, Ar-*H*-3^2,7^2), 4.08 (t, *J* = 7.6 Hz, 4H, -C*H*), 1.99–1.87 (m, 8H, -CH_2), 0.92 (t, *J* = 7.0 Hz, 12H, -CH_3). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 145.20 (Ar-*C*-1^4,1^6,5^4,5^6), 142.48 (Ar-*C*-3^1,3^3,7^1,7^3), 138.22 (Ar-*C*-1^1,1^3,5^1,5^3), 128.92 (Ar-*C*-1^2,5^2), 128.65 (Ar-*C*-3^5,7^5), 127.36 (Ar-*C*-3^2,7^2), 126.90 (Ar-*C*-3^4,3^6,7^4,7^6), 118.52 (q, J_{CF} = 320 Hz, -OTf), 114.68 (Ar-*C*-1^5,5^5), 45.57 (-*C*H), 27.97 (-*C*H_2-), 12.43 (-*C*H_3). ^{19}F-NMR (470 MHz, $CDCl_3$): δ –74.0 (s, -OTf). HR-ESI-MS: calcd [M+Na]$^+$ ($C_{40}H_{36}F_{12}O_{12}S_4Na$) *m/z* 1087.079; found 1087.081. Anal. calcd [$C_{40}H_{36}F_{12}O_{12}S_4$·0.2$CH_2Cl_2$]: C 44.35, H 3.35; found C 44.31, H 3.32.

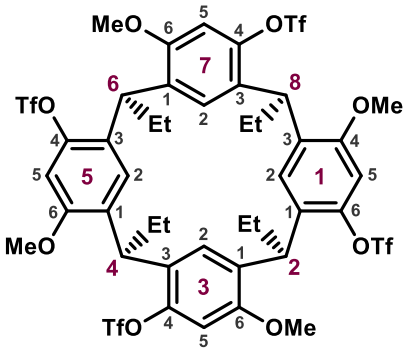
2.2.4 2,4,6,8-Tetraethyl-$1^4,1^6,5^4,5^6$-tetra(3',4'-dimethoxyphenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (**2-C_{2v}**)



Tetratriflate **9-C_{2v}** (400 mg, 0.38 mmol), 3,4-dimethoxyphenyl boronic acid (692 mg, 3.76 mmol) and cesium carbonate (2.45 g, 7.52 mmol) were suspended in toluene (15 mL), water (7 mL) and *n*-propanol (1 mL), and the mixture deoxygenated with gentle argon bubbling for 10 min. Dichloro[1,1'-bis(diphenylphosphino)ferrocene] palladium(II) (27 mg, 0.038 mmol) was added and the mixture heated at 70 °C for 48 h with vigorous stirring. After cooling, the dark mixture was diluted with CH_2Cl_2, the organic phase washed with water, brine, then dried over $MgSO_4$ and the solvents removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, 2% acetone/CH_2Cl_2) affording **2-C_{2v}** as a white solid (295 mg, 0.29 mmol, 76%). Crystals suitable for X-ray diffraction were grown by the layered diffusion of MeOH into a $CHCl_3$ solution of **2-C_4**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.25 (s, 2H, Ar-*H*-1^2,5^2), 7.04 (s, 2H, Ar-*H*-3^2,7^2), 6.99–6.96 (m, 4H, Ar-*H*-1^5,3^5,5^5,7^5), 6.83 (d, *J* = 8.1 Hz, 4H, Ph-*H*$_{5'}$), 6.76–6.74 (m, 8H, Ph-*H*$_{2',6'}$), 6.66 (dd, *J* = 7.7, 1.7 Hz, 4H, Ar-*H*-3^4,3^6,7^4,7^6), 4.01 (t, *J* = 7.7 Hz, 4H, -C*H*), 3.92 (s, 12H, C$_{4'}$-OCH_3), 3.77 (s, 12H, C$_{3'}$-OCH_3), 1.99 (quin, *J* = 7.2 Hz, 8H, -CH_2-), 0.80 (t, *J* = 7.2 Hz, 12H, -CH_3). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 148.35 (Ph-*C*$_{3'}$), 148.06 (Ph-*C*$_4$), 145.34 (Ar-*C*-3^1,3^3,7^1,7^3), 141.60 (Ar-*C*-1^1,1^3,5^1,5^3), 139.52 (Ar-*C*-1^4,1^6,5^4,5^6), 134.54 (Ph-*C*$_{1'}$), 131.86 (Ar-*C*-3^2,7^2), 127.41 (Ar-*C*-3^5,7^5), 127.00 (Ar-*C*-3^4,3^6,7^4,7^6) 126.07 (Ar-*C*-1^5,5^5), 125.68 (Ar-*C*-1^2,5^2), 122.20 (P*C*$_{6'}$), 113.64 (Ph-*C*$_{2'}$), 110.75 (Ph-*C*$_{5'}$), 56.05 (C$_{4'}$-O*C*H$_3$), 56.01 (C$_{3'}$-O*C*H$_3$), 48.60 (-*C*H), 29.92 (-*C*H_2-), 12.96 (-*C*H_3). HR-ESI-MS: calcd [M+Na]$^+$

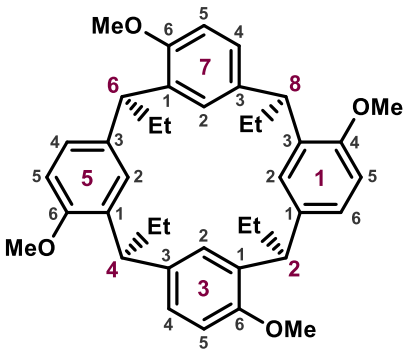
($C_{68}H_{72}O_8Na$) *m/z* 1039.512; found 1039.511. Anal. calcd [$C_{68}H_{72}O_8$·0.75MeOH]: C 79.30, H 7.26; found C 79.18, H 7.54. $\lambda_{max}(CH_2Cl_2)$/nm 250 (ε/dm^3 mol^{-1} cm^{-1} 98000).

2.2.5 *rac*-2,4,6,8-Tetraethyl-*1^4,3^6,5^6,7^6*-tetramethoxy-*1^6,3^4,5^4,7^4*-tetra(triflyloxy)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (**6-*C*$_4$**)



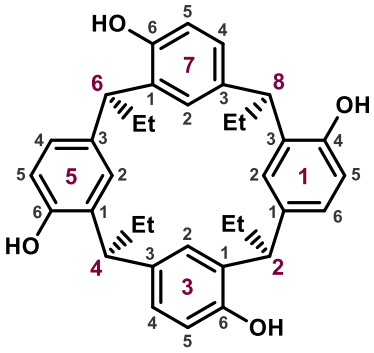
Tetrol **5-*C*$_4$** (1.00 g, 1.52 mmol) was dissolved in dry CH_2Cl_2 (20 mL), pyridine (2.95 mL, 36.5 mmol) added and the solution cooled on an ice-water bath under an argon atmosphere. Triflic anhydride (1.53 mL, 2.58 g, 9.14 mmol) was added dropwise and the resulting light-purple solution stirred cold for 30 min before allowing to warm to rt overnight. The reaction was quenched by the dropwise addition of aqueous HCl (5 M, 10 mL) with vigorous stirring, washed twice with water and then brine, dried over $MgSO_4$ and filtered. The removal of solvents under reduced pressure afforded **6-*C*$_4$** as an off-white solid (1.80 g, 1.51 mmol, 99%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.79 (s, 4H, Ar-*H*-1^2,3^2,5^2,7^2), 6.61 (s, 4H, Ar-*H*-1^5,3^5,5^5,7^5), 4.41 (dd, *J* = 8.3, 6.8 Hz, 4H, -C*H*), 3.68 (s, 12H, -OCH_3), 1.98 (m, 4H, -CH_2-), 1.84 (m, 4H, -CH_2-), 0.93 (s, 12H, -CH_3). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 156.16 (Ar-*C*-1^4,3^6,5^6,7^6), 147.14 (Ar-*C*-1^6,3^4,5^4,7^4), 131.96 (Ar-*C*-1^3,3^1,5^1,7^1), 127.03 (Ar-*C*-1^1,3^3,5^3,7^3), 126.63 (Ar-*C*-1^2,3^2,5^2,7^2), 118.61 (q, J_{CF} = 320 Hz, -OTf), 103.41 (Ar-*C*-1^5,3^5,5^5,7^5), 55.49 (-O*C*H$_3$), 37.78 (-*C*H), 27.99 (-*C*H$_2$-), 12.40 (-*C*H$_3$). ^{19}F-NMR (470 MHz, $CDCl_3$): δ –74.6 (s, -OTf). HR-ESI-MS: calcd [M+Na]$^+$ ($C_{44}H_{44}F_{12}O_{16}S_4Na$) *m/z* 1207.121; found 1207.120. Anal. calcd [$C_{44}H_{44}F_{12}O_{16}S_4$]: C 44.60, H 3.74; found C 44.64, H 3.69.

2.2.6 *rac*-2,4,6,8-Tetraethyl-*1^4,3^6,5^6,7^6*-tetramethoxy-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (**7-*C*$_4$**)



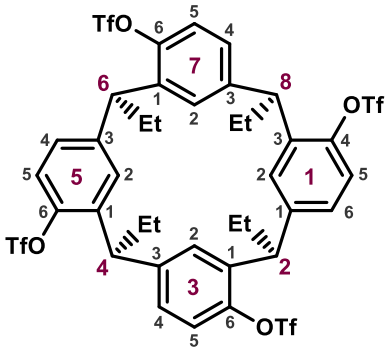
Tetratriflate **6-*C*$_4$** (2.50 g, 2.11 mmol) was dissolved in toluene (30 mL) and triethylamine (3.50 mL, 25.3 mmol) under an argon atmosphere and the solution deoxygenated with gentle argon bubbling for 15 min. Formic acid (0.96 mL, 25.3 mmol) was added dropwise, followed by tris(dibenzylideneacetone)dipalladium(0) (192 mg, 0.21 mmol) and (±)-BINAP (261 mg, 0.42 mmol), and the dark-purple mixture heated at 100 °C for 24 h. After cooling, the mixture was diluted with CH_2Cl_2, and the organic phase washed with water, dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, 25% CH_2Cl_2/petrol) affording **7-*C*$_4$** as a white solid (970 mg, 1.64 mmol, 78%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.07 (dd, *J* = 8.3, 2.2 Hz, 4H, Ar-*H*-1^6,3^4,5^4,7^4), 7.00 (d, *J* = 2.2 Hz, 4H, Ar-*H*-1^2,3^2,5^2,7^2), 6.66 (d, *J* = 8.3 Hz, 4H, Ar-*H*-1^5,3^5,5^5,7^5), 4.18 (t, *J* = 7.9 Hz, 4H, -C*H*), 3.73 (s, 12H, -OCH_3), 2.03 (m, 8H, -CH_2-), 0.87 (t, *J* = 7.2 Hz, 12H, -CH_3). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 157.55 (Ar-*C*-1^4,3^6,5^6,7^6), 139.61 (Ar-*C*-1^1,3^3,5^3,7^3), 136.50 (Ar-*C*-1^3,3^1,5^1,7^1), 130.19 (Ar-*C*-1^6,3^4,5^4,7^4), 127.64 (Ar-*C*-1^2,3^2,5^2,7^2), 112.82 (Ar-*C*-1^5,3^5,5^5,7^5), 58.20 (-O*C*H$_3$), 46.63 (-*C*H), 30.29 (-*C*H$_2$-), 15.36 (-*C*H$_3$). HR-ESI-MS: calcd [M+Na]$^+$ ($C_{40}H_{48}O_4Na$) *m/z* 615.345; found 615.343. Anal. calcd [$C_{40}H_{48}O_4$·0.7$CHCl_3$]: C 72.27, H 7.26; found C 72.33, H 7.52.

2.2.7 *rac*-2,4,6,8-Tetraethyl-*1⁴,3⁶,5⁶,7⁶*-tetrahydroxy-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (**8-*C*₄**)



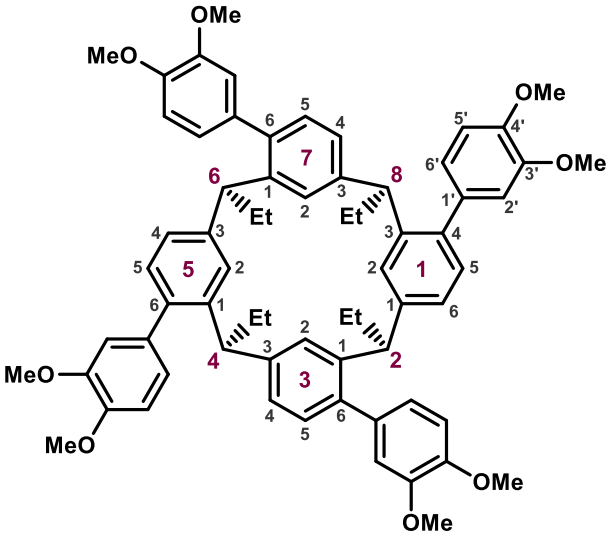
Tetramethoxy **7-*C*₄** (1.65 g, 2.78 mmol) was dissolved in dry CH_2Cl_2 (50 mL) under argon and the solution cooled in an ice water bath. BBr_3 (1 M, 27.8 mL, 27.8 mmol) was added dropwise, the resulting purple solution stirred cold for 30 min before allowing to warm to rt over 4 h. The reaction was quenched with MeOH and diluted with Et_2O, the organic phase washed with water, brine, then dried over $MgSO_4$, filtered and the solvents removed under reduced pressure affording **8-*C*₄** as a white solid (1.37 g, 2.55 mmol, 92%). ^{1}H-NMR (500 MHz, d_6-acetone): δ 7.80 (s, 4H, -O*H*), 7.38 (d, *J* = 2.2 Hz, 4H, Ar-*H*-1²,3²,5²,7²), 6.93 (dd, *J* = 8.1, 2.2 Hz, 4H, Ar-*H*-1⁶,3⁴,5⁴,7⁴), 6.55 (d, *J* = 8.1 Hz, 4H, Ar-*H*-1⁵,3⁵,5⁵,7⁵), 4.23 (t, *J* = 8.0 Hz, 4H, -C*H*), 2.15 (m, 8H, -CH_2-), 0.87 (t, *J* = 7.3 Hz, 12H, -CH_3). ^{13}C-NMR (126 MHz, d_6-acetone): δ 153.05 (Ar-*C*-1⁴,3⁶,5⁶,7⁶), 137.44 (Ar-*C*-1³,3¹,5¹,7¹), 133.06 (Ar-*C*-1¹,3³,5³,7³), 128.65 (Ar-*C*-1⁶,3⁴,5⁴,7⁴), 124.92 (Ar-*C*-1²,3²,5²,7²), 115.02 (Ar-*C*-1⁵,3⁵,5⁵,7⁵), 44.68 (-*C*H), 28.48 (-*C*H_2-), 13.14 (-*C*H_3). HR-ESI-MS: calcd $[M+Na]^+$ ($C_{36}H_{40}O_4Na$) *m/z* 559.282; found 559.280. Anal. calcd [$C_{36}H_{40}O_4 \cdot Et_2O \cdot 0.5H_2O$]: C 77.51, H 8.29; found C 77.56, H 8.29.

2.2.8 *rac*-2,4,6,8-Tetraethyl-*1⁴,3⁶,5⁶,7⁶*-tetra(triflyloxy)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (**9-*C*₄**)



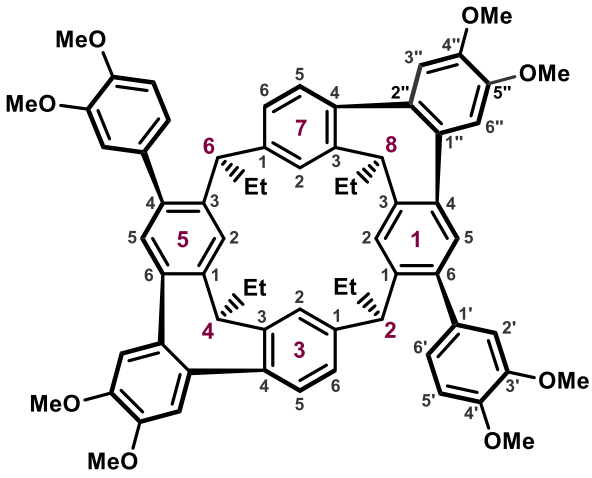
Tetrol **8-*C*₄** (500 mg, 0.93 mmol) was suspended in dry CH_2Cl_2 (30 mL) under argon and the mixture cooled in an ice water bath. Pyridine (1.80 mL, 1.77 g, 22.3 mmol) was added before the dropwise addition of triflic anhydride (1.60 mL, 2.62 g, 9.30 mmol). The resulting yellow solution was stirred cold for 30 min before allowing to warm to rt over 5 h. The reaction was quenched with HCl (5 M, 15 mL), and the organic phase washed with water, brine, then dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, 25% CH_2Cl_2/petrol) affording **9-*C*₄** as a white solid (900 mg, 0.85 mmol, 91%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.15 (dd, *J* = 8.6, 2.1 Hz, 4H, Ar-*H*-1⁶,3⁴,5⁴,7⁴), 7.13 (d, *J* = 8.6 Hz, 4H, Ar-*H*-1⁵,3⁵,5⁵,7⁵), 6.94 (d, *J* = 2.1 Hz, 4H, Ar-*H*-1²,3²,5²,7²), 4.19 (t, *J* = 7.6 Hz, 4H, -C*H*), 2.13–1.96 (m, 8H, -CH_2-), 0.95 (t, *J* = 7.3 Hz, 12H, -CH_3). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 146.37 (Ar-*C*-1⁴,3⁶,5⁶,7⁶), 143.56 (Ar-*C*-1³,3¹,5¹,7¹), 136.77 (Ar-*C*-1¹,3³,5³,7³), 130.22 (Ar-*C*-1⁶,3⁴,5⁴,7⁴), 126.45 (Ar-*C*-1²,3²,5²,7²), 121.43 (Ar-*C*-1⁵,3⁵,5⁵,7⁵), 118.61 (q, J_{CF} = 320 Hz, -OTf), 45.03 (-*C*H), 28.41 (-*C*H_2-), 12.37 (-*C*H_3). ^{19}F-NMR (376 MHz, $CDCl_3$): δ −74.0 (s, -OTf). HR-ESI-MS: calcd $[M+Na]^+$ ($C_{40}H_{36}F_{12}O_{12}S_4Na$) *m/z* 1087.079; found 1087.078. Anal. calcd [$C_{40}H_{36}F_{12}O_{12}S_4$]: C 45.11, H 3.41; found C 45.34, H 3.15.

2.2.9 *rac*-2,4,6,8-Tetraethyl-$1^4,3^6,5^6,7^6$-tetra(3',4'-dimethoxyphenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (**2-C_4**)



Tetratriflate **9-C_4** (400 mg, 0.38 mmol), 3,4-dimethoxyphenyl boronic acid (692 mg, 3.76 mmol) and cesium carbonate (2.45 g, 7.52 mmol) were suspended in toluene (15 mL), water (7 mL) and *n*-propanol (1 mL) and the mixture deoxygenated with gentle argon bubbling for 10 min. Dichloro[1,1'-bis(diphenylphosphino)ferrocene] palladium(II) (27 mg, 0.038 mmol) was added and the mixture heated at 70 °C for 48 h. After cooling, the dark mixture was diluted with CH_2Cl_2, the organic phase washed with water, brine, then dried over $MgSO_4$ and the solvents removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, 2% acetone/CH_2Cl_2) affording **2-C_4** as a white solid (355 mg, 0.35 mmol, 93%). Crystals suitable for X-ray diffraction were grown by the layered diffusion of MeOH into a $CHCl_3$ solution of **2-C_4**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.16 (br s, 4H, Ar-*H*-1^2,3^2,5^2,7^2), 6.96 (d, *J* = 7.8 Hz, 4H, Ph-$H_{5'}$), 6.87 (d, *J* = 8.2 Hz, 4H, Ph-$H_{6'}$), 6.74 (d, *J* = 8.0 Hz, 4H, Ar-*H*-1^5,3^5,5^5,7^5), 6.68 (dd, *J* = 8.0, 1.8 Hz, 4H, Ar-*H*-1^6,3^4,5^4,7^4), 6.49 (br s, 4H, Ph-$H_{2'}$), 4.00 (t, *J* = 7.4 Hz, 4H, -C*H*), 3.91 (s, 12H, $C_{4'}$-OCH_3), 3.72 (s, 12H, $C_{3'}$-OCH_3), 2.12–1.94 (m, 8H, -CH_2-), 0.84 (t, *J* = 7.2 Hz, 12H, -CH_3). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 148.20 (Ph-$C_{4'}$), 147.96 (Ar-*C*-1^1,3^3,5^3,7^3), 144.99 (Ph-$C_{1'}$), 142.42 (Ph-$C_{3'}$), 139.78 (Ar-*C*-1^4,3^6,5^6,7^6), 134.83 (Ar-*C*-1^3,3^1,5^1,7^1), 129.69 (Ph-$C_{5'}$), 127.29 (Ar-*C*-1^6,3^4,5^4,7^4), 125.63 (Ar-*C*-1^2,3^2,5^2,7^2), 121.55 (Ar-*C*-1^5,3^5,5^5,7^5), 113.33 (Ph-$C_{2'}$), 110.87 (Ph-$C_{6'}$), 56.07 ($C_{4'}$-O*C*H_3), 55.72 ($C_{3'}$-O*C*H_3), 47.84 (-*C*H), 29.73 (-*C*H_2-), 12.93 (-*C*H_3). HR-ESI-MS: calcd [M+Na]$^+$ ($C_{68}H_{72}O_8$Na) *m/z* 1039.512; found 1039.512. Anal. calcd [$C_{68}H_{72}O_8$·0.6$CHCl_3$]: C 75.67, H 6.72; found C 75.88, H 7.04. λ_{max}(CH_2Cl_2)/nm 250 (ε/dm^3 mol^{-1} cm^{-1} 96000).

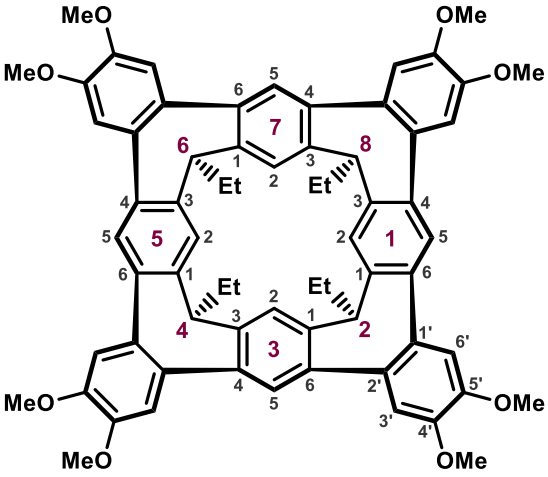
2.2.10 $1^4,7^4$:$3^4,5^6$-Bis(4,5-dimethoxy[1,2]benzeno)-$1^6,5^4$-bis(3,4-dimethoxyphenyl)-2,4,6,8-tetraethyl-1,3,5,7(1,3)tetrabenzenacyclooctaphane (**3**)



Macrocycle **2-C_{2v}** (300 mg, 0.30 mmol) was dissolved in CH_2Cl_2 (150 mL, AR grade) and the solution purged with gentle argon bubbling for 10 min. $FeCl_3$ (1.15 g, 7.10 mmol) in CH_3NO_2 (5 mL) was added dropwise and the resulting dark green solution stirred at rt with continued argon bubbling. After 30 min, the reaction mixture was washed with water brine, then dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, 2% acetone/CH_2Cl_2) affording **3** as an off-white solid (270 mg, 0.27 mmol, 90%). Crystals suitable for X-ray diffraction were grown by the layered diffusion of MeOH into a $CHCl_3$ solution of **3**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.64 (s, 2H, Ar-*H*-1^2,5^2), 7.55 (s, 2H, Ar-*H*-

$3^2,7^2$), 7.18 (s, 2H, Ar-*H*-$1^5,5^5$), 7.07 (s, 2H, $H_{3''}$), 7.05 (d, *J* = 7.8 Hz, 2H, Ar-*H*-$3^5,7^5$), 7.02 (s, 2H, $H_{6''}$), 6.97 (br d, *J* =7.8 Hz, 2H, Ph-$H_{5'}$), 6.92 (br m, 4H, Ph-$H_{2',6'}$), 6.38 (d, *J* = 7.8 Hz, Ar-*H*-$3^6,7^6$), 4.07 (t, *J* = 8.0 Hz, 2H, 4, 8-C*H*), 3.97 (s, 6H, $C_{4'}$-OCH_3), 3.93 (s, 6H, $C_{5''}$-OCH_3), 3.91 (s, 6H, $C_{4''}$-OCH_3), 3.81 (br s, 6H, $C_{3'}$-OCH_3), 3.40 (t, *J* = 7.6 Hz, 2H, 2, 6-C*H*), 2.68–2.60 (m, 4H, 2, 6-CH_2), 2.45–2.23 (m, 4H, 4, 8-CH_2), 1.22 (t, *J* = 7.2 Hz, 6H, 2, 6-CH_3), 1.04 (t, *J* = 7.2 Hz, 6H, 4-CH_3, 8-CH_3). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 148.48 (Ph-$C_{5'}$), 148.23 ($C_{5''}$), 148.21 ($C_{4''}$), 148.04 (Ph-$C_{4'}$), 145.31 (Ar-*C*-$3^1,7^1$), 144.23 (Ar-*C*-$3^3,7^3$), 143.01 (Ar-*C*-$1^3,5^1$), 142.52 (Ar-*C*-$1^1,5^3$), 138.77 (Ar-*C*-$1^6,5^4$), 136.30 (Ar-*C*-$3^4,7^4$), 135.52 (Ar-*C*-$1^4,5^6$), 134.72 ($C_{1''}$), 131.74 ($C_{2''}$), 131.19 (Ph-$C_{1'}$), 130.28 (Ar-*C*-$1^5,5^5$), 128.52 (Ar-*C*-$3^5,7^5$), 126.63 (Ar-*C*-$3^6,7^6$), 122.01 (Ph-$C_{2'}$), 119.49 (Ar-*C*-$1^2,5^2$), 118.49 (Ph-*C*-$3^2,7^2$), 113.61 (Ph-$C_{6'}$), 112.04 ($C_{6''}$), 111.75 ($C_{3''}$), 110.90 (Ph-$C_{3'}$), 56.17 ($C_{4''}$-OCH_3), 56.10 ($C_{5''}$-OCH_3), 56.08 ($C_{4'}$-OCH_3), 56.07 ($C_{3'}$-OCH_3), 47.90 (4, 8-*C*H), 45.10 (2, 6-*C*H), 29.17 (4, 8-*C*H_2), 21.95 (2, 6-*C*H_2), 13.20 (4, 8-*C*H_3), 12.78 (2, 6-*C*H_3). HR-ESI-MS: calcd $[M+Na]^+$ ($C_{68}H_{68}NaO_8$) *m/z* 1035.481; found 1035.481. Anal. calcd [$C_{68}H_{68}O_8$·1.5Me_2CO]: C 79.13, H 7.05; found C 78.87, H 6.89. λ_{max}(CH_2Cl_2)/nm 262 (ε/dm^3 mol^{-1} cm^{-1} 200000).

2.2.11 $1^4,7^4$:$1^6,3^6$:$3^4,5^6$:$5^4,7^6$-Tetrakis(4,5-dimethoxy[1,2]benzeno)-2,4,6,8-tetraethyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (**4**)

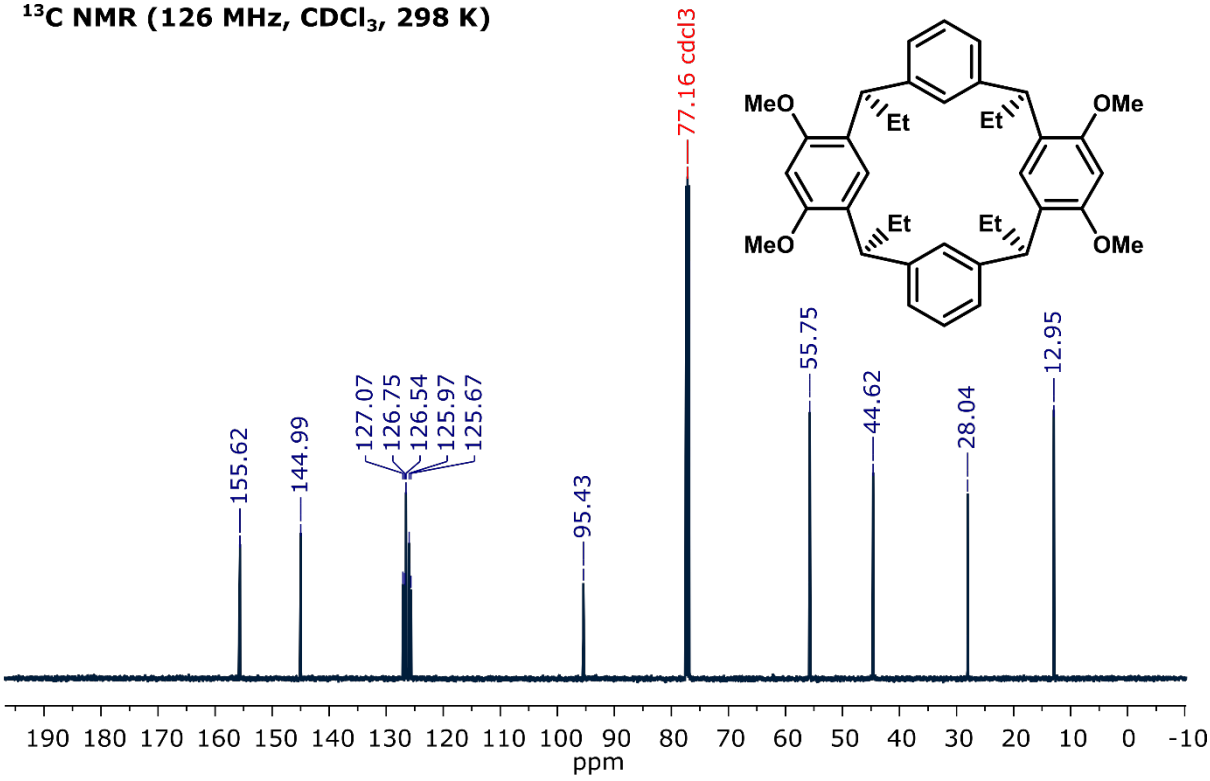


Bis-bridged macrocycle **3** (650 mg, 0.64 mmol) was dissolved in CH_2Cl_2 (dry, 50 mL) under an argon atmosphere and cooled on a ice/brine bath to −10 °C. Triflic acid (5.65 mL, 9.60 g, 64.0 mmol) was added dropwise giving a deep purple solution. DDQ (655 mg, 2.89 mmol) was added immediately in one aliquot and the resulting deep blue solution was stirred at −10 °C for 30 min. The reaction was quenched with NaOH (2 M, 10 mL), diluted with water and separated. The organic phase was washed with HCl (2 M, 20 ml), dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, 5% ethyl acetate/CH_2Cl_2) affording **4** as a white solid (312 mg, 0.30 mmol, 48%) with a trace amount of deep red impurity. Crystals suitable for X-ray diffraction were grown by the layered diffusion of MeOH into a CH_2Cl_2 solution of **4**, or the evaporation of $CHCl_3$/DMSO mixtures. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.16 (s, 8H, $H_{3',6'}$), 7.12 (s, 4H, Ar-*H*-$1^5,3^5,5^5,7^5$), 7.09 (s, 4H, Ar-*H*-$1^2,3^2,5^2,7^2$), 3.99 (s, 24H, −OCH_3), 3.51 (t, *J* = 7.7 Hz, 4H, −C*H*), 2.53 (p, *J* = 7.3 Hz, 8H, −CH_2−), 1.17 (t, *J* = 7.2 Hz, 12H, −CH_3). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 148.34 ($C_{4',5'}$), 143.36 (Ar-*C*-$1^1,1^3$), 135.47 (Ar-*C*-$1^4,1^6$), 131.85 ($C_{1',2'}$), 130.08 (Ar-*C*-1^5), 113.72 (Ar-*C*-1^2), 111.60 ($C_{3',6'}$), 56.37 (−OCH_3), 44.81 (−*C*H), 20.97 (−*C*H_2−), 12.47 (−*C*H_3). HR MS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{68}H_{64}NaO_8$ 1031.449; found 1031.447. Anal. Calcd for $C_{68}H_{64}O_8$·0.7CH_2Cl_2·0.6MeOH: C, 76.40; H, 6.51: Found C, 76.51; H, 6.28. λ_{max}(CH_2Cl_2)/nm 264 (ε/dm^3 mol^{-1} cm^{-1} 164000).

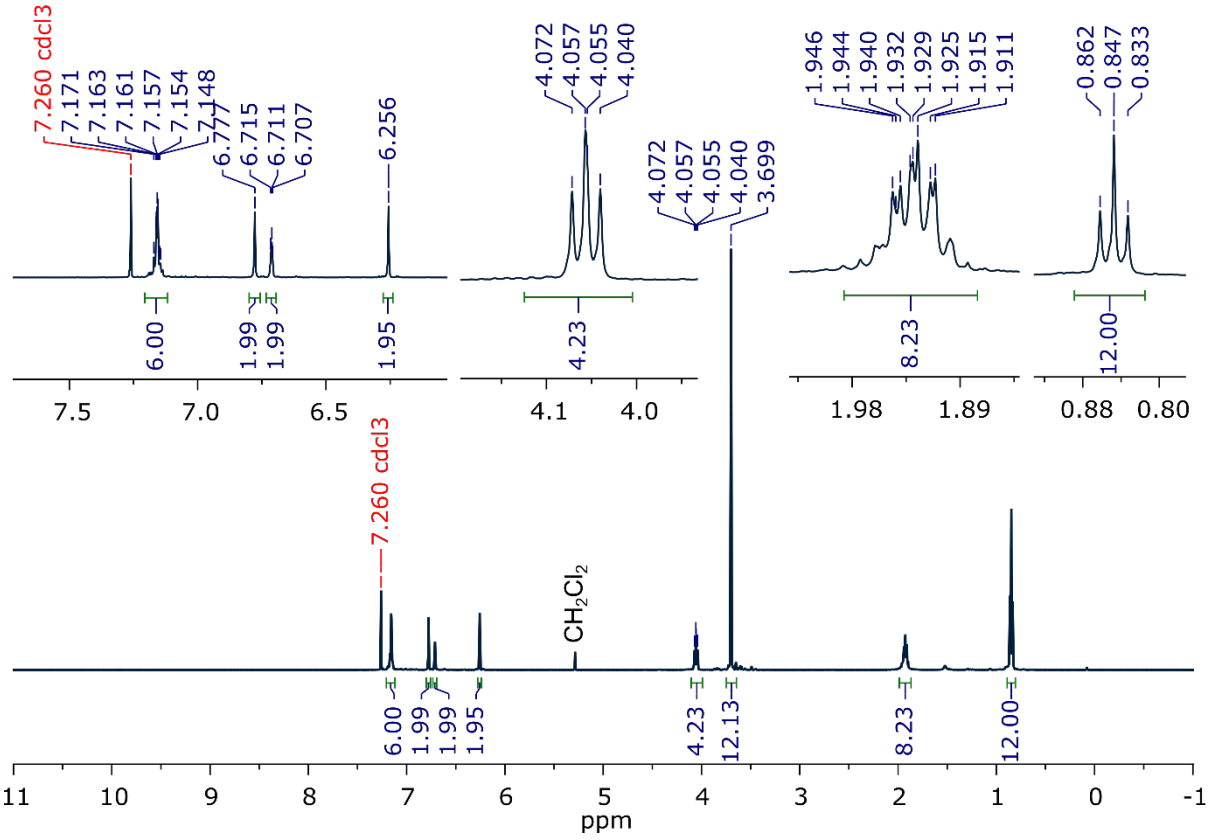
3. NMR Spectra

Compound **7-C_{2v}**

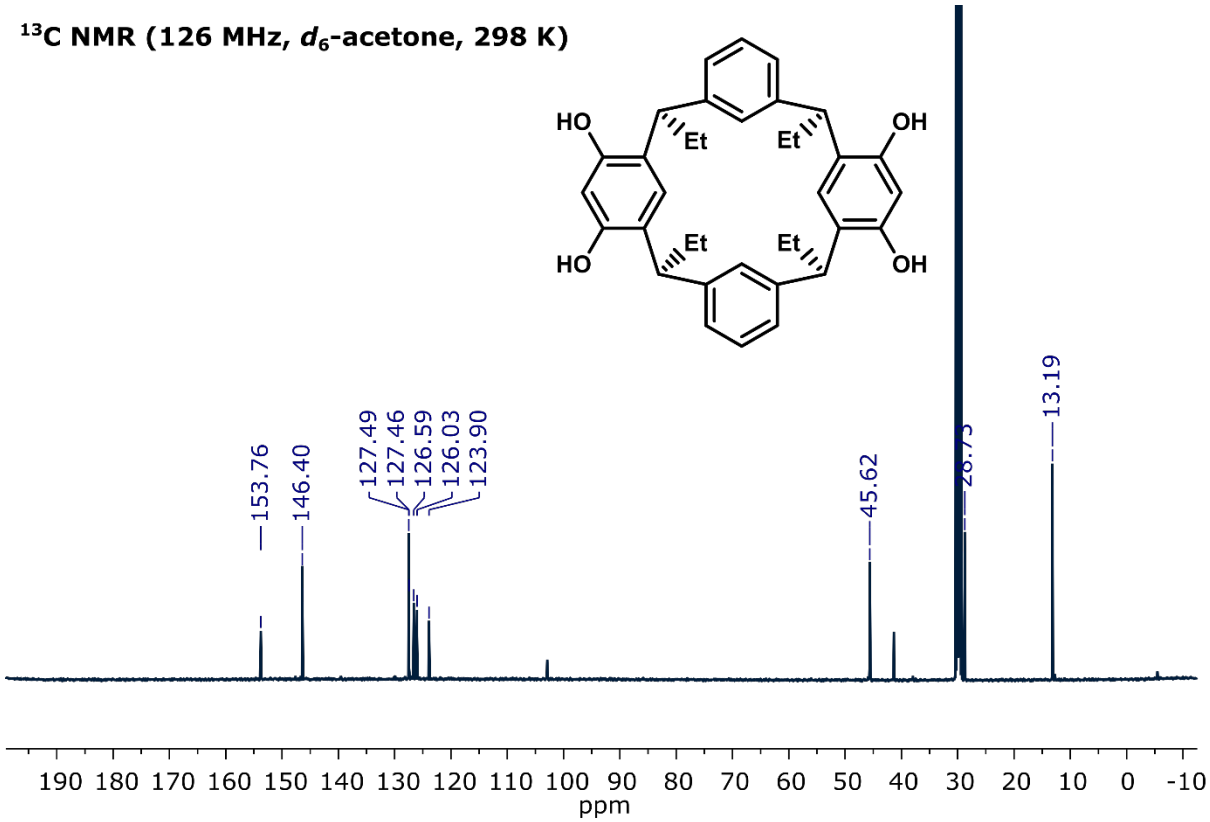
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)

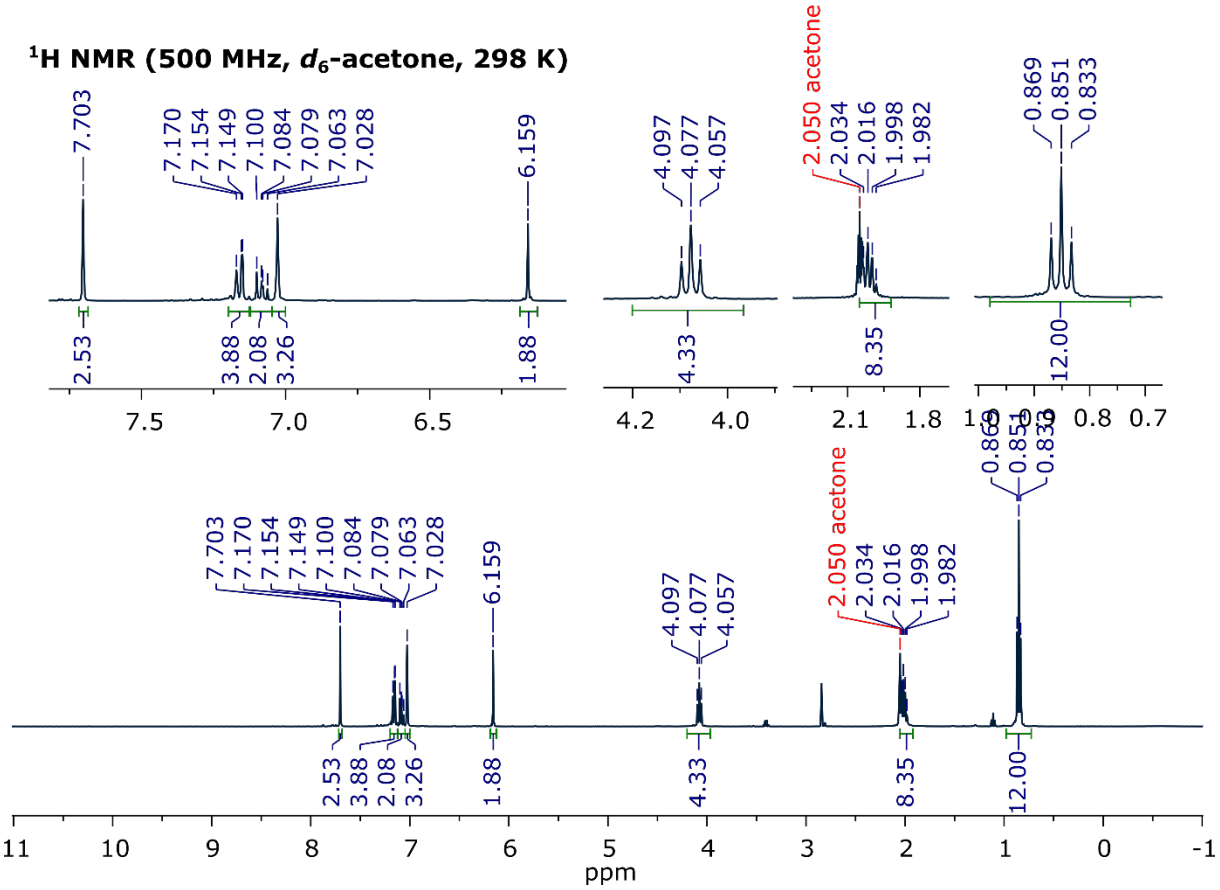


^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



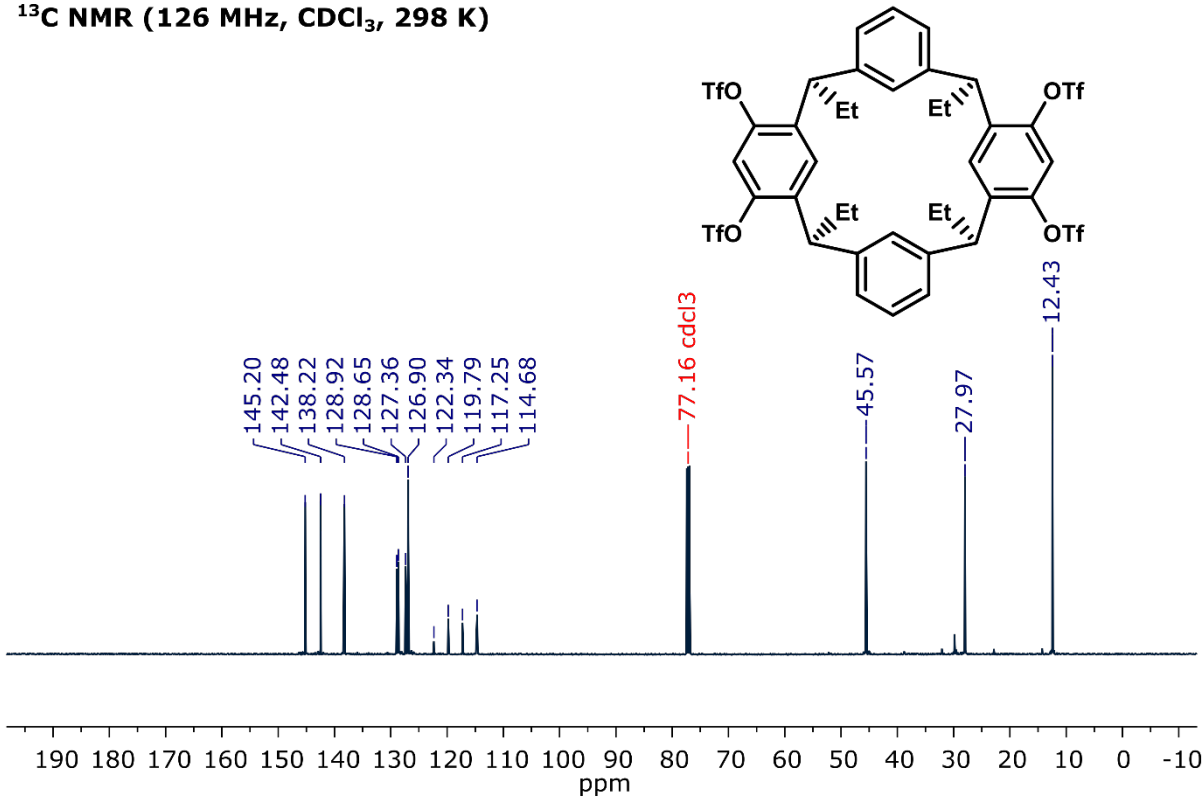
Compound **8**-C_{2v}



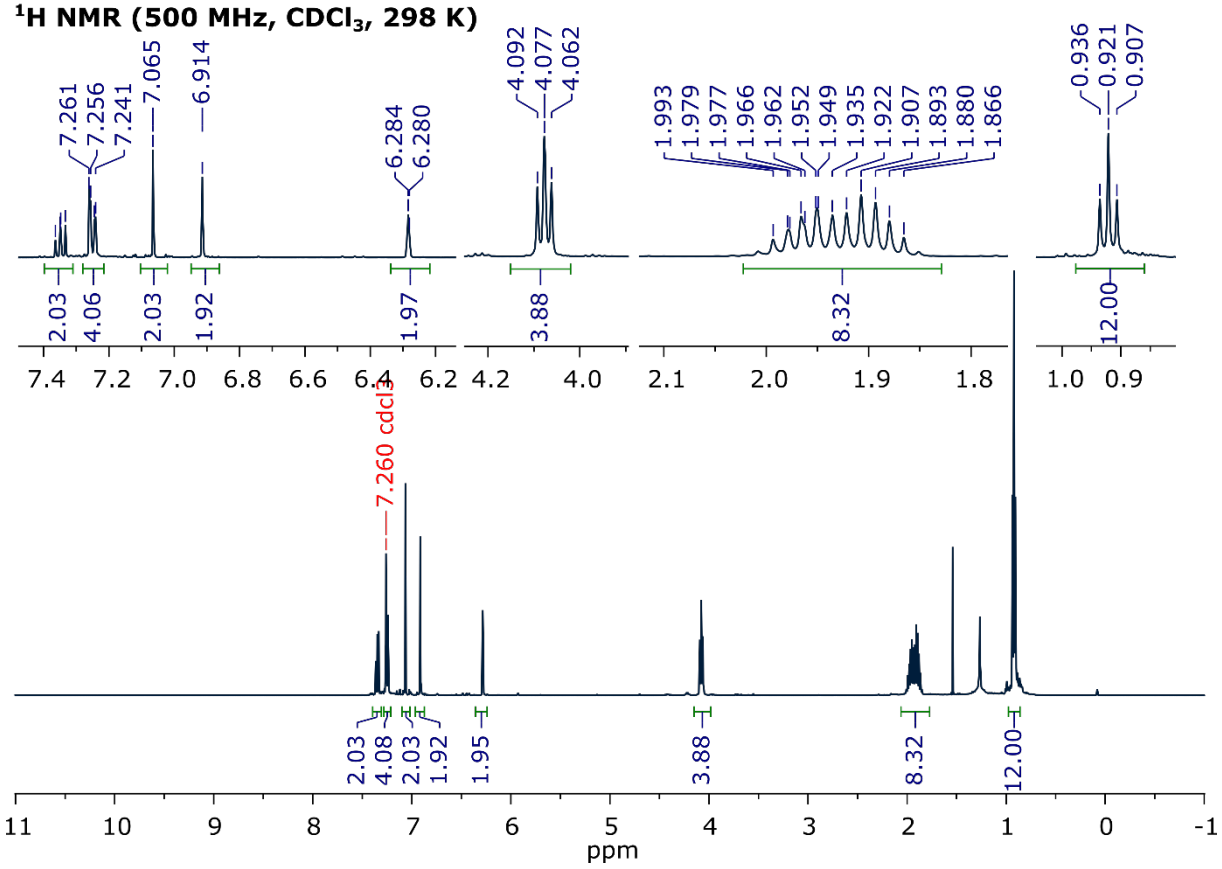


Compound **9-C_{2v}**

^{13}C NMR (126 MHz, $CDCl_3$, 298 K)

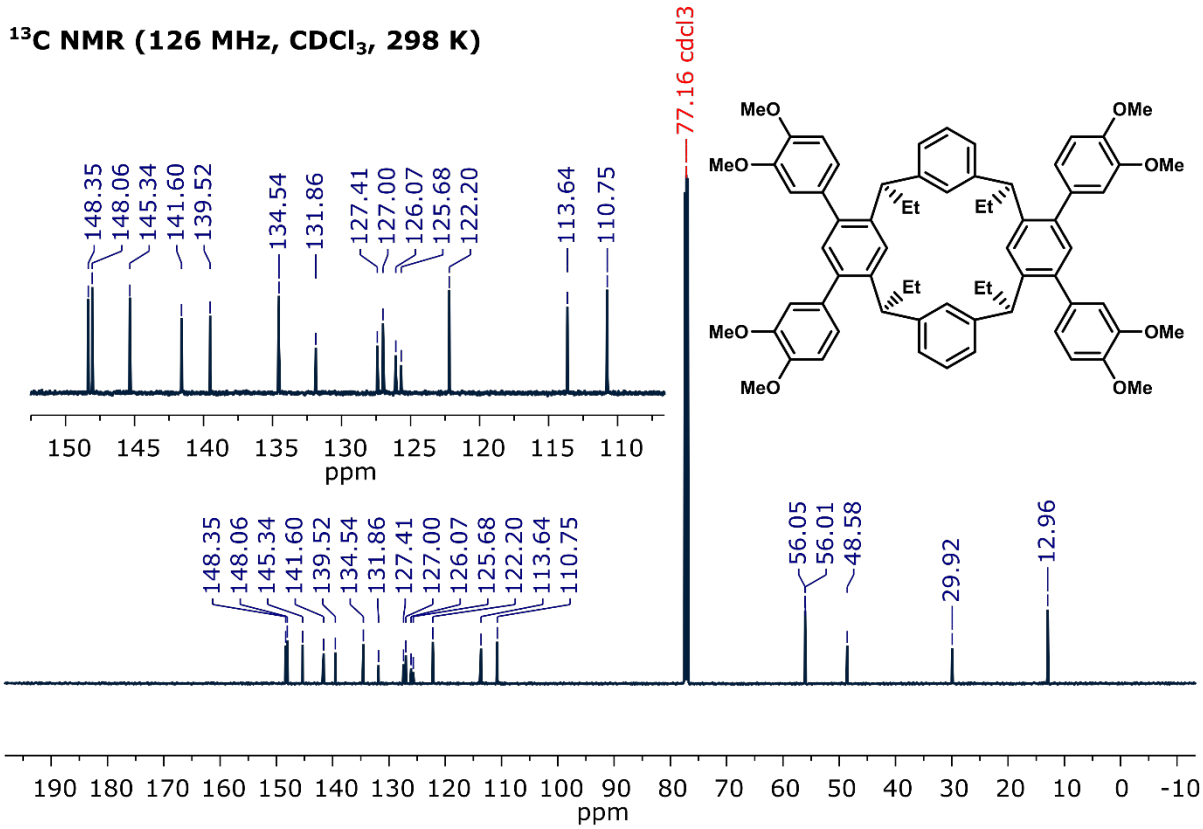


^{1}H NMR (500 MHz, $CDCl_3$, 298 K)

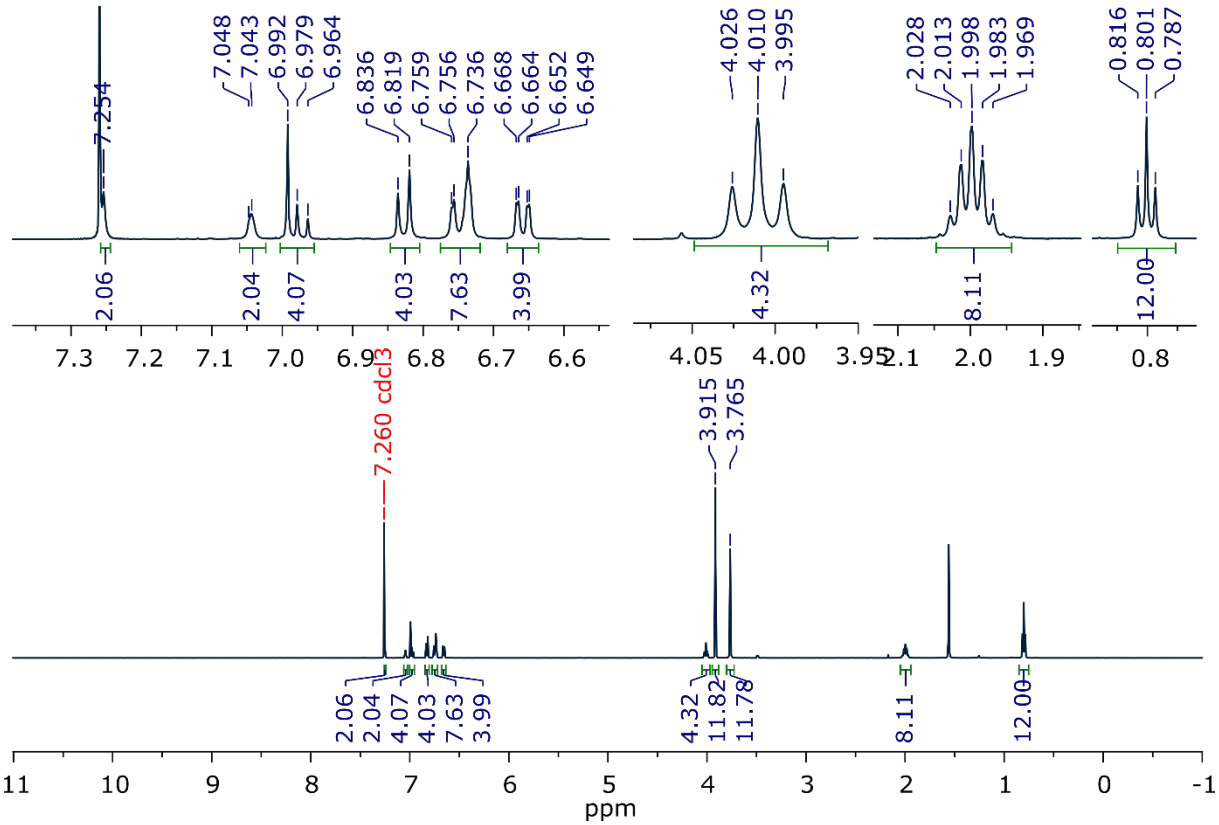


Compound **2-C_{2v}**

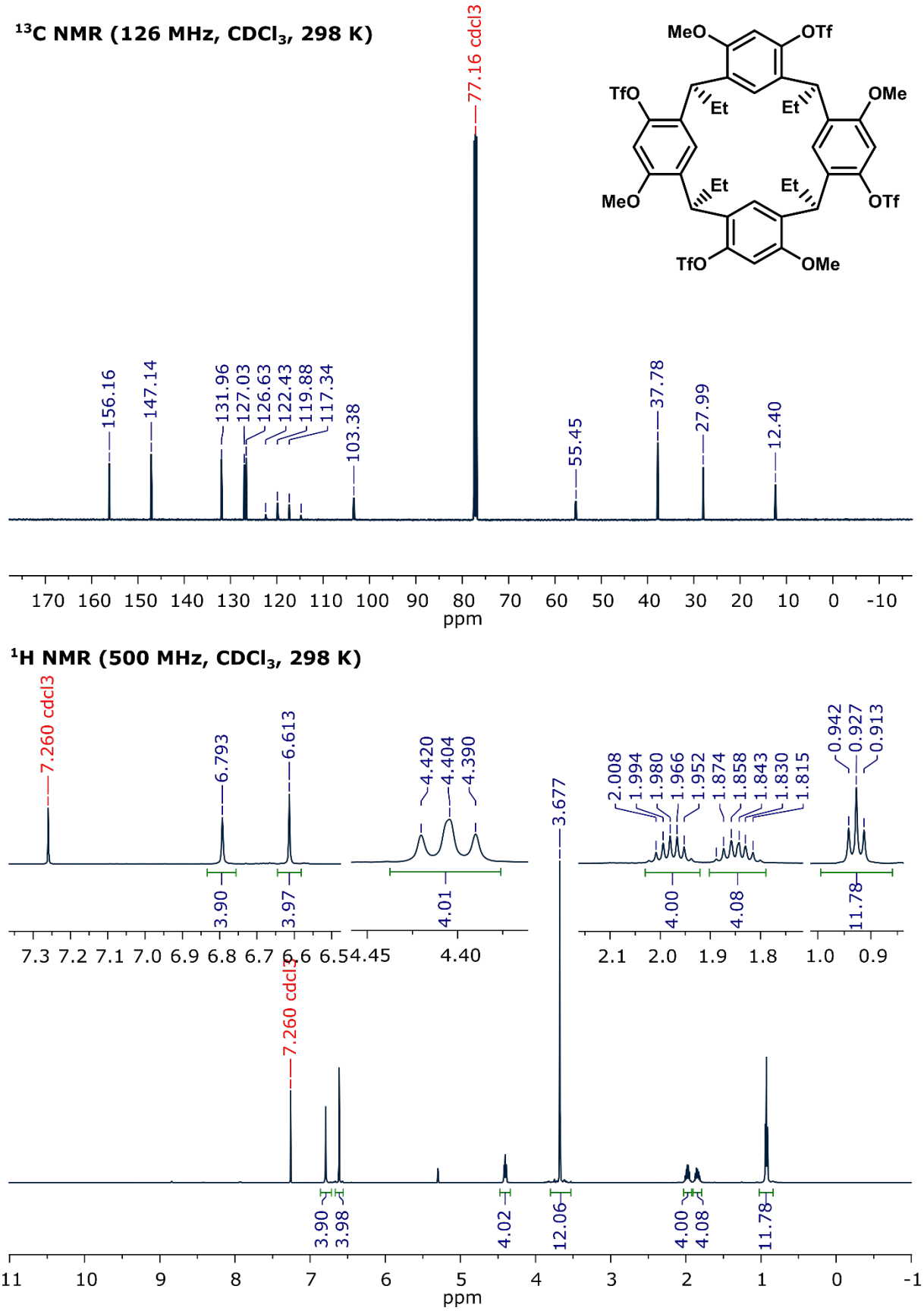
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)



^{1}H NMR (500 MHz, $CDCl_3$, 298 K)

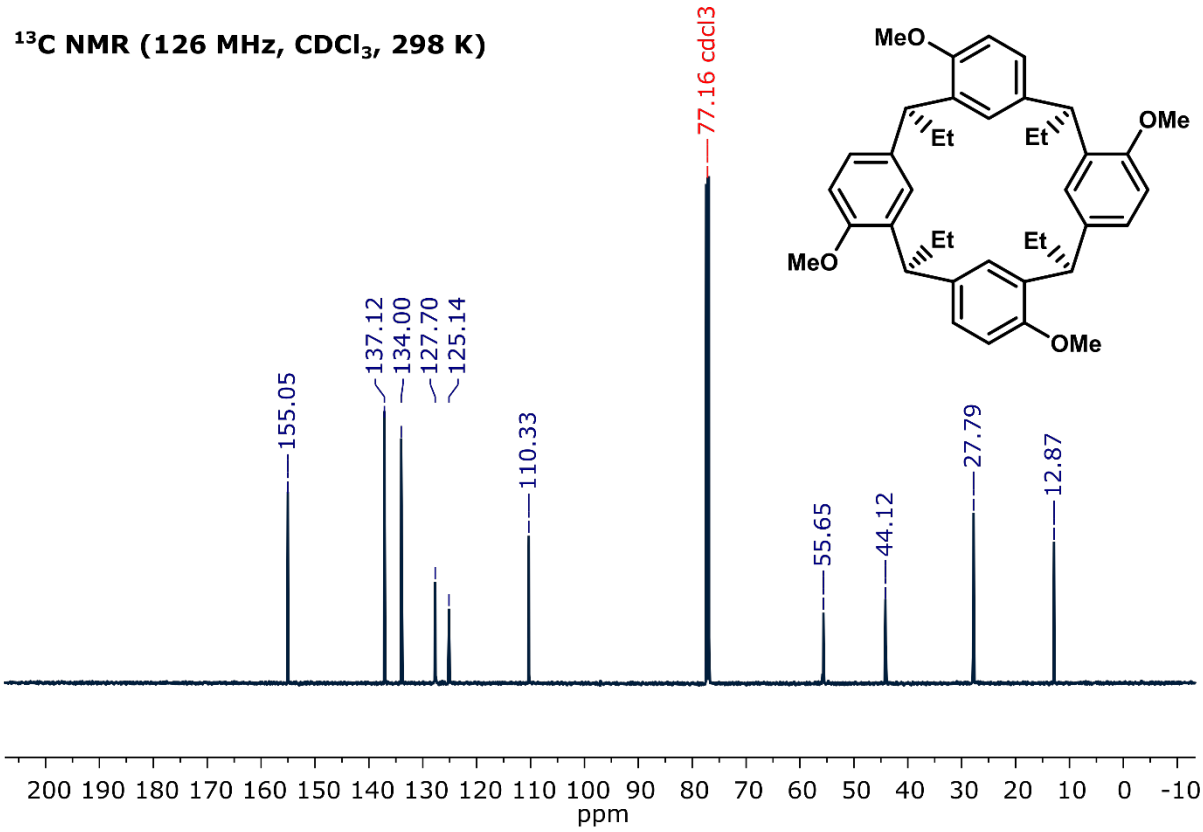


Compound **6-C_4**

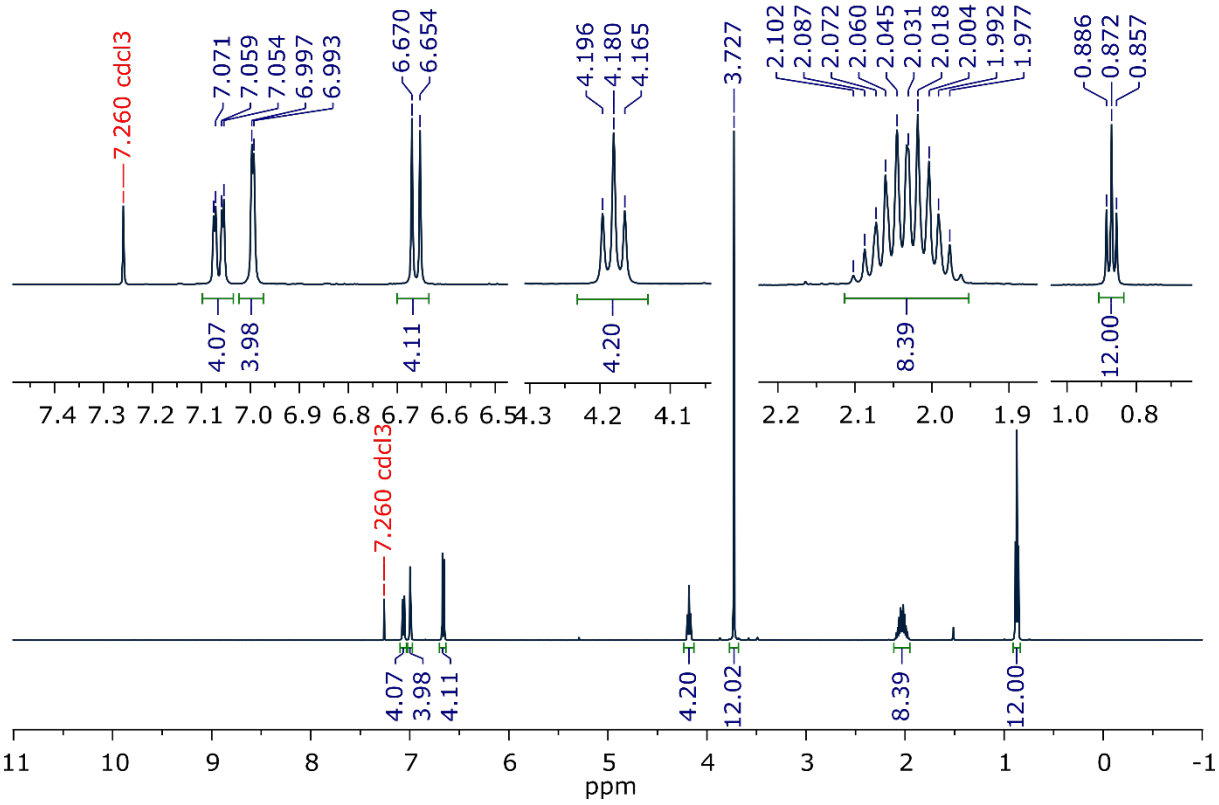


Compound **7-C_4**

^{13}C NMR (126 MHz, $CDCl_3$, 298 K)

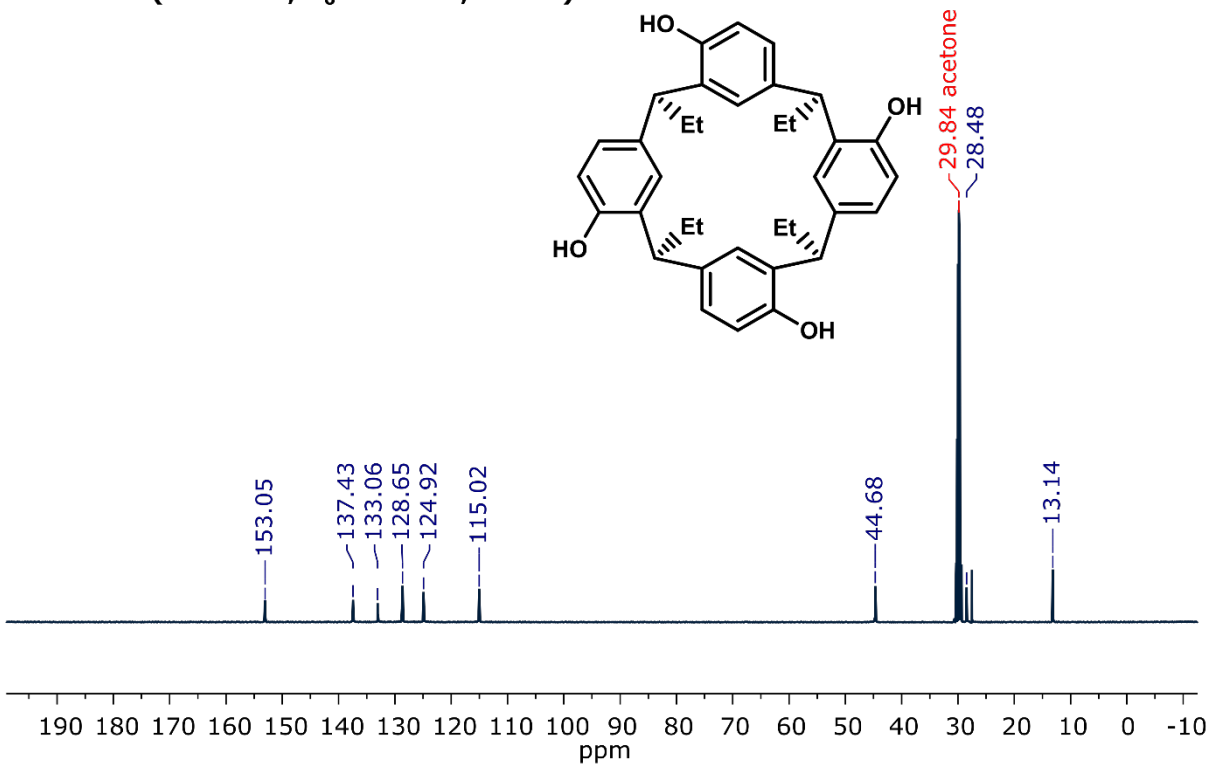


^{1}H NMR (500 MHz, $CDCl_3$, 298 K)

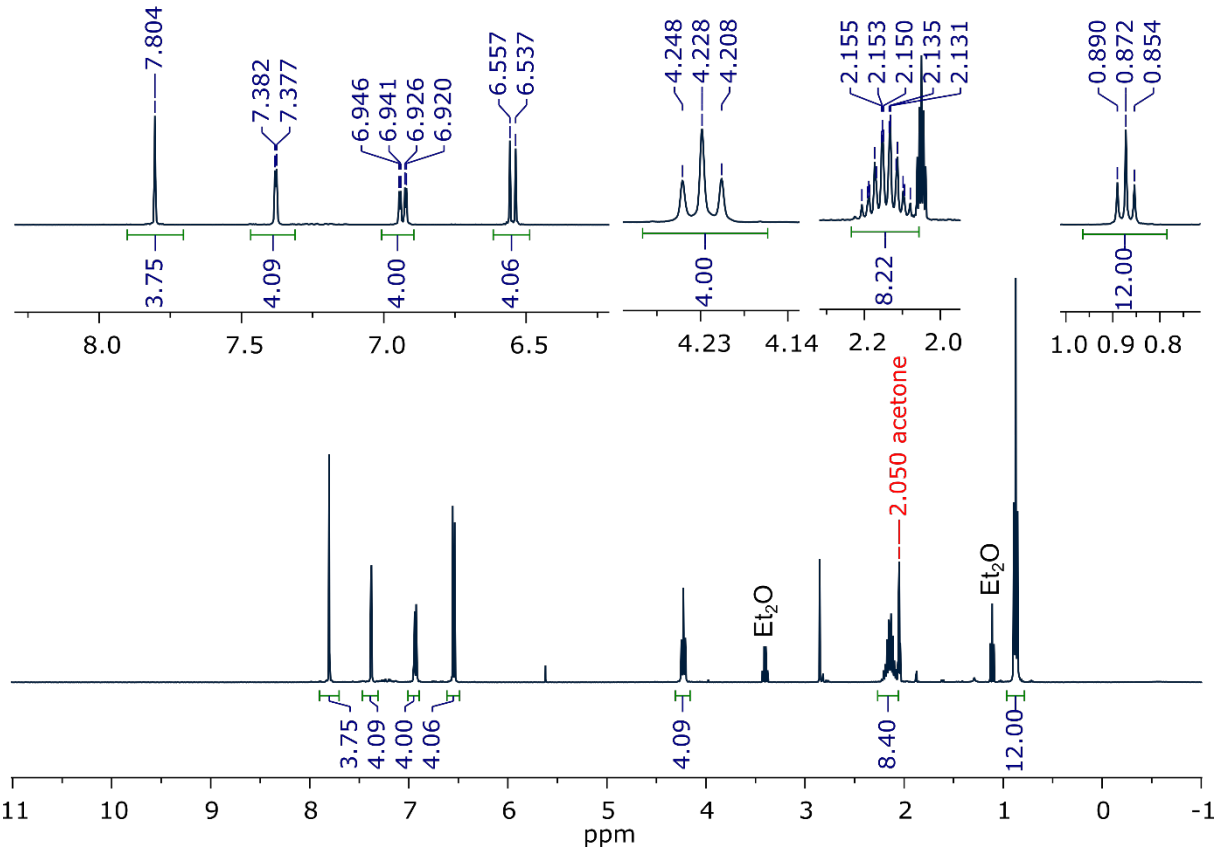


Compound **8-C_4**

^{13}C NMR (126 MHz, d_6-acetone, 298 K)

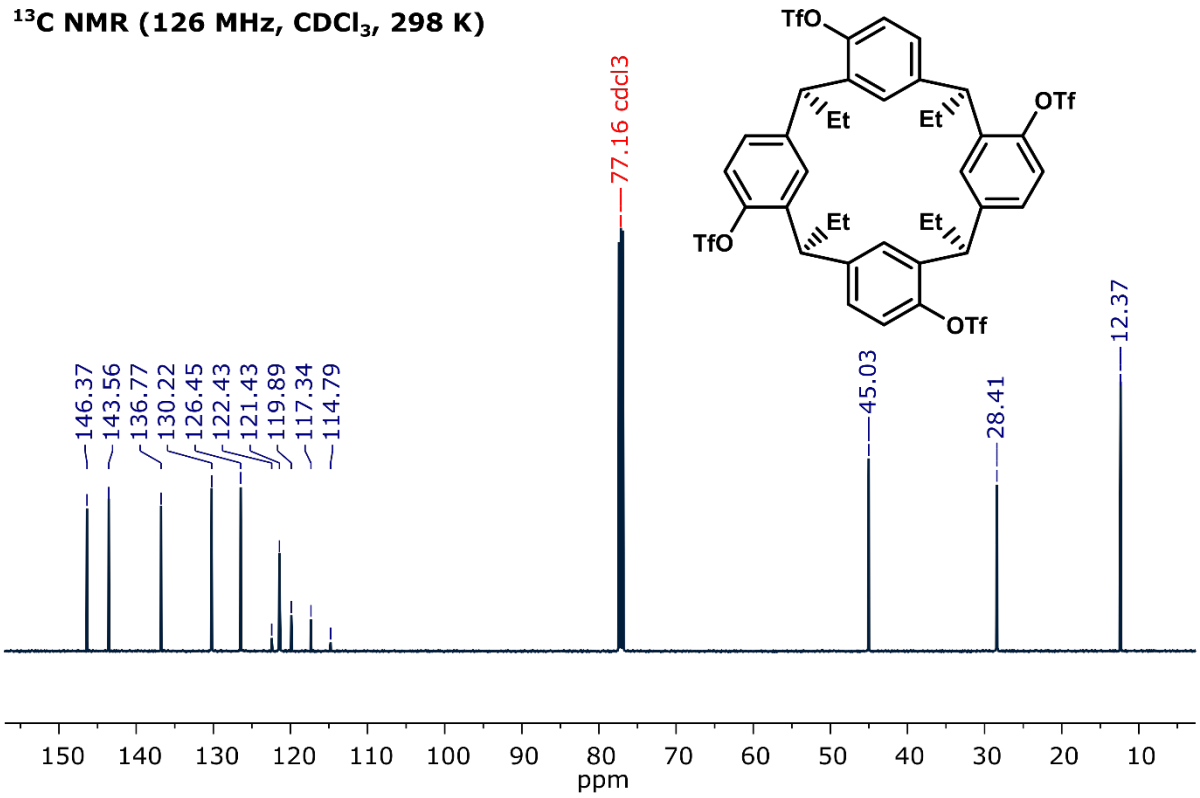


^{1}H NMR (500 MHz, d_6-acetone, 298 K)

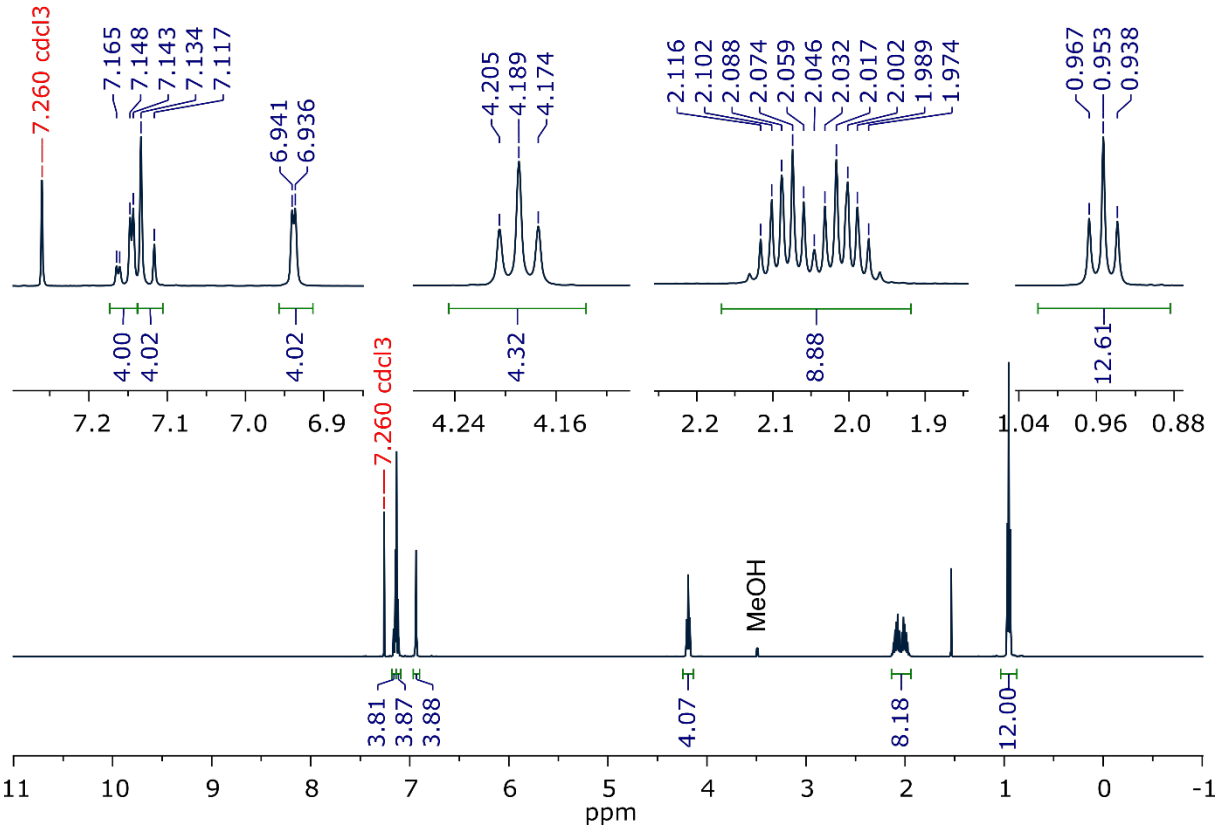


Compound **9-C_4**

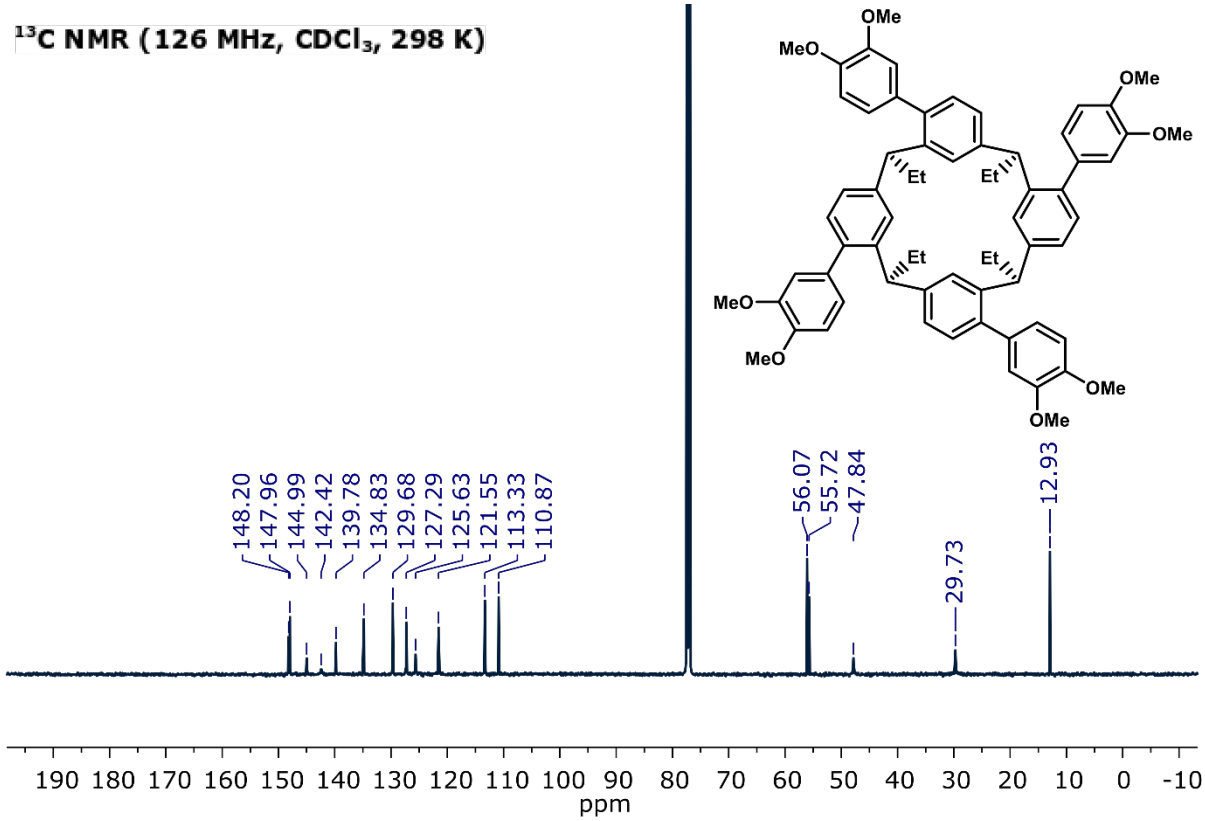
^{13}C NMR (126 MHz, $CDCl_3$, 298 K)

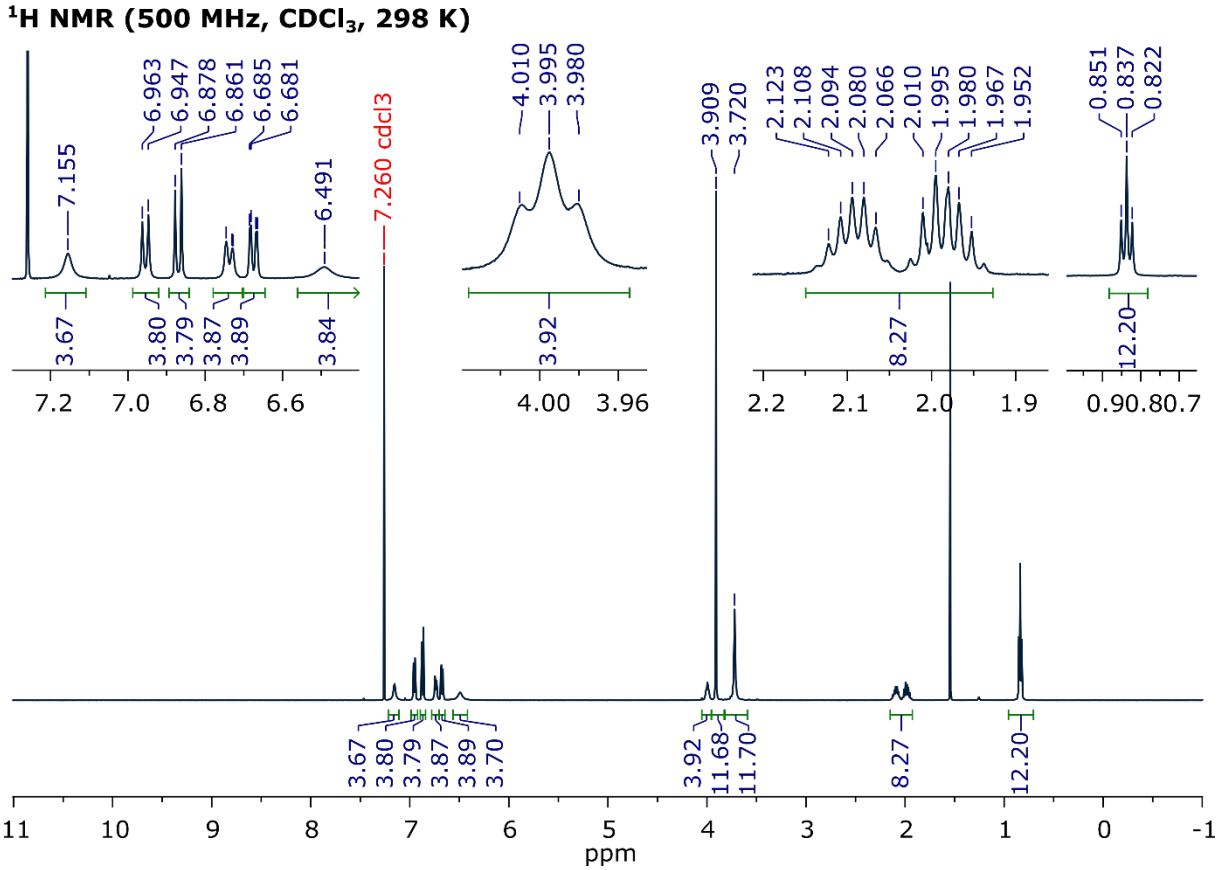


^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



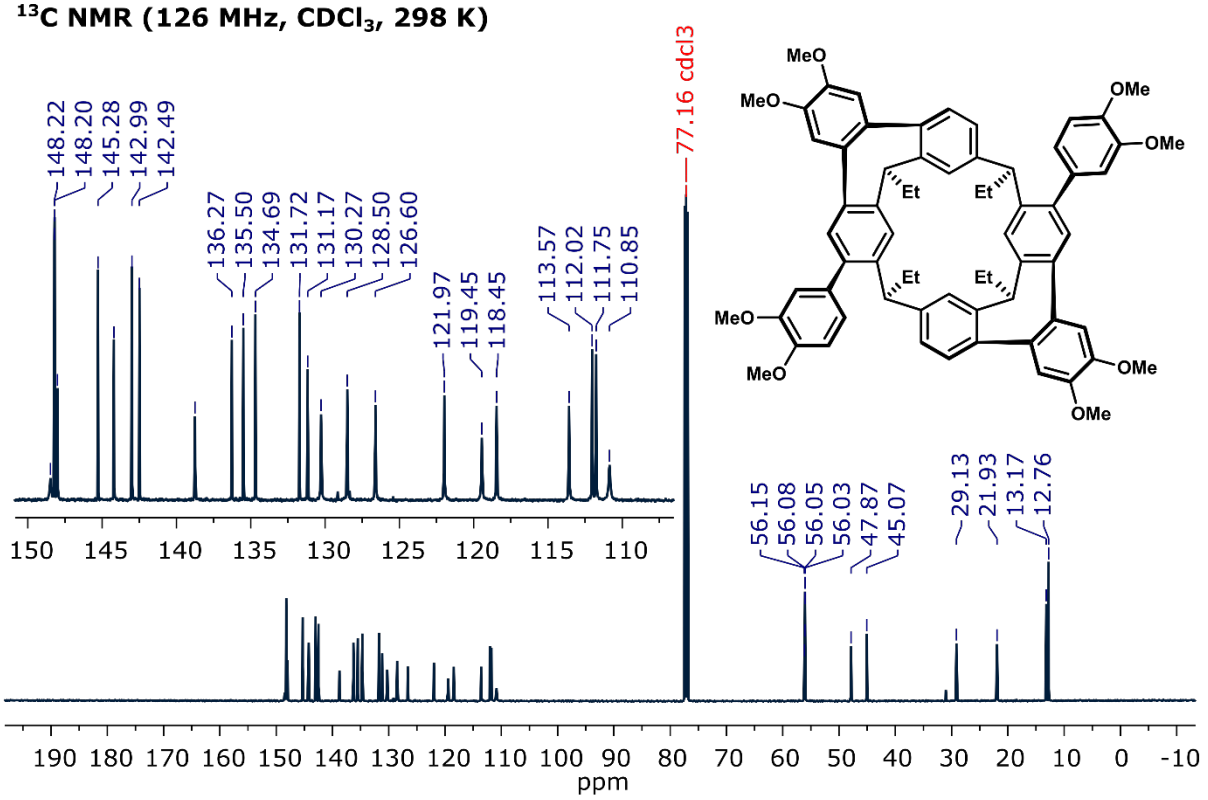
Compound **2-C_4**



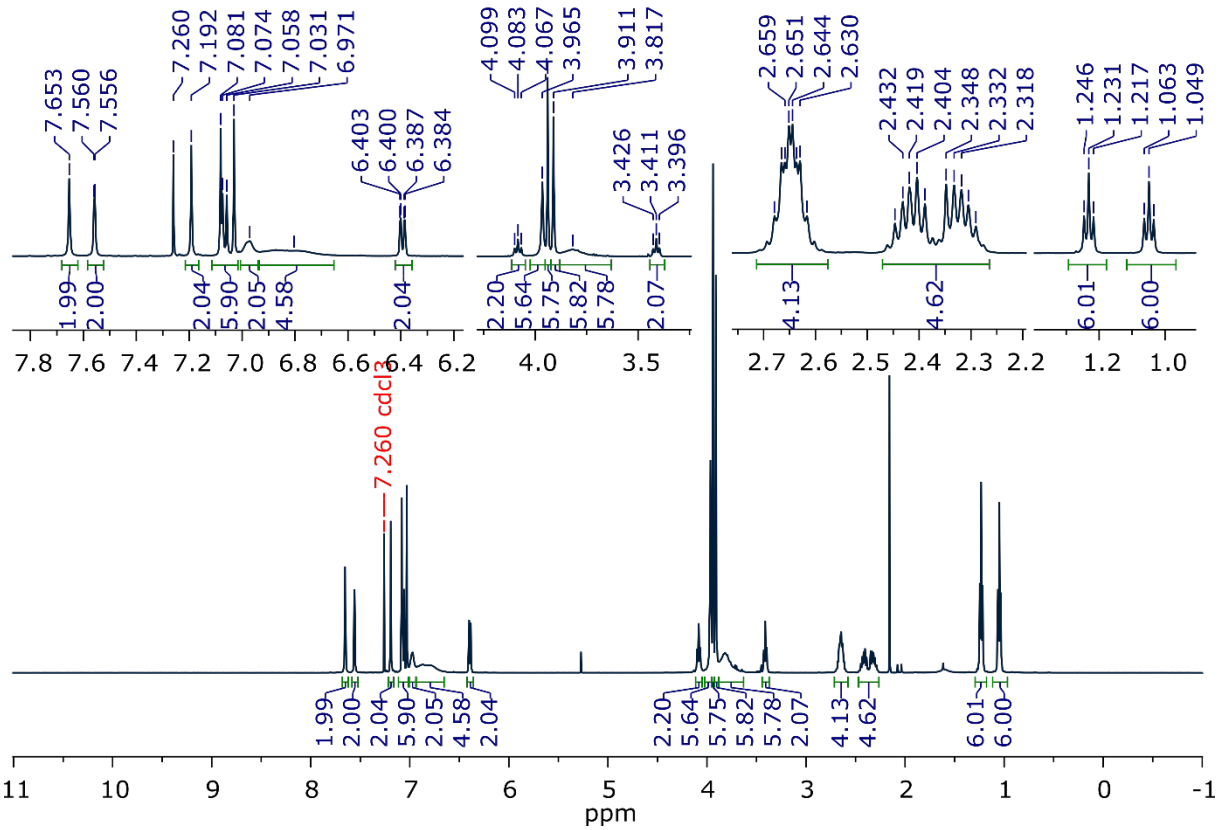


Compound **3**

^{13}C NMR (126 MHz, $CDCl_3$, 298 K)

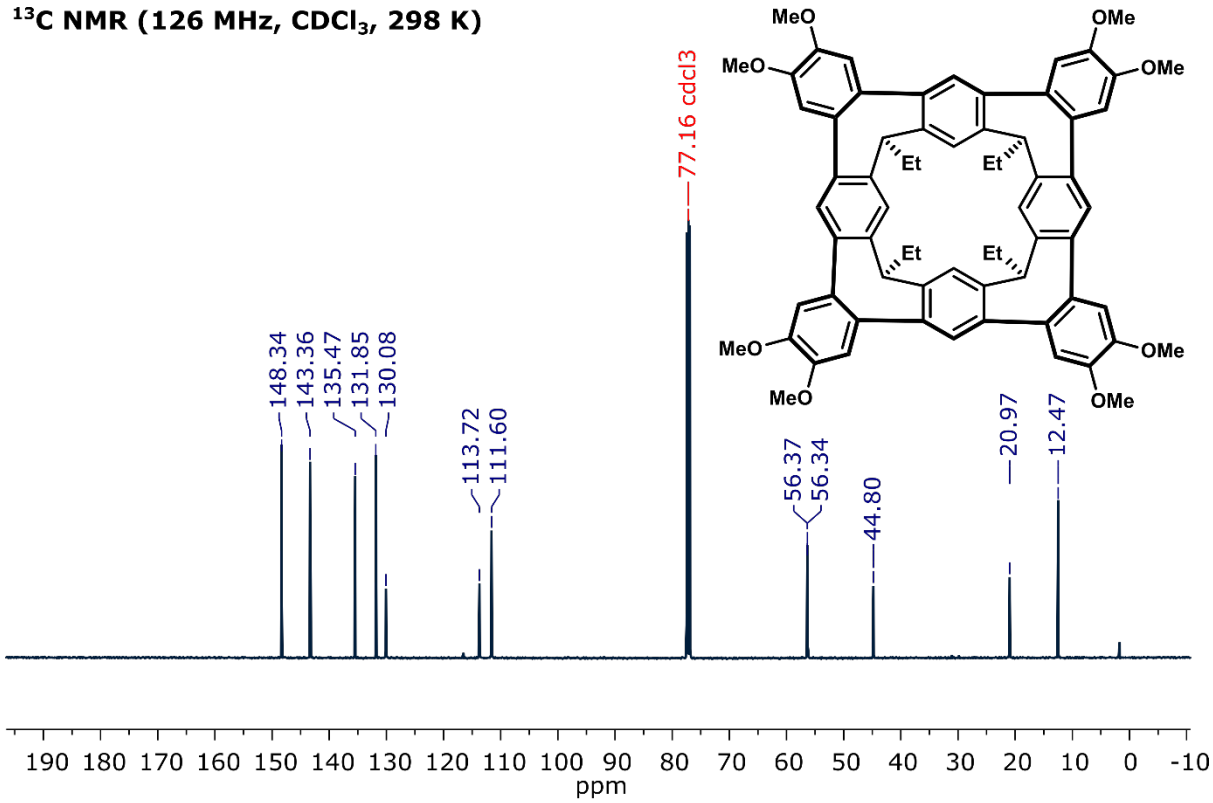


^{1}H NMR (500 MHz, $CDCl_3$, 298 K)

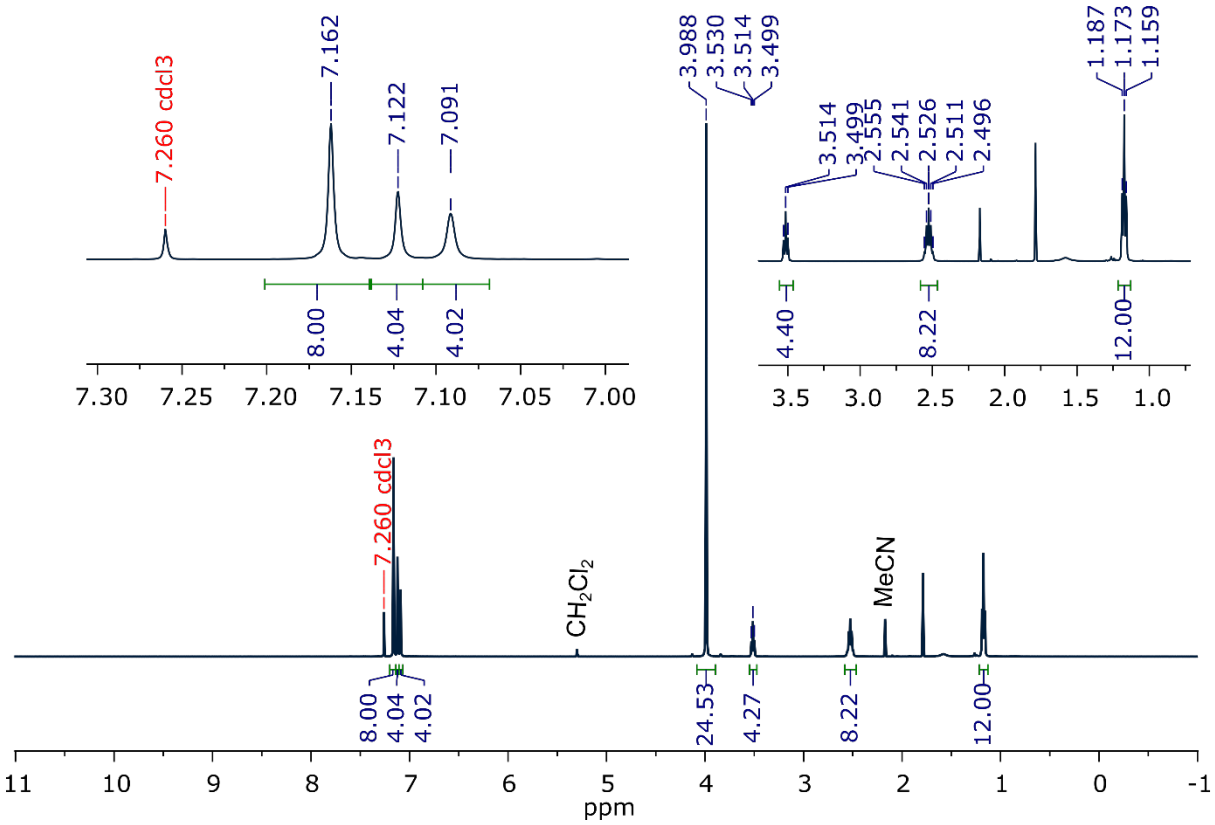


Compound **4**

^{13}C NMR (126 MHz, $CDCl_3$, 298 K)

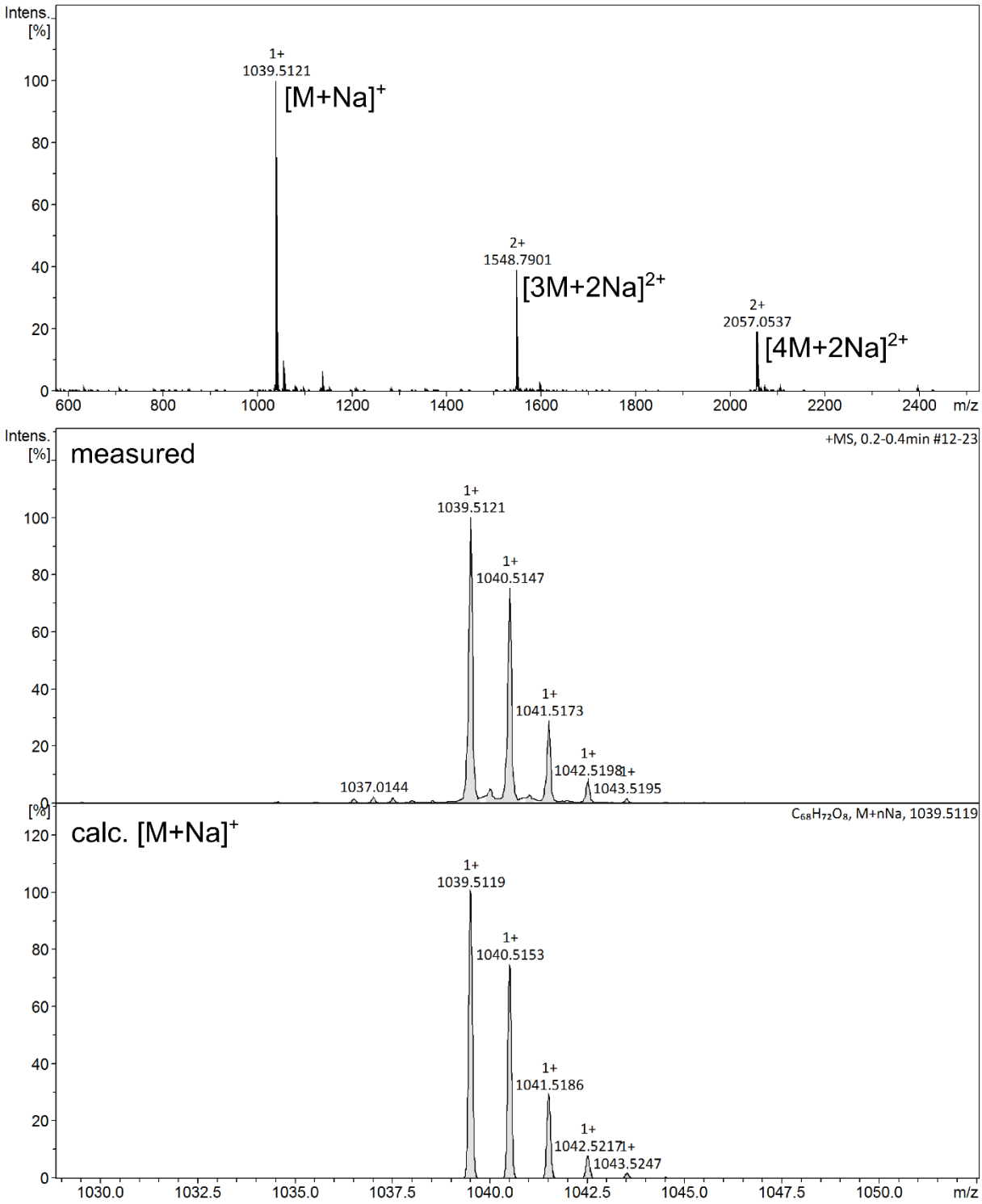


^{1}H NMR (500 MHz, $CDCl_3$, 298 K)

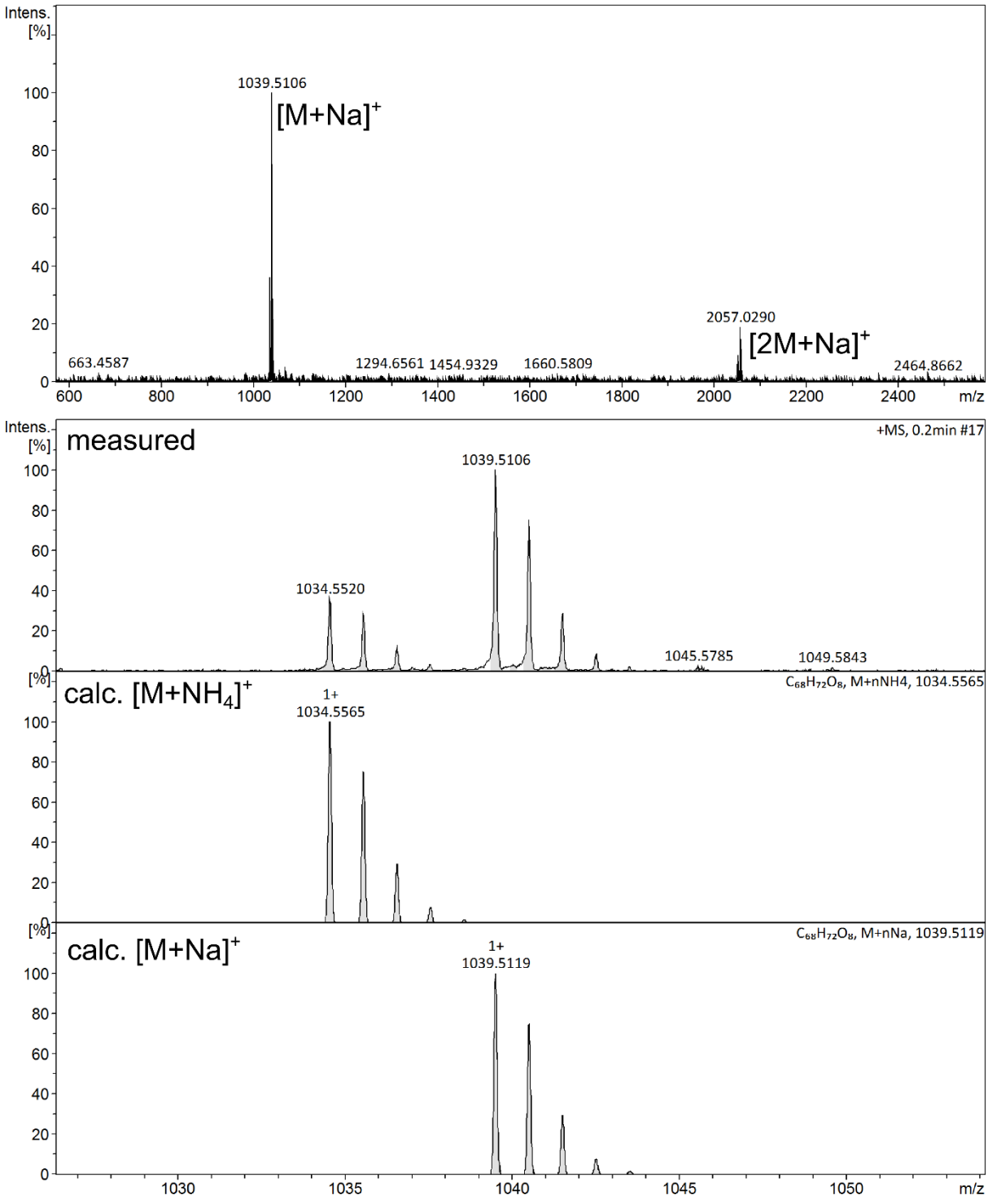


4. ESI-MS

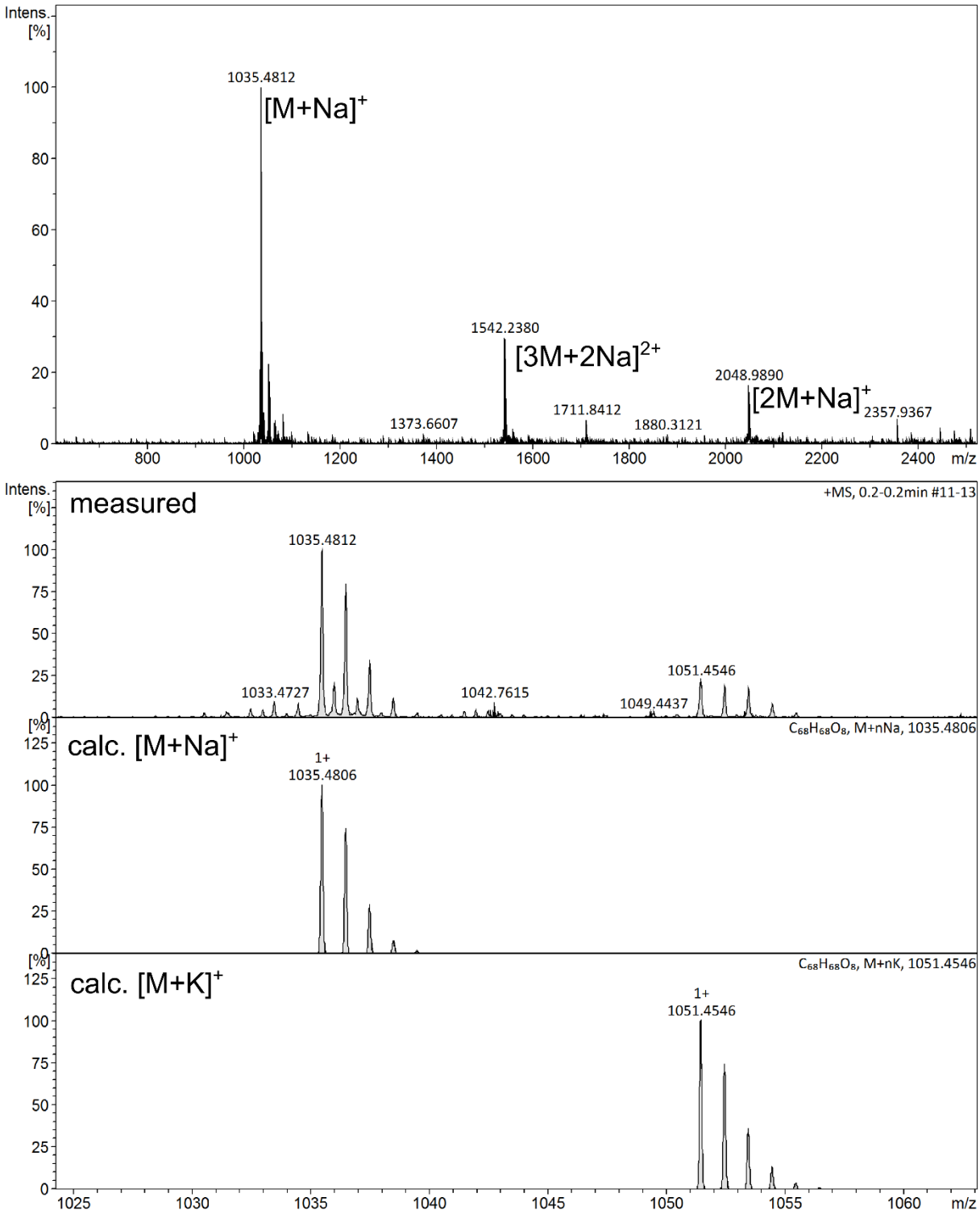
Compound **2-C_4**



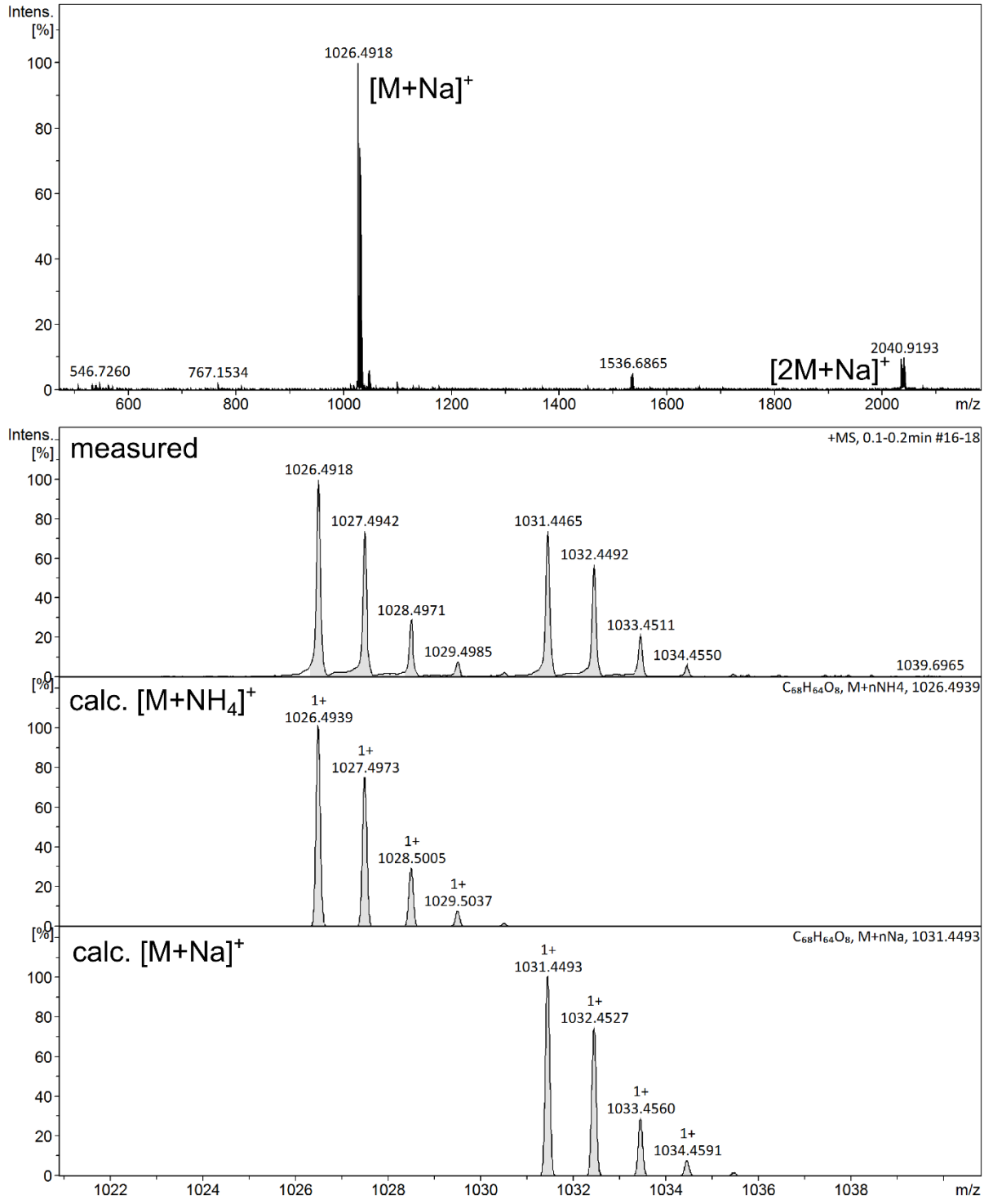
Compound **2-C_{2v}**



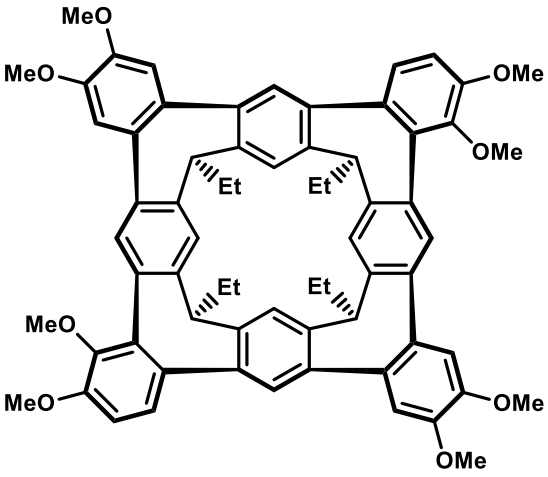
Compound **3**


Intens.
[%]
1035.4812
[M+Na]+
1542.2380
[3M+2Na]2+
2048.9890
[2M+Na]+
1373.6607
1711.8412
1880.3121
2357.9367
m/z
measured
+MS, 0.2-0.2min #11-13
1033.4727
1042.7615
1049.4437
1051.4546
C68H68O8, M+nNa, 1035.4806
calc. [M+Na]+
1+
1035.4806
C68H68O8, M+nK, 1051.4546
calc. [M+K]+
1+
1051.4546

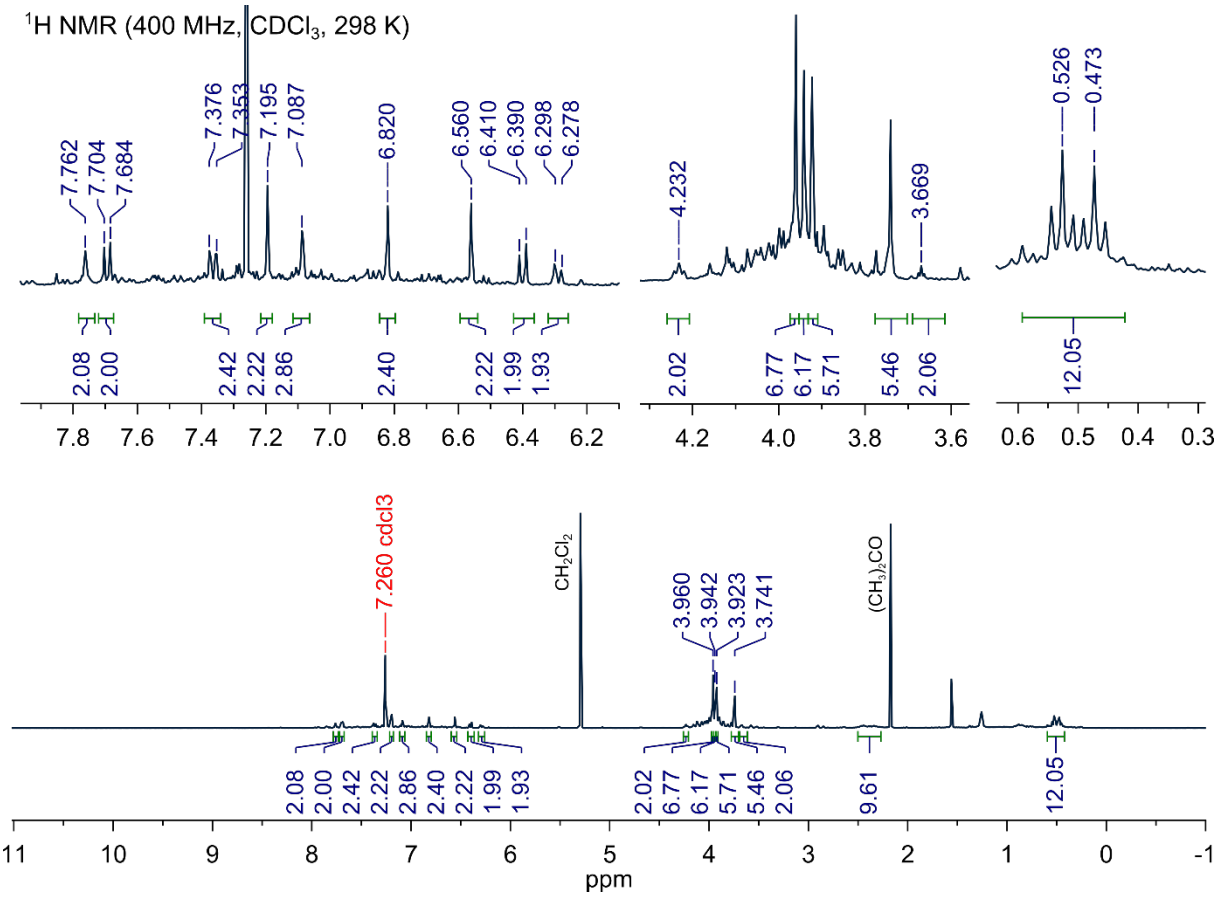
Compound **4.**


Intens.
[%]
1026.4918
[M+Na]+
546.7260
767.1534
1536.6865
2040.9193
[2M+Na]+
m/z
measured
+MS, 0.1-0.2min #16-18
1026.4918
1027.4942
1028.4971
1029.4985
1031.4465
1032.4492
1033.4511
1034.4550
1039.6965
calc. [M+NH4]+
C68H64O8, M+nNH4, 1026.4939
1+
1026.4939
1+
1027.4973
1+
1028.5005
1+
1029.5037
calc. [M+Na]+
C68H64O8, M+nNa, 1031.4493
1+
1031.4493
1+
1032.4527
1+
1033.4560
1+
1034.4591

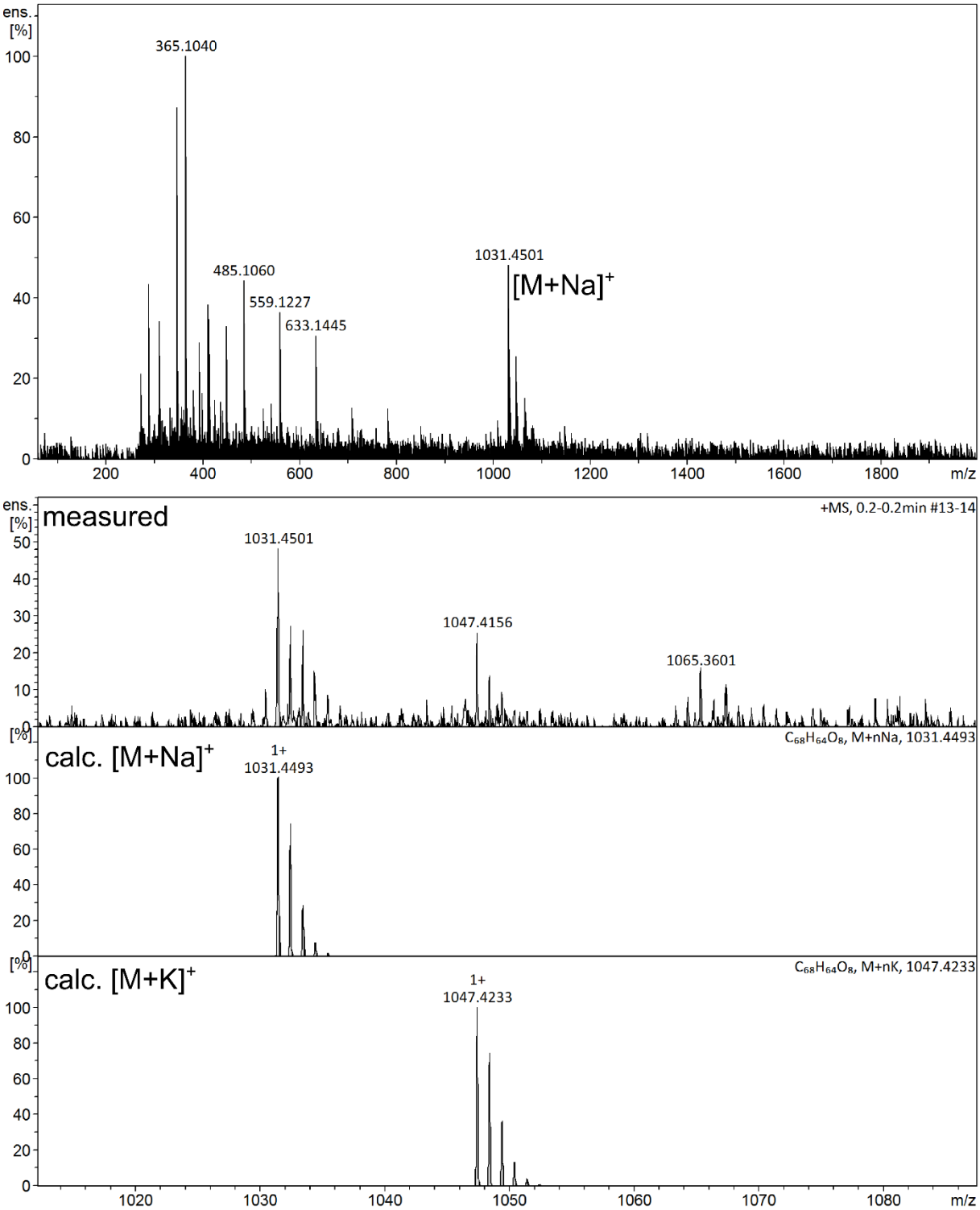
5. Compound 10



The oxidative cyclodehydrogenation of **2-C_4** using the $FeCl_3/CH_3NO_2$ method returned a complex mixture of products that could not be separated by column chromatography. A single, impure fraction contained a compound, likely possessing two-fold symmetry as consistent with **10**. Repeated attempts at crystallisation were unsuccessful. The ^{1}H NMR spectrum shows four signals at ca 3.9 ppm, consistent with methoxy-protons. Two triplets at similar frequency are seen at ca. 0.5 ppm, consistent with the methyl protons of the ethyl feet. Nine aromatic signals are seen where eight are expected, likely due to the obvious impurities. HR-ESI-MS supports the structural assignment for this fraction.



ESI-MS for Compound **10**



6. Crystallography

6.1 Experimental Details

Data were collected on an Agilent SuperNova with Atlas CCD using mirror monochromated microfocus Cu K_α radiation (λ = 1.54184 Å) at 40 W. The data processing was undertaken within CrysAlisPro,[4] including a numerical absorption correction over a face-indexed model and/or a multiscan empirical correction. The structures were solved by direct methods with SHELXT2014 or SHELXS2014[5-6] and extended and refined against all F^2 data with SHELXL2014[5] using the X-Seed[7] interface. The non-hydrogen atoms in the asymmetric unit were modelled with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined using a riding model with fixed C−H distances (sp^2 CH 0.95 Å, sp^3 CH_3 0.98 Å, sp^3 CH_2 0.99 Å; sp^3 CH 1.00 Å,) and isotropic displacement parameters estimated as U_{iso}(H) = 1.2U_{eq}(C), except for CH_3, where U_{iso}(H) = 1.5U_{eq}(C).

Many structures contained disordered fragments and/or solvent molecules that were modelled with the aid of geometric (SADI, DFIX, FLAT, EXYZ) and ADP (RIGU, SIMU, EADP, ISOR) restraints/constraints. Where structures contained regions of highly disordered solvent that could not be adequately modelled, the PLATON SQUEEZE[8] function was used. Details of the SQUEEZE process for each structure, including the volume and electron count for the disordered regions (per unit cell), and suggested solvent contents, are included in Table S1. Water molecules in structures **2-C_{2v}** were modelled without hydrogen atoms as insufficient residual electron density was observed for their localisation.

CCDC 1826428–1826432, 1834922 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Table S1. X-ray crystallography data and structure refinement parameters

	2-C_{2v}·0.5H_2O	**2-C_4**·2$CHCl_3$	**3**·1.5$CHCl_3$
CCDC No.	**1826428**	**1826429**	**1826430**
Formula	$C_{68}H_{73}O_{8.5}$	$C_{70}H_{74}Cl_6O_8$	$C_{139}H_{139}Cl_9O_{16}$
M	1026.25	1255.98	2384.54
T (K)	100	100	100
Crystal system	triclinic	triclinic	triclinic
Space group	P–1 (#2)	P–1 (#2)	P–1 (#2)
a (Å)	12.3530(4)	13.6525(4)	14.3309(4)
b (Å)	14.6695(4)	15.3663(4)	18.0783(5)
c (Å)	16.1299(5)	17.4716(5)	24.9943(5)
α (°)	93.266(2)	109.493(3)	72.549(2)
β (°)	105.038(3)	102.788(3)	80.550(2)
γ (°)	100.126(3)	99.544(2)	75.159(2)
V (Å^3)	2762.64(15)	3253.02(17)	5944.5(3)
Z [Z']	2	2	2 [2]
Crystal description	colourless block	colourless prism	pale yellow irregular
Crystal size (mm^3)	0.20 × 0.08 ×0.05	0.24 × 0.09 ×0.08	0.31 × 0.16 × 0.08
μ (mm^{-1})	0.633	2.841	2.477
$2\theta_{max}$, $2\theta_{full}$ (°)	149.63, 134.00	148.38, 134.00	148.53, 134.00
$N_{measured\ refl}$	31061	24041	45719
$N_{independent\ refl}$ [R_{int}]	11056 [0.0355]	12810 [0.0292]	23441 [0.0360]
$N_{observed\ refl}$ [$I > 2\sigma(I)$]	8798	10680	17397
$N_{parameters}$	906	812	1632
$N_{restraints}$	78	0	348
R [$I > 2\sigma(I)$]	0.0559	0.0449	0.0984
wR [all data]	0.1570	0.1274	0.3244
GOF	1.027	1.031	1.248
SQUEEZE details (per unit cell)	-	-	-
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.750, –0.502	0.923, –0.547	1.537, –0.835

Table S1 (continued). X-ray crystallography data and structure refinement parameters

	4·CH_2Cl_2	**4**·7DMSO	**4**·3.5(EtPh)
CCDC No.	**1826431**	**1826432**	**1834922**
Formula	$C_{138}H_{132}Cl_4O_{16}$	$C_{164}H_{212}O_{30}S_{14}$	$C_{96}H_{99}O_8$
M	2188.22	3112.16	1380.75
T (K)	100	100	100
Crystal system	triclinic	triclinic	triclinic
Space group	P–1 (#2)	P–1 (#2)	P–1 (#2)
a (Å)	17.7109(5)	16.7858(4)	14.2685(3)
b (Å)	19.3230(7)	20.0431(4)	14.5929(2)
c (Å)	21.2976(7)	25.8482(5)	19.2492(3)
α (°)	78.212(3)	87.859(2)	101.4820(10)
β (°)	65.437(3)	88.846(2)	91.2600(10)
γ (°)	66.098(3)	68.982(2)	95.4360(10)
V (Å^3)	6054.9(4)	8111.9(3)	3906.74(12)
Z [Z']	2 [2]	2 [2]	2
Crystal description	colourless plate	light yellow block	colourless plate
Crystal size (mm^3)	0.17 × 0.15 × 0.08	0.41 × 0.27 × 0.18	0.25 × 0.23 × 0.05
μ (mm^{-1})	1.398	2.307	0.570
$2\theta_{max}$, $2\theta_{full}$ (°)	149.69, 134.00	149.09, 134.00	149.77, 134.00
$N_{measured\ refl}$	45912	63304	73852
$N_{independent\ refl}$ [R_{int}]	24089 [0.0408]	32042 [0.0260]	15664 [0.0249]
$N_{observed\ refl}$ [$I > 2\sigma(I)$]	18185	27481	13432
$N_{parameters}$	1499	2000	998
$N_{restraints}$	34	249	315
R [$I > 2\sigma(I)$]	0.0667	0.1001	0.0885
wR [all data]	0.1820	0.2868	0.0970
GOF	1.022	1.040	1.025
SQUEEZE details	10 CH_3OH, 2 H_2O	4 H_2O	-
(per unit cell)	(697 Å^3, 214 e)	(160 Å^3, 50 e)	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.671, –0.449	2.533, –2.463	0.916, –0.696

6.2 Crystal structures not detailed in main text

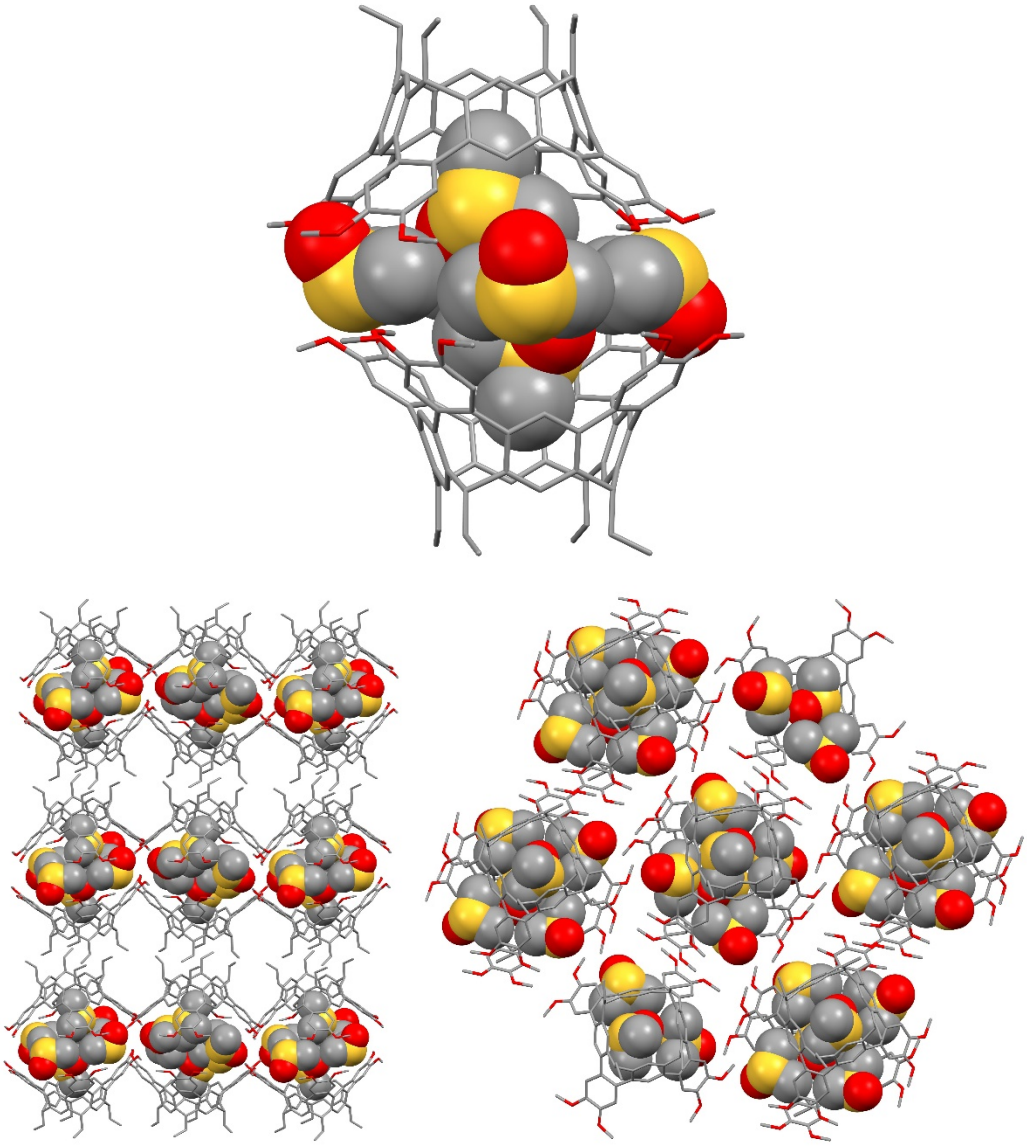


Figure S1. Stick diagrams of **4** showing encapsulation of 6 DMSO molecules in space-filling representation. Hydrogen atoms and non-encapsulated DMSO molecules omitted for clarity.

6.3 ORTEP Diagrams

Representative ORTEP diagrams of the asymmetric unit (ASU) with 50% probability ellipsoids are shown for all compounds analysed crystallographically. Labels are omitted as required for clarity.

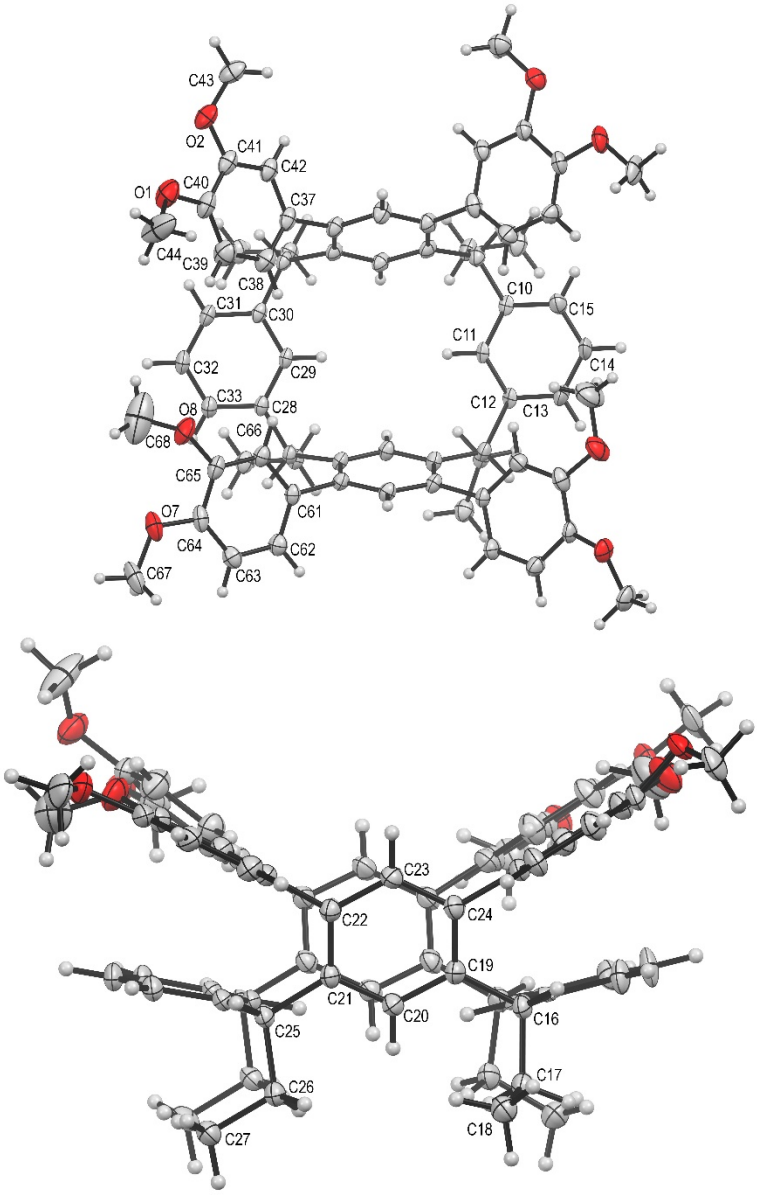


Figure S2. ORTEP diagram of the ASU of **2-C_{2v}**·0.5H_2O shown in top and side views. The 2nd component of disorder is omitted for clarity. The partial water molecule split over three sites in a highly disordered region of the structure.

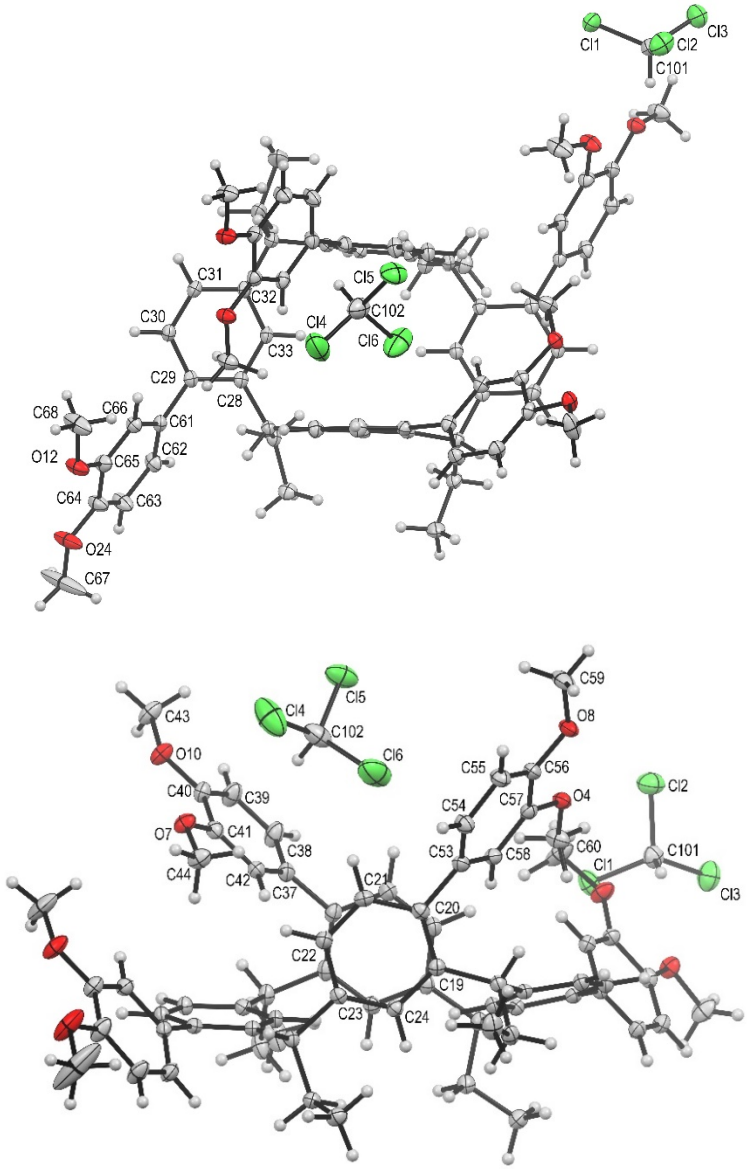


Figure S3. ORTEP diagram of the ASU of **2-*C*$_4$**·2CHCl$_3$ shown in top and side views.

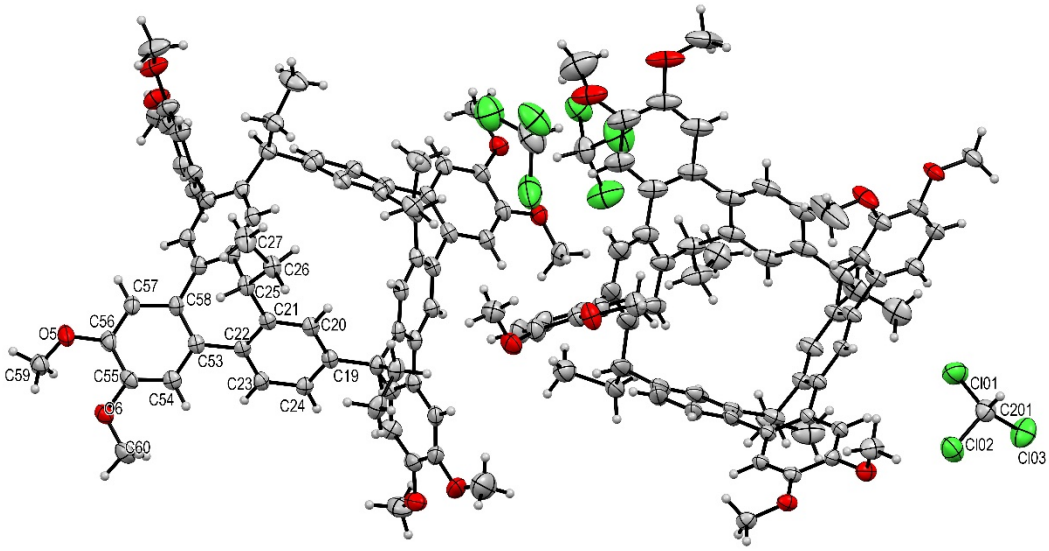


Figure S4. ORTEP diagram of the ASU of **3**·1.5CHCl$_3$. The 2nd component of disorder is omitted for clarity

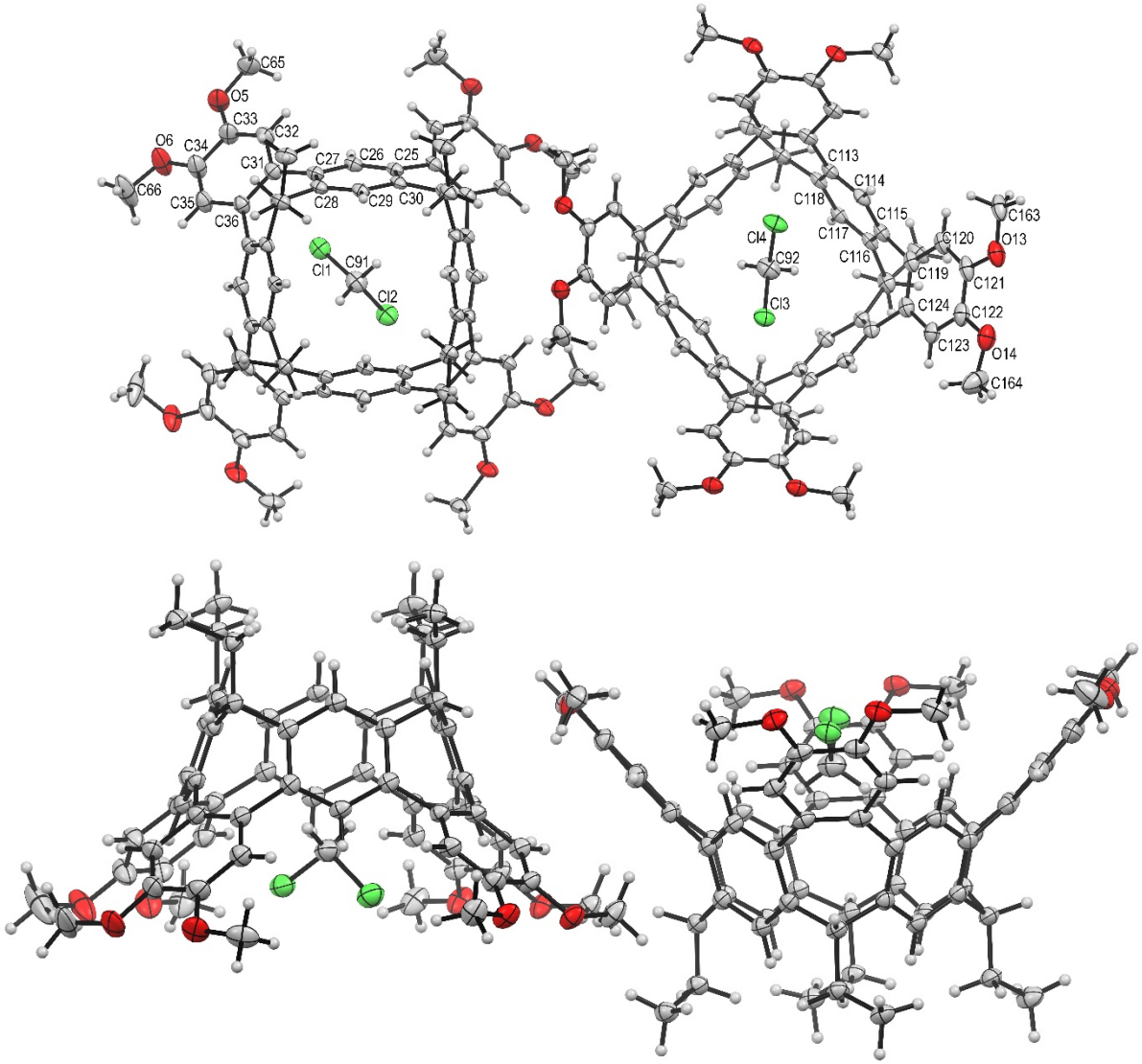


Figure S5. ORTEP diagram of the ASU of **4**·CH_2Cl_2 shown in top and side views. The 2nd component of disorder is omitted for clarity.

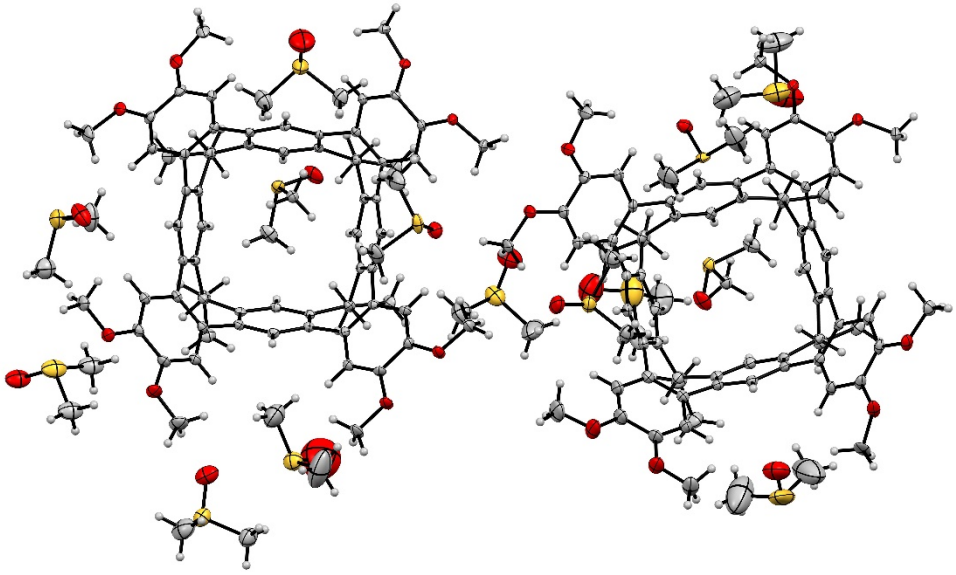


Figure S6. ORTEP diagram of the ASU of **4**·7DMSO. 10 of the 14 DMSO molecules in the ASU are disordered, with the 2nd component omitted for clarity.

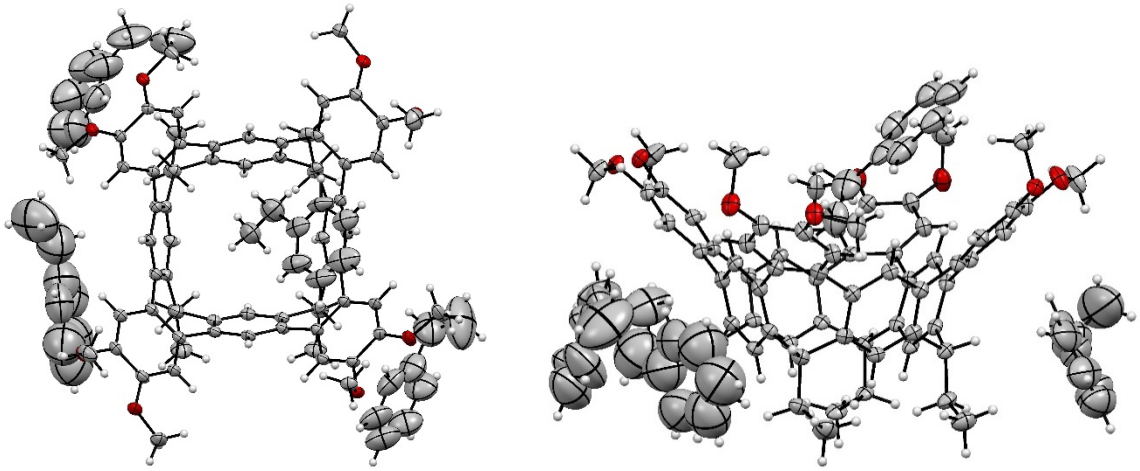


Figure S7. ORTEP diagram of the ASU of **4**·3.5(EtPh) in top and side views. The 2nd component of disorder is omitted for clarity.

6.4 Structural Comparison of 4 to Related Structures

Structural dissimilarities in the solid state between **4** and Cram-type caviplexes **1a** and **1b** are primarily in the angles of the conical core and extended walls, driven by the size of the unsaturated rings and flexibility in the walls (Figure S7, Table S2). The angle at the conical core (α) of **4** is approximately half that of **1b** and increases across the series with increasing size of the unsaturated ring. The angle between arylene walls of **4** approaches 90°, while the angle of **1b** in the vase conformation shows an inward inflection with a β angle of –18.8°.

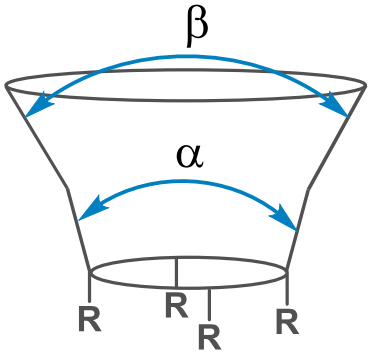


Figure S8. Diagram of cavitand showing angles α and β.

Table S2. Structural comparison between cavitands **4**, **1a** and **1b** in the solid state

Cavitand	**4**	**1a**[a]	**1b**[b]
Ring size	7	8	9
α (°)	36.3	58.2	73.7
β (°)	88.3	-	–18.8

[a]R = Me, caviplex binding CH_2Cl_2.[9] [b]R = $CH_2CH_2CH_2COOMe$, caviplex in vase conformation binding MeCN.[10]

7. References

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