*Electronic Supporting Information*

*for:*

# One-pot regioselective synthesis and X-ray crystal structure of a stable [60]fullerene trisadduct with the $e_{\text{edge}}$,$e_{\text{face}}$,*trans*-1 addition pattern

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## General experimental

All starting materials were purchased from commercial sources and used without further purification. The solvents were dried using standard techniques. Reactions were monitored by thin layer chromatography on silica gel 60 $F_{254}$ (Merck) aluminum plates. After development TLC plates were stained with phosphomolybdic acid (PMA). Products were isolated by column chromatography (silica gel 60, particle size 0.04-0.063 mm, Merck). $^1$H- and $^{13}$C NMR spectra were recorded on a Bruker Avance 300 MHz and a Bruker Avance III 500 Ultrashield Plus 500 MHz spectrometers. The chemical shifts are given in ppm relative to the appropriate solvent peak as standard reference. The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), or combinations of those. Broad resonances are designated with br. High resolution (EI and ESI) mass spectra were recorded on a Thermo Finnigan Mat 95 instrument. Atmospheric pressure chemical ionisation (APCI) mass spectra were recorded on a Micromass Platform II spectrometer. High resolution MALDI TOF mass spectra were recorded on a Bruker Autoflex III Smartbeam instrument using graphite as a matrix. UV/Vis spectra were recorded on a Shimadzu UV-3600 spectrometer. IR spectra were recorded on a Shimadzu IR Prestige-21 spectrometer. The spectra were measured as a film on NaCl plates. Melting points (mp) were determined on a Stuart Scientific SMP10 apparatus and were uncorrected.

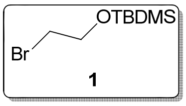
## X-ray Crystallography

Data were collected on an Oxford-Diffraction diffractometer, equipped with a CCD area detector and a graphite monochromator utilizing Mo-$K_a$ radiation (l = 0.71073 Å). Suitable crystals were attached to glass fibers using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Unit cell dimensions were determined and refined by using 9172 ($2.94 \leq \theta \leq 28.95^\circ$) and 22893 ($2.89 \leq \theta \leq 28.98^\circ$) reflections for **9**·$2CH_2Cl_2$ and **10**·$1CH_2Cl_2$ respectively. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software.[1] The structures were solved by direct methods using SIR92[2a] and refined on $F^2$ using full-matrix least squares using SHELXL97.[2b] Programs used: CrysAlis CCD[1] for data collection, CrysAlis RED[1] for cell refinement and data reduction, and DIAMOND[3a] and MERCURY[3b] for molecular graphics. The non-H atoms were treated anisotropically whereas, the hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms.

Unit cell data and structure refinement details are listed in Table S1, page S22. Full details can be found in the CIF files provided in the Supporting Information material.

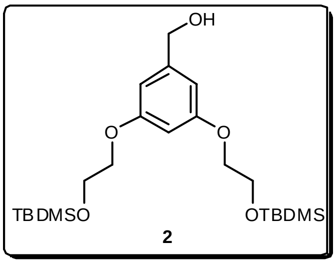
Compound **10**·1$CH_2Cl_2$ contains severely disordered lattice $CH_2Cl_2$ molecules that could not be modeled properly thus, program SQUEEZE, a part of the PLATON package of crystallographic software was used to calculate the solvent disorder area and remove its contribution from the intensity data.[4]

### (2-Bromoethoxy)(*tert*-butyl)dimethylsilane (1)[5,6]



(2-Bromo-ethoxy)-*tert*-butyl-dimethyl-silane **1** was synthesized according to a literature procedure.[1] $^1$H-, $^{13}$C NMR resonances and IR were in good agreement with the data reported in the literature.[6]

### [3,5-Bis(2-{[*tert*-butyl(dimethyl)silyl]oxy}ethoxy)phenyl]methanol (2)[7]



3,5-Dihydroxybenzyl alcohol (2.12 g, 15.10 mmol), 18-crown-6 (3.00 g, 12.80 mmol), anhydrous $K_2CO_3$ (26.13 g, 18.90 mmol), dry acetone (500 mL) and (2-bromoethoxy)(*tert*-butyl)dimethylsilane **1** (18.00 g, 75.60 mmol) were placed in a dry 1000 mL single-necked round-bottomed flask fitted with a condenser and a magnetic stirrer. The resulting mixture was stirred for two days at 56 °C, under nitrogen atmosphere. The solution was concentrated and the residue was partitioned between equal volumes of $CH_2Cl_2$ and water. The organic layer was separated, washed with water, brine and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave an oil which was purified by column chromatography on silica gel (hexane : EtOAc = 7 : 3) to afford product **2** as a yellow oil (5.27 g, 76%).

***R<sub></sub>***$R_f$ = 0.33 ($SiO_2$, hexane : EtOAc = 7 : 3, stain: PMA).

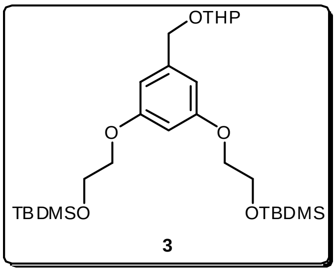
**$^1$H NMR** (300 MHz, $CDCl_3$): $\delta_H$ 6.52 (2H, d, $^4J_{H\text{-}H}$ = 2.4 Hz, 2 x *ortho*-C*H* ar.), 6.40 (1H, apparent t, $^4J_{H\text{-}H}$ = 2.4 Hz, *para*-C*H* ar.), 4.62 (2H, d, $J$ = 5.7 Hz, C$H_2$OH), 4.04-4.00 (4H, m, OC$H_2$C$H_2$O), 3.97-3.93 (4H, m, OC$H_2$C$H_2$O), 1.61 (1H, t, $J$ = 6.0 Hz, O*H*), 0.91 (18H, s, 2 x C(C$H_3$)$_3$), 0.10 (12H, s, 2 x Si(C$H_3$)$_2$).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): $\delta_C$ 160.29 (*meta*-*C* ar.), 143.23 (*C* ar.), 105.24 (*ortho*-*C*H ar.), 100.83 (*para*-*C*H ar.), 69.35 (O*C*$H_2CH_2$O), 65.41 (C*C*$H_2$OH), 61.95 (O$CH_2$*C*$H_2$O), 25.91 (-SiC(*C*$H_3$)$_3$), 18.41 (-Si*C*($CH_3$)$_3$), -5.19 (-Si(*C*$H_3$)$_2$).

**IR**, $\nu_{max}$ (NaCl, evap. film)/cm$^{-1}$: 3385, 3084, 2955, 2936, 2858, 1603, 1464, 1398, 1359, 1254, 1173, 1014, 841.

**HRMS** (EI+): calculated for $C_{23}H_{44}O_5Si_2$ [M]$^+$ requires 456.2722; found: 456.2718.

### ***tert*-Butyl(2-{3-(2-{[isopropyl(dimethyl)silyl]oxy}ethoxy)-5-[(tetrahydro-2*H*-pyran-2-yloxy)methyl]phenoxy}ethoxy)dimethylsilane (3)**[8]



**3**

Pyridinium *p*-toluenesulfonate (PPTS) (0.40 g, 1.59 mmol) was added into a dry 250 mL single-necked round-bottomed flask, containing a stirred solution of **2** (5.10 g, 11.18 mmol) and dihydropyran (DHP) (2.70 mL, 2.49 g, 29.59 mmol) in dry $CH_2Cl_2$ (80 mL), under a nitrogen atmosphere. The resulting mixture was stirred for twelve hours at room temperature. The solution was then washed with brine and finally dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave an oil which was purified by column chromatography on silica gel ($CH_2Cl_2$ : EtOAc = 9.5 : 0.5) to afford product **3** as a yellow oil (5.30 g, 87%).

***$R_f$*** = 0.88 ($SiO_2$, $CH_2Cl_2$ : EtOAc = 9.5 : 0.5, stain: PMA).

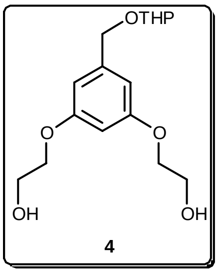
**$^1$H NMR** (300 MHz, $CDCl_3$): $\delta_H$ 6.52 (2H, d, $^4J_{H\text{-}H}$ = 2.1 Hz, 2 x *ortho*-C*H* ar.), 6.39 (1H, apparent t, $^4J_{H\text{-}H}$ = 2.2 Hz, *para*-C*H* ar.), 4.71 (1H, d, *J* = 12.3 Hz, CC*H*$_2$OCH), 4.69 (1H, t, *J* = 3.4 Hz, OC*H*O), 4.44 (1H, d, *J* = 12.3 Hz, CC*H*$_2$OCH), 4.03-3.93 (8H, m, 2 x OC*H*$_2$C*H*$_2$O), 3.92-3.88 (1H, m, $CH_2$C*H*$_2$O), 3.58-3.50 (1H, m, $CH_2$C*H*$_2$O), 1.94-1.51 (6H, m, C*H*$_2$C*H*$_2$C*H*$_2$$CH_2$O), 0.91 (18H, s, 2 x C(C*H*$_3$)$_3$), 0.10 (12H, s, 2 x Si(C*H*$_3$)$_2$).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): $\delta_C$ 160.09 (*meta*-*C* ar.), 140.59 (*C* ar.), 106.23 (*ortho*-*C*H ar.), 100.72 (*para*-*C*H ar.), 97.64 (O*C*HO), 69.29 (O*C*$H_2CH_2$O), 68.66 (C*C*$H_2$OCH), 62.16 ($CH_2CH_2CH_2$*C*$H_2$O), 61.95 (O$CH_2$*C*$H_2$O), 30.56 (*C*$H_2$ from THP), 25.92 (-SiC(*C*$H_3$)$_3$), 25.46 (*C*$H_2$ from THP), 19.36 (*C*$H_2$ from THP), 18.40 (-Si*C*($CH_3$)$_3$), -5.20 (-Si(*C*$H_3$)$_2$).

**IR**, $\nu_{max}$ (NaCl, evap. film)/cm$^{-1}$: 3083, 2934, 2858, 1601, 1460, 1391, 1352, 1290, 1254, 1171, 1126, 1068, 1030, 837, 777.

**HRMS** (EI+): calculated for $C_{28}H_{52}O_6Si_2$ [M – $CH_3$]$^+$ requires 525.3062; found: 525.3069.

## 2,2'-[{5-[(Tetrahydro-2*H*-pyran-2-yloxy)methyl]-1,3-phenylene}bis(oxy)]diethanol (4)[9]

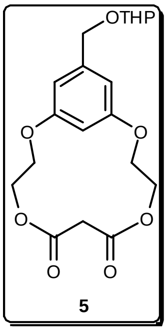


**4**

In a dry 100 mL single-necked round-bottomed flask equipped with a magnetic stirrer, **3** (4.40 g, 8.14 mmol) was dissolved in dry THF (40 mL) under a nitrogen atmosphere. Tetrabutylammonium fluoride (TBAF) (7.30 mL, 6.59 g, 25.22 mmol) was then added and the resulting mixture was stirred for four hours at room temperature. The solvent was then removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc : hexane = 9 : 1) to afford product **4** as a colourless oil (2.40 g, 94%).

***R**$_f$* = 0.29 ($SiO_2$, EtOAc : hexane = 9 : 1, stain: PMA).
$^1$**H NMR** (300 MHz, $CDCl_3$): $\delta_H$ 6.56 (2H, d, $^4J_{H\text{-}H}$ = 2.1 Hz, 2 x *ortho*-C*H* ar.), 6.42 (1H, apparent t, $^4J_{H\text{-}H}$ = 2.1 Hz, *para*-C*H* ar.), 4.72 (1H, d, *J* = 12.3 Hz, $CC\mathit{H}_2OCHO$), 4.69 (1H, t, *J* = 3.9 Hz, $CCH_2OC\mathit{H}O$), 4.44 (1H, d, *J* = 12.3 Hz, $CC\mathit{H}_2OCHO$), 4.08-4.05 (4H, m, $OC\mathit{H}_2C\mathit{H}_2O$), 3.97-3.92 (4H, m, $OC\mathit{H}_2C\mathit{H}_2O$), 3.91-3.87 (1H, m, $CH_2CH_2CH_2C\mathit{H}_2O$), 3.58-3.51 (1H, m, $CH_2CH_2CH_2C\mathit{H}_2O$), 2.07 (2H, t, *J* = 6.0 Hz, 2 x O*H*), 1.89-1.52 (6H, m, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_2O$).
$^{13}$**C NMR** (75 MHz, $CDCl_3$): $\delta_C$ 159.80 (*meta*-*C* ar.), 140.96 (*C* ar.), 106.47 (*ortho*-*C*H ar.), 100.68 (*para*-*C*H ar.), 97.74 (O*C*HO), 69.22 ($O\mathit{C}H_2CH_2O$), 68.55 ($C\mathit{C}H_2OCH$), 62.20 ($CH_2CH_2CH_2\mathit{C}H_2O$), 61.42 ($OCH_2\mathit{C}H_2O$), 30.53 (*C*$H_2$ from THP), 25.41 (*C*$H_2$ from THP), 19.34 (*C*$H_2$ from THP).
**IR**, $\nu_{max}$ (NaCl, evap. film)/cm$^{-1}$: 3364, 3031, 2926, 2866, 1597, 1448, 1358, 1321, 1294, 1167, 1061, 901, 835, 743, 696.
**HRMS** (ESI-): calculated for $C_{16}H_{23}O_6$ $[M - H]^-$ requires 311.1500; found: 311.1488.

## 15-[(Tetrahydro-2*H*-pyran-2-yloxy)methyl]-2,5,9,12-tetraoxabicyclo[11.3.1]heptadeca-1(17),13,15-triene-6,8-dione (5)

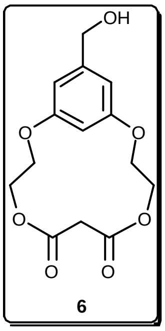


**5**

In a dry 1000 mL three-necked round-bottomed flask equipped with gas inlet, dropping funnel and magnetic stirrer, **4** (0.25 g, 0.66 mmol) was dissolved in dry $CH_2Cl_2$ (550 mL) followed by the addition of pyridine (0.11 mL, 1.32 mmol) and $KBF_4$ (0.83 g, 6.60 mmol). The mixture was stirred at room temperature for 15 minutes. Subsequently, a solution of malonyl dichloride (0.08 mL, 0.79 mmol) in dry $CH_2Cl_2$ (125 mL) was added dropwise during a period of 7 hours. After stirring overnight at room temperature the mixture was filtered to remove the remaining $KBF_4$ and the filtrate was washed with water. The organic phase was dried over anhydrous $MgSO_4$, filtered, absorbed on $SiO_2$ and chromatographed on a $SiO_2$ column (hexane : EtOAc = 6 : 4) to afford the product **5** as a white solid (0.018 mg, 7%).

***$R_f$***= 0.37 ($SiO_2$, hexane : EtOAc = 6 : 4, stain: PMA).
**m.p.** 108 °C.
**$^1$H NMR** (300 MHz, $CDCl_3$): $\delta_H$ 6.73 (1H, br s, *para*-C*H* ar.), 6.58 (2H, d, $^4J_{H\text{-}H}$ = 1.8 Hz, 2 x *ortho*-C*H* ar.), 4.72-4.68 (2H, m, $CCH_2OCHO$), 4.43-4.38 (9H, m, $CCH_2OCHO$ and 2 x $OCH_2CH_2O$), 3.94-3.87 (1H, m, $CH_2CH_2CH_2CH_2O$), 3.57-3.52 (1H, m, $CH_2CH_2CH_2CH_2O$), 3.37 (2H, s, $COCH_2CO$), 1.93-1.52 (6H, m, $CH_2CH_2CH_2CH_2O$).
**$^{13}$C NMR** (75 MHz, $CDCl_3$): $\delta_C$ 165.87 (*C*=O), 160.00 (*meta*-*C* ar.), 141.01 (*C* ar.), 110.11 (*ortho*-CH ar.), 100.08 (*para*-CH ar.), 97.74 (OCHO), 68.19 ($CCH_2OCH$), 66.72 ($OCH_2CH_2O$), 66.54 ($OCH_2CH_2O$), 62.02 ($CH_2CH_2CH_2CH_2O$), 41.84 ($COCH_2CO$), 30.49 ($CH_2$ from THP), 25.43 ($CH_2$ from THP), 19.23 ($CH_2$ from THP).
**IR**, $\nu_{max}$ (NaCl, evap. film)/cm$^{-1}$: 2918, 2849, 2361, 2332, 1738, 1611, 1589, 1454, 1367, 1312, 1259, 1161, 1117, 1074, 1032, 970, 905, 868, 814, 683.
**HRMS** (EI+): calculated for $C_{14}H_{15}O_6$ $[M - C_5H_9O_2]^+$ requires 279.0863; found: 279.0851.

### 15-(Hydroxymethyl)-2,5,9,12-tetraoxabicyclo[11.3.1]heptadeca-1(17),13,15-triene-6,8-dione (6)



**6**

In a 50 mL single-necked round-bottomed flask equipped with magnetic stirrer, **5** (0.130 g, 0.340 mmol) was dissolved in MeOH-$CH_2Cl_2$ (5 : 2, 14 mL) followed by the addition of a catalytic amount of PPTS (0.008 g, 0.034 mmol). After stirring at room temperature for 48 hours, the mixture was diluted with $CH_2Cl_2$ and washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent under reduced pressure afforded the crude mixture which was chromatographed on a $SiO_2$ column ($CH_2Cl_2$ : EtOAc = 7 : 3) to afford product **6** as a white solid (0.091 g, 90%).

***$R_f$***= 0.40 ($SiO_2$, $CH_2Cl_2$ : EtOAc = 7 : 3, stain: PMA).
**m.p.** 150 °C.

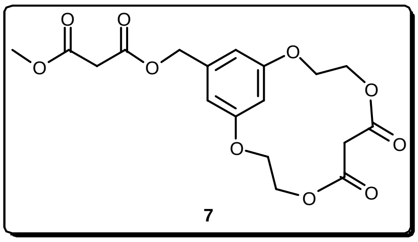
**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta_H$ 6.73 (1H, br s, *para*-C*H* ar.), 6.58 (2H, d, $^4J_{H\text{-}H}$ = 1.5 Hz, 2 x *ortho*-C*H* ar.), 4.60 (2H, d, *J* = 6.0 Hz, $CCH_2OH$), 4.47-4.45 (4H, m, $OCH_2CH_2O$), 4.43-4.41 (4H, m, $OCH_2CH_2O$), 3.36 (2H, s, $COCH_2CO$), 1.63 (1H, t, *J* = 6.0 Hz, O*H*).

**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta_C$ 165.85 (*C*=O), 160.20 (*meta*-*C* ar.), 143.55 (*C* ar.), 109.36 (*ortho*-*C*H ar.), 100.22 (*para*-*C*H ar.), 66.70 ($OCH_2CH_2O$), 66.53 ($OCH_2CH_2O$), 64.90 ($CCH_2OH$), 41.83 ($COCH_2CO$).

**IR**, $\nu_{max}$ (NaCl, evap. film)/cm$^{-1}$: 3298, 2955, 2361, 2340, 1736, 1609, 1595, 1468, 1410, 1367, 1313, 1252, 1169, 1080, 1036, 1015, 972, 957, 843, 816, 702.

**HRMS** (EI+): calculated for $C_{14}H_{16}O_7$ $[M]^+$ requires 296.0890; found: 296.0892.

### [6,8-Dioxo-2,5,9,12-tetraoxabicyclo[11.3.1]heptadeca-1(17),13,15-trien-15-yl]methyl methyl malonate (7)[10]


7

In a dry 15 mL three-necked round-bottomed flask equipped with gas inlet, dropping funnel and magnetic stirrer, **6** (0.03 g, 0.10 mmol) was dissolved in dry $CH_2Cl_2$ (3 mL) followed by the addition of pyridine (8.00 µL, 0.10 mmol). The mixture was cooled to 0 °C and a solution of methyl malonyl chloride (14.00 µL, 0.13 mmol) in dry $CH_2Cl_2$ (1 mL) was added dropwise during a period of 20 minutes. After stirring at 0 °C for 2 hours the mixture was allowed to warm at room temperature and stirred for another 12 hours. The crude mixture was absorbed on $SiO_2$ and chromatographed on a $SiO_2$ column ($CH_2Cl_2$ : EtOAc = 7 : 3) to afford product **7** as a white solid (0.04 mg, 99%).

***R$_f$***= 0.82 ($SiO_2$, $CH_2Cl_2$ : EtOAc = 7 : 3, stain: PMA).

**m.p.** 113 °C.

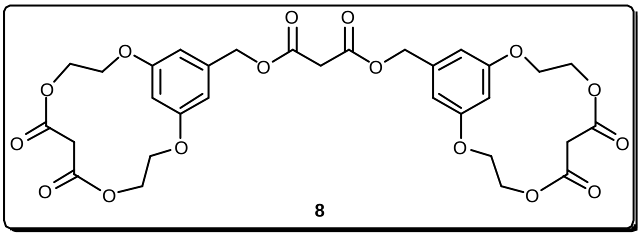
**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta_H$ 6.77 (1H, apparent t, $^4J_{H\text{-}H}$ = 2.2 Hz, *para*-C*H* ar.), 6.55 (2H, d, $^4J_{H\text{-}H}$ = 2.5 Hz, 2 x *ortho*-C*H* ar.), 5.09 (2H, s, $CCH_2OCO$), 4.46 (4H, m, $OCH_2CH_2O$), 4.42 (4H, m, $OCH_2CH_2O$), 3.76 (3H, s, $OCH_3$), 3.45 (2H, s, $COCH_2CO$), 3.37 (2H, s, $COCH_2CO$).

**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta_C$ 166.78 (*C*=O), 166.22 (*C*=O), 165.81 (*C*=O), 160.17 (*meta*-*C* ar.), 137.67 (*C* ar.), 110.41 (*ortho*-*C*H ar.), 100.68 (*para*-*C*H ar.), 66.71 ($OCH_2CH_2O$), 66.55 ($CCH_2OCO$), 66.49 ($OCH_2CH_2O$), 52.54 ($CO_2CH_3$), 41.81 ($COCH_2CO$), 41.28 ($COCH_2CO$).

**IR**, $\nu_{max}$ (NaCl, evap. film)/cm$^{-1}$: 2920, 2853, 2359, 2340, 1751, 1722, 1591, 1462, 1371, 1323, 1263, 1161, 1080, 1020, 872, 837.

**HRMS** (EI+): calculated for $C_{18}H_{20}O_{10}$ [M]$^+$ requires 396.1051; found: 396.1051.

### Bis{[6,8-dioxo-2,5,9,12-tetraoxabicyclo[11.3.1]heptadeca-1(17),13,15-trien-15-yl]methyl} malonate (8)[10]


**8**

In a dry 15 mL three-necked round-bottomed flask equipped with gas inlet, dropping funnel and magnetic stirrer, **6** (0.06 g, 0.20 mmol) was dissolved in dry $CH_2Cl_2$ (2 mL) followed by the addition of pyridine (16.00 μL, 0.20 mmol). The mixture was cooled to 0 °C and a solution of malonyl dichloride (9.00 μL, 0.09 mmol) in dry $CH_2Cl_2$ (1 mL) was added dropwise during a period of 20 minutes. After stirring at 0 °C for 2 hours the reaction mixture was allowed to warm at room temperature and stirred for another 12 h. The crude mixture was absorbed on $SiO_2$ and chromatographed on a $SiO_2$ column ($CH_2Cl_2$ : EtOAc = 7 : 3) to afford product **8** as a white solid (0.03 g, 50%) and unreacted **6** (17.00 mg, 29%).

***$R_f$***= 0.73 ($SiO_2$, $CH_2Cl_2$ : EtOAc = 7 : 3, stain: PMA).

**m.p.** 173 °C.

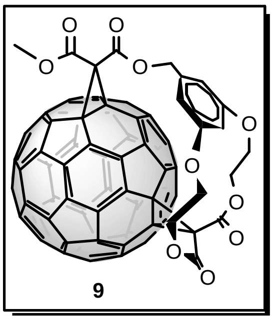
**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta_H$ 6.77 (2H, br s, 2 x *para*-C*H* ar.), 6.56 (4H, br s, 4 x *ortho*-C*H* ar.), 5.09 (4H, s, 2 x $CCH_2OCO$), 4.46-4.45 (8H, m, 2 x $OCH_2CH_2O$), 4.42-4.40 (8H, m, 2 x $OCH_2CH_2O$), 3.49 (2H, s, $COCH_2CO$), 3.36 (4H, s, 2 x $COCH_2CO$).

**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta_C$ 166.11 (*C*=O), 165.83 (*C*=O), 160.19 (*meta*-*C* ar.), 137.65 (*C* ar.), 110.49 (*ortho*-*C*H ar.), 100.78 (*para*-*C*H ar.), 66.74 ($OCH_2CH_2O$), 66.62 ($CCH_2O$-), 66.50 ($OCH_2CH_2O$), 41.81 ($COCH_2CO$), 41.46 ($COCH_2CO$).

**IR**, $\nu_{max}$ (NaCl, evap. film)/cm$^{-1}$: 2924, 2853, 2359, 2342, 1724, 1611, 1587, 1450, 1367, 1310, 1259, 1161, 1142, 1078, 1042, 957, 831, 667.

**MS** (APCI-), *m/z* (rel. intensity %): 659 ([M - H]$^-$, 30%).

## *Equatorial* bisadduct (9)



9

In a dry 250 mL three-necked round-bottomed flask equipped with gas inlet, dropping funnel and magnetic stirrer, $C_{60}$ (0.064 mg, 0.089 mmol) was dissolved in dry toluene (70 mL) under an argon atmosphere. A solution of tether **7** (0.032 mg, 0.081 mmol) in dry $CH_2Cl_2$ (30 mL) was added to the reaction mixture followed by the addition of iodine (0.041 mg, 0.162 mmol). Subsequently, a solution of DBU (0.050 mL, 0.324 mmol) in dry toluene (25 mL) was added dropwise. After stirring at room temperature for one day the crude reaction mixture was subjected to flash column chromatography on $SiO_2$. Unreacted $C_{60}$ and other impurities were eluted with toluene and the fullerene bisadduct **9** was then eluted with toluene : EtOAc = 9 : 1. Precipitation from $CHCl_3$-pentane afforded product **9** as a dark red solid (0.062 g, 68%).

***$R_f$***= 0.40 (toluene : EtOAc = 9 :1).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta_H$ 7.07 (1H, br s, *para*-C*H* ar.), 6.56 (2H, br s, 2 x *ortho*-C*H* ar.), 5.21 (2H, s, $CCH_2OCO$), 4.87-4.78 (4H, m, $OCH_2CH_2O$), 4.53 (2H, apparent t, $J$ = 13.0 Hz, $OCH_2CH_2O$), 4.23 (2H, apparent d, $J$ = 14.0 Hz, $OCH_2CH_2O$), 4.06 (3H, s, $OCH_3$).

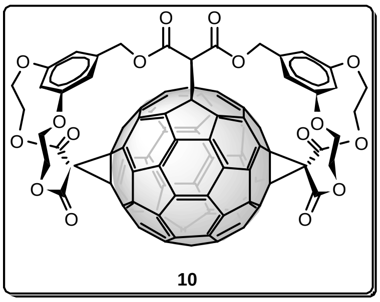
**$^{13}$C NMR** (125 MHz, $CDCl_3$): $\delta_C$ 164.75 (*C*=O), 164.11 (*C*=O), 161.56 (*C*=O), 159.78 (*meta*-*C* ar.), 147.92,$^*$ 147.29, 146.46, 146.13, 146.06, 145.57, 145.15, 145.02, 144.84, 144.79, 144.66, 144.58, 144.33, 143.99, 143.93, 143.87, 143.55, 143.33, 142.85, 142.10, 141.95, 141.58, 140.99, 140.94, 138.65, 138.52,$^*$ 135.32 (*C* ar.), 113.25 (*ortho*-CH ar.), 101.86 (*para*-*C*H ar.), 71.79 ($sp^3$ *C* of $C_{60}$), 71.42 ($sp^3$ *C* of $C_{60}$), 69.43 ($sp^3$ *C* of $C_{60}$), 69.33 ($CCH_2O$-), 67.44 ($OCH_2CH_2O$), 64.13 ($OCH_2CH_2O$), 54.03 ($CO_2CH_3$), 52.70 (COCCO), 52.31 (COCCO).

$^*$ *26 Signals from 147.92 to 138.52 ppm for $sp^2$ carbons of $C_{60}$*

**UV/Vis** ($CHCl_3$) $\lambda_{max}$/nm ($\varepsilon$/$dm^3mol^{-1}cm^{-1}$): 253 (97006), 311 (34726), 362 (12467), 397 (3805), 408 (2494), 421 (2123), 481 (2593), 689 (108).

**HRMS** (MALDI TOF, negative mode, graphite): calculated for $C_{78}H_{16}O_{10}$ $[M]^-$ requires 1112.0738; found: 1112.0739.

### *$E_{edge}$,$e_{face}$,trans*-1 trisadduct (10)



**10**

In a dry 100 mL three-necked round-bottomed flask equipped with gas inlet, dropping funnel and magnetic stirrer, $C_{60}$ (0.033 g, 0.045 mmol) was dissolved in dry toluene (35 mL) under an argon atmosphere. A solution of tether **8** (0.027 g, 0.041 mmol) in dry $CH_2Cl_2$ (15 mL) was added to the reaction mixture followed by the addition of iodine (0.031 g, 0.121 mmol). Subsequently, a solution of DBU (0.050 mL, 0.337 mmol) in dry toluene (20 mL) was added dropwise. After stirring at room temperature for one day the crude reaction mixture was subjected to flash column chromatography on $SiO_2$. Unreacted $C_{60}$ and other impurities were eluted with toluene and the fullerene trisadduct **10** was then eluted with toluene : EtOAc = 7 : 3. Precipitation from $CHCl_3$-pentane afforded product **10** as a dark red solid (0.037 g, 65%).

***$R_f$***= 0.58 ($SiO_2$, toluene : EtOAc = 7 : 3).

**$^1$H NMR** (500 MHz, $C_2D_4Cl_2$): $\delta_H$ 7.15 (2H, apparent t, $J$ = 2 Hz, 2 x *para*-C*H* ar.), 6.59 (4H, d, $J$ = 2.5 Hz, 4 x *ortho*-C*H* ar.), 5.22 (4H, s, 2 x CC*H*$_2$OCO), 4.91-4.85 (8H, m, 2 x OC*H*$_2$C*H*$_2$O), 4.60-4.56 (4H, m, OC*H*$_2$C*H*$_2$O), 4.28-4.53 (4H, m, OC*H*$_2$C*H*$_2$O), 4.30-4.26 (4H, m, OC*H*$_2$C*H*$_2$O).

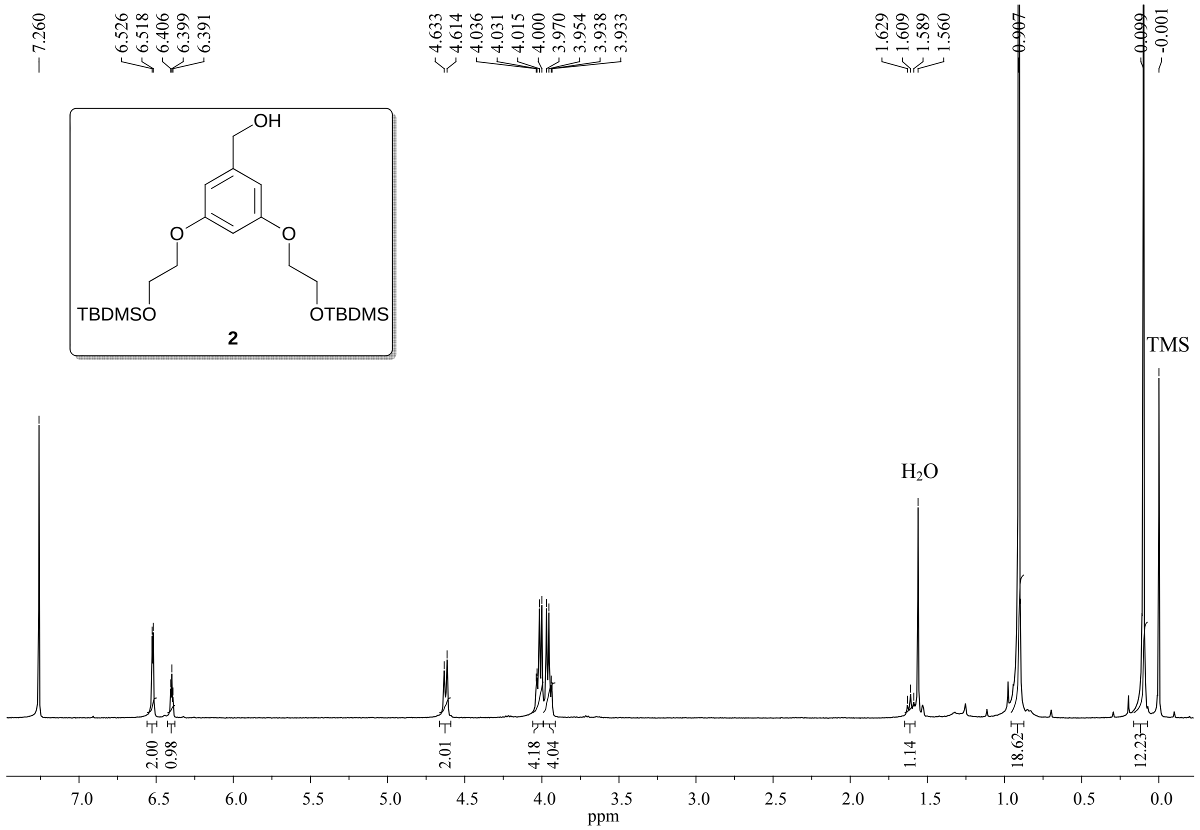
**$^{13}$C NMR** (125 MHz, $C_2D_4Cl_2$): $\delta_C$ 164.77 (*C*=O), 161.98 (*C*=O), 160.15 (*meta*-*C* ar.), 147.38,$^*$ 146.20, 146.02, 145.08, 144.76, 144.68, 144.34, 143.81, 143.70, 142.93, 141.77, 141.23, 139.93, 139.52,$^*$ 135.93 (*C* ar.), 113.22 (*ortho*-*C*H ar.), 101.76 (*para*-*C*H ar.), 72.27 (sp$^3$ *C* of $C_{60}$), 70.66 (sp$^3$ *C* of $C_{60}$), 69.35 (C*C*H$_2$O-), 68.53 (sp$^3$ *C* of $C_{60}$), 67.91 (O*C*H$_2$CH$_2$O), 64.30 (OCH$_2$*C*H$_2$O), 53.27 (CO*C*CO), 46.73 (CO*C*CO).

$^*$ *14 Signals from 147.38 to 139.52 ppm for sp$^2$ carbons of $C_{60}$*

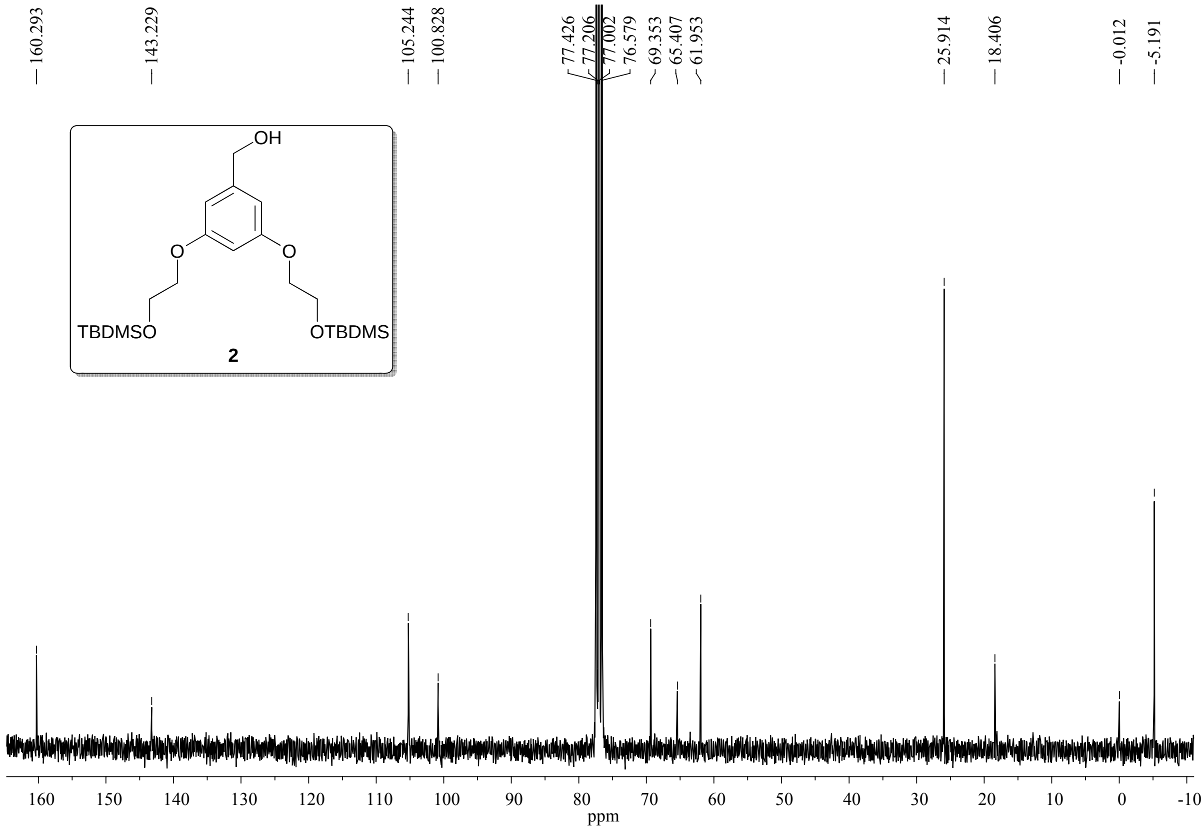
**UV/Vis** ($CHCl_3$) $\lambda_{max}$/nm ($\varepsilon$/dm$^3$mol$^{-1}$cm$^{-1}$): 251 (105227), 279 (77869), 305 (47816), 338 (29296), 405 (4188), 434 (3189), 462 (5125), 503 (2330), 622 (496), 695 (211).

**HRMS** (MALDI TOF, negative mode, graphite): calculated for $C_{91}H_{26}O_{16}K_2$ [M + 2K]$^-$ requires 1453.0523; found: 1453.0534.

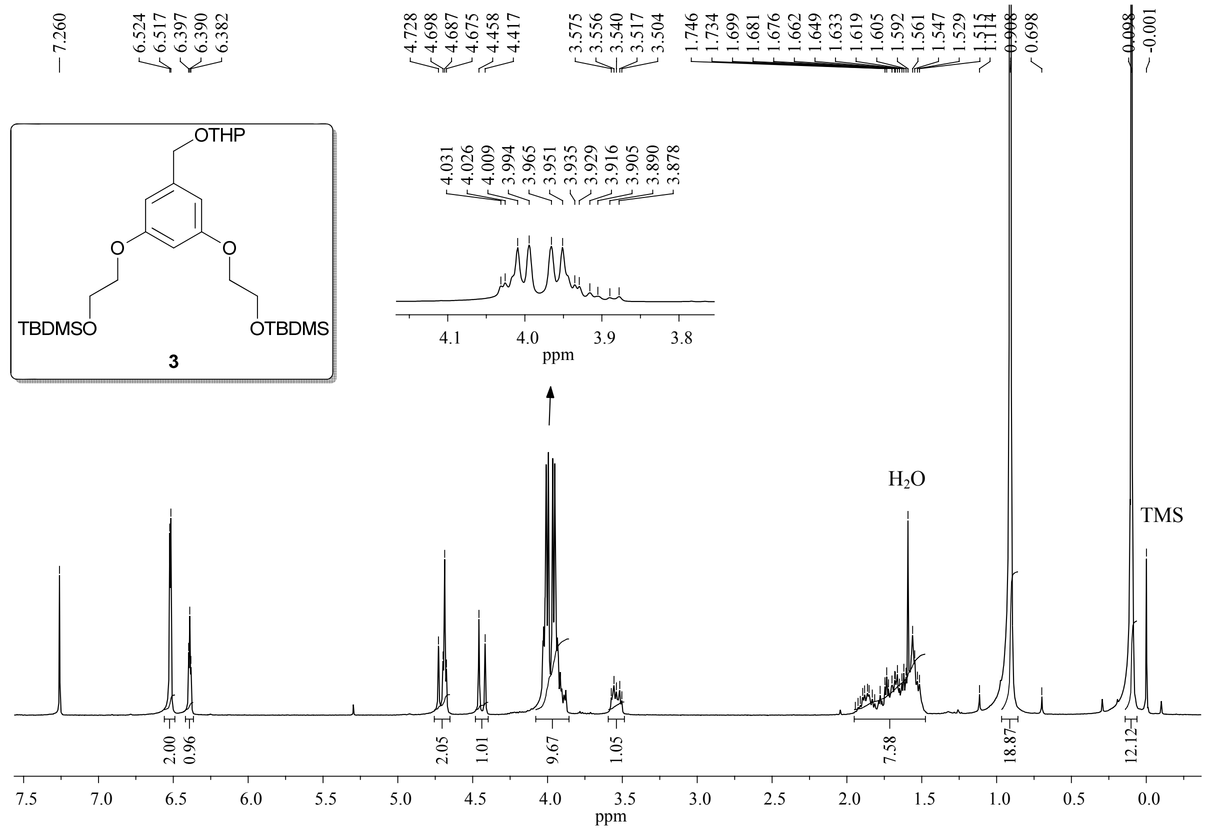
## $^1$H NMR spectrum of 2 (300 MHz, $CDCl_3$, 25 °C)



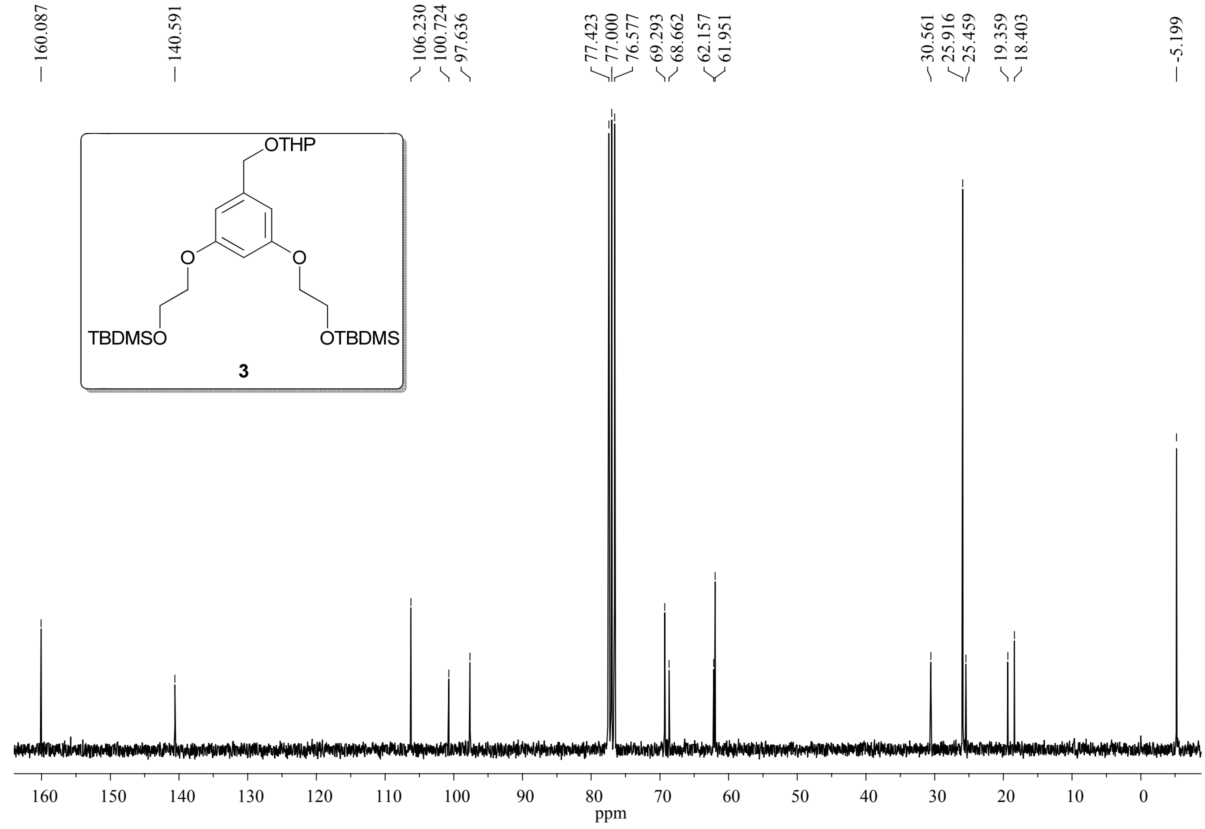
## $^{13}$C NMR spectrum of 2 (75 MHz, $CDCl_3$, 25 °C)



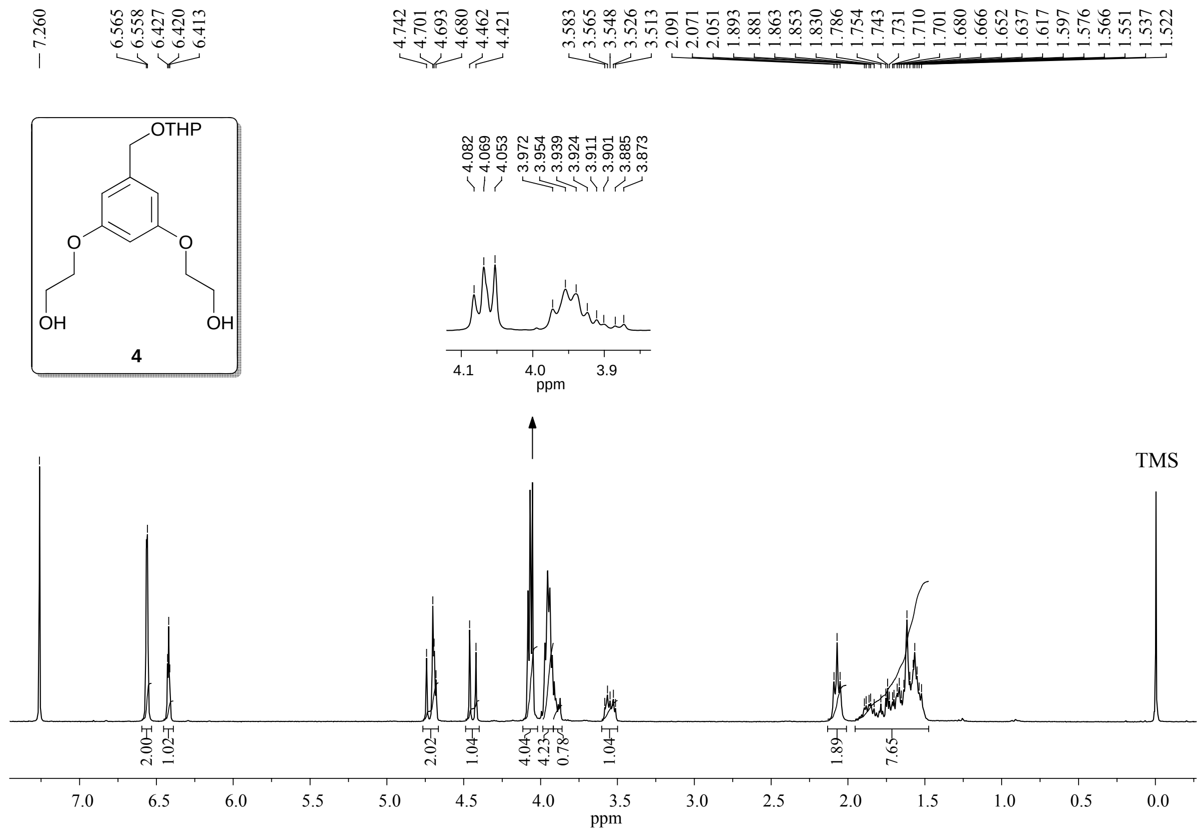
## $^1$H NMR spectrum of 3 (300 MHz, $CDCl_3$, 25 °C)



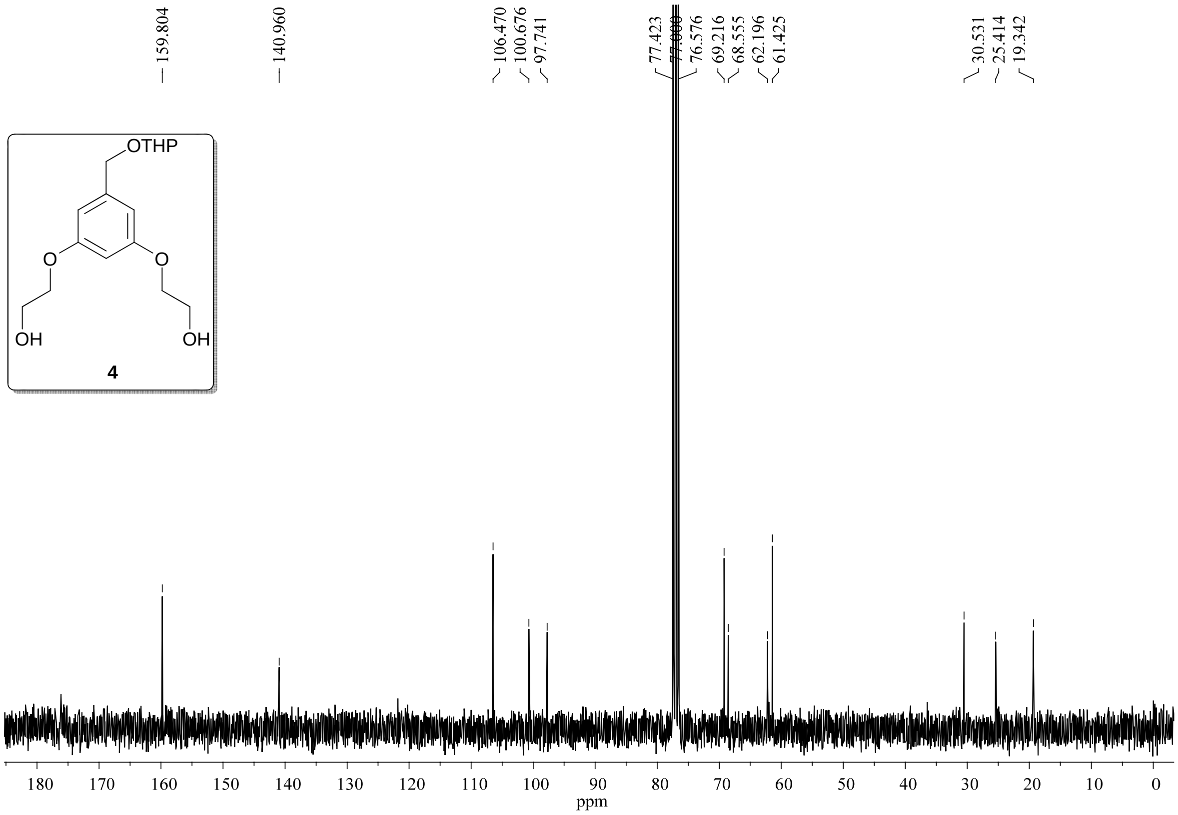
## $^{13}$C NMR spectrum of 3 (75 MHz, $CDCl_3$, 25 °C)



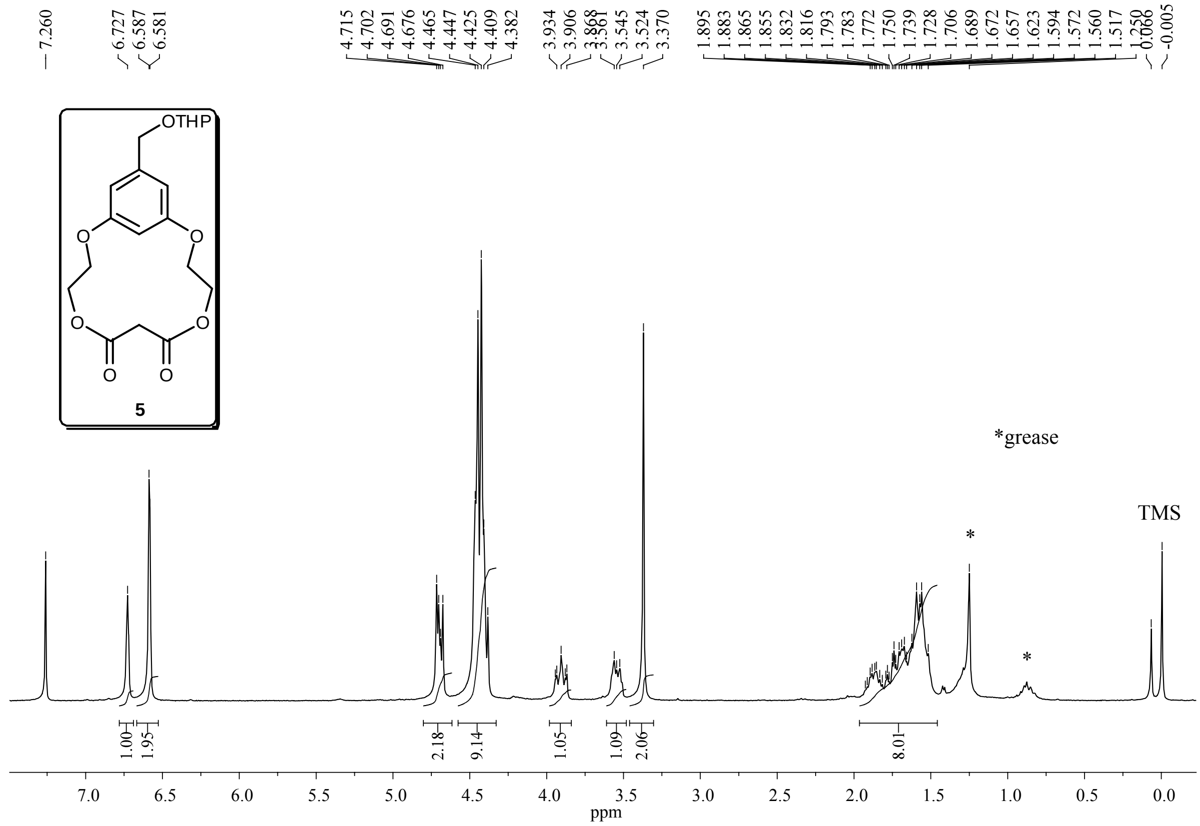
## $^{1}$H NMR spectrum of 4 (300 MHz, $CDCl_3$, 25 °C)



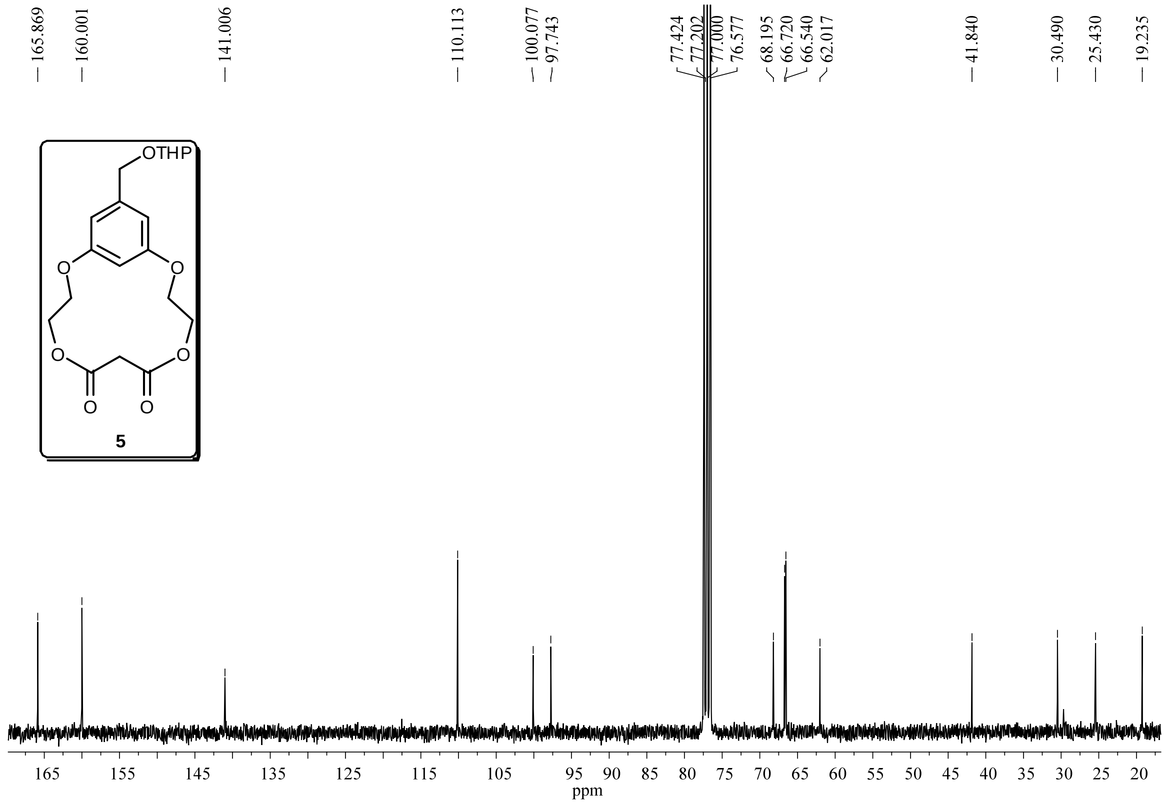
## $^{13}$C NMR spectrum of 4 (75 MHz, $CDCl_3$, 25 °C)



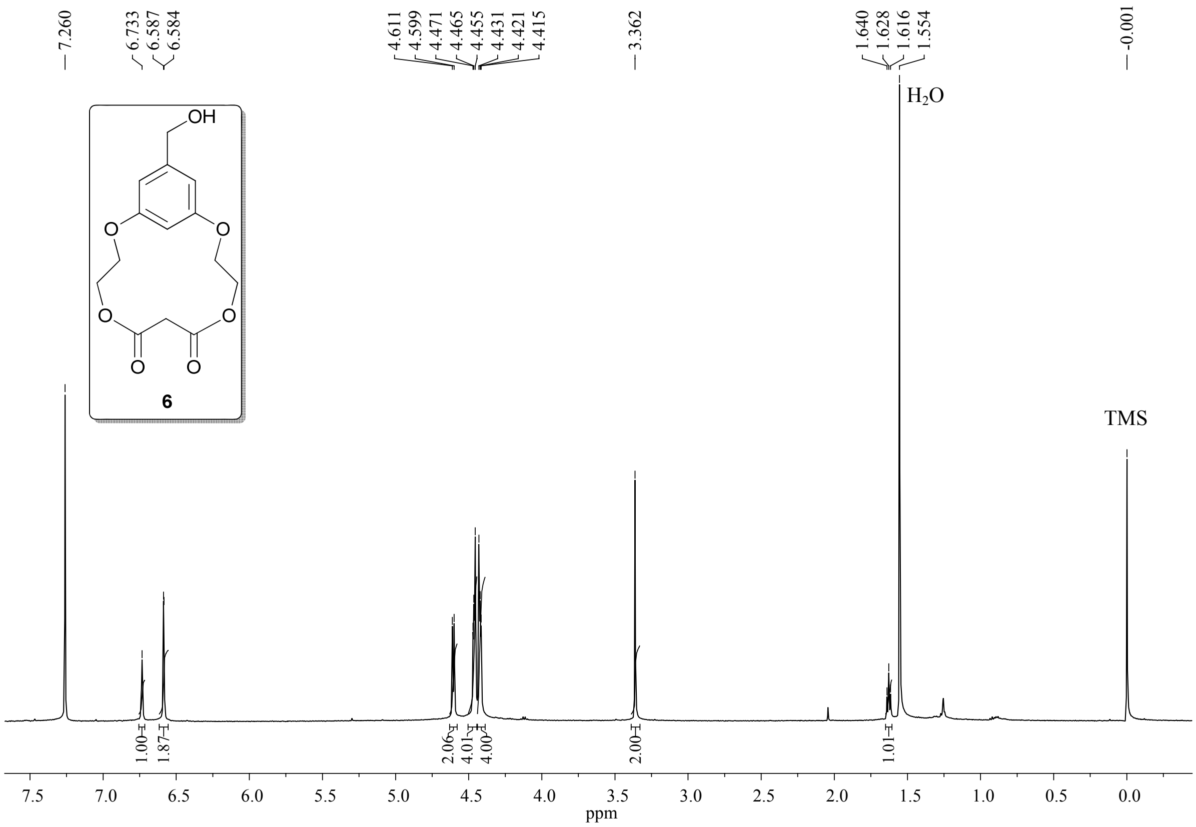
## $^1$H NMR spectrum of 5 (300 MHz, $CDCl_3$, 25 °C)



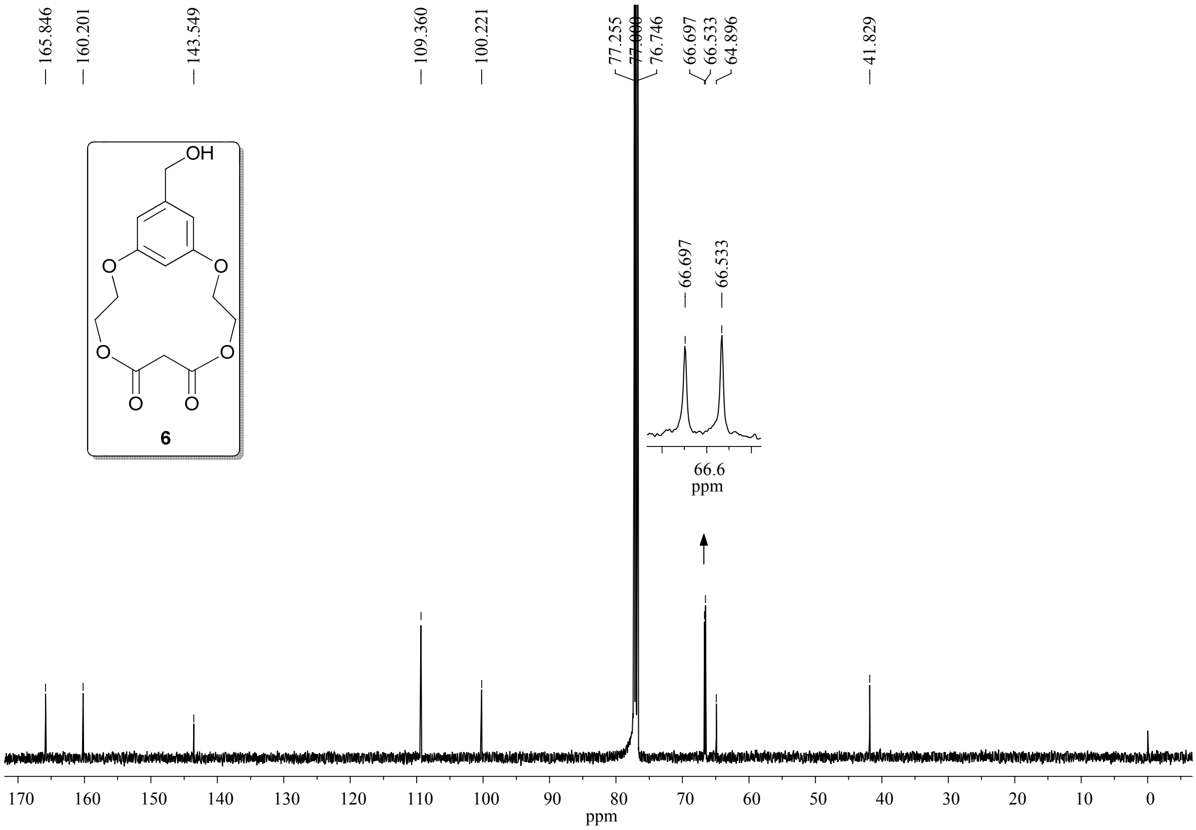
## $^{13}$C NMR spectrum of 5 (75 MHz, $CDCl_3$, 25 °C)



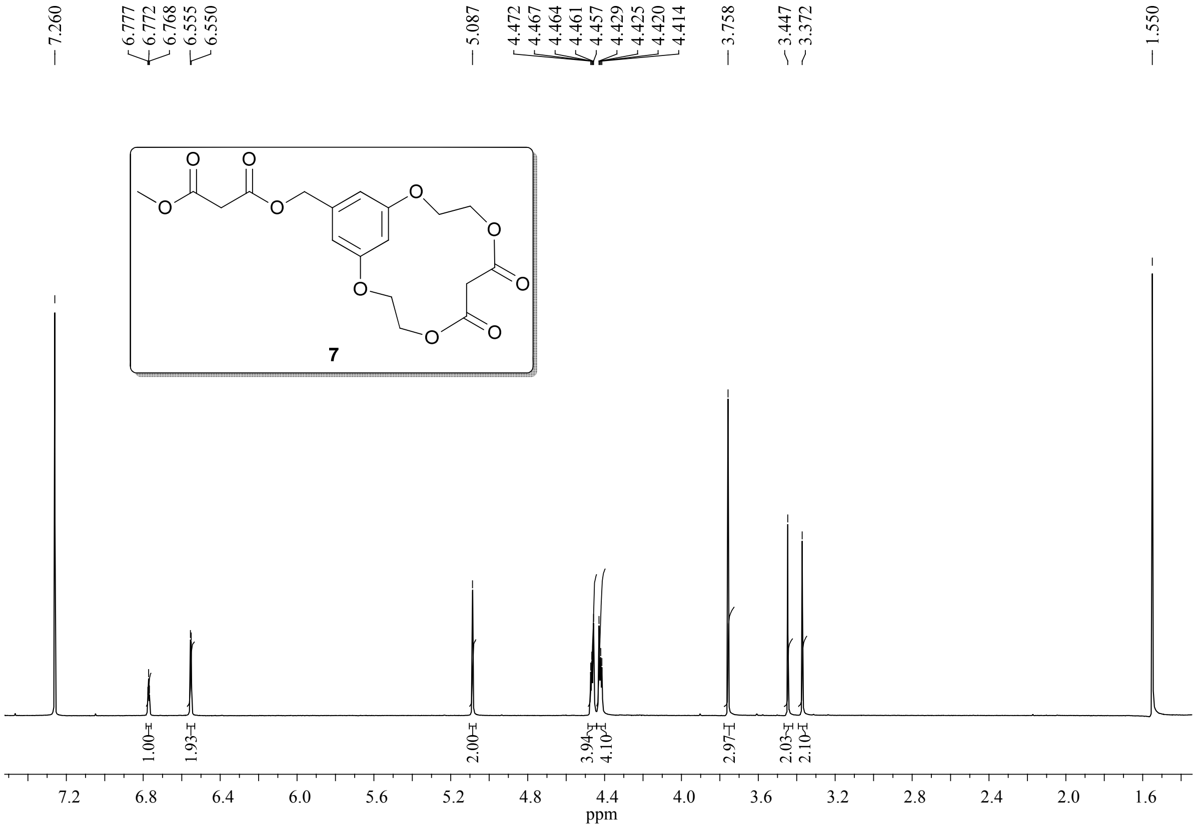
## $^{1}$H NMR spectrum of 6 (500 MHz, $CDCl_3$, 25 °C)



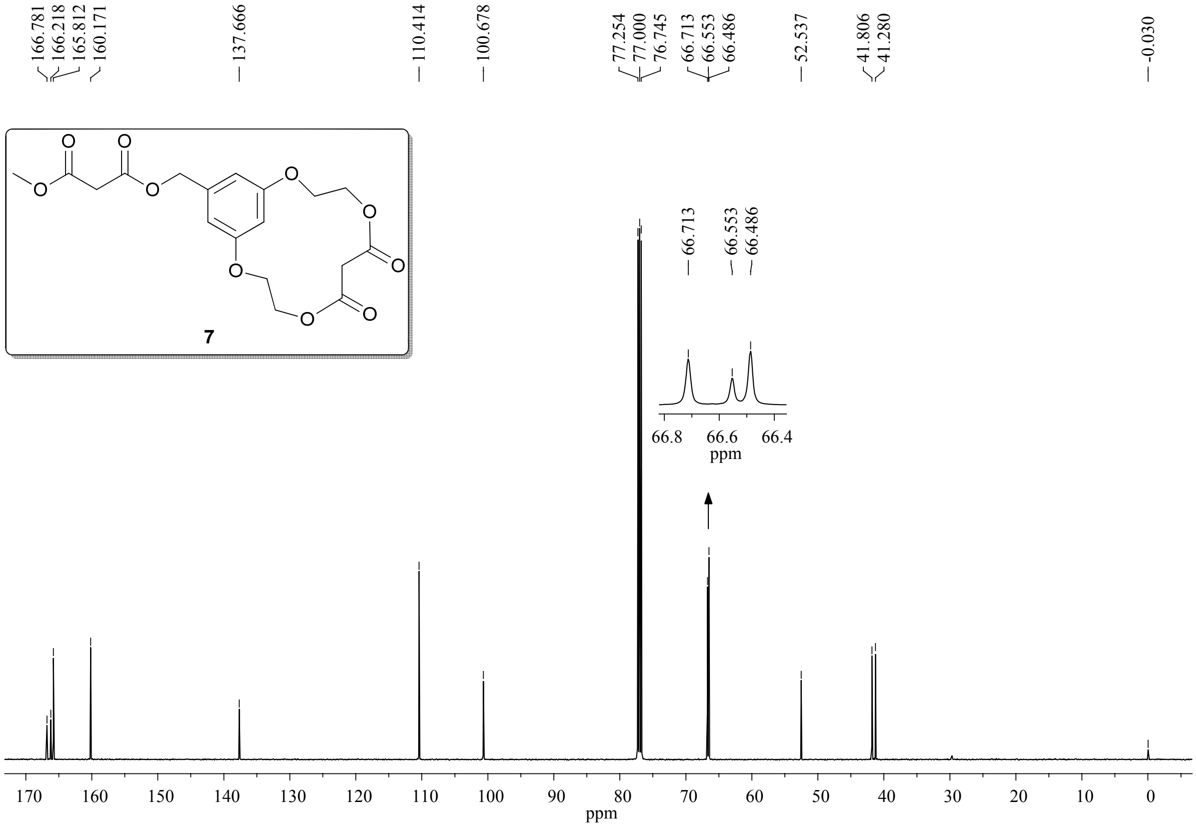
## $^{13}$C NMR spectrum of 6 (125 MHz, $CDCl_3$, 25 °C)



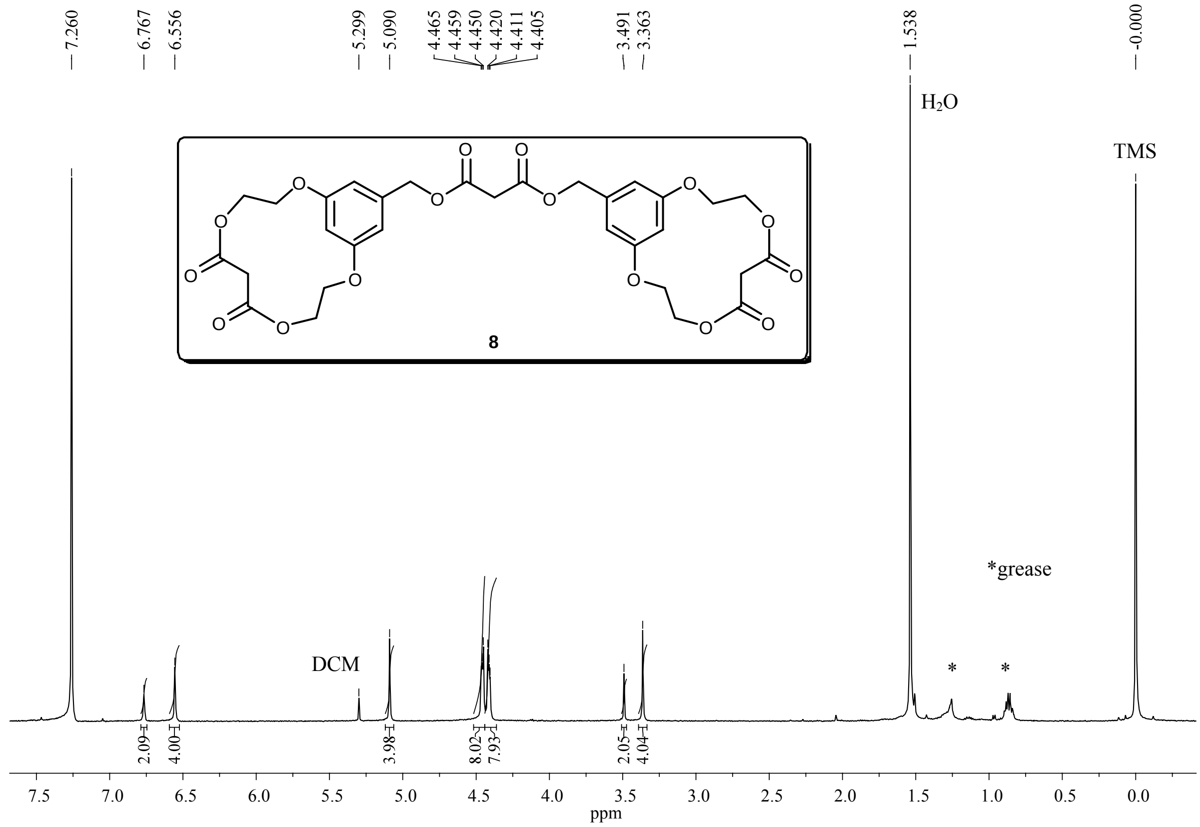
## $^1$H NMR spectrum of 7 (500 MHz, $CDCl_3$, 25 °C)



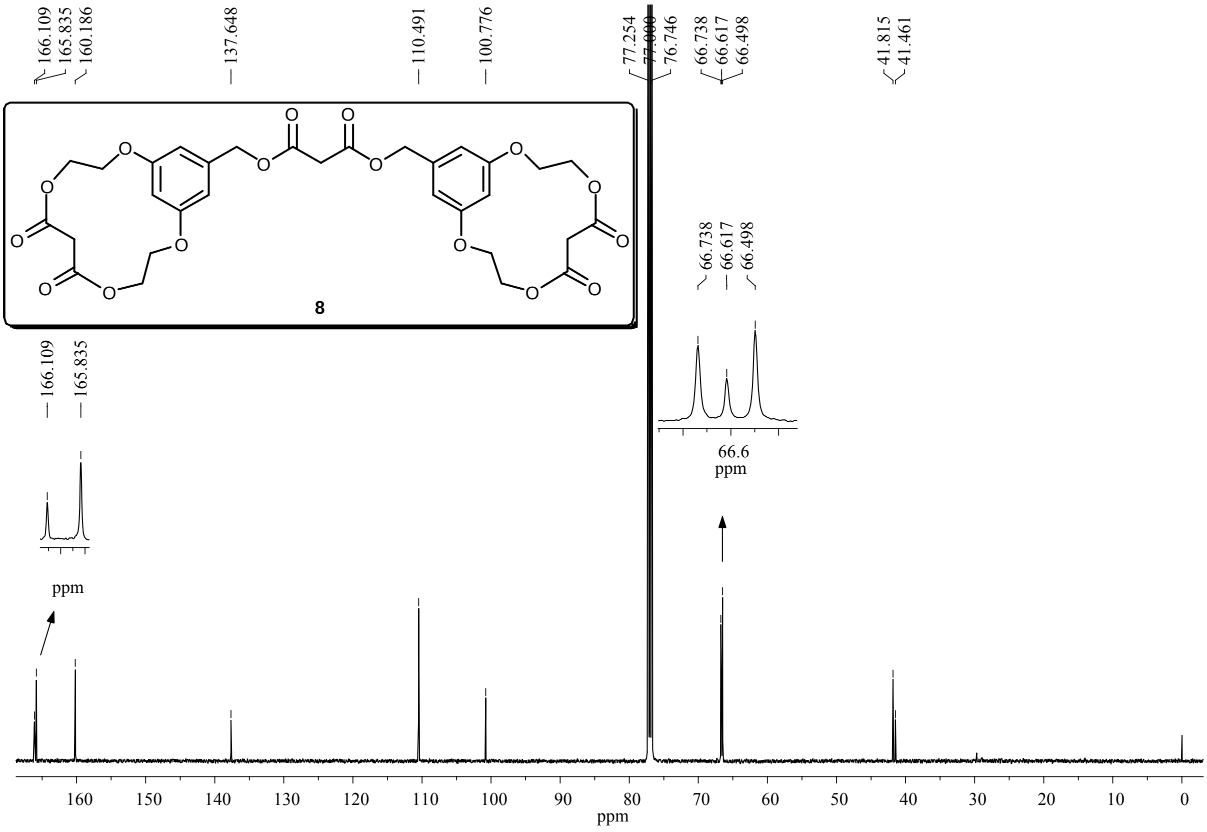
## $^{13}$C NMR spectrum of 7 (125 MHz, $CDCl_3$, 25 °C)



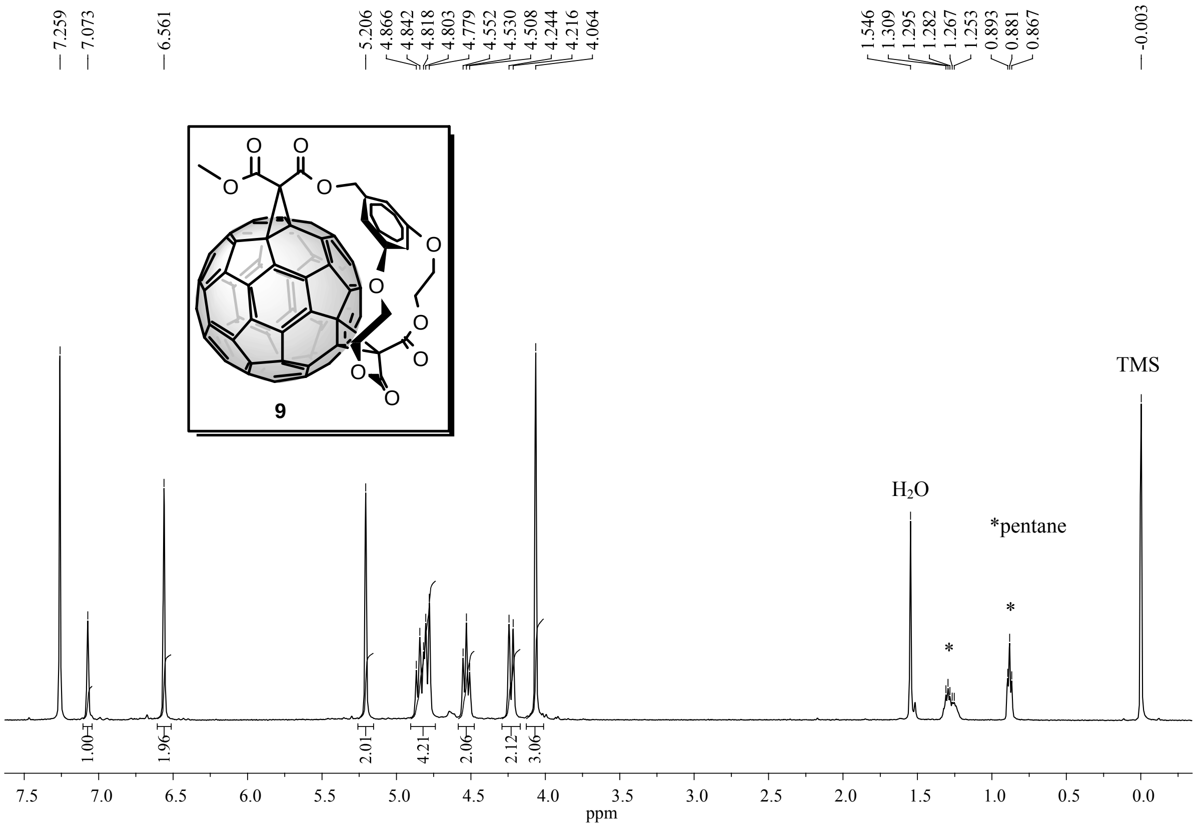
## $^1$H NMR spectrum of 8 (500 MHz, $CDCl_3$, 25 °C)



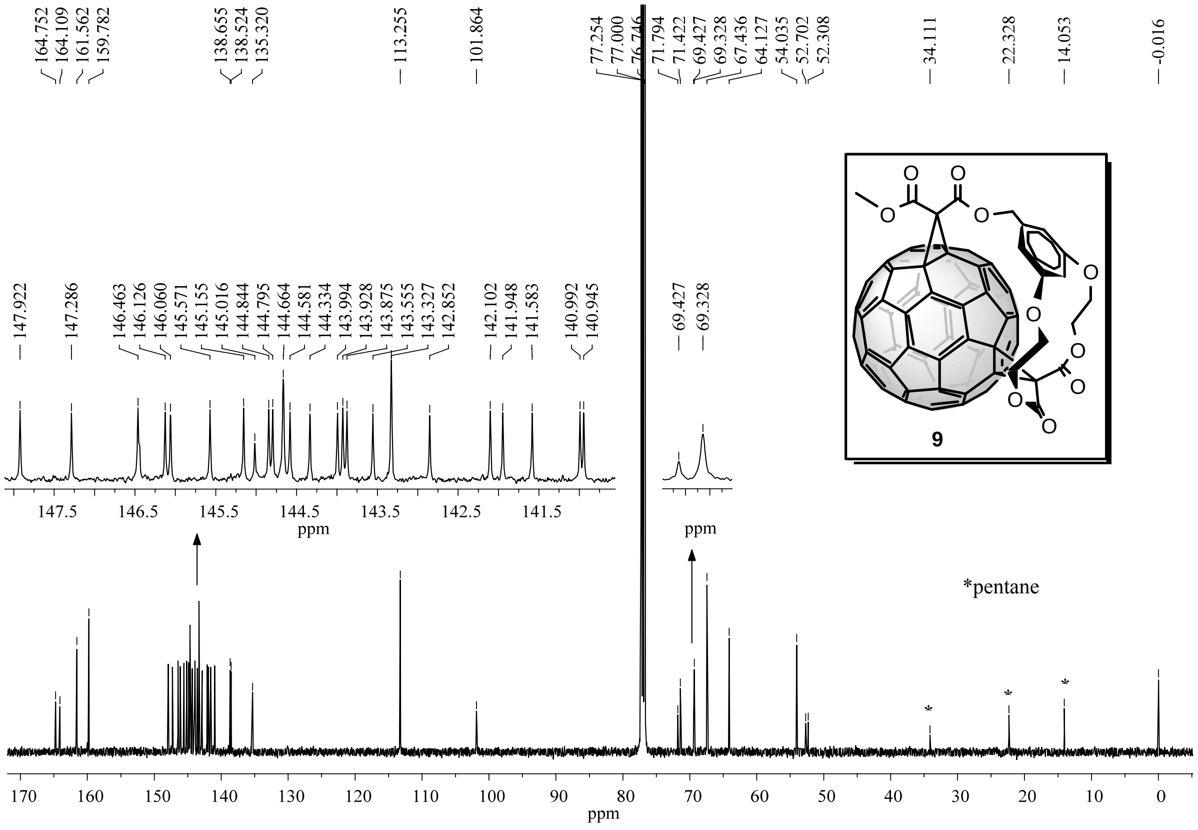
## $^{13}$C NMR spectrum of 8 (125 MHz, $CDCl_3$, 25 °C)



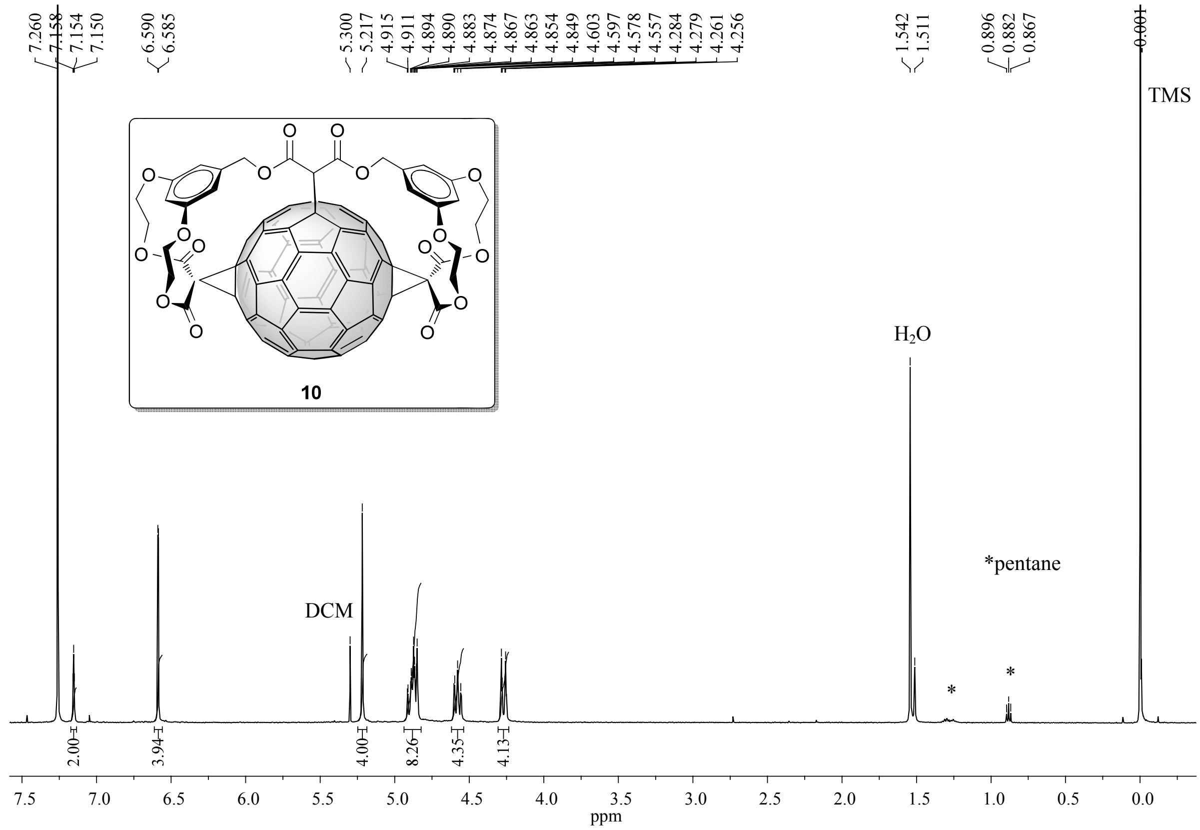
## $^1$H NMR spectrum of 9 (500 MHz, CDCl$_3$, 25 °C)



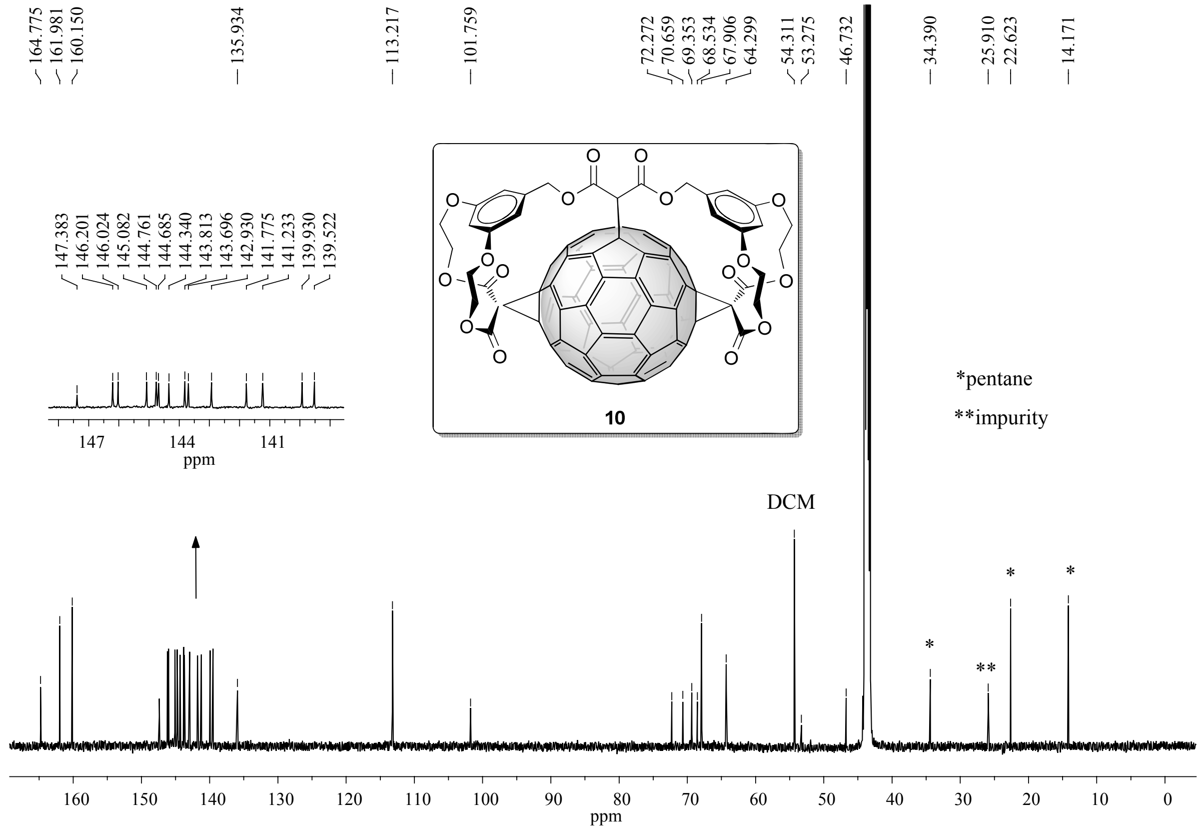
## $^{13}$C NMR spectrum of 9 (125 MHz, CDCl$_3$, 25 °C)



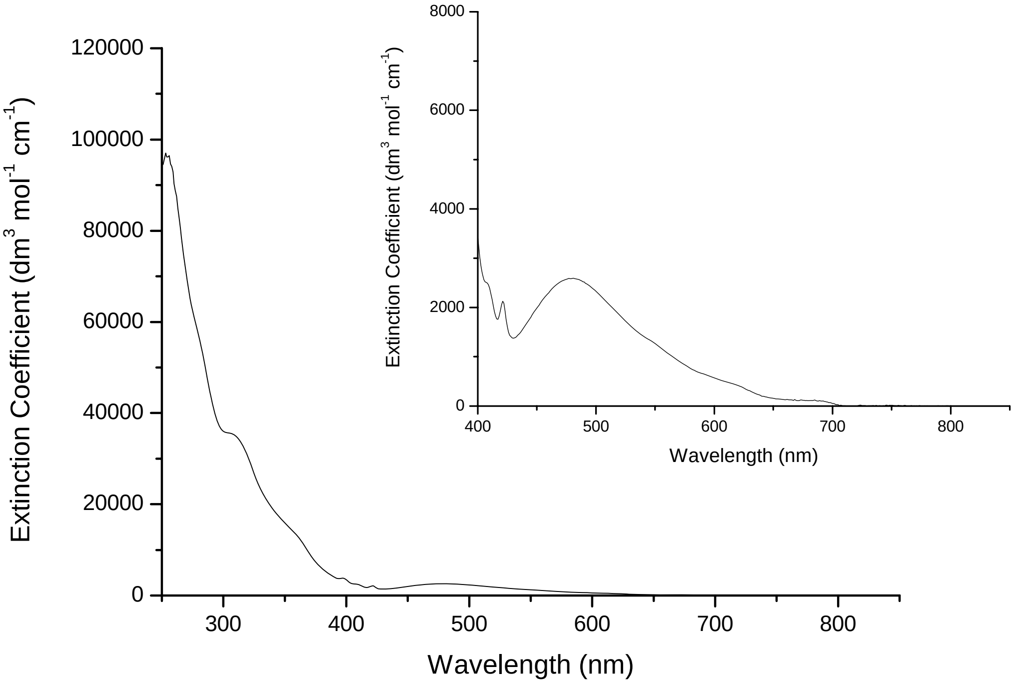
## $^1$H NMR spectrum of 10 (500 MHz, CDCl$_3$, 25 °C)



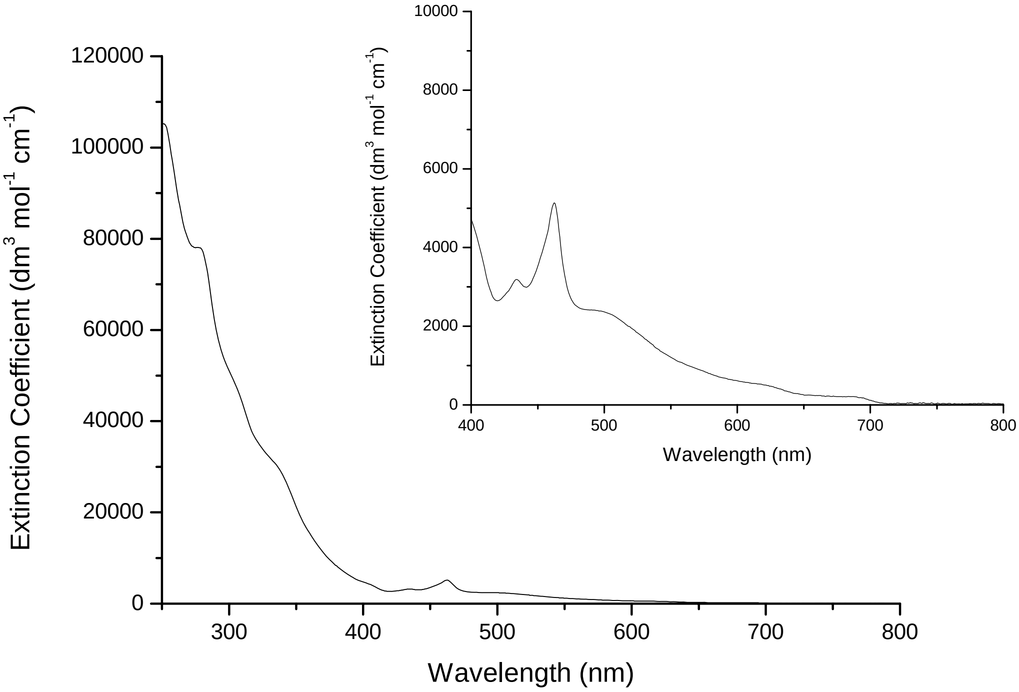
## $^{13}$C NMR spectrum of 10 (125 MHz, C$_2$D$_4$Cl$_2$, 25 °C)



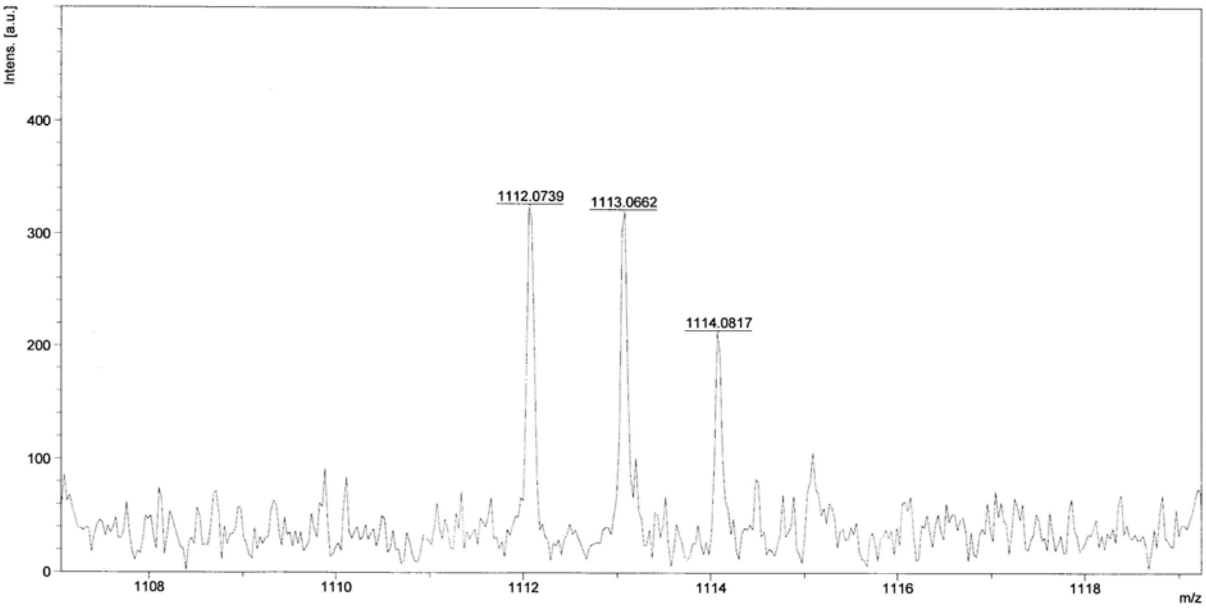
## UV-Vis spectrum of 9 ($CHCl_3$)



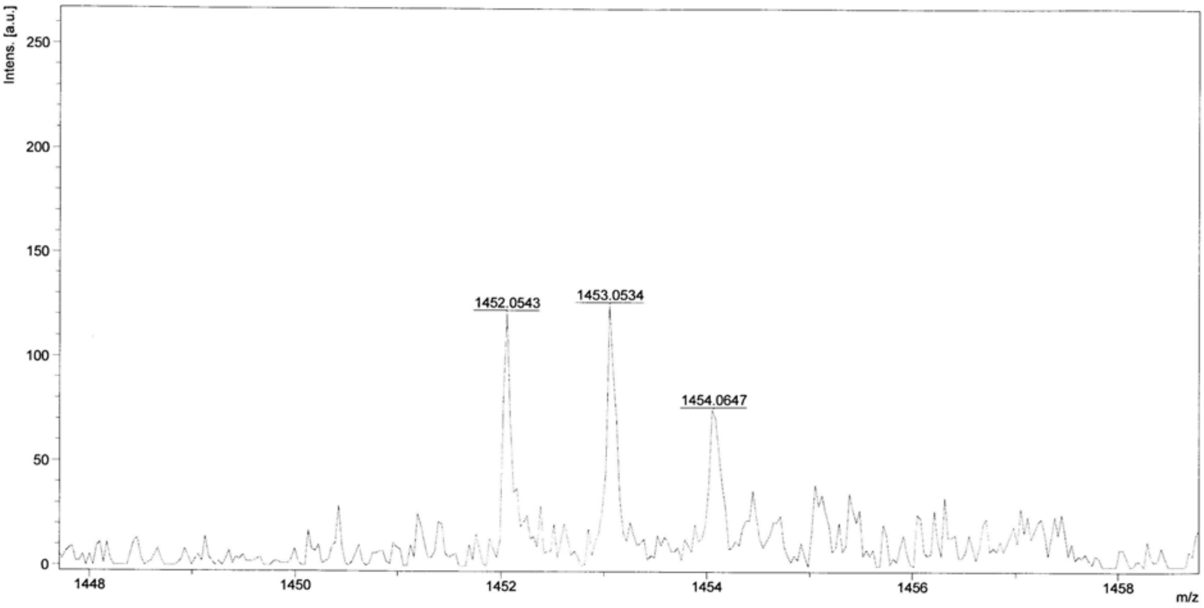
## UV-Vis spectrum of 10 ($CHCl_3$)



## High resolution MALDI-TOF mass spectrum of 9 (negative mode, graphite)



## High resolution MALDI-TOF mass spectrum of 10 (negative mode, graphite)



## X-ray crystallographic information (crystal data/structure refinement) of 9 and 10

**Table S1.** Crystallographic Data for Compounds **9** and **10**

| | **Compound 9** | **Compound 10** |
|---|---|---|
| **Formula** | $C_{80}H_{20}Cl_4O_{10}$ | $C_{92}H_{28}Cl_2O_{16}$ |
| **$M_r$** | 1282.76 | 1460.05 |
| **Crystal system** | Triclinic | Triclinic |
| **Space group** | P -1 | P -1 |
| **Temperature** | 100(2) | 100(2) |
| **$a$ (Å)** | 10.4435(4) | 13.4764(4) |
| **$b$ (Å)** | 12.5513(7) | 19.7789(4) |
| **$c$ (Å)** | 19.9229(6) | 26.0709(7) |
| **$\alpha$ (deg)** | 79.988(4) | 72.890(2) |
| **$\beta$ (deg)** | 89.625(3) | 78.690(2) |
| **$\gamma$ (deg)** | 71.533(4) | 70.885(2) |
| **$V$ (Å$^3$)** | 2435.99(19) | 6237.0(3) |
| **$Z$** | 2 | 4 |
| **$D_{calc.}$ (g cm$^{-3}$)** | 1.743 | 1.555 |
| **$F$ (000)** | 1296.0 | 2968 |
| **$R_1[I>2\sigma(I)]$** | 0.0452 | 0.0875 |
| **$wR_2[I>2\sigma(I)]$** | 0.1273 | 0.2324 |
| **$R_1$ (all data)** | 0.0545 | 0.1038 |
| **$wR_2$ (all data)** | 0.1273 | 0.2453 |
| **GOOF** | 1.052 | 1.114 |

## Crystal packing, interactions and measured distances in the crystal structure of 9

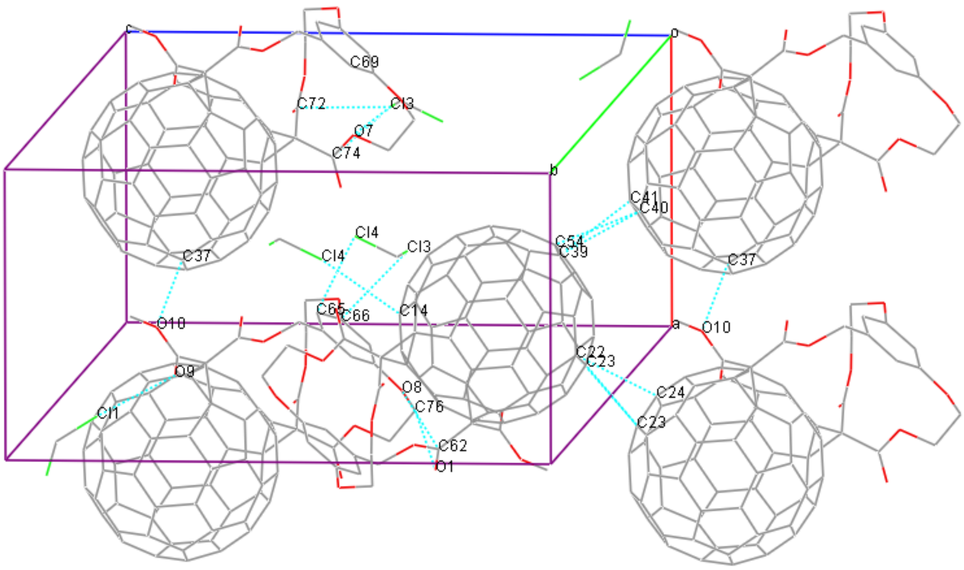


Figure S1

**Table S2**: Interactions and measured distances (Å) in the crystal structure of **9**

| **Cl(x)···O(y)** | **d [Cl(x)···O(y)], (Å)** |
|---|---|
| Cl(1)···O(9) | 3.219 |
| Cl(3)···O(7) | 3.203 |
| **Cl(x)···C(y)** | **d [Cl(x)···C(y)], (Å)** |
| Cl(4)···C(14) | 3.429 |
| Cl(3)···C(66) | 3.442 |
| Cl(4)···C(65) | 3.393 |
| Cl(3)···C(72) | 3.385 |
| Cl(3)···C(74) | 3.375 |
| **C(x)···O(y)** | **d [C(x)···O(y)], (Å)** |
| C(37)···O(10) | 3.123 |
| C(76)···O(1) | 3.190 |
| C(62)···O(8) | 3.190 |
| C(73)···O(10) | 3.123 |
| **C(x)···C(y)** | **d [C(x)···C(y)], (Å)** |
| C(22)···C(23) | 3.339 |
| C(22)···C(24) | 3.367 |
| C(23)···C(23) | 3.242 |
| C(39)···C(40) | 3.387 |
| C(39)···C(41) | 3.248 |
| C(54)···C(40) | 3.342 |

## Crystal packing, interactions and measured distances in the crystal structure of 10

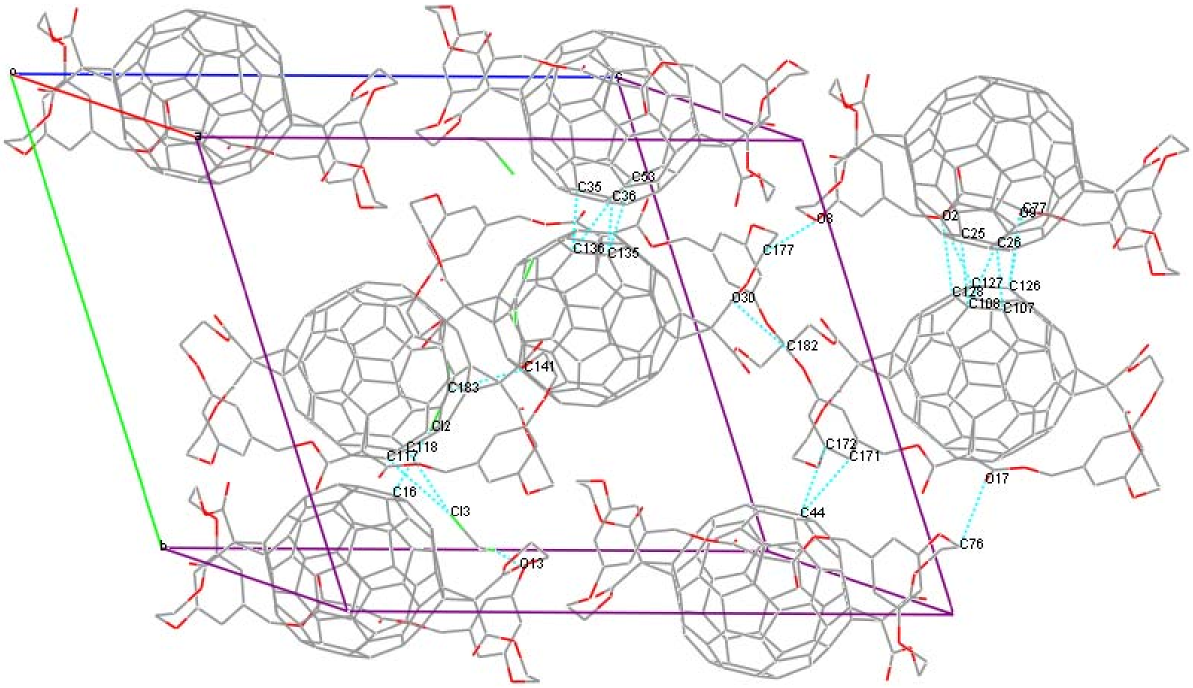


**Figure S2**

**Table S3**: Interactions and measured distances (Å) in the crystal structure of **10**

| **Cl(x)···O(y)** | **d [Cl(x)···O(y)], (Å)** |
|---|---|
| Cl(4)···O(13) | 3.159 |
| **Cl(x)···C(y)** | **d [Cl(x)···C(y)], (Å)** |
| Cl(2)···C(16) | 3.129 |
| Cl(3)···C(117) | 3.373 |
| Cl(3)···C(118) | 3.299 |
| **C(x)···O(y)** | **d [C(x)···O(y)], (Å)** |
| C(76)···O(17) | 3.190 |
| C(177)···O(8) | 3.141 |
| C(182)···O(30) | 3.182 |
| C(126)···O(9) | 3.193 |
| C(127)···O(2) | 2.940 |
| C(128)···O(2) | 3.203 |
| **C(x)···C(y)** | **d [C(x)···C(y)], (Å)** |
| C(44)···C(171) | 3.102 |
| C(44)···C(172) | 3.392 |
| C(135)···C(36) | 3.052 |
| C(135)···C(53) | 3.347 |

| | |
|---|---|
| C(136)···C(35) | 3.174 |
| C(136)···C(36) | 3.387 |
| C(107)···C(26) | 3.224 |
| C(108)···C(25) | 3.378 |
| C(108)···C(26) | 3.356 |
| C(126)···C(77) | 3.143 |
| C(183)···C(141) | 3.340 |

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