Supporting Information

Upper-rim functionalization and supramolecular polymerization of a feet-to-feet-connected biscavitand

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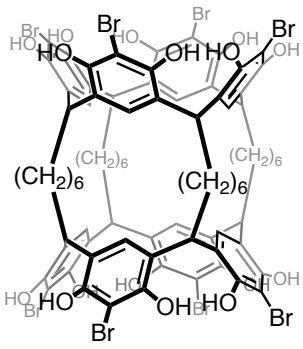
Experimental Section

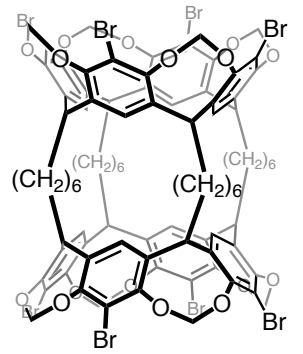
General: Commercially supplied CuI (Kanto Chemical Co., Ltd.) were dissolved in hot saturated aqueous sodium iodide. Pure CuI is obtained by cooling and diluting the solution with water, followed by filtering and washing sequentially with distilled water, then drying *in vacuo* over P_2O_5 at 70 ºC.[1] KI (Nacalai Tesuque, Inc.) was recrystallised from distilled water/ethanol, then drying *in vacuo* over P_2O_5 at 70 ºC.[1] DMI, 2-butanone, dioxane, THF, and isopropylamine were distilled prior to use according to the standard protocols. All other reagents and solvents were purchased from Kanto Chemical Co., Ltd., Wako Pure Chemical Co., Ltd., Tokyo Kasei Kogyo Co., Ltd., and Sigma-Aldrich Co., Ltd., and Nacalai Tesuque, Inc. were used as received without further purification. ^{1}H and ^{13}C spectra were recorded on a VARIAN Mercury 300 spectrometer. Chemical shifts are quoted as parts per million (ppm) relative to chloroform (chloroform-d_1, δ = 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C), tetrachloroethane (tetrachloroethane-d_2, δ = 6.00 ppm for ^{1}H and 74.0 ppm for ^{13}C), dimethylformamide (DMF-d_7, δ = 8.03 ppm for ^{1}H and 163.2 ppm for ^{13}C). IR spectra were recorded on a JASCO FT/IR-4600 spectrometer. High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific LTQ Orbitrap XL by electron splay ionization (ESI) method. Melting points were measured with a Yanagimoto micro melting point apparatus and uncorrected.

X-ray Crystallography

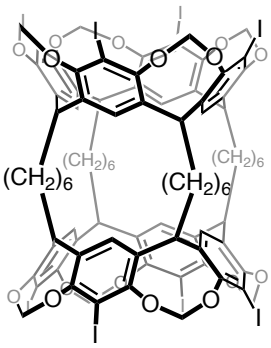
X-ray quality single crystals of **4** were grown from chloroform solutions by slow evaporation of hexane at room temperature. X-ray crystallographic data were collected on a Bruker SMART AEPX II ULTRA CCD diffractometer. The crystals were irradiation using Mo-Kα radiation (λ = 0.71073 Å) at 90 K. The crystal structures were solved by the direct method using the SHELXS-2013 program and refined by successive differential Fourier syntheses and full-matrix least-squares procedures using the SHELXL-2013 program.[2] Due to the weak diffractions, anisotropic thermal factors were not applied to all atoms. Diffuse electron densities arising from the disordered solvents were treated with the SQUEEZE routine in the PLATON program.[3] A summary of data collection and structure refinement details is provided in Table S1.



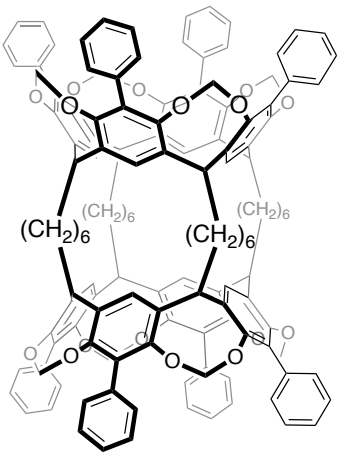
Octabromobisresorcinarene 6: To a solution of bisresorcinarene **5**[4] (6.40 g, 4.90 mmol) in dry 2-butanone (61 mL) were added NBS (8.38 g, 47.1 mmol) under argon atmosphere. The mixture was stirred at 0 ºC for 12 h. After the reaction the crude product was washed with methanol and water several times to give **6** as a white solid (7.50 g, 79%). M.p. >300 ºC; ^{1}H NMR (300 MHz, DMF-d_7): δ 9.48 (s, 16H), 7.28 (s, 8H), 4.54 (t, J = 6.5 Hz, 8H), 2.16–2.33 (m, 16H), 1.43–1.59 (m, 16H), 1.24–1.42 (m, 16H) ppm; ^{13}C{^{1}H} NMR (75 MHz, DMF-d_7): δ 149.6 125.4, 122.1, 101.5, 36.1, 34.7, 29.9, 28.9 ppm; FTIR-ATR(neat): ν 3301, 2926, 2851, 1652, 1470 cm^{-1}; HRMS (ESI-Orbitrap) m/z: [M – H]$^-$ Calcd for $C_{80}H_{79}O_{16}Br_8$ 1926.8841; found 1926.8834.



Octabromobiscavitand 2: A mixture of **6** (1.00 g, 0.516 mmol), Cs_2CO_3 (5.05 g, 15.5 mmol), and bromochloromethane (4.70 mL, 70.1 mmol) in dry DMSO (30 mL) was stirred in a sealed tube (Ace pressure tube, Aldrich) for 12 h at 88 °C with the use of an oil bath. After cooling, the mixture was poured into 2% HCl, and the solid formed was filtered and washed with $NaHCO_3$ aq., water, and chloroform to give **2** as a white solid (1.47 g, 70%) M.p. >300 ºC; ^{1}H NMR (300 MHz, tetrachloroethane-d_2): δ 7.18 (s, 8H), 6.02 (d, J = 3.8 Hz, 8H), 4.82 (t, J =7.2 Hz, 8H), 4.20 (d, J = 3.8 Hz, 8H), 2.18–2.42 (m, 16H), 1.62–1.71 (m, 16H), 1.35–1.51 (m, 16H) ppm; ^{13}C{^{1}H} NMR (75 MHz, tetrachloroethane-d_2): δ 152.1, 139.0, 118.6, 113.6, 98.8, 37.9, 30.0, 29.8, 28.2 ppm; FTIR-ATR(neat): ν 2926, 2854, 1737, 1470, 1090, 1018 cm^{-1}; HRMS (ESI-Orbitrap) m/z: [M]$^{+\cdot}$ Calcd for $C_{88}H_{80}O_{16}Br_8$ 2023.8908; found 2023.8901.

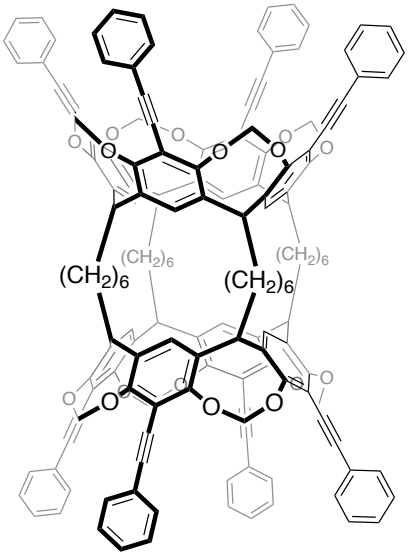


Octaiodobiscavitand 1: A mixture of **2** (500 mg, 0.246 mmol), KI (56 g, 337 mmol), and CuI (21.2 g, 111 mmol) in dry DMI (120 mL) was stirred under nitrogen atmosphere. After being stirred for 60 h at 145 ºC with the use of an oil bath, the reaction mixture was extracted with chloroform. The organic layer was washed with sodium thiosulfate aq. and brine, dried over sodium sulfate and concentrated *in vacuo*. The crude product was washed with water and chloroform several times to give **1** as a white solid (480 mg, 81%). M.p. >300 ºC; ^{1}H NMR (300 MHz, chloroform-d_1): δ 7.18 (s, 8H), 5.99 (d, 8H, J = 6.5 Hz), 4.85 (d, 8H, J = 7.1 Hz), 4.35 (d, 8H, J = 6.5 Hz), 2.18–2.41 (m, 16H), 1.54–1.63 (s, 16H), 1.38–1.52 (s, 16H) ppm; ^{13}C{^{1}H} NMR (75 MHz, chloroform-d_1): δ 154.9, 138.5, 120.0, 98.7, 93.3, 38.1, 30.1, 29.7, 28.1 ppm; FTIR-ATR(neat): ν 2926, 2859, 1697, 1444, 1089, 1016 cm^{-1}; HRMS (ESI-Orbitrap) m/z: $[M]^{+\cdot}$ Calcd for $C_{88}H_{80}O_{16}Br_8$ 2407.7798; found 2407.7833.



Biscavitand 3: H_2O (0.33 mL), Phenylboronic acid pinacol ester (120 mg, 10.6 mmol), and $AsPh_3$ (50.0 mg, 0.163 mmol) in dioxane (3.27 mL) were added to a mixture of **1** (59 mg, 20.8 μmol), $PdCl_2(PPh_3)_2$ (4.20 mg, 6.03 μmol), and Cs_2CO_3 (402 mg, 1.23 mmol). After stirring for 12 h at 110 °C with the use of an oil bath in the dark, the reaction mixture was filtered on a celite pad and the solution was concentrated in vacuo. The residue was purified by GPC to afford **3** as white solid (36.9 mg, 18.4 μmol) in 75% yield. M.p. >300 ºC; ^{1}H NMR (300 MHz, chloroform-d_1): δ 7.51 (s, 8H), 7.38–7.27 (m, 24H), 7.05 (d, J = 7.7 Hz, 16H), 5.25 (d, J = 7.4 Hz, 8H), 4.88 (t, J = 6.2 Hz, 8H), 4.28 (d, J = 7.4 Hz, 8H), 2.42–2.58 (m, 16H), 1.69–1.79 (m, 16H), 1.48–1.63 (m, 16H) ppm; ^{13}C{^{1}H} NMR (75 MHz, chloroform-d_1): δ 152.7, 138.2, 133.9, 129.8, 129.7, 127.9, 127.1, 119.3, 100.6, 37.4, 30.6, 30.1,

28.5 ppm; FTIR-ATR(neat): *v* 2927, 2854, 1731, 1435, 1088, 1015 cm^{-1}; HRMS (ESI-Orbitrap) m/z: $[M]^{+\cdot}$ Calcd for $C_{136}H_{120}O_{16}$ *m/z* 2008.8571; found 2008.8602.



Biscavitand 4: To a solution of **1** (59.0 mg, 0.0246 mmol) in dry THF (12.6 mL) were added phenylacetylene (60 mg, 0.592 mmol), isopropylamine (12.6 mL), CuI (1.89 mg, 46 μmol), and $PdCl_2(PPh_3)_2$ (5.20 mg, 7.47 μmol) and the mixture was stirred for 12 h at 50 °C with the use of an oil bath in the dark. The reaction mixture was filtered on a celite pad and the solution was concentrated in vacuo. The residue was purified by GPC to afford **4** as white solid (43.3 mg, 19.7 μmol) in 80% yield. M.p. >300 ºC; ^{1}H NMR (300 MHz, chloroform-d_1): δ 7.50–7.44 (m, 16H), 7.37–7.33 (m, 24H), 7.24 (s, 8H), 6.04 (d, J =7.5 Hz, 8H), 4.88 (t, J =7.5 Hz, 8H), 4.67 (d, J =7.5 Hz, 8H), 2.28–2.44 (m, 16H), 1.62–1.72 (m, 16H), 1.48–1.58 (m, 16H) ppm; ^{13}C{^{1}H} NMR (75 MHz, chloroform-d_1): δ 155.4, 138.3, 131.7, 128.6, 128.4, 123.0, 119.4, 113.5, 98.4, 97.8, 81.0, 36.8, 29.9, 29.7, 28.2 ppm; FTIR-ATR(neat): *v* 2926, 2859, 2218, 1738, 1446, 1085, 1015 cm^{-1}; HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ Calcd for $C_{152}H_{120}O_{16}Na$ 2223.8469; found 2223.8468.

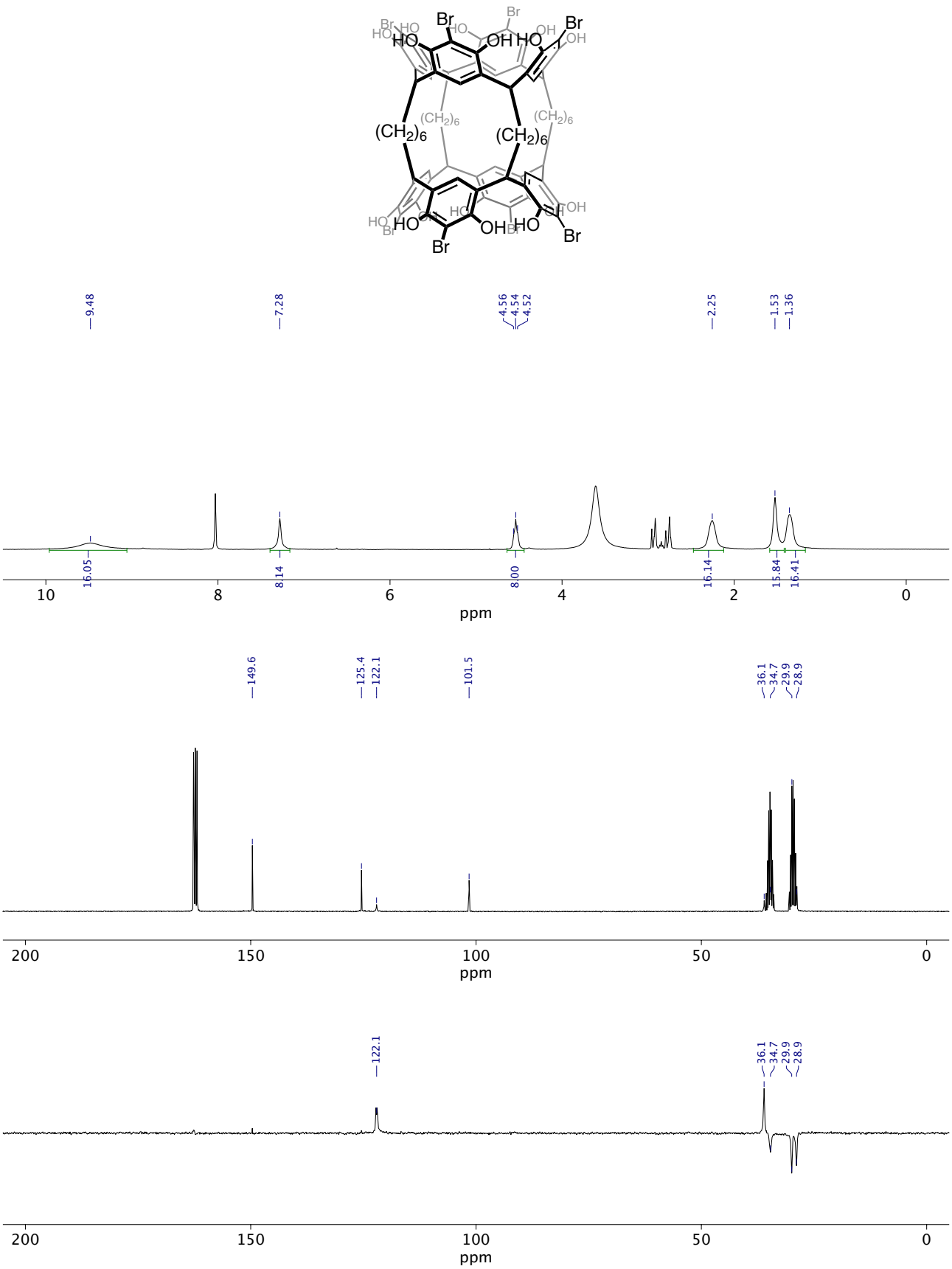


Figure S1. ^{1}H, ^{13}C NMR and DEPT-135 NMR spectra of **6** in DMF-d_7.

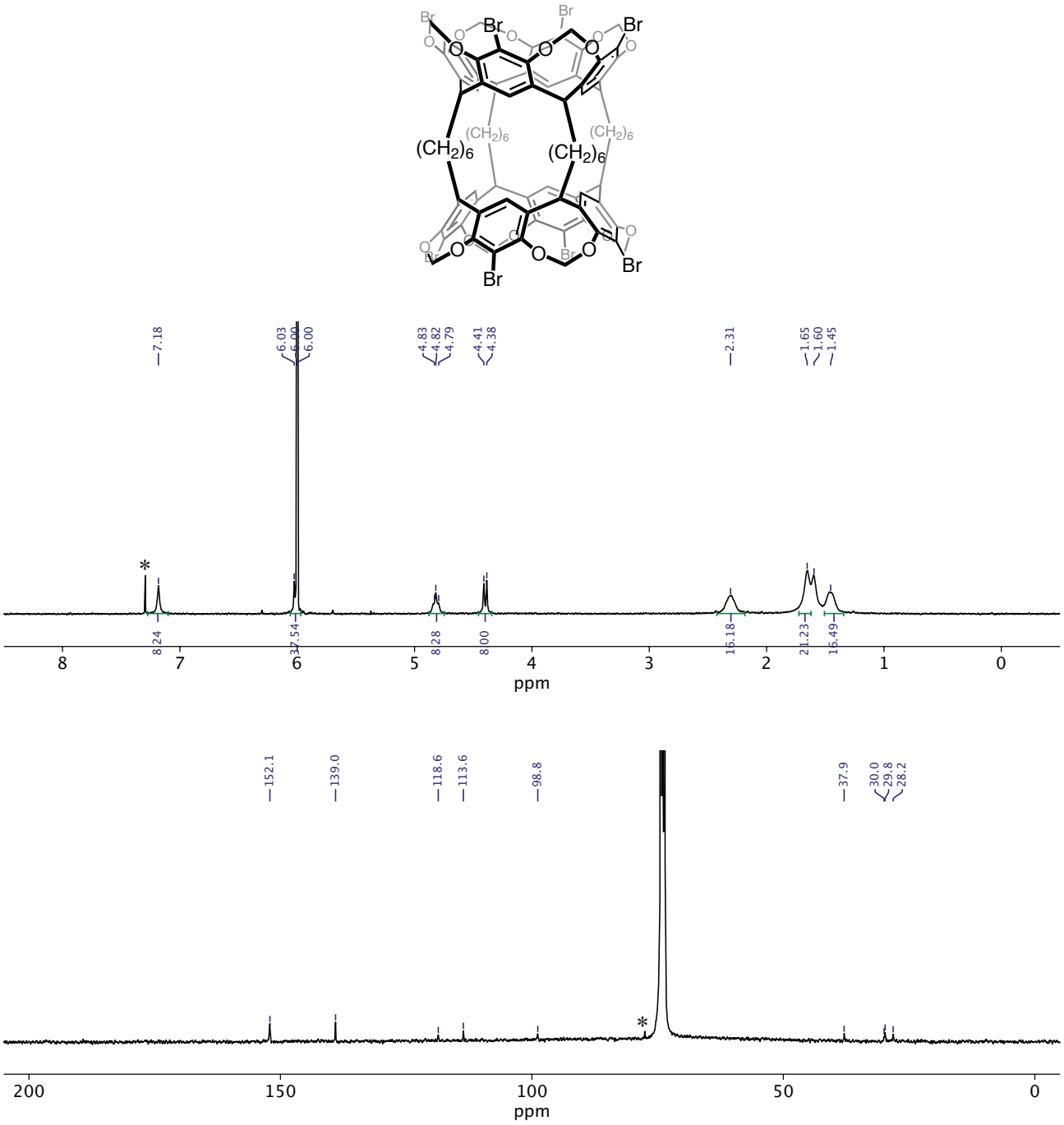


Figure S2. ^{1}H and ^{13}C NMR spectra of **2** in tetrachloroethane-d_2. *chloroform signal.

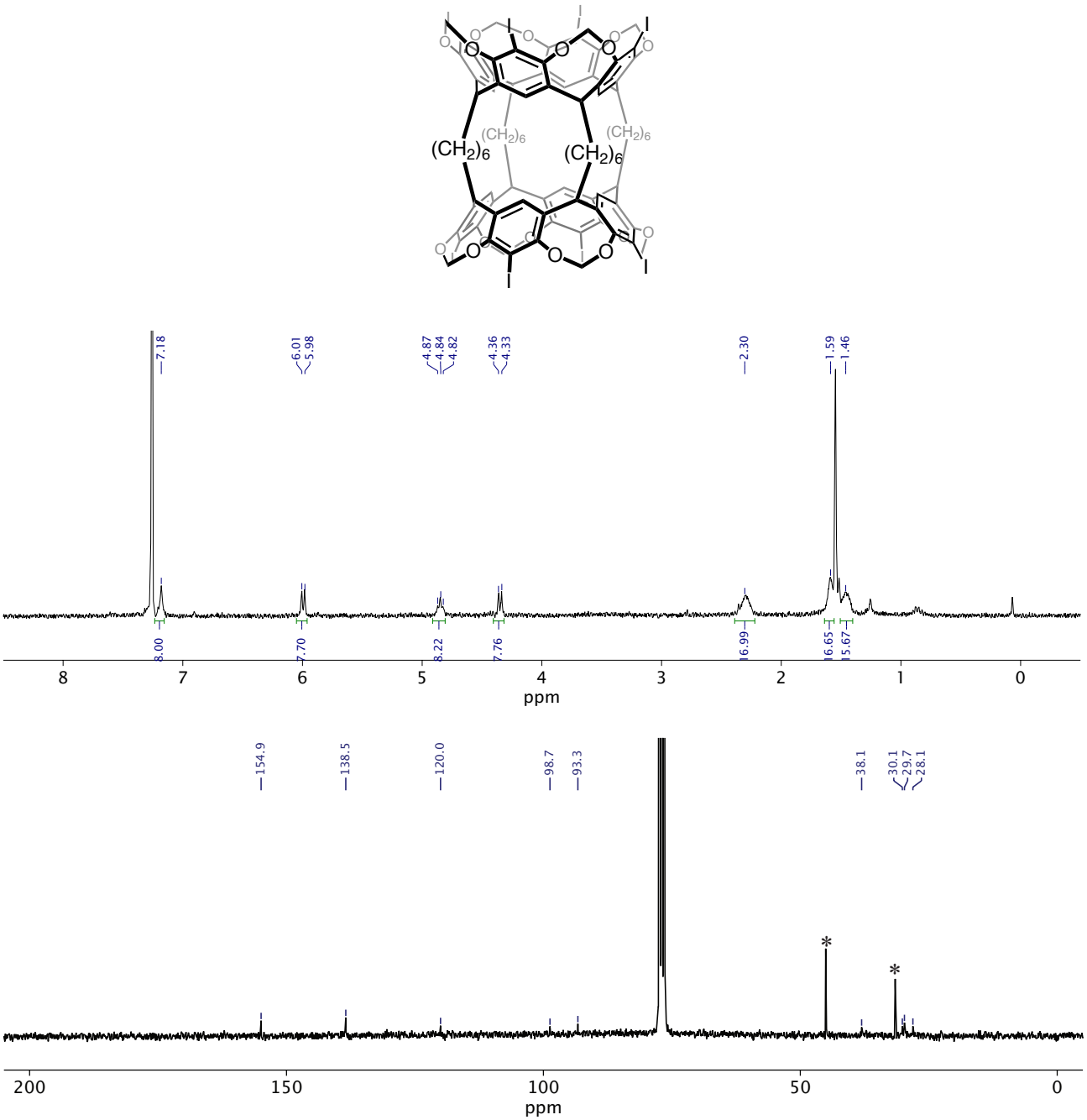


Figure S3. ^{1}H and ^{13}C NMR spectra of **1** in chloroform-d_1. *DMI signal.

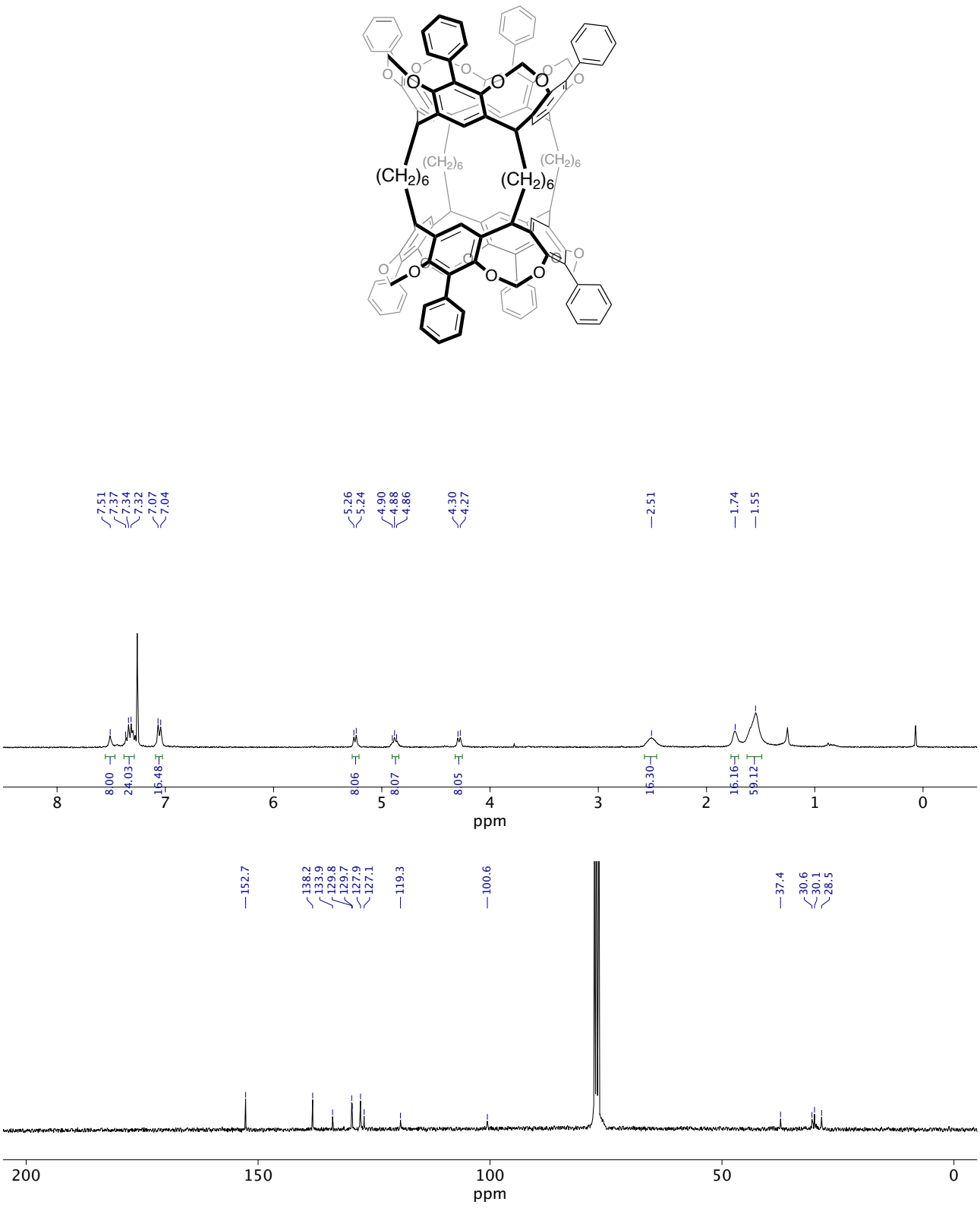


Figure S4. ^{1}H and ^{13}C NMR spectra of **3** in chloroform-d_1.

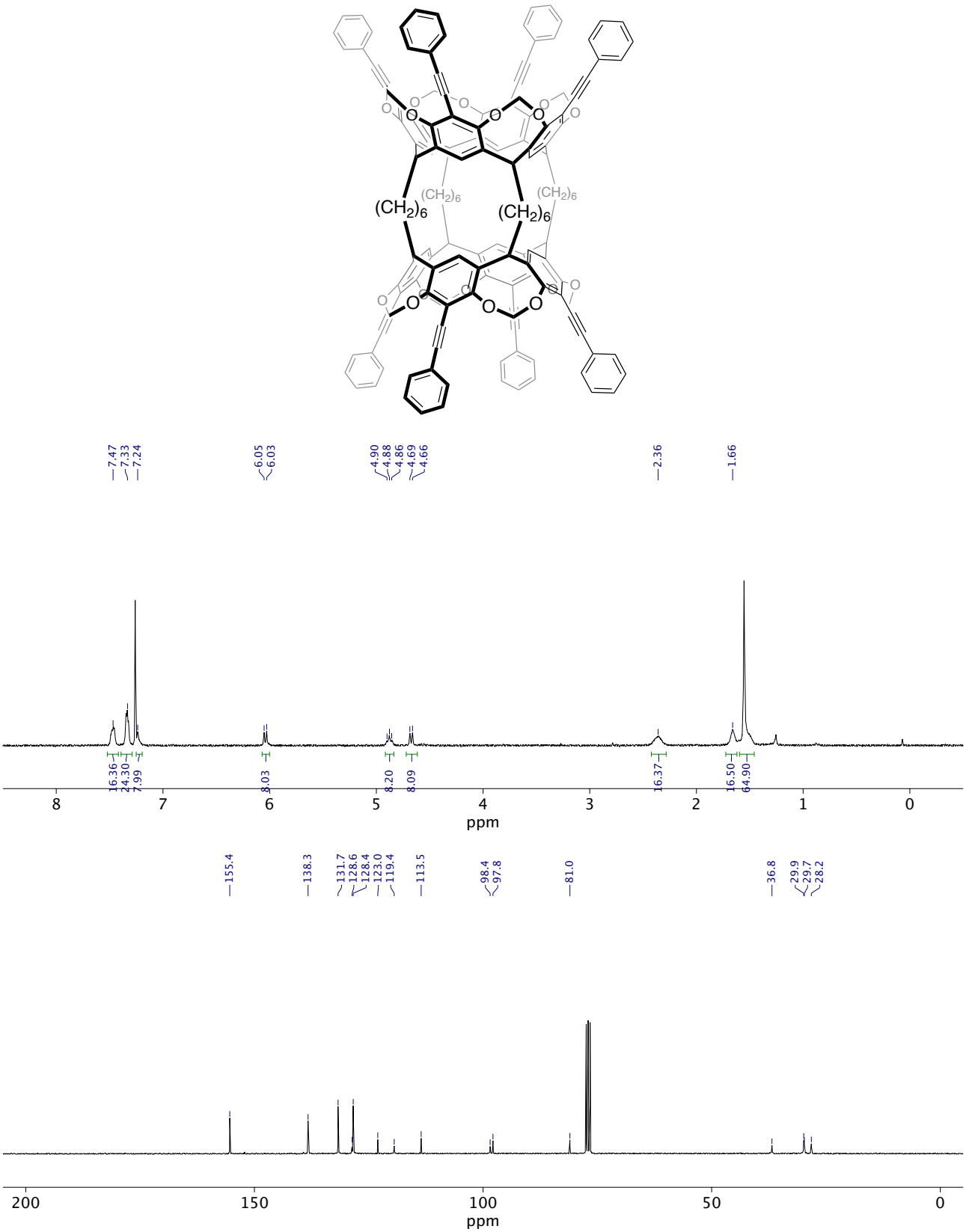


Figure S5. ^{1}H and ^{13}C NMR spectra of **4** in chloroform-d_1.

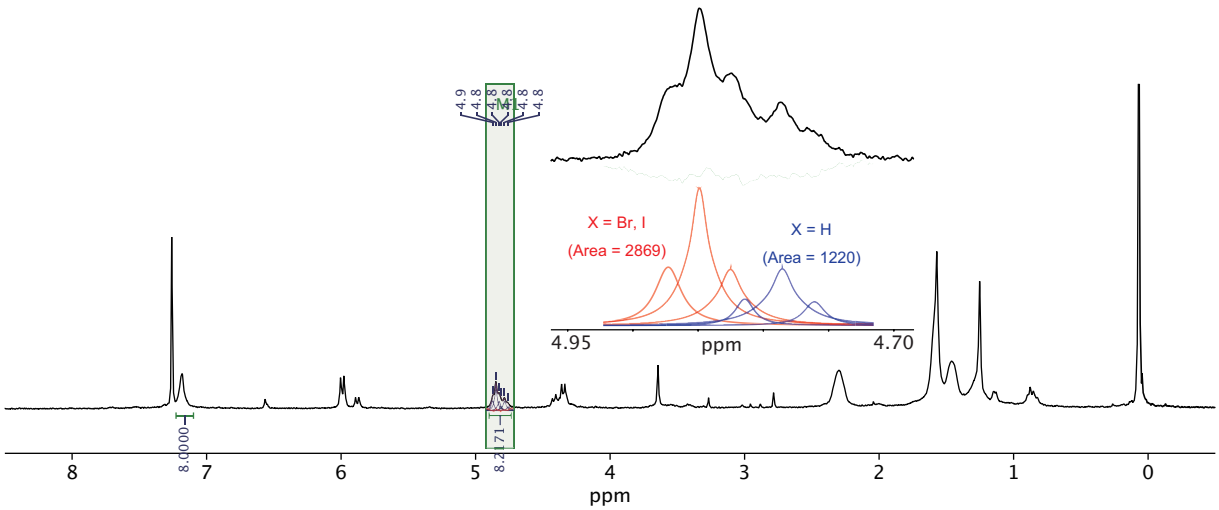


Figure S6. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of the crude mixtures of reaction for entry 1.

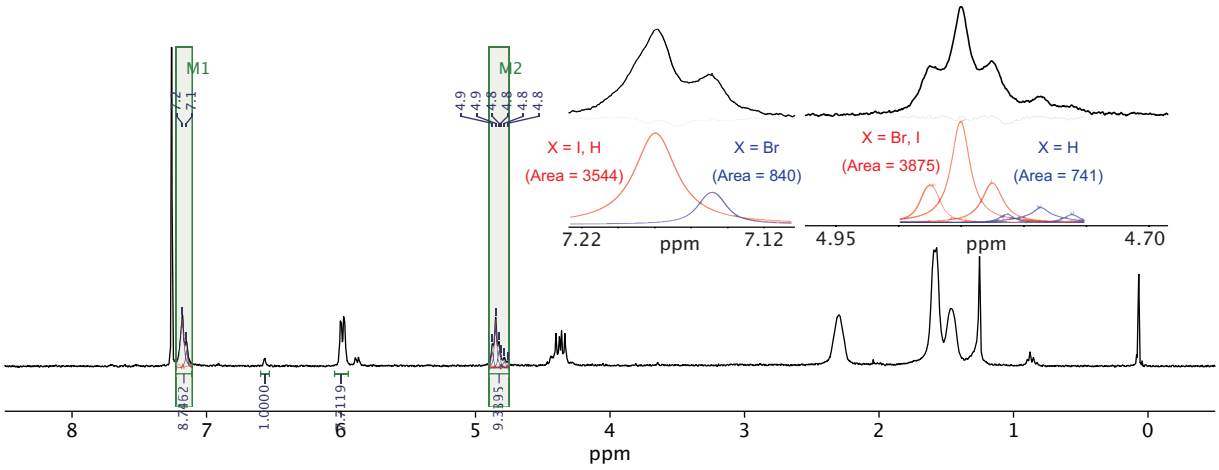


Figure S7. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of the crude mixtures of reaction for entry 2.

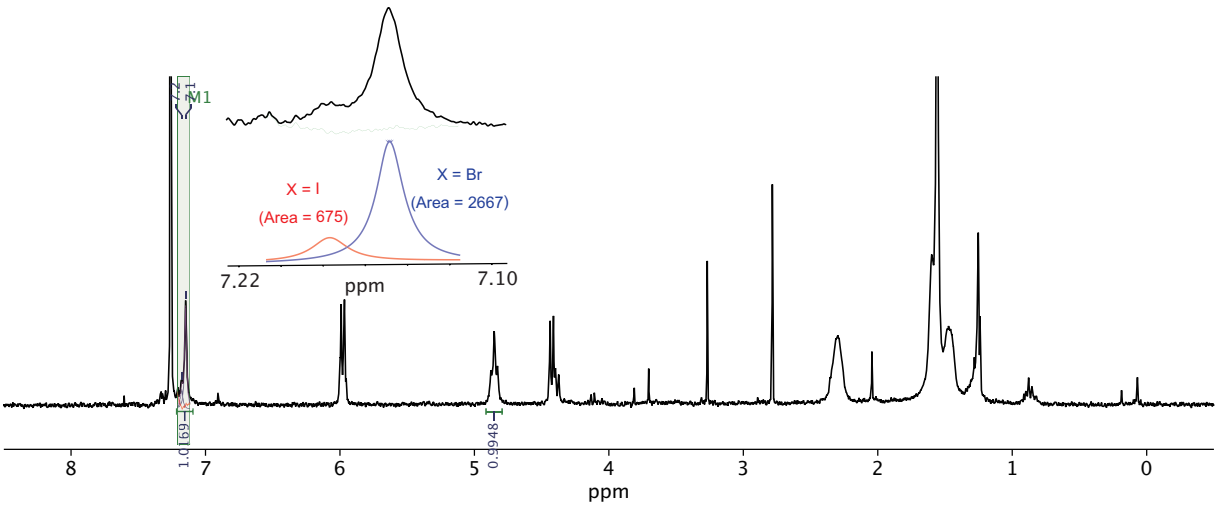


Figure S8. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of the crude mixtures of reaction for entry 3.

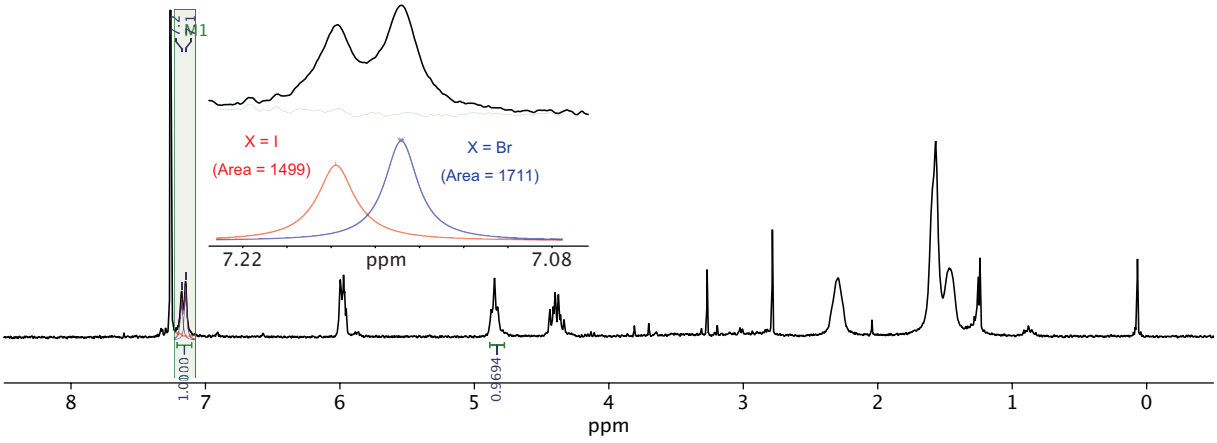


Figure S9. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of the crude mixtures of reaction for entry 4.

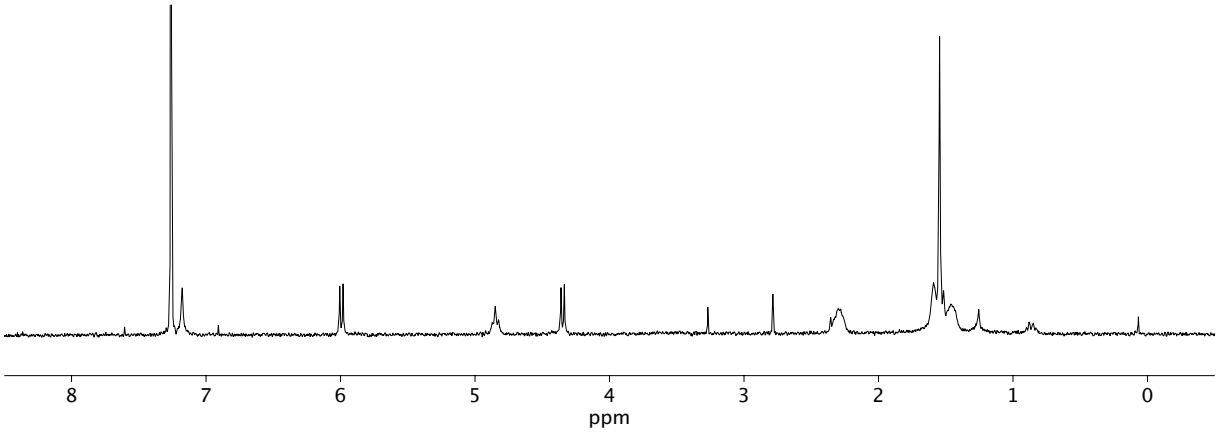


Figure S10. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of the crude mixtures of reaction for entry 5.

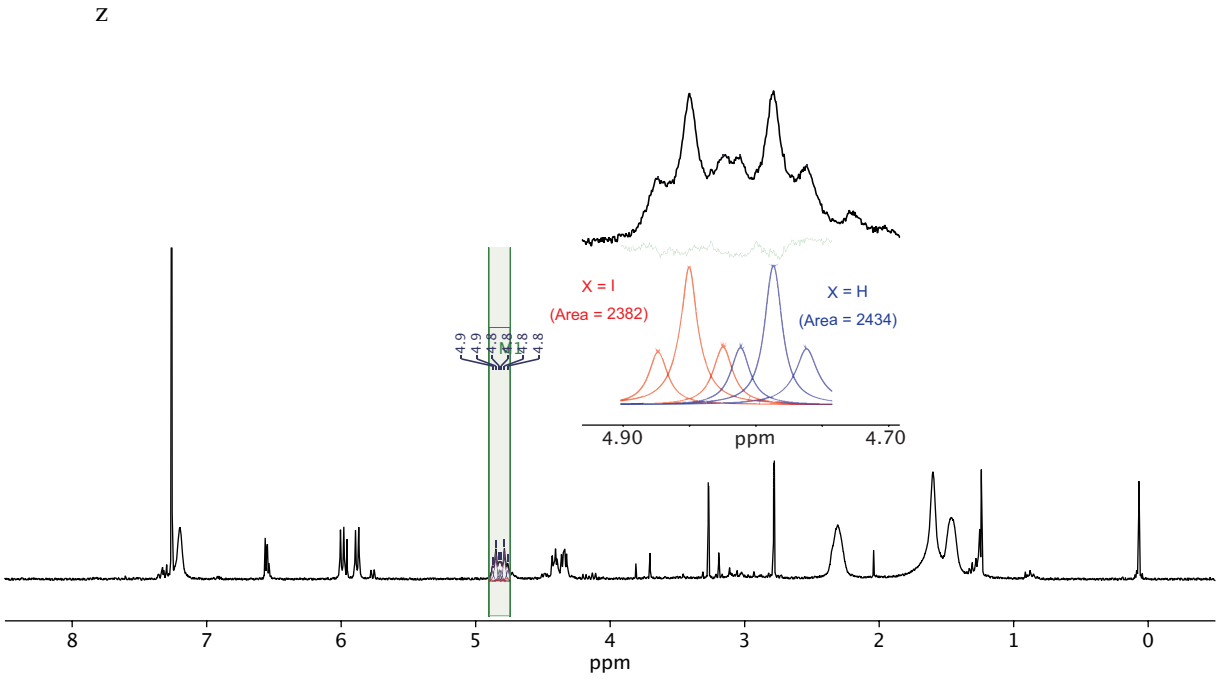


Figure S11. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of the crude mixtures of reaction for entry 6.

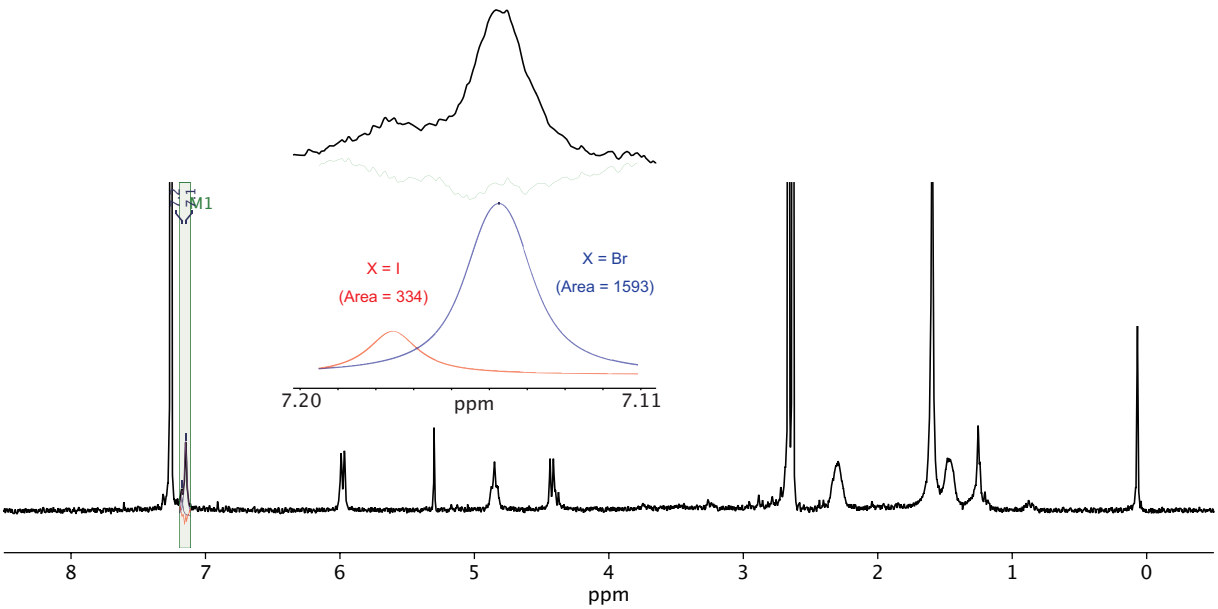


Figure S12. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of the crude mixtures of reaction for entry 7.

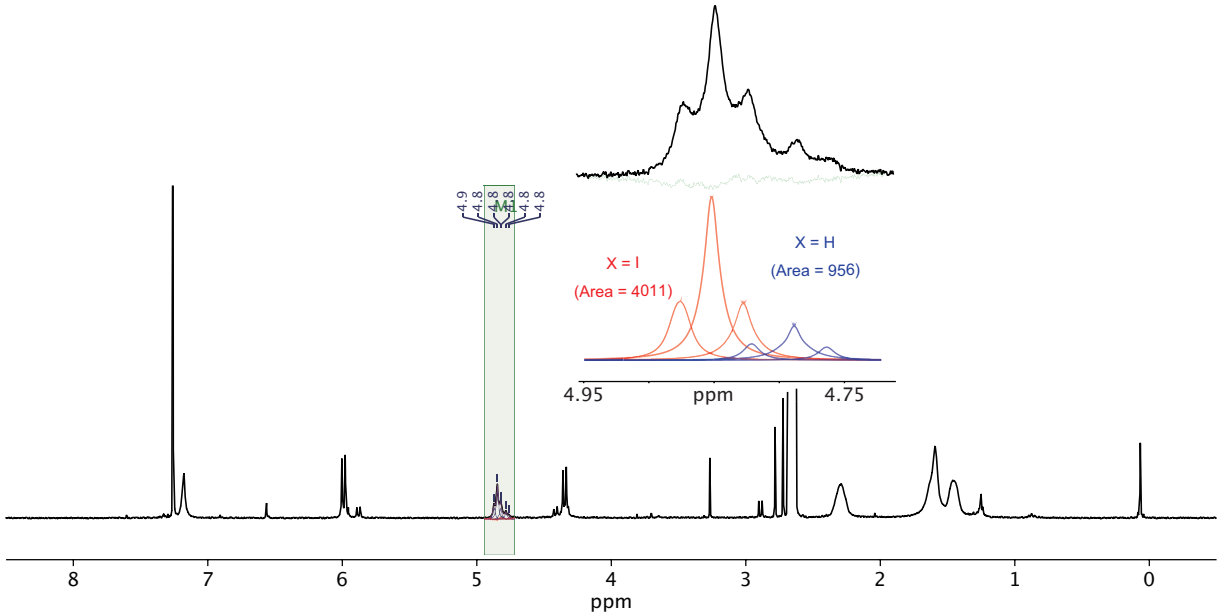


Figure S13. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of the crude mixtures of reaction for entry 8.

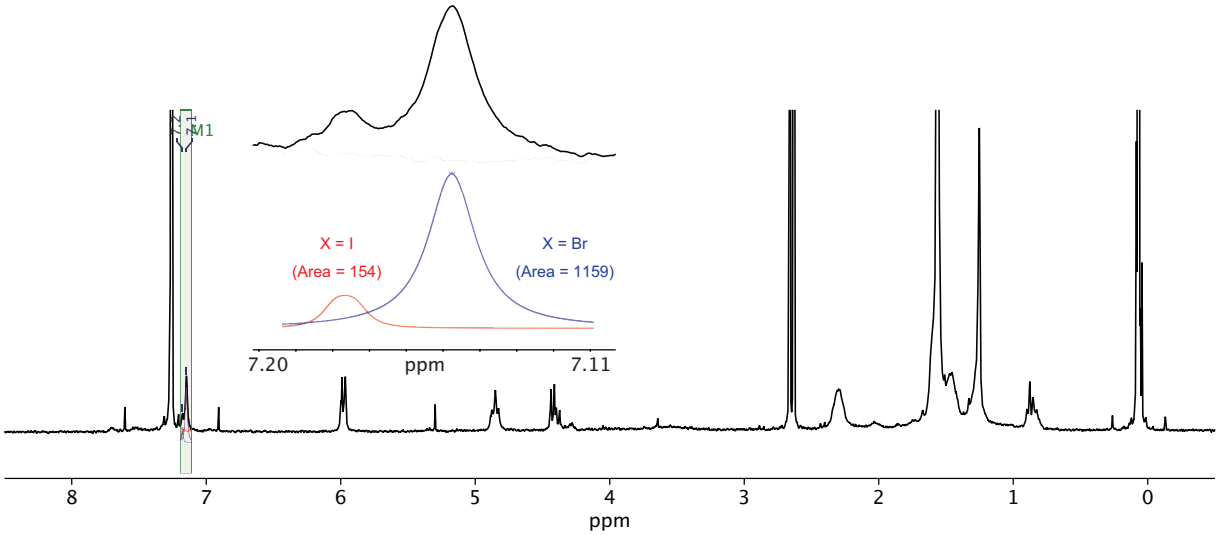


Figure S14. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of the crude mixtures of reaction for entry 9.

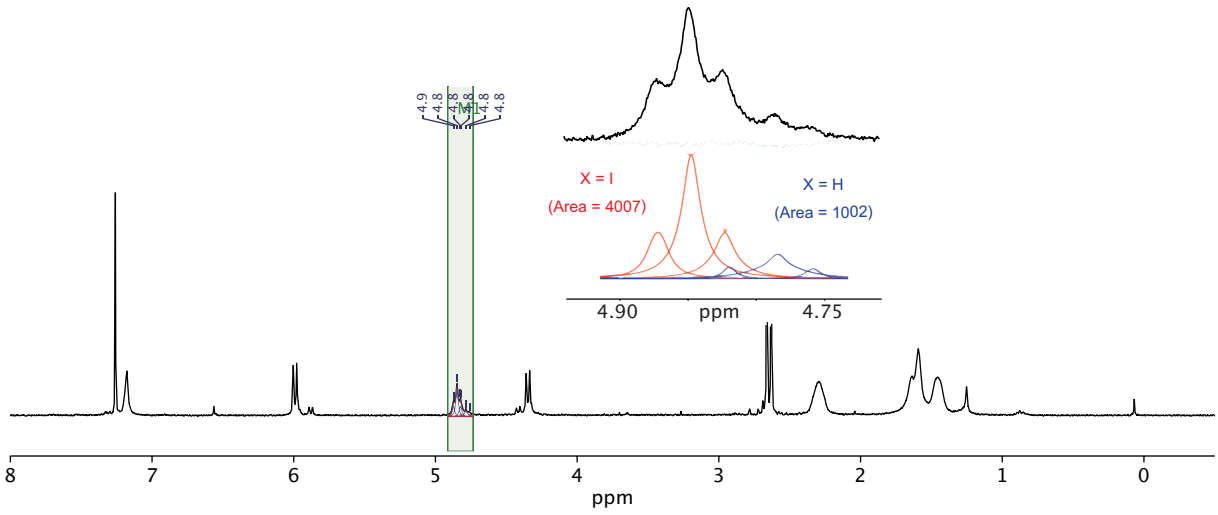


Figure S15. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of the crude mixtures of reaction for entry 10.

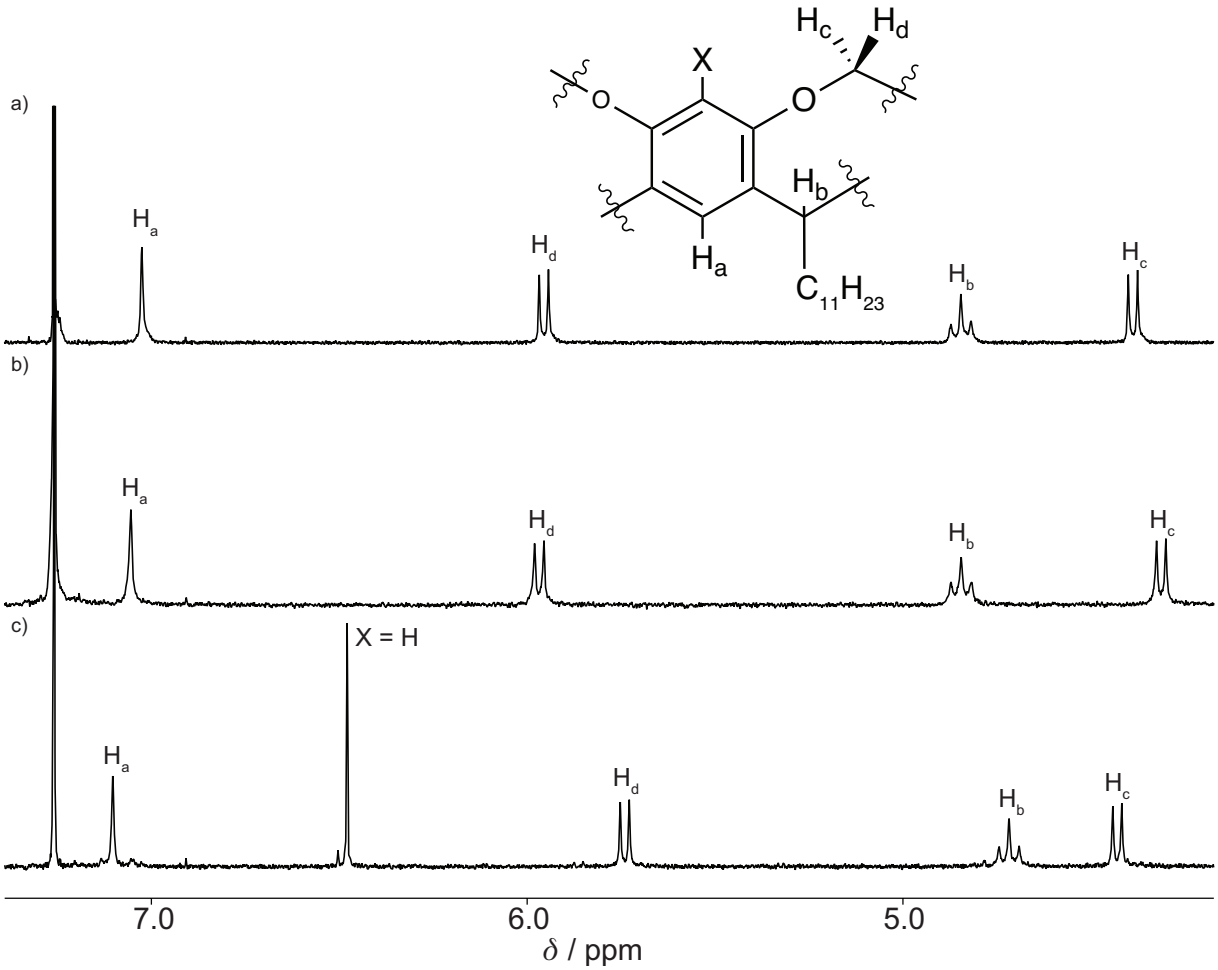


Figure S16. ^{1}H NMR spectrum (300 MHz, chloroform-d_1) of a) tetrabromomonocavitand (X = Br), b) tetraiodomonocavitand (X = I), and c) monocavitand **7**.

Table S1. Crystallographic parameters of biscavitand **4**.

Formula	$C_{154}H_{122}Cl_6O_{16}$	Temperature/ K	93
Formula weight	3172.1(11)	Crystal form	plate
Crystal system	triclinic	Crystal size/ mm^3	0.13 × 0.08 ×0.01
Space group	*P*–1	Crystal color	colorless
a/ Å	11.895(6)	# of total reflections	34209
b/ Å	13.566(6)	# of unique reflections	14926
c/ Å	21.429(10)	# of observed reflections	6755
α/ º	89.762(5)	R_{int}	0.0767
β/ º	74.368(5)	$R1(F_o)$	0.149
γ/ º	73.348(5)	$wR2(F_o^2)$	0.3844
V/ $Å^3$	3180(3)	*G. O. F.*	1.283
$d_{calc.}$/ g cm^{-3}	1.275	# of parameters used	775
Z	1	$\Delta\rho_{max}$/ $eÅ^{-3}$	2.193
$2\theta_{max}$/ º	3.580≤2θ≤56.358	$\Delta\rho_{min}$/ $eÅ^{-3}$	–1.419
ρ (MoKα)/ mm^{-1}	0.202	*CCDC* number	1981472

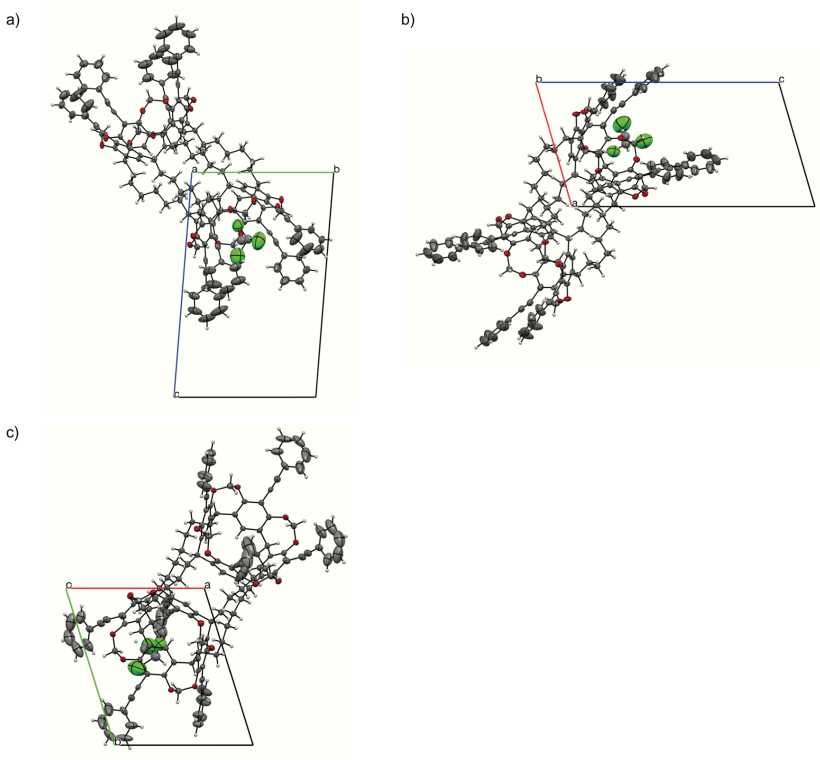


Figure S17. ORTEP drawing of the X-ray crystal structure of **4**. Views along (a) *a*-, (b) *b*-, and (c) *c*-axes. Ellipsoids are shown at 50%. Hydrogen atoms are omitted for clarity. (Crystals were obtained by slow diffusion of hexane vapor into the solution of chloroform.)

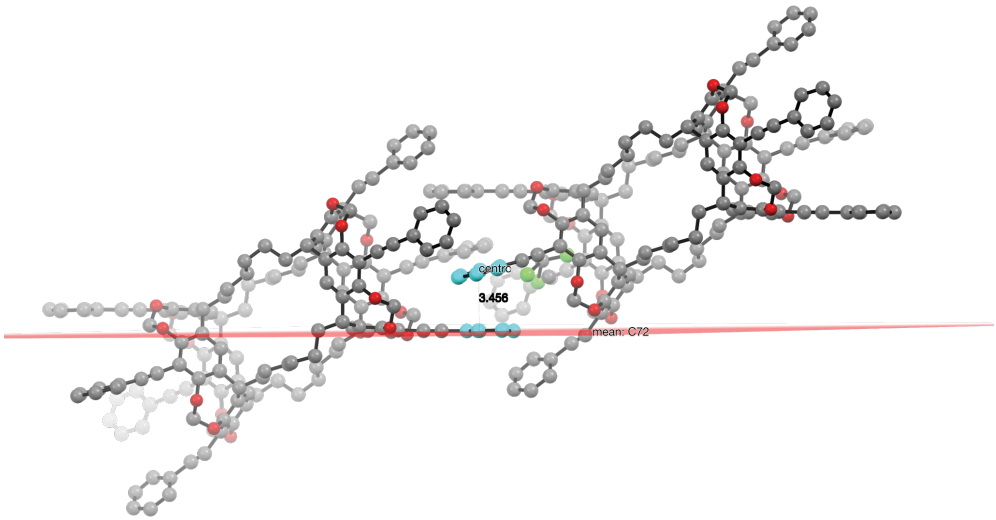


Figure S18. π-Stacking in the crystal structure of **4**.

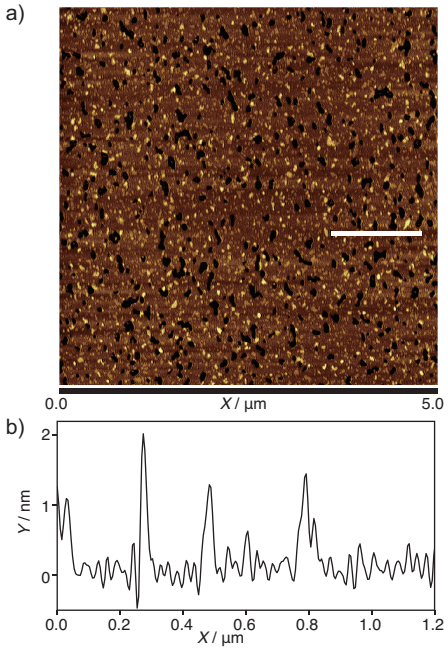


Figure S19. (a) AFM images of cast films prepared from chloroform solutions of **1**. (b) The height profile of the white line in (a).

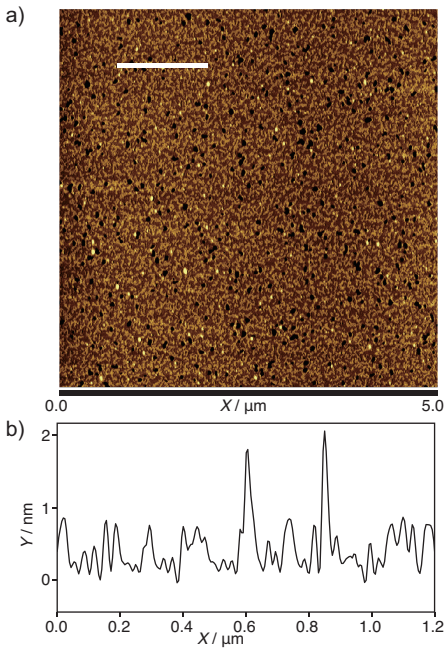


Figure S20. (a) AFM images of cast films prepared from chloroform solutions of **3**. (b) The height profile of the white line in (a).

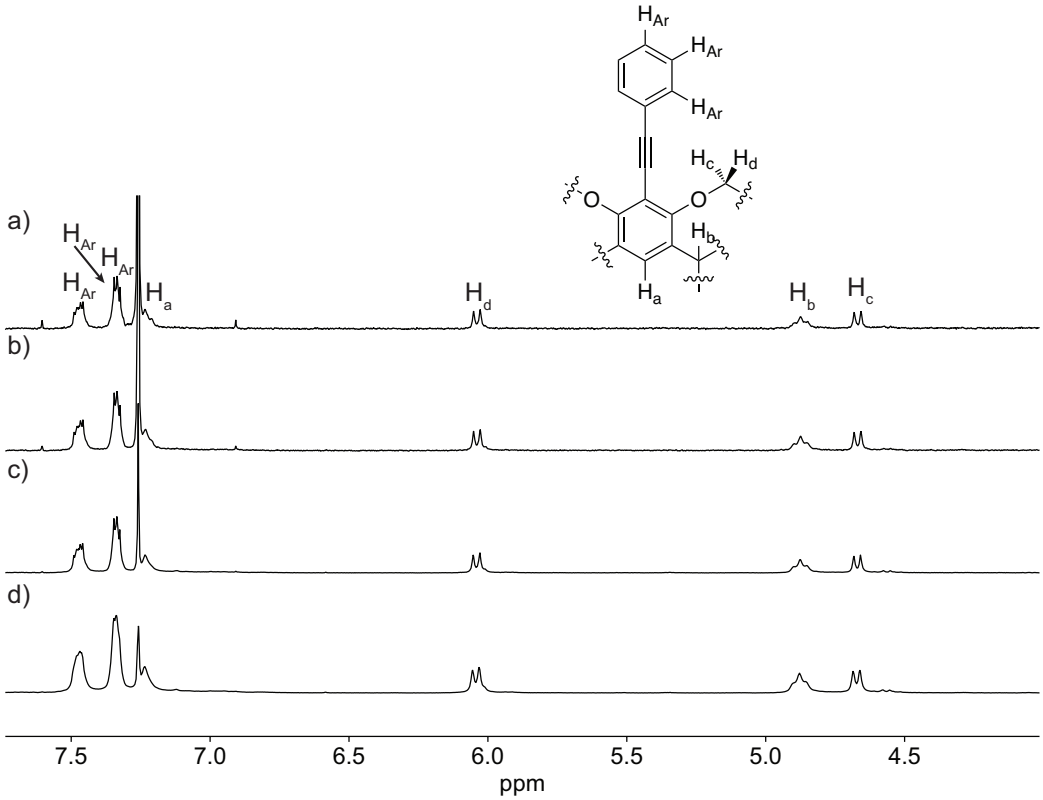


Figure S21. Concentration-dependent ^{1}H NMR spectra of **4** at 25 °C in chloroform-d_1. The concentrations of **4** are (a) 0.5, (b) 1.0, (c) 5.0, and (d) 10.0 mmol L^{-1}.

References

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