Synthesis of Highly Strained π-Bowls from Sumanene

Toru Amaya, Takuto Nakata, and Toshikazu Hirao*

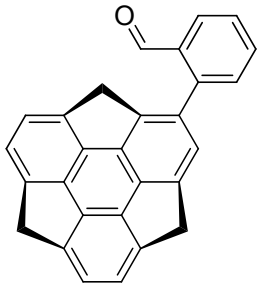
Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan

Supporting Information

Experimental Section

General. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra were measured on a Varian INOVA 600 spectrometer. CD_2Cl_2, THF-d_8, and mesitylene-d_{12} were used as a solvent and the residual solvent peak (^{1}H, δ 5.32, 3.58 and 2.11 for CD_2Cl_2, THF-d_8 and mesitylene-d_{12}, respectively; ^{13}C, 53.8, 66.6 ppm for CD_2Cl_2 and THF-d_8, respectively) was used as a reference. Infrared spectra were recorded on JASCO FT/IR-480plus. Mass spectra were measured on a JEOL JMS-DX-303 spectrometer using electron impact (EI) mode. Column chromatography was conducted on silica gel (Wakogel C-200). All reagents and solvents were purchased from commercial sources.

Monoaldehyde 5 :

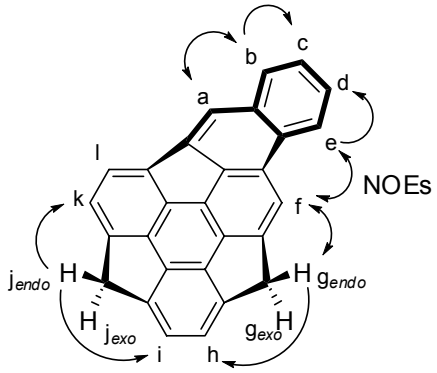


5

To a dioxane (2.5 mL) solution of **4** (8 mg, 0.0233 mmol), 2-formylphenylboronic acid (10.5 mg, 0.0700 mmol), Cs_2CO_3 (15.2 mg, 0.0467 mmol), and P(*t*-Bu)$_3$ (9.4 mg, 0.0465 mmol) was added $Pd_2(dba)_3$ (10.6 mg, 0.0116 mmol) at room temperature. The mixture was stirred at 80 ^{o}C for 24 h. After concentration, the residue was purified by preparative thin-layer silica-gel chromatography (CH_2Cl_2) to give the product **5** as a yellow oil (8 mg, 0.0217 mmol, 93%). IR (neat) cm^{-1}: 1686, 1595, 1391, 1264, 787, 735; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 3.09 (d, *J* = 19.8 Hz, 1H), 3.46 (d, *J* = 19.8 Hz, 1H), 3.58 (d, *J* = 19.8 Hz, 1H), 4.53 (d, *J* = 19.8 Hz, 1H), 4.73 (d, *J* = 19.8 Hz, 1H), 4.80 (d, *J* = 19.8 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.20 (s, 1H), 7.33 (brs, 1H), 7.51 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.62 (dd, *J* = 7.8, 7.8 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 10.20 (brs, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2) 42.0, 42.1, 42.2, 123.7, 123.8, 124.1, 125.5, 127.7, 128.2, 131.3, 133.97, 134.01, 145.2, 148.5, 148.7, 148.8, 148.9x2, 149.3, 149.5, 149.59x2, 149.63x2, 149.7x2, 150.4, 192.8 ppm; HRMS (EI) Found: *m/z* 368.1194; calcd for

$C_{28}H_{16}O$: M, 368.1201.

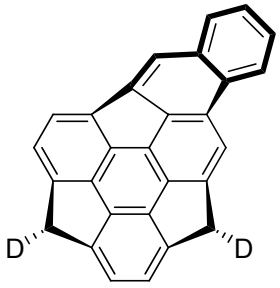
Naphtosumanene 6 :



6

Monoaldehyde **5** (4 mg, 0.0109 mmol) was charged in an NMR tube attached with a resealable J-Young valve. In glove box, to a THF-d_8 (500 μL) solution of **5** was added $KN(SiMe_3)_2$ (0.91 M, THF solution; 100 μL, 0.0912 mmol) at below -80 ^oC using liq. nitrogen/silica gel bath. The mixture was shaken at room temperature for 1 h. After checking the disappearance of **5** by ^1H NMR, the reaction mixture was poured into the mixed solution of ether and aqueous saturated ammonium chloride. The aqueous layer was extracted with ether, and the combined organic layer was washed with aqueous saturated $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by preparative thin-layer silica-gel chromatography (hexane-CH_2Cl_2) to give the product **6** as a yellow solid (3.7 mg, 0.0106 mmol, 98%). IR (neat) cm^{-1}: 1640, 752, 695, 673; ^1H NMR (600 MHz, CD_2Cl_2) δ 3.36 (d, J = 19.2 Hz, 1H, j_{endo}), 3.52 (d, J = 19.2 Hz, 1H, g_{endo}), 4.79 (d, J = 19.2 Hz, 1H, j_{exo}), 4.95 (d, J = 19.2 Hz, 1H, g_{exo}), 7.06 (d, J = 7.8 Hz, 1H, i), 7.10 (d, J = 7.8 Hz, 1H, h), 7.29 (d, J = 7.8 Hz, 1H, k), 7.53 (d, J = 7.8 Hz, 1H, l), 7.57 (dd, J = 7.8, 7.8 Hz, 1H, c), 7.66 (dd, J = 7.8, 7.8 Hz, 1H, d), 7.97 (s, 1H, a), 8.00 (d, J = 7.8 Hz, 1H, b), 8.08 (s, 1H, f), 8.55 (d, J = 7.8 Hz, 1H, e); ^{13}C NMR (150 MHz, CD_2Cl_2) 42.0, 42.7, 121.4, 122.1, 122.8, 123.71, 123.74, 124.0, 125.7, 126.5, 127.6, 130.8, 132.3, 135.3, 138.4, 138.6, 141.6, 144.8, 148.6, 149.8, 150.1, 150.2, 150.78, 150.84, 151.6, 152.4, 153.0 ppm; HRMS (EI) Found: *m/z* 350.1093; calcd for $C_{28}H_{14}$: M, 350.1096.

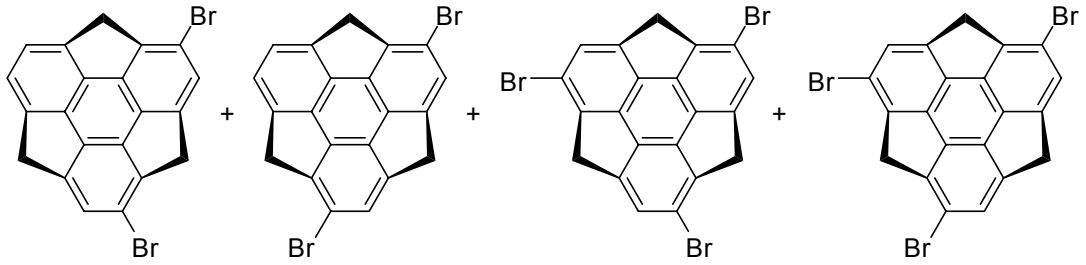
Dideuterated naphtosumanene 7a :



7a

Naphtosumanene **6** (4 mg, 0.0114 mmol) was charged in an NMR tube attached with a resealable J-Young valve. In glove box, to a THF-d_8 (500 μL) solution of **6** was added *t*-BuLi (1.57 M, pentane solution; 27.3 μL, 0.0429 mmol) at below -80 ^{o}C using liq. nitrogen/silica gel bath. After checking the dianion of **6** by ^{1}H NMR, MeOD (1 mL) was added at below -80 ^{o}C using liq. nitrogen/silica gel bath in glove box. The mixture was shaken at room temperature for 1 h. The reaction mixture was poured into the mixed solution of ether and aqueous saturated ammonium chloride. The aqueous layer was extracted with ether, and the combined organic layer was washed with aqueous saturated $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by preparative thin-layer silica-gel chromatography (hexane-CH_2Cl_2) to give **7a** as a yellow solid (4 mg, 0.0114 mmol, quant.); dianion of **6**: ^{1}H NMR (600 MHz, THF-d_8) δ 5.20 (s, 1H), 5.59 (s, 1H), 6.15 (d, J = 9.0 Hz, 1H), 6.57 (d, J = 9.0 Hz, 1H), 6.74 (d, J = 9.0 Hz, 1H), 6.82 (d, J = 9.0 Hz, 1H), 6.82 (s, 1H), 7.15-7.20 (m, 2H), 7.49 (s, 1H), 7.68 (d, J = 7.2 Hz, 1H), 8.50 (d, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, THF-d_8) 89.6, 93.2, 106.7, 107.9, 113.7, 118.2, 119.6, 120.9, 122.4, 122.5, 123.1, 124.4, 128.3, 128.5, 131.9, 132.3, 133.2, 134.2, 136.0, 136.2, 136.5, 137.5, 137.7, 138.2, 143.9, 144.8, 145.9, 158.4 ppm; **7a**: IR (neat) cm^{-1}: 1717, 1282, 1014, 804, 759; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 3.35 (s, 1H), 3.50 (s, 1H), 7.06 (d, J = 7.8 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.57 (dd, J = 7.8, 7.8 Hz, 1H), 7.66 (dd, J = 7.8, 7.8 Hz, 1H), 7.97 (s, 1H), 8.00 (d, J = 7.8 Hz, 1H), 8.08 (s, 1H), 8.55 (d, J = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, CD_2Cl_2) 41.6 (t, J = 19.9 Hz), 42.3 (t, J = 20.0 Hz), 121.3, 121.9, 122.6, 123.5, 123.6, 123.8, 125.6, 126.3, 127.4, 130.6, 132.1, 135.1, 138.2, 138.4, 141.5, 144.6, 148.5, 149.6, 149.9, 150.0, 150.60, 150.64, 151.5, 152.2, 152.7 ppm; HRMS (EI) Found: *m/z* 352.1226; calcd for $C_{28}H_{12}D_2$: M, 352.1221.

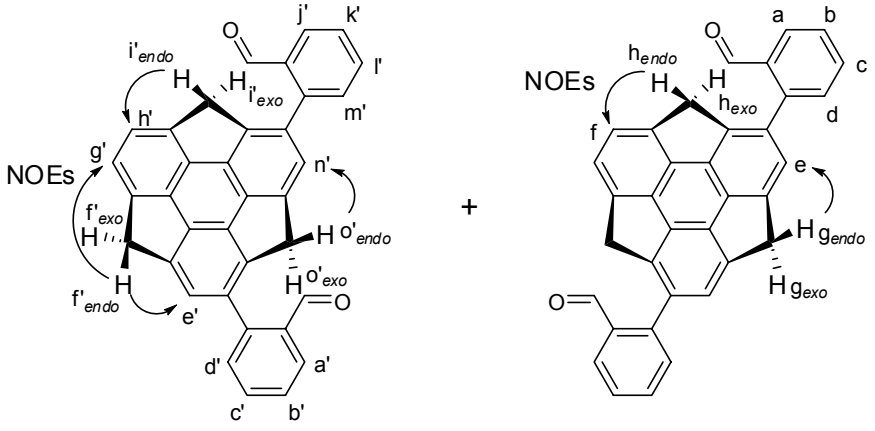
Dibromides 8a,b and tribromides 3a,b :



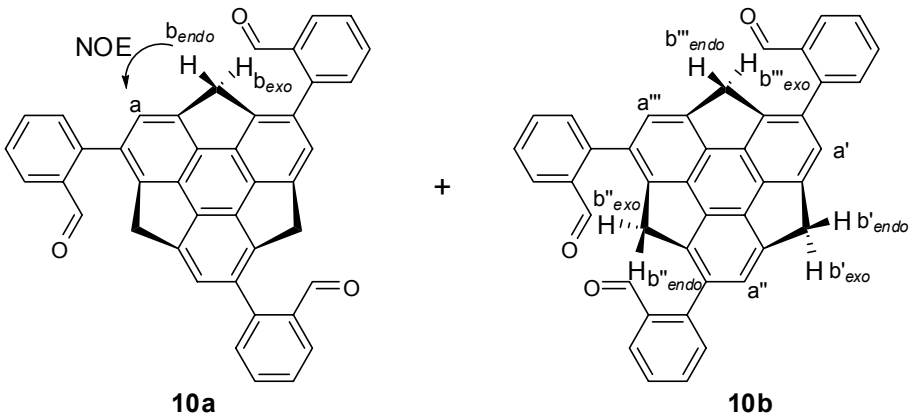
8a **8b** **3a** **3b**

To a $CHCl_3/CH_3CN$ (2 mL/0.5 mL) solution of **1** (10 mg, 0.0378 mmol) was added Br_2 (20 mg, 0.125 mmol) at 60 ^oC. The mixture was stirred for 4.5 h. After work-up with saturated $Na_2S_2O_3$ and saturated $NaHCO_3$, the mixture was extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by preparative thin-layer silica-gel chromatography (hexane-CH_2Cl_2) to give a mixture of **8a**,**b** and **3a**,**b** (16 mg). **8a**,**b**: HRMS (EI) Found: *m/z* 419.9133; calcd for $C_{21}H_{10}Br_2$: M, 419.9149; **3a**,**b**: HRMS (EI) Found: *m/z* 497.8246; calcd for $C_{21}H_9Br_3$: M, 497.8254.

Dialdehyde 9a,b and trialdehyde 10a,b :



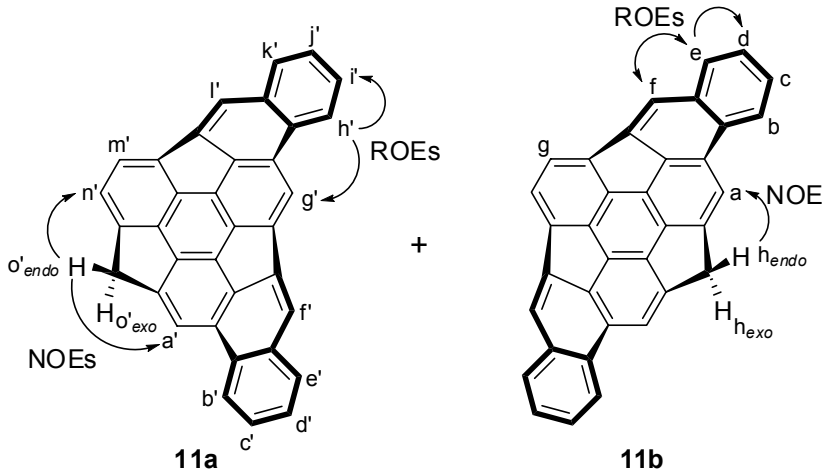
9a **9b**



10a **10b**

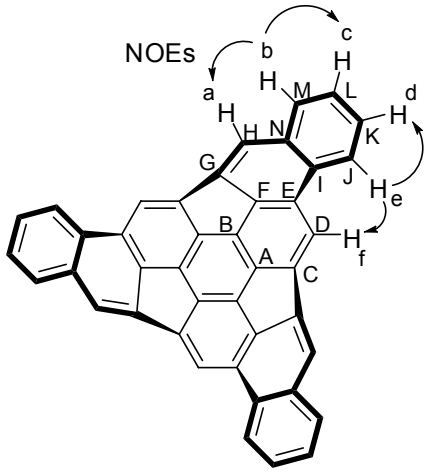
To a dioxane (3 mL) solution of **8a**,**b** and **3a**,**b** (16 mg), 2-formylphenylboronic acid (43 mg, 0.287 mmol), Cs_2CO_3 (21 mg, 0.0645 mmol), and P(*t*-Bu)$_3$ (19 mg, 0.0941 mmol) was added $Pd_2(dba)_3$ (44 mg, 0.0481 mmol) at room temperature. The mixture was stirred at 80 ^oC for 24 h. After concentration, the residue was purified by preparative thin-layer silica-gel chromatography (hexane-ethyl acetate) to give a mixture of **9a**,**b** as a yellow oil (**9a**/**9b** = 1/1.2, 8 mg, 0.0169 mmol, 2 steps 45%) and a mixture of **10a**,**b** as a yellow oil (**10a**/**10b** = 1/5, 9 mg, 0.0156 mmol, 2 steps 41%). **9a,b**: IR (neat) cm^{-1}: 1687, 1595, 1396, 1266, 1193, 769, 735; ^1H NMR (600 MHz, CD_2Cl_2) δ 3.13 (d, *J* = 19.8 Hz, 1H+2H, i'$_{endo}$, h$_{endo}$), 3.24 (d, *J* = 19.8 Hz, 1H, o'$_{endo}$), 3.62 (d, *J* = 19.8 Hz, 1H, f'$_{endo}$), 3.73 (d, *J* = 19.8 Hz, 1H, g$_{endo}$), 4.56 (d, *J* = 19.8 Hz, 1H+2H, i'$_{exo}$, h$_{exo}$), 4.62 (d, *J* = 19.8 Hz, 1H, o'$_{exo}$), 4.83 (d, *J* = 19.8 Hz, 1H, f'$_{exo}$), 4.90 (d, *J* = 19.8 Hz, 1H, g$_{exo}$), 7.05 (s, 2H, f), 7.09 (d, *J* = 7.2 Hz, 1H, h'), 7.12 (s, 1H, n'), 7.19 (d, *J* = 7.2 Hz, 1H, g'), 7.27 (brs, 1H+2H, e', e), 7.38 (brs, 1H+2H, d' or m', d), 7.49-7.55 (m, 3H+2H, b', d' or m', k', b), 7.60 (dd, *J* = 7.2, 7.2 Hz, 1H, c' or l'), 7.61-7.67 (m, 1H+2H, c' or l', c), 8.01 (d, *J* = 7.2 Hz, 1H, a' or j'), 8.04 (d, *J* = 7.8 Hz, 2H, a), 8.05 (d, *J* = 7.2 Hz, 1H, a' or j'), 10.2 (brs, 4H, -CHO); ^{13}C NMR (150 MHz, CD_2Cl_2) 42.16x2, 42.19, 42.3, 42.4, 124.1, 124.2, 125.7, 127.71, 127.76, 127.77, 128.24, 128.27, 128.28, 131.3, 133.99, 134.03, 134.04, 134.2, 134.4, 134.5, 144.9, 145.01, 145.03, 148.3, 148.5, 148.7, 148.8, 148.90, 148.94, 149.09, 149.10, 149.11, 149.15, 149.2, 149.3, 149.8, 149.9, 150.5, 150.6, 192.7 ppm; HRMS (EI) Found: *m/z* 472.1459; calcd for $C_{35}H_{20}O_2$: M, 472.1463. **10a**,**b**: IR (neat) cm^{-1}: 1690, 1595, 1194, 871, 768, 738; ^1H NMR (600 MHz, CD_2Cl_2) δ 2.78 (d, *J* = 19.8 Hz, 1H, b'$_{endo}$ or b''$_{endo}$ or b'''$_{endo}$), 3.28 (d, *J* = 19.8 Hz, 1H, b$_{endo}$, b'$_{endo}$ or b''$_{endo}$ or b'''$_{endo}$), 3.77 (d, *J* = 19.8 Hz, 1H, b'$_{endo}$ or b''$_{endo}$ or b'''$_{endo}$), 4.40 (d, *J* = 19.8 Hz, 1H, b'$_{exo}$ or b''$_{exo}$ or b'''$_{exo}$), 4.65 (d, *J* = 19.8 Hz, 1H, b$_{exo}$, b'$_{exo}$ or b''$_{exo}$ or b'''$_{exo}$), 4.93 (d, *J* = 19.8 Hz, 1H, b'$_{exo}$ or b''$_{exo}$ or b'''$_{exo}$), 7.13 (s, 1H, a' or a'' or a'''), 7.18 (s, 1H, a), 7.24 (brs, 2H, a' or a'' or a'''), 7.32 (brs, 2H, a' or a'' or a'''), 7.41-7.47 (m, 3H), 7.52-7.59 (m, 3H), 7.63 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.68 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 10.20 (br, 4H, -CHO); ^{13}C NMR (150 MHz, CD_2Cl_2) 42.2, 42.3x2, 42.5, 126.0, 126.2, 127.82, 127.87, 127.88, 128.29, 128.31, 128.37, 128.39, 131.3, 134.01, 134.05, 134.07, 134.10, 134.57, 134.60, 134.8, 135.0, 144.59, 144.68, 144.76, 144.84, 148.3, 148.47, 148.50, 148.6, 148.7, 148.8, 148.9, 149.0, 149.3, 149.9, 150.1, 150.6, 150.7, 192.5x2, 192.7x2 ppm; HRMS (EI) Found: *m/z* 576.1730; calcd for $C_{42}H_{24}O_3$: M, 576.1725.

Dinaphtosumanene 11a,b :



Dialdehyde **9a,b** (**9a**/**9b** = 1/1.2, 6 mg, 0.0127 mmol) was charged in an NMR tube attached with a resealable J-Young valve. In glove box, to a THF-d_8 (500 μL) solution of **9a,b** was added $KN(SiMe_3)_2$ (0.91 M, THF solution; 56 μL, 0.0510 mmol) at below -80 ^oC using liq. nitrogen/silica gel bath. The mixture was shaken at room temperature for 1 h. This reaction was monitored by ^1H NMR. After checking the disappearance of the peaks for **9a,b**, the reaction mixture was poured into the mixed solution of ether and aqueous saturated ammonium chloride. The aqueous layer was extracted with ether, and the combined organic layer was washed with aqueous saturated $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by preparative thin-layer silica-gel chromatography (hexane-CH_2Cl_2) to give a mixture of **11a,b** as a yellow solid (**11a**/**11b** = 1/1.2, 6 mg, 0.0127 mmol, quant.). These compounds are independent with isolable peaks in the ^1H NMR spectrum. IR (neat) cm^{-1}: 3019, 1216, 770, 669; ^1H NMR (600 MHz, CD_2Cl_2) δ 3.43 (d, *J* = 19.2 Hz, 1H, h_{endo}), 3.57 (d, *J* = 18.6 Hz, 1H, o'_{endo}), 5.02 (d, *J* = 19.2 Hz, 1H, h_{exo}), 5.08 (d, *J* = 18.6 Hz, 1H, o'_{exo}), 7.27 (d, *J* = 7.8 Hz, 1H, n'), 7.48 (d, *J* = 7.8 Hz, 1H, m'), 7.49 (dd, *J* = 7.8, 7.8 Hz, 2H, d), 7.54-7.60 (m, 3H+2H, c, d', j', e' or k', f' or l'), 7.64 (dd, *J* = 7.8, 7.8 Hz, 1H, c'), 7.70 (dd, *J* = 7.8, 7.8 Hz, 1H, i'), 7.81 (s, 2H, f), 7.89 (d, *J* = 7.8 Hz, 2H, e), 7.94 (s, 2H, a), 7.98 (brs, 1H+2H, a', g), 7.99 (d, *J* = 7.8 Hz, 1H, e' or k'), 8.02 (s, 1H, f' or l'), 8.43 (d, *J* = 7.8 Hz, 2H, b), 8.46 (s, 1H, g'), 8.51 (d, *J* = 7.8 Hz, 1H, b'), 8.63 (d, *J* = 7.8 Hz, 1H, h'); ^{13}C NMR (150 MHz, CD_2Cl_2) 42.7, 43.4, 120.2, 121.4, 121.6, 122.6, 122.8, 123.0, 123.8, 124.1, 126.0, 126.7, 127.7, 127.9, 130.3, 130.8, 132.1, 132.4, 132.5, 133.1, 135.2, 135.3, 135.5, 137.6, 138.0, 138.2, 138.4, 139.0, 139.6, 141.2, 142.1, 145.3, 146.3, 146.4, 147.6, 150.3, 150.6, 151.0, 151.4, 151.7, 152.6, 152.8, 153.1, 155.0 ppm; HRMS (EI) Found: *m/z* 436.1246; calcd for $C_{35}H_{16}$: M, 436.1252.

Trinaphtosumanene 2 :



2

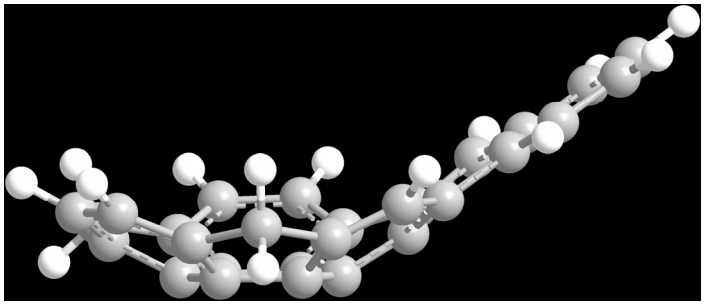
Trialdehyde **10a,b** (**10a**/**10b** = 1/5, 9 mg, 0.0156 mmol) was charged in an NMR tube attached with a resealable J-Young valve. In glove box, to a THF-d_8 (500 μL) solution of **10a,b** was added $KN(SiMe_3)_2$ (0.91 M, THF solution; 154 μL, 0.140 mmol) at below -80 ^oC using liq. nitrogen/silica gel bath. The mixture was shaken at room temperature for 1 h. This reaction was monitored by ^1H NMR. After checking the disappearance of the peaks for **10a,b**, the reaction mixture was poured into the mixed solution of ether and aqueous saturated ammonium chloride. The aqueous layer was extracted with ether, and the combined organic layer was washed with aqueous saturated $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by preparative thin-layer silica-gel chromatography (hexane-CH_2Cl_2) to give the product **2** as a yellow solid (1.4 mg, 0.00268 mmol, quant. based on **10a**). IR (neat) cm^{-1}: 2915, 2849, 1663, 1260, 1094, 804; ^1H NMR (600 MHz, CD_2Cl_2/CS_2 = 1/1) δ 7.56 (dd, *J* = 7.2, 7.8 Hz, 3H, c), 7.68 (dd, *J* = 7.8, 8.4 Hz, 3H, d), 7.97 (d, *J* = 7.2 Hz, 3H, b), 8.04 (s, 3H, a), 8.44 (s, 3H, f), 8.60 (d, *J* = 8.4 Hz, 3H, e; ^{13}C NMR chemical shifts from HMQC and HMBC (600 MHz, CD_2Cl_2/CS_2 = 1/1) 122.3x2 (D, H), 123.9 (J), 126.9 (L), 128.3 (K), 130.7 (M), 132.4 (I), 133.1 (E), 135.1 (N), 138.4x2 (F, G), 145.7 (C), 153.5 (A) ppm; HRMS (EI) Found: *m/z* 522.1406; calcd for $C_{42}H_{24}O_3$: M, 522.1409.

Theoretical calculations:

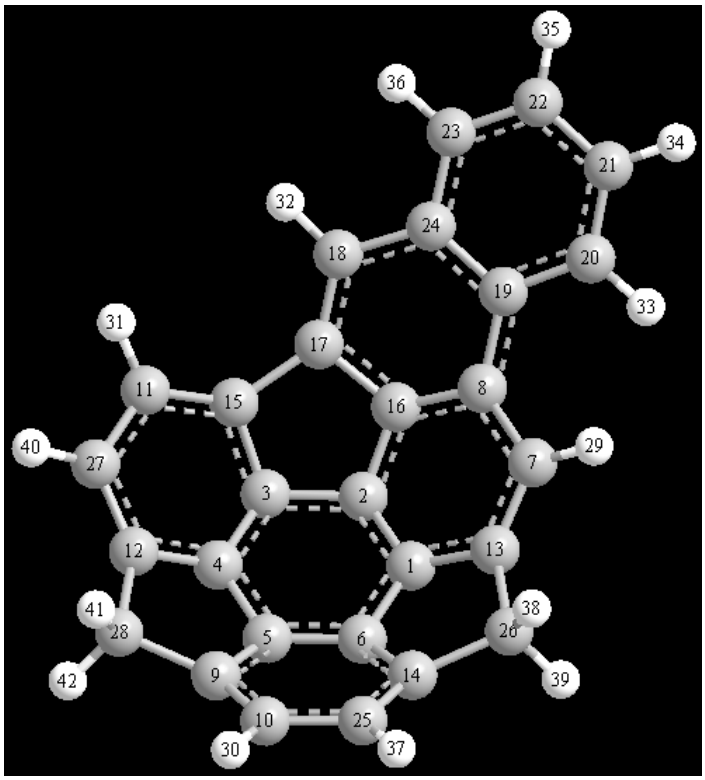
The calculations were carried out using the Gaussian 03 program.

The optimized structure of **6** (B3LYP/6-31G**)

(a)



Side view



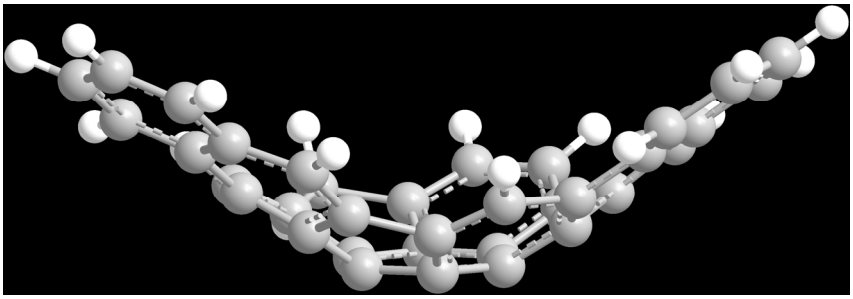
Top view

Center Number	Atomic Type	Coordinates X	Y	(Angstroms) Z
1	C	-0.871	-1.235	-1.021
2	C	-0.263	-0.018	-1.23
3	C	-0.959	1.217	-1.025

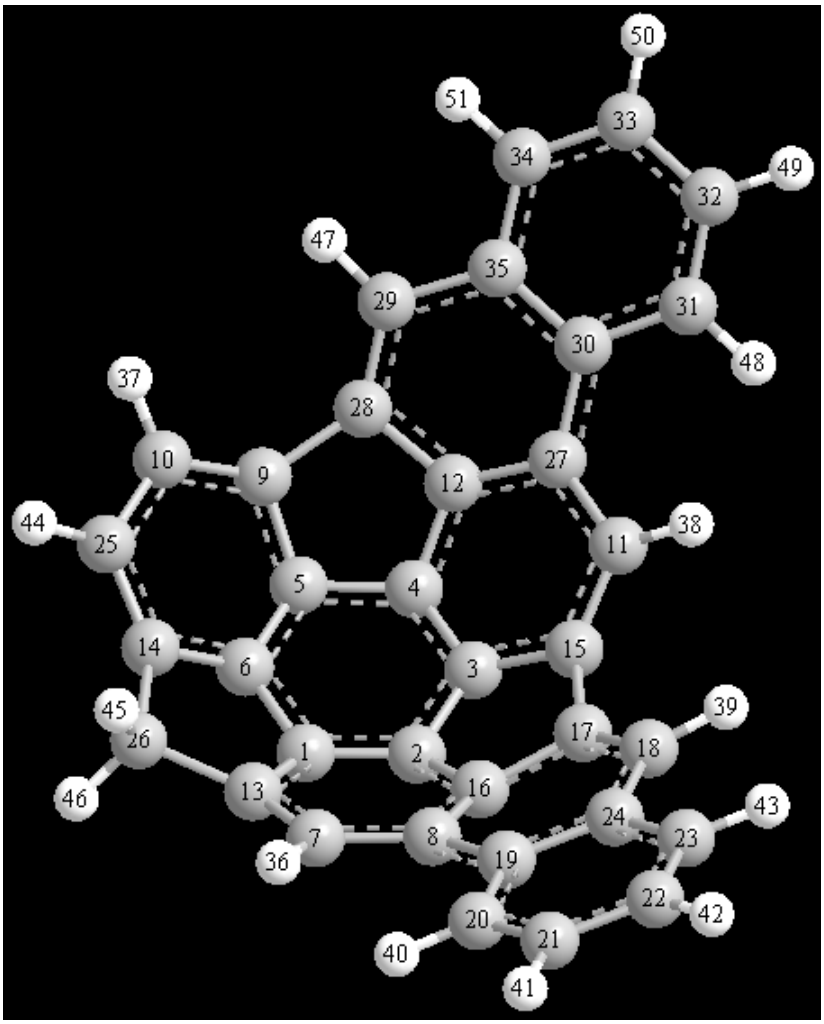
4	C	-2.291	1.178	-0.643
5	C	-2.944	-0.087	-0.443
6	C	-2.245	-1.277	-0.626
7	C	1.21	-2.203	-0.292
8	C	1.864	-0.92	-0.47
9	C	-3.966	0.03	0.507
10	C	-4.334	-1.141	1.176
11	C	-0.661	3.275	0.147
12	C	-2.86	2.16	0.18
13	C	-0.16	-2.343	-0.5
14	C	-2.502	-2.422	0.141
15	C	-0.069	2.215	-0.558
16	C	1.078	0.165	-0.884
17	C	1.293	1.561	-0.536
18	C	2.514	1.876	-0.01
19	C	3.196	-0.559	-0.009
20	C	4.196	-1.514	0.273
21	C	5.451	-1.137	0.719
22	C	5.753	0.223	0.912
23	C	4.793	1.183	0.652
24	C	3.503	0.837	0.185
25	C	-3.604	-2.359	0.998
26	C	-1.232	-3.316	0.071
27	C	-2.044	3.251	0.503
28	C	-4.138	1.544	0.807
29	H	1.773	-3.003	0.182
30	H	-5.097	-1.122	1.95
31	H	-0.052	4.071	0.566
32	H	2.761	2.88	0.324
33	H	3.981	-2.566	0.109
34	H	6.205	-1.893	0.916
35	H	6.737	0.518	1.264
36	H	5.022	2.235	0.804
37	H	-3.854	-3.193	1.648
38	H	-0.95	-3.696	1.058
39	H	-1.38	-4.19	-0.578
40	H	-2.407	4.041	1.156

41	H	-4.196	1.739	1.883
42	H	-5.056	1.952	0.361

The optimized structure of **11a** (B3LYP/6-31G**)



Side view

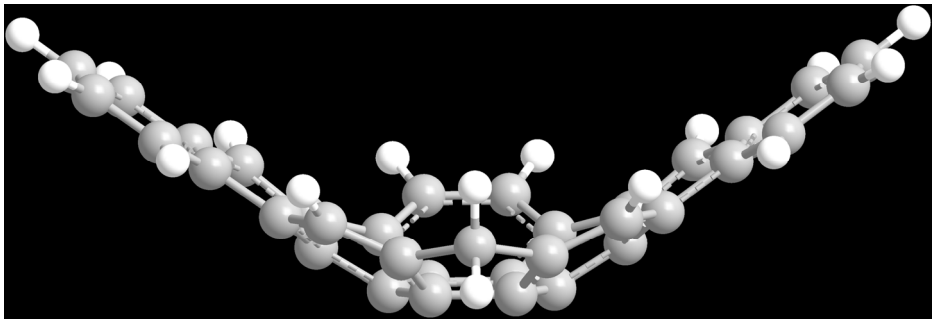


Top view

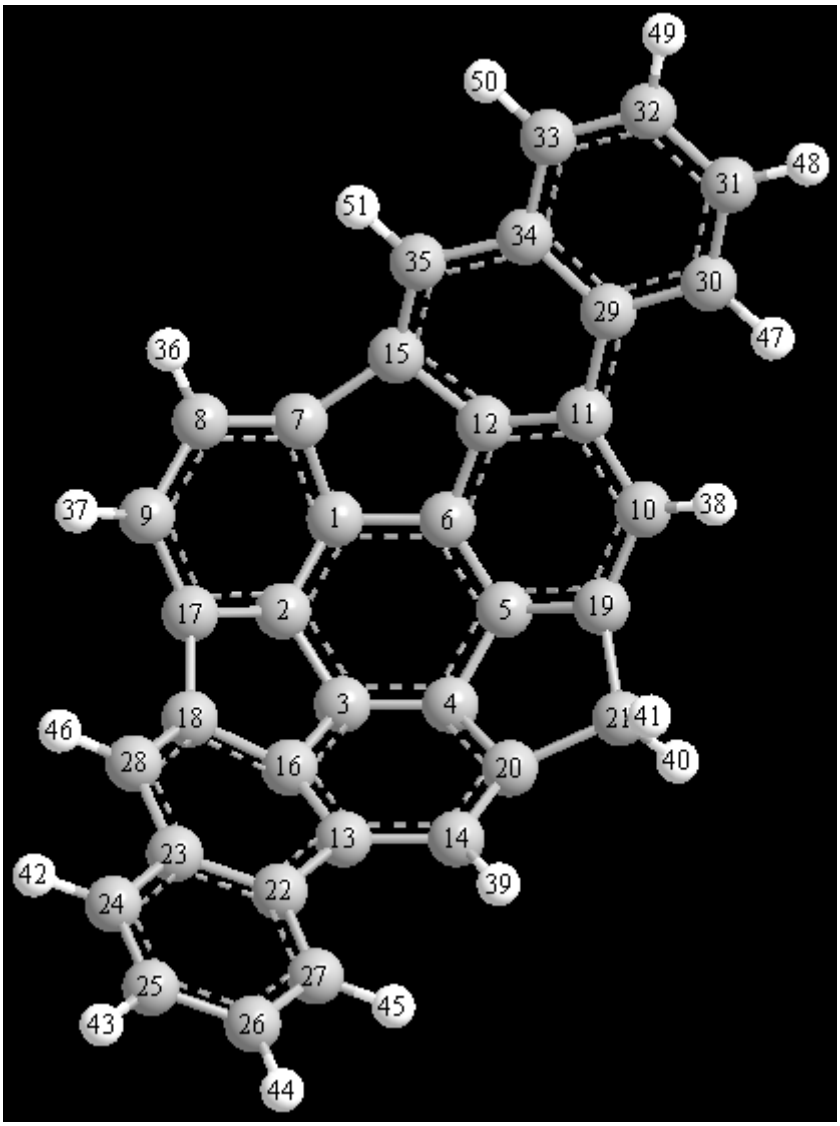
Center Number	Atomic Type	Coordinates X	Y	(Angstroms) Z
1	C	1.265	2.173	0.863
2	C	1.218	0.895	1.386
3	C	-0.028	0.237	1.63
4	C	-1.192	0.927	1.374
5	C	-1.176	2.255	0.828
6	C	0.045	2.875	0.58
7	C	3.307	1.655	-0.311
8	C	3.249	0.295	0.187
9	C	-2.297	2.451	-0.016
10	C	-2.161	3.445	-0.997
11	C	-1.08	-1.853	1.019
12	C	-2.309	0.255	0.868
13	C	2.288	2.563	-0.035
14	C	0.23	3.758	-0.494
15	C	0.086	-1.167	1.376
16	C	2.151	-0.065	0.982
17	C	1.545	-1.386	1.047
18	C	2.277	-2.419	0.532
19	C	4.065	-0.822	-0.264
20	C	5.308	-0.654	-0.909
21	C	6.056	-1.739	-1.333
22	C	5.579	-3.047	-1.132
23	C	4.362	-3.246	-0.508
24	C	3.574	-2.162	-0.054
25	C	-0.911	4.096	-1.229
26	C	1.752	3.809	-0.795
27	C	-2.313	-1.145	0.752
28	C	-3.098	1.174	0.067
29	C	-4.14	0.635	-0.635
30	C	-3.489	-1.695	0.092
31	C	-3.771	-3.076	0.054
32	C	-4.893	-3.566	-0.594
33	C	-5.777	-2.685	-1.241
34	C	-5.525	-1.326	-1.226

35	C	-4.396	-0.787	-0.566
36	H	4.06	1.896	-1.057
37	H	-2.962	3.636	-1.706
38	H	-1.024	-2.9	0.734
39	H	1.895	-3.437	0.494
40	H	5.696	0.35	-1.053
41	H	7.015	-1.58	-1.817
42	H	6.166	-3.897	-1.466
43	H	3.989	-4.256	-0.356
44	H	-0.842	4.755	-2.091
45	H	1.956	3.75	-1.869
46	H	2.212	4.739	-0.434
47	H	-4.763	1.232	-1.297
48	H	-3.107	-3.764	0.567
49	H	-5.092	-4.634	-0.597
50	H	-6.655	-3.071	-1.749
51	H	-6.205	-0.642	-1.729

The optimized structure of **11b** (B3LYP/6-31G**)



Side view



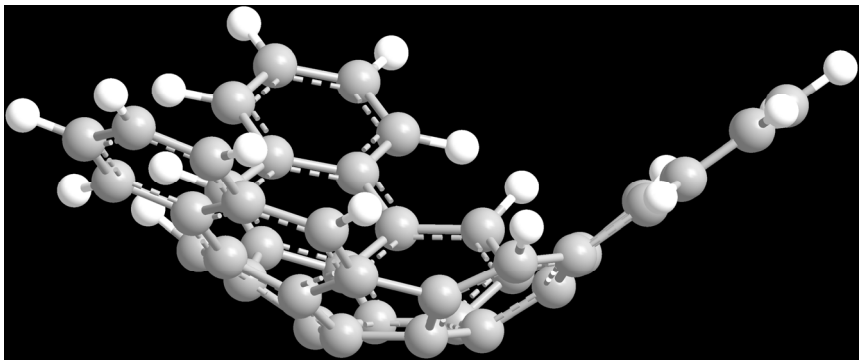
Top view

Center Number	Atomic Type	Coordinates X	Y	(Angstroms) Z
1	C	0.693	1.305	-1.548
2	C	-0.693	1.305	-1.548
3	C	-1.385	0.047	-1.604
4	C	-0.715	-1.16	-1.62
5	C	0.715	-1.16	-1.62
6	C	1.385	0.047	-1.604
7	C	1.447	2.245	-0.801
8	C	0.713	3.291	-0.215
9	C	-0.713	3.291	-0.215

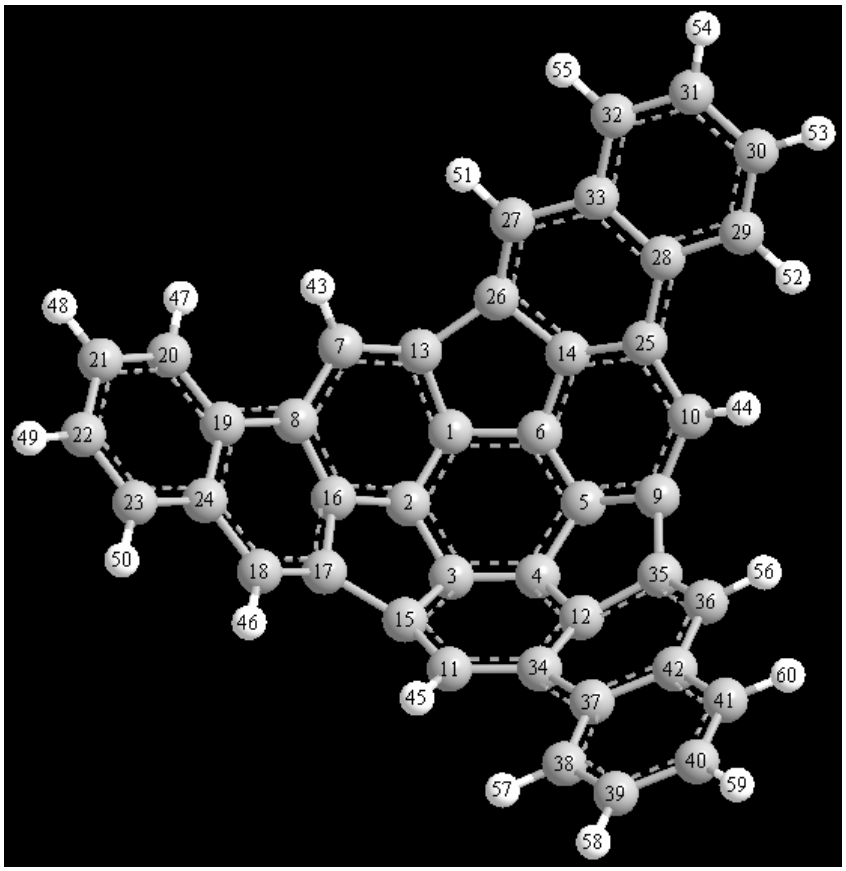
10	C	2.474	-2.214	-0.355
11	C	3.188	-0.953	-0.309
12	C	2.581	0.169	-0.889
13	C	-3.188	-0.953	-0.309
14	C	-2.474	-2.214	-0.355
15	C	2.731	1.543	-0.438
16	C	-2.581	0.169	-0.889
17	C	-1.447	2.245	-0.801
18	C	-2.731	1.543	-0.438
19	C	1.216	-2.301	-0.945
20	C	-1.216	-2.301	-0.945
21	C	0	-3.245	-0.712
22	C	-4.353	-0.657	0.514
23	C	-4.636	0.72	0.836
24	C	-5.758	1.004	1.649
25	C	-6.582	0.001	2.124
26	C	-6.305	-1.34	1.806
27	C	-5.209	-1.656	1.02
28	C	-3.766	1.798	0.417
29	C	4.353	-0.657	0.514
30	C	5.209	-1.656	1.02
31	C	6.305	-1.34	1.806
32	C	6.582	0.001	2.124
33	C	5.758	1.004	1.649
34	C	4.636	0.72	0.836
35	C	3.766	1.798	0.417
36	H	1.211	4.043	0.391
37	H	-1.211	4.043	0.391
38	H	2.854	-3.041	0.238
39	H	-2.854	-3.041	0.238
40	H	0	-4.09	-1.414
41	H	0	-3.667	0.297
42	H	-5.966	2.042	1.898
43	H	-7.441	0.248	2.741
44	H	-6.954	-2.13	2.171
45	H	-5.017	-2.694	0.765
46	H	-3.936	2.783	0.845

47	H	5.017	-2.694	0.765
48	H	6.954	-2.13	2.171
49	H	7.441	0.248	2.741
50	H	5.966	2.042	1.898
51	H	3.936	2.783	0.845

The optimized structure of **2** (B3LYP/6-31G**)



Side view

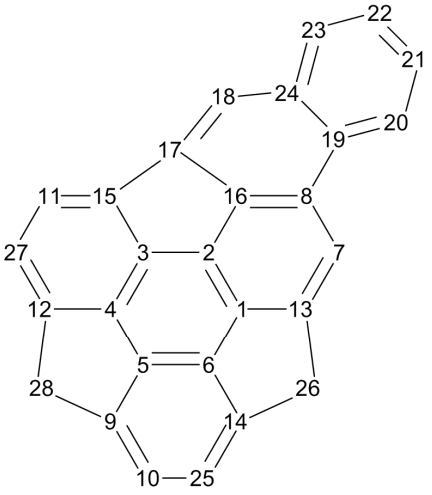


Top view

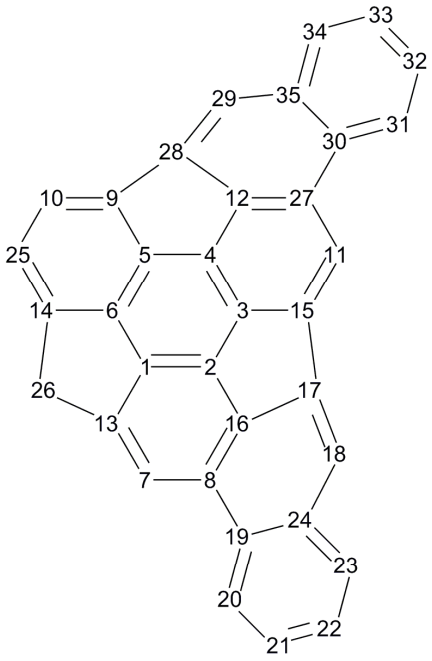
Center	Atomic	Coordinates		(Angstroms)
Number	Type	X	Y	Z
1	C	-1.365	0.377	-1.856
2	C	-1.018	-0.959	-1.868
3	C	0.355	-1.371	-1.855
4	C	1.34	-0.402	-1.868
5	C	1.01	0.992	-1.855
6	C	-0.322	1.36	-1.868
7	C	-3.316	-0.108	-0.505
8	C	-2.961	-1.51	-0.504
9	C	1.978	1.727	-1.097
10	C	1.563	2.923	-0.502
11	C	1.75	-2.816	-0.501
12	C	2.515	-0.582	-1.127
13	C	-2.486	0.849	-1.099
14	C	-0.754	2.468	-1.128
15	C	0.507	-2.576	-1.096
16	C	-1.761	-1.887	-1.128
17	C	-0.896	-2.975	-0.705
18	C	-1.436	-3.888	0.159
19	C	-3.567	-2.543	0.325
20	C	-4.863	-2.429	0.868
21	C	-5.404	-3.426	1.662
22	C	-4.657	-4.582	1.952
23	C	-3.381	-4.722	1.439
24	C	-2.799	-3.729	0.616
25	C	0.172	3.317	-0.501
26	C	-2.13	2.264	-0.708
27	C	-2.65	3.187	0.156
28	C	-0.42	4.358	0.327
29	C	0.326	5.424	0.872
30	C	-0.268	6.392	1.664
31	C	-1.643	6.323	1.951
32	C	-2.401	5.288	1.437
33	C	-1.831	4.287	0.616
34	C	2.788	-1.809	-0.501
35	C	3.026	0.712	-0.707

36	C	4.088	0.701	0.154
37	C	3.986	-1.816	0.327
38	C	4.535	-2.995	0.873
39	C	5.671	-2.963	1.664
40	C	6.301	-1.738	1.948
41	C	5.784	-0.564	1.433
42	C	4.631	-0.558	0.613
43	H	-4.125	0.212	0.146
44	H	2.244	3.464	0.15
45	H	1.878	-3.676	0.151
46	H	-0.856	-4.713	0.566
47	H	-5.458	-1.551	0.634
48	H	-6.411	-3.317	2.057
49	H	-5.082	-5.363	2.575
50	H	-2.799	-5.613	1.664
51	H	-3.656	3.098	0.562
52	H	1.385	5.499	0.64
53	H	0.33	7.208	2.06
54	H	-2.107	7.083	2.573
55	H	-3.464	5.23	1.661
56	H	4.515	1.616	0.558
57	H	4.071	-3.949	0.643
58	H	6.08	-3.889	2.061
59	H	7.192	-1.715	2.57
60	H	6.266	0.385	1.654

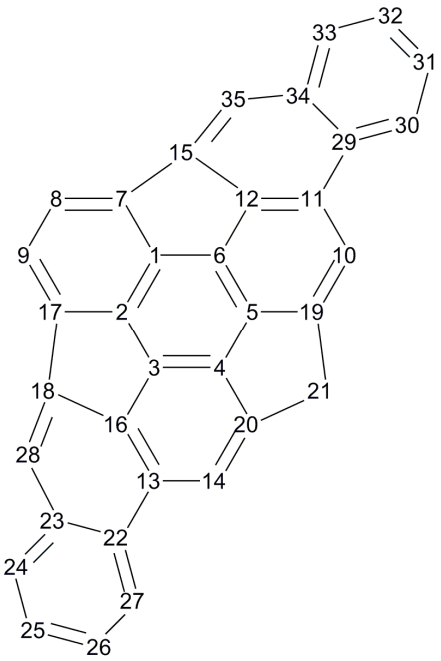
(b)



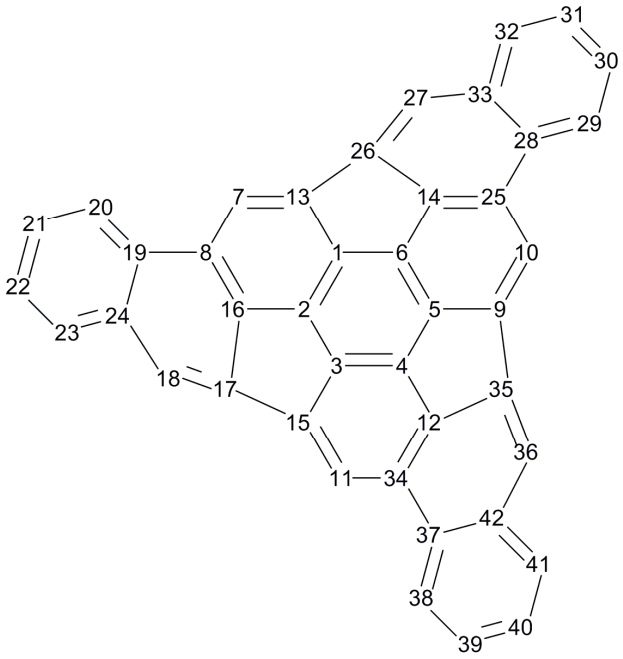
Atom	Bond Atom	Bond Length (Å)
C(2)	C(1)	1.3764
C(3)	C(2)	1.4324
C(16)	C(2)	1.3970
C(4)	C(3)	1.3862
C(15)	C(3)	1.4164
C(5)	C(4)	1.4376
C(12)	C(4)	1.4019
C(6)	C(1)	1.4303
C(9)	C(5)	1.4002
C(13)	C(1)	1.4158
C(14)	C(6)	1.4019
C(7)	C(13)	1.3928
C(26)	C(13)	1.5563
C(25)	C(14)	1.3974
C(8)	C(16)	1.4023
C(17)	C(16)	1.4547
C(11)	C(15)	1.4040
C(18)	C(17)	1.3663
C(19)	C(8)	1.4550
C(10)	C(9)	1.3979
C(28)	C(9)	1.5530
C(27)	C(12)	1.4002
C(20)	C(19)	1.4112
C(24)	C(19)	1.4425
C(23)	C(24)	1.4149
C(21)	C(20)	1.3842
C(22)	C(23)	1.3823



Atom	Bond Atom	Bond Length (Å)
C(2)	C(1)	1.3817
C(3)	C(2)	1.4300
C(16)	C(2)	1.3983
C(4)	C(3)	1.3771
C(15)	C(3)	1.4313
C(5)	C(4)	1.4360
C(12)	C(4)	1.3983
C(6)	C(1)	1.4357
C(9)	C(5)	1.4168
C(13)	C(1)	1.4160
C(14)	C(6)	1.4026
C(7)	C(13)	1.3925
C(26)	C(13)	1.5548
C(25)	C(14)	1.3987
C(8)	C(16)	1.4026
C(17)	C(16)	1.4548
C(11)	C(15)	1.3991
C(18)	C(17)	1.3668
C(19)	C(8)	1.4550
C(10)	C(9)	1.4032
C(28)	C(9)	1.5097
C(27)	C(12)	1.4048
C(29)	C(28)	1.3671
C(30)	C(27)	1.4564
C(20)	C(19)	1.4104
C(24)	C(19)	1.4425
C(23)	C(24)	1.4150
C(21)	C(20)	1.3844
C(22)	C(23)	1.3821
C(31)	C(30)	1.4100
C(35)	C(30)	1.4422
C(34)	C(35)	1.4145
C(32)	C(31)	1.3852
C(33)	C(34)	1.3822

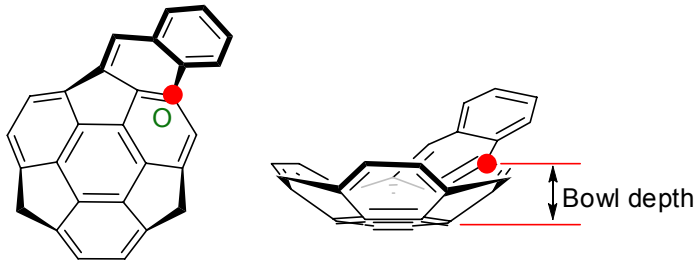


Atom	Bond Atom	Bond Length (Å)
C(2)	C(1)	1.3860
C(5)	C(4)	1.4300
C(6)	C(1)	1.4369
C(7)	C(1)	1.4178
C(12)	C(6)	1.3988
C(19)	C(5)	1.4172
C(8)	C(7)	1.4058
C(15)	C(7)	1.5077
C(11)	C(12)	1.4013
C(35)	C(15)	1.3665
C(10)	C(19)	1.3922
C(21)	C(19)	1.5569
C(29)	C(11)	1.4568
C(30)	C(29)	1.4095
C(34)	C(29)	1.4422
C(33)	C(34)	1.4144
C(31)	C(30)	1.3852
C(32)	C(33)	1.3822

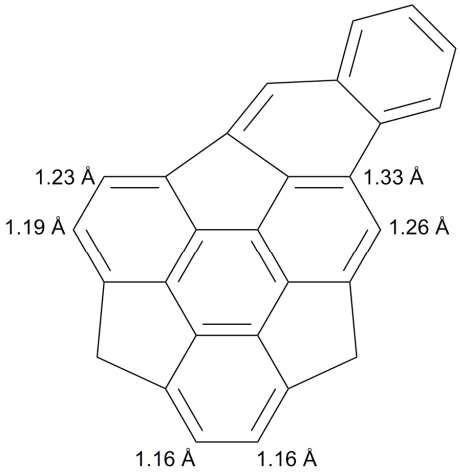


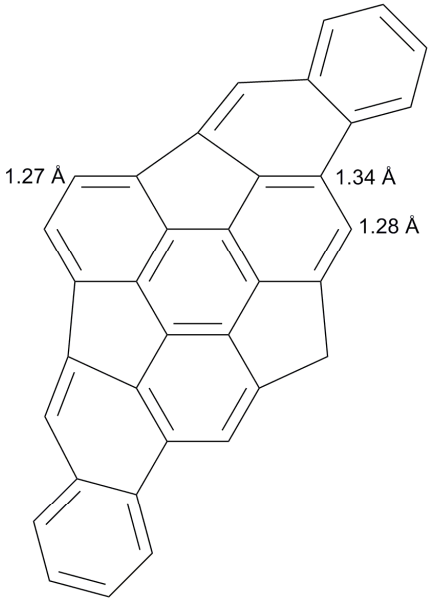
Atom	Bond Atom	Bond Length (Å)
C(2)	C(1)	1.3804
C(3)	C(2)	1.4335
C(16)	C(2)	1.4003
C(6)	C(1)	1.4333
C(13)	C(1)	1.4326
C(7)	C(13)	1.3991
C(26)	C(13)	1.5106
C(8)	C(16)	1.4041
C(17)	C(16)	1.4529
C(18)	C(17)	1.3681
C(19)	C(8)	1.4566
C(20)	C(19)	1.4098
C(24)	C(19)	1.4426
C(23)	C(24)	1.4150
C(21)	C(20)	1.3846
C(22)	C(23)	1.3824

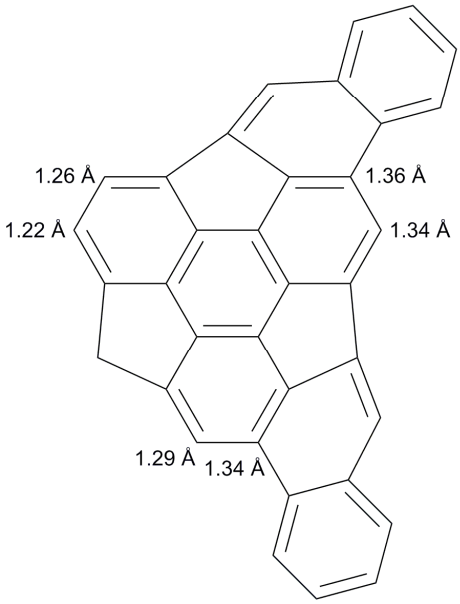
(c) Bowl depth is defined here as the distance between the plane of the 6-membered ring at the base and the rim carbon on the sumanene skeleton in the structure, see below as an example.

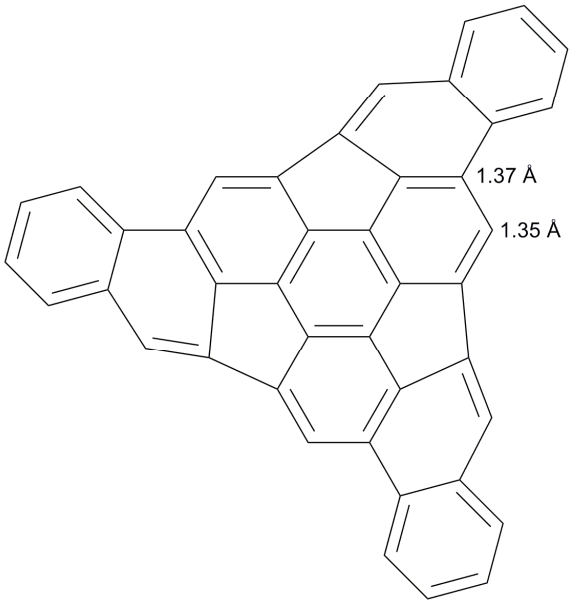


6









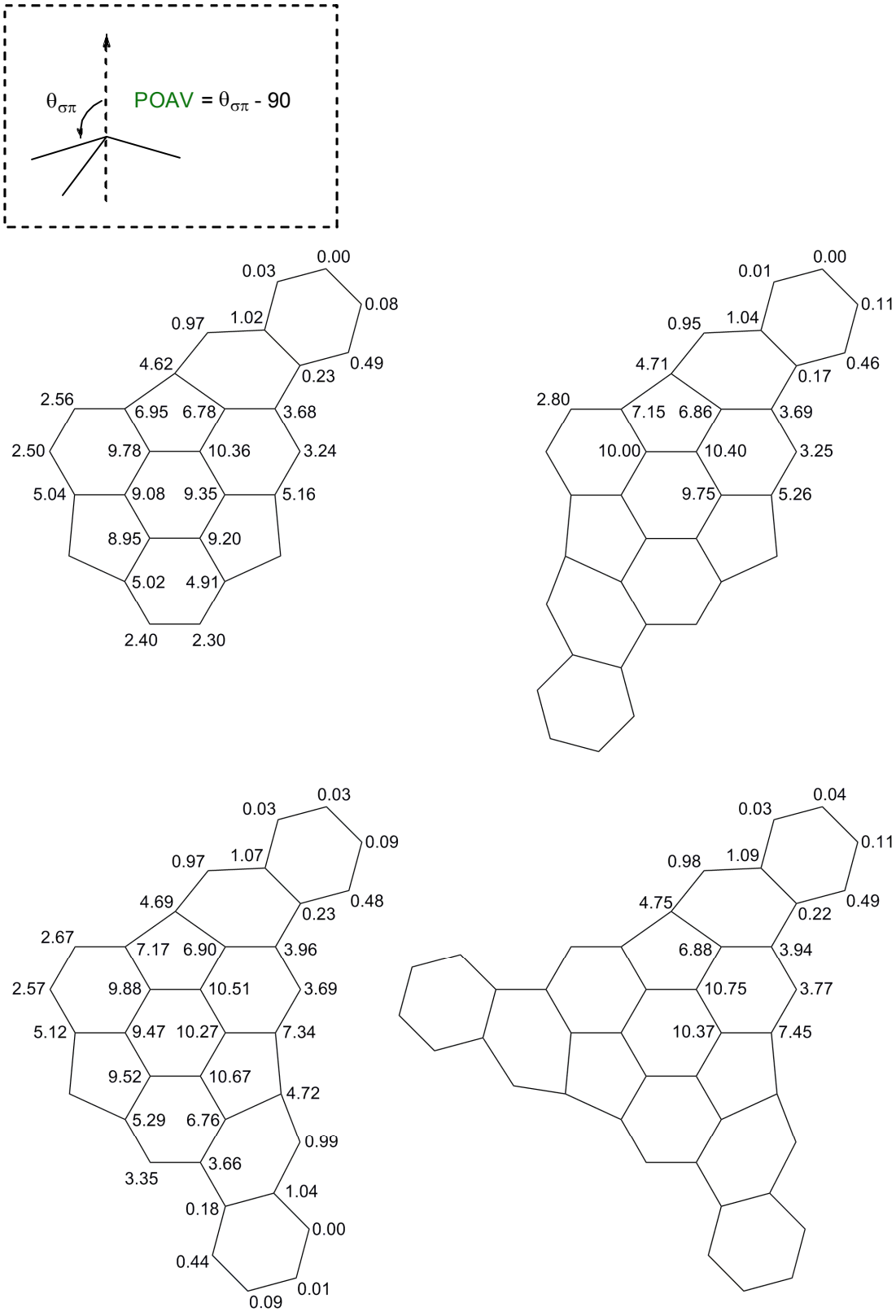
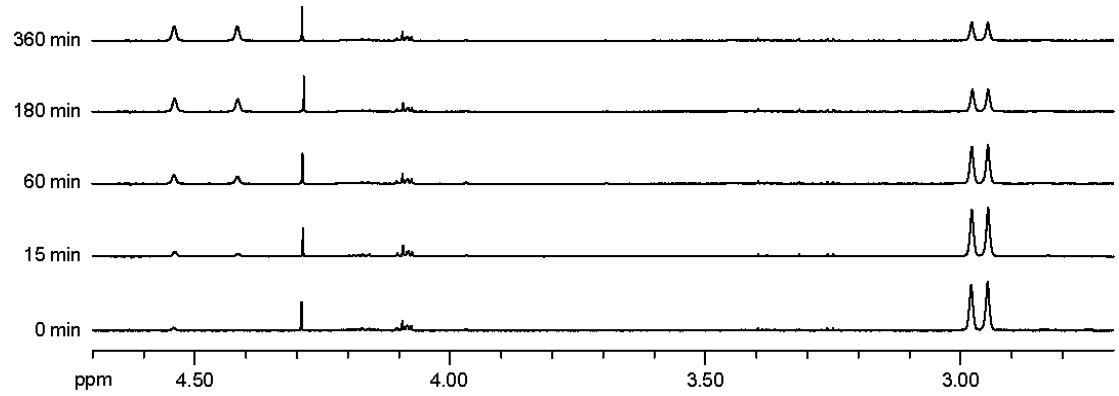


Figure S1. (a) Optimized structures and coordinations, (b) bond-lengths, (c) bowl-depths and POAVs of naphtosumanenes **6**, **11a,b**, and **2** (B3LYP/6-31G**).

(a)



(b)

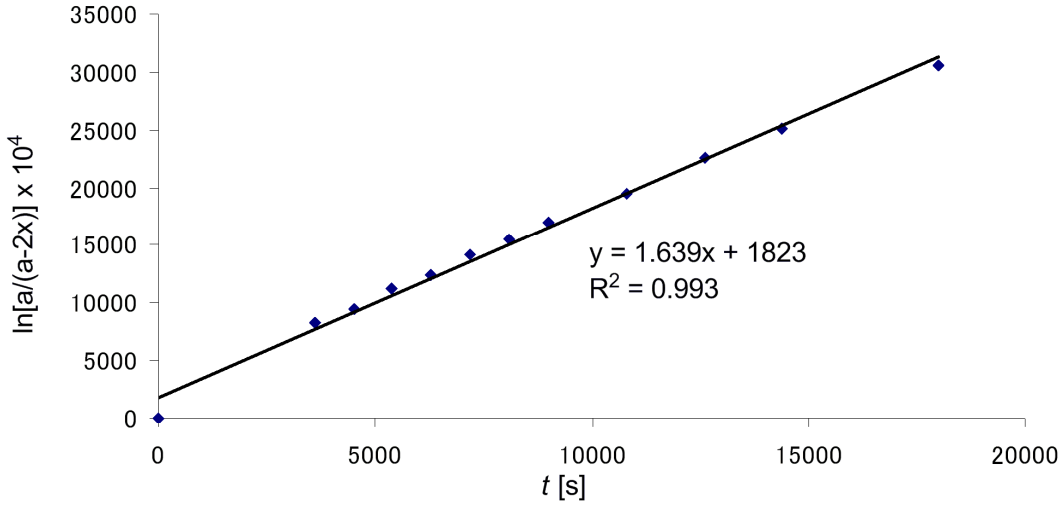
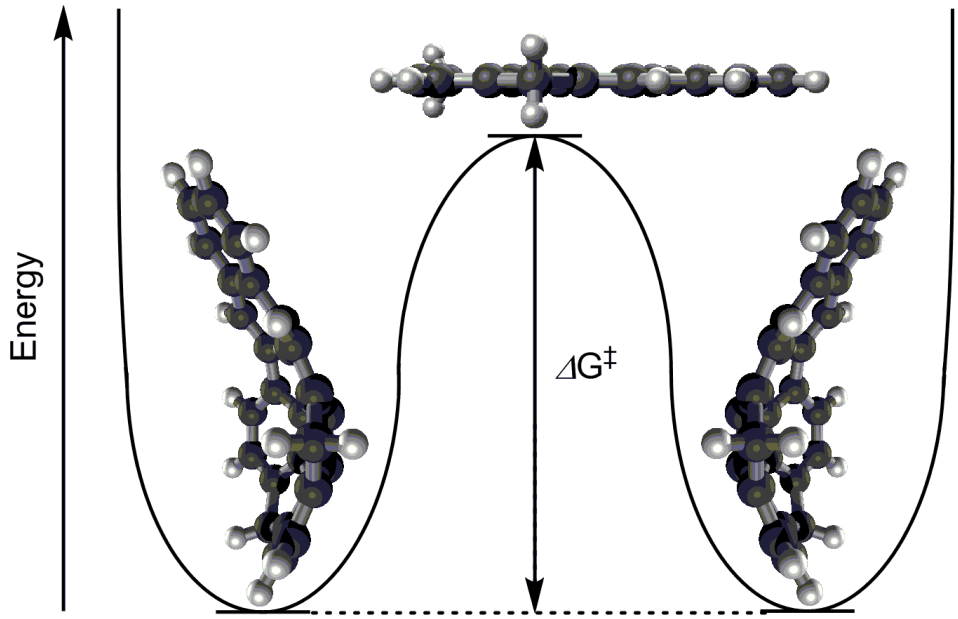


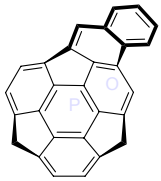
Figure S2. Bowl-to-bowl inversion of **7a**. (a) ^{1}H NMR spectra after keeping at 140 ^{o}C over 0, 15, 60, 180, and 360 min (600 MHz, mesitylene-d_{12}). (b) Plot of ln[a/(a-$2x$)] vs t (s)

Bowl-to-bowl inversion of 7a :

The NMR tube was charged with ca. 4 mg portions of **7a** dissolved in mesitylene-d_{12} (500 μL), then sealed under Ar. The sample was kept in a thermostat for the appropriate period of time at 140 ℃ (±0.1 ℃), then removed, and quickly cooled in ice-water. The progress of equilibration was monitored by ^{1}H NMR at ambient temperature (0, 15, 25, 40, 60, 75, 90, 105, 120, 135, 150, 180, 210, 240, 300, 360, 480, 600 min). The benzylic region of each spectrum was carefully phase- and baseline-corrected before integration, the rate constants (k) for the reversible equilibration were determined by regression analysis using the equation $2kt$ = ln[a/(a-2x)] where a is the initial concentration of *endo*-proton (fixed on 1) and x is the concentration of *exo*-proton at time t. Correlation coefficients of the linear regressions were 0.992 or higher. The rate constant k was further substituted to the Eyring equation to derive the activation energy ($\Delta G^{\ddagger}$).

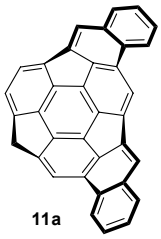


The bowl-to-bowl inversion barrier $\Delta G^{\ddagger}$ was estimated from the energy difference between the optimized bowl structure and the flat structure for a transition state as reported previously (see : Priyakumar, U. D.; Sastry, G. N. *J. Phys. Chem. A* **2001**, *105*, 4488.)



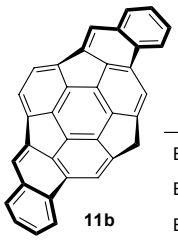
6

	⊿G‡ [kcal/mol]
B3LYP/6-31G(d,p)	29.1
B3LYP/6-31+G(d,p)	30.5
B3LYP/6-311+G(2d,p)	31.4



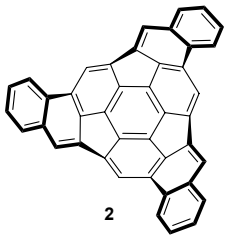
11a

	⊿G‡ [kcal/mol]
B3LYP/6-31G(d,p)	43.7
B3LYP/6-31+G(d,p)	45.4
B3LYP/6-311+G(2d,p)	46.4



11b

	⊿G‡ [kcal/mol]
B3LYP/6-31G(d,p)	42.5
B3LYP/6-31+G(d,p)	44.2
B3LYP/6-311+G(2d,p)	45.2



2

	⊿G‡ [kcal/mol]
B3LYP/6-31G(d,p)	61.0
B3LYP/6-31+G(d,p)	63.0
B3LYP/6-311+G(2d,p)	63.8

Figure S3. Estimated bowl-to-bowl inversion barrier of naphtosumanenes **6**, **11a**, **11b**, and **2** (geometry optimization was performed at the B3LYP density functional level of theory using the 6-31G** basis set).

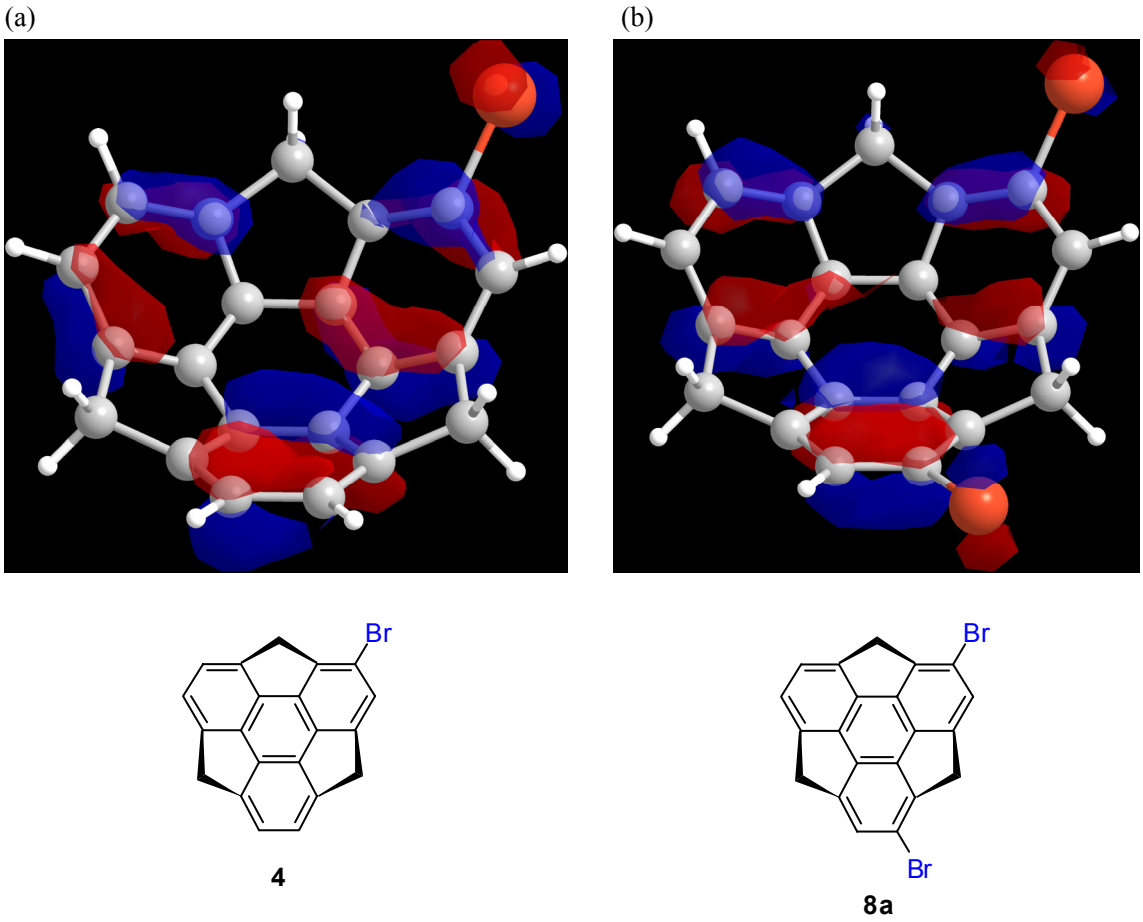
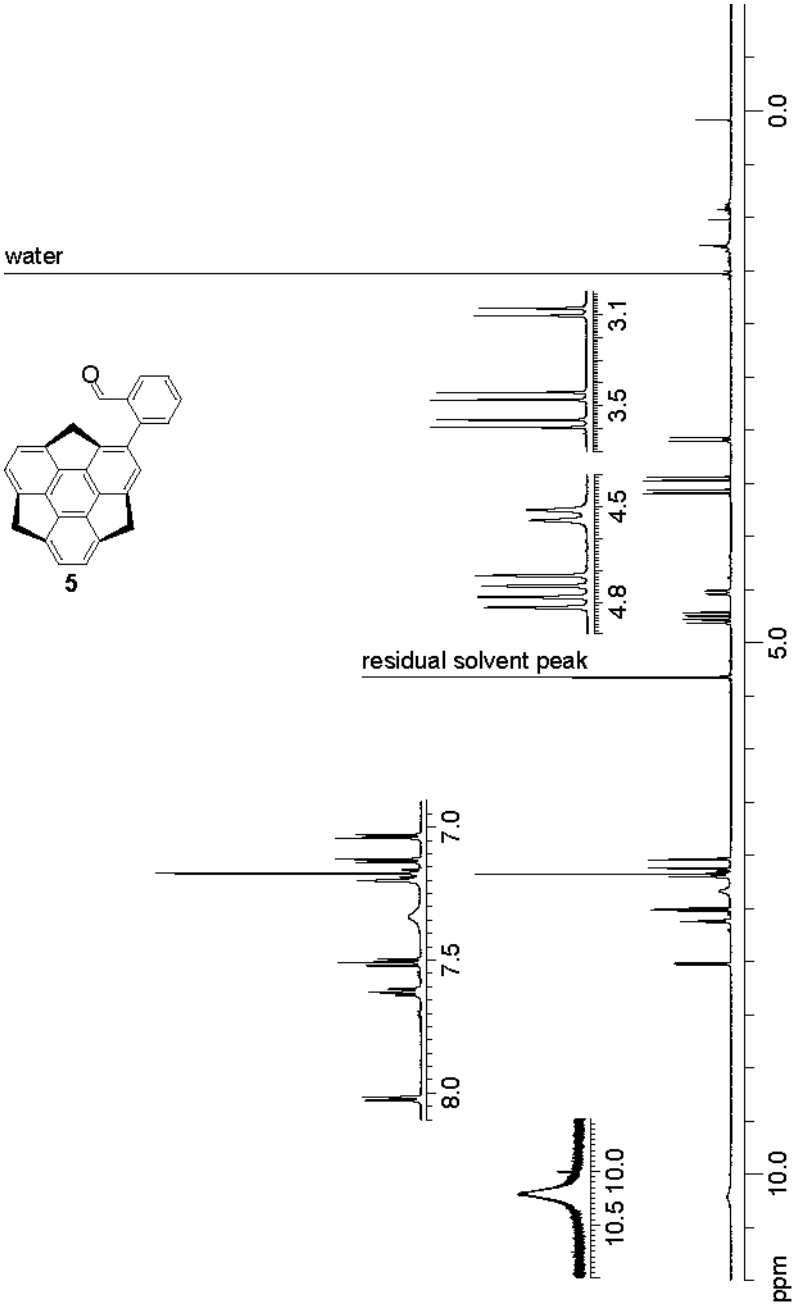


Figure S4 HOMOs of (a) monobromide **4** and (b) dibromide **8a** (B3LYP/6-31G**).

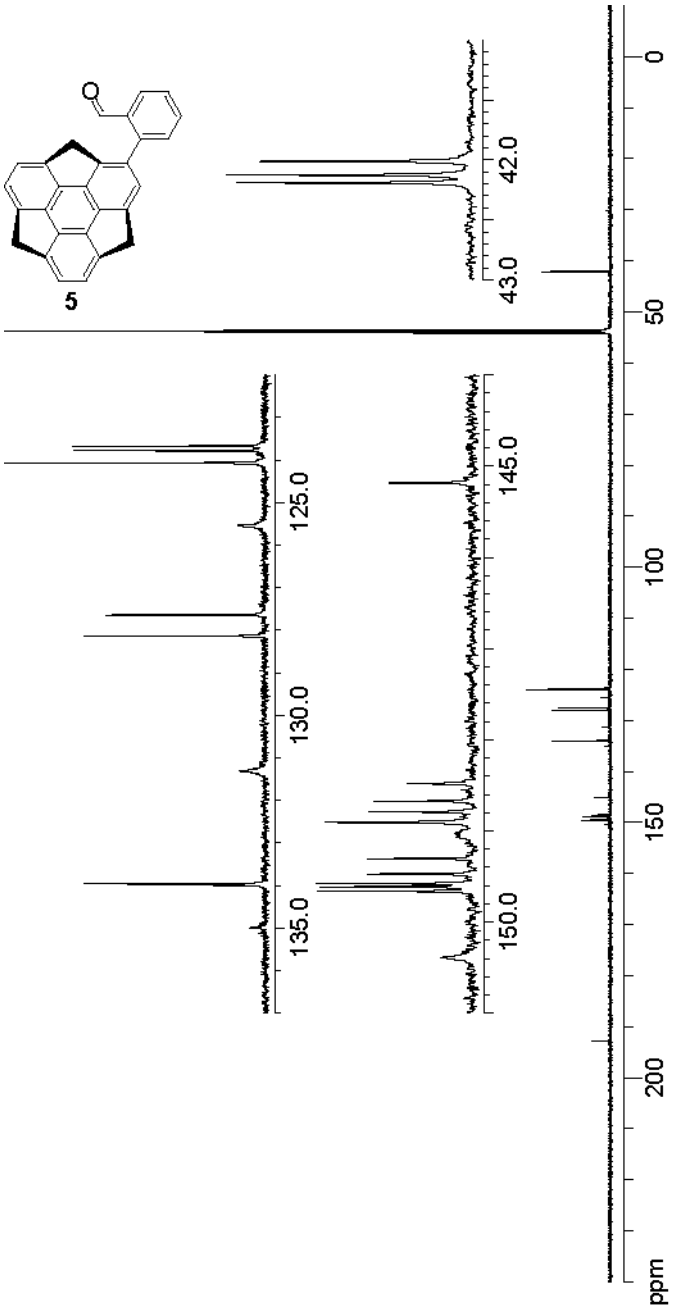
^{1}H NMR spectra of **5**

(600 MHz, CD_2Cl_2)



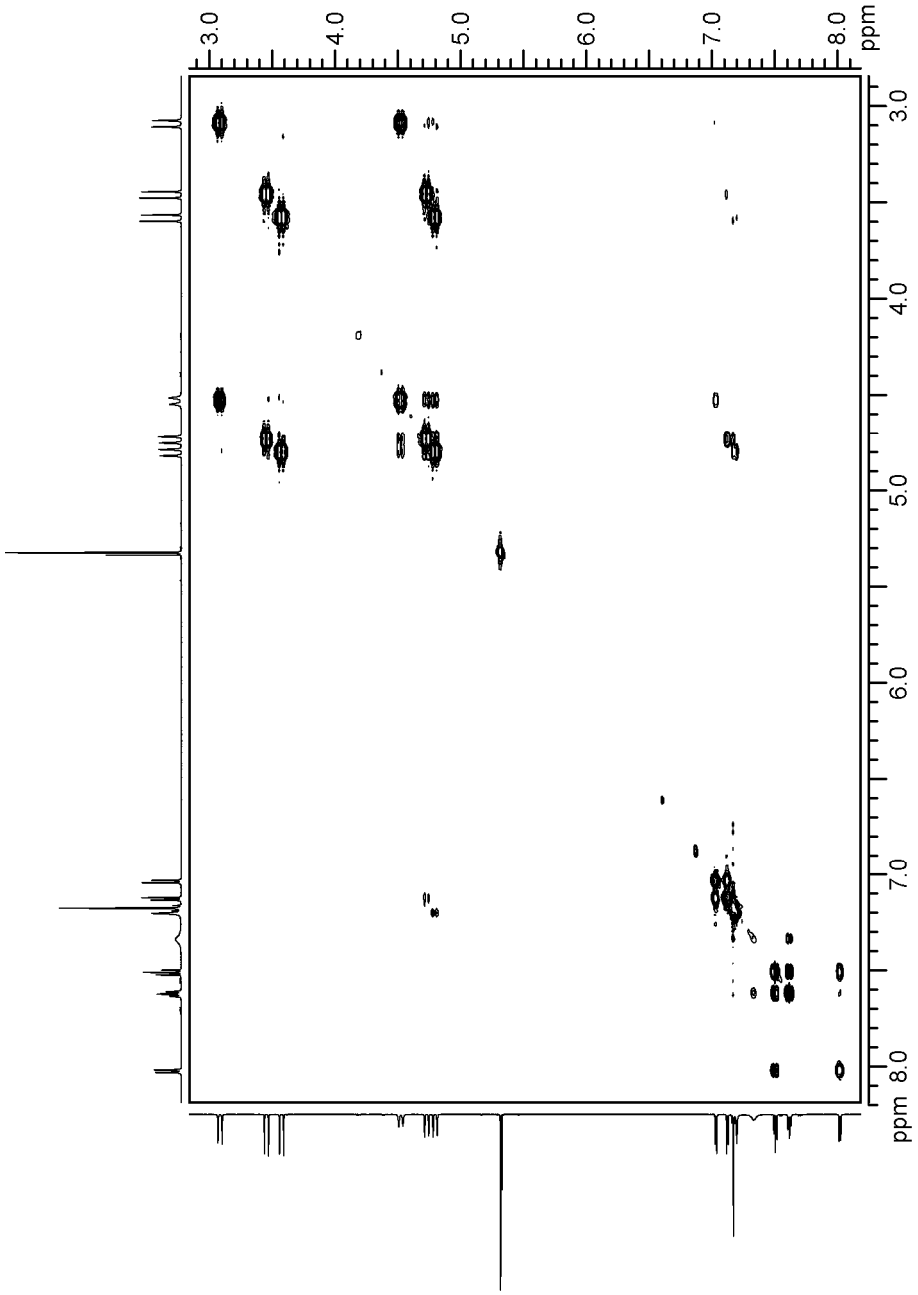
^{13}C NMR spectra of **5**

(150 MHz, CD_2Cl_2)



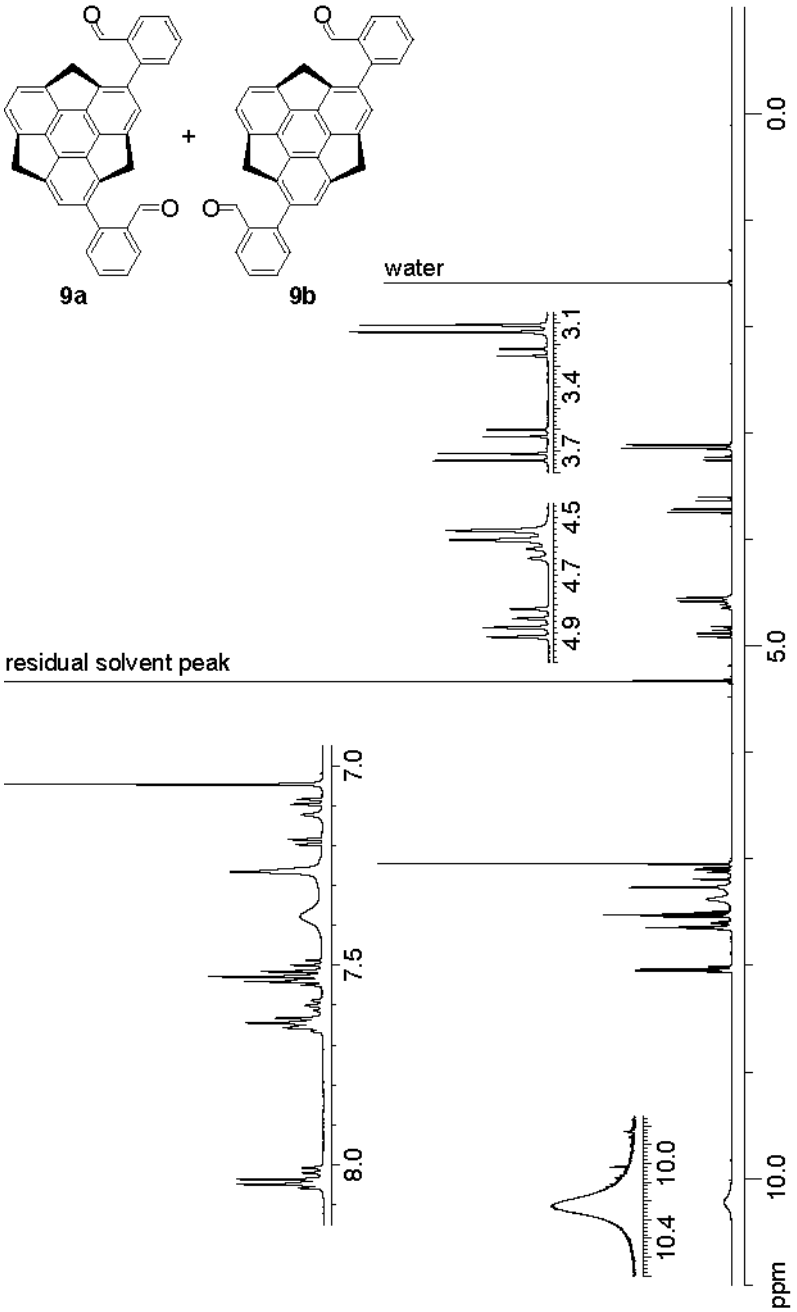
^{1}H-^{1}H COSY spectrum of **5**

(600 MHz, CD_2Cl_2)



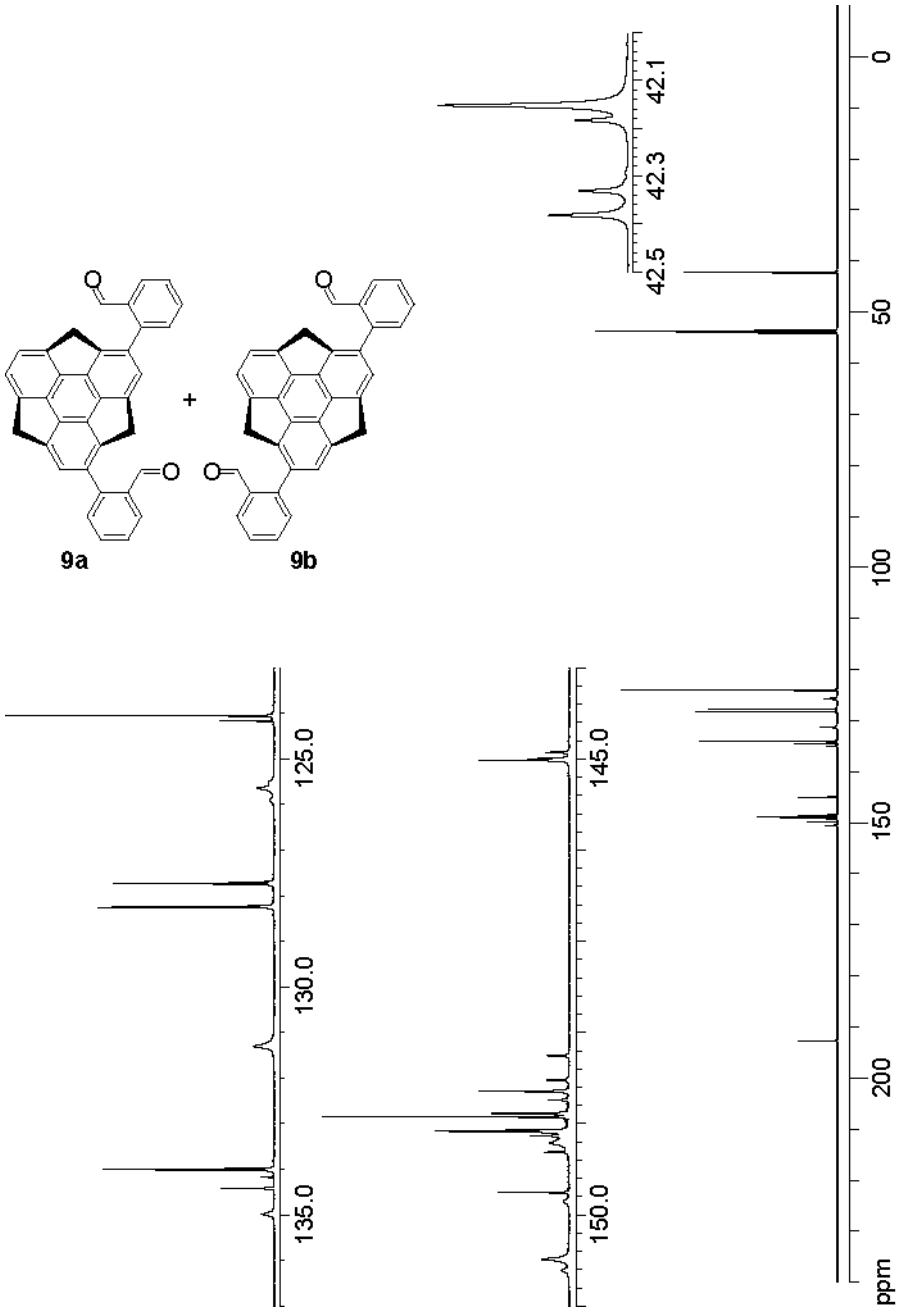
^{1}H NMR spectra of **9a** and **9b**

(600 MHz, CD_2Cl_2)



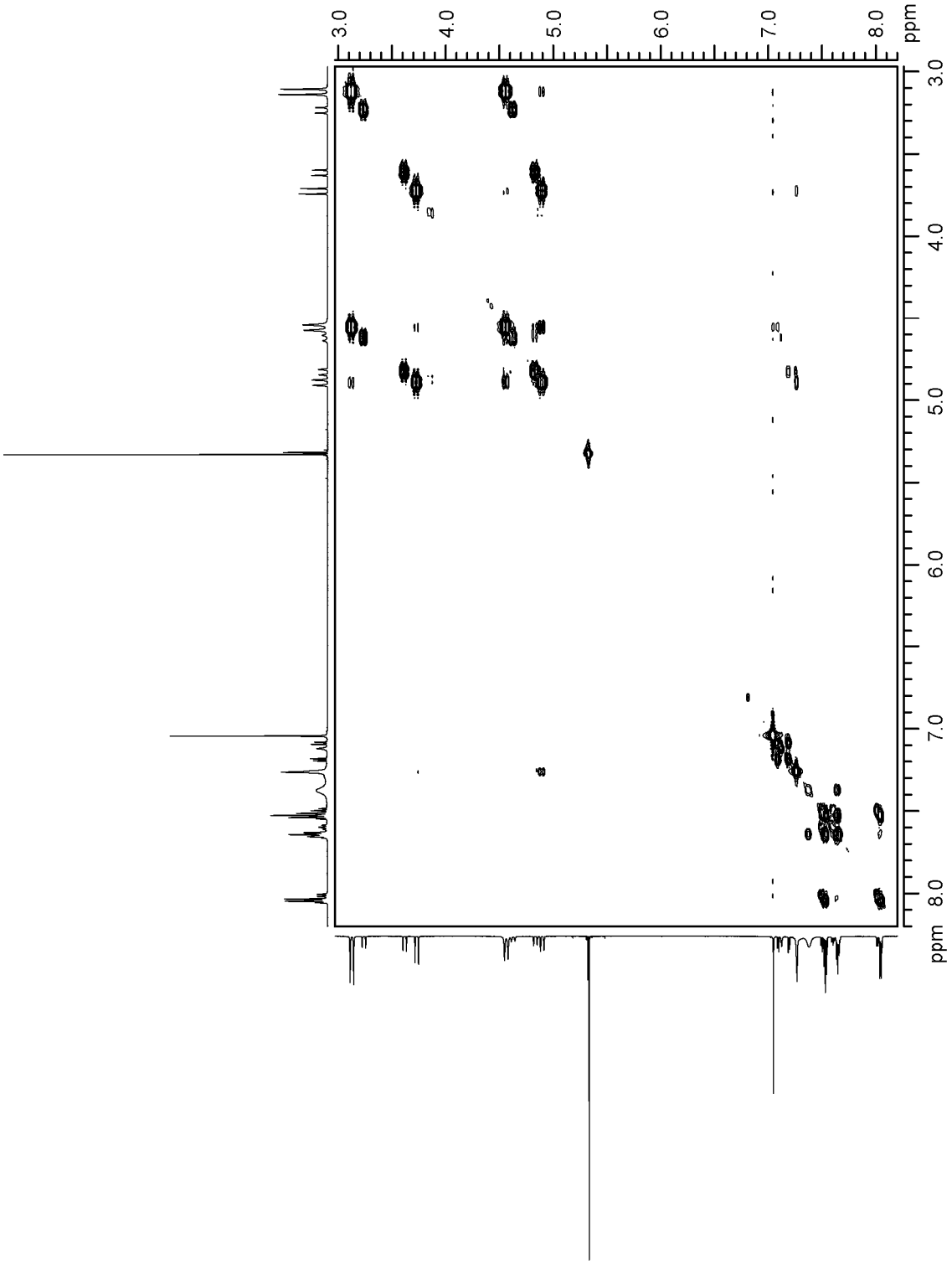
^{13}C NMR spectra of **9a** and **9b**

(150 MHz, CD_2Cl_2)



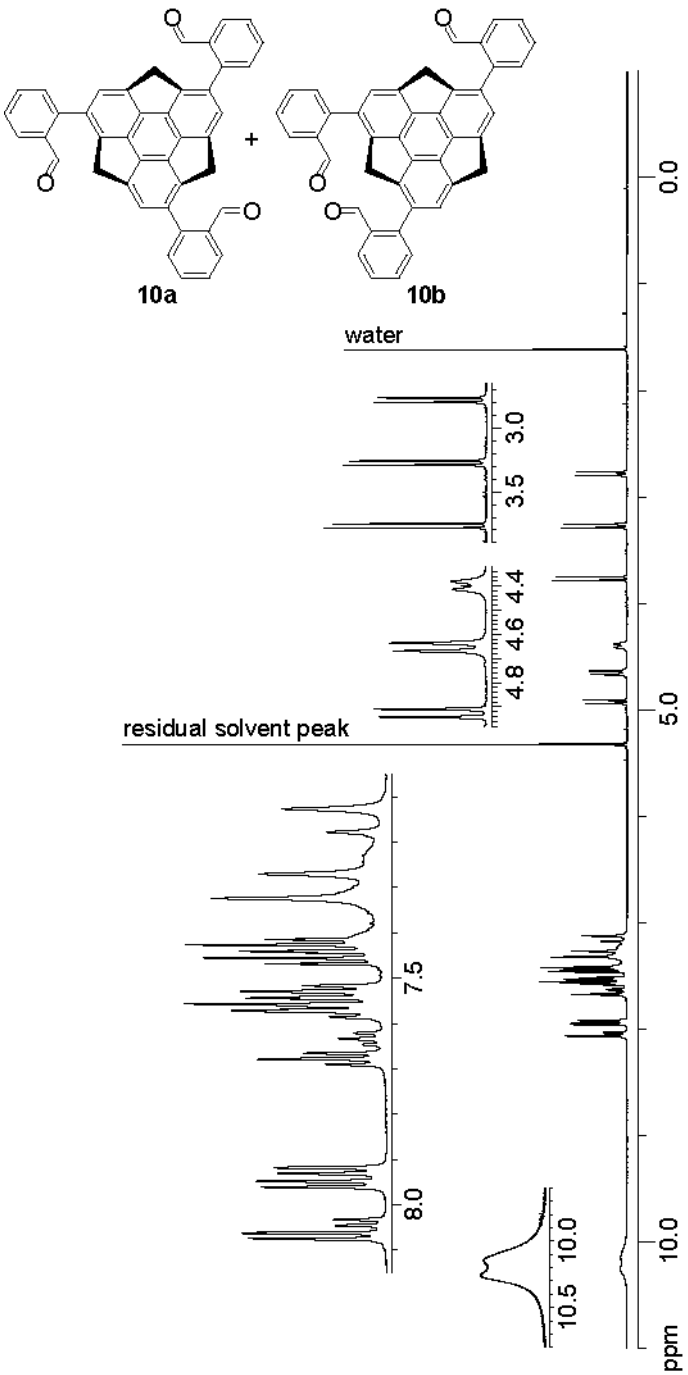
^{1}H-^{1}H COSY spectrum of **9a** and **9b**

(600 MHz, CD_2Cl_2)



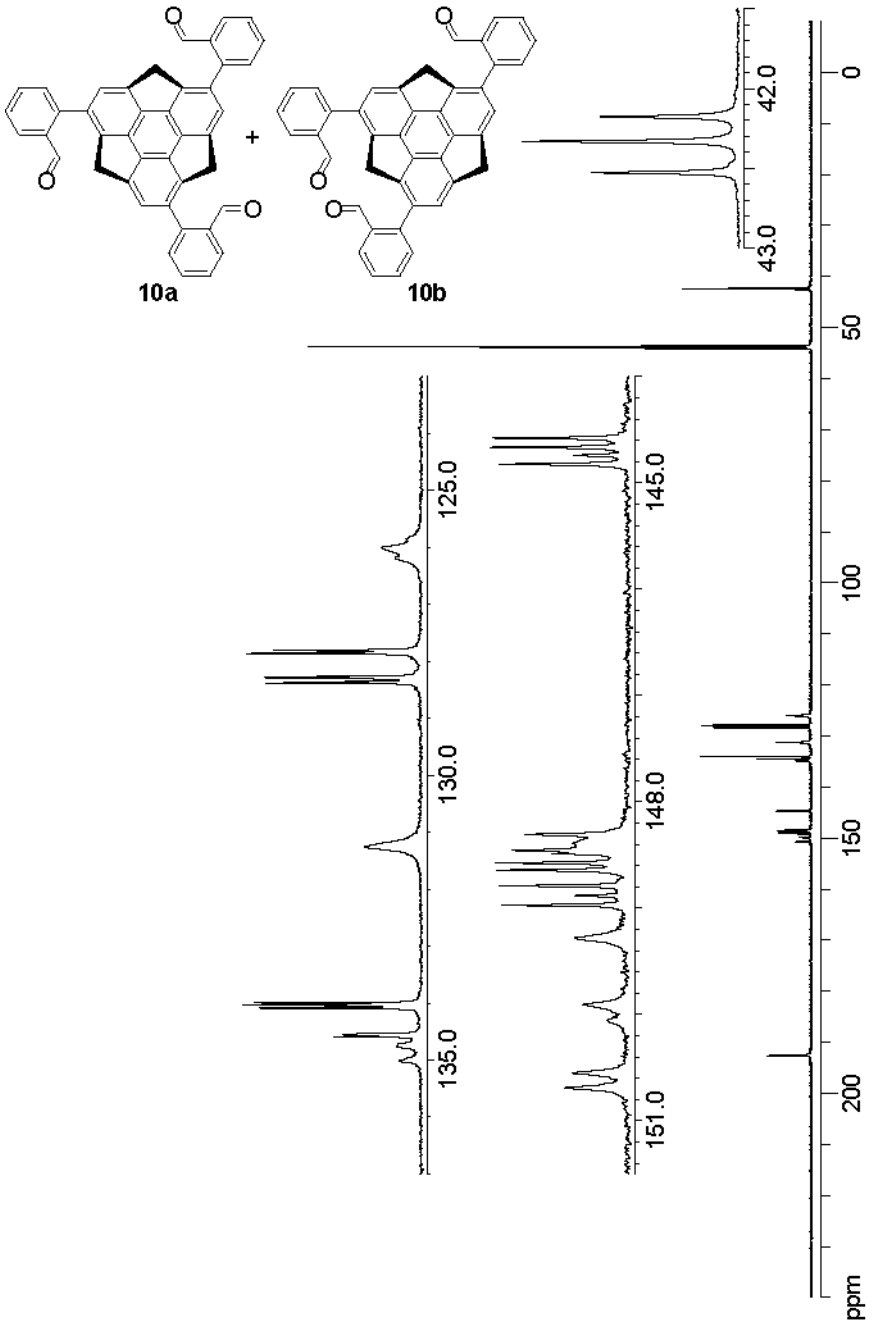
^{1}H NMR spectra of **10a** and **10b**

(600 MHz, CD_2Cl_2)



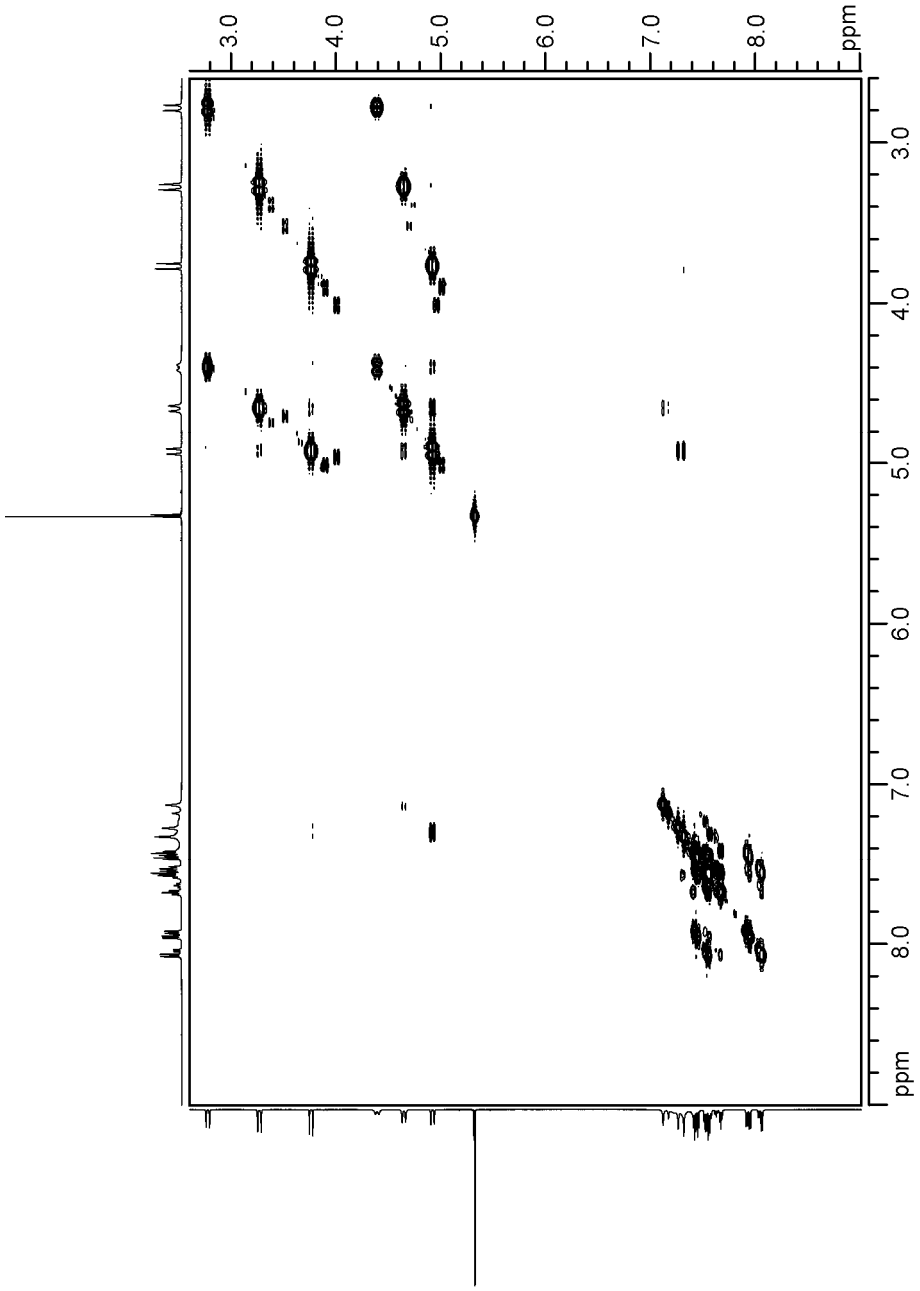
^{13}C NMR spectra of **10a** and **10b**

(150 MHz, CD_2Cl_2)



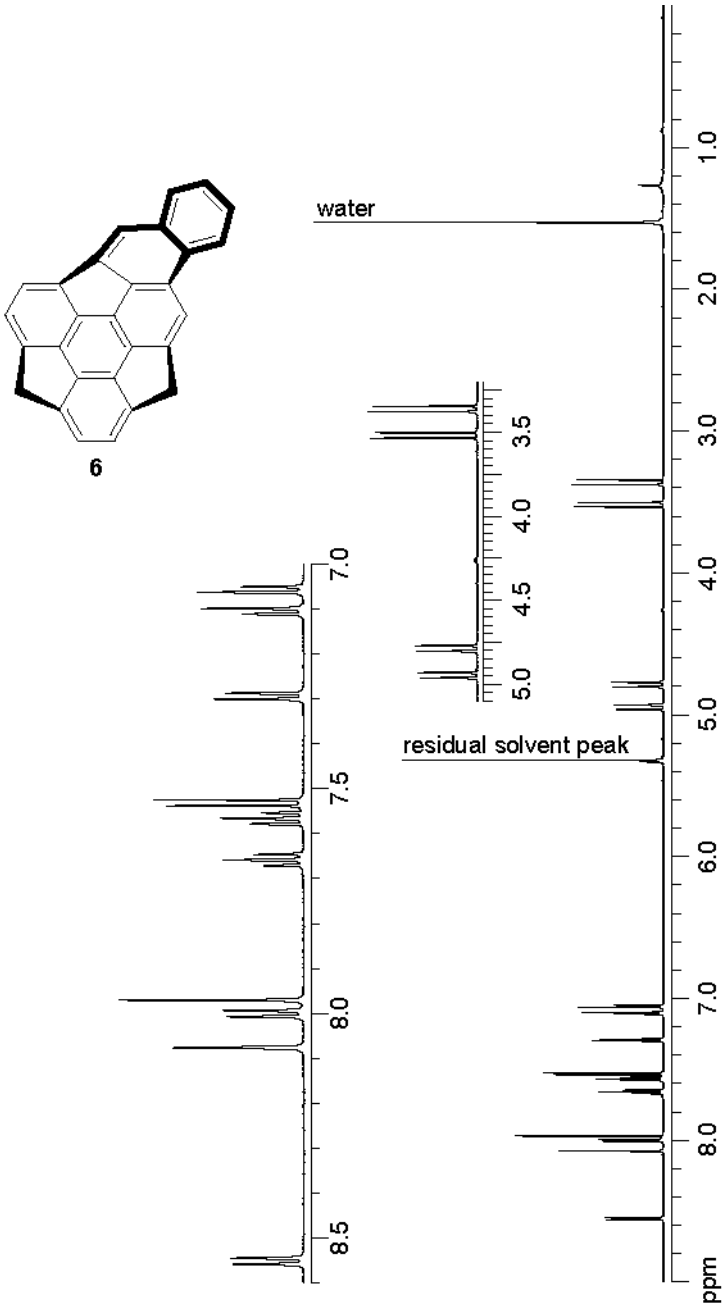
^{1}H-^{1}H COSY spectrum of **10a** and **10b**

(600 MHz, CD_2Cl_2)



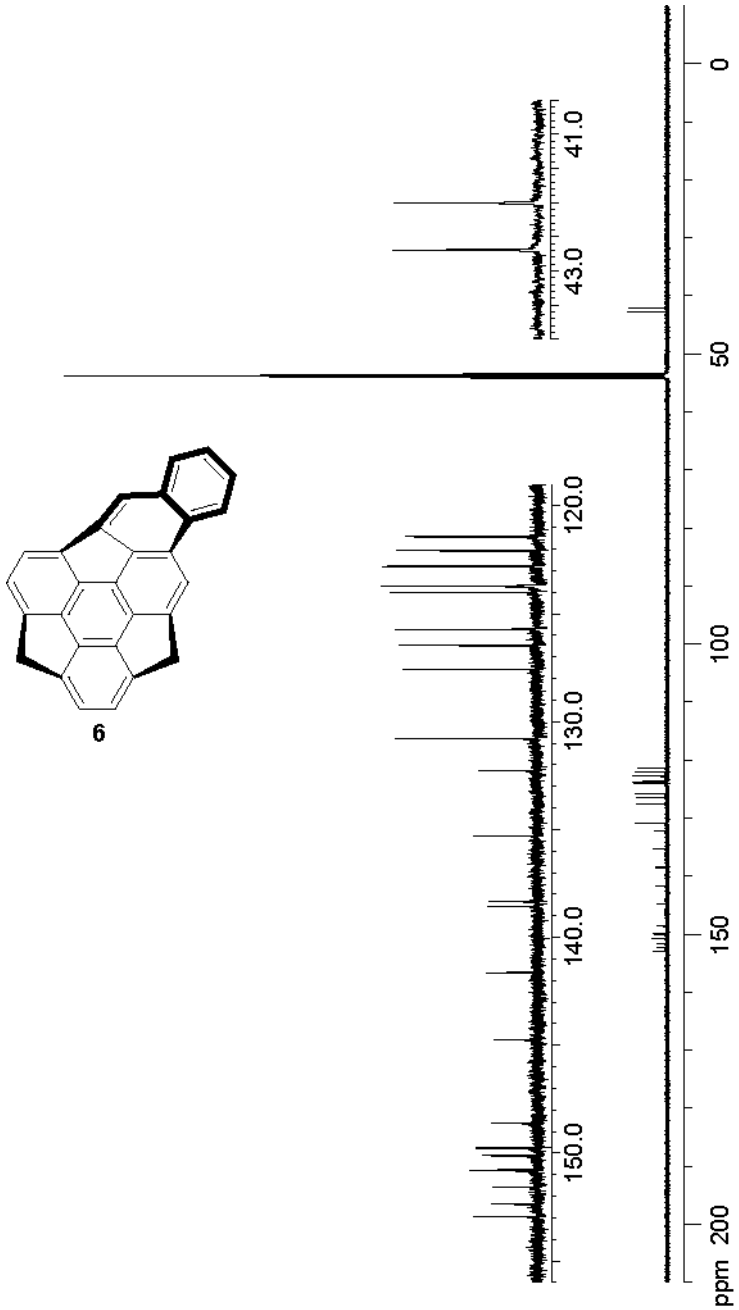
^{1}H NMR spectra of **6**

(600 MHz, CD_2Cl_2)



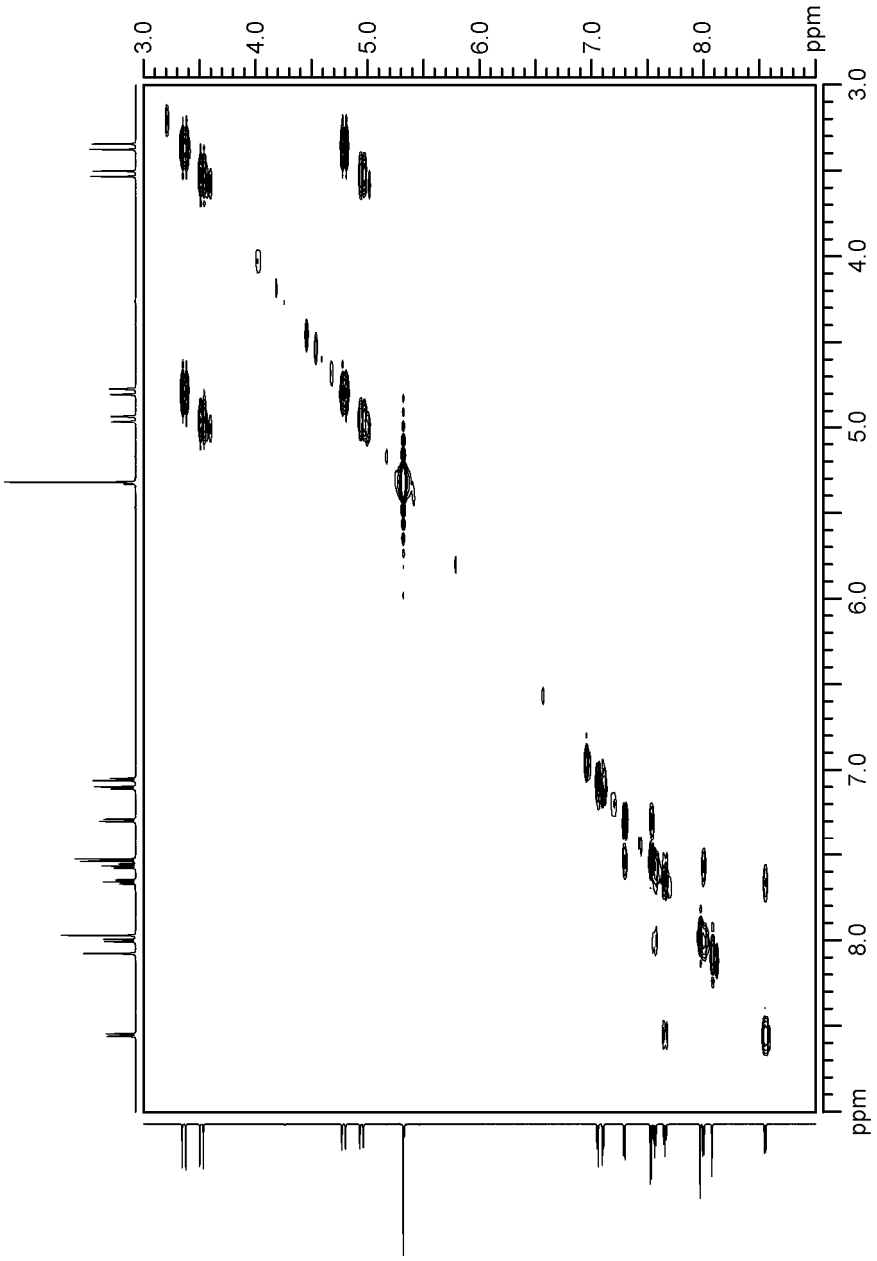
^{13}C NMR spectra of **6**

(150 MHz, CD_2Cl_2)



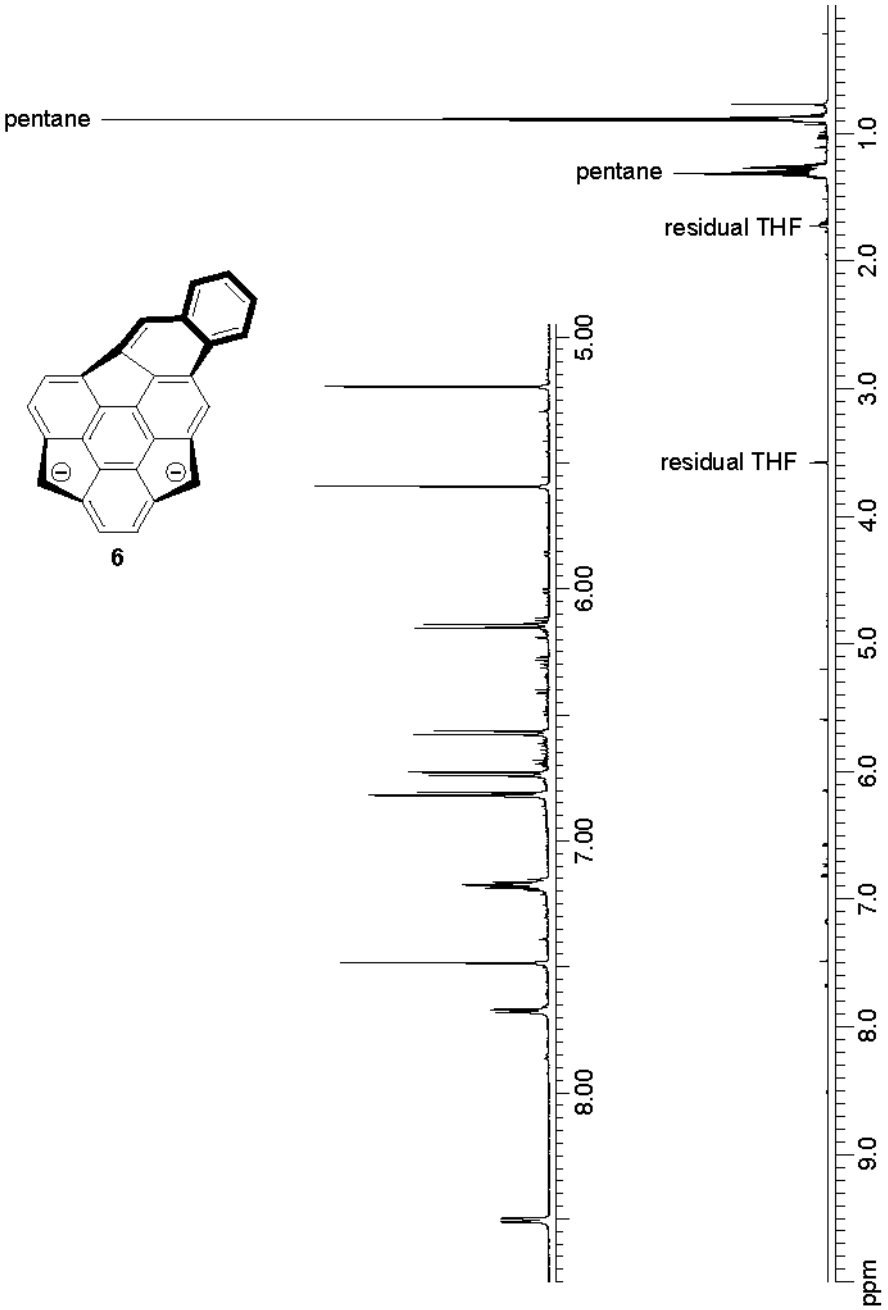
^{1}H-^{1}H COSY spectrum of **6**

(600 MHz, CD_2Cl_2)



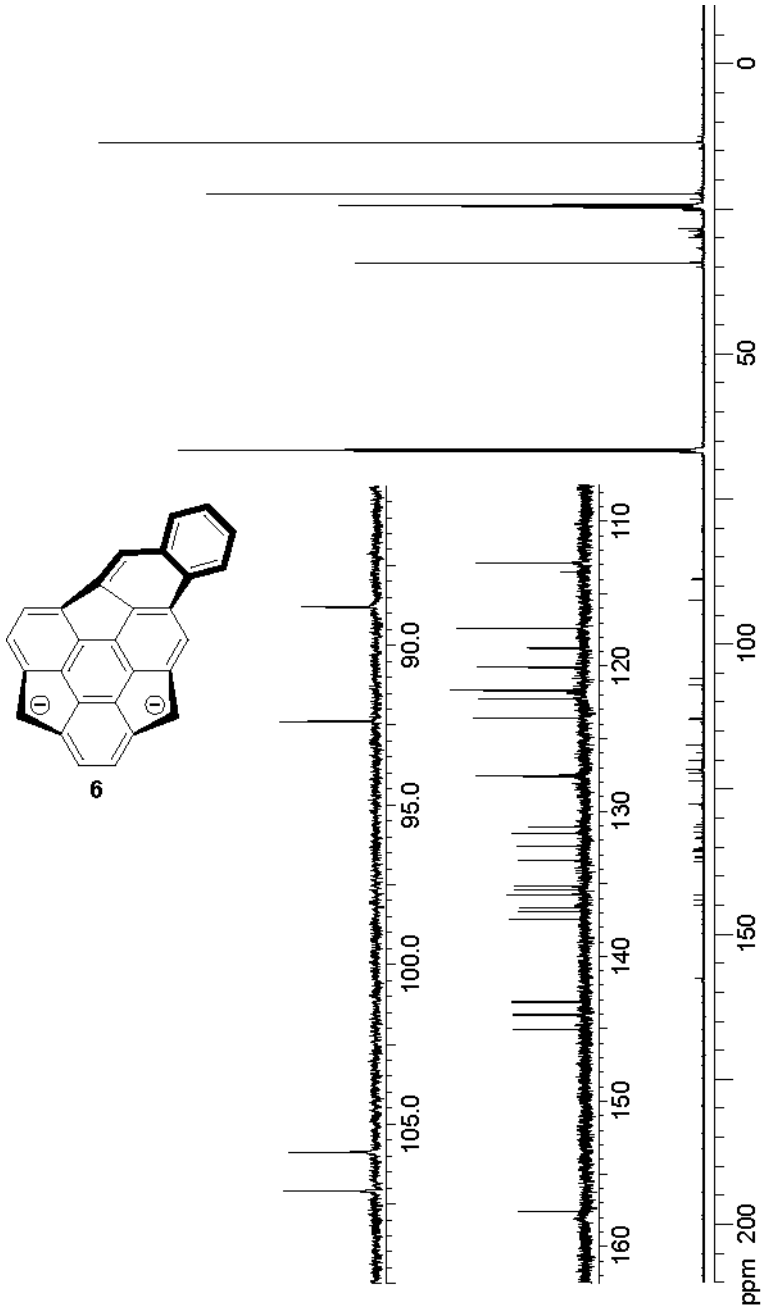
^{1}H NMR spectra of dianion **6**

(600 MHz, THF-d_8)



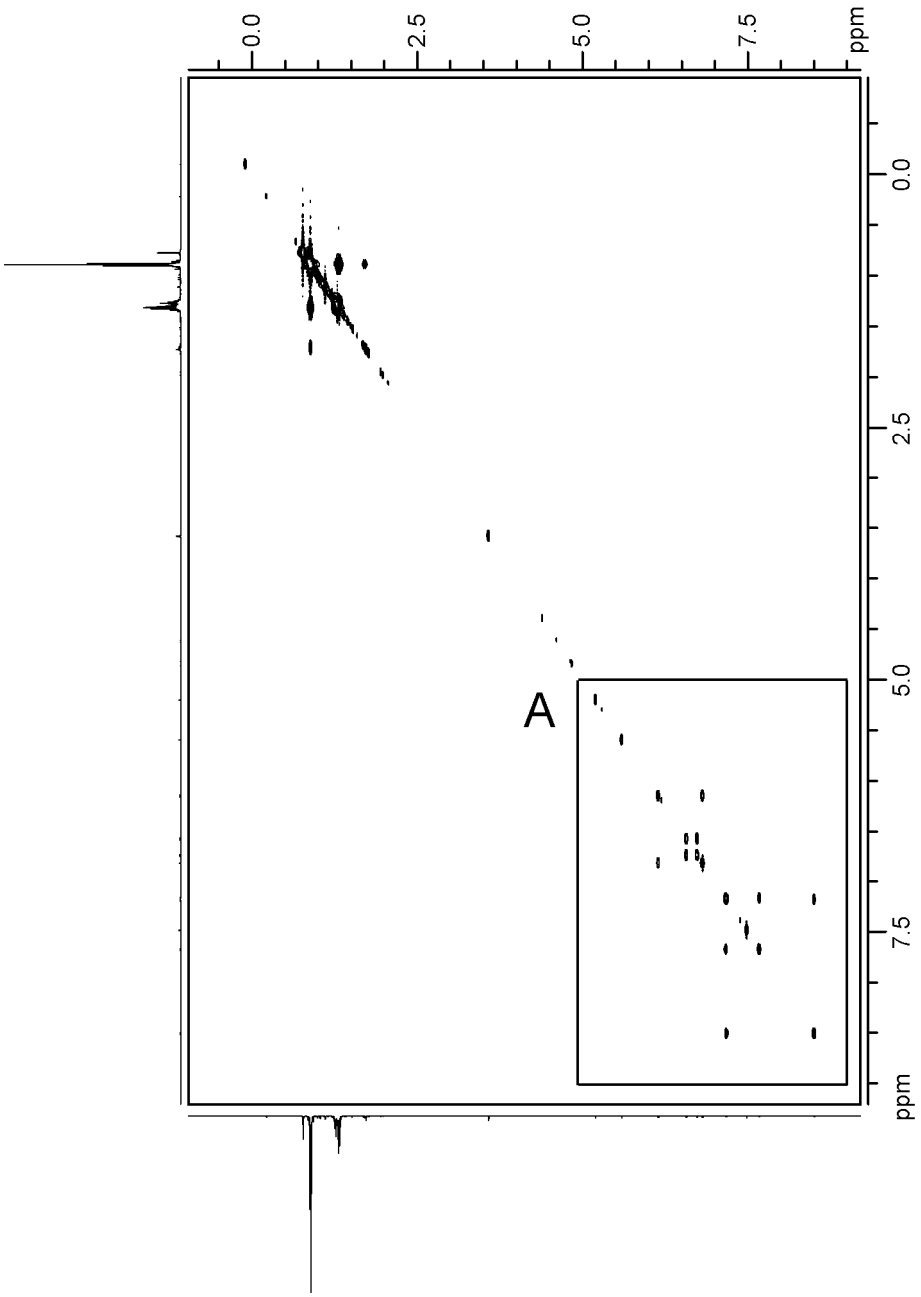
^{13}C NMR spectra of dianion **6**

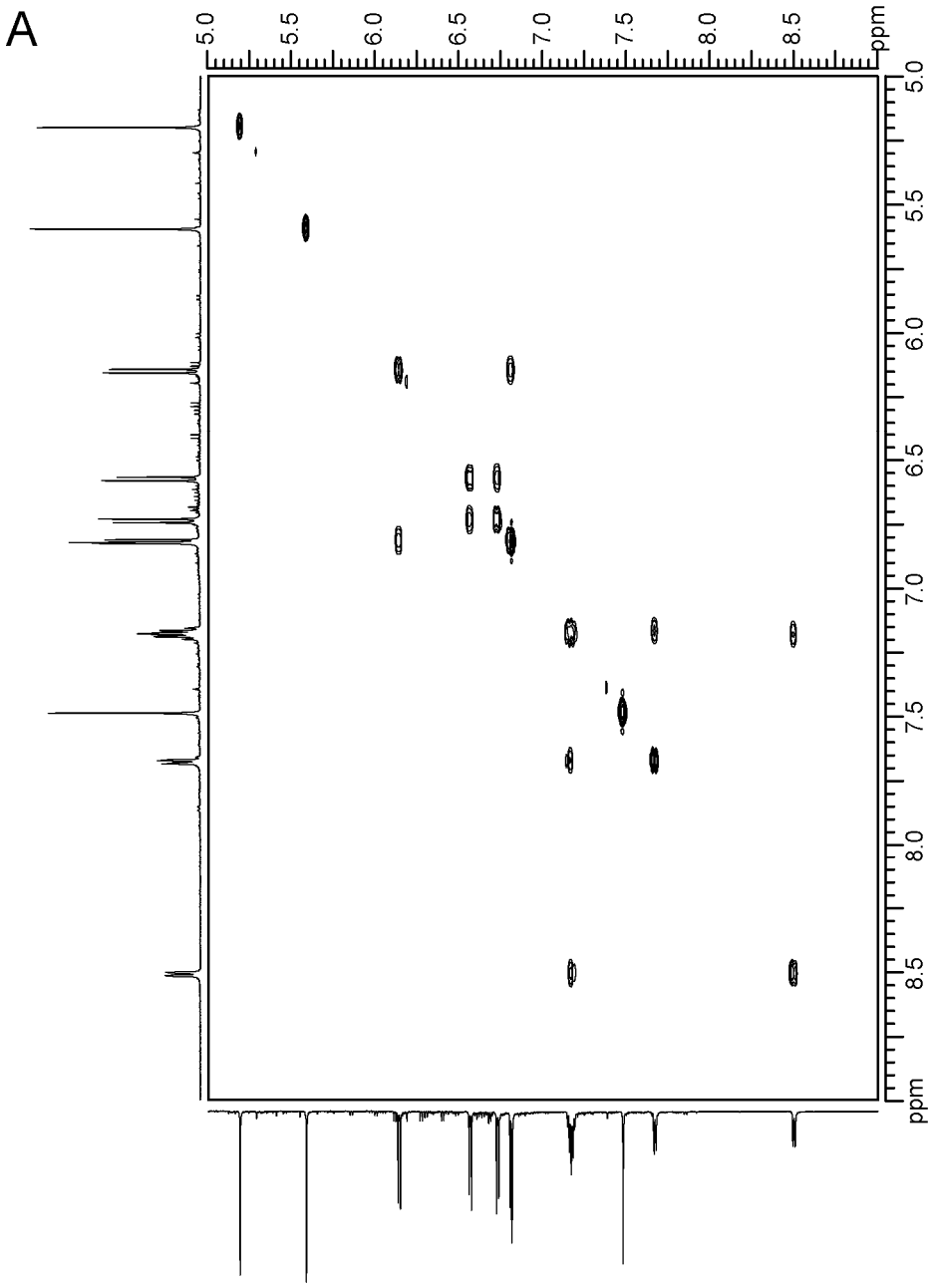
(150 MHz, THF-d_8)



^{1}H-^{1}H COSY spectra of dianion **6**

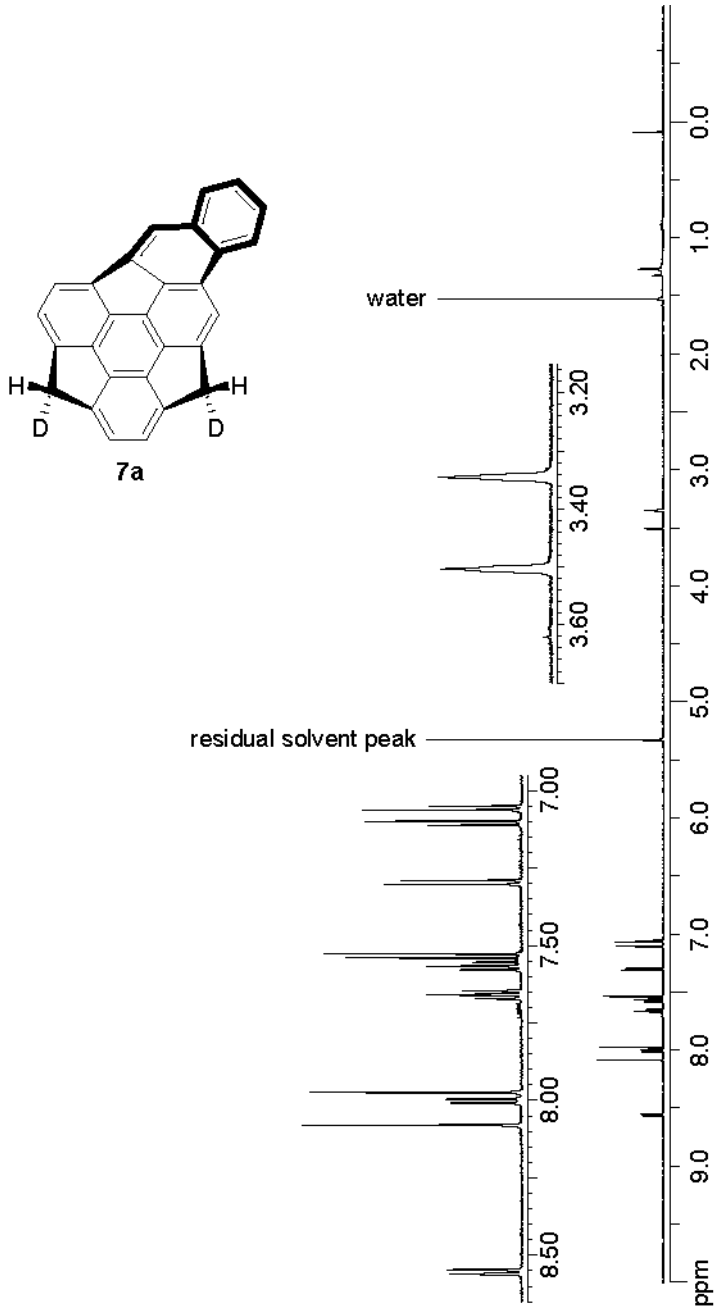
(600 MHz, THF-d_8)




A
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
ppm

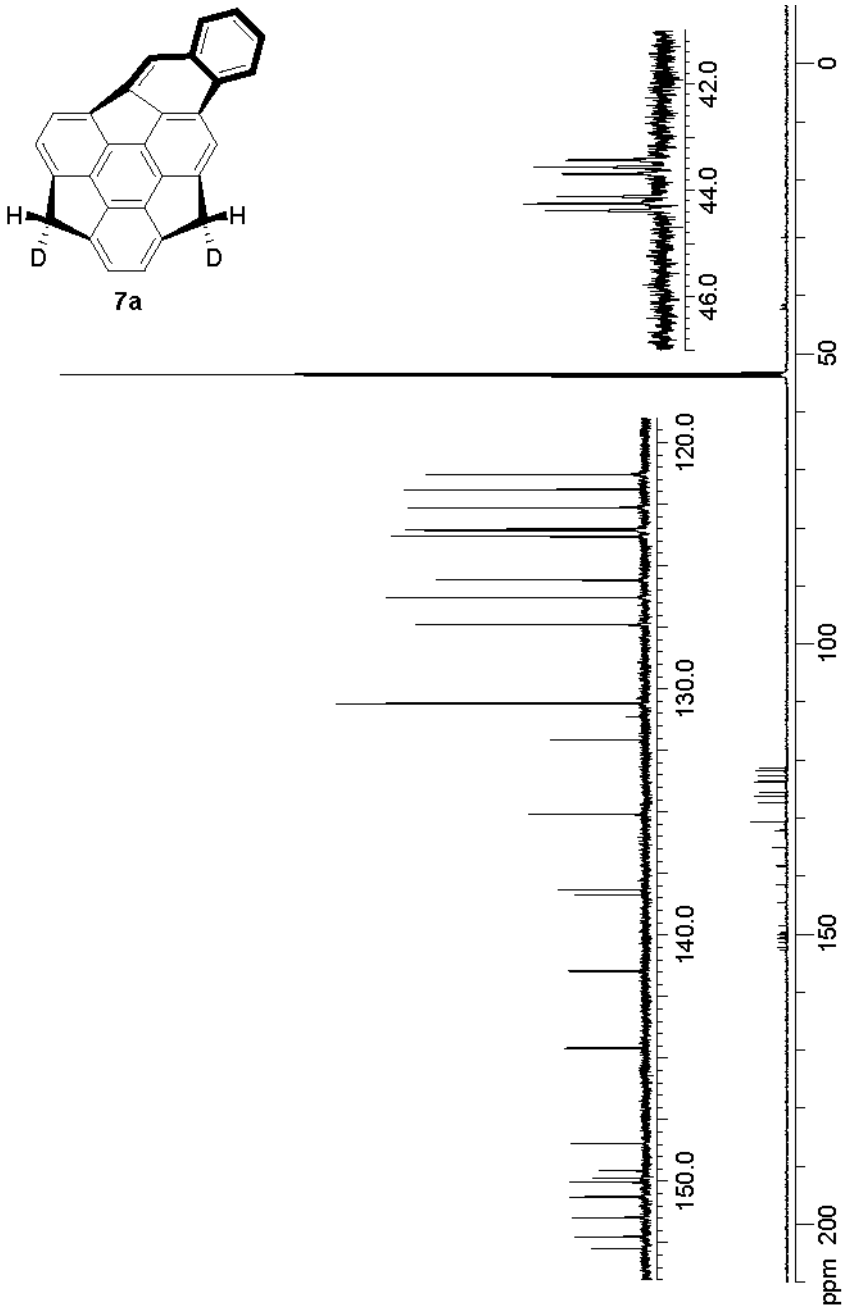
^{1}H NMR spectra of **7a**

(600 MHz, CD_2Cl_2)



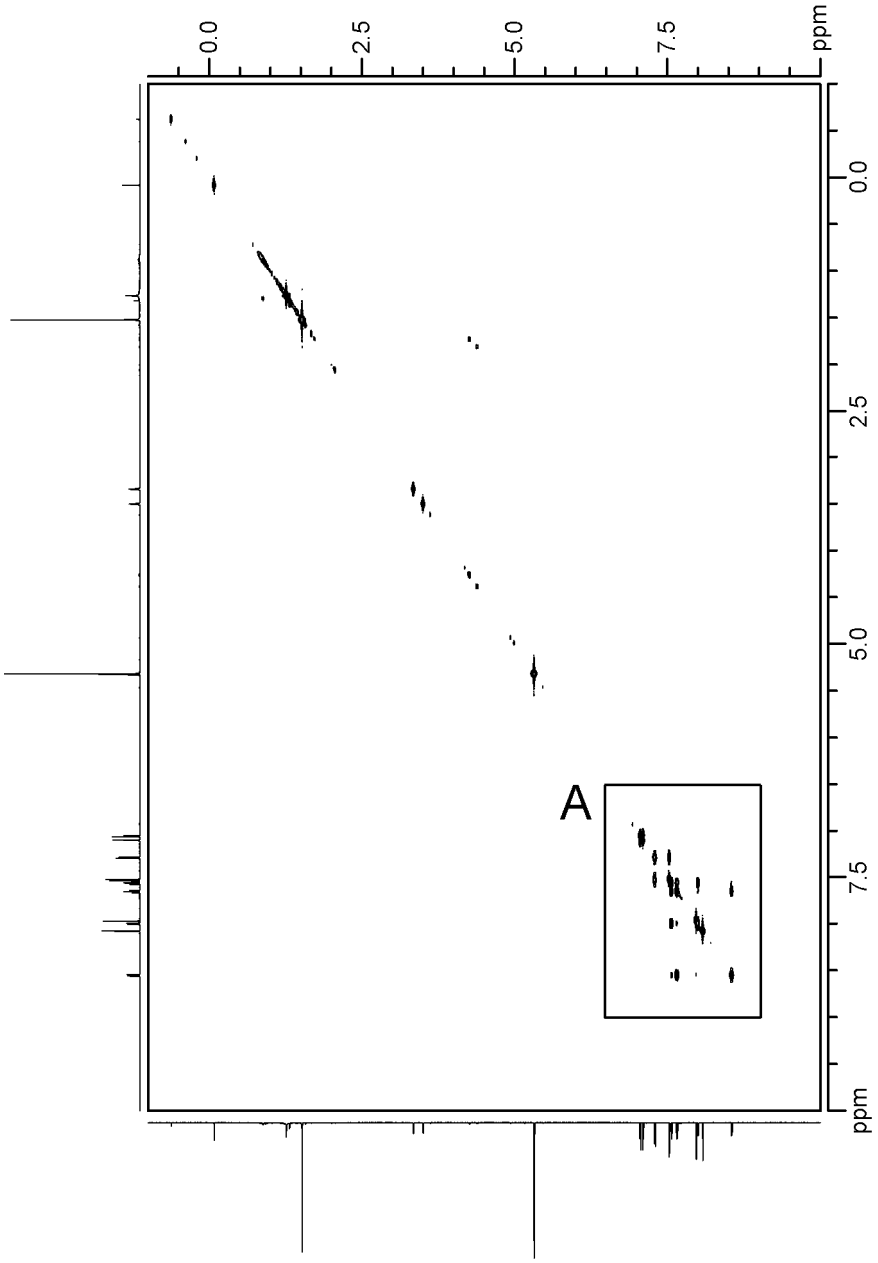
^{13}C NMR spectra of **7a**

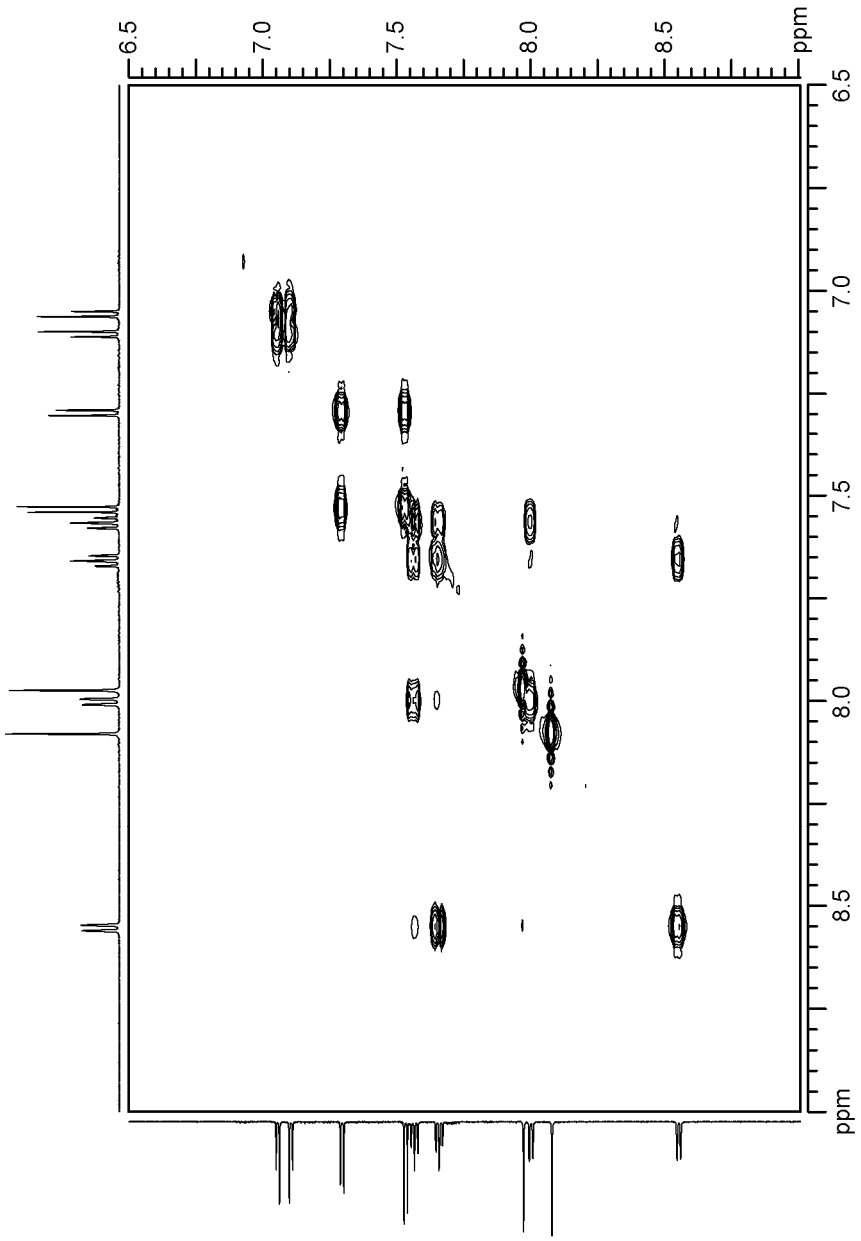
(150 MHz, CD_2Cl_2)



^{1}H-^{1}H COSY of **7a**

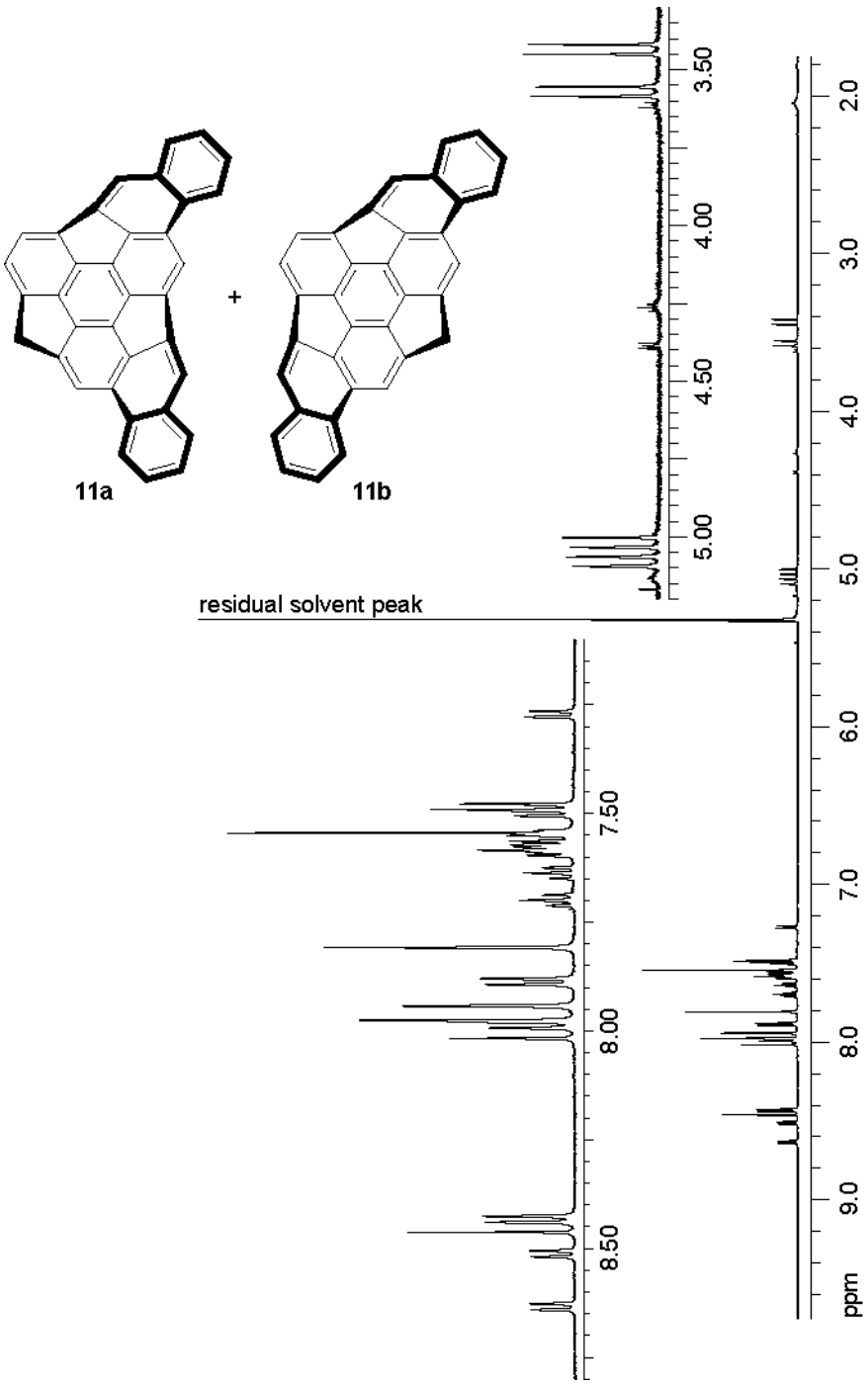
(600 MHz, CD_2Cl_2)




6.5
7.0
7.5
8.0
8.5
ppm
6.5
7.0
7.5
8.0
8.5
ppm

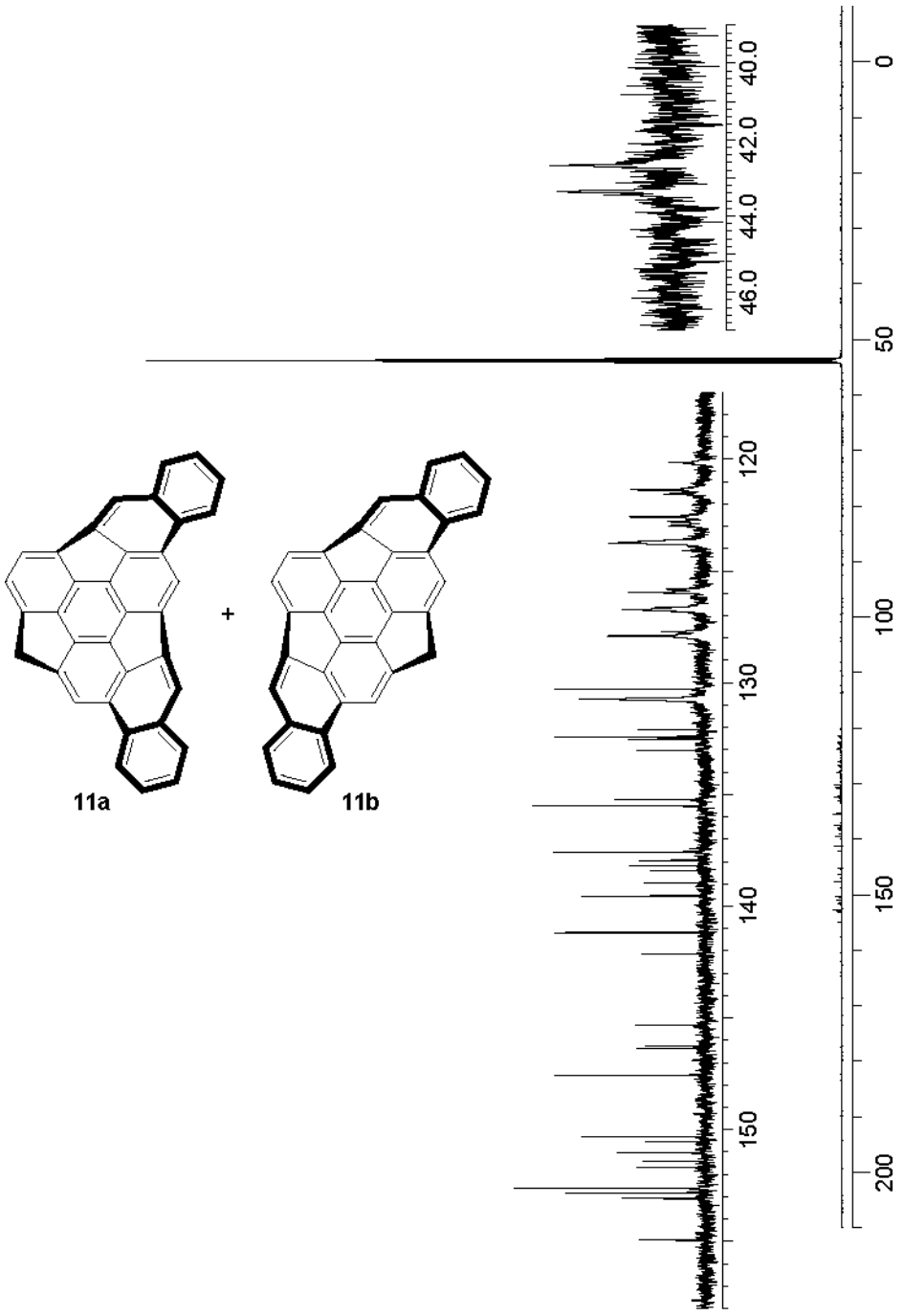
^{1}H NMR spectra of **11a** and **11b**

(600 MHz, CD_2Cl_2)



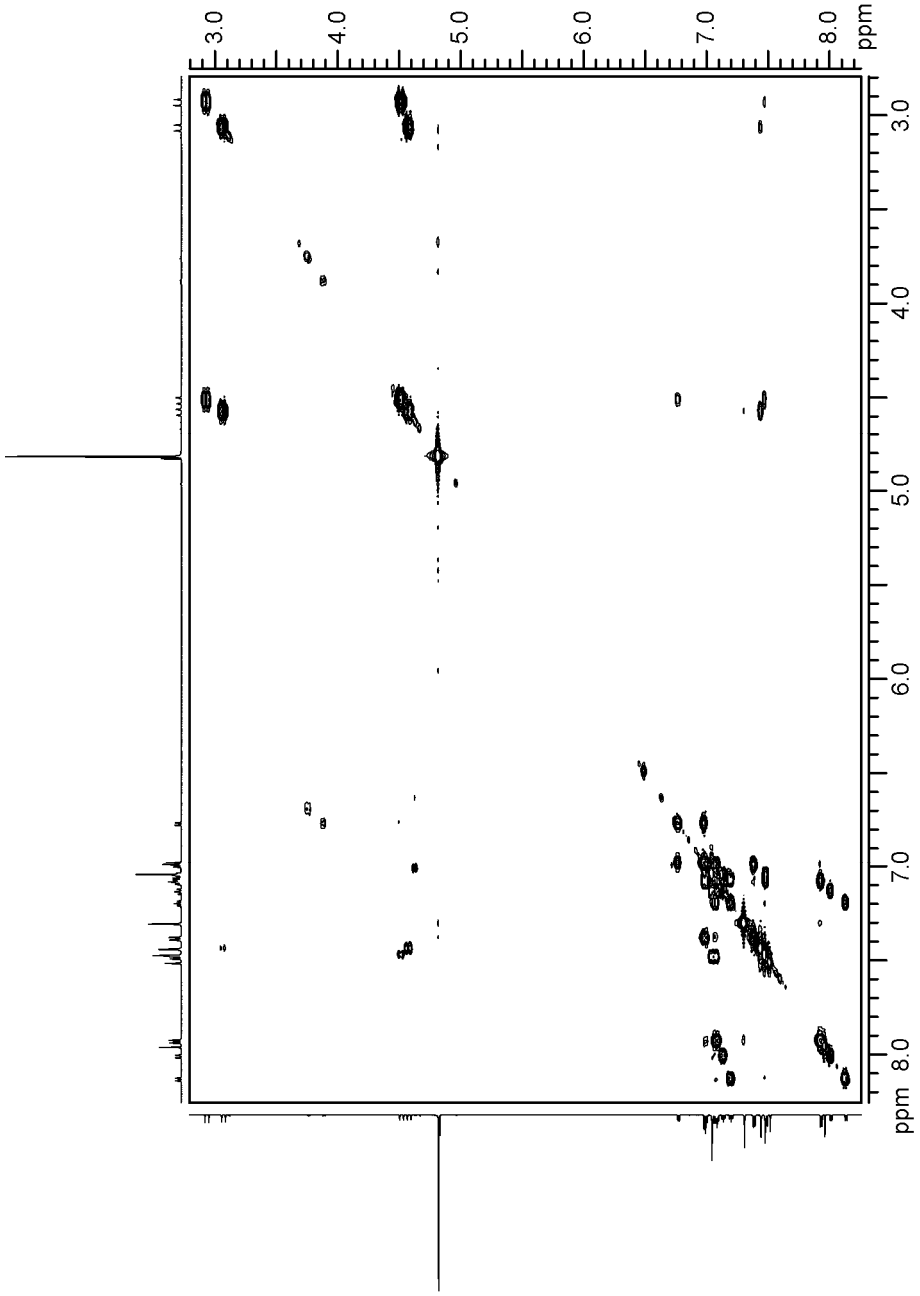
^{13}C NMR spectra of **11a** and **11b**

(150 MHz, CD_2Cl_2)



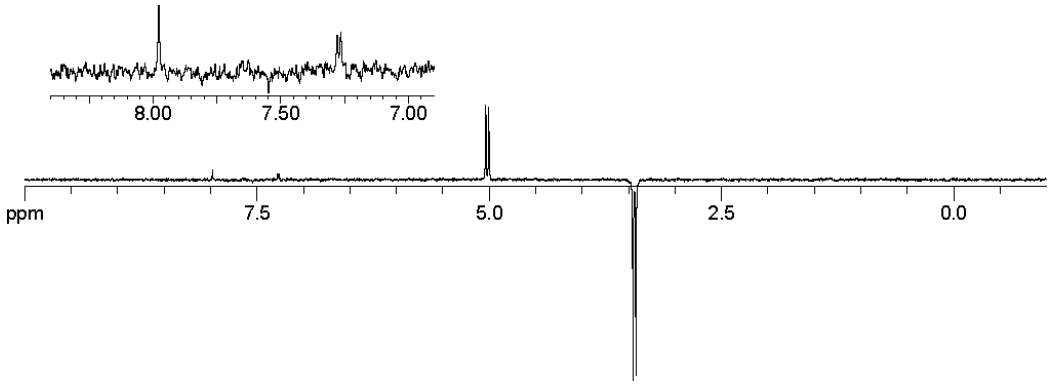
^{1}H-^{1}H COSY spectrum of **11a** and **11b**

(600 MHz, CD_2Cl_2)

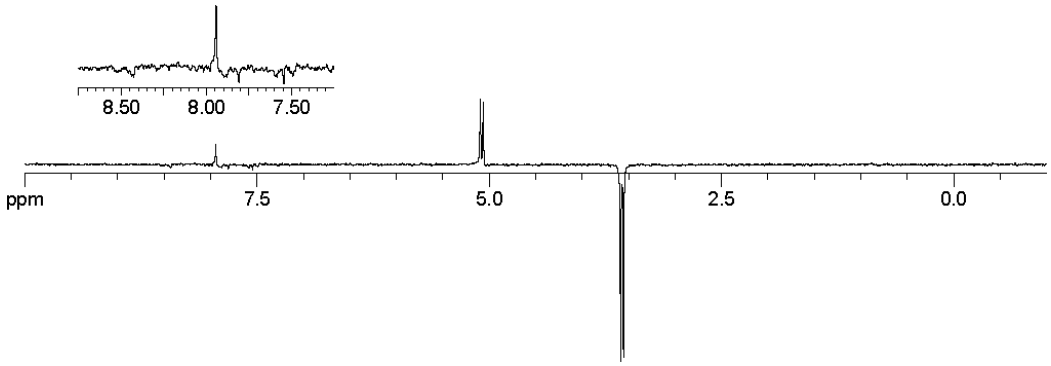


NOESY 1D spectra of **11a** and **11b** (600 MHz, CD_2Cl_2)

Irradiated at 3.43 ppm

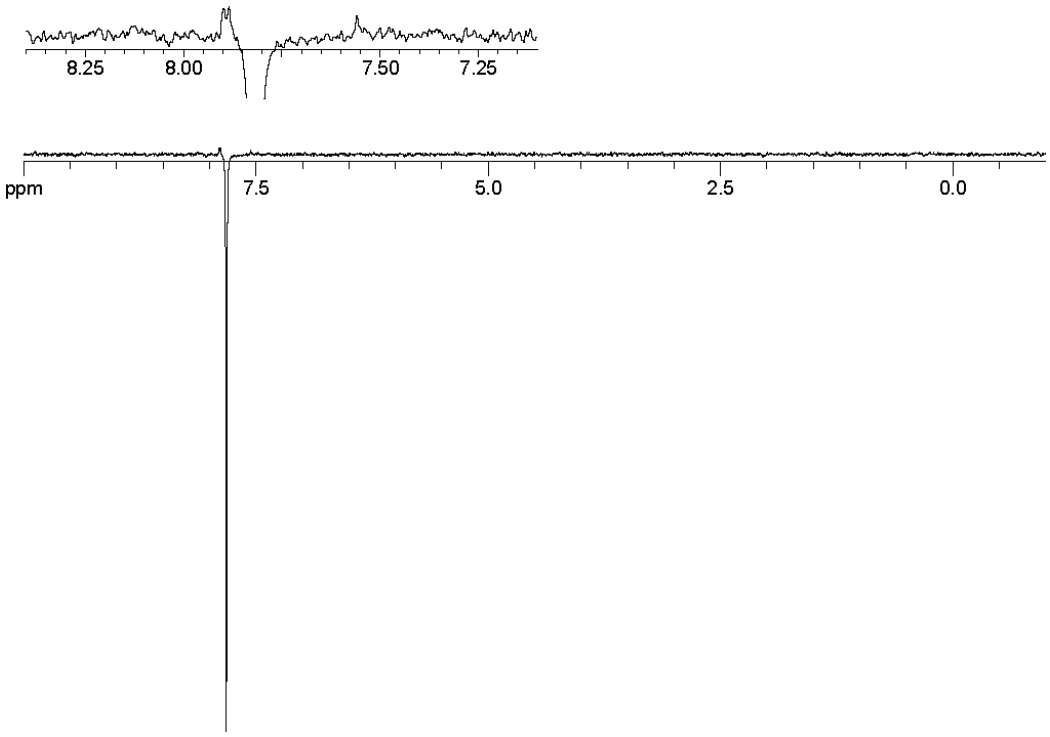


Irradiated at 3.57 ppm

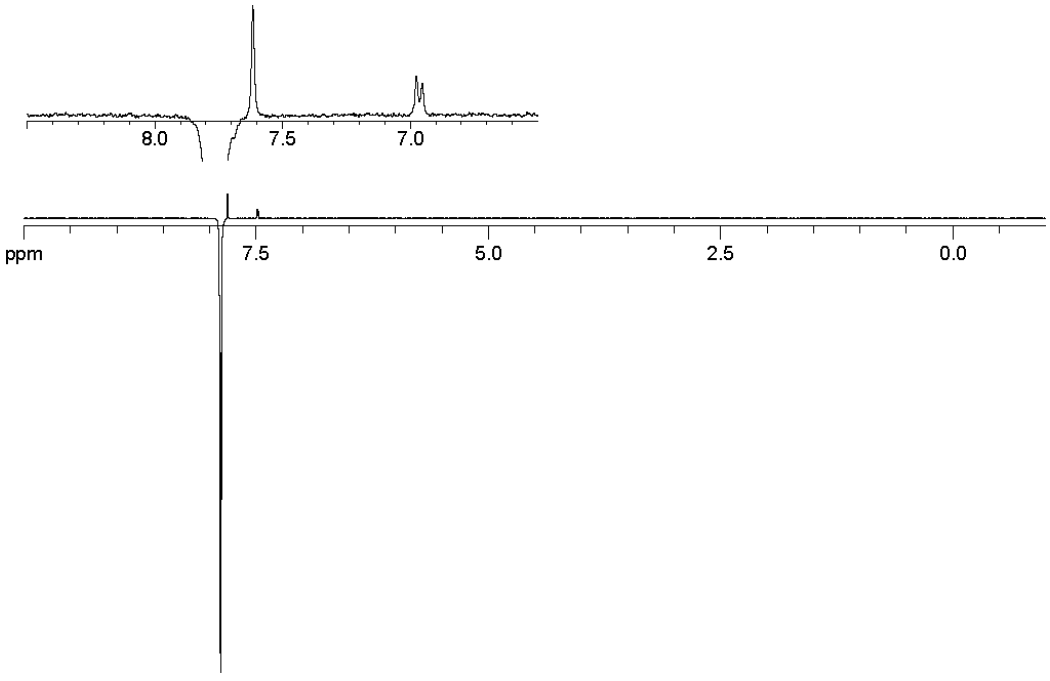


ROESY 1D spectra of **11a** and **11b** (600 MHz, CD_2Cl_2)

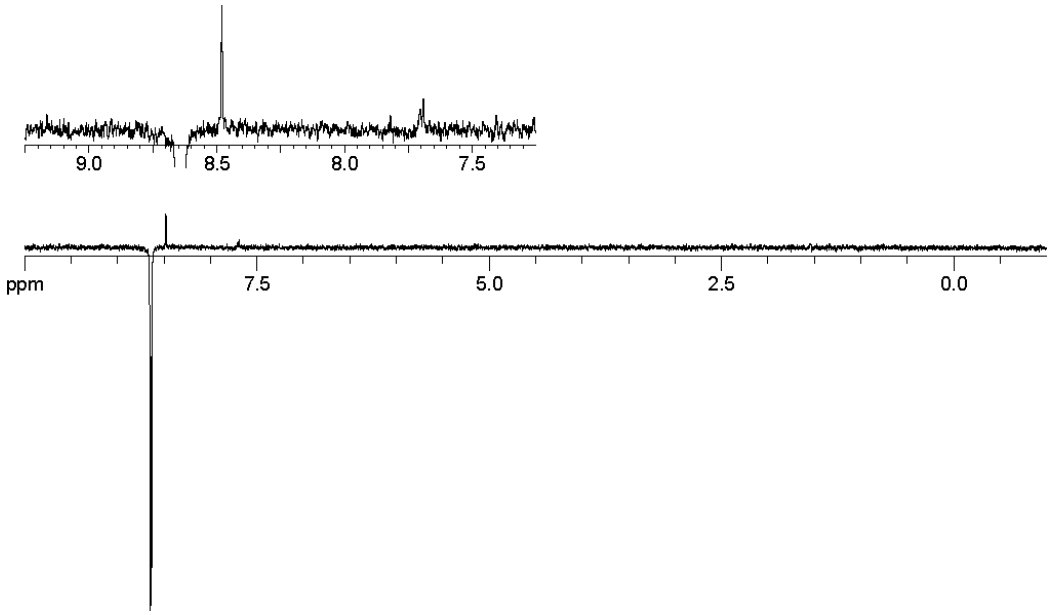
Irradiated at 7.81 ppm



Irradiated at 7.89 ppm

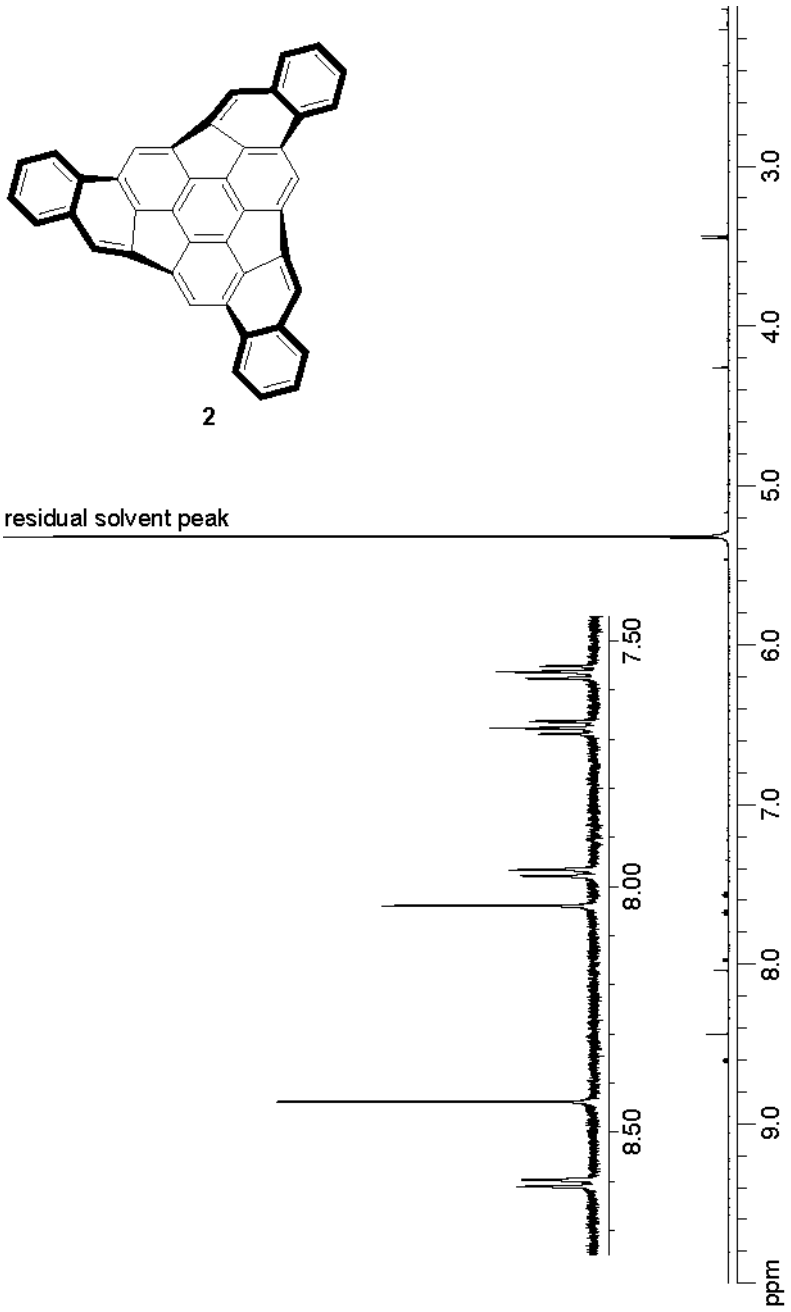


Irradiated at 8.64 ppm



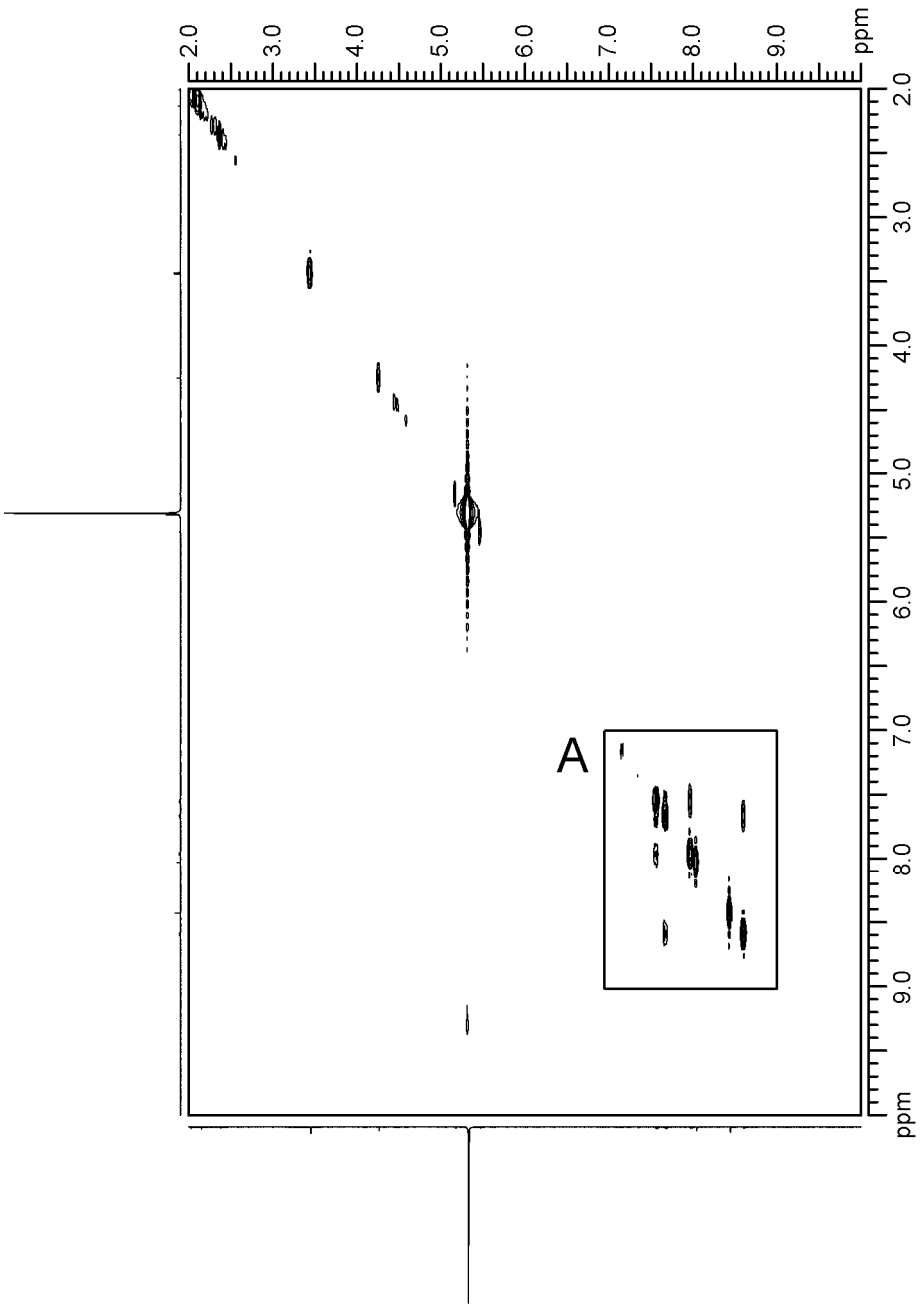
^{1}H NMR spectra of **2**

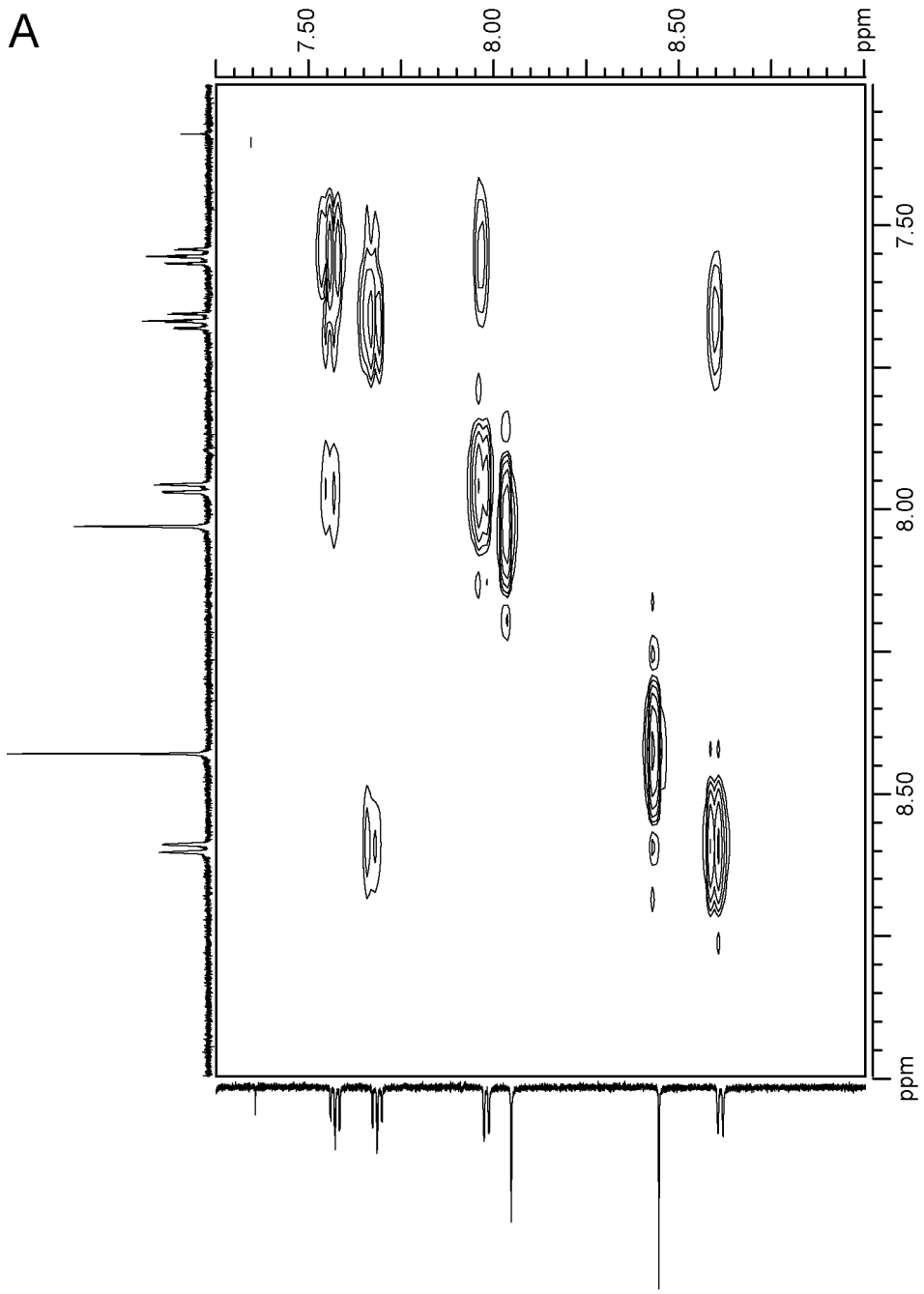
(600 MHz, CD_2Cl_2/CS_2 = 1/1)



^{1}H-^{1}H COSY spectra of **2**

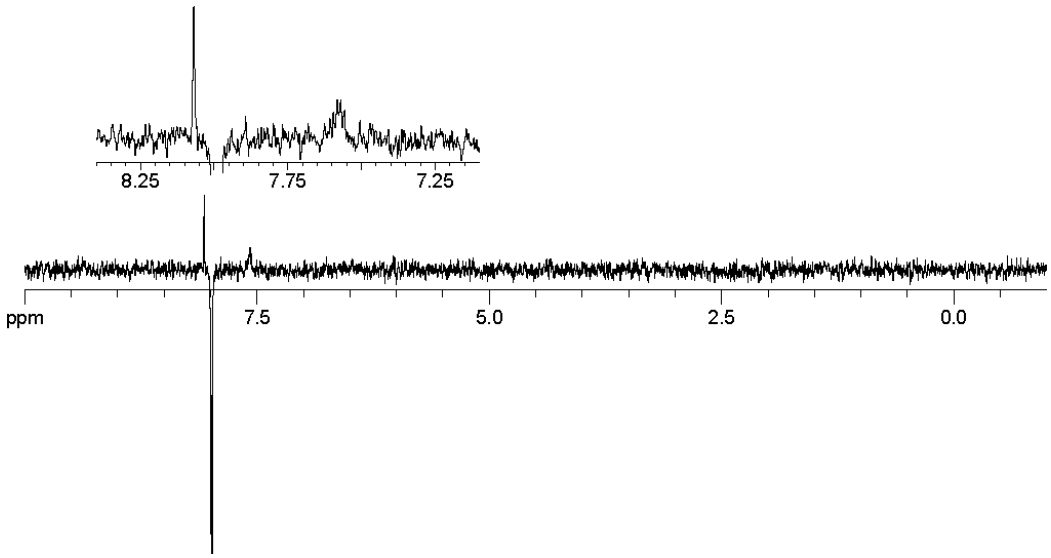
(600 MHz, CD_2Cl_2/CS_2 = 1/1)



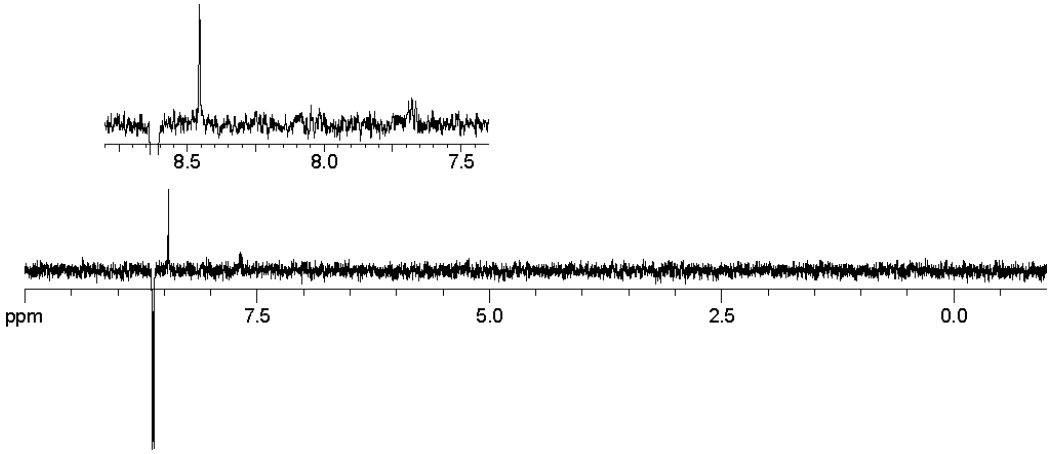

A
7.50
8.00
8.50
ppm
7.50
8.00
8.50
ppm

NOESY 1D spectra of **2** (600 MHz, CD_2Cl_2)

Irradiated at 8.0 ppm

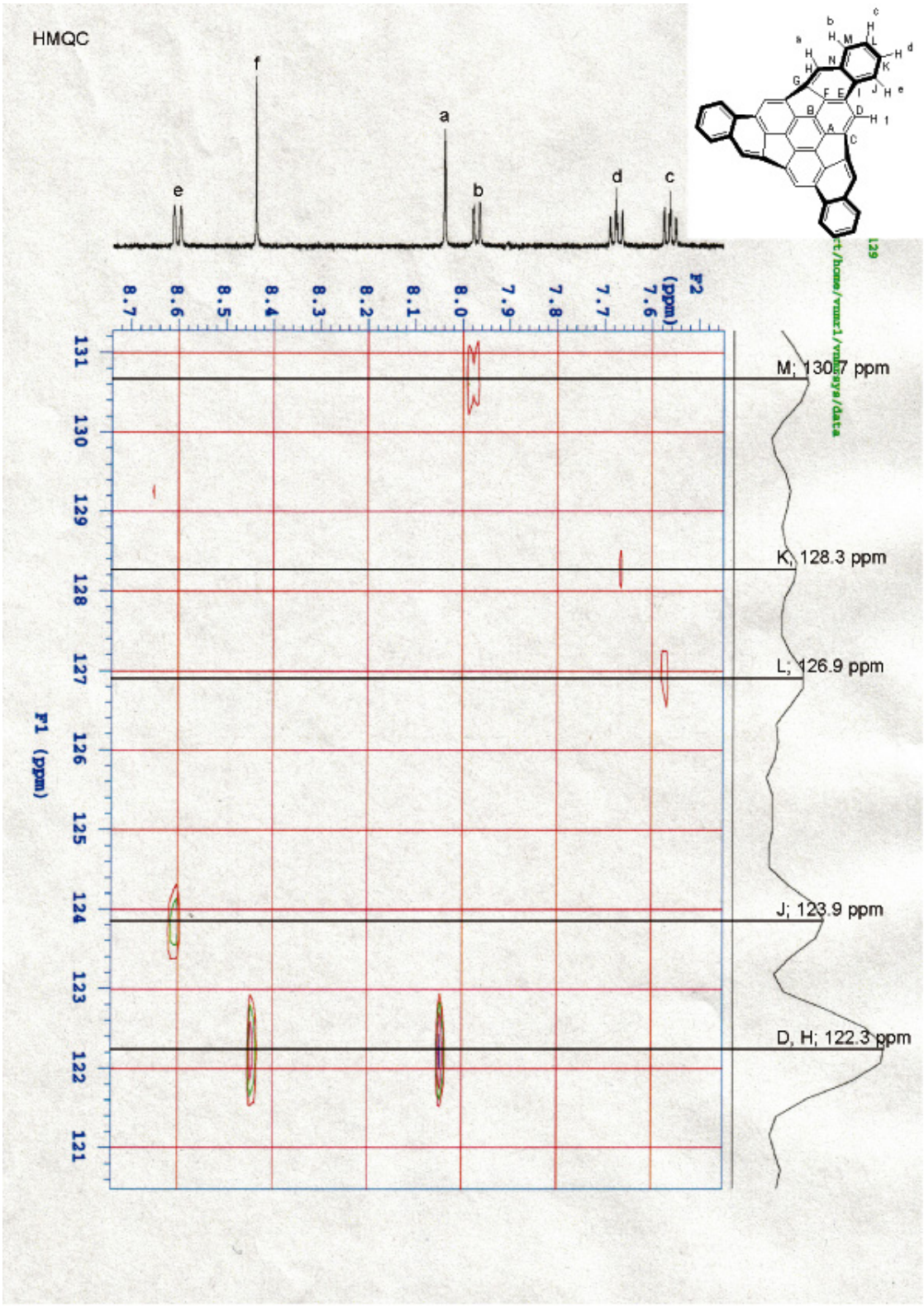


Irradiated at 8.62 ppm



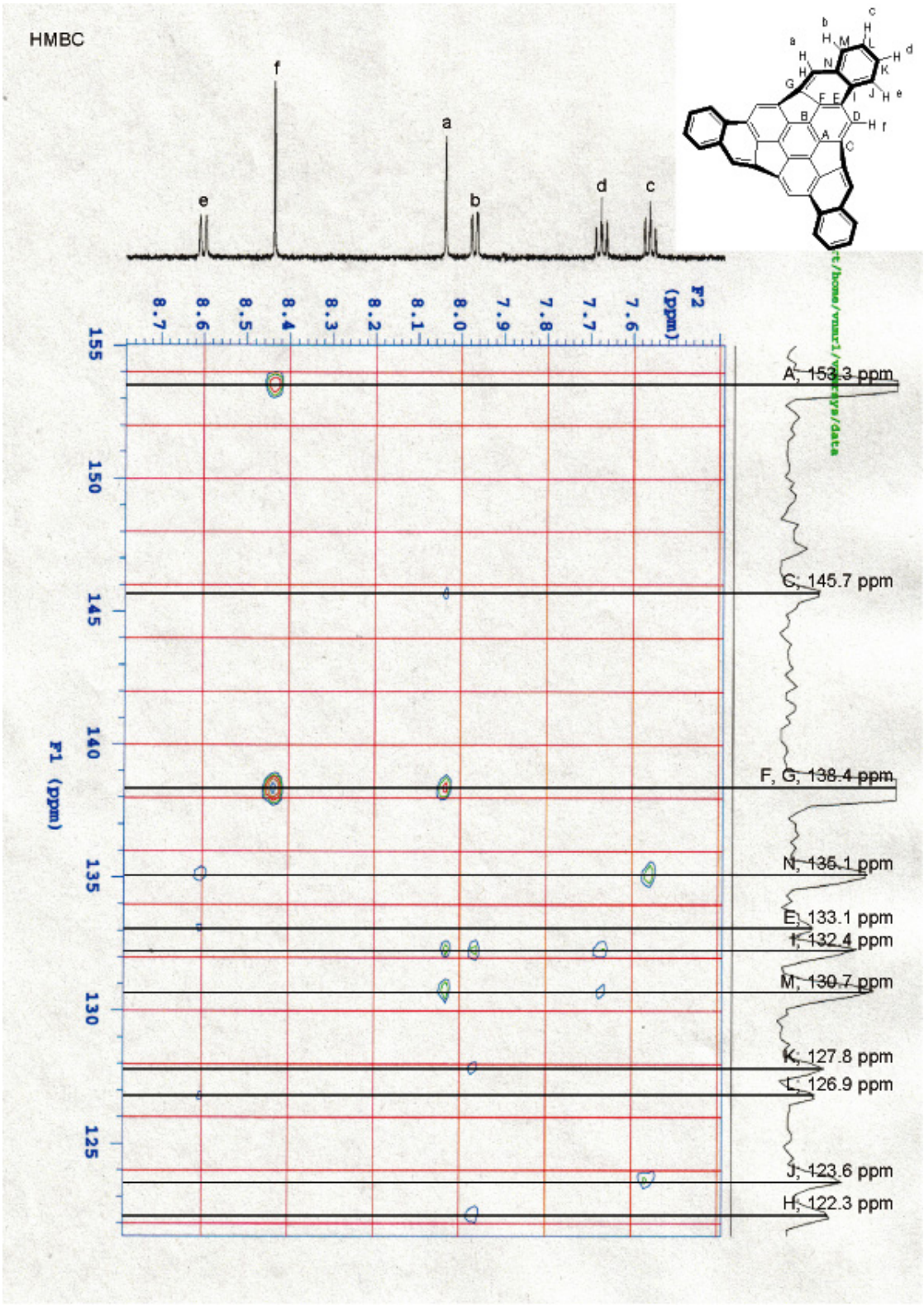
HMQC Experiment of **2**

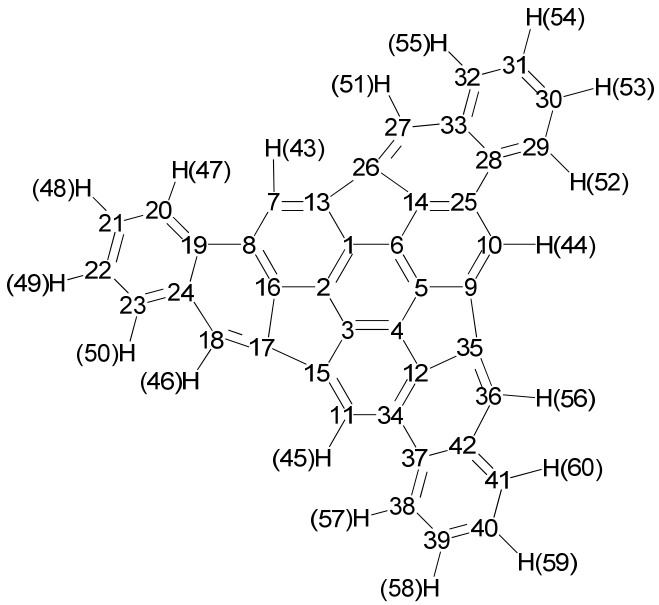
(600 MHz, CD_2Cl_2/CS_2 = 1/1)



HMBC Experiment of **2**

(600 MHz, CD_2Cl_2/CS_2 = 1/1)





GIAO/6-31G(d,p)	^{1}H NMR
H(47); 8.66	H(47); 8.60
H(43); 8.48	H(43); 8.44
H(46); 7.97	H(46); 8.04
H(50); 7.96	H(50); 7.97
H(48); 7.75	H(48); 7.68
H(49); 7.65	H(49); 7.56

GIAO/6-31G(d,p)	correlation value (HMQC and HMBC)
C(1); 150.4	C(1); 153.5
C(2); 142.8	C(2); -----
C(13); 142.3	C(13); 145.7
C(7); 118.3	C(7); 122.3
C(8); 129.8	C(8); 133.1
C(16); 135.4	C(16); 138.4
C(17); 135.7	C(17); 138.4
C(18); 118.8	C(18); 122.3
C(19); 128.8	C(19); 132.4
C(20); 118.7	C(20); 123.9
C(21); 122.2	C(21); 128.3
C(22); 120.7	C(22); 126.9
C(23); 126.2	C(23); 130.7
C(24); 130.9	C(24); 135.1

The predicted and observed chemical shifts of ^{1}Hs and ^{13}Cs of **2** (GIAO/6-31G**//B3LYP/6-31G**).