Transition Metal-Free vs. Metal-Catalyzed Cyclotrimerization of Didehydro[8]annulenes (COTynes): A Complex Pathway to Non-Planar PAHs – Dewar Benzenes vs. Benzotri[8]annulenes

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Electronic Supplementary Information

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1. General Information

All reactions were performed under an inert atmosphere of argon and with anhydrous solvents in glassware oven or flame dried at 80 ºC unless otherwise stated. Commercially available chemicals were purchased from Acros Organics Ltd., Aldrich Chemical Co. Ltd., Alfa Aesar, Fluorochem Ltd., Strem Chemicals Inc. or TCI Europe N.V. chemical companies and used without further purification, unless otherwise stated.

Analytical thin-layer chromatography was carried out on silica-coated aluminum plates (silica gel 60 F254 Merck) using UV light as visualizing agent (254 nm) and $KMnO_4$ (solution of 1.5 g of potassium permanganate, 10 g of potassium bicarbonate and 1.25 mL of 10% sodium hydroxide in 200 mL of water) with heat as a developing agent. Flash column chromatography was performed on silica gel 60 (Merck, 230-400 mesh) with the indicated eluent.[1]

The complex [Ru (η^5-(C_5Me_5) ($CH_3CN)_3$]PF_6 was synthesized by the reduction of [Ru (η^5-(C_5Me_5)Cl_2]$_n$ with $LiEt_3BH$ according to published procedures.[2]

Caution! Trimethylsilyldiazomethane should be regarded as extremely toxic and should only be handled by individuals trained in its proper and safe use. All operations must be carried out in a well-ventilated fume hood and all skin contact should be avoided.[3]

^{1}H- and ^{13}C-NMR experiments were carried out using a Bruker NEO 750 MHz, a Varian Inova 500MHz, a Varian Inova 400 MHz, a Varian Mercury 300MHz or a Bruker DPX 250 or a Bruker Avance 300 NMR spectrometer. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C(1H)). Coupling constants (*J*) are given in Hertz (Hz). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or as a combination of them. The multiplicities of ^{13}C NMR signals were determined by DEPT experiments.

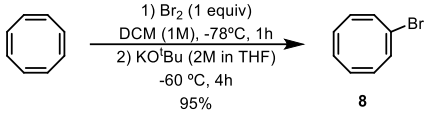
Mass spectrometry was carried out on a Bruker micro TOF spectrometer.

Yields refer to isolated compounds estimated to be > 95% pure as determined by ^{1}HNMR and capillary GC analysis.

X-ray crystallographic analysis was performed at the CACTUS facility of the University of Santiago de Compostela, Spain.

2. Synthesis of starting materials

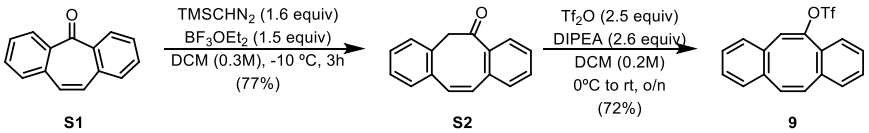
(1*E*,3*Z*,5*Z*,7*Z*)-1-Bromocycloocta-1,3,5,7-tetraene **8**[4]



A solution of Br_2 (0.1 mL, 2 mmol, 1 equiv) in DCM (0.5 mL) was slowly added to a solution of COT (0.23 mL, 2 mmol) in DCM (1.5 mL, 1 M) cooled to -78 ºC. After stirring for 1h, a solution of KO^{t}Bu in THF (1.4 mL, 2 M) was added dropwise. The resulting mixture was stirred at -60 ºC for 4h, warmed to -10ºC, and poured into ice water with a small amount of solid $MgSO_4$ to break the formed emulsions. The organic layer was removed, and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford BrCOT **8** (0.35 g, 95%) as a light yellow oil. The characterization data are consistent with those reported in the literature.

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.22 (s, 1H), 5.97 – 5.75 (m, 5H), 5.64 (d, *J* = 10.5 Hz, 1H).

(5*E*,11*Z*)-Dibenzo[*a*,*e*][8]annulen-5-yl trifluoromethanesulfonate **9**[5]



A solution of trimethylsilyl diazomethane (5.8 mL, 2 M in hexane) in DCM (10 mL) was added dropwise over a period of 1h to a solution of dibenzosuberenone **S1** (1.53 g, 7.2 mmol) and $BF_3.OEt_2$ (1.3 mL, 10.8 mmol, 1.5 equiv) in DCM (16 mL, 0.3 M) at -10 ºC. The resulting mixture was stirred at the same temperature for another 2h and then poured into ice water. The aqueous layer was extracted with DCM (3 x 15 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography through silica gel using a mixture of DCM/Hex (1:2) to afford (*Z*)-dibenzo[*a*,*e*][8]annulen-5(6H)-one **S2** (1.2 g, 77%) as a yellow solid. The characterization data are consistent with those reported in the literature.

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.26 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.40 – 7.18 (m, 5H), 7.05 (d, *J* = 2.2 Hz, 2H), 4.06 (s, 2H).

In a round-bottomed flask, DIPEA (1.9 mL, 11 mmol, 2.6 equiv) and triflic anhydride (1.8 mL, 10.5 mmol, 2.5 equiv) were dissolved in dry DCM (14 mL) at 0 ºC, and then a solution of

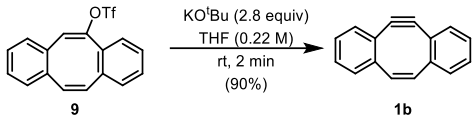
dibenzoannulenone **S2** (0.92 g, 4.2 mmol) in DCM (7 mL, 0.2 M) was added dropwise. The resulting mixture was stirred at room temperature until the starting material disappeared (TLC monitoring, o/n). The mixture was transferred to water (50 mL) and extracted with DCM (3 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of Hex/EtOAc (9:1) to give vinyl triflate **9** (1.07g, 72%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.35 – 7.18 (m, 5H), 7.11 – 7.06 (m, 3H), 6.92 (s, 1H), 6.82 (s, 2H).

^{13}C NMR, DEPT (126 MHz, $CDCl_3$), δ (ppm): 146.1 (C), 137.1 (C), 135.9 (C), 132.2 (CH), 131.5 (CH), 130.9 (C), 130.4 (C), 128.9 (CH), 128.3 (CH), 128.3 (CH), 128.1 (CH), 127.6 (CH), 127.1 (CH), 126.4 (CH), 126.3 (CH), 123.8 (CH), 117.5 (CF_3, *J* =320 Hz)

HRMS (APCI-Probe) calculated for $C_{17}H_{11}F_3O_3S$ $[M]^+$: 352.0376, found: 352.0381.

5,6-Didehydrodibenzo[*a*,*e*][8]annulene (dibenzoCOTyne) **1b**



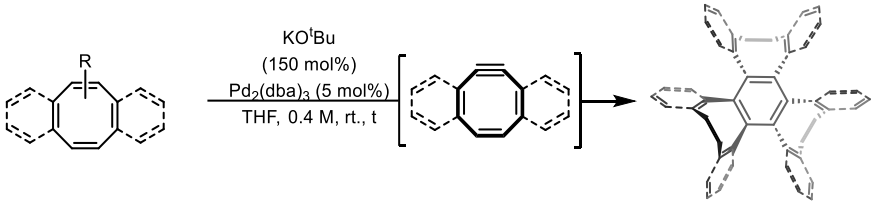
A solution of vinyl triflate **9** (0.2 g, 0.57 mmol) in THF (2.5 mL, 0.22 M) was added dropwise over 1 min to a stirred solution of sublimated KO^{t}Bu (0.18 mmol, 1.6 mmol, 2.8 equiv) in dry THF (20 mL, 0.08 M) at rt in a dry round-bottomed flask under Ar. After stirring the resulting mixture for another 1 min, aqueous HCl (10 mL, 2N) was added, followed by ether (20 mL). The ether extract was washed with water (2 x 10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on neutral alumina using a mixture of Hex/EtOAc (99:1) to give dibenzoCOTyne **1b** (0.1 g, 90%) as an orange crystalline solid.

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.95 – 6.78 (m, 4H), 6.67 (dd, *J* = 7.4, 1.7 Hz, 2H), 6.56 (dd, *J* = 7.2, 1.7 Hz, 2H), 5.49 (s, 2H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 146.8 (2 x C), 134.8 (2 x CH), 132.0 (2 x CH), 129.5 (2 x CH), 129.0 (2 x CH), 126.1 (2 x CH), 123.1 (2 x C), 108.6 (2 x C).

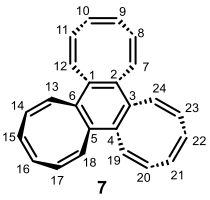
Note: After 10 min in solution ($CDCl_3$), decomposition into several products is observed.

3. Metal-catalyzed [2+2+2] cyclotrimerization of BrCOT 8 and vinyl triflate 9



In a dry round-bottomed flask under argon, BrCOT **8** (1 equiv) and $Pd_2(dba)_3$ (5 mol%) (or $Pd(PPh_3)_4$ (10 mol%) were dissolved in anhydrous THF (0.4 M). The resulting mixture was stirred for 10 min and then solid KO^{t}Bu (1.5 equiv) was added. The resulting mixture was stirred at rt until the starting material disappeared (TLC monitoring). After completion, the reaction mixture was concentrated to dryness and the residue was purified by flash column chromatography on silica gel using a Hex/EtOAc mixture to give the corresponding tri[8]annulene.

*(α,α,β)-Benzotri[8]annulene **7***



7

$Pd_2(dba)_3$ as catalyst

(α,α,β)-Benzotri[8]annulene **7** was obtained using BrCOT **8** (0.036 g , 0.2 mmol), $Pd_2(dba)_3$ (0.009 g, 0.01 mmol, 5 mol%), KO^{t}Bu (0.034 g, 0.3 mmol, 1.5 equiv) and THF (0.5 mL, 0.4 M) at rt for 4 hours with stirring. Purification conditions: Hex/EtOAc (98:2).

Yield: 7 mg (35%) as a yellow solid.

Rf: 0.56 (SiO_2; Hexane/ethyl acetate 98:2).

Mp (ºC): 195.3 – 196.8

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 6.42 (d, *J* = 11.6 Hz, 2H), 6.29 (d, *J* = 11.5 Hz, 4H), 6.03 (d, *J* = 11.3 Hz, 4H), 6.00 (d, *J* = 13.3 Hz, 2H), 5.94 (s, 2H), 5.93 (s, 4H).

^{13}C NMR, DEPT (126 MHz, $CDCl_3$), δ (ppm): 135.3 (2 x C), 134.8 (2 x C), 134.7 (2 x C), 131.7 (2 x CH), 131.3 (2 x CH), 131.2 (2 x CH), 130.1 (2 x CH), 130.1 (2 x CH), 130.0 (2 x CH), 129.1 (2 x CH), 129.0 (2 x CH), 129.0 (2 x CH).

^{1}H NMR (750 MHz, $C_6D_4Cl_2$), δ (ppm): 6.55 (d, *J* = 11.7 Hz, 2H, $H_{7,24}$), 6.51 (d, *J* = 11.7 Hz, 2H, $H_{12,19}$), 6.48 (d, *J* = 11.6 Hz, 2H, $H_{13,18}$), 6.19 (d, *J* = 11.4 Hz, 2H, $H_{14,17}$), 6.17 (dd, *J* = 11.8, 3.2

Hz, 2H, $H_{11, 20}$), 6.13 (dd, *J* = 12.0, 3.3 Hz, 2H, $H_{8, 23}$), 6.11 (s, 2H, $H_{15, 16}$), 6.03 (dd, *J* = 11.5, 3.2 Hz, 2H, $H_{9, 22}$), 6.00 (dd, *J* = 11.5, 3.3 Hz, 2H, $H_{10, 21}$).

^{13}C NMR, DEPT (188 MHz, $C_6D_4Cl_2$), δ (ppm):136.0 (2 x $C_{1, 2}$), 135.6 (2 x $C_{4, 5}$), 135.5 (2 x $C_{3, 6}$), 132.5 (2 x CH, $C_{13, 18}$), 132.2 (2 x CH, $C_{12, 19}$), 132.0 (2 x CH, $C_{7, 24}$), 130.9 (2 x CH, $C_{15, 16}$), 130.8 (2 x CH, $C_{9, 22}$), 130.6 (2 x CH, $C_{10, 21}$), 129.9 (2 x CH, $C_{14, 17}$), 129.8 (2 x CH, $C_{8, 23}$), 129.7 (2 x CH, $C_{11, 20}$).

HRMS (APCI) calculated for $C_{24}H_{19}$ $[M+H]^+$: 307.1481, found: 307.1481.

$Pd(PPh_3)_4$ as catalyst

(α,α,β)-Benzotri[8]annulene **7** was obtained using BrCOT **8** (0.031 g , 0.17 mmol), $Pd(PPh_3)_4$ (0.020 g, 0.017 mmol, 10 mol%), KO^{t}Bu (0.029 g, 0.25 mmol, 1.5 equiv) and THF (0.42 mL, 0.4 M) at rt for 4 hours with stirring. Purification conditions: Hex/EtOAc (98/2).

Yield: 6 mg (33%) as a yellow solid.

Scale-up reaction

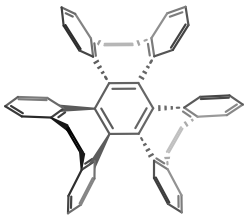
Amounts: BrCOT **8** (0.183 g, 1 mmol), $Pd_2(dba)_3$ (0.046 g, 0.05 mmol, 5 mol%), KO^{t}Bu (0.168 g, 1.5 mmol, 1.5 equiv) and THF (2.5 mL, 0.4 M).

Yield: 31 mg (30%) as a yellow solid.

Amounts: BrCOT **8** (0.9 g, 4.9 mmol), $Pd_2(dba)_3$ (0.23 g, 0.25 mmol, 5 mol%), KO^{t}Bu (0.83 g, 7.4 mmol, 1.5 equiv) and THF (12.3 mL, 0.4 M).

Yield: 140 mg (27%) as a light yellow solid.

*Benzo-fused tri(dibenzo[8]annulene) **3** ((α,α,β)-TDBA)*



3

Benzo-fused tri(dibenzo[8]annulene) **3** ((α,α,β)-TDBA) was obtained using vinyl triflate **9** (0.073 g, 0.2 mmol), $Pd_2(dba)_3$ (0.01 mmol, 5 mol%), KO^{t}Bu (0.034 g, 0.3 mmol, 1.5 equiv) and THF (0.5 mL, 0.4 M) at rt for 6h with stirring. Purification conditions: Hex/EtOAc (90/10).

Yield: 10 mg (25%) as a pale yellow solid.

Rf: 0.30 (SiO_2; Hexane/ethyl acetate 90:10).

Mp (°C): > 350

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.24 – 7.20 (m, 2H), 7.07 (s, 2H), 6.95 (dd, *J* = 7.6, 1.4 Hz, 2H), 6.90 – 6.84 (m, 14H), 6.80 – 6.77 (m, 2H), 6.64 (ddd, *J* = 7.7, 6.5, 2.1 Hz, 2H), 6.60 (td, *J* = 7.6, 1.4 Hz, 2H), 6.51 (dt, *J* = 7.6, 1.1 Hz, 2H), 6.38 (dd, *J* = 8.0, 1.5 Hz, 2H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 141.2 (2 x C), 140.5 (2 x C), 139.9 (2 x C), 139.7 (2 x C), 139.7 (2 x C), 139.2 (2 x C), 138.9 (2 x C), 138.4 (2 x C), 137.9 (2 x C), 133.6 (2 x CH), 133.4 (2 x CH), 133.1 (2 x CH), 131.6 (2 x CH), 130.3 (2 x CH), 129.5 (2 x CH), 126.7 (2 x CH), 126.7 (2 x CH), 126.4 (2 x CH), 126.1 (2 x CH), 126.1 (2 x CH), 126.0 (2 x CH), 126.0 (2 x CH), 125.9 (2 x CH), 125.1 (2 x CH).

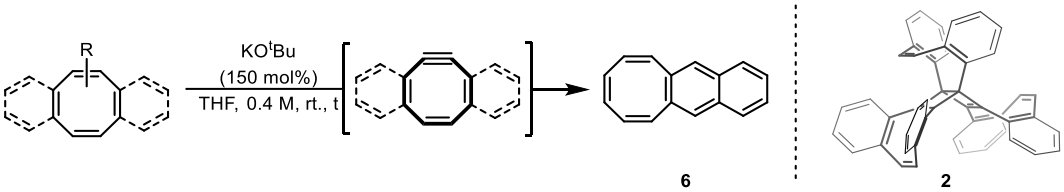
HRMS (APCI) calculated for $C_{48}H_{31}$ $[M+H]^+$: 607.2425, found: 607.2420.

Scale-up reaction

Amounts: Vinyl triflate **9** (0.352 g, 1 mmol), $Pd_2(dba)_3$ (0.46 g, 0.05 mmol, 5 mol%), KO^tBu (0.168 g, 1.5 mmol, 1.5 equiv) and THF (2.5 mL, 0.4 M).

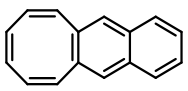
Yield: 48 mg (24%)as off-white crystals after washing with MeOH.

4. Transition metal-free cycloadditions of BrCOT 8 and vinyl triflate 9



BrCOT **8** or vinyl triflate **9** (1 equiv) was dissolved in anhydrous THF (0.4 M) in a dry round-bottomed flask under argon and then KO^{t}Bu (1.5 equiv) was added. The resulting mixture was stirred at rt until the starting material disappeared (TLC monitoring). After completion, the reaction mixture was concentrated to dryness and the residue was purified by flash column chromatography on silica gel using a Hex/EtOAc mixture to give the corresponding product.

*NaphthoCOT **6***



6

NaphthoCOT **6** was obtained using BrCOT **8** (0.036 g, 0.2 mmol), KO^{t}Bu (0.034 g, 0.3 mmol, 1.5 equiv) and THF (0.5 mL, 0.4 M) at rt for 4 hours with stirring. Purification conditions: Hex/EtOAc (98/2).

Yield: 4 mg (20%) as a yellow solid.

Rf: 0.67 (SiO_2; Hexane/ethyl acetate 98:2).

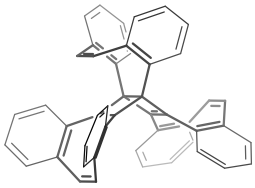
Mp (°C): 93.7 – 94.3

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.72 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.45 (s, 2H), 7.39 (dd, *J* = 6.3, 3.2 Hz, 2H), 6.78 (d, *J* = 11.5 Hz, 2H), 6.13 (ddd, *J* = 11.5, 2.2, 1.4 Hz, 2H), 5.90 (dd, *J* = 2.2, 1.2 Hz, 2H).

^{13}C NMR, DEPT (126 MHz, $CDCl_3$), δ (ppm): 136.0 (2 x C), 133.1 (2 x CH), 132.5 (2 x C), 131.3 (2 x CH), 130.3 (2 x CH), 128.7 (2 x CH), 127.5 (2 x CH), 126.0 (2 x CH).

HRMS (APCI) calculated for $C_{16}H_{13}$ $[M+H]^+$: 205.1012, found: 205.1010.

*Dewar benzene **2***



2

Dewar benzene **2** was obtained using vinyl triflate **9** (0.071 g, 0.2 mmol), KO^{t}Bu (0.034 g, 0.3 mmol, 1.5 equiv) and THF (0.5 mL, 0.4 M) at rt for 6h with stirring. Purification conditions: Hex/EtOAc (90/10).

Yield: 24 mg (60%)as a yellow solid.

Rf: 0.32 (SiO_2; Hexane/ethyl acetate 90:10).

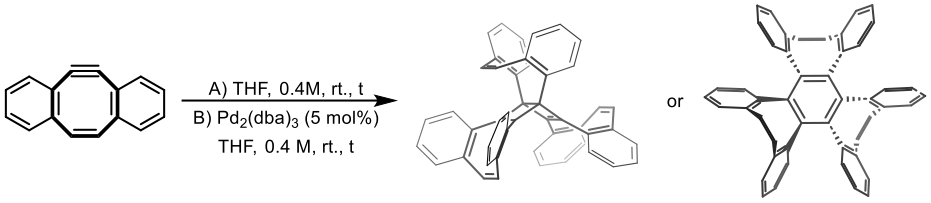
Mp (ºC): 281.9 – 282.3

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.19 (td, *J* = 7.6, 1.3 Hz, 2H), 7.14 (q, *J* = 2.9, 2.4 Hz, 8H), 7.12 (s, 2H), 7.08 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.04 (td, *J* = 7.6, 1.4 Hz, 2H), 7.00 (s, 2H), 6.95 (td, *J* = 7.5, 1.7 Hz, 2H), 6.87 – 6.75 (m, 4H), 6.72 (s, 2H), 6.59 (d, *J* = 7.8 Hz, 2H), 6.35 (s, 2H).

^{13}C NMR, DEPT (126 MHz, $CDCl_3$), δ (ppm): 153.0 (2 x C), 149.9 (2 x C), 138.2 (2 x C), 137.5 (2 x C), 137.0 (2 x C), 136.3 (2 x C), 135.6 (2 x C), 134.6 (2 x C), 133.9 (2 x CH), 133.0 (2 x CH), 132.1 (2 x CH), 131.3 (2 x CH), 130.5 (2 x CH), 130.2 (2 x CH), 129.0 (2 x CH), 127.7 (2 x CH), 127.5 (2 x CH), 127.4 (2 x CH), 127.4 (2 x CH), 127.1 (2 x CH), 127.1 (2 x CH), 126.8 (2 x CH), 126.3 (2 x CH), 69.7 (2 x C).

HRMS (APCI) calculated for $C_{48}H_{31}$ $[M+H]^+$: 607.2420, found 607.2418.

5. 5,6-Didehydrodibenzo[*a*,*e*][8]annulene (DibenzoCOTyne) 1b: a) transition metal-free and b) metal-catalyzed reactivities

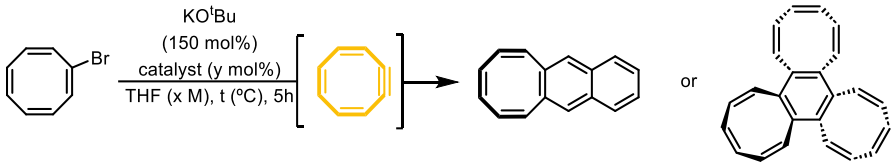


1b **2** **3**

a) Conditions A: DibenzoCOTyne **1b** (0.050g, 0.25 mmol) was dissolved in anhydrous THF (0.62 mL, 0.4 M) in a dry round-bottom flask under argon. The mixture was stirred at rt until the starting material disappeared (TLC monitoring). After completion, the solvent was removed, and the residue was purified by flash column chromatography on silica gel using a mixture of Hex/EtOAc (90/10), yielding Dewar benzene **2** as a yellow solid (9 mg, 17%).

b) Conditions B: A Pd(0)-catalyzed cycloaddition was performed using the same procedure with dibenzoCOTyne **1b** (0.050g, 0.25 mmol) and $Pd_2(dba)_3$ (0.011 g, 0.012 mmol, 0.05 equiv) in THF (0.62 mL, 0.4 M), yielding benzo-fused tri(dibenzo[8]annulene) **3** ((α,α,β)-TDBA) as a yellow solid (11 mg, 40%).

6. Transition metal-free and metal-catalyzed cycloadditions of BrCOT 8: Screening of reaction conditions



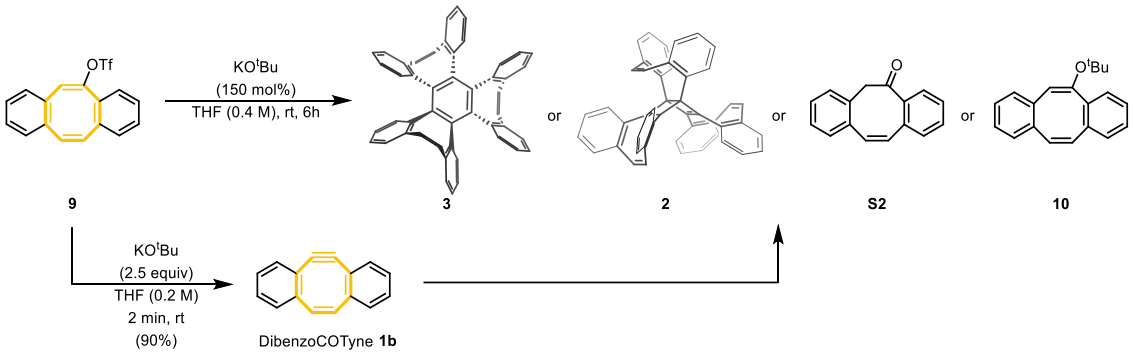
8 **6** **7**

BrCOT **8** (0.091 g, 0.5 mmol, 1 equiv) and a metal catalyst (y mol%) were dissolved in anhydrous THF (x M) in a dry round-bottom flask under argon. The mixture was stirred at rt and degassed with an Ar balloon for 10 min, then freshly sublimated KO^{t}Bu (0.084 g, 0.75 mmol, 1.5 equiv) was added. Stirring continued at the appropriate temperature until the starting material disappeared (TLC monitoring). After work-up and purification by flash column chromatography under general conditions, the results obtained are summarized in Table S1.

Entry	Catalyst (y mol%)	Conditions	Product[a]
1	$Pd_2(dba)_3$ (5)	0.4 M at rt, 5h	Tri[8]annulene **7** (35%)
2		0.33 M at rt, 5h	Tri[8]annulene **7** (35%)
5	$Pd(PPh_3)_4$ (10)	0.4 M at rt, 5h	Tri[8]annulene **7** (33%)
9	-	0.4 M at rt, 5h	NaphthoCOT **6** (20%)
10		0.4 M at 50 °C, 5h	NaphthoCOT **6** (12%)

Table S1. [a] Isolated yield.

7. Transition metal-free and metal-catalyzed cycloadditions of vinyl triflate 9 and dibenzoCOTyne 1b: screening of reaction conditions

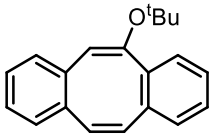


Vinyl triflate **9** (0.071 g, 0.2 mmol, 1 equiv) or dibenzoCOTyne **1b** (0.040 g, 0.2 mmol, 1 equiv) and a metal catalyst (y mol%) were dissolved in anhydrous THF (x M) in a dry round-bottom flask under argon. The mixture was stirred at rt and degassed with an Ar balloon for 10 min, then freshly sublimated KO^{t}Bu (0.084 g, 0.75 mmol, 1.5 equiv) was added. Stirring continued at the appropriate temperature until the starting material disappeared (TLC monitoring). After work-up and purification by flash column chromatography under general conditions, the results obtained are summarized in Table S2.

Entry	Starting material	Catalyst (y mol%)	Conditions	Product[a]
1	Triflate **9**	$Pd_2(dba)_3$ (5)	THF (0.4 M) at rt, 6h	TDBA **3** (25%)
2	Triflate **9**		THF (0.33 M) at rt, 6h	TDBA **3** (24%)
3	Triflate **9**	$[CpRu(CH_3CN)_3]PF_6$ (10)	THF (0.4 M) at rt, 6h	Dewar benzene **2** (44%)
4	Triflate **9**		DCM (0.4 M) at rt, 6h	Ketone **S2** (40%)
5	Triflate **9**	-	THF (0.4 M) at rt, 6h	Dewar benzene **2** (60%)
6	Triflate **9**		THF (0.4 M) at 0 °C, 6h	DibenzoCOTyne **1b** (20%) + Dewar benzene **2** (35%)
7	Triflate **9**		THF (0.4 M) at 50 °C, 6h	Dewar benzene **2** + ketone **S2** (70%)[b]
8	COTyne **1b**	$Pd_2(dba)_3$ (5)	THF (0.4 M) at rt, 6h	TDBA **3** (40%)
9	COTyne **1b**	$[CpRu(CH_3CN)_3]PF_6$ (10)	DCM (0.4 M) at rt, 6h	TDBA **3** (30%) + Dewar benzene **2** (13%)
10	COTyne **1b**	$[Cp^*Ru(CH_3CN)_3]PF_6$ (10)	DCM (0.4 M) at rt, 6h	TDBA **3** (8%) + Dewar benzene **2** (33%)
11	COTyne **1b**	Cp*RuCl(cod) (10)	DCM (0.4 M) at rt, 6h	Dewar benzene **2** (52%)
12	COTyne **1b**	-	THF (0.4 M) at rt, 6h	Dewar benzene **2** (17%)
13	COTyne **1b**		DCM (0.4 M) at rt, 6h	Complex mixture
14[c]	COTyne **1b**		THF (0.4 M) at rt, 6h	Dewar benzene **2** (17%)
15[d]	COTyne **1b**		THF (0.4 M) at rt, 6h	Ether **10** (50%) + Dewar benzene **2** / ketone **S2** (30%)[e]

Table S2. [a] Isolated yield. [b] 3:1 NMR ratio. [c] In the presence of $K[B(ArF_5)_4]$ (1.5 equiv). [d] In the presence of KO^tBu (1.5 equiv).[e] 1:2 ratio

*(5E,11Z)-5-(tert-butoxy)dibenzo[a,e][8]annulene (**10**)*



10

Rf: 0.5 (SiO_2; Hexane/ethyl acetate 90:10).

Mp (ºC): 68.3 – 69.7

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.43 – 7.36 (m, 1H), 7.21 – 6.98 (m, 7H), 6.93 – 6.77 (m, 2H), 6.43 (s, 1H), 1.22 (s, 9H).

^{13}C NMR, DEPT (75 MHz, $CDCl_3$), δ (ppm): 152.2 (C), 138.8 (C), 137.3 (C), 136.7 (C), 136.2 (C), 134.3 (CH), 132.9 (CH), 129.8 (2 x CH), 128.8 (CH), 128.5 (CH), 127.7 (CH), 127.1 (CH), 126.8 (CH), 126.4 (CH), 120.3 (CH), 78.5 (C), 29.3 (3 x CH_3).

HRMS (APCI) calculated for $C_{20}H_{21}O$ $[M+H]^+$: 277.1587, found 277.1584.

8. Variable-Temperature 1H NMR Studies

8.1. Variable-Temperature 1H NMR of (α,α,β)-TDBA 3

The ^{1}H-NMR experiment of TDBA **3** in deuterated 1,1,2,2-tetrachloroethane from 25 to 100 ºC (Figure S1) showed no significant changes, indicating no interconversion between its conformers.

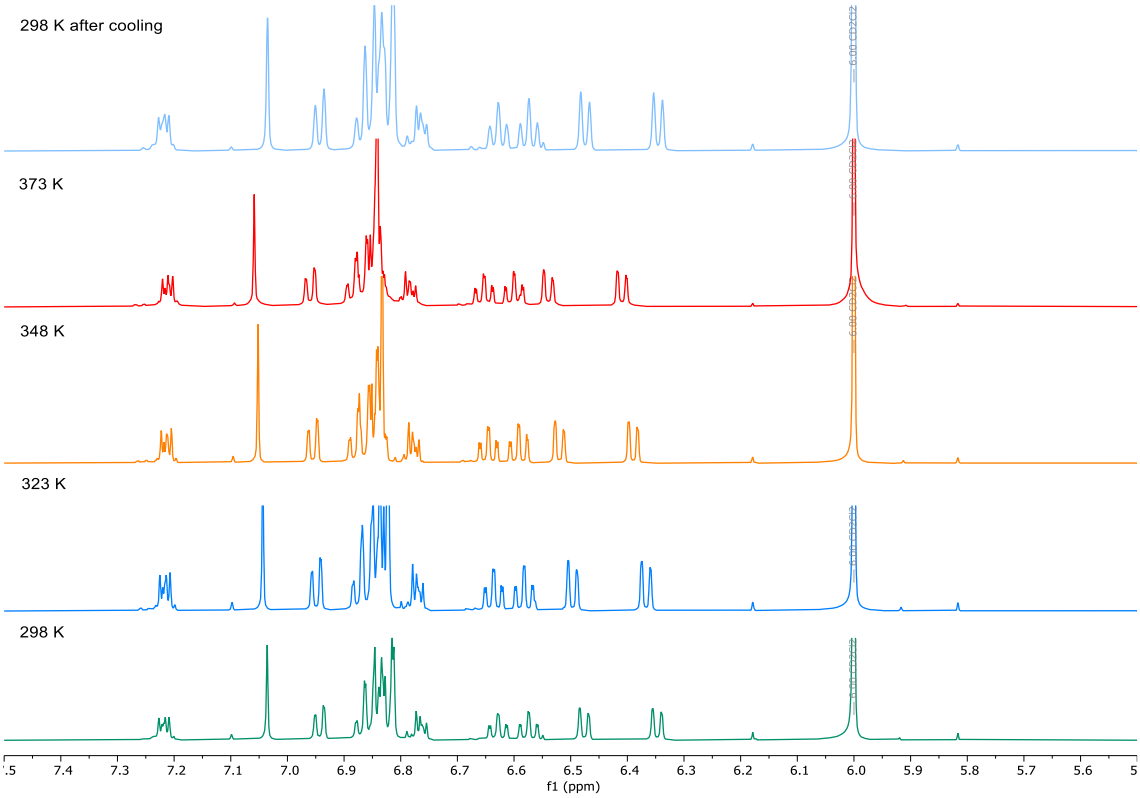


*Figure S1. Variable-temperature ^{1}H-NMR spectra (500 MHz) of (α,α,β)-TDBA **3** in $C_2D_2Cl_4$*

8.2. Variable-Temperature 1H NMR of (α,α,β)-Benzotri[8]annulene 7

Variable-temperature ^{1}H-NMR spectra of (α,α,β)–benzotri[8]annulene **7** were recorded from 273 to 293 K using deuterated 1,2-dichlorobenzene as the solvent (Figure S2). At lower and room temperature, nine signals were observed, which merged into three signals at 388 K, indicating rapid hydrogen exchange within each of the three signals sets of **7**. This exchange is attributed to fast conformational interconversion among the three degenerate (α,α,β) isomers.

^{1}H NMR (750 MHz, 1,2-dichlorobenzene-d_4, 393 K): δ 6.51 (d, J = 11.7 Hz, protons 1, 6 and 7), 6.14 (d, J = 11.7 Hz, protons 2, 5 and 8), 6.02 (s, protons 3, 4 and 9).

Upon cooling to room temperature, the three distinct proton signal sets were fully recovered.

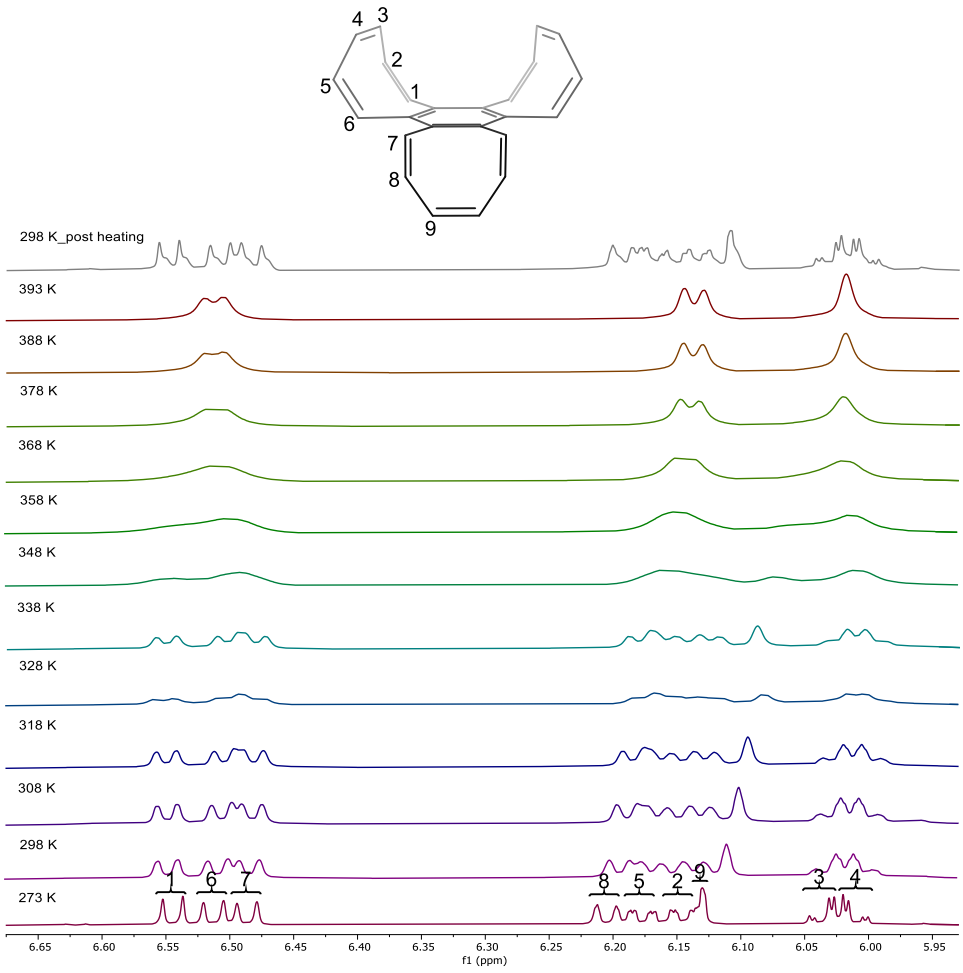


*Figure S2. Variable-temperature ^{1}H-NMR spectra (750 MHz) of (α,α,β)-benzotri[8]annulene **7** in $C_6D_4Cl_2$*

Crude estimates of rate constants were obtained using the following approximate equations:[6]

- For the uncoupled 6 and 7 protons $k = \frac{\pi}{\sqrt{2}}\nu_{6,7}$ at coalescence, being $\nu_{6,7}$ = 19.25 Hz and $T_{coalescence}$ = 348 K.

- For the coupled 3 and 4 protons $k = \frac{\pi}{\sqrt{2}}\sqrt{\nu_{3,4}^2 + J_{3,4}^2}$ at coalescence, being $\nu_{3,4}$ = 19.7 Hz, $J_{3,4}$ = 11.44 Hz and $T_{coalescence}$ = 348 K.

$\Delta G^{\ddagger}$ can be determined using the Eyring equation $k(T) = \frac{K_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$. The calculated values are $\Delta G^{\ddagger}$ = 17.8 kcal mol^{-1} for protons 6 and 7, and $\Delta G^{\ddagger}$ = 17.7 kcal mol^{-1} for protons 3 and 4.

9. Absorption spectra of (α,α,β)-benzotri[8]annulene 7 and (α,α,β)-TDBA 3

UV/Vis spectra of diluted solutions (1.10^{-5} M) in cyclohexane of (α,α,β)-benzotri[8]annulene **7** and (α,α,β)-TDBA **3** were taken in quartz cuvettes at room temperature (Figure S3).

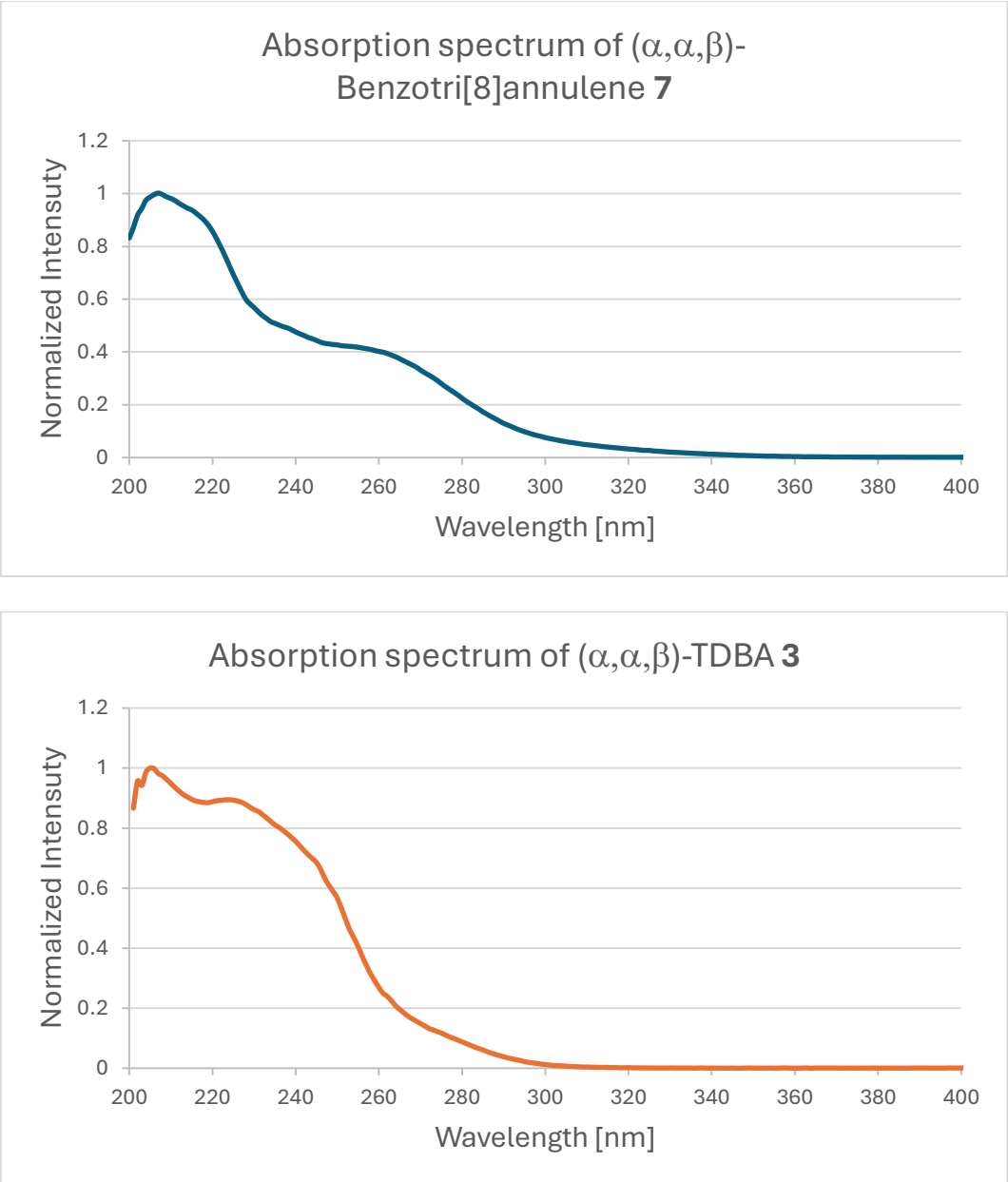


*Figure S3. Absorption spectra of (α,α,β)-Benzotri[8]annulene **7** and (α,α,β)-TDBA **3** in cyclohexane.*

10. Crystallographic data

10.1. Crystallographic data of naphthoCOT 6

An X-ray crystal of naphthoCOT **6** was grown by vapor diffusion using a DCM /hexanes solvent mixture.

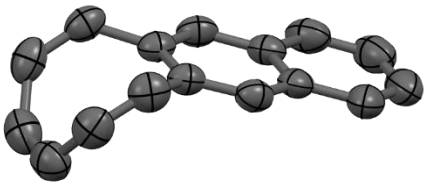


Figure S4. ORTEP drawing of ***6*** showing thermal ellipsoids at the 50% contour probability level.

*Table S3. Crystal data and structure refinement of naphthoCOT **6***

Deposition Number CCDC	2418247
Chemical formula	$C_{16}H_{12}$
Molecular weigh	204.26 g/mol
Temperature	299 K
Wavelength	1.54178 Å
Crystal Size	0.20 × 0.18 × 0.05 mm
Crystal habit	Plate, colourless
Crystal system	Orthorhombic,
Space group	$P2_12_12_1$
Unit cell dimensions	a = 6.4618 (2) Å
	b = 7.8144 (2) Å
	c = 22.3901 (6) Å
Volume	1130.59 (5) $Å^3$
Z	4
Density (calculated)	1.2 g/cm^3
Absorption coefficient	0.51 mm^{-1}
F(000)	432

10.2. Crystallographic data of (α,α,β)-benzotri[8]annulene 7

An X-ray crystal of (α,α,β)-benzotri[8]annulene **7** was grown by slow diffusion using a solvent mixture of DCM, Et_2O, and hexanes.

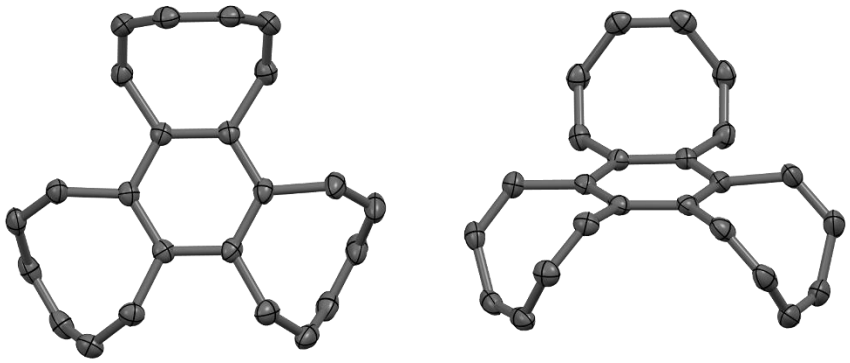
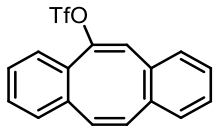


Figure S5. ORTEP drawing of (α,α,β)-benzotri[8]annulene ***7*** showing thermal ellipsoids at the 50% contour probability level. Hydrogen atoms were removed for clarity.

*Table S4. Crystal data and structure refinement of (α,α,β)-benzotri[8]annulene **7***

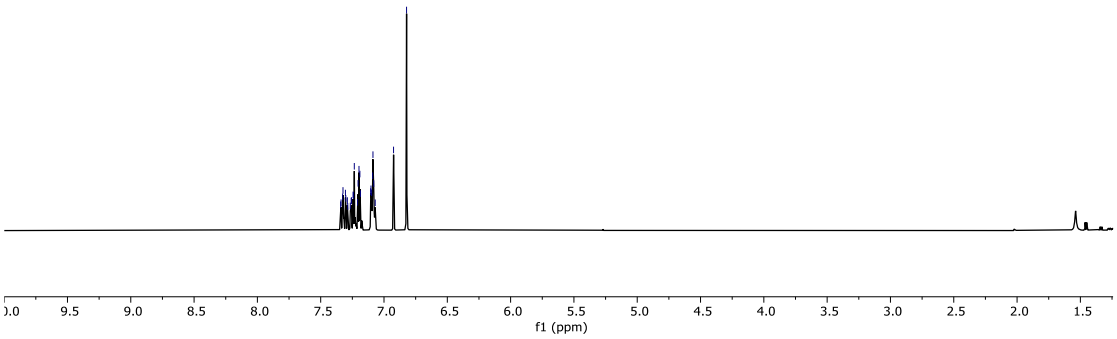
Deposition Number CCDC	2427818	
Chemical formula	$C_{24}H_{18}$	
Molecular weigh	306.38	
Temperature	100 K	
Wavelength	1.54184 Å	
Crystal Size	0.15 × 0.04 × 0.03 mm	
Crystal habit	Prism, clear light colourless	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 9.4244 (4) Å	α = 75.257 (5) º
	b = 9.6598 (5) Å	β = 82.012 (4) º
	c =10.1931 (5) Å	γ = 67.210 (4) º
Volume	826.50 (8) $Å^3$	
Z	2	
Density (calculated)	1.231 g/cm^3	
Absorption coefficient	0.53 mm^{-1}	
F(000)	324	

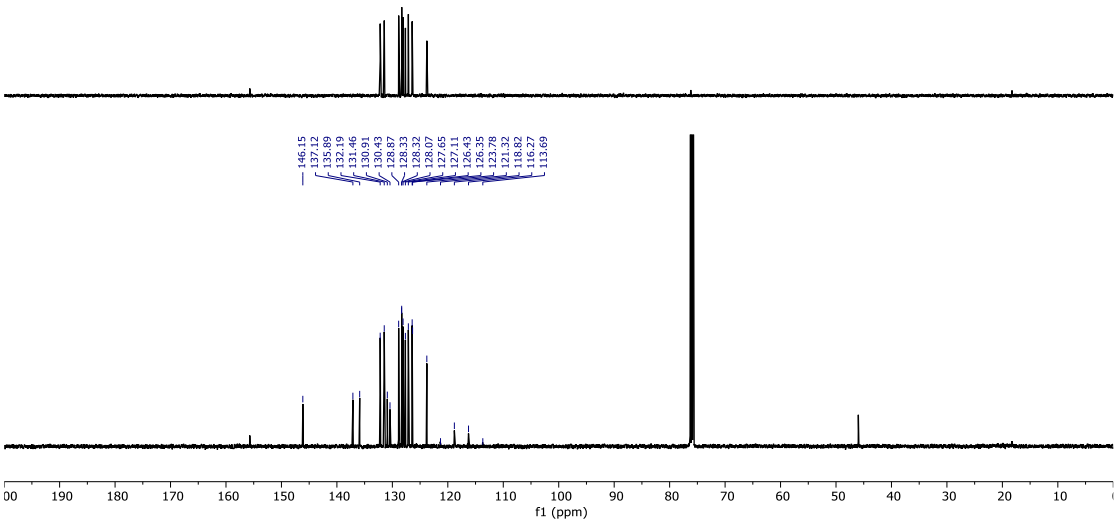
11. NMR Spectra

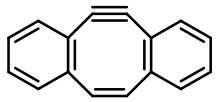


9

^{1}H-NMR (300 MHz) and ^{13}C-NMR, DEPT (75 MHz) in $CDCl_3$

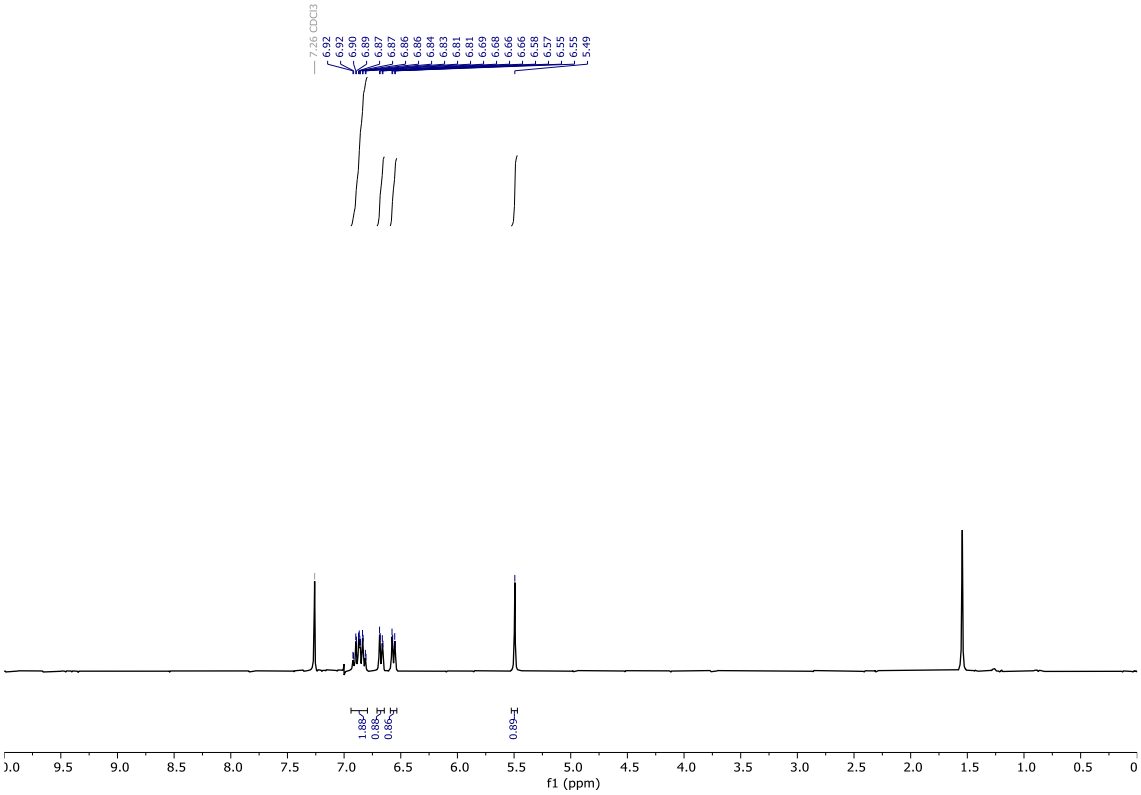


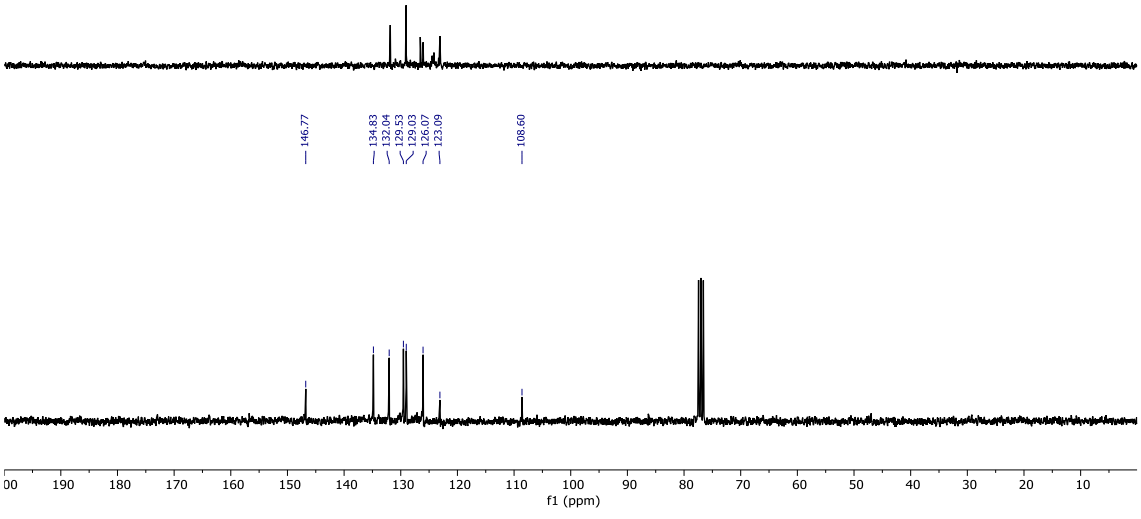


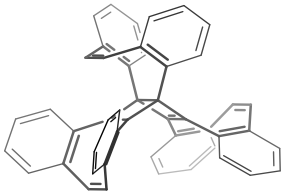


1b

^{1}H-NMR (300 MHz) and ^{13}C-NMR, DEPT (75 MHz) in $CDCl_3$

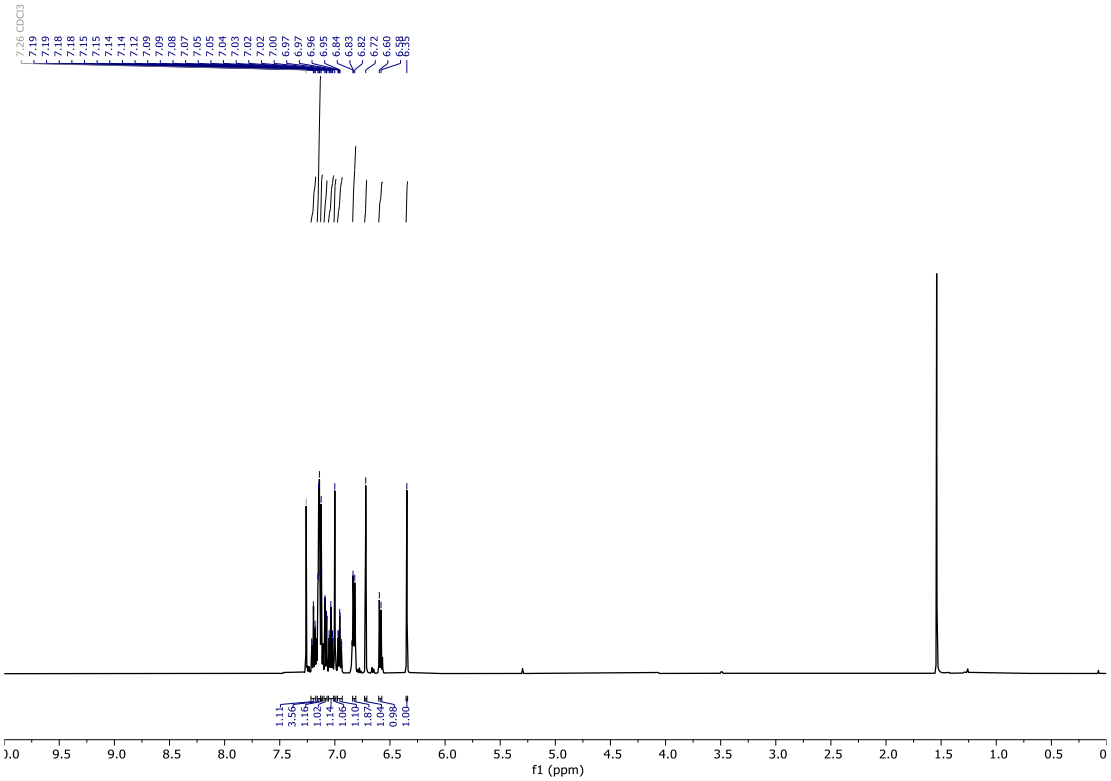


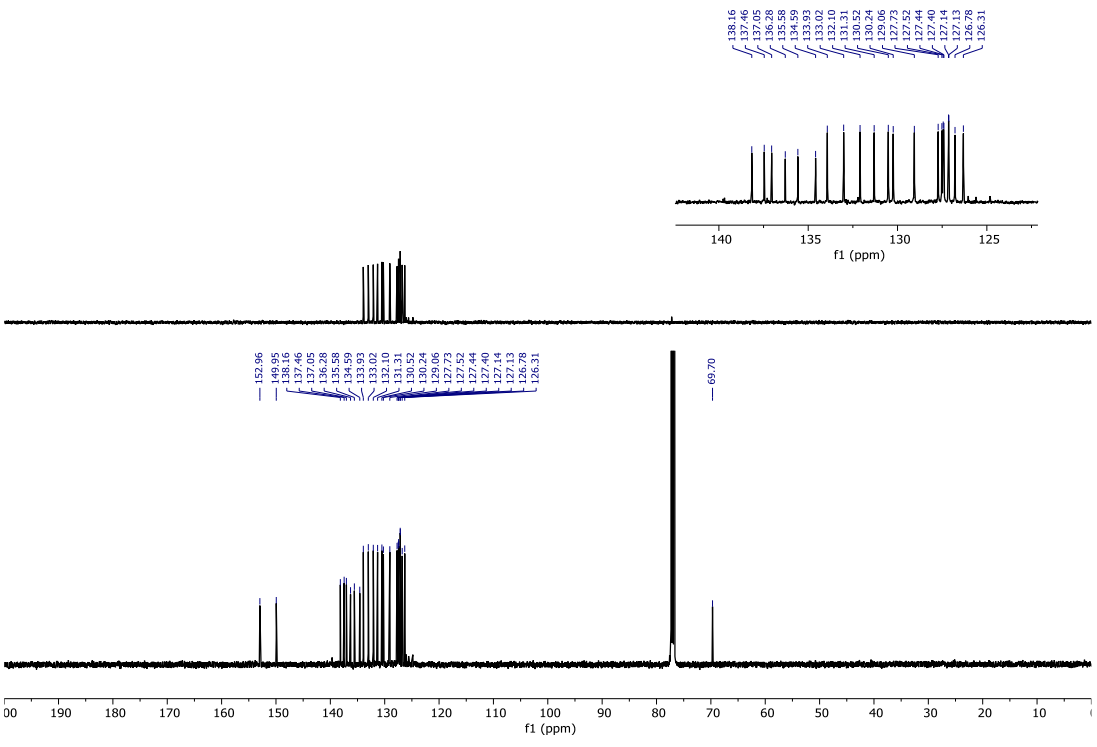


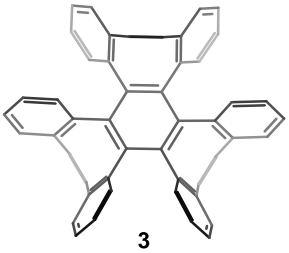


2

^{1}H-NMR (500 MHz) and ^{13}C-NMR, DEPT (126 MHz) in $CDCl_3$

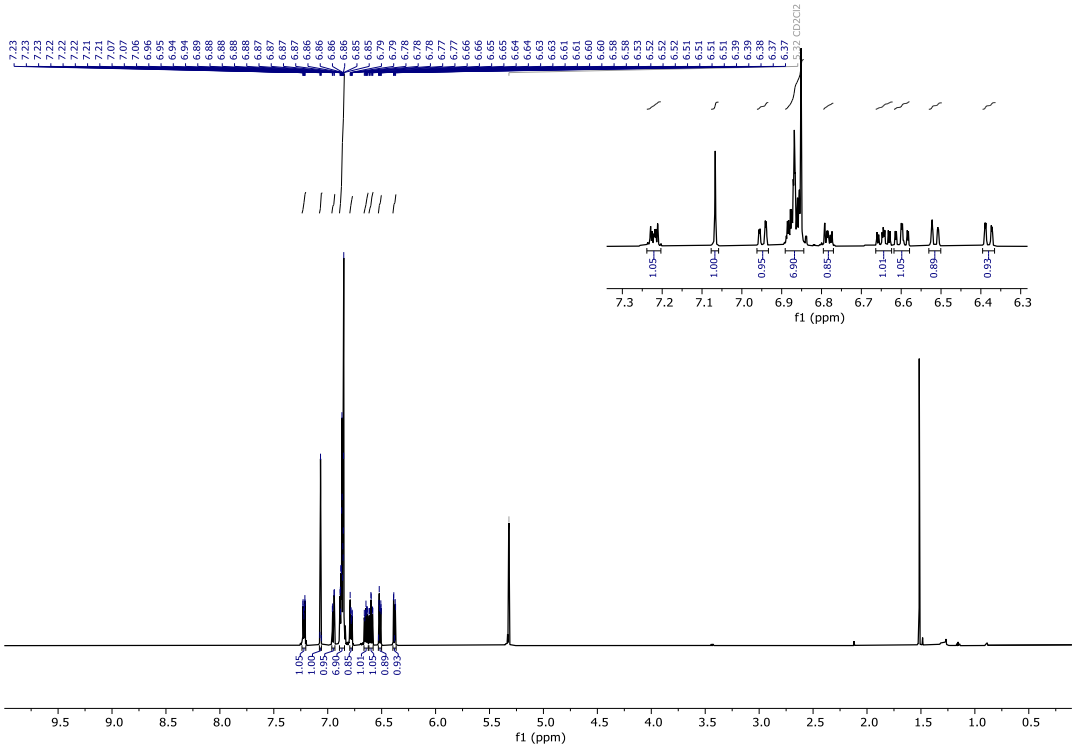


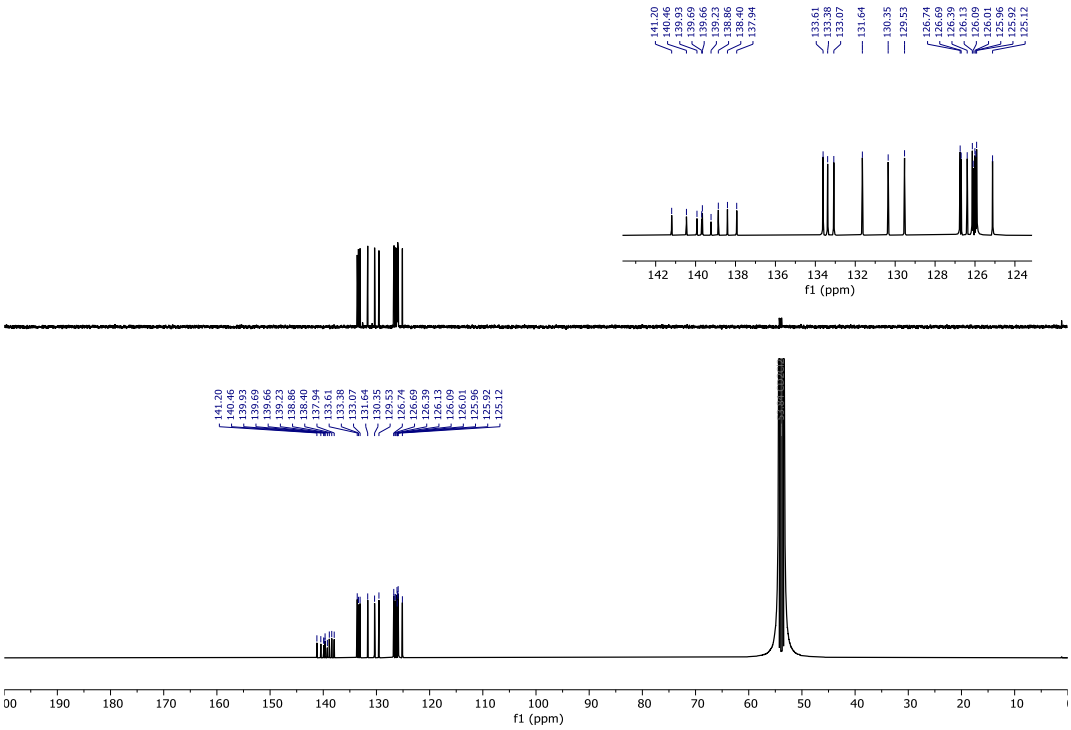


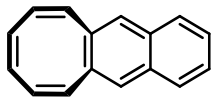


3

^{1}H-NMR (500 MHz) and ^{13}C-NMR, DEPT (126 MHz) in CD_2Cl_2

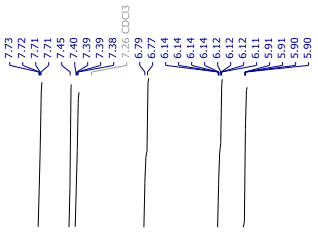


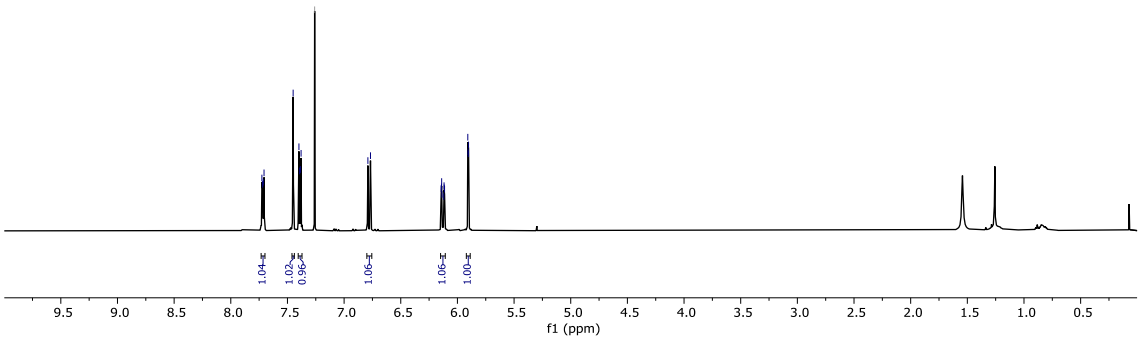


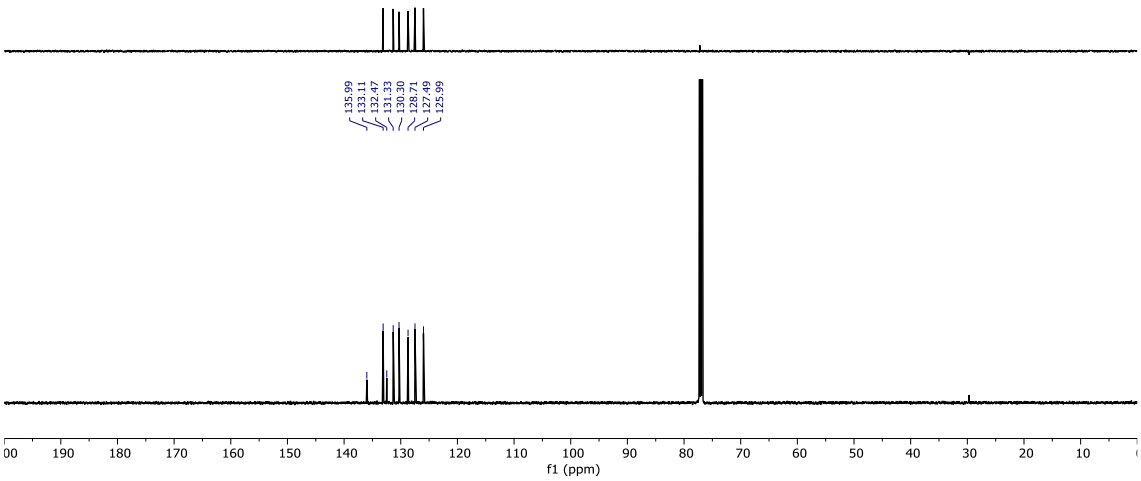


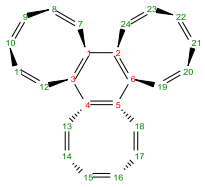
6

^{1}H-NMR (300 MHz) and ^{13}C-NMR, DEPT (75 MHz) in $CDCl_3$



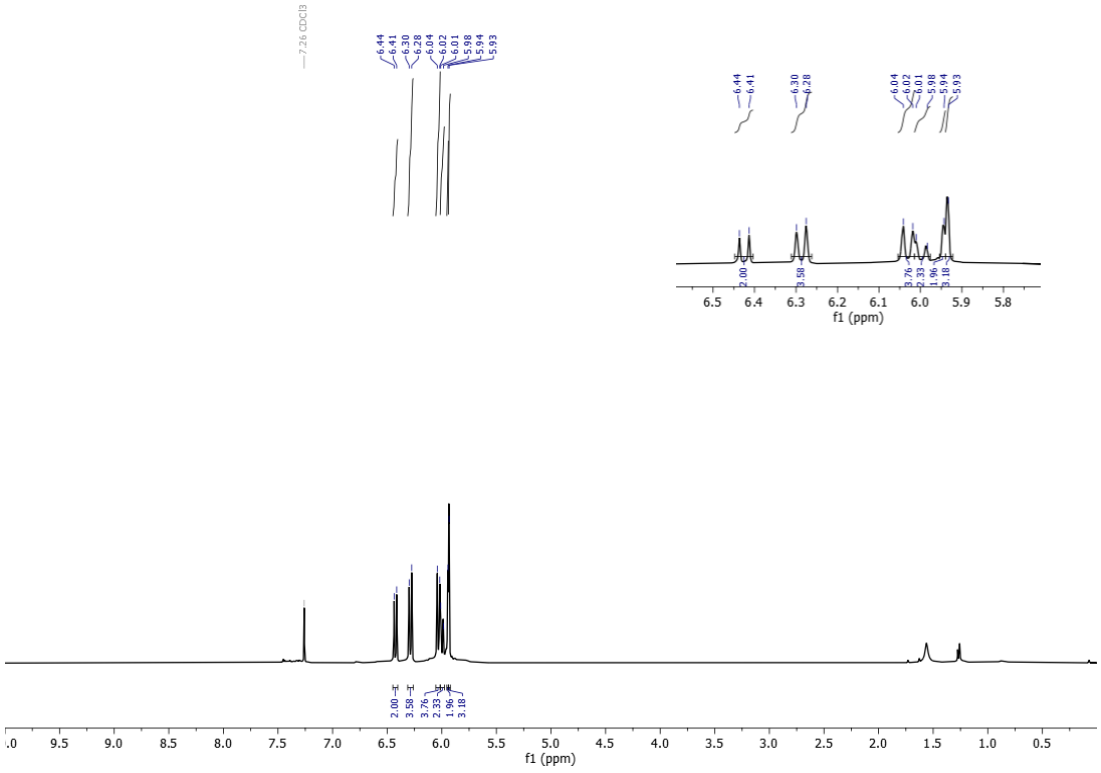


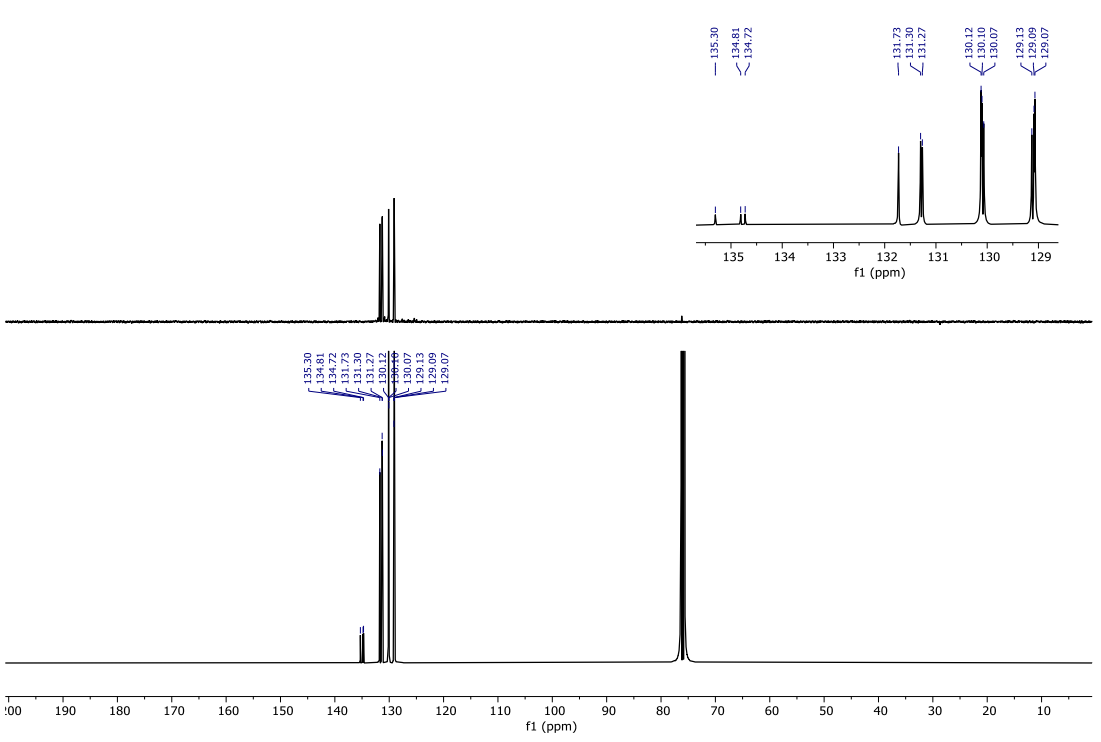


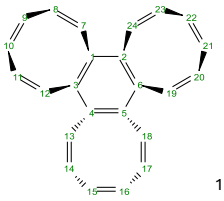


7

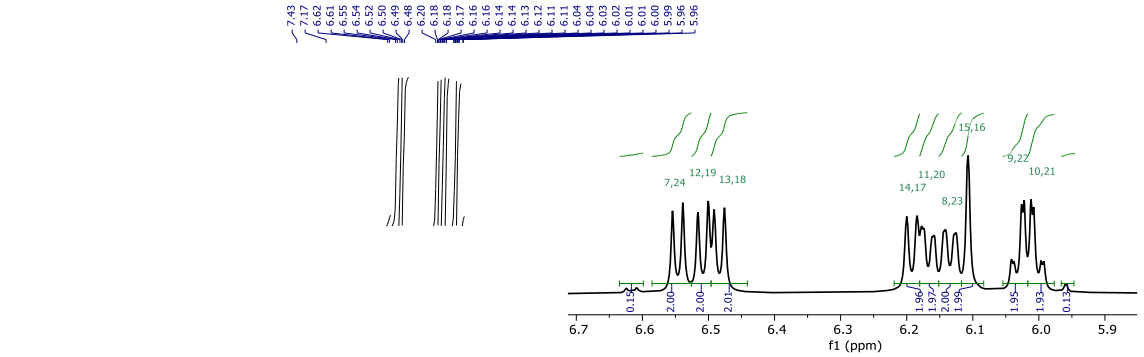
^{1}H-NMR (500 MHz) and ^{13}C-NMR, DEPT (75 MHz) in $CDCl_3$

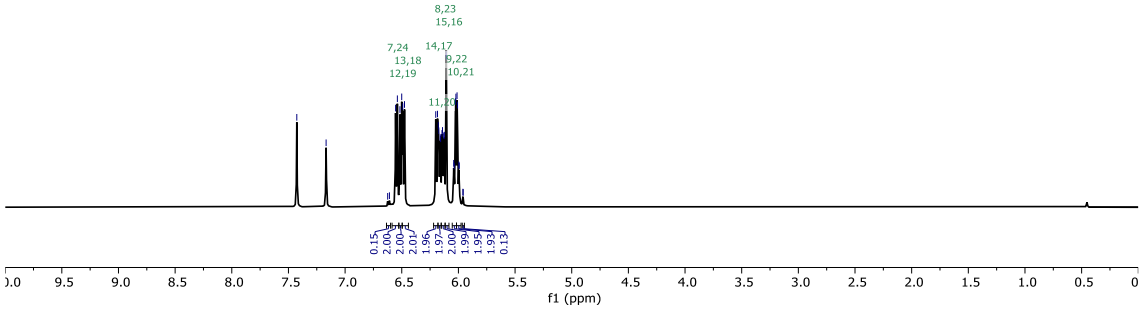


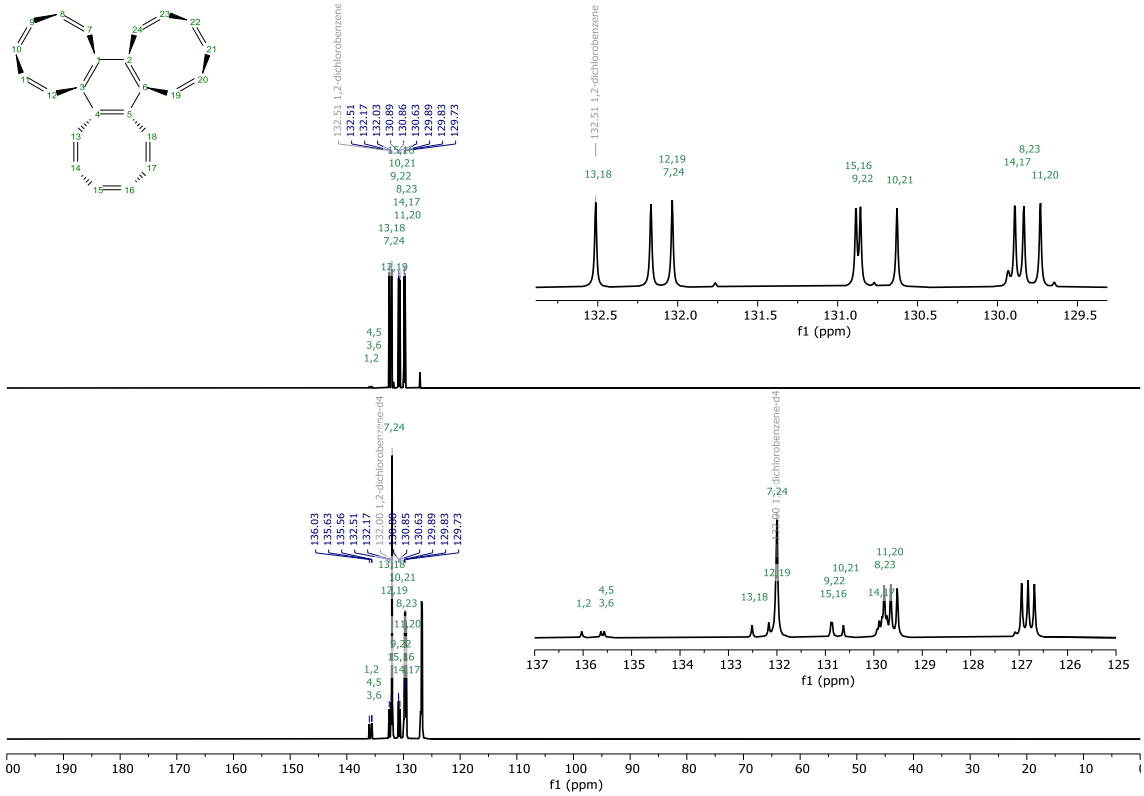




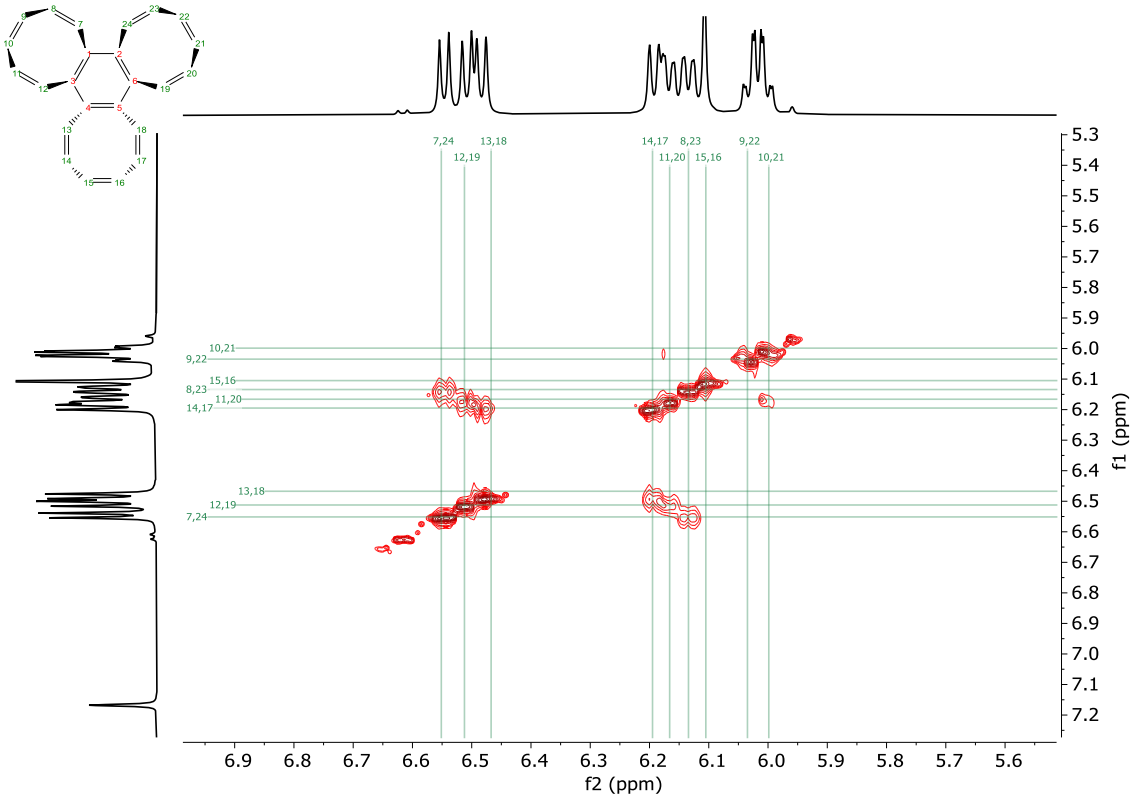
^{1}H-NMR (750 MHz) and ^{13}C-NMR, DEPT (188 MHz) in $C_6D_4Cl_2$



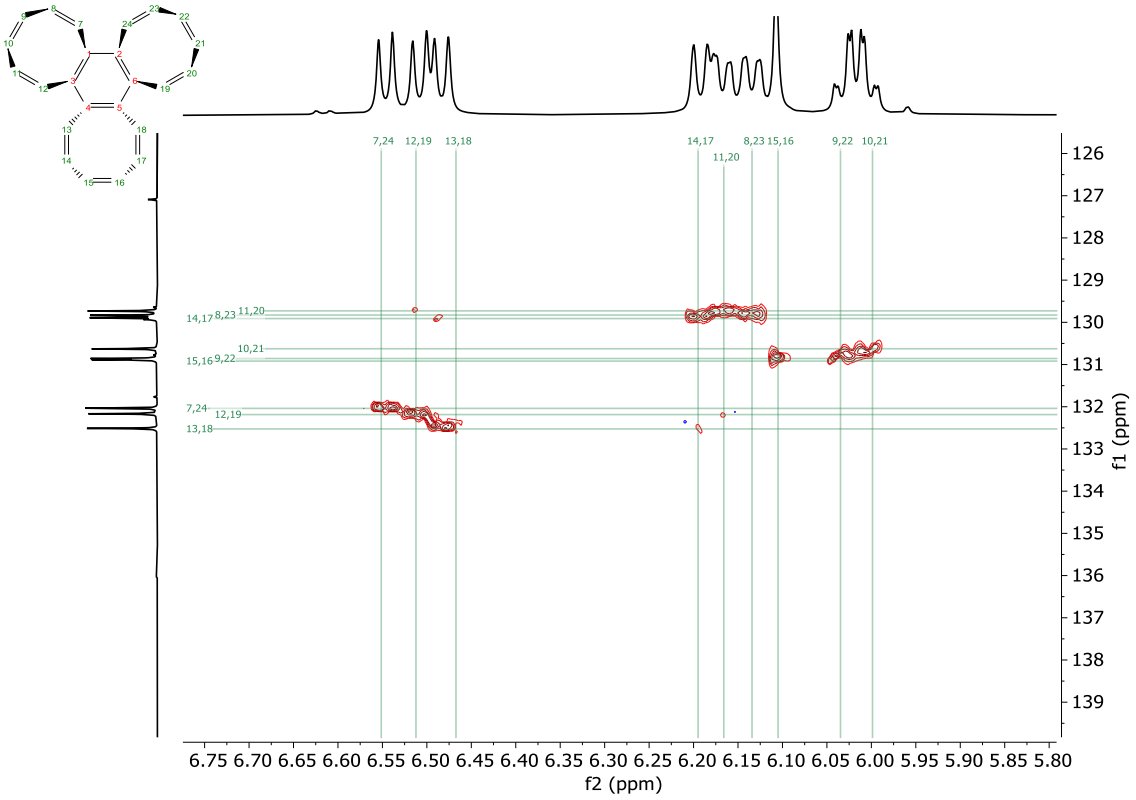




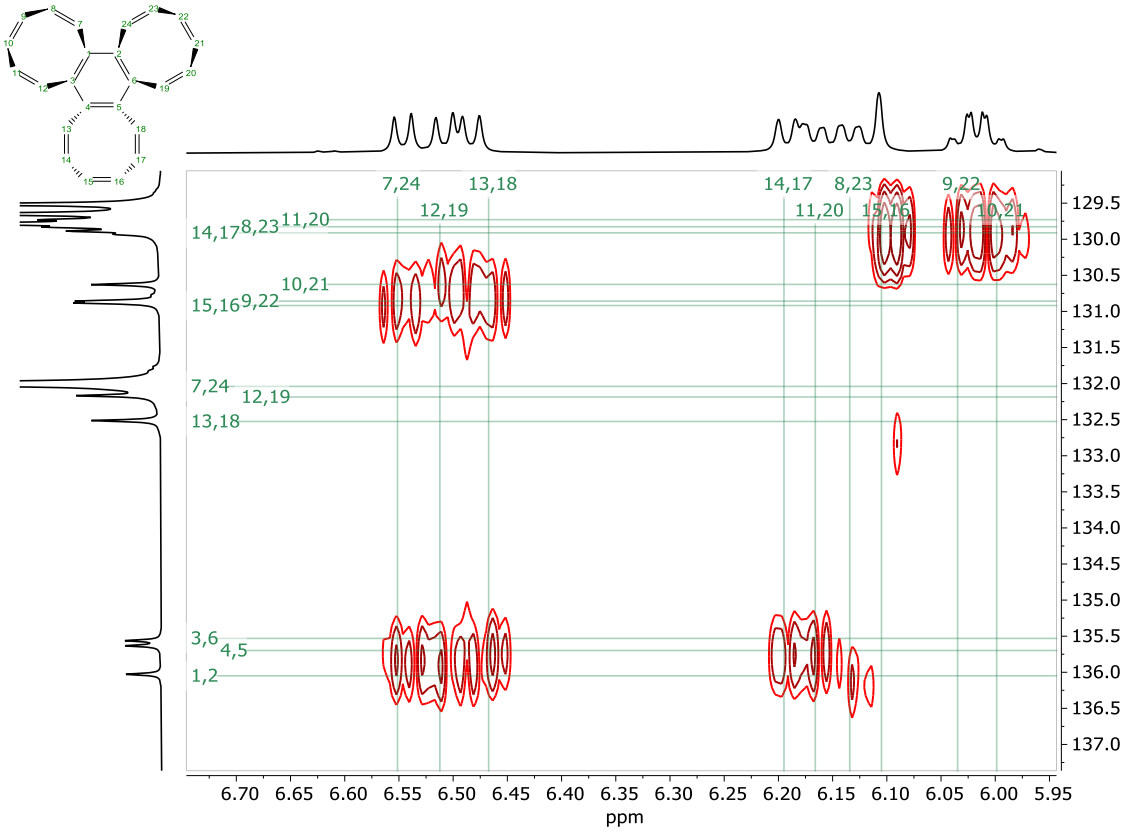
COSY (750 MHz) in $C_6D_4Cl_2$

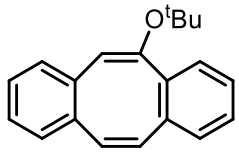


HSQC (750 and 188 MHz) in $C_6D_4Cl_2$



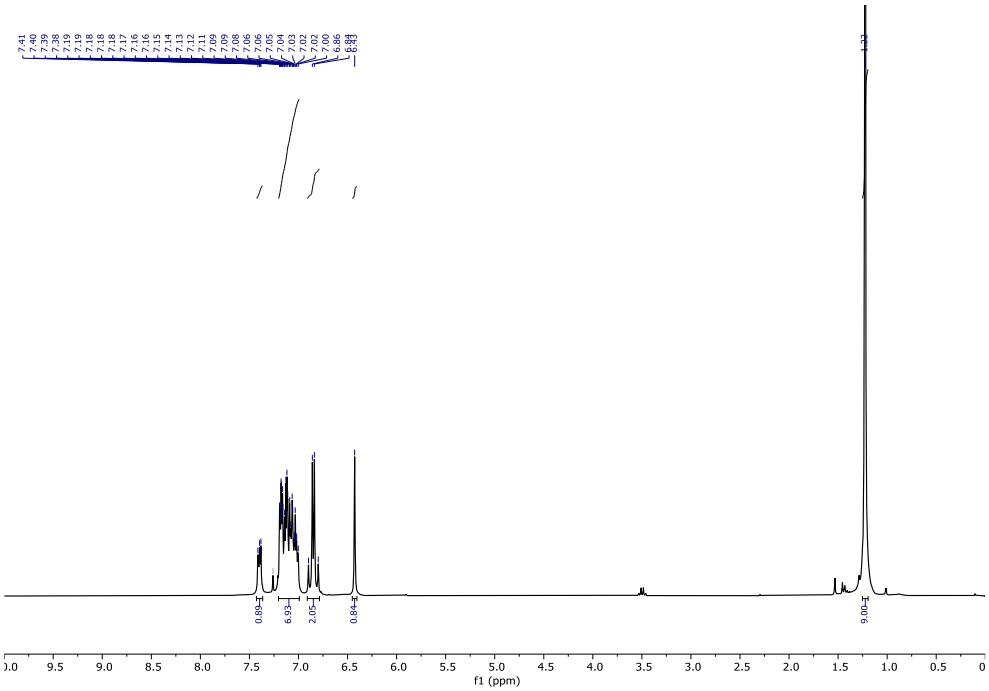
HMBC (750 and 188 MHz) in $C_6D_4Cl_2$

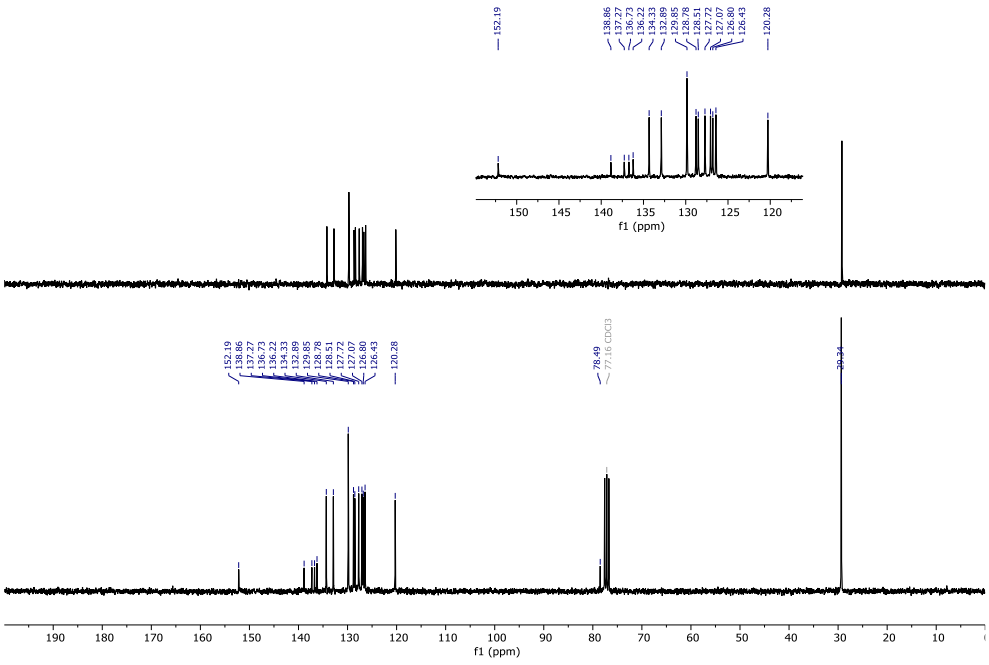




10

^{1}H-NMR (300 MHz) and ^{13}C-NMR, DEPT (75 MHz) in $CDCl_3$





12. Computational Details

All electronic structure calculations were performed using the Gaussian 16 software package[7] at the CESGA facilities. The geometries of all minima and transition states involved were optimized in the gas phase at the B3LYP[8] level with the addition of Grimme's D3 dispersion corrections[9] (B3LYP-D3) with the 6-31G(d,p)[10] basis set (BS1). Frequency calculations were performed at the same level to evaluate the zero-point vibrational energy and thermal corrections at 298 K and to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minimum. Each transition state was further confirmed by following the steepest descent to both sides and identifying the minima present in the reaction energy profile. Single-point energies were calculated using B3LYP-D3 with the 6-311++G(d,p)[11] basis set (BS2). The resulting energies were used to correct the gas-phase energies obtained from initial B3LYP-D3/6-31G(d,p) calculations. The reaction profiles were built up in terms of ΔG.

13. Free Energy Profile for the Isomerization of Benzotri[8]annulene 7 and Benzo-Fused tri(Dibenzo[8]annulene) 3 (TDBA)

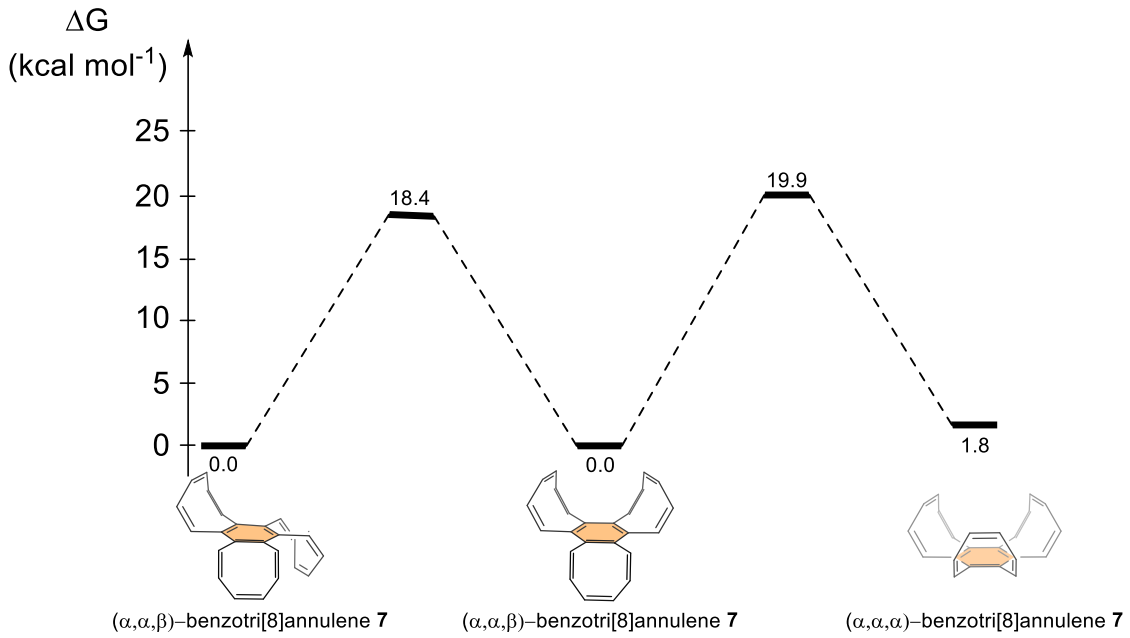


*Figure S6. Free energy profile for the isomerization of benzotri[8]annulene **7**.*

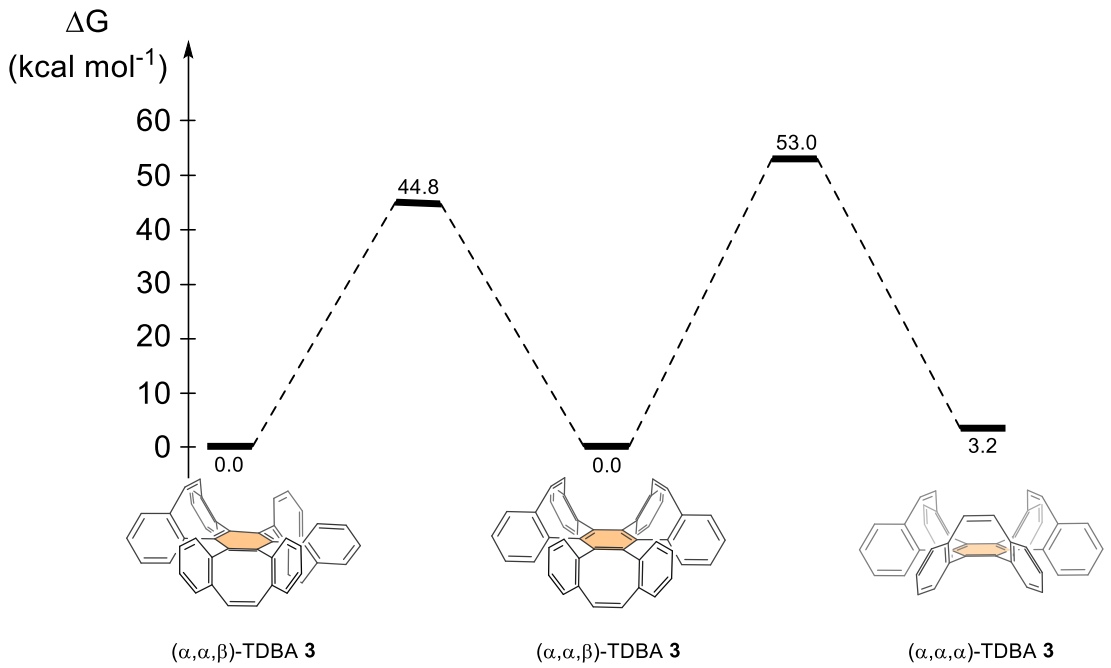


*Figure S7. Free energy profile for the isomerization of benzo-fused tri(dibenzo[8]annulene) **3** (TDBA).*

14. Cartesian Coordinates

(α,α,β)-3

Electronic Energy BS1 = -1847.29568765 Hartree

Electronic Energy BS2 = -1847.68262237 Hartree

Zero-point Energy Correction = 0.621453 Hartree

Thermal Correction to Enthalpy = 0.657181 Hartree

Thermal Correction to Free Energy = 0.555436 Hartree

Chemical symbol	X	Y	Z
C	2.481290	-1.459062	-0.458629
C	1.191293	-0.705480	-0.348637
C	1.217311	-2.802207	2.140797
C	-0.014300	-1.403815	-0.182854
C	0.509649	-3.536776	1.061304
C	-0.009244	-2.895600	-0.083801
C	3.079670	-2.014711	0.689972
C	2.358290	-2.113123	1.980909
C	0.343291	-4.924047	1.194502
H	0.724127	-5.414657	2.086417
C	-0.278051	-5.675775	0.200885
H	-0.386878	-6.749663	0.321415
C	-0.754926	-5.043414	-0.948983
H	-1.239662	-5.619680	-1.731395
C	-0.626647	-3.663854	-1.079214
H	-1.032973	-3.157949	-1.949397
C	3.143762	-1.565780	-1.687695
H	2.661527	-1.175757	-2.577612
C	4.403404	-2.152205	-1.780695
H	4.899233	-2.220941	-2.744403
C	5.029638	-2.631786	-0.629274
C	4.366598	-2.565017	0.593188
C	-1.232369	0.701553	-0.068139
C	-1.232525	-0.701273	-0.068141
H	6.020676	-3.072380	-0.686448
H	4.832405	-2.972432	1.486600
C	-0.013988	1.403825	-0.182850
C	1.191450	0.705221	-0.348636
C	-0.008603	2.895608	-0.083791
C	2.481613	1.458517	-0.458644
C	0.510442	3.536668	1.061311
C	-0.625845	3.664001	-1.079196

C	3.080129	2.014044	0.689943	C	-3.399505	-0.670712	-2.131835
C	3.144089	1.565080	-1.687720	C	-3.477380	-1.512851	-0.914305
C	1.217960	2.801946	2.140794	C	-2.508145	-1.462953	0.107712
C	0.344385	4.923975	1.194514	C	-2.698445	-2.228057	1.266919
C	-0.753824	5.043589	-0.948960	C	-3.805795	-3.057816	1.410473
H	-1.032289	3.158188	-1.949378	C	-4.740180	-3.148052	0.376559
C	2.358789	2.112617	1.980890	C	-4.571194	-2.381861	-0.772927
C	4.367174	2.564074	0.593136	C	-4.570692	2.382834	-0.772922
C	4.403857	2.151229	-1.780743	C	-4.739517	3.149060	0.376563
H	2.661757	1.175156	-2.577628	C	-3.805144	3.058642	1.410471
C	-0.276801	5.675842	0.200906	C	-2.697964	2.228657	1.266915
H	0.725338	5.414499	2.086427	H	-1.946426	-2.183918	2.048021
H	-1.238441	5.619963	-1.731367	H	-3.930014	-3.644563	2.315718
C	5.030211	2.630690	-0.629336	H	-5.599083	-3.806355	0.468835
H	4.833081	2.971399	1.486537	H	-5.305164	-2.435099	-1.572757
H	4.899688	2.219848	-2.744459	H	-5.304655	2.436216	-1.572747
H	-0.385392	6.749753	0.321440	H	-5.598287	3.807537	0.468842
H	6.021343	3.071070	-0.686529	H	-3.929239	3.645418	2.315715
C	-2.507824	1.463509	0.107711	H	-1.945950	2.184369	2.048014
C	-3.477052	1.513602	-0.914303	H	2.843163	-1.690224	2.859538
C	-3.399358	0.671446	-2.131834	H	0.815413	-2.914129	3.147387

H	-3.448290	1.189969	-3.088764
H	-3.448553	-1.189222	-3.088766
H	0.816100	2.913952	3.147389
H	2.843582	1.689613	2.859514

$TS_{(\alpha,\alpha,\beta)3\text{-}(\alpha,\alpha,\beta)3}$

Imaginary Freq = -28.3442 (cm^{-1})

Electronic Energy BS1 = -1847.22899651 Hartree

Electronic Energy BS2 = -1847.61392420 Hartree

Zero-point Energy Correction = 0.621880 Hartree

Thermal Correction to Enthalpy = 0.656606 Hartree

Thermal Correction to Free Energy = 0.558137 Hartree

Chemical symbol X, Y, Z

C	-1.528106	-2.356329	-0.852740
C	-0.706809	-1.361555	-0.081581
C	0.612311	-4.733473	0.284818
C	0.707230	-1.361320	0.081584
C	1.544245	-3.775484	0.872236
C	1.528857	-2.355818	0.852758
C	-1.542862	-3.776001	-0.872385
C	-0.610461	-4.733675	-0.285185
C	0.672196	1.081421	-0.223400
C	1.370969	-0.129333	-0.227788
C	-0.672564	1.081205	0.223385
C	-1.370938	-0.129777	0.227814
C	-1.254638	2.371172	0.705631
C	-2.798540	-0.207385	0.677367
C	-2.275297	3.064915	0.029399
C	-3.865556	0.465774	0.044475
C	-2.983053	2.498648	-1.139405
C	-3.685756	1.357081	-1.126802
C	1.253843	2.371561	-0.705701
C	2.274244	3.065693	-0.029481
C	2.982154	2.499728	1.139374
C	3.685224	1.358387	1.126862
C	3.865373	0.467076	-0.044360
C	2.798616	-0.206482	-0.677265
H	-0.961542	-5.749017	-0.458010
H	0.963831	-5.748696	0.457449
H	3.006493	3.115252	2.037934

H	4.251144	1.090603	2.018923	C	-1.053548	4.222604	2.278711
H	-3.007619	3.114112	-2.038000	H	-0.578478	4.660365	3.151748
H	-4.251622	1.089062	-2.018827	C	-2.044105	4.923325	1.587828
C	3.082520	-1.048265	-1.765212	H	-2.349257	5.912220	1.917139
H	2.258746	-1.566636	-2.245714	C	-2.639838	4.347039	0.470159
C	4.383948	-1.235179	-2.222267	H	-3.412862	4.886691	-0.070594
H	4.572548	-1.891887	-3.066325	C	-5.174536	0.246519	0.498876
C	5.439388	-0.585961	-1.581545	H	-5.993688	0.749291	-0.008485
H	6.461386	-0.729357	-1.919750	C	-5.439141	-0.587718	1.581785
C	5.174448	0.248243	-0.498693	H	-6.461075	-0.731447	1.920043
H	5.993406	0.751321	0.008678	C	-4.383448	-1.236539	2.222498
C	2.638360	4.347915	-0.470305	H	-4.571785	-1.893266	3.066598
H	3.411183	4.887863	0.070438	C	-3.082105	-1.049203	1.765374
C	2.042461	4.923930	-1.588026	H	-2.258131	-1.567266	2.245866
H	2.347284	5.912910	-1.917388	C	-2.351199	-1.707149	-1.805116
C	1.052163	4.222830	-2.278895	H	-2.249745	-0.636189	-1.919987
H	0.576969	4.660376	-3.151972	C	-3.277872	-2.362216	-2.604888
C	0.658581	2.966274	-1.829298	H	-3.889879	-1.791539	-3.296922
H	-0.139918	2.431360	-2.334925	C	-3.404952	-3.743445	-2.498415
C	-0.659550	2.966157	1.829177	H	-4.137887	-4.291081	-3.082876
H	0.139143	2.431545	2.334815	C	-2.530039	-4.417908	-1.661749

H	-2.575704	-5.502481	-1.628823
C	2.351587	-1.706366	1.805254
H	2.249689	-0.635452	1.920181
C	3.278459	-2.361118	2.605058
H	3.890163	-1.790249	3.297201
C	3.406142	-3.742279	2.498462
H	4.139260	-4.289653	3.082939
C	2.531621	-4.417046	1.661626
H	2.577773	-5.501595	1.628587

$TS_{(\alpha,\alpha,\beta)3-(\alpha,\alpha,\alpha)3}$

Imaginary Freq = -27.7679 (cm^{-1})

Electronic Energy BS1 = -1847.21425051 Hartree

Electronic Energy BS2 = -1847.59996660 Hartree

Zero-point Energy Correction = 0.621475 Hartree

Thermal Correction to Enthalpy = 0.656280 Hartree

Thermal Correction to Free Energy = 0.557199 Hartree

Chemical symbol X, Y, Z

C	-1.015031	-2.587144	-0.145808
C	-0.391261	-1.288241	0.252910
C	0.826191	-1.781095	-2.618529
C	0.988564	-1.098362	0.202174
C	1.828058	-2.421931	-1.724835
C	1.873996	-2.199061	-0.325811
C	-1.145462	-2.856729	-1.526185
C	-0.497073	-1.995095	-2.545544
C	2.726237	-3.327754	-2.307365
H	2.694391	-3.475091	-3.383617
C	3.624876	-4.055181	-1.532100
H	4.305761	-4.758708	-2.002199
C	3.625891	-3.884642	-0.148911
H	4.303193	-4.459959	0.475433
C	2.762347	-2.963141	0.440928
H	2.790693	-2.833204	1.513480
C	-1.561268	-3.481331	0.780331
H	-1.452504	-3.275414	1.839070
C	-2.261463	-4.610647	0.359567
H	-2.681494	-5.290981	1.094461
C	-2.434383	-4.852433	-1.003806
C	-1.878428	-3.978949	-1.936283

C	0.688688	1.287871	0.045338	H	-4.314372	3.920738	-0.690766
C	1.551251	0.208030	0.383927	H	-1.564701	5.183137	2.360007
H	-2.991539	-5.722162	-1.339748	C	-5.138234	-1.214716	1.988707
H	-1.991150	-4.174893	-2.999394	H	-5.851578	-0.630182	0.044680
C	-0.698642	1.098476	0.347113	H	-4.135879	-1.667743	3.846651
C	-1.218196	-0.180989	0.563290	H	-3.601294	5.603017	0.979334
C	-1.567961	2.306616	0.512760	H	-6.116840	-1.531085	2.337575
C	-2.607788	-0.422365	1.056467	C	1.014525	2.407415	-0.901828
C	-2.730704	2.536685	-0.256670	C	2.148403	3.254111	-1.031189
C	-1.171614	3.275211	1.447880	C	3.470134	3.163074	-0.414659
C	-3.736851	-0.285114	0.228762	C	4.179719	2.302290	0.344416
C	-2.776371	-0.909871	2.360291	C	3.920821	1.136279	1.183058
C	-3.216483	1.602547	-1.304903	C	2.781811	0.291645	1.230230
C	-3.433663	3.737681	-0.080814	C	2.667879	-0.553228	2.361624
C	-1.894061	4.451436	1.628253	C	3.667183	-0.708325	3.316098
H	-0.273703	3.093446	2.030207	C	4.849148	0.010677	3.176234
C	-3.653971	0.350712	-1.103321	C	4.947602	0.919879	2.133193
C	-4.987367	-0.715038	0.698159	C	2.089474	4.293957	-1.993650
C	-4.029005	-1.293134	2.832886	C	1.044839	4.456373	-2.889472
H	-1.901693	-1.000582	2.997983	C	0.022470	3.512720	-2.881924
C	-3.031938	4.686423	0.856249	C	0.033235	2.514967	-1.916830

H	1.743458	-1.103562	2.487420
H	3.516421	-1.387386	4.149847
H	5.665330	-0.102755	3.883084
H	5.843980	1.528350	2.056575
H	2.931481	4.977596	-2.049775
H	1.057617	5.271699	-3.606199
H	-0.779244	3.544470	-3.613662
H	-0.746389	1.766130	-1.949744
H	-1.139150	-1.570157	-3.315750
H	1.214337	-1.189001	-3.445986
H	4.093234	3.988391	-0.753226
H	5.209103	2.634151	0.465348
H	-3.293672	2.019594	-2.309000
H	-4.070547	-0.201199	-1.944549

(α,α,α)-3

Electronic Energy BS1 = -1847.29041137 Hartree

Electronic Energy BS2 = -1847.67684420 Hartree

Zero-point Energy Correction = 0.621219 Hartree

Thermal Correction to Enthalpy = 0.656984 Hartree

Thermal Correction to Free Energy = 0.554784 Hartree

Chemical symbol X, Y, Z

C	-0.911681	2.744912	-0.439269
C	-0.442692	1.334306	-0.612635
C	1.186212	2.449557	1.971519
C	0.931614	1.052884	-0.612423
C	2.094708	2.745321	0.835294
C	1.917244	2.165621	-0.438719
C	-0.847905	3.347725	0.834779
C	-0.129162	2.718827	1.971316
C	3.132861	3.669588	1.023628
H	3.280522	4.100126	2.010527
C	3.946477	4.064089	-0.035616
H	4.737296	4.790153	0.128755
C	3.729335	3.534777	-1.308534
H	4.347269	3.846778	-2.145295
C	2.726688	2.586998	-1.499561
H	2.569323	2.153710	-2.481984
C	-1.489538	3.450501	-1.500558

H	-1.514330	2.990196	-2.482982	C	-2.715010	-0.196678	1.971079
C	-2.039024	4.716142	-1.309974	C	-4.744872	0.878727	1.022477
H	-2.483902	5.245958	-2.147073	C	-4.925902	1.461882	-1.309936
C	-2.031630	5.288173	-0.037036	H	-3.149704	1.147321	-2.482995
C	-1.439334	4.605661	1.022668	C	-3.563950	-4.403712	-0.035786
C	0.446173	-1.333533	-0.612134	H	-3.679051	-3.747182	2.010491
C	1.377041	-0.284058	-0.612210	H	-3.300813	-4.775212	-2.145603
H	-2.473486	6.266663	0.126991	C	-5.493105	1.385736	-0.037091
H	-1.406591	5.059638	2.009567	H	-5.191759	0.791651	2.009313
C	-0.934391	-1.050804	-0.612363	H	-5.504928	1.840717	-2.146937
C	-1.377835	0.280088	-0.612719	H	-4.190365	-5.275601	0.128518
C	-1.921462	-2.162253	-0.438714	H	-6.517333	1.707639	0.126973
C	-2.834313	0.577479	-0.439411	C	0.916946	-2.743473	-0.438211
C	-2.475647	-2.407877	0.835337	C	1.330343	-3.186890	0.835809
C	-2.243365	-3.015951	-1.499689	C	1.528229	-2.252151	1.972011
C	-3.425305	0.441762	0.834538	C	2.418991	-1.247533	1.971884
C	-3.603760	1.067347	-1.500597	C	3.323190	-0.939505	0.835492
C	-2.290526	-1.470467	1.971474	C	2.833157	-0.583030	-0.438651
C	-3.269313	-3.549001	1.023589	C	3.733289	-0.435115	-1.499776
C	-3.064617	-4.124641	-1.308749	C	5.104121	-0.591613	-1.308928
H	-1.832208	-2.807666	-2.482149	C	5.595672	-0.883870	-0.035898

C	4.708315	-1.055847	1.023640
C	1.612038	-4.548024	1.024172
C	1.547040	-5.449927	-0.035046
C	1.197090	-4.997327	-1.307975
C	0.877378	-3.655185	-1.499050
H	3.347194	-0.183549	-2.482277
H	5.785512	-0.471016	-2.145898
H	6.664003	-0.990077	0.128332
H	5.085000	-1.311047	2.010614
H	1.911190	-4.891058	2.011070
H	1.780658	-6.497772	0.129349
H	1.158479	-5.688513	-2.144712
H	0.580839	-3.302324	-2.481502
H	-0.696988	2.555250	2.886098
H	1.643768	2.075991	2.886456
H	0.975751	-2.461567	2.886852
H	2.560937	-0.673847	2.886626
H	-1.864929	-1.879971	2.886456
H	-2.620241	0.386789	2.885744

(α,α,β)-7

Electronic Energy BS1 = -925.292299439 Hartree

Electronic Energy BS2 = -925.494580808 Hartree

Zero-point Energy Correction = 0.339005 Hartree

Thermal Correction to Enthalpy = 0.358911 Hartree

Thermal Correction to Free Energy = 0.292500 Hartree

Chemical symbol X, Y, Z

C	-1.236653	-2.239855	1.401845
C	-0.695943	-1.040424	0.708332
C	1.221801	-1.817271	3.440477
C	-0.234036	0.083601	1.407476
C	0.437276	-0.615717	3.750086
C	-0.237223	0.165359	2.891372
C	-0.583580	-3.060148	2.237309
C	0.773697	-2.894467	2.771276
C	0.200688	1.230908	-0.700699
C	0.200688	1.230908	0.700699
C	-0.234036	0.083601	-1.407476
C	-0.695943	-1.040424	-0.708332

C	-0.237223	0.165359	-2.891372
C	-1.236653	-2.239855	-1.401845
C	0.437276	-0.615717	-3.750086
C	-0.583580	-3.060148	-2.237309
C	1.221801	-1.817271	-3.440477
C	0.773697	-2.894467	-2.771276
C	0.724217	2.364238	-1.506649
C	0.275954	3.629148	-1.529104
C	-0.752718	4.231735	-0.672372
C	-0.752718	4.231735	0.672372
C	0.275954	3.629148	1.529104
C	0.724217	2.364238	1.506649
H	1.424236	-3.766823	2.706901
H	2.214764	-1.867148	3.887808
H	-1.518419	4.814498	-1.184964
H	-1.518419	4.814498	1.184964
H	2.214764	-1.867148	-3.887808
H	1.424236	-3.766823	-2.706901
H	0.695432	4.295138	-2.284824
H	1.479194	2.088865	-2.241353
H	0.695432	4.295138	2.284824
H	1.479194	2.088865	2.241353
H	-0.745836	1.036727	-3.300879
H	0.433831	-0.323605	-4.801433
H	-2.246352	-2.530935	-1.114755
H	-1.097728	-3.969367	-2.552649
H	-1.097728	-3.969367	2.552649
H	-2.246352	-2.530935	1.114755
H	0.433831	-0.323605	4.801433
H	-0.745836	1.036727	3.300879

$TS_{(\alpha,\alpha,\beta)7\text{-}(\alpha,\alpha,\beta)7}$

Imaginary Freq = -95.5460 (cm^{-1})

Electronic Energy BS1 = -925.267430397 Hartree

Electronic Energy BS2 = -925.467856408 Hartree

Zero-point Energy Correction = 0.340252 Hartree

Thermal Correction to Enthalpy = 0.359248 Hartree

Thermal Correction to Free Energy = 0.295061 Hartree

Chemical symbol X, Y, Z			
C	2.296347	1.641785	-0.094413

C	1.156660	0.695128	-0.152224	C	-0.583102	-3.834373	0.493886
C	4.721221	-0.673473	0.018897	C	-0.062976	-2.705925	1.001211
C	1.156660	-0.695128	0.152224	H	5.707139	1.135109	-0.022043
C	3.646743	-1.651467	0.025694	H	5.707139	-1.135109	0.022043
C	2.296347	-1.641785	0.094413	H	-3.151026	-3.605866	-1.810388
C	3.646743	1.651467	-0.025694	H	-1.112472	-4.758332	-1.408553
C	4.721221	0.673473	-0.018897	H	-3.151026	3.605866	1.810388
C	-1.309131	-0.664416	0.228372	H	-1.112472	4.758332	1.408553
C	-0.085633	-1.335336	0.412388	H	-4.234492	-2.557312	0.207664
C	-1.309131	0.664416	-0.228372	H	-3.268845	-0.662176	1.169320
C	-0.085633	1.335336	-0.412388	H	-0.359488	-4.766700	1.015010
C	-2.631103	1.269906	-0.529437	H	0.531111	-2.798593	1.909637
C	-0.062976	2.705925	-1.001211	H	-3.268845	0.662176	-1.169320
C	-3.186533	2.361172	0.024062	H	-4.234492	2.557312	-0.207664
C	-0.583102	3.834373	-0.493886	H	0.531111	2.798593	-1.909637
C	-2.563765	3.323842	0.936566	H	-0.359487	4.766700	-1.015010
C	-1.409032	3.976177	0.709777	H	4.042604	2.663318	0.057154
C	-2.631103	-1.269906	0.529437	H	1.907289	2.651850	-0.022526
C	-3.186533	-2.361172	-0.024062	H	4.042604	-2.663318	-0.057154
C	-2.563765	-3.323842	-0.936566	H	1.907289	-2.651850	0.022526
C	-1.409032	-3.976177	-0.709777				

$TS_{(\alpha,\alpha,\beta)7\text{-}(\alpha,\alpha,\alpha)7}$

Imaginary Freq = -117.5230 (cm^{-1})

Electronic Energy BS1 = -925.262338993 Hartree

Electronic Energy BS2 = -925.463262369 Hartree

Zero-point Energy Correction = 0.339808 Hartree

Thermal Correction to Enthalpy = 0.358980 Hartree

Thermal Correction to Free Energy = 0.292927 Hartree

Chemical symbol X, Y, Z

C	-2.597764	1.398990	-0.820300
C	-1.291802	0.703409	-0.694536
C	-1.390524	3.563098	1.234312
C	-0.069719	1.394462	-0.575479
C	-0.585519	3.807766	0.032483
C	-0.072743	2.876463	-0.783274
C	-3.153820	2.250934	0.057299
C	-2.538318	2.859491	1.240474
C	1.157140	-0.713862	-0.355134
C	1.158632	0.711513	-0.355589
C	-0.072530	-1.394369	-0.575364
C	-1.293175	-0.700875	-0.694840
C	-0.078341	-2.876391	-0.782834
C	-2.600449	-1.393832	-0.821795
C	-0.593809	-3.806539	0.032570
C	-3.159067	-2.244646	0.055244
C	-1.399366	-3.560227	1.233700
C	-2.545786	-2.854386	1.238960
C	2.298003	-1.640979	-0.154612
C	3.615171	-1.648400	0.150070
C	4.653459	-0.677200	0.453158
C	4.655013	0.668094	0.452048
C	3.618993	1.641190	0.147266
C	2.301733	1.636314	-0.157032
H	-3.127489	2.837595	2.157016
H	-1.094388	4.085677	2.143470
H	5.598822	-1.144076	0.723841
H	5.601465	1.133231	0.721922
H	-1.104967	-4.083365	2.143104
H	-3.135644	-2.831322	2.155028
H	4.010410	-2.662545	0.202917
H	1.944582	-2.659521	-0.247929

H	4.016701	2.654482	0.197919
H	1.950750	2.655512	-0.252361
H	0.457585	-3.220640	-1.667346
H	-0.415761	-4.854868	-0.211988
H	-3.229113	-1.067713	-1.648311
H	-4.200078	-2.522293	-0.117069
H	-4.194471	2.530559	-0.113993
H	-3.227988	1.074038	-1.646074
H	-0.405706	4.855715	-0.212410
H	0.462818	3.219438	-1.668507

(α,α,α)-7

Electronic Energy BS1 = -925.288064310 Hartree

Electronic Energy BS2 = -925.491021167 Hartree

Zero-point Energy Correction = 0.338620 Hartree

Thermal Correction to Enthalpy = 0.358603 Hartree

Thermal Correction to Free Energy = 0.291782 Hartree

Chemical symbol X, Y, Z

C	2.706543	1.028936	-0.802245
C	1.327737	0.471666	-0.776568
C	3.362682	-1.292807	1.329209
C	1.077930	-0.907413	-0.776551
C	3.110413	-2.110542	0.136628
C	2.173654	-1.912908	-0.802311
C	3.653212	0.885187	0.136630
C	3.602571	0.030871	1.329179
C	-1.324776	-0.479815	-0.776784
C	-0.255439	-1.385702	-0.776580
C	-1.072300	0.914050	-0.776659
C	0.246870	1.387263	-0.776585
C	-2.244333	1.829459	-0.801983
C	0.569664	2.838992	-0.802096
C	-2.593129	2.720793	0.137204
C	0.272477	3.748893	0.137062
C	-1.827851	3.103851	1.329783
C	-0.561613	3.558094	1.329736
C	-2.743433	-0.925899	-0.802398
C	-3.382931	-1.638197	0.136656
C	-2.800939	-2.265260	1.329387
C	-1.774557	-3.134903	1.329561

C	-1.060083	-3.606186	0.137088
C	-0.462319	-2.858442	-0.801968
H	3.890743	0.501568	2.269224
H	3.467339	-1.834674	2.269267
H	-3.322530	-2.084709	2.269398
H	-1.510982	-3.619583	2.269712
H	-2.379434	3.117727	2.269914
H	-0.144539	3.919419	2.269832
H	-4.461608	-1.760603	0.027235
H	-3.344959	-0.535930	-1.622576
H	-1.003729	-4.690338	0.027765
H	0.021023	-3.387795	-1.622195
H	-2.944487	1.675419	-1.622143
H	-3.560255	3.213976	0.027912
H	1.207907	3.165113	-1.622396
H	0.705541	4.744377	0.027679
H	4.563925	1.476048	0.027076
H	2.923131	1.712184	-1.622525
H	3.755881	-2.983395	0.027076
H	2.136728	-2.628689	-1.622619

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