Dibenzocycloheptatriene as end-group of Thiele and tetrabenzo-Chichibabin hydrocarbons

Vicente G. Jiménez,†[a] Paula Mayorga-Burrezo,†[b] Victor Blanco,[a] Vega Lloveras,[b] Carlos J. Gomez-Garcia,[c] Tomáš Šolomek,[d] Juan M. Cuerva,[a] Jaume Veciana*[b] and Araceli G. Campaña*[a]

[a] Departamento de Química Orgánica. Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain.

[b] Department of Molecular Nanoscience and Organic Materials, Institut de Ciència de Materials de Barcelona (ICMAB)/ CIBER-BBN. Campus Universitari de Bellaterra, E-08193, Cerdanyola, Barcelona (Spain).

[c] Department of Inorganic Chemistry and Instituto de Ciencia Molecular, Universidad de Valencia,Paterna 46980, Spain

[d] Department of Chemistry, University of Basel, St. Johanns-Ring 19, 4056 Basel (Switzerland).

*E-mail: vecianaj@icmab.es, araceligc@ugr.es

- Electronic Supporting Information -

Table of Contents

1. General Details 3
2. Synthetic procedures 4
3. Titration and variable temperature ^{1}H-NMR spectra 8
4. Crystallographic data 11
5. Optical properties 13
6. Electron Spin Resonance (ESR) measurements 14
7. Theoretical calculations 18
   - 7.1. Geometry optimizations 18
   - 7.2. Isotropic hyperfine coupling constants ($|a_H|$) 38
   - 7.3. TD-DFT calculations 39
   - 7.4. Energy barrier between geometries of DBHept-Anthracene 65
   - 7.5. Radical stabilization energies 69
8. Electrochemical properties 70
9. SQUID Measurements 71
10. References 72

ANNEX I: ^{1}H and ^{13}C NMR spectra of new compounds 73

ANNEX II: 2D-NMR and HRMS spectra of selected compounds 77

1. General Details

Unless otherwise stated, all reagents and solvents, either HPLC grade or anhydrous ones, were purchased from commercial sources and used without further purification, but anhydrous THF, that was freshly distilled over Na/benzophenone. Flash column chromatography was carried out using Silica gel 60 (230-400 mesh, Scharlab, Spain) as the stationary phase.

Analytical TLC was performed on aluminium sheets coated with silica gel with fluorescent indicator UV_{254} (Sigma-Aldrich) and observed under UV light (254 nm) or stained with phosphomolybdic acid (5% ethanol solution).

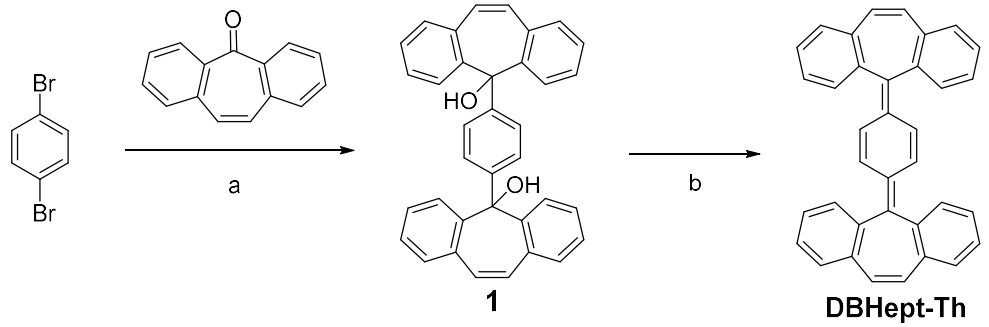
^{1}H and ^{13}C NMR spectra were recorded on a Varian Direct Drive (500 MHz or 600 MH), Bruker Avance III HD NanoBay (400 MHz), Bruker Avance Neo (400 MHz or 500 MHz) or a Bruker Biospin (600 MHz) spectrometers.

Chemical shifts are given in ppm and referenced to the signal of the residual protiated solvent (^{1}H: δ = 11.50 for CF_3COOD, δ = 7.26 for $CDCl_3$, δ = 5.32 for CD_2Cl_2, δ = 6.00 for $C_2D_2Cl_4$ and δ = 7.19 for *o*-dichlorobenzene-d_4 (*o*-DCB-d_4) or the ^{13}C signal of the solvents (^{13}C: δ = 164.2 and 116.2 for CF_3COOD, δ = 77.16 for $CDCl_3$, δ = 73.78 for $C_2D_2Cl_4$ and δ = 132.39 for [D_4]-*o*-DCB) or to the signal of the residual TMS (^{1}H: δ = 0.00). Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint. = quintet, q = quartet, t = triplet, d = doublet, s = singlet, br = broad. Assignment of the ^{13}C NMR multiplicities was accomplished by DEPT. Assignment of the ^{1}H signals was carried out with the help of 2D NMR experiments (COSY, HSQC and HMBC techniques).

The titration experiments monitored by ^{1}H NMR were carried out on a Bruker Avance Neo (400 MHz) spectrometer at a constant temperature of 298 K. All the solutions were prepared under Ar atmosphere.

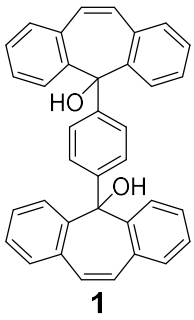
ESI-TOF mass spectra were recorded on a Waters XEVO G2-XS QTof mass spectrometer. APCI mass spectra were recorded on a Bruker MAXIS II mass spectrometer. IR-ATR spectra were recorded on a Perkin Elmer Spectrum Two IR Spectrometer.

2. Synthetic procedures



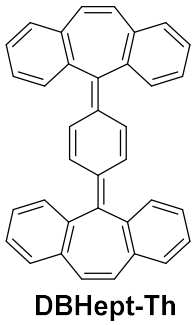
Scheme S1. Synthesis of **DBHept-Th**: a) *n*BuLi, THF, −78 ºC, 1 h; then dibenzosuberenone, THF −78 ºC to rt, 16h, 25%. b) $SnCl_2$, DCM, rt, 24h, 62%.

Compound 1



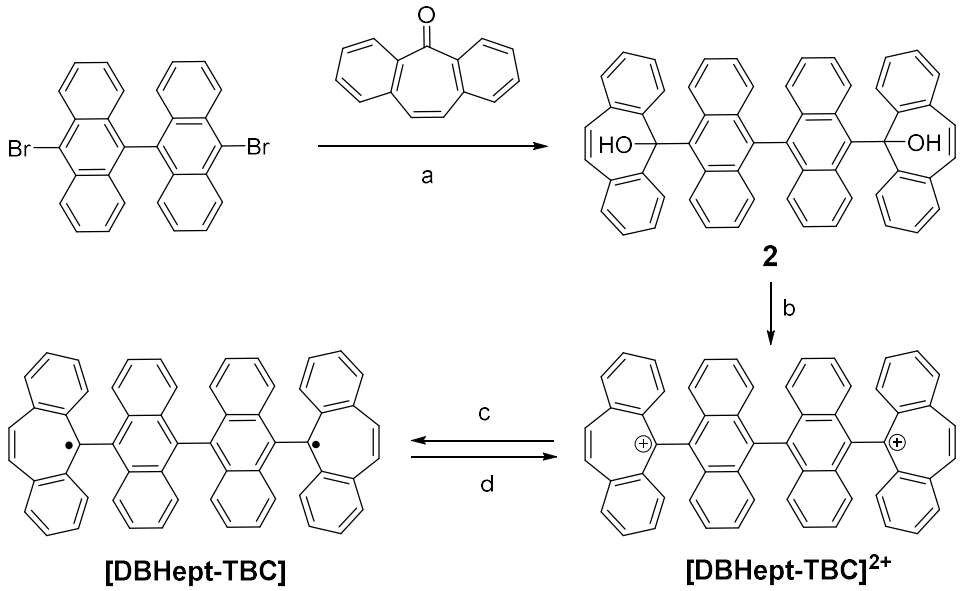
1,4-dibromobenzene (300 mg, 1.27 mmol) was dissolved in freshly distilled THF (15 mL) and the solution was cooled to −78 ºC under Ar atmosphere. Then, *n*-butyllithium (2.5 M in hexanes, 1.1 mL, 2.67 mmol) was added and the mixture was stirred for 1 h at the same temperature. After this time, a solution of dibenzosuberenone (551 mg, 2.67 mmol) in distilled THF (3 mL) was added dropwise. Finally, the reaction was heated up to room temperature and kept under stirring for 16 h. The mixture was diluted with EtOAc (100 mL) and washed with water (15 mL) and brine (15 mL). The organic phase was then separated and dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, CH_2Cl_2) affording diol **1** (156 mg, 25%) as a white solid (see **Scheme S1**, reaction (a)). **M.p.:** 222 ºC decomposition. **^{1}H NMR**: (600 MHz, CD_2Cl_2) δ = 8.06 (d, *J* = 8.0 Hz, 4H), 7.43 (t, *J* = 7.5 Hz, 4H), 7.27 (m, 8H), 6.59 (s, 4H), 6.28 (s, 4H), 2.39 (s, 2H). **^{13}C NMR**: (151 MHz, CD_2Cl_2) δ = 145.54 (C), 142.84 (C), 133.70 (C), 131.68 (CH), 129.14 (CH), 128.55 (CH), 127.20 (CH), 126.44 (CH), 124.80 (CH), 78.74 (C). **HR-MS (ESI-TOF):** *m/z* calcd. for $C_{36}H_{25}O$ $[M–OH]^+$: 473.1900, found: 473.1899. **IR (ATR):** 3544, 3447, 3071, 1488, 1005, 752 cm^{-1}.

DBHept-Th



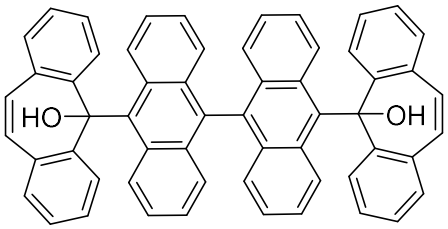
To a suspension of $SnCl_2$ (220 mg, 1.16 mmol) in anhydrous dichloromethane (6 mL), a solution of compound **1** (57 mg, 0.116 mmol) in dry dichloromethane (2 mL) was added under Ar atmosphere. After stirring for 24 h at room temperature, the solvent was removed under vacuum and the crude was purified by flash column chromatography (SiO_2, CH_2Cl_2/Hexane 5:95) affording **DBHept-Th** (33 mg, 62%) as a 1:1 mixture of the *syn* and *anti*-isomers as a yellow solid (see **Scheme S1**, reaction (b)). **M.p:** > 250 ºC. **^{1}H NMR**: (500 MHz, $C_2Cl_4D_2$) δ = 7.41 – 7.25 (m, 16H), 6.95 (s, 2H), 6.87 (s, 2H), 6.61 (s, 2H) 6.49 (s, 2H). **^{13}C NMR**: (126 MHz, $C_2Cl_4D_2$) δ = 137.89 (C), 137.65 (C), 137.18 (C), 134.72 (C), 134.65 (C), 131.10 (CH), 131.05 (CH), 130.81 (C), 128.99 (CH), 128.76 (CH), 128.52

(CH), 128.47 (CH), 127.87 (CH), 127.77 (CH), 126.94 (CH), 126.90 (CH), 126.28 (CH), 126.15 (CH). **HR-MS (ESI-TOF):** *m/z* calcd. for $C_{36}H_{24}$ $[M]^+$: 456.1878, found: 456.1875. **IR (ATR)**: 3017, 1483, 833, 798, 753 cm^{-1}.



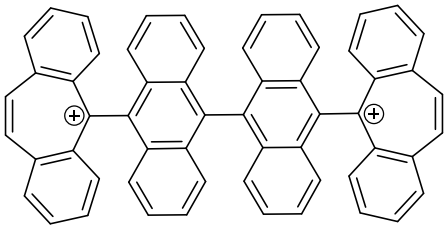
Scheme S2. Synthesis of **DBHept-TBC**. a) *n*BuLi, THF, −78 ºC, 1 h; then dibenzosuberenone, THF −78 ºC to rt, 16 h, 86%. b) CF_3CO_2D, CD_2Cl_2, 1 min, rt, 100 %. c) Ferrocene (Fc), CD_2Cl_2, 1 min, RT, 100%. d) tris(4-bromophenyl) ammoniumyl hexachloroantimonate (*Magic Blue*), CD_2Cl_2, 1 min, 100%.

Compound 2



Firstly, 10,10´-dibromo-9,9´-bianthracene (400 mg, 0.78 mmol) was dissolved in freshly distilled THF (15 mL) under an Ar atmosphere and cooled to −78 ºC. Secondly, *n*-butyllithium (2.5 M in hexanes, 0.7 mL, 1.72 mmol) was added and stirred for 1 h at the same temperature. After this time, a solution of dibenzosuberenone (354 mg, 1.72 mmol) in distilled THF (2 mL) was added dropwise to the orange mixture. The reaction was then heated up to room temperature and stirred for 16 h. After this time, the mixture was diluted with EtOAc (100 mL) and washed with water (15 mL) and brine (15 mL). The organic phase was separated and dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, CH_2Cl_2/Hexane 1:1) affording diol **2** (517 mg, 86%) as a yellow solid (see**Scheme S2**, reaction (a)). **M.p.:** 260 ºC decomposition. **^{1}H NMR**: (600 MHz, CD_2Cl_2) δ = 8.54 (d, *J* = 8.4 Hz, 4H), 7.70 (d, *J* = 9.3 Hz, 2H), 7.68 (d, *J* = 9.1 Hz, 2H), 7.62 (t, *J* = 7.7 Hz, 4H), 7.21 (td, *J* = 7.4, 1.3 Hz, 4H), 7.01 (d, *J* = 7.5 Hz, 2H), 6.97 (m, 4H), 6.91 (d, *J* = 8.8 Hz, 4H), 6.79 (m, 4H), 6.72 (m, 2H), 6.22 (d, *J* = 11.4 Hz, 2H), 6.18 (d, *J* = 11.4 Hz, 2H), 3.97 (s, 2H). **^{13}C NMR**: (151 MHz, CD_2Cl_2) δ = 146.95 (C), 146.91 (C), 136.37 (C), 135.74 (C), 132.47 (C), 131.89 (C), 131.69 (C), 131.23 (CH), 131.15 (CH), 130.65 (C), 130.26 (C), 129.06 (C), 129.02 (CH), 128.36 (CH), 128.30 (CH), 127.09 (CH), 126.80 (CH), 126.42 (CH), 126.37 (CH), 126.14 (CH), 125.00 (CH), 124.65 (CH), 123.34 (CH), 123.32 (CH), 122.46 (CH), 122.44 (CH), 80.38 (C). **HR-MS (ESI-TOF):** *m/z* calcd. for $C_{58}H_{37}O$ $[M–OH]^+$: 749.2839, found:749.2850 **IR (ATR):** 3456, 2917, 1716, 1248, 761 cm^{-1}.

[DBHept-TBC]$^{2+}$



[DBHept-TBC]$^{2+}$

Compound **2** (5.0 mg, 6.5 × 10^{-3} mmol) was dissolved in CD_2Cl_2 (2 mL) under Ar atmosphere. An aliquot (0.5 mL) of this solution was transferred into a sealed NMR tube under Ar atmosphere, where a solution of CF_3CO_2D (0.019 mmol) in CD_2Cl_2 (2 mL) was added stepwise (see **Scheme S2**, reaction (b)) and monitored *in-situ* by ^{1}H NMR, (**Figure S1**). An immediate colour change from yellow to red was observed and a quantitative conversion towards **[DBHept-TBC]$^{2+}$** was obtained. **^{1}H NMR:** (400 MHz, CD_2Cl_2) δ = 9.47 (s, 4H), 8.96 (d, *J* = 8.1 Hz, 4H), 8.69 (t, *J* = 7.5 Hz, 4H), 8.39 (d, *J* = 9.0 Hz, 4H), 8.16 (t, *J* = 7.9 Hz, 4H), 7.59 (d, *J* = 8.7 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.6 Hz, 4H), 6.96 (d, *J* = 8.7 Hz, 4H). **^{13}C NMR:** (101 MHz, CD_2Cl_2) δ = 147.30 (C), 146.28 (CH), 142.51 (CH), 140.80 (C), 139.63 (CH), 137.51 (CH), 137.00 (C), 135.44 (C), 135.33 (CH), 131.49 (C), 131.40 (C), 129.33 (CH), 127.85 (CH), 126.77 (CH). **HR-MS (ESI-TOF):** *m/z* calcd. for $C_{58}H_{36}$ $[M]^{2+}$: 366.1408, found: 366.1414.

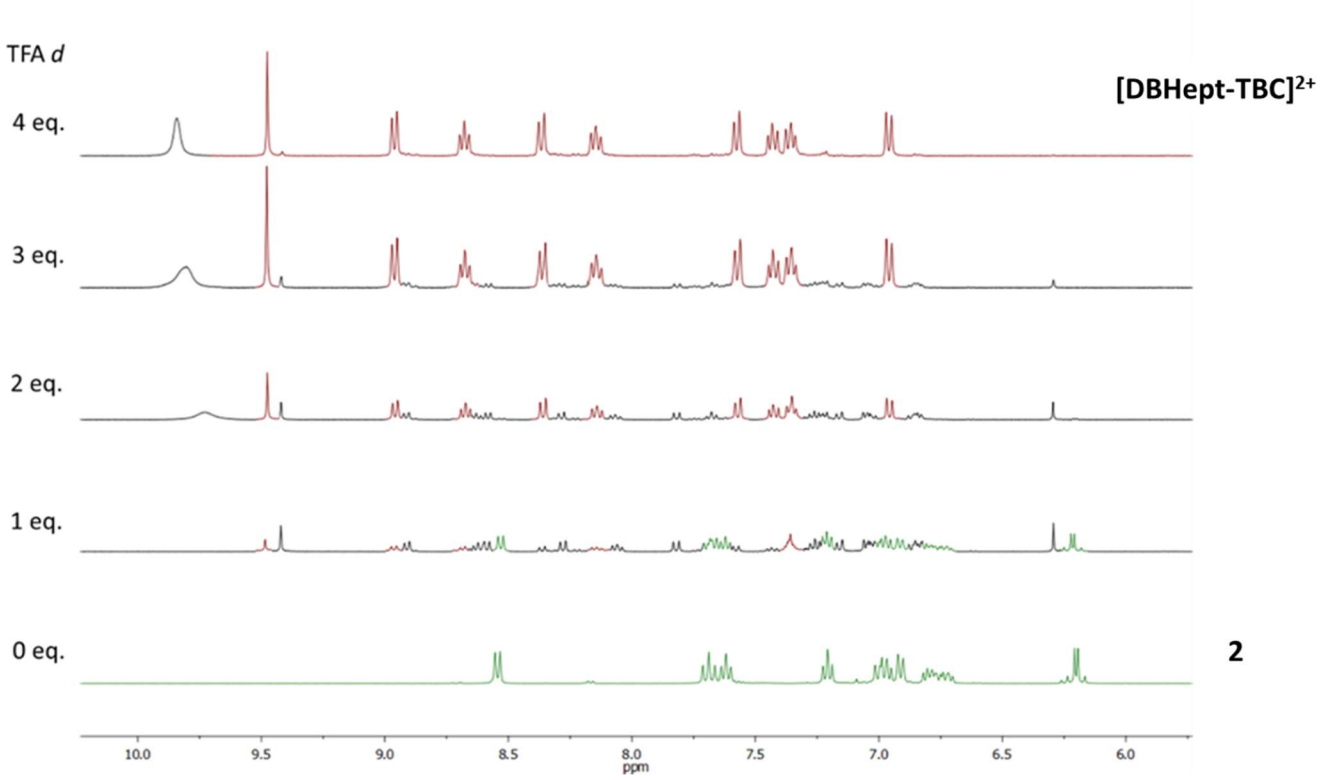
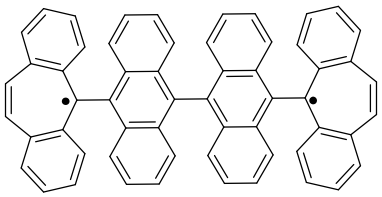


Figure S1. ^{1}H NMR (400 MHz, CD_2Cl_2) spectra for the generation of **[DBHept-TBC]$^{2+}$** (red) by addition of increasing amounts of CF_3CO_2D (≈ 10 mM) to a solution of diol **2** (green).

DBHept-TBC



[DBHept-TBC]

A solution of **[DBHept-TBC]$^{2+}$** (3.2 mM) in CD_2Cl_2 (0.5 mL) was prepared in a sealed NMR tube under Ar atmosphere. A solution of ferrocene (10 mM, 3.8 mg, 0.020 mmol) in CD_2Cl_2 (2 mL) was added (i.e., from 0.15 to 0.75 mL. see**Scheme S2**, reaction (c)). The reaction was monitored by ^{1}H-NMR with quantitative conversion towards **DBHept-TBC** once the ^{1}H-NMR signals of **[DBHept-TBC]$^{2+}$** either disappeared or broadened (see **Figure S2**). On the other hand, a solution of tris(4-bromophenyl) ammoniumyl hexachloroantimonate, (*Magic Blue*)[S1] (5.3 mg, 6.5 × 10^{-3} mmol) in CD_2Cl_2 (1 mL) was used to check the reversibility of the resulting **DBHept-TBC** (see **Figure S3**). **HR-MS (ESI-TOF):** *m/z* calcd. for $C_{58}H_{36}$ [M]$^+$: 732.2817, found: 732.2820.

The isolation of **DBHept-TBC** as solid was performed by the addition of anhydrous Et_2O (70 mL) to a solution of **DBHept-TBC** (88 mg, 0.12 mmol) in CD_2Cl_2 (8 mL) under Ar atmosphere. After the addition of Et_2O a red solid precipitate appeared, then the solvent was removed using a syringe and the red solid was dried under an Ar flow.

3. Titration and variable temperature ^{1}H-NMR spectra

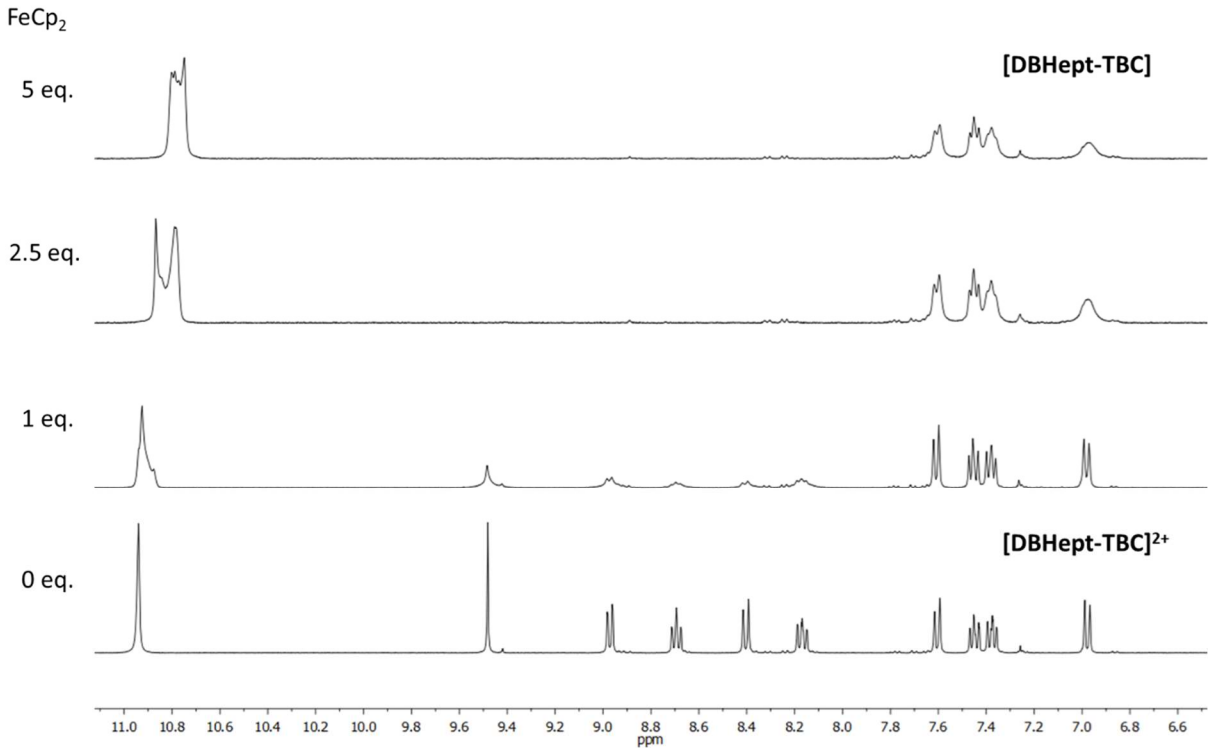


Figure S2. ^{1}H NMR (400 MHz, CD_2Cl_2) spectra for the generation of **DBHept-TBC** from a solution of **[DBHept-TBC]$^{2+}$** (3.2 mM) in CD_2Cl_2 (0.5 mL) by the addition of several aliquots of a 10 mM solution of $FeCp_2$ (3.8 mg, 0.02 mmol) in CD_2Cl_2 (2 mL).

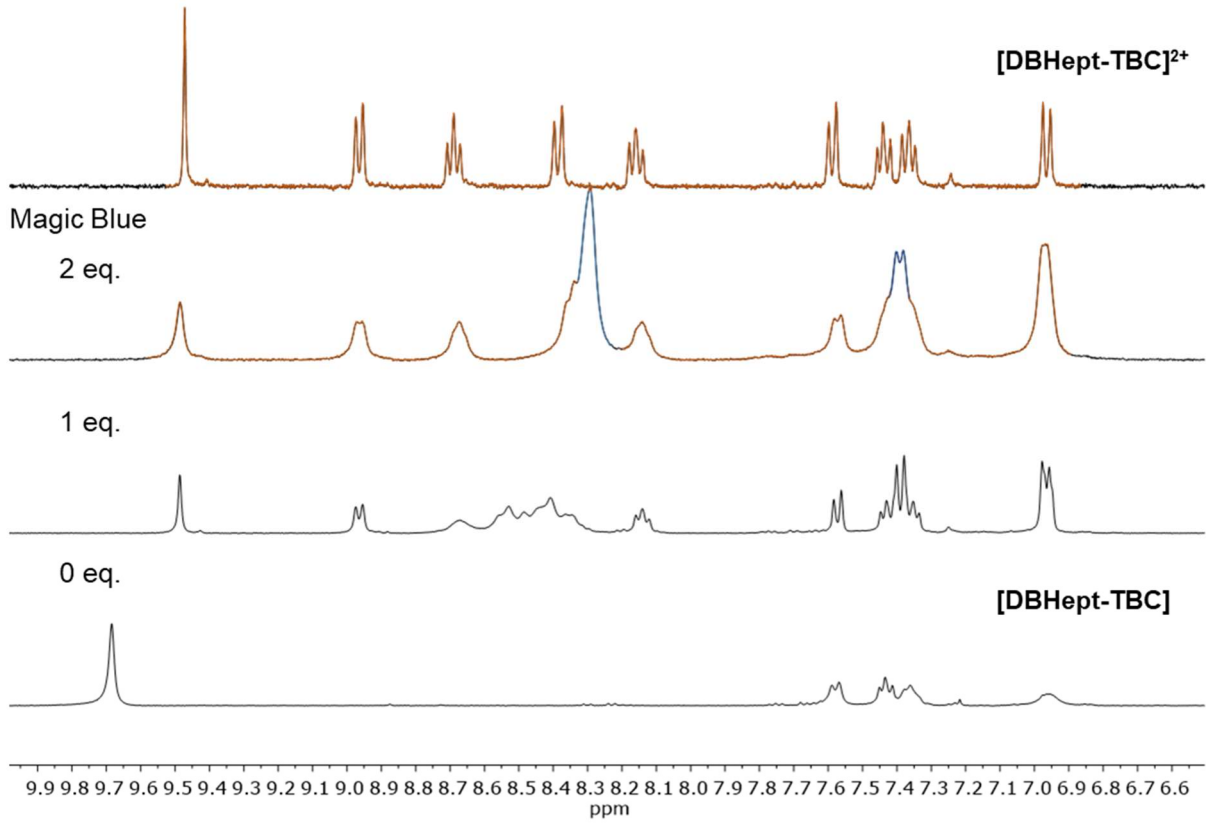


Figure S3. ^{1}H NMR (400 MHz, CD_2Cl_2) spectra for the generation of **[DBHept-TBC]$^{2+}$** from a solution of **DBHept-TBC** (3.2 mM) in CD_2Cl_2 (0.5 mL) by the addition of *Magic Blue* (tris(4-bromophenyl)ammoniumyl hexachloroantimonate).[S1] ^{1}H NMR signals of *Magic Blue*: δ = 8.36 and 7.39 ppm.

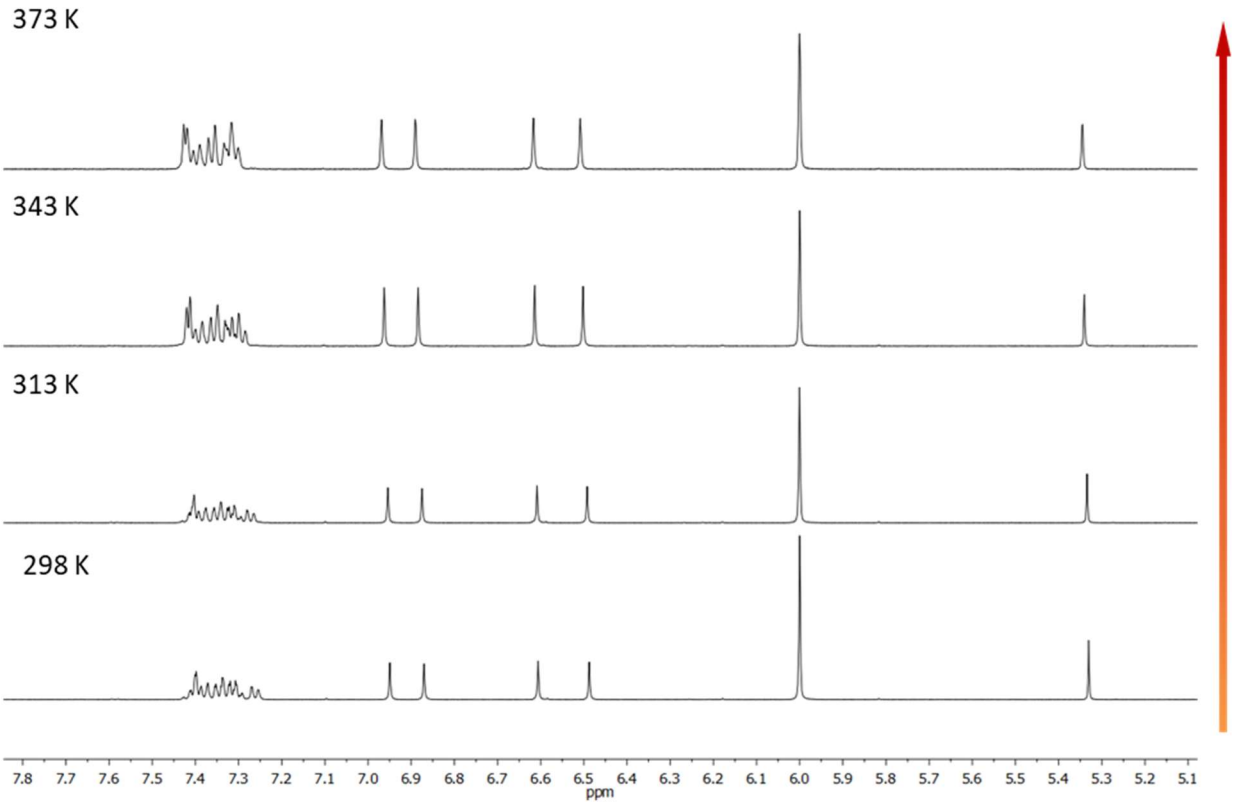


Figure S4. Partial VT ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) spectra of **DBHept-Th**. (From 298 K to 373 K).

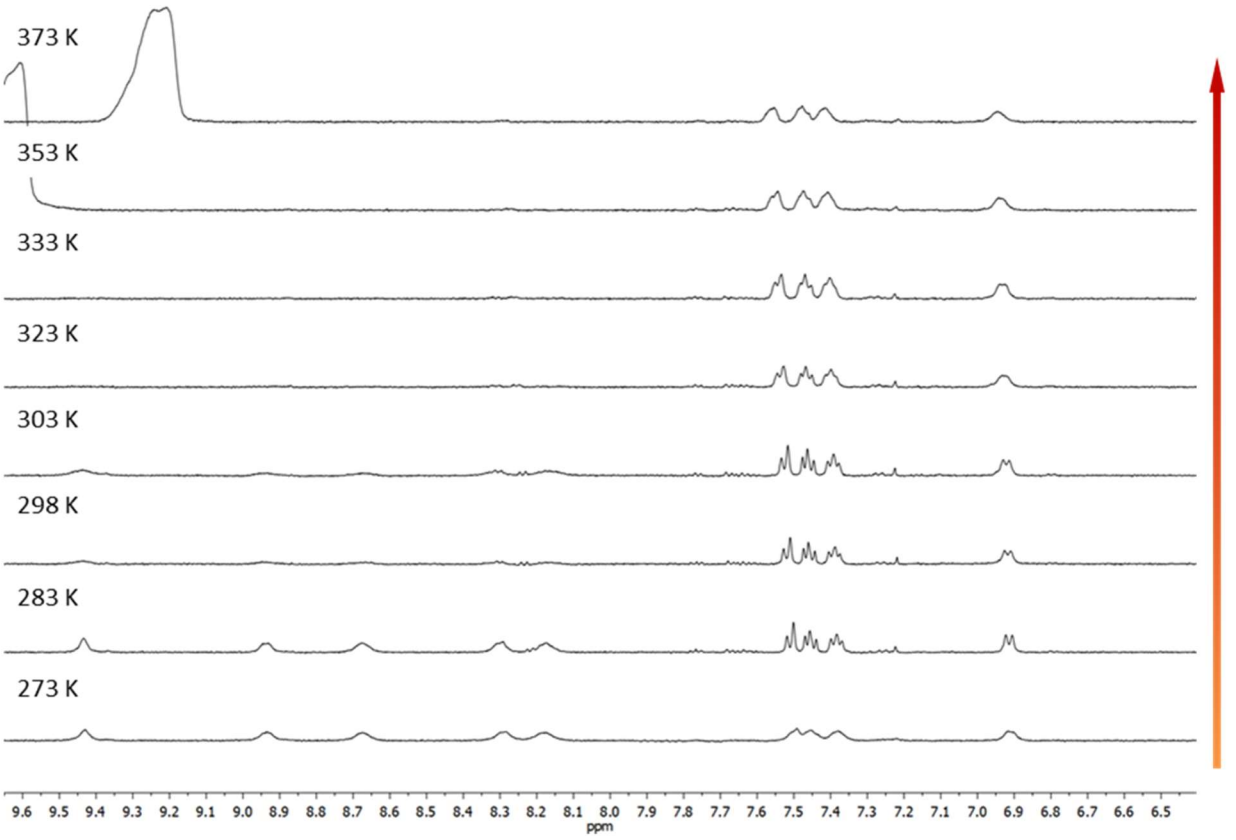


Figure S5. Partial VT ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) spectra of **DBHept-TBC**. (From 273 K to 373 K).

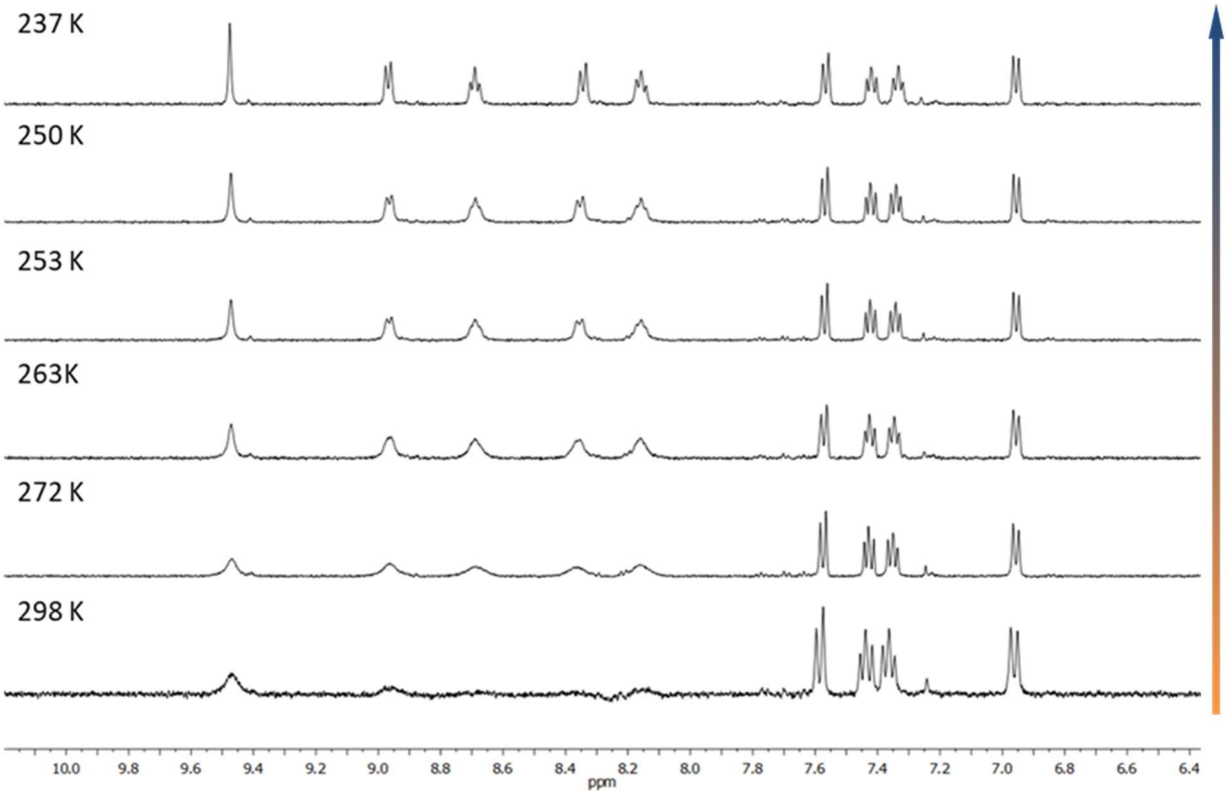


Figure S6. Partial VT ^{1}H NMR (500 MHz, CD_2Cl_2) spectra of **DBHept-TBC**. (From 298 K to 237 K).

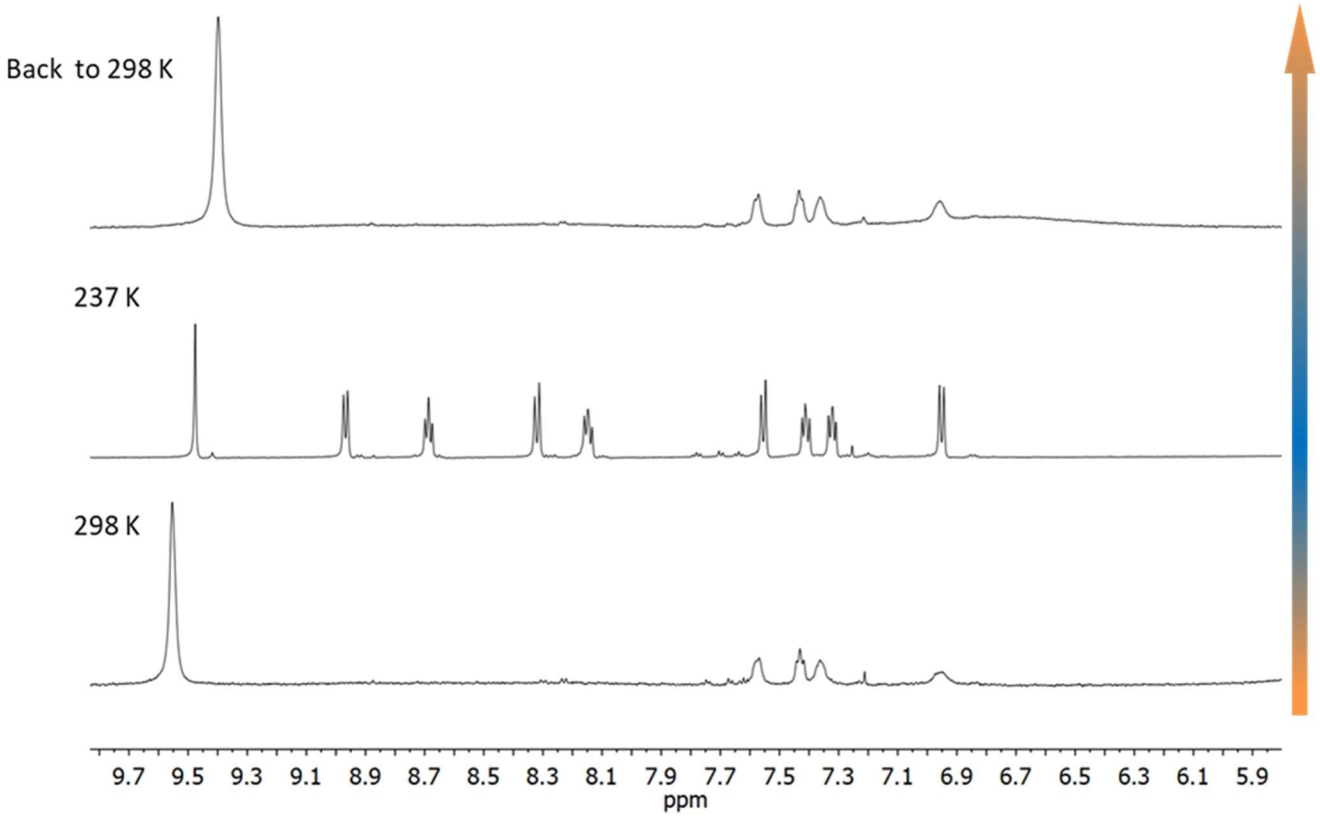


Figure S7. Partial VT ^{1}H NMR (600 MHz, CD_2Cl_2) spectra of **DBHept-TBC**: from 298K to 237 K and back to 298 K.

4. Crystallographic data

Single crystals of suitable quality for X-ray diffraction analysis of **DBHept-Th** and **2** were grown by slow evaporation of solutions of the corresponding compound in a CH_2Cl_2/hexane mixture or in CH_2Cl_2, respectively. X-ray diffraction measurements were carried out on a Bruker D8 Venture diffractometer equipped with a Photon 100 detector using a Mo radiation. The SHELXT[S2] or SIR2014[S3] software was used to solve the structures, which were refined with SHELX 2018[S4] (full-matrix least-squares against F^2 procedure) using the WinGX32[S5] suite. C–H hydrogen atoms were placed in idealized positions (U_{eg}(H) = 1.2U_{eg}(C) or U_{eg}(H) = 1.5U_{eg}(C)) and were allowed to ride on their parent atoms.

2 was refined as a 2-component inversion twin. For **DBHept-Th**, the space group was initially determined as *P*2/*c* in a monoclinic system. However, the ADDSYM tool in PLATON[S6] suggested a *Cmca* symmetry in an orthorrombic system with 100% of confidence. Therefore, the structure was solved again in the *Cmca* group using the SIR2014[S2] software. For this reason, the value of the beta angle in the unit cell was constrained to 90º to fit the requirements of the crystalline group (initially measured as 90.013º. Moreover, after the refinement, there was some density corresponding to what it seemed hexane solvent molecules which could not be modelled and were removed using the SQUEEZE[S7] routine in PLATON, which showed an electron density removed of 119 electrons/cell which fits with approximately 2 molecules of hexane per unit cell. These molecules were included in the formula. The refinement gave a wR_2 of 0.104 while the wR_2 value obtained in the refinement using the *P*2/*c* group was 0.17. Only the *anti*-**DBHept-Th** conformer was present in the unit cell.

The diffraction measurement and refinement data are summarized in Table S1.

CCDC-2012097 (**DBHept-Th**) and CCDC-2012098 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/

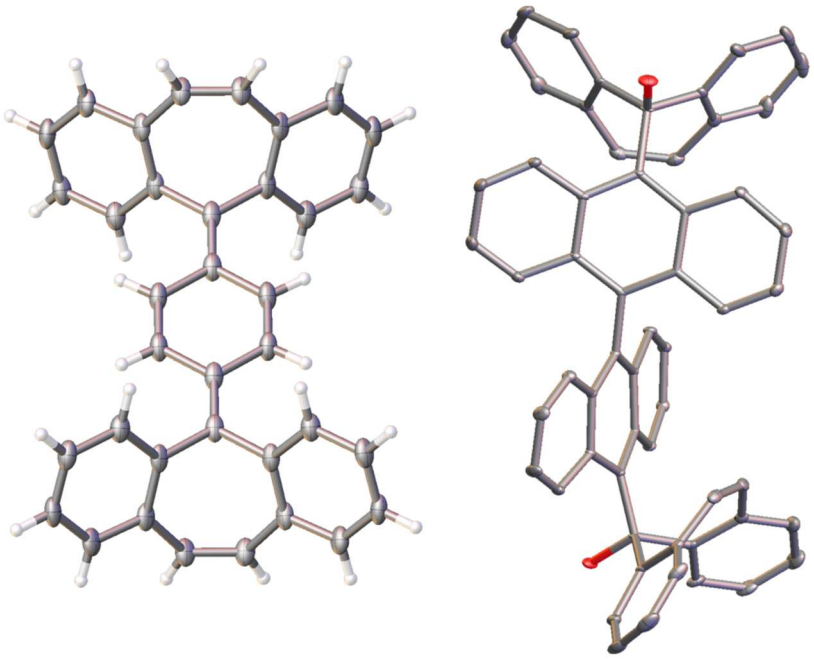


Figure S8. ORTEP-type[S7] representation of the X-ray diffraction structure of **DBHept-Th** (left) and **2** (right) showing the 50% probability thermal ellipsoids: a) Colour code: C: gray, O: red, H: white. Hydrogen atoms for **2** and solvent molecules have been omitted for clarity.

Table S1. Summary of the single-crystal X-ray diffraction measurement and refinement data for **DBHept-Th** and **2**[a]

	DBHept-Th	**2**·CH_2Cl_2
Chemical formula	$C_{9.75}H_{7.75}$[b]	$C_{59}H_{40}Cl_2O_2$
M_r	124.91 [b]	851.81
Crystal size [mm^3]	0.387 × 0.142 × 0.071	0.286 × 0.274 × 0.070
Crystal system	Orthorhombic	Triclinic
Space group	*C m c a*	*P*-1
a [Å]	20.1550(15)	10.9191(6)
b [Å]	4.7512(4)	14.2474(8)
c [Å]	26.999(2)	15.1184(9)
α [°]	90	87.560(2)
β [°]	90	70.753(2)
γ [°]	90	71.905(2)
V [$Å^3$]	2585.4(4)	2106.0(2)
Z	16	2
ρ_{calcd} [Mg m^{-3}]	1.284	1.343
μ [mm^{-1}]	0.072	0.202
F(000)	1060	888
θ range [°]	2.522 to 26.349	2.231 to 28.369
hkl ranges	-25/22,-5/5,-33/33	-14/14,-19/19,-20/20
Reflections collected	12788	54168
Independent reflections	1349	10509
R_{int}	0.0266	0.0534
Completeness [%]	99.8 (*Θ* = 25.242)	99.8 (*Θ* = 25.242)
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0392 wR_2 = 0.1015	R_1 = 0.0669 wR_2 = 0.1845
R indices (all data)	R_1 = 0.0437 wR_2 = 0.1044	R_1 = 0.0849 wR_2 = 0.1951
Goodness-of-fit on F^2	1.089	1.103

[a]In common: Wavelength: 0.71073 Å. Temperature, 100 K. Refinement method, full-matrix least-squares on F^2. Absorption correction: Numerical. [b] Two molecules of hexane per unit cell were included as compatible electron density was removed with SQUEEZE.

5. Optical properties

UV-Vis electronic absorption spectra were obtained at room temperature in an Analitik Jena SPECORD® 200 Plus spectrophotometer equipped with an UV-Vis lamp and working with a double beam configuration. For this purpose, solutions of the compounds in HPLC grade CH_2Cl_2 at *ca.* 1×10^{-6} M and 5×10^{-4} M for **DBHept-Th** and **DBHept-TBC** respectively were used,

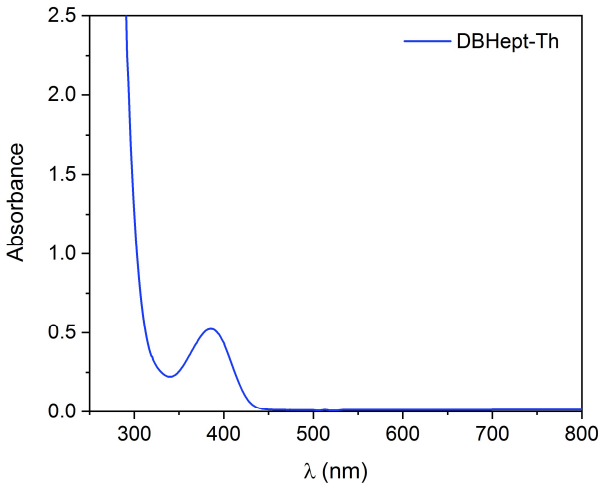


Figure S9. UV-Vis electronic absorption spectrum of **DBHept-Th** (blue) in CH_2Cl_2.

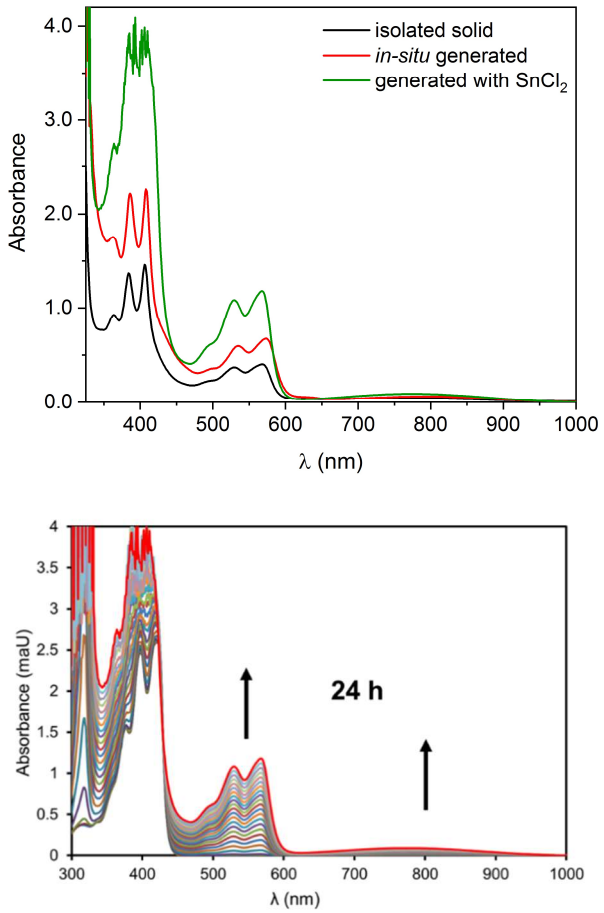


Figure S10. TOP UV-Vis electronic absorption spectra in CH_2Cl_2 of **DBHept-TBC** obtained by different ways: generated by reduction of **2** with $SnCl_2$ (green line); generated *in situ* by reduction of [**DBHept-TBC**]$^{2+}$ with Fc (red line) and as isolated solid by precipitation with Et_2O (black line). **BOTTOM**: Time-evolution (24 h) of the UV-Vis absorption spectra of freshly generated **DBHept-TBC** from **2** (10^{-5} M in CH_2Cl_2) in the presence of excess of $SnCl_2$.

6. Electron Spin Resonance (ESR) measurements

ESR spectra for **DBHept-Th** and **DBHept-TBC** were recorded on a X-Band (9.4 GHz) Bruker ELEXSYS E500 spectrometer equipped with a TE102 microwave cavity, a Bruker variable temperature unit, a field frequency lock system Bruker ER 033 M and a NMR Gaussmeter Bruker ER 035 M. Samples were prepared following the same procedure described in section 2 for the *in situ* generation of **DBHept-TBC** from [**DBHept-TBC**]$^{2+}$ in *o*-DCB-d_4 using 5 equiv. of ferrocene (Fc). Two different concentrations (10^{-4} M and 10^{-3} M in *o*-DCB-d_4) were chosen for the given purpose. In both cases, a temperature range varying from 300 to 400 K was explored, considering the reversibility of the experiments. The signal-to-noise ratio of spectra was increased by accumulation of scans. Precautions to avoid undesirable spectral distortion and line broadenings, such as those arising from microwave power saturation and magnetic field over modulation, were also taken into account to improve sensitivity. All samples were previously degassed with Ar.

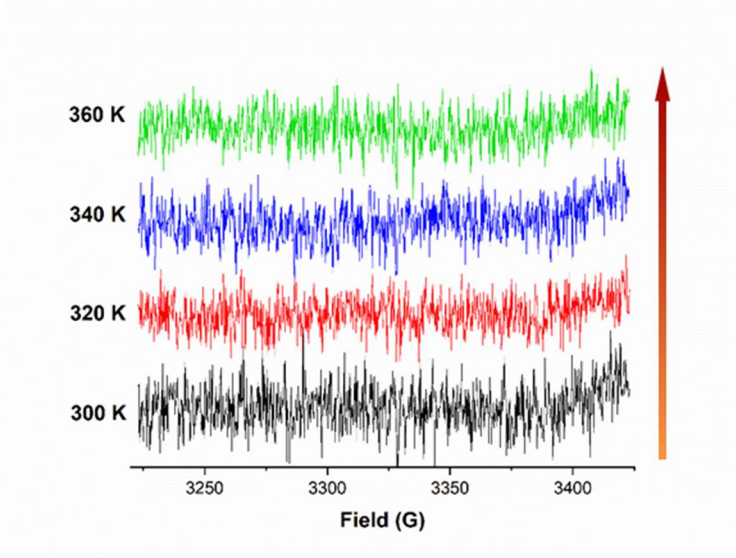


Figure S11. ESR spectra of **DBHept-Th** (in *o*-DCB-d_4 at 10^{-4} M) at different temperatures (from 300 to 360K).

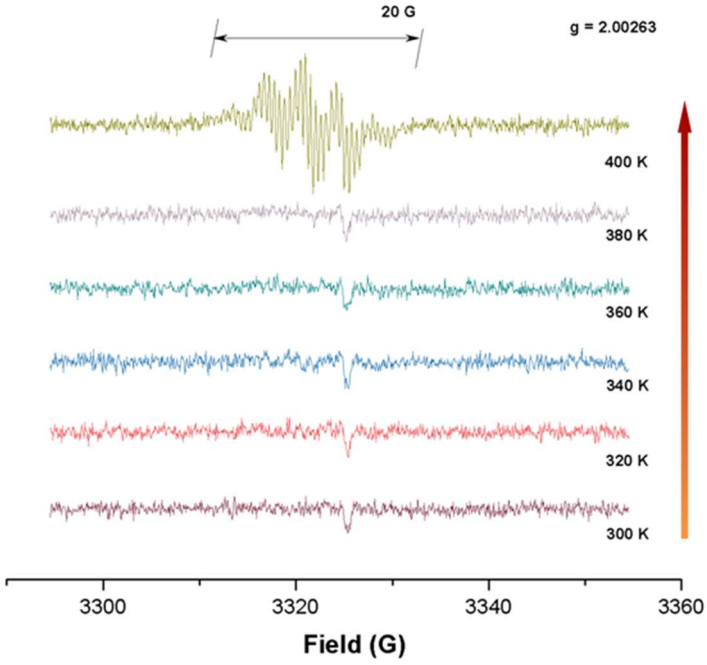


Figure S12. ESR spectra of **DBHept-TBC** (in *o*-DCB-d_4 at 10^{-4} M) at different temperatures (from 300 to 400 K) (first heating cycle).

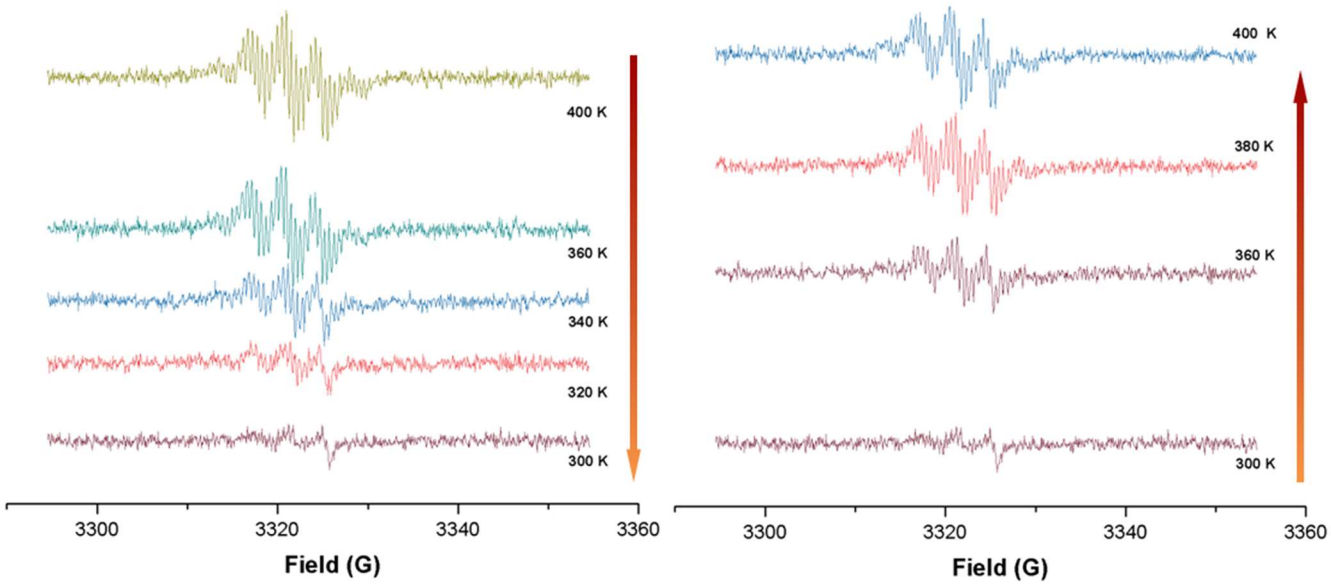


Figure S13. ESR spectra of **DBHept-TBC** (in *o*-DCB-d_4 at 10^{-4} M) at different temperatures: from 400 to 300 K (left), going back to room temperature, and from 300 to 400 K (right) during a second heating process.

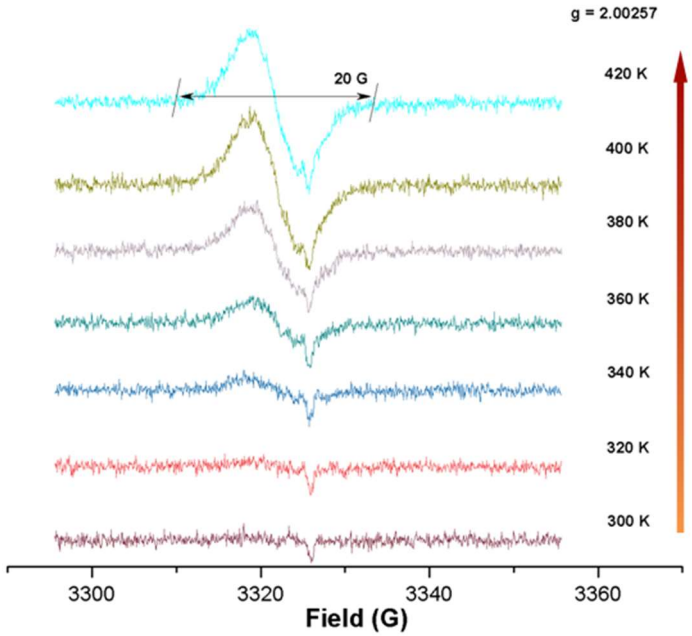


Figure S14. ESR spectra of **DBHept-TBC** (in *o*-DCB-d_4 at 10^{-3} M) at different temperatures (from 300 to 400 K).

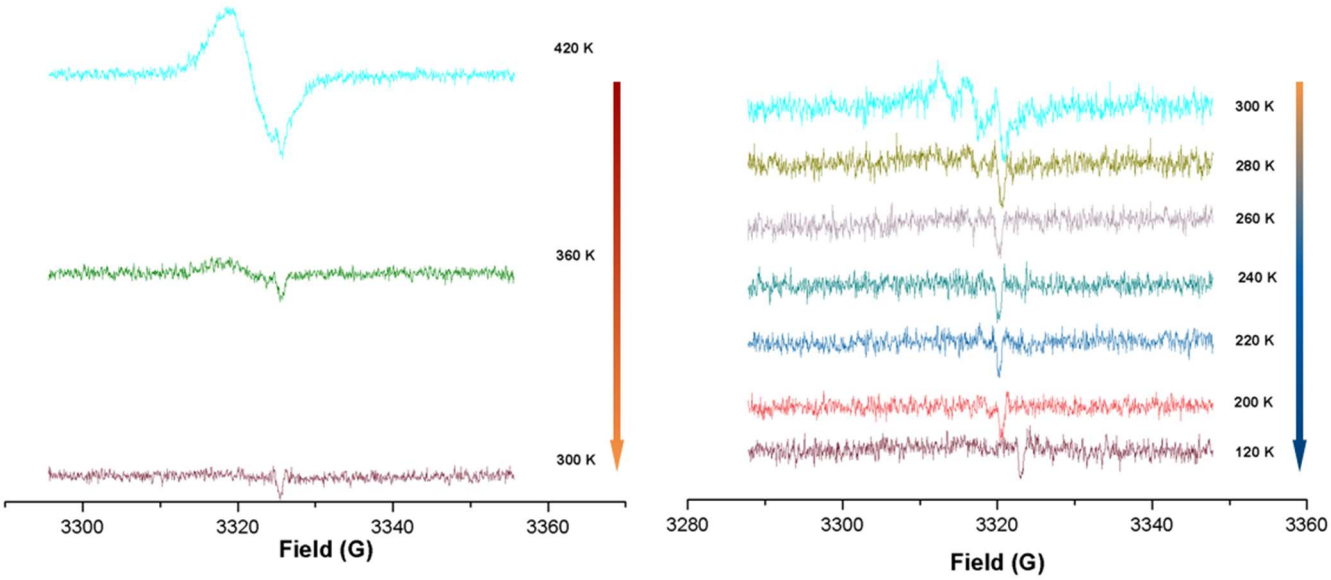


Figure S15. ESR spectra of **DBHept-TBC** (*ca*. 10^{-3} M) at different temperatures: from 420 to 300 K (in *o*-DCB-d_4, left) and from 300 to 120 K (in Toluene/DCM 1:1, right).

Figures S16 and **S17** show the ESR experiments of a solution of the sample of **DBHept-TBC** previously isolated as solid by precipitation with Et_2O. In this case, samples were prepared by redissolving the isolated solid in *o*-DCB at 10^{-4} M.

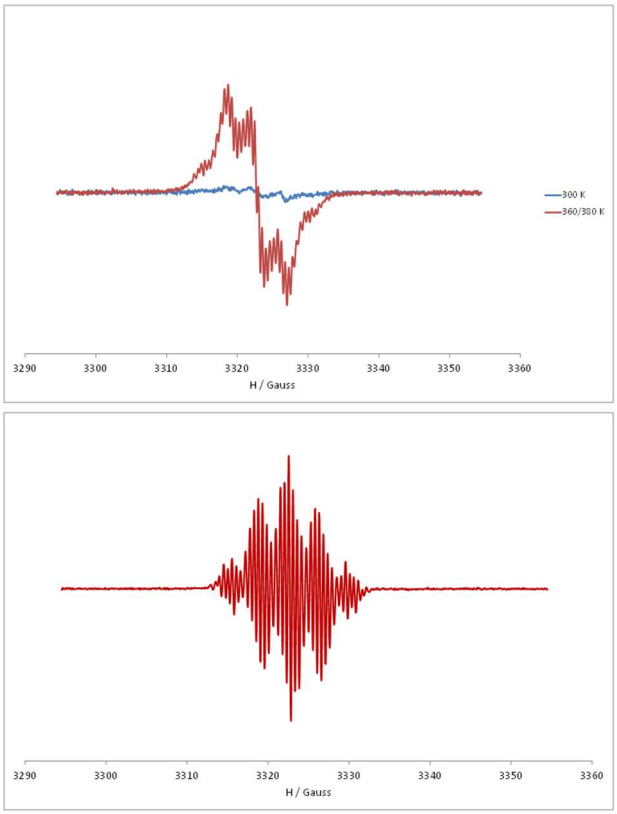


Figure S16. ESR spectra of **DBHept-TBC** (in *o*-DCB-d_4 at 10^{-4} M). Top: from 300 K (blue) to 380 K (red) (first heating cycle). Bottom: well-resolved EPR spectrum at 380 K

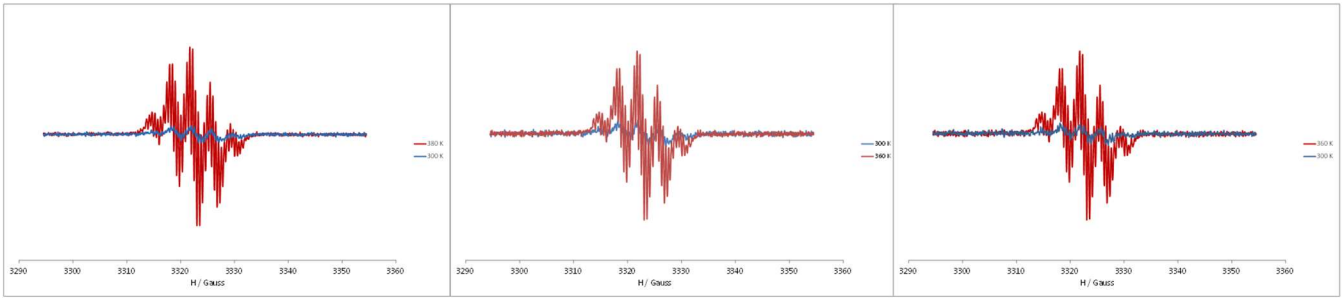


Figure S17. ESR spectra of **DBHept-TBC** (in *o*-DCB-d_4 at 10^{-4} M) at different temperatures: left: from 380 (red) back to 300 K (blue); middle: second cycle from 300 (blue) to 380 K (red); right: second cycle from 380 K (red) back to 300 K (blue).

7. Theoretical calculations

7.1. Geometry optimizations

Gaussian 09[S9] suite of electronic structure programs was used to optimize the geometries of **[DBHept-TBC]$^{2+}$** and the singlet and triplet state of **DBHept-TBC** in its contorted butterfly-like and orthogonal conformations, namely: **DBHept-TBC-CS** (*p*-QDM, contorted butterfly-like geometry singlet closed shell)**, DBHept-TBC-TOS** (orthogonal conformation, triplet open-shell state – Table S5), **DBHept-TBC-SOS** (orthogonal conformation, singlet open-shell state – Table S6), ***syn*-DBHept-Th-CS**, ***anti*-DBHept-Th-CS** and **DBHept-Th-TOS** by density functional theory. The optimizations were carried out at the B3LYP/6-31G(d,p) level of theory in gas phase or dichloromethane as solvent modelled as a polarizable continuum with the integral equation formalism (IEFPCM) model.[S10] The optimized structures were analysed by analytical frequency calculation to demonstrate that they correspond to energy minima. Unrestricted DFT formalism was used for the calculations of the triplet states and broken symmetry (BS) formalism for the calculations of open-shell singlet states. An ultrafine integration grid was used for the calculation of the different **DBHept-Th** structures. The atomic coordinates of the optimized geometries either in solution or in the gas phase are shown in Tables S3-S14. The colour coding used is: C, gray; H, white.

The single point calculations to obtain the energies in Tables S2 and S23 were performed with a set of functionals (B3LYP, BMK, M06-2X, M11L, and PBE0) and cc-pVTZ basis set in gas phase. The final energies are reported as the sum of the electronic energy and the B3LYP/6-31G(d,p) zero-point vibrational energies used without scaling (E_{el} + *ZPVE*, 0K).

CASSCF calculations were performed using Molpro 2012[S11] suite of electronic structure programs for **DBHept-TBC-TOS** (orthogonal conformation, triplet state), **DBHept-TBC-SOS** (orthogonal conformation, open-shell singlet state). The active space of two electrons in two degenerate orbitals (the two SOMOs residing on the end-groups in **DBHept-TBC-TOS**, see Figure S19) were used in connection with 6-31G(d) basis set. The geometries used in these calculations were generated by relaxed potential energy surface scan on geometries obtained by changing **DBHept-TBC-TOS** molecular coordinates along a number of low-frequency vibrational modes from the gas phase B3LYP/6-31G(d,p) D_{2d}–point-group-optimized geometry in Gaussian 09.

Table S2. Energies of individual singlet/triplet states of DBHept-TBC in different (p-QDM or twisted) geometries with respect to the most stable diastereomer of DBHept-TBC-SCS (p-QDM geometry, closed shell singlet).

State	Geometry[a]	Energy[b] (0K, in kcal mol^{-1})				
		B3LYP	BMK	M06-2X	M11L	PBE0
CS, closed-shell singlet	*p*-QDM,[c] diastereomer 1	0	0	0	0	0
CS, closed-shell singlet	*p*-QDM, [c] diastereomer 2	4.7	5.1	5.0	4.8	4.9
CS, closed-shell singlet	*p*-QDM, [c] diastereomer 3	9.4	10.2	10.1	9.7	9.8
TOS, triplet state	Butterfly-like geometry,[c] diastereomer 1	45.1	49.6	52.5	42.7	44.1
TOS, triplet state	Orthogonal geometry[c]	10.6	18.0	24.9	8.0	9.9
SOS, open-shell singlet	Orthogonal geometry[c]	10.8	18.2	25.2	8.3	10.2

[a] The geometries were optimized in gas phase at B3LYP/6-31G(d,p) level of theory. [b] The energies were calculated with the respective functional using cc-pVTZ basis set and the zero-point vibrational energy correction that was used unscaled (*Energy* = E_{el} + *ZPVE*, 0K) with respect to **DBHept-TBC-CS** (Table S7, closed-shell singlet in contorted butterfly-like geometry). [c] Geometries are defined according to Chart 1D, (*p*-QDM: left, orthogonal geometry: right); individual *p*-QDM diastereomers of **DBHept-TBC-CS** (in contorted butterfly-like geometry) are depicted in Figure S18; **DBHept-TBC-TOS** in orthogonal geometry is shown in Table S5; **DBHept-TBC-SOS** in orthogonal geometry is shown in Table S6)

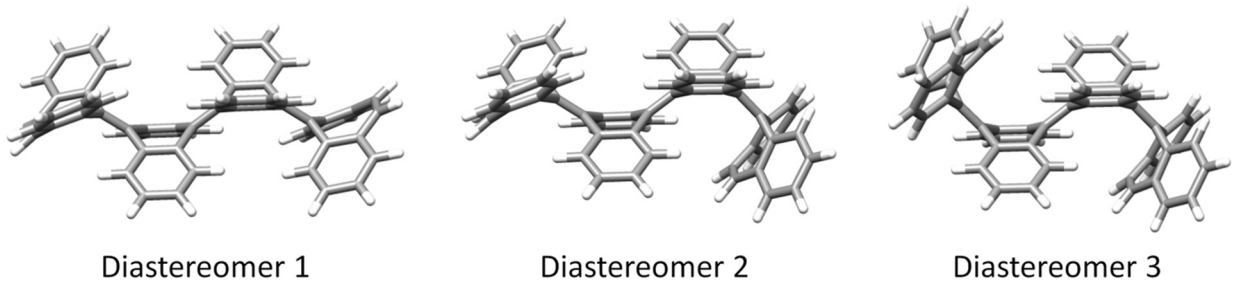


Figure S18. DFT optimized structures of the three different diastereomers considered for **DBHept-TBC-SCS**.

a) DBHept-TBC

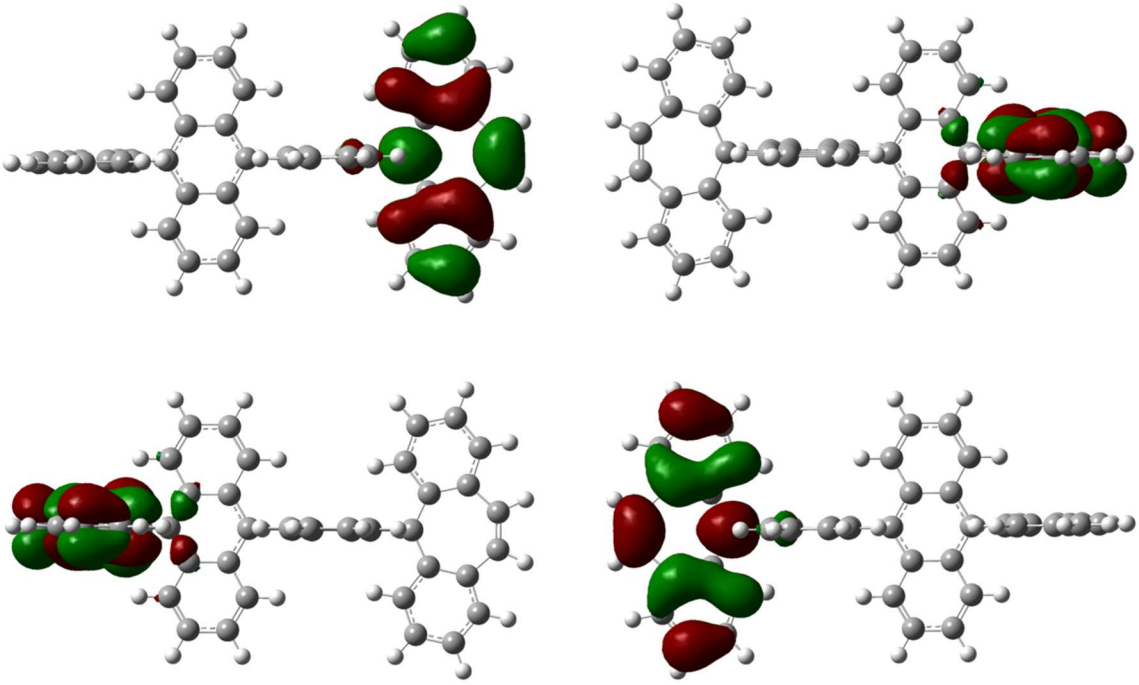


Figure S19. Top (left) and side (right) views of the SOMOs (isovalue = 0.02) (αMO = 192 and 193) for **DBHept-TBC-TOS**.

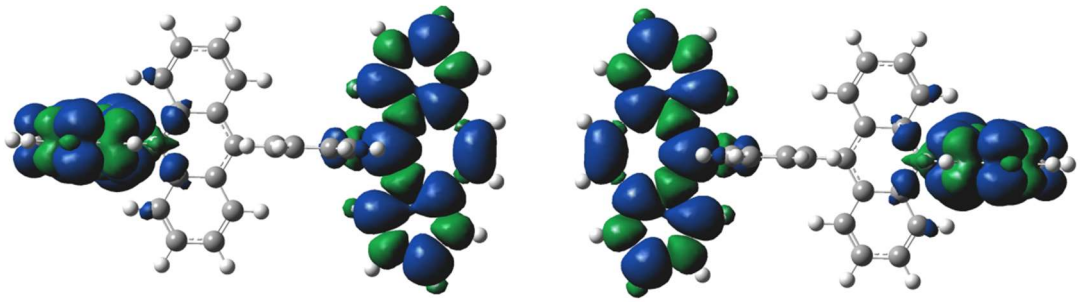
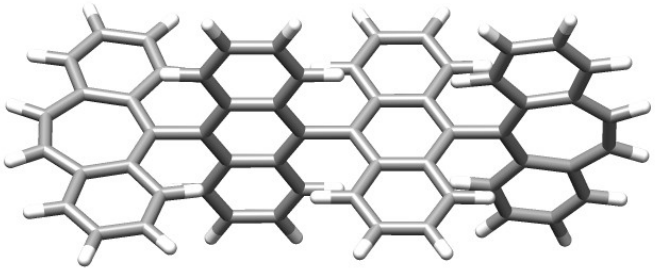


Figure S20. Top (left) and side (right) views of the electron density from the spin SCF density (isovalue = 0.0004) for **DBHept-TBC-TOS**.

Table S3. Atomic coordinates for the optimized structure of **[DBHept-TBC]$^{2+}$** (solution)

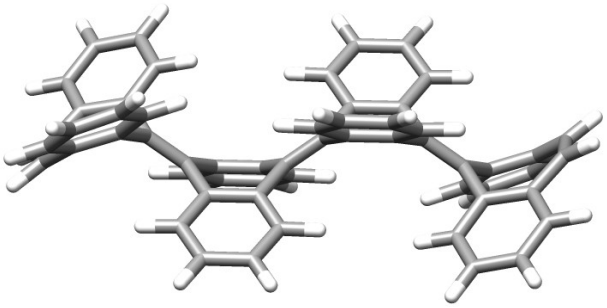


Atom	X	Y	Z
C	5.113022	-0.000050	-0.000037
C	5.717202	0.948482	-0.893469
C	7.136243	1.189118	-1.089669
C	8.209737	0.507247	-0.457648
H	9.195232	0.847986	-0.760707
C	8.209818	-0.506955	0.457415
H	9.195371	-0.847592	0.760396
C	7.136438	-1.188881	1.089583
C	5.717356	-0.948452	0.893427
C	7.544618	-2.195141	2.005201
H	8.608068	-2.363198	2.134660
C	6.644091	-2.947875	2.723311
H	6.995017	-3.707259	3.413888
C	5.264203	-2.719195	2.555413
H	4.542500	-3.300311	3.118670
C	4.826821	-1.758563	1.676142
H	3.763265	-1.610145	1.572127
C	7.544252	2.195525	-2.005191
H	8.607675	2.363741	-2.134654
C	6.643597	2.948254	-2.723142
H	6.994397	3.707775	-3.413631
C	5.263747	2.719355	-2.555236
H	4.541941	3.300426	-3.118406
C	4.826530	1.758547	-1.676084
H	3.762999	1.609923	-1.572101
C	3.598456	-0.000127	0.000013
C	2.902585	-0.860825	-0.875602
C	3.581665	-1.742330	-1.777861
H	4.665758	-1.751782	-1.795560
C	2.888159	-2.572107	-2.617919
H	3.424719	-3.231635	-3.292556
C	1.465778	-2.575589	-2.612553
H	0.928347	-3.238867	-3.282743
C	0.776621	-1.747020	-1.768155
H	-0.306971	-1.753323	-1.769088
C	1.456260	-0.860196	-0.871672
C	0.751246	-0.000227	0.000032
C	1.456215	0.859773	0.871736
C	0.776529	1.746587	1.768188
H	-0.307063	1.752885	1.769068
C	1.465642	2.575207	2.612572
H	0.928173	3.238476	3.282740
C	2.888023	2.571750	2.617994
H	3.424545	3.231320	3.292621
C	3.581573	1.741971	1.777973
H	4.665667	1.751460	1.795683
C	2.902537	0.860470	0.875679
C	-0.751241	-0.000172	-0.000048
C	-1.456321	-0.859999	0.871739
C	-0.776754	-1.746719	1.768379
H	0.306837	-1.753092	1.769331
C	-1.465978	-2.575167	2.612842
H	-0.928600	-3.238391	3.283128
C	-2.888358	-2.571613	2.618167
H	-3.424969	-3.231053	3.292850
C	-3.581796	-1.741893	1.777995
H	-4.665892	-1.751303	1.795640
C	-2.902644	-0.860555	0.875632
C	-3.598449	0.000008	-0.000159
C	-2.902465	0.860511	-0.875873
C	-3.581431	1.742018	-1.778219
H	-4.665522	1.751598	-1.795926
C	-2.887816	2.571666	-2.618314

H	-3.424287	3.231209	-3.293007	H	-8.608120	-2.363372	-2.134334
C	-1.465436	2.575018	-2.612889	C	-6.644166	-2.948007	-2.723098
H	-0.927919	3.238207	-3.283098	H	-6.995115	-3.707451	-3.413596
C	-0.776388	1.746444	-1.768407	C	-5.264276	-2.719275	-2.555305
H	0.307204	1.752665	-1.769279	H	-4.542587	-3.300430	-3.118540
C	-1.456142	0.859737	-0.871898	C	-4.826871	-1.758540	-1.676161
C	-5.113016	0.000153	-0.000145	H	-3.763314	-1.610055	-1.572259
C	-5.717173	0.948682	0.893312	C	-4.826486	1.758871	1.675781
C	-7.136216	1.189115	1.089749	H	-3.762950	1.610457	1.571568
C	-8.209723	0.507081	0.457919	C	-5.263697	2.719620	2.555006
H	-9.195213	0.847649	0.761184	H	-4.541882	3.300822	3.118029
C	-8.209829	-0.507101	-0.457164	C	-6.643552	2.948310	2.723159
H	-9.195389	-0.847869	-0.759978	H	-6.994342	3.707788	3.413700
C	-7.136466	-1.188920	-1.089467	C	-7.544218	2.195463	2.005347
C	-5.717381	-0.948377	-0.893462	H	-8.607644	2.363507	2.135016
C	-7.544668	-2.195240	-2.004998				

Charge = 2; multiplicity = 1; (0 imaginary frequencies)
Zero-point correction = 0.753700 (Hartree/Particle)
Thermal correction to Energy = 0.795934
Thermal correction to Enthalpy = 0.796879
Thermal correction to Gibbs Free Energy = 0.676591
Sum of electronic and zero-point Energies = −2230.819778
Sum of electronic and thermal Energies = −2230.777543
Sum of electronic and thermal Enthalpies = −2230.776599
Sum of electronic and thermal Free Energies = −2230.896886

Table S4. Atomic coordinates for the optimized structure of **DBHept-TBC-SCS** (solution) (contorted butterfly-like geometry)



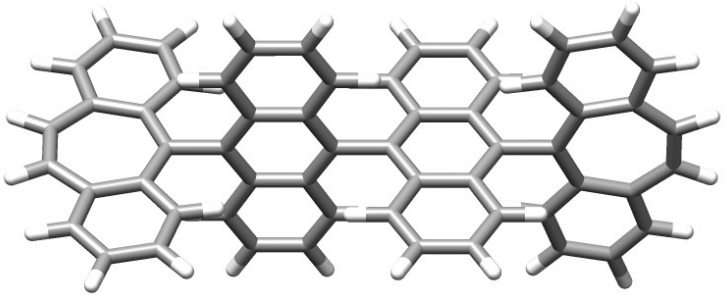
Atom	X	Y	Z	C	-3.283737	-0.000001	0.720593
C	-7.237814	0.676134	0.882525	C	-2.552476	1.227036	1.152278
C	-7.237815	-0.676128	0.882542	C	-2.552474	-1.227023	1.152317
C	-6.439100	-1.570278	0.043087	C	-3.182803	2.317689	1.769816
C	-6.439097	1.570262	0.043048	C	-1.143002	1.223504	1.024642
C	-5.137918	-1.249433	-0.416127	C	-1.142999	-1.223491	1.024683
C	-5.137916	1.249401	-0.416158	C	-3.182799	-2.317652	1.769901
C	-4.458741	-0.000011	0.036833	C	-2.438210	3.389982	2.254836
H	-7.992231	1.167924	1.493764	H	-4.260164	2.311983	1.888900

C	-0.405559	2.303551	1.532502	C	-5.078019	3.322988	-1.693659
C	-0.509592	-0.000001	0.452642	H	-7.984261	3.070959	0.045954
C	-0.405554	-2.303508	1.532607	H	-6.796159	4.615543	-1.478165
H	-4.260160	-2.311943	1.888983	H	-4.553408	3.986983	-2.374043
C	-2.438204	-3.389920	2.254972	H	-7.992233	-1.167902	1.493793
C	-1.045319	3.381463	2.138640	C	-7.000097	-2.807988	-0.332613
H	-2.941658	4.220248	2.741097	C	-4.488822	-2.124527	-1.300624
H	0.676202	2.288970	1.462430	C	-6.335615	-3.674625	-1.192614
C	-1.045312	-3.381396	2.138788	C	-5.078029	-3.323049	-1.693580
H	0.676208	-2.288921	1.462550	H	-7.984269	-3.070971	0.046028
H	-2.941651	-4.220166	2.741269	H	-6.796173	-4.615594	-1.478055
H	-0.457987	4.204207	2.535363	H	-4.553421	-3.987062	-2.373950
H	-0.457977	-4.204117	2.535557	H	-3.502636	-1.858474	-1.667656
C	0.509592	-0.000002	-0.452642	C	4.458741	-0.000009	-0.036834
C	1.143000	-1.223491	-1.024682	C	5.137917	-1.249432	0.416127
C	1.143001	1.223504	-1.024643	C	5.137917	1.249402	0.416158
C	0.405556	-2.303509	-1.532605	C	6.439098	-1.570280	-0.043088
C	2.552475	-1.227022	-1.152316	C	4.488819	-2.124525	1.300623
C	2.552476	1.227037	-1.152279	C	6.439099	1.570260	-0.043047
C	0.405557	2.303550	-1.532503	C	4.488819	2.124475	1.300674
C	1.045315	-3.381397	-2.138786	C	7.237814	-0.676130	-0.882543
H	-0.676206	-2.288923	-1.462548	C	7.000092	-2.807991	0.332610
C	3.182801	-2.317651	-1.769899	C	5.078024	-3.323049	1.693579
C	3.283737	0.000001	-0.720593	C	7.237815	0.676132	-0.882525
C	3.182801	2.317690	-1.769819	C	7.000094	2.807961	0.332683
H	-0.676204	2.288968	-1.462430	H	3.502632	1.858412	1.667698
C	1.045316	3.381462	-2.138642	C	5.078024	3.322989	1.693660
C	2.438207	-3.389920	-2.254969	H	7.992232	-1.167905	-1.493794
H	0.457981	-4.204119	-2.535554	C	6.335609	-3.674627	1.192611
H	4.260162	-2.311942	-1.888980	H	7.984264	-3.070976	-0.046031
C	2.438207	3.389982	-2.254839	H	4.553415	-3.987061	2.373948
H	4.260162	2.311984	-1.888903	H	7.992233	1.167922	-1.493764
H	0.457983	4.204206	-2.535365	C	6.335611	3.674577	1.192704
H	2.941654	-4.220167	-2.741265	H	7.984267	3.070954	-0.045951
H	2.941654	4.220249	-2.741101	H	4.553414	3.986984	2.374044
C	-4.488816	2.124473	-1.300674	H	6.796165	-4.615597	1.478052
C	-7.000089	2.807964	-0.332681	H	6.796167	4.615539	1.478168
H	-3.502629	1.858409	-1.667698	H	3.502634	-1.858470	1.667655
C	-6.335604	3.674579	-1.192702				

Charge = 0; multiplicity = 1; (0 imaginary frequencies)
Zero-point correction = 0.749691 (Hartree/Particle)

Thermal correction to Energy = 0.791883
Thermal correction to Enthalpy = 0.792827
Thermal correction to Gibbs Free Energy = 0.673756
Sum of electronic and zero-point Energies = −2231.157575
Sum of electronic and thermal Energies = −2231.115383
Sum of electronic and thermal Enthalpies = −2231.114439
Sum of electronic and thermal Free Energies = −2231.233511

Table S5. Atomic coordinates for the optimized structure of **DBHept-TBC-TOS** (solution) (orthogonal geometry)

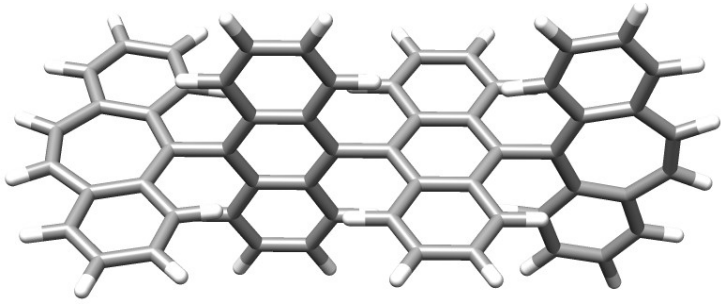


Atom	X	Y	Z
C	5.129924	0.000001	-0.000004
C	5.739978	0.934829	0.935139
C	7.146854	1.155715	1.156017
C	8.233236	0.476765	0.476830
H	9.218453	0.802764	0.802873
C	8.233227	-0.476747	-0.476918
H	9.218439	-0.802725	-0.803000
C	7.146833	-1.155722	-1.156058
C	5.739961	-0.934843	-0.935147
C	7.559774	-2.108422	-2.108993
H	8.627383	-2.250590	-2.251158
C	6.669472	-2.861493	-2.862304
H	7.031576	-3.584783	-3.585769
C	5.301686	-2.660955	-2.661803
H	4.571332	-3.229132	-3.230192
C	4.863192	-1.731308	-1.731917
H	3.796592	-1.609270	-1.609916
C	7.559814	2.108402	2.108957
H	8.627426	2.250574	2.251095
C	6.669527	2.861453	2.862304
H	7.031645	3.584733	3.585773
C	5.301737	2.660913	2.661833
H	4.571394	3.229076	3.230248
C	4.863224	1.731280	1.731941
H	3.796622	1.609240	1.609964
C	3.618284	0.000008	-0.000004
C	2.907111	0.863778	-0.863394
C	3.586687	1.756038	-1.755256
H	4.670870	1.757926	-1.757159
C	2.897651	2.593131	-2.591926
H	3.435934	3.260149	-3.258625
C	1.474449	2.593754	-2.592508
H	0.937484	3.261338	-3.259756
C	0.782916	1.757721	-1.756868
H	-0.301120	1.761856	-1.760960
C	1.460399	0.864412	-0.864013
C	0.750891	0.000025	-0.000012
C	1.460384	-0.864370	0.863993
C	0.782885	-1.757674	1.756841
H	-0.301152	-1.761796	1.760926
C	1.474402	-2.593716	2.592483
H	0.937426	-3.261295	3.259727
C	2.897605	-2.593111	2.591910
H	3.435876	-3.260136	3.258611
C	3.586656	-1.756025	1.755245
H	4.670839	-1.757926	1.757155
C	2.907096	-0.863754	0.863382
C	-0.750890	0.000030	-0.000017
C	-1.460390	-0.864055	-0.864326
C	-0.782898	-1.757034	-1.757505
H	0.301139	-1.761147	-1.761606
C	-1.474422	-2.592770	-2.593448
H	-0.937450	-3.260105	-3.260940

C	-2.897624	-2.592171	-2.592857	C	-8.233259	0.476768	-0.476705
H	-3.435900	-3.258949	-3.259802	H	-9.218493	0.802797	-0.802669
C	-3.586669	-1.755399	-1.755873	C	-7.146912	1.156012	-1.155653
H	-4.670852	-1.757297	-1.757778	C	-5.740023	0.935112	-0.934865
C	-2.907102	-0.863443	-0.863700	C	-7.559927	2.108994	-2.108274
C	-3.618284	0.000034	-0.000024	H	-8.627547	2.251162	-2.250355
C	-2.907103	0.863491	0.863674	C	-6.669684	2.862330	-2.861389
C	-3.586672	1.755427	1.755866	H	-7.031844	3.585833	-3.584612
H	-4.670855	1.757322	1.757772	C	-5.301883	2.661781	-2.661004
C	-2.897630	2.592186	2.592864	H	-4.571574	3.230158	-3.229249
H	-3.435907	3.258951	3.259821	C	-4.863316	1.731865	-1.731421
C	-1.474427	2.592790	2.593454	H	-3.796708	1.609833	-1.609505
H	-0.937457	3.260114	3.260958	C	-4.863101	-1.731736	1.731426
C	-0.782902	1.757071	1.757495	H	-3.796508	-1.609589	1.609466
H	0.301135	1.761184	1.761598	C	-5.301542	-2.661665	2.661055
C	-1.460392	0.864107	0.864300	H	-4.571155	-3.229944	3.229298
C	-5.129925	0.000015	-0.000011	C	-6.669317	-2.862351	2.861485
C	-5.739918	-0.935106	0.934876	H	-7.031380	-3.585867	3.584744
C	-7.146776	-1.156147	1.155700	C	-7.559663	-2.109140	2.108365
C	-8.233205	-0.477050	0.476736	H	-8.627264	-2.251423	2.250476
H	-9.218400	-0.803205	0.802690				

Charge = 0; multiplicity = 3; (0 imaginary frequencies)
Zero-point correction = 0.748478 (Hartree/Particle)
Thermal correction to Energy = 0.790982
Thermal correction to Enthalpy = 0.791926
Thermal correction to Gibbs Free Energy = 0.668965
Sum of electronic and zero-point Energies = −2231.142438
Sum of electronic and thermal Energies = −2231.099934
Sum of electronic and thermal Enthalpies = −2231.098990
Sum of electronic and thermal Free Energies = −2231.221951

Table S6. Atomic coordinates for the optimized structure of **DBHept-TBC-SOS** (gas phase) (orthogonal geometry)



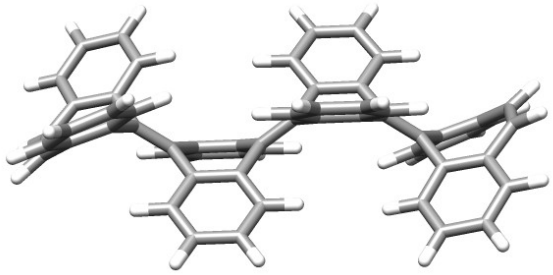
Atom	X	Y	Z	H	0.803081	-0.802935	-9.217529
C	0.000000	0.000000	-5.130112	C	-0.476643	0.476558	-8.232270
C	0.934824	-0.934711	-5.740419	H	-0.803081	0.802935	-9.217529
C	1.155815	-1.155638	-7.146807	C	-1.155815	1.155638	-7.146807
C	0.476643	-0.476558	-8.232270	C	-0.934824	0.934711	-5.740419

C	-2.108248	2.107919	-7.559084	C	-1.756876	1.756895	0.783525
H	-2.250092	2.249714	-8.626967	H	-1.759850	1.759852	-0.300347
C	-2.861203	2.860789	-6.669356	C	-2.592065	2.592107	1.475277
H	-3.584753	3.584223	-7.031443	H	-3.259522	3.259564	0.938065
C	-2.660456	2.660119	-5.302370	C	-2.591464	2.591532	2.897761
H	-3.228707	3.228319	-4.571766	H	-3.258274	3.258366	3.436426
C	-1.731134	1.730940	-4.863967	C	-1.755221	1.755283	3.587015
H	-1.607805	1.607666	-3.797866	H	-1.756283	1.756365	4.671051
C	2.108248	-2.107919	-7.559084	C	-0.863580	0.863609	2.907356
H	2.250092	-2.249714	-8.626967	C	0.000000	0.000000	3.618369
C	2.861203	-2.860789	-6.669356	C	0.863580	-0.863609	2.907356
H	3.584753	-3.584223	-7.031443	C	1.755221	-1.755283	3.587015
C	2.660456	-2.660119	-5.302370	H	1.756283	-1.756365	4.671051
H	3.228707	-3.228319	-4.571766	C	2.591464	-2.591532	2.897761
C	1.731134	-1.730940	-4.863967	H	3.258274	-3.258366	3.436426
H	1.607805	-1.607666	-3.797866	C	2.592065	-2.592107	1.475277
C	0.000000	0.000000	-3.618369	H	3.259522	-3.259564	0.938065
C	0.863580	0.863609	-2.907356	C	1.756876	-1.756895	0.783525
C	1.755221	1.755283	-3.587015	H	1.759850	-1.759852	-0.300347
H	1.756283	1.756365	-4.671051	C	0.864129	-0.864147	1.460749
C	2.591464	2.591532	-2.897761	C	0.000000	0.000000	5.130112
H	3.258274	3.258366	-3.436426	C	-0.934824	-0.934711	5.740419
C	2.592065	2.592107	-1.475277	C	-1.155815	-1.155638	7.146807
H	3.259522	3.259564	-0.938065	C	-0.476643	-0.476558	8.232270
C	1.756876	1.756895	-0.783525	H	-0.803081	-0.802935	9.217529
H	1.759850	1.759852	0.300347	C	0.476643	0.476558	8.232270
C	0.864129	0.864147	-1.460749	H	0.803081	0.802935	9.217529
C	0.000000	0.000000	-0.751020	C	1.155815	1.155638	7.146807
C	-0.864129	-0.864147	-1.460749	C	0.934824	0.934711	5.740419
C	-1.756876	-1.756895	-0.783525	C	2.108248	2.107919	7.559084
H	-1.759850	-1.759852	0.300347	H	2.250092	2.249714	8.626967
C	-2.592065	-2.592107	-1.475277	C	2.861203	2.860789	6.669356
H	-3.259522	-3.259564	-0.938065	H	3.584753	3.584223	7.031443
C	-2.591464	-2.591532	-2.897761	C	2.660456	2.660119	5.302370
H	-3.258274	-3.258366	-3.436426	H	3.228707	3.228319	4.571766
C	-1.755221	-1.755283	-3.587015	C	1.731134	1.730940	4.863967
H	-1.756283	-1.756365	-4.671051	H	1.607805	1.607666	3.797866
C	-0.863580	-0.863609	-2.907356	C	-1.731134	-1.730940	4.863967
C	0.000000	0.000000	0.751020	H	-1.607805	-1.607666	3.797866
C	-0.864129	0.864147	1.460749	C	-2.660456	-2.660119	5.302370

H	-3.228707	-3.228319	4.571766	C	-2.108248	-2.107919	7.559084
C	-2.861203	-2.860789	6.669356	H	-2.250092	-2.249714	8.626967
H	-3.584753	-3.584223	7.031443				

Charge = 0; multiplicity = 1
Energy = −2231.88003229 Hartree

Table S7. Atomic coordinates for the optimized structure of **DBHept-TBC-SCS** (diastereomer 1, gas phase)

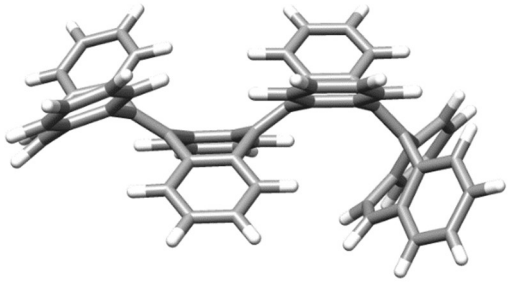


Atom	X	Y	Z	H	1.425735	0.721693	-2.292827
C	1.106902	-7.210738	-0.675768	H	2.823815	-2.851328	-4.224825
C	1.106902	-7.210738	0.675768	H	2.532867	-0.376730	4.210635
C	0.247454	-6.435475	1.570504	H	2.532867	-0.376730	-4.210635
C	0.247454	-6.435475	-1.570504	C	-0.469040	0.494738	0.000000
C	-0.247449	-5.147858	1.249766	C	-1.059981	1.109510	-1.223697
C	-0.247449	-5.147858	-1.249766	C	-1.059981	1.109510	1.223697
C	0.183789	-4.455438	0.000000	C	-1.537444	0.356559	-2.306212
H	1.739111	-7.948136	-1.167459	C	-1.234840	2.513526	-1.227135
C	0.828645	-3.258521	0.000000	C	-1.234840	2.513526	1.227135
C	1.234840	-2.513526	1.227135	C	-1.537444	0.356559	2.306212
C	1.234840	-2.513526	-1.227135	C	-2.160777	0.976348	-3.385075
C	1.869087	-3.123518	2.319096	H	-1.425735	-0.721693	-2.292827
C	1.059981	-1.109510	1.223697	C	-1.869087	3.123518	-2.319096
C	1.059981	-1.109510	-1.223697	C	-0.828645	3.258521	0.000000
C	1.869087	-3.123518	-2.319096	C	-1.869087	3.123518	2.319096
C	2.324443	-2.363734	3.392756	H	-1.425735	-0.721693	2.292827
H	2.022849	-4.196327	2.312996	C	-2.160777	0.976348	3.385075
C	1.537444	-0.356559	2.306212	C	-2.324443	2.363734	-3.392756
C	0.469040	-0.494738	0.000000	H	-2.532867	0.376730	-4.210635
C	1.537444	-0.356559	-2.306212	H	-2.022849	4.196327	-2.312996
H	2.022849	-4.196327	-2.312996	C	-2.324443	2.363734	3.392756
C	2.324443	-2.363734	-3.392756	H	-2.022849	4.196327	2.312996
C	2.160777	-0.976348	3.385075	H	-2.532867	0.376730	4.210635
H	2.823815	-2.851328	4.224825	H	-2.823815	2.851328	-4.224825
H	1.425735	0.721693	2.292827	H	-2.823815	2.851328	4.224825
C	2.160777	-0.976348	-3.385075	C	-1.146851	-4.523805	-2.127104

C	-0.110516	-7.005766	-2.808429	C	-0.247454	6.435475	1.570504
H	-1.539792	-3.547659	-1.861159	C	1.146851	4.523805	2.127104
C	-0.985497	-6.365260	-3.676874	C	-1.106902	7.210738	-0.675768
C	-1.520448	-5.122409	-3.326357	C	0.110516	7.005766	-2.808429
H	0.293755	-7.980379	-3.069549	C	1.520448	5.122409	-3.326357
H	-1.256576	-6.833526	-4.618435	C	-1.106902	7.210738	0.675768
H	-2.212693	-4.615730	-3.992149	C	0.110516	7.005766	2.808429
H	1.739111	-7.948136	1.167459	H	1.539792	3.547659	1.861159
C	-0.110516	-7.005766	2.808429	C	1.520448	5.122409	3.326357
C	-1.146851	-4.523805	2.127104	H	-1.739111	7.948136	-1.167459
C	-0.985497	-6.365260	3.676874	C	0.985497	6.365260	-3.676874
C	-1.520448	-5.122409	3.326357	H	-0.293755	7.980379	-3.069549
H	0.293755	-7.980379	3.069549	H	2.212693	4.615730	-3.992149
H	-1.256576	-6.833526	4.618435	H	-1.739111	7.948136	1.167459
H	-2.212693	-4.615730	3.992149	C	0.985497	6.365260	3.676874
H	-1.539792	-3.547659	1.861159	H	-0.293755	7.980379	3.069549
C	-0.183789	4.455438	0.000000	H	2.212693	4.615730	3.992149
C	0.247449	5.147858	-1.249766	H	1.256576	6.833526	-4.618435
C	0.247449	5.147858	1.249766	H	1.256576	6.833526	4.618435
C	-0.247454	6.435475	-1.570504	H	1.539792	3.547659	-1.861159
C	1.146851	4.523805	-2.127104				

Charge = 0; multiplicity = 1

Table S8. Atomic coordinates for the optimized structure of **DBHept-TBC-SCS** (diastereomer 2, gas phase)

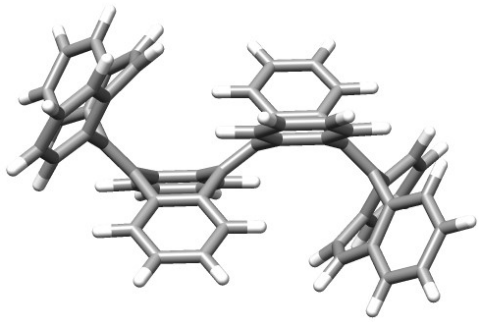


Atom	X	Y	Z	C	2.207085	1.227898	-1.043057
C	6.902918	0.675696	-1.217016	C	2.207028	-1.227816	-1.043195
C	6.902886	-0.675820	-1.217090	C	2.774547	2.321143	-1.713536
C	6.184263	-1.570607	-0.309822	C	0.816908	1.223804	-0.780705
C	6.184337	1.570418	-0.309650	C	0.816847	-1.223685	-0.780852
C	4.930998	-1.249870	0.266611	C	2.774443	-2.320991	-1.713831
C	4.931057	1.249678	0.266748	C	1.985502	3.393665	-2.119671
C	4.212302	-0.000058	-0.119106	H	3.835587	2.317380	-1.934506
H	7.598223	1.167413	-1.895242	C	0.031634	2.303142	-1.211212
C	2.976372	0.000003	-0.685739	C	0.241870	0.000041	-0.152870

C	0.031513	-2.302875	-1.211628	H	7.723108	3.069445	-0.455160
H	3.835486	-2.317251	-1.934782	H	6.677826	4.618800	1.164922
C	1.985344	-3.393394	-2.120170	H	4.525513	3.992974	2.260842
C	0.610682	3.383079	-1.871322	H	7.598168	-1.167496	-1.895369
H	2.439825	4.227091	-2.647494	C	6.776259	-2.808658	0.010478
H	-1.038447	2.283303	-1.038505	C	4.365736	-2.127715	1.203605
C	0.610512	-3.382740	-1.871897	C	6.193028	-3.677449	0.924291
H	-1.038579	-2.282977	-1.039004	C	4.986885	-3.327163	1.537660
H	2.439629	-4.226758	-2.648123	H	7.722964	-3.069690	-0.455494
H	-0.012256	4.207525	-2.205827	H	6.677610	-4.619171	1.164422
H	-0.012475	-4.207073	-2.206591	H	4.525328	-3.993360	2.260412
C	-0.688662	0.000068	0.841758	H	3.416340	-1.862185	1.657598
C	-1.274496	-1.223537	1.462414	C	-4.478417	0.000000	0.425662
C	-1.274512	1.223773	1.462180	C	-5.043483	-1.238398	-0.189644
C	-0.504192	-2.303001	1.912975	C	-5.043500	1.238270	-0.189886
C	-2.672130	-1.225890	1.689024	C	-4.644159	-1.566984	-1.509064
C	-2.672143	1.226154	1.688794	C	-5.957737	-2.064691	0.475620
C	-0.504225	2.303386	1.912409	C	-4.644184	1.566602	-1.509372
C	-1.100916	-3.380745	2.563249	C	-5.957767	2.064678	0.475215
H	0.568799	-2.291305	1.757261	C	-3.824525	-0.677078	-2.334220
C	-3.256293	-2.311223	2.351795	C	-5.089067	-2.782492	-2.063773
C	-3.410273	0.000087	1.261710	C	-6.421241	-3.241784	-0.108138
C	-3.256313	2.311623	2.351336	C	-3.824536	0.676546	-2.334354
H	0.568757	2.291697	1.756623	C	-5.089111	2.781993	-2.064320
C	-1.100959	3.381267	2.562448	H	-6.300290	1.780218	1.465690
C	-2.479124	-3.386118	2.780992	C	-6.421291	3.241649	-0.108774
H	-0.488256	-4.206512	2.912925	H	-3.239567	-1.168871	-3.109362
H	-4.319883	-2.303530	2.553755	C	-5.967476	-3.612106	-1.376682
C	-2.479157	3.386638	2.780259	H	-4.757120	-3.054196	-3.062511
H	-4.319900	2.303957	2.553314	H	-7.120454	-3.874783	0.430193
H	-0.488315	4.207147	2.911886	H	-3.239587	1.168195	-3.109593
H	-2.947945	-4.216137	3.301355	C	-5.967533	3.611729	-1.377391
H	-2.947984	4.216769	3.300436	H	-4.757171	3.053506	-3.063112
C	4.365835	2.127449	1.203834	H	-7.120514	3.874743	0.429433
C	6.776391	2.808407	0.010784	H	-6.308251	-4.537540	-1.831386
H	3.416426	1.861915	1.657797	H	-6.308323	4.537068	-1.832277
C	6.193200	3.677127	0.924690	H	-6.300264	-1.780042	1.466039
C	4.987040	3.326832	1.538019				

Charge = 0; multiplicity = 1

Table S9. Atomic coordinates for the optimized structure of **DBHept-TBC-SCS** (diastereomer 3, gas phase)

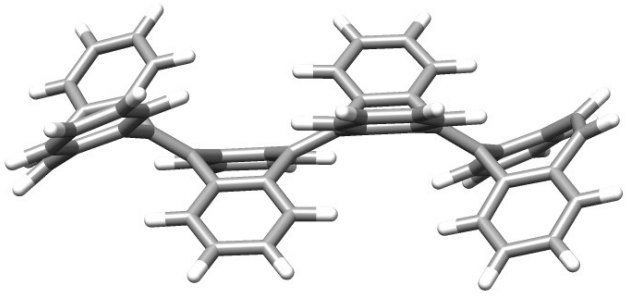


Atom	X	Y	Z
C	0.000021	-4.494852	-0.676811
C	0.000021	-4.494852	0.676811
C	-1.151387	-4.658590	1.566745
C	-1.151387	-4.658590	-1.566745
C	-2.447771	-4.189884	1.238137
C	-2.447771	-4.189884	-1.238137
C	-2.603337	-3.368722	0.000000
H	0.971164	-4.490016	-1.168529
C	-2.634948	-2.012656	0.000000
C	-2.536810	-1.165611	-1.226713
C	-2.536810	-1.165611	1.226713
C	-3.415950	-1.238376	-2.313133
C	-1.521926	-0.178546	-1.223684
C	-1.521926	-0.178546	1.223684
C	-3.415950	-1.238376	2.313133
C	-3.295747	-0.356774	-3.386624
H	-4.212451	-1.971646	-2.307675
C	-1.423143	0.712358	-2.299971
C	-0.675717	-0.079092	0.000000
C	-1.423143	0.712358	2.299971
H	-4.212451	-1.971646	2.307675
C	-3.295747	-0.356774	3.386624
C	-2.300418	0.621232	-3.378489
H	-3.991834	-0.422479	-4.217746
H	-0.662522	1.484934	-2.281909
C	-2.300418	0.621232	3.378489
H	-0.662522	1.484934	2.281909
H	-3.991834	-0.422479	4.217746
H	-2.215981	1.323075	-4.203043
H	-2.215981	1.323075	4.203043
C	0.675659	0.079078	0.000000
C	1.521866	0.178534	1.223676
C	1.521866	0.178534	-1.223676
C	1.423080	-0.712366	2.299966
C	2.536749	1.165599	1.226706
C	2.536749	1.165599	-1.226706
C	1.423080	-0.712366	-2.299966
C	2.300349	-0.621232	3.378488
H	0.662460	-1.484944	2.281904
C	3.415881	1.238376	2.313132
C	2.634895	2.012640	0.000000
C	3.415881	1.238376	-2.313132
H	0.662460	-1.484944	-2.281904
C	2.300349	-0.621232	-3.378488
C	3.295674	0.356778	3.386625
H	2.215910	-1.323071	4.203045
H	4.212376	1.971652	2.307676
C	3.295674	0.356778	-3.386625
H	4.212376	1.971652	-2.307676
H	2.215910	-1.323071	-4.203045
H	3.991755	0.422491	4.217752
H	3.991755	0.422491	-4.217752
C	-3.527542	-4.525676	-2.064328
C	-0.972569	-5.347152	-2.782051
H	-4.526256	-4.208050	-1.779829
C	-2.048439	-5.641045	-3.611548
C	-3.336655	-5.246592	-3.241185
H	0.026550	-5.678022	-3.053702
H	-1.887572	-6.186266	-4.536836
H	-4.186219	-5.485545	-3.874055
H	0.971164	-4.490016	1.168529

C	-0.972569	-5.347152	2.782051	C	3.336732	5.246486	3.241210
C	-3.527542	-4.525676	2.064328	C	0.000021	4.494969	-0.676814
C	-2.048439	-5.641045	3.611548	C	0.972655	5.347193	-2.782065
C	-3.336655	-5.246592	3.241185	H	4.526280	4.207904	-1.779842
H	0.026550	-5.678022	3.053702	C	3.336732	5.246486	-3.241210
H	-1.887572	-6.186266	4.536836	H	-0.971123	4.490182	1.168532
H	-4.186219	-5.485545	3.874055	C	2.048537	5.641012	3.611570
H	-4.526256	-4.208050	1.779829	H	-0.026446	5.678117	3.053717
C	2.603322	3.368706	0.000000	H	4.186307	5.485378	3.874089
C	2.447796	4.189873	1.238141	H	-0.971123	4.490182	-1.168532
C	2.447796	4.189873	-1.238141	C	2.048537	5.641012	-3.611570
C	1.151437	4.658648	1.566747	H	-0.026446	5.678117	-3.053717
C	3.527584	4.525576	2.064344	H	4.186307	5.485378	-3.874089
C	1.151437	4.658648	-1.566747	H	1.887698	6.186230	4.536865
C	3.527584	4.525576	-2.064344	H	1.887698	6.186230	-4.536865
C	0.000021	4.494969	0.676814	H	4.526280	4.207904	1.779842
C	0.972655	5.347193	2.782065				

Charge = 0; multiplicity = 1

Table S10. Atomic coordinates for the optimized structure of **DBHept-TBC-TOS** (saddle butterfly geometry, gas phase)

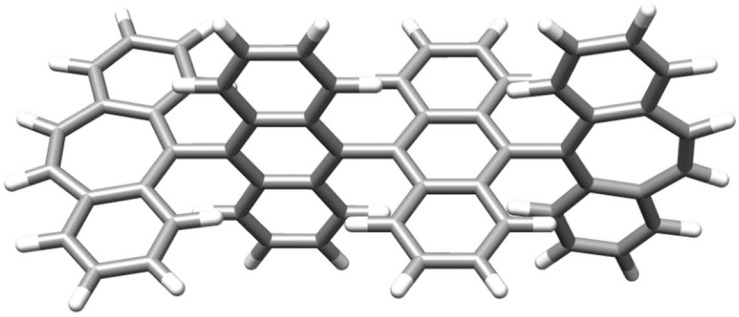


Atom	X	Y	Z	C	-1.652520	3.318999	2.325113
C	-0.931097	7.424494	0.675657	C	-0.889327	1.277287	1.206488
C	-0.931097	7.424494	-0.675657	C	-0.889327	1.277287	-1.206488
C	-0.075253	6.642722	-1.567933	C	-1.652520	3.318999	-2.325113
C	-0.075253	6.642722	1.567933	C	-2.090199	2.577175	3.417662
C	0.405397	5.349171	-1.247634	H	-1.794647	4.393054	2.314740
C	0.405397	5.349171	1.247634	C	-1.354270	0.547653	2.333529
C	-0.030383	4.658360	0.000000	C	-0.392033	0.638325	0.000000
H	-1.557832	8.165858	1.168370	C	-1.354270	0.547653	-2.333529
C	-0.667662	3.446253	0.000000	H	-1.794647	4.393054	-2.314740
C	-1.058883	2.701135	1.216839	C	-2.090199	2.577175	-3.417662
C	-1.058883	2.701135	-1.216839	C	-1.945332	1.183945	3.412415

H	-2.564537	3.077401	4.256465
H	-1.294426	-0.532240	2.323994
C	-1.945332	1.183945	-3.412415
H	-1.294426	-0.532240	-2.323994
H	-2.564537	3.077401	-4.256465
H	-2.316656	0.592943	4.244592
H	-2.316656	0.592943	-4.244592
C	0.392033	-0.638325	0.000000
C	0.889327	-1.277287	-1.206488
C	0.889327	-1.277287	1.206488
C	1.354270	-0.547653	-2.333529
C	1.058883	-2.701135	-1.216839
C	1.058883	-2.701135	1.216839
C	1.354270	-0.547653	2.333529
C	1.945332	-1.183945	-3.412415
H	1.294426	0.532240	-2.323994
C	1.652520	-3.318999	-2.325113
C	0.667662	-3.446253	0.000000
C	1.652520	-3.318999	2.325113
H	1.294426	0.532240	2.323994
C	1.945332	-1.183945	3.412415
C	2.090199	-2.577175	-3.417662
H	2.316656	-0.592943	-4.244592
H	1.794647	-4.393054	-2.314740
C	2.090199	-2.577175	3.417662
H	1.794647	-4.393054	2.314740
H	2.316656	-0.592943	4.244592
H	2.564537	-3.077401	-4.256465
H	2.564537	-3.077401	4.256465
C	1.302145	4.718763	2.124775
C	0.292541	7.212321	2.803467
H	1.682759	3.737039	1.861858
C	1.164270	6.565865	3.670338
C	1.685867	5.316731	3.320493
H	-0.101686	8.191342	3.063461
H	1.443476	7.033758	4.609691
H	2.376332	4.805243	3.984478
H	-1.557832	8.165858	-1.168370
C	0.292541	7.212321	-2.803467
C	1.302145	4.718763	-2.124775
C	1.164270	6.565865	-3.670338
C	1.685867	5.316731	-3.320493
H	-0.101686	8.191342	-3.063461
H	1.443476	7.033758	-4.609691
H	2.376332	4.805243	-3.984478
H	1.682759	3.737039	-1.861858
C	0.030383	-4.658360	0.000000
C	-0.405397	-5.349171	-1.247634
C	-0.405397	-5.349171	1.247634
C	0.075253	-6.642722	-1.567933
C	-1.302145	-4.718763	-2.124775
C	0.075253	-6.642722	1.567933
C	-1.302145	-4.718763	2.124775
C	0.931097	-7.424494	-0.675657
C	-0.292541	-7.212321	-2.803467
C	-1.685867	-5.316731	-3.320493
C	0.931097	-7.424494	0.675657
C	-0.292541	-7.212321	2.803467
H	-1.682759	-3.737039	1.861858
C	-1.685867	-5.316731	3.320493
H	1.557832	-8.165858	-1.168370
C	-1.164270	-6.565865	-3.670338
H	0.101686	-8.191342	-3.063461
H	-2.376332	-4.805243	-3.984478
H	1.557832	-8.165858	1.168370
C	-1.164270	-6.565865	3.670338
H	0.101686	-8.191342	3.063461
H	-2.376332	-4.805243	3.984478
H	-1.443476	-7.033758	-4.609691
H	-1.443476	-7.033758	4.609691
H	-1.682759	-3.737039	-1.861858

Charge = 0; multiplicity = 3

Table S11. Atomic coordinates for the optimized structure of **DBHept-TBC-TOS** (orthogonal planar geometry, gas phase)



Atom	X	Y	Z
C	0.000000	0.000000	5.129885
C	0.000000	-1.321836	5.740026
C	0.000000	-1.634252	7.146271
C	0.000000	-0.673996	8.231801
H	0.000000	-1.135660	9.216987
C	0.000000	0.673996	8.231801
H	0.000000	1.135660	9.216987
C	0.000000	1.634252	7.146271
C	0.000000	1.321836	5.740026
C	0.000000	2.980994	7.558725
H	0.000000	3.181641	8.626556
C	0.000000	4.045747	6.669084
H	0.000000	5.068906	7.031222
C	0.000000	3.761974	5.302141
H	0.000000	4.565550	4.571588
C	0.000000	2.447860	4.863681
H	0.000000	2.273877	3.797528
C	0.000000	-2.980994	7.558725
H	0.000000	-3.181641	8.626556
C	0.000000	-4.045747	6.669084
H	0.000000	-5.068906	7.031222
C	0.000000	-3.761974	5.302141
H	0.000000	-4.565550	4.571588
C	0.000000	-2.447860	4.863681
H	0.000000	-2.273877	3.797528
C	0.000000	0.000000	3.618108
C	-1.221240	0.000000	2.907194
C	-2.481975	0.000000	3.587042
H	-2.482979	0.000000	4.671122
C	-3.664739	0.000000	2.898182
H	-4.607611	0.000000	3.437045
C	-3.665746	0.000000	1.475596
H	-4.609659	0.000000	0.938450
C	-2.484679	0.000000	0.783756
H	-2.489163	0.000000	-0.300137
C	-1.222101	0.000000	1.460684
C	0.000000	0.000000	0.751078
C	1.222101	0.000000	1.460684
C	2.484679	0.000000	0.783756
H	2.489163	0.000000	-0.300137
C	3.665746	0.000000	1.475596
H	4.609659	0.000000	0.938450
C	3.664739	0.000000	2.898182
H	4.607611	0.000000	3.437045
C	2.481975	0.000000	3.587042
H	2.482979	0.000000	4.671122
C	1.221240	0.000000	2.907194
C	0.000000	0.000000	-0.751078
C	0.000000	1.222101	-1.460684
C	0.000000	2.484679	-0.783756
H	0.000000	2.489163	0.300137
C	0.000000	3.665746	-1.475596
H	0.000000	4.609659	-0.938450
C	0.000000	3.664739	-2.898182
H	0.000000	4.607611	-3.437045
C	0.000000	2.481975	-3.587042
H	0.000000	2.482979	-4.671122
C	0.000000	1.221240	-2.907194
C	0.000000	0.000000	-3.618108
C	0.000000	-1.221240	-2.907194
C	0.000000	-2.481975	-3.587042
H	0.000000	-2.482979	-4.671122
C	0.000000	-3.664739	-2.898182

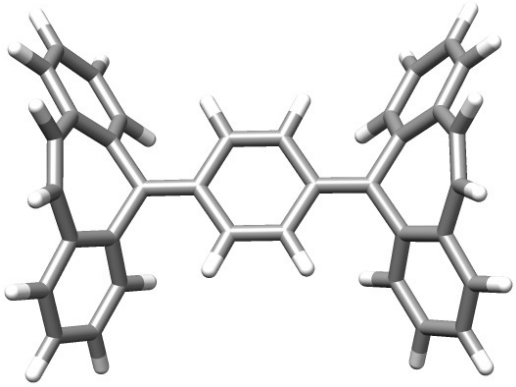
H	0.000000	-4.607611	-3.437045	H	-3.181641	0.000000	-8.626556
C	0.000000	-3.665746	-1.475596	C	-4.045747	0.000000	-6.669084
H	0.000000	-4.609659	-0.938450	H	-5.068906	0.000000	-7.031222
C	0.000000	-2.484679	-0.783756	C	-3.761974	0.000000	-5.302141
H	0.000000	-2.489163	0.300137	H	-4.565550	0.000000	-4.571588
C	0.000000	-1.222101	-1.460684	C	-2.447860	0.000000	-4.863681
C	0.000000	0.000000	-5.129885	H	-2.273877	0.000000	-3.797528
C	1.321836	0.000000	-5.740026	C	2.447860	0.000000	-4.863681
C	1.634252	0.000000	-7.146271	H	2.273877	0.000000	-3.797528
C	0.673996	0.000000	-8.231801	C	3.761974	0.000000	-5.302141
H	1.135660	0.000000	-9.216987	H	4.565550	0.000000	-4.571588
C	-0.673996	0.000000	-8.231801	C	4.045747	0.000000	-6.669084
H	-1.135660	0.000000	-9.216987	H	5.068906	0.000000	-7.031222
C	-1.634252	0.000000	-7.146271	C	2.980994	0.000000	-7.558725
C	-1.321836	0.000000	-5.740026	H	3.181641	0.000000	-8.626556
C	-2.980994	0.000000	-7.558725				

Charge = 0; multiplicity = 3

b) DBHept-Th

DFT calculations in solution show two possible conformers (*syn* and *anti*) for **DBHept-Th-SCS** depending on the relative orientation of the DBHept groups. The calculations predict that very similar energies for both conformers, which, as result, should coexist, being the *syn* form slightly more stable (ΔG = 0.63 kcal/mol). Moreover, the triplet state is higher in energy in comparison with the closed shell structures (ΔG = 16.9 kcal/mol respect to the most stable *syn*-CS conformer).

Table S12. Atomic coordinates for the optimized structure of ***syn*-DBHept-Th-CS**

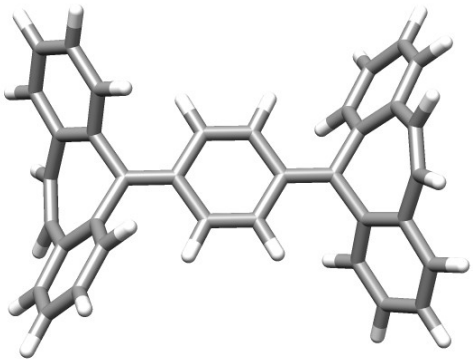


Atom	X	Y	Z	C	-0.090622	-0.677068	1.226030
C	-0.188858	-2.843231	0.000000	H	-0.022435	-1.200466	2.172424
C	0.794958	-4.561252	1.576667	C	-0.155761	-1.463930	0.000000
C	-0.232220	-3.636083	1.257603	C	-0.294038	-5.014377	3.717416
C	0.754501	-5.211578	2.826263	H	-0.305783	-5.539331	4.667781
H	1.558862	-5.895939	3.082626	C	-1.332131	-4.141820	3.378504
C	-1.292469	-3.460793	2.164267	H	-2.161745	-3.983320	4.060904
H	-2.089560	-2.770582	1.906041	C	1.901844	-4.880929	0.675762

H	2.795595	-5.263050	1.165447	C	-0.090622	0.677068	-1.226030
C	-0.188858	2.843231	0.000000	H	-0.022435	1.200466	-2.172424
C	0.794957	4.561253	-1.576667	C	-0.294039	5.014376	3.717416
C	-0.232220	3.636083	-1.257603	H	-0.305784	5.539329	4.667782
C	0.754500	5.211579	-2.826263	C	-1.332131	4.141818	3.378504
H	1.558860	5.895940	-3.082626	H	-2.161745	3.983316	4.060905
C	-1.292469	3.460792	-2.164267	C	1.901842	4.880932	0.675762
H	-2.089559	2.770580	-1.906042	H	2.795593	5.263054	1.165447
C	-0.090622	0.677068	1.226030	C	0.794958	-4.561252	-1.576667
H	-0.022435	1.200466	2.172424	C	-0.232220	-3.636083	-1.257603
C	-0.155761	1.463931	0.000000	C	0.754501	-5.211578	-2.826263
C	-0.294039	5.014376	-3.717416	H	1.558862	-5.895939	-3.082626
H	-0.305784	5.539329	-4.667782	C	-1.292469	-3.460793	-2.164267
C	-1.332131	4.141818	-3.378504	H	-2.089560	-2.770582	-1.906041
H	-2.161745	3.983316	-4.060905	C	-0.090622	-0.677068	-1.226030
C	1.901842	4.880932	-0.675762	H	-0.022435	-1.200466	-2.172424
H	2.795593	5.263054	-1.165447	C	-0.294038	-5.014377	-3.717416
C	0.794957	4.561253	1.576667	H	-0.305783	-5.539331	-4.667781
C	-0.232220	3.636083	1.257603	C	-1.332131	-4.141820	-3.378504
C	0.754500	5.211579	2.826263	H	-2.161745	-3.983320	-4.060904
H	1.558860	5.895940	3.082626	C	1.901844	-4.880929	-0.675762
C	-1.292469	3.460792	2.164267	H	2.795595	-5.263050	-1.165447
H	-2.089559	2.770580	1.906042				

Charge = 0; multiplicity = 1; (0 imaginary frequencies)
Zero-point correction = 0.482994 (Hartree/Particle)
Thermal correction to Energy = 0.509364
Thermal correction to Enthalpy = 0.510308
Thermal correction to Gibbs Free Energy = 0.425878
Sum of electronic and zero-point Energies = −1385.814824
Sum of electronic and thermal Energies = −1385.788454
Sum of electronic and thermal Enthalpies = −1385.787510
Sum of electronic and thermal Free Energies = −1385.871941

Table S13. Atomic coordinates for the optimized structure of *anti*-DBHept-Th-SCS

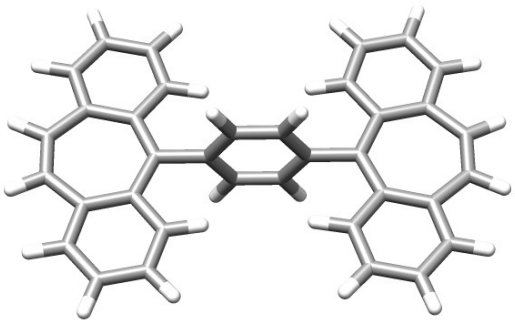


Atom	X	Y	Z	C	0.269902	2.831955	0.000000

C	-0.635185	4.590082	1.575811	H	2.609265	-5.365724	1.165830
C	0.353922	3.624954	1.255886	C	0.635185	-4.590082	-1.575811
C	-0.564120	5.242697	2.822852	C	-0.353922	-3.624954	-1.255886
H	-1.340060	5.958754	3.080360	C	0.564120	-5.242697	-2.822852
C	1.412040	3.412826	2.156788	H	1.340060	-5.958754	-3.080360
H	2.181366	2.692312	1.896860	C	-1.412040	-3.412826	-2.156788
C	0.065659	0.673884	1.226611	H	-2.181366	-2.692312	-1.896860
H	0.109631	1.193923	2.176036	C	-0.065659	-0.673884	-1.226611
C	0.154039	1.457279	0.000000	H	-0.109631	-1.193923	-2.176036
C	0.480469	5.008101	3.709624	C	-0.480469	-5.008101	-3.709624
H	0.516964	5.535120	4.658222	H	-0.516964	-5.535120	-4.658222
C	1.483305	4.095949	3.368497	C	-1.483305	-4.095949	-3.368497
H	2.309767	3.908554	4.047386	H	-2.309767	-3.908554	-4.047386
C	-1.730695	4.950196	0.675846	C	1.730695	-4.950196	-0.675846
H	-2.609265	5.365724	1.165830	H	2.609265	-5.365724	-1.165830
C	-0.269902	-2.831955	0.000000	C	-0.635185	4.590082	-1.575811
C	0.635185	-4.590082	1.575811	C	0.353922	3.624954	-1.255886
C	-0.353922	-3.624954	1.255886	C	-0.564120	5.242697	-2.822852
C	0.564120	-5.242697	2.822852	H	-1.340060	5.958754	-3.080360
H	1.340060	-5.958754	3.080360	C	1.412040	3.412826	-2.156788
C	-1.412040	-3.412826	2.156788	H	2.181366	2.692312	-1.896860
H	-2.181366	-2.692312	1.896860	C	0.065659	0.673884	-1.226611
C	-0.065659	-0.673884	1.226611	H	0.109631	1.193923	-2.176036
H	-0.109631	-1.193923	2.176036	C	0.480469	5.008101	-3.709624
C	-0.154039	-1.457279	0.000000	H	0.516964	5.535120	-4.658222
C	-0.480469	-5.008101	3.709624	C	1.483305	4.095949	-3.368497
H	-0.516964	-5.535120	4.658222	H	2.309767	3.908554	-4.047386
C	-1.483305	-4.095949	3.368497	C	-1.730695	4.950196	-0.675846
H	-2.309767	-3.908554	4.047386	H	-2.609265	5.365724	-1.165830
C	1.730695	-4.950196	0.675846				

Charge = 0; multiplicity = 1; (0 imaginary frequencies)
Zero-point correction = 0.482962 (Hartree/Particle)
Thermal correction to Energy = 0.509358
Thermal correction to Enthalpy = 0.510302
Thermal correction to Gibbs Free Energy = 0.426354
Sum of electronic and zero-point Energies = −1385.814329
Sum of electronic and thermal Energies = −1385.787933
Sum of electronic and thermal Enthalpies = −1385.786989
Sum of electronic and thermal Free Energies = −1385.870937

Table S14. Atomic coordinates for the optimized structure of **DBHept-Th-T**



Atom	X	Y	Z
C	-1.420386	-0.000001	-0.007245
C	-0.703810	-0.000001	1.198800
C	0.691576	-0.000001	1.206036
C	1.420386	-0.000001	0.007247
C	0.703810	-0.000001	-1.198798
C	-0.691577	-0.000001	-1.206035
C	2.928720	0.000000	0.010599
C	3.536761	-1.322197	0.013566
C	4.943805	-1.634866	-0.012092
C	6.029505	-0.674205	-0.049833
H	7.014267	-1.135348	-0.080625
C	6.029505	0.674207	-0.049826
H	7.014267	1.135351	-0.080612
C	4.943804	1.634867	-0.012076
C	3.536761	1.322197	0.013576
C	5.357831	2.981614	-0.005809
H	6.425427	3.181787	-0.026603
C	4.469023	4.047988	0.025329
H	4.832239	5.070600	0.029533
C	3.101614	3.764942	0.049882
H	2.372010	4.569055	0.074238
C	2.661400	2.450293	0.043249
H	1.595133	2.279819	0.063703
C	2.661402	-2.450294	0.043232
H	1.595135	-2.279821	0.063692
C	3.101617	-3.764943	0.049852
H	2.372013	-4.569056	0.074204
C	4.469025	-4.047988	0.025292
H	4.832242	-5.070599	0.029485
C	5.357833	-2.981613	-0.005839
H	6.425429	-3.181785	-0.026638
C	-2.928720	0.000000	-0.010598
C	-3.536761	-1.322197	-0.013565
C	-3.536760	1.322196	-0.013576
C	-4.943805	-1.634866	0.012090
C	-2.661402	-2.450294	-0.043229
C	-4.943804	1.634867	0.012074
C	-2.661400	2.450293	-0.043245
C	-6.029505	-0.674205	0.049827
C	-5.357833	-2.981613	0.005837
C	-3.101616	-3.764943	-0.049848
C	-6.029505	0.674206	0.049819
C	-5.357831	2.981614	0.005807
C	-3.101614	3.764942	-0.049878
H	-7.014267	-1.135348	0.080615
H	-6.425429	-3.181785	0.026633
C	-4.469025	-4.047988	-0.025291
H	-2.372013	-4.569056	-0.074197
H	-7.014267	1.135351	0.080603
H	-6.425427	3.181787	0.026598
C	-4.469023	4.047988	-0.025328
H	-2.372010	4.569055	-0.074231
H	-4.832242	-5.070599	-0.029484
H	-4.832239	5.070600	-0.029532
H	1.245563	-0.000001	-2.140479
H	-1.223591	-0.000001	-2.153272
H	-1.245563	-0.000001	2.140481
H	1.223591	-0.000001	2.153273
H	-1.595133	2.279819	-0.063697
H	-1.595135	-2.279821	-0.063686

Charge = 0; multiplicity = 3; (0 imaginary frequencies)

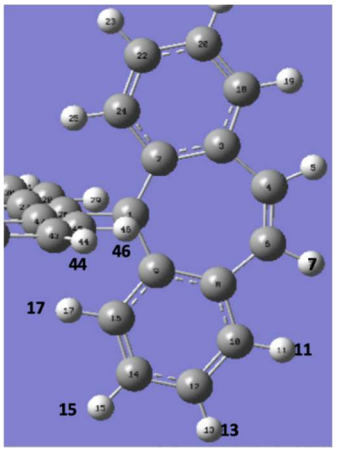
Zero-point correction = 0.480792 (Hartree/Particle)
Thermal correction to Energy = 0.507594
Thermal correction to Enthalpy = 0.419224
Thermal correction to Gibbs Free Energy = 0.670270
Sum of electronic and zero-point Energies = −1385.783452
Sum of electronic and thermal Energies = −1385.756651
Sum of electronic and thermal Enthalpies = −1385.755707
Sum of electronic and thermal Free Energies = −1385.845021

7.2. Isotropic hyperfine coupling constants ($|a_H|$)

The performance of DFT methodology was tested to predict the $|a_H|$ by means of the "prop=epr" keyword. To this end, calculations based on the spin-unrestricted (U) approach with B3LYP and CAM-B3LYP functionals were run, in combination with 6-31G(d) or 6-31G(d,p) basis sets, and compared to the obtained experimental data. A triplet (m = 3) state was considered, as the most plausible electronic configuration, in line with the above reported data on energy differences. In all cases, same functional/basis coupling were applied for the structure optimization and the subsequent EPR calculations. Finally, actual $|a_H|$ data were extracted from the "Isotropic Fermi Contact Couplings" section of the output log file.

Table S15. $|a_H|$ calculated value (in G) at different level of theory, together with the experimentally determined ones for **DBHept-TBC-TOS**

	UCAM-B3LYP		UB3LYP		
H	**6-31G(d)**	**6-31G(d,p)**	**6-31G(d)**	**6-31G(d,p)**	**EXPERIMENTAL.**
7	-0.52	-0.51	-0.55	-0.55	**0.54**
11	1.11	1.09	0.68	0.67	**1.06**
13	-2.41	-2.38	-2.12	-2.10	**3.78**
15	1.16	1.14	0.75	0.74	**0.95**
17	-2.35	-2.33	-1.98	-1.97	**3.22**
46	-0.03	-0.01	-0.04	-0.02	
44	0.02	0.02	0.03	0.03	



7.3. TD-DFT calculations

Time-dependent DFT calculations were carried out to model the electronic transitions for the **[DBHept-TBC]$^{2+}$**, **DBHept-TBC-SCS** and **DBHept-TBC-TOS** and **DBHept-TBC-SOS** species. The calculations were performed at the (U)CAM-B3LYP/def2TZV or (U)CAM-B3LYP/6-31G(d,p) (only for **DBHept-TBC-SOS**) level of theory for using Gaussian 09.[S9] The first 75 excited states were considered and the optimized coordinates shown in Tables S3-S6 were used for the calculations. An ultrafine integration grid was used in the calculations. Dichloromethane was used as solvent using the IEFPCM model also applied in the structure optimization. A correction of −0.3 eV was applied to the calculated values.

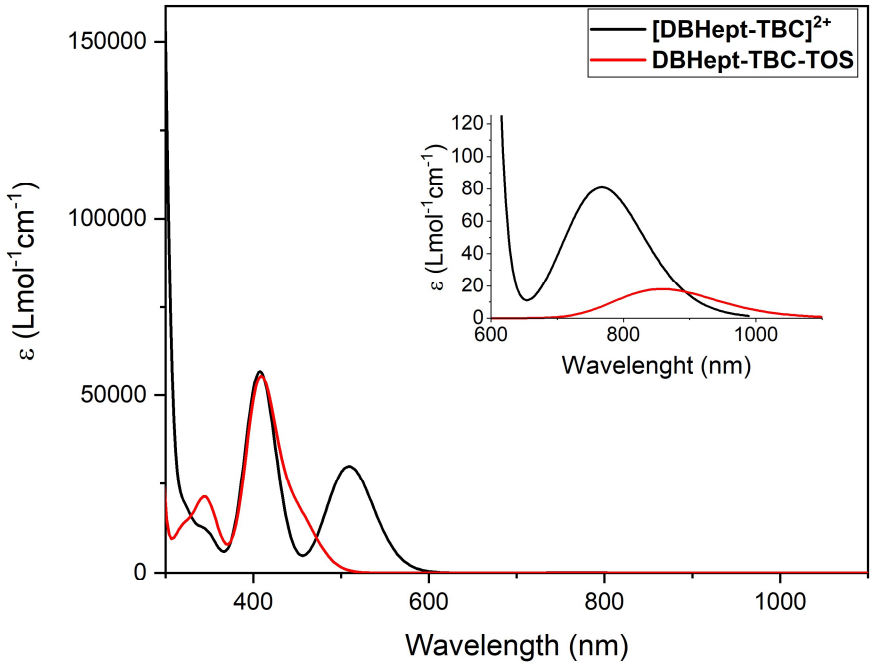


Figure S21. Calculated UV-Vis spectrum of **[DBHept-TBC]$^{2+}$** (black line) and **DBHept-TBC-TOS** (red line).

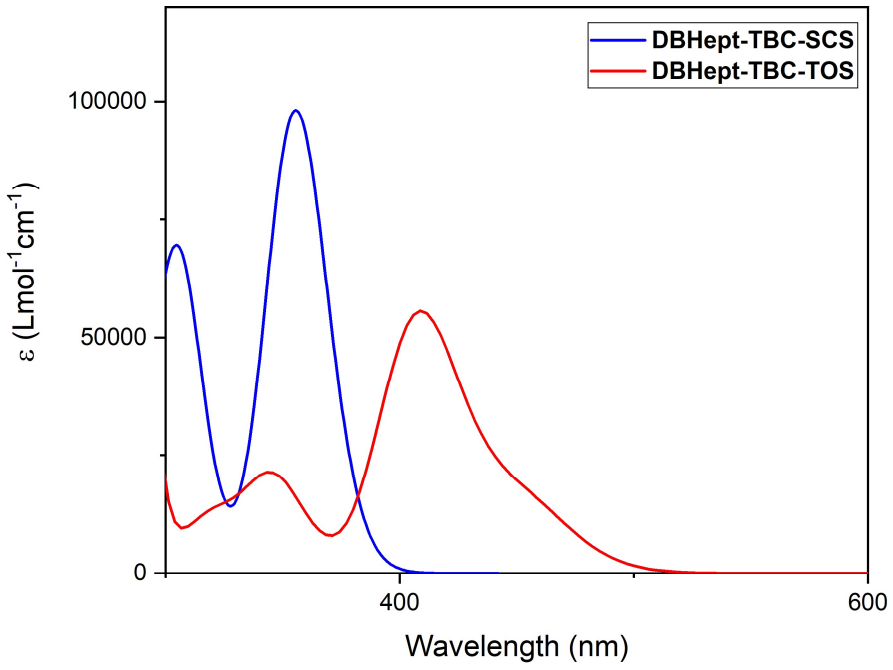


Figure S22. Calculated UV-Vis spectrum of **DBHept-TBC-SCS** (blue line) and **DBHept-TBC-TOS** (red line).

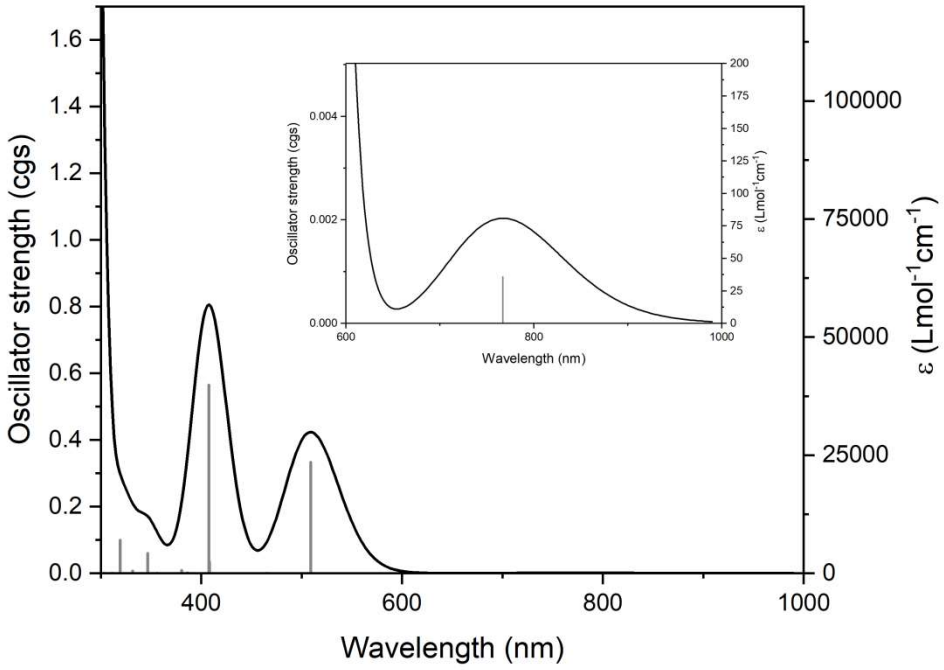


Figure S23. Calculated UV-Vis spectrum of **[DBHept-TBC]$^{2+}$**.

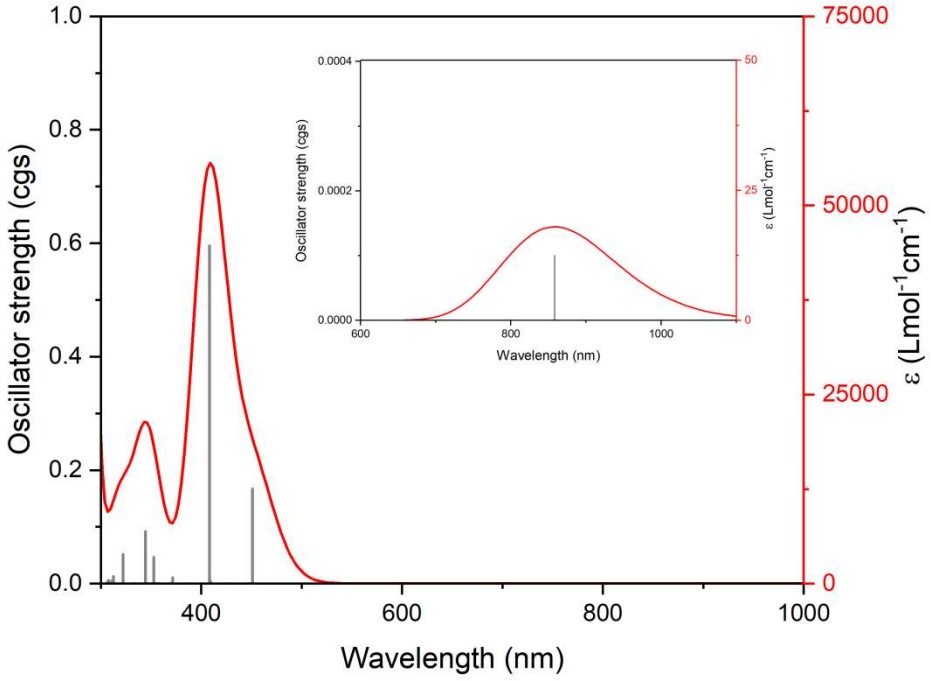


Figure S24. Calculated UV-Vis spectrum of **DBHept-TBC-TOS**.

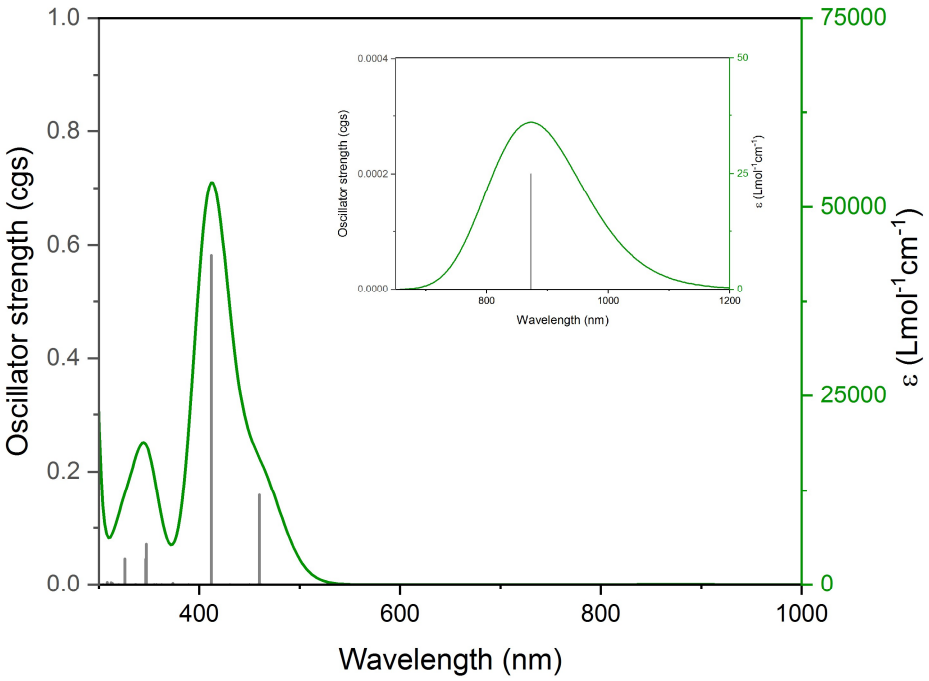


Figure S25. Calculated UV-Vis spectrum of **DBHept-TBC-SOS**.

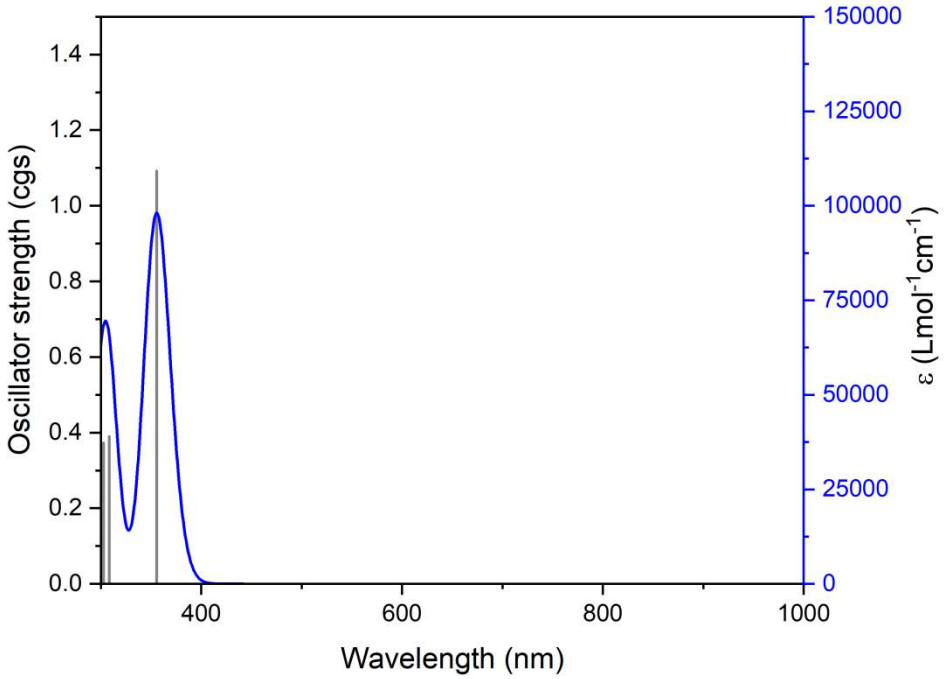


Figure S26. Calculated UV-Vis spectrum of **DBHept-TBC-SCS**.

Table S16. Lower energy electronic transitions (>300 nm) predicted by TDDFT at the CAM-B3LYP/def2TZV level for **[DBHept-TBC]$^{2+}$** in dichloromethane showing the molecular orbitals involved, the CI coefficients, the wavelength of the transition (nm) and the oscillator strength. The energy values obtained have been corrected by −0.3 eV. The most intense calculated transitions for each of the absorption bands predicted are highlighted in red.

State	λ_{cal} (nm)		CI	f
S_1	767.06	190 →193	0.48850	0.0009
		191 (H) →192 (L)	0.49514	
S_2	766.99	190 →192	-0.48860	0.0000
		191 →193	0.49507	
S_3	509.09	188 →193	0.48765	0.3326
		189 →192	0.48772	
S_4	505.92	188 →192	0.49207	0.0000
		189 →193	0.49212	
S_5	465.34	190 →192	0.19805	0.0000
		190 →193	0.46064	
		191 →192	0.48035	
		191 →193	0.12781	
S_6	465.34	190 →192	0.46056	0.0000
		190 →193	-0.19823	
		191 →192	-0.12761	
		191 →193	0.48040	
S_7	408.14	182 →193	-0.13773	0.0285
		183 →192	0.17292	
		184 →193	-0.19348	
		185 →192	0.26280	
		186 →193	0.40854	
		187 →192	-0.35906	
		188 →194	0.13161	
		189 →195	-0.13150	
S_8	408.13	182 →192	-0.13764	0.0343
		183 →193	0.17284	
		184 →192	-0.19351	
		185 →193	0.26279	
		186 →192	0.40851	
		187 →193	-0.35889	
		188 →195	-0.13165	
		189 →194	0.13189	
S_9	407.73	190 →197	-0.48332	0.5645
		191 →196	0.49992	
S_{10}	386.37	190 →194	-0.10509	0.0009
		190 →195	0.47943	
		191 →194	0.48401	
		191 →195	-0.10955	
S_{11}	386.36	190 →194	0.48035	0.0015
		190 →195	0.10471	
		191 →194	0.10976	
		191 →195	0.48375	
S_{12}	385.90	190 →196	-0.49353	0.0000
		191 →197	0.49382	
S_{13}	380.38	182 →193	-0.20445	0.0093
		183 →192	0.26195	
		184 →193	-0.25033	
		185 →192	0.16373	
		186 →193	-0.23731	
		187 →192	0.35271	
		188 →194	0.22039	
		189 →195	-0.21869	
S_{14}	380.38	182 →192	-0.20432	0.0092
		183 →193	0.26180	
		184 →192	-0.25026	
		185 →193	0.16370	
		186 →192	-0.23711	
		187 →193	0.35232	
		188 →195	-0.21847	
		189 →194	0.22053	

S_{15}	356.09	190 →197	0.50205	0.0001
		191 →196	0.48540	
S_{16}	355.89	190 →196	0.49399	0.0000
		191 →197	0.49365	
S_{17}	346.61	180 →192	0.19158	0.0598
		181 →193	-0.20495	
		182 →192	0.19175	
		183 →193	-0.13565	
		184 →192	-0.25385	
		185 →193	0.36639	
		187 →193	0.19922	
		188 →195	0.23873	
		189 →194	-0.23850	
S_{18}	346.60	180 →193	0.19155	0.0574
		181 →192	-0.20492	
		182 →193	0.19172	
		183 →192	-0.13566	
		184 →193	-0.25380	
		185 →192	0.36650	
		187 →192	0.19946	
		188 →194	-0.23839	
		189 →195	0.23855	
S_{19}	331.71	186 →197	-0.34732	0.0068
		187 →196	0.38030	
		190 →199	-0.22139	
		190 →201	-0.19691	
		191 →198	0.33632	
		191 →200	-0.11224	
S_{20}	331.62	186 →196	-0.35009	0.0055
		187 →197	0.37822	
		190 →198	-0.33422	
		190 →200	0.11163	
		191 →199	0.22273	
		191 →201	0.19807	
S_{21}	319.35	180 →193	0.36361	0.0871
		181 →192	-0.35653	
		182 →193	-0.21412	
		183 →192	0.23143	
		185 →192	-0.21883	
		186 →193	-0.16868	
		187 →192	-0.15798	
		188 →194	-0.10865	
		189 →195	0.10851	
S_{22}	319.32	180 →192	0.36395	0.0996
		181 →193	-0.35685	
		182 →192	-0.21368	
		183 →193	0.23091	
		185 →193	-0.21887	
		186 →192	-0.16887	
		187 →193	-0.15833	
		188 →195	0.10786	
		189 →194	-0.10806	
S_{23}	310.79	190 →194	0.49866	0.0001
		191 →195	-0.49410	
S_{24}	303.72	190 →195	0.49968	0.0001
		191 →194	-0.49308	
S_{25}	303.72	184 →192	0.10090	0.0005
		185 →192	-0.14883	
		185 →193	-0.15902	
		186 →192	0.39939	
		186 →193	0.27669	
		187 →192	0.28577	
		187 →193	0.30527	

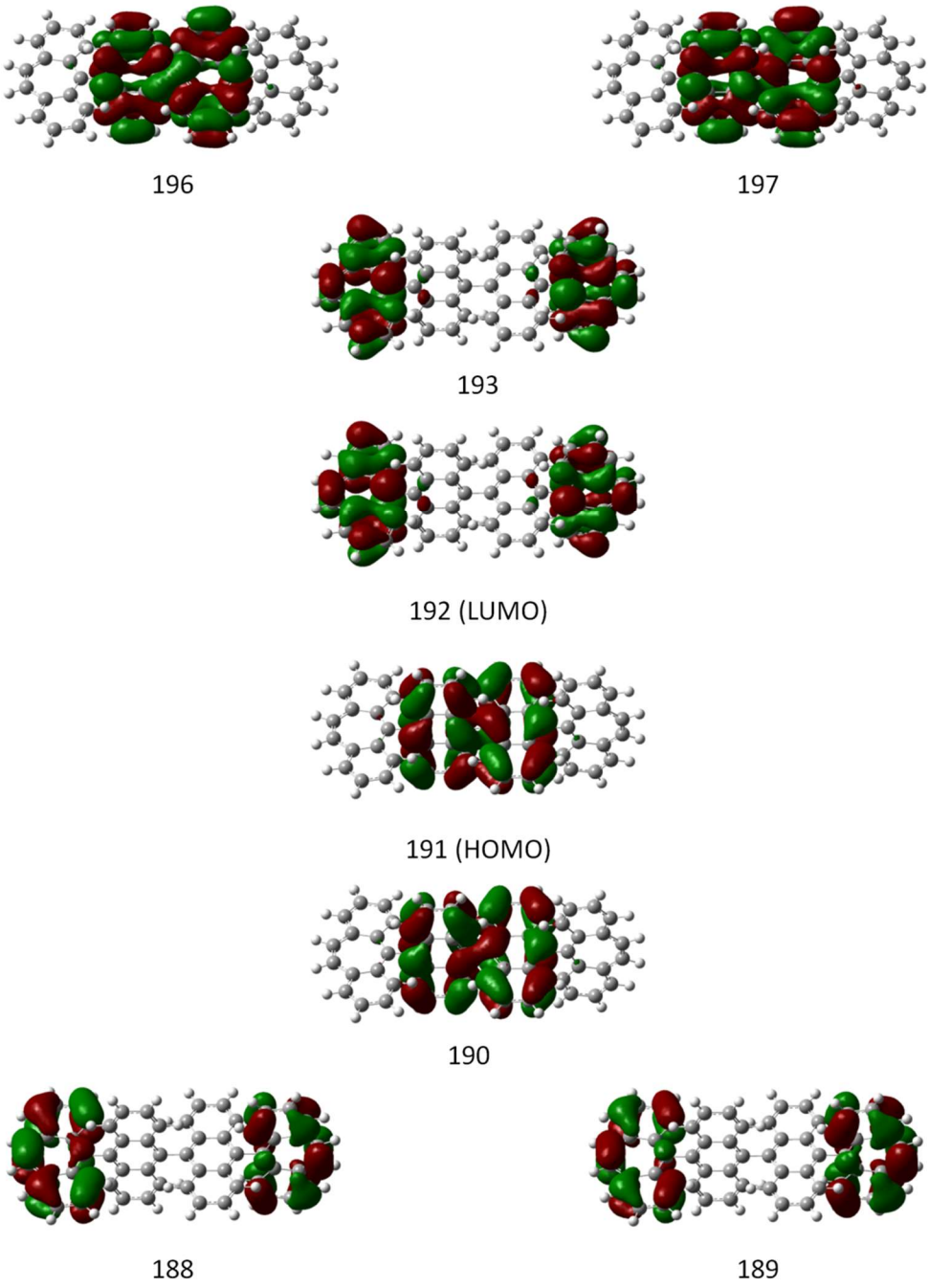


Figure S27. Molecular orbitals (isovalue = 0.02) involved in the excited states with more intense oscillator strengths calculated for [**DBHept-TBC**]$^{2+}$.

Table S17. Lower energy electronic transitions (>300 nm) predicted by TDDFT at the UCAM-B3LYP/def2TZV level for **DBHept-TBC-TOS** in dichloromethane showing the molecular orbitals involved, the CI coefficients, the wavelength of the transition (nm) and the oscillator strength. The energy values obtained have been corrected by –0.3 eV. The most intense calculated transitions for each of the absorption bands predicted are highlighted in red.

State	λ_{cal} (nm)		CI	f
S_1	1085.44	185A→204A	-0.10119	0.0000
		187A→198A	0.10614	
		190A→194A	0.49529	
		191A→195A	-0.49530	
		187B→198B	0.10641	
		190B→194B	-0.49546	
		191B→195B	0.49547	
		190A←194A	0.16836	
		191A←195A	-0.16836	
		190B←194B	-0.16831	
		191B←195B	0.16831	
S_2	1066.79	185A→205A	-0.10137	0.0000
		186A→198A	0.10629	
		190A→195A	0.49504	
		191A→194A	-0.49505	
		190B→195B	-0.49526	
		191B→194B	0.49526	
		190A←195A	0.16528	
		191A←194A	-0.16528	
		190B←195B	-0.16524	
		191B←194B	0.16524	
S_3	858.28	189A→196A	-0.13238	0.0001
		189A→197A	-0.13157	
		193A (SOMO)→196A	0.64564	
		193A (SOMO)→197A	0.64103	
		189B→196B	-0.18724	
		189B→197B	-0.18565	
S_4	858.27	188A→196A	-0.13154	0.0001
		188A→197A	0.13242	
		192A (SOMO)→196A	-0.64154	
		192A (SOMO)→197A	0.64514	
		188B→196B	-0.18567	
		188B→197B	0.18722	
S_5	533.91	192A→194A	0.38697	0.0000
		192A→195A	-0.33381	
		193A→194A	0.60154	
		193A→195A	0.57841	
S_6	533.91	192A→194A	-0.50911	0.0000
		192A→195A	0.66122	
		193A→194A	0.43219	
		193A→195A	0.27274	
S_7	451.07	192A→202A	0.11805	0.1671
		193A→203A	0.11807	
		188B→192B	-0.59162	
		188B→193B	-0.29518	
		189B→192B	-0.29526	
		189B→193B	0.59176	
S_8	449.74	192A→202A	-0.10588	0.0000
		193A→203A	0.10585	
		188B→192B	0.56974	
		188B→193B	0.34645	
		189B→192B	-0.34638	
		189B→193B	0.56960	
S_9	449.30	189A→196A	0.30359	0.0000
		189A→197A	0.3016	
		193A→196A	0.25473	
		193A→197A	0.25262	
		193A→200A	-0.10298	
		189B→196B	0.52009	
		189B→197B	0.51562	
S_{10}	449.30	188A→196A	-0.30166	0.0000
		188A→197A	0.30353	
		192A→196A	0.25311	
		192A→197A	-0.25424	
		192A→200A	0.10299	

		188B→196B	-0.51574	
		188B→197B	0.51998	
S_{11}	446.86	190B→192B	0.19675	0.0000
		190B→193B	0.66641	
		191B→192B	0.66638	
		191B→192B	-0.19696	
S_{12}	446.86	190B→192B	0.66889	0.0000
		190B→193B	-0.18818	
		191B→192B	0.18839	
		191B→192B	0.66885	
S_{13}	424.53	178A→204A	-0.10488	0.0000
		179A→205A	0.10903	
		180A→195A	-0.11702	
		182A→195A	0.22065	
		183A→194A	0.17663	
		184A→195A	0.19170	
		185A→194A	0.32798	
		190A→204A	-0.29484	
		191A→205A	0.29051	
		177B→203B	-0.10876	
		180B→195B	-0.25228	
		181B→194B	0.13481	
		182B→195B	0.14902	
		183B→194B	-0.23490	
		184B→195B	0.10437	
		185B→194B	0.26695	
		186B→195B	-0.10880	
		190B→200B	0.17904	
		190B→202B	0.23794	
		191B→203B	-0.29000	
S_{14}	424.53	178A→205A	-0.10902	0.0000
		179A→204A	0.10489	
		180A→194A	-0.11702	
		182A→194A	0.22066	
		183A→195A	0.17663	
		184A→194A	0.1917	
		185A→195A	0.32797	
		190A→205A	-0.29052	
		191A→204A	0.29484	
		176B→203B	0.10875	
		180B→194B	-0.25229	
		181B→195B	0.13481	
		182B→194B	0.14902	
		183B→195B	-0.2349	
		184B→194B	0.10437	
		185B→195B	0.26694	
		186B→194B	-0.1088	
		190B→203B	0.29001	
		191B→200B	-0.17903	
		191B→202B	-0.23794	
S_{15}	409.32	192A→198A	0.16522	0.0043
		192A→199A	-0.25198	
		192A→200A	0.46968	
		192A→201A	0.43065	
		180B→192B	0.10297	
		181B→192B	0.11779	
		183B→192B	-0.12456	
		184B→192B	0.27489	
		184B→193B	0.15400	
		185B→192B	-0.28534	
		185B→193B	-0.15533	
		186B→192B	-0.20802	
		186B→193B	-0.11654	
		187B→192B	0.14317	
S_{16}	409.32	193A→198A	0.16522	0.0043
		193A→199A	0.25198	
		193A→200A	0.46965	
		193A→201A	-0.43069	
		180B→193B	-0.10297	
		181B→193B	0.11779	
		183B→193B	-0.12456	
		184B→192B	0.15400	
		184B→193B	-0.27490	
		185B→192B	0.15533	

		185B→193B	-0.28534	
		186B→192B	-0.11653	
		186B→193B	0.20801	
		187B→193B	0.14317	
S_{17}	408.19	190A→194B	-0.48848	0.5957
		191A→195A	0.48852	
		190B→194B	-0.48793	
		191B→195B	0.48797	
S_{18}	386.29	190A→195B	-0.49264	0.0000
		191A→194A	0.49274	
		190B→195B	-0.49212	
		191B→194B	0.49222	
S_{19}	371.38	180A→196A	-0.16565	0.0106
		181A→197A	0.19647	
		182A→196A	-0.16775	
		183A→197A	-0.15224	
		184A→196A	0.10098	
		188A→202A	0.14383	
		188A→203A	-0.11832	
		189A→202A	-0.12033	
		189A→203A	-0.14698	
		192A→202A	0.27844	
		192A→203A	-0.16532	
		192A→209A	0.12074	
		192A→210A	0.14074	
		193A→202A	0.16958	
		193A→203A	0.28332	
		193A→209A	-0.14309	
		193A→210A	0.12362	
		178B→192B	0.13193	
		179B→193B	-0.13190	
		181B→197B	-0.20828	
		182B→196B	0.27441	
		183B→197B	-0.22957	
		184B→196B	-0.1551	
		185B→197B	-0.11647	
		188B→204B	-0.15112	
		188B→205B	0.12291	
		189B→204B	0.12511	
		189B→205B	0.15435	
S_{20}	371.36	180A→197A	0.16571	0.0000
		181A→196A	-0.19638	
		182A→197A	0.16767	
		183A→196A	0.1524	
		184A→197A	-0.10075	
		184A→200A	0.10287	
		188A→202A	0.16013	
		188A→203A	-0.10255	
		189A→202A	0.10018	
		189A→203A	0.15725	
		192A→202A	0.24837	
		192A→203A	-0.21621	
		192A→209A	0.14709	
		192A→210A	0.11925	
		193A→202A	-0.21289	
		193A→203A	-0.24281	
		193A→209A	0.11645	
		193A→210A	-0.14464	
		178B→193B	0.15614	
		179B→192B	-0.15782	
		181B→196B	0.2084	
		182B→197B	-0.27455	
		183B→196B	0.22973	
		184B→197B	0.15502	
		185B→196B	0.11675	
		188B→204B	-0.16414	
		188B→205B	0.11211	
		189B→204B	-0.10965	
		189B→205B	-0.16111	
S_{21}	368.01	184A→194A	0.10869	0.0000
		186A→194A	-0.35519	
		186A→195A	-0.11039	
		187A→194A	-0.17569	
		187A→195A	-0.36354	
		190A→198A	-0.10093	

		190A→199A	-0.21227	
		191A→198A	0.26037	
		184B→194B	0.17277	
		186B→194B	0.34211	
		186B→195B	0.10411	
		187B→194B	0.18041	
		187B→195B	0.36775	
		190B→199B	0.21398	
		191B→198B	0.25242	
S_{22}	368.01	184A→195A	0.10869	0.0000
		186A→194A	0.11039	
		186A→195A	-0.3552	
		187A→194A	-0.36354	
		187A→195A	0.17568	
		190A→198A	-0.26036	
		191A→198A	-0.10093	
		191A→199A	0.21227	
		184B→195B	0.17277	
		186B→194B	-0.10412	
		186B→195B	0.34211	
		187B→194B	0.36775	
		187B→195B	-0.1804	
		190B→198B	-0.25241	
		191B→199B	-0.21399	
S_{23}	367.382	192A→194A	-0.56928	0.0000
		192A→195A	-0.40602	
		193A→194A	-0.41281	
		193A→195A	0.57585	
S_{24}	367.382	192A→194A	0.49357	0.0000
		192A→195A	0.50819	
		193A→194A	-0.50270	
		193A→195A	0.48588	
S_{25}	357.39	190A→195A	-0.45197	0.0000
		191A→194A	-0.45199	
		190B→195B	0.52856	
		191B→194B	0.52857	
S_{26}	357.20	190A→194A	-0.42859	0.0000
		191A→195A	-0.4286	
		190B→194B	0.54826	
		191B→195B	0.54827	
S_{27}	356.46	190A→194A	0.54894	0.0000
		191A→195A	0.54889	
		190B→194B	0.42898	
		191B→195B	0.42893	
S_{28}	356.25	190A→195A	0.52923	0.0000
		191A→194A	0.52912	
		190B→195B	0.45215	
		191B→194B	0.45204	
S_{29}	352.86	183A→200A	-0.12918	0.0467
		184A→201A	-0.11260	
		192A→202A	0.46627	
		192A→203A	-0.27808	
		192A→209A	-0.13067	
		192A→210A	-0.15171	
		193A→202A	0.27744	
		193A→203A	0.46553	
		193A→209A	0.15150	
		193A→210A	-0.13038	
		178B→192B	-0.20386	
		178B→193B	0.13059	
		179B→192B	0.13103	
		179B→193B	0.20386	
		184B→201B	-0.10791	
		188B→192B	0.12713	
		189B→193B	-0.12691	
S_{30}	352.80	183A→201A	0.12001	0.0000
		184A→200A	0.12118	
		192A→202A	-0.40836	
		192A→203A	0.35685	
		192A→209A	0.15578	
		192A→210A	0.1258	

		193A→202A	0.35735	
		193A→203A	0.40918	
		193A→209A	0.12609	
		193A→210A	-0.15599	
		178B→193B	0.24197	
		179B→192B	-0.24173	
		185B→201B	-0.10408	
		188B→192B	-0.1217	
		189B→193B	-0.12193	
S_{31}	346.87	186A→194A	0.24831	0.0000
		187A→195A	0.26570	
		190A→196A	-0.12227	
		190A→198A	-0.10903	
		190A→199A	-0.31403	
		190A→201A	-0.12244	
		191A→197A	0.13087	
		191A→198A	0.39548	
		184B→194B	-0.11072	
		186B→194B	-0.23636	
		187B→195B	-0.26330	
		190B→196B	-0.12600	
		190B→198B	-0.10928	
		190B→199B	0.32905	
		191B→197B	0.13298	
		191B→198B	0.39715	
S_{32}	346.87	186A→195A	-0.24831	0.0000
		187A→194A	-0.26570	
		190A→197A	0.13109	
		190A→198A	0.39547	
		191A→196A	-0.12205	
		191A→198A	0.10903	
		191A→199A	-0.31404	
		191A→201A	-0.12244	
		184B→195B	0.11071	
		186B→195B	0.23636	
		187B→194B	0.2633	
		190B→197B	0.13328	
		190B→198B	0.39714	
		191B→196B	-0.12570	
		191B→198B	0.10928	
		191B→199B	0.32907	
S_{33}	344.57	188A→196A	-0.10135	0.092
		188A→197A	0.13563	
		189A→196A	0.28953	
		189A→197A	0.27370	
		192A→199A	0.14744	
		192A→201A	-0.11842	
		193A→198A	0.27305	
		193A→199A	0.27735	
		193A→200A	0.29425	
		193A→201A	-0.22277	
		183B→192B	-0.15245	
		183B→193B	0.12024	
		184B→193B	0.32486	
		185B→192B	-0.26638	
		185B→193B	0.21010	
		186B→193B	-0.26654	
		187B→192B	0.14854	
		187B→193B	-0.11715	
S_{34}	344.57	188A→196A	-0.28777	0.092
		188A→197A	0.27554	
		189A→196A	-0.10222	
		189A→197A	-0.13498	
		192A→198A	-0.27304	
		192A→200A	0.27735	
		192A→201A	-0.29427	
		193A→199A	-0.22275	
		193A→199A	-0.14744	
		193A→201A	0.11843	
		183B→192B	-0.12024	
		183B→193B	-0.15245	
		184B→192B	0.32485	
		185B→192B	-0.21010	
		185B→193B	-0.26638	
		186B→192B	-0.26654	
		187B→192B	0.11715	

		187B→193B	0.14854	
S_{35}	333.79	186A→194A	0.31509	0.0001
		187A→194A	0.14881	
		187A→195A	0.32893	
		190A→196A	-0.13030	
		190A→198A	-0.11519	
		190A→199A	-0.25301	
		190A→201A	-0.10004	
		191A→197A	0.13780	
		191A→198A	0.32107	
		184B→194B	0.12697	
		186B→194B	0.28126	
		187B→194B	0.14109	
		187B→195B	0.30704	
		190B→196B	0.14550	
		190B→198B	0.11712	
		190B→199B	-0.26872	
		191B→197B	-0.15182	
		191B→198B	-0.32695	
		191B→199B	0.10018	
S_{36}	333.79	186A→195A	0.31509	0.0001
		187A→194A	0.32893	
		187A→195A	-0.14880	
		190A→197A	-0.13810	
		190A→198A	-0.32106	
		191A→196A	0.12999	
		191A→198A	-0.11520	
		191A→199A	0.25302	
		191A→201A	0.10005	
		184B→195B	0.12697	
		186B→195B	0.28127	
		187B→194B	0.30704	
		187B→195B	-0.14109	
		190B→197B	0.15227	
		190B→198B	0.32694	
		190B→199B	0.10018	
		191B→196B	-0.14505	
		191B→198B	0.11713	
		191B→199B	0.26873	
S_{37}	333.02	178A→194A	0.31566	0.0000
		179A→195A	-0.31566	
		182A→205A	-0.13811	
		183A→204A	-0.10510	
		184A→205A	-0.10950	
		185A→204A	-0.18481	
		190A→207A	-0.28631	
		191A→206A	0.28635	
		176B→194B	-0.31584	
		177B→195B	0.31584	
		180B→203B	0.15816	
		183B→202B	0.10955	
		185B→202B	-0.12110	
		190B→207B	0.29186	
		191B→206B	-0.29186	
S_{38}	332.24	178A→195A	0.31342	0.0000
		179A→194A	-0.31343	
		182A→204A	-0.13780	
		183A→205A	-0.10981	
		184A→204A	-0.11636	
		185A→205A	-0.18506	
		190A→206A	-0.28546	
		191A→207A	0.28542	
		176B→195B	-0.31376	
		177B→194B	0.31378	
		180B→202B	0.12852	
		183B→203B	0.14061	
		185B→203B	-0.14475	
		190B→206B	0.29095	
		191B→207B	-0.29094	
S_{39}	321.97	189A→196A	-0.18909	0.0518
		189A→197A	-0.18725	
		189A→200A	-0.15646	
		189A→201A	0.15199	
		193A→198A	0.20838	
		193A→199A	0.18378	

		193A→200A	0.11057	
		180B→193B	0.17461	
		181B→192B	0.19899	
		181B→193B	-0.34719	
		182B→192B	-0.21485	
		182B→193B	0.40406	
		183B→192B	0.15469	
		183B→193B	-0.26988	
		189B→196B	0.17844	
		189B→197B	0.17623	
		189B→200B	0.19771	
		189B→201B	-0.22842	
		189B→202B	-0.12954	
S_{40}	321.97	188A→196A	0.18789	0.0518
		188A→197A	-0.18846	
		188A→200A	-0.15647	
		188A→201A	-0.15198	
		192A→198A	-0.20837	
		192A→199A	0.18377	
		192A→200A	-0.11057	
		180B→192B	0.17461	
		181B→192B	0.34719	
		181B→193B	0.19900	
		182B→192B	0.40406	
		182B→193B	0.21485	
		183B→192B	0.26988	
		183B→193B	0.15468	
		188B→196B	-0.17695	
		188B→197B	0.17772	
		188B→200B	0.19772	
		188B→201B	0.22842	
		188B→202B	-0.12954	
S_{41}	318.79	190B→192B	-0.19688	0.0000
		190B→193B	-0.67754	
		191B→192B	0.68087	
		191B→193B	-0.18551	
S_{42}	318.79	190B→192B	-0.67501	0.0000
		190B→193B	0.20558	
		191B→192B	0.19416	
		191B→193B	0.67819	
S_{43}	312.54	189A→198A	0.10296	0.0123
		193A→198A	0.67916	
		193A→199A	0.39406	
		193A→200A	-0.32739	
		193A→201A	0.37750	
		193A→205A	-0.12625	
S_{44}	312.54	188A→198A	-0.10296	0.0123
		192A→198A	0.67916	
		192A→199A	-0.39406	
		192A→200A	-0.32742	
		192A→201A	-0.37747	
		192A→205A	0.12625	
S_{45}	310.88	190B→196B	-0.47165	0.0048
		190B→197B	-0.46229	
		190B→198B	0.14358	
		190B→199B	-0.11207	
		191B→196B	0.47700	
		191B→197B	0.46906	
		191B→198B	-0.14568	
		191B→199B	0.11334	
S_{46}	310.88	190B→196B	-0.47301	0.0048
		190B→197B	0.47302	
		190B→198B	-0.14567	
		190B→199B	-0.11333	
		191B→196B	-0.46777	
		191B→197B	0.46627	
		191B→198B	-0.14358	
		191B→199B	-0.11207	
S_{47}	307.86	180A→196A	-0.15618	0.0057
		181A→197A	0.14327	
		183A→197A	0.19164	
		184A→196A	-0.24882	

		185A→197A	-0.21744	
		186A→196A	-0.14204	
		188A→202A	0.17211	
		188A→203A	-0.14159	
		189A→202A	-0.14405	
		189A→203A	-0.17595	
		192A→209A	-0.11836	
		192A→210A	-0.13796	
		193A→209A	0.14032	
		193A→210A	-0.12123	
		180B→196B	0.16141	
		181B→197B	-0.2116	
		184B→196B	0.31350	
		185B→197B	0.33466	
		186B→196B	-0.25403	
		187B→197B	-0.17541	
		188B→204B	-0.16256	
		188B→205B	0.13222	
		189B→204B	0.13463	
		189B→205B	0.16610	
S_{48}	307.85	180A→197A	-0.15630	0.0000
		181A→196A	0.14334	
		183A→196A	0.19175	
		184A→197A	-0.24866	
		185A→196A	-0.21725	
		186A→197A	-0.14210	
		188A→202A	-0.19141	
		188A→203A	0.12259	
		189A→202A	-0.11969	
		189A→203A	-0.18788	
		192A→209A	0.14372	
		192A→210A	0.11652	
		193A→209A	0.11372	
		193A→210A	-0.14127	
		178B→193B	0.10229	
		179B→192B	-0.10342	
		180B→197B	0.16131	
		181B→196B	-0.21154	
		184B→197B	0.31360	
		185B→196B	0.33502	
		186B→197B	-0.25443	
		187B→196B	-0.17552	
		188B→204B	0.17660	
		188B→205B	-0.12063	
		189B→204B	0.11792	
		189B→205B	0.17327	
S_{49}	306.84	190A→196A	-0.44219	0.0039
		190A→197A	-0.48931	
		190A→198A	0.15578	
		190A→199A	0.10992	
		191A→196A	0.50356	
		191A→197A	0.43947	
		191A→198A	-0.14001	
		191A→199A	-0.12526	
S_{50}	306.84	190A→196A	0.50071	0.0040
		190A→197A	-0.44265	
		190A→198A	0.14001	
		190A→199A	-0.12526	
		191A→196A	0.43908	
		191A→197A	-0.49216	
		191A→198A	0.15578	
		191A→199A	-0.10992	

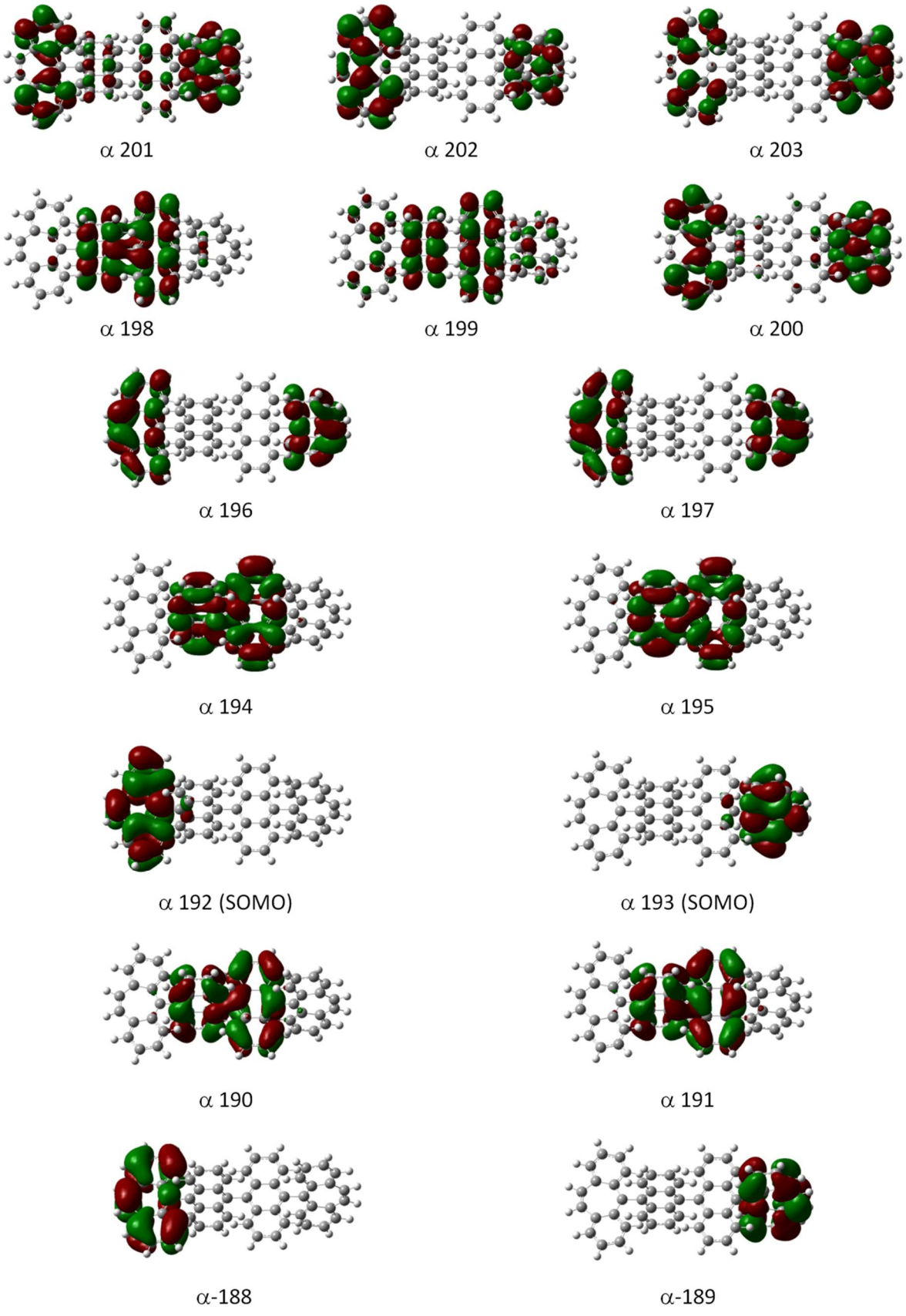


Figure S28. Molecular orbitals (α spin, isovalue = 0.02) involved in the excited states with more intense oscillator strengths calculated for **DBHept-TBC-TOS**.

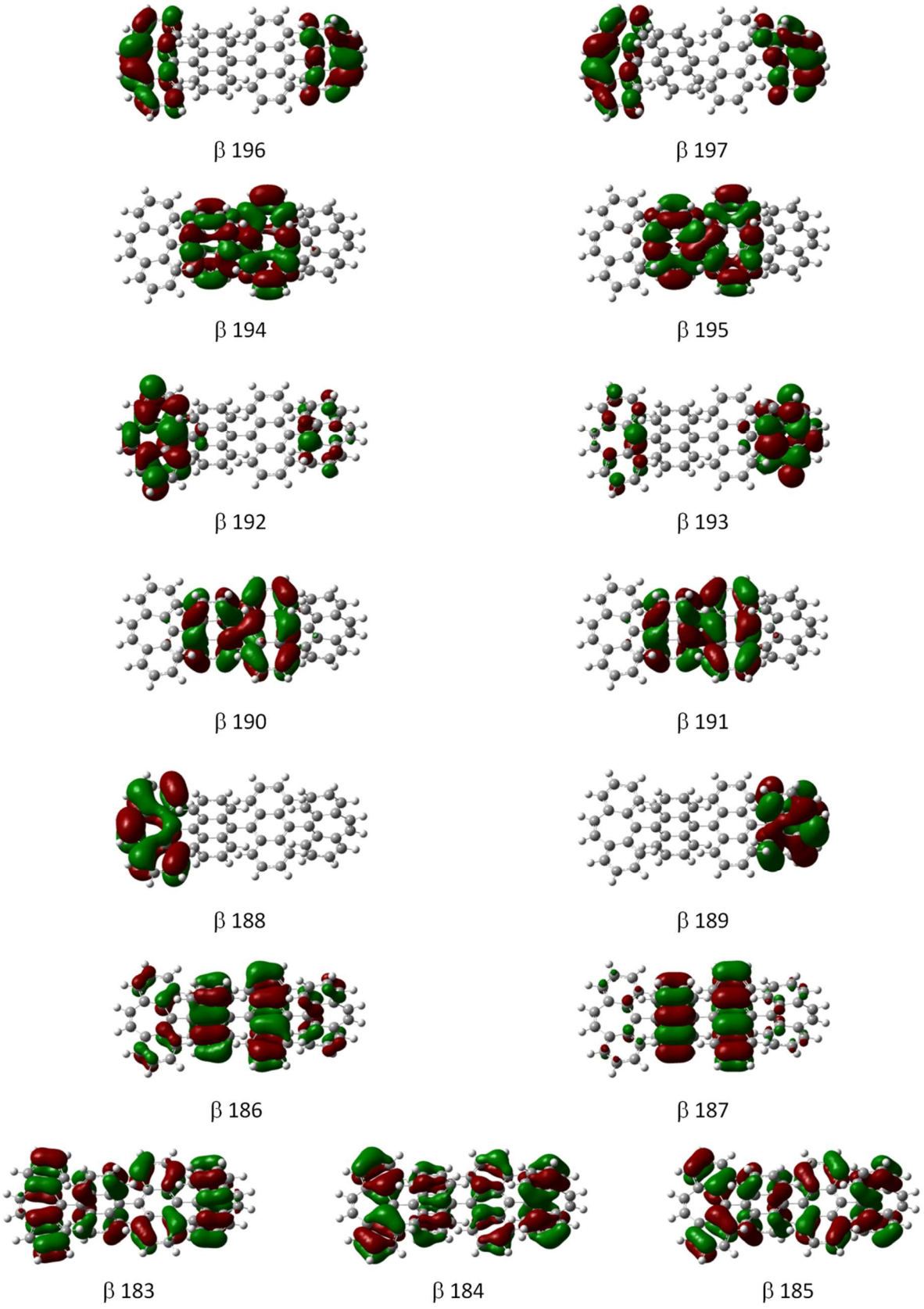


Figure S29. Molecular orbitals (β spin, isovalue = 0.02) involved in the excited states with more intense oscillator strengths calculated for **DBHept-TBC-TOS**.

Table S18. Lower energy electronic transitions (>300 nm) predicted by TDDFT at the UCAM-B3LYP/6-31G(d,p) level for **DBHept-TBC-SOS** in dichloromethane showing the molecular orbitals involved, the CI coefficients, the wavelength of the transition (nm) and the oscillator strength. The energy values obtained have been corrected by –0.3 eV. The most intense calculated transitions for each of the absorption bands predicted are highlighted in red.

State	λ_{cal} (nm)		CI	f
S_1	1097.95	187A → 198A	-0.10388	0.0000
		190A → 194A	-0.49868	
		191A → 195A	0.49813	
		187B → 198B	-0.10388	
		190B → 194B	0.49868	
		191B → 195B	-0.49813	
		190A ← 194A	-0.17013	
		191A ← 195A	0.17009	
		190B ← 194B	0.17013	
		191B ← 195B	-0.17009	
S_2	1083.47	190A → 194A	0.49813	0.0000
		191A → 195A	0.49754	
		190B → 194B	0.49813	
		191B → 195B	0.49754	
		190A ← 194A	0.16763	
		191A ← 195A	0.16758	
		190B ← 194B	0.16763	
		191B ← 195B	0.16758	
S_3	872.85	188A → 197A	0.19256	0.0002
		188A → 200A	0.10006	
		192A (SOMO) → 197A	0.91225	
		189B → 196B	-0.26628	
S_4	872.85	189A → 196A	-0.26628	0.0002
		188B → 197B	0.19256	
		188B → 200B	0.10006	
		192B (SOMO) → 197B	0.91225	
S_5	526.85	192A → 195A	0.72522	0.0000
		192B → 195B	-0.65530	
S_6	526.85	192A → 195A	0.65530	0.0000
		192B → 195B	0.72522	
S_7	461.35	180A → 201A	-0.10244	0.0000
		188A → 197A	-0.42765	
		192A → 197A	0.36455	
		192A → 200A	-0.12867	
		172B → 196B	0.10923	
		172B → 215B	0.10166	
		185B → 193B	0.1007	
		189B → 196B	0.73702	
S_8	461.35	172A → 196A	0.10923	0.0000
		172A → 215A	0.10166	
		185A → 193A	0.10070	
		189A → 196A	0.73702	
		180B → 201B	-0.10244	
		188B → 197B	-0.42765	
		192B → 197B	0.36455	
		192B → 200B	-0.12867	
S_9	459.89	189A → 193A	0.66571	0.1584
		192A → 201A	0.12138	
		189B → 193B	-0.66569	
		192B → 201B	-0.12138	
S_{10}	458.53	189A → 193A	0.67063	0.0000
		192A → 201A	-0.12383	
		189B → 193B	0.67065	
		192B → 201B	-0.12382	
S_{11}	449.95	190A → 193A	0.70631	0.0000
		190B → 193B	-0.68253	
S_{12}	449.95	190A → 193A	0.68253	0.0000
		190B → 193B	0.70631	
S_{13}	430.67	181A → 194A	0.17282	0.0000
		181A → 195A	0.16968	
		182A → 194A	-0.10463	
		182A → 195A	0.11118	

		183A → 194A	0.19750	
		184A → 195A	0.22727	
		185A → 194A	-0.19471	
		185A → 195A	0.15061	
		190A → 203A	-0.20123	
		190A → 204A	-0.21159	
		191A → 203A	-0.19470	
		191A → 204A	0.20461	
		181B → 194B	0.17019	
		181B → 195B	-0.17229	
		182B → 194B	-0.10305	
		182B → 195B	-0.11289	
		183B → 194B	0.19450	
		184B → 195B	0.23078	
		185B → 194B	-0.19176	
		185B → 195B	-0.15294	
		190B → 203B	-0.19816	
		190B → 204B	-0.20839	
		191B → 203B	0.19768	
		191B → 204B	-0.20778	
S_{14}	430.67	181A → 194A	-0.17071	0.0000
		181A → 195A	0.17177	
		182A → 194A	0.10270	
		182A → 195A	0.11321	
		183A → 194A	-0.19452	
		184A → 195A	0.23093	
		185A → 194A	0.19129	
		185A → 195A	0.15352	
		190A → 203A	0.19906	
		190A → 204A	0.20744	
		191A → 203A	-0.19678	
		191A → 204A	0.20872	
		181B → 194B	0.17333	
		181B → 195B	0.16916	
		182B → 194B	-0.10429	
		182B → 195B	0.11149	
		183B → 194B	0.19752	
		184B → 195B	-0.22743	
		185B → 194B	-0.19425	
		185B → 195B	0.15120	
		190B → 203B	-0.20211	
		190B → 204B	-0.21065	
		191B → 203B	-0.19378	
		191B → 204B	0.20557	
S_{15}	412.17	188A → 200A	-0.13574	0.0013
		192A → 197A	0.11992	
		192A → 198A	-0.14600	
		192A → 199A	0.21126	
		192A → 200A	0.62284	
		179B → 202B	0.13343	
		181B → 193B	0.11406	
		182B → 193B	-0.15199	
		184B → 193B	0.22215	
		185B → 193B	0.43251	
		186B → 193B	0.23437	
		187B → 193B	-0.22919	
		189B → 202B	0.12531	
S_{16}	412.17	179A → 202A	0.13343	0.0013
		181A → 193A	0.11406	
		182A → 193A	-0.15199	
		184A → 193A	-0.22215	
		185A → 193A	0.43251	
		186A → 193A	-0.23437	
		187A → 193A	0.22919	
		189A → 202A	0.12531	
		188B → 200B	-0.13574	
		192B → 197B	0.11992	
		192B → 198B	0.14600	
		192B → 199B	-0.21126	
		192B →200B	0.62284	
S_{17}	412.06	190A → 194A	-0.49005	0.5820
		191A → 195A	0.49048	
		190B → 194B	-0.49005	
		191B →195B	0.49048	
S_{18}	389.34	190A → 194A	0.49306	0.0000

		191A → 195A	0.49350	
		190B → 194B	-0.49306	
		191B → 195B	-0.49350	
S_{19}	374.80	185A → 194A	-0.12371	0.0000
		186A → 194A	-0.18464	
		186A → 195A	-0.32625	
		187A → 194A	0.36022	
		187A → 195A	-0.22305	
		190A → 198A	0.17590	
		190A → 199A	0.15545	
		191A → 198A	0.17664	
		191A → 199A	-0.14432	
		185B → 194B	-0.11862	
		186B → 194B	0.17701	
		186B → 195B	-0.34021	
		187B → 194B	-0.34544	
		187B → 195B	-0.23266	
		190B → 198B	0.16864	
		190B → 199B	0.14909	
		191B → 198B	-0.18418	
		191B → 199B	0.15053	
S_{20}	374.80	185A → 194A	-0.11875	0.0000
		186A → 194A	-0.17805	
		186A → 195A	0.33967	
		187A → 194A	0.34473	
		187A → 195A	0.23371	
		190A → 198A	0.16947	
		190A → 199A	0.14840	
		191A → 198A	-0.18341	
		191A → 199A	0.15121	
		185B → 194B	0.12384	
		186B → 194B	-0.18564	
		186B → 195B	-0.32569	
		187B → 194B	0.35954	
		187B → 195B	-0.22414	
		190B → 198B	-0.17670	
		190B → 199B	-0.15479	
		191B → 198B	-0.17584	
		191B → 199B	0.14503	
S_{21}	373.91	179A → 193A	0.19620	0.0024
		180A → 197A	-0.19873	
		181A → 197A	-0.12944	
		182A → 196A	-0.16662	
		183A → 196A	-0.23565	
		184A → 196A	0.11546	
		185A → 196A	-0.13303	
		188A → 201A	-0.19729	
		189A → 205A	0.20193	
		192A → 201A	-0.21723	
		192A → 208A	-0.21472	
		179B → 193B	-0.19620	
		180B → 197B	0.19874	
		181B → 197B	0.12944	
		182B → 196B	0.16662	
		183B → 196B	0.23565	
		184B → 196B	0.11546	
		185B → 196B	0.13303	
		188B → 201B	0.19729	
		189B → 205B	-0.20193	
		192B → 201B	0.21724	
		192B → 208B	0.21472	
S_{22}	373.91	179A → 193A	0.19625	0.0000
		180A → 197A	0.19869	
		181A → 197A	0.12921	
		182A → 196A	-0.16641	
		183A → 196A	-0.23579	
		184A → 196A	0.11532	
		185A → 196A	-0.13304	
		188A → 201A	0.19732	
		189A → 205A	0.20192	
		192A → 201A	0.21696	
		192A → 208A	0.21473	
		179B → 193B	0.19625	
		180B → 197B	0.19869	
		181B → 197B	0.12920	
		182B →196B	-0.16641	

		183B → 196B	-0.23579	
		184B →196B	-0.11532	
		185B →196B	-0.13304	
		188B →201B	0.19731	
		189B →205B	0.20193	
		192B →201B	0.21695	
		192B → 208B	0.21473	
S_{23}	372.40	192A → 193A	0.99077	0.0000
		192B → 193B	-0.13197	
S_{24}	372.40	192A → 193A	-0.13197	0.0000
		192B → 193B	0.99077	
S_{25}	362.72	192A → 194A	0.73389	0.0000
		192B → 194B	0.67522	
S_{26}	362.72	192A → 194A	-0.67520	0.0000
		192B → 194B	0.73388	
S_{27}	357.57	186A → 194A	0.10421	0.0000
		186A → 195A	0.20161	
		187A → 194A	-0.20928	
		187A → 195A	0.14161	
		190A → 196A	-0.13057	
		190A → 198A	0.29658	
		190A → 199A	0.25685	
		191A → 197A	-0.13292	
		191A → 198A	0.30920	
		191A → 199A	-0.24701	
		186B → 194B	-0.10663	
		186B → 195B	0.19707	
		187B → 194B	0.21410	
		187B → 195B	0.13840	
		190B → 196B	0.13359	
		190B → 198B	0.30346	
		190B → 199B	0.26275	
		191B → 197B	-0.12993	
		191B → 198B	-0.30225	
		191B → 199B	0.24141	
S_{28}	357.57	186A → 194A	-0.10723	0.0000
		186A → 195A	0.19675	
		187A → 194A	0.21367	
		187A → 195A	0.13905	
		190A → 196A	0.13361	
		190A → 198A	-0.30483	
		190A → 199A	-0.26165	
		191A → 197A	-0.12990	
		191A → 198A	0.30086	
		191A → 199A	-0.24261	
		186B → 194B	-0.10482	
		186B → 195B	-0.20130	
		187B → 194B	0.20884	
		187B → 195B	-0.14224	
		190B → 196B	0.13060	
		190B → 198B	0.29798	
		190B → 199B	0.25572	
		191B → 197B	0.13290	
		191B → 198B	0.30784	
		191B → 199B	-0.24818	
S_{29}	357.57	190A → 195A	0.16744	0.0000
		191A → 194A	0.67715	
		190B → 195B	-0.16745	
		191B → 194B	-0.67709	
S_{30}	357.18	190A → 195A	-0.15014	0.0000
		191A → 194A	0.68109	
		190B → 195B	-0.15012	
		191B → 194B	0.68116	
S_{31}	355.14	190A → 195A	-0.67737	0.0000
		191A → 194A	0.16801	
		190B → 195B	0.67746	
		191B →194B	-0.16800	
S_{32}	354.84	190A → 195A	0.68149	0.0000
		191A → 194A	0.15088	
		190B → 195B	0.68140	

		191B → 194B	0.15090	
S_{33}	347.39	183A → 193A	0.13785	0.0714
		184A → 193A	-0.17433	
		185A → 193A	0.32156	
		186A → 193A	-0.18462	
		187A → 193A	0.18744	
		188A → 197A	0.27887	
		192A → 198A	0.15780	
		192A → 199A	-0.16877	
		192A → 200A	-0.26081	
		183B → 193B	0.10117	
		184B → 193B	0.12795	
		185B →193B	0.23600	
		186B → 193B	0.13550	
		187B →193B	-0.13757	
		188B → 197B	0.37996	
		192B → 198B	-0.21501	
		192B → 199B	0.22995	
		192B → 200B	-0.35535	
		192B → 212B	0.10701	
S_{34}	347.39	183A → 193A	-0.10117	0.0714
		184A → 193A	0.12795	
		185A → 193A	-0.23600	
		186A → 193A	0.13550	
		187A → 193A	-0.13757	
		188A → 197A	0.37996	
		192A → 198A	0.21501	
		192A → 199A	-0.22995	
		192A → 200A	-0.35535	
		192A → 212A	0.10701	
		183B → 193B	0.13785	
		184B → 193B	0.17433	
		185B → 193B	0.32156	
		186B →193B	0.18462	
		187B → 193B	-0.18744	
		188B → 197B	-0.27887	
		192B → 198B	0.15780	
		192B → 199B	-0.16877	
		192B → 200B	0.26081	
S_{35}	346.76	179A → 193A	0.22525	0.0449
		189A → 193A	-0.12615	
		192A → 201A	0.58162	
		192A → 208A	-0.16717	
		179B → 193B	-0.22531	
		189B → 193B	0.12618	
		192B → 201B	-0.58146	
		192B → 208B	0.16713	
S_{36}	346.70	179A → 193A	-0.22502	0.0000
		189A → 193A	0.12670	
		192A → 201A	0.58146	
		192A → 208A	-0.16774	
		179B → 193B	-0.22496	
		189B → 193B	0.12666	
		192B → 201B	0.58162	
		192B → 208B	-0.16779	
S_{37}	337.08	177A → 195A	0.31827	0.0000
		178A → 194A	0.31980	
		181A → 204A	0.15071	
		184A → 203A	-0.10640	
		185A → 203A	-0.13165	
		190A → 206A	-0.28936	
		191A → 207A	0.29519	
		177B → 195B	-0.31827	
		178B → 194B	0.31981	
		181B → 204B	-0.15071	
		184B → 203B	-0.10640	
		185B → 203B	0.13165	
		190B → 206B	-0.28936	
		191B → 207B	-0.29519	
S_{38}	336.46	177A → 195A	0.31718	0.0000
		178A → 194A	-0.31864	
		181A →203A	-0.14177	
		184A → 204A	0.11594	
		185A → 204A	0.13604	

		190A → 206A	0.28793	
		191A → 207A	0.29375	
		177B → 195B	0.31718	
		178B → 194B	0.31864	
		181B →203B	-0.14177	
		184B → 204B	-0.11594	
		185B → 204B	0.13604	
		190B → 206B	-0.28793	
		191B →> 207B	0.29375	
S_{39}	336.23	186A → 194A	-0.14234	0.0002
		186A → 195A	-0.28042	
		187A → 194A	0.28282	
		187A → 195A	-0.19535	
		190A → 196A	0.16356	
		190A → 198A	-0.23926	
		190A → 199A	-0.20429	
		191A →197A	0.14962	
		191A → 198A	-0.24417	
		191A → 199A	0.19232	
		186B → 194B	-0.14314	
		186B → 195B	0.27886	
		187B → 194B	0.28440	
		187B → 195B	0.19426	
		190B → 196B	0.16447	
		190B → 198B	0.24061	
		190B → 199B	0.20543	
		191B → 197B	-0.14878	
		191B → 198B	-0.24282	
		191B → 199B	0.19125	
S_{40}	336.23	186A → 194A	-0.14400	0.0002
		186A → 195A	0.27842	
		187A → 194A	0.28380	
		187A → 195A	0.19512	
		190A → 196A	0.16450	
		190A →198A	-0.24171	
		190A → 199A	-0.20456	
		191A → 197A	-0.14876	
		191A →198A	0.24171	
		191A → 199A	-0.19218	
		186B → 194B	0.14320	
		186B → 195B	0.27999	
		187B → 194B	-0.28222	
		187B → 195B	0.19621	
		190B → 196B	-0.16358	
		190B → 198B	-0.24037	
		190B →199B	-0.20341	
		191B → 197B	-0.14959	
		191B → 198B	-0.24307	
		191B → 199B	0.19326	
S_{41}	326.06	181A → 193A	-0.18409	0.0454
		182A → 193A	0.43803	
		183A → 193A	0.47981	
		184A → 193A	-0.12727	
		189A → 196A	0.19837	
		189A → 202A	-0.30052	
		189A → 203A	0.10797	
		180B → 201B	0.11714	
		182B → 193B	0.16547	
		183B → 193B	0.18125	
		188B → 197B	0.19268	
		188B → 200B	0.22539	
		189B → 202B	-0.11352	
		192B → 198B	0.15999	
		192B →199B	-0.15021	
		192B → 200B	0.18977	
S_{42}	326.06	180A → 201A	0.11714	0.0454
		182A → 193A	-0.16547	
		183A → 193A	-0.18125	
		188A → 197A	0.19268	
		188A → 200A	0.22539	
		189A → 202A	0.11352	
		192A → 198A	-0.15999	
		192A → 199A	0.15021	
		192A → 200A	0.18977	
		181B → 193B	-0.18409	
		182B → 193B	0.43803	

		183B → 193B	0.47981	
		184B → 193B	0.12727	
		189B → 196B	0.19837	
		189B → 202B	-0.30052	
		189B → 203B	-0.10797	
S_{43}	319.95	191A → 193A	0.72148	0.0000
		191B → 193B	-0.68971	
S_{44}	319.94	191A → 193A	0.68967	0.0000
		191B → 193B	0.72144	
S_{45}	313.52	179A → 193A	0.10646	0.0022
		180A → 197A	0.15701	
		181A → 196A	-0.11187	
		182A → 196A	0.17698	
		182A → 197A	-0.11874	
		183A → 197A	0.11719	
		184A → 196A	0.13717	
		184A → 197A	0.19162	
		185A → 196A	-0.29417	
		186A → 196A	0.16714	
		186A → 197A	0.10598	
		187A → 196A	-0.16490	
		188A → 201A	0.22146	
		189A → 205A	-0.20543	
		192A → 208A	-0.17136	
		179B → 193B	-0.10671	
		180B → 197B	-0.15664	
		181B → 196B	0.11213	
		182B → 196B	-0.17740	
		182B → 197B	0.11847	
		183B → 197B	-0.11692	
		184B → 196B	0.13749	
		184B → 197B	0.19116	
		185B →196B	0.29486	
		186B → 196B	0.16753	
		186B →197B	0.10573	
		187B → 196B	-0.16529	
		188B → 201B	-0.22094	
		189B → 205B	0.20592	
		192B → 208B	0.17096	
S_{46}	313.52	179A → 193A	-0.10676	0.0000
		180A → 197A	0.15678	
		181A → 196A	0.11200	
		182A → 196A	-0.17767	
		182A → 197A	-0.11764	
		183A → 197A	0.11682	
		184A → 196A	-0.13685	
		184A → 197A	0.19184	
		185A → 196A	0.29539	
		186A → 196A	-0.16692	
		186A → 197A	0.10618	
		187A → 196A	0.16583	
		188A → 201A	0.22089	
		189A → 205A	0.20593	
		192A → 208A	-0.17069	
		179B → 193B	-0.10651	
		180B → 197B	0.15715	
		181B → 196B	0.11174	
		182B → 196B	-0.17726	
		182B → 197B	-0.11792	
		183B → 197B	0.11709	
		184B → 196B	0.13653	
		184B → 197B	-0.19229	
		185B → 196B	0.2947	
		186B → 196B	0.16653	
		186B → 197B	-0.10643	
		187B → 196B	-0.16544	
		188B → 201B	0.22141	
		189B → 205B	0.20544	
		192B → 208B	-0.17109	
S_{47}	312.23	190A → 196A	0.52014	0.0031
		190A → 198A	0.11356	
		190B → 196B	0.76098	
		190B → 198B	-0.16613	
		190B → 199B	-0.13203	
		192B → 198B	-0.11763	

S_{48}	312.23	190A → 196A	0.76103	0.0031
		190A → 198A	0.16611	
		190A → 199A	0.13209	
		192A → 198A	0.11742	
		190B → 196B	-0.52025	
		190B → 198B	0.11354	
S_{49}	312.15	188A → 197A	-0.13544	0.0035
		190A → 196A	-0.16604	
		192A → 198A	0.61876	
		192A → 199A	-0.37943	
		192A → 200A	0.38759	
		192B → 198B	0.31034	
		192B → 199B	-0.19030	
		192B → 200B	-0.19439	
S_{50}	312.15	192A → 198A	-0.31025	0.0035
		192A → 199A	0.19025	
		192A → 200A	-0.19434	
		188B → 197B	0.13543	
		190B → 196B	0.16625	
		192B → 198B	0.61873	
		192B → 199B	-0.37941	
		192B → 200B	-0.38757	
S_{51}	308.27	191A → 197A	0.82607	0.0041
		191A → 198A	0.18742	
		191A → 199A	-0.14664	
		191B →197B	-0.44740	
		191B → 198B	0.10146	
S_{52}	308.27	191A → 197A	0.44739	0.0041
		191A → 198A	0.10158	
		191B →197B	0.82607	
		191B →198B	-0.18748	
		191B → 199B	0.14657	
S_{53}	304.29	192A -> 196A	0.99271	0.0000
S_{54}	304.29	192B -> 196B	0.99271	0.0000

Table S19. Lower energy electronic transitions (>300 nm) predicted by TDDFT at the CAM-B3LYP/def2TZV level for **DBHept-TBC-SCS** in dichloromethane showing the molecular orbitals involved, the CI coefficients, the wavelength of the transition (nm) and the oscillator strength. The energy values obtained have been corrected by −0.3 eV. The most intense calculated transitions for each of the absorption bands predicted are highlighted in red.

State	λ_{cal} (nm)		CI	f
S_1	355.67	190 →193	0.15704	1.0915
		191 →196	0.12052	
		192 (H) →193 (L)	0.65620	
S_2	309.80	188 →196	-0.10242	0.0000
		189 →193	-0.21086	
		190 →196	-0.19587	
		191 →193	0.50130	
		191 →197	-0.16707	
		192 →196	0.32655	
S_3	308.89	190 →195	0.32039	0.0000
		191 →194	0.47009	
		192 →195	-0.38856	
S_4	308.23	190 →194	0.31778	0.3899
		191 →195	0.46936	
		192 →194	-0.39209	
S_5	302.67	188 →193	0.33118	0.3728
		190 →193	0.47893	
		191 →196	-0.30790	
		192 →197	0.12540	

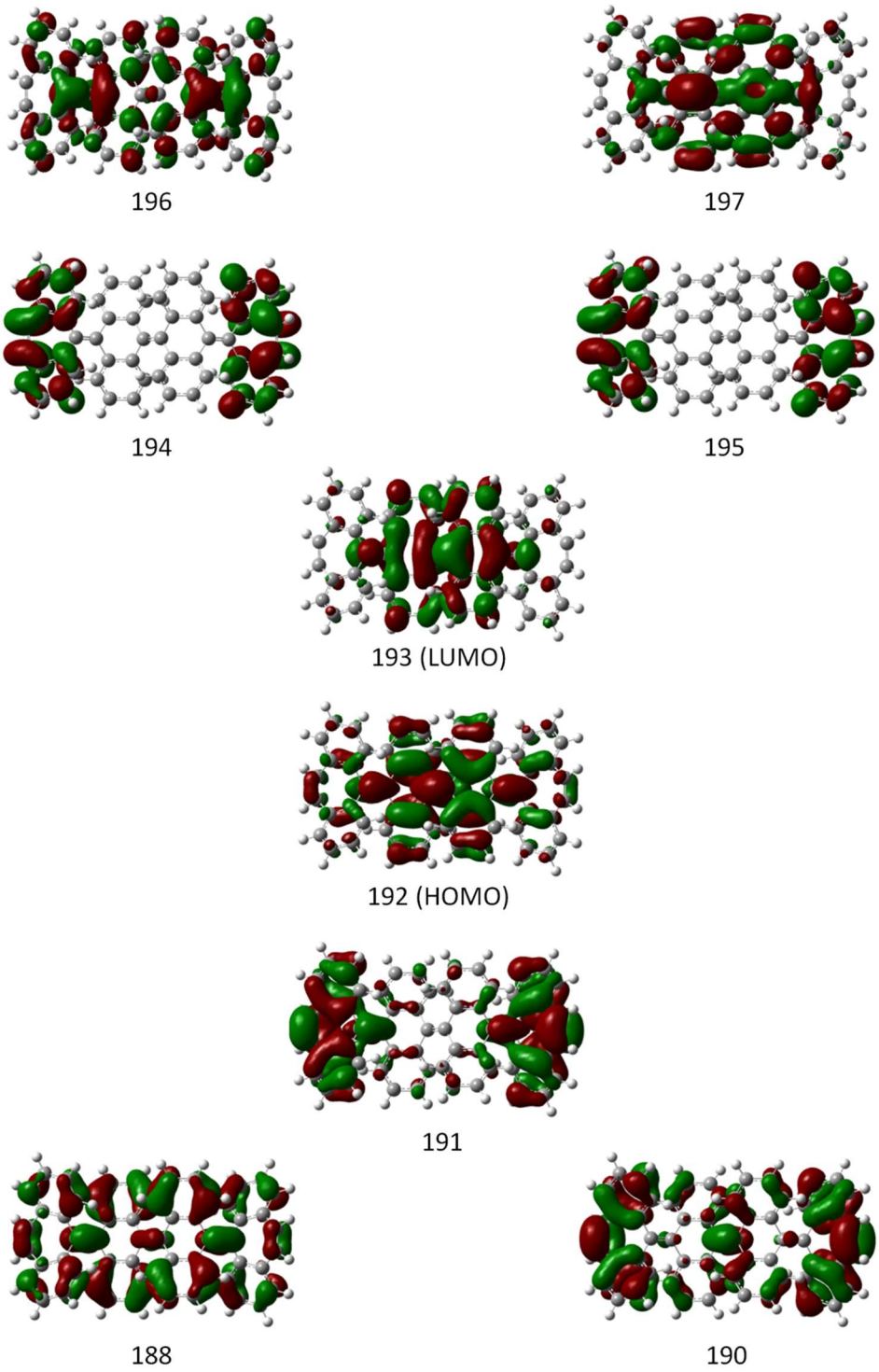


Figure S30. Molecular orbitals (isovalue = 0.02) involved in the excited states with more intense oscillator strengths calculated for **DBHept-TBC-SCS**.

7.4. Energy barrier between geometries of DBHept-Anthracene

To evaluate the energy barrier between the orthogonal planar geometry of **DBHept-TBC-TOS** and the saddle-butterfly shape of **DBHept-TBC-SCS**, we considered the simple model radical compound **DBHept-Anthracene**, incorporating a dibenzocycloheptatriene (DBHept) unit and an anthracene moiety (Figure S31), previously studied by Nishiuchi, Kubo and co-workers.[S12] We repeated the optimization of this model compound by DFT methods in both geometries and calculated the corresponding transition state between them at our level of theory, different from that employed in the original paper. Thus, the calculations were performed at the UB3LYP/6-31G(d,p) level of theory in dichloromethane as solvent using the polarizable continuum model with the integral equation formalism (IEFPCM) model.[S10] The transition state was calculated using the synchronous transit-guided quasi-Newton method[S13] implemented in Gaussian 09 (QST2 or QST3). Analytical frequencies were also calculated for all the structures to corroborate they corresponded to an energy minimum or a transition state, respectively. The calculated coordinates and structures are shown in Tables S20-S22.

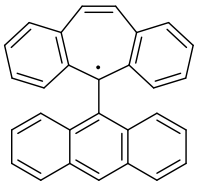


Figure S31. Structure of the model compound **DBHept-Anthracene** modelled to evaluate the energy barrier between geometries.[S12]

In this radical model compound the orthogonal planar geometry is more stable ($\Delta G \approx 36$ kcal/mol) in agreement with the results on **DBHept-TBC**, where this planar structure is also the more stable geometry in an open shell configuration such as the triplet, as the saddle butterfly geometry is higher in energy ($\Delta E \approx 34.5$ kcal/mol, see Table S2). Therefore, starting from this orthogonal geometry, the transition state in the interconversion path to the saddle geometry is *ca.* 20 kcal/mol higher in free energy. These results agree with those already reported.[S12]

It should be noted that this model system probably underestimates the real energy barrier in **DBHept-TBC** as only the steric clash between the DBHept and the anthracene unit is considered but not the one that could arise from two connected anthracene units. Therefore, these results suggest that this energy barrier between geometries makes that, at room temperature, the orthogonal planar geometry of **DBHept-TBC** should be maintained upon reduction of the cation species, giving rise to an open shell system rather than the overall more stable **DBHept-TBC-SCS** geometry. The relative energies of the different species are shown in Figure S32.

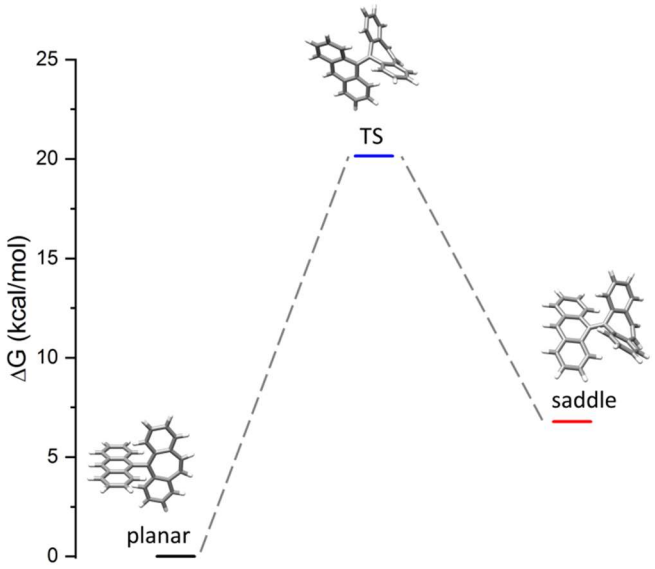
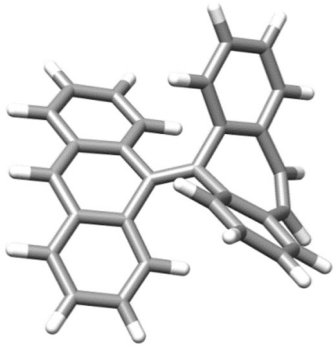


Figure S32. DFT-calculated relative free energies of the different geometries for the radical model compound and the corresponding transition state.

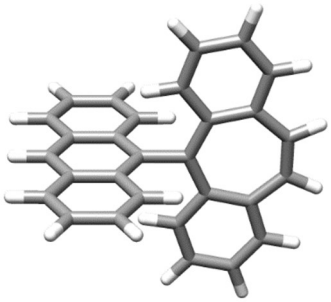
Table S20. Atomic coordinates for the saddle-butterfly geometry of **DBHept-Anthracene**



Atom	X	Y	Z
C	-0.599236	-0.000154	0.079743
C	-1.409384	1.231023	0.314356
C	-2.485810	1.555670	-0.547606
C	-2.935303	0.675600	-1.627689
C	-2.935008	-0.676805	-1.627720
C	-2.485157	-1.556727	-0.547662
C	-1.408897	-1.231658	0.314348
C	-3.168241	-2.773582	-0.345250
C	-2.858219	-3.609096	0.721248
C	-1.843324	-3.245619	1.613470
C	-1.126186	-2.071959	1.403651
C	-3.169405	2.772226	-0.345128
C	-2.859723	3.607826	0.721399
C	-1.844622	3.244768	1.613558
C	-1.126988	2.071417	1.403679
C	0.753430	0.000135	-0.184280
C	1.550918	-1.247213	-0.283226
C	1.066125	-2.444169	-0.838347
C	1.830222	-3.606919	-0.840759
C	3.114695	-3.613822	-0.269047
C	3.641384	-2.441296	0.238212
C	2.900070	-1.230086	0.202280
C	3.506119	0.000801	0.556334
C	2.899483	1.231393	0.202241
C	3.640201	2.442971	0.238149
C	3.112939	3.615229	-0.269135
C	1.828479	3.607683	-0.840866
C	1.064965	2.444553	-0.838456
C	1.550342	1.247840	-0.283302
H	-3.427123	1.172399	-2.461930
H	-3.426601	-1.173780	-2.461991
H	-3.970483	-3.041931	-1.027624
H	-3.409495	-4.533467	0.864968
H	-1.602207	-3.883742	2.458340
H	-0.315626	-1.804040	2.073957
H	-3.971790	3.040252	-1.027458
H	-3.411409	4.531942	0.865188
H	-1.603769	3.882963	2.458449
H	-0.316317	1.803807	2.073975
H	0.080150	-2.463634	-1.284671
H	1.428079	-4.511533	-1.286564
H	3.700025	-4.528355	-0.252458
H	4.651738	-2.418658	0.637709
H	4.518395	0.001037	0.951214
H	4.650565	2.420839	0.637653
H	3.697814	4.530054	-0.252553
H	1.425879	4.512107	-1.286647
H	0.078956	2.463542	-1.284733

Charge = 0; multiplicity = 2; (0 imaginary frequencies)
Zero-point correction = 0.383683 (Hartree/Particle)
Thermal correction to Energy = 0.404372
Thermal correction to Enthalpy = 0.405316
Thermal correction to Gibbs Free Energy = 0.334147
Sum of electronic and zero-point Energies = −1116.155176
Sum of electronic and thermal Energies = −1116.134487
Sum of electronic and thermal Enthalpies = −1116.133543
Sum of electronic and thermal Free Energies = −1116.204712

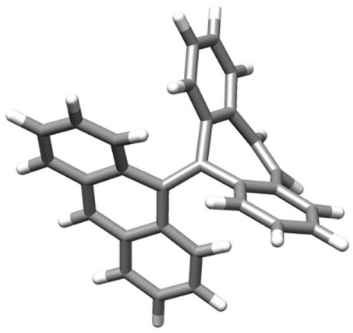
Table S21. Atomic coordinates for the orthogonal planar geometry of **DBHept-Anthracene**



Atom	X	Y	Z
C	0.762488	0.000000	-0.000002
C	1.372113	-1.322338	0.001336
C	2.778919	-1.634995	0.001460
C	3.865105	-0.674212	0.000562
C	3.865050	0.674468	-0.000472
C	2.778784	1.635160	-0.001450
C	1.372006	1.322381	-0.001357
C	3.191166	2.982698	-0.002665
C	2.300234	4.047495	-0.003812
C	0.932465	3.763428	-0.003776
C	0.494284	2.448475	-0.002598
C	3.191422	-2.982496	0.002641
C	2.300588	-4.047374	0.003726
C	0.932794	-3.763430	0.003667
C	0.494494	-2.448517	0.002522
C	-0.748352	-0.000038	0.000006
C	-1.457600	0.001315	1.224950
C	-0.793070	0.002685	2.494214
C	-1.500908	0.004061	3.668053
C	-2.926041	0.004139	3.658180
C	-3.603607	0.002797	2.468331
C	-2.903581	0.001329	1.220113
C	-3.587593	-0.000088	0.000026
C	-2.903597	-0.001471	-1.220071
C	-3.603641	-0.002959	-2.468279
C	-2.926091	-0.004265	-3.658138
C	-1.500958	-0.004129	-3.668030
C	-0.793105	-0.002732	-2.494200
C	-1.457617	-0.001400	-1.224928
H	4.850389	-1.135180	0.000904
H	4.850296	1.135517	-0.000750
H	4.258668	3.184330	-0.002705
H	2.661964	5.070660	-0.004708
H	0.201802	4.566849	-0.004686
H	-0.572223	2.275120	-0.002596
H	4.258943	-3.184032	0.002705
H	2.662411	-5.070506	0.004595
H	0.202204	-4.566918	0.004533
H	-0.572028	-2.275265	0.002501
H	0.291261	0.002636	2.514050
H	-0.973989	0.005104	4.617638
H	-3.469197	0.005249	4.598426
H	-4.690196	0.002836	2.449384
H	-4.674910	-0.000108	0.000033
H	-4.690230	-0.003042	-2.449318
H	-3.469260	-0.005390	-4.598376
H	-0.974052	-0.005145	-4.617622
H	0.291227	-0.002640	-2.514051

Charge = 0; multiplicity = 2; (0 imaginary frequencies)
Zero-point correction = 0.384369 (Hartree/Particle)
Thermal correction to Energy = 0.405161
Thermal correction to Enthalpy = 0.406105
Thermal correction to Gibbs Free Energy = 0.333551
Sum of electronic and zero-point Energies = −1116.164708
Sum of electronic and thermal Energies = −1116.143916
Sum of electronic and thermal Enthalpies = −1116.142971
Sum of electronic and thermal Free Energies = −1116.215526

Table S22. Atomic coordinates for the transition state between geometries of **DBHept-Anthracene**

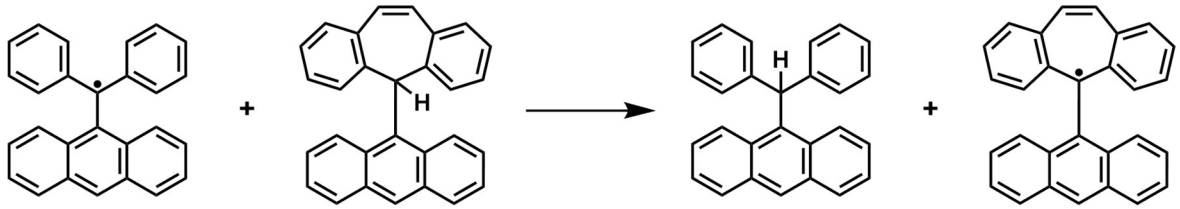


Atom	X	Y	Z
C	0.509170	0.433920	0.375123
C	1.808621	-0.076092	0.870947
C	2.959132	-0.213897	0.048797
C	2.932324	0.053725	-1.385934
C	2.157105	0.940853	-2.045826
C	1.274113	1.954693	-1.467545
C	0.570229	1.810164	-0.235047
C	1.200620	3.176582	-2.165790
C	0.544967	4.282744	-1.640732
C	-0.042478	4.180419	-0.380672
C	-0.025992	2.964379	0.301633
C	4.138847	-0.732640	0.616937
C	4.210304	-1.075458	1.962781
C	3.079370	-0.932994	2.773225
C	1.894561	-0.448544	2.225946
C	-0.674737	-0.392694	0.305881
C	-1.983795	0.151100	0.597649
C	-2.166811	1.173089	1.565089
C	-3.408966	1.713305	1.832999
C	-4.553051	1.248924	1.140620
C	-4.436511	0.191555	0.269593
C	-3.171527	-0.420801	0.023158
C	-3.067308	-1.615866	-0.699761
C	-1.855645	-2.324181	-0.753959
C	-1.830538	-3.616379	-1.361215
C	-0.678238	-4.357692	-1.422377
C	0.511573	-3.822626	-0.875614
C	0.529401	-2.567377	-0.304868
C	-0.638315	-1.757468	-0.212364
H	3.662055	-0.500089	-1.973550
H	2.320592	1.032934	-3.117712
H	1.704957	3.252665	-3.125356
H	0.513747	5.215903	-2.194843
H	-0.527580	5.039424	0.073185
H	-0.491506	2.924635	1.273357
H	5.008808	-0.865975	-0.020676
H	5.136561	-1.462508	2.376445
H	3.117574	-1.210741	3.822253
H	1.008938	-0.355198	2.847187
H	-1.314741	1.472815	2.161858
H	-3.512289	2.478966	2.595864
H	-5.524116	1.692891	1.338021
H	-5.315179	-0.227742	-0.212987
H	-3.954171	-2.045030	-1.158524
H	-2.761464	-4.006056	-1.764209
H	-0.677466	-5.343925	-1.876408
H	1.426986	-4.406502	-0.901776
H	1.459759	-2.210918	0.105843

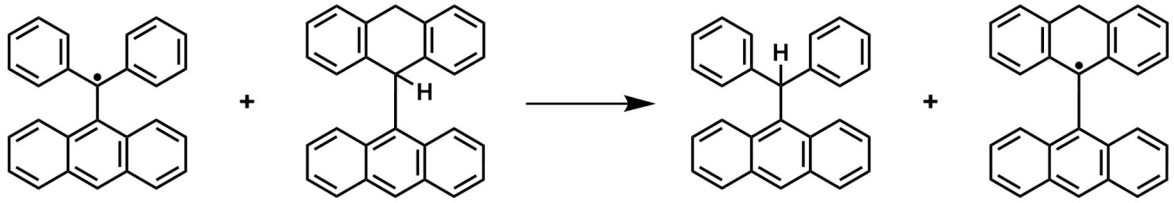
Charge = 0; multiplicity = 2; (1 imaginary frequency)
Zero-point correction = 0.383320 (Hartree/Particle)
Thermal correction to Energy = 0.403285Thermal correction to Enthalpy = 0.404229
Thermal correction to Gibbs Free Energy = 0.335098
Sum of electronic and zero-point Energies = −1116.135183
Sum of electronic and thermal Energies = −1116.115218
Sum of electronic and thermal Enthalpies = −1116.114274
Sum of electronic and thermal Free Energies = −1116.183405

7.5. Radical stabilization energies

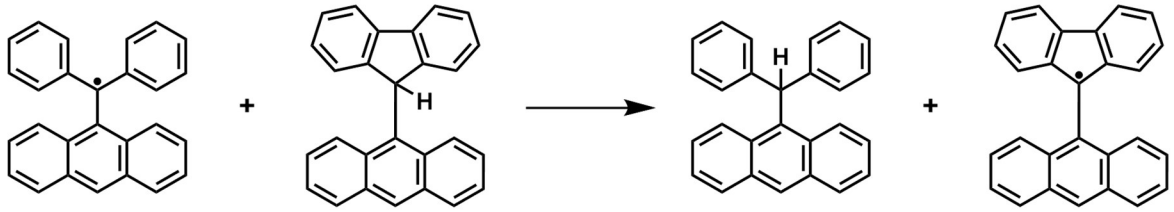
Reaction 1:



Reaction 2:



Reaction 3:



Scheme S3. Isodesmic reactions used to calculate the radical stabilization energies (RSEs) of different end-groups relative to (9-anthryldiphenyl)methyl radical (see Table S23).

Table S23. Radical stabilization energies (RSEs) of substituted (9-anthryl)methyl radicals employing the end-groups considered in this and previous studies according to isodesmic reactions displayed in Scheme S3.

Reaction[a]	*RSE*[b] (0K, in kcal mol^{-1})				
	B3LYP	BMK	M06-2X	M11L	PBE0
1	–2.0	–1.0	–0.2	–2.1	–1.5
2	–3.4	–2.8	–2.3	–2.5	–2.8
3	–0.7	–1.2	–1.0	–1.1	–0.5

[a] According to Scheme S3. [b] Calculated *via* isodesmic reactions depicted in Scheme S3 with cc-pVTZ basis set and the corresponding density functional (gas phase) at B3LYP/6-31G(d,p) gas phase optimized geometries. The final energies (kcal mol^{-1}) of individual molecules individual are the sum of the electronic energy and the unscaled zero-point vibrational energy corrections ($RSE = E_{el} + ZVPE$). UKS formalism was used for the radicals.

We evaluated the RSEs to investigate their relative ability to stabilize radical centers. We used to (9-anthryldiphenyl)methyl radical as simplified model. In this case, as shown in Table S23, all groups exert a similar stabilization of a radical center and are, therefore, all alike. Therefore, in our case, the orthogonal diradical might be kinetically stabilized due to the size of planar DBHept, that enhances the steric clash with central anthracenes. Previous works of Wu (ref 13a in the manuscript) and Kubo (ref 18e in the manuscript) suggested that fluorenyl end-group can exert an extra radical stabilization ability because it is not fully orthogonal to the anthracene unit. As a result, the triplet diradical form of a Chichibabin PAH synthesized by Wu was shown to be the thermodynamic product of the precursor diol reduction. However, fluorenyl could also increase the energy of the closed-shell singlet state in the “butterfly-like” geommetry.

8. Electrochemical properties

Cyclic voltammograms (CV) and square wave voltammograms (SWV) were recorded on a *PGSTAT204* potentiostat/galvanostat (*Metrohm Autolab B. V.*) in a conventional three-electrode cell under inert atmosphere at 25 ºC. WE = glassy carbon disk, CE= Pt wire and RE= silver wire, were used together with ferrocene as an internal reference. Potential values were referenced to the ferrocenium/ferrocene (Fc^+/Fc) system. All the experiments were carried out at *ca*. 4 × 10^{-3} M in HPLC grade DCM with a 0.1 M solution of tetra-*n*-butylammonium hexfluorophosphate ($TBAPF_6$) as electrolyte.

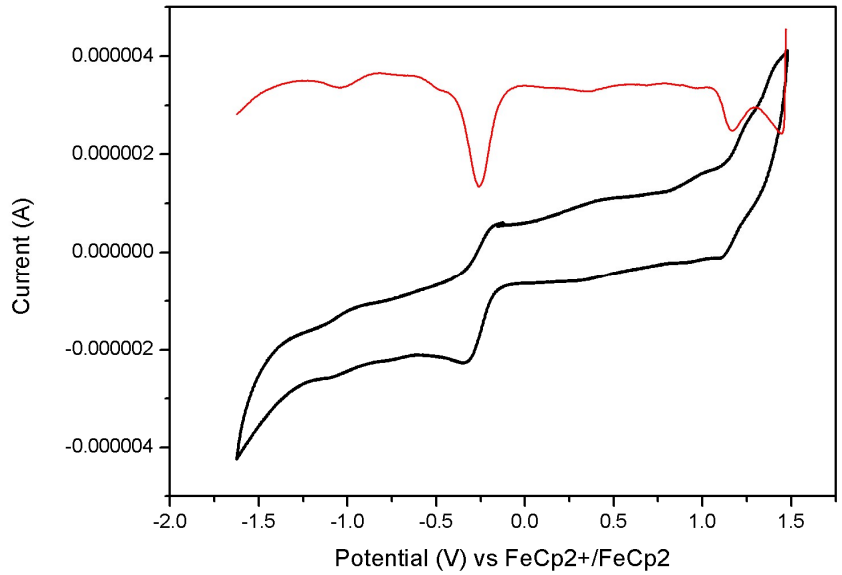


Figure S33. Cyclic (black line) and square wave (red line) voltammograms of **[DBHept-TBC]$^{2+}$** (c.a. 10^{-3} M) in DCM (internal standard Fc/Fc^+, scan rate = 0.1 V/s).

In-situ UV-Vis spectroelectrochemical studies were conducted on a JASCO V-780 UV-visible/NIR spectrophotometer together with an Autolab electrochemical analyzer (PGSTAT 204 potentiostat/galvanostat) with NOVA 1.9 software, connected to a thin-layer cell from a demountable omni cell from Specac (WE = CE = Pt gauze and RE= silver wire). All the spectra were collected at constant potential electrolysis at room temperature and a 400 nm/min scan rate. The electrochemical medium used was 0.2 M $TBAPF_6$ in fresh distilled CD_2Cl_2, at room temperature with a sample concentration of 10^{-3} M.

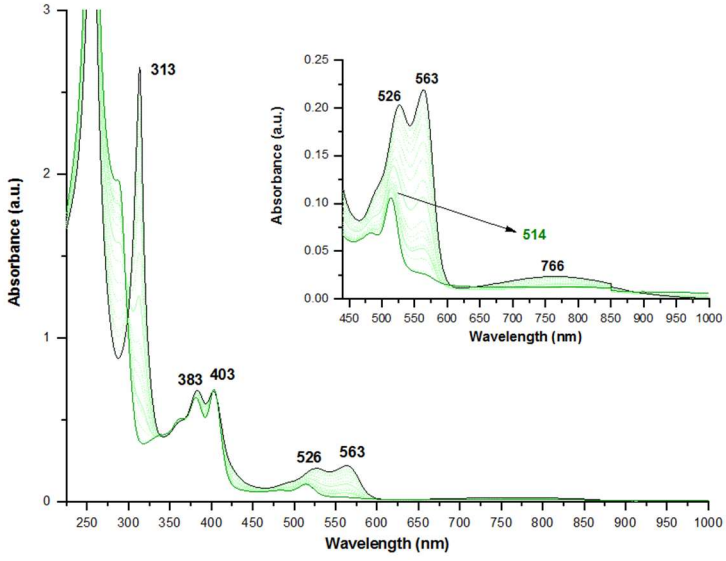


Figure S34. Spectroelectrochemistry measurement of **[DBHept-TBC]$^{2+}$** (10^{-3} M) in dry DCM: UV-Vis absorption spectrum of **[DBHept-TBC]$^{2+}$** (black); UV-Vis absorption spectrum with external potential of −1.4V (dark green); UV-Vis spectra after removal of the external potential (light green).

9. SQUID Measurements

Experimental. Magnetic susceptibility measurements were carried out in the temperature range 2-350 K with an applied magnetic field of 0.1 T on a solid sample of compound **DBHept-TBC** (with a mass of 21.334 mg) with a Quantum Design MPMS-XL-5 SQUID susceptometer. Susceptibility data were corrected for the sample holder and for the diamagnetic contribution of the salts using Pascal's constants.[S14]

To fit the thermal variation of $\chi_m T$ (Figure S35) we have used the classic Bleaney Bowers model[S15] for a S = ½ dimer including interdimer interactions (zJ') using the mean field approximation. This model reproduces very satisfactorily the magnetic properties of compound **DBHept-TBC** in the whole temperature range with g = 2.06, J = −258 cm^{-1}, zJ' = -17 cm^{-1} and a paramagnetic impurity of 12.9 % (solid line in Figure S35, the Exchange hamiltonian is written as $H = -JS_1S_2$ and, therefore, J represents the singlet-triple gap: ΔE_{S-T} = 258 cm^{-1} = 0.74 kcal/mol). The interdimer interaction (zJ') may be attributed to the presence of intermolecular π-π interactions of the radical centres in the solid state.

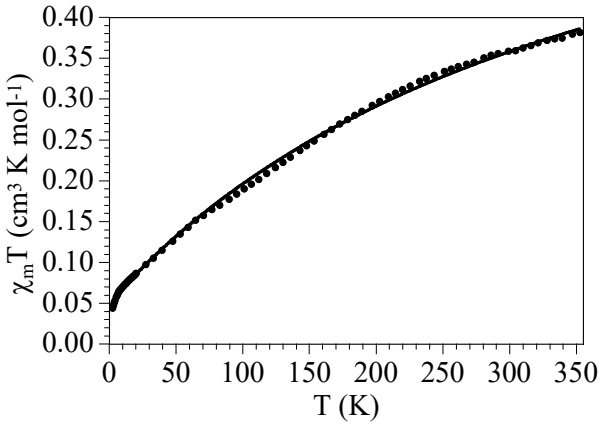


Figure S35. Thermal variation of $\chi_m T$ for compound **1**. Solid line is the best fit to the model (see text).

10. References

S1 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.

S2 G. M. Sheldrick, *Acta Cryst.,* 2015, **A71**, 3.

S3 M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone and G. Polidori, *J. Appl. Cryst.,* 2015, **48**, 306.

S4 a) G. M. Sheldrick, *Acta Cryst.,* 2008, **A64**, 112; (b) G. M. Sheldrick, *Acta Cryst.,* 2015, **C71**, 3.

S5 L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849.

S6 A. L. Spek, *Acta Cryst.,* 2009, **D65**, 148.

S7 A. L. Spek, *Acta Cryst.,* 2015, **C71**, 9.

S8 The ellipsoid image was generated with the OLEX2 software package: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

S9 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.

S10 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.* 2005, **105**, 2999.

S11 H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, S. J. Bennie, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, S. J. R. Lee, Y. Liu, A. W. Lloyd, Q. Ma, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, T. F. {Miller III}, M. E. Mura, A. Nicklaß, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang and M. Welborn, MOLPRO 2012.

S12 T. Nishiuchi, R. Ito, A. Takada, Y. Yasuda, T. Nagata, E. Stratmann and T. Kubo, *Chem. Asian J.*, 2019, **14**, 1830.

S13 a) C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, *J. Comput. Chem.,* 1996, **17**, 49; b) C. Peng and H. B. Schlegel*, Isr. J. Chem.*, 1994**, 33**, 449.

S14 G. A. Bain and J. F. Berry, *J. Chem. Educ.,* 2008, **85**, 532.

S15 B. Bleaney and K. D. Bowers, *Proc. R. Soc. Lond. A.* **1952***, 214*, 451.

ANNEX I: ^{1}H and ^{13}C NMR spectra of new compounds

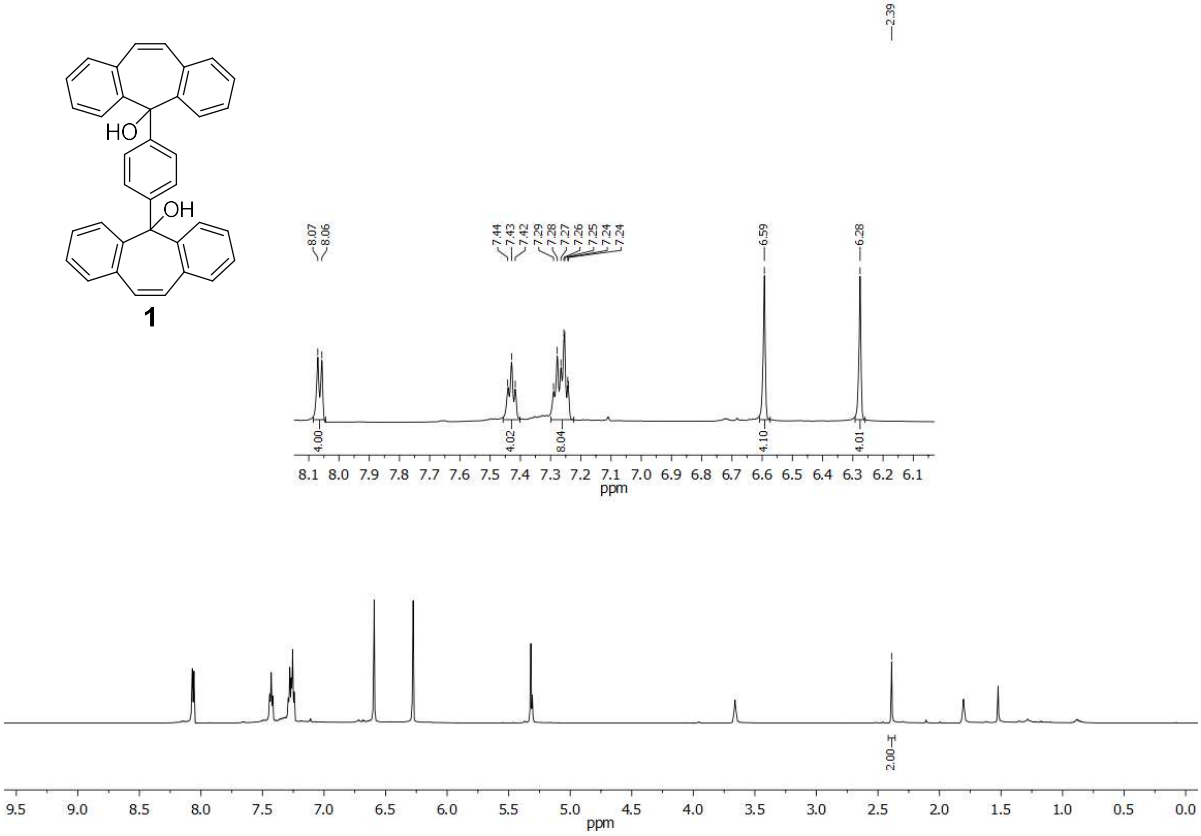


Figure S36. ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of **1**.

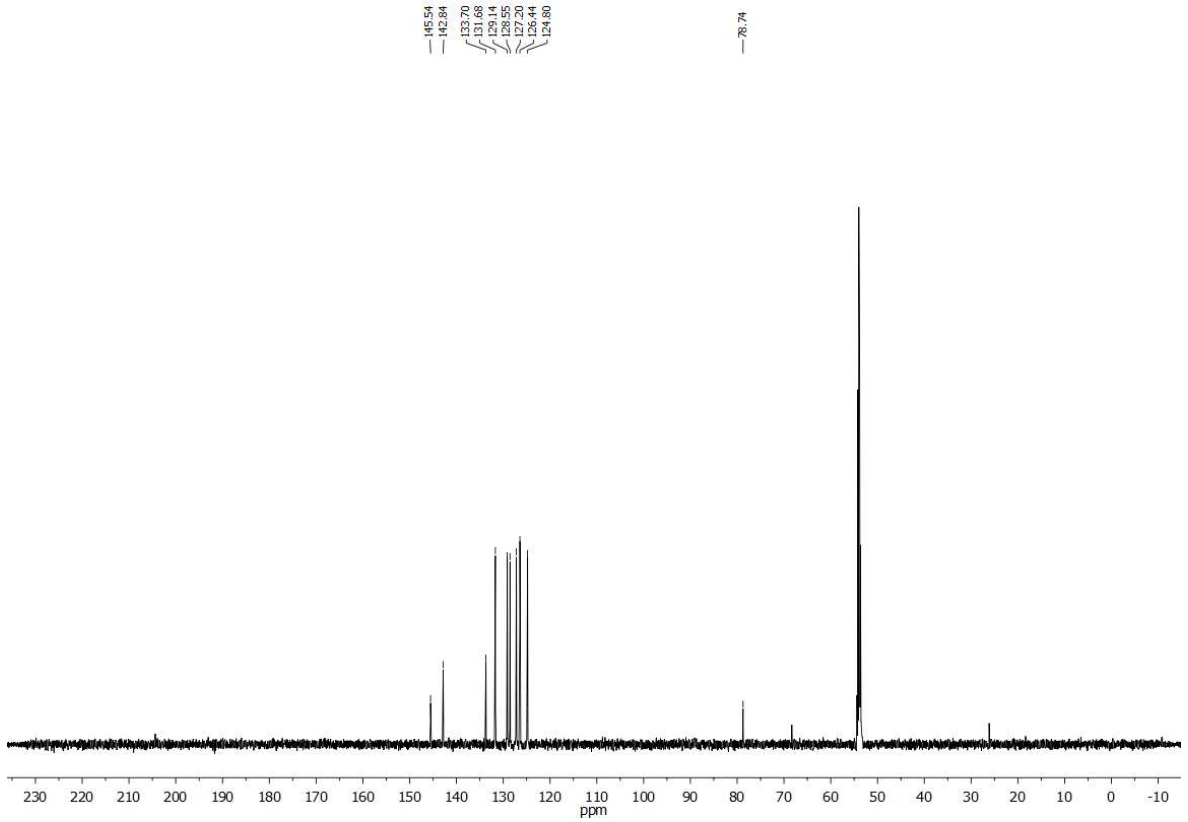


Figure S37. ^{13}C NMR (150 MHz, CD_2Cl_2) spectrum of **1**.

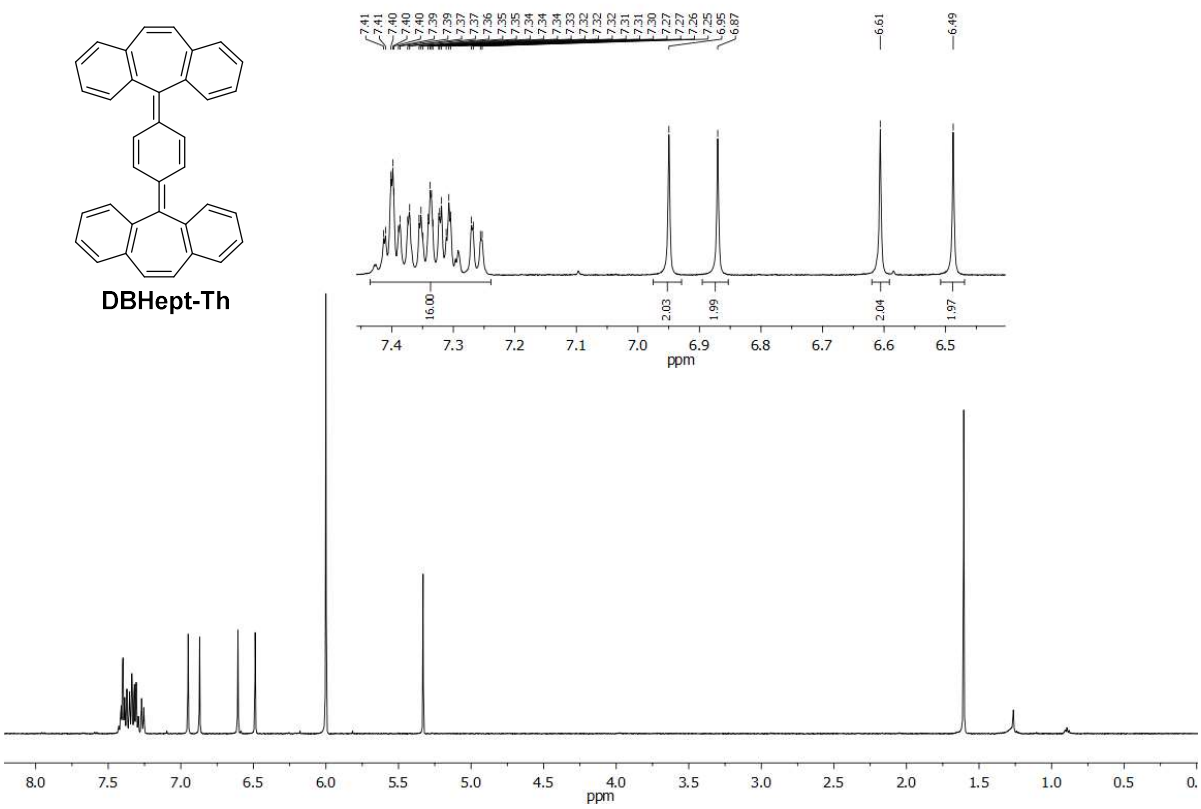


Figure S38. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) spectrum of **DBHept-Th**.

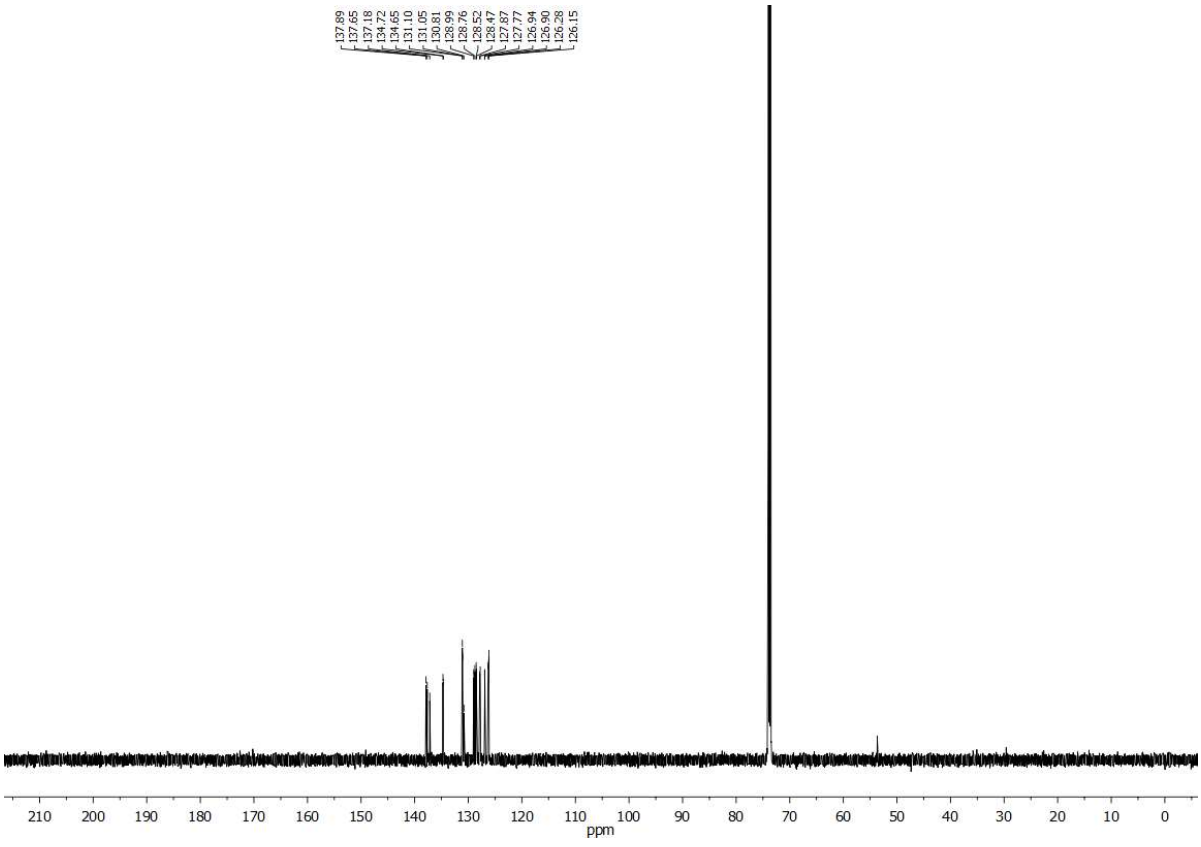


Figure S39. ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) spectrum of **DBHept-Th**.

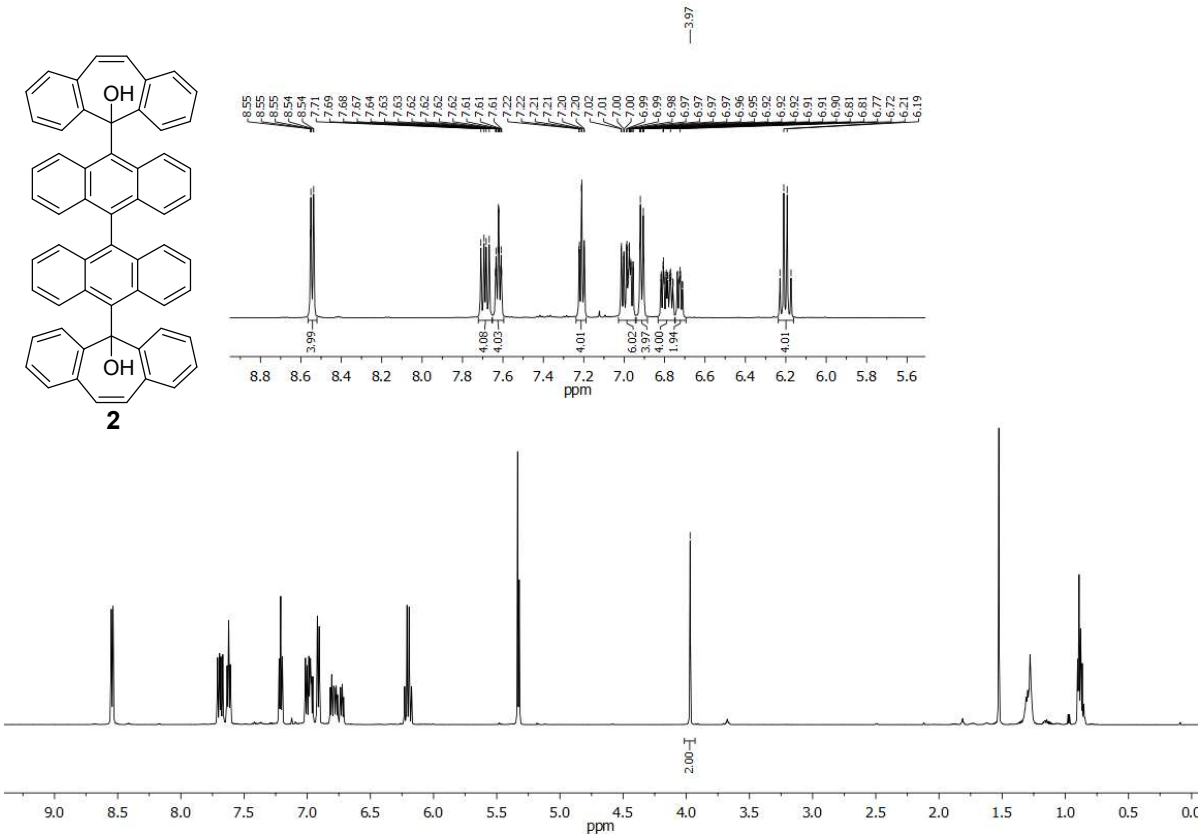


Figure S40. ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of **2**.

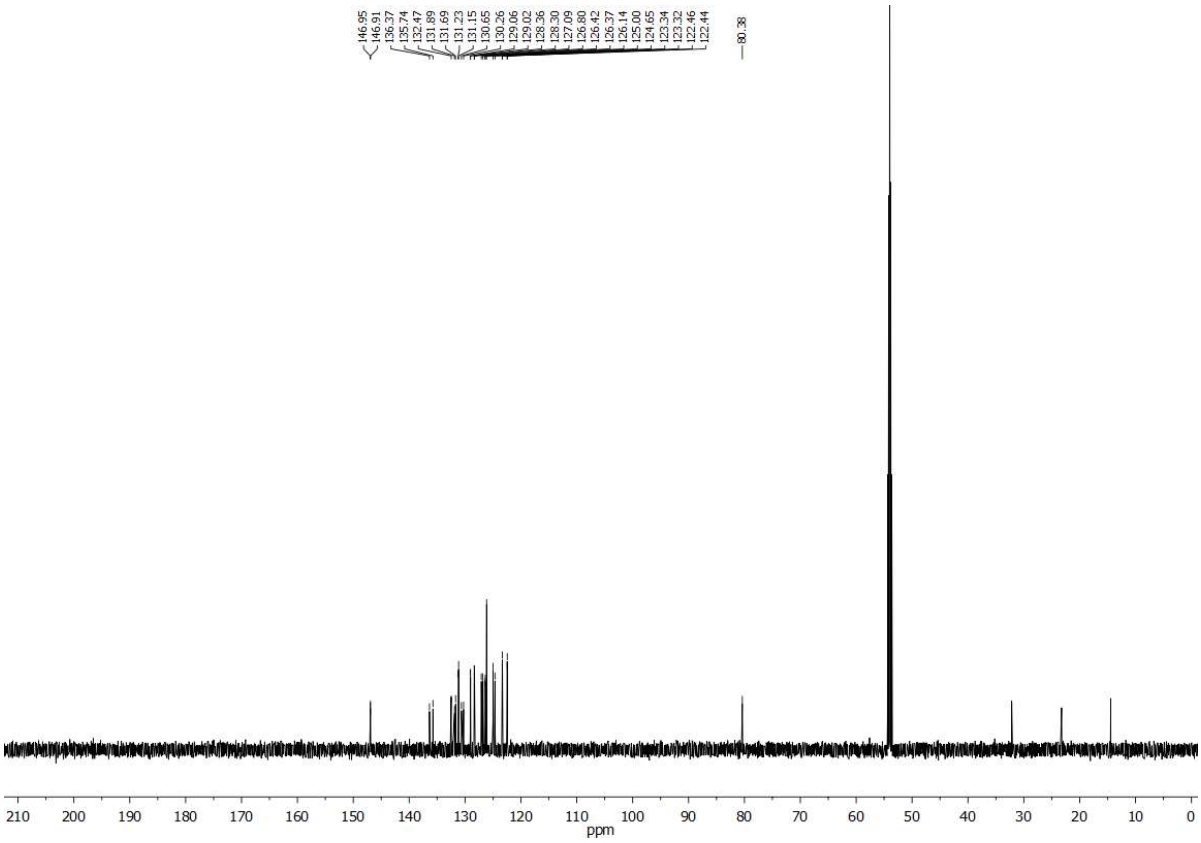


Figure S41. ^{13}C NMR (150 MHz, CD_2Cl_2) spectrum of **2**.

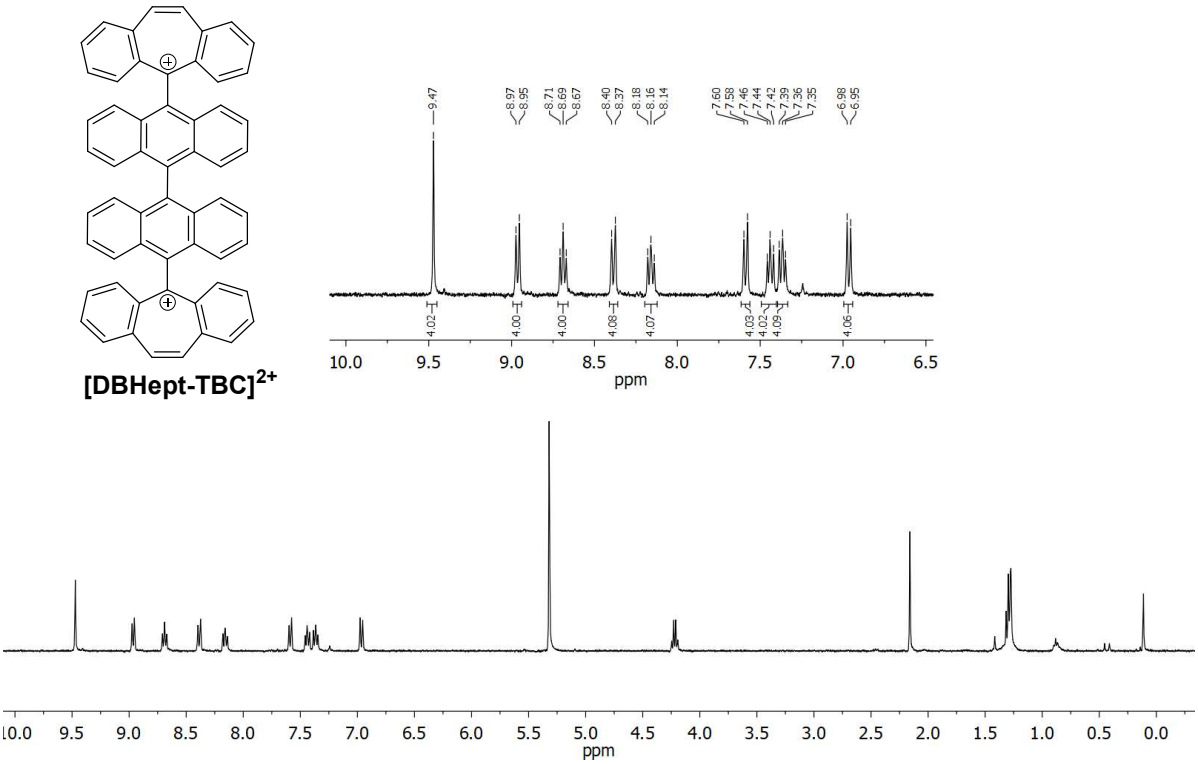


Figure S42. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **[DBHept-TBC]$^{2+}$**.

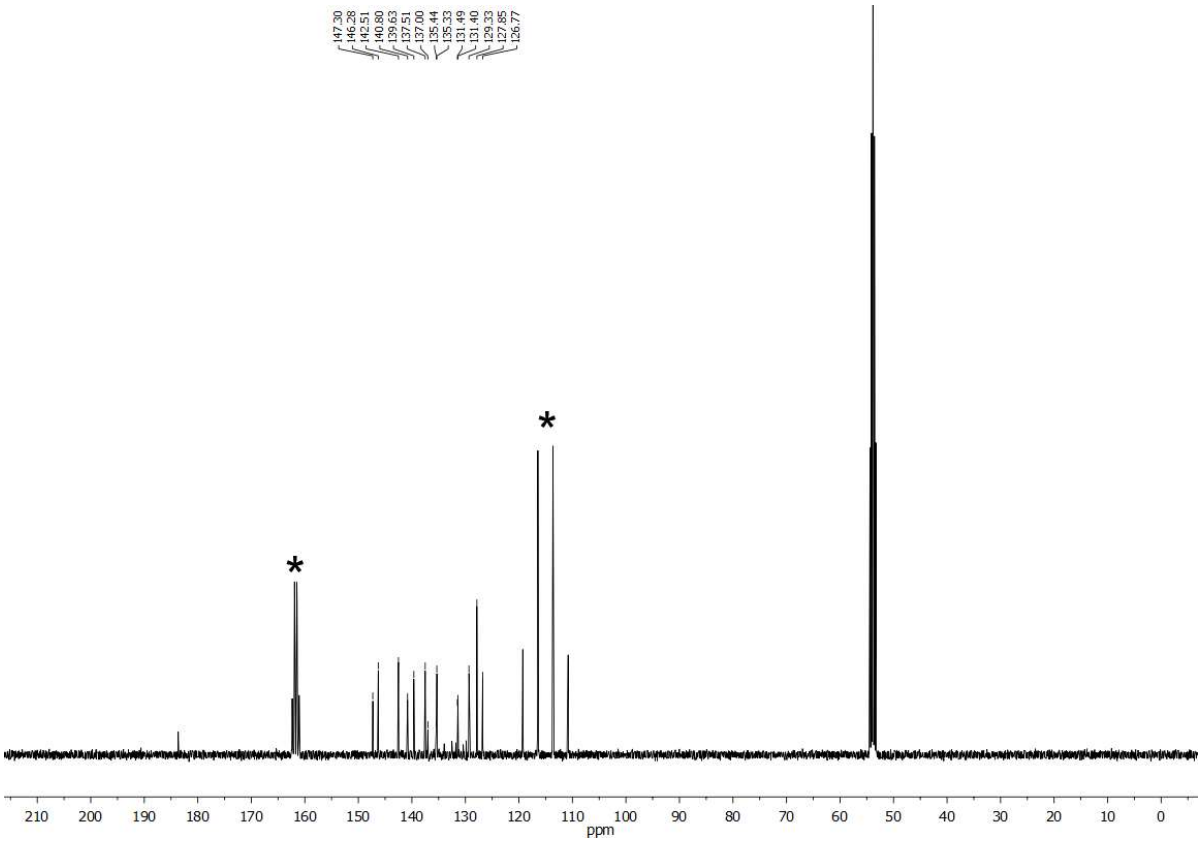


Figure S43. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **[DBHept-TBC]$^{2+}$.** The signals marked with a * correspond to CF_3CO_2D.

ANNEX II: 2D-NMR and HRMS spectra of selected compounds

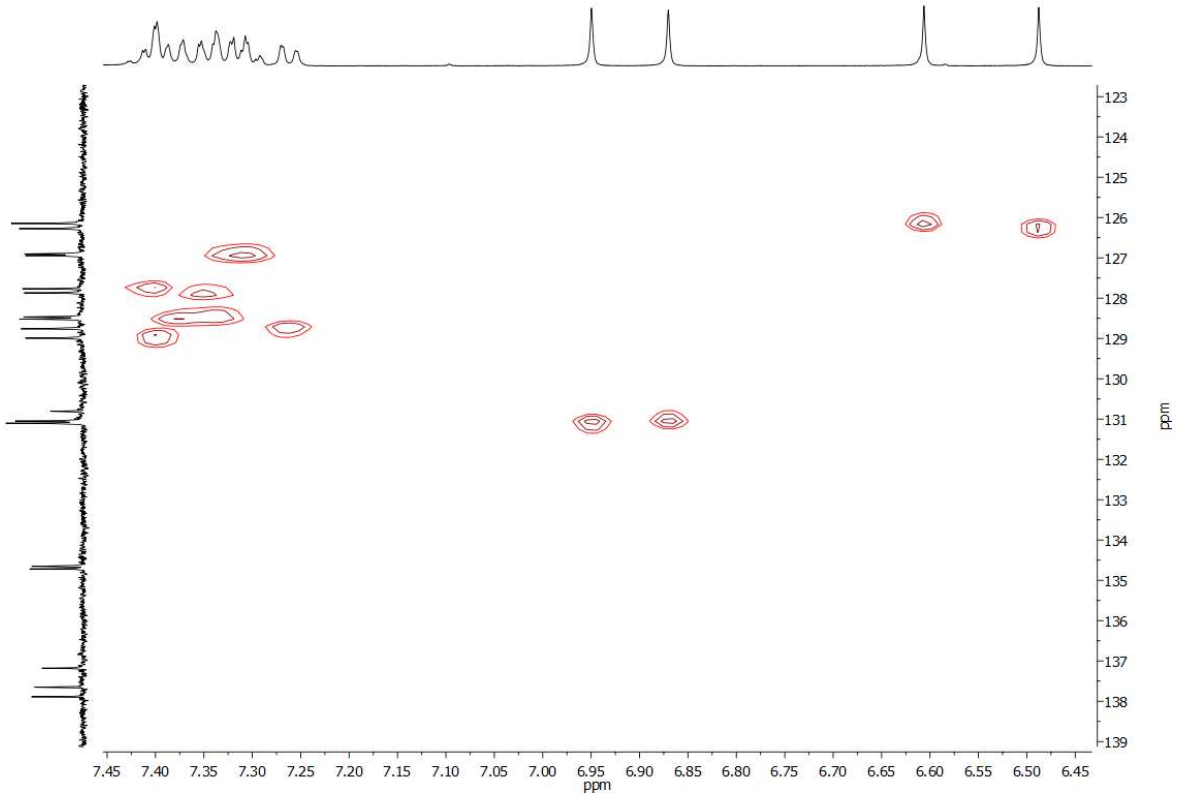


Figure S44. Partial HSQC NMR (500 MHz and 125MHz $C_2D_2Cl_4$) spectrum **DBHept-Th**.

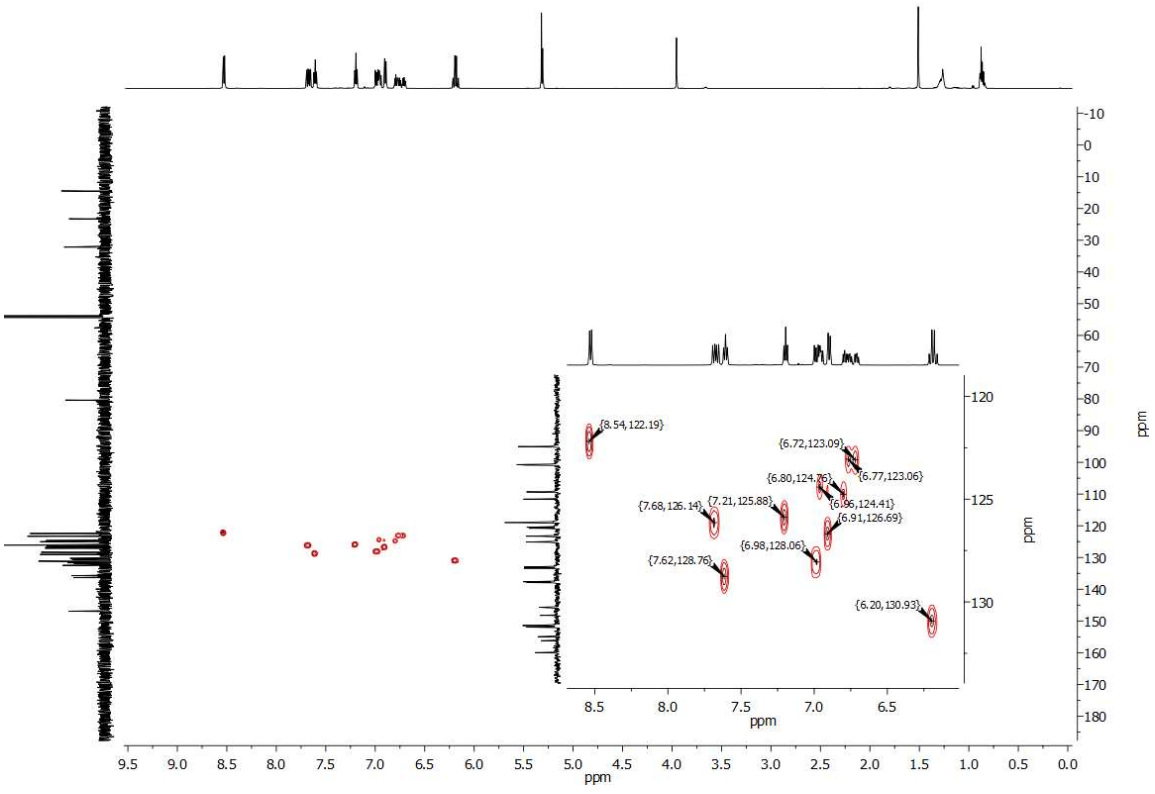


Figure S45. HSQC NMR (600 MHz and 150 MHz CD_2Cl_2) spectrum of **2**.

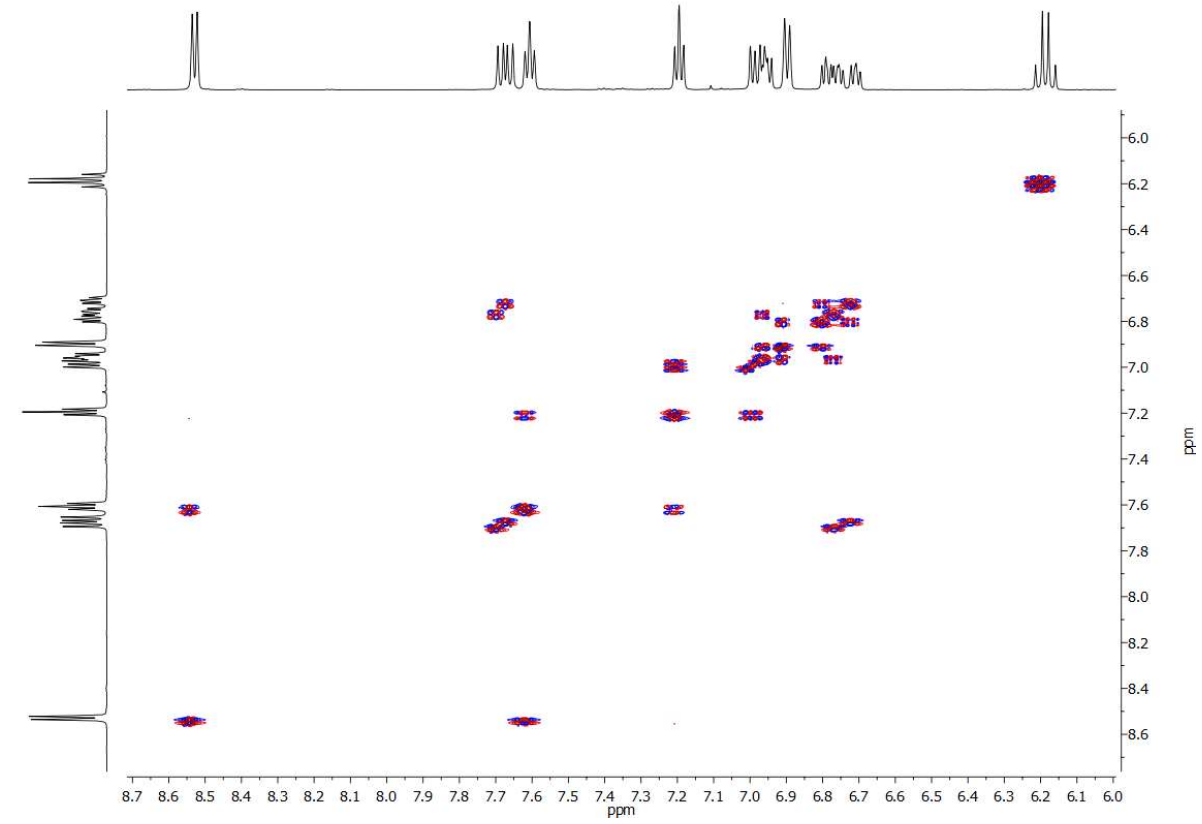


Figure S46. Partial COSY NMR (600 MHz, CD_2Cl_2) spectrum of **2**.

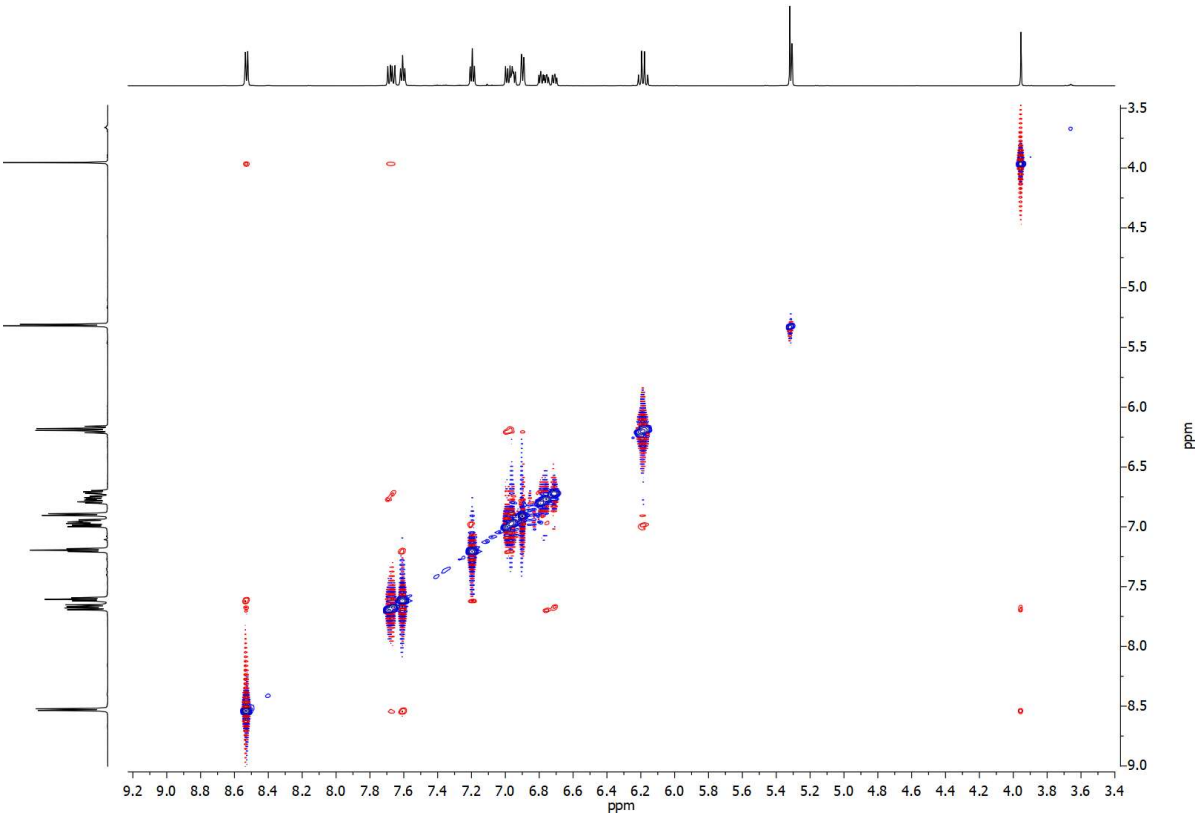


Figure S47. Partial NOESY NMR (600 MHz, CD_2Cl_2) spectrum of **2**.

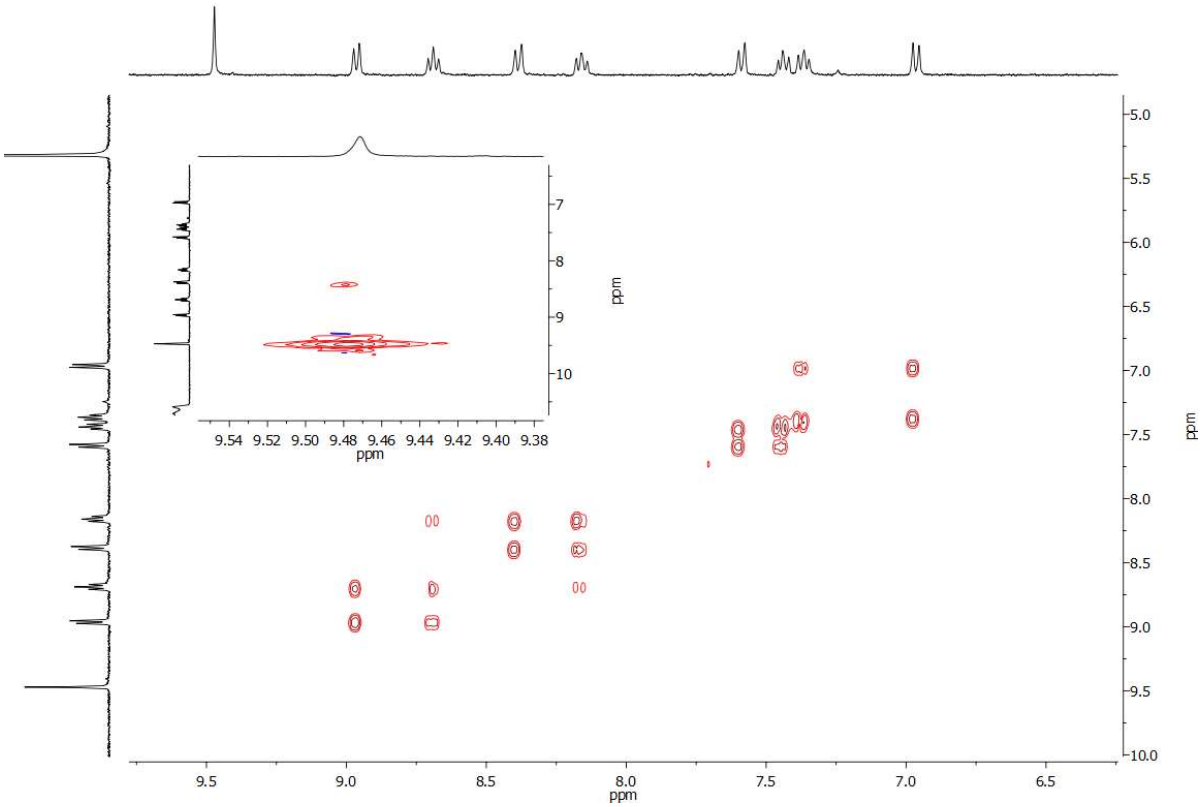


Figure S48. Partial COSY NMR (500 MHz, CD_2Cl_2) spectrum of compound [**DBHept-TBC**]$^{2+}$.

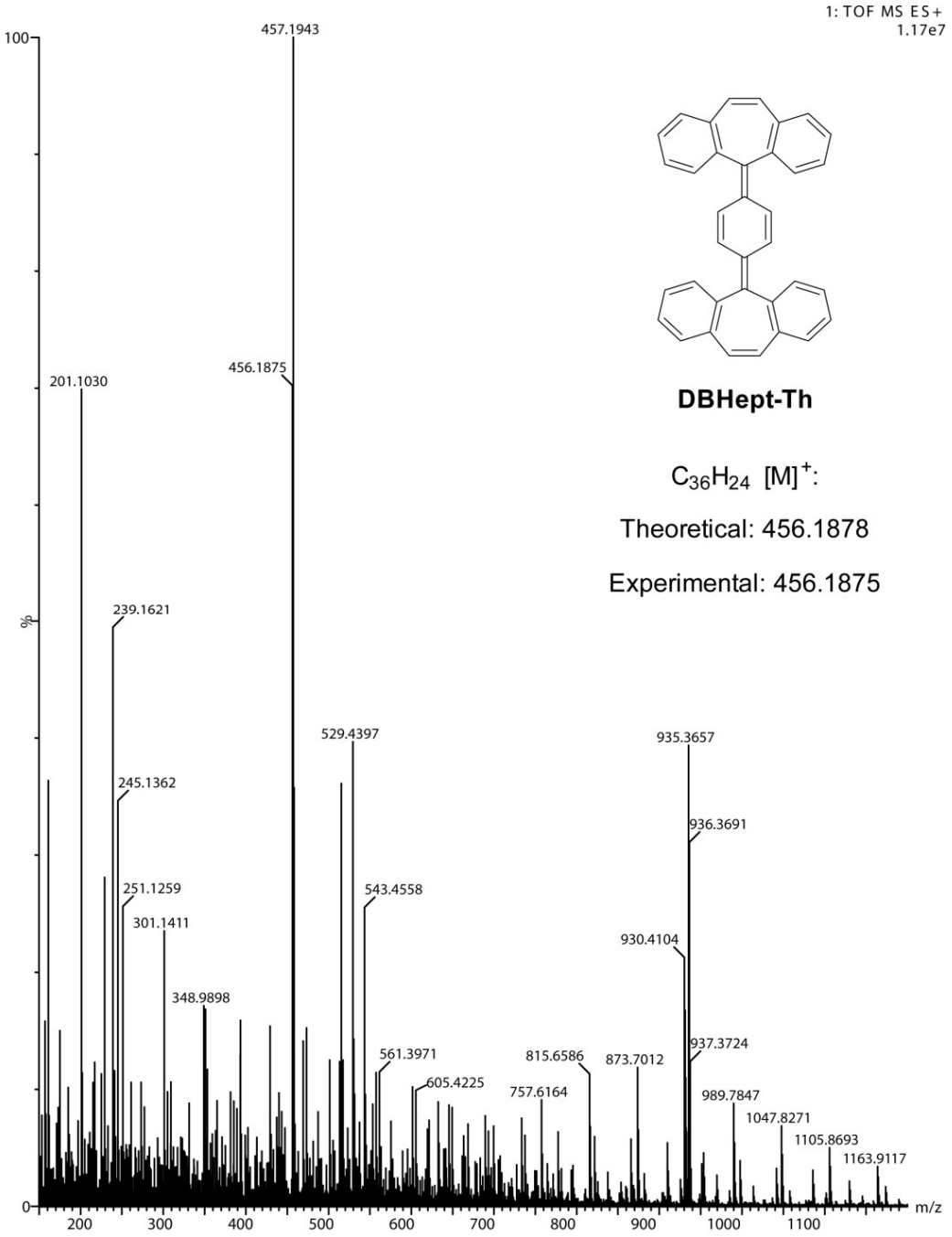


Figure S49. HRMS (ESI$^+$-TOF) of **DBHept-Th**.

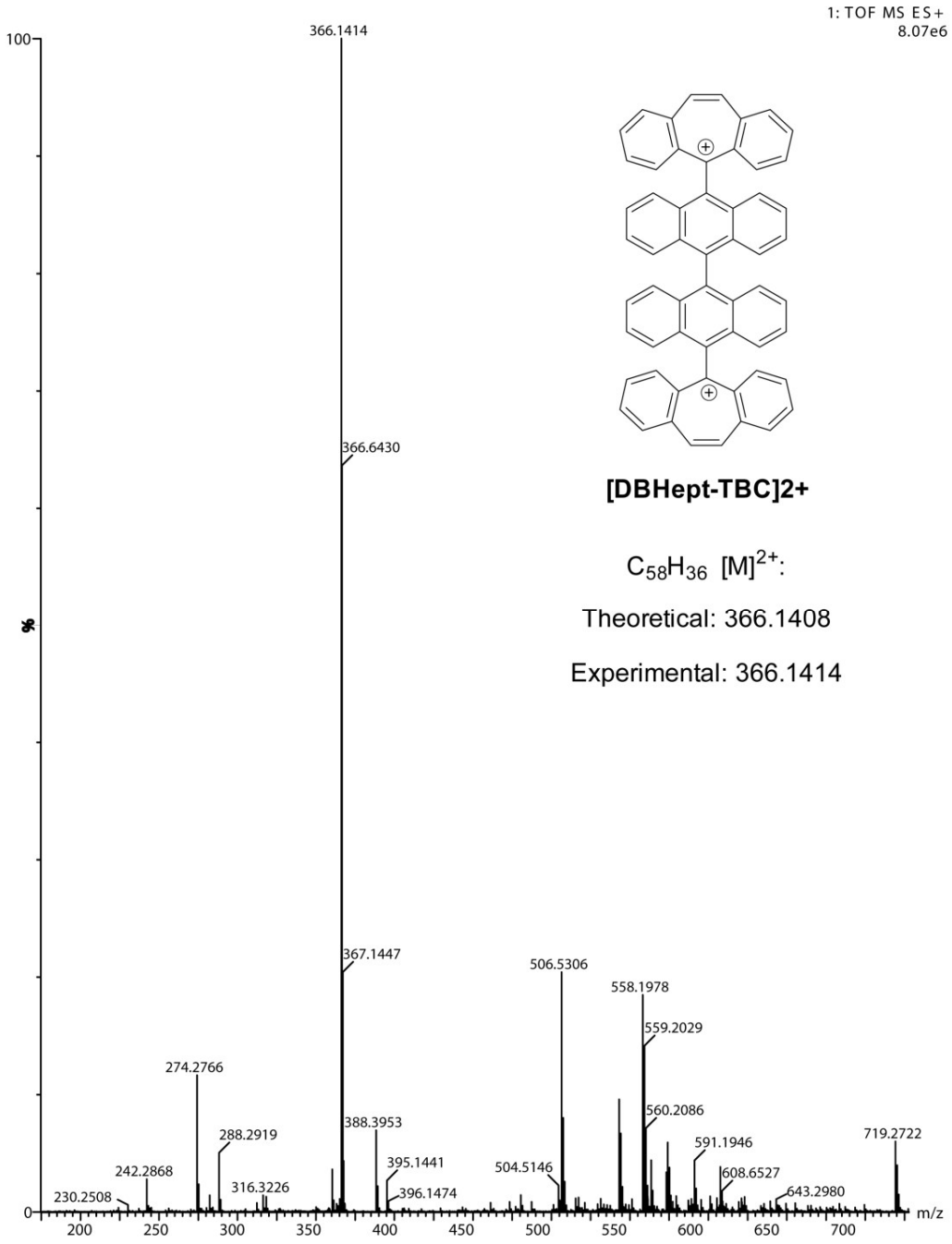


Figure S50. Partial HRMS (ESI$^+$-TOF) of **[DBHept-TBC]$^{2+}$**.

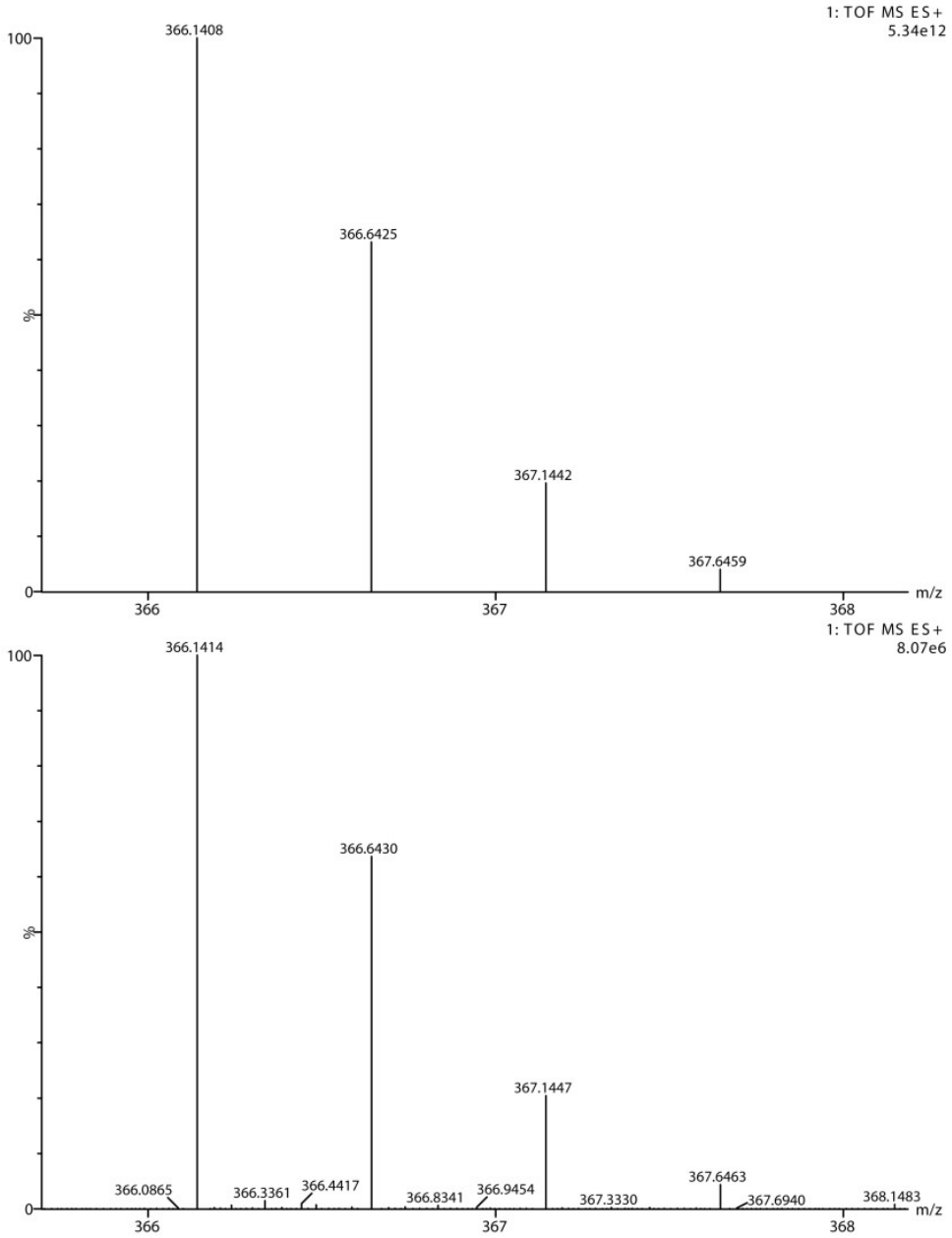


Figure S51. Theoretical (top) and experimental (bottom) isotopic for the signal of the $[M]^{2+}$ ion in the HRMS (ESI^+-TOF) of **$[DBHept\text{-}TBC]^{2+}$**.

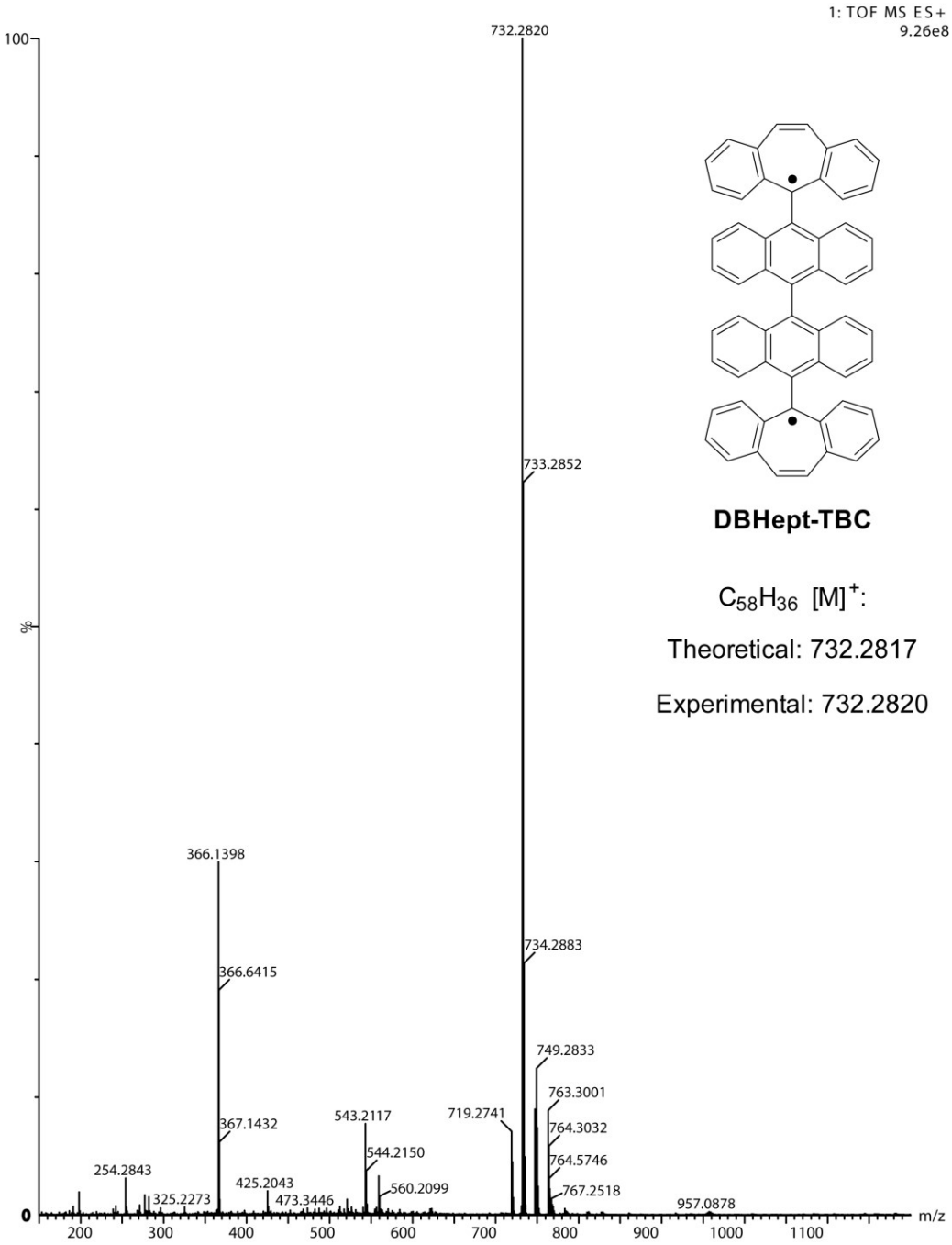


Figure S52. HRMS (ESI$^+$-TOF) of **DBHept-TBC.**

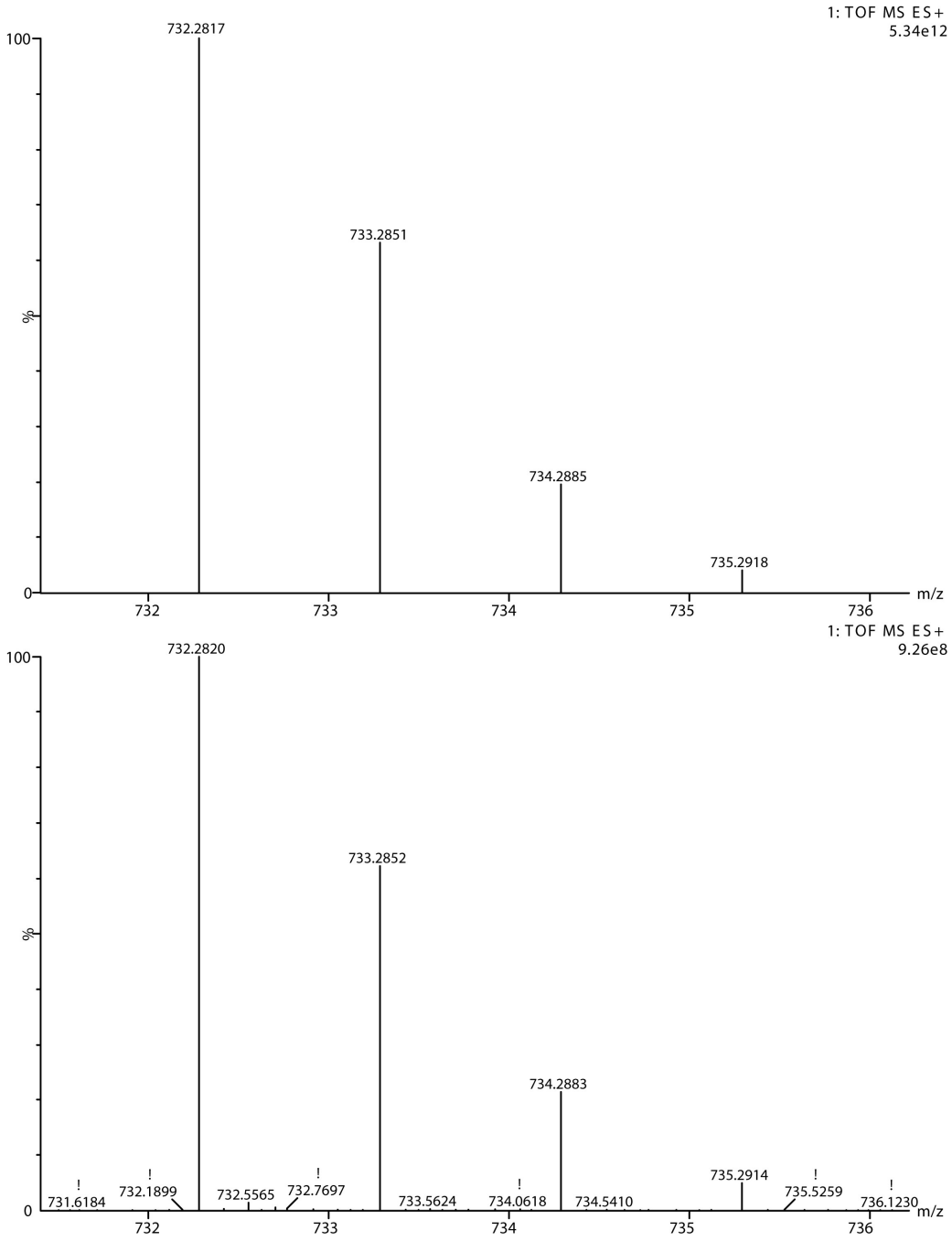


Figure S53. Theoretical (top) and experimental (bottom) isotopic distribution for the signal of the $[M]^+$ ion in the HRMS (ESI^+-TOF) of **DBHept-TBC**.