Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Thia-bridged triarylamine heterohelicene radical cations as redox-driven molecular switches

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1SI Synthetic Procedures

1.1SI Materials and Methods

Chloroform, dichloromethane (DCM) and toluene, were dried following standard procedures.

All reactions were monitored by tlc on commercially available precoated plates (silica gel 60 F254) and the products were visualized with acid vanillin solution.

Silica gel 60, 230–400 mesh, was used for column chromatography.

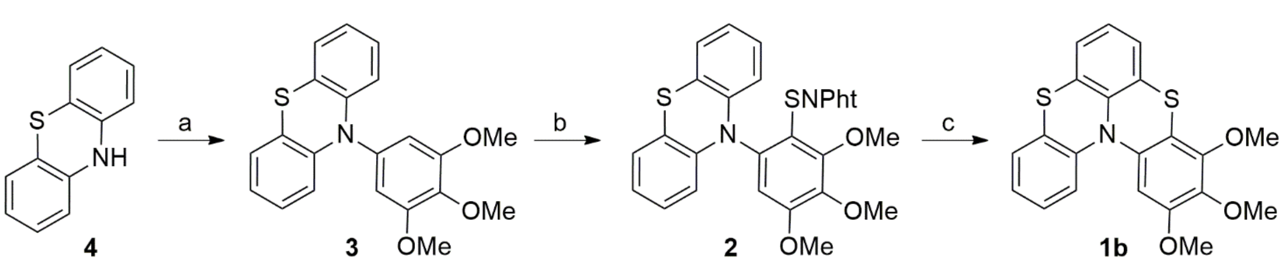
Melting points were measured with Melting Point Buchi 510 and are uncorrected.

^{1}H and ^{13}C NMR spectra were recorded with Varian Gemini 200 and 50 MHz respectively or Varian Mercury Plus 400 and 100 MHz respectively. Residual $CHCl_3$ at 7.26 for ^{1}H NMR. Central line of CDCl3 at 77.00 ppm was used as reference for ^{13}C NMR.

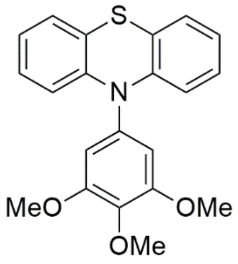
Elemental analysis was measured with Elemental Analyser 2400 series II Perkin- Elmer.

Mass spectra were measured with a Shimadzu QP5050.

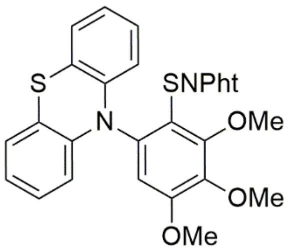
Commercial available reagents, catalysts and ligands were used as obtained from freshly open container without further purifications. Phthalimide sulfenyl chloride was prepared from the corresponding commercial available disulfide (purchased from Chemper snc) as reported elsewhere.[1] Thia-bridged heterohelicene **1a** was prepared as reported elsewhere (see ref. 9 of the manuscript).



Scheme 1SI. General synthetic scheme for helicene **1b**. (a) NaOt-Bu, $P(tBu)_2$-o-biphenyl, $Pd_2(dba)_3$, 5-bromo-1,2,3-trimethoxybenzene, toluene, 110 °C, 18 h, 96%. (b) PhtNSCl, $CHCl_3$, 0-25 °C, 42h, 96%. (c) $AlCl_3$, 25 °C, DCM, 3h, 88%.

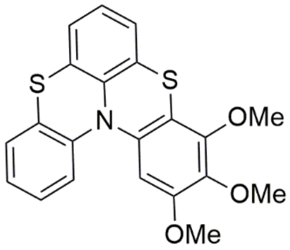


10-(3,4,5-trimethoxyphenyl)-10H-phenothiazine (3) was prepared via Buchwald-Hartwig cross-coupling as it follows: An oven-dried Schlenk flask was charged with phenothiazine **4** (1500 mg, 7.53 mmol), NaOt-Bu (2170 mg, 22.59 mmol), P(*t*Bu)2 -o-biphenyl (89 mg, 0.3 mmol), $Pd_2(dba)_3$ (69 mg, 0.07 mmol) and 5-bromo-1,2,3-trimethoxybenzene (2050 mg, 8.28 mmol). The tube was purged of air by a vacuum-nitrogen cycle repeated three times, before being added dry toluene (45 mL). The mixture was stirred at 110 °C for 18 h under nitrogen. Upon cooling, the reaction mixture was diluted with diethyl ether (250 mL), washed with brine (3x300 mL), dried over Na_2SO_4 and concentrated in vacuum. The product 10-(3,4,5-trimethoxyphenyl)-10H-phenothiazine **3** was obtained, after column chromatography (DCM), as a white solid (2630 mg, 7.20 mmol, 96% yield), m.p. 187 °C; **^{1}H-NMR** (200 MHz, CDCl3) δ 3.85 (s, 6H), 3.96 (s, 3H), 6.29 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 2H), 6.62 (s, 2H), 6.76-6.92 (m, 4H), 6.99 (dd, *J* = 7.0 Hz, *J* = 2.2 Hz, 2H) ppm. **^{13}C-NMR** (50 MHz, $CDCl_3$) δ 56.3, 61.0, 107.7, 115.5, 119.5, 122.4, 126.5, 126.8, 136.1, 137.8, 144.0, 154.7 ppm. **MS** *m/z* **(**int. rel. %): 365 (100, $M^{\bullet+}$), 350 (80), 198 (46). **Elemental Analysis** calcd. (%) for $C_{21}H_{19}NO_3S$: C 69.02, H 5.24, N 3.83; found: C 69.16, H 5.03, N 3.69.

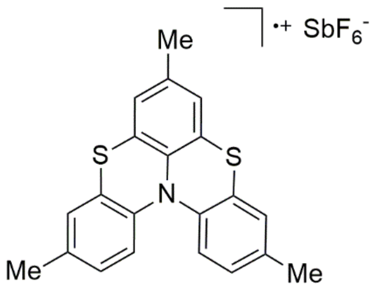


2-((2,3,4-trimethoxy-6-(10H-phenothiazin-10-yl)phenyl)thio)isoindoline-1,3-dione (2). To a solution of 10-(3,4,5-trimethoxyphenyl)-10H-phenothiazine **3** (300 mg, 0.82 mmol) in dry $CHCl_3$ (30 mL) was added phthalimidesulfenyl chloride (217 mg, 1.02 mmol) under a nitrogen atmosphere at 0 C°. After stirring at room temperature for 42h, the reaction mixture was diluted with DCM (100 mL), washed with a saturated $NaHCO_3$ solution (2x150 mL) and water (150 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated under reduced pressure. The crude material was purified by flash chromatography (DCM) to provide the product 2-((2,3,4-trimethoxy-6-(10H-phenothiazin-10-

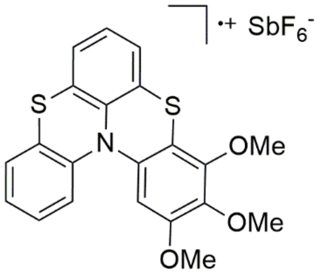
yl)phenyl)thio)isoindoline-1,3-dione **2** as an orange solid (430 mg, 0.79 mmol, 96% yield), m.p. 182 °C (dec.); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.96 (s, 3H), 4.11 (s, 3H), 5.90 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 2H), 6.51-6.55 (m, 2H), 6.61-6.66 (m, 3H), 6.70 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 2H), 7.58-7.60 (m, 2H), 7.70-7.72 (m, 2H) ppm. **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 56.3, 61.1, 61.4, 111.3, 115.1, 118.3, 121.7, 122.3, 124.3, 126.7, 132.0, 133.8, 134.9, 136.0, 141.6, 143.0, 154.8, 155.9, 167.2 ppm. **MS** *m/z* (int. rel. %): 542 (6, $M^{\bullet+}$), 147 (50), 76 (100). **Elemental Analysis** calcd. (%) for $C_{29}H_{22}N_2O_5S_2$: C 69.10, H 4.09, N 5.16; found: C 69.36, H 4.33, N 5.29.



Helicene 1b: To a solution of 2-((2,3,4-trimethoxy-6-(10H-phenothiazin-10-yl)phenyl)thio)isoindoline-1,3-dione **2** (880 mg, 1.62 mmol) in dry DCM (50 mL) was added $AlCl_3$ (325 mg, 2.43 mmol) under a nitrogen atmosphere. After 3h of stirring at room temperature, the mixture was diluted with DCM (30 mL), washed with a saturated Na_2CO_3 solution (2x60 mL) and the organic layer was dried over Na_2SO_4. Evaporation of the solvent gives a crude that was purified by flash chromatography (petroleum ether/AcOEt=5/1) to afford the heterohelicene **1b** as a white solid (560 mg, 1.42 mmol, 88% yield) m.p. 193 °C (dec.). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.86 (s, 3H), 3.97 (s, 3H) , 6.50 (s, 1H), 6.92-7.07 (m, 4H), 7.10-7.24 (m, 3H) ppm. **^{13}C-NMR** (100 MHz, CDCl3) δ 56.3, 61.0, 61.2, 101.2, 113.0, 120.4, 124.4, 126.7, 125.4, 125.5, 125.8, 126.9, 127.3, 127.9, 137.5, 139.4, 142.9, 149.5, 152.9 ppm 19 signals for 21 non equivalent carbons. **MS** *m/z* (int. rel. %): 395 (100, $M^{\bullet+}$), 380 (23), 365 (10). **Elemental Analysis** calcd. for $C_{21}H_{17}NO_3S_2$: C 63.77, H 4.33, N 3.54; found: C 63.42, H 4.15, N 3.62.



Radical cation $1a^{\bullet+}$: A solution of $AgSbF_6$ (75 mg, 0.215 mmol) in CH_2Cl_2 dry (5 mL) was added dropwise to a solution of **1a** (60 mg, 0.215 mmol) in DCM dry (10 mL) at room temperature. The mixture was stirred for few minutes, filtered through a short pad of celite and washed twice with dry DCM. The solvent was removed under vacuum to give **$1a^{\bullet+}$** in quantitative yields as a purple solid, m.p. 230 °C. **UV-Vis** (DCM $1.6\cdot10^{-4}$ M): λmax = 311 nm, 398 nm, 560 nm, 723 nm. **Elemental Analysis** calcd. for $C_{21}H_{17}NS_2SbF_6$: C 43.24, H 2.94, N 2.40; found: C 43.53, H 2.96, N 2.64.



Radical cation $1b^{\bullet+}$: A solution of $AgSbF_6$ (67 mg, 0.195 mmol) in dry DCM (5 mL) was added dropwise to a solution of **1b** (80 mg, 0.195 mmol) in dry DCM (10 mL) at room temperature. The mixture was stirred for few minutes, filtered through a short pad of celite and washed twice with dry DCM. The solvent was removed under vacuum to give **$1b^{\bullet+}$** in quantitative yields as a green solid m.p. 185 °C. **UV-Vis** (DCM $1.6\cdot10^{-4}$ M): λ max = 318 nm, 509 nm, 661 nm, 806 nm. **Elemental Analysis** calcd. for $C_{21}H_{17}NO_3S_2SbF_6$: C 39.96, H 2.71, N 2.22; found: C 40.21, H 2.55 N 2.39.

Reduction of radical cations $1a^{\bullet+}$ and $1b^{\bullet+}$ with $Na_2S_2O_4$: To a solution 1.6 10^{-4} M of **$1a^{\bullet+}$** (or **$1b^{\bullet+}$**) (0.017 mmol) in DCM (100 mL) solid sodium dithionite $Na_2S_2O_4$ (118 mg, 0.68 mmol) was added. The heterogeneous mixture, manually shacked time by time, was left at room temperature for 65h while monitored by UV-Vis.

2SI Cyclic Voltammetry

Cyclic voltammetries were recorded in 0.2 M (t-Bu)$_4$NPF$_6$ DCM solution at room temperature, using a conventional three-electrode set up. The working electrode was a Teflon supported platinum disk mechanically polished with 0.05 μm alumina powder before each set of measurements. Pseudoreference and counter electrodes were platinum wires. Applied potentials were measured against the Pt wire as a pseudoreference electrode but are referred to the ferrocene/ferrocinium, Fc/Fc$^+$, redox couple formal potential. Electroactive species were added at a final concentration of 0.5 mM. Before the addition of the proper amount of the electroactive compounds, the absence of interfering species was tested by recording the cyclic voltammogram of the pure electrolyte solution over the whole potential range of interest.

3SI EPR and ENDOR Spectroscopy

3.1SI General Information

Electron paramagnetic resonance (EPR) measurements were performed on a Bruker ER200D spectrometer operating at X-band (ν 9-10 GHz). The Electron nuclear double resonance (ENDOR) experiments were performed using a Bruker ER200D spectrometer equipped with a Bruker EN801 cavity, a frequency modulated RF signal generator (Rohde&Schwartz SMX), an RF power amplifier (ENI A-300W), an EG&G 5208 lock-in amplifier and LabView software for the control system. The spectra EPR and ENDOR were carried out between 120K and 310K with a Bruker BVT2000 variable-temperature controller used to control the sample temperature with nitrogen gas. For the EPR or ENDOR experiments samples were prepared by dissolving radicals **1a**$^{\bullet+}$ and **1b**$^{\bullet+}$ in DCM ($\approx 10^{-4}$M) and using 0.1 mL of this solution in a quartz tube (1 mm diameter). The simulations of the EPR spectra were performed using the EasySpin Matlab™ toolbox programmed for EPR simulations.[2] EPR experimental setup: microwave power 2mW, sweep 80 Gauss, sweep time 30s, 10 scans, modulation amplitude 0.5 gauss. ENDOR spectra were recorded in the frequency range of 10 MHz - 20 MHz, setting a magnetic field at the centre of the EPR lines and with a RF power of 200W, RF frequency modulation 25 KHz, RF amplitude modulation 15 KHz. Calculation of *g* factors (error ±0.0005) and isotropic hyperfine coupling constants were performed with the Gaussian09 using unrestricted DFT and B3LYP hybrid functional methods with 6-311G** basis set at the optimized geometry starting from X-ray crystallographic structure.

3.2SI Experimental Data

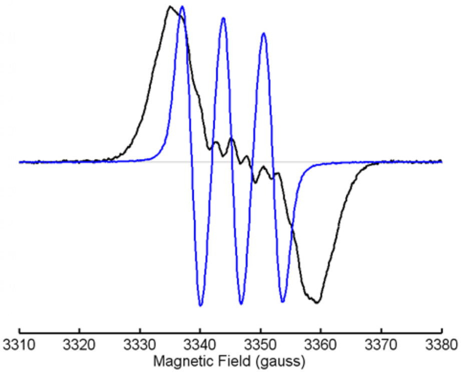


Figure 3.2SI-1. EPR Spectra of **1a**$^{\bullet+}$ (black line) and **1b**$^{\bullet+}$ (blue line) in CH_2Cl_2 at T=200K.

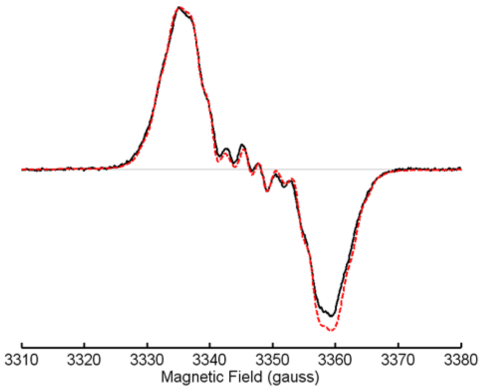


Figure 3.2SI-2. Experimental EPR spectrum of radical **1a**$^{\bullet+}$ (black line) and calculated spectrum (*g* = 2.0042, red dashed line).

	Hyperfine constant (Gauss)	**Number of equivalent nuclei**
a$_N$	7.92	**1**
a$_{H1}$	2.20	**3**
a$_{H2}$	2.44	**6**
a$_{H3}$	**1.18**	**2**

Table 3.2SI-1. Hyperfine coupling constants obtained by simulated EPR spectrum of radical **1a**$^{\cdot+}$.

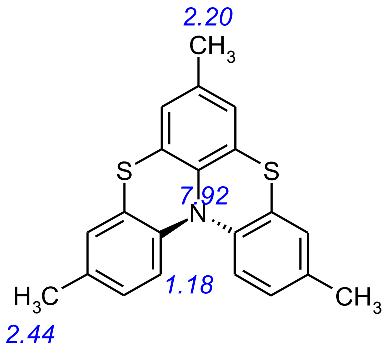


Figure 3.2SI-3. Hyperfine coupling constants (Gauss) determined and assigned using spectrum simulation of radical **1a**$^{\bullet+}$.

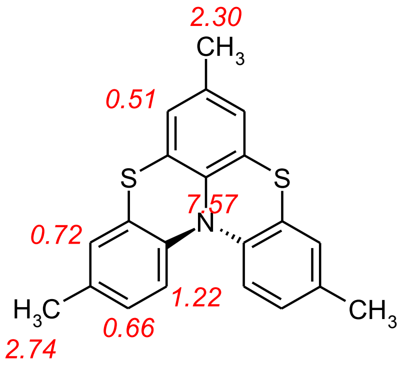


Figure 3.2SI-4. Hyperfine coupling constants (in Gauss) for H and N in the radical **1a**$^{\bullet+}$ by DFT calculations (calculated *g* factor =2.0049).

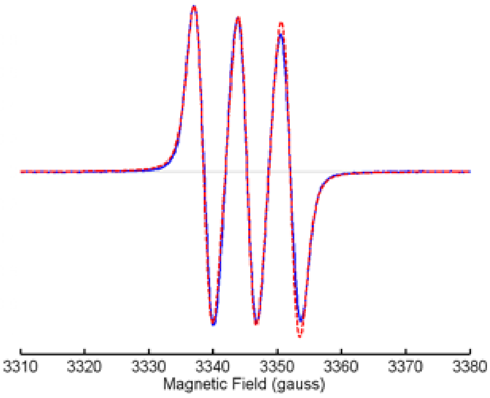


Figure Figure 3.2SI-5. Experimental EPR spectrum of radical **1b**$^{\bullet+}$ (blue line) and calculated spectrum (*g* = 2.0056, red dashed line).

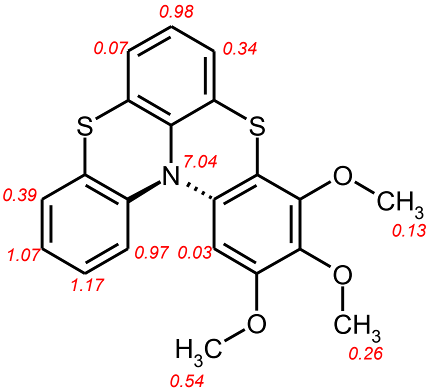


Figure 3.2SI-6. Hyperfine coupling constants (in Gauss) for H and N in the radical **1b**$^{\bullet+}$ by DFT calculations (calculated *g* factor = 2.0053).

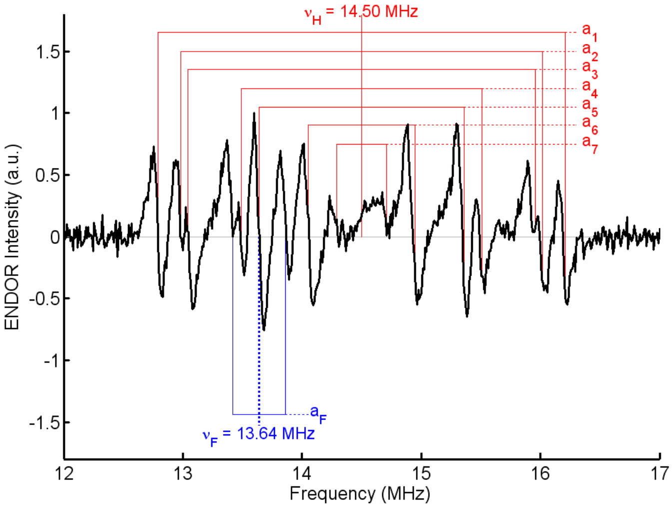


Figure 3.2SI-7. ENDOR spectrum of radical **1b**$^{\bullet+}$ at 220K, hyperfine coupling constants for Hydrogen (red), hyperfine coupling constants for Fluoro (blue).

	Hyperfine constant (MHz)	**Hyperfine constant (Gauss)**
$\mathbf{a_F}$	0.44	**0.16**
$\mathbf{a_{H1}}$	3.40	**1.22**
$\mathbf{a_{H2}}$	3.02	**1.08**
$\mathbf{a_{H3}}$	2.90	**1.04**
$\mathbf{a_{H4}}$	2.00	**0.72**
$\mathbf{a_{H5}}$	1.70	**0.61**
$\mathbf{a_{H6}}$	0.88	**0.32**
$\mathbf{a_{H7}}$	**0.40**	**0.14**

Table 3.2SI-2. Hyperfine coupling constants for radical **1b**$^{\bullet+}$ by ENDOR experiments.

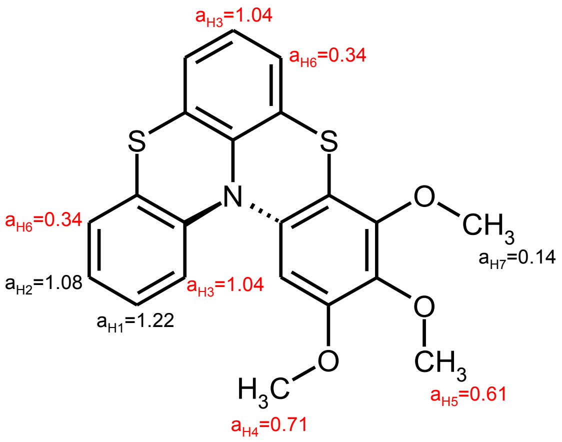


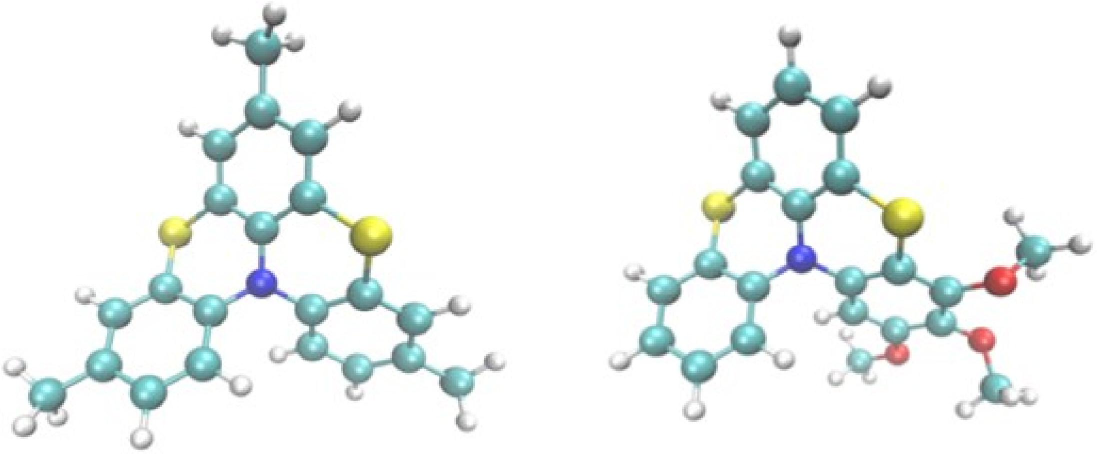
Figure 3.2SI-8. Hyperfine coupling constants (Gauss) for radical **1b**$^{\bullet+}$ by ENDOR experiments.

4SI DFT Calculations

4.1SI General Information

X-ray structures of all compounds underwent geometry optimization using Density functional Theory (DFT) with the Becke, three-parameter, Lee-Yang-Parr hybrid functional (B3LYP)[3] using the 6-31G(d) basis set and the Polarizable Continuum Model[4] with the Integral Equation Formalism variant (IEFPCM) for accounting of the solvent effect. The dielectric constant in the IEFPCM approach was taken to be that of dichlorometane (ε=8.93). The IEFPCM-B3LYP ground state energies at the optimized geometries were re-calculated switching to the correlation consistent Dunning[5] basis set cc-pVDZ. UV spectra were calculated at the optimized geometry using Time Dependent Density Functional Theory (TD-DFT) with the Coulomb Attenuated[6] CAM-B3LYP/IEFPCM functional and the cc-pVDZ basis using 24 states. All ab initio calculations were done with the program Gaussian,[7] version 9.

4.2SI HOMO/SOMO LUMO energies



1a, 1a$^{\cdot+}$ **1b, 1b$^{\cdot+}$**

Figure 4.2SI-1. Ball and stick 3D representation of the thia-bridged heterohelicenes.

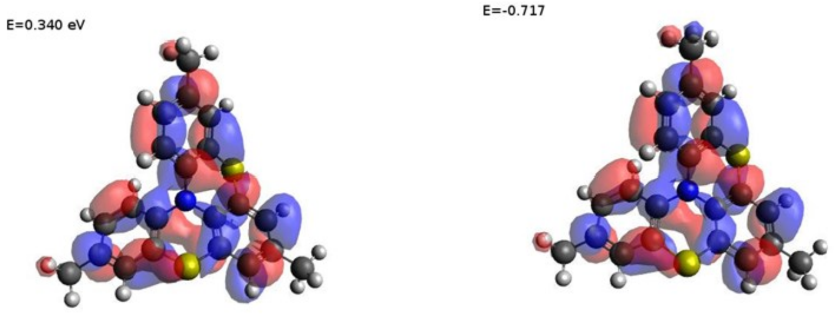
In the table below we report the spin state, aryl-aryl angle at the optimized geometry, and energies for the neutral and charged species. The Θ angle refers to mean angle between the two terminal aryl moieties computed by averaging over 36 possible pairs of planes, defined picking up three consecutive atoms on the rings. The observed variance in the Θ angle is a measure of the distortion of the aryl planes.

Compound	S	Θ (degrees)	Energy (A.U.)
1a	S=1	66.82	-1661.71399
1a$^{\bullet+}$	S=2	60.02	-1661.53262
1b	S=1	68.32	-1887.33537
1b$^{\bullet+}$	S=2	61.13	-1887.150716

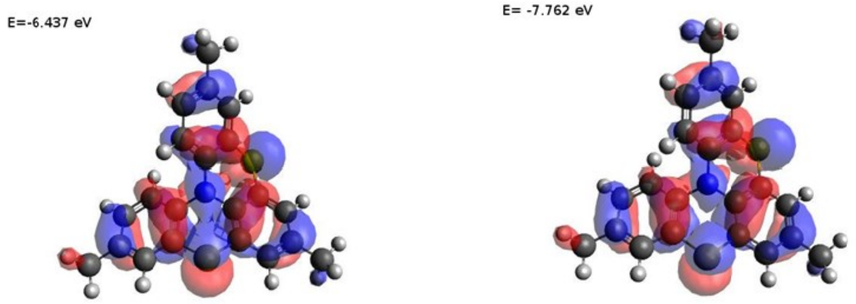
Table 4.2SI-1. Energy in Hartree computed at the B3-LYP/cc-pVDZ level of theory. The Θ angle is calculated on the B3LYP/6-31G(d) optimized geometry. The energy difference $E_{1a}^{\cdot+}$-E_{1a} is equal to 113.811 kcal/mol. The energy difference $E_{1b}^{\cdot+}$-E_{1b} is equal to 115.872 kcal/mol.

Compound	HOMO/SOMO (eV)	LUMO (eV)
1a	-6.437	0.340
1a$^{\bullet+}$	-7.762	-0.717
1b	-6.510	0.349
1b$^{\bullet+}$	-7.617	0.763

Table 4.2SI-2. HOMO/SOMO LUMO energies (in eV)

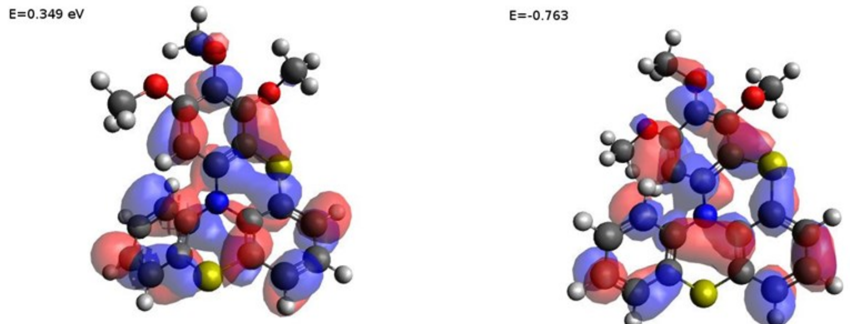


1a *(LUMO)* **1a**$^{\cdot+}$ *(LUMO)*

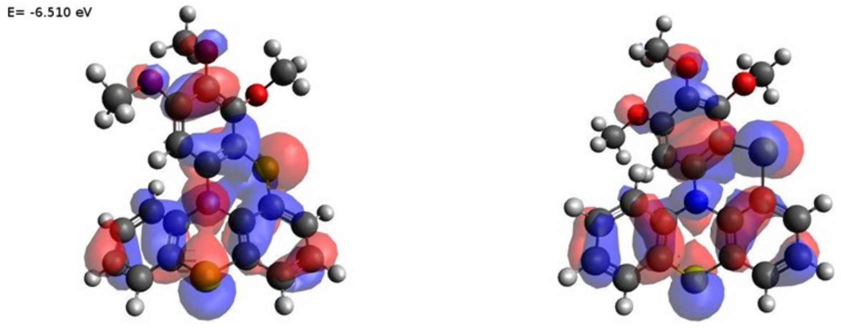


1a *(HOMO)* **1a**$^{\cdot+}$ *(HOMO)*

Figure 4.2SI-2. HOMO/SOMO LUMO for helicene **1a** and radical cation **1a**$^{\bullet+}$



1b *(LUMO)* **1b**$^{\cdot+}$ *(LUMO)*



1b *(HOMO)* **1b**$^{\cdot+}$ *(HOMO)*

Figure 4.2SI-3. HOMO/SOMO LUMO for helicene **1b** and radical cation **1b**$^{\bullet+}$

4.3SI Experimental and calculated UV-vis spectra

In the Figures below, along with experimental UV-Vis spectra of **1a**/**1a**$^{\bullet+}$ and **1b**/**1b**$^{\bullet+}$, for each excitation peak, we report the orbital indexes of the largest coefficients (c>0.4) in the TD-DFT expansion. The HOMO/SOMO index for the **1a**/**1a**$^{\bullet+}$ and **1b**/**1b**$^{\bullet+}$ pairs is 91 and 103, respectively. In the radical cations, low energy transitions, involving the SOMO (arrival) orbital, refer to excitations where a beta inner electron is moved to the singly occupied SOMO.

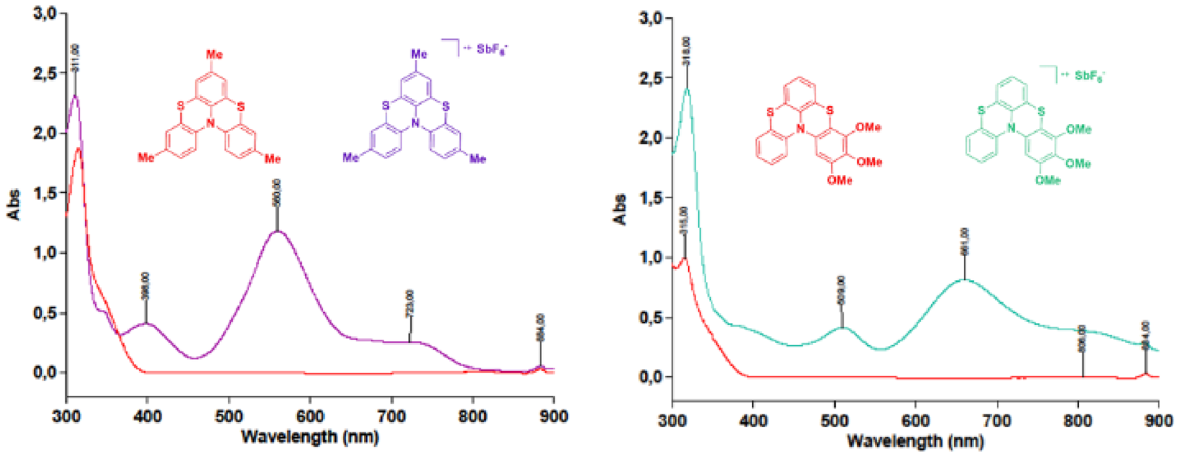


Figure 4.3SI-1. UV-Vis absorptions of **1a** *vs* **1a**$^{\bullet+}$ (left) and **1b** *vs* **1b**$^{\bullet+}$ (right) in DCM $1.6 \cdot 10^{-4}$M

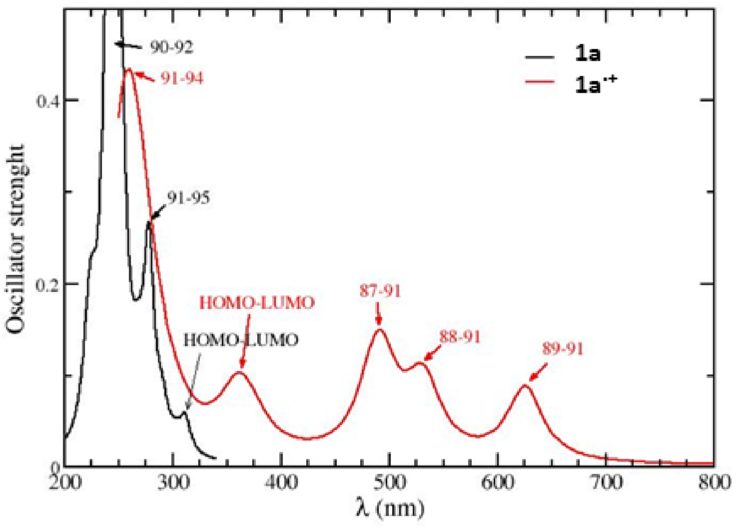


Figure 4.3SI-2. UV spectra (CAM-B3LYP/cc-pVDZ) for **1a** (black line) and **1a**$^{\bullet+}$ (red line) with assignment

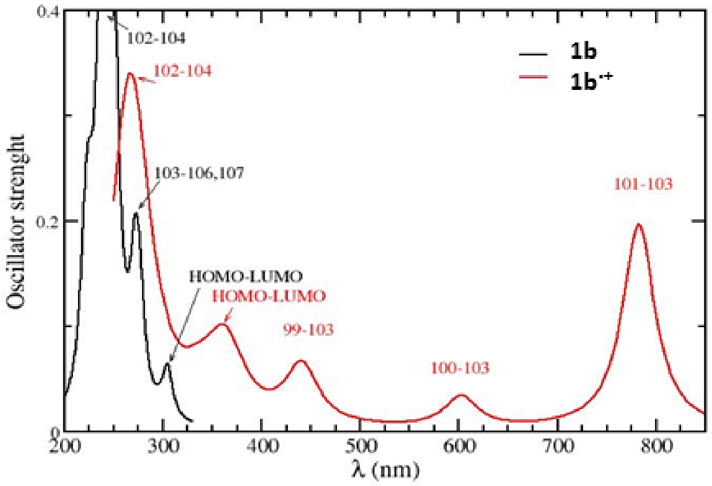


Figure 4.3SI-3. UV spectra (CAM-B3LYP/cc-pVDZ) for **1b** (black line) and **1b**$^{\bullet+}$ (red line) with assignment.

4.4SI Mulliken atomic spin densities

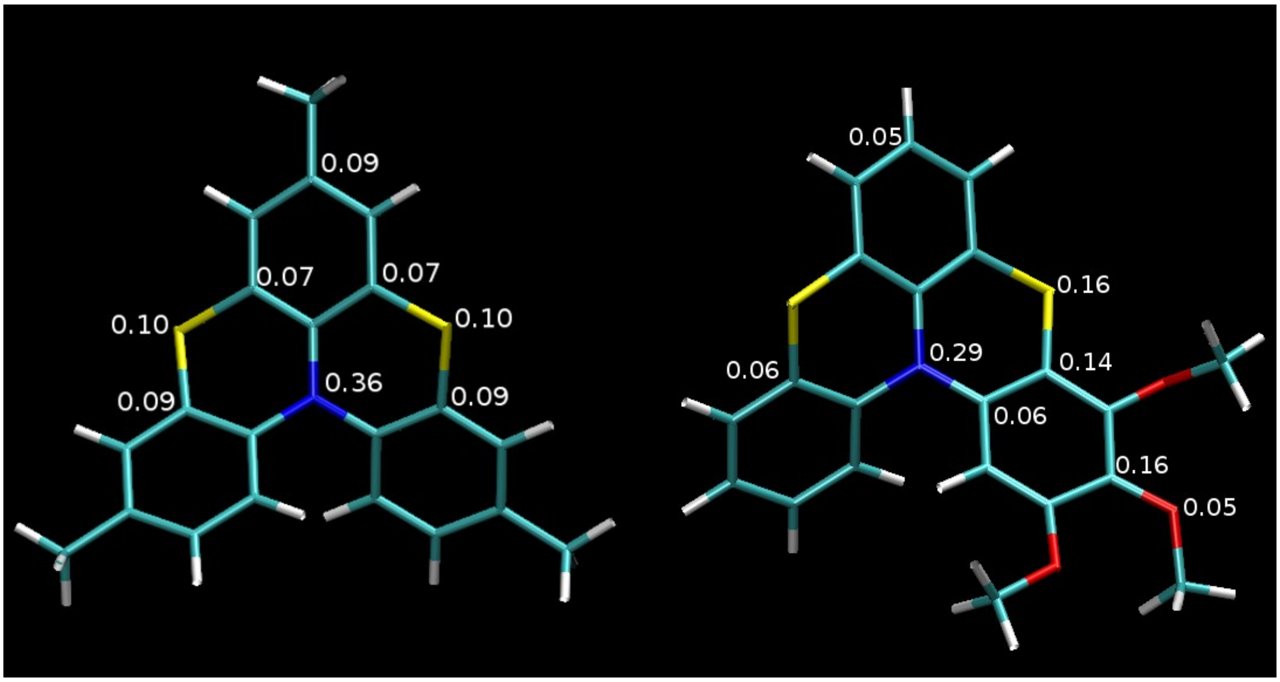


Figure 4.4SI-1. Main Mulliken atomic spin densities on radical cations **1a**$^{\bullet+}$ (left) and **1b**$^{\bullet+}$ (right) as computed at the CAM-B3LYP/cc-DZV level of theory.

5SI X-Ray Data Collection

5.1SI General information

Crystals were mounted on a glass fiber then they were analyzed using a Goniometer Oxford Diffraction KM4 Xcalibur2 with a graphite-monochromated Cu/Kα radiation (40mA/-40KV). The measures were carried out at room temperature, except for compound exp_732 which was analysed at 150°K.

5.2SI Structures refinement

The integrated intensities, measured using the ω scan mode, were corrected for Lorentz and polarization effects.[8] The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of symmetry-equivalent reflections. Structures were solved by direct methods of SIR2002[9] and refined using the full-matrix least squares on F^2 provided by SHELXL97.[10] The non-hydrogen atoms were refined anisotropically. In all three cases hydrogen atoms were assigned in calculated positions, all of them were refined as isotropic. Copies of the data can be obtained, free of charge, from CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (e-mail: deposit@ccdc.cam.ac.uk; internet://www.ccdc.cam.ac.uk) with the deposition numbers reported below for each compound.

5.3SI Cristallographic data radical cation 1a$^{\bullet +}$

$C_{21}H_{17}NS_2SbF_6$, M=583.23, Monoclinic, space group P 21/n, a=8.543(1), b=15.622(1), c=16.383(1)Å, β=94.989(4), V=2178.2(3)Å^3, Z=4 D_c=1.779, μ=12.396 mm^{-1}, F(000)=1148. 8286 Reflections were collected with a 3.92<θ<71.50 range with a completeness to theta 92.7%; 3934 were independent, the parameters were 281 and the final R index was 0.0662 for reflections having I>2σI. Deposition number at the Cambridge Crystallographic Data Center: CCDC 931340. No significant H-bonds or short interactions were detectable. Angle between ring planes is 52.2°. The analogue angle in the case of the corresponding neutral molecule is 61.4°

5.3SI Table 1. Crystal data and structure refinement for exp_77.

Identification code	exp_77
Empirical formula	C21 H17 F6 N S2 Sb
Formula weight	583.23
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 8.543(1) A alpha = 90.000 deg. b = 15.622(1) A beta = 94.989(4) deg. c = 16.383(1) A gamma = 90.000 deg.
Volume	2178.2(3) A^3
Z, Calculated density	4, 1.779 Mg/m^3
Absorption coefficient	12.396 mm^-1
F(000)	1148
Crystal size	0.13 x 0.10 x 0.09 mm
Theta range for data collection	3.92 to 71.50 deg.
Limiting indices	-8<=h<=10, -18<=k<=18, -18<=l<=20
Reflections collected / unique	8286 / 3934 [R(int) = 0.0747]
Completeness to theta = 71.50	92.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3934 / 0 / 281
Goodness-of-fit on F^2	0.931
Final R indices [I>2sigma(I)]	R1 = 0.0662, wR2 = 0.1719
R indices (all data)	R1 = 0.1271, wR2 = 0.2120
Extinction coefficient	0.00038(14)
Largest diff. peak and hole	0.831 and -1.523 e.A^-3

5.3SI Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for exp_77. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	2288(7)	4802(4)	7636(4)	44(2)
F(1)	2621(13)	1832(6)	5481(5)	181(5)
F(2)	3920(13)	1805(6)	6961(7)	184(5)
F(3)	5538(15)	2270(7)	5749(13)	293(11)
F(4)	4783(10)	3430(5)	6821(5)	116(3)
F(5)	3481(16)	3448(6)	5356(5)	194(6)
F(6)	1894(10)	2966(8)	6559(6)	156(4)
S(1)	3444(3)	3314(1)	8771(2)	60(1)
S(2)	-1098(3)	5250(1)	7038(2)	59(1)
Sb(1)	3720(1)	2605(1)	6151(1)	69(1)
C(1)	-1163(11)	3020(6)	8229(5)	57(2)
C(2)	409(11)	2930(5)	8556(5)	52(2)
C(3)	1516(9)	3526(5)	8379(5)	47(2)
C(4)	1142(9)	4228(5)	7880(4)	41(2)
C(5)	-430(10)	4325(5)	7577(5)	49(2)
C(6)	-1541(10)	3713(6)	7745(5)	54(2)
C(7)	581(10)	5457(5)	6530(5)	50(2)
C(8)	2063(10)	5217(5)	6870(5)	48(2)
C(9)	3349(11)	5339(6)	6419(5)	56(2)
C(10)	3169(11)	5768(5)	5665(5)	61(2)
C(11)	1675(12)	6068(5)	5348(5)	61(2)
C(12)	420(11)	5883(5)	5784(5)	54(2)
C(13)	3699(9)	4940(5)	8138(5)	45(2)
C(14)	4332(9)	4301(5)	8671(5)	48(2)
C(15)	5769(10)	4443(6)	9131(5)	58(2)
C(16)	6574(10)	5203(7)	9060(5)	59(2)
C(17)	5902(11)	5844(6)	8561(5)	64(3)
C(18)	4465(10)	5728(5)	8112(5)	53(2)
C(19)	-2371(12)	2361(7)	8394(7)	78(3)
C(20)	1496(13)	6533(7)	4545(6)	80(3)
C(21)	8159(11)	5315(8)	9551(6)	82(3)

5.3SI Table 3. Bond lengths [A] and angles [deg] for exp_77.

N(1)-C(13)	1.415(9)
N(1)-C(4)	1.410(10)
N(1)-C(8)	1.412(10)
F(1)-Sb(1)	1.835(7)
F(2)-Sb(1)	1.821(9)
F(3)-Sb(1)	1.816(10)
F(4)-Sb(1)	1.876(6)
F(5)-Sb(1)	1.852(9)
F(6)-Sb(1)	1.838(8)
S(1)-C(14)	1.733(8)
S(1)-C(3)	1.747(8)
S(2)-C(7)	1.750(9)
S(2)-C(5)	1.762(8)
C(1)-C(6)	1.365(12)
C(1)-C(2)	1.409(12)
C(1)-C(19)	1.499(12)
C(2)-C(3)	1.376(11)
C(3)-C(4)	1.388(11)
C(4)-C(5)	1.399(10)
C(5)-C(6)	1.391(12)
C(7)-C(8)	1.390(11)
C(7)-C(12)	1.387(11)
C(8)-C(9)	1.389(12)
C(9)-C(10)	1.403(11)
C(10)-C(11)	1.415(13)
C(11)-C(12)	1.370(13)
C(11)-C(20)	1.498(12)
C(13)-C(14)	1.402(11)
C(13)-C(18)	1.397(11)
C(14)-C(15)	1.401(11)
C(15)-C(16)	1.383(13)
C(16)-C(17)	1.385(13)
C(16)-C(21)	1.524(12)
C(17)-C(18)	1.388(11)

C(13)-N(1)-C(4)	120.6(6)
C(13)-N(1)-C(8)	119.3(7)
C(4)-N(1)-C(8)	120.0(6)
C(14)-S(1)-C(3)	101.6(4)
C(7)-S(2)-C(5)	98.5(4)
F(2)-Sb(1)-F(3)	92.1(7)
F(2)-Sb(1)-F(6)	88.6(6)
F(3)-Sb(1)-F(6)	178.8(4)
F(2)-Sb(1)-F(1)	89.7(5)
F(3)-Sb(1)-F(1)	90.1(6)
F(6)-Sb(1)-F(1)	90.8(5)
F(2)-Sb(1)-F(5)	177.7(5)
F(3)-Sb(1)-F(5)	89.7(7)
F(6)-Sb(1)-F(5)	89.6(6)
F(1)-Sb(1)-F(5)	91.6(5)
F(2)-Sb(1)-F(4)	92.0(4)
F(3)-Sb(1)-F(4)	91.4(6)
F(6)-Sb(1)-F(4)	87.7(4)
F(1)-Sb(1)-F(4)	177.7(4)
F(5)-Sb(1)-F(4)	86.6(4)
C(6)-C(1)-C(2)	118.0(8)
C(6)-C(1)-C(19)	121.2(9)
C(2)-C(1)-C(19)	120.8(8)
C(3)-C(2)-C(1)	120.2(8)

C(2)-C(3)-C(4)	122.1(7)
C(2)-C(3)-S(1)	115.9(6)
C(4)-C(3)-S(1)	121.9(6)
C(3)-C(4)-C(5)	117.3(7)
C(3)-C(4)-N(1)	122.6(7)
C(5)-C(4)-N(1)	120.0(7)
C(6)-C(5)-C(4)	120.4(8)
C(6)-C(5)-S(2)	117.7(6)
C(4)-C(5)-S(2)	121.7(6)
C(1)-C(6)-C(5)	121.9(8)
C(8)-C(7)-C(12)	120.0(8)
C(8)-C(7)-S(2)	121.0(7)
C(12)-C(7)-S(2)	119.0(7)
C(7)-C(8)-C(9)	119.0(8)
C(7)-C(8)-N(1)	122.0(8)
C(9)-C(8)-N(1)	118.8(8)
C(8)-C(9)-C(10)	120.2(8)
C(9)-C(10)-C(11)	120.5(9)
C(12)-C(11)-C(10)	117.5(8)
C(12)-C(11)-C(20)	122.4(9)
C(10)-C(11)-C(20)	120.1(9)
C(11)-C(12)-C(7)	122.6(8)
C(14)-C(13)-C(18)	119.3(7)
C(14)-C(13)-N(1)	121.0(7)
C(18)-C(13)-N(1)	119.6(7)
C(13)-C(14)-C(15)	119.7(8)
C(13)-C(14)-S(1)	123.0(6)
C(15)-C(14)-S(1)	117.3(7)
C(16)-C(15)-C(14)	120.6(8)
C(17)-C(16)-C(15)	119.2(8)
C(17)-C(16)-C(21)	122.1(9)
C(15)-C(16)-C(21)	118.7(9)
C(16)-C(17)-C(18)	121.3(9)
C(17)-C(18)-C(13)	119.6(8)

5.3SI Table 4. Anisotropic displacement parameters (A^2 x 10^3) for exp_77.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	53(4)	33(3)	45(4)	3(3)	1(3)	4(3)
F(1)	275(13)	156(8)	117(7)	-78(6)	57(7)	-129(9)
F(2)	199(11)	118(7)	222(11)	91(8)	-50(8)	-46(7)
F(3)	172(11)	140(9)	600(30)	-110(14)	226(15)	-23(8)
F(4)	137(6)	85(5)	117(6)	-5(4)	-30(5)	-25(5)
F(5)	349(16)	135(8)	89(6)	26(6)	-35(8)	-101(9)
F(6)	90(6)	207(10)	170(9)	-75(8)	16(5)	35(6)
S(1)	59(1)	47(1)	75(2)	16(1)	1(1)	4(1)
S(2)	53(1)	46(1)	78(2)	10(1)	3(1)	9(1)
Sb(1)	76(1)	57(1)	74(1)	-12(1)	14(1)	-6(1)
C(1)	70(6)	53(5)	48(5)	5(4)	9(4)	-15(5)
C(2)	63(6)	43(4)	49(5)	18(4)	5(4)	-10(4)
C(3)	52(5)	37(4)	51(5)	3(4)	2(4)	9(4)
C(4)	49(5)	35(4)	38(4)	-8(3)	5(3)	-3(3)
C(5)	54(5)	45(5)	47(5)	0(4)	-1(4)	6(4)
C(6)	52(5)	55(5)	53(5)	-5(4)	-5(4)	-5(4)
C(7)	55(5)	33(4)	61(5)	-4(4)	0(4)	3(4)
C(8)	58(5)	31(4)	56(5)	7(4)	3(4)	-4(4)
C(9)	69(6)	43(5)	55(5)	-1(4)	6(4)	1(4)
C(10)	81(7)	45(5)	59(6)	3(5)	21(5)	-9(5)
C(11)	85(7)	41(5)	53(5)	2(4)	-8(5)	-14(5)
C(12)	64(6)	41(4)	56(5)	7(4)	-1(4)	3(4)
C(13)	38(4)	46(4)	50(5)	0(4)	1(4)	-2(4)
C(14)	42(4)	51(5)	51(5)	1(4)	7(4)	2(4)
C(15)	57(5)	63(6)	53(5)	2(5)	6(4)	7(5)
C(16)	50(5)	77(7)	50(5)	-12(5)	3(4)	-2(5)
C(17)	69(6)	57(6)	65(6)	0(5)	1(5)	-17(5)
C(18)	53(5)	47(5)	61(5)	5(4)	3(4)	-1(4)
C(19)	74(7)	66(6)	94(8)	8(6)	9(6)	-29(5)
C(20)	100(8)	76(7)	62(6)	20(6)	-12(6)	-10(6)
C(21)	56(6)	110(9)	78(7)	-16(7)	-3(5)	-13(6)

5.4SI Cristallographic data radical cation 1b$^{\bullet+}$

$C_{21}H_{17}NS_2O_3SbF_6$+CH_2Cl_2, M=716.15, Triclinic, space group P-1, a=9.106(1), b=10.580(1), c=15.856(1)Å, α=102.819(5), β=97.906(4), γ=112.771(5) V=1330.3(2)Å^3, Z=2 D_c=1.788, μ=12.175 mm^{-1}, F(000)=706. 7657 Reflections were collected with a 4.75<θ< 61.82 range with a completeness to theta 97.1%; 4050 were independent, the parameters were 325 and the final R index was 0.0687 for reflections having I>2σI, and 0.0981 for all data. No significant H-bonds or short interactions were detectable. Deposition number at the Cambridge Crystallographic Data Center: CCDC 931338. Angle between ring planes is 54.5°.

5.4SI Table 1. Crystal data and structure refinement for exp_711.

Identification code	exp_711
Empirical formula	C22 H19 Cl2 F6 N O3 S2 Sb
Formula weight	716.15
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.106(1) A alpha = 102.819(5) deg. b = 10.580(1) A beta = 97.906(4) deg. c = 15.856(1) A gamma = 112.771(5) deg.
Volume	1330.3(2) A^3
Z, Calculated density	2, 1.788 Mg/m^3
Absorption coefficient	12.175 mm^-1
F(000)	706
Crystal size	0.10 x 0.06 x 0.04 mm
Theta range for data collection	4.75 to 61.82 deg.
Limiting indices	-8<=h<=10, -11<=k<=11, -18<=l<=17
Reflections collected / unique	7657 / 4050 [R(int) = 0.0525]
Completeness to theta = 61.82	97.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4050 / 0 / 325
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0687, wR2 = 0.1821
R indices (all data)	R1 = 0.0981, wR2 = 0.2068
Largest diff. peak and hole	1.689 and -1.258 e.A^-3

5.4SI Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for exp_711.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	5005(8)	-2339(7)	936(4)	46(2)
O(1)	1294(8)	-5027(7)	2429(5)	65(2)
O(2)	3503(9)	-3343(8)	4070(4)	74(2)
O(3)	6470(8)	-1293(7)	4138(4)	64(2)
F(1)	1674(10)	1165(9)	3724(5)	119(3)
F(2)	474(16)	-1607(10)	3055(8)	170(5)
F(3)	3597(12)	-51(12)	3229(7)	151(4)
F(4)	-285(12)	-133(15)	2154(8)	183(5)
F(5)	1646(11)	-1305(9)	1662(6)	130(3)
F(6)	2890(13)	1492(10)	2370(6)	134(3)
S(1)	7172(4)	-1952(4)	-364(2)	77(1)
S(2)	1706(3)	-4896(3)	736(2)	59(1)
Sb(1)	1634(1)	-64(1)	2686(1)	66(1)
C(1)	4359(11)	-3430(10)	119(6)	53(2)
C(2)	5188(12)	-3313(12)	-558(6)	61(3)
C(3)	4489(17)	-4358(14)	-1387(7)	77(3)
C(4)	2986(16)	-5516(12)	-1553(6)	69(3)
C(5)	2189(14)	-5636(11)	-888(6)	69(3)
C(6)	2854(11)	-4637(10)	-60(6)	54(2)
C(7)	5971(10)	-889(10)	958(6)	50(2)
C(8)	6990(11)	-575(11)	398(6)	57(2)
C(9)	7903(12)	855(14)	444(8)	72(3)
C(10)	7773(14)	1946(14)	1034(9)	83(4)
C(11)	6720(12)	1637(11)	1555(8)	68(3)
C(12)	5761(11)	212(10)	1535(7)	57(2)
C(13)	4656(10)	-2639(8)	1726(5)	44(2)
C(14)	3191(10)	-3755(8)	1712(6)	45(2)
C(15)	2807(10)	-3964(9)	2504(6)	47(2)
C(16)	3914(11)	-3093(10)	3318(6)	53(2)
C(17)	5449(10)	-2023(10)	3321(6)	51(2)
C(18)	5818(10)	-1787(9)	2544(5)	44(2)
C(19)	1208(18)	-6074(15)	2841(10)	122(6)
C(20)	3520(18)	-2226(15)	4750(9)	98(4)
C(21)	8091(4)	-129(4)	4184(3)	84(4)
Cl(1)	4327(4)	-4357(4)	6183(3)	142(2)
Cl(2)	1153(4)	-6470(4)	5787(3)	299(5)
C(22)	2951(4)	-5789(4)	5405(3)	143(6)

5.4SI Table 3. Bond lengths [A] and angles [deg] for exp_711.

N(1)-C(1)	1.400(11)
N(1)-C(13)	1.406(10)
N(1)-C(7)	1.432(11)
O(1)-C(15)	1.369(10)
O(1)-C(19)	1.389(13)
O(2)-C(16)	1.348(10)
O(2)-C(20)	1.406(14)
O(3)-C(17)	1.345(10)
O(3)-C(21)	1.492(7)
F(1)-Sb(1)	1.843(7)
F(2)-Sb(1)	1.839(8)
F(3)-Sb(1)	1.867(8)
F(4)-Sb(1)	1.800(8)
F(5)-Sb(1)	1.853(7)
F(6)-Sb(1)	1.826(8)
S(1)-C(8)	1.752(11)
S(1)-C(2)	1.751(11)
S(2)-C(14)	1.735(8)
S(2)-C(6)	1.748(10)
C(1)-C(2)	1.396(13)
C(1)-C(6)	1.402(13)
C(2)-C(3)	1.391(15)
C(3)-C(4)	1.380(16)
C(4)-C(5)	1.361(15)
C(5)-C(6)	1.370(12)
C(7)-C(8)	1.371(12)
C(7)-C(12)	1.406(13)
C(8)-C(9)	1.395(14)
C(9)-C(10)	1.370(17)
C(10)-C(11)	1.344(16)
C(11)-C(12)	1.410(13)
C(13)-C(14)	1.391(11)
C(13)-C(18)	1.407(11)
C(14)-C(15)	1.390(11)
C(15)-C(16)	1.388(12)
C(16)-C(17)	1.417(12)
C(17)-C(18)	1.370(11)
Cl(1)-C(22)	1.6320
Cl(2)-C(22)	1.7663

C(1)-N(1)-C(13)	120.8(7)
C(1)-N(1)-C(7)	119.3(7)
C(13)-N(1)-C(7)	119.8(7)
C(15)-O(1)-C(19)	118.5(9)
C(16)-O(2)-C(20)	119.9(8)
C(17)-O(3)-C(21)	116.5(6)
C(8)-S(1)-C(2)	98.7(4)
C(14)-S(2)-C(6)	101.1(4)
F(4)-Sb(1)-F(6)	94.2(6)
F(4)-Sb(1)-F(2)	89.0(6)
F(6)-Sb(1)-F(2)	176.7(5)
F(4)-Sb(1)-F(1)	90.0(5)
F(6)-Sb(1)-F(1)	89.2(4)
F(2)-Sb(1)-F(1)	89.7(4)
F(4)-Sb(1)-F(5)	91.7(5)
F(6)-Sb(1)-F(5)	91.0(4)
F(2)-Sb(1)-F(5)	90.0(4)
F(1)-Sb(1)-F(5)	178.3(4)

F(4)-Sb(1)-F(3)	178.3(5)
F(6)-Sb(1)-F(3)	87.2(5)
F(2)-Sb(1)-F(3)	89.7(6)
F(1)-Sb(1)-F(3)	91.1(4)
F(5)-Sb(1)-F(3)	87.3(4)
C(2)-C(1)-N(1)	120.1(9)
C(2)-C(1)-C(6)	118.0(9)
N(1)-C(1)-C(6)	121.9(8)
C(3)-C(2)-C(1)	119.7(10)
C(3)-C(2)-S(1)	118.7(8)
C(1)-C(2)-S(1)	121.4(8)
C(4)-C(3)-C(2)	121.2(10)
C(5)-C(4)-C(3)	119.0(9)
C(4)-C(5)-C(6)	121.3(11)
C(5)-C(6)-C(1)	120.8(10)
C(5)-C(6)-S(2)	117.2(8)
C(1)-C(6)-S(2)	122.0(7)
C(8)-C(7)-C(12)	120.4(9)
C(8)-C(7)-N(1)	121.8(9)
C(12)-C(7)-N(1)	117.7(8)
C(7)-C(8)-C(9)	119.5(10)
C(7)-C(8)-S(1)	120.6(8)
C(9)-C(8)-S(1)	119.9(8)
C(10)-C(9)-C(8)	120.7(10)
C(11)-C(10)-C(9)	119.8(11)
C(10)-C(11)-C(12)	122.0(12)
C(7)-C(12)-C(11)	117.4(10)
C(14)-C(13)-C(18)	119.7(7)
C(14)-C(13)-N(1)	121.3(7)
C(18)-C(13)-N(1)	118.9(7)
C(15)-C(14)-C(13)	120.5(8)
C(15)-C(14)-S(2)	116.1(6)
C(13)-C(14)-S(2)	123.2(6)
O(1)-C(15)-C(14)	116.6(7)
O(1)-C(15)-C(16)	123.2(8)
C(14)-C(15)-C(16)	120.2(8)
O(2)-C(16)-C(15)	118.4(8)
O(2)-C(16)-C(17)	122.9(8)
C(15)-C(16)-C(17)	118.7(8)
O(3)-C(17)-C(18)	124.5(8)
O(3)-C(17)-C(16)	114.1(7)
C(18)-C(17)-C(16)	121.4(8)
C(17)-C(18)-C(13)	119.3(8)
Cl(1)-C(22)-Cl(2)	108.6

5.4SI Table 4. Anisotropic displacement parameters (A^2 x 10^3) for exp_711.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	46(4)	51(4)	43(4)	15(3)	16(3)	22(3)
O(1)	50(4)	62(4)	69(4)	25(3)	13(3)	8(3)
O(2)	90(5)	73(5)	47(4)	20(3)	24(4)	18(4)
O(3)	58(4)	78(5)	38(3)	13(3)	6(3)	16(3)
F(1)	127(6)	107(6)	104(6)	6(5)	60(5)	34(5)
F(2)	225(11)	91(6)	183(10)	58(6)	109(9)	30(6)
F(3)	126(7)	197(10)	133(8)	17(7)	-7(6)	105(7)
F(4)	119(7)	269(14)	172(10)	53(10)	-7(7)	117(9)
F(5)	126(6)	125(6)	100(6)	-15(5)	42(5)	35(5)
F(6)	171(8)	113(6)	122(7)	60(5)	66(6)	42(6)
S(1)	77(2)	111(2)	67(2)	40(2)	39(1)	49(2)
S(2)	51(1)	57(1)	51(1)	13(1)	4(1)	11(1)
Sb(1)	64(1)	73(1)	60(1)	18(1)	22(1)	28(1)
C(1)	63(6)	65(6)	42(5)	16(4)	7(4)	39(5)
C(2)	70(6)	90(7)	50(6)	29(5)	20(5)	54(6)
C(3)	108(10)	105(9)	47(6)	18(6)	24(6)	78(9)
C(4)	112(9)	66(7)	34(5)	2(5)	3(5)	55(7)
C(5)	90(8)	60(6)	46(6)	-7(5)	-13(5)	44(6)
C(6)	58(6)	57(6)	47(5)	11(4)	4(4)	30(5)
C(7)	39(5)	58(6)	60(6)	29(5)	9(4)	21(4)
C(8)	46(5)	74(6)	56(6)	36(5)	12(4)	21(5)
C(9)	56(6)	100(9)	63(7)	49(7)	12(5)	25(6)
C(10)	71(8)	79(8)	88(9)	44(7)	-3(7)	19(7)
C(11)	55(6)	59(6)	92(8)	36(6)	11(6)	20(5)
C(12)	47(5)	50(5)	75(7)	27(5)	6(5)	20(4)
C(13)	49(5)	42(5)	41(5)	9(4)	11(4)	23(4)
C(14)	44(5)	37(4)	50(5)	13(4)	11(4)	12(4)
C(15)	44(5)	48(5)	47(5)	12(4)	17(4)	18(4)
C(16)	57(6)	59(6)	41(5)	14(4)	15(4)	22(5)
C(17)	41(5)	64(6)	44(5)	13(4)	9(4)	19(4)
C(18)	46(5)	47(5)	41(5)	10(4)	16(4)	21(4)
C(19)	117(11)	85(9)	128(13)	66(9)	-8(9)	1(8)
C(20)	117(11)	107(10)	88(9)	36(8)	56(8)	53(9)
C(21)	53(6)	97(9)	60(7)	9(6)	3(5)	2(6)
Cl(1)	135(3)	158(4)	101(3)	22(3)	5(2)	50(3)
Cl(2)	130(5)	259(9)	388(14)	34(9)	92(7)	-12(5)
C(22)	182(18)	124(13)	111(13)	14(11)	18(12)	72(13)

5.5SI Cristallographic data helicene 1b

$C_{21}H_{17}NO_3S_2$, M=395.48, Orthorhombic, space group P b c a, a=10.641(1), b=14.807(1), c=23.076(1)Å, V=3635.9(4)Å^3, Z=8 D$_c$=1.445, μ=2.844 mm^{-1}, F(000)=1648. 10195 Reflections were collected with a 5.47<θ< 70.96 range with a completeness to theta 95,3%; 3344 were independent, the parameters were 245 and the final R index was 0.0440 for reflections having I>2σI, and 0.0803 for all data. No significant H-bonds or short interactions were detectable. Deposition number at the Cambridge Crystallographic Data Center: CCDC 931339. Angle between ring planes is 70.8°.

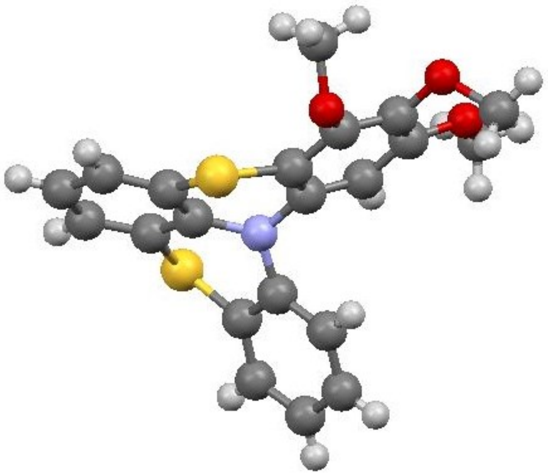


Figure 5.5SI-1. Ortep draw of helicene **1b**

5.5SI Table 1. Crystal data and structure refinement for **1b**.

Identification code	exp_732
Empirical formula	C21 H17 N O3 S2
Formula weight	395.48
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Orthorhombic, P b c a
Unit cell dimensions	a = 10.641(1) A alpha = 90 deg. b = 14.807(1) A beta = 90 deg. c = 23.076(1) A gamma = 90 deg.
Volume	3635.9(4) A^3
Z, Calculated density	8, 1.445 Mg/m^3
Absorption coefficient	2.844 mm^-1
F(000)	1648
Crystal size	0.09 x 0.04 x 0.03 mm
Theta range for data collection	5.47 to 70.96 deg.
Limiting indices	-12<=h<=12, -16<=k<=17, -27<=l<=21
Reflections collected / unique	10195 / 3344 [R(int) = 0.0574]
Completeness to theta = 70.96	95.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3344 / 0 / 245
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.0947
R indices (all data)	R1 = 0.0803, wR2 = 0.1131
Extinction coefficient	0.00042(7)
Largest diff. peak and hole	0.276 and -0.318 e.A^-3

5.5SI Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for exp_732.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	7710(2)	2824(2)	8353(1)	20(1)
O(1)	10447(2)	376(1)	8961(1)	27(1)
O(2)	11852(2)	1537(1)	9588(1)	29(1)
O(3)	11233(2)	3376(1)	9605(1)	26(1)
S(1)	6135(1)	2893(1)	7293(1)	23(1)
S(2)	9355(1)	4284(1)	8922(1)	23(1)
C(1)	7806(3)	3652(2)	8044(1)	19(1)
C(2)	7106(3)	3778(2)	7540(1)	21(1)
C(3)	7167(3)	4592(2)	7241(1)	24(1)
C(4)	7965(3)	5265(2)	7431(1)	25(1)
C(5)	8668(3)	5147(2)	7932(1)	24(1)
C(6)	8568(3)	4353(2)	8247(1)	20(1)
C(7)	6500(3)	2438(2)	8433(1)	19(1)
C(8)	5646(3)	2477(2)	7976(1)	19(1)
C(9)	4426(3)	2153(2)	8050(1)	23(1)
C(10)	4077(3)	1762(2)	8570(1)	27(1)
C(11)	4936(3)	1706(2)	9022(1)	25(1)
C(12)	6135(3)	2050(2)	8954(1)	21(1)
C(13)	8758(3)	2505(2)	8676(1)	20(1)
C(14)	9536(3)	3101(2)	8966(1)	19(1)
C(15)	10565(3)	2762(2)	9281(1)	21(1)
C(16)	10824(3)	1848(2)	9285(1)	22(1)
C(17)	10075(3)	1258(2)	8956(1)	21(1)
C(18)	9036(3)	1586(2)	8663(1)	22(1)
C(19)	12507(3)	3523(3)	9423(2)	42(1)
C(20)	11530(3)	1019(2)	10089(1)	35(1)
C(21)	9730(3)	-242(2)	8619(1)	30(1)

5.5SI Table 3. Bond lengths [A] and angles [deg] for exp_732.

N(1)-C(7)	1.420(4)
N(1)-C(13)	1.423(3)
N(1)-C(1)	1.422(4)
O(1)-C(17)	1.365(3)
O(1)-C(21)	1.429(3)
O(2)-C(16)	1.379(3)
O(2)-C(20)	1.428(4)
O(3)-C(15)	1.375(3)
O(3)-C(19)	1.435(4)
S(1)-C(2)	1.763(3)
S(1)-C(8)	1.770(3)
S(2)-C(14)	1.765(3)
S(2)-C(6)	1.772(3)
C(1)-C(2)	1.394(4)
C(1)-C(6)	1.397(4)
C(2)-C(3)	1.391(4)
C(3)-C(4)	1.381(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.388(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.386(4)
C(5)-H(5)	0.9300
C(7)-C(12)	1.390(4)
C(7)-C(8)	1.392(4)
C(8)-C(9)	1.395(4)
C(9)-C(10)	1.382(4)
C(9)-H(9)	0.9300
C(10)-C(11)	1.389(4)
C(10)-H(10)	0.9300
C(11)-C(12)	1.382(4)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(13)-C(14)	1.383(4)
C(13)-C(18)	1.392(4)
C(14)-C(15)	1.407(4)
C(15)-C(16)	1.382(4)
C(16)-C(17)	1.405(4)
C(17)-C(18)	1.383(4)
C(18)-H(18)	0.9300
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600

C(7)-N(1)-C(13)	120.6(2)
C(7)-N(1)-C(1)	118.5(2)
C(13)-N(1)-C(1)	119.5(2)
C(17)-O(1)-C(21)	117.0(2)
C(16)-O(2)-C(20)	113.6(2)
C(15)-O(3)-C(19)	115.5(2)
C(2)-S(1)-C(8)	98.24(14)
C(14)-S(2)-C(6)	99.14(13)
C(2)-C(1)-C(6)	119.4(3)
C(2)-C(1)-N(1)	119.6(3)

C(6)-C(1)-N(1)	121.0(2)
C(3)-C(2)-C(1)	120.3(3)
C(3)-C(2)-S(1)	120.7(2)
C(1)-C(2)-S(1)	118.9(2)
C(4)-C(3)-C(2)	119.8(3)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(3)-C(4)-C(5)	120.3(3)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
C(6)-C(5)-C(4)	120.2(3)
C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9
C(5)-C(6)-C(1)	119.9(3)
C(5)-C(6)-S(2)	118.3(2)
C(1)-C(6)-S(2)	121.7(2)
C(12)-C(7)-C(8)	119.4(3)
C(12)-C(7)-N(1)	122.1(2)
C(8)-C(7)-N(1)	118.4(3)
C(7)-C(8)-C(9)	120.0(3)
C(7)-C(8)-S(1)	119.7(2)
C(9)-C(8)-S(1)	120.2(2)
C(10)-C(9)-C(8)	120.0(3)
C(10)-C(9)-H(9)	120.0
C(8)-C(9)-H(9)	120.0
C(9)-C(10)-C(11)	120.0(3)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
C(12)-C(11)-C(10)	120.0(3)
C(12)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0
C(11)-C(12)-C(7)	120.5(3)
C(11)-C(12)-H(12)	119.7
C(7)-C(12)-H(12)	119.7
C(14)-C(13)-C(18)	120.5(3)
C(14)-C(13)-N(1)	120.7(3)
C(18)-C(13)-N(1)	118.7(3)
C(13)-C(14)-C(15)	119.2(3)
C(13)-C(14)-S(2)	122.8(2)
C(15)-C(14)-S(2)	117.9(2)
O(3)-C(15)-C(16)	122.8(3)
O(3)-C(15)-C(14)	116.6(3)
C(16)-C(15)-C(14)	120.5(3)
O(2)-C(16)-C(15)	119.3(3)
O(2)-C(16)-C(17)	121.1(3)
C(15)-C(16)-C(17)	119.5(3)
O(1)-C(17)-C(18)	124.8(3)
O(1)-C(17)-C(16)	115.2(2)
C(18)-C(17)-C(16)	119.9(3)
C(17)-C(18)-C(13)	120.2(3)
C(17)-C(18)-H(18)	119.9
C(13)-C(18)-H(18)	119.9
O(3)-C(19)-H(19A)	109.5
O(3)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(3)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(2)-C(20)-H(20A)	109.5
O(2)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(2)-C(20)-H(20C)	109.5

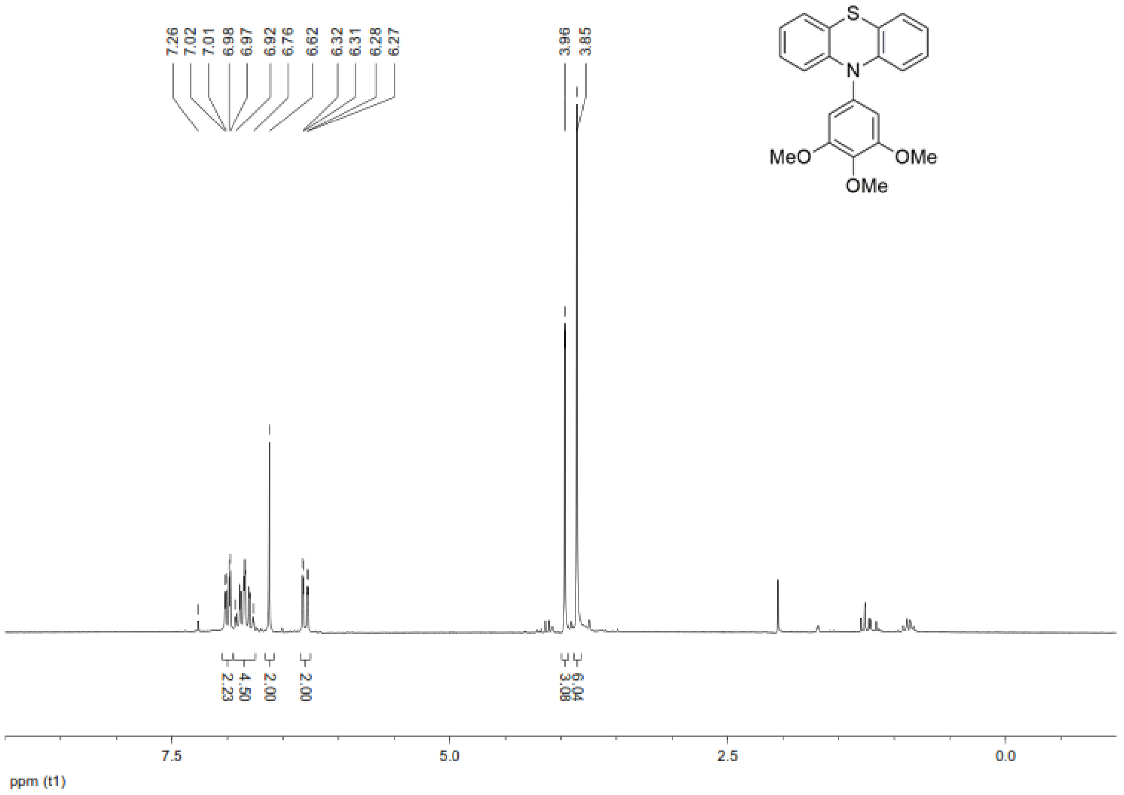
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(1)-C(21)-H(21A)	109.5
O(1)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(1)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

5.5SI Table 4. Anisotropic displacement parameters (A^2 x 10^3) for exp_732.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

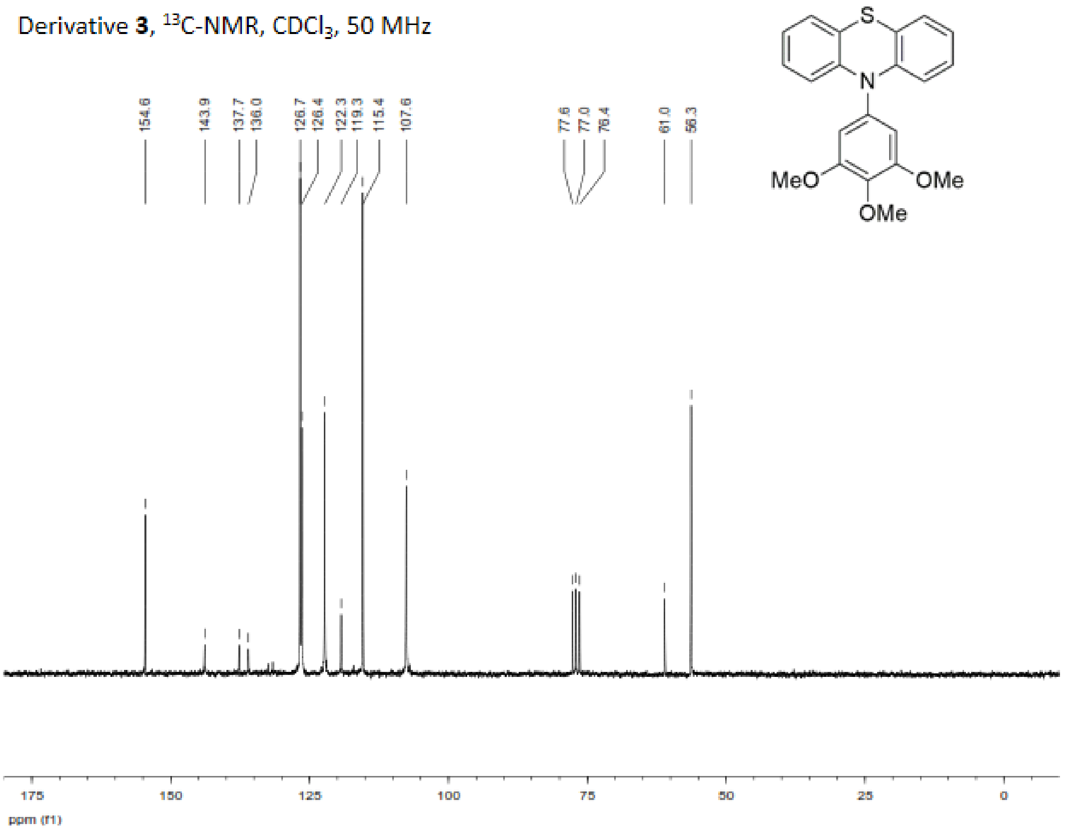
	U11	U22	U33	U23	U13	U12
N(1)	17(1)	20(1)	24(1)	6(1)	-4(1)	-1(1)
O(1)	29(1)	20(1)	32(1)	-1(1)	-9(1)	0(1)
O(2)	24(1)	35(1)	28(1)	8(1)	-7(1)	0(1)
O(3)	24(1)	33(1)	21(1)	-7(1)	-4(1)	-3(1)
S(1)	24(1)	24(1)	21(1)	1(1)	-4(1)	-1(1)
S(2)	25(1)	21(1)	22(1)	-2(1)	-1(1)	-3(1)
C(1)	16(1)	17(2)	22(2)	3(1)	4(1)	4(1)
C(2)	18(1)	24(2)	21(2)	-2(1)	1(1)	2(1)
C(3)	25(2)	26(2)	22(2)	6(1)	1(1)	4(2)
C(4)	27(2)	20(2)	30(2)	7(2)	4(1)	-1(1)
C(5)	23(2)	20(2)	28(2)	-3(1)	3(1)	2(1)
C(6)	21(2)	17(2)	21(2)	0(1)	1(1)	0(1)
C(7)	18(1)	16(2)	24(2)	-1(1)	-3(1)	1(1)
C(8)	22(2)	14(1)	23(2)	-2(1)	1(1)	2(1)
C(9)	20(2)	22(2)	27(2)	-5(1)	-5(1)	1(1)
C(10)	22(2)	25(2)	35(2)	-3(2)	2(1)	-3(1)
C(11)	30(2)	23(2)	24(2)	-2(1)	6(1)	-2(2)
C(12)	23(2)	21(2)	20(2)	2(1)	-1(1)	-2(1)
C(13)	20(2)	25(2)	15(1)	6(1)	0(1)	1(1)
C(14)	20(2)	21(2)	16(1)	-1(1)	3(1)	-2(1)
C(15)	21(2)	27(2)	14(1)	-5(1)	1(1)	-5(1)
C(16)	19(2)	29(2)	19(2)	4(1)	-3(1)	2(1)
C(17)	22(2)	22(2)	20(2)	2(1)	-1(1)	0(1)
C(18)	23(2)	22(2)	19(2)	1(1)	-4(1)	-3(1)
C(19)	25(2)	48(2)	51(2)	-10(2)	2(2)	-17(2)
C(20)	43(2)	32(2)	29(2)	4(2)	-13(2)	1(2)
C(21)	31(2)	23(2)	35(2)	-1(2)	-7(1)	-3(2)

6SI NMR Spectra of New Compounds

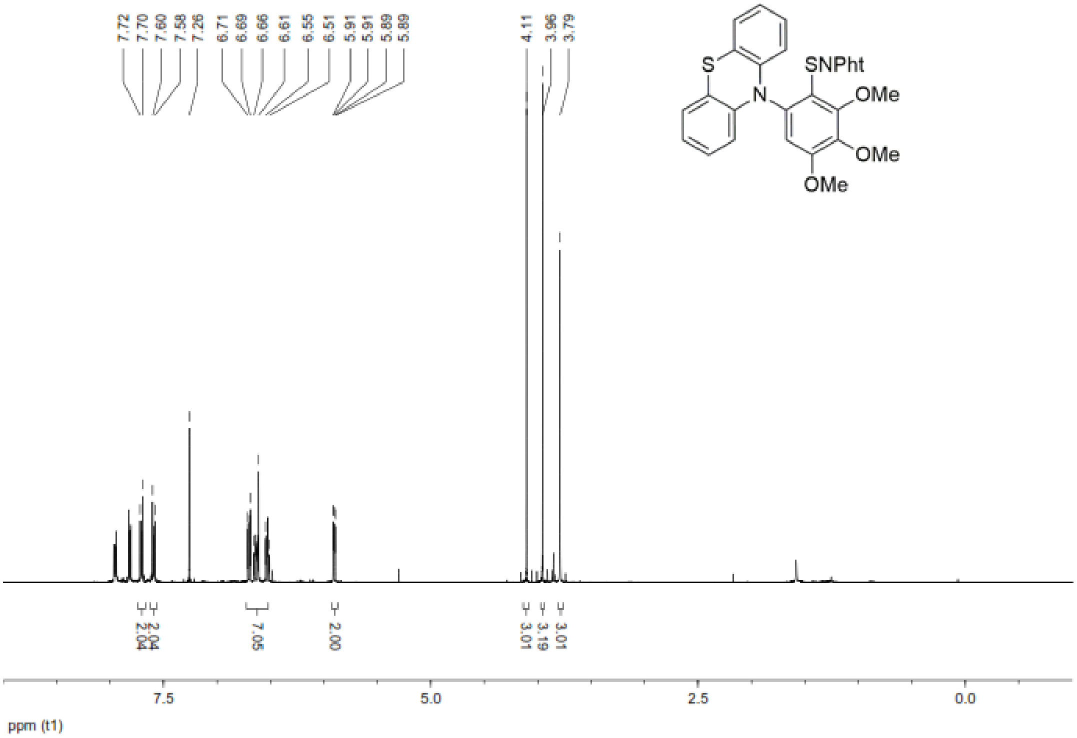
Derivative **3**, ^{1}H-NMR, CDCl$_3$, 200 MHz



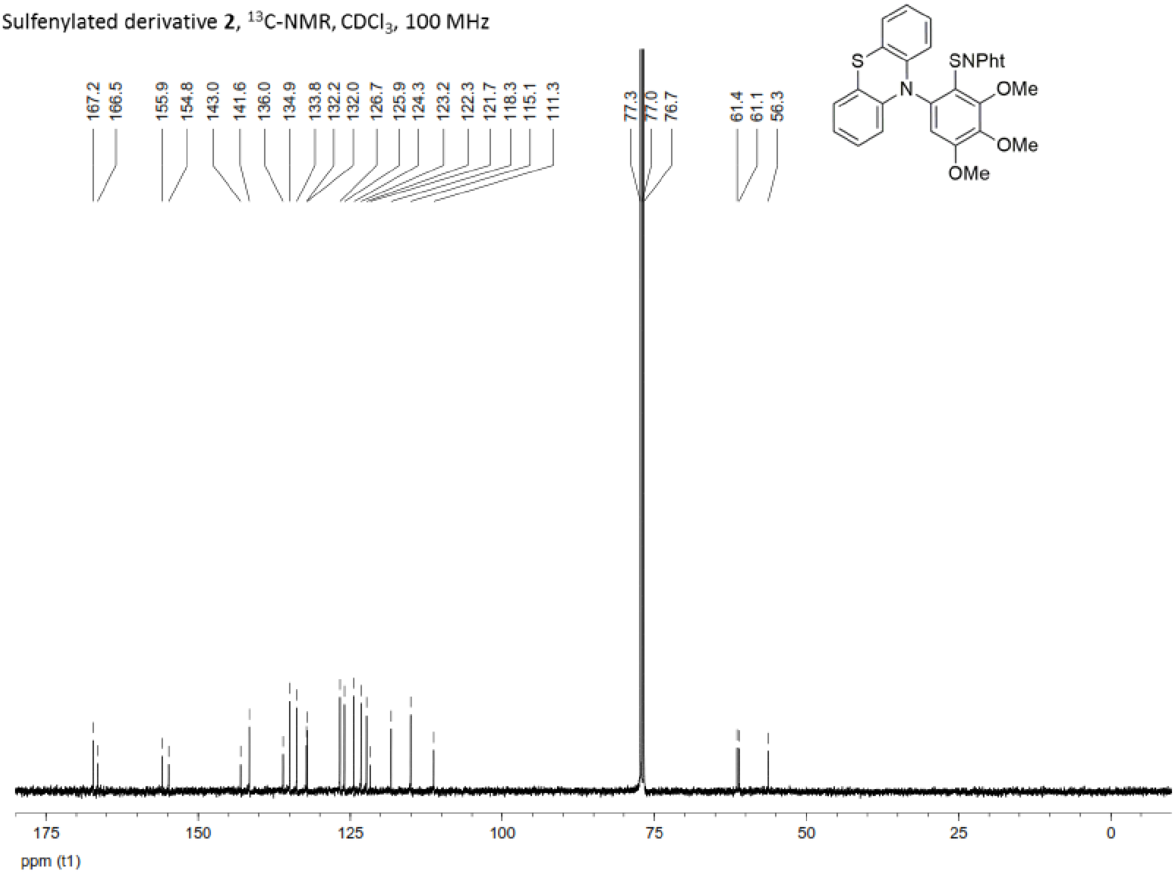
Derivative **3**, ^{13}C-NMR, CDCl$_3$, 50 MHz



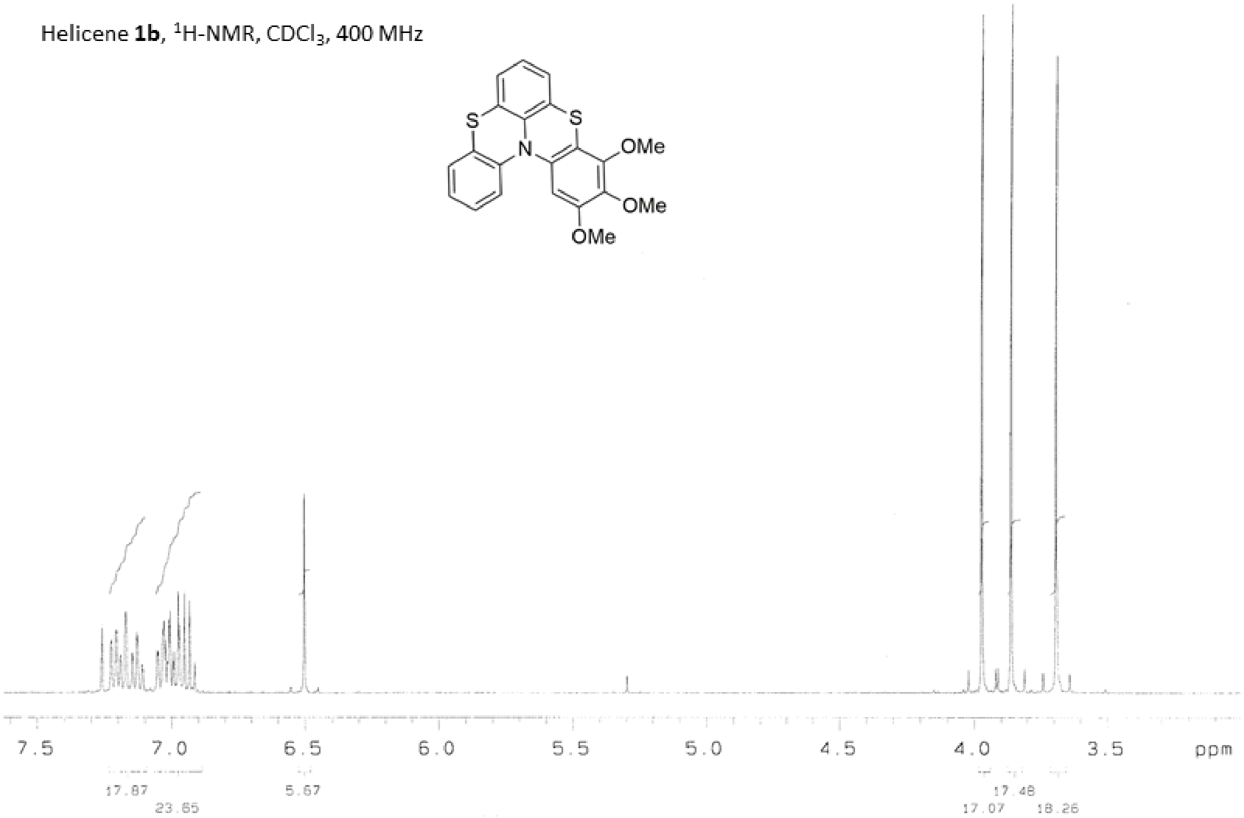
Sulfenylated derivative **2**, ^{1}H-NMR, $CDCl_3$, 400 MHz



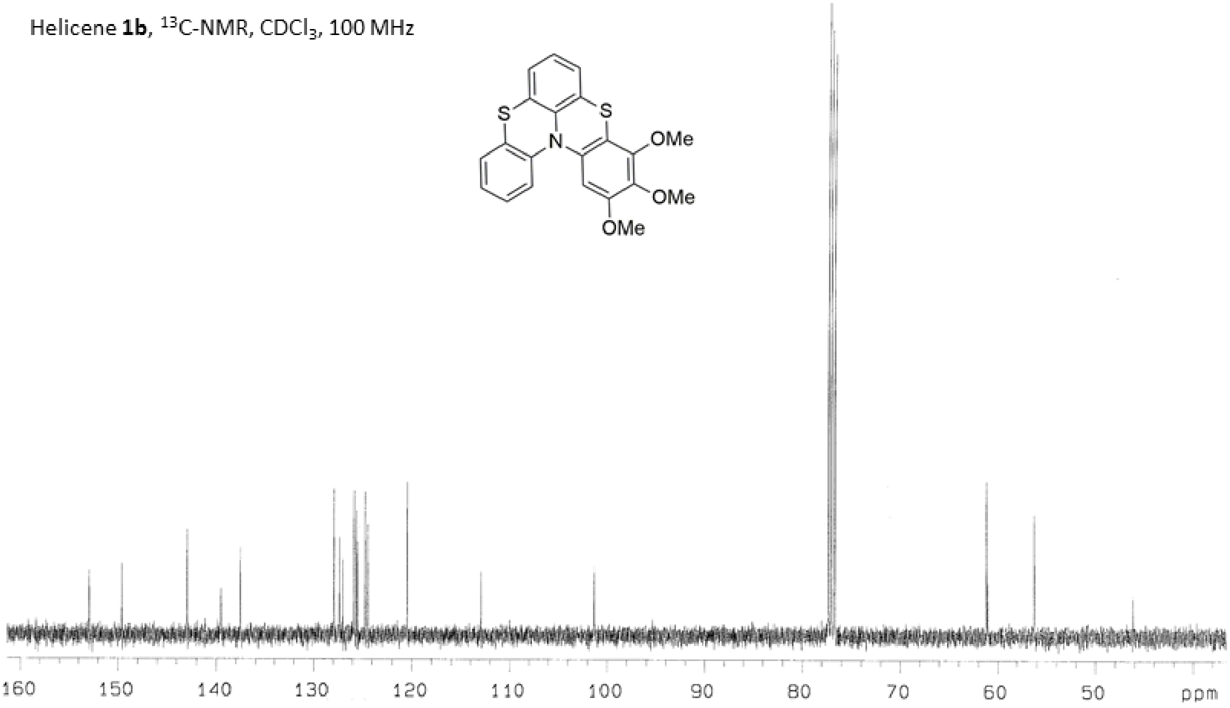
Sulfenylated derivative **2**, ^{13}C-NMR, $CDCl_3$, 100 MHz



Helicene **1b**, ^{1}H-NMR, CDCl$_3$, 400 MHz



Helicene **1b**, ^{13}C-NMR, CDCl$_3$, 100 MHz



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