*Supporting information for*

# Dithia[9]helicenes: Molecular Design, Surface Imaging, and Circularly Polarized Luminescence with Enhanced Dissymmetry Factors

Bianca C. Baciu,[a] Pawel J. Bronk,[a] Tamara de Ara,[b] Rafael Rodriguez,[c] Pierpaolo Morgante,[e] Nicolas Vanthuyne,[d] Carlos Sabater,[b] Carlos Untiedt,[b] Jochen Autschbach[*,e] Jeanne Crassous,[*,c] Albert Guijarro.[*,a]

[a] *Departamento de Química Orgánica and Instituto Universitario de Síntesis Orgánica, Unidad asociada CSIC, Universidad de Alicante, Campus de San Vicente del Raspeig, E-03080, Alicante, Spain*

[b] *Departamento de Física Aplicada and Unidad asociada CSIC, Universidad de Alicante, Campus de San Vicente del Raspeig, E-03080, Alicante, Spain*

[c] *Université Rennes, CNRS, ISCR-UMR 6226, Rennes F-35000, France*

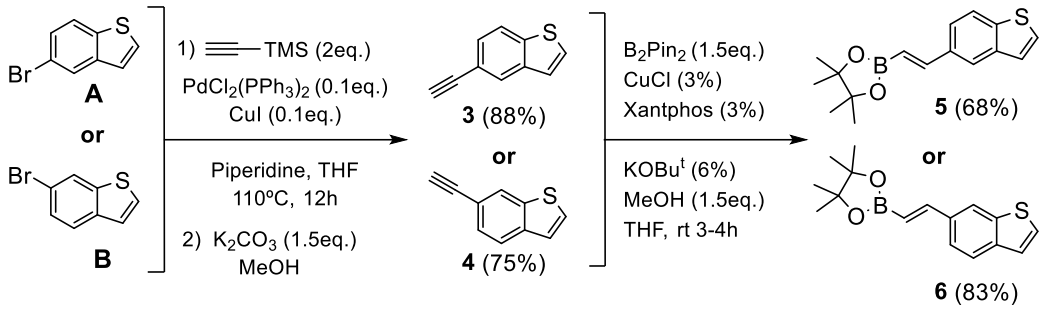
[d] *Aix Marseille University, CNRS, Centrale Marseille, iSm2, Marseille, France*

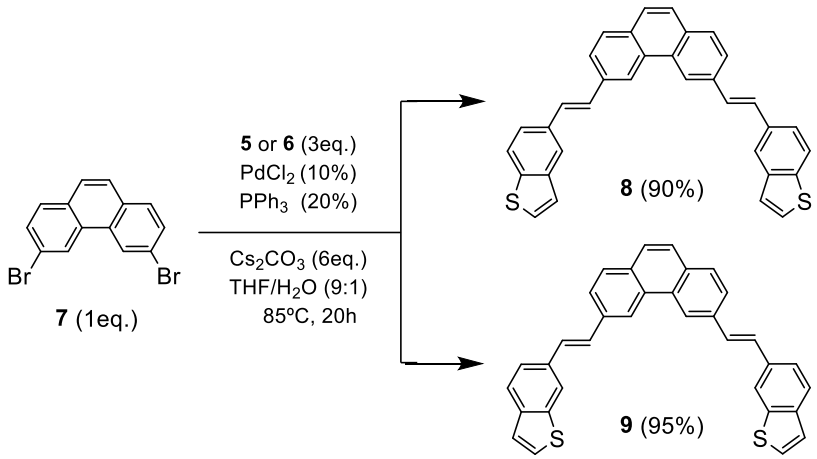
[e] *Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14260, United States*

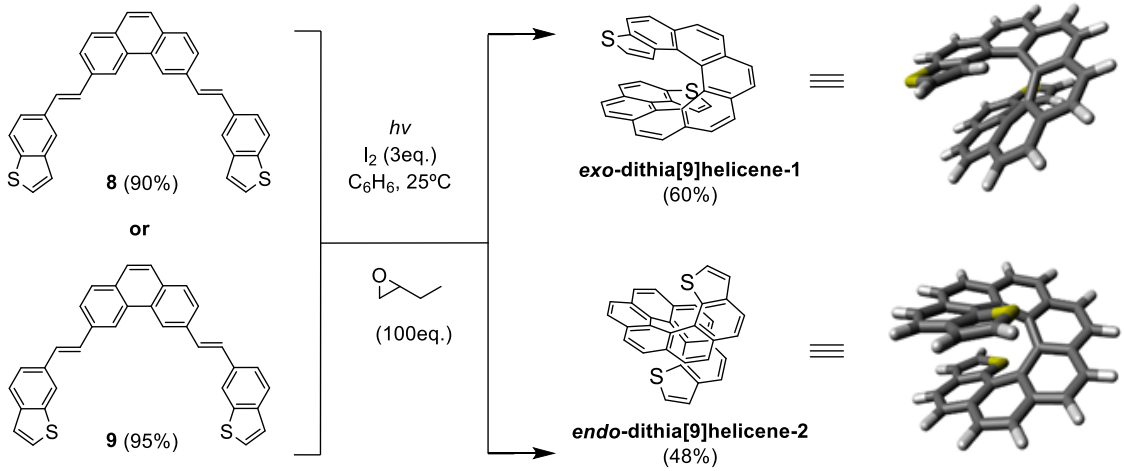
# Table of Contents

# Section S1: Experimental part

## 1. Synthesis of *exo*-dithia[9]helicene and *endo*-dithia[9]helicene



## 2. General Methods

Commercially starting materials and solvents for photochemistry, chromatography and recrystallization were used without further purification, unless otherwise stated. THF, benzene and cyclohexane were dried and distilled over Na/K alloy right before. Commercially unavailable reagents were synthesized via different methods that will be explained separately.

Gas chromatography analyses (GLC) were carried out with a Hewlett Packard HP-5890 instrument equipped with a flame ionization detector and a 30 m HP-5 capillary column (0.32 mm diam, 0.25 µm film thickness), using nitrogen as carrier gas (12 psi). Column chromatography was performed with Merck silica gel 60 (0.040-0.063 µm, 240-400 mesh). Thin-layer chromatography (TLC) was performed on precoated silica gel plates (Merck 60, F254, 0.25 mm). TLC detection was done by $UV_{254}$ light, $R_f$ values are given under these conditions. NMR spectra were recorded on a Bruker Avance 300 and Bruker Avance 400 (300 and 400 MHz for $^{1}$H-NMR, and 75 and 100 MHz for $^{13}$C-NMR respectively) using $CDCl_3$ as a solvent and TMS as internal standard. Chemical shifts ($\delta$) are given in ppm vs. TMS. Infrared (IR) analysis was performed with a JASCO FT/IR 4100 spectrophotometer equipped with an ATR component. LRMS were performed using the electron impact (EI) mode at 70 eV in an AGILENT 5973N mass spectrometer coupled with an AGILENT 6890N gas chromatographer. Melting points were performed with a Reichert Thermovar polarizing light microscope and melting points apparatus and have been corrected. Differential scanning calorimetry (DSC) analyses were performed with a calorimeter of TA INSTRUMENTS model Q100 mDSC.

Absorption spectra of UV-Visible (UV-vis, in $M^{-1}$ $cm^{-1}$) were recorded on a UV-2401PC Shimadzu spectrophotometer. Fluorescence spectra were recorded on a FL 920 Edinburgh fluorimeter. Fluorescence quantum yields Ø were measured in diluted solutions using the following equation:

$$\emptyset_X = \emptyset_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta^2{}_X}{\eta^2{}_{ST}}\right)$$

The parameters that appear in the equation mean: the subscripts ST and X denote standard and sample respectively, Ø is the fluorescence quantum yield, Grad is the gradient from the plot of integrated fluorescence intensity vs absorbance, and η the refractive index of the solvent. Quantum yield measurements were carried out using quinine in sulfuric acid as reference (excitation of reference and sample compounds was performed at the same wavelength). Spectra were recorded in $CH_2Cl_2$ at room temperature and in 1-methyl-THF (Me-THF) at 77 K. Optical Rotations were measured on a Jasco P-200.

Electronic circular dichroism (ECD, in $M^{-1}$ $cm^{-1}$) was measured on a Jasco J-815 Circular dichroism Spectrometer (IFR140 facility- Biosit- Université de Rennes 1). The circularly polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter (constructed with the help of the JASCO Company). The samples were excited using a 90° geometry with a Xenon ozone-free lamp 150 W LS. The concentration of the sample was ca. $10^{-5}$ M. Spectra were recorded in $CH_2Cl_2$ with 10 accumulations.

## 3. Photochemistry

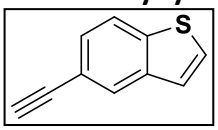
Two different photochemical setups (400 W high-pressure Hg lamps and 2×50 W, 365 nm LED board) were used for the final Mallory-Katz photocyclizations reaction.

A 400-watt high-pressure mercury lamp (Osram HQL MBF-U) was modified by cutting away the outer glass envelope from the screw base (preserving the inner quartz arc tube containing Hg) and was mounted in a porcelain lamp holder provided with a reflector. The lamp was connected to a corresponding power unit and the light beam was focused horizontally to a number of 100mL Schlenck's tubes provided with magnetic stirring and a vertical condenser ending up with a bubbler and refrigerated with a recirculating chiller. 30% ethylene glycol -water mixture as a coolant. The chemical hood was lined with aluminum foil to avoid unwanted exposure to UV radiation. We used cyclohexane or benzene under reflux as solvents. For the degassed reaction, Ar was mildly bubbled through the reaction mixture using a 2 mm flexible Teflon tube.

Two 50 W LED boards were fixed to the walls of a vertical aluminum cylinder (15 cm diameter × 25 cm height) facing each other on opposite sides and connected to the corresponding power units. Small heat dissipaters provided with fans were attached to the LED boards to prevent overheating. This constituted the irradiation chamber. A 250 mL Schlenk 0.6 mm thick single-walled borosilicate tube was placed in the middle of this chamber containing the reaction mixture and was irradiated from opposite sides, at ca. 4 cm distance from each LED plate, while being magnetically stirred from the bottom. With this setup, we worked without reflux and no additional refrigeration of the central reaction tube was needed. We use cyclohexane or benzene as solvents. For the degassed reaction, Ar was mildly bubbled through the reaction as explained above.

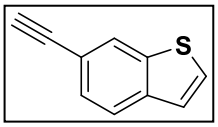
## 4. Synthesis and characterization of compounds

### 4.1. **5-Ethynylbenzo[b]thiophene (3)[1]**




This compound was prepared by adapting a Sonogashira coupling described in the literature to our substrates[1]. A pressure tube was charged with a stirbar, $Pd(PPh_3)_2Cl_2$ (145.80 mg; 0.2 mmol; 0.1 eq.), CuI (39.71 mg; 0.2 mmol; 0.1 eq.) and 5-bromobenzo[b]tiophene (426.18 mg; 2 mmol; 1eq.). The tube was sealed with septum and three cycles vacuum/argon were then performed. Then 4.4mL of dry THF and 2.2mL of dry piperidine followed by trimethylsilylacetylene (0.56mL, 4 mmol; 2 eq.) were added via syringe. The tube was closed and heated in an oil bath at 110°C overnight. The reaction was monitored by TLC. After completion, the dark solution was filtered through a pad of celite. The crude product was purified by column chromatography (silica gel, hexane). The combined fractions were evaporated, and the yellow solid was immediately dissolved in MeOH (20mL) and treated with solid $K_2CO_3$ (418 mg; 3 mmol) with vigorous stirring for 3 hours. The work up consisted in an extraction using 5mL of $H_2O$ and 3×10mL of EtOAc. The organic phase was then dried over magnesium sulfate, filtered and the solvent evaporated under reduced pressure (15 Torr). The residue was purified by column chromatography on silica gel (hexane) to obtain a yellow oil in 88% yield.

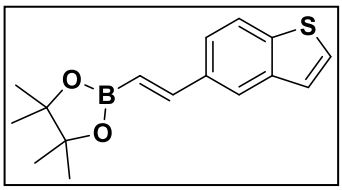
Yellow oil; $R_f$=0.44 (hexane); $^1$H-NMR ($CDCl_3$, 300MHz): $\delta$= 7.99 (d, $J$= 1.1 Hz, 1H), 7.83 (d, $J$=8.4 Hz, 1H), 7.51-7.43 (m, 2H), 7.35-7.29 (m, 1H), 3.11 (s, 1H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): $\delta$= 140.26, 139.55, 127.71, 127.70, 127.61, 123.75, 122.57, 118.08, 84.08, 76.82. MS (EI) *m/z* 160.05 ($M^+$+2, 4.7), 159.10 ($M^+$+1, 11.6), 158.10 ($M^+$, 100), 114.10 (14.5), 113.10 (6.2), 79.10 (3.9). IR (neat) $\nu_{max}$ 3292.86, 1432.85, 1314.25, 1156.12, 1116.58, 895.77, 824.42, 808.99, 753.10, 732.82, 696.18cm$^{-1}$.



### 6-Ethynylbenzo[b]thiophene (4)[2]

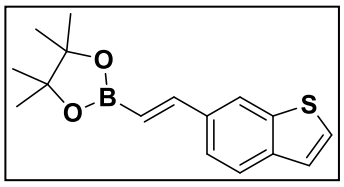
This compound was prepared following the previous procedure, but in this case replacing 5-bromobenzo[b]thiophene by 6-bromobenzo[b]thiophene. Yellow oil in 75% yield; $R_f$=0.48 (hexane); $^1$H-NMR ($CDCl_3$, 300MHz): $\delta$= 8.05 (s, 1H), 7.77 (d, *J*= 8.3 Hz, 1H), 7.52 (d, *J*=5.4 Hz, 1H), 7.49 (dd, *J*= 8.3, 1.4 Hz, 1H), 7.33 (dd, *J*= 5.4, 0.7 Hz, 1H), 3.14 (s, 1H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): $\delta$= 139.80, 139.62, 128.28, 128.02, 126.57, 123.91, 123.52, 117.99, 84.02, 77.35. MS (EI) *m/z* 160.10 ($M^+$+2, 5.1), 159.10 ($M^+$+1, 12.0), 158.10 ($M^+$, 100), 114.10 (13.5), 113.10 (6.3), 79.10 (3.8). IR (neat) $\nu_{max}$ 3297.68, 1455.03, 1385.6, 1214.93, 1080.91, 1046.19, 907.34, 823.45, 753.20, 732.78, 697.14. 663.39cm$^{-1}$.

## 4.2. (*E*)-2-(2-(Benzo[*b*]thiophen-5-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (5)[3]



The compound was prepared by adapting to our substrates a procedure of hydroboration of alkynes[4]. In an oven-dried Schlenk tube, CuCl (8.17 mg; 0.082 mmol; 0.03 eq.), NaOt-Bu (15.86 mg; 0.164 mmol; 0.06 eq.) and Xantphos ligand (47.33 mg; 0.082 mmol; 0.03 eq.) were added. After three cycles of vacuum/argon, 2.5mL of dry THF were injected and the solution was stirred for 30 minutes at room temperature. Then bis(pinacolato)diboron (1.39 g; 5.46 mmol; 2 eq.) in 1.6mL of dry THF were added, the reaction mixture being stirred for 10 minutes more at room temperature. 5-Ethynylbenzo[*b*]tiophene (431.34 mg; 2.73 mmol; 1 eq.) was then added followed by dry MeOH (218.40 µL, 5.4 mmol). The reaction mixture was stirred at room temperature until no starting material was detected by TLC (4 hours). After this time, the reaction mixture was filtered through a pad of celite and the residue was purified by column chromatography on silica gel (hexane-EtOAc 9:1) obtaining a white solid in 68% yield.

White solid; $R_f$=0.51 (hexane-EtOAc 9:1); $^1$H-NMR ($CDCl_3$, 300MHz): $\delta$= 7.88 (d, *J*=1.5 Hz, 1H), 7.83 (d, *J*=8.3 Hz, 1H), 7.58-7.46 (m, 2H), 7.44 (d, *J*=5.5 Hz, 1H), 7.33 (dd, *J*=5.5, 0.7 Hz, 1H), 6.23 (d, J=18.4 Hz, 1H), 1.33 (s, 12H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): $\delta$= 149.77, 140.37, 140.05, 134.14, 127.09, 124.27, 122.94, 122.84, 122.64, 83.48, 24.96. MS (EI) *m/z* 288.15 ($M^+$+2, 6.3), 287.15 ($M^+$+1, 19.3), 286.10 ($M^+$, 100), 285.15 ($M^+$-1, 24.7), 228.10 (7.4), 201.10 (21.8), 186.00 (95), 170.00 (74.5), 160.00 (14.9), 134.00 (14.7), 115.05 (13.1), 89.05 (5.2), 57.10 (3.9). IR (neat) $\nu_{max}$ 2977.55, 2937.41, 1693.19, 1619.91, 1430.92, 1353.78, 1322.93, 1214.93, 1137.80, 1049.09, 998.95, 971. 95, 898.67, 844.67, 798.39, 759.82, 698.11, 659.54cm$^{-1}$.



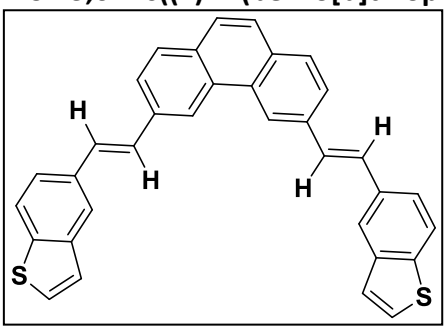
### (*E*)-2-(2-(Benzo[*b*]thiophen-6-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (6)[5]

This compound was prepared employing the previous procedure, replacing the terminal alkyne by 6-ethynylbenzo[*b*]thiophene.

Yellow oil in 83% yield; $R_f$=0.44 (hexane-EtOAc 9:1); $^1$H-NMR ($CDCl_3$, 300MHz): $\delta$= 7.94 (d, *J*=0.6 Hz, 1H), 7.77 (d, *J*=8.3 Hz, 1H), 7.55 (dd, *J*=8.1, 1.6 Hz, 1H), 7.51 (d, *J*= 18.4 Hz, 1H), 7.45 (d, *J*=5.4 Hz, 1H), 7.30 (d, *J*=5.4 Hz, 1H), 6.24 (d, *J*=18.4 Hz, 1H), 1.33 (s, 12H). $^{13}$C-NMR ($CDCl_3$, 75 MHz): $\delta$= 149.51, 140.27, 140.21, 134.07, 127.66, 123.87, 123.71, 123.06, 121.80, 83.48, 24.94. MS (EI) *m/z* 288.10 ($M^+$+2, 6.7), 287.10 ($M^+$+1, 19.3), 286.10 ($M^+$, 100), 285.15 ($M^+$-1, 24.2), 271.10 (12.6), 228.10 (5.9), 201.10 (20.9), 186.00 (82.9), 170.00 (69.3), 161.00 (15.4), 134.00 (12.5),

115.05 (11.1), 89.05 (4.6), 57.10 (3.4). IR (neat) $\nu_{max}$ 2977.55, 2927.41, 1689.34, 1619.91, 1457.92, 1346.07, 1265.07, 1207.22, 1141.65, 1041.37, 998.95, 894.81, 844.67, 813.81, 736.67, 694.25cm$^{-1}$.

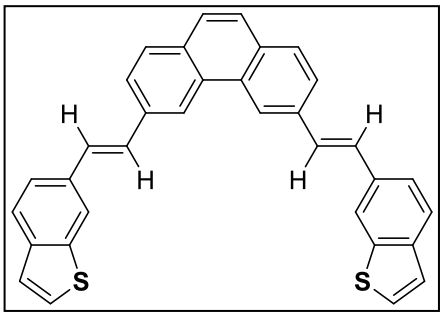
### 4.3. **3,6-Bis((*E*)-2-(benzo[*b*]thiophen-5-yl)vinyl)phenanthrene (8)**



This compound was prepared by adapting to our substrates a Suzuki coupling described in the literature[6]. In an over-dried pressure tube $PdCl_2$ (19.30 mg; 0.11 mmol; 0.20 eq.), $PPh_3$ (62.50 mg; 0.21 mmol; 0.40 eq.), $Cs_2CO_3$ (1.03 g; 3.42 mmol; 6 eq.), (E)-2-(2-(benzo[b]tiophen-5-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (524.40 mg; 1.71 mmol; 3 eq.) and 3,6-dibromophenanthrene (176.40 mg; 0.57 mmol; 1 eq.) were added. The tube was sealed with a septum and after three cycles of vacuum/argon, 3.6mL of THF and 0.4mL of $H_2O$ were added with a syringe. Then the tube was closed and heated in an oil bath at 85°C for 20 hours. An insoluble solid in suspension was observed in the tube. The insoluble solid, a greenish yellow solid, was filtered and washed with $H_2O$ and $CH_2Cl_2$ (10 mL each).

Greenish solid in 90% yield; $R_f$= 0.48 (hexane-EtOAc 9:1); $^1$H-NMR ($CDCl_3$, 400MHz): $\delta$= 8.80 (s, 2H), 8.03 (s, 2H), 7.91 (d, *J*= 8.4 Hz, 2H), 7.89 (m, 4H), 7.72 (s, 2H), 7.69 (dd, *J*= 8.4, 1.5 Hz, 2H), 7.53-7.44 (m, 6H), 7.39 (d, *J*= 5.4 Hz, 2H). MS (EI, DIP) *m/z* 496.2 ($M^+$+2, 14.33), 495.2 ($M^+$+1, 32.40), 494.2 (M+, 100), 358.2 (11.33), 247.1 (16.42). IR (neat) $\nu_{max}$ 3054.69, 1511.92, 1434.78, 1326.79, 1261.22, 1045.23, 960.37, 887.09, 840.81, 806.09, 752.10, 694.24.

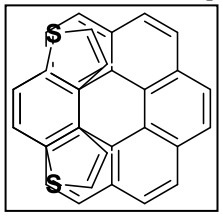
### **3,6-Bis((*E*)-2-(benzo[*b*]thiophen-6-yl)vinyl)phenanthrene (9)**



This compound was prepared following the previous procedure, but as starting reagents (*E*)-2-(2-(benzo[b]tiophen-6-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane and 3,6-dibromophenanthrene were used.

Greenish solid in 95% yield; $R_f$=0.44 (hexane-EtOAc 9:1); $^1$H-NMR ($CDCl_3$, 300MHz): $\delta$= 8.81 (s, 2H), 8.10 (s, 2H), 7.89 (s, 4H), 7.86 (d, *J*=8.3 Hz, 2H), 7.72 (s, 2H), 7.69 (dd. *J*=8.3, 1.5 Hz, 2H), 7.50-7.46 (m, 6H), 7.36 (d, *J*=4.7 Hz, 2H). MS (EI, DIP) *m/z* 496.2 ($M^+$+2, 16.33), 495.2 ($M^+$+1, 38.06), 494.2 ($M^+$, 100), 358.2 (11.64), 247.1 (16.07). IR (neat) $\nu_{max}$ 3062.41, 3023.84, 1600.63, 1392.35, 1083.80, 1041.37, 956.52, 879.38, 836.95, 752.10, 694.25.

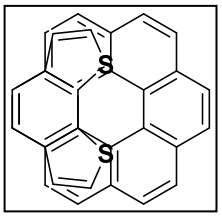
### 4.4. ***Exo*-dithia[9]helicene (1)**



The synthesis of this compound has been carried out by three photochemical methods (A, B and C) in line what was explained above (photochemistry). Method A) in three oven-dried Schlenk tubes were loaded with 3,6-bis((*E*)-2-(benzo[*b*]thiophen-5-yl)vinyl)phenanthrene (49.42 mg; 0.1 mmol; 1 eq.), KI (33.2 mg; 0.2 mmol; 2 eq.) and 200mL of benzene each. The tubes were provided with vertical condensers connected in line to a chiller. The recirculation chiller was turned on and the mixture was irradiated with a 400 W high-pressure Hg lamp for 3-4 hours under continuous reflux. Methos B) in a different procedure under inert atmosphere a suspension of 3,6-bis((*E*)-2-(benzo[*b*]thiophen-5-

yl)vinyl)phenanthrene (24.71 mg; 0.05 mmol; 1 eq.), iodine (38.07 mg; 0.15 mmol; 3 eq.), 1,2-epoxybutane (360.5 mg; 5 mmol; 100 eq.) and 100mL of benzene were placed in an oven-dried Schlenk tubes. As in the former method, the recirculation chiller was turned on and the mixture was irradiated with 400 W high-pressure Hg lamp for 3-4 hours in refluxing benzene under Ar. Method C) LED technology. In here we used the same amount of reagents a in B to compare reaction time and yields. The Schlenk tubes were safely irradiated with our LED setup overnight (12 h) at room temperature. In all cases, (A, B and C) the advance of the reaction was followed by TLC. After the reaction was completed, it was washed with aqueous $NaHSO_3$, dried over magnesium sulfate, filtered and the solvent evaporated under reduced pressure (15 Torr). The residue was purified by column chromatography on silica gel (hexane- $CH_2Cl_2$ 8:2) to obtain a greenish yellow solid. The isolated yields are: Methos A) 3-4 h, 52%. Methos B) 3-4 h, 49%. Method C) 12 h, 60%.

Greenish yellow crystals; approximated melting point 365.3℃ (DSC, with decomposition); $R_f$= 0.39 (hexane-$CH_2Cl_2$/8:2); $^1$H-NMR (Methylene chloride-$d_2$, 400MHz): $\delta$= 8.09 (s, 2H), 7.98 (d, *J*=8.1 Hz, 2H), 7.67 (d, *J*=8.2 Hz, 2H), 7.44 (dd, *J*=8.5 0.8 Hz, 2H), 7.27 (d, *J*=8.4 Hz, 2H), 7.23 (d, *J*=8.4 Hz, 2H), 7.18 (d, *J*=8.5 Hz, 2H), 6.50 (dd, *J*=5.5 0.4 Hz, 2H), 6.00 (dd, *J*=5.5 0.8 Hz, 2H). $^{13}$C-NMR (Methylene Chloride-$d_2$, 101 MHz): $\delta$= 138.23, 134.04, 132.82, 131.86, 129.93, 127.81, 127.14, 127.08, 127.02, 126.93, 126.17, 125.91, 124.96, 124.70, 122.98, 122.69, 120.56. MS (EI, DIP) *m/z* 492.1 ($M^+$+2, 14.80), 491.1 ($M^+$+1, 37.81), 490.1 ($M^+$, 100), 456.1 (12.38), 278.1 (13.31), 245.0 (10.78), 228.1 (17.32). HRMS (ESI): $M^+$ found 490.0834 $[C_{34}H_{18}S_2]^+$, requires 490.0850. IR (neat) $\nu_{max}$ 3035.41, 1465.63, 1346.07, 1315.21, 1191.79, 1157.08, 1130.08, 1091.51, 1014.37, 948.81, 883.24, 836.95, 744.39, 694.25 $cm^{-1}$.



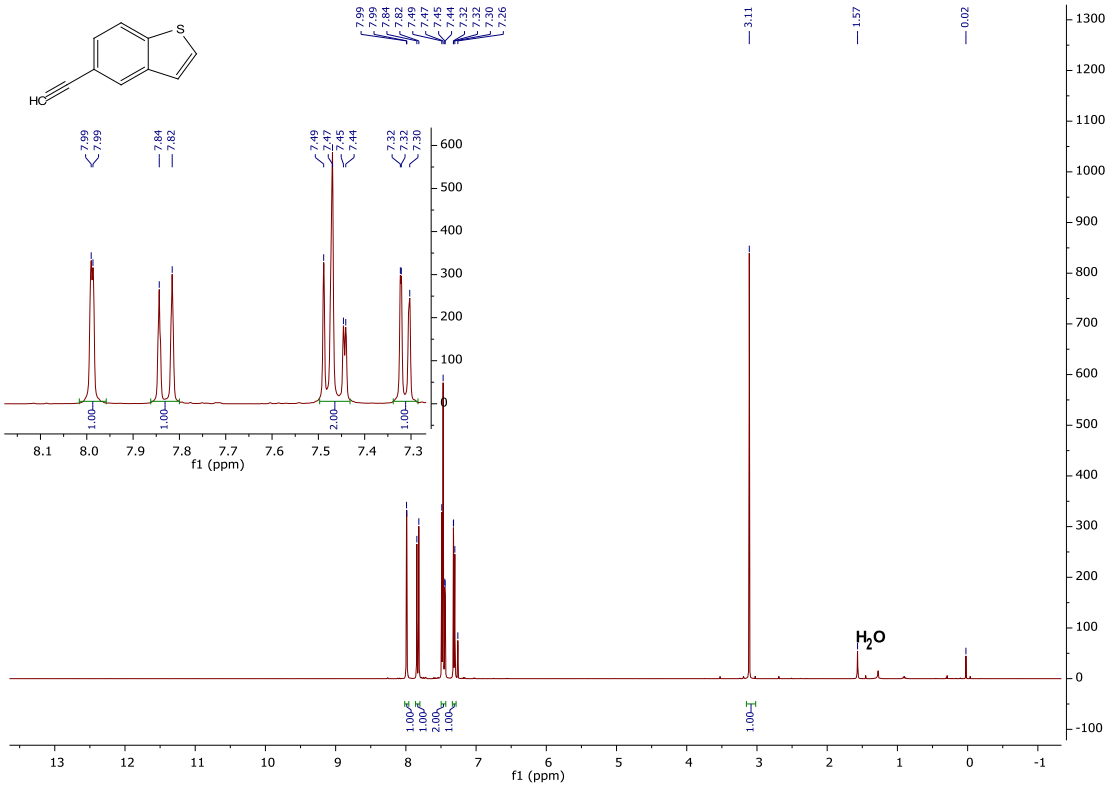

### *Endo*-dithia[9]helicene (2)

In this case a suspension of 3,6-bis((E)-2-(benzo[b]tiophen-6-yl)vinyl)phenanthrene, iodine and 1,2-epoxybutane in benzene under Ar, was irradiated following the same methodology described above for the *exo* isomer. The isolated yields are: Method B) 38%. Method C) 48%. The reaction affords only a mixture of unidentifiable products in the presence of air.

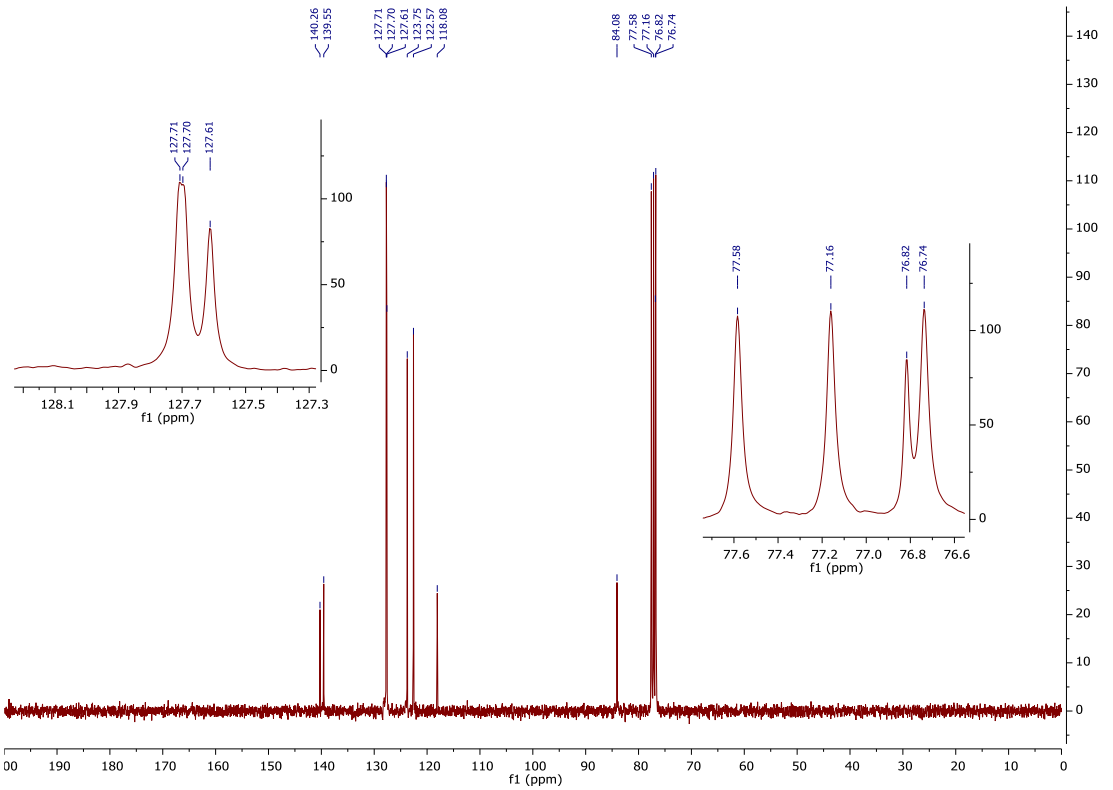
Greenish yellow crystals; approximated 332.3℃ melting point (DSC, with decomposition); $R_f$= 0.40 (Hexane-$CH_2Cl_2$/8:2); $^1$H-NMR ($CDCl_3$, 300MHz): $\delta$= 8.16 (s, 2H), 8.01 (d, *J*=8.1 Hz, 2H), 7.70 (d, *J*=8.2 Hz, 2H), 7.40 (d, *J*=8.4 Hz, 2H), 7.26 (d, *J*=8.4 Hz, 2H), 7.22-7.18 (m, 4H), 6.88 (d, *J*=5.4 Hz, 2H), 6.72 (d, *J*=5.4 Hz, 2H). $^{13}$C-NMR ($CDCl_3$, 101 MHz): $\delta$= 137.80, 134.96, 132.63, 132.38, 129.17, 127.42, 127.31, 127.07, 126.59, 126.06, 125.43, 124.74, 124.58, 124.12, 123.69, 122.12, 121.23. MS (EI, DIP) *m/z* 492.2 ($M^+$+2, 15.66), 491.2 ($M^+$+1, 39.86), 490.2 ($M^+$, 100), 443.2 (25.25), 228.1 (15.25). HRMS (ESI): $M^+$ found 490.0840 $[C_{34}H_{18}S_2]^+$, requires 490.0850. IR (neat) $\nu_{max}$ 3039.26, 1488.78, 1353.78, 1292.07, 1249.65, 1133.94, 1079.94, 948.81, 894.81, 833.10, 736.67, 701.96 $cm^{-1}$.

## 5. $^{1}$H NMR and $^{13}$C NMR spectra of compounds

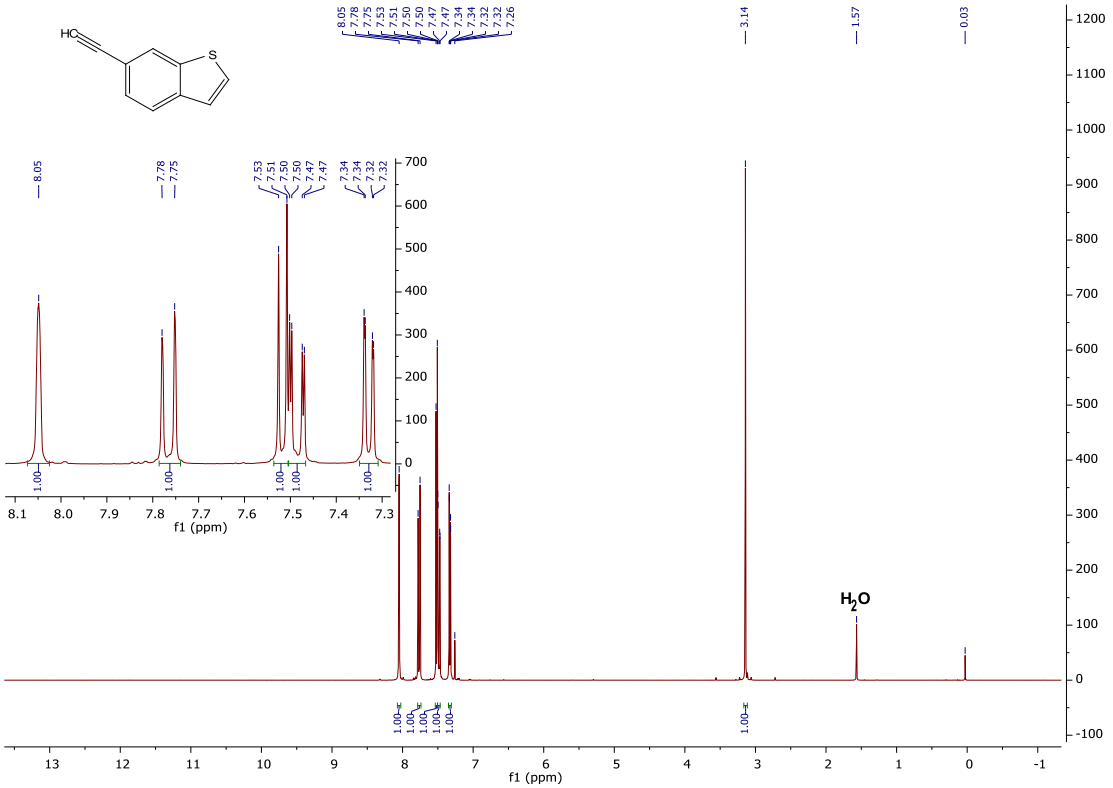
### 5.1. 5-Ethynylbenzo[*b*]tiophene (300MHz, $CDCl_3$)



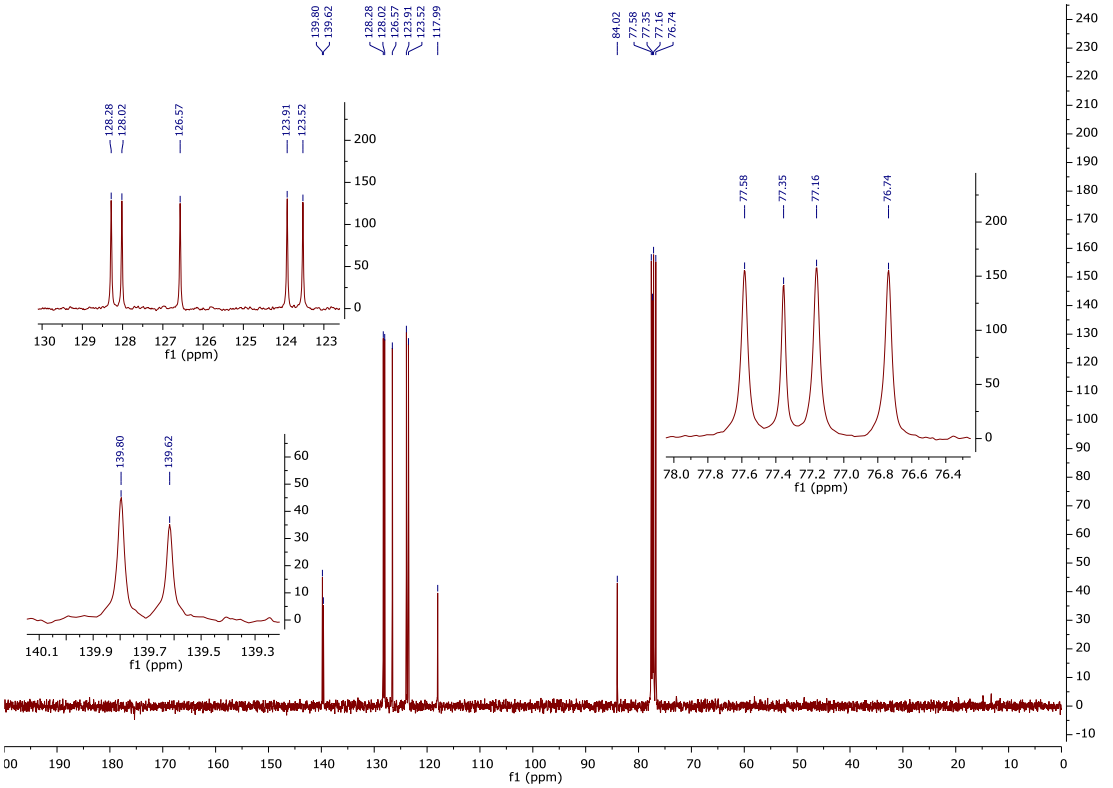

5-Ethynylbenzo[*b*]tiophene (75MHz, $CDCl_3$)



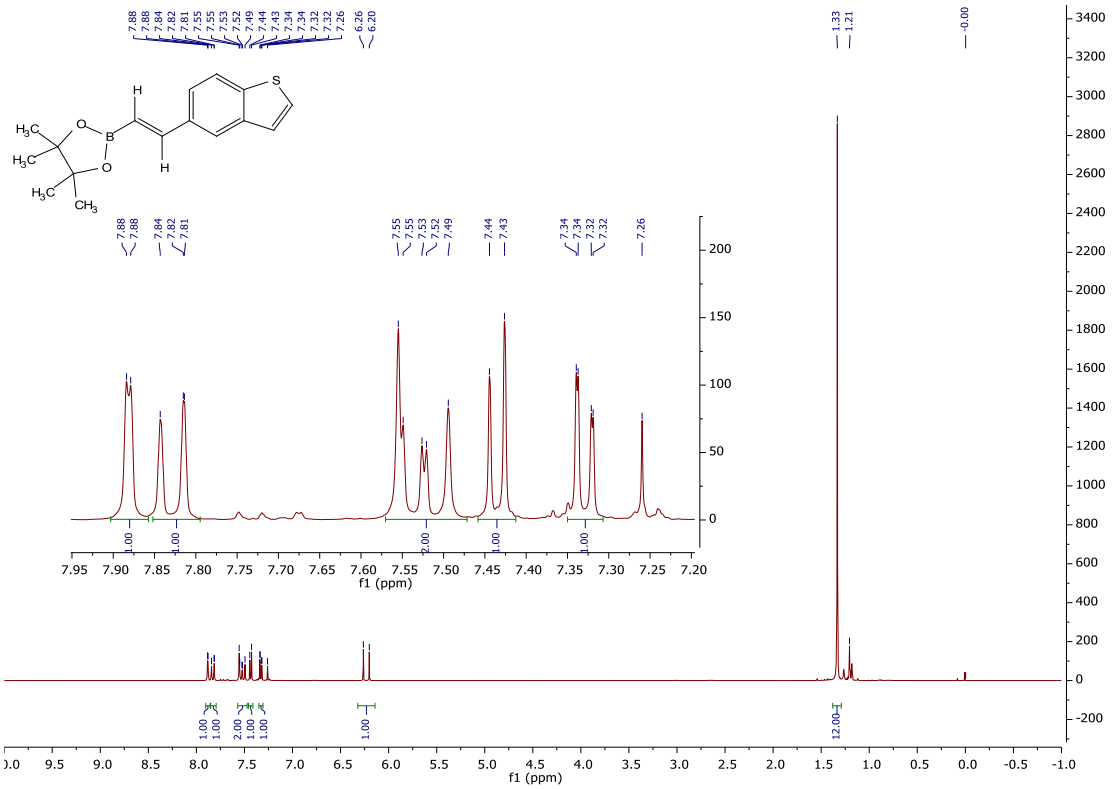
## 5.2. 6-Ethynylbenzo[*b*]tiophene (300MHz, $CDCl_3$)



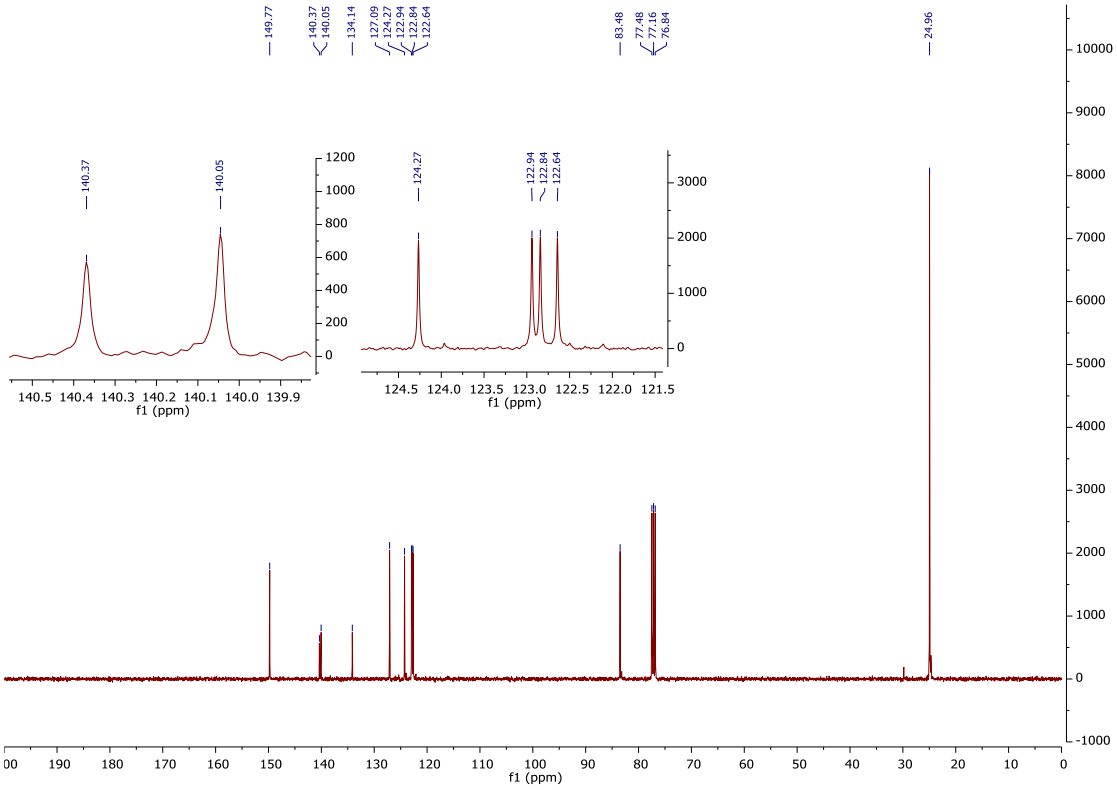

## 6-Ethynylbenzo[*b*]tiophene (75MHz, $CDCl_3$)



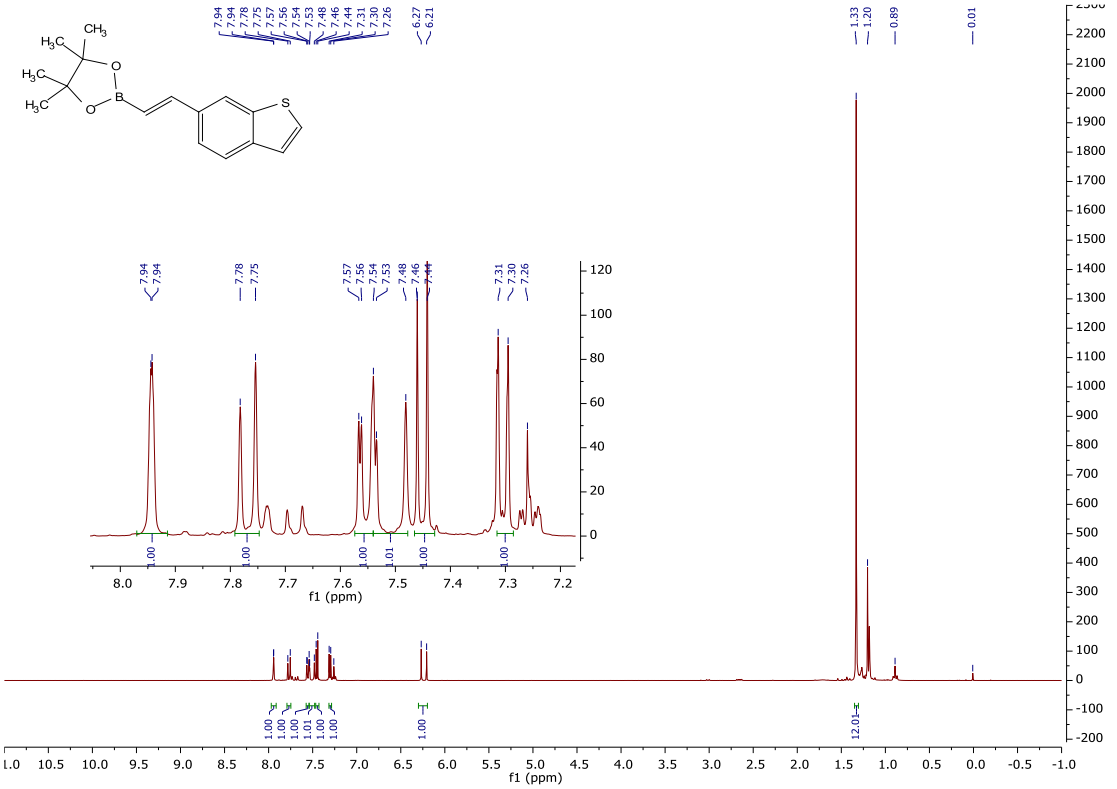
5.3. (*E*)-2-(2-(Benzo[*b*]tiophene-5-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (300MHz, $CDCl_3$)



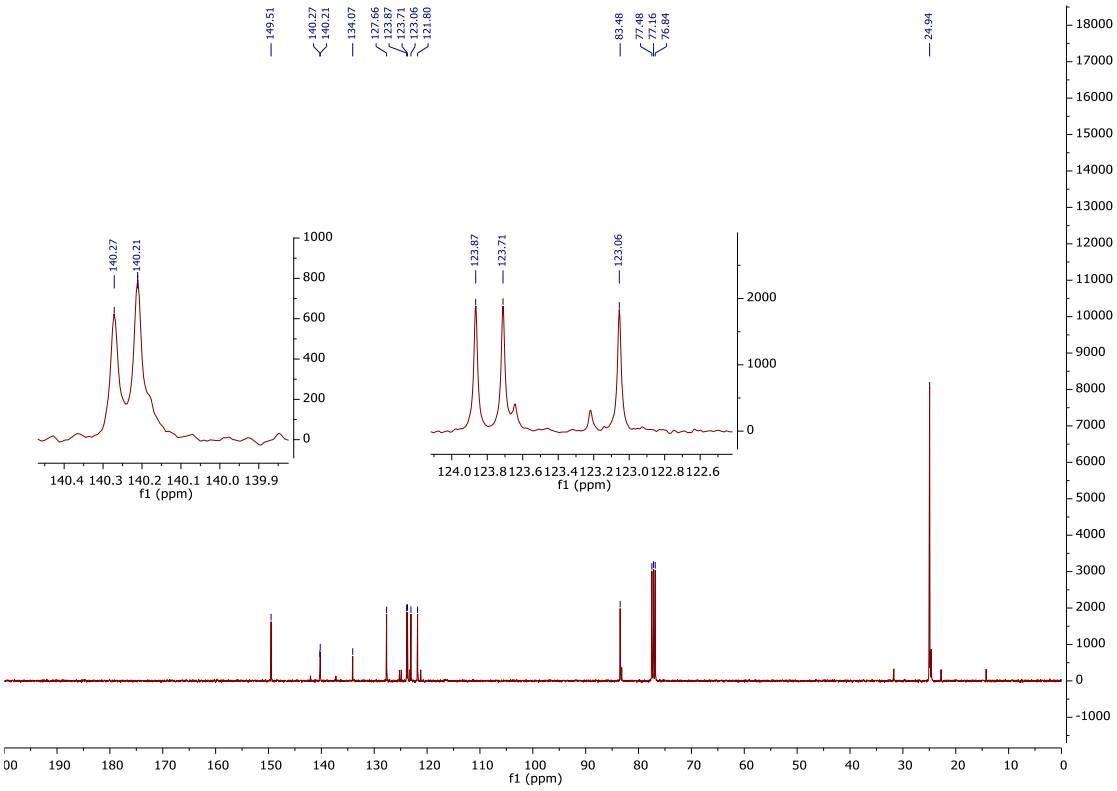

(*E*)-2-(2-(Benzo[*b*]tiophene-5-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (75MHz, $CDCl_3$)



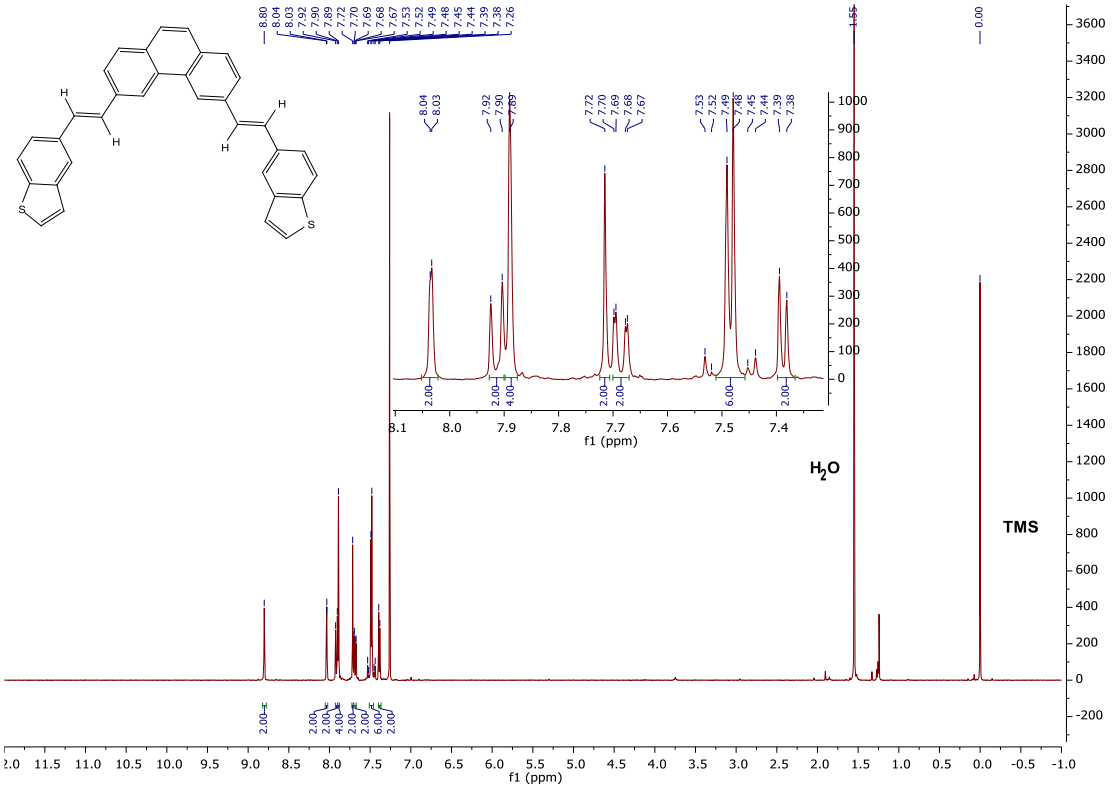
5.4. (*E*)-2-(2-(Benzo[*b*]thiophene-6-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (300MHz, $CDCl_3$)



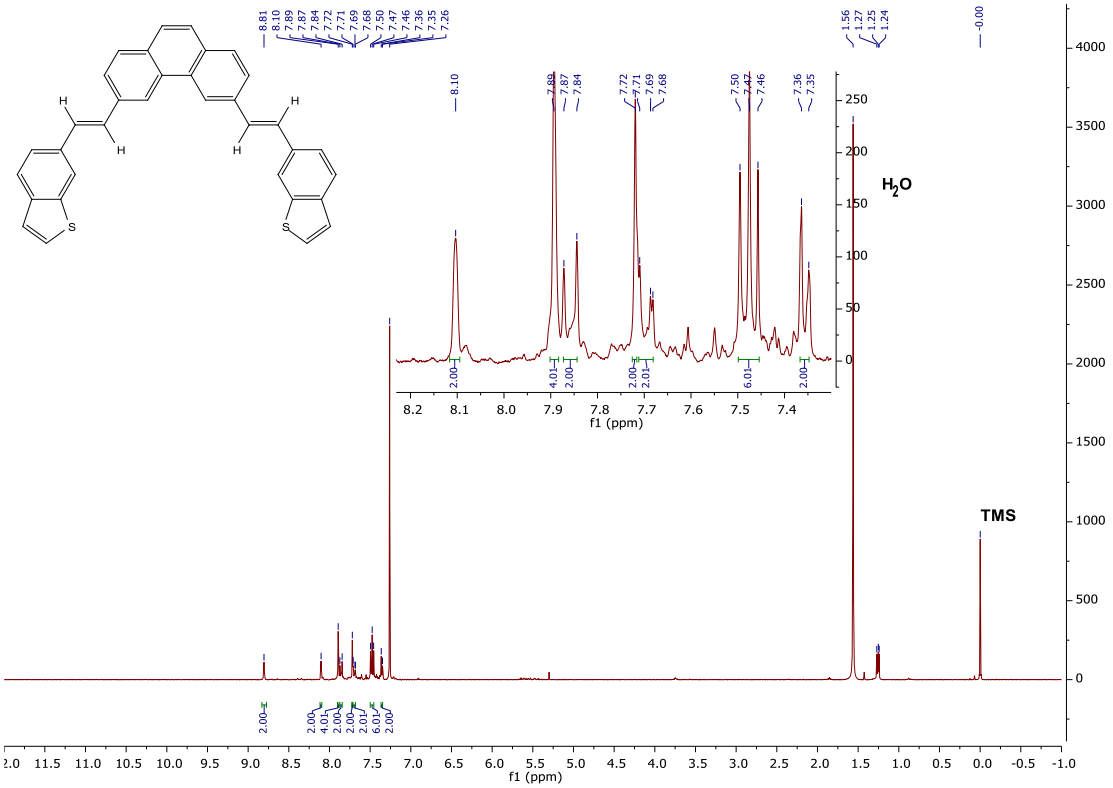
(*E*)-2-(2-(Benzo[*b*]thiophene-6-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (75MHz, $CDCl_3$)



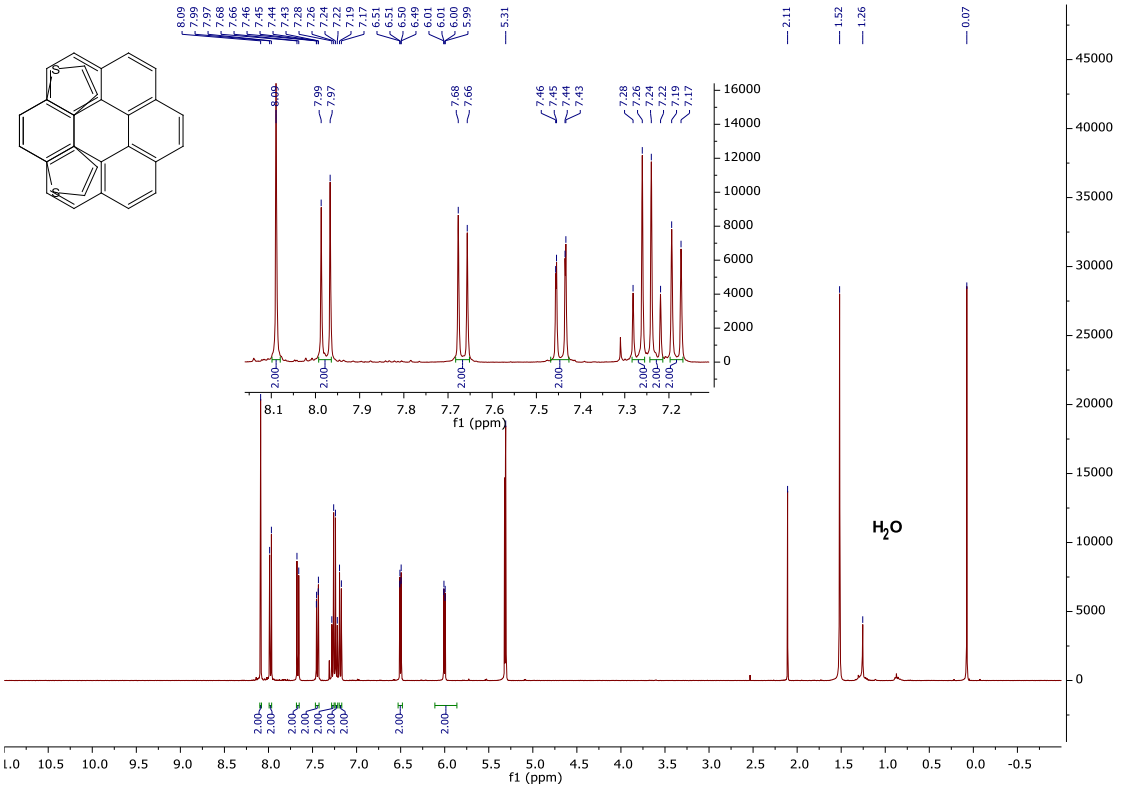
## 5.5. 3,6-Bis((*E*)-2-(benzo[*b*]tiophen-5-yl)vinyl)phenanthrene (400MHz, $CDCl_3$)



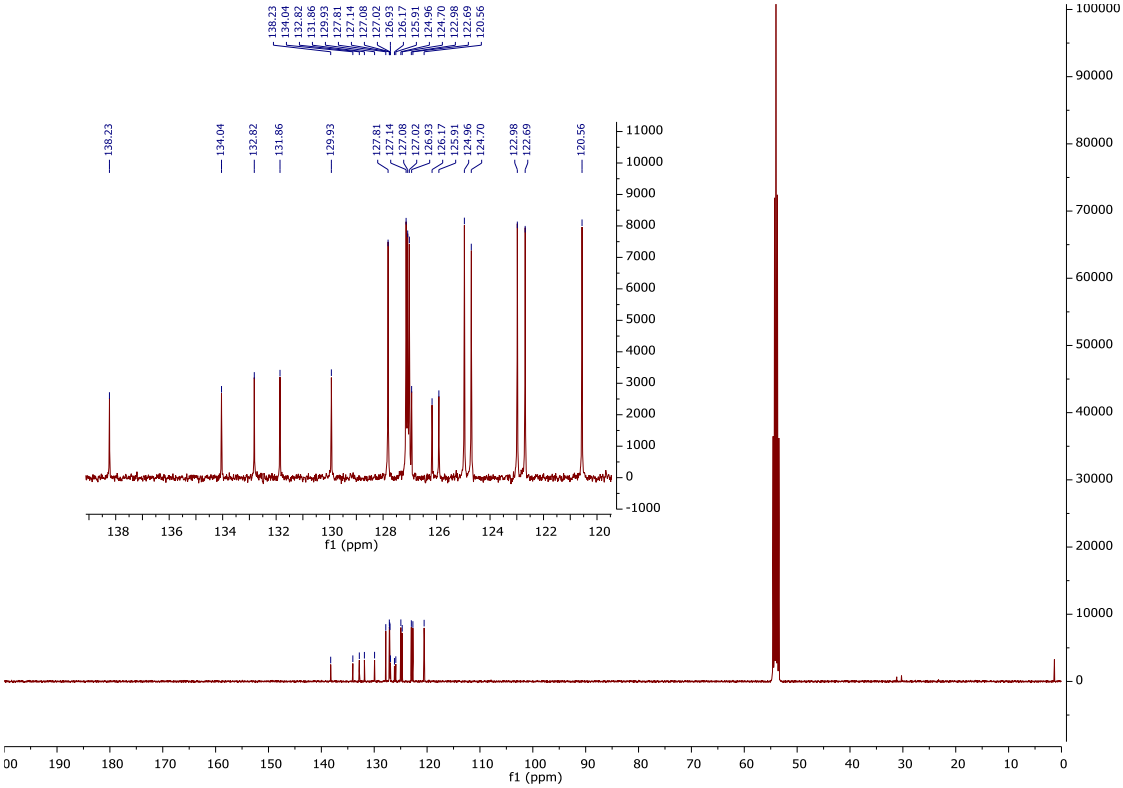

## 5.6. 3,6-Bis((*E*)-2-(benzo[*b*]tiophen-6-yl)vinyl)phenanthrene (300MHz, $CDCl_3$)



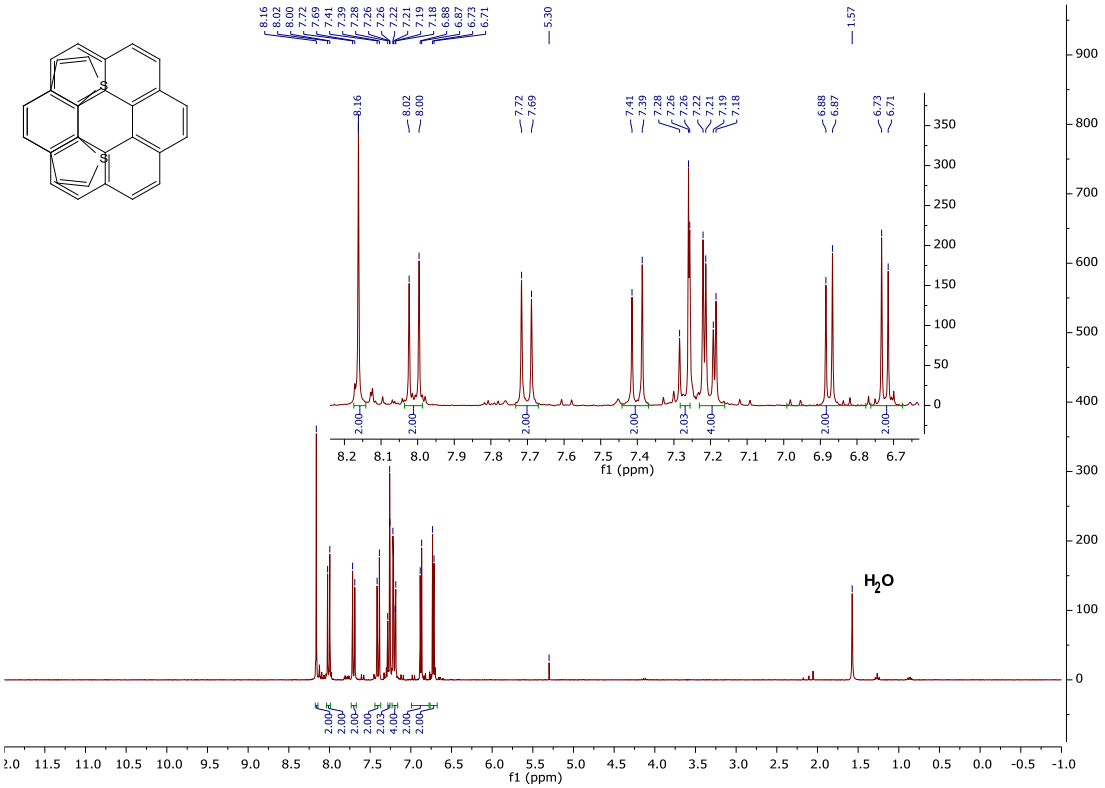
5.7. *Exo*-dithia[9]helicene (400MHz, Methylene chloride-$d_2$)



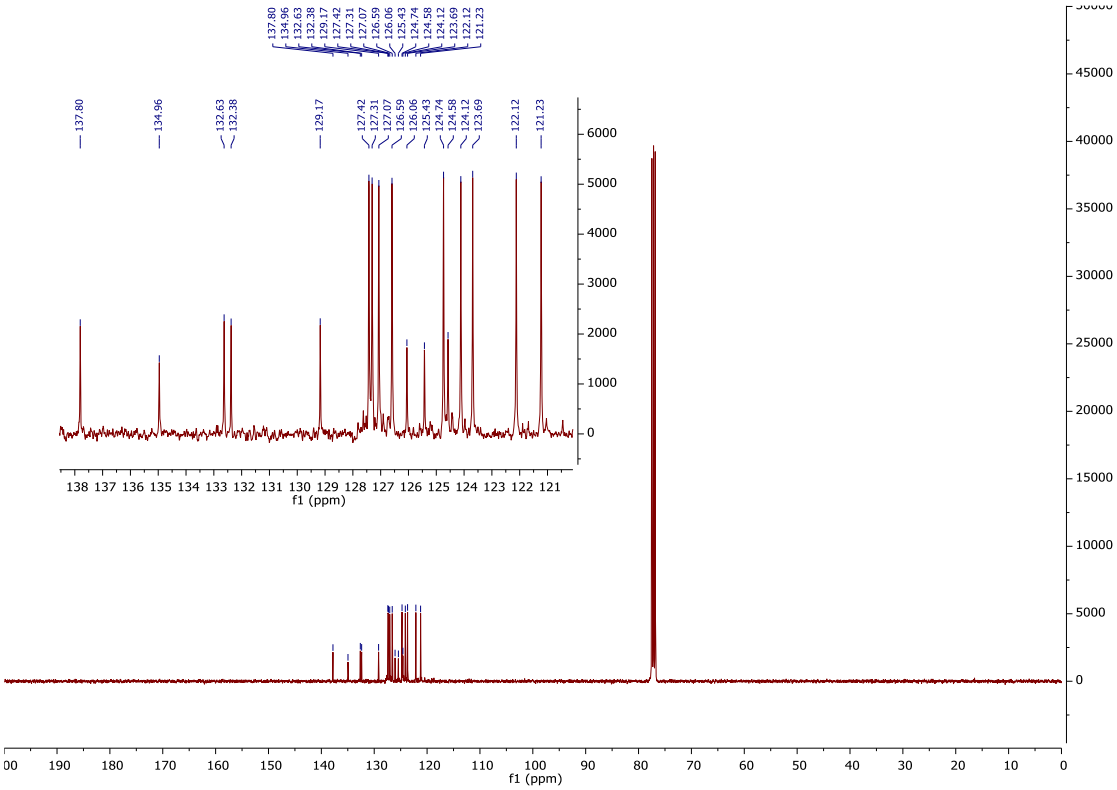

*Exo*-dithia[9]helicene (101MHz, Methylene chloride-$d_2$)



## 5.8. *Endo*-dithia[9]helicene (300MHz, $CDCl_3$)




## *Endo*-dithia[9]helicene (101MHz, $CDCl_3$)



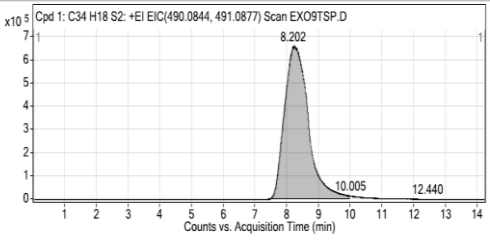
# 6. HMRS (ESI)

*Exo*-dithia[9]dithiahelicene

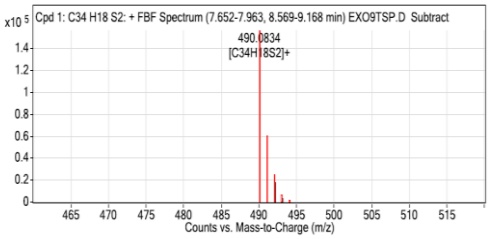
Compound Table

| Tgt Formula | Tgt Mass | Obs. Mass | Tgt Score | Mass Error (ppm) | Obs. m/z | Ret.T | Find Comp. Algorith |
|---|---|---|---|---|---|---|---|
| C34 H18 S2 | 490.085 | 490.084 | 94.03 | -2.12 | 490.0834 | 8.202 | Find By Formula |

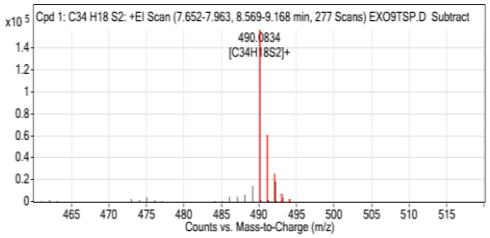
| Tgt Formula | Tgt Mass | Obs. Mass | Tgt Score | Mass error (ppm) | *Obs. m/z* | Find Cpds Algorith |
|---|---|---|---|---|---|---|
| C34 H18 S2 | 490.085 | 490.084 | 94.03 | -2.12 | 490.0834 | Find By Formula |




MS Zoomed Spectrum




## Target Compound Screening Report




MS Spectrum Peak List

| *Obs. m/z* | Charge | Abund | Formula | Ion/Isotope | Tgt Mass Error (ppm) |
|---|---|---|---|---|---|
| 490.0834 | 1 | 156467.05 | C34H18S2 | M+ | |
| 491.0864 | 1 | 53191.29 | C34H18S2 | M+ | |
| 492.0845 | 1 | 18245.49 | C34H18S2 | M+ | |
| 493.0851 | 1 | 4272.97 | C34H18S2 | M+ | |
| 494.0849 | 1 | 905.35 | C34H18S2 | M+ | |
| 495.084 | 1 | 174.7 | C34H18S2 | M+ | |
| 490.0834 | 1 | 156467.05 | C34H18S2 | M+ | 2.17 |
| 491.0864 | 1 | 53191.29 | C34H18S2 | M+ | 2.45 |
| 492.0845 | 1 | 18245.49 | C34H18S2 | M+ | 1.05 |
| 493.0851 | 1 | 4272.97 | C34H18S2 | M+ | 1.21 |
| 494.0849 | 1 | 905.35 | C34H18S2 | M+ | 0.48 |
| 495.084 | 1 | 174.7 | C34H18S2 | M+ | 2.32 |

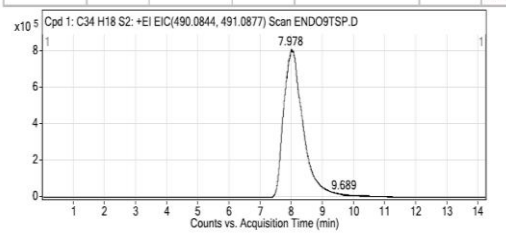
--- End Of Report ---

*Endo*- dithia[9]helicene

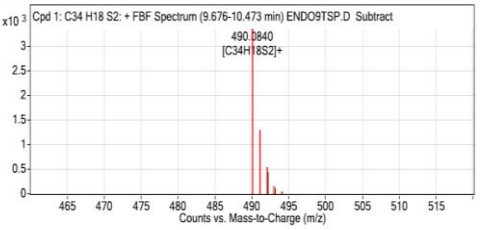
Compound Table

| Tgt Formula | Tgt Mass | Obs. Mass | Tgt Score | Mass Error (ppm) | Obs. m/z | Ret.T | Find Comp. Algorith |
|---|---|---|---|---|---|---|---|
| C34 H18 S2 | 490.085 | 490.0846 | 98.21 | -0.77 | 490.084 | 9.689 | Find By Formula |

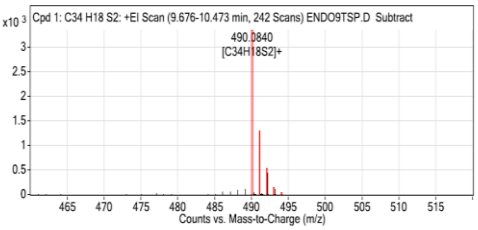
| Tgt Formula | Tgt Mass | Obs. Mass | Tgt Score | Mass error (ppm) | *Obs. m/z* | Find Cpds Algorith |
|---|---|---|---|---|---|---|
| C34 H18 S2 | 490.085 | 490.0846 | 98.21 | -0.77 | 490.084 | Find By Formula |




MS Zoomed Spectrum




## Target Compound Screening Report




MS Spectrum Peak List

| *Obs. m/z* | Charge | Abund | Formula | Ion/Isotope | Tgt Mass Error (ppm) |
|---|---|---|---|---|---|
| 490.084 | 1 | 3339.65 | C34H18S2 | M+ | |
| 491.0872 | 1 | 1190.11 | C34H18S2 | M+ | |
| 492.085 | 1 | 446.68 | C34H18S2 | M+ | |
| 493.0857 | 1 | 124.15 | C34H18S2 | M+ | |
| 494.0846 | 1 | 32.72 | C34H18S2 | M+ | |
| 490.084 | 1 | 3339.65 | C34H18S2 | M+ | 0.84 |
| 491.0872 | 1 | 1190.11 | C34H18S2 | M+ | 0.92 |
| 492.085 | 1 | 446.68 | C34H18S2 | M+ | 0 |
| 493.0857 | 1 | 124.15 | C34H18S2 | M+ | 0.06 |
| 494.0846 | 1 | 32.72 | C34H18S2 | M+ | 1.09 |

--- End Of Report ---

## 7. X-ray diffraction (XRD) analysis

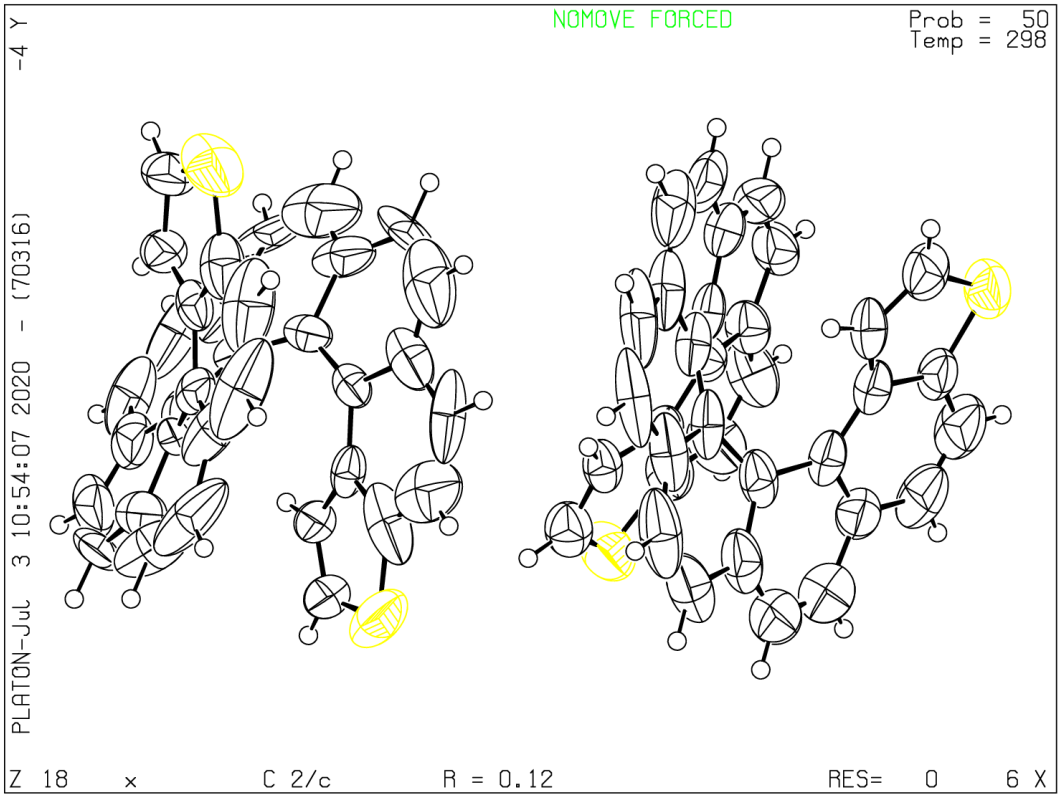
The crystals of *exo*-dithia[9]helicene-**1** and *endo*-dithia[9]helicene-**2** were analyzed using a Bruker CCD-Apex single crystal X-Ray diffraction kit equipped with an X-ray tube with Mo anode and KRYOFLEX low temperature equipment.

***Exo*-dithia[9]helicene-1**

Bond precision: C-C = 0.0176 A
Wavelength=0.71073
Cell: a=33.075(4) b=9.8984(11) c=28.178(3)
alpha=90 beta=94.890(2) gamma=90
Temperature: 298 K

| | Calculated | Reported |
|---|---|---|
| Volume | 9191.6 (18) | 9191.7 (17) |
| Space group | C 2/c | C 2/c |
| Hall group | -C 2yc | |
| Moiety formula | $C_{34}$ $H_{18}$ $S_2$ | $C_{34}$ $H_{18}$ $S_2$ |
| Sum formula | $C_{34}$ $H_{18}$ $S_2$ | $C_{34}$ $H_{18}$ $S_2$ |
| Mr | 490.60 | 490.60 |
| Dx, g $cm^{-3}$ | 1.418 | 1.418 |
| Z | 16 | 16 |
| Mu ($mm^{-1}$) | 0.255 | 0.255 |
| F 0 0 0 | 4064.0 | 4064.0 |
| F 0 0 0′ | 4069.33 | |
| h, k, l max | 39, 11, 33 | 39, 11, 33 |
| Nref | 8147 | 8132 |
| Tmin, Tmax | 0.982, 0.995 | 0.932, 0.995 |
| Tmin′ | 0.912 | |

Correction method= # Reported T Limits: Tmin=0.932 Tmax=0.995
AbsCorr = MULTI-SCAN
Data completeness= 0.998 Theta(max)= 25.050
R(reflections)= 0.1173( 3653) wR2(reflections)= 0.3000( 8132)
S = 1.021 Npar= 649




Comments to the checkCIF/Platon Exo-dithia[9]helicene-1: deposition number 2184340.
Associated files: x_finalfile001.cif and a380.fcf
**a380**

Level A

**PLAT234** Large Hirshfeld Difference C5 --C6. 0.41 Å.

Response: The most probable cause in here is dynamic disorder along with a limited quality of the crystal. The structure was determined at room temperature, as a low temperature setup was not operative in our facilities. Analysis done considering higher symmetry groups or potential twinning did not afford better results, as neither did several attempts to recrystallize the compound under different conditions. Substitutional disorder or misassignment of atom positions are not the causes for this, nor has the structure been over-refined.

Level B. Response: The same arguments stated above apply in here.

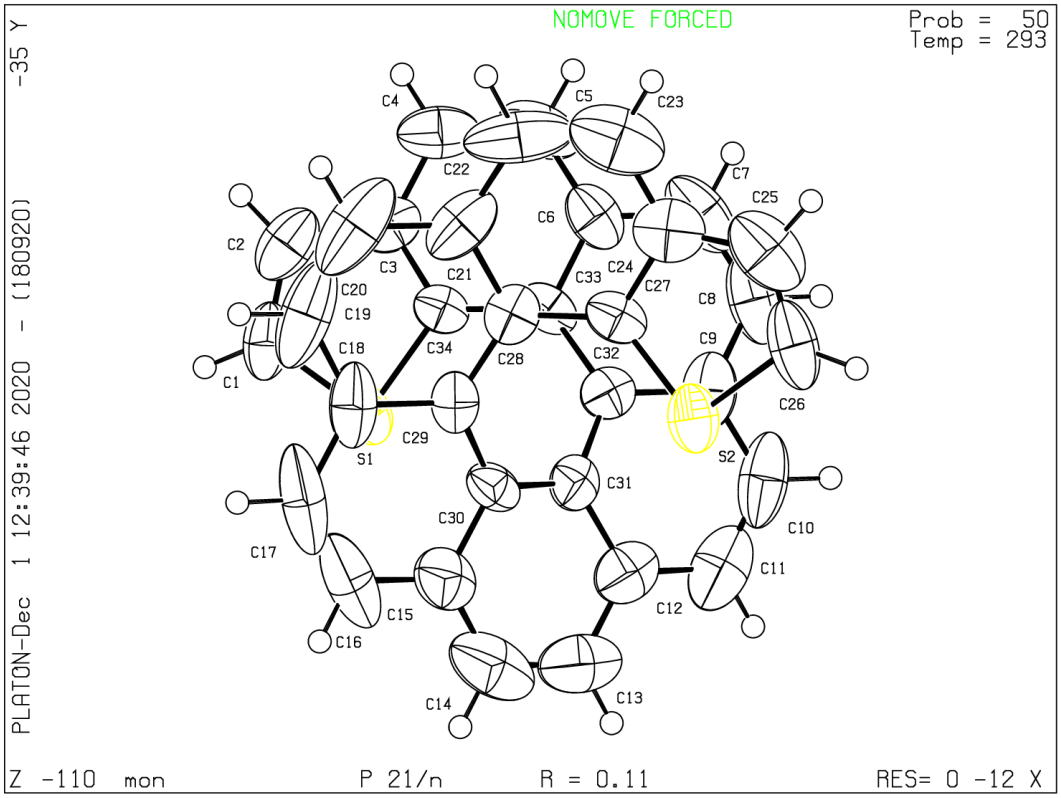
***Endo*-dithia[9]helicene-2**

```
Bond precision: C-C = 0.0140 A
Wavelength=0.71073
Cell: a=9.712(2) b=9.709(3) c=25.072(6)
      alpha=90 beta=94.401(7) gamma=90
Temperature: 293 K
```

| | Calculated | Reported |
|---|---|---|
| Volume | 2357.2 (10) | 2357.2 (10) |

| | | |
|---|---|---|
| Space group | P 21/n | P 21/n |
| Hall group | -P 2yn | |
| Moiety formula | $C_{34}$ $H_{18}$ $S_2$ | $C_{34}$ $H_{18}$ $S_2$ |
| Sum formula | $C_{34}$ $H_{18}$ $S_2$ | $C_{34}$ $H_{18}$ $S_2$ |
| Mr | 490.60 | 490.60 |
| Dx, g $cm^{-3}$ | 1.382 | 1.382 |
| Z | 4 | 4 |
| Mu ($mm^{-1}$) | 0.249 | 0.249 |
| F 0 0 0 | 1016.0 | 1016.0 |
| F 0 0 0' | 1017.33 | |
| h, k, l max | 11, 11, 29 | 11, 11, 29 |
| Nref | 4203 | 4193 |
| Tmin, Tmax | 0.905, 0.995 | 0.526, 0.995 |
| Tmin' | 0.905 | |

Correction method= # Reported T Limits: Tmin=0.526 Tmax=0.995
AbsCorr = MULTI-SCAN
Data completeness= 0.998 Theta(max)= 25.110
R(reflections)= 0.1078( 1054) wR2(reflections)= 0.1439( 4193)
S = 0.686 Npar= 325




Comments to the checkCIF/Platon Endo-dithia[9]helicene-2: deposition number 2184341.
Associated files: mon_final003.cif and a387.fcf
**a387**

**RINTA01** The value of Rint is greater than 0.25

Response: The overall quality of the data may be somewhat low because the crystal diffracts only weakly in one of its dimensions. Unfortunately, attempts to obtain better quality crystals

by recrystallizing the compound under different conditions (T/solvent) did not afford better quality data. The structure was determined at room temperature, as a low temperature setup was not operative in our facilities.

**PLAT020** The Value of Rint is Greater Than 0.12 ..... 0.446 Report

Response: Similar arguments to those described before apply in here.

**PLAT026** Ratio Observed / Unique Reflections (too) Low .. 25% Check

Response: Again, a poor diffraction in one of the directions of the crystal may be responsible for this issue. Unfortunately, it could not be solved using different crystals obtained under different conditions of recrystallization, which afforded similar data.

Level B. Response: The same arguments stated above apply in here.

## 8. List of possible isomeric structures in the synthesis of *exo*-1 and *endo*-2

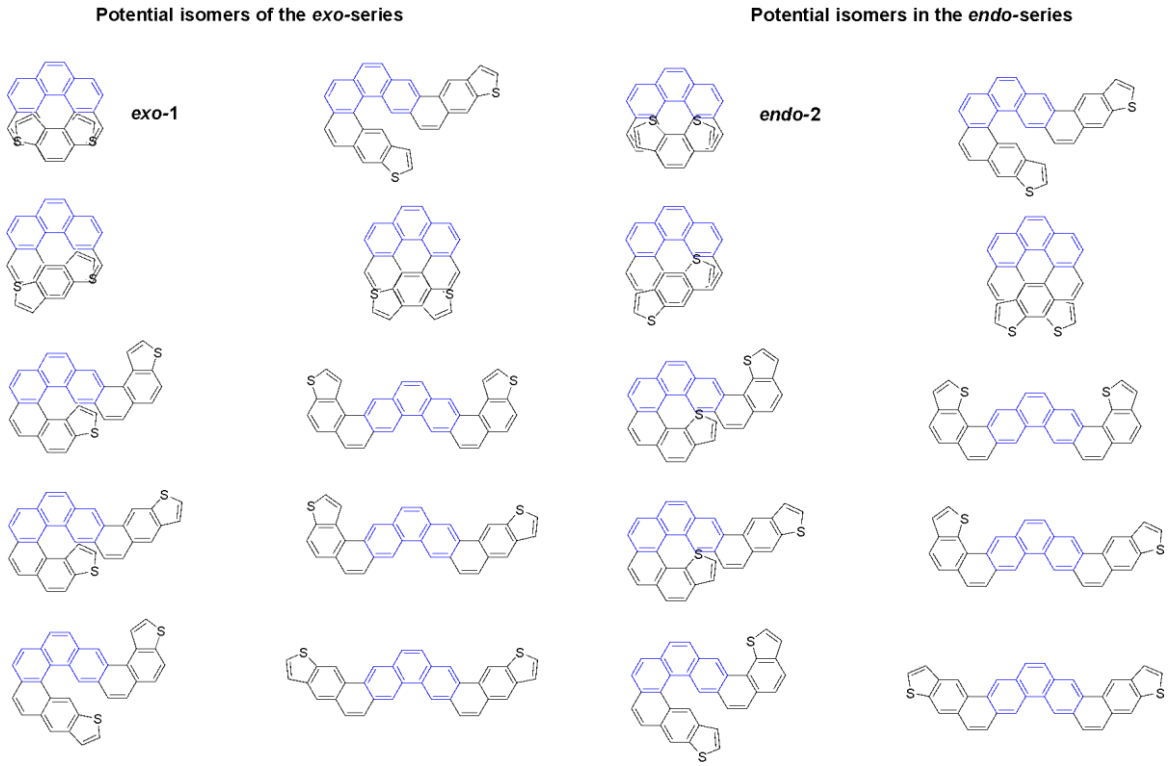


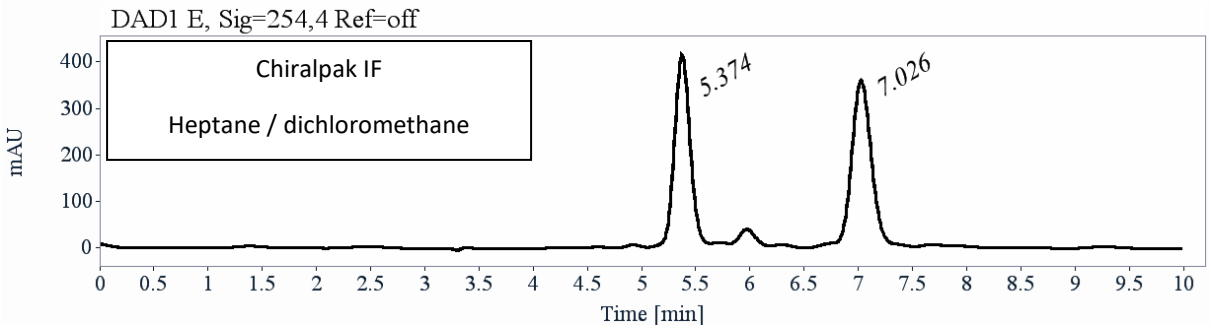

Figure S1. The 10 possible isomers of the *exo* and *endo* series

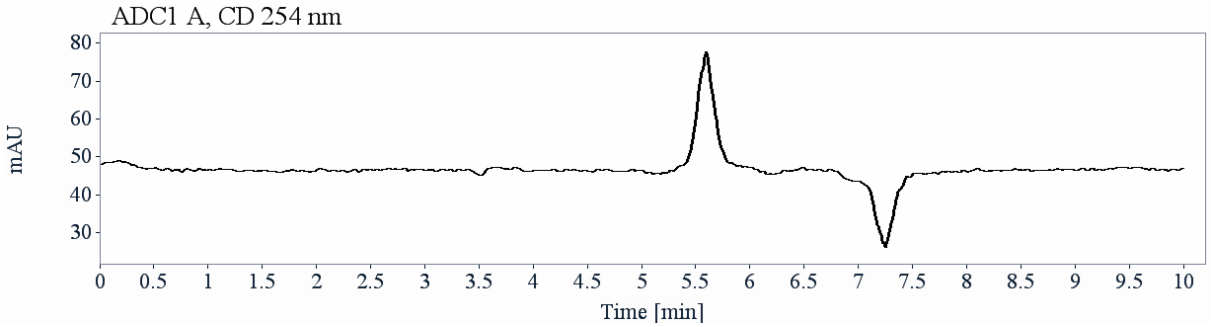
## 9. HPLC separations

Analytical chiral HPLC separation for compound **1**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with a UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

| Column | Mobile Phase | t1 | k1 | t2 | k2 | α | Rs |
|---|---|---|---|---|---|---|---|
| **Chiralpak IF** | Heptane / dichloromethane (70/30) | 5.37 (+) | 0.82 | 7.03 (-) | 1.38 | 1.68 | 5.61 |




| RT [min] | Area | Area% | Capacity Factor | Enantioselectivity | Resolution (USP) |
|---|---|---|---|---|---|
| 5.37 | 4079 | 48.54 | 0.82 | | |
| 7.03 | 4324 | 51.46 | 1.38 | 1.68 | 5.61 |
| Sum | 8402 | 100.00 | | | |

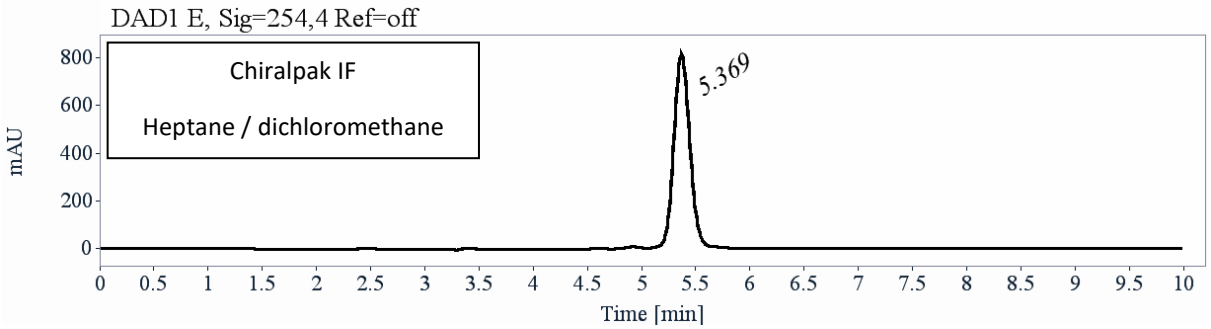
<u>Preparative separation for compound **1**:</u>

• Sample preparation: About 40 mg of compound **1** were dissolved in 11 mL of dichloromethane.

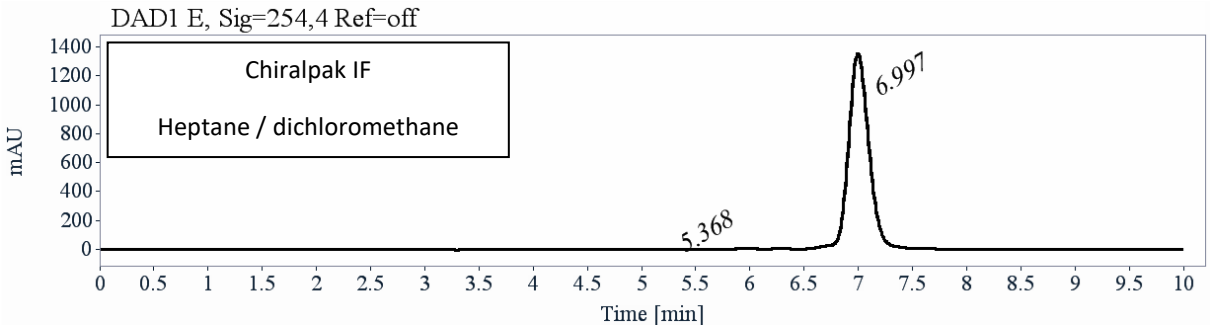
• Chromatographic conditions: Chiralpak IF (250 x 4.6 mm), hexane / dichloromethane (70/30) as mobile phase, flow-rate = 1 mL/min, UV detection at 254 nm.

• Injections (stacked): 74 times 150 µL, every 8.4 minutes.

• First fraction: 12 mg of the first eluted with ee > 99.5 %



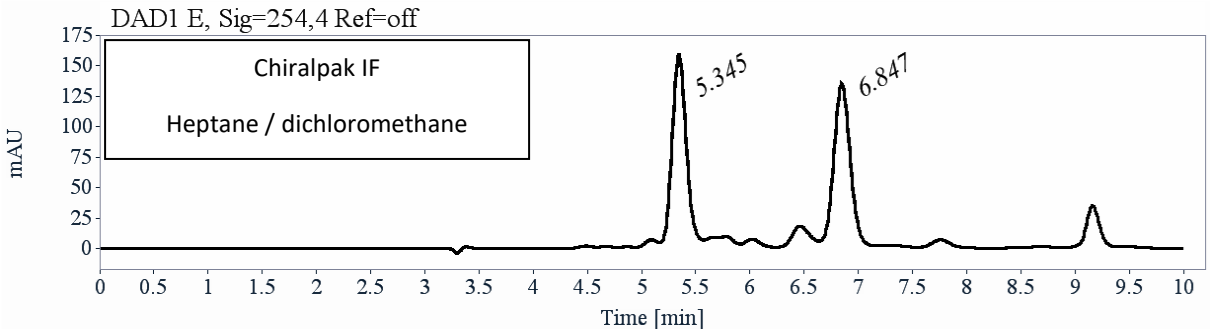
• Second fraction: 14 mg of the second eluted with ee > 99.5 %

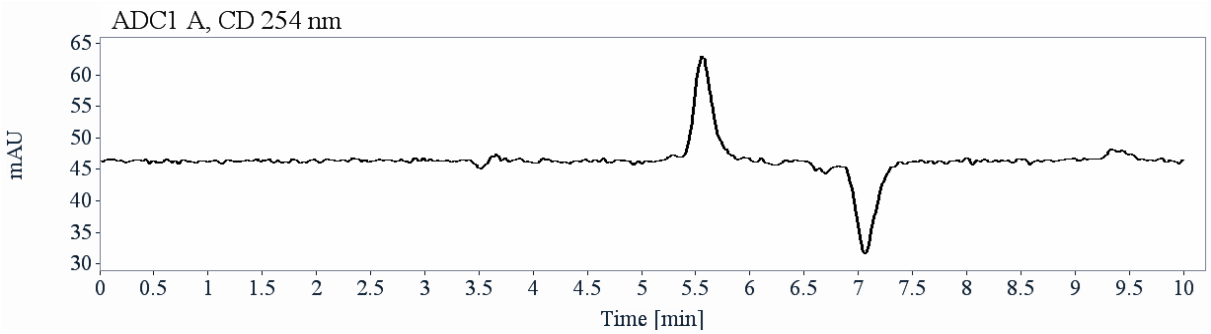



Analytical chiral HPLC separation for compound **2**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with a UV detector at 254 nm and a circular dichroism detector at 254nm. The flow-rate is 1 mL/min.

| Column | Mobile Phase | t1 | k1 | t2 | k2 | α | Rs |
|---|---|---|---|---|---|---|---|
| **Chiralpak IF** | Heptane / dichloromethane (70/30) | 5.34 (+) | 0.81 | 6.85 (-) | 1.32 | 1.63 | 5.95 |



| RT [min] | Area | Area% | Capacity Factor | Enantioselectivity | Resolution (USP) |
|---|---|---|---|---|---|
| 5.34 | 1344 | 50.17 | 0.81 | | |
| 6.85 | 1335 | 49.83 | 1.32 | 1.63 | 5.95 |
| Sum | 2678 | 100.00 | | | |

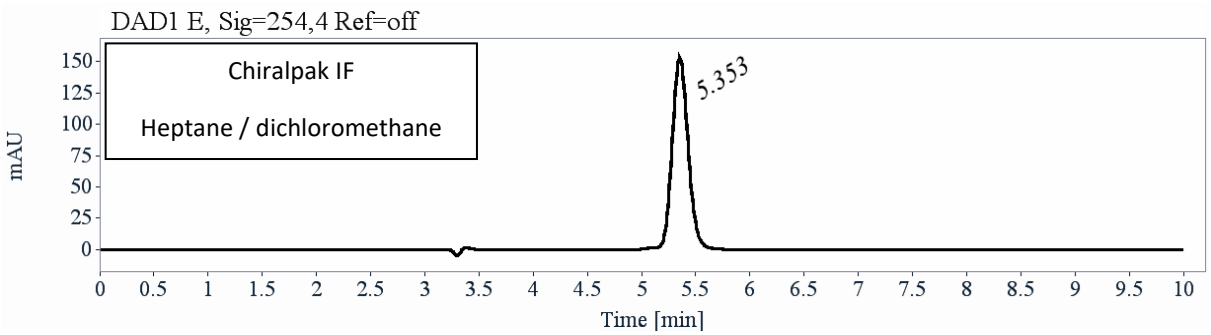
Preparative separation for compound **2**:

• Sample preparation: About 16 mg of compound **2** were dissolved in 4 mL of a mixture of dichloromethane and hexane (50/50).

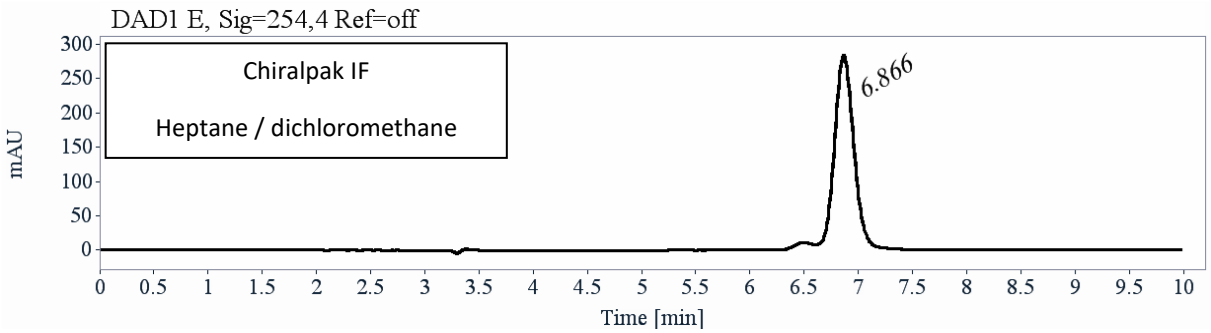
• Chromatographic conditions: Chiralpak IF (250 x 4.6 mm), hexane / dichloromethane (70/30) as mobile phase, flow-rate = 1 mL/min, UV detection at 254 nm.

• Injections (stacked): 20 times 200 μL, every 8.4 minutes.

• First fraction: 2.5 mg of the first eluted with ee > 99.5 %



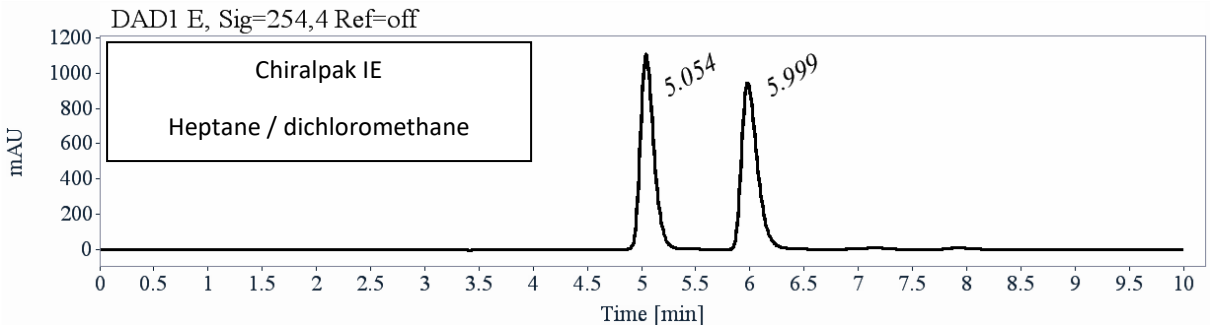

• Second fraction: 3.3 mg of the second eluted with ee > 99.5 %




Analytical chiral HPLC separation for compound **10**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with a UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

| Column | Mobile Phase | t1 | k1 | t2 | k2 | α | Rs |
|---|---|---|---|---|---|---|---|
| **Chiralpak IE** | Heptane / dichloromethane (70/30) | 5.05 | 0.71 | 6 | 1.03 | 1.45 | 3.85 |



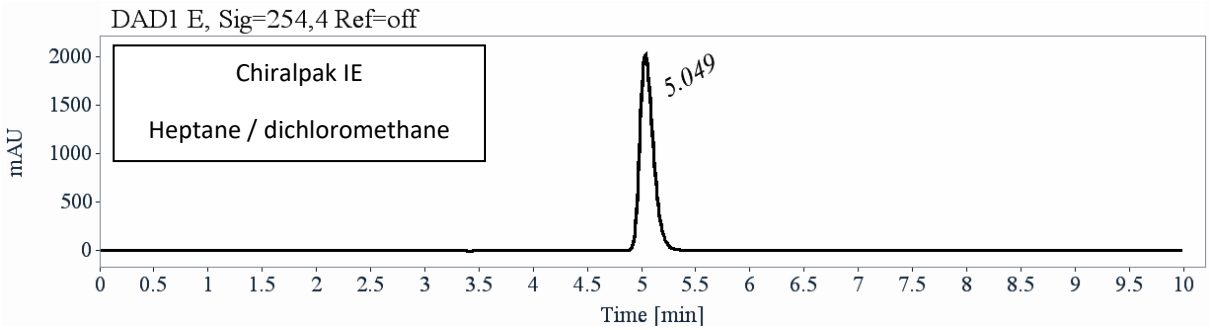

| RT [min] | Area | Area% | Capacity Factor | Enantioselectivity | Resolution (USP) |
|---|---|---|---|---|---|
| 5.05 | 9627 | 50.00 | 0.71 | | |
| 6.00 | 9627 | 50.00 | 1.03 | 1.45 | 3.85 |
| Sum | 19254 | 100.00 | | | |

• Sample preparation: About 90 mg of compound **10** were dissolved in 4.25 mL of dichloromethane.

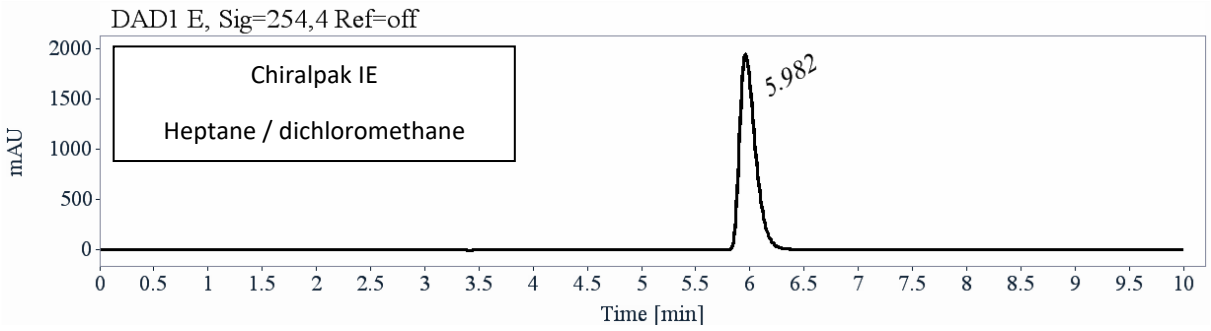
• Chromatographic conditions: Chiralpak IE (250 x 10 mm), hexane / dichloromethane (70/30) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections (stacked): 85 times 50 μL, every 6.7 minutes.

• First fraction: 40 mg of the first eluted with ee > 99.5 %



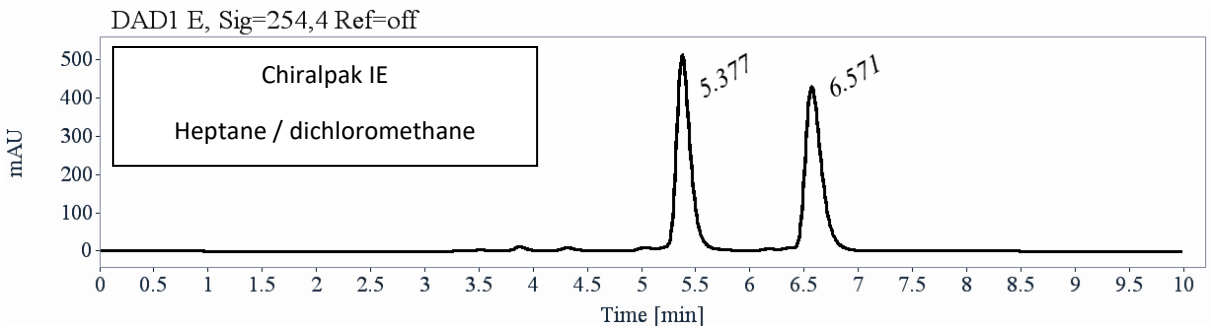

• Second fraction: 40 mg of the second eluted with ee > 99.5 %

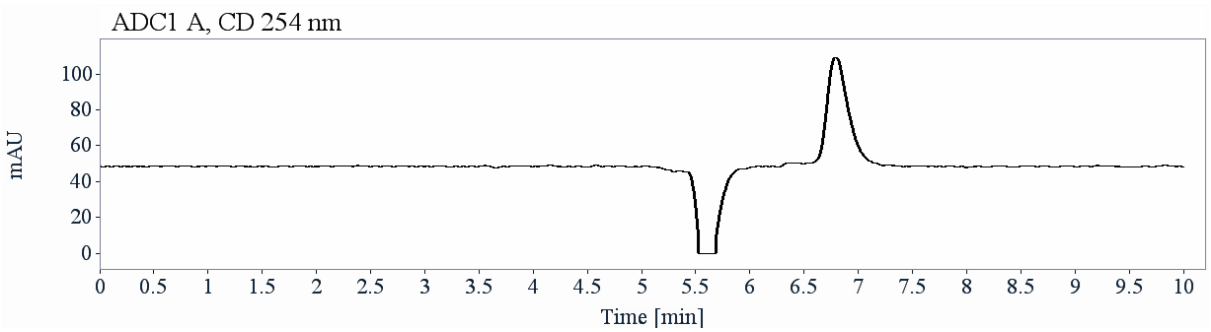


Analytical chiral HPLC separation for compound **11**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with a UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

| Column | Mobile Phase | t1 | k1 | t2 | k2 | α | Rs |
|---|---|---|---|---|---|---|---|
| **Chiralpak IE** | Heptane / dichloromethane (70/30) | 5.38 (-) | 0.82 | 6.57 (+) | 1.23 | 1.49 | 4.79 |




| RT [min] | Area | Area% | Capacity Factor | Enantioselectivity | Resolution (USP) |
|---|---|---|---|---|---|
| 5.38 | 4446 | 49.95 | 0.82 | | |
| 6.57 | 4455 | 50.05 | 1.23 | 1.49 | 4.79 |
| Sum | 8900 | 100.00 | | | |

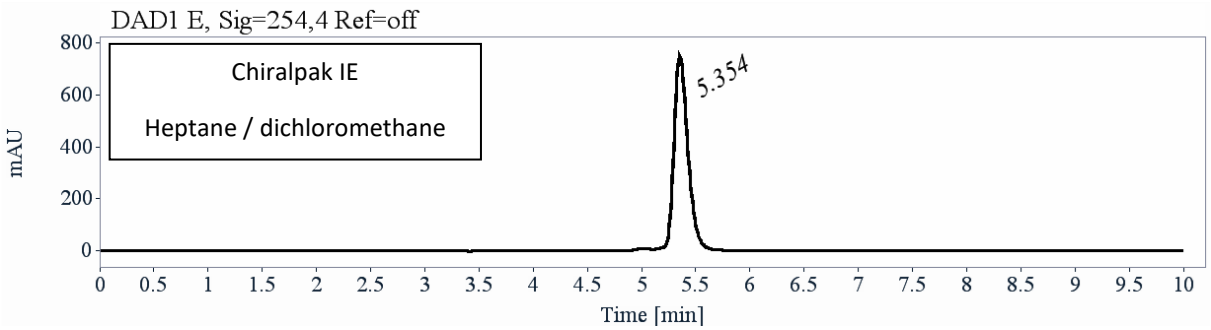
Preparative separation for compound **11**:

• Sample preparation: About 24 mg of compound **Endo-S2-H7** were dissolved in 5.2 mL of dichloromethane.

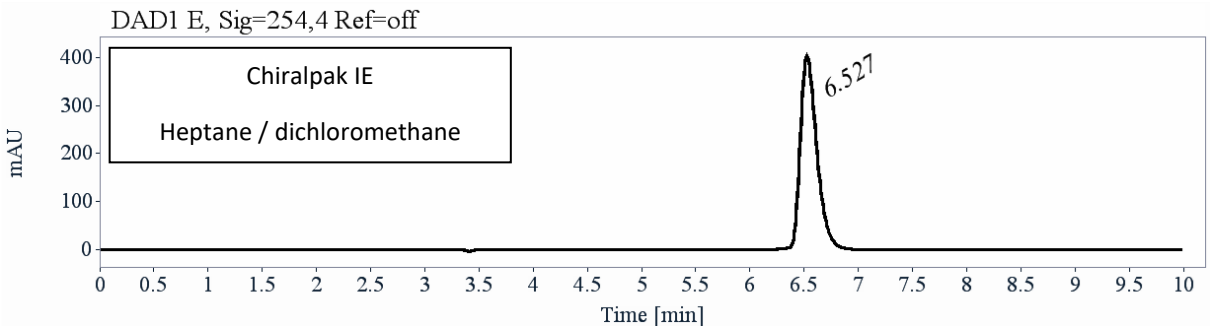
• Chromatographic conditions: Chiralpak IE (250 x 10 mm), hexane / dichloromethane (70/30) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections (stacked): 35 times 150 μL, every 7.5 minutes.

• First fraction: 5 mg of the first eluted with ee > 99.5 %




• Second fraction: 5 mg of the second eluted with ee > 99.5 %



# 10. Photophysical and chiroptical studies

## 10.1. CD and CPL measurements

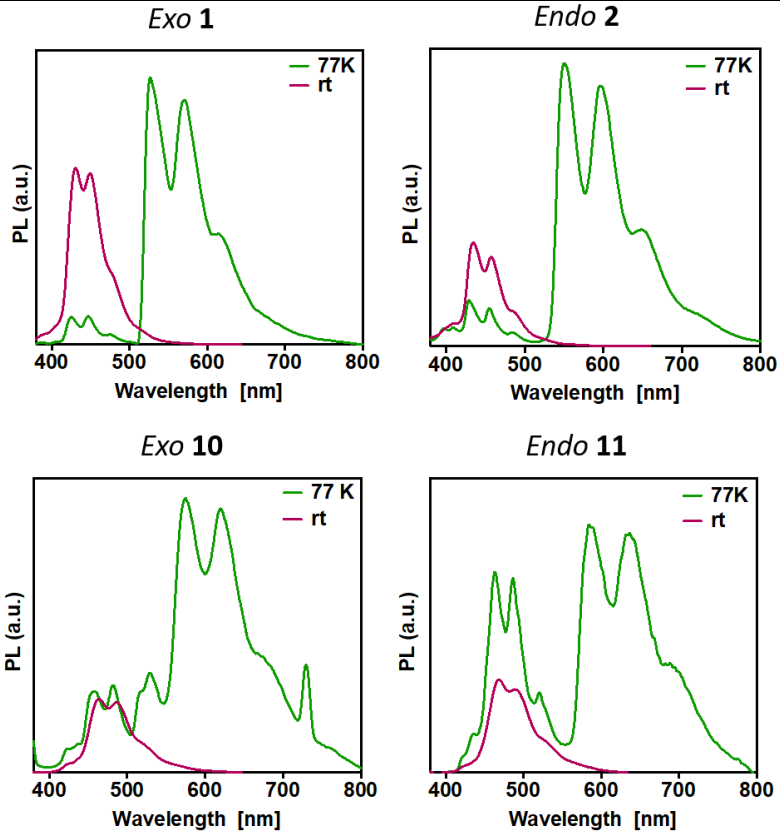



Figure S2-1 Room and low temperature emission spectra of compounds **1**,**2** and **10**,**11** (MeTHF, C = $10^{-5}$ M).

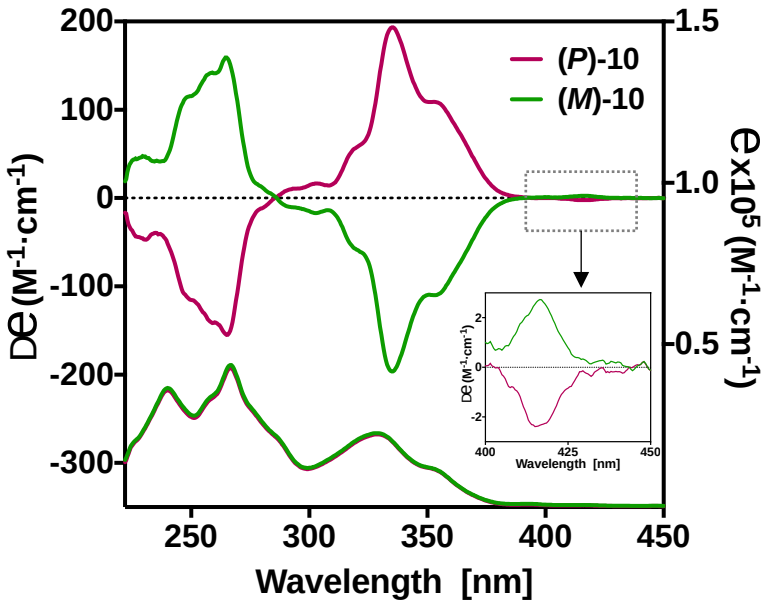



Figure S2-2 Experimental UV-vis (bottom) and ECD (top) spectra (*P*) and (*M*)-**10**; inset: magnified view of the 400-450 nm region.

## 11. Scanning Tunneling Microscopy (STM)

For general information and description of the methods used in STM imaging, refer to reference 14 in the main text. Additional graphic material is shown below.

Supplemental graphic material by STM

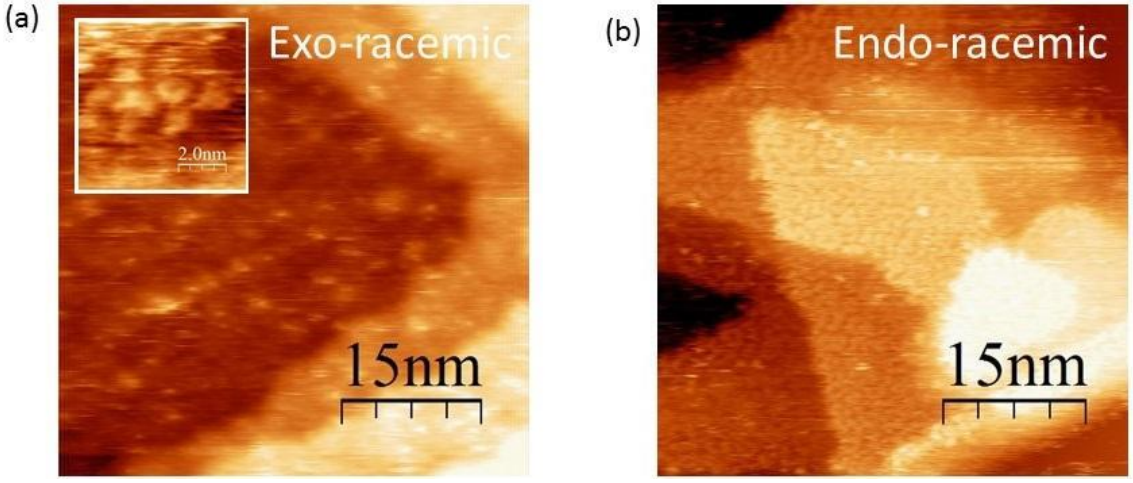



Figure S3. STM image of both topologies (a) *exo*- and (b) *endo*- dithia[9]helicenes racemic in benzene solution (in a concentration of 0.25 mg·ml$^{-1}$) on (111)gold substrates deposited via drop casting. Set parameters are $V_{bias}$= 0.5 V and $I_t$=0.1×10$^{-9}$ A for both panels whereas for the inset image are $V_{bias}$= 0.4 V and $I_t$=0.1×10$^{-9}$ A. No order is observed in either panel. Inset of panel (a) shows a zoom in of single molecules on gold substrates.

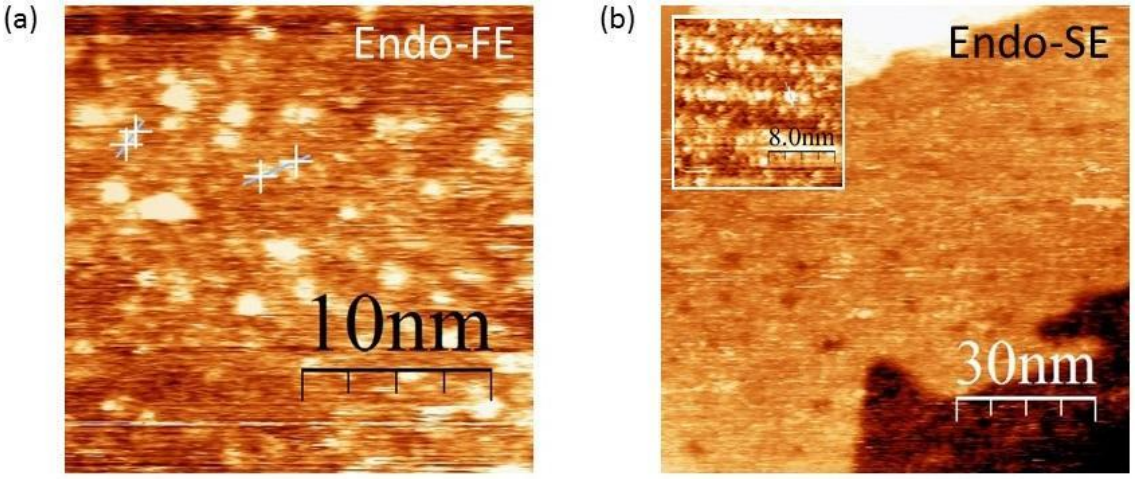



Figure S4. Topographic images of pure enantiomers of *endo*-dithia[9]helicene. Panel (a) shows the FE (firs eluted = (+)-*P*) and (b) the SE (second eluted = (−)-*M*) enantiomer. Set parameters for panel (a) are $V_{bias}$= -1.5 V and $I_t$=0.1×10$^{-9}$ A and for (b), $V_{bias}$= 0.9 V and $I_t$=0.1×10$^{-9}$ A. Inset of panel (b) shows the molecular distribution along the herringbone of the gold structure. For the inset case, the set parameters are $V_{bias}$= 1.3 V and $I_t$=0.03×10$^{-9}$ A.

# Section S2: Theoretical part

## 1. Computational details.

All calculations were performed with Kohn–Sham density functional theory (KS DFT) and KS time-dependent DFT (TD-DFT) linear response methods. Geometry optimizations and vibrational frequency calculations with the CAM-B3LYP functional[7] and the def2-SV(P) Gaussian-type basis set[8] were performed with Gaussian 16, version A.03 (G16).[9] $S_1$ equilibrium structures were optimized with excited state gradients from TD-DFT. Ground-state equilibrium structures were optimized with spin-restricted DFT. All structures were characterized as minima via harmonic vibrational frequency calculations. Calculations were performed with the (*P*) isomer of *exo*-dithia[9]helicene and endo-dithia[7]helicene, but the (*M*)-isomer was considered for comparison with the experimental data in the main text. Accordingly, the sign of the calculated chiroptical properties was inverted prior to reporting them in figures and tables.

Absorption and electronic circular dichroism (ECD) spectra were obtained considering the 30 lowest-lying excitations calculated using TD-DFT with the ground-state optimized geometries. The transitions were Gaussian broadened with a σ of 0.20 eV to obtain the corresponding spectra. Vibrationally resolved singlet emission and circularly polarized luminescence (CPL) spectra including Franck-Condon (FC) and Herzberg-Teller (HT) effects were calculated as implemented in G16.[10] The vibronic transitions were Gaussian broadened with a σ of 0.0248 eV. Regarding general strategies for calculating natural optical activity parameters, in particular with DFT/TD-DFT, see, for example, References 11 and 12.

The CAM-B3LYP/def2-SV(P) level of theory yielded the correct signs for the ECD and CPL spectra except for the (*M*)-*exo*-dithia[7]helicene compound. Its ECD spectrum was investigated with a selection of functionals (M06-HF,[13] M11,[14] ωB97X-D,[15] and LC-ωHPBE[16]) and the def2-SV(P) basis set, confirming that CAM-B3LYP predicts the correct ECD sign (**Figure S5**, Panels A and B). We chose the functionals listed above based on their known excellent performance for excitation energies.[17] The ωB97X-D functional was used to re-optimize the $S_0$ and $S_1$ structures to obtain the vibrationally resolved CPL spectrum reported in **Figure S6**. The $S_1$ geometry obtained with this functional and basis set was then used as starting point in another geometry optimization with CAM-B3LYP. The optimized geometry obtained in this way was used to re-calculate the emission and CPL spectra, yielding the correct CPL sign as shown in **Figure S7**.

The dissymmetry factors ($g_{lum}$) reported in Table S7 were calculated as $\Delta I/I$, i.e. as the ratio between the broadened calculated CPL ($\Delta I$) and emission ($I$) intensities at the experimental wavelengths, instead of using the rotatory and dipole strengths of the electronic transitions.[18] This way was chosen because for the two dithia[9]helicenes the purely electronic spectrum of these compounds, unlike the experimental CPL band, has a positive rotatory strength for the $S_0$ - $S_1$ transition, whose contribution can still be observed as a weak feature around the wavelength of the 0-0 transition in the vibrationally resolved calculated CPL spectrum for the *exo* isomer (**Figure S11**). To further investigate the origin of this negative band, calculations were performed for the FC and HT intensities separately from each other. The experimental spectra shown in **Figure S16** were arbitrarily scaled to match the calculated intensities.[18]

It has been reported that HT effects heavily influence the shape and sign of ECD and CPL spectra for [6]helicene and its 2-methyl-, 5-aza-, and 2-bromo-derivatives through the modification of

the FC spectral features.[18] As revealed by the present calculations, this is also the case for (*M*)-*exo*-dithia[7]helicene and the two dithia[9]helicenes. For the first compound, the FC spectrum already reproduces the shape and sign of the experimental equivalent well, although the relative intensity of the two experimental bands around 430 and 450 nm is not correctly reproduced. The experimental spectrum shows two bands of roughly the same intensity. The calculated FC spectrum, instead, shows two peaks of different intensity, with the first band being more intense than the second. HT effects alone are not enough to obtain a satisfactory agreement with the experiment. The combined FCHT spectrum appears less intense than the one including FC effects only due to FC and HT spectra having opposite signs. This reduces the intensity of both bands in the 430–450 nm range by roughly the same amount (panel A of **Figure S16**).

The CPL spectrum obtained including only FC contributions for the two [9]helicenes exhibits the wrong sign. For (*M*)-*endo*-dithia[9]helicene, the intensity of the FC spectrum is very weak in the whole spectral range, and the HT spectrum accounts for most of the spectral shape. The experimental spectrum is overall not well resolved, showing a major negative band whose intensity is largest around 460–470 nm. Individual bands are not clearly visible, instead. The computed HT and FCHT spectra exhibit the same pattern, with the most intense peak around 470 nm accompanied by two less intense shoulders. The FC spectrum of (*M*)-*exo*-dithia[9]helicene is opposite in sign to the HT spectrum, as for the (*M*)-*endo*-dithia[9]helicene compound. HT effects are responsible for the satisfactory agreement with the experimental data exhibited by the HT and FCHT spectra. The experimental spectrum shows three maxima, although not well resolved, that are matched by the calculated pattern. FC effects are responsible for the positive band observed between 450 and 460 nm, while the sign change is due to HT effects.

Overall, HT effects are responsible for sign changes, relative to the purely electronic spectra, for the calculated CPL of some of the systems. In addition, the simultaneous inclusion of FC and HT effects is necessary to obtain satisfactory agreement with the experimental data, similar to what was shown previously for hexahelicene and its derivatives in reference 18. As discussed in the main text, this is partially due to small rotatory strengths for the $S_1$–$S_0$ transition of these compounds, reported in **Tables S1**–**S3** below.

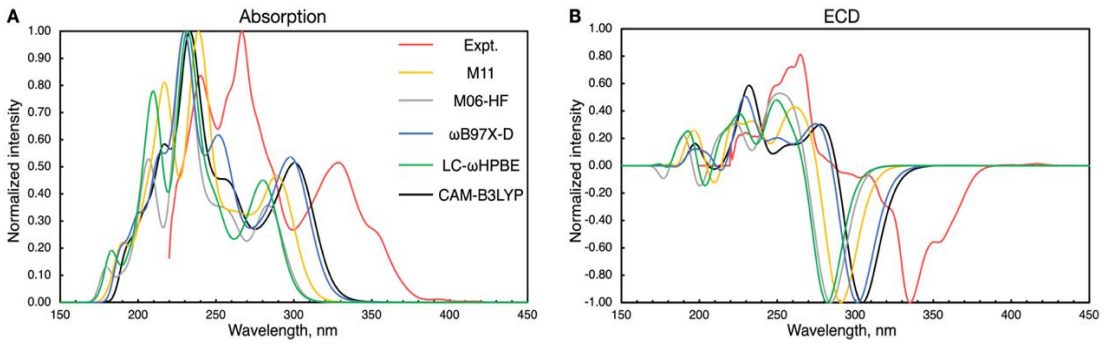



**Figure S5** Normalized absorption (Panel **A**) and ECD (Panel **B**) spectra calculated with the CAM-B3LYP, LC-ωHPBE, M11, M06-HF, ωB97X-D functionals and the def2-SV(P) basis set on CAM-B3LYP/def2-SV(P) optimized geometries of (*M*)-*exo*-dithia[7]helicene. A Gaussian broadening with σ = 0.20 eV was applied to the transitions. Calculated spectra are unshifted.

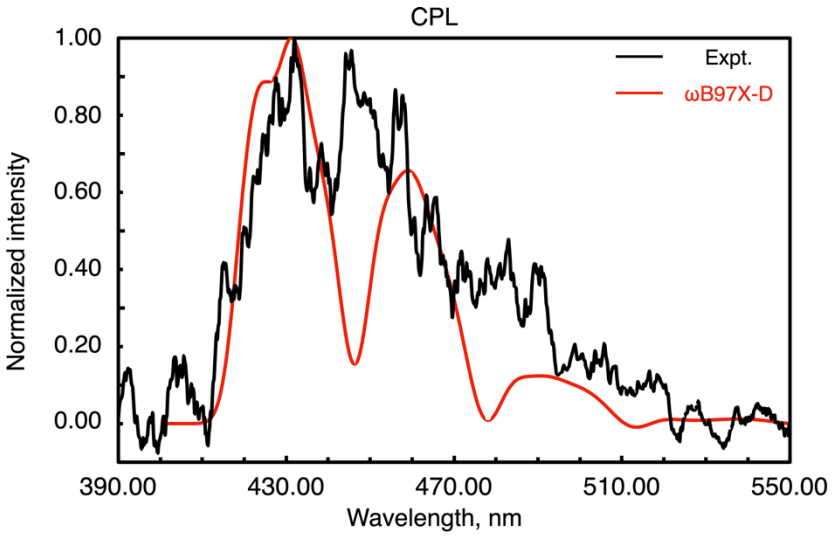



**Figure S6** Normalized CPL spectrum for (*M*)-*exo*-dithia[7]helicene obtained with ωB97X-D/def2-SV(P). A Gaussian broadening with σ = 0.0248 eV was applied. A shift of –0.40 eV was applied to the computed spectrum.

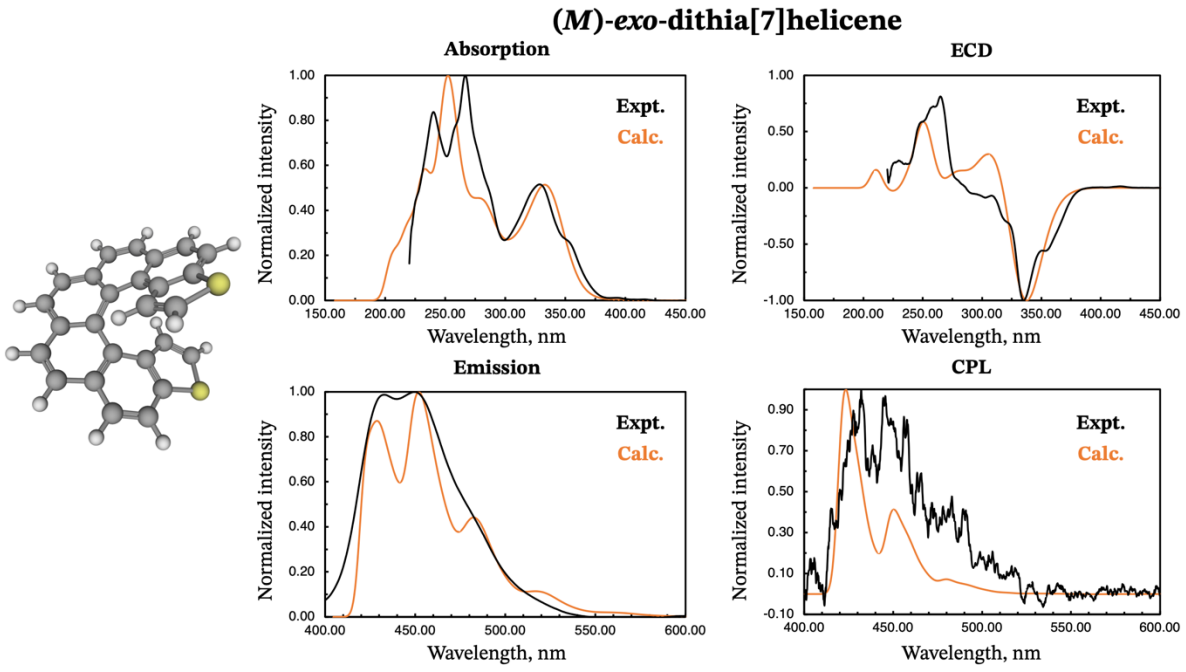



**Figure S7** Normalized absorption, ECD, vibrationally resolved singlet emission and CPL spectra alongside the optimized ground state structure of (*M*)-*exo*-dithia[7]helicene obtained with CAM-B3LYP/def2-SV(P). Calculated spectra were shifted by –0.40 eV (orange curves). Hydrogen atoms are white, carbon atoms are black, sulfur atoms are yellow.

**Table S1** Twenty lowest excitation energies, oscillator strengths, rotatory strengths, and orbital contributions for the transitions (greater than 15.0 %) of (*M*)-*exo*-dithia[7]helicene. The values in parentheses are rotatory strengths calculated for the $S_1$– $S_0$ transition (on the $S_1$ geometry).

| Excitation number | Excitation energy[a] | Wavelength[b] | Oscillator strength[c] | Rotatory strength[d] | Occupied orbital | Virtual orbital | Percentage[e] |
|---|---|---|---|---|---|---|---|
| 1 | 3.594 | 345 | 0.0012 | 3.61 (5.89) | 100 | 103 | 34.6% |
| | | | | | 101 | 102 | 53.3% |
| 2 | 3.834 | 323 | 0.0065 | -28.17 (-30.00) | 100 | 102 | 56.7% |
| | | | | | 101 | 103 | 36.7% |
| 3 | 4.087 | 303 | 0.3564 | -904.80 (-878.67) | 100 | 102 | 31.7% |
| | | | | | 101 | 103 | 45.7% |
| 4 | 4.228 | 293 | 0.0046 | -30.09 (-7.60) | 98 | 102 | 34.8% |
| | | | | | 99 | 103 | 25.0% |
| | | | | | 101 | 105 | 17.2% |
| 5 | 4.293 | 289 | 0.1390 | 191.46 (322.26) | 99 | 102 | 38.0% |
| | | | | | 101 | 102 | 20.3% |
| 6 | 4.483 | 277 | 0.1158 | 175.55 (40.20) | 99 | 102 | 29.1% |
| | | | | | 100 | 103 | 45.8% |
| | | | | | 101 | 102 | 19.4% |
| 7 | 4.740 | 262 | 0.1935 | 5.97 (-3.36) | 98 | 102 | 29.5% |
| | | | | | 99 | 103 | 48.7% |
| 8 | 4.844 | 256 | 0.1243 | 99.51 (90.36) | 98 | 103 | 36.4% |
| | | | | | 99 | 102 | 24.5% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | 100 | 105 | 24.1% |
| 9 | 4.955 | 250 | 0.0403 | -9.31 (-12.01) | 98 | 105 | 15.9% |
| | | | | | 99 | 104 | 22.4% |
| | | | | | 101 | 104 | 18.9% |
| 10 | 5.041 | 246 | 0.0848 | 6.18 (-2.94) | 98 | 102 | 18.8% |
| | | | | | 99 | 105 | 20.7% |
| | | | | | 100 | 104 | 23.5% |
| 11 | 5.043 | 246 | 0.0328 | 41.75 (46.36) | 98 | 103 | 33.4% |
| | | | | | 101 | 104 | 32.2% |
| 12 | 5.096 | 243 | 0.0866 | -69.98 (-79.81) | 101 | 105 | 60.4% |
| 13 | 5.235 | 237 | 0.1009 | 0.58 (9.66) | 97 | 102 | 26.8% |
| | | | | | 100 | 104 | 44.7% |
| 14 | 5.327 | 233 | 0.6304 | 372.46 (411.10) | 100 | 105 | 51.2% |
| | | | | | 101 | 104 | 24.0% |
| 15 | 5.438 | 228 | 0.0294 | 13.46 (26.48) | 97 | 102 | 27.5% |
| | | | | | 99 | 105 | 40.7% |
| 16 | 5.497 | 226 | 0.0057 | -15.61 (15.66) | 96 | 102 | 25.0% |
| | | | | | 99 | 104 | 45.8% |
| 17 | 5.553 | 223 | 0.1254 | 47.29 (31.13) | 96 | 103 | 24.8% |
| 18 | 5.567 | 223 | 0.0017 | 27.79 (-51.13) | 97 | 103 | 62.2% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | 98 | 105 | 20.8% |
| 19 | 5.747 | 216 | 0.2113 | 226.84<br>(251.78) | 96 | 102 | 25.7% |
| | | | | | 98 | 105 | 46.4% |
| 20 | 5.754 | 215 | 0.1756 | -234.34<br>(-247.23) | 96 | 103 | 25.2% |
| | | | | | 98 | 104 | 39.1% |

[a]In units of eV; [b]In units of nm; [c]Dimensionless; [d]In units of $10^{-40}$ $esu^2$ $cm^2$;

[e]Calculated using the square of the coefficients printed by the G16 program.

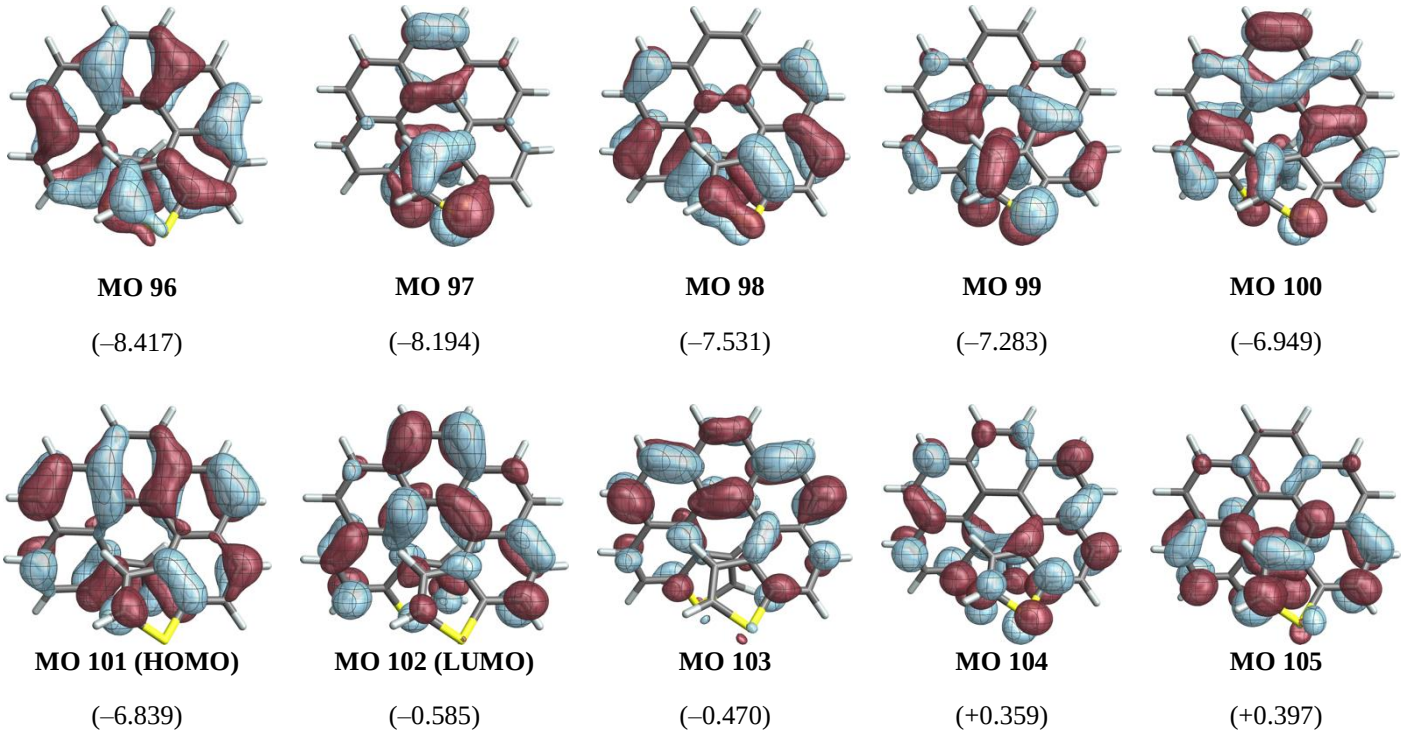



**Figure S8** Molecular orbitals involved in the excitations for (*M*)-*exo*-dithia[7]helicene. Values in parentheses are orbital energies in eV. Iso values ±0.030 a.u., ground state geometry.

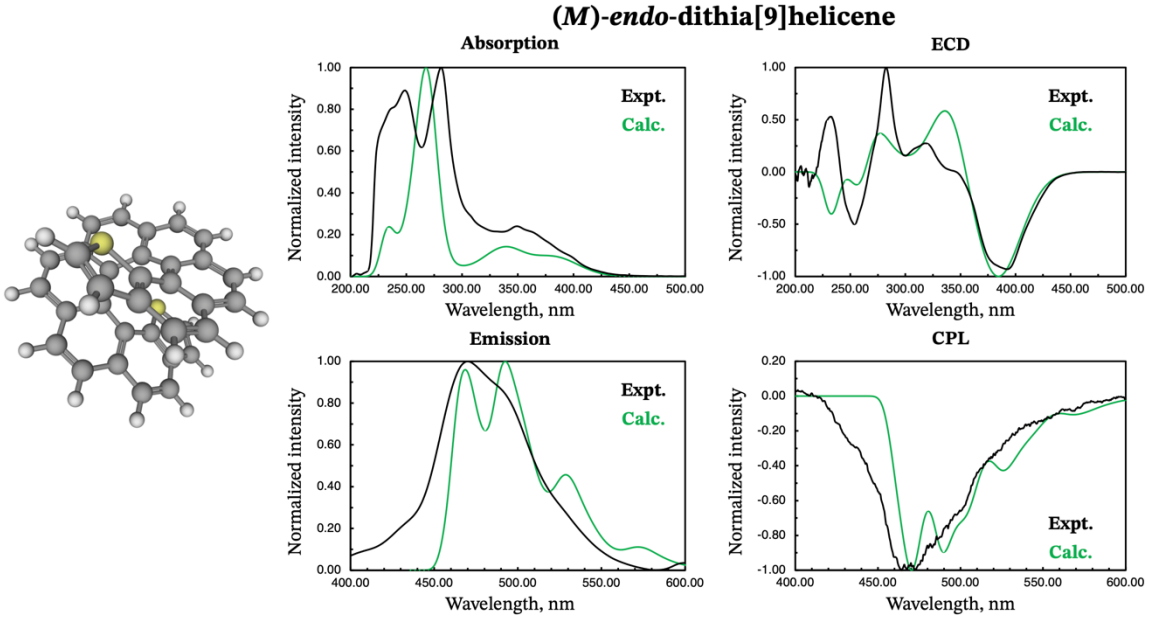



**Figure S9** Normalized absorption, ECD, vibrationally resolved singlet emission and CPL spectra alongside the optimized ground state structure of (*M*)-*endo*-dithia[9]helicene obtained with CAM-B3LYP/def2-SV(P). Calculated spectra were shifted by –0.40 eV (green curves). Hydrogen atoms are white, carbon atoms are black, sulfur atoms are yellow.

**Table S2** Twenty lowest excitation energies, oscillator strengths, rotatory strengths, and orbital contributions for the transitions (greater than 15.0 %) of (*M*)-*endo*-dithia[9]helicene. The values in parentheses are rotatory strengths calculated for the $S_1$– $S_0$ transition (on the $S_1$ geometry).

| Excitation number | Excitation energy[a] | Wavelength[b] | Oscillator strength[c] | Rotatory strength[d] | Occupied orbital | Virtual orbital | Percentage[e] |
|---|---|---|---|---|---|---|---|
| 1 | 3.364 | 369 | 0.0001 | 0.20 (0.21) | 126 | 128 | 32.8% |
| | | | | | 127 | 129 | 48.4% |
| 2 | 3.534 | 351 | 0.0492 | -433.79 (-399.67) | 127 | 128 | 84.0% |
| 3 | 3.652 | 340 | 0.0630 | -584.39 (-741.53) | 125 | 128 | 29.6% |
| | | | | | 126 | 129 | 55.8% |
| 4 | 3.817 | 325 | 0.0529 | -244.22 (-56.83) | 124 | 129 | 42.0% |
| | | | | | 125 | 128 | 19.6% |
| 5 | 3.915 | 317 | 0.0015 | 7.92 (2.39) | 124 | 128 | 19.3% |
| | | | | | 125 | 129 | 56.1% |
| 6 | 4.026 | 308 | 0.1342 | 487.33 (372.31) | 126 | 128 | 53.5% |
| | | | | | 127 | 129 | 34.8% |
| 7 | 4.210 | 295 | 0.0015 | 17.33 (152.41) | 124 | 128 | 44.6% |
| | | | | | 125 | 129 | 22.5% |
| 8 | 4.219 | 294 | 0.0750 | 160.26 (148.47) | 124 | 129 | 34.0% |
| | | | | | 125 | 128 | 33.9% |
| | | | | | 126 | 129 | 16.4% |
| 9 | 4.363 | 284 | 0.0226 | 35.77 (14.13) | 122 | 129 | 18.1% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | 123 | 128 | 18.9% |
| | | | | | 125 | 130 | 19.8% |
| 10 | 4.527 | 274 | 0.0198 | 38.52 (46.06) | 124 | 128 | 15.8% |
| | | | | | 127 | 130 | 67.2% |
| 11 | 4.557 | 272 | 0.0107 | 3.37 (12.26) | 122 | 128 | 18.5% |
| | | | | | 123 | 129 | 42.0% |
| 12 | 4.589 | 270 | 0.0088 | 21.72 (3.74) | 124 | 129 | 16.4% |
| | | | | | 126 | 130 | 17.6% |
| | | | | | 127 | 131 | 36.4% |
| 13 | 4.750 | 261 | 0.0129 | 72.65 (112.08) | 125 | 131 | 31.7% |
| 14 | 4.801 | 258 | 0.0002 | 6.87 (101.54) | 123 | 128 | 39.5% |
| | | | | | 124 | 131 | 32.1% |
| 15 | 4.824 | 257 | 0.0145 | 81.65 (-8.44) | 122 | 129 | 17.3% |
| | | | | | 125 | 130 | 45.0% |
| 16 | 4.843 | 256 | 0.0317 | -11.81 (11.09) | 122 | 128 | 20.1% |
| | | | | | 124 | 130 | 17.4% |
| | | | | | 126 | 130 | 23.6% |
| | | | | | 127 | 131 | 25.0% |
| 17 | 4.993 | 248 | 0.3515 | 272.04 (228.68) | 122 | 128 | 23.0% |
| | | | | | 123 | 129 | 25.3% |
| 18 | 4.997 | 248 | 0.4663 | 211.35 (258.32) | 122 | 129 | 39.6% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | 123 | 128 | 16.0% |
| 19 | 5.022 | 247 | 0.0841 | -133.94 (-169.21) | 124 | 131 | 27.8% |
| | | | | | 126 | 131 | 32.0% |
| 20 | 5.040 | 246 | 0.2230 | -203.58 (-161.17) | 124 | 130 | 33.9% |
| | | | | | 125 | 131 | 19.0% |
| | | | | | 126 | 130 | 18.3% |

[a]In units of eV; [b]In units of nm; [c]Dimensionless; [d]In units of $10^{-40}$ esu$^2$ cm$^2$;

[e]Calculated using the square of the coefficients printed by the G16 program.

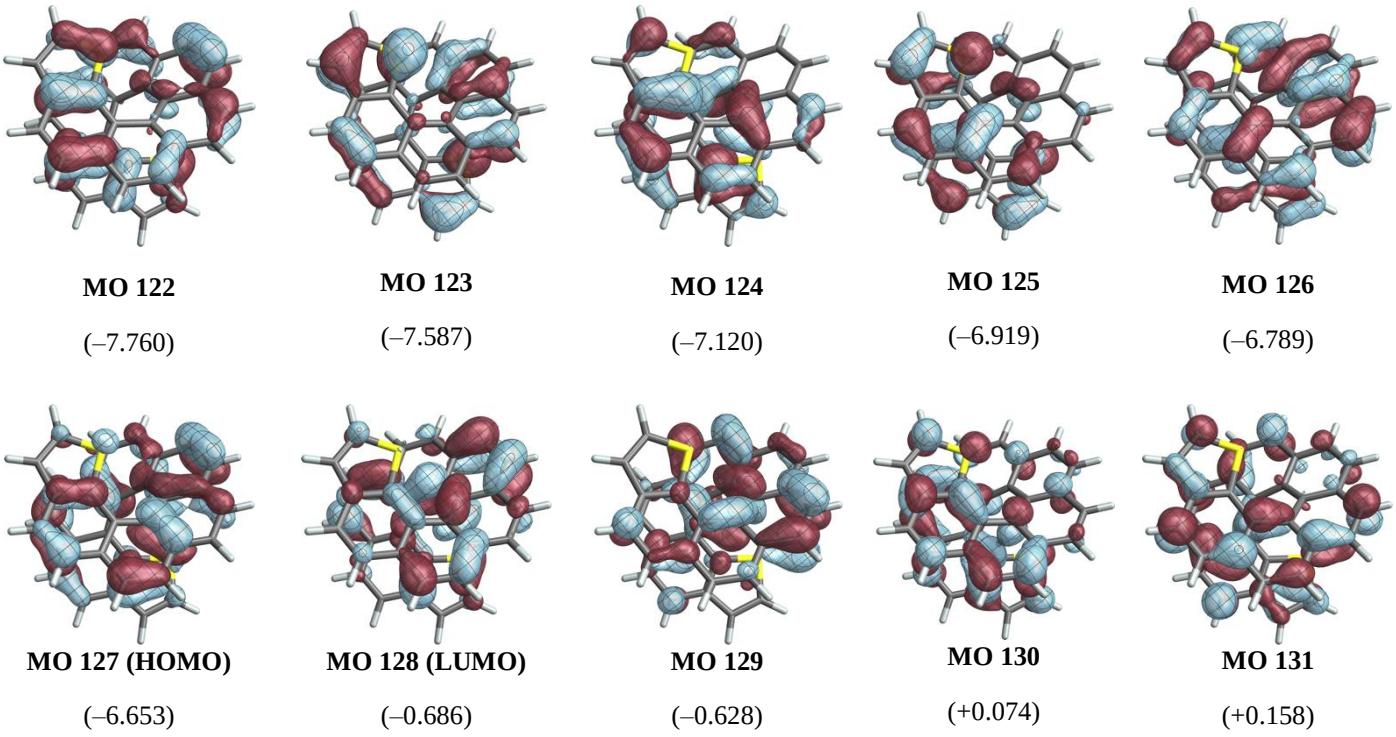



**Figure S10** Molecular orbitals involved in the excitations for (*M*)-*endo*-dithia[9]helicene. Values in parentheses are orbital energies in eV. Iso values ±0.030 a.u., ground state geometry.

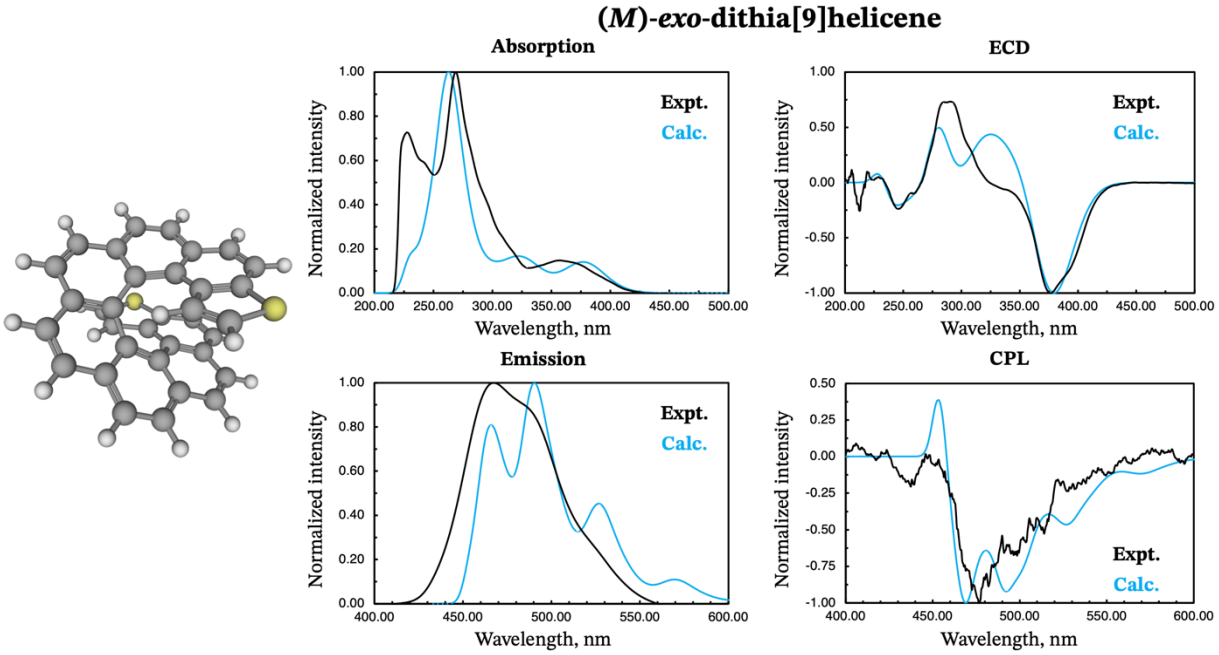



**Figure S11** Normalized absorption, ECD, vibrationally resolved singlet emission and CPL spectra alongside the ground state structure of (*M*)-*exo*-dithia[9]helicene obtained with CAM-B3LYP/def2-SV(P). Calculations were performed with the (*P*) isomer. The sign of the ECD and CPL spectra and the optimized geometry were inverted. Calculated spectra were shifted by –0.40 eV (blue curves). Hydrogen atoms are white, carbon atoms are black, sulfur atoms are yellow.

**Table S3** Twenty lowest excitation energies, oscillator strengths, rotatory strengths, and orbital contributions for the transitions (greater than 15.0 %) of (*M*)-*exo*-dithia[9]helicene. Calculations were performed with the (*P*) isomer, the sign of the rotatory strength was inverted for the (*M*) enantiomer. The values in parentheses are rotatory strengths calculated for the $S_1$– $S_0$ transition (on the $S_1$ geometry).

| Excitation number | Excitation energy[a] | Wavelength[b] | Oscillator strength[c] | Rotatory strength[d] | Occupied orbital | Virtual orbital | Percentage[e] |
|---|---|---|---|---|---|---|---|
| 1 | 3.384 | 366 | 0.0002 | 2.52 (3.13) | 126 | 129 | 32.9% |
| | | | | | 127 | 128 | 47.7% |
| 2 | 3.597 | 345 | 0.0081 | -22.40 (4.59) | 126 | 128 | 27.9% |
| | | | | | 127 | 129 | 60.4% |
| 3 | 3.677 | 337 | 0.1460 | -1180.00 (-1112.06) | 126 | 128 | 56.9% |
| | | | | | 127 | 129 | 18.9% |
| 4 | 3.842 | 323 | 0.0019 | 3.40 | 124 | 128 | 34.3% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | (2.76) | | | |
| | | | | | 125 | 129 | 32.3% |
| 5 | 3.908 | 317 | 0.0339 | 140.03 (239.19) | 125 | 128 | 33.7% |
| | | | | | 127 | 128 | 30.3% |
| 6 | 4.125 | 301 | 0.0978 | 254.27 (87.22) | 126 | 129 | 51.7% |
| | | | | | 127 | 128 | 17.1% |
| 7 | 4.275 | 290 | 0.0733 | 125.50 (104.77) | 124 | 128 | 31.6% |
| | | | | | 125 | 129 | 42.0% |
| 8 | 4.346 | 285 | 0.0536 | 161.48 (188.31) | 124 | 129 | 56.7% |
| | | | | | 125 | 128 | 32.3% |
| 9 | 4.442 | 279 | 0.0157 | 3.11 (2.26) | 122 | 128 | 15.9% |
| | | | | | 124 | 131 | 22.7% |
| | | | | | 125 | 130 | 24.8% |
| 10 | 4.564 | 272 | 0.0100 | -15.85 (-44.57) | 126 | 131 | 23.3% |
| | | | | | 127 | 130 | 52.3% |
| 11 | 4.568 | 271 | 0.0256 | 33.73 (-3.62) | 125 | 131 | 25.3% |
| 12 | 4.590 | 270 | 0.0633 | -23.62 47.20) | 127 | 131 | 49.4% |
| 13 | 4.794 | 259 | 0.0443 | 60.63 (107.44) | 123 | 128 | 24.7% |
| | | | | | 124 | 130 | 18.2% |
| | | | | | 126 | 130 | 15.6% |
| 14 | 4.837 | 256 | 0.1638 | 383.84 | 124 | 131 | 25.1% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | (419.90) | | | |
| | | | | | 126 | 131 | 34.4% |
| | | | | | 127 | 130 | 15.0% |
| 15 | 4.881 | 254 | 0.0014 | -13.78<br>(-24.29) | 122 | 128 | 26.0% |
| | | | | | 123 | 129 | 21.7% |
| | | | | | 125 | 130 | 34.8% |
| 16 | 4.900 | 253 | 0.0677 | 68.05<br>(19.17) | 125 | 131 | 30.3% |
| | | | | | 126 | 130 | 37.4% |
| 17 | 5.005 | 248 | 0.0777 | 27.12<br>(115.52) | 123 | 128 | 38.0% |
| | | | | | 125 | 131 | 22.1% |
| 18 | 5.020 | 247 | 0.2650 | -218.70<br>(1.61) | 123 | 129 | 15.9% |
| | | | | | 124 | 131 | 18.6% |
| | | | | | 126 | 131 | 26.2% |
| | | | | | 127 | 130 | 16.9% |
| 19 | 5.081 | 244 | 0.1872 | 213.87<br>(0.43) | 122 | 128 | 39.7% |
| | | | | | 123 | 129 | 30.8% |
| | | | | | 124 | 131 | 18.2% |
| 20 | 5.129 | 242 | 0.2593 | -212.97<br>(27.70) | 124 | 130 | 42.8% |

[a]In units of eV; [b]In units of nm; [c]Dimensionless; [d]In units of $10^{-40}$ esu$^2$ cm$^2$;

[e]Calculated using the square of the coefficients printed by the G16 program.

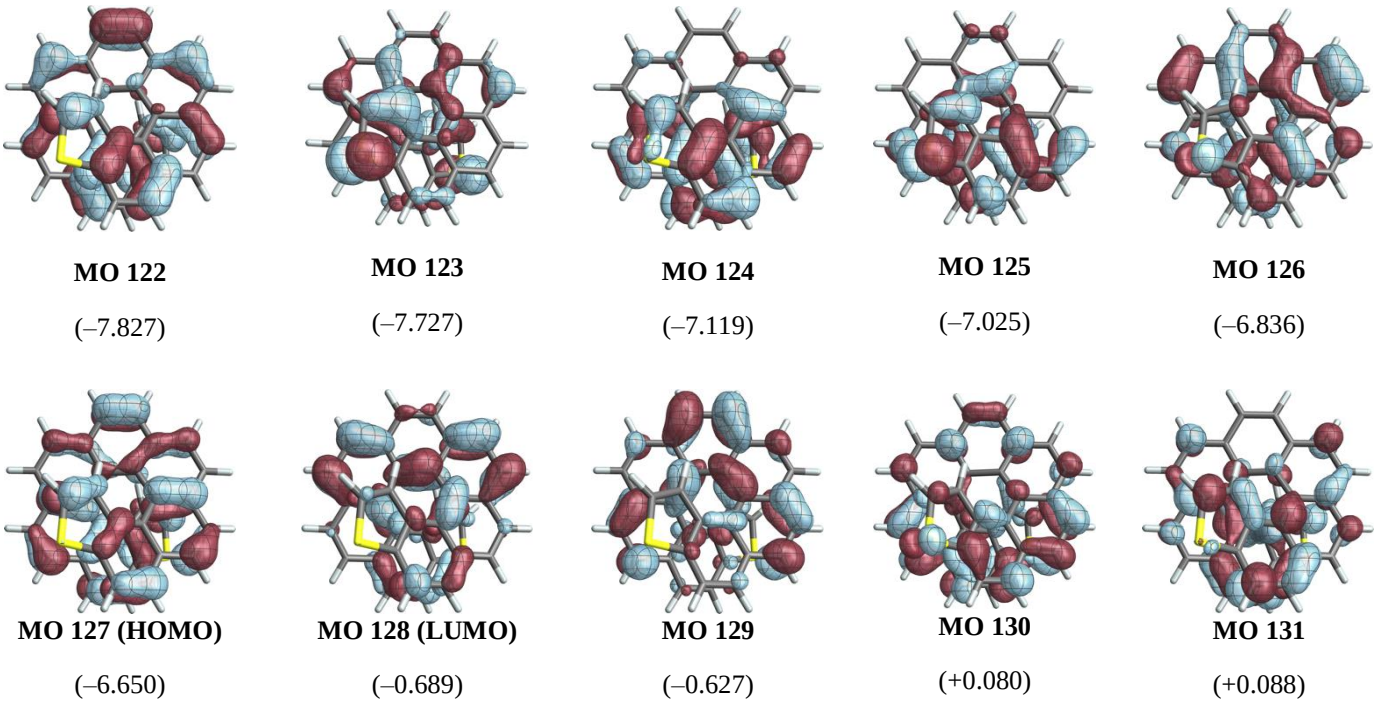



**Figure S12** Molecular orbitals involved in the excitations for (*M*)-*exo*-dithia[9]helicene. Values in parentheses are orbital energies in eV. Iso values ±0.030 a.u., ground state geometry calculated with the (*P*) isomer and subsequently inverted.

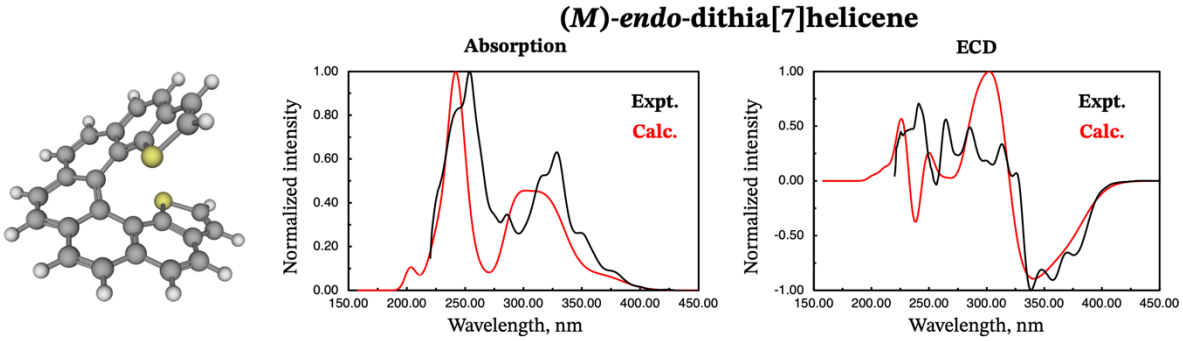



**Figure S13** Normalized absorption and ECD spectra alongside the optimized ground state structure of (*M*)-*endo*-dithia[7]helicene obtained with CAM-B3LYP/def2-SV(P). Calculations were performed with the (*P*) isomer. The sign of the ECD spectrum and the optimized geometry were inverted. Calculated spectra were shifted by –0.40 eV (red curves). Hydrogen atoms are white, carbon atoms are black, sulfur atoms are yellow.

**Table S4** Twenty lowest excitation energies, oscillator strengths, rotatory strengths, and orbital contributions for the transitions (greater than 15.0 %) of (*M*)-*endo*-dithia[7]helicene. Calculations were performed with the (*P*) isomer, the sign of the rotatory strength was inverted for the (*M*) enantiomer.

| Excitation number | Excitation energy[a] | Wavelength[b] | Oscillator strength[c] | Rotatory strength[d] | Occupied orbital | Virtual orbital | Percentage[e] |
|---|---|---|---|---|---|---|---|
| 1 | 3.548 | 349 | 0.0011 | -1.87 | 100 | 102 | 38.8% |
| | | | | | 101 | 103 | 51.3% |
| 2 | 3.730 | 332 | 0.0525 | -258.66 | 101 | 102 | 80.3% |
| 3 | 3.967 | 313 | 0.0533 | -334.17 | 99 | 102 | 50.5% |
| | | | | | 100 | 103 | 35.4% |
| 4 | 4.196 | 296 | 0.2680 | -411.72 | 98 | 103 | 28.1% |
| | | | | | 100 | 103 | 35.4% |
| 5 | 4.241 | 292 | 0.0101 | 20.72 | 98 | 102 | 15.6% |
| | | | | | 99 | 103 | 62.5% |
| 6 | 4.401 | 282 | 0.2757 | 493.59 | 100 | 102 | 45.4% |
| | | | | | 101 | 103 | 40.6% |
| 7 | 4.615 | 269 | 0.2020 | 26.07 | 98 | 103 | 43.6% |
| | | | | | 99 | 102 | 24.5% |
| 8 | 4.669 | 266 | 0.1603 | 303.15 | 98 | 102 | 58.9% |
| | | | | | 99 | 103 | 26.0% |
| 9 | 4.881 | 254 | 0.0173 | -57.68 | 96 | 103 | 16.0% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | 97 | 102 | 34.3% |
| | | | | | 99 | 104 | 23.3% |
| 10 | 5.065 | 245 | 0.0345 | 48.63 | 101 | 104 | 69.3% |
| 11 | 5.113 | 243 | 0.0030 | -5.85 | 97 | 103 | 56.9% |
| 12 | 5.170 | 240 | 0.0258 | -5.34 | 98 | 103 | 20.6% |
| | | | | | 100 | 104 | 17.9% |
| | | | | | 101 | 105 | 42.7% |
| 13 | 5.306 | 234 | 0.0283 | -61.75 | 97 | 102 | 50.5% |
| | | | | | 98 | 105 | 15.8% |
| 14 | 5.317 | 233 | 0.0799 | -9.51 | 96 | 102 | 23.8% |
| | | | | | 99 | 105 | 15.4% |
| | | | | | 100 | 104 | 37.4% |
| 15 | 5.448 | 228 | 0.2459 | 410.02 | 99 | 104 | 36.2% |
| | | | | | 100 | 105 | 38.9% |
| 16 | 5.464 | 227 | 0.0854 | -1.56 | 97 | 103 | 23.8% |
| | | | | | 99 | 105 | 33.5% |
| 17 | 5.540 | 224 | 0.4434 | -255.44 | 96 | 102 | 25.1% |
| | | | | | 100 | 104 | 22.9% |
| | | | | | 101 | 105 | 23.9% |
| 18 | 5.596 | 222 | 0.2679 | -191.57 | 96 | 103 | 27.8% |
| | | | | | 99 | 104 | 15.5% |
| | | | | | 100 | 105 | 30.9% |
| 19 | 5.791 | 214 | 0.0500 | -72.18 | 98 | 104 | 61.4% |
| | | | | | 99 | 105 | 17.1% |
| 20 | 5.841 | 212 | 0.1786 | 333.58 | 96 | 103 | 19.3% |
| | | | | | 98 | 105 | 47.0% |

[a]In units of eV; [b]In units of nm; [c]Dimensionless; [d]In units of $10^{-40}$ esu$^2$ cm$^2$;

[e]Calculated using the square of the coefficients printed by the G16 program.

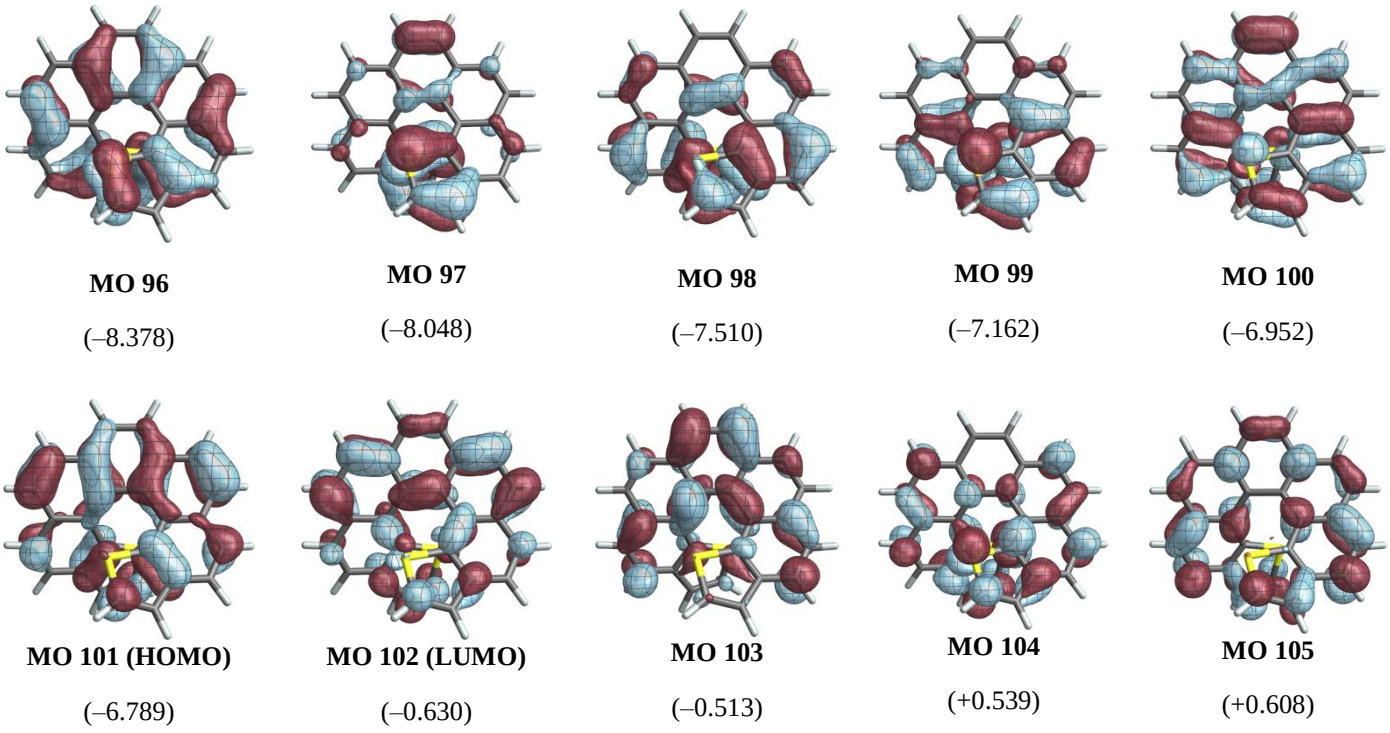
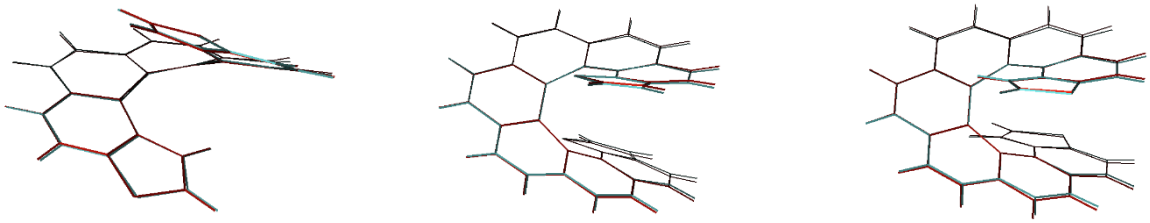



**Figure S14** Molecular orbitals involved in the excitations for (*M*)-*endo*-dithia[7]helicene. Values in parentheses are orbital energies in eV. Iso values ±0.030 a.u., ground state geometry calculated with the (*P*) isomer and subsequently inverted.

**Table S7** Experimental and calculated dissymmetry factors ($g_{LUM}$) for (*M*)-*exo*-dithia[7]helicene, (*M*)-*endo*-dithia[9]helicene, and (*M*)-*exo*-dithia[9]helicene.

| Compound | $g_{LUM}$, expt[a] | Expt. wavelength[b] | $g_{LUM}$, calc[a,c] | Calc. wavelength[b,d] | Excitation energy[e] | Excitation energy, shifted[e] |
|---|---|---|---|---|---|---|
| (*M*)-*exo*-thia-heptahelicene | 0.005 | 470 | 0.0024 | 470.0 | 3.04 | 2.64 |
| (*M*)-*endo*-thia-nonahelicene | –0.0123 | 470 | –0.024 | 470.4 | 3.04 | 2.64 |
| (*M*)-*exo*-thia-nonahelicene | –0.0042 | 475 | –0.019[f] | 469.0 | 3.04 | 2.64 |

[a]Dimensionless; [b]In nm; [c]Calculated as Δ*I*/*I* at the wavelengths given in column 5 (see text); [d]After shifting; [e]In eV; [f]After sign change from the calculations with the (*P*) enantiomer.



(*M*)-*exo*-dithia[9]helicene (*M*)-*endo*-dithia[9]helicene (*M*)-*exo*-dithia[9]helicene

**Figure S15** Optimized $S_0$ (red) and $S_1$ (blue) geometries superimposed with one another for (*M*)-*exo*-thia-heptahelicene (left), (*M*)-*endo*-thia-nonahelicene (middle), and (*M*)-*exo*-thia-nonahelicene (right).

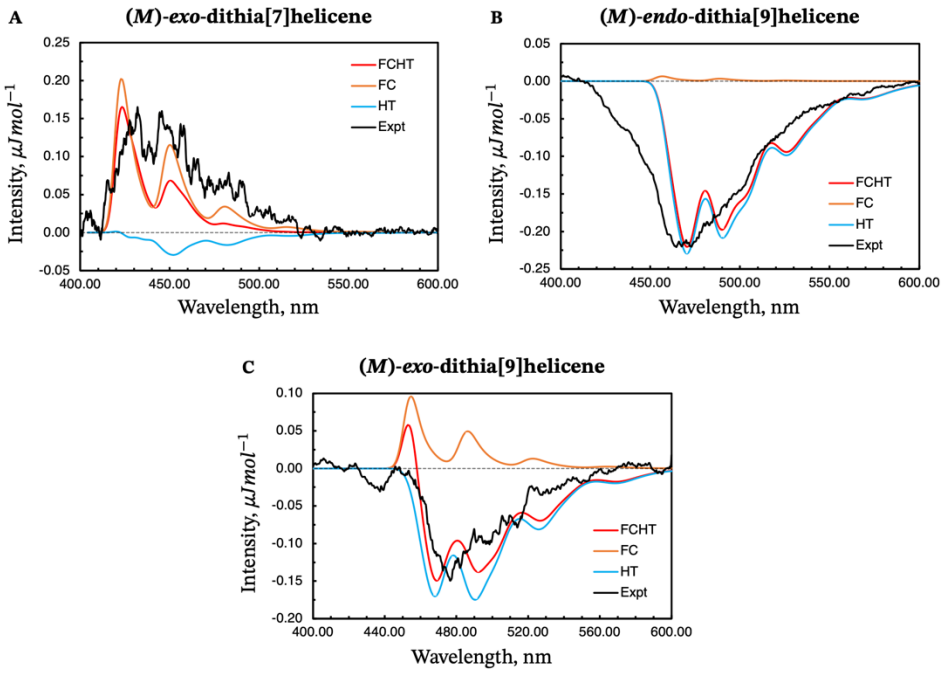



**Figure S16** Calculated CPL spectra including Franck-Condon (FC, orange lines), Herzberg-Teller (HT, blue lines), and FCHT effects (red lines) compared to the experimental spectra for (*M*)-*exo*-dithia[7]helicene (top left, panel A), (*M*)-*endo*-dithia[9]helicene (top right, panel B), and (*M*)-*exo*-dithia[9]helicene (bottom, panel C; calculations were performed with (*P*)-*exo*-dithia[9]helicene and the sign of the CPL spectra was inverted). Calculated spectra are Gaussian broadened (σ = 0.0248 eV) and shifted by –0.40 eV. Experimental spectra were scaled to match the calculated intensities.

**Table S8** Vibrational normal modes implied in the most intense vibronic transitions for the *M* isomers of *exo*-dithia[7]helicene, *endo*-dithia[9]helicene, and *exo*-dithia[9]helicene. The numbering follows the G16 output.

| Molecule | Normal modes # | Wavenumber ($cm^{-1}$) |
|---|---|---|
| (*M*)-*exo*-dithia[7]helicene | 2 | 56 |
| | 4 | 97 |
| | 9 | 215 |
| | 15 | 338 |
| | 89 | 1428 |
| | 92 | 1455 |
| (*M*)-*endo*-dithia[9]helicene | 3 | 54 |
| | 11 | 154 |
| | 19 | 312 |
| | 22 | 370 |
| | 25 | 428 |
| | 42 | 630 |
| | 113 | 1421 |
| | 115 | 1428 |
| | 121 | 1467 |
| | 128 | 1584 |
| (*M*)-*exo*-dithia[9]helicene | 3 | 55 |
| | 7 | 107 |
| | 25 | 421 |
| | 42 | 631 |
| | 115 | 1426 |
| | 117 | 1437 |
| | 119 | 1453 |
| | 120 | 1453 |
| | 128 | 1593 |
| | 133 | 1676 |

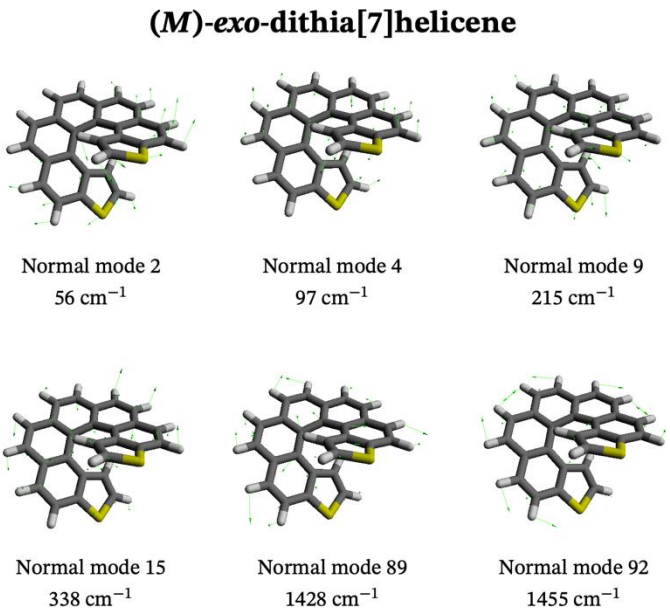



**Figure S17** Selected vibrational normal modes for (*M*)-*exo*-dithia[7]helicene related to the most intense vibronic peaks in the calculated CPL spectra. The green vectors indicate the direction of the displacement for the corresponding frequency (in $cm^{-1}$). The numbers refer to the order the normal modes appear in the G16 output.

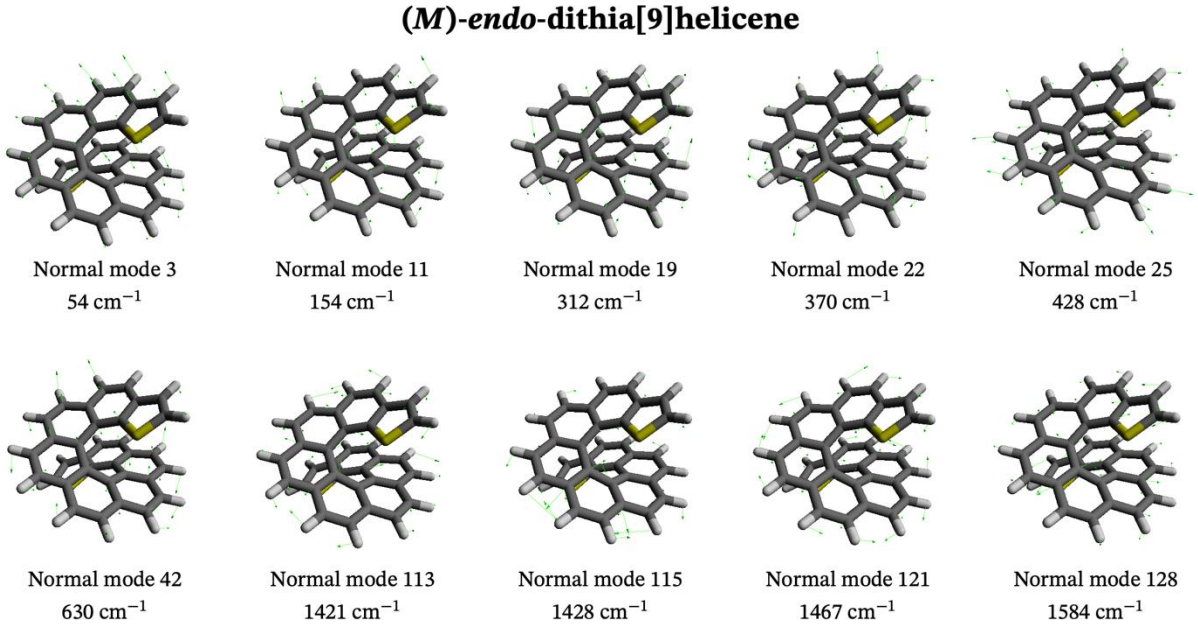



**Figure S18** Selected vibrational normal modes for (*M*)-*endo*-dithia[9]helicene related to the most intense vibronic peaks in the calculated CPL spectra. The green vectors indicate the direction of the displacement for the corresponding frequency (in $cm^{-1}$). The numbers refer to the order the normal modes appear in the G16 output.

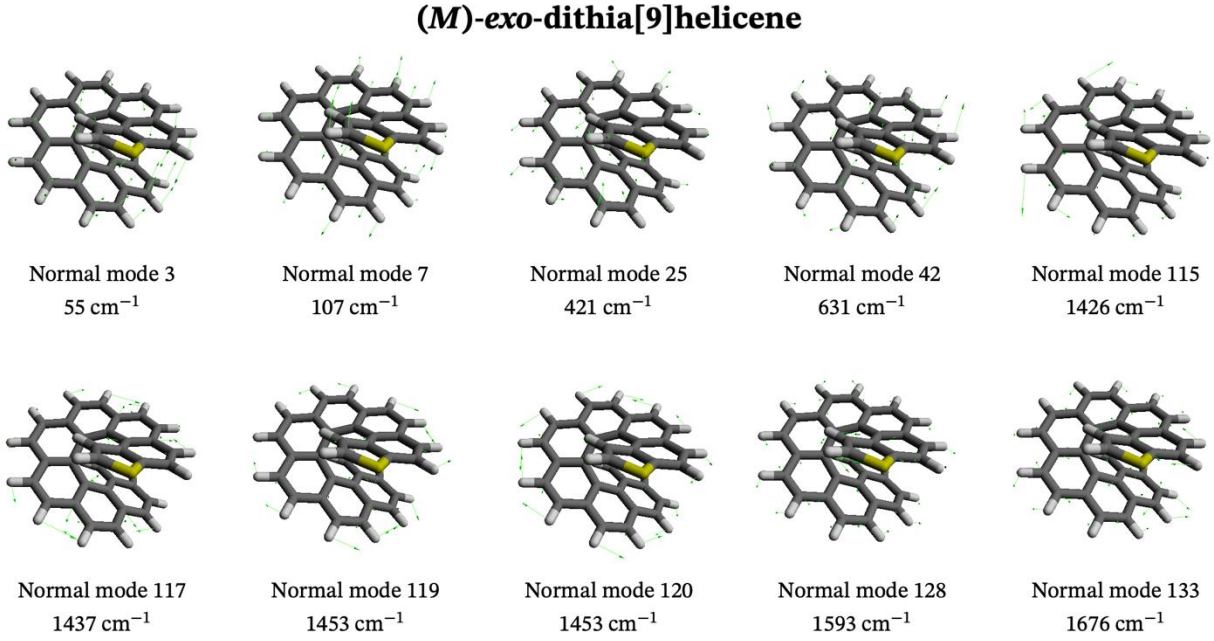



**Figure S19** Selected vibrational normal modes for (*M*)-*exo*-dithia[9]helicene related to the most intense vibronic peaks in the calculated CPL spectra. The green vectors indicate the direction of the displacement for the corresponding frequency (in $cm^{-1}$). The numbers refer to the order the normal modes appear in the G16 output.

## 2. Optimized structures in Cartesian coordinates (xyz format).

(*P*)-*endo*-dithia[7]helicene, $S_0$.

| | | | |
|---|---|---|---|
| S | 0.022427 | -0.977779 | 2.079089 |
| C | -0.619896 | -2.461030 | 2.686901 |
| H | -0.074606 | -3.003020 | 3.459903 |
| C | -1.788297 | -2.811961 | 2.095641 |
| H | -2.352626 | -3.714159 | 2.337761 |
| C | -2.221458 | -1.843856 | 1.127865 |
| C | -3.443396 | -1.842831 | 0.413676 |
| H | -4.127754 | -2.689874 | 0.508340 |
| C | -3.778465 | -0.745513 | -0.326903 |
| H | -4.748980 | -0.690497 | -0.827102 |
| C | -2.904462 | 0.372490 | -0.434878 |
| C | -3.384043 | 1.571254 | -1.045337 |
| H | -4.387279 | 1.570078 | -1.479627 |
| C | -2.654755 | 2.715014 | -0.981517 |
| H | -3.065191 | 3.664582 | -1.335155 |
| C | -1.323161 | 2.698979 | -0.466537 |
| C | -0.619763 | 3.922723 | -0.280841 |
| H | -1.124696 | 4.859746 | -0.530157 |
| C | 0.620797 | 3.922565 | 0.280892 |
| H | 1.125990 | 4.859464 | 0.530159 |
| C | 1.323882 | 2.698644 | 0.466599 |
| C | 2.655500 | 2.714339 | 0.981544 |
| H | 3.066184 | 3.663805 | 1.335172 |
| C | 3.384511 | 1.570407 | 1.045310 |
| H | 4.387770 | 1.568978 | 1.479544 |
| C | 2.904616 | 0.371771 | 0.434824 |
| C | 3.778366 | -0.746409 | 0.326730 |
| H | 4.748932 | -0.691647 | 0.826862 |
| C | 3.443007 | -1.843600 | -0.413910 |
| H | 4.127142 | -2.690816 | -0.508633 |

| | | | |
|---|---|---|---|
| C | 2.221007 | -1.844312 | -1.127981 |
| C | 1.787441 | -2.812394 | -2.095595 |
| H | 2.351511 | -3.714753 | -2.337726 |
| C | 0.619182 | -2.461076 | -2.686897 |
| H | 0.073710 | -3.002890 | -3.459891 |
| S | -0.022739 | -0.977671 | -2.079020 |
| C | 1.318406 | -0.776436 | -0.980701 |
| C | 1.599917 | 0.339615 | -0.128414 |
| C | 0.718490 | 1.471944 | 0.100875 |
| C | -0.718110 | 1.472133 | -0.100728 |
| C | -1.599838 | 0.340035 | 0.128512 |
| C | -1.318661 | -0.776128 | 0.980774 |

(*M*)-*exo*-dithia[7]helicene, $S_0$.

| | | | |
|---|---|---|---|
| S | -2.951929 | -1.695065 | 1.999248 |
| C | -1.707859 | -2.190401 | 0.894692 |
| C | -1.730163 | -3.376745 | 0.134322 |
| H | -2.606338 | -4.029124 | 0.141831 |
| C | -0.596269 | -3.718651 | -0.549446 |
| H | -0.544678 | -4.668135 | -1.088923 |
| C | 0.550600 | -2.874762 | -0.560192 |
| C | 1.762724 | -3.354134 | -1.146676 |
| H | 1.762225 | -4.341539 | -1.615996 |
| C | 2.911566 | -2.640262 | -1.028168 |
| H | 3.865337 | -3.048796 | -1.372657 |
| C | 2.895472 | -1.320913 | -0.480126 |
| C | 4.120866 | -0.622363 | -0.283488 |
| H | 5.057395 | -1.126761 | -0.535846 |
| C | 4.121986 | 0.614978 | 0.283588 |
| H | 5.059426 | 1.117669 | 0.535973 |
| C | 2.897858 | 1.315760 | 0.480171 |
| C | 2.916313 | 2.635085 | 1.028203 |
| H | 3.870810 | 3.041895 | 1.372713 |

| | | | |
|---|---|---|---|
| C | 1.768761 | 3.351041 | 1.146657 |
| H | 1.770027 | 4.338454 | 1.615953 |
| C | 0.555790 | 2.873852 | 0.560140 |
| C | -0.589569 | 3.719798 | 0.549330 |
| H | -0.536304 | 4.669188 | 1.088806 |
| C | -1.724054 | 3.379888 | -0.134447 |
| H | -2.599076 | 4.033808 | -0.141984 |
| C | -1.703869 | 2.193457 | -0.894751 |
| S | -2.948889 | 1.700176 | -1.999157 |
| C | -1.991138 | 0.359901 | -2.522994 |
| H | -2.362839 | -0.301790 | -3.305129 |
| C | -0.801130 | 0.272568 | -1.877694 |
| H | -0.065984 | -0.491906 | -2.113651 |
| C | -0.609176 | 1.313917 | -0.897922 |
| C | 0.525474 | 1.597828 | -0.061281 |
| C | 1.669123 | 0.715968 | 0.111762 |
| C | 1.667811 | -0.718901 | -0.111749 |
| C | 0.522558 | -1.598698 | 0.061262 |
| C | -0.611588 | -1.312820 | 0.897913 |
| C | -0.801674 | -0.271218 | 1.877786 |
| H | -0.065170 | 0.491932 | 2.113788 |
| C | -1.991944 | -0.356301 | 2.522892 |
| H | -2.362555 | 0.306085 | 3.304959 |

(*M*)-*exo*-dithia[7]helicene, $S_1$.

| | | | |
|---|---|---|---|
| S | -2.9476010 | -1.6193400 | 2.0400590 |
| C | -1.7107500 | -2.1515770 | 0.9483820 |
| C | -1.7591800 | -3.3294820 | 0.1795540 |
| H | -2.6474940 | -3.9644140 | 0.1816740 |
| C | -0.6284040 | -3.6864750 | -0.5201050 |
| H | -0.6045400 | -4.6287250 | -1.0742830 |
| C | 0.5315470 | -2.8738820 | -0.5305960 |
| C | 1.7193170 | -3.3353350 | -1.1565780 |

| | | | |
|---|---|---|---|
| H | 1.7073410 | -4.3135420 | -1.6446220 |
| C | 2.8909640 | -2.6147930 | -1.0789750 |
| H | 3.8205480 | -3.0294400 | -1.4783720 |
| C | 2.9189820 | -1.3298280 | -0.4925470 |
| C | 4.1306320 | -0.6376000 | -0.2883670 |
| H | 5.0700180 | -1.1331220 | -0.5462850 |
| C | 4.1329200 | 0.6228270 | 0.2885790 |
| H | 5.0741020 | 1.1149570 | 0.5464460 |
| C | 2.9237970 | 1.3194820 | 0.4926780 |
| C | 2.9004540 | 2.6046580 | 1.0788520 |
| H | 3.8315380 | 3.0159920 | 1.4781840 |
| C | 1.7314590 | 3.3295320 | 1.1561960 |
| H | 1.7230530 | 4.3078980 | 1.6439950 |
| C | 0.5420390 | 2.8723010 | 0.5302460 |
| C | -0.6149260 | 3.6891400 | 0.5194510 |
| H | -0.5876300 | 4.6314690 | 1.0733390 |
| C | -1.7469790 | 3.3360770 | -0.1801450 |
| H | -2.6329620 | 3.9742610 | -0.1824940 |
| C | -1.7028740 | 2.1577170 | -0.9485380 |
| S | -2.9416570 | 1.6295850 | -2.0400210 |
| C | -1.9618020 | 0.2998240 | -2.5623460 |
| H | -2.3300820 | -0.3759290 | -3.3338840 |
| C | -0.7644270 | 0.2426390 | -1.9261290 |
| H | -0.0148010 | -0.5114240 | -2.1535530 |
| C | -0.5854580 | 1.2942690 | -0.9582230 |
| C | 0.5401850 | 1.5851690 | -0.1200150 |
| C | 1.6628140 | 0.7114030 | 0.0842790 |
| C | 1.6602170 | -0.7172230 | -0.0840640 |
| C | 0.5343830 | -1.5869270 | 0.1200200 |
| C | -0.5901730 | -1.2922320 | 0.9583860 |
| C | -0.7652200 | -0.2404610 | 1.9268630 |
| H | -0.0127870 | 0.5106630 | 2.1547160 |
| C | -1.9627910 | -0.2935170 | 2.5630660 |

| | | | |
|---|---|---|---|
| H | -2.3285360 | 0.3831900 | 3.3349750 |

(*M*)-*endo*-dithia[9]helicene, $S_0$.

| | | | |
|---|---|---|---|
| S | -2.596477 | 0.736645 | 1.350663 |
| C | -4.011172 | -0.249243 | 1.456835 |
| H | -4.994475 | 0.220994 | 1.431960 |
| C | -3.727270 | -1.570989 | 1.561880 |
| H | -4.481264 | -2.355656 | 1.645576 |
| C | -2.313550 | -1.825312 | 1.588930 |
| C | -1.670694 | -3.064067 | 1.832001 |
| H | -2.265262 | -3.977762 | 1.912753 |
| C | -0.321781 | -3.080569 | 2.045883 |
| H | 0.183821 | -4.010539 | 2.319144 |
| C | 0.457907 | -1.890936 | 1.968736 |
| C | 1.810438 | -1.906032 | 2.430674 |
| H | 2.239862 | -2.857227 | 2.756152 |
| C | 2.502502 | -0.745581 | 2.572386 |
| H | 3.491346 | -0.734638 | 3.038495 |
| C | 1.970893 | 0.483352 | 2.073927 |
| C | 2.674324 | 1.706454 | 2.279659 |
| H | 3.599086 | 1.685198 | 2.862606 |
| C | 2.160736 | 2.883078 | 1.826100 |
| H | 2.639531 | 3.836040 | 2.066923 |
| C | 1.034567 | 2.885649 | 0.953174 |
| C | 0.531439 | 4.111962 | 0.425764 |
| H | 0.983891 | 5.049483 | 0.759978 |
| C | -0.529850 | 4.112110 | -0.426003 |
| H | -0.982025 | 5.049754 | -0.760258 |
| C | -1.033426 | 2.885943 | -0.953338 |
| C | -2.159649 | 2.883737 | -1.826169 |
| H | -2.638123 | 3.836853 | -2.066997 |
| C | -2.673681 | 1.707260 | -2.279659 |
| H | -3.598447 | 1.686299 | -2.862606 |

| | | | |
|---|---|---|---|
| C | -1.970694 | 0.483920 | -2.073911 |
| C | -2.502738 | -0.744842 | -2.572384 |
| H | -3.491554 | -0.733491 | -3.038532 |
| C | -1.811101 | -1.905547 | -2.430663 |
| H | -2.240807 | -2.856592 | -2.756204 |
| C | -0.458556 | -1.890919 | -1.968713 |
| C | 0.320785 | -3.080806 | -2.045903 |
| H | -0.185134 | -4.010579 | -2.319234 |
| C | 1.669688 | -3.064728 | -1.831956 |
| H | 2.264003 | -3.978574 | -1.912690 |
| C | 2.312898 | -1.826137 | -1.588834 |
| C | 3.726709 | -1.572183 | -1.561832 |
| H | 4.480453 | -2.357070 | -1.645532 |
| C | 4.010921 | -0.250500 | -1.456794 |
| H | 4.994360 | 0.219480 | -1.431956 |
| S | 2.596518 | 0.735789 | -1.350577 |
| C | 1.548271 | -0.656803 | -1.444548 |
| C | 0.120519 | -0.668520 | -1.539283 |
| C | -0.742722 | 0.487980 | -1.377358 |
| C | -0.428744 | 1.660245 | -0.584758 |
| C | 0.429501 | 1.660157 | 0.584610 |
| C | 0.742917 | 0.487855 | 1.377411 |
| C | -0.120802 | -0.668324 | 1.539366 |
| C | -1.548572 | -0.656148 | 1.444612 |

(*M*)-*endo*-dithia[9]helicene, $S_1$.

| | | | |
|---|---|---|---|
| S | 2.6144610 | 0.7588340 | -1.3521070 |
| C | 4.0335190 | -0.2268340 | -1.3955320 |
| H | 5.0151380 | 0.2458330 | -1.3552400 |
| C | 3.7566980 | -1.5531670 | -1.4776190 |
| H | 4.5161960 | -2.3356490 | -1.5226400 |
| C | 2.3468380 | -1.8144400 | -1.5349620 |
| C | 1.7087680 | -3.0597140 | -1.7512530 |

| | | | |
|---|---|---|---|
| H | 2.3045720 | -3.9748950 | -1.7951110 |
| C | 0.3582420 | -3.0861340 | -1.9803550 |
| H | -0.1411030 | -4.0269440 | -2.2265420 |
| C | -0.4259130 | -1.9017440 | -1.9451190 |
| C | -1.7820430 | -1.9314280 | -2.3747160 |
| H | -2.2138570 | -2.8903210 | -2.6729910 |
| C | -2.5016020 | -0.7738850 | -2.5114200 |
| H | -3.5054710 | -0.7923230 | -2.9440790 |
| C | -1.9784000 | 0.4661180 | -2.0658120 |
| C | -2.6913960 | 1.6741810 | -2.2567770 |
| H | -3.6294440 | 1.6463690 | -2.8171560 |
| C | -2.1857320 | 2.8717480 | -1.7942570 |
| H | -2.6922060 | 3.8134040 | -2.0225860 |
| C | -1.0493230 | 2.8986500 | -0.9589660 |
| C | -0.5351050 | 4.1078480 | -0.4397600 |
| H | -0.9777220 | 5.0511070 | -0.7710100 |
| C | 0.5317440 | 4.1085490 | 0.4379240 |
| H | 0.9734060 | 5.0523660 | 0.7688610 |
| C | 1.0471420 | 2.9000440 | 0.9575560 |
| C | 2.1834640 | 2.8744230 | 1.7929540 |
| H | 2.6891960 | 3.8165690 | 2.0208850 |
| C | 2.6900640 | 1.6774050 | 2.2561400 |
| H | 3.6281430 | 1.6506820 | 2.8165300 |
| C | 1.9781560 | 0.4687130 | 2.0656440 |
| C | 2.5022810 | -0.7707640 | 2.5113760 |
| H | 3.5062120 | -0.7884870 | 2.9439330 |
| C | 1.7835230 | -1.9289720 | 2.3750640 |
| H | 2.2162240 | -2.8874090 | 2.6735230 |
| C | 0.4273450 | -1.9004780 | 1.9457530 |
| C | -0.3560260 | -3.0853720 | 1.9813490 |
| H | 0.1439570 | -4.0258150 | 2.2276540 |
| C | -1.7066260 | -3.0599270 | 1.7524770 |
| H | -2.3017480 | -3.9755300 | 1.7966500 |

| | | | |
|---|---|---|---|
| C | -2.3455750 | -1.8151580 | 1.5359230 |
| C | -3.7555520 | -1.5547400 | 1.4785630 |
| H | -4.5145960 | -2.3376440 | 1.5238740 |
| C | -4.0331990 | -0.2285770 | 1.3960770 |
| H | -5.0151360 | 0.2434200 | 1.3556850 |
| S | -2.6147900 | 0.7579780 | 1.3520820 |
| C | -1.5756810 | -0.6398940 | 1.4407500 |
| C | -0.1531440 | -0.6545610 | 1.5506320 |
| C | 0.7099610 | 0.4907400 | 1.3893680 |
| C | 0.4127110 | 1.6473690 | 0.5863150 |
| C | -0.4139060 | 1.6467550 | -0.5872230 |
| C | -0.7104180 | 0.4893810 | -1.3895890 |
| C | 0.1535930 | -0.6554100 | -1.5503100 |
| C | 1.5761760 | -0.6396830 | -1.4401660 |

(*P*)-*exo*-dithia[9]helicene, $S_0$.

| | | | |
|---|---|---|---|
| S | -3.956099 | -1.470825 | -1.409333 |
| C | -2.238556 | -1.711280 | -1.505148 |
| C | -1.606585 | -2.948871 | -1.744316 |
| H | -2.186700 | -3.873434 | -1.789206 |
| C | -0.262404 | -2.941719 | -1.995764 |
| H | 0.251502 | -3.868428 | -2.264458 |
| C | 0.498856 | -1.738827 | -1.948974 |
| C | 1.850544 | -1.745851 | -2.414351 |
| H | 2.288653 | -2.694783 | -2.734790 |
| C | 2.534627 | -0.581200 | -2.556295 |
| H | 3.525216 | -0.564214 | -3.018393 |
| C | 1.993927 | 0.644193 | -2.059237 |
| C | 2.696570 | 1.868640 | -2.259030 |
| H | 3.624508 | 1.849957 | -2.836927 |
| C | 2.180253 | 3.042976 | -1.803669 |
| H | 2.658849 | 3.997477 | -2.038693 |
| C | 1.046215 | 3.041057 | -0.939667 |

| | | | |
|---|---|---|---|
| C | 0.535623 | 4.268567 | -0.418898 |
| H | 0.991605 | 5.205997 | -0.748528 |
| C | -0.536062 | 4.268520 | 0.418823 |
| H | -0.992162 | 5.205907 | 0.748396 |
| C | -1.046524 | 3.040970 | 0.939635 |
| C | -2.180564 | 3.042784 | 1.803602 |
| H | -2.659313 | 3.997221 | 2.038575 |
| C | -2.696720 | 1.868403 | 2.259054 |
| H | -3.624634 | 1.849668 | 2.836996 |
| C | -1.993943 | 0.644053 | 2.059297 |
| C | -2.534540 | -0.581396 | 2.556348 |
| H | -3.525142 | -0.564488 | 3.018426 |
| C | -1.850392 | -1.745997 | 2.414389 |
| H | -2.288459 | -2.694970 | 2.734771 |
| C | -0.498710 | -1.738857 | 1.948985 |
| C | 0.262631 | -2.941695 | 1.995696 |
| H | -0.251206 | -3.868470 | 2.264319 |
| C | 1.606802 | -2.948772 | 1.744194 |
| H | 2.186926 | -3.873338 | 1.788966 |
| C | 2.238709 | -1.711139 | 1.505101 |
| S | 3.956232 | -1.470539 | 1.409320 |
| C | 3.739819 | 0.243364 | 1.327088 |
| H | 4.608189 | 0.900020 | 1.277748 |
| C | 2.435423 | 0.614365 | 1.340974 |
| H | 2.124011 | 1.655834 | 1.326449 |
| C | 1.527589 | -0.504582 | 1.417805 |
| C | 0.094125 | -0.521009 | 1.530333 |
| C | -0.760422 | 0.643088 | 1.370310 |
| C | -0.437768 | 1.814950 | 0.579528 |
| C | 0.437672 | 1.814986 | -0.579476 |
| C | 0.760417 | 0.643112 | -1.370263 |
| C | -0.094066 | -0.521015 | -1.530296 |
| C | -1.527536 | -0.504674 | -1.417775 |

| | | | |
|---|---|---|---|
| C | -2.435452 | 0.614187 | -1.340908 |
| H | -2.124151 | 1.655681 | -1.326328 |
| C | -3.739828 | 0.243078 | -1.327015 |
| H | -4.608200 | 0.899720 | -1.277592 |

(*P*)-*exo*-dithia[9]helicene, $S_1$.

| | | | |
|---|---|---|---|
| S | -3.9714570 | -1.4472340 | -1.3476280 |
| C | -2.2566110 | -1.6972110 | -1.4682000 |
| C | -1.6288630 | -2.9403940 | -1.6727340 |
| H | -2.2096490 | -3.8652670 | -1.6866550 |
| C | -0.2792450 | -2.9443670 | -1.9266200 |
| H | 0.2304480 | -3.8822320 | -2.1626750 |
| C | 0.4853090 | -1.7490990 | -1.9140130 |
| C | 1.8479630 | -1.7731430 | -2.3290750 |
| H | 2.2908480 | -2.7311100 | -2.6139480 |
| C | 2.5635920 | -0.6137360 | -2.4573350 |
| H | 3.5758990 | -0.6289420 | -2.8698220 |
| C | 2.0270440 | 0.6253420 | -2.0226880 |
| C | 2.7435660 | 1.8334330 | -2.1991450 |
| H | 3.6918420 | 1.8065660 | -2.7419100 |
| C | 2.2290260 | 3.0293790 | -1.7425180 |
| H | 2.7375700 | 3.9725940 | -1.9596950 |
| C | 1.0749430 | 3.0521750 | -0.9299290 |
| C | 0.5453030 | 4.2611460 | -0.4242280 |
| H | 0.9949470 | 5.2052410 | -0.7436590 |
| C | -0.5461620 | 4.2611700 | 0.4232050 |
| H | -0.9959820 | 5.2052710 | 0.7423600 |
| C | -1.0755130 | 3.0522500 | 0.9293300 |
| C | -2.2294680 | 3.0294930 | 1.7421030 |
| H | -2.7381280 | 3.9726870 | 1.9591070 |
| C | -2.7437250 | 1.8335960 | 2.1991690 |
| H | -3.6919400 | 1.8067480 | 2.7420480 |
| C | -2.0270450 | 0.6255700 | 2.0229230 |

| | | | |
|---|---|---|---|
| C | -2.5633580 | -0.6134900 | 2.4578630 |
| H | -3.5756020 | -0.6287830 | 2.8705120 |
| C | -1.8476250 | -1.7728490 | 2.3296520 |
| H | -2.2904070 | -2.7308160 | 2.6146970 |
| C | -0.4850340 | -1.7487200 | 1.9143930 |
| C | 0.2796570 | -2.9438920 | 1.9270150 |
| H | -0.2299010 | -3.8818060 | 2.1631670 |
| C | 1.6292500 | -2.9397930 | 1.6729950 |
| H | 2.2101170 | -3.8646160 | 1.6868740 |
| C | 2.2568510 | -1.6965630 | 1.4683200 |
| S | 3.9716540 | -1.4464010 | 1.3474620 |
| C | 3.7488440 | 0.2698570 | 1.3126450 |
| H | 4.6147660 | 0.9296320 | 1.2624190 |
| C | 2.4435490 | 0.6365260 | 1.3616110 |
| H | 2.1264580 | 1.6767530 | 1.3735320 |
| C | 1.5417810 | -0.4851190 | 1.4259220 |
| C | 0.1108860 | -0.5063090 | 1.5398150 |
| C | -0.7439930 | 0.6443330 | 1.3715260 |
| C | -0.4295300 | 1.8012470 | 0.5749350 |
| C | 0.4291290 | 1.8011710 | -0.5752520 |
| C | 0.7439090 | 0.6440570 | -1.3714680 |
| C | -0.1107890 | -0.5067160 | -1.5396210 |
| C | -1.5416980 | -0.4856800 | -1.4258520 |
| C | -2.4435870 | 0.6358600 | -1.3616010 |
| H | -2.1266270 | 1.6761250 | -1.3734550 |
| C | -3.7488530 | 0.2690380 | -1.3127560 |
| H | -4.6148220 | 0.9287510 | -1.2625600 |

## 3. Additional structures optimized with ωB97X-D/def2-SV(P).

(*M*)-*exo*-dithia[7]helicene, $S_0$.

| | | | |
|---|---|---|---|
| S | -3.0001210 | -1.4270700 | 1.9286820 |
| C | -1.7296070 | -2.0378780 | 0.9151940 |
| C | -1.7707830 | -3.2542670 | 0.2008810 |
| H | -2.6756520 | -3.8671780 | 0.1902590 |
| C | -0.6208520 | -3.6767840 | -0.4117790 |
| H | -0.5895110 | -4.6520580 | -0.9064020 |
| C | 0.5590660 | -2.8767710 | -0.4152520 |
| C | 1.7763310 | -3.4087070 | -0.9477580 |
| H | 1.7694650 | -4.4201740 | -1.3645530 |
| C | 2.9372140 | -2.7065030 | -0.8490840 |
| H | 3.8885030 | -3.1510520 | -1.1560060 |
| C | 2.9327470 | -1.3528230 | -0.3862420 |
| C | 4.1586990 | -0.6397550 | -0.2375710 |
| H | 5.0979200 | -1.1582050 | -0.4516410 |
| C | 4.1589190 | 0.6383750 | 0.2377700 |
| H | 5.0983130 | 1.1564710 | 0.4519470 |
| C | 2.9332110 | 1.3518830 | 0.3863050 |
| C | 2.9381000 | 2.7055900 | 0.8490630 |
| H | 3.8895170 | 3.1498240 | 1.1560310 |
| C | 1.7774880 | 3.4082430 | 0.9475670 |
| H | 1.7709830 | 4.4197310 | 1.3643090 |
| C | 0.5600550 | 2.8767360 | 0.4150350 |
| C | -0.6195980 | 3.6771380 | 0.4115050 |
| H | -0.5879650 | 4.6524330 | 0.9060610 |
| C | -1.7696810 | 3.2549310 | -0.2010590 |
| H | -2.6743790 | 3.8680890 | -0.1903590 |
| C | -1.7289420 | 2.0384740 | -0.9152690 |
| S | -2.9998510 | 1.4277750 | -1.9283260 |
| C | -1.9965420 | 0.1193550 | -2.4505760 |
| H | -2.3711900 | -0.5944650 | -3.1847640 |

| | | | |
|---|---|---|---|
| C | -0.7694390 | 0.1262300 | -1.8692510 |
| H | -0.0018900 | -0.6048650 | -2.1147310 |
| C | -0.5923900 | 1.2150680 | -0.9401190 |
| C | 0.5513130 | 1.5750470 | -0.1483610 |
| C | 1.7079630 | 0.7220000 | 0.0628890 |
| C | 1.7077050 | -0.7225150 | -0.0629070 |
| C | 0.5507590 | -1.5751370 | 0.1482490 |
| C | -0.5927890 | -1.2148550 | 0.9400500 |
| C | -0.7693790 | -0.1260880 | 1.8693560 |
| H | -0.0015600 | 0.6047560 | 2.1147520 |
| C | -1.9965640 | -0.1186460 | 2.4504960 |
| H | -2.3710180 | 0.5953490 | 3.1846150 |

(*M*)-*exo*-dithia[7]helicene, $S_1$.

| | | | |
|---|---|---|---|
| S | -3.0097380 | 1.2258080 | -1.9294310 |
| C | -1.7398670 | 1.9233820 | -0.9767960 |
| C | -1.8134600 | 3.1438690 | -0.2750750 |
| H | -2.7406260 | 3.7212290 | -0.2489690 |
| C | -0.6619080 | 3.6191450 | 0.3166380 |
| H | -0.6655760 | 4.5979080 | 0.8056760 |
| C | 0.5433240 | 2.8721260 | 0.3115480 |
| C | 1.7409630 | 3.4142910 | 0.8526200 |
| H | 1.7206950 | 4.4293600 | 1.2602840 |
| C | 2.9293310 | 2.7130400 | 0.8049420 |
| H | 3.8575460 | 3.1817640 | 1.1453590 |
| C | 2.9700620 | 1.3747630 | 0.3476240 |
| C | 4.1817600 | 0.6600700 | 0.2153040 |
| H | 5.1248100 | 1.1772940 | 0.4138480 |
| C | 4.1817570 | -0.6600600 | -0.2153260 |
| H | 5.1248060 | -1.1772810 | -0.4138850 |
| C | 2.9700600 | -1.3747600 | -0.3476350 |
| C | 2.9293370 | -2.7130350 | -0.8049500 |
| H | 3.8575530 | -3.1817620 | -1.1453650 |

| | | | |
|---|---|---|---|
| C | 1.7409650 | -3.4142900 | -0.8526150 |
| H | 1.7207040 | -4.4293630 | -1.2602720 |
| C | 0.5433310 | -2.8721240 | -0.3115430 |
| C | -0.6618990 | -3.6191450 | -0.3166320 |
| H | -0.6655680 | -4.5979040 | -0.8056800 |
| C | -1.8134560 | -3.1438710 | 0.2750830 |
| H | -2.7406240 | -3.7212310 | 0.2489630 |
| C | -1.7398580 | -1.9233880 | 0.9768060 |
| S | -3.0097370 | -1.2257940 | 1.9294050 |
| C | -1.9658280 | 0.0558630 | 2.4508690 |
| H | -2.3351360 | 0.8070030 | 3.1495650 |
| C | -0.7209780 | -0.0241070 | 1.9127640 |
| H | 0.0727680 | 0.6812100 | 2.1543770 |
| C | -0.5648050 | -1.1438710 | 1.0211670 |
| C | 0.5726380 | -1.5459260 | 0.2497750 |
| C | 1.7156690 | -0.7175920 | -0.0110490 |
| C | 1.7156760 | 0.7175990 | 0.0110430 |
| C | 0.5726370 | 1.5459430 | -0.2497770 |
| C | -0.5648160 | 1.1438690 | -1.0211660 |
| C | -0.7209960 | 0.0240910 | -1.9127460 |
| H | 0.0727370 | -0.6812400 | -2.1543510 |
| C | -1.9658640 | -0.0559050 | -2.4508100 |
| H | -2.3351670 | -0.8070690 | -3.1494810 |

## Section S3: Additional references.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