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Supporting Information

Electronic Circular Dichroism Unravels Atropisomers of a Broadly Absorbing Fulgide Derivative

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Table of contents

1. General information	2
2. Experimental Details	2
3. Computational Details.....	11
4. References	12

1. General information

All reagents and solvents were purchased from TCI, Acros Organics (ThermoFisher), Sigma Aldrich (Merck) and Fluorochem and were used as received.

NMR spectra were measured on a Bruker AV 400 device. Deuterated solvents (purchased at Eurisotop) were used for sample preparation. Spectra were referenced to the solvent peak. (Toluene- d_8 1H : 2.08, 6.97, 7.01, 7.09).

Synthesis of the fulgide derivative was performed according literature.(1,2)

2. Experimental Details

The separation of different isomers was performed on a *Young Lin SP930D* HPLC from *Techlab*. We used a *CHIRALPAK® IA 5 μ m* column from *Daicel Corporation*. (semi-preparative, 20 mm x 250 mm). As solvent, we used a mixture of 85% n-Hexan and 15% Ethanol. The isocratic separation was performed with a flow rate of 7 mL/min at room temperature.

All CD measurements were performed on a JASCO J-710 spectrometer. The temperature range of the measurements was between room temperature to 90 °C. We used standard sensitivity (100 mdeg) and a continuous scanmode with 3 spectral accumulations of each measurement. Analysis of the CD-spectra and the thermal rates of the different isomers were performed according literature.(3)

UV-vis spectra were measured in 1.0 cm quartz fluorescence cuvette (QS) from Hellma-Analytix. Ocean Optics USB4000 detector connected via optical fiber and convex lens, mounted in an adapter, to cuvette holder CVH100 (Thorlabs). In the opposed side of cuvette holder DH-mini light source (Ocean Optics) was connected in the same way. For more details in terms of the setup see Reinfelds et al.(1) Irradiation experiments were done in 1.0 cm quartz fluorescence cuvette (QS) from Hellma-Analytix equipped with a magnetic stirrer or for CD measurements in 0.1 cm quartz cuvette (QS) from Hellma-Analytix. Light sources (365 nm LED M365L2, 405 nm LED M405L4, 455 nm LED M455L4 and 595 nm LED M595L4) were operated by DC2100 LED driver in external trigger mode (both from Thorlabs). As external trigger was used an in-house programmed software PHITS.(1)

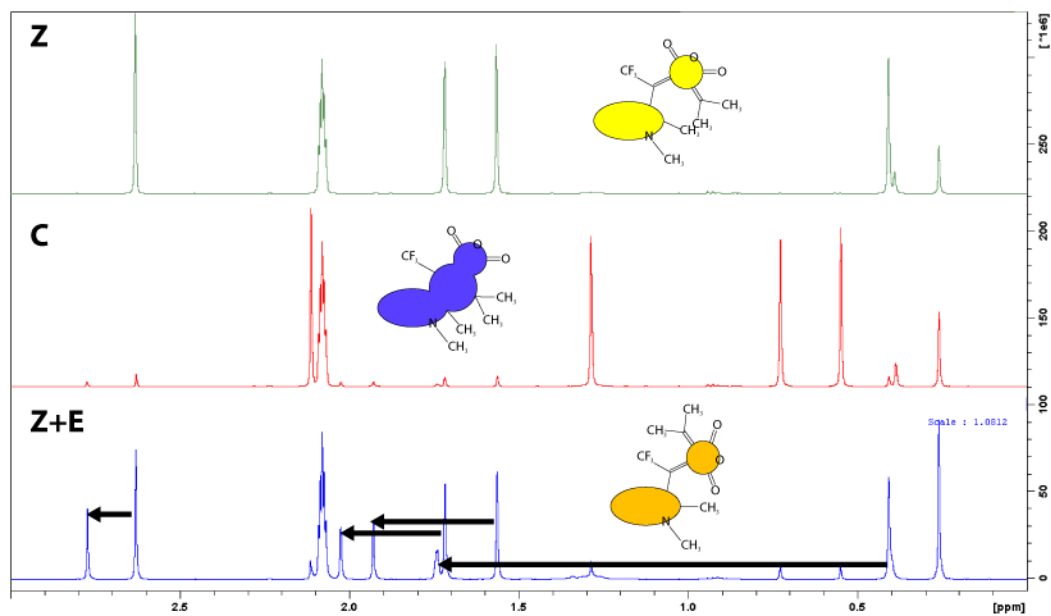


Figure S1: NMR Spectra of the CH_3 -signals of the three accumulated photo-isomers measured in toluene.

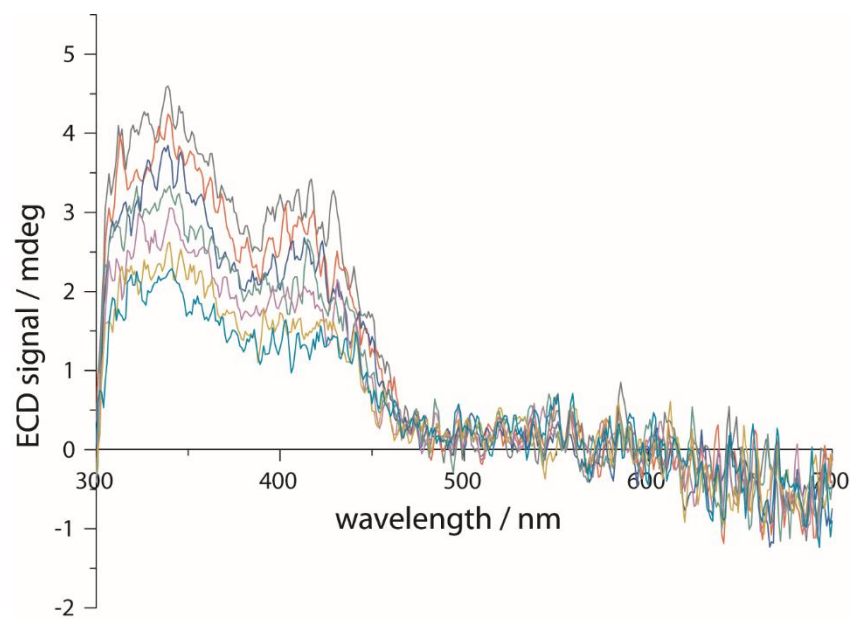


Figure S2: Series of Z_p -ECD spectra measured in toluene at 35 °C.

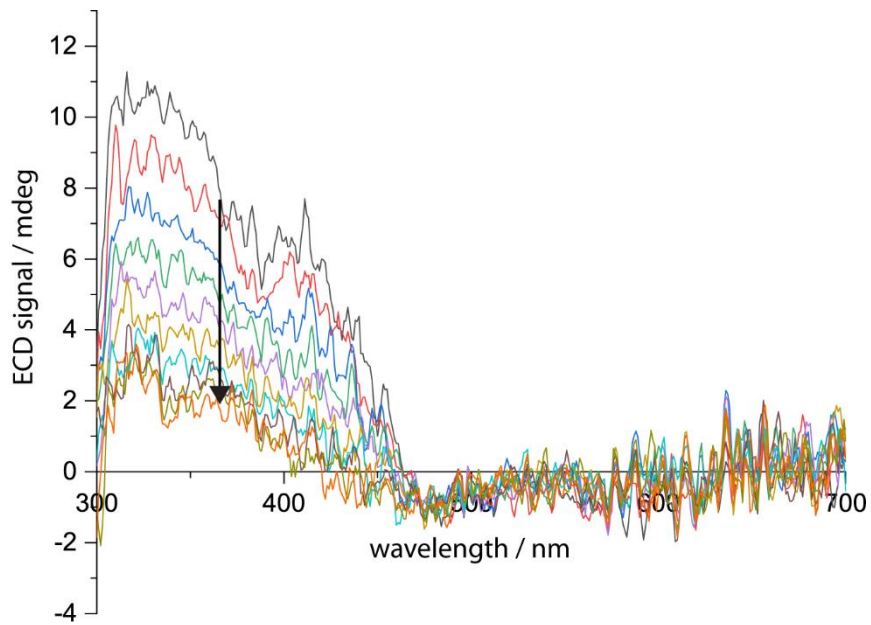


Figure S3: Series of Z_p -ECD spectra measured in toluene at 50 °C.

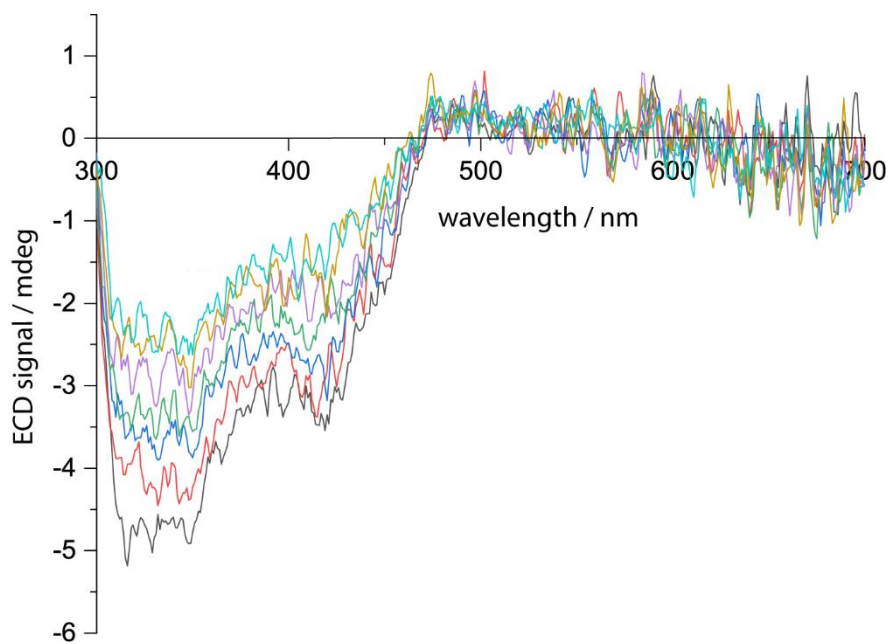


Figure S4: Series of Z_M -ECD spectra measured in toluene at 35 °C.

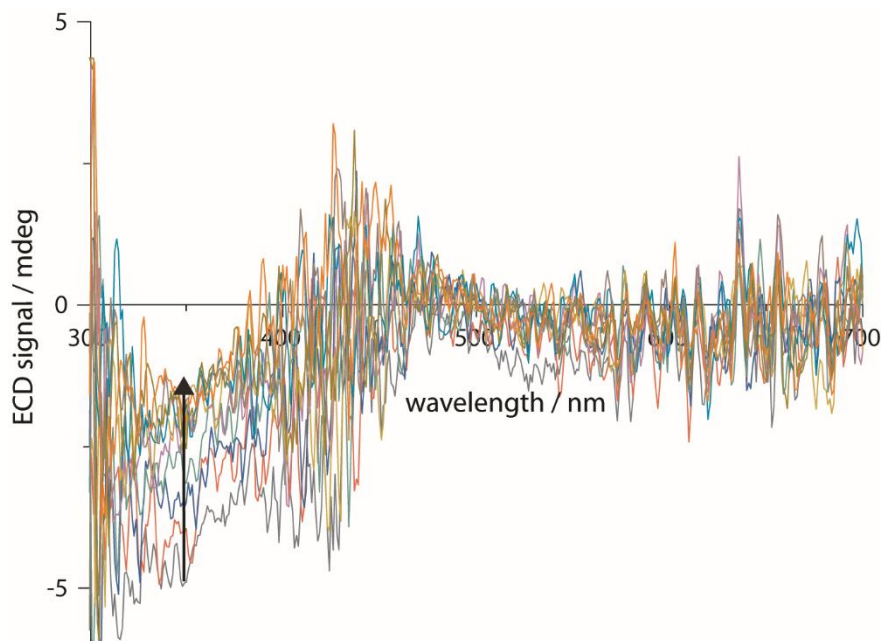


Figure S5: Series of Z_M -ECD spectra measured in toluene at 50 °C.

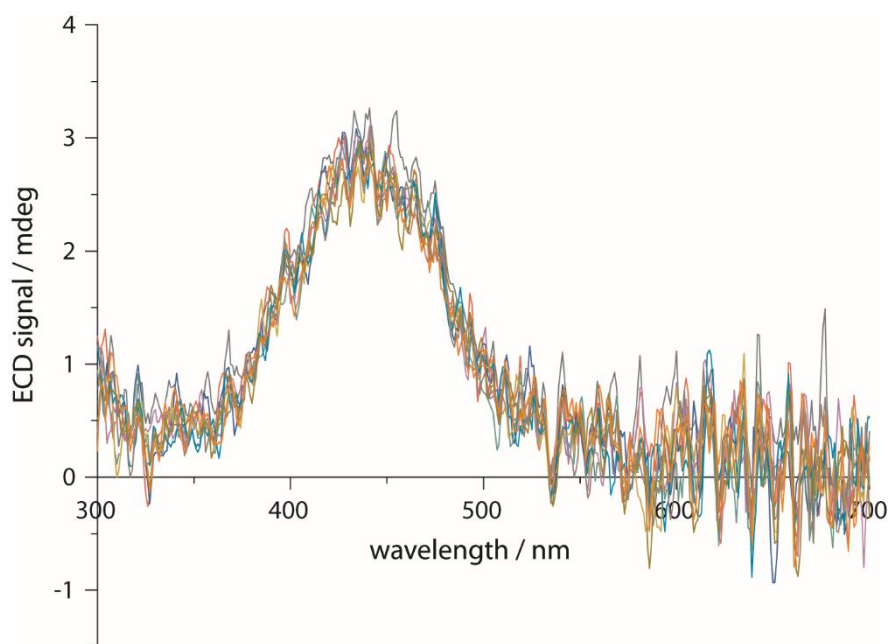


Figure S6: Series of E_P -ECD spectra measured in toluene at 50 °C.

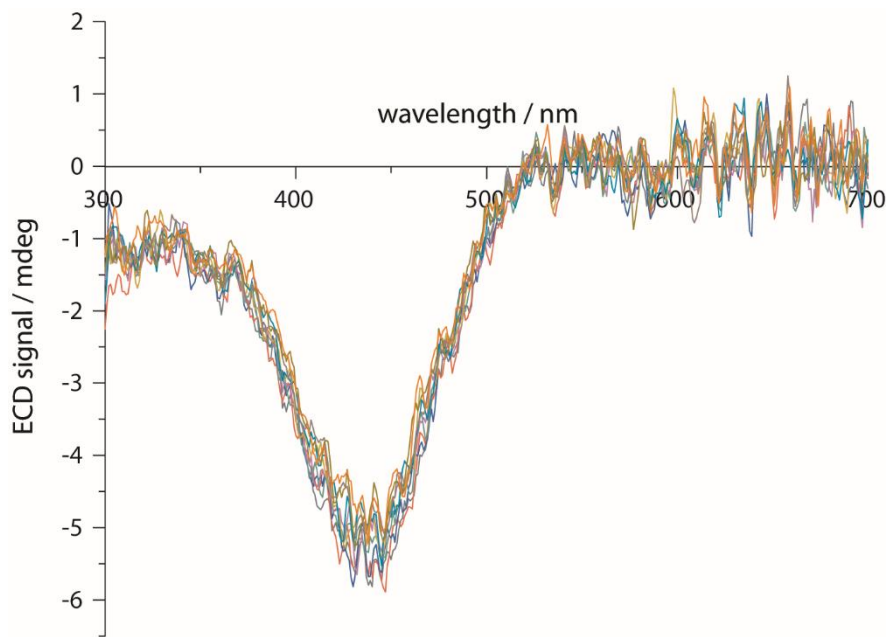


Figure S7: Series of E_M -ECD spectra measured in toluene at 50 °C.

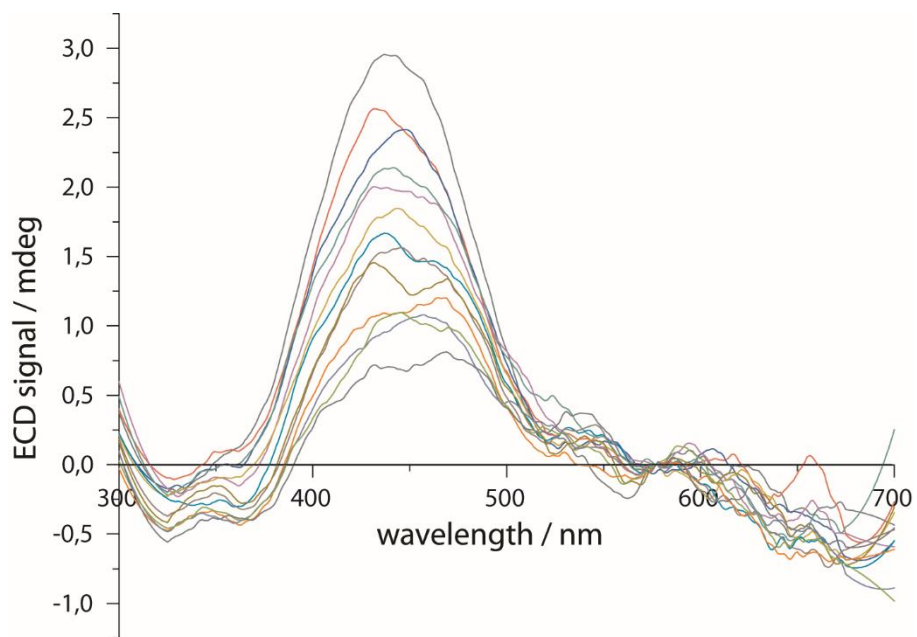


Figure S8: Series of E_P -ECD spectra measured in toluene at 70 °C.

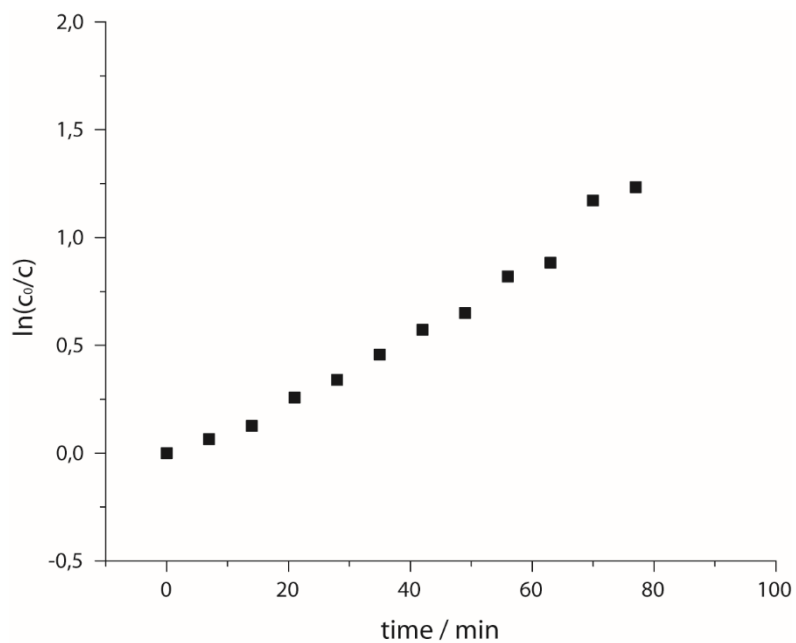


Figure S9: Thermal racemization for E_P at 70 °C. The y-axis shows the integral over the respective ECD curves – indicative for the enantiomeric excess. All measurements were performed in toluene.

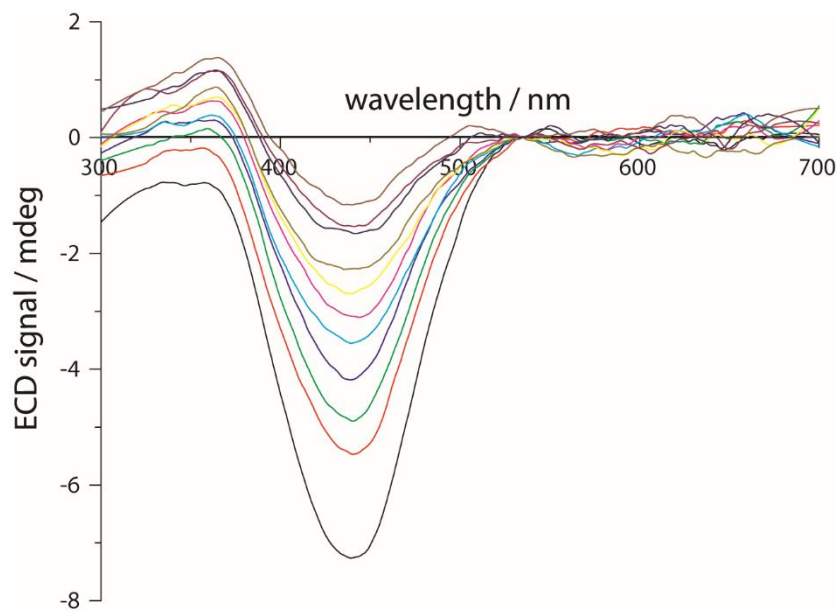


Figure S10: Series of E_M -ECD spectra measured in toluene at 70 °C.

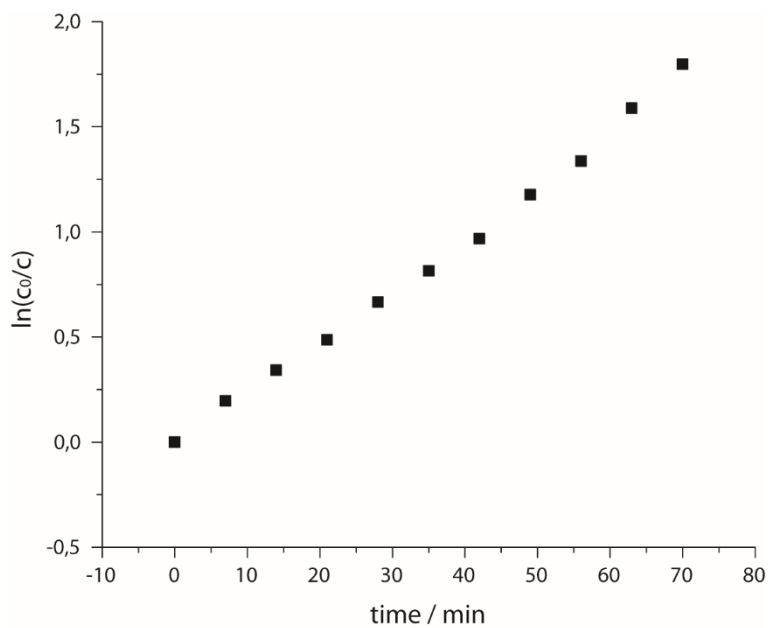


Figure S11: Thermal racemization for E_M at 70 °C. The y-axis shows the integral over the respective ECD curves – indicative for the enantiomeric excess. All measurements were performed in toluene.

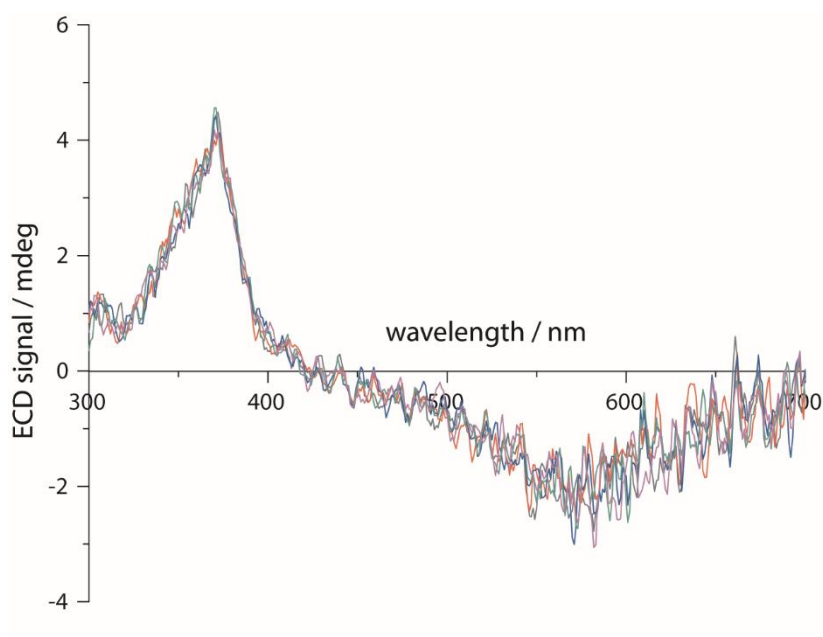


Figure S12: Series of C_R -ECD spectra measured in toluene at 70 °C.

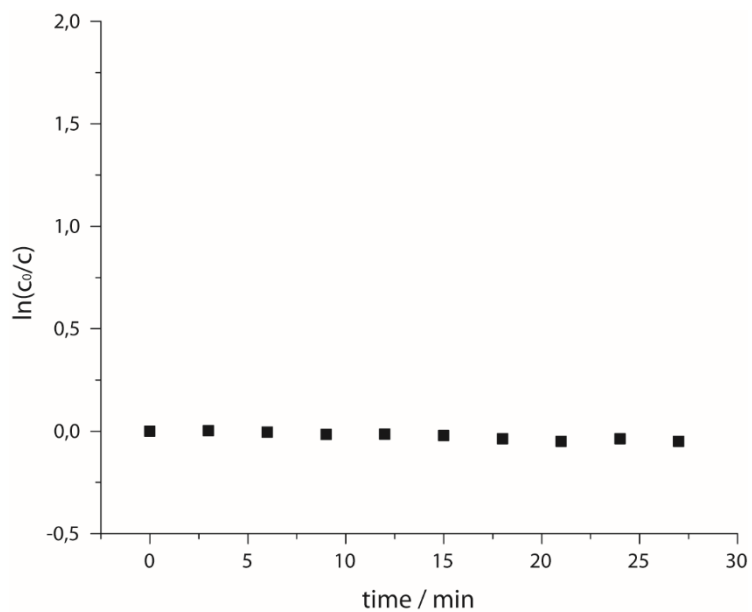


Figure S13: Thermal racemization for C_R at 70 °C. The y-axis shows the integral over the respective ECD curves – indicative for the enantiomeric excess. All measurements were performed in toluene.

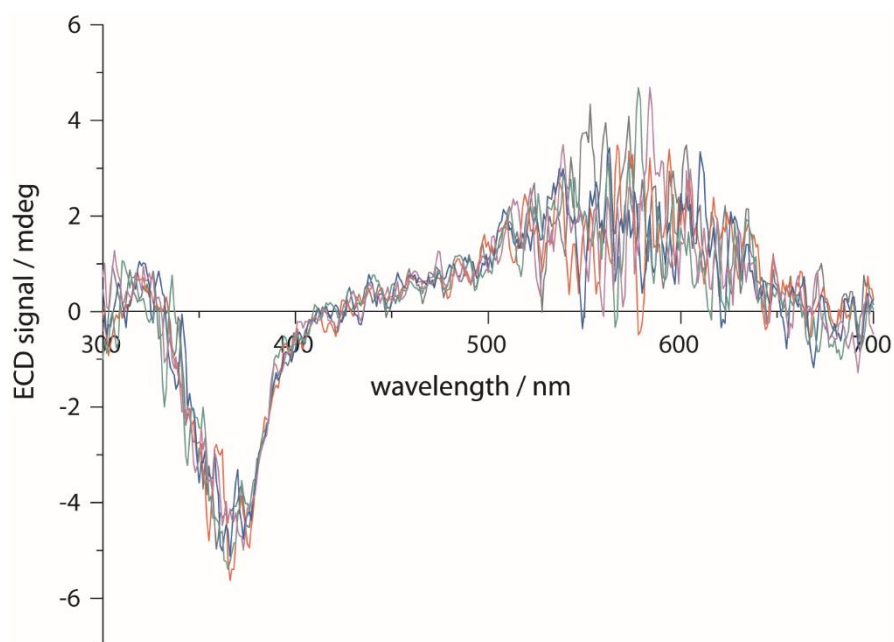


Figure S14: Series of C_S -ECD spectra measured in toluene at 70 °C.

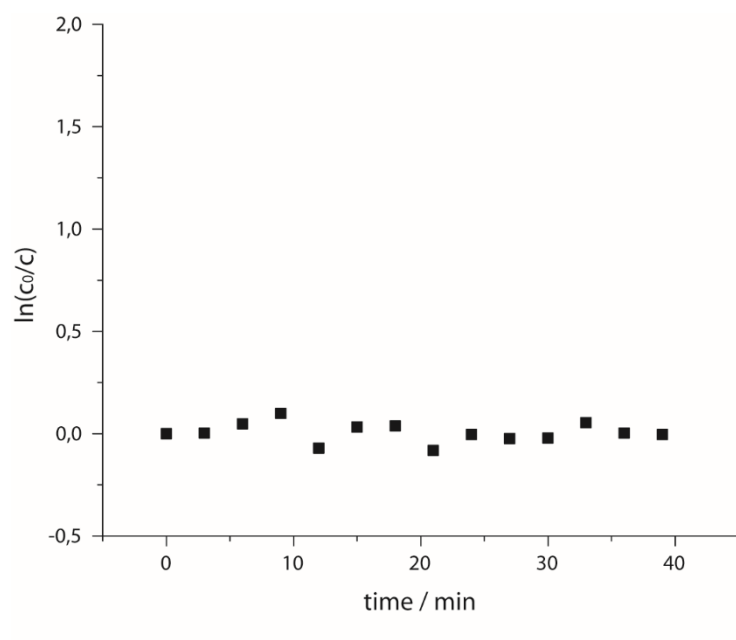


Figure S15: Thermal racemization for C_5 at 70 °C. The y-axis shows the integral over the respective ECD curves – indicative for the enantiomeric excess. All measurements were performed in toluene.

3. Computational Details

All calculations were carried out using Psi4, version 1.4dev (4) at the CAM-B3LYP/def2-SVP level of theory. (5, 6) Relaxed torsion scans for the E- and Z-isomers were run with torsiondrive (7) interfaced to Psi4 with an angle step size of 15°. Subsequently, local minima of the PES were extracted and re-optimized with Psi4 without any constraints. In the same manner, both stereoisomers of the cyclized fulgide were optimized. This resulted in six optimized geometries (two representative atropisomers of E and Z, and two stereoisomers of C). For the calculation of the relaxed scans along the dihedral angle (Figure 5 of the main manuscript) the convergence criteria for the geometry optimization was increased by one order of magnitude relative to the default settings to avoid hysteresis artefacts. All optimized geometries and scan trajectories can be found in a ZIP folder in the SI. For all structures, the 10 lowest excited singlet states were computed with TD-CAM-B3LYP/def2-SVP. Rotatory strengths were obtained and convoluted using Psi4-internal functions with a Lorentzian function ($\gamma = 0.124$ eV) to yield the final ECD spectra (Figure S19). The ECD spectra were then mapped to the corresponding experimental spectrum, shown in the main part of the manuscript. Molecular structures were visualized using VMD.(8)

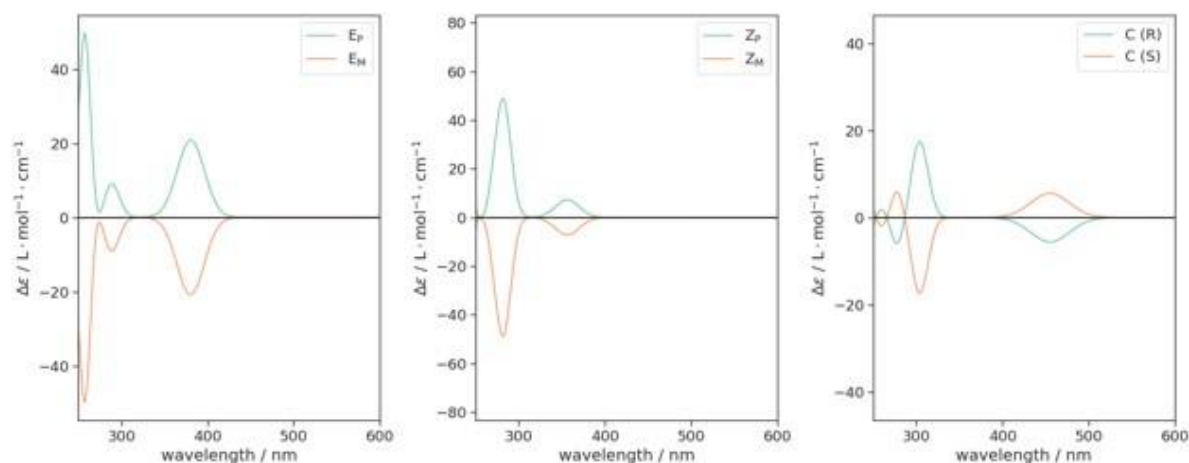


Figure S16: ECD spectra computed at the TD-CAM-B3LYP/def2-SVP level of theory. Rotatory strength stick spectra were convoluted a Lorentzian function ($\gamma = 0.124$ eV).

4. References

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