Chemistry–A European Journal

Supporting Information

Palladium Complexes of *N*-Methylcorroles

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Reagents and solvents (Aldrich) were of the highest grade available and were used without further purification. Thin-layer chromatography (TLC) was performed on Sigma-Aldrich silica gel plates. Chromatographic purification of the reaction products was accomplished by using silica gel 60 (70–230 mesh, Sigma-Aldrich, St. Louis, MO, USA) as a stationary phase. UV-vis spectra were measured on a Varian Cary 50 Spectrophotometer using CH_2Cl_2 as solvent. Electronic circular dichroism (ECD) spectra were recorded at room temperature with a JASCO J815 spectropolarimeter in a 0.5 mm quartz cell and CH_2Cl_2 solvent.
NMR experiments were performed in deuterated acetone at 15 °C and recorded with a Bruker Avance spectrometer operating at 700 MHz for ^1H, equipped with a 5 mm inverse TXI probe and z-axis gradients.
High-resolution mass spectra were recorded on an Agilent 6520 Q-TOF instrument.
UV–Vis absorption spectra were recorded with a Perkin-Elmer Lambda 45 spectrophotometer (Boston, MA, USA), while the fluorescence spectra were recorded with a Horiba Jobin Yvon Fluoromax-4 (Kyoto, Japan). The fluorescence quantum yields were determined using tetraphenylporphyrin (TPP) in toluene as a reference with $\Phi = 0.11$. Excited state lifetime measurements were performed using an Edinburgh Analytical Instruments FLS920 spectrofluorimeter, equipped with an LDH-C 405 nm pulsed diode laser and with a Time Correlated Single Photon Counting (TCSPC) device, which is able to measure lifetimes in a range between 0.5 ns and 30 μs. The same instrument was used for the analyses in the NIR region, using an Edinburgh Instruments Xe900 xenon lamp for the excitation and an Edinburgh Instruments EI-L germanium detector.

For all the measurements at room temperature, the spectra of 1 μM solutions in CH_2Cl_2 were recorded using quartz cells with path length of 1.0 cm. For the measurements at 77K, 10 μM solutions in CH_2Cl_2:MeOH = 1:1 (v/v) were analysed in glass tubes with a diameter of 0.1 cm, immersed in liquid nitrogen. For the analyses in absence of oxygen, the solutions were degassed with the freeze-thaw-pump methodology, using six cycles.

Chiral HPLC enantiomers separation.
The racemic mixture of compound **2** was eluted on (*R,R*)-Whelk-O1 c.s.p., revealing the peaks at λ = 350 nm. Isocratic (hexane:isopropanol 99:1 *v:v* mobile phase and 1.0 mL/min flow were employed. The two enantiomers were eluted at tr_1 = 35.49 min and tr_2 = 44.47 min. Compound **3** was separated on a Chiralcel OD-H c.s.p. with isocratic hexane:IPA 99:1 *v:v* mixture and 0.5 mL/min flow, detecting the peaks at λ = 350 nm. The two enantiomers were eluted tr_1 = 20.72 min and tr_2 = 23.13 min. Enantiomers of **2** and **3** were collected after HPLC separation. For **2** 1.8 mg (90 ee%) of the first eluted enantiomer and 1.1 mg (84 ee%) of the second eluted enantiomer were recovered. For **3** 2.0 mg of the first eluted enantiomer (30% ee) and 2.0 mg of the second eluted enantiomer (80% ee) were recovered.

Computational details.
Arbitrarily fixing the (*R*)-**3** and (*S*)-**2** absolute configurations, preliminary molecular mechanics (MM) conformational analyses were carried out by Spartan02 package[31] employing MMFF94s force field and Monte Carlo search. All possible conformers within an energy range of 30 kcal/mole were collected. Further Density Functional Theory (DFT) optimization was carried out on conformers found by MM by Gaussian09 package[32] using DFT/B3LYP/6-311++G(d,p)/IEFPCM(CH_2Cl_2) level of theory. IEFPCM implicit solvation model[33] allowed to take into account solvent effect of CH_2Cl_2. Conformer structures were employed as input geometries for TDDFT/ωB97XD/def2-TZVP/IEF-PCM(CH_2Cl_2 computations of UV and ECD spectra. The first 100 excited states were taken into account. Spec Dis v1.51 package[34] allowed to obtain ECD spectra from calculated excitation energies and rotational strengths, as a sum of Gaussian functions centered at the transitions wavelength and applying a σ (width of the band at ½ height) parameter of 0.2 eV. The ECD spectra of enantiomers (*S*)-**3** and (*R*)-**2** were obtained by multiplying the computed spectra by -1.

Amplex Red assay.
Materials
10-Acetyl-3,7-dihydroxyphenoxazine (Amplex Red) (Cat. No. 90101); Type VI-A Peroxidase from horseradish lyophilized powder (HRP) (Cat. No. P6782); Hydrogen Peroxide Solution 30% (w/w) (Cat. No. 31642-M);

The Amplex Red assay allowed the quantification of peroxides in a solution. It is based on the reaction between the not fluorescent Amplex Red with hydrogen peroxide. The reaction is catalyzed by horseradish peroxidase (HRP) and produces the fluorescent Resorufin. A working solution (WS), containing Amplex Red and HRP dissolved in PB, was freshly prepared. 90 μL of each sample were loaded into the wells of a 96-multiwell plate. One plate was irradiated, while an identical plate was kept in the dark.
The irradiated plate was exposed to a light source (Valex 30 W, 6500 K, cold white LED) for 30 min (irradiance = 1.5 mW cm^{-2},). The irradiance was measured with the photo-radiometer Delta Ohm LP 471 RAD.
Then, 10 μL of the WS was added to each sample and both the plates were kept in incubation for 30 min in dark conditions at room temperature. The absorbance of the resorufin produced was recorded at 560 nm. To convert the absorbance values to the equivalent H_2O_2 concentration, a calibration curve was created using standard solutions of H_2O_2. The contribution of the H_2O_2 produced by the samples kept in the dark was subtracted from the H_2O_2 concentration that was estimated for the corresponding irradiated samples. All the measurements were performed using an EnSpire® Multimode Plate Reader (PerkinElmer).

Docking studies
The possible interaction sites between **5**/**6** and HSA were determined by docking. By using the crystallographic structure of HSA (PDB = 1n5u) deposited in the protein data bank (PDB), and the crystallographic structures of **5** and **6** the PatchDock software was used.

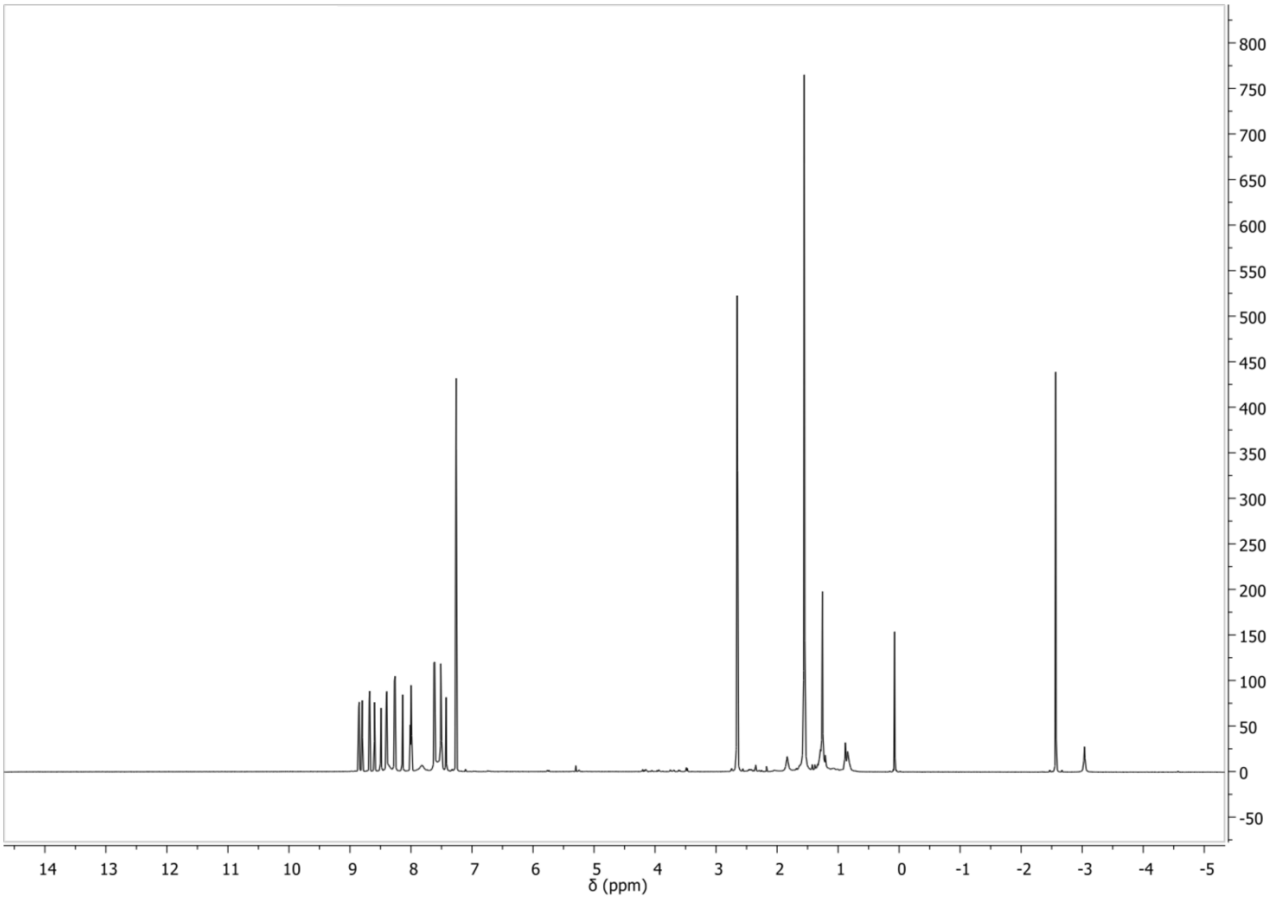


Figure S1. ^{1}H-NMR spectrum of **2** in $CDCl_3$ (700 MHz, *298K)*.

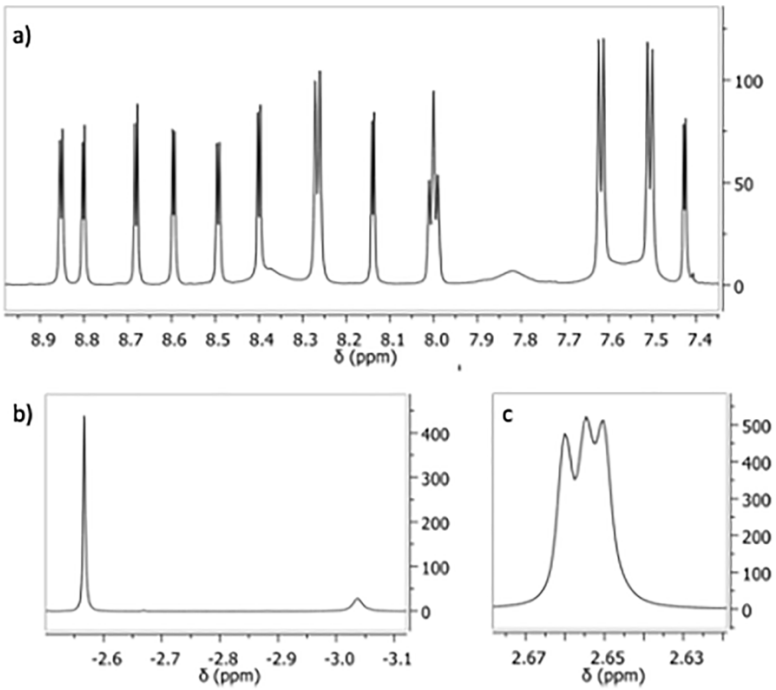


Figure S2. Selected region of the ^{1}H-NMR spectrum of **2** in $CDCl_3$ (700 MHz, *298K)*: a) aromatic region, b) N-21 methyl resonance, c) CH_3 signals of tolyl group

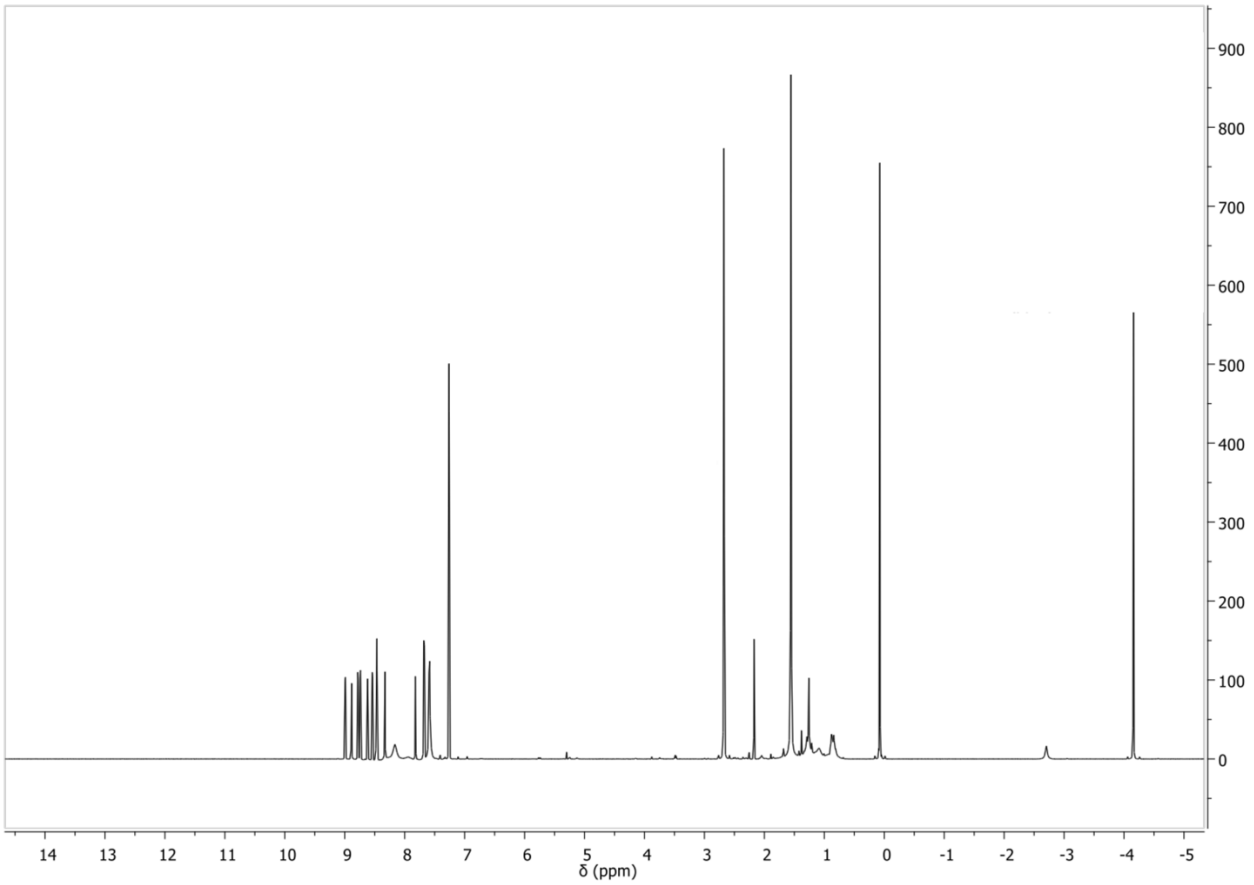


Figure S3. ^{1}H-NMR spectrum of **3** in $CDCl_3$ (700 MHz, *298K)*.

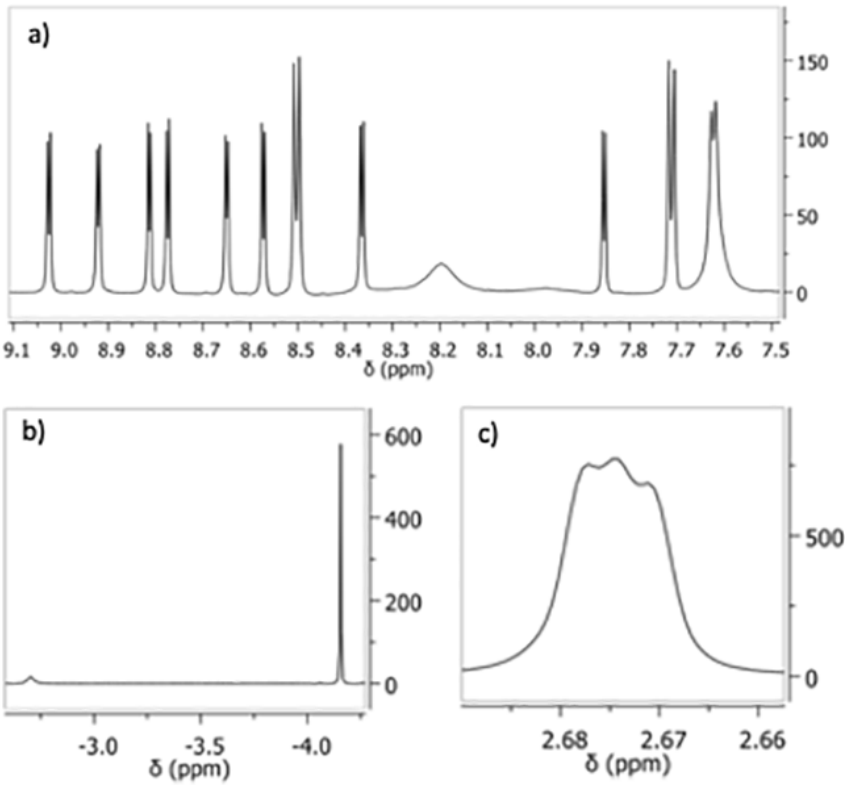


Figure S4. Selected region of the ^{1}H-NMR spectrum of **3** in $CDCl_3$ (700 MHz, *298K)*: a) aromatic region, b) N-21 methyl resonance, c) CH_3 signals of tolyl group

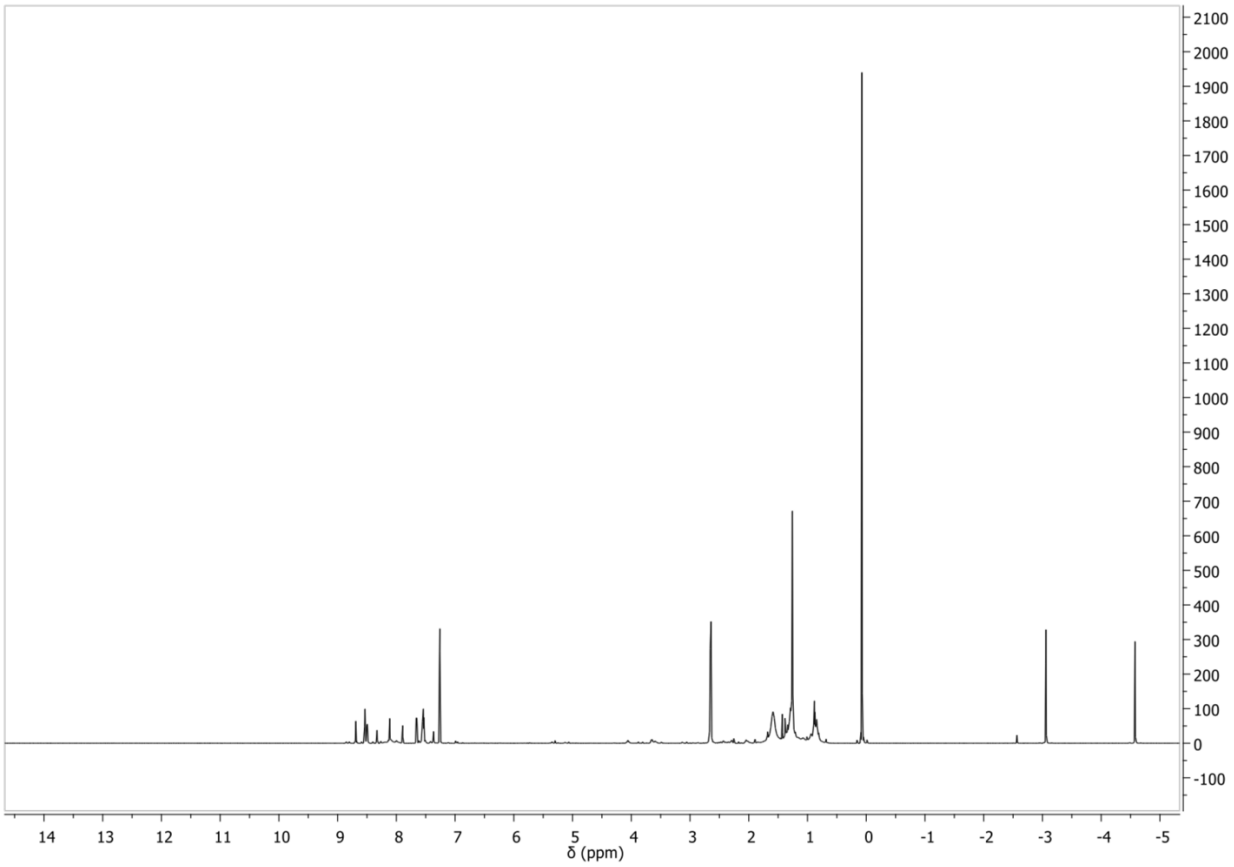


Figure S5. ^{1}H-NMR spectrum of **4** in $CDCl_3$ (700 MHz, *298K).*

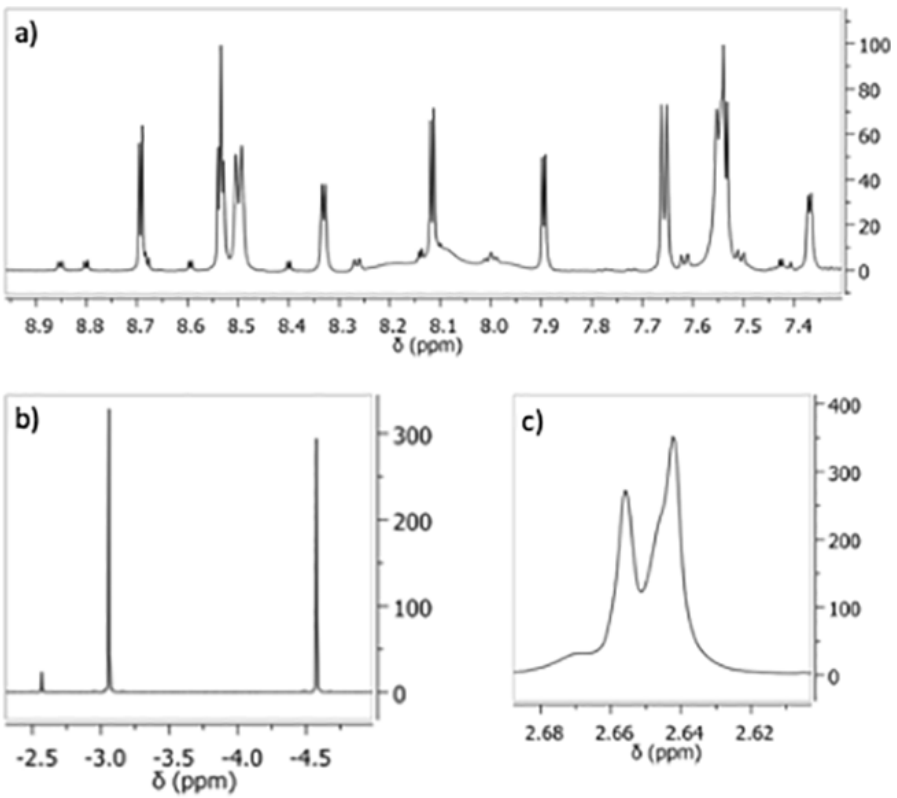


Figure S6. Selected region of the ^{1}H-NMR spectrum of **4** in $CDCl_3$ (700 MHz, *298K)*: a) aromatic region, b) N-21 methyl resonance, c) CH_3 signals of tolyl group

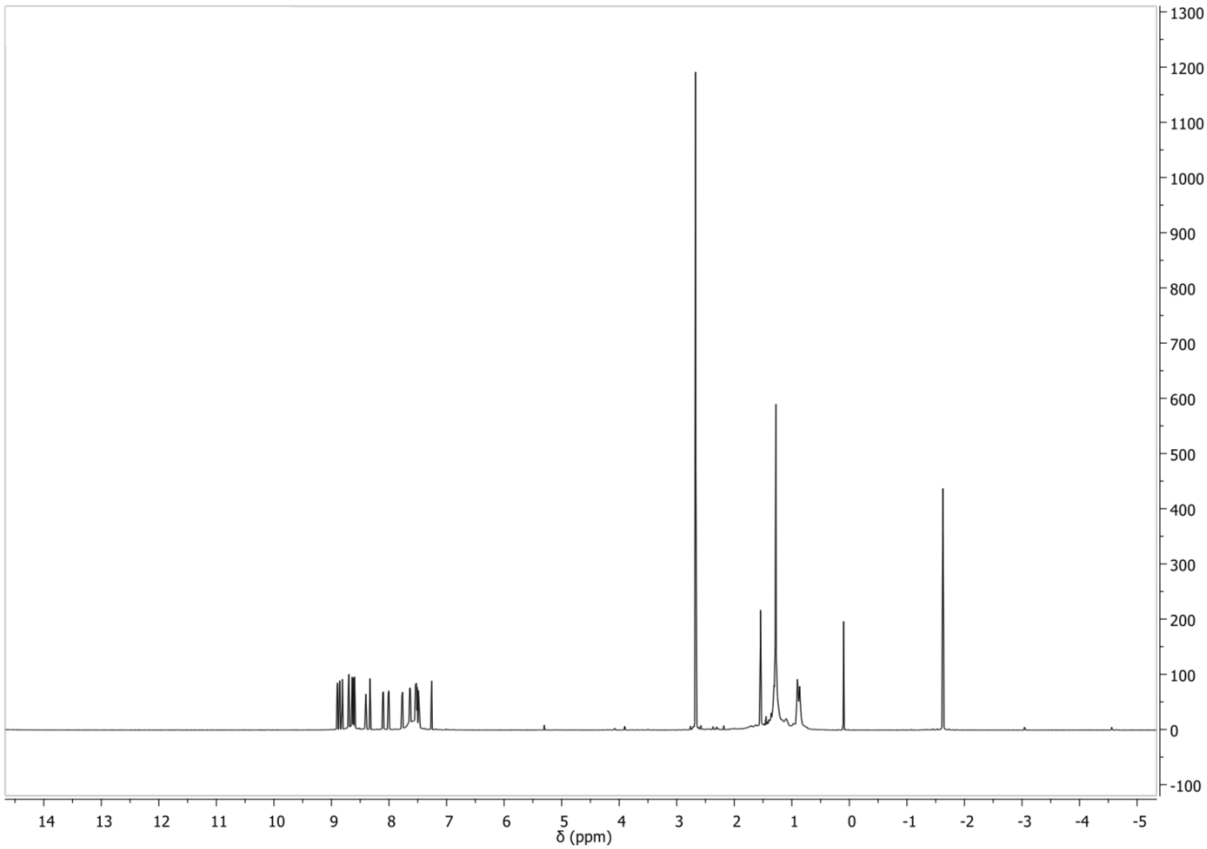


Figure S7. ^{1}H-NMR spectrum of **5** in $CDCl_3$ (700 MHz, *298K).*

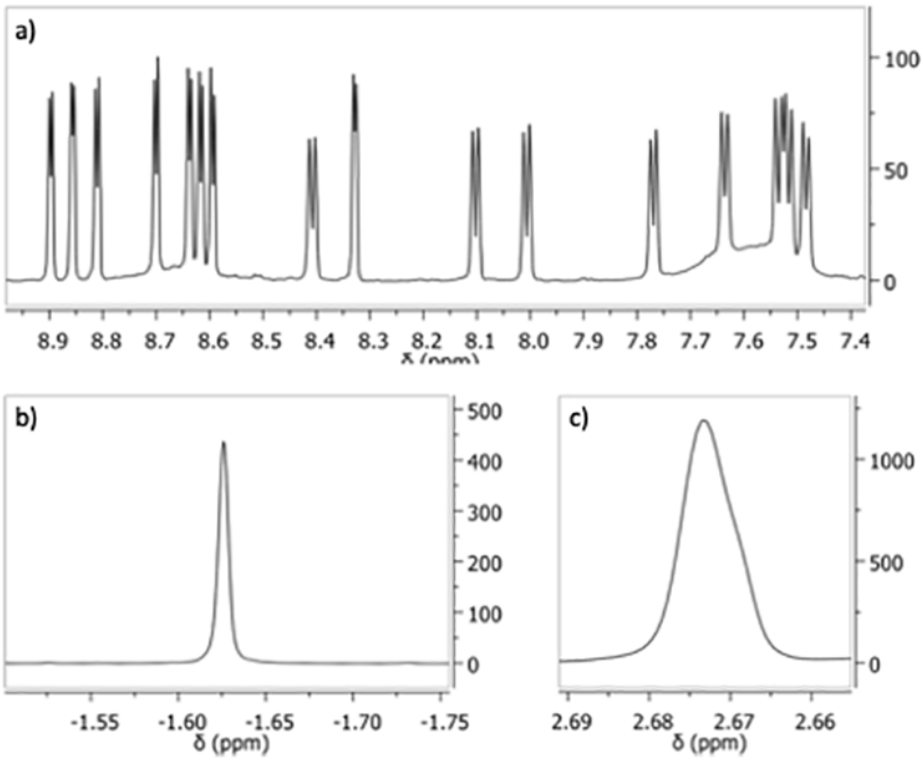


Figure S8. Selected region of the ^{1}H-NMR spectrum of **5** in $CDCl_3$ (700 MHz, *298K)*: a) aromatic region, b) N-21 methyl resonance, c) CH_3 signals of tolyl group

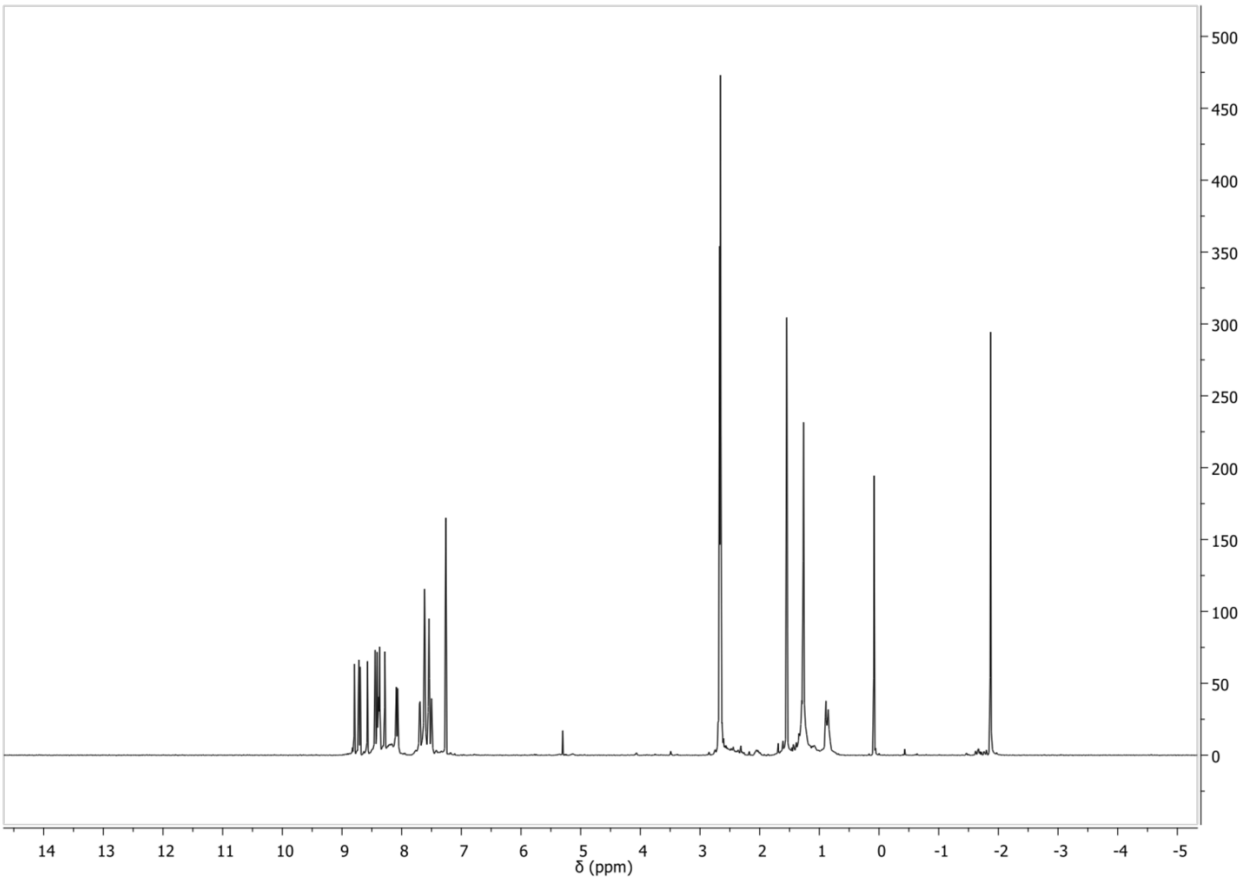


Figure S9. ^{1}H-NMR spectrum of **6** in $CDCl_3$ (700 MHz, *298K).*

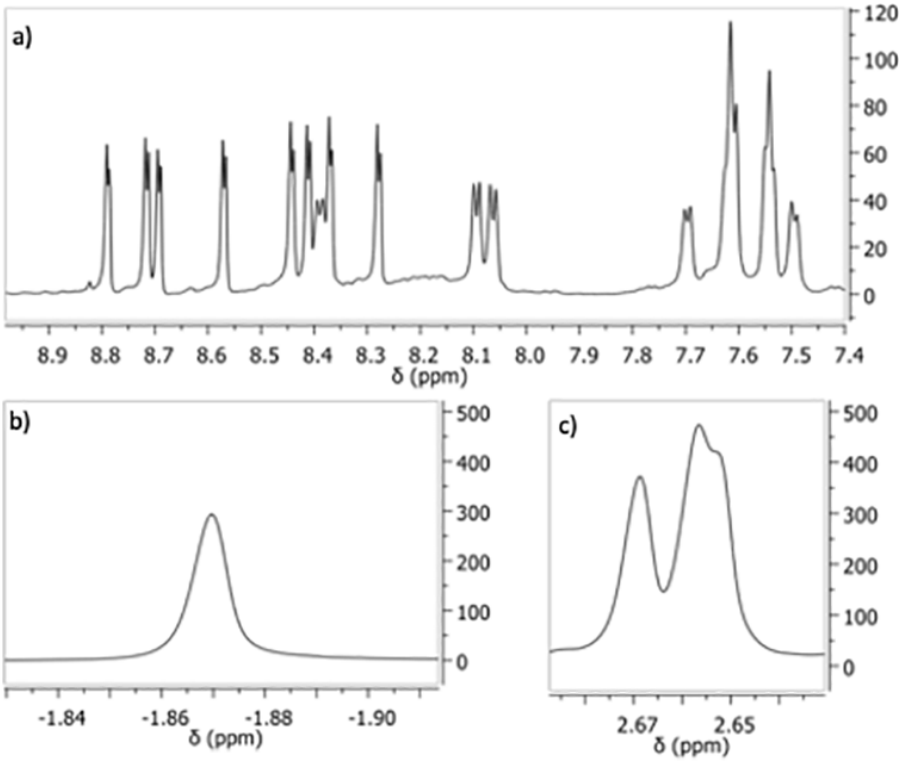


Figure S10. Selected region of the ^{1}H-NMR spectrum of **6** in $CDCl_3$ (700 MHz, *298K)*: a) aromatic region, b) N-21 methyl resonance, c) CH_3 signals of tolyl group

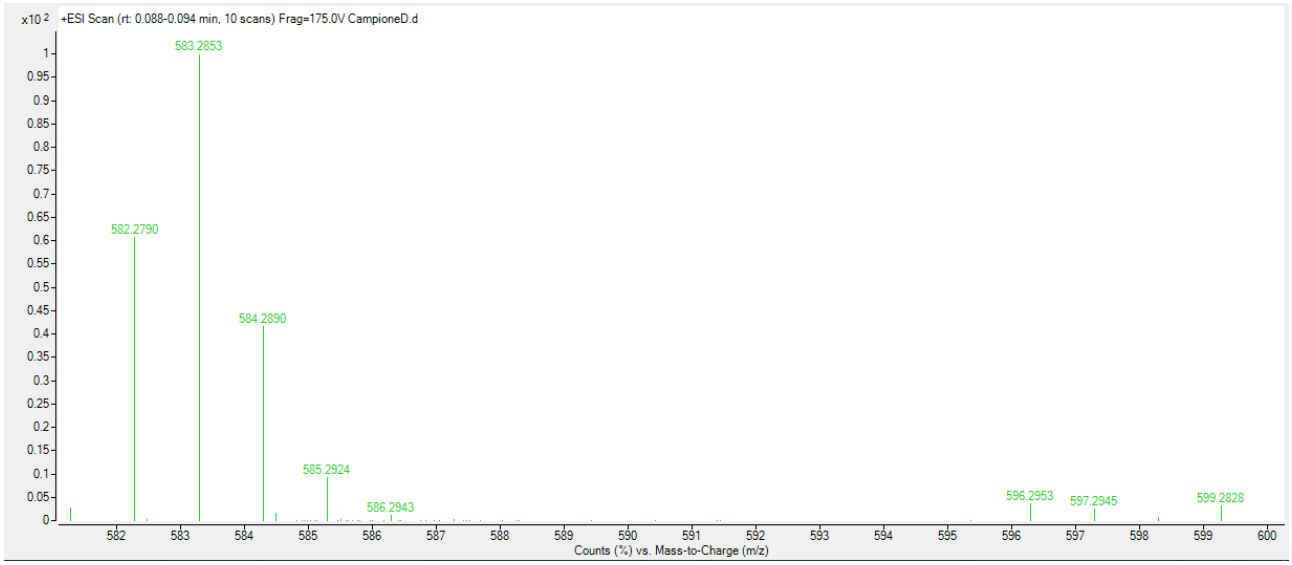


Figure S11. Mass spectrum of **2**.

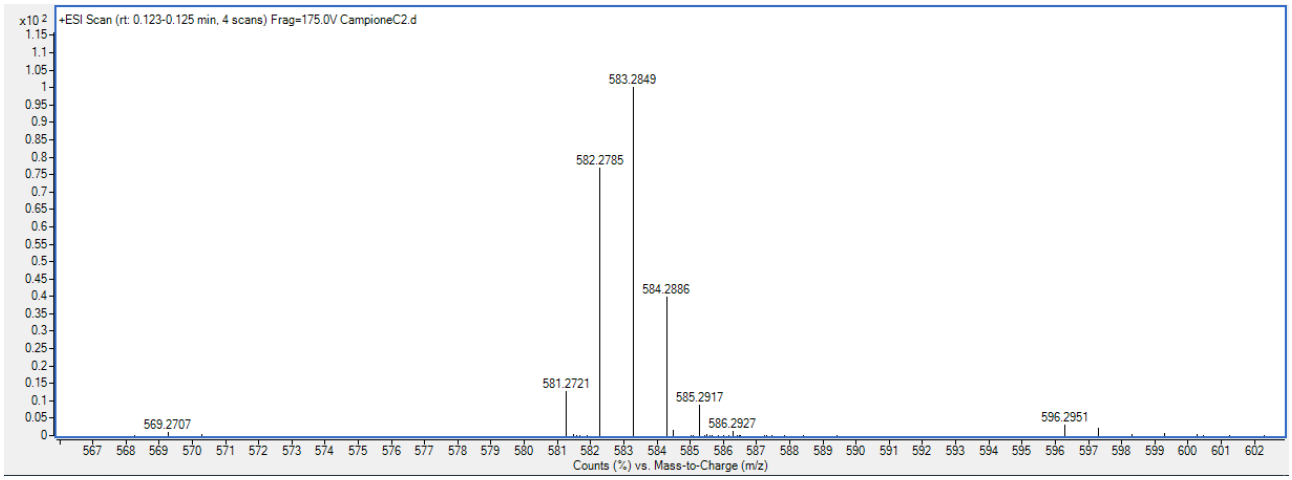


Figure S12. Mass spectrum of **3**.

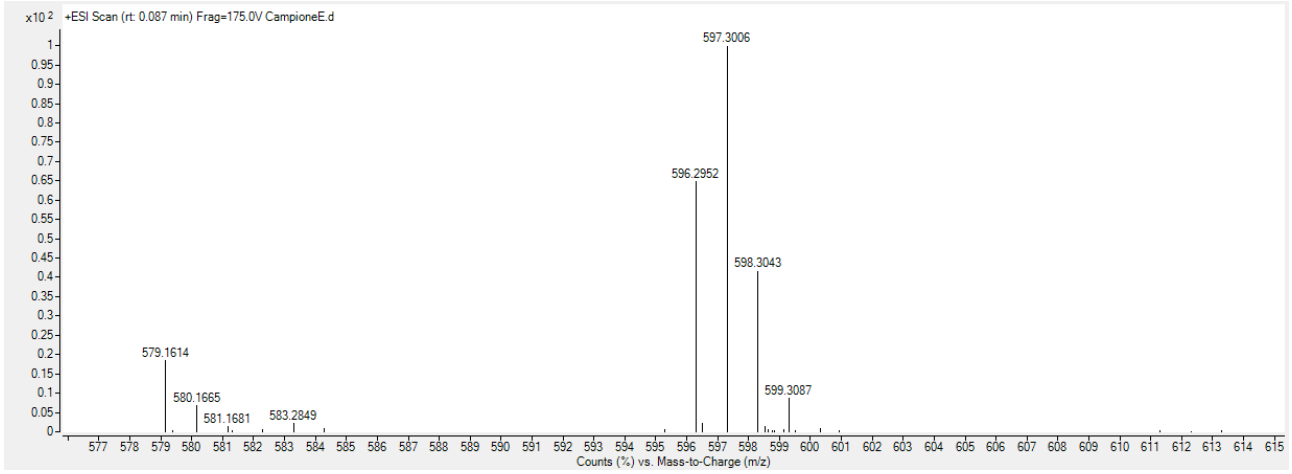


Figure S13. Mass spectrum of **4**.

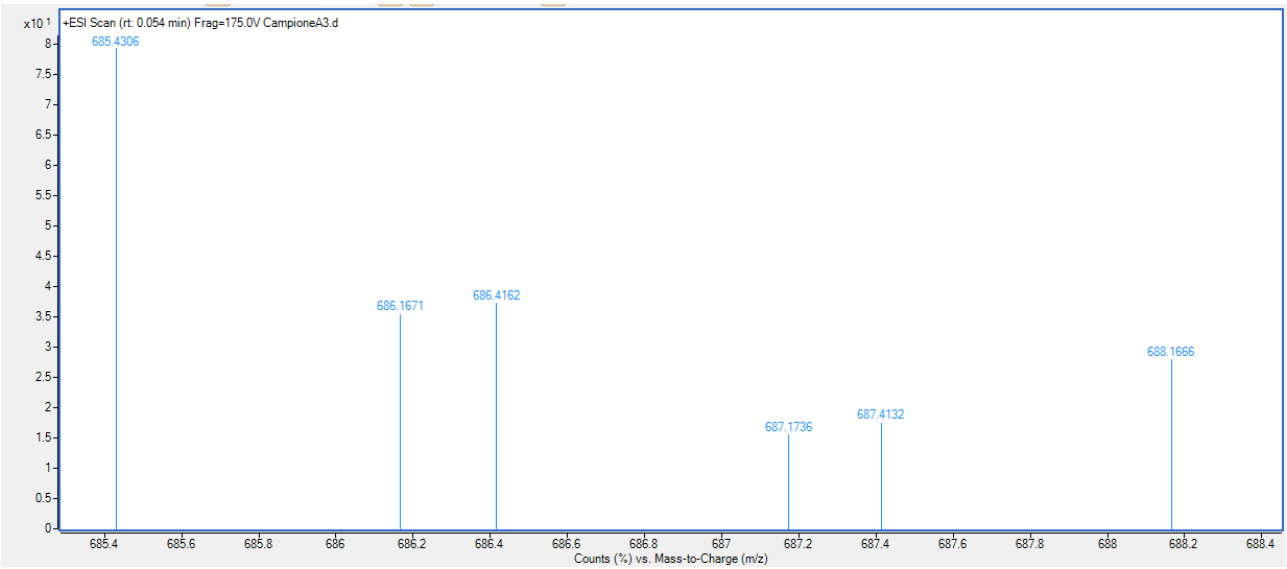


Figure S14. Mass spectrum of **5**

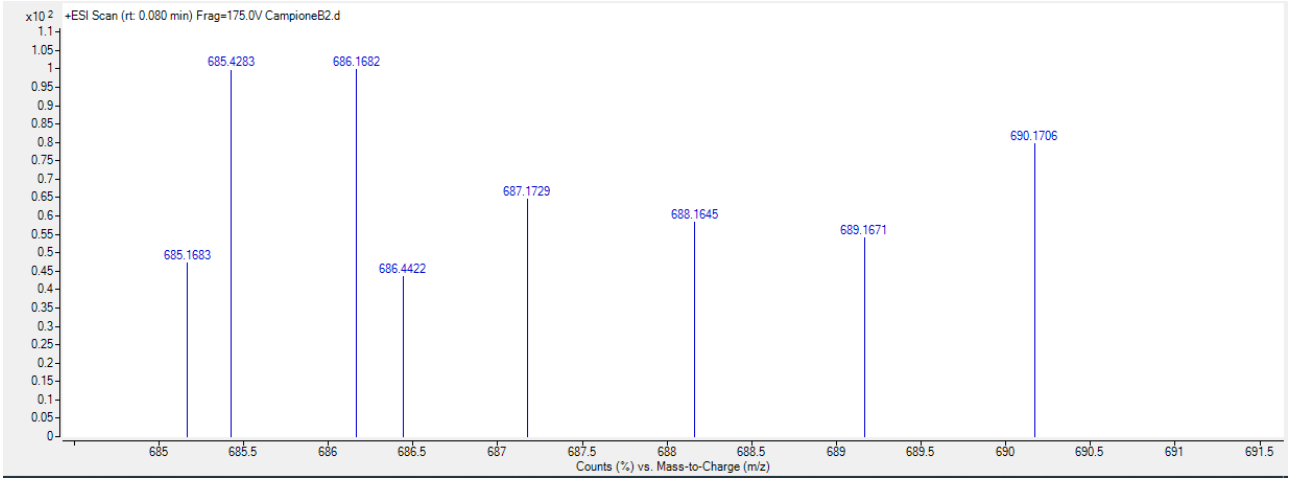


Figure S15. Mass spectrum of **6**

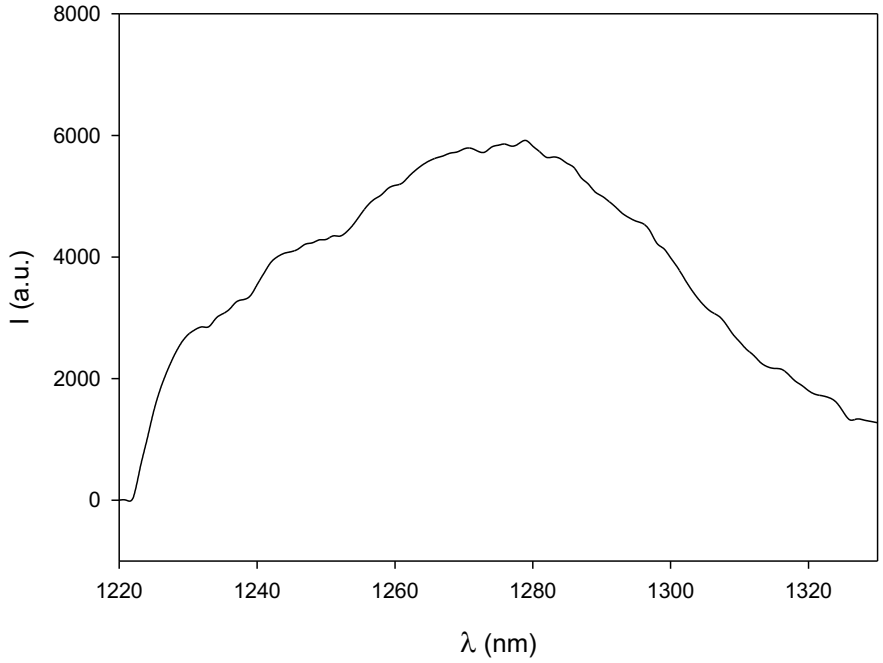


Figure S16. Emission spectra of **2** in aerated DCM solution in the NIR region at room temperature (λ_{exc} = 400 nm).

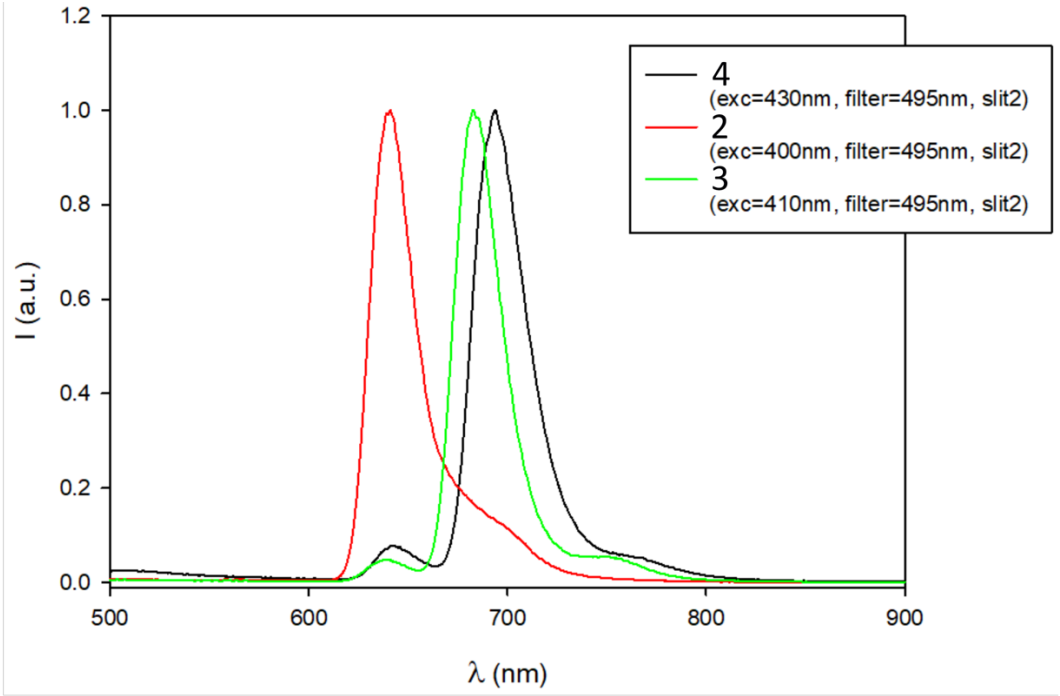


Figure S17. Normalized emission spectra of corroles **2**-**4** in CH_2Cl_2:CH_3OH 1:1 at 77 K.

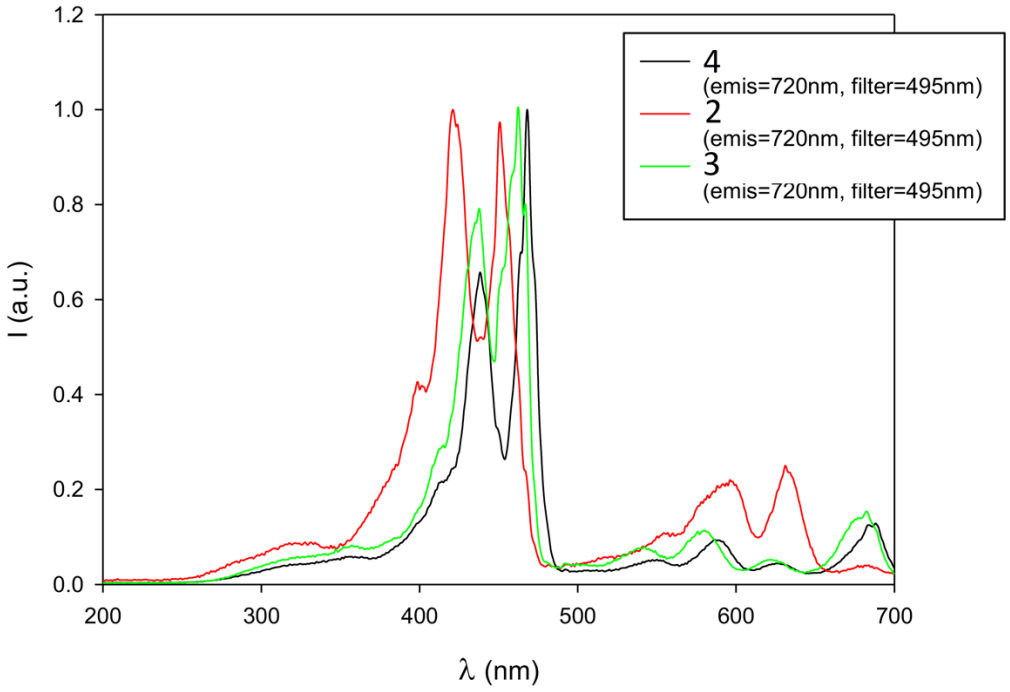


Figure S18. Normalized excitation spectra of corroles **2**-**4** in CH_2Cl_2:CH_3OH 1:1 at 77 K.

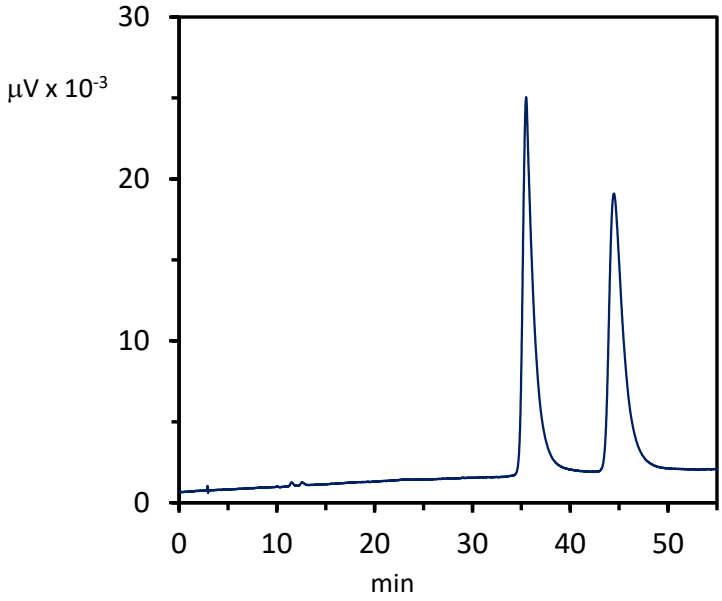


Figure S19. HPLC separation of **2**. Column: (*R*,*R*)-Whelk-O1 250 mm × 4.6 mm (5 μ); mobile phase: hexane:isopropanol (99:1 v/v); flow rate: 1.0 mL min^{-1}. UV detection at 350 nm. *T* = 25 °C. First enantiomer t_{r1} = 35.49 min, second enantiomer t_{r2} = 44.47 min.

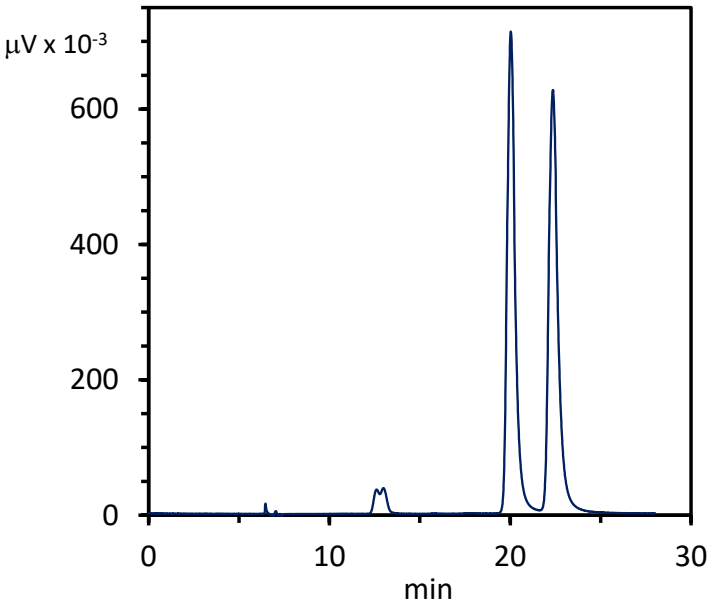
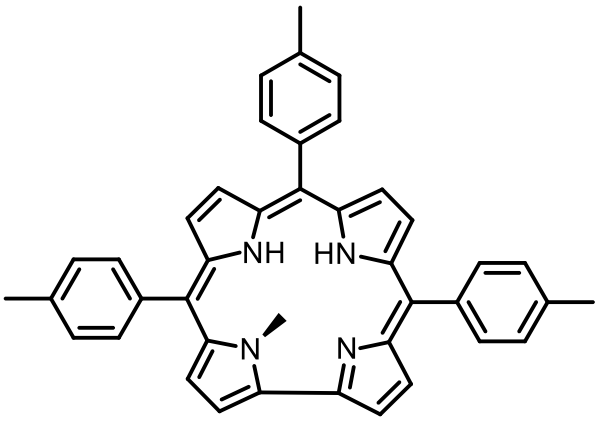
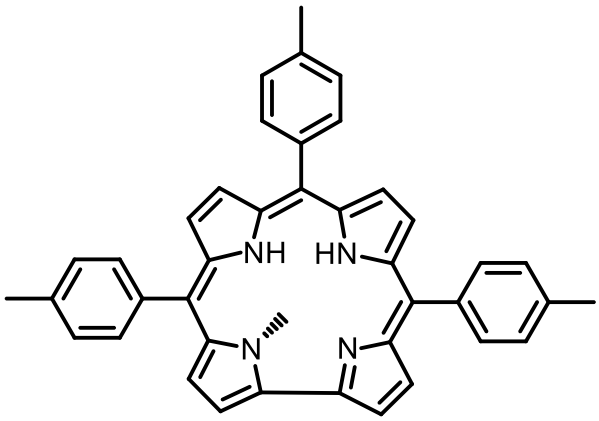


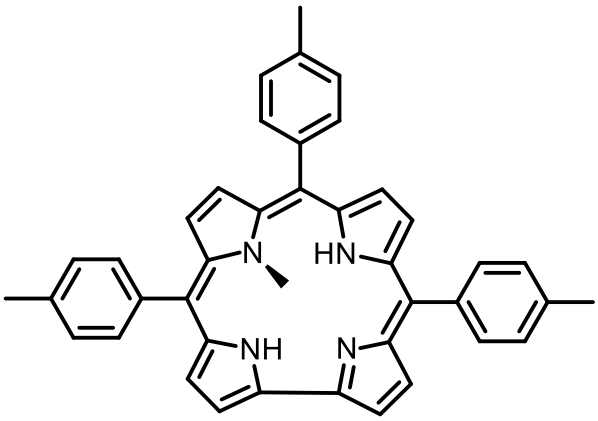
Figure S20. HPLC separation of **3**. Column: Chiralcel OD-H 250 mm × 4.6 mm (5 μ); mobile phase: hexane:isopropanol (99:1 v/v); flow rate: 0.5 mL min^{-1}. UV detection at 350 nm. *T* = 25 °C. First enantiomer t_{r1} = 20.72 min, second enantiomer t_{r2} = 23.13 min.



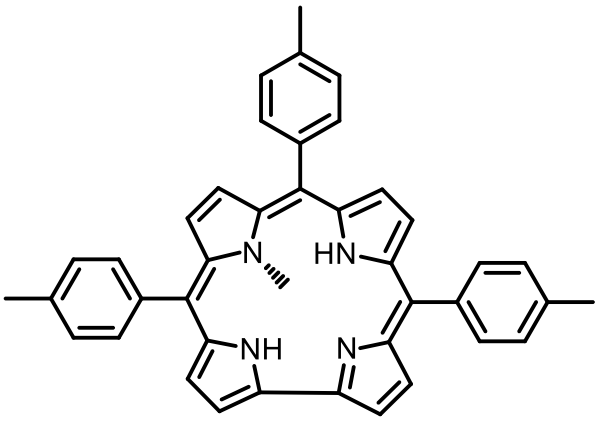
(*R*)-**2**



(*S*)-**2**



(*R*)-**3**



(*S*)-**3**

Figure S21. Structures of stereoisomers of corroles **2** and **3**. Absolute configuration on the stereogenic nitrogen assigned on the basis of the CIP rules.

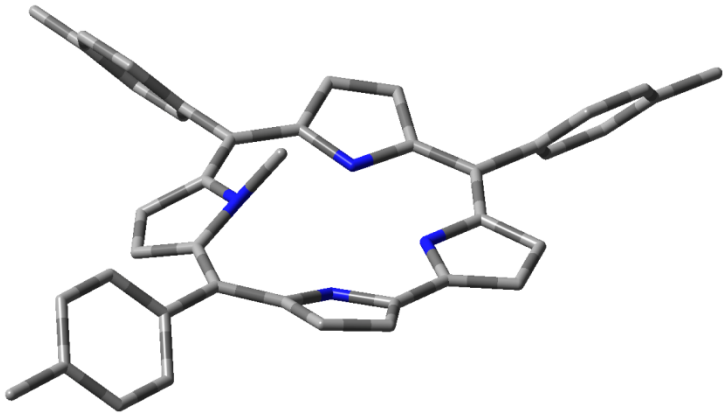


Figure S22. Structure of corrole (*R*)-**3** conformer (DFT/B3LYP/6-311++G(d,p)/IEFPCM(CH_2Cl_2).

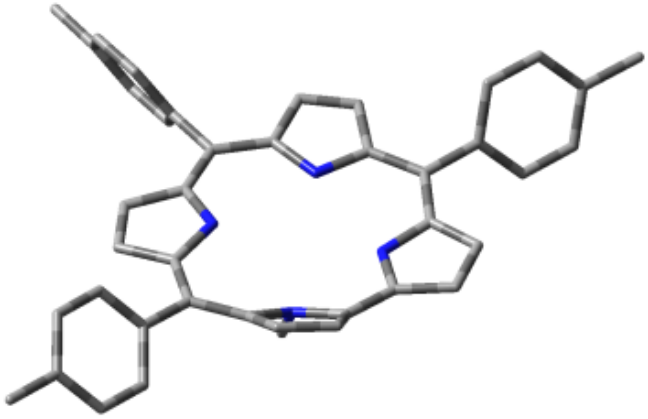


Figure S23. Structure of corrole (*S*)-**2** conformer (DFT/B3LYP/6-311++G(d,p)/IEFPCM(CH_2Cl_2).