SUPPORTING INFORMATION

Synthesis of a helicene-fused porphyrin leading to a π–extended chiral chromophore

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EXPERIMENTAL PROCEDURES

I General method

NMR spectra were recorded on Bruker Advance 300 (300 MHz), 400 (400 MHz), 500 (500 MHz), 600 (600 MHz) spectrometers. Chemical shifts are given in parts per million (ppm) by taking the solvent as a reference: $\delta(CHCl_3)$ = 7.26 ppm, $\delta(CH_2Cl_2)$ = 5.33 ppm for ^1H NMR and $\delta(CHCl_3)$ = 77.16 ppm for ^{13}C NMR (relative to TMS signal). The coupling constants (*J*) are given in Hertz (Hz) and the multiplicity of the signals are expressed as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal.

Mass spectrometry (MS and HRMS) experiments were performed on a Bruker Daltonics microTOF spectrometer equipped with an ESI source (Bruker Daltonik GmgH, Bremen, Germany) by the Service de Spectrométrie de Masse de la Fédération de Chimie "Le Bel" (FR 2010).

UV/vis spectra were recorded on a Cary 5000 UV/vis/NIR double-beam spectrometer in dichloromethane. Extinction coefficients were determined for samples with analyte concentrations ranging from 5.10^{-6} to 1.10^{-4} M. All experiments were performed in dry CH_2Cl_2 (distilled over CaH_2) at 298 K.

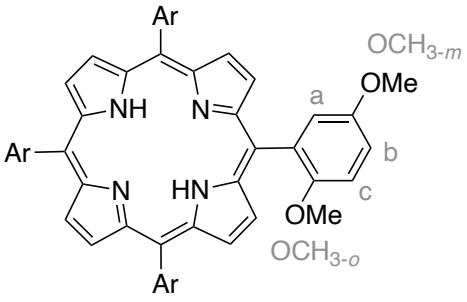
X-ray analyses and structural resolutions were performed by Dr. L. Karmazin, Dr. C. Bailly and N. Grüber (Service de radiocristallographie, Fédération de Chimie, Strasbourg) using a Bruker APEX II DUO Kappa-CCD diffractometer using MoK\$\alpha$ radiation (λ = 0.71073 Å) or CuK\$\alpha$ radiation (λ = 1.54178 Å)

Electrochemical measurements were performed using a three-electrode cell connected to a computerized electrochemical device (SP150 from BioLogic). Measurements were usually performed using a glassy carbon electrode as the working electrode and the compound were dissolved in distilled dichloromethane with NBu_4PF_6 (0.1 M) as electrolyte. Electrochemical potentials were referenced to the Ferrocene/Ferrocenium couple (Fc/Fc^+).

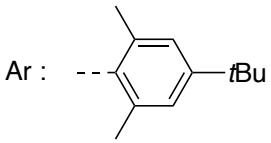
ECD spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2 °C

II Synthetic procedures and characterisation

II.1 Synthesis and characterisation of the free base porphyrin



Chemical Formula: $C_{64}H_{70}N_4O_2$
Exact Mass: 926.5499
Molecular Weight: 927.2900



A solution of 2,6-dimethyl-4-*tert*-butylbenzaldehyde (1.72 g, 9.03 mmol, 3 eq.), 2,5-dimethoxybenzaldehyde (500 mg, 3.01 mmol, 1 eq.), pyrrole (0.84 mL, 12.04 mmol, 4 eq.) in $CHCl_3$ (390 mL) was degassed in the dark for 30 minutes by argon bubbling. Under argon, $BF_3{\cdot}OEt_2$ (0.28 mL, 5.7 mM) was added and the solution was stirred in the dark at room temperature for 1 h. *p*-chloranil (2.22 g, 9.03 mmol, 3 eq.) was added and the solution was heated to reflux for an additional hour. The solution was filtered through a silica pad and evaporated to dryness. The desired porphyrin was isolated by column chromatography (silica gel, cyclohexane/CH_2Cl_2 8/2 to 6/4) followed by precipitation from an acetone/hexane/methanol mixture to afford the desired porphyrin (320 mg, 0.35 mmol, 11%) as a purple solid.

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 8.74 (d, *J* = 4.7 Hz, 2H, H_{pyrr}), 8.64 (d, *J* = 4.7 Hz, 2H, H_{pyrr}), 8.60 (br s, 4H, H_{pyrr}), 7.61 (d, *J* = 3.0 Hz, 1H, H_a), 7.43 (br s, 6H, H_{Ar}), 7.33 – 7.21 (m, 2H, H_b + H_c), 3.93 (s, 3H, $OCH_{3\text{-}m}$), 3.51 (s, 3H, $OCH_{3\text{-}o}$), 1.91 (s, 3H, CH_{3Ar}), 1.89 (s, 6H, CH_{3Ar}), 1.88 (s, 6H, CH_{3Ar}), 1.85 (s, 3H, CH_{3Ar}), 1.60 – 1.50 (m, 27H, $H_{t\text{Bu}}$), -2.51 (s, 2H, NH).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 157.4, 154.4, 152.5, 151.0, 139.15, 139.08, 139.0, 138.5, 138.4 (CH), 132.3, 127.0, 124.01, 123.98 (CH), 121.7 (CH), 118.2, 118.1, 118.0, 114.81 (CH), 114.79, 112.5 (CH), 56.8 (OCH_3), 56.1 (OCH_3), 34.8, 31.9 (*t*Bu), 22.21 (CH_3), 22.18 (CH_3).

ESI-TOF-HR-MS (m/z): Calcd for ([M+H$^+$]) 927.5572; found 927.5566.

UV-vis (CH_2Cl_2): λ_{max} = 418 nm (ε = 188000 L.cm^{-1}.mol^{-1}), 514 (10000), 548 (3200), 593 (2900), 647 (1800).

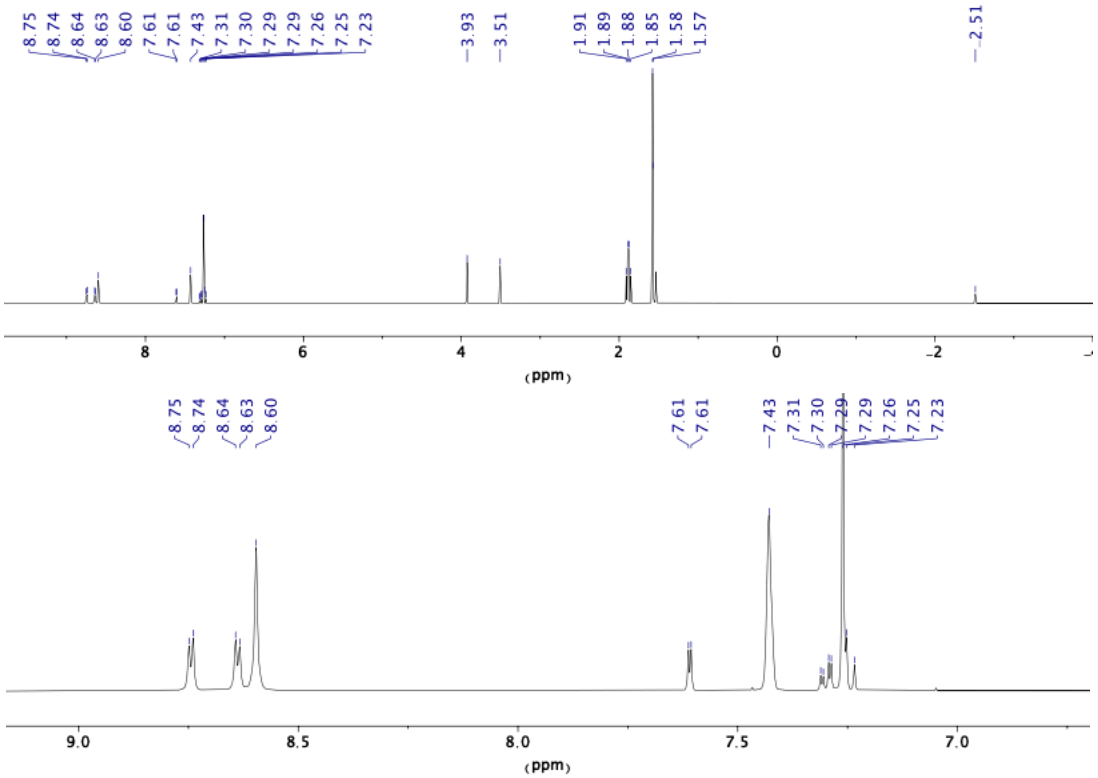


Figure S1: ^{1}H spectrum of the free-base porphyrin in $CDCl_3$ at 298 K (500 MHz).

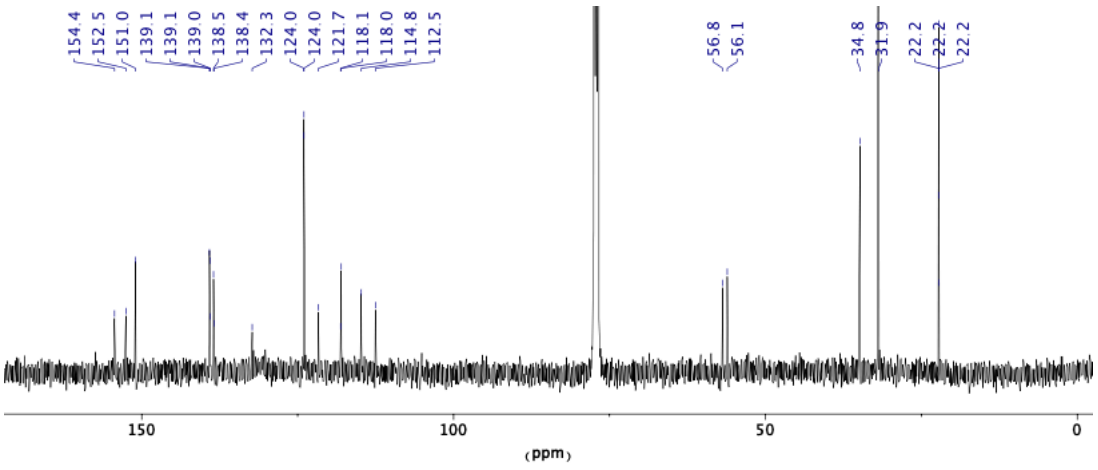


Figure S2: ^{13}C spectrum of the free-base porphyrin in $CDCl_3$ at 298 K (126 MHz).

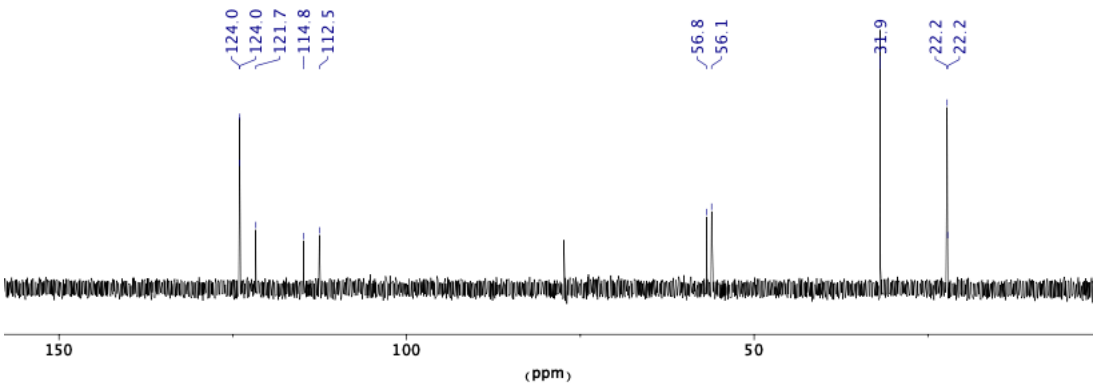
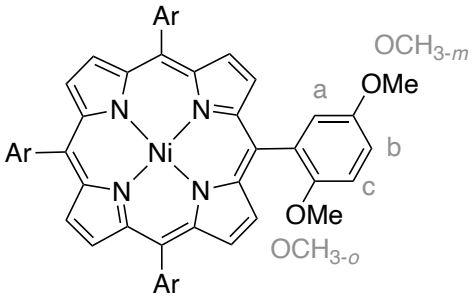
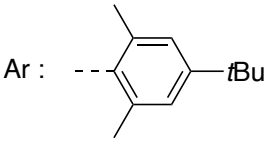


Figure S3: ^{13}C DEPT spectrum of the free-base porphyrin in $CDCl_3$ at 298 K (126 MHz).

II.2 Synthesis of the Ni(II)-porphyrin 1



Chemical Formula: $C_{64}H_{68}N_4NiO_2$
Exact Mass: 982.4696
Molecular Weight: 983.9674



A solution containing the free-base porphyrin (320 mg, 0.35 mmol, 1 eq.) and $Ni(acac)_2$ (440 mg, 1.73 mmol, 5 eq.) in toluene (100 mL) was refluxed overnight. The mixture was filtered through an alumina pad. The solvent was evaporated under vacuum and the resulting solid was further purified by precipitation from an acetone/hexane/methanol mixture to afford the desired metallo-porphyrin **1** (344 mg, 1.57 mmol, quant.) as a red solid.

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 8.67 (d, *J* = 4.9 Hz, 2H, H_{pyrr}), 8.56 (d, *J* = 4.9 Hz, 2H, H_{pyrr}), 8.55 – 8.52 (m, 4H, H_{pyrr}), 7.45 (d, *J* = 3.0 Hz, 1H, H_a), 7.24 (dd, *J* = 9.0, 3.0 Hz, 1H, H_b), 7.20 (d, *J* = 9.0 Hz, 1H, H_c), 3.87 (s, 3H, $OCH_{3\text{-}m}$), 3.59 (s, 3H, $OCH_{3\text{-}o}$), 1.90 – 1.80 (m, 18H, CH_{3Ar}), 1.55-156 (2s, 27H, H_{tBu}).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 156.8, 153.7, 152.5, 150.91, 150.89, 142.9, 142.6, 142.5, 142.4, 141.4, 138.74, 138.71, 138.6, 137.5, 137.4, 132.0 (CH), 131.5 (CH), 131.4 (CH), 131.3 (CH), 131.0, 127.0 (CH), 125.1 (CH), 124.0 (CH), 123.97 (CH), 121.0 (CH), 117.22, 117.18, 114.9 (CH), 114.1, 112.2 (CH), 56.6 (OCH_3), 56.0 (OCH_3), 34.83, 34.80, 31.8 (*t*Bu), 22.04 (CH_3), 22.02 (CH_3), 21.9 (CH_3), 21.1 (CH_3), 20.7 (CH_3).

ESI-TOF-HR-MS (m/z): Calcd for ([$M^{\cdot+}$]) 982.4690; found 982.4695.

UV-vis (CH_2Cl_2): λ_{max} = 419 nm (ε = 140000 L.cm^{-1}.mol^{-1}), 527 (13000), 565 (3500).

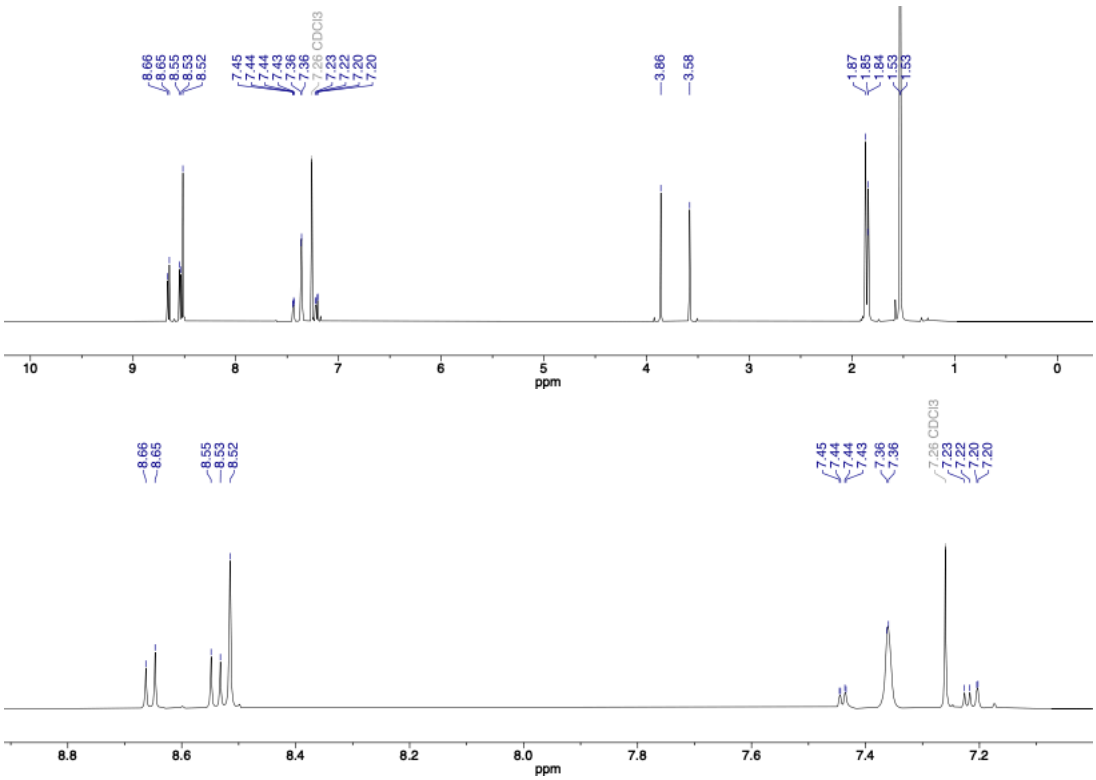


Figure S4: ^{1}H spectrum of **1** in $CDCl_3$ at 298 K (500 MHz).

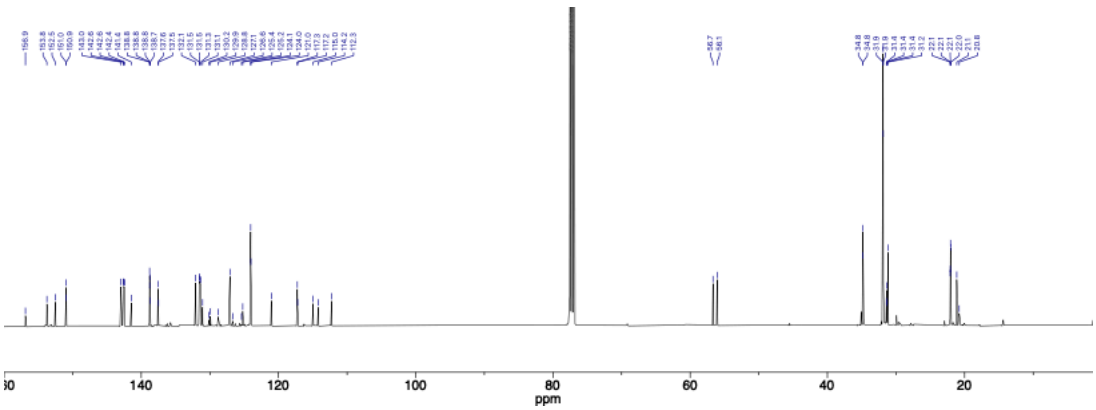


Figure S5: ^{13}C spectrum of **1** in $CDCl_3$ at 298 K (126 MHz).

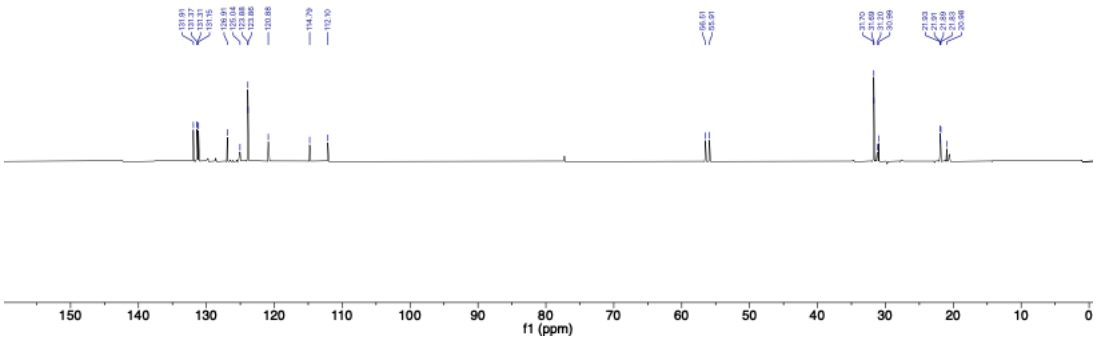
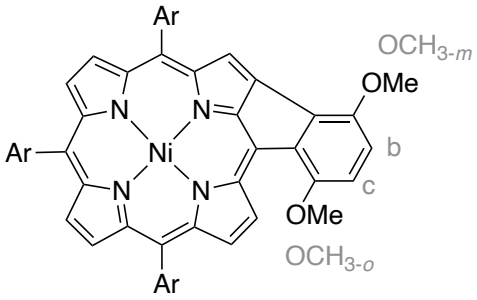
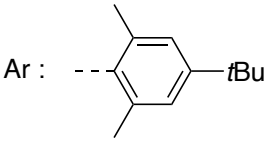


Figure S6: ^{13}C DEPT spectrum of **1** in $CDCl_3$ at 298 K (126 MHz).

II.3 Synthesis and characterisation of the fused porphyrin 2



Chemical Formula: $C_{64}H_{66}N_4NiO_2$
Exact Mass: 980.4539
Molecular Weight: 981.9514



A solution of the porphyrin **1** (60 mg, 61 mmol, 1 eq.) in chlorobenzene (3 mL) was degassed by argon bubbling for 30 minutes. In a second flask, anhydrous $FeCl_3$ (100 mg, 0.61 mmol, 10 eq.) was dissolved in $MeNO_2$ (1mL) and degassed by argon bubbling for 30 minutes. The iron chloride solution was cannulated to the porphyrin solution and the resulting mixture instantly turned to dark green upon addition. The solution was heated for 4 h at 50 °C while maintaining the argon bubbling. The solution was allowed to cool to room temperature and NEt_3 (5 mL) and MeOH (5 mL) were added. The solvents were removed under reduced pressure and CH_2Cl_2 (50 mL) and H_2O (50 mL) were added. The organic layer was collected, washed thrice with H_2O (3 x 20 mL), dried over Na_2SO_4, filtered and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 1/1) to afford the desired porphyrin **2** (35 mg, 35.6 mmol, 58%) as a green solid.

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.76 (d, J = 5.0 Hz, 1H, H_{pyrr}), 8.37 (d, J = 5.0 Hz, 1H, H_{pyrr}), 8.15 (d, J = 4.8 Hz, 1H, H_{pyrr}), 8.09 (d, J = 4.8 Hz, 1H, H_{pyrr}), 8.06 (br s, 2H, H_{pyrr}), 7.69 (s, 1H, H_{pyrr}), 7.35 (s, 2H, H_{Ar}), 7.35 (s, 2H, H_{Ar}), 7.33 (s, 2H, H_{Ar}), 6.76 (d, J = 9.0 Hz, 1H, H_c), 6.62 (d, J = 9.0 Hz, 1H, H_b), 4.13 (s, 3H, $OCH_{3\text{-}o}$), 3.99 (s, 3H, $OCH_{3\text{-}m}$), 1.98 (s, 6H, CH_{3Ar}), 1.91 (s, 6H, CH_{3Ar}), 1.90 (s, 6H, CH_{3Ar}), 1.54 (br s, 18H, H_{tBu}), 1.52 (s, 9H, H_{tBu}).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 153.9, 150.94, 150.89, 150.87, 150.81, 150.6, 146.1, 145.8, 145.4, 144.8, 144.0, 143.4, 143.2, 143.0, 138.6, 138.4, 138.3, 137.6, 137.0, 136.9, 136.1, 132.8 (CH), 132.0 (CH), 131.4 (CH), 130.5 (CH), 129.9 (CH), 129.4 (CH), 126.9, 124.0 (CH), 122.8 (CH), 122.2, 121.0, 117.2, 116.4 (CH), 113.7 (CH), 112.5, 56.4 (OCH_3), 56.1 (OCH_3), 34.74, 34.72, 31.79 (*t*Bu), 31.76 (*t*Bu), 22.0 (CH_3), 21.9 (CH_3), 21.8 (CH_3).

ESI-TOF-HR-MS (m/z): Calcd for ([$M^{\cdot+}$]) 980.4534; found 980.4527.

UV-vis (CH_2Cl_2): λ_{max} = 424 nm (ε = 50000 L.cm^{-1}.mol^{-1}), 473 (75000), 570 (6700), 618 (5400), 645 (1000).

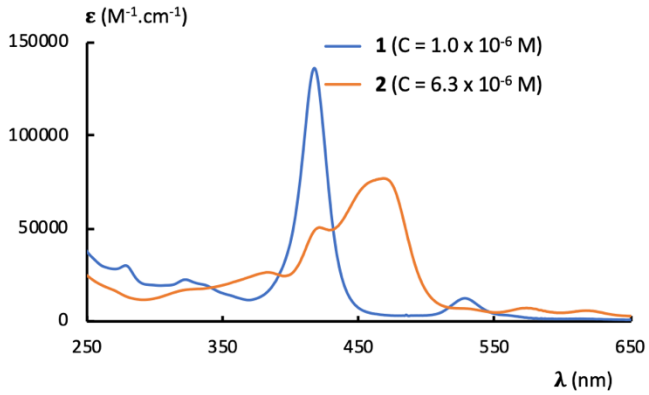


Figure S7: Electronic spectra of **1** and **2** in dichloromethane.

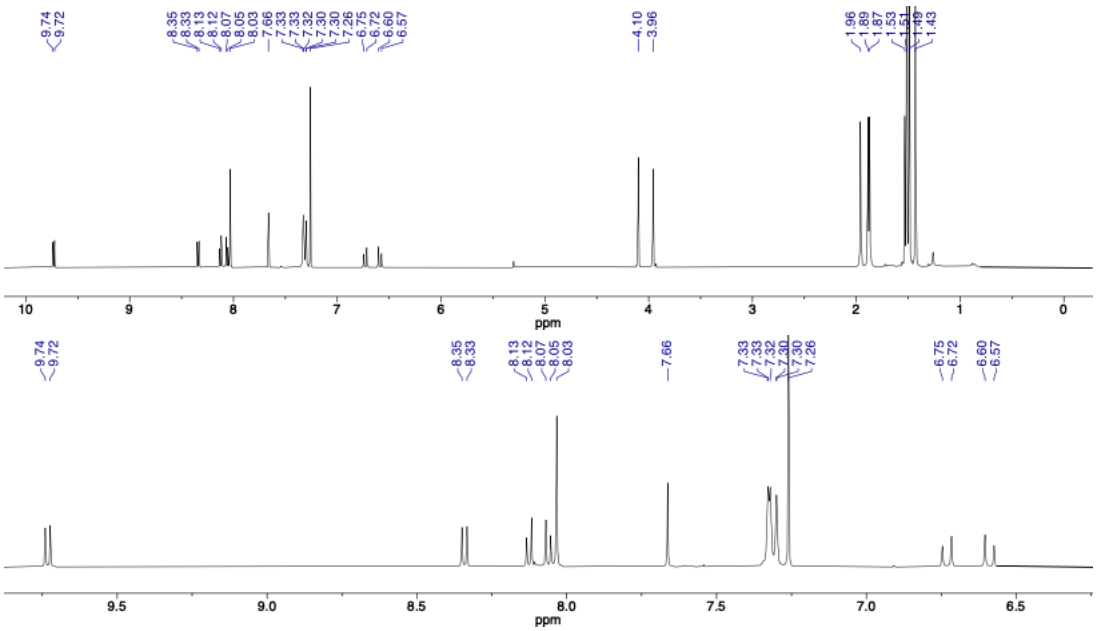


Figure S8: ^{1}H spectrum of **2** in $CDCl_3$ at 298 K (500 MHz) and aromatic area.

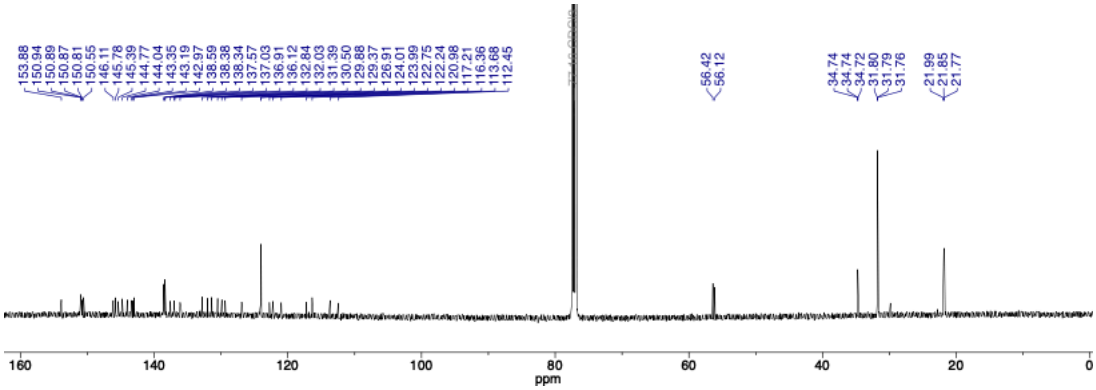


Figure S9: ^{13}C spectrum of **2** in $CDCl_3$ at 298 K (126 MHz).

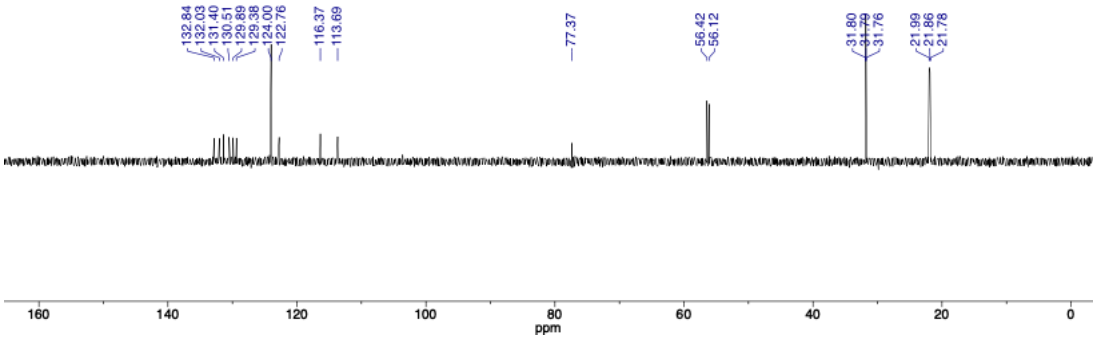


Figure S10: ^{13}C DEPT spectrum of **2** in $CDCl_3$ at 298 K (126 MHz).

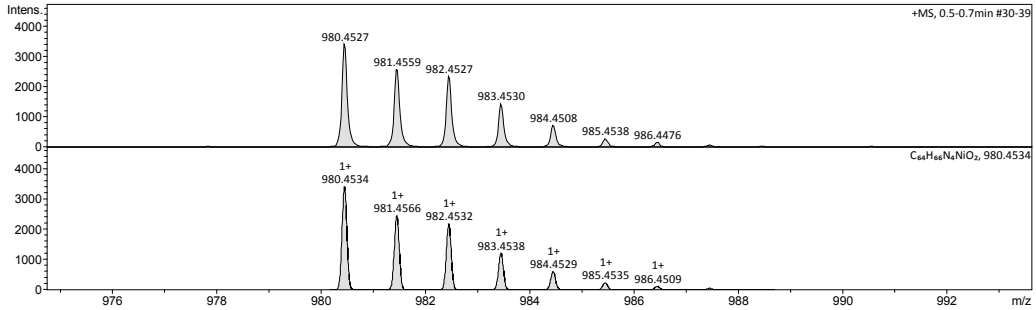
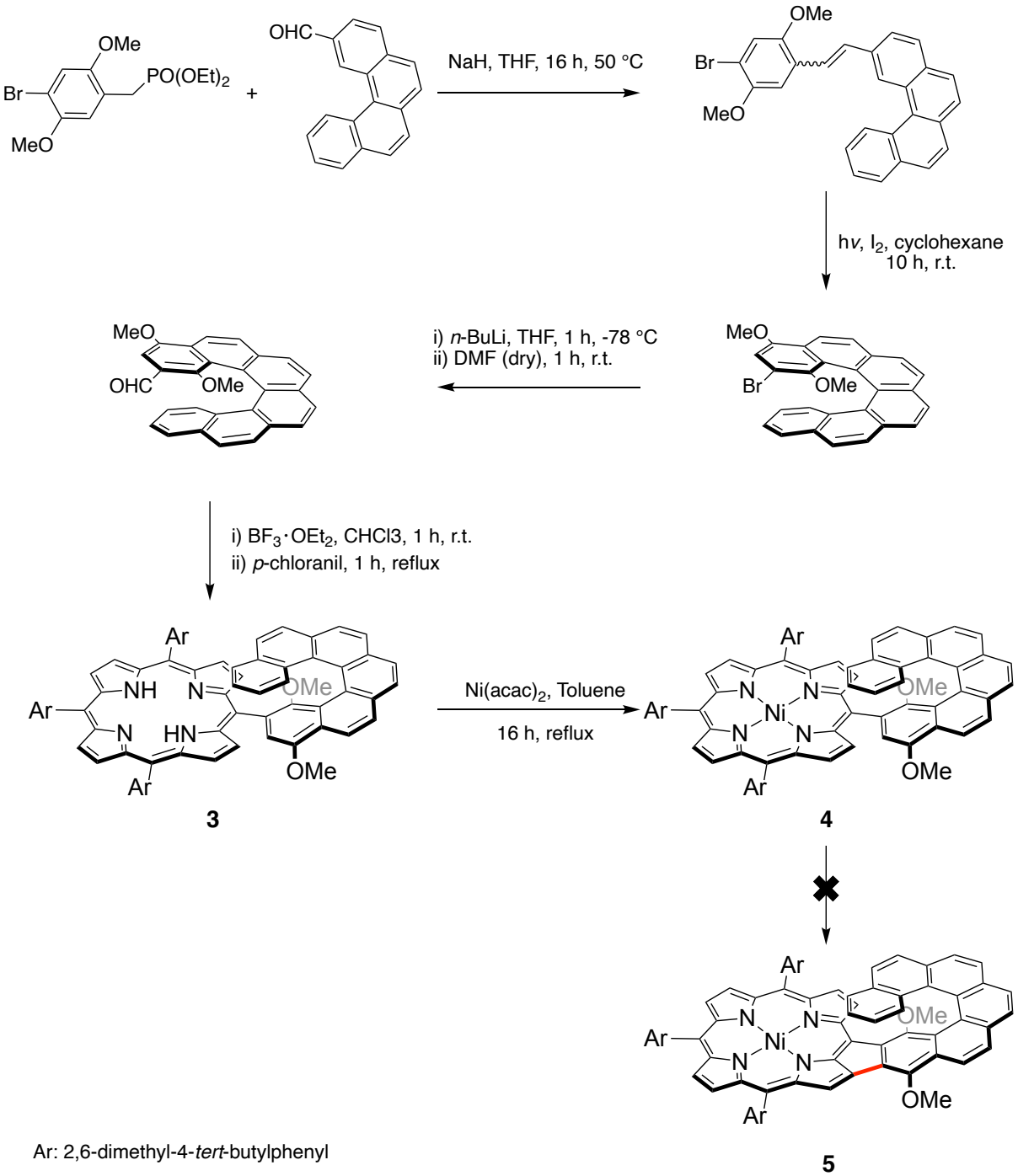


Figure S11: HR-ESI mass of compound **2** (top) and simulation (bottom).

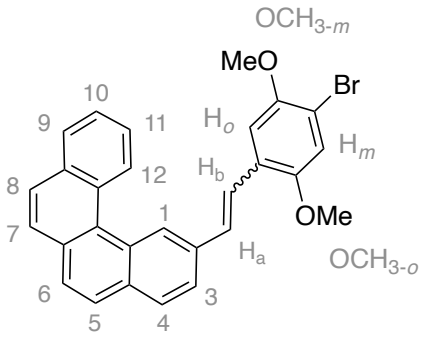
III Synthesis of the non-fused helicene-porphyrin 4



Ar: 2,6-dimethyl-4-*tert*-butylphenyl

Figure S12. Proposed synthesis of the five-membered ring helicene-fused porphyrin **5**.

III.1 Synthesis of the 2-(4-bromo-2,5-dimethoxystyryl)benzo[*c*]phenanthrene



Chemical Formula: $C_{28}H_{21}BrO_2$
Exact Mass: 468.0725
Molecular Weight: 469.3780

Under argon, NaH (60% in mineral oil) (220 mg, 5.49 mmol, 1.1 eq.) was added to a solution of diethyl 4-bromo-2,5-dimethoxybenzylphosphonate (2.02 g, 5.49 mmol, 1.1 eq.) in freshly distilled THF (50 mL). After 15 min of stirring at room temperature, a solution of benzo[*c*]phenanthrene-2-carbaldehyde (1.28 g, 4.99 mmol, 1.0 eq.) in freshly distilled THF (30 mL) was added dropwise and the resulting solution was heated at 50 °C for 16 h. The solution was allowed to cool to room temperature and H_2O (50 mL) was added. The solvents were evaporated under reduced pressure and the resulting solid was dissolved in CH_2Cl_2 (50 mL). The resulting solution was washed with a saturated aqueous solution of NH_4Cl (3 x 20 mL), dried over $MgSO_4$, and filtered. Subsequent purification of the crude product by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 40/60 to 50/50) afforded the desired product as a yellow solid (2.23 mg, 4.74 mmol, 95%).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.17 (dd, *J* = 8.5, 1.1 Hz, 1H, H_{12}), 9.15 (br s, 1H, H_1), 8.04 (dd, *J* = 8.0, 1.5 Hz, 1H H_9), 8.01 (d, *J* = 8.3 Hz, 1H, H_4), 7.96 – 7.87 (m, 3H, H_3 + 2*$H_{5\text{-}8}$), 7.85 – 7.80 (m, 2H, $H_{5\text{-}8}$), 7.74 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H, H_{11}), 7.65 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H, H_{10}), 7.61 (d, *J* = 16.4 Hz, 1H, H_b), 7.38 (d, *J* = 16.4 Hz, 1H, H_a), 7.24 (s, 1H, H_o), 7.14 (s, 1H, H_m), 3.97 (s, 3H, $OCH_{3\text{-}m}$), 3.89 (s, 3H, $OCH_{3\text{-}o}$).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 151.6, 150.4, 135.6, 133.7, 133.2, 131.5, 130.8, 130.5, 130.2 (CH), 129.1 (CH), 128.8 (CH), 128.0 (CH), 127.7 (CH), 127.52 (CH), 127.49, 127.3 (CH), 127.1 (CH), 127.0 (CH), 126.5, 126.3 (CH), 126.0 (CH), 123.4 (CH), 123.3 (CH), 116.8 (CH), 111.2, 109.9 (CH), 57.2 (OCH_3), 56.6 (OCH_3).

ESI-TOF-HR-MS (m/z): Calcd for ([M+K^+]) 507.0357; found 507.0329.

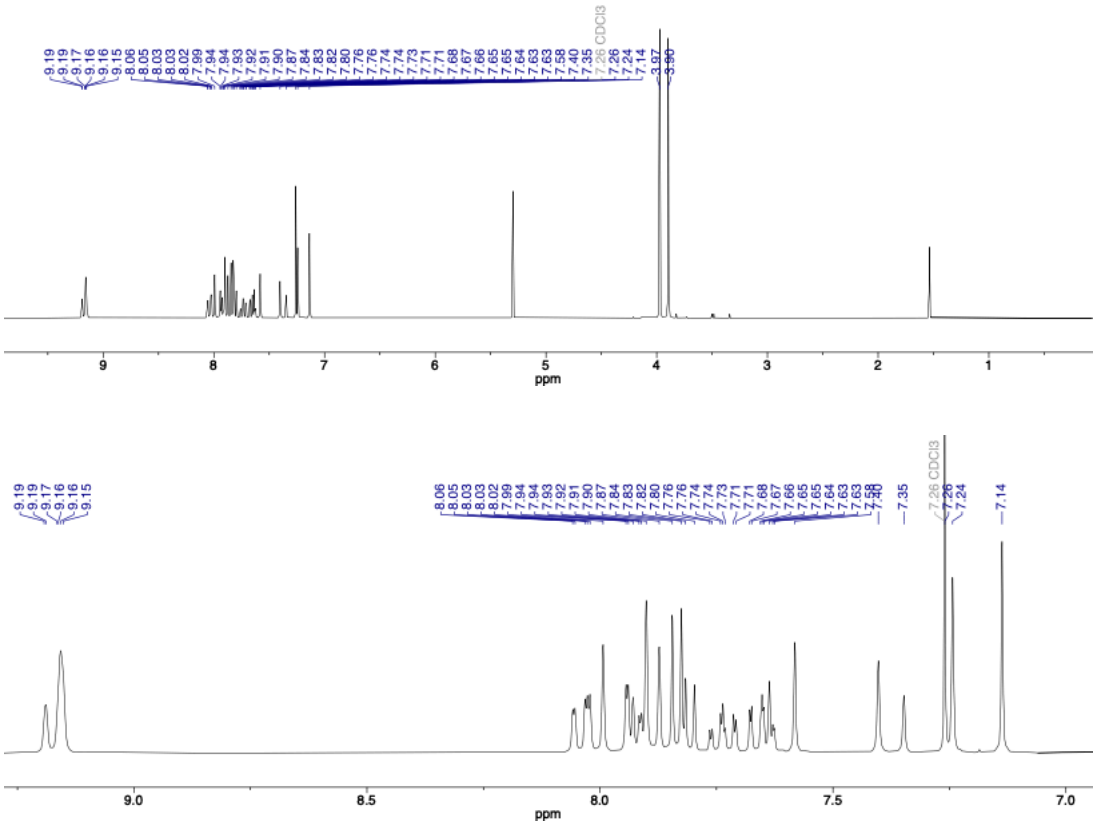


Figure S13: ^{1}H spectrum of the 2-(4-bromo-2,5-dimethoxystyryl)benzo[c]phenanthrene in $CDCl_3$ at 298 K (300 MHz, at 5.3 and 1.5 ppm: residual CH_2Cl_2 and H_2O) and aromatic area.

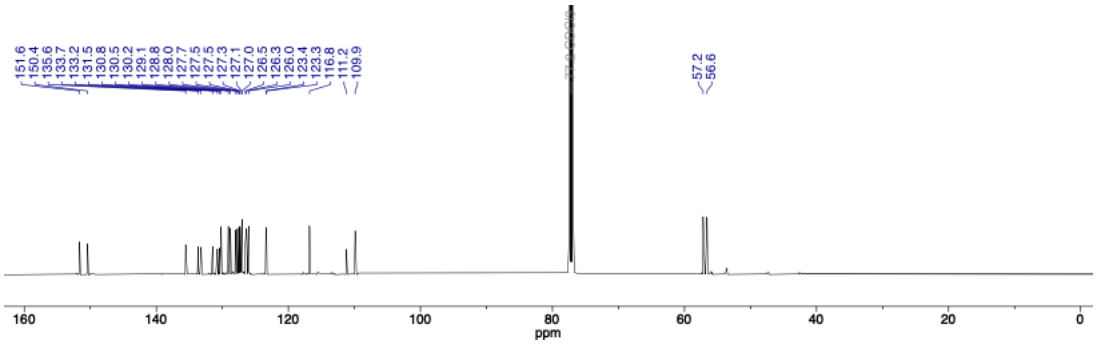


Figure S14: ^{13}C spectrum of the 2-(4-bromo-2,5-dimethoxystyryl)benzo[c]phenanthrene in $CDCl_3$ at 298 K (126 MHz).

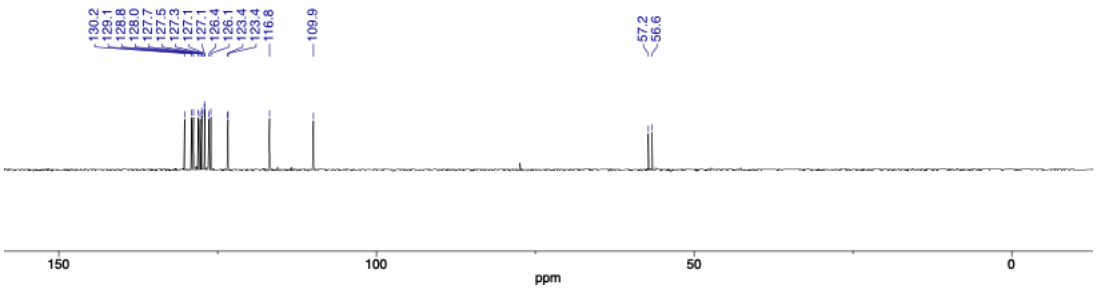
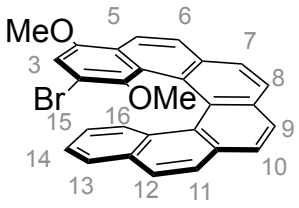


Figure S15: ^{13}C DEPT spectrum of the 2-(4-bromo-2,5-dimethoxystyryl)benzo[c]phenanthrene in $CDCl_3$ at 298 K (126 MHz).

III.2 Synthesis of the 2-bromo-1,4-dimethoxyhexahelicene (±)



Chemical Formula: $C_{28}H_{19}BrO_2$
Exact Mass: 466.0568
Molecular Weight: 467.3620

A solution of 2-(4-bromo-2,5-dimethoxystyryl)benzo[c]phenanthrene (1.12 g, 2.56 mmol, 1 eq.) and iodine (≃ 0.015 eq.) in cyclohexane (400 mL) was irradiated in a photoreactor equipped with an immersion lamp (150 W) for 10 h. Sodium thiosulfate (5 g) was added and the solution was stirred overnight. The solvent was evaporated, and the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 40/60) to afford the 2-bromo-1,4-dimethoxyhexahelicene (±) as a yellow solid (580 mg, 1.24 mmol, 52%).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 8.39 (d, *J* = 8.7 Hz, 1H, H_5), 8.10 – 7.87 (m, 7H, H_6 + H_7 + H_8 + H_9 + H_{10} + H_{11} + H_{12}) 7.81 (dd, *J* = 8.0, 1.4 Hz, 1H, H_{13}), 7.28 – 7.20 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H, H_{14}), 7.07 (dd, *J* = 8.5, 1.1 Hz, 1H, H_{16}), 6.87 (s, 1H, H_3), 6.60 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H, H_{15}), 4.02 (s, 3H, OCH_{3out}), 2.08 (s, 3H, OCH_{3in}).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 151.9, 147.8, 132.6, 132.19, 132.17, 130.8, 129.12, 129.09, 128.1 (CH), 127.9 (CH), 127.5 (CH), 127.4 (CH), 126.3 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 125.6, 125.33 (CH), 125.29 (CH), 124.7, 124.1, 123.7, 123.3 (CH), 121.4 (CH), 114.4, 109.9 (CH), 58.4 (OCH_3), 56.4 (OCH_3).

ESI-TOF-HR-MS (m/z): Calcd for ([M+Na$^+$]) 489.0461; found 489.0465.

Crystal data: From $CHCl_3$, $C_{28}H_{19}BrO_2$, M = 467.34 g.mol^{-1}, monoclinic space group P 21/c, a = 14.6897 (5) Å, b = 14.0457 (6) Å, c = 20.6528 (7) Å, α = 90.0°, β = 104.4410°, γ = 90.0°, V = 4126.6 (3) Å^3, Z = 8, T = 120 K, MoK\α = 0.71073, 2.43 < θ < 27.89, 31304 reflections measured, R_1 = 2.94%, *w*R_2 = 7.6%, GoF = 1.00626. CCDC : 2092869

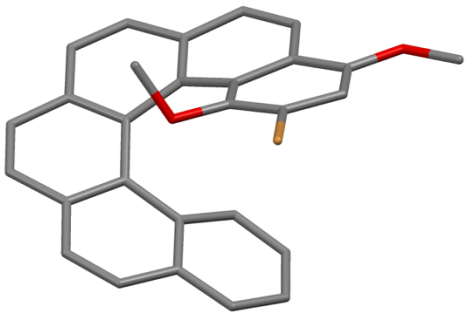


Figure S16. X-Ray structure of the 1,4-dimethoxy-2-bromo-[6]helicene

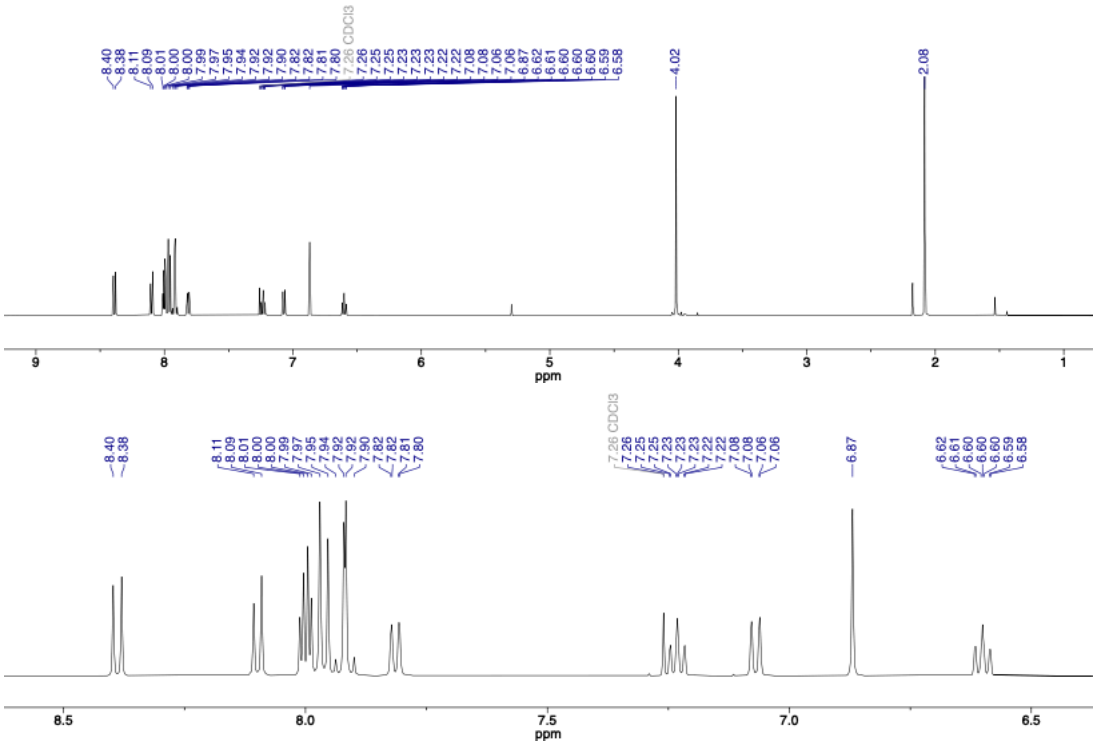


Figure S17: ^{1}H spectrum of the 2-bromo-1,4-dimethoxyhexahelicene (±) in $CDCl_3$ at 298 K (500 MHz) and aromatic area (bottom).

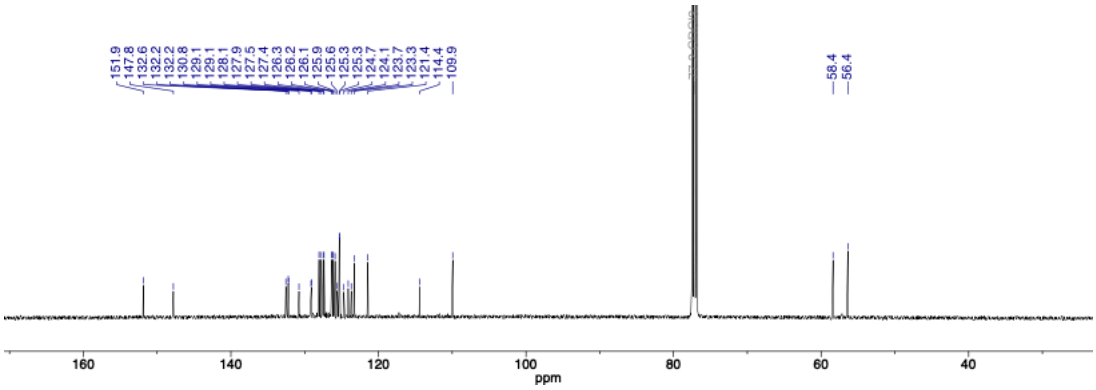


Figure S18: ^{13}C spectrum of the 2-bromo-1,4-dimethoxyhexahelicene (±) in $CDCl_3$ at 298 K (126 MHz).

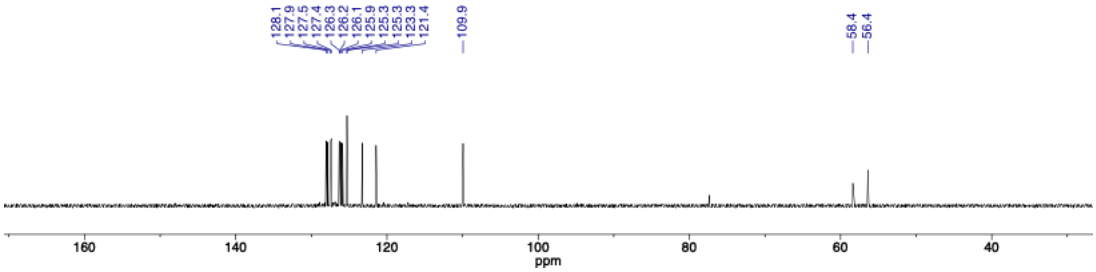
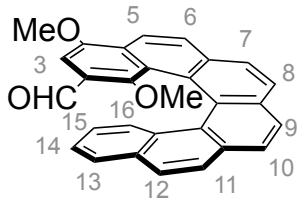


Figure S19: ^{13}C DEPT spectrum of the 2-bromo-1,4-dimethoxyhexahelicene (±) in $CDCl_3$ at 298 K (126 MHz).

III.3 Synthesis of the 2-formyl-1,4-dimethoxyhexahelicene (±)



Chemical Formula: $C_{29}H_{20}O_3$
Exact Mass: 416.1412
Molecular Weight: 416.4760

Under argon at -78 °C, a solution of *n*-BuLi (1.6 M in hexanes) (0.74 mL, 1.18 mmol, 1.1 eq.) was added to a solution of 2-bromo-1,4-dimethoxyhexahelicene (±) (500 mg, 1.07 mmol, 1.0 eq.) in distilled THF (20 mL). After 1 h of stirring at this temperature, dry DMF (0.3 mL, 3.2 mmol, 3 eq.) was added, the solution was allowed to warm to room temperature and H_2O (10 mL) was added. The solution was concentrated under reduced pressure and CH_2Cl_2 (20 mL) was added. The organic layer was washed with a saturated aqueous solution of NH_4Cl (5 x 30 mL), dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure. The crude solid was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 40/60) to afford the 2-formyl-1,4-dimethoxyhexahelicene (±) as a yellow solid (355 mg, 0.85 mmol, 79%).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.63 (s, 1H, CHO), 8.46 (d, *J* = 8.7 Hz, 1H, H_5), 8.14 (d, *J* = 8.1 Hz, 1H, H_9), 8.11 (d, *J* = 8.7 Hz, 1H, H_6), 8.04 (d, *J* = 8.1 Hz, 1H, H_{10}), 8.03 (d, *J* = 8.1 Hz, 1H, $H_{7\text{-}8}$), 7.99 (d, *J* = 8.1 Hz, 1H, $H_{7\text{-}8}$), 7.91 (d, *J* = 8.5 Hz, 1H, H_{11}), 7.88 (d, *J* = 8.5 Hz, 1H, H_{12}), 7.75 (dd, *J* = 8.0, 1.4 Hz, 1H, H_{13}), 7.11 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H, H_{14}), 7.06 (s, 1H, H_3), 7.02 (dd, *J* = 8.4, 1.2 Hz, 1H, H_{16}), 6.55 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, H_{15}), 4.07 (s, 3H, $OCH_{3\text{-}out}$), 2.15 (s, 3H, $OCH_{3\text{-}in}$).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 190.1 (CH), 156.9, 152.0, 132.7, 132.2, 131.9, 130.7, 129.5 (CH), 129.4, 129.1, 129.0, 128.2 (CH), 128.0 (CH), 127.9 (CH), 127.5 (CH), 126.51 (CH), 126.48 (CH), 126.0 (CH), 125.6 (CH), 125.5, 125.4 (CH), 125.0, 124.5, 124.4, 123.6 (CH), 121.5 (CH), 100.9 (CH), 60.9 (OCH_3), 56.3 (OCH_3).

ESI-TOF-HR-MS (m/z): Calcd for ([M+K$^+$]) 455.1044; found 455.1041.

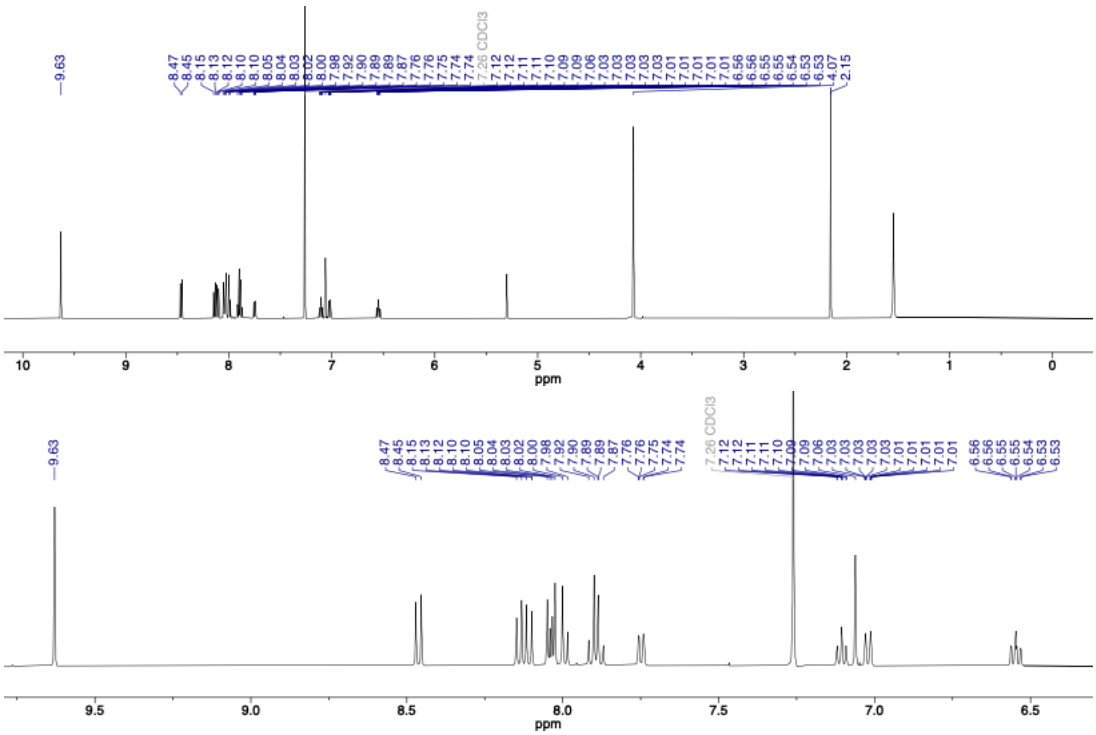


Figure S20: ^{1}H spectrum of the 2-formyl-1,4-dimethoxyhexahelicene (±) in $CDCl_3$ at 298 K (500 MHz) and aromatic area.

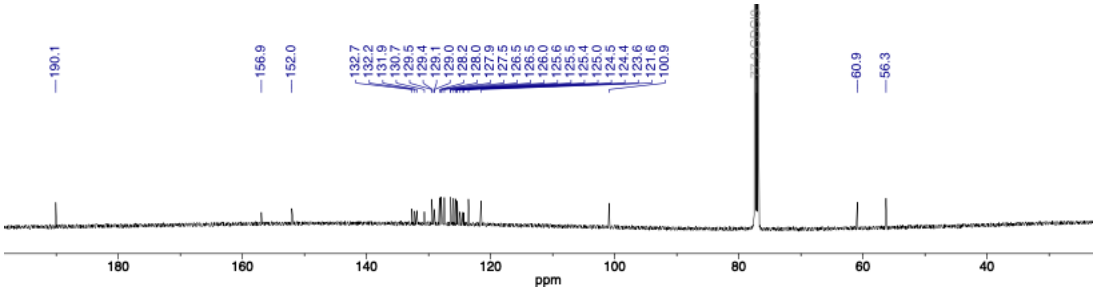


Figure S21: ^{13}C spectrum of the 2-formyl-1,4-dimethoxyhexahelicene (±) in $CDCl_3$ at 298 K (126 MHz).

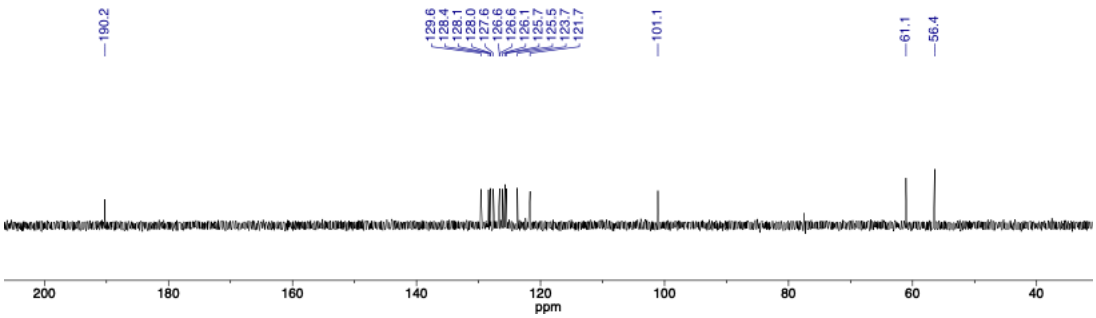
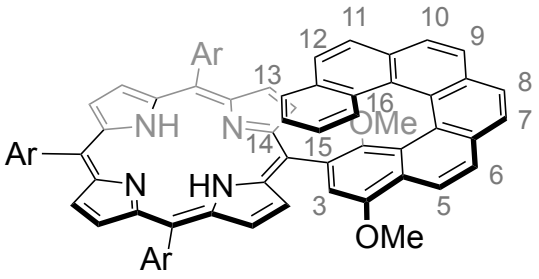
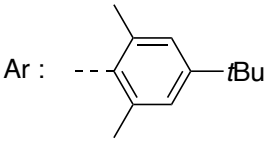


Figure S22: ^{13}C DEPT spectrum of the 2-formyl-1,4-dimethoxyhexahelicene (±) in $CDCl_3$ at 298 K (126 MHz).

III.4 Synthesis of the porphyrin 3 (±)



Chemical Formula: $C_{84}H_{80}N_4O_2$
Exact Mass: 1176.63
Molecular Weight: 1177.59



A solution of 2,6-dimethyl-4-*tert*-butylbenzaldehyde (137 mg, 0.72 mmol, 3 eq.), 1,4-dimethoxy-2-formyl-[6]helicene (100 mg, 0.24 mmol, 1 eq.) and pyrrole (67 µL, 0.96 mmol, 4 eq.) in $CHCl_3$ (50 mL) was degassed in the dark for 30 minutes by argon bubbling. Under argon, $BF_3{\cdot}OEt_2$ (25 µL, 5.7 mM)) was added and the solution was stirred in the dark at room temperature for 1 h. *p*-chloranil (177 mg, 0.72 mmol, 3 eq.) was added and the solution was heated to reflux for an additional hour. The solution was filtered through a silica pad and evaporated to dryness. The desired porphyrin was isolated by column chromatography (silica gel, cyclohexane/CH_2Cl_2 8/2 to 6/4) followed by precipitation from an acetone/hexane/methanol mixture to afford the porphyrin **6** (25 mg, 0.24 mmol, 9%) as a purple solid.

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 8.81 (d, *J* = 8.9 Hz, 1H, H_5), 8.62 – 8.57 (m, 3H, H_{pyrr}), 8.53 (d, *J* = 4.6 Hz, 1H, H_{pyrr}), 8.50 (d, *J* = 4.7 Hz, 1H, H_{pyrr}), 8.29 (d, *J* = 4.7 Hz, 1H, H_{pyrr}), 8.20 (d, *J* = 8.9 Hz, 1H, H_6), 8.10 (d, *J* = 8.2 Hz, 1H, H_9), 8.05 – 8.02 (m , 2H, H_{pyrr} + H_{10}), 7.87 (dd, *J* = 7.9, 1.4 Hz, 1H, H_{13}), 7.77 (d, *J* = 8.1 Hz, 1H, H_8), 7.70 – 7.61 (m, 4H, H_{Ar} + H_{14} + H_{16} + H_7), 7.56 (s, 1H, H_3) 7.52 (d, *J* = 2.0 Hz, 1H, H_{Ar}), 7.43 (br s, 1H, H_{Ar}), 7.42 – 7.35 (m, 4H, 2*H_{Ar} + H_{11} + H_{12}), 7.30 (d, *J* = 2.0 Hz, 1H, H_{Ar}), 7.26 (d, *J* = 4.7 Hz, H_{pyrr}) 7.17 (ddd, *J* = 8.4, 6.7, 1.4 Hz, 1H, H_{15}), 4.08 (s, 3H, OCH_{3out}), 2.14 (s, 3H, CH_{3Ar}), 1.94 (s, 3H, CH_{3Ar}), 1.88 (s, 3H, CH_{3Ar}), 1.81 (s, 3H, CH_{3Ar}), 1.79 (s, 3H, CH_{3Ar}), 1.69 (s, 9H, H_{tBu}), 1.62 (s, 3H, CH_{3Ar}), 1.57 (s, 9H, H_{tBu}), 1.50 (s, 9H, H_{tBu}), 1.36 (s, 3H, OCH_{3in}), -2.74 (s, 2H, NH).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 151.4, 151.2, 151.0, 150.9, 149.2, 139.3, 139.2, 139.1, 139.00, 139.95, 138.8, 138.6, 138.4, 138.3, 132.7, 132.33, 132.31, 132.2, 131.4, 129.7, 129.1 (CH), 128.6, 127.52 (CH), 127.48 (CH), 127.3 (CH), 127.1 (CH), 126.5, 126.4 (CH), 125.8 (CH), 125.7 (CH), 125.4, 125.33, 125.26, 125.1, 124.74 (CH), 124.67 (CH), 124.1 (CH), 124.03 (CH), 123.98 (CH), 123.94 (CH), 123.91 (CH), 123.88 (CH), 122.2 (CH), 117.82, 117.80, 117.7, 115.9, 112.7 (CH), 58.0 (OCH_3), 56.4 (OCH_3), 35.0, 34.8, 34.7, 32.0 (*t*Bu), 31.84 (*t*Bu), 31.77 (*t*Bu), 22.4 (CH_3), 22.3 (CH_3), 22.24 (CH_3), 22.18 (CH_3), 22.16 (CH_3), 21.9 (CH_3).

ESI-TOF-HR-MS (m/z): Calcd for ([M+H$^+$]) 1177.6354; found 1177.6405.

UV-vis (CH_2Cl_2): λ_{max} = 422 nm (ε = 345000 L.cm^{-1}.mol^{-1}), 519 (21900), 531 (6900) 552 (4700), 593 (6000), 649 (3900).

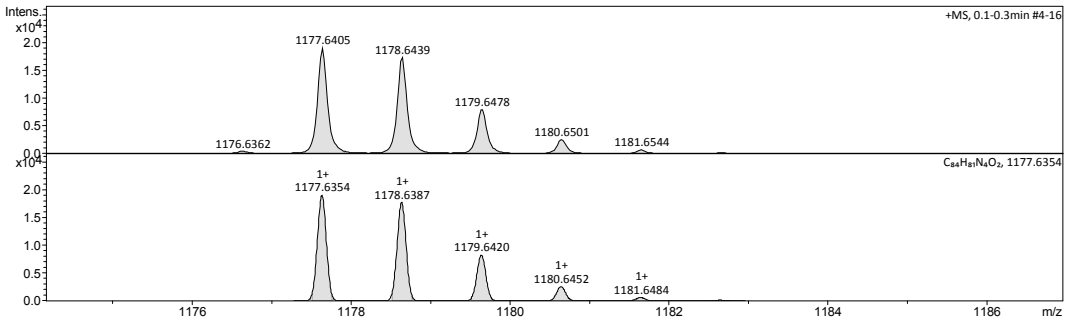


Figure S23: HR-ESI-TOF spectrum of **3** and simulation (bottom).

Crystal data: From CH_2Cl_2-MeOH, $C_{84}H_{80}N_4O_2$, M = 1177.52 g.mol^{-1}, monoclinic space group P 21/c, a = 13.2857 (5) Å, b = 15.5135 (6) Å, c = 35.8022 (15) Å, α = 90.0°, β = 95.347°, γ = 90.0°, V = 7347.0 (5) Å^3, Z = 4, T = 120 K, CuK\α λ = 1.54178, 2.48 < θ < 66.33, 86405 reflections measured, R_1 = 6.49%, *w*R_2 = 23.2%, GoF = 1.21705. CCDC: 2157003

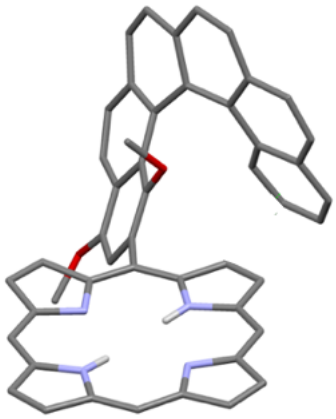


Figure S24. X-ray structure of the porphyrin **3**. H atoms and *meso* substituents were omitted for clarity.

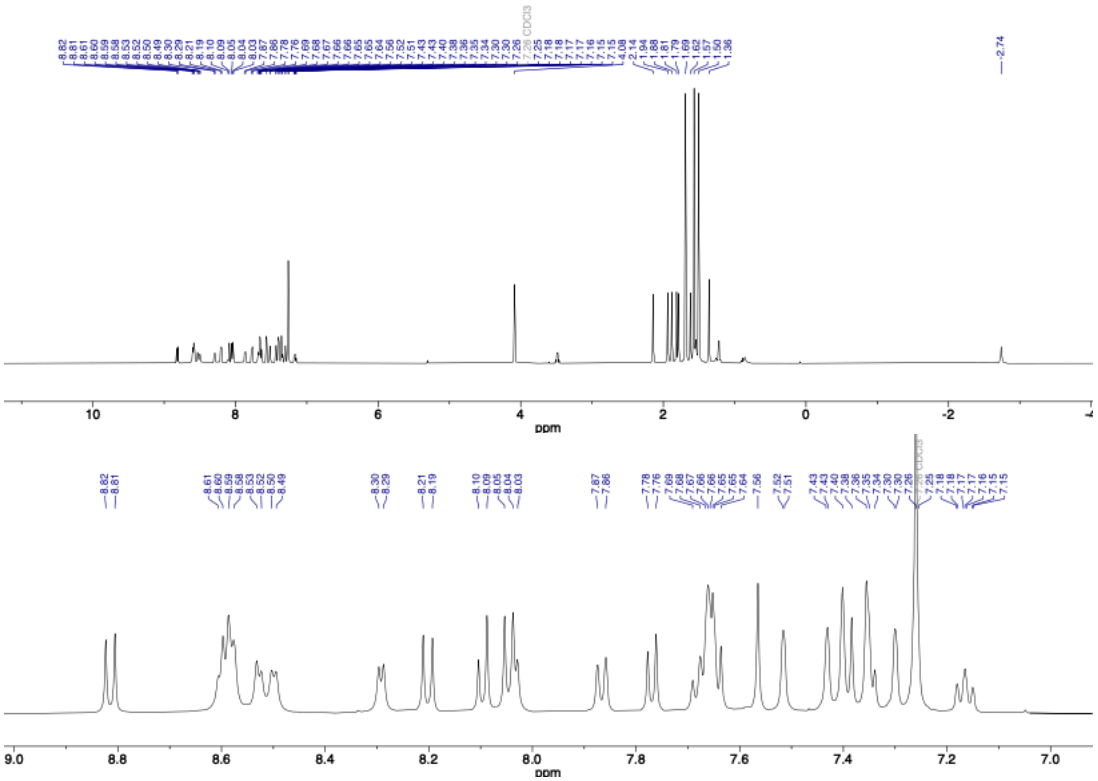


Figure S25: ^{1}H spectrum of **3** in $CDCl_3$ at 298 K (500 MHz) and aromatic area (bottom).

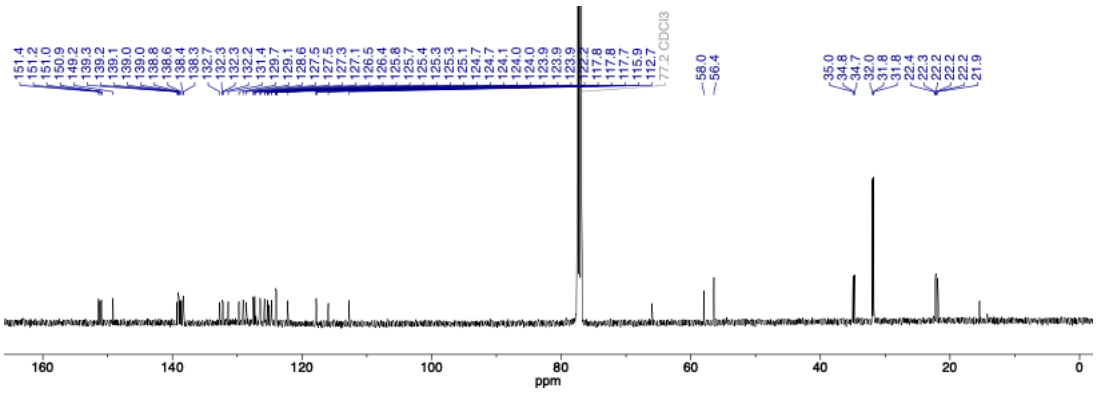


Figure S26: ^{13}C spectrum of **3** in $CDCl_3$ at 298 K (126 MHz).

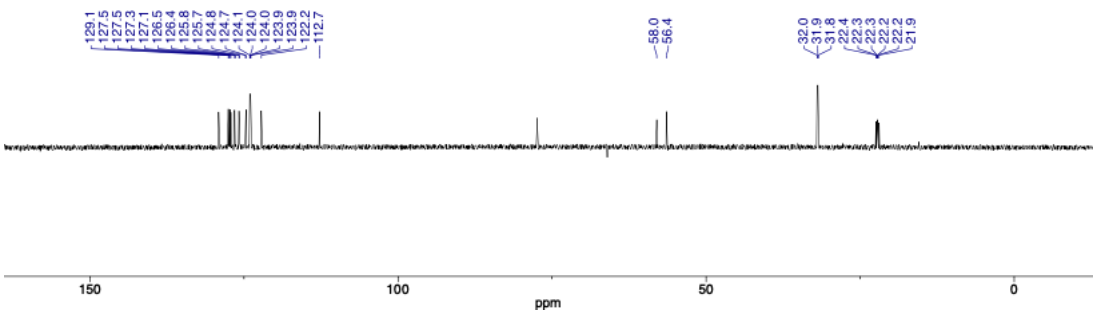
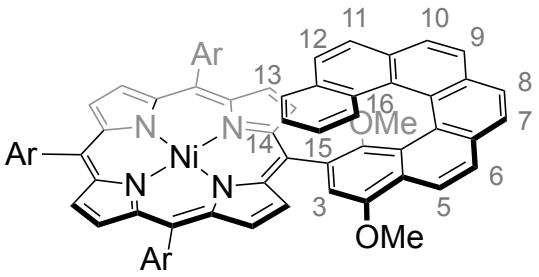
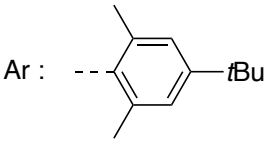


Figure S27: ^{13}C DEPT spectrum of **3** in $CDCl_3$ at 298 K (126 MHz).

Synthesis of the porphyrin 4 (±)



Chemical Formula: $C_{84}H_{78}N_4NiO_2$
Exact Mass: 1232.5478
Molecular Weight: 1234.2674



A solution containing the free-base porphyrin **3** (20 mg, 17 μmol, 1 eq.) and $Ni(acac)_2$ (22 mg, 85 μmol, 5 eq.) in toluene (20 mL) was refluxed overnight. The mixture was filtered through an alumina pad. The solvent was evaporated under vacuum and the resulting solid was further purified by precipitation from an acetone/hexane/methanol mixture to afford the desired metallo-porphyrin **4** (219 mg, 0.18 mmol, 99%) as a red solid.

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 8.68 (d, *J* = 8.8 Hz, 1H, H_5), 8.48 – 8.42 (m, 2H, H_{pyrr}), 8.38 (d, *J* = 4.8 Hz, 1H, H_{pyrr}), 8.34 (d, *J* = 4.7 Hz, 1H, H_{pyrr}), 8.31 (d, *J* = 4.8 Hz, 1H, H_{pyrr}), 8.16 (d, *J* = 4.9 Hz, 1H, H_{pyrr}), 8.08 (d, *J* = 8.8 Hz, 1H, H_6), 7.99 (d, *J* = 8.2 Hz, 1H, $H_{7\text{-}12}$), 7.96 (d, *J* = 8.2 Hz, 1H, $H_{7\text{-}12}$), 7.93 (d, *J* = 5.0 Hz, 1H, H_{pyrr}), 7.81 – 7.69 (m, 3H, 2*$H_{7\text{-}12}$ + H_{13}), 7.61 (d, *J* = 8.1 Hz, 1H, $H_{7\text{-}12}$), 7.55 – 7.50 (m, 2H, H_{Ar} + H_{14}), 7.48 (d, *J* = 8.4 Hz, 1H, H_{16}), 7.46 (s, 1H, H_3), 7.40 (d, *J* = 8.7 Hz, 1H, $H_{7\text{-}12}$), 7.35 (d, *J* = 8.7 Hz, 1H, $H_{7\text{-}12}$), 7.32 (br s, 1H, H_{Ar}), 7.31 (br s, 1H, H_{Ar}), 7.21 (br s, 2H, H_{Ar}), 7.17 (br s, 1H, H_{Ar}), 7.12 (d, *J* = 4.7 Hz, 1H, H_{pyrr}), 7.01 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H, H_{15}), 4.00 (s, 3H, OCH_{3out}), 2.21 (s, 3H, CH_{3Ar}), 2.00 (s, 3H, CH_{3Ar}), 1.71 (s, 3H, CH_{3Ar}), 1.56 (s, 12H, CH_{3Ar} + H_{tBu}), 1.52 (s, 3H, CH_{3Ar}), 1.51 (s, 3H, CH_{3Ar}), 1.45 (s, 9H, H_{tBu}), 1.39 (s, 9H, H_{tBu}), 1.31 (s, 3H, OCH_{3in}).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 151.0, 150.9, 150.8, 149.3, 143.1, 142.6, 142.5, 142.44, 142.42, 142.37, 142.0, 138.82, 138.79, 138.62, 138.60, 138.4, 137.7, 137.5, 137.4, 134.2 (CH), 132.7, 132.31, 132.29, 131.43 (CH), 131.39 (CH), 131.20 (CH), 131.18 (CH), 131.11 (CH), 131.09, 131.0 (CH), 130.4 (CH), 129.5, 128.8 (CH), 128.7, 127.6 (CH), 127.5 (CH), 127.3 (CH), 127.1 (CH), 126.5 (CH), 126.3 (CH), 125.9 (CH), 125.7 (CH), 125.4, 125.3, 125.2, 125.0 (CH), 124.9, 124.5 (CH), 124.05 (CH), 123.97 (CH), 123.94 (CH), 123.87 (CH), 122.1 (CH), 117.07, 117.04, 115.4, 112.9 (CH), 58.3 (OCH_3), 56.4 (OCH_3), 34.9, 34.74, 34.71, 31.9 (*t*Bu), 31.8 (*t*Bu), 31.7 (*t*Bu), 22.3 (CH_3), 22.2 (CH_3), 21.9 (CH_3), 21.81 (CH_3), 21.78 (CH_3), 21.7 (CH_3).

ESI-TOF-HR-MS (m/z): Calcd for ([M+H$^+$]) 1233.5551; found 1233.5568.

UV-vis (CH_2Cl_2): λ_{max} = 418 nm (ε = 182000 L.cm^{-1}.mol^{-1}), 515 (9900), 548 (3000), 591 (3000), 646 (1800).

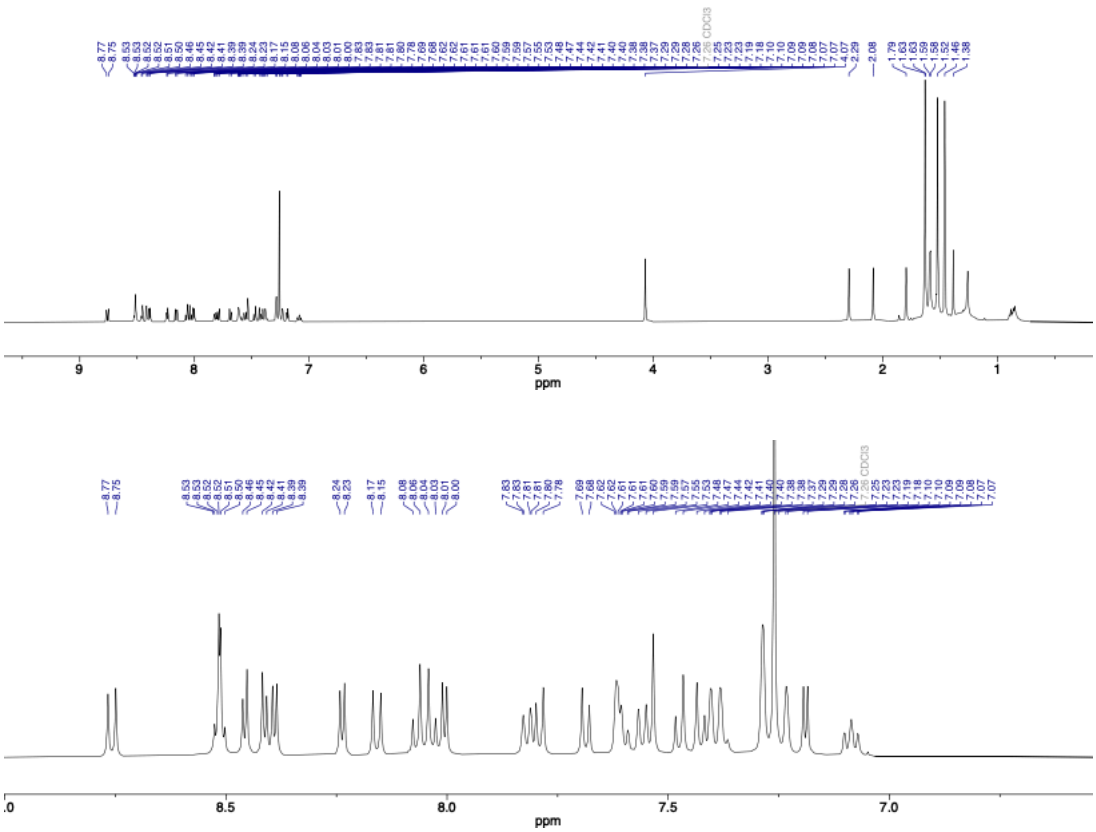


Figure S28: ^{1}H spectrum of **4** in $CDCl_3$ at 298 K (500 MHz).

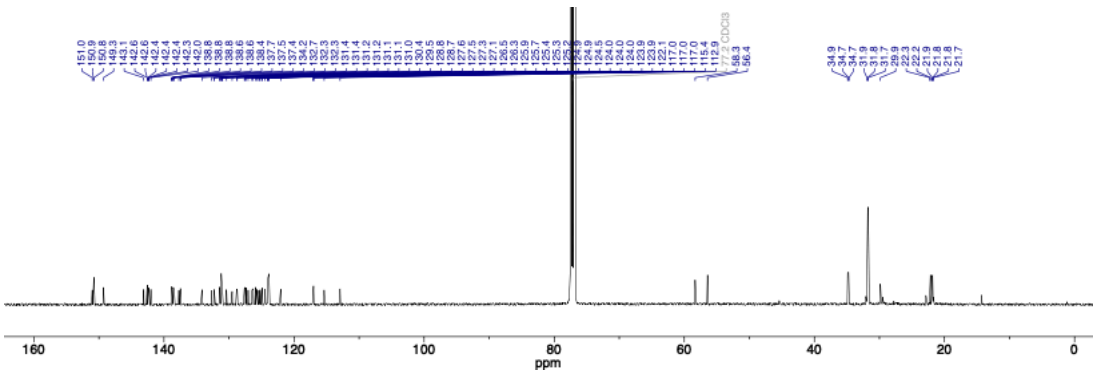


Figure S29: ^{13}C spectrum of **4** in $CDCl_3$ at 298 K (126 MHz).

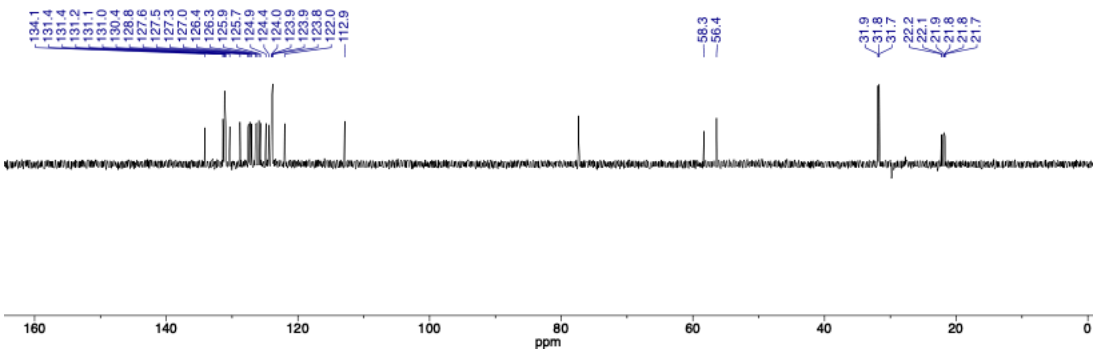


Figure S30: ^{13}C DEPT spectrum of **4** in $CDCl_3$ at 298 K (126 MHz).

IV Synthesis of the six-membered ring helicene-fused porphyrin

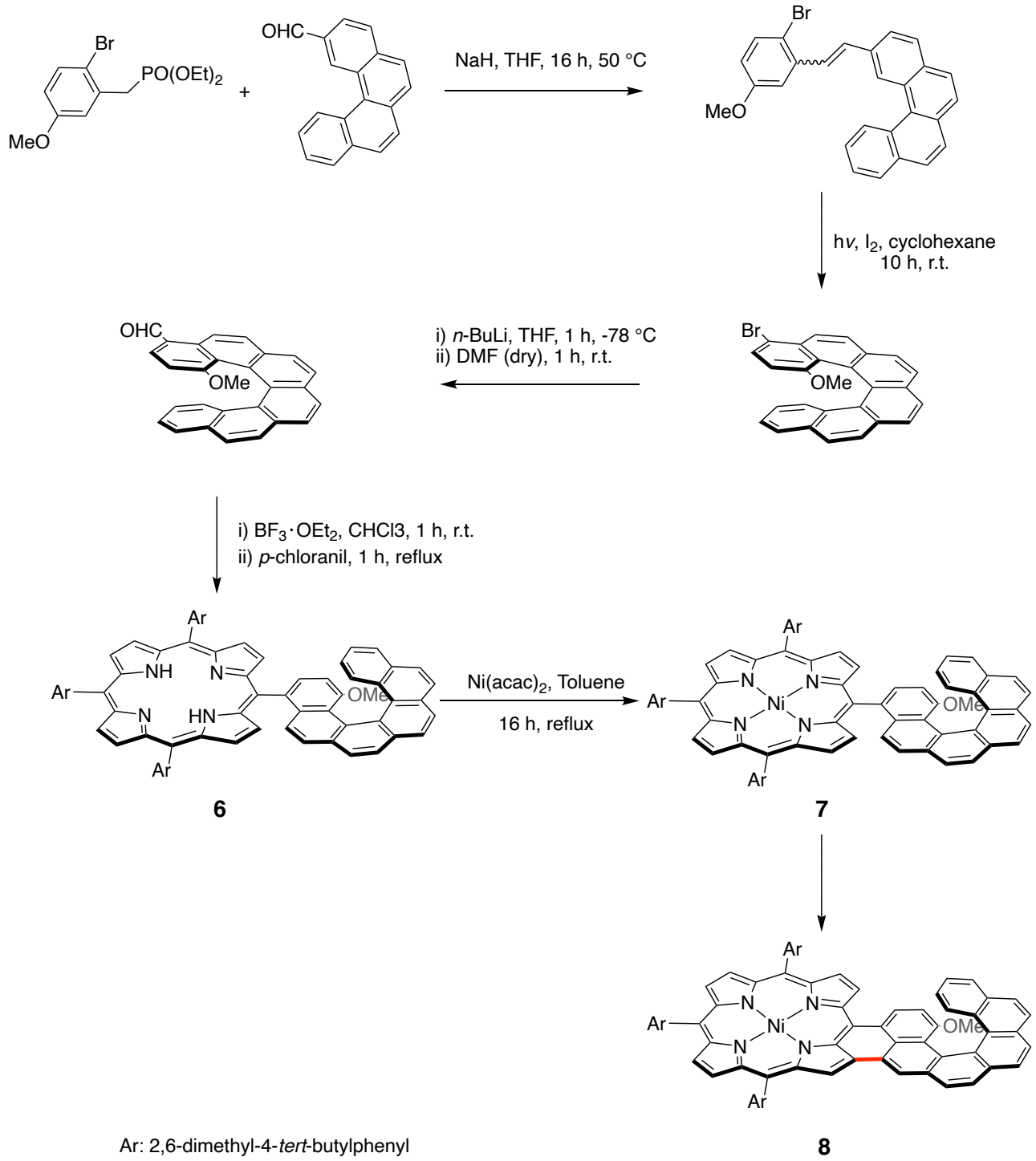
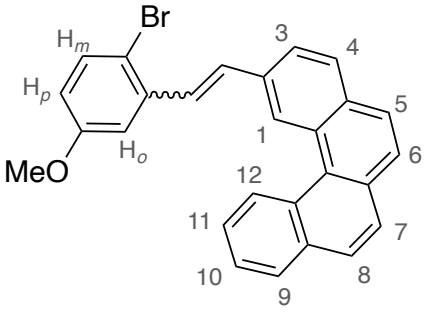


Figure S29. Synthesis of the six-membered ring helicene-fused porphyrin **8**.

IV.1 Synthesis of the 2-(2-bromo-5-methoxystyryl)benzo[*c*]phenanthrene



Chemical Formula: $C_{27}H_{19}BrO$
Exact Mass: 438.0619
Molecular Weight: 439.3520

Under argon, NaH (60% in mineral oil) (552 mg, 13.8 mmol, 1.0 eq.) was added to a solution of diethyl 2-bromo-5-methoxybenzylphosphonate (4.65 g, 13.8 mmol, 1.0 eq.) in freshly distilled THF (50 mL). After 15 min of stirring at room temperature, a solution of 2-formyl-[4]helicene (3.18 g, 12.4 mmol, 0.9 eq.) in freshly distilled THF (35 mL) was added dropwise. The resulting solution was heated at 50 °C for 16 h. The solution was allowed to cool to room temperature and H_2O (50 mL) was added. The solution was concentrated under reduced pressure. The resulting solid was dissolved in CH_2Cl_2 (50 mL) and the solution was washed with a saturated aqueous solution of NH_4Cl (3 x 20 mL), dried over $MgSO_4$, and filtered. Subsequent purification of the crude product by column chromatography afforded the desired product as a yellow solid (5.26 g, 12.0 mmol, 87%).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.21 (d, J = 1.5 Hz, 1H, H_1), 9.17 (d, J = 8.5 Hz, 1H, H_{12}), 8.11 – 8.00 (m, 2H, $H_{5\text{-}8}$ + H_9), 7.96 – 7.88 (m, 3H, $H_{5\text{-}8}$ + H_3), 7.84 (m, 1H, H_4), 7.83 (m, 1H, $H_{5\text{-}8}$), 7.74 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H, H_{11}), 7.69 – 7.61 (m, 2H, H_{alkene} + H_{10}), 7.51 (d, J = 8.8 Hz, 1H, H_m), 7.35 – 7.29 (m, 2H, H_{alkene} + H_o), 6.75 (dd, J = 8.8, 3.0 Hz, 1H, H_p), 3.89 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 159.2, 137.9, 134.9, 133.8 (CH), 133.7, 133.4, 132.1 (CH), 131.5, 130.7, 130.4, 129.2 (CH), 128.8 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 127.32 (CH), 127.29, 127.0 (CH), 126.5 (CH), 126.1 (CH), 123.6 (CH), 115.3 (CH), 115.2, 111.9 (CH), 55.8 (OCH_3).

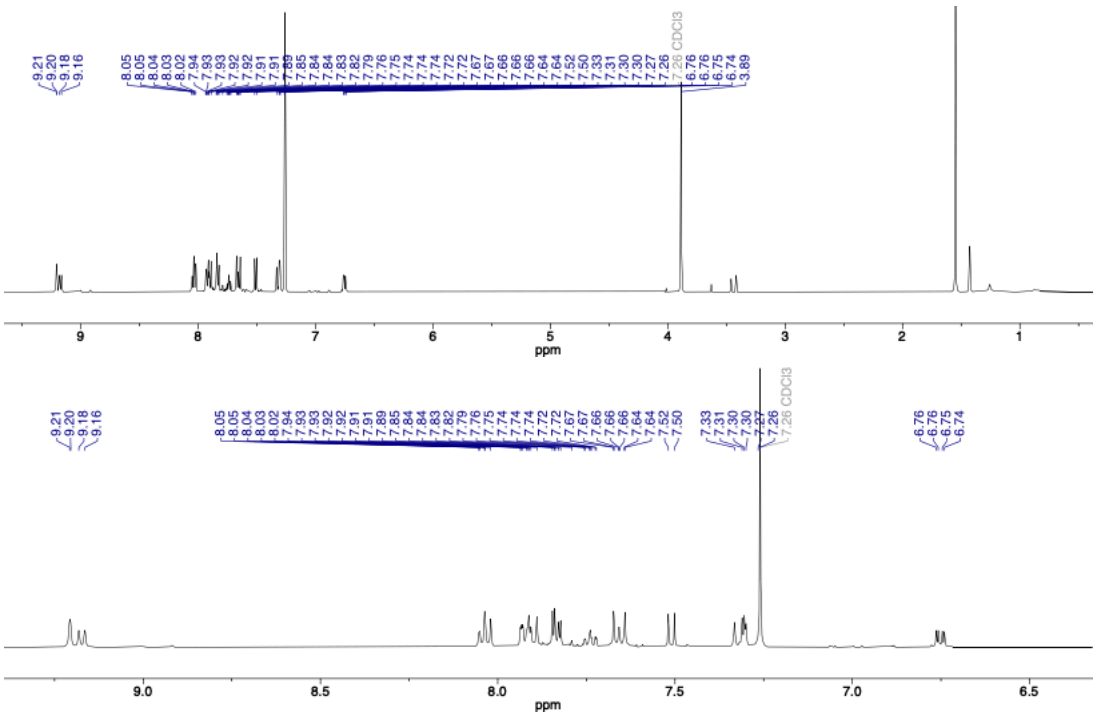


Figure S30: ^{1}H spectrum of the 2-(2-bromo-5-methoxystyryl)benzo[c]phenanthrene in $CDCl_3$ at 298 K (500 MHz) and aromatic area (bottom).

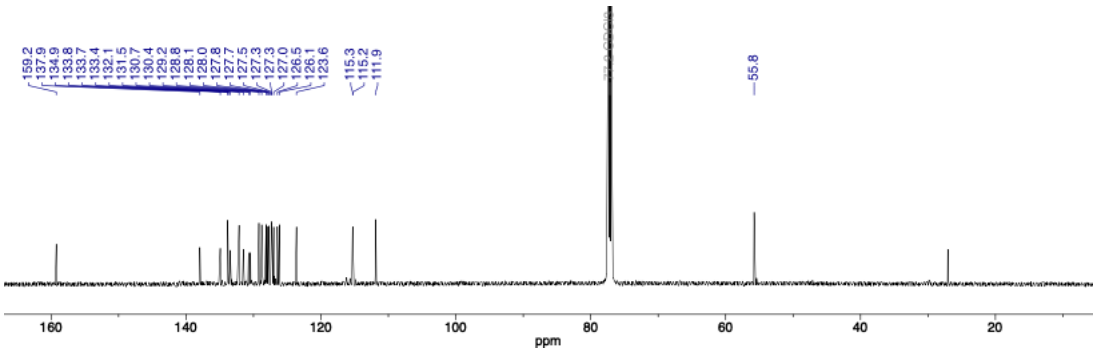


Figure S31: ^{13}C spectrum of the 2-(2-bromo-5-methoxystyryl)benzo[c]phenanthrene in $CDCl_3$ at 298 K (126 MHz) with residual cyclohexane.

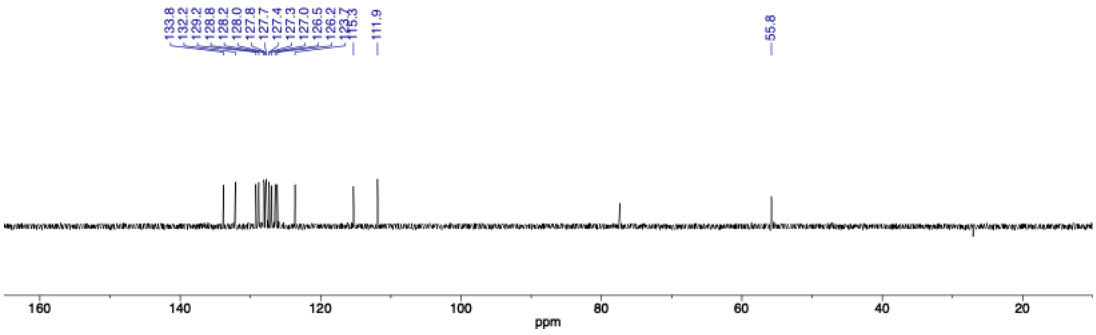
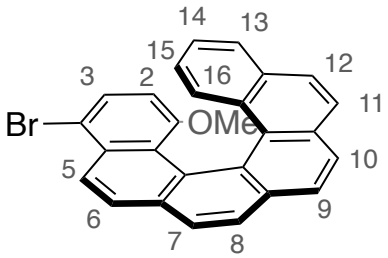


Figure S32: ^{13}C DEPT spectrum of the 2-(2-bromo-5-methoxystyryl)benzo[c]phenanthrene in $CDCl_3$ at 298 K (126 MHz).

IV.2 Synthesis of the 1-methoxy-4-bromo-[6]helicene (±)



Chemical Formula: $C_{27}H_{17}BrO$
Exact Mass: 436.0463
Molecular Weight: 437.3360

A solution of 2-(2-bromo-5-methoxystyryl)benzo[*c*]phenanthrene (1.00 g, 2.56 mmol, 1 eq.) and iodine (≃ 0.015 eq.) in a mixture of cyclohexane (390 mL) and propylene oxide (10 mL) was irradiated in a photoreactor equipped with an immersion lamp (150 W) for 10 h. Sodium thiosulfate (5 g) was added and the solution was stirred overnight. The solvent was evaporated, and the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 40/60) to afford the 1-methoxy-4-bromo-[6]helicene (±) as a yellow solid (511 mg, 1.10 mmol, 51%).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 8.36 (d, *J* = 8.8 Hz, 1H, H_5), 8.09 (d, *J* = 8.1 Hz, 1H, $H_{7\text{-}12}$), 8.04 (d, *J* = 8.8 Hz, 1H, $H_{7\text{-}12}$), 8.02 – 7.95 (m, 3H, H_6 + 2$H_{7\text{-}12}$), 7.93 (d, *J* = 8.5 Hz, 1H, $H_{7\text{-}12}$), 7.86 (d, *J* = 8.5 Hz, 1H, $H_{7\text{-}12}$), 7.77 (dd, *J* = 8.1, 1.4 Hz, 1H, H_{13}), 7.49 (d, *J* = 8.4 Hz, 1H, H_3), 7.16 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H, H_{14}), 7.06 (dd, *J* = 8.5, 1.2 Hz, 1H, H_{16}), 6.60 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, H_{15}), 5.97 (d, *J* = 8.5 Hz, 1H, H_2), 2.57 (s, 3H, OCH_3).
^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 154.8, 132.1, 132.0, 131.9, 131.3, 130.6, 130.1 (CH), 129.0, 128.5 (CH), 128.3, 127.9 (CH), 127.4 (CH), 127.1 (CH), 126.9 (CH), 126.6 (CH), 126.4 (CH), 126.30 (CH), 126.29 (CH), 125.5 (CH), 125.3, 124.2, 123.90 (CH), 123.87, 113.3, 106.0 (CH), 54.0 (CH_3).
ESI-TOF-MS (m/z): Calcd for ([M·$^+$]) 436.0457; found 436.0436.

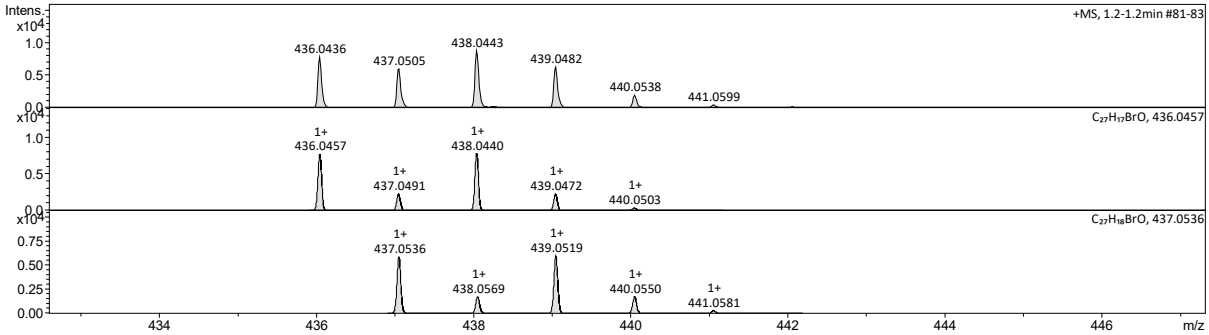


Figure S33: ESI-HR exper. mass spectrum (top) and simulations of M^+ and $M+H^+$ (bottom).

Crystal data: From CH_2Cl_2, $C_{27}H_{17}BrO$, M = 437.32 g.mol^{-1}, monoclinic space group, P 21/c, a = 8.4721 (3) Å, b = 16.1858 (7) Å, c = 14.3123 (6) Å, α = 90.0°, β = 105.9750°, γ = 90.0°, V = 1886.82 (13) Å^3, Z = 4, T = 120 (2) K, MoK\α = 0.71073, 1.943 < θ < 29.192, 68068 reflections measured, R_1 = 2.78%, *w*R_2 = 6.9%, GoF = 1.061. CCDC : 2157002

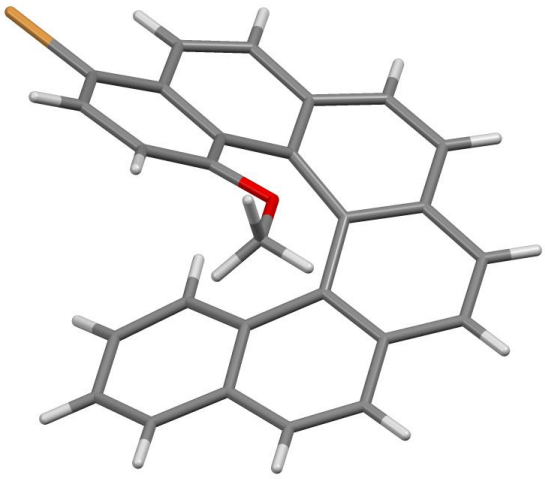


Figure S34. X-Ray structure of the 1-methoxy-4-bromo-[6]helicene.

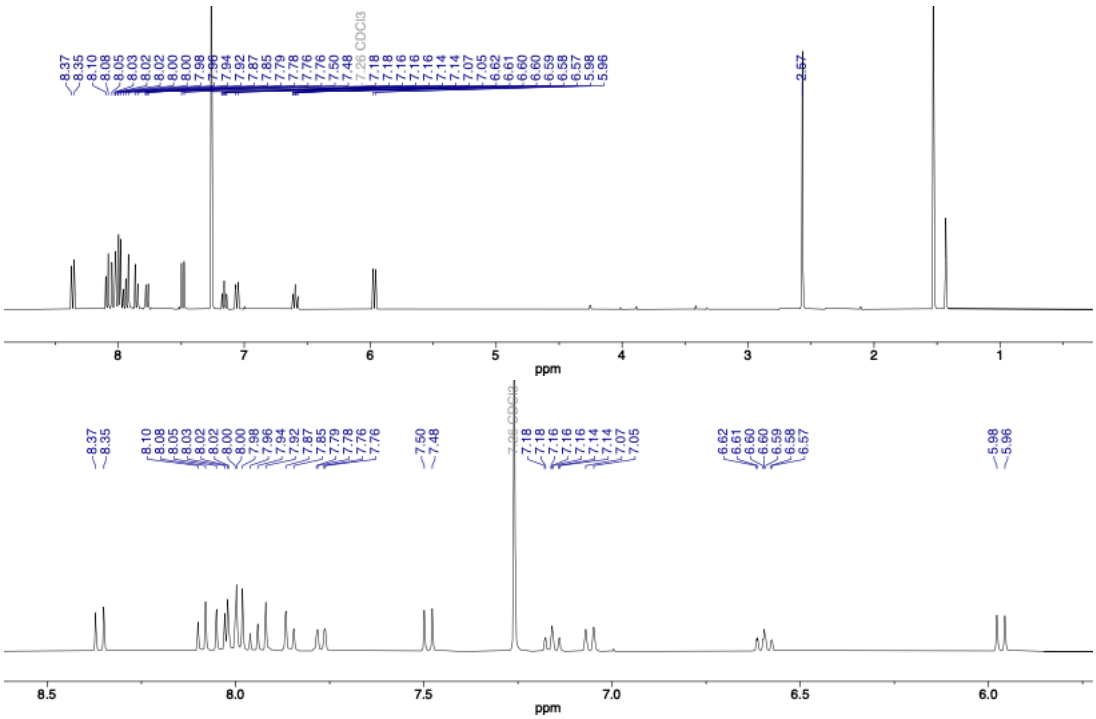


Figure S35: ^{1}H spectrum of the 1-methoxy-4-bromo-[6]helicene (±) in $CDCl_3$ at 298 K (500 MHz).

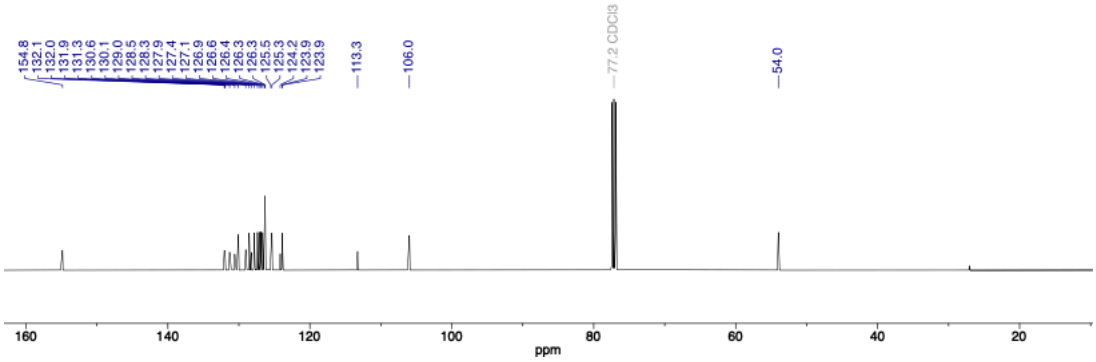


Figure S36: ^{13}C spectrum of the 1-methoxy-4-bromo-[6]helicene (±) in $CDCl_3$ at 298 K (126 MHz).

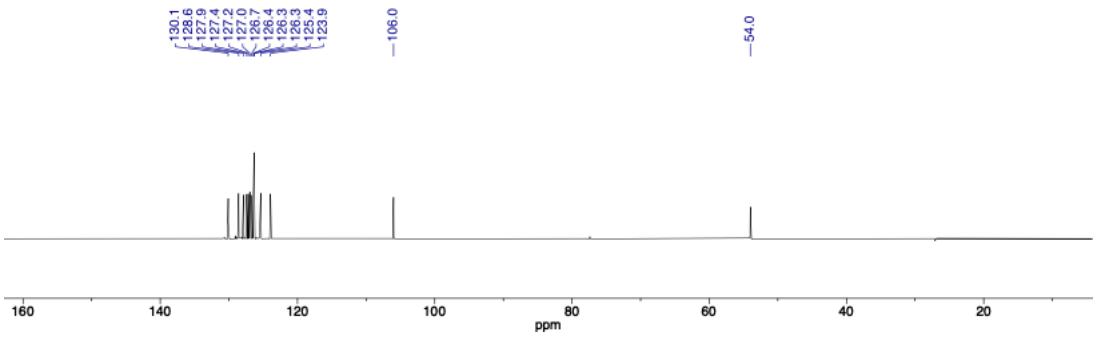
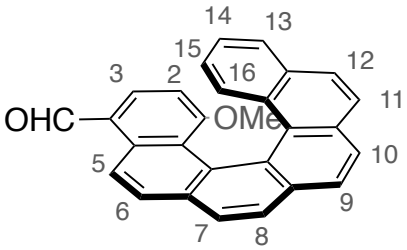


Figure S37: ^{13}C DEPT spectrum of the 1-methoxy-4-bromo-[6]helicene (±) in $CDCl_3$ at 298 K (126 MHz).

IV.3 Synthesis of the 1-methoxy-4-formyl-[6]helicene (±)



Chemical Formula: $C_{28}H_{18}O_2$
Exact Mass: 386.1307
Molecular Weight: 386.4500

Under argon at -78 °C, a solution of *n*-BuLi (1.6 M in hexanes) (2.21 mL, 3.54 mmol, 1.2 eq.) was added to a solution of 1-methoxy-4-bromo-[6]helicene (1.29 g, 2.95 mmol, 1.0 eq.) in distilled THF (30 mL). After 1 h of stirring at this temperature, dry DMF (0.82 mL, 8.85 mmol, 3 eq.) was added, the solution was allowed to warm to room temperature and H_2O (30 mL) was added. The solution was concentrated under reduced pressure and CH_2Cl_2 (30 mL) was added. The organic layer was washed with a saturated aqueous solution of NH_4Cl (5 x 30 mL), dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure. The desired compound was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 40/60) to afford the desired product as a yellow solid (784 mg, 2.03 mmol, 69%).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 10.33 (s, 1H, CHO), 9.45 (d, J = 8.8 Hz, 1H, H_5), 8.14 (d, J = 8.9 Hz, 1H, H_6), 8.10 (d, J = 8.1 Hz, 1H, $H_{7\text{-}12}$), 8.06 – 7.99 (m, 2H, 2*$H_{7\text{-}12}$), 7.97 (d, J = 8.1 Hz, 1H, $H_{7\text{-}12}$), 7.93 (d, J = 8.5 Hz, 1H, $H_{7\text{-}12}$), 7.86 (d, J = 8.5 Hz, 1H, $H_{7\text{-}12}$), 7.78 (dd, J = 8.0, 1.4 Hz, 1H, H_{13}), 7.72 (d, J = 8.2 Hz, 1H, H_3), 7.15 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H, H_{14}), 7.09 (dd, J = 8.6, 1.1 Hz, 1H, H_{16}), 6.53 (ddd, J = 8.5, 6.9, 1.4 Hz, 1H, H_{15}), 6.18 (d, J = 8.2 Hz, 1H, H_2), 2.68 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 192.7 (CH), 160.1, 138.0 (CH), 132.2, 132.03, 131.99, 131.8, 130.5, 130.3 (CH), 129.2, 128.3, 127.9 (CH), 127.5 (CH), 127.2 (CH), 127.1 (CH), 126.9 (CH), 126.51 (CH), 126.47 (CH), 126.4 (CH), 125.6 (CH), 125.4, 124.3, 123.97 (CH), 123.96, 123.3 (CH), 122.4, 104.4 (CH), 54.4 (CH_3).

ESI-TOF-MS (m/z): Calcd for ([M + H^+]) 387.1380; found 387.1376.

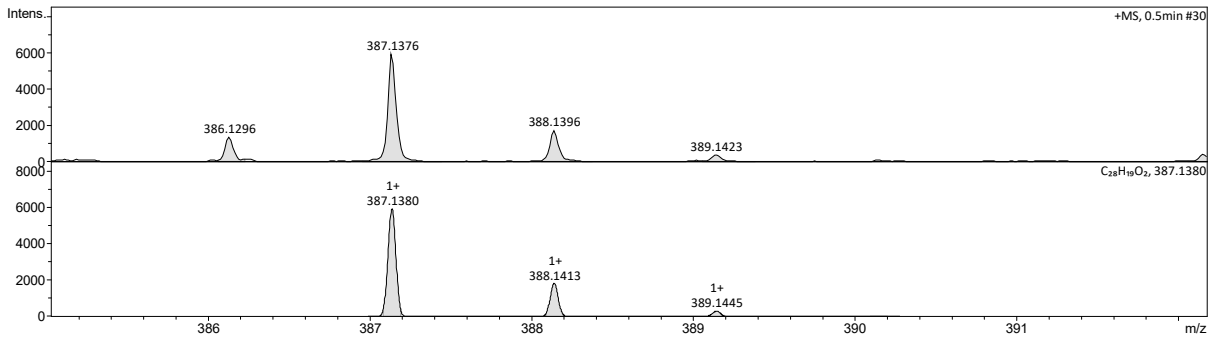


Figure S38: Experimental HR ESI-TOF spectrum (top) and simulation (bottom).

Crystal data: From CH_2Cl_2, $C_{28}H_{18}O_2$, M = 386.42 g.mol^{-1}, monoclinic space group, P 21/n, a = 11.5972 (4) Å, b = 12.8994 (5) Å, c = 13.7902 (5) Å, α = 90.0°, β = 114.2170°, γ = 90.0°, V = 1881.43 (12) Å^3, Z = 4, T = 120 (2) K, MoK\α = 0.71073, 2.262 < θ < 27.921, 71287 reflections measured, R_1 = 3.75%, wR_2 = 10.3%, GoF = 1.01708. CCDC : 2157005

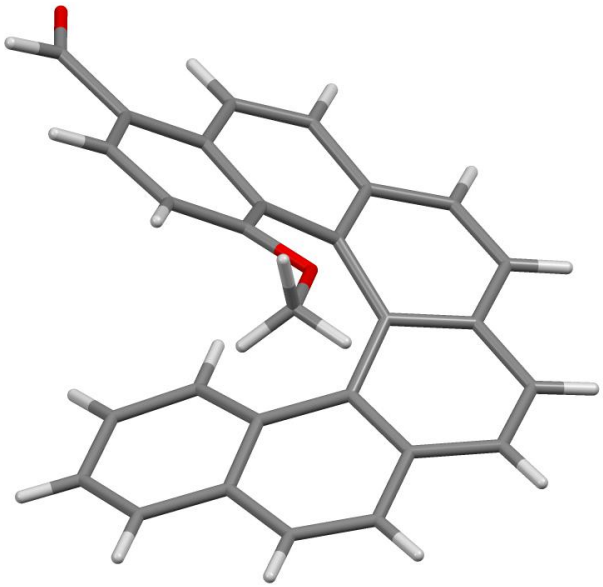


Figure S39. X-Ray structure of the 1-methoxy-4-formyl-[6]helicene (±).

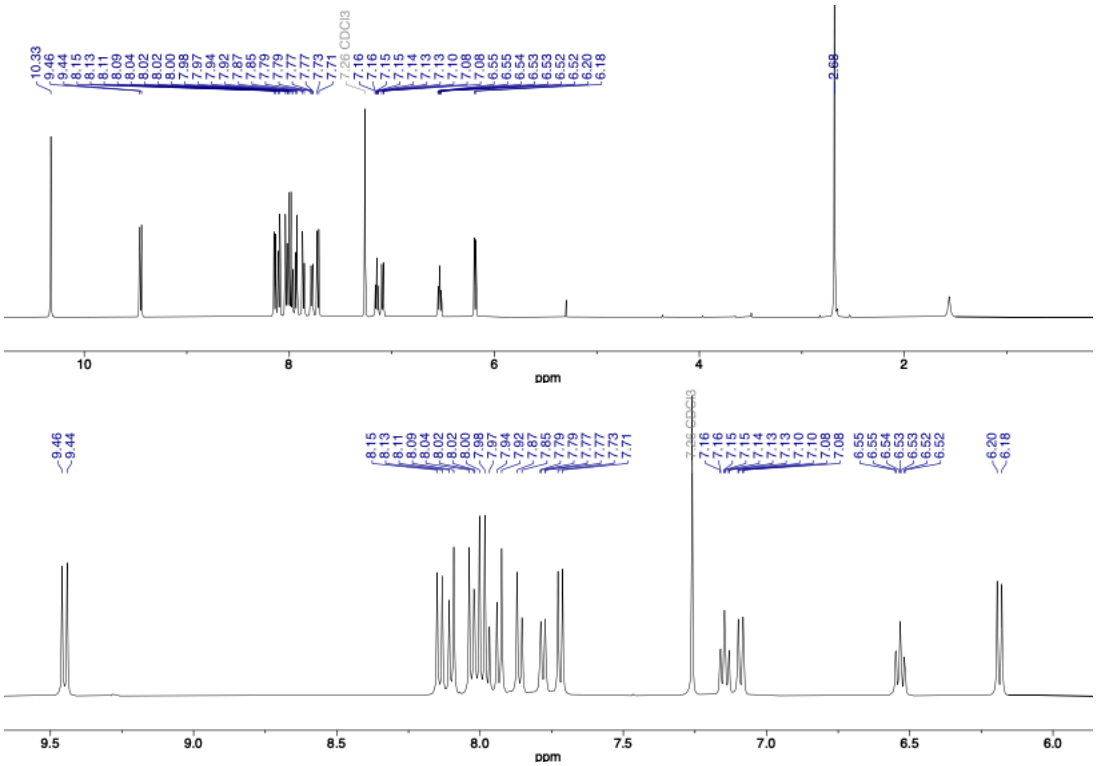


Figure S40: ^{1}H spectrum of the 1-methoxy-4-formyl-[6]helicene (±) in $CDCl_3$ at 298 K (500 MHz) and aromatic area.

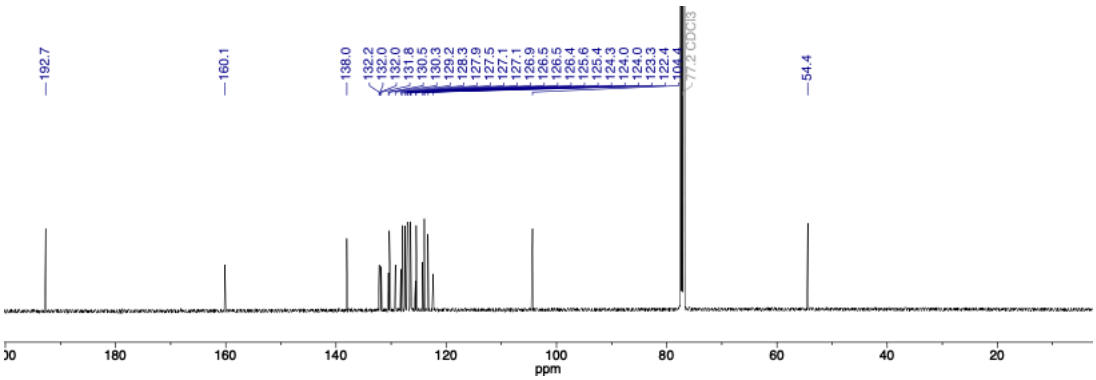


Figure S41: ^{13}C spectrum of the 1-methoxy-4-formyl-[6]helicene (±) in $CDCl_3$ at 298 K (126 MHz).

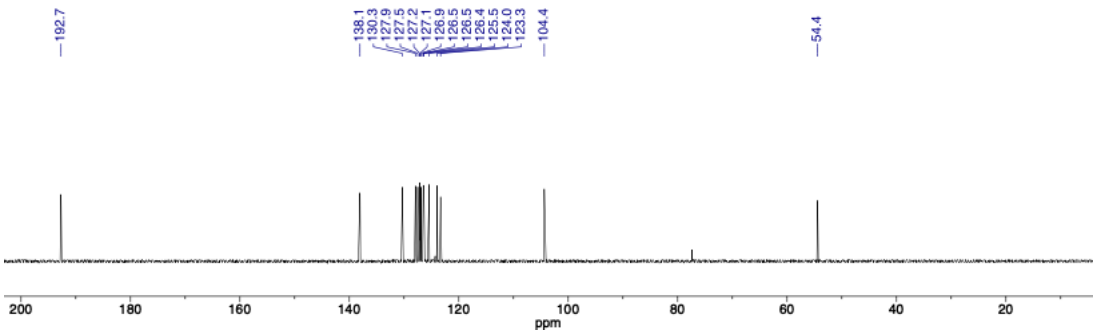
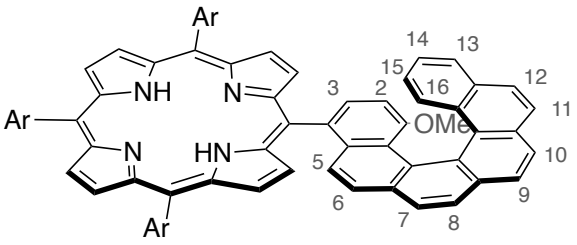
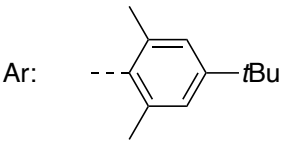


Figure S42: ^{13}C DEPT spectrum of the 1-methoxy-4-formyl-[6]helicene (±) in $CDCl_3$ at 298 K (126 MHz).

IV.4 Synthesis of the free-base porphyrin 6 (±)



Chemical Formula: $C_{83}H_{78}N_4O$
Exact Mass: 1146.6176
Molecular Weight: 1147.5640



A solution of 2,6-dimethyl-4-*tert*-butylbenzaldehyde (1.18 g, 6.22 mmol, 3 eq.), 1-methoxy-4-formyl-[6]helicene (0.80 g, 2.07 mmol, 1 eq.) and pyrrole (0.58 mL, 8.29 mmol, 4 eq.) in $CHCl_3$ (260 mL) was degassed in the dark for 30 minutes by argon bubbling. Under argon, $BF_3{\cdot}OEt_2$ (0.18 m mL, 0.74 mmol, 5.7 mM) was added and the solution was stirred in the dark at room temperature for 1 h. *p*-chloranil (1.53 g, 6.22 mmol, 3 eq.) was added and the solution was heated to reflux for an additional hour. The solution was filtered through a silica pad and evaporated to dryness. The desired porphyrin **6** was isolated by column chromatography (silica gel, cyclohexane/CH_2Cl_2 8/2 to 6/4) followed by precipitation from an acetone/hexane/methanol mixture to afford (0.22 g, 0.19 mmol, 9%) of a purple solid.

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.12 (d, *J* = 4.7 Hz, 1H, H_{pyrr}), 8.79 (d, *J* = 4.7 Hz, 1H, H_{pyrr}), 8.72 – 8.61 (m, 4H, H_{pyrr}), 8.56 (d, *J* = 4.7 Hz, 1H, H_{pyrr}), 8.39 (d, *J* = 4.8 Hz, 1H, H_{pyrr}), 8.09 (d, *J* = 8.0 Hz, 1H, H_5-H_{12}), 8.08 – 8.05 (m, 2H, H_5-H_{12}), 8.02 (d, *J* = 8.0 Hz, 1H, H_5-H_{12}), 8.00 (d, *J* = 8.6 Hz, 1H, H_5-H_{12}), 7.97 – 7.92 (m, 1H, H_{13}), 7.89 (d, *J* = 8.0 Hz, 1H, H_3), 7.74 (m, 1H, H_{16}), 7.54 (d, *J* = 8.9 Hz, 1H,), 7.48 – 7.38 (m, 7H, H_5-H_{12} + 6*H_{Ar}), 7.33 (d, *J* = 8.9 Hz, 1H, $H_{5\text{-}12}$), 7.26 (m, 1H, H_{15}), 6.52 (d, *J* = 7.9 Hz, 1H, H_2), 2.88 (s, 3H, OCH_3), 1.98 (s, 3H, CH_{3Ar}), 1.96 (s, 3H, CH_{3Ar}), 1.94 (s, 3H, CH_{3Ar}), 1.94 (s, 3H, CH_{3Ar}), 1.92 (s, 3H, CH_{3Ar}), 1.89 (s, 3H, CH_{3Ar}), 1.60 (s, 9H, H_{tBu}), 1.59 (s, 9H, H_{tBu}), 1.55 (s, 9H, H_{tBu}), -2.34 (s, 2H, NH).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 155.6, 151.09, 151.07, 151.0, 139.2, 139.13, 139.07, 139.0, 138.4, 138.31, 138.30, 136.29, 133.27 (CH), 132.4, 132.1, 131.5, 131.2, 131.1, 129.0, 128.9, 128.1 (CH), 127.5, 127.4 (CH), 127.21 (CH), 127.17 (CH), 127.0 (CH), 126.7 (CH), 126.5 (CH), 126.4 (CH), 126.0, 125.6 (CH), 124.5 (CH), 124.2 (CH), 124.1 (CH), 124.00 (CH), 123.96 (CH), 121.3, 118.4, 118.30, 118.27, 117.4, 103.7 (CH), 54.2 (OCH_3), 34.84, 34.79, 31.95 CH_3), 31.81 CH_3), 22.34 CH_3), 22.28 CH_3), 22.2 CH_3).

ESI-TOF-MS (m/z): Calcd for ([M + H^+]) 1147.6176; found 1147.6248.

UV-vis (CH_2Cl_2): λ_{max} = 423 nm (ε = 326000 L.cm^{-1}.mol^{-1}), 521 (20000), 556 (5100), 597 (6000), 650 (5200).

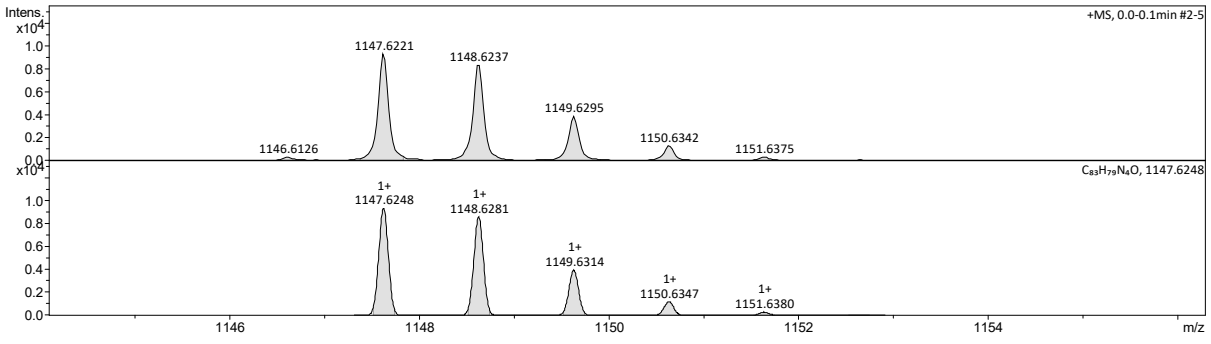


Figure S43: HR ESI-TOF spectrum of **6** and simulation.

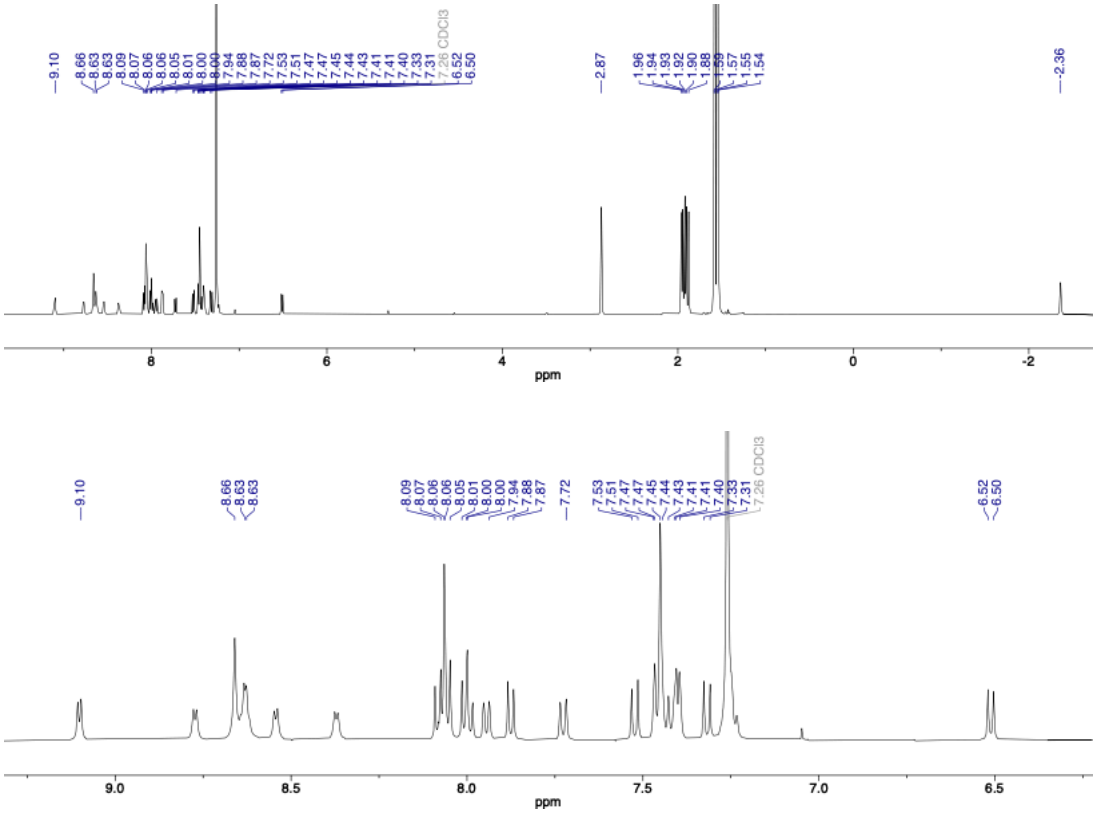


Figure S44: ^{1}H spectrum of **6** in $CDCl_3$ at 298 K (500 MHz) and aromatic area.

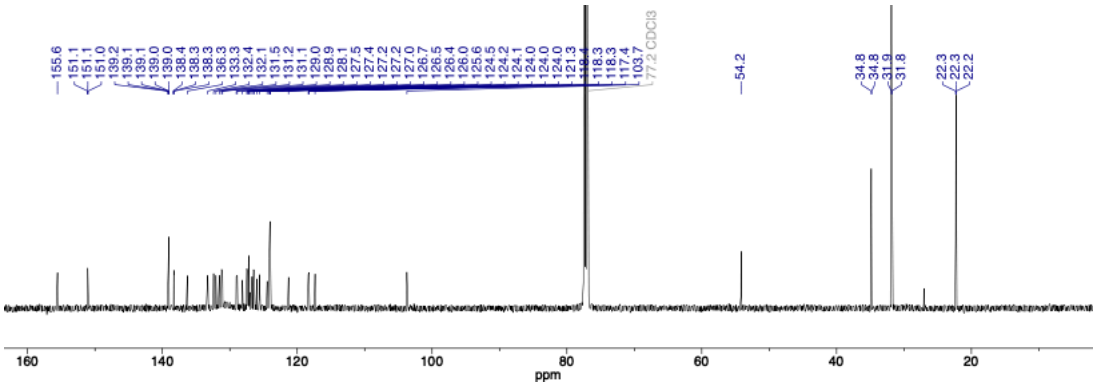


Figure S45: ^{13}C spectrum of **6** in $CDCl_3$ at 298 K (126 MHz).

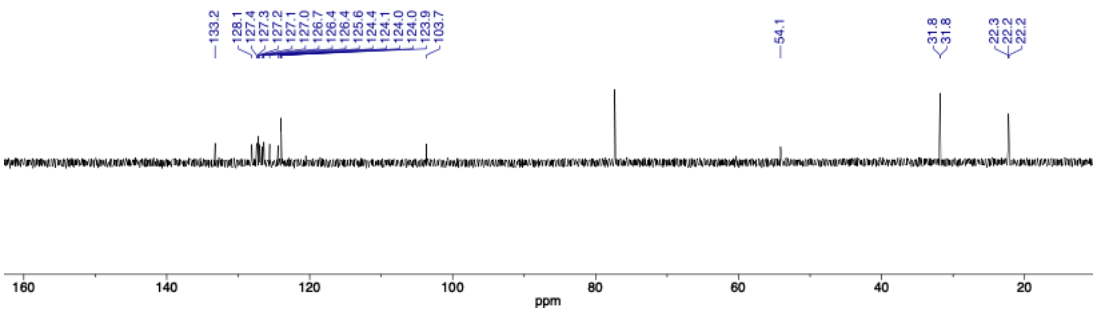
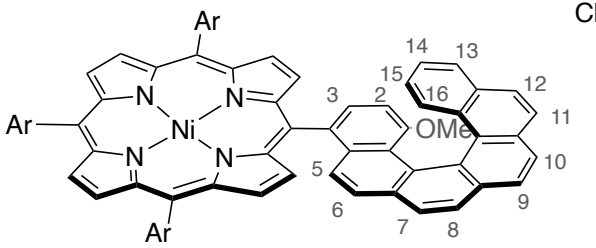
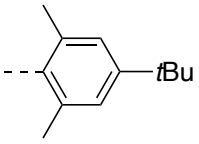


Figure S46: ^{13}C DEPT spectrum of **6** in $CDCl_3$ at 298 K (126 MHz).

IV.5 Synthesis of the Ni(II)-porphyrin 7 (±)



Chemical Formula: $C_{83}H_{76}N_4NiO$
Exact Mass: 1202.5373
Molecular Weight: 1204.2414

Ar: 

A solution containing the free-base porphyrin **6** (210 mg, 0.18 mmol, 1 eq.) and $Ni(acac)_2$ (235 g, 0.92 mmol, 5 eq.) in toluene (50 mL) was refluxed overnight. The mixture was filtered through an alumina pad. The solvent was evaporated under vacuum and the resulting solid was further purified by precipitation from an acetone/hexane/methanol mixture to afford the desired metallo-porphyrin **7** (219 mg, 0.18 mmol, 99%) as a red solid.

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.01 (d, J = 4.8 Hz, 1H, H_{pyrr}), 8.67 (d, J = 4.8 Hz, 1H, H_{pyrr}), 8.61 – 8.54 (m, 4H, H_{pyrr}), 8.46 (d, J = 4.9 Hz, 1H, H_{pyrr}), 8.33 (d, J = 4.8 Hz, 1H, H_{pyrr}), 8.10 – 8.00 (m, 4H, $H_{7\text{-}12}$), 7.97 (d, J = 8.7 Hz, 1H, $H_{7\text{-}12}$), 7.93 – 7.85 (m, 3H, H_3 + $H_{7\text{-}12}$ + H_{13}), 7.64 (d, J = 8.5 Hz, 1H, H_{16}), 7.55 (m, 1H, H_6), 7.48 – 7.34 (m, 6H, H_{14} + H_{Ar}), 7.32 (d, J = 2.0 Hz, 1H, H_{Ar}), 7.24 (m, 1H, H_5), 7.13 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H, H_{15}), 6.45 (d, J = 8.0 Hz, 1H, H_2), 2.83 (s, 3H, OCH_3), 1.99 (s, 3H, CH_{3Ar}), 1.94 (m, 6H, CH_{3Ar}), 1.88 (m, 6H, CH_{3Ar}), 1.87 (s, 3H, CH_{3Ar}), 1.80 (s, 3H, CH_{3Ar}), 1.55 (s, 9H, $H_{t\text{Bu}}$), 1.53 (s, 9H, $H_{t\text{Bu}}$), 1.50 (s, 9H, $H_{t\text{Bu}}$).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 155.4, 151.0, 150.9, 144.22, 144.17, 142.80, 142.77, 142.71, 142.69, 142.67, 138.8, 138.74, 138.68, 138.6, 137.5, 137.44, 137.41, 135.7, 132.7 (CH), 132.6 (CH), 132.39 (CH), 132.36, 132.0, 131.6, 131.54 (CH), 131.52 (CH), 131.3 (CH), 131.1 (CH), 131.0, 130.4, 129.0, 128.8, 127.9 (CH), 127.4 (CH), 127.3 (CH), 127.16 (CH), 127.14 (CH), 127.0 (CH), 126.7 (CH), 126.5 (CH), 126.4 (CH), 126.0, 125.6 (CH), 124.4 (CH), 124.2, 124.1 (CH), 124.03 (CH), 123.99 (CH), 123.96 (CH), 121.3, 117.6, 117.5, 117.4, 116.7, 103.8 (CH), 54.1 (OCH_3), 34.8, 34.7, 31.81 (CH_3), 31.77 (CH_3), 22.10 (CH_3), 22.08 (CH_3), 22.05 (CH_3), 22.0 (CH_3), 21.9 (CH_3)

ESI-TOF-MS (m/z): Calcd for ([M + H^+]) 1202.5367; found 1202.5315.

UV-vis (CH_2Cl_2): λ_{max} = 419 nm (ε = 263000 L.cm^{-1}.mol^{-1}), 530 (22700), 563 (3700).

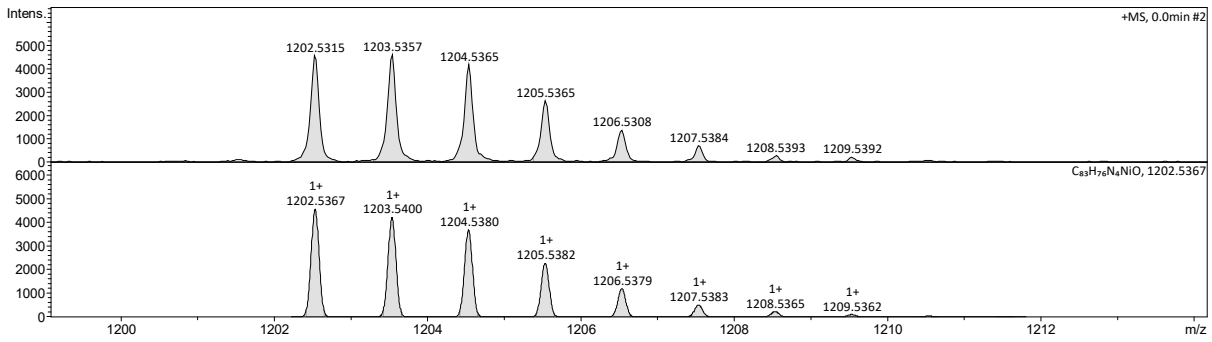


Figure S47: HR ESI-TOF spectrum of **7** and simulation.

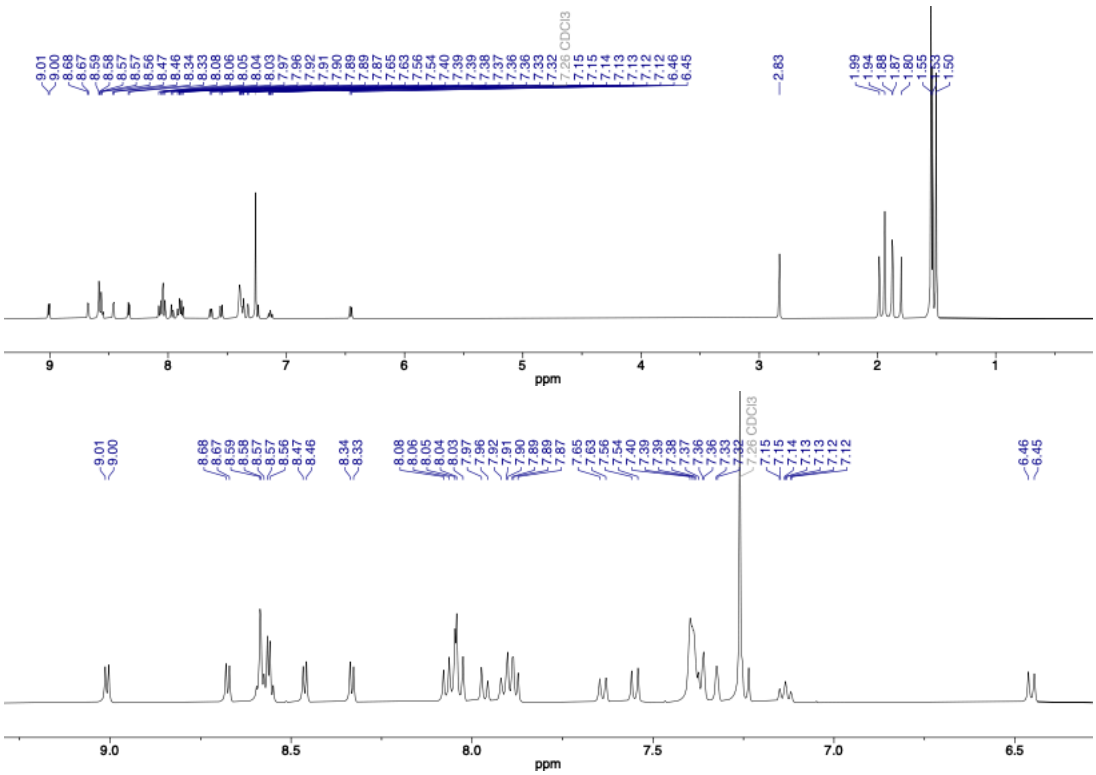


Figure S48: ^{1}H spectrum of **7** in $CDCl_3$ at 298 K (500 MHz).

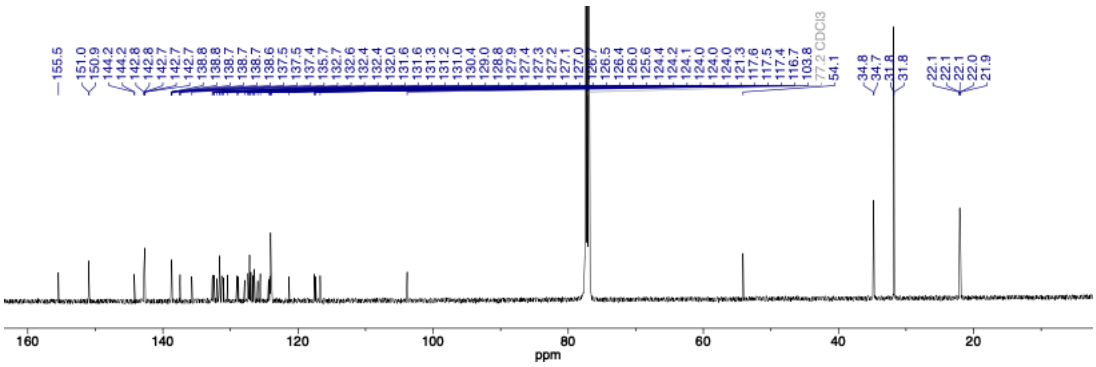


Figure S49: ^{13}C spectrum of **7** in $CDCl_3$ at 298 K (126 MHz).

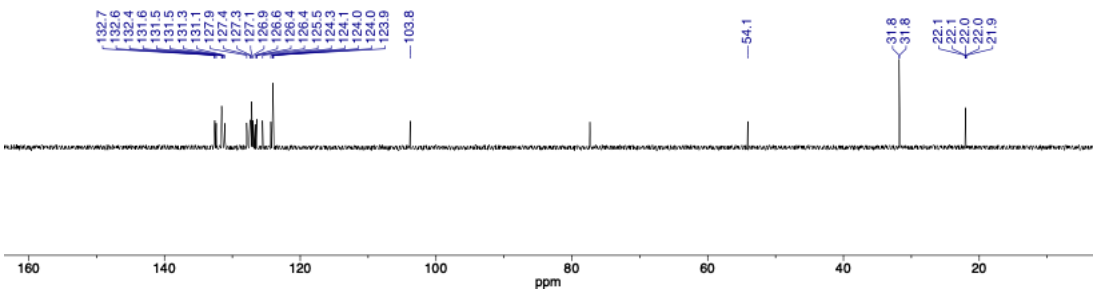
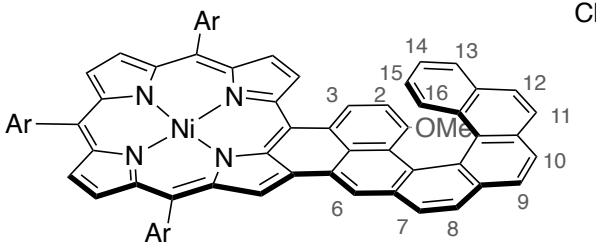
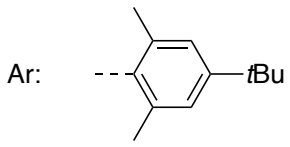


Figure S50: ^{13}C DEPT spectrum of **7** in $CDCl_3$ at 298 K (126 MHz).

IV.6 Synthesis and characterisation of the helicene-fused porphyrin 8 (±)



Chemical Formula: $C_{83}H_{74}N_4NiO$
Exact Mass: 1200.5216
Molecular Weight: 1202.2254



A solution of the Ni(II)-porphyrin **7** (15.0 mg, 13.6 mmol, 1 eq.) in chlorobenzene (6 mL) was degassed for 30 min by argon bubbling. A solution of anhydrous iron (III) chloride (22 mg, 136 mmol, 10 eq.) in $MeNO_2$ (1 mL) was degassed by argon bubbling for 30 min and added to the former solution. The resulting dark green solution was heated to 50 °C while maintaining an argon bubbling for 4 h. The mixture was allowed to cool to room temperature and NEt_3 (3 mL) was added, followed by MeOH (5 mL). H_2O (50 mL) and CH_2Cl_2 (50 mL) were added. The organic layer was isolated, washed twice with water, dried over Na_2SO_4 and the solvents were evaporated under vacuum. The resulting crude solid was purified by column chromatography (SiO_2, CH_2Cl_2/cyclohexane 15/85 to 40/60) to afford the helicene-fused porphyrin **8** (13.3 mg, 12.1 mmol, 89%) as a green solid.

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ_H (ppm) = 9.13 (s, 1H, H_{pyrr}), 9.08 (m, 2H, H_6 + H_{pyrr}), 8.67 (d, J = 4.8 Hz, 1H, H_{pyrr}), 8.40 (m, 2H, H_{pyrr}), 8.36 (m, 2H, H_{pyrr}), 8.26 (d, J = 8.2 Hz, 1H, H_7), 8.15 (d, J = 8.2 Hz, 1H, H_8), 8.04 (d, J = 8.1 Hz, 1H, $H_{9\text{-}12}$), 8.00 (d, J = 8.1 Hz, 1H, $H_{9\text{-}12}$), 7.96 (d, J = 8.5 Hz, 1H, $H_{9\text{-}12}$), 7.92 (d, J = 8.5 Hz, 1H, $H_{9\text{-}12}$), 7.89 (m, 2H, H_3 + H_{14}), 7.58 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.58 – 7.54 (m, J = 8.3 Hz, 1H, H_{16}), 7.50 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.45 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.39 – 7.34 (m, 1H, H_{Ar}), 7.31 – 7.27 (m, 1H, H_{14}), 7.25 (d, J = 2.1 Hz, 1H, H_{Ar}), 7.23 (d, J = 2.1 Hz, 1H, H_{Ar}), 6.77 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H, H_{15}), 6.51 (d, J = 8.5 Hz, 1H, H_2), 2.77 (s, 3H, OCH_3), 2.42 (s, 3H, CH_{3Ar}), 2.37 (s, 3H, CH_{3Ar}), 2.35 (s, 3H, CH_{3Ar}), 1.66 (s, 3H, CH_{3Ar}), 1.62 (s, 9H, $H_{t\text{Bu}}$), 1.54 (s, 9H, $H_{t\text{Bu}}$), 1.51 (s, 12H, CH_{3Ar} + $H_{t\text{Bu}}$), 1.50 (s, 3H, CH_{3Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C (ppm) = 154.9, 151.0, 150.90, 150.87, 143.0, 142.9, 142.4, 142.1, 141.3, 140.8, 140.2, 139.2, 139.1 (CH), 139.0, 138.83, 138.76, 138.6, 138.51, 138.47, 137.1, 137.0, 136.9, 134.8 (CH), 132.8 (CH), 132.5, 132.3, 132.2, 132.1 (CH), 131.7 (CH), 131.6 (CH), 131.5 (CH), 130.9, 130.0, 129.6, 128.6, 128.0 (CH), 127.7 (CH), 127.5 (CH), 127.3 (CH), 127.1 (CH), 126.9 (CH), 126.6 (CH), 126.5 (CH), 126.2, 126.1, 125.9, 125.4 (CH), 124.9, 124.5 (CH), 124.3 (CH), 124.2 (CH), 124.1 (CH), 123.9 (CH), 123.6, 120.7 (CH), 118.2, 117.1, 116.3, 111.8, 107.3 (CH), 106.3, 105.6, 54.4 (OCH_3), 34.9, 34.8, 34.7, 31.9 (CH_3), 31.8 (CH_3), 31.7 (CH_3), 22.21 (CH_3), 22.20 (CH_3), 21.9 (CH_3), 21.8 (CH_3), 21.7 (CH_3).

ESI-TOF-MS (m/z): Calcd for ([M + H$^+$]) 1200.5216; found 1200.5167.

UV-vis (CH_2Cl_2): λ_{max} = 466 nm (ε = 63000 L.cm^{-1}.mol^{-1}), 496 (106000), 594 (12000), 663 (39000).

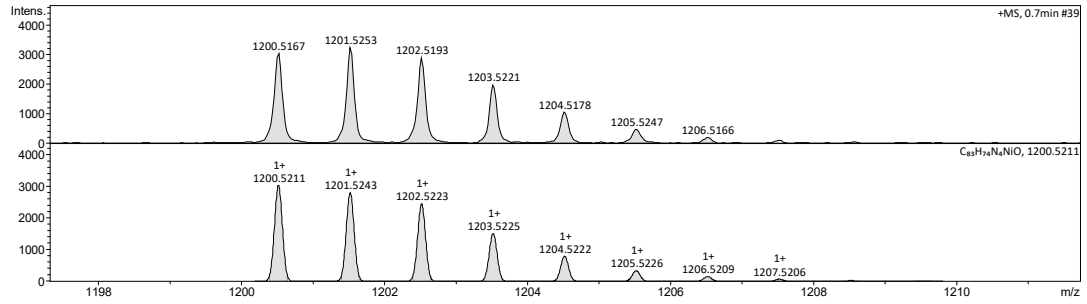


Figure S51: HR ESI-TOF spectrum of **8** and simulation.

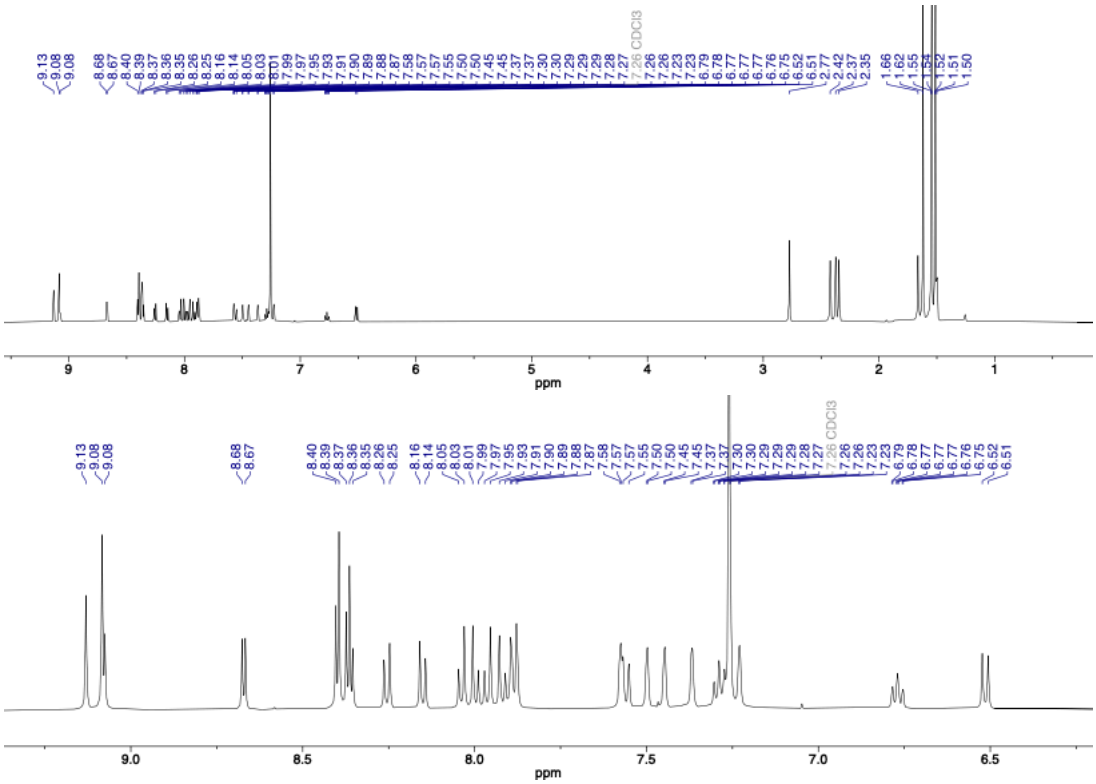


Figure S52: ^{1}H spectrum of **8** in $CDCl_3$ at 298 K (500 MHz) and aromatic area.

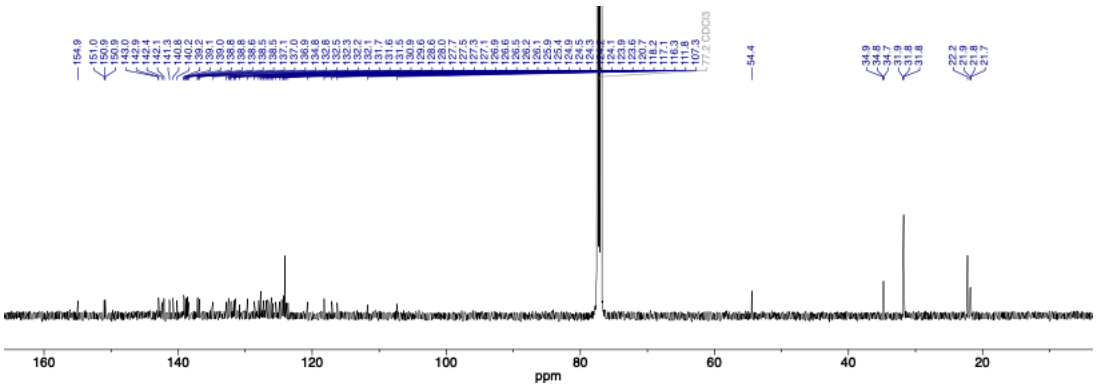


Figure S53: ^{13}C spectrum of **8** in $CDCl_3$ at 298 K (126 MHz).

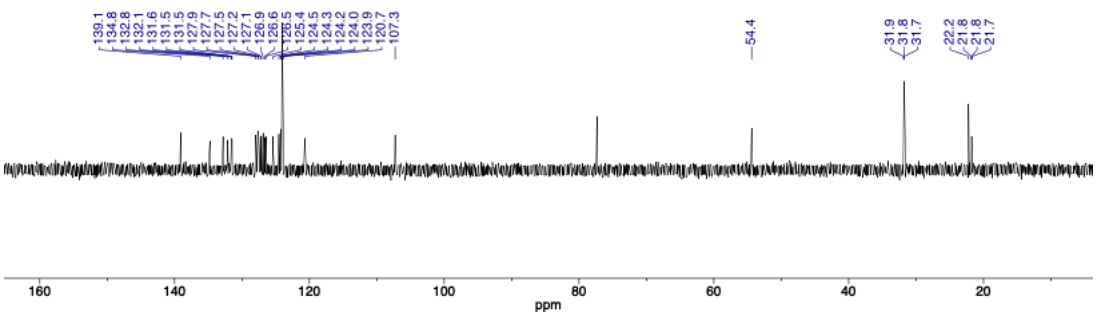


Figure S54: ^{13}C DEPT spectrum of **8** in $CDCl_3$ at 298 K (126 MHz).

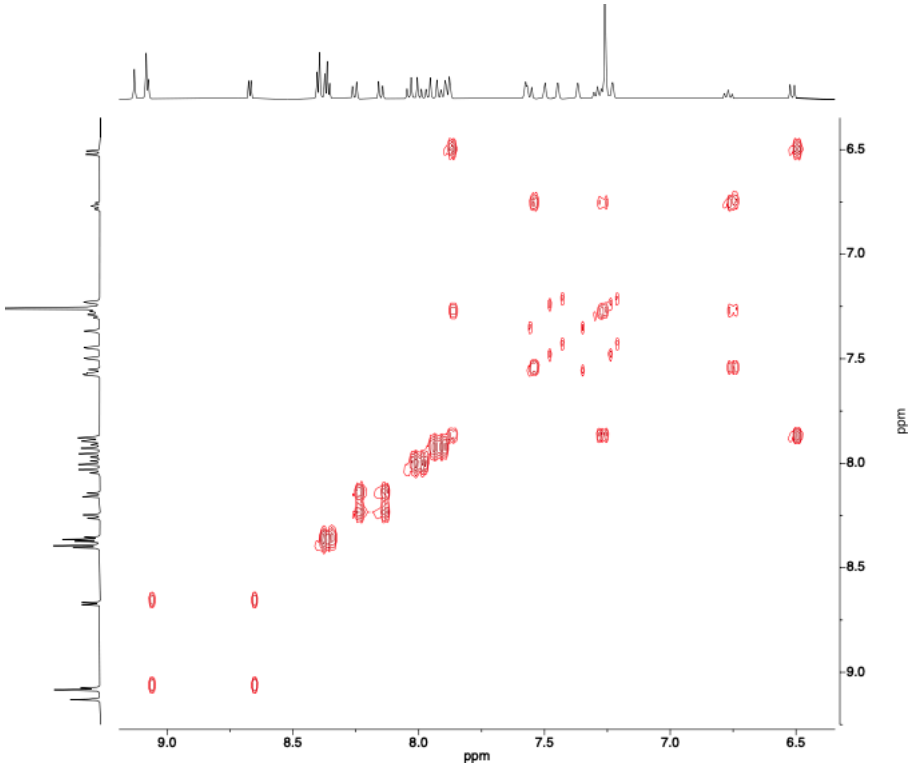


Figure S55: ^{1}H-1H COSY spectrum of **8** in $CDCl_3$ at 298 K, aromatic area.

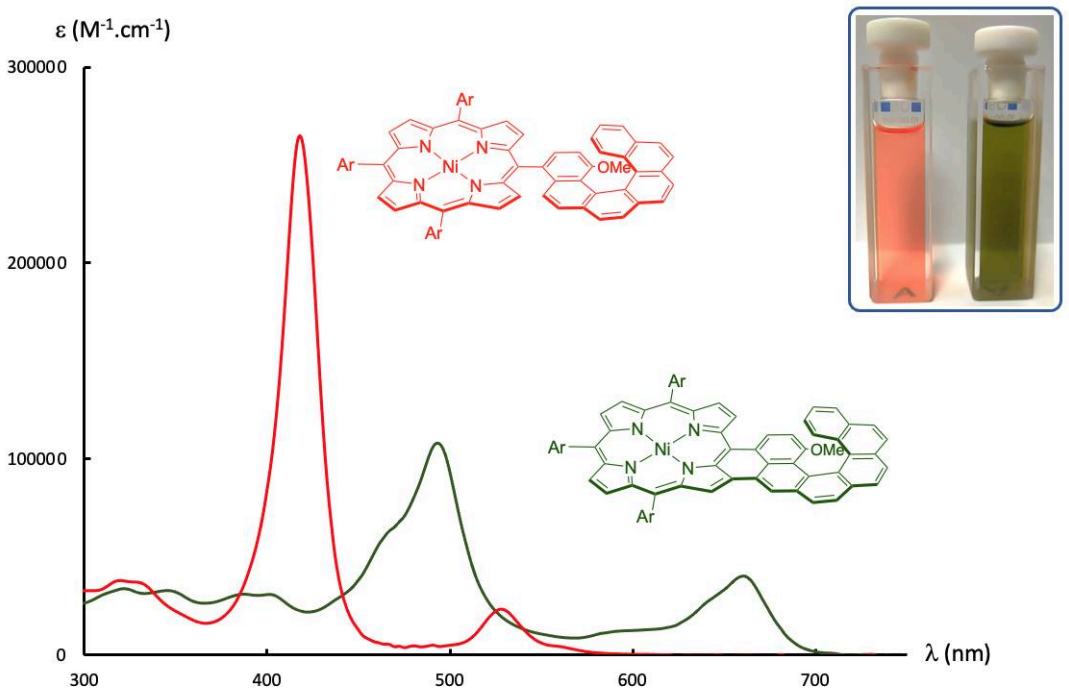


Figure S56: Electronic spectra of nickel(II) porphyrin **7** and nickel(II) fused porphyrin **8**.

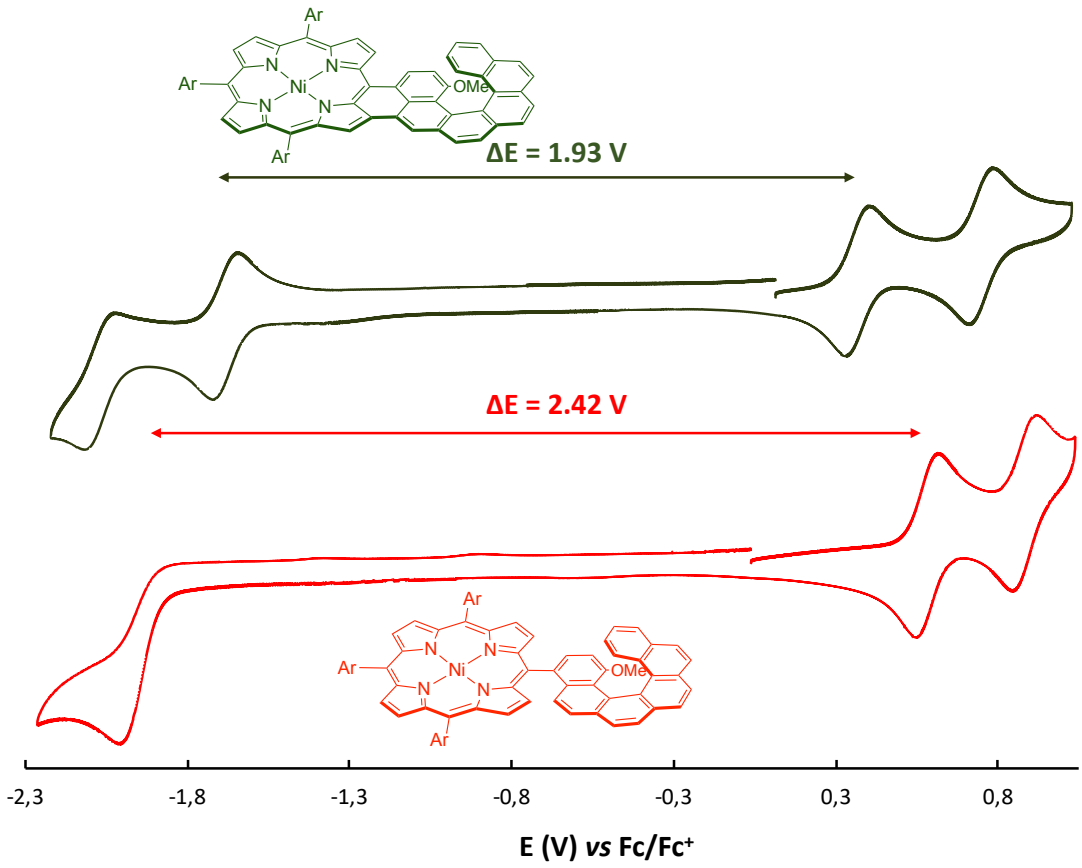
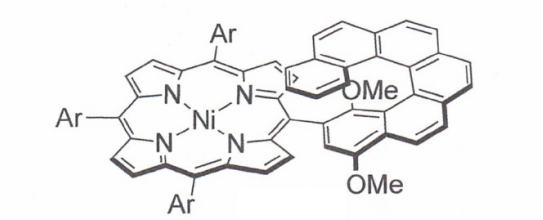


Figure S57. Cyclic voltammetry of compound **7** (bottom) and fused compound **8** (top): in dichloromethane, 0.1 M NBu_4PF_6, glassy carbon electrode, 100 mV/s.

V Resolution of enantiomers by chiral HPLC

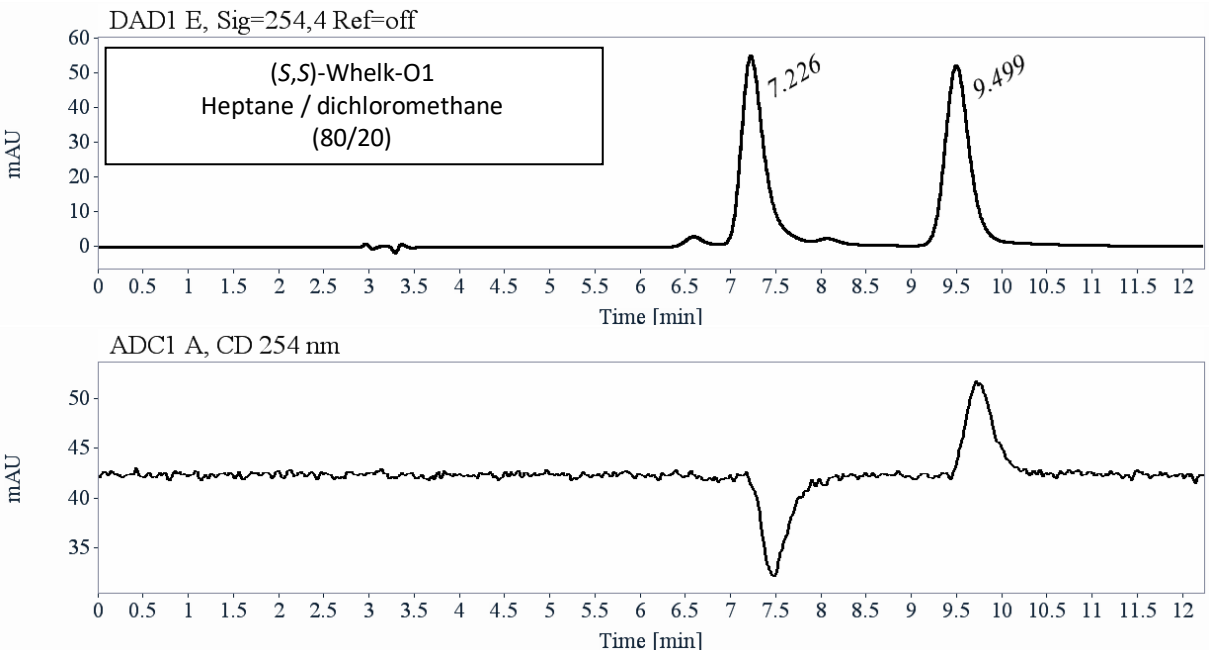
V.1 Porphyrin 4

Analytical chiral HPLC separation for compound **4**



• 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
(*S*,*S*)-Whelk-O1	Heptane / dichloromethane (80/20)	7.23 (-)	1.45	9.50 (+)	2.22	1.53	4.89

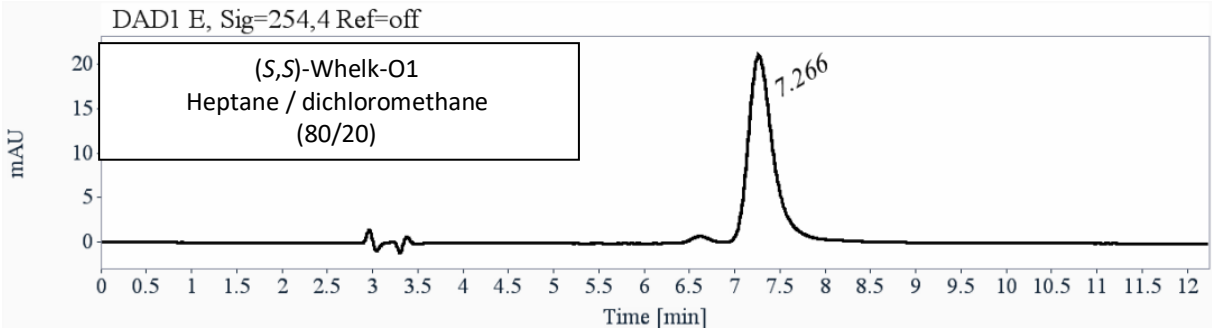


RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.23	986	51.05	1.45		
9.50	945	48.95	2.22	1.53	4.89
Sum	1931	100.00			

Preparative separation for compound **4**

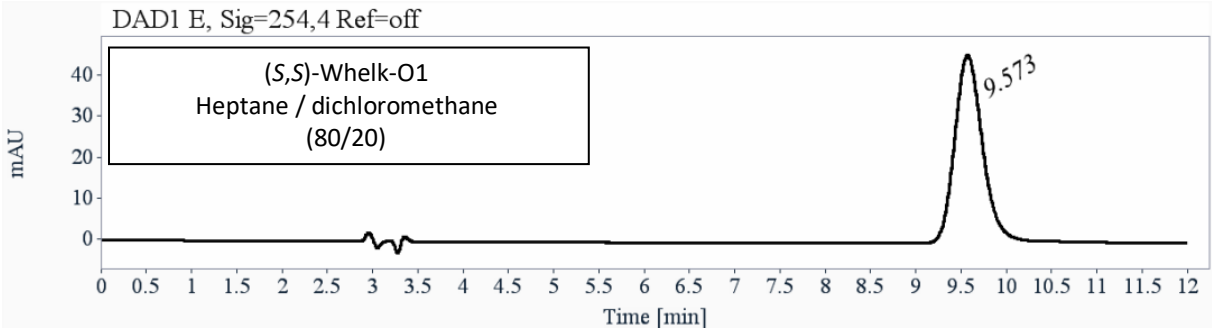
• Sample preparation: About 2.0 mg of compound **4** are dissolved in 1.8 mL of a mixture of dichloromethane and hexane (50/50).
• Chromatographic conditions: (*S*,*S*)-Whelk-O1 (250 x 10 mm), hexane / dichloromethane (80/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
• Injections (stacked): 12 times 160 µL, every 10.8 minutes.

• First fraction: 0.8 mg of the first eluted enantiomer with ee > 99.5 %



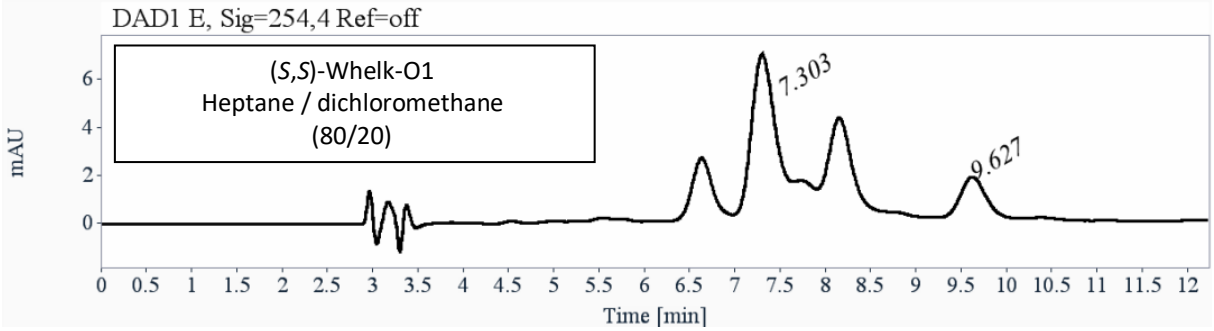
RT [min]	Area	Area%
7.27	420	100.00
Sum	420	100.00

• Second fraction: 0.9 mg of the second eluted enantiomer with ee > 99.5 %



RT [min]	Area	Area%
9.57	1010	100.00
Sum	1010	100.00

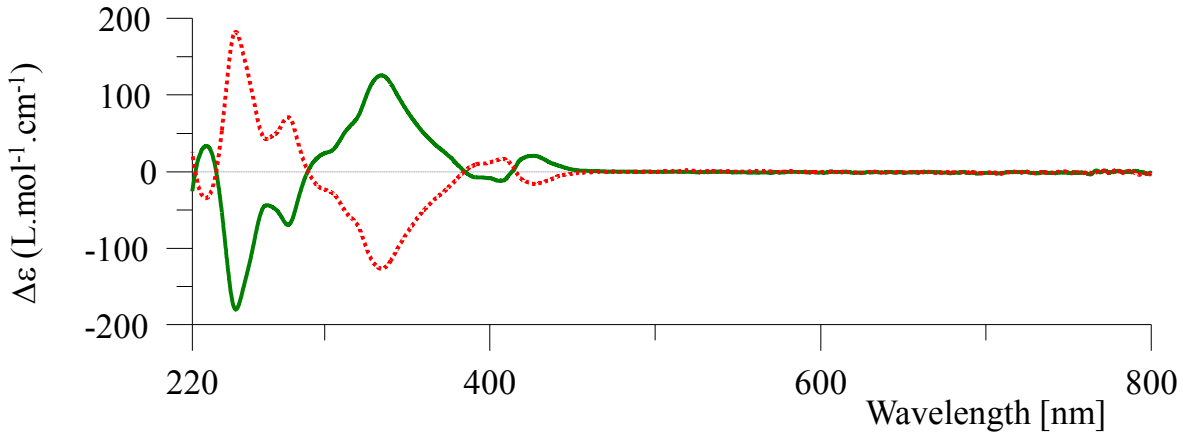
Intermediate: 0.2 mg

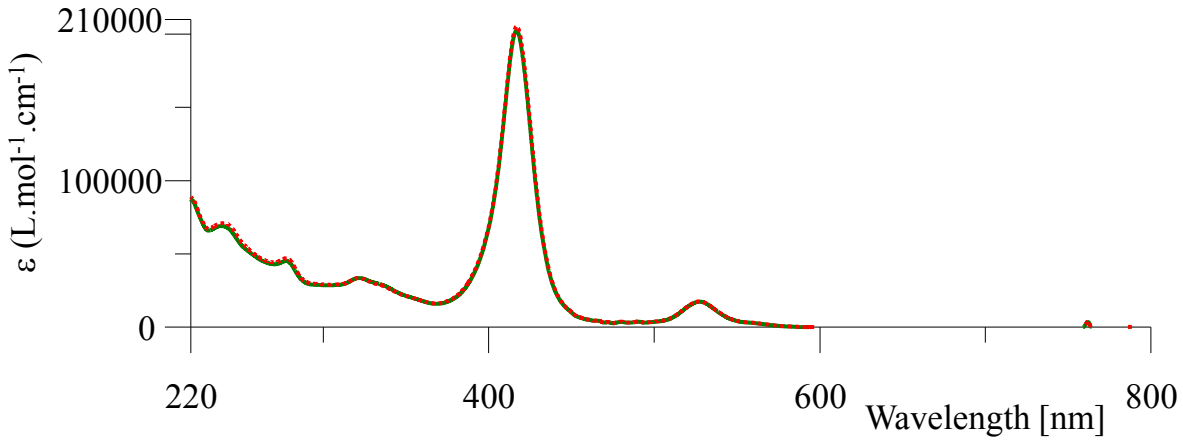


Electronic Circular Dichroism

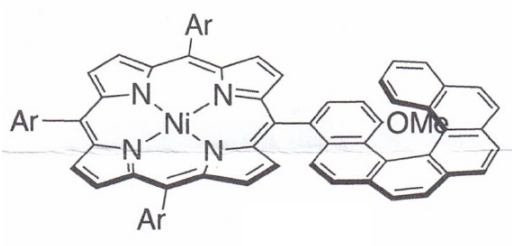
ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted.
The baseline was always measured for the same solvent and in the same cell as the samples.
The spectra are presented without smoothing and further data processing.

4, first eluted on (*S*,*S*)-Whelk-O1: green solid line, concentration = 0.074 mmol.L^{-1} in dichloromethane.
4, second eluted on (*S*,*S*)-Whelk-O1: red dotted line, concentration = 0.077 mmol.L^{-1} in dichloromethane.
Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.





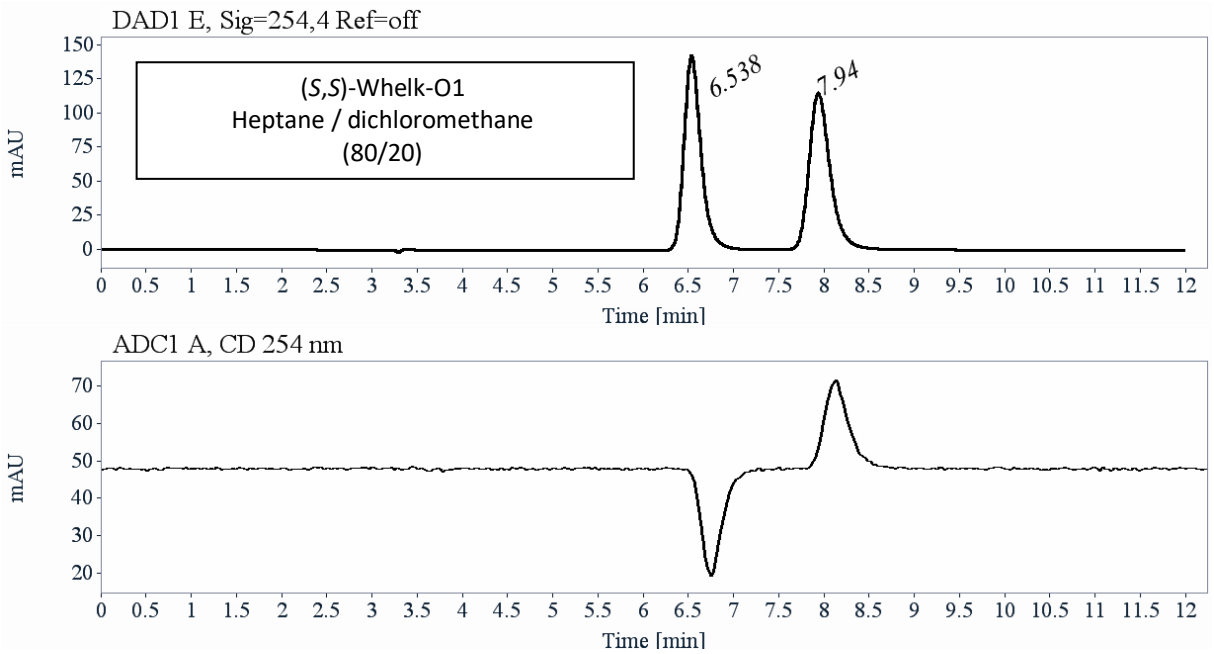
V.2 Porphyrin 7



Analytical chiral HPLC separation for compound **7**

• 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
(*S*,*S*)-Whelk-O1	Heptane / dichloromethane (80/20)	6.54 (-)	1.22	7.94 (+)	1.69	1.39	3.74



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.54	1873	50.11	1.22		
7.94	1864	49.89	1.69	1.39	3.74
Sum	3737	100.00			

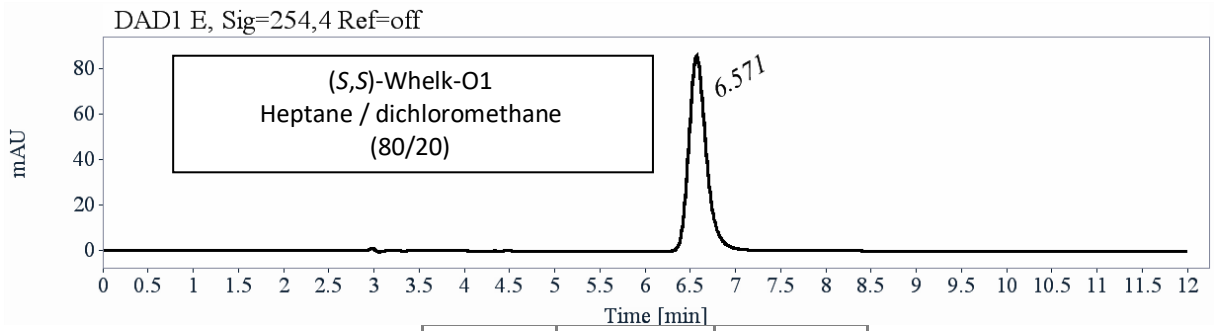
Preparative separation for compound **7**:

• Sample preparation: About 12 mg of compound **7** are dissolved in 1.5 mL of dichloromethane.

• Chromatographic conditions: (*S*,*S*)-Whelk-O1 (250 x 10 mm), hexane / dichloromethane (80/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 310 nm.

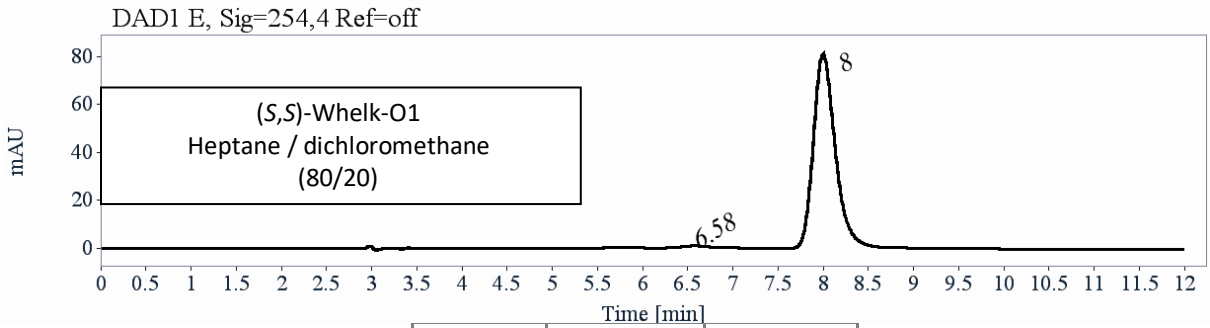
• Injections (stacked): 60 times 25 μL, every 8.2 minutes.

• First fraction: 6.4 mg of the first eluted enantiomer with ee > 99.5 %



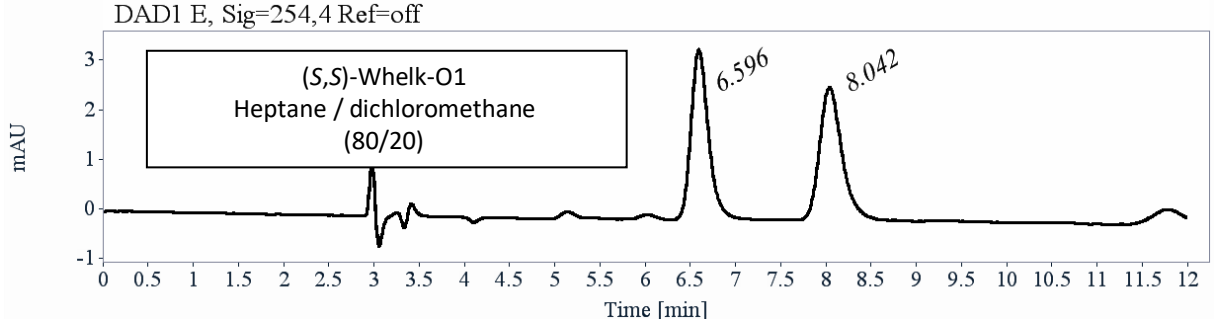
RT [min]	Area	Area%
6.57	1155	100.00
Sum	1155	100.00

• Second fraction: 5.4 mg of the second eluted enantiomer with ee > 97.5 %



RT [min]	Area	Area%
6.58	14	1.01
8.00	1376	98.99
Sum	1390	100.00

Intermediate: 0.7 mg

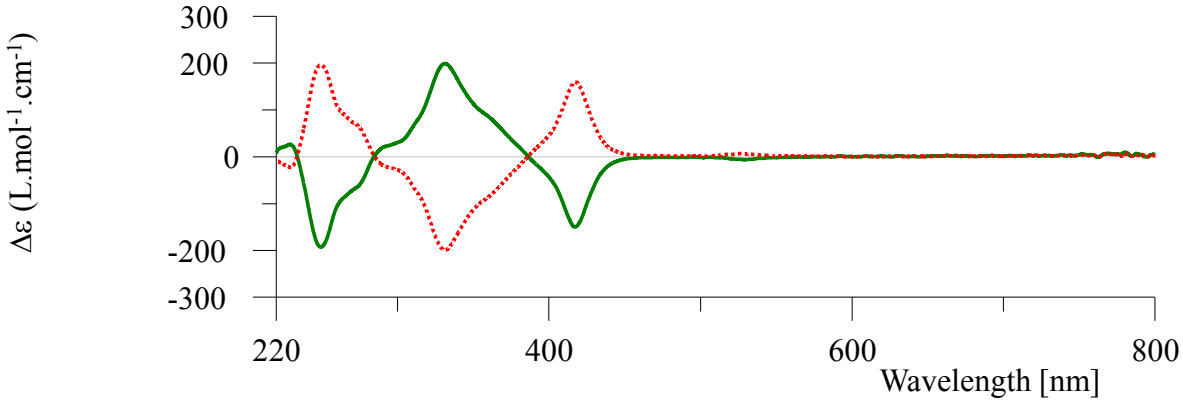


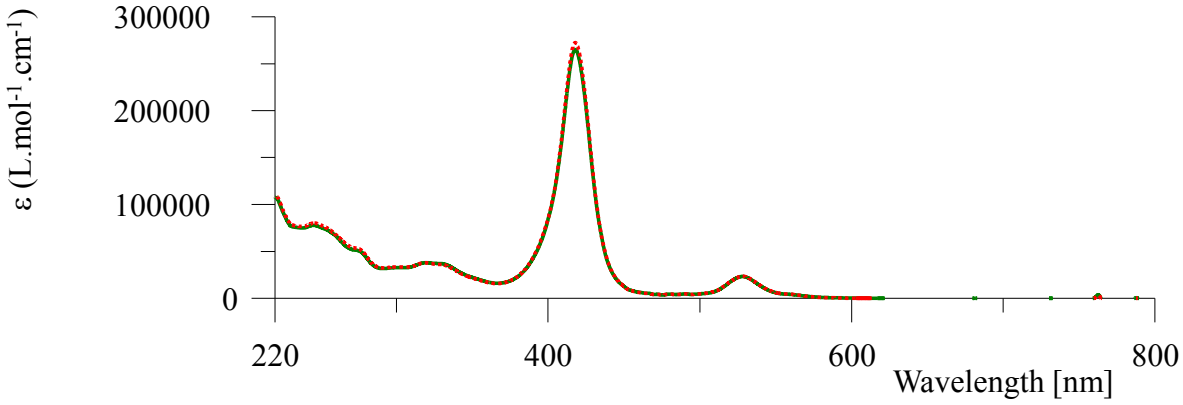
Electronic Circular Dichroism

ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical

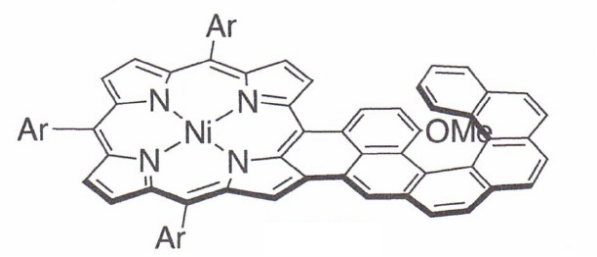
pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted.
The baseline was always measured for the same solvent and in the same cell as the samples.
The spectra are presented without smoothing and further data processing.

7, first eluted on (*S*,*S*)-Whelk-O1: green solid line, concentration = 0.055 mmol.L^{-1} in dichloromethane.
7, second eluted on (*S*,*S*)-Whelk-O1: red dotted line, concentration = 0.066 mmol.L^{-1} in dichloromethane.
Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.





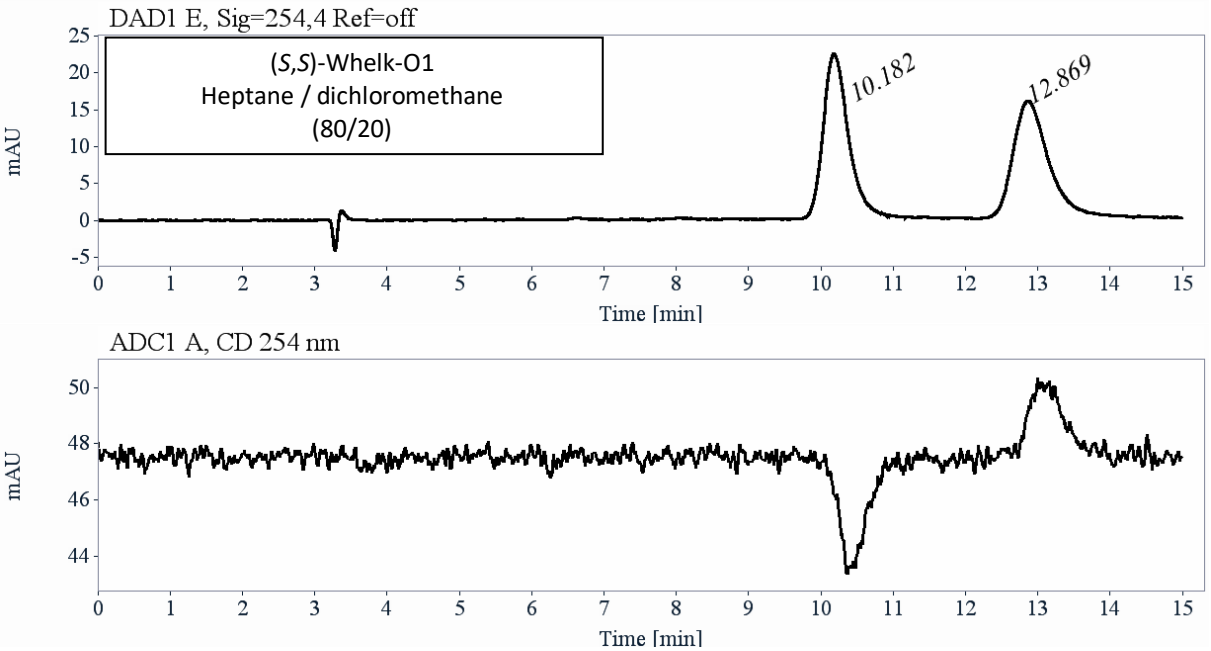
V.3 Porphyrin 8



Analytical chiral HPLC separation for compound **8**

• 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
(*S*,*S*)-Whelk-O1	Heptane / dichloromethane (80/20)	10.18 (-)	2.45	12.87 (+)	3.36	1.37	3.67



RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
10.18	545	49.81	2.45		
12.87	549	50.19	3.36	1.37	3.67
Sum	1094	100.00			

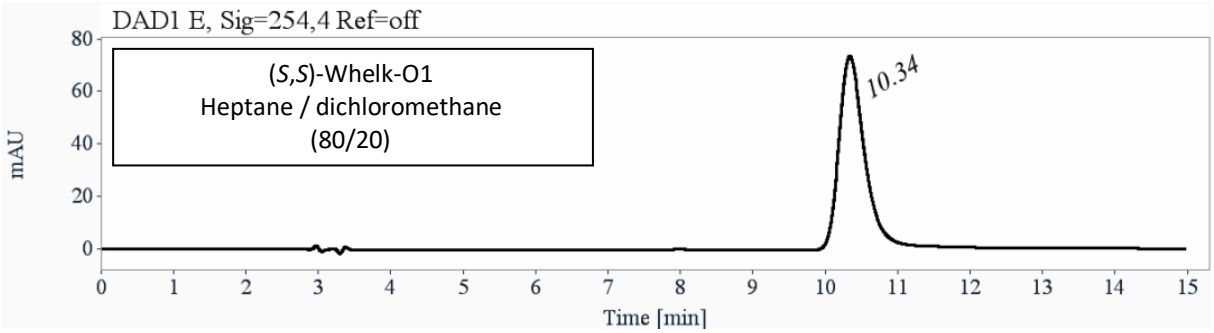
Preparative separation for compound **8**:

• Sample preparation: About 10 mg of compound **8** are dissolved in 1.8 mL of a mixture of dichloromethane and hexane (50/50).

• Chromatographic conditions: (*S*,*S*)-Whelk-O1 (250 x 10 mm), hexane / dichloromethane (80/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

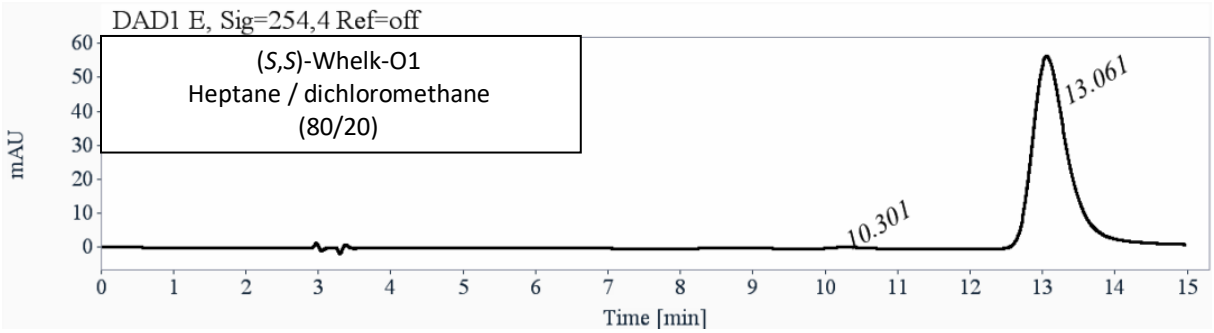
• Injections (stacked): 18 times 100 µL, every 15.5 minutes.

• First fraction: 4.2 mg of the first eluted enantiomer with ee > 99.5 %



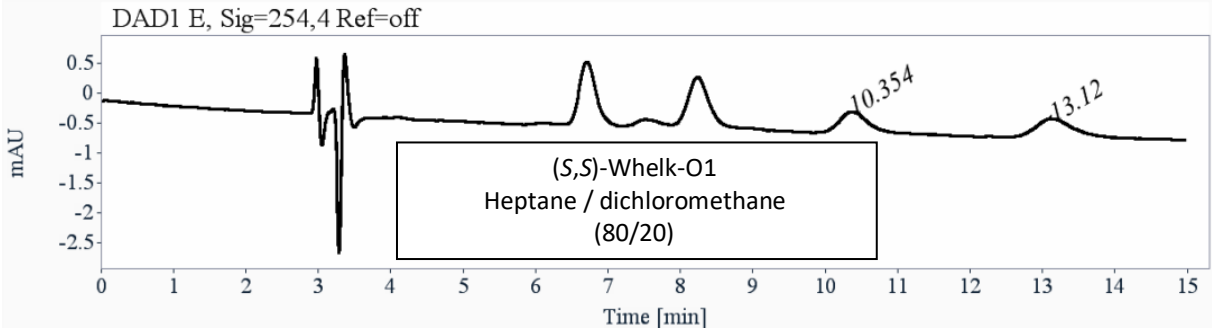
RT [min]	Area	Area%
10.34	1940	100.00
Sum	1940	100.00

• Second fraction: 4.3 mg of the second eluted enantiomer with ee > 98.5 %



RT [min]	Area	Area%
10.30	14	0.70
13.06	1923	99.30
Sum	1936	100.00

Intermediate: 0.6 mg



Electronic Circular Dichroism

ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted.
The baseline was always measured for the same solvent and in the same cell as the samples.
The spectra are presented without smoothing and further data processing.

8, first eluted on (*S*,*S*)-Whelk-O1: green solid line, concentration = 0.149 mmol.L^{-1} in dichloromethane.
8, second eluted on (*S*,*S*)-Whelk-O1: red dotted line, concentration = 0.137 mmol.L^{-1} in dichloromethane.
Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.