Electronic Supplementary Material (ESI) for Dalton Transactions.

A Synthetic Tactic to Substitute Axial Ligands in Sterically Demanding Ru(II)Porphyrinates

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SUPPORTING INFORMATION

Table of contents:

1. General Information

1.1. Materials

All chemicals were purchased from Sigma-Aldrich and Labsynth and used without further purification unless otherwise noted. For moisture-sensitive reactions, solvents were freshly distilled. Dichloromethane (DCM) was dried over calcium hydride, whereas tetrahydrofuran (THF) was dried using the sodium/benzophenone system. Anhydrous methanol (MeOH), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were P.A. ACS grade reagents and were used as received. Technical grade ethyl acetate (EtOAc) and hexanes were used as received in extractions and as eluent in column chromatography purifications. All syntheses were carried out using Schlenk line techniques. Moisture-sensitive liquids were transferred by cannula or syringe. The progress of the reactions was monitored by thin-layer chromatography (TLC) whenever possible. TLC was performed using pre-coated aluminum plates (SiliaPlate from Silicycle with 200 μm thickness) containing a 254 nm fluorescent indicator. Column chromatography was carried out using Fluka Silica Gel 60 (230-400 mesh particle size). Complexes **1**[S1] and **S1**[S1] and half-thread **4**[S2] were prepared according to our previous works.

1.2. Nuclear Magnetic Resonance – NMR

^{1}H, ^{13}C, ^{31}P, COSY and NOESY NMR spectra were obtained either on a Bruker AVANCE 250 (250 MHz), a Bruker AVANCE 400 (400 MHz) or a Bruker AVANCE 500 (500 MHz), in all cases using deuterated solvents as the lock. The spectra were collected at 298 K, and chemical shifts reported in parts per million (δ, ppm) were referenced to the residual solvent peak. In the assignments, the chemical shift (in ppm) is given first, followed, in parentheses, by multiplicity (s, singlet; d, doublet; t, triplet; q, quartet and quintet; m, multiplet; br, broad), the values of the *J*-coupling constants in Hz (if applicable), the number of protons implied and finally the assignment. Residual solvent peaks and eventual aliphatic impurities were assigned according to literature.[S3]

1.3. Mass Spectrometry

Mass spectrometry analyses were carried out at the Mass Spectrometry Service, Institute of Chemistry, University of Campinas (UNICAMP).

Low-resolution MALDI-TOF mass spectra were recorded in a Bruker Daltonics Microflex LT MALDI-TOF MS. The mass spectra represent an average over 512 consecutive laser shots in linear mode using (1E,3E)-1,4-diphenylbuta-1,3-diene (DPB) as matrix (unless otherwise noted), which was purchased from Sigma-Aldrich. The mass scale was calibrated using the peptide calibration standard purchase from Bruker and α-cyano-4-hydroxycinnamic acid (HCCA) as matrix. Data processing was carried out using the software package Compass for Flex series available from Bruker. Mentioned *m/z* values correspond to monoisotopic masses. High-resolution mass spectra (HRMS) were recorded on a Q-TOF (ESI-QTOF) equipment operating in positive mode. Pure samples were prepared for analysis by mass spectrometry by dissolution of a small quantity (ca. 1 mg) in the minimum amount of a suitable solvent (typically THF), followed by dilution with CH_3OH or CH_3CN (to a final concentration of approximately 1 mg/mL) and filtration.

1.4. Fourier-Transform Infrared Spectroscopy – FTIR

FTIR spectra were obtained from an Agilent Cary 630 spectrometer equipped with Attenuated Total Reflection (ATR) accessory and 4 cm^{-1} resolution. All samples were analyzed in the solid state.

1.5. Steady-State Ultraviolet-Visible Absorption Spectroscopy – UV-Vis

UV-Vis spectra were obtained from an Agilent Cary 50 spectrometer with 1.0 nm resolution. All samples were analyzed in dichloromethane solutions (10^{-5} mol/L) at room temperature in quartz cuvettes with 1 cm width.

2. Spectroscopic Data and Compound Structures Mentioned in the Manuscript

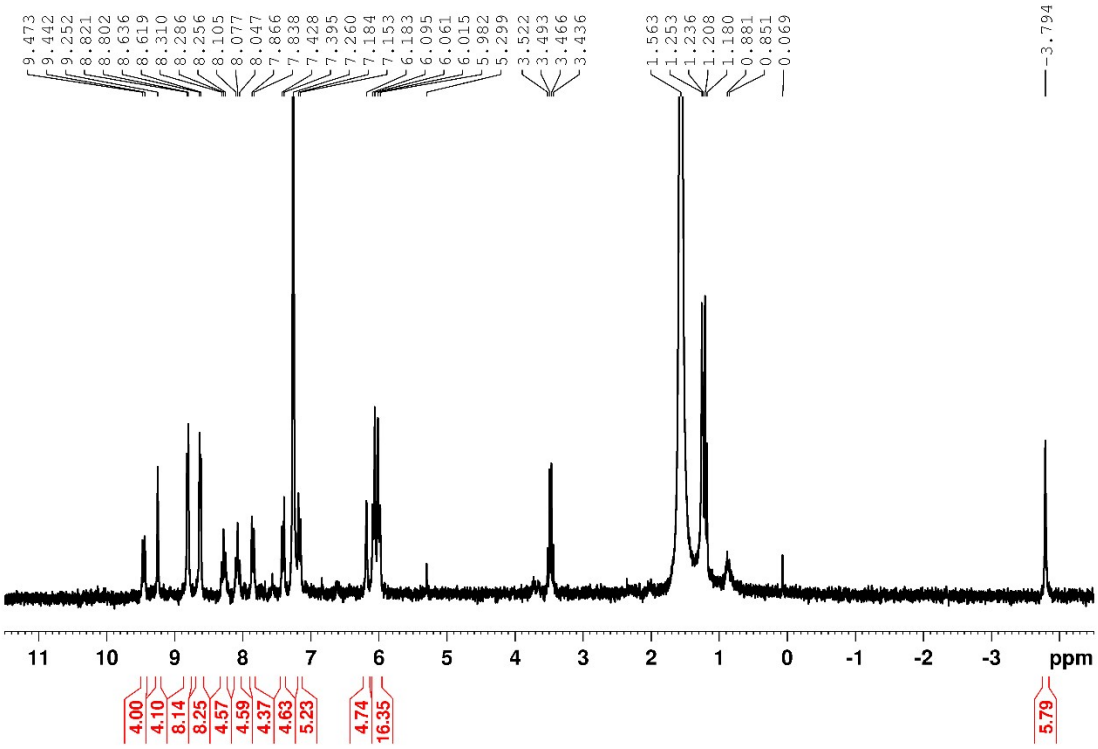


Figure S1. Full scale ^{1}H NMR spectrum of complex **2**. Integral ratio of the shielded singlet at -3.79 ppm informs the right proton proportion for two methoxy axial ligands in **2**. Experimental conditions: 250 MHz, $CDCl_3$, 298 K.

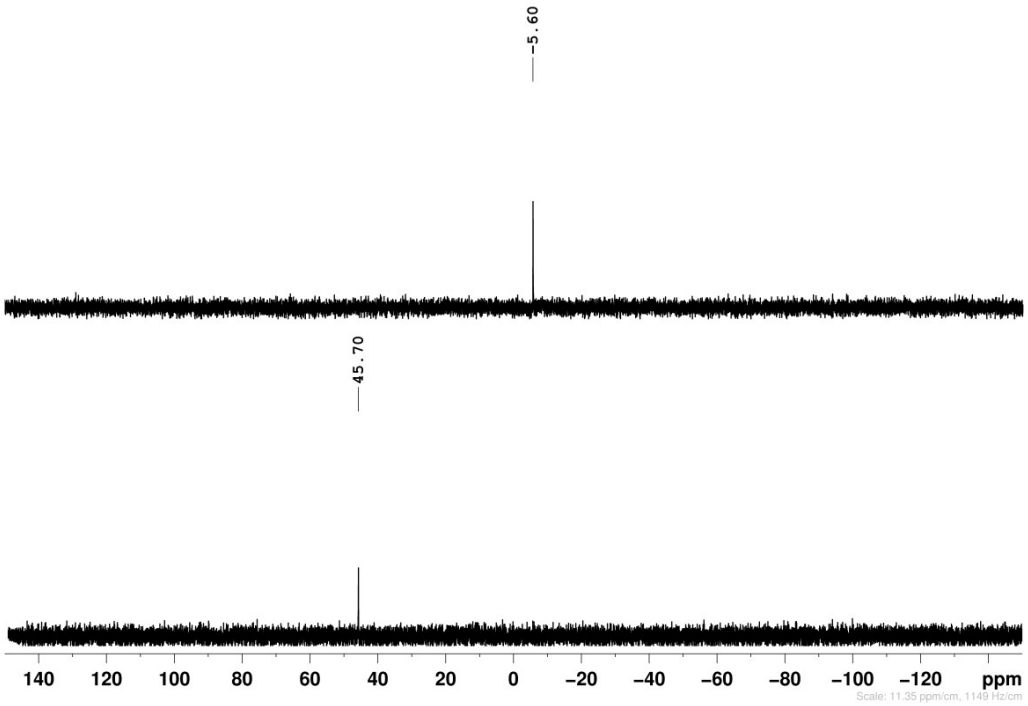
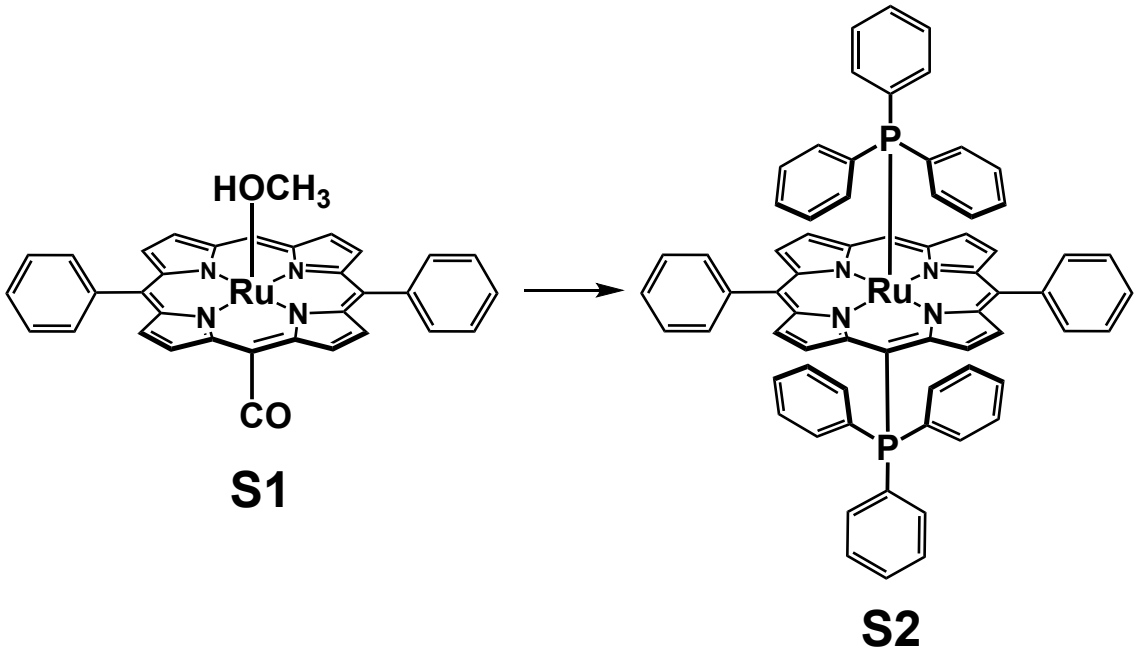


Figure S2. Full scale ^{31}P NMR spectra of pristine triphenylphosphine (top) and complex **3** (bottom). Experimental conditions: 250 MHz, $CDCl_3$, 298 K.

Scheme 1. Axial ligand substitution reaction via the stepwise redox process using acyclic carbonyl Ru(II)porphyrinate model compound **S1** as a starting material. Under the exact same experimental conditions as those applied to **1**, the homoleptic *bis*-PPh_3 Ru(II)porphyrinate **S2** was the solely isolated complex by precipitation.



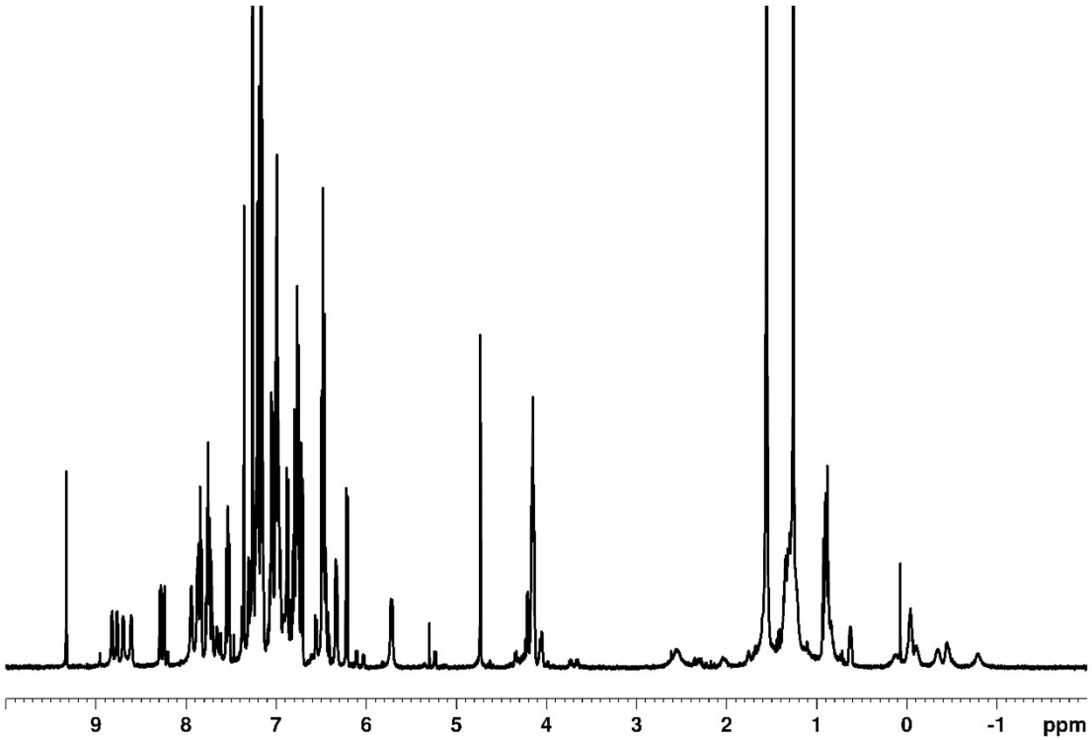
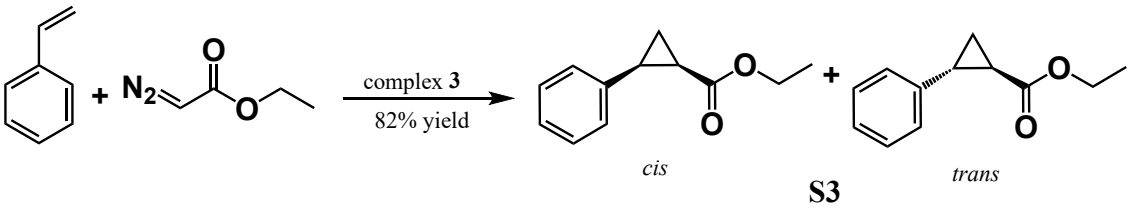


Figure S3. Full scale ^{1}H NMR spectrum of rotaxane **6**. Experimental conditions: 500 MHz, $CDCl_3$, 298 K.

Scheme 2. Cyclopropanation model reaction between styrene and ethyldiazoacetate promoted by complex **3** to afford non-interlocked **S3** as a mixture of stereoisomers. Reaction conditions are identical to that described for the assembly of rotaxane **6** (see, Section 3).



S3

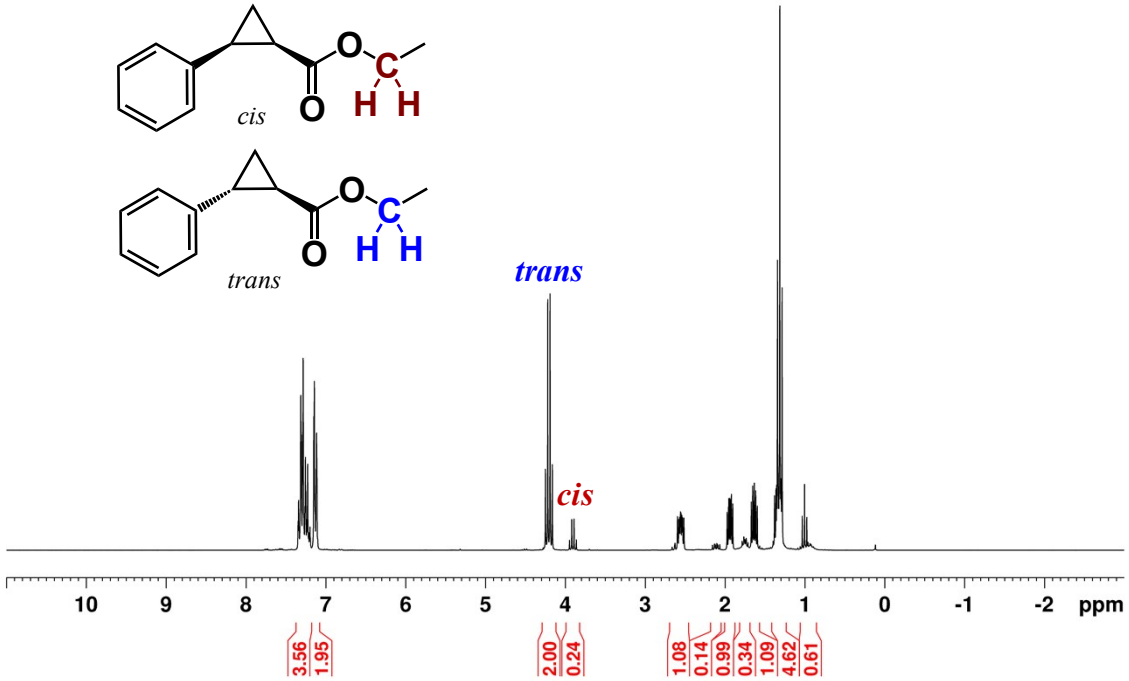


Figure S4 - Full scale ^{1}H NMR spectrum of model compound **S3**. Experimental conditions: 250 MHz, $CDCl_3$, 298 K. According to literature[S4], the ester-methylene protons of the isolated stereoisomers resonate as a quartet at 4.17 ppm (*trans*) and 3.88 ppm (*cis*).

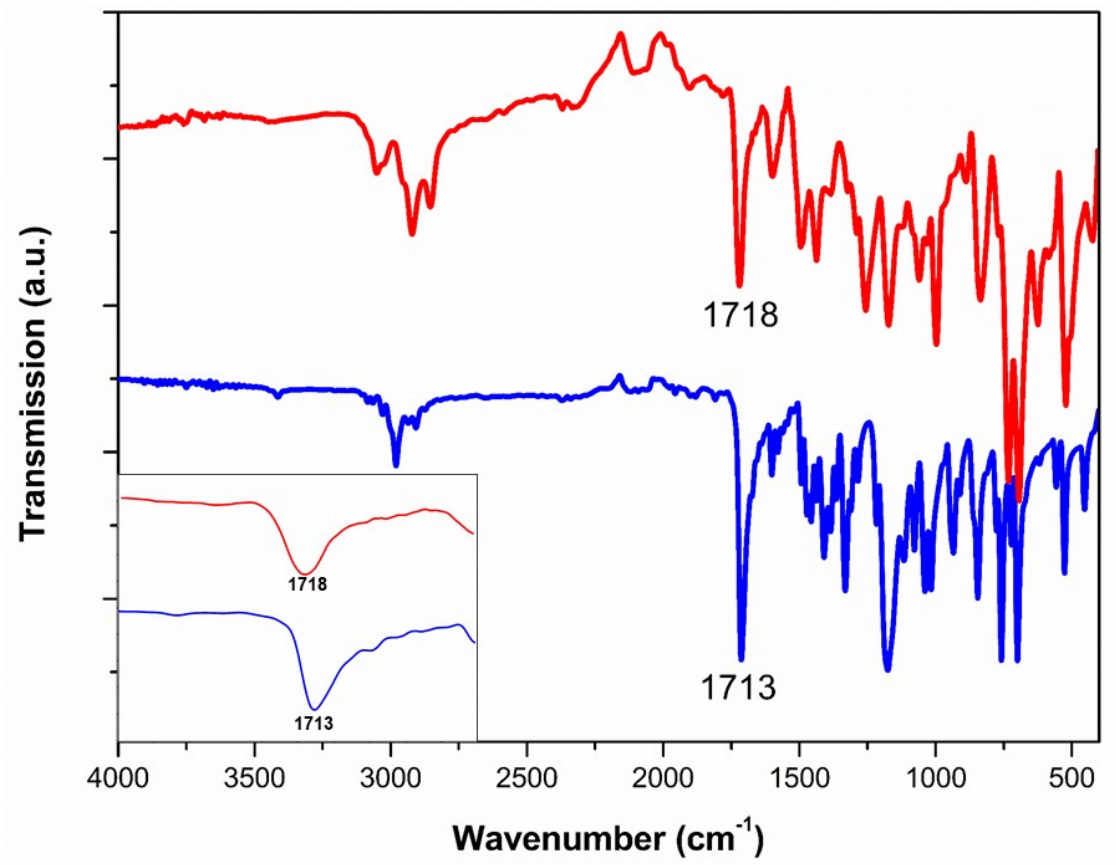
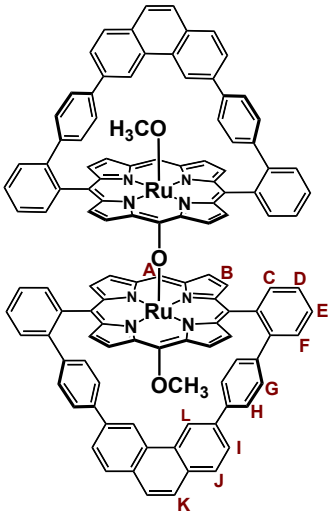


Figure S5 - FTIR vibrational spectrum of rotaxane **6** (red) and model compound **S3** (blue). The vibrational band at 1718 cm-[1] is attributed to the carbonyl stretching mode of the thread component in **6**. *Inset*: Zoom in the carbonyl stretching region of the spectra.

3. Synthesis

Synthesis of complex **2**



For the success of this synthesis, starting material complex **1** must be freshly prepared. In a 50 mL Schlenk flask under inert atmosphere, complex **1** (0.016 g, 0.017 mmol, 1 equiv) was dissolved in 12 mL of a mixture of dichloromethane/methanol (1:1, v/v) under magnetic stirring at room temperature. Commercially available *meta*-chloroperoxybenzoic acid (*m*CPBA) (purity 77%, 0.088 g, 0.39 mmol, 23 equiv) was added as a solid and the resulting mixture was stirred at room temperature for 5 minutes. A saturated aqueous solution of K_2CO_3 (10 mL) was added and the resulting biphasic mixture was transferred to an extraction funnel and the organic phase was separated, washed with water (3 x 10 mL), dried over Na_2SO_4, filtered through paper and the solvent evaporated to dryness. The crude product was purified by silica-gel chromatography column, using a mixture of dichloromethane/methanol (99.5:0.5, v/v) as eluent to afford target complex **2** as a red solid in 69% yield (5.95 µmol, 11.0 mg).

R.F. (dichloromethane/methanol, 99.5:0.5) = 0.21.

^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 9.45 (d, J = 7.82 Hz, 4H, H_C); 9.25 (s, 4H, H_A); 8.81 (d, J = 4.67 Hz, 8H, H_B); 8.63 (d, J = 4.32 Hz, 8H, H_B); 8.28 (t, J = 7.37 Hz, 4H, H_D); 8.07 (t, J = 7.67 Hz, 4H, H_E); 7.85 (d, J = 7.12, 4H, H_F); 7.41 (d, J = 8.42 Hz, 4H, H_J); 7.16 (d, J = 7.80 Hz, 4H, H_I); 6.18 (s, 4H, H_L); 6.12-5.95 (m, 16H, H_G and H_H); -3.79 (s, 6H, O-CH_3). Impurities: 5.30 (residual dichloromethane); 3.48 and 1.21 (diethyl ether); 1.26 and 0.88 (aliphatic impurities); 0.07 (silicone grease).

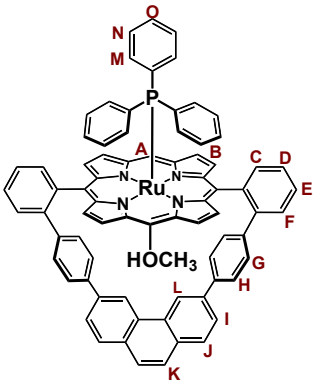
^{13}C NMR (60 MHz, $CDCl_3$) δ (ppm): Macrocycle **2** was too insoluble to record ^{13}C NMR.

MALDI-TOF (pristine) (+): Calculated for $C_{118}H_{74}N_8O_3Ru_2$, 1854.397. Found *m/z* 1822.767 $[M - OCH_3]^+$.

UV-Vis (CH_2Cl_2), 10^{-5} mol/L, λ_{max} (nm): 319 (phenanthrene moiety); 401, 517, 557 (porphyrinate core).

FTIR (ATR), ν (cm^{-1}): 1016 (ruthenium oxidation state marker band).

Synthesis of complex **3**:



In a 25 mL Schlenk flask under inert atmosphere, complex **2** (0.032 g, 0.017 mmol, 1 equiv) and triphenylphosphine (0.018 g, 0.068 mmol, 4.0 equiv) were dissolved in 10 mL of tetrahydrofuran under magnetic stirring at room temperature. Sodium borohydride ($NaBH_4$) (0.038 g, 1.02 mmol, 60 equiv) was added as a solid and the resulting mixture was stirred at room temperature for 24 hours. The mixture was concentrated to dryness under reduced pressure and dichloromethane (25 mL) was added to the crude material. The resulting solution was filtered through paper to remove solid impurities, methanol (10 mL) was added and the resulting solution was concentrated under reduced pressure to about 1/5 of its original volume to give a red solid as a precipitate. The red solid was decanted and the remaining solvent was carefully removed with a pipette. The resulting red solid was washed with methanol (3 x 5 mL) and with petroleum ether (3 x 10 mL) to afford complex **3** as a red solid in 65% isolated yield (0.022 mmol, 26.0 mg).

^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 9.15 (s, 2H, H_A); 8.55 (d, J = 4.77 Hz, 4H, H_B); 8.33 (d, J = 4.75 Hz, 4H, H_B); 8.10 (d, J = 7.35 Hz, 2H, H_C); 7.90-7.82 (m, 4H, H_D + H_F); 7.79-7.71 (m, 2H, H_E); 7.62 (d, J = 8.27 Hz, 2H, H_J); 7.46 (s, Hz, 2H, H_K); 7.42 (d, J = 8.30 Hz, 2H, H_I); 6.96-6.88 (m, 6H, H_L + H_G); 6.83 (t, J = 7.45 Hz, 3H, H_O); 6.57-6.45 (m, 10H, H_H + H_N); 4.24-4.09 (m, 6H, H_M); 2.43 (br, 3H, CH_3OH); -0.69 (br, 1H,

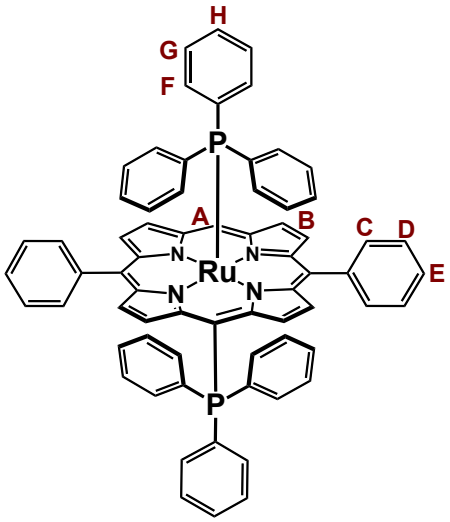
CH_3OH). Impurities: 5.30 (residual dichloromethane); 1.26 and 0.99 (aliphatic impurities); 0.07 (silicone grease).

^{31}P NMR (250 MHz, $CDCl_3$), δ (ppm): 45.70.

MALDI-TOF (pristine) (+): Calculated for $C_{77}H_{53}N_4OPRu$, 1182.300. Found *m/z* 1149.630 $[M - HOCH_3]^+$.

UV-Vis (CH_2Cl_2), 10^{-5} mol/L, λ_{max} (nm): 320 (phenanthrene moiety); 410, 499, 524 (porphyrinate core).

Synthesis of complex **S2**:



S2

Oxidation step: In a 50 mL Schlenk flask under inert atmosphere, complex **S1** (0.011 g, 0.018 mmol, 1 equiv) was dissolved in 12 mL of a mixture of dichloromethane/methanol (1:1, v/v) under magnetic stirring and at room temperature. Commercially available *meta*-chloroperoxybenzoic acid (*m*CPBA) (purity 77%, 0.086 g, 0.41 mmol, 23 equiv) was added as a solid and the resulting mixture was stirred at room temperature for 5 minutes. A saturated aqueous solution of K_2CO_3 (10 mL) was added and the resulting biphasic mixture was transferred to an extraction funnel and the organic phase was separated, washed with water (3 x 10 mL), dried over Na_2SO_4, filtered through paper and the solvent evaporated to dryness. The crude product was purified by silica-gel chromatography column, using a mixture of dichloromethane/methanol (99.5:0.5, v/v) as eluent to afford the corresponding μ-oxo-dimeric-Ru(IV) complex as a red solid in 83% yield (0.015 mmol, 18 mg).

Reduction step: In a 25 mL Schlenk flask under inert atmosphere, the μ-oxo-dimer-Ru(IV) complex (0.020 g, 0.017 mmol, 1 equiv) and triphenylphosphine (0.018 g, 0.068

mmol, 4.0 equiv) were dissolved in 10 mL of tetrahydrofuran under magnetic stirring at room temperature. Sodium borohydride ($NaBH_4$) (0.038 g, 1.02 mmol, 60 equiv) was added as a solid and the resulting mixture was stirred at room temperature for 24 hours. The mixture was concentrated to dryness under reduced pressure and dichloromethane (25 mL) was added to the crude material. The resulting solution was filtered through paper to remove solid impurities, methanol (10 mL) was added and the resulting solution was concentrated under reduced pressure to about 1/5 of its original volume to give a red solid as a precipitate. The red solid was decanted and the remaining solvent was carefully removed with a pipette. The resulting red solid was washed with methanol (3 x 5 mL) and with petroleum ether (3 x 10 mL) to afford complex **S2** as a red solid in 88% isolated yield (0.030 mmol, 32.5 mg).

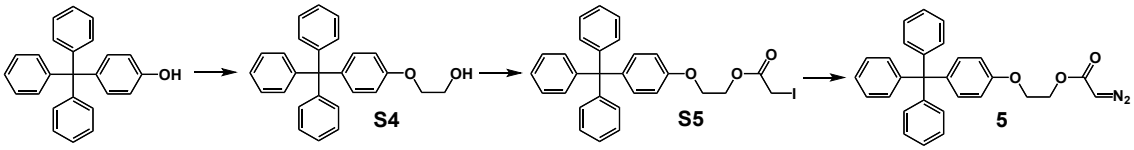
^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 8.78 (s, 2H, H_A); 8.46 (d, J = 4.75 Hz, 4H, H_B) 8.24 (d, J = 4.75 Hz, 4H, H_B); 7.67-7.50 (m, 10H, H_C + H_D + H_E); 6.76 (t, J = 7.57 Hz, 6H, H_H); 6.43 (t, J = 7.67 Hz, 12H, H_G); 4.08 (br, 12H, H_F). Impurities: 5.30 (residual dichloromethane).

^{31}P NMR (250 MHz, $CDCl_3$), δ (ppm): 7.01.

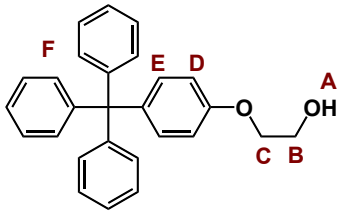
MALDI-TOF (pristine) (+): Calculated for $C_{68}H_{50}N_4P_2Ru$, 1086.2554. Found *m/z* 824.0935 $[M - PPh_3]^+$.

UV-Vis (CH_2Cl_2), 10^{-5} mol/L, λ_{max} (nm): 404, 426, 508.

Synthetic strategy used to prepare half-thread **5**.



Synthesis of compound **S4**



In a 100 mL Schlenk flask under inert atmosphere, tritylphenol (0.67 g, 2.00 mmol, 1.0 equiv), sodium iodide (0.12 g, 0.80 mmol, 0.4 equiv) and 2-chloroethanol (0.32 g, 4.00 mmol, 2.0 equiv) were dissolved in 20 mL of dimethylformamide under magnetic

stirring at room temperature. The reaction mixture was heated at 80°C and potassium carbonate (2.76 g, 20.00 mmol, 10.0 equiv) was added to the reaction flask. The reaction mixture was kept at 80°C for 30h. After cooling to room temperature, the crude product was filtered through paper to remove solid impurities. The crude product was concentrated under reduced pressure and redissolved in 100 mL of dichloromethane. The crude was washed with water (3 x 50 mL), dried over Na_2SO_4, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography on SiO_2 using a mixture of hexanes/ethyl acetate (80:20, v/v) as eluent to afford **S4** as a white solid in 65% yield (1.29 mmol, 0.49 g).

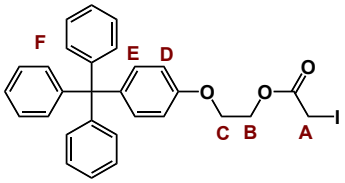
R.F. (hexanes/ethylacetate, 70:30, v/v) = 0.34

^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.30-7.16 (m, 15H, H_F); 7.12 (d, *J* = 8.50 Hz, 2H, H_E); 6.80 (d, *J* = 8.51 Hz, 4H, H_D); 4.10-4.02 (m, 2H, H_C); 4.00-3.89 (m, 2H, H_B); 2.01 (t, *J* = 6.17 Hz, 1H, H_A). Impurities: 4.12, 2.05 and 1.26 (residual ethyl acetate); 0.07 (silicone grease).

^{13}C NMR (60 MHz, $CDCl_3$) δ (ppm): 156.7; 147.1; 139.6; 132.4; 131.2; 127.6; 126.0; 113.4; 69.1; 64.4; 61.6.

HRMS (ESI) (+): Calculated for $[C_{27}H_{24}O_2]$, 380.16685. Found *m/z* 403.16602 $[M+Na]^+$.

Synthesis of compound **S5**



In a 100 mL Schlenk flask under inert atmosphere, compound **S4** (0.57 g, 1.50 mmol, 1.0 equiv) and iodoacetic acid (0.34 g, 1.83 mmol, 1.22 equiv) were dissolved in 20 mL of dichloromethane under magnetic stirring at room temperature for 10 minutes. *N*,*N*'-dicyclohexylcarbodiimide (DCC) (0.93 g, 4.51 mmol, 3.0 equiv) and 4-dimethylaminepyridine (DMAP) (0.056 g, 0.46 mmol, 0.30 equiv) were added to the reaction flask and the mixture was kept at room temperature for 24h. The crude product was diluted with 80 mL of dichloromethane, washed with a 2% aqueous $NaHCO_3$ (3 x 50 mL), dried over Na_2SO_4, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography on SiO_2 using a

mixture of hexanes/ethyl acetate (80:20, v/v) as eluent to afford **S5** as a light yellow solid in 48% yield (0.71 mmol, 0.39 g).

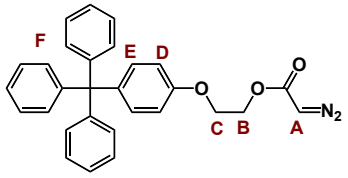
R.F. (hexanes/ethylacetate, 80:20, v/v) = 0.60

^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.30-7.08 (m, 17H, H_F + H_E); 6.80 (d, *J* = 7.50 Hz, 4H, H_D); 4.51-4.44 (m, Hz, 2H, H_C); 4.20-4.13 (m, 2H, H_B); 3.72 (s, 2H, H_A). Impurities: 5.30 (residual dichloromethane) 4.12, 2.05 and 1.26 (residual ethyl acetate); 0.08 (silicone grease).

^{13}C NMR (60 MHz, $CDCl_3$) δ (ppm): 168.9; 156.4; 147.0; 139.8; 132.4; 131.2; 127,6; 126.0; 113.5; 65.5; 64.5; 64.4; -5.7.

HRMS (ESI) (+): Calculated for [$C_{29}H_{25}O_3I$], 548.07406. Found *m/z* 571.07335 $[M+Na]^+$.

Synthesis of half-thread **5**



In a 50 mL Schlenk flask under inert atmosphere, compound **S5** (0.36 g, 0.66 mmol, 1.0 equiv) and *N*-*N*'-*bis*(*p*-toluenesulfonil)hidrazine (0.34 g, 1.00 mmol, 1.5 equiv) were dissolved in 10 mL of freshly distilled tetrahydrofuran under magnetic stirring at room temperature. The reaction mixture was cooled with an ice bath to about 0°C and stirred for 5 minutes and 1,8-diazabiciclo[5.4.0]undec-7-ene (DBU) (0.4 g, 2.63 mmol, 4.0 equiv) was added dropwise. The reaction mixture was stirred in the ice bath for 45 min. The ice bath was removed, the reaction was quenched by addition of 10 mL of saturated aqueous $NaHCO_3$ and then allowed to warm to rt (about 10 minutes). The crude product was extracted with diethyl ether (3x50 mL), the combining organic phases was dried over Na_2SO_4, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography on SiO_2 using a mixture of hexanes/ethyl acetate (75:25, v/v) as eluent to afford **5** as a light yellow solid in 40% yield (0.26 mmol, 0.12 g).

R.F. (hexanes/ethylacetate, 75:25, v/v) = 0.50

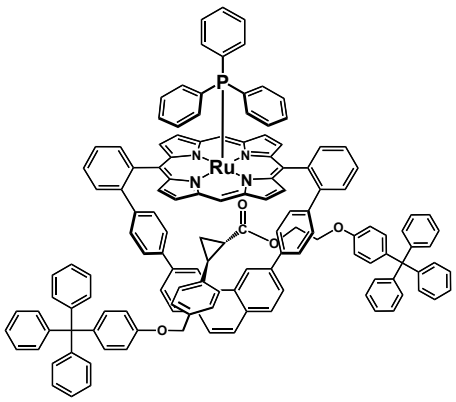
^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.32-7.07 (m, 17H, H_F + H_E); 6.78 (d, *J* = 9.32 Hz, 2H, H_D); 4.79 (br, 1H, H_A); 4.5 (t, *J* = 4.57 Hz, 4H, H_C); 4.16 (t, *J* = 4.85 Hz; 4H, H_B). Impurities: 1.26 and 0.88 (aliphatic impurities); 0.08 (silicone grease).

^{13}C NMR (60 MHz, $CDCl_3$) δ (ppm): 156.4; 146.9; 139.6; 132.3; 131.1; 127.4; 125.9; 113.4; 65.9; 64.3; 63.2; 46.4.

HRMS (ESI) (+): Calculated for [$C_{29}H_{24}N_2O_3$], 448.16791. Found *m/z* 471.16712 $[M+Na]^+$.

FTIR (ATR), ν (cm^{-1}): 2110 (C=N_2).

Synthesis of rotaxane **6**



In a 10 mL Schlenk flask under inert atmosphere, complex **3** (0.010 g, 8.45 μmol, 1.0 equiv) and styrene half-thread **4** (0.020 g, 44.2 μmol, 5.0 equiv) were dissolved in 1.2 mL of dry and freshly distilled DCM under magnetic stirring at room temperature. Diazoacetate half-thread **5** (0.006 g, 13.37 μmol, 1.5 equiv) was added as a solid in 3 portions of 0.002 g each to the reaction flask every 2h at room temperature. After complete addition of half-thread **5**, the reaction mixture was stirred for additional 6h at room temperature, thereby making a total of 12h reaction time. Thin layer chromatography on neutral alumina revealed total interlocked of macrocycle **3** and formation of rotaxane **6** in quantitative yield. The crude product was directly loaded into a neutral alumina column chromatography and flash chromatography allowed isolation of two products. The first fraction corresponded to excess of olefin half-thread **4**, which was eluted using hexanes/DCM (40:60, v/v) as eluent. A second fraction eluted with DCM corresponded to target rotaxane **6**, which was isolated as a red solid in about 90% isolated yield (relative to **3**) (7.61 μmol, 15.5 mg).

R.F. (neutral alumina, DCM/hexanes, 60:40, v/v) = 0.60

MALDI-TOF (pristine) (+): Calculated for $C_{139}H_{101}N_4O_4PRu$, 2022.660. Found *m/z* 2022.29 $[M]^+$.

UV-Vis (CH_2Cl_2), 10^{-5} mol/L, λ_{max} (nm): 316 (phenanthrene moiety); 412, 499 and 525 (porphyrinate core).

FTIR (ATR), ν (cm^{-1}): 1718 (carbonyl).

Synthesis of model compound **S3**:

Compound **S3** was prepared under the exactly same conditions as those described for rotaxane **6**. The crude product was purified by column chromatography on silica to afford the target compound as a mixture of stereoisomers.[S4] Yellow oil, 82% yield.

^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm): 7.33-7.05 (m, 5H, *cis* + *trans*); 4.17 (q, *J* = 7.15 Hz, 2H, *trans*); 3.87 (q, *J* = 7.13 Hz, 2H, *cis*); 2.64-2.46 (m, 1H, *cis* + *trans*); 2.07 (ddd, *J* = 9.25, 7.80 and 5.62 Hz, 1H, *cis*); 1.90 (ddd, *J* = 8.42, 5.27, and 4.23 Hz, 1H, *trans*), 1.77-1.66 (m, 1H, *cis*), 1.65-1.54 (m, 1H, *trans*), 1.39-1.18 (m, 4H, *cis* + *trans*), 0.97 (t, *J* = 7.13 Hz, 3H, *cis*).

4. Spectral Data

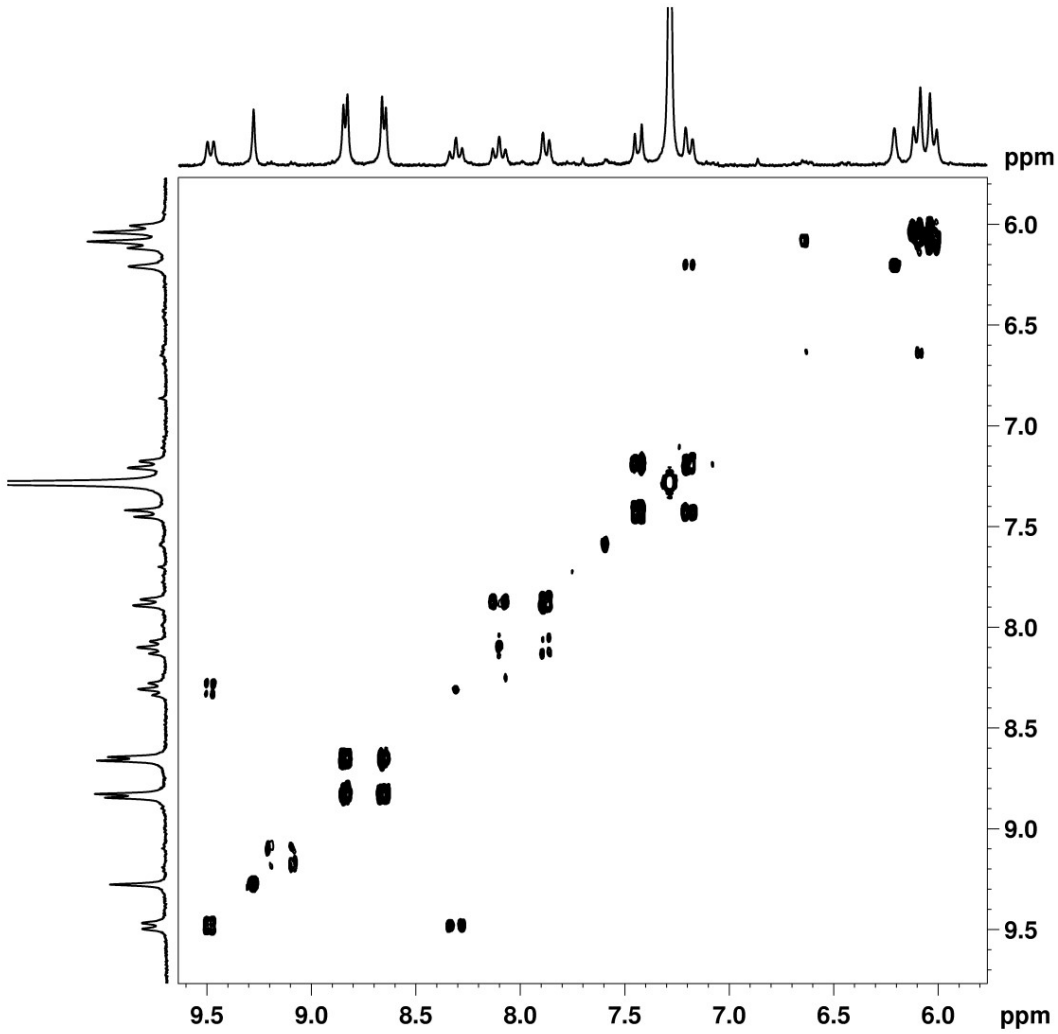


Figure S6 – Two-dimensional (^{1}H-^{1}H) COSY NMR spectrum of complex **2** (250 MHz, $CDCl_3$, 298 K).

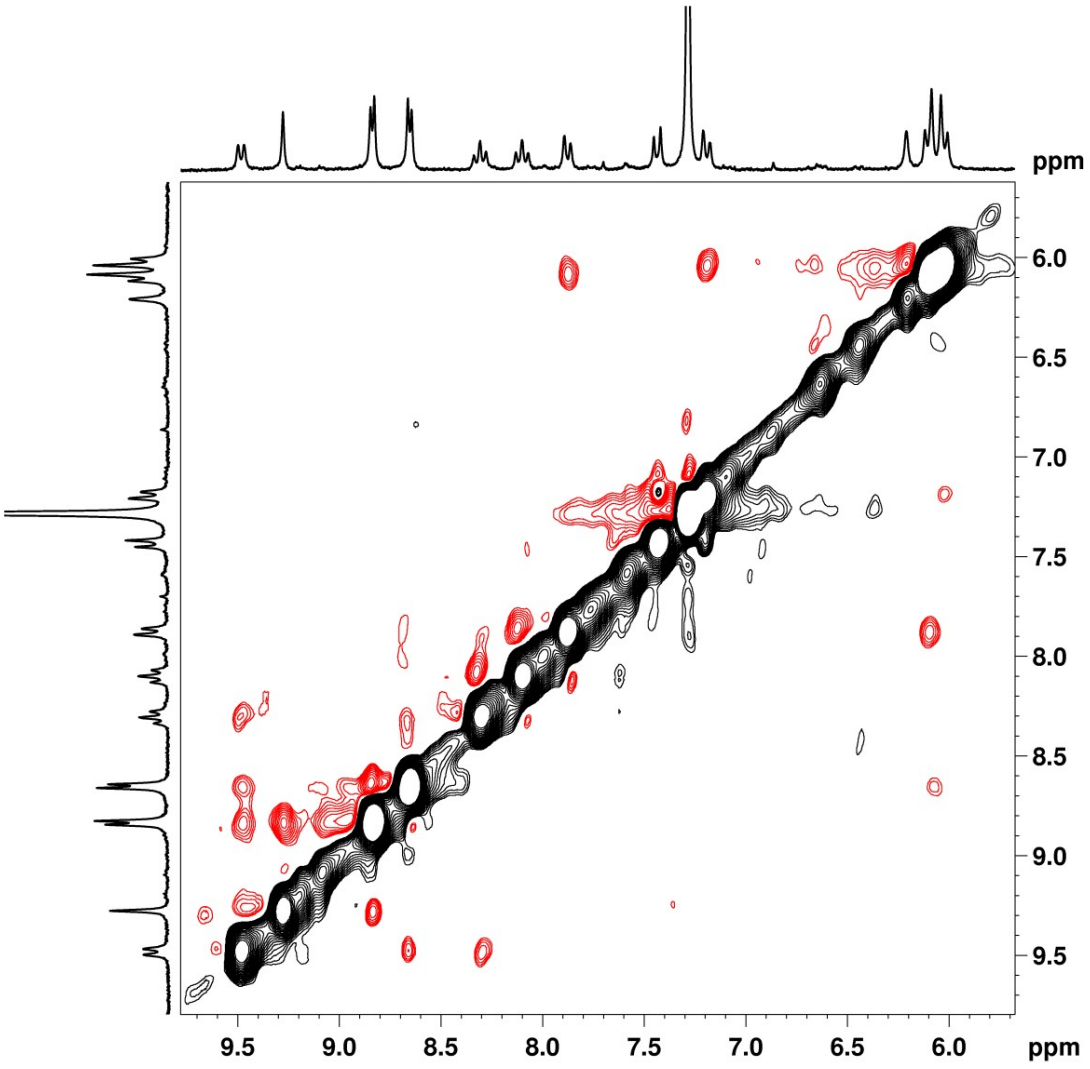


Figure S7 – Two-dimensional (^{1}H-^{1}H) NOESY NMR spectrum of complex **2** (250 MHz, $CDCl_3$, 298 K).

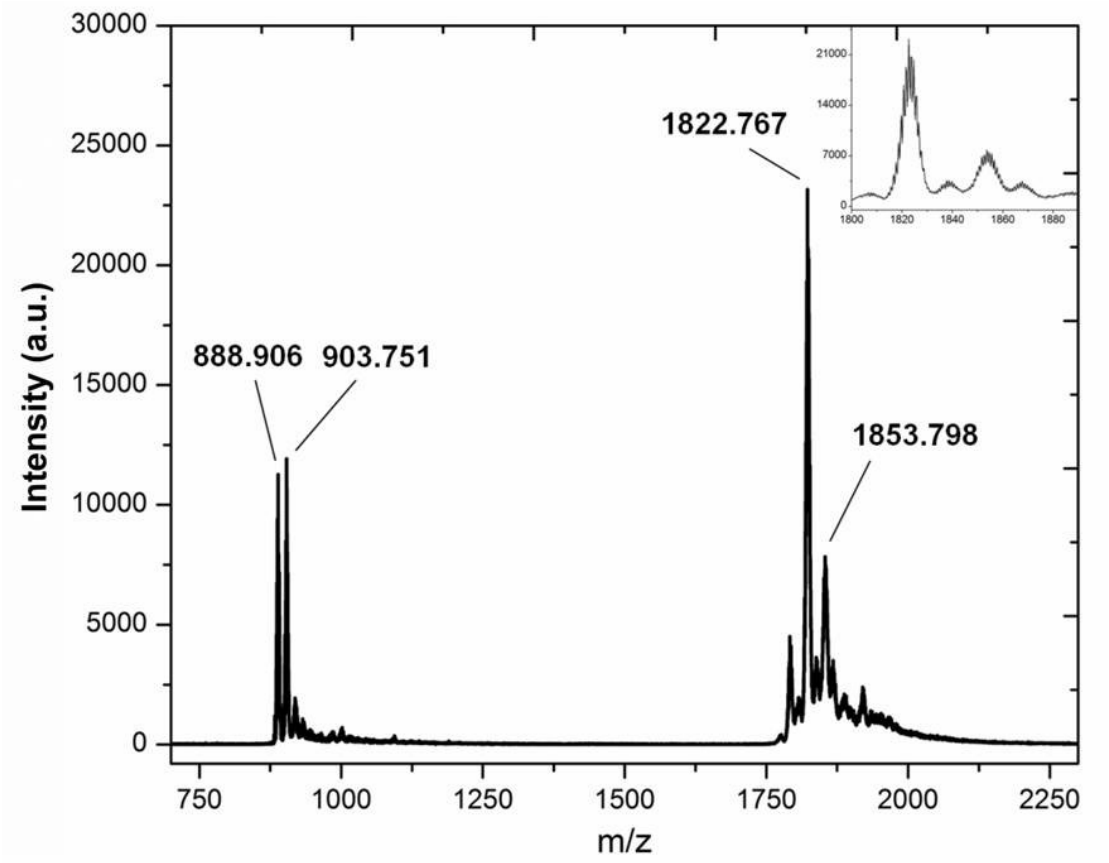


Figure S8 - Low-resolution MALDI-TOF mass spectrum of complex **2**. The correct molecular ion peak for **2** is observed at *m/z* 1853.798. The strong signal at *m/z* 1822.767 corresponds to a species lacking one of the methoxy axial ligands, suggesting photolysis of the CH_3O–Ru(IV) coordinative bond. Such rupture of axial coordinative bonds in Ru-porphyrinates is well-established.[S1,S5]

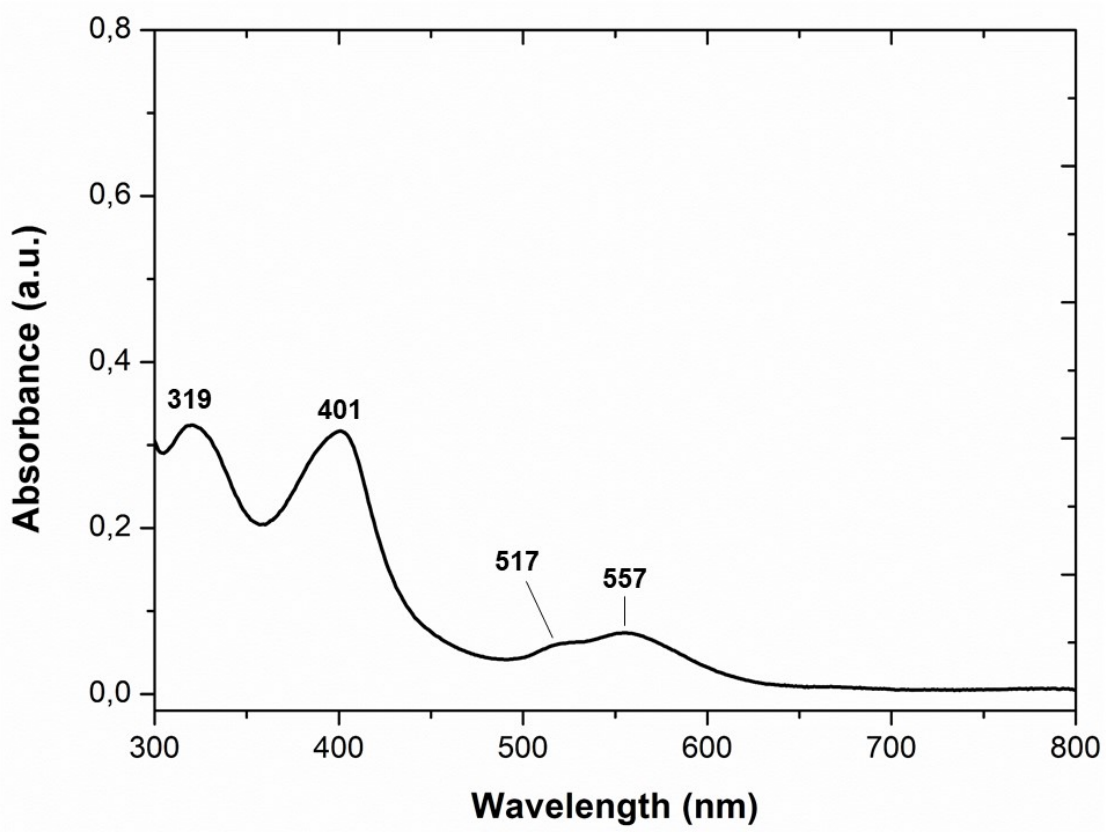


Figure S9 - Ground State UV-Vis absorption spectrum of complex **2**. Experimental conditions: DCM solutions at 10^{-5} M concentration, room temperature.

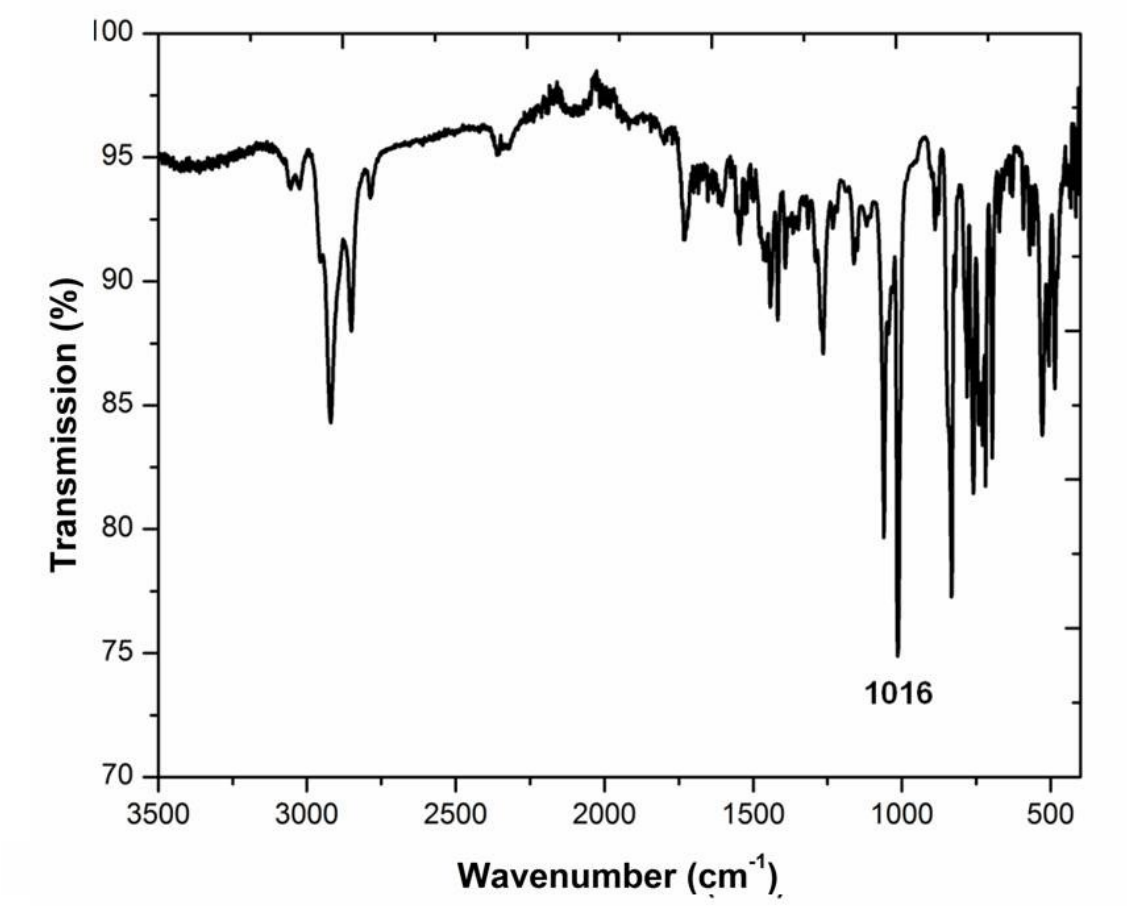


Figure S10 - FTIR-ATR vibrational spectrum of complex **2**. FTIR-ATR spectrum reveals the complete disappearance of the strong carbonyl stretching band at 1927 cm^{-1} observed for **1**[S1] along with the shift to higher frequency of the ruthenium oxidation state marker band from ν = 1004 cm^{-1} for the Ru(II)porphyrinate subunit in **1**[S1] to ν = 1016 cm^{-1} in **2**, which is consistent with the Ru(IV) oxidation state.[S6]

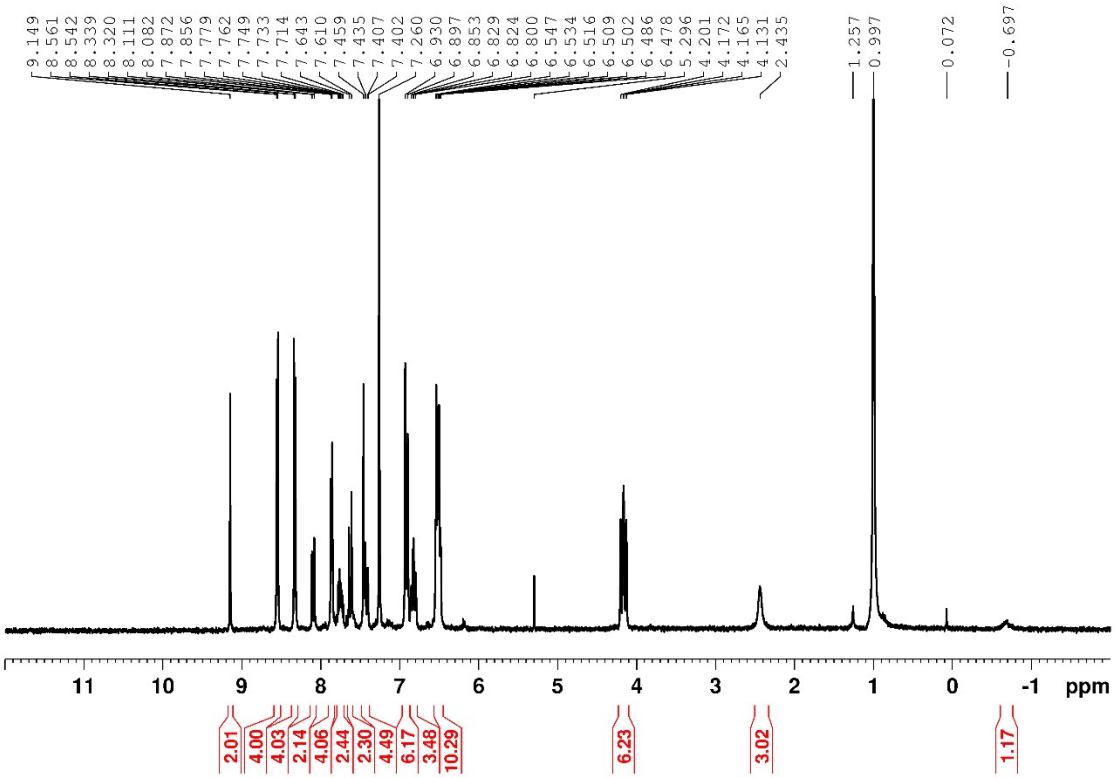


Figure S11 - Full scale ^{1}H NMR spectrum of complex **3**. Experimental conditions: 250 MHz, $CDCl_3$, 298 K.

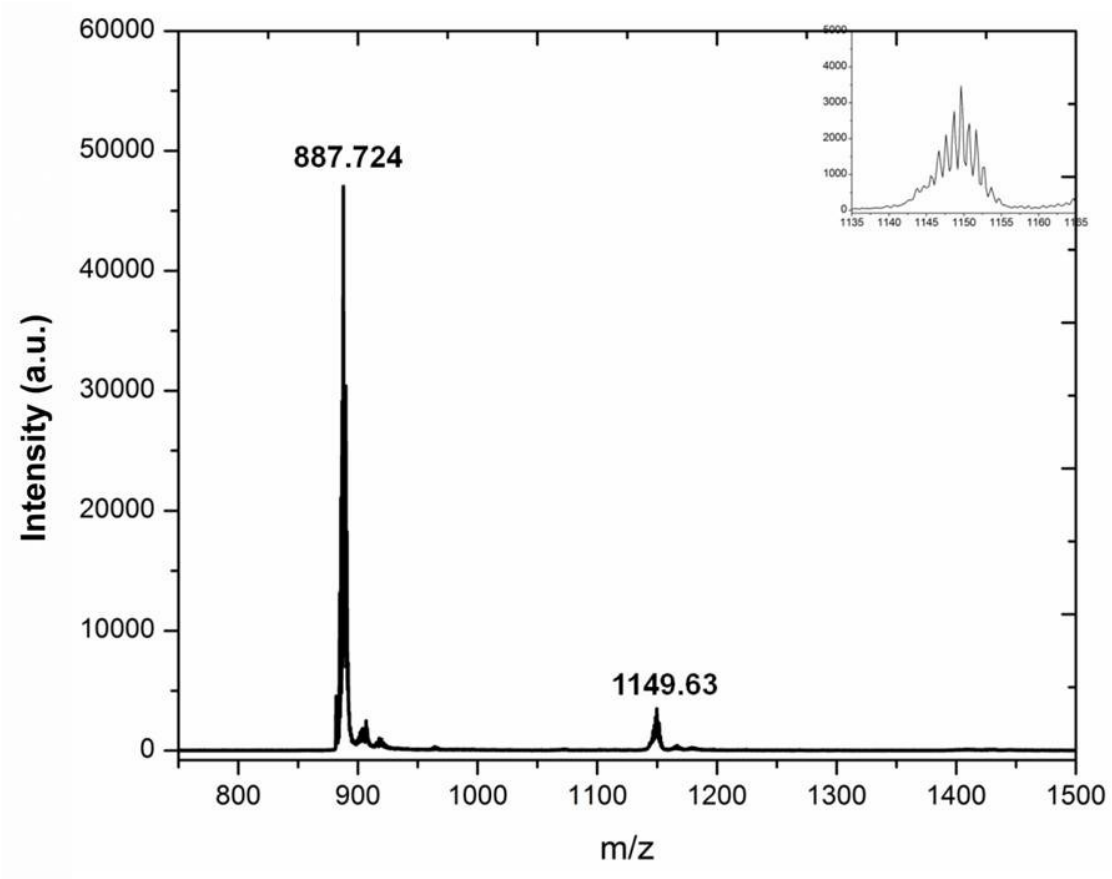


Figure S12 - Low-resolution MALDI-TOF mass spectrum of complex **3**. The molecular ion peak observed at *m/z* 1149.63 corresponds to a species lacking the loosely bound methanol axial ligand, which is lost during the MALDI-TOF ionization process. The strong signal at *m/z* 887.72 corresponds to a species lacking both axial ligands. Rupture of the axial coordinative bonds in Ru-porphyrinates is usually observed in the MALDI-TOF mass spectrum as such bonds are well-known to be light sensitive.[S1,S5]

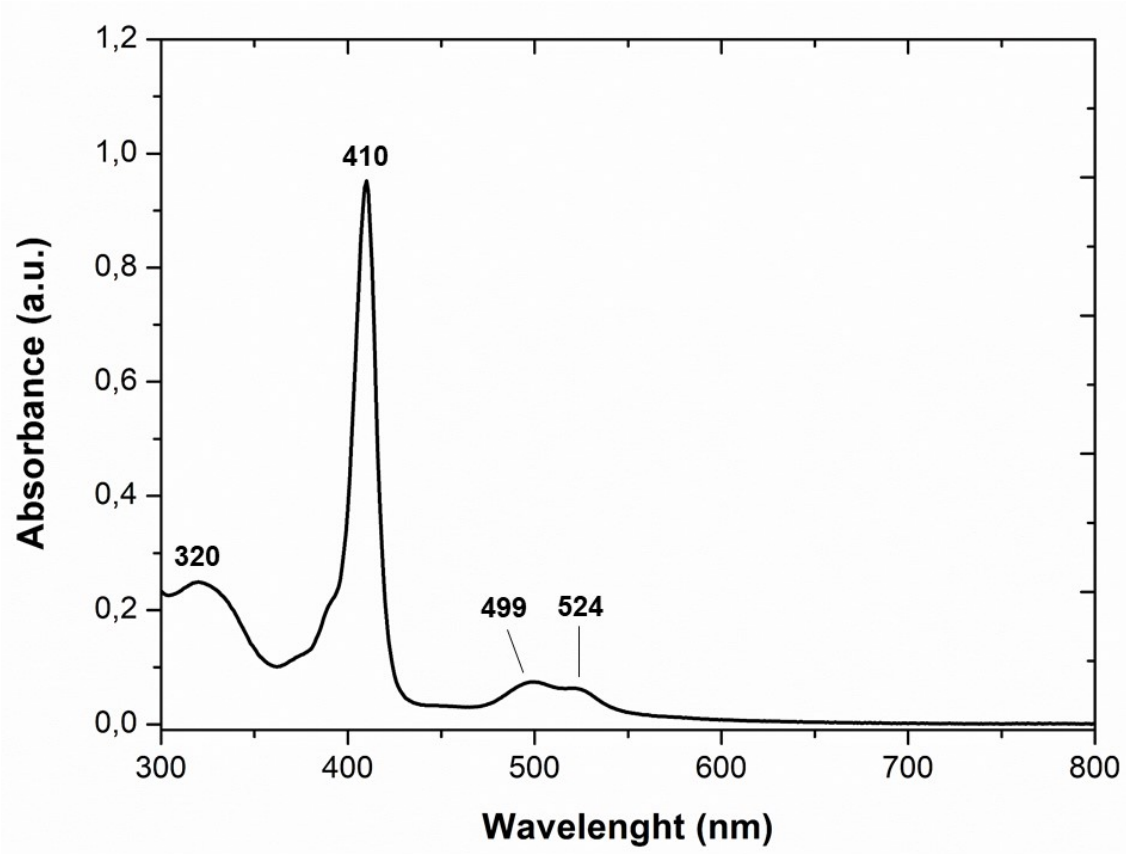


Figure S13 - Ground State UV-Vis absorption spectrum of complex **3**. Experimental conditions: DCM solutions at 10^{-5} M concentration, room temperature.

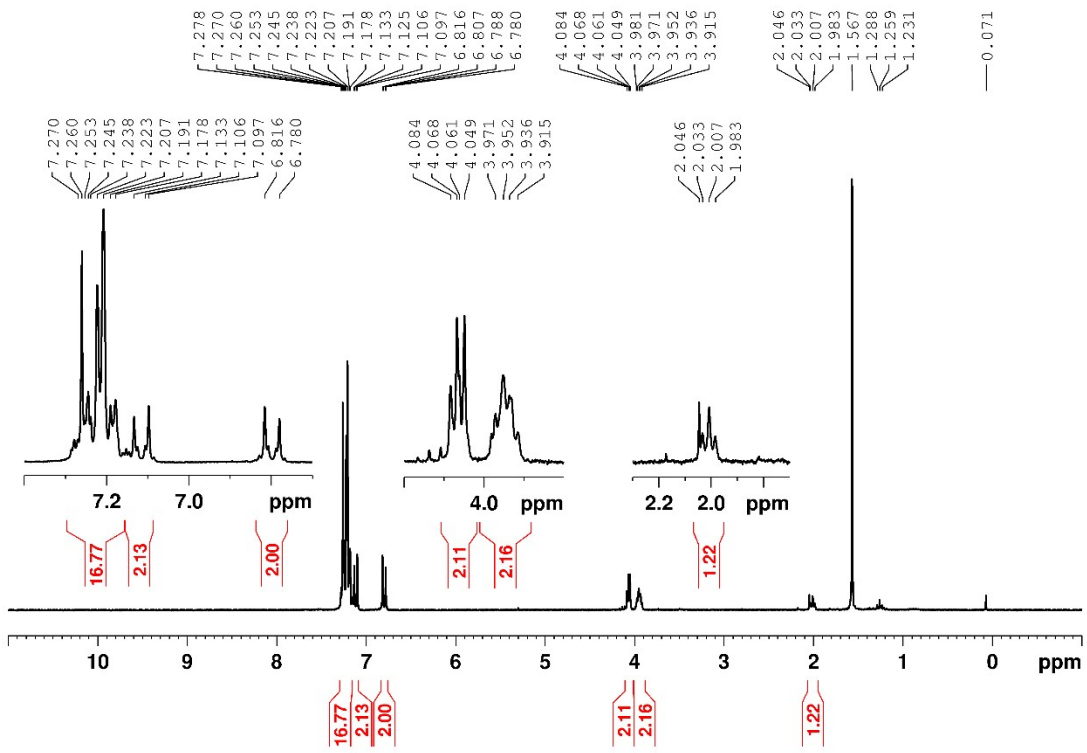


Figure S14 - Full scale ^{1}H NMR spectrum of compound **S4**. Experimental conditions: 250 MHz, $CDCl_3$, 298 K.

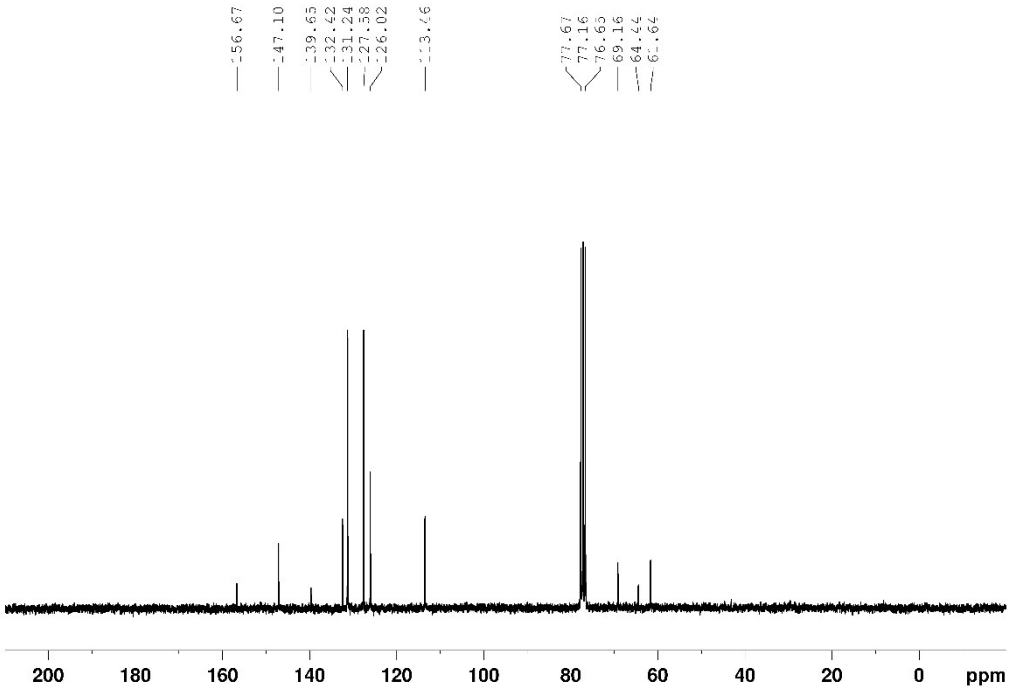


Figure S15 - Full scale ^{13}C NMR spectrum of compound **S4**. Experimental conditions: 60 MHz, $CDCl_3$, 298 K.

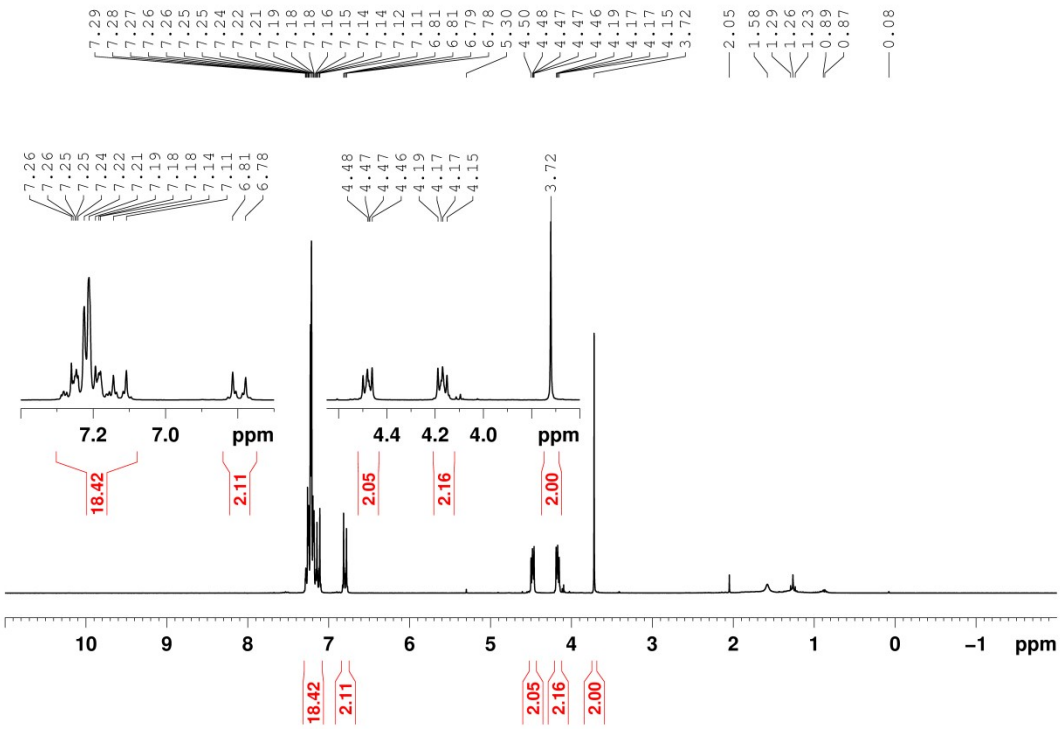


Figure S16 - Full scale ^{1}H NMR spectrum of compound **S5**. Experimental conditions: 250 MHz, $CDCl_3$, 298 K.

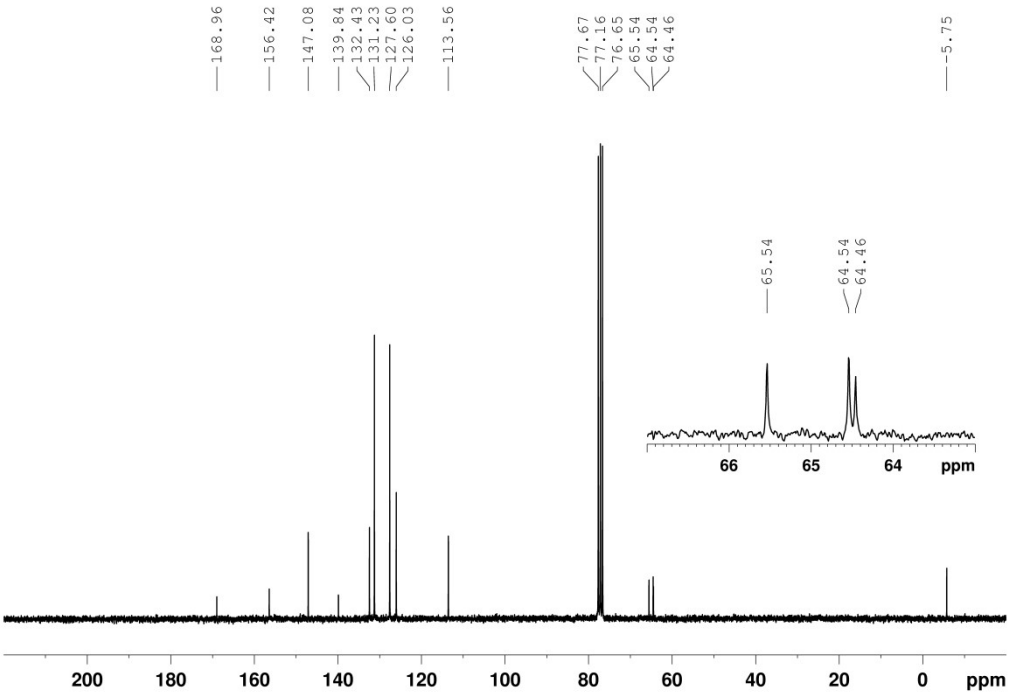


Figure S17 - Full scale ^{13}C NMR spectrum of compound **S5**. Experimental conditions: 60 MHz, $CDCl_3$, 298 K.

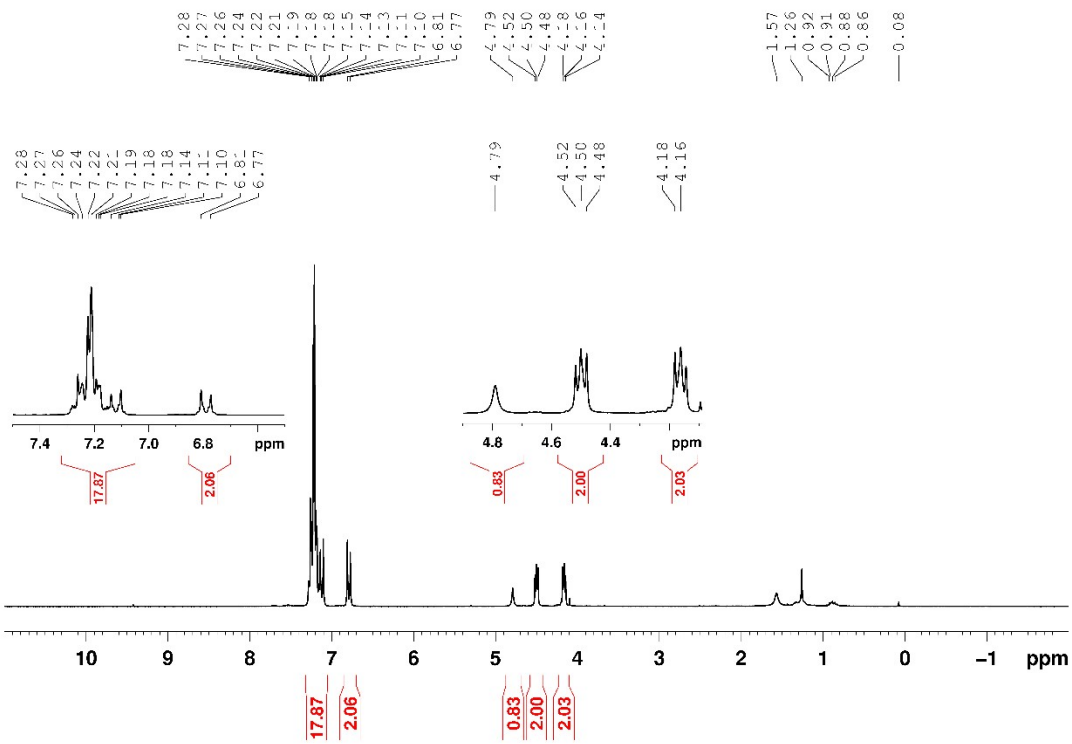


Figure S18 - Full scale ^{1}H NMR spectrum of half-thread **5**. Experimental conditions: 250 MHz, $CDCl_3$, 298 K.

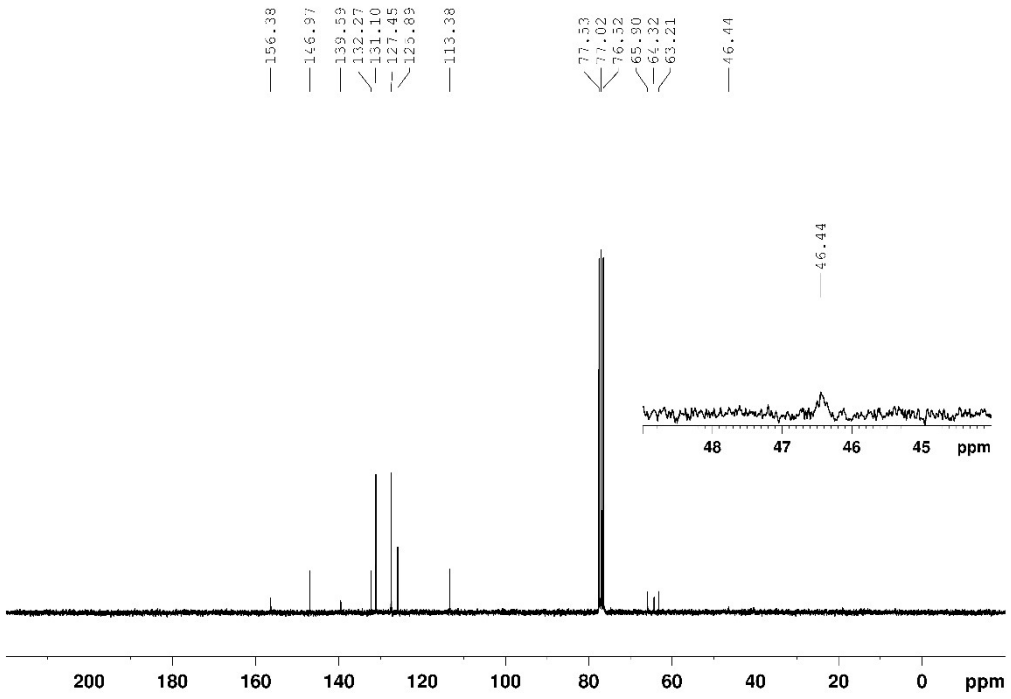


Figure S19 - Full scale ^{13}C NMR spectrum of half-thread **5**. Experimental conditions: 60 MHz, $CDCl_3$, 298 K.

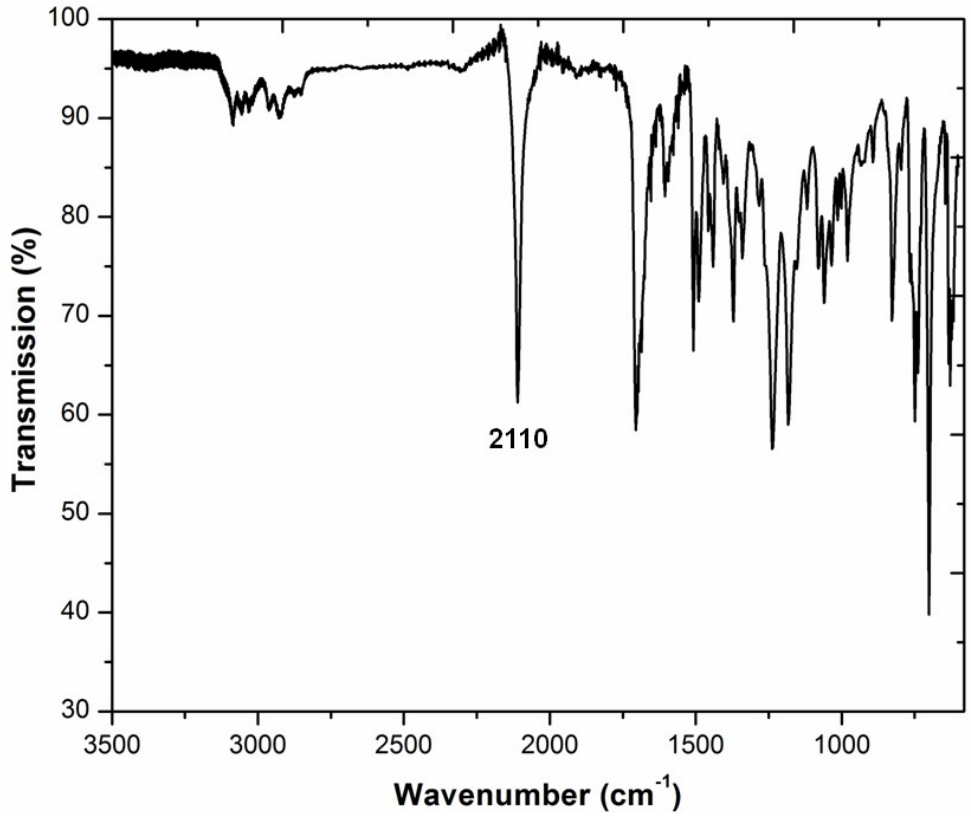


Figure S20 - FTIR-ATR vibrational spectrum of half-thread **5**.

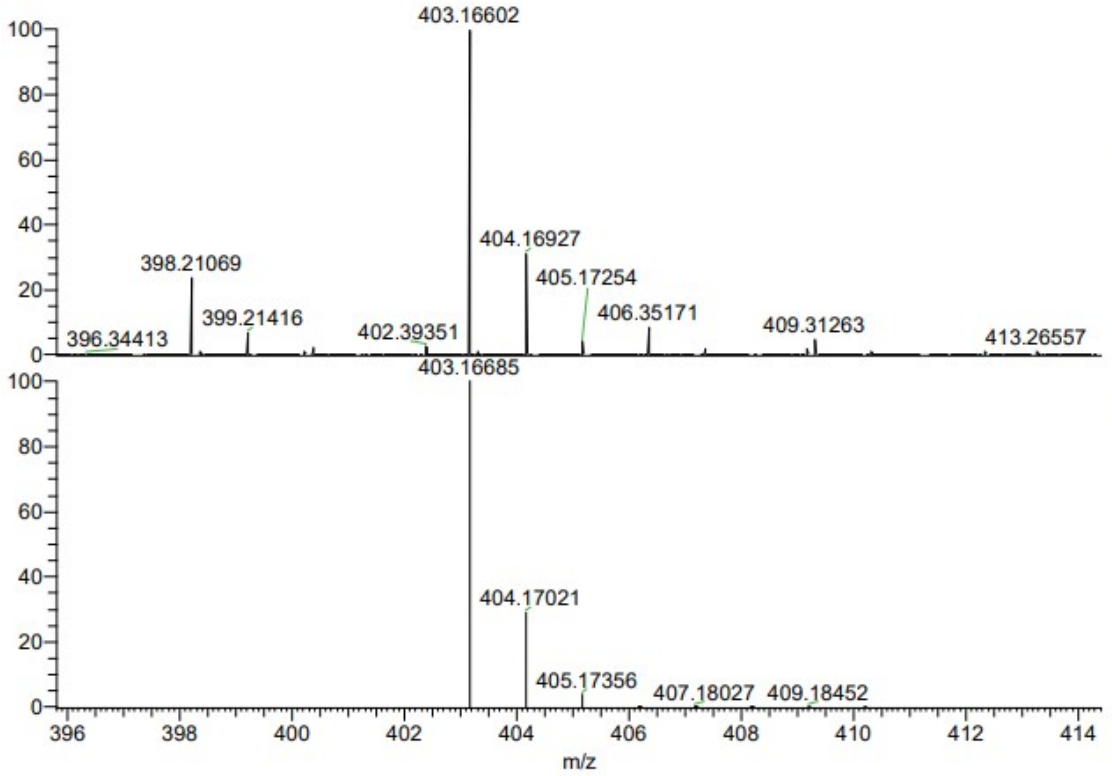


Figure S21 – High-Resolution mass spectrum of compound **S4**. Simulated (bottom) and experimental (top) spectra.

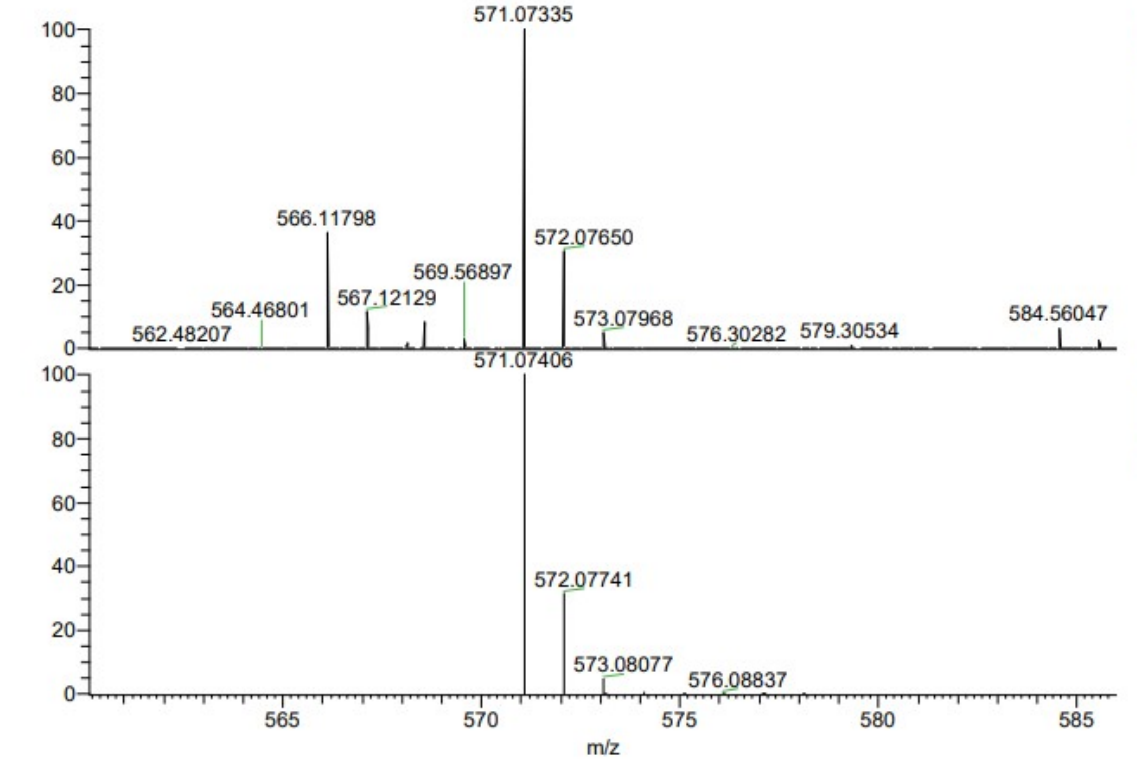


Figure S22 – High-Resolution mass spectrum of compound **S5**. Simulated (bottom) and experimental (top) spectra.

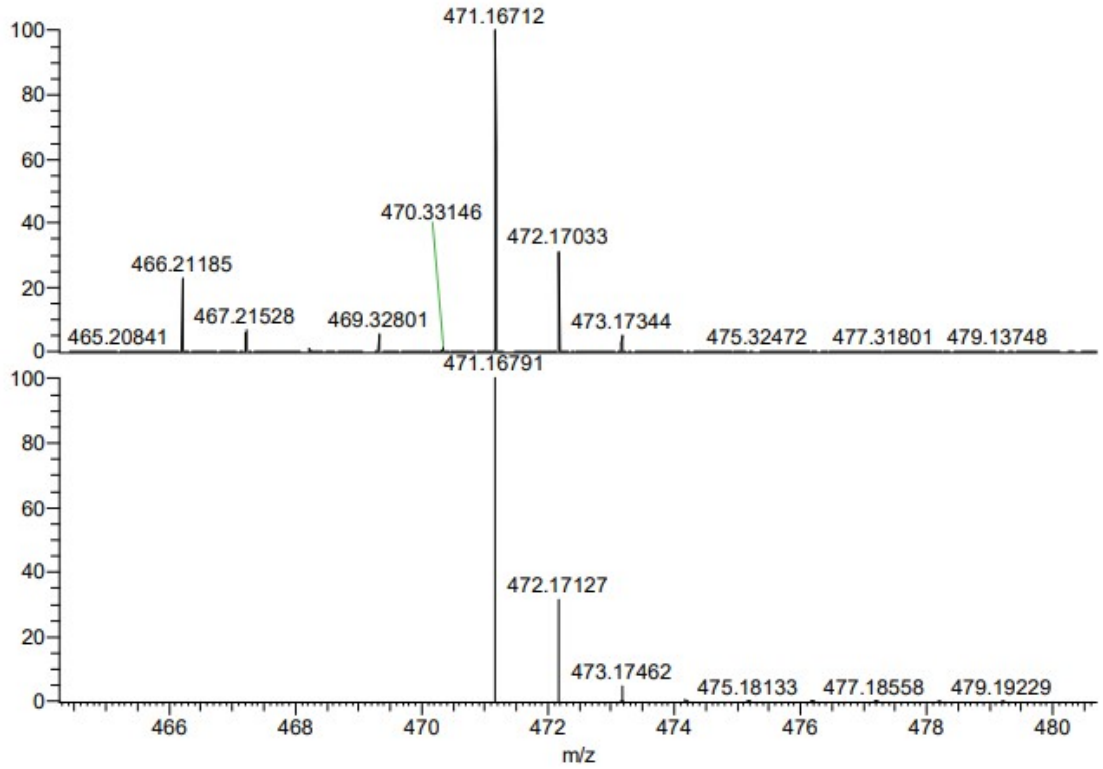


Figure S23 – High-Resolution mass spectrum of half-thread **5**. Simulated (bottom) and experimental (top) spectra.

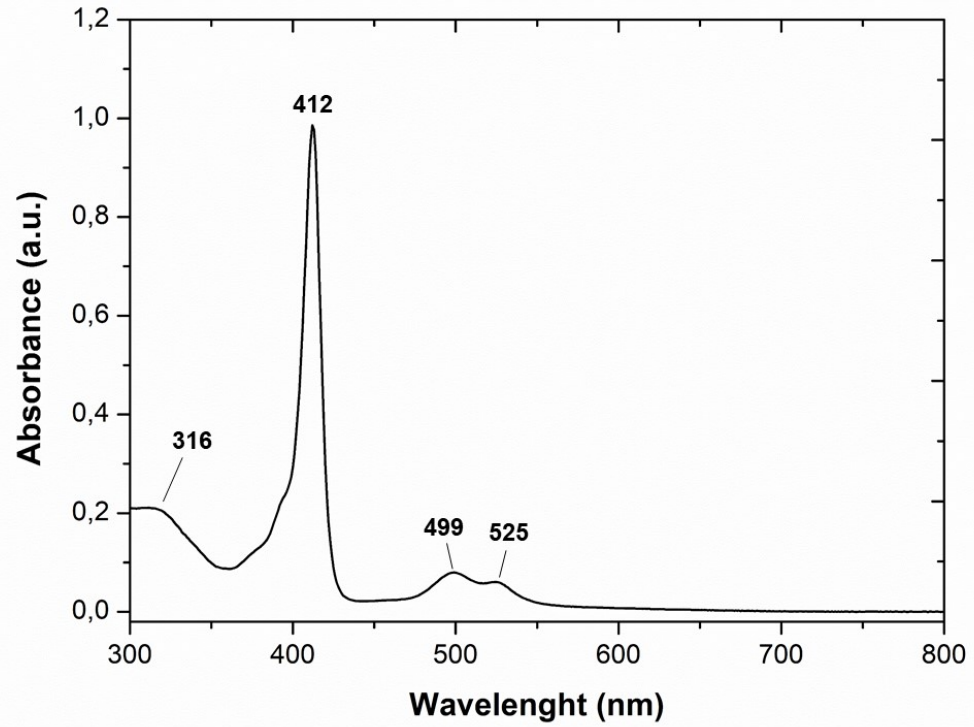


Figure S24 - Ground State UV-Vis absorption spectrum of rotaxane **6**. Experimental conditions: DCM solutions at 10^{-5} M concentration, room temperature.

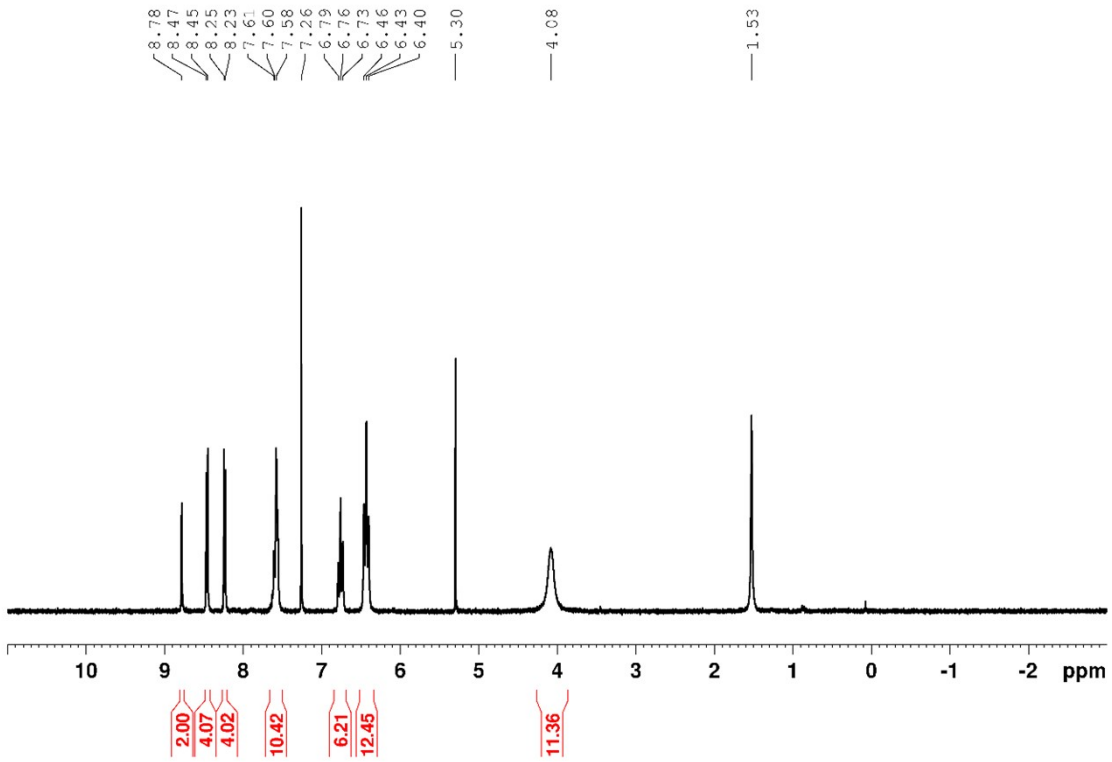


Figure S25 - Full scale ^{1}H NMR spectrum of complex **S2**. Experimental conditions: 250 MHz, $CDCl_3$, 298 K.

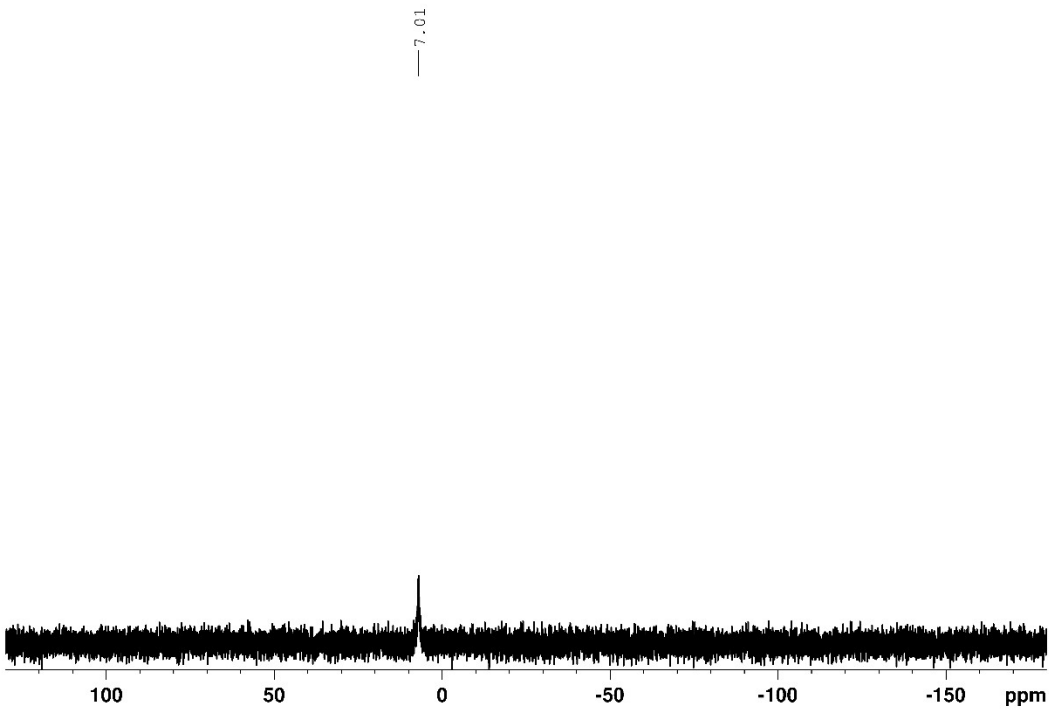


Figure S26 - Full scale ^{31}P NMR spectra of complex **S2**. Experimental conditions: 250 MHz, $CDCl_3$, 298 K.

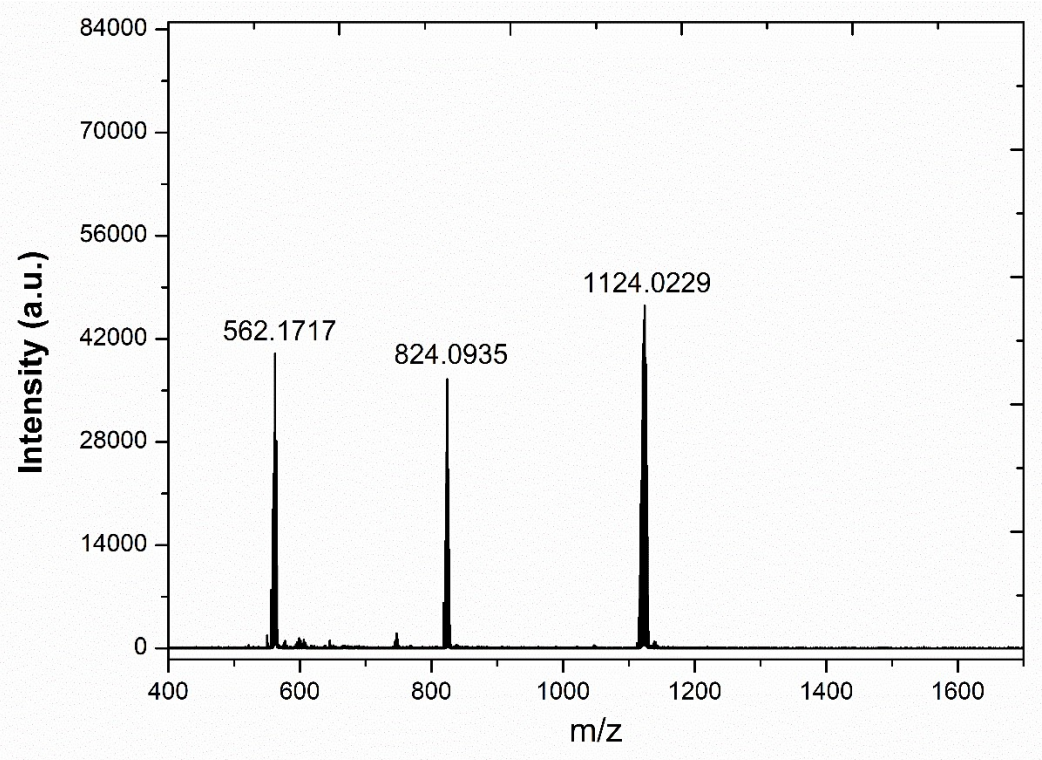


Figure S27 - High-resolution MALDI-TOF mass spectrum of complex **S2**. The molecular ion peak observed at *m/z* 824.0935 and 562.1717 correspond to species lacking one and both PPh_3 axial ligands, respectively. Rupture of the axial coordinative

bonds in Ru-porphyrinates is usually observed in the MALDI-TOF mass spectrum as such bonds are well-known to be light sensitive.[S1,S5] The molecular ion peak at *m/z* 1124.0229 correspond to a Ru(II)porphyrinate dimer containing a Ru-Ru bond, which is well-known to form upon irradiation.[S7]

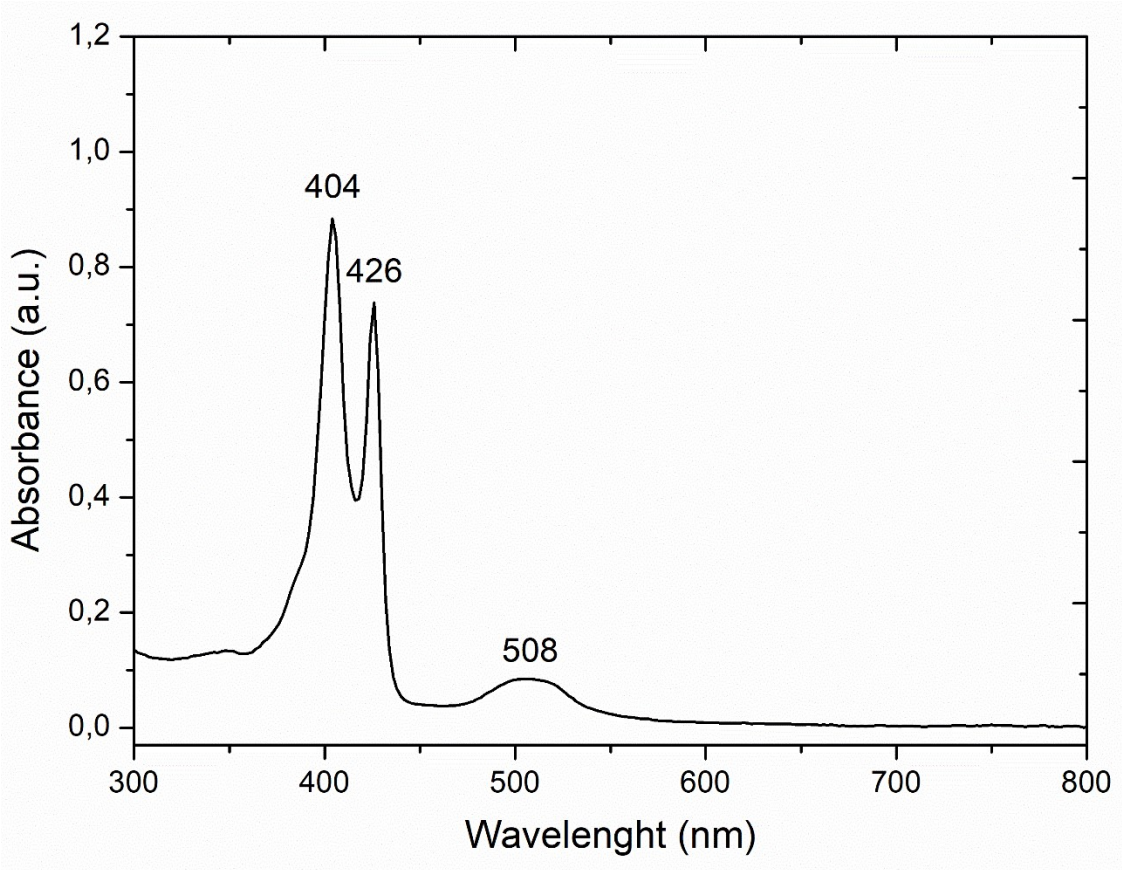


Figure S28 - Ground State UV-Vis absorption spectrum of complex **S2**. Experimental conditions: DCM solutions at 10^{-5} M concentration, room temperature.

5. Crystal Data

The X-ray diffraction experiments were performed at MX2 beamline.[S8] MX2 is a wiggler beamline dedicated to Macromolecular Crystallography at the UVX synchrotron source at the Brazilian Synchrotron Light Source. It operates on a 2.0 T hybrid 30-pole wiggler and its optical layout includes collimating mirror, Si(111) double-crystal monochromator and toroidal bendable mirror. The MX2 beamline provides wide tunability between 5 and 15 keV with maximum flux at 8.5 keV. The beamline is equipped with PILATUS2M detector from Dectris and a mini-Kappa goniometer from Arinax. For the data collection of the crystals of complex **3**, 360

frames were collected using phi-scans (1°/frame, 10s of exposition for scan, kappa 0°) and additional 360 frames were collected using phi-scans with kappa axis at kappa 45° to improve completeness. The wavelength used for these samples was 0.82602 Å. The single crystals were kept at 100 ± 2 K during the X-ray diffraction experiments.

Single crystals were grown from a dichloromethane/methanol (9:1, v/v) saturated solution by slow evaporation. The approximate dimensions for the crystals were (0.025 x 0.015 x 0.05 mm). The harvested crystals were placed in a Micromount supported with mineral oil. Crystal reflections indexing, unit-cell parameters refinement, integration and corrections were performed by CCP4 7.1.013,[S9] XIA2 0.6.475-g7ac7bb6b-dials-2.2,[S10] XDS (v. Feb 5,2021 built=20210323) [S11] Data merging and scale were performed using XDS1 Using Olex2,[S12] the structures were solved with the ShelXT[S13] structure solution program using Intrinsic Phasing and refined with the XL[S14] refinement package using Least Squares minimization. The position of all non-hydrogen atoms was refined anisotropically. The hydrogen atoms on the complex were added to the structures in idealized positions and further refined according to the riding model. Uiso(H) = 1.2Ueq(C) for aromatic and Uiso(H) = 1.5Ueq(C) for methyl groups and O groups. Table S1 presents crystal data, data collection and refinement data for complex **3**.

Table S1 – Crystallographic details for complex **3**.

Formula	$C_{77}H_{52}N_4OPRu$
Formula weight	1181.26
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.57760(10)
b (Å)	26.8909(3)
c (Å)	22.0304(2)
α (°)	90
β (°)	97.4850(10)
γ (°)	90
V (Å^3)	5625.59(10)
Z	4
Wavelength (Å)	0.82602 (Synchrotron radiation)
T (K)	100
ρ_{calc}(mg m^{-3})	1.395
μ (mm^{-1})	0.538
F(000)	2436
θ range(°)	1.4–29.8
Refl. Collected	115112
Independent refl.	9777 [Rint=0.048]
Completeness to θ max (%)	95.2
Data, restraints, parameters	977, 7, 758
Goodness-of-fit on F^2	1.21
R, w*R* [$I > 2\sigma(I)$]	0.101, 0.2177
R, w*R* (all data)	0.1074, 0.2209
*Largest diff. peak and hole (*e.Å^{-3}*)*	2.150, -2.181
CCDC	2084961

Table S2 – Main bond lengths (Å) and angles (°) for compounds **3**

Ru1—P1	2.3338 (18)	N1—Ru1—P1	95.58 (17)
Ru1—N3	2.041 (6)	N1—Ru1—O1	83.8 (2)
Ru1—N1	2.054 (6)	N2—Ru1—P1	94.90 (15)
Ru1—N2	2.048 (6)	N2—Ru1—N1	90.7 (2)
Ru1—N4	2.050 (6)	N2—Ru1—N4	170.5 (2)
Ru1—O1	2.154 (6)	N2—Ru1—O1	87.4 (2)
N3—Ru1—P1	91.00 (16)	N4—Ru1—P1	94.65 (17)
N3—Ru1—N1	173.4 (2)	N4—Ru1—N1	88.3 (2)
N3—Ru1—N2	88.9 (2)	N4—Ru1—O1	83.0 (3)
N3—Ru1—N4	91.0 (2)	O1—Ru1—P1	177.6 (2)
N3—Ru1—O1	89.6 (2)		

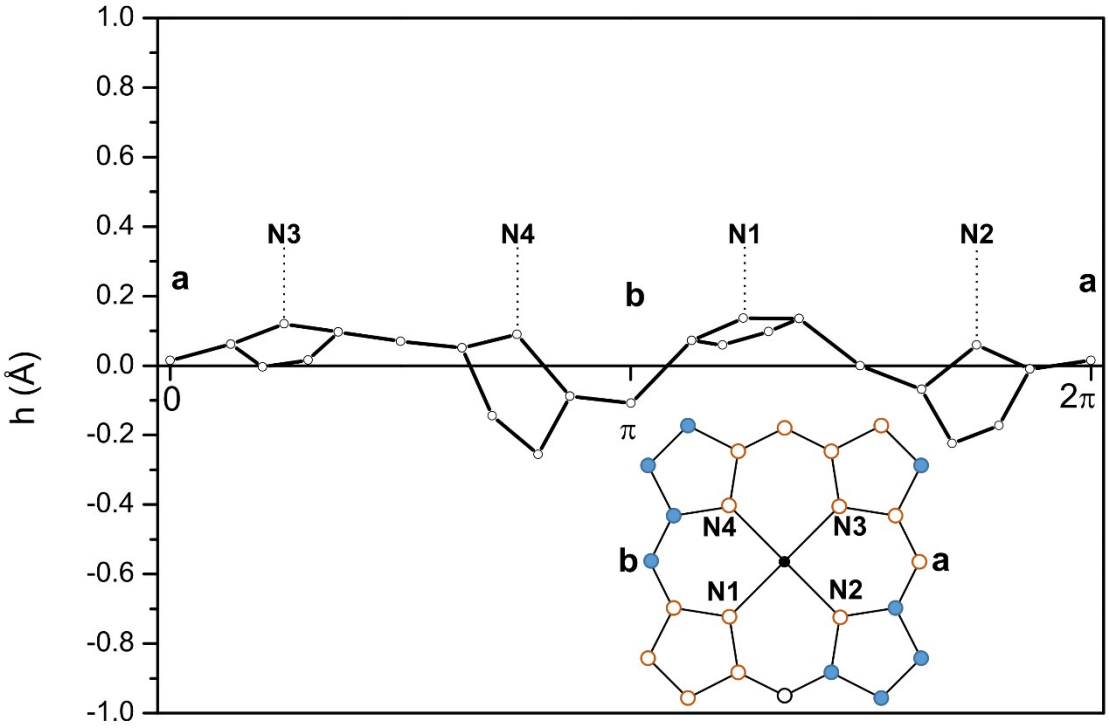


Figure S29 - Cylindrical projection of the porphyrin moiety in complex **3** with the z-coordinate displacement relative to the porphyrin mean plane on the vertical axis (h, in Å), and the azimuthal angle on the horizontal axis. The inset scheme shows the porphyrin-core conformation with open-orange circles and closed-blue circles representing atoms lying above and below the porphyrin mean plane, respectively.

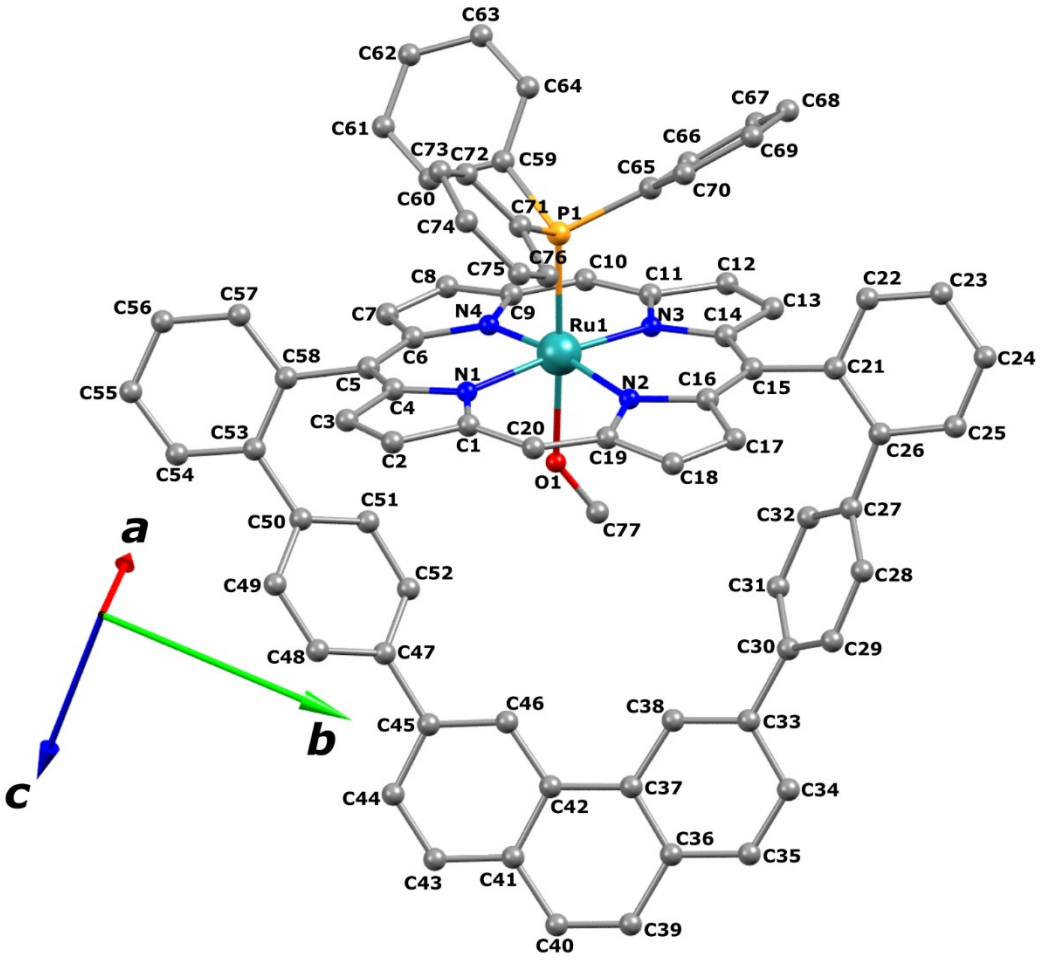


Figure S30. Representation of the single crystal structure of complex **3** with atom numbering. Carbon atoms are shown in gray, nitrogen in blue, oxygen in red, ruthenium in cyan and phosphorus in yellow. Hydrogen atoms are omitted for clarity purposes.

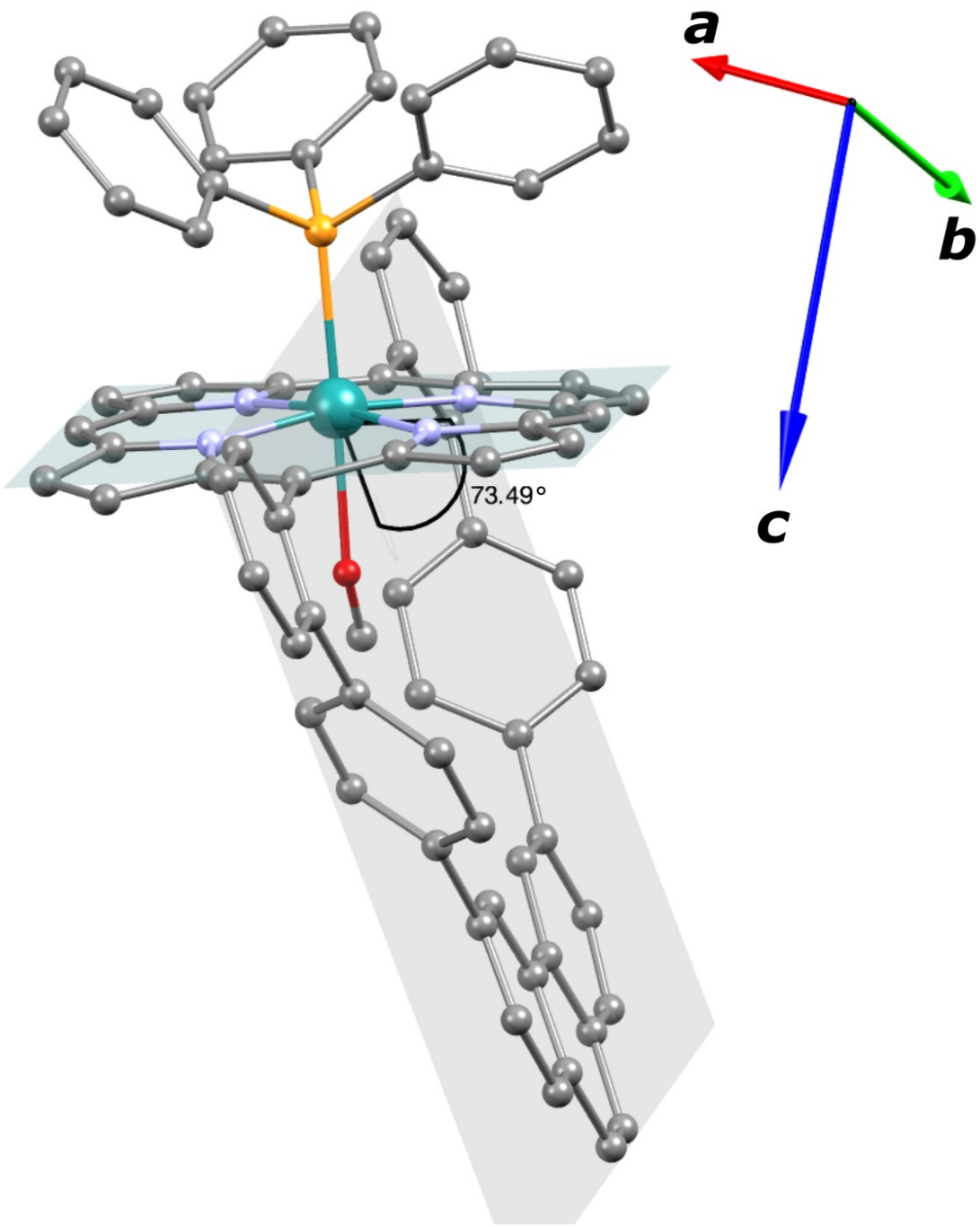


Figure S31. Side-view of the crystal structure of complex **3** highlighting the angle between the porphyrin core and the molecular aromatic backbone mean planes of 73.49°.

According to the crystallographic data, complex **3** reveals structural similarities to the relative free base macrocycle ligand and complex **1**, both reported in our previous work.[S1] The porphyrin core is virtually flat, as noticed by the low z-coordinate

displacements for each atom (h, in Å, Figure S31) from the porphyrin mean plane (root-mean-square out-of-plane value of 0.11 Å), and the dimensions of the central cavity formed between the aromatic backbone and the porphyrin moiety are 8.582 and 7.608 Å (centroid-to-centroid of the phenyl spacers and porphyrin centroid-to-midpoint of C37–C42 bond on the phenanthrene moiety, respectively; see Figure 3 in the manuscript). The complex has a distorted octahedral symmetry with a methanol molecule loosely bound at the internal axial position [Ru1–O1 of 2.156(7) Å] of the Ru(II)porphyrinate and a PPh_3 molecule at the external axial position [Ru1–P1 of 2.334(2)]. The Ru(II) ion is slightly displaced from the porphyrin mean plane toward the phosphine ligand (0.245 Å).

6. References

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S2 - (a) A. F. P. Alcântara, L. A. Fontana, V. H. Rigolin, Y. F. S. Andrade, M. A. Ribeiro, W. P. Barros, J. D. Megiatto, Jr. *Angew. Chem. Int. Ed.* **2018**, *57*, 8979-8983; (b) A. F. P. Alcântara, L. A. Fontana, M. A. Profeta, V. H. Rigolin, M. A. Ribeiro, W. P. Barros, J. D. Megiatto, Jr. *Chem. Eur. J.* **2020**, *26*, 7808-7822.

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