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SUPPORTING INFORMATION

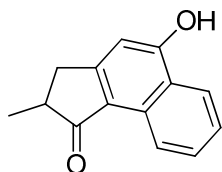
DRIVING UNIDIRECTIONAL MOLECULAR ROTARY MOTORS WITH VISIBLE LIGHT BY INTRA- AND INTERMOLECULAR ENERGY TRANSFER FROM PALLADIUM PORPHYRIN

Arjen Cnossen, Lili Hou, Michael M. Pollard, Philana V. Wesenhagen, Wesley R. Browne, Ben L. Feringa

Synthesis

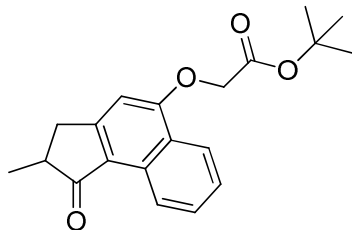
Unless stated otherwise all reagents were obtained from commercial sources and used as received without further purification. Solvents for reactions were reagent grade and distilled and dried according to standard procedures. Flash column chromatography was performed over silica gel (Aldrich 60, 230-400 mesh) using positive pressure. Solvents for spectroscopic studies were of spectrophotometric grade (UVASOL Merck). NMR spectra were recorded on a Varian Gemini-200 (^1H : 200 MHz, ^{13}C : 50 MHz), Varian VXR-300 (^1H : 300 MHz), Varian AMX400 (^1H : 400 MHz, ^{13}C : 100 MHz) or Varian Unity Plus (^1H : 500 MHz, ^{13}C : 125 MHz) spectrometer. Chemical shifts are denoted in δ -units (ppm) relative to the residual solvent peak (CDCl_3 : ^1H δ = 7.26, ^{13}C δ = 77.0; DMSO: ^1H δ = 2.49, ^{13}C δ = 39.5). The splitting parameters are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad. (HR)MS spectra were obtained with an AEI MS-902. HPLC was performed on a Shimadzu semi-prep system consisting of a LC-20T pump, a DGU-20A degasser, a CBM-20A control module, a SIL-20AC autosampler, a SPD-M20A diode array detector and a FRC-10A fraction collector. Palladium tetraphenylporphyrin,¹ motors **1** and **2**,² 9-diazo fluorenone and ketone **3**,³ porphyrins **10** and **11**⁴ and potassium reineckate⁵ were synthesized according to literature procedures.

Enantioresolution of **2** was performed using chiral stationary phase HPLC: Chiralpak AD column, 99:1 *n*-heptane:2-propanol, T = 40 °C, flow rate 1 mL/min, retention times 6.5 min (*E*), 7.5 min (*Z*), 9.5 min (*Z*), 13 min (*E*).



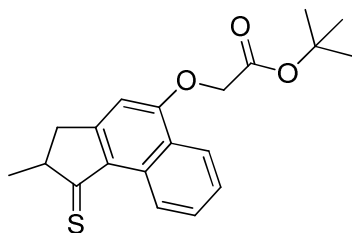
5-hydroxy-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one **5**

To pyridine hydrochloride (6.0 g, 52 mmol) at 150 °C was added **4** (550 mg, 2.43 mmol). The mixture was heated to 190 °C for 2 h, after which it was allowed to cool to rt. The solid mass was partitioned between H_2O (200 mL) and ethyl acetate (200 mL). The organic layer was washed with 0.5 M aqueous HCl (100 mL), H_2O (100 mL) and brine (100 mL) and dried on Na_2SO_4 . The solvent was removed *in vacuo* and the crude product was purified by column chromatography (SiO_2 , 2:1 pentane:ethyl acetate, R_f = 0.3) yielding **5** (286 mg, 56 %) as an orange solid. mp >200 °C; ^1H NMR (300 MHz, DMSO) δ 11.35 (br s, 1H), 8.93 (d, J = 8.1 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.63 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.3 Hz, 1H), 6.88 (s, 1H), 3.32 (overlaps with H_2O , dd, J = 17.9 Hz, 7.3 Hz, 1H), 2.65 (d, J = 17.2 Hz, 2H), 1.17 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, DMSO) δ 207.6 (C), 161.0 (C), 160.4 (C), 131.2 (C), 129.8 (CH), 126.0 (CH), 124.7 (C), 123.6 (CH), 123.5 (CH), 121.8 (C), 106.3 (CH), 42.1 (CH), 35.6 (CH_2), 17.2 (CH_3); HRMS (ESI^+) calcd. for $\text{C}_{14}\text{H}_{13}\text{O}_2$ [$\text{M}+\text{H}$] 213.0910, found 213.0910.



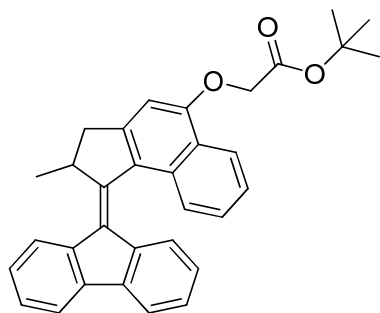
tert-butyl 2-((2-methyl-1-oxo-2,3-dihydro-1H-cyclopenta[a]naphthalen-5-yl)oxy)acetate 6

To a suspension of **5** (235 mg, 1.11 mmol) and K_2CO_3 (209 mg, 1.5 mmol) in DMF (12 mL) at 50 °C was added *t*-butyl chloroacetate (0.5 mL, 3.5 mmol) and the mixture was stirred at 50 °C for 2 h. The reaction mixture was diluted with ethyl acetate (100 mL) and washed with H_2O (3 x 100 mL) and brine (100 mL) and dried on Na_2SO_4 . The volatiles were removed *in vacuo* and the crude product was purified by column chromatography (SiO_2 , 5:2 pentane:ethyl acetate, $R_f = 0.5$) yielding **6** (305 mg, 84%) as a yellow solid. mp 129.6-131.5 °C; 1H NMR (300 MHz, $CDCl_3$) δ 9.13 (d, $J = 8.7$ Hz, 1H), 8.38 (d, $J = 8.1$ Hz, 1H), 7.69 (t, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 6.66 (s, 1H), 4.79 (s, 2H), 3.42 (dd, $J = 18.3$ Hz, 7.8 Hz, 1H), 2.79 (m, 2H), 1.53 (s, 9H), 1.36 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.3 (C), 166.9 (C), 159.7 (C), 158.5 (C), 130.6 (C), 129.4 (CH), 126.1 (CH), 125.0 (C), 124.1 (C), 123.7 (CH), 122.6 (CH), 102.3 (CH), 82.8 (C), 65.9 (CH₂), 42.1 (CH), 35.7 (CH₂), 28.0 (3CH₃), 16.7 (CH₃); HRMS (ESI⁺) calcd. for $C_{20}H_{23}O_4$ [M+H] 327.1591, found 327.1590.



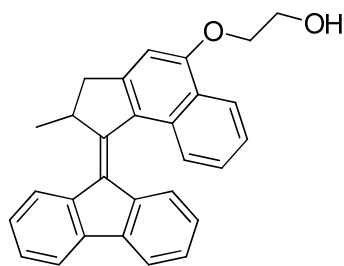
tert-butyl 2-((2-methyl-1-thioxo-2,3-dihydro-1H-cyclopenta[a]naphthalen-5-yl)oxy)-acetate 7

To a solution of **6** (50 mg, 0.15 mmol) in THF (2 mL) was added Lawesson's reagent (74 mg, 0.18 mmol). The reaction mixture was stirred for 3.5 h at 50 °C. The solvent was removed *in vacuo* and the crude product was purified by column chromatography (SiO_2 , toluene, $R_f = 0.5$) yielding **7** (40 mg, 78%) as a purple-red solid. Thioketone **7** could be stored at rt under inert atmosphere for at least three days without degradation. 1H NMR (300 MHz, $CDCl_3$) δ 10.15 (d, $J = 8.4$ Hz, 1H), 8.40 (d, $J = 8.1$ Hz, 1H), 7.73 (t, $J = 7.7$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 6.63 (s, 1H), 4.76 (s, 2H), 3.39 (dd, $J = 6.4, 18.1$ Hz, 1H), 3.10 (m, $J = 7.0$ Hz, 1H), 2.81 (d, $J = 18.0$ Hz, 1H), 1.53 (s, 9H), 1.47 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 245.6 (C), 166.9 (C), 161.5 (C), 160.1 (C), 134.3 (C), 131.6 (C), 131.0 (CH), 126.6 (CH), 125.5 (C), 124.3 (CH), 123.1 (CH), 102.1 (CH), 83.2 (C), 66.1 (CH₂), 55.1 (CH), 40.5 (CH₂), 28.3 (3CH₃), 22.0 (CH₃); HRMS (ESI⁺) calcd. for $C_{20}H_{23}O_3S$ [M+H] 343.1362, found 343.1358.



tert-butyl 2-((1-(9H-fluoren-9-ylidene)-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-5-yl)oxy)acetate **8**

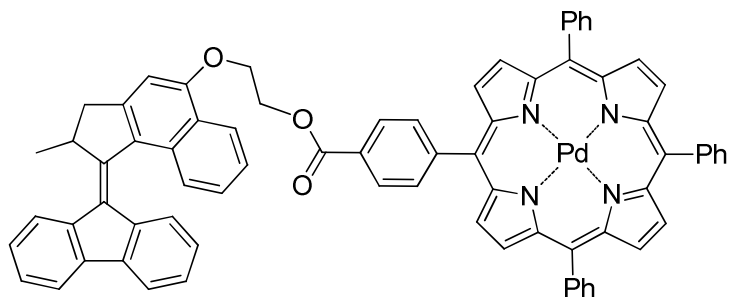
A solution of **7** (108 mg, 0.316 mmol) and 9-diazafluorenone (100 mg, 0.521 mmol) in toluene (10 mL) was stirred at 50 °C for 16 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography (SiO₂, 1:1 heptane:toluene, R_f = 0.2) yielding a mixture of **8** and the corresponding episulfide. This mixture was dissolved in toluene (10 mL) and PPh₃ (250 mg, 0.95 mmol) was added and the solution was heated to reflux for 16 h. The volatiles were removed *in vacuo* and the residue was redissolved in Et₂O (10 mL). Methyl iodide (0.1 mL) was added and the mixture was stirred at rt for 3 h. A white precipitate was filtered off and the filtrate was concentrated. Column chromatography (SiO₂, 1:1 pentane:toluene) yielded **8** (98 mg, 65%) as a yellow solid. mp 153.5-154.3 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.48 (d, *J* = 8.1 Hz, 1H), 7.99 (m, 1H), 7.87 (m, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.40-7.32 (m, 4H), 7.20 (t, *J* = 6.9 Hz, 1H), 6.83 (s, 1H), 6.80 (d, *J* = 7.1 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 4.84 (s, 2H), 4.35 (m, *J* = 6.3 Hz, 1H), 3.57 (dd, *J* = 5.6, 15.0 Hz, 1H), 2.72 (d, *J* = 15.1 Hz, 1H), 1.57 (s, 9H), 1.43 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.3 (C), 158.9 (C), 154.0 (C), 151.2 (C), 142.6 (C), 141.9 (C), 139.9 (C), 133.3 (C), 132.3 (C), 131.3 (C), 130.1 (CH), 130.0 (CH), 129.5 (CH), 129.2 (CH), 129.1 (CH), 128.5 (CH), 128.4 (CH), 127.7 (CH), 127.3 (C), 126.5 (CH), 125.7 (CH), 122.3 (CH), 121.6 (CH), 106.3 (CH), 85.3 (C), 68.9 (CH₂), 47.9 (CH), 45.2 (CH₂), 30.8 (3CH₃), 22.3 (CH₃); HRMS (ESI⁺) calcd. for C₃₃H₃₀O₃Na [M+Na] 497.2087, found 497.2097. Elemental analysis calcd. C: 83.51 H: 6.37 found C: 83.14 H: 6.27.



2-((1-(9H-fluoren-9-ylidene)-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-5-yl)oxy)ethanol **9**

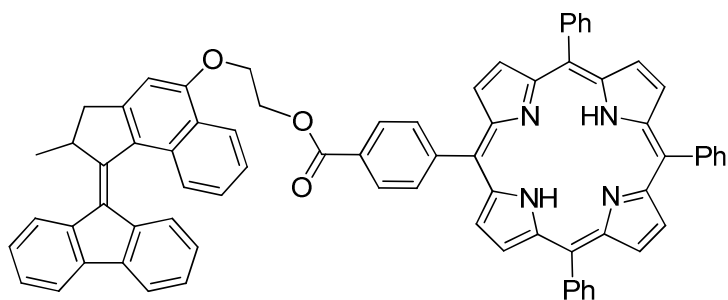
To a solution of **8** (100 mg, 0.210 mmol) in THF (4 mL) at 0 °C was added LiAlH₄ (70 mg, 1.84 mmol). After stirring for 3 h at 0 °C the reaction was quenched by addition of excess Na₂SO₄·10H₂O. The mixture was allowed to warm to rt, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO₂, 2:1 pentane:ethyl acetate, R_f = 0.2) yielding **9** (68 mg, 80%) as a yellow solid. ¹H NMR (300 MHz, DMSO) δ 8.39 (d, *J* = 8.4 Hz, 1H), 7.93 (m, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.52-7.30 (m, 5H), 7.19 (m, *J* = 7.1 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 8.1 Hz, 1H), 5.07 (t, *J* = 5.7 Hz, 1H), 4.33-4.18 (m, 3H), 3.91 (m,

2H), 3.34 (dd, $J = 5.5, 15.6$ Hz, 1H), 2.72 (d, $J = 15.7$ Hz, 1H), 1.28 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (50 MHz, DMSO) δ 157.8 (C), 152.5 (C), 150.6 (C), 139.8 (C), 139.6 (C), 139.3 (C), 137.1 (C), 130.5 (C), 127.9 (CH), 127.8 (CH), 127.7 (C), 127.2 (2CH), 127.1 (2CH), 126.4 (CH), 125.6 (CH), 125.3 (CH), 124.7 (C), 124.2 (CH), 123.8 (CH), 120.6 (CH), 120.0 (CH), 104.7 (CH), 71.1 (CH₂), 60.3 (CH₂), 45.4 (CH), 42.7 (CH₂), 20.2 (CH₃); HRMS (ESI) calcd. for C₂₉H₂₅O₂ [M+H] 405.1849, found 405.1848.



PdTPP-motor hybrid **12**

A solution of **9** (41 mg, 0.101 mmol), **10** (77 mg, 0.1 mmol), 4-dimethylaminopyridine (DMAP) (15 mg, 0.12 mmol) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (21 mg, 0.11 mmol) in CH₂Cl₂ (3 mL) at rt was stirred for 16 h in the dark. Another batch of EDC (5 mg, 0.026 mmol) was added and stirring was continued for 4 h. The volatiles were removed *in vacuo* and the residue was subjected to column chromatography (SiO₂, 1:1 pentane:CHCl₃) yielding **12** (103 mg, 88%) as a purple solid. ^1H NMR (500 MHz, CDCl₃) δ 8.87 (s, 6H), 8.80 (d, $J = 4.8$ Hz, 2H), 8.54 (d, $J = 8.5$ Hz, 1H), 8.50 (d, $J = 8.0$ Hz, 2H), 8.30 (d, $J = 7.9$ Hz, 2H), 8.19 (d, $J = 6.6$ Hz, 6H), 8.0 (d, $J = 7.1$ Hz, 1H), 7.88 (d, $J = 7.3$ Hz, 1H), 7.83-7.72 (m, 11H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.47-7.37 (m, 2H), 7.22 (t, $J = 7.4$ Hz, 1H), 6.95 (s, 1H), 6.86 (t, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 6.78$, 1H), 4.97 (s, 2H), 4.55 (s, 2H), 4.33 (m, 1H), 3.52 (dd, $J = 15.0, 5.2$ Hz, 1H), 2.72 (d, $J = 15.2$ Hz, 1H), 1.27 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl₃) δ 166.9 (C), 157.2 (C), 151.6 (C), 149.1 (C), 147.3 (C), 142.3 (2C), 142.2 (2C), 142.1 (3C), 142.0 (2C), 141.4 (2C), 140.3 (C), 140.2 (C), 139.6 (C), 137.6 (C), 134.6 (2CH), 134.4 (6CH), 131.8 (2CH), 131.6 (2CH), 131.5 (2CH), 131.1 (C), 130.9 (CH), 129.8 (C), 129.7 (C), 129.0 (C), 128.5 (2CH), 128.1 (3CH), 127.8 (CH), 127.7 (CH), 127.1 (7CH), 126.8 (2CH), 126.1 (2CH), 125.3 (CH), 125.2 (C), 124.1 (CH), 123.3 (CH), 122.5 (C), 122.4 (2C), 120.6 (C), 119.9 (CH), 119.1 (CH), 104.1 (CH), 104.0 (CH), 67.0 (CH₂), 63.7 (CH₂), 45.5 (CH), 42.9 (CH₂), 19.9 (CH₃); MS (EI) calcd. for C₇₄H₅₁N₄O₃Pd [M+H] 1149.29, found 1149.17. HPLC Chiralpak AD column, 80:20 *n*-heptane:2-propanol, $T = 50$ °C, flow rate 1 mL/min, retention times 14 min, 18 min.



H₂TPP-motor hybrid **13**

A solution of **9** (25 mg, 0.062 mmol), **11** (41 mg, 0.062 mmol), 4-dimethylaminopyridine (DMAP) (7.5 mg, 0.061 mmol) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (14 mg, 0.073 mmol) in CH₂Cl₂ (3 mL) at rt was stirred for 2 d in the dark. The volatiles were removed *in vacuo* and the residue was loaded on a silica column. Unreacted starting material was eluted with 1:1 pentane:CH₂Cl₂, after which the porphyrin fraction was eluted with CHCl₃. The crude product was purified by recrystallization (CH₂Cl₂/MeOH, layer addition) yielding **13** (42 mg, 65%) as a purple solid. ¹H NMR (400 MHz, CDCl₃) δ 8.90 (s, 6H), 8.84 (d, *J* = 4.7 Hz, 2H), 8.60-8.52 (m, 3H), 8.37 (d, *J* = 8.0 Hz, 2H), 8.29-8.23 (m, 6H), 8.05-7.96 (m, 1H), 7.93-7.84 (m, 1H), 7.84-7.66 (m, 11H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.46-7.33 (m, 3H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.08 (s, 1H), 6.90-6.76 (m, 2H), 5.19-4.93 (m, 2H), 4.72 (d, *J* = 3.3 Hz, 2H), 4.43-4.28 (m, 1H), 3.60 (dd, *J* = 15.1, 5.6 Hz, 1H), 2.77 (d, *J* = 15.1 Hz, 1H), 1.45 (d, *J* = 6.6, 3H), -2.71 (s, 2H). ¹³C NMR (50 MHz, CDCl₃) δ = 167.1 (C), 157.1 (C), 151.7 (C), 149.2 (2C), 147.7 (2C), 142.3 (4C), 140.1 (C), 140.0 (C), 139.5 (C), 137.5 (C), 134.9 (2CH), 134.8 (6CH), 130.9 (C), 129.5 (2C), 128.7 (C), 128.4 (3CH), 128.1 (4CH), 127.6 (3CH), 127.0 (8CH), 126.7 (2CH), 126.1 (CH), 126.0 (2CH), 125.3 (CH), 124.9 (C), 124.0 (CH), 123.2 (CH), 120.9 (C), 120.7 (2C), 119.9 (CH), 119.2 (CH), 118.7 (C), 103.8 (CH), 67.0 (CH₂), 63.8 (CH₂), 45.5 (CH), 42.8 (CH₂), 19.9 (CH₃). MS (EI) calcd. for C₇₄H₅₁N₄O₃Pd [M+H] 1149.29, found 1149.17. HPLC Chiralpak AD column, 90:10 *n*-heptane:2-propanol, *T* = 50 °C, flow rate 1 mL/min, retention times 16 min, 21 min.

Irradiation experiments

UV/Vis absorption spectra were measured on Jasco V-630 spectrometer. Emission spectra were measured using a Jasco FP-6200 spectrofluorimeter. Room temperature phosphorescence spectra were obtained in 1,2-dichloroethane under Argon atmosphere with degassing by at least three freeze-pump-thaw cycles. Phosphorescence lifetimes were obtained using a home built system. Excitation was performed using the second harmonic (532 nm, 10 Hz, 25 mJ, 10 ns) of a Q-switched Nd:YAG laser (Innolas 400) with a Si-diode trigger sensor. The emission from the sample was focused into a Zolix Omni-λ 300 monochromator coupled with a Zolix PMTH-S1-CR131 side-on PMT. Emission decay traces were recorded with 50 Ohm termination on a Tetrionix DPO 4032 digital phosphor Oscilloscope and transferred to a PC for data analysis using homebuilt software written in National Instruments LabVIEW 8.2.

Solutions of **1**, **2**, **12** and **13** were bubbled with Argon for at least two minutes before irradiation. For fluorescence and phosphorescence emission and lifetime measurements, the solutions were deoxygenated with at least three freeze-pump-thaw cycles. For irradiation with a fluorescent

lamp, a 546 ± 5 nm bandpass filter was used and the solutions were cooled to -40 °C using a cryostat. Depending on the concentration, irradiation times were up to 1 h at $\sim 10^{-5}$ M and overnight for samples used for NMR spectroscopy ($\sim 10^{-3}$ M). Laser irradiation we employed at rt with care taken to perform measurements within 30 s of irradiation. In general, PSS was reached within 10 s of irradiation. To be certain photostationary states were reached, several spectra at set intervals were recorded. Thermal isomerization was performed by leaving the solutions in the dark at 20 - 40 °C for at least 20 min. The solution was then cooled again to the temperature at which irradiation was performed before further measurement.

The photochemical and thermal isomerizations of **2** in chloroform in the presence of PdTPP were also followed using CD spectroscopy (Figure S1). Upon irradiation at 532 nm, a decrease in the intensity is observed, caused by the formation of the thermally unstable isomer. Upon warming, the spectral changes are reverted; a complete recovery is not observed because *E-2a* and *Z-2a* have slightly different CD spectra.

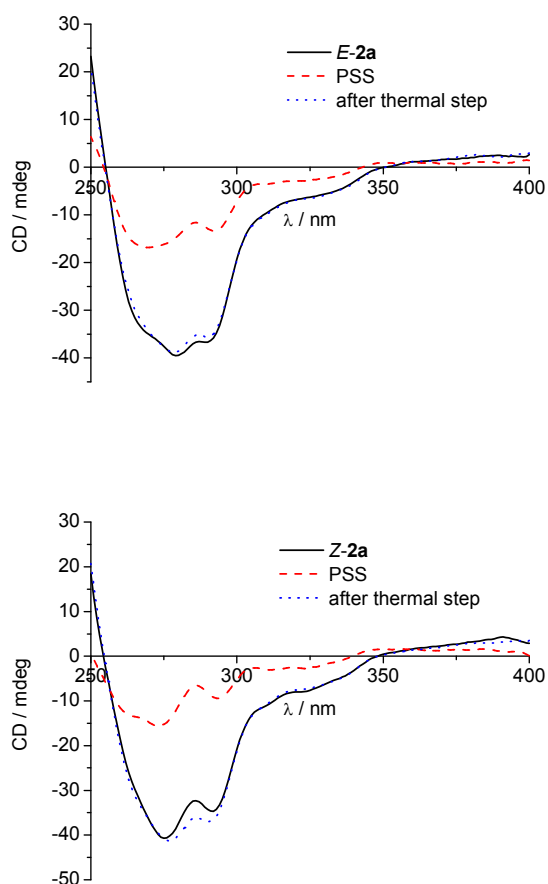


Figure S1 Left: CD spectra of *E-2a* mixed with 1 equivalent of PdTPP (solid line), the mixture of *E-2a* and *Z-2b* obtained after irradiation at 532 nm (dashed line) and the mixture of *E-2a* and *Z-2a* obtained after the thermal step. Right: CD spectra of *Z-2a* mixed with 1 equivalent of PdTPP (solid line), the mixture of *Z-2a* and *E-2b* obtained after irradiation at 532 nm (dashed line) and the mixture of *Z-2a* and *E-2a* obtained after the thermal step.

Phosphorescence lifetime measurements show quenching of the phosphorescence of PdTPP in the presence of motor **1** (Figure S2). In motor-PdTPP conjugate **12** the quenching is more efficient and the lifetime is reduced further.

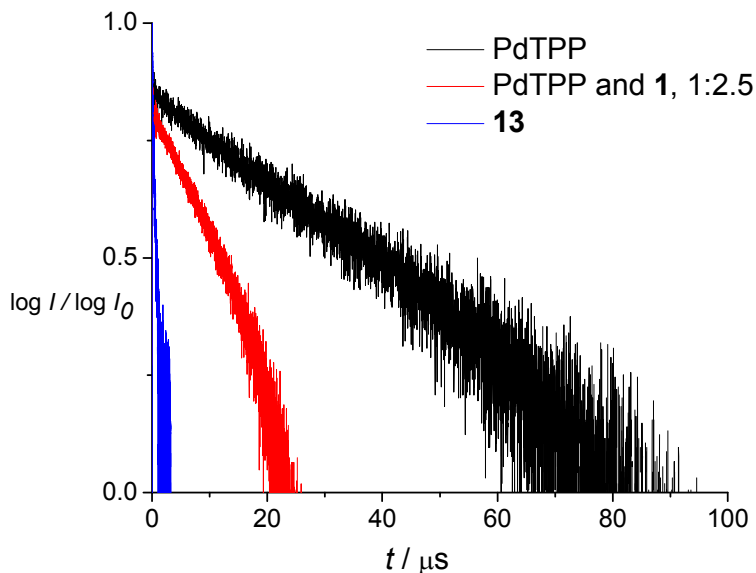


Figure S2 Room temperature phosphorescence lifetime measurements of PdTPP (black line), a 1:2.5 mixture of PdTPP and **1** (red line), and **12** (blue line) in 1,2-dichloroethane in Argon-saturated solution. Measured at 710 nm with excitation at 532 nm (6 ns, 10 Hz).

The photochemical quantum yield of the visible light-driven photoisomerization of **12** was determined using potassium reineckate ($\text{K}[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$, $\Phi = 0.29$) as a standard. A solution of **12** in 1,2-dichloroethane was irradiated and the change in CD was followed in time (Figure S3). From the comparison to the standard under the same irradiation conditions, the quantum yield was determined to be 0.11 ± 2 .

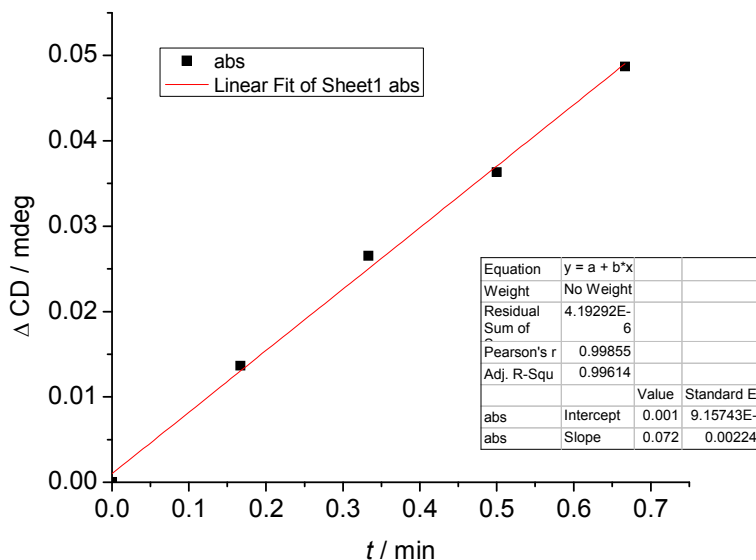


Figure S3 Changes in CD upon irradiation of a solution of **12** plotted against time.

Control experiments with free-base porphyrin

To confirm that energy transferred from a porphyrin triplet state, irradiation of PdTPP-motor **12** was repeated with the free-base analogue **13**. No changes were observed by CD spectroscopy after 10 s irradiation at 532 nm. Continued irradiation results in a decrease in the intensity across the entire spectrum (Figure S4). These changes are irreversible, even with heating, and are attributed to degradation.

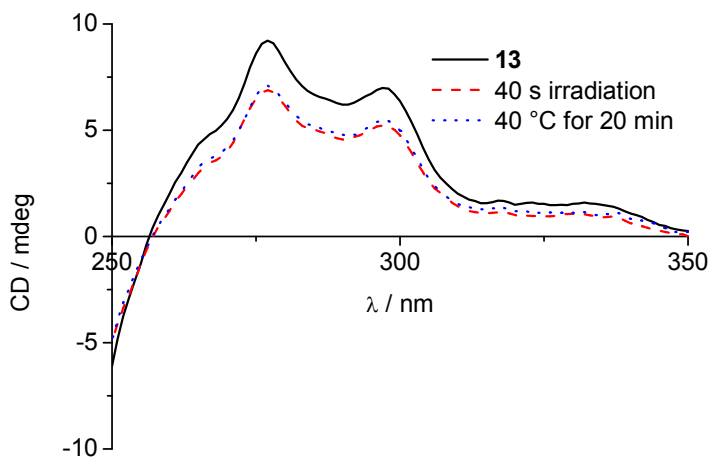


Figure S4 CD spectra of **13** before (black line) and after 40 s irradiation at 532 nm (red dashed line) and after to 40 °C for 20 min (blue dotted line).

Further evidence that energy transfer from the free-base porphyrin does not occur is obtained from the emission spectra of H₂TPP and H₂TPP-motor **13** (Figure S5). From the spectra it is apparent that there is no decrease in fluorescence quantum yield.

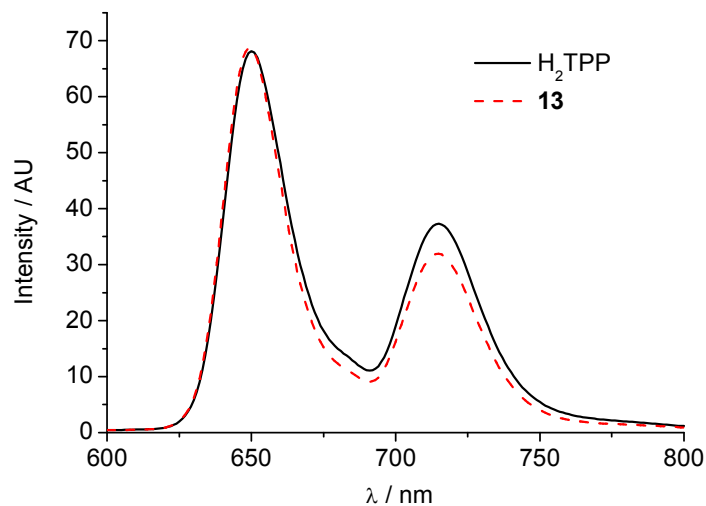
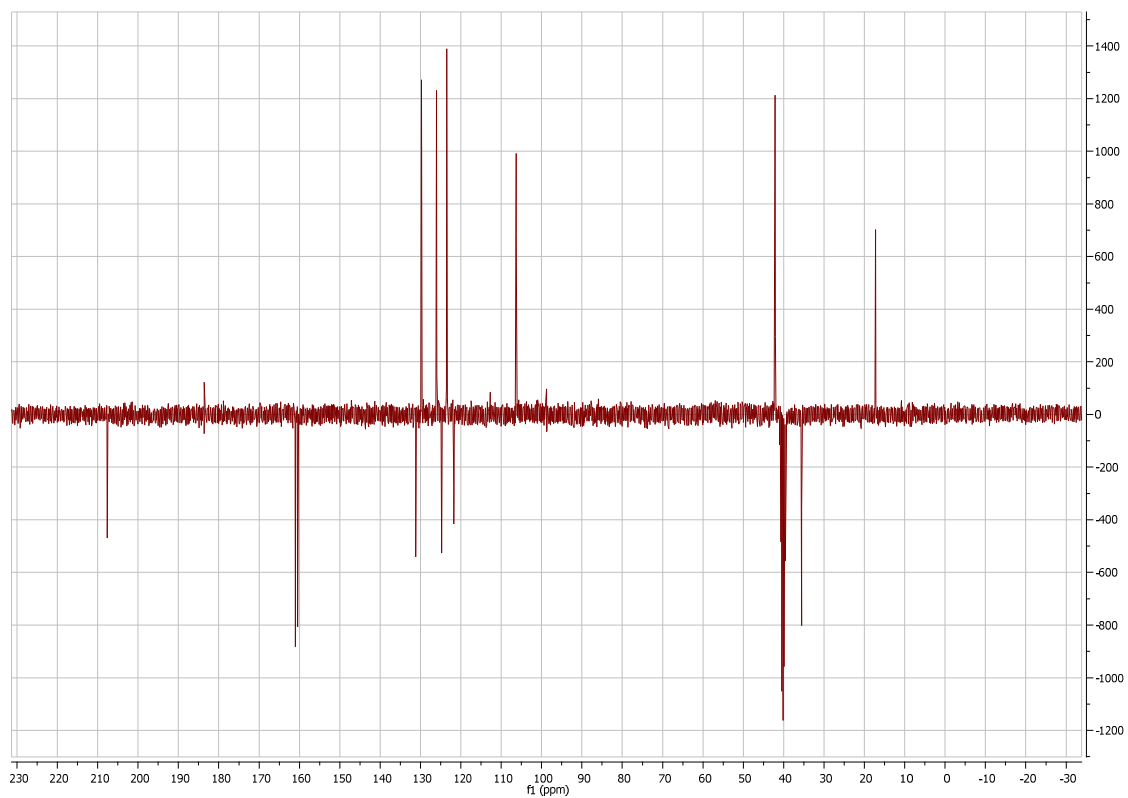
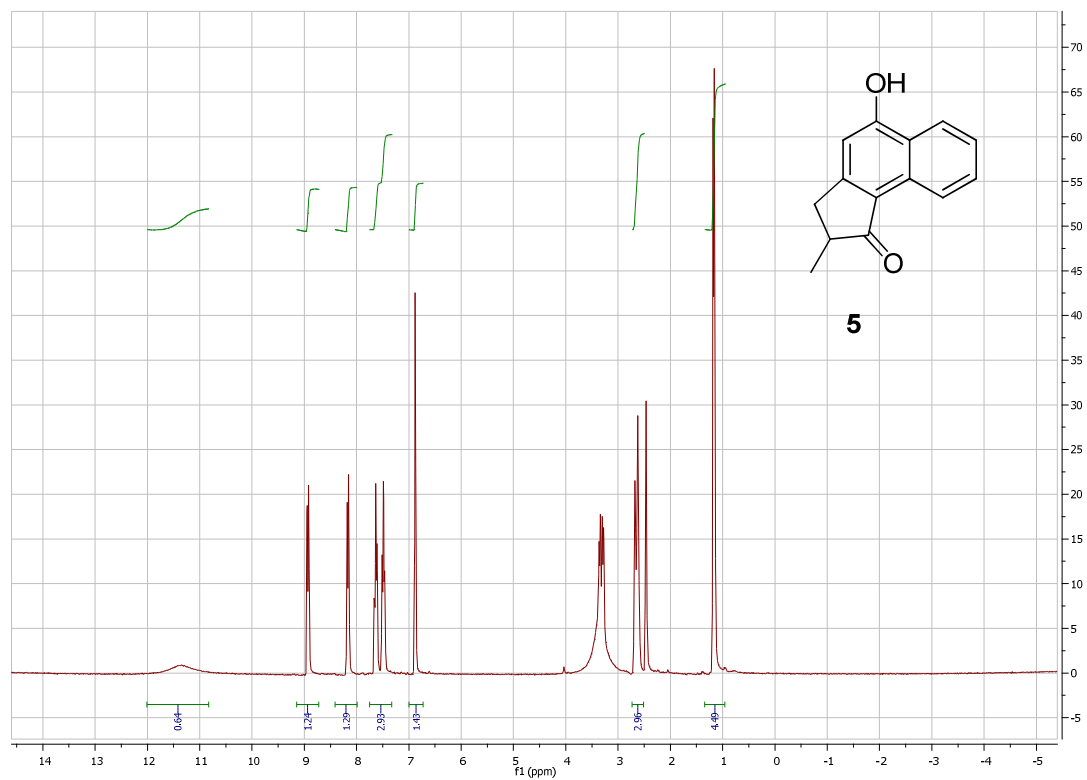


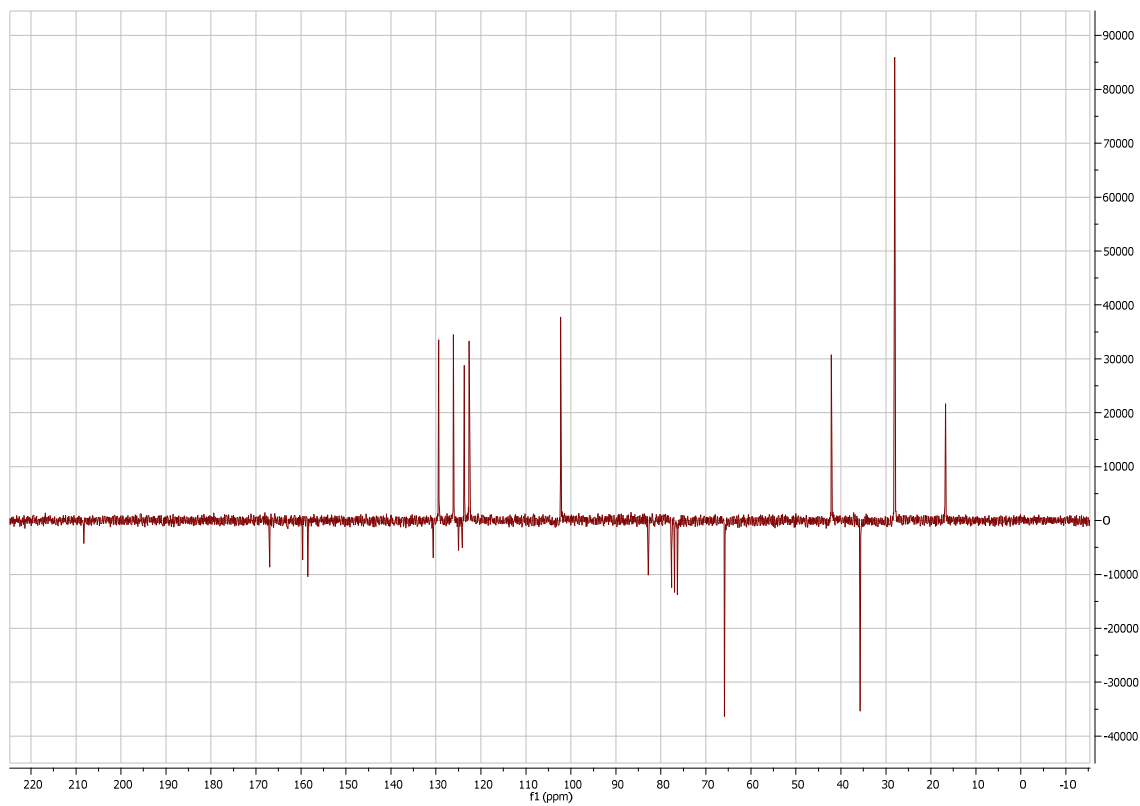
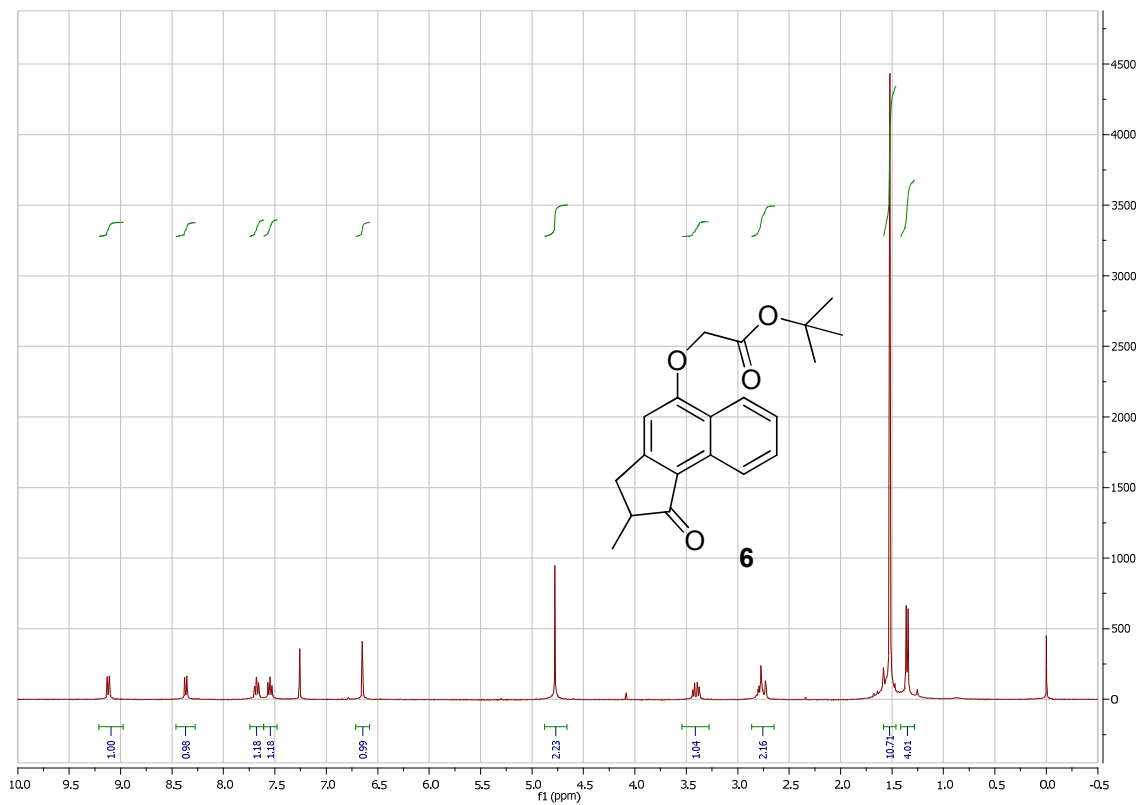
Figure S5 Emission spectra of H₂TPP (black line) and **13** (red dashed line) excited at 418 nm (chloroform solution, 1×10^{-5} M).

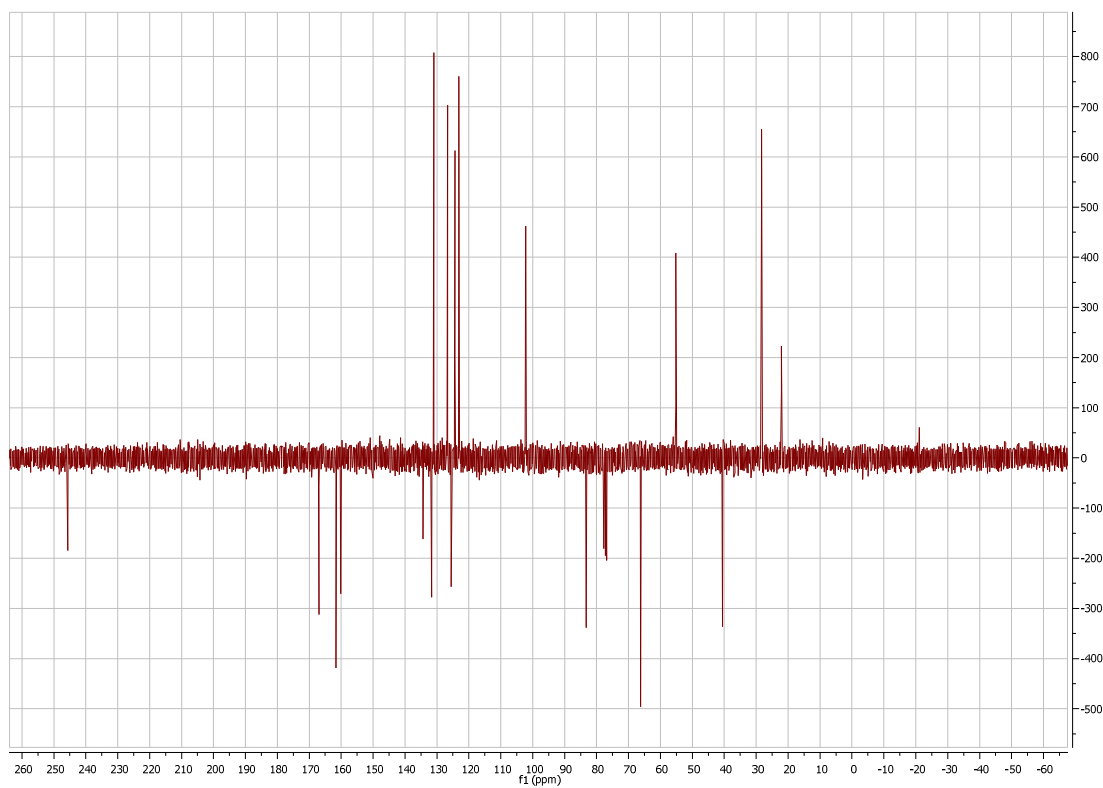
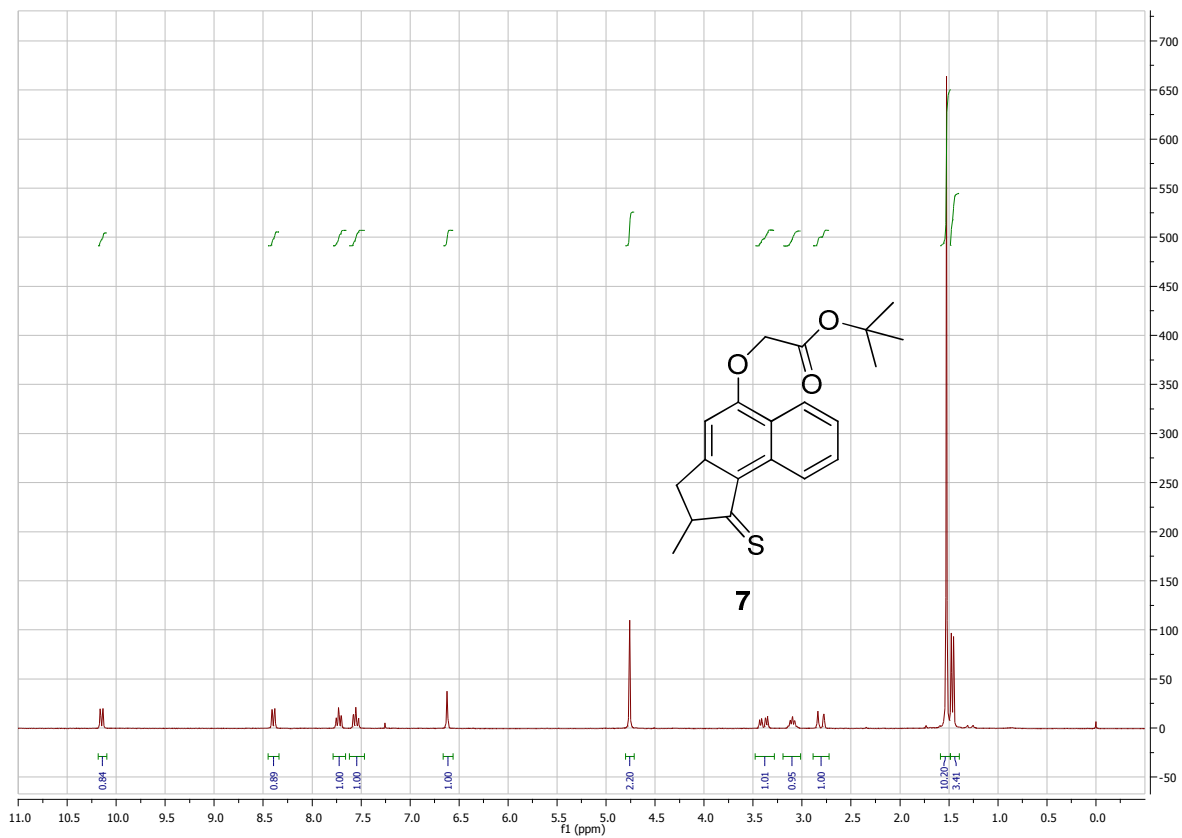
Computational details

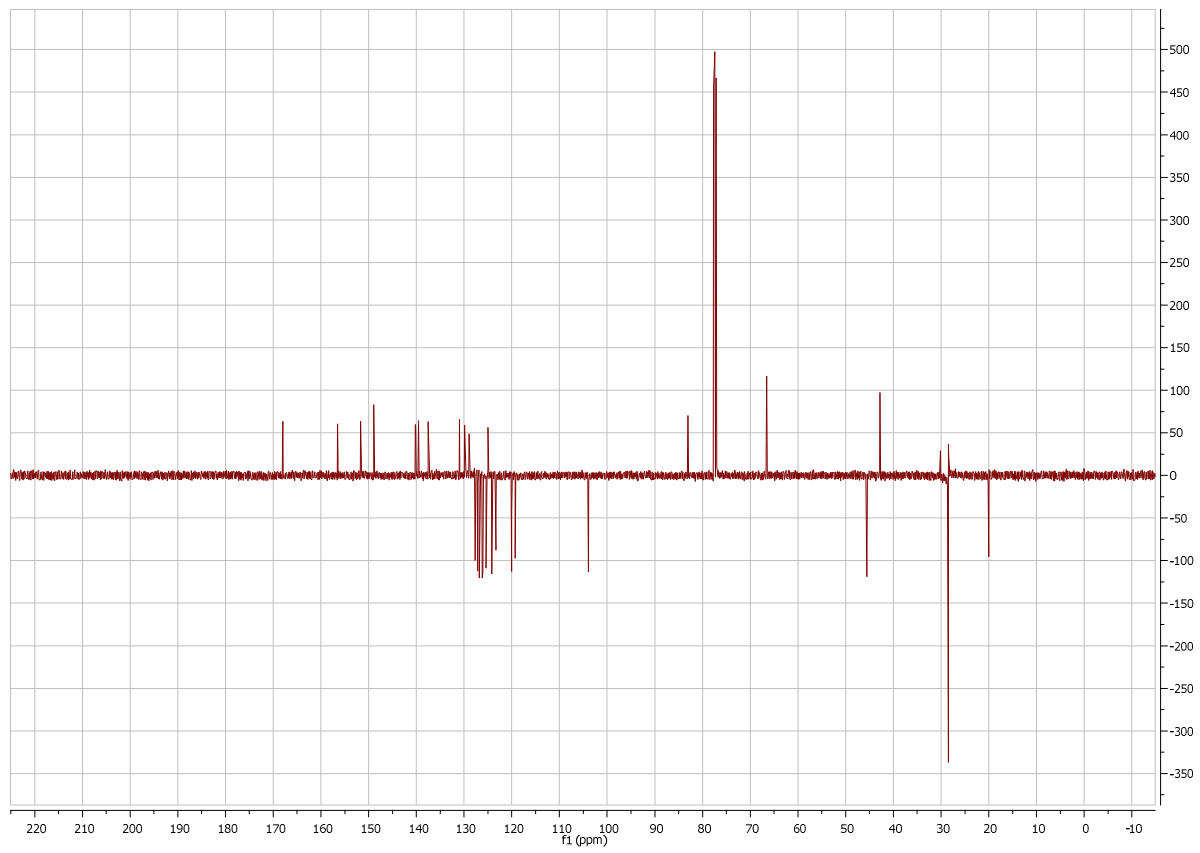
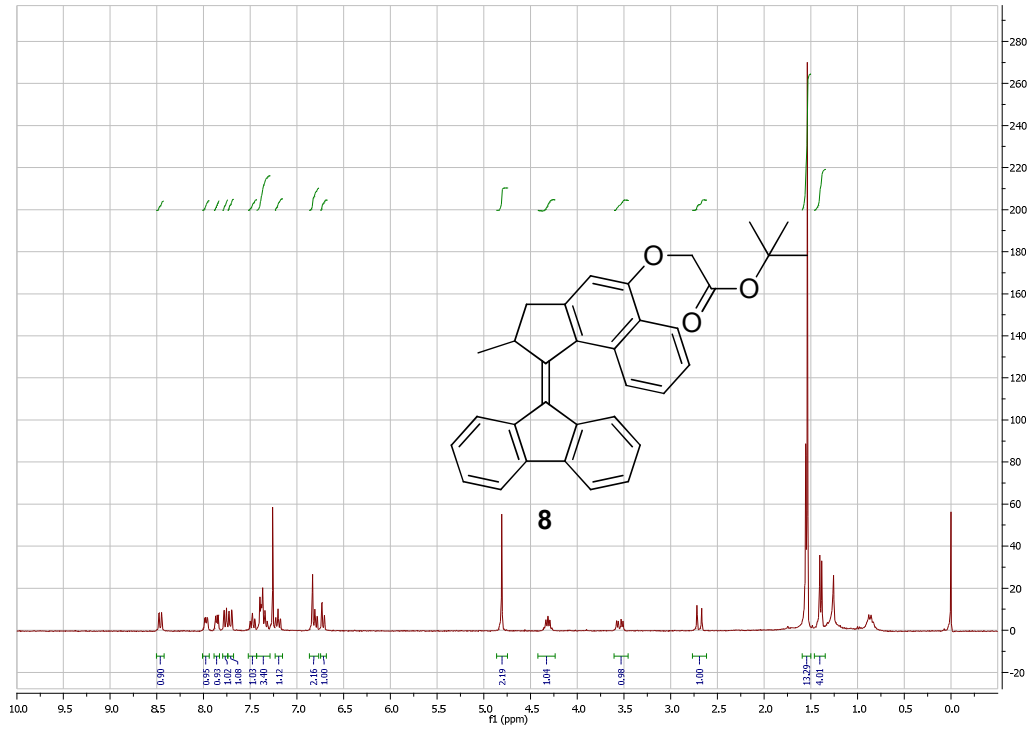
Calculations of triplet excited state energy and CD spectra were performed using the Gaussian 09 program.⁶ Geometry optimizations were performed on B3LYP/6-31G(d,p) using tight convergence criteria. Frequency analysis was performed on the optimized structures to ensure a true energy minimum was reached. CD spectra were calculated on B3LYP/6-31G++(d,p) and normalized to the highest band in the experimental spectrum.

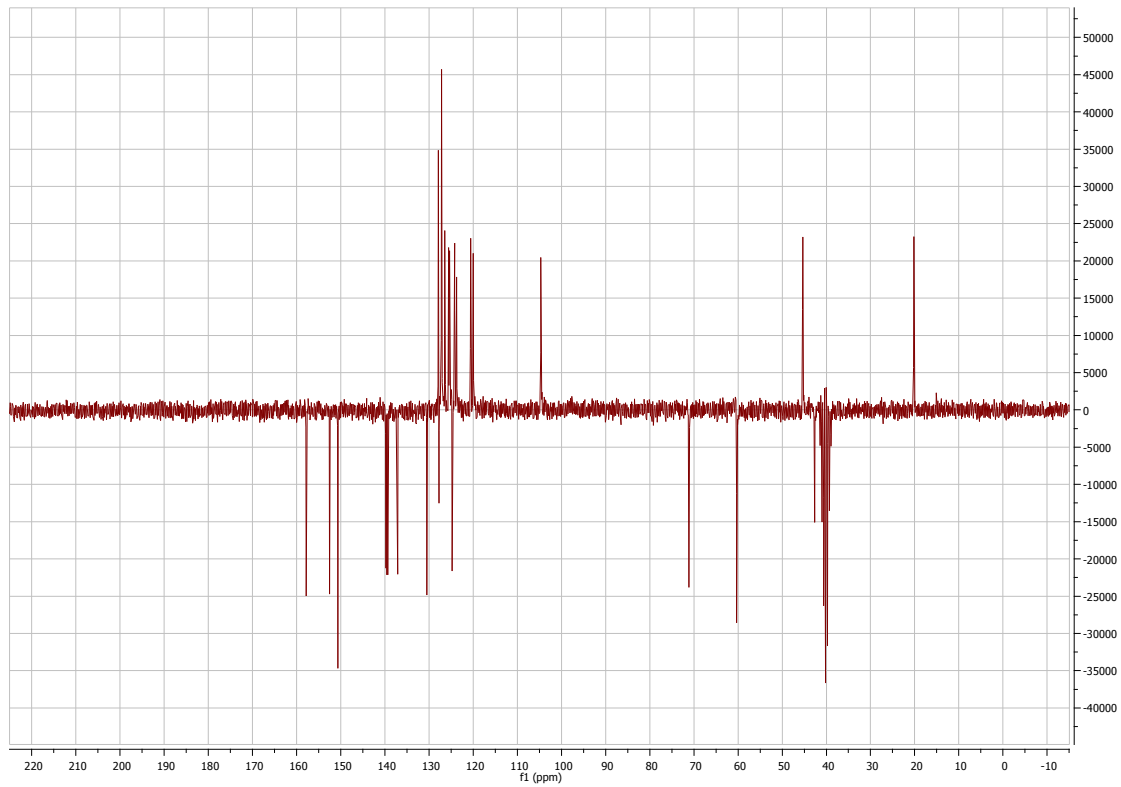
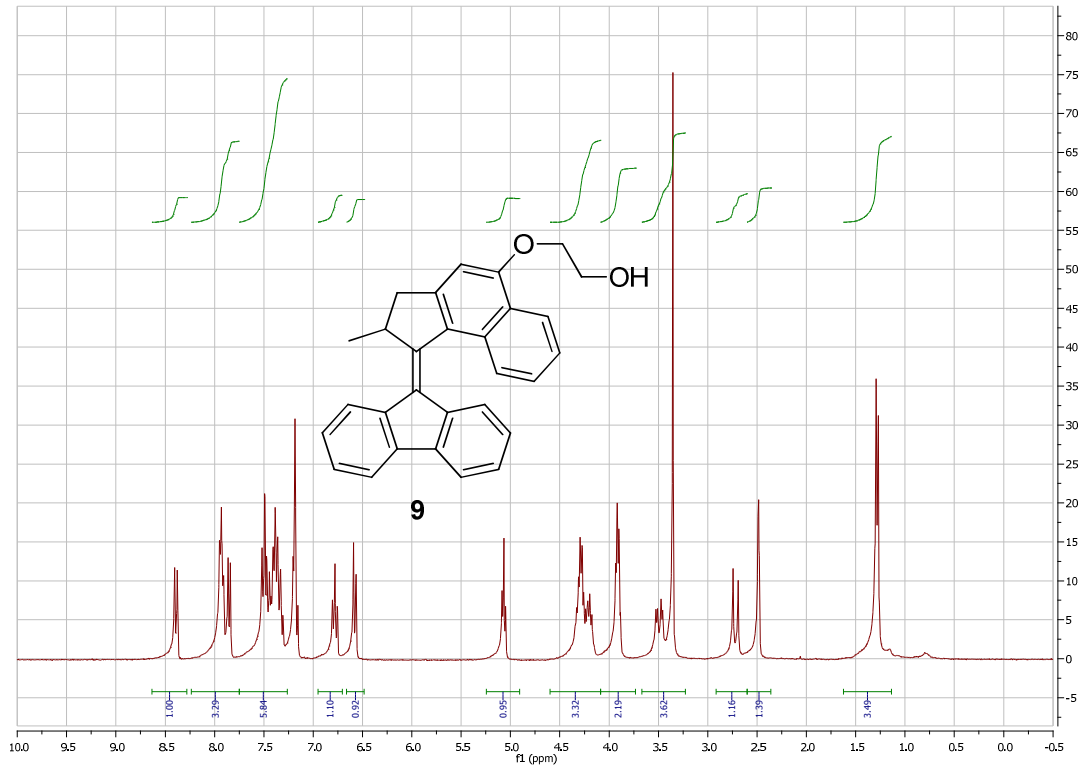
^1H and ^{13}C NMR spectra of 5-9, 12 and 13

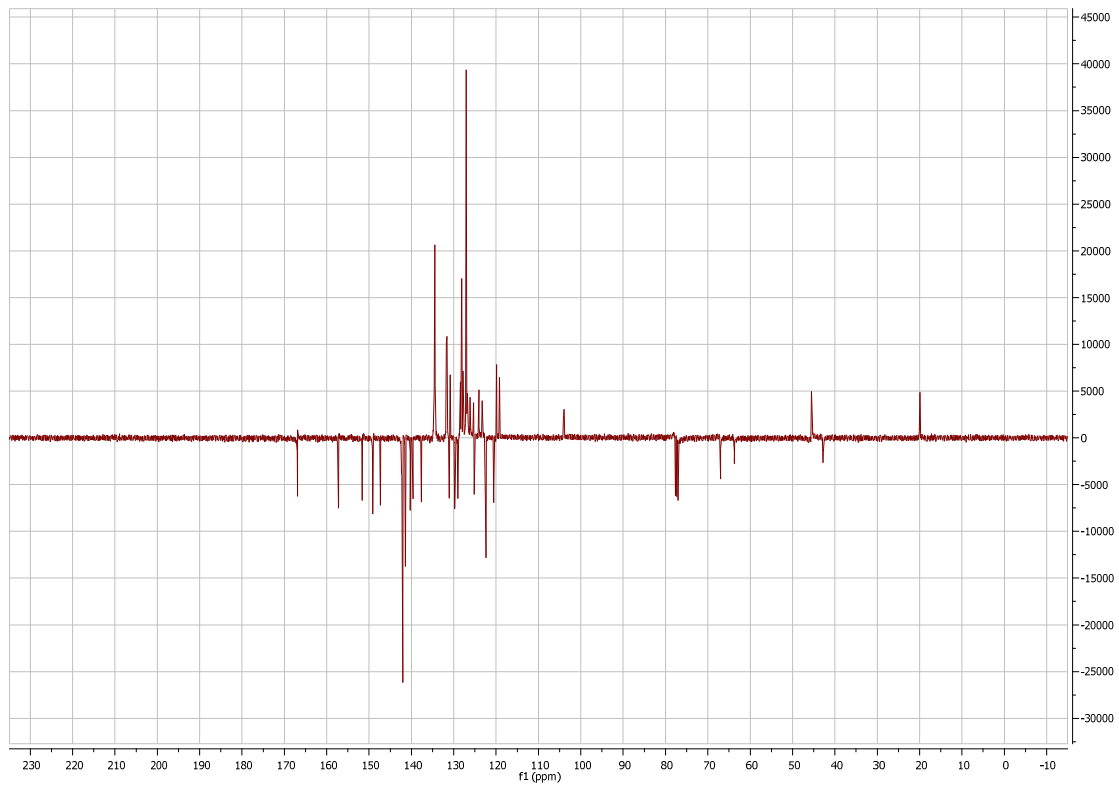
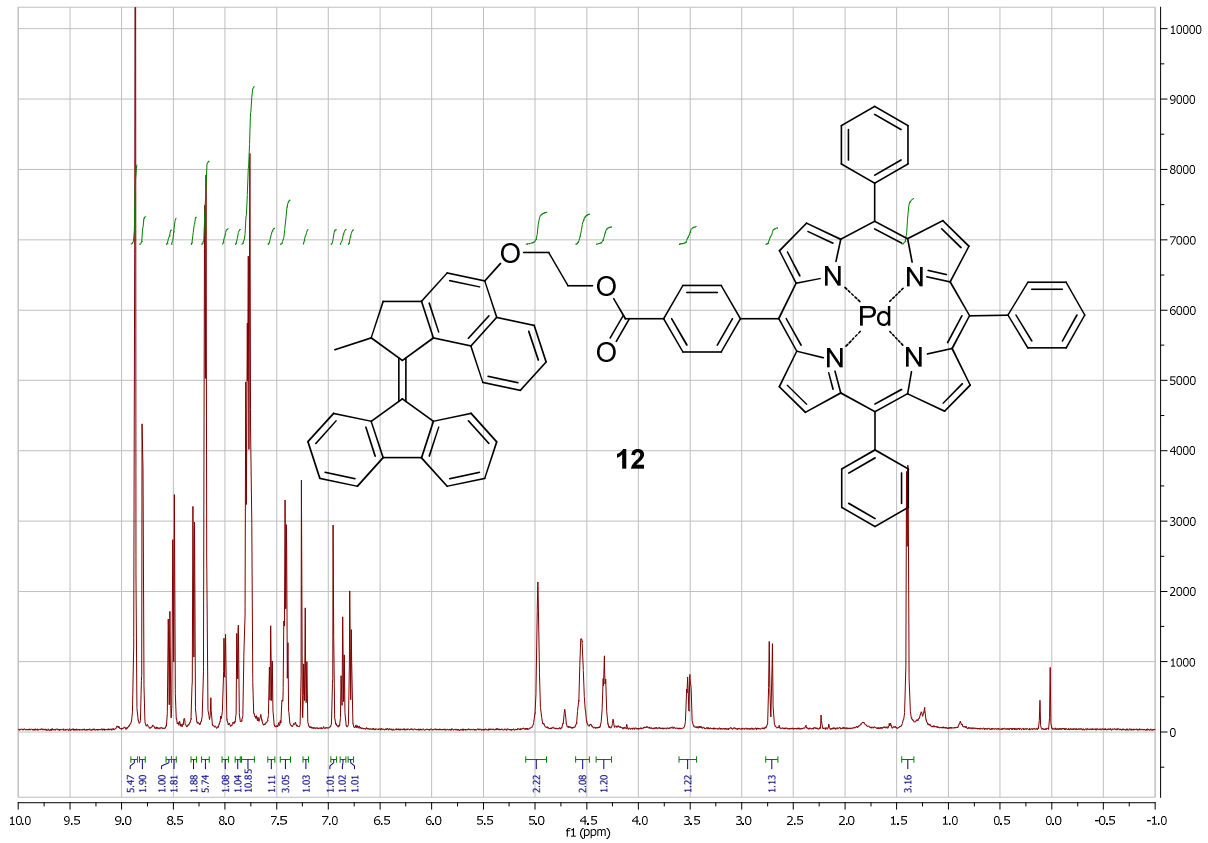


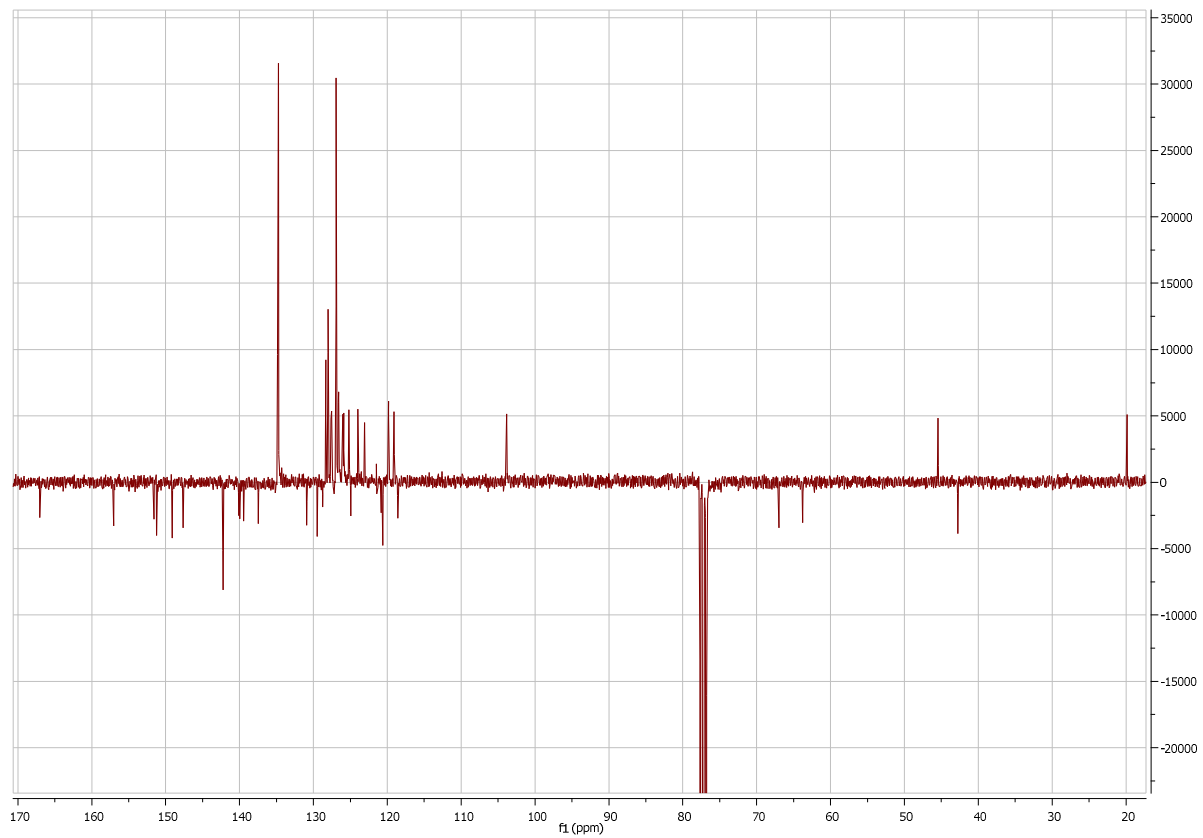
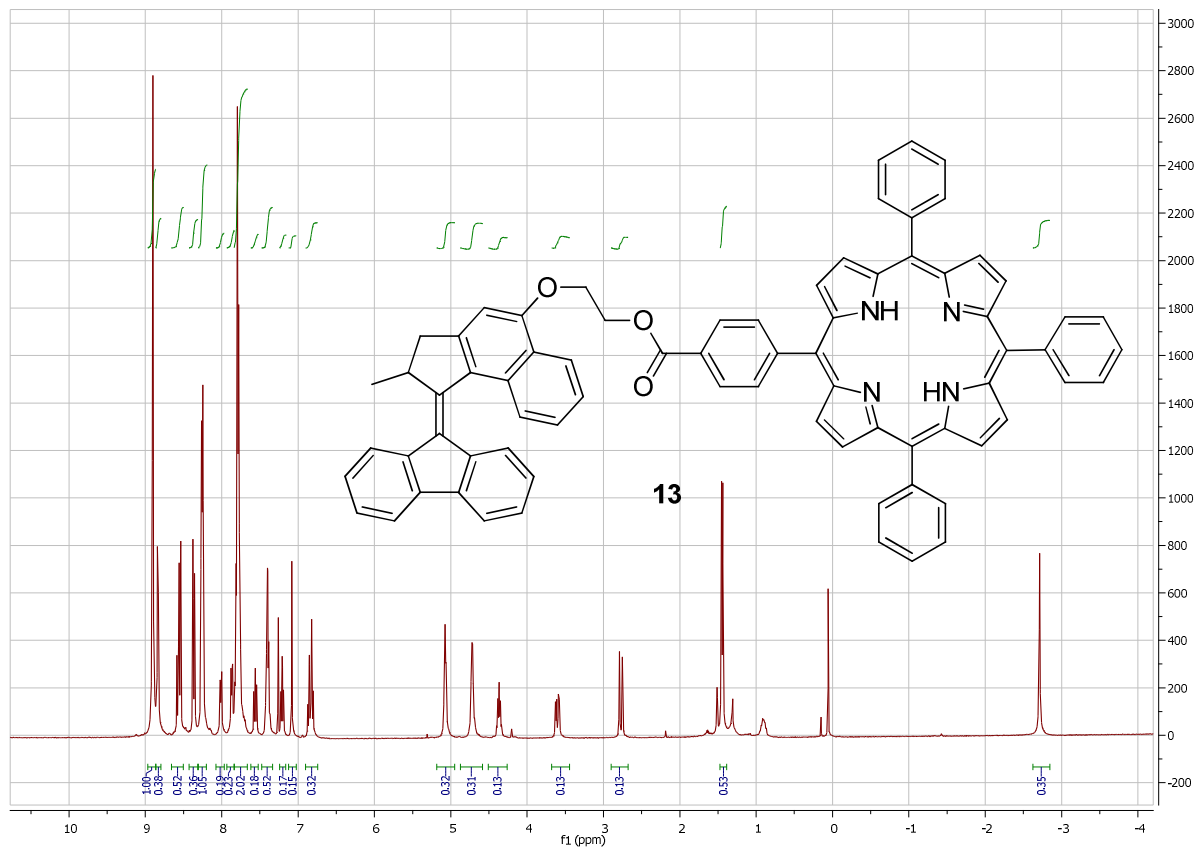












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