Supporting Information

Turn-on fluorescence switching and radical formation of a dual-functional negative photochromic dimethyldihydropyrene

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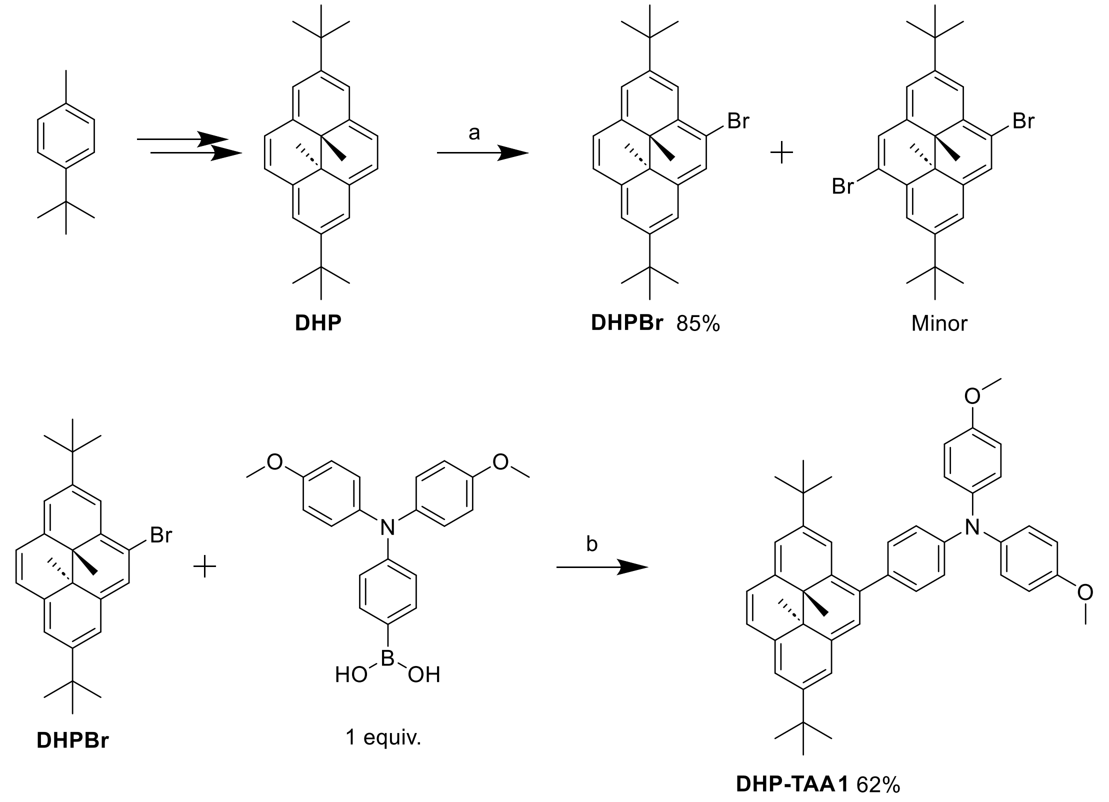
1. Procedures and Synthesis

1.1 Materials and methods

The reagents used in this study were sourced from commercial suppliers and utilized without additional purification unless specified. Standard methods were applied to purify and dry solvents, with Tetrahydrofuran (THF) freshly distilled over sodium/benzophenone and anhydrous CaH_2, respectively, before use. All other solvents used for synthesis and purification were freshly distilled prior to use, including toluene. A dry nitrogen/argon atmosphere was maintained during reactions, employing flame-dried glassware unless otherwise noted. Column chromatography utilized Merck silica gel (100-200 mesh). Thin-layer chromatography (TLC) was performed on Merck plates (TLC Silica Gel 60 F254) to monitor reactions. Yields reported pertain to the use of chromatographically and spectroscopically pure compounds. Compound structures were characterized through NMR spectroscopy, mass spectrometry, and various spectroscopic techniques. ^{1}H NMR spectra were acquired on a 400 MHz JEOL and 500 MHz Bruker spectrometer, with chemical shifts reported as δ values relative to tetramethylsilane (TMS) for ^{1}H NMR or the solvent peak. Photochemical isomerization studies were performed in toluene for all compounds at 25 °C, unless otherwise indicated. Closed to open photoisomerization reactions have been carried out under 525 nm green light, 640 nm red light, and 740 nm NIR light. 1 mL cuvette was kept under ice-cold conditions to minimize the effect of heat during irradiation. The UV-vis absorbance data were recorded subsequently with a Cary 60 UV-Vis spectrophotometer. The open-to-closed isomerization under the thermal conditions was carried out in the spectrophotometer itself using a Peltier heating system accessory with an accuracy of ± 1 °C. Photoisomerization followed by fluorescence spectroscopy, before and after the isomerization, was studied in quartz fluorescence cuvettes (Starna). The photoisomerization conditions are the same as described for the absorption studies. Fluorescence measurements were carried out with a Horiba Duetta (Xe-150 W, 200−1100 nm) and Jasco Fluoromax spectrometer. Single crystal X-ray diffraction (SCXRD) data were recorded using a Rigaku XtaLAB Synergy Dualflex four-circle diffractometer with a HyPix3000 detector. X-band electron paramagnetic resonance (EPR) spectra were recorded using an EMX MICRO X Bruker EPR instrument.

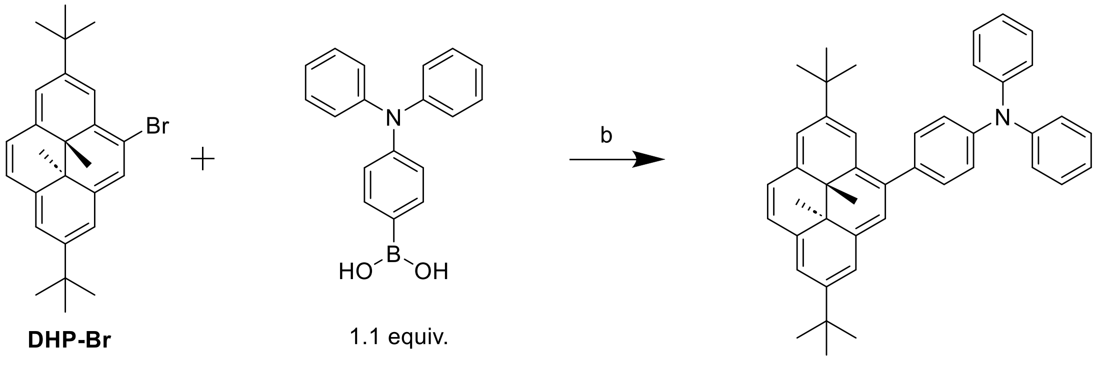
1.2 Synthesis

Synthetic scheme:



Scheme S1: (a) NBS (1 eq), CH_2Cl_2, 0 °C, 2 h; **(b)** $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (1.2 eq), toluene: H_2O (4:1), reflux, N_2, 24 h.

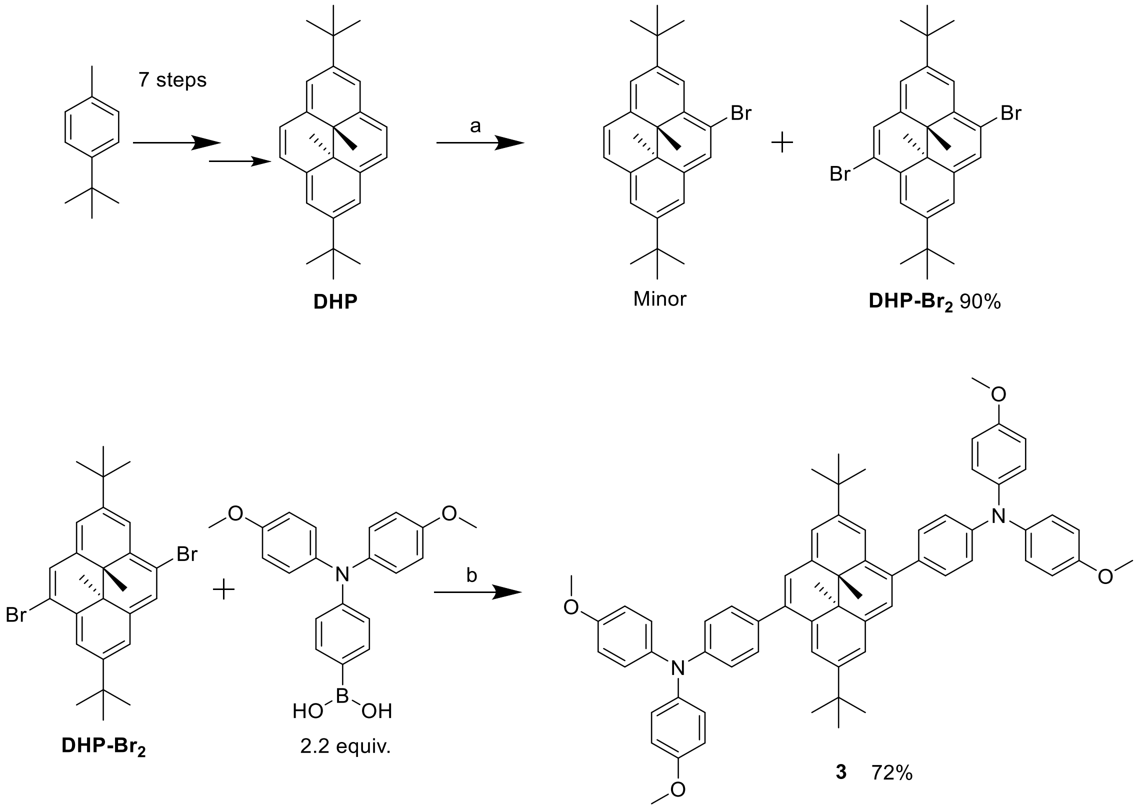
The unsubstituted DHP was synthesized according to the literature report.[1] The purity of the synthesized compound was confirmed with the ^{1}H NMR and ^{13}C NMR data, which were consistent with the reported values. Bromination of the DHP was done following the reported procedure to afford the mono-substituted DHP-Br**;** the ^{1}H NMR and ^{13}C data were consistent with the literature.[2] **4-((3a1R,5a1R)-2,7-di-tert-butyl-3a1,5a1-dimethyl-3a1,5a1-dihydropyren-4-yl)-N,N-bis(4-methoxyphenyl)aniline (1).** (4-(bis(4 methoxyphenyl)amino)phenyl)boronic acid (91 mg, 0.260 mmol) was added to a mixture of DHP-Br (100 mg, 0.236 mmol), K_2CO_3 (36 mg, 0.260 mmol), and 4 ml toluene, 1 ml water. The mixture was purged with argon for 30 minutes before the addition of $Pd(PPh_3)_4$ (15 mg, 0.013 mmol). The mixture was stirred for 24 h at 80 °C. After cooling to the ambient temperature, the mixture was filtered through celite. The organic compound was extracted with dichloromethane, and washed with water (2 × 15 mL), brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4. After the removal of the volatiles in rotavapor, the residue was purified by column chromatography (silica gel, eluent: 5% ethyl acetate in hexane) to give 95 mg of pure compound **1** (yield 62%); **^{1}H NMR**(400 MHz, benzene-d$_6$) δ = 9.19 (s, 1H), 8.69 – 8.60 (m, 4H), 8.49 (d, *J*=1.3, 2H), 7.90 (d, *J*=8.6, 2H), 7.47 (d, *J*=8.6, 2H), 7.28 (d, *J*=8.9, 4H), 6.81 (d, *J*=9.0, 4H), 3.33 (s, 6H), 1.64 (s, 9H), 1.59 (s, 9H), -3.45 (d, *J*=12.4, 6H). **^{13}C{^{1}H} NMR** (125 MHz, C6D6) δ = 156.25, 148.14, 145.63, 145.26, 141.38, 137.17, 136.90, 136.68, 135.34, 135.31, 133.50, 132.02, 126.73, 125.48, 123.23, 122.71, 121.18, 120.99, 120.79, 120.60, 120.52, 114.92, 54.70, 35.85, 35.67, 34.08, 31.69, 31.64, 30.52, 30.15, 26.88. **HRMS (ESI)**: *m/z* (Calc): $C_{46}H_{49}NO_2$ [M]$^+$ 647.3763; found: 647.3729



2 75%

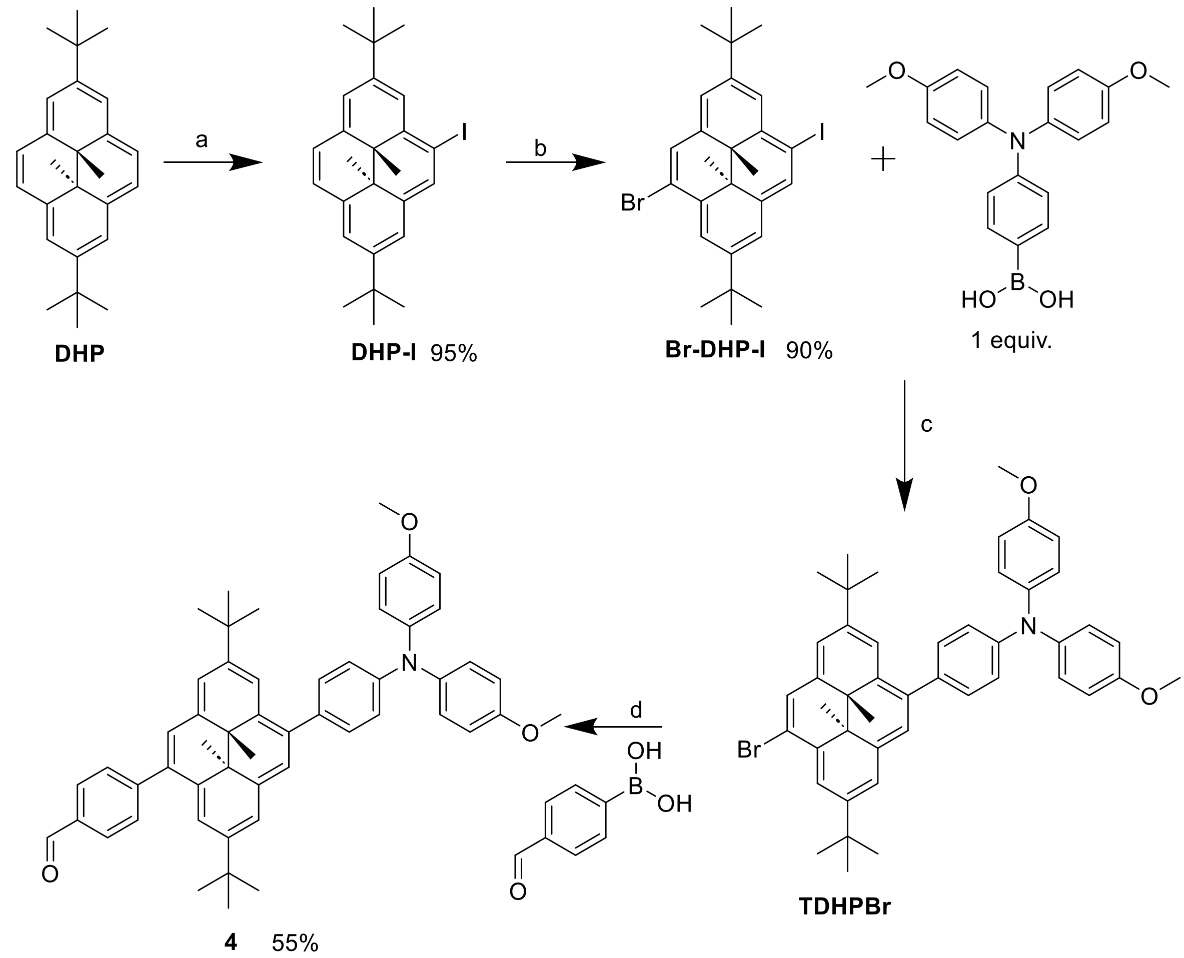
Scheme S2: (a) Pd(PPh$_3$)$_4$ (10 mol%), K_2CO_3 (1.2 eq), toluene : H_2O (3:1), reflux, N_2, 24 h.

4-((3a1R,5a1R)-2,7-di-tert-butyl-3a1,5a1-dimethyl-3a1,5a1-dihydropyren-4-yl)-N,N-diphenylaniline (2). (4-(diphenylamino)phenyl)boronic acid (75 mg, 0.260 mmol) was added to a mixture of DHP-Br (100 mg, 0.236 mmol), K_2CO_3 (36 mg, 0.260 mmol) in 3 ml toluene, 1 ml water, and the mixture was purged with argon for 30 minutes. Then, Pd(PPh$_3$)$_4$ (15 mg, 0.013 mmol) was added, and the reaction mixture was purged for an additional 10 minutes. The mixture was stirred for 24 h at 80 °C. After cooling to the ambient temperature, the mixture was filtered through celite. The organic compound was extracted with dichloromethane, and washed with water (2 × 15 mL), brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4. After the removal of the volatiles in rotavapor, the residue was purified by column chromatography (silica gel, eluent: 5% ethyl acetate in hexane) to give 104 mg of pure compound **2** (yield 62%). **^{1}H NMR**(400 MHz, benzene-d$_6$) δ 9.04 (d, *J* = 1.3 Hz, 1H), 8.60 – 8.52 (m, 4H), 8.43 (s, 2H), 7.80 – 7.72 (m, 2H), 7.39 – 7.31 (m, 2H), 7.25 (s, 1H), 7.12 – 7.02 (m, 4H), 6.88 – 6.79 (m, 1H), 1.58 (s, 9H), 1.51 (s, 9H), -3.54 (d, *J* = 9.6 Hz, 6H).**^{13}C{^{1}H} NMR** (101 MHz, benzene-d6) δ = 148.55, 147.40, 146.07, 145.75, 137.67, 137.57, 137.26, 136.96, 135.30, 133.78, 132.54, 129.74, 129.67, 128.30, 128.06, 127.82, 125.73, 124.86, 124.26, 123.66, 123.24, 121.60, 121.45, 121.10, 120.68, 36.21, 36.04, 34.97, 32.05, 31.97, 30.84, 30.45, 25.64. **HRMS(ESI)**: m/z (Calc): $C_{44}H_{55}N$ $[M]^+$ 587.3552; found: 587.3492



Scheme S3: (a) NBS (1 eq), CH_2Cl_2, 0 °C, 2 h; **(b)**$Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (1.2 eq), toluene:H_2O (3:1), reflux, N_2, 24 h.

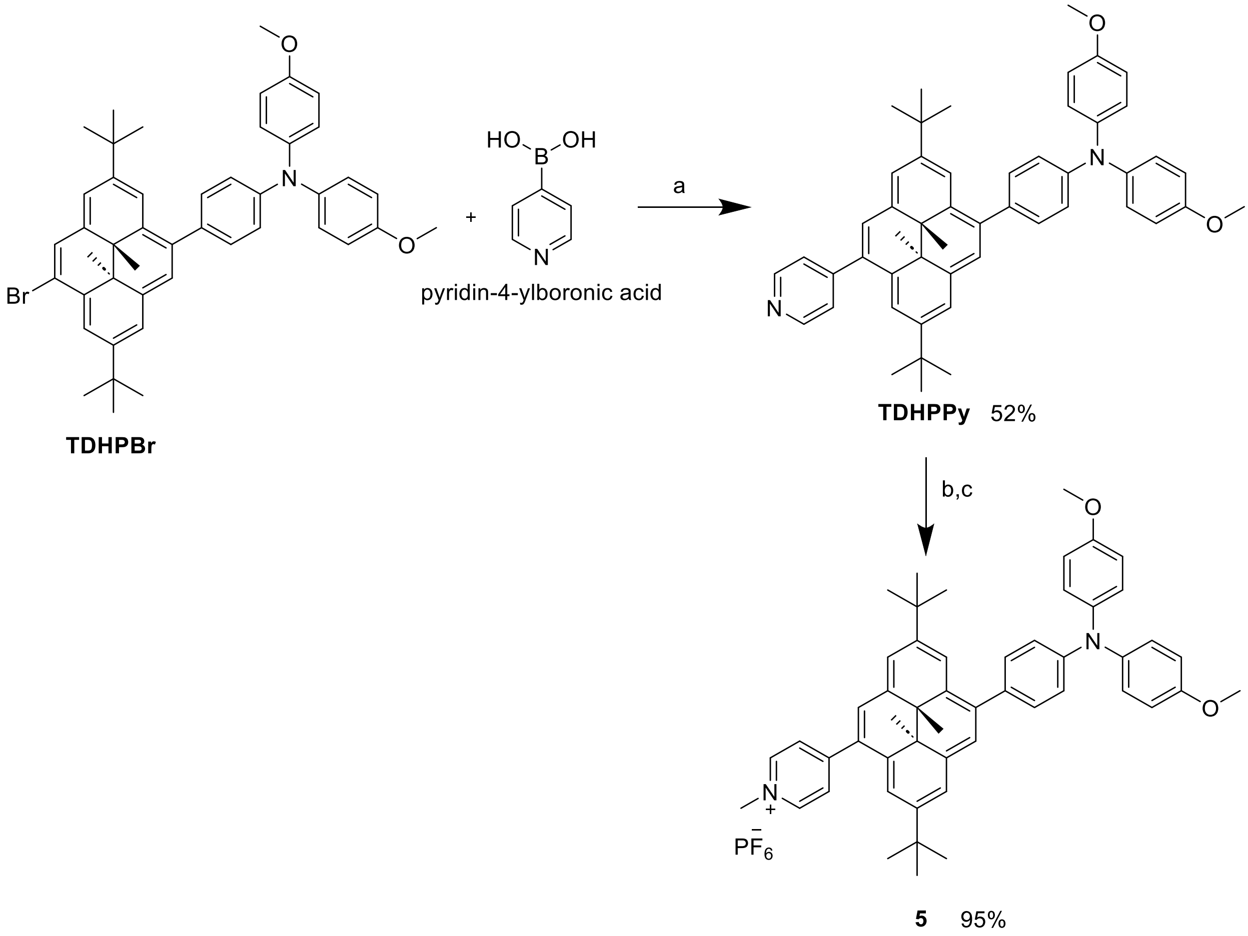
4,4'-(2,7-di-tert-butyl-3a1,5a1-dimethyl-3a1,5a1-dihydropyrene-4,9-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (3). (4-(bis(4 methoxyphenyl)amino)phenyl)boronic acid (152 mg, 0.438 mmol) was added to a mixture of DHP-Br_2 (100 mg, 0.199 mmol), K_2CO_3 (36 mg, 0.260 mmol) in 3 ml toluene, 1 ml water, and the mixture was purged with argon for 30 minutes. Then, $Pd(PPh_3)_4$ (23 mg, 0.019 mmol) was added, and the reaction mixture was purged for an additional 10 minutes. The mixture was stirred for 24 h at 80 °C. After cooling to the ambient temperature, the mixture was filtered through celite. The organic compound was extracted with dichloromethane and washed with water (2 × 15 mL), brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4. After the removal of the volatiles in rotavapor, the residue was purified by column chromatography (silica gel, eluent: 5% ethyl acetate in hexane) to give 136 mg of pure compound **3** (yield 72%). **^{1}H NMR**(400 MHz, benzene-d_6) δ = 9.18 (s, 2H), 8.67 (s, 2H), 8.62 (s, 2H), 7.93 (d, *J*=8.6, 4H), 7.49 (d, *J*=8.7, 4H), 7.29 (d, *J*=9.0, 8H), 6.81 (d, *J*=9.0, 8H), 3.33 (s, 12H), 1.60 (s, 18H), -3.26 (s, 6H).**^{13}C{^{1}H} NMR** (100 MHz, benzene-d6) δ = 156.60, 148.47, 145.96, 141.76, 137.39, 135.66, 135.26, 133.83, 132.36, 127.09, 126.05, 121.66, 121.21, 120.49, 115.28, 55.05, 36.21, 31.99, 31.10. **HRMS (ESI):** *m/z* (Calc): $C_{66}H_{66}N_2O_4$ $[M]^+$ 950.5023; found: 950.4910



Scheme S4: (a) Ag(collidine)$_2PF_6$, I_2, Dry CH_2Cl_2, (b) NBS (1 equiv.), Dry CH_2Cl_2, 0 °C, 2 h; (c)Pd$(PPh_3)_4$ (10 mol%), K_2CO_3 (1.2 eq), toluene : H_2O (3:1), reflux, N_2, 24 h. (d)Pd$(PPh_3)_4$ (10 mol%), K_2CO_3 (1.2 eq), toluene : H_2O (3:1), reflux, N_2, 24 h.

Br-DHP-I was synthesized following the reported procedure, and the purity of the sample was verified by ^{1}H NMR spectroscopy.[3]

4-((3a1S,5a1R)-9-(4-(bis(4-methoxyphenyl)amino)phenyl)-2,7-di-tert-butyl-3a1,5a1-dimethyl-3a1,5a1-dihydropyren-4-yl)benzaldehyde (4). By following the same procedure as stated in the synthesis of derivative **1**, we go **TDHPBr** from **Br-DHP-I** and without further purification, and repeated the same procedure with **TDHPBr** (100 mg, 0.137 mmol) and 4-formylphenyl)boronic acid (23 mg, 0152 mmol) to get the 75 mg of pure compound **4** (yield 55% with respect to Br-DHP-I); ^{1}H NMR (400 MHz, *benzene-d*$_6$) δ 9.85 (s, 1H), 9.15 (d, *J* = 1.3 Hz, 1H), 8.79 (d, *J* = 1.3 Hz, 1H), 8.60 (s, 1H), 8.54 (dd, *J* = 8.6, 1.3 Hz, 2H), 8.33 (s, 1H), 7.87 – 7.77 (m, 6H), 7.45 – 7.42 (m, 2H), 7.25 – 7.22 (m, 4H), 6.77 – 6.74 (m, 4H), 3.27 (s, 6H), 1.54 (s, 9H), 1.48 (s, 9H), -3.39 (d, *J* = 6.5 Hz, 6H). **^{13}C{^{1}H} NMR** (101 MHz, benzene-d6) δ 191.25, 170.50, 158.25, 156.72, 153.93, 149.11, 146.85, 146.35, 141.64, 139.97, 138.84, 137.69, 135.70, 133.99, 133.73, 132.33, 131.96, 129.75, 128.30, 128.06, 127.82, 127.20, 126.30, 125.43, 122.28, 121.35, 121.03, 119.59, 116.50, 115.33, 112.47, 104.63, 55.07, 36.24, 31.95, 31.85, 31.05, 30.92, 30.22, 1.41. **HRMS (ESI)**: *m/z* (Calc): $C_{66}H_{66}N_2O_4$ [M]$^+$ 751.4025; found: 751.4030



Scheme S5: (a) $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (1.2 eq), toluene : H_2O (3:1), reflux, N_2, 24 h, (b) MeI (1mL, excess), CH_2Cl_2, r.t., 12 h; (c) aq. KPF_6, MeOH

4-((3a1R,5a1S)-2,7-di-tert-butyl-3a1,5a1-dimethyl-9-(pyridin-4-yl)-3a1,5a1-dihydropyren-4-yl)-N,N-bis(4-methoxyphenyl)aniline (TDHPPy). Similarly, TDHPPy was synthesized using the same procedure as that for compound **4**. **TDHPBr** (100 mg, 0.137 mmol) and pyridin-4-ylboronic acid (19 mg, 0.151 mmol) to get the 68 mg of pure compound **TDHPPy** (yield 52% with respect to Br-DHP-I)**;** ^{1}H NMR (400 MHz, *benzene-d*$_6$) δ 9.14 (s, 1H), 8.85 – 8.76 (m, 1H), 8.59 – 8.50 (m, 1H), 7.89 – 7.80 (m, 1H), 7.50 (td, *J* = 3.6, 1.6 Hz, 1H), 7.46 – 7.36 (m, 1H), 7.23 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.09 (dt, *J* = 3.9, 1.9 Hz, 2H), 6.79 – 6.71 (m, 1H), 3.30 – 3.21 (m, 2H), 1.54 (s, 1H), 1.47 (s, 1H), -3.43 (d, *J* = 8.3 Hz, 2H). **^{13}C{^{1}H} NMR**

(101 MHz, *benzene-d*$_6$) δ = 156.42, 150.53, 150.10, 150.00, 148.44, 146.70, 146.02, 141.31, 137.40, 136.65, 134.83, 133.68, 133.12, 132.03, 131.74, 128.89, 128.02, 128.00, 127.78, 127.76, 127.74, 127.54, 127.52, 127.50, 126.93, 126.90, 125.99, 125.84, 124.77, 122.06, 121.54, 121.29, 121.13, 120.70, 118.92, 115.02, 54.77, 35.93, 35.91, 31.70, 31.65, 31.53, 31.46, 30.67, 30.54, 29.91. **HRMS (ESI):** *m/z* (Calc): $C_{51}H_{52}N_2O_2$ $[M+H]^+$ 725.4102; found: 725.4111

4-((3a1S,5a1R)-9-(4-(bis(4-methoxyphenyl)amino)phenyl)-2,7-di-tert-butyl-3a1,5a1-dimethyl-3a1,5a1-dihydropyren-4-yl)-1-methylpyridin-1-ium (5). A solution of **TDHPPy** (65 mg, 0.089 mmol) in CH_2Cl_2 (5 mL) was prepared. Methyl iodide (1 mL, excess) was added to the previous solution, and the resulting mixture was allowed to stir for 12 h at room temperature. The solvent was then evaporated under vacuo and the residue was washed with diethyl ether (3 × 10 mL). The solid was then dried under reduced pressure to give the targeted product as a brown powder (yield 95%, 112 mg). followed by an anion exchange using a saturated aqueous solution of KPF_6 (1 mL) in methanol (1 mL). **^{1}H NMR** (400 MHz, ACETONITRILE-*D*$_3$) δ 8.84 (d, *J* = 1.2 Hz, 1H), 8.74 (t, *J* = 9.0 Hz, 4H), 8.69 (s, 1H), 8.60 (d, *J* = 4.9 Hz, 2H), 8.43 (d, *J* = 6.6 Hz, 2H), 7.69 – 7.66 (m, 2H), 7.22 – 7.19 (m, 4H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.98 – 6.95 (m, 4H), 4.39 (s, 3H), 3.81 (s, 6H), 1.64 (s, 9H), 1.61 (s, 9H), -3.68 (d, *J* = 5.2 Hz, 6H).**^{13}C{^{1}H} NMR** (101 MHz, ACETONITRILE-*D*$_3$) δ 159.63, 157.40, 150.37, 149.43, 147.85, 145.37, 141.58, 139.70, 138.06, 137.33, 134.73, 134.46, 134.16, 132.46, 129.93, 128.07, 127.61, 126.49, 124.58, 124.26, 123.25, 122.81, 120.24, 115.80, 56.08, 48.32, 37.01, 36.71, 31.83, 31.72, 31.62, 30.85, 15.43, 15.36. **HRMS (ESI):** *m/z* (Calc): $C_{52}H_{55}N_2O_2^+$ $[M]^+$ 739.4258; found: 739.4252

1.3 ^{1}H and ^{13}C NMR of the synthesized compounds:

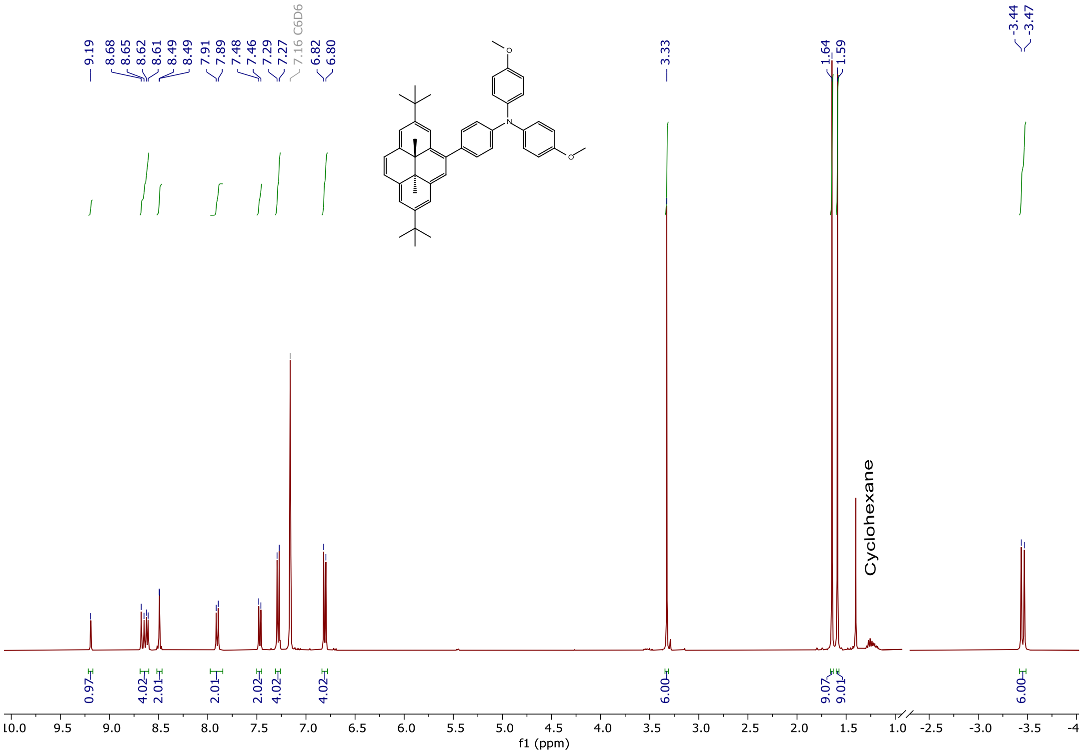


Figure S1: ^{1}H NMR spectrum of **1** in *benzene-d*$_6$.

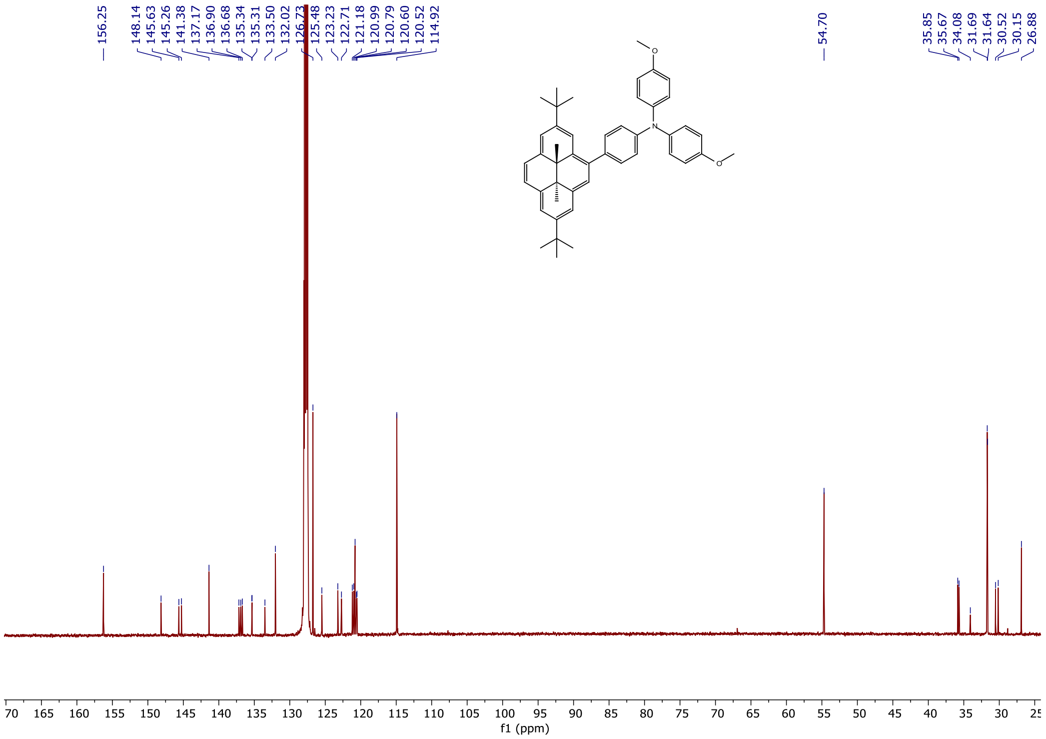


Figure S2: ^{13}C NMR spectrum of **1** in *benzene-d*$_6$.

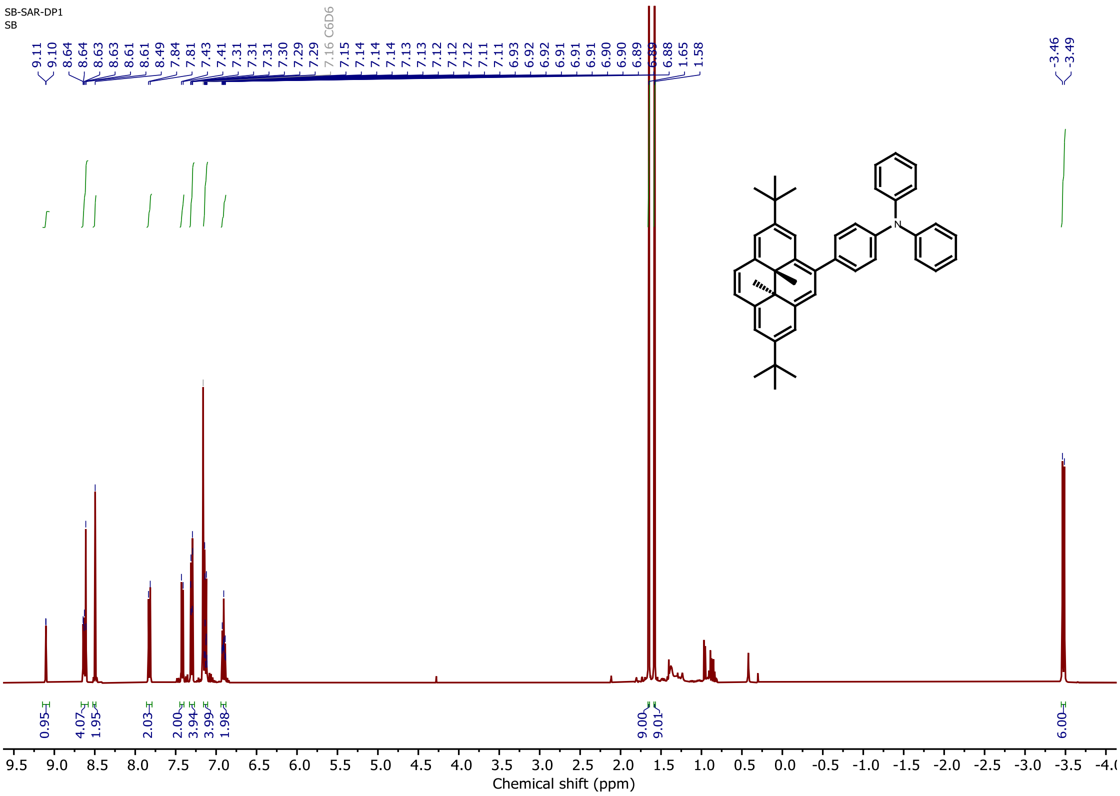


Figure S3: ^{1}H NMR spectrum of **2** in *benzene-d*$_6$.

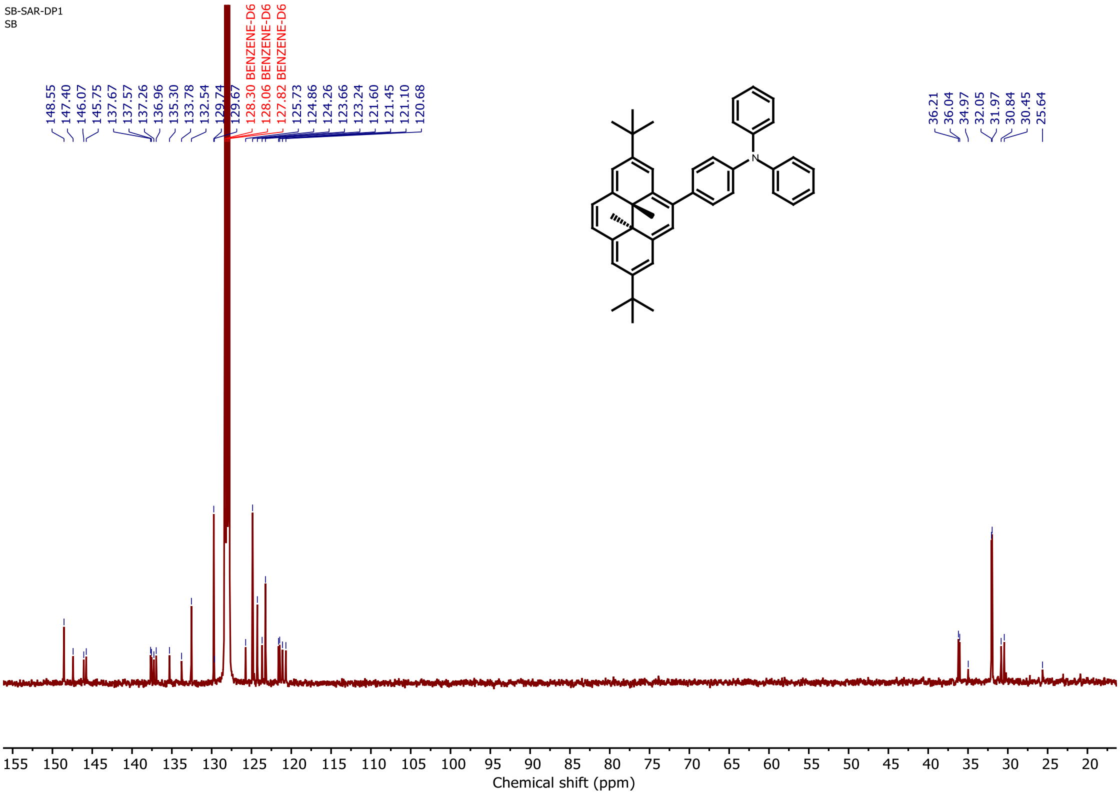


Figure S4: ^{13}C NMR spectrum of **2** in *benzene-d*$_6$.

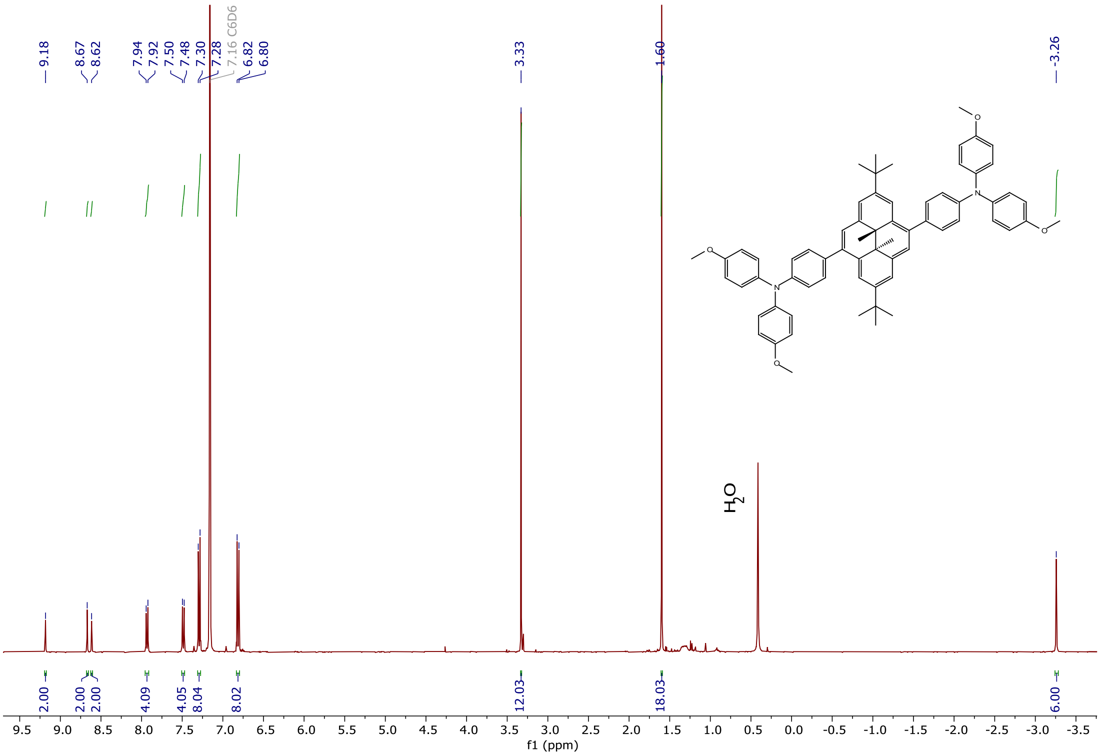


Figure S5: ^1H NMR spectrum of **3** in benzene-*d*$_6$.

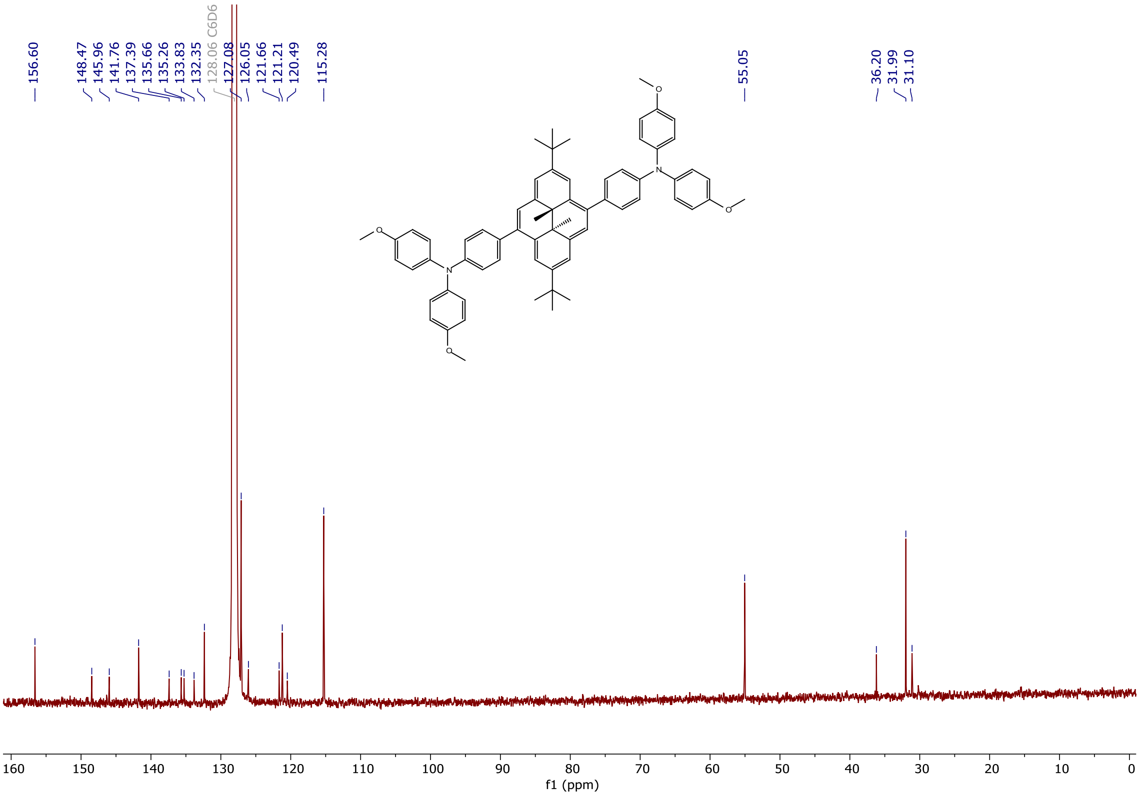


Figure S6: ^{13}C NMR spectrum of **3** in benzene-*d*$_6$.

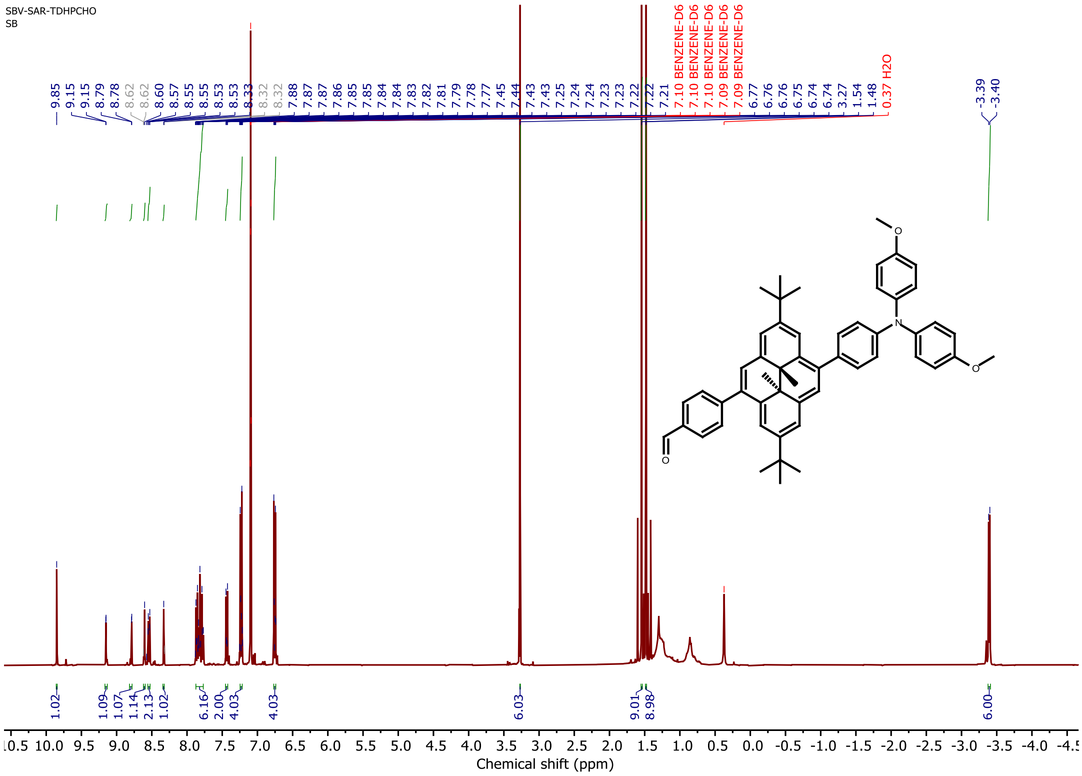


Figure S7: ^{1}H NMR spectrum of **4** in benzene-d_6.

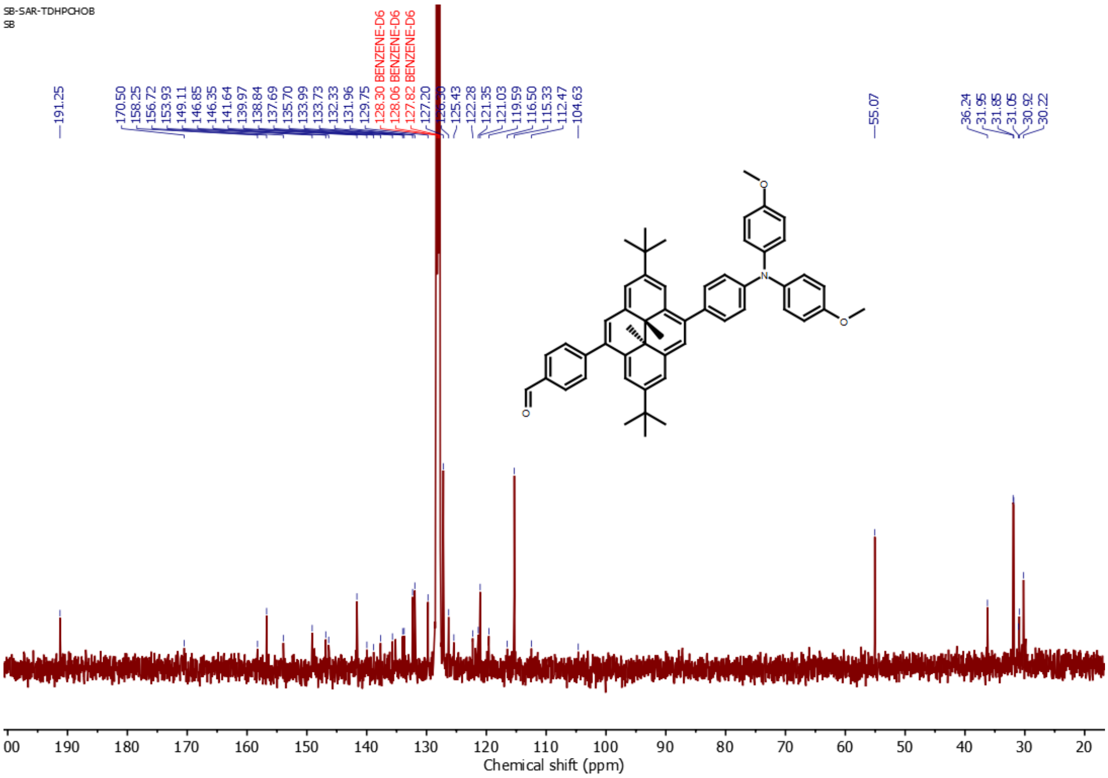


Figure S8: ^{13}C NMR spectrum of **4** in benzene-d_6.

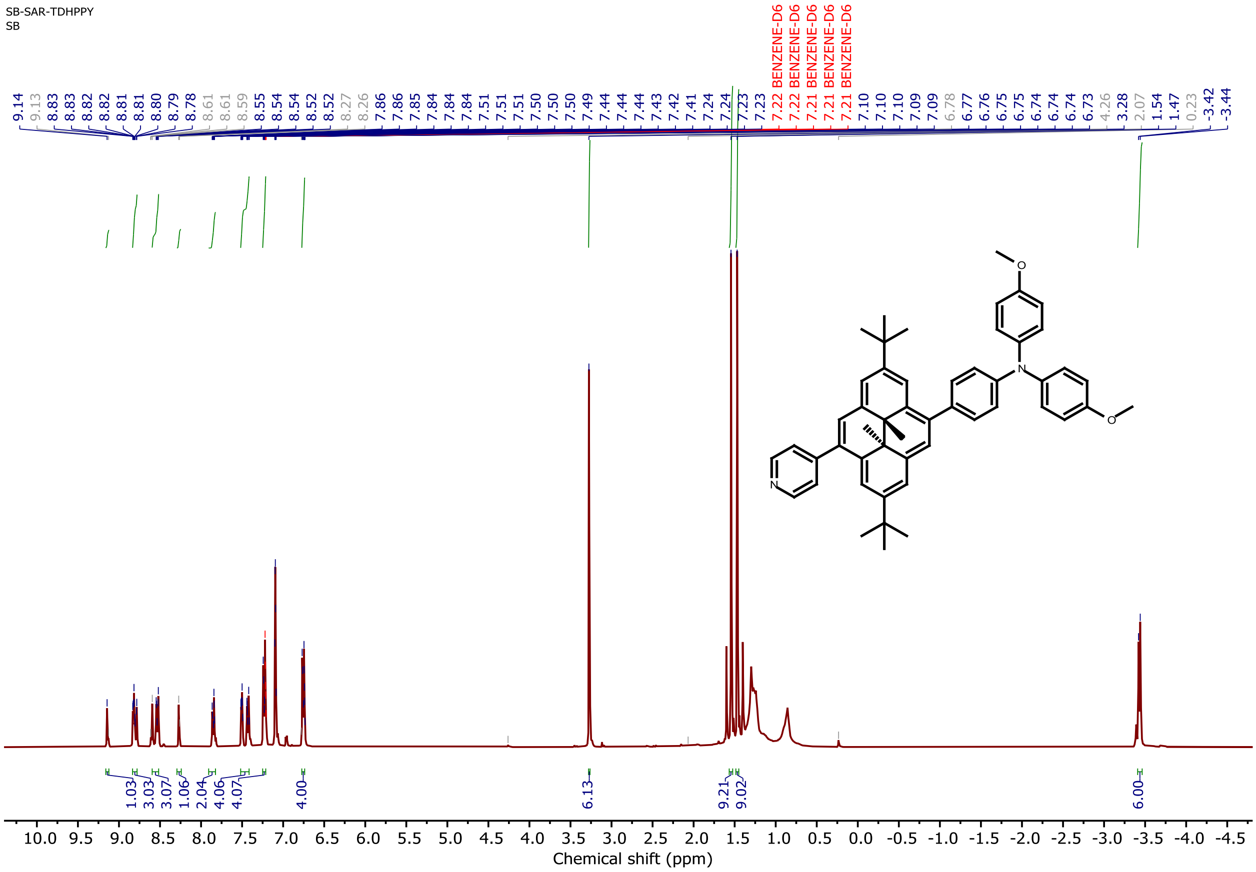


Figure S9: ^{1}H NMR spectrum of **TDHPPy** in benzene-d_6.

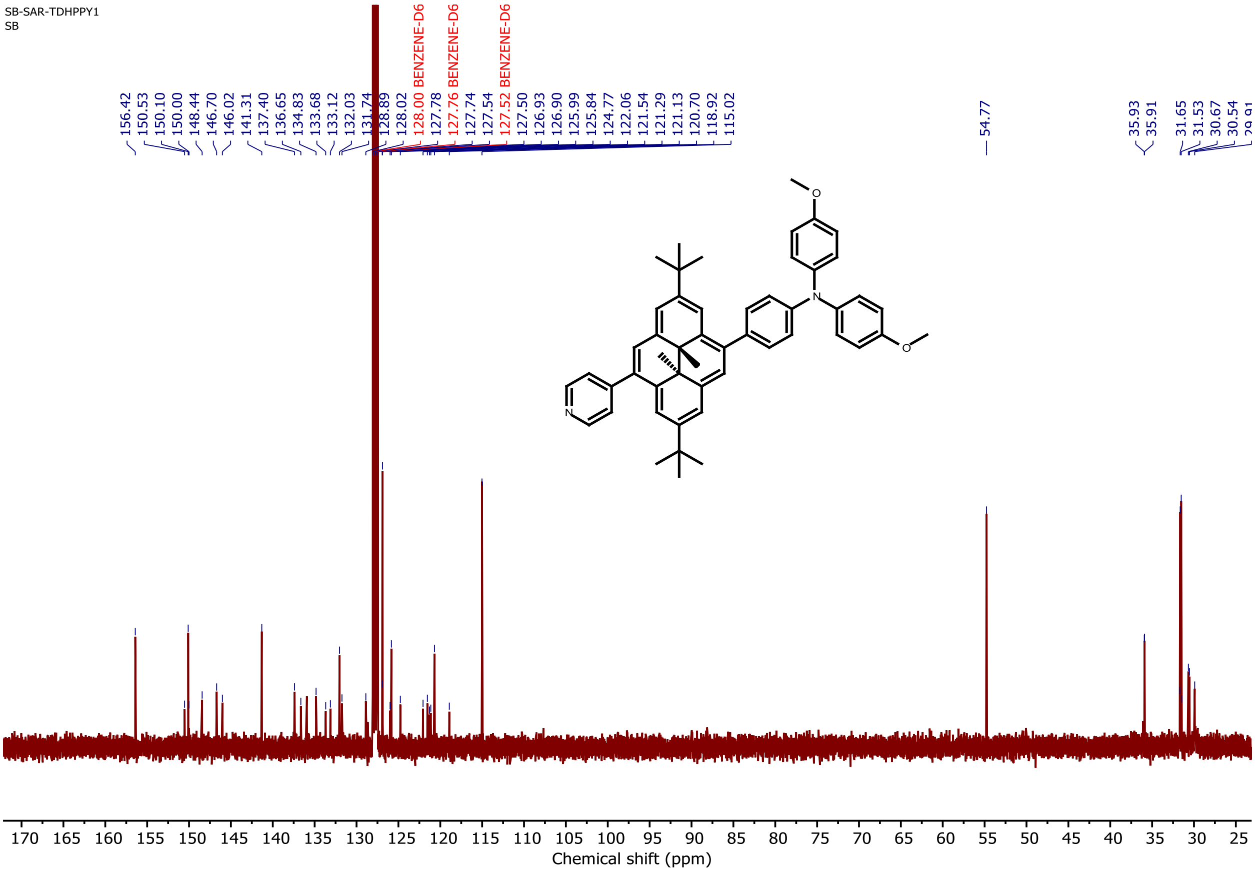


Figure S10: ^{13}C NMR spectrum of **TDHPPy** in benzene-*d*$_6$.

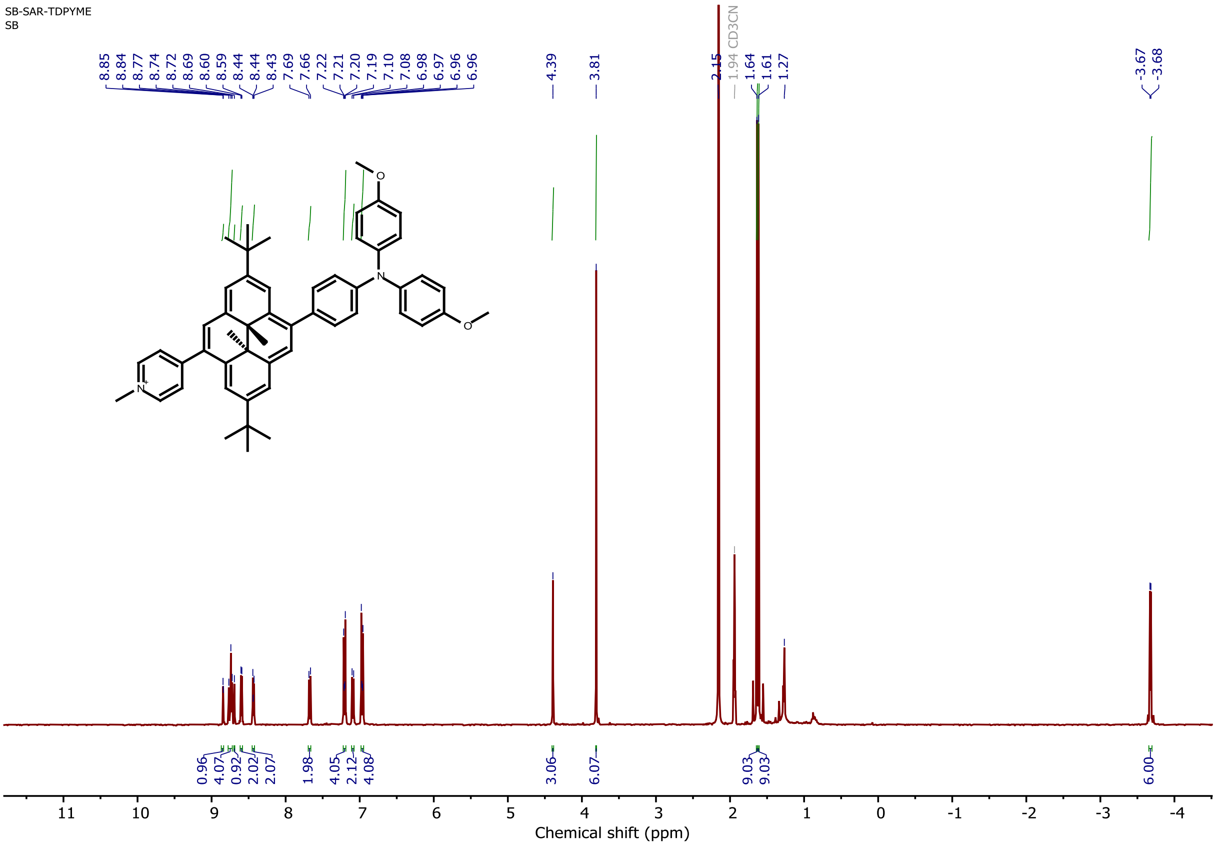


Figure S11: ^{1}H NMR spectrum of **5** in acetonitrile-*d*$_3$.

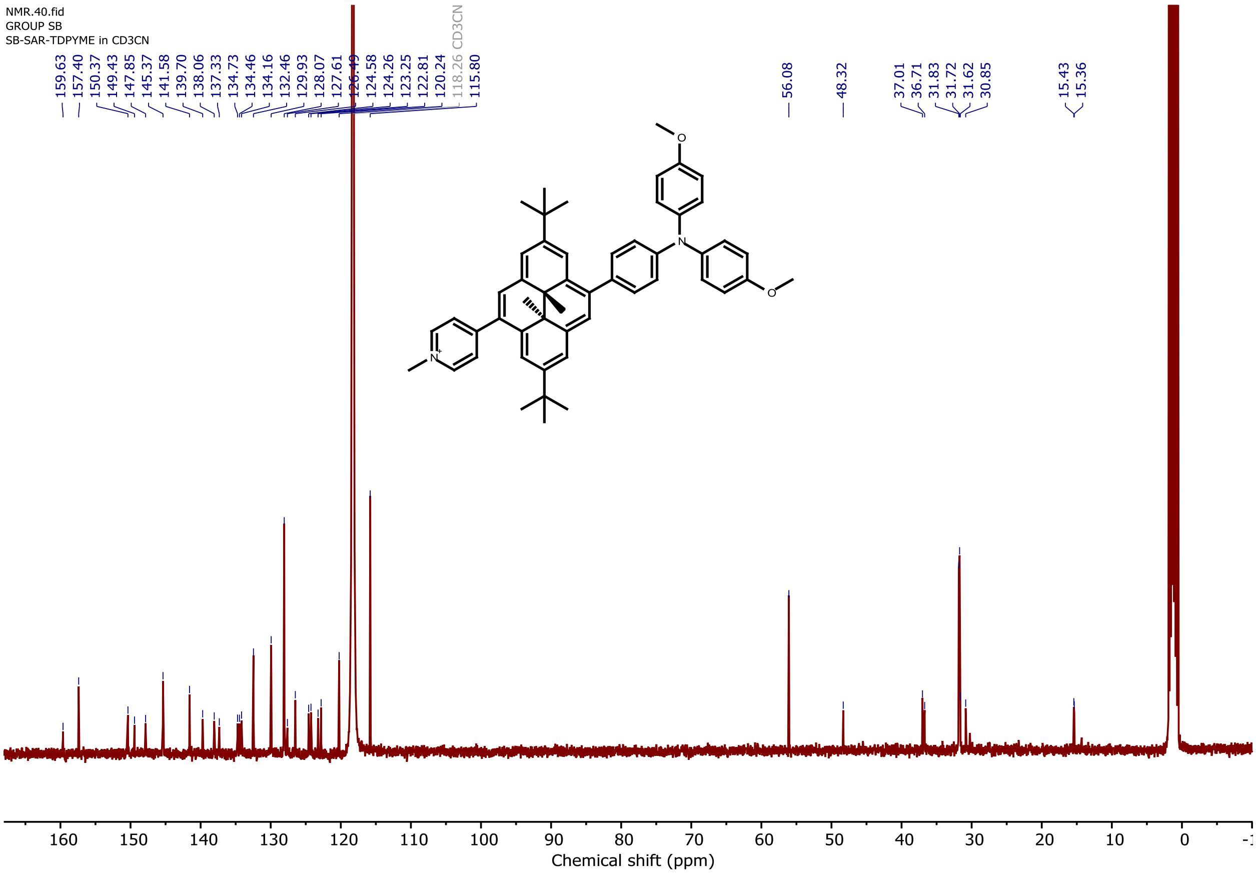


Figure S12: ^{13}C NMR spectrum of **5** in acetonitrile-d_3.

2. Photoisomerization Studies

Photoisomerization, a fascinating process in which the absorption of photons triggers changes in molecular configuration, was systematically explored in this solvent environment. Throughout our research, we subjected the photochromic compounds to carefully controlled light exposure, continuously monitoring the ensuing structural changes and characterizing the resulting isomers in acetonitrile. Employing a combination of analytical techniques, including UV-vis spectroscopy.

Absorption spectra of photoswitching:

The photoisomerization studies were carried out using various light sources, including UV (370 nm, 254 nm), blue (456 nm), green (525 nm), and red (640 nm) Kessil lamps, with a light source of 35 mW/cm^2 (measured from a 5 cm distance).

Photoisomerization transformations are performed in HPLC-grade solvent without further drying, and before each isomerization study, the solvent is purged with N_2 gas. The experiments were performed in quartz glass cuvettes with a path length of 1 cm and HPLC-grade solvents were used. Considering the photochemical equilibrium between closed and opened photoisomers. The photostationary state (PSS) distributions were calculated using the

following equation:

$$\chi_{open} = (A_0 - A_{PSS} / A_0) \times 100\%$$

where, χ= Ring opened isomer percentage at the PSS

A_0 = Absorbance at initial state at λ_{max}

A_{PSS} = Absorbance at PSS at λ_{max}

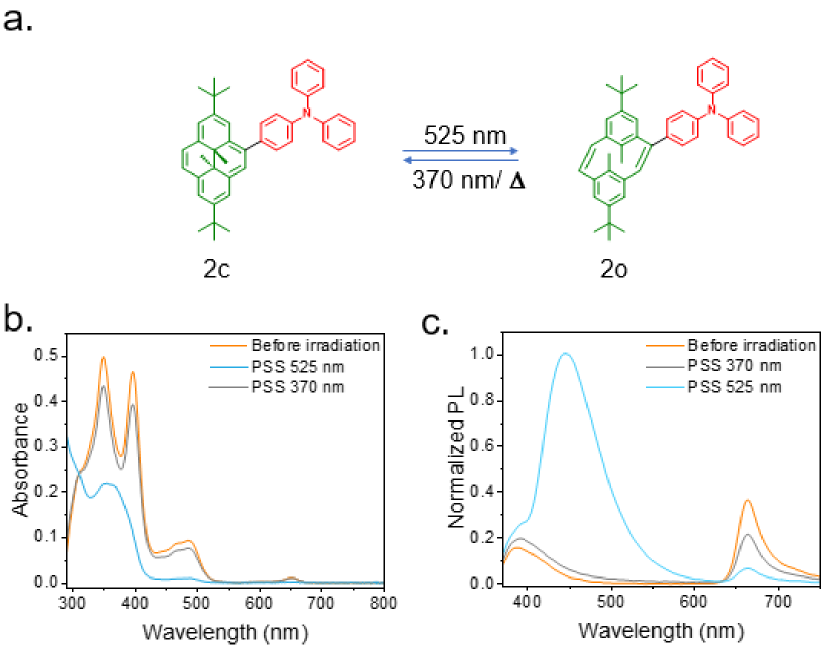


Figure S13: a) The photoisomerization between **2c** and **2o**. b) UV-vis absorption and c) PL emission spectral changes upon the photoisomerization of **2** in toluene (10 μM).

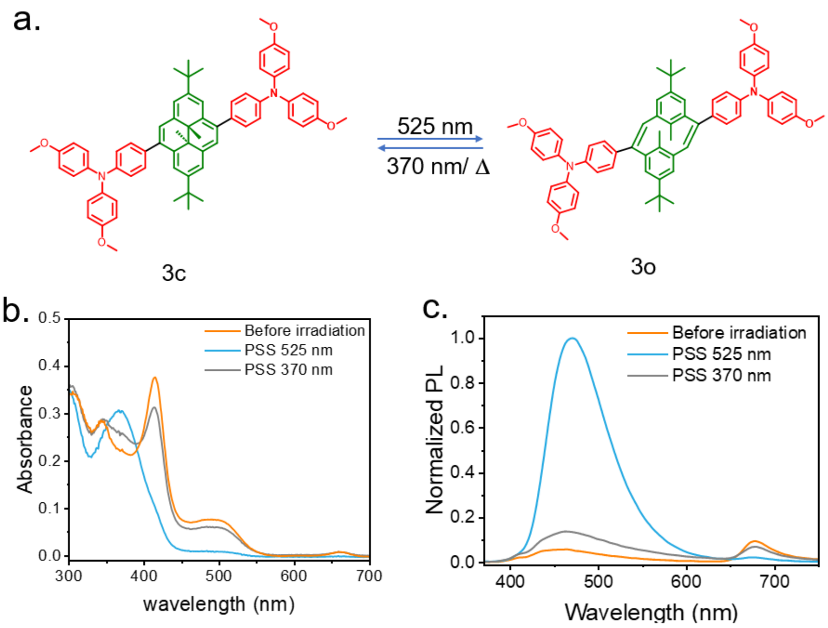


Figure S14: a) The photoisomerization between **3c** and **3o**. b) UV-vis absorption and c) PL emission spectral changes upon the photoisomerization of **3** in toluene (10 μM).

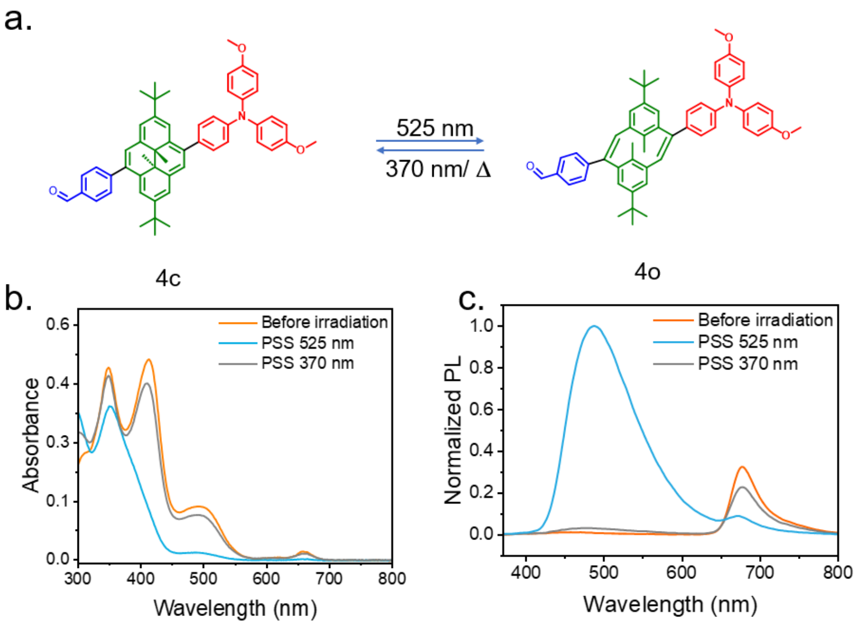


Figure S15: a) The photoisomerization between **4c** and **4o**. b) UV-vis absorption and c) PL emission spectral changes upon the photoisomerization of **4** in toluene (10 μM).

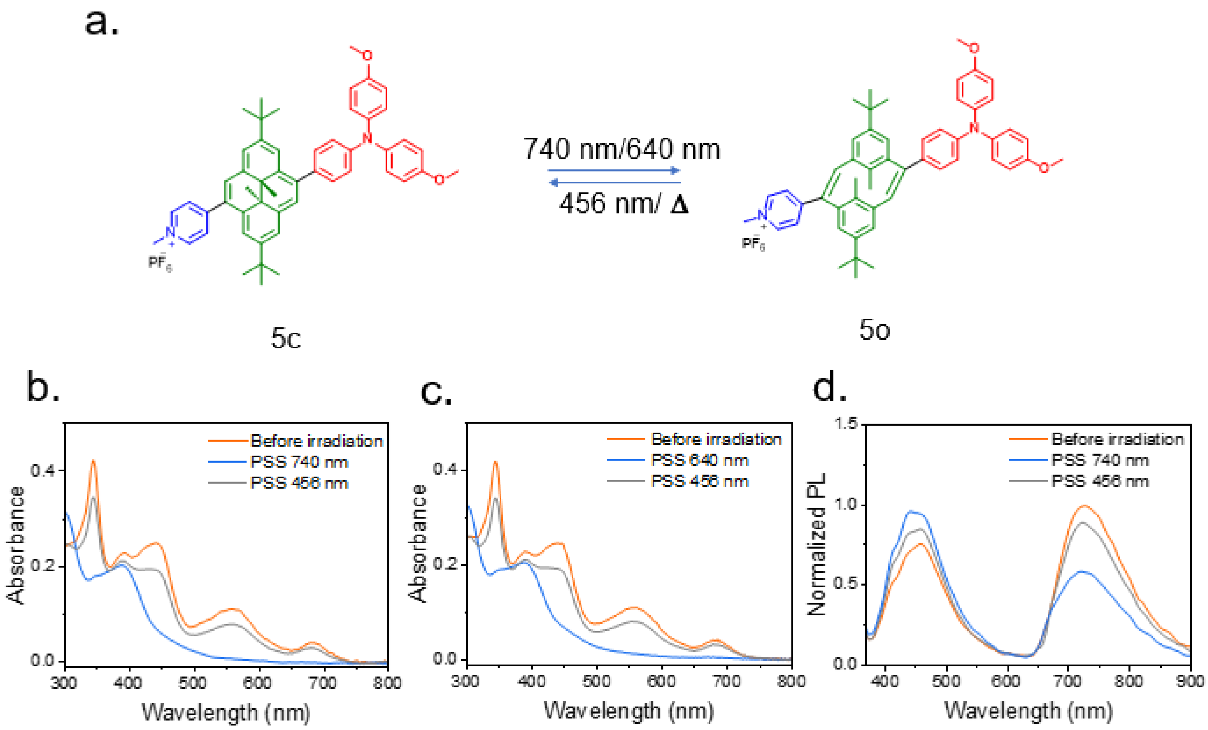


Figure S16: a) The photoisomerization between **5c** and **5o**. b) & c) UV-vis absorption and c) PL emission spectral changes upon the photoisomerization of **5** in toluene (10 μM).

3. Studies of fatigue resistance

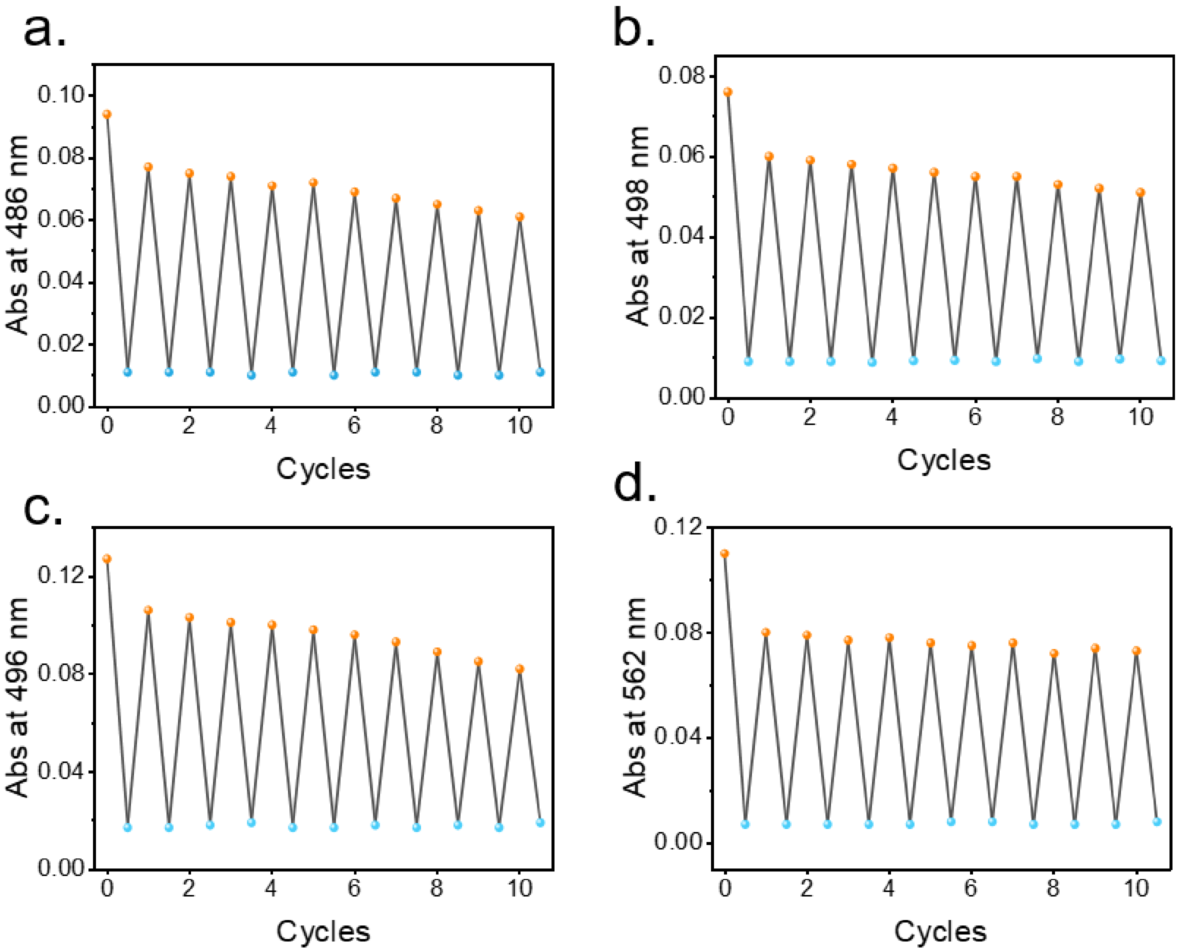


Figure S17: Up to 10 switching cycles for a) **2** (**2c**/**2o**), b) **3** (**2c**/**3o**), c) **4** (**4c**/**4o**), and d) **5** (**5c**/**5o**) have been monitored upon alternate irradiation with an appropriate wavelength of light (10 μM in toluene).

4. Arrhenius and Eyring plots

Newly prepared solutions of the studied compounds were exposed to light at distinct wavelengths (525 nm or 640 nm) corresponding to their photochemical characteristics until a photostationary state (PSS) was reached. To initiate the reverse reaction, samples rich in the opened form of PSS were promptly transferred to a dark setting within a Peltier module (temperature details specified below the graphs), as outlined in the experiment. The thermal reversal was assumed to follow first-order kinetics.

The rate constants (*k*) for the thermal reversal were determined using the following equation:

$$\boldsymbol{ln\,(A_0/A_t) \;=\; kt}$$

Half-life, $\boldsymbol{t_{1/2} = 0.693/k}$

From the plot of $\boldsymbol{ln\ k\ vs\ 1/T}$ of the Arrhenius equation, $\boldsymbol{ln\ k = ln\ A - E_a/RT}$), the $\boldsymbol{slope} = -\boldsymbol{E_a/R}$ was obtained. Similarly, from the plot of $\boldsymbol{ln\ (k/T)\ vs\ 1/T}$ of the Eyring equation, $\boldsymbol{ln\ (k/T) = -(\Delta H^{\neq}/RT) + ln\ (k_b/h) + \Delta S^{\neq}/R}$, we obtained the $\boldsymbol{slope = -(\Delta H^{\neq}/R)}$ and the $\boldsymbol{intercept = ln\ (k_b/h) + \Delta S^{\neq}/R}$

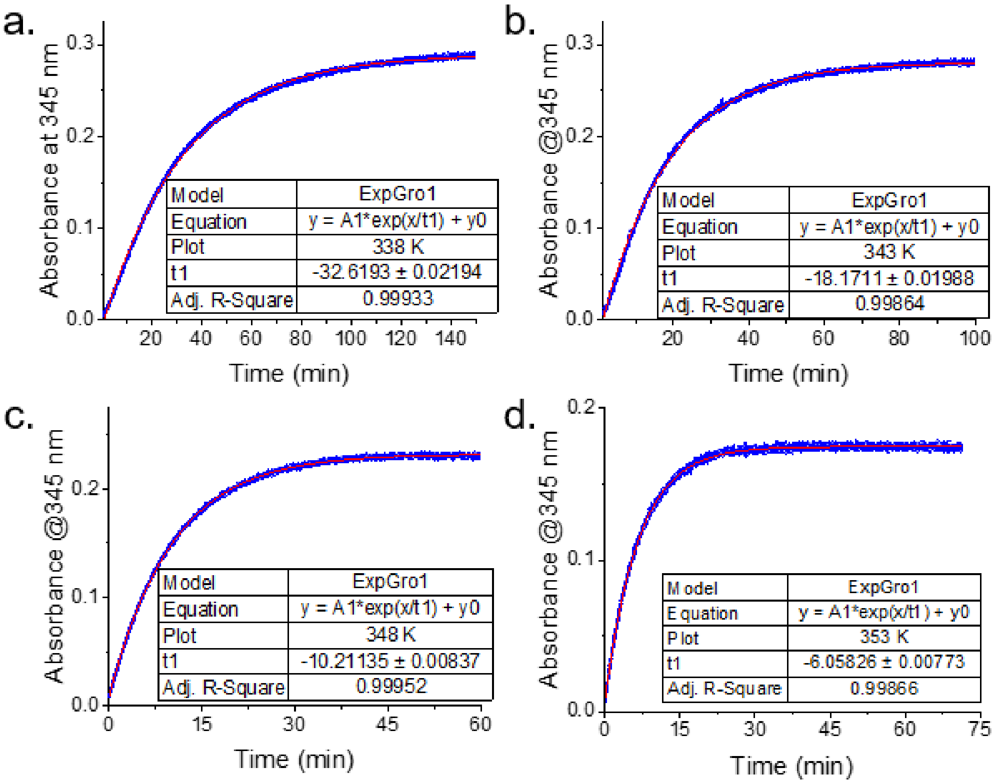


Figure S18: Kinetics plot of **1** at variable temperatures (338 K, 343 K, 348 K, and 353 K, respectively) for the open to closed isomer thermal reversal.

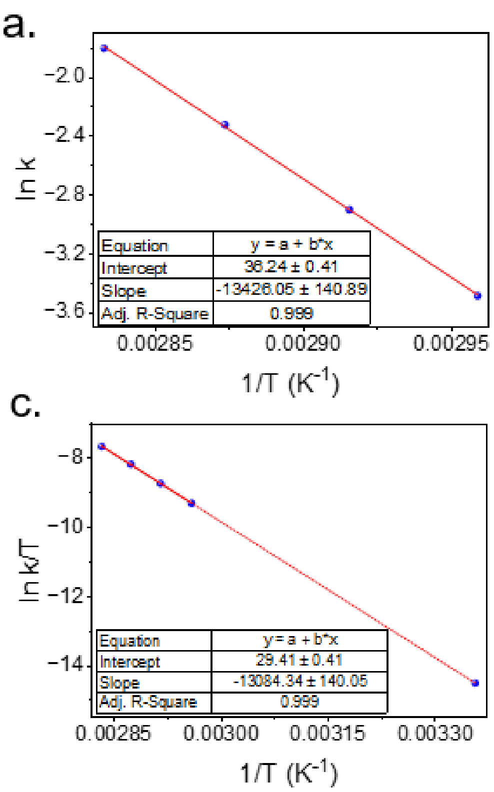


Figure S19: Arrhenius plot and Eyring plot of compound **1**.

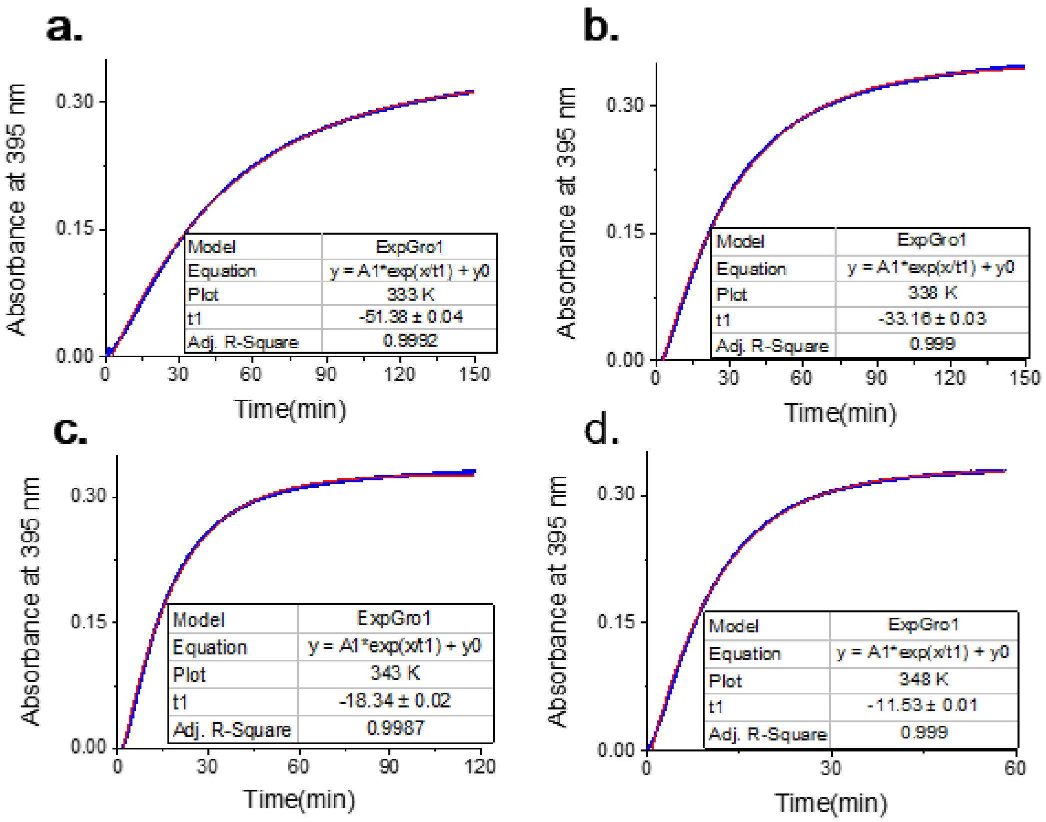
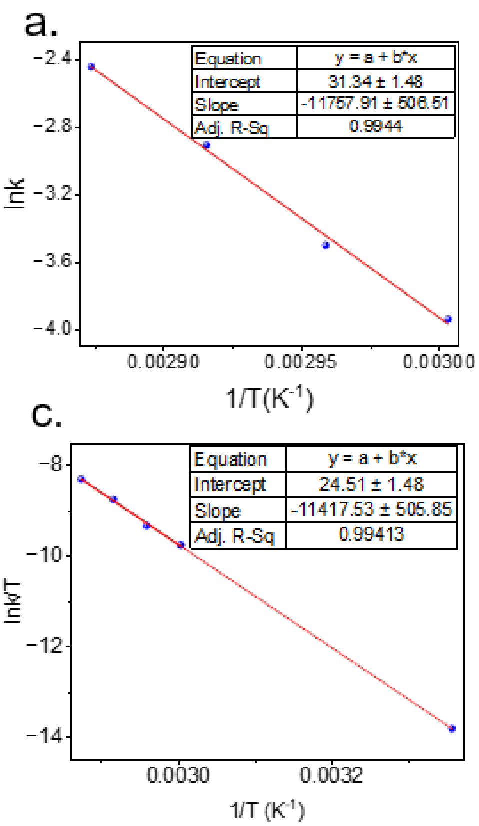


Figure S20: Kinetics plot of **2** at variable temperatures (333 K, 338 K, 343 K, and 348 K respectively) for the open to closed isomer thermal reversal.



a.

Equation	y = a + b*x
Intercept	31.34 ± 1.48
Slope	-11757.91 ± 506.51
Adj. R-Sq	0.9944

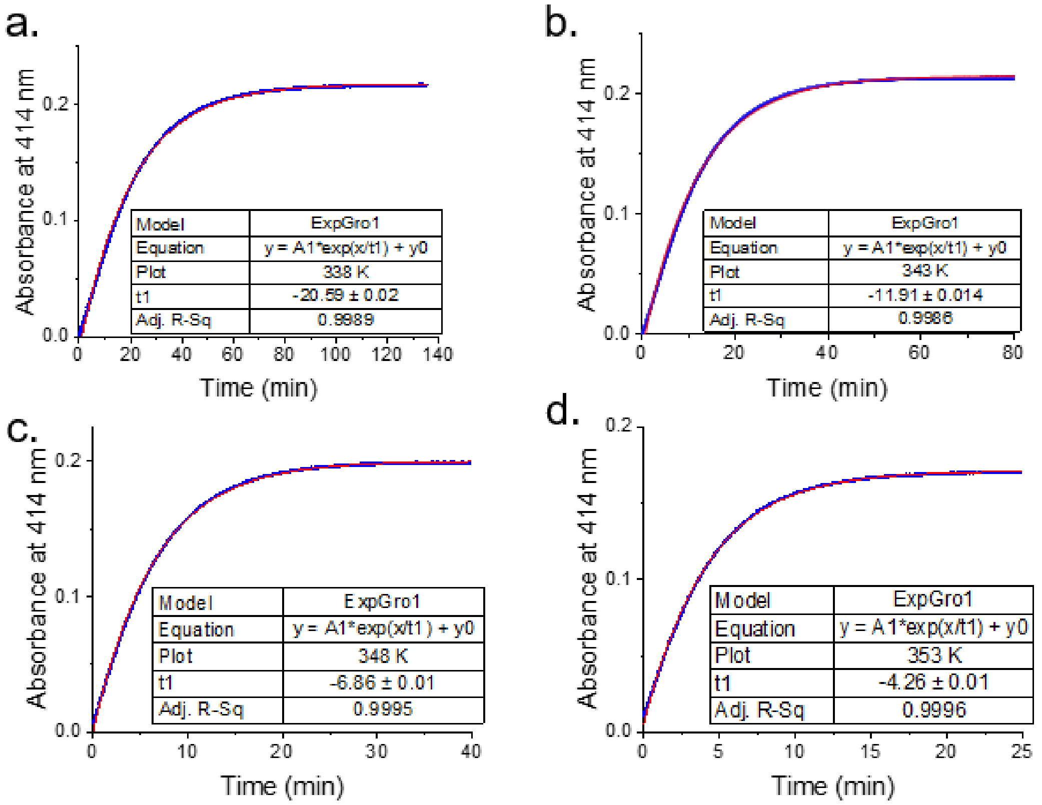
b.

Equation	y = a + b*x
Intercept	24.51 ± 1.48
Slope	-11417.54 ± 505.85
Adj. R-Sq	0.9941

c.

Equation	y = a + b*x
Intercept	24.51 ± 1.48
Slope	-11417.53 ± 505.85
Adj. R-Sq	0.99413

Figure S21: Arrhenius plot and Eyring plot of compound **2**.



a.

Model	ExpGro1
Equation	y = A1*exp(x/t1) + y0
Plot	338 K
t1	-20.59 ± 0.02
Adj. R-Sq	0.9989

b.

Model	ExpGro1
Equation	y = A1*exp(x/t1) + y0
Plot	343 K
t1	-11.91 ± 0.014
Adj. R-Sq	0.9986

c.

Model	ExpGro1
Equation	y = A1*exp(x/t1) + y0
Plot	348 K
t1	-6.86 ± 0.01
Adj. R-Sq	0.9995

d.

Model	ExpGro1
Equation	y = A1*exp(x/t1) + y0
Plot	353 K
t1	-4.26 ± 0.01
Adj. R-Sq	0.9996

Figure S22: Kinetics plot of **3** at variable temperatures (338 K, 343 K, 348 K, and 353 K respectively) for the open to closed isomer thermal reversal.

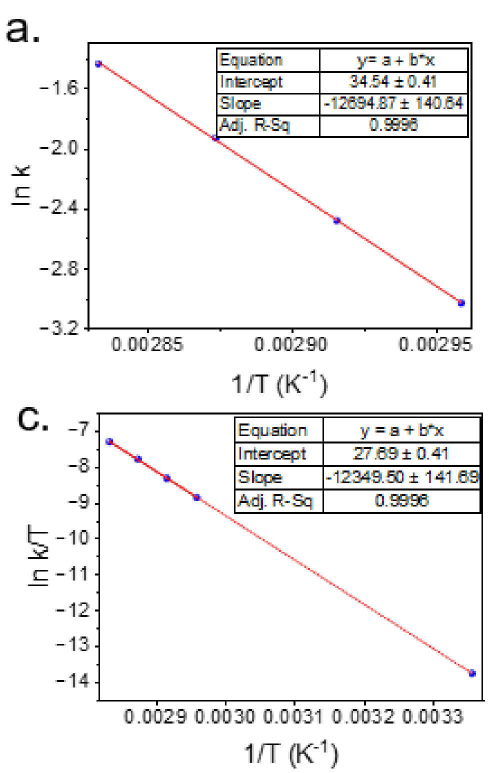


Figure S23: Arrhenius plot and Eyring plot of compound **3**.

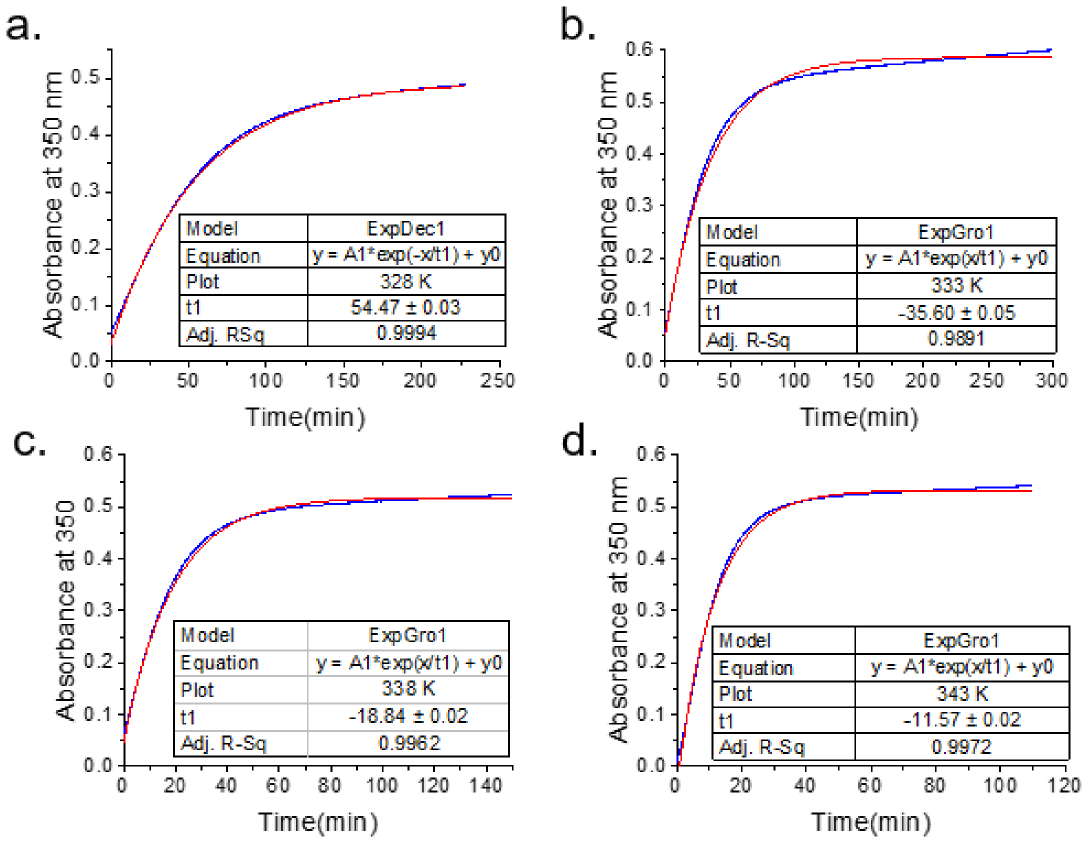


Figure S24: Kinetics plot of **4** at variable temperatures (328 K, 333 K, 338 K, and 343 K, respectively) for the open-to-closed isomer thermal reversal.

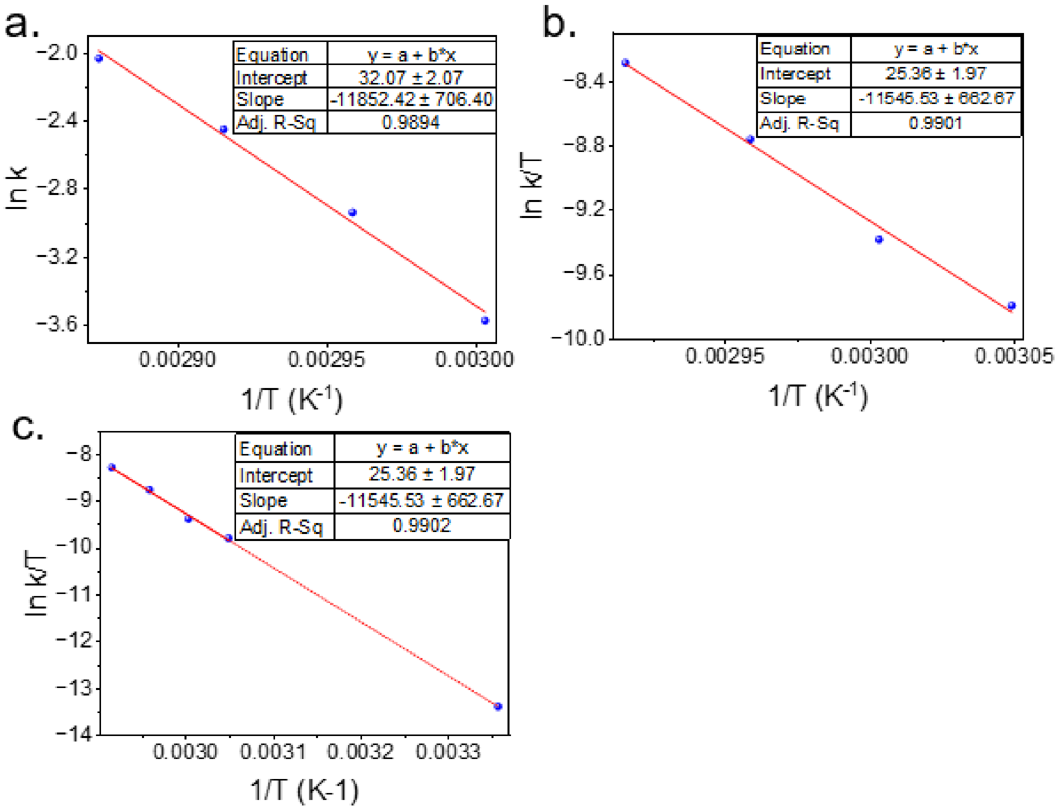


Figure S25: Arrhenius plot and Eyring plot of compound **4**.

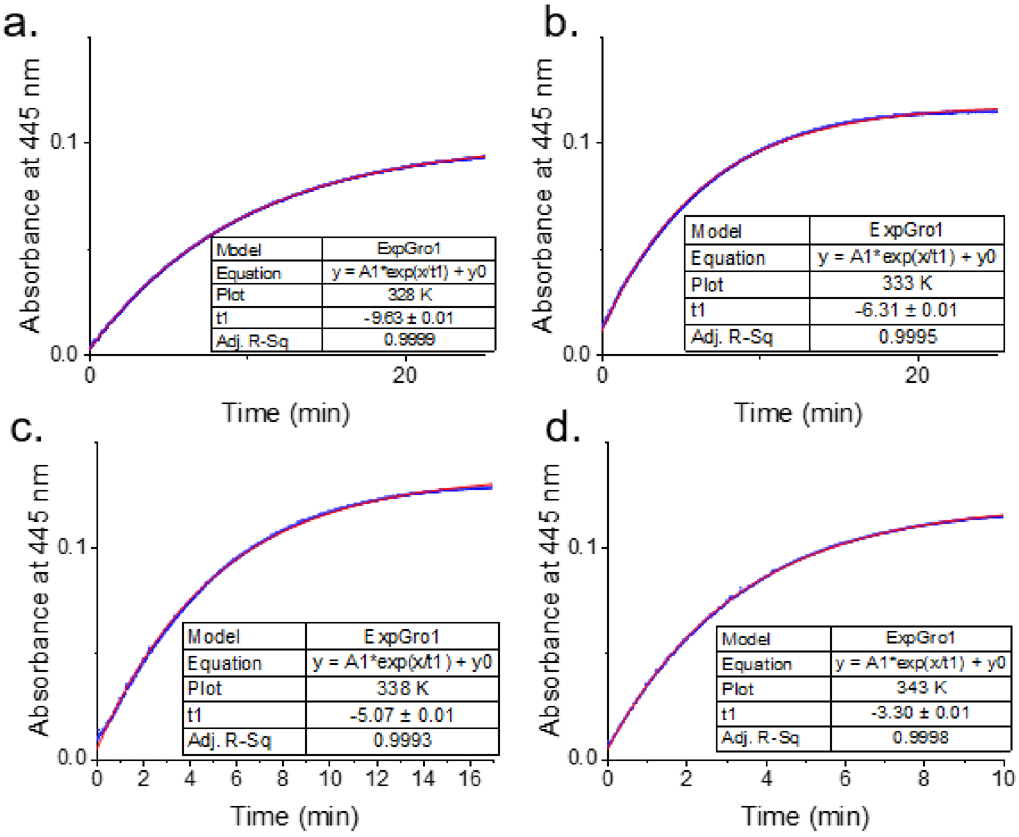


Figure S26: Kinetics plot of **5** at variable temperatures (328 K, 333 K, 338 K, and 343 K, respectively) for the open to closed isomer thermal reversal.

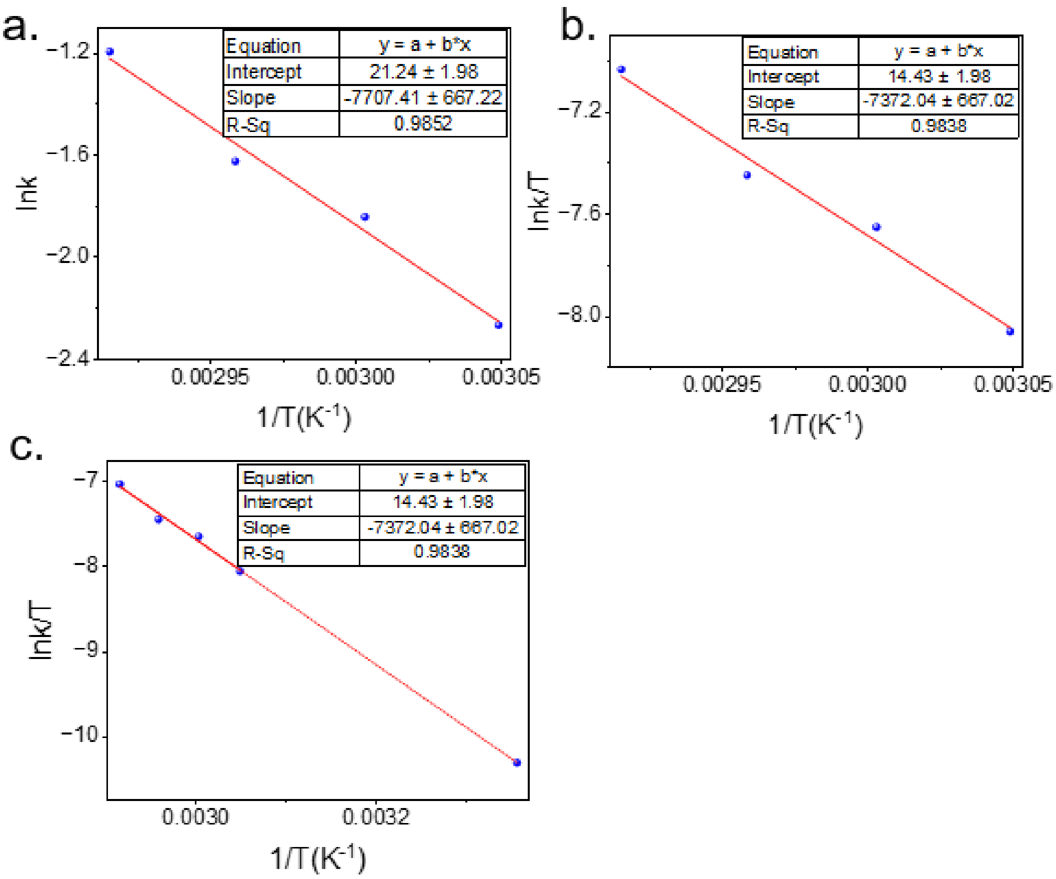


Figure S27: Arrhenius plot and Eyring plot of compound **5**.

Table S1: Photochemical and thermodynamic properties of 1-5 in solution (10 µM in Toluene).

Compounds	Activation energy (E_a) for reverse Reaction (kcal/mol)	Enthalpy of activation ($\Delta H^{\neq}$) for reverse reaction (kcal/mol)	Entropy of activation ($\Delta S^{\neq}$) for reverse reaction (Cal/mol)	$t_{1/2}$ (h) at 298K
1	26.6 ± 0.2	25.9 ± 0.3	11.18 ± 0.3	77
2	23.3± 0.2	22.6± 0.3	1.48± 0.3	38
3	25.1 ± 0.2	24.5 ± 0.2	7.79 ± 0.2	36
4	23.4 ± 0.5	22.9 ± 0.5	3.18± 0.5	25
5	15.3± 0.8	14.6± 0.8	18.47 ± 1.2	1

5. Isomerization studies with ^{1}H-NMR

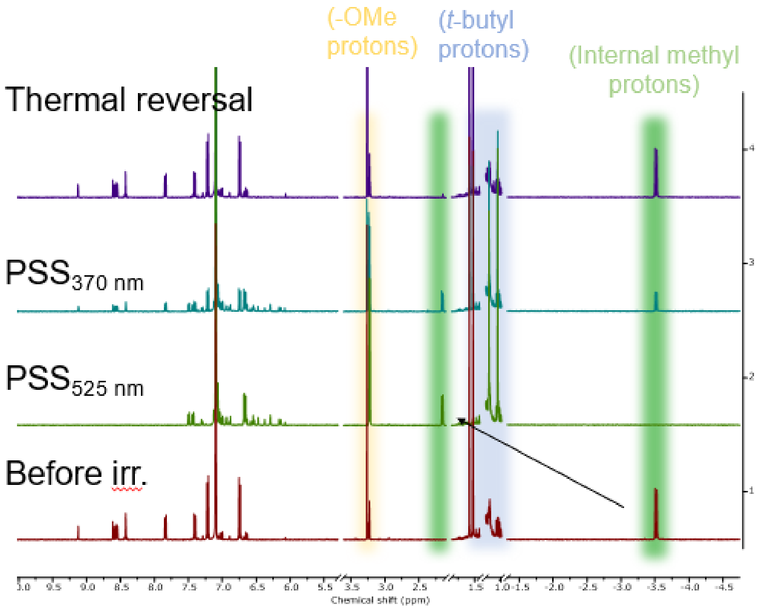


Figure S28: ^{1}H NMR (400 MHz, benzene-d_6, 298 K) isomerization spectra of **1**. 10 mM solutions were used for the NMR isomerization studies. The reversible shift of the internal methyl protons (green) and t-Bu protons (grey) depicts the isomerization process.

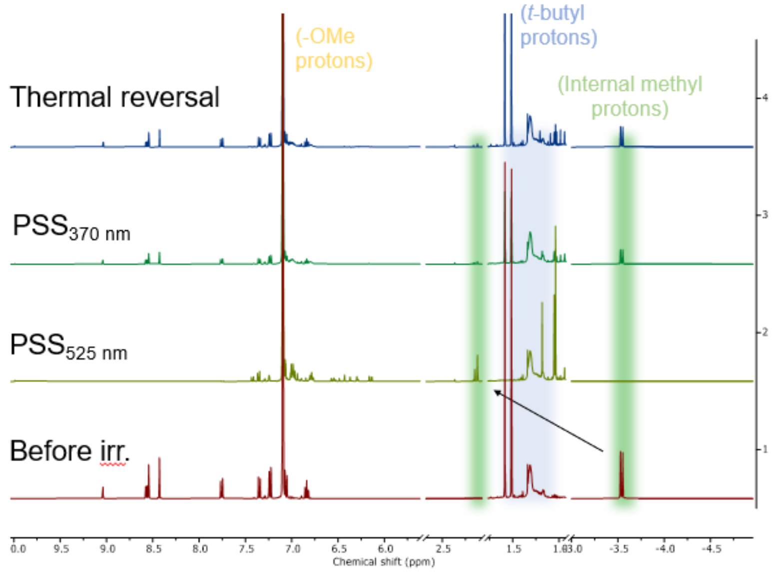


Figure S29: ^{1}H NMR (400 MHz, benzene-d_6, 298 K) isomerization spectra of **2**. 10 mM solutions were used for the NMR isomerization studies. The reversible shift of the internal methyl protons (green) and t-Bu protons (grey) depicts the isomerization process.

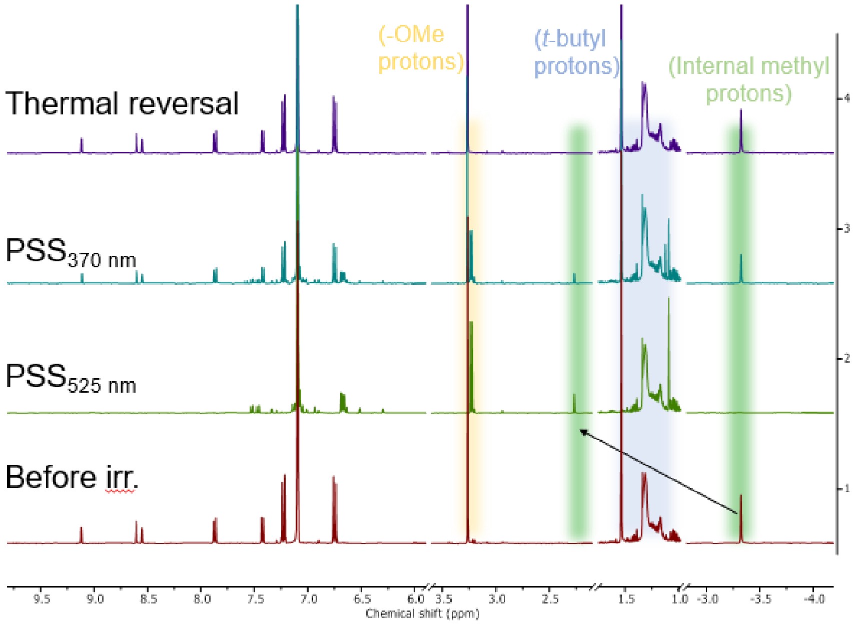


Figure S30: ^{1}H NMR (400 MHz, benzene-d$_6$, 298 K) isomerization spectra of **3**. 10 mM solutions were used for the isomerization studies. The reversible shift of the internal methyl protons (green) and t-Bu protons (grey) depicts the isomerization process.

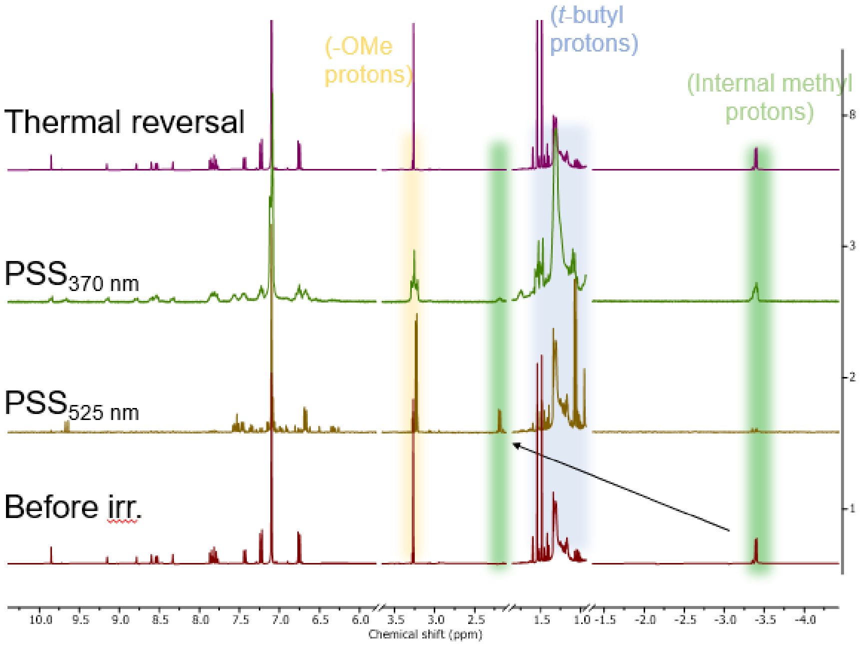


Figure S31: ^{1}H NMR (400 MHz, benzene-d$_6$, 298 K) isomerization spectra of **4**. 10 mM solutions were used for the NMR isomerization studies. The reversible shift of the internal methyl protons (green) and t-Bu protons (grey) depicts the isomerization process.

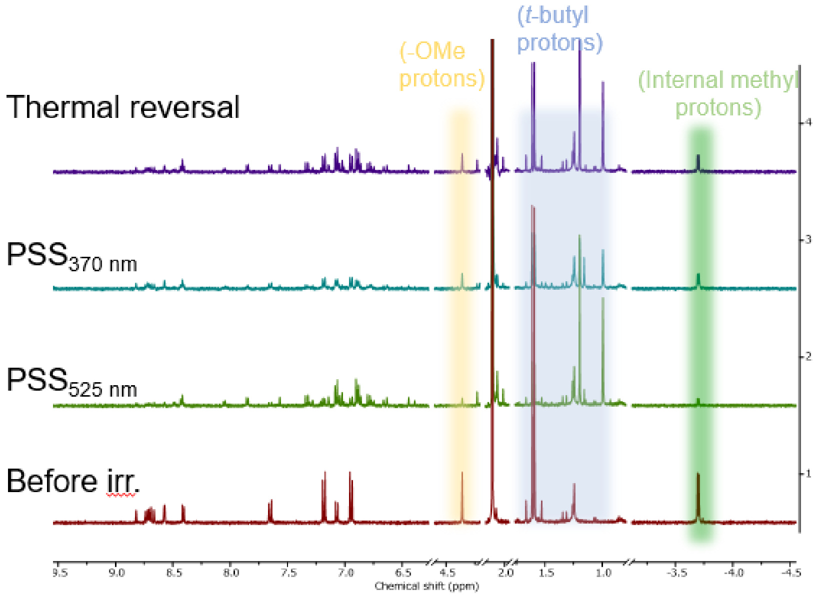


Figure S32: ^{1}H NMR (400 MHz, acetonitrile-d3, 298 K) isomerization spectra of **5**. 10 mM solutions were used for the NMR isomerization studies. The reversible shift of the internal methyl protons (green, after isomerization, the peak merges with the protons of the water molecule in acetonitrile-d$_3$) and t-Bu protons (grey) depicts the isomerization process.

6. Photoisomerization quantum yield

Quantum yields have been calculated following the reported method.[4]

The rate of a unidirectional photochemical reaction initiated with monochromatic light is given by:

$$r_{A\to B} = \frac{q_{in}\Phi_{A\to B}}{V}\left(1 - 10^{-\varepsilon_A[A]l}\right) \qquad (1)$$

In our case, since the value of absorbance of the compounds **1** (at 525 nm), and **2** (at 640 nm, wavelength at which the quantum yield was measured) was much less than 0.4, Taylor series expansion of the exponential function and subsequent truncation at the linear term was carried out leading to a first-order rate equation (2). This equation can be further expressed in terms of the quantum yield and the observed first-order rate constant, photon flux and other known measurable quantities for the sample (see below), leading to equation (3):

$$r_{A\to B} = q_{in}\Phi_{A\to B}\varepsilon_A l\, V\, [A] \qquad (2)$$

$$\Phi_{A\to B} = \frac{k\, V}{q_{in}\varepsilon_A l\, ln\, 10} \qquad (3)$$

Where Φ = quantum yield; k= rate constant (obtained from the exponential fit of a graph of A vs. time); V = sample volume; ε_A= molar extinction coefficient; l = pathlength; and q = molar photon flux.

Molar photon flux:

$$q_{in} = \frac{P\lambda}{hcN_A} \qquad (4)$$

where P = power (of the laser); λ = pump wavelength; h = Planck's constant; c = speed of light; and N_A = Avogadro's number.

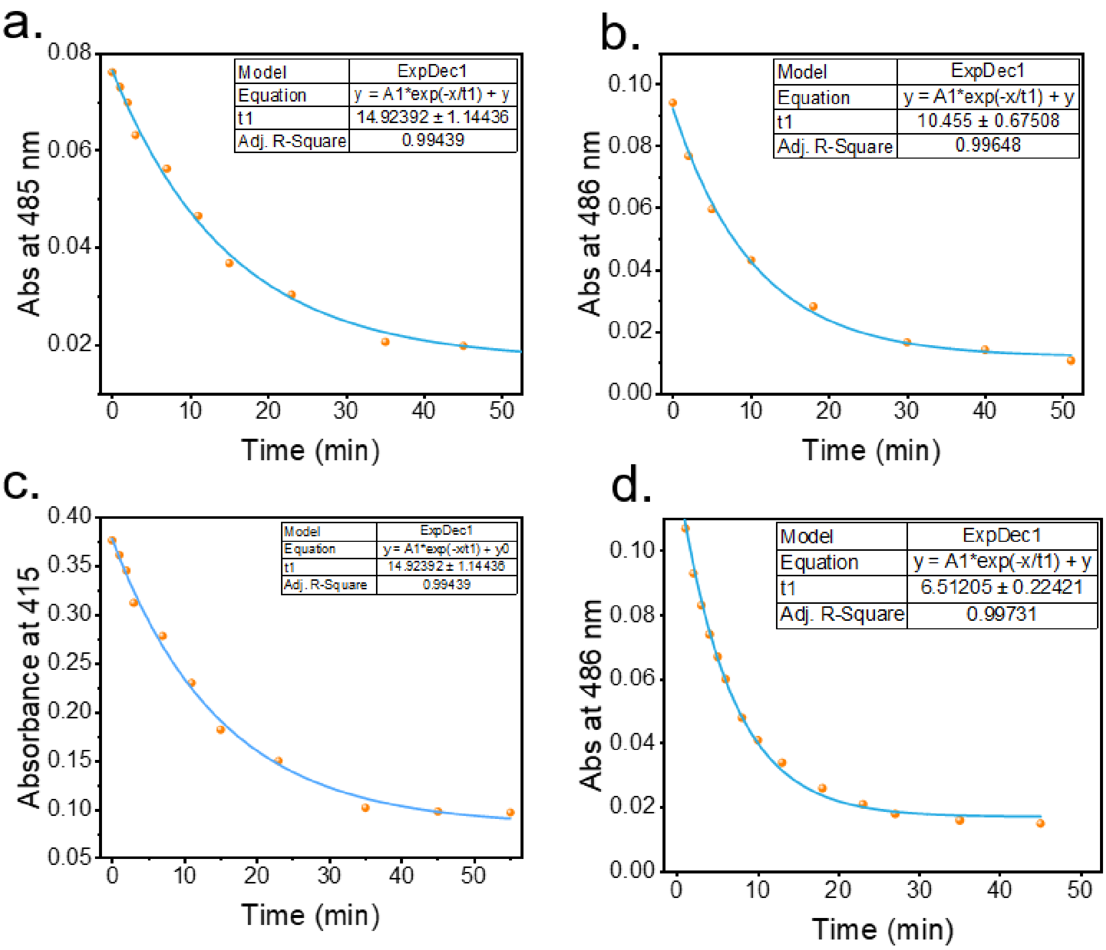


Figure S33: Kinetics of ring opening (c→o) photoisomerization of DHP unit for compounds a) **1**, b) **2**, c) **3**, and d) **4** upon irradiation with 525 nm.

Table S2. Estimation of quantum yield for the forward photoisomerization of in toluene.

Compound	Wavelength (λ)(nm)	Extinction coefficient (ε_A) at λ(Lmol^{-1}cm^{-1})	Rate constant (k) s^{-1}	Photon Flux (q_{in}) (10^{-7})	Quantum yield (Φ) (10^{-3})
1	525	1000 ± 60	0.001117	6.01	0.80
2	525	700 ± 80	0.001594	6.01	1.65
3	525	4500 ± 50	0.0011170	6.01	0.18
4	525	8000 ± 50	0.0025601	6.01	0.23

7. Fluorescence quantum yield

To estimate the fluorescence quantum yields (QY) of **1c** and **1o**, the relative quantum yield method was used with quinine sulphate in 0.1 M H_2SO_4 standards (QY = 0.547, λ_{ex} = 350 nm).[5] Solutions with an absorbance (OD) of less than 0.05 were chosen to prevent concentration-related errors. Each sample's QY was calculated using the same excitation wavelength as the reference. The QY was computed using the following equation:

$$\Phi = \Phi_R \times (\frac{OD_R}{OD}) \times (\frac{I}{I_R}) \times (\frac{\eta^2}{\eta_R^2})$$

Φ, Φ_R = quantum yield, Subscript R stands for reference (standard fluorescein dye)

OD, OD_R = optical density

I, I_R = integrated fluorescence intensity

η, η_R = refractive index of the solvents

8. Solvatochromism of isomer **1o**

Calculations were done by following a reported procedure.[6]

Table S3 Table of Lippert-Mataga plot for isomer **1o**.

Solvent	f(ε,n)	λ_{abs} (max)(nm)	λ_{em} (max)(nm)	υ_{abs}-υ_{em} (cm^{-1})
Hexane	0.001	370	446	4605
Toluene	0.014	376	470	5319
Chloroform	0.148	368	497	7053
Ethyl acetate	0.167	369	499	7060
DCM	0.217	372	514	7426
DMF	0.276	371	544	8571
Acetone	0.284	368	527	8198
Acetonitrile	0.305	365	547	9115

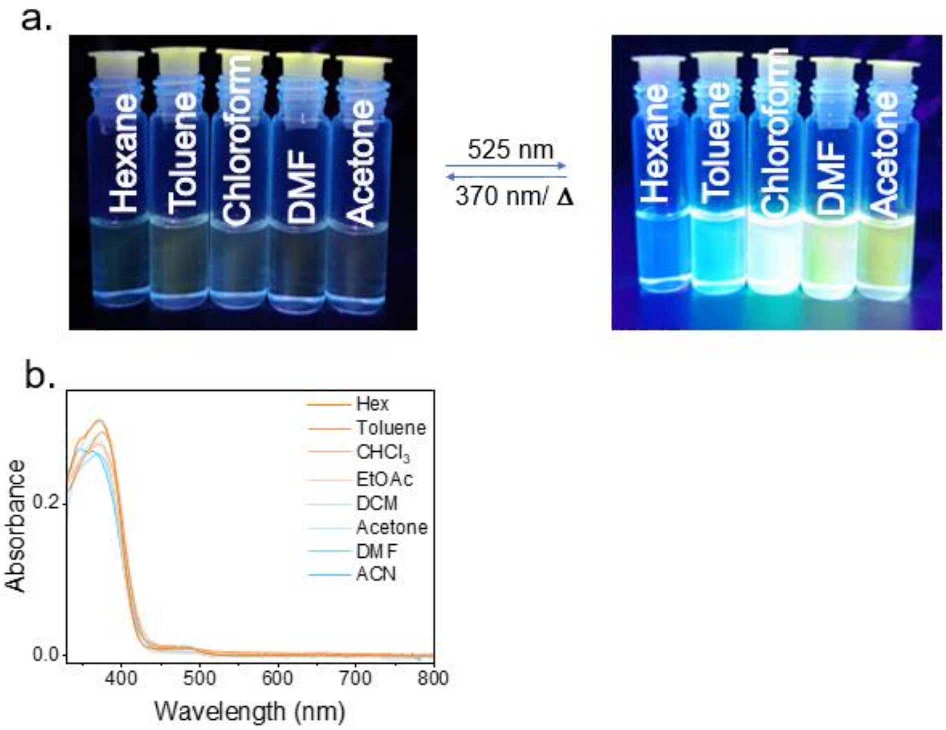


Figure S34 (a) Visual color change upon isomerization in different solvents. (b) UV-vis absorption spectra of **1o** isomer in different solvents.

9. Summary of the fluorescence lifetimes of **1o** in different solvents.

Table S4. time-resolved photophysical data of **1o**, the samples were excited at 340 nm.

DHPs	λ_{max}^{abs}[nm]	λ_{max}^{em}[nm]	τ_1[ns]	τ_2[ns]	τ_{av}[ns]	χ^2
Hexane	370	446	0.71	2.12	1.37	1.2
Toluene	376	470	1.12	2.23	2.22	1.2
DMF	371	544	2.87	4.19	3.56	1.2
Acetone	368	527	5.28	4.60	5.15	1.3

10. Computational Details.

All calculations were performed using Gaussian 16 (Revision A.03).[7] Ground-state geometries were optimized at the B3LYP/6-311G(d,p) level[8-11] which has been shown to provide reliable structural parameters for DHP-based systems[12,13] and vibrational frequency calculations confirmed all structures as true minima. Excited-state properties were investigated using TD-DFT[14,15] with the long-range-corrected CAM-B3LYP[16] functional and the 6-311G(d,p) basis set, which is well suited for describing charge-transfer (CT) excitations due to its correct asymptotic exchange behavior. Solvent effects were included using the polarizable continuum model (PCM)[17] in all the calculations, with PCM(toluene) employed for TD-DFT calculations related to absorption and emission and PCM ($CHCl_3$) used for spin-density analyses to match experimental conditions. Low-energy emissive states were examined by optimizing the lowest singlet excited state (S_1) at the CAM-B3LYP/6-311G(d,p) level, followed by TD-DFT single-point calculations on the S_1-optimized geometries to obtain emission energies and oscillator strengths; frequency calculations confirmed the S_1 structures as excited-state minima. Spin-density distributions were visualized using GaussView.

Table S5. Dihedral angles in the first excited state for the remaining compounds (**2**–**5**), reported for the closed and open forms.

Compounds	Dihedral angle in the excited state	
	Closed	Open
2	48°	19°
3	50°	22°
4	50°	21°
5	53°	23°

Table S6. Simulated emission wavelengths and corresponding oscillator strengths for the closed and open forms of the remaining derivatives.

Compounds	Simulated emission maximum	
	Closed	Open
1	610.08 nm f = 0.0271	441.90 nm f = 0.3672
2	608.58 nm f = 0.0260	438.52 nm f = 0.3312
3	625.61 nm f = 0.0480	452.38 nm f = 0.3513
4	622.02 nm f = 0.0476	470.64 nm f = 0.2805

11. Radical cation generation by Cu^{2+}

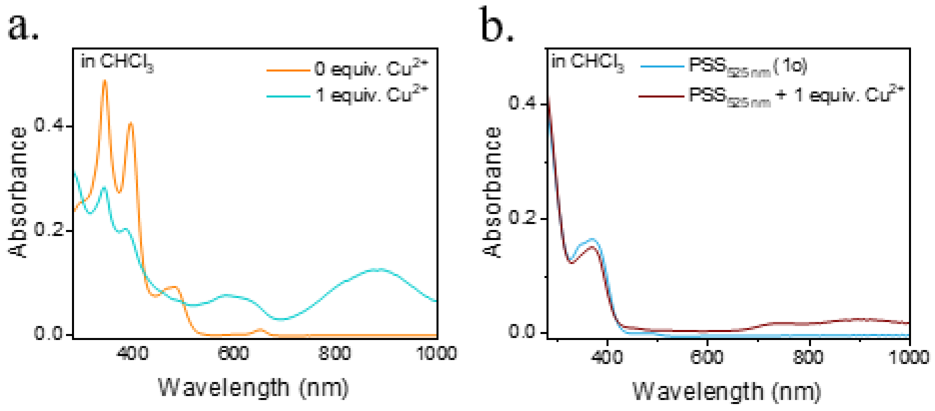


Figure S35: (a) **1c** and (b) **1o**, before and after addition of 1 equivalent of $Cu(ClO_4)_2$.

12. Compound **1** in different solvents under 370 nm irradiation.

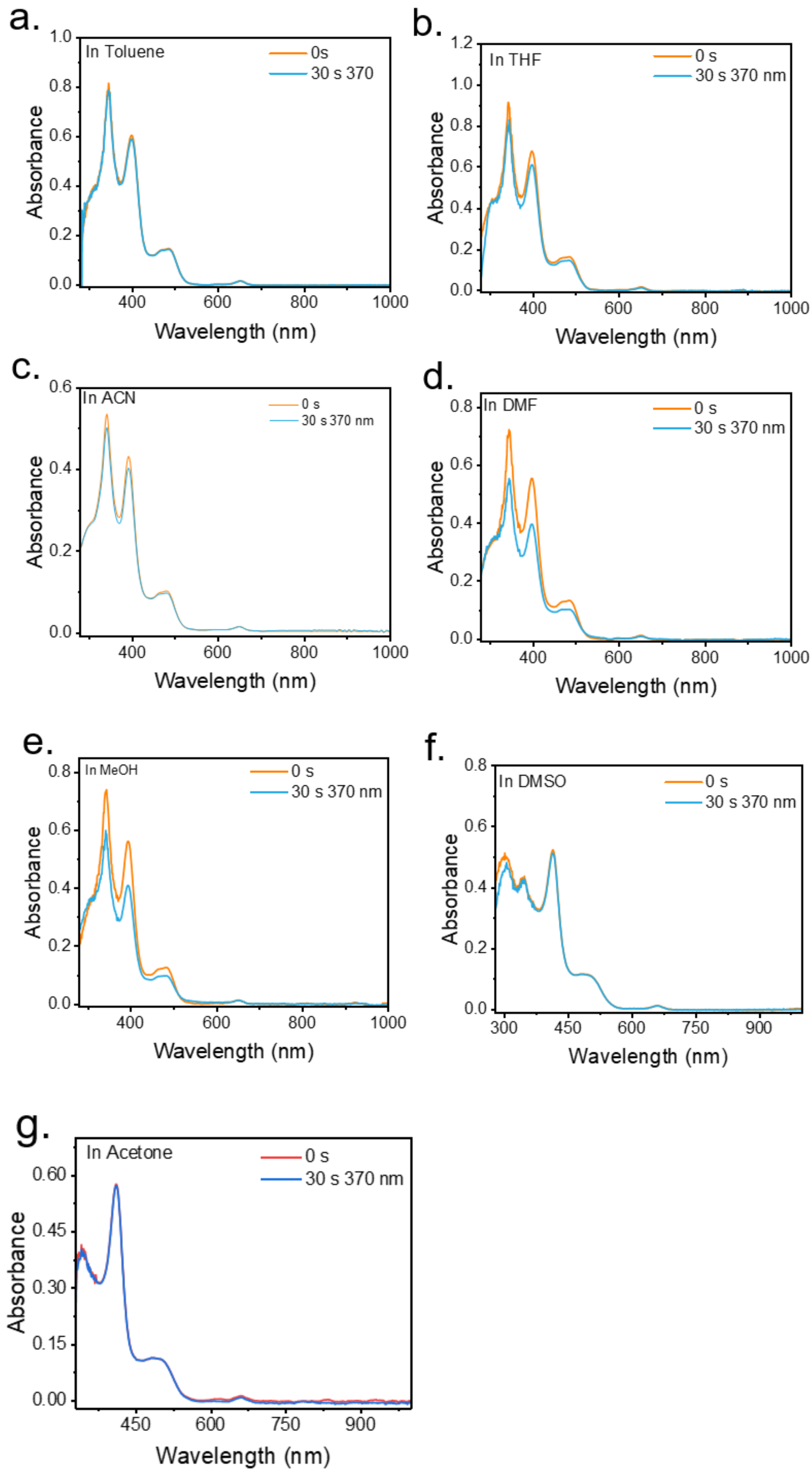


Figure S36: Before and after irradiation with 370 nm light in different solvents: (a) toluene, (b) THF, (c) ACN, (d) DMF, (e) MeOH, (f) DMSO, and (g) Acetone, showing that the formation of radical cation takes place only in chlorinated solvents e.g., chloroform.

13. Control experiments of radical generation

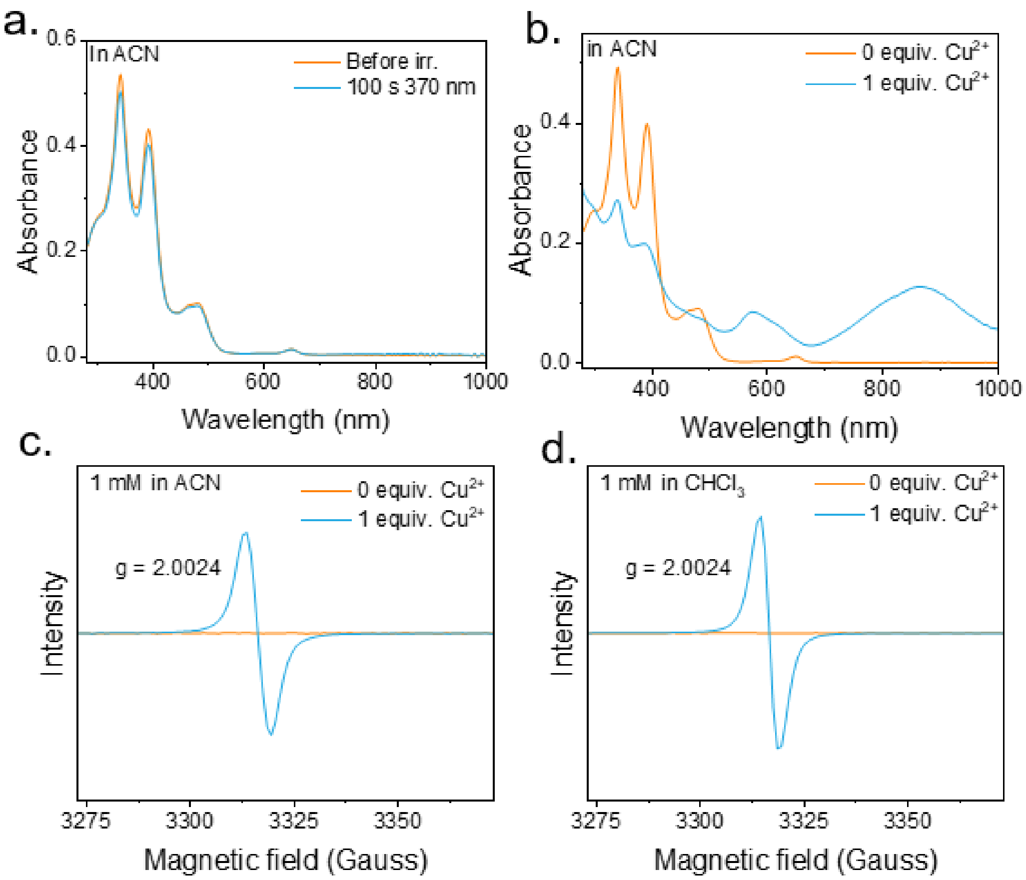


Figure S37: (a) **1c** upon 370 nm irradiation. [observation: no radical formation.] (b) **1c**, when 1 equivalent of Cu^{2+} was added. [observation: radical cation forms chemically in non-chlorinated solvents like ACN.] (c) and (d) are EPR spectra of compound **1** upon chemical oxidation with Cu^{2+} in ACN and $CHCl_3$, respectively.

14. EPR measurements

For radical generation experiments, we used $CHCl_3$ without purging with N_2 or Ar gas. We tried purging with N_2, but did not observe any changes in its properties.

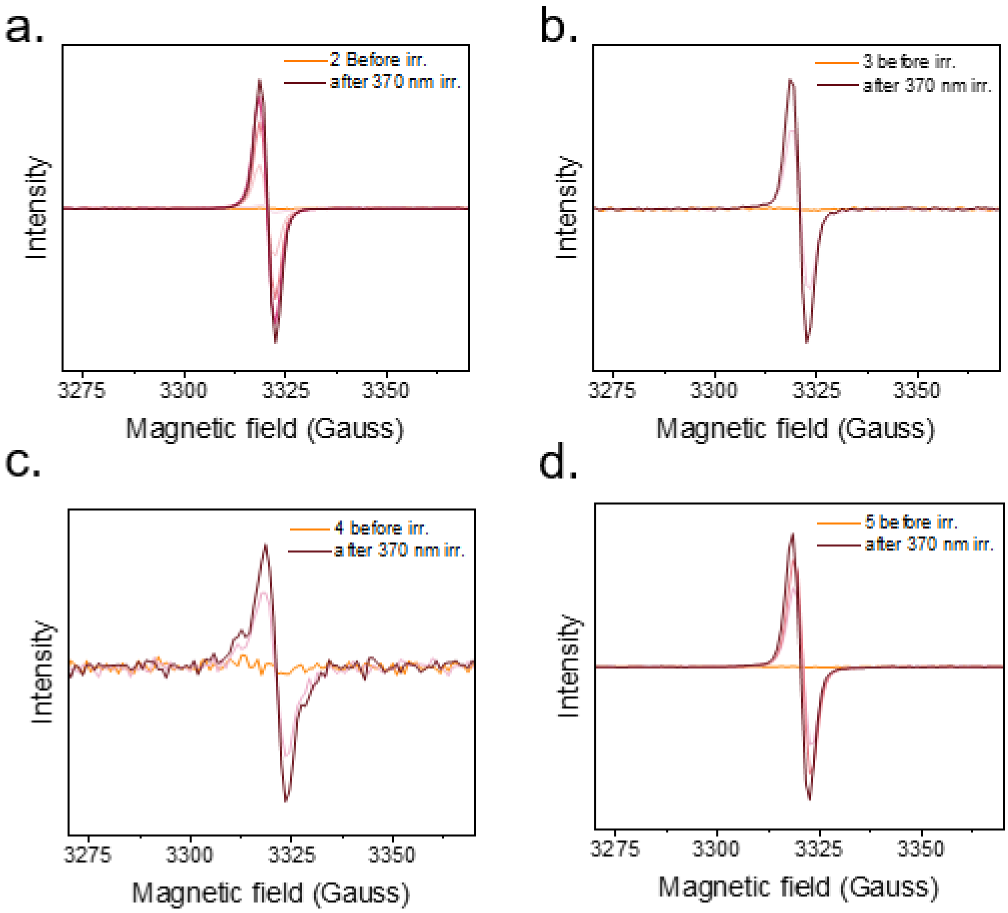


Figure S38: EPR spectra of (a) **2** (b) **3** (c) **4**, and (d) **5** upon 370 nm irradiation. [observation: radical formation after 370 nm light irradiation in $CHCl_3$.

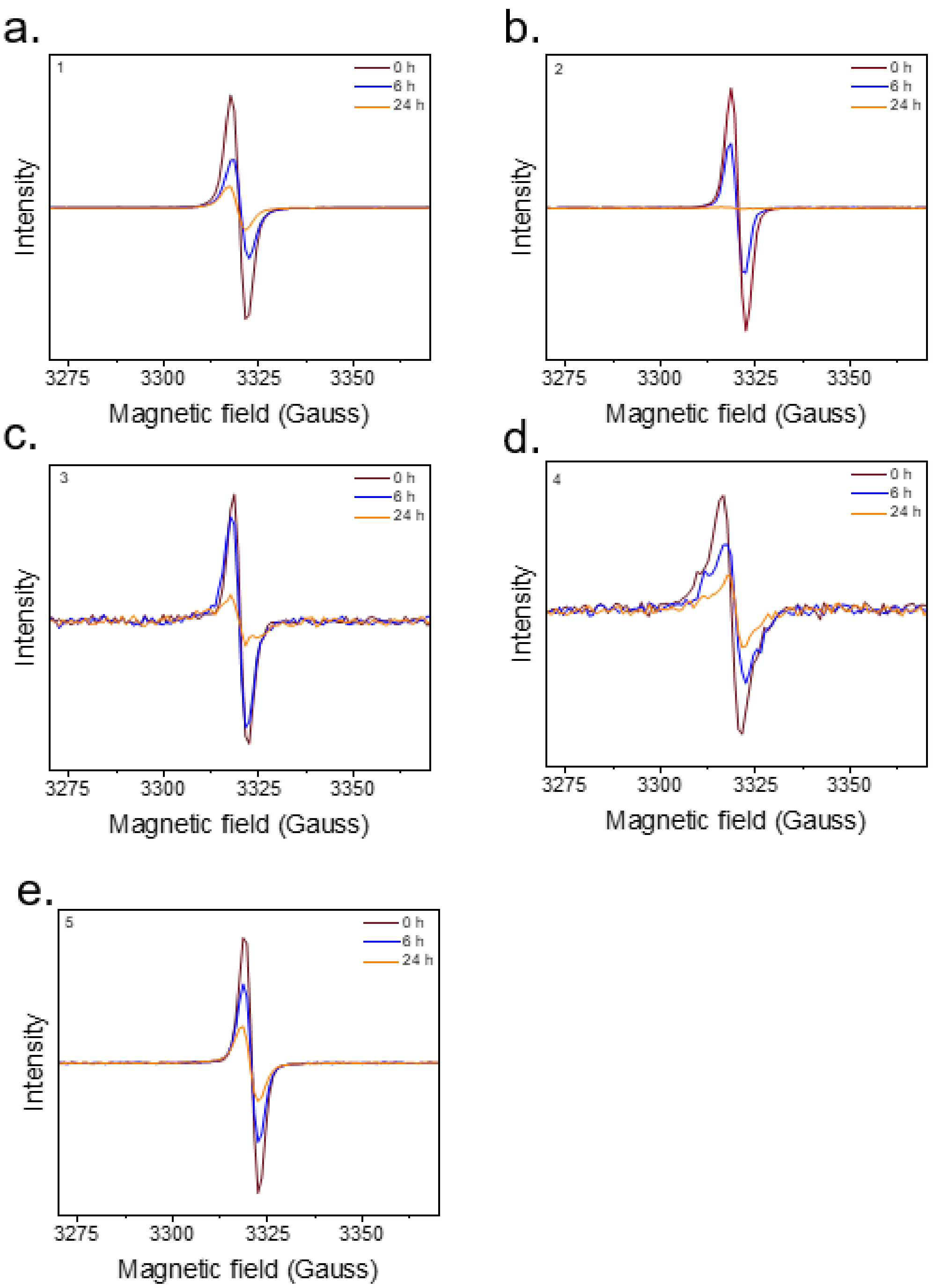


Figure S39: EPR spectra of (a) **1** (b) **2** (c) **3** (d) **4**, and (e) **5** monitored over intervals up to 24 h after exposure to 370 nm light for 180 s. [observation: Even after 24 h, reduced EPR signals were still detected for derivatives **1**, **3**, **4**, and **5**, whereas the signal corresponding to compound **2** completely disappeared]

15. SCXRD data of compounds **1** and **2**

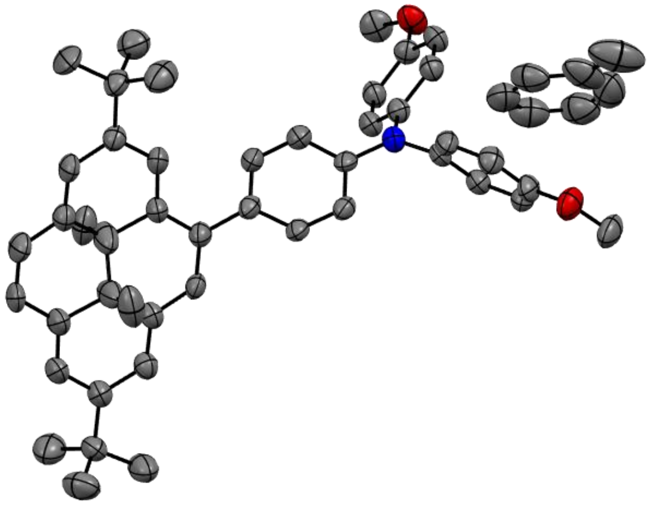


Figure S40: ORTEP diagram (with 50% thermal ellipsoid probability) of **1**. Hydrogen atoms are omitted for clarity.

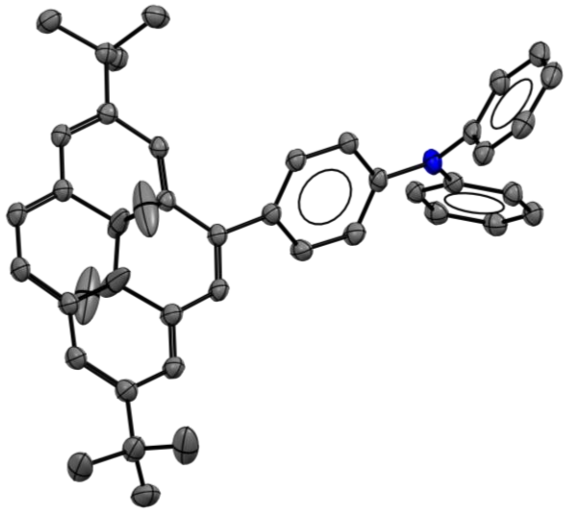


Figure S41: ORTEP diagram (with 50% thermal ellipsoid probability) of **2**. Hydrogen atoms are omitted for clarity.

Table S7 Crystal data and structure refinement for **1** and **2**.

CCDC	2507057	2507332
Identification code	SM_DT1	SB_SM_DP1_auto
Empirical formula	$C_{46}H_{49}N_{1}O_{2}$, $C_{7}H_{8}$	$C_{44}H_{45}N$
Formula weight	734.40	587.81
Temperature/K	106(9)	100.00(10)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a/Å	10.2446(2)	10.4823(2)
b/Å	42.1839(8)	12.4252(2)
c/Å	9.66550(10)	13.6567(3)
α/°	90	83.446(2)
β/°	92.302(2)	79.691(2)
γ/°	90	73.563(2)
Volume/Å^3	4173.64(12)	1674.67(6)
Z	4	2
ρ_{calc}g/cm^3	1.169	1.166
μ/mm^{-1}	0.532	0.497
F(000)	1579.0	632.0
Crystal size/mm^3	0.2 × 0.15 × 0.1	0.5 × 0.5 × 0.05
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.19 to 137.314	6.594 to 136.77
Index ranges	-12 ≤ h ≤ 12, -50 ≤ k ≤ 45, -11 ≤ l ≤ 11	-12 ≤ h ≤ 11, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	28717	33880
Independent reflections	7405 [R_{int} = 0.0756, R_{sigma} = 0.0528]	6110 [R_{int} = 0.0328, R_{sigma} = 0.0206]
Data/restraints/parameters	7405/93/552	6110/0/414
Goodness-of-fit on F^2	1.117	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0989, wR_2 = 0.2707	R_1 = 0.0827, wR_2 = 0.1882

Final R indexes [all data]	R_1 = 0.1339, wR_2 = 0.3464	R_1 = 0.0895, wR_2 = 0.1932
Largest diff. peak/hole / e Å^{-3}	0.91/-0.57	1.10/-1.11

16. Optimized coordinates

Ground state for 1, closed, neutral

C	-5.88993500	2.30886500	0.16208700
C	-6.57391600	1.09052900	0.12109300
C	-5.90167500	-0.12692800	-0.03173600
C	-4.41374400	-0.05583000	-0.34684500
C	-3.74666400	1.06975200	0.46751200
C	-4.49220000	2.37591600	0.22451600
C	-3.68056400	-1.36256900	-0.10884000
C	-2.28701300	-1.30087000	-0.01101700
C	-1.56268200	-0.09652000	0.04501500
C	-2.25321600	1.13746900	0.15158700
C	-1.65022000	2.39007400	0.08425900
C	-2.36768700	3.60102300	0.13756300
C	-3.77107100	3.56368200	0.18620500
C	-6.52887200	-1.37140400	-0.04181900
C	-5.81793400	-2.58107800	-0.11484000
C	-4.40910200	-2.54666700	-0.10771000
C	-0.07708100	-0.17585800	0.02231700
C	0.58724400	-0.90791300	-0.97334800
C	1.97052300	-1.03431000	-0.99001200
C	2.75943000	-0.42303000	-0.00194900
C	2.10334600	0.30844000	1.00238900
C	0.71918600	0.42160200	1.01157900
N	4.16586200	-0.54193400	-0.01582200
C	4.90331800	-0.58505800	1.20326900
C	4.87609300	-0.62201400	-1.24899800
C	5.86791500	-1.59619600	-1.43979400
C	6.57451300	-1.66622600	-2.62976500
C	6.29840300	-0.77621200	-3.67555400
C	5.30729300	0.19323500	-3.49939100
C	4.61623100	0.27120400	-2.29036800
C	6.04415500	0.21348500	1.37597100
C	6.77575900	0.16119200	2.55162200
C	6.37859900	-0.67764900	3.60084500
C	5.23933900	-1.47153500	3.44278300
C	4.52134500	-1.42935700	2.24773000
O	7.04159200	-0.93588900	-4.80886300
C	6.80594300	-0.05739000	-5.90097100
O	7.15986800	-0.64743000	4.71921100
C	6.80768400	-1.48442400	5.81258900

C	-1.66041900	4.96789100	0.06765000
C	-0.12701900	4.84366100	0.01803600
C	-2.11694900	5.72839500	-1.19938000
C	-2.02893200	5.79745100	1.31972700
C	-6.52913300	-3.94694300	-0.12901000
C	-8.06284400	-3.81785400	-0.14096500
C	-6.10862300	-4.72882700	-1.39518800
C	-6.12922500	-4.75693600	1.12633300
C	-3.83845100	0.81878200	2.01215900
C	-4.32199500	0.20385800	-1.89107600
H	-6.45682200	3.23654200	0.16591600
H	-7.65965900	1.08727300	0.17689100
H	-1.73261900	-2.23515800	0.02158500
H	-0.58033200	2.42499000	-0.06605100
H	-4.33175900	4.49259300	0.13072900
H	-7.60843300	-1.38840500	0.05701200
H	-3.85534500	-3.47961400	-0.05358800
H	0.00701000	-1.38738000	-1.75566100
H	2.44643000	-1.60965100	-1.77550200
H	2.68405300	0.78542900	1.78325400
H	0.24470700	0.97991900	1.81179100
H	6.08570200	-2.29936000	-0.64366500
H	7.34231700	-2.41770100	-2.77768000
H	5.07184600	0.90235200	-4.28286900
H	3.85931000	1.03676700	-2.16066100
H	6.35797100	0.87571000	0.57677700
H	7.65872400	0.77645400	2.68556800
H	4.90684400	-2.13676800	4.22957900
H	3.64729100	-2.06055200	2.13148400
H	7.49660600	-0.36474300	-6.68375500
H	5.77886600	-0.14359000	-6.27075600
H	7.00814300	0.98385700	-5.62916900
H	7.55557700	-1.29939800	6.58112800
H	5.81640600	-1.23538000	6.20552500
H	6.83203800	-2.54249900	5.53188200
H	0.32103500	5.84082700	0.00026000
H	0.27155400	4.32142400	0.89190100
H	0.21609000	4.31797900	-0.87691400
H	-1.61852400	6.70095600	-1.26000300
H	-3.19398600	5.90980400	-1.20528400
H	-1.86935300	5.16606500	-2.10391200
H	-1.70527500	5.29221700	2.23404200
H	-1.54127800	6.77673000	1.28553500
H	-3.10522200	5.96675500	1.39746200
H	-8.51472300	-4.81257600	-0.18120200
H	-8.44238400	-3.32583500	0.75855300
H	-8.42041100	-3.26036500	-1.01094200

H	-6.59936100	-5.70683100	-1.41988300
H	-5.03035900	-4.89882700	-1.43261700
H	-6.39129600	-4.18743000	-2.30234900
H	-6.41472900	-4.22914200	2.04044400
H	-6.63152700	-5.72935600	1.12745900
H	-5.05384900	-4.94220500	1.17169400
H	-3.32737400	-0.10229400	2.29561100
H	-3.36004800	1.64955600	2.53450800
H	-4.87589900	0.76109800	2.34428900
H	-4.79961500	-0.62336800	-2.41919500
H	-4.83238500	1.12697800	-2.16863800
H	-3.28358000	0.26481200	-2.22013800

Ground state for 1, open, neutral

C	-5.90663700	1.38395800	1.48395800
C	-6.55531200	0.69668500	0.51619000
C	-5.89896500	-0.17617300	-0.49363700
C	-4.69482600	0.20402200	-1.11867300
C	-3.48886200	0.60463200	1.29168300
C	-4.43600700	1.62858500	1.53401300
C	-3.75409500	-0.82363400	-1.36112700
C	-2.28492100	-0.62868900	-1.26885800
C	-1.59715200	0.06357100	-0.31477900
C	-2.29558000	0.98236000	0.65049200
C	-1.89057100	2.33002600	0.68863800
C	-2.69257700	3.33047000	1.23916000
C	-4.00467200	2.95808200	1.56817400
C	-6.33439300	-1.50968500	-0.58964700
C	-5.54007400	-2.50451100	-1.16616400
C	-4.21519300	-2.14568900	-1.45117000
C	-0.11531800	0.00304200	-0.27608900
C	0.66871700	-0.11741600	-1.43505700
C	2.05148400	-0.22631900	-1.37569000
C	2.72393000	-0.20289300	-0.14215600
C	1.95054000	-0.05841200	1.02273500
C	0.56899500	0.04341900	0.95058700
N	4.12859500	-0.30554500	-0.07396100
C	4.75726400	-0.94873200	1.03235900
C	4.94656200	0.20084000	-1.12633800
C	4.75892900	1.50126700	-1.62053100
C	5.55867400	1.99527900	-2.63798800
C	6.58713100	1.21241000	-3.17969400
C	6.79160300	-0.07823600	-2.68565600
C	5.96776500	-0.57585000	-1.67548900
C	5.84687200	-0.34754500	1.68078400
C	6.47398200	-0.97568100	2.74467100

C	6.01917600	-2.21752100	3.20716700
C	4.92982500	-2.82169500	2.57384100
C	4.31809100	-2.19265600	1.48936200
O	7.32368600	1.79566900	-4.16898500
C	8.37795100	1.04613700	-4.75807100
O	6.69781400	-2.74608300	4.26630600
C	6.28042800	-4.00560400	4.77587000
C	-2.23470300	4.79095500	1.39010500
C	-0.77030400	4.98820900	0.96045000
C	-3.11820100	5.71902700	0.52594000
C	-2.36100500	5.20643400	2.87349200
C	-6.02237900	-3.94858400	-1.38552300
C	-7.50081900	-4.13178900	-0.99983600
C	-5.86759000	-4.30888000	-2.88052900
C	-5.17974700	-4.92773900	-0.53721000
C	-3.73605200	-0.82097300	1.71906700
C	-4.45002700	1.62867500	-1.54405900
H	-6.51900700	1.92549200	2.20294500
H	-7.64158000	0.65689900	0.57666600
H	-1.69534700	-1.27960500	-1.91099000
H	-0.93738600	2.58051900	0.24045900
H	-4.73730000	3.72211300	1.81101200
H	-7.29605800	-1.75915600	-0.15571600
H	-3.49278400	-2.91529900	-1.70618000
H	0.18948600	-0.11294400	-2.40846300
H	2.61912600	-0.32024300	-2.29395500
H	2.43999600	-0.02279900	1.98895200
H	0.00339200	0.15896100	1.86937900
H	3.97688000	2.12442000	-1.20115900
H	5.41509300	2.99957500	-3.02128000
H	7.57558300	-0.71165200	-3.08091800
H	6.12949400	-1.58252100	-1.30627400
H	6.20298900	0.61871200	1.34126300
H	7.31658800	-0.51263700	3.24640900
H	4.55516500	-3.78374800	2.89980500
H	3.48210300	-2.67748800	0.99752000
H	8.82178400	1.69721400	-5.50860700
H	9.13901400	0.77503200	-4.01898200
H	8.00249900	0.13899600	-5.24288500
H	6.94941200	-4.22690500	5.60513500
H	5.24956700	-3.96797900	5.14309200
H	6.36862300	-4.79312200	4.02023700
H	-0.47292600	6.02733200	1.12605200
H	-0.08809000	4.35461900	1.53357900
H	-0.62071300	4.77312800	-0.10110100
H	-2.79337500	6.75926000	0.62818900
H	-4.17005400	5.67392000	0.81768600

H	-3.05411000	5.44899200	-0.53178500
H	-3.38972500	5.12208900	3.23222400
H	-1.73438000	4.57738900	3.51191400
H	-2.04524400	6.24568100	3.00947300
H	-7.81525700	-5.15694500	-1.21377600
H	-7.67277600	-3.95575300	0.06560000
H	-8.15497000	-3.46190900	-1.56459900
H	-6.20029200	-5.33530900	-3.06523200
H	-4.82876700	-4.23167500	-3.21028000
H	-6.46516400	-3.64237300	-3.50871200
H	-5.26469900	-4.69712200	0.52837700
H	-5.52227200	-5.95642600	-0.68772200
H	-4.12033100	-4.89268800	-0.80138300
H	-3.71801500	-0.85565100	2.81467600
H	-4.69697800	-1.22353000	1.40477700
H	-2.95121000	-1.48562200	1.36031100
H	-4.57079700	1.67487800	-2.63337400
H	-5.17940900	2.31131100	-1.11117800
H	-3.45156700	1.99762100	-1.32061700

Ground state for 1c+

C	-5.93154300	2.18989400	-0.56071600
C	-6.58155700	1.04864600	-0.13170400
C	-5.88028300	-0.15367900	0.13618400
C	-4.42204100	-0.20211800	-0.27454500
C	-3.73246600	1.15224400	0.02776200
C	-4.51994800	2.26664700	-0.62953600
C	-3.64809600	-1.32669000	0.36819300
C	-2.25560700	-1.24278700	0.36975900
C	-1.54061900	-0.09522300	-0.02170500
C	-2.26786500	1.09912300	-0.37205600
C	-1.71015800	2.19082900	-1.00964300
C	-2.45534800	3.33449500	-1.38853800
C	-3.84709100	3.33710400	-1.19723700
C	-6.47834300	-1.28511700	0.64839600
C	-5.74279200	-2.45446000	0.98153500
C	-4.35059300	-2.43060300	0.86516500
C	-0.07696500	-0.15216800	-0.02183100
C	0.59906600	-1.32220600	-0.43476700
C	1.97385700	-1.42600500	-0.39172900
C	2.76218100	-0.36207100	0.10374200
C	2.09695400	0.80837200	0.53466400
C	0.72291000	0.90824700	0.46010500
N	4.14720700	-0.46559600	0.17352000
C	4.88812100	0.26382200	1.15304800

C	4.87139000	-1.31088200	-0.72017900
C	5.85274100	-2.18421500	-0.22539700
C	6.57103600	-2.99043100	-1.08831000
C	6.32905700	-2.94962800	-2.47110000
C	5.35364000	-2.07741200	-2.97045200
C	4.63916500	-1.26278700	-2.09702000
C	6.02075500	1.00198400	0.77668800
C	6.75143900	1.69367400	1.72481600
C	6.37118400	1.66833100	3.07650200
C	5.24462900	0.92880900	3.45781400
C	4.51682800	0.23010100	2.49921200
O	7.08494100	-3.77975800	-3.22684800
C	6.90524900	-3.78183900	-4.64180900
O	7.15155000	2.37989700	3.92293500
C	6.83326000	2.38798900	5.31336400
C	-1.79112200	4.54479600	-2.06067100
C	-0.26654100	4.38737400	-2.20177500
C	-2.38882200	4.74112900	-3.47518400
C	-2.06829000	5.80536800	-1.20606500
C	-6.43259300	-3.71599500	1.52530700
C	-7.96422200	-3.57648400	1.58742400
C	-6.09638400	-4.91024500	0.60071100
C	-5.91667200	-4.01188400	2.95396000
C	-3.73877200	1.47821500	1.56528100
C	-4.42146700	-0.51333200	-1.81417500
H	-6.51235300	3.06035700	-0.85017000
H	-7.66149300	1.05709900	-0.01807800
H	-1.69740300	-2.09653400	0.73947900
H	-0.66446300	2.14932400	-1.27561700
H	-4.43395000	4.17263500	-1.56308100
H	-7.54414200	-1.25465300	0.83821700
H	-3.77203200	-3.28148900	1.20930000
H	0.02768700	-2.15990200	-0.81888400
H	2.45202100	-2.33872400	-0.72332200
H	2.67248000	1.63888900	0.92271000
H	0.25076200	1.81464300	0.81925800
H	6.04426300	-2.22922000	0.84043500
H	7.32646900	-3.67230900	-0.71540900
H	5.15436800	-2.01012500	-4.03193900
H	3.90154200	-0.57484800	-2.49447100
H	6.32058800	1.03270200	-0.26443200
H	7.62386700	2.27197400	1.44354700
H	4.93622100	0.87511700	4.49349800
H	3.65723700	-0.35542600	2.80558400
H	7.60786700	-4.51772000	-5.02529900
H	5.88668200	-4.07560300	-4.91154900
H	7.13373100	-2.80220800	-5.07150500

H	7.58607300	3.01650500	5.78284100
H	5.84133400	2.81380200	5.49118100
H	6.88450000	1.38089800	5.73714700
H	0.15126700	5.28886100	-2.65539700
H	0.22517800	4.25292900	-1.23449800
H	0.00629200	3.54707600	-2.84572800
H	-1.91143700	5.59399500	-3.96513300
H	-3.46274500	4.93703300	-3.44916700
H	-2.22338800	3.85912700	-4.09945100
H	-1.64729000	5.70235600	-0.20218600
H	-1.61094400	6.68143800	-1.67369800
H	-3.13629300	6.00786800	-1.10189300
H	-8.39936700	-4.50860200	1.95478400
H	-8.28142500	-2.78302800	2.26919000
H	-8.40017000	-3.38022600	0.60421900
H	-6.57925900	-5.81804200	0.97236900
H	-5.02271600	-5.10387000	0.55158900
H	-6.45261600	-4.73351400	-0.41769600
H	-6.13360100	-3.18237200	3.63226800
H	-6.40689400	-4.90576300	3.34920900
H	-4.83960800	-4.19102200	2.97681700
H	-3.18842800	0.72415600	2.12792300
H	-3.26456600	2.44662000	1.73159000
H	-4.75837600	1.52776500	1.94842200
H	-4.89263200	-1.48128700	-1.98885000
H	-4.97707700	0.24313000	-2.36868400
H	-3.40170700	-0.55533100	-2.19972000

Excited state for 1, closed

C	-5.86654700	2.29562500	-0.27079200
C	-6.54417900	1.08814600	-0.09384100
C	-5.87817800	-0.13842200	-0.01422900
C	-4.39998400	-0.13051600	-0.31997000
C	-3.72415100	1.14812800	0.24043200
C	-4.46925200	2.37662700	-0.22666900
C	-3.66617900	-1.36034800	0.14521000
C	-2.27754400	-1.27743300	0.23523300
C	-1.55720100	-0.07813100	0.07667500
C	-2.24144700	1.15293600	-0.06289800
C	-1.62651100	2.35893700	-0.41031500
C	-2.35668200	3.54050800	-0.60676700
C	-3.75334300	3.54206000	-0.50884000
C	-6.51875600	-1.35325600	0.24268900
C	-5.79548300	-2.54099600	0.42106100
C	-4.39469200	-2.53103800	0.38763300
C	-0.07913500	-0.15875000	0.06136500
C	0.57525100	-1.11274900	-0.72134600

C	1.95309300	-1.24087400	-0.71465600
C	2.74346700	-0.41053000	0.08523600
C	2.09704100	0.54393600	0.87839400
C	0.71927500	0.66058100	0.86425300
N	4.14334200	-0.53111500	0.09376300
C	4.89150900	-0.23517200	1.26548600
C	4.84291000	-0.95412200	-1.06911800
C	5.81418300	-1.95433900	-0.98722900
C	6.51090700	-2.35491800	-2.10930300
C	6.24290200	-1.78030900	-3.35155500
C	5.27273600	-0.78836300	-3.44584900
C	4.59195100	-0.37545900	-2.30633800
C	6.02359600	0.57979500	1.19573000
C	6.76630200	0.85411400	2.32616500
C	6.38712500	0.33749300	3.56497500
C	5.25724500	-0.46909700	3.64729900
C	4.52842200	-0.75874600	2.49941000
O	6.97270600	-2.25003600	-4.39654700
C	6.74495200	-1.69377600	-5.67559300
O	7.17569600	0.67427500	4.61856200
C	6.83845700	0.17034600	5.89511200
C	-1.65215600	4.84780400	-0.97873000
C	-0.12810700	4.71066600	-1.05033000
C	-2.15229000	5.32178400	-2.35460800
C	-1.98435100	5.91330400	0.08064900
C	-6.50778300	-3.86650100	0.70380700
C	-8.03416000	-3.73750200	0.70658000
C	-6.11904200	-4.88612700	-0.38087300
C	-6.07263800	-4.39555400	2.08155300
C	-3.83270500	1.17466900	1.79709600
C	-4.29241300	-0.14983000	-1.87629900
H	-6.43283200	3.20410200	-0.44916200
H	-7.62796200	1.09294000	-0.02528900
H	-1.72461500	-2.18181200	0.46689200
H	-0.56324300	2.35796900	-0.58591900
H	-4.31243900	4.44260900	-0.73162500
H	-7.59417600	-1.34564300	0.35380800
H	-3.84193100	-3.43573600	0.60956200
H	-0.01056400	-1.76939300	-1.35542600
H	2.42436500	-1.99236500	-1.33583500
H	2.68276900	1.19675400	1.51355700
H	0.24975000	1.40271900	1.49984300
H	6.02456400	-2.41502400	-0.02913700
H	7.26747200	-3.12843500	-2.05055300
H	5.04417100	-0.31683100	-4.39220700
H	3.84669400	0.40728700	-2.38664300
H	6.32258600	0.99489800	0.24036600
H	7.64719000	1.48322500	2.27686200
H	4.93819600	-0.89177100	4.59058100
H	3.65710900	-1.39929500	2.57053700
H	7.42426900	-2.20690900	-6.35174100

H	5.71522100	-1.85835500	-6.00614200
H	6.96321600	-0.62199600	-5.69048800
H	7.58912200	0.55825900	6.57921600
H	5.84973300	0.51415000	6.21267100
H	6.86501900	-0.92304300	5.91361700
H	0.31275600	5.67974500	-1.29348500
H	0.29957400	4.38485200	-0.10012800
H	0.18578700	4.00692000	-1.82361300
H	-1.64640400	6.24873600	-2.63659300
H	-3.22542500	5.51392100	-2.35948100
H	-1.94264600	4.57657400	-3.12522000
H	-1.64004400	5.60307800	1.06990500
H	-1.48796400	6.85489100	-0.16755500
H	-3.05506300	6.10799000	0.14645100
H	-8.48201600	-4.71671700	0.88862700
H	-8.38800900	-3.06666600	1.49194000
H	-8.41550900	-3.37467100	-0.24997500
H	-6.62144100	-5.83922300	-0.19645500
H	-5.04517200	-5.07324300	-0.40188300
H	-6.41618300	-4.53607900	-1.37213700
H	-6.32257700	-3.68346100	2.87125200
H	-6.58664300	-5.33504500	2.30054600
H	-5.00001000	-4.58443700	2.13010000
H	-3.31938800	0.31508400	2.22695800
H	-3.37478100	2.08480200	2.18498600
H	-4.87779500	1.15306200	2.10529900
H	-4.75093200	-1.05762700	-2.26809800
H	-4.80581000	0.71201600	-2.30201800
H	-3.24709400	-0.12653100	-2.18459900

Excited state for 1, open

C	-5.81860300	2.04335600	0.41637600
C	-6.49453800	0.82807300	0.22083600
C	-5.86651400	-0.43201600	-0.12374800
C	-4.68610500	-0.49284700	-0.89969300
C	-3.44087300	1.23082100	0.63173200
C	-4.39235000	2.24754700	0.30517500
C	-3.75731100	-1.50591100	-0.57552500
C	-2.30928800	-1.32840400	-0.69718600
C	-1.56625500	-0.13941400	-0.36555100
C	-2.28514400	1.15671500	-0.15405000
C	-1.91783800	2.25974200	-0.93037600
C	-2.67992000	3.43715600	-0.97117500
C	-3.93618700	3.38481200	-0.38587800
C	-6.31058000	-1.60707200	0.52272900
C	-5.53148900	-2.74704400	0.58458400
C	-4.21511800	-2.63438800	0.10339000
C	-0.13777500	-0.18518600	-0.28406300
C	0.64008500	-1.23773000	-0.84308000

C	2.00939900	-1.27375300	-0.73226000
C	2.71362500	-0.26418900	-0.05237000
C	1.96485300	0.78869300	0.50843300
C	0.59675600	0.82550900	0.39539200
N	4.10874500	-0.30116900	0.06163000
C	4.75661900	0.22999700	1.20985100
C	4.90265200	-0.90397800	-0.95133600
C	4.69793400	-0.59138000	-2.29791900
C	5.47153200	-1.17250200	-3.28104300
C	6.48807000	-2.06801300	-2.94605600
C	6.70853600	-2.37568800	-1.60829100
C	5.91058200	-1.80118800	-0.62511700
C	5.86722600	1.06628000	1.07226900
C	6.50853700	1.57369400	2.18325500
C	6.04730800	1.27467300	3.46581000
C	4.93839900	0.44887700	3.61355600
C	4.31061200	-0.07490100	2.48897200
O	7.20004400	-2.57635000	-3.98462300
C	8.23999100	-3.49018900	-3.69993700
O	6.73989500	1.83110300	4.49284000
C	6.31335200	1.56020200	5.81287300
C	-2.22377700	4.69608300	-1.71667400
C	-0.80758200	4.55202300	-2.28226100
C	-3.17748200	4.99239600	-2.88534300
C	-2.23106600	5.88609000	-0.74373800
C	-5.99776200	-4.05073000	1.23773200
C	-7.45876200	-3.97840300	1.69009400
C	-5.86762000	-5.19609300	0.22056800
C	-5.13036800	-4.36472900	2.46750800
C	-3.62119700	0.37033200	1.85040700
C	-4.49437800	0.37218700	-2.11223800
H	-6.43508900	2.93327100	0.52028300
H	-7.55459900	0.80926000	0.46099300
H	-1.74088800	-2.25054000	-0.73659200
H	-1.01672400	2.17922300	-1.52344700
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H	-7.26793100	-1.56647100	1.02888900
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H	0.15472400	-2.02960800	-1.39894200
H	2.55693200	-2.09531700	-1.17774200
H	2.47765400	1.58156700	1.03901600
H	0.05811500	1.64637500	0.85149400
H	3.92118100	0.11383900	-2.56917700
H	5.31700700	-0.93459600	-4.32680900
H	7.48707600	-3.06632800	-1.31322700
H	6.08314600	-2.05321200	0.41461700
H	6.22784900	1.31412400	0.08089300

H	7.37069400	2.22235700	2.08292700
H	4.55758900	0.19202100	4.59291600
H	3.45456500	-0.72773200	2.61299500
H	8.66932000	-3.76536900	-4.66006300
H	9.01424300	-3.03357300	-3.07656200
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H	6.99503600	2.09982400	6.46556800
H	5.29315100	1.91556300	5.98429700
H	6.36786300	0.49148800	6.03953700
H	-0.50407600	5.48720000	-2.75814400
H	-0.07750700	4.32693400	-1.50162300
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H	-2.85209100	5.88440800	-3.42758800
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H	-4.93389800	1.36153800	-2.01423300
H	-3.44808900	0.47936600	-2.38875500

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