

Supporting Information  
for

## **White-Light Emission from a Structurally Simple Hydrazone**

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## **Table of Contents**

<b>1. General Methods</b>	<b>S3</b>
<b>2. Synthesis</b>	<b>S5</b>
<b>3. NMR Characterization</b>	<b>S8</b>
<b>4. Photoisomerization Studies</b>	<b>S12</b>
<b>5. Fluorescence Emission Studies</b>	<b>S15</b>
<b>6. Crystallography</b>	<b>S19</b>
<b>7. Low-Temperature (77 K) Fluorescence Emission Studies</b>	<b>S23</b>

# 1 General Methods

All reagents and starting materials were purchased from commercial vendors and used as supplied unless otherwise indicated. All experiments were conducted under air unless otherwise noted. Compounds were purified by column chromatography using silica gel (SiliCycle<sup>®</sup>, 60 Å, 230-400 mesh) as stationary phase and solvents mixtures used during chromatography were reported as volume ratios unless otherwise noted. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and used as received. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 500 or 600 MHz NMR spectrometer, with working frequencies of 500.13 or 600.13 MHz for <sup>1</sup>H nuclei, and 150.9 MHz for <sup>13</sup>C nuclei, respectively. Chemical shifts are quoted in ppm relative to tetramethylsilane (TMS), using the residual solvent peak as the reference standard. ESI mass spectra were obtained on a Waters Quattro II ESI mass spectrometer. Elemental analysis was performed by Intertek Pharmaceutical Services (Whitehouse, NJ). Melting points were measured on an Electrothermal Thermo Scientific IA9100X1 digital melting point instrument. UV-Vis spectra were recorded on a Shimadzu UV-1800 UV-Vis spectrophotometer.

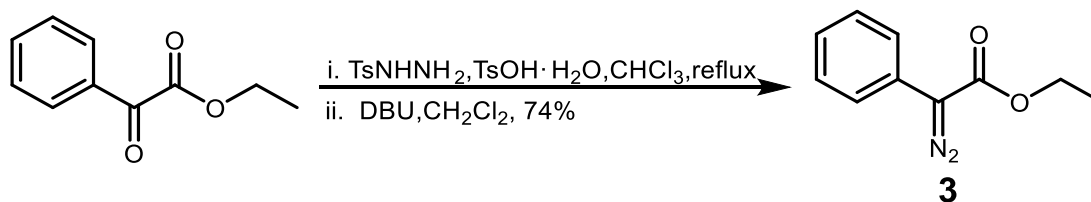
Stock solutions were prepared by dissolving appropriate amounts of **1** or **2** in toluene, followed by stirring to ensure sample homogeneity. The desired concentration was reached by consecutive dilutions. The fluorescence spectra were collected immediately after the sample was prepared. A Photon Technology International QuantaMaster 4 spectrofluorometer outfitted with an LPS-100 lamp power supply and Xenon arc lamp housing, ASOC-10 electronics interface, MD-4 motor driver control, and a model 914D photomultiplier detector system was used to collect fluorescence spectra. Data were acquired with a step size of 0.5 nm, an integration time of 0.1 s, and slit widths of 5 nm.

For fluorescence lifetime measurements, toluene solutions of **1** or **2** ( $5 \times 10^{-6}$  M) were used. The lifetimes were determined by time-correlated single photon-counting (TCSPC) using a Photon Technology International QuantaMaster 4 spectrofluorometer integrated with Deltadiode-375L diode laser ( $\lambda_{\text{ex}} = 373$  nm, < 70 ps pulse width) as the excitation source. The fluorescence decays were detected using a fast PPD-850 detector. In all cases, decays were recorded until peak counts reached 10,000. The decay traces were analyzed by the multi-exponential fitting method using Felix data analysis from Horiba Scientific Ltd. The emission quantum yield of solid powder of **1** was measured

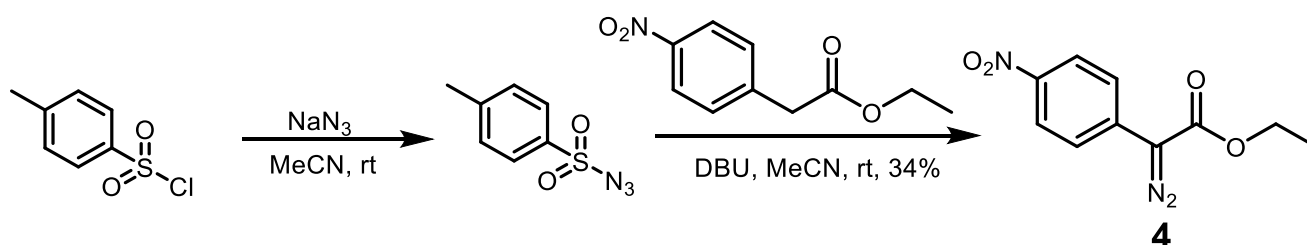
using a Horiba model 914D photomultiplier detector system with a calibrated integrating sphere.

All low temperature (77 K) fluorescence experiments were done using a Photon Technology International QuantaMaster 4 spectrofluorometer with a LPS-220B lamp power supply, A-1010B arc lamp housing, ASOC-10 electronics interface, MD-4000 motor driver, and a model 814 photomultiplier detection system. All spectra were collected using a step size of 0.5 nm, an integration time of 0.1 s, and slit widths of 1 nm. Data were collected in triplicate. The fluorescence of toluene at 77 K was subtracted from the raw fluorescence data of the compounds.

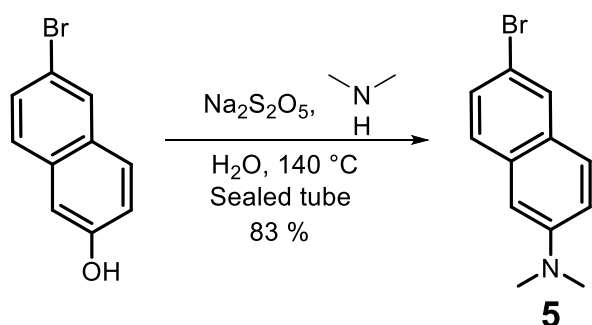
## 2 Synthesis



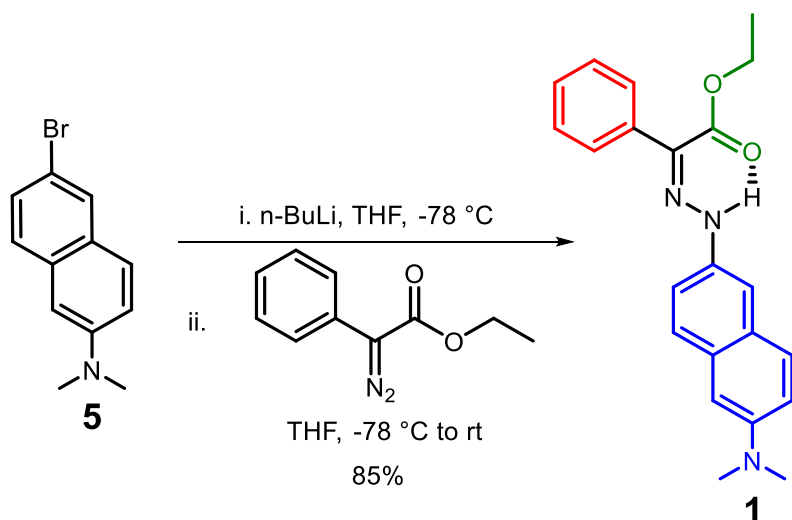
**3:** This compound was synthesized using a reported procedure,<sup>S1</sup> and its identity was confirmed by comparing the obtained <sup>1</sup>H NMR spectrum with the published one. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.39 (dd, *J* = 7.4 Hz, 2H), 7.34 – 7.28 (tt, *J* = 7.5, 1.9 Hz, 2H), 7.11 (tt, *J* = 7.4, 1.2 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).



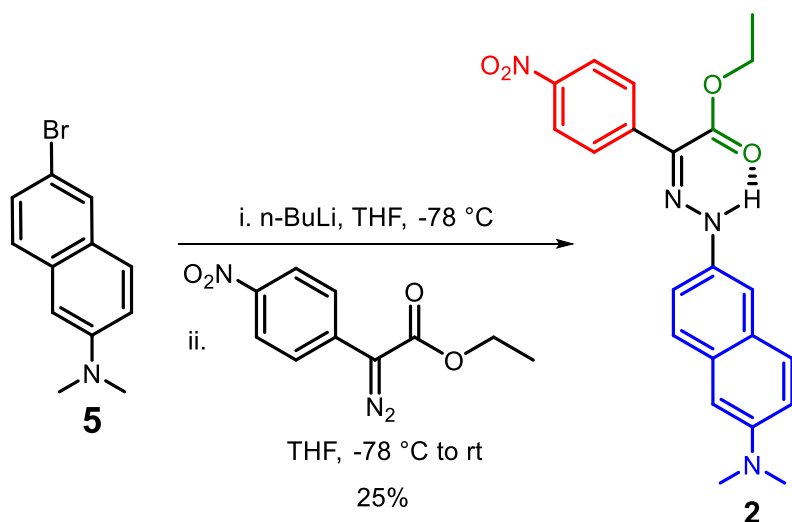
**4:** This compound was synthesized using a reported procedure,<sup>S2</sup> and its identity was confirmed by comparing the obtained <sup>1</sup>H NMR spectrum with the published one. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.31 – 8.17 (m, 2H), 7.73 – 7.62 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).



**5:** This compound was synthesized using a reported procedure,<sup>S3</sup> and its identity was confirmed by comparing the obtained <sup>1</sup>H NMR spectrum with the published one. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 2.0 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.17 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.86 (d, *J* = 2.5 Hz, 1H), 3.05 (s, 6H).

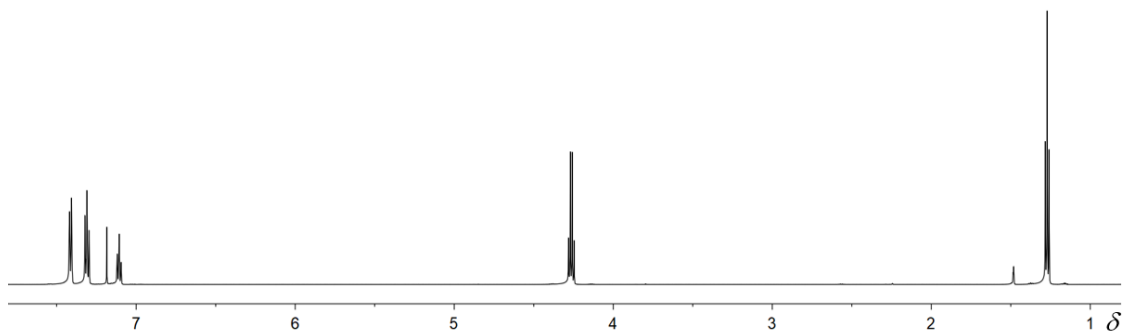
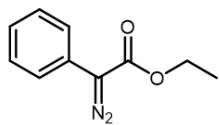


**1**: 6-Bromo-*N,N*-dimethylnaphthalen-2-amine (**5**, 2.0 g, 7.9 mmol, 1.5 equiv.) in THF (30 ml) was added to a flame-dried flask and the solution was cooled to  $-78\text{ }^{\circ}\text{C}$ . 2.5 M *n*-BuLi in hexanes (3.4 ml, 8.4 mmol, 1.6 equiv.) was then added dropwise to the solution, which was left to stir for 30 min at low temperature. Ethyl 2-diazo-2-phenylacetate (**3**, 1.0 g, 5.3 mmol, 1.0 equiv.) dissolved in THF (15 ml) was added dropwise to the lithium reagent, and the mixture was stirred for 1 hour at low temperature. The mixture was then left to warm up to room temperature and stirred for another 2 hours. The mixture was quenched with aqueous ammonium chloride. The mixture was then diluted with water (50 ml) and extracted with  $\text{CH}_2\text{Cl}_2$  (50 ml  $\times$  3). The organic layer was separated and washed with brine (100 ml). After removal of the solvent under reduced pressure, the crude product was subjected to column chromatography (20:1 to 10:1 hexane/ethyl acetate). Compound **1** was obtained as an orange solid (1.6 g, 85 %). m.p.  $100.6\text{--}101.4\text{ }^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  12.42 (s, 1H), 7.76 – 7.71 (m, 2H), 7.71 – 7.66 (m, 2H), 7.57 (d,  $J = 2.0\text{ Hz}$ , 1H), 7.49 (dd,  $J = 8.9, 2.2\text{ Hz}$ , 1H), 7.43 (t,  $J = 7.5\text{ Hz}$ , 2H), 7.37 (t,  $J = 7.3\text{ Hz}$ , 1H), 7.24 (dd,  $J = 9.1, 2.6\text{ Hz}$ , 1H), 7.00 (d,  $J = 2.4\text{ Hz}$ , 1H), 4.38 (q,  $J = 7.1\text{ Hz}$ , 2H), 3.02 (s, 6H), 1.35 (t,  $J = 7.1\text{ Hz}$ , 3H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  164.16, 148.54, 138.76, 137.50, 132.35, 129.95, 129.86, 129.83, 129.19, 128.41, 128.25, 128.10, 128.00, 127.90, 118.12, 116.51, 110.02, 107.23, 61.60, 40.73, 13.99 ppm. ESI-HRMS:  $m/z$  found  $[\text{M}-\text{H}^+]$  for  $\text{C}_{22}\text{H}_{24}\text{N}_3\text{O}_2^+$  362.1861 (calcd. 362.1863). Elemental Analysis:  $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_2$ , calculated C 73.11%, H 6.41%, N 11.63%; found: C 72.78%, 6.27%, N 11.45%.

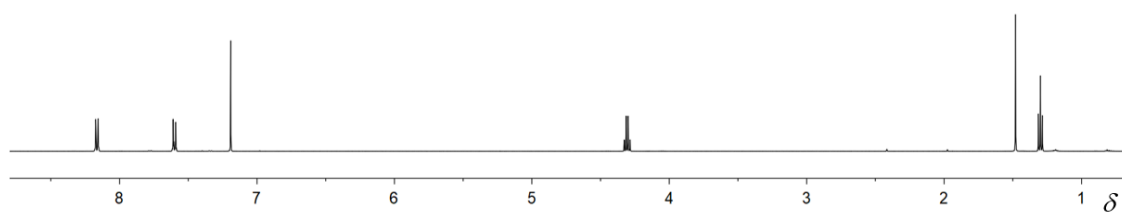
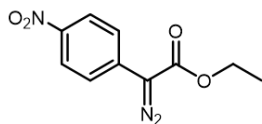


**2**: 6-Bromo-*N,N*-dimethylnaphthalen-2-amine (**5**, 102 mg, 0.5 mmol, 1.5 equiv.) in THF (10 ml) was added to a flame-dried flask and the solution was cooled to -78 °C. 2.5 M *n*-BuLi in hexane (0.22 ml, 0.6 mmol, 1.6 equiv.) was then added dropwise to the solution, which was left to stir for 30 min at low temperature. Ethyl 2-diazo-2-(4-nitrophenyl) acetate (**4**, 87 mg, 0.4 mmol, 1.0 equiv.) dissolved in THF (5 ml) was added dropwise to lithium reagent, and the mixture was stirred for 1 hours at low temperature. Then reaction was then left to warm up to room temperature and stirred for another 3 hours. The mixture was quenched with aqueous ammonium chloride. The mixture was then diluted with water (20 ml) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 ml × 3). The organic layer was separated and washed with brine (20 ml). After removal of the solvent under reduced pressure, the crude was subjected to column chromatography (30:1 to 20:1 hexane/ethyl acetate). Compound **2** was obtained as a red solid (22 mg, 25 %). m.p. 153.1-153.6 °C; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN) δ 12.71 (s, 1H), 8.27 – 8.22 (m, 2H), 8.04 – 7.99 (m, 2H), 7.71 (t, *J* = 9.0 Hz, 2H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.55 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.26 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.03 (s, 6H), 1.38 (t, *J* = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN) δ 163.74, 148.81, 147.17, 143.90, 138.08, 132.86, 129.51, 128.44, 128.22, 127.63, 123.62, 118.13, 116.51, 111.15, 107.06, 61.95, 40.64, 13.95 ppm. ESI-HRMS: *m/z* found [M-H<sup>+</sup>] for C<sub>22</sub>H<sub>23</sub>N<sub>4</sub>O<sub>4</sub><sup>+</sup> 407.1713 (calcd. 407.1714)

### 3 NMR Characterization

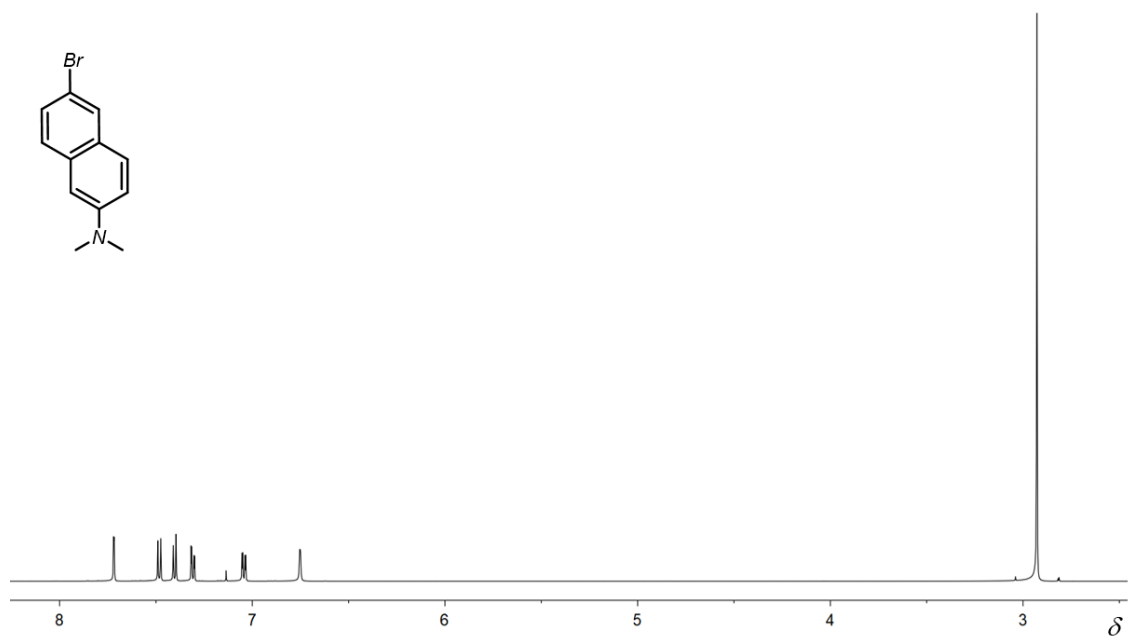


**Figure S1.**  $^1\text{H}$  NMR spectrum of **3** in  $\text{CDCl}_3$  at 294 K.

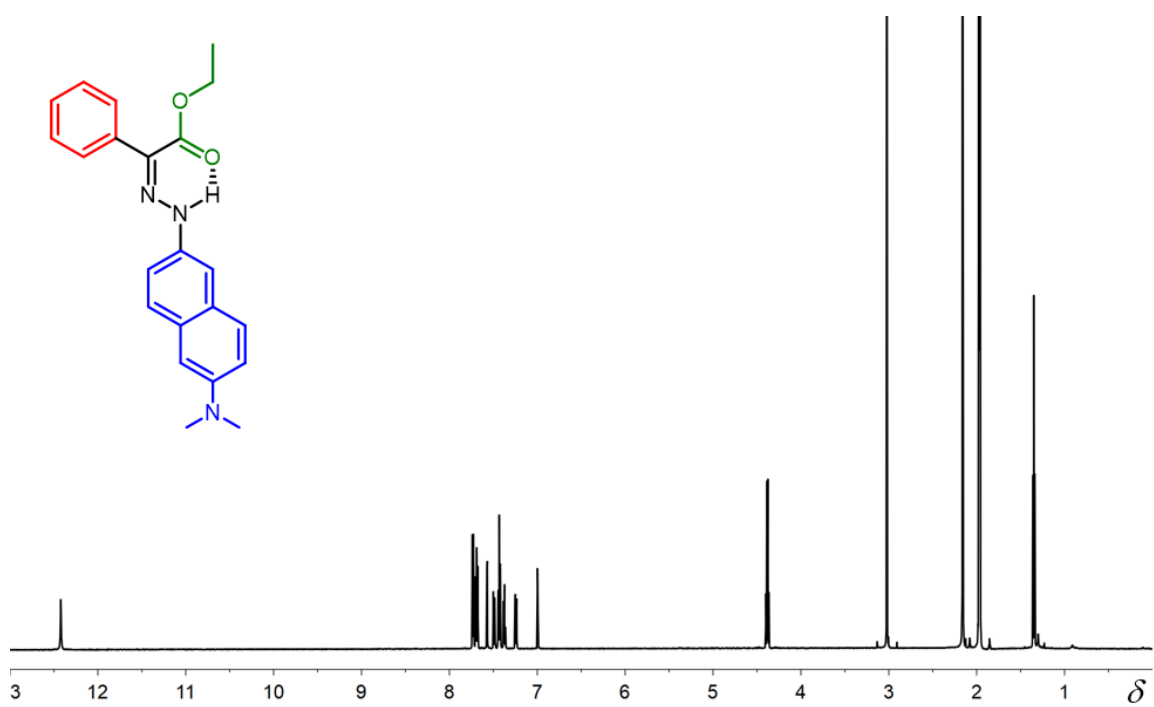


**Figure S2.**  $^1\text{H}$  NMR spectrum of **4** in  $\text{CDCl}_3$  at 294 K.

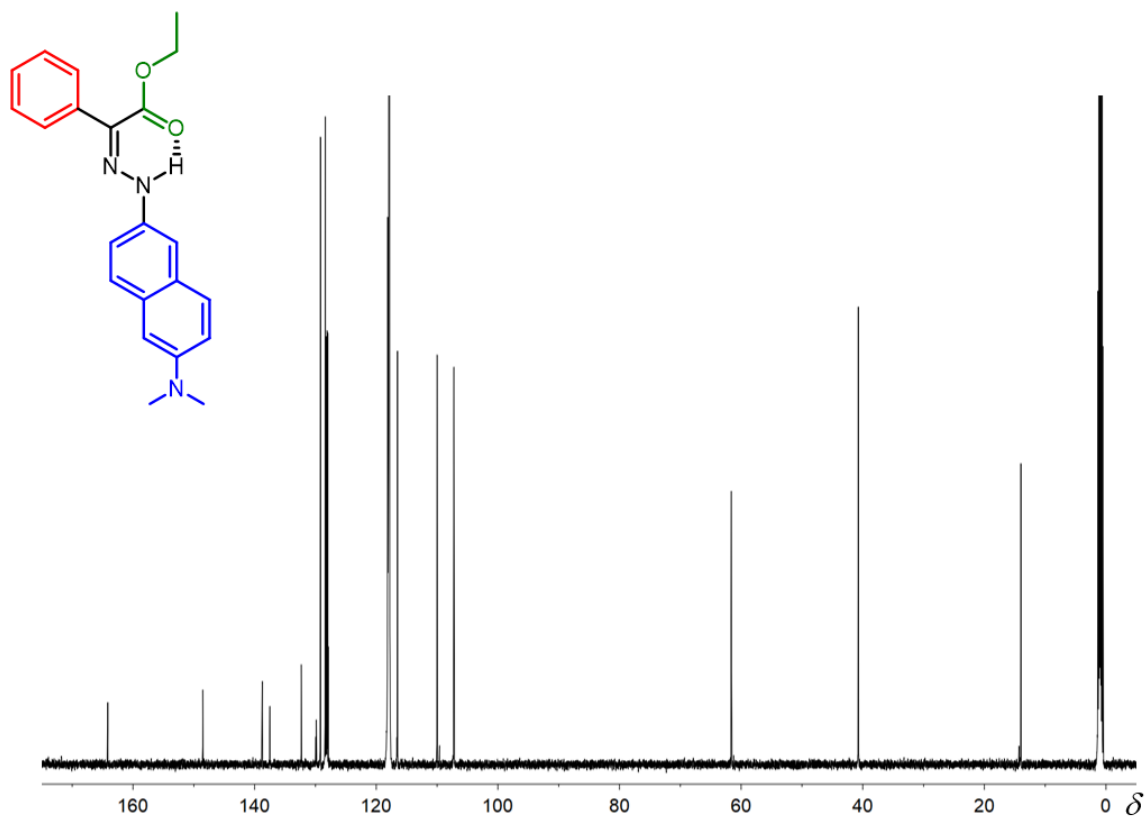




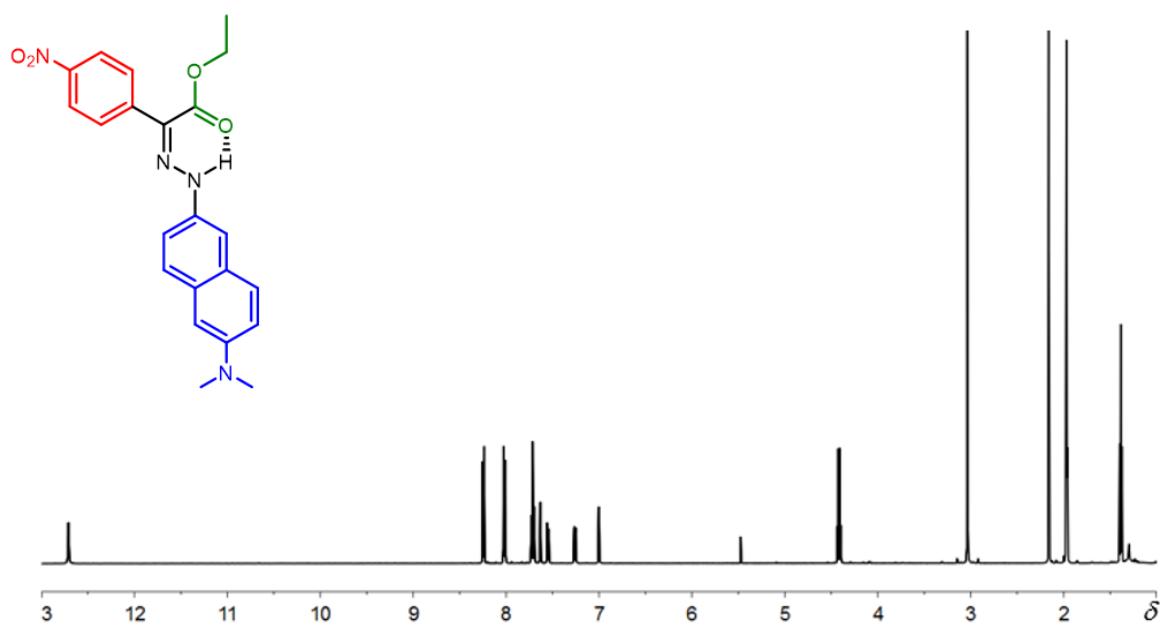
**Figure S3.** <sup>1</sup>H NMR spectrum of **5** in CDCl<sub>3</sub> at 294 K.



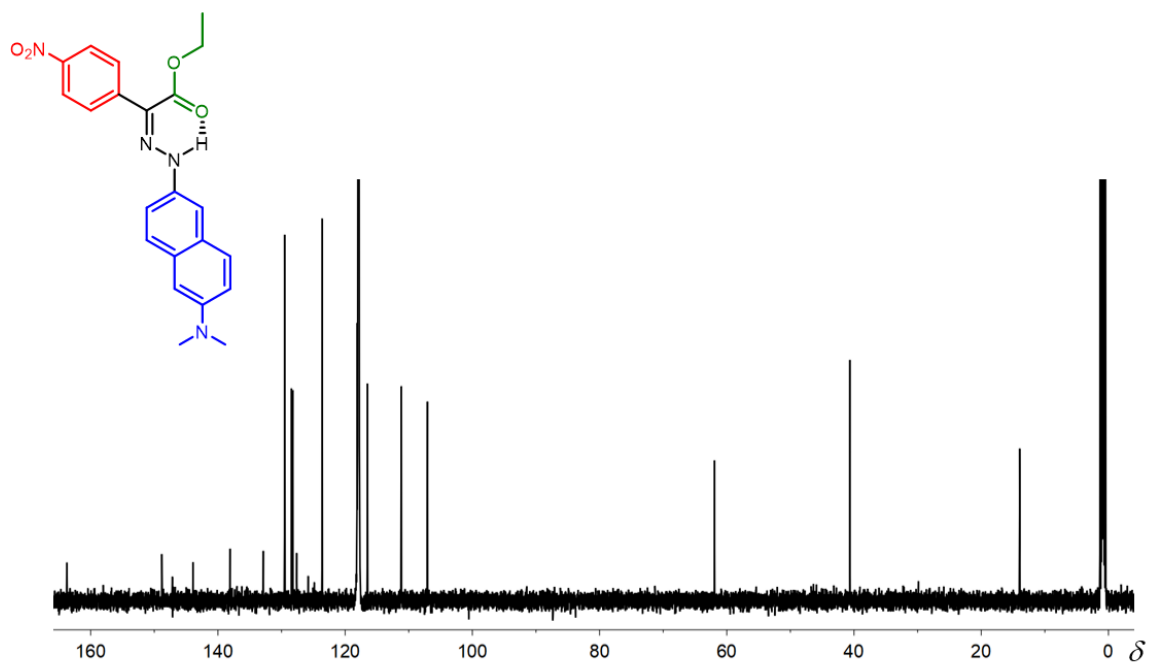
**Figure S4.** <sup>1</sup>H NMR spectrum of **1** in CD<sub>3</sub>CN at 294 K.



**Figure S5.**  $^{13}\text{C}$  NMR spectrum of **1** in  $\text{CD}_3\text{CN}$  at 294 K.



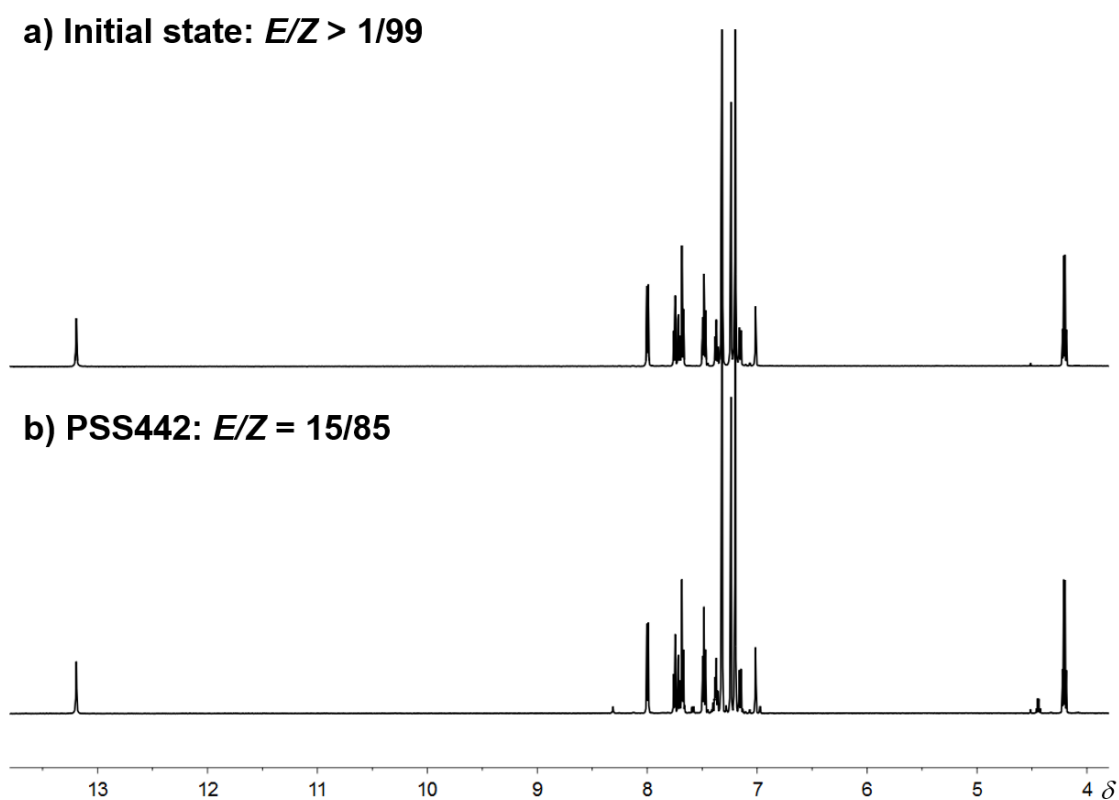
**Figure S6.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_3\text{CN}$  at 294 K.



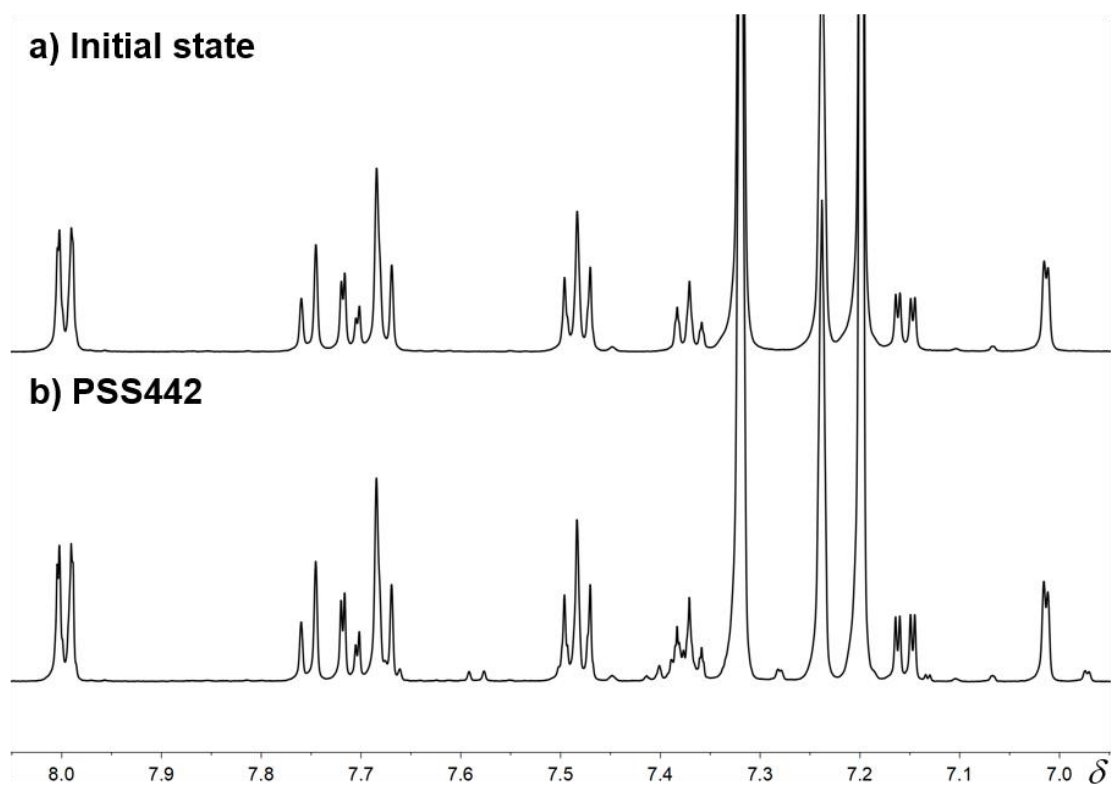
**Figure S7.**  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{CD}_3\text{CN}$  at 294 K.

## 4 Photoisomerization Studies

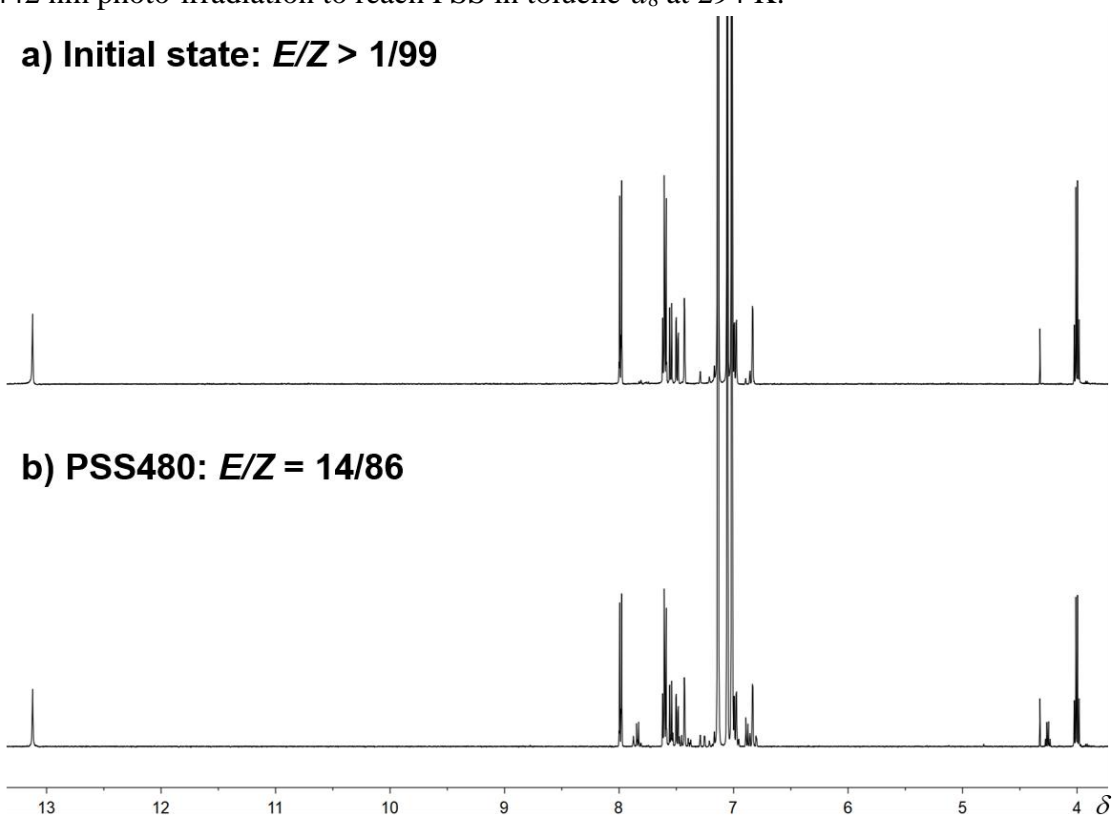
$^1\text{H}$  NMR and UV/Vis spectroscopies were employed in the study of the photoisomerization process of the of hydrazone switches. Spectrophotometric grade solvents were used for the UV/Vis spectroscopy studies. The photostationary states (PSSs) were determined upon continuous irradiation of the sample until no further isomerization was observed using  $^1\text{H}$  NMR spectroscopy.



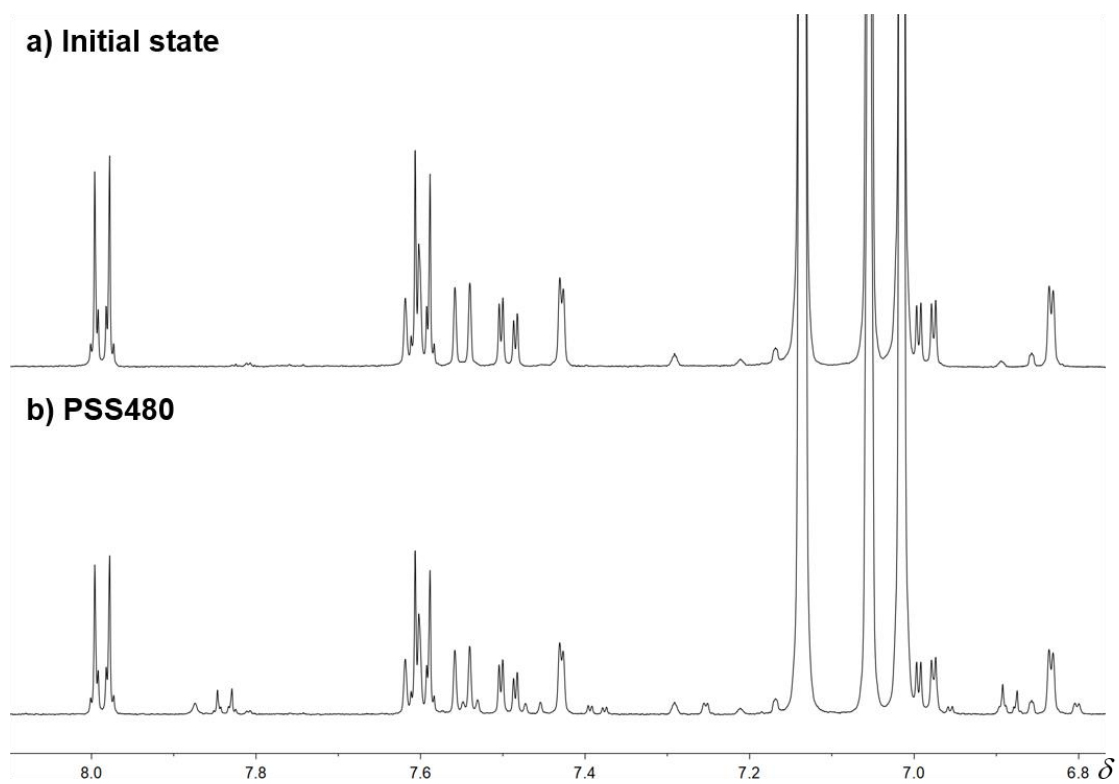
**Figure S8.**  $^1\text{H}$  NMR spectra of hydrazone switch **1** a) before and b) after 442 nm photo-irradiation to reach PSS in toluene- $d_8$  at 294 K.



**Figure S9.** Zoom-in on the aromatic area of  $^1\text{H}$  NMR spectra of hydrazone switch **1** a) before and b) after 442 nm photo-irradiation to reach PSS in toluene- $d_8$  at 294 K.



**Figure S10.**  $^1\text{H}$  NMR spectra of hydrazone switch **2** a) before and b) after 480 nm photo-irradiation to reach PSS in toluene- $d_8$  at 294 K.



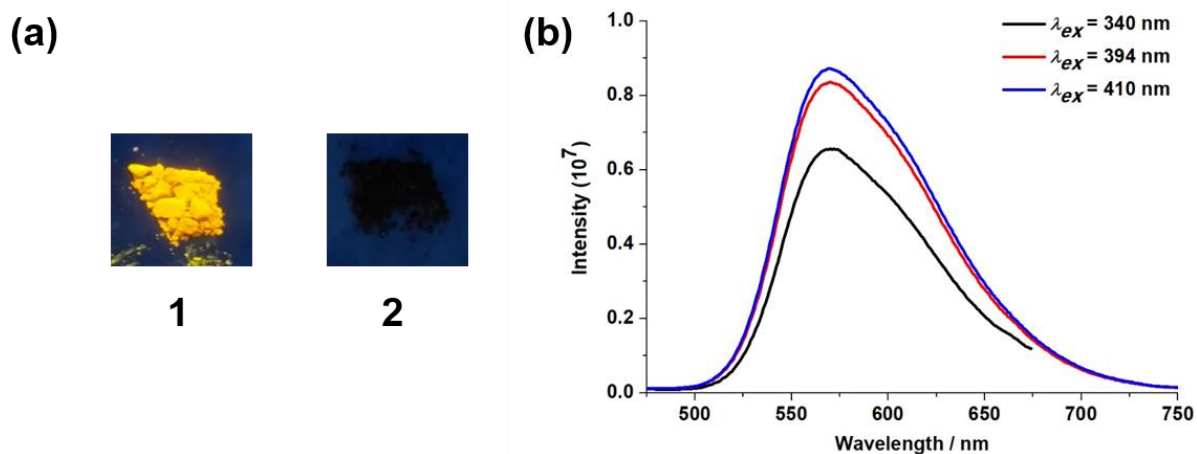
**Figure S11.** Zoom-in on the aromatic area of  $^1\text{H}$  NMR spectra of hydrazone switch **2** a) before and b) after 480 nm photo-irradiation to reach PSS in toluene- $d_8$  at 294 K.

## 5 Fluorescence Emission Studies

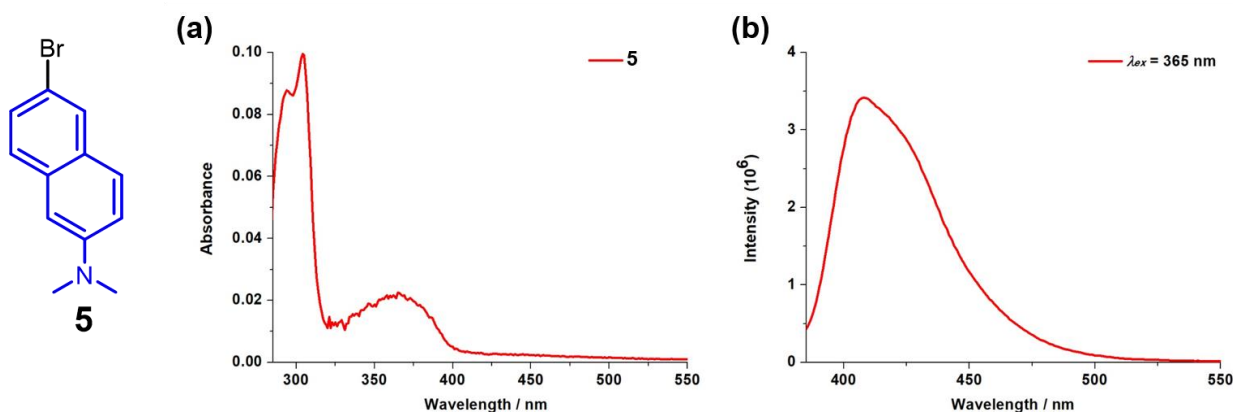
The fluorescence quantum yields for **1** and **2** were determined using Quinine Sulfate ( $\Phi_{FL} = 0.55$  in 0.1M H<sub>2</sub>SO<sub>4</sub>) and Coumarin 153 ( $\Phi_{FL} = 0.38$  in EtOH) as reference fluorophores.<sup>S4</sup> After the acquisition of the emission spectra of **1** and **2** in toluene ( $5 \times 10^{-6}$  M), the quantum yields were calculated using the following equation:

$$\Phi_{sample} = \Phi_{reference} \times \frac{Abs_{reference} \times \Sigma F_{sample} \times n_{sample}^2}{Abs_{sample} \times \Sigma F_{reference} \times n_{reference}^2}$$

where  $\Phi$  is quantum yield,  $Abs$  is the absorption at corresponding excitation wavelength,  $\Sigma F$  is the integrated fluorescence intensity, and  $n$  is the refractive index of solvent (1.33 for 0.1M H<sub>2</sub>SO<sub>4</sub>; 1.36 for EtOH; 1.50 for toluene).



**Figure S12.** (a) Photographs of powders of **1** and **2** under 365 nm UV lamp; (b) Fluorescence spectra of powder **1** upon excitation at 340, 394, and 410 nm.

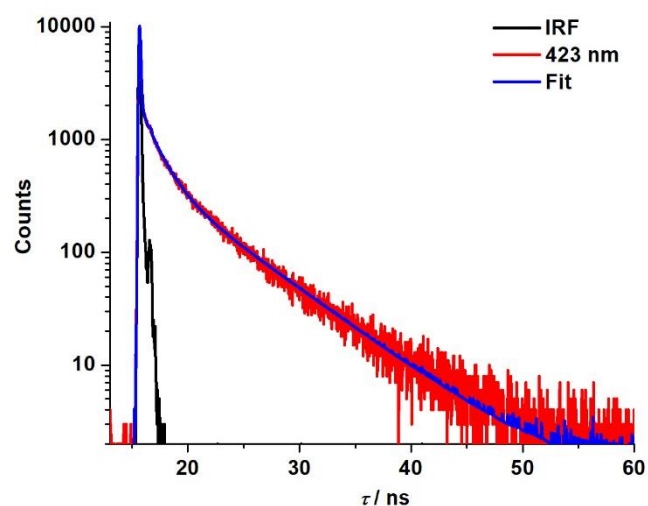
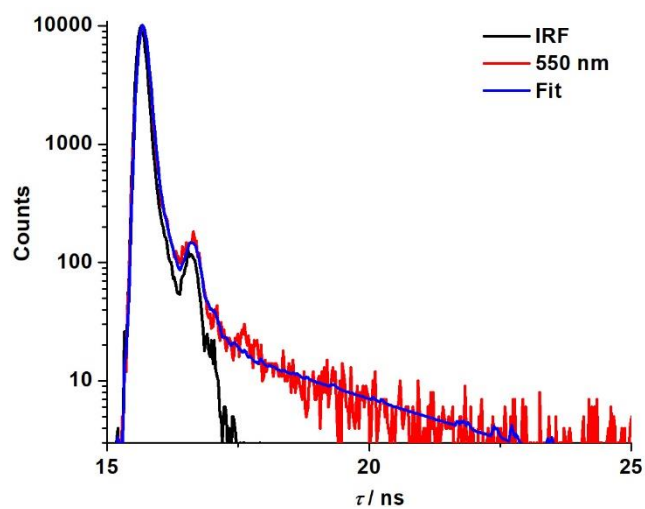


**Figure S13.** (a) UV-Vis spectrum of compound **5** ( $5 \times 10^{-6}$  M) in toluene; (b) Fluorescence emission spectrum of the solution upon excitation at 365 nm light.

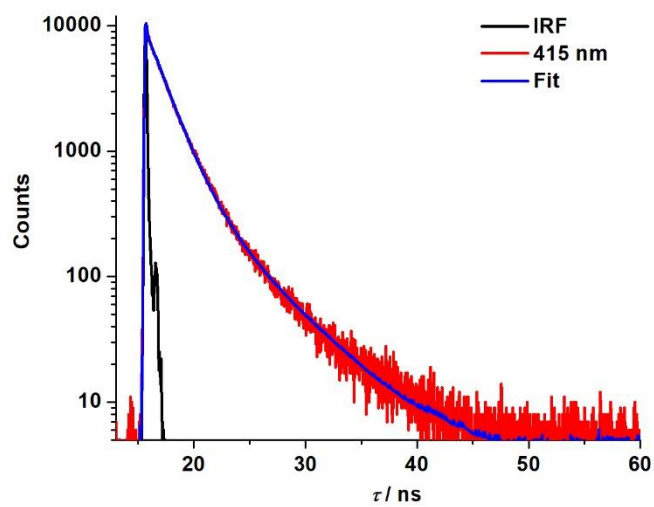
**Table S1. Summary of fluorescence decay lifetimes of 1 and 2.**

Compound	$\lambda_{em}$ (nm)	$\alpha^a$ (%)	$\tau$ (ns)	$\chi^2$
1	423	$98.0 \pm 3.7$	$0.020 \pm 0.001$	1.04
		$1.47 \pm 0.01$	$1.51 \pm 0.02$	
		$0.50 \pm 0.01$	$6.21 \pm 0.04$	
	550	$99.9 \pm 2.6$	$0.037 \pm 0.001$	1.06
	$0.04 \pm 0.01$	$2.94 \pm 0.08$		
2	415	$89.7 \pm 3.8$	$0.010 \pm 0.001$	1.20
		$9.21 \pm 0.02$	$1.61 \pm 0.01$	
		$1.05 \pm 0.02$	$4.60 \pm 0.04$	
	615	100	$0.062 \pm 0.001$	1.92

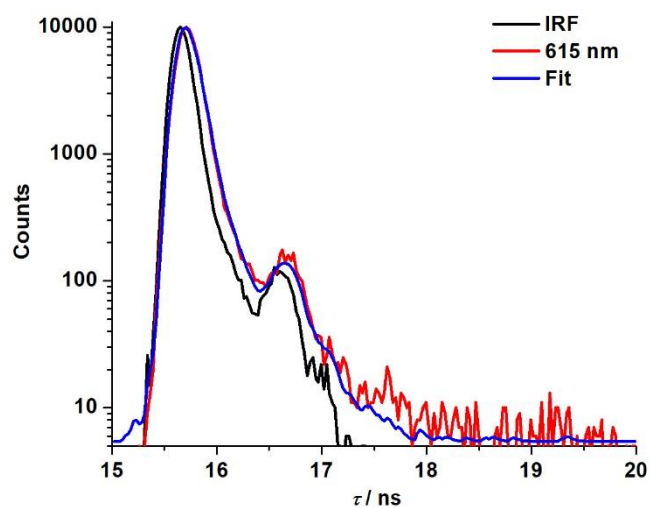
<sup>a</sup> Pre-exponential factor.

**Figure S14.** Fluorescence lifetime decay of the emission band (423 nm) of 1-Z ( $5 \times 10^{-6}$  M) in toluene.**Figure S15.** Fluorescence lifetime decay of the emission band (550 nm) of 1-Z ( $5 \times 10^{-6}$  M) in toluene.

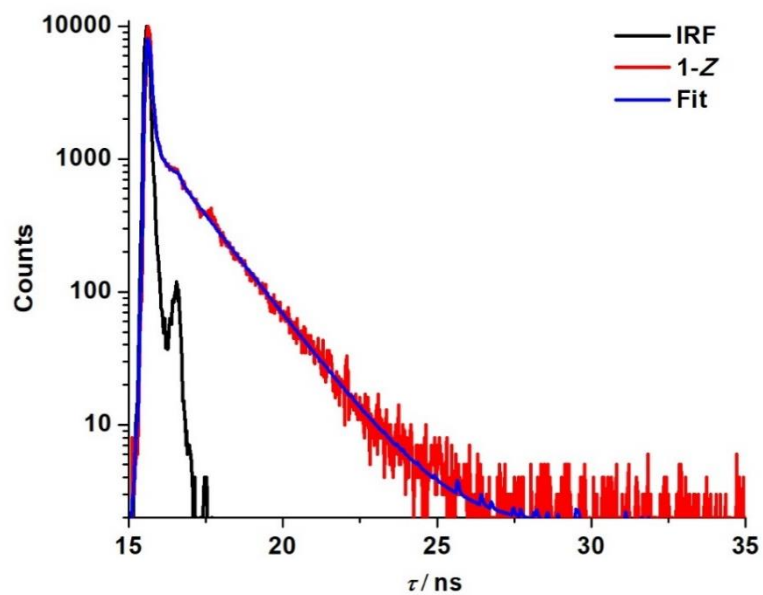




**Figure S16.** Fluorescence lifetime decay of the emission band (415 nm) of 2-Z ( $5 \times 10^{-6}$  M) in toluene.



**Figure S17.** Fluorescence lifetime decay of the emission band (615 nm) of 2-Z ( $5 \times 10^{-6}$  M) in toluene.

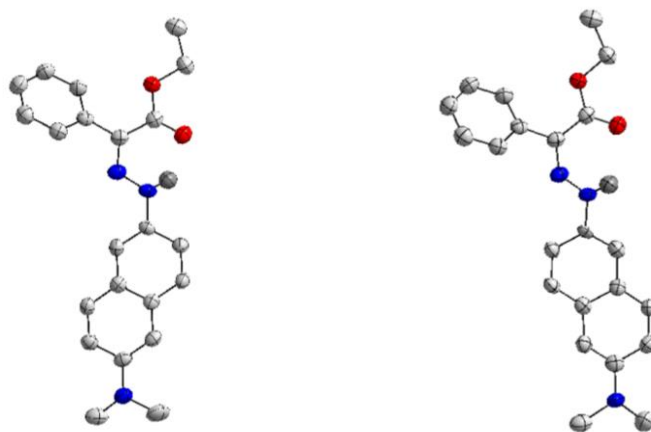


**Figure S18.** Fluorescence lifetime decay of **1-Z** powder. Multi-exponential fitting ( $\chi^2 = 1.10$ ) gave fluorescence decay lifetimes of  $0.050 \pm 0.002$  ns ( $96.1 \pm 3.7\%$ ), and  $1.45 \pm 0.06$  ns ( $3.9 \pm 0.1\%$ ). The pre-exponential factors are shown in brackets.

## 6 Crystallography

### 6.1 Crystallography of 1-Z

An orange chunk-shaped crystal with dimensions (0.35×0.22×0.21) mm<sup>3</sup> was mounted on a nylon loop with paratone oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at  $T = 173(2)$  K. Data were measured using scans of 1.00° per frame for 151.21 s using MoK $\alpha$  radiation (sealed tube, 50 kV, 40 mA). The total number of runs and images was based on the strategy calculation from the program **COSMO** (BRUKER, V1.61, 2009).<sup>S5</sup> The actually achieved resolution was  $\theta = 25.400$ . Cell parameters were retrieved using the **SAINT** (Bruker, V8.34A, 2013) software and refined using **SAINT** (Bruker, V8.34A, 2013) on 1415 reflections, 35% of the observed reflections.<sup>S6</sup> Data reduction was performed using the **SAINT** (Bruker, V8.34A, 2013) software which corrects for Lorentz polarisation. The final completeness is 100.00 out to 25.400 in  $\theta$ . The absorption coefficient ( $\mu$ ) of this material is 0.083 mm<sup>-1</sup> and the minimum and maximum transmissions are 0.6857 and 0.7452. The structure was solved in the space group  $P2_1/c$  (# 14) by Direct Methods using the **ShelXS** (Sheldrick, 2008) structure solution program<sup>S7</sup> and refined by Least Squares using **XL** (Sheldrick, 2008).<sup>S8</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.



**Figure S19.** ORTEP (50% probability) drawing of two possible structures of **1-Z** in the unit cell. There is disorder at the bottom naphthalene ring (C-H hydrogens have been removed for clarity).

**Table S2. Crystal data and structure refinement for 1-Z**

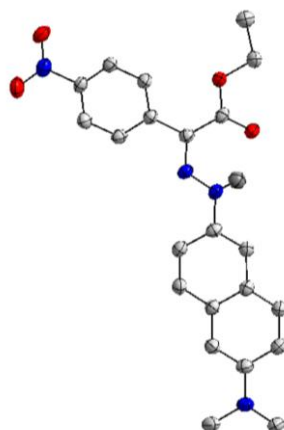
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CCDC	1851243
Empirical formula	C <sub>22</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub>
Formula weight	361.43
Temperature	173(2) K
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>C</i>
Unit cell dimensions	9.8408(14) Å 7.6010(11) Å 25.340(4) Å 90° 92.827(2) ° 90°
Volume	1893.1(5) Å <sup>3</sup>
<i>Z</i>	4
<i>Z</i> '	1
Density (Calcd.)	1.268 g/cm <sup>-3</sup>
Absorption coefficient	0.083 mm <sup>-1</sup>
Crystal size	0.35×0.22×0.21 mm <sup>3</sup>
$\theta$ range for data collection	1.609 to 25.400°
Index ranges	-11 ≤ <i>h</i> ≤ 11 0 ≤ <i>k</i> ≤ 9 0 ≤ <i>l</i> ≤ 30
Reflections Measured	28100
Independent reflections	3462 [ <i>R</i> <sub>int</sub> = 0.0426, <i>R</i> <sub>sigma</sub> = 0.0306]
Data / restraints / parameters	2719/ 2 / 358
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.029
Final <i>R</i> indexes [ <i>I</i> ≥ 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0429, ω <i>R</i> <sub>2</sub> = 0.1134
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0562, ω <i>R</i> <sub>2</sub> = 0.1246
Largest diff. peak and hole	0.162 and -0.185 e Å <sup>-3</sup>

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## 6.2 Crystallography of 2-Z

A red plate-shaped crystal with dimensions (0.20×0.17×0.03) mm<sup>3</sup> was mounted on a nylon loop with paratone oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at  $T = 173(2)$  K. Data were measured using scans of 1.00° per frame for 100.00 s using CuK $\alpha$  radiation (sealed tube, 40 kV, 30 mA). The total number of runs and images was based on the strategy calculation from the program **COSMO** (BRUKER, V1.61, 2009).<sup>S5</sup> The actually achieved resolution was  $\Theta = 70.027$ . Cell parameters were retrieved using the **SAINT** (Bruker, V8.34A, 2013) software and refined using **SAINT** (Bruker, V8.34A, 2013) on 3911 reflections, 28% of the observed reflections.<sup>S6</sup> Data reduction was performed using the **SAINT** (Bruker, V8.34A, 2013) software which corrects for Lorentz polarisation. The final completeness is 97.20 out to 70.027 in  $\Theta$ . The absorption coefficient ( $\mu$ ) of this material is 0.789 mm<sup>-1</sup> and the minimum and maximum transmissions are 0.669 and 0.753. The structure was solved in the space group  $P-1$  (# 2) by Direct Methods using the **ShelXS** (Sheldrick, 2008) structure solution program<sup>S7</sup> and refined by Least Squares using **XL** (Sheldrick, 2008).<sup>S8</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.



**Figure S20.** ORTEP (50% probability) drawing of the crystal structure of **2-Z** (C-H hydrogens have been removed for clarity).

**Table S3. Crystal data and structure refinement for 2-Z**

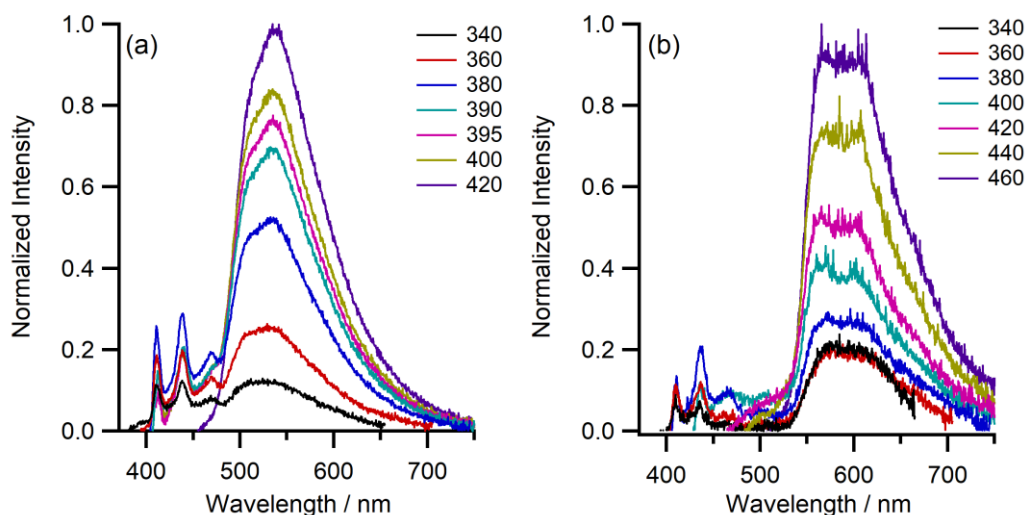
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CCDC	1860816
Empirical formula	C <sub>22</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub>
Formula weight	406.43
Temperature	173(2) K
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	8.18900(10) Å 10.2031(2) Å 12.0424(2) Å 81.6260(10) ° 83.0170(10) ° 89.0430(10) °
Volume	988.07(3) Å <sup>3</sup>
<i>Z</i>	2
<i>Z</i> '	1
Density (Calcd.)	1.366 g/cm <sup>-3</sup>
Absorption coefficient	0.789 mm <sup>-1</sup>
Crystal size	0.20×0.17×0.03 mm <sup>3</sup>
$\theta$ range for data collection	6.972 to 70.027°
Index ranges	-9 ≤ <i>h</i> ≤ 9 -12 ≤ <i>k</i> ≤ 12 -14 ≤ <i>l</i> ≤ 0
Reflections Measured	14174
Independent reflections	3625 [ <i>R</i> <sub>int</sub> = 0.0443, <i>R</i> <sub>sigma</sub> = 0.033]
Data / restraints / parameters	2573/ 0 / 278
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.022
Final <i>R</i> indexes [ <i>I</i> ≥ 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0454, ω <i>R</i> <sub>2</sub> = 0.1100
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0696, ω <i>R</i> <sub>2</sub> = 0.1241
Largest diff. peak and hole	0.228 and -0.207 e Å <sup>-3</sup>

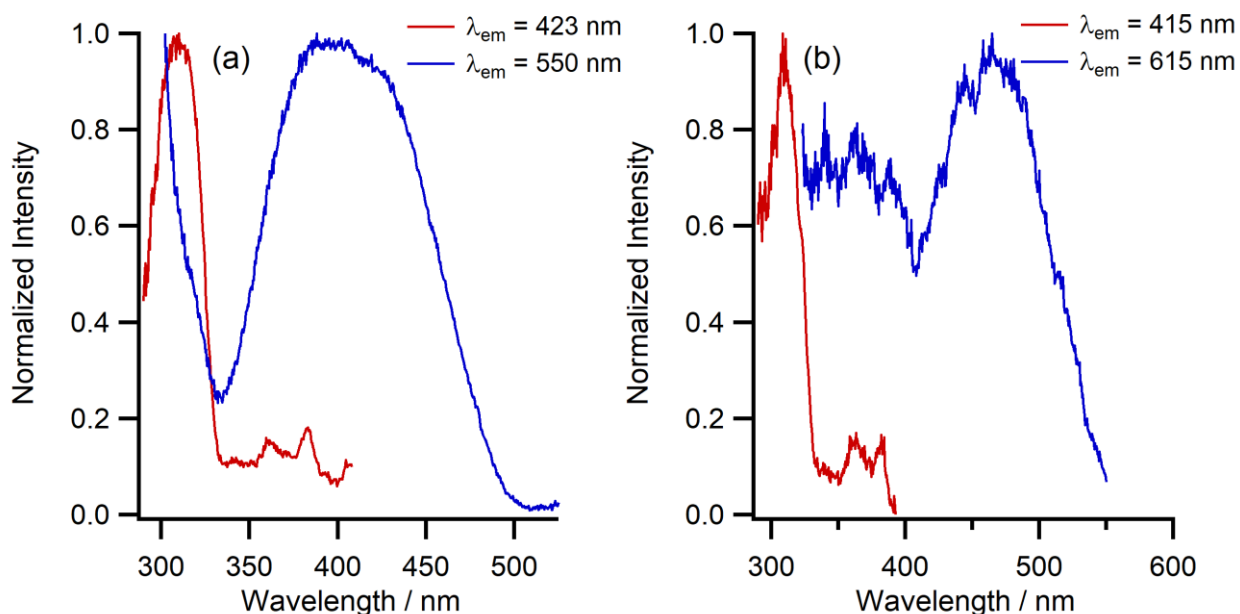
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## 7 Low-Temperature (77 K) Fluorescence Emission Studies

Solutions of compounds **1** and **2** in toluene were prepared by dissolving the solid compound in toluene and diluting in series to the desired concentration. The solution was added to a quartz NMR tube and flash-frozen in liquid nitrogen. The sample tube was loaded into a quartz Dewar containing liquid nitrogen to acquire fluorescence data at 77 K.

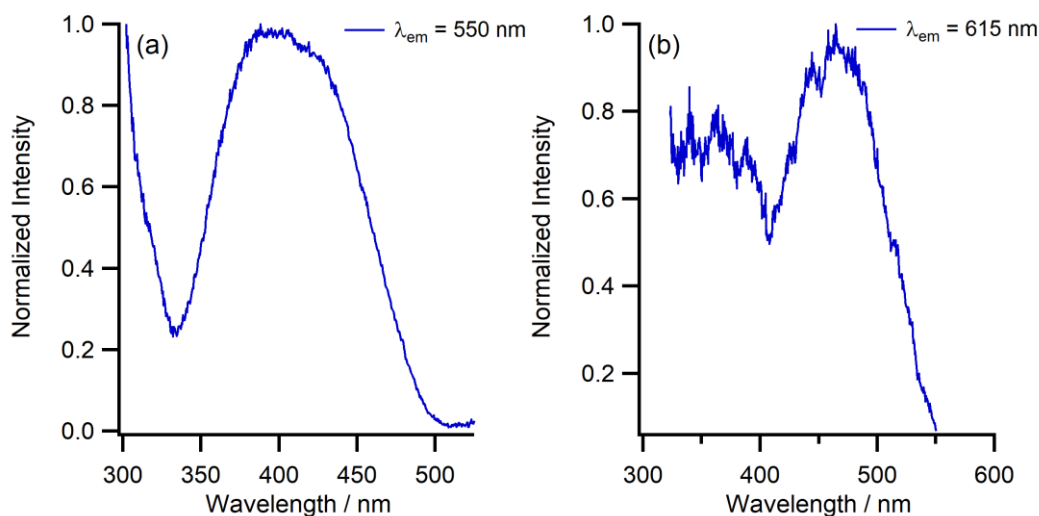


**Figure S21.** (a) Normalized 77 K fluorescence emission spectra of **1** ( $5 \times 10^{-6}$  M) in toluene, under excitation wavelengths ranging from 340 to 420 nm; (b) Normalized 77 K fluorescence emission spectra of **2** ( $5 \times 10^{-6}$  M) in toluene, under excitation wavelengths ranging from 340 to 460 nm.



**Figure S22.** (a) Normalized 77 K fluorescence excitation spectra of **1** ( $5 \times 10^{-6}$  M) in toluene, monitored at the emission wavelengths of 423 nm (red) and 550 nm (blue); (b) Normalized 77 K fluorescence excitation spectra of **2** ( $5 \times 10^{-6}$  M) in toluene, monitored at the emission wavelengths of

415 nm (red) and 415 nm (blue).



**Figure S23.** (a) Normalized 77 K fluorescence excitation spectrum of **1** ( $5 \times 10^{-6}$  M) in toluene, monitored at the emission wavelength of 550 nm; (b) Normalized 77 K fluorescence excitation spectrum of **2** ( $5 \times 10^{-6}$  M) in toluene, monitored at the emission wavelength of 615 nm.

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