

## **Supporting Information**

### **Waste Management of Chemically Activated Switches: Using a Photoacid to Eliminate Accumulation of Side Products**

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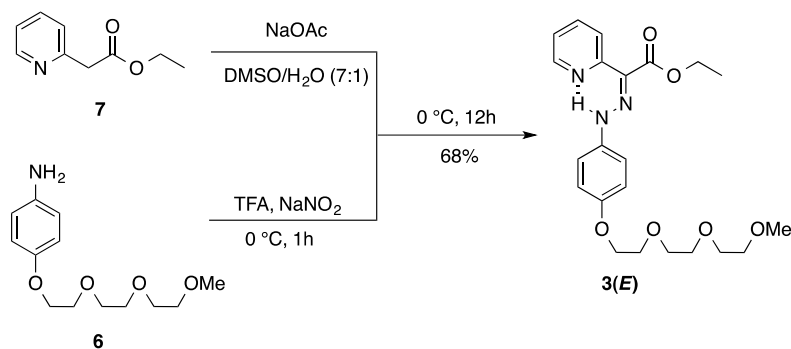
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<b>Table of contents</b>	<b>pages</b>
1. Experimental details	S3–S4
1.1 Synthesis	S3–S4
1.2 Irradiation studies	S4
2. NMR spectroscopy	S5–S13
4. References	S13

**1. General Methods.** All reagents and starting materials were purchased from Acros and used without further purification. Column chromatography was performed on silica gel (Silicycle, 230-400 mesh). Silicycle glass backed thin layer chromatography (TLC) plates (extra hard layer, 60 Å, F-254 indicator) were used for all TLCs. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. NMR spectra were recorded on a 500 MHz spectrometer, with working frequencies of 499.8 and 125.7 MHz for the  $^1\text{H}$  and  $^{13}\text{C}$  nuclei, respectively. Chemical shifts are quoted in ppm relative to tetramethylsilane, using the residual solvent peak as a reference standard. High-resolution mass spectra were measured on a Micromass Q-TOF Ultima at the University of Illinois, Urbana-Champaign. All spectroscopy samples were taken at room temperature. Irradiation studies were performed using 430 nm LEDs with radiant powers of 880-960 mW at 700 mA, purchased from LED groupbuy. The LEDs were affixed in a custom irradiation chamber fitted with a cooling fan to maintain ambient temperature. Compounds **1-MEH**<sup>S1</sup>, **2**<sup>S2</sup>, **4**<sup>S3</sup>, **5-6**<sup>S4</sup> and **7**<sup>S2</sup> were synthesized as previously reported.

## 1.1 Synthesis

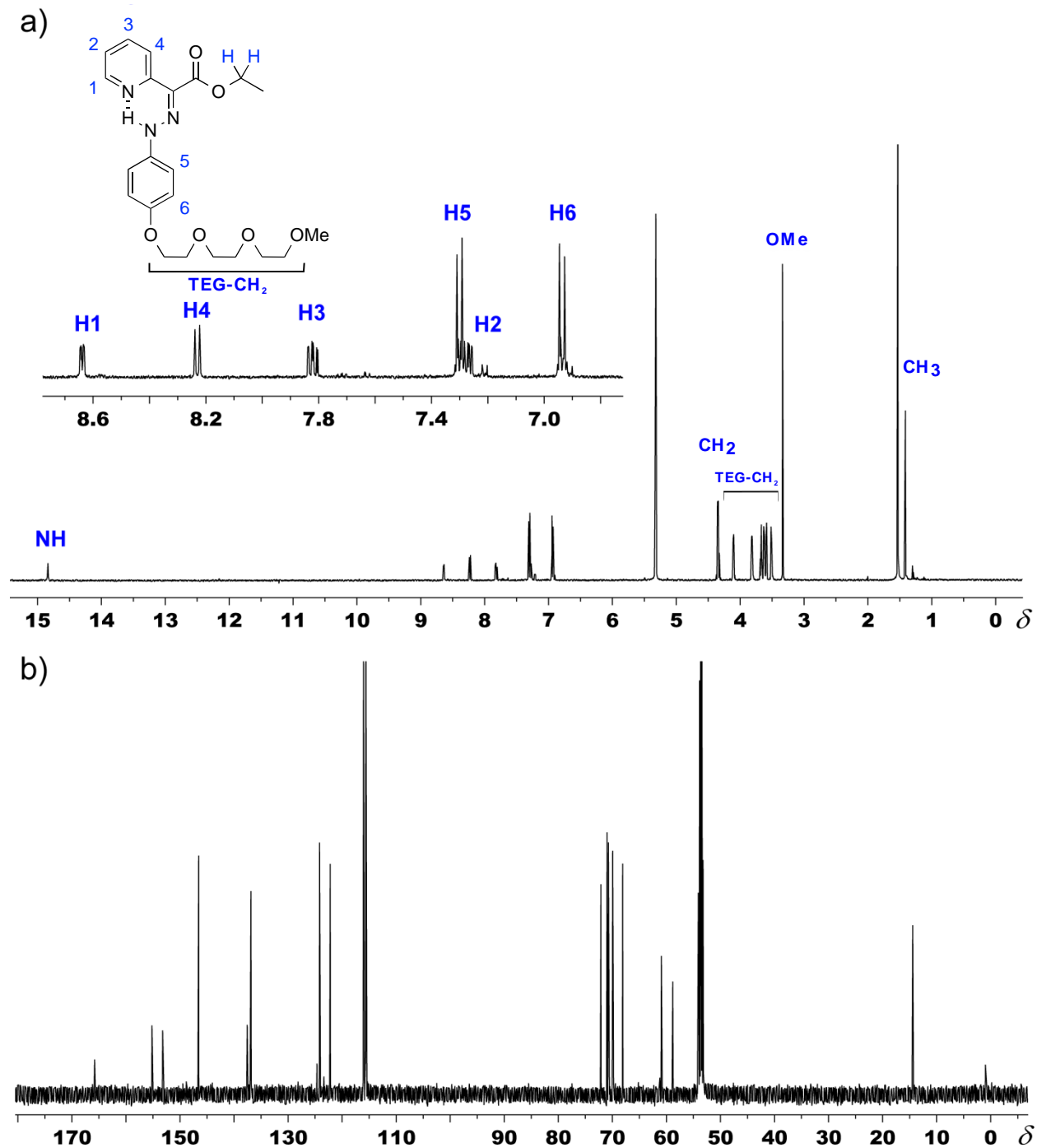


**3(E).** TFA (314  $\mu\text{L}$ , 4.1 mmol) was added dropwise to a cooled (0 °C) solution (10 mL, CH<sub>3</sub>CN) of aniline **6** (0.500 g, 2.0 mmol) followed by stirring for 30 min. A solution of NaNO<sub>2</sub> (0.1351 g,

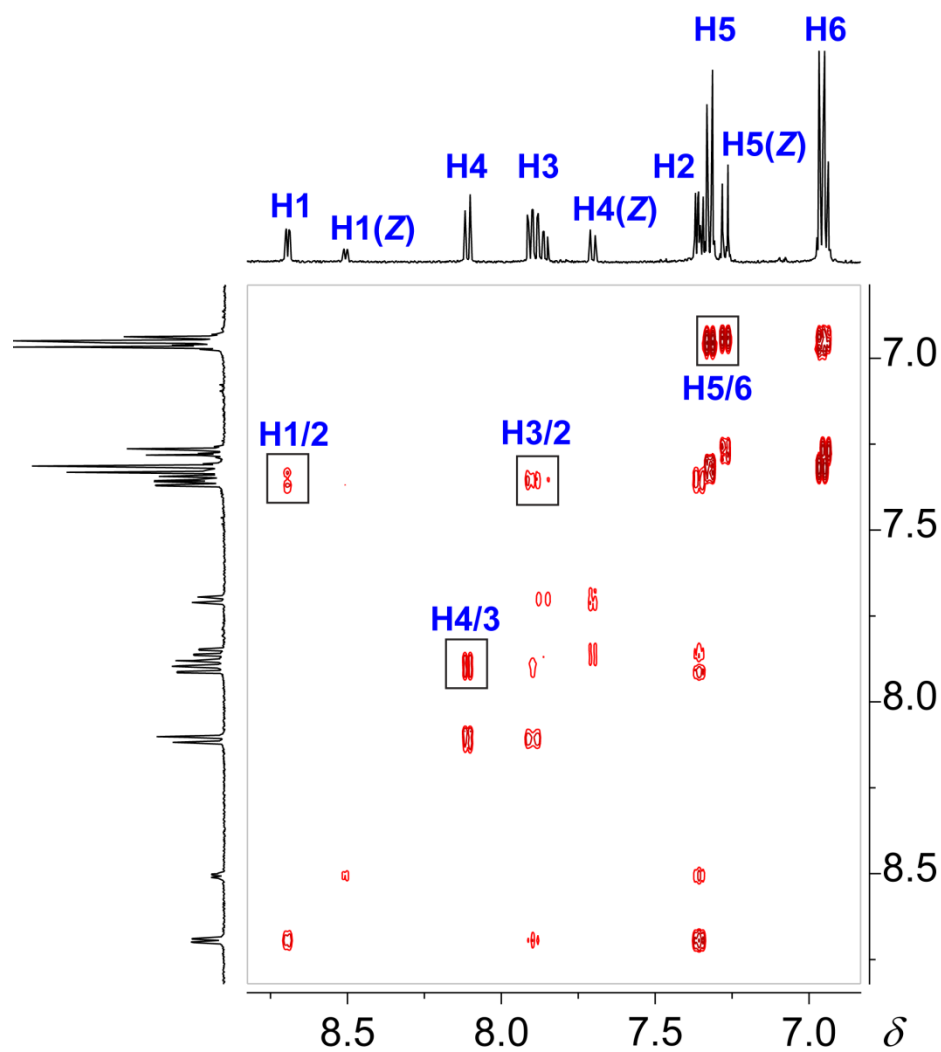
2 mmol) in H<sub>2</sub>O (1 mL) was added dropwise to the mixture at 0 °C over a period of 1 h, followed by stirring for an additional 1 h. In a separate flask, a solution of NaOAc (1.124 g, 13.7 mmol) in H<sub>2</sub>O (1 mL) was added to ethyl 2-pyridyl acetate (0.3234 g, 2 mmol) dissolved in DMSO (1 mL) at 0 °C, and then left to stir for 1 h. Subsequently, the mixture containing the diazotized aniline **6** was added dropwise over 30 min, and the mixture was allowed to stir overnight warming to room temperature. The crude reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL), washed with brine (15 mL) and dried over sodium sulfate. After removal of solvent under vacuum the crude mixture was purified using flash column chromatography (3:2, hexanes/ethyl acetate) to yield 0.5784 g (68%) hydrazone product **3(E)** as a yellow oil. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 14.84 (s, 1H), 8.63 (ddd, *J* = 5.0, 1.8, 1.0 Hz, 1H), 8.23 (d, *J* = 8.3, 1H), 7.82 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.31–7.29 (m, 2H), 7.28–7.26 (m, 1H), 6.95–6.93 (m, 2H), 4.35 (q, *J* = 7.1, 5.0 Hz, 2H), 4.12–4.10 (m, 2H), 3.82–3.80 (m, 2H), 3.69–3.67 (m, 2H), 3.63–3.59 (m, 4H), 3.52–3.50 (m, 2H), 3.34 (dt, *J* = 3.3, 1.6 Hz, 3H), 1.41 (t, *J* = 7.1 Hz, 3H) ppm; <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 165.59, 154.99, 153.01, 146.33, 137.36, 136.67, 124.45, 123.96, 121.99, 115.83, 115.41, 71.91, 70.76, 70.52, 70.43, 69.72, 67.89, 58.61, 60.72, 14.20 ppm. HRMS (ESI) *m/z* calcd for C<sub>22</sub>H<sub>30</sub>N<sub>3</sub>O<sub>6</sub>: 432.2129, found [M-H<sup>+</sup>]: 432.2120.

**1.2 Irradiation Studies.** A 2:1 molar equivalent mixture of **1-MEH** and hydrazone (either **2** or **3**, ~10<sup>-4</sup> M) was irradiated in an NMR tube with 430 nm light for 5 min. The switching process was monitored using <sup>1</sup>H NMR spectroscopy. Leaving the NMR tube under dark reverted the system to its original state. Cycling studies were performed by irradiating the sample mixture then leaving it in the dark to reverse the switching process (60 minutes for **3** in D<sub>2</sub>O and 150 minutes for **2** in MeOD).

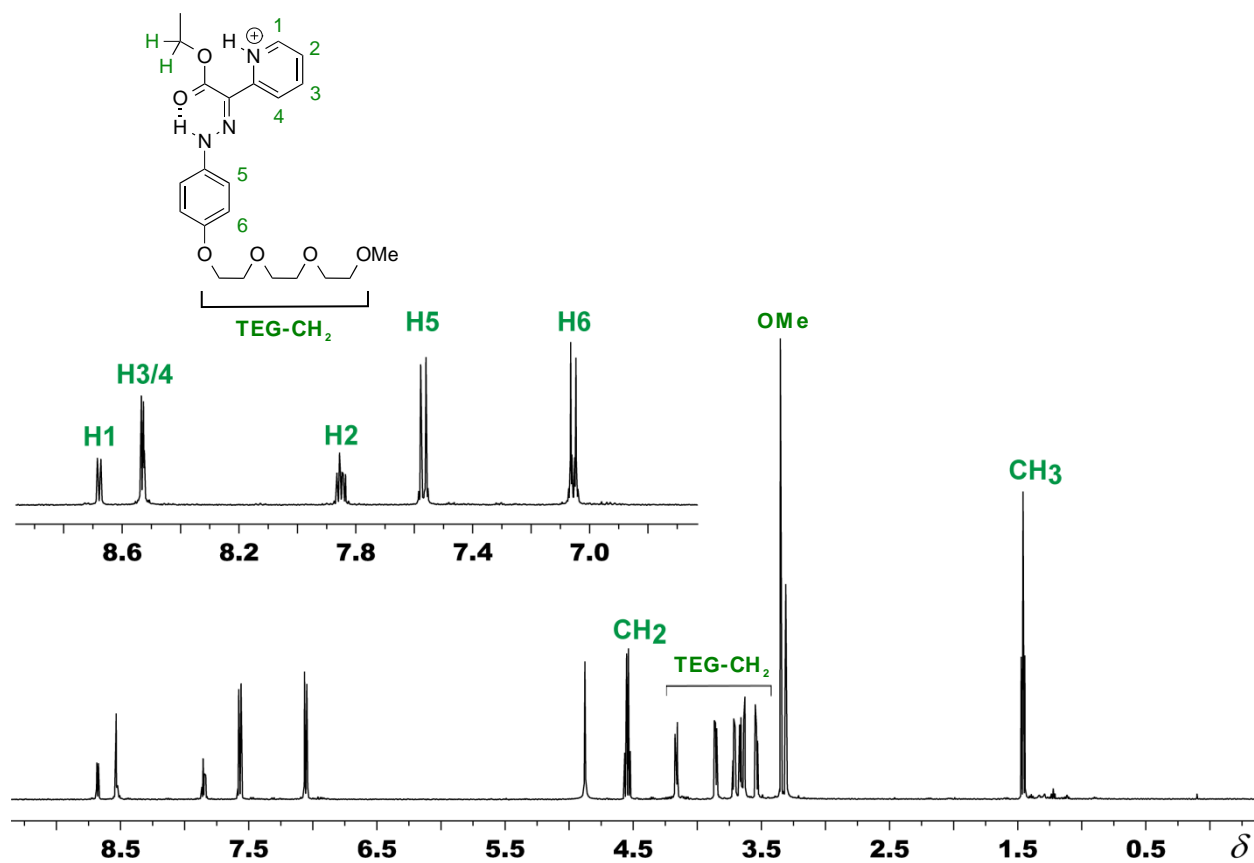
## 2. NMR Spectroscopy



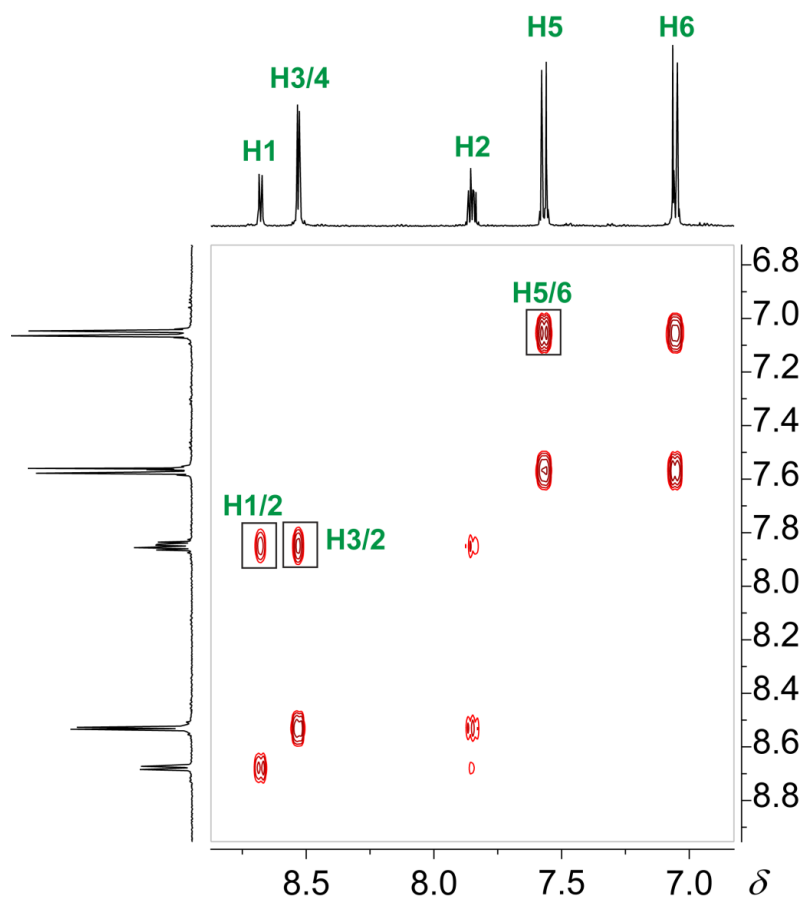
**Figure S1.** The a)  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) and b)  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectra of 3.



**Figure S2.** The COSY spectrum (500 MHz, CD<sub>3</sub>OD) of the aromatic region of **3**.

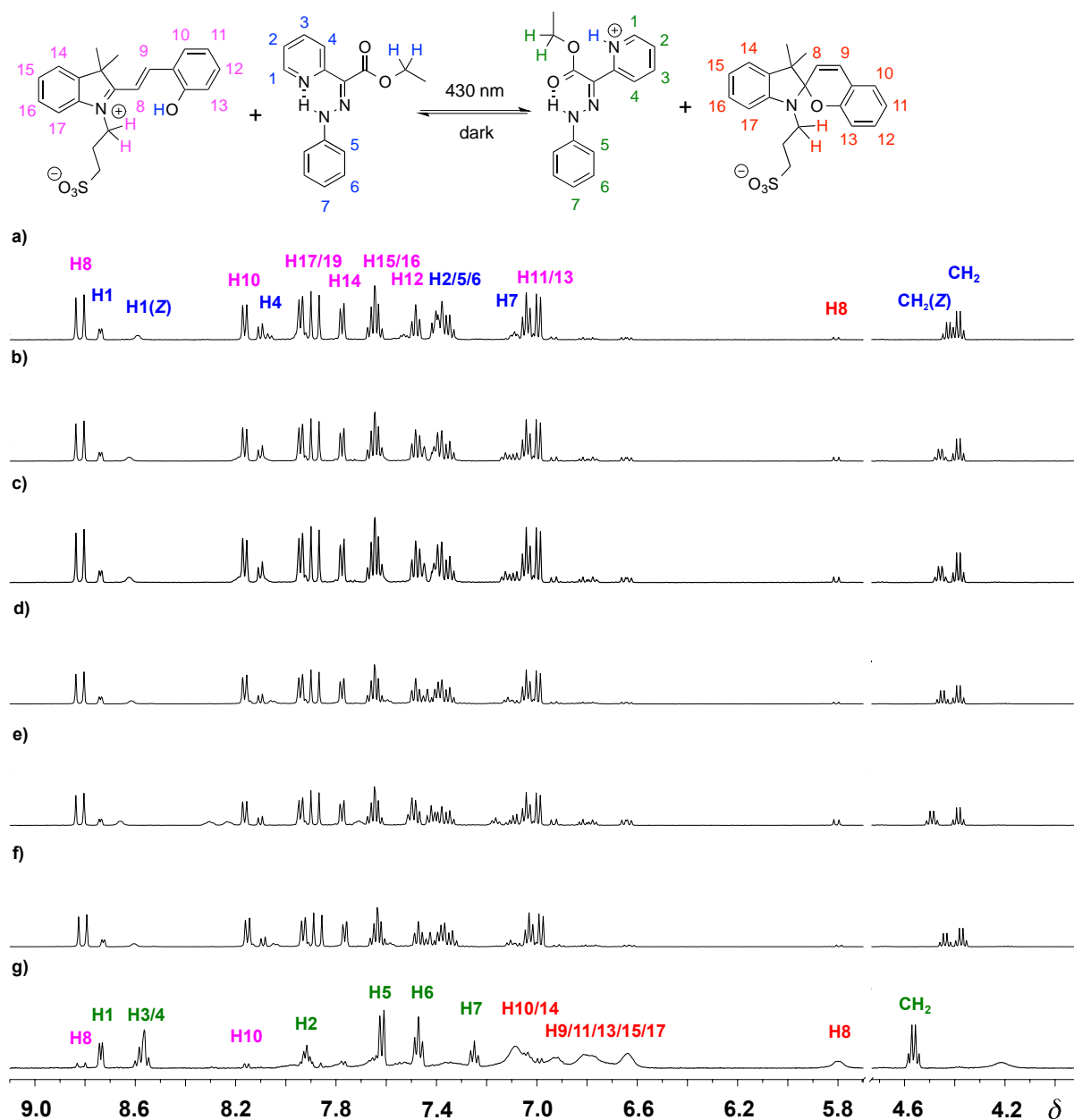


**Figure S3.** The <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) of **3(ZH<sup>+</sup>)**, obtained after the addition of 2 equivalents of TFA.

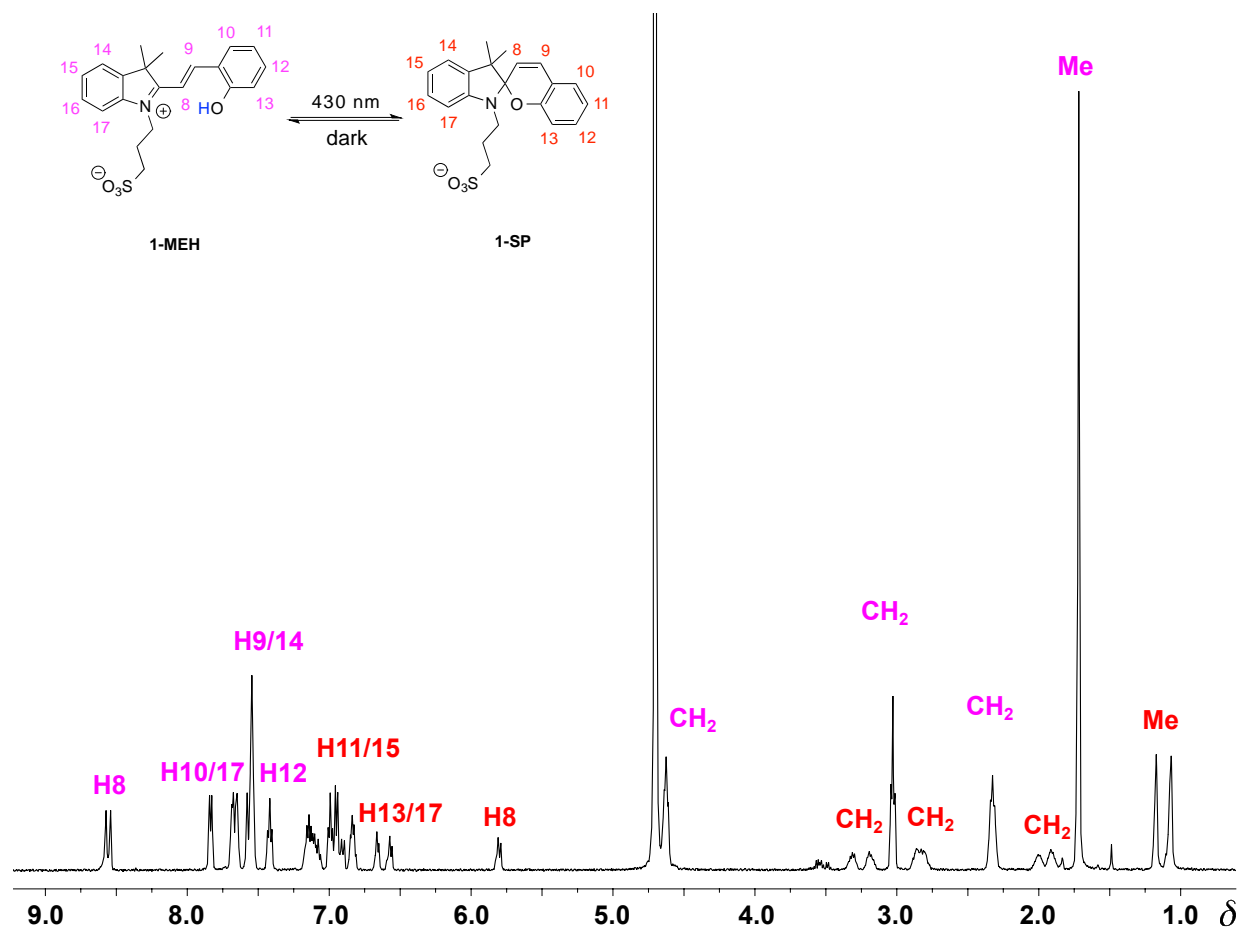


**Figure S4.** The COSY spectrum (500 MHz, CD<sub>3</sub>OD) of **3**(ZH<sup>+</sup>).

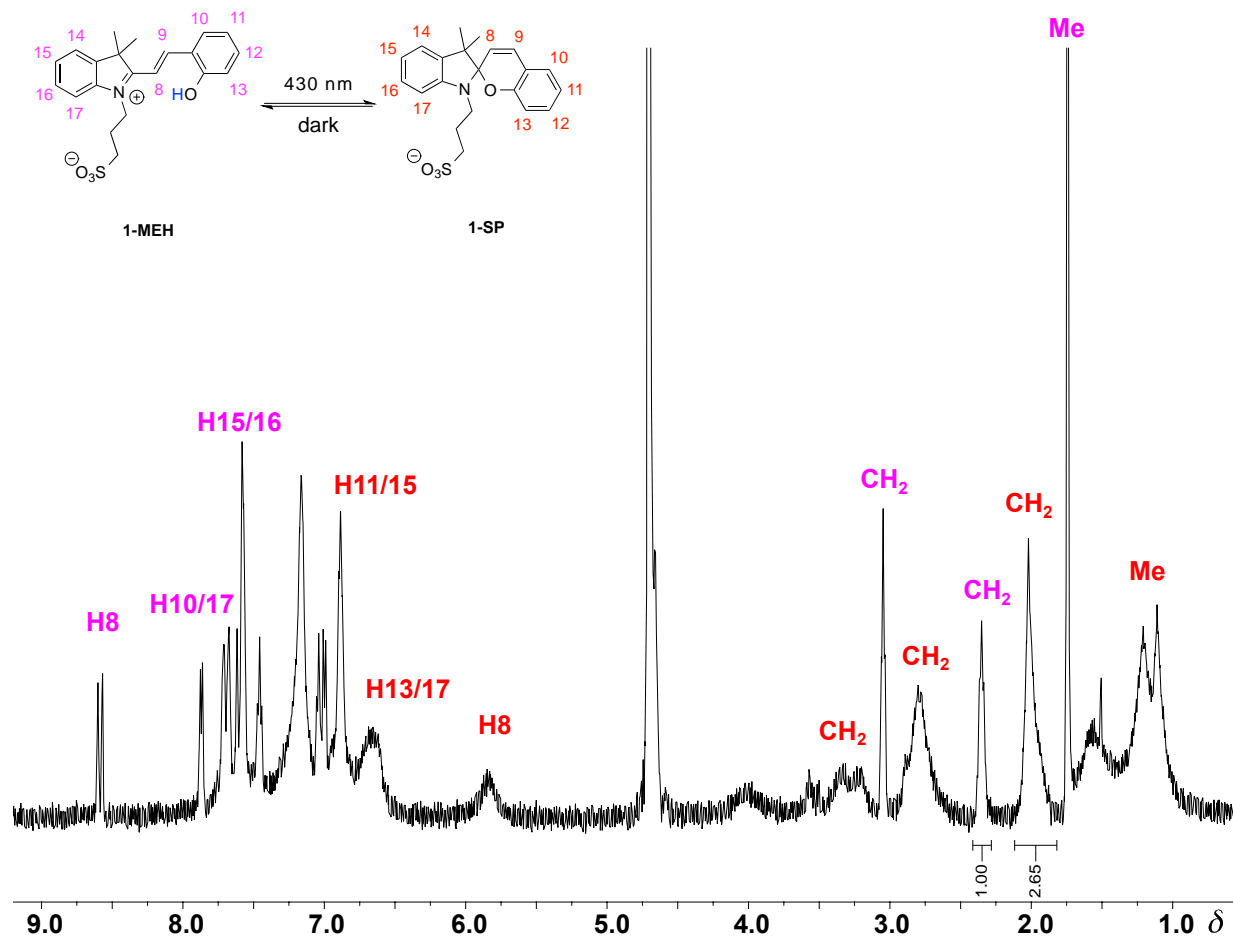




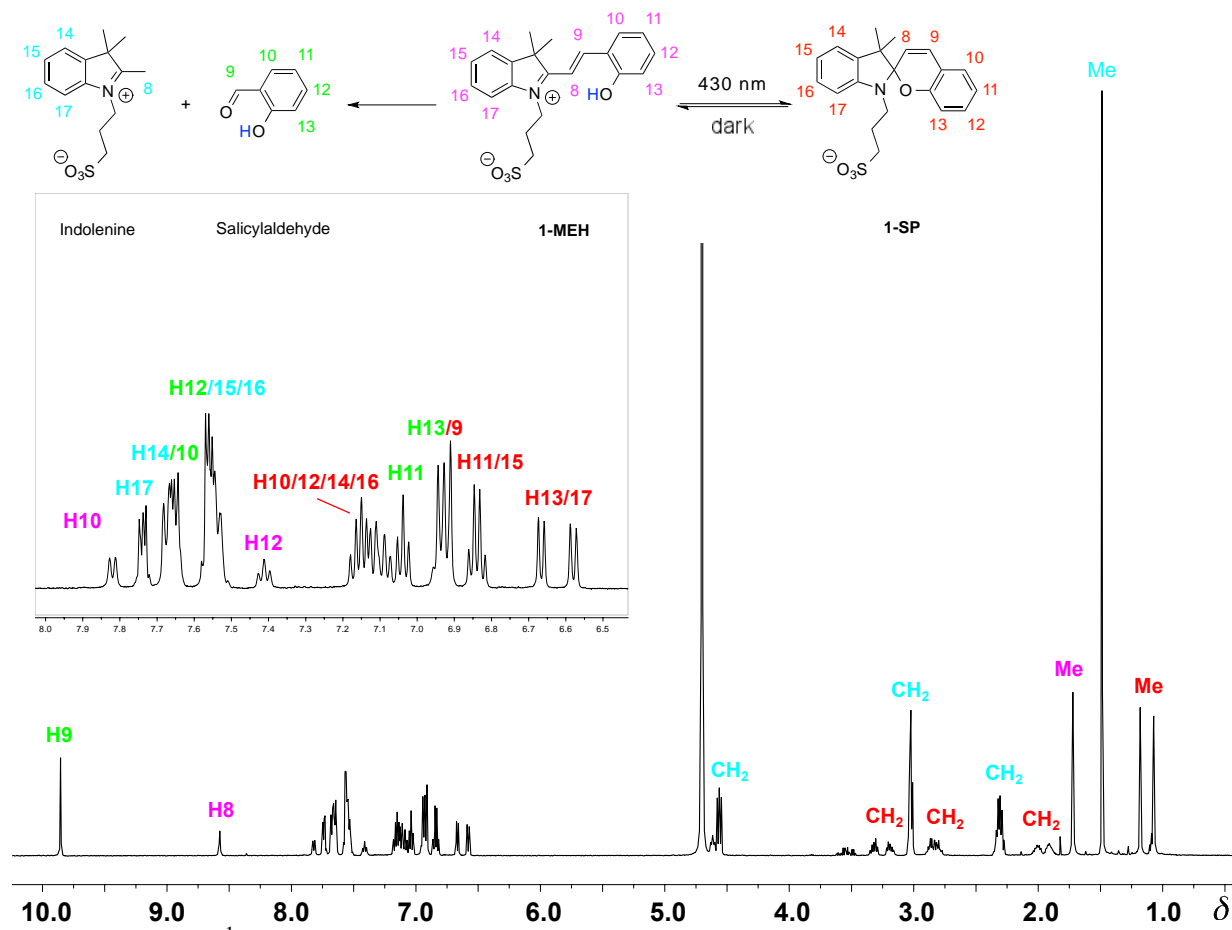
**Figure S5.** The  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CD}_3\text{OD}$ ) of **1-MEH** and **2** (a) no irradiation, (b) before irradiating for the 20<sup>th</sup> time, (c) before irradiating for the 40<sup>th</sup> time, (d) before irradiating for the 60<sup>th</sup> time, (e) before irradiating for the 80<sup>th</sup> time, (f) before irradiating for the 100<sup>th</sup> time, and (g) after 100<sup>th</sup> irradiation.



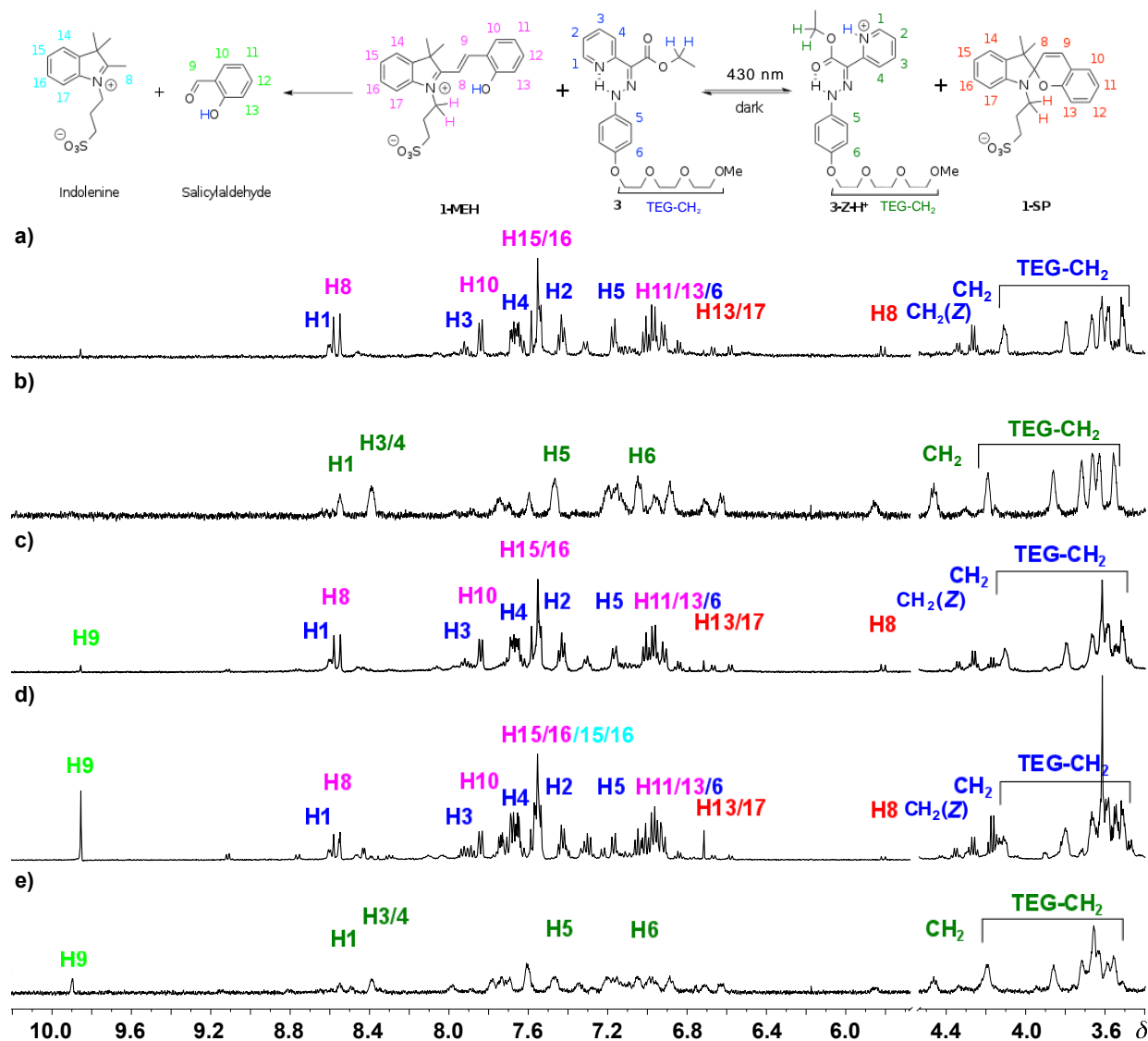
**Figure S6.** The <sup>1</sup>H NMR spectrum (500 MHz, D<sub>2</sub>O) of **1-MEH** before irradiation in water.



**Figure S7.** The <sup>1</sup>H NMR spectrum (500 MHz, D<sub>2</sub>O) of **1-SP** after irradiation for 5 min in water demonstrating rapid reversion to the SP form.



**Figure S8.** The <sup>1</sup>H NMR spectrum (500 MHz, D<sub>2</sub>O) of **1-MEH** after 10 irradiation cycles in water.



**Figure S9.** the  $^1\text{H}$  NMR spectra (500 MHz,  $\text{D}_2\text{O}$ ) of **1-MEH** and **3** (a) no irradiation, (b) after 5 min irradiation, 1<sup>st</sup> cycle, (c) before 10<sup>th</sup> irradiation cycle, (d) before 20<sup>th</sup> irradiation cycle, and (e) after 5 min irradiation for the 20<sup>th</sup> time.

### 3. References

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