

## Supplementary Material

### Visible light-promoted metal-free reduction reaction of organohalides by 2-naphthyl or 2-hydroxynaphthyl substituted 1,3-dimethylbenzimidazolines

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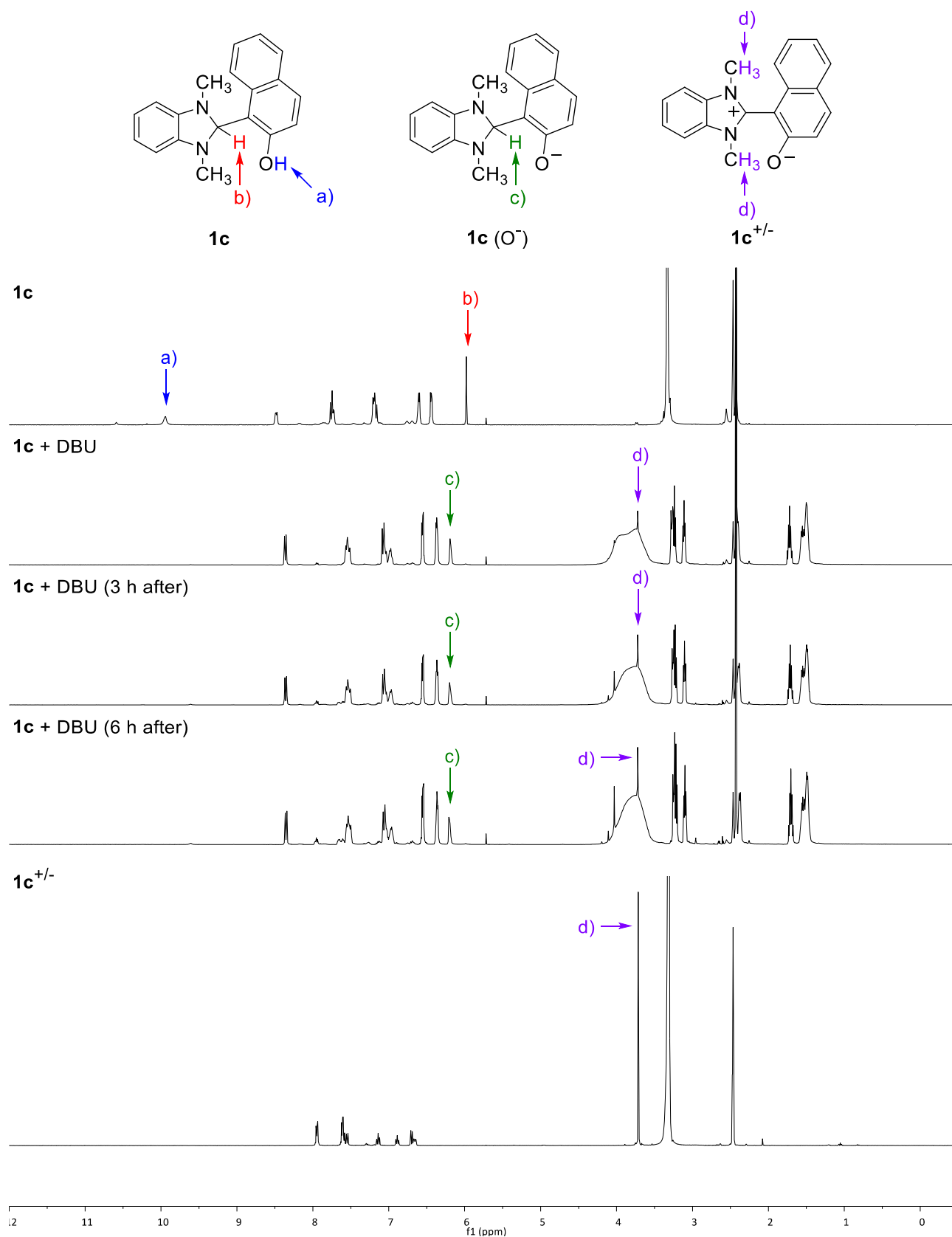
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**General Methods.** NMR spectra were recorded using CDCl<sub>3</sub> or DMSO solutions with tetramethylsilane (Me<sub>4</sub>Si) as an internal standard at 400 MHz for <sup>1</sup>H NMR. Column chromatography was performed using silica gel. Preparative thin-layer chromatography (TLC) was performed on 20 x 20 cm plates coated with silica gel. Anhydrous dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were purchased and used without distillation. MeCN was distilled over P<sub>2</sub>O<sub>5</sub> and subsequently distilled with K<sub>2</sub>CO<sub>3</sub>. CH<sub>2</sub>Cl<sub>2</sub> and PhCH<sub>3</sub> were purified in a same manner by the treatment with H<sub>2</sub>SO<sub>4</sub>, water, 5% NaOH, water, and CaCl<sub>2</sub> and then distilled over CaH<sub>2</sub>. Tetrahydrofuran (THF) was distilled over sodium-benzophenone under N<sub>2</sub>. Other reagents and solvents were purchased and used without purification. Benzimidazoline **1a**,<sup>[1]</sup> **1b**,<sup>[2]</sup> **1c**<sup>[2]</sup> and substrates **2a-c**,<sup>[3]</sup> **6**,<sup>[4]</sup> **8a**,<sup>[5]</sup> and **8b**<sup>[6]</sup> which are known compounds, were prepared by using reported procedures. Known products **3**,<sup>[2]</sup> **7**,<sup>[3]</sup> **9**<sup>[4]</sup> and **10**<sup>[4]</sup> were characterized by comparing their <sup>1</sup>H NMR data with those reported earlier.

**Preparations of 2-Aryl-1,3-dimethylbenzimidazoline (DMBIH) (1).** A typical procedure for preparation of **1a** is described below. To a CH<sub>2</sub>Cl<sub>2</sub> (10 mL) containing *N,N'*-dimethyl-*o*-phenylenediamine (DMPDA) (1.38 g, 10.1 mmol) with molecular sieves 4A (ca. 10g) under N<sub>2</sub> seated in ice-water bath was slowly added 1-naphthoaldehyde (1.42 mL, 10.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). After addition of acetic acid (0.23 mL, 4.0 mmol), the resulting mixture was stirred for 6 h in an ice-water bath and then molecular sieves were removed by filtration. The residue obtained after concentration of the filtrate in vacuo was subjected to column chromatography (benzene with 1% triethylamine) to give **1a** (1.85 g, 6.8 mmol, 67%). In a similar fashion, **1b** (1.61 g, 5.9 mmol, 71%) from DMPDA (1.12 g, 8.2 mmol) was prepared. **1a** and **1b** were crystallized from dimethoxyethane and EtOH before using for the photoreactions. **1c** (595 mg, 2.1 mmol, 49%) from DMPDA (584

mg, 4.3 mmol) was obtained by rinsing the solid with EtOH after column chromatography (AcOEt / benzene = 1/6 with 1% triethylamine), and then used for the photoreaction.

**Photoreaction procedure.** *Photoreactions of 2-Aryl-1,3-dimethylbenzimidazoline 1 with allyloxy halobenzene 2, alkene tethered bromoalkyl ketone 6, or bromoalkyl keto ester 8.* Photoreactions were conducted using solutions in Pyrex test tubes (1.4 cm diameter) immersed in a water bath at room temperature and irradiated using a 500 W Xe lamp. Same solution was also irradiated with 7.3 W white LED without being immersed in a water bath. General procedure is described below. A solution of a substrate **2**, **6** or **8** (0.20 or 0.40 mmol) and **1** (0.24 or 0.48 mmol) in a solvent (2 mL or 4 mL) was purged with N<sub>2</sub> for 5 min prior to irradiation. Each solution was irradiated. When DMSO or DMF was used as a solvent, the photolysate was diluted with water and extracted with Et<sub>2</sub>O. Each extract was washed with water, sat NaHCO<sub>3</sub>, brine, and dried over anhydrous MgSO<sub>4</sub>. When CH<sub>2</sub>Cl<sub>2</sub> was used, the precipitate formed by addition of Et<sub>2</sub>O to the photolysate was separated by filtration. The conversion of **2** and **6** as well as the yields of **3** and **7** were determined by using <sup>1</sup>H-NMR and appropriate internal references such as triphenylmethane and 1,3,5-trimethoxybenzene. In the reaction of **8**, the residue obtained by the concentration of the extract or filtrate was subjected to column chromatography (n-hexane / EtOAc = 3/1) and TLC (benzene / EtOAc = 20/1) to give recovered **8** and products **9** and **10**. Since separation of **8** and **10** by chromatography could not be achieved, yields were determined by using <sup>1</sup>H-NMR.



**Figure 1.**  $^1\text{H-NMR}$  of **1c** in the absence or presence of DBU, and **1c<sup>+/-</sup>** in DMSO.

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