Supporting Information

Visible-Light-Induced Radical Cascade Sulfonylation/Cyclization

towards Indole-fused Pyridine Derivatives

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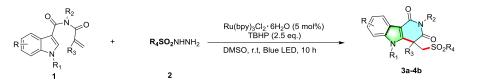
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1. General Information

All reagents and solvents were purchased from commercial suppliers and used without purifications. TLC was performed on silica gel plates (200-300 mesh) using UV light (254/365 nm) for detection and column chromatography was performed on silica gel (200-300 mesh). The ¹H NMR and ¹³C NMR spectra were recorded at 25 °C in CDCl₃ at 400 and 100 MHz, respectively, with TMS as the internal standard. Chemical shifts (δ) are expressed in ppm and coupling constants *J* are given in Hz. All reactions were performed on the photoreaction instrument (WP-TEC-1020SL), which are purchased from WATTCAS, China. Fluorescence spectra were performed on a F-7000 spectrophotometer (Hitachi Ltd., Japan) with excitation and emission lit widths of 5 nm.

2. General procedure

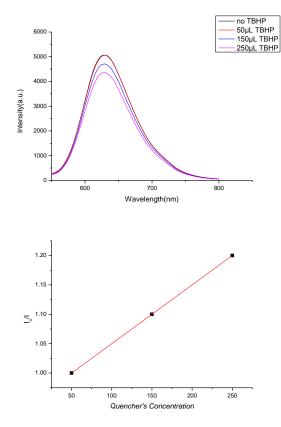


Experimental Procedure: To a stirred solution of **1** (0.25 mmol) in DMSO (2.0 mL) were added **2** (2.5 eq., 0.625 mmol), Ru(bpy)₃Cl₂ $6H_2O$ (5 mol%) and TBHP (70% aqueous solution, 2.5 eq., 0.625 mmol). The resulting mixture was stirred in air under a 10W blue LEDs (460~465nm) and irradiated for 10 h. The temperature was maintained at 20~25 °C when the LED light was on. After the reaction was complete, the reaction mixture was diluted with a brine solution (25 mL) and extracted with EtOAc (30 mL×3). The combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by flash column chromatography to afford the desired products **3a-4b**.

3. Stern-Volmer fluorescence quenching experiments

The fluorescence emission intensities were carried out on an F-7000 FL spectrophotometer (Hitachi Ltd, Japan) with excitation slit set at 5 nm and emission at 5 nm. The excitation wavelength was fixed at 450 nm, and the emission wavelength

was measured at 550~800 nm. The samples were prepared by mixing Ru(bpy)₃Cl₂ 6H₂O (5.0 μ m in DMSO) and different amount of TBHP (0.01M in DMSO) in a light path quartz fluorescence cuvette. For each quenching experiment, 0 μ L $_{\sim}$ 50 μ L $_{\sim}$ 150 μ L and 250 μ L stock solution of TBHP was titrated to the solution of Ru(bpy)₃Cl₂ 6H₂O. Then the emission intensity was collected and the results were presented as follows:



4. ¹H NMR and ¹³C NMR spectra of products

