

Supporting Information

Visible-light-induced a tandem oxidative cyclization of 2-alkynylanilines with disulfides(diselenides) to 3-sulfenyl- and 3-selenylindoles under transition-metal-free and photocatalyst-free conditions

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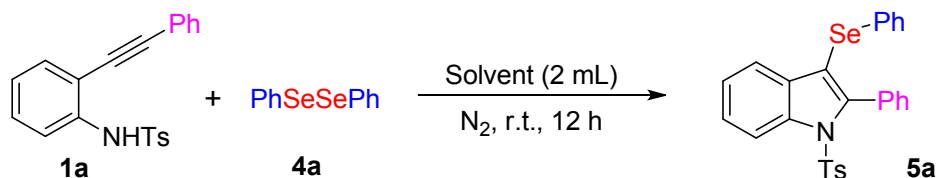
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1. Optimization of the reaction conditions^a (Table S1)

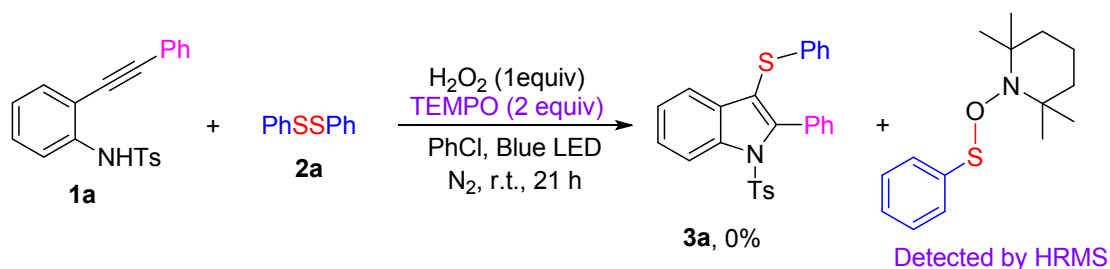


Entry	Oxidant	Solvent	Light Source	Yield ^b (%)
1	H ₂ O ₂	PhCl	Blue LED	72
2	H ₂ O ₂	PhMe	Blue LED	75
3	H ₂ O ₂	Acetone	Blue LED	28
4	H ₂ O ₂	CH ₃ CN	Blue LED	97
5	H ₂ O ₂	DMC	Blue LED	33
6	H ₂ O ₂	DCE	Blue LED	54
7	H ₂ O ₂	MeOH	Blue LED	n.r.
8	H ₂ O ₂	EtOH	Blue LED	n.r.
9	H ₂ O ₂	DMF	Blue LED	n.r.
10	H ₂ O ₂	DMSO	Blue LED	n.r.
11	H ₂ O ₂	1,4-Dioxane	Blue LED	n.r.
12	H ₂ O ₂	CH ₃ CN	Blue LED	69 ^c , 88 ^d
13	H ₂ O ₂	CH ₃ CN	Blue LED	73 ^e , 98 ^f
14	H ₂ O ₂	CH ₃ CN	Blue LED	68 ^g , 83 ^h , 97 ⁱ

^a Reaction conditions: **1a** (0.20 mmol), **4a** (0.125 mmol), H₂O₂ (1.0 equiv, 30% aqueous solution), solvent (2.0 mL), nitrogen atmosphere at room temperature under 3 W LED irradiation for 12 h. ^b isolated yield of the product based on compound **1a**; ^c H₂O₂ (0.50 equiv, 30% aqueous solution) was used. ^d H₂O₂ (1.5 equiv, 30% aqueous solution) was added. ^e **4a** (0.10 mmol) was used. ^f **4a** (0.15 mmol) was added. ^g 6 h. ^h 9 h. ⁱ 15 h.

2. Reaction mechanism study

2.1 Free radical-trapping experiment (I)



4-Methyl-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide (**1a**, 0.20 mmol), diphenyl disulfide (**2a**, 0.125 mmol), H_2O_2 (1.0 equiv, 30% aqueous solution) and chlorobenzene (2.0 mL) and (2,2,6,6-tetramethylpiperidine)-1-oxyl (TEMPO, 0.40 mmol, 2.0 equiv) was added to an oven-dried Schlenk tube equipped with magnetic stirring bar, and the reaction tube was irradiated using 3 W blue LED at room temperature under N_2 atmosphere for 21 h. After the reaction was completed, no desired product **3a** was obtained, and a free radical-trapping adduct of PhS^\bullet with TEMPO was observed by HPLC-HRMS analysis of the reaction solution (Figure S1).

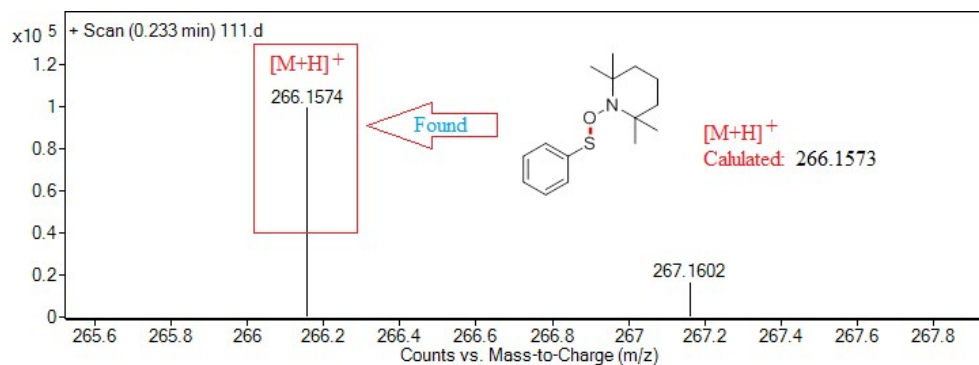
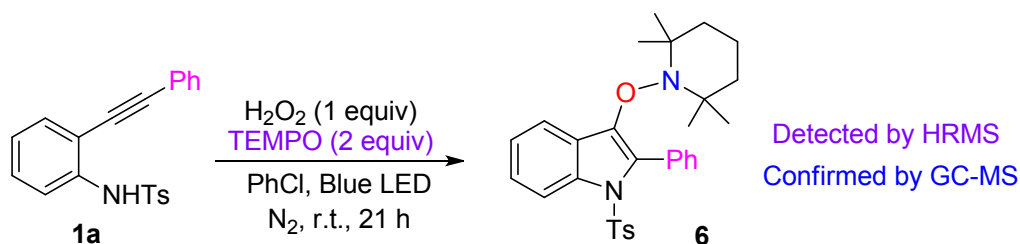


Figure S1. HRMS analysis of the adduct of PhS^\bullet with TEMPO

2.2 Free radical-trapping experiment (II)



4-Methyl-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide (**1a**, 0.20 mmol), H₂O₂ (1.0 equiv, 30% aqueous solution) and chlorobenzene (2.0 mL) and (2,2,6,6-tetramethylpiperidine)-1-oxyl (TEMPO, 0.40 mmol, 2.0 equiv) was added to an oven-dried Schlenk tube equipped with magnetic stirring bar, and the reaction tube was irradiated using 3 W blue LED at room temperature under N₂ atmosphere for 21 h. After the reaction was completed, a free radical-trapping adduct (**6**) of indole radical with TEMPO, which was confirmed by HPLC-HRMS and GC-MS analysis of the reaction solution (Figure S2 and S3).

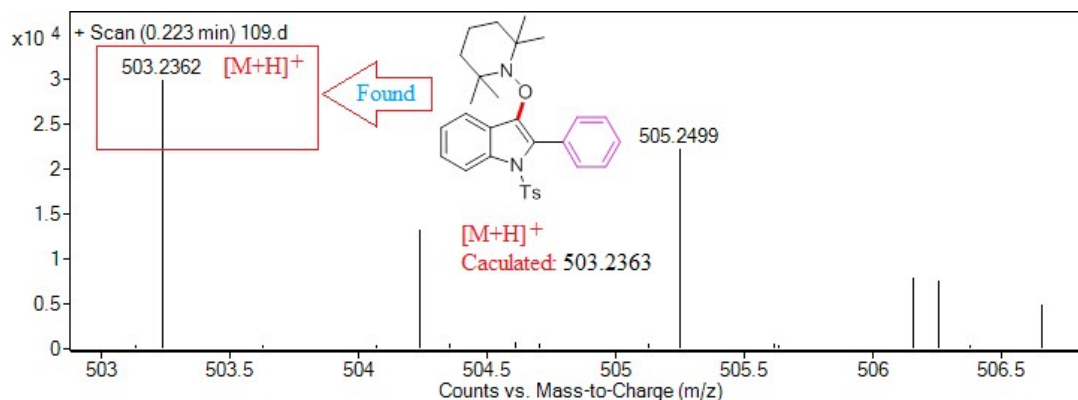


Figure S2. HRMS analysis of the adduct of adduct (**6**) of indole radical with TEMPO

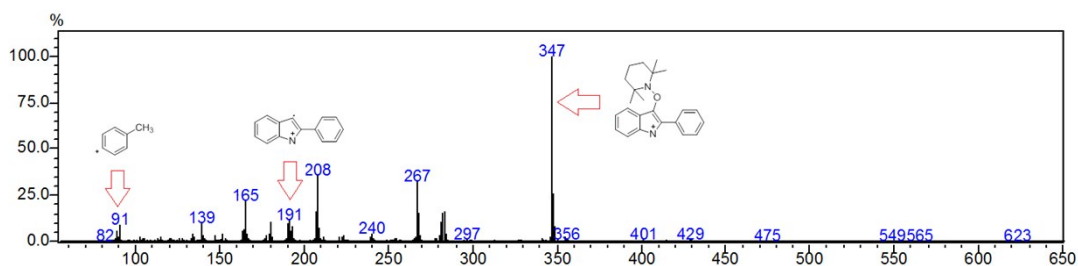


Figure S3. GC-MS analysis of the adduct of adduct (**6**) of indole radical with TEMPO

3. ^1H and ^{13}C NMR spectra of the products

