

**Visible-light-induced decarboxylative sulfonylation of cinnamic acids
with sodium sulfinates by using Merrifield resin supported Rose
Bengal as catalyst sulfinates**

Pinhua Li^{*a,b} and Guan-Wu Wang^{*a}

^a Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China, E-mail: pphuali@126.com; gwang@ustc.edu.cn

^b Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P R China

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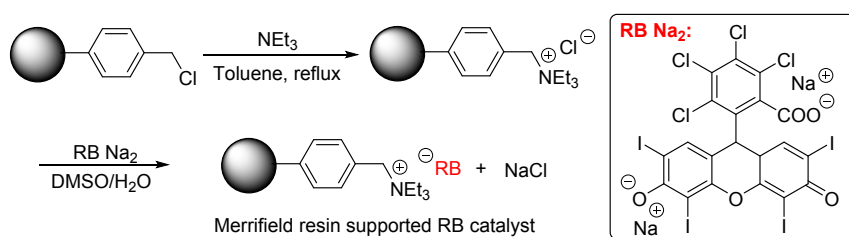
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1. General considerations

The ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400 MHz and 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). CHN analysis was performed using a Vario EL III elemental. Scanning electron micrographs (SEM) were obtained using a FESEM-SU8220 scanning electron microscope. All the solvents and commercially available reagents were purchased from commercial suppliers. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2 .

2. Experimental Section

2.1 The preparation of Merrifield resin immobilized Rose Bengal catalyst



Under nitrogen atmosphere, triethylamine (0.3 g) and Merrifield Resin (3.0 g, loading 1.0 mmol/g active Cl from GL Biochem Shanghai Ltd.) were mixed in toluene (20 mL). The solution was kept at 70 °C and stirred for 24 h, then the solution was filtered and the solid was washed with ethanol and ethyl ether, respectively, and dried under vacuo at 60 °C, 3.06 g of benzyltriethylammonium chloride functionalized Merrifield resin as pale solid was obtained, and the loading of benzyltriethylammonium chloride was quantified by CHN microanalysis and was found to be 0.36 mmol·g⁻¹ based on nitrogen content determination.

In a sealable reaction tube, Rose Bengal sodium salt (51.0 mg, 0.05 mmol) was added to a solution of DMSO and H_2O (15.0 mL, $V_{\text{DMSO}} : V_{\text{water}} = 1:1$), and the mixture was shaking at room temperature for 20 min., then the above

benzyltriethylammonium chloride functionalized Merrifield resin (2.0 g) were added, and the mixture was shaking at room temperature for 3 h. Finally, the catalyst was separated by filtration, and the solid was washed with water (10.0 mL*2), EtOH (10.0 mL*2), and ethyl ether (10.0 mL*2), respectively, and then dried under vacuum at 50 °C for 2 h. It was found that Rose Bengal sodium salt could be immobilized successfully through overall ion-exchange, and there was minimal level of RB leaching in the solution determined via spectrophotometric method, and the supported catalyst was obtained with a loading of 0.025 mmol of RB per gram.



Fig. S1. The prepared supported catalyst: (1) the benzyltriethylammonium chloride functionalized Merrifield resin (left); (2) The supported Rose Bengal ammonium salt (right).

2.2 SEM images of the catalytic materials

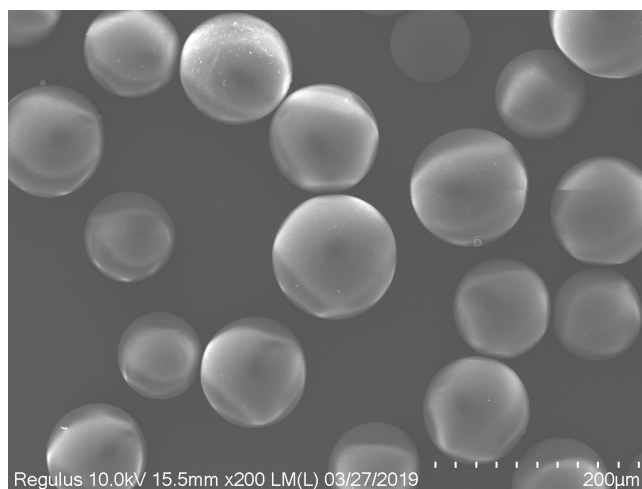


Fig. S2. (a) SEM images for the benzyltriethylammonium chloride functionalized Merrifield resin.

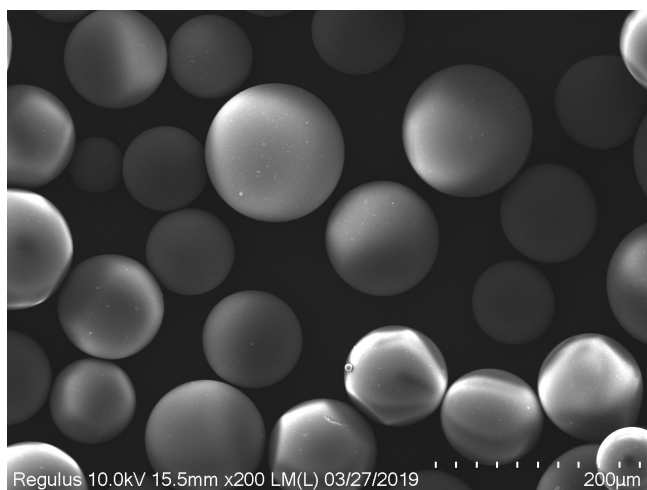


Fig. S2. (b) SEM images for Merrifield resin supported RB catalyst

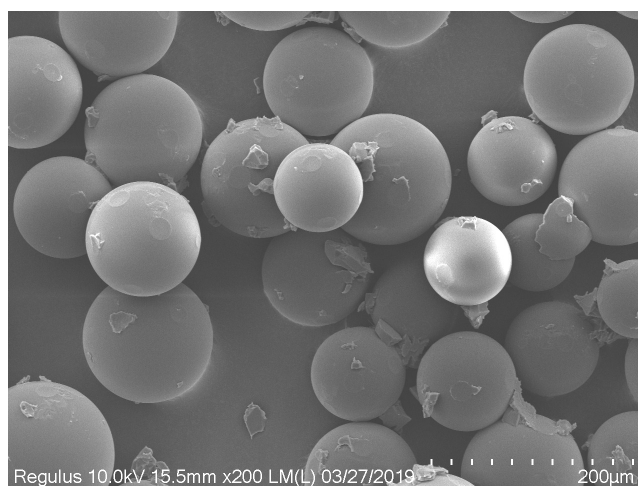


Fig. S2. (c) SEM images for the 4th recycled Merrifield resin supported RB catalyst

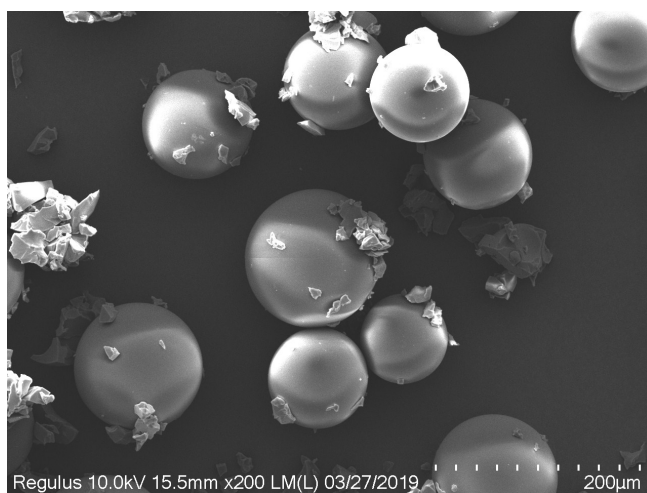
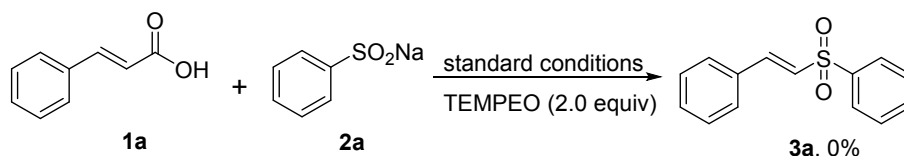


Fig. S2. (d) SEM images for the 6th recycled Merrifield resin supported RB catalyst

2.3 Preliminary mechanistic study

2.3.1 Free radical-inhibiting experiment

When the model reaction was carried out in the presence of a radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 2.0 equiv.) under the standard conditions, the decarboxylative sulfonylation was completely inhibited.



2.3.2 Determination of hydroxyl radicals

In order to determine the active radical species involved in the present reaction, 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) was employed to capture OH[•]. There was no signal when DMPO was added into a solution of supported catalyst, TBHP and sodium benzenesulfinate (2a) in air in the absence of light irradiation (Figure S3A). Irradiation of the above reaction solution in air with LED (530–535 nm, 3 W) resulted in the formation of a strong characteristic signal of OH[•] adduct with DMPO (Figure S3B). When the reaction time was prolonged, a series of weaker characteristic signal of OH[•] were observed (Figure S3C and S3D), indicating the formation and the consumption of OH[•] in the reaction.

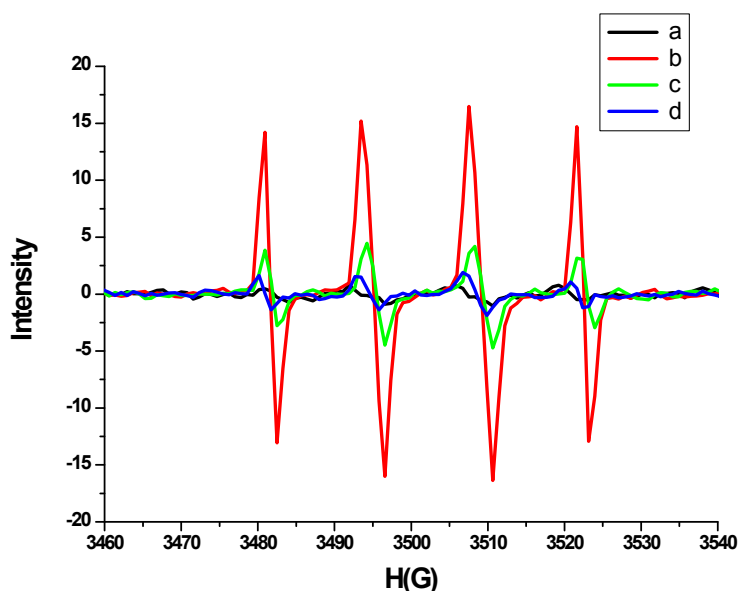


Figure S3. Electron spin resonance (ESR) spectra of 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) with OH[•]

(A) A solution of DMPO (0.20 mol/L) with the reaction mixture in aqueous DMSO

solution without light irradiation.

(B) A solution of DMPO (0.20 mol/L) with the reaction mixture in aqueous DMSO solution under LED (530–535 nm, 3 W) irradiation for 30 s.

(C) A solution of DMPO (0.20 mol/L) with the reaction mixture in aqueous DMSO solution under LED (530–535 nm, 3 W) irradiation for 60 s.

(D) A solution of DMPO (0.20 mol/L) with the reaction mixture in aqueous DMSO solution under LED (530–535 nm, 3 W) irradiation for 90 s.

2.4 General procedure for the decarboxylative sulfonylation of cinnamic acid with sodium arylsulfonates

A 10 mL reaction vessel equipped with a magnetic stirrer bar was charged with cinnamic acid (**1a**, 0.25 mmol), sodium benzenesulfinate (**2a**, 0.50 mmol), Merrifield resin supported Rose Bengal ammonium salt (5.0 mol%, 0.5 g, contain RB 0.0125 mmol), TBHP (70% in water, 0.50 mmol, 2.0 equiv.) and DMSO/H₂O (2.5 mL, V/V = 4:1). The reaction vessel was irradiated under green LED irradiation (530–535 nm, 3.0 W) at room temperature for 12 h. After completion of the reaction, the mixture was transferred to the separating funnel, diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate and the combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuum to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate) to give the desired product (*E*)-(2-(phenylsulfonyl)vinyl)benzene (**3a**) in 76% yield.

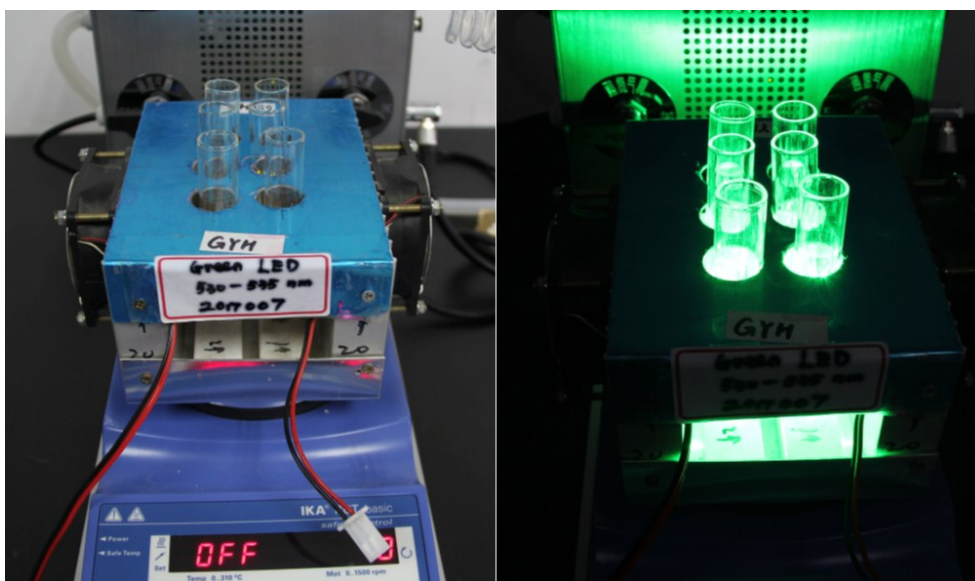


Figure S4. The experimental apparatus.

The green LED (3 W, 530-535 nm) located 1.0 cm away from the tube wall of the reaction vessel was used as light source to drive the photocatalytic of the reaction.

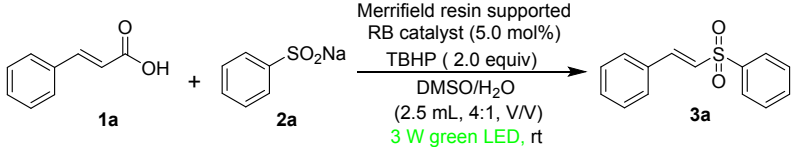
2.5 General procedure for the decarboxylative sulfonylation of cinnamic acid with sodium benzenesulfinate in gram-scale

A 50 mL reaction vessel equipped with a magnetic stirrer bar was charged with cinnamic acid (**1a**, 5.0 mmol), sodium benzenesulfinate (**2a**, 10.0 mmol), Merrifield resin supported Rose Bengal ammonium salt (5.0 mol%, 10 g, contain RB 0.25 mmol), TBHP (70% in water, 10.0 mmol, 2.0 equiv.) and DMSO/H₂O (30 mL, V/V = 4:1). The reaction vessel was irradiated under green LED irradiation (530–535 nm, 3 W*2, two lamp) at room temperature for 18 h. After completion of the reaction, the mixture was transferred to the separating funnel, diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate and the combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuum to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate) to give the desired product (*E*)-(2-(phenylsulfonyl)vinyl)benzene (**3a**) in 62% yield.

2.6 The recovery and reuse of the Merrifield resin immobilized Rose Bengal catalyst

The supported catalyst was separated from the reaction mixture by filtration and the separated catalyst was washed with ethanol, ethyl acetate and diethyl ether, respectively. After being dried in air, it was reused directly in the model reaction without any further treatment. Notably, the supported catalyst can be recycled at least six times without a significant loss of activity. While the yield of the product was decreased dramatically in the 7th run, and only 33% yield of **3a** was obtained. For a better understanding of this result, the catalyst was analyzed by scanning electron microscope (SEM) again, and the SEM photographs indicate that the resin is damaged after long-term stirring (Fig. S2d), and the eosin Y leaching has been founded.

Table S1. Recycling Merrifield resin immobilized Rose Bengal ammonium salt for the decarboxylative sulfonylation of cinnamic acid and sodium benzenesulfinate^a



Reaction scheme showing the decarboxylative sulfonylation of cinnamic acid (**1a**) with sodium benzenesulfinate (**2a**) to form cinnamic sulfone (**3a**). The reaction conditions are: Merrifield resin supported RB catalyst (5.0 mol%), TBHP (2.0 equiv), DMSO/H₂O (2.5 mL, 4:1, V/V), 3 W green LED, rt.

Run	Yield ^b (%)	Run	Yield ^b (%)
1	76	5	71
2	77	6	69
3	74	7	33
4	70	8	26

^a Reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), photocatalyst (5.0 mol%), oxidant (0.50 mmol, 2.0 equiv.), solvent (2.5 mL, $V_{\text{DMSO}}/V_{\text{H}_2\text{O}} = 4:1$) at room temperature under LED irradiation (1.5 W) in air for 12 h. ^b Isolated yield.

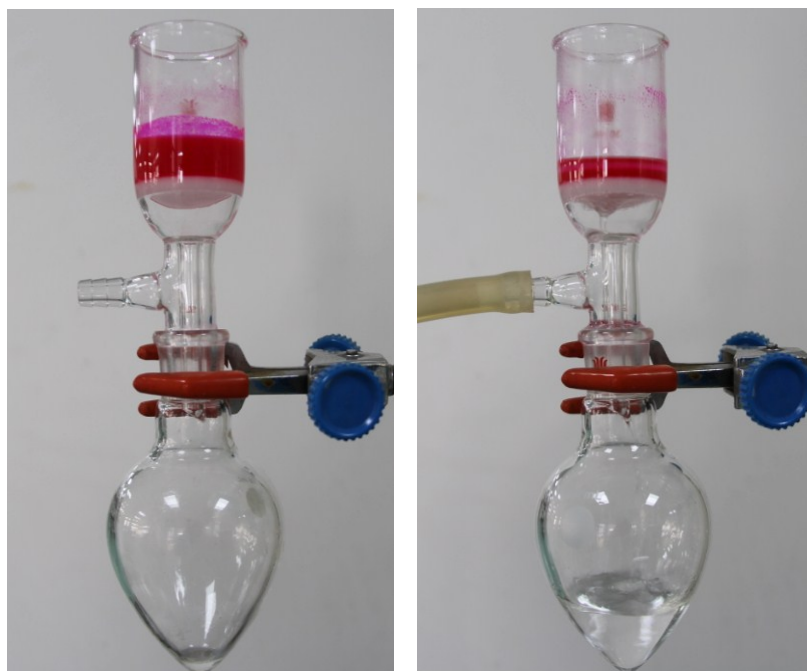


Fig. S5. Separation of the supported catalyst: (a) The reaction mixture, the supported catalyst was dispersed in the reaction solution (left); (b) after the reaction, the supported catalyst was separated from the reaction solution by filtration(right).

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

