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ARTICLE

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

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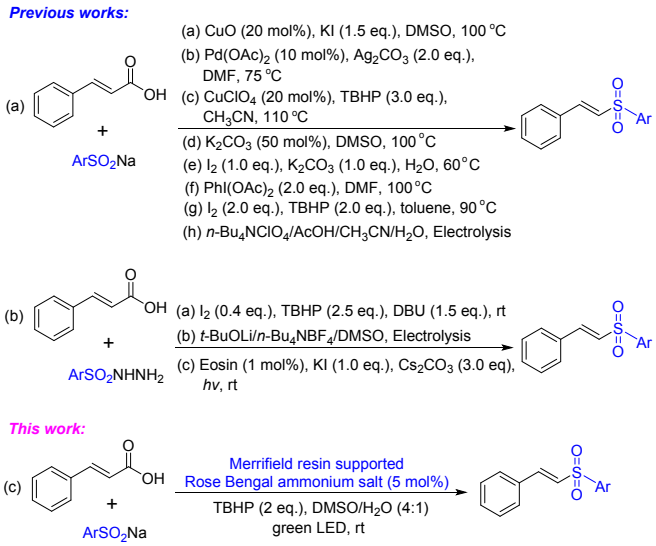
A visible-light-induced decarboxylative sulfonylation of cinnamic acids with sodium sulfinates for the synthesis of vinyl sulfones were developed. The reaction underwent smoothly in the presence of Merrifield resin supported Rose Bengal ammonium salt as a photocatalyst, *tert*-butyl hydroperoxide (70% in water) as an oxidant in aqueous DMSO solution at room temperature under green LED (530−535 nm) irradiation in air atmosphere, generating the desired products in good yields. Notably, the supported catalyst can easily be separated from the reaction mixture by filtration and can be recycled at least six times without a significant loss of activity.

Introduction

Vinyl sulfones are valuable synthetic intermediates and constitute a significant component in natural products and in drug discovery.[1] In the past few years, the synthesis of vinyl sulfones has received much attention and a lot of synthetic routes have been established. The classic vinyl sulfone preparations are based on the Knoevenagel condensation and the Horner–Emmons reaction.[2] Recently, decarboxylative sulfonylation of cinnamic acids with sodium arylsulfonates or aromatic sulfonylhydrazides are one of the most attractive methods for the preparation of vinyl sulfones (Scheme 1a and 1b). For the elegant examples, Guo reported the synthesis of vinyl sulfones by a Cu(II)-catalyzed decarboxylative sulfonylation of cinnamic acids with sodium sulfonates in 2014,[3] and Tan's group realized this transformation by a Pd catalyst.[4] Moreover, the I_2, $PhI(OAc)_2$ or bases or electrolysis could also promote this decarboxylative sulfonylation with satisfactory results.[5] In addition, Singh developed an I_2/TBHP-promoted decarboxylative sulfonylation of cinnamic acids with sulfonyl hydrazides in 2015,[6] and Cai realized a visible-light-induced decarboxylative sulfonylation of cinnamic acids with sulfonyl hydrazides using eosin Y as a photoredox catalyst,[7] and Huang demonstrated an electrochemical decarboxylative sulfonylation of cinnamic acids with aromatic sulfonylhydrazides in 2017.[8] It is note that the sulfonylation of alkenes with sodium sulfonates or aromatic sulfonylhydrazides have also been developed. Jiang reported a copper/air catalytic system for the regioselective sulfonation of alkene in 2014,[9] and König also realized the sulfonation of alkene with sodium sulfonates through visible light photoredox catalysis.[10] Despite those established methodologies are efficient, limitations or drawbacks still remain, such as the use of transition metals, strong oxidants or harsh reaction conditions. Accordingly, the development of more practical and alternative route to prepare vinyl sulfones is still highly desirable.



Scheme 1. The strategies for Synthesis of vinyl sulfones

As a continuation of our interest in visible-light photochemistry[11] and inspired by the recent studies of decarboxylative sulfonylation of cinnamic acids with sodium sulfonates, we would like to realize this transformation by visible light photoredox catalysis. Fortunately, we have achieved this assumed process, the decarboxylative sulfonylation of cinnamic acids with sodium

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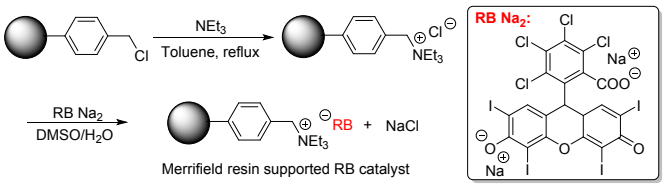
sulfinates underwent smoothly in the presence of Rose Bengal sodium salt (5 mol%) as a photocatalyst, *tert*-butyl hydroperoxide (70% in water) as an oxidant in aqueous DMSO solution at room temperature under green LED (530−535 nm) irradiation in air atmosphere. In continuing our efforts to develop economical and ecofriendly synthetic protocols for organic transformations from the view of sustainable chemistry,[12] a very convenient method for immobilization of Rose Bengal ammonium salt on Merrifield resin by overall ion-exchange process has been developed. To our pleasure, the supported catalyst exhibits high photo-catalytic activity for the decarboxylative sulfonylation of cinnamic acids with sodium sulfinates (Scheme 1c). More importantly, the supported catalyst could be recovered and reused well at least six times without significant loss of catalytic activity.

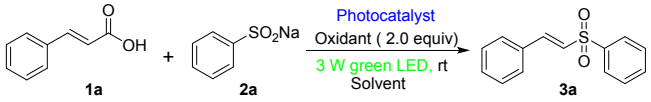
The Merrifield resin immobilized Rose Bengal ammonium salt was easily prepared from the commercially available Merrifield resin (loading 1.0 mmol/g active Cl, from GL Biochem Shanghai Ltd.) according to Scheme 2. At first, Merrifield resin reacted with triethylamine in toluene under reflux condition for 12 h to generate the benzyltriethylammonium chloride functionalized Merrifield resin. Then, the resin supported Rose Bengal ammonium salt was obtained by simply dissolving Rose Bengal sodium salt in the mixture of DMSO and water (1:1, V/V), and treating it with the above quaternary ammonium salt functionalized Merrifield resin, with a loading of 0.025 mmol of RB per gram determined via spectrophotometric method, and there was no noticeable level of Rose Bengal leaching in the solution. For a better understanding of the morphologies of the supported catalysts, SEM photographs were taken at different synthesis stages. It is clearly visible that the particles were on the order of micrometer in size, and the relative smooth surface of the starting polymer changed after immobilization of the RB catalyst. The recovered catalyst after being reused five times was also characterized by SEM, and displayed rather rough surfaces in comparison with the fresh catalyst (Fig. S2, See supporting information). It means that the mechanical strength of the Merrifield resin is not good enough, and the surface of the resin is damaged after long-term stirring.



Scheme 2 Preparation of the Merrifield resin supported Rose Bengal catalyst.

Firstly, a model reaction of cinnamic acid (**1a**, 0.25 mmol) and sodium benzenesulfinate (**2a**, 0.50 mmol) was chosen to optimize the reaction conditions, as shown in Table 1. When the model reaction was performed in the presence of eosin Y as a photocatalyst, *tert*-butyl hydroperoxide (TBHP, 70% in water) as an oxidant in aqueous DMSO solution at room temperature under green LED (530−535 nm) irradiation in air atmosphere, the corresponding product (*E*)-(2-(phenylsulfonyl)vinyl)benzene (**3a**) was obtained in 65% yield (Table 1, entry 1). In the absence of visible-light irradiation, no desired product was formed, and only a trace amount of **3a** was detected without a photocatalyst (Table 1, entries 2 and 3). A slightly improved yield of **3a** was achieved when

Table 1 Optimization of the reaction conditions[a]

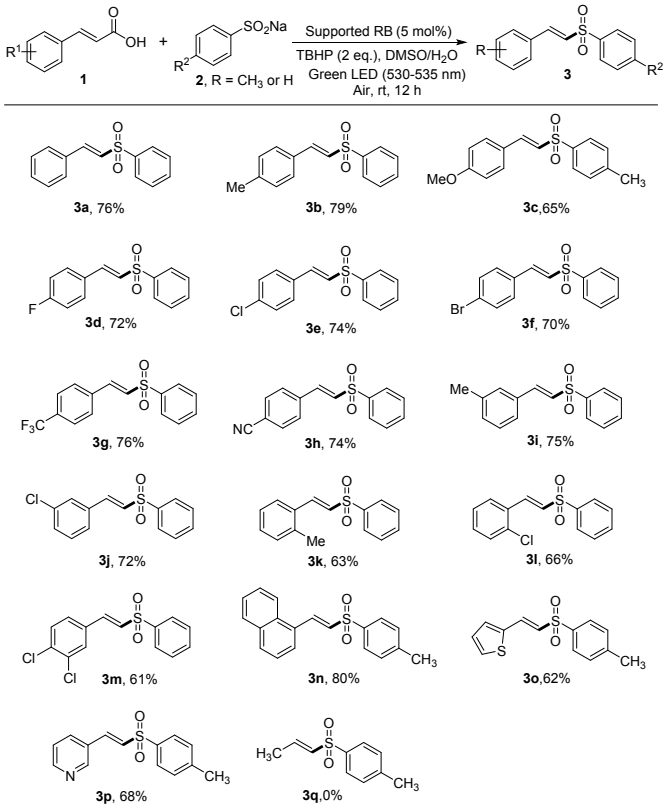


Entry	Photocatalyst	Oxidant	Solvent	Yield of **3a** (%)[b]
1	Eosin Y-Na_2	TBHP	DMSO/H_2O	65
2	Eosin Y-Na_2	TBHP	DMSO/H_2O	NR[c]
3	–	TBHP	DMSO/H_2O	Trace
4	Rose Bengal	TBHP	DMSO/H_2O	71
5	Rose Bengal	TBHP	DMSO	61[d]
6	Rose Bengal	DTBP	DMSO/H_2O	41
7	Rose Bengal	O_2	DMSO/H_2O	Trace
8	Rose Bengal	H_2O_2	DMSO/H_2O	Trace
9	Rose Bengal	$K_2S_2O_8$	DMSO/H_2O	Trace
10	Rose Bengal	TBHP	CH_3CN/H_2O	Trace
11	Rose Bengal	TBHP	DMF/H_2O	Trace
12	Rose Bengal	TBHP	THF/H_2O	Trace
13	Rose Bengal	TBHP	EtOH/H_2O	Trace
14	Rose Bengal	TBHP	Acetone/ H_2O	Trace
15	Supported RB	TBHP	DMSO/H_2O	76[e]
16	Supported RB	TBHP	DMSO/H_2O	75[f]
17	Supported RB	TBHP	DMSO/H_2O	49[g], 75[h]
18	Supported RB	TBHP	DMSO/H_2O	40[i], 70[j]
19	Supported RB	TBHP	DMSO/H_2O	50[k], 73[l]
20	Supported RB	TBHP	DMSO/H2O	55[m], 70[n]
21	Supported RB	TBHP	DMSO/H_2O	55[o], 72[p]

[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_{DMSO}/V_{H2O} = 4:1) at room temperature under LED irradiation (3.0 W) in air for 12 h. [b]Isolated yield. [c]In dark. [d]anhydrous DMSO (2.5 mL) was used. [e]Merrifield resin immobilized Rose Bengal ammonium salt was added (0.5 g, contain RB 0.0125 mmol). [f]Nitrogen atmosphere. [g]Merrifield resin immobilized Rose Bengal ammonium salt was added (0.25 g, contain RB 0.00625 mmol). [h]Merrifield resin immobilized Rose Bengal ammonium salt was added (1.0 g, contain RB 0.025 mmol). [i]TBHP (0.25 mmol, 1.0 equiv.) was used. [j]TBHP (0.75 mmol, 3.0 equiv.) was added. [k]Sodium benzenesulfinate (**2a**, 0.30 mmol) was added. [l]Sodium benzenesulfinate (**2a**, 0.75 mmol) was added. [m]DMSO/H_2O (V/V = 4:1). [n]DMSO/H_2O (V/V = 5:1). [o]For 8 h. [p]For 16 h. NR = no reaction.

Rose Bengal sodium salt was used as the photocatalyst (Table 1, entry 4). However, there was only 61% yield of **3a** was obtained when the reaction was performed in anhydrous DMSO (Table 1, entry 5). The oxidants screening showed that di-*tert*-butyl peroxide (DTBP) exhibited inferior reactivity, generating **3a** in 41% yields (Table 1, entry 6), but oxygen, hydrogen peroxide (30% in water) and potassium persulfate were failed (Table 1, entries 7−9). The solvent also plays an important role in the reaction and the aqueous DMSO solution is the best of choice among the tested solvents. When the model reaction was carried out in the aqueous solution of CH_3CN, DMF, THF, CH_3CH_2OH and acetone (The volume ratio of organic solvent to H_2O was 4:1), only a trace amount of **3a** was detected (Table 1, entries 10−14). It was pleasing to find that when

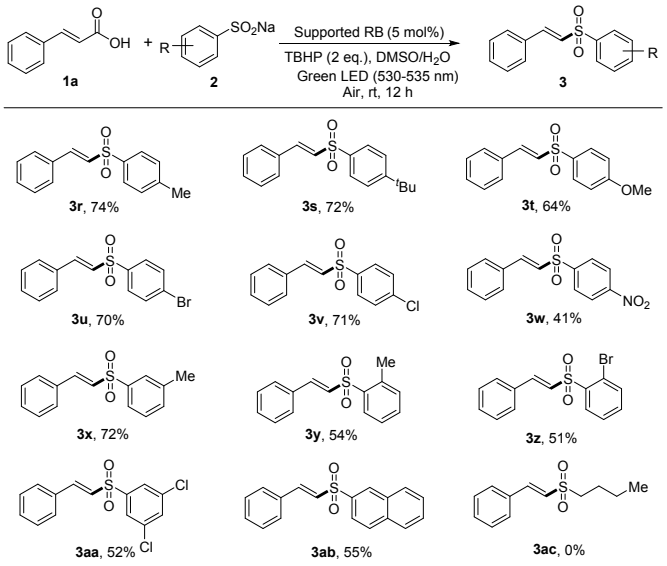
the Merrifield resin immobilized Rose Bengal ammonium salt was used as the photocatalyst, 76% yield of the desired product **3a** was obtained (Table 1, entry 15). Moreover, When the model reaction was conducted under nitrogen atmosphere, the desired product was obtained in a comparable yield (Table 1, entry 16). Further investigation on the loading of supported catalyst and oxidant, molar ratio of **1a** to **2a**, volume ratio of DMSO to H_2O, as well as reaction time was also optimized and presented in Table 1 (entries 17−21). After all, the optimized reaction conditions are consisted of the supported photocatalyst (5.0 mol%) and TBHP (2.0 equiv) in aqueous DMSO solution at room temperature under green LED irradiation (530**–**535 nm, 3 W) for 12 h.



Scheme 3. The scope of cinnamic acids [*Reaction conditions:* **1** (0.25 mmol), **2a** or **2b** (0.50 mmol), Merrifield resin immobilized Rose Bengal ammonium salt (0.5 g, contain RB 0.0125 mmol), TBHP (0.50 mmol, 2.0 equiv.), DMSO/H_2O (2.5 mL, V/V = 4:1) at room temperature under green LED irradiation (530−535 nm, 3 W) for 12 h; isolated yield of the product.]

To explore the generality of this decarboxylative sulfonylation reaction, different substituted cinnamic acids reacted with sodium benzenesulfinate (**2a**) or sodium toluene-4-sulphinate (**2b**) under the optimized conditions. The results are listed in Scheme 3. In general, a variety of cinnamic acids were attempted to react with **2a** or **2b**, and a broad tolerance of the reaction towards substituents on the aromatic rings was observed. When cinnamic acids with an electron-donating group, such as Me, OCH_3 on the *para*-position of benzene rings reacted smoothly with **2a** or **2b** to generate the corresponding products (**3b** and **3c**) in 79% and 65% yields, respectively. When the cinnamic acids having an electron-withdrawing group including fluoro, chloro, bromo, trifluoromethyl and cyano groups on the phenyl rings reacted all with **2a** efficiently to deliver the corresponding products (**3d**−**3h**) in 72−76% yields. Moreover, *m*- and *o*-substituted cinnamic acids with an electron-donating or electron-withdrawing group, such as *m*-methyl, *m*-chloro, *o*-methyl and *o*-chloro) on the benzene rings could also be applied to the reaction with **2a** and afforded the desired products (**3i**–**3l**) in 63−75% yields, and no obvious steric effect was observed. It is worth mentioning that this strategy could also be used to the reactions of *(E)*-3-(3,4-dichlorophenyl)acrylic acid and *(E)*-3-(1-naphthyl)acrylic acid with **2a** or **2b**, affording **3m** and **3n** in 60% and 80% yields, respectively. It should be noted that (*E*)-3-(2-thienyl)acrylic acid and 3-pyridineacrylic acid were proved to be the amenable substrates to afford the desired product **3o** and **3p** in 62% and 68% yields. Unfortunately, when crotonic acid was used as substrate, the decarboxylative sulfonylation reaction was failed, and no any product was obtained.

Next, the scope of sodium arylsulfinates were also investigated under optimized reaction conditions, and the results are presented in Scheme 4. It was observed that a variety of sodium arylsulfinates are valid substrates for this reaction. The reaction could tolerate a number of sodium arylsulfinates with an electron-rich substitute such as Me, *t*-Bu and OMe at the *para*-position of the phenyl rings, affording the desired products **3r**–**3t** in 64−74% yields. Meanwhile, sodium arylsulfinates with an electron-poor substitute such as Cl, Br and NO_2 at the *para*-position of the phenyl rings, providing the corresponding products **3u**–**3w** in 41−71% yields. In addition, sodium toluene-3-sulphinate was also converted to the corresponding product **3x** in 72% yield. However, the *ortho*-substitute sodium benzenesulfinate afforded the products **3y** and **3z** in lower yields. It should be noted that sodium 3,5-dichlorophenylsulfinate and sodium 2-naphthalenesulfinate were also compatible in this reaction, afford the desired product **3aa** and **3ab** in 52% and 55% yields, respectively. In order to further extend the scope of the reaction, sodium alkyl sulfinate, such as sodium *n*-butylsulfinate, was also employed in this transformation, however, no desired product **3ac** was isolated.

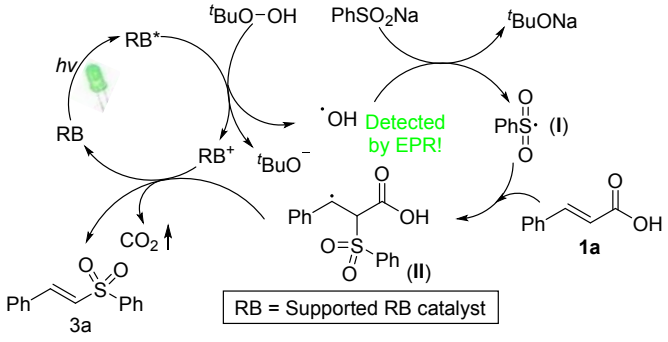


Scheme 4. The scope of sodium sulfinates [*Reaction conditions:* **1a** (0.25 mmol), **2** (0.50 mmol), Merrifield resin immobilized Rose Bengal ammonium salt (0.5 g, contain RB 0.0125 mmol), TBHP (0.50 mmol, 2.0 equiv.),

DMSO/H_2O (2.5 mL, V/V = 4:1) at room temperature under green LED irradiation (530−535 nm, 3 W) for 12 h; isolated yield of the product.]

To further illustrate the utility of the developed methodology, a gram-scale experiment was conducted. The reaction of cinnamic acid (**1a**, 5.0 mmol) and sodium toluene-4-sulphinate (**2b**, 10.0 mmol) could be performed on 5 mmol scale, providing the desired product **3a** in 62% yield (0.8 g).

To understand this transformation, a free radical-inhibiting experiment and analytical survey were conducted. 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, suggesting that a radical process might be involved in the reaction. Additionally, the electron paramagnetic resonance (EPR) spectra were recorded using 5,5-dimethyl-pyrroline-N-oxide (DMPO) for capturing OH•, and the result indicated that OH• was formed and consumed in the reaction. Based on the preliminary study and the related reports,[13] a possible mechanism is proposed in Scheme 5. Initially, a *tert*-butoxyl radical is produced by a SET from the reaction of excited state of Rose Bengal* with *tert*-butyl hydroperoxide (TBHP). Then, a single electron oxidation of sodium benzenesulfinate (**2a**) by *tert*-butoxyl radical to give the corresponding sulfonyl radical (**I**) and *t*-BuONa. Subsequently, the addition of sulfonyl radical (**I**) to cinnamic acid (**1a**) to afford an important intermediate (**II**), which reacts with RB^+ via SET to afford the desired product **3a** along with the release of CO_2 as the sole by-product and the regeneration of RB.



Scheme 5. The proposed mechanism

Finally, the viability of recovering and reusing the Merrifield resin supported Rose Bengal ammonium salt as a photocatalyst for the visible-light-induced decarboxylative sulfonylation of cinnamic acid (**1a**) with sodium toluene-4-sulphinate (**2b**) was examined. It was found that the catalyst could be reused at least six times without a noticeable loss of catalytic activity with minimal levels of Rose Bengal leaching (See supporting information for detail). The supported catalyst could be collected and reused by filtration and the separated catalyst was washed with DMSO, ethyl acetate and diethyl ether, respectively. After being dried in air, it can be reused directly without any further treatment.

Conclusions

In conclusion, we have developed a visible-light-induced decarboxylative sulfonylation of cinnamic acids with sodium arylsulfinates for the preparation of vinyl sulfones. The reaction underwent smoothly in the presence of Merrifield resin supported Rose Bengal ammonium salt as a photocatalyst, *tert*-butyl hydroperoxide (70% in water) as an oxidant in aqueous DMSO solution at room temperature under green LED (530−535 nm) irradiation in air atmosphere, generating the desired products in good yields. Notably, the supported catalyst can be recycled at least six times without a significant loss of activity. The supported catalyst can be easily separated from the reaction mixture by simple filtration and its further applications in organic synthesis is underway in our laboratory.

Experimental section

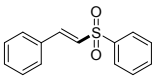
General remarks

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). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). CHN analysis was performed using a Vario EL III elementar. 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.

Typical procedure for the decarboxylative sulfonylation of cinnamic acid with sodium arylsulfinates.

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/H_2O (2.5 mL, V/V = 4:1). The reaction vessel was irradiated under green LED irradiation (530−535 nm, 3 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 Na_2SO_4, 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.

Characterization data for all products



(*E*)-(2-(Phenylsulfonyl)vinyl)benzene (3a)[7]**:** White solid. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 14.8 Hz, 1H), 7.62−7.59 (m, 1H), 7.55−7.52 (m, 2H), 7.48−7.46 (m, 2H), 7.41−7.35

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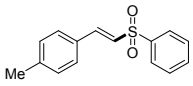
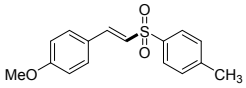
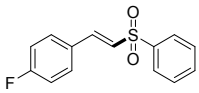
(m, 3H), 6.88 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.4, 140.6, 133.3, 132.2, 131.1, 129.2, 129.0, 128.5, 127.5, 127.2.



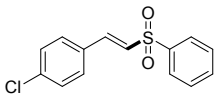
(*E*)–1-Methyl-4-(2-(phenylsulfonyl)vinyl)benzene (3b)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95–7.93 (m, 2H), 7.66 (d, *J* = 15.2 Hz, 1H), 7.63–7.58 (m, 1H), 7.55–7.51 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 14.8 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.5, 141.8, 141.0, 133.2, 129.7, 129.6, 129.2, 128.5, 127.5, 126.1, 21.4.



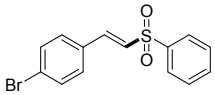
(*E*)-1-methoxy-4-(2-tosylvinyl)benzene (3c)[6]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 15.6 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 15.6 Hz, 1H), 3.83 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.0, 144.1, 141.7, 138.2, 130.3, 129.9, 127.5, 125.1, 124.8, 114.5, 55.4, 21.5.



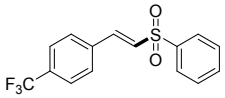
(*E*)-1-Fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (3d)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96–7.94 (m, 2H), 7.67–7.60 (m, 2H), 7.57–7.53 (m, 2H), 7.50–7.47 (m, 2H), 7.10–7.05 (m, 2H), 6.81 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3 (d, *J* = 251.3 Hz), 141.1, 140.7, 133.4, 130.6 (d, *J* = 8.5 Hz), 129.3, 128.6 (d, J = 3.2 Hz), 127.6, 127.1 (d, *J* = 2.4 Hz), 116.3 (d, *J* = 21.7 Hz).



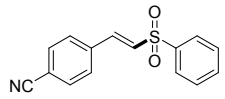
(*E*)-1-Chloro-4-(2-(phenylsulfonyl)vinyl)benzene (3e)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96–7.94 (m, 2H), 7.65–7.61 (m, 2H), 7.57–7.54 (m, 2H), 7.43–7.41 (m, 2H), 7.37–7.35 (m, 2H), 6.85 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.9, 140.5, 137.2, 133.5, 130.9, 129.7, 129.4, 128.0, 127.7.



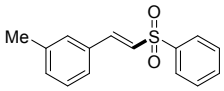
(*E*)-1-Bromo-4-(2-(phenylsulfonyl)vinyl)benzene (3f)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96–7.94 (m, 2H), 7.64–7.60 (m, 2H), 7.57–7.54 (m, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.0, 140.5, 133.5, 132.3, 131.3, 129.9, 129.4, 128.1, 127.7, 125.6.



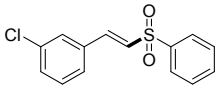
(*E*)-1-(2-(Phenylsulfonyl)vinyl)-4-(trifluoromethyl)benzene (3g)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98–7.96 (m, 2H), 7.71 (d, *J* = 15.2 Hz, 1H), 7.67–7.63 (m, 3H), 7.61–7.55 (m, 4H), 7.00 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 140.1, 135.7, 133.6, 132.5 (q, *J* = 32.5 Hz), 130.1, 129.4, 128.7, 127.7, 126.0 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 270.7 Hz).



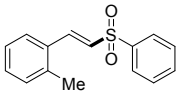
(*E*)-4-(2-(Phenylsulfonyl)vinyl)benzonitrile (3h)[14]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 7.6 Hz, 2H), 7.70–7.65 (m, 4H), 7.61–7.56 (m, 4H), 7.01 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.7, 136.5, 133.8, 132.7, 131.0, 129.5, 128.9, 127.8, 117.9, 114.2.



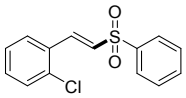
(*E*)-1-Methyl-3-(2-(phenylsulfonyl)vinyl)benzene (3i)[5f]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97–7.94 (m, 2H), 7.67–7.59 (m, 2H), 7.56–7.52 (m, 2H), 7.29–7.25 (m, 3H), 7.23–7.21 (m, 1H), 6.85 (d, *J* = 15.6 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.6, 140.8, 138.8, 133.2, 132.3, 132.0, 129.3, 129.1, 128.9, 127.6, 127.0, 125.8, 21.2.



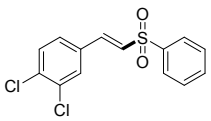
(*E*)-1-Chloro-3-(2-(phenylsulfonyl)vinyl)benzene (3j)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96–7.94 (m, 2H), 7.65–7.59 (m, 2H), 7.57–7.53 (m, 2H), 7.44 (s, 1H), 7.37–7.29 (m, 3H), 6.90 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.6, 140.3, 135.0, 134.1, 133.5, 130.9, 130.2, 129.3, 128.9, 128.1, 127.6, 126.7.



(*E*)-1-Methyl-2-(2-(phenylsulfonyl)vinyl)benzene (3k)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99–7.94 (m, 3H), 7.64–7.60 (m, 1H), 7.57–7.53 (m, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.31–7.26 (m, 1H), 7.22–7.16 (m, 2H), 6.79 (d, *J* = 15.6 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.7, 140.1, 138.1, 133.3, 131.2, 131.0, 130.9, 129.3, 128.2, 127.6, 126.8, 126.4, 19.7.

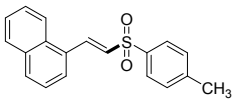


(*E*)-1-Chloro-2-(2-(phenylsulfonyl)vinyl)benzene (3l) [7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 15.2 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.65–7.61 (m, 1H), 7.58–7.54 (m, 2H), 7.50 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.42–7.40 (m, 1H), 7.33 (td, J_1 = 15.2 Hz, J_2 = 1.6 Hz, 1H), 7.28–7.24 (m, 1H), 6.92 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 138.3, 135.2, 133.5, 131.9, 130.6, 130.3, 130.0, 129.3, 128.2, 127.7, 127.2.

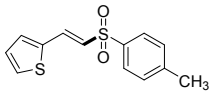


(*E*)-1,2-dichloro-4-(2-(phenylsulfonyl)vinyl)benzene (3m)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 7.6 Hz, 2H), 7.66–7.62 (m, 1H), 7.60–7.58 (m, 4H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.31

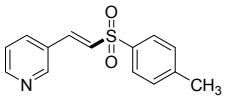
(d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.1, 139.5, 135.2, 133.6, 133.4, 132.3, 131.0, 130.0, 129.4, 129.3, 127.7, 127.5.



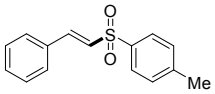
(*E*)-1-(2-tosylvinyl)naphthalene (3n)[15]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 15.2 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.89−7.83 (m, 4H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.59−7.55 (m, 1H), 7.54−7.50 (m, 1H), 7.43−7.39 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 15.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.3, 138.8, 137.6, 133.5, 131.3, 131.2, 129.9 (double), 129.4, 128.7, 127.7, 127.2, 126.4, 125.5, 125.2, 122.9, 21.5.



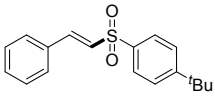
(*E*)-2-(2-tosylvinyl)thiophene (3o)[5b]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 15.2 Hz, 1H), 7.42 (d, *J* = 5.2 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 3.6 Hz, 1H), 7.07−7.05 (m, 1H), 6.63 (d, *J* = 15.2 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.3, 137.9, 137.0, 134.6, 132.2, 129.9, 129.8, 128.3, 127.6, 125.8, 21.6.



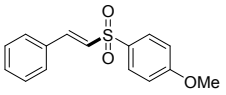
(*E*)-3-(2-tosylvinyl)pyridine (3p)[14]: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72−8.63 (m, 2H), 7.84 (br, 3H), 7.66 (d, *J* = 14.0 Hz, 1H), 7.36 (br, 3H), 6.97 (d, *J* = 14.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.6, 149.9, 144.7, 138.1, 137.0, 134.7, 130.0, 129.9, 128.3, 127.8, 123.8, 21.5.



(*E*)-1-Methyl-4-(styrylsulfonyl)benzene (3r)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 15.2 Hz, 1H), 7.46−7.44 (m, 2H), 7.37−7.36 (m, 3H), 7.34−7.32 (m, 2H), 6.87 (d, *J* = 15.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2, 141.7, 137.6, 132.3, 130.9, 129.8, 128.9, 128.4, 127.6, 127.5, 21.4.



(*E*)-1-(*tert*-Butyl)-4-(styrylsulfonyl)benzene (3s)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J = 8.8 Hz, 2H), 7.67 (d, *J* = 15.6 Hz, 1H), 7.56−7.54 (m, 2H), 7.48−7.46 (m, 2H), 7.40−7.36 (m, 3H), 6.87 (d, *J* = 15.6 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.3, 141.9, 137.6, 132.4, 131.0, 129.0, 128.4, 127.7, 127.5, 126.3, 35.1, 31.0.



(*E*)-1-Methoxy-4-(styrylsulfonyl)benzene (3t)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 15.2 Hz, 1H), 7.48−7.45 (m, 2H), 7.40−7.36 (m, 3H), 7.01−6.99 (m, 2H), 6.86 (d, *J* = 15.2 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.5, 141.3, 132.4, 132.1, 130.9, 129.8, 129.0, 128.4, 127.9, 114.5, 55.6.

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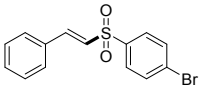
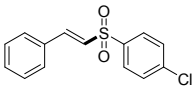
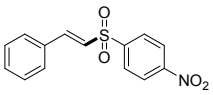


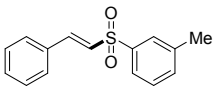
(*E*)-1-Bromo-4-(styrylsulfonyl)benzene (3u)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.8 Hz, 2H), 7.71−7.66 (m, 3H), 7.49−7.47 (m, 2H), 7.42−7.37 (m, 3H), 6.85 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.0, 139.8, 132.6, 132.1, 131.4, 129.2, 129.1, 128.6, 126.8.



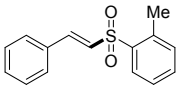
(*E*)-1-Chloro-4-(styrylsulfonyl)benzene (3v)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 15.2 Hz, 1H), 7.52−7.50 (m, 2H), 7.49−7.47 (m, 2H), 7.42−7.37 (m, 3H), 6.85 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.0, 140.0, 139.3, 132.1, 131.3, 129.6, 129.1(double), 128.6, 126.9.



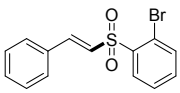
(*E*)-1-Nitro-4-(styrylsulfonyl)benzene (3w)[7]**:** Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 9.2 Hz, 2H), 7.78 (d, *J* = 15.2 Hz, 1H), 7.52−7.50 (m, 2H), 7.48−7.40 (m, 3H), 6.86 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.5, 146.6, 145.0, 131.9, 129.2, 129.0, 128.8, 125.7, 124.5.



(*E*)-1-Methyl-3-(styrylsulfonyl)benzene (3x)[16]**:** Pale solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76−7.74 (m, 2H), 7.67 (d, *J* = 15.2 Hz, 1H), 7.48−7.46 (m, 2H), 7.42−7.41 (m, 2H), 7.39−7.37 (m, 3H), 6.88 (d, *J* = 15.2 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.1, 140.5, 139.5, 134.1, 132.3, 131.0, 129.1, 128.9, 128.4, 127.8, 127.4, 124.7, 21.2.

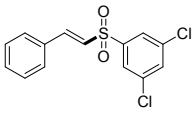


(*E*)-1-methyl-2-(styrylsulfonyl)benzene (3y)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.51−7.48 (m, 3H), 7.41−7.39 (m, 4H), 7.30 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 15.6 Hz, 1H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.8, 138.3, 138.0, 133.6, 132.6, 132.3, 131.2, 129.4, 129.1, 128.5, 126.7, 124.7, 20.3.

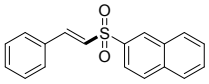


(*E*)-1-Bromo-2-(styrylsulfonyl)benzene (3z)[17]**:** Pale solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.78 (d, *J* = 15.6 Hz, 1H), 7.72 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.54−7.50 (m, 3H), 7.46−7.43 (m, 1H), 7.42−7.37 (m, 3H), 7.11 (d, *J* = 15.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.3, 139.8, 135.4, 134.4, 132.3, 131.3, 131.0, 129.0, 128.6, 128.0, 125.0, 120.9.



(*E*)-1,3-Dichloro-5-(styrylsulfonyl)benzene (3aa): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 2.0 Hz, 2H), 7.72 (d, *J* = 15.2 Hz, 1H), 7.57−7.56 (m, 1H), 7.52−7.50 (m, 2H), 7.45−7.39 (m, 3H), 6.84 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.4, 143.8, 136.3, 133.3, 131.9, 131.7, 129.2, 128.8, 126.0, 125.9. HRMS (EI): Calcd. for $C_{14}H_{10}Cl_2NaO_2S$: 334.9671, found: 334.9671.



(*E*)-2-(Styrylsulfonyl)naphthalene (3ab)[7]**:** White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (d, *J* = 1.2 Hz, 1H), 8.00−7.97 (m, 2H), 7.92−7.87 (m, 2H), 7.74 (d, *J* = 15.2 Hz, 1H), 7.67−7.59 (m, 2H), 7.50−7.47 (m, 2H), 7.41−7.36 (m, 3H), 6.92 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.5, 137.5, 135.1, 132.4, 132.3, 131.2, 129.6, 129.4, 129.2 (double), 129.1, 128.6, 127.9, 127.6, 127.4, 122.5.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and reference

1. For selected examples, see: (*a*) W. R. Roush, S. L. Gwaltney II, J. Cheng, K. A. Scheidt, J. H. McKerrow and E. Hansell, *J. Am. Chem. Soc.,* 1998, **120**, 10994; (*b*) J. J. Reddick, J. Cheng and W. R. Roush, *Org. Lett.,* 2003, **5**, 1967; (*c*) T. Llamas, R. G. Arrayas and J. C. Carretero, *Org. Lett.,* 2006, **8**, 1795; (*d*) D. Sahu, S. Dey, T. Pathak and B. Ganguly, *Org. Lett.,* 2014, **16**, 2100; (*e*) J. K. Laha, *Chem. Nat. Compd.,* 2010, **46**, 254; (*f*) R. Ettari, E. Nizi, M. E. D. Francesco, M.-A. Dude, G. Pradel, R. Vičík, T. Schirmeister, N. Micale, S. Grasso and M. Zappalà, *J. Med. Chem.,* 2008, **51**, 988; (g) M. V. R. Reddy, P. Venkatapuram, M. R. Mallireddigari, V. R. Pallela, S. C. Cosenza, K. A. Robell, B. Akula, B. S. Hoffman and E. P. Reddy, *J. Med. Chem.*, 2011, **54**, 6254; (*h*) X. Ning, Y. Guo, X. Wang, X. Ma, C. Tian, X. Shi, R. Zhu, C. Cheng, Y. Du, Z. Ma, Z. Zhang and J. Liu, *J. Med. Chem.*, 2014, **57**, 4302; (*i*) S. Y. Woo, J. H. Kim, M. K. Moon, S.-H. Han, S. K. Yeon, J. W. Choi, B. K. Jang, H. J. Song, Y. G. Kang, J. W. Kim, J. Lee, D. J. Kim, O. Hwang and K. D. Park, *J. Med. Chem.,* 2014, **57**, 1473.
2. (*a*) S. Chodroff, W. F. Whitmore, *J. Am. Chem. Soc.*, 1950, **72**, 1073; (*b*) D. A. R. Happer, B. E. Steenson, *Synthesis*, 1980, 806; (*c*) I. C. Popoff, J. L. Dever, G. R. Leader, *J. Org. Chem.*, 1969, **34**, 1128.
3. Q. Jiang, B. Xu, A. Zhao, Y. Zhao, Y. Li, N. He and C. Guo, *J. Org. Chem.,* 2014, **79**, 7372.
4. R. Guo, Q. Gui, D. Wang and Z. Tan, *Catal. Lett.,* 2014, **144**, 1377.
5. (*a*) Y. Xu, X. Tang, W. Hu, W. Wu and H. Jiang, *Green Chem.,* 2014, **16**, 3720; (*b*) B. V. Rokade and K. R. Prabhu, *J. Org. Chem.*, 2014, **79**, 8110; (*c*) J. Gao, J. Lai and G. Yuan, *RSC Adv.,* 2015, **5**, 66723; (*d*) P. Katrun, S. Hlekhlai, J. Meesin, M. Pohmakotr, V. Reutrakul, T. Jaipetch, D. Soorukram and C. Kuhakarn, *Org. Biomol. Chem.,* 2015, **13**, 4785; (*e*) J. Chen, J. Mao, Y. Zheng, D. Liu, G. Rong, H. Yan, C. Zhang and D. Shi, *Tetrahedron,* 2015, **71**, 5059; (*f*) P. Qian, M. Bi, J. Su, Z. Zha and Z. Wang, *J. Org. Chem.,* 2016, **81**, 4876.
6. R. Singh, B. K. Allam, N. Singh, K. Kumari, S. K. Singh and K. N. Singh, *Org. Lett.*, 2015, **17**, 2656.
7. S. Cai, Y. Xu, D. Chen, L. Li, Q. Chen, M. Huang and W. Weng, *Org. Lett.*, 2016, **18**, 2990.
8. Y. Zhao, Y.-L. Lai, K.-S. Du, D.-Z. Lin and J.-M. Huang, *J. Org. Chem.,* 2017, **82**, 9655.
9. X. Li, Y. Xu, W. Wu, C. Jiang, C. Qi and H. Jiang, *Chem. Eur. J.*, 2014, **20**, 7911.
10. A. U. Meyer, S. Jäger, D. P. Hari and B. König, *Adv. Synth. Catal.*, 2015, **357**, 2050.
11. (*a*) W. Yang, S. Yang, P. Li and Lei Wang, *Chem. Commun.*, 2015, **51**, 7520; (*b*) X. Zhu, M.-Y. Han, P. Li and L. Wang, *Org. Chem. Front.*, 2017, **4**, 1640; (*c*) Y. Zhang, W. Chen, X. Jia, L. Wang and P. Li, *Chem. Commun.*, 2019, **55**, 2785.
12. (*a*) P. Li, L. Wang, Y. Zhang and M. Wang, *Tetrahedron Lett.*, 2008, **49**, 6650; (*b*) P. Li, L. Wang, M. Wang and Y. Zhang, *Eur. J. Org. Chem.*, 2008, 1157; (*c*) J. Liu, P. Li, Y. Zhang, K. Ren, L. Wang and G.-W. Wang, Chirality, 2010, **22**, 432; (*d*) P. Li, L. Wang, L. Zhang and G.-W. Wang, *Adv. Synth. Catal.*, 2012, **354**, 1307.
13. (*a*) J.-Y. Luo, H.-L. Hua, Z.-S. Chen, Z.-Z. Zhou, Y.-F. Yang, P.-X. Zhou, Y.-T. He, X.-Y. Liu and Y.-M. Liang, *Chem. Commun.*, 2014, **50**, 1564; (*b*) W.-T. Wei, R.-J. Song, X.-H. Ouyang, Y. Li, H.-B. Li and J.-H. Li, *Org. Chem. Front.*, 2014, **1**, 484; (*c*) X.-H. Ouyang, R.-J. Song, Y. Li, B. Liu and J.-H. Li, *J. Org. Chem.*, 2014, **79**, 4582; (*d*) W. Yang, S. Yang, P. Li and L. Wang, *Chem. Commun.*, 2015, **51**, 7520.
14. G. Rong, J. Mao, H. Yan, Y. Zheng, G. Zhang, *J. Org. Chem.*, 2015, **80**, 4697.
15. S. Mao, Y.-R. Gao, X.-Q. Zhu, D.-D. Guo, Y.-Q. Wang, *Org. Lett.*, 2015, **17**, 1692.
16. L. Wang, H. Yue, D. Yang, H. Cui, M. Zhu, J. Wang, W. Wei, H. Wang, *J. Org. Chem.*, 2017, **82**, 6857.
17. W. Wei, J. Wen, D. Yang, H. Jing, J. You, H. Wang, *RSC Advances*, 2015, **5**, 4416.