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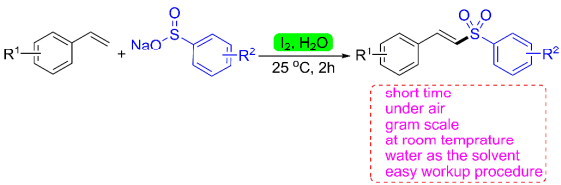


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ARTICLE TYPE

Metal-free iodine-mediated synthesis of vinyl sulfones at room temperature using water as solvent

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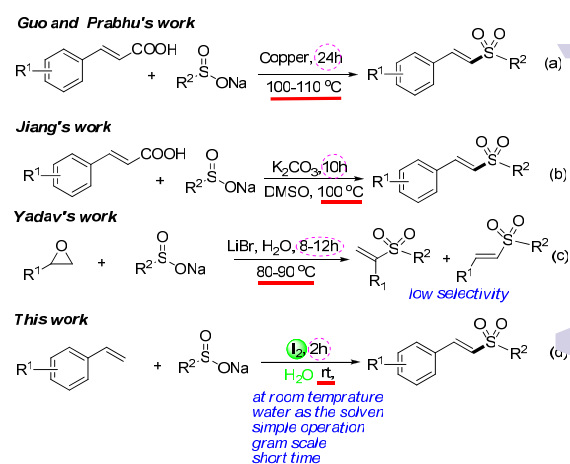
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Metal-free efficient iodine-mediated synthesis of vinyl sulfones utilizing aryl sulfonates and alkenes has been realized under mild conditions in water. Notably, when sodium methanesulfonate was used in this transformation, affording the β -iodo sulfones in good yields. This simple, efficient and environmentally benign transformation provides an attractive approach to various vinyl sulfones or β -iodo sulfones.

10 Introduction

Vinyl sulfone derivatives show a wide range of useful biological and pharmacological activities.¹ As a consequence, development of more practical and efficient methods for the formation of these compounds is of great interest. Traditionally, Knoevenagel condensation of aromatic aldehydes with sulfonylacetic acids,² β -elimination of selenosulfones or halosulfones,³ Wittig reaction of α -sulfinyl phosphonium ylides,⁴ and the oxidation of the corresponding sulfides⁵ are perhaps the most common. However, the preparation of vinyl sulfones with these methods depends on the availability of the requisite *p*-tolylsulfonylacetic acids, Wittig reagents or vinylic sulfides, and they are sometimes more difficult to prepare. Besides that, the multi-steps, strong bases and strong oxidants involving in these transformations might limit their wide applications. Transition-metal-catalyzed transformations are reliable tools in the synthetic chemistry.⁶ In recent years, Pd- or Cu-catalyzed cross-coupling of sulfinate salts with vinyl halides⁷ or alkenyl boronic acids⁸ leading to vinyl sulfones have made great progress. Very recently, Guo' group and Prabhu' group respectively developed a new copper-catalyzed method for the synthesis of vinyl sulfones through decarboxylative sulfonylation of cinnamic acids with sodium sulfonates (Scheme 1, a).^{9a, 9b} Despite some great advantages of these reactions, there are still certain limitations including harsh reaction conditions, the uneasily available precursors and especially toxic metal catalysts. As a result, there are increasing demands for metal-free reactions owing to trace-metal impurities can be avoided in the end products.¹⁰ For example, Jiang and co-workers developed an efficient metal-free approach for the

synthesis of vinyl sulfones through cross-decarboxylative/coupling reaction of sodium sulfonates and cinnamic acids using dimethyl sulfoxide (DMSO) as solvent at 100 °C (Scheme 1, b).¹¹



45 **Scheme 1.** Methods for the construction of vinyl sulfones

In view of the principles of green chemistry, the development of some synthesis methods under mild reaction conditions using environmental-friendly catalysts and medium has been being a challenging but attractive task in the current synthesis chemistry.¹² As is well-known, replacement of common hazardous organic solvents by green and safe reaction media is an ongoing interest. In recent years, using water as an ideal medium in synthetic chemistry has attracted considerable attentions owing to its non-toxic characters. Importantly, water is also known to affect the selectivity and to enhance the reaction rates in organic transformations.¹³ As a wonderful example, Yadav and co-workers developed a LiBr catalysed one-pot method for synthesis of vinyl sulfones from terminal epoxides and sodium sulfonates in water (Scheme 1, c).¹⁴ Gracefully excellent as this work could be the terminal epoxides in some cases are not available, and the transformation is low regioselective. Alternatively, molecular iodine as an inexpensive, green and efficient reagent has been

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extensively used in organic transformation.¹⁵ In the present work, a metal-free molecular iodine-mediated synthesis approach has been developed for preparing vinyl sulfones from readily available alkenes and sodium sulfinates by using environmentally benign water as the solvent under mild conditions.

Results and Discussion

As shown in Table 1, phenylethylene (**1a**) and benzenesulfonic acid sodium salt (**2a**) were used as the model substrates to optimize the catalysis conditions including solvents and the amount of catalyst under air atmosphere. First, solvent (1 mL) including 1,2-dichloroethane, acetonitrile and methanol were investigated in the presence of 1 equiv of iodine (relative to amount of **1a**) at room temperature, and no obvious reaction activity was observed in this transformation, and we chose the most green and environmentally friendly water as the solvent. When the amount of the catalyst was changed to 0.5 equiv from 2 equiv the reaction yield decreased, only 46% yield was provided (Table 1, entry 4-7). No target product was observed in the absence of molecular iodine (Table 1, entry 8). After the optimization process of the amount of catalyst and solvent, the following reactions were carried out under our standard conditions: I₂ (1.5 equiv) and H₂O (1mL) under air atmosphere at room temperature for 2 h.

Table 1. Optimization of the reaction conditions^a

Entry	I ₂ (equiv)	Solvent	Yield (%) ^b
1	1	DCE	88
2	1	CH ₃ CN	86
3	1	MeOH	89
4	1	H ₂ O	90
5	1.5	H ₂ O	94
6	2	H ₂ O	94
7	0.5	H ₂ O	46
8	--	H ₂ O	n.d. ^c

^a Reaction conditions: under air atmosphere, **1a** (0.5 mmol), **2a** (0.75 equiv.), solvent (1 mL), at room temperature (2 h). ^b Isolated yield. ^c n.d.= not detected

The scope of iodine-mediated reactions of the substituted alkenes with sodium sulfinates was investigated under the optimized conditions. As shown in Table 2, the tested substrates afforded good to excellent yields. For substituted alkenes, the substrates containing electron-withdrawing groups exhibited slightly higher reactivity than the others. Electron-effect of the substituted groups in sodium sulfinates including electron-rich, -neutral, -deficient groups did not display evidently difference of reactivity. The steric hindrance in alkenes such as 1-methyl-2-vinylbenzene, did not significantly affect the catalytic efficiency (Table 2, **3c** and **3g**). Interestingly, when sodium methanesulfinate was employed in this transformation, affording the β-iodo sulfones in good yields (Table 2, **3n** and **3o**), and no vinyl sulfones were observed. The reason might be the acidity of 2-H in the intermediate **C** is lower than aryl sodium sulfinates, which would

Table 2. Scope of the reaction of various alkenes and sodium sulfinates^{a,b}

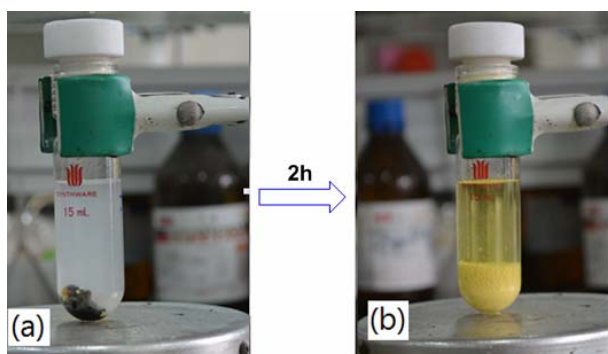
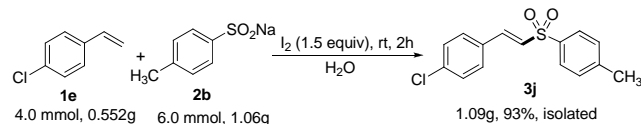
Entry	1	2	3	Yield(%)
1				94%
2				91%
3				88%
4				96%
5				90%
6				90%
7				85%
8				87%
9				91%
10				84%
11				95%
12				91%
13				98%
14				93%
15				90%

^a Reaction conditions: the substituted alkenes (1 mmol), molecular iodine (1.5 mmol), H₂O (2 ml), at room temperature, 2h, under air atmosphere. ^b Isolated yield.

not be easy to be attacked by iodine anion (see scheme 4. formation mechanism). The cascade reactions could tolerate some

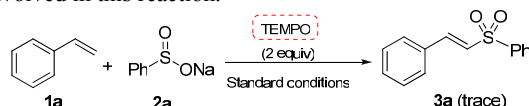
functional groups such as methyl, C-Cl bond and C-Br bond, which could be used for further modifications at the substituted positions.

Further, we explored the synthetic applicability of the method. The gram-scale reaction was performed in the usual laboratory flask, and the reaction afforded **3j** in 93% yield. As can be seen from Scheme 2, after two hours, the desired product **3j** was completely precipitated in the flask owing to its poor solubility in water, and the pure **3j** can be easily obtained through column chromatography after simple filtration. This example clearly demonstrates the practical aspect of this newly developed method.



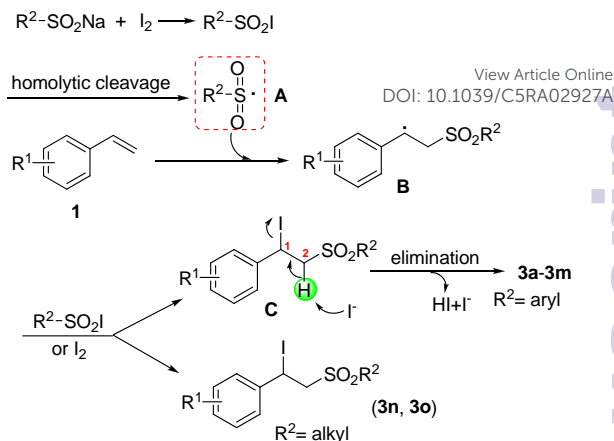
Scheme 2. Synthesis of **3j** on gram scale; Reaction mixture (a) before and (b) after reaction

To understand the mechanism further, the reaction of **1a** with **2a** was carried out in the presence of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl, a well-known radical inhibitor). As expected, the formation of **3a** was completely inhibited in the reactions (Scheme 3), demonstrating that a radical process should be involved in this reaction.



Scheme 3. Control experiments.

On the basis of these preliminary results above, together with literature reports,¹⁶ we proposed the mechanism in Scheme 4. Sodium sulfinate first interacted with molecular iodine to give sulfonyl iodide **A**, which then underwent homolytic cleavage to generate a sulfonyl radical. Addition of the sulfonyl radical to the substituted alkenes produced the reactive alkyl radical **B**, which could be trapped by iodine radical from homolytic cleavage the sulfonyl iodide or the molecular iodine to form intermediate **C** or the product **3n** and **3o** (if the R^2 is alkyl). Elimination of HI from **C** finally generated the desired product **3a-3m** (if the R^2 is aryl).



Scheme 4. A proposed mechanism for the direct transformation.

Experimental Section

General: All reagents and solvents were obtained from commercial suppliers and used without further purification. Flash chromatography was performed on silica gel (200 ~ 300 mesh). 1H and ^{13}C NMR data were recorded at 400 and 100 MHz on a BRUKER 400 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm) coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (1H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard (1H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.28 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm).

General procedure for synthesis of substituted vinyl sulfones:

A 15 mL Schlenk tube equipped with a magnetic stirring bar was charged with I_2 (1.5 equiv, 190 mg), alkenes (0.5 mmol), substituted various sodium sulfonates (0.75 mmol) and H_2O (2 mL). The mixture was then stirred at room temperature for 2 h under air atmosphere, and then a saturated aqueous $Na_2S_2O_3$ solution (2 mL) was added. Following that, the solution was extracted with ethyl acetate (3-2 mL). Finally, the combined organic phases were concentrated and the remaining residue was purified by column chromatography on silica gel to provide the desired product **3**.

(E)-(2-(phenylsulfonyl)vinyl)benzene (3a):^[1] Eluent petroleum ether/ethyl acetate (10:1), pale yellow viscous liquid. 1H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.97 (d, 2H, J = 8.0 Hz), 7.70 (d, 1H, J = 16 Hz), 7.63 (d, 1H, J = 8.0 Hz), 7.59-7.55 (m, 2H), 7.51-7.49 (m, 2H), 7.42-7.40 (m, 3H), 6.88 (d, 1H, J = 16 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 142.5, 140.7, 133.4, 132.4, 131.3, 129.4, 129.1, 128.6, 127.7, 127.3. ESI-MS $[M+H]^+$ m/z 245.2.

(E)-1-methyl-3-(2-(phenylsulfonyl)vinyl)benzene (3b):^[2] Eluent petroleum ether/ethyl acetate (10:1), pale yellow solid, mp 104-106 °C. 1H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.96 (d, 2H, J = 8.0 Hz), 7.68 (d, 1H, J = 16 Hz), 7.63 (d, 1H, J = 8.0 Hz), 7.59-7.57 (m, 2H), 7.32-7.30 (m, 3H), 7.25-7.26 (m, 1H), 6.87 (d, 1H, J = 16 Hz), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 142.7, 140.8, 138.9, 133.3, 132.4, 132.1, 129.3, 129.2, 129.0, 127.6, 127.0, 125.9, 21.3. ESI-MS $[M+H]^+$ m/z 259.1.

(E)-1-methyl-2-(2-(phenylsulfonyl)vinyl)benzene (3c): Eluent petroleum ether/ethyl acetate (10:1), white solid, mp = 112–115 °C. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.98–7.93 (m, 3H), 7.61–7.59 (m, 1H), 7.56–7.52 (m, 2H), 7.42 (d, 1H, *J* = 8.0 Hz), 7.27 (dd, 1H, *J* = 8.0 Hz), 7.21–7.27 (m, 2H), 6.78 (d, 1H, *J* = 16 Hz), 2.44 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 140.8, 140.2, 138.3, 133.4, 131.4, 131.1, 131.0, 129.4, 128.3, 127.7, 127.0, 126.6, 19.8. ESI-MS [M+H]⁺ *m/z* 259.1.

(E)-1-fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (3d): Eluent petroleum ether/ethyl acetate (10:1), pale yellow solid, mp = 110–112 °C. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.97 (d, 2H, *J* = 8.0 Hz), 7.68 (d, 1H, *J* = 16 Hz), 7.63 (d, 1H, *J* = 8.0 Hz), 7.60–7.56 (m, 2H), 7.53–7.49 (m, 2H), 7.11 (t, 2H, *J* = 8.0 Hz), 6.81 (d, 1H, *J* = 16 Hz). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 166.6, 163.1, 140.3 (d, *J* = 100.1 Hz), 133.5, 130.5 (d, *J* = 18.2 Hz), 129.4, 128.6 (d, *J* = 6.0 Hz), 127.7, 127.1 (d, *J* = 6.0 Hz), 116.5, 116.2. ESI-MS [M+H]⁺ *m/z* 263.2.

(E)-1-chloro-4-(2-(phenylsulfonyl)vinyl)benzene (3e):^[3] Eluent petroleum ether/ethyl acetate (10:1), colorless solid, mp = 127–129 °C. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.97 (d, 2H, *J* = 8.0 Hz), 7.67 (d, 1H, *J* = 16 Hz), 7.60–7.56 (m, 3H), 7.44 (d, 2H, *J* = 8 Hz), 7.38 (d, 2H, *J* = 8 Hz), 6.87 (d, 1H, *J* = 16 Hz). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 141.0, 140.7, 137.3, 133.5, 130.9, 129.8, 129.4, 128.9, 127.9, 127.7. ESI-MS [M+H]⁺ *m/z* 279.2.

(E)-1-methyl-4-(styrylsulfonyl)benzene (3f):^[1] Eluent petroleum ether/ethyl acetate (10:1), pale yellow solid, mp 102–103 °C. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.85 (d, 2H, *J* = 8.0 Hz), 7.68 (d, 1H, *J* = 16 Hz), 7.51–7.49 (m, 2H), 7.42–7.36 (m, 5H), 6.87 (d, 1H, *J* = 16 Hz), 2.46 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 144.4, 141.9, 137.8, 132.4, 131.1, 130.0, 129.1, 128.5, 127.7, 127.6, 21.6. ESI-MS [M+H]⁺ *m/z* 259.3.

(E)-1-methyl-2-(2-tosylvinyl)benzene (3g): Eluent petroleum ether/ethyl acetate (10:1), white solid, mp 126–127 °C. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.94 (d, 1H, *J* = 16 Hz), 7.84 (d, 2H, *J* = 8 Hz), 7.65 (d, 1H, *J* = 16 Hz), 7.34 (d, 2H, *J* = 8 Hz), 7.32–7.29 (m, 3H), 6.85 (d, 1H, *J* = 16 Hz), 2.46 (s, 3H), 2.37 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 144.4, 139.7, 138.2, 137.9, 131.5, 131.1, 130.9, 130.1, 128.7, 127.8, 126.9, 126.5, 21.7, 19.9. ESI-MS [M+H]⁺ *m/z* 273.3.

(E)-1-methyl-3-(2-tosylvinyl)benzene (3h): Eluent petroleum ether/ethyl acetate (10:1), white solid, mp 82–83 °C. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.93 (d, 1H, *J* = 16 Hz), 7.82 (d, 2H, *J* = 8 Hz), 7.41 (d, 1H, *J* = 8 Hz), 7.33 (d, 2H, *J* = 8 Hz), 7.25–7.21 (m, 1H), 7.20 (t, 2H, *J* = 8 Hz), 6.76 (d, 1H, *J* = 16 Hz), 2.44 (s, 3H), 2.43 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 144.3, 142.2, 138.8, 137.9, 132.4, 131.9, 129.9, 129.1, 128.9, 127.7, 127.4, 125.8, 21.6, 21.3. ESI-MS [M+H]⁺ *m/z* 273.3.

(E)-1-fluoro-4-(2-tosylvinyl)benzene (3i): Eluent petroleum ether/ethyl acetate (10:1), yellow oil. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.84 (d, 2H, *J* = 8 Hz), 7.63 (d, 1H, *J* = 16 Hz), 7.50–7.47 (m, 2H), 7.36 (d, 2H, *J* = 8 Hz), 7.11–7.06 (m, 2H), 6.81 (d, 1H, *J* = 16 Hz), 2.45 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 144.5, 140.7, 137.8, 130.7, 130.6, 130.1, 128.9, 127.8, 127.5, 116.5, 116.3, 21.7. ESI-MS [M+H]⁺ *m/z* 278.1.

(E)-1-chloro-4-(2-tosylvinyl)benzene (3j):^[4] Eluent petroleum ether/ethyl acetate (10:1), white solid, mp = 140–141 °C. ¹H

NMR (CDCl₃, 400 MHz, ppm) δ 7.84 (d, 2H, *J* = 8 Hz), 7.62 (d, 1H, *J* = 16 Hz), 7.43 (d, 2H, *J* = 8 Hz), 7.39–7.36 (m, 4H), 6.85 (d, 1H, *J* = 16 Hz), 2.46 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 144.6, 140.4, 137.5, 137.2, 131.0, 130.0, 129.7, 129.4, 128.3, 127.8, 21.6. ESI-MS [M+H]⁺ *m/z* 294.2.

(E)-1-chloro-4-(styrylsulfonyl)benzene (3k):^[1] Eluent petroleum ether/ethyl acetate (10:1), pale yellow solid, mp = 85–87 °C. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.91 (d, 2H, *J* = 8 Hz), 7.71 (d, 1H, *J* = 16 Hz), 7.56–7.52 (m, 4H), 7.45–7.42 (m, 3H), 6.86 (d, 1H, *J* = 16 Hz). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 143.1, 140.1, 139.3, 132.2, 131.4, 129.7, 129.2, 128.7, 126.9, 125.7. HRMS *m/z* calcd. for C₁₄H₁₂ClO₂S [M+H]⁺: 279.0247, found: 279.0238.

(E)-1-(2-(4-chlorophenylsulfonyl)vinyl)-3-methylbenzene (3l): Eluent petroleum ether/ethyl acetate (10:1), colorless oil. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.86 (d, 2H, *J* = 4 Hz), 7.62 (d, 1H, *J* = 12 Hz), 7.50 (d, 2H, *J* = 4 Hz), 7.28–7.21 (m, 4H), 6.80 (d, 1H, *J* = 12 Hz), 2.35 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 143.4, 140.2, 139.4, 139.0, 132.3, 132.2, 129.7, 129.3, 129.2, 129.1, 126.7, 126.0, 21.3. ESI-MS [M+H]⁺ *m/z* 294.2.

(E)-1-chloro-4-(2-(4-chlorophenylsulfonyl)vinyl)benzene (3m): Eluent petroleum ether/ethyl acetate (10:1), pale yellow solid, mp = 164–166 °C. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.90 (d, 2H, *J* = 8 Hz), 7.64 (d, 1H, *J* = 16 Hz), 7.56 (d, 2H, *J* = 8 Hz), 7.51–7.49 (m, 1H), 7.42–7.37 (m, 3H), 6.87 (d, 1H, *J* = 16 Hz). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 141.5, 140.3, 139.0, 137.5, 130.6, 129.8, 129.7, 129.5, 129.2, 127.5. ESI-MS [M+H]⁺ *m/z* 313.1.

1-chloro-3-(1-iodo-2-(methylsulfonyl)ethyl)benzene (3n): Eluent petroleum ether/ethyl acetate (10:1), pale yellow solid, mp = 85–87 °C. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.52 (s, 1H), 7.42–7.39 (m, 1H), 7.33–7.31 (m, 2H), 5.53 (dd, 1H, *J* = 8 Hz), 4.14–4.08 (dd, 1H, *J*₁ = 8 Hz, *J*₂ = 12 Hz), 3.95–3.90 (dd, 1H, *J*₁ = 8 Hz, *J*₂ = 12 Hz), 2.51 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 143.0, 135.1, 130.6, 129.4, 127.7, 125.6, 65.4, 42.6, 15.5. ESI-MS [M+H]⁺ *m/z* 361.3.

(1-iodo-2-(methylsulfonyl)ethyl)benzene (3o): Eluent petroleum ether/ethyl acetate (10:1), colorless oil. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.53 (d, 1H, *J* = 8 Hz), 7.41–7.34 (m, 3H), 5.58 (dd, 1H, *J* = 4 Hz), 4.17 (dd, 1H, *J*₁ = 8 Hz, *J*₂ = 12 Hz), 3.94 (dd, 1H, *J*₁ = 8 Hz, *J*₂ = 4 Hz), 2.35 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 140.9, 129.4, 127.5, 125.7, 65.7, 42.4, 17.5. ESI-MS [M+H]⁺ *m/z* 311.1.

Conclusions

In conclusion, we have developed a highly efficient, green and practical iodine-mediated method for the synthesis of vinyl sulfones. The method enjoys the following advantages of: (a) commercially available and non-toxic molecular iodine as the catalyst; (b) environmentally friendly water as the solvent (c) no addition of any base or additive; (d) all the reactions performed at room temperature; (e) easy workup procedure; (f) outstanding tolerance of functional groups. All these merits can meet the requirements of green and sustainable chemistry. Therefore, the developed synthesis method will attract much attention in academic and industrial fields. Further investigation on the applications of this method is in progress.

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