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PII: S0040-4020(16)30953-X

DOI: 10.1016/j.tet.2016.09.037

Reference: TET 28108

To appear in: *Tetrahedron*

Received Date: 19 June 2016

Revised Date: 18 September 2016

Accepted Date: 19 September 2016

Please cite this article as: Jiang J, Wu Y, Wang R, He Y, Xu C, Deng W, Zeng Z, Xiang J, A direct catalyst-free and stereoselective sulfonylation of propargyl esters for efficient synthesis of (*Z*)-β-sulfonyl enoates in water, *Tetrahedron* (2016), doi: 10.1016/j.tet.2016.09.037.

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A Direct Catalyst-free and Stereoselective Sulfonylation of Propargyl Esters for Efficient Synthesis of (Z)-β-Sulfonyl Enoates in Water

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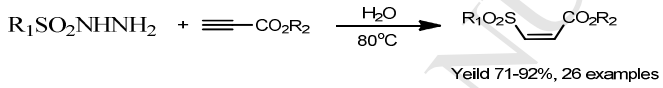

Tetrahedron
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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
propargyl esters
arylsulfonyl hydrazides
green chemistry
(*Z*)-β-sulfonyl enoates

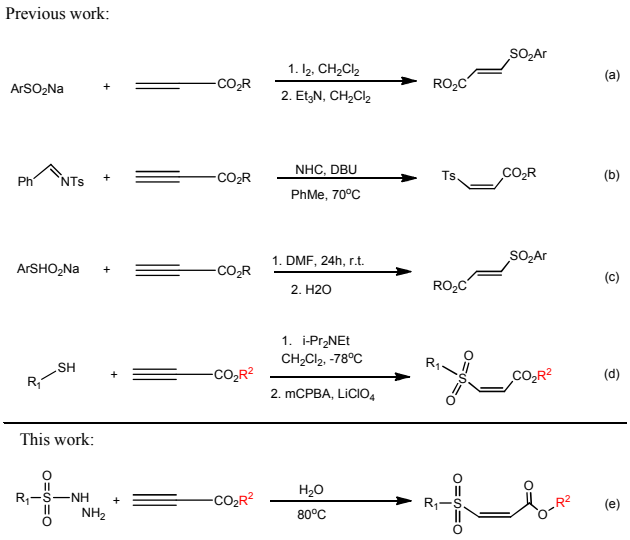
ABSTRACT

Water-promoted sulfonylation of propargyl esters leading to highly regioselective and stereoselective formation of (*Z*)-β-sulfonyl enoates in excellent yields, by a simple, mild, and environmentally benign reaction procedure without employing any ligand or additive is reported.

Introduction

Sulfones display a diverse range of behaviors and possess unique features that make them worthful to be ingredients for various synthesis reactions.[1] For instance, sulfones have been described as “chemical chameleons” by Trost and as “pluripotent” by Fuchs et al.[2] ~~Besides~~ In addition, the β-sulfonyl enoates are present in many bioactive molecules and serve as useful building blocks in organic synthesis.[3] The significance of sulfones and the difficulties in their preparation have gained intensive attention (scheme 1). Traditionally, β-sulfonyl enoates were prepared by the reaction of cross-coupling of organostannanes with sulfonyl chlorides,[4] iodosulphonylation-dehydroiodination (Scheme **1a**)[5] or imines with ethyl propiolate (Scheme **1b**).[6] Recently, a sulfonylation using sodium arylsulfinate of alkyl propiolate leading to (*E*)-β-sulfonyl enoates in DMF was reported by Khalili (Scheme **1c**).[7] Moreover, a two-step thioconjugate addition-oxidation reaction of ethyl propiolate with numerous types of thiols and *meta*-chloroperbenzoic acid (*m*-CPBA) in the presence of $LiClO_4$ leading to (*Z*)-β-sulfonyl enoates was reported (Scheme **1d**).[8] However, a majority of them employed a catalyst, an addition agent or a toxic organic solvent and proceeded via two steps. In particular, few researches that refer to the mild and rapid synthesis of (*Z*)-β-sulfonyl enoates were reported. In consequence, there is still an urgent need for the exploitation of milder and more rapid synthetic method of (*Z*)-β-sulfonyl enoates.

Water, as a proton source, is the best solvent for organic synthesis for its natural, inexpensive, and environmentally friendly characteristics.[9] Besides, alkynes, as versatile structural motif, are extensively employed in synthetic sequences.[10] Taking the significance of sulfur-containing organic compounds and related scaffolds into account,[11] we exploited an efficient sulfonylation of propargyl esters with sulfohydrazides to afford (*Z*)-β-sulfonyl enoates via an anion process (Scheme **1e**). These conversions can be easily completed in water under green conditions. These transformations did not involve any catalyst, ligand, additive or organic solvent.

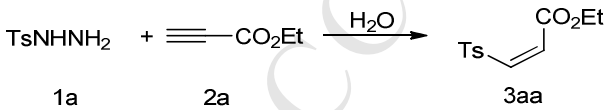


Scheme 1 (a) Iodosulphonylation-dehydroiodination leading to (E)-β-sulfonyl enoates; (b) imines with ethyl propiolate; (c) sulfonylation using sodium arylsulfinate of alkyl propiolate leading to (E)-β-sulfonyl enoates; (d) two-step thioconjugate addition-oxidation reaction of ethyl propiolate; (e) Catalyst-free sulfonylation of activated alkynes.

Results and discussion

Firstly, the reaction of 4-methylbenzenesulfonohydrazide (**1a**) and ethyl propiolate (**2a**) under air atmosphere in water at 60°C for 24h (Table 1, entry 1), gave the desired product (*Z*)-ethyl 3-tosylacrylate (**3aa**) in 65% yield. Subsequently, the temperature was tested and 80°C was the best choice (entries 1 - 4). Then, further optimization suggested that solvents had a strong effect on this process and H_2O was found to be the best medium for this reaction (entries 3 vs. 5-10). ~~Besides~~ In addition, control experiments showed that reaction time could be reduced to 2 h (entries 13-15). We also studied the influence of the amount of water, and 2 ml was the best (entries 3 vs. 11-12). ~~In addition~~ Moreover, the ratio of **1a** and **2a** was investigated to improve the reaction efficiency and ratio of 1:3 gave the highest field (~~Table 1,~~ entries 3 vs. 16-17). Thus, the best conditions for this process comprised ratio (1a:2a = 1:3) under air atmosphere in water (2 ml) at 80°C for 2 h.

Table 1. Optimization of the Reaction Conditions [a]

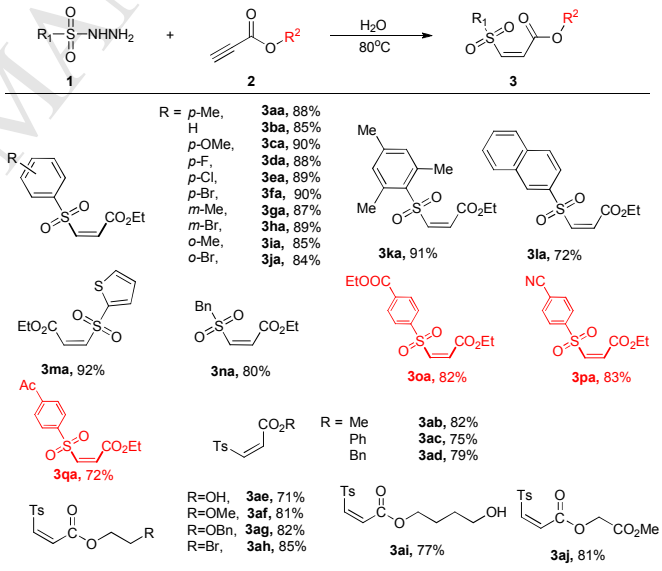


Entry	Solvent	Time (h)	Temp. (°C)	Yield[b] (%)
1	H_2O	24	60	65
2	H_2O	24	70	75
3	H_2O	24	80	88
4	H_2O	24	100	87
5	CH_3CN	24	80	12
6	DMF	24	80	Trace
7	EtOH	24	80	27
8	EtOAc	24	80	33
9	CH_2Cl_2	24	80	19
10	MeOH	24	80	36
11[c]	H_2O	24	80	72
12[d]	H_2O	24	80	84
13	H_2O	4	80	88
14	**H_2O**	**2**	**80**	**88**
15	H_2O	1	80	84
16[e]	H_2O	2	80	82
17[f]	H_2O	2	80	88

[a] All reactions were performed with 4-methylbenzenesulfonohydrazide (**1a**, 0.25 mmol), ethyl propiolate (**2a**, 0.75 mmol), solvent (2 mL), under air. [b] Estimated by ^{1}H NMR spectroscopy using methylene bromide as an internal reference. [c] 1ml of water. [d] 3ml of water. [e] 0.5 mmol of **2a**. [f] 1 mmol of **2a**.

Under the optimized reaction conditions (Table 1, entry 14), we then explored the scope of the reaction (Table 2). First, a series of aromatic sulfonyl hydrazides were tested and the corresponding products were furnished in good to excellent yields. The electronic effect of substituents at the *para* position of the aryl acetylene was evaluated (**3aa** − **3fa**). The reaction tolerated both electron-donating and electron-withdrawing groups. Aromatic sulfonyl hydrazides with substituents at *meta* (**3ga** − **3ha**) and *ortho* (**3ia** – **3ja)** positions also worked well, although giving slightly lower yields. 2,4,6-Trimethylbenzene sulfonyl hydrazide can also be used as reaction substrate, afforded the desired product 3**ka** in good yield. It is notable that the naphthalene substrate **1l**, the thiophene substrate **1m** and benzyl substrate **1n** can also be transformed into the desired products **3la–3na** in good yields.

Table 2. Reaction Scope [a, b]

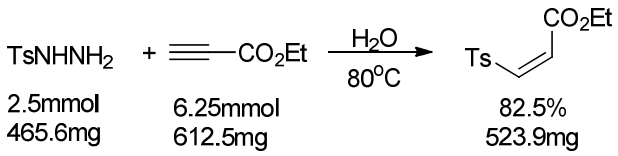


[a] Conditions: 1 (0.25mmol) and 2 (0.75mmol) in 2ml of H_2O, 80°C, under air, 2h.
[b] After column chromatography.

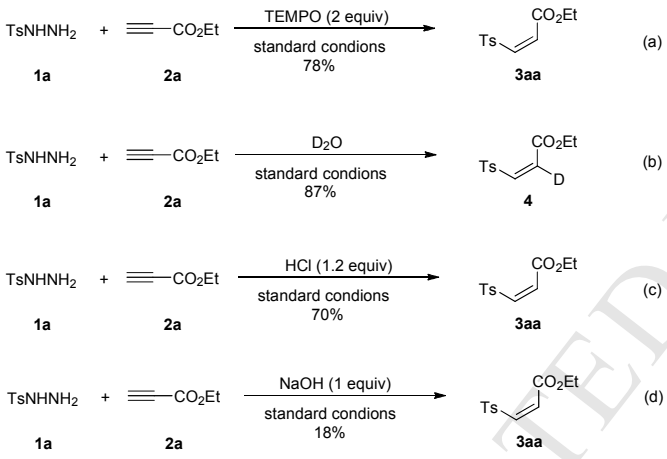
To further exploit the generality of this catalytic reaction, propargyl esters were also investigated. Propargyl esters generally led to the corresponding products in good yield. Many synthetically important functional groups were readily tolerated, including an alkyl (**3ab**), a phenyl (**3ac**), a benzyl (**3ac**), a free hydroxyl moiety (**3ae** and **3ai**), a protected OH (**3af** – **3ag**), a bromide (**3ah**) and an ester (**3aj**).

To demonstrate the reaction efficiency of this sulfonylation system, we managed to enlarge the transformation to a 2.5 mmol scale. In so far as **3aa**, the amount of ethyl propiolate and H_2O could be reduced to 2.5 equiv. and 8 ml, respectively, by increasing the reaction time to 3h to ensure completion (Scheme 2).

Scheme 2. Gram Scale Synthesis



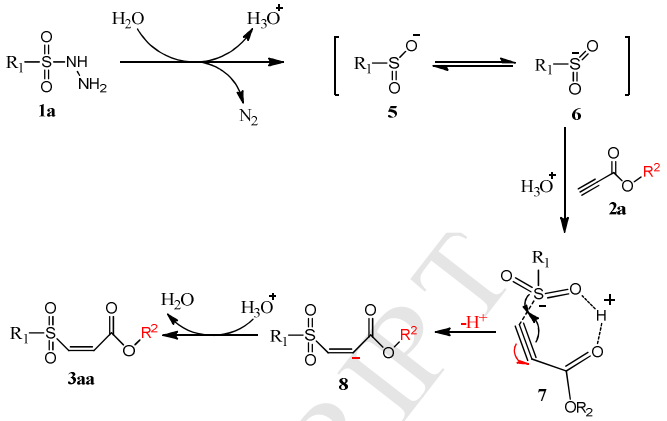
Control experiments were carried out in order to get an insight into the reaction mechanism (Scheme 3). When the radical inhibitor 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO—~~2equiv.~~) was employed under standard conditions, the reaction afforded **3aa** in 83% yield (Scheme **3a**), which implied that the transformation did not proceed via a free-radical pathway[12]. Then, with D_2O (2 mL) as the solvent, the transformation gave a deuterium generation product **4** in 87% yield (Scheme 3b). The deuterium generation experiment implied that the α-hydrogen atom of (*Z*)-β-sulfonyl enoates resulted from water.



Scheme 3 Mechanistic investigations of the sulfonylation process.

Furthermore, when HCl (1 equiv) was employed, the reaction of **3aa** could be completed in 30 mins (Scheme 3c). However, the reaction of 3aa reduced to 18% at the basic condition of 1 equiv. of NaOH (Scheme 3d). The acid and alkaline tests indicated that hydronium ions played an important role in the reaction. Notably, a small number of acid was generated in the transformation, because the reaction system was weak acidity at the end.

Based on our experimental results and previous reports,[13] a possible reaction mechanism was proposed in Scheme **4**. Firstly, sulfonyl hydrazides is quickly turned into a sulfinyl anion **5**, which can resonate with the sulfur-centered anions **6** in the presence of water, with the generation of hydrion and the freeing of N_2. Then, the sulfur-centered anions **6** is selectively added into the propargyl esters **2a** leading to the intermediate **7** in the presence of hydrion, which can turned into the carbon-centered anions **8**. In the end, the intermediate **8** transforms into (*Z*)-β-sulfonyl enoate **3aa** by a protonation from hydrion.



Scheme 4 The proposed mechanism for the reaction.

Conclusion

In summary, a simple and ~~mild~~ efficient regioselective sulfonylation of propargyl esters in water has been developed, ~~giving (*Z*)-β-sulfonyl enoates in good to excellent yields~~. The reaction proceeded under mild conditions without any catalyst or organic solvent. A broad range of sulfonyl hydrazides and propargyl esters were tolerated in this method, and all the sulfonylation products could be obtained in good to excellent yields. Additionally, this methodology can be performed on a large scale without any problems. Further research, including further mechanical experiments, extending the substrate range and applications in industry are currently underway.

Experimental Section

4.1. General Information

Commercially available reagents were of reagent grade (AR grade) and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silicycle silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz NMR plus spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with IR spectrometer and are reported in reciprocal centimeter (cm^{-1}). High resolution mass spectra were obtained using GCT-TOF instrument with ESI source. Sulfonyl hydrazides and propargyl esters except ethyl propiolate, methyl propiolate were prepared according to literature procedures. Rest of the chemicals was purchased from Sigma Aldrich and Alfa Aesar, and was used without further purification. Solvents were purified by standard methods.

1.2. General Procedure of 3.

A mixture of arylsulfonyl hydrazides[14] (0.25 mmol) and propargyl esters[15] (0.75 mmol) in water (2 mL) was put into an oil bath at 80 °C under magnetic stirring for 2 h under air. After the reaction was complete, the mixture was extracted with CH_2Cl_2 (3 × 15 mL) and then the combined organic extract was washed with brine (15 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the

corresponding product.

4.3. Characterization of the compounds

*(Z)-ethyl 3-tosylacrylate **(3aa)***.

White Solid; Yield = 88% (55.9 mg); mp = 37 °C (Lit. mp = 36–38 °C); [1] NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.42 (ABq, 2H, ΔδAB = 0.04, J_{AB} = 12.0 Hz), 4.29 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.06, 145.20, 136.50, 135.41, 131.42, 129.96, 128.28, 62.15, 21.69, 13.98. The data meet the literature report.[8]

*(Z)-ethyl 3-(phenylsulfonyl)acrylate **(3ba)***.

White Solid; Yield = 85% (51.1 mg); mp = 70 °C (Lit. mp = 69–71 °C); [1] NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.68 – 7.59 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 6.50 (ABq, 2H, ΔδAB = 0.03, J_{AB} = 10.0 Hz), 4.34 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.10, 139.59, 135.29, 134.18, 132.08, 129.46, 128.35, 62.34, 14.11. The data meet the literature report.[8]

*(Z)-ethyl 3-((4-methoxyphenyl)sulfonyl)acrylate **(3ca)***.

White Solid; Yield = 90% (60.8 mg); mp = 76 °C (Lit. mp = 75–77 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.45 (ABq, 2H, ΔδAB = 0.06, J_{AB} = 12.0 Hz), 4.34 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.29, 164.26, 135.81, 131.02, 130.73, 114.70, 62.25, 55.85, 14.13. The data meet the literature report.[8]

*(Z)-ethyl 3-((4-fluorophenyl)sulfonyl)acrylate **(3da)***.

White Solid; Yield = 88% (56.8 mg); mp = 53 °C (Lit. mp = 52–53 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.8, 5.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.56 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.35, 164.79, 163.89, 135.53, 135.18, 132.19, 131.33, 131.23, 116.77, 116.55, 62.27, 13.98. The data meet the literature report.[8]

*(Z)-ethyl 3-((4-chlorophenyl)sulfonyl)acrylate **(3ea)***.

White Solid; Yield = 89% (66.1 mg); mp = 55 °C (Lit. mp = 54–56 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 6.52 (s, 2H), 4.36 (q, *J* = 7.3 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.81, 140.91, 137.96, 135.04, 132.51, 129.79, 129.66, 62.30, 13.98; IR (neat) 2992, 1984, 1794, 1602, 1549, 1347, 1050 cm^{-1}; HRMS Calcd for $C_{11}H_{11}ClO_4S$ (M + Na^+): 296.9964, found: 296.9966.

*(Z)-ethyl 3-((4-bromophenyl)sulfonyl)acrylate **(3fa)***.

White Solid; Yield = 90% (71.6 mg); mp = 56 °C (Lit. mp = 55–57 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 6.52 (t, *J* = 12.0 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.79, 138.50, 135.00, 132.66, 132.55, 129.83, 129.54, 62.30, 13.98. The data meet the literature report.[8]

*(Z)-ethyl 3-(m-tolylsulfonyl)acrylate **(3ga)***.

Colorless oil; Yield = 87% (60.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.38 (t, *J* = 4.0 Hz, 2H), 6.44 (ABq, 2H, ΔδAB = 0.03, J_{AB} = 10.0 Hz), 4.29 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H) ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.00, 138.63, 138.27, 134.14, 133.83, 130.66, 128.19, 127.43, 124.32, 61.14, 20.31, 12.97; IR (neat) 1985, 1796, 1601, 1548, 1348, 1051 cm^{-1}; HRMS Calcd for $C_{12}H_{14}O_4S$ (M + Na^+): 277.0510, found: 277.0513.

*(Z)-ethyl 3-((3-bromophenyl)sulfonyl)acrylate **(3ha)***.

White Solid; Yield = 89% (75.9 mg); mp = 47 °C (Lit. mp = 47–48 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, *J* = 1.9 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 6.53 (ABq, 2H, ΔδAB = 0.03, J_{AB} = 12.0 Hz), 4.35 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.69, 141.35, 137.10, 134.69, 132.93, 131.13, 130.85, 126.83, 123.25, 62.37, 13.98; IR (neat) 2990, 1983, 1795, 1601, 1548, 1346, 1052 cm^{-1}; HRMS Calcd for $C_{11}H_{11}BrO_4S$ (M + Na^+): 340.9459, found: 340.9458.

*(Z)-ethyl 3-(o-tolylsulfonyl)acrylate **(3ia)***.

White Solid; Yield = 85% (58.9 mg); mp = 56 °C (Lit. mp = 55–56 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 11.7 Hz, 1H), 6.51 (d, *J* = 11.7 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.65 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.54, 138.43, 137.80, 135.66, 134.02, 132.58, 131.57, 129.77, 126.55, 62.09, 20.30, 13.90; IR (neat) 1984, 1796, 1603, 1549, 1347, 1050 cm^{-1}; HRMS Calcd for $C_{12}H_{14}O_4S$ (M + Na^+): 277.0510, found: 277.0511.

*(Z)-ethyl 3-((2-bromophenyl)sulfonyl)acrylate **(3ja)***.

White Solid; Yield = 84% (71.6 mg); mp = 47 °C (Lit. mp = 46–48 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.73 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.58 – 7.43 (m, 2H), 7.05 (d, *J* = 11.6 Hz, 1H), 6.54 (d, *J* = 11.6 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.98, 140.15, 136.77, 135.06, 134.81, 132.63, 131.47, 127.79, 120.69, 62.02, 13.91; IR (neat) 2994, 1984, 1796, 1600, 1548, 1348, 1052 cm^{-1}; HRMS Calcd for $C_{11}H_{11}BrO_4S$ (M + Na^+): 340.9459, found: 340.9457.

*(Z)-ethyl 3-(mesitylsulfonyl)acrylate **(3ka).***

White Solid; Yield = 91% (69.4 mg); mp = 67 °C (Lit. mp = 66–68 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.65 (d, *J* = 11.7 Hz, 1H), 6.41 (d, *J* = 11.7 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.64 (s, 6H), 2.30 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.50, 143.68, 140.21, 138.15, 133.60, 132.10, 129.45, 61.94, 22.60, 21.03, 13.88; IR (neat) 2996, 1986, 1793, 1605, 1547, 1348, 1052 cm^{-1}; HRMS Calcd for $C_{14}H_{18}O_4S$ (M + Na^+): 305.0823, found: 305.0826.

*(Z)-ethyl 3-(naphthalen-2-ylsulfonyl)acrylate **(3la).***

Yellow Solid; Yield = 72% (56.4 mg); mp = 77 °C (Lit. mp = 76–78 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.7 Hz, 1H), 8.05 – 7.90 (m, 4H), 7.66 (dt, *J* = 21.1, 7.1 Hz, 2H), 6.56 (ABq, 2H, ΔδAB = 0.06, J_{AB} = 10.0 Hz), 4.39 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.01, 136.29, 135.52, 135.17, 132.21, 131.89, 130.23, 129.68, 129.55, 129.50, 128.00, 127.71, 122.73, 62.24, 14.02. The data meet the literature report.[8]

*(Z)-ethyl 3-(thiophen-2-ylsulfonyl)acrylate **(3ma)***.

White Solid; Yield = 92% (61.9 mg); mp = 56 °C (Lit. mp = 55–57 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 4.0 Hz,

1H), 7.75 (d, *J* = 4.0 Hz, 1H), 7.17 (t, *J* = 4.0 Hz, 1H), 6.64 (d, *J* = 11.5 Hz, 1H), 6.49 (d, *J* = 11.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.70, 140.60, 135.77, 135.10, 135.04, 131.49, 128.19, 62.24, 14.00. The data meet the literature report.[8]

(Z)-ethyl 3-(benzylsulfonyl)acrylate ***(3na).***

White Solid; Yield = 80% (59.4 mg); mp = 44 °C (Lit. mp = 43–45 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (q, *J* = 3.4 Hz, 5H), 6.57 (d, *J* = 11.6 Hz, 1H), 6.35 (d, *J* = 11.6 Hz, 1H), 4.53 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.51, 136.30, 134.48, 131.07, 129.10, 128.95, 127.19, 62.30, 62.05, 13.97. The data meet the literature report.[8]

(Z)-ethyl 4-((3-ethoxy-3-oxoprop-1-en-1-yl)sulfonyl)benzoate ***(3oa).***

White Solid; Yield = 82% (59.4 mg); mp = 56 °C (Lit. mp = 55–57 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 6.55 (s, 2H), 4.40 (dq, *J* = 22.0, 7.1 Hz, 4H), 1.40 (dt, *J* = 13.5, 7.1 Hz, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.110, 163.836, 143.3 43, 135.594, 134.971, 133.140, 130.537, 128.420, 62.482, 61 .981, 14.392, 14.137; IR (neat) 2995, 1986, 1794, 1605, 15 49, 1346, 1051 cm^{-1}; HRMS Calcd for $C_{14}H_{16}O_6S$ (M + Na $^+$): 335.0565, found: 335.0568.

(Z)-ethyl 3-((4-cyanophenyl)sulfonyl)acrylate ***(3pa)***.

White Solid; Yield = 83% (59.4 mg); mp = 85 °C (Lit. mp = 84–86 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 11.4 Hz, 1H), 6.55 (d, *J* = 11.5 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.521, 143.654, 134.502, 134.066, 133. 034, 128.986, 117.742, 117.099, 62.475, 13.981; IR (neat) 2994, 2226, 1985, 1792, 1604, 1548, 1344, 1053 cm^{-1}; HR MS Calcd for $C_{12}H_{11}NO_4S$ (M + Na^+): 288.0306, found: 28 8.0304.

(Z)-ethyl 3-((4-acetylphenyl)sulfonyl)acrylate ***(3qa).***

White Solid; Yield = 72% (50.8 mg); mp = 82 °C (Lit. mp = 81–83 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 4 H), 6.56 (m, 2H), 4.36 (q, *J* = 7.2, 6.6 Hz, 2H), 2.65 (s , 3H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.815, 163.831, 143.364, 141.164, 134.901, 1 33.287, 129.152, 128.763, 62.487, 27.080, 14.121. IR (ne at) 2992, 1792, 1735, 1603, 1547, 1342, 1051 cm^{-1}; HRMS Calcd for $C_{13}H_{14}O_5S$ (M + Na^+): 305.0454, found: 305.045 1.

(Z)-methyl 3-tosylacrylate ***(3ab)***.

Colorless oil; Yield = 82% (53.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.50 (ABq, 2H, ΔδAB = 0.06, J_{AB} = 12.0 Hz), 3.88 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.51, 145.28, 136.40, 135.88, 131.02, 130.00, 128.29, 52.76, 21.6 9; IR (neat) 1984, 1795, 1601, 1548, 1347, 1050 cm^{-1}; HR MS Calcd for $C_{11}H_{12}O_4S$ (M + Na^+): 263.0354, found: 263. 0351.

(Z)-phenyl 3-tosylacrylate ***(3ac)***.

Yellow Solid; Yield = 75% (60.8 mg); mp = 86 °C (Lit. mp = 85–87 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.39 (m, 2H), 7.37 – 7.28 (m, 5H), 6.67 (ABq, 2H, ΔδAB = 0.03, J_{AB} = 12.0 Hz), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.80, 150.07, 145.44, 136.22, 130.52, 130.09, 129.63, 128.41, 126.48, 121.57, 21.70; IR (neat) 1984, 1791, 1601, 1549, 1542, 1348, 1052 cm^{-1}; HRMS Calcd for $C_{16}H_{14}O_4S$ (M + Na^+): 325.0510, found: 325.0494.

(Z)-benzyl 3-tosylacrylate ***(3ad).***

White Solid; Yield = 79% (66.9 mg); mp = 103 °C (Lit. mp = 102–103 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.26 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.44 (ABq, 2H, ΔδAB = 0.04, J_{AB} = 12.0 Hz), 5.23 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.88, 145.21, 136.37, 135.85, 134.75, 131.00, 129.93, 128.91, 128.67, 128.64, 128.34, 68.02, 21.69; IR (neat) 2996, 1985, 1794, 1602, 1549, 1541, 1348, 1052 cm^{-1}; HRMS Calcd for $C_{17}H_{16}O_4S$ (M + Na^+): 339.0667, found: 339.0671.

(Z)-2-hydroxyethyl 3-tosylacrylate ***(3ae).***

Colorless oil; Yield = 71% (52.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.52 (ABq, 2H, ΔδAB = 0.04, J_{AB} = 12.0 Hz), 4.49 – 4.46 (m, 2H), 3.95 (t, *J* = 4.3 Hz, 2H), 2.87 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.15, 145.59, 136.02, 135.38, 130.82, 130.17, 128.17, 68.08, 60.68, 21.71; IR (neat) 3362, 2991, 1985, 1794, 1603, 1548, 1348, 1052 cm^{-1}; HRMS Calcd for $C_{12}H_{14}O_5S$ (M + Na^+): 293.0460, found: 293.0451.

(Z)-2-methoxyethyl 3-tosylacrylate ***(3af).***

White Solid; Yield = 81% (62.2 mg); mp = 78 °C (Lit. mp = 77–79 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.49 (ABq, 2H, ΔδAB = 0.04, J_{AB} = 12.0 Hz), 4.44 (t, *J* = 4.8 Hz, 2H), 3.92 (t, *J* = 4.4 Hz, 2H), 3.49 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.151, 145.593, 136.015, 135.384, 130.819, 130.171, 128.167, 68.080, 60.681, 53.406, 21.712; IR (neat) 1985, 1795, 1602, 1548, 1347, 1051 cm^{-1}; HRMS Calcd for $C_{13}H_{16}O_5S$ (M + Na^+): 307.0616, found: 307.0617.

(Z)-2-(benzyloxy)ethyl 3-tosylacrylate ***(3ag).***

White Solid; Yield = 82% (78.5 mg); mp = 100 °C (Lit. mp = 99–101 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.26 (m, 7H), 6.50 (ABq, 2H, ΔδAB = 0.03, J_{AB} = 12.0 Hz), 4.60 (s, 2H), 4.52 – 4.45 (m, 2H), 3.81 (dd, *J* = 5.5, 3.9 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.05, 144.17, 136.80, 135.29, 134.51, 130.03, 128.95, 127.41, 127.36, 126.83, 126.74, 72.22, 66.67, 64.05, 20.66; IR (neat) 2994, 1985, 1792, 1604, 1547, 1348, 1051 cm^{-1}; HRMS Calcd for $C_{19}H_{20}O_5S$ (M + Na^+): 383.0929, found: 383.0927.

(Z)-2-bromoethyl 3-tosylacrylate ***(3ah).***

White Solid; Yield = 85% (75.4 mg); mp = 85 °C (Lit. mp = 84–86 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.52 (ABq, 2H, ΔδAB = 0.04, J_{AB} = 12.0 Hz), 4.61 (t, *J* = 6.3 Hz, 2H), 3.63 (t, *J* = 6.3 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.67, 145.42, 136.17, 135.94, 130.40, 130.07, 128.33, 65.08, 27.86, 21.72; IR (neat) 2992, 1984, 1793, 1602, 1548, 1348, 1051 cm^{-1}; HRMS Calcd for $C_{12}H_{13}BrO_4S$ (M + Na^+): 354.9616, found: 354.9618.

(Z)-4-hydroxybutyl 3-tosylacrylate ***(3ai).***

Colorless oil; Yield = 77% (61.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.49

(ABq, 2H, ΔδAB = 0.04, J_{AB} = 12.0 Hz), 4.35 (t, *J* = 6.5 Hz, 2H), 3.71 (t, *J* = 6.3 Hz, 2H), 2.45 (s, 3H), 1.92 – 1.81 (m, 2H), 1.72 (dq, *J* = 9.7, 6.4 Hz, 2H), 1.25 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.18, 145.29, 136.39, 135.36, 131.26, 130.01, 128.29, 66.00, 62.31, 29.02, 24.88, 21.70; IR (neat) 3386, 2991, 1984, 1795, 1602, 1547, 1347, 1048 cm^{-1}; HRMS Calcd for $C_{14}H_{18}O_5S$ (M + Na^+): 321.0773, found: 321.0775.

(Z)-2-methoxy-2-oxoethyl 3-tosylacrylate ***(3aj).***

Colorless oil; Yield = 81% (60.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.58 (ABq, 2H, ΔδAB = 0.04, J_{AB} = 12.0 Hz), 4.84 (s, 2H), 3.81 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.51, 162.28, 144.40, 135.69, 129.03, 128.98, 127.40, 60.61, 51.40, 20.70; IR (neat) 2991, 1984, 1794, 1742, 1602, 1548, 1347, 1051 cm^{-1}; HRMS Calcd for $C_{13}H_{14}O_6S$ (M + Na^+): 298.0511, found: 298.0508.

Deuterium generation (Z)-ethyl 3-tosylacrylate ***(4).***

White Solid; Yield = 87% (55.5 mg); mp = 37 °C (Lit. mp = 36–38 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 6.51 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.02, 144.18, 135.46, 134.37, 128.94, 127.28, 61.14, 20.69, 12.97; IR (neat) 2994, 1985, 1794, 1602, 1548, 1348, 1051 cm^{-1}; HRMS Calcd for $C_{12}H_{13}DO_4S$ (M + Na^+): 278.0573, found: 278.0575.

Acknowledgment

We are grateful for financial support from the National Natural Science Foundation of China (No. 21502049 and 51573040) and the Planned Science and Technology Project of Hunan Province, China (No. 2015WK3003).

Supporting Information

^{1}H and ^{13}C NMR spectra of compounds **3aa-3na, 3ab-3aj and 4**.

References

(1) (a) Back, T. G.; Clary, K. N.; Gao, D. *Chem. Rev.* **2010,** *110*, 4498. (b) Kotha, S.; Khedkar, P. *Chem. Rev.* **2012,** *112*, 1650.

(2) (a) El-Awa, A.; Noshi, M. N.; Jourdin, X. M.; Fuchs, P. L. *Chem. Rev.* **2009,** *109*, 2315. (b) Trost, B. M. *The Chemical Society of Japan.* **1988,** *61*, 107.

(3) (a) Masand, V. H.; Mahajan, D. T.; Hadda, T. B.; Jawarkar, R. D. and Ali, M. A. *Med. Chem. Res.*, 2013, **23**, 1742. (b) Ettari, R.; Nizi, E.; Di Francesco, M. E.; Dude, M.A.; G. Pradel, R. Vičík, Micale, N.; Grasso, S. and Zappalà, M. *J. Med. Chem.*, 2008, **51**, 988. (c) Moon, J. T.; Ha, S. H.; Lee, S. H.; Kwon, T. H.; Oh, C. R.; Kim, Y. D.; Kim, J., Choo, D. J. and Lee, J. Y. *Bioorg. Med. Chem. Lett.*, 2010, **20**, 52; (d) Hayakawa, K.; Yodo, M.; Ohsuki S. and Kanematsu, K. *J. Am. Chem. Soc.*, 1984, **106**, 6735.

(4) Labadie, S. S. *J. Org. Chem.* **1989,** *54*, 2496.

(5) Nájera, C.; Baldó, B.; Yus, M. *J. Chem. Soc., Perkin Trans. 1*. **1988**, 1029.

(6) Chen, D. D.; Hou, X. L.; Dai, L. X. *J. Org. Chem.* **2008,** *73*, 5578.

(7) Khalili, G. *Journal of Sulfur Chemistry.* **2013,** *34*, 532.

(8) Downey, C. W.; Craciun, S.; Neferu, A. M.; Vivelo, C. A.; Mueller, C. J.; Southall, B. C.; Corsi, S.; Etchill, E. W.; Sault, R. J. *Tetrahedron Lett.* **2012,** *53*, 5763.

(9) (a) Herrerıas, C. I.; Yao, X. Q.; Li, Z. P.; Li, C. J. *Chem. Rev.* **2007,** *107*, 2546. (b) Chanda, A.; Fokin, V. V. *Chem. Rev.* **2009,** *109*, 725. (c) Butler, R. N.; Coyne, A. G. *Chem. Rev.* **2010,** *110*, 6302. (d) Lindstrom, U. M. *Chem. Rev.* **2002,** *102*, 2751. (e) Bai, C.; Li, A.; Yao, X.; Liu, H.; Li, Y. *Green Chem.* **2016,** *18*, 1061. (f) Xiao, F.; Chen, S.; Tian, J.; Huang, H.; Liu, Y.; Deng, G.-J. *Green Chem.* **2016,** *18*, 1538. (g) Yang, Y.; Zhang, S.; Tang, L.; Hu, Y.; Zha, Z.; Wang, Z. *Green Chem.* **2016**.

(10) (a) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2014,** *114*, 1783. (b) Dorel, R.; Echavarren, A. M. *Chem. Rev.* **2015,** *115*, 9028. (c) Godoi, B.; Schumacher, R. F.; Zeni, G. *Chem. Rev.* **2011,** *111*, 2937. (d) Oger, C.; Balas, L.; Durand, T.; Galano, J.-M. *Chem. Rev.* **2013,** *113*, 1313.

(11) (a) Singh, R.; Allam, B. K.; Singh, N.; Kumari, K.; Singh, S. K.; Singh, K. N. *Org. Lett.* **2015,** *17*, 2656. (b) Xu, K.; Khakyzadeh, V.; Bury, T.; Breit, B. *J. Am. Chem. Soc.* **2014,** *136*, 16124.

(12) Yang, F. L.; Ma, X. T.; Tian, S. K. *Chemistry, a European journal.* **2012,** *18*, 1582.

(13) (a) Ji, X.; Huang, H.; Wu, W.; Jiang, H. *J. Am. Chem. Soc.* **2013,** *135*, 5286. (b) Lu, Q.; Zhang, J.; Zhao, G.; Qi, Y.; Wang, H.; Lei, A. *J. Am. Chem. Soc.* **2013,** *135*, 11481. (c) Pinter, A.; Sud, A.; Sureshkumar, D.; Klussmann, M. *Angew. Chem. Int. Ed. Engl.* **2010,** *49*, 5004.

(14) Friedman, L.; Litle, R. L.; Reichle, W. R. *Organic Syntheses.* 1960, *40*, 93.

(15) (a) Bio, M.; Nkepang, G.; You, Y. *Chem. Commun. (Camb.).* 2012, *48*, 6517. (b) Doohan, R. A.; Hannan, J. J.; Geraghty, N. W. *Organic & biomolecular chemistry.* 2006, *4*, 942. (c) Jim, C. K. W.; Qin, A.; Lam, J. W. Y.; Häussler, M.; Liu, J.; Yuen, M. M. F.; Kim, J. K.; Ng, K. M.; Tang, B. Z. *Macromolecules.* 2009, *42*, 4099. (d) Ramachandran, P. V.; Rudd, M. T.; Reddy, M. V. R. *Tetrahedron Lett.* 2005, *46*, 2547