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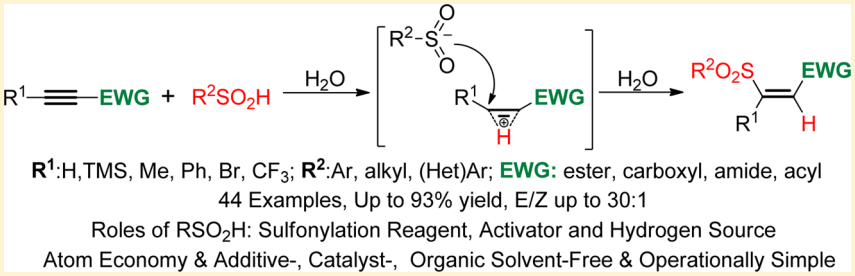
Regio- and Stereoselective Hydrosulfonation of Alkynylcarbonyl Compounds with Sulfinic Acid in Water

Chao Wu, Panpan Yang, Zhimin Fu, Yong Peng, Xin Wang, Zuozhi Zhang, Fang Liu, Wenyi Li, Zhizhang Li, and Weimin He*

Key Laboratory of Comprehensive Utilization of Advantage Plants Resources in Hunan South, College of Chemistry and Bioengineering, Hunan University of Science and Engineering, Yongzhou 425100, China

Supporting Information



ABSTRACT: We report the atom-economic and environmentally friendly synthesis of *Z*-*β*-sulfonyl-a,*β*-unsaturated carbonyl compounds in water. The mechanism study reveals that the hydrosulfonylation of alkynylcarbonyl compounds with sulfinic acids proceeds via a mechanism that features a sulfinic acid molecule protonating an alkynyl motif to form the ethenium intermediate, which subsequently reacted with a sulfonyl anion to afford the desired products. The ethenium intermediate differentiated electronic and steric demands between the two substituents on the C≡C triple bond of the alkyne substrates to exhibit high regio- and stereoselectivity from a wide range of *Z*-*β*-sulfonyl-a,*β*-unsaturated carbonyl compounds.

INTRODUCTION

Complex organic molecules play a crucial role in the study and treatment of disease. The extent to which they can be utilized in these endeavors depends on the efficient and selective chemical methods for their construction from simple and readily accessible starting materials. *β*-Sulfonyl-*α*,*β*-unsaturated carbonyl compounds are widely represented in biologically active molecules[1] and serve as versatile building blocks in organic synthesis.[2] Consequently, the selective assembly of *β*-sulfonyl-*α*,*β*-unsaturated carbonyl compounds from commercially available raw materials is a prominent objective in chemical research. There are a number of powerful methods for the preparation of the (*E*) isomer of *β*-sulfonyl-*α*,*β*-unsaturated carbonyl compounds.[3] However, the synthesis of the corresponding (*Z*) isomers are more challenging and typically require multistep routes that are potentially complicated by competing isomerization to the more thermodynamically favored (*E*) isomer. Examples of direct production of *Z*-*β*-sulfonyl-*α*,*β*-unsaturated carbonyl compounds from alkynylcarbonyl compounds are rare. Dai and co-workers reported a single example of NHC catalyzed sulfonylation of ethyl propiolate with *N*-tosylbenzaldimine in the presence of DBU as a base to give *Z*-ethyl 3-tosyl acrylate only in low yield (Scheme 1, eq 1).[4] In addition, the reaction is intrinsically limited to costly catalysts and requires an additional prefunctionalization process of benzenesulfonamide.[5] Downey et al. developed a different method to *Z*-*β*-sulfonyl enoates involving a sequential intermolecular C−S bond forming step via nucleophilic addition at low temperature, followed by an oxidation reaction (Scheme 1, eq 2).[6] However, sulfide sources are frequently reported to have unstable, toxic, and odorous properties; the use of hazardous additives (*N*,*N*-diisopropylethylamine, potassium *tert*-butylate, and lithium perchlorate) have greatly hindered its application in synthetic chemistry. Most importantly, these methods are not atom economical, as only a part of the reagent used for the introduction of sulfonyl group is retained.

Reactions in aqueous media are of paramount importance in organic syntheses.[7] The use of many toxic and volatile organic solvents, particularly chlorinated hydrocarbons, as reaction media contributes to the environment pollution, and it is highly desirable to develop environmentally benign processes that can be conducted in aqueous media. Furthermore, using water as a solvent offers many advantages such as simple operation, nonflammability, and high efficiency in many organic reactions that involve insoluble reagents.[8]

Continuing with our interest in alkyne chemistry,[9] we herein disclose our investigation on the synthesis of *Z*-*β*-sulfonyl-*α*,*β*-unsaturated carbonyl compounds through hydrosulfonation of alkynylcarbonyl compounds with sulfinic acid[10] under environmentally friendly conditions. In addition to the impressive

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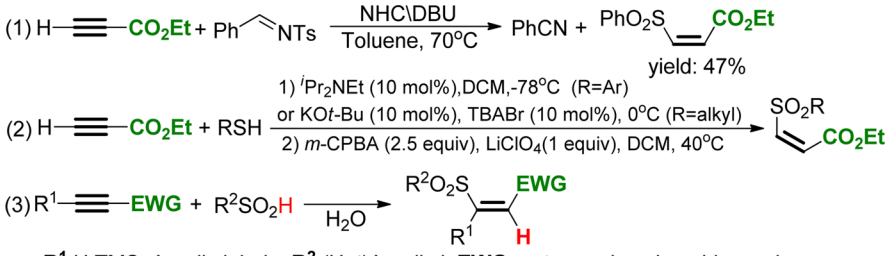
Scheme 1. Synthesis of *Z*-*β*-Sulfonyl Enoates

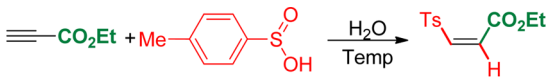


scope, important novel aspects are the organic solvent-, external catalyst-, additive-free reaction conditions and excellent chemo-, regio-, and stereoselectivity. Moreover, large-scale synthesis of (*Z*)-ethyl 3-tosyl acrylate is described (Scheme 1, eq 3).

RESULTS AND DISCUSSION

Initially, we performed the hydrosulfonation of the readily available ethyl propiolate (**1a**) with 4-methylbenzenesulfinic acid (**2a**) in water at room temperature. To our delight, an 18% NMR yield of ethyl 3-tosyl acrylate (**3aa**) based on 21% conversion of the starting material **1a** was obtained after 24 h (Table 1, entry 1). To check the effect of temperature on the reaction, the test reaction was carried out at different temperatures (entries 2−4). It was found that the maximum conversion occurred at 60 °C, providing the desired product **3aa** in 55% yield after 4 h (entry 3). A higher temperature (80 °C) did not improve the yield (entry 4). Significantly, employment of a slight excess of **2a** (1.1−1.3 equiv) was found to provide the desirable product **3aa** in good to excellent yields with high stereoselectivity for *E*/*Z* = 16:1 isomers (entries 5−7). These results indicated that the proton has a significant role in the reactions. Conducting the reaction at a concentration of 0.05 M did not affect the reaction yield (entry 8 vs 7); however, a higher concentration of 0.2 M was selected to provide conditions that minimize solvent waste and reduce the reaction time from 1.5 to 1 h (entry 9 vs 7). Mild reaction conditions, shorter reaction times, cost-effectiveness, operational simplicity, excellent yields, and high stereoselectivity make this transformation an alternative method for the facile construction of numerous *Z*-*β*-sulfonyl enoates.

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3aa**

entry	ratio	temp (°C)	time	concn (M)	yield[b]	*E*/*Z*[b]
1	1:1	rt	24 h	0.1	18	14:1
2	1:1	40	8 h	0.1	24	14:1
3	1:1	60	4 h	0.1	55	16:1
4	1:1	80	4 h	0.1	55	15:1
5	1.1.1	60	2 h	0.1	72	16:1
6	1:1.2	60	1.5 h	0.1	92	16:1
7	1:1.3	60	1.5 h	0.1	92	16:1
8[c]	1:1.2	60	1.5 h	0.05	90	16:1
9[d]	**1:1.2**	**60**	**1 h**	**0.2**	**92**	**16:1**

[a]Unless otherwise specified, the reactions were carried out in sealed tubes in the presence of **1a** (0.1 mmol), **2a**, and water (1 mL). [b]Estimated by ^{1}H NMR spectroscopy using diethyl phthalate as an internal reference. [c]2 mL of water were used as the solvent. [d]0.5 mL water was used as the solvent. rt = room temperature.

With the optimum conditions in hand, the reaction scope with regard to the sulfinic acids was first examined (Table 2). No matter what substitute group (electron-neutral, electron-rich, electron-deficient, or steric hindrance group) the benzene ring of benzenesulphinic acid carries, in all cases the sulfonated products (**3aa**−**ao**) were obtained in good to excellent yields and a satisfactory range of *Z*/*E* ratios from 14:1 to 30:1 (based on the analysis of ^{1}H NMR spectra). Various functional groups were readily well tolerated, including alkoxyl (**3ac** and **3ad**), amide (**3ae**), halide (**3af** − **ai**), trifluoromethyl (**3aj**), acyl (**3ak**), cyano (**3al**), and nitro (**3am**) groups. Furthermore, benzenesulphinic acids bearing two- or three-substituents on the arene rings could also be converted to corresponding products (**3ap** and **3aq**) in good yields. We were pleased that the sulfonating of the polycyclic and heterocyclic aromatic motif was possible and proceeded in good yields as well as high *Z*/*E* ratios (**3ar** and **3as**), thus further enhancing the scope of our reaction. In addition, aliphatic sulfinic acids were good coupling partners (**3at** and **3au**). The reaction proceeded efficiently to afford their corresponding hydrosulfonation products in moderate to good yields even for the substrates bearing functional groups such as free chloro.

Subsequently, we further investigated the scope of alkynylcarbonyl compounds (Table 3). To our satisfaction, propargylic carboxylates with various chain lengths and isomeric structures undergo hydrosulfonation to furnish the *β*-sulfonyl enoates in good yields with high stereoselectivity in favor of the (*Z*)-isomer. Excellent functional group compatibility was exhibited, tolerating alkyl (**3ba**−**3ca**), Ph (**3da**), cyclopropylmethyl (**3ea**), cyclopentyl (**3fa**), free OH (**3ga**), Br (**3ha**), and thiophenemethyl (**3ia**) moieties. Notably, the reaction could be extended to thermodynamically more stable internal propargylic carboxylates possessing substituents with various electronic and steric properties (**3ja**−**na**). Subjecting the substrate ethyl 3-(trimethylsilyl)propiolate **1j** to the standard reaction conditions could successfully afford the (*Z*)-ethyl 3-tosyl acrylate in 84% yield, allowing access to ethyl propiolate via deprotection of the TMS group. Compared with alkyl-substituted substrates (**3ka**), phenyl-substituted ethyl propiolate (**3la**) exhibit relatively poor reactivity and the examples indicate steric hindrance play a key role in these transformations. The electron-rich groups attached to ethyl propiolate led usually to higher yields than did the electron-deficient groups (**3ka** vs **3ma** and **3na**). Gratifyingly, the present catalytic reaction was also successfully applied to other electron-withdrawing group substituted acetylenes, including carboxyl (**3oa**), amide (**3pa** and **3qa**), sulfonic ester (**3ra**), and

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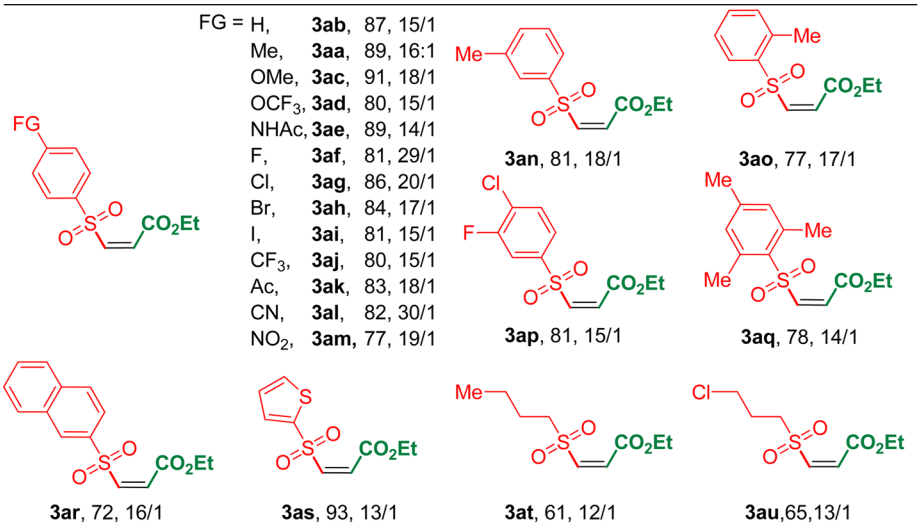
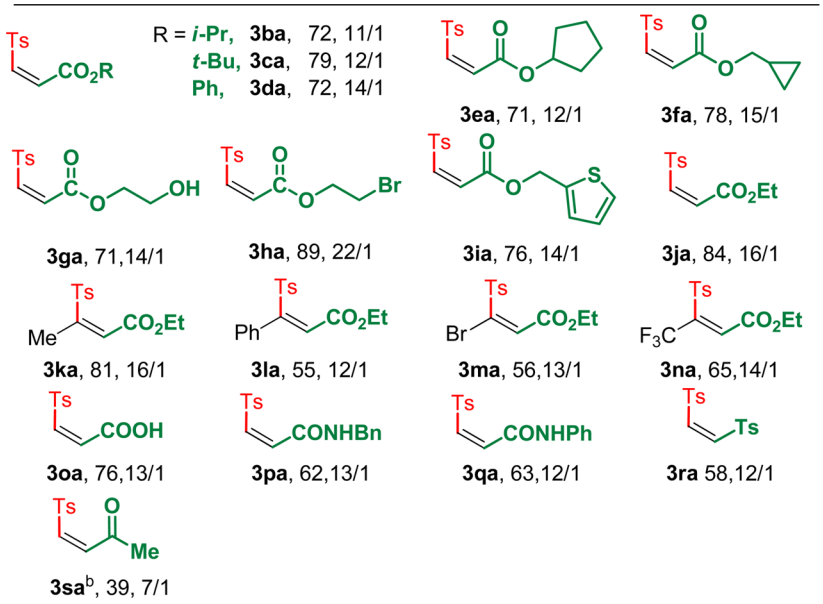
Table 2. Reaction Scope of Sulfinic Acids[a]



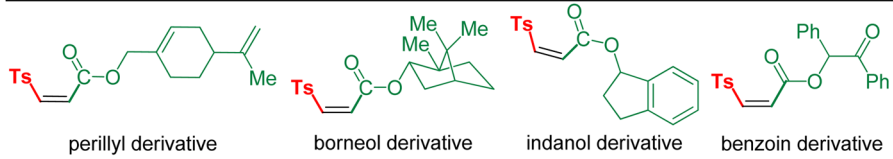
[a] All reactions were carried out in a sealed tube in the presence of 1 (0.2 mmol), 2 (0.24 mmol) and water (1 ml).

Table 3. Reaction Scope of Substituted Alkynes[a]



[a] All reactions were carried out in a sealed tube in the presence of 1 (0.2 mmol), 2 (0.24 mmol) and water (1 ml). [b] After 24 h, 51% of 1s was detected.

Table 4. Reaction Scope of Late-Stage Modification[a]



[a] All reactions were carried out in a sealed tube in the presence of 1 (0.2 mmol), 2 (0.24 mmol) and water (1 ml).

acetyl (**3sa**) groups, which gave the corresponding hydrosulfonation products in moderate to good yields.

β-Sulfonylenoates are important multifunctional motifs present in a wide range of bioactive compounds, synthetic intermediates, and pharmaceuticals. In addition, late-stage modification is a valuable strategy for medicinal chemistry research. Therefore, the hydrosulfonylation method was applied for the synthesis of vinyl sulfones containing bioactive moieties (Table 4). Derivatives bearing natural groups such as perillyl, borneol, indanol, and benzoin could well react with 4-

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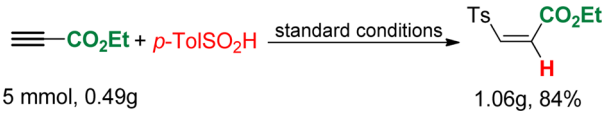
methylbenzenesulfinic acid **2a** to give the desired products (**4aa**−**da**) in 50−79% yields and with *Z*/*E* ratios ranging from 9:1 to 14:1. These results demonstrate that the present protocol could be applied in late-stage bioactive compound modification.

For the small-scale reaction, 1.2 equiv of sulfinic acid **2a** was required, and the decrease in **2a** loading would dramatically decrease the yield (Table 1, entry 6 vs 5). Delightedly, the use of 1.1 equiv of **2a** could afford the desired product in 84% yield (1.06 g) with an increase in the scale of the reaction by 25-fold (Scheme 2), demonstrating the synthetic utility of this protocol

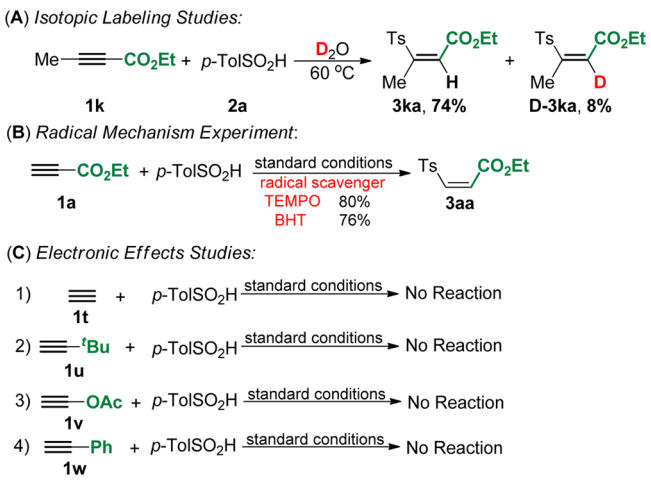
Scheme 2. Gram Scale Synthesis of (*Z*)-Ethyl 3-Tosylacrylate



from a practical point of view. Importantly, the products were easily recrystallized to afford the pure *Z*-isomer of *β*-sulfonyl enoates. No column chromatography was used at all during the purification process.

In order to gain information on the reaction mechanism, several control experiments were conducted. First, the hydrosulfonylation reaction of **1k** in D_2O gave **3ka** and **D-3ka** in 74% and 8% NMR yields, respectively (Scheme 3A).

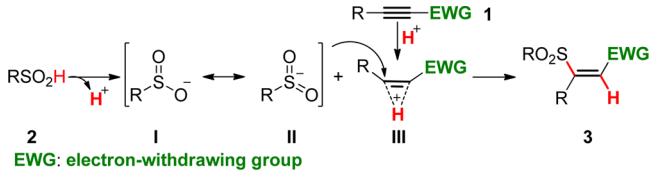
Scheme 3. Mechanism Study Experiments



This result clearly demonstrated that the *α*-hydrogen atom of *β*-sulfonyl-*α*,*β*-unsaturated carbonyl compound **3** originated from sulfinic acid **2**. Next, addition of a radical scavenger (for example, TEMPO and BHT) to the reaction mixture under the standard reaction conditions did not make this hydrosulfonylation reaction completely suppressed, excluding the possibility of a radical process (Scheme 3B).[10e−i,11] Moreover, the acetylene **1t**, 3,3-dimethylbut-1-yne **1u**, ethynyl acetate **1v**, and phenylacetylene **1w** were subjected to the reaction with **2a**, but no sulfonylated products were observed (Scheme 3C), confirming the electron-withdraw group is essential for this transformation. These observations indicating the electron-donating substitution, which may promote the electrophilic addition of alkynyl group, has a negative influence on the reaction. These results exclude the possibility of the electrophilic mechanism.

Based on the above results, we propose a potential mechanistic pathway for this hydrosulfonation of alkynylcarbonyl compound (Scheme 4). Initially, sulfinic acid **2** was

Scheme 4. Plausible Reaction Mechanism



converted into an oxygen-centered anion **I** resonating with the sulfonyl anion **II** via the single electron transfer (SET) and deprotonation process in water. Simultaneously, propargylic carboxylates **1** were protonated by sulfinic acid to give the activated ethenium intermediate **III**.[12] Subsequently, the regio- and antiselective nucleophilic addition of the sulfonyl anion **II** to intermediate **III** generated the corresponding *Z*-*β*-sulfonyl enoates **3**. We speculate that a relatively weak acidity (pH around 6) of the reaction mixture is crucial. Most of the sulfinic acid is quickly consumed via reaction with intermediate **III**; therefore, the overall acidity of the reaction is dominated by the acidity of excess sulfinic acid.

CONCLUSIONS

In conclusion, we have developed the atom-economic hydrosulfonation of activated alkynes with sulfinic acid to afford valuable *Z*-*β*-sulfonyl-*α*,*β*-unsaturated carbonyl compounds in environmentally friendly conditions. In this reaction, the sulfinic acid plays three roles, acting as the sulfonation reagent, hydrogen source, and activating reagent. This transformation can also tolerate a range of functional groups due to its weak acidity and redox-neutral conditions. The intermolecular hydrosulfonation of activated alkynes shows excellent chemo- and regioselectivity as well as high stereoselectivity. Finally, the proposed mechanism was carefully explored through competition experiments, control experiments, and deuterium-labeling experiments. We expect this detailed study would shed light on the scope and potential of the activation strategy of activated alkynes.

EXPERIMENTAL SECTION

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 precoated silica gel plates. Chromatographic purifications were carried out on a Biotage Isolera Four instrument. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 and 500 MHz NMR plus spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with an IR spectrometer and are reported in reciprocal centimeter (cm^{-1}). High resolution mass spectra were obtained using a GCT-TOF instrument with an EI or ESI source.

General Procedure for the Synthesis of *Z*-*β*-Sulfonyl Enoates. In a sealed tube were placed alkynylcarbonyl compound (0.2 mmol), sulfinic acid (0.24 mmol), and H_2O (1 mL), and then the contents were stirred at 60 °C. The progress of the reaction was monitored by TLC. The reaction typically took 1−2 h. Upon completion, the reaction was cooled down to room temperature, mixed with silica gel, and concentrated under vacuum. Gradient elution with ethyl acetate/hexane was accomplished in both instances. This residue was purified by flash chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford **3**−**4**.

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The Experimental Procedure for Larger-Scale Synthesis of 3aa. In a sealed tube were placed ethyl propiolate (5 mmol, 0.49 g), 4-methylbenzenesulfinic acid (5.5 mmol, 0.855 g), and H_2O (10 mL), and then the contents were stirred at 60 °C for 1.5 h. The reaction was cooled down to room temperature and concentrated under vacuum. This residue was recrystallized by hexane and tetrahydrofuran to give **3aa** (1.06 g, yield 84%).

*(Z)-Ethyl 3-Tosyl Acrylate (**3aa**).*[6] White solid (45.2 mg, 89%), mp 41−42 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 11.6 Hz, 1H), 6.48 (d, J = 11.6 Hz, 1H), 4.32 (q, J = 6.8 Hz, 2H), 2.45 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.0, 145.1, 136.4, 135.3, 131.4, 130.0, 128.2, 62.1, 21.7, 13.9.

*(Z)-Ethyl 3-(Phenylsulfonyl)acrylate (**3ab**).*[6] Colorless oil (41.7 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.69−7.65 (m, 1H), 7.61−7.56 (m, 2H), 6.54 (d, J = 11.2 Hz, 1H), 6.50 (d, J = 11.2 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.0, 139.4, 135.1, 134.0, 131.9, 129.4, 128.2, 62.2, 14.0.

*(Z)-Ethyl 3-(4-Methoxyphenylsulfonyl)acrylate (**3ac**).*[6] White solid (49.1 mg, 91%), mp 47−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.49 (d, J = 11.2 Hz, 1H), 6.45 (d, J = 11.2 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 3.88 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.2, 164.1, 135.6, 130.9, 130.6, 114.6, 62.1, 55.7, 14.0.

*(Z)-Ethyl 3-(4-(Trifluoromethoxy)phenylsulfonyl)acrylate (**3ad**).* Light yellow solid (51.8 mg, 80%), mp 46−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 2H), 7.83(d, J = 8.4 Hz, 2H), 6.60 (d, J = 11.2 Hz, 1H), 6.55 (d, J = 11.2 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.7, 142.9, 135.6 (d, J = 32.6 Hz), 134.5, 133.5, 128.9, 126.4 (q, J = 3.8 Hz), 123.0 (d, J = 271.8 Hz), 62.3, 13.9. IR (neat, cm^{-1}): 3076, 2981, 1732, 1669, 1313, 1150, 735, 701. HRMS calcd (ESI) m/z: for $C_{12}H_{11}NaF_3O_5S$ [M + Na]$^+$, 347.0171; found, 347.0177.

*(Z)-Ethyl 3-(4-Acetamidophenylsulfonyl)acrylate (**3ae**).*[13] White solid (52.8 mg, 89%), mp 52−54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.8 Hz, 2H), 7.64 (s, 1H), 6.53 (d, J = 11.2 Hz, 1H), 6.49 (d, J = 11.2 Hz, 1H), 4.36 (q, J = 6.8 Hz, 2H), 2.22 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 168.6, 164.0, 143.2, 135.4, 133.9, 131.5, 129.7, 119.3, 62.1, 24.6, 13.8.

*(Z)-Ethyl 3-(4-Fluorophenylsulfonyl)acrylate (**3af**).*[6] Light yellow solid (41.8 mg, 81%), mp 46−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.06 (m, 2H), 7.29 (d, J = 8.0 Hz 2H), 6.57 (s, 2H), 4.40 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 165.8 (d, J = 255.5 Hz), 163.8, 135.3 (d, J = 3.0 Hz), 134.9, 132.2, 131.1 (d, J = 9.7 Hz), 116.5 (d, J = 22.7 Hz), 62.3, 14.0.

*(Z)-Ethyl 3-(4-Chlorophenylsulfonyl)acrylate (**3ag**).*[13] Colorless oil (47.1 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.8 Hz 2H), 6.52 (s, 2H), 4.36 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 2.8 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.9, 140.9, 138.0, 135.0, 132.5, 129.8, 129.7, 62.3, 14.0.

*(Z)-Ethyl 3-(4-Bromophenylsulfonyl)acrylate (**3ah**).*[6] White solid (53.3 mg, 84%), mp 65−66 °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), 6.53 (s, 2H), 4.36 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.9, 138.6, 135.1, 132.7, 132.5, 129.9, 129.5, 62.4, 14.0.

*(Z)-Ethyl 3-(4-Iodophenylsulfonyl)acrylate (**3ai**).* White solid (59.3 mg, 81%), mp 72−73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 6.54 (d, J = 11.2 Hz, 1H), 6.50 (d, J = 11.6 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.8, 139.0, 138.7, 134.8, 132.5, 129.6, 102.2, 62.3, 13.9. IR (neat, cm^{-1}): 3081, 2978, 1723, 1670, 1323, 1172, 735. HRMS calcd (ESI) m/z: for $C_{11}H_{11}NaIO_4S$ [M + Na]$^+$, 388.9315; found, 388.9311.

*(Z)-ethyl 3-(4-(trifluoromethyl)phenylsulfonyl)acrylate (**3aj**).* White solid (49.2 mg, 80%), mp 61−62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 11.6 Hz, 1H), 6.57 (d, J = 11.6 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 6.8 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.9, 142.9, 135.6 (q, J = 32.7 Hz), 134.5, 133.5, 128.8, 126.4 (q, J = 3.8 Hz), 123.1 (q, J = 271.8 Hz), 62.3, 13.9. IR (neat, cm^{-1}): 3077, 2989, 1726, 1680, 1320, 1086, 755. HRMS calcd (ESI) m/z: for $C_{12}H_{11}NaF_3O_4S$ [M + Na]$^+$, 331.0222; found, 331.0217.

*(Z)-Ethyl 3-((4-Acetylphenyl)sulfonyl)acrylate (**3ak**).* White solid (46.8 mg, 83%), mp 53−54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.05 (m, 4H), 6.56 (d, J = 11.2 Hz, 1H), 6.53 (d, J = 11.6 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 2.63 (s, 3H), 1.35 (t, J = 6.8 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 196.6, 163.6, 143.0, 140.8, 134.5, 133.0, 128.8, 128.4, 62.1, 26.8, 13.8. IR (neat, cm^{-1}): 3077, 2956, 1732, 1720, 1659, 1298, 1106, 752. HRMS calcd (ESI) m/z: for $C_{13}H_{14}NaO_5S$ [M + Na]$^+$, 305.0454; found, 305.0448.

*(Z)-Ethyl 3-(4-Cyanophenylsulfonyl)acrylate (**3al**).* White solid (43.5 mg, 82%), mp 66−67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 11.2 Hz, 1H), 6.55 (d, J = 11.6 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.5, 143.6, 134.5, 134.0, 133.0, 128.9, 117.7, 117.0, 62.4, 13.9. IR (neat, cm^{-1}): 3074, 2982, 2224, 1730, 1680, 1086, 793. HRMS calcd (ESI) m/z: for $C_{12}H_{11}NaNO_4S$ [M + Na]$^+$, 288.0301; found, 288.0298.

*(Z)-ethyl 3-(4-Nitrophenylsulfonyl)acrylate (**3am**).*[14] White solid (43.9 mg, 77%), mp 59−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.8 Hz, 2H), 8.23 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 11.6 Hz, 1H), 6.58 (d, J = 11.2 Hz, 1H), 4.38 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.4, 151.0, 145.2, 134.5, 134.3, 129.8, 124.4, 62.5, 13.8.

*(Z)-Ethyl 3-(m-Tolylsulfonyl)acrylate (**3an**).* Colorless oil (41.1 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.77 (m, 2H), 7.46−7.2 (m, 2H), 6.52 (d, J = 11.2 Hz, 1H), 6.48 (d, J = 11.6 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.0, 138.6, 138.3, 134.1, 133.8, 130.7, 128.2, 127.4, 124.3, 61.1, 20.3, 13.0. IR (neat, cm^{-1}): 3081, 2979, 1723, 1339, 1141, 789. HRMS calcd (ESI) m/z: for $C_{12}H_{14}NaO_4S$ [M + Na]$^+$, 277.0505; found, 277.0501.

*(Z)-Ethyl 3-(Phenylsulfonyl)acrylate (**3ao**).* Colorless oil (40.1 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.38(t, J = 7.6 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 6.61 (d, J = 12 Hz, 1H), 6.51 (d, J = 11.6 Hz, 1H), 4.28 (q, J = 6.8 Hz, 2H), 2.65 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.6, 138.4, 137.8, 135.6, 134.0, 132.6, 131.6, 129.7, 126.5, 62.1, 20.3, 13.9. IR (neat, cm^{-1}): 3070, 2972, 1729, 1669, 1327, 1081, 722. HRMS calcd (ESI) m/z: for $C_{12}H_{14}NaO_4S$ [M + Na]$^+$, 277.0505; found, 277.0501.

*(Z)-Ethyl 3-(4-Chloro-3-fluorophenylsulfonyl)acrylate (**3ap**).* White solid (47.3 mg, 81%), mp 77−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.08 (m, 1H), 7.94−7.90 (m, 1H), 7.33 (t, J = 8.4 Hz, 1H), 6.58 (d, J = 11.6 Hz, 1H), 6.53 (d, J = 11.6 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H).^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 166.1 (d, J = 271.2 Hz), 163.9, 135.5 (d, J = 3.7 Hz), 135.2, 132.2, 131.3 (d, J = 9.4 Hz), 116.7 (d, J = 22.6 Hz), 62.3, 13.9. IR (neat, cm^{-1}): 3077, 2985, 1732, 1324, 1153, 822. HRMS calcd (ESI) m/z: for $C_{11}H_{10}NaClFO_4S$ [M + Na]$^+$, 314.9865; found, 314.9860.

*(Z)-Ethyl 3-(Mesitylsulfonyl)acrylate (**3aq**).* Light yellow solid (44.0 mg, 78%), mp 82−83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.66 (d, J = 12 Hz, 1H), 6.42 (d, J = 12 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 2.65 (s, 6H), 2.31 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.5, 143.7, 140.2, 138.2, 133.6, 132.1, 129.5, 61.9, 22.6, 21.0, 13.9. IR (neat, cm^{-1}): 3072, 2928, 1726, 1677, 1310, 1143, 782. HRMS calcd (ESI) m/z: for $C_{14}H_{18}NaO_4S$ [M + Na]$^+$, 305.0818; found, 305.0815.

*(Z)-Ethyl 3-(Naphthalen-2-ylsulfonyl)acrylate (**3ar**).*[6] White solid (41.8 mg, 72%), mp 83−84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.03−7.93 (m, 4H), 7.70−7.63 (m, 2H), 6.60 (d, J = 11.6 Hz, 1H), 6.53 (d, J = 11.6 Hz, 1H), 4.40 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.0, 136.3, 135.5, 135.2, 132.2, 131.9, 130.2, 129.7, 129.6, 129.5, 128.0, 127.7, 122.7, 62.2, 14.0.

*(Z)-Ethyl 3-(Thiophen-2-ylsulfonyl)acrylate (**3as**).* White solid (45.8 mg, 93%), mp 73−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 3.6 Hz, 1H), 7.74 (d, J = 5.6 Hz, 1H), 7.17 (t, J = 4.4 Hz,

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1H), 6.64 (d, J = 11.6 Hz, 1H), 6.48 (d, J = 11.2 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H).^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ163.8, 140.7, 135.9, 135.2, 135.2, 131.6, 128.3, 62.4, 14.1. IR (neat, cm^{-1}): 3068, 2954, 1738, 1666, 1298, 1073, 811. HRMS calcd (ESI) m/z: for $C_9H_{10}NaO_4S_2$ [M + Na]$^+$, 268.9913; found, 268.9906.

(Z)-Ethyl 3-(Butylsulfonyl)acrylate (**3at**). Colorless oil (26.8 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (d, J = 11.2 Hz, 1H), 6.57 (d, J = 11.6 Hz, 1H), 4.28 (q, J = 7.6 Hz, 2H), 3.20 (t, J = 8.0 Hz, 2H), 1.81−1.75 (m, 2H), 1.47−1.40 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.4, 135.8, 134.1, 62.1, 55.1, 23.8, 21.6, 13.8, 13.4. IR (neat, cm^{-1}): 3076, 2974, 1732, 1651, 1314, 1147, 742. HRMS calcd (ESI) m/z: for $C_9H_{16}NaO_4S$ [M + Na]$^+$, 243.0662; found, 243.0658.

(Z)-Ethyl 3-(3-Chloropropylsulfonyl)acrylate (**3au**). White solid (31.2 mg, 65%), mp 55−56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (d, J = 12.0 Hz, 1H), 6.59 (d, J = 11.6 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 3.69 (t, J = 6.4 Hz, 2H), 3.43 (t, J = 7.6 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H), 1.31−1.24 (m, 2H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.3, 135.7, 134.8, 62.4, 52.7, 42.7, 25.2, 13.9. IR (neat, cm^{-1}): 3070, 2970, 1737, 1340, 1089, 904. HRMS calcd (ESI) m/z: for $C_8H_{13}NaClO_4S$ [M + Na]$^+$, 263.0115; found, 263.0111.

(Z)-Isopropyl 3-Tosyl Acrylate (**3ba**). White solid (38.6 mg, 72%), mp 102−103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.48 (d, J = 11.6 Hz, 1H), 6.44 (d, J = 11.6 Hz, 1H), 5.28−5.19 (m, 1H), 2.45 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.6, 145.1, 136.6, 134.9, 131.8, 129.9, 128.3, 70.3, 21.7, 21.6. IR (neat, cm^{-1}): 3082, 2956, 1741, 1662, 1086, 977, 755. HRMS calcd (ESI) m/z: for $C_{13}H_{16}NaO_4S$ [M + Na]$^+$, 291.0662; found, 291.0657.

(Z)-tert-Butyl 3-Tosyl Acrylate (**3ca**). White solid (44.6 mg, 79%), mp 114−115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 6.40 (s, 2H), 2.44 (s, 3H), 1.58 (s, 9H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.0, 145.0, 136.7, 133.6, 132.5, 129.9, 128.1, 83.9, 28.0, 21.83. IR (neat, cm^{-1}): 3076, 2956, 1743, 1697, 1311, 1128, 820. HRMS calcd (ESI) m/z: for $C_{14}H_{18}NaO_4S$ [M + Na]$^+$, 305.0818; found, 305.0815.

(Z)-Phenyl 3-Tosyl Acrylate (**3da**). White solid (43.5 mg, 72%), mp 113−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.46−7.42 (m, 2H), 7.37−7.29 (m, 5H), 6.69 (d, J = 11.6 Hz, 1H), 6.65 (d, J = 11.6 Hz, 1H), 2.45 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.0, 150.2, 145.6, 136.4, 130.7, 130.2, 129.8, 129.6, 128.6, 126.6, 121.7, 21.9. IR (neat, cm^{-1}): 3068, 2932, 1733, 1675, 1135, 976, 747. HRMS calcd (ESI) m/z: for $C_{16}H_{14}NaO_4S$ [M + Na]$^+$ 325.0505; found, 325.0501.

(Z)-Cyclopentyl 3-Tosyl Acrylate (**3ea**). White solid (41.7 mg, 71%), mp 128−129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.47 (d, J = 11.6 Hz, 1H), 6.44 (d, J = 11.2 Hz, 1H), 5.40−5.35 (m, 1H), 2.45 (s, 2H), 1.95−1.90 (m, 4H), 1.82−1.77 (m, 2H), 1.68−1.61 (m, 2H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.9, 145.1, 136.6, 134.9, 131.8, 129.9, 128.3, 79.6, 32.4, 23.7, 21.7. IR (neat, cm^{-1}): 3066, 2971, 1740, 1162, 947, 702. HRMS calcd (ESI) m/z: for $C_{15}H_{18}NaO_4S$ [M + Na]$^+$, 317.0818; found, 317.0812.

(Z)-Cyclopropylmethyl 3-Tosyl Acrylate (**3fa**). Light yellow solid (43.7 mg, 78%), mp 97−98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 11.2 Hz, 1H), 6.48 (d, J = 11.6 Hz, 1H), 4.13 (d, J = 7.6 Hz, 2H), 2.45 (s, 3H), 1.28−1.23 (m, 1H), 0.64 (d, J = 5.6 Hz, 2H), 0.38 (d, J = 4.8 Hz, 2H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.2, 145.2, 136.6, 135.4, 131.4, 139.9, 128.4, 71.1, 21.7, 9.52, 3.53. IR (neat, cm^{-1}): 3078, 2946, 1731, 1643, 1116, 953, 782. HRMS calcd (ESI) m/z: for $C_{14}H_{16}NaO_4S$ [M + Na]$^+$, 303.0662; found, 303.0658.

(Z)-2-Hydroxyethyl 3-Tosyl Acrylate (**3ga**). White solid (38.3 mg, 71%), mp 59−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 11.6 Hz, 1H), 6.51 (d, J = 11.6 Hz, 1H), 4.48 (t, J = 4.4 Hz, 2H), 3.96 (t, J = 4.0 Hz, 2H), 2.88 (s, 1H), 2.46 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.2, 145.6, 136.0, 135.3, 130.8, 130.1, 128.2, 68.1, 60.7, 21.7. IR (neat, cm^{-1}): 3069, 2970, 1746, 1317, 1143, 872, 763. HRMS calcd (ESI) m/z: for $C_{12}H_{14}NaO_5S$ [M + Na]$^+$, 293.0454; found, 293.0451.

(Z)-2-Bromoethyl 3-Tosyl Acrylate (**3ha**). White solid (59.1 mg, 89%), mp 63−64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.55 (d, J = 11.6 Hz, 1H), 6.50 (d, J = 11.6 Hz, 1H), 4.61 (t, J = 6.4 Hz, 2H), 3.63 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.7, 145.4, 136.2, 135.9, 130.4, 130.1, 128.3, 65.1, 27.9, 21.7. IR (neat, cm^{-1}): 3063, 2968, 1738, 1673, 1327, 1148, 923, 748. HRMS calcd (ESI) m/z: for $C_{12}H_{13}NaBrO_4S$ [M + Na]$^+$, 354.9610; found, 354.9603.

(Z)-Thiophen-2-ylmethyl 3-Tosyl Acrylate (**3ia**). White solid (48.9 mg, 76%), mp 133−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 4.8 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 3.2 Hz, 1H), 7.02 (m, 1H), 6.52 (d, J = 11.2 Hz, 1H), 6.46 (d, J = 11.2 Hz, 1H), 5.47 (s, 2H), 2.43 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.6, 145.1, 136.3, 136.1, 135.8, 130.6, 129.8, 129.1, 128.2, 127.3, 126.9, 61.8, 21.6. IR (neat, cm^{-1}): 3078, 2973, 1744, 1670, 1146, 965, 781. HRMS calcd (ESI) m/z: for $C_{15}H_{14}NaO_4S_2$ [M + Na]$^+$, 345.0226; found, 345.0223.

(Z)-Ethyl 3-tosyl acrylate (**3ja**).[6] White solid (42.7 mg, 84%), mp 41−42 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 11.6 Hz, 1H), 6.27 (d, J = 11.6 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.1, 145.2, 136.5, 135.4, 131.4, 123.0, 128.3, 62.2, 21.7, 14.0.

(Z)-Ethyl 3-Tosylbut-2-enoate (**3ka**). White solid (43.4 mg, 81%), mp 47−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.26 (s, 1H), 4.35 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.96 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 165.1, 145.1, 142.4, 135.3, 129.9, 128.8, 128.6, 61.9, 21.7, 17.9, 14.0. IR (neat, cm^{-1}): 3081, 2977, 1724, 1327, 1139, 861, 784. HRMS calcd (ESI) m/z: for $C_{13}H_{16}NaO_4S$ [M + Na]$^+$, 291.0662; found, 291.0658.

(Z)-Ethyl 3-Phenyl-3-tosyl Acrylate (**3la**).[15] White solid (36.3 mg, 55%), mp 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.36−7.31 (m, 1H), 7.27−7.25 (m, 4H), 7.19 (d, J = 8.0 Hz, 2H), 6.39 (s, 1H), 4.41 (q, J = 7.2 Hz, 2H), 2.36 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 165.1, 146.2, 144.8, 135.5, 132.3, 130.4, 129.6, 129.6, 129.5, 128.7, 128.2, 62.1, 21.6, 14.0.

(E)-Ethyl 3-Bromo-3-tosyl acrylate (**3ma**). White solid (37.2 mg, 56%), mp 94−95 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.79 (s, 1H), 4.42 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ 161.6, 144.6, 135.1, 132.5, 129.2, 127.2, 124.7, 62.5, 20.7, 12.8. IR (neat, cm^{-1}): 3064, 2968, 1730, 1344, 1142, 927, 762. HRMS calcd (ESI) m/z: for $C_{12}H_{13}NaBrO_4S$ [M + Na]$^+$ 354.9610; found, 354.9606.

(Z)-Ethyl 4,4,4-Trifluoro-3-tosylbut-2-enoate (**3na**). Yellow solid (41.9 mg, 65%), mp 90−91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 6.8 Hz, 2H), 7.38 (d, J = 6.4 Hz, 2H), 7.04 (s, 1H), 4.45 (q, J = 5.6 Hz, 2H), 2.46 (s, 3H), 1.43 (t, J = 5.6 Hz, 3H). ^{13}C{^{1}H}NMR (123 MHz, $CDCl_3$) δ 162.8, 146.1, 136.1, 135.4, 135.3,129.9, 128.9, 119.1, 62.8, 21.7, 13.8. IR: 2973, 1722, 1345, 1143, 734, 705. IR (neat, cm^{-1}): 3077, 2972, 1728, 1681, 1076, 765. HRMS calcd (ESI) m/z: for $C_{13}H_{13}F_3NaO_4S$ [M + Na]$^+$ 345.0379; found, 345.0373.

(Z)-3-Tosylacrylic Acid (**3oa**). Light yellow oil (34.4 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (brs, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.35 (d, J = 7.6 Hz, 2H), 6.57 (d, J = 11.6 Hz, 1H), 6.53 (d, J = 11.6 Hz, 1H), 2.42 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 166.6, 144.5, 134.8, 134.7, 130.0, 129.1, 127.3, 20.7. IR (neat, cm^{-1}): 3085, 2970, 1725, 1672, 1147, 931, 791. HRMS calcd (ESI) m/z: for $C_{10}H_{10}NaO_4S$ [M + Na]$^+$, 249.0192, found 249.0188.

(Z)-N-Benzyl-3-tosylacrylamide (**3pa**). Light yellow solid (39.1 mg, 62%), mp 77−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 2H), 7.33−7.24 (m, 7H), 6.80 (s, 1H), 6.46 (d, J = 12.0 Hz, 1H), 6.43 (d, J = 12.0 Hz, 1H), 4.49 (d, J = 5.6 Hz, 2H), 2.37 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 163.0, 145.4, 137.1, 136.4, 134.8, 130.1, 128.9, 128.8, 128.2, 128.0, 127.8, 44.13, 21.72. IR (neat, cm^{-1}): 3073, 2976, 1724, 1337, 1028, 972, 740. HRMS calcd (ESI) m/z: for $C_{17}H_{17}NaNO_3S$ [M + Na]$^+$, 338.0821; found, 338.0816.

(Z)-N-Phenyl-3-tosylacrylamide (**3qa**). Light yellow solid (37.9 mg, 63%), mp 69−70 °C. ^{1}H NMR (400 MHz, DMSO-d6) δ 9.51 (s,

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1H), 6.96 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 8.0 Hz, 2H), 6.47 (t, J = 8.0 Hz, 2H), 6.23 (t, J = 8.0 Hz, 1H), 6.14 (d, J = 8.0 Hz, 1H), 6.02 (d, J = 8.0 Hz, 1H), 1.59 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, DMSO-d6) δ 162.1, 144.7, 138.6, 137.0, 136.3, 133.1, 19.9, 128.8, 127.8, 123.8, 119.6, 21.1. IR (neat, cm^{-1}): 3076, 2969, 1747, 1681, 1210, 1012, 785. HRMS calcd (ESI) m/z: for $C_{16}H_{15}NaNO_3S$ $[M + Na]^+$, 324.0665; found, 324.0661.

*(Z)-1,2-Ditosylethene (**3ra**).* White solid (38.9 mg, 58%), mp 75−76 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 4H), 7.38 (d, J = 8.0 Hz, 4H), 6.77 (s, 2H), 2.48 (s, 6H).$^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 145.8, 140.4, 136.6, 129.9, 128.9, 21.8. IR (neat, cm^{-1}): 3072, 2964, 1736, 1675, 1240, 827. HRMS calcd (ESI) m/z: for $C_{16}H_{16}NaO_4S_2$ $[M + Na]^+$, 359.0382; found, 359.0379.

*(Z)-4-Tosylbut-3-en-2-one (**3sa**).*[16] White solid (17.5 mg, 39%), mp 45−46 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 15.2 Hz, 1H), 6.97 (d, J = 15.6 Hz, 1H), 2.47 (s, 3H), 2.35 (s, 3H).$^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 196.8, 141.4, 138.0, 135.7, 131.9, 130.4, 128.4, 29.1, 26.9.

*(Z)-(4-(Prop-1-en-2-yl)cyclohex-1-enyl)methyl 3-tosyl Acrylate (**4aa**).* White solid (56.9 mg, 79%), mp 94−95 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 11.2 Hz, 1H), 6.51 (d, J = 11.6 Hz, 1H), 5.89 (s, 1H), 4.76−4.74 (m, 2H), 4.69 (s, 1H), 2.47 (s, 3H), 2.24−2.17 (m, 4H), 2.06−1.98 (m, 1H), 1.92−1.85 (m, 1H), 1.77 (s, 3H), 1.58−1.49 (m, 1H), 1.28 (s, 2H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 164.3, 149.7, 145.4, 136.6, 135.6, 132.0, 131.5, 130.1, 128.5, 127.6, 109.0, 70.4, 40.8, 30.7, 27.4, 26.5, 21.8, 20.9. IR (neat, cm^{-1}): 3078, 2967, 1739, 1672, 1312, 1042, 783. HRMS calcd (ESI) m/z: for $C_{20}H_{24}NaO_4S$ $[M + Na]^+$, 383.1288; found, 383.1284.

*(Z)-(1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-tosyl Acrylate (**4ba**).* Yellow solid (36.2 mg, 50%), mp 107−108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.51 (d, J = 11.6 Hz, 1H), 6.62 (d, J = 11.2 Hz, 1H), 5.07 (d, J = 7.6 Hz, 1H), 2.43 (s, 3H), 2.04−1.60 (m, 1H), 1.80−1.73 (m, 2H), 1.40−1.26 (m, 4H), 0.94 (s, 3H), 0.93 (s, 3H), 0.90 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 164.4, 145.1, 136.5, 134.6, 131.6, 129.9, 128.3, 82.5, 51.4, 48.8, 47.9, 44.7, 35.8, 27.8, 27.1, 19.7, 18.7. IR (neat, cm^{-1}): 3082, 2947, 1731, 1385, 1160, 1034, 827. HRMS calcd (ESI) m/z: for $C_{20}H_{26}NaO_4S$ $[M + Na]^+$, 385.1444; found, 385.1441.

*(Z)-2,3-dihydro-1H-inden-1-yl 3-tosyl acrylate (**4ca**).* Light yellow solid (39.7 mg, 58%), mp 110−111 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.35−7.33 (m, 2H), 7.30−7.28 (m, 3H), 6.49 (d, J = 11.2 Hz, 1H), 6.46 (d, J = 11.2 Hz, 1H), 6.43−6.41 (m, 1H), 3.23−3.16 (m, 1H), 3.24−3.15 (m, 1H), 2.98−2.91 (m, 1H), 2.62−2.53 (m, 1H), 2.44 (s, 3H), 2.44−2.35 (m, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 164.1, 145.4, 145.1, 140.3, 136.8, 135.5, 131.7, 130.2, 129.5, 128.6, 127.1, 126.3, 125.0, 80.8, 32.2, 30.6, 21.8. IR (neat, cm^{-1}): 3077, 2964, 1746, 1372, 1041, 860, 782. HRMS calcd (ESI) m/z: for $C_{19}H_{18}NaO_4S$ $[M + Na]^+$, 365.0818; found, 365.0815.

*(Z)-2-Oxo-1,2-diphenylethyl 3-Tosyl Acrylate (**4da**).* White solid (47.0 mg, 56%), mp 123−124 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.53−7.47 (m, 3H), 7.39−7.33 (m, 5H), 7.11 (d, J = 8.0 Hz, 2H), 7.05 (s, 1H), 6.58 (d, J = 11.6 Hz, 1H), 7.63 (d, J = 11.6 Hz, 1H), 2.34 (s, 3H). $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ 193.0, 163.4, 145.7, 126.1, 134.4, 133.6, 132.9, 130.5, 129.9, 129.8, 129.2, 129.2, 128.9, 128.8, 128.7, 128.3, 79.0, 21.7. IR (neat, cm^{-1}): 3073, 2961, 1748, 1286, 1124, 942, 728. HRMS calcd (ESI) m/z: for $C_{24}H_{20}NaO_5S$ $[M + Na]^+$, 443.0924; found, 443.0920.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01549.

^1H and ^{13}C NMR spectra of compounds **3aa**−**3ja**, **4**−**7** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: weiminhe2016@yeah.net.

Notes

The authors declare no competing financial interest.

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