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ARTICLE

Visible-light promoted aerobic difunctionalization of alkenes with sulfonyl hydrazides for the synthesis of β -keto/hydroxyl sulfones

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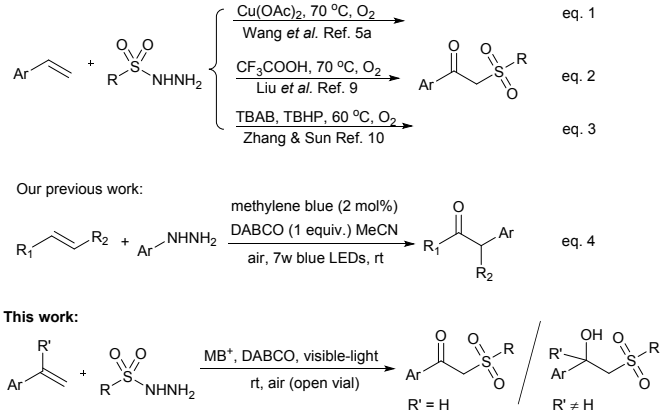
A practical method has been developed for the conversion of alkenes to β-keto/hydroxyl sulfones by their reaction with sulfonyl hydrazides under metal-free conditions. This reaction proceeds through the oxidative addition of alkenes by sulfonyl radicals that are generated by visible-light induced oxidation of sulfonyl hydrazides. Notaly the reaction uses O_2 as the terminal oxidant, instead of metal catalysts or oxidants like TBHP, leading to H_2O and N_2 as the clean by-products.The key features of this reaction include readily available reagents, mild reaction conditions and broad substrate scope.

Introduction

Alkenes have been exploited as starting materials for chemical production in industry due to their diverse and abundant availability from petrochemical sources.[1] Among the numerous utilizations of alkenes, difunctionalization of alkenes has evolved to be one of the most powerful and straightforward tools to integrate small molecules into intricate molecular architectures via one-step introduction of two functional groups that possess significantly synthetic utility in chemical synthesis.[2] In this regard, the oxysulfonylation of alkenes has emerged as an ideal strategy for the synthesis of β -keto sulfones, which are valuable skeletons found in many organic compounds due to their biological properties[3] and widespread synthetic applications[4]. As a consequence, extensive research efforts have been devoted to this transformation by the study of sulphur sources, oxidants and catalysts. For example, Wei and Wang reported copper-catalyzed aerobic difunctionalization of alkenes with sulfonylhydrazides for the synthesis of β -ketosulfones (Eq. 1, Scheme 1). [5] Yadav et al. accomplished $K_2S_2O_8$-mediated aqueous oxysulfonylation of simple alkenes with sodium arenesulfinates in the presence of O_2.[6] Later, they also reported $AgNO_3$-catalyzed oxysulfonylation of alkenes with thiophenols as the sulphur source in the presence of O_2 (air) and $K_2S_2O_8$ as oxidants.[7] The same group also achieved the transformation with sodium arenesulfinates by using the $AgNO_3/K_2S_2O_8$ combination.[8] Liu and co-workers disclosed CF_3COOH-promoted oxysulfonylation of alkenes with sulfonyl hydrazides in the presence of O_2 under elevated temperature (Eq. 2, Scheme 1).[9] Zhang and Sun reported tetra-*n*-butylammonium bromide-mediated aerobic oxysulfonylation of styrenes with sulfonylhydrazides for the synthesis of β-ketosulfones (Eq. 3, Scheme 1).[10]



Scheme 1. Syntheses of β-ketosulfones by difunctionalization of alkenes with sulfonyl hydrazides.

Recently, visible light photoredox catalysis (VLPC)[11] has received increasing attention from the synthetic community due to the mild conditions and high efficiency, and this strategy has also been introduced to the oxidative difunctionalization of alkenes[12]. In this context, major advance has been made in the synthesis of β -ketosulfones by using visible light photoredox catalysis. For example, Yang and co-workers developed a visible-light-promoted oxysulfonylation reaction of alkenes with sulfinic acids by using tert-butyl hydroperoxide (TBHP) as oxidant for the synthesis of β -keto sulfones.[13] Niu and co-workers reported a $Ir(ppy)_2(dtbbpy)PF_6$-catalyzed visible-light-induced oxidative difunctionalization of alkenes with sulfonyl chlorides using air under mild conditions without any other additives.[14] Lipshutz and co-workers accomplished the aqueous sulfonylation of various alkenes and enol acetates using arenesulfonyl chlorides in the presence of a novel amphoteric PQS-attached photocatalyst.[15] As a continuation of our interest in the utilization of hydrazine derivatives under photocatalytic conditions[16], we reported a metal-free protocol for the conversion of alkenes to ketones through oxidative radical

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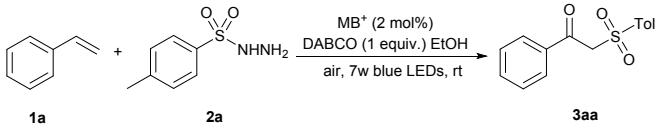
addition with arylhydrazines (Eq. 4, Scheme 1)[16b]. Now, by replacing arylhydrazines with sulfonyl hydrazides, we discovered a visible-light promoted aerobic difunctionalization of alkenes for the synthesis of β-keto/hydroxyl sulfones (Scheme 1). Herein we would like to report the details of this transformation.

Results and discussion

Table 1. Effect of Reaction Parameters on the difunctionalization of alkenes with sulfonyl hydrazides [a]



1a 2a 3aa

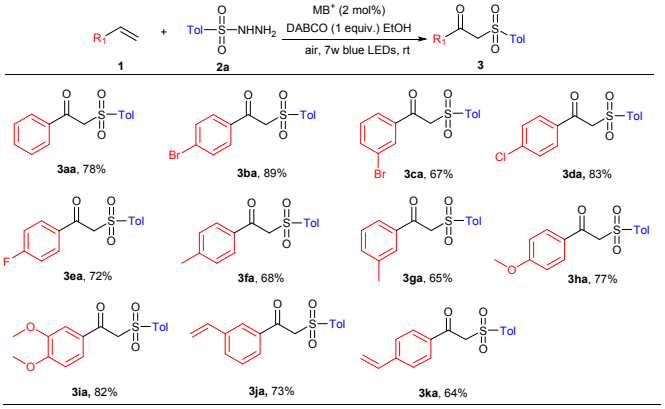
entry	variation from the standard conditions	yield/%[b]
1	None	78
2	No MB^+	<10
3	No visible light, no MB^+	trace
4	Eosin Y, instead of MB^+	40
5	Rhodamine B, instead of MB^+	33
6	No DABCO	29
7	DBU, instead of DABCO	56
8	Et_3N,instead of DABCO	43
9	Pyridine, instead of DABCO	31
10	Piperidine, instead of DABCO	46
11	Cs_2CO_3,instead of DABCO	42
12	K_2CO_3,instead of DABCO	30
13	MeOH, instead of EtOH	69
14	CH_2Cl_2,instead of EtOH	62
15	THF, instead of EtOH	31
16	DMSO, instead of EtOH	37
17	DMF, instead of EtOH	30
18	MeCN, instead of EtOH	67
19[c]	Green LEDs instead of blue LEDs	76

[a]Standard conditions: 1.5 mmol of **1a**, 0.5 mmol of **2a**, 0.01 mmol of methylene blue, 0.5 mmol of DABCO, air (open flask), and EtOH (1.5 mL) at room temperature under the irradiation of 7 W blue LEDs; MB^+ = methylene blue, DABCO = 1,4-Diazabicyclo[2.2.2]octane. [b]isolated yield. [c]The reaction was irradiated by 7 W green LEDs

At the outset, the reactivity towards this difunctionalization of alkenes was evaluated by studying the reaction of styrene **1a** and 4-methylbenzenesulfonohydrazide **2a** (Table 1). To our delight, the reaction was found to work smoothly in the presence of methylene blue (MB^+, 2 mol %), DABCO (1 equiv.) and air (open flask) in EtOH at room temperature under the irradiation of 7 W blue LEDs, leading to the production of β-keto sulfones **3aa** in a good yield (78%) (entry 1). Without photocatalyst, the reaction became sluggish, resulting in a yield less than 10% (entry 2). The reaction performed in dark environment was totally shut down, indicating light is indispensable for this reaction (entries 3). Compared to methylene blue, other commercially available organic photocatalysts including rhodamine B and eosin Y, are less effective (entries 4–5), probably due to the lower oxidation potential of eosin Y [$E_{1/2}(PC^*/PC^-)$ = +0.83 V vs SCE for eosin Y; $E_{1/2}(PC^*/PC^-)$ = +1.14 V vs SCE for MB^+] [11l]. Moreover, without DABCO or replacing it with other bases, the reactions lead to inferior results (entries 6–12). This phenomenon can be explained by the fact that base can significantly lower the redox potential of toluene sulfonyl hydrazide from +1.24 V vs SCE to +0.53 V vs SCE by deprotonation[17], making it easier to be oxidized by the excited MB^+. The screening of solvents revealed that EtOH is superior to other solvents, such as MeOH, CH_2Cl_2, THF, DMSO, DMF and MeCN (Table 1 entries 13-18). Finally, a reaction was performed under the irradiation of green LEDs, and it gave a yield of 76% that is close to the one under standard conditions.

With the optimized conditions in hand, we proceeded to evaluate the scope and generality of this difunctionalization of alkenes. Initial studies began by holding the hydrazine reagent constant (i.e., 4-methylbenzenesulfonohydrazide **2a**) when reacting alkenes with various substitution groups/patterns. The reaction tolerated a range of functional groups including electron-withdrawing groups (F, Cl and Br) and -donating groups (Me and OMe). Some of these functional groups are useful for further synthetic diversification. Notably, divinylbenzene substrates could react with 4-methylbenzenesulfonohydrazide at one side selectively in good yields (**3ja** and **3ka**). For internal olefins, the reaction of (*E*)-prop-1-en-1-ylbenzene with 4-methylbenzenesulfonohydrazide was tried, however, it gave a disordered mixture.

Table 2. Reaction of 4-methylbenzenesulfonohydrazide **2a** with different alkenes **1**[a]



[a]1.5 mmol of **1a**, 0.5 mmol of **2a**, 0.01 mmol of methylene blue, 0.5 mmol of DABCO, air (open flask), and EtOH (1.5 mL) at room temperature under the irradiation of 7 W blue LEDs

Table 3. Reaction of 4-methylbenzenesulfonohydrazide **2a** with 1,1-disubstituted alkenes[a]

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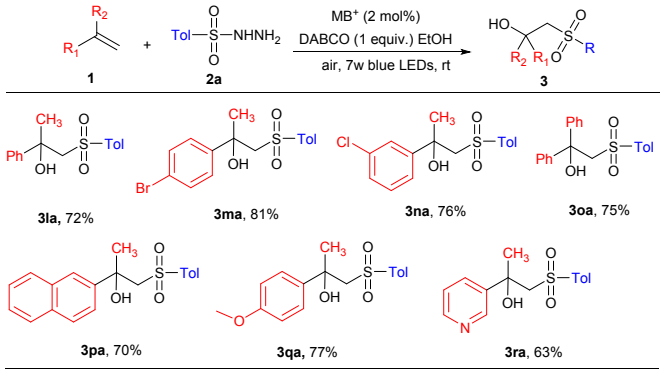
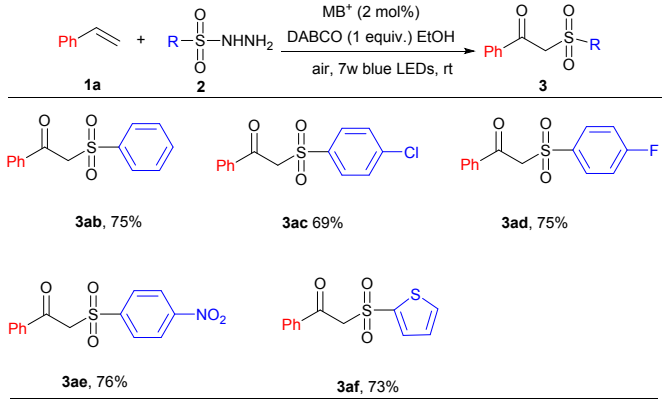


[a]1.5 mmol of **1a**, 0.5 mmol of **2a**, 0.01 mmol of methylene blue, 0.5 mmol of DABCO, air (open flask), and EtOH (1.5 mL) at room temperature under the irradiation of 7 W blue LEDs

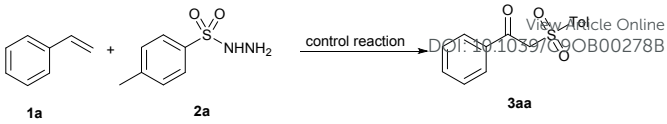
When α-methyl styrene was subjected to the reaction, β-hydroxyl sulfone was generated in good yield (Table 3, **3la**). Other α-methyl styrenes bearing diverse substituents including Cl, Br and OMe, also underwent this reaction smoothly, leading to the corresponding β-hydroxyl sulfones in good yields (**3ma**, **3na** and **3qa**). Replacing benzene ring with other aromatic rings such as naphthalene and pyridine, the reaction worked as well (**3pa** and **3ra**). Notably, this reaction is also applicable to ethene-1,1-diyldibenzene, permitting the synthesis of a tertiary alcohol bearing two phenyl groups (**3oa**).

This difunctionalization of alkenes with a focused substrate scope of hydrazine derivatives was also explored. As shown in Table 4, arylsulfonohydrazide with different groups on the benzene ring reacted smoothly with styrene under the standard conditions, leading to various β-keto sulfones in good yields (**3ab**-**3ae**). In addition, thiophene-2-sulfonohydrazide also worked for the transformation to generate the desired product **3af** in 73% yield.

Table 4. Reaction of styrene **1a** with substituted sulfonohydrazide **2**[a]

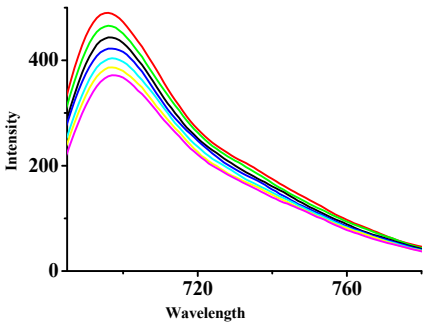


[a]1.5 mmol of **1a**, 0.5 mmol of **2a**, 0.01 mmol of methylene blue, 0.5 mmol of DABCO, air (open flask), and EtOH (1.5 mL) at room temperature under the irradiation of 7 W blue LEDs

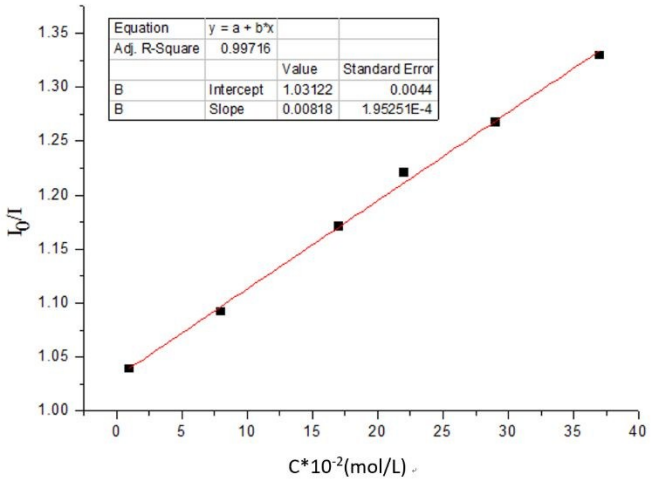


Variation from the standard conditions	yield	
Addition of **TEMPO** (2.0 equiv.)	0	eq. 1
Under N_2 (instead of air) atmosphere	<10%	eq. 2

Scheme 2. Control reactions



Scheme 3. Luminescence quenching of methylene blue with excitation at 664 nm by **2a**.



Scheme 4. The Stern- Volmer plot.

To provide some insights into the mechanism of this reaction, control experiment in the presence of radical trapper TEMPO (2.0 equiv.) was carried out. The reaction was found to be inhibited, as no desired **3aa** was isolated and the starting styrene **1a** was recovered (eq. 1, Scheme 2). This observation supports the idea that the reaction probably proceeds through a radical pathway. A reaction in N_2 atmosphere was performed, and only trace amount of product was isolated (eq.2, Scheme 2), indicating O_2 is necessary for this reaction. Also the luminescence of methylene blue with excitation at 664 nm could be readily quenched by **2a** following Stern–Volmer kinetics (Scheme 3-4), and styrene **1a** cannot serve as the emission quenchers.

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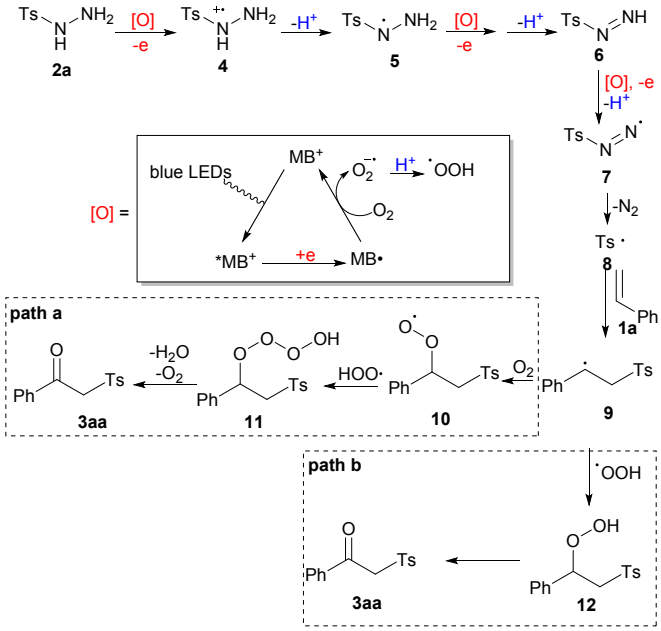

Scheme 5. Plausible mechanistic pathways for the reaction

On the basis of these experimental observations and our previous studies on the reaction of hydrazine derivatives[16], a plausible mechanism is proposed for this reaction (Scheme 5). First, methylene blue is irradiated to the excited state $*MB^+$ using blue LEDs, and this excited state is then reductively quenched by **2a** along with the generation of ionic radical **4** and methylene blue radical (MB•). After deprotonation, ionic radical **4** is transformed to radical **5**, which can also quench the excited state $*MB^+$ and lose a proton to give intermediate **6**. Another single-electron oxidation by $*MB^+$, followed by deprotonation, results in the formation of Ts• **8**. During the course MB• is oxidized back to MB^+ by molecular oxygen with itself being reduced to hydroperoxyl radical (HOO•). Furthermore, intermediate **10**, which is generated from the addition of Ts• to styrene **1a** followed by incorporation of dioxygen, could react with hydroperoxyl radical to form **11.** Then **11** decomposes to afford the desired product **3aa**, with concomitant formation of molecular oxygen and water through Russell fragmentation[18]. Another possible pathway from intermediate **9** to **3aa** is the combination of **9** with HOO• to form intermediate **12**, followed by its decomposition to final product **3aa** (path b).

Conclusions

In conclusion, we have developed a metal-free protocol for the conversion of alkenes to β-keto/hydroxyl sulfones through difunctionalization of alkenes with sulfonyl hydrazides. This reaction avoids the need for the use of metal catalysts or oxidants like TBHP. Instead, by using O_2 as the terminal oxidant, this visible-light induced reaction leads to H_2O and N_2 as the clean by-products. Preliminary mechanistic studies suggested the reaction goes through VLPC-promoted oxidation of sulfonyl hydrazides to sulfonyl radical followed by its addition to alkenes. Taken together with its operational simplicity, readily available reagents and broad substrates scope, this reaction will find practical application for the transformation of alkenes.

Experimental

General information

Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^1H (400 MHz) and ^{13}C NMR (100 MHz) data were recorded on Bruker AVANCE Ⅲ 400MHz spectrometer using $CDCl_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^1H NMR spectra was recorded with tetramethylsilane (δ=0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ=77.00 ppm) as internal reference. All starting materials commercially available were used directly.

Typical procedure for the synthesis of products 3

To a solution of sulfonhydrazide **2** (0.5 mmol) and alkene **1** (1.5 mmol) in EtOH (1.5 mL) was added Methylene Blue (0.01 mmol) and DABCO (1 mmol). The reaction mixture was stirred at 25℃ under air atmosphere (open vial) and irradiated by blue LED (7 W). After the completion of the reaction which was indicated by TLC (usually 24 hours), removal of solvent followed by column chromatography afforded desired products.

Characterization of products 3

1-phenyl-2-tosylethan-1-one (3aa) [19]**.** Petroleum ether/ethyl acetate =10:1, white solid, 78% yield (106 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.15, 145.36, 135.82, 134.31, 129.84, 129.34, 128.84, 128.62, 63.61, 21.70.

1-(4-bromophenyl)-2-tosylethan-1-one (3ba) [19]**.** Petroleum ether/ethyl acetate =10:1, white solid, 89% yield (155 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, *J* = 1.8 Hz, 1H), 7.91 (ddd, *J* = 7.8, 1.6, 1.0 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.38 (dd, *J* = 15.3, 7.8 Hz, 3H), 4.70 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.69, 144.92, 137.41, 132.04, 130.34, 128.55, 127.98, 123.18, 63.98.

1-(3-bromophenyl)-2-tosylethan-1-one (3ca) [19]**.** Petroleum ether/ethyl acetate =10:1, white solid, 67% yield (118 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, *J* = 1.6 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 6.9 Hz, 3H), 7.38 (dd, *J* = 15.3, 7.8 Hz, 3H), 4.70 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.98, 145.64, 137.41, 137.12, 135.54, 132.09, 130.40, 129.95, 128.60, 128.03, 123.18, 63.68, 21.75.

1-(4-chlorophenyl)-2-tosylethan-1-one (3da) [19]**.** Petroleum ether/ethyl acetate =10:1, white solid, 83% yield (130 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 6.8 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 4.70 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.90, 145.56, 141.08, 135.62, 134.11, 130.79, 129.91, 129.21, 128.58, 63.74, 21.72.

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1-(4-fluorophenyl)-2-tosylethan-1-one (3ea) [19]**.** Petroleum ether/ethyl acetate =10:1, white solid, 72% yield (106 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.94 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.08 (m, 2H), 4.71 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.58, 167.76, 165.20, 145.52, 135.66, 132.51 – 132.12 (m), 129.90, 128.56, 116.21, 115.99, 63.75, 21.71.

1-(p-tolyl)-2-tosylethan-1-one (3fa) [19]**.** Petroleum ether/ethyl acetate =20:1, white solid, 68% yield (98 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.71 (s, 2H), 2.46 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.67, 145.57, 145.30, 135.82, 133.39, 129.82, 129.54 (d, *J* = 3.7 Hz), 128.61, 63.58, 21.76 (d, *J* = 7.4 Hz).

1-(m-tolyl)-2-tosylethan-1-one (3ga) [19]**.** Petroleum ether/ethyl acetate =20:1, white solid, 65% yield (93mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.77 (s, 2H), 7.75 (s, 1H), 7.73 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.37 (dd, *J* = 15.3, 7.8 Hz, 3H), 4.72 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 188.30, 145.33, 138.74, 135.83, 135.15, 129.76 (d, *J* = 10.2 Hz), 128.67 (d, *J* = 5.5 Hz), 126.66, 63.58, 21.68, 21.31.

1-(4-methoxyphenyl)-2-tosylethan-1-one (3ha) [19]**.** Petroleum ether/ethyl acetate =5:1, white solid, 77% yield (117mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.68 (s, 2H), 3.96 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.36, 164.55, 145.26, 135.85, 131.93, 129.81, 128.92, 128.57, 114.07, 63.55, 55.64, 21.71.

1-(3,4-dimethoxyphenyl)-2-tosylethan-1-one (3ia). Petroleum ether/ethyl acetate =5:1, white solid, 82% yield (136mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 10.3 Hz, 1H), 7.48 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 4.70 (s, 2H), 3.96 (s, 3H), 3.91 (s, 3H), 2.45 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 186.41, 154.48, 149.23, 145.27, 135.85, 129.81, 129.04, 128.57, 125.15, 110.67, 110.13, 63.48, 56.12 (d, *J* = 19.0 Hz), 21.71. MS (ESI, *m/z*) 335.1 (M + H^+), 357.1 (M + Na^+). Anal. calcd for $C_{17}H_{18}O_5S$: C, 61.06; H, 5.43. Found: C, 60.84; H, 5.56.

2-tosyl-1-(3-vinylphenyl) ethan-1-one (3ja). Petroleum ether/ethyl acetate =20:1, white solid, 73% yield (109mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.84 (d, *J* = 17.6 Hz, 1H), 5.38 (d, *J* = 10.9 Hz, 1H), 4.75 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.12, 145.42, 138.36, 137.42, 136.08, 135.54, 131.74, 129.85, 129.04, 128.63, 126.96, 115.88, 63.69, 21.70. MS (ESI, *m/z*) 301.1 (M + H^+), 323.1 (M + Na^+). Anal. calcd for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found: C, 67.74; H, 5.26.

2-tosyl-1-(4-vinylphenyl) ethan-1-one (3ka). Petroleum ether/ethyl acetate =40:1, white solid, 64% yield (96mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.78 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.69 (dd, *J* = 189.7, 19.5 Hz, 2H), 4.72 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.46, 145.38, 143.33 (s), 135.77, 135.68, 134.89, 129.83 (d, *J* = 1.9 Hz), 128.61, 126.53, 117.76, 63.68, 21.71. MS (ESI, *m/z*) 301.1 (M + H^+), 323.1 (M + Na^+). Anal. calcd for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found: C, 67.86; H, 5.24.

2-phenyl-1-tosylpropan-2-ol (3la) [20]**.** Petroleum ether/ethyl acetate =10:1, white solid, 72% yield (103mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.14 (m, 5H), 4.66 (s, 1H), 3.67 (dd, *J* = 45.6, 14.6 Hz, 2H), 2.40 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.53, 137.39, 133.62, 129.71, 128.25, 127.56, 127.13, 124.65, 73.17, 66.69, 30.76, 21.57.

2-(4-bromophenyl)-1-tosylpropan-2-ol (3ma) [20]**.** Petroleum ether/ethyl acetate =10:1, white solid, 81% yield (183mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 13.3, 5.4 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.08 (m, 2H), 4.72 (s, 1H), 3.66 (dd, *J* = 53.1, 14.7 Hz, 2H), 2.45 (d, *J* = 7.6 Hz, 3H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.81, 143.28, 136.84, 131.17, 129.75, 127.51, 126.61, 121.32, 72.80, 66.25, 31.02, 21.62.

2-(3-chlorophenyl)-1-tosylpropan-2-ol (3na) [20]**.** Petroleum ether/ethyl acetate =10:1, white solid, 76% yield (161mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, *J* = 1.6 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 6.9 Hz, 3H), 7.38 (dd, *J* = 15.3, 7.8 Hz, 3H), 4.70 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.98, 145.64, 137.41, 137.12, 135.54, 132.09, 130.40, 129.95, 128.60, 128.03, 123.18, 63.68, 21.75.

1,1-diphenyl-2-tosylethan-1-ol (3oa) [20]**.** Petroleum ether/ethyl acetate =10:1, white solid, 75% yield (132mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.26 – 7.19 (m, 6H), 7.15 (d, *J* = 8.1 Hz, 2H), 5.41 (s, 1H), 4.21 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.51, 143.73, 137.42, 129.70, 128.28, 127.57 (d, *J* = 18.7 Hz), 125.87, 65.51, 21.61.

2-(naphthalen-2-yl)-1-tosylpropan-2-ol (3pa) [20]**.** Petroleum ether/ethyl acetate =10:1, white solid, 70% yield (119mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.93 (m, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.67 (dd, *J* = 8.7, 4.1 Hz, 2H), 7.49 – 7.40 (m, 1H), 7.39 – 7.32 (m, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.78 (d, *J* = 8.1 Hz, 2H), 4.87 (s, 1H), 4.13 (dd, *J* = 220.5, 15.0 Hz, 2H), 2.21 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.70, 139.04, 134.54, 129.37, 129.20, 128.82, 126.94, 125.72, 125.09, 124.77, 124.55, 124.38, 73.52, 65.00, 30.14, 21.35.

2-(4-methoxyphenyl)-1-tosylpropan-2-ol (3qa) [20]**.** Petroleum ether/ethyl acetate =5:1, white solid, 77% yield (123mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.1 Hz, 2H), 7.19 (dd, *J* = 8.6, 3.3 Hz, 4H), 6.71 (d, *J* = 8.8 Hz, 2H), 4.61 (s, 1H), 3.77 (s, 3H), 3.64 (dd, *J* = 49.7, 14.6 Hz, 2H), 2.40 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.70, 144.41, 136.64, 129.65, 127.57, 125.87, 113.50, 72.89, 66.85, 55.24, 30.70, 21.57.

2-(pyridin-3-yl)-1-tosylpropan-2-ol (3ra) [21]**.** Petroleum ether/ethyl acetate =10:1, white solid, 63% yield (92mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 4.7 Hz, 1H), 7.66 (q, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.07 (ddd, *J* = 6.6, 4.8, 1.7 Hz, 1H), 3.90 (dd, *J* = 152.0, 14.5 Hz, 2H), 2.38 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.51, 147.95, 144.23, 137.45, 136.93, 129.55, 127.70, 122.13, 119.34, 74.04, 65.17, 30.11, 21.56.

1-phenyl-2-(phenylsulfonyl) ethan-1-one (3ab) [22]**.** Petroleum ether/ethyl acetate =10:1, white solid, 75% yield (98mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 2H), 7.48(tt, *J* = 7.8, 1.6 Hz, 2H),

7.55 (tt, *J* = 7.8, 1.6 Hz, 2H), 7.62 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.66 (tt, *J* =7.6, 1.2 Hz, 1H), 7.90 (m, 2H), 7.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 138.8, 135.8, 134.5, 134.4, 129.4, 129.3, 129.0, 128.7, 63.6.

2-((4-fluorophenyl) sulfonyl)-1-phenylethan-1-one (3ac) [22]**.** Petroleum ether/ethyl acetate =10:1, white solid, 75% yield (104mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 (s, 2H),7.20-7.26 (m, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.90-7.95 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 166.3 (d, *1JCF* = 245.4 Hz), 135.7, 134.8 (d, *4JCF* = 3.1 Hz), 134.7, 131.8 (d, *3JCF* = 9.7 Hz), 129.4, 129.1, 116.7 (d, *2JCF* = 22.6 Hz), 63.6.

2-((4-chlorophenyl) sulfonyl)-1-phenylethan-1-one (3ad) [22]**.** Petroleum ether/ethyl acetate =10:1, white solid, 69% yield (101mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 (s, 2H),7.48-7.53 (m, 4H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 141.3, 137.2, 135.7, 134.7, 130.3, 129.7, 129.4, 129.1, 63.5.

2-((4-nitrophenyl) sulfonyl)-1-phenylethan-1-one (3ae) [22]**.** Petroleum ether/ethyl acetate =10:1, white solid, 77% yield (117mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.35 (m, 1H), 8.14 (ddt, *J* = 11.3, 9.3, 2.4 Hz, 1H), 7.94 (dt, *J* = 7.1, 1.4 Hz, 1H), 7.72 – 7.63 (m, 0H), 7.52 (t, *J* = 7.8 Hz, 1H), 4.82 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.60, 144.03, 135.33, 134.86, 130.34, 129.19, 129.09, 124.31, 63.00.

1-phenyl-2-(thiophen-2-ylsulfonyl) ethan-1-one (3af) [23]**.** Petroleum ether/ethyl acetate =5:1, white solid, 73% yield(102mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.4 Hz, 2 H), 7.74 (dd, *J* = 4.9, 1.3 Hz, 1 H), 7.69 (dd, *J* = 3.8, 1.2 Hz, 1 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.49 (t, *J* = 7.4 Hz, 2 H), 7.13 (dd, *J* = 4.9, 3.9 Hz, 1 H), 4.83 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 139.4, 135.7, 135.5, 135.0, 134.5, 129.2, 128.9, 127.9, 64.4.

Conflicts of interest

There are no conflicts to declare.

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