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Catalyst-Free Imidation of Allyl Sulfides with Chloramine-T and Subsequent [2,3]-Sigmatropic Rearrangement†

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A facile synthesis of various allyl sulfonamides based on imidation of allyl sulfides with chloramine-T and subsequent [2,3]-sigmatropic rearrangement has been achieved without metal catalysts. The reaction completes smoothly within 10 min, providing excellent yields in environment friendly solvent of alcohol. Functional groups such as bromine, hydroxyl, protected amido and aldehyde are tolerant under this condition.

Keywords allyl sulfonamide, allyl sulfide, transition-metal-free reaction, sigmatropic rearrangement, nitrene

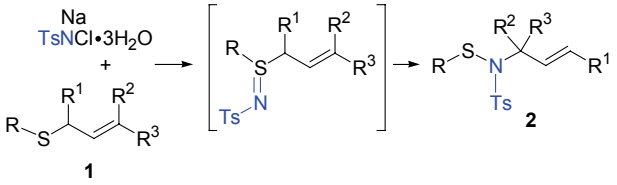
Introduction

The construction of carbon-nitrogen bond is one of the major topics in organic synthesis as the nitrogen is ubiquitous in natural products and biologically active agents. Similar to the related carbene species, nitrene is highly reactive species and can undergo various transformations, such as C—H bond insertions and aziridinations.[1] These reactions can serve as useful approaches toward carbon-nitrogen bond formation. The reaction of nitrene with sulfides affords sulfilimines, which have diverse reactivities.[2] When allylsulfides are employed in this reaction, the corresponding sulfilimines bearing allylic substituent will undergo [2,3]-sigmatropic rearrangement to afford allylic amides.[3] This unique transformation is considered as an interesting method for the synthesis of allylic amine derivatives.

Copper-catalyzed formation of sulfimides and selenimides and subsequent [2,3]-sigmatropic rearrangement to the corresponding allylic sulfonamides using [*N*-(*p*-tolylsulfonyl)imino] phenyliodinane (TsN＝IPh) as nitrogen source has been reported by Uemura and coworkers.[4] The iron-catalyzed imidation of sulfides with *tert*-butoxycarbonyl azide and [2,3]-sigmatropic rearrangement has been investigated by Bach[5] and van Vranken[6] respectively. Very recently, the synthesis of allenamides has been achieved by Armstrong[7] through this rearrangement by employing CbzNHOTf as the nitrene precursor.

As the continuation of our own interest in [2,3]-sigmatropic rearrangement of sulfide ylides[8] and transition-metal-free transformations,[9] we have investigated the metal-free imidation of allyl sulfides **1** by using chloramine-T (TsNClNa) as the nitrogen source.[3] The subsequent [2,3]-sigmatropic rearrangement affords allyl sulfonamides **2** in good yields (Scheme 1).

Scheme 1 Imidation/[2,3]-sigmatropic rearrangement



The products contains sulfonamide segment which serves as one of the common structural features in drugs.[10] Furthermore, they can also be converted to allyl sulfonamides and allyl amides by removal of the protecting group (Ts).[5,11]

Results and Discussion

The allyl sulfides were prepared and their reactions with chloramine-T were investigated. The allyl(phenyl)-sulfane **1a** was selected to optimize the reaction conditions (Table 1). Initially, only trace of product could be detected when we conducted the reaction in toluene as the solvent under room temperature (Table 1, Eentry 1).

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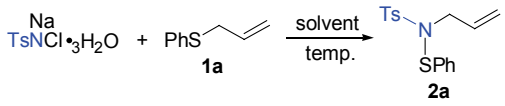
The yield was increased to 50% when we elevated the reaction temperature to 70 ℃ (Table 2, Eentry 1). We continued to tried other solvents and found that DCE, THF, DMF and dioxane could afford moderate yields (Table 2, Entries 3—6), while MeCN and EtOH afforded excellent yields (Table 2, Entries 7—12). Moderate yields can also be obtained when H_2O was used as the solvent under heating or microwave conditions (Table 1, Entries 14—16). Notably, more favored yields can be achieved under room temperature other than 70 ℃ when MeCN or EtOH was chosen as the medium (Table 1, Entries 10, 12).

Table 1 Optimization of the reaction conditions with **1a**



Entry	Solvent	Equv. of TsNClNa	Temp./℃	Time[a]	Yield[b]/%
1	PhMe	1.2	r.t.	5 h	<5
2	PhMe	1.2	70	2 h	50
3	DCE	1.2	70	1 h	58 (50)[c]
4	THF	1.2	70	10 min	57
5	DMF	1.2	r.t.	5 min	50
6	Dioxane	1.2	r.t.	5 min	57
7	MeCN	1.2	70	5 min	70
8	MeCN	1.3	70	5 min	78
9	MeCN	1.4	70	5 min	78
10	MeCN	1.3	r.t.	10 min	81
11	EtOH	1.3	70	5 min	80
12	EtOH	1.3	r.t.	10 min	82
13[d]	DCM	1.3	r.t.	12 h	<5
14	H_2O	1.3	70	12 h	64
15[d]	H_2O	1.3	70 (MW)	5 min	52
16[d]	H_2O	1.3	100 (MW)	30 min	58

[a] Determined by TLC. [b] Isolated yields. [c] Yield using anhydrous chloramine-T was given in parentheses. [d] Amount of recovered staring material was not determined.

The optimized reaction conditions (EtOH/room temperature) were then applied to a series of allyl sulfides **1b**—**1q** and the results were summarized in Table 2. All aromatic allyl sulfides reacted smoothly with chloramines-T and afforded excellent yields. The substituents on the aromatic ring had some influences on the reaction. When electron-donating aromatic allyl sulfides were subjected to the reaction, the yields slightly increased (Table 2, Entries 1, 2, 4, 9), while the yields decreased when the aromatic ring bears electron-withdrawing group (Table 2, Entries 3, 5). Various substituted and cyclic allyl sulfides could also be used for the construction of C—N bonds (Table 2, Entries 6—9). The benzyl and alkyl allyl sulfides react slowly at room temperature, they could work successfully when heated to 70 ℃ (Table 2, Entries 10, 11). Moreover, functional groups such as bromine, hydroxyl, protected amido and aldehyde on allyl part are tolerant in this system (Table 2, Entries 12—16). It is worth noting that this reaction proceeds very fast and could complete within 10 min in all cases.

Conclusions

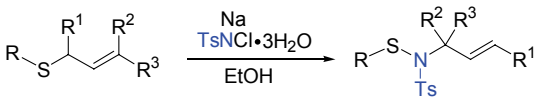
In summary, we have developed a process of metal-catalyst free imidation of allyl sulfides with Chloramines-T and subsequent [2,3]-sigmatropic rearrangement. Various substituted and functionalized allyl sulfonamides or allyl amides can be easily obtained through this approach. It affords an efficient strategy for the construction of carbon-nitrogen bond. Compared to other procedures, this method has wider scope and higher efficiency.

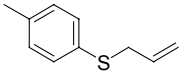
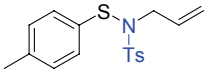
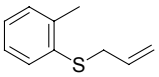
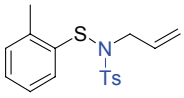
Experimental

General

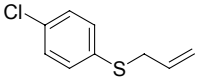
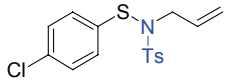
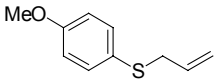
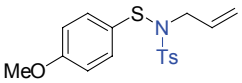
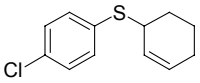
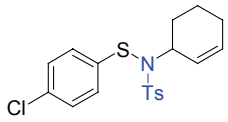
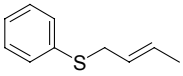
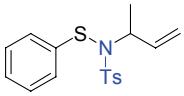
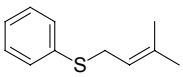
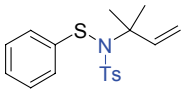
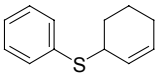
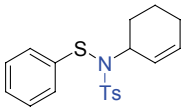
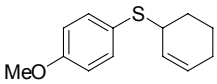
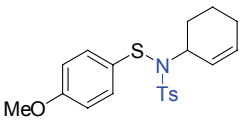
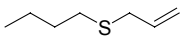
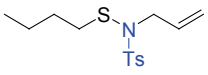
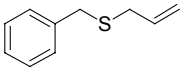
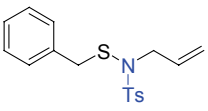
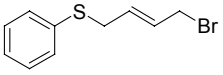
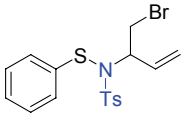
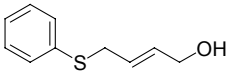
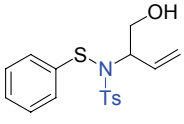
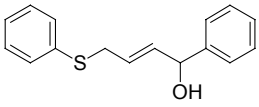
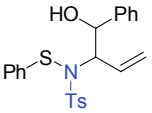
Aryl mercaptans, bromides and chloramine-T were

Table 2 Reaction of **1b**—**1q** with chloramine-T under qptimization conditions

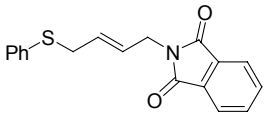
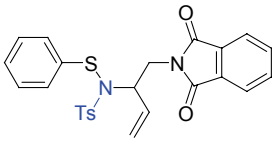
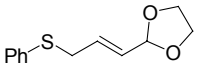
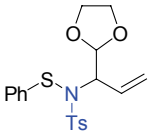


Entry	Allyl sulfide **1**	Product **2**	Yield[a]/%
1	 **1b**	 **2b**	90
2	 **1c**	 **2c**	92

Continued

Entry	Allyl sulfide **1**	Product **2**	Yield[a]/%
3	 **1d**	 **2d**	72
4	 **1e**	 **2e**	97
5	 **1f**	 **2f**	78
6	 **1g**	 **2g**	78
7	 **1h**	 **2h**	77
8	 **1i**	 **2i**	93
9	 **1j**	 **2j**	95
10[b]	 **1k**	 **2k**	45
11[b]	 **1l**	 **2l**	91
12	 **1m**	 **2m**	84
13	 **1n**	 **2n**	83
14[c]	 **1o**	 **2o**	82

Continued

Entry	Allyl sulfide **1**	Product **2**	Yield[a]/%
15	 **1p**	 **2p**	84
16[b]	 **1q**	 **2q**	68

[a] Isolated yields. [b] The reaction was carried out at 70 ℃ [c] *d.r.*＝60∶40.

purchased from Alfa Aesar. Chloroform-*d* and dimethylsulfoxide-d_6 were purchased from Cambridge Isotope Laboratories. All solvents were distilled prior to use. THF was freshly distilled from Na before use. All reactions were performed in air atmosphere. For chromatography, 200—300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR (300 or 200 MHz) and ^{13}C NMR (75 or 50 MHz) spectra were measured on Varian 300 MHz spectrometers; ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Bruker ARX 400 MHz spectrometer. $CDCl_3$ was used as solvent with tetramethylsilane (TMS) as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer.

Synthesis and spectral data for the substrates 1a—1q and 3—4

(*E*)-Ethyl 4-(phenylthio)but-2-enoate (**3**):[12] A 2.05 mL portion of thiophenol (2.2 g, 20 mmol) and 5.13 g of (*E*)-ethyl 4-bromobut-2-enoate (22 mmol) were dissolved in 30 mL of dry diethyl ether and cooled to −10 ℃. A 2.2 g portion of triethylamine (22 mmol) was added dropwise during 0.5 h. After being stirred at −10 ℃ for 30 min, the mixture was refluxed for 1 h and stirred overnight at room temperature. The precipitate was removed by filtration and washed with diethyl ether. The filtrate was washed with aqueous NaOH and dried over $MgSO_4$. After the solvent was removed the residue was purified by column chromatography. 4.35 g (98%) of **3** was obtained as a colorless liquid.

(*E*)-4-(Phenylthio)but-2-enal (**4**):[13] A 0.72 g (4 mmol) portion of (*E*)-ethyl-4-(phenylthio)but-2-enoate (**3**), 0.672 g $NaHCO_3$ and 2.035 g of DMP were added to 20 mL of CH_2Cl_2 under 0 ℃ and the reaction was conducted by TLC. Flash chromatography provided crude product which was further purified by column chromatography providing 0.584 g (82%) **4** as a colorless liquid.

General procedure for the preparation of **1a**—**1m**:[14-19] To a 15 mL of dry THF was added 12 mmol of NaH, 10 mmol of thiol (slowly added) and stirred at 0 ℃ for 15 min. To the system was then added 12 mmol of allyl bromide and stirred overnight at room temperature. The precipitate was removed by filtration and washed with diethyl ether. After the solvent was removed the residue was purified by column chromatography.

(4-Chlorophenyl)(cyclohex-2-enyl)sulfane (**1f**): Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J=8.4 Hz, 2H), 7.25 (d, J=8.5 Hz, 2H), 5.85 (dd, J=3.50, 9.9 Hz, 1H), 5.74 (dd, J=1.8, 10.0 Hz, 1H), 3.81 (s, br, 1H), 2.04—1.58 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.3, 132.6, 130.7, 128.9, 126.5, 44.2, 28.7, 24.8, 19.3; IR (film) v: 2933, 1476, 1096, 1013, 815 cm^{-1}; EI-MS (relative intensity) m/z (%): 224 (11), 143 (16), 108 (18), 81 (100), 53 (14); HRMS calcd for $C_{12}H_{13}ClSK$ $(M+Na)^+$: 263.0058, found 263.0053.

Cyclohex-2-enyl(4-methoxyphenyl)sulfane (**1j**): Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.62 Hz, 2H), 5.81—5.73 (m, 2H), 3.79 (s, 3H), 3.65 (br s, 1H), 2.00—1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3, 135.1, 130.0, 127.2, 125.7, 114.3, 55.2, 45.4, 28.7, 24.9, 19.4; IR (film) v: 2933, 1492, 1243, 1029, 823 cm^{-1}; EI-MS (relative intensity) m/z (%): 220 (21), 140 (100), 81 (55); HRMS calcd for $C_{13}H_{15}OS$ $(M-H)^+$: 219.0838, found 219.0838.

(*E*)-4-(Phenylthio)but-2-en-1-ol (**1n**):[20] A 0.666 g (3 mmol) portion of (*E*)-ethyl-4-(phenylthio) but-2-enoate (**3**) was dissolved in 10 mL of dry THF and cooled to 0 ℃. A 6 mL portion of Dibal-H (6 mmol, **1n** in hexane) was added, and after the mixture was stirred at 0 ℃ for 1 h, 2 mL of methanol, 10 mL of water, 1 mL of saturated NaOH aqueous, and 10 mL of aqueous KNa tartrate (30%, *W*/*W*) were added successively. The mixture was stirred at room temperature for 1 h, and the layers were separated. The aqueous layer was extracted with 30 mL Et_2O for three times, and the combined

organic layers were washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography. Compound **1n** (0.443 g, 82%) was obtained as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.34—7.16 (m, 5H), 5.75—5.70 (m, 2H), 4.04 (d, J=4.2 Hz, 2H), 3.54 (d, J=5.8 Hz, 2H), 1.73 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 135.6, 132.3, 129.8, 128.7, 126.8, 126.2, 62.7, 35.7.

(*E*)-1-Phenyl-4-(phenylthio)but-2-en-1-ol (**1o**): In a 25 mL round bottom flask a magnetic stir bar was placed and the apparatus was flame dried. Then, dried diethyl ether (10 mL), phenylmagnesium bromide (4.5 mmol, 3 mol/L in diethyl ether) and 0.534 g (3 mmol) of (*E*)-4-(phenylthio)-but-2-enal (**4**) were added to the flask under 0 ℃. After stirred at room temperature for 30 min, the reaction was quenched by slow addition of a saturated NH_4Cl solution followed by extraction with diethyl ether (15 mL×3). The combined organic layers were washed with brine, dried (Na_2SO_4), concentrated and the crude product was purified by column chromatography to afford 0.66 g of **1o** as a light yellow oil, yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.33—7.14 (m, 10H), 5.85—5.62 (m, 2H), 5.09 (d, J=5.4 Hz, 1H), 3.52 (d, J=6.8 Hz, 2H), 1.97 (d, J=2.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.3, 135.3, 135.3, 130.4, 128.7, 128.4, 127.5, 126.6, 126.4, 126.1, 74.2, 36.0; IR (film) v: 967, 699, 738 cm^{-1}; EI-MS (relative intensity) m/z (%): 256 (27), 146 (49), 129 (29), 110 (100), 105 (80), 77 (52), 65 (15); HRMS calcd for $C_{16}H_{16}OSNa$ $(M+Na)^+$: 279.0814, found 279.0807.

(*E*)-2-(4-(Phenylthio)but-2-enyl)isoindoline-1,3-dione (**1p**): Triphenylphosphane (1.179 g, 4.5 mmol) and phthalimide (0.529 g, 3.6 mmol) were added at room temperature to a solution of 0.540 g (3 mmol) of (*E*)-4-(phenylthio)but-2-en-1-ol (**1n**) in THF (10 mL). Diethyl azodicarboxylate (0.783 mg, 4.5 mmol) was added dropwise to the reaction mixture at 0 ℃. After complete consumption (the reaction was monitored by TLC), the solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel to afford the corresponding **1p** as a white solid, 0.917 g, yield 99%. m.p. 114—115 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84—7.82 (m, 2H), 7.73—7.71 (m, 2H), 7.30—7.26 (m, 2H), 7.17—7.14 (m, 2H), 7.06—7.02 (m, 1H), 5.81—5.75 (m, 1H), 5.56—5.51 (m, 1H), 4.18 (d, J=6.3 Hz, 2H), 3.46 (d, J=7.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.6, 135.0, 133.8, 132.0, 130.9, 129.7, 128.6, 126.5, 126.4, 123.2, 38.8, 36.2; IR (film) v: 1709, 1392, 717 cm^{-1}; EI-MS (relative intensity) m/z (%): 309 (36), 200 (100), 182 (40), 130 (38), 109 (35), 53 (49); HRMS calcd for $C_{18}H_{15}NO_2SNa$ $(M+Na)^+$: 332.0716, found 332.0708.

(*E*)-2-(3-(Phenylthio)prop-1-enyl)-1,3-dioxolane (**1q**): To a 25 mL two-necked, round-bottomed flask, equipped with a Dean-Stark adapter and a condenser, containing the (*E*)-4-(phenylthio)but-2-enal (**4**) (0.534 g, 3 mmol), *p*-toluenesulfonic acid (14 mg, 0.075 mmol), in benzene (15 mL) was added ethylene glycol (0.279 g, 4.5 mmol) in benzene (10 mL). The reaction mixture was heated to reflux and was monitored by TLC until no starting aldehyde was detected. The reaction mixture was then filtered through a pad of anhydrous $NaHCO_3$, and the filter cake was washed with CH_2Cl_2 (10 mL×3). Concentration of the filtrate gave the crude product which was further purified by column chromatography on silica gel to give 0.373 g of **1q** as a light yellow oil, yield 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34—7.16 (m, 5H), 3.96—3.83 (m, 4H), 5.97 (td, J=6.93, 6.93, 15.17 Hz, 1H), 5.57 (dd, J=5.8, 15.40 Hz, 1H), 5.21 (d, J=5.8 Hz, 1H), 3.55 (d, J=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.5, 131.3, 129.9, 129.4, 128.8, 126.3, 102.8, 64.7, 35.5; EI-MS (relative intensity) m/z (%): 222 (24), 112 (100), 73 (47), 41 (87); IR (film) v: 1141, 1404, 961, 738, 687 cm^{-1}; HRMS calcd for $C_{12}H_{14}O_2SK$ $(M+Na)^+$: 261.0556, found 261.0552.

Synthesis and spectral data for products 2a—2q

General procedure for the reaction of allyl sulfides with chloramine-T: To a flask was added 1 mmol allyl sulfides (**1**), 1.3 mmol chloramine-T, 2 mL of EtOH and the system was stirred at the assigned temperature. After the reaction finished, the solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel to afford the corresponding product.

N-Allyl-4-methyl-*N*-(phenylthio)benzenesulfonamide (**2a**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J=8.3 Hz, 2H), 7.39 (d, J=7.6 Hz, 2H), 7.33—7.20 (m, 5H), 5.71 (tdd, J=6.5, 6.47, 10.1, 16.7 Hz, 1H), 5.15 (t, J=14.1, 14.1 Hz, 2H), 4.15 (d, J=6.5 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.0, 137.0, 136.1, 132.3, 129.6, 128.9, 127.8, 127.4, 126.3, 119.6, 56.9, 21.5; IR (film) v: 1349, 1160, 827, 812, 659 cm^{-1}; EI-MS (relative intensity) m/z (%): 319 (M^+, 13), 164 (56), 109 (72), 91 (100), 65 (54), 56 (44), 41 (45); HRMS calcd for $C_{16}H_{17}NO_2S_2K$ $(M+Na)^+$: 358.0332, found 358.0326.

N-Allyl-4-methyl-*N*-(*p*-tolylthio)benzenesulfonamide (**2b**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J=8.3 Hz, 2H), 7.35 (d, J=8.1 Hz, 2H), 7.29 (d, J=8.2 Hz, 2H), 7.12 (d, J=8.1 Hz, 2H), 5.71 (tdd, J=6.4, 6.4, 10.1, 16.7 Hz, 1H), 5.16 (dd, J=5.2, 21.1 Hz, 2H), 4.12 (d, J=6.4 Hz, 2H), 2.42 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.9, 138.2, 136.4, 133.1, 132.6, 129.6, 129.5, 128.3, 127.8, 119.4, 56.7, 21.5, 21.1; IR (film) v: 1352, 1160, 827, 809, 659 cm^{-1}; EI-MS (relative intensity) m/z (%): 333 (13), 178 (67), 123 (100), 91 (57), 65 (27); HRMS calcd for $C_{17}H_{19}NO_2S_2Na$ $(M+Na)^+$: 356.0749, found 356.0742.

N-Allyl-4-methyl-*N*-(*o*-tolylthio)benzenesulfonamide (**2c**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J=8.3 Hz, 2H), 7.47 (d, J=7.8 Hz, 1H), 7.30 (d, J=8.1 Hz, 2H), 7.22—7.18 (m, 1H), 7.11—7.06 (m, 2H), 5.71 (tdd, J=6.5, 6.5, 10.1, 16.7 Hz, 1H), 5.13 (ddd, J=1.2, 13.6, 11.2 Hz, 2H), 4.16 (d, J=6.5 Hz,

2H), 2.43 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.0, 136.2, 136.2, 132.8, 132.1, 130.1, 129.6, 127.8, 126.6, 126.3, 124.4, 119.7, 56.9, 21.6, 18.8; IR (film) *v*: 1352, 1166, 827, 812, 659 cm^{-1}; EI-MS (relative intensity) *m/z* (%): 333 (27), 178 (80), 137 (40), 123 (74), 91 (100), 65 (46), 45 (69); HRMS calcd for $C_{17}H_{19}NO_2S_2Na$ $(M+Na)^+$: 356.0749, found 356.0749.

N-Allyl-*N*-(4-chlorophenylthio)-4-methylbenzenesulfonamide (**2d**): White solid, m.p. 64—65 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J=8.3 Hz, 2H), 7.36—7.26 (m, 6H), 5.70 (tdd, J=6.5, 6.5, 10.1, 16.7 Hz, 1H), 5.19—5.13 (m, 2H), 4.13 (d, J=6.5 Hz, 2H), 2.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2, 136.0, 135.6, 133.5, 132.2, 129.6, 129.0, 128.0, 127.7, 119.9, 77.3, 77.0, 76.7, 57.0, 21.5; IR (film) *v*: 1474, 1349, 1086, 812, 659 cm^{-1}; EI-MS (relative intensity) *m/z* (%): 353 (11), 198 (49), 143 (68), 91 (100), 108 (30), 65 (46); HRMS calcd for $C_{16}H_{16}ClNO_2S_2Na$ $(M+Na)^+$: 376.0202, found 376.0203.

N-Allyl-*N*-(4-methoxyphenylthio)-4-methylbenzenesulfonamide (**2e**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, J=8.3 Hz, 1H), 7.52 (d, J=8.9 Hz, 2H), 7.30 (d, J=8.0 Hz, 2H), 6.85 (d, J=8.9 Hz, 2H), 5.72 (tdd, J=6.4, 6.4, 10.1, 16.5 Hz, 1H), 5.17 (ddd, J=1.3, 9.3, 7.1 Hz, 2H), 4.08 (d, J=6.4 Hz, 2H), 3.81 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.6, 143.7, 136.5, 133.6, 132.9, 129.5, 127.7, 126.5, 119.1, 114.4, 56.3, 55.3, 21.5; IR (film) *v*: 1590, 1492, 1346, 1245, 1086, 824, 812, 662 cm^{-1}; EI-MS (relative intensity) *m/z* (%): 349 (12), 194 (56), 139 (100), 91 (50); HRMS calcd for $C_{17}H_{19}NO_3S_2Na$ $(M+Na)^+$: 372.0698, found 372.0699.

N-(4-Chlorophenylthio)-*N*-(cyclohex-2-enyl)-4-methylbenzenesulfonamide (**2f**): White solid, m.p. 79—80 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J=8.3 Hz, 2H), 7.40 (d, J=8.6 Hz, 2H), 7.33—7.27 (m, 4H), 5.77—5.73 (m, 1H), 4.92 (br s, 2H), 2.24 (s, 3H), 1.91—1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 132.6, 129.7, 128.8, 127.6, 126.8, 59.8, 24.2, 21.5, 21.1; IR (film) *v*: 1474, 1355, 1166, 1086, 873, 814, 729, 665 cm^{-1}; EI-MS (relative intensity) *m/z* (%): 393 (12), 313 (66), 91 (100), 65 (44), 41 (42); HRMS calcd for $C_{19}H_{20}ClNO_2S_2Na$ $(M+Na)^+$: 416.0516, found 416.0512.

N-(Cyclohex-2-enyl)-4-methyl-*N*-(phenylthio)benzenesulfonamide (**2i**): White solid, m.p. 101—102 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J=8.3 Hz, 2H), 7.44 (d, J=7.5 Hz, 2H), 7.33—7.30 (m, 4H), 7.21—7.17 (m, 1H), 5.75—5.72 (m, 1H), 4.93—4.91 (m, 2H), 2.24 (s, 3H), 1.90—1.57 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.9, 137.0, 137.0, 132.4, 129.6, 128.7, 127.6, 127.0, 126.6, 124.8, 59.8, 24.2, 21.5, 21.2; IR (film) *v*: 1355, 1163, 873, 854, 812, 665 cm^{-1}; EI-MS (relative intensity) *m/z* (%): 359 (2), 279 (59), 124 (100), 109 (37), 91 (66), 81 (34), 65 (44); HRMS calcd for $C_{19}H_{21}NO_2S_2Na$ $(M+Na)^+$: 382.0906, found 382.0905.

N-(Cyclohex-2-enyl)-*N*-(4-methoxyphenylthio)-4-methylbenzenesulfonamide (**2j**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, J=8.3 Hz, 2H), 7.57 (d, J=8.8 Hz, 2H), 7.30 (d, J=8.0 Hz, 2H), 6.86 (d, J=8.9 Hz, 2H), 5.79—5.75 (m, 1H), 5.04 (s, br, 1H), 4.83—4.81 (m, 1H), 3.81 (s, 3H), 2.43 (s, 3H), 1.95—1.59 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.9, 143.6, 137.4, 131.9, 129.5, 127.7, 127.6, 114.3, 59.7, 55.3, 24.3, 21.5, 21.3; IR (film) *v*: 1590, 1492, 1346, 1251, 1160, 1083, 1028, 873, 854, 812, 729, 665 cm^{-1}; EI-MS (relative intensity) *m/z* (%): 389 (5), 309 (36), 154 (100), 139 (74), 91 (56), 65 (26); HRMS calcd for $C_{20}H_{24}NO_3S_2$ $(M+H)^+$: 390.1192, found 390.1191.

N-Allyl-*N*-(butylthio)-4-methylbenzenesulfonamide (**2k**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J=8.3 Hz, 2H), 7.30 (d, J=8.2 Hz, 2H), 5.77 (tdd, J=6.5, 6.5, 10.08, 16.7 Hz, 1H), 5.19 (ddd, J=1.3, 10.9, 8.7 Hz, 2H), 4.04 (d, J=6.5 Hz, 2H), 2.88 (t, J=7.4 Hz, 2H), 2.43 (s, 3H), 1.59—1.52 (m, 2H), 1.43—1.36 (m, 2H), (t, J=7.33, 7.33 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.6, 136.0, 133.1, 129.4, 127.8, 119.1, 57.6, 39.8, 29.1, 21.8, 21.5, 13.6; IR (film) *v*: 1345, 1160, 1089, 912, 827, 812, 732, 662 cm^{-1}; EI-MS (relative intensity) *m/z* (%): 299 (30), 344 (52), 103 (70), 91 (100), 65 (44), 56 (97), 41 (70), 29 (53); HRMS calcd for $C_{14}H_{21}NO_2S_2Na$ $(M+Na)^+$: 322.0907, found 322.0906.

N-Allyl-*N*-(benzylthio)-4-methylbenzenesulfonamide (**2l**): White solid, m.p. 52—53 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J=8.3 Hz, 2H), 7.32—7.26 (m, 7H), 5.52 (tdd, J=6.5, 6.5, 10.4, 16.8 Hz, 1H), 5.06—5.01 (m, 2H), 4.10 (s, 2H), 3.81 (d, J=6.4 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.7, 136.2, 134.9, 132.7, 129.7, 129.4, 128.6, 127.8, 127.6, 118.9, 57.2, 44.8, 21.5; IR (film) *v*: 1349, 1160, 1086, 925, 827, 812, 711, 699, 662 cm^{-1}; EI-MS (relative intensity) *m/z* (%): 333 (10), 123 (20), 91 (100), 65 (19); HRMS calcd for $C_{17}H_{19}NO_2S_2Na$ $(M+Na)^+$: 356.0749, found 356.0741.

N-(1-Bromobut-3-en-2-yl)-4-methyl-*N*-(phenylthio)-benzenesulfonamide (**2m**): White solid, m.p. 83—84 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, J=8.3 Hz, 2H), 7.52 (d, J=7.4 Hz, 2H), 7.34—7.23 (m, 5H), 5.64 (ddd, J=7.8, 10.3, 17.3 Hz, 1H), 5.15 (d, J=10.4 Hz, 2H), 4.91 (q, J=7.4, 7.4, 7.7 Hz, 1H), 3.45 (dd, J=6.9, 10.4 Hz, 1H), 3.34 (t, J=8.7, 8.7 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2, 137.7, 136.1, 133.2, 129.4, 128.9, 128.1, 127.7, 126.6, 120.6, 66.0, 32.1, 21.6; IR (film) *v*: 1358, 1163, 1086, 888, 836, 812, 741, 668 cm^{-1}; EI-MS (relative intensity) *m/z* (%): 413 (8), 411 (7), 258 (37), 256 (36), 124 (44), 109 (69), 91 (100), 65(63); HRMS calcd for $C_{17}H_{18}BrNO_2S_2Na$ $(M+Na)^+$: 433.9855, found 433.9847.

N-(1-Hydroxybut-3-en-2-yl)-4-methyl-*N*-(phenylthio)benzenesulfonamide (**2n**): White solid, m.p. 107—108 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, J=8.3 Hz, 2H), 7.58 (s, 2H), 7.36—7.24 (m, 5H), 5.56 (ddd, J=8.0, 10.0, 17.6 Hz, 1H), 5.09 (d, J=10.5 Hz, 2H), 4.81 (dt, J=5.3, 8.0, 7.7 Hz, 1H), 3.70 (t, J=10.0,

CHINESE JOURNAL OF CHEMISTRY

10.0 Hz, 1H), 3.56 (s, 1H), 2.42 (s, 3H), 1.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 137.9, 136.2, 132.5, 129.4, 129.1, 128.0, 127.8, 126.7, 119.8, 66.5, 62.7, 21.5; IR (film) v: 1349, 1160, 1086, 1041, 870, 812, 738, 665 cm^{-1}; EI-MS (relative intensity) m/z (%): 349 (7), 318 (40), 164 (58), 124 (44), 109 (78), 91 (100), 65 (57); HRMS calcd for $C_{17}H_{19}NO_3S_2Na$ $(M+Na)^+$: 372.0699, found 372.0690.

N-(1-Hydroxy-1-phenylbut-3-en-2-yl)-4-methyl-*N*-(phenylthio) benzenesulfonamide (**2o**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J=8.2 Hz, 2H), 7.74—7.69 (m, 2H), 7.37—7.21 (m, 10H), 5.52 (ddd, J=8.4, 10.4, 17.2 Hz, 1H), (d, J=10.1 Hz, 2H), 4.70 (s, 1H), 4.57 (s, 1H), 2.39 (s, 3H), 2.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.0, 139.6, 137.5, 136.0, 131.7, 129.2, 129.1, 128.3, 128.1, 128.1, 127.6, 127.4, 120.7, 74.0, 71.7, 21.5; IR (film) v: 1346, 1160, 1086, 1022, 906, 812, 732, 699, 668 cm^{-1}; EI-MS (relative intensity) m/z (%): 318 (32), 210 (98), 163 (69), 155 (48), 109 (47), 91 (100), 79 (52), 65 (44); HRMS calcd for $C_{23}H_{23}NO_3S_2Na$ $(M+Na)^+$: 448.1011, found 448.1003.

N-(1-(1,3-Dioxoisoindolin-2-yl)but-3-en-2-yl)-4-methyl-*N*-(phenylthio)benzenesulfonamide (**2p**): White solid, m.p. 183—185 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78—7.75 (m, 4H), 7.71—7.68 (m, 2H), 7.46 (s, 2H), 7.30—7.11 (m, 5H), 5.77—5.68 (m, 1H), 5.22—5.03 (m, 3H), 3.83 (d, J=13.4 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.7, 143.8, 138.3, 133.9, 131.8, 129.4, 128.7, 127.8, 127.1, 125.8, 123.2, 120.4, 120.3, 62.4, 39.9, 21.5; EI-MS (relative intensity) m/z (%): 478 (2), 318 (30), 200 (24), 160 (100), 91 (49); HRMS calcd for $C_{25}H_{22}N_2O_4S_2Na$ $(M+Na)^+$: 501.0905, found 501.0913.

N-(1-(1,3-Dioxolan-2-yl)allyl)-4-methyl-*N*-(phenylthio)benzenesulfonamide (**2q**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J=8.2 Hz, 2 H), 7.47 (s, 2H), 7.30—7.12 (m, 5H), 5.82 (ddd, J=7.8, 10.4, 17.9 Hz, 1H), 5.19 (d, J=10.5 Hz, 2H), 5.01 (s, 1H), 5.01—4.69 (m, 1H), 3.86—3.83 (m, 4H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.8, 138.2, 136.3, 131.4, 129.2, 128.5, 128.2, 126.9, 125.6, 120.8, 103.1, 65.9, 65.3, 64.5, 21.5; IR (film) v: 1349, 1163, 1086, 866, 814, 665 cm^{-1}; EI-MS (relative intensity) m/z (%): 282 (8), 109 (11), 91 (14), 73 (100), 45 (23); HRMS calcd for $C_{19}H_{21}NO_4S_2Na$ $(M+Na)^+$: 414.0804, found 414.0800.

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