JOC The Journal of Organic Chemistry

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Synthesis of α,β-Unsaturated *N*-Sulfonyl Imides through Zinc-Catalyzed Intermolecular Oxidation of *N*-Sulfonyl Ynamides

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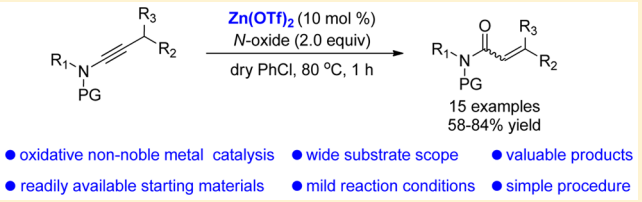
Supporting Information

ABSTRACT: A novel zinc-catalyzed intermolecular oxidation of *N*-sulfonyl ynamides has been developed. A variety of functionalized α,β-unsaturated *N*-sulfonyl imides are readily accessed by utilizing this approach, thus providing a viable alternative to synthetically useful α,β-unsaturated imides. Importantly, the reaction is proposed to proceed by a vinyligous E2-type elimination pathway, but not metal carbene pathway.

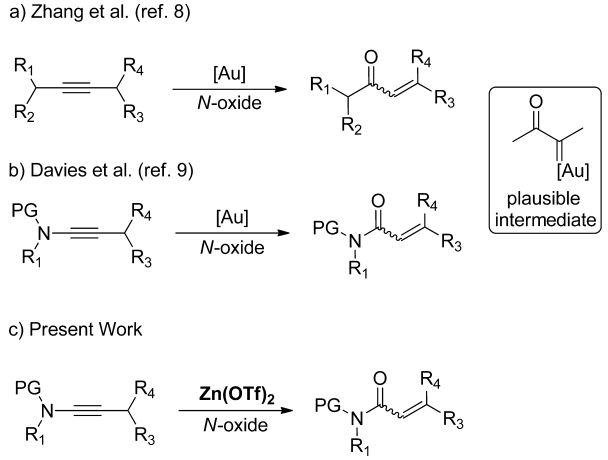


INTRODUCTION

α,β-Unsaturated amides represent an important type of organic compounds because of their frequent occurrence in many bioactive natural products as well as pharmaceuticals.[1] In addition, they can also serve as valuable building blocks used in a wide range of organic reactions[2] and in the synthesis of polymeric materials.[3] However, compared to the synthesis of α,β-unsaturated esters and amides, access to α,β-unsaturated *N*-sulfonyl imides remains scarce.[4] Therefore, the development of novel and general methods for their efficient and practical synthesis is highly desirable.

In recent years, particular attention has been paid to the gold-catalyzed intermolecular alkyne oxidation by *N*-oxides.[5,6] This approach has enabled an easy access to α,β-unsaturated carbonyl compounds using readily available and safer alkynes to replace hazardous α-diazo ketones as precursors in the realm of carbene chemistry.[7] For example, Zhang and co-workers reported a gold-catalyzed intermolecular alkyne oxidation, involving a gold carbene as the most likely intermediate, for the highly regioselective synthesis of α,β-unsaturated carbonyls (Scheme 1a).[8] Simultaneously, Davies and co-workers also described a general route for the synthesis of α,β-unsaturated imides by a gold-catalyzed intermolecular oxidation of ynamides, where a 1,2-C−H insertion into the gold carbenoid intermediate was proposed (Scheme 1b).[9] In our recent study on the ynamide chemistry,[10,11] we developed the first non-noble metal-catalyzed alkyne oxidation, leading to the highly site-selective synthesis of versatile isoquinolones and β-carbolines.[11a] With this in mind, we envisioned that the synthesis of α,β-unsaturated imides might be achieved by a non-noble metal-catalyzed ynamide oxidation (Scheme 1c).[12] In this context, we wish to report a zinc-catalyzed intermolecular oxidation of *N*-sulfonyl ynamides providing ready access to various α,β-unsaturated *N*-sulfonyl imides in moderate to good yields. Importantly, mechanistic studies reveal that the reaction is proposed to occur by a vinyligous E2-type elimination pathway, which is substantially different from the related gold-catalyzed alkyne oxidation.

Scheme 1. Synthesis of α,β-Unsaturated Imides by Intermolecular Oxidation of Ynamides



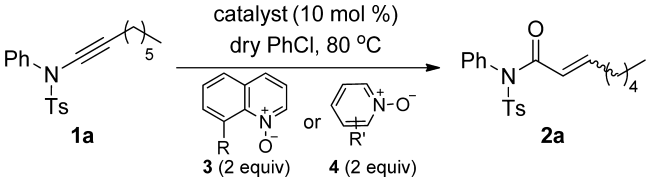
RESULTS AND DISCUSSION

At the outset, *N*-sulfonyl ynamide **1a** was chosen as the model substrate and some of the results are outlined in Table 1. To our delight, the initial catalyst investigation showed that most Lewis acid catalysts displayed good reactivity to furnish the desired α,β-unsaturated *N*-sulfonyl imide **2a** (Table 1, entries 1−6), and $Zn(OTf)_2$ was found to be the best one (Table 1,

Received: July 12, 2015
Published: September 30, 2015

DOI: 10.1021/acs.joc.5b01608
J. Org. Chem. 2015, 80, 10009−10015

Table 1. Optimization of Reaction Conditions[a]



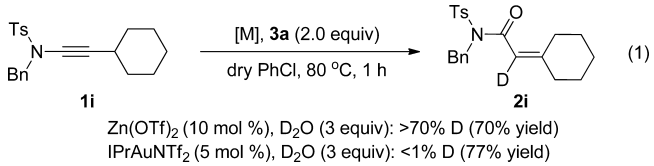
entry	catalyst	oxidant (3/4)	E/Z[b]	yield (%)[c]
1	$In(OTf)_3$	**3a** (R = Et)	2.5/1	72
2	$Sm(OTf)_3$	**3a** (R = Et)	2.5/1	64
3	$Sc(OTf)_3$	**3a** (R = Et)	2.3/1	66
4	$Y(OTf)_3$	**3a** (R = Et)	2.5/1	62
5	$Yb(OTf)_3$	**3a** (R = Et)	2.1/1	69
6	$Zn(OTf)_2$	**3a** (R = Et)	2.6/1	80
7	MsOH	**3a** (R = Et)	-	<5
8	HOTf	**3a** (R = Et)	2.0/1	22
9	$Zn(OTf)_2$	**3b** (R = Me)	1.9/1	61
10	$Zn(OTf)_2$	**3c** (R = ^{i}Pr)	1.8/1	77
11	$Zn(OTf)_2$	**4a** (R' = H)	2.2/1	56
12	$Zn(OTf)_2$	**4b** (R' = 2-Br)	2.1/1	44
13	$Zn(OTf)_2$	**4c** (R' = 2,6-Br_2)	2.1/1	50
14[d]	$Zn(OTf)_2$	**3a** (R = Et)	2.0/1	78
15[e]	$Zn(OTf)_2$	**3a** (R = Et)	2.6/1	69
16[f]	$Zn(OTf)_2$	**3a** (R = Et)	1.4/1	75
17[g]	$Zn(OTf)_2$	**3a** (R = Et)	2.1/1	51

[a]Reaction conditions: [**1a**] = 0.05 M. [b]Determined by crude ^{1}H NMR. [c]Estimated by ^{1}H NMR using diethyl phthalate as internal standard. [d]3.0 equiv of **3a** was used. [e]1.5 equiv of **3a** was used. [f]In DCE. [g]In toluene.

entry 6). These results suggest that the metal carbene pathway is less likely in such an oxidative catalysis. Notably, proton acids such as MsOH and HOTf were not effective in promoting this reaction (Table 1, entries 7 and 8).[13] A subsequent *N*-oxide screening revealed that 8-ethylquinoline *N*-oxide **3a** gave the best result, and *E*:*Z* selectivity slightly varied with different *N*-oxides (Table 1, entries 9−13). In addition, it was found that the screening of the amount of the *N*-oxide (Table 1, entries 14−15) and other solvents such as DCE and toluene (Table 1, entries 16−17) could not further improve the reaction.

With the optimized conditions established (Table 1, entry 6), the reaction scope was then studied. As shown in Table 2, moderate to good yields (58−84%) of the corresponding *α*,*β*-unsaturated *N*-sulfonyl imides **2a**−**2o** were obtained, and the (*E*)-isomer was formed as the major, or sole product in all cases. Of note, the reaction was tolerant of a range of functional groups including a remote chloro, protected hydroxyl and amino (Table 2, entries 2−5). In addition, the investigation of the *N*-protecting groups demonstrated that this reaction could work well with different *N*-protecting groups, such as Ms, Bs (*p*-bromobenzenesulfonyl), MBS (*p*-methoxylbenzenesulfonyl) and Ns (*o*-nitrobenzenesulfonyl) (Table 2, entries 11−14). Interestingly, it was found that conjugated *N*-sulfonyl ynamide **1o** was also suitable substrate for this transformation, allowing the synthesis of the desired *α*,*β*,*γ*,*δ*-unsaturated *N*-sulfonyl imide **2o** in 68% yield (Table 2, entry 15).[14] Thus, this protocol provides an efficient and practical route for the construction of synthetically important *α*,*β*-unsaturated imide derivatives from readily accessible materials. Attempts to expand this chemistry to oxazolidinone derived ynamide were not successful presumably due to product inhibition as a good zinc chelate system is generated in this reaction system.

To further clarify the reaction mechanism, we also performed the deuterium-labeling studies, as depicted in eq 1. It was found



that in the presence of 3 equiv of D_2O, >70% deuterium incorporation at the alkenyl position was observed by using $Zn(OTf)_2$ as catalyst, while almost no deuterium was incorporated by using $IPrAuNTf_2$ as catalyst. These results further support that the reaction pathway of the current zinc catalysis is distinctively different from the related gold catalysis, where the metal carbenoid intermediate is presumably involved.[8,9]

On the basis of these experimental observations, a plausible mechanism to rationalize this zinc-promoted oxidative catalysis is proposed, as illustrated in Scheme 2. Taking *N*-sulfonyl ynamide **1i** for example, the *N*-oxide **3a** first attacked the Zn-activated alkyne to form vinyl zinc intermediate **A**, which could then undergo a vinyligous E2-type elimination to generate intermediate **B**.[15] Finally, protodemetalation ought to deliver the product **2i**.

CONCLUSION

In summary, we have developed a convenient and viable alternative for the synthesis of various *α*,*β*-unsaturated *N*-sulfonyl imides via a zinc-catalyzed alkyne oxidation. Importantly, the reaction is proposed to proceed by a vinyligous E2-type elimination pathway, but not metal carbene pathway. Other notable features of this method include widespread availability of the substrates, compatibility with a broad range of functional groups, the simple procedure and mild reaction conditions. Further application of this non-noble metal-promoted oxidative catalysis will be pursued in our laboratory.

EXPERIMENTAL SECTION

General Information. Ethyl acetate (ACS grade), hexanes (ACS grade) and anhydrous 1, 2-dichloroethane (ACS grade) were obtained commercially and used without further purification. Methylene chloride, tetrahydrofuran, and diethyl ether were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. High-resolution mass spectra were obtained using electrospray ionization using an ICR analyzer (ESI-MS).

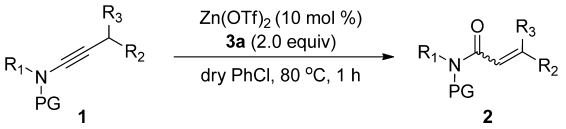
^{1}H NMR spectra were recorded in chloroform-d_3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration).

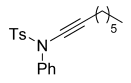
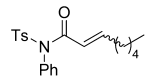
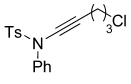
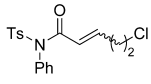
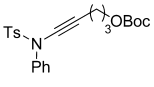
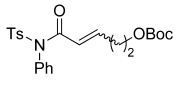
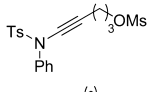
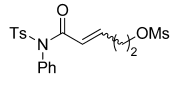
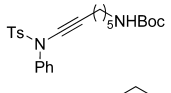
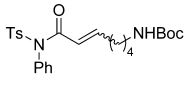
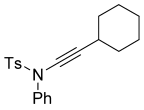
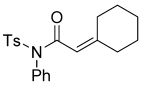
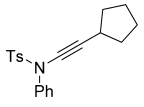
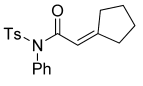
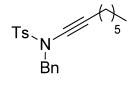
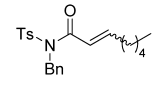
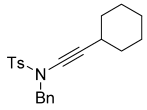
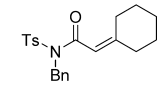
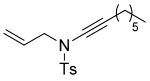
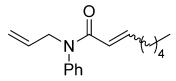
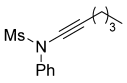
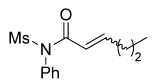
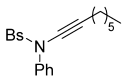
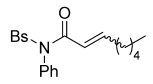
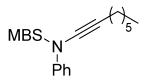
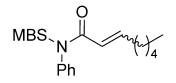
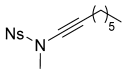
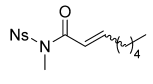
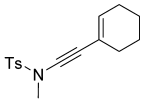
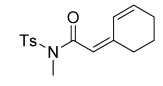
^{13}C NMR spectra were recorded in chloroform-d_3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

Representative Synthetic Procedures for the Preparation of *N*-Sulfonyl Ynamides 1 (1b, 1h, 1l, 1o)..[11f,16] Alkynyl bromide (1.1 mmol) and DMEDA (0.2 mmol, 17.6 mg) were added to a stirred solution of amide (1.0 mmol), K_2CO_3 (2.0 mmol, 276.4 mg), $FeCl_3\cdot 6H_2O$ (0.1 mmol, 27.0 mg), and toluene (5 mL) under air, and the resulting mixture was stirred at 90 °C for 12 h. The suspension was filtered, and the residue was washed with diethyl ether (3 × 15 mL). The purification of products was achieved by flash chromatography

DOI: 10.1021/acs.joc.5b01608
J. Org. Chem. 2015, 80, 10009−10015

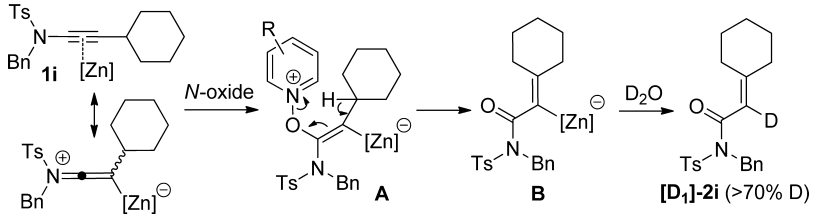
Table 2. Reaction Scope Study[a]



entry	substrate	1	product	2	E/Z[b]	yield (%)
1		**1a**		**2a**	2.6/1	78
2		**1b**		**2b**	4.0/1	65
3		**1c**		**2c**	2.5/1	75
4		**1d**		**2d**	2.9/1	77
5		**1e**		**2e**	2.3/1	73
6		**1f**		**2f**		84
7		**1g**		**2g**		78
8		**1h**		**2h**	1.7/1	74
9		**1i**		**2i**		75
10		**1j**		**2j**	2.3 /1	69
11		**1k**		**2k**	2.8/1	72
12		**1l**		**2l**	2.4/1	58
13		**1m**		**2m**	2.4 /1	80
14		**1n**		**2n**	1.9/1	65
15		**1o**		**2o**		68

[a]Reaction conditions: 0.3 mmol of ynamide **1**, 0.6 mmol of oxidant **3a** and 0.03 mmol of $Zn(OTf)_2$ in 6 mL of dry PhCl. [b]Determined by crude ^1H NMR. [c]Isolated yield.

Scheme 2. Plausible Reaction Mechanism



(eluent: hexanes/ethyl acetate) to afford the desired *N*-sulfonyl ynamide **1**.

Representative Synthetic Procedures for the Preparation of *N*-Sulfonyl Ynamides 1 (1a, 1c–1g, 1i–1k, 1m–1n).[9] $CuCl_2$ (0.1 mmol, 13.5 mg), amide (5.0 mmol), and Na_2CO_3 (3.0 mmol, 318.0 mg) were added to a flame-dried 50 mL three-necked round-bottomed flask. The flask was purged with oxygen for 15 min, and a solution of pyridine (2.0 mmol, 158.2 mg) in dry toluene (10 mL) was added. A balloon filled with oxygen was connected to the flask, and the stirred mixture was heated at 70 °C. After 15 min, a solution of alkyne (1 mmol) in dry toluene (10 mL) was added by syringe pump over 4 h. The mixture was allowed to stir at 70 °C for another 4 h and was then cooled to rt. The reaction mixture was concentrated under reduced pressure, and the residue was purified by flash chromatography (eluent: hexanes/ethyl acetate) to afford the desired *N*-sulfonyl ynamide **1**.

*4-Methyl-N-(oct-1-yn-1-yl)-N-phenylbenzenesulfonamide (**1a**).*[11d] Pale yellow oil (199.1 mg, 56%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2H, J = 8.4 Hz), 7.33–7.27 (m, 7H), 2.44 (s, 3H), 2.31 (t, 2H, J = 7.2 Hz), 1.54–1.51 (m, 2H), 1.40–1.30 (m, 6H), 0.91 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 139.4, 133.1, 129.3, 128.8, 128.2, 127.8, 126.0, 73.8, 70.4, 31.3, 28.8, 28.4, 22.5, 21.6, 18.4, 14.0; IR (neat): 2930, 2253, 1592, 1489, 1373, 1177, 1092.

*N-(5-Chloropent-1-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide (**1b**).* Pale yellow oil (183.9 mg, 52%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, 2H, J = 8.4 Hz), 7.35–7.21 (m, 7H), 3.62 (t, 2H, J = 6.4 Hz), 2.50 (t, 2H, J = 6.8 Hz), 2.44 (s, 3H), 1.98–1.93 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 138.9, 132.7, 129.3, 128.9, 128.0, 127.9, 125.9, 74.8, 68.3, 43.5, 31.3, 21.5, 15.8; IR (neat): 2958, 2923, 2851, 2254, 1594, 1489, 1454, 1371, 1175; MS (ESI, m/z) 370 ($M + Na^+$); HRMS (ESI) Calcd for $[C_{18}H_{18}ClNNaO_2S]^+$ ($M + Na^+$) 370.0639, found 370.0632.

DOI: 10.1021/acs.joc.5b01608
J. Org. Chem. 2015, 80, 10009–10015

*tert-Butyl (5-(4-Methyl-N-phenylphenylsulfonamido)pent-4-yn-1-yl) Carbonate (**1c**).* Pale yellow oil (300.7 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H, J = 8.4 Hz), 7.33−7.20 (m, 7H), 4.12 (t, 2H, J = 6.4 Hz), 2.47−2.38 (m, 5H), 1.89−1.80 (m, 2H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 144.6, 139.0, 132.7, 129.3, 128.8, 128.0, 127.8, 125.9, 81.7, 74.4, 68.6, 65.3, 27.8, 27.6, 21.4, 15.0; IR (neat): 2978, 2929, 2254, 1739(s), 1595, 1489, 1455, 1371, 1278, 1174; MS (ESI, m/z) 452 (M + Na^+); HRMS (ESI) Calcd for $[C_{23}H_{27}NNaO_5S]^+$ (M + Na^+) 452.1502, found 452.1501.

*5-(4-Methyl-N-phenylphenylsulfonamido)pent-4-yn-1-yl Methanesulfonate (**1d**).* Pale yellow oil (256.7 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 2H, J = 8.4 Hz), 7.36−7.19 (m, 7H), 4.32 (t, 2H, J = 6.0 Hz), 3.00 (s, 3H), 2.47 (t, 2H, J = 6.8 Hz), 2.42 (s, 3H), 1.99−1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 138.7, 132.6, 129.4, 128.9, 128.0, 127.8, 125.8, 75.0, 68.4, 67.8, 36.8, 28.0, 21.4, 14.6; IR (neat): 3030, 2937, 2851, 2254, 1594, 1489, 1454, 1358, 1174; MS (ESI, m/z) 430 (M + Na^+); HRMS (ESI) Calcd for $[C_{19}H_{21}NNaO_5S_2]^+$ (M + Na^+) 430.0753, found 430.0759.

*tert-Butyl (7-((4-Methyl-N-phenylphenyl)sulfonamido)hept-6-yn-1-yl)carbamate (**1e**).* White solid (mp 78−80 °C, 241.9 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H, J = 8.4 Hz), 7.34−7.19 (m, 7H), 4.65 (s, 1H), 3.18−3.01 (m, 2H), 2.42 (s, 1H), 2.29 (t, 2H, J = 6.8 Hz), 1.56−1.30 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 144.6, 139.2, 132.9, 129.2, 128.8, 128.1, 127.8, 125.9, 78.8, 74.0, 69.9, 40.4, 29.4, 27.5, 25.8, 21.5, 18.3; IR (neat): 3418, 2932, 2253, 1715(s), 1595, 1489; MS (ESI, m/z) 479 (M + Na^+); HRMS (ESI) Calcd for $[C_{25}H_{32}N_2NaO_4S]^+$ (M + Na^+) 479.1975, found 479.1972.

*N-(Cyclohexylethynyl)-4-methyl-N-phenylbenzenesulfonamide (**1f**).* Pale yellow oil (212.1 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H, J = 8.0 Hz), 7.31−7.20 (m, 7H), 2.57−2.46 (m, 1H), 2.41 (s, 3H), 1.83−1.72 (m, 2H), 1.71−1.61 (m, 2H), 1.53−1.42 (m, 2H), 1.37−1.23 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 139.4, 132.7, 129.1, 128.7, 128.1, 127.7, 125.8, 74.2, 74.1, 32.6, 28.6, 25.8, 24.5, 21.5; IR (neat): 2929, 2853, 2246, 1595, 1488, 1448, 1373, 1175; MS (ESI, m/z) 376 (M + Na^+); HRMS (ESI) Calcd for $[C_{21}H_{23}NNaO_2S]^+$ 376.1342, found 376.1341.

*N-(Cyclopentylethynyl)-4-methyl-N-phenylbenzenesulfonamide (**1g**).* Pale yellow oil (159.5 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 2H, J = 8.4 Hz), 7.35−7.15 (m, 7H), 2.76−2.69 (m, 1H), 2.42 (s, 3H), 1.95−1.81 (m, 2H), 1.81−1.66 (m, 2H), 1.66−1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 139.3, 132.7, 129.2, 128.8, 128.1, 127.7, 125.9, 74.5, 73.6, 33.8, 29.9, 24.7, 21.6; IR (neat): 2959, 2869, 2247, 1595, 1489, 1453, 1372, 1175; MS (ESI, m/z) 362 (M + Na^+); HRMS (ESI) Calcd for $[C_{20}H_{21}NNaO_2S]^+$ 362.1185, found 362.1183.

*N-Benzyl-4-methyl-N-(oct-1-yn-1-yl)benzenesulfonamide (**1h**).* Pale yellow oil (258.7 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.4 Hz), 7.34−7.22 (m, 7H), 4.44 (s, 2H), 2.43 (s, 3H), 2.15 (t, 2H, J = 6.8 Hz), 1.42−1.32 (m, 2H), 1.30−1.13 (m, 6H), 0.86 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 134.8, 134.7, 129.4, 128.6, 128.3, 128.0, 127.6, 73.3, 70.8, 55.5, 31.2, 28.6, 28.2, 22.4, 21.5, 18.3, 14.0; IR (neat): 2929, 2857, 2252, 1597, 1495, 1455, 1365, 1169; MS (ESI, m/z) 392 (M + Na^+); HRMS (ESI) Calcd for $[C_{22}H_{27}NNaO_2S]^+$ 392.1655, found 392.1654.

*N-Benzyl-N-(cyclohexylethynyl)-4-methylbenzenesulfonamide (**1i**).* White solid (mp 68−70 °C, 258.7 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.4 Hz,), 7.32−7.21 (m, 7H), 4.43 (s, 2H), 2.43 (s, 3H), 2.40−2.35 (m, 1H), 1.68−1.60 (m, 2H), 1.55−1.48 (m, 2H), 1.47−1.17 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 134.8, 134.7, 129.4, 128.8, 128.3, 128.0, 127.7, 74.8, 73.7, 55.6, 32.6, 28.6, 25.8, 24.4, 21.6; IR (neat): 2929, 2853, 1365, 1169, 599; MS (ESI, m/z) 390.1498 (M + Na^+); HRMS (ESI) Calcd for $[C_{22}H_{25}NNaO_2S]^+$ 390.1498, found 390.1492.

*N-Allyl-4-methyl-N-(oct-1-yn-1-yl)benzenesulfonamide (**1j**).* Pale yellow oil (210.9 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H, J = 8.0 Hz), 7.33 (d, 2H, J = 8.0 Hz), 5.77−5.67 (m, 1H), 5.27−5.13 (m, 2H), 3.91 (d, 2H, J = 6.4 Hz), 2.44 (s, 3H), 2.23 (t, 2H, J = 6.8 Hz), 1.52−1.42 (m, 2H), 1.39−1.16 (m, 6H), 0.88 (t, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 134.7, 131.1, 129.5, 127.6, 119.4, 72.9, 70.4, 54.2, 31.2, 28.7, 28.2, 22.4, 21.5, 18.3, 13.9; IR (neat): 2929, 2857, 2251, 1643, 1597, 1494, 1454, 1366, 1170; MS (ESI, m/z) 342 (M + Na^+); HRMS (ESI) Calcd for $[C_{18}H_{25}NNaO_2S]^+$ 342.1498, found 342.1497.

*N-(Hex-1-yn-1-yl)-N-phenylmethanesulfonamide (**1k**).*[11b] Pale yellow oil (145.8 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.47 (m, 2H), 7.46−7.38 (m, 2H), 7.37−7.29 (m, 1H), 3.06 (s, 3H), 2.35 (t, 2H, J = 7.2 Hz), 1.58−1.51 (m, 2H), 1.48−1.37 (m, 2H), 0.92 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 129.1, 127.8, 125.2, 73.0, 70.9, 35.9, 30.7, 21.8, 18.0, 13.4; IR (neat): 2957, 2858, 2256, 1593, 1490, 1456, 1362, 1270, 1168, 1075, 1027.

*4-Bromo-N-(oct-1-yn-1-yl)-N-phenylbenzenesulfonamide (**1l**).* Pale yellow oil (281.7 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.60 (m, 2H), 7.54−7.50 (m, 2H), 7.35−7.23 (m, 5H), 2.29 (t, 2H, J = 7.2 Hz), 1.54−1.45 (m, 2H), 1.41−1.21 (m, 6H), 0.89 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 134. 6, 131.9, 129.5, 128.9, 128.8, 128.0, 125.8, 73.3, 70.7, 31.1, 28.6, 28.3, 22.4, 18.2, 13.9; IR (neat): 2929, 2857, 2253, 1592, 1573, 1488, 1470, 1389, 1377, 1183; MS (ESI, m/z) 442 (M + Na^+); HRMS (ESI) Calcd for $[C_{20}H_{22}BrNNaO_2S]^+$ 442.0447, found 442.0446.

*4-Methoxy-N-(oct-1-yn-1-yl)-N-phenylbenzenesulfonamide (**1m**).* Pale yellow oil (267.5 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.56 (m, 2H), 7.34−7.22 (m, 5H), 6.95−6.88 (m, 2H), 3.84 (s, 3H), 2.28 (t, 2H, J = 6.8 Hz), 1.55−1.44 (m, 2H), 1.41−1.30 (m, 6H), 0.88 (t, 2H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 139.3, 130.3, 128.8, 127.7, 127.3, 126.0, 113.7, 73.9, 70.3, 55.5, 31.2, 28.7, 28.3, 22.4, 18.3, 13.9; IR (neat): 2929, 2856, 2253, 1594, 1577, 1496, 1456, 1370, 1262, 1165; MS (ESI, m/z) 394 (M + Na^+); HRMS (ESI) Calcd for $[C_{21}H_{25}NNaO_3S]^+$ 394.1447, found 394.1446.

*N-Methyl-2-nitro-N-(oct-1-yn-1-yl)benzenesulfonamide (**1n**).* Pale yellow oil (259.5 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, 1H, J = 1.6, J = 7.6 Hz), 7.82−7.65 (m, 3H), 3.27 (s, 3H), 2.23 (t, 2H, J = 7.2 Hz), 1.50−1.39 (m, 2H), 1.35−1.18 (m, 6H), 0.88 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 134.5, 131.5, 131.2, 129.6, 124.0, 73.0, 69.9, 39.5, 31.0, 28.4, 28.1, 22.2, 18.0, 13.7; IR (neat): 2930, 2857, 2256, 1589, 1548, 1465, 1440, 1374, 1181; MS (ESI, m/z): 347 (M + Na^+); HRMS (ESI) Calcd for $[C_{15}H_{20}N_2NaO_4S]^+$ 347.1036, found 347.1038.

*N-(Cyclohex-1-en-1-ylethynyl)-N,4-dimethylbenzenesulfonamide (**1o**).* Pale yellow oil (153.4 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.4 Hz), 7.36 (d, 2H, J = 8.0 Hz), 6.00 (s, 1H), 3.05 (s, 3H), 2.45 (s, 3H), 2.03−2.13 (m, 4H), 1.69−1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 134.1, 133.3, 129.6, 127.8, 119.8, 81.5, 70.6, 39.4, 29.4, 25.6, 22.3, 21.5, 21.4; IR (neat): 2929, 2857, 2225, 1363, 1165, 913; MS (ESI, m/z): 312 (M + Na^+); HRMS (ESI) Calcd for $[C_{16}H_{19}NNaO_2S]^+$ 312.1029, found 312.1031.

General Procedure of the Synthesis of α,β-Unsaturated *N*-Sulfonyl Imide 2 from *N*-Sulfonyl Ynamide 1. 8-Ethylquinoline *N*-oxide **3a** (103.9 mg, 0.60 mmol) and $Zn(OTf)_2$ (10.8 mg, 0.03 mmol) were added to a solution of the **N**-sulfonyl ynamide **1** (0.30 mmol) in dry PhCl (6.0 mL) under N_2 at room temperature. The reaction mixture was stirred at 80 °C and the progress of the reaction was monitored by TLC. The reaction typically took 1 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired product **2**.

*(E)-N-Phenyl-N-tosyloct-2-enamide (**2a**).* Pale yellow oil (62.8 mg, 56%). This compound is known and the spectroscopic data match those reported.[11d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, 2H, J = 8.4 Hz), 7.48−7.46 (m, 3H), 7.32 (d, 2H, J = 8.4 Hz), 7.33−7.26 (m, 2H), 6.98−6.91 (m, 1H), 5.45 (d, 1H, J = 15.2 Hz), 2.43 (s, 3H), 2.00−1.95 (m, 2H), 1.28−1.11 (m, 6H), 0.80 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 151.0, 144.6, 136.2, 140.0, 130.2, 129.5, 129.2, 129.1, 121.1, 32.1, 30.9, 27.4, 22.1, 21.5, 13.7.

*(Z)-N-Phenyl-N-tosyloct-2-enamide (**2a**).* Pale yellow oil (24.5 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, 2H, J = 8.4 Hz), 7.50−7.40 (m, 3H), 7.33 (d, 2H, J = 8.0 Hz), 7.25−7.21 (m, 2H), 6.01−5.92 (m, 1H), 5.43−5.37 (m, 1H), 2.61−2.50 (m, 2H), 2.44 (s, 3H), 1.37−1.29 (m, 2H), 1.29−1.18 (m, 4H), 0.84 (t, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 151.4, 144.6, 136.4, 136.3, 130.2, 129.6, 129.5, 129.2, 129.0, 120.1, 31.3, 29.0, 28.4, 22.3, 21.6, 13.9; IR (neat):

DOI: 10.1021/acs.joc.5b01608
J. Org. Chem. 2015, 80, 10009−10015

2956, 1693 (s), 1625, 1595, 1489, 1364, 1174, 1158, 578; MS (ESI, *m*/*z*) 394 (M + Na^+); HRMS (ESI) Calcd for $[C_{21}H_{25}NNaO_3S]^+$ 394.1447, found 394.1442.

(E)-6-Chloro-N-phenyl-N-tosylhex-2-enamide (**2b**). Pale yellow oil (70.9 mg, 65% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, 2H, *J* = 8.4 Hz), 7.56−7.47 (m, 3H), 7.36 (d, 2H, *J* = 8.4 Hz), 7.30−7.26 (m, 2H), 6.93−6.83 (m, 1H), 5.61−5.53 (m, 1H), 3.45 (t, 2H, *J* = 6.8 Hz), 2.53−2.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 145.1, 144.9, 136.0, 135.8, 130.3, 129.9, 129.7, 129.3, 129.2, 123.8, 42.0, 34.9, 21.6; IR (neat): 2919, 2850, 1692 (s), 1639, 1595, 1488, 1360, 1169, 574; MS (ESI, *m*/*z*): 386 (M + Na^+); HRMS (ESI) Calcd for $[C_{18}H_{18}ClNNaO_3S]^+$ 386.0588, found 386.0591.

tert-Butyl (E)-(5-(4-Methyl-N-phenylphenylsulfonamido)-5-oxopent-3-en-1-yl) Carbonate (**2c**). Pale yellow oil (100.2 mg, 75% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, 2H, *J* = 8.4 Hz), 7.53−7.44 (m, 3H), 7.34 (d, 2H, *J* = 8.0 Hz), 7.28−7.22 (m, 2H), 6.97−6.84 (m, 1H), 5.61−5.51 (m, 1H), 3.97 (t, 2H, *J* = 6.4 Hz), 2.45 (s, 3H), 2.39−2.30 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 153.1, 145.4, 144.8, 136.1, 135.8, 130.3, 129.9, 129.7, 129.3, 129.2, 123.4, 82.2, 64.5, 31.5, 27.7, 21.6; IR (neat): 2925, 2853, 1740 (s), 1694 (s), 1639, 1595, 1488, 1454, 1367, 1163, 696, 575; MS (ESI, *m*/*z*) 468 (M + Na^+); HRMS (ESI) Calcd for $[C_{23}H_{27}NNaO_6S]^+$ 468.1451, found 468.1453.

(E)-5-(4-Methyl-N-phenylphenylsulfonamido)-5-oxopent-3-en-1-yl methanesulfonate (**2d**). Pale yellow oil (97.8 mg, 77% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, 2H, *J* = 8.4 Hz), 7.54−7.45 (m, 3H), 7.34 (d, 2H, *J* = 8.0 Hz), 7.29−7.20 (m, 2H), 6.92−6.77 (m, 1H), 5.62 (d, 1H, *J* = 15.2 Hz), 4.19−4.07 (m, 2H), 2.90 (s, 3H), 2.51−2.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 144.9, 143.5, 135.9, 135.7, 130.2, 130.0, 129.7, 129.3, 129.1, 124.2, 66.8, 37.4, 31.8, 21.6; IR (neat): 2923, 2852, 2256, 1690, 1640, 1593, 1486, 1260; MS (ESI, *m*/*z*) 446 (M + Na^+); HRMS (ESI) Calcd for $[C_{19}H_{21}NNaO_6S_2]^+$ 446.0702, found 446.0707.

tert-Butyl (E)-(7-((4-Methyl-N-phenylphenyl)sulfonamido)-7-oxohept-5-en-1-yl)carbamate (**2e**). Pale yellow oil (103.5 mg, 73% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, 2H, *J* = 8.4 Hz), 7.51−7.47 (m, 3H), 7.33 (d, 2H, *J* = 8.0 Hz), 7.26−7.23 (m, 2H), 6.94−6.87 (m, 1H), 5.44 (d, 1H, *J* = 15.2 Hz,), 4.48 (s, 1H), 3.07−2.92 (m, 2H), 2.44 (s, 3H), 2.04−1.98 (m, 2H), 1.41 (s, 9H), 1.35−1.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 155.8, 150.2, 144.7, 136.1, 135.9, 130.3, 129.8, 129.6, 129.3, 129.1, 121.5, 67.9, 39.9, 31.8, 28.3, 25.5, 24.9, 21.6; IR (neat): 3407, 2928, 1695 (s), 1364, 1172, 697, 575; MS (ESI, *m*/*z*) 495 (M + Na^+); HRMS (ESI) Calcd for $[C_{25}H_{32}N_2NaO_5S]^+$ 495.1924, found 495.1921.

2-Cyclohexylidene-N-phenyl-N-tosylacetamide (**2f**). Pale yellow oil (93.1 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, 2H, *J* = 8.4 Hz), 7.51−7.42 (m, 3H), 7.32 (d, 2H, *J* = 8.0 Hz), 7.28−7.21 (m, 2H), 5.21 (s, 1H), 2.70−2.62 (m, 2H), 2.43 (s, 3H), 1.95−1.86 (m, 2H), 1.61−1.41 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 164.7, 144.4, 136.6, 136.5, 130.2, 129.4, 129.2, 129.0, 114.0, 38.1, 30.0, 28.4, 27.6, 25.9, 21.6; IR (neat): 2925, 2855, 1692 (s), 1627, 1596, 1488, 1448, 1359; MS (ESI, *m*/*z*) 392 (M + Na^+); HRMS (ESI) Calcd for $[C_{21}H_{23}NNaO_3S]^+$ 392.1291, found: 392.1291.

2-Cyclopentylidene-N-phenyl-N-tosylacetamide (**2g**). Pale yellow oil (83.3 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, 2H, *J* = 8.4 Hz), 7.50−7.43 (m, 3H), 7.32 (d, 2H, *J* = 8.0 Hz), 7.28−7.23 (m, 2H), 5.44−5.41 (m, 1H), 2.78−2.72 (m, 2H), 2.44 (s, 3H), 2.22−2.15 (m, 2H), 1.70−1.62 (m, 2H), 1.58−1.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 165.3, 144.3, 136.7, 136.6, 130.3, 129.5, 129.4, 129.2, 129.0, 111.5, 36.6, 33.2, 26.2, 25.1, 21.6; IR (neat): 2921, 2851, 1691 (s), 1629, 1595, 1488, 1452, 1363, 1168, 697, 565; MS (ESI, *m*/*z*) 378 (M + Na^+); HRMS (ESI) Calcd for $[C_{20}H_{21}NNaO_3S]^+$ 378.1134, found 378.1130.

(E)-N-Benzyl-N-phenyloct-2-enamide (**2h**). Pale yellow oil (85.6 mg, 74% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, 2H, *J* = 8.4 Hz), 7.40−7.21 (m, 7H), 7.01−6.87 (m, 1H), 6.58−6.53 (m, 1H), 5.10 (s, 2H), 2.40 (s, 3H), 2.09−2.14 (m, 2H), 1.40−1.30 (m, 2H), 1.30−1.16 (m, 4H), 0.85 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 151.5, 144.6, 137.0, 136.7, 129.5, 128.5, 127.9, 127.7, 127.6, 121.3, 49.3, 32.5, 31.2, 27.5, 22.3, 21.5, 13.9; IR (neat): 2925, 2854, 1685 (s), 1633, 1597, 1495, 1454, 1356, 1162, 589; MS (ESI, *m*/*z*) 408 (M + Na^+); HRMS (ESI) Calcd for $[C_{22}H_{27}NNaO_3S]^+$ 408.1604, found 408.1602.

N-Benzyl-2-cyclohexylidene-N-tosylacetamide (**2i**). Pale yellow oil (86.3 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, 2H, *J* = 8.0 Hz), 7.40−7.36 (m, 2H), 7.35−7.27 (m, 3H), 7.25−7.18 (m, 2H), 6.11 (s, 1H), 5.10 (s, 1H), 2.38 (s, 3H), 2.34−2.31 (m, 2H), 2.08−2.05 (m, 2H), 1.52−1.45 (m, 4H), 1.40−1.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 161.5, 144.3, 137.0, 136.9, 129.3, 128.4, 127.8, 127.7, 127.4, 114.9, 49.0, 37.5, 30.4, 28.0, 27.4, 25.9, 21.4; IR (neat): 2930, 2855, 1682 (s), 1634, 1496, 1353, 1160, 588; MS (ESI, *m*/*z*) 406 (M + Na^+); HRMS (ESI) Calcd for $[C_{22}H_{25}NNaO_3S]^+$ 406.1447, found 406.1448.

(E)-N-Allyl-N-phenyloct-2-enamide (**2j**). Pale yellow oil (69.4 mg, 69% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, 2H, *J* = 8.0 Hz), 7.31 (d, 2H, *J* = 8.0 Hz), 7.04−6.88 (m, 1H), 6.50 (d, 1H, *J* = 15.2 Hz), 5.98−5.82 (m, 1H), 5.36−5.21 (m, 2H), 4.49 (d, 2H, *J* = 5.2 Hz), 2.42 (s, 3H), 2.19−2.14 (m, 2H), 1.45−1.35 (m, 2H), 1.35−1.17 (m, 4H), 0.87 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 151.3, 144.6, 137.0, 132.9, 129.5, 127.9, 121.1, 118.1, 48.3, 32.5, 31.2, 27.5, 22.3, 21.5, 13.8; IR (neat): 2925, 2927, 1686 (s), 1635, 1597, 1494, 1433, 1356, 1167, 666, 590; MS (ESI, *m*/*z*) 358 (M + Na^+); HRMS (ESI) Calcd for $[C_{18}H_{25}NNaO_3S]^+$ 358.1447, found 358.1449.

(E)-N-(Methylsulfonyl)-N-phenylhex-2-enamide (**2k**). Pale yellow oil (57.7 mg, 72% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.45 (m, 3H), 7.34−7.25 (m, 2H), 7.13−7.06 (m, 1H), 5.51 (d, 1H, *J* = 15.2 Hz), 3.47 (s, 3H), 2.10−1.98 (m, 2H), 1.40−1.32 (m, 2H), 0.83 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 151.6, 135.2, 130.0, 129.9, 129.7, 121.0, 41.8, 34.3, 21.1, 13.4; IR (neat): 2923, 2852, 1686 (s), 1635, 1592, 1488, 1353, 1155, 964, 695, 541; MS (ESI, *m*/*z*) 290 (M + Na^+); HRMS (ESI) Calcd for $[C_{13}H_{17}NNaO_3S]^+$ 290.0821, found 290.0826.

(E)-N-((4-Bromophenyl)sulfonyl)-N-phenyloct-2-enamide (**2l**). Pale yellow oil (75.9 mg, 58% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.88 (m, 2H), 7.74−7.65 (m, 2H), 7.58−7.43 (m, 3H), 7.27−7.22 (m, 2H), 7.01−6.91 (m, 1H), 5.45−5.38 (m, 1H), 2.04−1.96 (m, 2H), 1.33−1.24 (m, 2H), 1.21−1.10 (m, 4H), 0.81 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 151.8, 138.1, 135.7, 132.0, 130.7, 130.2, 130.0, 129.8, 129.0, 120.9, 32.3, 31.0, 27.4, 22.2, 13.8; IR (neat): 2920, 2851, 1692 (s), 1633, 1573, 1469, 1367, 1162, 746, 600, 596; MS (ESI, *m*/*z*) 458 (M + Na^+); HRMS (ESI) Calcd for $[C_{20}H_{22}BrNNaO_3S]^+$ 458.0396, found 458.0399.

(E)-N-((4-Methoxyphenyl)sulfonyl)-N-phenyloct-2-enamide (**2m**). Pale yellow oil (93.0 mg, 80% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.95 (m, 2H), 7.51−7.44 (m, 3H), 7.31−7.22 (m, 2H), 7.04−6.90 (m, 3H), 5.46−5.41 (m, 1H), 3.87 (s, 3H), 2.01−1.92 (m, 2H), 1.32−1.21 (m, 2H), 1.21−1.09 (m, 4H), 0.81 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 163.7, 150.9, 136.2, 131.5, 130.6, 130.3, 129.7, 129.6, 121.2, 113.8, 55.6, 32.2, 31.0, 27.4, 22.2, 13.8; IR (neat): 2926, 2854, 1691 (s), 1634, 1594, 1496, 1363, 1165, 912, 743; MS (ESI, *m*/*z*) 410 (M + Na^+); HRMS (ESI) Calcd for $[C_{21}H_{25}NNaO_4S]^+$ 410.1397, found 410.1392.

(E)-N-((4-Bromophenyl)sulfonyl)-N-methyloct-2-enamide (**2n**). Pale yellow oil (66.3 mg, 65% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45−8.40 (m, 1H), 7.79−7.74 (m, 3H), 7.09−7.00 (m, 1H), 6.32 (d, 1H, *J* = 15.2 Hz,), 3.46 (s, 3H), 2.28−2.19 (m, 2H), 1.49−1.39 (m, 2H), 1.35−1.23 (m, 4H), 0.88 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 152.9, 134.4, 134.2, 132.0, 124.5, 119.7, 33.5, 32.7, 31.2, 27.6, 22.4, 13.9; IR (neat): 2919, 1683 (s), 1634, 1542, 1457, 1360, 1175; MS (ESI, *m*/*z*) 363 (M + Na^+); HRMS (ESI) Calcd for $[C_{15}H_{20}N_2NaO_5S]^+$ 363.0985, found 363.0989.

(Z)-2-(Cyclohex-2-en-1-ylidene)-N-methyl-N-tosylacetamide (**2o**). Pale yellow oil (62.4 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, 2H, *J* = 8.4 Hz), 7.30 (d, 2H, *J* = 8.0 Hz), 6.31−6.19 (m, 2H), 6.15−6.10 (m, 1H), 3.29 (s, 2H), 2.69−2.63 (m, 2H), 2.42 (s, 3H), 2.20−2.12 (m, 2H), 1.65−1.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 153.5, 144.4, 138.4, 130.2, 129.7, 127.3, 116.3, 32.8, 27.1, 25.6, 21.7, 21.5; IR (neat): 2922, 1674 (s), 1355, 1160, 1035; MS

DOI: 10.1021/acs.joc.5b01608
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(ESI, m/z) 328 ($M + Na^+$); HRMS (ESI) Calcd for $[C_{16}H_{19}NNaO_3S]^+$ 328.0978, found 328.0980.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01608.

^1H and ^{13}C NMR spectra for all described compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the National Natural Science Foundation of China (No. 21272191), the Natural Science Foundation of Fujian Province for Distinguished Young Scholars (No. 2015J06003), the President Research Funds from Xiamen University (No. 20720150045), PCSIRT, NFFTBS (No. J1310024) and XMU Training Program of Innovation and Enterpreneurship for Undergraduates (Nos. 201510384008 and 201510384018).

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