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Note

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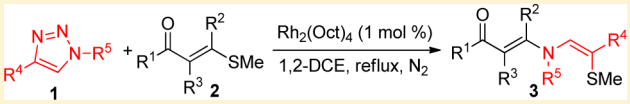
Synthesis of β-Amino-α,β-unsaturated Ketone Derivatives via Sequential Rhodium-Catalyzed Sulfur Ylide Formation/Rearrangement

Jun He, Zengming Man, Yinping Shi, and Chuan-Ying Li*

Department of Chemistry, Zhejiang Sci-Tech University, Xiasha West Higher Education District, Hangzhou 310018, China

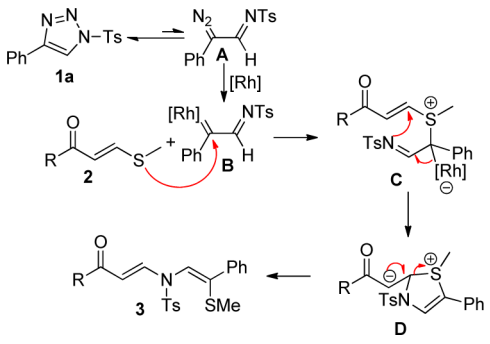
Supporting Information

ABSTRACT: In the presence of a Rh(II) catalyst and β-(methylthio)-α,β-unsaturated ketones, 1-sulfonyl-1,2,3-triazoles can be converted into functionalized β-amino-α,β-unsaturated ketones via formation of α-imino rhodium carbene/sulfur ylide and subsequent rearrangement. The products decompose to useful 2-methylthiopyrrole derivatives conveniently in high yield.



Transition-metal carbenoids are versatile intermediates in modern synthetic chemistry that undergo a wide variety of chemical transformations leading to the formation of complex molecules.[1] Although diazo compounds and *N*-tosylhydrazones are traditional precursors for metal carbenes,[2] nondiazo approaches to metal carbenes have attracted considerable attention recently.[3] In 2008, Fokin and Gevorgyan demonstrated that in the presence of rhodium(II) catalyst 1-sulfonyl-1,2,3-triazole underwent transannulation with nitrile to furnish imidazole.[4] Noticeably, the author proposed a Dimroth-type equilibrium and denitrogenative decomposition of the open chain form **A**, which led to the formation of critical intermediate α-imino carbenoid **B** (Scheme 1). This report

Scheme 1. Mechanistic Hypothesis



opens a new era for triazole chemistry,[5] and many novel transformations based on the electrophilic activity of carbene carbon and nucleophilic ability of imino nitrogen atom have been explored by Fokin, Gevorgyan, Murakami, Davies, and other groups.[6] In our related research,[7] we used ketene silyl acetal, nitrosobenzene, and a tethered carbonyl group to trap α-imino rhodium carbenoid, and 3-pyrrolin-2-one,[7a] *N*-acylamidine,[7b] and furan derivatives[7c] were obtained, respectively. Ylide formation and subsequent reactions[8] are among the most important transformations of transition metal carbenoids. α-Imino carbenoid derived from 1-sulfonyl-1,2,3-triazole could also be trapped by heteroatoms such as sulfur,[9] oxygen,[10] and nitrogen,[11] and subsequent [2,3]-sigmatropic rearrangement or cycloaddition resulted in the formation of heterocycles or compounds bearing heteroatom-substituted quaternary carbon atoms. We envisioned that if we used β-methylthio-α,β-unsaturated ketone **2** to react with in situ generated α-imino carbenoid **B** (Scheme 1), sulfur ylide **C** may be formed, and subsequent Michael addition of nitrogen would furnish zwitterionic intermediate **D**, which would lead to the formation of **3** by cleavage of carbon sulfur bond and reformation of carbon carbon double bond. Thus, the unusual insertion of three atoms into the carbon sulfur bond would be realized.

To test the above hypothesis, 3-oxobis(methylthio)ketene acetal **2a** was synthesized conveniently from acetophenone, carbon disulfide, and iodomethane.[12] Compound **2a** was treated with triazole **1a** in the presence of 1 mol % of $Rh_2(OAc)_4$ in refluxing DCE (Table 1, entry 1). After 5 h, compound **3aa** was obtained as a single isomer in 81% yield. The use of $Rh_2(Oct)_4$ substantially improved the reaction (entry 2). $Rh_2(esp)_2$ and $Rh_2(piv)_4$ worked almost equally well (entries 3 and 4), while $Rh_2(s\text{-}ntv)_4$ and $Rh_2(TFA)_4$ led to much decreased yield (entries 5 and 6). High temperature was necessary to achieve high yield (entries 7 and 9). Among the different solvent we examined (entries 2 and 8−10), 1,2-DCE was proven to be the best. Fine tuning the ratio of **1a** and **2a** did not improve the yield of **3aa** (entries 11 and 12).

In order to explore the scope of this novel transformation, a wide range of 1-sulfonyl-1,2,3-triazoles underwent the rhodium-catalyzed reaction with **2a** (Table 2). Gratifyingly, in most cases, this procedure worked well and the corresponding product **3** could be obtained in moderate to good yield. Moreover, this reaction is compatible with all kinds of functional groups including fluoro, chloro, bromo, trifluoromethyl, methoxycarbonyl, cyano, methoxy, and thienyl groups.

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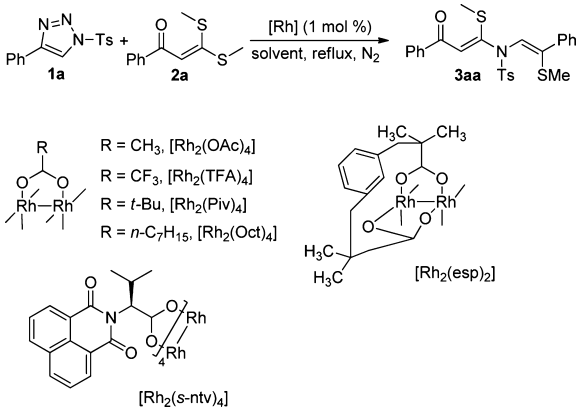
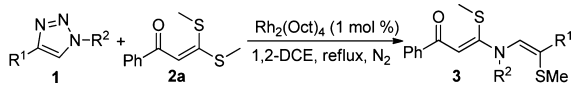
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	solvent	time (h)	yield[b] (%)
1	$Rh_2(OAc)_4$	DCE	5.0	81
2	$Rh_2(Oct)_4$	DCE	4.5	96
3	$Rh_2(esp)_2$	DCE	4.0	91
4	$Rh_2(piv)_4$	DCE	4.3	95
5	$Rh_2(s\text{-}ntv)_4$	DCE	9.0	53
6	$Rh_2(TFA)_4$	DCE	10.0	N.R.[c]
7[d]	$Rh_2(Oct)_4$	DCE	7.0	N.R.
8	$Rh_2(Oct)_4$	toluene	1.3	34
9	$Rh_2(Oct)_4$	DCM	11.0	N.R.
10	$Rh_2(Oct)_4$	$CHCl_3$	11.0	42
11[e]	$Rh_2(Oct)_4$	DCE	1.7	91
12[f]	$Rh_2(Oct)_4$	DCE	4.0	93

[a]0.2 mmol of **1a**, 0.2 mmol of **2a**, and 0.002 mmol of rhodium(II) catalyst dissolved in 2 mL of refluxing solvent under N_2. [b]Average of two runs. [c]No reaction. [d]The reaction temperature was 70 °C. [e]0.3 mmol of **1a** and 0.2 mmol of **2a** were used. [f]0.2 mmol of **1a** and 0.3 mmol of **2a** were used.

Table 2. Reaction Scope with 1-Sulfonyl-1,2,3-triazoles[a]



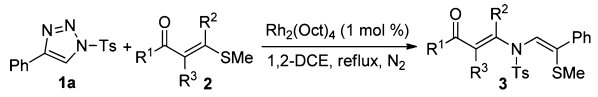
entry	**1** (R^1, R^2)	time (h)	yield[b] (%)
1	**1b** (*p*-FC_6H_4, Ts)	4.5	**3ba** (77)
2	**1c** (*p*-ClC_6H_4, Ts)	2.0	**3ca** (85)
3	**1d** (*p*-BrC_6H_4, Ts)	4.0	**3da** (88)
4	**1e** (*p*-$CF_3C_6H_4$, Ts)	5.5	**3ea** (72)
5	**1f** (*p*-$MeOOCC_6H_4$, Ts)	4.3	**3fa** (72)
6	**1g** (*p*-NCC_6H_4, Ts)	7.5	**3ga** (53)
7	**1h** (*p*-MeC_6H_4, Ts)	1.5	**3ha** (94)
8	**1i** (*p*-EtC_6H_4, Ts)	1.5	**3ia** (84)
9	**1j** (*p*-$^tBuC_6H_4$, Ts)	2.3	**3ja** (77)
10	**1k** (*p*-$MeOC_6H_4$, Ts)	1.4	**3ka** (86)
11	**1l** (*o*-$MeOC_6H_4$, Ts)	2.3	**3la** (76)
12	**1m** (*m*-$MeOC_6H_4$, Ts)	1.6	**3ma** (87)
13	**1n** (*m*-FC_6H_4, Ts)	3.8	**3na** (98)
14	**1o** (2-thienyl, Ts)	0.7	**3oa** (55)
15	**1p** (Ph, Ms)	4.4	**3pa** (88)[c]
16	**1q** (Ph, *p*-$BrC_6H_4SO_2$)	2.4	**3qa** (82)
17	**1r** (Ph, *p*-$MeOC_6H_4SO_2$)	7.0	**3ra** (64)

[a]In the presence of 0.002 mmol of $Rh_2(Oct)_4$, 0.2 mmol of triazole **1** and 0.2 mmol of **2a** were reacted in 2 mL of refluxing DCE under N_2. [b]Average of two runs. [c]Two inseparable isomers were obtained (1:0.8).

For the aryl group with different substitution patterns (R^1 in triazole **1**), the *o*-methoxy-substituted substrate **1l** led to the formation of **3la** in 76% yield (entry 11). Likely due to the steric hindrance of *o*-group, the yield of **3la** is lower than corresponding *m*eta- or *para*-isomers (entries 10 and 12). Of note is that the resulting products **3** were obtained exclusively as single isomers, except in the case of **3pa** (entry 15), for which two inseparable isomers (1:0.8) were obtained in 88% yield.

This reaction also permitted the use of a variety of different *β*-(methylthio)-*α*,*β*-unsaturated ketones (Table 3). For 3-oxobis(methylthio)keteneacetals bearing different aromatic rings (entries 1−5), **3ab**−**af** were obtained in 76−89% yield. The presence of chloro or bromo on the aromatic rings had a negative effect on the process (entries 3 and 4). Alkyl ketones **2g** and **2h** were also suitable nucleophilic reagents, leading to the formation of **3ag** and **3ah** in moderate yield, although two inseparable isomers were obtained in these cases (entries 6 and 7, the molar ratio of the isomers is 1:0.35). This reaction also worked well for **2i** and **2j**, which have only one methylthio group at the *β*-position (entries 8 and 9). Compound **2i** delivered a 1:0.4 mixture of the desired **3ai**, while **3aj** was isolated as the *trans*-isomer.

Table 3. Reaction Scope with *β*-(Methylthio)-*α*,*β*-unsaturated Ketones[a]



entry	**2** (R^1, R^2, R^3)	time (h)	yield[b] (%)
1	**2b** (*o*-MeC_6H_4, SMe, H)	1.6	**3ab** (89)
2	**2c** (*p*-$MeOC_6H_4$, SMe, H)	4.5	**3ac** (86)
3	**2d** (*p*-ClC_6H_4, SMe, H)	2.8	**3ad** (77)
4	**2e** (*p*-BrC_6H_4, SMe, H)	1.3	**3ae** (76)
5	**2f** (2-thienyl, SMe, H)	0.9	**3af** (84)
6	**2g** (Me, SMe, H)	2.0	**3ag** (59)[c]
7	**2h** (Me, SMe, Me)	5.2	**3ah** (63)[d]
8	**2i** (Ph, Ph, H)	2.0	**3ai** (82)[e]
9	**2j** (Ph, H, H)	2.4	**3aj** (86)

[a]In the presence of 0.002 mmol of $Rh_2(Oct)_4$, 0.2 mmol of triazole **1a** and 0.2 mmol of **2** were reacted in 2 mL of refluxing DCE under N_2. [b]Average of two runs. [c]Two inseparable isomers were obtained (1:0.35). [d]Two inseparable isomers were obtained (1:0.35). [e]Two inseparable isomers were obtained (1:0.4).

When we optimized the reaction conditions, we found that if we prolonged the reaction time, 2-(methylthio)-4-phenyl-1-tosyl-1*H*-pyrrole **4aa** could be isolated in about 10% yield. We were interested in this transformation and tried to improve the yield of **4aa**. Finally, we found that **4aa** was obtained in 90% yield when **3aa** was heated in refluxing toluene for 2.5 h (Table 4, entry 1). For most of the *β*-amino-*α*,*β*-unsaturated ketones we tested, the corresponding substituted pyrroles could be obtained in high yield. The mixture of the *E*- and *Z*-isomer led to the formation of **4** smoothly (Table 4, entries 3, 6, 7, and 8). When treated with 20% hydrochloric acid in THF at 30 °C, **3af** furnished compound **6** in 70% yield, together with 2-methylthioenamine **7** in 40% yield (eq 1).

In summary, *α*-imino rhodium carbenes derived from 1-sulfonyl-1,2,3-triazoles are efficiently trapped with *β*-(methylthio)-*α*,*β*-unsaturated ketones, and the in situ generated sulfur ylides undergo rearrangement to afford *β*-amino-*α*,*β*-unsatu-

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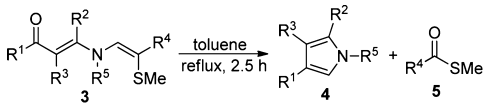
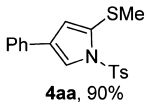
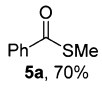
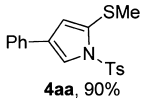
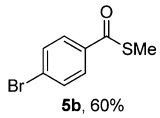
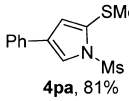
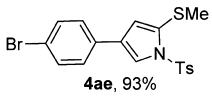
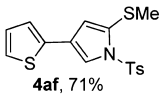
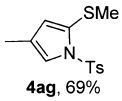
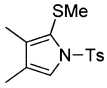
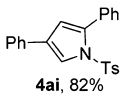
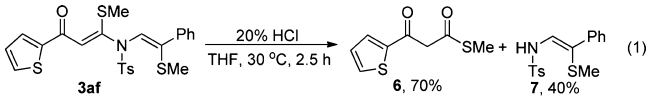
Table 4. Synthesis of Pyrrole 4[a]



3 4 5

entry	substrate 3	product 4	product 5
1	3aa	 4aa, 90%	 5a, 70%
2	3da	 4aa, 90%	 5b, 60%
3	3pa	 4pa, 81%	5a, 64%
4	3ae	 4ae, 93%	5a, 65%
5	3af	 4af, 71%	5a, 76%
6	3ag	 4ag, 69%	5a, 68%
7	3ah	 4ah, 90%	5a, 92%
8	3ai	 4ai, 82%	5a, 73%

[a]0.2 mmol of **3** was dissolved in 2 mL of dry toluene, and then the reaction mixture was stirred at 110 °C for 2.5 h.



3af 6, 70% 7, 40% (1)

rated ketones in mostly good to excellent yields. The transformation is featured with broad scope and a formal insertion of three atoms into C−S bond. The synthetic potential of the reaction is highlighted by the synthesis of 2-(methylthio)pyrrole derivatives.

EXPERIMENTAL SECTION

General Information. For proton nuclear magnetic resonance (^{1}H NMR) spectra, the chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm) or $CDCl_3$ (7.26 ppm). Coupling constants (J) are reported in hertz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. For carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra, the chemical shift is reported in ppm relative to the carbon resonance of $CDCl_3$ (77.00 ppm). High-resolution mass spectra (HRMS) were recorded using the ESI mode (TOF). All of the substituted acetophenones were commercially purchased, and the *S*-ethyl ester[13] and dithioacetals **2**[14] were prepared according to the reported methods in the literature.

Preparation of α-Oxo Ketene Dithioacetal 2. *General Procedure for Preparation of Substituted 3,3-Bis(methylthio)-1-phenylprop-2-en-1-ones* ***2****.*[14] To a stirred solution of NaH (800 mg, 20 mmol) in THF (20 mL) at 0 °C was added appropriately substituted acetophenone (10 mmol) dropwise, the suspension was stirred for 20 min, and CS_2 (11 mmol) was added dropwise. The reaction mixture (RM) was allowed to stir for 30 min, and MeI (25 mmol) was added dropwise. The RM was slowly brought up to room temperature (rt) and stirring continued for another 3 h with monitoring by TLC. The RM was poured into ice-cold water, extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under reduced pressure. The crude was recrystallized with dichloromethane and petroleum ether to give the desired product **2**. The compound **2a**,[14] **2b**,[14] **2c**,[14] **2d**,[14] **2e**,[14] **2f**,[15] **2g**,[15] and **2h**[15]were reported in the literature.

*3,3-Bis(methylthio)-1-phenylprop-2-en-1-one (**2a**):* yellow solid, 1.36 g; yield 61%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.92 (d, J = 7.2 Hz, 2H), 7.52−7.42 (m, 3H), 6.77 (s, 1H), 2.57 (s, 3H), 2.54 (s, 3H).

*3,3-Bis(methylthio)-1-(o-tolyl)prop-2-en-1-one (**2b**):* yellow solid, 1.53 g; yield 64%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.48 (d, J = 7.2 Hz, 1H), 7.33−7.30 (m, 1H), 7.23−7.21 (m, 2H), 6.41 (s, 1H), 2.54 (s, 3H), 2.49 (s, 3H), 2.48 (s, 3H).

*1-(4-Methoxyphenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2c**):* yellow solid, 1.50 g; yield 59%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.92 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.75 (s, 1H), 3.86 (s, 3H), 2.56 (s, 3H), 2.53 (s, 3H).

*1-(4-Chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2d**):* yellow solid, 1.13 g; yield 44%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.86 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 6.70 (s, 1H), 2.57 (s, 3H), 2.54 (s, 3H).

*1-(4-Bromophenyl)-3,3-bis(methylthio)prop-2-en-1-one (**2e**):* yellow solid, 1.29 g; yield 43%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.78 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 6.70 (s, 1H), 2.57 (s, 3H), 2.54 (s, 3H).

*3,3-Bis(methylthio)-1-(thiophene-2-yl)prop-2-en-1-one (**2f**):* brown solid, 1.24 g; yield 54%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.66 (d, J = 3.6 Hz, 1H), 7.55 (d, J = 4.8 Hz, 1H), 7.10 (t, J = 4.4 Hz, 1H), 6.62 (s, 1H), 2.56 (s, 3H), 2.53 (s, 3H).

*4,4-Bis(methylthio)but-3-en-2-one (**2g**):* yellow solid, 0.83 g, yield 51%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 6.04 (s, 1H), 2.47 (s, 3H), 2.43 (s, 3H), 2.20 (s, 3H).

*3-Methyl-4,4-bis(methylthio)but-3-en-2-one (**2h**):* yellow viscous liquid, 0.96 g; yield 54%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 2.39 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 2.11 (s, 3H).

Procedure for the Preparation of 3-(Methylthio)-1,3-diphenylprop-2-en-1-one ***2i****.*[16] To a stirred suspension of NaH (160 mg, 4.0 mmol) in DMF (25 mL) under an N_2 atmosphere was added dropwise a solution of aryl methyl ketone (3.7 mmol) and aryl dithioester[13] (800 mg, 4.4 mmol) in DMF (15 mL) at 0 °C, and the reaction mixture was further stirred at room temperature for 1 h. After complete formation of monothiodiketone (monitored by TLC), the reaction mixture was cooled to 0 °C, followed by dropwise addition of methyl iodide (4.4 mmol) and further stirring at room temperature for 2 h (monitored by TLC). The mixture was then poured into water (40 mL) and extracted with EtOAc (3 × 40 mL). The combined organic extracts were washed with H_2O (3 × 40 mL) followed by brine (1 × 40 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give crude products **2i**, which were purified by column chromatography using PE/EtOAc (40:1) as eluent to give the desired product **2i**.[16] The compound **2i** was reported in the literature.

*3-(Methylthio)-1,3-diphenylprop-2-en-1-one (**2i**):* yellow solid, 0.39 g; yield 42%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.98 (d, J

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J. Org. Chem. 2015, 80, 4816−4823

= 7.2 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.46−7.42 (m, 5H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.11 (s, 1H), 1.96 (s, 3H).

Procedure for the Preparation of (E)-3-(Methylthio)-1-phenylprop-2-en-1-one ***2j****.*[17] To a stirred suspension of nickel chloride hexahydrate (1.706 g, 7.2 mmol) in ethanol (10 mL) was added sodium borohydride (340 mg, 9.0 mmol), in small portions (15 min) and the mixture was further stirred for 10 min. A solution of ketene *S*,*S*-acetal **2a** (650 mg, 2.7 mmol) in ethanol (5 mL) was added to the black suspension, and the mixture was further stirred at room temperature for 10 min. It was then heated under reflux on an oil bath with stirring for 48 h until the starting material has disappeared completely (TLC). The mixture was filtered hot through a sintered funnel, and the black residue was washed with boiling chloroform (3 × 30 mL). The combined filtrate was washed with water (2 × 40 mL), and the organic layer was dried with sodium sulfate and evaporated to give a yellow viscous liquid, which was passed through a silica gel column. Elution with PE/EtOAc (30:1) as eluent gave the desired product **2j**. The compound **2j** was reported in the literature.

(E)-3-(Methylthio)-1-phenylprop-2-en-1-one ***(2j)****:* yellow viscous liquid, 78 mg; yield 16%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.98 (d, *J* = 14.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.49−7.44 (m, 2H), 6.80 (d, *J* = 14.4 Hz, 1H), 2.46 (s, 3H).

General Procedures for Formation of 1-Sulfonyl-1,2,3-triazoles 1.[5b] A scintillation vial was charged with copper(I) thiophene-2-carboxylate (CuTC, 0.095 g, 0.5 mmol, 0.1 equiv in regards to alkyne), toluene (20 mL), and the alkyne (5.0 mmol, 1 equiv). The reaction mixture was cooled in an ice−water bath. Subsequently, the sulfonyl azide (5.0 mmol, 1 equiv) was added slowly as the limiting reagent to avoid a runaway exotherm, and the reaction mixture allowed to warm to room temperature and stirred overnight. The reaction was diluted with saturated aq NH_4Cl and extracted into DCM (2 × 20 mL). The combined organics were dried (Na_2SO_4) and filtered through Celite. The eluent was concentrated in vacuo. The obtained crude product was purified by SiO_2 column chromatography (PE/EA = 30:1) to give the desired product **1**. The compounds **1a**,[5b] **1b**,[18] **1c**,[9b] **1d**,[5a] **1e**,[19] **1f**,[7a] **1g**,[6j] **1h**,[19] **1i**,[20] **1j**,[21] **1k**,[19] **1l**,[22] **1m**,[11a] **1n**,[21] **1p**,[23] **1q**,[5b] and **1r**[4]were reported in the literature.

4-Phenyl-1-tosyl-1H-1,2,3-triazole ***(1a)****:* white solid, 1.42 g; yield 95%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.32 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.48−7.34 (m, 5H), 2.44 (s, 3H).

4-(4-Fluorophenyl)-1-tosyl-1H-1,2,3-triazole ***(1b)****:* white solid, 0.82 g; yield 52%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.28 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.81 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 2H), 2.46 (s, 3H).

4-(4-Chlorophenyl)-1-tosyl-1H-1,2,3-triazole ***(1c)****:* white solid, 1.12 g; yield 76%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.30 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), δ 7.43−7.38 (m, 4H), 2.45 (s, 3H).

4-(4-Bromophenyl)-1-tosyl-1H-1,2,3-triazole ***(1d)****:* white solid, 1.05 g; yield 56%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.32 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H).

1-Tosyl-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole ***(1e)****:* white solid, 1.11 g; yield 60%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.40 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H).

Methyl 4-(1-tosyl-1H-1,2,3-triazol-4-yl)benzoate ***(1f)****:* white solid, 1.37 g; yield 77%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.40 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 3H), 2.46 (s, 3H).

4-(1-Tosyl-1H-1,2,3-triazol-4-yl)benzonitrile ***(1g)****:* white solid, 1.23 g; yield 76%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.42 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H).

4-p-Tolyl-1-tosyl-1H-1,2,3-triazole ***(1h)****:* white solid, 1.25 g; yield 80%; ^{1}H NMR (400 MHz, Chloro- form-d) δ 8.27 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 2.38 (s, 3H).

4-(4-Ethylphenyl)-1-tosyl-1H-1,2,3-triazole ***(1i)****:* white solid, 0.98 g; yield 60%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.27 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 2H), 2.67 (d, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H).

4-(4-(tert-Butyl)phenyl)-1-tosyl-1H-1,2,3-triazole ***(1j)****:* white solid, 1.05 g; yield 59%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.27 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 2.45 (s, 3H), 1.33 (s, 9H).

4-(4-Methoxyphenyl)-1-tosyl-1H-1,2,3-triazole ***(1k)****:* white solid, 1.39 g; yield 85%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.22 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 2.43 (s, 3H).

4-(2-Methoxyphenyl)-1-tosyl-1H-1,2,3-triazole ***(1l)****:* yellow solid, 1.14 g; yield 69%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.57 (s, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.39−7.31 (m, 3H), 7.10−7.02 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 3H), 2.43 (s, 3H).

4-(3-Methoxyphenyl)-1-tosyl-1H-1,2,3-triazole ***(1m)****:* white solid, 1.29 g; yield 65%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.31 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.43−7.31 (m, 5H), 6.92 (d, *J* = 7.6 Hz, 1H), 3.86 (s, 3H), 2.45 (s, 3H).

4-(3-Fluorophenyl)-1-tosyl-1H-1,2,3-triazole ***(1n)****:* white solid, 0.48 g; yield 30%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.32 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 10.2 Hz, 2H), 7.44−7.35 (m, 3H), 7.07 (t, *J* = 8.6 Hz, 1H), 2.46 (s, 3H).

4-(Thiophene-2-yl)-1-tosyl-1H-1,2,3-triazole ***(1o)****:* white solid, 0.37 g, yield 24%; mp 140−141 °C; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.21 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 3.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 5.2 Hz, 1H), 7.09 (t, *J* = 4.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 147.4, 142.5, 133.0, 130.8, 130.5, 128.7, 127.8, 126.3, 125.6, 118.1, 21.8; HRMS (ESI) calcd for $C_{13}H_{12}N_3O_2S_2^+$ 306.0371, found 306.0366.

1-(Methylsulfonyl)-4-phenyl-1H-1,2,3-triazole ***(1p)****:* white solid, 0.96 g; yield 86%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.32 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.53−7.44 (m, 2H), 7.46−7.39 (m, 1H), 3.58 (s, 3H).

1-(4-Bromophenylsulfonyl)-4-phenyl-1H-1,2,3-triazole ***(1q)****:* white solid, 1.60 g; yield 88%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.32 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.49−7.36 (m, 3H).

1-(4-Methoxyphenylsulfonyl)-4-phenyl-1H-1,2,3-triazole ***(1r)****:* white solid, 0.87 g; yield 55%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.31 (s, 1H), 8.09 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.48−7.39 (m, 2H), 7.42−7.33 (m, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H).

General Procedure for the Synthesis of β-Amino-α,β-unsaturated Ketone Derivatives 3. Under a nitrogen atmosphere, DCE (1.0 mL) was added to reaction flask charged with $Rh_2(Oct)_4$ (1.6 mg, 1 mol %) and 1-sulfonyl-1,2,3-triazoles **1** (0.2 mmol). Then a solution of α-oxo ketene dithioacetal compound **2** (0.2 mmol) in DCE (1.0 mL) was added dropwise at room temperature. The reaction mixture was stirred at reflux until TLC analysis showed that **2** was completely consumed. The reaction mixture cooled to room temperature and filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography elution with PE/DCM (1:2) as eluent to give the corresponding product **3**.

4-Methyl-N-((Z)-2-(methylthio)-2-phenylvinyl)-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide ***(3aa)****:* yellow oil, 95 mg; yield 96%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.46−7.33 (m, 9H), 6.74 (s, 1H), 6.68 (s, 1H), 2.47 (s, 3H), 2.45 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.3, 156.7, 144.9, 138.3, 136.8, 136.2, 135.2, 132.4, 129.8, 128.6, 128.5, 128.4, 127.9, 125.0, 120.8, 21.6, 16.3, 15.5; HRMS (ESI) calcd for $C_{26}H_{26}NO_3S_3^+$ 496.1075, found 496.1079.

N-((Z)-2-(4-Fluorophenyl)-2-(methylthio)vinyl)-4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide ***(3ba)****:* yellow oil, 79 mg; yield 77%; ^{1}H NMR (400 MHz, chloroform-

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J. Org. Chem. 2015, 80, 4816−4823

d) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.45−7.40 (m, 4H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.06−7.11 (m, 2H), 6.75 (s, 1H), 6.65 (s, 1H), 2.46 (s, 3H), 2.44 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.4, 164.1 (q, *J* = 124.0 Hz), 156.5, 145.0, 138.3, 135.1 (d, *J* = 3.5 Hz), 132.5, 130.2, 130.1, 129.9, 128.5, 128.0, 128.0, 125.2, 120.9 (d, *J* = 4.6 Hz), 115.8, 115.6, 21.6, 16.3, 15.6; HRMS (ESI) calcd for $C_{26}H_{25}FNO_3S_3^+$ 514.0980, found 514.0986.

N-((Z)-2-(4-Chlorophenyl)-2-(methylthio)vinyl)-4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**3ca**)*:* yellow oil, 89 mg; yield 85%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.35−7.24 (m, 8H), 6.65 (s, 1H), 6.63 (s, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.2, 156.3, 145.0, 138.2, 135.5, 135.1, 134.4, 133.8, 132.5, 129.9, 129.6, 128.8, 128.4, 127.9, 127.8, 125.7, 120.9, 21.6, 16.2, 15.6; HRMS (ESI) calcd for $C_{26}H_{25}ClNO_3S_3^+$ 530.0685, found 530.0692.

N-((Z)-2-(4-Bromophenyl)-2-(methylthio)vinyl)-4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**3da**)*:* yellow oil, 101 mg; yield 88%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.35−7.31 (m, 3H), 7.27−7.23 (m, 4H), 6.64 (s, 2H), 2.36 (s, 3H), 2.35 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.3, 156.4, 145.0, 138.2, 136.0, 135.1, 133.7, 132.5, 131.8, 129.9, 128.4, 128.3, 127.9, 127.6, 125.8, 122.6, 120.9, 21.6, 16.3, 15.7; HRMS (ESI) calcd for $C_{26}H_{25}BrNO_3S_3^+$ 574.0180, found 574.0186.

4-Methyl-N-((Z)-2-(methylthio)-2-(4-(trifluoromethyl)phenyl)-vinyl)-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)-benzenesulfonamide (**3ea**)*:* yellow oil, 81 mg; yield 72%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.45−7.34 (m, 5H), 6.85 (s, 1H), 6.72 (s, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.2, 156.4, 145.2, 140.9, 139.3 (q, *J* = 193.4 Hz), 138.1, 134.9, 132.5, 131.7, 130.0, 128.6, 128.5, 127.92, 127.90 (q, *J* = 1.1 Hz), 127.1, 125.6 (q, *J* = 1.9 Hz), 120.9, 115.7, 21.6, 16.2, 15.7; HRMS (ESI) calcd for $C_{27}H_{25}F_3NO_3S_3^+$ 564.0948, found 564.0954.

Methyl 4-((Z)-2-(4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)phenylsulfonamido)-1-(methylthio)vinyl)benzoate (**3fa**)*:* yellow oil, 80 mg; yield 72%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.68(d, *J* = 7.6 Hz, 2H), 7.46(d, *J* = 8.4 Hz, 2H), 7.37−7.32 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 6.63 (s, 1H), 3.86 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.3, 166.5, 156.5, 145.1, 141.8, 138.2, 135.0, 132.5, 132.3, 130.0, 129.9, 129.7, 129.4, 128.5, 128.3, 128.0, 126.9, 120.9, 52.2, 21.6, 16.3, 15.8; HRMS (ESI) calcd for $C_{28}H_{28}NO_5S_3^+$ 554.1129, found 554.1135.

N-((Z)-2-(4-Cyanophenyl)-2-(methylthio)vinyl)-4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**3ga**)*:* yellow oil, 55 mg; yield 53%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.36−7.44 (m, 4H), 6.96 (s, 1H), 6.70 (s, 1H), 2.46 (s, 3H), 2.41 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.1, 156.1, 145.3, 142.2, 138.0, 134.7, 132.6, 132.5, 130.0, 129.6, 128.8, 128.5, 128.2, 127.92, 127.89, 118.4, 121.1, 111.9, 21.6, 16.2, 15.9; HRMS (ESI) calcd for $C_{27}H_{25}N_2O_3S_3^+$ 521.1027, found 521.1034.

4-Methyl-N-((Z)-2-(methylthio)-2-p-tolylvinyl)-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**3ha**)*:* yellow oil, 92 mg; yield 94%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.34 (m, 4H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.74 (s, 1H), 6.63 (s, 1H), 2.47 (s, 3H), 2.44 (s, 3H), 2.37 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.4, 156.9, 144.8, 138.6, 138.3, 136.9, 135.3, 133.8, 132.4, 129.8, 129.3, 129.0, 128.4, 128.3, 127.9, 124.4, 120.6, 21.6, 21.1, 16.3, 15.5; HRMS (ESI) calcd for $C_{27}H_{28}NO_3S_3^+$ 510.1231, found 510.1232.

N-((Z)-2-(4-Ethylphenyl)-2-(methylthio)vinyl)-4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**3ia**)*:* yellow oil, 87 mg; yield 84%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.35−7.23 (m, 6H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.66 (s, 1H), 6.55 (s, 1H), 2.58 (q, *J* = 7.4 Hz, 2H), 2.39 (s, 3H), 2.35 (s, 3H), 1.71 (s, 3H), 1.16 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.3, 156.9, 144.9, 144.8, 138.3, 136.9, 135.2, 134.0, 132.4, 129.8, 129.2, 128.4, 128.3, 128.1, 127.9, 124.5, 120.6, 28.5, 21.6, 16.3, 15.5, 15.3; HRMS (ESI) calcd for $C_{28}H_{30}NO_3S_3^+$ 524.1388, found 524.1393.

N-((Z)-2-(4-tert-Butylphenyl)-2-(methylthio)vinyl)-4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)-benzenesulfonamide (**3ja**)*:* yellow oil, 84 mg; yield 77%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.33−7.30 (m, 6H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 1H), 6.57 (s, 1H), 2.39 (s, 3H), 2.35 (s, 3H), 1.72 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.3, 157.0, 151.8, 144.8, 138.3, 136.6, 135.2, 133.7, 132.4, 129.8, 128.4, 128.1, 127.9, 125.5, 125.2, 124.6, 120.6, 34.6, 31.2, 21.6, 16.3, 15.6; HRMS (ESI) calcd for $C_{30}H_{34}NO_3S_3^+$ 552.1701, found 552.1706.

N-((Z)-2-(4-Methoxyphenyl)-2-(methylthio)vinyl)-4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)-benzenesulfonamide (**3ka**)*:* yellow oil, 90 mg; yield 86%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.44−7.32 (m, 6H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.77 (s, 1H), 6.58 (s, 1H), 3.82 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.4, 160.0, 156.7, 144.8, 138.3, 137.5, 135.4, 132.4, 129.8, 129.7, 128.9, 128.4, 127.94, 127.90, 123.8, 120.7, 114.0, 55.3, 21.6, 16.3, 15.5; HRMS (ESI) calcd for $C_{27}H_{28}NO_4S_3^+$ 526.1180, found 526.1182.

N-((Z)-2-(2-Methoxyphenyl)-2-(methylthio)vinyl)-4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)-benzenesulfonamide (**3la**)*:* yellow oil, 80 mg; yield 76%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.23−7.27 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.70 (s, 1H), 6.39 (s, 1H), 3.73 (s, 3H), 2.43 (s, 3H), 2.36 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.3, 157.2, 157.1, 144.6, 138.5, 135.6, 134.0, 132.3, 131.0, 130.8, 129.8, 129.7, 128.4, 127.9, 125.1, 123.6, 120.5, 120.3, 111.0, 55.6, 21.6, 16.3, 14.6; HRMS (ESI) calcd for $C_{27}H_{28}NO_4S_3^+$ 526.1180, found 526.1182.

N-((Z)-2-(3-Methoxyphenyl)-2-(methylthio)vinyl)-4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)-benzenesulfonamide (**3ma**)*:* yellow oil, 92 mg; yield 87%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.05−6.98 (m, 2H), 6.92−6.88 (m, 1H), 6.72 (s, 1H), 6.71 (s, 1H), 3.83 (s, 3H), 2.47 (s, 3H), 2.45 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.3, 159.7, 157.0, 144.9, 138.22, 138.16, 135.6, 135.0, 132.4, 129.8, 129.6, 129.3, 128.4, 127.9, 125.1, 120.7, 120.5, 114.0, 113.8, 55.3, 21.6, 16.3, 15.5; HRMS (ESI) calcd for $C_{27}H_{28}NO_4S_3^+$ 526.1180, found 526.1182.

N-((Z)-2-(3-Fluorophenyl)-2-(methylthio)vinyl)-4-methyl-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**3na**)*:* yellow oil, 101 mg; yield 98%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.16−7.25 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.74 (s, 1H), 2.48 (s, 3H), 2.47 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.2, 164.0, 161.5, 156.6, 145.1, 139.4, 138.1 (q, *J* = 147.0 Hz), 134.9, 132.5, 130.1 (q, *J* = 4.2 Hz), 129.9, 129.3, 128.4, 127.9, 126.2, 123.94, 123.91, 120.7, 115.3 (q, *J* = 21.3 Hz), 21.6, 16.2, 15.7; HRMS (ESI) calcd for $C_{26}H_{25}FNO_3S_3^+$ 514.0980, found 514.0986.

4-Methyl-N-((Z)-2-(methylthio)-2-(thiophene-2-yl)vinyl)-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**3oa**)*:* yellow oil, 55 mg; yield 55%; 1H NMR (400 MHz, chloroform-*d*) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.46−7.36 (m, 5H), 7.32 (d, *J* = 5.2 Hz, 1H), 7.21(d, *J* = 3.2 Hz, 1H), 7.07 (s, 1H), 6.76 (s, 1H), 2.47 (s, 3H), 2.40 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.3, 156.33, 156.25, 145.1, 141.7, 138.1, 135.2, 132.5, 130.0, 128.5, 128.0, 127.9, 127.6,

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J. Org. Chem. 2015, 80, 4816−4823

126.2, 125.7, 120.7, 120.6, 21.6, 16.4, 16.1; HRMS (ESI) calcd for $C_{24}H_{24}NO_3S_4^+$ 502.0639, found 502.0645.

N-((Z)-2-(Methylthio)-2-phenylvinyl)-N-(1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)methanesulfonamide (**3pa**): yellow oil, 74 mg; two inseparable isomers were obtained (1:0.8); yield 88%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.89 (d, J = 7.2 Hz, 1.6H), 7.86 (d, J = 7.2 Hz, 2H), 7.48−7.43 (m, 2H), 7.42−7.32 (m, 6H), 7.31−7.22 (m, 6.4H), 7.13 (s, 0.8H), 6.86 (s, 1H), 6.68 (s, 1H), 6.54 (s, 0.8H), 3.27 (s, 3H), 3.19 (s, 2.4H), 2.45 (s, 3H), 2.39 (s, 2.4H), 1.83 (s, 2.4H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.9, 185.9, 155.4, 153.3, 139.2, 138.7, 138.4, 136.7, 136.1, 134.4, 132.6, 132.5, 128.9, 128.7, 128.56, 128.51, 128.50, 128.48, 128.43, 128.33, 128.15, 128.12, 125.2, 123.9, 121.5, 116.2, 41.0, 40.9, 16.9, 16.6, 15.4, 15.3; HRMS (ESI) calcd for $C_{20}H_{22}NO_3S_3^+$ 420.0762, found 420.0760.

4-Bromo-N-((Z)-2-(methylthio)-2-phenylvinyl)-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**3qa**): yellow oil, 91 mg; yield 82%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.79 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.56−7.52 (m, 1H), 7.47−7.37 (m, 7H), 6.75 (s, 1H), 6.59 (s, 1H), 2.49 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.3, 156.2, 138.5, 138.1, 137.3, 136.4, 132.6, 132.5, 129.3, 129.0, 128.8, 128.7, 128.5, 128.4, 127.9, 124.0, 121.1, 16.4, 15.5; HRMS (ESI) calcd for $C_{25}H_{23}BrNO_3S_3^+$ 560.0023, found 560.0026.

4-Methoxy-N-((Z)-2-(methylthio)-2-phenylvinyl)-N-((Z)-1-(methylthio)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**3ra**): yellow oil, 64 mg; yield 64%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.86 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.47−7.33 (m, 7H), 7.00 (d, J = 8.8 Hz, 2H), 6.76 (s, 1H), 6.68 (s, 1H), 3.86 (s, 3H), 2.48 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 188.3, 163.8, 157.1, 138.3, 136.8, 135.8, 132.4, 130.2, 129.5, 128.6, 128.5, 128.43, 128.40, 127.9, 125.2, 120.5, 114.4, 55.7, 16.3, 15.6; HRMS (ESI) calcd for $C_{26}H_{26}NO_4S_3^+$ 512.1024, found 512.1021.

4-Methyl-N-((Z)-2-(methylthio)-2-phenylvinyl)-N-((Z)-1-(methylthio)-3-oxo-3-(o-tolyl)prop-1-en-1-yl)benzenesulfonamide (**3ab**): yellow oil, 90 mg; yield 89%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.79 (d, J = 8.0 Hz, 2H), 7.48−7.28 (m, 9H), 7.20 (d, J = 8.4 Hz, 2H), 6.65 (s, 1H), 6.44 (s, 1H), 2.50 (s, 3H), 2.49 (s, 3H), 2.41 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 192.3, 156.2, 156.0, 144.8, 139.0, 137.8, 136.6, 136.2, 135.0, 131.4, 130.7, 129.8, 128.6, 128.5, 128.3, 127.8, 125.3, 125.1, 123.8, 21.5, 20.7, 16.3, 15.5; HRMS (ESI) calcd for $C_{27}H_{28}NO_3S_3^+$ 510.1231, found 510.1232.

N-((Z)-3-(4-Methoxyphenyl)-1-(methylthio)-3-oxoprop-1-en-1-yl)-4-methyl-N-((Z)-2-(methylthio)-2-phenylvinyl)benzenesulfonamide (**3ac**): yellow oil, 90 mg; yield 86%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.81 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 7.2 Hz, 2H), 7.41−7.33 (m, 5H), 6.90 (d, J = 8.8 Hz, 2H), 6.73 (s, 1H), 6.68 (s, 1H), 3.86 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 187.1, 163.1, 155.2, 144.8, 136.8, 136.1, 135.2, 131.2, 130.2, 129.8, 128.6, 128.5, 128.4, 127.9, 125.0, 121.1, 113.6, 55.4, 21.6, 16.2, 15.5; HRMS (EI) calcd for $C_{27}H_{28}NO_4S_3^+$ 526.1180, found 526.1182.

N-((Z)-3-(4-Chlorophenyl)-1-(methylthio)-3-oxoprop-1-en-1-yl)-4-methyl-N-((Z)-2-(methylthio)-2-phenylvinyl)benzenesulfonamide (**3ad**): yellow oil, 81 mg; yield 77%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.81 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.47−7.32 (m, 9H), 6.70 (s, 1H), 6.68 (s, 1H), 2.45 (s, 6H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 187.0, 157.5, 145.0, 138.7, 136.6, 136.3, 135.1, 129.9, 129.3, 128.7, 128.6, 128.4, 127.8, 127.0, 126.5, 124.8, 120.1, 21.6, 16.3, 15.5; HRMS (ESI) calcd for $C_{26}H_{25}ClNO_3S_3^+$ 530.0685, found 530.0687.

N-((Z)-3-(4-Bromophenyl)-1-(methylthio)-3-oxoprop-1-en-1-yl)-4-methyl-N-((Z)-2-(methylthio)-2-phenylvinyl)benzenesulfonamide (**3ae**): yellow oil, 87 mg; yield 76%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.81 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.45−7.33 (m, 7H), 6.70 (s, 1H), 6.67 (s, 1H), 2.45 (s, 6H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 187.2, 157.3, 144.9, 137.1, 136.6, 136.4, 135.2, 131.7, 129.9, 129.5, 128.63, 128.60, 128.4, 127.9, 127.4, 124.8, 120.1, 21.6, 16.3, 15.5; HRMS (ESI) calcd for $C_{26}H_{25}BrNO_3S_3^+$ 574.0180, found 574.0194.

4-Methyl-N-((Z)-2-(methylthio)-2-phenylvinyl)-N-((Z)-1-(methylthio)-3-oxo-3-(thiophene-2-yl)prop-1-en-1-yl)benzenesulfonamide (**3af**): yellow oil, 84 mg; yield 84%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.81 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 4.8 Hz, 1H), 7.46−7.34 (m, 8H), 7.08 (t, J = 4.2 Hz, 1H), 6.67 (s, 1H), 6.61 (s, 1H), 2.48 (s, 3H), 2.45 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 180.5, 157.0, 145.8, 144.9, 136.7, 136.0, 135.0, 133.2, 130.6, 129.9, 128.6, 128.5, 128.4, 128.0, 127.9, 124.9, 120.0, 21.6, 16.4, 15.5; HRMS (ESI) calcd for $C_{24}H_{24}NO_3S_4^+$ 502.0639, found 502.0645.

4-Methyl-N-((Z)-2-(methylthio)-2-phenylvinyl)-N-(1-(methylthio)-3-oxobut-1-en-1-yl)benzenesulfonamide (**3ag**): yellow oil, 51 mg; two inseparable isomers were obtained (1:0.35), yield 59%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.78 (d, J = 8.0 Hz, 0.71H), 7.76 (d, J = 8.0 Hz, 2H), 7.41−7.32 (m, 9.5H), 6.68 (s, 0.35H), 6.58 (s, 1H), 5.99 (s, 1.36H), 2.48 (s, 3H), 2.45 (s, 3H), 2.43 (s, 1H), 2.33 (s, 1H), 2.18 (s, 4H), 1.84 (s, 1H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 195.7, 195.2, 155.2, 155.1, 151.6, 144.8, 137.2, 136.7, 135.92, 135.88, 134.9, 134.8, 134.4, 131.0, 129.7, 129.5, 128.6, 128.5, 128.3, 128.2, 127.9, 125.9, 124.9, 123.5, 123.4, 123.1, 30.8, 29.7, 29.2, 21.6, 16.9, 16.2, 15.5, 15.4; HRMS (ESI) calcd for $C_{21}H_{24}NO_3S_3^+$ 434.0918, found 434.0923.

4-Methyl-N-(2-methyl-1-(methylthio)-3-oxobut-1-en-1-yl)-N-((Z)-2-(methylthio)-2-phenylvinyl)benzenesulfonamide (**3ah**): yellow oil, 56 mg; two inseparable isomers were obtained (1:0.35); yield 63%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.79 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 0.71H), 7.40−7.30 (m, 9.5H), 6.89 (s, 0.35H), 6.64 (s, 1H), 2.51 (s, 3H), 2.43 (s, 5H), 2.21 (s, 3H), 2.16 (s, 1H), 2.14 (s, 1H), 1.95 (s, 3H), 1.81 (s, 3H), 1.79 (s, 1H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 203.3, 201.1, 144.9, 144.6, 144.4, 141.1, 139.0, 137.7, 136.9, 135.8, 135.6, 134.3, 133.8, 129.62, 129.57, 128.54, 128.50, 128.42, 128.32, 128.29, 127.99, 127.94, 127.7, 127.1, 126.9, 124.5, 29.4, 29.3, 21.59, 21.57, 18.9, 18.4, 18.3, 17.0, 15.7, 15.3; HRMS (ESI) calcd for $C_{22}H_{26}NO_3S_3^+$ 448.1075, found 448.1072.

4-Methyl-N-((Z)-2-(methylthio)-2-phenylvinyl)-N-(3-oxo-1,3-diphenylprop-1-en-1-yl)benzenesulfonamide (**3ai**): yellow oil, 83 mg; two inseparable isomers were obtained (1:0.4); yield 82%; ^{1}H NMR (400 MHz, chloroform-*d*) δ ^{1}H NMR (400 MHz, CDCl3) δ 7.91 (d, J = 7.6 Hz, 2H), 7.86−7.83 (m, 1.4H), 7.74 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.44−7.29 (m, 9H), 7.24−7.18 (m, 9H), 6.91 (s, 1.4H), 6.86 (s, 1H), 6.39 (s, 0.4H), 2.45 (s, 1.2H), 2.39 (s, 3H), 1.73 (s, 1.2H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 192.2, 187.8, 150.0, 149.0, 144.6, 144.1, 140.2, 138.3, 138.2, 138.0, 137.1, 136.3, 136.1, 135.6, 134.7, 132.5, 132.4, 130.1, 129.9, 129.5, 129.40, 129.35, 129.26, 128.7, 128.6, 128.40, 128.33, 128.29, 128.20, 128.14, 127.96, 127.87, 127.67, 127.59, 127.42, 124.0, 119.7, 116.8, 21.61, 21.57, 15.5, 15.4. HRMS (ESI) calcd for $C_{31}H_{28}NO_3S_2^+$ 526.1510, found 526.1512.

4-Methyl-N-((Z)-2-(methylthio)-2-phenylvinyl)-N-((E)-3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**3aj**): yellow oil, 78 mg; yield 86%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.28 (d, J = 14.4 Hz, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.55−7.41 (m, 8H), 7.34 (d, J = 8.4 Hz, 2H), 6.19 (d, J = 14.4 Hz, 2H), 2.43 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 189.8, 148.9, 145.0, 141.7, 138.6, 135.3, 134.6, 132.2, 129.7, 129.5, 128.8, 128.39, 128.37, 128.0, 127.9, 118.0, 104.1, 21.5, 15.1; HRMS (ESI) calcd for $C_{25}H_{24}NO_3S_2^+$ 450.1198, found 450.1199.

Procedure for Formation of *S*-Methyl-3-Oxo-3-(thiophene-2-yl)propanethioate 6 and (*Z*)-4-Methyl-*N*-(2-(methylthio)-2-phenylvinyl)benzenesulfonamide 7. To a solvent of **3af** (100 mg, 0.2 mmol) in THF (4.0 mL) was added 20% hydrochloric acid (2 mL), and the reaction mixture was stirred at 30 °C for 2.5 h. After completion of reaction, the reaction was filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography elution with PE/DCM (1:2) as eluent to give the corresponding product **6** (28 mg, 70%) and **7** (25 mg, 40%) as a yellow viscous liquid.

S-Methyl-3-oxo-3-(thiophene-2-yl)propanethioate (**6**): yellow viscous liquid, 28 mg; yield 70%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.79 (d, J = 3.2 Hz, 1H), 7.72 (d, J = 4.8 Hz, 1H), 7.16 (t, J = 4.4 Hz, 1H), 4.16 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz,

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chloroform-*d*) δ 191.8, 184.1, 143.2, 135.3, 133.8, 128.4, 54.5, 12.2; HRMS (ESI) calcd for $C_8H_9O_2S_2^+$ 201.0044, found 201.0042.

*(Z)-4-Methyl-N-(2-(methylthio)-2-phenylvinyl)-benzenesulfonamide (**7**):* yellow viscous liquid, 25 mg; yield 40%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.49−7.43 (m, 3H), 7.36−7.29 (m, 4H), 6.87 (d, *J* = 11.2 Hz, 1H), 2.42 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 144.1, 137.0, 136.7, 129.9, 128.6, 127.6, 126.8, 126.7, 126.4, 117.9, 21.6, 16.3; HRMS (ESI) calcd for $C_{16}H_{18}NO_2S_2^+$ 320.0779, found 320.0766.

General Procedure for Formation of Pyrrole Derivative 4 and *S*-Methyl Benzothioate 5. Compound **3** (0.2 mmol) was dissolved in the dry toluene (2 mL), and then the reaction mixture was stirred at 110 °C for 2.5 h. After completion of the reaction, the reaction mixture cooled to the room temperature and filtered through a short plug of silica gel. The solution of mixture was concentrated and purified by flash chromatography (elution with PE/DCM as eluent) to give the corresponding product **4** and **5**.

*2-(Methylthio)-4-phenyl-1-tosyl-1H-pyrrole (**4aa**):* yellow viscous liquid, 62 mg, yield 90%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.64 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.30−7.25 (m, 2H), 7.22−7.16 (m, 3H), 6.53 (s, 1H), 2.31 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 145.1, 135.3, 132.9, 129.7, 128.8, 127.8, 127.4, 127.3, 127.1, 125.3, 120.3, 118.1, 21.6, 20.8; HRMS (ESI) calcd for $C_{18}H_{18}NO_2S_2^+$ 344.0779, found 344.0777.

*1-(Methylsulfonyl)-2-(methylthio)-4-phenyl-1H-pyrrole (**4pa**):* yellow viscous liquid, 43 mg; yield 81%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.57 (s, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.39−7.35 (m, 2H), 7.29−7.25 (m, 1H), 6.78 (s, 1H), 3.40 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 132.8, 128.8, 127.2, 127.1, 126.3, 125.3, 120.2, 119.2, 42.4, 21.2; HRMS (ESI) calcd for $C_{12}H_{14}NO_2S_2^+$ 268.0466, found 268.0460.

*4-(4-Bromophenyl)-2-(methylthio)-1-tosyl-1H-pyrrole (**4ae**):* yellow viscous liquid; 78 mg, yield 93%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.70 (s, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.56 (s, 1H), 2.40 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 145.3, 135.2, 132.0, 131.8, 129.8, 127.8, 127.7, 126.8, 126.2, 120.7, 120.3, 117.7, 21.7, 20.7; HRMS (ESI) calcd for $C_{18}H_{17}BrNO_2S_2^+$ 421.9884, found 421.9887.

*2-(Methylthio)-4-(thiophene-2-yl)-1-tosyl-1H-pyrrole (**4af**):* yellow viscous liquid, 50 mg; yield 71%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.63 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 4.8 Hz, 1H), 7.08 (d, *J* = 3.2 Hz, 1H), 7.01−6.99 (m, 1H), 6.49 (s, 1H), 2.41 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 145.3, 135.2, 132.0, 131.8, 129.8, 127.84, 127.78, 126.8, 126.2, 120.7, 120.3, 117.7, 21.7, 20.7; HRMS (ESI) calcd for $C_{16}H_{16}NO_2S_3^+$ 350.0343, found 350.0344.

*4-Methyl-2-(methylthio)-1-tosyl-1H-pyrrole (**4ag**):* yellow viscous liquid, 39 mg; yield 69%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.17 (s, 1H), 6.14 (s, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 144.7, 135.8, 129.6, 127.6, 126.1, 122.5, 122.0, 121.9, 21.6, 20.7, 11.8; HRMS (ESI) calcd for $C_{13}H_{16}NO_2S_2^+$ 282.0622, found 282.0617.

*3,4-Dimethyl-2-(methylthio)-1-tosyl-1H-pyrrole (**4ah**):* yellow viscous liquid, 53 mg; yield 90%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.27 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.14 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 144.4, 136.3, 133.0, 129.5, 127.7, 122.1, 122.0, 121.0, 21.6, 21.0, 10.6, 10.2; HRMS (ESI) calcd for $C_{14}H_{18}NO_2S_2^+$ 296.0779, found 296.0776.

*2,4-Diphenyl-1-tosyl-1H-pyrrole (**4ai**):* yellow viscous liquid, 61 mg; yield 82%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.73 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.39−7.24 (m, 10H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.48 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, chloroform-*d*) δ 144.8, 136.9, 135.4, 133.3, 131.2, 130.8, 129.4, 128.8, 128.4, 127.5, 127.4, 127.1, 127.0, 125.5, 119.5, 114.3, 21.6; HRMS (ESI) calcd for $C_{23}H_{20}NO_2S^+$ 374.1214, found 374.1217.

*S-Methyl benzothioate (**5a**):* yellow viscous liquid, 21 mg; yield 70%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.59−7.55 (t, *J* = 7.4 Hz, 1H), 7.47−7.43 (m, 2H), 2.48 (s, 3H).

*S-Methyl-4-bromobenzothioate (**5b**):* yellow viscous liquid, 28 mg; yield 60%; ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 2.48 (s, 3H).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra for **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: licy@zstu.edu.cn.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. (b) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (c) Lebel, H.; Marcoux, J. F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977.

(2) (a) Aggarwal, V. K.; Winn, C. L. *Acc. Chem. Res.* **2004**, *37*, 611. (b) Xiao, Q.; Zhang, Y.; Wang, J. *Acc. Chem. Res.* **2013**, *46*, 236. (c) Guo, X.; Hu, W. *Acc. Chem. Res.* **2013**, *46*, 2427. (d) Xu, X.; Doyle, M. P. *Acc. Chem. Res.* **2014**, *47*, 1396.

(3) For reviews, see: (a) Xiao, J.; Li, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 7226. (b) Zhang, L. *Acc. Chem. Res.* **2014**, *47*, 877. (c) Yeom, H.-S.; Shin, S. *Acc. Chem. Res.* **2014**, *47*, 966. For publications from our group, see: (d) Xu, C.-F.; Xu, M.; Jia, Y.-X.; Li, C.-Y. *Org. Lett.* **2011**, *13*, 1556. (e) Xu, M.; Ren, T.-T.; Li, C.-Y. *Org. Lett.* **2012**, *14*, 4902. (f) Wang, K.-B.; Ran, R.-Q.; Xiu, S.-D.; Li, C.-Y. *Org. Lett.* **2013**, *15*, 2374. (g) Yang, L.-Q.; Wang, K.-B.; Li, C.-Y. *Eur. J. Org. Chem.* **2013**, 2775. (h) Xu, M.; Ren, T.-T.; Wang, K.-B.; Li, C.-Y. *Adv. Synth. Catal.* **2013**, *355*, 2488.

(4) Horneff, T.; Chuprakov, S.; Chernyak, N.; Gevorgyan, V.; Fokin, V. V. *J. Am. Chem. Soc.* **2008**, *130*, 14972.

(5) *N*-Sulfonyl-1,2,3-triazoles are easily available by a Cu-catalyzed alkyne−azide cycloaddition (CuAAC) reaction: (a) Yoo, E. J.; Ahlquist, M.; Kim, S. H.; Bae, I.; Fokin, V. V.; Sharpless, K. B.; Chang, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 1730. (b) Raushel, J.; Fokin, V. V. *Org. Lett.* **2010**, *12*, 4952. (c) Liu, Y.; Wang, X.; Xu, J.; Zhang, Q.; Zhao, Y.; Hu, Y. *Tetrahedron* **2011**, *67*, 6294.

(6) For reviews, see: (a) Chattopadhyay, B.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2012**, *51*, 862. (b) Gulevich, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2013**, *52*, 1371. (c) Davies, H. M. L.; Alford, J. S. *Chem. Soc. Rev.* **2014**, *43*, 5151. For selected recent reports, see: (d) Miura, T.; Nakamuro, T.; Liang, C.-J.; Murakami, M. *J. Am. Chem. Soc.* **2014**, *136*, 15905. (e) Kwok, S. W.; Zhang, L.; Grimster, N. P.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2014**, *53*, 3452. (f) Yang, J.-M.; Zhu, C.-Z.; Tang, X.-Y.; Shi, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 5142. (g) Shang, H.; Wang, Y.; Tian, Y.; Feng, J.; Tang, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 5662. (h) Schultz, E. E.; Lindsay, V. N. G.; Sarpong, R. *Angew. Chem., Int. Ed.* **2014**, *53*, 9904. (i) Shi, Y.; Gulevich, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2014**, *53*, 14191. (j) Jung, D. J.; Jeon, H. J.; Kim, J. H.; Kim, Y.; Lee, S. *Org. Lett.* **2014**, *16*, 2208. (k) Miura, T.; Funakoshi, Y.; Tanaka, T.; Yada, A.; Murakami, M. *Org. Lett.* **2014**, *16*, 2760. (l) Ma, X.-J.; Pan, S.-F.; Wang, H.-X.; Chen, W.-Z. *Org. Lett.* **2014**, *16*, 4554. (m) Shen, H.; Fu, J.; Gong, J.; Yang, Z. *Org. Lett.* **2014**, *16*, 5588. (n) Zhang, Y.-S.; Tang, X.-Y.; Shi, M. *Chem. Commun.* **2014**, *50*, 15971. (o) Lee, D. J.; Shin, J.; Yoo, E. J. *Chem.*

DOI: 10.1021/acs.joc.5b00521
J. Org. Chem. 2015, 80, 4816−4823

Commun. **2014**, *50*, 6620. (p) Miura, T.; Nakamuro, T.; Hiraga, K.; Murakami, M. *Chem. Commun.* **2014**, *50*, 10474. (q) Tang, X.-Y.; Zhang, Y.-S.; He, L.; Wei, Y.; Shi, M. *Chem. Commun.* **2015**, *51*, 133. (r) Miura, T.; Tanaka, T.; Matsumoto, K.; Murakami, M. *Chem.—Eur. J.* **2014**, *20*, 16078. (s) Jeon, H. J.; Jung, D. J.; Kim, J. H.; Kim, Y.; Bouffard, J.; Lee, S. *J. Org. Chem.* **2014**, *79*, 9865. (t) Feng, J.; Wang, Y.; Li, Q.; Jiang, R.; Tang, Y. *Tetrahedron Lett.* **2014**, *55*, 6455. (u) Tian, Y.; Wang, Y.; Shang, H.; Xu, X.; Tang, Y. *Org. Biomol. Chem.* **2015**, *13*, 612.

(7) (a) Ran, R.-Q.; He, J.; Xiu, S.-D.; Wang, K.-B.; Li, C.-Y. *Org. Lett.* **2014**, *16*, 3704. (b) Ran, R.-Q.; Xiu, S.-D.; Li, C.-Y. *Org. Lett.* **2014**, *16*, 6394. (c) Zhang, W.-B.; Xiu, S.-D.; Li, C.-Y. *Org. Chem. Front.* **2015**, *2*, 47.

(8) For reviews, see: (a) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. *Chem. Rev.* **1997**, *97*, 2341. (b) Dai, L.-X.; Hou, X.-L.; Zhou, Y.-G. *Pure Appl. Chem.* **1999**, *71*, 369. (c) Aggarwal, V. K.; Winn, C. L. *Acc. Chem. Res.* **2004**, *37*, 611. (d) Ye, S.; Tang, Y.; Sun, X.-L. *Synlett.* **2005**, 2720. (e) Sun, X.-L.; Tang, Y. *Acc. Chem. Res.* **2008**, *41*, 937.

(9) (a) Miura, T.; Tanaka, T.; Yada, A.; Murakami, M. *Chem. Lett.* **2013**, *42*, 1308. (b) Yadagiri, D.; Anbarasan, P. *Chem.—Eur. J.* **2013**, *19*, 15115.

(10) (a) Boyer, A. *Org. Lett.* **2014**, *16*, 1660. (b) Medina, F.; Besnard, C.; Lacour, J. *Org. Lett.* **2014**, *16*, 3232. (c) Boyer, A. *Org. Lett.* **2014**, *16*, 5878.

(11) (a) Lee, D. J.; Han, H. S.; Shin, J.; Yoo, E. J. *J. Am. Chem. Soc.* **2014**, *136*, 11606. (b) Xu, H.-D.; Jia, Z.-H.; Xu, K.; Zhou, H.; Shen, M.-H. *Org. Lett.* **2015**, *17*, 66.

(12) Lubbe, M.; Bendrath, F.; Trabhardt, T.; Villinger, A.; Fischer, C.; Langer, P. *Tetrahedron* **2013**, *69*, 5998.

(13) Cohen, O.; Mishani, E.; Rozen, S. *Tetrahedron* **2010**, *66*, 3579.

(14) Konreddy, A. K.; Toyama, M.; Ito, W.; Bal, C.; Baba, M.; Sharon, A. *ACS Med. Chem. Lett.* **2014**, *5*, 259.

(15) Lubbe, M.; Bendrath, F.; Trabhardt, T.; Villinger, A.; Fischer, C.; Langer, P. *Tetrahedron* **2013**, *69*, 5998.

(16) Kumar, S. V.; Yadav, S. K.; Raghava, B.; Saraiah, B.; Ila, H.; Rangappa, K. S.; Hazra, A. *J. Org. Chem.* **2013**, *78*, 4960.

(17) Myrboh, B.; Singh, L. M.; Ila, H.; Junjappa, H. *Synthesis* **1982**, 307.

(18) Parr, B. T.; Green, S. A.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 4716.

(19) Miura, T.; Biyajima, T.; Fuji, T.; Murakami, M. *J. Am. Chem. Soc.* **2012**, *134*, 194.

(20) Yadagiri, D.; Anbarasan, P. *Org. Lett.* **2014**, *16*, 2510.

(21) Wang, K.; Bi, X.-H.; Xing, S.-X.; Liao, P.-Q.; Fang, Z.-X.; Meng, X.-Y.; Zhang, Q.; Liu, Q.; Ji, Y. *Green Chem.* **2011**, *13*, 562.

(22) Chuprakov, S.; Worrell, B. T.; Selander, N.; Sit, R. K.; Fokin, V. V. *J. Am. Chem. Soc.* **2014**, *136*, 195.

(23) Spangler, J. E.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 6802.

DOI: 10.1021/acs.joc.5b00521
J. Org. Chem. 2015, 80, 4816−4823