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Iron Halide-Mediated Regio- and Stereoselective Halosulfonylation of Terminal Alkynes with Sulfonylhydrazides: Synthesis of (*E*)-β-Chloro and Bromo Vinylsulfones

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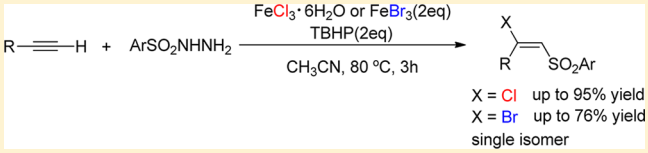
Supporting Information

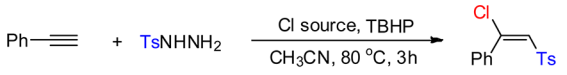
ABSTRACT: Halosulfonylation of terminal alkynes was achieved with sulfonylhydrazides as the sulfonyl precursor and inexpensive iron halide as halide source in the presence of TBHP, allowing the regio- and stereoselective generation of (*E*)-β-chloro and bromo vinylsulfones.



Functionalized alkenes are one of the most broadly existing structural motifs present in organic molecules. The difunctionalization of alkynes represents a particularly useful contribution to their synthesis.[1] In this context, halosulfonylation of terminal alkynes has attracted considerable attention[2,3] because both the vinyl halide[4] and vinyl sulfone moiety[5] in the resulting β-halide vinylsulfones are important intermediates in organic synthesis. Generally, sulfonyl bromides and iodides were applied as halosulfonylation reagents under thermal or photochemical conditions.[2] Alternative copper-catalyzed methods using more practical sulfonyl chlorides are also investigated.[3] Recently, Nakamura and co-workers demonstrated a highly regio- and stereoselective $Fe(acac)_2$-catalyzed chlorosulfonylation with aromatic sulfonyl chlorides.[6] However, the usage of a phosphine ligand and harsh reaction conditions restricted their practical utility on a larger scale process. In recent years, we have focused our efforts on the construction of sulfone-containing molecules based on sulfonyl radical addition using sulfonylhydrazides as the sulfonyl precursor.[7] It has been found that $FeCl_3$ could act as Cl source in some radical reactions.[8] In light of these factors, we hypothesized that the combination of sulfonylhydrazides with $FeCl_3$ might be utilized to allow chlorosulfonylation of alkynes. Herein, we present a full account of this work including extension to bromosulfonylation by using $FeBr_3$ as the Br source.

We initially examined the chlorosulfonylation of phenylacetylene **1a** with *p*-toluenesulfonylhydrazide ($TsNHNH_2$) **2a** and $FeCl_3·6H_2O$ in the presence of 2 equiv of TBHP as the oxidant (Table 1). After screening the loading of $FeCl_3·6H_2O$ (entries 1−3), 2.0 equiv afforded the best result, providing (*E*)-β-chloro vinylsulfone **3aa** in 95% yield (entry 2). Notably, this reaction exhibited high selectivity, and no other isomers were observed. The reaction worked equally well with anhydrous $FeCl_3$ (entry 4), whereas no desired product was isolated by using LiCl as the chloride source (entry 5). Reducing the amount of $TsNHNH_2$ led to a lower yield (entry 6). The reaction in water did not work (entry 7), while other solvents, such as EtOAc, DCE, toluene, and dioxane, were less effective (entries 8−11).

Table 1. Optimized Reaction Conditions[a]



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

entry	Cl source (equiv)	solvent	yield (%)
1	$FeCl_3·6H_2O$ (1.5)	MeCN	74
2	$FeCl_3·6H_2O$ (2.0)	MeCN	95
3	$FeCl_3·6H_2O$ (2.5)	MeCN	87
4	$FeCl_3$ (2.0)	MeCN	94
5	LiCl (2.0)	MeCN	trace
6[b]	$FeCl_3·6H_2O$ (2.0)	MeCN	88
7	$FeCl_3·6H_2O$ (2.0)	H_2O	trace
8	$FeCl_3·6H_2O$ (2.0)	EtOAc	83
9	$FeCl_3·6H_2O$ (2.0)	DCE	64
10	$FeCl_3·6H_2O$ (2.0)	toluene	67
11	$FeCl_3·6H_2O$ (2.0)	dioxane	68

[a]Reaction conditions: alkynes (0.5 mmol), sulfonylhydrazides (1.4 equiv), Cl source, and TBHP (2 equiv, 70% water solution) in CH_3CN (2 mL) at 80 °C for 3 h. [b]1.2 equiv of $TsNHNH_2$ was used.

Encouraged by these results, we applied the above chlorosulfonylation protocol to a range of alkynes **1** and arylsulfonylhydrazides **2** (Table 2). The scope of arylsulfonylhydrazides **2** was initially explored in the presence of phenylacetylene **1a**. Gratifyingly, introduction of Me, MeO, and halogen groups into the phenyl ring of sulfonylhydrazides was well-tolerated, and the chlorosulfonylation products were isolated in good to excellent yield. Then, the scope of alkynes **1** was explored in the reaction with $TsNHNH_2$ (**2a**). Aromatic alkynes with a wide range of functional groups, such as Me, $(CH_2)_4CH_3$, MeO, $CH_3(CH_2)_4O$, F, Cl, Br, and CF_3, were well-tolerated (products

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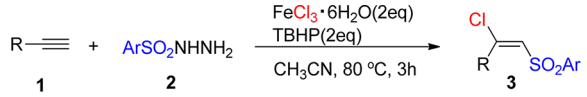
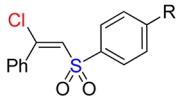
Table 2. $FeCl_3·6H_2O$-Mediated Chlorosulfonylation of Alkynes with Sulfonylhydrazides[a]



1 2 3



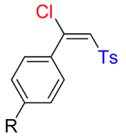
3aa, R = Me 95%

3ab, R = H 78%

3ac, R = MeO 82%

3ad, R = Cl 80%

3ae, R = Br 90%



3ba, R = Me 82%

3ca, R = $(CH_2)_4CH_3$ 85%

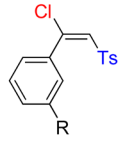
3da, R = MeO 74%

3ea, R = $CH_3(CH_2)_4O$ 58%

3fa, R = F 83%

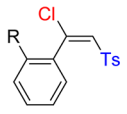
3ga, R = Cl 79%

3ha, R = Br 75%



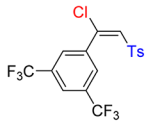
3ia, R= Cl 67%

3ja, R= Br 67%

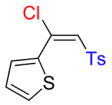


3ka, R= Me 69%

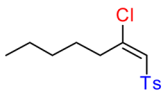
3la, R= Cl 70%



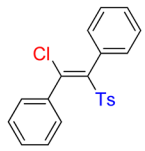
3ma, 61%



3na, 49%



3oa, 36%



3pa, trace

[a]Reaction conditions: alkynes (0.5 mmol), sulfonylhydrazides (1.4 equiv), $FeCl_3·6H_2O$ (2 equiv), and TBHP (2 equiv, 70% water solution) in CH_3CN (2 mL) at 80 °C for 3 h.

3ba–**3ma**). The majority of the alkynes with *para*-substitutions gave good yields, while the *ortho*- and *meta*-substituted alkynes afforded a slightly lower yield. Thiophenyl-substituted alkyne could also be employed in this reaction to afford the product **3na** in moderate yields. Notably, aliphatic alkyne successfully underwent halosulfonylation give **3oa**, albeit in a low yield. However, the internal alkyne failed in the reaction to give the desired product **3pa** due to the steric effect. To our delight, the known compounds are formed in higher yields under milder reaction conditions compared with the reported method.[9]

Inspired by the excellent results above, we initiated further studies of bromosulfonylation by replacing $FeCl_3·6H_2O$ with $FeBr_3$. As described in Table 3, with various alkynes and sulfonylhydrazides examined in the chlorosulfonylation reaction (Table 2), the desired (*E*)-*β*-bromo vinylsulfones were successfully achieved in the presence of $FeBr_3$ under the optimal reaction conditions. Generally, bromosulfonylation exhibited slightly lower reactivity than chlorosulfonylation, giving moderate yields.

On the basis of the above results and literature reports,[4,6,10] the proposed mechanism is illustrated in Scheme 1. Initially, the *tert*-butoxyl and *tert*-butylperoxy radicals were generated in an iron catalyst–TBHP catalytic system.[10] Then, hydrogen abstraction of sulfonylhydrazides by the resultant radicals generated sulfonyl radicals from a series of steps with the release of molecular nitrogen.[4] The iron halide also acted as a Lewis acid to activate the alkynes. Subsequently, the radical addition of sulfonyl radicals to the Fe-coordinated alkynes (**A**) from the opposite side of the Fe moiety at the terminal position would lead to regio- and stereoselective formation of the Fe(IV) intermediate (**B**). Finally, reductive elimination of Fe(IV) intermediate **B** occurred to afford the (*E*)-*β*-halo-vinylsulfones with the generation of the Fe(II) catalyst. Notably, the formation of sulfonyl halide (**C**) was detected in the halosulfonylation, which probably was due to the direct trapping of the sulfonyl radicals with a halide atom of the iron halide.[8] Thus we speculated that the difference in the reactivity between chlorosulfonylation and bromosulfonylation might result from the easier abstraction of Br than Cl by sulfonyl radicals.

In summary, we have developed a highly regio- and stereoselective oxidative halosulfonylation of alkynes using sulfonylhydrazides as the sulfonyl precursor and inexpensive iron halide as the halide source. It provides efficient and general access to both (*E*)-*β*-chloro and bromo vinylsulfones.

EXPERIMENTAL SECTION

General Procedures. All reagents and solvents were used without purification. $FeCl_3·6H_2O$ and $FeCl_3$ was purchased from Sinopharm Chemical (≥99 and ≥97%, respectively). $FeBr_3$ was purchased from J&K Chemical (97%). Melting points are uncorrected. The ^1H NMR

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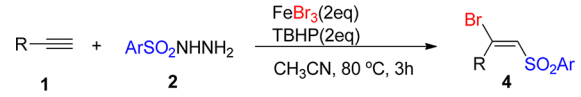
Table 3. $FeBr_3$-Mediated Bromosulfonylation of Alkynes with Sulfonylhydrazides[a]



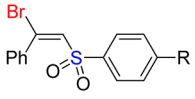
4aa, R = Me 53%

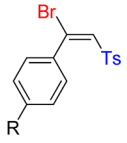
4ab, R = H 40%

4ac, R = MeO 60%

4ad, R = Cl 48%

4ae, R = Br 37%





4ba, R = Me 51%

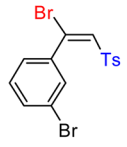
4ca, R = $(CH_2)_4CH_3$ 50%

4da, R = MeO 54%

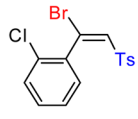
4ea, R = F 36%

4fa, R = Cl 76%

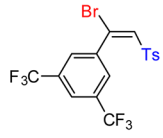
4ga, R = Br 68%



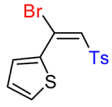
4ha, 47%



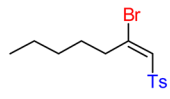
4ia, 49%



4ja, 49%



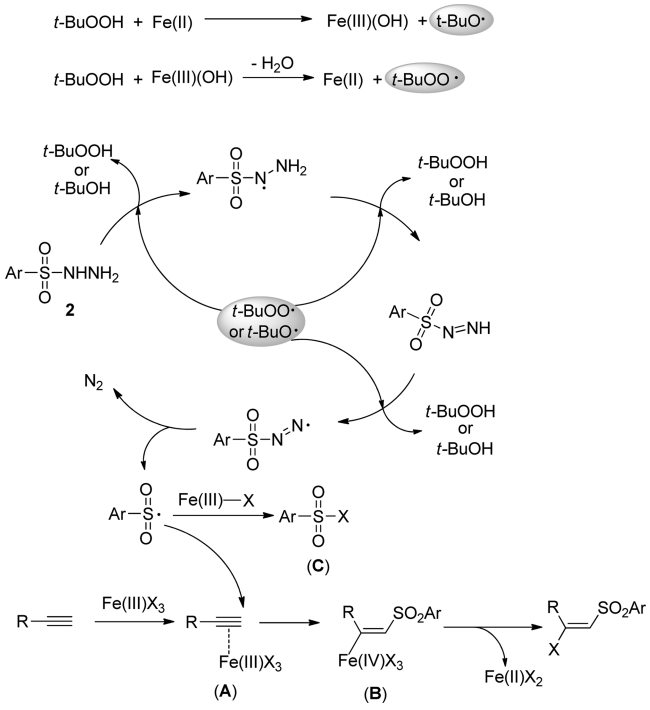
4ka, 42%



4la, 36%

[a]Reaction conditions: alkynes (0.5 mmol), sulfonylhydrazides (1.4 equiv), $FeBr_3$ (2 equiv), and TBHP (2 equiv, 70% water solution) in CH_3CN (2 mL) at 80 °C for 3 h.

Scheme 1. Proposed Mechanism



and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ at 500 and 125 MHz, respectively, with TMS as the internal standard. Chemical shifts (δ) are expressed in parts per million, and coupling constants J are given in hertz. High-resolution mass spectra (HRMS) were obtained on a TOF MS instrument with APCI source.

Typical Procedure for the Synthesis of (*E*)-β-Halovinylsulfones. To a solution of sulfonylhydrazides (0.7 mmol), $FeCl_3 \cdot 6H_2O$, or $FeBr_3$ (1.0 mmol) in CH_3CN (2 mL) were added alkynes (0.5 mmol) and TBHP (1.0 mmol, 70% water solution), and the mixture was stirred at 80 °C for 3 h. After removal of solvent under reduced pressure, the residue was purified by chromatography (petroleum/ethyl acetate = 20:1) to give the desired products.

*(E)-1-((2-Chloro-2-phenylvinyl)sulfonyl)-4-methylbenzene (**3aa**):*[6] white solid (138.8 mg, 95%); mp 97–98 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.3 Hz, 2H), 7.42 (m, 1H), 7.39–7.33 (m, 4H), 7.20 (d, J = 8.2 Hz, 2H), 6.92 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 144.6, 137.6, 134.4, 131.0, 130.6, 129.6, 128.8, 128.0, 127.8, 21.6.

*(E)-(1-Chloro-2-(phenylsulfonyl)vinyl)benzene (**3ab**):* white solid (108.5 mg, 78%); mp 73–74 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.5, 1.2 Hz, 2H), 7.56–7.52 (m, 1H), 7.44–7.40 (m, 2H), 7.40–7.32 (m, 5H), 6.95 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 140.5, 134.3, 133.5, 130.9, 130.7, 129.0, 128.8, 128.1, 127.7; HRMS (APCI) calcd for $C_{14}H_{12}ClO_2S$ $(M + H)^+$ 279.0247, found 279.0244.

*(E)-1-((2-Chloro-2-phenylvinyl)sulfonyl)-4-methoxybenzene (**3ac**):*[6] white solid (126.4 mg, 82%); mp 104–106 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.9 Hz, 2H), 7.42 (m, 1H), 7.39–7.34 (m, 4H), 6.93 (s, 1H), 6.85 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 147.5, 134.4, 132.0, 131.4, 130.6, 130.0, 128.9, 128.0, 114.2, 55.7.

*(E)-1-Chloro-4-((2-chloro-2-phenylvinyl)sulfonyl)benzene (**3ad**):*[6] white solid (125.0 mg, 80%); mp 107–108 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.7 Hz, 2H), 7.45–7.41 (m, 1H), 7.36–7.33 (m, 6H), 6.94 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 140.3, 138.9, 134.1, 130.9, 130.7, 129.2, 129.2, 128.8, 128.1.

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(E)-1-Bromo-4-((2-chloro-2-phenylvinyl)sulfonyl)benzene (**3ae**): white solid (161.3 mg, 90%); mp 103−104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.7 Hz, 2H), 7.43 (t, J = 2.1 Hz, 2H), 7.41 (d, J = 1.8 Hz, 1H), 7.34 (d, J = 1.6 Hz, 2H), 7.34 (s, 2H), 6.94 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 139.4, 134.1, 132.2, 130.8, 130.6, 129.2, 128.8, 128.7, 128.0; HRMS (APCI) calcd for $C_{14}H_{11}BrClO_2S$ (M + H)$^+$ 356.9352, found 356.9348.

(E)-1-((2-Chloro-2-(p-tolyl)vinyl)sulfonyl)-4-methylbenzene (**3ba**): white solid (125.5 mg, 82%); mp 135−137 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.86 (s, 1H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 144.6, 141.2, 137.8, 131.5, 130.3, 129.6, 128.9, 128.7, 127.8, 21.6, 21.5; HRMS (APCI) calcd for $C_{16}H_{16}ClO_2S$ (M + H)$^+$ 307.0560, found 307.0557.

(E)-1-((2-Chloro-2-(4-pentylphenyl)vinyl)sulfonyl)-4-methylbenzene (**3ca**): pale oil (154.7 mg, 85%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 6.89 (s, 1H), 2.64−2.61 (m, 2H), 2.38 (s, 3H), 1.65−1.61 (m, 2H), 1.37−1.33 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 146.2, 144.4, 137.8, 131.6, 130.5, 129.5, 129.0, 128.0, 127.8, 35.8, 31.5, 30.9, 22.5, 21.6, 14.0; HRMS (APCI) calcd for $C_{20}H_{24}ClO_2S$ (M + H)$^+$ 363.1186, found 363.1182.

(E)-1-((2-Chloro-2-(4-methoxyphenyl)vinyl)sulfonyl)-4-methylbenzene (**3da**):[6] white solid (118.7 mg, 74%); mp 85−86 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.9 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 6.83 (s, 1H), 3.85 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 148.0, 144.5, 137.9, 131.0, 129.7, 129.6, 127.7, 126.5, 113.4, 55.4, 21.6.

(E)-1-((2-Chloro-2-(4-(pentyloxy)phenyl)vinyl)sulfonyl)-4-methylbenzene (**3ea**): pale oil (110.3 mg, 52%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.84 (s, 1H), 3.99 (t, J = 6.5 Hz, 2H), 2.40 (s, 3H), 1.83−1.79 (m, 2H), 1.48−1.40 (m, 4H), 0.96 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 148.0, 144.4, 137.8, 130.9, 129.6, 129.4, 127.6, 126.1, 113.7, 68.1, 28.7, 28.1, 22.3, 21.5, 13.9; HRMS (APCI) calcd for $C_{20}H_{24}ClO_3S$ (M + H)$^+$ 379.1135, found 379.1132.

(E)-1-((2-Chloro-2-(4-fluorophenyl)vinyl)sulfonyl)-4-methylbenzene (**3fa**):[6] white solid (128.3 mg, 83%); mp 98−99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.41 (dd, J = 8.9, 5.2 Hz, 2H), 7.24 (dd, J = 8.4, 0.5 Hz, 2H), 7.05 (t, J = 8.7 Hz, 2H), 6.91 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0 (d, J = 250.6 Hz), 146.7, 144.9, 137.6, 131.3, 131.2, 130.4 (d, J = 3.4 Hz), 129.8, 127.7, 115.3 (d, J = 22.0 Hz), 21.6.

(E)-1-Chloro-4-(1-chloro-2-tosylvinyl)benzene (**3ga**): white solid (128.9 mg, 79%); mp 96−98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.34 (s, 4H), 7.25 (d, J = 8.0 Hz, 2H), 6.91 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 144.9, 137.5, 137.0, 132.7, 131.4, 130.3, 129.8, 128.3, 127.8, 21.6; HRMS (APCI) calcd for $C_{15}H_{13}Cl_2O_2S$ (M + H)$^+$ 327.0013, found 327.0015.

(E)-1-Bromo-4-(1-chloro-2-tosylvinyl)benzene (**3ha**): white solid (139.6 mg, 75%); mp 101−103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.91 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 145.0, 137.4, 133.2, 131.5, 131.3, 130.5, 129.8, 127.8, 125.3, 21.6; HRMS (APCI) calcd for $C_{15}H_{13}BrClO_2S$ (M + H)$^+$ 370.9508, found 370.9506.

(E)-1-Chloro-3-(1-chloro-2-tosylvinyl)benzene (**3ia**): white solid (109.9 mg, 67%); mp 87−89 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.3 Hz, 2H), 7.340−7.37 (m, 1H), 7.31 (d, J = 5.0 Hz, 2H), 7.23 (dd, J = 14.5, 6.4 Hz, 3H), 6.96 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 145.0, 137.3, 135.9, 134.1, 132.2, 130.6, 129.8, 129.39, 128.5, 127.8, 127.2, 21.6; HRMS (APCI) calcd for $C_{15}H_{13}Cl_2O_2S$ (M + H)$^+$ 327.0013, found 327.0011.

(E)-1-Bromo-3-(1-chloro-2-tosylvinyl)benzene (**3ja**): white solid (128.4 mg, 69%); mp 91−92 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.34 (s, 4H), 7.25 (d, J = 8.3 Hz, 2H), 6.91 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 144.9, 137.5, 137.0, 132.7, 131.4, 130.3, 129.8, 128.3, 127.8, 21.6; HRMS (APCI) calcd for $C_{15}H_{13}BrClO_2S$ (M + H)$^+$ 370.9508, found 370.9503.

(E)-1-(1-Chloro-2-tosylvinyl)-2-methylbenzene (**3ka**): white solid (105.5 mg, 69%); mp 80−81 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 8.3 Hz, 2H), 7.30 (m, 1H), 7.17 (dd, J = 7.6, 5.3 Hz, 3H), 7.13−7.08 (m, 2H), 7.00 (s, 1H), 2.40 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 144.6, 137.4, 135.9, 133.9, 132.6, 130.3, 130.2, 129.6, 128.6, 127.9, 125.5, 21.6, 19.1; HRMS (APCI) calcd for $C_{16}H_{16}ClO_2S$ (M + H)$^+$ 307.0560, found 307.0557.

(E)-1-Chloro-2-(1-chloro-2-tosylvinyl)benzene (**3la**): white solid (114.8 mg, 70%); mp 112−114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.37−7.31 (m, 4H), 7.23 (d, J = 8.0 Hz, 2H), 6.97 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 144.7, 137.0, 133.5, 133.0, 132.2, 131.4, 130.6, 129.7, 129.6, 128.0, 126.6, 21.6; HRMS (APCI) calcd for $C_{15}H_{13}Cl_2O_2S$ (M + H)$^+$ 327.0013, found 327.0011.

(E)-1-(1-Chloro-2-tosylvinyl)-3,5-bis(trifluoromethyl)benzene (**3ma**): white solid (130.9 mg, 61%); mp 169−170 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.78 (s, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.09 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 143.4, 136.9, 136.4, 133.8, 131.7 (q, J = 33.9 Hz), 130.0, 129.0 (d, J = 2.8 Hz), 127.7, 124.1 (m), 122.8 (q, J = 271.4 Hz), 21.5; HRMS (APCI) calcd for $C_{17}H_{12}ClF_6O_2S$ (M + H)$^+$ 429.0151, found 429.0149.

(E)-2-(1-Chloro-2-tosylvinyl)thiophene (**3na**): brown solid (72.6 mg, 49%); mp 54−57 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, J = 3.8, 1.1 Hz, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.54 (dd, J = 5.1, 1.1 Hz, 1H), 7.25 (d, J = 7.8 Hz, 2H), 7.05 (dd, J = 5.0, 3.8 Hz, 1H), 6.82 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 139.9, 137.6, 135.3, 133.8, 131.5, 129.7, 129.3, 127.6, 127.4, 21.6; HRMS (APCI) calcd for $C_{13}H_{12}ClO_2S_2$ (M + H)$^+$ 298.9967, found 298.9964.

(E)-1-((2-Chlorohept-1-en-1-yl)sulfonyl)-4-methylbenzene (**3oa**): pale oil (51.3 mg, 36%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.52 (s, 1H), 2.95−2.91 (m, 2H), 2.45 (s, 3H), 1.62−1.56 (m, 2H), 1.32 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 144.8, 138.5, 130.0, 128.9, 127.4, 34.8, 30.9, 27.2, 22.3, 21.6, 13.8; HRMS (APCI) calcd for $C_{14}H_{20}ClO_2S$ (M + H)$^+$ 287.0873, found 287.0868.

(E)-1-((2-Bromo-2-phenylvinyl)sulfonyl)-4-methylbenzene (**4aa**):[11] white solid (89.5 mg, 53%); mp 94−96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.3 Hz, 2H), 7.40−7.37 (m, 1H), 7.33 (dd, J = 4.9, 1.5 Hz, 4H), 7.20 (d, J = 8.0 Hz, 2H), 7.14 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 138.3, 137.5, 136.1, 134.3, 130.4, 129.7, 128.6, 128.0, 127.9, 21.6.

(E)-(1-Bromo-2-(phenylsulfonyl)vinyl)benzene (**4ab**):[11] white solid (64.5 mg, 40%); mp 77−78 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J = 8.3, 1.1 Hz, 2H), 7.54 (dd, J = 11.7, 4.2 Hz, 1H), 7.41−7.36 (m, 3H), 7.33−7.29 (m, 4H), 7.17 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 138.8, 136.0, 134.2, 133.6, 130.5, 129.0, 128.6, 128.1, 127.8.

(E)-1-((2-Bromo-2-phenylvinyl)sulfonyl)-4-methoxybenzene (**4ac**): white solid (106.5 mg, 60%); mp 96−98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.9 Hz, 2H), 7.39−7.31 (m, 5H), 7.15 (s, 1H), 6.85 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 137.8, 136.2, 134.7, 131.9, 130.3, 130.0, 128.6, 128.0, 114.3, 55.7; HRMS (APCI) calcd for $C_{15}H_{14}BrO_3S$ (M + H)$^+$ 352.9847, found 352.9844.

(E)-1-((2-Bromo-2-phenylvinyl)sulfonyl)-4-chlorobenzene (**4ad**): white solid (86.2 mg, 48%); mp 124−125 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.47 (m, 2H), 7.42−7.48 (m, 1H), 7.36−7.31 (m, 4H), 7.28 (dd, J = 8.3, 1.3 Hz, 2H), 7.16 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 139.4, 138.8, 135.9, 134.1, 130.6, 129.3, 129.3, 128.6, 128.1; HRMS (APCI) calcd for $C_{14}H_{11}BrClO_2S$ (M + H)$^+$ 356.9352, found 356.9348.

(E)-1-Bromo-4-((2-bromo-2-phenylvinyl)sulfonyl)benzene (**4ae**): white solid (74.4 mg, 37%); mp 121−123 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.7 Hz, 2H), 7.42−7.38 (m, 3H), 7.35−7.32 (m, 2H), 7.29−7.26 (m, 2H), 7.16 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 139.3, 135.9, 134.0, 132.3, 130.6, 129.3, 128.9, 128.6, 128.1;

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HRMS (APCI) calcd for $C_{14}H_{11}Br_2O_2S$ $(M + H)^+$ 400.8847, found 400.8843.

*(E)-1-((2-Bromo-2-(p-tolyl)vinyl)sulfonyl)-4-methylbenzene (**4ba**):*[12] white solid (89.2 mg, 51%); mp 125−126 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 7.08 (s, 1H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 140.9, 138.7, 137.6, 133.7, 133.3, 129.7, 128.7, 128.6, 127.8, 21.6, 21.5.

*(E)-1-((2-Bromo-2-(4-pentylphenyl)vinyl)sulfonyl)-4-methylbenzene (**4ca**):* pale oil (101.6 mg, 50%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 4.1 Hz, 3H), 2.63−2.59 (m, 2H), 2.37 (s, 3H), 1.66−1.59 (m, 2H), 1.39−1.31 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 144.5, 138.8, 137.5, 136.5, 134.0, 129.6, 128.8, 128.0, 127.8, 35.8, 31.5, 30.9, 22.5, 21.6, 14.0; HRMS (APCI) calcd for $C_{20}H_{24}BrO_2S$ $(M + H)^+$ 407.0680, found 407.0684.

*(E)-1-((2-Bromo-2-(4-methoxyphenyl)vinyl)sulfonyl)-4-methylbenzene (**4da**):*[12] white solid (99.5 mg, 54%); mp 101−103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.06 (s, 1H), 6.84 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 144.6, 138.7, 137.7, 133.1, 130.8, 129.7, 128.2, 127.8, 113.3, 55.4, 21.6.

*(E)-1-((2-Bromo-2-(4-fluorophenyl)vinyl)sulfonyl)-4-methylbenzene (**4ea**):*[12] white solid (64.2 mg, 36%); mp 89−91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.37−7.34 (m, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.13 (s, 1H), 7.03 (t, J = 8.6 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (d, J = 250.6 Hz), 144.9, 137.4, 136.9, 134.6, 132.1 (d, J = 3.4 Hz), 131.0 (d, J = 8.7 Hz), 129.8, 127.8, 115.2 (d, J = 22.0 Hz), 21.6.

*(E)-1-((2-Bromo-2-(4-chlorophenyl)vinyl)sulfonyl)-4-methylbenzene (**4fa**):* white solid (140.8 mg, 76%); mp 123−124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.13 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 137.3, 136.7, 136.5, 134.8, 134.5, 130.1, 129.8, 128.3, 127.8, 21.6; HRMS (APCI) calcd for $C_{15}H_{13}BrClO_2S$ $(M + H)^+$ 370.9508, found 370.9505.

*(E)-1-Bromo-4-(1-bromo-2-tosylvinyl)benzene (**4ga**):* white solid (141.5 mg, 68%); mp 137−139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 7.13 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 137.3, 136.5, 135.0, 134.8, 131.3, 130.2, 129.8, 127.8, 125.0, 21.7; HRMS (APCI) calcd for $C_{15}H_{13}Br_2O_2S$ $(M + H)^+$ 414.9003, found 414.9001.

*(E)-1-Bromo-3-(1-bromo-2-tosylvinyl)benzene (**4ha**):* white solid (97.5 mg, 47%); mp 111−112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.47 (m, 3H), 7.31−7.29 (m, 1H), 7.25−7.21 (m, 4H), 7.18 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 137.8, 137.1, 135.7, 135.6, 133.2, 130.9, 129.8, 129.6, 127.9, 127.3, 121.9, 21.7; HRMS (APCI) calcd for $C_{15}H_{13}Br_2O_2S$ $(M + H)^+$ 414.9003, found 414.9006.

*(E)-1-(1-Bromo-2-tosylvinyl)-2-chlorobenzene (**4ia**):* white solid (91.4 mg, 49%); mp 97−98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.35−7.31 (m, 4H), 7.24 (d, J = 8.0 Hz, 2H), 7.16 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 136.8, 135.9, 135.0, 134.3, 131.9, 131.2, 130.1, 129.8, 129.7, 128.0, 126.6, 21.7; HRMS (APCI) calcd for $C_{15}H_{13}BrClO_2S$ $(M + H)^+$ 370.9508, found 370.9507.

*(E)-1-(1-Bromo-2-tosylvinyl)-3,5-bis(trifluoromethyl)benzene (**4ja**):* white solid (123.2 mg 54%); mp 147−149 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.71 (s, 2H), 7.48 (d, J = 8.3 Hz, 2H), 7.30 (s, 1H), 7.24 (d, J = 8.1 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 138.1, 137.1, 136.7, 133.0, 131.7 (q, J = 33.8 Hz), 130.0, 128.7 (d, J = 3.2 Hz), 127.7, 123.8 (m), 122.7 (q, J = 271.3 Hz), 21.5; HRMS (APCI) calcd for $C_{17}H_{12}BrF_6O_2S$ $(M + H)^+$ 472.9646, found 472.9641.

*(E)-2-(1-Bromo-2-tosylvinyl)thiophene (**4ka**):* brown solid (71.9 mg, 42%); mp 84−86 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, J = 3.8, 1.2 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.53 (dd, J = 5.1, 1.2 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.07 (s, 1H), 7.04 (dd, J = 5.1, 3.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 137.3, 137.1, 133.3, 133.3, 131.3, 129.7, 129.4, 127.7, 127.3, 21.6; HRMS (APCI) calcd for $C_{13}H_{12}BrO_2S_2$ $(M + H)^+$ 342.9462, found 342.9465.

*(E)-1-((2-Bromohept-1-en-1-yl)sulfonyl)-4-methylbenzene (**4la**):*[12] pale oil (59.6 mg, 36%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.68 (s, 1H), 2.98−2.95 (m, 2H), 2.38 (s, 3H), 1.54−1.50 (m, 2H), 1.25 (m, 4H), 0.83 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 144.9, 138.3, 132.1, 130.1, 127.5, 36.8, 30.8, 28.1, 22.4, 21.7, 13.9.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For recent selected examples of difunctionalization of terminal alkyne, see: (a) Goossen, L. J.; Rodríguez, N.; Goossen, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 9592. (b) Mizuno, A.; Kusama, H.; Iwasawa, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 8318. (c) Sha, F.; Huang, X. *Angew. Chem., Int. Ed.* **2009**, *48*, 3458. (d) Ye, L.; Cui, L.; Zhang, G.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 3258. (e) Dutta, B.; Gilboa, N.; Marek, I. *J. Am. Chem. Soc.* **2010**, *132*, 5588. (f) Zhang, C.; Jiao, N. *J. Am. Chem. Soc.* **2010**, *132*, 28. (g) Kuang, J.; Ma, S. *J. Am. Chem. Soc.* **2010**, *132*, 1786. (h) Li, Y.; Liu, X.; Ma, D.; Liu, B.; Jiang, H. *Adv. Synth. Catal.* **2012**, *354*, 2683. (i) Chen, Z.; Li, J.; Jiang, H.; Zhu, S.; Li, Y.; Qi, C. *Org. Lett.* **2010**, *12*, 3262.

(2) (a) Amiel, Y. *Tetrahedron Lett.* **1971**, *8*, 661. (b) Amiel, Y. *J. Org. Chem.* **1971**, *36*, 3691. (c) Amiel, Y. *J. Org. Chem.* **1971**, *36*, 3697. (d) Liu, X.; Duan, X.; Pan, Z.; Han, Y.; Liang, Y. *Synlett* **2005**, *11*, 1752.

(3) (a) Truce, W. E.; Wolf, G. C. *J. Org. Chem.* **1971**, *36*, 1727. (b) Amiel, Y. *J. Org. Chem.* **1974**, *39*, 3867.

(4) For recent selected examples, see: (a) Corbet, J. P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651. (b) Cahiez, G.; Moyeux, A. *Chem. Rev.* **2010**, *110*, 1435. (c) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314. (d) Bettinger, H. F.; Filthaus, M. *J. Org. Chem.* **2007**, *72*, 9750. (e) Uchiyama, M.; Furuyama, T.; Kobayashi, M.; Matsumoto, Y.; Tanaka, K. *J. Am. Chem. Soc.* **2006**, *128*, 8404. (f) Boukouvalas, J.; Loach, R. P. *J. Org. Chem.* **2008**, *73*, 8109.

(5) For recent selected examples, see: (a) Kumar, R.; Kumar, T.; Mobin, S. M.; Nambothiri, I. N. N. *J. Org. Chem.* **2013**, *78*, 5073. (b) Opekar, S.; Pohl, R.; Eigner, V.; Beier, P. *J. Org. Chem.* **2013**, *78*, 4573. (c) Urones, B.; Arrayas, R. G.; Carretero, J. C. *Org. Lett.* **2013**, *15*, 1120. (d) Suresh, R. C.; Wieczysty, M. D.; Khan, I.; Lam, H. W. *Org. Lett.* **2013**, *15*, 570. (e) Zhao, P.; Beaudry, C. M. *Org. Lett.* **2013**, *15*, 402. (f) Huang, Z.; Kaur, J.; Bhardwaj, A.; Alsaleh, N. *J. Med. Chem.* **2012**, *55*, 10262.

(6) Zeng, X.; Ilies, L.; Nakamura, E. *Org. Lett.* **2012**, *14*, 954.

(7) (a) Li, X.; Xu, X.; Zhou, C. *Chem. Commun.* **2012**, *48*, 12240. (b) Li, X.; Xu, X.; Hu, P.; Xiao, X.; Zhou, C. *J. Org. Chem.* **2013**, *78*,

7343. (c) Li, X.; Xu, X.; Tang, Y. *Org. Biomol. Chem.* **2013**, *11*, 1739. (d) Li, X.; Xu, X.; Shi, X. *Tetrahedron Lett.* **2013**, *54*, 3071.
(8) Taniguchi, T.; Fujii, T.; Ishibashi, H. *J. Org. Chem.* **2010**, *75*, 8126.
(9) The compounds **3aa**, **3ac**, **3ad**, **3da**, and **3fa** are synthesized in 66, 55, 67, 52, and 63% yields, respectively, in ref 6.
(10) Liu, W.; Li, Y.; Liu, K.; Li, Z. *J. Am. Chem. Soc.* **2011**, *133*, 10756.
(11) Taniguchi, N. *Synlett* **2011**, 1308.
(12) Gilmore, K.; Gold, B.; Alabugin, L. V. *Aust. J. Chem.* **2013**, *66*, 336.