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Article

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Iodine-catalyzed Sulfonylation of Arylacetylenic Acids and Arylacetylenes with Sodium Sulfinates: Synthesis of Arylacetylenic Sulfones

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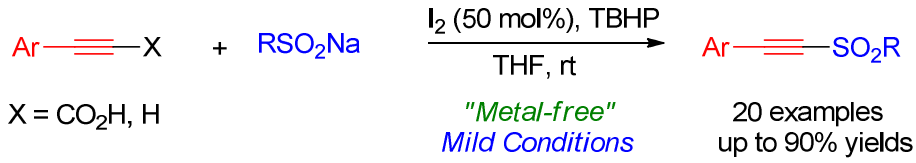


A highly efficient and generally applicable iodine-catalyzed reaction of arylacetylenic acids and arylacetylenes with sodium sulfinates for the synthesis of arylacetylenic sulfones was developed. The methodology has advantages of a metal-free strategy, easy to handle reagents, functional group tolerance, a wide range of arylacetylenic acids and arylacetylenes and easy access to arylacetylenic sulfones.

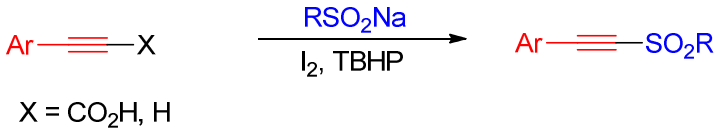
Introduction

Sulfur-containing compounds are of great importance in organic synthesis, pharmaceuticals, bioactive products, medicines, agrochemicals, semiconductors, and organic dyes. Among them, organosulfone compounds have attracted enormous attention, because they occur in a number of compounds exhibiting important biological activities[1] and show tremendous synthetic utilities.[2] Therefore, the development of general methods for the synthesis of organosulfone compounds is consequently an important goal in organic chemistry. The construction of the C–SO_2 bond is important, and the installation of sulfone moiety into the organic molecules via C–SO_2 bond formation has thereby drawn remarked attentions.[3] A number of sulfonyl precursors including sulfonyl halides,[4] sulfonyl selenides,[5] sulfonyl cyanides,[6] sulfonyl azides,[7] sulfonyl hydrazides,[8] sodium sulfinates,[9] sulfinic acids[10] and sulfoxides[11] were employed to access organosulfone compounds.

Acetylenic sulfones are important class of organosulfone compounds and their synthetic applications are well documented.[12] A number of synthetic routes are available toward the synthesis of acetylenic sulfones.[13] Most recently, Singh and coworkers described, in part, a combination of arylsulfonyl hydrazide, molecular iodine (I_2), *tert*-butyl hydroperoxide (TBHP), DBU in aqueous acetonitrile to access acetylenic sulfones from 3-phenylpropiolic acid.[13e] Although the reported methods for acetylenic sulfone synthesis are highly efficient, alternative methodologies employing commercially available starting materials and operationally simple methods are still desirable. With our continuing interests in developing efficient methods for the synthesis of organosulfur compounds,[14] we report herein our research results on the combination of I_2-TBHP mediated decarboxylative sulfonylation of arylacetylenic acids and sulfonylation of arylacetylenes employing sodium sulfinates as sulfur sources (Scheme 1). Our method offers

several advantages, including being transition-metal-free, employing stable reagents, involving simple handling under air-stable conditions, accommodating a variety of substrates, and avoiding the formation of toxic byproducts.

Scheme 1. Iodine-catalyzed Sulfonylation of Arylacetylenic Acids and Arylacetylenes with Sodium Sulfinates

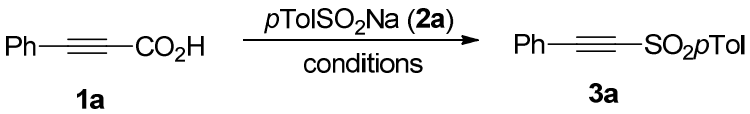


Results and Discussion

To evaluate the potential for acetylenic sulfone formation, the reaction between 3-phenylpropiolic acid (**1a**) and sodium *p*-toluenesulfinate (**2a**) was examined under various reaction parameters in order to screen for the optimum reaction conditions and the results are summarized in Table 1. To our delight, when 3-phenylpropiolic acid (**1a**, 0.5 mmol) was treated with sodium *p*-toluenesulfinate (**2a**, 3 equiv) with molecular iodine (I_2, 1 equiv), *tert*-butylhydroperoxide (TBHP, 5 equiv), potassium carbonate (K_2CO_3, 1 equiv) in acetonitrile (2 mL) and the resulting mixture was stirred at room temperature (30–32 ^oC) for 24 h, the corresponding acetylenic sulfone **3a** was obtained in 51% yield (Table 1, entry 1). Next various solvents, including ethanol, tetrahydrofuran, 1,4-dioxane, dichloroethane and toluene, were screened (Table 1, entries 2–6). Among those, tetrahydrofuran was found being an optimum solvent yielding **3a** in significantly improved yield (88% yield, Table 1, entry 3). It is pleasing to find that reaction time can be shortened (from 24 h to 16 h) and comparable yield of **3a** was observed (Table 1, entry 7). The amount of sodium *p*-toluenesulfinate (**2a**) employed can be as low as 2 equivalents; further reduction of the amount of **2a** caused drastic decrease in product yield (Table 1, entries 8–9). Further attempts to highlight the role of reagents employed were

also investigated. External base (K_2CO_3) can be excluded from the reaction without affecting the reaction efficiency (Table 1, entry 10). Furthermore, the stoichiometry of TBHP can be lowered (from 5 equiv to 3 equiv) and molecular iodine can be employed in substoichiometric quantity (50 mol%) (Table 1, entries 11–12). Effort to drive the reaction to completion by conducting the reaction in refluxing THF for 9 h was unsuccessful; there was no improvement in yield but a significant decrease in product yield was observed (Table 1, entry 12). Further decrease in the iodine quantity (from 0.5 equiv to 0.25 equiv) led to poorer results (Table 1, entry 13). Finally, the reaction did not take place in the absence of molecular iodine catalyst and only trace amount of **3a** was observed (TLC analysis) when TBHP was excluded from the reaction (Table 1, entries 14–15). The observed results further emphasized the important roles of both molecular iodine and TBHP in the present reaction. It is worth also mentioned here that attempts to replace aqueous TBHP with TBHP in decane or other peroxide reagents including aqueous hydrogen peroxide, cumene hydroperoxide, di-*tert*-butyl peroxide, di-cumyl peroxide, and *tert*-butyl benzoperoxoate gave inferior results.

Table 1. Optimization of the Reaction Conditions for Iodine-catalyzed Decarboxylative Sulfonylation of 3-Phenylpropiolic acid (1a)[a]



1a **3a**

entry	**2a** (equiv)	I_2 (equiv)	aq TBHP (equiv)	K_2CO_3 (equiv)	Solvent	time (h)	yield[b] (%)
1	3	1	5	1	CH_3CN	24	51
2	3	1	5	1	EtOH	24	43
3	3	1	5	1	THF	24	88
4	3	1	5	1	1,4-Dioxane	24	72
5	3	1	5	1	Dichloroethane	24	Trace
6	3	1	5	1	Toluene	24	Trace
7	3	1	5	1	THF	16	88
8	2	1	5	1	THF	16	86
9	1	1	5	1	THF	16	59
10	2	1	5	–	THF	16	87
11	2	1	3	–	THF	16	85
12	**2**	**0.5**	**3**	**–**	**THF**	**16**	**86 (65)**[c]
13	2	0.25	3	–	THF	16	59
14	2	–	3	–	THF	16	–[d]
15	2	0.5	–	–	THF	16	Trace

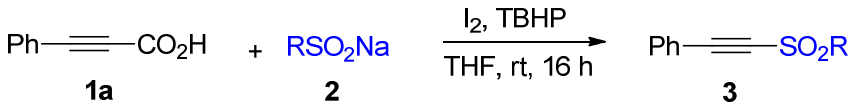
[a] Reaction conditions: **1a** (0.5 mmol) in solvent (2 mL), rt (30–32 °C), open air. [b] Isolated yields after column chromatography (SiO_2). [c] Reaction was performed in refluxing THF (9 h). [d] **3a** was not observed (TLC analysis).

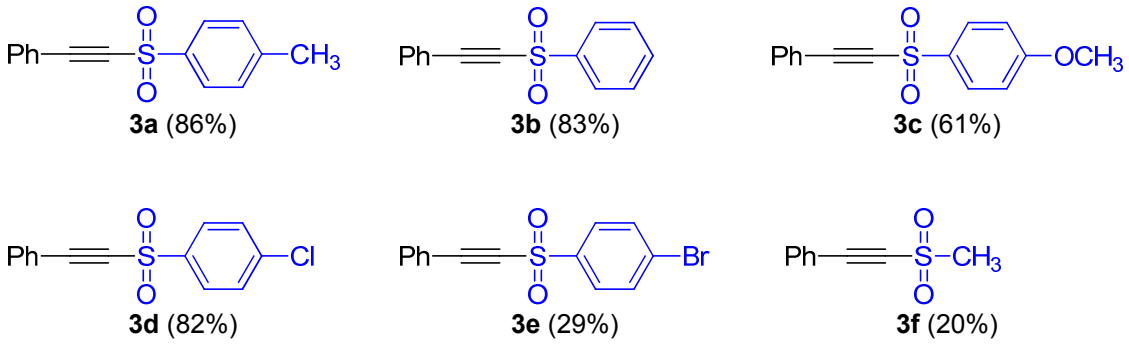
After extensive experimentation, the optimum reaction conditions for the iodine-catalyzed decarboxylative sulfonylation of arylacetylenic acids were chosen as follows: **1a** (1 equiv), **2a** (2 equiv), I_2 (50 mol%), TBHP (3 equiv) in THF at room temperature for 16 h (Table 1, entry 12). With the optimized reaction conditions in hand, we next explored the generality and functional group compatibility of this transformation under the established reaction conditions and the results are summarized in Tables 2 and 3.

Initially, the scope of the decarboxylative sulfonylation of 3-phenylpropiolic acid (**1a**) with a collection of sodium sulfinates was investigated as shown in Table 2. The reactions of 3-phenylpropiolic acid (**1a**) with sodium arenesulfinates bearing electronically different groups on the *para* position (*p*-CH_3, *p*-OCH_3, *p*-Cl, *p*-Br) gave the corresponding products **3a**–**3e** in low to

good yields (29–86% yields); sodium *p*-bromobenzenesulfinates is being a poor sulfinate salt. Under standard reaction conditions, sodium methanesulfinate gave the corresponding product **3f** in low yield (20% yield). On the other hand, we observed no acetylenic sulfones formed when sterically hindered sodium mesitylenesulfinate and electron deficient sulfinates including sodium 2,4-dinitrobenzenesulfinate and sodium trifluoromethanesulfinate were employed; unidentifiable polar mixture was observed (TLC analysis).

Table 2. Scope of Sodium Sulfinates[a]



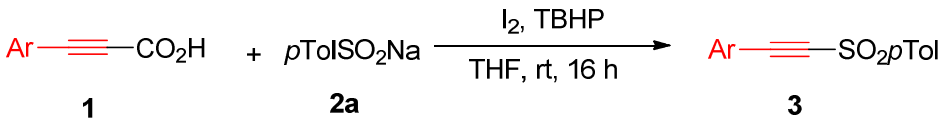


[a] Conditions: **1a** (0.5 mmol), **2** (2 equiv), I_2 (0.5 equiv), 70% TBHP in H_2O (3 equiv) in THF (2 mL), rt (30–32 °C), 16 h. In parenthesis: isolated yields after chromatographic purification (SiO_2 column chromatography).

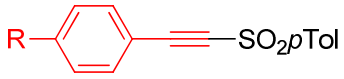
Next, the reactions between various types of arylacetylenic acids **1** with sodium *p*-toluenesulfinate (**2a**) were examined as shown in Table 3. Under the established reaction conditions, the reactions of sodium *p*-toluenesulfinate (**2a**) with electronically different *para*-substituted arylacetylenic acid derivatives (*p*-CH_3, *p*-OCH_3, and *p*-CF_3) smoothly gave the corresponding products **3g**–**3i** in good yields (68–90% yields). In case of *para*-halosubstituted arylacetylenic acids (*p*-F and *p*-Br), the corresponding acetylenic sulfones **3j**–**3k** were obtained

in moderate quantities (47–80% yields). Arylacetylenic acid bearing strong electron-attracting group (*p*-NO_2) was also suitable for this process, albeit diverting to the corresponding acetylenic sulfone **3l** in relatively low yield (32% yield). Arylacetylenic acids bearing substituents at the *meta* position (*m*-CH_3, and *m*-Cl) could also be converted to their corresponding acetylenic sulfones **3m**–**3n** in high yields (69–90% yields). The electronic and steric effects were evident when 3-(2-bromophenyl)propiolic acid was employed as a starting material; an evident decrease of reaction yield of **3o** was observed. Notably, arylacetylenic acids bearing substituents at the *ortho* and *para* positions were also effective substrates in this transformation furnishing the corresponding products **3p**–**3q** in good yields (67–83% yields). 3-(Naphthalen-2-yl)propiolic acid and 3-heteroarylpropiolic acid, *i.e.* 3-(thiophen-2-yl)propiolic acid, are also good substrates providing **3r** and **3s** in 53% and 63% yields, respectively. Nevertheless, the present protocol was found incompatible with β-alkyl- and β-silyl-substituted propiolic acids. 2-Butynoic acid failed to give any desired acetylenic sulfone product. Efforts to employ 3-(triisopropylsilyl)propiolic acid and 3-(*tert*-butyldimethylsilyl)propiolic acid as the substrates were also examined albeit without success; the starting acids were recovered in both cases. Noteworthy, a scaling up experiment (5 mmol) between **1a** and **2a** was also investigated under the optimized conditions and **3a** was obtained in comparable efficiency (82% yield).

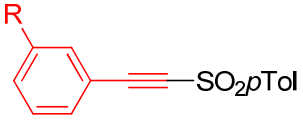
Table 3. Scope of Arylacetylenic Acids[a]



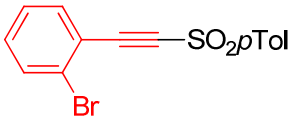
1 **2a** **3**



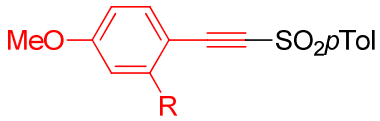
3g	R = CH_3	(90%)
3h	R = OCH_3	(80%)
3i	R = CF_3	(68%)
3j	R =F	(47%)
3k	R =Br	(80%)
3l	R = NO_2	(32%)



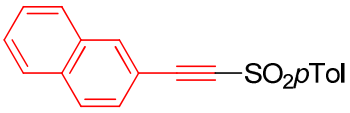
3m	R = CH_3	(90%)
3n	R = Cl	(69%)



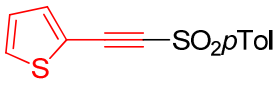
3o (35%)



3p	R = CH_3	(67%)
3q	R = OCH_3	(83%)



3r (53%)



3s (63%)

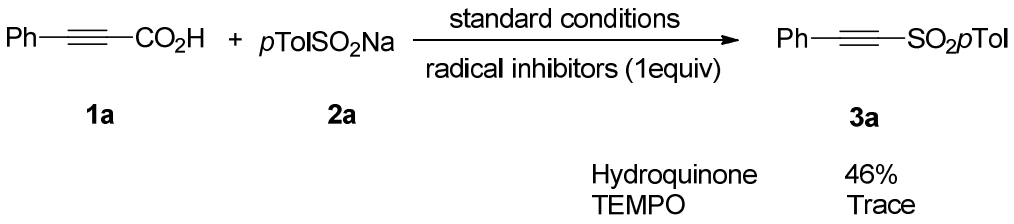
[a] Conditions: **1a** (0.5 mmol), **2** (2 equiv), I_2 (0.5 equiv), 70% TBHP in H_2O (3 equiv) in THF (2 mL), rt (30–32 °C), 16 h. In parenthesis: isolated yields after chromatographic purification (SiO_2 column chromatography).

To gain a better understanding of the reaction mechanism, a series of control experiments were carried out (Scheme 2). The reaction of 3-phenylpropiolic acid (**1a**) with sodium *p*-toluenesulfinate (**2a**) was conducted under the standard reaction conditions in the presence of radical inhibitors, including hydroquinone and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) [Scheme 2, (a)]. Hydroquinone was found to retard the reaction while TEMPO almost ceased the reaction. Although the radical-trapping adducts were not isolated, the observed results implied that the reaction is likely to involve a radical pathway. There has been a previous report that arylpropiolic acids were capable of undergoing halodecarboxylation to provide 1-haloalkynes.[15] We then separately prepared (iodoethynyl)benzene (**4**)[16] and employed **4** in place of 3-

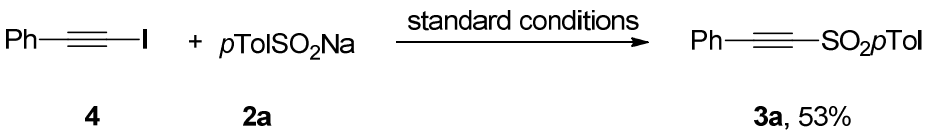
phenylpropiolic acid (**1a**) the under standard reaction conditions. Interestingly, **3a** was isolated in 53% yield, suggesting that **4** might also be an intermediate in the present reaction [Scheme 2, (b)]. However, under the standard reaction conditions but in the absence of **2a**, **1a** did not provide any isolable products [Scheme 2, (c)]. GC/MS analysis of the reaction mixture before aqueous work-up indicated the formation of phenylacetylene (**5a**). However, after aqueous work-up, **1a** was recovered in 90% yield. This observation suggested that under the reaction conditions, **1a** was unlikely converted to either **4** or **5a**. Indeed, decarboxylative sulfonylation of **1a** to **3a** is unlikely to proceed through the intermediate **4** or **5a**. The detection of **5a** urged us to investigate the reaction of phenylacetylene (**5a**) and sodium *p*-toluenesulfinate (**2a**) under our standard reaction conditions [Scheme 2, (d)]. Gratifyingly, we were pleased to observe that **5a** reacted with **2a** under the standard conditions, yielding the corresponding acetylenic sulfone **3a** in moderate yield (56% yield). Next, the reactions of 3-phenylpropiolic acid (**1a**) and phenylacetylene (**5a**) with *p*-toluenesulfonyl iodide[17] were examined [Scheme 2, (e)]. To our surprise, acetylenic sulfone **3a** was not observed in both cases; interestingly, phenylacetylene (**5a**) yielded (*E*)-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (**6a**) in 83% yield. This outcome suggested that sulfonyl iodide is unlikely being a key precursor to react with **1a** or **5a** to lead to acetylenic sulfone **3a**. Finally, it was found that sulfonyl iodide cannot be generated upon treatment of sodium *p*-toluenesulfinate (**2a**) with molecular iodine in THF at room temperature [Scheme 2, (f)]. On the contrary, under our standard reaction conditions (I_2, TBHP, THF, rt), the sulfonyl iodide can be detected (TLC analysis) but disappeared upon stirring overnight [Scheme 2, (f)].

Scheme 2. Control Experiments

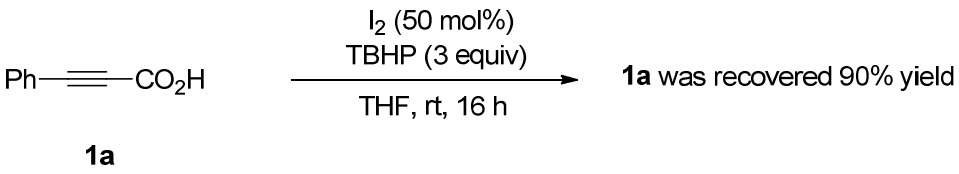
(a)



(b)

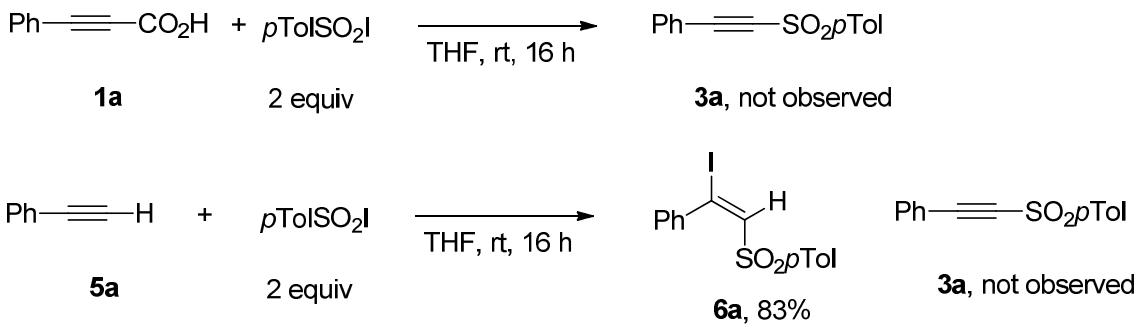


(c)

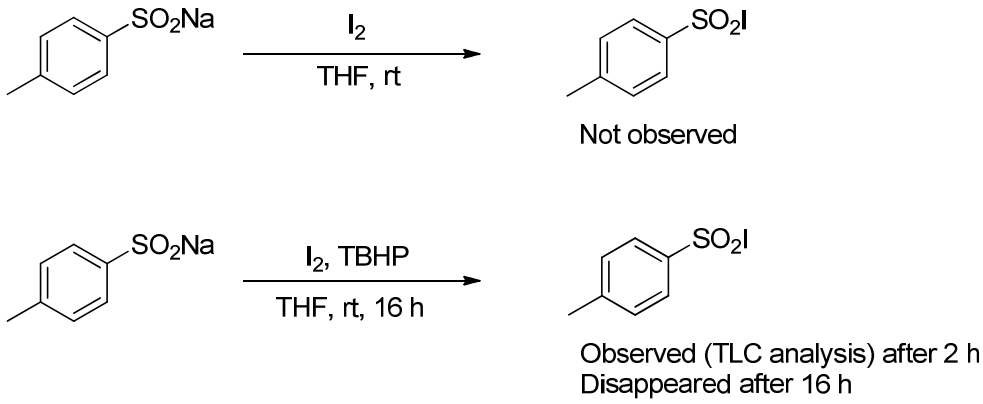


(d)

(e)



(f)

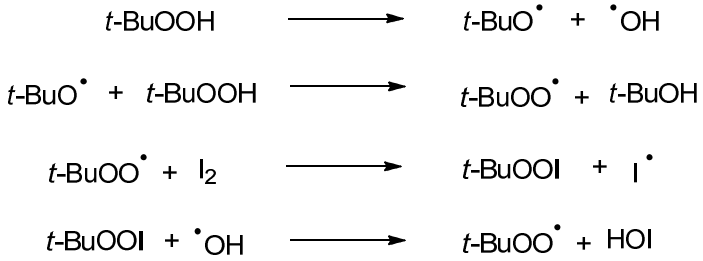


On the basis of the results described above and relevant literature,[13] tentative reaction mechanisms for this metal-free decarboxylative sulfonylation of arylacetylenic acids is proposed using 3-phenylpropiolic acid (**1a**) and sodium *p*-toluenesulfinate (**2a**) as the model substrates (Scheme 3). Since the reactions were extremely sluggish or did not occur if neither I_2 nor TBHP was employed under the typical reaction conditions (Table 1, entries 14–15), this observation implied that to lead to the desired acetylenic sulfones both of the I_2 and TBHP did not directly react with substrates during the reaction. Indeed, two possible pathways are proposed for the *in situ* generation of sulfonyl radical intermediate [Scheme 3, (b)]. In the presence of iodine/TBHP, sodium *p*-toluenesulfinate will be oxidized to preferably generate the oxygen-centered sulfonyl radical **A**. The oxygen-centered radical **A** exists as an equilibrium with the sulfur-centered sulfonyl radical **B** which then react with the substrates (3-arylpropiolic acids or arylacetylenes) (Path A). Alternatively, iodine/TBHP readily reacted to form a more reactive electrophilic iodine species [Scheme 3, (a)][13e] which then reacted with sodium *p*-toluenesulfinates to generate *p*-toluenesulfinylhypoiodite **C** (Path B). The *p*-toluenesulfinylhypoiodite **C** could exist in equilibrium with its corresponding *p*-toluenesulfonyl iodide **D** and subsequently underwent homolytic cleavage to yield oxygen-centered sulfonyl radical **A**, and finally to the sulfur-

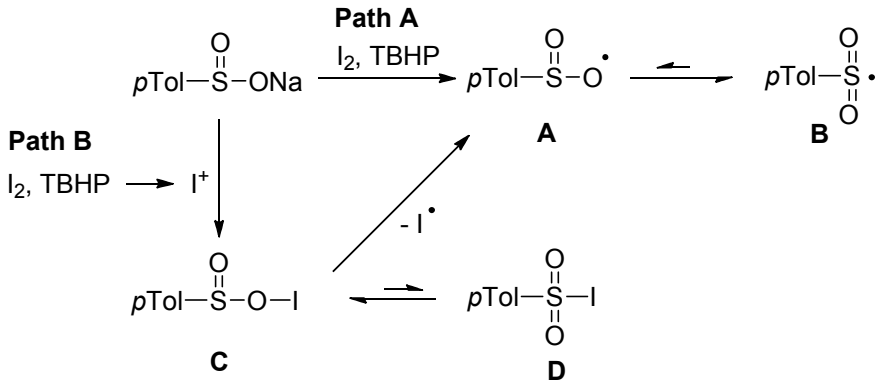
centered sulfonyl radical **B**. Upon employing 3-phenylpropiolic acid (**1a**) as a starting compound, the sulfonyl radical **B** underwent direct addition to **1a** to generate the vinyl radical intermediate **E** which then subsequently underwent decarboxylation to provide the acetylenic sulfone **3a** [Scheme 3, (c)].[18] For the conversion of phenylacetylene (**5a**) to acetylenic sulfone **3a**, addition of the sulfonyl radical **B** to **5a** generated a vinyl radical intermediate **F** [Scheme 3, (c)].[13d] The acetylenic sulfone **3a** was obtained upon elimination of hydrogen radical. In this work, the (iodoethynyl)benzene (**4**) can also be converted to acetylenic sulfone **3a** through a similar pathway via a proposed intermediate **G** [Scheme 3, (c)]. Finally, the HI generated in the reaction could be reoxidized leading to I_2 to resume the catalytic cycle [Scheme 3, (d)].[19]

Scheme 3. Proposed Reaction Mechanism

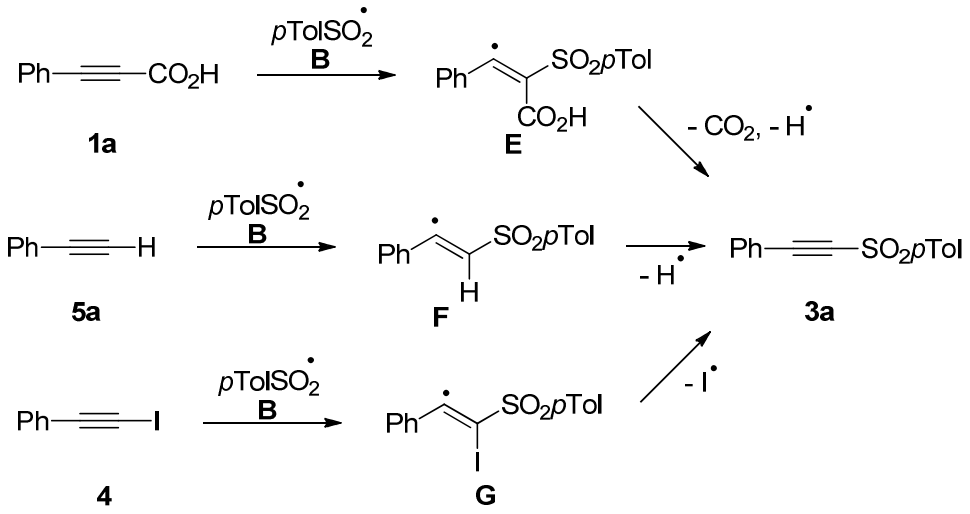
(a) Formation of electrophilic iodine species



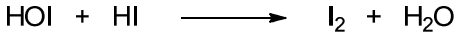
(b) Formation of sulfonyl radical



c) Formation of acetylenic sulfones



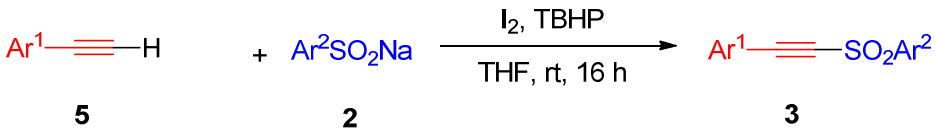
d) Regeneration of molecular iodine



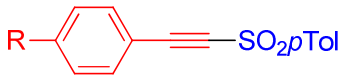
The synthetic utility of the present protocol was further extended to the sulfonylation of arylacetylenes. The reaction of electronically different arylacetylenes **5** with sodium arenesulfinates **2** under the established reaction conditions for decarboxylative sulfonylaion of arylacetylenic acids **1** was evaluated and the results were summarized in Table 4. Delightfully, arylacetylenes **5** were found capable of undergoing sulfonylation reaction to yield the respective arylacetylenic sulfones **3**, albeit in lower efficiency. Except for **3l** where trace amount of the product was observed (TLC analysis), the yields were moderate (42–68% yields). Arylacetylenes bearing electron-withdrawing substituents gave poorer yields in comparison to those bearing electron-releasing substituents. While the reaction of phenylacetylene with sodium *p*-bromobenzenesulfinate gave acetylenic sulfone **3e** in low yield (17% yield), those with sodium

mesitylenesulfinate and sodium 2,4-dinitrobenzenesulfinate did not provide the desired products. This observation is in accordance with those observed when arylacetylenic acids were employed as the starting compounds (Tables 2 and 3). Interestingly, under the standard reaction conditions [I_2 (0.5 equiv), 70% TBHP in H_2O (3 equiv), THF, rt, 16 h], terminal aliphatic alkyne, 1-octyne, did not yield alkylacetylenic sulfone but led to the corresponding (*E*)-β-iodovinyl sulfone **6b** (confirmed by NOE experiments) in low yield (26% yield) [Scheme 4, (a)]. Notably, internal alkynes, under the established reaction conditions, also yielded the corresponding (*E*)-β-iodovinyl sulfones **6c**–**6e**, albeit in low yields (14–27% yields) [Scheme 4, (b)].

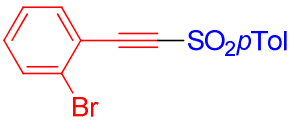
Table 4. Sulfonylation of Arylacetylenes 5[a]



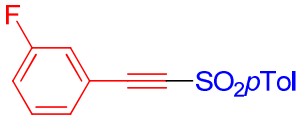
5 **2** **3**



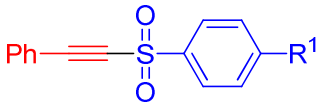
3a	R = H	(56%)
3g	R = CH_3	(68%)
3h	R = OCH_3	(62%)
3j	R = F	(55%)
3l	R = NO_2	Trace



3o (49%)



3t (42%)

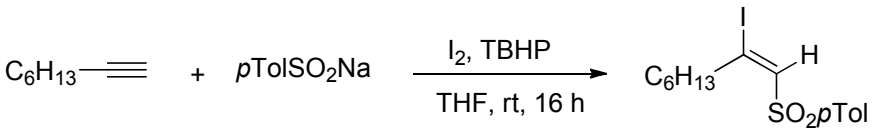


3b	R^1 = H	(54%)
3c	R^1 = OCH_3	(45%)
3d	R^1 = Cl	(46%)
3e	R^1 = Br	(17%)

[a] Conditions: **1a** (0.5 mmol), **2** (2 equiv), I_2 (0.5 equiv), 70% TBHP in H_2O (3 equiv) in THF (2 mL), rt (30–32 °C), 16 h. In parenthesis: isolated yields after chromatographic purification (SiO_2 column chromatography).

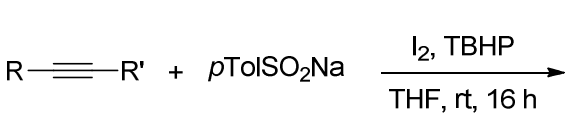
Scheme 4. Reaction of Terminal Aliphatic Alkyne and Internal Alkynes

(a) Terminal aliphatic alkyne



6b, 26%

(b) Internal alkynes



6c, R = R' =Ph, 19%
6d, R = Ph R' = CH_3, 27%
6e, R = R' = *n*Pr, 14%

Conclusion

In summary, a highly efficient synthesis of arylacetylenic sulfones has been developed. Under identical reaction conditions, arylacetylenic acids underwent decarboxylative sulfonylation while arylacetylenes underwent sulfonylation to yield the acetylenic sulfones in moderate to excellent yields. The established methodology offers a benign metal-free protocol, ease of experimentation (room temperature) and open-flask reaction. The expansion of the synthetic application of this chemistry is currently under investigation in our laboratory.

Experimental Section

General Procedure: All isolated compounds were characterized on the basis of ^{1}H NMR, ^{13}C NMR spectroscopic data, IR spectra and HRMS data. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in ppm using tetramethylsilane (TMS) as an internal standard or residual non-deuterated solvent peak as an internal standard.

General Procedure for the Synthesis of Arylpropiolic acids[20]

Aryl iodide (5.0 mmol), DBU (1.83 g, 12 mmol, 2.4 equiv.), $Pd(PPh_3)_4$ (144 mg, 2.5 mol%) were mixed in DMSO (6 mL). The solution of propiolic acid (420 mg, 6.0 mmol, 1.2 equiv.) in DMSO (6 mL) was poured to the flask. The mixture was stirred at room temperature for 12 h. After the reaction completely occurred, EtOAc (20 mL) was poured into the reaction mixture. The reaction mixture was extracted with saturated aqueous $NaHCO_3$ solution. The aqueous layer was separated, acidified to pH 2.0 by adding cold HCl (1 N), and extracted with CH_2Cl_2. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel.

General Procedure for the Synthesis of Acetylenic Sulfones from Arylacetylenic acids or Arylacetylenes: To a solution of arylacetylenic acid or arylacetylene (0.5 mmol) with sodium sulfinate (1 mmol), and iodine (0.25 mmol) in THF (2 mL) was added TBHP (70% in water, 1.5 mmol). The resulting mixture was stirred at room temperature for 16 h. The reaction mixture was quenched by the addition of saturated aqueous $Na_2S_2O_3$ (5 mL). Further stirring was followed by extraction with EtOAc (2 × 20 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (20 mL), dried ($MgSO_4$), filtered, and concentrated (aspirator). The residue was purified by column chromatography using EtOAc/hexanes as eluent to afford the corresponding product.

*1-Methyl-4-((phenylethynyl)sulfonyl)benzene (**3a**):*[13e] pale yellow solid (110.2 mg, 86% yield from 3-phenylpropiolic acid; 71.8 mg, 56% yield from phenylacetylene); mp = 76–77 °C (from CH_2Cl_2/hexanes) (lit.[13e] mp 74 °C); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2 H), 7.52–7.45 (m, 3 H), 7.40–7.34 (m, 4 H), 2.46 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.4 (C), 138.8 (C), 132.7 (2 × CH), 131.4 (CH), 130.0 (2 × CH), 128.6 (2 × CH), 127.4 (2 × CH),

117.9 (C), 92.9 (C), 85.5 (C), 21.7 (CH_3) ppm; IR (neat) *v* 2179 (C≡C), 1322 and 1152 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{12}O_2SNa$ 279.0456, found 279.0469.

*((Phenylethynyl)sulfonyl)benzene (**3b**):*[12i] pale yellow solid (100.6 mg, 83% yield from 3-phenylpropiolic acid; 65.4 mg, 54% yield from phenylacetylene); mp = 66–68 °C (from CH_2Cl_2/hexanes) (lit.[12i] mp 62–63 °C); ^1H NMR (400 MHz; $CDCl_3$) δ 8.08 (d, *J* = 9.0 Hz, 2 H), 7.70–7.67 (m, 1 H), 7.62–7.58 (m, 2 H), 7.52–7.44 (m, 3 H), 7.36 (t, *J* = 7.6 Hz, 2 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 141.8 (C), 134.1 (CH), 132.7 (2 × CH), 131.5 (CH), 129.3 (2 × CH), 128.7 (2 × CH), 127.3 (2 × CH), 117.8 (C), 93.5 (C), 85.3 (C) ppm; IR (neat) *v* 2180 (C≡C), 1322 and 1154 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{14}H_{10}O_2SNa$ 265.0299, found 265.0294.

*1-Methoxy-4-((phenylethynyl)sulfonyl)benzene (**3c**):*[13e] pale yellow solid (83.1 mg, 61% yield from 3-phenylpropiolic acid; 61.3 mg, 45% yield from phenylacetylene); mp = 77−78 °C (from CH_2Cl_2/hexanes) (lit.[13e] mp 77 °C); ^1H NMR (400 MHz; $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2 H), 7.51–7.44 (m, 3 H), 7.36 (t, *J* = 7.6 Hz, 2 H), 7.05 (d, *J* = 8.9 Hz, 2 H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 164.1 (C), 133.2 (C), 132.5 (2 × CH), 131.3 (CH), 129.7 (2 × CH), 128.6 (2 × CH), 117.9 (C), 114.5 (2 × CH), 92.4 (C), 85.8 (C), 55.7 (CH_3) ppm; IR (neat) *v* 2182 (C≡C), 1328 and 1149 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{12}O_3SNa$ 295.0405, found 295.0410.

*1-Chloro-4-((phenylethynyl)sulfonyl)benzene (**3d**):*[12j] pale yellow solid (113.5 mg, 82% yield from 3-phenylpropiolic acid; 63.7 mg, 46% yield from phenylacetylene); mp = 97−100 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2 H), 7.59–7.47 (m, 5 H), 7.38 (t, *J* = 7.6 Hz, 2 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 141.0 (C), 140.2 (C), 132.8 (2 × CH), 131.7 (CH), 129.7 (2 × CH), 128.9 (2 × CH), 128.7 (2 × CH), 117.6 (C), 94.0 (C), 85.0 (C)

ppm; IR (neat) *v* 2180 (C≡C), 1323 and 1149 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{14}H_9ClO_2SNa$ 298.9909, found 298.9910.

*1-Bromo-4-((phenylethynyl)sulfonyl)benzene (**3e**):* white solid (46.6 mg, 29% yield from 3-phenylpropiolic acid; 27.3 mg, 17% yield from phenylacetylene); mp = 98−100 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.96–7.92 (m, 2 H), 7.76–7.72 (m, 2 H), 7.54–7.47 (m, 3 H), 7.40–7.36 (m, 2 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 140.8 (C), 132.8 (2 × CH), 132.7 (2 × CH), 131.7 (CH), 129.6 (C), 128.9 (2 × CH), 128.7 (2 × CH), 117.6 (C), 94.0 (C), 85.0 (C) ppm; IR (neat) *v* 2179 (C≡C), 1326 and 1151 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{14}H_9BrO_2SNa$ 342.9404, found 342.9418.

*((Methylsulfonyl)ethynyl)benzene (**3f**):*[12h] yellow liquid (18.0 mg, 20% yield from 3-phenylpropiolic acid); ^1H NMR (400 MHz; $CDCl_3$) δ 7.59–7.57 (m, 2 H), 7.51 (t, *J* = 7.5 Hz, 1 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 3.30 (s, 3H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 132.8 (2 × CH), 131.7 (CH), 128.7 (2 × CH), 117.4 (C), 91.4 (C), 84.4 (C), 46.7 (CH_3) ppm; IR (neat) *v* 2180 (C≡C), 1316 and 1139 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_9H_8O_2SNa$ 203.0143, found 203.0142.

*1-Methyl-4-((p-tolylethynyl)sulfonyl)benzene (**3g**):*[13b] pale yellow solid (121.6 mg, 90% yield from 3-(*p*-tolyl)propiolic acid; 91.9 mg, 68% yield from 1-ethynyl-4-methylbenzene); mp = 101−103 °C (from CH_2Cl_2/hexanes) (lit.[13b] mp 100–101 °C); ^1H NMR (400 MHz; $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2 H), 7.40–7.37 (m, 4 H), 7.16 (d, *J* = 7.9 Hz, 2 H), 2.45 (s, 3 H), 2.35 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.2 (C), 142.2 (C), 139.0 (C), 132.5 (2 × CH), 129.9 (2 × CH), 129.3 (2 × CH), 127.3 (2 × CH), 114.7 (C), 93.6 (C), 85.1 (C), 21.6 (CH_3), 21.5 (CH_3) ppm; IR (neat) *v* 2176 (C≡C), 1327 and 1154 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{14}O_2SNa$ 293.0612, found 293.0616.

*1-Methoxy-4-((p-tolylethynyl)sulfonyl)benzene (**3h**):*[13b] yellow amorphous solid (114.5 mg, 80% yield from 3-(4-methoxyphenyl)propiolic acid; 88.8 mg, 62% yield from 1-ethynyl-4-methoxybenzene); mp = 77−79 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2 H), 7.45 (d, *J* = 8.9 Hz, 2 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 6.86 (d, *J* = 8.9 Hz, 2 H), 3.82 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 162.1 (C), 145.1 (C), 139.2 (C), 134.6 (2 × CH), 129.9 (2 × CH), 127.3 (2 × CH), 114.4 (2 × CH), 109.5 (C), 94.1 (C), 84.8 (C), 55.4 (CH_3), 21.6 (CH_3) ppm; IR (neat) *v* 2169 (C≡C), 1324 and 1151 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{14}O_3SNa$ 309.0561, found 309.0554.

*1-Methyl-4-(((4-trifluoromethyl)phenyl)ethynyl)sulfonyl)benzene (**3i**):*[12c] pale yellow solid (110.3 mg, 68% yield from 3-(4-(trifluoromethyl)phenyl)propiolic acid); mp = 112−113 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2 H), 7.63 (s, 4 H), 7.41 (d, *J* = 8.2 Hz, 2 H), 2.47 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.8 (C), 138.4 (C), 133.0 (2 × CH), 132.9 (q, *J* = 33 Hz, C), 130.1 (2 × CH), 127.6 (2 × CH), 125.6 (q, *J* = 3 Hz, 2 × CH), 123.3 (q, *J* = 271.0 Hz, C), 121.8 (C), 90.3 (C), 87.3 (C), 21.7 (CH_3) ppm; IR (neat) *v* 2188 (C≡C), 1319 and 1155 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{11}F_3O_2SNa$ 347.0330, found 347.0331.

*1-Fluoro-4-(tosylethynyl)benzene (**3j**):*[12e] pale yellow solid (64.5 mg, 47% yield from 3-(4-fluorophenyl)propiolic acid; 75.4 mg, 55% yield from 1-ethynyl-4-fluorobenzene); mp = 75−77 °C (from CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2 H), 7.51 (dd, *J* = 8.7, 5.4 Hz, 2 H), 7.39 (d, *J* = 8.0 Hz, 2 H), 7.06 (t, *J* = 8.6 Hz, 2 H), 2.46 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 164.2 (d, *J* = 253 Hz, C), 145.4 (C), 138.8 (C), 135.0 (d, *J* = 9 Hz, 2 × CH), 130.0 (2 × CH), 128.7 (d, *J* = 198 Hz, C), 127.4 (2 × CH), 116.3 (d, *J* = 23 Hz, 2 × CH),

91.8 (C), 85.5 (C), 21.7 (CH_3) ppm; IR (neat) *v* 2179 (C≡C), 1330 and 1151 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{11}FO_2SNa$ 297.0361, found 297.0365.

*1-Bromo-4-(tosylethynyl)benzene (**3k**):*[13c] white solid (134.1 mg, 80% yield from 3-(4-bromophenyl)propiolic acid); mp = 107−108 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2 H), 7.52 (d, *J* = 8.5 Hz, 2 H), 7.41–7.36 (m, 4 H), 2.47 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.6 (C), 138.7 (C), 133.9 (2 × CH), 132.1 (2 × CH), 130.0 (2 × CH), 127.6 (2 × CH), 126.4 (C), 116.9 (C), 91.5 (C), 86.6 (C), 21.7 (CH_3) ppm; IR (neat) *v* 2179 (C≡C), 1330 and 1156 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{11}BrO_2SNa$ 356.9561, found 356.9570.

*1-Methyl-4-(((4-nitrophenyl)ethynyl)sulfonyl)benzene (**3l**):*[13a] pale yellow solid (48.2 mg, 32% yield from 3-(4-nitrophenyl)propiolic acid); mp = 164−165 °C (from CH_2Cl_2/hexanes) (lit.[13a] mp 166–167 °C); ^1H NMR (400 MHz; $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2 H), 7.96 (d, *J* = 8.3 Hz, 2 H), 7.69 (d, *J* = 8.8 Hz, 2 H), 7.42 (d, *J* = 8.1 Hz, 2 H), 2.48 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 148.9 (C), 146.1 (C), 138.1 (C), 133.6 (2 × CH), 130.2 (2 × CH), 127.7 (2 × CH), 124.5 (C), 123.8 (2 × CH), 89.2 (C), 89.1 (C), 21.8 (CH_3) ppm; IR (neat) *v* 2181 (C≡C), 1337 and 1155 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{11}NO_4SNa$ 324.0306, found 324.0308.

*1-Methyl-3-(tosylethynyl)benzene (**3m**):* pale yellow solid (121.6 mg, 90% yield from 3-(*m*-tolyl)propiolic acid); mp = 77−78 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 2 H), 7.33–7.24 (m, 4 H), 2.46 (s, 3 H), 2.32 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.3 (C), 139.0 (C), 138.5 (C), 133.1 (CH), 132.4 (CH), 129.9 (2 × CH), 129.8 (CH), 128.5 (CH), 127.4 (2 × CH), 117.7 (C), 93.3 (C), 85.3 (C),

21.7 (CH_3), 21.0 (CH_3) ppm; IR (neat) *v* 2160 (C≡C), 1334 and 1159 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{14}O_2SNa$ 293.0612, found 293.0605.

*1-Chloro-3-(tosylethynyl)benzene (**3n**):* pale yellow solid (83.9 mg, 69% yield from 3-(3-chlorophenyl)propiolic acid); mp = 108−110 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2 H), 7.38–7.30 (m, 5 H), 7.22 (t, *J* = 7.9 Hz, 1 H), 2.38 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.6 (C), 138.5 (C), 134.5 (C), 132.2 (CH), 131.7 (CH), 130.7 (CH), 130.0 (2 × CH), 129.9 (CH), 127.5 (2 × CH), 119.6 (C), 90.7 (C), 86.4 (C), 21.7 (CH_3) ppm; IR (neat) *v* 2182 (C≡C), 1336 and 1163 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{11}ClO_2SNa$ 313.0066, found 313.0073.

*1-Bromo-2-(tosylethynyl)benzene (**3o**):* pale yellow solid (58.7 mg, 35% yield from 3-(2-bromophenyl)propiolic acid; 82.1 mg, 49% yield from 1-bromo-2-ethynylbenzene); mp = 50−52 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2 H), 7.59–7.57 (m, 1 H), 7.51–7.49 (m, 1 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.33–7.28 (m, 2 H), 2.47 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.5 (C), 138.7 (C), 134.3 (CH), 132.8 (C), 132.4 (CH), 129.9 (2 × CH), 127.4 (2 × CH), 127.2 (CH), 126.4 (C), 120.6 (C), 90.9 (C), 89.0 (C), 21.7 (CH_3) ppm; IR (neat) *v* 2182 (C≡C), 1329 and 1152 (SO_2) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{11}BrO_2SNa$ 356.9561, found 356.9558.

*4-Methoxy-2-methyl-1-(tosylethynyl)benzene (**3p**):* amorphous solid (100.6 mg, 67% yield from 3-(4-methoxy-2-methylphenyl)propiolic acid); ^1H NMR (400 MHz; $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2 H), 7.39–7.35 (m, 3 H), 6.71–6.67 (m, 2 H), 3.79 (s, 3 H), 2.45 (s, 3 H), 2.34 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 162.0 (C), 145.0 (C), 144.6 (C), 139.5 (C), 134.7 (CH), 129.8 (2 × CH), 127.1 (2 × CH), 115.4 (CH), 111.8 (CH), 109.6 (C), 93.8 (C), 88.4 (C), 55.3

(CH_3), 21.6 (CH_3), 20.6 (CH_3) ppm; IR (neat) *v* 2161 (C≡C), 1321 and 1152 (SO_2) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}O_3SNa$ 323.0718, found 323.0717.

*2,4-Dimethoxy-1-(tosylethynyl)benzene (**3q**):* yellow liquid (262.6 mg, 83% yield from 3-(2,4-dimethoxyphenyl)propiolic acid); ^1H NMR (400 MHz; $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2 H), 7.35–7.32 (m, 3 H), 6.42 (dd, *J* = 8.6, 2.0 Hz, 1 H), 6.36 (d, *J* = 1.6 Hz, 1 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 2.43 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 163.9 (C), 163.3 (C), 144.7 (C), 139.6 (C), 135.6 (CH), 129.7 (2 × CH), 127.1 (2 × CH), 105.6 (CH), 99.4 (C), 98.1 (CH), 92.3 (C), 88.2 (C), 55.7 (CH_3), 55.5 (CH_3), 21.6 (CH_3) ppm; IR (neat) *v* 2161 (C≡C), 1321 and 1151 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{17}H_{16}O_4SNa$ 339.0667, found 339.0663.

*2-(Tosylethynyl)naphthalene (**3r**):* pale yellow solid (81.2 mg, 53% yield from 3-(naphthalen-2-yl)propiolic acid); mp = 132−134 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 8.07 (s, 1 H), 8.00 (d, *J* = 8.2 Hz, 2 H), 7.82–7.78 (m, 3 H), 7.58–7.51 (m, 2 H), 7.47 (d, *J* = 8.5 Hz, 1 H), 7.40 (d, *J* = 8.0 Hz, 2 H), 2.46 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.3 (C), 138.9 (C), 134.2 (CH), 134.0 (C), 132.3 (C), 130.0 (2 × CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.4 (2 × CH), 127.3 (CH), 127.2 (CH), 115.0 (C), 93.4 (C), 85.7 (C), 21.7 (CH_3) ppm; IR (neat) *v* 2181 (C≡C), 1334 and 1161 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{19}H_{14}O_2SNa$ 329.0612, found 329.0609.

*2-(Tosylethynyl)thiophene (**3s**):* yellow solid (82.6 mg, 63% yield from 3-(thiophen-2-yl)propiolic acid); mp = 87−88 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2 H), 7.49 (dd, *J* = 5.0, 1.0 Hz, 1 H), 7.44 (dd, *J* = 3.7, 1.0 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.03 (dd, *J* = 5.0, 3.8 Hz, 1 H), 2.45 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.4 (C), 138.7 (C), 137.0 (CH), 132.1 (CH), 130.0 (2 × CH), 127.6 (CH), 127.4 (2 × CH),

117.3 (C), 89.1 (C), 87.1 (C), 21.7 (CH_3) ppm; IR (neat) *v* 2157 (C≡C), 1330 and 1159 (SO_2) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{13}H_{10}O_2S_2Na$ 285.0020, found 285.0024.

*1-Fluoro-3-(tosylethynyl)benzene (**3t**):* white solid (57.6 mg, 42% yield from 1-ethynyl-3-fluorobenzene); mp = 88−90 °C (from CH_2Cl_2/hexanes); ^1H NMR (400 MHz; $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2 H), 7.42–7.27 (m, 4 H), 7.21–7.16 (m, 2 H), 2.47 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 162.0 (d, *J* = 247 Hz, C), 145.6 (C), 138.6 (C), 130.5 (d, *J* = 8 Hz, CH), 130.0 (2 × CH), 128.6 (d, *J* = 3 Hz, CH), 127.5 (2 × CH), 119.7 (d, *J* = 9 Hz, C), 119.3 (d, *J* = 24 Hz, CH), 118.9 (d, *J* = 21 Hz, CH), 90.9 (d, *J* = 4 Hz, C), 86.1 (C), 21.7 (CH_3) ppm; IR (neat) *v* 2175 (C≡C), 1333 and 1152 (SO_2) cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{11}FO_2SNa$ 297.0361, found 297.0369.

Synthesis of (*E*)-1-((2-Iodo-2-phenylvinyl)sulfonyl)-4-methylbenzene (6a):[14a] A solution of phenylacetylene (**5a**) (50.1 mg, 0.5 mmol) with *p*-toluenesulfonyliodide (282.1 mg, 1 mmol) in THF (2 mL) was stirred at room temperature for 16 h. The reaction mixture was quenched by the addition of saturated aqueous $Na_2S_2O_3$ (5 mL). Further stirring was followed by extraction with EtOAc (2 × 20 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (20 mL), dried ($MgSO_4$), filtered, and concentrated (aspirator). The residue was purified by column chromatography using EtOAc/hexanes as eluent to afford **6a**; white solid (167.4 mg, 83% yield); mp = 80−82 °C (from CH_2Cl_2/hexanes) (lit.[14a] mp 77–79 °C); ^1H NMR (400 MHz; $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2 H), 7.36 (s, 1 H), 7.32–7.26 (m, 3 H), 7.24–7.21 (m, 2 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 2.38 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 114.5 (C), 141.2 (CH), 139.6 (C), 137.2 (C), 129.7 (CH), 129.6 (2 × CH), 127.9 (2 × CH), 127.8 (2 × CH), 127.6 (2 × CH), 114.1 (C), 21.6 (CH_3) ppm; IR (neat) *v* 3057, 2920, 1585, 1326, 1141, 1083 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{13}IO_2SNa$ 406.9579, found 406.9583.

General Procedure for the Synthesis of *β*-Iodovinyl Sulfones from Terminal Aliphatic Alkyne and Internal Alkynes: To a solution of alkyne (0.5 mmol) with sodium sulfinate (1 mmol) and iodine (0.25 mmol) in THF (2 mL) was added TBHP (70% in water, 1.5 mmol). The resulting mixture was stirred at room temperature for 16 h. The reaction mixture was quenched by the addition of saturated aqueous $Na_2S_2O_3$ (5 mL). Further stirring was followed by extraction with EtOAc (2 × 20 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (20 mL), dried ($MgSO_4$), filtered, and concentrated (aspirator). The residue was purified by column chromatography using EtOAc/hexanes as eluent to afford the corresponding product.

*(E)-1-((2-Iodooct-1-en-1-yl)sulfonyl)-4-methylbenzene (**6b**):*[14a] colorless viscous liquid (42.8 mg, 26% yield); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.00 (s, 1 H), 3.00 (t, *J* = 7.4 Hz, 2 H), 2.44 (s, 3 H), 1.53–1.49 (m, 2 H), 1.32–1.25 (m, 6 H), 0.90–0.85 (m, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.8 (C), 138.9 (CH), 138.1 (C), 130.0 (2 × CH), 127.5 (2 × CH), 125.7 (C), 39.9 (CH_2), 31.5 (CH_2), 29.8 (CH_2), 28.1 (CH_2), 22.4 (CH_2), 21.6 (CH_3), 14.0 (CH_3) ppm; IR (neat): *ν* = 3044, 2956, 2929, 2858, 1597, 1456, 1379, 1322, 1303, 1147, 1086, 1018, 816, 768 cm^{-1}; HRMS (ESI-TOF): *m/z* calcd for $C_{15}H_{21}IO_2SNa$ [M + Na]+: 415.0205; found: 415.0204.

*(E)-(1-Iodo-2-tosylethene-1,2-diyl)dibenzene (**6c**):*[18d] white solid (43.4 mg, 19% yield); mp = 191−193 °C (from CH_2Cl_2/hexanes) (lit.[18d] mp 192–193 °C); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.37–7.32 (m, 8 H), 7.26 (d, *J* = 8.2 Hz, 2 H), 7.18–7.16 (m, 2 H), 7.09 (d, *J* = 8.1 Hz, 2 H), 2.36 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 149.1 (C), 144.2 (C), 142.5 (C), 139.3 (C), 136.7 (C), 130.3 (2 × CH), 129.2 (3 × CH), 129.0 (CH), 128.5 (2 × CH), 128.3 (2 × CH), 127.8 (2 × CH), 127.3 (2 × CH), 118.0 (C), 21.6 (CH_3) ppm; IR (neat) ν 3053, 2922, 1619, 1596, 1318,

1150, 1087 cm^{-1}; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{21}H_{17}IO_2SNa$ 482.9892, found 482.9899.

(E)-1-((1-Iodo-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene ***(6d)****:*[18a] white solid (49.3 mg, 27% yield); mp = 128–129 °C (from CH_2Cl_2/hexanes) (lit.[18a] mp 133–135 °C); ^1H NMR (400 MHz; $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2 H), 7.24–7.22 (m, 3 H), 7.16 (d, *J* = 8.1 Hz, 2 H), 7.12–7.10 (m, 2 H), 2.51 (s, 3 H), 2.39 (s, 3 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 144.1 (C), 143.9 (C), 142.9 (C), 137.2 (C), 129.5 (2 × CH), 128.6 (CH), 127.7 (2 × CH), 127.6 (2 × CH), 127.5 (2 × CH), 115.7 (C), 27.0 (CH_3), 21.6 (CH_3) ppm; IR (neat) *v* 3059, 2922, 1623, 1593, 1315, 1151, 1079 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{15}IO_2SNa$ 420.9735, found 420.9738.

(E)-1-((5-Iodooct-4-en-4-yl)sulfonyl)-4-methylbenzene ***(6e)****:* yellowish liquid (32.3 mg, 14% yield); ^1H NMR (400 MHz; $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 3.15–3.11 (m, 2 H), 2.58–2.54 (m, 2 H), 2.44 (s, 3 H), 1.61–1.49 (m, 4 H), 0.94–0.88 (m, 6 H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 143.7 (C), 143.4 (C), 137.6 (C), 128.8 (2 × CH), 126.8 (C), 126.3 (2 × CH), 44.0 (CH_2), 41.4 (CH_2), 22.8 (CH_2), 20.8 (CH_2), 20.6 (CH_3), 13.0 (CH_3), 11.9 (CH_3) ppm; IR (neat) *v* 2960, 2929, 1594, 1461, 1314, 1151, 1081 cm^{-1}; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{21}IO_2SNa$ 415.0205, found 415.0212.

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Supporting Information

Copies of ^{1}H- and ^{13}C-NMR spectra for all acetylenic sulfones **3** presented in Tables 2–4 and β-iodovinyl sulfones **6**. This material is available free of charge via the internet http://pub.acs.org.

References

(1) For vinyl sulfones see: (a) Uttamchandani, M.; Liu, K.; Panicker, R. C.; Yao, S. Q. *Chem. Commun.* **2007**, 1518–1520. (b) Steert, K.; El-Sayed, I.; Van der Veken, P.; Krishtal, A.; Van Alsenoy, C.; Westrop, G. D.; Mottram, J. C.; Coombs, G. H.; Augustyns, K.; Haemers, A. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6563–6566. (c) Ettari, R.; Nizi, E.; Francesco, M. E. D.; Dude, M.-A.; Pradel, G.; Vičík, R.; Schirmeister, T.; Micale, N.; Grasso, S.; Zappalà, M. *J. Med. Chem.* **2008**, *51*, 988–996. For β-ketosulfones see: (d) Curti, C.; Laget, M.; Carle, A. O.; Gellis, A.; Vanelle, P. *Eur. J. Med. Chem.* **2007**, *42*, 880–884. For β-hydroxysulfones see: (e) Oida, S.; Tajima, Y.; Konosu, T.; Nakamura, Y.; Somada, A.; Tanaka, T.; Habuki, S.; Harasaki, T.; Kamai, Y.; Fukuoka, T.; Ohya, S.; Yasuda, H. *Chem. Pharm. Bull.* **2000**, *48*, 694–707. And references cited therein.

(2) For vinyl sulfones see: (a) Llamas, T.; Arrayás, R. G.; Carretero, J. C. *Org. Lett.* **2006**, *8*, 1795–1798. (b) Sulzer-Mossé, S.; Alexakis, A.; Mareda, J.; Bollot, G.; Bernardinelli, G.; Filinchuk, Y. *Chem. Eur. J.* **2009**, *15*, 3204–3220. (c) Zhu, Q.; Cheng, L.; Lu, Y. *Chem. Commun.* **2008**, 6315–6317. (d) Sun, X.; Yu, F.; Ye, T.; Liang, X.; Ye, J. *Chem. Eur. J.* **2011**, *17*, 430–434. For β-ketosulfones see: (e) Yang, H.; Carter, R. G.; Zakharov, L. N. *J. Am. Chem. Soc.* **2008**, *130*, 9238–9239. (f) Alemán, J.; Marcos, V.; Marzo, L.; Ruano, J. L. G. *Eur. J. Org. Chem.* **2010**, 4482–4491. And references cited therein.

(3) (a) Simpkins, N. S. In *Sulfones in Organic Synthesis*; Baldwin, J. E., Ed.; Pergamon Press: Oxford, 1993. (b) Trost, B. M. In *Comprehensive Organic Chemistry*; Oxford: Pergamon Press,

1991. (c) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205–3220. (d) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400–5449.

(4) (a) Kang, S.-K.; Seo, H.-W.; Ha, Y.-H. *Synthesis* **2001**, 1321–1326. (b) Thommes, K.; Içli, B.; Scopelliti, R.; Severin, K. *Chem.–Eur. J.* **2007**, *13*, 6899–6907. (c) Li, H.-H.; Dong, D.-J.; Jin, Y.-H.; Tian, S.-K. *J. Org. Chem.* **2009**, *74*, 9501–9504. (d) Jiang, H.; Cheng, Y.; Zhang, Y.; Yu, S. *Eur. J. Org. Chem*. **2013**, 5485–5492.

(5) (a) Barton, D. H. R.; Csiba, M. A.; Jaszberenyi, J. C. *Tetrahedron Lett.* **1994**, *35*, 2869–2872. (b) Yoshimatsu, M.; Hayashi, M.; Tanabe, G.; Muraoka, O. *Tetrahedron Lett.* **1996**, *37*, 4161–4164. (c) Qian, H.; Huang, X. *Synthesis* **2006**, 1934–1936.

(6) (a) Fang, J.-M.; Chen, M.-Y. *Tetrahedron Lett.* **1987**, *28*, 2853–2856. (b) Reddy, L. R.; Hu, B.; Prashad, M.; Prasad, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 172–174.

(7) Mantrand, N.; Renaud, P. *Tetrahedron* **2008**, *64*, 11860–11864.

(8) (a) Taniguchi, T.; Idota, A.; Ishibashi, H. *Org. Biomol. Chem.* **2011**, *9*, 3151–3153. (b) Li, X.; Xu, X.; Zhou, C. *Chem. Commun.* **2012**, *48*, 12240–12242. (c) Li, X.; Xu, X.; Tang, Y. *Org. Biomol. Chem.* **2013**, *11*, 1739–1742. (d) Li, X.; Shi, X.; Fang, M.; Xu, X. *J. Org. Chem.* **2013**, *78*, 9499–9504. (e) Li, X.; Xu, X.; Hu, P.; Xiao, X.; Zhou, C. *J. Org. Chem.* **2013**, *78*, 7343–7348.

(9) (a) Taniguchi, N. *Synlett* **2012**, 1245–1249. (b) Chawla, R.; Singh, A. K.; Yadav, L. D. S. *Eur. J. Org. Chem.* **2014**, 2032–2036. (c) Mochizuki, T.; Hayakawa, S.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2317–2325. (d) Wang, S.-F.; Chuang, C.-P.; Lee, J.-H.; Liu, S.-T. *Tetrahedron* **1999**, *55*, 2273–2288. (e) Singh, A. K.; Chawla, R.; Yadav, L. D. S. *Tetrahedron Lett.* **2014**, *55*, 4742–4746.

(10) (a) Lu, Q.; Zhang, J.; Zhao, G.; Qi , Y.; Wang, H.; Lei, A. W. *J. Am. Chem. Soc.* **2013**, *135*, 11481–11484. (b) Wei, W.; Li, J.; Yang, D.; Wen, J.; Jiao, Y.; You, J.; Wang, H. *Org. Biomol. Chem.* **2014**, *12*, 1861–1864. (c) Shen, T.; Yuan, Y.; Song, S.; Jiao, N. *Chem. Commun.* **2014**, *50*, 4115–4118. (d) Wei, W.; Wen, J.; Yang, D.; Du, J.; You, J.; Wang, H. *Green Chem*. **2014**,

16, 2988–2991. (e) Lu, Q.; Zhang, J.; Wei, F.; Qi, Y.; Wang, H.; Liu, Z.; Lei, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 7156–7159.

(11) Shi, X.; Ren, X.; Ren, Z.; Li, J.; Wang, Y.; Yang, S.; Gu, J.; Gao, Q.; Huang, G. *Eur. J. Org. Chem.* **2014**, 5083–5088.

(12) (a) Gao, D.; Back, T. G. *Chem. Eur. J.* **2012**, *18*, 14828–14840. (b) Zhao, H.; Yang, W.; Xie, S.; Cai, M. *Eur. J. Org. Chem.* **2012**, 831–836. (c) Ruano, J. L. G.; Alemán, J.; Marzo, L.; Alvarado, C.; Tortosa, M.; Díaz-Tendero, S.; Fraile, A. *Chem. Eur. J.* **2012**, *18*, 8414–8422. (d) Ruano, J. L. G.; Alemán, J.; Marzo, L.; Alvarado, C.; Tortosa, M.; Díaz-Tendero, S.; Fraile, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 2712–2716. (e) Fang, K.; Xie, M.; Zhang, Z.; Ning, P.; Shu, G. *Tetrahedron Lett.* **2013**, *54*, 3819–3821. (f) Ruano, J. L. G.; Alemán, J.; Parra, A.; Marzo, L. *Eur. J. Org. Chem.* **2014**, 1577–1588. (g) Marzo, L.; Pérez, I.; Yuste, F.; Alemán, J.; Ruano, J. L. G. *Chem. Commun.* **2015**, *51*, 346–349. (h) Yang, J.; Zhang, J.; Qi, L.; Hu, C.; Chen, Y. *Chem. Commun.* **2015**, *51*, 5275–5278. (i) Riddell, N.; Tam, W. *J. Org. Chem.* **2006**, *71*, 1934–1937. (j) Huang, X.; Duan, D.; Zheng, W. *J. Org. Chem*. **2003**, *68*, 1958–1963. And references cited therein.

(13) (a) Abe, H.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 787–798. (b) Nair, V.; Augustine, A.; Suja, T. D. *Synthesis* **2002**, 2259–2265. (c) Qian, H.; Huang, X. *Tetrahedron Lett.* **2002**, *43*, 1059–1061. (d) Wei, W.; Wen, J.; Yang, D.; Jing, H.; You, J.; Wang, H. *RSC Adv.* **2015**, *5*, 4416–4419. (e) Singh, R.; Allam, B. K.; Singh, N.; Kumari, K.; Singh, S. K.; Singh, K. N. *Org. Lett.* **2015**, *17*, 2656–2659. And references cited therein.

(14) (a) Katrun, P.; Chiampanichayakul, S.; Korworapan, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Kuhakarn, C. *Eur. J. Org. Chem.* **2010**, 5633–5641. (b) Samakkanad, N.; Katrun, P.; Techajaroonjit, T.; Hlekhlai, S.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. *Synthesis* **2012**, *44*, 1693–1699. (c) Sawangphon, T.; Katrun, P.; Chaisiwamongkhol, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. *Synth. Commun.* **2013**, *43*, 1692–1707. (d) Muangkaew, C.; Katrun, P.; Kanchanarugee, P.; Pohmakotr, M.; Reutrakul, V.; Soorukram, D.; Jaipetch, T.; Kuhakarn, C. *Tetrahedron* **2013**, *69*, 8847–18856. (e) Katrun, P.; Mueangkaew, C.; Pohmakotr, M.; Reutrakul,

V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. *J. Org. Chem.* **2014**, *79*, 1778–1785. (f) Katrun, P.; Hongthong, S.; Hlekhlai, S.; Pohmakotr, M.; Reutrakul, V.; Soorukram, D.; Jaipetch, T.; Kuhakarn, C. *RSC Adv.* **2014**, *4*, 18933–18938. (g) Katrun, P.; Hlekhlai, S.; Meesin, J.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. *Org. Biomol. Chem.* **2015**, *13*, 4785–4794.

(15) Naskar, D.; Roy, S. *J. Org. Chem.* **1999**, *64*, 6896–6897.

(16) (a) Reddy, K. R.; Venkateshwar, M.; Maheswari, C. U.; Kumar, P. S. *Tetrahedron Lett.* **2010**, *51*, 2170–2173. (b) Kulbitski, K.; Nisnevich, G.; Gandelman, M. *Adv. Synth. Catal.* **2011**, *353*, 1438–1442.

(17) Liu, L. K.; Chi, Y.; Jen, K.-Y. *J. Org. Chem.* **1980**, *45*, 406–410.

(18) (a) Tanuguchi, N. *Tetrahedron* **2014**, *70*, 1984–1990. (b) Rong, G.; Mao, J.; Yan, H.; Zheng, Y.; Zhang, G. *J. Org. Chem.* **2015**, *80*, 7652–7657. (c) Li, S.; Li, X.; Yang, F.; Wu, Y. *Org. Chem. Front.* **2015**, *2*, 1076–1079. (d) Truce, W. E.; Wolf. G. C. *J. Org. Chem.* **1971**, *36*, 1727–1732.

(19) (a) Reddy, K. R.; Maheswari, C. U.; Venkateshwar, M.; Kantam, M. L. *Eur. J. Org. Chem.* **2008**, 3619–3622. (b) Lamani, M.; Prabhu, K. R. *J. Org. Chem.* **2011**, *76*, 7938–7944. (c) Froehr, T.; Sindlinger, C. P.; Kloeckner, U.; Finkbeiner, P.; Nachtsheim, B. J. *Org. Lett.* **2011**, *13*, 3754–3757. (d) Zeng, L. Y.; Yi, W. B.; Cai, C. *Eur. J. Org. Chem.* **2012**, 559–566. (e) Jia, Z.; Nagano, T.; Li, X.; Chan, A. S. C. *Eur. J. Org. Chem.* **2013**, 858–861. (f) Wu, X.-F.; Gong, J.-L.; Qi, X. *Org. Biomol. Chem.* **2014**, *12*, 5807–5817. (g) Zhao, J.; Li, P.; Xia, C.; Li, F. *Chem. Commun.* **2014**, *50*, 4751–4754. (h) Guo, S.; Yu, J.-T.; Dai, Q.; Yang, H.; Cheng, J. *Chem. Commun.* **2014**, *50*, 6240–6242.

(20) (a) Park, K.; Heo, Y.; Lee, S. *Org. Lett*. **2013**, *15*, 3322–3325. (b) Hwang, J.; Choi, J.; Park, K.; Kim, W.; Song, K. H.; Lee, S. *Eur. J. Org. Chem.* **2015**, *10*, 2235–2243. (c) Zhou, M.; Chen, M.; Zhou, Y.; Yang, K.; Su, J.; Du, J.; Song, Q. *Org. Lett.* **2015**, *17*, 1786–1789.