Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201300945

Chemoselective Synthesis of Unsymmetrical Internal Alkynes or Vinyl Sulfones *via* Palladium-Catalyzed Cross-Coupling Reaction of Sodium Sulfinates with Alkynes

Yanli Xu,[a] Jinwu Zhao,[a] Xiaodong Tang,[a] Wanqing Wu,[a] and Huanfeng Jiang[a,*]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China
Fax: (+86)-20-8711-2906; e-mail: jianghf@scut.edu.cn

Received: October 24, 2013; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300945.

Abstract: A highly efficient and mild palladium-catalyzed cross-coupling of sodium sulfinates and alkynes for the selective synthesis of unsymmetrical internal alkynes and vinyl sulfones has been developed. This methodology has advantages of easily accessible starting materials, functional group tolerance and a wide range of substrates, which provides rapid access to alkynes and vinyl sulfones.

Keywords: alkynes; cross-coupling; palladium catalyst; sodium sulfinates; vinyl sulfones

Introduction

Significant efforts have been devoted to the development of transition metal-catalyzed cross-coupling reactions, allowing for the construction of novel and biologically relevant molecules.[1] Among them, the palladium-catalyzed coupling reactions for the formation of C–C and C–heteroatom bonds has been widely used both in preparative laboratories and industrial applications.[2]

The alkyne moiety is an important structural motif in many biologically active natural products and pharmaceutical compounds,[3] as well as useful synthetic intermediates.[4] In general, the palladium-catalyzed Sonogashira coupling is one of the most powerful and straightforward tools for the preparation of alkynes, which involves an aryl halide (C_{sp2}–X) and an alkyne (C_{sp}–H) substrate in the presence of a phosphane ligand and base under a nitrogen atmosphere. Usually, butadiyne was also formed as the by-product.[5]

Vinyl sulfones occur in a number of compounds exhibiting potential biological activities.[6] For example, substituted vinyl sulfones have proved to be potent inhibitors of a variety of enzymatic processes which mainly include inducible VCAM-1 expression inhibition and cysteine proteases, making them lead candidates for drug design and have thus received overwhelming attention in the pharmaceutical industry (Figure 1).[7] They also exhibit interesting chemical properties and are useful intermediates in organic synthesis.[8] Thus, numerous procedures for their preparation have been developed, which mainly included the oxidation of the corresponding sulfides,[9a–e] manipulation of acetylenic sulfones,[9f] condensation of aromatic aldehydes with sulfonylacetic acids,[9g] and β-elimination of selenosulfones or halosulfones.[9h,i] Re-

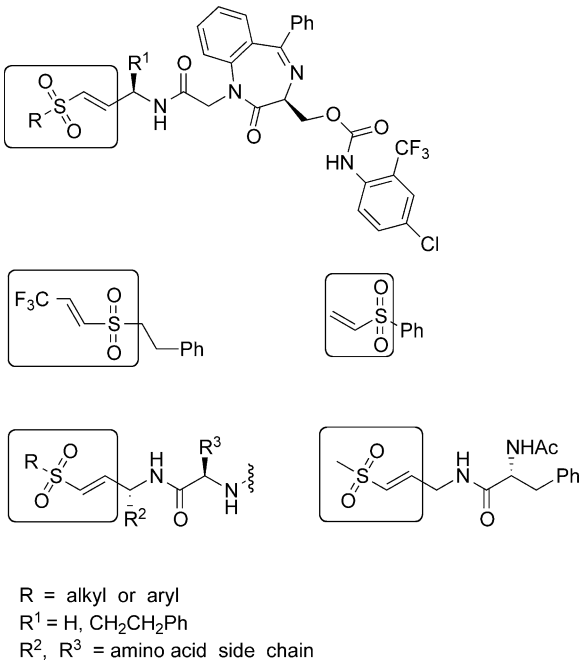
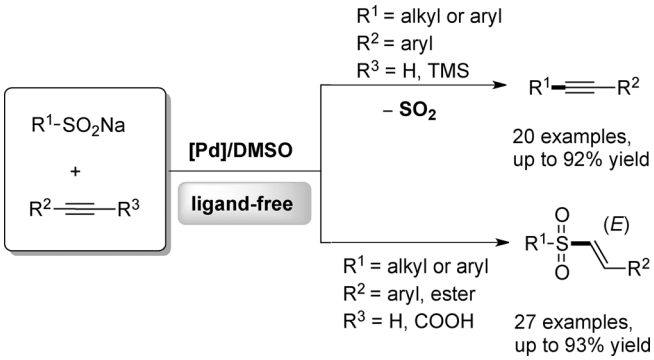


Figure 1. Examples of vinyl sulfone enzyme inhibitors.



Scheme 1.

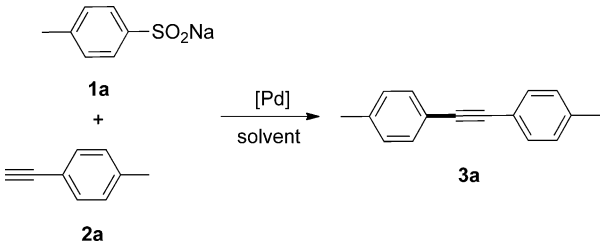
cently, a newly uncovered and efficient method to vinyl sulfones is the cross-coupling of sulfinate salts with vinyl halides,[10a–c] vinyl tosylates,[10d] vinyl triflates,[10e] alkenylboronic acids,[10f] or alkenes[10g] in the presence of a Pd or Cu catalyst. Besides, Li's group has also described a new and selective method for the preparation of (*E*)-vinyl sulfones through palladium-catalyzed conjugated addition of electron-deficient alkynes with benzenesulfinic acid derivatives such as 2-bis(phenylsulfonyl)ethane.[11] Although diverse approaches toward the synthesis of vinyl sulfones have been exploited, the development of efficient and practical synthetic methods for vinyl sulfones with high regioselectivity is still needed.

As we all known, sulfinic acid sodium salts are relatively stable, simple to handle, and easy to prepare from their corresponding sulfonyl chlorides, and when necessary, could be used as aryl sources in cross-coupling reaction *via* release of SO_2.[12] As part of our continuing interest in sodium sulfinates as substrates,[13] herein, we would like to desicribe a simple and efficient palladium-catalyzed cross-coupling of sodium sulfinates and alkynes for the selective synthesis of unsymmetrical internal alkynes and vinyl sulfones. This transformation proceeds under ligand-free and mild conditions, providing excellent yields of coupling products and tolerating a variety of functional groups (Scheme 1).

Results and Discussion

Firstly, the reaction of *para*-toluenesulfinic acid sodium salt (**1a**) and 4-ethynyltoluene (**2a**) in the presence of 5 mol% $PdCl_2$ in *N*,*N*-dimethylformamide (DMF) at 80 °C for 8 h, gave the desired product 1,2-di-*para*-tolylethyne (**3a**) in 35% GC yield (Table 1, entry 1). Subsequently, ligands such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and PPh_3 were added, however, lower yields of **3a** were detected (Table 1, entries 2 and 3). To our delight, when the reaction was carried out in dimethyl sulfoxide (DMSO), the yield of **3a** was increased to 87% (Table 1, entry 4). Other Pd catalysts including $Pd_2(dba)_3$, $Pd(OAc)_2$, $Pd(PPh_3)_2Cl_2$, $Pd(TFA)_2$ could also afford the desired product, and $PdCl_2$ proved to be optimal (Table 1, entries 4 *vs.* 5–8). In addition, further optimization suggested that solvents had a strong effect on this process and DMSO was found to be the best medium for this reaction (Table 1, entries 4 *vs.* 9–12). Besides, control experiments showed that no desired product **3a** was formed when the catalyst $PdCl_2$ was omitted from the reaction. Thus, the best conditions for this process comprised 5 mol% $PdCl_2$ in DMSO at 80 °C for 8 h.

Table 1. Optimization of the reaction conditions.[a]

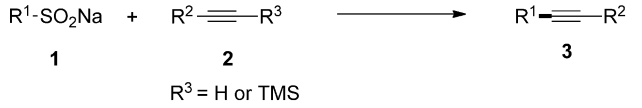


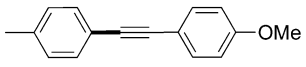
Entry	Catalyst	Solvent	Yield [%][b]
1	$PdCl_2$	DMF	35
2[c]	$PdCl_2$	DMF	32
3[d]	$PdCl_2$	DMF	19
4	$PdCl_2$	DMSO	87 (79)
5	$Pd_2(dba)_3$	DMSO	<10
6	$Pd(OAc)_2$	DMSO	73
7	$Pd(PPh_3)_2Cl_2$	DMSO	65
8	$Pd(TFA)_2$	DMSO	62
9	$PdCl_2$	CH_3CN	n.d.
10	$PdCl_2$	1,4-dioxane	n.d.
11	$PdCl_2$	toluene	10
12	$PdCl_2$	DCE	n.d.

[a] *Reaction conditions:* unless otherwise noted, all reactions were performed with **1a** (0.3 mmol), **2a** (0.2 mmol) Pd catalyst (5 mol%), in the indicated solvent (2 mL) at 80 °C for 8 h.
[b] Determined by GC using dodecane as the internal standard. Data in parentheses are the yields of isolated product. n.d. = not detected.
[c] 10 mol% DABCO was added.
[d] 10 mol% PPh_3 was added.

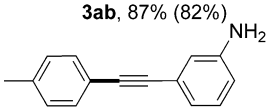
With the optimal reaction conditions in hand, we then evaluated the scope of the reaction and the results are summarized in Table 2. The coupling of *para*-toluenesulfinic acid sodium salt with 1-ethynyl-4-methoxybenzene or 3-ethynylaniline, gave the corresponding products **3ab** and **3ac** in excellent yields, respectively. Also, benzenesulfinic acid sodium salt could react with phenylacetylenes bearing electron-donating groups such as Me, OMe, OEt, NH_2, and OH or weak electron-withdrawing substituents such as COOMe on the aromatic ring, affording the de-

Table 2. Formation of C–C bonds for the synthesis of internal alkynes.[a,b]

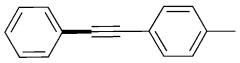




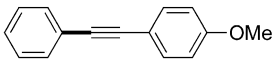
3ab, 87% (82%)



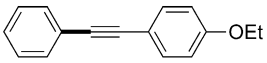
3ac,[c] 92% (85%)



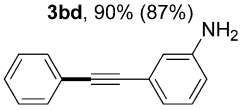
3ba, 78% (80%)



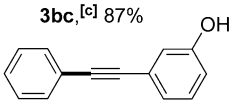
3bb, 88%



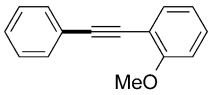
3bd, 90% (87%)



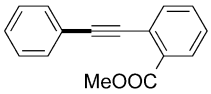
3bc,[c] 87%



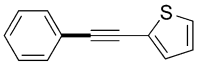
3bd,[d] 86% (78%)



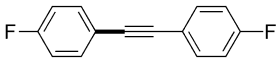
3bf, 89% (86%)



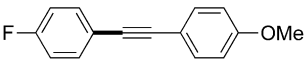
3bh,[e] 64% (70%)



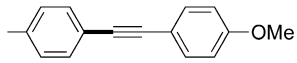
3bi, 67% (71%)



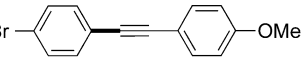
3cj,[e] 69% (68%)



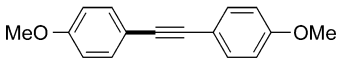
3cb,[f] 82%



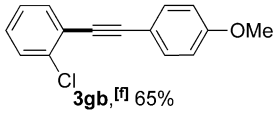
3db,[f] 78%



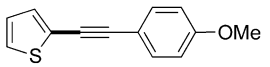
3eb,[f] 72%



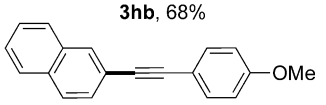
3fb, 89%



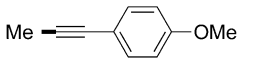
3gb,[f] 65%



3hb, 68%



3ib,[g] 81%



3nb,[h] 42%

[a] *Reaction conditions:* unless otherwise noted, all reactions were performed with **1** (0.75 mmol), **2** (0.5 mmol) $PdCl_2$ (5 mol%), in DMSO (2 mL) at 80 °C (R^3 = H, for 8 h and R^3 = TMS, for 10–16 h).

[b] Yields of isolated products base on **2**, and data in parentheses are the yields for starting material **2** when R^3 isTMS.

[c] R^3 = H, at 120 °C for 24 h and R^3 = TMS, for 32 h.

[d] R^3 = H, at 110 °C for 8 h and R^3 = TMS, for 12 h.

[e] R^3 = H, at 50 °C for 8 h and R^3 = TMS, for 10 h.

[f] R^3 = H, at 50 °C for 8 h.

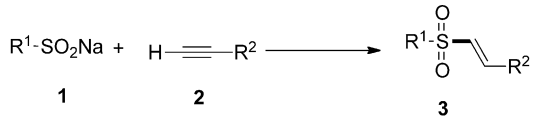
[g] R^3 = H, at 50 °C for 24 h.

[h] R^3 = H, at 100 °C for 8 h.

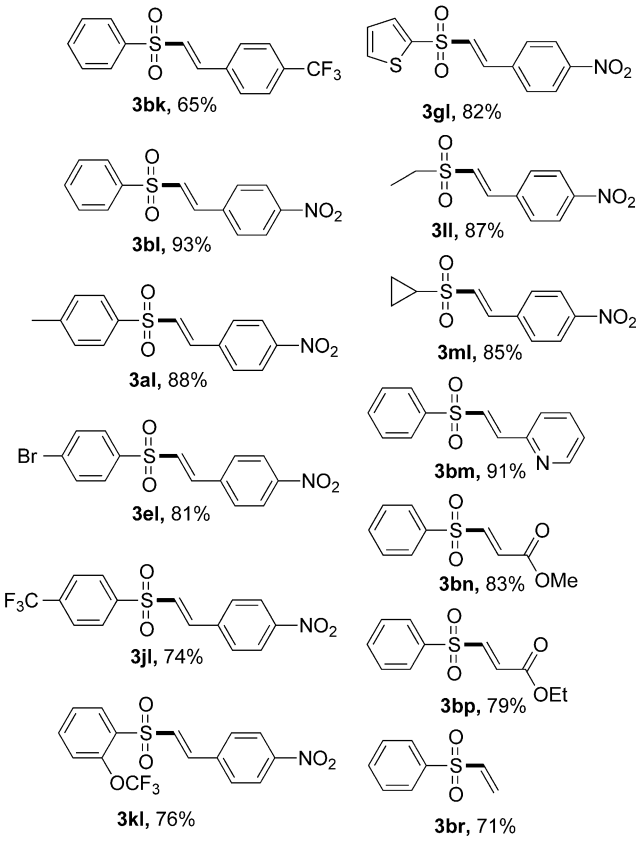
sired products in good to excellent yields. These results showed that the position of the substituents on benzene ring did not affect the reaction significantly. 4-Flurobenzenesulfinic acid sodium salt was treated with ethynyl-4-fluorobenzene in the presence of 2 mol% $PdCl_2$ at 50 °C for 8 h, giving 1,2-bis(4-fluorophenyl)ethyne (**3cj**) in 69% yield, and with 1-ethynyl-4-methoxybenzene to give the desired product **3cb** in 82% yield, which suggested that electron-rich terminal alkynes provided the desired products in higher yields than did electron-poor terminal alkynes. In addition, alkynes bearing a heterocyclic aromatic substituent such as 2-ethynylthiophene (R^2 = 2-thienyl), giving the desired product **3bi** in 67% yield. And the reactions of 4-chlorobenzenesulfinic acid sodium, 4-bromobenzenesulfinic acid sodium, or 4-methoxybenzenesulfinic acid sodium with 1-ethynyl-4-methoxybenzene also proceeded smoothly and afforded the desired products **3db**–**3fb** in high yields. Moreover, 2-chlorobenzenesulfinic acid sodium could provide the desired product in 65% yield, when it reacted with 1-ethynyl-4-methoxybenzene. Besides, 2-thienylsulfinic acid sodium salt and 2-naphthylsulfinic acid sodium salt also participated well in this process, and gave the corresponding products **3hb** and **3ib** in 68% and 81% yields. In addition, when methanesulfinic acid sodium salt was used as substrate, the desired product **3nb** could be obtained in 42% yield. Besides, substituted phenylethynyl(trimethyl)silanes were also suitable for this transformation, on the whole, giving the desired products in good to high yields with extension of the reaction time compared to the corresponding substituted phenylacetylenes. Unfortunately, the coupling reactions between benzenesulfinic acid sodium salt and 1-octyne or trimethylsilylacetylene failed to give the desired products.

To our surprise, the coupling reaction of benzenesulfinic acid sodium salt and 1-ethynyl-4-(trifluoromethyl)benzene in the presence of 5 mol% $PdCl_2$ provided (*E*)-1-[2-(phenylsulfonyl)vinyl]-4-(trifluoromethyl)-benzene (**3bk**) in 65% yield together with 10% of 1-(phenylethynyl)-4-(trifluoromethyl)benzene (Table 3). When benzenesulfinic acid sodium salt was treated with 1-ethynyl-4-nitrobenzene, a 93% yield of (*E*)-1-nitro-4-[2-(phenylsulfonyl)vinyl]benzene **3bl** only was obtained. These results suggest that electronic effects on the aromatic ring of the phenylacetylene play a crucial role in the selective formation of C–C and C–S bonds. Other substituted benzenesulfinic acid sodium salts also reacted with 1-ethynyl-4-nitrobenzene smoothly, giving the corresponding products **3al**–**3kl** in excellent yields. In addition, 2-thienylsulfinic acid sodium salt reacted well in this process and led to the desired product **3gl** in 82% yield. It should be noted that ethanesulfinic acid sodium salt or cyclopropanesulfinic acid sodium salt were also successfully employed in this process, affording the desired products **3ll** and **3ml** in 87% and 85% yields, respectively. Benzenesulfinic acid sodium salt when treated with 2-

Table 3. Formation of C–S bonds for the synthesis of vinyl sulfones.[a,b]



1 2 3



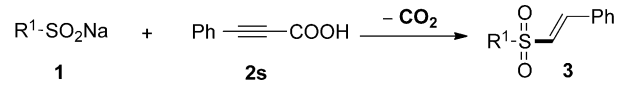
[a] *Reaction conditions:* unless otherwise noted, all reactions were performed with **1** (0.75 mmol), **2** (0.5 mmol), $PdCl_2$ (5 mol%), in DMSO (2 mL) at 50 °C for 8 h.
[b] Yields of isolated products.

ethynylpyridine gave the desired product **3bm** in 91% yield, as well. Reactions of benzenesulfinic acid sodium salt and methyl propiolate or ethyl propiolate in the presence of 5 mol% $PdCl_2$ afforded **3bn** and **3bp** in 83% and 79% yields, respectively. Additionally, propiolic acid also reacted well under the same conditions, however, the reaction did not give the corresponding product (*E*)-3-(phenylsulfonyl)acrylic acid, but rather (vinylsulfonyl)benzene **3br** in 71% yield, which was the result of decarboxylation.

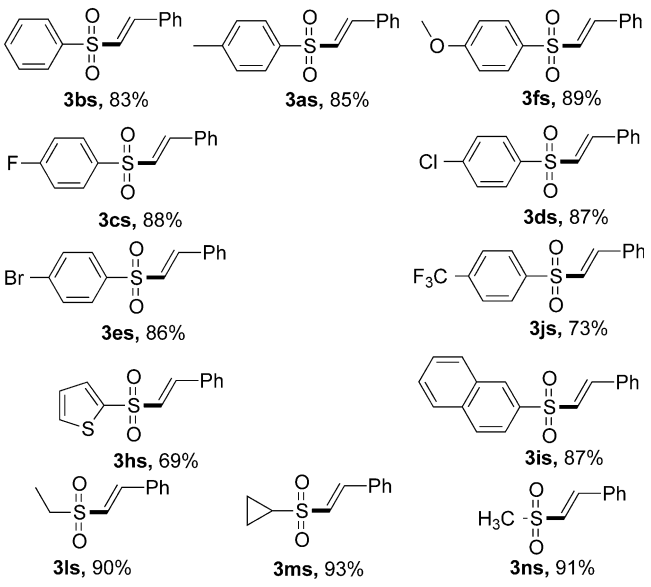
Inspired by the result of decarboxylation of propiolic acid, the coupling reaction between benzenesulfinic acid sodium salt and 3-phenylpropiolic acid was preformed in the presence of 5 mol% $PdCl_2$ in DMSO at 50 °C, and a product mixture of 1,2-diphenylethyne, 1,4-diphenylbuta-1,3-diyne and a vinyl sulfone was detected by GC-MS. When the reaction solution was heated to 100 °C, the vinyl sulfone product was isolated in 83% yield, and further confirmation showed it to be (*E*)-[2-(phenylsulfonyl)vinyl]benzene and not [1-(phenylsulfonyl)vinyl]benzene (Table 4). This result suggested that the substrate 3-phenylpropiolic acid reacted as phenylacetylene by releasing CO_2 in this process.[14] Other arylsulfinic acid sodium salts bearing methyl, methoxy, fluoro, chloro, bromo, and trifluoromethyl on the benzene ring reacted smoothly and afforded the desired products in good to high yield. Also, a 69% yield of **3hs** was obtained when 2-thienylsulfinic acid sodium salt reacted with **2s**. More sterically impaired substrates such as 2-naphthylsulfinic acid sodium salt also efficiently reacted with **2s** and gave the product **3is** in 83% yield. Besides, methanesulfinic acid sodium salt, ethanesulfinic acid sodium salt or cyclopropanesulfinic acid sodium salt were also employed well in this process, affording the corresponding products in excellent yields.

Additionally, when *ortho*-substituted arylsulfinic acid sodium salts, such as 2-chlorobenzenesulfinic acid sodium or 2-trifluoromethoxybenzenesulfinic acid sodium, were treated with **2t**, they gave 2-[(2-chlorophenyl)sulfonyl]-1-phenylethanone and 1-phenyl-2-[(2-(trifluoromethoxy)phenyl]sulfonyl)ethanone in 86% and 76% yields, respectively (Scheme 2).[15]

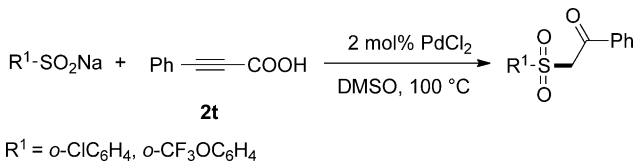
Table 4. Formation of C–S bonds for the synthesis of vinyl sulfones.[a,b]



1 2s 3



[a] *Reaction conditions:* unless otherwise noted, all reactions were performed with **1** (0.75 mmol), **2s** (0.5 mmol), $PdCl_2$ (5 mol%), in DMSO (2 mL) at 100 °C for 8 h.
[b] Yields of isolated products.

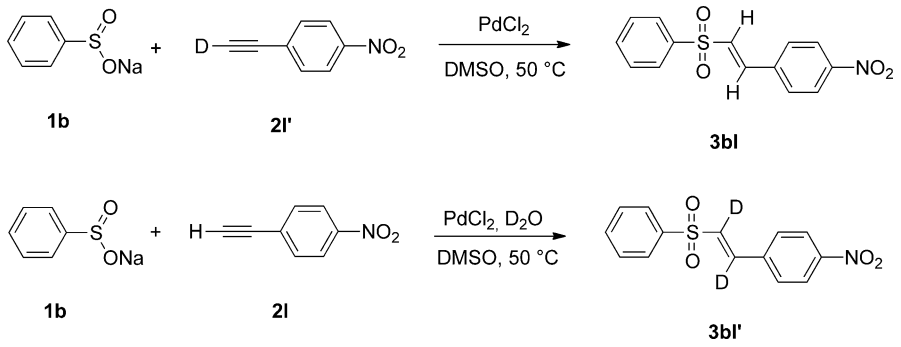


Scheme 2. Synthesis of β-keto sulfones.

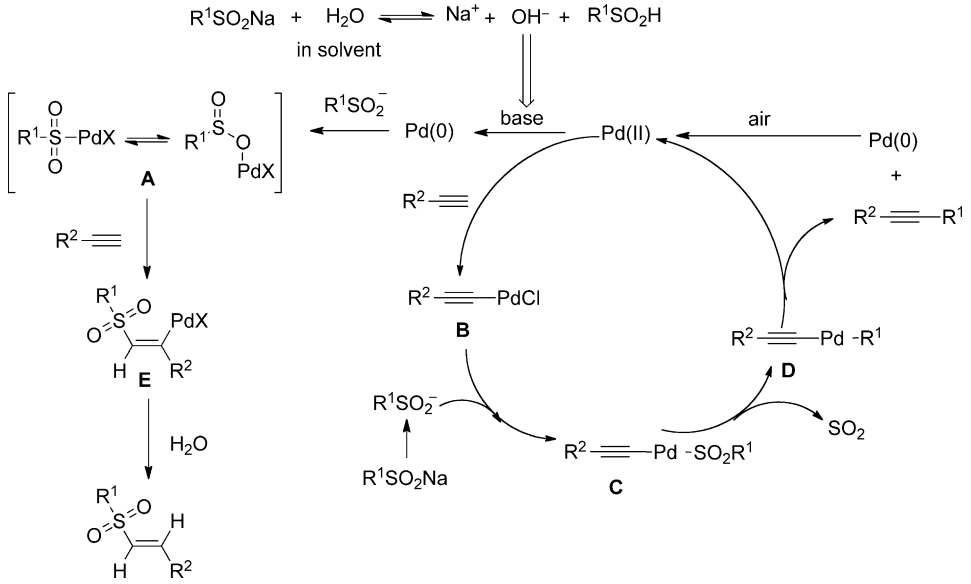
In order to study the mechanism for the synthesis of vinyl sulfones, control experiments have been done as shown in Scheme 3. The reaction of benzenesulfinic acid sodium salt (**1b**) and deuterated 1-ethynyl-4-nitrobenzene (**2l′**) was performed under the standard conditions, which gave product **3bl**, while the treatment of benzenesulfinic acid sodium salt (**1b**) 1-ethynyl-4-nitrobenzene (**2l**) in the presence of D_2O under the standard conditions resulted in product **3bl′**. These results suggested that (i) the formation of vinyl sulfones by water-assisted regeneration of complex **E** as in Scheme 4; (ii) the formation of **3bl′** might be due to the acidity of 1-ethynyl-4-nitrobenzene. It exchanged with the D_2O of DMSO under the weak basic reaction conditions at first, and then coupled with benzenesulfinic acid sodium salt to afford **3bl′**.

Plausible Reaction Mechanism

On the basis of the above results, a plausible mechanism for the selective formation of C–C and C–S bonds is proposed, as shown in Scheme 4. Firstly, coordination of terminal alkynes to $PdCl_2$ to give alkynyl palladium **B**, and then nucleophilic displacement of chlorine to generate intermediate **C**,[12a] followed by expulsion of SO_2 led to the formation of intermediate **D**. Subsequently, reductive elimination of a Pd(0) species occurred to give the desired product, and Pd(0) species was oxidized to the active Pd(II) species under the air atmosphere. On the other hand, oxidative addition of Pd(0) to sulfinic acid sodium salts



Scheme 3. The deuteration experiments.



Scheme 4. Plausible reaction mechanism.

(R^1SO_2Na) afforded intermediate **A**, which was treated with strong electron-withdrawing alkynes, whereby migratory insertion of the C≡C bond with complex **A** occurred to give complex **E**,[16] followed by protonation of water to form the vinyl sulfone products.

Conclusions

In summary, we have developed a simple and efficient palladium-catalyzed method for the formation of internal alkynes and vinyl sulfones from sodium sulfinates and alkynes. The electronic effect of the substituents on the triple bond plays a crucial role on this process. This reaction presents a convenient method with good functional group tolerance for the synthesis of unsymmetrical internal alkynes and vinyl sulfones in organic synthesis and medicinal chemistry. Further studies on the applications of vinyl sulfones in drug design are currently ongoing in our laboratory.

Experimental Section

General Methods

Solvents and all reagents were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz NMR spectrometer. The chemical shifts (δ) were referenced to TMS. GC-MS was obtained using electron ionization (EI). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. Melting points were measured with a micro melting point apparatus. TLC was performed using commercially prepared 100–400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. High resolution-mass spectra (ESI) were obtained with an LCMS-IT-TOF mass spectrometer.

General Procedure for the Synthesis of Internal Alkynes and Vinyl Sulfones

The reaction mixture of sodium sulfinate **1** (0.75 mmol), alkyne **2** (0.5 mmol), $PdCl_2$ (5 mol%, 44 mg) and DMSO (2 mL) in a 25-mL tube was stirred at the corresponding temperature under an air atmosphere and monitored periodically by TLC. Upon completion, the crude product was cooled to room temperature and then quenched by the addition of 10 mL water. The aqueous solution was extracted with ethyl acetate (3×10 mL) and the combined extracts were dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure by an aspirator, and the crude product was purified by silica gel column chromatography to give the pure product **3**.

1,2-Di-*para*-tolylethyne (3aa):[17] White solid; mp 126–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 131.4, 129.1, 120.4, 88.9, 21.5; IR (KBr): ν = 3064, 2924, 1647, 1513, 1454, 815, 747 cm^{-1}; MS (EI): m/z = 206, 191, 165, 115, 102, 89.

1-Methoxy-4-(*para*-tolylethynyl)benzene (3ab):[18] White solid; mp 130–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.06 (d, J = 7.8 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 3.74 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 138.0, 133.0, 131.3, 129.1, 120.5, 115.6, 114.0, 88.7, 88.2, 55.3, 21.5; IR (KBr): ν = 3064, 2924, 1645, 1511, 1455, 1247, 1175, 1104, 1028, 822, 750 cm^{-1}; MS (EI): m/z = 222, 207, 179, 152, 111, 94.

3-(*para*-Tolylethynyl)aniline (3ac):[19] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 7.13–7.11 (m, 1H), 6.95 (d, J = 7.0 Hz, 1H), 6.86 (s, 1H), 6.66 (d, J = 8.0 Hz, 1H), 3.33 (br, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2, 138.3, 131.5, 129.2, 129.1, 124.1, 122.1, 120.3, 117.8, 115.2, 89.0, 88.9, 21.45; IR (KBr): ν = 3458, 2922, 2358, 1632, 1448, 1105, 780, 623 cm^{-1}; MS (EI): m/z = 207, 189, 178, 165, 103, 90.

1-Methyl-4-(phenylethynyl)benzene (3ba):[17] White solid; mp 70–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (m, 2H), 7.44 (d, J = 7.8 Hz, 2H), 7.40–7.31 (m, 3H), 7.17 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 131.5, 131.4, 129.1, 128.3, 128.1, 123.5, 120.2, 89.6, 88.7, 21.5; IR (KBr): ν = 3065, 2925, 1648, 1509, 1441, 817, 755 cm^{-1}; MS (EI): m/z = 192, 189, 176, 165, 119, 77.

1-Methoxy-4-(phenylethynyl)benzene (3bb):[17] Yellow solid; mp 58–60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.50 (m, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.39–7.28 (m, 3H), 6.89 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ = 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3; IR (KBr): ν = 3064, 2928, 1601, 1510, 1441, 1250, 1179, 1029, 834, 754 cm^{-1}; MS (EI): m/z = 208, 193, 165, 139, 104, 77.

1-Ethoxy-4-(phenylethynyl)benzene (3bd):[20] White solid; mp 83–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, J = 8.6 Hz, 2H), 7.45 (m, 2H), 7.38–7.28 (m, 3H), 6.87 (d, J = 8.6 Hz, 2H), 4.05 (q, J = 7.0 Hz, 2H), 1.43 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 133.0, 131.4, 128.3, 127.9, 123.6, 115.2, 114.5, 89.4, 88.0, 63.5, 14.8. IR (KBr): ν = 3064, 2927, 1603, 1511, 1389, 1252, 1115, 1025, 832, 756 cm^{-1}; MS (EI): m/z = 222, 194, 165, 139, 115, 89.

3-(Phenylethynyl)aniline (3bc):[21] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.50 (m, 1H), 7.44–6.80 (m, 7H), 6.73–6.59 (m, 1H), 3.30 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2, 131.6, 129.3, 128.3, 128.1, 123.9, 123.4, 122.1, 117.8, 115.4, 89.6, 88.8. IR (KBr): ν = 3459, 3377, 3055, 2925, 1601, 1492, 1446, 1251, 1129, 1028, 756, 691 cm^{-1}; MS (EI): m/z = 193, 165, 139, 115, 97, 77.

3-(Phenylethynyl)phenol (3be):[22] Pale yellow solid; mp 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.54 (m, 2H), 7.41–7.40 (m, 3H), 7.33–7.27 (m, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.07 (s, 1H), 6.89 (d, J = 8.0 Hz, 1H), 5.20 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 131.6, 129.6, 128.3, 124.5, 124.3, 123.1, 118.2, 115.8, 89.4, 89.0; IR (KBr): ν = 3610, 3292, 3060, 2925, 1582, 1497, 1443, 1309, 1215, 1125, 755, 687 cm^{-1}; MS (EI): m/z = 194, 165, 137, 115, 97, 82.

Methoxy-2-(phenylethynyl)benzene (3bf):[21] Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.56 (m, 2H), 7.52–7.50 (m, 1H), 7.39–7.28 (m, 4H), 7.00–6.88 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 133.6, 131.6, 129.7, 128.2, 128.1, 123.6, 120.5, 112.5, 110.7, 93.4, 85.7, 55.8; IR (KBr): ν = 3062, 2928, 1644, 1595, 1492, 1275,

1246, 1107, 1023, 752, 690 cm^{-1}; MS (EI): m/z = 208, 189, 178, 165, 131, 115.

Methyl 2-(phenylethynyl)benzoate (3bh):[23] Yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 7.9 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.61–7.55 (m, 2H), 7.50 (t, J = 7.6 Hz, 1H), 7.40–7.35 (m, 4H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 134.0, 131.9, 131.7, 131.7, 130.5, 128.5, 128.3, 127.9, 123.7, 123.4, 94.3, 88.2, 52.2; IR (KBr): ν = 3053, 2924, 1728, 1603, 1438, 1125, 757, 620 cm^{-1}; MS (EI): m/z = 236, 221, 193, 165, 151, 88.

2-(Phenylethynyl)thiophene (3bi):[21] Yellow solid; mp 46–47 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 3.9 Hz, 1H), 7.55 (d, J = 5.2 Hz, 1H), 7.41–7.35 (m, 3H), 7.36–7.29 (m, 2H), 7.04 (dd, J = 5.2, 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.8, 131.4, 128.4, 128.3, 127.2, 127.0, 123.3, 122.9, 93.0, 82.6; IR (KBr): ν = 3073, 2924, 1654, 1598, 1521,1427, 1215, 846, 754, 697 cm^{-1}; MS (EI): m/z = 184, 152, 139, 126, 113, 92.

1,2-Bis(4-fluorophenyl)ethyne (3cj):[24] White solid; mp 92–94 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.48 (m, 4H), 7.07–7.03 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6, 133.4, 119.2, 115.7, 88.0; IR (KBr): ν = 3053, 2924, 1588, 1509, 1405, 1157, 836, 761 cm^{-1}; MS (EI): m/z = 214, 193, 188, 168, 107, 94.

1-Fluoro-4-[(4-methoxyphenyl)ethynyl]benzene (3cb):[18] White solid; mp 85–86 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.41 (m, 4H), 7.03 (t, J = 8.5 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 161.1, 159.7, 133.0, 119.7, 115.4, 115.2, 114.0, 89.0, 87.0, 55.3; IR (KBr): ν = 3064, 2969, 1605, 1512, 1464, 1254, 1179, 1028, 834, 754 cm^{-1}; MS (EI): m/z = 226, 211, 183, 157, 133, 113.

1-Chloro-4-[(4-methoxyphenyl)ethynyl]benzene (3db):[18] White solid; mp 112–113 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (dd, J = 11.0, 8.6 Hz, 4H), 7.31 (d, J = 8.4 Hz, 2H), 6.87 (t, J = 6.9 Hz, 2H), 3.83 (s, 3H): ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 133.95, 133.1, 132.6, 128.6, 122.1, 115.0, 114.0, 90.4, 87.0, 55.3; IR (KBr): ν = 3064, 2926, 1604, 1512, 1462, 1396, 1252, 1108, 1029, 831, 750 cm^{-1}; MS (EI): m/z = 244, 242, 227, 199, 163, 137, 99.

1-Bromo-4-[(4-methoxyphenyl)ethynyl]benzene (3eb):[14a] White solid; mp 153–154 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.41 (m, 4H), 7.36 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 133.1, 132.8, 131.5, 122.6, 122.0, 115.0, 114.1, 90.6, 87.0, 55.3; IR (KBr): ν = 3064, 2931, 1603, 1511, 1459, 1390, 1250, 1110, 1029, 827, 754 cm^{-1}; MS (EI): m/z = 288, 286, 273, 243, 163, 144, 88.

1,2-Bis(4-methoxyphenyl)ethyne (3fb):[18] White solid; mp 113–114 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.2 Hz, 4H), 6.87 (d, J = 8.2 Hz, 4H), 3.82 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 132.9, 115.7, 114.0, 87.9, 55.3. IR (KBr): ν = 3062, 2923, 2843, 1651, 1604, 1557, 1456, 1245, 1170, 1024, 829, 751 cm^{-1}; MS (EI): m/z = 238, 223, 195, 180, 152, 119.

1-Chloro-2-[(4-methoxyphenyl)ethynyl]benzene (3gb):[25] White solid; mp 52–53 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.55 (m, 1H), 7.54 (d, J = 8.8 Hz, 2H), 7.43 (dd, J = 5.9, 3.4 Hz, 1H), 7.27–7.21 (m, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 135.6, 133.1, 132.9, 129.2, 128.8, 126.4, 123.5, 114.9, 114.0, 94.7, 85.0, 55.2. IR (KBr): ν = 3063, 2929, 2838, 1604, 1510, 1465, 1288, 1249, 1029, 752, 696 cm^{-1}; MS (EI): m/z = 242, 227, 199, 163, 121, 87.

2-[(4-Methoxyphenyl)ethynyl]thiophene (3hb):[18] White solid; mp 53–54 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 3.7 Hz, 1H), 7.27 (d, J = 5.1 Hz, 1H), 7.02 (dd, J = 5.1, 3.7 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 132.9, 131.4, 127.0, 126.8, 123.7, 115.0, 114.0, 93.0, 81.2, 55.3; IR (KBr): ν = 3064, 2920, 2847, 1607, 1508, 1462, 1246, 1172, 1109, 1026, 826, 754 cm^{-1}; MS (EI): m/z = 214, 199, 171, 127, 107, 63.

2-[(4-Methoxyphenyl)ethynyl]naphthalene (3ib):[18] White solid; mp 119–120 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.87–7.81 (m, 3H), 7.61–7.59 (m, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.51–7.49 (m, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 133.1, 133.0, 132.7, 131.1, 128.4, 127.9, 127.7, 127.7, 126.5, 120.9, 115.4, 114.1, 89.8, 88.5, 55.3; IR (KBr): ν = 3053, 2926, 2845, 1648, 1598, 1510, 1247, 1173, 1029, 827, 745 cm^{-1}; MS (EI): m/z = 258, 243, 215, 189, 129, 94.

1-Methoxy-4-(prop-1-yn-1-yl)benzene (3nb):[14d] Pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H), 3.80 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 132.8, 116.2, 113.8, 84.1, 79.4, 55.2, 4.3; IR (KBr): ν = 3052, 2926, 2845, 1651, 1598, 1509, 1247, 1173, 1029, 829, 746 cm^{-1}; MS (EI): m/z = 146, 131, 115, 103, 77.

(*E*)-1-[2-(Phenylsulfonyl)vinyl]-4-(trifluoromethyl)benzene (3bk):[26] Yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.95 (m, 1H), 7.54 (m, 9H), 6.96 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 140.2, 135.7, 133.7, 130.1, 129.5, 128.7, 127.8, 126.1, 126.0; IR (KBr): ν = 3064, 2925, 1613, 1383, 1325, 1169, 1120, 1067, 845, 750 cm^{-1}; MS (EI): m/z = 312, 247, 187, 159, 125, 97.

(*E*)-1-Nitro-4-[2-(phenylsulfonyl)vinyl]benzene (3bl): Yellow solid; mp 139–140 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 15.5 Hz, 1H), 7.67–7.53 (m, 5H), 7.04 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 139.7, 139.2, 138.4, 133.8, 131.7, 129.5, 129.2, 127.8, 124.2; IR (KBr): ν = 3064, 2925, 1595, 1520, 1346, 1308, 1275, 1147, 811, 751 cm^{-1}; MS (EI): m/z = 289, 259, 225, 178, 148, 125; ESI-HR-MS: m/z = 312.0290, calcd. for $C_{14}H_{11}NNaO_4S$ $[M+Na]^+$: 312.0301.

(*E*)-1-Methyl-4-[(4-nitrostyryl)sulfonyl]benzene (3al): Yellow solid; mp 167–168 °; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.3 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.68 (d, J = 15.5 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 15.5 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 145.1, 138.6, 138.5, 136.8, 132.1, 130.2, 129.2, 128.0, 124.2, 21.6; IR (KBr): ν = 3116, 2925, 1596, 1520, 1346, 1310, 1147, 1085, 813, 745 cm^{-1}; MS (EI): m/z = 303, 239, 192, 178, 139, 92; ESI-HR-MS: m/z = 326.0455, calcd. for $C_{15}H_{13}NNaO_4S$ $[M+Na]^+$: 326.0457.

(*E*)-1-Bromo-4-[(4-nitrostyryl)sulfonyl]benzene (3el): Yellow solid; mp 172–173 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.6 Hz, 2H), 7.82 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 15.5 Hz, 1H), 7.65 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 139.8, 138.8, 138.1, 132.9, 131.2, 129.4, 129.3, 129.2, 124.3; IR (KBr): ν = 3052, 2924, 1596, 1524, 1648, 1345, 1311, 1141, 842, 743 cm^{-1}; MS (EI): m/z = 368, 366, 204, 177,

148, 117, 89; ESI-HR-MS: m/z = 389.9399, calcd. for $C_{14}H_{10}BrNNaO_4S$ $[M+Na]^+$: 389.9406.

(*E*)-1-Nitro-4-(2-{[4-(trifluoromethyl)phenyl]sulfonyl}vinyl)benzene (3jl): Yellow solid; mp 169–171 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.27 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 15.5 Hz, 1H), 7.88 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 148.6, 143.9, 140.9, 138.5, 131.2, 130.3, 128.5, 126.9, 126.9, 124.0; IR (KBr): ν = 3052, 2923, 2853, 1647, 1529, 1320, 1137, 836, 746 cm^{-1}; MS (EI): m/z = 357, 327, 193, 165, 118, 102; ESI-HR-MS: m/z = 380.0176, calcd. for $C_{15}H_{10}F_3NNaO_4S$ $[M+Na]^+$: 380.0175.

(*E*)-1-[(4-Nitrostyryl)sulfonyl]-2-(trifluoromethoxy)benzene (3kl): Yellow solid; mp 158–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.3 Hz, 2H), 8.15 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 15.4 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.11 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 146.7, 142.1, 138.2, 135.8, 131.8, 130.5, 130.2, 129.3, 126.9, 124.3 120.0; IR (KBr): ν = 3063, 2925, 1596, 1522 1344, 1248, 1151, 1068, 841, 746, 695 cm^{-1}; MS (EI): m/z = 373, 309, 262, 209, 115, 89; ESI-HR-MS: m/z = 396.0124, calcd. for $C_{15}H_{10}F_3NNaO_5S$ $[M+Na]^+$: 396.0124.

(*E*)-2-[(4-Nitrostyryl)sulfonyl]thiophene (3gl): Yellow solid; mp 143–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 3.6 Hz, 2H), 7.71 (d, J = 15.5 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.18 (t, J = 4.2 Hz, 1H), 7.11 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 141.1, 138.9, 138.3, 134.8, 134.2, 132.2, 129.3, 128.3, 124.3; IR (KBr): ν = 3063, 2925, 1655, 1518, 1342, 1307, 1243, 1139, 1060, 812, 747 cm^{-1}; MS (EI): m/z = 295, 231, 184, 152, 131, 102; ESI-HR-MS: m/z = 317.9872, calcd. for $C_{12}H_9NNaO_4S_2$ $[M+Na]^+$: 317.9865.

(*E*)-1-[2-(Ethylsulfonyl)vinyl]-4-nitrobenzene (3ll): Yellow solid; mp 161–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 15.5 Hz, 1H), 6.99 (d, J = 15.5 Hz, 1H), 3.13 (q, J = 7.4 Hz, 2H), 1.40 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 142.1, 138.2, 129.3, 128.5, 124.3, 49.3, 7.1; IR (KBr): ν = 3060, 2927, 2363, 1596, 1520, 1345, 1308, 1271, 843, 749 cm^{-1}; MS (EI): m/z = 241, 212, 164, 148, 118, 102; ESI-HR-MS: m/z = 264.0297, calcd. for $C_{10}H_{11}NNaO_4S$ $[M+Na]^+$: 264.0301.

(*E*)-1-[2-(Cyclopropylsulfonyl)vinyl]-4-nitrobenzene (3ml): Yellow solid; mp 157–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 15.5 Hz, 1H), 7.05 (d, J = 15.5 Hz, 1H), 2.56–2.40 (m, 1H), 1.38–1.29 (m, 2H), 1.15–1.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0, 140.1, 138.5, 123.0, 129.2, 124.3, 31.1, 5.5; IR (KBr): ν = 3048, 2924, 1597, 1519, 1345, 1295, 1131, 843, 745 cm^{-1}; MS (EI): m/z = 253, 204, 148, 118, 102, 89; ESI-HR-MS: m/z = 276.0295, calcd. for $C_{11}H_{11}NNaO_4S$ $[M+Na]^+$: 276.0301.

(*E*)-2-[2-(Phenylsulfonyl)vinyl]pyridine (3bm): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 4.7 Hz, 1H), 7.92 (d, J = 15.2 Hz, 1H), 7.91–7.89 (m, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.63–7.55 (m, 2H), 7.53–7.47 (m, 2H), 7.43 (d, J = 15.2 Hz, 1H), 7.40–7.35 (m, 1H), 7.25–7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9, 150.2, 140.5, 137.0, 133.5, 131.8, 129.3, 127.8, 127.3, 125.4, 125.0; IR (KBr): ν = 3054, 2920, 1647, 1549, 1463, 1305, 1144, 819, 754 cm^{-1}; MS (EI): m/z = 245, 216, 180, 125, 104, 92; ESI-HR-MS: m/z = 268.0411, calcd. for $C_{13}H_{11}NNaO_2S$ $[M+Na]^+$: 268.0403.

(*E*)-Methyl 3-(phenylsulfonyl)acrylate (3bn):[27] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, J = 7.7 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.7 Hz, 2H), 7.34 (d, J = 15.2 Hz, 1H), 6.84 (d, J = 15.2 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163. 9, 143. 5, 138.5, 134.4, 130.5, 129.6, 128.3, 52.8; IR (KBr): ν = 2924, 1729, 1584, 1441, 1303, 1274, 1232, 817, 754, 571 cm^{-1}; MS (EI): m/z = 226, 195, 161, 125, 97, 77.

(*E*)-Ethyl 3-(phenylsulfonyl)acrylate (3bp):[27] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, J = 7.8 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 15.2 Hz, 1H), 6.83 (d, J = 15.2 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 1.29 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4, 143.2, 138.5, 134.4, 131.0, 129.6, 128.3, 62.0, 14.0; IR (KBr): ν = 2984, 1724, 1583, 1447, 1384, 1298, 1231, 736, 689, 571 cm^{-1}; MS (EI): m/z = 240, 195, 167, 125, 97, 77.

(Vinylsulfonyl)benzene (3br):[11] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 7.8 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 6.66 (dd, J = 16.5, 9.8 Hz, 1H), 6.46 (d, J = 16.5 Hz, 1H), 6.04 (d, J = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.6, 138.5, 133.6, 129.3, 127.9, 127.7; IR (KBr): ν = 3061, 2923, 1635, 1448, 1383, 1310, 1143, 976, 744, 694, 558 cm^{-1}; MS (EI): m/z = 168, 141, 125, 97, 77, 65.

(*E*)-[2-(Phenylsulfonyl)vinyl]benzene (3bs):[28] Pale yellow solid; mp 67–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 7.7 Hz, 2H), 7.69 (d, J = 15.4 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.48 (d, J = 6.8 Hz, 2H), 7.39 (d, J = 6.2 Hz, 3H), 6.87 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 140.7, 133.3, 132.3, 131.2, 129.3, 129.0, 128.5, 127.6, 127.3; IR (KBr): ν = 3059, 2924, 1615, 1492, 1447, 1309, 1146, 1084, 975, 817, 749, 689 cm^{-1}; MS (EI): m/z = 244, 179, 125, 102, 92, 77.

(*E*)-1-Methyl-4-(styrylsulfonyl)benzene (3as):[28] Pale yellow solid; mp 100–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 7.8 Hz, 2H), 7.65 (d, J = 15.4 Hz, 1H), 7.47 (d, J = 7.8 Hz, 2H), 7.41–7.32 (m, 5H), 6.85 (d, J = 15.4 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 141.9, 137.8, 132.5, 131.1, 129.9, 129.0, 128.5, 127.7, 127.6, 21.6; IR (KBr): ν = 3056, 2920, 1659, 1549, 1299, 1120, 973, 815, 748, 685 cm^{-1}; MS (EI): m/z = 258, 193, 179, 139, 119, 102.

(*E*)-1-Methoxy-4-(styrylsulfonyl)benzene (3fs):[28] Pale yellow solid; mp 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 15.5 Hz, 1H), 7.48–7.46 (m, 2H), 7.43–7.33 (m, 3H), 7.00 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 15.5 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 141.4, 132.5, 132.2, 131.0, 129.9, 129.0, 128.5, 127.9, 114.6, 55.7; IR (KBr): ν = 3058, 2923, 1586, 1496, 1454, 1259, 1139, 1085, 817, 749 cm^{-1}; MS (EI): m/z = 274, 210, 194, 155, 123, 77.

(*E*)-1-Fluoro-4-(styrylsulfonyl)benzene (3cs):[28] Pale yellow solid; mp 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 15.4 Hz, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.43–7.38 (m, 3H), 7.24–7.20 (m, 2H), 6.84 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 164.4, 142.7, 132.2, 131.3, 130.5, 129.11, 128.7, 127.1, 116.7, 116.5; IR (KBr): ν = 3058, 2919, 1654, 1563, 1410, 1272,

1138, 1079, 806, 751 cm^{-1}; MS (EI): m/z = 262, 197, 143, 119, 102, 92, 77.

(*E*)-1-Chloro-4-(styrylsulfonyl)benzene (3ds):[28] Pale yellow solid; mp 107–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 15.4 Hz, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 6.4 Hz, 2H), 7.40 (q, J = 6.4 Hz, 3H), 6.83 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0, 140.1, 139.3, 132.2, 131.4, 129.7, 129.1, 128.6, 126.9; IR (KBr): ν = 3060, 2925, 1614, 1578, 1476, 1394, 1318, 1147, 1088, 816, 753 cm^{-1}; MS (EI): m/z = 280, 278, 213, 178, 159, 119, 102, 77.

(*E*)-1-Bromo-4-(styrylsulfonyl)benzene (3es): Yellow solid; mp 115–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 15.4 Hz, 1H), 7.48 (d, J = 6.6 Hz, 2H), 7.40 (q, J = 6.6 Hz, 3H), 6.83 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 139.8, 132.6, 132.2, 131.4, 129.2, 129.1, 128.6, 126.8; IR (KBr): ν = 3055, 2924, 1663, 1516, 1462, 1382, 1247, 1078, 811, 750 cm^{-1}; MS (EI): m/z = 324, 322, 206, 178, 119, 102, 92; ESI-HR-MS: m/z = 344.9554, calcd. for $C_{14}H_{11}BrNaO_2S$ $[M+Na]^+$: 344.9555.

(*E*)-1-(Styrylsulfonyl)-4-(trifluoromethyl)benzene (3js): Pale yellow solid; mp 77–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 15.4 Hz, 1H), 7.53–7.47 (m, 2H), 7.46–7.36 (m, 3H), 6.86 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 132.0, 131.6, 129.2, 128.7, 128.2, 126.4, 126.3; IR (KBr): ν = 3054, 2925, 1614, 1571, 1451, 1323, 1141, 1061, 816, 746 cm^{-1}; MS (EI): m/z = 312, 227, 178, 145, 119, 102, 91; ESI-HR-MS: m/z = 335.0328, calcd. for $C_{15}H_{11}F_3NaO_2S$ $[M+Na]^+$: 335.0324.

(*E*)-2-(Styrylsulfonyl)thiophene (3hs):[29] Pale yellow solid; mp 55–57 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 3.6 Hz, 1H), 7.70–7.64 (m, 2H), 7.50 (d, J = 15.4 Hz, 1H), 7.49 (d, J = 4.9 Hz, 1H),7.44–7.36 (m, 3H), 7.14 (dd, J = 4.9, 3.6 Hz, 1H), 6.96 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.3, 142.2, 133.9, 133.4, 132.3, 131.3, 129.1, 128.5, 127.9, 127.9; IR (KBr): ν = 3092, 2922, 1651, 1548, 1396, 1306, 1226, 1137, 1015, 805, 721 cm^{-1}; MS (EI): m/z = 250, 202, 185, 152, 131, 105, 92.

(*E*)-2-(Styrylsulfonyl)naphthalene (3is):[30] White solid; mp 115–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 15.4 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.50–7.48 (m, 2H), 7.41–7.36 (m, 3H), 6.93 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 137.5, 135.1, 132.4, 132.3, 131.2, 129.7, 129.4, 129.2, 129.1, 129.0, 128.6, 127.9, 127.6, 127.3, 122.5; IR (KBr): ν = 3057, 2959, 1510, 1452, 1378, 1308, 1244, 1136, 810, 749, 661 cm^{-1}; MS (EI): m/z = 294, 229, 192, 175, 127, 92, 77.

(*E*)-[2-(Methylsulfonyl)vinyl]benzene (3ns):[28] Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 15.5 Hz, 1H), 7.52 (d, J = 6.7 Hz, 2H), 7.43 (t, J = 6.7 Hz, 3H), 6.92 (d, J = 15.5 Hz, 1H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 132.1, 131.4, 129.1, 128.5, 126.2, 43.3; IR (KBr): ν = 3054, 2923, 1622, 1545, 1498, 1280, 1125, 946, 820, 752, 687 cm^{-1}; MS (EI): m/z = 182, 167, 119, 102, 91, 77.

(*E*)-[2-(Ethylsulfonyl)vinyl]benzene (3ls): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 15.5 Hz, 1H), 7.52 (d, J = 6.7 Hz, 2H), 7.46–7.40 (m, 3H), 6.81 (d, J = 15.4 Hz, 1H), 3.09 (q, J = 7.4 Hz, 2H), 1.39 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 132.3, 131.4, 129.2, 128.6, 124.1, 49.5, 7.2; IR (KBr): ν = 3054, 2923, 1622, 1545, 1498, 1280, 1125, 946,820, 752, 687 cm^{-1}; MS (EI): m/z = 196, 167, 119, 103, 92, 77. ESI-HR-MS: m/z = 219.0454, calcd. for $C_{10}H_{12}NaO_2S$ $[M+Na]^+$: 219.0450.

(*E*)-[2-(Cyclopropylsulfonyl)vinyl]benzene (3ms): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 15.5 Hz, 1H), 7.53 (d, J = 6.3 Hz, 2H), 7.47–7.39 (m, 3H), 6.89 (d, J = 15.5 Hz, 1H), 2.47–2.40 (m, 1H), 1.34–1.28 (m, 2H), 1.11–1.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 132.5, 131.1, 129.1, 128.5, 125.7, 31.4, 5.3; IR (KBr): ν = 3054, 2918, 1652, 1544, 1275, 1122, 969, 882, 746, 681 cm^{-1}; MS (EI): m/z = 208, 167, 129, 119, 91, 77; ESI-HR-MS: m/z = 231.0457, calcd. for $C_{11}H_{12}NaO_2S$ $[M+Na]^+$: 231.0450.

2-[(2-Chlorophenyl)sulfonyl]-1-phenylethanone (3gt): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 7.3 Hz, 2H), 7.63 (d, J = 7.4 Hz, 1H), 7.60–7.55 (m, 2H), 7.51–7.43 (m, 3H), 5.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.8, 136.5, 135.8, 135.1, 134.4, 132.7, 132.1, 131.8, 129.1, 128.9, 127.4, 61.0; IR (KBr): ν = 3054, 2920, 1759, 1652, 1544, 1275, 1122, 969, 820, 756 cm^{-1}; MS (EI): m/z = 294, 259, 230, 195, 128, 105; ESI-HR-MS: m/z = 317.0015, calcd. for $C_{14}H_{11}ClNaO_3S$ $[M+Na]^+$: 317.0010.

Phenyl-2-{[2-(trifluoromethoxy)phenyl]sulfonyl}ethanone (3kt): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 7.9 Hz, 2H), 7.75–7.68 (m, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.51–7.42 (m, 4H), 4.93 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.8, 146.9, 135.9, 135.7,134.5, 131.5, 130.8,129.1, 128.9, 126.7, 119.9, 62.0; IR (KBr): ν = 3052, 2920, 2853, 1764, 1677, 1477, 1389, 1330, 1252, 1153, 817, 753 cm^{-1}; MS (EI): m/z = 344, 280 225, 195, 178, 105; ESI-HR-MS: m/z = 367.0224, calcd. for $C_{15}H_{11}F_3NaO_4S$ $[M+Na]^+$: 367.0222.

Acknowledgements

The authors thank the National Natural Science Foundation of China (21172076 and 21202046), the National Basic Research Program of China (973 Program) (2011CB808600), the Changjiang Scholars and Innovation Team Project of Ministry of Education, Guangdong Natural Science Foundation (10351064101000000 and S2012040007088) and the Fundamental Research Funds for the Central Universities (2014ZP0004 and 2014ZZ0046) for financial support.

References

[1] a) F. Diederich, P. T. Stang, *Metal-Catalyzed Cross-coupling Reactions*, Wiley-VCH, Weinheim, Germany, **1998**; b) A. de Meijere, F. Diederich, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, Germany, **2004**; c) M. Beller, C. Bolm, *Transition Metals for Organic Synthesis*, Wiley-VCH, Weinheim, Germany, **1998**; d) M. Beller, C. Bolm, *Transition Metals for Organic Synthesis*, 2nd edn., Wiley-VCH, Weinheim, Germany, **2004**.

[2] a) A. R. Muci, S. L. Buchwald, in: *Topics in Current Chemistry*, Springer-Verlag, Berlin, **2002**, Vol. 219, pp 133–209, and references cited therein; b) J. F. Hartwig, *Acc. Chem. Res.* **1998**, *31*, 852; c) E. M. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, *Chem. Rev.* **2007**, *107*, 5318; d) T. Kondo, T. Motsudo, *Chem. Rev.* **2000**, *100*, 3205.

[3] a) L. Brandsma, *Synthesis of Acetylenes, Allenes and Cumulenes: Methods and Techniques*, Elsevier, Oxford, **2004**; b) F. Diederich, P. J. Stang, R. R. Tykwinski, *Acetylene Chemistry: Chemistry, Biology, and Material Science*, Wiley-VCH, Weinheim, Germany, **2005**.

[4] For excellent papers, see: a) J. D. Dooley, S. R. Chidipudi, H. W. Lam, *J. Am. Chem. Soc.* **2013**, *135*, 10829; b) M. Onoe, K. Baba, Y. Kim, Y. Kita, M. Tobisu, N. Chatani, *J. Am. Chem. Soc.* **2012**, *134*, 19477; c) Y. Minami, Y. Shiraishi, K. Yamada, T. Hiyama, *J. Am. Chem. Soc.* **2012**, *134*, 6124; d) H. Shiota, Y. Ano, Y. Aihara, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2011**, *133*, 14952; e) N. Guimond, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449; f) S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9585; g) R. M. Kuram, M. Bhanuchandra, A. K. Sahoo, *Angew. Chem. Int. Ed.* **2013**, *52*, 4607; h) Z. Shi, S. Ding, Y. Cui, N. Jiao, *Angew. Chem.* **2009**, *121*, 8035; *Angew. Chem. Int. Ed.* **2009**, *48*, 7895.

[5] a) R. R. Tykwinski, *Angew. Chem.* **2003**, *115*, 1604; *Angew. Chem. Int. Ed.* **2003**, *42*, 1566; b) E. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979; c) R. Chinchilla, C. Najera, *Chem. Rev.* **2007**, *107*, 874.

[6] a) U. Mahesh, K. Liu, R. C. Panicker, S. Q. Yao, *Chem. Commun.* **2007**, 1518; b) G. Wang, U. Mahesh, G. Y. J. Chen, S. Yao, *Org. Lett.* **2003**, *5*, 737; c) I. Forristal, *J. Sulfur Chem.* **2005**, *26*, 163; d) F. Hof, A. Schutz, C. Fah, S. Meyer, D. Bur, J. Liu, D. E. Goldberg, E. Diederich, *Angew. Chem.* **2006**, *118*, 2193; *Angew. Chem. Int. Ed.* **2006**, *45*, 2138.

[7] a) L. Ni, X. Zheng, P. K. Somers, L. K. Hoong, R. R. Hill, E. M. Marino, K. L. Suen, U. Saxena, C. Meng, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 745; b) J. T. Palmer, D. Rasnick, J. L. Klaus, D. Brömme, *J. Med. Chem.* **1995**, *38*, 3193; c) M. M. M. Santos, R. Moreira, *Mini-Rev. Med. Chem.* **2007**, *7*, 1040; d) R. Ettari, E. Nizi, M. E. D. Francesco, M. A. Dude, G. Pradel, R. Vicik, T. Schirmeister, N. Micale, S. Grasso, M. Zappala, *J. Med. Chem.* **2008**, *51*, 988.

[8] a) M. N. Noshi, A. El-Awa, E. Torres, P. L. Fuchs, *J. Am. Chem. Soc.* **2007**, *129*, 11242; b) J. N. Desrosiers, A. B. Charette, *Angew. Chem.* **2007**, *119*, 6059; *Angew. Chem. Int. Ed.* **2007**, *46*, 5955; c) G. Pandey, K. N. Tiwari, V. G. Puranik, *Org. Lett.* **2008**, *10*, 3611; d) K. Oh, *Org. Lett.* **2007**, *9*, 2973.

[9] a) S. Choi, J. Yang, M. Ji, H. Choi, M. Kee, K. Ahn, S. Byeon, W. Baik, S. Koo, *J. Org. Chem.* **2001**, *66*, 8192; b) A. A. Lindén, L. Krüger, J. Bäckvall, *J. Org. Chem.* **2003**, *68*, 5890; c) E. Baciocchi, M. F. Gerini, A. Lapi, *J. Org. Chem.* **2004**, *69*, 3586; d) F. G. Gelalcha, B. Schulze, *J. Org. Chem.* **2002**, *67*, 8400; e) M. Matteucci, G. Bhalay, M. Bradley, *Org. Lett.* **2003**, *5*, 235; f) X. Huang, D. Duan, W. Zheng, *J. Org. Chem.* **2003**, *68*, 1958; g) S. Chodroff, W. F. Whitmore, *J. Am. Chem. Soc.* **1950**, *72*, 1073; h) P. B. Hopkins, P. L. Fuchs, *J. Org. Chem.* **1978**, *43*, 1208; i) R. A. Gancarz, J. L. Kice, *Tetrahedron Lett.* **1980**, *21*, 4155.

[10] a) J. M. Baskin, Z. Wang, *Org. Lett.* **2002**, *4*, 4423; b) W. Zhu, D. Ma, *J.Org.Chem.* **2005**, *70*, 2696; c) M. Bian, F. Xu, C. Ma, *Synthesis* **2007**, 2951; d) D. C. Reeves, S. Rodriguez, H. Lee, N. Hahhad, D. Krishnamurthy, C. H. Senanayake, *Tetrahedron Lett.* **2009**, *50*, 2870; e) S. Cacchi, G. Fabrizi, A. Goggiamani, L. M. Parisi, R. Bernini, *J. Org. Chem.* **2004**, *69*, 5608; f) F. Huang, R. A. Batey, *Tetrahedron* **2007**, *63*, 7667; g) V. Nair, A. Augustine, T. G. George, L. G. Nair, *Tetrahedron Lett.* **2001**, *42*, 6763.

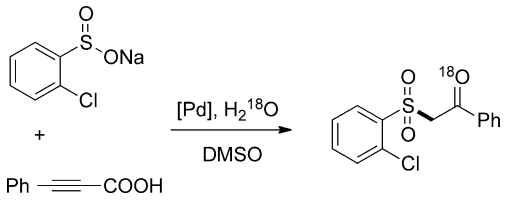
[11] R. Song, Y. Liu, Y. Liu, J. Li, *J. Org. Chem.* **2011**, *76*, 1001.

[12] a) S. Cacchi, G. Fabrizi, A. Goggiamani, L. M. Parisi, *Org. Lett.* **2002**, *4*, 4719; b) M. Wu, J. Luo, F. Xiao, S. Zhang, G. Deng, H. Luo, *Adv. Synth. Catal.* **2012**, *354*, 335; c) K. Cheng, S. Hu, B. Zhao, X. Zhang, C. Qi, *J. Org. Chem.* **2013**, *78*, 5022; d) F. Zhao, Q. Tan, F. Xiao, S. Zhang, G. Deng, *Org. Lett.* **2013**, *15*, 1520; e) G. Wang, T. Miao, *Chem. Commun.* **2011**, *47*, 9501; f) G. Wang, T. Miao, *Chem. Eur. J.* **2011**, *17*, 5787.

[13] a) X. Tang, L. Huang, C. Qi, X. Wu, W. Wu, H. Jiang, *Chem. Commun.* **2013**, *49*, 6102; b) G. Yuan, J. Zheng, X. Gao, X. Li, L. Huang, H. Chen, H. Jiang, *Chem. Commun.* **2012**, *48*, 7513.

[14] a) C. Feng, T. P. Loh, *Chem. Commun.* **2010**, *46*, 4779; b) J. Moon, M. Jeong, H. Nam, J. Ju, J. H. Moon, H. M. Jung, S. Lee, *Org. Lett.* **2008**, *10*, 945; c) J. Moon, M. Jang, S. Lee, *J. Org. Chem.* **2009**, *74*, 1403; d) X. Li, F. Yang, Y. Wu, *J. Org. Chem.* **2013**, *78*, 4543.

[15] Control experiments conformed that the oxygen atom of β-keto sulfones came from water in the solvent, which is different from Lei's report, for details see: Q. Lu, J. Zhang, G. Zhao, Y. Qi, H. Wang, A. Lei, *J. Am. Chem. Soc.* **2013**, *135*, 11481.



[16] a) P. Zhou, L. Huang, H. Jiang, A. Wang, X. Li, *J. Org. Chem.* **2010**, *75*, 8279; b) L. Zhao, X. Lu, *Org. Lett.* **2002**, *4*, 3903; c) A. Lei, X. Lu, *Org. Lett.* **2000**, *2*, 2699.

[17] A. K. Verma, M. Joshi, V. P. Singh, *Org. Lett.* **2011**, *13*, 1630.

[18] M. L. N. Rao, D. N. Jadhav, P. Dasgupta, *Org. Lett.* **2010**, *12*, 2048.

[19] Z. Wan, C. D. Jones, D. Mitchell, J. Y. Pu, T. Y. Zhang, *J. Org. Chem.* **2006**, *71*, 826.

[20] N. P. Bizier, J. W. Wackerly, E. D. Braunstein, M. Zhang, S. T. Nodder, S. M. Carlin, J. L. Katz, *J. Org. Chem.* **2013**, *78*, 5987.

[21] D. Zhao, C. Gao, X. Su, Y. He, J. You, Y. Xue, *Chem. Commun.* **2010**, *46*, 9049.

[22] H. R. Luckarift, G. R. Johnson, J. C. Spain, *Chem. Commun.* **2004**, 2402.

[23] C. Shi, Q. Zhang, K. Wang, *J. Org. Chem.* **1999**, *64*, 925.
[24] M. J. Mio, L. C. Kopel, J. B. Braun, T. J. Gadzikwa, K. L. Hull, R. G. Brisbois, *Org. Lett.* **2002**, *4*, 3199.
[25] Z. Novak, P. Nemes, A. Kotschy, *Org. Lett.* **2004**, *6*, 4917.
[26] P. R. Sacasa, J. Zayas, S. F. Wnuk, *Tetrahedron Lett.* **2009**, *50*, 5424.
[27] G. Khalili, *J. Sulfur Chem.* **2013**, *34*, 532.
[28] N. Taniguchi, *Synlett* **2012**, *23*, 1245.
[29] C. T. Goralski, *J. Org. Chem.* **1972**, *37*, 2355.
[30] S. S. Labadie, *J. Org. Chem.* **1989**, *54*, 2496.

12 Chemoselective Synthesis of Unsymmetrical Internal Alkynes or Vinyl Sulfones *via* Palladium-Catalyzed Cross-Coupling Reaction of Sodium Sulfinates with Alkynes

Adv. Synth. Catal. **2014**, *356*, 1 – 12

Yanli Xu, Jinwu Zhao, Xiaodong Tang, Wanqing Wu, Huanfeng Jiang*