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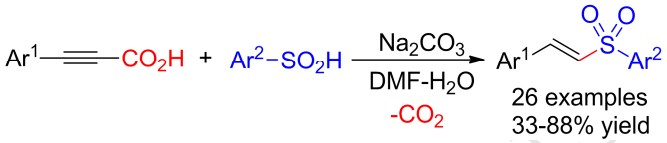

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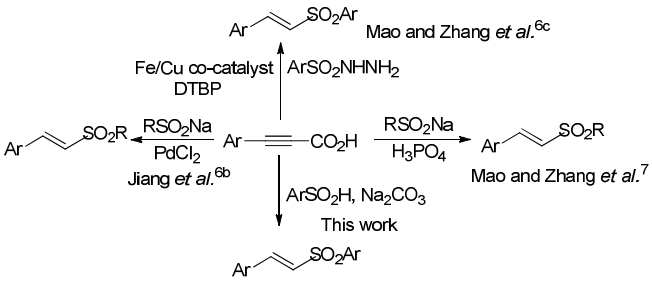
ABSTRACT

Decarboxylative sulfonylation of arylpropiolic acids has been achieved by simply employing Na_2CO_3 as a promoter and arenesulfinic acids as sulfonylating reagents. This simple and environmentally benign transformation offers an alternative approach and allows for easy and rapid synthesis of (*E*)-vinyl sulfones from arylpropiolic acids and arenesufinic acids.

1. Introduction

Vinyl sulfones constitute an important class of compounds owing to their potential utility in various fields including biology, medicines and synthetic chemistry. Vinyl sulfone scaffolds are present in many biologically active compounds and pharmaceuticals which display a broad range of bioactivities.[1] In view of organic synthesis, vinyl sulfones serve as versatile synthetic synthons for various synthetic transformations.[2] As a consequence, development of new approaches for the synthesis of vinyl sulfones is an important goal in organic chemistry. An enormous number of synthetic routes are available toward the synthesis of vinyl sulfones.[3] Recently, decarboxylative functionalization of carboxylic acids that involves C−heteroatom bond forming reactions has emerged as attractive transformation in organic synthesis.[4] In particular, decarboxylative C-S bond formation of α,β-unsaturated carboxylic acids has received a great deal of interest.[5] However, that of alkynyl carboxylic acids has received less attention.[6] Despite, being highly efficient, the previously reported protocols toward vinyl sulfones via decarboxylative coupling between alkynyl carboxylic acids with either sodium sulfinates or sulfonyl hydrazides required metal salts (Pd, Cu, Fe) (Scheme 1).



Scheme 1. Diverse approaches to access vinyl sulfones from arylpropiolic acid derivatives.

During our study on and in the process of preparation of this manuscript, a report on the use of the Brønsted acid-promoted reactions of arylpropiolic acid and sodium arenesulfinates for the synthesis of vinyl sulfones was disclosed by Mao and Zhang.[7] This encouraged us to report our findings (Scheme 1). Our research group has reported a series of efforts towards the devlopment of efficient methods for vinyl sulfone synthesis.[8] We describe herein Na_2CO_3-promoted decarboxylative sulfonylation of arylpropiolic acids with sulfinic acids in the absence of a transition metal catalyst.

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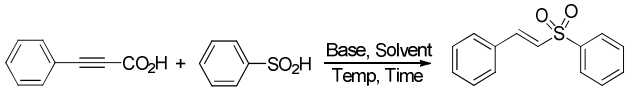
2. Results and discussion

Our investigation began with the search for the optimization conditions by using the commercially available phenylpropiolic acid (**1a**) and benzenesulfinic acid (**2a**) as benchmark substrates. Thus, treatment of **1a** (0.25 mmol) with **2a** (4 equiv.) in the presence of K_2CO_3 (1 equiv.) in dimethylformamide (DMF, 3 mL) at 100 ^oC for 2 h resulted in the formation of (*E*)-vinyl sulfone **3a** in 38% isolated yield (Table 1, entry 1). Reaction parameters were examined in order to obtain the optimized reaction conditions. Initially, types of base were screened including inorganic bases (Na_2CO_3, Cs_2CO_3, NaOH, and $NaHCO_3$) and organic bases (Et_3N and pyridine) (Table 1, entries 2–7). Vinyl sulfone **3a** was obtained in higher yield (50% yield) when Na_2CO_3 and NaOH were employed as the base. For the ease of the handling, Na_2CO_3 was chosen as a base in the present work. While increasing the stoichiometry of **2a** from 4 equivalents to 5 equivalents did not improve the yield, lowering the stoichiometry of **2a** from 4 equivalents to 3 equivalents significantly reduced the yield of **3a** from 50% yield to 35% yield (Table 1, entries 8–9). Reactions carried out at higher (120 ^oC) or lower (80 ^oC) temperature led to inferior results (Table 1, entries 10–11). Types of solvent were briefly screened (Table 1, entries 12–18). Among the solvents applied, DMSO gave comparable results under similar reaction conditions. (Table 1, entry 12 vs entry 2). The reaction also worked well in water with comparable yield although longer reaction time (20 h) was required (Table 1, entry 16). These promising results prompted us to further examine the possibility of using water as a co-solvent. Therefore, the reaction was performed in DMF-water mixture in the ratio of 2:1 v/v (Table 1, entry 17). However, higher content of water (DMF : H_2O = 1:2 v/v) led to poorer yield (Table 1, entry 18). On the basis of the optimization results shown in Table 1, the standard reaction conditions were identified as the following: arylpropiolic acid (1 equiv.), sulfinic acid (4 equiv.), Na_2CO_3 (1 equiv.) in DMF-H_2O (2:1 v/v; 3 mL) at 100 ^oC for 2 h (Table 1, entry 17). It is noteworthy that although we were unable to make additional improvement in the yield of **3a**, high yields were observed in some substrates studied in this work.

With the optimized conditions in hand, we next explored the scope of the reaction between various arylpropiolic acids **1** and arylsulfinic acids **2**, and the results are summarized in Table 2. A collection of arylpropiolic acids and aryl sulfinic acids bearing electronically different substituents furnished a variety of vinyl sulfones **3a**–**3y** in moderate to good yields ranging from 38–88%. The parent phenylpropiolic acid reacted with arylsulfinic acid bearing both electron-donating groups (R = OCH_3, CH_3) and electron-withdrawing groups (R = Cl, NO_2) to yield vinyl sulfones **3a**–**3e** in moderate yields (48–57% yields).

The reactions of *para*- and *meta*-halogen substituted arylpropiolic acids also readily proceeded under standard reaction conditions. Noteworthy, *para*-nitro substituted arylpropiolic acid reacted smoothly with arylsulfinic acids **2a**–**2d** to yield vinyl sulfones **3p**–**3s** in good to high yields (70–88% yields). In contrast, arylpropiolic acids bearing electron-donating groups (CH_3, OCH_3) were less effective substrates, and the corresponding vinyl sulfones **3t** and **3u** were obtained in somewhat lower yields. Moderate yields (47–63% yields) were observed from the reactions of 3-bromo-4-methoxylphenylpropiolic acid with arylsulfinic acids **2a**–**2d**. Finally, 3-(naphthalen-2-yl)propiolic acid readily reacted with benzenesulfinic acid (**2a**) to provide the corresponding vinyl sulfone **3z** in 50% yield.

Table 1
Optimization of the reaction conditions[a]



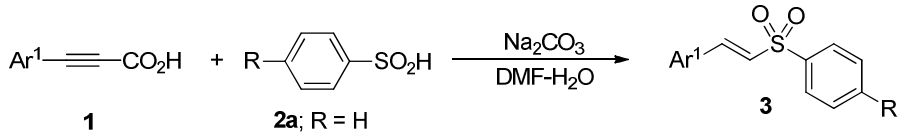
1a **2a** **3a**

Entry	Base	Solvent	Temp (^oC)	Time (h)	Yield[b] (%)
1	K_2CO_3	DMF	100	2	38
2	Na_2CO_3	DMF	100	2	50
3	Cs_2CO_3	DMF	100	2	39
4	NaOH	DMF	100	2	50
5	$NaHCO_3$	DMF	100	2	29
6	Et_3N	DMF	100	6	21
7	pyridine	DMF	100	3	22
8[c]	Na_2CO_3	DMF	100	2	50
9[d]	Na_2CO_3	DMF	100	2	35
10	Na_2CO_3	DMF	120	2	40
11	Na_2CO_3	DMF	80	2	27
12	Na_2CO_3	DMSO	100	2	46
13	Na_2CO_3	CH_3CN	80	5	Trace
14	Na_2CO_3	Dioxane	100	5	8
15	Na_2CO_3	DMA	100	5	19
16	Na_2CO_3	H_2O	100	20	46
17	**Na_2CO_3**	**DMF-H_2O (2:1 v/v)**	**100**	**2**	**53**
18	Na_2CO_3	DMF-H_2O (1:2 v/v)	100	2	29

[a] Reaction conditions: Phenylpropiolic acid (**1a**, 0.25 mmol), benzenesulfinic acid (**2a**, 4 equiv.), base (1 equiv.), and solvent (3 mL).
[b] Isolated yields after chromatographic purification (SiO_2).
[c] Reaction was carried out employing **2a** (5 equiv.).
[d] Reaction was carried out employing **2a** (3 equiv.).

At this stage, to gain better insight into the mechanistic pathway, a series of control experiments were examined (Scheme 2). Initially, the reaction of phenylpropiolic acid (**1a**) with benzenesulfinic acid (**2a**) was conducted under standard reaction conditions in the presence of radical inhibitor, TEMPO. As can be seen in Scheme 2, TEMPO suppressed the reaction. These experiments implied that the reaction is probably undergoing *via* a radical pathway (Scheme 2, a). The reaction carried out by using benzenesulfinate sodium salt in place of benzenesulfinic acid (**2a**) under the optimized reaction conditions did not furnish the expected vinyl sulfone **3a** (Scheme 2, b). It has been previously reported that arylacetylenes reacted with arenesulfinic acids to yield vinyl sulfones.[9] Thus, we were aware of prior decarboxylative-protonation to furnish phenylacetylene which further reacts with sulfinic acid to yield the corresponding vinyl sulfone **3a**. Therefore, phenylacetylene was allowed to react with benzenesulfinic acid (**2a**) under standard reaction conditions (Scheme 2, c). This reaction did not furnish the vinyl sulfone **3a** but instead yielded the corresponding β-ketosulfone **4a** in low yield (13% yield), suggesting that the reaction does not involve the corresponding phenylacetylene as an intermediate. Finally, when the reaction of phenylpropiolic acid (**1a**) with benzenesulfinic acid (**2a**) was conducted employing DMF:D_2O (2:1 v/v, 3 mL) as the solvent, a deuterated product **3a′** was obtained almost exclusively (Scheme 2, d) (See supplementary data for ^1H and ^{13}C data of **3a′**).

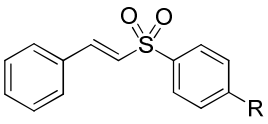
Table 2
Substrate scope[a]



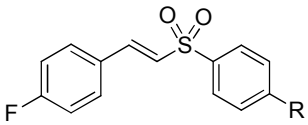
1

2a; R = H
2b; R = CH_3
2c; R = OCH_3
2d; R = Cl
2e; R = NO_2

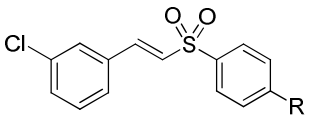
3



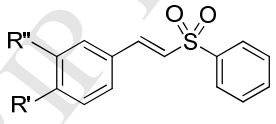
R = H, **3a**, 53%
R = CH_3, **3b**, 50%
R = OCH_3, **3c**, 50%
R = Cl, **3d**, 48%
R = NO_2, **3e**, 57%



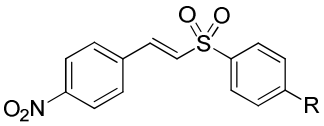
R = H, **3f**, 48%[b]
R = CH_3, **3g**, 44%[b]
R = OCH_3, **3h**, 39%
R = Cl, **3i**, 50%



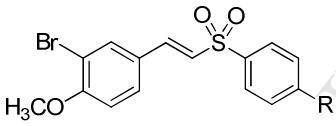
R = H, **3j**, 70%
R = CH_3, **3k**, 49%
R = OCH_3, **3l**, 74%
R = Cl, **3m**, 64%
R = NO_2, **3n**, 67%



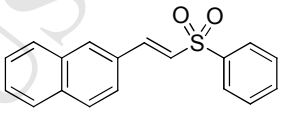
R' = Br; R'' = H, **3o**, 55%
R' = CH_3; R'' = H, **3t**, 43%[b]
R' = H; R'' = OCH_3, **3u**, 33%[b]



R = H, **3p**, 73%
R = CH_3, **3q**, 70%
R = OCH_3, **3r**, 82%
R = Cl, **3s**, 88%



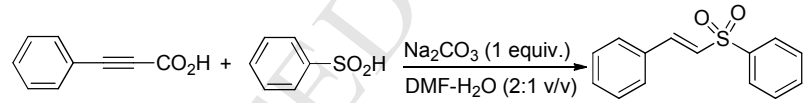
R = H, **3v**, 47%
R = CH_3, **3w**, 54%
R = OCH_3, **3x**, 59%
R = Cl, **3y**, 63%



3z, 50%

[a] Reaction conditions: **1** (0.25 mmol), **2** (4 equiv.), Na_2CO_3 (1 equiv.), DMF-H_2O (2:1v/v; 3 mL), 100 °C, 2 h.
[b] Reaction time: 4 h.

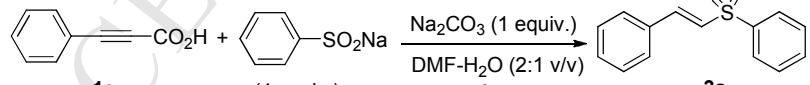
a)



1a **2a** (4 equiv.) **3a**

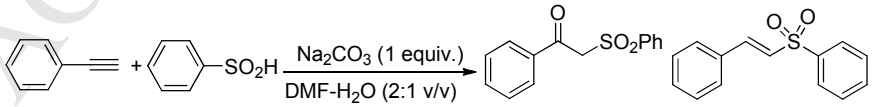
TEMPO (equiv.)	Yield (%)
1	50
2	19
3	5

b)



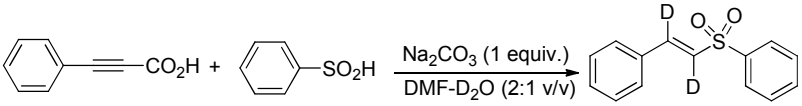
1a (4 equiv.) **3a** not observed

c)



1a **2a** (4 equiv.) **4a**, 13% yield **3a** not observed

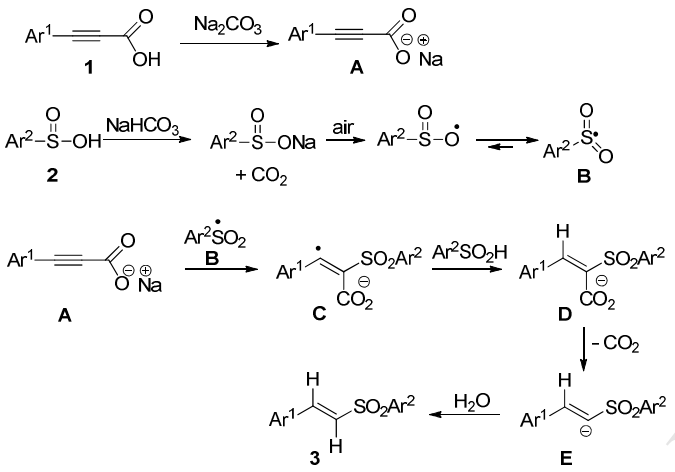
d)



1a **2a** (4 equiv.) **3a'**, 47% yield

Scheme 2. Control experiments.

On the basis of the control experiments described above and the previously reported literature,[7,9-10] a tentative mechanism for the decarboxylative sulfonylation of arylpropiolic acids has been proposed as depicted in Scheme 3. In the presence of base, arylpropiolic acid could be deprotonated to generate carboxylate anion **A**. Next, under the reaction conditions, the sulfonyl radical **B** can be generated from sulfinic acid **2**. Subsequently, the sulfonyl radical **B** can selectively attack the alkynyl moiety of **A** to produce the vinyl radical **C**. The high yields obtained when *para*-nitrophenylpropiolic acid was employed as the starting material imply that the step of sulfonyl radical addition to alkynyl moiety might be the rate controlling step (Table 2). Thereafter, the vinyl radical **C** can abstract a hydrogen radical from sulfinic acid to generate **D** which can subsequently undergo decarboxylation to give vinyl anion E followed by protonation leading to vinyl sulfone **3**.



Scheme 3. Postulated reaction mechanism.

3. Conclusions

In summary, a facile protocol for the synthesis of vinyl sulfones using a decarboxylation strategy via a radical pathway has been developed. In this work, for the first time sulfinic acids were employed to couple with a variety of arylpropiolic acids leading to vinyl sulfones in moderate to good yields. This reaction is selective and exclusively furnishes the corresponding (*E*)-vinyl sulfones. This method provides an alternative route for the synthesis of vinyl sulfones which are important scaffolds in various fields.

4. Experimental

4.1 General information

All isolated compounds were characterized on the basis of ^{1}H NMR and ^{13}C NMR spectroscopic data, IR spectra, and HRMS data. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ascend™ spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in ppm using tetramethylsilane (TMS) or residual nondeuterated solvent peak as an internal standard. Infrared spectra were recorded with a Bruker ALPHA FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded with a Bruker micro TOF spectrometer in the ESI mode. Melting points were recorded with a Sanyo Gallenkamp apparatus. Reactions were monitored by thin-layer chromatography and visualized by UV and a solution of $KMnO_4$. Except for phenylpropiolic acid, all arylpropiolic acids were prepared according to the literature procedure. Sulfinic acids were synthesized from the acidification of sodium sulfinate salt. Purification of the reaction products was carried out by column chromatography on silica gel (0.063–0.200 mm). After column chromatography, analytically pure solid was obtained by crystallization from CH_2Cl_2–hexanes and acetone–hexanes.

4.2 General procedure

To a mixture of arylpropiolic acid (0.25 mmol), arenesulfinic acid (1.0 mmol), and Na_2CO_3 (0.25 mmol) were added DMF (2 mL) and H_2O (1 mL). The reaction mixture was stirred at 100 °C under air atmosphere for 2 hours. After completion of the reaction, the reaction was cooled to room temperature and was diluted with water (10 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.

4.3 Spectroscopic data of compounds 3

*4.3.1 (E)-(2-(Phenylsulfonyl)vinyl)benzene (**3a**).*[8c] Colorless solid (32.6 mg, 53% yield); m.p. 62–63 °C. IR (neat): *v* 3044, 2918, 1611, 1574, 1446, 1298, 1142, 1084 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.5 Hz, 2 H), 7.69 (d, *J* = 15.4 Hz, 1 H), 7.61 (t, *J* = 7.3 Hz, 1 H), 7.56–7.52 (m, 2 H), 7.48–7.46 (m, 2 H), 7.42–7.35 (m, 3 H), 6.88 (d, *J* = 15.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4 (CH), 140.6 (C), 133.3 (CH), 132.3 (C), 131.1 (CH), 129.3 (2 × CH), 129.0 (2 × CH), 128.5 (2 × CH), 127.5 (2 × CH), 127.1 (CH) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{12}O_2S + Na]^+$: calcd. 267.0456, found 267.0455.

*4.3.2 (E)-1-Methyl-4-(styrylsulfonyl)benzene (**3b**).*[8c] Colorless solid (31.8 mg, 50% yield); m.p. 117–118 °C. IR (neat): *v* 3045, 2920, 2851, 1650, 1613, 1595, 1449, 1302, 1140, 1084 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.2 Hz, 2 H), 7.66 (d, *J* = 15.4 Hz, 1 H), 7.49-7.46 (m, 2 H), 7.41–7.38 (m, 3 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 6.85 (d, *J* = 15.4 HZ, 1 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4 (C), 141.9 (CH), 137.7 (C), 132.4 (C), 131.1 (CH), 130.0 (2 × CH), 129.0 (2 × CH), 128.5 (2 × CH), 127.7 (2 × CH), 127.6 (CH), 21.6 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{14}O_2S + Na]^+$: calcd. 281.0612, found 281.0618.

*4.3.3 (E)-1-Methoxy-4-(styrylsulfonyl)benzene (**3c**).*[8c] Colorless solid (35 mg, 50% yield); m.p. 75–76 °C. IR (neat): *v* 3038, 2949, 2844, 1591, 1574, 1496, 1448, 1296, 1260, 1135, 1082 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.9 Hz, 2 H), 7.63 (d, *J* = 15.4 Hz, 1 H), 7.48–7.46 (m, 2 H), 7.39–7.37 (m, 3 H), 7.00 (d, *J* = 8.9 Hz, 2 H), 6.85 (d, *J* = 15.4 Hz, 1 H), 3.86 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5 (C), 141.3 (CH), 132.4 (C), 132.1 (C), 131.0 (CH), 129.8 (2 × CH), 129.0 (2 × CH), 128.4 (2 × CH), 127.9 (CH), 114.5 (2 × CH), 55.7 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{14}O_3S + Na]^+$: calcd. 297.0561, found 297.0568.

*4.3.4 (E)-1-Chloro-4-(styrylsulfonyl)benzene (**3d**).*[8c] White solid (33.7 mg, 48% yield); m.p. 78–80 °C. IR (neat): *v* 3087, 3053, 1614, 1575, 1471, 1449, 1310, 1143, 1082 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.6 Hz, 2 H), 7.69 (d, *J* = 15.4 Hz,

1 H), 7.52 (d, *J* = 8.6 Hz, 2 H), 7.50–7.48 (m, 2 H), 7.45–7.37 (m, 3 H), 6.84 (d, *J* = 15.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0 (CH), 140.1 (C), 139.2 (C), 132.1 (C), 131.4 (CH), 129.6 (2 × CH), 129.1 (4 × CH), 128.6 (2 × CH), 126.8 (CH) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{11}ClO_2S + Na]^+$: calcd. 301.0066, found 301.0067.

*4.3.5 (E)-1-Nitro-4-(styrylsulfonyl)benzene (**3e**).*[7] Colorless solid (40.8 mg, 57% yield); m.p. 150–152 °C. IR (neat): *v* 3103, 3042, 2923, 1603, 1573, 1526, 1449, 1345, 1324, 1300, 1144, 1082 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.9 Hz, 2 H), 8.15 (d, *J* = 8.9 Hz, 2 H), 7.77 (d, *J* = 15.4 Hz, 1 H), 7.51 (d, *J* = 6.5 Hz, 2 H), 7.46–7.40 (m, 3 H), 6.86 (d, *J* = 15.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5 (C), 146.5 (2 × C), 145.0 (CH), 131.9 (CH), 129.2 (2 × CH), 129.0 (2 × CH), 128.8 (2 × CH), 125.6 (CH), 124.6 (2 × CH) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{11}NO_4S + Na]^+$: calcd. 312.0306, found 312.0305.

*4.3.6 (E)-1-Fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (**3f**).*[8c] Colorless solid (32.3 mg, 48% yield); m.p. 92–93 °C. IR (neat): *v* 3048, 1613, 1599, 1509, 1446, 1302, 1280, 1230, 1141, 1082 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.8 Hz, 2 H), 7.67–7.61 (m, 2 H), 7.55 (t, *J* = 7.8 Hz, 2 H), 7.50–7.47 (m, 2 H), 7.08 (t, *J* = 8.6 Hz, 2 H), 6.80 (d, *J* = 15.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3 (d, *J* = 251.0 Hz, C), 141.1 (CH), 140.6 (C), 133.4 (CH), 130.6 (d, *J* = 9.0 Hz, 2 × CH), 129.3 (2 × CH), 128.6 (d, *J* = 3.0 Hz, C), 127.6 (2 × CH), 127.0 (d, *J* = 1.9 Hz, CH), 116.3 (d, *J* = 22.0 Hz, 2 × CH) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{11}FO_2S + Na]^+$: calcd. 285.0361, found 285.0360.

*4.3.7 (E)-1-Fluoro-4-(2-tosylvinyl)benzene (**3g**).*[6c] White solid (30.5 mg, 44% yield); m.p. 94–95 °C. IR (neat): *v* 3053, 2920, 2851, 1615, 1597, 1507, 1321, 1303, 1230, 1139, 1081 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.3 Hz, 2 H), 7.62 (d, *J* = 15.4 Hz, 1 H), 7.47 (dd, *J* = 8.7, 5.3 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.08 (t, *J* = 8.6 Hz, 2 H), 6.78 (d, *J* = 15.4 Hz, 1 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3 (d, *J* = 252.0 Hz, C), 144.5 (C), 140.6 (CH), 137.6 (C), 130.5 (d, *J* = 8.0 Hz, 2 × CH), 130.0 (2 × CH), 128.7 (d, *J* = 3.3 Hz, C), 127.7 (2 × CH), 127.3 (d, *J* = 2.4 Hz, CH), 116.3 (d, *J* = 22.0 Hz, 2 × CH), 21.6 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{13}FO_2S + Na]^+$: calcd. 299.0518, found 299.0519.

*4.3.8 (E)-1-Fluoro-4-(2-(4-methoxyphenylsulfonyl)vinyl)-benzene (**3h**).*[3q'] White solid (23.8 mg, 39% yield); m.p. 94–95 °C. IR (neat): *v* 3057, 2920, 2847, 1591, 1496, 1317, 1295, 1254, 1226, 1135, 1086 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 9.0 Hz, 2 H), 7.59 (d, *J* = 15.4 Hz, 1 H), 7.47 (dd, *J* = 8.7, 5.3 Hz, 2 H), 7.08 (t, *J* = 8.6 Hz, 2 H), 7.01 (d, *J* = 8.9 Hz, 2 H), 6.77 (d, *J* = 15.4 Hz, 1 H), 3.87 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2 (d, *J* = 252.0 Hz, C), 163.6 (C), 140.0 (CH), 132.0 (C), 130.5 (d, *J* = 9.0 Hz, 2 × CH), 129.9 (2× CH), 128.8 (C), 127.7 (CH), 116.3 (d, *J* = 22.0 Hz, 2 × CH), 114.6 (2 × CH), 55.7 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{13}FO_3S + Na]^+$: calcd. 315.0467, found 315.0479.

*4.3.9 (E)-1-Fluoro-4-(2-(4-chlorophenylsulfonyl)vinyl)benzene (**3i**).* Colorless solid (36.5 mg, 50% yield); m.p. 116–117 °C. IR (neat): *v* 3058, 2922, 2853, 1618, 1503, 1319, 1230, 1143, 1084 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.7 Hz, 2 H), 7.65 (d, *J* = 15.4 Hz, 1 H), 7.54–7.47 (m, 4 H), 7.09 (t, *J* = 8.6 Hz, 2 H), 6.77 (d, *J* = 15.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4 (d, *J* = 252.0 Hz, C), 141.7 (CH), 140.2 (C), 139.0 (C), 130.7 (d, *J* = 9.0 Hz, 2 × CH), 129.7 (2 × CH), 129.1 (2 × CH), 128.4 (d, *J* = 4.0 Hz, C), 126.6 (d, *J* = 2.0 Hz, CH), 116.4 (d, *J* = 21.0 Hz, 2 × CH) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{10}ClFO_2S + Na]^+$: calcd. 318.9972, found 319.0052.

*4.3.10 (E)-1-Chloro-3-(2-(phenylsulfonyl)vinyl)benzene (**3j**).*[8c] White solid (48.4 mg, 70% yield); m.p. 83–84 °C. IR (neat): *v* 3048, 2919, 2850, 1617, 1562, 1446, 1318, 1142, 1084 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.4 Hz, 2 H), 7.66–7.55 (m, 4 H), 7.47 (s, 1 H), 7.40–7.31 (m, 3 H), 6.88 (d, *J* = 15.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.7 (CH), 140.3 (C), 135.1 (C), 134.1 (C), 133.6 (CH), 131.0 (CH), 130.3 (CH), 129.4 (2 × CH), 128.8 (CH), 128.2 (CH), 127.7 (2 × CH), 126.8 (CH) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{11}ClO_2S + Na]^+$: calcd. 301.0066, found 301.0069.

*4.3.11 (E)-1-Chloro-3-(2-tosylvinyl)benzene (**3k**).*[5f] Colorless solid (36.2 mg, 49% yield); m.p. 92–94 °C. IR (neat): ν 3061, 3041, 2923, 2852, 1614, 1592, 1563, 1430, 1300, 1146, 1082 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.3 Hz, 2 H), 7.58 (d, *J* = 15.4 Hz, 1 H), 7.45 (s, 1 H), 7.38–7.32 (m, 5 H), 6.86 (d, *J* = 15.4 Hz, 1 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6 (C), 140.1 (CH), 137.3 (C), 135.1 (C), 134.2 (C), 130.9 (CH), 130.3 (CH), 130.0 (2 × CH), 129.2 (CH), 128.1 (CH), 127.8 (2 × CH), 126.7 (CH), 21.6 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{13}ClO_2S + Na]^+$: calcd. 315.0222, found 315.0228.

*4.3.12 (E)-1-Chloro-3-(2-(4-methoxyphenylsulfonyl)vinyl)-benzene (**3l**).*[1l] Colorless solid (57.3 mg, 74% yield); m.p. 71–72 °C. IR (neat): *v* 3056, 2928, 2840, 1591, 1576, 1494, 1461, 1320, 1294, 1256, 1136, 1084 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.9 Hz, 2 H), 7.56 (d, *J* = 15.4 Hz, 1 H), 7.45 (s, 1 H), 7.36–7.32 (m, 3 H), 7.02 (d, *J* = 8.9 Hz, 2 H), 6.87 (d, *J* = 15.4 Hz, 1 H), 3.87 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7 (C), 139.6 (CH), 135.0 (C), 134.2 (C), 131.6 (C), 130.8 (CH), 130.3 (CH), 129.9 (2 × CH), 129.5 (CH), 128.0 (CH), 126.7 (CH), 114.6 (2 × CH), 55.7 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{13}ClO_3S + Na]^+$: calcd. 331.0172, found 331.0170.

*4.3.13 (E)-1-Chloro-3-(2-(4-chlorophenylsulfonyl)vinyl)-benzene (**3m**).*[1l] Colorless solid (50.2 mg, 64% yield); m.p. 126–129 °C. IR (neat): *v* 3056, 2921, 2851, 1616, 1580, 1562, 1470, 1299, 1144, 1083 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.6 Hz, 2 H), 7.61 (d, *J* = 15.4 Hz, 1 H), 7.52 (d, *J* = 8.6 Hz, 2 H), 7.46 (s, 1 H), 7.40–7.31 (m, 3 H), 6.86 (d, *J* = 15.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2 (CH), 140.3 (C), 138.8 (C), 135.1 (C), 133.9 (C), 131.2 (CH), 130.4 (CH), 129.7 (2 × CH), 129.2 (2 × CH), 128.4 (CH), 128.2 (CH), 126.8 (CH) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{10}Cl_2O_2S + Na]^+$: calcd. 334.9676, found 334.9679.

*4.3.14 (E)-1-Chloro-3-(2-(4-nitrophenylsulfonyl)vinyl)benzene (**3n**).* Pale yellow solid (54 mg, 67% yield); m.p. 130–132 °C. IR (neat): *v* 3059, 2921, 2852, 1613, 1521, 1470, 1345, 1297, 1143, 1080 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.9 Hz, 2 H), 8.14 (d, *J* = 8.9 Hz, 2 H), 7.70 (d, *J* = 15.4 Hz, 1 H), 7.49 (s, 1 H), 7.43–7.36 (m, 3 H), 6.88 (d, *J* = 15.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6 (C), 146.1 (C), 143.1 (CH), 135.3 (C), 133.5 (C), 131.7 (CH), 130.5 (CH), 129.1 (2 × CH), 128.4 (CH), 127.3 (CH), 127.1 (CH), 124.6 (2 × CH) ppm.

HRMS (ESI) (*m/z*) $[C_{14}H_{10}ClNO_4S + Na]^+$: calcd. 345.9917, found 345.9919.

*4.3.15 (E)-1-Bromo-4-(2-(phenylsulfonyl)vinyl)benzene (**3o**).*[8c] Colorless solid (44.3 mg, 55% yield); m.p. 138–139 °C. IR (neat): *v* 3054, 1610, 1582, 1481, 1446, 1397, 1305, 1141, 1067 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.9 Hz, 2 H), 7.65–7.51 (m, 6 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 6.86 (d, *J* = 15.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0 (CH), 140.4 (C), 133.5 (CH), 132.4 (2 × CH), 131.2 (C), 129.9 (2 × CH), 129.4 (2 × CH), 128.0 (CH), 127.7 (2 × CH), 125.6 (C) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{11}BrO_2S + Na]^+$: calcd. 346.9540, found 346.9543.

*4.3.16 (E)-1-Nitro-4-(2-(phenylsulfonyl)vinyl)benzene (**3p**).*[8c] Yellow solid (53.1 mg, 73% yield); m.p. 152–153 °C. IR (neat): *v* 3055, 1592, 1509, 1446, 1337, 1307, 1148, 1085 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): δ = 8.29 (d, *J* = 8.8 Hz, 2 H), 8.05–7.98 (m, 4 H), 7.81 (d, *J* = 15.5 Hz, 1 H), 7.77–7.73 (m, 1 H), 7.70–7.66 (m, 2 H), 7.61 (d, *J* = 15.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, acetone-d_6): δ 150.0 (C), 141.8 (C), 140.4 (CH), 140.1 (C), 134.8 (CH), 133.5 (CH), 130.9 (2 × CH), 130.6 (2 × CH), 128.8 (2 × CH), 125.0 (2 × CH) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{11}NO_4S + Na]^+$: calcd. 312.0306, found 312.0309.

*4.3.17 (E)-1-Nitro-4-(2-tosylvinyl)benzene (**3q**).*[5f] Pale yellow solid (52.7 mg, 70% yield); m.p. 166–168 °C. IR (neat): *v* 3052, 2921, 2851, 1595, 1514, 1341, 1301, 1287, 1144, 1082 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): δ = 8.29 (d, *J* = 8.8 Hz, 2 H), 8.02 (d, *J* = 8.8 Hz, 2 H), 7.85 (d, *J* = 8.3 Hz, 2 H), 7.77 (d, *J* = 15.5 Hz, 1 H), 7.58 (d, *J* = 15.5 Hz, 1 H), 7.48 (d, *J* = 8.2 Hz, 2 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (100 MHz, acetone-d_6): δ = 150.0 (C), 145.8 (C), 140.2 (C), 139.8 (CH), 138.8 (C), 133.8 (CH), 131.1 (2 × CH), 130.8 (2 × CH), 128.8 (2 × CH), 125.0 (2 × CH), 21.6 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{13}NO_4S + Na]^+$: calcd. 326.0463, found 326.0466.

*4.3.18 (E)-1-Nitro-4-(2-(4-methoxyphenylsulfonyl)vinyl)-benzene (**3r**).*[5f] White solid (64.3 mg, 82% yield); m.p. 186–188 °C. IR (neat): *v* 3111, 3083, 3056, 2921, 2845, 1590, 1521, 1493, 1341, 1295, 1253, 1136, 1088 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): δ = 8.29 (d, *J* = 8.9 Hz, 2 H), 8.01 (d, *J* = 8.8 Hz, 2 H), 7.90 (d, *J* = 9.0 Hz, 2 H), 7.73 (d, *J* = 15.5 Hz, 1 H), 7.56 (d, *J* = 15.5 Hz, 1 H), 7.17 (d, *J* = 9.0 Hz, 2 H), 3.91 (s, 3 H) ppm. ^{13}C NMR (100 MHz, acetone-d_6): δ = 165.0 (C), 149.9 (C), 140.3 (C), 139.1 (CH), 134.2 (CH), 133.1 (CH), 131.1 (2 × CH), 130.8 (2 × CH), 125.0 (2 × CH), 115.8 (2 × CH), 56.4 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{13}NO_5S + Na]^+$: calcd. 342.0412, found 342.0425.

*4.3.19 (E)-1-Nitro-4-(2-(4-chlorophenylsulfonyl)vinyl)benzene (**3s**).* Pale yellow solid (70.5 mg, 88% yield); m.p. 176–178 °C. IR (neat): *v* 3112, 3085, 3057, 2922, 2850, 1593, 1520, 1473, 1341, 1307, 1143, 1085 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): δ = 8.30 (d, *J* = 8.8 Hz, 2 H), 8.04–7.98 (m, 4 H), 7.83 (d, *J* = 15.5 Hz, 1 H), 7.72 (d, *J* = 8.7 Hz, 2 H), 7.63 (d, *J* = 15.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, acetone-d_6): δ = 150.1 (C), 140.9 (CH), 140.6 (C), 140.5 (C), 140.0 (C), 133.0 (CH), 131.0 (2 × CH), 130.8 (2 × CH), 130.7 (2 × CH), 125.0 (2 × CH) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{10}ClNO_4S + Na]^+$: calcd. 345.9917, found 345.9929.

*4.3.20 (E)-1-Methyl-4-(2-(phenylsulfonyl)vinyl)benzene (**3t**).*[8c] White solid (27.7 mg, 43% yield); m.p. 118–120 °C. IR (neat): *v* 3053, 2918, 1604, 1510, 1446, 1306, 1143, 1082 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.7 Hz, 2 H), 7.68–7.60 (m, 2 H), 7.54 (t, *J* = 7.8 Hz, 2 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 6.81 (d, *J* = 15.4 Hz, 1 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5 (CH), 141.9 (C), 140.9 (C), 133.3 (CH), 129.8 (2 × CH), 129.6 (C), 129.3 (2 × CH), 128.6 (2 × CH), 127.6 (2 × CH), 126.0 (CH), 21.5 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{14}O_2S + Na]^+$: calcd. 281.0612, found 281.0615.

*4.3.21 (E)-1-Methoxy-3-(2-(phenylsulfonyl)vinyl)benzene (**3u**).*[8c] Colorless solid (22.4 mg, 33% yield); m.p. 101–102 °C. IR (neat): *v* 3075, 3046, 3005, 2838, 1598, 1584, 1446, 1300, 1270, 1144, 1083 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.9 Hz, 2 H), 7.68–7.61 (m, 2 H), 7.55 (t, *J* = 7.8 Hz, 2 H), 7.30 (t, *J* = 7.9 Hz, 1 H), 7.08 (d, *J* = 7.6 Hz, 1 H), 6.99–6.95 (m, 2 H), 6.86 (d, *J* = 15.4 Hz, 1 H), 3.81 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9 (C), 142.4 (CH), 140.6 (C), 133.6 (C), 133.4 (CH), 130.1 (CH), 129.3 (2 × CH), 127.6 (2 × CH), 127.5 (CH), 121.2 (CH), 117.1 (CH), 113.3 (CH), 55.3 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{14}O_3S + Na]^+$: calcd. 297.0561, found 297.0567.

*4.3.22 (E)-1-Bromo-3-methoxy-4-(2-(phenylsulfonyl)vinyl)-benzene (**3v**).* Colorless solid (41.1 mg, 47% yield); m.p. 158–161 °C. IR (neat): *v* 3048, 2940, 2843, 1607, 1495, 1301, 1283, 1138, 1081 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.3 Hz, 2 H), 7.69 (d, *J* = 2.1 Hz, 1 H), 7.63–7.53 (m, 4 H), 7.40 (dd, *J* = 8.5, 2.1 Hz, 1 H), 6.89 (d, *J* = 8.6 Hz, 1 H), 6.73 (d, *J* = 15.4 Hz, 1 H), 3.92 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1 (C), 140.7 (C), 140.6 (CH), 133.3 (CH), 133.0 (CH), 129.7 (CH), 129.3 (2 × CH), 127.6 (2 × CH), 126.2 (C), 126.0 (CH), 112.4 (C), 111.8 (CH), 56.4 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{13}BrO_3S + Na]^+$: calcd. 376.9646, found 376.9649.

*4.3.23 (E)-1-Bromo-3-methoxy-4-(2-tosylvinyl)benzene (**3w**).* Pale yellow solid (49.3 mg, 54% yield); m.p. 166–168 °C. IR (neat): *v* 3066, 2920, 2851, 1607, 1594, 1493, 1462, 1287, 1261, 1135, 1080 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.3 Hz, 2 H), 7.67 (d, *J* = 2.0 Hz, 1 H), 7.52 (d, *J* = 15.4 Hz, 1 H), 7.39 (dd, *J* = 8.6, 2.0 Hz, 1 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 6.88 (d, *J* = 8.6 Hz, 1 H), 6.71 (d, *J* = 15.3 Hz, 1 H), 3.91 (s, 3 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9 (C), 144.3 (2 × C), 140.1 (CH), 137.7 (C), 132.9 (CH), 129.9 (2 × CH), 129.6 (CH), 127.6 (2 × CH), 126.3 (CH), 112.4 (C), 111.8 (CH), 56.4 (CH_3), 21.6 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{16}H_{15}BrO_3S + Na]^+$: calcd. 390.9803, found 390.9807.

*4.3.24 (E)-1-Bromo-3-methoxy-4-(2-(4-methoxyphenylsulfonyl)vinyl)benzene (**3x**).* White solid (57 mg, 59% yield); m.p. 155–158 °C. IR (neat): *v* 3054, 2918, 2846, 1591, 1492, 1291, 1254, 1133, 1085 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 9.0 Hz, 2 H), 7.67 (d, *J* = 2.1 Hz, 1 H), 7.50 (d, *J* = 15.4 Hz, 1 H), 7.39 (dd, *J* = 8.6, 2.2 Hz, 1 H), 7.00 (d, *J* = 9.0 Hz, 2 H), 6.89 (d, *J* = 8.6 Hz, 1 H), 6.71 (d, *J* = 15.3 Hz, 1 H), 3.92 (s, 3 H), 3.87 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5 (C), 157.9 (C), 139.5 (CH), 132.9 (CH), 132.2 (C), 129.8 (2 × CH), 129.6 (CH), 126.7 (CH), 126.4 (C), 114.5 (2 × CH), 112.4 (C), 111.8 (CH), 56.4 (CH_3), 55.7 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{16}H_{15}BrO_4S + Na]^+$: calcd. 406.9752, found 406.9748.

*4.3.25 (E)-1-Bromo-3-methoxy-4-(2-(4-chlorophenylsulfonyl)-vinyl)benzene (**3y**).* White solid (61 mg, 63% yield); m.p. 132–135 °C. IR (neat): *v* 3068, 2949, 2850, 1612, 1591, 1495, 1439,

1399, 1299, 1284, 1269, 1136, 1083 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.6 Hz, 2 H), 7.69 (d, J = 2.1 Hz, 1 H), 7.56 (d, J = 15.4 Hz, 1 H), 7.51 (d, J = 8.6 Hz, 2 H), 7.41 (dd, J = 8.5, 2.1 Hz, 1 H), 6.90 (d, J = 8.6 Hz, 1 H), 6.70 (d, J = 15.3 Hz, 1 H), 3.93 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2 (C), 141.2 (CH), 140.0 (C), 139.3 (C), 133.0 (CH), 129.8 (CH), 129.6 (2 × CH), 129.1 (2 × CH), 126.0 (C), 125.5 (CH), 112.5 (C), 111.9 (CH), 56.4 (CH_3) ppm. HRMS (ESI) (*m/z*) $[C_{15}H_{12}BrClO_3S + Na]^+$: calcd. 410.9256, found 410.9252.

*4.3.26 (E)-2-(2-(Phenylsulfonyl)vinyl)naphthalene (**3z**).*[8c] White solid (36.7 mg, 50% yield); m.p. 89–90 °C. IR (neat): ν 3046, 2919, 1611, 1445, 1304, 1286, 1139, 1083 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.3 Hz, 2 H), 7.94 (s, 1 H), 7.87–7.81 (m, 4 H), 7.63 (t, J = 7.4 Hz, 1 H), 7.58–7.51 (m, 5 H), 6.98 (d, J = 15.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5 (CH), 140.8 (C), 134.5 (C), 133.4 (CH), 133.1 (C), 130.9 (CH), 129.8 (C), 129.3 (2 × CH), 128.9 (CH), 128.7 (CH), 127.8 (2 × CH), 127.6 (2 × CH), 127.2 (CH), 127.0 (CH), 123.4 (CH) ppm. HRMS (ESI) (*m/z*) $[C_{18}H_{14}O_2S + Na]^+$: calcd. 317.0612, found 317.0610.

4.4 Preparation of compound 3a'

To a mixture of 3-phenylpropiolic acid (36.5 mg, 0.25 mmol), benzenesulfinic acid (142.2 mg, 1.0 mmol), and Na_2CO_3 (26.9 mg, 0.25 mmol) were added DMF (2 mL) and D_2O (1 mL). The reaction mixture was stirred at 100 °C under air atmosphere for 2 hours. After completion of the reaction, the reaction was cooled to room temperature and was diluted with water (10 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 **3a'**.

*(E)-(1,2-deutero-2-(phenylsulfonyl)vinyl)benzene (**3a'**).*[7] White solid (29 mg, 47% yield); m.p. 74–76 °C. IR (neat): ν 3057, 1568, 1446, 1295, 1144, 1086 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 7.4 Hz, 2 H), 7.64–7.60 (m, 1 H), 7.57–7.53 (m, 2 H), 7.50–7.48 (m, 2 H), 7.44–7.37 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4 (C), 140.7 (C), 133.4 (CH), 132.2 (C), 131.2 (CH), 129.3 (2 × CH), 129.1 (2 × CH), 128.6 (2 × CH), 127.7 (2 × CH), 127.1 (C) ppm. HRMS (ESI) (*m/z*) $[C_{14}H_{10}D_2O_2S + H]^+$: calcd. 247.0762, found 247.0769.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.

References and notes

1. (a) Liu, S.; Hanzlik, R. P. *J. Med. Chem.* **1992**, *35*, 1067–1075; (b) Palmer, J. T.; Rasnick, D.; Klaus, J. L.; Brömme, D. *J. Med. Chem.* **1995**, *38*, 3193–3196; (c) Roush, W. R.; Gwaltney II, S. L.; Cheng, J.; Scheidt, K. A.; McKerrow, J. H.; Hansell, E. *J. Am. Chem. Soc.* **1998**, *120*, 10994–10995; (d) Reddick, J. J.; Cheng, J.; Roush, W. R. *Org. Lett.* **2003**, *5*, 1967–1970; (e) Wang, G.; Mahesh, U.; Chen, G. Y. J.; Yao, S. Q. *Org. Lett.* **2003**, *5*, 737–740; (f) Shenai, B. R.; Lee, B. J.; Alvarez-Hernandez, A.; Chong, P. Y.; Emal, C. D.; Neitz, R. J.; Roush, W. R.; Rosenthal, P. J. *Antimicrob. Agents Chemother.* **2003**, *47*, 154–160; (g) Frankel, B. A.; Bentley, M.; Kruger, R. G.; McCafferty, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 3404–3405; (h) Meadows, D. C.; Sanchez, T.; Neamati, N.; North, T. W.; Gervay-Hague, J. *Bioorg. Med. Chem.* **2007**, *15*, 1127–1137; (i) Uttamchandani, M.; Liu, K.; Panicker, R. C.; Yao, S. Q. *Chem. Commun.* **2007**, 1518–1520; (j) 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; (k) 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; (l) Woo, S. Y.; Kim, J. H.; Moon, M. K.; Han, S.-H.; Yeon, S. K.; Choi, J. W.; Jang, B. K.; Song, H. J.; Kang, Y. G.; Kim, J. W.; Lee, J.; Kim, D. J.; Hwang, O.; Park, K. D. *J. Med. Chem.* **2014**, *57*, 1473–1487.
2. (a) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853–855; (b) Farthing, C. N.; Marsden, S. P. *Tetrahedron Lett.* **2000**, *41*, 4235–4238; (c) Krasovsky, A. L.; Nenajdenko, V. G.; Balenkova, E. S. *Tetrahedron* **2001**, *57*, 201–209; (d) Arjona, O.; Menchaca, R.; Plumet, J. *Org. Lett.* **2001**, *3*, 107–109; (e) Padwa, A.; Lipka, H.; Watterson, S. H.; Murphree, S. S. *J. Org. Chem.* **2003**, *68*, 6238–6250; (f) Llamas, T.; Arrayás, R. G.; Carretero, J. C. *Org. Lett.* **2006**, *8*, 1795–1798; (g) Wardrop, D. J.; Fritz, J. *Org. Lett.* **2006**, *8*, 3659–3662; (h) Noshi, M. N.; Elawa, A.; Torres, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **2007**, *129*, 11242–11247; (i) López-Pérez, A.; Robles-Machín, R.; Adrio, J.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 9261–9264; (j) Esteves, A. P.; Silva, M. E.; Rodrigues, L. M.; Oliveira-Campos, A. M. F.; Hrdina, R. *Tetrahedron Lett.* **2007**, *48*, 9040–9043; k) Gao, Y.; Lam, Y. *J. Comb. Chem.* **2008**, *10*, 327–332; (l) Kumamoto, H.; Deguchi, K.; Wagata, T.; Furuya, Y.; Odanaka, Y.; Kitade, Y.; Tanaka, H. *Tetrahedron* **2009**, *65*, 8007–8013; (m) Zhu, Q.; Lu, Y. *Org. Lett.* **2009**, *11*, 1721–1724; (n) Sulzer-Mossé, S.; Alexakis, A.; Mareda, J.; Bollot, G.; Bernardinelli, G.; Filinchuk, Y. *Chem.–Eur. J.* **2009**, *15*, 3204–3220.
3. A two-step method involving β-elimination of and sulfur oxidation or vice versa, see: (a) Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4976–4986; (b) Brace, N. O. *J. Org. Chem.* **1993**, *58*, 4506–4508; (c) Kroll, F. E. K.; Morphy, R.; Rees, D.; Gani, D. *Tetrahedron Lett.* **1997**, *38*, 8573–8576; (d) Orita, A.; Katakami, M.; Yasui, Y.; Kurihara, A.; Otera, J. *Green Chem.* **2001**, *3*, 13–16; (e) Magnier, E.; Tordeux, M.; Goumont, R.; Magder, K.; Wakselman, C. *J. Fluorine Chem.* **2003**, *124*, 55–59; Addition of $PhSO_2X$ (X = I, Cl, SePh, ONO_2, HgCl, etc.) to alkenes followed by β-elimination, see: (f) Liu, L. K.; Jen, K.-Y. *J. Org. Chem.* **1980**, *45*, 406–410; (g) Harwood, L. M.; Julia, M.; Thuillier, G. L. *Tetrahedron* **1980**, *36*, 2483–2487; (h) Nájera, C.; Baldó, B.; Yus, M. *J. Chem. Soc., Perkin Trans. 1*. **1988**, 1029–1032; (i) Nair, V.; Augustine, A.; George, T. G.; Nair, L. G. *Tetrahedron Lett.* **2001**, *42*, 6763–6765; (j) Nair, V.; Augustine, A.; Suja, T. D. *Synthesis* **2002**, 2259–2265; (k) Zhu, S.; Qin, C.; Xu, G.; Chu, Q. *Tetrahedron Lett.* **1998**, *39*, 5265–5268; (l) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249–3256; (m) Nair, V.; Augustine, A.; Panicker, S. B.; Suja, T. D.; Mathai, S. *Res. Chem. Intermed.* **2003**, *29*, 213–226; (n) Sas, W. *J. Chem. Soc., Chem. Commun.* **1984**, 862–863; (o) Qian, H.; Huang, X. *Synlett* **2001**, 1913–1916; (p) Das, B.; Lingaiah, M.; Damodar, K.; Bhunia, N. *Synthesis* **2011**, 2941–2944; (q) Zhang, N.; Yang, D.; Wei, W.; Yuan, L.; Cao, Y.; Wang, H. *RSC Adv.* **2015**, *5*, 37013–37017; Addition of $PhSO_2X$ (X = I, Cl, etc.) to alkynes, see: (r) Edwards, G. L.; Muldoon, C. A.; Sinclair, D. J. *Tetrahedron* **1996**, *52*, 7779–7788; (s) Liu, X.; Duan, X.; Pan, Z.; Han, Y.; Liang, Y. *Synlett* **2005**, 1752–1754; Horner–Wadsworth–Emmons reaction, see: (t) Popoff, I. C.; Dever, J. L.; Leader, G. R. *J. Org. Chem.* **1969**, *34*, 1128–1130; (u) Wang, G.; Yao, S. Q. *Org. Lett.* **2003**, *5*, 4437–4440; Hydrozirconation reaction of acetylenic sulfones, see: (v) Huang, X.; Duan, D.-H. *Chem. Commun.* **1999**, 1741–1742; (w) Huang, X.; Duan, D.-H.; Zheng, W. *J. Org. Chem.* **2003**, *68*, 1958–1963; Hydrozirconation of terminal alkynes followed by reaction with sulfonyl chloride, see: (x) Duan, D.-H.; Huang, X. *Synlett* **1999**, 317–318; Hydrotelluration of acetylenic sulfones, see: (y) Huang, X.; Liang, C.-G.; Xu, Q.; He, Q.-W. *J. Org. Chem.* **2001**, *66*, 74–80; Selenosulfonation to alkynes, see: (z) Back, T. G.; Collins, S.; Krishna, M. V.; Law, K.-W. *J. Org. Chem.* **1987**, *52*, 4258–4264; Nucleophilic

addition to 1-phenylseleno-2 (arenesulfonyl)ethyne, see: (a') Back, T. G.; Bethell, R. J.; Parvez, M.; Wehrli, D. *J. Org. Chem.* **1998**, *63*, 7908–7919; Addition of sodium benzenesulfinate to alkynylselenonium salts, see: (b') Watanabe, S.; Yamamoto, K.; Itagaki, Y.; Iwamura, T.; Iwama, T.; Kataoka, T.; Tanabe, G.; Muraoka, O. *J. Chem. Soc., Perkin Trans. 1* **2001**, 239–247; Displacement of β-bromostyrene derivatives with sodium arenesulfinates, see: (c') Baker, B. R.; Querry, M. V. *J. Org. Chem.* **1950**, *15*, 417–424; Reaction of alkenyltriphenylbismuthonium tetrafluoroborates with arylsulfinate salt, see: (d') Matano, Y.; Yoshimune, M.; Azuna, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1971–1977; Reaction of β-haloalkenylphenyliodonium salts with benzenesulfinate sodium salt, see: (e') Ochiai, M.; Kitagawa, Y.; Toyonari, M.; Uemura, K.; Oshima, K.; Shiro, M. *J. Org. Chem.* **1997**, *62*, 8001–8008; Palladium-catalyzed reactions, see: (f') Berteina, S.; Wendeborn, S.; Brill, W. K.-D.; Mesmaeker, A. D. *Synlett* **1998**, 676–678; (g') Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Parisi, L. M.; Bernini, R. *J. Org. Chem.* **2004**, *69*, 5608–5614; (h') Kabalka, G. W.; Guchhait, S. K. *Tetrahedron Lett.* **2004**, *45*, 4021–4022; (i') Reeves, D. C.; Rodriguez, S.; Lee, H.; Haddad, N.; Krishnamurthy, D.; Senanayake, C. H. *Tetrahedron Lett.* **2009**, *50*, 2870–2873; Copper-catalyzed reactions, see: (j') Bao, W.; Wang, C. *J. Chem. Res.* **2006**, *6*, 396–397; (k') M. Bian, F. Xu, C. Ma, *Synthesis* **2007**, 2951–2956; (l') Taniguchi, N. *Synthesis* **2011**, 1308–1312; Cross-metathesis, see: (m') Grela, K.; Bieniek, M. *Tetrahedron Lett*. **2001**, *42*, 6425–6428; (n') Michrowska, A.; Bieniek, M.; Kim, M.; Klajn, R.; Grela, K. *Tetrahedron* **2003**, *59*, 4525–4531; Carbomagnesiation of acetylenic sulfones, see: (o') Xie, M.; Liu, L.; Wang, J.; Wang, S. *J. Organomet. Chem.* **2005**, *690*, 4058–4062; Reaction of 1,2-dibromoalkanes with sulfinic acid sodium salts, see: (p') Guan, Z.-H.; Zuo, W.; Zhao, L.-B.; Ren, Z.-H.; Liang, Y.-M. *Synthesis* **2007**, 1465–1470; Addition of thiols with alkynes, see: (q') Xue, Q.; Mao, Z.; Shi, Y.; Mao, H.; Cheng, Y.; Zhu, C. *Tetrahedron Lett.* **2012**, *53*, 1851–1854; Addition of sulfonylhydrazides to alkynes and alkenes, see: (r') Li, X.; Shi, X.; Fang, M.; Xu, X. *J. Org. Chem.* **2013**, *78*, 9499–9504; (s') Tang, S.; Wu, Y.; Liao, W.; Bai, R.; Liu, C.; Lei, A. *Chem. Commun.* **2014**, *50*, 4496–4499; Copper catalyzed addition of sulfinic acids to alkynes, see: (t') Wei, W.; Li, J.; Yang, D.; Wen, J.; Jiao, Y.; You, J.; Wang, H. *Org. Biomol. Chem.* **2014**, *12*, 1861–1864; Ring opening of epoxides, see: (u') Chawla, R.; Kapoor, R.; Singh, A. K.; Yadav, L. D. S. *Green Chem.* **2012**, *14*, 1308–1313.

4. Selected examples for decarboxylative functionalization of aromatic carboxylic acids, see: (a) Pei, K.; Jie, X.; Zhao, H.; Su, W. *Eur. J. Org. Chem.* **2014**, 4230–4233; (b) Rao, A. S.; Srinivas, P. V.; Babu, K. S.; Rao, J. M. *Tetrahedron Lett.* **2005**, *46*, 8141–8143; Selected examples for decarboxylative functionalization of α,β-unsaturated carboxylic acids, see: (c) He, Z.; Luo, T. ; Hu, M.; Cao, Y.; Hu, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 3944–3947; (d) Yang, H.; Sun, P.; Zhu, Y.; Yan, H.; Lu, L.; Qu, X.; Li, T.; Mao, J. *Chem. Commun.* **2012**, *48*, 7847–7849; (e) Li, Z.; Cui, Z.; Liu, Z.-Q. *Org. Lett.* **2013**, *15*, 406–409; (f) Das, J. P.; Sinha, P.; Roy, S. *Org. Lett.* **2002**, *4*, 3055–3058; (g) Manna, S.; Jana, S.; Saboo, T.; Maji, A.; Maiti, D. *Chem. Commun.* **2013**, *49*, 5286–5288; (h) Rokade, B. V.; Prabhu, K. R. *Org. Biomol. Chem.* **2013**, *11*, 6713–6716; Selected examples for decarboxylative functionalization of alkynyl carboxylic acids, see: (i) Hwang, J.; Park, K.; Choe, J.; Min, H.; Song, K. H.; Lee, S. *J. Org. Chem.* **2014**, *79*, 3267–3271; (j) Jia, W.; Jiao, N. *Org. Lett.* **2010**, *12*, 2000–2003; Selected examples for decarboxylative functionalization of aliphatic carboxylic acids, see: (k) Liu, X.; Wang, Z.; Cheng, X.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 4258–4263; (l) Zuo, Z.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2014**, *136*, 5257–5260; (m) Song, Q.; Feng, Q.; Yang, K. *Org. Lett.* **2014**, *16*, 624–627; (n) Wang, Z.; Zhu, L.; Yin, F.; Su, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc*. **2012**, *134*, 4258–4263; (o) Yin, F.; Wang, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc*. **2012**, *134*, 10401–10404; (p) Mizuta, S.; Stenhagen, I. S. R.; O'Duill, M.; Wolstenhulme, J.; Kirjavainen, A. K.; Forsback, S. J.; Tredwell, M.; Sandford, G.; Moore, P. R.; Huiban, M.; Luthra, S. K.; Passchier, J.; Solin, O.; Gouverneur, V. *Org. Lett.* **2013**, *15*, 2648–2651; (q) Rueda-Becerril, M.; Mahé, O.; Drouin, M.; Majewski, M. B.; West, J. G.; Wolf, M. O.; Sammis, G. M.; Paquin, J.-F. *J. Am. Chem. Soc*. **2014**, *136*, 2637–2641.
5. Decarboxylative sulfonylation of α,β-unsaturated carboxylic acids, see: (a) Li, H.-S.; Liu, G. *J. Org. Chem.* **2014**, *79*, 509–516; (b) Xu, Y.; Tang, X.; Hu, W.; Wu, W.; Jiang, H. *Green Chem.* **2014**, *16*, 3720–3723; (c) Guo, R.; Gui, Q.; Wang, D.; Tan, Z. *Catal. Lett.* **2014**, *144*, 1377–1383; (d) Jiang, Q.; Xu, B.; Jia, J.; Zhao, A.; Zhao, -R. Y.; Li, -Y.Y.; He, -N. N. Guo, -C. C. *J. Org. Chem.* **2014**, *79*, 7372–7379; (e) Rokade, V. B.; Prabhu, R. K.; *J. Org. Chem.* **2014**, *79*, 8110–8117; (f) Singh, R.; Allam, K. B.; Singh, N.; Kumari, K.; Singh, K. S.; Singh, N. K. *Org. Lett.* **2015**, *17*, 2656–2659; (g) Chen, J.; Mao, J.; Zheng, Y.; Liu, D.; Rong, G.; Yan, H.; Zhang, C.; Shi, D. *Tetrahedron* **2015**, *71*, 5059–5063.
6. Decarboxylative C-S cross coupling of alkynyl acids, see: (a) Ranjit, S.; Duan, Z.; Zhang, P.; Liu, X. *Org. Lett.* **2010**, *12*, 4134–4136; (b) Xu, Y.; Zhao, J.; Tang, X.; Wu, W.; Jiang, H *Adv. Synth. Catal*. **2014**, *356*, 2029–2039; (c) Rong, G.; Mao, J.; Yan, H.; Zheng, Y.; Zhang, G. *J. Org. Chem.* **2015**, *80*, 4697–4703.
7. Rong, G.; Mao, J.; Yan, H.; Zheng, Y.; Zhang, G. *J. Org. Chem.* **2015**, *80*, 7652–7657.
8. (a) Katrun, P.; Chiampanichayakul, S.; Korworapan, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Kuhakarn, C. *Eur. J. Org. Chem.* **2010**, 5633–5641; (b) Sawangphon, T.; Katrun, P.; Chaisiwamongkhol, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. *Synth. Commun.* **2013**, *43*, 1692–1707; (c) Katrun, P.; Hlekhlai, S.; Meesin, J.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. *Org. Biomol. Chem.* **2015**, *13*, 4785–4794.
9. (a) Lu, Q.; Zhang, J.; Zhao, G.; Qi, Y.; Wang, H.; Lei, A. *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.
10. (a) Shen, T.; Yuan, Y.; Song, S.; Jiao, N. *Chem. Commun.* **2014**, *50*, 4115–4118; (b) Wei, W.; Wen, J.; Yang, D.; Du, J.; You, J.; Wang, H. *Green Chem.* **2014**, *16*, 2988–2991; (c) Lu, Q.; Zhang, J.; Wei, F.; Qi, Y.; Wang, H.; Liu, Z.; A. Lei, *Angew. Chem., Int. Ed.* **2013**, *52*, 7156–7159; (d) Wei, W.; Wen, J.; Yang, D.; Wu, M.; You, J.; Wang, H. *Org. Biomol. Chem.* **2014**, *12*, 7678–7681.