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Electrosynthesis of (*E*)-Vinyl Sulfones Directly from Cinnamic Acids and Sodium Sulfinates via Decarboxylative Sulfono Functionalization

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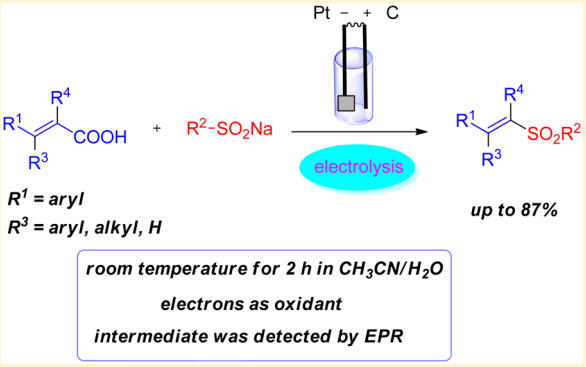
Supporting Information

ABSTRACT: A variety of (*E*)-vinyl sulfones were constructed directly from cinnamic acids and sodium sulfinates with high regioselectivity at room temperature by virtue of an electrocatalytic oxidation. A radical intermediate was detected, and the corresponding mechanism was investigated.



Vinyl sulfones widely exist in pharmaceutically active agents[1] and naturally active molecules and are the prevalent molecular skeleton for various organic transformations.[2] The invention of methodologies toward this building block is a long-standing goal in organic synthesis, and considerable progress has been made in this area. In terms of these synthetic methodologies,[3] the overwhelming majority were still not green enough, often involving a high-temperature, transition-metal catalysis and limited availability of raw materials. Therefore, a more modern and green strategy for the broadly rapid electrosynthesize (*E*)-vinyl sulfones directly from readily accessible starting materials at room temperature is still desired. Electrochemical synthesis has been extensively employed in a variety of chemical transformations and has become an interesting and attractive avenue for their benign properties, selectivity, and sustainability.[4,5] Our group has developed a series of electrochemical routes toward various organic transformations,[6] motivating us to accomplish a sulfo functionalization via an electrochemical decarboxylation oxidation. The reaction can be carried out directly from facile cinnamic acids and sodium sulfinates at room temperature under an elegant constant current with good selectivity and yield. As far as we know, this electrocatalytic decarboxylation coupling should be one of the best efficient methods to construct the (*E*)-vinyl sulfones under the mild conditions.

We commenced our studies by attempting the proposed decarboxylative coupling of cinnamic acid **1a** with sodium sulfinates **2a** in an undivided cell at room temperature. As shown in Table 1 (entry 1), the proposed decarboxylation sulfo functionalization was conducted smoothly via an electrocatalytic oxidation. The current optimization indicated that the high yield can be obtained when the 20 mA current was used (entries 2−4). Subsequently, it was found that the best anode was the carbon rod, while the best cathode was a platinum plate (entries 5−10). An investigation of electrolytes showed that electrolytes had a slight influence on yield (entries 11 and 12). Nevertheless, the solvent had an important influence on the reaction. For instance, the combination of CH_3CN and H_2O (7:1) favored the reaction, while other solvents disfavored the reaction (entries 13−15). In order to promote the reaction further, some additives were tested (entries 16−21). It was found that the appropriate AcOH was beneficial to this transformation (entries 20−23). A higher concentration of **2a** increased the yield from 75% to 77% (entries 24 and 25). On the other hand, only a trace amount of product was detected when the reaction was carried out in an oxygen atmosphere, while a nitrogen atmosphere led to a slightly lower yield. Taken together, the optimal conditions were obtained as below: cinnamic acids (0.5 mmol), sodium sulfinates (1.2 mmol), *n*-Bu_4NClO_4 (1 mmol), AcOH (0.25 mmol), CH_3CN/H_2O (7/1 mL), carbon rod as the anode, platinum plate as the cathode. All of the reactions were electrolyzed at a constant current of 20 mA for 2 h in an undivided cell at room temperature.

Having identified the optimized conditions for this electrocatalytic decarboxylative coupling, we then examined the compatibility of this reaction with respect to cinnamic acids and sodium sulfinates (Table 2). As shown in Table 2, a broad scope of cinnamic acids was found, and the cinnamic acids with

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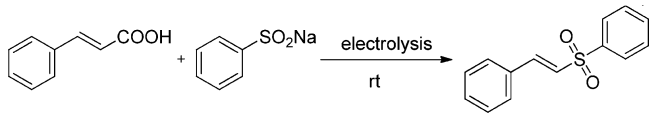
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

entry	electrode (anode/cathode)	electrolyte	additive (equiv)	current (mA)	solvent (mL)	yield[b] (%)
1	Pt/Pt	$LiClO_4$	none	40	CH_3CN/H_2O	26
2	Pt/Pt	$LiClO_4$	none	30	CH_3CN/H_2O	35
3	Pt/Pt	$LiClO_4$	none	20	CH_3CN/H_2O	43
4	Pt/Pt	$LiClO_4$	none	10	CH_3CN/H_2O	41
5	C/Pt	$LiClO_4$	none	20	CH_3CN/H_2O	66
6	C/C	$LiClO_4$	none	20	CH_3CN/H_2O	25
7	C/Ag	$LiClO_4$	none	20	CH_3CN/H_2O	52
8	C/Au	$LiClO_4$	none	20	CH_3CN/H_2O	55
9	C/Ti	$LiClO_4$	none	20	CH_3CN/H_2O	50
10	C/Zn	$LiClO_4$	none	20	CH_3CN/H_2O	40
11	C/Pt	n-Bu_4NClO_4	none	20	CH_3CN/H_2O	67
12	C/Pt	n-Bu_4NPF_6	none	20	CH_3CN/H_2O	66
13	C/Pt	n-Bu_4NClO_4	none	20	$MeOH/H_2O$	trace
14	C/Pt	n-Bu_4NClO_4	none	20	$EtOH/H_2O$	trace
15	C/Pt	n-Bu_4NClO_4	none	20	THF/H_2O	trace
16	C/Pt	n-Bu_4NClO_4	Et_3N (0.5)	20	CH_3CN/H_2O	61
17	C/Pt	n-Bu_4NClO_4	DBU (0.5)	20	CH_3CN/H_2O	60
18	C/Pt	n-Bu_4NClO_4	HFIP (0.5)	20	CH_3CN/H_2O	73
19	C/Pt	n-Bu_4NClO_4	CF_3CH_2OH (0.5)	20	CH_3CN/H_2O	34
20	C/Pt	n-Bu_4NClO_4	AcOH (0.5)	20	CH_3CN/H_2O	75
21	C/Pt	n-Bu_4NClO_4	H_3PO_4 (0.5)	20	CH_3CN/H_2O	trace
22	C/Pt	n-Bu_4NClO_4	AcOH (0.25)	20	CH_3CN/H_2O	68
23	C/Pt	n-Bu_4NClO_4	AcOH (1)	20	CH_3CN/H_2O	65
24[c]	**C/Pt**	**n-Bu_4NClO_4**	**AcOH (0.5)**	**20**	**CH_3CN/H_2O**	77
25[d]	C/Pt	n-Bu_4NClO_4	AcOH (0.5)	20	CH_3CN/H_2O	70
26[e]	C/Pt	n-Bu_4NClO_4	AcOH (0.5)	20	CH_3CN/H_2O	trace
27[f]	C/Pt	n-Bu_4NClO_4	AcOH (0.5)	20	CH_3CN/H_2O	73

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), electrolyte (1 mmol), solvent/H_2O = 7:1 (8 mL); the electrolysis was conducted at a constant current for 2 h in an undivided cell. [b]Yields of the isolated products. [c]1.2 mmol of **2a** was used. [d]1.5 mmol of **2a** was used. [e]O_2 was used instead of air. [f]N_2 was used instead of air. HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol.

different substituents were readily converted to the corresponding (*E*)-vinyl sulfones with moderate to good yields. Nevertheless, both the steric effect and the electronic effect of the substituents were observed in the reaction. Generally, the *ortho* substitution on the phenyl ring of the cinnamic acids disfavored this reaction in comparison with the *meta* and *para* substitutions (**3n** vs **3j** and **3b**; **3o** vs **3k** and **3c**; **3p** vs **3m** and **3e** **3q** vs **3f**). This implied that the hindrance had a negative influence on this reaction. On the other hand, the electron-rich cinnamic acids were more reactive than electron-deficient ones (**3b**,**c** vs **3g**−**i**), while weak electron-withdrawing (F, Cl, Br, **3d**−**f**) groups had little influence on the reaction yield. To our delight, the sterically congested substrate 1-naphthalene and multisubstituted cinnamic acid could proceed smoothly in this transformation, albeit with a slightly lower yield (**3r** and **3s**). However, ferulic acid gave a trace amount of product due to the effect of hydroxyl group. Further, pyridines, furans, and thiophenes were also good substrates in the reaction, affording the corresponding desired product in 45−67% yield (**3u**−**w**). Besides, when β-methyl- and phenyl-substituted cinnamic acid derivatives were used as the starting materials, the corresponding yields of the product were 62% and 50% (**3x** and **3y**), respectively. Nevertheless, α-methyl-substituted cinnamic acid gave a trace amount of the desired product, perhaps due to the steric hindrance. 2-Cyclohexylideneacetic acid was also examined in this reaction, no desired product was detected. In order to extend the scope of unsaturated acid substrate, phenylpropiolic acid was employed as the reaction substrate to give (phenylethynylsulfonyl)-benzene **3ab** smoothly, although the reaction afforded the product with a low yield of 29%. Finally, the scope of sodium sulfinates was also investigated. The electronic effect and steric hindrance of sodium phenylsulfinates had a great influence on the reaction, although the weak electron-donating sodium 4-toluenesulfinate and electron-withdrawing sodium 4-chlorobenzenesulfinate could provide the vinyl sulfones in 81% and 40% yield (**3ac** and **3ad**), respectively. When the more electron-rich (4-MeO) and electron-deficient (4-NO_2) sodium phenylsulfinates were used as substrates, the reactions hardly proceeded and gave a trace amount of the desired product (see details in the Supporting Information). The sodium mesitylenesulfinate could not give the desired product either, perhaps due to the steric hindrance. On the other hand, aliphatic sodium sulfinates (e.g., sodium methanesulfinate and sodium trifluoromethanesulfinate) were not compatible under the reaction conditions and no desired products were detected, perhaps due to the instability of the intermediate **A**.

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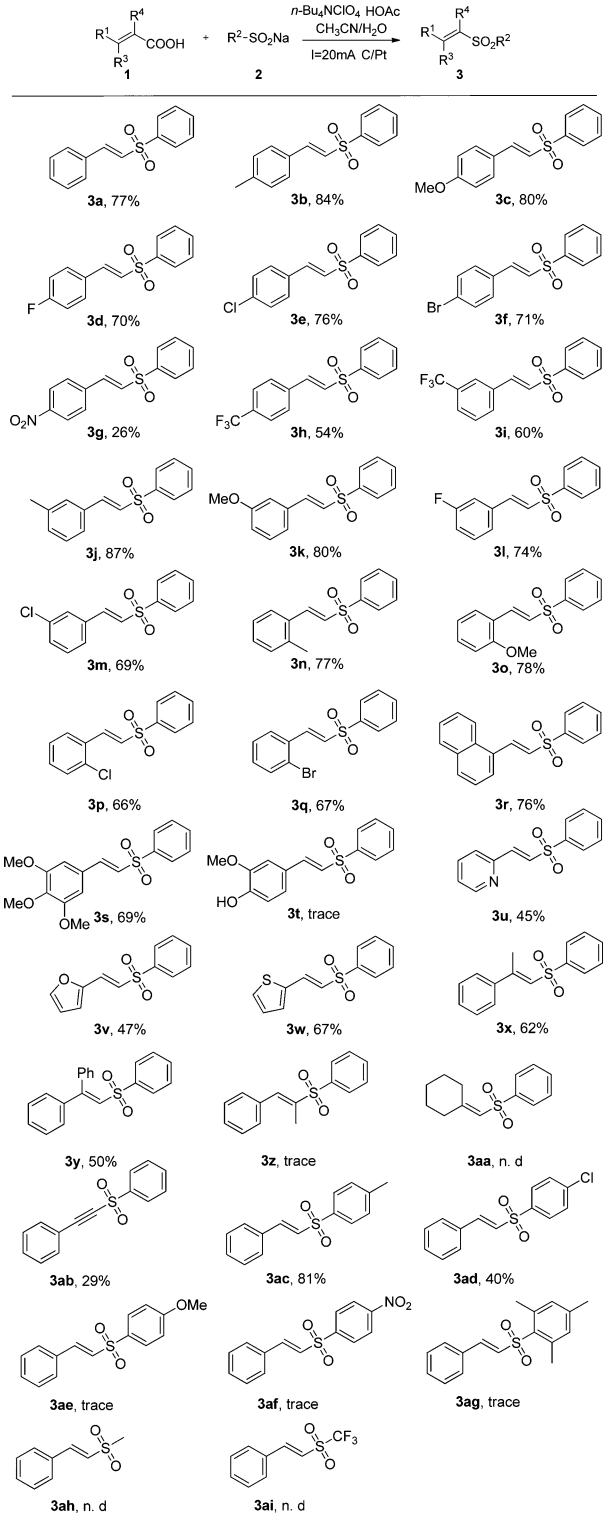
Table 2. Substrate Scope for the Decarboxylative Sulfono Functionalization[a]



[a]Reaction conditions: **1** (0.5 mmol), **2** (1.2 mmol), *n*-Bu_4NClO_4 (1.0 mmol), AcOH (0.25 mmol), CH_3CN/H_2O = 7:1 (8 mL). The electrolysis was conducted at a constant current of 20 mA about 2 h in an undivided cell at room temperature. nd: not detected.

To gain insight into the reaction mechanism, some control experiments were conducted (Scheme 1). First, the reaction was completely inhibited with the addition of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 2.4 equiv) (Scheme 1a), suggesting the reaction presumably involved a radical pathway. When styrene was employed as the coupling partner under the standard conditions, only a trace amount of vinyl sulfone was obtained, which implied styrene was not the mainly active intermediate of this reaction (Scheme 1b). Moreover, when methyl cinnamate and **2a** was carried out under the standard reaction conditions, the expected product was not detected, and almost all of the methyl cinnamate was recovered (Scheme 1c), which indicated that the carboxyl group was necessary for the reaction.

In an attempt to better understand this reaction, the EPR spin trapping and cyclic voltammetry (CV) were undertaken to monitor this progress. In the EPR experiments (Figure 1), 5,5-dimethyl-1-proline *N*-oxide (DMPO) was used to trap the potentially involved free radicals. As expected, the experimental EPR spectra (a) and the corresponding simulations (b–d) were achieved. The spectrum b was identified according to the hyperfine coupling constants for the nitrogen (A_{14N} = 16.2 G) and the β-proton (A_{1H} = 25.2 G), indicating the radical was centered at a carbon group between single and double bonds.[7] Another signal (c) was found to be the radical $^{\bullet}OH$, characterized by the hyperfine coupling constants for the nitrogen (A_{14N} = 14.7 G) and the β-proton (A_{1H} = 14.7 G).[7] When we overlapped the spectra b and c, the complicated spectrum d was formed, matching the experimental result (a). From the cyclic voltammogram (Figure 2), three oxidation waves were easily observed. One at 1.03 V was assigned to the oxidation of sodium sulfinates to sulfonyl radical, and the other, 1.73 V, was attributed to the oxidation of sulfonyl radical. Another, 2.20 V was also obtained, corresponding to the oxidation of cinnamic acid and water.[8]

In light of the mentioned experiments and preceding literature,[3f,9] a possible radical-based pathway is presented as shown in Scheme 2. A sulfonyl radical intermediate **A** is generated by the oxidation of sodium sulfinates in the anodic electrode and then is attacked by anion **B** to give rise to anion radical **C**, which is easy to be decarboxylated to afford the vinyl sulfone **3a** under the reaction conditions.

In conclusion, we developed an electrochemical decarboxylative sulfono functionalization protocol and demonstrated its utility directly from readily available starting materials at room temperature with high regioselectivity and good functional group tolerance, utilizing electrons as oxidant. Based on the EPR and CV experiments, a radical-based pathway was proposed.

EXPERIMENTAL SECTION

General Information. All products were characterized by ^1H NMR and ^{13}C NMR, using TMS as an internal reference (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz). HRMS (ESI) data were recorded on a Q-TOF Premier. Commercial reagent and compound were used without purification unless otherwise indicated. Various sodium sulfinates (sodium 4-methoxybenzenesulfinate, sodium 4-nitrobenzenesulfinate, and sodium mesitylenesulfinate),[3f] β-methyl-,[10,11] β-phenyl-,[10,11] and α-methyl-substituted[11,12] cinnamic acid derivatives as well as 2-cyclohexylideneacetic acid[10,11] were prepared according to literature procedures.

Representative Procedures for the Synthesis of (*E*)-Vinyl Sulfones. A mixture of cinnamic acid derivatives (0.5 mmol), sodium sulfinates (1.2 mmol), *n*-Bu_4NClO_4 (1 mmol), AcOH (0.25 mmol), and CH_3CN/H_2O (7/1 mL) was added to an undivided cell. The cell was equipped with carbon rod (d = 6 mm) as the anode with a platinum plate (1.5 × 1.5 cm^2) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA under room temperature for 2 h. When the reaction was finished, the solvent

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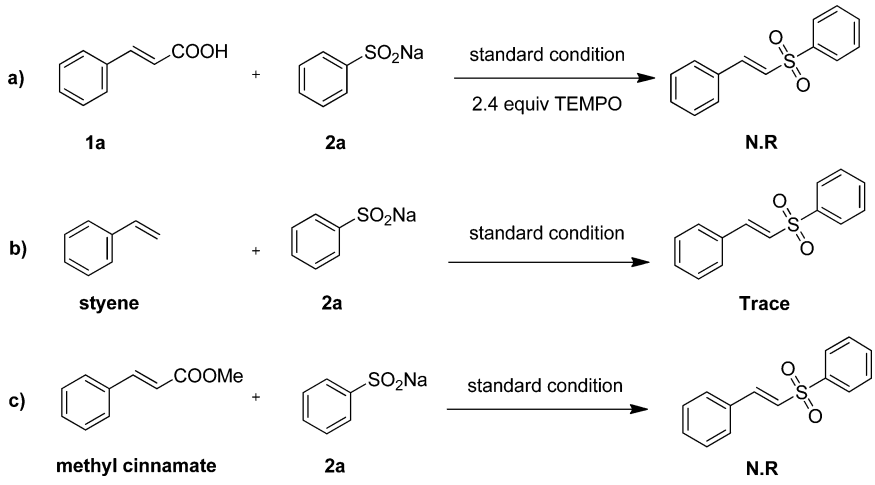
Scheme 1. Control Experiments for the Reaction



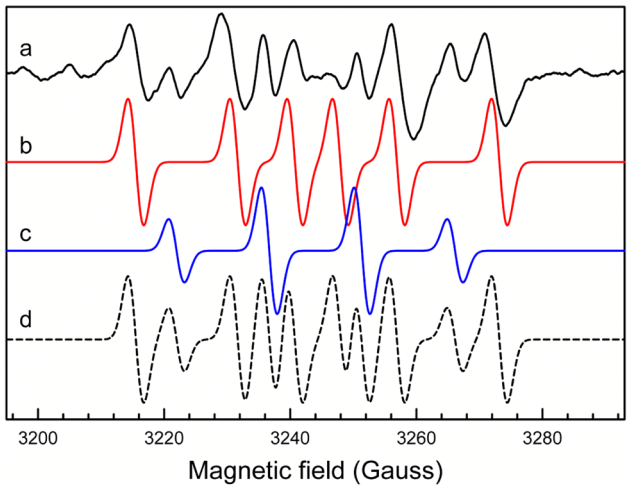


Figure 1. EPR spectra (X band, 9.7 GHz, room temperature) for reaction mixtures in the presence of the radical trapper DMPO. The complicated spectrum (a) is the experimental spectrum, and the others (b–d) were their simulations. Spectra b and c were assigned to a carbon group radical between single and double bonds and the radical •OH, respectively, while the complicated spectrum (d) was the overlapping of spectra b and c.

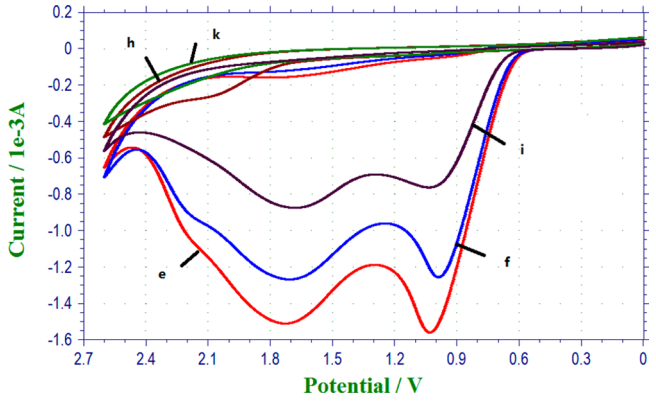
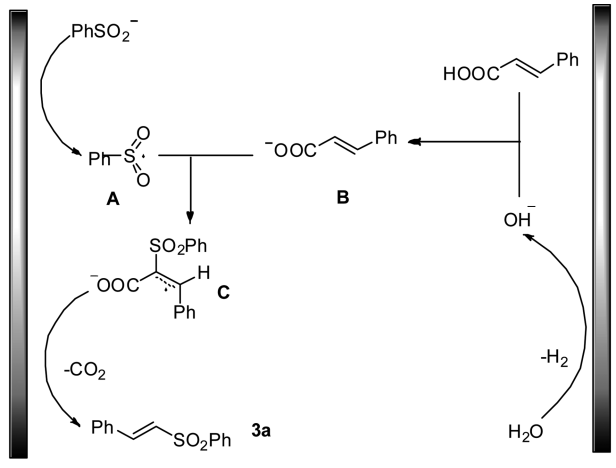


Figure 2. Cyclic voltammogram curves of **1a**, **2a** and AcOH in the solution of 0.125 M *n*-Bu_4NClO_4/CH_3CN/H_2O = 7:1 (8 mL), using GC disk as working electrode, Pt wire, and Ag/AgCl as counter and reference electrode at 50 mV/s scan rate: (e) **1a** (0.0625 M), **2a** (0.15 M) and AcOH (0.03125 M); (f) **1a** (0.0625 M) and **2a** (0.15 M); (h) **1a** (0.0625 M); (i) **2a** (0.15 M); (k) 0.125 M *n*-Bu_4NClO_4/CH_3CN/H_2O.

Scheme 2. Proposed Reaction Mechanism



was removed with a rotary evaporator. The solution was then added to 9 mL of water and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried with Na_2SO_4 and filtered. The solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica, and the product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

Experimental Details for the Capture of Radical. An undivided cell was equipped with a magnet stirrer, carbon rod (d = 6 mm) as the anode, and a platinum plate (1.5 × 1.5 cm^2) as the cathode, respectively. In the electrolytic cell, a solution of cinnamic acid (0.5 mmol), sodium sulfinates (1.2 mmol), *n*-Bu_4NClO_4 (1 mmol), AcOH (0.25 mmol), N_2 (balloon), and CH_3CN/H_2O (7/1 mL) was allowed to stir and electrolyze at a constant current of 20 mA for 40 min at 0 °C. A 0.05 mL portion of solution was added to a small tube and mixed well with 0.03 mL of DMPO. The mixture was quick-frozen with liquid nitrogen and measured at room temperature by EPR.

*(E)-[2-(Phenylsulfonyl)vinyl]benzene (**3a**).*[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 77% yield (94.1 mg); mp = 62–63 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.97–7.94 (m, 2H), 7.69 (d, J = 15.4 Hz, 1H), 7.64–7.60 (m, 1H), 7.57–7.53 (m, 2H), 7.50–7.48 (m, 2H), 7.42–7.37 (m, 3H), 6.86 (d, J = 15.4 Hz, 1H); ^{13}C NMR

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($CDCl_3$, 100 MHz) δ 142.5, 140.8, 133.4, 132.4, 131.2, 129.3, 129.1, 128.6, 127.7, 127.3; IR (KBr) 3044, 2918, 1611, 1574, 1446, 1298, 1142, 1084 cm^{-1}; HRMS calcd $[C_{14}H_{12}O_2S + Na]^+$ 267.0456, found 267.0458.

(E)-1-Methyl-4-[2-(phenylsulfonyl)vinyl]benzene (**3b**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as colorless solid: 84% yield (108.0 mg); mp = 118−120 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96−7.93 (m, 2H), 7.66 (d, J = 15.4 Hz, 1H), 7.61−7.59 (m, 1H), 7.56−7.52 (m, 2H), 7.38 (d, J = 8.08 Hz, 2H), 7.19 (d, J = 8.04 Hz, 2H), 6.81 (d, J = 15.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.6, 141.9, 140.9, 133.3, 129.8, 129.6, 129.3, 128.6, 127.6, 126.0. 21.5; IR (KBr) 3053, 2918, 1604, 1510, 1446, 1306, 1143, 1082 cm^{-1}; HRMS calcd $[C_{15}H_{14}O_2S+ Na]^+$ 281.0612, found 281.0610.

(E)-1-Methoxy-4-[2-(phenylsulfonyl)vinyl]benzene (**3c**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 80% yield (109.9 mg); mp = 100−101 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96−7.93 (m, 2H), 7.64 (d, J = 15.4 Hz, 1H), 7.61−7.59 (m, 1H), 7.56−7.52 (m, 2H), 7.45−7.42 (m, 2H), 6.91−6.89 (m, 2H), 6.72 (d, J = 15.4 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.1, 142.3, 141.1, 133.2, 130.4, 129.3, 127.5, 125.0, 124.4, 114.5, 55.5; IR (KBr) 3061, 2939, 2846, 1601, 1509, 1444, 1260, 1138, 1081 cm^{-1}; HRMS calcd $[C_{15}H_{14}O_3S + Na]^+$ 297.0561, found 297.0559.

(E)-1-Fluoro-4-[2-(phenylsulfonyl)vinyl]benzene (**3d**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography to give the product (petroleum ether/ethyl acetate = 10:1) as a colorless solid: 70% yield (92.2 mg); mp = 92−93 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.97−7.94 (m, 2H), 7.68−7.62 (m, 2H), 7.58−7.54 (m, 2H), 7.51−7.47 (m, 2H), 7.11−7.06 (m, 2H), 6.80 (d, J = 15.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.4 (d, J = 251.5 Hz), 141.2, 140.6, 133.5, 130.6 (d, J = 8.7 Hz), 129.4, 128.6 (d, J = 3.4 Hz), 127.6, 127.0 (d, J = 2.2 Hz), 116.4 (d, J = 22.0 Hz); IR (KBr) 3048, 1613, 1599, 1509, 1446, 1302, 1280, 1230, 1141, 1082 cm^{-1}; HRMS calcd $[C_{14}H_{11}FO_2S + Na]^+$ 285.0361, found 285.0361.

(E)-1-Chloro-4-[2-(phenylsulfonyl)vinyl]benzene (**3e**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a white solid: 76% yield (105.0 mg); mp = 128−130 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96−7.94 (m, 2H), 7.66−7.62 (m, 2H), 7.62−7.60 (m, 1H), 7.58−7.56 (m, 2H), 7.54−7.52 (m, 2H), 6.85 (d, J = 15.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.0, 140.4, 137.2, 133.5, 130.8, 129.7, 129.4, 129.4, 127.9, 127.7; IR (KBr) 3054, 1741, 1614, 1445, 1307, 1146, 1083 cm^{-1}; HRMS calcd $[C_{14}H_{11}ClO_2S + Na]^+$ 301.0066, found 301.0063.

(E)-1-Bromo-4-[2-(phenylsulfonyl)vinyl]benzene (**3f**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 71% yield (115.0 mg); mp 138−139 °C ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96−7.94 (m, 2H), 7.66−7.63 (m, 1H), 7.62−7.60 (m, 1H), 7.58−7.56 (m, 2H), 7.54−7.51 (m, 2H), 7.36−7.34 (m, 2H), 6.86 (d, J = 15.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.1, 140.4, 133.6, 132.4, 131.3, 129.9 129.4, 128.0, 127.7, 125.7; IR (KBr) 3054, 1610, 1582, 1481, 1446, 1397, 1305, 1141, 1067 cm^{-1}; HRMS calcd $[C_{14}H_{11}BrO_2S + Na]^+$ 344.9561, found 344.9562.

(E)-1-Nitro-4-(2-(phenylsulfonyl)vinyl)benzene (**3g**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 8:1) to give the product as a yellow solid: 26% yield (37.6 mg); mp = 152−153 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.27−8.24 (m, 2H), 7.98−7.96 (m, 2H), 7.73 (d, J = 15.4 Hz, 1H), 7.69−7.64 (m, 3H), 7.61−7.57 (m, 2H), 7.01 (d, J = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.0, 139.8, 139.2, 138.4, 133.9, 131.7, 129.6, 129.2, 127.9, 124.3; IR (KBr) 3055, 1592, 1509, 1446, 1337, 1307, 1148, 1085 cm^{-1}; HRMS calcd $[C_{14}H_{11}NO_4S + Na]^+$ 312.0306, found 312.0304.

(E)-1-(Trifluoromethyl)-4-(2-(phenylsulfonyl)vinyl)benzene (**3h**).[3k] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a yellow oil: 54% yield (85.0 mg); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.98−7.95 (m, 2H), 7.71 (d, J = 15.4 Hz, 1H), 7.67−7.63 (m, 3H), 7.61−7.56 (m, 4H), 6.96 (d, J = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.4, 140.1, 135.7, 133.7, 132.6(d, J = 32.5 Hz), 130.0, 129.5, 128.8, 127.8, 126.1 (q, J = 3.7 Hz), 123.6 (d, J = 270.9 Hz); IR (KBr) 3064, 2925, 1613, 1383, 1325, 1169, 1120, 1067, 845, 750 cm^{-1}; HRMS calcd $[C_{15}H_{11}F_3O_2S + Na]^+$ 335.0330, found 335.0325.

(E)-1-(Trifluoromethyl)-3-(2-(phenylsulfonyl)vinyl)benzene (**3i**).[3l] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 60% yield (93.0 mg); mp = 83−85 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.98−7.95 (m, 2H), 7.73 (s, 1H), 7.69−7.63 (m, 4H), 7.59−7.52 (m, 3H), 6.95 (d, J = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.5, 140.2, 133.7, 133.2, 131.9, 131.7, 131.5, 129.7, 129.5, 127.8, 127.6 (q, J = 3.7 Hz), 125.0 (q, J = 3.7 Hz), 122.2; IR (KBr) 3071, 2924, 1621, 1446, 1431, 1325, 1301, 1139, 1068 cm^{-1}; HRMS calcd $[C_{15}H_{11}F_3O_2S + Na]^+$ 335.0330, found 335.0331.

(E)-1-Methyl-3-[2-(phenylsulfonyl)vinyl]benzene (**3j**).[3f] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a pale yellow solid: 87% yield (112.1 mg); mp = 105−106 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96−7.94 (m, 2H), 7.66(d, J = 15.4 Hz, 1 H), 7.62−7.59 (m, 1H), 7.56−7.53 (m, 2H), 7.29−7.26(m, 3H), 7.23−7.21 (m, 1H), 6.85(d, J = 15.4 Hz, 1H), 2.35(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.7, 140.8, 138.9, 133.3, 132.3, 132.1, 129.3, 129.1, 129.0, 127.6. 127.0, 125.8, 21.3; IR (KBr) 3048, 2923, 1614, 1445, 1384, 1260, 1143, 1084, 747, 621 cm^{-1}; HRMS calcd $[C_{15}H_{14}O_2S + Na]^+$ 281.0612, found 281.0613.

(E)-1-Methoxy-3-[2-(phenylsulfonyl)vinyl]benzene (**3k**).[3j] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 80% yield (110.0 mg); mp = 101−102 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 7.2 Hz, 1H), 7.67−7.61 (m, 2H), 7.55 (t, J = 7.9 Hz, 2H), 7.30 (t, J = 7.9 Hz, 2H), 7.08 (d, J = 7.6 Hz, 1H), 6.99−6.95 (m, 2H), 6.85 (d, J = 15.4 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.0, 142.5, 140.7, 133.7, 133.4, 130.1, 129.4, 127.7, 127.5, 121.2, 117.1, 113.4, 55.4; IR (KBr) 3075, 3046, 3005, 2838, 1598, 1584, 1446, 1300, 1270, 1144, 1083 cm^{-1}; HRMS calcd $[C_{15}H_{14}O_3S + Na]^+$ 297.0561, found 297.0558.

(E)-1-Fluoro-3-[2-(phenylsulfonyl)vinyl]benzene (**3l**). The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless oil: 74% yield (96.9 mg); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.97−7.94 (m, 2H), 7.67−7.62 (m, 2H), 7.59−7.54 (m, 2 H), 7.40−7.35 (m, 1H), 7.28−7.26 (m, 1H), 7.19−7.16 (m, 1H), 7.14−7.09 (m, 1H), 6.87 (d, J = 15.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.9 (d, J = 246.5 Hz), 141.0 (d, J = 2.5 Hz), 140.3, 134.5 (d, J = 7.7 Hz), 133.6, 130.7 (d, J = 8.3 Hz), 129.4, 128.8, 127.8, 124.6 (d, J = 2.9 Hz), 118.1 (d, J = 21.4 Hz), 114.8 (d, J = 22.0 Hz); IR (KBr) 3061, 1614, 1581, 1555, 1485, 1446, 1304, 1262, 1230, 1145, 1084 cm^{-1}. HRMS calcd $[C_{14}H_{11}FO_2S + Na]^+$ 285.0361, found 285.0359.

(E)-1-Chloro-3-[2-(phenylsulfonyl)vinyl]benzene (**3m**). The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 69% yield (95.8 mg); mp = 103−105 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.97−7.94 (m, 2H), 7.66−7.54 (m, 4H), 7.47 (d, J = 1.7 Hz, 1H), 7.40−7.31 (m, 3H), 6.88 (d, J = 15.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.7, 140.3, 135.1, 134.1, 133.6, 131.1, 130.3, 129.4, 128.9, 128.2, 127.8, 126.8; IR (KBr) 3059, 1617, 1565, 1446, 1322, 1305, 1147, 1086 cm^{-1}; HRMS calcd $[C_{14}H_{11}ClO_2S + Na]^+$ 301.0066, found 301.0063.

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(E)-1-Methyl-2-[2-(phenylsulfonyl)vinyl]benzene (**3n**).[3m] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a white solid: 77% yield (100.2 mg); mp = 112−115 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99−7.94 (m, 3H), 7.65−7.60 (m, 1H), 7.57−7.53 (m, 2H), 7.44 (d, J = 7.8 Hz, 1H), 7.32−7.28 (m, 1H), 7.23−7.17 (m, 2H), 6.79 (d, J = 15.3 Hz, 1H), 2.46(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.8, 140.2, 138.2, 133.4, 131.3, 131.1, 130.9, 129.3, 128.2, 127.7. 126.9, 126.5, 19.8; IR (KBr) 3057, 1612, 1598, 1481, 1446, 1306, 1144, 1085 cm^{-1}; HRMS calcd $[C_{15}H_{14}O_2S + Na]^+$ 281.0612, found 281.0610.

(E)-1-Methoxy-2-[2-(phenylsulfonyl)vinyl]benzene (**3o**).[3f] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a pale yellow solid: 78% yield (107.0 mg); mp = 97−98 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97−7.94 (m, 2H), 7.90 (d, J = 15.5 Hz, 1H), 7.62−7.58 (m, 1H), 7.55−7.51 (m, 2H), 7.43−7.36 (m, 2H), 7.08 (d, J = 15.5 Hz, 1H), 6.98−6.91 (m, 2H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 141.2, 138.6, 133.1, 132.5, 130.8, 129.2, 127.9, 127.6, 121.2, 120.8, 111.3, 55.5; IR (KBr) 3052, 2920, 1648, 1465, 1385, 1277, 1142, 1023, 766, 638 cm^{-1}; HRMS calcd $[C_{15}H_{14}O_3S + Na]^+$ 297.0561, found 297.0558.

(E)-1-Chloro-2-[2-(phenylsulfonyl)vinyl]benzene (**3p**).[3f] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a pale yellow solid: 66% yield (91.9 mg); mp = 75−76 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, J = 15.4 Hz, 1H), 7.99−7.96 (m, 2H), 7.66−7.62 (m, 1H), 7.58−7.54 (m, 2H), 7.51 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.43 (dd, J_1 = 8 Hz, J_2 = 1.3 Hz, 1H), 7.36−7.31 (m, 1H), 7.28−7.24 (m, 1H), 6.91 (d, J = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.3, 138.4, 135.3, 133.6, 131.9, 130.7, 130.4, 130.1, 129.4, 128.3, 127.8, 127.2; IR (KBr) 3054, 2925, 1610, 1449, 1319, 1277, 1146, 1040, 820, 766 cm^{-1}; HRMS calcd $[C_{14}H_{11}ClO\ _2S + Na]^+$ 301.0066, found 301.0063.

(E)-1-Bromo-2-[2-(phenylsulfonyl)vinyl]benzene (**3q**). The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 67% yield (108.0 mg); mp = 97−99 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (d, J = 15.4 Hz, 1H), 7.99−7.96 (m, 2H), 7.67−7.61 (m, 2H), 7.59−7.55 (m, 2H), 7.49 (dd, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H), 7.33−7.29 (m, 1H), 7.27−7.23 (m, 1H), 6.85 (d, J = 15.4 Hz, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 141.0, 140.3, 133.6, 133.6, 132.5, 132.1, 130.2, 129.4, 128.3, 127.9, 125.6; IR (KBr) 3054, 2920, 2850, 1603, 1464, 1305, 1146, 1085 cm^{-1}; HRMS calcd $[C_{14}H_{11}BrO_2S + Na]^+$ 344.9561, found 344.9558.

(E)-1-(2-(Phenylsulfonyl)vinyl)naphthalene (**3r**). The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a white solid: 76% yield (112.0 mg); mp = 99−101 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.53 (d, J = 15.2 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1 H), 8.03−8.00 (m, 2H), 7.92−7.86 (m, 2H), 7.67−7.53 (m, 6H), 7.45 (t, J = 7.72 Hz, 1H), 6.97 (d, J = 15.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.6, 139.5, 133.7, 133.5, 131.5, 131.3, 129.6, 129.5, 129.4, 128.9, 127.8, 127.4, 126.5, 125.7, 125.3, 123.0; IR (KBr) 3055, 2922, 1604, 1510, 1445, 1304, 1144, 1084 cm^{-1}; HRMS calcd $[C_{18}H_{14}O_2S + Na]^+$ 317.0612, found 317.0609.

(E)-1,2,3-Trimethoxy-5-(2-(phenylsulfonyl)vinyl)benzene (**3s**).[3i] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 69% yield (115.2 mg); mp = 143−144 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97−7.95 (m, 2H), 7.65−7.54 (m, 4H), 6.79 (d, J = 15.3 Hz, 1H), 6.72 (s, 2H), 3.873 (s, 3H), 3.869 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.5, 142.6, 140.8, 133.4, 129.4, 127.7, 127.6, 126.3, 105.8, 61.0, 56.2; IR (KBr) 3048, 2942, 2841, 1579, 1506, 1421, 1280, 1254, 1127, 1081 cm^{-1}; HRMS calcd $[C_{17}H_{18}O_5S + Na]^+$ 357.0773, found 357.0769.

(E)-2-(2-(Phenylsulfonyl)vinyl)pyridine (**3u**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 45% yield (55.0 mg); mp = 85−86 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.61 (d, J = 4.6 Hz, 1H), 7.98−7.96 (m, 2H), 7.76−7.72 (m, 1H), 7.68−7.60 (m, 2H), 7.57−7.53 (m, 2H), 7.48−7.41 (m, 2H), 7.31−7.27 (m, 1H), 6.85 (d, J = 15.4 Hz, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 151.0, 150.3, 140.5, 140.2, 137.1, 133.6, 131.8, 129.4, 127.8, 125.5, 125.0; IR (KBr) 3056, 1579, 1443, 1428, 1309, 1299, 1142, 1082 cm^{-1}; HRMS calcd $[C_{13}H_{11}NO_2S + Na]^+$ 268.0408, found 268.0410.

(E)-2-(2-(Phenylsulfonyl)vinyl)furan (**3v**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a brown viscous oil: 47% yield (55.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95−7.92 (m, 2H), 7.63−7.59 (m, 1H), 7.56−7.52 (m, 2H), 7.48−7.43 (m, 2H), 6.75 (d, J = 15.0 Hz, 1H), 6.71 (d, J = 3.4 Hz, 1H), 6.49−6.48 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 148.7, 145.7, 140.9, 133.3, 129.3, 128.9, 127.6, 124.7, 117.0, 112.6; IR (KBr) 3058, 1781, 1722, 1621, 1446, 1304, 1138, 1082 cm^{-1}. HRMS calcd $[C_{12}H_{10}O_3S + Na]^+$ 257.0248, found 257.0244.

(E)-2-(2-(Phenylsulfonyl)vinyl)thiophene (**3w**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a brown solid: 67% yield (83.9 mg); mp = 79−80 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95−7.93 (m, 2H), 7.80 (d, J = 15.1 Hz, 1H), 7.64−7.60 (m, 1H), 7.57−7.53 (m, 2H), 7.44 (d, J = 5.0 Hz, 1H), 7.32 (d, J = 3.4 Hz, 1H), 7.08−7.06 (m, 2H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 140.8, 137.0, 135.2, 133.4, 132.5, 130.1, 129.4, 128.4, 127.6, 125.4; IR (KBr) 3119, 3038, 2919, 1599, 1443, 1418, 1306, 1279, 1141, 1081 cm^{-1}; HRMS calcd $[C_{12}H_{10}O_2S_2 + Na]^+$ 273.0020, found 273.0018.

(E)-((2-Phenylprop-1-en-1-yl)sulfonyl)benzene(**3x**).[3i] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 15:1) to give the product as a colorless oil: 60% yield (79.8 mg); ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.01−7.98 (m, 2H), 7.66−7.61 (m, 1H), 7.59−7.55 (m, 2H), 7.52−7.35 (m, 5H), 6.62 (d, J = 1.2 Hz, 1H), 2.54 (d, J = 1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.5, 141.1, 139.1, 132.2, 128.9, 128.2, 127.7, 126.4, 126.2, 125.3, 16.2.

(2-(Phenylsulfonyl)ethene-1,1-diyl)dibenzene (**3y**).[13] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 15:1) to give the product as a colorless oil: 50% yield (80.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52−7.50 (m, 2H), 7.43−7.39 (m, 1H), 7.30−7.25 (m, 5H), 7.21−7.19 (m, 3H), 7.15−7.13 (m, 2H), 7.01−6.99 (m, 2H), 6.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.2, 141.5, 139.1, 135.5, 132.8, 130.3, 129.8, 128.9, 128.8, 128.7, 128.6, 128.2, 127.9, 127.6.

(Phenylethynylsulfonyl)benzene (**3ab**). The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless oil: 29% yield (35.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10−8.08 (m, 2H), 7.72−7.68 (m, 1H), 7.63−7.59 (m, 2H), 7.54−7.46 (m, 3H), 7.39−7.36(m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.8, 134.2, 132.8, 131.6, 129.4, 128.7, 127.4, 117.9, 93.5, 85.3; IR (KBr) 2922, 2852, 2100, 1743, 1446, 1330, 1161, 1036, 850 cm^{-1}; HRMS calcd $[C_{14}H_{10}O_2S + Na]^+$ 265.0299, found 265.0298.

(E)-1-Methyl-4-(styrylsulfonyl)benzene (**3ac**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 81% yield (103.9 mg); mp = 117−118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83(d, J = 8.2 Hz, 2H), 7.66 (d, J = 15.4 Hz, 1 H), 7.49−7.46 (m, 2H), 7.41−7.35 (m, 3H), 7.34(d, J = 8.3 Hz, 2H), 6.85(d, J = 15.4 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.4, 141.9, 137.8, 132.5, 131.1, 130.0, 129.1, 128.5, 127.7, 127.6. 21.6; IR (KBr) 3045, 2921, 2851, 1613, 1595, 1449, 1302, 1140, 1084 cm^{-1}; HRMS calcd $[C_{15}H_{14}O_2S + Na]^+$ 281.0612, found 281.0611.

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(E)-1-Chloro-4-(styrylsulfonyl)benzene (**3ad**).[3g] The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product as a colorless solid: 40% yield (55.0 mg); mp = 78−80 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90−7.87 (m, 2H), 7.69 (d, J = 15.4 Hz, 1H), 7.54−7.48 (m, 4H), 7.44−7.38 (m, 3H), 6.84 (d, J = 15.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.1, 140.1, 139.2, 132.2, 131.4, 129.7, 129.2, 128.6, 126.8; IR (KBr) 3061, 3039, 1610, 1575, 1473, 1449, 1394, 1309, 1278, 1142, 1083 cm^{-1}; HRMS calcd $[C_{14}H_{11}ClO_2S + Na]^+$ 301.0066, found 301.0064.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00661.

^{1}H NMR and ^{13}C NMR spectra for all products (PDF)

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Notes

The authors declare no competing financial interest.

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