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PhI(OAc)$_2$ mediated decarboxylative sulfonylation of β-aryl-α,β-unsaturated carboxylic acids: a synthesis of (*E*)-vinyl sulfones†

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A highly efficient metal-free decarboxylative sulfonylation protocol for the preparation of (*E*)-vinyl sulfones from of β-aryl-α,β-unsaturated carboxylic acids using sodium sulfinates and (diacetoxyiodo)-benzene (PhI(OAc)$_2$) was developed. This strategy offers a simple and expedient synthesis of (*E*)-vinyl sulfones bearing a wide variety of functional groups. A radical-based pathway has been proposed for this decarboxylative sulfonylation reaction.

Introduction

Decarboxylation accompanied by a simultaneous functionalization reaction has emerged as a synthetically important transformation in current organic synthesis, leading to carbon–carbon and carbon–heteroatom bond formation. Aromatic, α,β-unsaturated, alkynyl as well as aliphatic carboxylic acids can be used as substrates to yield numerous more highly functionalized compounds.[1]

Vinyl sulfones are particularly valuable units in organic synthesis due to chemical versatility of the sulfonyl moiety which can be further manipulated into other useful functional groups. A vast number of synthetic routes are available toward the synthesis of vinyl sulfones.[2] Very recently, a few approaches were described for converting α,β-unsaturated carboxylic acids to vinyl sulfones and 2-sulfonylbenzofuran employing metal-catalyzed reactions.[3] Although the reported methods employing transition metal reagents are highly efficient, they require complex reaction conditions and long reaction times to facilitate product formation.

Hypervalent iodine reagents are widely employed in a variety of chemical transformations and their chemistry has become an area of growing interest due to their benign properties, selectivity and ease of handling. (Diacetoxyiodo)benzene (PhI(OAc)$_2$, DIB), a commercially available iodine(III) reagent, has received much interest and its synthetic utility as an efficient oxidative functionalization reagent has been demonstrated by several groups.[4] Our research group has long been interested in the functionalization of alkenes and alkynes promoted by hypervalent iodine compounds including iodoxybenzoic acid (IBX) and DIB.[5] In this context, we report herein our research results on the decarboxylative sulfonylation of unsaturated carboxylic acids mediated by (diacetoxyiodo) benzene (DIB). Our method offers several advantages, including being transition-metal-free, employing environmentally benign and stable reagents, and involving simple handling under air-stable conditions.

Results and discussion

We began our study employing (*E*)-cinnamic acid (**1a**) and sodium benzenesulfinate (**2a**) as benchmark substrates to screen for optimum reaction conditions. A variety of reaction parameters including reagent stoichiometry, additive and solvent were screened and the results are summarized in Table 1. When (*E*)-cinnamic acid (**1a**, 1 equiv.) was treated with sodium benzenesulfinate (**2a**, 1 equiv.) in the presence of DIB (1 equiv.) under air in *N*,*N*-dimethylformamide (DMF) as solvent at 100 °C for 1 h, (*E*)-(2-(phenylsulfonyl)vinyl)benzene (**3a**) was isolated in 17% yield (Table 1, entry 1). In order to improve the reaction yield, an excess quantity of DIB (2 equiv.) was employed (Table 1, entry 2). Unfortunately, no appreciable improvement was obtained. Increasing the stoichiometry of **2a** from 1 equivalent to 2–4 equivalents dramatically improved the yields of **3a** from 20% yield to 70% yield (Table 1, entries 3–5).

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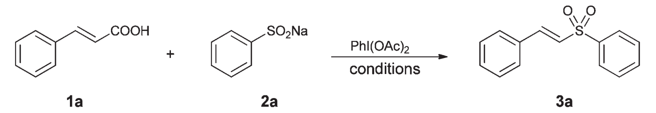
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ob00417a

Table 1 Optimization of the reaction conditions[a]



1a 2a 3a

Entry	2a (equiv.)	PhI(OAc)$_2$ (equiv.)	Solvent	Time (h)	Yield[b] (%)
1	1	1	DMF	1	17
2	1	2	DMF	1	20
3	2	2	DMF	1	37
4	3	2	DMF	1	60
5	4	2	DMF	1	70
6	4	1	DMF	1	45
7	4	3	DMF	1	72
8[c]	4	2	DMF	1	64
9[d]	4	2	DMF	1	58
10	**4**	**2**	**DMF**	**10 min**	**73**
11	4	2	DMSO	10 min	52
12	4	2	DMA	10 min	66
13[e]	4	2	DMF	1	60
14[f]	4	2	DMF	1	18
15[g]	4	2	DMF	1	69
16[h]	4	2	DMF	10 min	59

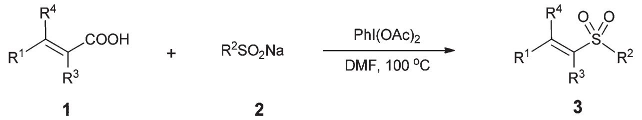
[a] Reaction conditions: **1a** (0.25 mmol) in solvent (3 mL), 100 °C, open air. [b] Isolated yield after column chromatography (SiO$_2$). [c] Reaction was carried out at room temperature. [d] Reaction was carried out at refluxing temperature. [e] Reaction was carried out employing KI (1 equiv.) as an additive. [f] Reaction was carried out employing I$_2$ (1 equiv.) as an additive. [g] Reaction was carried out employing K$_2$CO$_3$ (1 equiv.) as an additive. [h] Reaction was carried out under Ar.

While lowering the amount of DIB from 2 equivalents to 1 equivalent drastically reduced the yield of **3a** from 70% yield to 45% yield, increasing the amount of DIB from 2 equivalents to 3 equivalents did not show significantly higher yield (Table 1, entries 6–7). Lowering or elevating reaction temperature resulted in slightly lower yields (Table 1, entries 8–9). Much to our delight, it is pleasing to find that the reaction was exceptionally rapid and **3a** was isolated in 73% yield when the reaction was carried out within 10 minutes (Table 1, entry 10). A few solvents were screened including dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylacetamide (DMA) and DMF exhibited the optimal results (Table 1, entries 11–12). The presence of additives, including KI, I$_2$ and K$_2$CO$_3$ did not help enhancing the product yield (Table 1, entries 13–15).[5a,7,3b] Finally, the reaction performed under inert atmosphere (argon) gave poorer results (Table 1, entry 16). Based on the experimental results shown in Table 1, the optimized reaction conditions were chosen as follows: substrate (1 equiv.), sodium sulfinate (4 equiv.), DIB (2 equiv.) in DMF at 100 °C (Table 1, entry 10).

With the optimized reaction conditions in hand, the substrate scope and limitation of the method were evaluated and the results are summarized in Table 2. First the reactions of sodium benzenesulfinate (**2a**) with cinnamic acid derivatives were investigated. Those bearing electron-withdrawing substituents on the phenyl ring (4-F, 3-Cl, 2-Br, 4-Br, 4-NO$_2$, and 3-CF$_3$) afforded the corresponding products **3b–g** in 43–72% yields (Table 2, entries 2–7). Comparable results were observed with cinnamic acid derivatives containing electron-donating substituents on the phenyl ring (4-N(CH$_3$)$_2$, 4-CH$_3$, 2-OH, 3-OH, 4-OH, 3-OCH$_3$, 4-OCH$_3$, 2,3-(OCH$_3$)$_2$, 2,5-(OCH$_3$)$_2$, 3,4-OCH$_2$O, 2,4,5-(OCH$_3$)$_3$, and 3,4,5-(OCH$_3$)$_3$) yielding the respective products **3h–s** in 46–68% yields (Table 2, entries 8–19). (*E*)-3-(4-(Allyloxy)phenyl)acrylic acid reacted solely at the unsaturated carboxylic acid moiety to yield **3t** in 45% yield (Table 2, entry 20). Even though longer reaction times (15–30 minutes) were required for some substrates, it is evident that the method was compatible with a variety of electronically different substituents and with different steric environments on the phenyl ring of the cinnamic acid derivatives. The reactions of **2a** with (*E*)-3-(naphthalene-2-yl)acrylic acid and (2*E*,4*E*)-5-phenylpenta-2,4-dienoic acid were examined and gave the corresponding products **3u** and **3v** in 67% and 50% yields, respectively (Table 2, entries 21–22). It is also worth emphasizing that in all cases the vinyl sulfones **3a–v** were obtained as the *E* configuration. While (*E*)-3-phenylbut-2-enoic acid readily reacted with **2a** to yield the corresponding (*E*)-vinyl sulfone **3w** (44% yield) along with allyl sulfone **4w** (5% yield) as a minor product (Table 2, entry 23), (*E*)-2-methyl-3-phenylacrylic acid was found incompatible even with a prolonged reaction time (1 h). The reaction was also suitable for heteroaromatic-substituted acrylic acids; the reactions of (*E*)-3-(pyridin-3-yl)acrylic acid, (*E*)-3-(pyridin-2-yl)acrylic acid, (*E*)-3-(furan-2-yl)acrylic acid, (*E*)-3-(thiophen-2-yl)acrylic acid, and (*E*)-3-(2-pyrrolyl)acrylic acid provided the corresponding products in low to moderate yields (38–66% yields) (Table 2, entries 24–28). Next the reactions of cinnamic acid (**1a**) with a collection of sodium sulfinates were examined (Table 2, entries 29–32). Sodium benzenesulfinates bearing electronically different substituents on the *para* position (4-CH$_3$, 4-Cl, and 4-OCH$_3$) gave comparable results to those of the parent sodium benzenesulfinate (Table 2, entry 1 *vs.* entries 29–31). Although affording **3ad** in low yield (24% yield), the reaction with sodium methanesulfinate was found to be feasible under the reaction conditions (Table 2, entry 32). Unfortunately, the present protocol is not applicable to β-alkyl-α,β-unsaturated carboxylic acid; (*E*)-2-butenoic acid failed to give any desired vinyl sulfone product.

To help to better understand the reaction pathway, some control experiments were explored. The reaction of (*E*)-cinnamic acid (**1a**) with sodium benzenesulfinate (**2a**) was carried out under the standard reaction conditions in the presence of radical inhibitors, including 2,6-di-*tert*-butyl-4-methylphenol (BHT), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), and hydroquinone (Scheme 1a). BHT was found to suppress the reaction while TEMPO and hydroquinone totally stopped the reaction. The observed results implied that the reaction probably proceeded *via* a radical pathway. Next, when styrene was employed as a substrate in place of (*E*)-cinnamic acid (**1a**), only a trace amount of **3a** was observed (TLC analysis). These results suggested that styrene is not an intermediate in the present transformation (Scheme 1b). The product **3a** was not observed when ethyl cinnamate was employed as a substrate and almost all of the ethyl cinnamate was recovered (93%

Table 2 Decarboxylative sulfonylation of β-aryl-α,β-unsaturated carboxylic acids mediated by PhI(OAc)_2 [a]



1 2 3

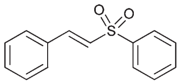
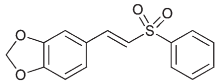
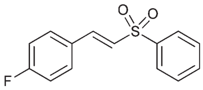
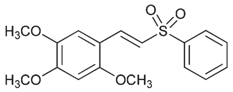
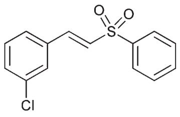
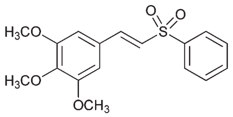
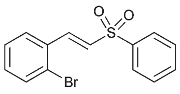
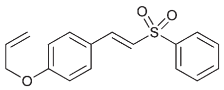
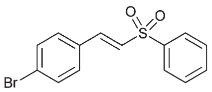
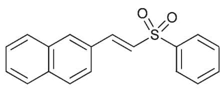
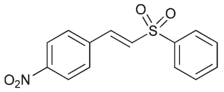
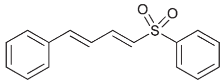
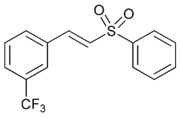
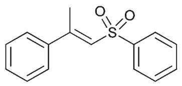
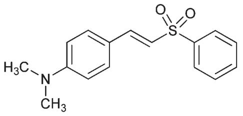
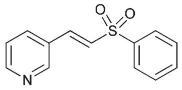
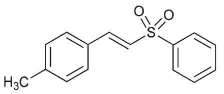
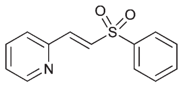
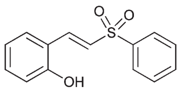
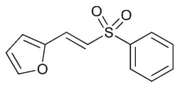
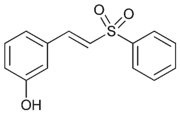
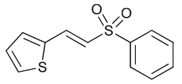
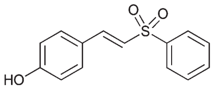
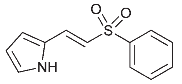
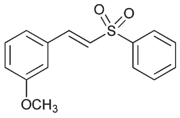
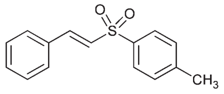
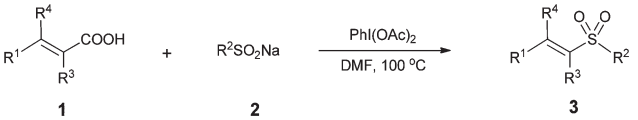
Entry	Product	Time (min)	Yield[b] (%)	Entry	Product	Time (min)	Yield[b] (%)
1		10	**3a**, 73	17		15	**3q**, 53
2		10	**3b**, 72	18		30	**3r**, 52
3		10	**3c**, 59	19		30	**3s**, 59
4		10	**3d**, 61	20		10	**3t**, 45
5		10	**3e**, 69	21		10	**3u**, 67
6		30	**3f**, 43	22		10	**3v**, 50
7		10	**3g**, 63	23		10	**3w**, 44[c]
8		30	**3h**, 46	24		10	**3x**, 66
9		15	**3i**, 58	25		10	**3y**, 61
10		15	**3j**, 64	26		10	**3z**, 52
11		15	**3k**, 57	27		10	**3za**, 54
12		15	**3l**, 47	28		30	**3zb**, 38
13		15	**3m**, 68	29		10	**3aa**, 79

Table 2 *(Contd.)*



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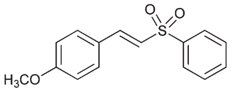
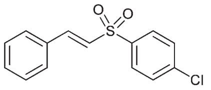
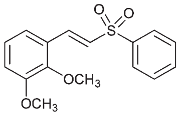
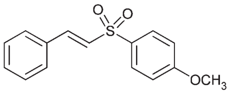
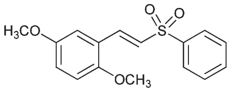
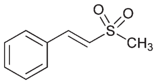
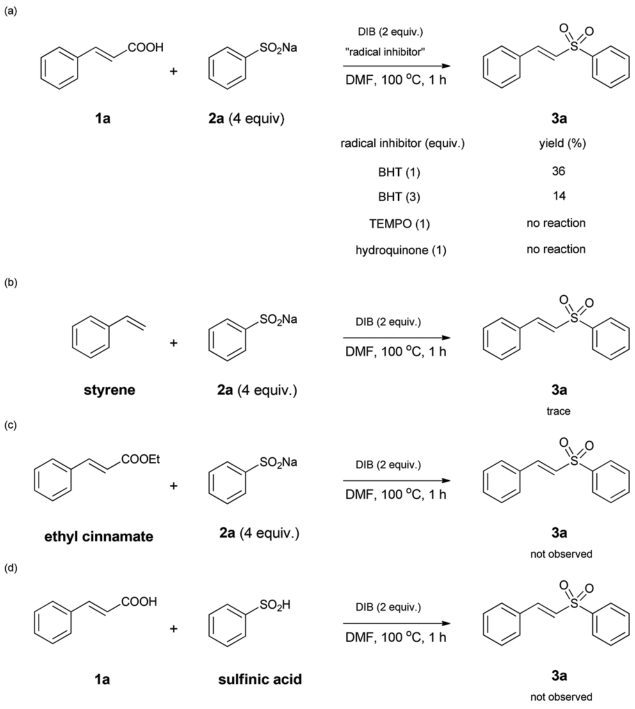
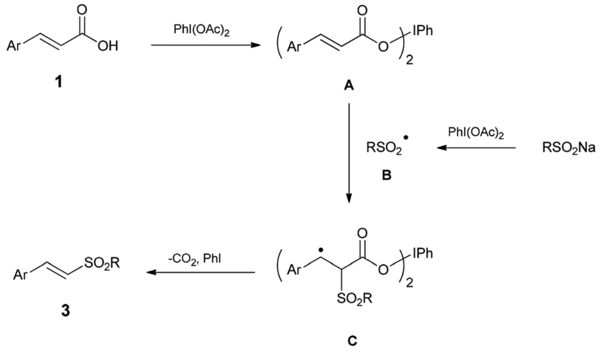
14		15	**3n**, 50	30		10	**3ab**, 71
15		15	**3o**, 64	31		10	**3ac**, 80
16		15	**3p**, 65	32		30	**3ad**, 24

[a] Reaction conditions: substrate **1** (0.25 mmol), sodium sulfinate (4 equiv.), $PhI(OAc)_2$ (2 equiv.) in DMF (3 mL), 100 °C, open air. [b] Isolated yield after column chromatography (SiO_2). [c] Allyl sulfone **4w** was isolated as a minor product (5% yield).



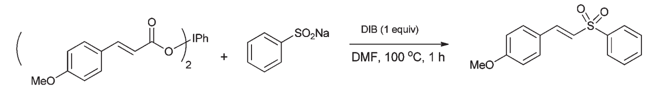
Scheme 1 Control experiments.



Scheme 2 Possible reaction mechanism.

yield) (Scheme 1c). Finally, sodium sulfinate is essential for the reaction to proceed efficiently since the reaction of (*E*)-cinnamic acid (**1a**) with benzenesulfinic acid under the standard reaction conditions did not afford the expected product **3a** (Scheme 1d).

On the basis of the control experiments mentioned above and the previously reported literature, a possible reaction pathway for the decarboxylative sulfonylation of β-aryl-α,β-unsaturated carboxylic acids mediated by $PhI(OAc)_2$ was deduced as shown in Scheme 2. Ligand exchange between $PhI(OAc)_2$ and β-aryl-α,β-unsaturated carboxylic acid **1** leads to the formation of intermediate **A**.[7] Next, the sulfonyl radical generated *in situ* by the reaction of sodium sulfinate and $PhI(OAc)_2$ attacked the intermediate **A** at the α-carbon to furnish benzylic radical intermediate **C**. Subsequently, the intermediate **C** undergoes decarboxylation and PhI loss to provide the vinyl sulfone product **3** (Scheme 2). The validity of the intermediate **A** possibly formed in the reaction was proved by separate preparation of iodosobenzene dicinnamate **5**.[7a] Treatment of iodosobenzene dicinnamate **5** with sodium benzenesulfinate (**2a**, 4 equiv.) in the presence of DIB (1 equiv.) in DMF at



5 **2a** (4 equiv) **3n** (39%)

Scheme 3 Reaction of iodosobenzene dicinnamate **5** with sodium benzenesulfinate (**2a**).

100 °C for 1 h furnished the desired product **3n** in 39% yield. Therefore, the observed results implied that the intermediate **A** might be involved as an early intermediate formed in this reaction (Scheme 3). Additionally, the stability of the radical intermediate **C** is highly crucial since the reaction of **2a** with (*E*)-2-butenoic acid did not furnish the expected vinyl sulfone product.

Conclusions

In summary, we have developed a facile and expedient protocol for the formation of (*E*)-vinyl sulfones from β-aryl-α,β-unsaturated carboxylic acids and sodium sulfinates through a $PhI(OAc)_2$ mediated decarboxylative sulfonylation strategy. The reaction exhibits good substrate scope. A wide range of functionalities both in the unsaturated carboxylic acids and the sodium sulfinates are tolerated under the reaction conditions. The method offers an alternative facile synthetic route to (*E*)-vinyl sulfones which are valuable scaffolds found in biologically active substances and important synthetic intermediates. A preliminary study on the reaction mechanism also implies that the reaction is probably proceeding through a radical pathway. To the best of our knowledge, this is the first report of decarboxylative sulfonylation of δ-aryl-α,β-γ,δ-diene carboxylic acids.

Experimental

General information

All isolated compounds were characterized on the basis of ^1H NMR and ^{13}C NMR spectroscopic data, IR spectra, and HRMS data. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Ascend™ spectrometer. ^1H NMR and ^{13}C NMR chemical shifts are reported in ppm using tetramethylsilane (TMS) as an internal standard 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 $KMnO_4$. Cinnamic acids **1a**, **1g**, **1j**, **1k**, **1n**, **1q** and solvents were obtained from commercial sources and used without further purification. Unless otherwise noted, α,β-unsaturated carboxylic acid were synthesized according to literature procedures *via* Wittig reaction and Horner–Wadsworth–Emmons reaction. 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.

General procedure: synthesis of vinyl sulfone from β-aryl-α,β-unsaturated carboxylic acid and sodium sulfinate. DIB (161.1 mg, 0.50 mmol) was added to a solution of β-aryl-α,β-unsaturated carboxylic acid (0.25 mmol) and sodium sulfinate (1.0 mmol) in DMF (3 mL) at room temperature and then the reaction mixture was stirred at 100 °C under air for 10–30 minutes. 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.

(*E*)-(2-(Phenylsulfonyl)vinyl)benzene (3a).[3d] Colorless solid, mp 62–63 °C (CH_2Cl_2–hexanes); R_f = 0.43 (1 : 3 EtOAc–hexanes); IR (neat): ν 3044, 2918, 1611, 1574, 1446, 1298, 1142, 1084 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 15.4 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.55–7.51 (m, 2H), 7.47–7.45 (m, 2H), 7.39–7.34 (m, 3H), 6.85 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4 (CH), 140.7 (C), 133.3 (CH), 132.3 (C), 131.2 (CH), 129.3 (2 × CH), 129.0 (2 × CH), 128.5 (2 × CH), 127.6 (2 × CH), 127.3 (CH); HRMS *m*/*z* (ESI): calcd for $[C_{14}H_{12}O_2S + Na]^+$: 267.0456, found 267.0455.

(*E*)-1-Fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (3b).[3d] Colorless solid, mp 92–93 °C (CH_2Cl_2–hexanes); R_f = 0.41 (1 : 3 EtOAc–hexanes); IR (neat): ν 3048, 1613, 1599, 1509, 1446, 1302, 1280, 1230, 1141, 1082 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.6 Hz, 2H), 7.65–7.59 (m, 2H), 7.54 (t, J = 7.8 Hz, 2H), 7.48–7.45 (m, 2H), 7.07 (t, J = 8.6 Hz, 2H), 6.77 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3 (d, J = 251.5 Hz, C), 141.1 (CH), 140.6 (C), 133.4 (CH), 130.6 (d, J = 8.7 Hz, 2 × CH), 129.3 (2 × CH), 128.6 (d, J = 3.3 Hz, C), 127.6 (2 × CH), 127.0 (d, J = 1.9 Hz, CH), 116.3 (d, J = 21.9 Hz, 2 × CH); HRMS *m*/*z* (ESI): calcd for $[C_{14}H_{11}FO_2S + Na]^+$: 285.0361, found 285.0360.

(*E*)-1-Chloro-3-(2-(phenylsulfonyl)vinyl)benzene (3c).[6] Colorless solid, mp 83–84 °C (CH_2Cl_2–hexanes); R_f = 0.43 (1 : 3 EtOAc–hexanes); IR (neat): ν 3048, 2919, 2850, 1617, 1562, 1446, 1318, 1142, 1084 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.6 Hz, 2H), 7.64–7.53 (m, 4H), 7.45 (s, 1H), 7.38–7.29 (m, 3H), 6.86 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7 (CH), 140.3 (C), 135.1 (C), 134.1 (C), 133.6 (CH), 131.1 (CH), 130.3 (CH), 129.4 (2 × CH), 128.9 (CH), 128.2 (CH), 127.7 (2 × CH), 126.8 (CH); HRMS *m*/*z* (ESI): calcd for $[C_{14}H_{11}ClO_2S + Na]^+$: 301.0066, found 301.0069.

(*E*)-1-Bromo-2-(2-(phenylsulfonyl)vinyl)benzene (3d).[8] Colorless solid, mp 77–79 °C (CH_2Cl_2–hexanes); R_f = 0.36 (1 : 3 EtOAc–hexanes); IR (neat): ν 3049, 2918, 2849, 1603, 1584, 1447, 1437, 1299, 1282, 1142, 1083 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 15.4 Hz, 1H), 7.95 (d, J = 8.7 Hz, 2H), 7.64–7.59 (m, 2H), 7.55 (t, J = 7.8 Hz, 2H), 7.48 (dd, J = 7.7, 1.5 Hz, 1H), 7.31–7.21 (m, 2H), 6.83 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0 (CH), 140.2 (C), 133.6 (CH), 133.5 (CH), 132.5 (C), 132.0 (CH), 130.2 (CH), 129.4 (2 × CH), 128.2 (CH), 127.84 (2 × CH), 127.82 (CH), 125.6 (C); HRMS m/z (ESI): calcd for $[C_{14}H_{11}BrO_2S + Na]^+$: 346.9540, found 346.9546.

(*E*)-1-Bromo-4-(2-(phenylsulfonyl)vinyl)benzene (3e).^{3d} Colorless solid, mp 138–139 °C (CH_2Cl_2–hexanes); R_f = 0.48 (1 : 3 EtOAc–hexanes); IR (neat): ν 3054, 1610, 1582, 1481, 1446, 1397, 1305, 1141, 1067 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.7 Hz, 2H), 7.64–7.50 (m, 6H), 7.33 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0 (CH), 140.4 (C), 133.5 (CH), 132.4 (2 × CH), 131.3 (C), 129.9 (2 × CH), 129.4 (2 × CH), 128.0 (CH), 127.7 (2 × CH), 125.6 (C); HRMS m/z (ESI): calcd for $[C_{14}H_{11}BrO_2S + Na]^+$: 346.9540, found 346.9543.

(*E*)-1-Nitro-4-(2-(phenylsulfonyl)vinyl)benzene (3f).^{3d} Yellow solid, mp 152–153 °C (CH_2Cl_2–hexanes); R_f = 0.35 (1 : 3 EtOAc–hexanes); IR (neat): ν 3055, 1592, 1509, 1446, 1337, 1307, 1148, 1085 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 8.28 (d, J = 8.9 Hz, 2H), 8.02–7.98 (m, 4H), 7.81 (d, J = 15.5 Hz, 1H), 7.77–7.73 (m, 1H), 7.69–7.65 (m, 2H), 7.60 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6): δ 149.0 (C), 140.7 (C), 139.3 (CH), 139.1 (C), 133.8 (CH), 132.4 (CH), 129.8 (2 × CH), 129.6 (2 × CH), 127.7 (2 × CH), 124.0 (2 × CH); HRMS m/z (ESI): calcd for $[C_{14}H_{11}NO_4S + Na]^+$: 312.0306, found 312.0309.

(*E*)-1-(2-(Phenylsulfonyl)vinyl)-3-(trifluoromethyl)benzene (3g).^{9} Colorless solid, mp 83–85 °C (CH_2Cl_2–hexanes); R_f = 0.44 (1 : 3 EtOAc–hexanes); IR (neat): ν 3071, 2924, 1621, 1446, 1431, 1325, 1301, 1139, 1068 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.4 Hz, 2H), 7.70 (s, 1H), 7.67–7.60 (m, 4H), 7.56–7.49 (m, 3H), 6.95 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5 (CH), 140.1 (C), 133.6 (CH), 133.1 (C), 131.6 (CH), 131.5 (q, J = 32.6 Hz, C), 129.7 (CH), 129.4 (3 × CH), 127.7 (2 × CH), 127.5 (q, J = 4.0 Hz, CH), 124.9 (q, J = 4.0 Hz, CH), 122.1 (C); HRMS m/z (ESI): calcd for $[C_{15}H_{11}F_3O_2S + Na]^+$: 335.0330, found 335.0331.

(*E*)-*N*,*N*-Dimethyl-4-(2-(phenylsulfonyl)vinyl)aniline (3h).^{10} Yellow solid, mp 158–159 °C (CH_2Cl_2–hexanes); R_f = 0.29 (1 : 3 EtOAc–hexanes); IR (neat): ν 3045, 2896, 1581, 1519, 1302, 1285, 1139, 1080 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.6 Hz, 2H), 7.60–7.48 (m, 4H), 7.34 (d, J = 8.9 Hz, 2H), 6.62 (d, J = 8.9 Hz, 2H), 6.55 (d, J = 15.2 Hz, 1H), 3.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2 (C), 143.3 (CH), 141.9 (C), 132.8 (CH), 130.4 (2 × CH), 129.1 (2 × CH), 127.3 (2 × CH), 120.6 (CH), 119.8 (C), 111.7 (2 × CH), 40.0 (2 × CH_3); HRMS m/z (ESI): calcd for $[C_{16}H_{17}NO_2S + H]^+$: 288.1058, found 288.1055.

(*E*)-1-Methyl-4-(2-(phenylsulfonyl)vinyl)benzene (3i).^{3d} Colorless solid, mp 118–120 °C (CH_2Cl_2–hexanes); R_f = 0.49 (1 : 3 EtOAc–hexanes); IR (neat): ν 3053, 2918, 1604, 1510, 1446, 1306, 1143, 1082 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.7 Hz, 2H), 7.66–7.58 (m, 2H), 7.53 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 15.4 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5 (CH), 141.9 (C), 140.9 (C), 133.2 (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); HRMS m/z (ESI): calcd for $[C_{15}H_{14}O_2S + Na]^+$: 281.0612, found 281.0615.

(*E*)-2-(2-(Phenylsulfonyl)vinyl)phenol (3j).^{3d} Colorless solid, mp 151–152 °C (CH_2Cl_2–hexanes); R_f = 0.40 (1 : 1 EtOAc–hexanes); IR (neat): ν 3317, 3100, 2921, 2851, 1602, 1580, 1444, 1286, 1274, 1135, 1080 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 9.42 (s, 1H), 7.96 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 15.5 Hz, 1H), 7.72–7.60 (m, 4H), 7.34 (d, J = 15.5 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 6.99 (d, J = 8.2 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6): δ 156.7 (C), 141.7 (C), 137.5 (CH), 132.8 (CH), 132.1 (CH), 129.9 (CH), 129.1 (2 × CH), 127.6 (CH), 127.1 (2 × CH), 119.8 (CH), 119.3 (C), 116.0 (CH); HRMS m/z (ESI): calcd for $[C_{14}H_{12}O_3S + Na]^+$: 283.0405, found 283.0409.

(*E*)-3-(2-(Phenylsulfonyl)vinyl)phenol (3k). Pale yellow solid, mp 86–88 °C (CH_2Cl_2–hexanes); R_f = 0.38 (1 : 1 EtOAc–hexanes); IR (neat): ν 3417, 3051, 2923, 2853, 1589, 1443, 1288, 1147, 1084 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.6 Hz, 2H), 7.60–7.51 (m, 4H), 7.21 (t, J = 7.9 Hz, 1H), 7.00–6.95 (m, 2H), 6.89 (dd, J = 8.1, 1.9 Hz, 1H), 6.81 (d, J = 15.4 Hz, 1H), 6.01 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3 (C), 142.6 (CH), 140.3 (C), 133.6 (C), 133.5 (CH), 130.3 (CH), 129.4 (2 × CH), 127.6 (2 × CH), 127.1 (CH), 121.2 (CH), 118.6 (CH), 114.9 (CH); HRMS m/z (ESI): calcd for $[C_{14}H_{12}O_3S + Na]^+$: 283.0405, found 283.0407.

(*E*)-4-(2-(Phenylsulfonyl)vinyl)phenol (3l).^{3d} Viscous oil; R_f = 0.34 (1 : 1 EtOAc–hexanes); IR (neat): ν 3361, 3058, 2924, 1598, 1582, 1512, 1444, 1279, 1134, 1080 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.4 Hz, 2H), 7.61–7.50 (m, 4H), 7.31 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 15.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0 (C), 142.7 (CH), 140.8 (C), 133.4 (CH), 130.7 (2 × CH), 129.4 (2 × CH), 127.5 (2 × CH), 124.7 (C), 123.8 (CH), 116.2 (2 × CH); HRMS m/z (ESI): calcd for $[C_{14}H_{12}O_3S + Na]^+$: 283.0405, found 283.0400.

(*E*)-1-Methoxy-3-(2-(phenylsulfonyl)vinyl)benzene (3m).^{3a} Colorless solid, mp 101–102 °C (CH_2Cl_2–hexanes); R_f = 0.39 (1 : 3 EtOAc–hexanes); IR (neat): ν 3075, 3046, 3005, 2838, 1598, 1584, 1446, 1300, 1270, 1144, 1083 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.6 Hz, 2H), 7.66–7.59 (m, 2H), 7.53 (t, J = 7.8 Hz, 2H), 7.29 (t, J = 7.9 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.97–6.93 (m, 2H), 6.83 (d, J = 15.4 Hz, 1H), 3.79 (s, 3H); ^{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); HRMS m/z (ESI): calcd for $[C_{15}H_{14}O_3S + Na]^+$: 297.0561, found 297.0567.

(*E*)-1-Methoxy-4-(2-(phenylsulfonyl)vinyl)benzene (3n).^{3d} Colorless solid, mp 100–101 °C (CH_2Cl_2–hexanes); R_f = 0.33 (1 : 3 EtOAc–hexanes); IR (neat): ν 3061, 2939, 2846, 1601, 1509, 1444, 1260, 1138, 1081 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.8 Hz, 2H), 7.63–7.57 (m, 2H), 7.52 (t, J = 7.8 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 15.3 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (C), 142.3 (CH), 141.1 (C), 133.1 (CH), 130.4 (2 × CH), 129.2 (2 × CH), 127.5 (2 × CH), 124.9 (C), 124.4 (CH), 114.5

(2 × CH), 55.4 (CH_3); HRMS *m*/*z* (ESI): calcd for $[C_{15}H_{14}O_3S + Na]^+$: 297.0561, found 297.0566.

(*E*)-1,2-Dimethoxy-3-(2-(phenylsulfonyl)vinyl)benzene (3o). Colorless solid, mp 99–100 °C (CH_2Cl_2–hexanes); R_f = 0.31 (1 : 3 EtOAc–hexanes); IR (neat): *ν* 3048, 2922, 2848, 1577, 1463, 1445, 1426, 1282, 1271, 1141, 1058 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.94–7.90 (m, 3H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.05–6.93 (m, 4H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 153.1 (C), 148.8 (C), 140.8 (C), 137.7 (CH), 133.2 (CH), 129.3 (2 × CH), 128.7 (CH), 127.6 (2 × CH), 126.4 (C), 124.2 (CH), 120.2 (CH), 114.9 (CH), 61.2 (CH_3), 55.9 (CH_3); HRMS *m*/*z* (ESI): calcd for $[C_{16}H_{16}O_4S + Na]^+$: 327.0667 found 327.0668.

(*E*)-1,4-Dimethoxy-2-(2-(phenylsulfonyl)vinyl)benzene (3p).[11] Pale yellow solid, mp 120–122 °C (CH_2Cl_2–hexanes); R_f = 0.30 (1 : 3 EtOAc–hexanes); IR (neat): *ν* 3081, 2957, 2928, 2835, 1577, 1500, 1442, 1273, 1138, 1082, 1022 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.93 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 15.4 Hz, 1H), 7.60–7.57 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 15.4 Hz, 1H), 6.92–6.90 (m, 2H), 6.84–6.82 (m, 1H), 3.81 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 153.4 (C), 153.3 (C), 141.1 (C), 138.3 (CH), 133.1 (CH), 129.2 (2 × CH), 128.1 (CH), 127.6 (2 × CH), 121.6 (C), 118.2 (CH), 114.9 (CH), 112.4 (CH), 55.9 (CH_3), 55.8 (CH_3); HRMS *m*/*z* (ESI): calcd for $[C_{16}H_{16}O_4S + Na]^+$: 327.0667 found 327.0663.

(*E*)-5-(2-(Phenylsulfonyl)vinyl)benzo[*d*][1,3]dioxole (3q).[12] Colorless solid, mp 95–96 °C (CH_2Cl_2–hexanes); R_f = 0.38 (1 : 3 EtOAc–hexanes); IR (neat): *ν* 3053, 2904, 1595, 1500, 1488, 1447, 1307, 1257, 1139, 1082 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.91 (d, *J* = 8.6 Hz, 2H), 7.61–7.50 (m, 4H), 6.98 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.91 (d, *J* = 1.5 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 15.3 Hz, 1H), 5.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 150.4 (C), 148.5 (C), 142.2 (CH), 141.0 (C), 133.2 (CH), 129.3 (2 × CH), 127.5 (2 × CH), 126.6 (C), 125.3 (CH), 124.9 (CH), 108.6 (CH), 106.8 (CH), 101.8 (CH_2); HRMS *m*/*z* (ESI): calcd for $[C_{15}H_{12}O_4S + Na]^+$: 311.0354, found 311.0352.

(*E*)-1,2,4-Trimethoxy-5-(2-(phenylsulfonyl)vinyl)benzene (3r). Pale yellow solid, mp 158–160 °C (CH_2Cl_2–hexanes); R_f = 0.28 (1 : 1 EtOAc–hexanes); IR (neat): *ν* 3052, 2925, 2835, 1595, 1514, 1446, 1296, 1211, 1138, 1083, 1029 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.92 (d, *J* = 7.4 Hz, 2H), 7.84 (d, *J* = 15.4 Hz, 1H), 7.56–7.48 (m, 3H), 6.88–6.84 (m, 2H), 6.45 (s, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 154.6 (C), 152.8 (C), 143.1 (C), 141.5 (C), 138.1 (CH), 132.9 (CH), 129.1 (2 × CH), 127.4 (2 × CH), 124.6 (CH), 112.5 (C), 112.4 (CH), 96.4 (CH), 56.4 (CH_3), 56.1 (CH_3), 56.0 (CH_3); HRMS *m*/*z* (ESI): calcd for $[C_{17}H_{18}O_5S + Na]^+$: 357.0773, found 357.0770.

(*E*)-1,2,3-Trimethoxy-5-(2-(phenylsulfonyl)vinyl)benzene (3s). Colorless solid, mp 143–144 °C (CH_2Cl_2–hexanes); R_f = 0.23 (1 : 3 EtOAc–hexanes); IR (neat): *ν* 3048, 2942, 2841, 1579, 1506, 1421, 1280, 1254, 1127, 1081 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.93 (d, *J* = 8.5 Hz, 2H), 7.62–7.51 (m, 4H), 6.76 (d, *J* = 15.3 Hz, 1H), 6.69 (s, 2H), 3.840 (s, 3H), 3.837 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 153.5 (2 × C), 142.6 (CH), 140.8 (C), 133.3 (CH), 129.3 (2 × CH), 127.7 (2 × C), 127.6 (2 × CH), 126.3 (CH), 105.8 (2 × CH), 61.0 (CH_3), 56.2 (2 × CH_3); HRMS *m*/*z* (ESI): calcd for $[C_{17}H_{18}O_5S + H]^+$: 335.0953, found 335.0954.

(*E*)-1-(Allyloxy)-4-(2-(phenylsulfonyl)vinyl)benzene (3t). Colorless solid, mp 116–117 °C (CH_2Cl_2–hexanes); R_f = 0.48 (1 : 3 EtOAc–hexanes); IR (neat): *ν* 3054, 2919, 2856, 1599, 1569, 1505, 1304, 1238, 1173, 1141, 1082 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.92 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 15.4 Hz, 1H), 7.60–7.56 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 15.4 Hz, 1H), 6.05–5.96 (m, 1H), 5.38 (dd, *J* = 17.3, 1.4 Hz, 1H), 5.28 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.54 (dt, *J* = 5.2, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 161.0 (C), 142.2 (CH), 141.1 (C), 133.2 (CH), 132.5 (CH), 130.3 (2 × CH), 129.2 (2 × CH), 127.5 (2 × CH), 125.0 (C), 124.5 (CH), 118.1 (CH_2), 115.2 (2 × CH), 68.8 (CH_2); HRMS *m*/*z* (ESI): calcd for $[C_{17}H_{16}O_3S + Na]^+$: 323.0718, found 323.0715.

(*E*)-2-(2-(Phenylsulfonyl)vinyl)naphthalene (3u).[3a] Pale yellow solid, mp 89–90 °C (CH_2Cl_2–hexanes); R_f = 0.45 (1 : 3 EtOAc–hexanes); IR (neat): *ν* 3046, 2919, 1611, 1445, 1304, 1286, 1139, 1083 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.98 (d, *J* = 8.4 Hz, 2H), 7.92 (s, 1H), 7.85–7.79 (m, 4H), 7.63–7.49 (m, 6H), 6.96 (d, *J* = 15.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 142.5 (CH), 140.8 (C), 134.5 (C), 133.3 (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), 127.3 (CH), 127.0 (CH), 123.4 (CH); HRMS *m*/*z* (ESI): calcd for $[C_{18}H_{14}O_2S + Na]^+$: 317.0612, found 317.0610.

(((1*E*,3*E*)-4-Phenylbuta-1,3-dien-1-yl)sulfonyl)benzene (3v).[13] Colorless solid, mp 89–90 °C (CH_2Cl_2–hexanes); R_f = 0.54 (1 : 3 EtOAc–hexanes); IR (neat): *ν* 3057, 2921, 1615, 1584, 1446, 1307, 1275, 1137, 1083 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.90 (d, *J* = 8.8 Hz, 2H), 7.59 (t, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.45–7.39 (m, 3H), 7.37–7.31 (m, 3H), 6.97 (d, *J* = 15.5 Hz, 1H), 6.76 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.43 (d, *J* = 14.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.0 (CH), 142.4 (CH), 140.9 (C), 135.3 (C), 133.2 (CH), 129.7 (CH), 129.3 (3 × CH), 128.9 (2 × CH), 127.5 (2 × CH), 127.4 (2 × CH), 123.6 (CH); HRMS *m*/*z* (ESI): calcd for $[C_{16}H_{14}O_2S + Na]^+$: 293.0612, found 293.0611.

(*E*)-((2-Phenylprop-1-en-1-yl)sulfonyl)benzene (3w).[14] Colorless oil; R_f = 0.60 (1 : 3 EtOAc–hexanes); IR (neat): *ν* 3058, 2924, 2853, 1601, 1572, 1444, 1300, 1140, 1083 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.96 (d, *J* = 8.6 Hz, 2H), 7.63–7.59 (m, 1H), 7.56–7.52 (m, 2H), 7.39–7.32 (m, 5H), 6.59 (d, *J* = 1.2 Hz, 1H), 2.51 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 153.5 (C), 142.1 (C), 140.1 (C), 133.2 (CH), 129.9 (CH), 129.2 (2 × CH), 128.7 (2 × CH), 127.4 (CH), 127.2 (2 × CH), 126.3 (2 × CH), 17.2 (CH_3); HRMS *m*/*z* (ESI): calcd for $[C_{15}H_{14}O_2S + Na]^+$: 281.0612, found 281.0619.

((2-Phenylallyl)sulfonyl)benzene (4w).[15] Colorless oil; R_f = 0.53 (1 : 3 EtOAc–hexanes); IR (neat): *ν* 3060, 2926, 2853, 1446, 1304, 1136, 1083 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.79 (d, *J* = 8.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.28–7.23 (m, 5H), 5.60 (s, 1H), 5.23 (s, 1H), 4.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 138.7 (C), 138.4 (C), 136.4 (C), 133.6 (CH), 128.9 (2 × CH), 128.6 (2 × CH), 128.4

(2 × CH), 128.0 (CH), 126.2 (2 × CH), 121.9 (CH_2), 62.0 (CH_2); HRMS *m*/*z* (ESI): calcd for $[C_{15}H_{14}O_2S + Na]^+$: 281.0612, found 281.0611.

(*E*)-3-(2-(Phenylsulfonyl)vinyl)pyridine (3x).[3d] Pale yellow solid, mp 83–85 °C (CH_2Cl_2–hexanes); R_f = 0.16 (1 : 1 EtOAc–hexanes); IR (neat): ν 3060, 2920, 1617, 1445, 1410, 1304, 1144, 1082 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 1.8 Hz, 1H), 8.60 (dd, *J* = 4.7, 1.1 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 15.5 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.56–7.53 (m, 2H), 7.31 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.94 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8 (CH), 149.9 (CH), 140.2 (C), 138.7 (CH), 134.8 (CH), 133.7 (CH), 129.7 (CH), 129.4 (2 × CH), 128.3 (C), 127.8 (2 × CH), 123.8 (CH); HRMS *m*/*z* (ESI): calcd for $[C_{13}H_{11}NO_2S + H]^+$: 246.0589, found 246.0591.

(*E*)-2-(2-(Phenylsulfonyl)vinyl)pyridine (3y).[3d] Colorless solid, mp 85–86 °C (CH_2Cl_2–hexanes); R_f = 0.20 (1 : 3 EtOAc–hexanes); IR (neat): ν 3056, 1579, 1443, 1428, 1309, 1299, 1142, 1082 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 4.4 Hz, 1H), 7.95 (d, *J* = 7.4 Hz, 2H), 7.72 (td, *J* = 7.7 Hz, *J* = 1.6 Hz, 1H), 7.66–7.59 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.45–7.38 (m, 2H), 7.28 (dd, *J* = 7.3, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0 (C), 150.3 (CH), 140.5 (CH), 140.2 (C), 137.0 (CH), 133.5 (CH), 131.8 (CH), 129.3 (2 × CH), 127.9 (2 × CH), 125.5 (CH), 125.0 (CH); HRMS *m*/*z* (ESI): calcd for $[C_{13}H_{11}NO_2S + H]^+$: 246.0589, found 246.0582.

(*E*)-2-(2-(Phenylsulfonyl)vinyl)furan (3z).[3d] Brown viscous oil; R_f = 0.40 (1 : 3 EtOAc–hexanes); IR (neat): ν 3058, 1781, 1722, 1621, 1446, 1304, 1138, 1082 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 1.0 Hz, 1H), 7.42 (d, *J* = 15.0 Hz, 1H), 6.72 (d, *J* = 15.0 Hz, 1H), 6.68 (d, *J* = 3.4 Hz, 1H), 6.46 (dd, *J* = 3.4, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7 (C), 145.6 (CH), 140.8 (C), 133.3 (CH), 129.3 (2 × CH), 128.9 (CH), 127.5 (2 × CH), 124.7 (CH), 116.9 (CH), 112.6 (CH); HRMS *m*/*z* (ESI): calcd for $[C_{12}H_{10}O_3S + H]^+$: 235.0429, found 235.0426.

(*E*)-2-(2-(Phenylsulfonyl)vinyl)thiophene (3za).[3d] Brown solid, mp 79–80 °C (CH_2Cl_2–hexanes); R_f = 0.44 (1 : 3 EtOAc–hexanes); IR (neat): ν 3119, 3038, 2919, 1599, 1443, 1418, 1306, 1279, 1141, 1081 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 15.1 Hz, 1H), 7.61–7.57 (m, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 5.1 Hz, 1H), 7.29 (d, *J* = 3.6 Hz, 1H), 7.04 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.62 (d, *J* = 15.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8 (C), 136.9 (C), 135.1 (CH), 133.3 (CH), 132.4 (CH), 130.0 (CH), 129.3 (2 × CH), 128.3 (CH), 127.5 (2 × CH), 125.3 (CH); HRMS *m*/*z* (ESI): calcd for $[C_{12}H_{10}O_2S_2 + Na]^+$: 273.0020, found 273.0016.

(*E*)-2-(2-(Phenylsulfonyl)vinyl)-1*H*-pyrrole (3zb). Brown solid, mp 98–99 °C (CH_2Cl_2–hexanes); R_f = 0.25 (1 : 3 EtOAc–hexanes); IR (neat): ν 3336, 3056, 2921, 1607, 1444, 1409, 1298, 1137, 1084 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (br s, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.59–7.54 (m, 2H), 7.49–7.45 (m, 2H), 6.92 (s, 1H), 6.59 (d, *J* = 3.9 Hz, 1H), 6.58 (d, *J* = 15.1 Hz, 1H), 6.25–6.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5 (C), 133.03 (CH), 133.01 (CH), 129.3 (2 × CH), 127.1 (2 × CH), 126.1 (C), 124.1 (CH), 118.9 (CH), 116.2 (CH), 111.2 (CH); HRMS *m*/*z* (ESI): calcd for $[C_{12}H_{11}NO_2S + Na]^+$: 256.0408, found 256.0404.

(*E*)-1-Methyl-4-(styrylsulfonyl)benzene (3aa).[3d] Colorless solid, mp 117–118 °C (CH_2Cl_2–hexanes); R_f = 0.49 (1 : 3 EtOAc–hexanes); IR (neat): ν 3045, 2921, 2851, 1613, 1595, 1449, 1302, 1140, 1084 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.47–7.44 (m, 2H), 7.39–7.31 (m, 5H), 6.83 (d, *J* = 15.4 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4 (C), 141.9 (CH), 137.7 (C), 132.4 (C), 131.1 (CH), 129.9 (2 × CH), 129.0 (2 × CH), 128.5 (2 × CH), 127.7 (2 × CH), 127.6 (CH), 21.6 (CH_3); HRMS *m*/*z* (ESI): calcd for $[C_{15}H_{14}O_2S + Na]^+$: 281.0612, found 281.0618.

(*E*)-1-Chloro-4-(styrylsulfonyl)benzene (3ab).[3d] Colorless solid, mp 78–80 °C (CH_2Cl_2–hexanes); R_f = 0.55 (1 : 3 EtOAc–hexanes); IR (neat): ν 3061, 3039, 1610, 1575, 1473, 1449, 1394, 1309, 1278, 1142, 1083 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 15.4 Hz, 1H), 7.51–7.46 (m, 4H), 7.43–7.36 (m, 3H), 6.82 (d, *J* = 15.4 Hz, 1H); ^{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); HRMS *m*/*z* (ESI): calcd for $[C_{14}H_{11}ClO_2S + Na]^+$: 301.0066, found 301.0067.

(*E*)-1-Methoxy-4-(styrylsulfonyl)benzene (3ac).[3a] Colorless solid, mp 75–76 °C (CH_2Cl_2–hexanes); R_f = 0.33 (1 : 3 EtOAc–hexanes); IR (neat): ν 3038, 2918, 2847, 1591, 1574, 1496, 1296, 1260, 1135, 1082 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.9 Hz, 2H), 7.61 (d, *J* = 15.4 Hz, 1H), 7.45–7.43 (m, 2H), 7.37–7.34 (m, 3H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 15.4 Hz, 1H), 3.84 (s, 3H); ^{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), 127.8 (CH), 114.5 (2 × CH), 55.6 (CH_3); HRMS *m*/*z* (ESI): calcd for $[C_{15}H_{14}O_3S + Na]^+$: 297.0561, found 297.0568.

(*E*)-(2-(Methylsulfonyl)vinyl)benzene (3ad).[3d] Colorless solid, mp 67–68 °C (CH_2Cl_2–hexanes); R_f = 0.21 (1 : 3 EtOAc–hexanes); IR (neat): ν 3047, 3026, 2926, 1622, 1451, 1273, 1130, 1113 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 15.5 Hz, 1H), 7.50–7.48 (m, 2H), 7.42–7.39 (m, 3H), 6.91 (d, *J* = 15.5 Hz, 1H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0 (CH), 132.1 (C), 131.4 (CH), 129.2 (2 × CH), 128.6 (2 × CH), 126.1 (CH), 43.3 (CH_3); HRMS *m*/*z* (ESI): calcd for $[C_9H_{10}O_2S + Na]^+$: 205.0299, found 205.0300.

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