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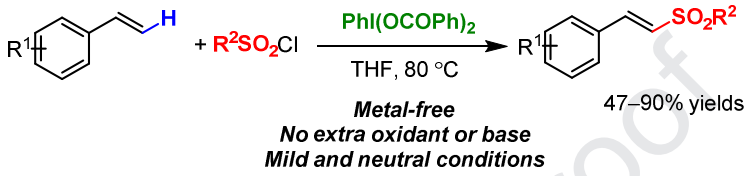

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Synthesis of vinyl sulfones through sulfonylation of styrenes with sulfonyl chlorides under metal-free conditions

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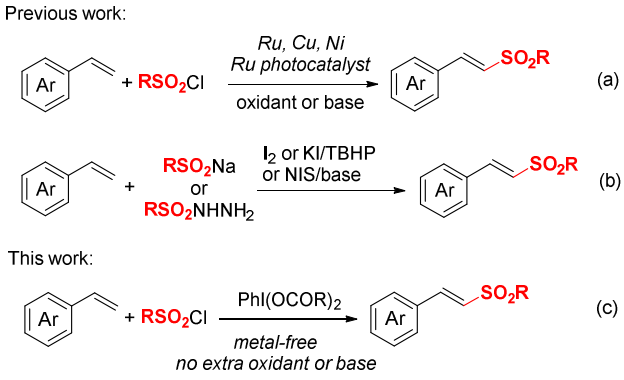
ABSTRACT

A hypervalent iodine reagent-mediated sulfonylation of styrenes with sulfonyl chlorides was developed for the synthesis of vinyl sulfones. The reaction proceeded under metal-free, mild and neutral conditions without extra oxidants or bases. It also exhibited good air and moisture tolerance, broad substrate scope and high chemo-selectivity, affording the vinyl sulfones in moderate to good yields.

1. Introduction

Sulfur-containing compound is of great importance as it finds widespread utilization in various fields of organic, biological and materials chemistry.[1] Among them, vinyl sulfones are versatile building blocks and convenient intermediates in organic synthesis and also important moieties in many natural products and biologically active compounds.[2] Classical methods to synthesize vinyl sulfones are mainly based on condensation, olefination or transition-metal-catalyzed cross coupling reactions.[3] Alkenes are among the most basic and cheap starting materials in organic synthesis. Thus direct sulfonylation of alkenes emerged as a more powerful and efficient method for preparation of vinyl sulfones. Kimigata and coworkers first reported a ruthenium-catalyzed sulfonylation of styrenes with sulfonyl chlorides in 1983.[4] In the past decade, the transformations under copper, silver or photoredox catalysis were also accomplished.[5] However, these sulfonylation methods required the involvement of metal catalysts, and sometimes also expensive ligands, extra stoichiometric oxidants or bases (Scheme 1a). In this regard, synthesis methods for vinyl sulfones under metal-free conditions are considerably desired on account of sustainable and green chemistry.[6]

Efforts have also been devoted to metal-free sulfonylation of alkenes in recent years. It was mainly achieved through sulfonylation using sulfonyl hydrazides or sodium sulfinates under iodine, hypervalent iodine or photoredox catalysis.[7] For a recent instance, Gevorgyan and coworkers developed a light-induced sulfonylation of styrenes with sulfonate esters.[8] Very recently, Mal and coworkers reported an *N*-iodosuccinimide-mediated sulfonylation of styrenes with sulfonyl hydrazides.[9] However, most of these methods still required a strong oxidant like TBHP or extra bases (Scheme 1b). More concise and milder reaction conditions are still demanded. On the other hand, sulfonyl chloride is a preferable sulfonylation reagent due to its high stability, ready availability and easy handling.



Scheme 1. Synthesis of vinyl sulfones from styrenes

Hypervalent iodine reagents have attracted much attention in organic synthesis as easily accessible, stable, efficient and environmentally benign oxidants in recent years.[10] Significant progress has also been made in hypervalent iodine reagents-

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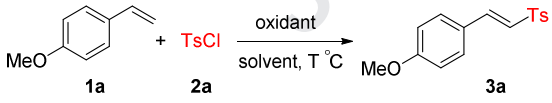
promoted selective C−H bond functionalization under metal-free conditions.[11] In 2015 Kuhakarn and coworkers reported a hypervalent iodine reagent-mediated decarboxylative sulfonylation of β-aryl-α,β-unsaturated carboxylic acids with sodium sulfinates for the preparation of vinyl sulfones.[12] In 2016, our group developed a hypervalent iodine reagent-mediated site-selective oxidative C–H sulfonylation of 8-amidoquinolines and anilides with sulfonyl chlorides.[13] Along with our study on the hypervalent iodine chemistry,[14] herein we report the hypervalent iodine reagent-mediated sulfonylation of styrenes with sulfonyl chlorides under metal-free conditions, which provided a novel method for the synthesis of vinyl sulfones (Scheme 1c).

2. Results and discussion

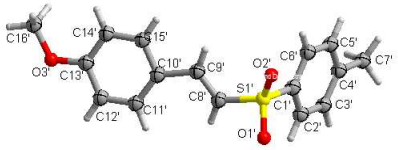
Initial study was carried out with 4-methoxystyrene (**1a**) (0.2 mmol) and TsCl (**2a**) (0.4 mmol) as the model reaction and the results were summarized in Table 1. The sulfonylation occurred in the presence of 2 equivalents of $PhI(OAc)_2$ (0.4 mmol) in THF at 80 °C for 12 h which produced the desired product (**3a**) in 50% yield (entry 1). The structure of **3a** was unambiguously confirmed by X-ray crystallography (Figure 1).[15] Other solvents such as CH_3CN, DCM, toluene, chlorobenzene, and DCE were subsequently examined but did not provide better results than THF (entries 2–6). Then other hypervalent iodine reagents were tested in THF. The employment of PhIO and $PhI(OTFA)_2$ resulted in no reaction (entries 7 and 8). $PhI(OPiv)_2$ provided similar product yield as $PhI(OAc)_2$ (entry 9). Notably a better result (65% yield) was obtained using $PhI(OCOPh)_2$ (entries 10). The reactions under reduced or elevated temperatures were investigated but no improvement was observed (entries 11–13). Shortening the reaction time to 8 h resulted in a lower yield but prolonging the reaction time to 16 h afforded the product in 71% yield (entries 14 and 15). Further prolonging the reaction time to 24 h did not give better result (entry 16). Thus the conditions showed in entry 15 were chose as the best one and subsequently applied to explore the scope of this reaction.

Table 1. Optimization of reaction conditions[a,b]



Entry	Oxidant	Solvent	T (°C)	Yield (%)[b]
1	$PhI(OAc)_2$	THF	80	50
2	$PhI(OAc)_2$	CH_3CN	80	11
3	$PhI(OAc)_2$	DCM	80	20
4	$PhI(OAc)_2$	PhCl	80	10
5	$PhI(OAc)_2$	toluene	80	10
6	$PhI(OAc)_2$	DCE	80	0
7	PhIO	THF	80	0
8	$PhI(OTFA)_2$	THF	80	0
9	$PhI(OPiv)_2$	THF	80	51
10	$PhI(OCOPh)_2$	THF	80	65
11	$PhI(OCOPh)_2$	THF	40	15
12	$PhI(OCOPh)_2$	THF	60	54
13	$PhI(OCOPh)_2$	THF	100	47
14[c]	$PhI(OCOPh)_2$	THF	80	50
15[d]	**$PhI(OOCPh)_2$**	**THF**	**80**	**71**
16[e]	$PhI(OCOPh)_2$	THF	80	52

[a]Reaction conditions: 4-methoxylstyrene (**1a**) (0.2 mmol), 4-tolysufonyl chloride (**2a**) (0.4 mmol), oxidant (0.4 mmol) in solvent (2.0 mL) stirring under air for 12 h. [b]Isolated yield. [c]Reaction time 8 h. [d]Reaction time 16 h. [e]Reaction time 24 h.

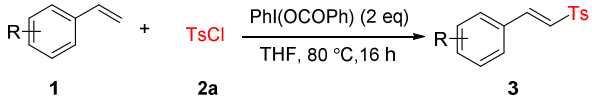


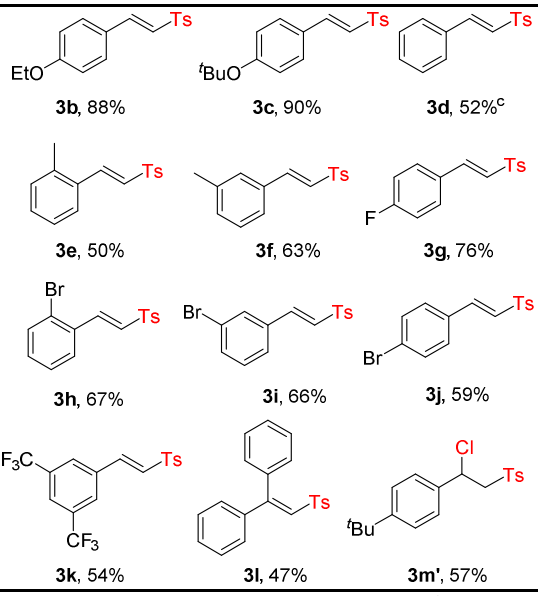
Fugure 1. X-ray crystallography of **3a**

Under the optimized conditions, the substrate scope of styrenes (**1**) with TsCl (**2a**) was explored as shown in Table 2. It's pleasant to find that good functional group compatibility was demonstrated for a variety of styrenes on the phenyl group such as alkoxyl, F, Br, and CF_3. The desired vinyl sulfone products were obtained in moderate to good yields (**3b**–**3k**). Electronic effect was observed in this reaction that the electron-rich styrene (**3b** and **3c**) gave higher yields than the electron-poor substrates (**3g**–**3k**). Substrates with a substituent on *ortho*-, *meta*- or *para*-position gave similar results without significant steric hindrance effect (**3e** and **3f, 3h**–**3j**). Notably, 1,1-diphenylethylene could also provide 47% yield of desired product (**3l**). However, when *p-tert*-butylstyrene was used the vinyl sulfone product was not obtained. Instead, a *β*-chlorosulfone **3m'** was isolated in 57% yield through chlorosulfonylation of the double bond.

The substrate scope of other sulfonyl chlorides (**2**) was investigated subsequently as shown in Table 3. Benzenesulfonyl chloride reacted with 4-methoxystyrene (**1a**) to give the vinyl sulfone **3n** in 67% yield. The *o*-tosyl chloride also underwent the reaction smoothly to provide 85% product yield without influence of steric hindrance effect (**3o**). Other functional groups such as MeO, F, Cl and Br were also tolerated on the sulfonyl

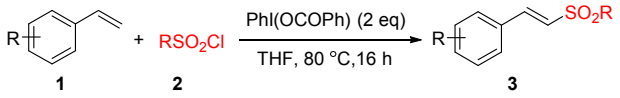
Table 2. Substrate scope of styrenes (**1**)[a,b]

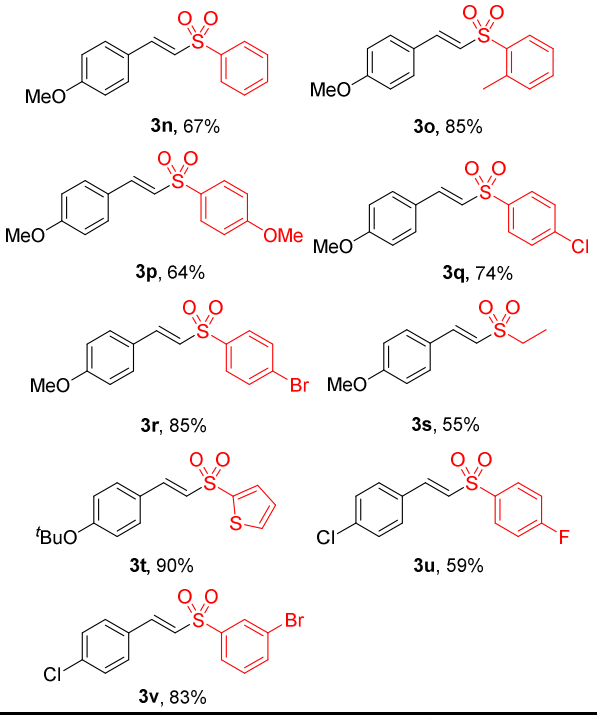




[a]Reaction conditions: styrene (**1**) (0.2 mmol), 4-tolysufonyl chloride (**2a**) (0.4 mmol), $PhI(OCOPh)_2$ (0.4 mmol) in THF (2.0 mL) stirring at 80 °C under air for 16 h. [b]Isolated yield; [c]$PhI(OAc)_2$ (0.4 mmol) is used.

Table 3. Substrate scope of sulfonyl chlorides (**2**)[a,b]



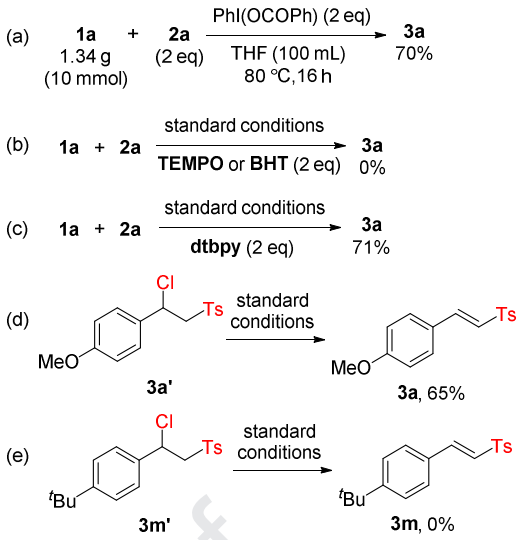


[a]Reaction conditions: styrene (**1**) (0.2 mmol), sufonyl chloride (**2**) (0.4 mmol), $PhI(OCOPh)_2$ (0.4 mmol) in THF (2.0 mL) stirring at 80 °C under air for 16 h. [b]Isolated yield.

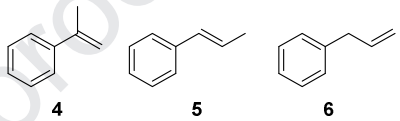
chlorides and the desired products were obtained in moderate to good yields (**3p**–**3r**, **3u** and **3v**). Notably, the alkyl and 2-thienyl sulfonyl chloride were also applicable in this protocol and gave the desired products in yields of 55% and 90% respectively (**3s** and **3t**).

We also carried out the standard reaction in gram-scale to examine the application potential of this method. With 10 mmol (1.34 g) substrate **1a** in 100 mL THF, the sulfonylation proceeded smoothly to give the product in 70% yield (Scheme 2a). Control experiments were conducted for clarification of the reaction mechanism. The sulfonylation of **1a** and **2a** in the presence of a radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylated hydroxytoluene (BHT) gave no desired products although no radical trapping product was detected either (Scheme 2b). But a proton scavenger 2,6-di-*tert*-butylpyridine (dtbpy) exhibited little influence to this reaction (Scheme 2c). It implied that the reaction proceeded through a radical mechanism. The study of possible reaction intermediate was also conducted. A pre-synthesized *β*-chlorosulfone **3a'** was handled under standard conditions which converted to the vinyl sulfone **3a** in 65% yield (Scheme 2d).[16] But the same treatment of **3m'** did not produce the vinyl sulfone product **3m** (Scheme 2e). It indicated the formation of a chlorosulfonylation intermediate in this process which might convert to the final product or remain unchangebly under reaction conditions.

Furthermore, some other styrene derivatives were also examined and found to be inapplicable in this method (Scheme 3). The 2-phenyl-propene (**4**) only gave trace amount of product. And 1-phenyl-propene (**5**) and allylbenzene (**6**) both resulted in no reaction.

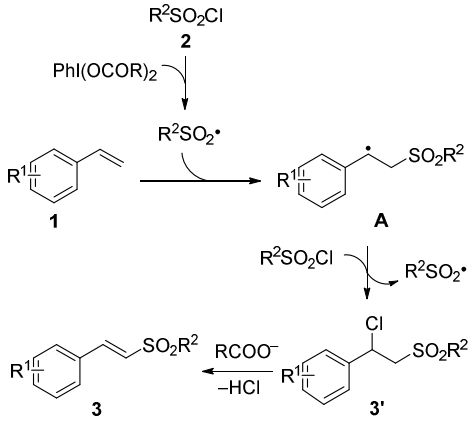


Scheme 2. Gram-scale synthesis and control experiments.



Scheme 3. Inapplicable substrates

Based on these results and previous reports, a plausible mechanism for this sulfonylation was proposed in Scheme 4. In the presence of hypervalent iodine reagent, the sulfonyl chloride converted to a sulfonyl radical.[17] The sulfonyl radical subsequently added to the styrene (**1**) to form a carbon-centered radical **A**. Electron-rich styrenes were more reactive towards the sulfonyl radical. Then intermediate **A** was trapped by chlorine radical from homolytic cleavage of sulfonyl chloride to form the chlorosulfonylation product **3'**. Then, in some cases (for instance if R^1 is *tert*-butyl), **3'** was more stable than the corresponding vinyl sulfones and did not proceed elimination reaction under the reaction conditions stable which can be isolated as the product (**3m'**). In other cases, elimination of HCl from **3'** generated the vinyl sulfone products **3**.



Scheme 4. Plausible reaction mechanism

3. Conclusions

In summary, we have developed a hypervalent iodine reagent-mediated sulfonylation of styrenes with sulfonyl chlorides. The reaction proceeded under metal-free, mild and neutral conditions and showed good air and moisture tolerance. Broad substrate scope and high chemo-selectivity were exhibited which afford the vinyl sulfones in moderate to good yields. It provides a novel and facile strategy for synthesis of vinyl sulfones.

4. Experimental section

4.1. General experimental

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard, operating at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR. Melting points were measured by SGW X-4A microscopic apparatus. The X-ray crystallography was measured on Bruker D8 VENTURE PHOTON instrument. HRMS was measured by Q Exactive LC/HRMS spectrometer. Ethyl acetate and hexane were used for column chromatography without further purification. All solvents and chemicals were obtained from commercial sources and used as received unless otherwise noted.

4.2. General procedure for the sulfonylation of styrenes (1).

A mixture of styrene (**1**, 0.2 mmol), sulfonyl chloride (**2**, 0.4 mmol), $PhI(OOCPh)_2$ (0.4mmol) were added into a vial containing a stirring bar and sealed with a Teflon-lined cap. Then THF (2 mL) was introduced. The resulting mixture was stirred at 80 °C for 16 h. Then the mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After removal of the solvent in vacuo, the residue was purified by column chromatography (ethyl acetate/hexane) to afford the pure product.

4.3. Characterization data of products 3

4.3.1. *(E)-1-Methoxy-4-(2-tosylvinyl)benzene (**3a**)*. Yellow solid, mp 100–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.83 (s, 3H), 6.70 (d, *J* = 15.32 Hz, 1H), 6.88–6.91 (m, 2H), 7.33 (d, *J* = 8.08 Hz, 2H), 7.42 (d, *J* = 8.76 Hz, 2H), 7.60 (d, *J* = 15.32 Hz, 1H), 7.82 (d, *J* = 8.24 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.60, 55.44, 114.49, 124.80, 125.07, 127.57, 129.91, 130.32, 138.18, 141.76, 144.14, 161.98. HRMS-ESI(m/z): calcd for $C_{16}H_{17}O_3S$ ($M+H^+$): 288.0898, found 288.0896.

4.3.2. *(E)-1-Ethoxy-4-(2-tosylvinyl)benzene (**3b**)*. Light yellow solid, mp 75–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (td, *J* = 6.98 Hz, *J* = 2.72 Hz, 3H), 2.43 (s, 3H), 4.03–4.09 (m, 2H), 6.69 (d, *J* = 15.32 Hz, 1H), 6.86–6.89 (m, 2H), 7.33 (d, *J* = 8.04 Hz, 2H), 7.39–7.43 (m, 2H), 7.60 (d, *J* = 15.36 Hz, 1H), 7.81–7.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.67, 21.60, 63.71, 114.95, 124.65, 124.89, 127.57, 129.90, 130.32, 138.24, 141.83, 144.10, 161.41. HRMS-ESI(m/z): calcd for $C_{17}H_{19}O_3S$ ($M+H^+$): 302.1055, found 302.1054.

4.3.3. *(E)-1-(tert-Butoxy)-4-(2-tosylvinyl)benzene (**3c**)*. Light yellow solid, mp 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 9H), 2.43 (s, 3H), 6.73 (d, *J* = 15.36 Hz, 1H), 6.98 (d, *J* = 8.56 Hz, 2H), 7.33 (d, *J* = 8.08 Hz, 2H), 7.39 (d, *J* = 8.60 Hz, 2H), 7.61 (d, *J* = 15.36 Hz, 1H), 7.82 (d, *J* = 8.24 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.61, 28.87, 79.59, 123.67, 125.76, 127.05, 127.62, 129.59, 129.92, 138.08, 141.67, 144.20, 158.55. HRMS-ESI(m/z): calcd for $C_{19}H_{23}O_3S$ ($M+H^+$): 330.1368, found 330.1370.

4.3.4. *(E)-1-Methyl-4-(styrylsulfonyl)benzene (**3d**)*. Light yellow solid, mp 90–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 6.85 (d, *J* = 15.40 Hz, 1H), 7.35 (d, *J* = 8.12 Hz, 2H), 7.38–7.41 (m, 3H), 7.47–7.49 (m, 2H), 7.66 (d, *J* = 15.44 Hz, 1H), 7.83 (d, J = 8.24 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.62, 127.63, 127.72, 128.53, 129.07, 129.97, 131.11, 132.46, 137.74, 141.95, 144.40. HRMS-ESI(m/z): calcd for $C_{15}H_{15}O_2S$ ($M+H^+$): 259.0793, found 259.0794.

4.3.5. *(E)-1-Methyl-2-(2-tosylvinyl)benzene (**3e**)*. Light yellow solid, mp 62–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 2.46 (s, 3H), 6.77 (d, *J* = 15.28 Hz, 1H), 7.19–7.23 (m, 2H), 7.28–7.30 (m, 1H), 7.35 (d, *J* = 7.96 Hz, 2H), 7.42–7.44 (m, 1H), 7.82–7.85 (m, 2H) 7.94 (d, *J* = 15.32 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.80, 21.64, 126.45, 126.80, 127.70, 128.39, 129.97, 130.84, 131.02, 131.29, 137.64, 138.15, 139.58, 144.37. HRMS-ESI(m/z): calcd for $C_{16}H_{17}O_2S$ ($M+H^+$): 273.0949, found 273.0948.

4.3.6. *(E)-1-Methyl-3-(2-tosylvinyl)benzene (**3f**)*. Light yellow solid, mp 74–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.43 (s, 3H), 6.83 (d, *J* = 15.40 Hz, 1H), 7.27–7.28 (m, 3H), 7.34 (d, *J* = 8.00 Hz, 2H), 7.39 (d, *J* = 8.28 Hz, 1H), 7.63 (d, *J* = 15.40 Hz, 1H) 7.82 (d, *J* = 8.28 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.27, 21.63, 124.34, 125.76, 127.22, 127.66, 127.91, 128.92, 129.09, 129.94, 131.94, 138.79, 142.12, 144.34. HRMS-ESI(m/z): calcd for $C_{16}H_{17}O_2S$ ($M+H^+$): 273.0949, found 273.0946.

4.3.7. *(E)-1-Fluoro-4-(2-tosylvinyl)benzene (**3g**)*. White solid, mp 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 6.78 (d, *J* = 15.40 Hz, 1H), 7.05–7.11 (m, 2H), 7.35 (d, *J* = 8.04 Hz, 2H), 7.45–7.50 (m, 2H), 7.62 (d, *J* = 15.40 Hz, 1H), 7.81–7.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.64, 116.32 (d, *J* = 21.94 Hz), 127.42, 127.73, 128.73, 130.02, 130.55, 137.67, 140.62, 144.49, 164.32 (d, *J* = 251.29 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): –111.73. HRMS-ESI(m/z): calcd for $C_{15}H_{14}FO_2S$ ($M+H^+$): 276.0699, found 276.0702.

4.3.8. *(E)-1-Bromo-2-(2-tosylvinyl)benzene (**3h**)*. Yellow solid, mp 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 6.84 (d, *J* = 15.36 Hz, 1H), 7.22–7.26 (m, 1H), 7.28–7.32 (m, 1H), 7.36 (d, *J* = 8.00 Hz, 2H), 7.47–7.50 (m, 1H), 7.84 (d, *J* = 8.28 Hz, 2H), 8.03 (d, *J* = 15.40 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.65, 125.49, 127.82, 127.85, 128.17, 130.02, 130.40, 131.97, 132.47, 133.55, 137.14, 140.35, 144.62. HRMS-ESI(m/z): calcd for $C_{15}H_{14}BrO_2S$ ($M+H^+$): 336.9898, found 336.9895.

4.3.9. *(E)-1-Bromo-3-(2-tosylvinyl)benzene (**3i**)*. Yellow solid, mp 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 6.86 (d, *J* = 15.40 Hz, 1H), 7.36 (d, *J* = 8.16 Hz, 2H), 7.38–7.41 (m, 2H), 7.52–7.54 (m, 1H), 7.58 (d, *J* = 15.44 Hz, 1H), 7.61–7.62 (m, 1H), 7.82 (d, *J* = 8.28 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.66, 123.11, 127.21, 127.79, 129.11, 129.70, 130.05, 130.56, 131.04, 133.84, 134.43, 140.06, 144.68. HRMS-ESI(m/z): calcd for $C_{15}H_{14}BrO_2S$ ($M+H^+$): 336.9898, found 336.9897.

4.3.10. *(E)-1-Bromo-4-(2-tosylvinyl)benzene (**3j**)*. Yellow solid, mp 80–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 6.84 (d, *J* = 15.40 Hz, 1H), 7.32–7.36 (m, 4H), 7.51–7.54 (m,

2H), 7.59 (d, *J* = 15.44 Hz, 1H), 7.82 (d, *J* = 8.28 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.66, 125.52, 127.76, 128.25, 129.87, 130.04, 131.32, 132.33, 137.37, 140.49, 144.61. HRMS-ESI(m/z): calcd for $C_{15}H_{14}BrO_2S$ ($M+H^+$): 336.9898, found 336.9897.

4.3.11. *(E)-1-(2-Tosylvinyl)-3,5-bis(trifluoromethyl)benzene (**3k**)*. Light yellow solid, mp 64–66 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 7.02 (d, *J* = 15.48 Hz, 1H), 7.38 (d, *J* = 8.24 Hz, 2H), 7.70 (d, *J* = 15.52 Hz, 1H), 7.85 (d, J = 8.28 Hz, 2H), 7.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.71, 121.42, 124.15, 128.03, 130.23, 131.23, 132.51, 134.61, 136.59, 137.99, 145.19; ^{19}F NMR (376 MHz, $CDCl_3$): –63.01. HRMS-ESI(m/z): calcd for $C_{17}H_{13}F_6O_2S$ ($M+H^+$): 395.0540, found 395.0540.

4.3.12. *(2-Tosylethene-1,1-diyl)dibenzene (**3l**)*. Light yellow solid, mp 56–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.99 (s, 1H), 7.08–7.11 (m, 2H), 7.15 (d, *J* = 8.04 Hz, 2H), 7.19–7.21 (m, 2H), 7.28–7.32 (m, 4H), 7.35–7.38 (m, 2H), 7.47 (d, *J* = 8.28 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.57, 127.70, 127.81, 128.21, 128.57, 128.84, 128.94, 129.33, 129.77, 130.23, 135.57. HRMS-ESI(m/z): calcd for $C_{21}H_{19}O_2S$ ($M+H^+$): 335.1106, found 335.1104.

4.3.13. *1-(tert-Butyl)-4-(1-chloro-2-tosylethyl)benzene (**3m'**)*. Light yellow solid, mp 91–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 9H), 2.38 (s, 3H), 3.85-3.98 (m, 2H), 5.33 (t, *J* = 6.96 Hz, 1H), 7.15–7.20 (m, 4H), 7.23–7.24 (m, 1H) 7.41 (s, 1H), 7.58 (d, *J* = 6.96 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.62, 31.24, 34.62, 55.10, 64.05, 125.77, 126.85, 128.16, 129.65, 135.39, 136.29, 144.61, 152.30. HRMS-ESI(m/z): calcd for $C_{19}H_{24}ClO_2S$ ($M+H^+$): 351.1186, found 351.1187.

4.3.14. *(E)-1-Methoxy-4-(2-(phenylsulfonyl)vinyl)benzene (**3n**)*. Light yellow solid, mp 69–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.71 (d, *J* = 15.36 Hz, 1H), 6.88–6.92 (m, 2H), 7.42–7.46 (m, 2H), 7.52–7.56 (m, 2H), 7.59–7.66 (m, 2H), 7.93–7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.45, 114.53, 124.43, 124.99, 127.52, 129.28, 130.40, 133.18, 141.15, 142.32, 162.09. HRMS-ESI(m/z): calcd for $C_{15}H_{15}O_3S$ ($M+H^+$): 275.0742, found 275.0745.

4.3.15. *(E)-1-((4-Methoxystyryl)sulfonyl)-2-methylbenzene (**3o**)*. Light yellow solid, mp 83–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (s, 3H), 3.84 (s, 3H), 6.70 (dd, *J* = 15.36 Hz, *J* = 3.00 Hz, 1H), 6.90–6.92 (m, 2H), 7.28–7.32 (m, 1H), 7.36–7.40 (m, 1H), 7.43–7.46 (m, 2H), 7.49 (td, *J* = 7.50 Hz, *J* = 1.30 Hz, 1H), 7.63 (d, *J* = 15.36 Hz, 1H), 8.11 (dd, *J* = 7.88 Hz, *J* = 1.16 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.33, 55.46, 114.54, 123.81, 124.99, 126.65, 129.29, 130.35, 132.55, 133.42, 137.93, 142.66, 162.08. HRMS-ESI(m/z): calcd for $C_{16}H_{17}O_3S$ ($M+H^+$): 289.0898, found 289.0897.

4.3.16. *(E)-1-Methoxy-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (**3p**)*. Brown yellow solid, mp 79–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 3.87 (s, 3H), 6.69 (d, *J* = 15.36 Hz, 1H), 6.88–6.91 (m, 2H), 6.98–7.02 (m, 2H), 7.40-7.44 (m, 2H), 7.58 (d, *J* = 15.36 Hz, 1H), 7.84–7.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.43, 55.68, 114.48, 114.49, 125.12, 125.15, 129.74, 130.25, 132.68, 141.20, 161.91, 163.41. HRMS-ESI(m/z): calcd for $C_{16}H_{17}O_4S$ ($M+H^+$): 305.0848, found 305.0852.

4.3.17. *(E)-1-Chloro-4-((4-methoxystyryl)sulfonyl)benzene (**3q**)*. Light yellow solid, mp 112–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.68 (d, *J* = 15.32 Hz, 1H), 6.91 (d, *J* = 8.36 Hz, 2H), 7.44 (d, *J* = 8.36 Hz, 2H), 7.51 (d, *J* = 8.20 Hz, 2H), 7.63 (d, *J* = 15.28 Hz, 1H), 7.87 (d, J = 8.24 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.47, 114.58, 123.95, 124.80, 129.03, 129.60, 130.49, 139.71, 139.85, 142.87, 162.25. HRMS-ESI(m/z): calcd for $C_{15}H_{14}ClO_3S$ ($M+H^+$): 309.0352, found 309.0354.

4.3.18. *(E)-1-Bromo-4-((4-methoxystyryl)sulfonyl)benzene (**3r**)*. Yellow solid, mp 114–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.68 (d, *J* = 15.32 Hz, 1H), 6.91 (d, *J* = 8.56 Hz, 2H), 7.43 (d, *J* = 8.60 Hz, 2H), 7.61–7.68 (m, 3H), 7.80 (d, *J* = 8.44 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.47, 114.58, 123.88, 124.78, 128.38, 129.10, 130.49, 132.58, 140.24, 142.92, 162.25. HRMS-ESI(m/z): calcd for $C_{15}H_{14}BrO_3S$ ($M+H^+$): 352.9847, found 352.9848.

4.3.19. *(E)-1-(2-(Ethylsulfonyl)vinyl)-4-methoxybenzene (**3s**)*. Yellow solid, mp 78–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (t, *J* = 7.46 Hz, 3H), 3.08 (q, *J* = 7.45 Hz, 2H), 3.85 (s, 3H), 6.66 (d, *J* = 15.44 Hz, 1H), 6.92–6.95 (m, 2H), 7.46–7.49 (m, 2H), 7.54 (d, *J* = 15.44 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.34, 49.57, 55.48, 114.58, 121.08, 124.87, 130.39, 144.88, 162.19. HRMS-ESI(m/z): calcd for $C_{11}H_{15}O_3S$ ($M+H^+$): 227.0742, found 227.0744.

4.3.20. *(E)-2-((4-(tert-Butoxy)styryl)sulfonyl)thiophene (**3t**)*. Light yellow solid, mp 68–70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (s, 9H), 6.84 (d, *J* = 15.28 Hz, 1H), 6.98–7.01 (m, 2H), 7.12–7.14 (m, 1H), 7.42 (d, *J* = 8.60 Hz, 2H), 7.64 (d, *J* = 15.32 Hz, 1H), 7.67 (dd, *J* = 4.96 Hz, *J* = 1.24 Hz, 1H), 7.70 (dd, *J* = 3.76 Hz, *J* = 1.24 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.86, 79.67, 123.64, 125.93, 126.78, 127.96, 129.74, 133.22, 133.66, 141.94, 158.75. HRMS-ESI(m/z): calcd for $C_{16}H_{19}O_3S_2$ ($M+H^+$): 323.0776, found 323.0774.

4.3.21. *(E)-1-Chloro-4-(2-((4-fluorophenyl)sulfonyl)vinyl)benzene (**3u**)*. White solid, mp 93–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (d, *J* = 15.36 Hz, 1H), 7.20–7.26 (m, 2H), 7.36–7.43 (m, 4H), 7.63 (d, *J* = 15.40 Hz, 1H), 7.94–7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.74 (d, *J* = 22.54 Hz), 127.72, 129.47, 129.77, 130.59, 130.71, 136.56, 137.43, 141.18, 165.72 (d, *J* = 254.78 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): –103.34. HRMS-ESI(m/z): calcd for $C_{14}H_{11}ClFO_2S$ ($M+H^+$): 297.0152, found 297.0150.

4.3.22. *(E)-1-Bromo-3-((4-chlorostyryl)sulfonyl)benzene (**3v**)*. Yellow solid, mp 65–67 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (d, *J* = 15.40 Hz, 1H), 7.37–7.39 (m, 2H), 7.42–7.46 (m, 3H), 7.65 (d, *J* = 15.40 Hz, 1H), 7.74–7.77 (m, 1H), 7.87–7.89 (m, 1H), 8.08 (t, *J* = 1.76 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.36, 126.26, 127.11, 129.48, 129.88, 130.60, 130.93, 136.58, 137.59, 141.99, 142.37. HRMS-ESI(m/z): calcd for $C_{14}H_{11}BrClO_2S$ ($M+H^+$): 356.9352, found 356.9351.

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Supplementary Material

Supplementary data associated with this article can be found, in the online version, at doi:

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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