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Note

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Electron Donor-Acceptor (EDA) Complex Enabled Decarboxylative Sulfonylation of Cinnamic Acids under Visible Light Irradiation

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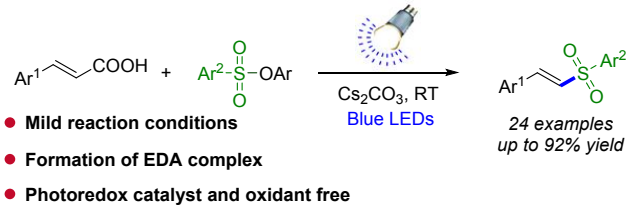
Supporting Information

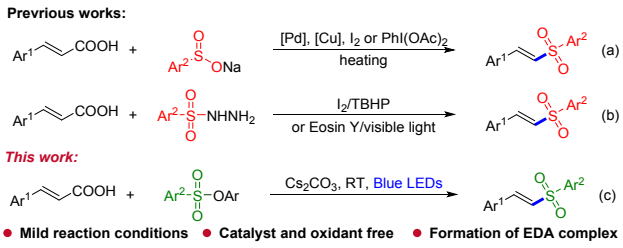


ABSTRACT: Visible light-induced decarboxylative sulfonylation of cinnamic acids with aryl sulfonate phenol esters enabled by the electron donor-acceptor (EDA) complex is developed. The method offers a mild and green approach for the synthesis of vinyl sulfones with excellent functional group compatibility under photocatalyst and oxidant free conditions.

Decarboxylative cross-couplings of carboxylic acids are widely used in biological and chemical synthesis[1] owing to the abundance of carboxylic acids and producing CO_2, an innocuous compound, as the sole by-product.[2] Apart from the transition-metal catalyzed decarboxylative processes,[3] recently, visible light-promoted decarboxylative functionalization of carboxylic acids or their derivatives has attracted considerable research interests due to its high efficiency and excellent functional group compatibility.[4] However, most of the developed decarboxylative reactions enabled by visible light photoredox catalysis required the use of photosensitizers (the polypyridyl metal complexes[5] and organic dyes[6]) and the complicated preparation procedures make its commercial application obstructed. There is no doubt that the development of photocatalyst-free decarboxylation reactions is highly desirable, yet a challenging goal.[7]

Vinyl sulfones (α,β-unsaturated sulfones) are commonly used subunits in organic compounds and important raw materials in the fields ranging from pharmaceuticals to materials science.[8] They can be further manipulated into other useful functional groups due to its chemical versatility.[9] Consequently, a large number of synthetic methodologies have been devoted towards the facile synthesis of vinyl sulfones.[10] Among the reactions developed, decarboxylative sulfonylation of cinnamic acids are one of the most attractive methods. In 2014, Guo and co-workers reported a vinyl sulfones synthesis through a Cu(II)-catalyzed decarboxylative sulfonylation of cinnamic acids with sodium sulfonates (Scheme 1a).[11a] Apart from copper, other transition metal salts or strong oxidants can also promote this transformation with good results (Scheme 1a).[11b-d] Similar at the same time, Singh *et al.* reported a I_2/TBHP (tert-butyl hydroperoxide)-promoted decarboxylative sulfonylation of cinnamic acids with sulfonyl hydrazides (Scheme 1b).[12] Despite those established methodologies are efficient, limitations or drawbacks still remain, such as harsh reaction conditions, the requirement of strong oxidants or transition-metals. Recently, the group of Cai realized a visible light-promoted decarboxylative sulfonylation of cinnamic acids with sulfonyl hydrazides by using oxygen as the sole terminal oxidant (Scheme 1b).[13] However, eosin Y are required to serve as the photoredox catalyst to run the process. It is still an important objective to discover new and efficient decarboxylative method to facile synthesis of vinyl sulfones from cinnamic acids, especially under oxidant and catalyst free reaction conditions.

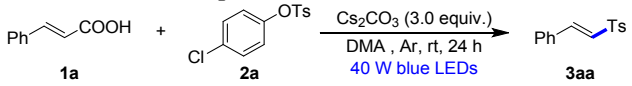
Scheme 1. Synthesis of Vinyl Sulfones from Cinnamic Acids



Within the frame of our ongoing research interests devoted to the development of valuable and efficient radical reactions,[14] we describe herein a visible light-induced radical

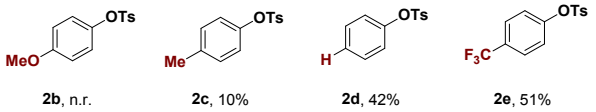
decarboxylative sulfonylation of cinnamic acids with aryl sulfonate phenol esters (Scheme 1c). It is worth noting that photoredox catalyst and oxidant were not required to run the reaction and this transformation proceeded at room temperature under blue LED irradiation by the formation of electron donor-acceptor (EDA) complex.[18]

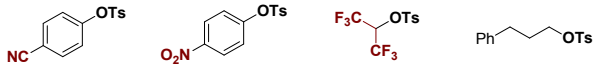
Table 1. Reaction Optimization between 1a and 2a[a]



1a 2a 3aa

entry	deviation from standard conditions	yield (%)[b]
1	None	85
2	DMF instead of DMA	65
3	DMSO instead of DMA	75
4	THF instead of DMA	N.R.
5	Acetone instead of DMA	N.R.
6	CH_3CN instead of DMA	N.R.
7	K_2CO_3 instead of Cs_2CO_3	trace
8	Na_2CO_3 instead of Cs_2CO_3	N.R.
9	K_2HPO_4 instead of Cs_2CO_3	N.R.
10	Cs_2CO_3 (2.0 equiv.)	55
11	**2a** (2.0 equiv.)	71
12	**2a** (5.0 equiv.)	87
13	Without Cs_2CO_3	N.R.
14	In the dark	N.R.

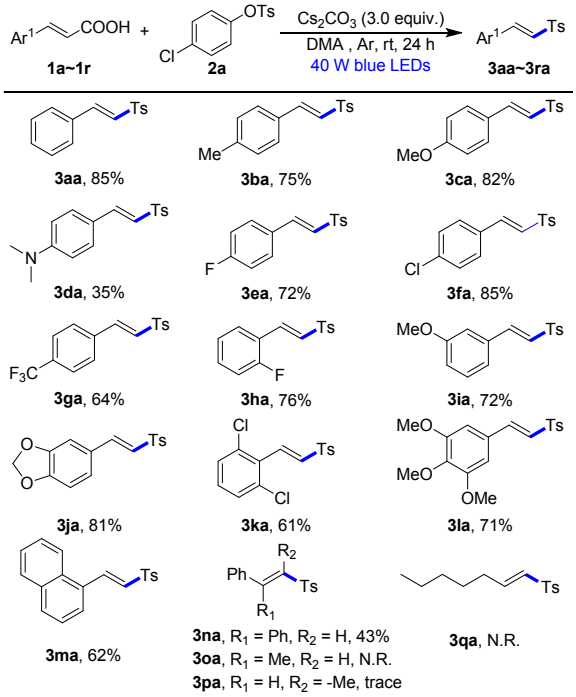




[a] Reaction conditions: Reaction condition: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), Cs_2CO_3 (0.6 mmol, 3.0 equiv.) in DMA (2.0 mL), irradiation by 40 W blue LEDs at room temperature for 24 h under argon atmosphere. [b] Isolated yield.

The optimized reaction condition is displayed in entry 1, Table 1. Irradiation of a mixture of (*E*)-cinnamic acid **1a**, 4-chlorophenyl 4-methylbenzenesulfonate **2a** and Cs_2CO_3 in N,N-dimethylacetamide (DMA) at room temperature for 24 h delivered the desired (*E*)-1-methyl-4-(styrylsulfonyl)benzene 3aa in 85% isolated yield. Employment of DMSO (dimethyl sulfoxide) and DMF (dimethylformamide) as the solvent instead of DMA resulted in a decreased yield (Table 1, entries 2 and 3). Switching to other reaction medias commonly used in chemical synthesis was not productive (Table 1, entries 4-6). It should be pointed out that other Brønsted bases, such as K_2CO_3, Na_2CO_3 and K_2HPO_4 were not suitable for this decarboxylative sulfonylation process (Table 1, entries 7-9). Lowering the equivalents of base and tosylate **2a** played a detrimental role as well (Table 1, entries 10 and 11). However, no obviously increased yield was observed by increasing the amount of tosylate **2a** from 3 equivalents to 5 equivalents (Table 1, entry 12). Moreover, control experiments clearly revealed that the reaction was completely shut down in the absence of light or Brønsted base (Table 1, entries 13 and 14). Interestingly, it was observed that the electronic effect of the tosylates **2** played a crucial role for the highly efficient transformation. Replacement of the chlorine atom of **2a** with other substituents ranging from electron donating to electron-withdrawing in character exhibited less efficiency (**2b-2g**). The aliphatic alcohol derived tosylates **2h** and **2i** were also not suitable for this transformation.

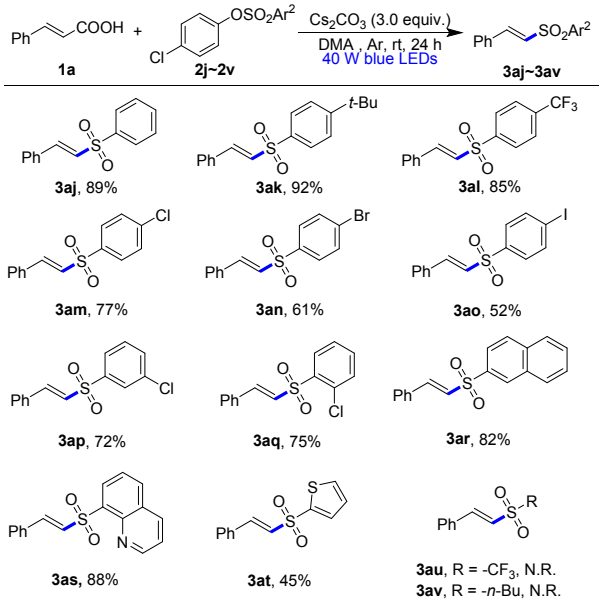
Scheme 2. Reaction Scope with Respect to Cinnamic Acids [ab]



[a] **1a~1q** (0.2 mmol), **2a** (0.6 mmol), Cs_2CO_3 (0.6 mmol) in DMA (2.0 mL), irradiation by 40 W blue LEDs at room temperature for 24 h under argon atmosphere. [b] Isolated yield.

With the optimal reaction conditions in hand, we next set out to investigate the scope with respect to cinnamic acids. As the results summarized in Scheme 2, a wide range of electron-rich and electron-deficient substituents can be successfully introduced at different positions on the aryl ring of cinnamic acids, affording the corresponding vinyl sulfones **3aa-3ia** in good yields. The aryl di-substituted cinnamic acids **1j**, **1k** and aryl tri-substituted cinnamic acid **1l** are also amenable substrates for the transformation. Moreover, the mild reaction conditions enable a broad range of functional groups to be tolerated, including ester (**3ca**), dimethylamine (**3da**), fluorine (**3ea**, **3ha**), chlorine (**3fa**), trifluoromethyl (**3ga**), and acetal groups (**3ja**). The 3,3-diphenylacrylic acid **3n** is also suitable, albeit with relatively low yield (**3na**, 43%). Unfortunately, for the cinnamic acid derivatives bearing alkyl substituents at alpha- or beta-carbon (**3o–3q)**, the reaction was limited.

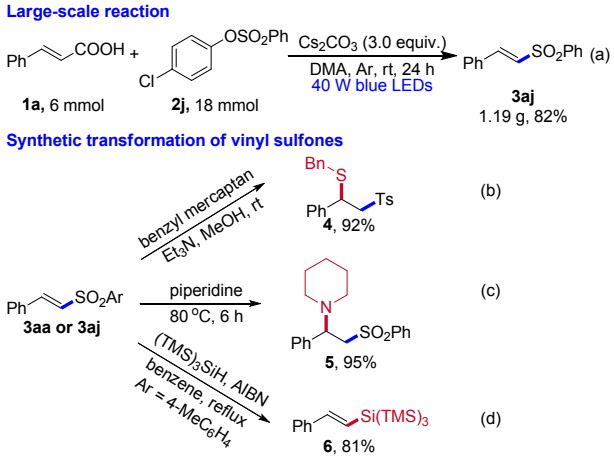
Scheme 3. Reaction Scope with Respect to Aryl Sulfonate Phenol Esters 2[a]



[a]**1a** (0.2 mmol), **2j~2v** (0.6 mmol), Cs_2CO_3 (0.6 mmol) in DMA (2.0 mL), irradiation by 40 W blue LEDs at room temperature for 24 h under argon atmosphere. [b] Isolated yield.

Next, the scope of the reaction with respect to aryl sulfonate phenol esters 2 was examined (Scheme 3). Incorporation of both electron-donating group (-^{t}Bu) and electron-withdrawing group (-CF_3, -Cl, -Br, -I) at the para-position of Ar^2 ring did not affect the reaction efficiency apparently, giving the corresponding coupling adducts **3ak**-**3ao** in good to excellent yields. Moreover, the arylsulfonate phenol esters bearing substituents at *meta*- and *ortho*-position were also amenable substrates under the optimum condition (**3ap, 3aq**). Substrates possessing a naphthalenyl (**2r**), quinoline (**2s**) or thiophene (**2t**) skeleton were also accommodated in the transformation, which demonstrated the potential application in the synthesis of the medical intermediates. Unfortunately, alkylsulfonates such as butylsulfonate and trifluoromethylsulfonate were unreactive (**2u**, **2v**).

Scheme 4. Follow-up Chemistry



The preparative utility of this method can be further demonstrated by investigating the follow-up chemistry as shown in Scheme 4. First, a large-scale experiment of **1a** (6 mmol) and **2j** (18 mmol) was carried out to give the desired product **3aj** in 82% isolated yield (Scheme 4a). More significantly, the vinyl sulfone products can be easily converted to other important organic molecules. For instance, conjugate Michael addition of vinyl sulfones with benzenemethanethiol[15] and pyrrolidine[16] was conducted to deliver the adduct **4** and **5** in excellent yield (Scheme 4b and 4c). Vinyl silane **6**, a valuable synthetic intermediate, can also be easily prepared in high yield with vinyl sulfone as the starting material under radical reaction conditions (Scheme 4d).[17]

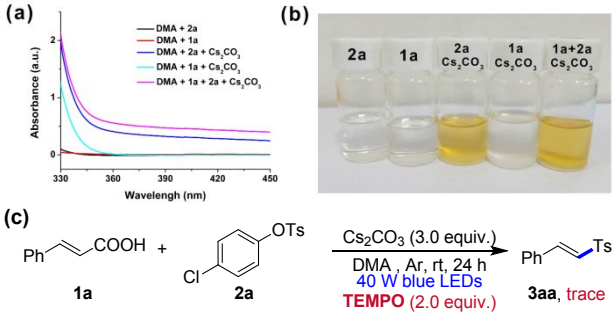
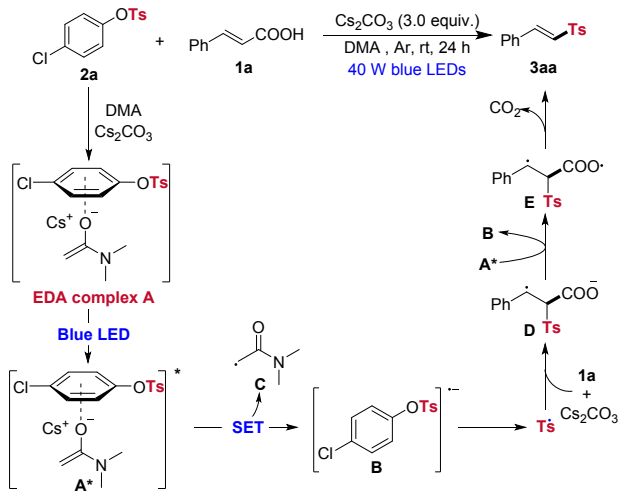


Figure 1. (a) UV-vis experiments; (b) Electronic photos of DMA solution with different components; (c) Radical trapping experiment.

To confirm the photoactive species of this catalyst-free decarboxylative process, a series of optical absorption spectra of the solution were recorded. Ultraviolet-visible spectroscopy (UV/Vis) measurements were conducted with a mixture of stoichiometric amounts of cinnamic acid **1a**, aryl sulfonate phenol ester **2a**, and Cs_2CO_3 in DMA (Figure 1a). The reaction mixture exhibited a clear absorption onset that overlaps with the blue LED wavelength, which explained the essential role of visible light irradiation. Control experiments indicated that no obvious change of the absorption was observed when the cinnamic acid **1a** was removed from the reaction mixture. As shown in Figure 1b, the solution developed a yellowish colour change from colourless when **2a** was mixed with Cs_2CO_3 in DMA, and its optical absorption spectra showed a bathochromic displacement in the visible region, which is diagnostic of an EDA complex.[18] Furthermore, the radical trapping experiment was conducted using the TEMPO (2,2,6,6-tetramethyl-4-piperidinol) as the

radical scavenger (Figure 1c). Only trace amount of product **3aa** was observed indicating a radical mechanism.

Scheme 5. Plausible Reaction Mechanism



Based on the experimental evidence in combination with previous literature reports, a plausible reaction mechanism was proposed in Scheme 5. Initially, an electron donor-acceptor (EDA) complex **A**[18,10j] was formed between aryl sulfonate phenol ester and DMA with the assistance of Cs_2CO_3. Under visible light irradiation, the excited complex **A*** underwent a single electron transfer (SET)[19] to deliver radical anion species **B** and carbon-centered radical intermediate **C**. Fragmentation of **B** provided the sulfonyl radical which subsequently added to the double bond of cinnamic acid to give benzyl radical **D**. Single electron oxidation of benzyl radical **D** by excited complex **A*** afforded **E** and regenerated anion radical **B**.[20] Finally, decarboxylation of **E** produced the final vinyl sulfone product **3aa**.

In summary, we have developed a visible light-induced decarboxylative sulfonylation of cinnamic acids with aryl sulfonate phenol esters under photoredox catalyst and oxidant free conditions. Mechanistic investigation revealed that the EDA complex was formed as the key photoactive species in the reaction system. This method provided a green and convenient approach for the preparation of important vinyl sulfones in good yields with excellent functional group compatibility. More importantly, the large-scale reaction and the synthetic application of the formed vinyl sulfones to other important organic molecules further rendered this approach attractive and valuable

EXPERIMENTAL SECTION

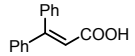
General Information. All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard Schlenk techniques. All other solvents and reagents were purified according to standard procedures or were used as received from Alfa Aesar, TCI, Aldrich, Fluka, Acros or ABCR. The starting materials were synthesized according to literature procedures. TLC was performed using Merck silica gel 60 F-254 plates, detection of compounds with UV light. Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63 µm) applying a pressure of about 0.2 bar. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ^{1}H NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). Mass spectra were recorded on a Finnigan MAT 4200S, a Bruker Daltonics Micro Tof, a Waters-Micromass Quatro LCZ (ESI); peaks are given in m/z (% of basis peak). All photolytic reactions were performed using 40 W Kessil Blue LED lamps (PR160-456 nm, 100% intensity).

Follow-up Chemistry. Cinnamic acid **1a** (1.0 equiv., 6 mmol), arene sulfonate ester 2 h (3 equiv., 18 mmol), Cs_2CO_3 (3.0 equiv., 18 mmol) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three cycles). To these solids, anhydrous DMA (50 mL) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under the irradiation of a 40 W blue LEDs at room temperature for 24 h. The mixture was quenched with saturated NaCl solution and extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and concentrated under vacuo. The product 3ah was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate = 10:1 as eluent (1.19 g, 82% yield).

General Procedure for the synthesis of aryl sulfonate esters: An oven dried round bottom flask was charged under stream of argon with corresponding arenesulfonyl chloride (12 mmol, 1.2 equiv.), DCM (40 mL), corresponding phenol (10 mmol, 1 equiv.), triethylamine (2.12 mL, 15 mmol, 1.5 equiv.) and stirred at 0 ℃ until completion (monitored by GC/MS). Reaction mixture was then diluted with 40 mL H_2O and extracted 3 times with 25 mL DCM. Combined organic phases were dried over magnesium sulfate, filtered through short celite pad and concentrated under reduced pressure. Purification by column chromatography (petroleum ether/ethyl acetate) afforded corresponding arene sulfonate ester.

General Procedure one (GP 1) for the synthesis of vinyl sulfones: Cinnamic acid 1 (1.0 equiv., 0.2 mmol), arene sulfonate ester 2 (3.0 equiv., 0.6 mmol), Cs_2CO_3 (3.0 equiv., 0.6 mmol) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (three times). Then, anhydrous DMA (2.0 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of a 40 W blue LEDs at room temperature for 24 h. After that, the mixture was quenched with sat. NaCl solution and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuo. The crude product was purified by flash column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate as eluent.

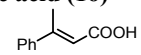
3,3-diphenylacrylic acid (1n)[21]



1n was synthesized according to the reported procedure as white solid (1.38g, 62%). Eluent: petroleum ether/ethyl acetate/acetic acid = 2:2:0.01. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.38 – 7.17 (m, 10H), 6.31 (s, 1H). ^{13}C{^{1}H}

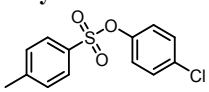
NMR (101 MHz, $CDCl_3$) δ 171.2, 159.0, 140.8, 138.4, 129.7, 129.3, 128.7, 128.5, 128.4, 127.9, 116.5.

***(E)*-3-phenylbut-2-enoic acid (1o)**[22]



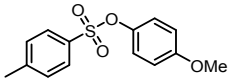
1o was synthesized according to the reported procedure as white solid (1.54g, 95%). Eluent: petroleum ether/ethyl acetate/acetic acid = 2:2:0.01. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.42 – 7.37 (m, 3H), 6.20 – 6.16 (m, 1H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 158.5, 142.0, 129.3, 128.5, 126.4, 116.4, 18.3.

4-chlorophenyl 4-methylbenzenesulfonate (2a)[23]



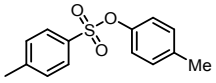
2a was synthesized according to the General Procedure as a white solid in 95% yield (2.68 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.27 – 7.21 (m, 2H), 6.96 – 6.87 (m, 2H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.0, 145.6, 132.7, 132.0, 129.8, 129.7, 128.5, 123.7, 21.7.

4-methoxyphenyl 4-methylbenzenesulfonate (2b)[24]



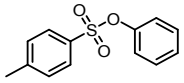
2b was synthesized according to the General Procedure as a white solid in 86% yield (2.39 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 10.2 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 6.92 – 6.84 (m, 2H), 6.80 – 6.73 (m, 2H), 3.76 (s, 3H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.2, 145.2, 143.1, 132.4, 129.6, 128.5, 123.3, 114.4, 55.5, 21.6.

***p*-tolyl 4-methylbenzenesulfonate (2c)**[24]



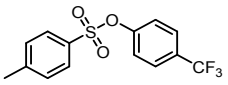
2c was synthesized according to the General Procedure as a white solid in 90% yield (2.36 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.7 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 7.06 (d, J = 7.9 Hz, 2H), 6.85 (d, J = 7.7 Hz, 2H), 2.44 (s, 3H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.5, 145.1, 136.9, 132.5, 130.0, 129.6, 128.5, 122.0, 21.6, 20.8.

phenyl 4-methylbenzenesulfonate (2d)[24]



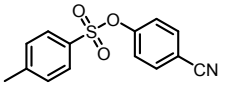
2d was synthesized according to the General Procedure as a white solid in 96% yield (2.38 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 2H), 7.34 – 7.20 (m, 5H), 6.99 – 6.96 (m, 2H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.6, 145.3, 132.4, 129.7, 129.6, 128.5, 127.1, 122.4, 21.7.

4-(trifluoromethyl)phenyl 4-methylbenzenesulfonate (2e)[25]



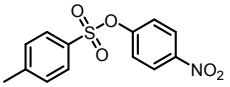
2e was synthesized according to the General Procedure as a white solid in 92% yield (2.91 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.9, 145.8, 132.0, 129.9, 129.3 (d, J = 33.0 Hz), 128.5, 127.0 (q, J = 3.7 Hz), 123.5 (d, J = 272.2 Hz), 122.8, 21.7.

4-cyanophenyl 4-methylbenzenesulfonate (2f) [26]



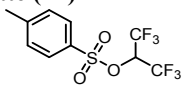
2f was synthesized according to the General Procedure as a white solid in 68% yield (1.86 g). Eluent: petroleum ether/ethyl acetate = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.64 – 7.59 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.17 – 7.10 (m, 2H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.5, 146.1, 133.9, 131.8, 130.0, 128.4, 123.4, 117.7, 111.1, 21.7.

4-nitrophenyl 4-methylbenzenesulfonate (2g)



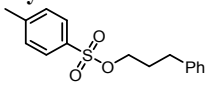
2g was synthesized according to the General Procedure as a white solid in 85% yield (2.5 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.15 (m, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 9.2 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 146.2, 146.1, 131.7, 130.1, 128.4, 125.4, 123.2, 21.7. HRMS (ESI) exact mass calculated for $C_{13}H_{12}NO_5S$: 294.0431 ([M+H]$^+$), found: 294.0430.

1,1,1,3,3,3-hexafluoropropan-2-yl 4-methylbenzenesulfonate (2h)[27]



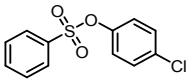
2h was synthesized according to 2j was synthesized according to the General Procedure as a colorless liquid in 95% yield (3.06 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 5.25 – 5.14 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.66 (s), 130.15 (s), 128.14 (s), 120.1 (q, J = 282 Hz), 72.1 (septet, J = 32.5 Hz).

3-phenylpropyl 4-methylbenzenesulfonate (2i)[28]



2i was synthesized according to the reported procedure as a colorless liquid (2.41g, 83%). Eluent: petroleum ether/ethyl acetate = 10:1.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.25 – 7.14 (m, 3H), 7.09 – 7.01 (m, 2H), 4.01 (t, J = 6.2 Hz, 2H), 2.67 – 2.57 (m, 2H), 2.43 (s, 3H), 2.00 – 1.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 140.4, 133.1, 129.9, 128.5, 128.4, 127.9, 126.1, 69.7, 31.4, 30.4, 21.6.

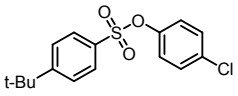
4-chlorophenyl benzenesulfonate (2j) [23]



2j was synthesized according to the General Procedure as a white solid in 95% yield (2.55 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.72 – 7.64 (m, 1H), 7.58 – 7.50 (m, 2H), 7.28 – 7.21 (m, 2H), 6.95 – 6.87 (m, 2H). ^{13}C{^{1}H}

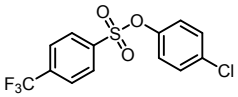
NMR (101 MHz, $CDCl_3$) δ 147.9, 135.0, 134.4, 132.9, 129.7, 129.2, 128.5, 123.7.

4-chlorophenyl 4-(tert-butyl)benzenesulfonate (2k)



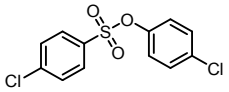
2k was synthesized according to the General Procedure as a white solid in 81% yield (2.62 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.29 – 7.22 (m, 2H), 6.98 – 6.91 (m, 2H), 1.35 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.6, 148.0, 132.7, 132.0, 129.7, 128.3, 126.2, 123.7, 35.3, 31.0. HRMS (ESI) exact mass calculated for $C_{16}H_{18}ClO_3S$: 325.0660 ([M+H]$^+$), found: 325.0662.

4-chlorophenyl 4-(trifluoromethyl)benzenesulfonate (2l)



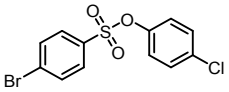
2l was synthesized according to the General Procedure as a white solid in 88% yield (2.96 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.34 – 7.24 (m, 2H), 6.99 – 6.91 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.6, 138.6, 136.0 (q, J = 33.4 Hz), 133.3, 130.0, 129.1, 126.4 (q, J = 3.7 Hz), 123.6, 122.9 (d, J = 273.3 Hz). HRMS (ESI) exact mass calculated for $C_{13}H_9ClF_3O_3S$: 336.9908 ([M+H]$^+$), found: 336.9912.

4-chlorophenyl 4-chlorobenzenesulfonate (2m) [23]



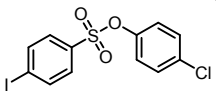
2m was synthesized according to the General Procedure as a white solid in 75% yield (2.26 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.55 – 7.46 (m, 2H), 7.32 – 7.23 (m, 2H), 6.98 – 6.89 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.8, 141.2, 133.5, 133.1, 129.9, 129.6, 123.6. (One carbon is overlapped).

4-chlorophenyl 4-bromobenzenesulfonate (2n) [23]



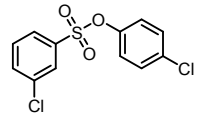
2n was synthesized according to the General Procedure as a white solid in 78% yield (2.70 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.29 – 7.23 (m, 2H), 6.97 – 6.90 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.8, 134.0, 133.1, 132.6, 129.9, 129.3, 123.6, 116.8.

4-chlorophenyl 4-iodobenzenesulfonate (2o)



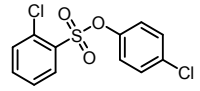
2o was synthesized according to the General Procedure as a white solid in 71% yield (2.80 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.55 – 7.48 (m, 2H), 7.30 – 7.24 (m, 2H), 6.98 – 6.89 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.8, 138.5, 134.7, 133.1, 129.9, 129.6, 123.5, 102.5. HRMS (ESI) exact mass calculated for $C_{12}H_9ClIO_3S$: 394.9000 ([M+H]$^+$), found: 394.9000.

4-chlorophenyl 3-chlorobenzenesulfonate (2p)



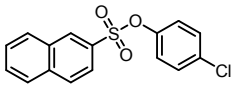
2p was synthesized according to the General Procedure as a white solid in 75% yield (2.25 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, J = 1.8 Hz, 1H), 7.75 – 7.64 (m, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.33 – 7.22 (m, 2H), 6.99 – 6.92 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 136.6, 135.6, 134.6, 133.1, 130.6, 129.9, 128.4, 126.6, 123.6. HRMS (ESI) exact mass calculated for $C_{12}H_9Cl_2O_3S$: 302.9644 ([M+H]$^+$), found: 302.9644.

4-chlorophenyl 2-chlorobenzenesulfonate (2q)



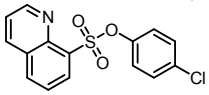
2q was synthesized according to the General Procedure as a white solid in 81% yield (2.43 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 1H), 7.66 – 7.54 (m, 2H), 7.40 –7.36 (m, 1H), 7.30 – 7.22 (m, 2H), 7.11 – 7.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 135.4, 133.3, 133.1, 133.0, 132.5, 132.2, 129.8, 127.1, 123.4. HRMS (ESI) exact mass calculated for $C_{12}H_9Cl_2O_3S$: 302.9644 ([M+H]$^+$), found: 302.9644.

4-chlorophenyl naphthalene-2-sulfonate (2r)



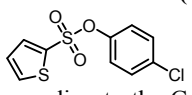
2r was synthesized according to the General Procedure as a colorless solid in 85% yield (2.70 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.0, 135.5, 132.9, 131.9, 131.8, 130.6, 129.8, 129.7, 129.6, 128.1, 128.0, 123.7, 122.8 (One carbon is overlapped). HRMS (ESI) exact mass calculated for $C_{16}H_{12}ClO_3S$: 319.0190 ([M+H]$^+$), found: 319.0193.

4-chlorophenyl quinoline-8-sulfonate (2s)



2s was synthesized according to the General Procedure as a white solid in 72% yield (2.30 g). Eluent: petroleum ether/ethyl acetate = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (dd, J = 4.2, 1.7 Hz, 1H), 8.37 (dd, J = 7.4, 1.3 Hz, 1H), 8.31 (dd, J = 8.4, 1.7 Hz, 1H), 8.15 (dd, J = 8.2, 1.3 Hz, 1H), 7.66 – 7.55 (m, 2H), 7.22 – 7.13 (m, 2H), 7.05 – 6.95 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.4, 148.3, 144.0, 136.7, 135.6, 134.2, 132.6, 129.6, 129.0, 125.3, 123.6, 122.7, 116.8. HRMS (ESI) exact mass calculated for $C_{15}H_{11}ClNO_3S$: 320.0143 ([M+H]$^+$), found: 320.0141.

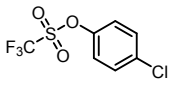
4-chlorophenyl thiophene-2-sulfonate (2t)



2t was synthesized according to the General Procedure as a white solid in 65% yield (1.78 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ

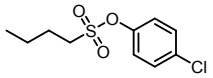
7.74 (dd, J = 5.0, 1.3 Hz, 1H), 7.59 (dd, J = 3.8, 1.3 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.12 (dd, J = 5.0, 3.9 Hz, 1H), 7.02 – 6.94 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.0, 135.6, 134.9, 134.2, 133.1, 129.8, 127.6, 123.6. HRMS (ESI) exact mass calculated for $C_{10}H_8ClO_3S_2$: 274.9598 ($[M+H]^+$), found: 274.9601.

4-chlorophenyl trifluoromethanesulfonate (2u)[29]



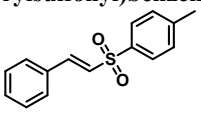
2u was synthesized according to the General Procedure as a colorless liquid in 90% yield (2.34 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 2H), 7.26 – 7.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 134.4, 130.5, 122.8, 118.7 (q, J = 320.9 Hz).

4-chlorophenyl butane-1-sulfonate (2v)



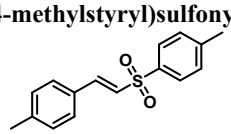
2v was synthesized according to the General Procedure as a colorless liquid in 81% yield (2.01 g). Eluent: petroleum ether/ethyl acetate = 10:1. ^1H NMR (400 MHz, CDCl3) δ 7.40 – 7.32 (m, 2H), 7.24 – 7.18 (m, 2H), 3.25 (dd, J = 8.4, 7.4 Hz, 2H), 1.96 – 1.92 (m, 2H), 1.59 – 1.45 (m, 2H), 0.99 – 0.95 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 132.8, 130.0, 123.4, 50.3, 25.4, 21.3, 13.4. HRMS (ESI) exact mass calculated for $C_{10}H_{14}ClO_3S$: 249.0347 ($[M+H]^+$), found: 249.0349.

***(E)*-1-methyl-4-(styrylsulfonyl)benzene (3aa)[30]**



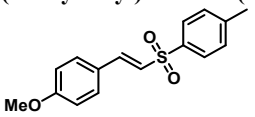
According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3aa** as a colorless solid in 85% yield (43.8 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3aa** were consistent with those in previously reported literature. ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.76 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 15.4 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.34 – 7.26 (m, 5H), 6.78 (d, J = 15.4 Hz, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.3, 141.9, 137.7, 132.4, 131.1, 129.9, 129.0, 128.5, 127.7, 127.6, 21.5.

***(E)*-1-methyl-4-((4-methylstyryl)sulfonyl)benzene (3ba)[11b]**



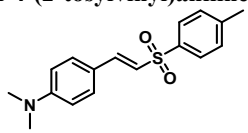
According to GP 1 with **1b** (32.4 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ba** as a colorless solid in 75% yield (40.8 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3ba** were consistent with those in previously reported literature. ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.74 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 15.4 Hz, 1H), 7.27 (dd, J = 12.4, 8.1 Hz, 4H), 7.11 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 15.4 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.2, 141.9, 141.6, 137.9, 129.8, 129.7, 129.6, 128.5, 127.6, 126.4, 21.6, 21.5.

***(E)*-1-methoxy-4-(2-tosylvinyl)benzene (3ca)[10j]**



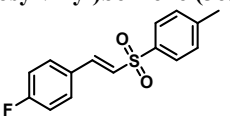
According to GP 1 with **1c** (35.6 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ca** as a colorless solid in 82% yield (47.2 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3ca** were consistent with those in previously reported literature. ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.83 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 15.4 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.95 – 6.87 (m, 2H), 6.71 (d, J = 15.4 Hz, 1H), 3.84 (s, 3H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 161.9, 144.1, 141.7, 138.1, 130.3, 129.9, 127.5, 125.0, 124.7, 114.5, 55.4, 21.6.

***(E)*-N,N-dimethyl-4-(2-tosylvinyl)aniline (3da)**



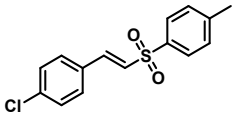
According to GP 1 with **1d** (38.2 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3da** as a pale-yellow solid in 35% yield (21.1 mg, eluent: PE/EA = 5:1). ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 15.2 Hz, 1H), 7.33 (dd, J = 17.1, 8.5 Hz, 4H), 6.61 (dd, J = 35.3, 12.0 Hz, 3H), 3.02 (s, 6H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.0, 143.7, 142.7, 138.9, 130.3, 129.7, 129.4, 127.4, 121.3, 111.9, 40.2, 21.5. HRMS (ESI) exact mass calculated for $C_{17}H_{20}NO_2S$: 302.1209 ($[M+H]^+$), found: 302.1211.

***(E)*-1-fluoro-4-(2-tosylvinyl)benzene (3ea)[31]**



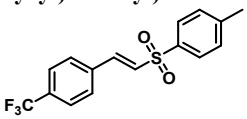
According to GP 1 with **1e** (33.2 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ea** as a colorless solid in 72% yield (39.7 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3ea** were consistent with those in previously reported literature. ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.83 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 15.4 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 8.6 Hz, 2H), 6.78 (d, J = 15.4 Hz, 1H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 164.4 (d, J = 251.8 Hz), 144.5, 140.6, 137.7, 130.5 (d, J = 8.7 Hz), 130.0, 128.7 (d, J = 3.4 Hz), 127.7, 127.4 (d, J = 2.4 Hz), 116.3 (d, J = 22.1 Hz), 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -107.92.

***(E)*-1-chloro-4-(2-tosylvinyl)benzene (3fa)[31]**



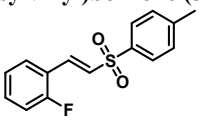
According to GP 1 with **1f** (36.5 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3fa** as a colorless solid in 85% yield (49.6 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3fa** were consistent with those in previously reported literature. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.74 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 15.4 Hz, 1H), 7.37 – 7.24 (m, 6H), 6.76 (d, J = 15.4 Hz, 1H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.5, 140.3, 137.4, 137.0, 130.9, 129.9, 129.6, 129.3, 128.2, 127.7, 21.6.

***(E)*-1-methyl-4-((4-(trifluoromethyl)styryl)sulfonyl)benzene (3ga)**



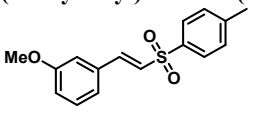
According to GP 1 with **1g** (43.2 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ga** as a colorless solid in 64% yield (41.7 mg, eluent: PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 (d, J = 8.3 Hz, 2H), 7.72 – 7.56 (m, 5H), 7.37 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 15.5 Hz, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CDCl3, 300 K): δ (ppm) = 144.8, 139.8, 137.1, 135.8, 132.5(d, J = 32.9 Hz), 130.3, 130.0, 128.66, 127.8, 126.01 (q, J = 3.8 Hz), 123.59 (d, J = 272.3 Hz), 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = - 62.97. HRMS (ESI) exact mass calculated for $C_{16}H_{14}F_3O_2S$: 327.0661 ([M+H]$^+$), found: 327.0664.

***(E)*-1-fluoro-2-(2-tosylvinyl)benzene (3ha)**



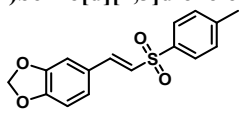
According to GP 1 with **1h** (33.2 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ha** as a colorless solid in 76% yield (41.9 mg, eluent: PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.75 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 15.6 Hz, 1H), 7.41 – 7.24 (m, 4H), 7.13 – 6.98 (m, 2H), 6.93 (d, J = 15.6 Hz, 1H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 161.5 (d, J = 255.3 Hz), 144.4, 137.5, 134.9 (d, J = 2.2 Hz), 132.5 (d, J = 8.9 Hz), 130.5 (d, J = 8.5 Hz), 130.2 (d, J = 2.6 Hz), 129.9, 127.8, 124.6 (d, J = 3.7 Hz), 120.6 (d, J = 11.5 Hz), 116.4 (d, J = 21.7 Hz), 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -112.48. HRMS (ESI) exact mass calculated for $C_{15}H_{14}FO_2S$: 277.0693 ([M+H]$^+$), found: 277.0691.

***(E)*-1-methoxy-3-(2-tosylvinyl)benzene (3ia)**[11b]



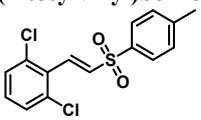
According to GP 1 with **1i** (35.6 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ia** as a colorless solid in 72% yield (41.4 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3ia** were consistent with those in previously reported literature. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.75 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 15.4 Hz, 1H), 7.30 – 7.19 (m, 3H), 6.99 (d, J = 7.6 Hz, 1H), 6.92 – 6.84 (m, 2H), 6.76 (d, J = 15.4 Hz, 1H), 3.74 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.9, 144.4, 141.8, 137.7, 133.7, 130.0, 129.9, 127.8, 127.7, 121.1, 117.0, 113.3, 55.3, 21.5.

***(E)*-5-(2-tosylvinyl)benzo[d][1,3]dioxole (3ja)**



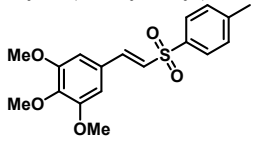
According to GP 1 with **1j** (38.4 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ja** as a colorless solid in 81% yield (48.9 mg, eluent: PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 15.3 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.03 – 6.91 (m, 2H), 6.82 (s, 1H), 6.66 (d, J = 15.3 Hz, 1H), 6.00 (s, 2H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.3, 148.5, 144.2, 141.7, 138.0, 129.9, 127.6, 126.7, 125.4, 125.2, 108.5, 106.8, 101.7, 21.6. HRMS (ESI) exact mass calculated for $C_{16}H_{15}O_4S$: 303.0686 ([M+H]$^+$), found: 303.0689.

***(E)*-1,3-dichloro-2-(2-tosylvinyl)benzene (3ka)**



According to GP 1 with **1k** (43.4 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ka** as a colorless solid in 61% yield (39.8 mg, eluent: PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 – 7.75 (m, 3H), 7.29 (dd, J = 8.2, 4.9 Hz, 4H), 7.15 (dd, J = 8.5, 7.6 Hz, 1H), 7.06 (d, J = 15.8 Hz, 1H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.6, 136.0, 134.7, 134.3, 134.2, 129.6, 128.9, 128.8, 127.9, 126.9, 20.6. HRMS (ESI) exact mass calculated for $C_{15}H_{13}C_{l2}O_2S$: 327.0008 ([M+H]$^+$), found: 327.0010.

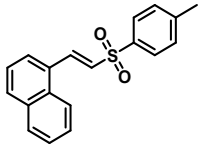
***(E)*-1,2,3-trimethoxy-5-(2-tosylvinyl)benzene (3la)**



According to GP 1 with **1l** (47.6 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3la** as a colorless solid in 71% yield (49.4 mg, eluent: PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.83 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 15.3 Hz, 1H),

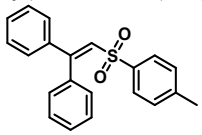
7.35 (d, J = 8.1 Hz, 2H), 6.76 (d, J = 15.3 Hz, 1H), 6.70 (s, 2H), 3.87 (d, J = 2.8 Hz, 9H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 153.5, 144.3, 142.0, 140.7, 137.9, 129.9, 127.8, 127.7, 126.7, 105.8, 61.0, 56.2, 21.6. HRMS (ESI) exact mass calculated for $C_{18}H_{21}O_5S$: 349.1104 ($[M+H]^+$), found: 349.1101.

***(E)*-1-(2-tosylvinyl)naphthalene (3ma)**



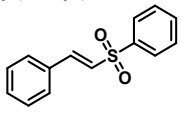
According to GP 1 with **1m** (39.6 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ma** as a colorless solid in 62% yield (38.2 mg, eluent: PE/EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.42 (d, J = 15.2 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.83 (dd, J = 12.1, 8.3 Hz, 4H), 7.69 – 7.46 (m, 3H), 7.41 – 7.35 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 15.2 Hz, 1H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.4, 138.9, 137.6, 133.6, 131.3, 131.2, 130.1, 130.0, 129.6, 128.82, 127.7, 127.2, 126.4, 125.6, 125.2, 123.0, 21.9. HRMS (ESI) exact mass calculated for $C_{19}H_{17}O_2S$: 309.0944 ($[M+H]^+$), found: 309.0945.

(2-tosylethene-1,1-diyl)dibenzene (3na)[10j]



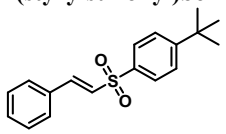
According to GP 1 with **1n** (44.9 mg, 0.200 mmol, 1.0 equiv.), **2a** (169.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3na** as a colorless solid in 43% yield (28.7 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3na** were consistent with those in previously reported literature. ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.40 (d, J = 8.3 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.19 (m, 5H), 7.14 – 7.01 (m, 5H), 6.92 (s, 1H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 154.7, 143.7, 139.3, 138.6, 135.6, 130.2, 129.8, 129.3, 128.9, 128.8 128.5, 128.2, 127.7, 127.6, 21.5.

***(E)*-(2-(phenylsulfonyl)vinyl)benzene (3aj)**[30]



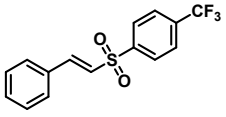
According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2j** (161.2 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3aj** as a colorless solid in 89% yield (43.4 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3aj** were consistent with those in previously reported literature. ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 – 7.81 (m, 2H), 7.62 (d, J = 15.4 Hz, 1H), 7.58 – 7.28 (m, 8H), 6.79 (d, J = 15.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.4, 140.7, 133.3, 132.3, 131.2, 129.3, 129.0, 128.5, 127.6, 127.3.

***(E)*-1-(tert-butyl)-4-(styrylsulfonyl)benzene (3ak)**[13]



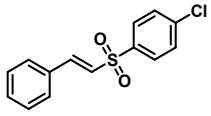
According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2k** (194.5 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ak** as a colorless solid in 92% yield (55.2 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3ak** were consistent with those in previously reported literature. ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.87 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 15.4 Hz, 1H), 7.58 – 7.34 (m, 7H), 6.86 (d, J = 15.4 Hz, 1H), 1.34 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 157.3, 141.9, 137.7, 132.5, 131.0, 129.0, 128.5, 127.6, 127.5, 126.3, 35.2, 31.0.

***(E)*-1-(styrylsulfonyl)-4-(trifluoromethyl)benzene (3al)**[32]



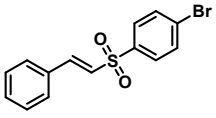
According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2l** (202.0 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3al** as a colorless solid in 85% yield (53.0 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3al** were consistent with those in previously reported literature. ^1H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.01 (d, J = 8.2 Hz, 2H), 7.70 (dd, J = 28.1, 11.8 Hz, 3H), 7.41 – 7.31 (m, 5H), 6.78 (d, J = 15.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.3, 144.0, 135.01 (q, J = 33.1 Hz), 131.9, 131.6, 129.1, 128.7, 128.2, 126.46 (q, J = 3.7 Hz), 126.2, 123.12 (d, J = 273.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = - 63.15.

***(E)*-1-chloro-4-(styrylsulfonyl)benzene1 (3am)**[30]



According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2m** (181.9 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3am** as a colorless solid in 77% yield (42.8 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3am** were consistent with those in previously reported literature. ^1H NMR c7.81 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 15.4 Hz, 1H), 7.49 – 7.30 (m, 7H), 6.76 (d, J = 15.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.0, 140.1, 139.3, 132.2, 131.4, 129.6, 129.2, 129.1, 128.5, 126.9.

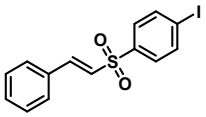
***(E)*-1-bromo-4-(styrylsulfonyl)benzene (3an)**[32]



According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2n** (208.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3an** as a colorless solid in 61% yield (39.3 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3an** were

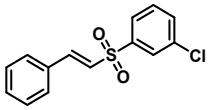
consistent with those in previously reported literature. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.74 (d, J = 8.7 Hz, 2H), 7.64 – 7.60 (m, 3H), 7.45 – 7.29 (m, 5H), 6.76 (d, J = 15.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.1, 139.8, 132.6, 132.2, 131.4, 129.2, 129.1, 128.6, 126.8.

***(E)*-1-iodo-4-(styrylsulfonyl)benzene (3ao)**



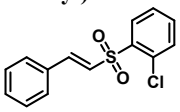
According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2o** (236.7 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ao** as a colorless solid in 52% yield (38.5 mg, eluent: PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.88 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 15.4 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.51 – 7.46 (m, 2H), 7.44 – 7.39 (m, 2H), 7.33 (dd, J = 4.7, 2.7 Hz, 2H), 6.79 (d, J = 15.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5, 140.7, 133.3, 132.4, 131.2, 129.3, 129.0, 128.5, 127.6, 127.3. HRMS (ESI) exact mass calculated for $C_{14}H_{12}IO_2S$: 370.9597 ($[M+H]^+$), found: 370.9595.

(*E*)-1-chloro-3-(styrylsulfonyl)benzene (3ap)



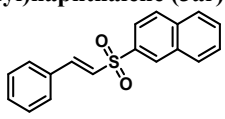
According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2p** (180.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ap** as a colorless solid in 72% yield (40.0 mg, eluent: PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 7.8, 1.5 Hz, 1H), 7.77 (d, J = 15.4 Hz, 1H), 7.57 – 7.39 (m, 8H), 7.08 (d, J = 15.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 138.2, 134.5, 132.8, 132.3, 131.9, 131.4, 130.7, 129.1, 128.7, 127.4, 125.2. HRMS (ESI) exact mass calculated for $C_{14}H_{12}ClO_2S$: 279.0241 ($[M+H]^+$), found: 279.0241.

***(E)*-1-chloro-2-(styrylsulfonyl)benzene (3aq)**



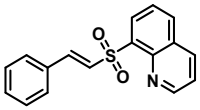
According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2q** (180.6 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3aq** as a colorless solid in 75% yield (41.7 mg, eluent: PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, J = 1.9 Hz, 1H), 7.88 – 7.80 (m, 1H), 7.71 (d, J = 15.4 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.52 – 7.38 (m, 6H), 6.85 (d, J = 15.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 141.5, 134.5, 132.5, 131.0, 130.4, 129.6, 128.1, 127.6, 126.7, 125.5, 124.7. HRMS (ESI) exact mass calculated for $C_{14}H_{12}ClO_2S$: 279.0241 ($[M+H]^+$), found: 279.0241.

***(E)*-2-(styrylsulfonyl)naphthalene (3ar)**[32]



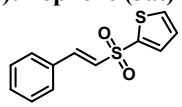
According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2r** (191.2 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3ar** as a colorless solid in 82% yield (48.2 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3ar** were consistent with those in previously reported literature. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.48 (s, 1H), 7.94 – 7.91 (m, 2H), 7.87 – 7.79 (m, 2H), 7.68 (d, J = 15.4 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.47 – 7.39 (m, 2H), 7.38 – 7.26 (m, 3H), 6.85 (d, J = 15.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5, 137.5, 135.1, 132.4, 132.3, 131.2, 129.6, 129.3, 129.2, 129.1, 129.0, 128.5, 127.9, 127.6, 127.3, 122.5.

***(E)*-8-(styrylsulfonyl)quinoline (3as)**



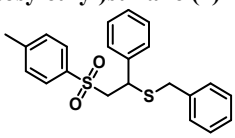
According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2s** (191.8 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3as** as a colorless solid in 88% yield (51.9 mg, eluent: PE/EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.17 (s, 1H), 8.58 (d, J = 7.1 Hz, 1H), 8.27 (d, J = 8.1 Hz, 1H), 8.08 (d, J = 18.6 Hz, 1H), 7.84 (dd, J = 41.3, 15.6 Hz, 2H), 7.69 (t, J = 7.7 Hz, 1H), 7.59 – 7.46 (m, 3H), 7.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.4, 144.0, 143.2, 138.3, 136.7, 134.1, 132.9, 130.9, 130.6, 128.9, 128.8, 128.5, 128.4, 125.7, 122.2. HRMS (ESI) exact mass calculated for $C_{17}H_{14}NO_2S$: 296.0740 ($[M+H]^+$), found: 296.0743.

***(E)*-2-(styrylsulfonyl)thiophene (3at)**[13]



According to GP 1 with **1a** (29.6 mg, 0.200 mmol, 1.0 equiv.), **2t** (164.8 mg, 0.600 mmol, 3.0 equiv.), Cs_2CO_3 (195.5 mg, 0.600 mmol, 3.0 equiv.) in 2.0 mL DMA. Purification by silica gel chromatography afforded the desired **3at** as a colorless solid in 45% yield (22.5 mg, eluent: PE/EA = 10:1). The spectroscopic data of **3at** were consistent with those in previously reported literature. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 – 7.61 (m, 3H), 7.43 – 7.37 (m, 5H), 7.17 – 7.11 (m, 1H), 6.96 (d, J = 15.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.3, 142.2, 133.8, 133.4, 132.2, 131.2, 129.0, 128.6, 127.9, 127.8.

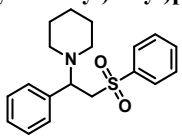
benzyl(1-phenyl-2-tosylethyl)sulfane (4)



Synthesis of 4: An oven-dried vial equipped with stirring bar was charged with vinyl sulfone **3aa** (0.2 mmol, 1.0 equiv.), benzyl mercaptan (1.0 mmol, 5.0 equiv.), triethylamine (0.3 mmol, 1.5 equiv), dry MeOH (1.0 mL) and stirred for 6 h at room temperature. After completion, the reaction mixture was concentrated under vacuo, purified by flash column chromatography on silica gel with a mixture

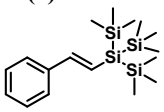
of petroleum ether and ethyl acetate (10:1) as eluent, affording the final product **4** in 92% yield (70.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.39 (d, J = 8.3 Hz, 2H), 7.22 – 7.17 (m, 3H), 7.14 – 7.00 (m, 9H), 4.08 (dd, J = 9.2, 4.8 Hz, 1H), 3.62 (dd, J = 14.6, 9.2 Hz, 1H), 3.63 – 3.37 (m, 3H), 2.30 (s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.3, 138.8, 137.1, 136.4, 129.5, 128.9, 128.7, 128.6, 127.9, 127.8, 127.7, 127.2, 61.5, 43.0, 36.0, 21.5; HRMS (ESI) exact mass calculated for C21H21S2O2: 369.0977 ([M+H]+), found: 369.0979.

1-(1-phenyl-2-(phenylsulfonyl)ethyl)piperidine (5)



Synthesis of 5: An oven-dried vial equipped with stirring bar was charged with vinyl sulfone **3aj** (0.2 mmol, 1.0 equiv.), piperidine (2.0 mmol, 10 equiv.) and stirred at 80 ℃ for 6 h. After completion, the reaction mixture was concentrated under vacuo, purified by flash column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (10:1) as eluent, affording the final product **5** in 95% yield (62.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.85 (d, J = 8.6 Hz, 2H), 7.57 (t, J = 8.5 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.26 (dd, J = 11.3, 3.2 Hz, 3H), 7.11 – 6.93 (m, 2H), 4.19 (dd, J = 8.1, 5.6 Hz, 1H), 4.04 – 3.88 (m, 1H), 3.50 (dd, J = 14.6, 5.4 Hz, 1H), 2.32 – 2.00 (m, 4H), 1.35 – 1.07 (m, 6H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.5, 134.8, 133.1, 128.7, 128.6, 128.2, 128.1, 127.7, 64.7, 57.9, 50.1 25.5, 24.0; HRMS (ESI) exact mass calculated for C19H24NO2S: 330.1522 ([M+H]+), found: 330.1525.

***(E)*-1,1,1,3,3,3-hexamethyl-2-styryl-2-(trimethylsilyl)trisilane (6)**[17]



Synthesis of 6: An oven-dried 2-neck round-bottom-flask equipped with stirring bar was charged under argon atmosphere with vinyl sulfone **3aa** (0.2 mmol, 1.0 equiv.), tris(trimethylsilyl)silane (0.6 mmol, 3.0 equiv.), AIBN (0.5 mmol, 2.5 equiv.), dry benzene (2.0 mL) and stirred under reflux for 12 h. After completion, the reaction mixture was concentrated under vacuo, purified by flash column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (10:1) as eluent, affording the final product **6** in 81% yield (56.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.44 – 7.39 (m, 2H), 7.38 – 7.33 (m, 2H), 7.28 – 7.20 (m, 1H), 6.93 (d, J = 18.8 Hz, 1H), 6.47 (d, J = 18.8 Hz, 1H), 0.27 – 0.23 (m, 27H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.4, 139.0, 128.4, 127.4, 125.9,) 122.7, 0.9.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Mechanistic studies and copies of ^{1}H NMR and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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