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Gram-Scale Synthesis of β-Sulfonyl Styrenes

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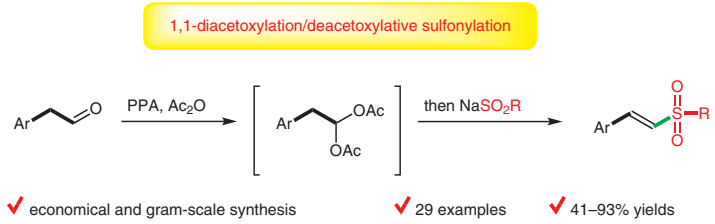

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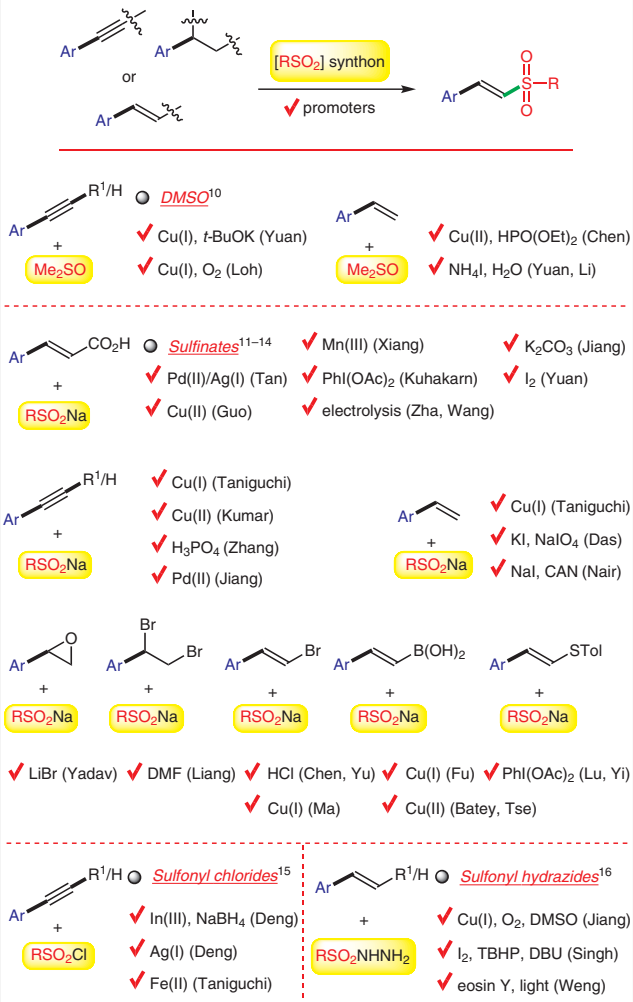
Abstract A simple and gram-scale synthesis of β-sulfonyl styrenes has been developed starting from one-pot PPA (polyphosphoric acid)-catalyzed 1,1-diacetoxylation of arylacetaldehydes ($ArCH_2CHO$) with acetic anhydride (Ac_2O) followed by deacetoxylative sulfonylation of the resulting 1,1-diacetate intermediate with sodium sulfinates (RSO_2Na) in good yields under solvent-free conditions.

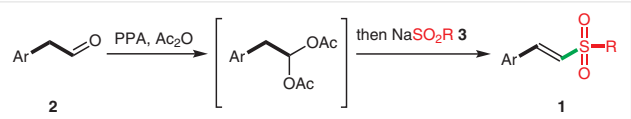
Key words β-sufonyl styrenes, sodium sulfinates, arylacetaldehydes, gram-scale synthesis

Among the sulfur-containing structures, β-sulfonyl styrenes (styryl sulfones) have attracted much attention in different fields, resulting in various synthetic strategies for their applications,[1] especially in organic building blocks,[2] natural product synthesis,[3] bioactive molecules,[4] and functionalized emitter materials.[5] Conventional synthesis for this skeleton includes (1) oxidation of vinyl sulfides,[6] (2) elimination of halosulfones,[7] (3) Horner–Wadsworth–Emmons olefination of β-phosphonate sulfones with carbonyl compounds,[8] and (4) the addition of sulfonyl halides to alkynes.[9] In contrast to these traditional strategies, recent works have focused on various sulfonyl synthon-mediated cross-coupling of aryl substrates with a triple bond (for arylacetylenes), a double bond (for cinnamic acids, styryl bromides, boronic acids, or sulfides), and a single bond (for epoxides, dibromides) under versatile reagent-initiated conditions (e.g., transition metals, oxidants, bases, acids, salts, LEDs, solvents, or electrolytes). As shown in Scheme 1, these sulfonyl sources are involved with dimethyl sulfoxide (DMSO),[10] sodium sulfinate (RSO_2Na),[11–14] sulfonyl chloride (RSO_2Cl),[15] and sulfonyl hydrazide (RSO_2HNH_2).[16] Thus, the development of a one-pot, open-vessel, and gram-scale method is highly in demand. In comparison to the above reports, we wanted to develop an economical and gram-scale synthesis of β-sulfonyl styrenes **1** without air-sensitive conditions and expensive transitional-metal catalysts. Herein, we disclose a PPA (polyphosphoric acid)-catalyzed 1,1-diacetoxylation of arylacetaldehydes **2** ($ArCH_2CHO$) with acetic anhydride (Ac_2O) followed by deacetoxylative sulfonylation of the resulting 1,1-diacetate intermediate with sodium sulfinates **3** (RSO_2Na) in moderate to good yields on a gram scale under solvent-free conditions (Scheme 2).[17] As far as we know, there have been no reports on the use of arylacetaldehydes serving as the starting materials in the formation of β-sulfonyl styrenes.

Continuing our research on Brønsted acid mediated synthetic applications,[18] herein, PPA was chosen first as the model promoter to seek optimal reaction conditions for synthesizing β-sulfonyl styrenes **1** in the presence of Ac_2O by the cross coupling of 3,4-dimethoxyphenylacetaldehyde (**2a**) [Ar = 3,4-$(MeO)_2C_6H_3$] and $TolSO_2Na$ (**3a**) at room temperature. Initially, we checked the solvent system, including solvent-containing and solvent-free conditions, respectively (Table 1, entries 1–5). When the volume of reaction solvents ($MeNO_2$ or DMAc) was increased gradually (0 → 1 → 2 → 4 mL), we were surprised to find that the reaction hardly proceeded in the presence of the solvent, while the reaction provided the desired **1a** in good yield (90%) under the solvent-free conditions. Moreover, product **1a** possessed complete *E*-stereoselectivity. With this idea in mind, four promoters (H_2SO_4, *p*-TsOH, AcOH, H_3BO_3) were examined. When the reaction mixture was treated with H_2SO_4 at room temperature for 1 hour (entry 6), a complex mixture was isolated. Changing to *p*-TsOH, 66% of **1a** was provided (entry 7). After changing promoters from stronger sulfonic-type acids to weaker acids, AcOH or H_3BO_3, the results showed that **1a** was produced in trace amounts (10% or 5%, entries 8, 9). After elevating the temperature (25 → 80 °C), the iso-



Scheme 1 Synthetic routes for β-sulfonyl styrenes

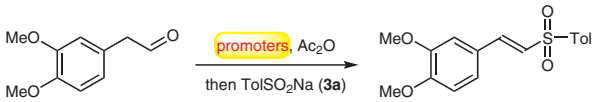


Scheme 2 Our route for β-sulfonyl styrenes

lated yields of the desired **1a** decreased slightly to 81% (entry 10). Attempts to adjust the time (4 → 10 h) afforded a similar yield (88%, entry 11). Furthermore, when we decreased the equivalent of PPA (1.0 → 0.5 → 0.1), the yields of **1a** decreased as well (entries 12, 13).

For the generation β-sulfonyl styrenes **1**, we believe that PPA should be an optimal promoter. With the results in hand, three Lewis acids ($ZnCl_2$, $InCl_3$, $BiCl_3$)[17f] were explored next. Under similar conditions, catalytic amounts (10% mol) of $InCl_3$ or $BiCl_3$ gave 69% and 76% yield, respectively; however, there was no reaction for $ZnCl_2$. Regarding a cheaper promoter, higher yield and activity, we believe that the PPA/Ac_2O combination system should be an optimal combination for the formation of **1a**. On the basis of the above optimal reaction conditions, the substrate scope and the results were explored are shown in Table 2. Using different Ar groups in **2a–p** [Ar = **a**, 3,4-$(MeO)_2C_6H_3$; **b**, Ph; **c**, 4-$MeOC_6H_4$; **d**, 3-$MeOC_6H_4$; **e**, 4-FC_6H_4; **f**, Tol; **g**, 4-PhC_6H_4; **h**, 2-naphthyl; **i**, 3,4-$CH_2O_2C_6H_3$; **j**, 3,4-$Cl_2C_6H_3$; **k**, 3,4,5-$(MeO)_3C_6H_2$; **l**, 2-furyl; **m**, 2-thienyl; **n**, 2-pyridyl; **o**, Me; **p**, 2-AcO], and different R groups in **3a–m** [Ar = **a**, Tol, **b**, Ph; **c**, Me; **d**, *n*-Bu; **e**, 4-FC_6H_4; **f**, 4-$MeOC_6H_4$; **g**, 3-MeC_6H_4; **h**, 4-*i*-PrC_6H_4; **i**, 4-BuC_6H_4; **j**, 4-*t*-BuC_6H_4; **k**, 2-styryl; **l**, (*E*)-1-CH=CH-3,4-$(MeO)_2C_6H_3$; **m**, benzyl], products **1a–ac** were synthesized in yields ranging from 41–93%. For Ar and R substituents, the electron-donating aryl groups, electron-neutral aryl groups, and electron-withdrawing aryl groups were well tolerated. Moreover, divinyl sulfones **1k** and **1l** could be prepared by the present route.[19] Especially, functionalized divinyl sulfones displayed some diverse applications in synthetic synthons, precursors of polymeric macrocycles, and biological molecules (Table 2, entries 11, 12).[19c] For the reaction of **2l–n** with a heterocyclic ring, **1z** was formed in an 84% yield; however, **1y** and **1aa** were obtained in 69% and 41% yield, respectively (entries 25–27). The reason for this could be that the furan ring (for **1y**) with lower aromaticity was more unstable than the thiophene ring (for

Table 1 Reaction Conditions[a]

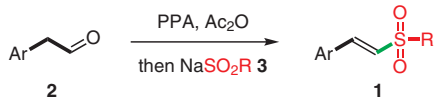


Entry	Promoters (equiv)	Solvent (mL)	Temp (°C)	Time (h)	Yield (%)[b] of **1a**
1	PPA (1.0)	–[c]	25	4	90
2	PPA 1.0)	$MeNO_2$ (1)	25	4	65
3	PPA 1.0)	$MeNO_2$ (2)	25	4	52
4	PPA (1.0)	$MeNO_2$ (4)	25	4	40
5	PPA (1.0)	DMAc (4)	25	4	18
6	H_2SO_4 (1.0)	–[c]	25	4	–[d]
7	*p*-TsOH (1.0)	–[c]	25	4	66
8	AcOH (1.0)	–[c]	25	4	10[e]
9	H_3BO_3 (1.0)	–[c]	25	4	~5[e]
10	PPA (1.0)	–[c]	80	4	81
11	PPA (1.0)	–[c]	25	10	88
12	PPA (0.5)	–[c]	25	4	57
13	PPA (0.1)	–[c]	25	4	12[e]

[a] Reactions were run on a 5.0 mmol scale with **2a**, Ac_2O (1.0 equiv), $TolSO_2Na$ (**3a**; 2.0 equiv).
[b] Isolated yields.
[c] Solvent-free conditions.
[d] Complex mixture.
[e] Compound **2a** was recovered in major amount.

1z) in a concentrated solution. Also, the nitrogen atom of the pyridine ring (for **1aa**) could block the proton to form a pyridinium such that **1a** was isolated in a lower yield. Besides the aromatic ring, reaction with **2o** with a methyl substituent (an aliphatic group) was performed (entry 28); however, **1ab** was isolated in only a 67% yield. The reason could be that **2o** has no aryl group so the double bond was not easy to form in comparison with the Ar group on skeleton **2**. As shown in Figure 1, the surrogates of ON013100,

Table 2 Synthesis of **1**[a]



2 **1**

Entry	**2**, Ar	**3**, R	**1** (%)[b]
1	**2a**, 3,4-$(MeO)_2C_6H_3$	**3a**, Tol	**1a**, 90
2	**2a**, 3,4-$(MeO)_2C_6H_3$	**3b**, Ph	**1b**, 86
3	**2a**, 3,4-$(MeO)_2C_6H_3$	**3c**, Me	**1c**, 89
4	**2a**, 3,4-$(MeO)_2C_6H_3$	**3d**, *n*-Bu	**1d**, 86
5	**2a**, 3,4-$(MeO)_2C_6H_3$	**3e**, 4-FC_6H_4	**1e**, 88
6	**2a**, 3,4-$(MeO)_2C_6H_3$	**3f**, 4-$MeOC_6H_4$	**1f**, 92
7	**2a**, 3,4-$(MeO)_2C_6H_3$	**3g**, 3-MeC_6H_4	**1g**, 90
8	**2a**, 3,4-$(MeO)_2C_6H_3$	**3h**, 4-*i*-PrC_6H_4	**1h**, 93
9	**2a**, 3,4-$(MeO)_2C_6H_3$	**3i**, 4-BuC_6H_4	**1i**, 93
10	**2a**, 3,4-$(MeO)_2C_6H_3$	**3j**, 4-*t*-BuC_6H_4	**1j**, 90
11	**2b**, Ph	**3k**, 2-styryl	**1k**, 80
12	**2a**, 3,4-$(MeO)_2C_6H_3$	**3l**, CH=CH-3,4-$(MeO)_2C_6H_3$	**1l**, 86
13	**2b**, Ph	**3m**, CH_2Ph	**1m**, 74
14	**2a**, 3,4-$(MeO)_2C_6H_3$	**3m**, CH_2Ph	**1n**, 86
15	**2b**, Ph	**3a**, Tol	**1o**, 80
16	**2c**, 4-$MeOC_6H_4$	**3a**, Tol	**1p**, 83
17	**2d**, 3-$MeOC_6H_4$	**3a**, Tol	**1q**, 80
18	**2e**, 4-FC_6H_4	**3a**, Tol	**1r**, 72
19	**2f**, Tol	**3a**, Tol	**1s**, 70
20	**2g**, 4-PhC_6H_4	**3a**, Tol	**1t**, 76
21	**2h**, 2-naphthyl	**3a**, Tol	**1u**, 81
22	**2i**, 3,4-$CH_2O_2C_6H_3$	**3a**, Tol	**1v**, 86
23	**2j**, 3,4-$Cl_2C_6H_3$	**3a**, Tol	**1w**, 82
24	**2k**, 3,4,5-$(MeO)_3C_6H_2$	**3a**, Tol	**1x**, 89
25	**2l**, 2-furyl	**3a**, Tol	**1y**, 69
26	**2m**, 2-thienyl	**3a**, Tol	**1z**, 84
27	**2n**, 2-pyridyl	**3a**, Tol	**1aa**, 41
28	**2o**, Me	**3b**, Ph	**1ab**, 67
29	**2p**, 2-AcO	**3a**, Tol	**1ac**, 80

[a] Reactions were carried out on a 5.0 mmol scale with **2**, PPA (490 mg, 1.0 equiv), Ac_2O (510 mg, 1.0 equiv), 25 °C, 10 min; then RSO_2Na **3** (2.0 equiv), 25 °C, 4 h.
[b] Isolated yields.

1m and **1n** with a skeleton of benzyl styryl sulfone, were synthesized by the gram-scale route. ON013100 has been reported as a class of non-ATP competitive molecules, and it is under evaluation as an anticancer agent.[20] Moreover, when the scale for the PPA/Ac_2O-mediated reaction of **2a** with **3m** was increased to 10 mmol (1.8 g) and 20 mmol (3.6 g), **1n** was isolated in 84% (2.67 g) and 82% (5.22 g) yield, respectively, under optimal conditions.

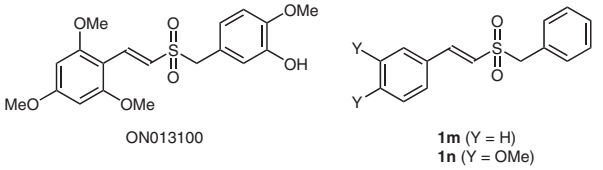
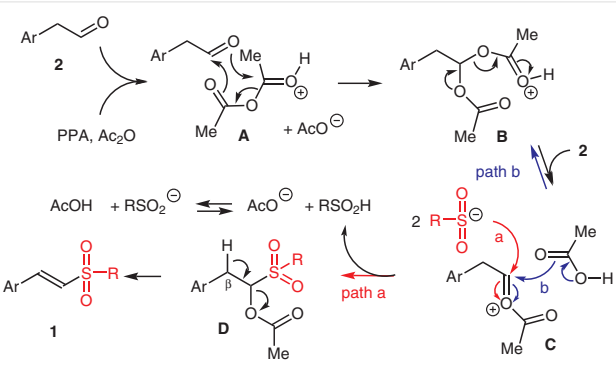


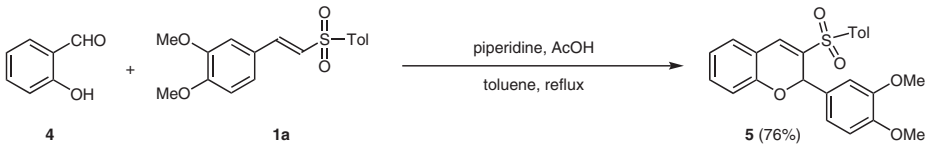
Figure 1 Structures of ON013100 and **1m**,**n**

On the basis of the above-mentioned experimental results, a possible reaction mechanism is shown in Scheme 3. Initially, the intermolecular reaction of **2** with the in situ formed **A** (derived from PPA mediated protonation of Ac_2O) generated **B** via a possible six-membered transition state. Next, protonated diacetate **B** was converted into **C** having an oxonium ion and AcOH. By the involvement of RSO_2Na **3** (2 equiv), **D** was produced along with the removal of acetate ion and sulfinic acid via the addition of **C** with one equivalent of RSO_2Na (path a). In another way, the in situ formed AcOH could react with **C** to go back into **B** under the equilibrium (path b). Subsequently, the released acetate ion or another equivalent of the sulfinate ion trapped the β-proton to provide **1** via the elimination pathway. Following a protonation–deprotonation process, the reaction equation for 'AcONa + RSO_2H ⇄ AcOH + RSO_2Na' was achieved.



Scheme 3 Possible mechanism

As an extension for the application of β-sulfonyl styrenes **1**, the synthesis of sulfonyl 2*H*-chromene **5** was explored next, as shown in Scheme 4. Under the Dean–Stark distillation conditions, treatment of **1a** with *o*-hydroxybenzaldehyde (**4**) provided **5** in a 76% yield via a domino sequence of oxa-Michael addition and Knoevengel condensation. The 2*H*-chromene skeleton is an important substruc-



Scheme 4 Synthesis of **5**

ture in a wide range of bioactive heterocycles.[21] This implies that β-sulfonyl styrene **1** is an excellent block for the formation of sulfonyl 2*H*-chromene **5**.

In summary, we have developed a simple and gram-scale synthesis of β-sulfonyl styrenes in moderate to good yields via one-pot PPA-catalyzed 1,1-diacetoxylation of arylacetaldehydes with acetic anhydride followed by deacetoxylative sulfonylation of the resulting 1,1-diacetate intermediate with sodium sulfinates under solvent-free conditions. A plausible mechanism has been discussed and proposed. The synthetic extension of β-sulfonyl styrenes in the preparation of a 2*H*-chromene skeleton has been included. Further investigation regarding synthetic applications of sodium sulfinates will be conducted and published in due course.

All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of air with magnetic stirring. Products in organic solvents were dried with anhyd $MgSO_4$ before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (*J*) are given in hertz. High-resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL.

β-Sulfonyl Styrenes 1a–ac; General Procedure

Ac_2O (510 mg, 5.0 mmol) was added to a stirred solution of the respective arylacetaldehyde **2** (5.0 mmol) at 25 °C. The reaction mixture was stirred at 25 °C for 2 min. PPA (490 mg, 5.0 mmol) was added slowly to the reaction mixture at 25 °C over 3 min. The mixture was stirred at 25 °C for 5 min. Then, the corresponding sodium sulfinate RSO_2Na **3** (10.0 mmol) was added to the mixture at 25 °C and the mixture was stirred at 25 °C for 4 h. The residue was diluted with H_2O (20 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with aq $NaHCO_3$ (3 × 10 mL), brine, dried, filtered and evaporated to afford the crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc 8:1 to 4:1) afforded compounds **1a–ac** (Table 2).

(*E*)-1,2-Dimethoxy-4-[2-(4-methylbenzene)sulfonylvinyl]benzene (1a)[22a]

Yield: 1.43 g (90%); white solid; mp 125–127 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 15.6 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.06 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.95 (d, *J* = 2.0 Hz, 1 H), 6.83 (d, *J* = 8.4 Hz, 1 H), 6.73 (d, *J* = 15.2 Hz, 1 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6, 149.1, 144.0, 141.9, 138.0, 129.8 (2 ×), 127.4 (2 ×), 125.2, 124.9, 123.3, 110.9, 109.7, 55.9, 55.8, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}O_4S$: 319.1004; found: 319.1005.

(*E*)-4-(2-Benzenesulfonylvinyl)-1,2-dimethoxybenzene (1b)[22b]

Yield: 1.31 g (86%); white solid; mp 149–151 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.90 (m, 2 H), 7.59 (d, *J* = 15.2 Hz, 1 H), 7.57–7.54 (m, 1 H), 7.51–7.47 (m, 2 H), 7.05 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.95 (d, *J* = 2.0 Hz, 1 H), 6.82 (d, *J* = 8.4 Hz, 1 H), 6.75 (d, *J* = 15.6 Hz, 1 H), 3.85 (s, 3 H), 3.83 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6, 149.1, 142.4, 140.9, 133.0, 129.1 (2 ×), 127.3 (2 ×), 125.0, 124.4, 123.4, 110.9, 109.7, 55.8, 55.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{17}O_4S$: 305.0848; found: 305.0849.

(*E*)-1,2-Dimethoxy-4-(methylsulfonylvinyl)benzene (1c)

Yield: 1.08 g (89%); white solid; mp 127–128 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 15.6 Hz, 1 H), 7.07 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.99 (d, *J* = 2.0 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 6.79 (d, *J* = 15.2 Hz, 1 H), 3.88 (s, 3 H), 3.87 (s, 3 H), 3.00 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8, 149.2, 143.7, 124.8, 123.5, 123.4, 111.0, 109.8, 55.9, 55.8, 43.3.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{15}O_4S$: 243.0691; found: 243.0693.

(*E*)-4-(Butylsulfonylvinyl)-1,2-dimethoxybenzene (1d)

Yield: 1.22 g (86%); viscous gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 15.6 Hz, 1 H), 7.06 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.99 (d, *J* = 2.0 Hz, 1 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 6.69 (d, *J* = 15.2 Hz, 1 H), 3.86 (s, 6 H), 3.02–2.98 (m, 2 H), 1.78–1.70 (m, 2 H), 1.44–1.35 (m, 2 H), 0.88 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6, 149.1, 144.4, 124.9, 123.3, 121.9, 110.9, 109.8, 55.80, 55.76, 54.8, 24.4, 21.4, 13.4.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{21}O_4S$: 285.1161; found: 285.1161.

(*E*)-4-[2-(4-Fluorbenzene)sulfonylvinyl]-1,2-dimethoxybenzene (1e)

Yield: 1.42 g (88%); white solid; mp 120–122 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.87 (m, 2 H), 7.56 (d, *J* = 15.6 Hz, 1 H), 7.17–7.11 (m, 2 H), 7.04 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.95 (d, *J* = 2.0 Hz, 1 H), 6.81 (d, *J* = 8.4 Hz, 1 H), 6.74 (d, *J* = 15.2 Hz, 1 H), 3.83 (s, 3 H), 3.81 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2 (d, *J* = 254.0 Hz), 151.7, 149.1, 142.5, 137.0 (d, *J* = 3.0 Hz), 130.1 (d, *J* = 9.8 Hz, 2 ×), 124.8, 124.2, 123.4, 116.3 (d, *J* = 22.7 Hz, 2 ×), 110.8, 109.7, 55.74, 55.67.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{16}FO_4S$: 323.0753; found: 323.0752.

(*E*)-1,2-Dimethoxy-4-[2-(4-methoxybenzene)sulfonylvinyl]benzene (1f)

Yield: 1.54 g (92%); viscous gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.8 Hz, 2 H), 7.51 (d, *J* = 15.6 Hz, 1 H), 7.02 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.95–6.91 (m, 3 H), 6.80 (d, *J* = 8.4 Hz, 1 H), 6.73 (d, *J* = 15.2 Hz, 1 H), 3.83 (s, 3 H), 3.81 (s, 3 H), 3.78 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2, 151.4, 149.0, 141.2, 132.3, 129.4 (2 ×), 125.12, 125.06, 123.1, 114.3 (2 ×), 110.8, 109.6, 55.72, 55.66, 55.4.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}O_5S$: 335.0953; found: 335.0955.

(*E*)-1,2-Dimethoxy-4-[2-(3-methylbenzene)sulfonylvinyl]benzene (1g)

Yield: 1.43 g (90%); white solid; mp 129–131 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.67 (m, 2 H), 7.56 (d, *J* = 15.2 Hz, 1 H), 7.36–7.30 (m, 2 H), 7.03 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.96 (d, *J* = 2.0 Hz, 1 H), 6.79 (d, *J* = 8.4 Hz, 1 H), 6.77 (d, *J* = 15.6 Hz, 1 H), 3.81 (s, 3 H), 3.79 (s, 3 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4, 148.9, 142.0, 140.6, 139.2, 133.7, 128.9, 127.4, 124.9, 124.5, 124.3, 123.3, 110.7, 109.6, 55.7, 55.6, 21.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}O_4S$: 319.1004; found: 319.1005.

(*E*)-4-[2-(4-Isopropylbenzene)sulfonylvinyl]-1,2-dimethoxybenzene (1h)

Yield: 1.61 g (93%); viscous gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 15.2 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.04 (dd, *J* = 2.0, 8.0 Hz, 1 H), 6.96 (d, *J* = 2.0 Hz, 1 H), 6.81 (d, *J* = 8.4 Hz, 1 H), 6.75 (d, *J* = 15.6 Hz, 1 H), 3.84 (s, 3 H), 3.82 (s, 3 H), 2.96–2.89 (m, 1 H), 1.20 (d, *J* = 7.2 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 151.5, 149.0, 141.9, 138.2, 127.5 (2 ×), 127.2 (2 ×), 125.1, 124.8, 123.3, 110.8, 109.7, 55.8, 55.7, 34.0, 23.4 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{23}O_4S$: 347.1317; found: 347.1320.

(*E*)-4-[2-(4-Butylbenzene)sulfonylvinyl]-1,2-dimethoxybenzene (1i)

Yield: 1.67 g (93%); viscous gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 15.6 Hz, 1 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.06 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.96 (d, *J* = 2.0 Hz, 1 H), 6.83 (d, *J* = 8.4 Hz, 1 H), 6.74 (d, *J* = 15.6 Hz, 1 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 2.66 (t, *J* = 7.6 Hz, 2 H), 1.61–1.53 (m, 2 H), 1.36–1.27 (m, 2 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6, 149.1, 148.9, 141.9, 138.1, 129.2 (2 ×), 127.4 (2 ×), 125.2, 124.9, 123.3, 110.9, 109.7, 55.9, 55.8, 35.4, 33.1, 22.1, 13.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{25}O_4S$: 361.0474; found: 361.0474.

(*E*)-4-[2-(4-*tert*-Butylbenzene)sulfonylvinyl]-1,2-dimethoxybenzene (1j)

Yield: 1.62 g (90%); viscous gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.8 Hz, 2 H), 7.58 (d, *J* = 15.2 Hz, 1 H), 7.50 (d, *J* = 8.8 Hz, 2 H), 7.05 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.96 (d, *J* = 2.0 Hz, 1 H), 6.82 (d, *J* = 8.4 Hz, 1 H), 6.76 (d, *J* = 15.6 Hz, 1 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 1.28 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 151.5, 149.1, 141.9, 137.9, 127.2 (2 ×), 126.1 (2 ×), 125.1, 124.8, 123.3, 110.8, 109.7, 55.8, 55.7, 35.0, 30.9 (3 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{25}O_4S$: 361.0474; found: 361.0474.

(*E*)-2-(Vinylbenzenesulfonyl)vinylbenzene (1k)[19a]

Yield: 1.08 g (80%); viscous gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 15.6 Hz, 2 H), 7.53–7.48 (m, 4 H), 7.44–7.39 (m, 6 H), 6.86 (d, *J* = 15.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5 (2 ×), 132.5 (2 ×), 131.3 (2 ×), 129.1 (4 ×), 128.5 (4 ×), 126.3 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}O_2S$: 271.0793; found: 271.0792.

(*E*)-1,2-Dimethoxy-4-[2-(3,4-dimethoxybenzene)sulfonylvinyl]benzene (1l)

Yield: 1.68 g (86%); white solid; mp 158–160 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 15.6 Hz, 2 H), 7.08 (dd, *J* = 2.0, 8.4 Hz, 2 H), 6.99 (d, *J* = 1.6 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 6.71 (d, *J* = 15.6 Hz, 2 H), 3.90 (s, 6 H), 3.88 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7 (2 ×), 149.2 (2 ×), 142.8 (2 ×), 125.4 (2 ×), 124.0 (2 ×), 123.3 (2 ×), 111.0 (2 ×), 109.8 (2 ×), 55.9 (2 ×), 55.8 (2 ×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}O_6S$: 391.1215; found: 391.1216.

(*E*)-2-(Benzylsulfonyl)vinylbenzene (1m)

Yield: 955 mg (74%); white solid; mp 140–142 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.37 (m, 11 H), 6.71 (d, *J* = 15.6 Hz, 1 H), 4.32 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 132.1, 131.3, 130.9 (2 ×), 129.0 (2 ×), 128.83, 128.77 (2 ×), 128.4 (2 ×), 128.0, 123.8, 61.8.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{15}O_2S$: 259.0793; found: 259.0795.

(*E*)-4-(2-Benzylsulfonylvinyl)-1,2-dimethoxybenzene (1n)[22c]

Yield: 1.37 g (86%); white solid; mp 141–143 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.34 (m, 5 H), 7.32 (d, *J* = 15.6 Hz, 1 H), 7.00 (dd, *J* = 2.0, 8.0 Hz, 1 H), 6.90 (d, *J* = 2.0 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 6.57 (d, *J* = 15.2 Hz, 1 H), 4.29 (s, 2 H), 3.90 (s, 3 H), 3.86 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8, 149.2, 145.5, 130.9 (2 ×), 128.8 (2 ×), 128.7, 128.2, 125.0, 123.2, 121.2, 111.0, 110.0, 61.9, 55.93, 55.87.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}O_4S$: 319.1004; found: 319.1003.

(*E*)-2-[(4-Methylbenzene)sulfonylvinyl]benzene (1o)[11g]

Yield: 1.03 g (80%); white solid; mp 119–121 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.4 Hz, 2 H), 7.65 (d, *J* = 15.2 Hz, 1 H), 7.48–7.45 (m, 2 H), 7.40–7.37 (m, 3 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 6.85 (d, *J* = 15.2 Hz, 1 H), 2.42 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.32, 141.85, 137.70, 132.38, 131.03, 129.90 (2 ×), 128.99 (2 ×), 128.44 (2 ×), 127.63 (2 ×), 127.59, 21.53.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{15}O_2S$: 259.0793; found: 259.0795.

(*E*)-1-Methoxy-4-[2-(4-methylbenzene)sulfonylvinyl]benzene (1p)[22d]

Yield: 1.20 g (83%); white solid; mp 81–83 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.4 Hz, 2 H), 7.59 (d, *J* = 15.2 Hz, 1 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 6.70 (d, *J* = 15.6 Hz, 1 H), 3.81 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9, 144.0, 141.6, 138.1, 130.2 (2 ×), 129.8 (2 ×), 127.4 (2 ×), 124.9, 124.7, 114.4 (2 ×), 55.3, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{17}O_3S$: 289.0898; found: 289.0899.

(*E*)-1-Methoxy-3-[2-(4-methylbenzene)sulfonylvinyl]benzene (1q)[22d]

Yield: 1.15 g (80%); white solid; mp 53–55 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.4 Hz, 2 H), 7.61 (d, *J* = 15.6 Hz, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.27 (t, *J* = 8.0 Hz, 1 H), 7.05 (d, *J* = 8.0 Hz, 1 H), 6.97 (t, *J* = 1.6 Hz, 1 H), 6.93 (dt, *J* = 1.6, 8.4 Hz, 1 H), 6.67 (d, *J* = 15.2 Hz, 1 H), 3.78 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 144.3, 141.7, 137.6, 133.6, 129.94, 129.85 (2 ×), 127.8, 127.6 (2 ×), 121.0, 116.9, 113.2, 55.2, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{17}O_3S$: 289.0898; found: 289.0897.

(*E*)-1-Fluoro-3-[2-(4-methylbenzene)sulfonylvinyl]benzene (1r)[22d]

Yield: 994 mg (72%); white solid; mp 86–88 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 2 H), 7.61 (d, *J* = 15.2 Hz, 1 H), 7.49–7.44 (m, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.09–7.04 (m, 2 H), 6.79 (d, *J* = 15.6 Hz, 1 H), 2.42 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2 (d, *J* = 251.7 Hz), 144.4, 140.5, 137.6, 130.5 (d, *J* = 8.4 Hz, 2 ×), 1299 (2 ×), 128.7 (d, *J* = 3.1 Hz), 127.6 (2 ×), 127.4 (d, *J* = 2.3 Hz), 116.2 (d, *J* = 22.0 Hz, 2 ×), 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{14}FO_2S$: 277.0699; found: 277.0697.

(*E*)-1-Methyl-3-[2-(4-methylbenzene)sulfonylvinyl]benzene (1s)[22d]

Yield: 952 mg (70%); white solid; mp 149–151 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 15.6 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 6.79 (d, *J* = 15.2 Hz, 1 H), 2.42 (s, 3 H), 2.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 141.9, 141.7, 137.9, 129.9 (2 ×), 129.7 (2 ×), 129.6, 128.5 (2 ×), 127.6 (2 ×), 126.4, 21.5, 21.4.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{17}O_2S$: 273.0949; found: 273.0951.

(*E*)-3-[2-(4-Methylbenzene)sulfonylvinyl]-1-phenylbenzene (1t)

Yield: 1.27 g (76%); white solid; mp 225–226 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 15.6 Hz, 1 H), 7.63–7.54 (m, 6 H), 7.47–7.43 (m, 2 H), 7.40–7.34 (m, 3 H), 6.70 (d, *J* = 15.2 Hz, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 143.9, 141.5, 139.8, 137.8, 131.4, 130.0 (2 ×), 129.0 (2 ×), 128.9 (2 ×), 128.1, 127.7 (2 ×), 127.7 (2 ×), 127.3, 127.0 (2 ×), 21.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{19}O_2S$: 335.1106; found: 335.1106.

(*E*)-2-[2-(4-methylbenzene)sulfonylvinyl]naphthalene (1u)[22e]

Yield: 1.25 g (81%); white solid; mp 126–128 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 7.88–7.80 (m, 6 H), 7.56–7.50 (m, 3 H), 7.35 (d, *J* = 7.6 Hz, 2 H), 6.96 (d, *J* = 15.2 Hz, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 142.0, 137.8, 134.4, 133.1, 130.8, 130.0 (2 ×), 129.9, 128.9, 128.6, 127.8, 127.7 (3 ×), 127.6, 126.9, 123.4, 21.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{17}O_2S$: 309.0949; found: 309.0950.

(*E*)-1,2-Dimethylenedioxy-4-[2-(4-methylbenzene)sulfonylvinyl]benzene (1v)

Yield: 1.30 g (86%); white solid; mp 112–113 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 15.2 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 6.98 (dd, *J* = 1.6, 8.0 Hz, 1 H), 6.92 (d, *J* = 2.0 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 6.65 (d, *J* = 15.2 Hz, 1 H), 5.99 (s, 2 H), 2.42 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2, 148.4, 144.2, 141.7, 138.0, 129.9 (2 ×), 127.5 (2 ×), 126.7, 125.3, 125.2, 108.6, 106.8, 101.7, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}O_4S$: 303.0691; found: 303.0693.

(*E*)-1,2-Dichloro-4-[2-(4-methylbenzene)sulfonylvinyl]benzene (1w)

Yield: 1.34 g (82%); white solid; mp 166–167 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.4 Hz, 2 H), 7.55 (d, *J* = 2.4 Hz, 1 H), 7.54 (d, *J* = 15.2 Hz, 1 H), 7.46 (d, *J* = 8.4 Hz, 1 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.29 (dd, *J* = 2.4, 8.4 Hz, 1 H), 6.85 (d, *J* = 15.2 Hz, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 139.0, 137.1, 135.1, 133.5, 132.4, 131.0, 130.1 (2 ×), 129.9, 129.6, 127.8 (2 ×), 127.5, 21.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}Cl_2O_2S$: 327.0013; found: 327.0015.

(*E*)-1,2,3-Trimethoxy-5-[2-(4-methylbenzene)sulfonylvinyl]benzene (1x)

Yield: 1.55 g (89%); white solid; mp 107–109 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 15.2 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 6.79 (d, *J* = 15.2 Hz, 1 H), 6.70 (s, 2 H), 3.84 (s, 3 H), 3.83 (s, 6 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4 (2 ×), 144.2, 141.9, 140.6, 137.8, 129.9 (2 ×), 127.7, 127.5 (2 ×), 126.6, 105.7 (2 ×), 60.8, 56.1 (2 ×), 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{21}O_5S$: 349.1110; found: 349.1112.

(*E*)-2-[4-Methylbenzene)sulfonylvinyl]furan (1y)[22f]

Yield: 856 mg (69%); white solid; mp 96–98 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 1.6 Hz, 1 H), 7.39 (d, *J* = 15.2 Hz, 1 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 6.71 (d, *J* = 15.2 Hz, 1 H), 6.67 (d, *J* = 3.2 Hz, 1 H), 6.45 (dd, *J* = 1.6, 3.2 Hz, 1 H), 2.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.6, 145.5, 144.2, 137.8, 129.8 (2 ×), 128.3, 127.4 (2 ×), 125.0, 116.6, 112.5, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}O_3S$: 249.0586; found: 249.0587.

(*E*)-2-(4-Methylbenzene)sulfonylvinyl)thiophene (1z)[22f]

Yield: 1.11 g (84%); white solid; mp 131–132 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.4 Hz, 2 H), 7.75 (d, *J* = 14.8 Hz, 1 H), 7.41 (d, *J* = 4.8 Hz, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 3.6 Hz, 1 H), 7.04 (dd, *J* = 3.6, 4.8 Hz, 1 H), 6.63 (d, *J* = 14.8 Hz, 1 H), 2.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 137.8, 136.9, 134.5, 132.2, 129.9 (2 ×), 129.8, 128.2, 127.5 (2 ×), 125.7, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}O_2S_2$: 265.0357; found: 265.0358.

(*E*)-2-[(4-Methylbenzene)sulfonylvinyl]pyridine (1aa)[22f]

Yield: 531 mg (41%); white solid; mp 90–92 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (br d, *J* = 8.8 Hz, 1 H), 7.81 (d, *J* = 8.4 Hz, 2 H), 7.70 (dt, *J* = 1.6, 7.6 Hz, 1 H), 7.59 (d, *J* = 14.8 Hz, 1 H), 7.41 (d, *J* = 14.8 Hz, 1 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.25 (ddd, *J* = 0.8, 4.4, 8.4 Hz, 1 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9, 150.1, 144.5, 140.0, 137.1, 137.0, 132.0, 129.9 (2 ×), 127.8 (2 ×), 125.3, 124.8, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{14}NO_2S$: 260.0745; found: 260.0746.

(*E*)-1-(Benzenesulfonylvinyl)prop-1-ene (1ab)

Yield: 610 mg (67%); white solid; mp 58–60 °C (hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.68 (m, 2 H), 7.43–7.38 (m, 1 H), 7.38–7.32 (m, 2 H), 6.78 (dq, *J* = 6.8, 14.0 Hz, 1 H), 6.22 (dq, *J* = 1.6, 14.0 Hz, 1 H), 1.69 (dd, *J* = 1.2, 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2, 140.1, 132.7, 131.1, 128.7 (2 ×), 126.8 (2 ×), 16.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_9H_{11}O_2S$: 183.0480; found: 183.0481.

Acetic Acid 2-[2-(Toluene-4-sulfonyl)vinyl]phenyl Ester (1ac)

Yield: 1.26 g (80%); viscous gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.4 Hz, 2 H), 7.70 (d, *J* = 15.6 Hz, 1 H), 7.51 (dd, *J* = 2.0, 8.0 Hz, 1 H), 7.42 (dt, *J* = 2.0, 8.4 Hz, 1 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.23 (dt, *J* = 1.2, 8.4 Hz, 1 H), 7.14 (dd, *J* = 1.2, 8.4 Hz, 1 H), 6.70 (d, *J* = 15.2 Hz, 1 H), 2.43 (s, 3 H), 2.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9, 149.4, 144.5, 137.2, 135.4, 131.9, 130.0 (2 ×), 129.7, 128.1, 127.7 (2 ×), 126.3, 125.1, 123.2, 21.6, 20.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}O_4S$: 317.0848; found: 317.0850.

2-(3,4-Dimethoxyphenyl)-3-(toluene-4-sulfonyl)-2*H*-chromene (5)

Piperidine (51 mg, 0.6 mmol) and AcOH (54 mg, 0.9 mmol) were added to a solution of **1a** (1.0 mmol) in toluene at r.t. The reaction mixture was stirred at r.t. for 10 min. The mixture was stirred at reflux for 10 h using the Dean–Stark distillation apparatus. The mixture was cooled to r.t. and the solvent was evaporated. The residue was diluted with H_2O (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated under reduced pressure to afford the crude product. Purification on silica gel (hexanes/EtOAc 8:1 to 3:1) afforded **5**; yield: 242 mg (76%); colorless gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (s, 1 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.23 (dt, *J* = 1.6, 7.6 Hz, 1 H), 7.19 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 6.92 (dt, *J* = 1.6, 7.6 Hz, 1 H), 6.74 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.72 (d, *J* = 8.4 Hz, 1 H), 6.67 (d, *J* = 2.0 Hz, 1 H), 6.58 (d, *J* = 8.4 Hz, 1 H), 6.07 (s, 1 H), 3.79 (s, 3 H), 3.67 (s, 3 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 149.6, 148.7, 144.3, 136.8, 134.0, 133.0, 132.9, 129.5 (2 ×), 129.1, 129.0, 127.9 (2 ×), 121.9, 120.7, 119.5, 117.0, 110.7, 110.5, 74.9, 55.8, 55.6, 21.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{23}O_5S$: 423.1266; found: 423.1267.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-xxxxxxx.

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