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Copper/Silver-Mediated Cascade Reactions for the Construction of 2-Sulfonylbenzo[*b*]furans from *trans*-2-Hydroxycinnamic Acids and Sodium Sulfinates

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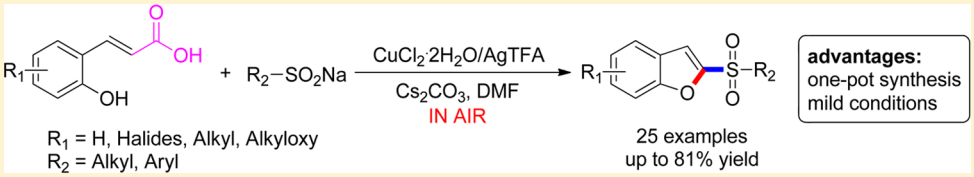
Supporting Information



ABSTRACT: Efficient construction of 2-sulfonylbenzo[*b*]furans is achieved from readily available *trans*-2-hydroxycinnamic acids and sodium sulfinates mediated by the $CuCl_2·2H_2O$/AgTFA system under mild conditions. This unprecedented synthetic protocol provides expedient access to a series of products in one step via a protodecarboxylation/C−S bond formation/C−O bond formation cascade.

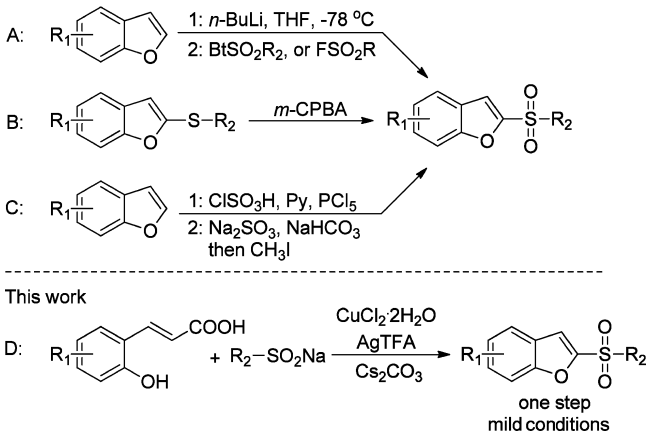
INTRODUCTION

Benzo[*b*]furan, as a ubiquitous heterocyclic structural motif, constitutes a significant component in naturally occurring products and in drug discovery[1] and thus has attracted considerable interest from organic chemists in pursuing synthetic efficiency.[2] Among these abundant functionalized structures, 2-sulfonylbenzo[*b*]furans have versatile pharmaceutical activities, such as antimalarial, MMP-13 inhibitor, aldose reductase inhibitor, 5-HT modulator, and cognitive enhancer.[3] Typical strategies for the synthesis of 2-sulfonylbenzo[*b*]furans involve the following: (i) deprotonation of benzofurans using *n*-BuLi followed by treatment with activated 1-sulfonylbenzotriazoles or arenesulfonyl fluorides (Scheme 1, route A);[4,3c,d] (ii) a multistep synthesis of sulfide with subsequent oxidation with *m*-CPBA (route B);[3a,b] and (iii) methylation after reduction of benzofuran-2-sulfonyl chloride to sodium sulfinate (route C).[3h] In view of the harsh conditions and tedious procedures required, it is desirable to develop a more facile and efficient approach for constructing this scaffold.

In continuation of our research on the functionalization of benzo[*b*]furan,[5] herein we disclose a cascade reaction involving a protodecarboxylation, an oxidative sulfonylation, and an intramolecular C−O cyclization to afford 2-sulfonylbenzo[*b*]furans under $CuCl_2·2H_2O$/AgTFA-mediated conditions (Scheme 1, route D).

In past decades, protodecarboxylations of carboxylic acids[6] mediated by transition metals (TMs) such as silver[7] or copper[8] have been exquisitely investigated. Among diverse carboxylic acids, the protodecarboxylation of cinnamic acid was successfully exploited with the Cu_2O/1,10-phenanthroline catalyst system.[9] Other approaches, including pH-dependent,[10] biocatalyzed,[11] or base-catalyzed[12] decarboxylations, have also been employed. Furthermore, styrenes as the decarboxylation products were reported to be able to react with sodium sulfinates to furnish α,β-unsaturated sulfones (vinyl sulfones) under various oxidative conditions, including $PhI(OAc)_2$/KI,[13] CAN/NaI,[14] $NaIO_4$/KI,[15] I_2/NaOAc,[16] and CuI-bpy/KI in

Scheme 1. Methods for the Synthesis of 2-Sulfonylbenzo[*b*]furans



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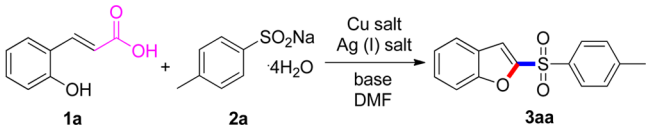
air.[17] In light of the harsh reaction conditions involved in the preparation of structure-diversified styrenes,[18] it would be advantageous to use cinnamic acids (readily prepared by Horner–Wittig reaction[19] or Knoevenagel condensation[20]) as alternatives to perform oxidative sulfonylation after in situ decarboxylation.

Recently, a number of methods have been developed for the transformation of *o*-alkenyl phenols into 2-substituted benzo[*b*]furans using the $VO(acac)_2$/TBHP/acid catalyst system,[21] I_2/K_2CO_3,[22] $CuBr_2$,[23] $PhI(OAc)_2$,[24] DDQ,[25] or *m*-CPBA/TsOH.[25a,26] Additionally, Dominguez and co-workers demonstrated an interesting cyclization of 2-hydroxy-α-arylstyrenes to benzofurans by employing the CuOAc/8-hydroxyquinoline/DMA/O_2 system.[27] Inspired by the intramolecular oxidative cyclization, we envisioned that the anticipated 2-sulfonylbenzo[*b*]furans could be accessible via cascade reactions[28] from *trans*-2-hydroxycinnamic acids and sodium sulfinates in the presence of a decarboxylation mediator and oxidants.

RESULTS AND DISCUSSION

In our initial studies, commercially available *trans*-2-hydroxycinnamic acid (**1a**) and *p*-toluenesulfinic acid sodium salt tetrahydrate (**2a**) were chosen as model substrates for optimization of the reaction conditions, and the results are depicted in Table 1. When **1a** was treated with **2a** in the presence of $Cu(OAc)_2$ (20 mol %), AgTFA (2 equiv), and Cs_2CO_3 (2 equiv) under ambient atmosphere in commercial-grade DMF (6 mL) at 100 °C for 12 h, 2-[(4-methylphenyl)-sulfonyl]benzofuran (**3aa**) was isolated in 31% yield (entry 1); ^{1}H NMR and ^{13}C NMR analyses of the product were in agreement with the published data.[4b] Intrigued by this unexpected cascade reaction, an array of assays was subsequently carried out to examine the reaction parameters. Among the copper salts screened (entries 2–6), $CuCl_2{\cdot}2H_2O$ produced a higher yield than other copper species; an isolated yield of 53% was obtained (entry 6). Therefore, $CuCl_2{\cdot}2H_2O$ was employed as the copper source on the basis of its cheapness and high efficiency, although $Cu(OTf)_2$ delivered a comparable yield (entry 4). Nevertheless, the product yield was lowered to 41% when the reaction was performed under an atmosphere of oxygen (entry 7). It was observed that increasing the copper loading resulted in an enhanced yield (59% with 30 mol % $CuCl_2{\cdot}2H_2O$; entry 8). Furthermore, employing 50 mol % $CuCl_2{\cdot}2H_2O$ increased the yield of **3aa** to 67% when the reaction was conducted at 80 °C for 18 h (entry 9).

Table 1. Optimization Studies for the Construction of 2-Sulfonylbenzo[*b*]furans[a]



1a 2a 3aa

entry	Cu salt (equiv)	Ag salt[b] (equiv)	*T* (°C)/*t* (h)	yield (%)[c]
1	$Cu(OAc)_2$ (0.2)	AgTFA (2)	100/12	31
2	$CuSO_4$ (0.2)	AgTFA (2)	100/12	6
3	$Cu(TFA)_2$ (0.2)	AgTFA (2)	100/12	46
4	$Cu(OTf)_2$ (0.2)	AgTFA (2)	100/12	51
5	CuCl (0.2)	AgTFA (2)	100/12	34
6	$CuCl_2{\cdot}2H_2O$ (0.2)	AgTFA (2)	100/12	53
7[d]	$CuCl_2{\cdot}2H_2O$ (0.2)	AgTFA (2)	100/12	41
8	$CuCl_2{\cdot}2H_2O$ (0.3)	AgTFA (2)	100/12	59
9	$CuCl_2{\cdot}2H_2O$ (0.5)	AgTFA (2)	80/18	67
10	$CuCl_2{\cdot}2H_2O$ (0.5)	AgTFA (1.2)	80/18	11
11	$CuCl_2{\cdot}2H_2O$ (0.5)	AgOAc (2)	80/18	9
12	$CuCl_2{\cdot}2H_2O$ (0.5)	Ag_2CO_3 (2)	80/18	14
13[e]	$CuCl_2{\cdot}2H_2O$ (0.5)	AgTFA (2)	80/18	65
14[f]	$CuCl_2{\cdot}2H_2O$ (0.5)	AgTFA (2)	80/18	58
15	**$CuCl_2{\cdot}2H_2O$ (0.5)**	**AgTFA (2.5)**	**80/18**	**79**

[a]Unless otherwise noted, the reactions were carried out in air using **1a** (1 equiv), **2a** (1.2 equiv), and Cs_2CO_3 (2 equiv) in 6 mL of DMF. [b]AgTFA = silver trifluoroacetate. [c]Isolated yields. [d]Under an atmosphere of O_2 (1 atm). [e]2 equiv of *t*-BuOK was used. [f]2 equiv of K_2CO_3 was used.

Moreover, the amount and choice of silver salt were pivotal. Decreasing the amount of AgTFA to 1.2 equiv was detrimental, providing **3aa** in a very poor yield (entry 10). In contrast, 2.5 equiv of AgTFA was beneficial in promoting the reaction and afforded a good yield (entry 15). Other silver salts such as AgOAc and Ag_2CO_3 were far less effective than AgTFA (entries 11 and 12, respectively). The effect of bases on the reaction turnover was also investigated. Although the yield was slightly diminished when K_2CO_3 was used as a base (entry 14), the reaction in the presence of a strong base such as *t*-BuOK provided a yield similar to that achieved with Cs_2CO_3 (entry 13).

Having established the optimized conditions for the construction of 2-sulfonylbenzo[*b*]furans, we next explored the substrate scope of the reaction. As summarized in Table 2, a variety of sodium sulfinates could be reacted with *trans*-2-hydroxycinnamic acids, which were readily synthesized by the Horner–Wittig reaction.[29] Sodium sulfinates bearing electron-donating substituents such as methyl, methoxy and *tert*-butyl gave the desired products (**3aa**, **3ab**, **3ad**, and **3ae**) in good yields, with the exception of **3ac**, which was obtained in low yield because of the steric hindrance of *o*-methyl group. Good compatibility with functional groups for the single-step synthesis of 2-sulfonylbenzo[*b*]furans was observed, with fluoro (**3ah**), chloro (**3ai**), bromo (**3aj**), and acetamido groups (**3al**) all being well-tolerated. The yield with the electron-withdrawing CF_3 group fell to 44% (**3ak**). However, exposure of sodium sulfinate bearing a nitro group to the reaction conditions showed that almost no product was delivered. Electron-neutral benzenesulfinate **2f** as well as the bulkier 2-naphthylsulfinate **2g** underwent this reaction smoothly to furnish **3af** and **3ag** in 60% and 52% yield, respectively. It is noteworthy that this protocol could be extended to methanesulfinic acid sodium salt **2m**, from which a good yield of **3am** was isolated.

Meanwhile, the scope of *trans*-2-hydroxycinnamic acids was also evaluated. (*E*)-3-(2-Hydroxynaphthalen-1-yl)acrylic acid **1b** was readily transformed into the target product **3ba** in 81% yield. Various substituents such as methoxy (**1c**, **1d**), methyl (**1e**), fluoro (**1g**, **1h**), chloro (**1i**), and bromo (**1k**) were again found to be well-tolerated, except for the difunctional group of **1j**. This suggests that introducing substituents at the position *ortho* to the hydroxyl group on the substrate influences this cascade reaction, since no product was delivered either when a substrate with a methoxy group at the same position was used. The 5-HT modulator **3cn**[3g] could be produced under this $CuCl_2{\cdot}2H_2O$/AgTFA-mediated reaction, albeit in low yield. Unfortunately, the incorporation of benzofuran on the substrate with a free phenolic hydroxyl group failed. To our

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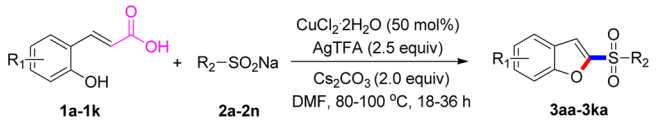
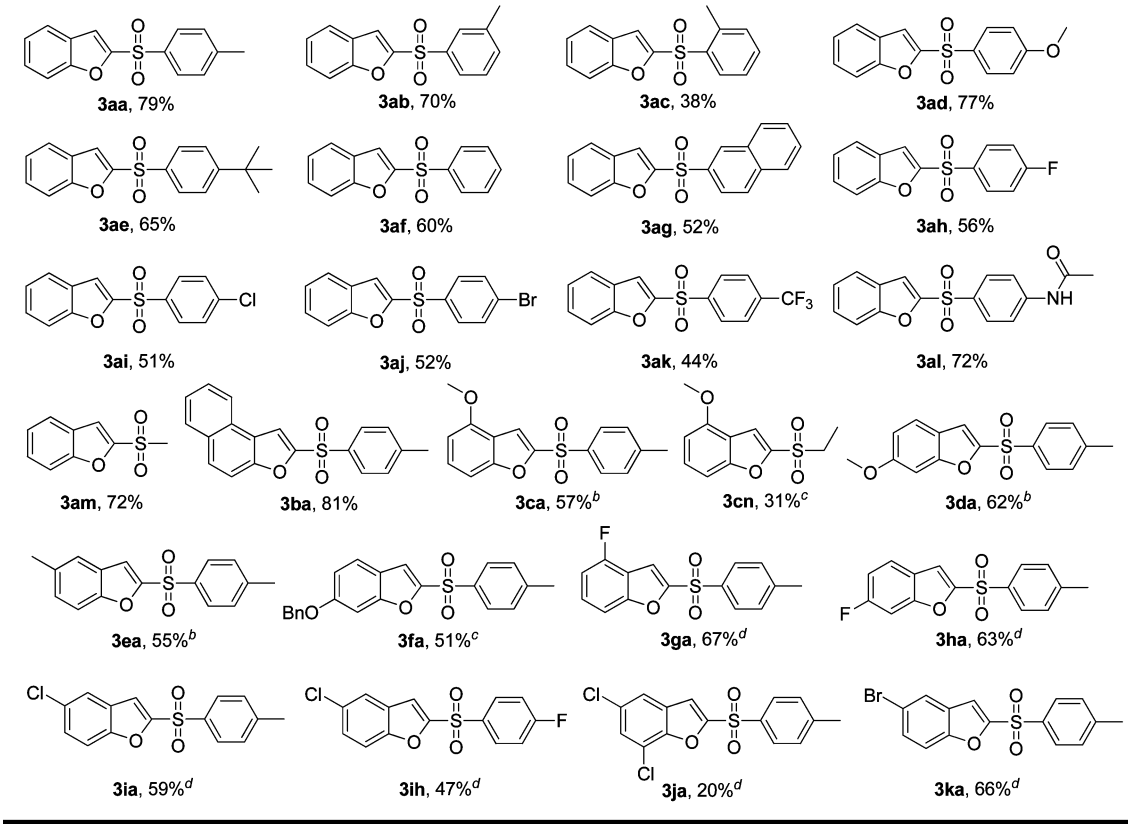
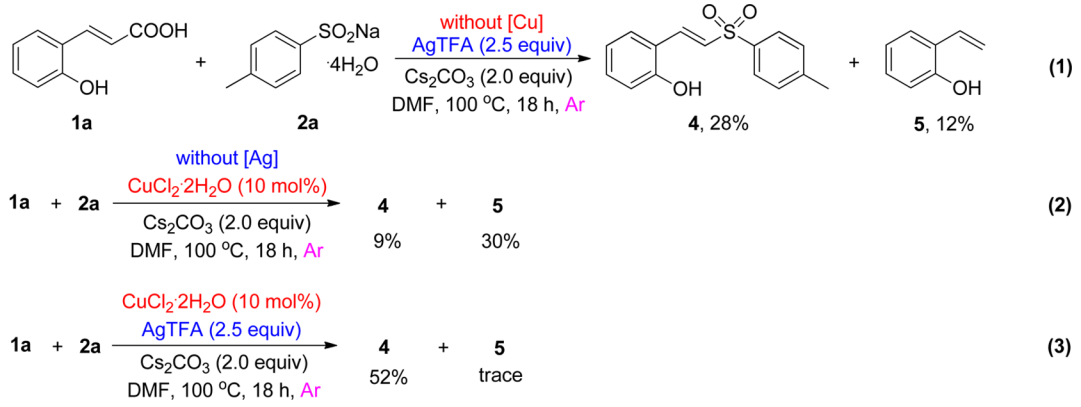
Table 2. Synthesis of Various 2-Sulfonylbenzo[*b*]furans[a]





[a]Reaction conditions: **1** (1 mmol), **2** (1.2 mmol), $CuCl_2·2H_2O$ (50 mol %), AgTFA (2.5 mmol), and Cs_2CO_3 (2.0 mmol) in 6 mL of DMF at 80 °C under air for 18 h, unless otherwise noted. [b]80 °C, 36 h. [c]90 °C, 24 h. [d]100 °C, 24 h.

Scheme 2. Control Experiments



delight, the monobenzyl-protected *trans*-2-hydroxycinnamic acid **2f** reacted readily, giving rise to **3fa** in 51% yield.

To shed light on the mechanism of this cascade reaction, control experiments were performed (Scheme 2). When **1a** was treated with **2a** in the presence of 2.5 equiv of AgTFA and 2 equiv of Cs_2CO_3 under an argon atmosphere, 2-(2-sulfonylvinyl)phenol **4** was produced in 28% isolated yield along with the protodecarboxylation product **5** in 12% isolated yield (eq 1). In addition, with 10 mol % $CuCl_2·2H_2O$, **5** was isolated as a major product (eq 2). Finally, combining the silver salt with a catalytic amount of the copper salt gave **4** in an acceptable yield (eq 3). Obviously, the copper salt improves the efficiency of formation of the α,β-unsaturated sulfone.

Scheme 3 exemplifies the two plausible pathways by isolating the key intermediates. On the one hand, when **5** formed by in situ decarboxylation of **1a** based on the silver salt was reacted with **2a** with and without a catalytic amount of $CuCl_2·2H_2O$ (10 mol %) under an argon atmosphere, **4** was obtained in

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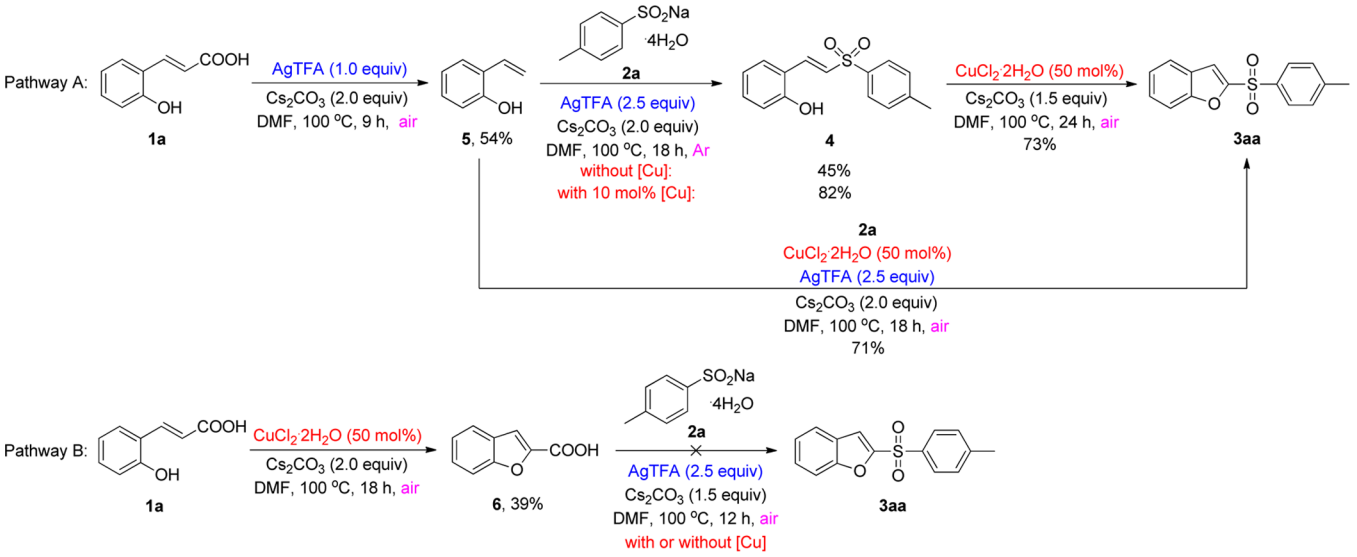
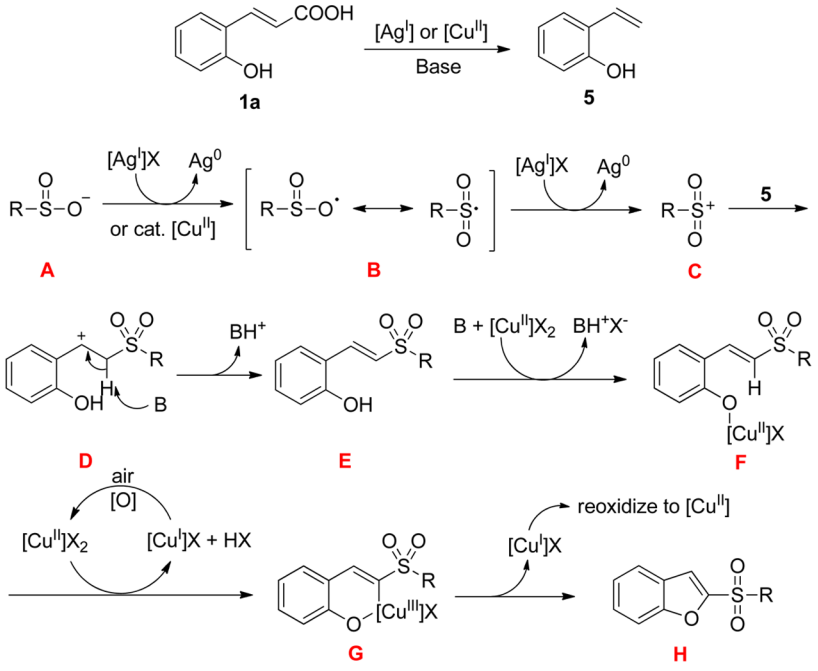
Scheme 3. Studies of Two Plausible Pathways



Scheme 4. Proposed Mechanism



isolated yields of 82% and 45%, respectively (pathway A). The results were in accordance with those of Scheme 2. Subsequent oxidative cyclization of **4** promoted by 50 mol % $CuCl_2{\cdot}2H_2O$ in air led to the formation of **3aa** in good yield. We observed that the reaction of **5** with **2a** under the standard conditions also provided the desired product **3aa** in 71% yield. However, only a trace amount of **3aa** was obtained when **1a** was treated with **2a** in the presence of 50 mol % copper salt only. On the other hand, benzofuran-2-carboxylic acid **6**, formed under the analogous oxidative conditions, was not observed to produce the sulfone **3aa** upon reaction of **2a** no matter the existence of the copper salt (pathway B). Furthermore, it should be mentioned that metallic silver is generated in all of these cascade reactions.

On the basis of the above investigations, a tentative mechanism for the construction of 2-sulfonylbenzo[*b*]furans is proposed, as illustrated in Scheme 4. Initial protodecarboxylation of *trans*-2-hydroxycinnamic acid mediated by Ag^{I} or Cu^{II} liberates 2-vinylphenol **5**, as established by Larrosa[7a] and Goossen.[9a] Meanwhile, the sodium sulfinate is oxidized by Ag^{I} to give sulfonyl radical **B** as well as metallic silver, and a second oxidation delivers sulfonyl cation **C**. It has been reported that Cu^{II} coupled with ligands can also catalyze the oxidation of sodium sulfinate, as indcated by Taniguchi.[17] Subsequent *anti* addition of **C** to alkene **5** and elimination of H^{+} produces *α,β*-unsaturated sulfone **E**. The Cu^{II} salt plays a key role in the oxidative cyclization step. In the presence of another Cu^{II} salt, the intermediate **F** undergoes C−H activation to generate the Cu^{III}−vinyl species **G**.[30] Finally, reductive elimination provides the target product **H**, and the Cu^{I} salt is reoxidized using air to regenerate the Cu^{II} salt. However, C−H functionalization/C−O cyclization cannot be ruled out in the second step.[31]

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CONCLUSION

An efficient strategy has been developed for constructing 2-sulfonylbenzo[*b*]furans induced by the $CuCl_2·2H_2O$/AgTFA system using readily available *trans*-2-hydroxycinnamic acids and sodium sulfinates as starting materials. The reaction proceeds via a protodecarboxylation/C−S bond formation/C−O bond formation cascade. This one-step protocol could complement the traditional methods for the preparation of 2-sulfonylbenzo[*b*]furans. Meanwhile, further applications of this method to the synthesis of other heterocycles are underway.

EXPERIMENTAL SECTION

General. All reagents and solvents of commercial grade were used without further purification. Melting points were performed with a micromelting point apparatus without correction. With $CDCl_3$, acetone-d_6, and DMSO-d_6 as solvents, ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. HRMS was carried out using electrospray ionization (ESI) as the ion source (linear ion trap Orbitrap). *trans*-2-Hydroxycinnamic acid (**1a**) and the substituted sulfinic acid sodium salts **2a**, **2f**, **2j**, **2m**, and **2n** were commercially available.

Preparation of *trans*-2-Hydroxycinnamic Acids. These acids (**1b**−**k**) were synthesized starting from substituted salicylaldehydes (5 mmol) according to the literature procedure[29] with the exception that EtOH was used as the solvent.

*(E)-3-(2-Hydroxynaphthalen-1-yl)acrylic Acid (**1b**).* Recrystallization from EtOH/H_2O; yellow solid, 611 mg (57%), mp 186−188 °C (lit.[29] 188−189 °C); ^{1}H NMR (400 MHz, acetone-d_6) δ 10.74 (br s, 1H), 9.49 (s, 1H), 8.41 (d, J = 16.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.57 (dt, J = 7.2, 1.6 Hz, 1H), 7.38 (dt, J = 7.6, 0.8 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 6.94 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.9, 156.3, 138.4, 134.1, 132.5, 129.7, 129.6, 128.3, 124.2, 123.33, 123.25, 119.1, 114.1; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{13}H_{11}O_3$ 215.0703, found 215.0698.

*(E)-3-(2-Hydroxy-6-methoxyphenyl)acrylic Acid (**1c**).* Recrystallization from MeOH/H_2O; light-red solid, 713 mg (73%), mp 186−188 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.18 (s, 1H), 8.20 (d, J = 16.4 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 16.4 Hz, 1H), 6.56−6.61 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 169.8, 161.2, 159.1, 137.0, 132.2, 120.7, 111.6, 109.5, 103.4, 56.1; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{10}H_{11}O_4$ 195.0652, found 195.0648.

*(E)-3-(2-Hydroxy-4-methoxyphenyl)acrylic Acid (**1d**).* Recrystallization from MeOH/H_2O; light-red solid, 596 mg (61%), mp 239−241 °C (lit.[29] 240−242 °C); ^{1}H NMR (400 MHz, acetone-d_6) δ 9.21 (s, 1H), 7.95 (d, J = 16.0 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 6.45−6.52 (m, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.7, 163.6, 158.8, 141.1, 131.1, 116.0, 115.6, 107.2, 102.3, 55.7; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{10}H_{11}O_4$ 195.0652, found 195.0649.

*(E)-3-(2-Hydroxy-5-methylphenyl)acrylic Acid (**1e**).* Recrystallization from MeOH/H_2O; light-yellow solid, 425 mg (48%), mp 184−186 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.83 (s, 1H), 8.00 (d, J = 16.0 Hz, 1H), 7.41 (d, J = 1.6 Hz, 1H), 7.06 (dd, J = 8.4, 1.6 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.6, 155.3, 141.3, 133.0, 129.8, 122.0, 118.4, 116.9, 20.4; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{10}H_{11}O_3$ 179.0703, found 179.0699.

*(E)-3-(4-Benzyloxy-2-hydroxyphenyl)acrylic Acid (**1f**).* **1f** was prepared by monobenzylation of 2,4-dihydroxybenzaldehyde[32] followed by Horner−Wittig reaction. Recrystallization from EtOH/H_2O; light-yellow solid, 757 mg (56%), mp 188−190 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 10.44 (br s, 1H), 9.15 (s, 1H), 7.94 (d, J = 16.0 Hz, 1H), 7.32−7.56 (m, 6H), 6.60−6.62 (m, 2H), 6.47 (d, J = 16.0 Hz, 1H), 5.13 (s, 2H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.7, 162.7, 158.9, 141.0, 138.0, 131.1, 129.4, 128.8, 128.5, 116.2, 115.9, 108.1, 103.3, 70.6; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{16}H_{15}O_4$ 271.0965, found 271.0960.

*(E)-3-(2-Fluoro-6-hydroxyphenyl)acrylic Acid (**1g**).* Recrystallization from MeOH/H_2O; light-red solid, 576 mg (63%), mp 191−193 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 10.74 (br s, 1H), 9.63 (s, 1H), 7.95 (d, J = 16.4 Hz, 1H), 7.26 (m, 1H), 6.81−6.85 (m, 2H), 6.71 (m, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.4, 163.4 (d, J = 248.3 Hz), 159.0 (d, J = 6.5 Hz), 134.2 (d, J = 3.6 Hz), 132.3 (d, J = 11.7 Hz), 122.8 (d, J = 8.8 Hz), 112.8 (d, J = 2.9 Hz), 111.4 (d, J = 13.5 Hz), 107.5 (d, J = 22.9 Hz); HRMS (ESI) m/z [M + H]$^+$ calcd for $C_9H_8FO_3$ 183.0452, found 183.0451.

*(E)-3-(4-Fluoro-2-hydroxyphenyl)acrylic Acid (**1h**).* Recrystallization from MeOH/H_2O; light-red solid, 663 mg (73%), mp 199−201 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.61 (br s, 1H), 7.95 (d, J = 16.0 Hz, 1H), 7.67 (dd, J = 8.8 Hz, 1H), 6.67−6.75 (m, 2H), 6.57 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.5, 165.3 (d, J = 247.0 Hz), 158.9 (d, J = 11.2 Hz), 140.1, 131.5 (d, J = 10.6 Hz), 119.3 (d, J = 3.0 Hz), 118.5 (d, J = 2.2 Hz), 108.0 (d, J = 22.0 Hz), 104.0 (d, J = 24.0 Hz); HRMS (ESI) m/z [M + H]$^+$ calcd for $C_9H_8FO_3$ 183.0452, found 183.0450.

*(E)-3-(5-Chloro-2-hydroxyphenyl)acrylic Acid (**1i**).* Recrystallization from MeOH/H_2O; yellow solid, 652 mg (66%), mp 217−219 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.38 (s, 1H), 7.93 (d, J = 16.4 Hz, 1H), 7.64 (d, J = 2.8 Hz, 1H), 7.25 (dd, J = 8.8, 2.8 Hz, 1H), 6.99 (d, J = 8.8 Hz, 1H), 6.66 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.0, 156.0, 139.5, 131.7, 128.9, 125.2, 124.1, 120.4, 118.6; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_9H_8ClO_3$ 199.0157, found 199.0154.

*(E)-3-(3,5-Dichloro-2-hydroxyphenyl)acrylic Acid (**1j**).* Recrystallization from acetone/H_2O; yellow solid, 676 mg (58%), mp 213−215 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.46 (br s, 1H), 10.24 (s, 1H), 7.78 (d, J = 16.0 Hz, 1H), 7.71 (d, J = 2.4 Hz, 1H), 7.53 (d, J = 2.4 Hz, 1H), 6.61 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.5, 150.6, 137.2, 130.2, 126.4, 125.6, 124.0, 122.9, 121.6; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_9H_7Cl_2O_3$ 232.9767, found 232.9765.

*(E)-3-(5-Bromo-2-hydroxyphenyl)acrylic Acid (**1k**).* Recrystallization from acetone/H_2O; yellow solid, 623 mg (51%), mp 215−217 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.44 (s, 1H), 7.92 (d, J = 16.0 Hz, 1H), 7.77 (d, J = 2.4 Hz, 1H), 7.37 (dd, J = 8.8, 2.4 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H), 6.66 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.1, 156.5, 139.4, 134.6, 131.9, 124.7, 120.4, 119.0, 112.3; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_9H_8BrO_3$ 242.9651, found 242.9650.

Preparation of Sodium Sulfinates. Sodium sulfinates **2b**−**e**, **2g**−**i**, **2k**, and **2l** were prepared according to the literature procedure.[33]

General Procedure for the Synthesis of 2-Sulfonylbenzo[*b*]furans. *trans*-2-Hydroxycinnamic acid (**1a**) (1 mmol, 164.2 mg), *p*-toluenesulfinic acid sodium salt tetrahydrate (**2a**) (1.2 mmol, 300.3 mg), $CuCl_2·2H_2O$ (0.5 mmol, 85.2 mg), AgTFA (2.5 mmol, 552.2 mg), and Cs_2CO_3 (2 mmol, 651.6 mg) were dissolved in 6 mL of DMF. The mixture was then stirred at 80 °C for 18 h under ambient atmosphere. After completion of the reaction, the reaction mixture was cooled to room temperature. DMF was removed under reduced pressure, and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (25:1) as the eluent followed by recrystallization in *n*-hexane to afford the product **3aa**.

*2-[(4-Methylphenyl)sulfonyl]benzofuran (**3aa**).* White solid, 215 mg (79%), mp 95−97 °C (lit.[4b] 95−96 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.53 (s, 1H), 7.49 (d, J = 8.8 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 152.0, 145.3, 136.4, 130.0, 128.3, 127.9, 126.0, 124.2, 123.1, 112.9, 112.4, 21.7; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{13}O_3S$ 273.0580, found 273.0576.

*2-[(3-Methylphenyl)sulfonyl]benzofuran (**3ab**).* White solid, 191 mg (70%), mp 116−118 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.88−7.90 (m, 2H), 7.82 (d, J = 7.6 Hz, 1H), 7.76 (s, 1H), 7.50−7.61 (m, 4H), 7.38 (t, J = 8.0 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 157.2, 153.0, 141.0, 140.5, 135.9, 130.4, 129.2, 129.0, 127.0, 126.1, 125.4, 124.4, 114.3, 113.0, 21.2; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{13}O_3S$ 273.0580, found 273.0577.

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*2-[(2-Methylphenyl)sulfonyl]benzofuran (**3ac**).* White solid, 103 mg (38%), mp 97−99 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.96 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 7.6 Hz, 1H), 7.74 (s, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.48−7.54 (m, 3H), 7.38 (t, J = 7.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 157.1, 153.2, 146.5, 137.7, 131.1, 129.1, 129.0, 127.1, 125.3, 124.4, 114.0, 113.0, 21.6; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{13}O_3S$ 273.0580, found 273.0577.

*2-[(4-Methoxyphenyl)sulfonyl]benzofuran (**3ad**).* White solid, 222 mg (77%), mp 78−80 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.02 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 7.6 Hz, 1H), 7.68 (s, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 165.3, 157.1, 153.7, 131.8, 131.4, 129.0, 127.1, 125.3, 124.3, 115.8, 113.4, 112.9, 56.3; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{13}O_4S$ 289.0529, found 289.0526.

*2-[(4-(tert-Butyl)phenyl)sulfonyl]benzofuran (**3ae**).* Light-yellow solid, 204 mg (65%), mp 155−157 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.01 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, acetone-d_6) δ 159.1, 157.2, 153.2, 137.7, 129.1, 128.9, 127.6, 127.1, 125.4, 124.4, 114.1, 113.0, 35.9, 31.2; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{18}H_{19}O_3S$ 315.1049, found 315.1048.

*2-(Phenylsulfonyl)benzofuran (**3af**).* Light-yellow solid, 155 mg (60%), mp 121−123 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.10 (d, J = 7.2 Hz, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.75−7.79 (m, 2H), 7.70 (t, J = 8.0 Hz, 2H), 7.61 (dd, J = 8.4, 0.8 Hz, 1H), 7.53 (dt, J = 7.2, 1.2 Hz, 1H), 7.39 (dt, J = 8.0, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 157.2, 152.9, 140.6, 135.3, 130.6, 129.2, 128.9, 127.0, 125.4, 124.4, 114.5, 113.0; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{14}H_{11}O_3S$ 259.0423, found 259.0421.

*2-(Naphthalen-2-ylsulfonyl)benzofuran (**3ag**).* White solid, 160 mg (52%), mp 158−160 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.77 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.04 (t, J = 7.6 Hz, 2H), 7.70−7.84 (m, 4H), 7.58 (d, J = 8.4 Hz, 1H), 7.51 (dt, J = 8.4, 1.2 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 157.2, 152.9, 137.5, 136.4, 133.2, 130.9, 130.8, 130.6, 130.5, 129.2, 128.93, 128.86, 127.1, 125.4, 124.4, 123.5, 114.6, 113.0; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{18}H_{13}O_3S$ 309.0580, found 309.0578.

*2-[(4-Fluorophenyl)sulfonyl]benzofuran (**3ah**).* Light-yellow solid, 155 mg (56%), mp 96−98 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.15−8.20 (m, 2H), 7.84 (d, J = 7.6 Hz, 1H), 7.79 (s, 1H), 7.62 (dd, J = 8.4, 0.8 Hz, 1H), 7.54 (dt, J = 7.2, 1.6 Hz, 1H), 7.47 (t, J = 8.4 Hz, 2H), 7.40 (dt, J = 8.0, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 167.0 (d, J = 254.0 Hz), 157.3, 152.6, 136.8 (d, J = 2.0 Hz), 132.2 (d, J = 10.0 Hz), 129.3, 127.0, 125.5, 124.5, 117.9 (d, J = 23.0 Hz), 114.6, 113.0; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{14}H_{10}FO_3S$ 277.0329, found 277.0327.

*2-[(4-Chlorophenyl)sulfonyl]benzofuran (**3ai**).* White solid, 149 mg (51%), mp 122−124 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.10 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 7.6 Hz, 1H), 7.81 (s, 1H), 7.73 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 157.3, 152.2, 141.2, 139.3, 130.9, 130.8, 129.4, 127.0, 125.5, 124.5, 114.9, 113.0; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{14}H_{10}ClO_3S$ 293.0034, found 293.0033.

*2-[(4-Bromophenyl)sulfonyl]benzofuran (**3aj**).* White solid, 175 mg (52%), mp 145−147 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.02 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 7.6 Hz, 1H), 7.81 (s, 1H), 7.62 (dd, J = 8.4, 0.8 Hz, 1H), 7.55 (dt, J = 8.4, 1.2 Hz, 1H), 7.40 (dt, J = 8.0, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 157.3, 152.2, 139.8, 133.9, 130.8, 129.9, 129.4, 127.0, 125.5, 124.5, 114.9, 113.1; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{14}H_{10}BrO_3S$ 336.9529, found 336.9531.

*2-[(4-(Trifluoromethyl)phenyl)sulfonyl]benzofuran (**3ak**).* White solid, 144 mg (44%), mp 123−125 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.33 (d, J = 8.0 Hz, 2H), 8.06 (d, J = 8.4 Hz, 2H), 7.89 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 157.5, 151.7, 144.4, 135.8 (q, J = 32.6 Hz), 129.9, 129.6, 127.8 (q, J = 3.7 Hz), 126.9, 125.6, 124.6, 124.3 (d, J = 270.8 Hz), 115.7, 113.1; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{10}F_3O_3S$ 327.0297, found 327.0301.

*N-[4-(Benzofuran-2-ylsulfonyl)phenyl]acetamide (**3al**).* White solid, 227 mg (72%), mp 179−181 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.62 (s, 1H), 8.00 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 9.2 Hz, 2H), 7.82 (d, J = 8.0 Hz, 1H), 7.70 (s, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.52 (dt, J = 7.2, 0.8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 169.7, 157.1, 153.5, 145.9, 133.9, 130.3, 129.0, 127.1, 125.3, 124.3, 119.9, 113.6, 113.0, 24.4; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{16}H_{14}NO_4S$ 316.0638, found 316.0637.

*2-(Methylsulfonyl)benzofuran (**3am**).* Light-yellow solid, 141 mg (72%), mp 69−71 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.86 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.64 (s, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 156.9, 152.9, 129.1, 127.0, 125.3, 124.4, 113.6, 113.1, 43.3; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_9H_9O_3S$ 197.0267, found 197.0268.

*2-[(4-Methylphenyl)sulfonyl]naphtho[2,1-b]furan (**3ba**).* Light-yellow solid, 261 mg (81%), mp 150−152 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.43 (d, J = 8.0 Hz, 1H), 8.36 (s, 1H), 7.98−8.07 (m, 4H), 7.71 (t, J = 8.0 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 155.5, 152.3, 146.4, 138.0, 131.6, 131.1, 130.7, 129.9, 128.88, 128.85, 128.5, 126.7, 124.5, 122.8, 113.4, 113.1, 21.5; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{19}H_{15}O_3S$ 323.0736, found 323.0737.

*4-Methoxy-2-[(4-methylphenyl)sulfonyl]benzofuran (**3ca**).* Light-yellow solid, 172 mg (57%), mp 152−154 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.96 (d, J = 8.4 Hz, 2H), 7.64 (s, 1H), 7.43−7.49 (m, 3H), 7.16 (d, J = 8.8 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 3.98 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 158.2, 155.8, 151.9, 146.4, 137.8, 131.1, 130.4, 129.0, 117.5, 111.4, 105.5, 105.4, 56.4, 21.5; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{16}H_{15}O_4S$ 303.0686, found 303.0682.

*2-(Ethylsulfonyl)-4-methoxybenzofuran (**3cn**).*[3g] Light-yellow solid, 75 mg (31%), mp 63−65 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.57 (s, 1H), 7.52 (t, J = 8.4 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 4.01 (s, 3H), 3.40 (q, J = 7.2 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 158.3, 155.9, 149.9, 130.4, 117.4, 112.5, 105.58, 105.52, 56.4, 50.1, 7.5; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{11}H_{13}O_4S$ 241.0529, found 241.0526.

*6-Methoxy-2-[(4-methylphenyl)sulfonyl]benzofuran (**3da**).* White solid, 187 mg (62%), mp 96−98 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.93 (d, J = 8.4 Hz, 2H), 7.65−7.68 (m, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.14 (s, 1H), 6.98 (dd, J = 8.4, 1.6 Hz, 1H), 3.86 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 161.9, 158.7, 151.8, 146.2, 138.1, 131.0, 128.8, 124.5, 120.0, 115.5, 114.4, 96.4, 56.2, 21.5; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{16}H_{15}O_4S$ 303.0686, found 303.0682.

*5-Methyl-2-[(4-methylphenyl)sulfonyl]benzofuran (**3ea**).* White solid, 157 mg (55%), mp 116−118 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.95 (d, J = 8.0 Hz, 2H), 7.65 (s, 1H), 7.58 (s, 1H), 7.45−7.49 (m, 3H), 7.33 (d, J = 8.0 Hz, 1H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, acetone-d_6) δ 155.7, 153.2, 146.4, 137.8, 135.0, 131.1, 130.5, 128.9, 127.1, 123.7, 113.7, 112.5, 21.5, 21.2; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{16}H_{15}O_3S$ 287.0736, found 287.0732.

*6-(Benzyloxy)-2-[(4-methylphenyl)sulfonyl]benzofuran (**3fa**).* Light-yellow solid, 193 mg (51%), mp 95−97 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.93 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.8 Hz, 1H), 7.65 (s, 1H), 7.46−7.50 (m, 4H), 7.31−7.41 (m, 3H), 7.24 (d, J = 2.0 Hz, 1H), 7.09 (dd, J = 8.4, 2.0 Hz, 1H), 5.21 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.9, 158.5, 152.0, 146.3, 138.1, 137.7, 131.1, 129.4, 128.9, 128.5, 124.6, 120.3, 116.1, 114.3, 97.7, 71.1, 21.5; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{22}H_{19}O_4S$ 379.0999, found 379.0995.

*4-Fluoro-2-[(4-methylphenyl)sulfonyl]benzofuran (**3ga**).* Light-yellow solid, 195 mg (67%), mp 125−127 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.98 (d, J = 8.0 Hz, 2H), 7.79 (s, 1H), 7.45−7.58 (m, 4H), 7.15 (t, J = 8.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz,

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acetone-d_6) δ 158.4 (d, J = 8.2 Hz), 157.4 (d, J = 251.2 Hz), 153.6, 146.8, 137.2, 131.2, 130.2 (d, J = 7.8 Hz), 129.1, 116.5 (d, J = 22.3 Hz), 110.6 (d, J = 18.4 Hz), 109.8 (d, J = 1.7 Hz), 109.5 (d, J = 4.5 Hz), 21.6; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{12}FO_3S$ 291.0486, found 291.0482.

*6-Fluoro-2-[(4-methylphenyl)sulfonyl]benzofuran (**3ha**).* Light-yellow solid, 183 mg (63%), mp 139−141 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.95 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 9.2 Hz, 1H), 7.23 (dt, J = 9.6, 1.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 163.6 (d, J = 244.6 Hz), 157.2 (d, J = 14.0 Hz), 154.0 (d, J = 4.3 Hz), 146.6, 137.5, 131.2, 129.0, 125.6 (d, J = 10.5 Hz), 123.6 (d, J = 1.7 Hz), 114.3, 114.0, 100.6 (d, J = 27.3 Hz), 21.6; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{12}FO_3S$ 291.0486, found 291.0483.

*5-Chloro-2-[(4-methylphenyl)sulfonyl]benzofuran (**3ia**).* Light-yellow solid, 181 mg (59%), mp 159−161 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.96 (d, J = 8.0 Hz, 2H), 7.85 (s, 1H), 7.72 (s, 1H), 7.63 (d, J = 9.2 Hz, 1H), 7.49−7.52 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 155.5, 154.6, 146.8, 137.2, 131.2, 130.4, 129.2, 129.1, 128.5, 123.7, 114.6, 113.4, 21.6; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{12}ClO_3S$ 307.0190, found 307.0188.

*5-Chloro-2-[(4-fluorophenyl)sulfonyl]benzofuran (**3ih**).* Light-yellow solid, 146 mg (47%), mp 146−148 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.18 (dd, J = 8.4, 5.2 Hz, 2H); 7.88 (s, 1H), 7.77 (s, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.55 (dd, J = 8.8, 1.2 Hz, 1H); 7.48 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6) δ 167.1 (d, J = 254.0 Hz), 155.6, 154.1, 136.4 (d, J = 3.0 Hz), 132.4 (d, J = 10.0 Hz), 130.5, 129.5, 128.5, 123.8, 118.0 (d, J = 23.0 Hz), 114.7, 114.0; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{14}H_9ClFO_3S$ 310.9940, found 310.9936.

*5,7-Dichloro-2-[(4-methylphenyl)sulfonyl]benzofuran (**3ja**).* Yellow solid, 68 mg (20%), mp 137−139 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.99 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 2.0 Hz, 1H), 7.80 (s, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 155.4, 151.4, 147.1, 136.9, 131.3, 130.7, 129.7, 129.2, 128.7, 122.9, 118.7, 114.1, 21.6; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{11}Cl_2O_3S$ 340.9801, found 340.9798.

*5-Bromo-2-[(4-methylphenyl)sulfonyl]benzofuran (**3ka**).* Light-yellow solid, 232 mg (66%), mp 166−168 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.01 (d, J = 1.6 Hz, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.72 (s, 1H), 7.65 (dd, J = 8.8, 2.0 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 155.9, 154.5, 146.8, 137.2, 131.9, 131.2, 129.13, 129.09, 126.9, 117.8, 115.0, 113.3, 21.6; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{12}BrO_3S$ 350.9685, found 350.9681.

Preparation of (*E*)-2-[2-(4-Methylphenyl)sulfonylvinyl]-phenol (4). A mixture of *trans*-2-hydroxycinnamic acid (**1a**) (1 mmol, 164.2 mg), *p*-toluenesulfinic acid sodium salt tetrahydrate (**2a**) (1.2 mmol, 300.3 mg), $CuCl_2{\cdot}2H_2O$ (0.1 mmol, 17.0 mg), AgTFA (2.5 mmol, 552.2 mg), and Cs_2CO_3 (2 mmol, 651.6 mg) was dissolved in 6 mL of DMF, and the reaction vessel was then charged three times with argon. The reaction mixture was stirred at 100 °C for 18 h until completion of the reaction and then cooled to room temperature. The mixture was washed with 1 N HCl (40 mL) and then extracted with ethyl acetate (30 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether 1:20 to 1:5) to obtain **4** as a light-yellow solid (143 mg, 52%, mp 129−131 °C). ^{1}H NMR (400 MHz, acetone-d_6) δ 9.31 (s, 1H), 7.89 (d, J = 15.6 Hz, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.59 (dd, J = 8.0, 1.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.26−7.33 (m, 2H), 6.98 (dd, J = 8.0, 0.8 Hz, 1H), 6.90 (dt, J = 8.0, 0.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 157.8, 144.9, 140.0, 138.2, 133.1, 131.0, 130.8, 129.2, 128.3, 121.0, 120.6, 117.1, 21.5; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{15}O_3S$ 275.0736, found 275.0731.

Preparation of 2-Vinylphenol (5).[12] A mixture of **1a** (1 mmol, 164.2 mg), AgTFA (1 mmol, 220.9 mg), and Cs_2CO_3 (2 mmol, 651.6 mg) was dissolved in 6 mL of DMF. The resulting mixture was then stirred at 100 °C for 9 h. After completion of the reaction, the reaction mixture was cooled to room temperature, washed with 1 N HCl (50 mL), and extracted with ethyl acetate (30 mL × 4). After the organic phases were combined, the solution was dried over anhydrous Na_2SO_4 and concentrated. Purification of the residue by silica gel column chromatography using ethyl acetate/petroleum ether (1:40) afforded **5** as a light-yellow oil (65 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.90−6.95 (m, 2H), 6.79 (d, J = 8.0 Hz, 1H), 5.74 (d, J = 18.0 Hz, 1H), 5.36 (d, J = 11.2 Hz, 1H), 5.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 131.5, 128.9, 127.4, 124.8, 120.9, 115.9, 115.8. HRMS (ESI) m/z [M + H]$^+$ calcd for C_8H_9O 121.0648, found 121.0651.

Preparation of Benzofuran-2-carboxylic Acid (6). The preparation of **6** was similar to that of **4** except that the eluent was DCM/MeOH (25:1). Light-yellow solid, 63 mg (39%), mp 194−196 (lit.[34] 194−195 °C); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.80 (d, J = 8.0 Hz, 1H), 7.63−7.66 (m, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 160.3, 156.6, 147.0, 128.5, 128.1, 124.7, 123.9, 114.7, 112.9; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_9H_7O_3$ 163.0390, found 163.0386.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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