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Copper-Catalyzed Decarboxylative Sulfonylation of α,β-Unsaturated Carboxylic Acids

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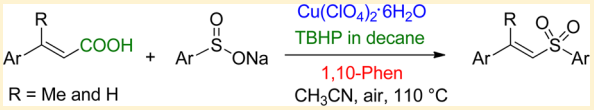
Supporting Information

ABSTRACT: Copper-catalyzed, ligand-promoted decarboxylative coupling of readily available α,β-unsaturated acids with sodium aryl sulfinates is presented. This method provides a new avenue for the synthesis of vinyl sulfones via a decarboxylative radical coupling strategy by employing a catalytic amount of $Cu(ClO_4)_2·6H_2O$, TBHP in decane as an oxidant, and 1,10-phenanthroline as a ligand. The salient feature of this method is that it furnishes exclusively the (*E*)-isomer.

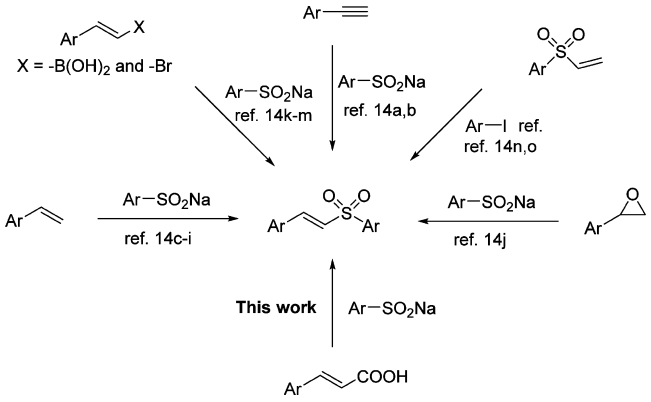


INTRODUCTION

Transition-metal-catalyzed decarboxylative coupling reactions have shown great promise in synthetic organic chemistry and are fast emerging as powerful tools for the formation of carbon−carbon[1] and carbon−heteroatom bonds.[2] Because carboxylic acids and their derivatives are inexpensive and commercially available or readily synthesized by Knoevenagel condensation[3] or Horner−Wittig reaction[4] followed by hydrolysis (for α,β-unsaturated acids), a number of reports on decarboxylative couplings of carboxylic acids or their salts with aromatic halides[5] or triflates,[6] amines,[2e] alcohols,[7] ethers,[7] hydrocarbons,[8] sodium trifluoromethanesulfinate,[9] *t*-BuONO,[10] etc., for synthesizing a variety of organic compounds have been reported.

Vinyl sulfones are versatile building blocks[11] that find their utility as Michael acceptors and are used in cycloaddition reactions. Vinyl sulfones are prominent in medicinal chemistry[11] owing to their wide presence in pharmaceutical molecules, such as enzyme inhibitors and biologically active antagonists; e.g., aspartic vinyl sulfones are inhibitors of a caspase-3-dependent pathway,[12] aza vinyl sulfones are well-known antiplasmodial agents,[13] eletriptan is a drug intended for treatment of migraine headaches, etc. Considering the significance of vinyl sulfones, various synthetic approaches have been reported in the literature.[14] For example, sulfonylation of alkynes,[14a,b] olefins,[14c−i] epoxides,[14j] vinyl halides,[14k,l] or boronic acids[14m] and Heck coupling[14n,o] are a few prominent methods of synthesizing sulfones[14p−r] (Scheme 1). Recently, Liu and co-workers reported a copper-catalyzed C−S cross-coupling reaction between arylpropionic acids and thiols to synthesize vinyl sulfides.[2b] In light of the literature precedence[1,2,5−10] and continuation of our work on the utility of copper catalyst for C-hetero bond-forming reactions,[10a,15] we thought it would be of interest to develop a method by a decarboxylative radical sulfonylation of α,β-unsaturated carboxylic acids using sodium aryl sulfinates. Herein, we disclose the synthesis of vinyl sulfone via decarboxylative coupling of α,β-unsaturated acids employing sodium aryl sulfinates through a ligand-promoted, copper-catalyzed radical pathway.

Scheme 1. Reported Methods for the Synthesis of Vinyl Sulfone derivatives



RESULTS AND DISCUSSION

Optimization Studies. The investigation for screening the reaction conditions began with (*E*)-4-methoxycinnamic acid (**1a**) and sodium *p*-toluenesulfinate (**2a**) as a model substrate using copper catalysts, and results are summarized in Table 1. Preliminary investigations were carried out by using **1a** (1 equiv), **2a** (1.2 equiv), and CuCl (10 mol %) as a catalyst with various oxidizing agents (2 equiv) such as TBHP in decane (*tert*-butyl hydroperoxide), TBHP in water, DTBP (di-*tert*-butyl peroxide), TBPB (*tert*-butyl perbenzoate), and $K_2S_2O_8$ at 80 °C using CH_3CN as a solvent (entries 1−5, Table 1). During the preliminary screening studies, it was found that TBHP in decane was a suitable oxidizing agent, which furnished the expected sulfone **3a** in 37% yield (entry 1, Table 1), while other oxidants were found to be less effective (entries 2−5, Table 1).

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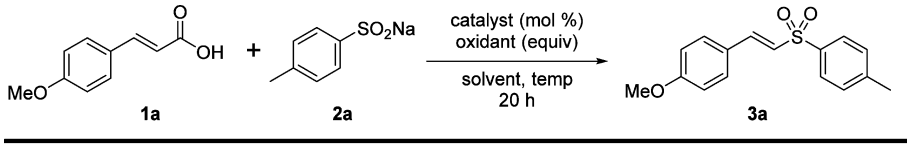
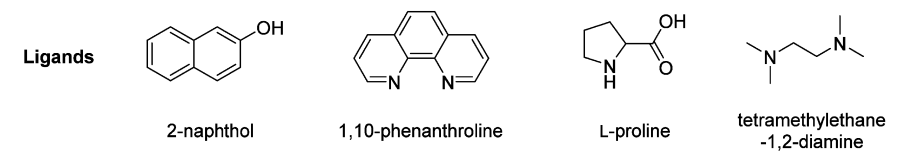
Table 1. Optimization Studies[a]





entry	**2a** (equiv)	catalyst (mol %)	oxidant (equiv)	temp (°C)	yield (%)
1	1.2	CuCl (10)	TBHP in decane (2)	80	37
2	1.2	CuCl (10)	TBHP in H_2O (2)	80	29
3	1.2	CuCl (10)	DTBP (2)	80	20
4	1.2	CuCl (10)	TBPB (2)	80	18
5	1.2	CuCl (10)	$K_2S_2O_8$ (2)	80	20
6	1.2	CuBr (10)	TBHP in decane (2)	80	32
7	1.2	$Cu(OTf)_2$ (10)	TBHP in decane (2)	80	31
8	1.2	$Cu(ClO_4)_2·6H_2O$ (10)	TBHP in decane (2)	80	44
9	1.2	$Cu(ClO_4)_2·6H_2O$ (10)	TBHP in decane (2)	80	25[b]
10	1.2	$Cu(ClO_4)_2·6H_2O$ (10)	TBHP in decane (2)	80	nr[c]
11	1.2	$Cu(ClO_4)_2·6H_2O$ (10)	TBHP in decane (2)	80	nr[d]
12	1.2	$Cu(ClO_4)_2·6H_2O$ (10)	TBHP in decane (2)	80	trace[e]
13	2	$Cu(ClO_4)_2·6H_2O$ (10)	TBHP in decane (2)	80	58[f]
14	2	$Cu(ClO_4)_2·6H_2O$ (10)	TBHP in decane (2)	80	63
15	2	$Cu(ClO_4)_2·6H_2O$ (10)	TBHP in decane (2)	110	67
16	3	$Cu(ClO_4)_2·6H_2O$ (10)	TBHP in decane (2)	110	70
17	2	$Cu(ClO_4)_2·6H_2O$ (20)	TBHP in decane (2)	110	74
18	2	$Cu(ClO_4)_2·6H_2O$ (10)	TBHP in decane (3)	110	76
19	2	$Cu(ClO_4)_2·6H_2O$ (20)	TBHP in decane (3)	110	81
20	2	$Cu(ClO_4)_2·6H_2O$ (20)	TBHP in decane (3)	120	70
21	**2**	**$Cu(ClO_4)_2·6H_2O$ (20)**	**TBHP in decane (3)**	**110**	**83**[g]
22	2	$Cu(ClO_4)_2·6H_2O$ (20)	TBHP in decane (3)	110	72[h]
23	2	$Cu(ClO_4)_2·6H_2O$ (20)	TBHP in decane (3)	110	66[i]
24	2	$FeCl_3$ (20)	$K_2S_2O_8$ (3)	110	nr
25	2	$NiCl_2·6H_2O$ (20)	$K_2S_2O_8$ (3)	110	nr
26	2	$Co(OAc)_2·4H_2O$ (20)	$K_2S_2O_8$ (3)	110	nr
27	2	V_2O_5 (20)	$K_2S_2O_8$ (3)	110	nr
28	2	$FeCl_3$ (20)	TBHP in decane (3)	110	nr[g]
29	2	$NiCl_2·6H_2O$ (20)	TBHP in decane (3)	110	nr[g]
30	2	$Co(OAc)_2·4H_2O$ (20)	TBHP in decane (3)	110	nr[g]
31	2	V_2O_5 (20)	TBHP in decane (3)	110	nr[g]

[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv), **2a** (equiv), catalyst (mol %), oxidant (equiv) in CH_3CN (2.0 mL), open air. [b]$ClCH_2CH_2Cl$ as a solvent instead of CH_3CN. [c]CH_3COOH as an additive. [d]TFA as an additive. [e]TfOH as an additive. [f]2-Naphthol as an additive (20 mol %). [g]1,10-Phen·H_2O as a ligand (20 mol %). [h]L-Proline as a ligand (20 mol %), [i]TMEDA (tetramethylethylenediamine) as a ligand (20 mol %).

Further, other copper salts such as CuBr and $Cu(OTf)_2$ yielded sulfone **3a** in 32% and 31% yields, respectively (entries 6 and 7, Table 1). Among the various copper catalysts that were screened, $Cu(ClO_4)_2·6H_2O$ was found to be the appropriate catalyst (44% yield, entry 8, Table 1). Changing the solvent to dichloroethane was not helpful (25% yield, entry 9, Table 1). Additives such as CH_3COOH, TFA (trifloroacetic acid), TfOH (triflic acid), and 2-naphthol were found to be ineffective (entries 10−13, Table 1). Interestingly, increasing the amount of sodium *p*-toluenesulfinate (**2a**) from 1.2 to 2 equiv increased the yield of the expected product **3a** to 63% (entry 14, Table 1). Increasing the temperature of the reaction to 110 °C has shown the formation of **3a** in 67% yield. Finally, by increasing the amount of catalyst ($Cu(ClO_4)_2·6H_2O$) and oxidant (TBHP in decane) the product **3a** was obtained in 81% yield (entries 15−19, Table 1). Unexpectedly, heating the reaction at 120 °C decreased the yield of **3a** to 70% (entry 20, Table 1). In addition, use of 1,10-phenanthroline as a ligand has brought a marginal increase in the yield of **3a** (81% to 83%, entry 21, Table 1). Later it was noticed that the addition of 1,10-phenanthroline as a ligand brought a considerable improvement in the yields.[16] On the other hand, the utility of ligands such as L-proline and TMEDA decreased the yield of product **3a** to 72% and 66%, respectively (entries 22 and 23, Table 1). Our attempts to enhance the yield by using a variety of metal catalysts such as $FeCl_3$, $NiCl_2·6H_2O$, $Co(OAc)_2·4H_2O$, and V_2O_5 in the presence of either $K_2S_2O_8$ or TBHP were not successful (entries 24−31, Table 1). Finally, it was pleasing to

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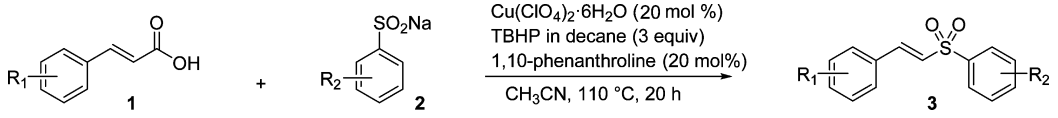
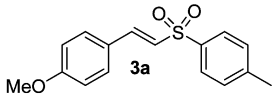
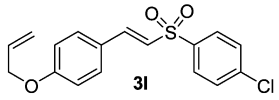
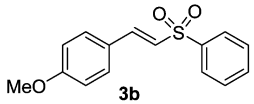
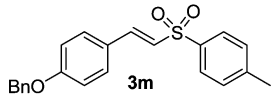
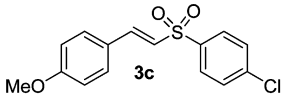
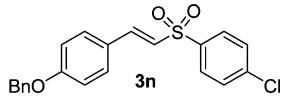
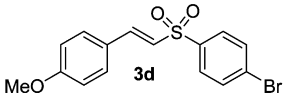
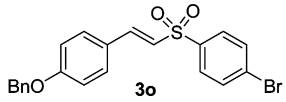
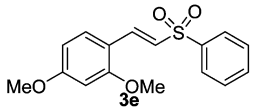
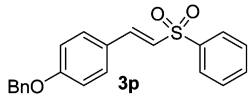
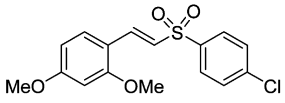
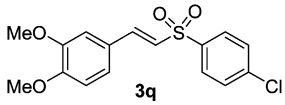
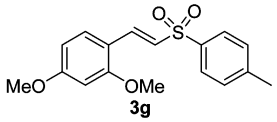
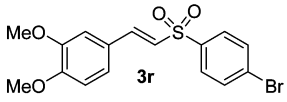
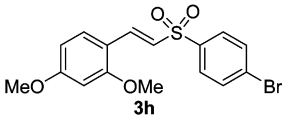
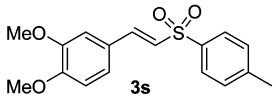
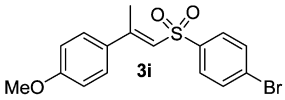
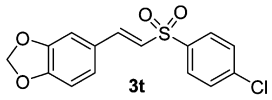
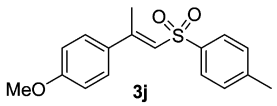
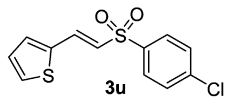
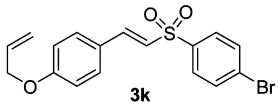
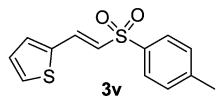
Table 2. Substrate Scope[a]



entry	product	yield (%)	entry	product	yield (%)
1	 **3a**	83	12	 **3l**	33 (38)[b]
2	 **3b**	51	13	 **3m**	45
3	 **3c**	44 (46)[b]	14	 **3n**	49
4	 **3d**	44	15	 **3o**	48
5	 **3e**	65	16	 **3p**	36
6	 **3f**	61	17	 **3q**	54
7	 **3g**	54	18	 **3r**	52
8	 **3h**	56	19	 **3s**	34 (38)[b]
9	 **3i**	62 (*E*:*Z* = 83:17)	20	 **3t**	52
10	 **3j**	49 (*E*:*Z* = 86:14)	21	 **3u**	33
11	 **3k**	42 (45)[b]	22	 **3v**	31

[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv), **2a** (0.50 mmol, 2 equiv), $Cu(ClO_4)_2·6H_2O$ (0.05 mmol, 20 mol %), TBHP in decane (0.75 mmol, 3 equiv), 1,10-Phen.H_2O (0.05 mmol, 20 mol %). [b]Yields in parentheses indicate the yields after 48 h.

find that **1a** (0.25 mmol), **2a** (0.50 mmol), $Cu(ClO_4)_2·6H_2O$ (0.050 mmol), TBHP in decane (0.750 mmol), and 1,10-phenanthroline (0.050 mmol) at 110 °C in CH_3CN as a solvent is required for the efficient synthesis of sulfone via a decarboxylative coupling reaction (entry 21, Table 1).

The scope of the decarboxylative coupling reaction has been explored with a variety of substituted carboxylic acids as presented in Table 2. (*E*)-4-Methoxycinnamic acid underwent a smooth decarboxylative coupling reaction with a variety of sulfinates such as sodium *p*-toluenesulfinate (**2a**), sodium benzenesulfinate (**2b**), sodium 4-bromobenzenesulfinate (**2c**), and sodium 4-chlorobenzenesulfinate (**2d**) to furnish the corresponding sulfones **3a**, **3b**, **3c**, and **3d** in good to moderate yields (entries 1−4, Table 2). (*E*)-3-(2,4-Dimethoxyphenyl)-

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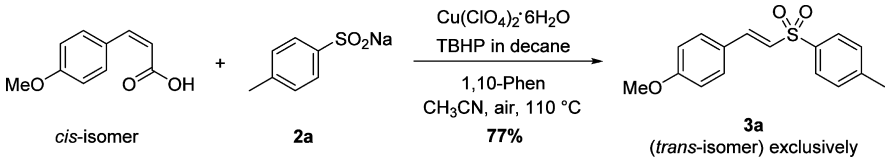
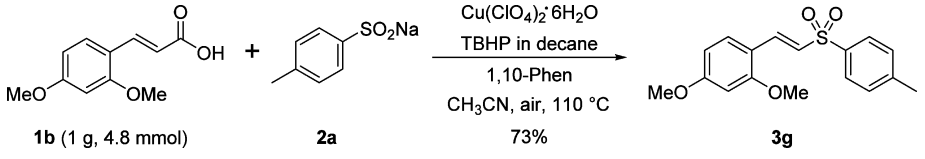
Scheme 2. Selectivity Study[a]



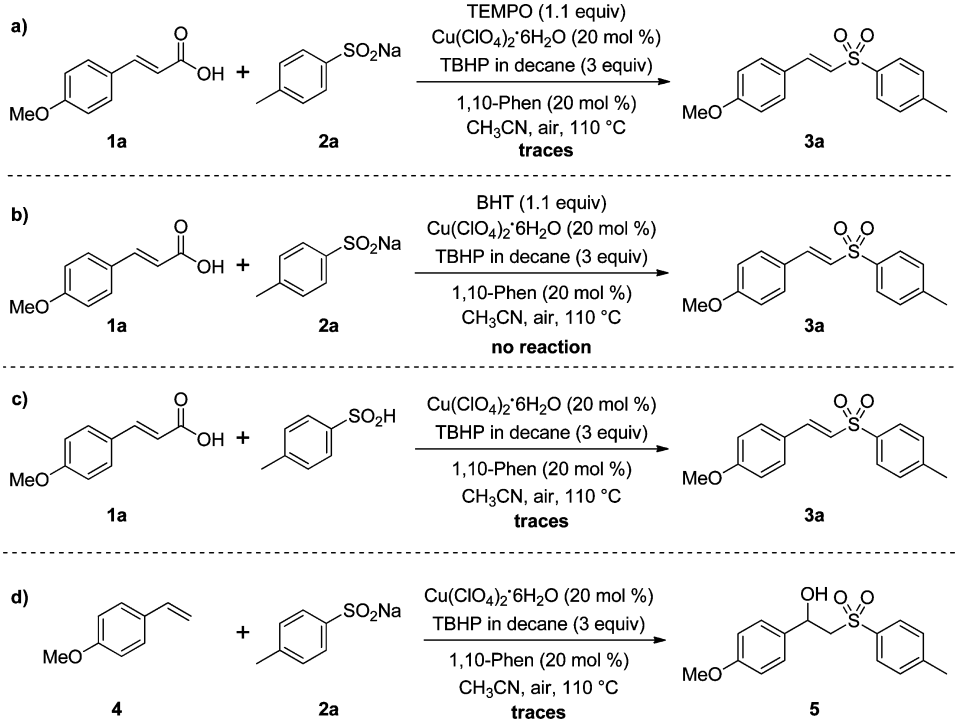
[a]Reaction conditions: *cis*-isomer of **1a** (0.25 mmol, 1 equiv), **2a** (0.50 mmol, 2 equiv), $Cu(ClO_4)_2{\cdot}6H_2O$ (0.05 mmol, 20 mol %), TBHP in decane (0.75 mmol, 3 equiv), 1,10-Phen·H_2O (0.05 mmol, 20 mol %, 20 h.

Scheme 3. Scaling up Experiment[a]



[a]Reaction conditions: **1b** (4.80 mmol), **2a** (2 equiv), $Cu(ClO_4)_2{\cdot}6H_2O$ (20 mol %), TBHP in decane (3 equiv), 1,10-Phen·H_2O (20 mol %), 20 h.

Scheme 4. Control Experiments



acrylic acid in reaction with **2b**, **2c**, **2a**, and **2d** yielded the products **3e**, **3f**, **3g**, and **3h** in moderate yields (65%, 61%, 54%, and 56%, respectively (entries 5−8, Table 2). Similarly, (*E*)-3-(4-methoxyphenyl)but-2-enoic acid reacted well with **2c** and **2a** to furnish the corresponding sulfones **3i** and **3j** in 62% (*E*:*Z*; 83:17) and 49% (*E*:*Z*; 86:14) yields, respectively (entries 9 and 10, Table 2). Further, it was noticed that acid such as (*E*)-3-(4-(allyloxy)phenyl)acrylic acid in a similar coupling reaction with **2c** and **2d** furnished the coupled products **3k** and **3l** in 42% and 33%, yields, respectively (entries 11 and 12, Table 2). The decarboxylative coupling of (*E*)-3-(4-(benzyloxy)phenyl)acrylic acid with **2a**, **2d**, **2c**, and **2b** resulted in the formation of **3m**, **3n**, **3o**, and **3p** in 45%, 49%, 48%, and 36% yields, respectively (entries 13−16, Table 2). The coupling reaction of (*E*)-3-(3,4-dimethoxyphenyl)acrylic acid with **2d**, **2c**, and **2a** proceeded well to afford the products **3q**, **3r**, and **3s** in 54%, 52%, and 34% yields, respectively (entries 17−19, Table 2). Further, (*E*)-3-(benzo[d][1,3]dioxol-5-yl)acrylic acid reacted with **2d** to afford the coupled products **3t** in 52% yield (entry 20, Table 2). The coupling reaction of heterocyclic derivatives such as (*E*)-3-(thiophene-2-yl)acrylic acid with **2d** and **2a** furnished the corresponding products **3u** and **3v** in 33% and 31% yield, respectively (entries 21 and 22, Table 2). To improve the yields of the reaction, a few of the substrates (**3c**, **3k**, **3l**, and **3s**) that were furnishing the products in low yields were allowed to undergo the reaction for extended reaction time (48 h). However, these reactions resulted in a marginal increase in the formation of products (2−5%).

As seen from these examples, various sodium aryl sulfinates furnished the vinyl sulfones in moderate to good yields.[17a] Although, in few examples, the yields are low, it is important to recognize that the present strategy provides a potentially useful

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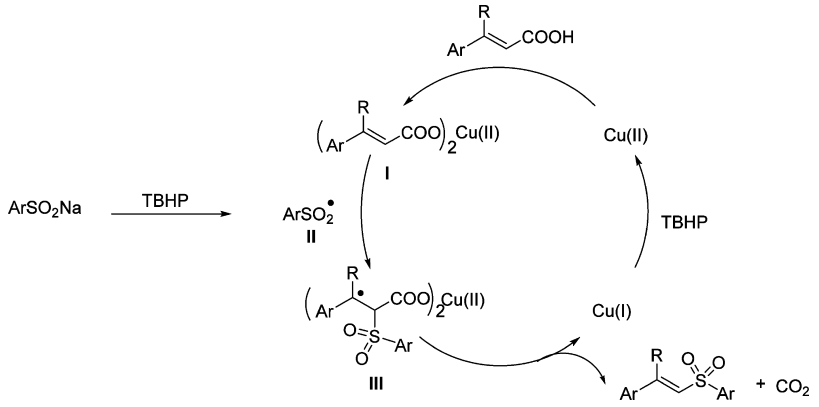
Scheme 5. Tentative Mechanism



method for the synthesis of vinyl sulfones.[17a] Under the reaction conditions, Br and Cl substituents were well tolerated, leading to the corresponding substituted sulfones in moderate yields, which can be further functionalized. Further, it was found that the reaction was stereoselective toward the formation of the *E*-isomer exclusively, which can be attributed to the thermodynamic stability of the product. This was further elaborated by the reaction of the *cis*-isomer of 4-methoxycinnamic acid with sodium *p*-toluenesulfinate (**2a**) under the optimal reaction conditions, which furnished the *E*-isomer of the product **3a** exclusively in 77% yield (Scheme 2). However, our attempts to explore the scope of this strategy using a variety of acid derivatives such as cinnamic acid, (*E*)-3-(4-nitrophenyl)-acrylic acid, (*E*)-3-(1*H*-indol-3-yl)acrylic acid, (*E*)-3-(4-aminophenyl)acrylic acid, (*E*)-3-(4-hydroxyphenyl)acrylic acid, 2-(4-methoxyphenyl)acrylic acid, (*E*)-3-(4-methoxyphenoxy)acrylic acid, (*E*)-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid, 2-(4-methoxyphenyl)acetic acid, 4-methoxybenzoic acid, and 1-benzylpyrrolidine-2-carboxylic acid was not fruitful (see SI-Table 1, Supporting Information).[17b] Further to this, our attempts on the reaction of sodium 2-nitrobenzenesulfinate and sodium 4-methoxy-3-nitrobenzenesulfinate were not successful. However, a similar reaction with sodium methyl sulfinate furnished trace amounts of corresponding sulfones.

A scaling up experiment between **1b** and **2a** under the optimized conditions furnished **3g** in 73% yield, indicating the reaction is more efficient on large scale (Scheme 3).

Mechanistic Considerations. A tentative mechanism has been proposed on the basis of literature precedence[7−10] and the following control experiments. The reaction of 4-methoxycinnamic acid (**1a**) with **2a** was conducted under the optimal reaction conditions in the presence of radical inhibitors such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and BHT (2,4-di-*tert*-butyl-4-methylphenol). As can be seen from Scheme 4, these two radical scavengers retarded the reaction, and the reaction did not proceed. These two experiments indicate that the reaction is probably proceeding via a radical intermediate (eqs *a* and *b*, Scheme 4). However, using sulfinic acid under the optimized reaction conditions did not furnish the expected product (eq c, Scheme 4), which shows the importance of sodium salt. We speculated that the decarboxylation reactions of cinnamic acid may proceed via a protodecarboxylation step to furnish styrene, which further reacts to yield the corresponding products. Therefore, a reaction was performed using a styrene derivative such as 1-methoxy-4-vinylbenzene **4** and **2a** (eq d, Scheme 4). This reaction did not furnish the expected product **3a** and instead produced trace amounts of **5**, indicating that the reaction does not involve a corresponding styrene as an intermediate. During preparation of this manuscript, Liu and co-workers reported a cascade reaction to obtain styrene 2-sulfonylbenzo[*b*]furans via styrene as an intermediate[18] using well-known reaction sequences.[14c−i,19]

On the basis of this information, a tentative reaction mechanism has been proposed as presented in Scheme 5. Cinnamic acid derivatives in the presence of Cu(II) form the corresponding intermediate **I**, which reacts with the sulfone radical **II**, which is generated by the reaction of sodium aryl sulfinate with Cu(II) and TBHP to furnish the radical species **III**.[7−9,20] Further, the species **III** undergoes a decarboxylation to provide the expected product.

■ CONCLUSION

In summary, formation of a C−S bond via ligand-promoted decarboxylative radical sulfonylation of a α,β-unsaturated carboxylic acids strategy has been developed to synthesize vinyl sulfones using Cu catalyst. This reaction is selective and exclusively furnishes the corresponding *E*-isomer. This method provides a new route for the synthesis of vinyl sulfones using a decarboxylation strategy to obtain vinyl sulfones via a radical pathway.

■ EXPERIMENTAL SECTION

General Experimental Procedures. All reactions were carried out using distilled solvents. Reactions were monitored by using precoated silica TLC plates. Mass spectra were recorded on EI, and ESI (TOF) modes. NMR spectra were recorded in at 400 MHz. Column chromatography was carried out on silica gel 230−400 mesh or 100−200 mesh. Chemicals obtained from commercial suppliers were used without further purification. Sodium sulphinates **2a**, **2b**, **2c** and **2d** were purchased from commercial suppliers. All cinnamic acid **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g** and **1h** were prepared according to literature procedure.[21−24] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Typical General Experimental Procedure: Synthesis of Vinyl Sulfone from α,β-Unsaturated Acid and Sodium Aryl Sulfinate. TBHP in decane (0.15 mL, 0.75 mmol, 3 equiv, 5. 0 M soluion) was added dropwise at room temperature to a well-stirred mixture of α,β-unsaturated acid (**1a**, 44.5 mg, 0.25 mmol, 1 equiv), sodium aryl sulfinate (**2a**, 90 mg, 0.50 mmol, 2 equiv), $Cu(ClO_4)_2{\cdot}6H_2O$ (18.5 mg, 0.05 mmol, 20 mol %), and 1,10-phenathroline·H_2O (9.9 mg, 0.05 mmol, 20 mol %) in CH_3CN (2 mL) and then heated at 110 °C until the reaction was complete (20 h, monitored by TLC). After completion of the reaction, the reaction mixture was cooled to room

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temperature, solvent was removed under reduced pressure, and the product was directly loaded on silica column for the purification.

*(E)-1-Methoxy-4-(2-tosylvinyl)benzene (**3a**):* white solid; yield 83% (59.8 mg); mp 176−178 °C (lit.[25] mp 177−180 °C); R_f (25% EtOAc/hexane) 0.40; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 2923, 1603, 1514, 1260, 1142; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8 Hz, 2H), 7.60 (d, J = 16 Hz, 1H), 7.43−7.32 (m, 4H), 6.89 (d, J = 8 Hz, 2H), 6.70 (d, J = 16 Hz, 1H), 3.82 (s, 3H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.9, 144.1, 141.7, 138.1, 130.2, 129.8, 127.5, 125.0, 124.7, 114.4, 55.4, 21.5; HRESI-MS (m/z) calcd for $C_{16}H_{16}O_3S$ (M + Na) 311.0718, found (M + Na) 311.0717.

*(E)-1-Methoxy-4-(2-(phenylsulfonyl)vinyl)benzene (**3b**):* yellow gummy liquid; yield 51% (34.9 mg); R_f (25% EtOAc/hexane) 0.60; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 3056, 2932, 1601, 1513, 1306, 1259, 1144; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8 Hz, 2H), 7.65−7.52 (m, 4H), 7.44 (d, J = 8 Hz, 2H), 6.90 (d, J = 8 Hz, 2H), 6.71 (d, J = 16 Hz, 1H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0, 142.3, 141.1, 133.1, 130.4, 129.2, 127.5, 124.9, 124.4, 114.5, 55.4; HRESI-MS (m/z) calcd for $C_{15}H_{14}O_3S$ (M + Na) 297.0561, found (M + Na) 297.0562.

*(E)-1-Chloro-4-((4-methoxystyryl)sulfonyl)benzene (**3c**):* white solid; yield 44% (33.9 mg); mp 140−142 °C (lit.[26] mp 144−145 °C); R_f (25% EtOAc/hexane) 0.60; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 2926, 1626, 1311, 1256, 1142; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8 Hz, 2H), 7.63 (d, J = 16 Hz, 1H), 7.51 (d, J = 8 Hz, 2H), 7.44 (d, J = 8 Hz, 2H), 6.91 (d, J = 8 Hz, 2H), 6.68 (d, J = 16 Hz, 1H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.2, 142.9, 139.8, 139.6, 130.5, 129.5, 129.0, 124.7, 123.8, 114.5, 55.4; HRESI-MS (m/z) calcd for $C_{15}H_{13}ClO_3S$ (M + Na) 331.0172, found (M + Na) 331.0173.

*(E)-1-Bromo-4-((4-methoxystyryl)sulfonyl)benzene (**3d**):* yellowish solid; yield 44% (38.8 mg); mp 144−147 °C (lit.[27] mp 149 °C); R_f (25% EtOAc/hexane) 0.60; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 2935, 1602, 1514, 1310, 1255, 1139; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8 Hz, 2H), 7.67 (d, J = 8 Hz, 2H), 7.63 (d, J = 16 Hz, 1H), 7.43 (d, J = 8 Hz, 2H), 6.90 (d, J = 8 Hz, 2H), 6.68 (d, J = 16 Hz, 1H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.2, 142.9, 140.2, 132.5, 130.5, 129.1, 128.3, 124.7, 123.8, 114.5, 55.4; HRESI-MS (m/z) calcd for $C_{15}H_{13}BrO_3S$ (M + Na) 374.9666, found (M + Na) 374.9666.

*(E)-2,4-Dimethoxy-1-(2-(phenylsulfonyl)vinyl)benzene (**3e**):* yellow gummy liquid; yield 65% (49.4 mg); R_f (25% EtOAc/hexane) 0.40; prepared as shown in the general experimental procedure; IR (neat, cm^{-1}) 2939, 1600, 1567, 1505, 1446, 1302, 1211, 1142, 1084, 1026; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2H), 7.79 (d, J = 15.6 Hz, 1H), 7.58−7.50 (m, 3H), 7.34 (d, J = 8.4 Hz, 1H), 6.96 (d, J = 15.2 Hz, 1H), 6.49 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.40 (d, J = 2 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.4, 160.4, 141.6, 138.6, 132.8, 132.5, 129.1, 127.4, 124.8, 114.4, 105.3, 98.5, 55.5, 55.4; HRESI-MS (m/z) calcd for $C_{16}H_{16}SO_4$ (M + Na) 327.0667, found (M + Na) 327.0665.

*(E)-1-(2-((4-Chlorophenyl)sulfonyl)vinyl)-2,4-dimethoxybenzene (**3f**):* yellow gummy liquid; yield 61% (51.6 mg); R_f (25% EtOAc/hexane) 0.40; prepared as shown in the general experimental procedure; IR (neat, cm^{-1}) 2939, 1601, 1505, 1468, 1439, 1303, 1277, 1212, 1144, 1086, 1028; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 15.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 1H), 6.93 (d, J = 15.2 Hz, 1H), 6.50 (dd, J_1 = 8.4 Hz, J_2 = 2 Hz, 1H), 6.44 (d, J = 2 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.6, 160.5, 140.2, 139.4, 139.2, 132.8, 129.4, 128.9, 124.4, 114.3, 105.4, 98.5, 55.5, 55.4; HRESI-MS (m/z) calcd for $C_{16}H_{15}SClO_4$ (M + Na): 361.0277, found (M + Na) 361.0277.

*(E)-2,4-Dimethoxy-1-(2-tosylvinyl)benzene (**3g**):* yellow gummy liquid; yield 73% (58.1 mg) and 54% (42.9 mg); R_f (25% EtOAc/hexane) 0.40; prepared as shown in the general experimental procedure. IR (neat, cm^{-1}) 2918, 1601, 1575, 1457, 1303, 1275, 1211, 1159, 1141; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8 Hz, 2H), 7.77 (d, J = 15.2 Hz, 1H), 7.34−7.30 (m, 3H), 6.94 (d, J = 15.6 Hz, 1H), 6.49 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.43 (d, J = 2 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 160.3, 143.7, 138.6, 138.0, 132.4, 129.7, 127.4, 125.2, 114.4, 105.3, 98.4, 55.5, 55.4, 21.5; HRESI-MS (m/z) calcd for $C_{17}H_{18}SO_4$ (M + Na) 341.0824, found (M + Na) 341.0827.

*(E)-1-(2-((4-Bromophenyl)sulfonyl)vinyl)-2,4-dimethoxybenzene (**3h**):* yellow gummy liquid; yield 56% (53.6 mg); R_f (25% EtOAc/hexane) 0.45; prepared as shown in the general experimental procedure; IR (neat, cm^{-1}) 2918, 1601, 1576, 1457, 1299, 1288, 1211, 1141, 1084, 1025; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80−7.72 (m, 3H), 7.65 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 15.2 Hz, 1H), 6.50 (dd, J_1 = 8.4 Hz, J_2 =2 Hz, 1H), 6.44 (d, J = 2 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.6, 160.5, 140.7, 139.2, 132.8, 132.4, 129.0, 127.9, 124.3, 114.2, 105.4, 98.5, 55.5, 55.4; HRESI-MS (m/z) calcd for $C_{16}H_{15}SBrO_4$ (M + Na) 404.9772, found (M + Na) 404.9775.

*(E)-1-Bromo-4-((2-(4-methoxyphenyl)prop-1-en-1-yl)sulfonyl)-benzene (**3i**):* E/Z = 83:17; yellowish gummy liquid; yield 62% (56.9 mg); R_f (25% EtOAc/hexane) 0.60; prepared as shown in the general experimental procedure; IR (neatr, cm^{-1}) 3422, 2933, 1637, 1307, 1257, 1141; major isomer E: ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8 Hz, 2H), 7.69 (d, J = 8 Hz, 2H), 7.37 (d, J = 8 Hz, 2H), 6.88 (d, J = 8 Hz, 2H), 6.56 (s, 1H), 3.82 (s, 3H), 2.49 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2, 153.6, 141.4, 132.4, 131.7, 128.7, 128.2, 127.8, 124.8, 114.1, 55.4, 16.9; HRESI-MS (m/z) calcd for $C_{16}H_{15}BrO_3S$ (M + Na) 388.9823, found (M + Na) 388.9824.

*(E)-1-Methoxy-4-(1-tosylprop-1-en-2-yl)benzene (**3j**):* E/Z = 86:14; yellow solid; yield 49% (37.0 mg); mp 66−69 °C; R_f (25% EtOAc/hexane) 0.50; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 3439, 2925, 1649, 1383, 1020; major isomer E: ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8 Hz, 2H), 7.37−7.33 (m, 4H), 6.87 (d, J = 8 Hz, 2H), 6.57 (s, 1H), 3.81 (s, 3H), 2.48 (s, 3H), 2.43 (s, 3H) ; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.0, 152.3, 143.9, 139.5, 132.1, 129.8, 127.7, 127.2, 125.8, 114.0, 55.3, 21.6, 16.8; HRESI-MS (m/z) calcd for $C_{17}H_{18}O_3S$ (M + Na) 325.0874, found (M + Na) 325.0871.

*(E)-1-(Allyloxy)-4-(2-((4-bromophenyl)sulfonyl)vinyl)benzene (**3k**):* white solid; yield 42% (39.8 mg); R_f (25% EtOAc/hexane) 0.40; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 3093, 2920, 1603, 1574, 1510, 1388, 1310, 1255, 1138, 1081, 1010, 810; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 15.2 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 15.2 Hz, 1H), 6.03 (m, 1H), 5.36 (dd, 2H), 4.57 (d, J = 5.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2, 142.8, 140.2, 132.5, 132.4, 130.4, 129.1, 128.3, 124.9, 123.9, 118.2, 115.3, 68.9; HRESI-MS (m/z) calcd for $C_{17}H_{15}BrO_3S$ (M + Na) 400.9823, found (M + Na) 400.9823.

*(E)-1-(Ellyloxy)-4-(2-((4-chlorophenyl)sulfonyl)vinyl)benzene (**3l**):* white solid; yield 33% (27.6 mg); mp 132−136 °C; R_f (25% EtOAc/hexane) 0.40; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 3094, 2923, 1603, 1583, 1509, 1395, 1311, 1255, 1142, 1087, 1014, 811; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 15.2 Hz, 1H), 7.50 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 15.2 Hz, 1H), 6.07−5.98 (m, 1H), 5.36 (dd, 2H), 4.57 (d, J = 5.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2, 142.8, 139.8, 139.7, 132.5, 130.4, 129.6, 129.0, 124.9, 124.0, 118.2, 115.3, 68.9; HRESI-MS (m/z) calcd for $C_{17}H_{15}BrO_3S$ (M + Na) 400.9823, found (M + Na) 400.9823.

*(E)-1-(Benzyloxy)-4-(2-tosylvinyl)benzene (**3m**):* yellow solid; yield 45% (41.0 mg); mp 156−161 °C; R_f (25% EtOAc/hexane) 0.60; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 3445, 1606, 1256, 1175, 1141, 1084; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.2 Hz, 2H), 7.60 (d, J = 15.2 Hz, 1H), 7.40−7.31 (m, 9H), 6.96 (d, J = 7.6 Hz, 2H), 6.79 (d, J = 15.2 Hz, 1H), 5.09 (s, 2H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.1, 144.1, 141.6, 138.1, 136.2, 130.3, 129.9, 128.6, 128.2, 127.5, 127.4, 125.2, 124.9, 115.3, 70.1, 21.6; HRESI-MS (m/z) calcd for $C_{22}H_{20}O_3S$ (M + Na) 387.1031, found (M + Na) 387.1032.

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(E)-1-(Benzyloxy)-4-(2-((4-chlorophenyl)sulfonyl)vinyl)benzene (**3n**): white solid; yield 49% (47.1 mg); mp 132−135 °C; R_f (15% EtOAc/hexane) 0.35; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 3438, 2920, 1625, 1261, 1140; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8 Hz, 2H), 7.62 (d, J = 16 Hz, 1H), 7.56−7.33 (m, 9H), 6.97 (d, J = 8 Hz, 2H), 6.67 (d, J = 16 Hz, 1H), 5.10 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3, 142.8, 139.8, 139.7, 136.1, 130.5, 129.6, 129.0, 128.7, 128.2, 127.4, 125.0, 124.1, 115.4, 70.1; HRESI-MS (m/z) calcd for $C_{21}H_{17}ClO_3S$(M + Na) 407.0485, found (M + Na) 407.0488.

(E)-1-(Benzyloxy)-4-(2-((4-bromophenyl)sulfonyl)vinyl)benzene (**3o**): yellow solid; yield 48% (51.5 mg); mp 129−133 °C; R_f (15% EtOAc/hexane) 0.40; Prepared as shown in the general experimental procedure. IR (KBr, cm^{-1}) 3448, 2921, 1602, 1314, 1261, 1143, 1086, 1013; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82−7.38 (m, 12H), 6.97 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 15.6 Hz, 1H), 5.10 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3, 142.8, 140.2, 136.1, 132.7, 132.6, 130.5, 129.1, 128.7, 128.2, 127.4, 125.0, 124.0, 115.4, 70.1; HRESI-MS (m/z) calcd for $C_{21}H_{17}BrO_3S$ (M + Na) 450.9979, found (M + Na) 450.9977.

(E)-1-(Benzyloxy)-4-(2-(phenylsulfonyl)vinyl)benzene (**3p**): white solid; yield 36% (31.5 mg); R_f (15% EtOAc/hexane) 0.40; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 3449, 2925, 2854, 1601, 1306, 1254, 1145, 1083, 1010, 974; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2H), 7.61−7.35 (m, 11H), 6.97 (d, J = 8 Hz, 2H), 6.71 (d, J = 15.6 Hz, 1H), 5.09 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2, 142.2, 141.8, 136.1, 133.2, 130.4, 129.2, 128.7, 128.2, 127.5, 127.4, 125.2, 124.5, 115.4, 70.1; HRESI-MS (m/z) calcd for $C_{21}H_{18}O_3S$ (M + Na) 373.0874, found (M + Na) 373.0874.

(E)-4-(2-((4-Chlorophenyl)sulfonyl)vinyl)-1,2-dimethoxybenzene (**3q**): yellowish gummy liquid; yield 54% (45.7 mg); R_f (25% EtOAc/hexane) 0.40; prepared as shown in the general experimental procedure; IR (neat, cm^{-1}) 3853, 3743, 3617, 1699, 1684, 1524, 1270, 1144, 1019; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8 Hz, 2H), 7.62 (d, J = 16 Hz, 1H), 7.51 (d, J = 8 Hz, 2H), 7.09 (d, J = 8 Hz, 1H), 6.97 (s, 1H), 6.87 (d, J = 8 Hz, 1H), 6.70 (d, J = 16 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.0, 149.3, 143.1, 139.8, 139.6, 129.6, 129.0, 125.0, 124.1, 123.6, 111.0, 109.9, 56.0, 55.9; HRESI-MS (m/z) calcd for $C_{16}H_{15}ClO_4S$ (M + Na) 361.0277, found (M + Na) 361.0277.

(E)-4-(2-((4-Bromophenyl)sulfonyl)vinyl)-1,2-dimethoxybenzene (**3r**): yellowish gummy liquid; yield 52% (49.8 mg); R_f (25% EtOAc/hexane) 0.40; prepared as shown in the general experimental procedure. IR (neat, cm^{-1}) 3853, 3744, 3617, 2934, 1699, 1521, 1270, 1141, 1022, 1010; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8 Hz, 2H), 7.68 (d, J = 8 Hz, 2H), 7.62 (d, J = 16 Hz, 1H), 7.10 (d, J = 8 Hz, 1H), 6.97 (s, 1H), 6.87 (d, J = 8 Hz, 1H), 6.70 (d, J = 16 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.0, 149.3, 143.1, 140.1, 132.5, 129.1, 128.4, 125.0, 124.0, 123.6, 111.0, 109.9, 56.0, 55.9; HRESI-MS (m/z) calcd for $C_{16}H_{15}BrO_4S$ (M + Na) 404.9772, found (M + Na) 404.9772.

(E)-1,2-Dimethoxy-4-(2-tosylvinyl)benzene (**3s**): yellow solid; yield 34% (27.0 mg); mp 125−127 °C (lit.[28] mp 126−127 °C); R_f (25% EtOAc/hexane) 0.30; prepared as shown in the general experimental procedure; IR (KBr, cm^{-1}) 3853, 3742, 3392, 2925, 1590, 1540, 1516, 1508, 1269, 1142, 1085, 1021; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8 Hz, 2H), 7.60 (d, J = 16 Hz, 1H), 7.34 (d, J = 8 Hz, 2H), 7.09 (d, J = 8 Hz, 1H), 6.97 (s, 1H), 6.87 (d, J = 8 Hz, 1H), 6.72 (d, J = 16 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.7, 149.2, 144.1, 142.0, 138.1, 129.1, 127.5, 125.2, 125.0, 123.3, 111.0, 109.9, 56.0, 55.9, 21.5; HRESI-MS (m/z) calcd for $C_{17}H_{18}O_4S$(M + Na) 341.0824, found (M + Na) 341.0824.

(E)-5-(2-((4-Chlorophenyl)sulfonyl)vinyl)benzo[d][1,3]dioxole (**3t**): yellow gummy solid; yield 52% (41.9 mg); R_f (25% EtOAc/hexane) 0.40; prepared as shown in the general experimental procedure. IR (KBr, cm^{-1}) 3393, 1684, 1522, 1257, 1146, 1086, 1037; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8 Hz, 2H), 7.58 (d, J = 15.2 Hz, 1H), 7.51 (d, J = 8 Hz, 2H), 7.00 (dd, J_1 = 1.2 Hz, J_2 = 8 Hz, 1H), 6.94 (d, J = 1.2 Hz, 1H), 6.82 (d, J = 8 Hz, 1H), 6.64 (d, J = 15.2 Hz, 1H), 6.01 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.5, 148.5, 142.8, 139.9, 139.5, 129.6, 129.0, 126.4, 125.5, 124.4, 108.7, 106.8, 101.8; HRESI-MS (m/z) calcd for $C_{15}H_{11}ClO_4S$(M + Na) 344.9964, found (M + Na) 344.9964.

(E)-2-(2-((4-Chlorophenyl)sulfonyl)vinyl)thiophene (**3u**): yellow gummy solid; yield 33% (23.4 mg); R_f (25% EtOAc/hexane) 0.70; prepared as shown in the general experimental procedure. IR (KBr, cm^{-1}) 3421, 2918, 1601, 1317, 1143, 1010, 960, 816; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81−7.77 (m, 3H), 7.69 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 4.8 Hz, 1H), 7.32 (d, J = 4.8 Hz, 1H), 7.08 (t, J = 4 Hz, 1H), 6.61 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.9, 136.8, 135.7, 132.7, 132.6, 130.3, 129.1, 128.6, 128.4, 124.9; HRESI-MS (m/z) calcd for $C_{12}H_9ClO_2S_2$ (M + Na) 306.9630, found (M + Na) 306.9626.

(E)-2-(2-Tosylvinyl)thiophene (**3v**): yellow solid; yield 31% (20.4 mg); mp 121−124 °C; R_f (15% EtOAc/hexane) 0.45; prepared as shown in the general experimental procedure. IR (KBr, cm^{-1}) 3454, 2922, 1605, 1303, 1142, 1085, 960, 814; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8 Hz, 2H), 7.77 (d, J = 16 Hz, 1H), 7.43 (d, J = 4 Hz, 1H), 7.34 (d, J = 8 Hz, 2H), 7.30 (d, J = 4 Hz, 1H), 7.06 (t, J = 4 Hz, 1H), 6.63 (d, J = 16 Hz, 1H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.3, 137.8, 137.0, 134.6, 132.3, 130.0, 129.8, 128.3, 127.6, 125.8, 21.6; HRESI-MS (m/z) calcd for $C_{13}H_{12}O_2S_2$ (M + Na) 287.0176, found (M + Na) 287.0174.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C spectra and spectral data . This material is available free of charge via the Internet. http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Professor H. Ila, JNCASR, Bangalore, on the occasion of her 70th birthday.

■ REFERENCES

(1) Some representative reviews: (a) Rodriguez, N.; Goossen, L. J. *Chem. Soc. Rev.* **2011**, *40*, 5030. (b) Rui, S.; Lei, L. *Sci. China. Chem.* **2011**, *54*, 1670. (c) Weaver, J. D.; Recio, A., III; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846. (d) Cornella, J.; Larrosa, I. *Synthesis* **2012**, *44*, 653. (e) Dzik, W. I.; Lange, P. P.; Goossen, L. J. *Chem. Sci.* **2012**, *3*, 2671. (f) Park, K.; Lee, S. *RSC Adv.* **2013**, *3*, 14165.

(2) Some representative examples: (a) Duan, Z.; Ranjit, S.; Zhang, P.; Liu, X. *Chem.—Eur. J.* **2009**, *15*, 3666. (b) Ranjit, S.; Duan, Z.; Zhang, P.; Liu, X. *Org. Lett.* **2010**, *12*, 4134. (c) Jia, W.; Jiao, N. *Org. Lett.* **2010**, *12*, 2000. (d) Hu, J.; Zhao, N.; Yang, B.; Wang, G.; Guo, L.-N.; Liang, Y.-M; Yang, S.-D. *Chem.—Eur. J.* **2011**, *17*, 5516. (e) Zhang, Y.; Patel, S.; Mainolfi, N. *Chem. Sci.* **2012**, *3*, 3196. (f) Bhadra, S.; Dzik, W. I.; Goossen, L. J. *J. Am. Chem. Soc.* **2012**, *134*, 9938. (g) Priebbenow, D. L.; Becker, P.; Bolm, C. *Org. Lett.* **2013**, *15*, 6155. (h) Duan, Z.; Ranjit, S.; Zhang, P.; Liu, X. *Chem.—Eur. J.* **2009**, *15*, 3666. (i) Becht, J.-M.; Le Drian, C. *J. Org. Chem.* **2011**, *76*, 6327. For additional references, see the reviews mentioned in ref 1.

(3) (a) De, A.; Karchaudhuri, N.; Mitra, A. K. *Synth. Commun.* **1999**, *29*, 573. (b) Chen, C.; Hu, P.; Wang, B.-Q.; Zhao, K.-Q.; Monobe, H.; Shimizu, Y. *Chem. Commun.* **2011**, *47*, 6290.
(4) (a) Dai, W.-M.; Fong, K. C.; Lau, C. W.; Lee, M. Y. H.; Wu, J. *J. Org. Chem.* **1999**, *64*, 5062. (b) Charette, A. B.; Brochu, C.; Molinaro, C. *J. Am. Chem. Soc.* **2001**, *123*, 12168.
(5) (a) Peschko, C.; Winklhofer, C.; Steglich, W. *Chem.—Eur. J.* **2000**, *6*, 1147. (b) Goossen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662. (c) Forgione, P.; Brochu, M. C.; St-Onge, M.; Thesen, K. H.; Bailey, M. D.; Bilodeau, F. *J. Am. Chem. Soc.* **2006**, *128*, 11350. (d) Goossen, L. J.; Rudolphi, F.; Oppel, C.; Rodriguez, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 3043.
(6) Goossen, L. J.; Rodriguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248.
(7) Cui, Z.; Shang, X.; Shao, X.-F.; Liu, Z.-Q. *Chem. Sci.* **2012**, *3*, 2853.
(8) Yang, H.; Sun, P.; Zhu, Y.; Yan, H.; Lu, L.; Qu, X.; Li, T.; Mao, J. *Chem. Commun.* **2012**, *48*, 7847.
(9) Li, Z.; Cui, Z.; Liu, Z.-Q. *Org. Lett.* **2013**, *15*, 406.
(10) (a) Rokade, B. V.; Prabhu, K. R. *Org. Biomol. Chem.* **2013**, *11*, 6713. (b) Manna, S.; Jana, S.; Saboo, T.; Maji, A.; Maiti, D. *Chem. Commun.* **2013**, *49*, 5286.
(11) (a) Meadows, D. C.; Gervay-Hague, J. *Med. Res. Rev.* **2006**, *26*, 793. (b) Francisco, J. L.-J.; Mariano, O.-M.; Alicia, M.-F.; Fernando, H.-M.; Francisco, S.-G. *Bioconjugate Chem.* **2012**, *23*, 846.
(12) Glória, P. M. C.; Coutinho, I.; Gonçalves, L. M.; Baptista, C.; Soares, J.; Newton, A. S.; Moreira, R.; Saraiva, L.; Santos, M. M. M. *Eur. J. Med. Chem.* **2011**, *46*, 2141.
(13) Glória, P. M. C.; Gut, J.; Gonçalves, L. M.; Rosenthal, P. J.; Moreira, R.; Santos, M. M. M. *Bioorg. Med. Chem.* **2011**, *19*, 7635.
(14) Some representative examples: (a) Taniguchi, N. *Synlett* **2012**, *23*, 1245. (b) Xue, Q.; Mao, Z.; Shi, Y.; Mao, H.; Cheng, Y.; Zhu, C. *Tetrahedron Lett.* **2012**, *53*, 1851. (c) Nair, V.; Augustine, A.; George, T. G.; Nair, L. G. *Tetrahedron Lett.* **2001**, *42*, 6763. (d) Katrun, P.; Chiampanichayakul, S.; Korworapan, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Kuhakarn, C. *Eur. J. Org. Chem.* **2010**, 5633. (e) Kamigata, N.; Sawada, H.; Kobayashi, M. *J. Org. Chem.* **1983**, *48*, 3793. (f) Taniguchi, N. *Synlett* **2011**, 1308. (g) Nair, V.; Augustine, A.; Suja, T. D. *Synthesis* **2002**, 2259. (h) Das, B.; Lingaiah, M.; Damodar, K.; Bhunia, N. *Synthesis* **2011**, 2941. (i) Sawangphon, T.; Katrun, P.; Chaisiwamongkhol, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. *Synth. Commun.* **2013**, *43*, 1692. (j) Chawla, R.; Kapoor, R.; Singh, A. K.; Yadav, L. D. S. *Green Chem.* **2012**, *14*, 1308. (k) Russell, G. A.; Ngoviwatchai, P.; Tashtoush, H. I.; Pla-Dalmau, A.; Khanna, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 3530. (l) Bian, M.; Xu, F.; Ma, C. *Synthesis* **2007**, 2951. (m) Huang, F.; Batey, R. A. *Tetrahedron* **2007**, *63*, 7667. (n) Na, Y.; Park, S.; Han, S. B.; Han, H.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2004**, *126*, 250. (o) Ruano, J. L. G.; Alemán, J.; Paredes, C. G. *Org. Lett.* **2006**, *8*, 2683. While our manuscript was under revision, similar reports appeared in the literature; see: (p) Guo, R.; Gui, Q.; Wang, D.; Tan, Z. *Catal. Lett.* **2014**, *144*, 1377. (q) Xu, Y.; Tang, X.; Hu, W.; Wu, W.; Jiang, H. *Green Chem.* **2014**, *16*, 3720. (r) Jiang, Q.; Xu, B.; Jia, J.; Zhao, A.; Zhao, Y.-R.; Li, Y.-Y.; He, N.-N.; Guo, C.-C. *J. Org. Chem.* **2014**, *79*, 7372.
(15) (a) Lamani, M.; Prabhu, K. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 6622. (b) Rokade, B. V.; Malekar, S. K.; Prabhu, K. R. *Chem. Commun.* **2012**, *48*, 5506. (c) Rokade, B. V.; Prabhu, K. R. *J. Org. Chem.* **2012**, *77*, 5364.
(16) The decarboxylative sulfonylation was successful with **1a** and **2a** in the absence of ligands (entry 19, Table 1). However, this observation could not be generalized, as many of the reactions in Table 2 gave low yields in the absence of ligand (1,10-Phen). Therefore, 1,10-Phen was used in all subsequent experiments.
(17) (a) In most of the examples (Table 2), the reaction did not go to completion. As a result, we observed that the acid precursors were present even after an extended reaction time. Interestingly, scale-up experiments resulted in the formation of product (**3g**) in better yield (Scheme 3). (b) Free hydroxy group is known to quench the radical intermediate. Therefore, we believe that substrates such as (*E*)-3-(4-hydroxyphenyl)acrylic acid do not undergo a facile decarboxylation. We believe on similar note that the compounds with free amino groups such as (*E*)-3-(1*H*-indol-3-yl)acrylic acid and (*E*)-3-(4-aminophenyl)acrylic acid are inert under the reaction conditions. Further, the decarboxylation of the substrates such as 2-(4-methoxyphenyl)acrylic acid, (*E*)-3-(4-methoxyphenoxy)acrylic acid, (*E*)-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid, 2-(4-methoxyphenyl)acetic acid, 4-methoxybenzoic acid, and 1-benzylpyrrolidine-2-carboxylic are difficult and need harsh reaction conditions See: Nishida, Y.; Yamashita, E.; Miki, W. *Carotenoid Sci.* **2007**, *11*, 16.
(18) Li, H.-S.; Liu, G. *J. Org. Chem.* **2014**, *79*, 509. In this paper, 2-hydroxycinnamic acid furnished the styrene derivative as an intermediate, which in turn was reacted with sodium aryl sulfinate to obtain corresponding vinyl sulfone derivative. Importantly, unlike our observation, this reaction proceeds via protodecarboxylation of 2-hydroxycinnamic acid to give the corresponding styrene as an intermediate. However, under our reaction conditions, 4-hydroxycinnamic acid with sodium aryl sulfinate under optimal reaction conditions failed to undergo the reaction and resulted in a quantitative recovery of 4-hydroxycinnamic acid. This result is in good agreement with our observation that BHT, a radical inhibitor (which contains a phenolic OH group), retards the reaction, which further strengthens proposed radical mechanism (eq b, Scheme 4). These observations suggest that both reactions are completely different and follow different pathways.
(19) See the following references for conversion of cinnamic acid to styrene: (a) Goossen, L. J.; Rodríguez, N.; Linder, C.; Lange, P. P.; Fromm, A. *Chem. Catal. Chem.* **2010**, *2*, 430. (b) Goossen, L. J.; Rodríguez, N.; Melzer, B.; Linder, C.; Deng, G.; Levy, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 4824.
(20) At this point in time, we are not clear about the role of the ligand in this reaction. However, based on the literature precedence, we believe that the ligand (1,10-phenanthroline) is stabilizing the intermediates **I** and **III**. See: (a) Ramakrishnan, S.; Palaniandavar, M. *J. Chem. Sci.* **2005**, *117*, 179. (b) Loganathan, R.; Ramakrishnan, S.; Suresh, E.; Riyasdeen, A.; Akbarsha, M. A.; Palaniandavar, M. *Inorg. Chem.* **2012**, *51*, 5512.
(21) Zhao, K. Q.; Chen, C.; Monobe, H.; Hu, P.; Wang, B. Q.; Shimizu, Y. *Chem. Commun.* **2011**, *47*, 6290.
(22) Xu, J.; Jin, Z.; Chi, Y. R. *Org. Lett.* **2013**, *15*, 5028.
(23) Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12168.
(24) Muhuhi, J.; Spaller, M. R. *J. Org. Chem.* **2006**, *71*, 5515.
(25) Supanimit, C.; Praewpan, K.; Kanokwan, K.; Chutima, K.; Manat, P.; Vichai, R.; Thaworn, J. *Eur. J. Org. Chem.* **2010**, *29*, 5633.
(26) Rao Naidu, M. S.; Reddy, D. B. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1091.
(27) Shahak, I.; Almog, J. *Synthesis* **1970**, 145.
(28) Rao Naidu, M. S.; Reddy, D. B. *Indian J. Chem.* **1975**, *13*, 534.