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Copper-Catalyzed Aerobic Decarboxylative Sulfonylation of Cinnamic Acids with Sodium Sulfinates: Stereospecific Synthesis of (*E*)-Alkenyl Sulfones

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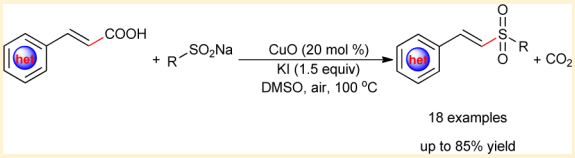
Supporting Information

ABSTRACT: A copper-catalyzed aerobic decarboxylative sulfonylation of alkenyl carboxylic acids with sodium sulfinates is developed. This study offers a new and expedient strategy for stereoselective synthesis of (*E*)-alkenyl sulfones that are widely present in biologically active natural products and therapeutic agents. Moreover, the transformation is proposed to proceed via a radical process and exhibits a broad substrate scope and good functional group tolerance.



INTRODUCTION

Transition-metal-catalyzed C−C and C−heteroatom bond-forming reactions are among the most powerful methods in modern synthetic chemistry and play a crucial role in fine chemicals, material science, and medicinal chemistry.[1] Among them, decarboxylative couplings[2] catalyzed by transition metals have proven to be one of the most powerful and versatile processes for the formation of C−C,[3] C−N,[4] C−S,[5] and C−P[6] bonds due to the "neutral " conditions, the readily available starting materials, and the nontoxic byproduct (CO_2). Notably, Pd catalysts have been shown to be extraordinarily versatile for decarboxylative coupling since the pioneering work of Myers and Goossen. However, those palladium-catalyzed methods suffer from some drawbacks: (1) palladium is quite expensive; (2) other additives, such as stoichiometric silver salts, are frequently encountered in the reactions; and (3) air- or moisture-sensitive, and very expensive, bulky phosphine ligands are always required for the success of the reactions. From a synthetic perspective, the development of analogous reactions using inexpensive metals such as copper and iron would be of significant importance. In this context, the copper-catalyzed decarboxylative coupling reactions have drawn considerable attention in recent years because of their low cost, commercially availability, and environmentally friendly character.[7] In this regard, different coupling partners, such as benzothiazoles,[7a] dialkyl H-phosphonates,[6a,b] amines,[4a−c] ammonia,[4e] thiols,[5a] sodium trifluoromethanesulfinate,[7b] and alkanes,[7c,i] have been employed to couple with carboxylic acids to provide higher functionalized molecules. During our investigation on mechanistic study and the process of preparation of this paper, Liu reported a copper/silver-mediated construction of 2-sulfonylbenzo[*b*]furans from *trans*-2-hydroxycinnamic acids and sodium sulfinates via a protodecarboxylation/sulfonylation/cyclization cascade.[5b] This prompted us to report our findings. As part of our continuing interest in C−C cleavage reactions,[8] we herein report a Cu(II)-catalyzed decarboxylative sulfonylation of alkenyl carboxylic acids with sodium sulfinates using air as the oxidant. The significance of the present chemistry is 3-fold: (1) this is the first aerobic decarboxylative sulfonylation of alkenyl carboxylic acids utilizing sodium sulfinates as the sulfur source without any silver additives for stereoselective synthesis of (*E*)-alkenyl sulfones, a structural motif considered to be both a useful synthetic intermediate[9] and a privileged medicinal target.[10] Although many synthetic methods have been developed for the preparation of vinyl sulfones, limitations, including the use of expensive or toxic reagents, narrow substrate scope, preinstalled functional groups, poor functional group tolerance, and multistep processes, restrict the applications of these methodologies.[11,12] (2) Inexpensive copper salt is employed as the catalyst, and molecular oxygen is used as a green oxidant and plays a very important role to initiate this transformation, which makes this protocol very easily handled. (3) The mechanistic study indicates that the initial sulfonyl cation addition and the following decarboxylation processes are involved in this transformation.

RESULTS AND DISCUSSION

We initiated our studies with the screening of the conditions for the decarboxylative coupling of cinnamic acid **1a** and sodium benzenesulfinate **2a**. It was found that, while a clean coupling occurred under an air atmosphere when CuO (20 mol %) was utilized as a catalyst, the desired product **3a** was isolated in only 38% yield due to low conversion (Table 1, entry 1). The yield of isolated **3a** was dramatically improved to 74% when KI as an additive was added to the reaction mixture (Table 1, entry 2). Addition of other additives including NaI, KBr, and AcOH failed to give any positive effect (Table 1, entries 3−6). Further

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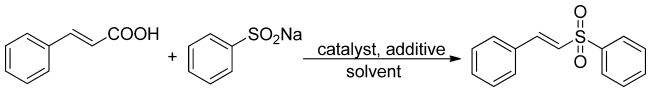
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

entry	catalyst (mol %)	additive	solvent	yield[b] (%)
1	CuO (20)	none	DMSO	38
2	CuO (20)	KI	DMSO	74
3	CuO (20)	NaI	DMSO	57
4	CuO (20)	NH_4I	DMSO	24
5	CuO (20)	KBr	DMSO	trace
6	CuO (20)	AcOH	DMSO	28
7	$CuCl_2$ (20)	KI	DMSO	23
8	CuCl (20)	KI	DMSO	37
9	$CuBr_2$ (20)	KI	DMSO	14
10	CuI (20)	KI	DMSO	54
11	$Cu(AcO)_2$ (20)	KI	DMSO	53
12	$FeCl_3$ (20)	KI	DMSO	12
13[c]	CuO (20)	KI	DMSO	42
14[d]	CuO (20)	KI	DMSO	60
15	CuO (20)	KI	DMF	20
16	CuO (20)	KI	DCE	9
17	CuO (20)	KI	CH_3CN	4
18	none	KI	DMSO	trace
19[e]	CuO (20)	KI	DMSO	trace
20	CuO (5)	KI	DMSO	56

[a]Reactions conditions: **1a** (0.5 mmol), **2a** (1.5 mmol), catalyst, additive (1.5 equiv), solvent (2 mL), 100 °C, 24 h, sealed tube under air. [b]Isolated yield. [c]80 °C. [d]110 °C. [e]Under N_2.

screening of different catalysts gave CuO as the best choice (Table 1, entries 7−12). Lowering or elevating the reaction temperature all gave rise to a much lower yield (Table 1, entries 13 and 14). A screening of solvents revealed that DMSO was optimal (Table 1, entries 15−17). Control experiments indicated that only a trace amount of **3a** was detected by HPLC in the absence of the catalyst (Table 1, entry 18), and air was necessary for the reaction to proceed (Table 1, entry 19). In addition, when the catalyst loading was reduced to 5 mol %, under which conditions product **3a** was isolated in 56% yield (Table 1, entry 20). Thus, the optimal conditions constitute a combination of CuO (20 mol %) and KI (1.5 equiv) in DMSO at 100 °C under an air atmosphere for 24 h.

With the optimized protocol in hand, the scope and limitation of this decarboxylation system were next explored. Cinnamic acids in reaction with **2a** was examined first (Table 2). The reaction worked very well for a range of cinnamic acids with various substituents at the phenyl ring, and the products were isolated in yields ranging from 34% to 85%. Cinnamic acid derivatives with electron-donating substituents at the phenyl ring afforded the desired vinyl sulfones in 34−54% yield (entries 2−4), whereas cinnamic acid derivatives bearing electron-withdrawing substituents at the phenyl ring provided the desired vinyl sulfones in 66−85% yield (entries 5−10). The experimental results indicated that *para*-, *meta*-, and *ortho*-nitro substituted cinnamic acid afforded similar yields (entries 5−7, 66−72% yield). Sterically hindered α-methylcinnamic acid was not suitable for this transformation (entry 11, 0% yield). Moreover, the arene ring is not limited to benzene rings. Pyridines, furans, and thiophenes also coupled with cinnamic acid, thus providing the corresponding desired products in 57−67% yield (entries 12−15). Finally, the scope of the sodium sulfinate substrate was explored in the coupling with cinnamic acid. Sodium benzenesulfinate bearing electron-donating and electron-withdrawing groups in the benzene ring, such as sodium 4-toluenesulfinate and sodium 4-chlorobenzenesulfinate, furnished **3p** and **3q** in 56% and 64% yield, respectively (entries 16 and 17). In addition, sodium methanesulfinate, a aliphatic sodium sulfinate, was also a viable partner, affording the vinyl sulfone **3r** in 33% yield (entry 18).

Though the exact mechanism of this coupling is still not clear, some information has been gathered. When radical inhibitors, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), hydroquinone, and 2,6-di-*tert*-butyl-4-methylphenol (BHT), were employed in the standard reaction, the reaction was obviously inhibited (Scheme 1a). The results implied that the reaction presumably underwent a radical pathway. When methyl cinnamate **4** was reacted with **2a** with and without a stoichiometric amount of AcOH (1.5 equiv) under the standard reaction conditions, the product **5** was not observed and almost all of the methyl cinnamate **4** remained intact (Scheme 1b). This result suggested that the carboxyl group is essential for the reaction to proceed efficiently. Moreover, no reaction occurred as determined by HPLC when only cinnamic acid was subjected to the standard reaction conditions (Scheme 1c). The reaction failed to give the desired product **3a** when **2a** was treated with styrene under the standard conditions, whereas, when this reaction was performed in the presence of AcOH under otherwise identical conditions, under the conditions that are similar to that developed by Taniguchi,[12a] the desired product **3a** was obtained in 18% yield (Scheme 1d). When the *trans*-2-hydroxy-cinnamic acid, which is a substrate studied in Li and Liu's work,[5b] was conducted under the standard conditions, the vinyl sulfone **3s** was obtained in 32% yield and no cyclization product **6** was observed (Scheme 1e). The above results indicated that the initial protodecarboxylation and the following sulfonylation processes might not be involved in the reaction mechanism.

On the basis of these results, a plausible mechanism is proposed and shown in Scheme 2 (using cinnamic acid and sodium benzenesulfinate as the model). Under the reaction conditions, benzenesulfinyl anion is first oxidized by Cu(II), air, or DMSO by single electron transfer (SET) to induce the formation of an oxygen-centered radical **A** resonating with sulfonyl radical **B**.[12a,13] Through further single electron oxidation, this carbon radical **B** would be converted to intermediate cation **C**.[5b] Subsequently, the addition of **C** to the α-position of the double bond in cupric cinnamate **D**,[7c] which is generated by the reaction of cinnamic acid **1a** with cupric oxide, would give an intermediate **E**, followed by trapping by the iodide ion to afford **F**. The validity of reaction intermediate **E** can be supported by the reaction results of nitro-substituted cinnamic acids (entries 5−7, Table 2). Among them, the pK_a of the *ortho*/*para*-nitro benzyl position would be significantly lower than the *meta*-nitro due to resonance. Therefore, the stability of the benzyl cation (species **E**) should have an inverse stability to the anion. In this case, the experimental results call the formation of cation **E** into question since the *ortho*-nitro cinnamic acid gives the highest yield, and to stabilize the benzyl cation, one of the resonance structures puts the cation onto the carbon attached to the nitro substituent. Therefore, an argument could be made that, even though the *ortho*- and *para*-nitro benzyl cations are difficult to form, they react much more quickly with the iodide if at all formed. Moreover, the result obtained from entry 2 in Table 1

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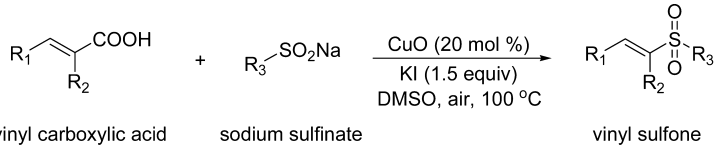
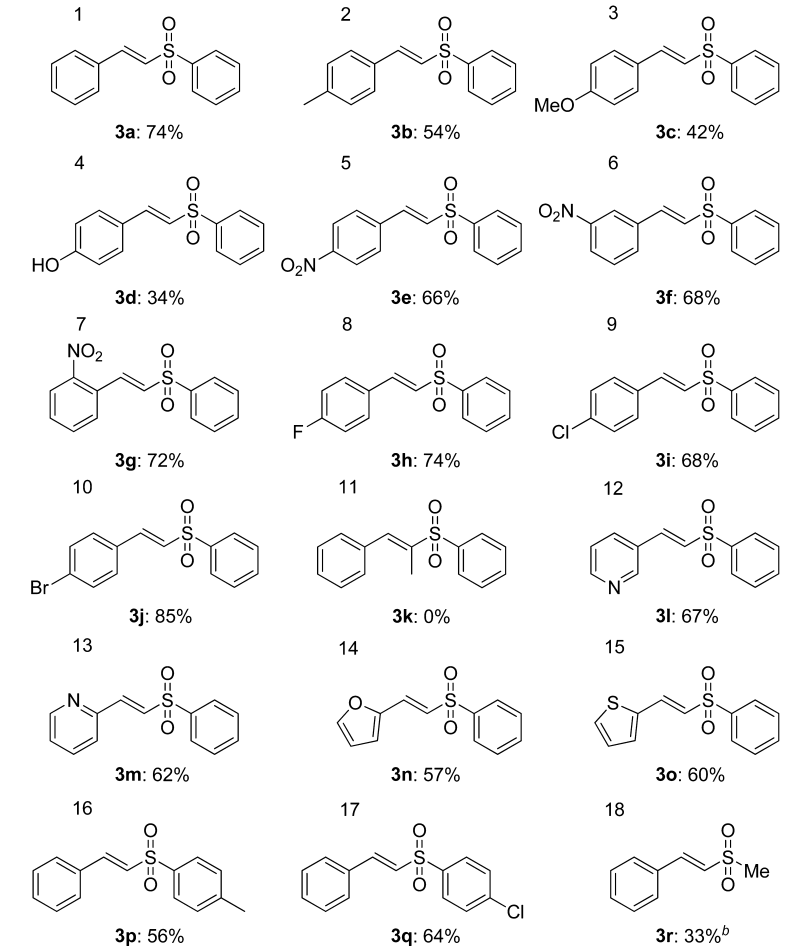
Table 2. Substrate Scope of the Aerobic Decarboxylative Sulfonylation of a Variety of Alkenyl Carboxylic Acids with Various Sodium Sulfinates[a,b,c]





[a]Reaction conditions: cinnamic acids (0.5 mmol), sodium sulfinates (1.5 mmol), CuO (20 mol %), KI (1.5 equiv), DMSO (2 mL), 100 °C, 24 h, sealed tube under air. [b]Sodium methanesulfinate (3.0 mmol). [c]The cited yields are of material isolated by column chromatography.

may also indicate that the Michael acceptor is undergoing conjugate addition with the iodide, thereby eliminating cation **E** as a reactive intermediate at least in the case of the nitrophenyl analogues. Finally, the **F** would undergo the *anti* elimination of Cu(I)I and carbon dioxide to afford the desired product **3a**. In addition, a direct pathway leading from **E** to **3a** is also likely.[7c] Then, the Cu(I) is reoxidized to Cu(II) by air, thus completing the catalytic cycle. However, it is very unlikely that these reaction conditions could induce such a high energy species as a phenyl radical, which would inhabit an electron-deficient orbital orthogonal to a node of the aromatic system because cinnamic acid derivatives with electron-withdrawing substituents at the phenyl ring provided the desired vinyl sulfones in good yields (entries 5−10, Table 2).

CONCLUSIONS

In summary, the first copper-catalyzed stereoselective decarboxylative C−S coupling reaction of cinnamic acids with sodium sulfinates has been developed using air as the oxidant. A wide range of cinnamic acid and sodium sulfinate substrates undergo decarboxylative coupling to produce the corresponding sulfonylation products in moderate to good yields. Preliminary mechanistic studies suggested that this reaction is likely to proceed through a radical pathway. This new and expedient synthetic protocol for vinyl sulfones may have wide applications to the industrial process in the future.

EXPERIMENTAL SECTION

General Comments. All reagents and solvents used were obtained commercially and used without further purification unless indicated otherwise. All products were characterized by ^{1}H NMR and ^{13}C NMR. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$ or DMSO-d_6, and ^{13}C NMR spectra were recorded on 101 MHz in $CDCl_3$ or DMSO-d_6 using TMS as internal standard. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet), and coupling constants (J) are reported in hertz. Copies of ^{1}H NMR and ^{13}C NMR spectra are provided as the Supporting Information.

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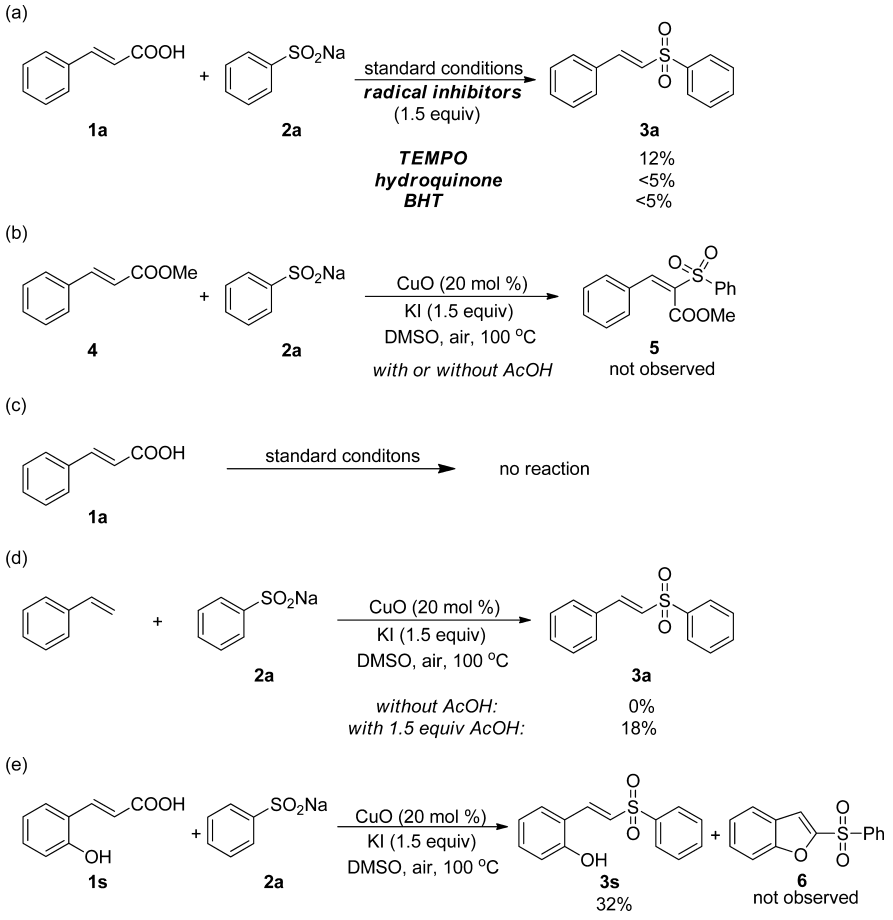
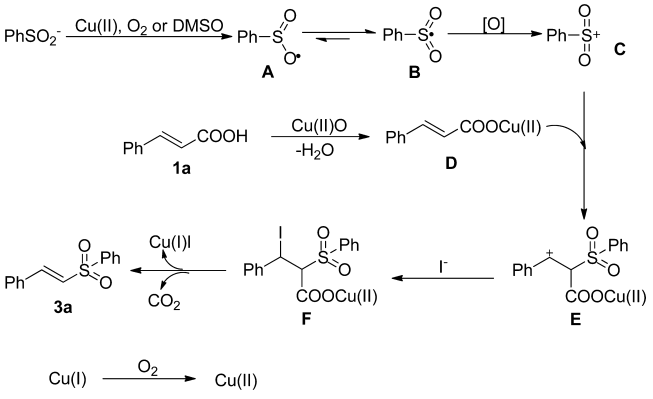
Scheme 1. Control Experiments



Scheme 2. Proposed Reaction Mechanism



Typical Procedure for the Aerobic Decarboxylative Sulfonylation of Cinnamic Acids with Sodium Sulfinates Catalyzed by Copper. A 25 mL sealed tube was charged with cinnamic acids (0.5 mmol, 1 equiv), sodium sulfinates (1.5 mmol, 3 equiv), CuO (0.1 mmol, 0.2 equiv), KI (0.75 mmol, 1.5 equiv), and DMSO (2 mL). The reaction was stirred at 100 °C for 24 h in air. Upon completion of the reaction, the reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the desired product (*E*)-alkenyl sulfones.

(*E*)-1-Phenylsulfonyl-2-phenylethene (3a). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), cinnamic acid (74 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (90.3 mg, 74%). Flash chromatography (petroleum ether/ethyl acetate, 10/1); colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.87 (d, J = 16.0 Hz, 1 H), 7.39−7.42 (m, 3 H), 7.47−7.50 (m, 2 H), 7.55 (t, J = 8.0 Hz, 2 H), 7.60−7.64 (m, 1 H), 7.69 (d, J = 16.0 Hz, 1 H), 7.95 (d, J = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 127.2, 127.6, 128.6, 129.1, 129.3, 131.2, 132.7, 133.4, 140.6, 142.5 ppm; LRMS: m/z calcd for $C_{13}H_{17}NO_2$ (M + H): 244, found: 244.

(*E*)-1-Methyl-4-(2-(phenylsulfonyl)vinyl)benzene (3b). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 4-methylcinnamic acid (81 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (69.7 mg, 54%). Flash chromatography (petroleum ether/ethyl acetate, 5/1); colorless solid, mp = 134.1−136.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3 H), 6.81 (d, J = 16.0 Hz, 1 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.38 (d, J = 8.0 Hz, 3 H), 7.52−7.68 (m, 4 H), 7.95 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 21.6, 126.1, 127.6, 128.6, 129.3, 129.6, 129.8, 133.3, 140.9, 141.9, 142.6 ppm; Anal.Calcd for $C_{15}H_{14}O_2S$ Elemental Analysis: C, 69.74; H, 5.46; Found: C, 69.67; H, 5.54.

(*E*)-1-Methoxyl-4-(2-(phenylsulfonyl)vinyl)benzene (3c). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 4-methoxylcinnamic acid (89 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was

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stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (57.5 mg, 42%). Flash chromatography (petroleum ether/ethyl acetate, 2/1); yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.83 (s, 1 H), 6.70 (d, J = 16.0 Hz, 1 H), 6.90 (d, J = 8.0 Hz, 2 H), 7.43−7.66 (m, 7 H), 7.95 (d, J = 6.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 55.5, 114.5, 124.4, 125.0, 127.5, 129.3, 130.4, 133.2, 141.2, 142.3, 162.1 ppm; LRMS: m/z calcd for $C_{15}H_{13}O_3S$ (M + H): 274, found: 274.

(*E*)-1-Hydroxyl-4-(2-(phenylsulfonyl)vinyl)benzene (3d). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 4-hydroxylcinnamic acid (82 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (44.2 mg, 34%). Flash chromatography (petroleum ether/ethyl acetate, 2/1); pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.66 (d, J = 16.0 Hz, 1 H), 6.86 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 7.51−7.61 (m, 4 H), 7.92 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 116.3, 123.3, 124.3, 127.4, 129.4, 130.7, 133.5, 140.7, 143.0, 159.4 ppm; LRMS: m/z calcd for $C_{14}H_{12}O_3S$ (M + H): 260, found: 260.

(*E*)-1-Nitro-4-(2-(phenylsulfonyl)vinyl)benzene (3e). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 4-nitrocinnamic acid (96.5 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (95.4 mg, 66%). Flash chromatography (petroleum ether/ethyl acetate, 3/1); yellow solid, mp = 170.2−172.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.04 (d, J = 16.0 Hz, 1 H), 7.59 (t, J = 8.0 Hz, 2 H), 7.67 (d, J = 8.0 Hz, 3 H), 7.74 (d, J = 12.0 Hz, 1 H), 7.97 (d, J = 8.0 Hz, 2 H), 8.25 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 124.3, 127.9, 129.3, 129.6, 131.7, 134.0, 138.4, 139.3, 139.8, 149.0 ppm; Anal.Calcd for $C_{14}H_{11}NO_4S$ Elemental Analysis: C, 58.12; H, 3.83; N, 4.84; Found: C, 58.01; H, 3.95; N, 4.74.

(*E*)-3-Nitro-4-(2-(phenylsulfonyl)vinyl)benzene (3f). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 3-nitrocinnamic acid (96.5 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (98.3 mg, 68%). Flash chromatography (petroleum ether/ethyl acetate, 4/1); colorless solid, mp = 136.5−138.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.05 (d, J = 16.0 Hz, 1 H), 7.57−7.69 (m, 4 H), 7.674 (d, J = 16.0 Hz, 1 H), 7.82 (d, J = 8.0 Hz, 1 H), 7.98 (d, J = 8.0 Hz, 2 H), 8.26 (d, J = 8.0 Hz, 1 H), 8.35 (s, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 122.8, 125.4, 127.9, 129.6, 130.3, 130.7, 133.9, 134.1, 134.3, 139.4, 139.9, 148.7 ppm; Anal.Calcd for $C_{14}H_{11}NO_4S$ Elemental Analysis: C, 58.12; H, 3.83; N, 4.84; Found: C, 58.04; H, 3.90; N, 4.74.

(*E*)-2-Nitro-4-(2-(phenylsulfonyl)vinyl)benzene (3g). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 2-nitrocinnamic acid (96.5 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (104.0 mg, 72%). Flash chromatography (petroleum ether/ethyl acetate, 3/1); yellow solid, mp = 101.2−103.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.81 (d, J = 16.0 Hz, 1 H), 7.55−7.60 (m, 4 H), 7.64−7.70 (m, 2 H), 8.00 (d, J = 8.0 Hz, 2 H), 8.12 (d, J = 8.0 Hz, 1 H), 8.17 (d, J = 16.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 125.2, 128.0, 129.0, 129.5, 129.6, 131.2, 132.2, 133.8, 134.1, 139.2, 139.8, 147.9 ppm; Anal.Calcd for $C_{14}H_{11}NO_4S$ Elemental Analysis: C, 58.12; H, 3.83; N, 4.84; Found: C, 58.02; H, 3.91; N, 4.72.

(*E*)-1-Fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (3i). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 4-fluorocinnamic acid (83 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (96.9 mg, 74%). Flash chromatography (petroleum ether/ethyl acetate, 2/1); colorless solid, mp = 108.5−110.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.80 (d, J = 16.0 Hz, 1 H), 7.09 (t, J = 8.0 Hz, 2 H), 7.47−7.68 (m, 6 H), 7.95 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 116.3 (d, J_{C-F} = 22.0 Hz), 127.0 (d, J_{C-F} = 2.0 Hz), 127.7, 128.6, 129.4, 130.6 (d, J_{C-F} = 9.0 Hz), 133.5, 140.6, 141.2, 164.6 (d, J_{C-F} = 252.0 Hz) ppm; Anal.Calcd for $C_{14}H_{11}FO_2S$ Elemental Analysis: C, 64.11; H, 4.23; Found: C, 64.01; H, 4.35.

(*E*)-1-Chloro-4-(2-(phenylsulfonyl)vinyl)benzene (3j). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 4-chlorocinnamic acid (91 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (94.5 mg, 68%). Flash chromatography (petroleum ether/ethyl acetate, 5/1); colorless solid, mp = 128.5−130.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.86 (d, J = 16.0 Hz, 1 H), 7.36 (d, J = 8.0 Hz, 2 H), 7.42 (d, J = 8.0 Hz, 2 H), 7.56 (t, J = 8.0 Hz, 2 H),7.62−7.66 (m, 2 H), 7.95 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 127.7, 127.9, 129.4, 129.4, 129.8, 130.9, 133.6, 137.3, 140.5, 141.0 ppm; Anal.Calcd for $C_{14}H_{11}ClO_2S$ Elemental Analysis: C, 60.32; H, 3.98; Found: C, 60.20; H, 4.08.

(*E*)-1-Bromo-4-(2-(phenylsulfonyl)vinyl)benzene (3k). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 4-bromocinnamic acid (113.5 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (137.3 mg, 85%). Flash chromatography (petroleum ether/ethyl acetate, 5/1); colorless solid, mp = 152.3−154.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.86 (d, J = 16.0 Hz, 1 H), 7.35 (d, J = 8.0 Hz, 2 H), 7.52−7.66 (m, 6 H), 7.95 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 125.7, 127.7, 128.0, 129.4, 129.9, 131.3, 132.4, 133.6, 140.4, 141.1 ppm; Anal.Calcd for $C_{14}H_{11}BrO_2S$ Elemental Analysis: C, 52.03; H, 3.43; Found: C, 51.91; H, 3.54.

(*E*)-1-(Pyridine-3-yl)-2-phenylsulfonylethene (3l). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 3-(3-pyridinyl)acrylic acid (74.5 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (82.1 mg, 67%). Flash chromatography (petroleum ether/ethyl acetate, 1/1); yellow solid, mp = 94.2−96.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.02 (d, J = 16.0 Hz, 1 H), 7.34−7.37 (m, 1 H), 7.28 (t, J = 8.0 Hz, 2 H), 7.64−7.72 (m,2 H), 7.82 (d, J = 8.0 Hz, 1 H), 7.87 (d, J = 8.0 Hz, 1 H), 8.63 (s, 1 H), 8.73 (s, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 123.9, 127.8, 128.3, 129.5, 129.6, 133.8, 134.9, 138.8, 140.1, 150.0, 151.8 ppm; Anal.Calcd

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for $C_{13}H_{11}NO_2S$ Elemental Analysis: C, 63.65; H, 4.52; N, 5.71; Found: C, 63.54; H, 4.64; N, 5.60.

(*E*)-1-(Pyridine-2-yl)-2-phenylsulfonylethene (3m). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 3-(2-pyridinyl)acrylic acid (74.5 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (76.0 mg, 62%). Flash chromatography (petroleum ether/ethyl acetate, 5/1); yellow solid, mp = 85.2−87.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29−7.32 (m, 1 H), 7.41−7.48 (m, 2 H), 7.55 (t, J = 8.0 Hz, 2 H), 7.61−7.68 (m, 2 H), 7.75 (t, J = 8.0 Hz, 1 H), 7.97 (d, J = 8.0 Hz, 2 H), 8.62 (d, J = 6.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 125.1, 125.5, 127.9, 129.4, 131.8, 133.6, 137.1, 140.2, 140.6, 150.3, 151.0 ppm; Anal.Calcd for $C_{13}H_{11}NO_2S$ Elemental Analysis: C, 63.65; H, 4.52; N, 5.71; Found: C, 63.53; H, 4.62; N, 5.61.

(*E*)-1-(Furan-2-yl)-2-phenylsulfonylethene (3n). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 3-(2-furyl)acrylic acid (69 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (66.7 mg, 57%). Flash chromatography (petroleum ether/ethyl acetate, 5/1); colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.49 (d, J = 6.2 Hz, 1 H), 6.71−6.75 (m, 2 H), 7.43−7.48 (m, 2 H), 7.54 (t, J = 8.0 Hz, 2 H), 7.61 (t, J = 8.0 Hz, 1 H), 7.93 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 112.6, 117.0, 124.7, 127.6, 128.9, 129.3, 133.3, 140.9, 145.7, 148.7 ppm; LRMS: m/z calcd for $C_{12}H_{10}O_3S$ (M + H): 234, found: 234.

(*E*)-1-(Thiophen-2-yl)-2-phenylsulfonylethene (3o). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 3-(2-thienyl)acrylic acid (77 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (75.0 mg, 60%). Flash chromatography (petroleum ether/ethyl acetate, 5/1); yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.57 (d, J = 16.0 Hz, 1 H), 6.99 (d, J = 6.2 Hz, 1 H), 7.23 (s, 1 H), 7.35 (d, J = 8.0 Hz, 1 H), 7.44−7.58 (m, 3 H), 7.71 (d, J = 16.0 Hz, 1 H), 7.85 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 125.4, 127.6, 128.4, 129.4, 130.1, 132.6, 133.4, 135.2, 136.9, 140.8 ppm; LRMS: m/z calcd for $C_{12}H_{10}O_2S_2$ (M + H): 250, found: 250.

(*E*)-1-(4-Methylphenyl)sulfonyl-2-phenylethene (3p). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), cinnamic acid (74 mg, 0.5 mmol, 1 equiv), and sodium 4-methylbenzenesulfinate (267 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (72.2 mg, 56%). Flash chromatography (petroleum ether/ethyl acetate, 8/1); colorless solid, mp = 112.3−114.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 1 H), 6.85 (d, J = 16.0 Hz, 1 H), 7.30−7.48 (m, 7 H), 7.66 (d, J = 16.0 Hz, 1 H), 7.83 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 21.7, 127.6, 127.7, 128.6, 129.1, 130.0, 131.1, 132.5, 137.7, 142.0, 144.4 ppm; Anal.Calcd for $C_{15}H_{14}O_2S$ Elemental Analysis: C, 69.74; H, 5.46; Found: C, 69.68; H, 5.58.

(*E*)-1-(4-Chlorophenyl)sulfonyl-2-phenylethene (3q). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), cinnamic acid (74 mg, 0.5 mmol, 1 equiv), and sodium 4-chlorobenzenesulfinate (298 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (89.0 mg, 64%). Flash chromatography (petroleum ether/ethyl acetate, 10/1); colorless solid, mp = 86.2−88.2 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.86 (d, J = 16.0 Hz, 1 H), 7.39−7.44 (m, 3 H), 7.50 (t, J = 8.0 Hz, 4 H), 7.69 (d, J = 16.0 Hz, 1 H), 7.89 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 126.8, 128.7, 129.1, 129.2, 129.7, 131.5, 132.2, 139.3, 140.1, 143.1 ppm; Anal.Calcd for $C_{14}H_{11}ClO_2S$ Elemental Analysis: C, 60.32; H, 3.98; Found: C, 60.22; H, 4.10.

(*E*)-1-Methylsulfonyl-2-phenylethene (3r). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), cinnamic acid (74 mg, 0.5 mmol, 1 equiv), and sodium methylsulfinate (306 mg, 3.0 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (30.0 mg, 33%). Flash chromatography (petroleum ether/ethyl acetate, 2/1); colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.04 (s, 1 H), 6.92 (d, J = 16.0 Hz, 1 H), 7.42−7.53 (m, 5 H), 7.64 (d, J = 16.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 43.3, 126.1, 128.6, 129.2, 131.5, 132.1, 144.1 ppm; LRMS: m/z calcd for $C_9H_{10}O_2S$ (M + H): 182, found: 182.

(*E*)-1-Hydroxyl-2-(2-(phenylsulfonyl)vinyl)benzene (3s). CuO (7.9 mg, 0.1 mmol, 0.2 equiv) was added to a mixture of KI (124.5 mg, 0.75 mmol, 1.5 equiv), 2-hydroxylcinnamic acid (82 mg, 0.5 mmol, 1 equiv), and sodium benzenesulfinate (246 mg, 1.5 mmol, 3 equiv) in DMSO (2 mL) at room temperature. The reaction was stirred at 100 °C for 24 h under air. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the vinyl sulfone (41.6 mg, 32%). Flash chromatography (petroleum ether/ethyl acetate, 3/1); colorless solid, mp = 159.2−161.8 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 10.53 (brs, 1 H), 7.91−7.93 (m, 2 H), 7.84 (d, J = 16.0 Hz, 1 H), 7.61−7.70 (m, 4 H), 7.46 (d, J = 16.0 Hz, 1 H), 7.27 (t, J = 8.0 Hz, 1 H), 6.94 (d, J = 8.0 Hz, 1 H), 6.83 (t, J = 8.0 Hz, 1 H); ^{13}C NMR (DMSO-d_6, 101 MHz) δ 116.6, 119.2, 119.8, 127.1, 127.4, 129.9, 130.2, 133.0, 133.7, 137.9, 141.4, 157.5 ppm; Anal. Calcd for $C_{14}H_{12}O_3S$ Elemental Analysis: C, 64.60; H, 4.65; Found: C, 64.65; H, 4.58.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for the products. 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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