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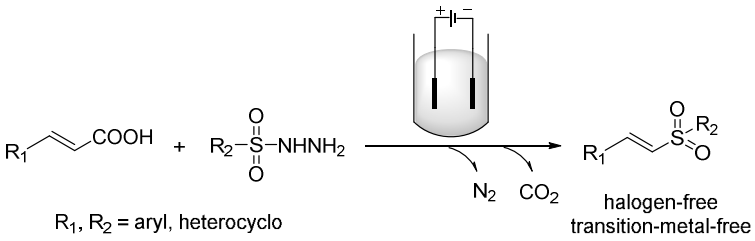


ABSTRACT: A stereoselective synthesis of (*E*)-vinyl sulfones has been developed via electrochemical oxidative N-S bond cleavage of aromatic sulfonylhydrazides, followed by cross-coupling reactions with cinnamic acids to form the C-S bond. The protocol proceeded smoothly to afford (*E*)-vinyl sulfones in good yields with wide substrate scope under metal-free and halogen-free conditions.

Introduction

Vinyl sulfones are particularly valuable units in organic synthesis[1] and biological chemistry.[2] As a consequence, considerable progress has been made in the development of methodologies toward this building block.[3] However, efficient methods for preparation of vinyl sulfones in terms of selectivity, availability of starting materials, operational simplicity, and environmentally friendly are still in demand.

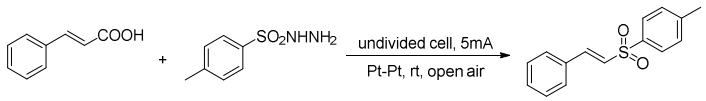
Recent years, decarboxylative cross-coupling reactions have attracted a great deal of interest[4] and the decarboxylative coupling of cinnamic acids with sodium sulfinates have been studied by several groups.[5] Sulfonylhydrazides are readily accessible synthetic intermediates that can also be served as sulfone sources by means of N-S bond cleavage.[6] Notably, N_2 and water are the only byproducts during this transformation. However, methods for decarboxylative sulfonylation of cinnamic acids with sulfonylhydrazides are quite rare.[7] In 2015, I_2/TBHP treated vinyl sulfones synthesis via decarboxylative sulfonylation of cinnamic acids with sulfonylhydrazides was first disclosed by Singh's group.[7a] Later, Cai et al. demonstrated a visible-light-promoted decarboxylative sulfonylation of cinnamic acids with sulfonylhydrazides in the presence of KI.[7b] Electrochemistry has been found to be a very useful mean for the synthesis of organic compounds and has demonstrated its advantages and environmentally friendly characteristics.[8] In continuation

of our interest in the application of electrochemical methods to organic synthesis,[9] herein we report the first efficient electrochemical decarboxylative sulfonylation of cinnamic acids with aromatic sulfonylhydrazides to afford the vinyl sulfones in good yields.

Results and Discussion

To start the investigation, we chose cinnamic acid **1a** and *p*-toluenesulfonylhydrazide **2a** as the model substrates. These two compounds were treated with K_2CO_3 in a solution of *n*- Bu_4NBF_4 (0.1 M) in DMSO in a one-compartment cell with two Pt foils (1×1.5 cm^2) as electrodes under a constant current (5 mA). The desired product **3a** was obtained in a yield of 38% after the reaction proceeded at room temperature for 10 h (Table 1, entry 1). A number of bases (Table 1, entries 2−8) were examined. And we found that 76% yield of product was obtained when *t*-BuOLi was employed (Table 1, entry 3). It was noted that only trace of the desired product could be obtained in the absence of base (Table 1, entry 9). Studies on the effect of solvent showed that the yield of product decreased sharply when DMF or NMP was used (Table 1, entries 10 and 11), while other solvents such as CH_3CN and THF disfavored the reaction (Table 1, entries 12 and 13). Hence, DMSO was the optimal solvent for this reaction. Other electrolytes, such as NH_4ClO_4, $NaBF_4$, $LiClO_4$, $KClO_4$ and *n*-Bu_4NClO_4 were screened and it was found that *n*-$(Bu)_4NBF_4$ was the most efficient electrolyte for this electrochemical reaction (Table 1, entries 4 and 14−18), perhaps due to a good solubility of *n*-$(Bu)_4NBF_4$ in DMSO.[10] In addition, attempts to vary the current intensity,

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3a**

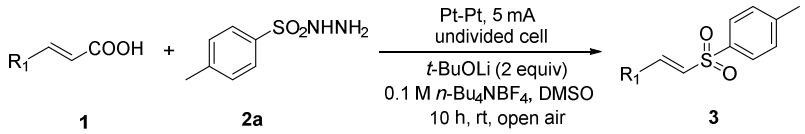
Entry	Solvent	Base	Electrolyte	Yield(%)[b]
1	DMSO	K_2CO_3	*n*-Bu_4NBF_4	38
2	DMSO	Cs_2CO_3	*n*-Bu_4NBF_4	50
3	DMSO	*t*-BuOLi	*n*-Bu_4NBF_4	76
4	DMSO	LiOH	*n*-Bu_4NBF_4	61
5	DMSO	*t*-BuONa	*n*-Bu_4NBF_4	68
6	DMSO	*t*-BuOK	*n*-Bu_4NBF_4	49
7	DMSO	DIPEA	*n*-Bu_4NBF_4	48
8	DMSO	TEA	*n*-Bu_4NBF_4	32
9	DMSO	-	*n*-Bu_4NBF_4	trace
10	DMF	*t*-BuOLi	*n*-Bu_4NBF_4	38
11	NMP	*t*-BuOLi	*n*-Bu_4NBF_4	41
12	CH_3CN	*t*-BuOLi	*n*-Bu_4NBF_4	trace
13	THF	*t*-BuOLi	*n*-Bu_4NBF_4	trace
14	DMSO	*t*-BuOLi	NH_4ClO_4	54
15	DMSO	*t*-BuOLi	$NaBF_4$	41
16	DMSO	*t*-BuOLi	$LiClO_4$	62
17	DMSO	*t*-BuOLi	$KClO_4$	65
18	DMSO	*t*-BuOLi	*n*-Bu_4NClO_4	58
19[c]	DMSO	*t*-BuOLi	*n*-Bu_4NBF_4	60
20[d]	DMSO	*t*-BuOLi	*n*-Bu_4NBF_4	45
21[e]	DMSO	*t*-BuOLi	*n*-Bu_4NBF_4	41
22[f]	DMSO	*t*-BuOLi	*n*-Bu_4NBF_4	0

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (1.0 mmol), and *t*-BuOLi (0.6 mmol) in solvent (5 mL) with 0.1 M electrolyte was electrolyzed at a constant current (5 mA) in an undivided cell at r.t., 10 h, open air. Anode: Pt foil (1×1.5 cm^2), cathode: Pt foil (1×1.5 cm^2). [b]Yields of isolated products. [c]The current was 3 mA. [d]The current was 10 mA. [e]Anode: graphite rod electrode (diameter = 0.5 cm, height = 1.8 cm). [f]No current.

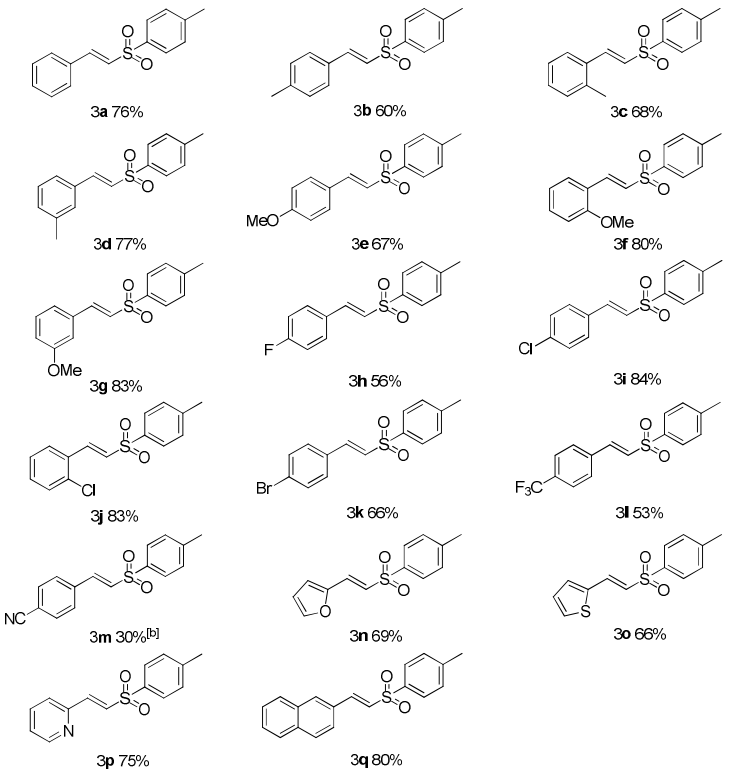
such as 3 mA or 10 mA led to a decrease of the product yield (Table 1, entries 19 and 20). Switching the Pt foils with graphite electrodes resulted in a yield of 41% only (Table 1, entry 21). Finally, it was found that no reaction occurred with starting materials recovered when the reaction was performed in the absence of current (Table 1, entry 22).

With the optimized reaction conditions in hand, we proceeded to examine the substrate scope. As presented in Table 2, the reactions of a series of *α,β*-unsaturated carboxylic acids with *p*-toluenesulfonylhydrazide **2a** were screened and moderate to good yields of the corresponding products were obtained. Firstly, cinnamic acids with a *para*-, *meta*-, or *ortho*- methyl substituent on the aromatic ring (**3b-d**) could be converted into the desired products in good yields. Cinnamic acids containing a methoxyl group (**3e-g**) underwent the reaction to give good yields. Additionally, a wide range of halogen-containing *α,β*-unsaturated carboxylic acids were tested. The results showed that halogen could be well tolerated under the electrochemical conditions (**3h- k**) and could thus provide a great opportunity for further transformation at the halide position. Strong electron- withdrawing groups such as trifluoromethyl (**3l**) and cyano (**3m**) had influence on the reaction and delivered lower yields. The reaction of **1m** was run at 3 mA and was stopped at 4 h to minimize the reduction of the cyano group on the cathode. Moreover, heteroarene-based acrylic

Table 2. Substrate Scope of *α,β*-Unsaturated Carboxylic Acids for Electrochemical Synthesis of 3a-q[a, b]



1 **2a** **3**

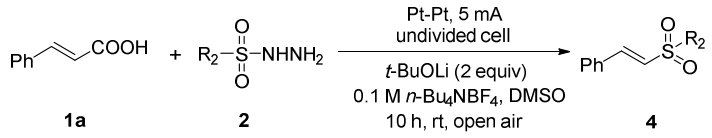


[a]Reaction conditions: **1** (0.3 mmol), **2a** (1.0 mmol), DMSO (5 mL), *t*-BuOLi (0.6 mmol), 0.1 M *n*-Bu_4NBF_4 as supporting electrolyte, 10 h at room temperature, anode: Pt foil (1×1.5 cm^2), cathode: Pt foil (1×1.5 cm^2), constant current (5 mA), undivided cell, open air. Yield of isolated products. [b]Constant current (3 mA), t = 4 h.

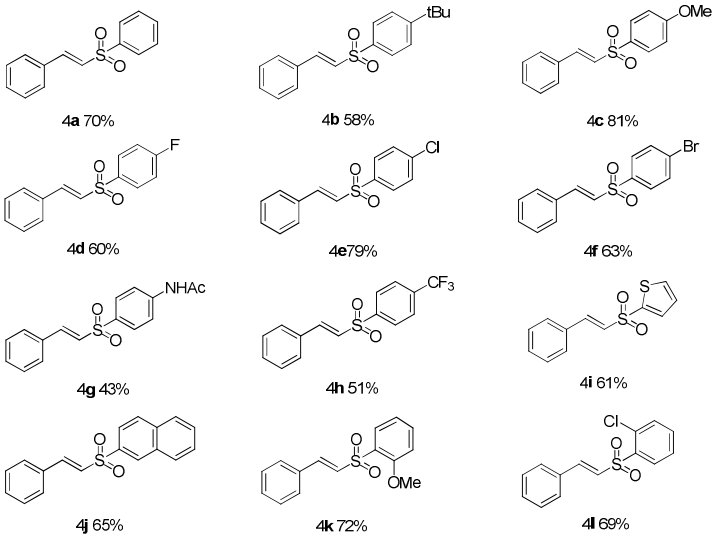
acids were good substrates for this process and afforded the desired product in moderate to good yields (**3n-p**). It was noteworthy that the cinnamic acid with a naphthyl group (**3q**) was also accommodated in the reaction and gave the desired product in a yield of 80%. In addition, 2-phenylacrylic acid and crotonic acid were examined in this reaction and no desired product were detected. Phenylpropiolic acid give a trace amount of the desired product.

To further examine the scope of this reaction, a range of sulfonylhydrazides were exposed to the optimal reaction conditions to react with the cinnamic acids **1a**. As shown in Table 3, cinnamic acids underwent decarboxylative sulfonylation with benzenesulfonohydrazide (**4a**) smoothly to afford the desired product in a yield of 70%. A series of sulfonylhydrazides with both the electron-donating (**4b, 4c** and **4k**) and electron-withdrawing (**4d-h** and **4l**) nature of the substituents on the aromatic ring were good partners with cinnamic acids, and the corresponding products were obtained in moderate to good yields. Moreover, sulfonylhydrazides with a naphthyl group or a thienyl group also participated in this reaction, and the desired products were afforded in yields of 61% and 65%, respectively (**4i** and **4j**). While aliphatic sulfonylhydrazide was not compatible with the reaction conditions and no desired products was detected. It was noteworthy that excellent *E* selectivity (*E*/*Z*>99:1) were observed in all product.

Table 3. Substrate Scope of Sulfonylhydrazides for Electrochemical Synthesis of 4a-j[a]



1a **2** **4**

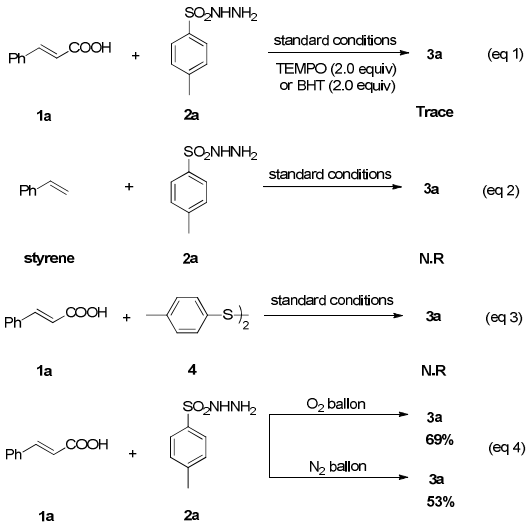


[a]Reaction conditions: **1a** (0.3 mmol), **2** (1.0 mmol), DMSO (5 mL), *t*-BuOLi (0.6 mmol), 0.1 M *n*-Bu_4NBF_4 as supporting electrolyte, 10 h at room temperature, anode: Pt foil (1×1.5 cm^2), cathode: Pt foil (1×1.5 cm^2), constant current (5 mA), undivided cell, open air. Yield of isolated products..

In order to gain some insights into the reaction mechanism, a series of control experiments were examined (Scheme 1). First, the reaction was inhibited with the addition of radical inhibitors such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Scheme 1, eq 1) under the standard conditions, suggesting the reaction presumably involved a radical pathway. Styrene was employed as the coupling partner under the standard reaction conditions and it was demonstrated that styrene was not the active intermediate of this reaction

(Scheme 1, eq 2). During the process of optimization of the reaction conditions, *p*-tolyl-disulfide (**4**) was detected. But when disulfide **4** was subjected to the reaction with **1a** under the standard conditions, no desired product was obtained. Thus, the involvement of *p*-tolyl disulfide (**4**) as an intermediate for this reaction was ruled out (Scheme 1, eq 3). In addition, the yield was 69% when the reaction was performed under an O_2 atmosphere, while the yield dropped to 53% under a N_2 atmosphere (Scheme 1, eq 4). Hence, air is the best atmosphere for the reaction. As the yield decreased in the absence of air[7b, 12] and the aromatic sulfonylhydazide was completely recovered without current (Table 1, entry 22), it was proposed that the aromatic sulfonylhydazide is oxidated by the synergistic effect of anodic oxidation and air.

Scheme 1. Control Experiments



Cyclic voltammetry (CV) experiments were then carried out. As shown in Figure 1, an oxidative peak at 1.24 V *vs*. Ag/AgCl (in Figure 1-Ⅰ, curve c) was detected, corresponding to the oxidation of *p*-toluenesulfonylhydrazide.[11] When *t*-BuOLi was added to the solution of *p*-toluenesulfonylhydrazide, one new oxidative peak at 0.53 V *vs*. Ag/AgCl (in Figure 1-Ⅰ, curve d) was obtained, which indicated that the oxidation of *p*-toluenesulfonylhydrazide was promoted by the base. While the anode potential of the cinnamic acid was observed at 1.38 V *vs*. Ag/AgCl in the presence of base (in Figure 1-Ⅱ, curve f). Therefore, the CV studies had shown that *p*-toluenesulfonylhydrazide oxidation could occur selectively during the initiation step of the reaction under the standard conditions.

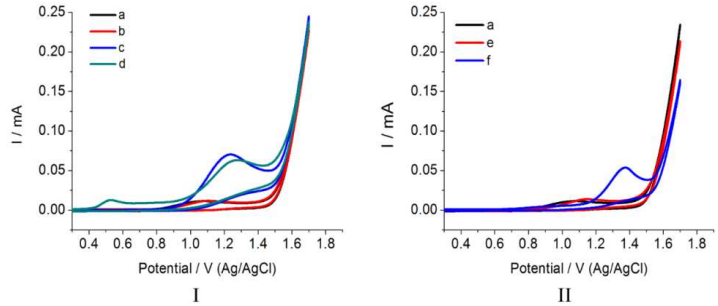
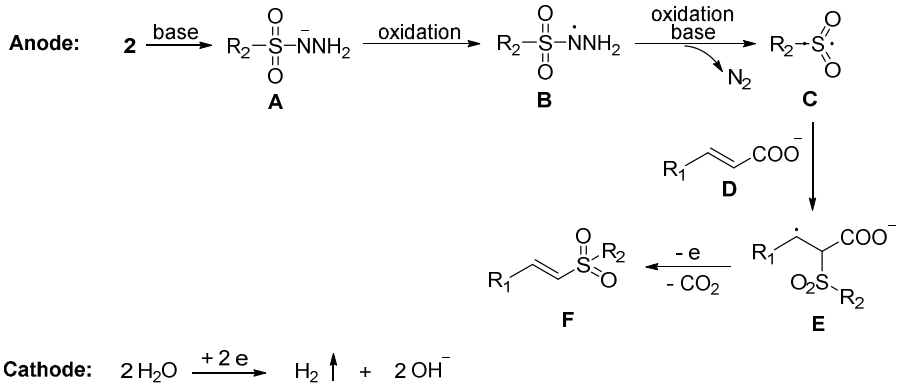


Figure 1. Cyclic voltammograms of 0.1 M *n*-Bu_4NBF_4 solution in DMSO, using glassy carbon electrode as working electrode (d = 3 mm), a Pt wire as counter electrode and Ag/AgCl as a reference electrode, at a scan rate of 50 mV/s: (a) none; (b) *t*-BuOLi (0.005 M); (c) **2a** (0.005 M); (d) **2a** (0.005 M) and *t*-BuOLi (0.005 M); (e) *t*-BuOLi (0.015 M); (f) **1a** (0.015 M) and *t*-BuOLi (0.015 M).

Scheme 2. Plausible Reaction Mechanism



On the basis of our experimental results and the precedent reports,[5d, 7, 11, 12] a possible mechanism for this reaction is proposed, as depicted in Scheme 2. Aromatic sulfonylhydazide is deprotonated to produce anion **A**, and anion **A** is then oxidized by the synergistic effect of anodic oxidation and air to produce a highly active radical **B**, followed by a further oxidation to the radical **C** with the release of nitrogen in the presence of a base. Subsequently, radical **C** reacted with the cinnamate **D** to furnish the radical species **E**, which is easy to be decarboxylated to afford the vinyl sulfone **F** under the standard conditions.

Conclusions

In conclusion, an electrochemical decarboxylative sulfonylation of cinnamic acids with aromatic sulfonylhydrazides to synthesize vinyl sulfones has been developed. Operating efficiently under air and at room temperature, this protocol refrains from using transition metal catalysts, strong oxidants and halogens. The electrochemical methodology provides a new method for the synthesis of vinyl sulfones using a decarboxylative strategy. Further investigation into the mechanistic details and applications of this method are underway in our laboratory.

Experimental Section

General Information. Unless otherwise noted, Solvents and reagents were commercially available and used as received without further treatment. Dimethyl sulfoxide (DMSO，H_2O≤0.5%) was purchased from Tianjing Fuyu Chemical Reagent Co. Reactions were monitored by thin-layer chromatography (TLC). ^{1}H NMR, ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts of ^{1}H NMR and ^{13}C NMR spectra were reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0 ppm) and relative to the signal of chloroform-d (δ 7.26 ppm for ^{1}H NMR and δ 77.1 ppm for ^{13}C NMR). Multiplicities were given as: s (singlet); br s (broad singlet); d (doublet); t (triplet); q (quartet); m (multiplets), etc. The number of protons (n) for a given resonance was indicated by nH. Highresolution mass spectra (ESI) were obtained with a LCMS-IT-TOF mass spectrometer. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer.

General procedure for Electrochemical Decarboxylative Sulfonylation of Cinnamic Acids with Sulfonylhydrazides to Vinyl Sulfones: In a round-bottomed flask (5 mL), (*E*)-cinnamic acid (0.3 mmol), *p*-toluenesulfonylhydrazide (1.0 mmol) and *t*-BuOLi (0.6 mmol) were dissolved in 5 mL DMSO with *n*-Bu_4NBF_4 (0.1 M) as an electrolyte. The reaction flask was equipped with Pt foils as anode and cathode (1.5 cm^2). The

solution was electrolyzed at a constant current (5 mA) for 10 h (6.2 F/mol) under open air at ambient temperature. After electrolysis, the mixture was quenched by water and extracted with ethyl acetate (3×15 mL). The combined organic layer was washed with brine (5 mL) and dried over $MgSO_4$. Purified product was obtained after column chromatography on silica gel using a solvent mixture of petroleum ether and ethyl acetate.

(*E*)-1-Methyl-4-(styrylsulfonyl)benzene **3a**. The product **3a** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (58.8 mg, 76% yield). Analytical data for **3a** was consistent with that previously reported.[7a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 15.4 Hz, 1H), 7.47-7.45 (m, 2H), 7.39-7.32 (m, 5H), 6.86 (d, *J* = 15.4 Hz, 1H), 2.42 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 144.4, 141.9, 137.8, 132.5, 131.1, 130.0, 129.1, 128.5, 127.7, 127.7, 21.6.

(*E*)-1-methyl-4-((4-methylstyryl)sulfonyl)benzene **3b**. The product **3b** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (49.0 mg, 60% yield). Analytical data for **3b** was consistent with that previously reported. [7a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 15.4 Hz, 1H), 7.37-7.32 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 15.4 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 144.3, 142.0, 141.7, 138.0 130.0, 129.8, 129.7, 128.6, 127.7, 126.5, 21.6, 21.5.

(*E*)-1-methyl-2-(2-tosylvinyl)benzene **3c.** The product **3c** was purified with silica gel chromatography (PE/EA=5:1) as a pale yellow solid solid (55.5 mg, 68% yield). Analytical data for **3c** was consistent with that previously reported. [5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 15.3 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.26-7.23 (m, 1H), 7.17-7.12 (m, 2H), 6.74 (d, *J* = 15.3 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 144.4, 139.6, 138.1, 137.8, 131.3, 131.0, 130.8, 130.0, 128.6, 127.7, 126.8, 126.5, 21.8, 19.8.

(*E*)-1-methyl-3-(2-tosylvinyl)benzene **3d.** The product **3d** was purified with silica gel chromatography (PE/EA=5:1) as a pale yellow solid (62.9 mg, 77% yield). Analytical data for **3d** was consistent with that previously reported. [5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.30-7.28 (m, 3H), 7.24-7.22 (m, 1H), 6.87 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 144.3, 142.1, 138.8, 137.9, 132.4, 131.9, 130.0, 129.1, 128.9, 127.7, 127.4, 125.8, 21.6, 21.2.

(*E*)-1-methoxy-4-(2-tosylvinyl)benzene **3e.** The product **3e** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (57.9 mg, 67% yield). Analytical data for **3e** was consistent with that previously reported. [5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 15.4 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 15.3 Hz, 1H), 3.80 (s, 3H), 2.40 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 162.0, 144.1, 141.6, 138.1, 130.3, 129.9, 127.5, 125.0, 124.8, 114.5, 55. 4, 21.5.

(*E*)-1-methoxy-2-(2-tosylvinyl)benzene **3f.** The product **3f** was purified with silica gel chromatography (PE/EA=5:1) as a colourless oil (69.1 mg, 80% yield). Analytical data for **3f** was consistent with that previously reported. [5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.81 (m, 3H), 7.40-7.31 (m, 4H), 7.06 (d, *J* = 15.5 Hz, 1H), 6.96-6.90 (m, 2H), 3.86 (s, 3H), 2.41 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 158.8, 144.1, 138.3, 138.0, 132.4, 130.7, 129.9, 128.3, 127.7, 121.3 120.8, 111.3, 55.5, 21.6.

(*E*)-1-methoxy-3-(2-tosylvinyl)benzene **3g.** The product **3g** was purified with silica gel chromatography (PE/EA=5:1) as a colourless oil (71.7 mg, 83% yield). Analytical data for **3g** was consistent with that previously reported. [5b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H),

7.61 (d, J = 15.4 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.29 (t, J = 7.9 Hz, 1H), 7.06 (d, J = 7.7 Hz, 1H), 6.97 (s, 2H), 6.84 (d, J = 15.4 Hz, 1H), 3.80 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 160.0, 144.5, 141.9, 137.8, 133.8, 130.1, 130.0, 128.0, 127.8, 121.2, 117.1, 113.4, 55.4, 21.7.

(*E*)-1-fluoro-4-(2-tosylvinyl)benzene **3h.** The product **3h** was purified with silica gel chromatography (PE/EA=5:1) as a colourless oil (46.4 mg, 56% yield). Analytical data for **3h** was consistent with that previously reported.[5c] ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 15.4 Hz, 1H), 7.48-7.44 (m, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.06 (t, J = 8.6 Hz, 2H), 6.79 (d, J = 15.4 Hz, 1H), 2.42 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 164.4 (d, $J_{C\text{-}F}$ = 251.3 Hz), 144.5, 140.6, 137.7, 130.6 (d, $J_{C\text{-}F}$ = 8.7 Hz), 130.0, 128.8 (d, $J_{C\text{-}F}$ = 3.3 Hz), 127.7, 127.5 (d, $J_{C\text{-}F}$ = 2.3 Hz), 116.3 (d, $J_{C\text{-}F}$ = 2.2 Hz), 21.6.

(*E*)-1-chloro-4-(2-tosylvinyl)benzene **3i.** The product **3i** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (73.6 mg, 84% yield). Analytical data for **3i** was consistent with that previously reported.[5c] ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 15.4 Hz, 1H), 7.41-7.39 (m, 2H), 7.36-7.33 (m, 4H), 6.83 (d, J = 15.4 Hz, 1H), 2.43 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 144.6, 140.5, 137.6, 137.2, 131.0, 130.1, 129.8, 129.4, 128.3, 127.8, 21.7.

(*E*)-1-Chloro-2-(2-tosylvinyl)benzene **3j.** The product **3j** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (72.7 mg, 83% yield). Analytical data for **3j** was consistent with that previously reported.[5a] ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 15.4 Hz, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 7.7 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.37-7.24 (m, 4H), 6.91 (d, J = 15.5 Hz, 1H), 2.44 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 144.6, 137.8, 137.4, 135.2, 131.9, 130.8, 130.4, 130.4 130.1, 128.2, 127.9, 127.2, 21.6.

(*E*)-1-bromo-4-(2-tosylvinyl)benzene **3k.** The product **3k** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (66.5 mg, 66% yield). Analytical data for **3k** was consistent with that previously reported.[5a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 15.4 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.35 (t, J = 7.5 Hz, 4H), 6.84 (d, J = 15.4 Hz, 1H), 2.44 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 144.7, 140. 6, 137.6, 132.4, 131.5, 130.1, 129.9, 128.5, 127. 9, 125.6, 21.7.

(*E*)-1-methyl-4-((4-(trifluoromethyl)styryl)sulfonyl)benzene **3l.** The product **3l** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (51.8 mg, 53% yield). Analytical data for **3l** was consistent with that previously reported.[5a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.68-7.61 (m, 3H), 7.57 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 6.97 (d, J = 15.4 Hz, 1H), 2.42 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 144.8, 139.9, 137.2, 135.9, 132.5 (q, $J_{C\text{-}F}$ = 32.6 Hz), 130.5, 130.1, 128.7, 127.9, 126.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.7(q, $J_{C\text{-}F}$ = 270.8 Hz), 21.5.

(*E*)-4-(2-Tosylvinyl)benzonitrile **3m.** The product **3m** was purified with silica gel chromatography (PE/EA=5:1) as a yellow solid (25.5 mg, 30% yield). Analytical data for **3m** was consistent with that previously reported.[7a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1 Hz, 2H), 7.69-7.55 (m, 5H), 7.36 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 15.4 Hz, 1H), 2.44 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 145.1, 139.3, 137.0, 136.8, 132.8, 131.5, 130.2, 128.9, 128.0, 118.1, 114.3, 21.7.

(*E*)-2-(2-tosylvinyl)furan **3n.** The product **3n** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (51.3 mg, 69% yield). Analytical data for **3n** was consistent with

that previously reported.[3g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.46 (s, 1H), 7.40 (d, *J* = 15.1 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 15.1 Hz, 1H), 6.68 (s, 1H), 6.46 (s, 1H), 2.41 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 148.8, 145.6, 144.3, 138.0, 130.0, 128.5, 127.6, 125.2, 116.7, 112.6, 21.6.

(*E*)-2-(2-tosylvinyl)thiophene **3o.** The product **3o** was purified with silica gel chromatography (PE/EA=5:1) as a brown solid (52.3 mg, 66% yield). Analytical data for **3o** was consistent with that previously reported.[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 15.1 Hz, 1H), 7.41 (d, *J* = 4.9 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 3.4 Hz, 1H), 7.10-7.01 (m, 1H), 6.63 (d, *J* = 15.1 Hz, 1H), 2.42 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 144.4, 137.9, 137.1, 134.6, 132.3, 130.0, 129.9, 128.3, 127.7, 125.9, 21.6.

(*E*)-2-(2-tosylvinyl)pyridine **3p.** The product **3p** was purified with silica gel chromatography (PE/EA=5:1) as a yellow oil (58.3 mg, 75% yield). Analytical data for **3p** was consistent with that previously reported.[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.7 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.74-7.70 (m, 1H), 7.61 (d, *J* = 14.9 Hz, 1H), 7.42 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.29-7.26 (m, 1H), 2.42 (s, 3H). $^{13}C\{^1H\}$NMR (100MHz, $CDCl_3$) δ 151.1, 150.3, 144.6, 140.1, 137.3, 137.1, 132.2, 130.0, 127.9, 125.4, 125.0, 21.6.

(*E*)-2-(2-tosylvinyl)naphthalene **3q.** The product **3q** was purified with silica gel chromatography (PE/EA=5:1) as a yellow solid (73.9 mg, 80% yield). Analytical data for **3q** was consistent with that previously reported.[3p] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 17.7 Hz, 2H), 7.86-7.80 (m, 5H), 7.55-7.51 (m, 3H), 7.35 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 144.5, 142.1, 137.9, 134.5, 133.2, 130.9, 130.0, 130.0, 129.0, 128.7, 127.9, 127.8, 127.7, 127.0, 123.5, 21.7.

(*E*)-(2-(phenylsulfonyl)vinyl)benzene **4a.** The product **4a** was purified with silica gel chromatography (PE/EA=5:1) as a pale yellow solid (51.3 mg, 70% yield). Analytical data for **4a** was consistent with that previously reported.[7b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.63-7.59 (m, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.48-7.46 (m, 2H), 7.38 (d, *J* = 6.7 Hz, 3H), 6.87 (d, *J* = 15.4 Hz, 1H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 142.5, 140.8, 133.4, 132.4, 131.3, 129.4, 129.1, 128.6, 127.7, 127.3.

(*E*)-1-*tert*-butyl-4-(styrylsulfonyl)benzene **4b.** The product **4b** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (52.2 mg, 58% yield). Analytical data for **4b** was consistent with that previously reported.[7b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 15.4 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.1 Hz, 2H), 7.38 (d, *J* = 6.0 Hz, 3H), 6.87 (d, *J* = 15.4 Hz, 1H), 1.33 (s, 9H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 157.4, 142.0, 137.7, 132.5, 131.1, 129.1, 128.6, 127.6, 127.6, 126.4, 35.3, 31.1.

(*E*)-1-methoxy-4-(styrylsulfonyl)benzene **4c.** The product **4c** was purified with silica gel chromatography (PE/EA=5:1) as a white oil (66.6 mg, 81% yield). Analytical data for **4c** was consistent with that previously reported.[7b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 15.4 Hz, 1H), 7.46-7.44 (m, 2H), 7.36 (d, *J* = 6.4 Hz, 3H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 15.4 Hz, 1H), 3.84 (s, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 163.6, 141.3, 132.5, 132.2 131.0, 129.8, 129.0, 128.5, 128.0, 114.6, 55.7.

(*E*)-1-fluoro-4-(styrylsulfonyl)benzene **4d.** The product **4d** was purified with silica gel chromatography (PE/EA=5:1) as a pale yellow solid (47.2 mg, 60% yield). Analytical data for **4d** was consistent with that previously reported.[7b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.94 (m, 2H), 7.68 (d, *J* = 15.4 Hz, 1H), 7.49-7.47 (m, 2H), 7.43-7.37 (m, 3H), 7.23-7.19 (m, 2H), 6.85 (d, *J* =

15.4 Hz, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 165.7(d, J_{C-F} = 254.4 Hz), 142.7, 136.8 (d, J_{C-F} = 3.1 Hz), 132.2, 131.4, 130.6 (d, J_{C-F} = 9.5 Hz), 129.2, 128.6, 127.1, 116.7(d, J_{C-F} = 22.5 Hz).

(*E*)-1-chloro-4-(styrylsulfonyl)benzene **4e.** The product **4e** was purified with silica gel chromatography (PE/EA=5:1) as a brown solid (65.9 mg, 79% yield). Analytical data for **4e** was consistent with that previously reported. [7b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 15.4 Hz, 1H), 7.41-7.36 (m, 4H), 7.31-7.26 (m, 3H), 6.77 (d, *J* = 15.4 Hz, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 143.0, 140.0, 139.3, 132.1, 131.4, 129.6, 129.1, 129.1, 128.6, 126.9.

(*E*)-1-bromo-4-(styrylsulfonyl)benzene **4f.** The product **4f** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (60.9 mg, 63% yield). Analytical data for **4f** was consistent with that previously reported. [5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.70-7.67(m, 3H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.42-7.39 (m, 3H), 6.84 (d, *J* = 15.4 Hz, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 143.2, 139.9, 132.7, 132.2, 131.5, 129.3, 129.2, 128.7, 126.9.

(*E*)-*N*-(4-(styrylsulfonyl)phenyl)acetamide **4g.** The product **4g** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (38.8 mg, 43% yield). Analytical data for **4g** was consistent with that previously reported. [7b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 15.4 Hz, 1H), 7.46 (d, *J* = 6.2 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 3H), 6.84 (d, *J* = 15.4 Hz, 1H), 2.19 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 169.5, 143.2, 142.3, 134.7, 132.2, 131.3, 129.1, 128.8, 128.6, 127.2, 119.8, 24.6.

(*E*)-1-(styrylsulfonyl)-4-(trifluoromethyl)benzene **4h.** The product **4h** was purified with silica gel chromatography (PE/EA=5:1) as a pale yellow solid (47.7 mg, 51% yield). Analytical data for **4h** was consistent with that previously reported. [7b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 15.4 Hz, 1H), 7.50-7.48 (m, 2H), 7.43-7.38 (m, 3H), 6.88 (d, *J* = 15.4 Hz, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 144.5, 144.1, 135.0 (q, J_{C-F} = 32.9 Hz), 132.1, 131.7, 129.2, 128.8, 128.3, 126.5 (q, J_{C-F} = 3.7 Hz), 126.3, 123.2(q, J_{C-F} = 271.4 Hz).

(*E*)-2-(styrylsulfonyl)thiophene **4i.** The product **4i** was purified with silica gel chromatography (PE/EA=5:1) as a yellow solid (45.8 mg, 61% yield). Analytical data for **4i** was consistent with that previously reported. [7b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.66 (m, 3H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.42-7.39 (m, 3H), 7.15-7.13 (m, 1H), 6.96 (d, *J* = 15.3 Hz, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 142.3, 142.2, 134.0, 133.5, 132.3, 131.4, 129.2, 128.7, 128.1, 128.0.

(*E*)-2-(styrylsulfonyl)naphthalene **4j.** The product **4j** was purified with silica gel chromatography (PE/EA=5:1) as a white solid (457.3 mg, 65% yield). Analytical data for **4j** was consistent with that previously reported.[3e] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.99-7.96 (m, 2H), 7.91-7.88 (m, 2H), 7.75 (d, *J* = 15.4 Hz, 1H), 7.67-7.59 (m, 2H), 7.49-7.47 (m, 2H), 7.40-7.37 (m, 3H), 6.94 (d, *J* = 15.4 Hz, 1H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 142.6, 137.6, 135.2, 132.4, 132.3, 131.3, 129.7, 129.4, 129.3, 129.2, 129.1, 128.6, 128.0, 127.7, 127.4, 122.6.

(*E*)-1-methoxy-2-(styrylsulfonyl)benzene **4k.** The product **4k** was purified with silica gel chromatography (PE/EA=5:1) as a yellow oil (59.2 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 15.5 Hz, 1H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.50-7.48 (m, 2H), 7.40- 7.38 (m, 3H), 7.15-7.09 (m, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 157.4, 143.3, 135.4, 132.9, 131.0, 129.5, 129.1, 128.7, 128.5, 127.0, 120.8, 112.5, 56.3. IR (KBr): 3060, 2926, 2846, 1585, 1471, 1297, 1137, 1013, 812, 748 cm^{-1}. HRMS calculated for $C_{15}H_{14}NaO_3S$ ($M + Na^+$): 297.0556, found:297.0559.

(*E*)-1-chloro-2-(styrylsulfonyl)benzene **4l.** The product **4l** was purified with silica gel chromatography (PE/EA=5:1) as a pale yellow solid (57.6 mg, 69% yield). Analytical data for **4l** was consistent with that previously reported.[5a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 15.4 Hz, 1H), 7.54-7.38 (m, 8H), 7.08 (d, *J* = 15.4 Hz, 1H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 145.3, 138.3, 134.6, 132.9, 132.4, 131.9, 131.5, 130.7, 129.2, 128.8, 127.5, 125.37.

ASSOCIATED CONTENT

Supporting Information

Experimental spectroscopic data. 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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