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Palladium(II)-Catalyzed Direct Alkenylation and Arylation of Arenes: Removable 2-Pyridylsulfinyl Group Assisted C−H Bond Activation

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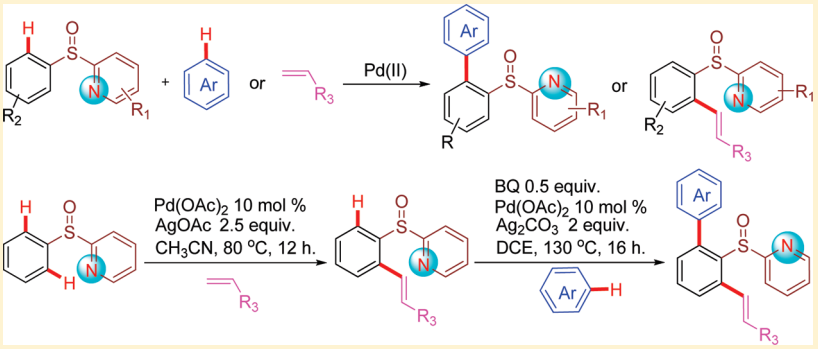
Supporting Information

ABSTRACT:



Palladium-catalyzed C−H activation reactions directed by a removable 2-pyridylsulfinyl group were developed. Aromatic olefination products were formed in good yields on treatment of 2-(phenylsulfinyl)pyridines with alkenes in the presence of a Pd catalyst. The reaction tolerates a wide range of substituted alkenes, including various acrylates and styrenes. The controlled experiments indicated that the 2-pyridyl moiety, rather than the sulfinyl, played the role of ligand. The final reductive desulfonylation affords the stilbenes, sulfides, and disulfides with different reductive conditions, respectively. More importantly, this transformation could also be applied in arylation through dual C−H activation.

INTRODUCTION

Transition-metal-catalyzed C−H functionalization has emerged as a valuable and atom-economical alternative to traditional metal-catalyzed cross-couplings in the construction of C−C and C−X (X = O, N, halogens) bonds.[1] Of particular interest is the palladium-catalyzed chelation-directed sp^2 C−H activation, which provides valuable products in a highly efficient way.[2] To date, diverse directing groups, including pyridine,[2a−c] imidazoline,[2d] pyrazole,[2e] oxazoline,[2f,g] amide,[2h,i] oxime ether,[2j] ketones,[2k] hydroxyl,[2l,m] and carboxylic acids,[2n,o] have been developed to assist aromatic C−H bond activation. However, in some cases, the practicality might be restricted when the directing groups cannot easily be removed from the products. Therefore, significant effort has been directed toward the discovery of efficient and removable directing groups. In a pioneering study, Gevorgyan and co-workers discovered that pyridyldiisopropylsilyl (PyDipSi) could be used successfully as the directing group for the transformation of C−H bonds to C−O and C−X (X = Cl, Br, and I) bonds via the sp^2 C−H bond activation and then be removed easily from the products.[3] Arrayas and Carretero made an advance in the directed C2-alkenylation of indoles by the use of removable pyridylsulfonyl (PyS(O_2)) as the directing group.[4] More recently, pyridylsulfonyl-directed olefination and acetoxylation were reported by the Carretero group and the Mancheño group, respectively.[5] Herein, we report the Pd-catalyzed alkenylation and arylation of arenes by the use of a 2-pyridylsulfinyl group as directing group. The (arylsulfinyl)pyridine compounds can be prepared very conveniently by thiophenols and 2-bromopyridine (see Supporting Information),[6] and the 2-pyridylsulfinyl group could be removed easily after the C−H bond functionalization under reductive conditions or afford diverse reduction products. The sequential alkenylation and arylation were achieved by suitable control of the reaction conditions.

RESULTS AND DISCUSSION

Alkenylation is an important transformation in organic synthesis,[7] and direct C−H bond olefination has received much attention in the past several years.[8,9] Although many efficient directing groups have been developed in the direct C−H alkenylation reactions, the difficulty removing such directing groups from the products remains a great challenge. Inspired by the use of the chiral sulfinyl group as chiral ligand in asymmetric synthesis, which can be easily cleaved after promoting asymmetric transformation,[10] we envisioned that the removable sulfides could be installed in arenes as the directing groups and then removed after the C−H bond functionalization under suitable reaction conditions. For this end, we designed different

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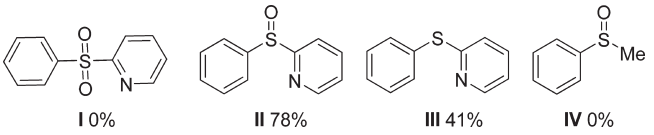


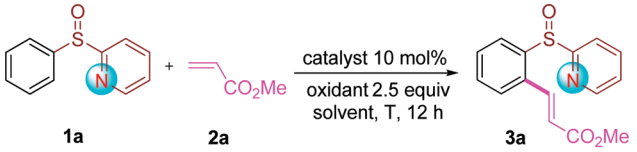
Figure 1. Directing group screening.

sulfur-containing directing groups to investigate their possibility in assisted C−H activation (Figure 1). We prepared 2-(phenylsulfonyl)pyridine (**I**) and examined the reactivity in the alkenylation reaction with methyl acrylate in the presence of $Pd(OAc)_2$ (10 mol %), AgOAc (2.5 equiv), and BQ (0.5 equiv) in DMF (1 mL) at 130 °C for 12 h. Unfortunately, it failed to provide the desired alkenylation product. To our delight, the use of (phenylsulfinyl)pyridine (**II**) as substrate delivered the desired *ortho*-alkenylation product **3a** (Table 1) in 78% yield, while 2-(phenylthio)pyridine (**III**) afforded the *ortho*-alkenylation product in 41% yield. Methylsulfinylbenzene (**IV**) was inactive.

The above results indicate that the use of (phenylsulfinyl)-pyridine (**II**) is a useful strategy to achieve the C−H activation. We optimized the reaction conditions by the use of 2-(phenylsulfinyl)pyridine and methyl acrylate as model substrates, and the selected results are listed in Table 1. First, a set of palladium catalysts were tested. The results indicated that $Pd(OAc)_2$ was superior to other palladium sources, such as $Pd(PPh_3)_4$, $Pd(dba)_2$, $PdCl_2$, $PdCl_2(PPh_3)_2$, and $PdCl_2(CH_3CN)_2$, to give the desired alkenylation product **3a** with 81% yield in the presence of AgOAc (2.5 equiv) in CH_3CN (1 mL) at 80 °C (entries 1−6). We also evaluated $RuCl_3$ as the catalyst under the reaction conditions, but there was no reaction in this system. It was found that the oxidants played a crucial role in the reaction. The best result was obtained by the use of AgOAc. A comparable reaction efficiency was presented by Ag_2CO_3, while other Ag(I) salts showed poor reactivity (entries 7−10). It should be noted that $Cu(OAc)_2$ can also afford the desire product with 44% yield (entry 11). No reaction took place without catalysts or oxidants in this system. Then, the effect of solvents was examined. We found that the alkenylation reaction of 2-(phenylsulfinyl)-pyridine can be carried out smoothly in CH_3CN, DCE, DME, DMF, and THF, and CH_3CN showed the best efficiency while other solvents such as DMSO, toluene, and 1,4-dioxane were inferior (entries 12−18). At last, the temperature effect was tested, and heat was found to favor the reaction (entries 19−22). When we performed the reaction of **1a** with **2a** in the presence of 10 mol % of $Pd(OAc)_2$ and 1 equiv of AgOAc in CH_3CN at 70 °C, 46% of the target product **3a** was obtained (entry 8). The yield of **3a** was profoundly increased to 81% at 80 °C under these reaction conditions, but it was helpless when the reaction temperature was increased to 100 or 130 °C.

The scope of the alkenylation reaction was investigated as summarized in Table 2. A variety of acrylates coupled cleanly with 2-(phenylsulfinyl)pyridine to give the corresponding alkenylation products in moderate to good yields with excellent *E*-stereoselectivity (entries 1−3). In the case of acrylonitrile, a higher yield was obtained but with a mixture of *Z* and *E* stereoisomers (entry 4). The more challenging styrene and its derivatives also reacted with 2-(phenylsulfinyl)pyridine efficiently (entries 5−12). The styrenes bearing both electron-donating and electron-withdrawing groups in the phenyl ring afforded the desired product smoothly. It should be noted that the presence of bromide in the phenyl ring of styrenes did not alter the reaction

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	oxidant	solvent	temp (°C)	yield (%)
1	$Pd(PPh_3)_4$	AgOAc	CH_3CN	80	62
2	$Pd(dba)_2$	AgOAc	CH_3CN	80	56
3	$Pd(CH_3CN)_2Cl_2$	AgOAc	CH_3CN	80	18
4	$Pd(PPh_3)_2Cl_2$	AgOAc	CH_3CN	80	23
5	$PdCl_2$	AgOAc	CH_3CN	80	75
6	**$Pd(OAc)_2$**	**AgOAc**	**CH_3CN**	**80**	**81**
7	$Pd(OAc)_2$	Ag_2CO_3	CH_3CN	80	68
8	$Pd(OAc)_2$	Ag_2O	CH_3CN	80	NR
9	$Pd(OAc)_2$	AgF	CH_3CN	80	NR
10	$Pd(OAc)_2$	$AgNO_3$	CH_3CN	80	35
11	$Pd(OAc)_2$	$Cu(OAc)_2$	CH_3CN	80	46
12	$Pd(OAc)_2$	AgOAc	DCE	80	67
13	$Pd(OAc)_2$	AgOAc	DME	80	70
14	$Pd(OAc)_2$	AgOAc	DMF	80	75
15	$Pd(OAc)_2$	AgOAc	THF	80	72
16	$Pd(OAc)_2$	AgOAc	DMSO	80	trace
17	$Pd(OAc)_2$	AgOAc	dioxane	80	32
18	$Pd(OAc)_2$	AgOAc	toluene	80	44
19	$Pd(OAc)_2$	AgOAc	CH_3CN	70	46
20	$Pd(OAc)_2$	AgOAc	CH_3CN	80	81
21	$Pd(OAc)_2$	AgOAc	CH_3CN	100	75
22	$Pd(OAc)_2$	AgOAc	CH_3CN	130	77

[a] Reaction conditions: 2-(phenylsulfinyl)pyridine **1a** (60.9 mg, 0.3 mmol), methyl acrylate **2a** (51.6 mg, 0.6 mmol), catalyst (0.03 mmol), solvent (1 mL), air, 12 h.

pathway, and the surviving C−Br bond could be further transformed to different useful functional groups (entry 12). In addition, this useful coupling reaction could be applied to various phenylsulfinyl substrates, and the electronic properties of the substituents influenced the reactivity of the reaction. For example, the reaction was carried out smoothly with electron-releasing substituents such as methyl and methoxyl to give good yields (entries 13−16), but higher temperature was required for the electron-withdrawing substituents in moderate yield (entry 17). When the arenes bearing stronger electron-withdrawing groups, such as 2-(4-nitrophenylsulfinyl)pyridine, cannot afford the desire alkenylation product, 2,2′-sulfinyldipyridine is also the inert substrate. The structure of this alkenylation product was further confirmed by the X-ray crystallography of **3f** (see Supporting Information).

Importantly, the (2-pyridyl)sulfinyl group could be easily removed by the treatment of the corresponding alkenylated product with *n*-BuLi, as shown in Scheme 1.[11] Furthermore, the alkenylated sulfoxide could be converted into the corresponding sulfide **4a** in 83% yield by the use of Zn dust as the reductant.[4,5] In the presence of sodium amalgam, disulfide **4g** resulted in good yield.

We noted that the 2-(arylsulfinyl)pyridines bearing electron-withdrawing groups in the aryl ring are less active under the reaction conditions. Thus, an electrophilic metalation mechanism

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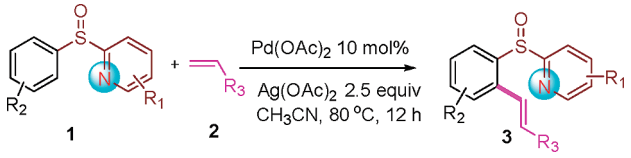
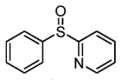
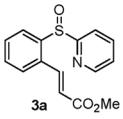
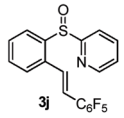
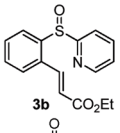
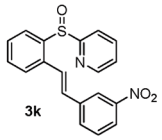
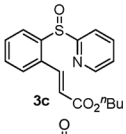
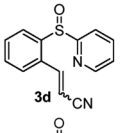
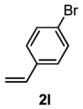
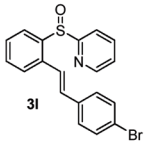
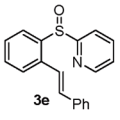
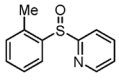
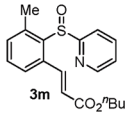
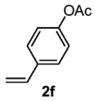
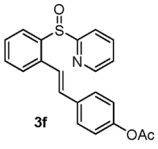
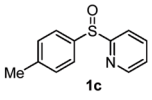
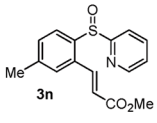
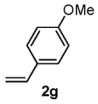
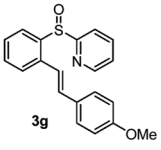
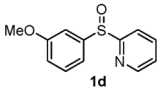
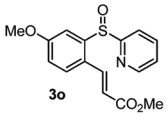
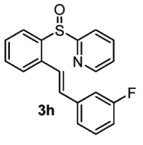
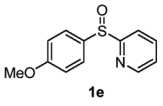
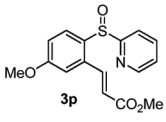
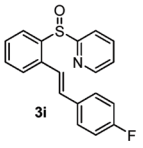
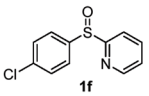
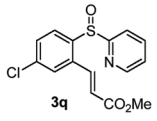
Table 2. Alkenylation of 2-(Phenylsulfinyl)pyridines with Alkenes[a]



entry	substrate 1	Substrate 2	Product 3	Yield (%)	entry	substrate 1	Substrate 2	Product 3	Yield (%)
1	 1a	 2a	 3a	81	10	1a	 2j	 3j	62 [b]
2	1a	 2b	 3b	76	11	1a	 2k	 3k	75
3	1a	 2c	 3c	72					
4	1a	 2d	 3d	83 [b] (E:Z = 11:1)	12	1a	 2l	 3l	68
5	1a	 2e	 3e	45[c]	13	 1b	2c	 3m	70
6	1a	 2f	 3f	74	14	 1c	2a	 3n	62
7	1a	 2g	 3g	62	15	 1d	2a	 3o	81
8	1a	 2h	 3h	77	16	 1e	2a	 3p	70
9	1a	 2i	 3i	65 [c]	17	 1f	2a	 3q	52 [c]

[a] Reaction conditions: 2-(phenylsulfinyl)pyridines **1** (0.3 mmol), alkenes **2** (0.6 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), and AgOAc (125 mg, 0.75 mmol) in CH_3CN (1 mL) under air at 80 °C for 12 h. [b] DCE/DMF (2 mL/0.2 mL) under air at 130 °C for 12 h. [c] The reaction temperature was 130 °C under air for 24 h.

is favored, as shown in Scheme 2.[12] Initially, the electronic attack of Pd(II) into 2-(phenylsulfinyl)pyridine forms the intermediate **I**, which inserts into olefins to afford the intermediate **II**. The subsequent β-hydro elimination results in the product and librates Pd(0) as well as acetic acid. The Pd(II) is regenerated from the oxidation of Pd(0) by silver(I) compounds.

In order to investigate the versatility of the 2-pyridyl sulfoxide directing group in C−H activation, we explored the arylation reaction of 2-(phenylsulfinyl)pyridines **1a** with arenes (Figure 2). After optimization of the reaction conditions, it was found that the arylation reaction[13] could proceed successfully in the presence of $Pd(OAc)_2$ (10 mol %), Ag_2CO_3 (2 equiv), and BQ (0.5 equiv) at 130 °C for 16 h. Both electron-rich (**5a**,**5b**) and electron-deficient arenes (**5c**−**5e**) took part in the arylation reaction. However, the electron-deficient arenes were more reactive to give the higher yields. The regioisomeric products

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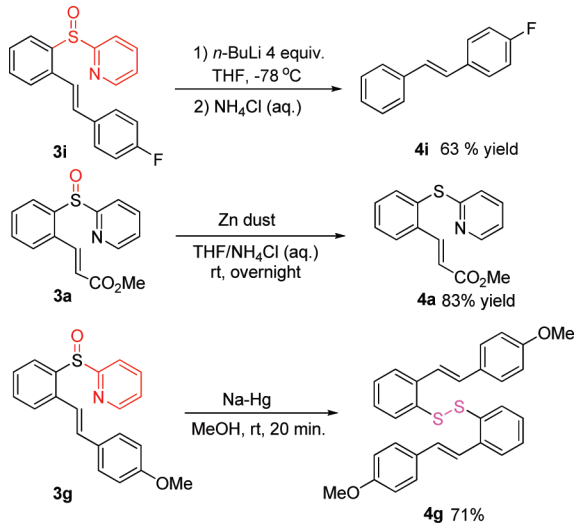
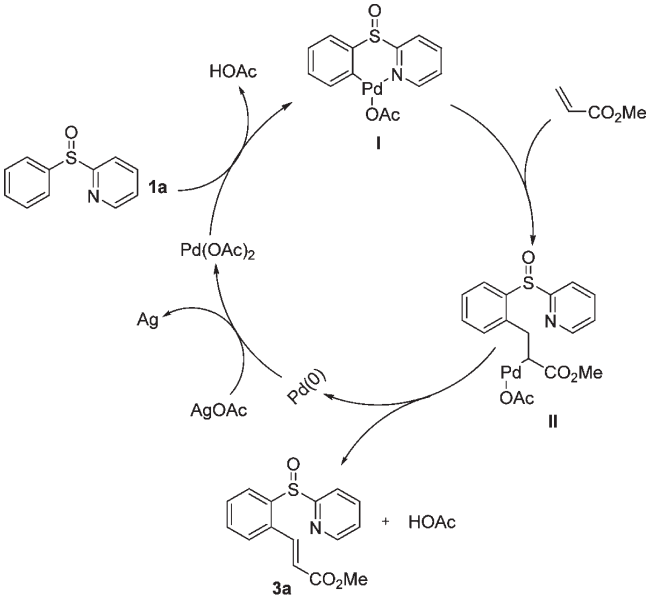
Scheme 1. Removing the Directing Group



Scheme 2. Possible Mechanism of the Alkenylation



were obtained when toluene was used (**5b**). 2-(*p*-Methoxylphenylsulfinyl)pyridine and 2-(*p*-methylphenylsulfinyl)pyridine reacted smoothly with 1,2,4,5-tetrafluorobenzene to give the arylated product in acceptable yields (**5f** and **5g**).

Notably, the arylation reaction occurred smoothly under the reaction conditions when the alkenylated products were used as substrates. Thus, the sequential alkenylation and arylation could be achieved by the treatment of compound **1a** under the alkenylation conditions first, and afterwords undergoing the arylation reaction under the arylation conditions (Scheme 3).

CONCLUSION

In summary, we have successfully developed an efficient palladium(II)-catalyzed methods for alkenylation and arylation of arenes by the use of 2-pyridyl sulfoxide as directing group. The directing group can be easily removed or converted to another useful synthetic moiety. Importantly, the sequential alkenylation and arylation of arenes was achieved by suitable control of reaction conditions.

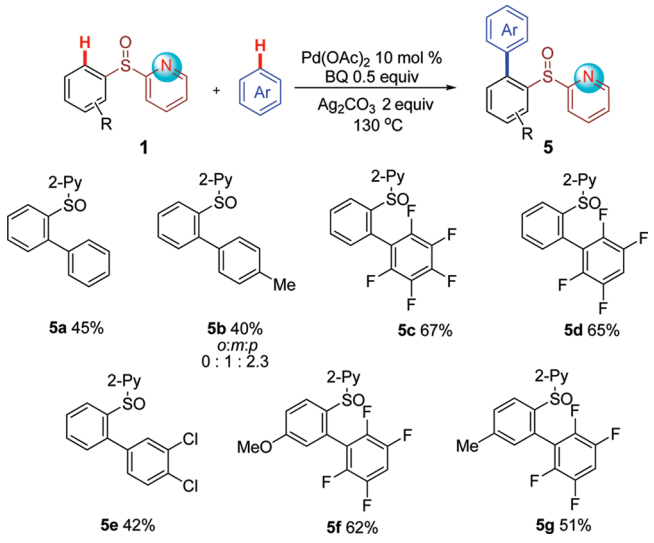


Figure 2. Arylation reaction of 2-(phenylsulfinyl)pyridines **1** with arenes. Conditions: **1** (0.3 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), BQ (16.2 mg, 0.15 mol), and Ag_2CO_3 (165.6 mg, 0.6 mmol) in arenes (0.5 mL) under air at 130 °C for 16 h.

EXPERIMENTAL SECTION

Typical Experimental Procedure for Preparation of Starting Material: A 100 mL flask was charged with 2-bromopyridines (30.0 mmol), thiophenols (35.0 mmol), DMF (25.00 mL), and K_2CO_3 (5.52 g, 40.0 mmol). The mixture was stirred at 110 °C for 20 h. The mixture was filtered through a pad of Celite, and the waste cake was washed with DMF (10 mL). The crude sulfide solution was transferred to another 100 mL flask. The subsequent oxidation was carried out by addition of glacial HOAc (2.00 mL) and heated to 80 °C. H_2O_2 solution (30 wt %, 3.47 g, 40.0 mol) was added slowly and stirred for 2 h at 80 °C. After the reaction, 20 mL of water was added into the reaction solution. The pH of the mixture was controlled to 9 by the use of 20% (w/v) NaOH solution, and the resulting slurry was cooled to <5 °C. The mixture was stirred below 5 °C for 1.5 h and filtered through a pad of Celite. The wet cake was washed with water (3 × 20 mL) and was redissolved in ethyl acetate (50 mL). The resulting solution was dried with anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to provide 2-benzenesulfonyl pyridines.

2-(Phenylsulfinyl)pyridine[5a] **1a:** White solid, mp 48 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.54 (d, J = 4.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.86 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.82−7.80 (m, 2H), 7.47−7.43 (m, 3H), 7.30−7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 150.0, 144.3, 138.4, 131.4, 129.4, 125.1, 124.9, 118.7.

2-(*o*-Tolylsulfinyl)pyridine[5a] **1b:** White solid, mp 103−105 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.49 (d, J = 4.0 Hz, 1H), 8.03 (d, J = 4.0 Hz, 1H), 7.86 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.79−7.77 (m, 1H), 7.32−7.25 (m, 3H), 7.21−7.19 (m, 1H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 149.5, 142.9, 137.9, 137.4, 130.9, 130.8, 126.8, 124.4, 118.9, 19.3.

2-(*p*-Tolylsulfinyl)pyridine[5a] **1c:** White solid, mp 66−67 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.53 (d, J = 4.0

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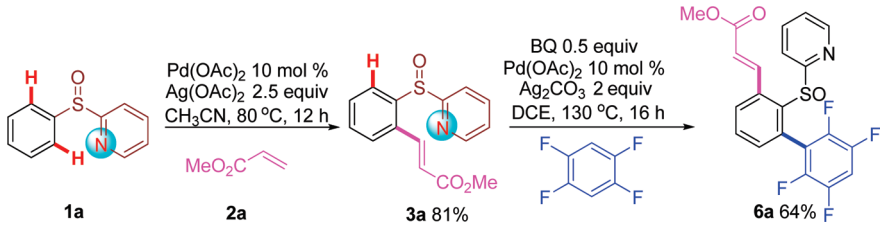
Scheme 3. Sequential Alkenylation and Arylation



Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.86 (t, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.82−7.80 (m, 2H), 7.30−7.24 (m, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 150.0, 141.9, 141.2, 138.3, 130.1, 125.3, 124.3, 118.7, 21.6.

2-(3-Methoxyphenylsulfinyl)pyridine[5a] 1d: Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.54 (d, J = 4.8 Hz, 1H), 8.07 (d, J = 7.2 Hz, 1H), 7.89 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.39−7.29 (m, 4H), 6.96−6.93 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 160.0, 149.6, 145.1, 138.0, 130.0, 124.7, 118.3, 117.4, 117.0, 108.9, 55.4.

2-(4-Methoxyphenylsulfinyl)pyridine[5a] 1e: White solid, mp 77−78 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.54 (d, J = 4.8 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.89 (td, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.70−7.67 (m, 2H), 7.31−7.28 (m, 1H), 6.96−6.94 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 162.0, 149.7, 138.0, 135.1, 127.2, 124.4, 118.5, 114.6, 55.6.

2-(4-Chlorophenylsulfinyl)pyridine[5a] 1f: White solid, mp 76−78 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.53 (d, J = 4.0 Hz, 1H), 8.01 (d, J = 4.0 Hz, 1H), 7.85 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.72 (d, J = 8.0 Hz, 2H), 8.39 (d, J = 8.0 Hz, 2H), 7.31−7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 149.7, 142.4, 138.1, 137.3, 129.7, 126.1, 124.7, 118.2.

Typical Experimental Procedure for the Alkenylation of 2-Pyridyl Sulfoxides: A mixture of 2-(phenylsulfinyl)pyridines (0.3 mmol), alkenes (0.6 mmol), Pd $(OAc)_2$ (6.7 mg, 10 mol %), and AgOAc (125.3 mg, 0.75 mmol) in acetonitrile (2 mL) was stirred at 80 °C for 12 h. Afterward, the reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite. The solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:3−5, v/v) to obtain the desired products.

(*E*)-Methyl 3-(2-(Pyridin-2-ylsulfinyl)phenyl)acrylate[5a] 3a: White solid, mp 76 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.51−8.47 (m, 2H), 8.05 (d, J = 8.0 Hz, 1H), 7.91−7.85 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.49−7.45 (m, 2H), 7.28−7.25 (m, 1H), 6.44 (d, J = 15.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.4, 149.7, 143.8, 139.7, 137.9, 134.2, 131.3, 130.6, 126.9, 125.3, 124.4, 121.1, 118.9, 51.7; HRMS (EI) calcd for $C_{15}H_{13}NO_3S$ (M^+) 287.0616, found 287.0614.

(*E*)-Ethyl 3-(2-(Pyridin-2-ylsulfinyl)phenyl)acrylate 3b: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.50−8.46 (m, 2H), 8.05 (d, J = 8.0 Hz, 1H), 7.91−7.87 (m, 2H), 7.63 (d, J_2 = 2.0 Hz, 1H), 7.49−7.45 (m, 2H), 7.28 (m, 1H), 6.43 (d, J = 16.0 Hz, 1 H), 4.28 (m, 2H), 1.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.7, 150.1, 144.1, 139.9, 138.2, 134.6, 131.7, 130.9, 127.2, 125.7, 124.8, 122.0, 119.3, 61.0, 14.5; HRMS (EI) calcd for $C_{16}H_{15}NO_3S$ (M^+) 301.0773, found 301.0763.

(*E*)-Butyl 3-(2-(Pyridin-2-ylsulfinyl)phenyl)acrylate[5a] 3c: Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.51−8.47 (m, 2H), 8.05 (d, J = 8.0 Hz, 1H), 7.91−7.85 (m, 2H), 7.64 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.51−7.43 (m, 2H), 7.29−7.25 (m, 1H), 6.43 (d, J = 15.6 Hz, 1H), 4.24 (t, J = 6.8 Hz, 2H), 1.75−1.68 (m, 2H), 1.51−1.42(m, 2H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.4, 149.8, 143.7, 140.0, 137.9, 134.3, 131.3, 130.6, 126.9, 125.3, 124.5, 121.6, 119.0, 64.6, 30.7, 19.1, 13.7; HRMS (EI) calcd for $C_{18}H_{19}NO_3S$ (M^+) 329.1086, found 329.1083.

(*E*)-3-(2-(Pyridin-2-ylsulfinyl)phenyl)acrylonitrile 3d: White solid, mp 88−90 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.49 (d, J = 4.0 Hz, 1H), 8.33 (d, J = 16.4 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.96−7.90 (m, 2H), 7.59 −7.54 (m, 2H), 7.51−7.47 (m, 1H), 7.33−7.30 (m, 1H), 5.95 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 149.7, 146.2, 143.6, 138.3, 133.1, 131.5, 131.4, 126.3, 125.2, 124.7, 118.6, 117.6, 99.5; HRMS (EI) calcd for $C_{14}H_{10}N_2OS$ (M^+) 254.0514, found 254.0513.

(*E*)-2-(2-Styrylphenylsulfinyl)pyridine[5a] 3e: White solid, mp 99−100 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.48 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 16.4 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.84 (t, J = 8.0 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.44−7.37 (m, 4H), 7.30 (t, J = 6.8 Hz, 1H), 7.26−7.24 (m, 1H), 7.05 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 149.5, 141.8, 137.8, 137.1, 136.8, 132.1, 131.2, 128.6, 128.3, 128.1, 126.9, 125.9, 125.1, 124.5, 123.9, 119.1; HRMS (EI) calcd for $C_{19}H_{15}NOS$ (M^+) 305.0874, found 305.0874.

(*E*)-4-(2-(Pyridin-2-ylsulfinyl)styryl)phenyl acetate[5a] 3f: White solid, mp 137−138 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.47 (d, J = 4.4 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.91−7.87 (m, 2H), 7.82 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.67 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.43−7.39 (m, 2H), 7.34−7.31 (m, 1H), 7.25−7.22 (m, 2H), 7.02 (d, J = 15.6 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 165.9, 150.4, 149.5, 141.8, 137.9, 136.9, 134.6, 131.2, 130.9, 128.3, 127.8, 125.8, 125.0, 124.5, 124.1, 121.8, 119.1, 21.0; HRMS (EI) calcd for $C_{21}H_{17}NO_3S$ (M^+) 363.0929, found 363.0922.

(*E*)-2-(2-(4-Methoxystyryl)phenylsulfinyl)pyridine[5a] 3g: Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.47 (d, J = 4.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 8.86−7.77 (m, 2H), 7.66 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 9.2 Hz, 2 H), 7.43−7.35 (m, 2H), 7.26 (m, 1H), 7.00 (d, J = 16.4 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 159.7, 149.5, 141.4, 137.8, 137.4, 131.6, 131.2, 129.6, 128.2, 127.8, 125.6, 125.0, 124.4, 121.6, 119.1, 114.1, 55.2; HRMS (EI) calcd for $C_{20}H_{17}NO_2S$ (M^+) 335.0980, found 335.0996.

(*E*)-2-(2-(3-Fluorostyryl)phenylsulfinyl)pyridine 3h: Yellow solid, mp 78−80 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.47 (d, J = 4.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 16.0 Hz, 1H), 7.89 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.83 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.68−7.66 (m, 1H), 7.46−7.39 (m, 2H), 7.34−7.31 (m, 2H), 7.28−7.23 (m, 2H), 7.00 (d, J = 16.0 Hz, 1H), 7.03−6.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 163.1 (d, J = 244.8 Hz, C−F), 149.5, 142.0, 139.1 (d, J = 7.3 Hz, 1C), 137.9, 137.4, 136.6, 131.3, 130.7 (d, J = 2.8 Hz, 1C), 130.0(d, J = 8.5 Hz, 1C), 128.6, 125.9, 125.3, 124.5, 122.7 (d, J = 2.6, Hz 1C), 119.0, 114.8 (d, J = 23.1 Hz, 1C), 113.2 (d, J = 20.8 Hz, 1C); HRMS (EI) calcd for $C_{19}H_{14}FNOS$ (M^+) 323.0780, found 323.0782.

(*E*)-2-(2-(4-Fluorostyryl)phenylsulfinyl)pyridine 3i: Yellow solid, mp 75−76 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$,

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TMS) δ 8.47 (d, J = 2.4 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.89−7.81 (m, 3H), 7.67−7.65 (m, 1H), 7.55−7.52 (m, 2H), 7.45−7.37 (m, 2H), 7.26−7.23 (m, 1H), 7.07 (t, J = 8.0 Hz, 2H), 7.01 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 162.4 (d, J = 247.0 Hz, C−F), 149.5, 141.9, 137.9, 137.0, 133.1 (d, J = 3.0 Hz, 2C), 131.3, 130.8, 128.5 (d, J = 8.4 Hz, 2C), 128.3, 125.8, 125.1, 124.5, 123.8, 119.1, 115.6 (d, J = 22.1 Hz, 2C); HRMS (EI) calcd for $C_{19}H_{14}FNOS$ (M^+) 323.0780, found 323.0782.

(*E*)-2-(2-(Perfluorostyryl)phenylsulfinyl)pyridine 3j: White solid, mp 158−159 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.49 (s, 1H), 8.29 (d, J = 16.4 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.90−7.86 (m, 2H), 7.71−7.69 (m, 1 H), 7.51−7.45 (m, 2H), 7.30−7.27 (m, 1H), 6.99 (d, J = 16.4, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 149.7, 142.7, 138.0, 136.3, 132.6 (d, C−C_6F_5), 131.5, 129.5, 126.1, 125.3, 124.6, 119.0, 116.2; HRMS (EI) calcd for $C_{19}H_{10}F_5NOS$ (M^+) 395.0403, found 395.0407.

(*E*)-2-(2-(3-Nitrostyryl)phenylsulfinyl)pyridine 3k: Yellow solid, mp 125−127 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.50 (d, J = 4.0 Hz, 1H), 8.39 (s, 1H), 8.15 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.11−8.06 (m, 2H), 7.94−7.86 (m, 3H), 7.72−7.70 (m, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.50−7.43 (m, 2H), 7.30−7.27 (m, 1H), 7.00 (d, J = 16 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 149.5, 148.6, 142.3, 138.7, 138.1, 135.9, 132.4, 131.3, 129.6, 129.3, 129.0, 127.1, 126.0, 125.1, 124.6, 122.4, 121.6, 119.1; HRMS (EI) calcd for $C_{19}H_{14}N_2O_3S$ (M^+) 350.0725, found 350.0717.

(*E*)-2-(2-(4-Bromostyryl)phenylsulfinyl)pyridine[5a] 3l: Yellow solid, mp 135−137 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.46 (d, J = 4.4 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 16.0 Hz, 1H), 7.89 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.84 (td, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.45−7.39 (m, 4H), 7.27−7.22 (m, 1H), 6.97 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 149.5, 142.0, 137.9, 136.8, 135.8, 131.8, 131.3, 130.7, 128.5, 128.4, 125.9, 125.2, 124.7, 124.5, 122.0, 119.1; HRMS (EI) calcd for $C_{19}H_{14}BrNOS$ (M^+) 382.9979, found 382.9979.

(*E*)-Methyl 3-(3-methyl-2-(pyridin-2-ylsulfinyl)phenyl)-acrylate[5a] 3m: Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.55 (d, J = 15.2 Hz, 1H), 8.45 (d, J = 4.0 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.88 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.39−7.35 (m, 2H), 7.27−7.24 (m, 2H), 6.12 (d, J = 16.0 Hz, 1H), 3.78 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.9, 150.1, 141.4, 140.9, 140.3, 137.4, 137.2, 133.3, 132.1, 126.5, 124.2, 121.5, 120.9, 52.0, 20.2; HRMS (EI) calcd for $C_{16}H_{15}NO_3S$ (M^+) 301.0773, found 301.0786.

(*E*)-Butyl 3-(5-Methyl-2-(pyridin-2-ylsulfinyl)phenyl)-acrylate 3n: Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.42−8.38 (m, 1H), 8.41 (d, J = 16.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.81 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.40 (s, 1H), 7.25−7.19 (m, 1H), 6.37 (d, J = 16.0 Hz, 1H), 4.18 (t, J = 6.8, 2H), 2.32 (s, 3H), 1.68−1.62 (m, 2H), 1.44−1.38 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 165.9, 150.0, 142.2, 141.0, 140.0, 138.2, 134.5, 131.8, 127.8, 126.0, 124.7, 121.3, 119.3, 64.8, 30.9, 21.6, 19.4, 13.9; HRMS (EI) calcd for $C_{19}H_{21}NO_3S$ (M^+) 343.1242, found 343.1246.

(*E*)-Methyl 3-(4-Methoxy-2-(pyridin-2-ylsulfinyl)phenyl)-acrylate 3o: White solid, mp 100−102 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.48 (d, J = 4 Hz, 1H), 8.41 (d, J = 15.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.89 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.43 (d, J = 2.4 Hz, 1H), 7.30−7.26 (m, 1H), 6.96 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 165.3, 161.7, 149.8, 145.5, 139.4, 137.9, 128.3, 126.3, 124.6, 118.9, 118.4, 118.3, 108.5, 55.7, 51.9; HRMS (EI) calcd for $C_{16}H_{15}NO_4S$ (M^+) 317.0722, found 317.0723.

(*E*)-Methyl 3-(5-Methoxy-2-(pyridin-2-ylsulfinyl)phenyl)-acrylate 3p: White solid, mp 142−143 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.48 (d, J = 3.2 Hz, 1H), 8.44 (d, J = 16.0 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.88 (t, J = 7.6 Hz, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.28−7.25 (m, 1H), 7.10 (d, J = 1.6 Hz, 1H), 6.99 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.7, 161.9, 149.8, 139.8, 137.9, 136.2, 135.2, 128.0, 124.3, 121.6, 119.1, 116.6, 111.9, 55.5, 51.8; HRMS (EI) calcd for $C_{16}H_{15}NO_4S$ (M^+) 317.0722, found 317.0737.

(*E*)-Methyl 3-(5-Chloro-2-(pyridin-2-ylsulfinyl)phenyl)-acrylate 3q: White solid, mp 128−129 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 (d, J = 3.2 Hz, 1H), 8.41 (d, J = 16.0 Hz, 1H), 8.04 (d, J = 8 Hz, 1H), 7.89 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 1.6 Hz, 1H), 7.44 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.31−7.28 (m, 1H), 6.45 (d, J = 16.0 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.2, 149.8, 142.3, 138.7, 138.1, 137.7, 135.7, 130.6, 126.8, 126.7, 124.6, 122.3, 118.9, 51.9; HRMS (EI) calcd for $C_{15}H_{12}ClNO_3S$ (M^+) 321.0226, found 321.0233.

The Reaction of Removing or Transforming Pyridylsulfinyl Group: Reduction of (*E*)-2-(2-(4-Fluorostyryl)phenylsulfinyl)pyridine 3i to (*E*)-1-Fluoro-4-styrylbenzene[14] 4i: To a solution of (*E*)-2-(2-(4-fluorostyryl)phenylsulfinyl)pyridine **3i** (97 mg, 0.3 mmol) in dry THF (2.5 mL) was added a 2.5 M solution of BuLi in hexane (0.48 mL, 1.2 mmol) at −78 °C under nitrogen atmosphere. The mixture was stirred at −78 °C for 10 min before a saturated aqueous solution of NH_4Cl was added. The two phases were separated, and the aqueous phase was extracted with EtOAc (2 × 5 mL). The combined organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography using petroleum ether as elute to afford (*E*)-1-fluoro-4-styrylbenzene **4i** with 63% yield: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53−7.48 (m, 4H), 7.39 (t, J = 1.2 Hz, 2H), 7.29 (t, J = 6.8 Hz, 1H), 7.12−7.02 (m, 4H); ^{1}H NMR (100 MHz, $CDCl_3$) δ 162.5 (J = 245.9 Hz, 1C), 137.1, 133.5 (J = 2.8 Hz, 1C), 128.7, 128.5, 128.0 (J = 8.2 Hz, 2C), 127.6, 127.5, 126.4, 115.7 (J = 22.3 Hz, 1C).

Reduction of (*E*)-Methyl 3-(2-(Pyridin-2-ylsulfinyl)phenyl)-acrylate 3a to (*E*)-Methyl 3-(2-(Pyridin-2-ylthio)phenyl)-acrylate 4a: A suspension of (*E*)-methyl 3-(2-(pyridin-2-ylsulfinyl)-phenyl)acrylate **3a** (86.0 mg, 0.3 mmol) and Zn dust (960.0 mg, 15 mmol) in a 1:1 mixture of THF/saturated aqueous NH_4Cl (2 mL) was stirred at room temperature overnight. The mixture was diluted with EtOAc (5 mL) and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/EtOAc 3:1) to give (*E*)-methyl 3-(2-(pyridin-2-ylthio)phenyl)acrylate **4a** as a colorless oil in 83% yield: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.35 (d, J = 4.4 Hz, 1H), 8.19 (d, J = 16.0 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.45−7.36 (m, 3H), 6.97−6.93 (m, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 160.3, 149.7, 142.3, 138.5, 137.1, 136.8, 131.6, 130.8, 130.0, 127.5, 121.3, 120.4, 120.0, 51.7; HRMS calcd for $C_{15}H_{13}NO_2S$ (M^+) 271.0677, found 271.0673.

Reduction of (*E*)-2-(2-(4-Methoxystyryl)phenylsulfinyl)-pyridine 3g to 2,2′-Bis(2-(4-methoxystyryl)phenyl)disulfide 4g: A suspension of (*E*)-2-(2-(4-methoxystyryl)phenylsulfinyl)pyridine **3g** (100.5 mg, 0.3 mmol) and 30% (w/w) Na−Hg (230.0 g, 10 mmol) in a MeOH (2 mL) was stirred at room temperature for 20 min. The mixture was diluted with EtOAc (5 mL) and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/EtOAc 50:1) to give 2,2′-bis(2-(4-methoxystyryl)phenyl)disulfide **4g** as a white solid in 71% yield: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (dd, J_1 = 7.6, J_2 = 1.2 Hz, 2H), 7.54 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 2H), 7.41 (d, J = 16.0 Hz, 2H), 7.37 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 4H), 7.22 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 2H), 7.14 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 2H), 6.92 (d, J = 16.0 Hz, 1H), 6.87 (dd, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 2H), 3.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 138.9, 134.8, 132.0, 130.5, 130.0,

128.4, 128.0, 127.6, 125.6, 123.6, 114.0, 55.2. HRMS calcd for $C_{30}H_{26}O_2S_2$ (M^+) 482.1374, found 482.1376.

Typical Experimental Procedure for the Arylation of 2-Pyridyl Sulfoxides: A mixture of 2-(phenylsulfinyl)pyridines **1** (0.3 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol %), BQ (16.2 mg, 0.15 mol), Ag_2CO_3 (165.6 mg, 0.6 mmol), and 0.5 mL of arenes was stirred at 130 °C for 16 h. Afterward, the reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite. The solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:3−5, v/v) to obtain the desired products.

2-(Biphenyl-2-ylsulfinyl)pyridine 5a: Yellow solid, mp 109−110 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.51 (d, J = 4.8 Hz, 1H), 7.87−7.80 (m, 3H), 7.63−7.60 (m, 2H), 7.52−7.38 (m, 6H), 7.27−7.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 149.8, 143.0, 142.6, 138.2, 137.6, 131.2, 130.5, 130.4, 128.6, 128.1, 128.0, 126.4, 124.3, 120.1; HRMS (EI) calcd for $C_{17}H_{13}NOS$ (M^+) 279.0718, found 279.0720.

2-(2′,3′,4′,5′,6′-Pentafluorobiphenyl-2-ylsulfinyl)pyridine 5c: White solid, mp 100−102 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.35 (d, J = 4.4, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.82 (t, J = 8.4 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.27−7.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 149.5, 144.5, 138.1, 131.6, 131.4, 130.6, 125.2, 124.8, 124.6, 118.4; HRMS (EI) calcd for $C_{17}H_8F_5NOS$ (M^+) 369.0247, found 369.0240.

2-(2′,3′,5′,6′-Tetrafluorobiphenyl-2-ylsulfinyl)pyridine 5d: White solid, mp 141−142 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.36 (d, J = 4.0 Hz, 1H), 8.06 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.84−7.79 (m, 2H), 7.61 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 755 (td, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.25−7.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 149.6, 144.3, 137.9, 131.3, 131.2, 130.4, 126.2, 124.7, 124.6, 118.6, 106.2 (m, 1C); HRMS (EI) calcd for $C_{17}H_9F_4NOS$ (M^+) 351.0341, found 351.0350.

2-(3′,4′-Dichlorobiphenyl-2-ylsulfinyl)pyridine 5e: White solid, mp 115−117 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.50 (d, J = 4.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.88 (d, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.80−7.76 (m, 1H), 7.74 (d, J = 2.0 Hz, 1H), 7.55−7.49 (m, 4H), 7.80−7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 149.7, 143.2, 140.2, 138.1, 137.9, 132.5, 132.2, 131.4, 130.3, 130.0, 129.9, 129.4, 128.9, 126.6, 124.5, 119.7; HRMS (EI) calcd for $C_{17}H_{11}Cl_2NOS$ (M^+) 346.9938, found 346.9934.

2-(2′,3′,5′,6′-Tetrafluoro-5-methoxybiphenyl-2-ylsulfinyl)-pyridine 5f: White solid, mp 159−160 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.40 (d, J = 4.0 Hz, 1H), 7.91 (d, J = 9.2 Hz, 1H), 7.82−7.80 (m, 1H), 7.24 (m, 1H), 7.18 (t, J = 8.4 Hz, 1H), 7.10 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 6.83 (d, J = 2.8 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ165.4, 161.6, 149.6, 137.8, 135.2, 128.1, 127.1, 124.5, 118.6, 116.9, 115.9, 106.2 (m, 1C), 55.6; HRMS (EI) calcd for $C_{18}H_{11}F_4NO_2S$ (M^+) 381.0477, found 381.0471.

2-(2′,3′,5′,6′-Tetrafluoro-5-methylbiphenyl-2-ylsulfinyl)-pyridine 5g: White solid, mp 145−147 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.37 (d, J = 4.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.84−7.77 (m, 2H), 7.41 (d, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.25−7.13 (m, 3H), 2.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 149.6, 142.0, 141.1, 137.9, 132.0, 131.3, 126.2, 124.9, 124.6, 118.6, 106.1, 21.2; HRMS (EI) calcd for $C_{18}H_{11}F_4NOS$ (M^+) 365.0497, found 365.0508.

Experimental Procedure for (2′,3′,5′,6′-Tetrafluoro-2-(pyridin-2-ylsulfinyl)biphenyl-3-yl)acrylate 6a: A mixture of (*E*)-methyl 3-(2-(pyridin-2-ylsulfinyl)phenyl)acrylate **3a** (86 mg, 0.3 mmol), Pd $(OAc)_2$ (6.7 mg, 10 mol %), BQ (16.2 mg, 0.15 mol), Ag_2CO_3 (165.6 mg, 0.6 mmol), and 0.25 mL of 2,3,5,6-tetrafluorobenzene and 0.5 mL of DCE was stirred at 130 °C for 16 h. Afterward, the reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite. The solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:3 v/v) to obtain the desired products: white solid, mp 179−180 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.58 (d, J = 15.6 Hz, 1H), 8.43 (d, J = 4.4 Hz, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.80 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.68 (d, J = 7.2 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.26−7.23 (m, 1H), 7.17−7.13 (m, 1H), 6.19 (d, J = 16.0 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.7, 149.9, 141.1, 139.9, 137.7, 137.1, 133.8, 132.1, 129.7, 129.6, 124.2, 122.3, 119.9, 106.2 (m, 1C), 51.8; HRMS (EI) calcd for $C_{21}H_{13}F_4NO_3S$ (M^+) 435.0552, found 435.0563.

■ ASSOCIATED CONTENT

Supporting Information. General experimental procedures and spectroscopic data (^{1}H NMR, ^{13}C NMR, HRMS, and MS) for the corresponding products. This material is available free of charge via the Internet at http://pubs.acs.org.

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