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2-Pyridyl Sulfoxide Directed Pd(II)-Catalyzed C–H Olefination of Arenes with Molecular Oxygen as the Sole Oxidant

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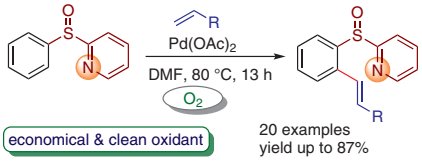

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Abstract Pd(II)-catalyzed C–H olefination of aryl 2-pyridyl sulfoxides with unactivated and activated olefins has been demonstrated. We employed environmentally benign and inexpensive molecular oxygen as the sole oxidant. The versatile nature of the 2-pyridyl sulfoxide directing group has been proven by its transformation to the sulfone functionality. Deuterium scrambling experiments and intramolecular kinetic isotopic studies were carried out to gain insights into the reaction pathway.

Key words C–H olefination, 2-pyridyl sulfoxides, molecular oxygen, palladium(II) catalysis

Transition-metal-catalyzed oxidative olefination of aryl C–H bonds with olefins has been considered as one of the straightforward methods to access functional materials.[1]

The Fujiwara–Moritani reaction, which represents the oxidative cross-coupling of arene C–H bonds with alkenes under palladium catalysis, is an attractive method in terms of the step economy feature.[2] Later on, numerous methods have been developed to tackle the regioselective issues in the oxidative olefination of aromatic C–H bonds with alkenes.[3] Cognizing the fact that the directing group can be an ultimate choice in controlling the regioselectivity of C–H olefination,[4] nitrogen-[5] and oxygen-based[3b,6] moieties have often been used as chelating groups for transition metals in C–H functionalization reactions. Even though excellent reactivity and regioselectivity have been achieved by introducing directing groups on arenes, removal of the chelating group from the final product is rather challenging.

In this regard, many research groups came up with the concept of removable and modifiable directing groups for the C(sp^2)–H bond functionalization of arenes, as this opens a plethora of synthetic applications in academia and industry. A few such directing groups are 8-aminoquinoline, picolinamide, sulfoximine,[7] pyridyldiisopropylsilyl (PyDipSi),[8] *N*-(2-pyridyl)sulfonyl,[9] and carboxylate.[10] Despite their labile oxido-redox nature and strong coordination ability towards transition metals, sulfur-containing directing groups have recently been used for *o*-C–H functionalization reactions.[1f,11] This is due to organosulfur compounds being widely found in biologically active molecules, natural products,[12] and smart materials.[13] Often, these motifs are used as building blocks, reagents, and chiral ligands[14] in organic synthesis. Of note, sulfoxide-directed C–H olefination allows installation of an alkene unit in the final product which then could be transformed to sulfur heterocycles.[11e,15] In particular, the versatile and removable 2-pyridyl sulfoxide group was proven to be efficient with Pd(II) catalysis in *o*-C–H functionalization reactions.[11a,b,16] For example, the Zhang[11a] group demonstrated efficient direct alkenylation of arenes with various acrylates and styrenes. With the same directing group, mono- and di-*ortho*-olefinated arenes were successfully synthesized by Arrayás, Carretero, and co-workers[16b] (Scheme 1). However, stoichiometric amounts of oxidants such as $K_2S_2O_8$ (2 equiv) and AgOAc (5 equiv) were employed in those reactions to complete the catalytic cycle. These oxidants ultimately produce undesired waste which may have ramifications on the environment. Considering the importance of the direct C–H olefination of arenes and vast applications of the sulfur moiety, we took the opportunity to develop a greener approach for the oxidative olefination of arenes with the 2-pyridyl sulfoxide directing group. We knew that molecular oxygen as oxidant would be the ultimate choice,[17] as it is rich in availability, nature-friendly, and inexpensive. Further, the sole byproduct produced in a molecular oxygen mediated C–H olefination reaction is H_2O.[18]

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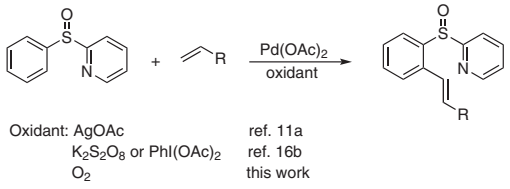
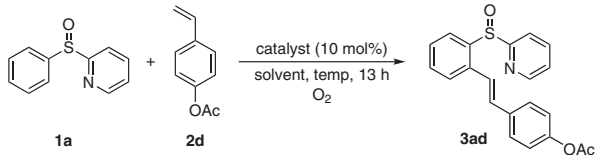


Scheme 1 Palladium-catalyzed *o*-C–H olefination of 2-pyridyl sulfoxides

Herein, we disclose our findings on the direct C–H olefination of arenes with unactivated and activated olefins using molecular oxygen as the sole oxidant.

We commenced our study by reacting 2-pyridyl sulfoxide **1a** with 4-acetoxystyrene (**2d**) using $Pd(OAc)_2$ (10 mol%) under oxygen atmosphere at 110 °C. At first, we screened the solvent in the olefination reaction and the results are summarized in Table 1. As per literature reports, DCE and MeCN proved to be effective solvents for C–H olefination of the 2-pyridyl sulfoxide.[11a,16b] However, the reactions in those solvents (DCE and MeCN) were not efficient and provided moderate yields of the desired product **3ad** (Table 1, entries 1 and 2).

Table 1 Optimization of the Reaction Conditions[a]



Entry	Catalyst	Solvent	Temp (°C)	Yield (%)[b]
1	$Pd(OAc)_2$	DCE	110	26
2	$Pd(OAc)_2$	MeCN	110	45
3	$Pd(OAc)_2$	THF	110	15
4	$Pd(OAc)_2$	1,4-dioxane	110	29
5	$Pd(OAc)_2$	DMSO	110	18
6	$Pd(OAc)_2$	DMF	110	52
7	$Pd(OAc)_2$	MeOH	110	NR[c]
8	$Pd(OAc)_2$	DMF	80	65
9	$Pd(PPh_3)_2Cl_2$	DMF	80	trace
10	$Pd(PPh_3)_4$	DMF	80	57
11	$Pd(dba)_2$	DMF	80	40
12	$PdCl_2$	DMF	80	54
13	$PdCl_2(C_6H_5CN)_2$	DMF	80	40

[a] Reaction conditions: **1a** (0.25 mmol), **2d** (0.5 mmol), solvent (2.5 mL), 13 h, O_2 atmosphere.
[b] Isolated yield.
[c] NR = no reaction.

Polar aprotic solvents, such as THF, 1,4-dioxane, and DMSO, were found to be inferior in this olefination reaction (entries 3–5). To our delight, the *o*-C–H olefination reaction worked well in DMF solvent to deliver **3ad** in 52% yield (entry 6). The reaction was completely turned off in protic MeOH (entry 7). The yield of **3ad** improved to 65% when the temperature was decreased from 110 °C to 80 °C in DMF (entry 8). The effect of the palladium catalyst was next examined in the *o*-C–H olefination reaction. Using $Pd(PPh_3)_2Cl_2$ gave trace amounts of the product (entry 9). The reactions with other palladium complexes, such as $Pd(PPh_3)_4$, $Pd(dba)_2$, $PdCl_2$, and $PdCl_2(C_6H_5CN)_2$, were found to be inefficient and the desired product was obtained in moderate yields (entries 10–13). Based on the above results, the optimized conditions for the *o*-C–H olefination reaction comprised $Pd(OAc)_2$ (10 mol%) in DMF at 80 °C under oxygen atmosphere. Under these conditions, we screened a few representative sulfur-based directing groups in the alkenylation reaction (Figure 1). The reaction did not proceed with the highly electron-withdrawing 2-pyridyl sulfone directing group. Reactions with diphenyl sulfoxide, methyl phenyl sulfoxide, and phenyl 2-pyridyl sulfide were found to be ineffective. Based on these results, we decided to choose 2-pyridyl sulfoxide as directing group to explore the scope of the olefination reaction.

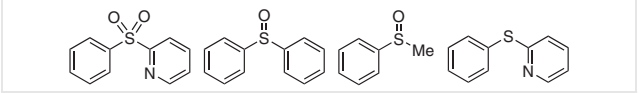
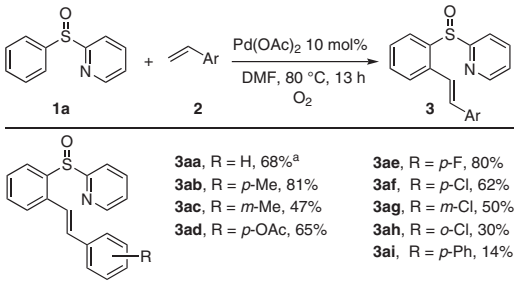


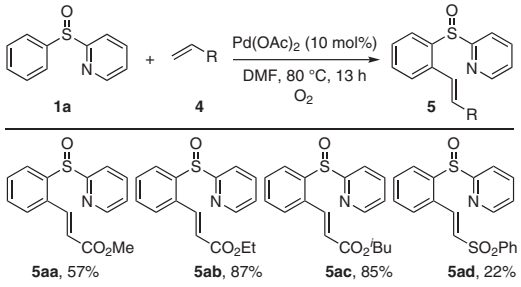
Figure 1 Directing groups that fail to provide *o*-C–H olefination product

At first, we investigated the scope of the *o*-C–H olefination reaction with unactivated styrene derivatives and the results are shown in Scheme 2. The reaction of styrene with **1a** afforded a mixture of mono- and di-*ortho*-alkenylated product in 68% and 10% yield, respectively. Substituents such as methyl and acetoxy at the *meta*- or *para*-position of the phenyl ring of styrene furnished the corresponding products **3ab–ad** in acceptable yields. Halo substituents such as fluoro and chloro were compatible under the optimized reaction conditions, delivering the *o*-alkenylated (arylsulfinyl)pyridines **3ae–ag** in good yields. Product **3ah** was obtained in lower yield due to steric factors. The presence of versatile halo substituents in the final C–H olefinated products may provide an opportunity to employ such products as starting materials in various cross-coupling reactions to synthesize complex molecules. The π-extended *o*-alkenylated (phenylsulfinyl)pyridine **3ai** was isolated, albeit in poor yield. Our efforts to obtain *o*-C–H olefinated products with heteroaryl substrates such as 4-vinylpyridine and 1-vinyl-1*H*-imidazole were unsuccessful.



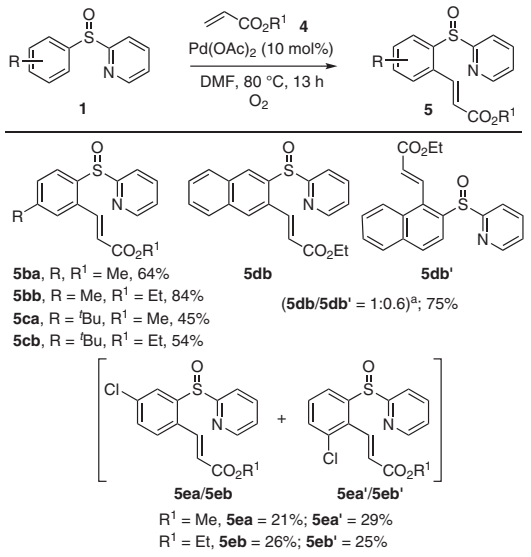
Scheme 2 Substrate scope of unactivated alkenes. *Reagents and conditions*: **1a** (0.25 mmol), **2** (0.5 mmol), DMF (2.5 mL), 13 h, O_2 atmosphere; isolated yields. [a] Di-*ortho*-olefination product **3aa′** was obtained in 10% yield.

We next turned our attention to examining the scope of the reaction with respect to activated olefins (Scheme 3). Acrylate derivatives such as methyl, ethyl, and isobutyl acrylate effectively participated in the *o*-C–H alkenylation reaction to afford the desired products **5aa–ac** in moderate to good yields. Interestingly, (vinylsulfonyl)benzene (**4d**) also participated in the reaction, providing **5ad** in 22% yield.



Scheme 3 Substrate scope of activated alkenes. *Reagents and conditions*: **1a** (0.25 mmol), **4** (0.5 mmol), DMF (2.5 mL), 13 h, O_2 atmosphere; isolated yields.

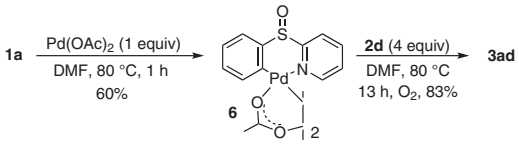
To study the scope of the sulfoxide, we prepared a few (arylsulfinyl)pyridine derivatives **1b–e** and subjected them to the optimized *o*-C–H olefination reaction conditions (Scheme 4). The reaction of 2-(*p*-tolylsulfinyl)pyridine (**1b**) individually with methyl acrylate (**4a**) as well as with ethyl acrylate (**4b**) provided **5ba** and **5bb** in good yields. (Arylsulfinyl)pyridine **1c** with a *tert*-butyl substituent at the *para*-position of the aromatic ring underwent the reaction with **4a** to give **5ca** in 45% yield and similarly reacted with **4b** to provide **5cb** in 54% yield. An inseparable mixture of regioisomers **5db**/**5db′** was isolated when 2-(naphthalen-2-ylsulfinyl)pyridine (**1d**) reacted with acrylate **4b**.[19] As anticipated, *meta*-chloro-substituted 2-pyridyl sulfoxide **1e** gave the two regioisomeric products **5ea** and **5ea′** in 21% and 29% yield, respectively, upon reaction with **4a**. A similar trend was observed for the C–H olefination of **1e** with **4b** to deliver the products **5eb** and **5eb′** in 51% combined yield. In



Scheme 4 Substrate scope of 2-pyridyl sulfoxides. *Reagents and conditions*: **1** (0.25 mmol), **4** (0.5 mmol), DMF (2.5 mL), 13 h, O_2 atmosphere; isolated yields. [a] Calculated by ^{1}H NMR.

these cases, both regioisomers were isolated in pure form through column chromatography.

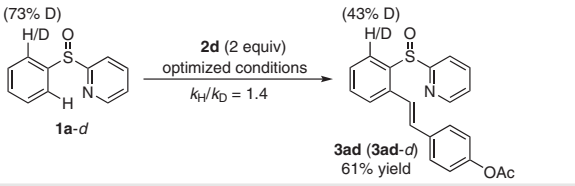
We conducted a few experiments to outline the plausible reaction mechanism for this *o*-C–H olefination reaction. Treatment of **1a** with $Pd(OAc)_2$ (1 equiv) in DMF at 80 °C provided the six-membered cyclopalladated complex **6** in 60% yield (Scheme 5).[11b,20] The formation of complex **6** was realized through coordination of the Pd(II) species to the nitrogen atom of the (arylsulfinyl)pyridine directing group and subsequent deprotonation, with Pd–C bond formation. Next, we subjected complex **6** to the C–H olefination reaction with **2d** in DMF at 80 °C in the presence of oxygen atmosphere. Finally, we were able to isolate the desired product **3ad** in 83% yield. This result indicates the involvement of a palladacycle in the *o*-C–H alkenylation reaction.



Scheme 5 Synthesis of palladacycle **6** and *o*-olefinated sulfoxide

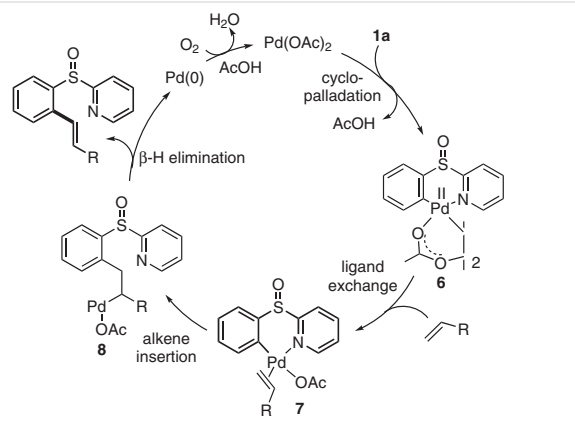
To gain further insight into the reaction mechanism, we performed deuterium scrambling experiments with D_2O. The reaction of **1a** with 10 equivalents of D_2O in the presence of 10 mol% $Pd(OAc)_2$ and DMF at 80 °C for 13 hours under O_2 atmosphere did not deliver deuterium incorporated product,[21] suggesting C–H bond palladation to be irreversible in nature. An intramolecular kinetic isotopic effect

k_H/k_D = 1.4 was observed for the reaction of **1a**-*d* with **2d**, implying that *o*-C–H bond breakage is most likely not involved in the rate-determining step (Scheme 6).



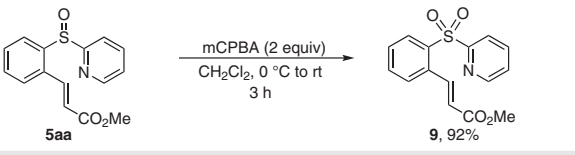
Scheme 6 Kinetic isotopic effect

On the basis of our findings and literature reports,[5e,11a,b,17c,d] a plausible reaction mechanism is proposed and depicted in Scheme 7. Initially, the Pd(II) species reacts with **1a** to form palladacycle **6**. Then, ligand exchange and alkene insertion probably leads to the generation of species **8**. Finally, β-hydride elimination from **8** provides the *o*-alkenylation product along with Pd(0). Molecular oxygen oxidizes Pd(0) to the Pd(II) active catalyst for completion of the catalytic cycle.



Scheme 7 Plausible catalytic cycle of the *o*-C–H olefination

Next, we envisioned demonstrating the synthetic versatility of the 2-pyridyl sulfoxide directing group. Oxidation of *o*-alkenylated 2-pyridyl sulfoxide **5aa** to the corresponding sulfone with mCPBA was efficient and provided **9** in 92% yield (Scheme 8).



Scheme 8 Transformation of the directing group

In conclusion, we have developed an efficient method for the *o*-C–H olefination of arenes with the aid of the 2-pyridyl sulfoxide directing group under palladium catalysis. Low cost and environmentally benign molecular oxygen was used as the sole oxidant in this process. A wide range of *o*-olefinated aryl 2-pyridyl sulfoxides was obtained in appreciable yields. Oxidation of the 2-pyridyl sulfoxide unit was efficient in providing the corresponding sulfone. Current efforts are focused on the carbon–heteroatom bond-formation reaction with the versatile 2-pyridyl sulfoxide directing group.

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were taken on a Bruker Avance 500 MHz NMR spectrometer. Chemical shifts (δ) are reported in parts per million, relative to chloroform at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.0 ppm for ^{13}C in $CDCl_3$. Data for ^{1}H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, bd = broad doublet, t = triplet, bt = broad triplet, q = quartet, m = multiplet), coupling constants, *J* (in Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm). High-resolution mass spectra were obtained using a TOF analyzer in ESI mode. TLC analysis was performed on commercial aluminum TLC plates, silica gel coated with fluorescent indicator F254. Silica gel (Merk 100–200 mesh and 230–400 mesh) was used for column chromatography. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Thiophenols, 2-bromopyridine, and alkenes were purchased from Sigma-Aldrich, India. *N*,*N*-Dimethylformamide (DMF) was distilled under reduced pressure and stored under nitrogen. All reactions were performed in oven-dried glass reaction tubes. Compounds **1a**,[16b] **1b**,[16c] **1d**,[16c] **1e**,[16b] **3aa**,[11a] **3aa′**,[16b] **3ad**,[11a] **3ae**,[11a] **5aa**,[11a] **5ab**,[11a] **5ad**,[16b] and **5ba**[11a] are previously reported and showed the identical spectra according to the literature.

2-((4-*tert*-Butylphenyl)sulfinyl)pyridine (1c); Typical Procedure for 2-(Arylsulfinyl)pyridines 1

4-*tert*-Butylbenzenethiol (500 mg, 3 mmol), 2-bromopyridine (470 mg, 3 mmol, 1 equiv), K_2CO_3 (830 mg, 6 mmol, 2 equiv), and DMSO (4 mL) were placed in an oven-dried round-bottom flask. The resulting solution was stirred at 110 °C for 20 h. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel (hexane/EtOAc, 9:1) to provide 2-((4-*tert*-butylphenyl)thio)pyridine. The thiol (710 mg, 3.0 mmol) was transferred to a 100 mL flask, CH_2Cl_2 (10 mL) was added, and the mixture was cooled to 0 °C. The subsequent oxidation was carried out by slow addition of mCPBA (510 mg, 3.0 mmol, 1 equiv) and stirring for 3–4 h at 0 °C to room temperature. Then, saturated aqueous $NaHCO_3$ solution was added and the mixture was stirred for 30 min, then extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel (hexane/EtOAc, 7:3) to provide **1c** as a white solid; yield: 553 mg (71%); mp 111–112 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.57–8.56 (m, 1 H), 8.08–8.06 (m, 1 H), 7.90–7.87 (m, 1 H), 7.71–7.69 (m, 2 H), 7.48–7.46 (m, 2 H), 7.32–7.29 (m, 1 H), 1.29 (s, 9 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.80, 154.59, 149.63, 140.70, 137.96, 126.18, 124.79, 124.47, 118.40, 34.56, 30.80.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{18}NOS^+$: 260.1104; found: 260.1103.

(*E*)-4-(2-(Pyridin-2-ylsulfinyl)styryl)phenyl Acetate (3ad); Typical Procedure for 2-Pyridyl Sulfoxide Directed Pd(II)-Catalyzed C–H Olefination of Arenes

An oven-dried glass reaction tube with a septum was charged with 2-(phenylsulfinyl)pyridine (**1a**; 51 mg, 0.25 mmol) and $Pd(OAc)_2$ (6 mg, 0.025 mmol, 0.1 equiv). The mixture was degassed with three vacuum–oxygen cycles before DMF (2.5 mL) and olefin **2d** (81 mg, 0.5 mmol, 2 equiv) were added at room temperature. Then the reaction mixture was purged with O_2 using a balloon and the reaction tube was closed with a screw cap. Finally, the mixture was stirred on a pre-heated heating block at 80 °C for 13 h. The reaction mixture was quenched with H_2O and extracted with ethyl acetate (3 × 10 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel (hexane/EtOAc, 4:1) to provide **3ad** as a yellow solid; yield: 59 mg (65%).

(*E*)-2-((2-(4-Methylstyryl)phenyl)sulfinyl)pyridine (3ab)

Light green solid; yield: 64 mg (81%); mp 88–89 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.49 (d, *J* = 4.0 Hz, 1 H), 8.02 (d, *J* = 8.0 Hz, 1 H), 7.89 (dd, *J* = 11.5, 6.0 Hz, 2 H), 7.83 (t, *J* = 9.0 Hz, 1 H), 7.69 (d, *J* = 7.5 Hz, 1 H), 7.48 (d, *J* = 8.5 Hz, 2 H), 7.44 (t, *J* = 7.0 Hz, 1 H), 7.38 (t, *J* = 6.5 Hz, 1 H), 7.26–7.24 (m, 1 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 16.0 Hz, 1 H), 2.39 (s, 3 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 165.90, 149.58, 141.63, 138.21, 137.88, 137.34, 134.06, 132.06, 131.27, 129.43, 128.11, 126.90, 125.79, 125.13, 124.49, 122.80, 119.21, 21.30.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{18}NOS^+$: 320.1104; found: 320.1105.

(*E*)-2-((2-(3-Methylstyryl)phenyl)sulfinyl)pyridine (3ac)

Colorless solid; yield: 38 mg (47%); mp 136–137 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.50 (d, *J* = 3.5 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.86–7.79 (m, 2 H), 7.71 (t, *J* = 7.5 Hz, 2 H), 7.46 (t, *J* = 7.0 Hz, 1 H), 7.41 (t, *J* = 7.5 Hz, 1 H), 7.32 (d, *J* = 15.5 Hz, 1 H), 7.29–7.20 (m, 4 H), 2.44 (s, 3 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.00, 149.57, 142.97, 137.91, 137.60, 136.04, 135.94, 131.28, 130.41, 130.30, 128.31, 128.07, 126.33, 126.23, 125.95, 125.30, 125.08, 124.47, 119.16, 19.91.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{18}NOS^+$: 320.1104; found: 320.1105.

(*E*)-2-((2-(4-Chlorostyryl)phenyl)sulfinyl)pyridine (3af)

Yellow solid; yield: 53 mg (62%); mp 124–125 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.48 (d, *J* = 4.0 Hz, 1 H), 8.03 (d, *J* = 8.0 Hz, 1 H), 7.95–7.89 (m, 2 H), 7.85 (t, *J* = 7.0 Hz, 1 H), 7.69 (d, *J* = 7.5 Hz, 1 H), 7.51 (d, *J* = 8.5 Hz, 2 H), 7.47–7.40 (m, 2 H), 7.37 (d, *J* = 8.5 Hz, 2 H), 7.27–7.25 (m, 1 H), 7.01 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 165.90, 149.54, 141.93, 137.97, 136.82, 135.35, 133.81, 131.34, 130.69, 128.91, 128.54, 128.13, 125.90, 125.19, 124.55, 119.13.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{15}ClNOS^+$: 340.0557; found: 340.0555.

(*E*)-2-((2-(3-Chlorostyryl)phenyl)sulfinyl)pyridine (3ag)

Yellow solid; yield: 43 mg (50%); mp 89–90 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.50 (d, *J* = 5.0 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 1 H), 7.95 (d, *J* = 16.5 Hz, 1 H), 7.90 (d, *J* = 7.5 Hz, 1 H), 7.86 (t, *J* = 8.0 Hz, 1 H), 7.68 (d, *J* = 7.5 Hz, 1 H), 7.55 (s, 1 H), 7.47–7.41 (m, 3 H), 7.33 (t, *J* = 7.5 Hz, 1 H), 7.29–7.26 (m, 2 H), 6.99 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 165.89, 149.58, 142.11, 138.76, 137.98, 136.66, 134.67, 131.35, 130.57, 129.94, 128.71, 128.05, 126.92, 126.02, 125.46, 125.23, 125.05, 124.57, 119.14.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{15}ClNOS^+$: 340.0557; found: 340.0556.

(*E*)-2-((2-(2-Chlorostyryl)phenyl)sulfinyl)pyridine (3ah)

Yellow solid; yield: 26 mg (30%); mp 123–124 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.49 (d, *J* = 4.0 Hz, 1 H), 8.02 (d, *J* = 8.0 Hz, 1 H), 7.95–7.91 (m, 2 H), 7.86–7.84 (m, 2 H), 7.76 (d, *J* = 7.0 Hz, 1 H), 7.49–7.40 (m, 4 H), 7.34 (t, *J* = 7.0 Hz, 1 H), 7.28–7.24 (m, 2 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.01, 149.67, 142.19, 138.08, 136.98, 135.10, 133.73, 131.50, 129.88, 129.19, 128.85, 128.10, 127.20 (2 C), 126.62, 126.47, 125.12, 124.67, 119.21.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{15}ClNOS^+$: 340.0557; found: 340.0556.

(*E*)-2-((2-([1,1′-Biphenyl]-4-yl)vinyl)phenyl)sulfinyl)pyridine (3ai)

Yellow solid; yield: 14 mg (14%); mp 157–158 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.51 (d, *J* = 4.0 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 1 H), 8.00 (d, *J* = 16.0 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.85 (t, *J* = 7.5 Hz, 1 H), 7.73 (d, *J* = 7.5 Hz, 1 H), 7.68–7.64 (m, 6 H), 7.49–7.36 (m, 5 H), 7.28–7.25 (m, 1 H), 7.12 (d, *J* = 16.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 165.95, 149.61, 141.85, 140.90, 140.51, 137.95, 137.17, 135.90, 131.59, 131.32, 128.83, 128.36, 127.45, 127.44, 127.40, 126.93, 125.89, 125.17, 124.55, 123.91, 119.20.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{20}NOS^+$: 382.1260; found: 382.1261.

Isobutyl (*E*)-3-(2-(Pyridin-2-ylsulfinyl)phenyl)acrylate (5ac)

Yellow oil; yield: 70 mg (85%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.53–8.47 (m, 2 H), 8.06 (d, *J* = 8.0 Hz, 1 H), 7.92–7.86 (m, 2 H), 7.66 (d, *J* = 7.5 Hz, 1 H), 7.51–7.45 (m, 2 H), 7.28–7.26 (m, 1 H), 6.54 (d, *J* = 16.0 Hz, 1 H), 4.07–4.00 (m, 2 H), 2.08–2.0 (m, 1 H), 1.01 (d, *J* = 7.0 Hz, 6 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.25, 165.36, 149.75, 143.69, 139.61, 137.95, 134.19, 131.35, 130.64, 126.90, 125.28, 124.50, 121.53, 118.98, 70.78, 27.78, 19.08.

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{20}NO_3S^+$: 330.1158; found: 330.1157.

Ethyl (*E*)-3-(5-Methyl-2-(pyridin-2-ylsulfinyl)phenyl)acrylate (5bb)

Yellow liquid; yield: 66 mg (84%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.47–8.42 (m, 2 H), 8.05 (d, *J* = 8.0 Hz, 1 H), 7.86 (t, *J* = 7.5 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.44 (s, 1 H), 7.29–7.24 (m, 2 H), 6.41 (d, *J* = 16.0 Hz, 1 H), 4.28 (q, *J* = 7.0 Hz, 2 H), 2.36 (s, 3 H), 1.35 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.35, 165.65, 149.92, 142.07, 140.80, 139.84, 138.00, 134.34, 131.66, 127.67, 125.92, 124.51, 121.57, 119.18, 60.77, 21.48, 14.10.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{18}NO_3S^+$: 316.1002; found: 316.1003.

Methyl (*E*)-3-(5-*tert*-Butyl-2-(pyridin-2-ylsulfinyl)phenyl)acrylate (5ca)

Yellow solid; yield: 38 mg (45%); mp 144–145 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.51–8.47 (m, 2 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 7.89 (t, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.63 (s, 1 H), 7.51 (d, *J* = 8.5 Hz, 1 H), 7.28–7.26 (m, 1 H), 6.47 (d, *J* = 16.0 Hz, 1 H), 3.85 (s, 3 H), 1.31 (s, 9 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.74, 165.57, 154.97, 149.81, 140.75, 140.52, 137.91, 133.91, 128.29, 125.58, 124.41, 124.01, 120.97, 119.09, 51.89, 35.02, 31.00.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{22}NO_3S^+$: 344.1315; found: 344.1310.

Ethyl (*E*)-3-(5-*tert*-Butyl-2-(pyridin-2-ylsulfinyl)phenyl)acrylate (5cb)

Brown solid; yield: 47 mg (54%); mp 107–108 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.51–8.46 (m, 2 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 7.88 (t, *J* = 6.5 Hz, 1 H), 7.77 (d, *J* = 8.5 Hz, 1 H), 7.63 (s, 1 H), 7.51 (dd, *J* = 8.5, 2.0 Hz, 1 H), 7.29–7.26 (m, 1 H), 6.45 (d, *J* = 16.0 Hz, 1 H), 4.31 (q, *J* = 7.5 Hz, 2 H), 1.37 (t, *J* = 7.5 Hz, 3 H), 1.31 (s, 9 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.30, 165.52, 154.97, 149.82, 140.66, 140.25, 137.88, 133.98, 128.21, 125.69, 124.40, 124.01, 121.39, 119.16, 60.70, 35.01, 31.01, 14.32.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{24}NO_3S^+$: 358.1471; found: 358.1466.

Ethyl (*E*)-3-(3-(Pyridin-2-ylsulfinyl)naphthalen-2-yl)acrylate (5db) and Ethyl (*E*)-3-(2-(Pyridin-2-ylsulfinyl)naphthalen-1-yl)acrylate (5db′)

Brown solid; yield: 66 mg (75%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.55–8.43 (m, 4 H), 8.21 (d, *J* = 8.0 Hz, 1 H), 8.14–8.09 (m, 3 H), 7.96–7.86 (m, 6 H), 7.76 (d, *J* = 9.0 Hz, 1 H), 7.62–7.57 (m, 4 H), 7.30–7.25 (m, 3 H), 6.85 (d, *J* = 16.0 Hz, 1 H) (**5db′**), 6.48 (d, *J* = 15.0 Hz, 1 H) (**5db**), 4.40–4.30 (m, 4 H), 1.42–1.37 (m, 6 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.25, 165.88 (3 C), 165.32, 149.97, 149.84, 149.74, 149.61, 140.72, 140.41, 138.70, 138.00, 134.66, 134.22, 134.12 (2 C), 133.22 (2 C), 130.94, 130.74, 129.75, 129.67, 128.66, 128.64, 128.62, 128.29, 127.56, 127.43, 127.02, 126.81, 124.47, 121.30, 121.23, 119.53, 119.38, 60.96, 60.67, 14.39, 14.29.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{18}NO_3S^+$: 352.1002; found: 352.0997.

Methyl (*E*)-3-(4-Chloro-2-(pyridin-2-ylsulfinyl)phenyl)acrylate (5ea)

White solid; yield: 17 mg (21%); mp 144–145 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.49 (d, *J* = 4.0 Hz, 1 H), 8.42 (d, *J* = 16.0 Hz, 1 H), 8.05 (d, *J* = 8.0 Hz, 1 H), 7.93–7.89 (m, 2 H), 7.59 (d, *J* = 8.5 Hz, 1 H), 7.41 (dd, *J* = 8.5, 2.0 Hz, 1 H), 7.32–7.30 (m, 1 H), 6.45 (d, *J* = 15.5 Hz, 1 H), 3.85 (s, 3 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.52, 165.10, 149.91, 145.68, 138.98, 138.25, 137.18, 132.44, 131.63, 128.21, 124.94, 124.80, 121.39, 118.97, 52.00.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}ClNO_3S^+$: 322.0299; found: 322.0298.

Methyl (*E*)-3-(2-Chloro-6-(pyridin-2-ylsulfinyl)phenyl)acrylate (5ea′)

Brown solid; yield: 23 mg (29%); mp 104–105 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.52 (d, *J* = 4.0 Hz, 1 H), 8.10 (d, *J* = 8.0 Hz, 1 H), 7.99–7.92 (m, 2 H), 7.76 (d, *J* = 7.5 Hz, 1 H), 7.51 (d, *J* = 7.0 Hz, 1 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.34–7.31 (m, 1 H), 6.84 (d, *J* = 16.0 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.17, 165.66, 149.84, 146.27, 138.20, 137.64, 134.33, 133.99, 132.31, 130.31, 128.63, 124.64, 124.42, 119.32, 52.03.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{13}ClNO_3S^+$: 322.0299; found: 322.0293.

Ethyl (*E*)-3-(4-Chloro-2-(pyridin-2-ylsulfinyl)phenyl)acrylate (5eb)

Yellow solid; yield: 22 mg (26%); mp 107–108 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.50 (d, *J* = 4.5 Hz, 1 H), 8.41 (d, *J* = 15.5 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 1 H), 7.92–7.89 (m, 2 H), 7.59 (d, *J* = 8.5 Hz, 1 H), 7.41 (d, *J* = 8.5 Hz, 1 H), 7.32–7.29 (m, 1 H), 6.43 (d, *J* = 15.5 Hz, 1 H), 4.31 (q, *J* = 7.0 Hz, 2 H), 1.36 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.07, 164.97, 149.91, 145.62, 138.69, 138.22, 137.07, 132.51, 131.62, 128.19, 124.97, 124.79, 121.85, 119.00, 60.84, 14.29.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}ClNO_3S^+$: 336.0456; found: 336.0446.

Ethyl (*E*)-3-(2-Chloro-6-(pyridin-2-ylsulfinyl)phenyl)acrylate (5eb′)

Brown solid; yield: 21 mg (25%); mp 79–80 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.52 (d, *J* = 3.5 Hz, 1 H), 8.09 (d, *J* = 8.0 Hz, 1 H), 7.98–7.90 (m, 2 H), 7.76 (d, *J* = 7.5 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 7.33–7.30 (m, 1 H), 6.79 (d, *J* = 16.0 Hz, 1 H), 4.31 (q, *J* = 5.5 Hz, 2 H), 1.37 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 165.74, 165.60, 149.86, 146.20, 138.15, 137.34, 134.32, 134.04, 132.33, 130.23, 129.00, 124.64, 124.44, 119.39, 60.93, 14.27.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}ClNO_3S^+$: 336.0456; found: 336.0446.

Palladacycle 6

Yellow solid; yield: 655 mg (60%); mp 191–192 °C (dec).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.19 (bd, *J* = 5.5 Hz, 1 H), 8.27 (bd, *J* = 5.5 Hz, 1 H), 8.08 (bt, *J* = 9.0 Hz, 1 H), 8.02 (bd, *J* = 9.0 Hz, 1 H), 7.92 (bt, *J* = 9.0 Hz, 1 H), 7.77 (bd, *J* = 10.5 Hz, 1 H), 7.67 (bs, 1 H), 7.57 (bt, *J* = 6.5 Hz, 1 H), 7.39 (bd, *J* = 9.0 Hz, 1 H), 7.26–7.22 (m, 3 H), 7.03 (bt, *J* = 7.5 Hz, 1 H), 6.71 (bt, *J* = 6.5 Hz, 1 H), 6.34 (bt, *J* = 8.0 Hz, 1 H), 6.12 (bs, *J* = 9.0 Hz, 1 H), 2.90 (bd, *J* = 7.5 Hz, 6 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 182.43, 182.00, 165.70, 165.43, 153.95, 152.67, 142.76, 142.50, 140.00, 139.91, 135.49, 135.17, 134.70, 134.30, 129.00, 128.90, 126.00, 125.60, 125.46, 124.47, 122.21, 122.12, 121.92, 121.65, 24.36 (2 C).

Methyl (*E*)-3-(2-(Pyridin-2-ylsulfonyl)phenyl)acrylate (9)

White solid; yield: 70 mg (92%); mp 141–142 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.62 (d, *J* = 6 Hz, 1 H), 8.42 (d, *J* = 20 Hz, 1 H), 8.36 (d, *J* = 9.5 Hz, 1 H), 8.31 (d, *J* = 10 Hz, 1 H), 7.96 (t, *J* = 10 Hz, 1 H), 7.65–7.59 (m, 3 H), 7.48–7.45 (m, 1 H), 6.15 (d, *J* = 20.0 Hz, 1 H), 3.79 (s, 3 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.20, 158.61, 150.37, 140.95, 137.97, 137.19, 134.97, 134.18, 130.78, 129.92, 128.49, 127.12, 122.58, 122.37, 51.91.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{14}NO_4S^+$: 304.0638; found: 304.0630.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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(19) The structures of regioisomers were assigned by analogy to compounds reported in the literature; see ref. 16b.

(20) Pd complex **6** has been synthesized in DCE and the structure unambiguously determined by X-ray analysis; see ref. 11b. Pd complex **6** synthesized in DCE and DMF showed identical peaks in the ^{1}H NMR spectra (see the Supporting Information).

(21) One of the referees suggested the use of 1–2 equivalents of D_2O instead of 10 equivalents of D_2O as it is too much for the reaction. However, no deuterium incorporation was found even with 2 equivalents of D_2O. Secondly, to avoid any interference of D_2O in the palladation step, a similar reaction was performed without D_2O and finally the reaction quenched with D_2O to capture deuterated product. But, the ^{1}H NMR data showed that no deuterated product was formed.

