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Palladium-Catalyzed Coupling of Arene C−H Bonds with Methyl- and Arylboron Reagents Assisted by the Removable 2-Pyridylsulfinyl Group

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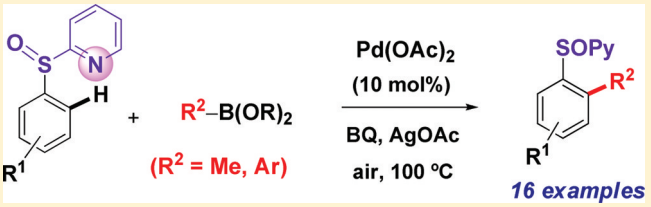
Supporting Information

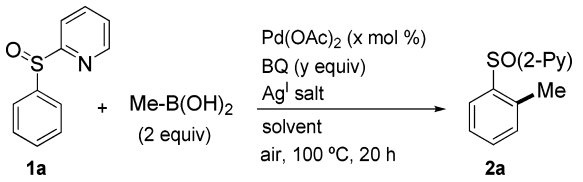
ABSTRACT: The Pd^{II}-catalyzed direct coupling of arene C−H bonds with organoboron reagents assisted by the 2-pyridylsulfinyl group is reported. Methylboronic acid and arylboronic acid neopentyl esters proved to be efficient coupling partners, furnishing methylated arenes and biaryl products in moderate to good yields. The 2-pyridylsulfinyl group can be easily removed to provide the free biaryls. The essential role of the 2-pyridyl unit in stabilizing the cyclopalladation complex was demonstrated by X-ray diffraction analysis of the palladacycle intermediate.



The Suzuki−Miyaura cross-coupling reaction is one of the most powerful and reliable tools for C−C bond construction for the synthesis of complex products.[1] In recent years, extensive efforts have been devoted to develop transition-metal-catalyzed direct coupling of arene C−H bonds with organoboron reagents. In comparison with the oxidative addition of a low-valent transition-metal complex to Ar-X (X = halide or pseudohalide), this strategy offers a more atom economical and environmentally benign alternative route to Ar-M (M = metal) intermediates.[2−13] Consequently, this Pd^{II}-catalyzed oxidative cross-coupling nicely complements the Pd^{0}-catalyzed direct C−H functionalization with aryl or alkyl halides/pseudohalides.[3] As in the majority of examples of C−H functionalization, a directing group has been mostly applied as a means of tuning the reactivity and achieving regiocontrol in the metal-catalyzed C−H coupling with organoboron reagents. Thus, a 2-pyridyl unit,[4] imines,[5] oxymes,[6] carboxylic acids,[7] and *N*-acetyl[8] or *N*-carbamoyl[9] anilines have been successfully used for this purpose under Pd catalysis, whereas a ketone directing group proved to be efficient under Ru catalysis.[10−13] However, despite their versatility, frequently these directing groups are not easily removed from the resulting products, thus compromising the generality of the reaction. Therefore, the development of novel directing groups, not only chemically versatile but also readily attachable and removable, is highly desirable. Recently, we[14] and others[15] have described the use of the 2-pyridyl sulfoxide as a chemically versatile and removable directing group in Pd^{II}-catalyzed C−H functionalization.[16] Herein, we report the extension of this concept to the oxidative cross-coupling of arenes with organoboron reagents.

The model reaction of phenyl 2-pyridyl sufoxide (**1a**) with methyl boronic acid (2 equiv) under a stoichiometric amount of $Pd(OAc)_2$ (1 equiv) in 1,2-dichloroethane (DCE) at 100 °C under aerobic conditions (air atmosphere) led us to find the key role of *p*-benzoquinone (BQ), likely for promoting the reductive elimination step as previously pointed out in seminal reports.[4b,17] As shown in Table 1, while the methylated product **2a** was not formed in the absence of BQ (entry 1), complete conversion was observed in the presence of BQ (1 equiv,

Table 1. Optimization of the Reaction Parameters



entry	*x*/*y*	Ag^{I} (equiv)	solvent	conv[a] (%)
1	100/0		DCE	0
2	100/1		DCE	>98
3	10/1	Ag_2O (2)	DCE	25
4	10/1	Ag_2O (2)	toluene	16
5	10/1	Ag_2O (2)	DMF	10
6	10/1	Ag_2O (2)	THF	47
7	10/1	Ag_2O (2)	AcOEt	54
8	10/1	Ag_2O (2)	*t*-AmOH	67
9	10/0.5	AgOAc (2)	*t*-AmOH	82
10	10/0.2	AgOAc (2)	*t*-AmOH	73
11	5/0.5	AgOAc (2)	*t*-AmOH	68
12	**10/0.5**	**AgOAc (3)**	***t*-AmOH**	**91** (74)[b]

[a]Conversion determined by ^{1}H NMR and/or GC. [b]Isolated yield.

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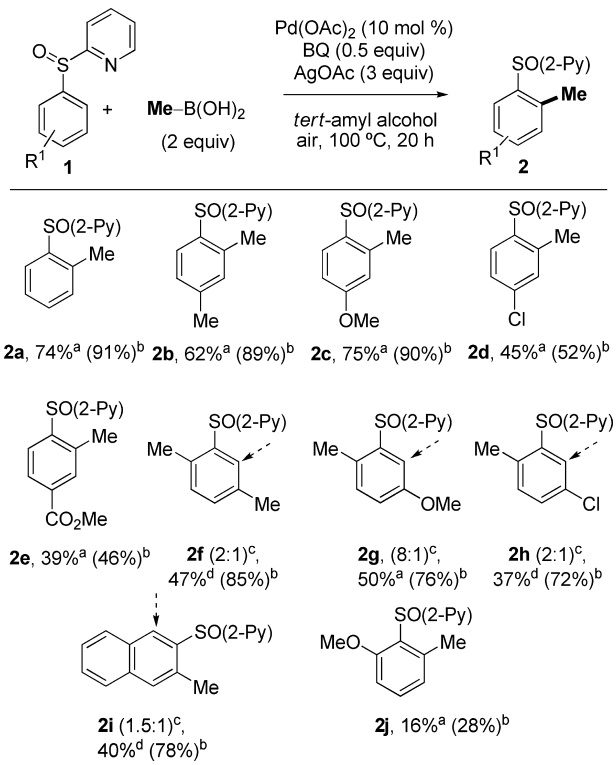
entry 2). To achieve effective catalytic turnover we focused on the choice of the optimal oxidant/base combination to facilitate transmetalation/catalyst regeneration. In this regard, Ag_2O has been reported to induce Suzuki–Miyaura cross-coupling, presumably by accelerating the B-to-Pd transfer step.[18] The model reaction using catalytic $Pd(OAc)_2$ (10 mol %) in the presence of BQ (1 equiv) and Ag_2O (2 equiv) in DCE at 100 °C for 20 h under air gave the methylated product **2a** in 25% conversion (entry 3). Screening of solvents (entries 4–8) allowed an increase in the conversion value to 67% using *tert*-amyl alcohol. Then, several silver salts were tested in our reaction system, among which AgOAc was found to be the most efficient, providing **2a** with 82% conversion and allowing the use of substoichiometric amount of BQ (0.5 equiv, entry 9). A further decrease of the amount of BQ (entry 10) or reducing the Pd-catalyst loading to 5 mol % (entry 11) led to lower conversions, whereas increasing to 3 equiv the amount of AgOAc provided the highest conversion (91%, 74% isolated yield of **2a**, entry 12).[19] The silver salt may work as both co-oxidant and base (promoter for transmetalation).[4b]

With the optimized reaction conditions in hand, the substrate scope with regard to the arene was examined. As in the model reaction, the conversions were never complete, and traces of dimethylated product were detected for some substrates. As shown in Table 2, this C–H alkylation process was amenable to

Table 2. Pd^{II}-Catalyzed C–H Methylation of Aryl 2-Pyridyl Sulfoxides with Methylboronic Acid



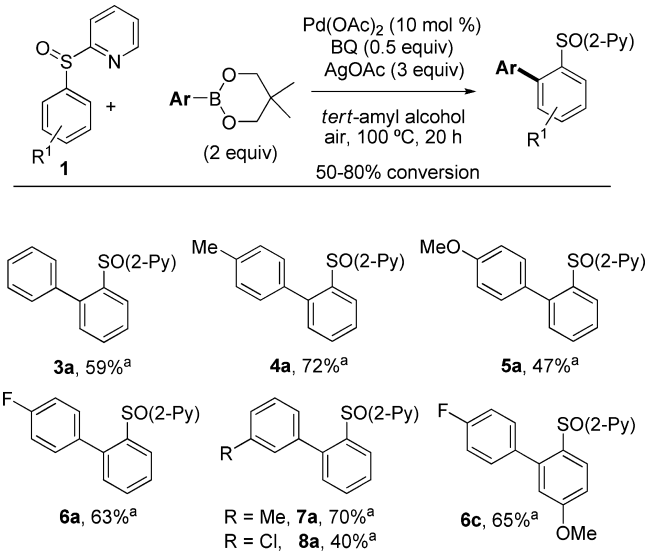
[a]Isolated yield. [b]Conversion determined by ^1H NMR. [c]Regioisomer methylation ratio. [d]Isolated yield of the major regioisomer.

different aryl 2-pyridyl sufoxides, yet the reaction was found to be deeply impacted by the electronic and steric effects of the substituents on the aryl sulfoxide. Thus, while electron-donating groups at the *para*-position had no influence on the methylation reaction (products **2b** and **2c**, 62% and 75% yield, respectively), electron-deficient groups at the *para*-position had a deleterious effect on the yield (products **2d** and **2e**, 45% and 39% yield, respectively). Acceptable yields for the major regioisomer (37–47%) but poor regioselectivity (1.5:1–2:1) in favor of the less hindered C–H bond were obtained with *meta*-substituted substrates (products **2f**, **2h**, and **2i**), except for the case of a *m*-methoxy substituent that induced a high regiocontrol (8:1) (product **2g**). Substituents at the *ortho*-position of the sulfoxide significantly compromised the reaction (product **2j**, 16% yield), indicating that the reaction is very sensitive to steric effects.

Unfortunately, the use of butylboronic acid as the coupling partner in the reaction with **1a** under various conditions failed to provide the desired alkylation product in practical yields (a maximum of 36% conversion was achieved using 2,2,5,5-tetramethyl-THF as solvent to minimize β-hydride elimination).[13a]

Driven by the wide range significance of biaryl systems as structural units in biologically active molecules and functional materials,[20] we sought to extend this coupling reaction to arylboronic acids. Unfortunately, the reaction of **1a** with phenylboronic acid (2 equiv) under the standard reaction conditions failed to provide the desired product. Only homocoupling of the organometallic reagent was observed, indicating that this undesired reaction is faster than the C–H activation process. To solve this problem, we tested other phenyl boron reagents such as potassium phenyltrifluoroborate and the pinacol or neopentyl phenylboronate esters under the optimized reaction conditions. Among them, the phenylboronic acid neopentyl ester provided the best result, affording the corresponding biphenyl sulfoxide **3a** in 79% conversion (59% isolated yield, Table 3).

Table 3. Pd^{II}-Catalyzed C–H Arylation of Aryl 2-Pyridyl Sulfoxides with Arylboronates



[a]Isolated yield.

The study of the scope of this reaction with regard to the organoboron reagent is shown in Table 3. In all these reactions, complete selectivity was observed, but full conversions were not achieved (50–80% conversion). The reaction was found to be marginally affected by the electronic effect of the substituents on the arylboronate, tolerating both electron-donating groups

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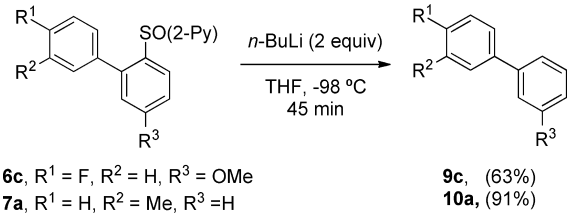
(products **4a**, **5a**, **7a**, 47−72% isolated yield) and electron-withdrawing groups (**6a**, **8a**, 40−63% isolated yield) at the *para*- or *meta*-positions. This biaryl coupling methodology allowed for the efficient coupling of two electronically dissimilar aromatic partners, as exemplified in the synthesis of **6c** (65% yield). In contrast, *ortho*-substituents at the boronate ester were not tolerated under the reaction conditions and completely suppressed the cross-coupling.[21]

Finally, to demostrate the synthetic potencial of this methodology, the 2-pyridylsulfinyl directing group was easily removed by sulfoxide/lithium exchange with *n*-BuLi in THF at −98 °C to provide the free corresponding biaryl products (Scheme 1).[14a,15,22]

Scheme 1. Removal of the 2-Pyridylsulfinyl Group

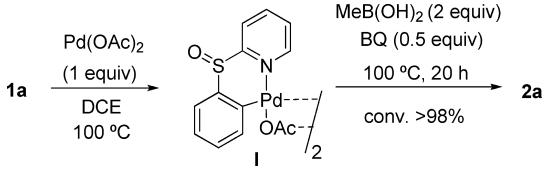


6c, R^1 = F, R^2 = H, R^3 = OMe
7a, R^1 = H, R^2 = Me, R^3 =H

9c, (63%)
10a, (91%)

To further understand this transformation, we carried out some mechanistic studies. First, treatment of **1a** with $Pd(OAc)_2$ (1 equiv) in DCE at 100 °C for 1 h led to the quantitative formation of the six-membered cyclopalladated complex **I**, which was isolated as an air stable solid (Scheme 2). X-ray

Scheme 2. Cyclopalladation and Methylation of 1a



diffraction analysis of suitable crystals established the acetate-bridged dimer structure of complex **I**, in which the Pd^{II} atom coordinates to the pyridyl nitrogen of the directing group, proving the directing ability of the 2-pyridylsulfinyl group in C−H functionalization reactions (see the Supporting Information). Complex **I** underwent methylation upon treatment with $MeB(OH)_2$ in DCE at 100 °C[23] to give full conversion to the *ortho*-methylated product **2a** in the presence of BQ.

Competitive experiments with electronically varied aryl 2-pyridyl sulfoxides in the reaction with methylboronic acid revealed higher reactivity of electron-rich arenes (Scheme 3a, **2d**/**2c**, k_{Cl}/k_{OMe} = 0.19). On the other hand, a very low intramolecular kinetic isotope effect was observed using 2-deuteriophenyl 2-pyridyl sulfoxide **1a-D** in the *ortho*-methylation with $MeB(OH)_2$ (Scheme 3b). These preliminary studies suggest as the most likely reaction mechanism the initial electrophilic C−H palladation of the arene with the assistance of the 2-pyridylsulfinyl group, followed by transmetalation of the boron reagent and subsequent reductive elimination to give the methylated or arylated product.

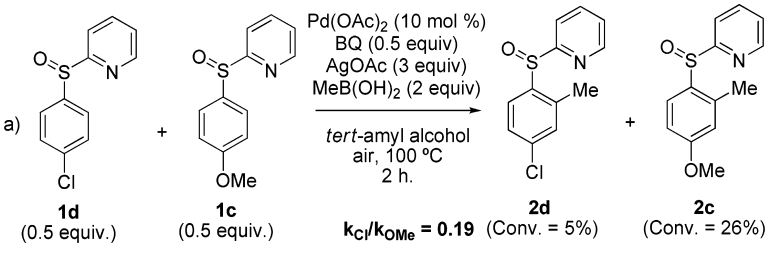
In conclusion, we have developed a Pd^{II}-catalyzed *ortho* C−H methylation and arylation with organoboron reagents directed by the removable 2-pyridylsulfinyl group. The origin of the directing ability of the 2-pyridylsulfinyl group has been attributed to the participation of the pyridinic nitrogen in the stabilization of the Pd^{II}-cyclopalladation intermediate complex, which has been evidenced by X-ray crystallographic study.

EXPERIMENTAL SECTION

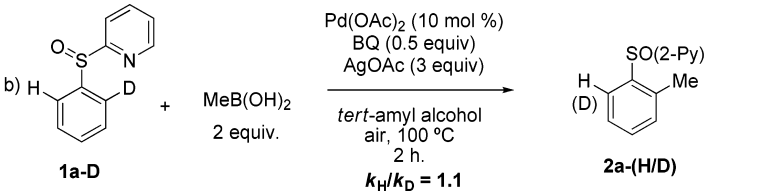
General Information. Chromatography: silica gel (230−400 mesh). TLC: silica gel (0.25 mm). Visualization of the chromatograms was performed by UV lamp and phosphomolybdic acid or potassium permanganate or Seebach's "magic" staining [a mixture of phosphomolybdic acid (25 g), cerium(IV) sulfate (7.5 g), H_2O (500 mL), and H_2SO_4 (25 mL)]. Mass spectra were recorded on a GC/EI or ESI (LC/MSD TOF by electrospray ionization time-of-flight) mass spectrometers. Progress and conversion of the reaction were determined by ^1H NMR (300 MHz) and GC. ^1H and ^{13}C NMR were recorded with ^1H at 300 MHz and ^{13}C at 75.4 MHz, respectively, using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^1H, δ 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Melting points were recorded on a melting point apparatus and are uncorrected. 2-Pyridyl aryl sulfoxides (**1a**−**j**)[14a] and boronic acid neopentyl esters[24] were synthesized following procedures described in the literature. *p*-Benzoquinone was purified by sublimation before use.

General Procedure for the Palladium(II)-Catalyzed C−H Activation/Suzuki−Miyaura-Type Coupling. In a screw-capped tube, the corresponding aryl 2-pyridyl sulfoxide (0.25 mmol), boronic

Scheme 3. Intermolecular Competition Experiment and Intramolecular Kinetic Isotopic Effect Studies



1d (0.5 equiv.) **1c** (0.5 equiv.) k_{Cl}/k_{OMe} = 0.19 **2d** (Conv. = 5%) **2c** (Conv. = 26%)



1a-D **2a-(H/D)**

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acid derivative (0.5 mmol, 2 equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 10 mol %), *p*-benzoquinone (13.5 mg, 0.125 mmol, 0.5 equiv), and AgOAc (125.2 mg, 0.75 mmol, 3 equiv) were dissolved in *tert*-amyl alcohol (2.5 mL) under atmospheric air. The reaction mixture was stirred at 100 °C for 20 h before it was allowed to reach room temperature. The mixture was filtered through a pad of Celite (washed with EtOAc), and the filtrate was concentrated under reduced pressure. The conversion was determined by ^{1}H NMR of the crude mixture before it was purified by flash column chromatography to give the desired product.[25]

2-[(2-Methylphenyl)sulfinyl]pyridine (2a).[14a] Compound **2a** was obtained from 2-(phenylsulfinyl)pyridine and methylboronic acid following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a white solid (yield 74%). Analytical data are in accordance with those from the literature.[14a] ^{1}H NMR δ: 8.51 (d, J = 4.3 Hz, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.88 (td, J = 7.8, 1.7 Hz, 1H), 7.83−7.71 (m, 1H), 7.38−7.16 (m, 4H), 1.53 (s, 3H).

2-[(2,4-Dimethylphenyl)sulfinyl]pyridine (2b). Compound **2b** was obtained from 2-(*p*-tolylsulfinyl)pyridine and methylboronic acid following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a white solid (yield 62%). Mp: 56−58 °C. ^{1}H NMR δ: 8.42 (ddd, J = 4.7, 1.7, 0.8 Hz, 1H), 7.97 (dt, J = 7.9, 1.0 Hz, 1H), 7.79 (td, J = 7.8, 1.8 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.19 (ddd, J = 7.5, 4.7, 1.2 Hz, 1H), 7.02 (d, J = 8.6 Hz, 1H), 6.95 (s, 1H), 2.54 (s, 3H), 2.23 (s, 3H). ^{13}C NMR δ: 166.5, 149.6, 141.5, 139.7, 137.9, 137.4, 131.7, 127.7, 124.9, 124.3, 119.0, 21.2, 19.2. MS (ESI) m/z: 126 (M^+ − 105), 232 (M^+ + H) (100), 254 (M^+ + Na), 485 ($2M^+$ + Na). HRMS: calcd for $C_{13}H_{14}NOS$ (M^+ + H) 232.0790, found 232.0784.

2-[(4-Methoxy-2-methylphenyl)sulfinyl]pyridine (2c). Compound **2c** was obtained from 2-[(4-methoxyphenyl)sulfinyl]pyridine and methylboronic acid following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a white solid (yield 75%). Mp: 85−87 °C. ^{1}H NMR δ: 8.43 (ddd, J = 4.7, 1.7, 0.8, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.81 (td, J = 7.7, 1.7 Hz, 1H), 7.55 (d, J = 8.7 Hz, 1H), 7.21 (ddd, J = 7.5, 4.7, 1.2 Hz, 1H), 6.73 (dd, J = 8.7, 2.6 Hz, 1H), 6.65 (d, J = 2.5 Hz, 1H), 3.72 (s, 3H), 2.56 (s, 3H). ^{13}C NMR δ: 166.5, 161.8, 149.6, 139.8, 137.9, 134.2, 127.3, 124.3, 119.0, 116.2, 112.6, 55.3, 19.4. MS (ESI) m/z: 122 (M^+ − 126) (100), 248 (M^+ + H), 270 (M^+ + Na), 571 ($2M^+$ + Na). HRMS: calcd for $C_{13}H_{14}NO_2S$ (M^+ + H) 248.0739, found 248.0742.

2-[(4-Chloro-2-methylphenyl)sulfinyl]pyridine (2d). Compound **2d** was obtained from 2-[(4-chlorophenyl)sulfinyl]pyridine and methylboronic acid following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a white solid (yield 45%). Mp: 76−78 °C. ^{1}H NMR δ: 8.49 (ddd, J = 4.7, 1.7, 0.9 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.89 (td, J = 7.7, 1.8 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.33−7.25 (m, 2H), 7.21 (d, J = 1.7 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR δ: 166.2, 149.7, 141.6, 139.3, 138.2, 137.1, 130.8, 127.2, 126.0, 124.6, 118.9, 19.3. MS (ESI) m/z: 126 (M^+ − 125), 252 (M^+ + H) (100), 274 (M^+ + Na), 527 ($2M^+$ + Na). HRMS: calcd for $C_{12}H_{11}ClNOS$ (M^+ + H) 252.0244, found 252.0241.

Methyl 3-Methyl-4-[(2-pyridyl)sulfinyl]benzoate (2e). Compound **2e** was obtained from methyl 4-[(2-pyridyl)sulfinyl]benzoate and methylboronic acid following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a white solid (yield 39%). Mp: 118−120 °C. ^{1}H NMR δ: 8.49 (ddd, J = 4.7, 1.7, 0.9 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.90−7.60 (m, 4H), 7.22 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 3.85 (s, 3H), 2.65 (s, 3H). ^{13}C NMR δ: 166.2, 166.0, 149.6, 147.9, 138.2, 137.5, 132.3, 132.0, 127.8, 124.7, 124.3, 119.0, 52.3, 19.4. MS (ESI) m/z: 276 (M^+ + H) (100), 298 (M^+ + Na), 573 ($2M^+$ + Na). HRMS: calcd for $C_{14}H_{14}NO_3S$ (M^+ + H) 276.0688, found 276.0699.

2-[(2,6-Dimethylphenyl)sulfinyl]pyridine (2f). Compound **2f** was obtained from 2-(*m*-tolylsulfinyl)pyridine and methylboronic acid following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a white solid (yield 47%). Mp: 72−74 °C. ^{1}H NMR δ: 8.53 (ddd, J = 4.7, 1.7, 0.8 Hz, 1H), 8.06 (d, J = 7.9 Hz, 1H), 7.90 (td, J = 7.7, 1.7 Hz, 1H), 7.60 (s, 1H), 7.30 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 7.19−7.06 (m, 2H), 2.64 (s, 3H), 2.33 (s, 3H). ^{13}C NMR δ: 166.5, 149.6, 142.4, 138.0, 136.8, 134.4, 131.9, 130.9, 124.6, 124.4, 119.0, 20.9, 18.9. MS (ESI) m/z: 232 (M^+ + H) (100), 254 (M^+ + Na), 485 ($2M^+$ + Na). HRMS: calcd for $C_{13}H_{14}NOS$ (M^+ + H) 232.0790, found 232.0789.

2-[(5-Methoxy-2-methylphenyl)sulfinyl]pyridine (2g). Compound **2g** was obtained from 2-[(3-methoxyphenyl)sulfinyl]pyridine and methylboronic acid following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a mixture 8:1 of regioisomers in favor of **2g** (yield 50%). ^{1}H NMR δ: 8.44 (ddd, J = 4.7, 1.7, 0.8 Hz, 1H), 7.93 (dd, J = 7.9, 0.8 Hz, 1H), 7.79 (td, J = 7.7, 1.8 Hz, 1H), 7.27 (d, J = 2.8 Hz, 1H), 7.24−7.18 (m, 1H), 7.04 (d, J = 8.4 Hz, 1H), 6.79 (dd, J = 8.4, 2.8 Hz, 1H), 3.71 (s, 3H), 2.50 (s, 3H). ^{13}C NMR δ: 166.4, 158.6, 149.6, 143.5, 138.0, 132.0, 129.2, 124.6, 118.9, 117.9, 108.2, 55.5, 18.4. MS (ESI) m/z: 248 (M^+ + H) (100), 270 (M^+ + Na), 517 ($2M^+$ + Na). HRMS: calcd for $C_{13}H_{14}NO_2S$ (M^+ + H) 248.0739, found 248.0741.

2-[(5-Chloro-2-methylphenyl)sulfinyl]pyridine (2h). Compound **2h** was obtained from 2-[(3-chlorophenyl)sulfinyl]pyridine and methylboronic acid following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a yellow solid (yield 37%). Mp: 114−116 °C. ^{1}H NMR δ: 8.43 (d, J = 4.7 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.83 (td, J = 7.7, 1.8 Hz, 1H), 7.69 (d, J = 2.2 Hz, 1H), 7.32−7.13 (m, 2H), 7.07 (d, J = 8.2 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR δ: 166.0, 149.6, 144.8, 138.3, 135.7, 133.0, 132.3, 131.1, 124.8, 124.1, 118.9, 19.0. MS (ESI) m/z: 252 (M^+ + H) (100), 274 (M^+ + Na), 525 ($2M^+$ + Na). HRMS: calcd for $C_{12}H_{11}ClNOS$ (M^+ + H) 252.0244, found 252.0251.

2-(3-Methylnaphthalene-2-ylsulfinyl)pyridine (2i). Compound **2i** was obtained from 2-(naphthalen-2-ylsulfinyl)pyridine and methylboronic acid following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a white solid (yield 40%). Mp: 172−174 °C. ^{1}H NMR δ: 8.49 (dd, J = 4.7, 0.8 Hz, 1H), 8.39 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.92−7.81 (m, 2H), 7.75 (d, J = 7.9 Hz, 1H), 7.63 (s, 1H), 7.54−7.41 (m, 2H), 7.30−7.23 (m, 1H), 2.74 (s, 3H). ^{13}C NMR δ: 166.4, 149.5, 141.6, 138.2, 134.6, 133.2, 131.6, 129.4, 128.4, 127.8, 127.0, 126.1, 125.4, 124.6, 119.2, 19.6. MS (EI) m/z: 267 (M^+), 251 (M^+ − 16), 236 (M^+ − 31), 218 (M^+ − 49) (100). HRMS: calcd for $C_{16}H_{13}NOS$ (M^+) 267.0718, found 267.0722.

2-[(2-Methoxy-6-methylphenyl)sulfinyl]pyridine (2j). Compound **2j** was obtained from 2-[(2-methoxyphenyl)sulfinyl]pyridine and methylboronic acid following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a white solid (yield 16%). Mp: 108−110 °C. ^{1}H NMR δ: 8.48 (d, J = 4.7 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.88 (td, J = 7.7, 1.7 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.29−7.23 (m, 1H), 6.84 (d, J = 7.7 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 3.59 (s, 3H), 2.64 (s, 3H). ^{13}C NMR δ: 165.3, 159.0, 149.2, 142.2, 136.7, 133.4, 129.7, 123.8, 123.5, 121.1, 110.3, 55.8, 19.7. MS (ESI) m/z: 122 (M^+ − 126) (100), 248 (M^+ + H), 280 (M^+ + Na), 517 ($2M^+$ + Na). HRMS: calcd for $C_{13}H_{14}NO_2S$ (M^+ + H) 248.0739, found 248.0744.

2-(Biphenyl-2-ylsulfinyl)pyridine (3a). Compound **3a** was obtained from 2-(phenylsulfinyl)pyridine and phenylboronic acid neopentylglycol ester following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a white solid (yield 59%). Mp: 112−115 °C. ^{1}H NMR δ: 8.50 (d, J = 4.5 Hz, 1H), 7.88−7.76 (m, 3H), 7.64−7.56 (m, 2H), 7.52−7.36 (m, 6H), 7.30−7.22 (m, 1H). ^{13}C NMR δ: 165.7, 149.8, 143.1, 142.7, 138.2, 137.6, 131.2, 130.5, 130.4, 128.6, 128.1, 128.0, 126.4, 124.3, 120.1. MS (EI) m/z: 279 (M^+), 262 (M^+ − 17) (100), 230 (M^+ − 49), 186 (M^+ − 93). HRMS: calcd for $C_{17}H_{13}NOS$ (M^+) 279.0718, found 279.0728.

2-[(4′-Methylbiphenyl-2-yl)sulfinyl]pyridine (4a). Compound **4a** was obtained from 2-(phenylsulfinyl)pyridine and 5,5-dimethyl-2-(*p*-tolyl)-1,3,2-dioxaborinane following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a yellow solid (yield 72%). Mp: 74−76 °C. ^{1}H NMR δ: 8.43 (d, J = 4.6, 1H), 7.79−7.67 (m, 3H), 7.47−7.07 (m, 8H), 2.32 (s, 3H). ^{13}C NMR δ: 165.7, 149.8, 143.0, 142.8, 138.2, 137.81, 137.6, 131.1, 130.9, 130.43, 128.7, 128.5, 128.0, 127.5, 126.4, 124.3, 120.3, 21.4. MS (EI)

m/z: 293 (M^+), 276 ($M^+ - 17$) (100), 244 ($M^+ - 49$), 186 ($M^+ - 107$). HRMS: calcd for $C_{18}H_{15}NOS$ (M^+) 293.0874, found 293.0876

2-[(4′-Methoxybiphenyl-2-yl)sulfinyl]pyridine (5a). Compound **5a** was obtained from 2-(phenylsulfinyl)pyridine and 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a yellow solid (yield 47%). Mp: 162−165 °C. ^{1}H NMR δ: 8.50 (d, J = 4.5 Hz, 1H), 7.97−7.78 (m, 2H), 7.74 (d, J = 7.4, 1H), 7.54 (d, J = 8.6 Hz, 2H), 7.50−7.39 (m, 2H), 7.35 (d, J = 7.2, 1H), 7.30−7.22 (m, 1H), 6.97 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR δ: 165.9, 159.6, 149.8, 143.1, 142.5, 137.7, 131.6, 131.2, 130.5, 128.3, 126.5, 124.3, 120.1, 113.6, 55.3. MS (EI) m/z: 309 (M^+), 292 ($M^+ - 17$) (100), 260 ($M^+ - 49$), 186 ($M^+ - 124$). HRMS: calcd for $C_{18}H_{15}NO_2S$ (M^+) 309.3824, found 309.0830.

2-[(4′-Fluorobiphenyl-2-yl)sulfinyl]pyridine (6a). Compound **6a** was obtained from 2-(phenylsulfinyl)pyridine and 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a white solid (yield 62%). Mp: 107−109 °C. ^{1}H NMR δ: 8.49 (d, J = 4.1 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.85 (td, J = 7.7, 1.6 Hz, 1H), 7.84−7.74 (m, 1H), 7.64−7.55 (m, 2H), 7.52−7.42 (m, 2H), 7.40−7.30 (m, 1H), 7.35−7.27 (m, 1H), 7.12 (t, J = 8.7 Hz, 2H). ^{13}C NMR δ: 165.7, 149.8, 143.1, 141.7, 137.8, 132.3, 132.1, 131.3, 130.5, 128.8, 126.6, 124.4, 119.9, 115.3, 114.9. MS (EI) m/z: 297 (M^+), 280 ($M^+ - 17$) (100), 248 ($M^+ - 49$), 186 ($M^+ - 111$). HRMS calcd for $C_{17}H_{12}FNOS$ (M^+) 297.0624, found 297.0612.

2-[(4′-Fluoro-5-methoxybiphenyl-2-yl)sulfinyl]pyridine (6c). Compound **6c** was obtained from 2-[(4-methoxyphenyl)-sulfinyl]pyridine and 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a yellow solid (yield 65%). Mp: 141−144 °C. ^{1}H NMR δ: 8.51 (d, J = 4.6 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.92−7.81 (m, 1H), 7.73−7.55 (m, 3H), 7.12 (t, J = 8.7 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 6.84 (d, J = 2.6 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR δ: 166.1, 161.3, 149.7, 144.0, 137.7, 132.2, 132.0, 129.1, 127.3, 124.5, 124.2, 119.8, 118.5, 115.4, 115.2, 114.9, 114.7, 55.5. MS (ESI) m/z: 202 ($M^+ - 125$), 310 ($M^+ - 17$), 328 ($M^+ + H$) (100), 350 ($M^+ + Na$), 677 ($2M^+ + Na$). HRMS: calcd for $C_{18}H_{15}FNO_2S$ ($M^+ + H$) 328.0802, found 328.0802.

2-[(3′-Methyl-2-yl)sulfinyl]pyridine (7a). Compound **7a** was obtained from 2-(phenylsulfinyl)pyridine and 5,5-dimethyl-2-(*m*-tolyl)-1,3,2-dioxaborinane following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a yellow solid (yield 70%). Mp: 73−76 °C. ^{1}H NMR δ: 8.50 (dt, J = 4.7, 1.4 Hz, 1H), 7.86−7.73 (m, 3H), 7.55−7.17 (m, 8H), 2.40 (s, 3H). ^{13}C NMR δ: 165.7, 149.8, 143.0, 142.8, 138.2, 137.8, 137.5, 131.1, 130.9, 130.4, 128.7, 128.5, 128.0, 127.5, 126.4, 124.3, 120.2, 21.4. MS (EI) m/z: 293 (M^+), 276 ($M^+ - 17$) (100), 244 ($M^+ - 49$), 186 ($M^+ - 107$). HRMS: calcd for $C_{18}H_{15}NOS$ (M^+) 293.0874, found 293.0865.

2-[(3′-Chlorobiphenyl-2-yl)sulfinyl]pyridine (8a). Compound **8a** was obtained from 2-(phenylsulfinyl)pyridine and 2-(3-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 2:1), as a yellow oil (yield 40%). ^{1}H NMR δ: 8.53 (d, J = 4.6 Hz, 1H), 7.98−7.79 (m, 3H), 7.64−7.22 (m, 8H). ^{13}C NMR δ: 165.7, 149.8, 143.2, 141.2, 139.9, 137.8, 134.0, 131.3, 130.4, 129.3, 129.1, 128.7, 128.2, 126.5, 124.9, 124.4, 119.9. MS (EI) m/z: 313 (M^+), 296 ($M^+ - 17$). 264 ($M^+ - 49$), 186 ($M^+ - 127$) (100). HRMS: calcd for $C_{17}H_{12}ClNOS$ (M^+) 313.0328, found 313.0319.

General Procedure for the Desulfinylation. To a solution of aryl 2-sulfinylpyridine (0.1 mmol) in dry THF (1 mL), cooled to −98 °C and under nitrogen atmosphere, was added a 1.6 M solution of BuLi in hexanes (0.125 mL, 0.2 mmol). The reaction mixture was stirred at −98 °C for 45 min before a saturated aqueous solution of NH_4Cl (5 mL) was added. The two phases were separated, and the aqueous phase was extracted with AcOEt (×3). The combined organic phase was dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography to give the corresponding biaryl products.

4′-Fluoro-3-methoxy-1,1′-biphenyl (9c).[26] Compound **9c** was obtained from 2-[(4′-fluoro-5-methoxybiphenyl-2-yl)sulfinyl]pyridine **6c** following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 3:1), as a yellow oil (yield 63%). Analytical data are in accordance with those reported in the literature.[26] ^{1}H NMR δ: 7.58−7.53 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.22−7.16 (m, 4H), 7.05 (dt, J = 7.5, 1.4 Hz, 1H), 3.81 (s, 3H).

3-Methylbiphenyl (10a).[27] Compound **10a** was obtained from 2-[(3′-methylbiphenyl]-2-yl)sulfinyl]pyridine **7a** following the general procedure, after purification by flash chromatography (*n*-hexane−EtOAc 3:1), as a colorless oil (yield 91%). Analytical data are in accordance with those from the literature.[27] ^{1}H NMR δ: 7.52 (d, J = 7.3 Hz, 2H), 7.45−7.33 (m, 4H), 7.21−7.11 (m, 3H), 2.35 (s, 3H).

Synthesis of the Palladacycle (I). A mixture of substrate **1a** (406.0 mg, 2 mmol) and $Pd(OAc)_2$ (448.0 mg, 2 mmol) in 1,2-dichloroethane (2 mL) was stirred at 100 °C for 30 min before the mixture was cooled down to room temperature. The reaction mixture was filtered through a pad of Celite (washed with EtOAc), and the filtrate was concentrated under reduced pressure. The residue was crystallized from a mixture DCE/heptane to give the palladacycle **I** as a yellow solid. Yield: 96%.

Reaction of the Palladacycle (I) with MeB(OH)$_2$. In a screw-capped tube, dimeric palladacycle **I** (73.5 mg, 0.1 mmol), methylboronic acid (23.8 mg, 0.4 mmol, 2 equiv according to Pd), and *p*-benzoquinone (10.8 mg, 0.1 mmol, 0.5 equiv according to Pd) were dissolved in *tert*-amyl alcohol (1 mL) under atmospheric air. The reaction mixture was stirred at 100 °C for 20 h before it was filtered through a pad of Celite (washed several times with EtOAc). The filtrate was concentrated under reduced pressure, and the conversion was determined to be >98% by ^{1}H NMR on the crude reaction mixture.

Intermolecular Competition Experiment. In a screw-capped tube, 2-[(4-chlorophenyl]sulfinyl)pyridine **1d** (11.8 mg, 0.05 mmol), 2-[(4-methoxyphenyl)sulfinyl]pyridine **1c** (11.6 mg, 0.05 mmol), methylboronic acid (11.9 mg, 0.2 mmol), $Pd(OAc)_2$ (2.2 mg, 10 mol %), *p*-benzoquinone (5.4 mg, 0.05 mmol), and AgOAc (49.9 mg, 0.3 mmol) were dissolved in *tert*-amyl alcohol (1 mL) under atmospheric air. The reaction mixture was stirred at 100 °C for 2 h before it was filtered through a pad of Celite (washed several times with EtOAc). The filtrate was concentrated under reduced pressure, and the residue was analyzed by ^{1}H NMR. The corresponding products **2d** and **2c** were obtained with 5% and 26% conversion, respectively (k_{Cl}/k_{OMe}= 0.19), along with the starting substrates.

Synthesis of 2-[(2-Deuteriophenyl)sulfinyl]pyridine (1a-D). To a solution of 2-[(2-bromophenyl)thio]pyridine (115.0 mg, 0.41 mmol) in dry THF (2 mL), cooled to −78 °C and under nitrogen atmosphere, was added dropwise a 1.6 M solution of BuLi in hexanes (0.51 mL, 0.81 mmol). The reaction mixture was stirred at −78 °C for 1 h before it was quenched with MeOD (1 mL). The reaction was allowed to reach room temperature and stirred for an extra 20 min. The reaction mixture was then diluted with H_2O (1 mL) and extracted with EtOAc (3 × 5 mL). The combined organic phase was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (*n*-hexane−EtOAc 4:1) to give the deuterated product as a colorless oil. Yield: 92%. This product was oxidized in the presence of *m*-chloroperbenzoic acid (1 equiv) to give 2-[(2-deuterophenyl)sulfinyl]pyridine **1a-D**.[14a] ^{1}H NMR δ: 8.55 (d, J = 4.1 Hz, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.87 (dt, J = 7.8, 1.6 Hz, 1H), 7.83−7.77 (m, 1H), 7.50−7.38 (m, 3H), 7.29 (ddd, J = 7.4, 4.7, 0.9 Hz, 1H).

Intramolecular Kinetic Isotope Effect. In a screw-capped tube, 2-[(2-deuterophenyl)sulfinyl]pyridine **1a-D** (20.3 mg, 0.1 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), *p*-benzoquinone (5.3 mg, 0.05 mmol), AgOAc (49.9 mg, 0.3 mmol), and methylboronic acid (11.9 mg, 0.2 mmol) were dissolved in *tert*-amyl alcohol (1 mL). The reaction mixture was stirred at 100 °C for 2 h before it was filtered through a pad of Celite (washed several times with EtOAc). The filtrate was concentrated under reduced pressure, and ^{1}H NMR analysis of the crude mixture showed a k_H/k_D value of 1.1.

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■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of new compounds and a X-ray crystallographic view for complex **I**. This material is available free of charge via the Internet at http://pubs.acs.org.

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