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Citation	Synlett, 27(10), 1582-1586 https://doi.org/10.1055/s-0035-1561578
Issue Date	2016-06
Doc URL	https://hdl.handle.net/2115/64699
Type	journal article
File Information	Ishiyama-S27(10).pdf

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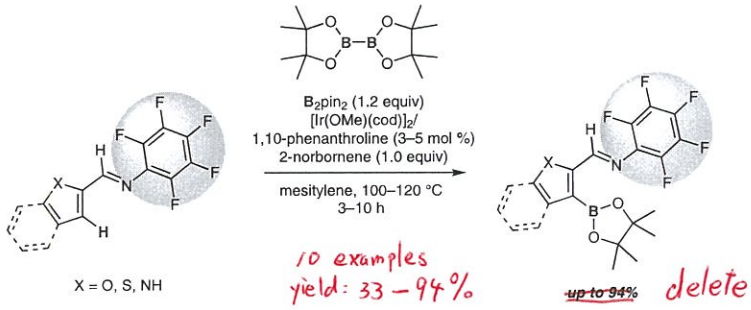
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Regioselective C–H Borylation of Heteroaromatic Aldimines with Iridium Complexes

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■■*give number of examples and yield range in GA*■■



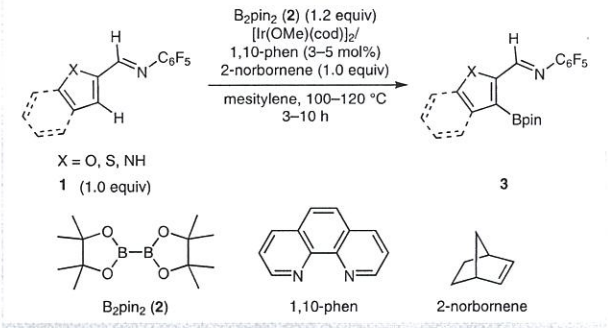
Received: 19.12.2015
Accepted after revision: 11.02.2016
Published online:
DOI: 10.1055/s-0035-1561578; Art ID: st-2015-u0985-l

Abstract An iridium-catalyzed regioselective C–H borylation of pentafluoroaniline-derived heteroaromatic aldimines has been developed. Various heteroaromatic aldimines underwent borylation by bis(pinacolato)diboron to afford the corresponding borylated products in good yields in the presence of an iridium complex formed in situ from bis(cyclooctadienyl)(methoxy)iridium {[Ir(OMe)(cod)]$_2$} and 1,10-phenanthroline.

Key words iridium, catalysis, borylation, heteroarenes, regioselectivity, aldimines

Heteroarylboronic acids and their derivatives are useful intermediates in organic synthesis because they can be readily converted into synthetic motifs for bioactive compounds and organic electronics materials.[1,2] Many groups have reported effective methods for synthesizing borylated heteroarenes by using a transition metal to catalyze regioselective borylation of C–H bonds.[3] For instance, our group previously reported on the use of an iridium complex, prepared from [Ir(OMe)(cod)]$_2$ and a 4,4′-di-*tert*-butylbipyridine (dtbpy) ligand, to catalyze C–H borylations of various heteroarenes.[4,5] The borylation occurred at the position α to the heteroatom in the substrate to afford either a 2- or a 5-borylated product in high yield. In this particular case, the regioselectivity for the reaction was determined by electronic effects. A sterically controlled C–H borylation reaction has also been reported by Smith's group; in this, borylation occurs at a position vicinal to a cyano group to afford the desired products in high yields and with good regioselectivities.[6] Our group and Sawamura's group[7–9] have developed carbonyl-directed borylations of heteroaromatic compounds with iridium catalysts. These studies established that the regioselectivity of the borylation reaction is governed by the interaction between the oxygen atom of the carbonyl group and the iridium metal center.[10] Although these reactions are regioselective, the directing groups are exclusively limited to ester or amide groups. Heteroaromatic aldehydes and their derivatives have received considerable attention from agricultural and medicinal chemists because of the various biological activities exhibited by these compounds.[11] However, to the best our knowledge, C–H borylation of heteroaromatic aldehydes derivatives has not been achieved, because aldehydes are extremely reactive under the established C–H borylation conditions.

We previously accomplished *ortho* C–H borylation of aromatic compounds containing a pentafluorophenyl aldimine moiety by using a combination of [Ir(OMe)(cod)]$_2$ and P(C$_6$F$_5$)$_3$ as the catalyst.[1,2] This reaction is suitable as an alternative to aldehyde-directed C–H borylation, because the hydrolysis of the pentafluorophenyl aldimine moiety readily affords the desired aldehyde. Here, we describe a regioselective C–H borylation of heteroaromatic aldimines **1** with

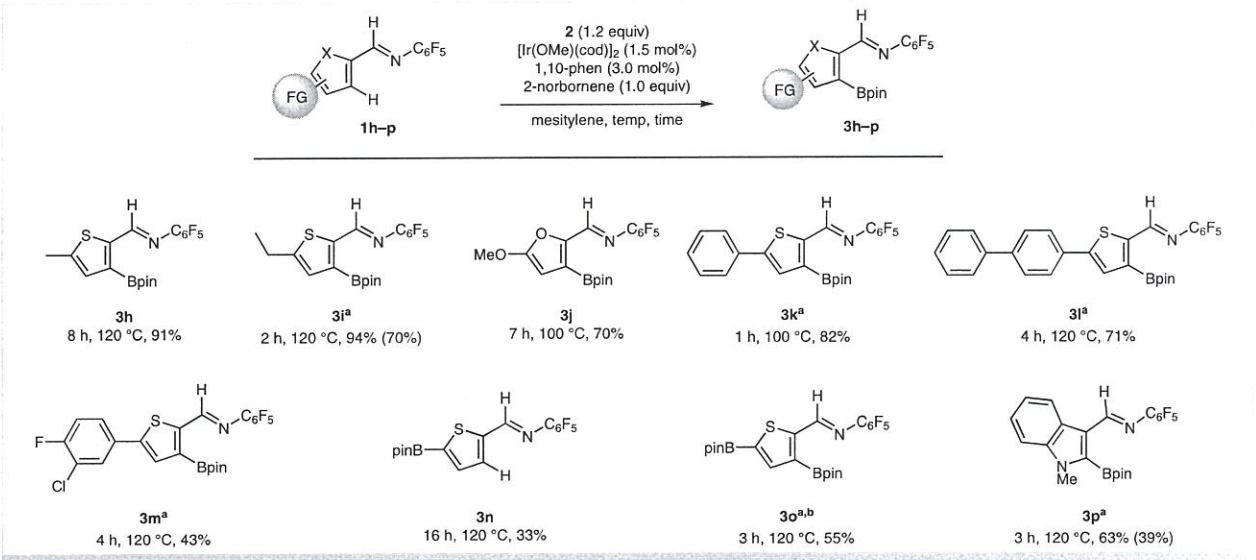


Scheme 1 Regioselective C–H borylation of heteroaromatic aldimines

of **3a** caused a marked decrease in the yield (38%) during the isolation procedure. These results indicate that the combination of $[Ir(OMe)(cod)]_2$ and 1,10-phen provides the best reaction conditions for the borylation of **1a**.

We then investigated the effect of an imino group *N*-substituent on the borylation of heteroaromatic aldimines under our optimized conditions (Scheme 2). The pentafluorophenyl moiety in **1a** was modified by replacing both *ortho* fluorine atoms with hydrogen atoms to afford the 3,4,5-trifluorophenyl aldimine **1b**. The reaction of **1b** with borane **2** gave **3b** in 74% NMR yield, but with an isolated yield of only 4%. Both the 3,5-bis(trifluoromethyl)phenyl aldimine **1c** and the 4-cyanophenyl aldimine **1d** gave negligible NMR yields. The reaction of phenyl aldimine **1e** with **2** occurred at 100 °C to afford **3e** in a 37% NMR yield; an attempt to isolate the product was unsuccessful, owing to its instability. The *ortho*-methoxyphenyl aldimine **1f** afforded the borylated product **3f** in a moderate yield. The reaction of aldoxime **1g** with **2** did not produce the desired borylated product **3g**. These results suggest that a pentafluorophenyl moiety on the imino group contributes to the reactivity of the substrate as well as to the stability of the product.

Next, we examined the borylation of *N*-pentafluorophenyl aldimines of various heteroarenes, such as furans, thiophenes, and indoles, under the optimized conditions (Scheme 3). These reactions proceeded regioselectively at the position vicinal to the imino group to afford the desired borylated products **3h–p** in good NMR yields. However, the yield still fell markedly during the isolation procedure, because the products are highly unstable in the presence of moisture and silica gel. The NMR yields are shown in Scheme 3. The 5-alkylthiophene aldimines **1h** and **1i** reacted with borane **2** to afford the corresponding borylated derivatives **3h** and **3i** in 91% and 94% yields, respectively. The reaction of the methoxy-substituted furan aldimine **1j** gave **3j** in 70% yield. In general, the C–H bonds on a phenyl group are easily transformed into C–B bonds under the established borylation reaction conditions. However, the regioselective borylation of the 5-phenylthiophene aldimine **1k** and the 5-biphenylthiophene aldimine **1l** proceeded at the vicinal position to afford the borylated products **3k** and **3l**, respectively, in high yields. Although some transition-metal complexes exhibit high reactivity toward C–Cl bonds, the 5-(3-chloro-4-fluorophenyl)thiophene aldimine **1m** underwent borylation with **2** exclusively at the vicinal C–H bonds to generate **3m** in 43% yield. The reaction of monosubstituted thiophene aldimine **1n** gave the 5-borylated thiophene **3n** in low yield. The selectivity toward borylation of the C–H bond at the 5-position (or the α-position relative to the sulfur atom) in **1n** was attributed to its higher acidity compared with the C–H bonds at the 3- and 4-positions. When two equivalents of borane **2** were used for the borylation of **1n**, diborylation occurred to afford **3o** in good yield. The *N*-methylindole derivative **1p** also underwent borylation to afford **3p** in 63% yield. These results indicate that the C–H borylation of various heteroarene aldimines with a combination of $[Ir(OMe)(cod)]_2$ and 1,10-phen shows good chemoselectivity and regioselectivity.

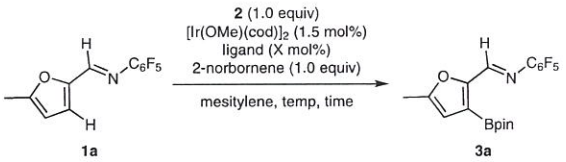


Scheme 3 Substrate scope. *Reagents and conditions*: aldimine **1a** (0.5 mmol), B_2pin_2 (0.5 mmol), 2-norbornene (0.5 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), 1,10-phen (3.0 mol%), mesitylene (3 mL). Yields were determined by ^1H NMR analysis (internal standard: 1,1,2,2-tetrachloroethane); isolated yields are shown in parentheses. [a] The reaction was conducted in the absence of 2-norbornene. [b] 2.0 equivalents of **2** were used.

bis(pinacolato)diborane (**2**; B_2pin_2), catalyzed by $[Ir(OMe)(cod)]_2$ and 1,10-phenanthroline (1,10-phen) in mesitylene as a solvent. The reaction proceeds regioselectively at either 100 or 120 °C in the presence of 2-norbornene (1.0 equiv) to afford the corresponding heteroaromatic boron compounds **3** in high yields (Scheme 1). The utility of this borylation strategy was demonstrated through transformation of a boryl-substituted heteroaromatic aldimine into a 3-aryl-2-formyl compound.

The borylation of the pentafluoroaniline-derived heteroaromatic aldimine **1a** was initially examined under the optimum conditions that we previously established for the borylation of aromatic aldimines (Table 1).[12,13] Unfortunately, the reaction of aldimine **1a** with borane **2** (1.0 equiv) in the presence of $[Ir(OMe)(cod)]_2$ (1.5 mol%), the ligand $P(C_6F_5)_3$ (6.0 mol%), and 2-norbornene (1.0 equiv) in mesitylene at 120 °C afforded the corresponding product **3a** in only 5% yield after 24 hours (Table 1, entry 1). We then screened other possible ligands (entries 2–7), and we discovered that no reaction occurred when Ph_3As was used as the ligand (entry 2). However, the use of 1,10-phen as the ligand markedly improved the yield of **3a**. Additionally, 1,10-phen also prevented the undesirable side reaction in which the imine group is reduced to an amine (61% and 3 hours; entry 3). Bipyridine ligands such as dtbpy or 4,4′-bipyridine (bpy) afforded **3a** in moderate yields (entries 4 and 5). Low yields of **3a** were obtained with other phenanthroline ligands, such as 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen) and 2,9-dimethyl-1,10-phenanthroline (2,9-Me_2phen) (entries 6 and 7, respectively). The borylation of **1a** with 1.2 equivalents of borane **2** proceeded at 100 °C to afford the corresponding product **3a** in high yield and good regioselectivity (62% and 3 h; entry 8). The reaction of **1a** proceeded even in the absence of 2-norbornene to afford **3a** in high yield (79% and 3 h; entry 9). However, the instability

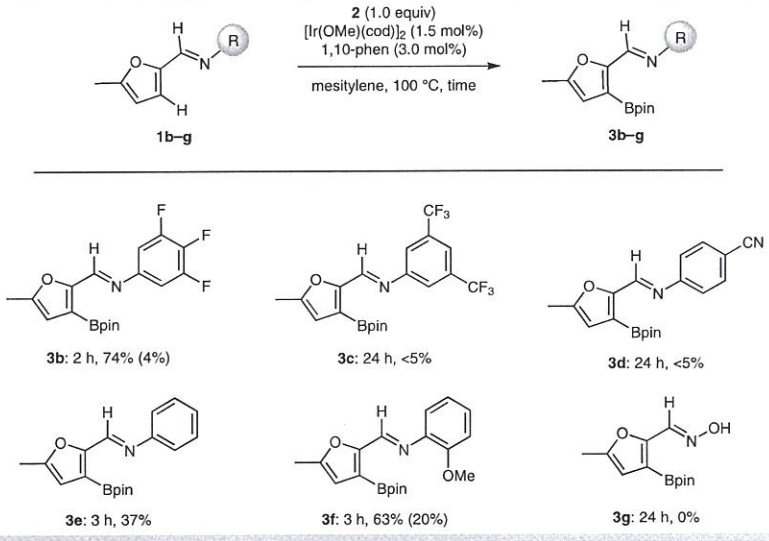
Table 1 Optimization of the Reaction Conditions for the Borylation of Aldimine **1a**[a]



1a 3a

Entry	Ligand (mol%)	Temp (°C)	Time (h)	Yield[b] of **3a** (%)
1	$(C_6F_5)_3P$ (6.0)	120	24	5
2	Ph_3As (6.0)	120	24	>5
3	1,10-phen (3.0)	120	3	61
4	dtbpy (3.0)	120	3	51
5	bpy (3.0)	120	3	31
6	4,7-Me_2phen (3.0)	120	3	8
7	2,9-Me_2phen (3.0)	120	3	>5
8[c]	1,10-phen (3.0)	100	3	62
9[c,d]	1,10-phen (3.0)	100	3	79 (38)[e]

[a] Reaction conditions: aldimine **1a** (0.5 mmol), B_2pin_2 (0.5 mmol), 2-norbornene (0.5 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), ligand (3.0–6.0 mol%), mesitylene (3 mL).
[b] Yields determined by ^1H NMR spectroscopy (internal standard: 1,1,2,2-tetrachloroethane).
[c] 1.2 equivalents of **2** were used.
[d] The reaction was conducted in the absence of 2-norbornene.
[e] Isolated yield.



Scheme 2 Investigation of the effects of various imino group substituents on the borylation of the neighboring C–H bond. *Reagents and conditions*: aldimine **1a** (0.5 mmol), B_2pin_2 (0.5 mmol), $[Ir(OMe)(cod)]_2$ (1.5 mol%), 1,10-phen (3.0 mol%), mesitylene (3 mL), 100 °C. Yields were determined by ^1H NMR analysis (internal standard: 1,1,2,2-tetrachloroethane). The isolated yields are shown in parentheses.

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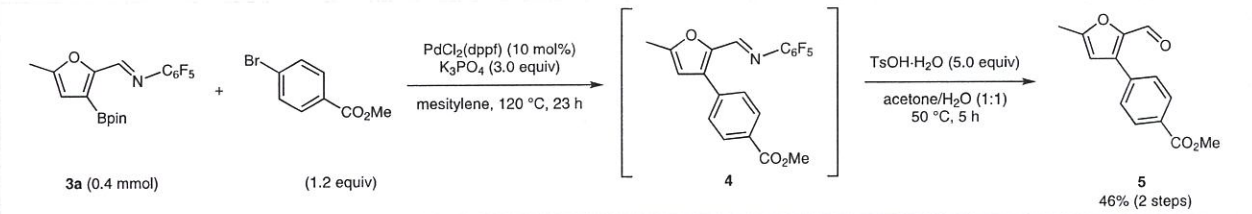
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(13) **Borylation of Heteroaromatic Aldimine 1a; General Procedure**

An oven-dried two-necked flask was charged with $[Ir(OMe)(cod)]_2$ (5.0 mg, 7.5 μmol), borane **2** (152.4 mg, 0.60 mmol), and 1,10-phen (2.7 mg, 15 μmol). The flask was connected to a vacuum/N_2 manifold through a rubber tube, evacuated, and backfilled with N_2. This cycle was repeated three times. Mesitylene (3.0 mL) was then added in the flask through a rubber septum by using a syringe and the mixture was stirred at r.t. for 15 min. Next, **1** (0.50 mmol) was added from a syringe and the mixture was stirred at r.t. When the reaction was complete, the mixture was initially purified by Kugelrohr distillation. The resulting mixture was crystallized from hexane. See the Supporting Information for characterization data of all compounds **3**. Data for **3a** are given here as an example.

The NMR yield of **3a** in the crude mixture was 79%. The reaction mixture was first purified by Kugelrohr distillation (34 Pa, 180 °C). Then, the resulting mixture was recrystallized from hexane to obtain **3a** (76.2 mg, 0.19 mmol, 38%) as a white solid from **1a** (137.6 mg, 0.50 mmol); mp 149 °C. ^{1}H NMR (396 MHz, $CDCl_3$): δ = 1.32 (s, 12 H), 2.45 (d, J = 1.2 Hz, 3 H), 6.40 (s, 1 H), 8.69 (s, 1 H). ^{13}C NMR (99 MHz, $CDCl_3$): δ = 13.7 (CH_3), 24.7 (CH_3), 84.2 (C), 113.5 (CH), 127.0 (dt, J = 4.2, 12.4 Hz, C), 136.4–136.8 (m, CF), 139.0–139.3 (m, CF), 141.5–141.6 (m, CF), 155.7 (C), 156.2 (CH), 158.1 (C). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. ^{19}F NMR (373 MHz, $CDCl_3$): δ = –153.6 (d, J = 14.2 Hz, 2 F), –161.5 (t, *J* = 21.6 Hz, 1 F), –163.9 (t, *J* = 17.9 Hz, 2 F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{17}{}^{10}BF_5NO_3$, 400.12580; found, 400.12638.■■sample data added–OK?■■ — o.k.

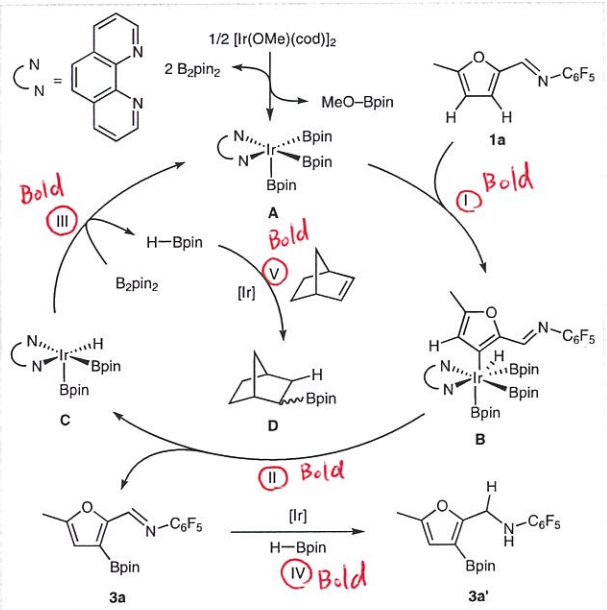
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Scheme 4 Synthesis of 3-aryl-2-formyl compound **5** from aldimine **3a** by sequential Suzuki–Miyaura cross-coupling and hydrolysis

The biological activities of 3-aryl 2-formyl heteroarene derivatives in medicinal and agricultural applications have been previously reported.[11a,b] The utility of these borylated heteroaromatic aldimines was demonstrated by transforming one of the products into the corresponding 3-aryl 2-formyl compound **5** (Scheme 4).[11] Cross-coupling of heteroaromatic aldimine **3a** with methyl 4-bromobenzoate (1.2 equiv) in the presence of $PdCl_2$(dppf) (10 mol%) and K_3PO_4 (3.0 equiv) in mesitylene was performed at 120 °C for 23 hours. The mixture was then concentrated, and the residue was treated with TsOH·H_2O (5.0 equiv) in 1:1 acetone–H_2O at 50 °C for five hours to remove the pentafluoroaniline moiety. The hydrolyzed product **5** was obtained in 46% isolated yield after these two sequential steps.

A possible mechanism for the reaction of aldimine **1a** is proposed in Scheme 5.[3d,e,14] The trisboryl iridium complex **A** is first produced by the reaction of $[Ir(OMe)(cod)]_2$ and 1,10-phen with B_2pin_2.[10] The oxidative addition of **1a** to complex **A** occurs at the C–H bond neighboring the imino group to produce complex **B** (step I). The regioselectivity of this oxidative addition is probably due to the acidity of the C–H bond, induced by the pentafluorophenyl substituent on the neighboring imino group acting as a powerful electron-withdrawing group. The Ir–hydride complex **C** and the product **3a** are produced (step II) after reductive elimination. In the final step (step III), the reaction of complex **C** with B_2pin_2 simultaneously regenerates **A** and produces H–Bpin as a byproduct. 2-Norbornene reacts with HBpin (step V), inhibiting the product-reduction pathway (step IV), so that amine **3a′** is not produced.



Scheme 5 Proposed mechanism of the regioselective borylation reaction

In summary, we have developed a regioselective C–H borylation of pentafluoroaniline-derived heteroaromatic aldimines by using B_2pin_2 in the presence of $[Ir(OMe)(cod)]_2$, 1,10-phen, and 2-norbornene. This reaction proceeds regioselectively to produce heteroaryl boronates in high yields. The C–H borylation of substrates containing aryl, methoxy, or halo (F, Cl) substituents afforded the corresponding borylated products in moderate to high yields without undesired side reactions of aryl C–H, C–F, or C–Cl bonds. Additionally, we demonstrated the utility of the borylated heteroaryl aldimine **3a** in medicinal and agricultural applications by transforming it into the 3-aryl 2-formyl compound **5**.

Acknowledgment

This study was financially supported by the NEXT (Japan) program (Strategic Molecular and Materials Chemistry through Innovative Coupling Reactions) of Hokkaido University and by JSPS KAKENHI Grant Numbers 15H03804 and 15K13633.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561578.

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