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Direct synthesis of hetero-biaryl compounds containing an unprotected NH_2 group via Suzuki–Miyaura reaction

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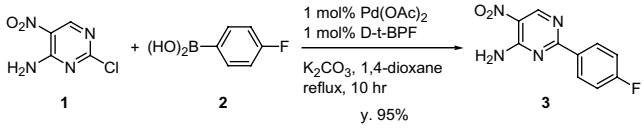
Abstract—Hetero-biaryl compounds were prepared via the Suzuki–Miyaura coupling reaction of hetero-aryl moieties containing an unprotected NH_2 group and arylboronic acids. D-*t*-BPF was found to be an efficient ligand for the cross-coupling of NH_2-unprotected hetero-aryl chlorides with phenylboronic acid.

1. Introduction

Biaryls are high value synthetic targets and can be found as substructures in numerous pharmaceutical and biological active compounds.[1] A large number of synthetic methods have been developed over the years for the preparation of biaryls,[2] however, the development of palladium- and nickel-catalyzed cross-coupling strategies has brought this methodology to the forefront of biaryl synthesis. Indeed, the methods of choice for the preparation of biaryls are cross-coupling reactions such as Stille[3] and Suzuki–Miyaura.[4] A few direct cross-coupling reactions involving NH_2-unprotected hetero-aryl moieties have been disclosed.[5] It is common practice to protection functional groups such as amines, alcohols/phenols, thiols/thiophenols and carboxylic acids[6] prior to the coupling step followed by deprotection later. In this letter, we present the first highly efficient and general Suzuki–Miyaura reaction between phenylboronic acid and NH_2-unprotected chloropyrimidines/pyridines.

Recently, we reported 1,1′-bis(di-*tert*-butyl phosphino)-ferrocene (D-*t*-BPF) was a highly effective ligand for synthesis of 4-amino-2-arylpyrimidines via the direct coupling of NH_2-unprotected 4-amino-2-chloropyrimidine with arylboronic acids under anhydrous conditions (Scheme 1).[7] In this reaction, $Pd(PPh_3)_2Cl_2$ or



Scheme 1.

$Pd(OAc)_2$/dppf were found to be less effective than $Pd(OAc)_2$ with D-*t*-BPF. Since we envisioned that our procedure would be applied in direct coupling of NH_2-unprotected hetero-aryl chlorides with arylboronic acids providing structurally diversified hetero-biaryl amino compounds, we have further investigated the role of D-*t*-BPF. Thus, we report the scope and limitation of this coupling reaction and the role of D-*t*-BPF in the coupling reaction under anhydrous conditions.

These reaction conditions were applied to the synthesis of an assortment of hetero-biaryl compounds having unprotected NH_2 group on the hetero-aryl moiety. The results of the Suzuki–Miyaura cross-coupling reaction employing D-*t*-BPF as ligand of the NH_2-unprotected various hetero-aryl chlorides with phenylboronic acid under our typical conditions are summarized in Table 1. Arylation of the activated aminochloropyrimidine afforded the corresponding biaryl products in high yield (entries 1 and 2). Coupling product of 4-amino-5-nitro-6-methoxy-2-chloropyrimidine with phenylboronic acid was also obtained in good yield (entry 3).

Quinazoline derivatives are important targets in the pharmaceutical industry. The Suzuki–Miyaura reaction at C-6,[8] C-4[9] and C-8[9] positions of the quinazoline ring

Keywords: Suzuki–Miyaura reaction; Unprotected NH_2 group; D-*t*-BPF.
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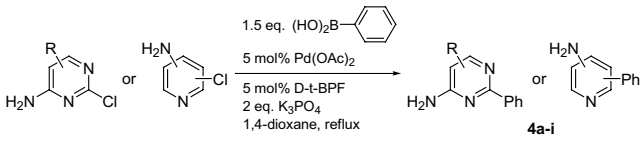
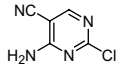
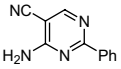
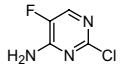
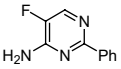
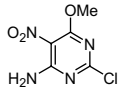
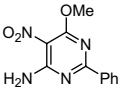
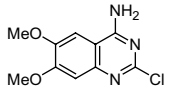
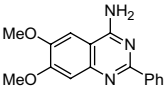
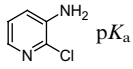
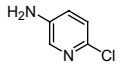
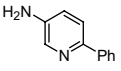
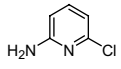
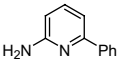
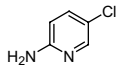
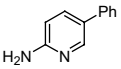
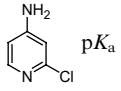
Table 1. Coupling of NH_2-unprotected aminochloropyrimidines/pyridines with phenylboronic acid



Entry	Substrates	Products		% Yield[a]
1			**4a**	91
2			**4b**	88
3			**4c**	82
4			**4d**	89
5	 pK_a 1.6		**4e**	93
6	 pK_a 2.1		**4f**	82
7	 pK_a 2.8		**4g**	68
8	 pK_a 4.5		**4h**	72
9	 pK_a 4.8		**4i**	30

[a] Yields refer to the average isolated yield of two runs.

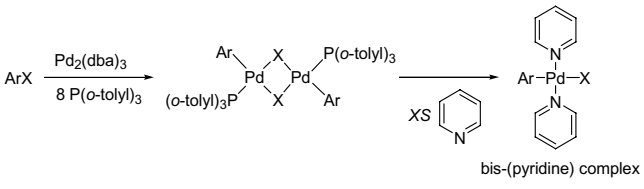
has been reported, but all examples reported do not contain an unprotected NH_2 group. As shown in entry 4, 4-amino-6,7-dimethoxy-2-chloroquinazoline was converted to the corresponding 2-phenylquinazoline derivative in high yield.

Next we evaluated the catalyst activity for the coupling of NH_2-unprotected chloropyridines with phenylboronic acid (entries 5–9). Traditionally, the NH_2 group on the pyridine ring has to be protected prior to the coupling reaction. The Pfizer group[10] reported that the protection of NH_2 group is crucial for the coupling of 3-amino-2-chloropyridine with phenylboronic acid. On the other hand, in our attempts, the direct coupling of NH_2-unprotected 3-amino-2-chloropyridine was successful using even 1 mol % $Pd(OAc)_2$ and 1 mol % D-*t*-BPF as ligand (entry 5).[11] Reaction of 2- or 3-amino-chloropyridine with phenylboronic acid afforded the desired phenylpyridine in good to moderate yields (entries 6–8[12]). The coupling of 4-amino-2-chloropyridine with phenylboronic acid resulted in incomplete reaction even after 48 h, and the product was obtained in only 30% yield with remaining starting material (entry 9). These results suggested that the yield depends on the basicity of aminochloropyridine. We infer that the strongly basic 4-aminopyridine could increase the propensity for coordination to palladium, which in turn could result in a bis-(pyridine) complex, thus terminating the catalytic cycle.

Wagaw and Buchwald reported that the bidentate ligand was an efficient for the amination of bromopyridines.[13] In the literature, he described that BINAP prevents the formation of bis-(pyridine) complex because of its bidentate nature (Scheme 2). Hamann and Hartwig also reported that the sterically hindered alkyl phosphines ligand D-*t*-BPF was efficient ligand for amination due to the acceleration of oxidative addition and reductive elimination.[14]

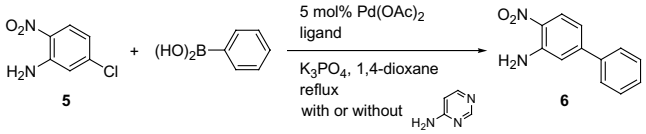
Lakshman et al.[15] and Western et al.[16] have observed that the use of a non-chelating *tert*-butyl-substituted phosphine in the Suzuki–Miyaura reaction of a protected 6- or 8-bromopurine nucleoside reduced the activity of the metal catalyst.

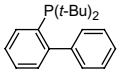
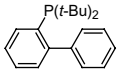
The selection of a ligand is one of the most important factors that affect the rate of oxidative addition and reductive elimination in the catalytic cycle. To facilitate reductive elimination, there are three key factors, the value of the bite angle P–Pd–P for bidentate ligands, the length P–Pd and steric hindrance around ligands including cone angles for monodentate ligands. For instance, larger P–Pd–P (angle, D-*t*-BPF 104°, DPPF 96°, DPPP 91°, DPPE 85°)[17] and longer P–Pd (length, D-*t*-BPF 2.419 Å, DPPF 2.292 Å, DPPP 2.247 Å, DPPE 2.230 Å) in the four complexes L_2 PdRX (L_2 = D-*t*-BPF, DPPF, DPPP, DPPE)[18,19] are well translated to smooth reductive elimination to form the coupling products.[19] Since D-*t*-BPF is one of the most sterically hindered analogues of ferrocenyl ligands, this ligand may generate a more active catalyst compared to other ferrocenyl ligands. In addition, the electron density of palladium is also increased by coordination of alkyl phosphines relative to aryl phosphines, therefore D-*t*-BFF is expected to accelerate the rate of oxidative addition step. Furthermore, since P–C bonds of alkyl phosphines are stronger than that of aryl phosphines, D-*t*-BPF should provide higher turnover numbers.[20] For these reasons, the complex resulting from Pd coordination to D-*t*-BPF exhibits higher reactivity towards the arylation of aminopyrimi-



Scheme 2.

Table 2. Influence of aminopyrimidine moiety for the cross-coupling



Entry	Ligand[a]	4-Aminopyrimidine	% Yield of **6**
1	D-*t*-BPF	None	92
2		None	91
3	D-*t*-BPF	50 mol %	90
4		50 mol %	26

[a] 5 mol % of D-*t*-BPF, 10 mol % of monodentate phosphine ligand.

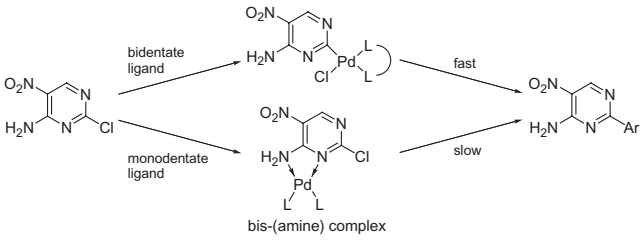
dine halides than complexes generated from DPPP, DPPF or 1,1′-bis(di-*iso*-propylphosphino)ferrocene (D-*i*-PrPF). In addition, the particular properties of D-*t*-BPF make it suitable for coupling of NH_2-unprotected pyrimidine/pyridine moieties.

In order to determine the coordination effect of the two nitrogen atoms on the aminopyrimidine moiety during the coupling reaction, aniline derivative **5** was coupled with phenylboronic acid in the absence or presence of 4-aminopyrimidine (Table 2).

For this study, we carried out the cross-coupling of 3-chloro-6-nitroaniline and phenylboronic acid with/without 4-aminopyrimidine. The coupling reaction proceeded smoothly in high yield regardless of the ligand used in the absence 4-aminopyrimidine (entries 1 and 2). These data suggests that the weak basicity of aniline should not detrimentally impact the coupling reaction. Next we examined the coupling reaction under the same conditions in the presence of 50 mol % of 4-aminopyrimidine. The presence of 4-aminopyrimidine does not affect the coupling when using D-*t*-BPF as ligand (entry 3), however dramatic affects with the monodentate ligand were observed (entry 4). These results showed that the addition of 4-aminopyrimidine significantly influences the catalytic activity due to its strong basicity when using the monodentate ligand. On the other hand, the bidentate nature of D-*t*-BPF coupled with its high electron density and bulkiness effectively suppresses coordination of 4-aminopyrimidine to the metal.

Taken together, we propose that the efficiency of this catalyst system ($Pd(OAc)_2$, D-*t*-BPF) is due to the ability of the chelating bis-(phosphine) ligand to inhibit the formation of bis-(amine) complex (Scheme 3).

In conclusion, the titled biaryls could be obtained in generally good yields and without any protection of the amino functional group using sterically hindered and electron rich alkyl bidentate phosphine ligand D-*t*-BPF with $Pd(OAc)_2$ under anhydrous conditions.



Scheme 3.

2. Experimental

2.1. General

The arylboronic acids, $Pd(OAc)_2$, ligands DPPF, D-*t*-BPF (purchased from Johnson Matthey), K_3PO_4 and anhydrous 1,4-dioxane, 2-MeTHF, were purchased from commercial sources and were used without additional purification. Reactions were monitored by HPLC and TLC (silica gel), and column chromatographic purifications were performed on 300 mesh silica gel. Proton and carbon NMR spectra were obtained at 500 MHz; chemical shifts (δ) were reported in parts per million, and coupling constants (J) are in hertz. All experiments were operated under a nitrogen atmosphere.

2.2. Typical procedure. The preparation of 4-amino-2-phenylpyrimidine-5-carbonitrile (4a)

To a round-bottom flask were added chloropyrimidine (1.0 g), the boronic acid (1.5 equiv), K_3PO_4 (2.0 equiv), dry 1,4-dioxane (30 mL) or 2-MeTHF (30 mL). The mixture was degassed by vacuum/N_2 cycle three times. Catalyst $Pd(OAc)_2$ (5 mol %) and D-*t*-BPF (5 mol %) were added and the mixture was degassed twice more. The mixture was heated to reflux temperature (~100 °C) for 4 h with vigorous stirring and HPLC confirmed the completion of the reaction. It was cooled to ambient temperature then the slurry was filtered to remove salt. The filter cake was washed with *i*-PrOAc. The filtrate was concentrated under vacuum to ca. 40 mL. To the solution was added *i*-PrOAc and 1 N NaOH aq to remove residual boronic acid. The organic layer was separated and then washed with fresh 1 N NaOH aq and 20% NaCl aq successively. After separation, the organic layer was evaporated to dryness. The product was purified by column chromatography on silica gel or crystallization using appropriate solvents (listed under individual compound headings, vide infra).

Compound **4a**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.74 (s, 1H, pyrimidine-H), 8.33 (d, J = 6.8, 8.5 Hz, 2H, Ar–H), 7.94 (br s, 2H, NH_2), 7.57–7.50 (m, 3H, Ar–H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.19, 162.98, 161.97, 136.83, 131.92, 128.90, 128.64, 116.11, 87.95; HRMS calcd for $C_{11}H_8N_4$ (M^++H), 197.0827. Found, 197.0819.

Compound **4b**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.25 (dd, J = 6.4, 8.8 Hz, 1H, Ar–H), 8.25 (dd, J = 7.8, 8.8 Hz, 1H, Ar–H), 8.25 (dd, J = 5.5, 7.8 Hz, 1H, Ar–H), 7.46 (d, J = 6.4 Hz, 1H, Ar–H), 7.45 (s, 1H,

pyrimidine-H), 7.45 (d, $J = 5.5$ Hz, 1H, Ar–H), 7.33 (s, 2H, NH_2); ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.07, 159.02, 153.94, 153.85, 145.89, 143.85, 139.97, 139.82, 137.70, 130.20; HRMS calcd for $C_{10}H_8FN_3$ (M^++H), 190.0780. Found, 190.0805.

Compound **4c**: crystallized from *i*-PrOAc/*n*-heptane. ^1H NMR (500 MHz, DMSO-d_6): δ 8.36 (d, $J = 7.1$ Hz, 2H, Ar–H), 8.35 (br s, 2H, NH_2), 7.59 (dd, $J = 7.0$, 7.4 Hz, 1H, Ar–H), 7.54 (dd, $J = 7.0$, 7.4 Hz, 2H, Ar–H), 4.12 (s, 3H, OMe); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.02, 162.98, 158.87, 136.07, 132.32, 128.96, 128.90, 114.26, 55.21; HRMS calcd for $C_{11}H_{10}N_4O_3$ (M^++H), 247.0831. Found, 247.0857.

Compound **4d**: crystallized from ^{i}PrOAc/*n*-heptane. ^1H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, $J = 8.8$ Hz, 1H, Ar–H), 8.44 (d, $J = 7.9$ Hz, 1H, Ar–H), 7.50–7.42 (m, 3H, Ar–H), 7.31 (s, 1H, quinazoline-H), 6.92 (s, 1H, quinazoline-H), 5.56 (s, 3H, OMe), 4.02 (s, 3H, OMe); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.12, 159.82, 155.01, 148.95, 148.40, 138.75, 129.81, 128.38, 128.02, 107.95, 106.92, 100.21, 56.27, 56.16; HRMS calcd for $C_{10}H_{11}N_3O_2$ (M^++H), 282.1243. Found, 282.1238.

Compound **4e**: ^1H NMR (500 MHz, $CDCl_3$): δ 8.16–8.13 (m, 1H), 7.71–7.67 (m, 2H), 7.53–7.28 (m, 3H), 7.11–7.02 (m, 2H), 3.84 (br s, 2H, NH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.43, 140.44, 140.33, 139.05, 129.20, 128.86, 128.62, 123.45, 123.06; HRMS calcd for $C_{11}H_{10}N_2$ (M^++H), 171.0922. Found, 171.0938.

Compound **4f**: ^1H NMR (500 MHz, DMSO-d_6): δ 8.15 (d, $J = 2.7$ Hz, 1H, Ar–H), 8.09 (d, $J = 9.0$ Hz, 1H, Ar–H), 8.00 (d, $J = 3.3$ Hz, 1H, Ar–H), 8.00 (d, $J = 7.2$ Hz, 1H, Ar–H), 7.74 (dd, $J = 2.7$ Hz, 1H, Ar–H), 7.59–7.52 (m, 3H, Ar–H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 176.50, 149.92, 138.20, 131.77, 130.43, 129.59, 129.09, 127.03, 126.34, 125.73; HRMS calcd for $C_{11}H_{10}N_2$ (M^++H), 171.0922. Found, 171.0911.

Compound **4g**: ^1H NMR (500 MHz, DMSO-d_6): δ 6.98 (d, $J = 8.5$ Hz, 1H, Ar–H), 3.50 (br s, 2H, NH_2); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.90, 144.33, 131.42, 129.61, 127.55, 112.14, 110.39; HRMS calcd for $C_{11}H_{10}N_2$ (M^++H), 171.0922. Found, 171.0948.

Compound **4h**: ^1H NMR (500 MHz, $CDCl_3$): δ 8.32 (d, $J = 2.4$ Hz, 1H, pyridine-H), 7.67 (dd, $J = 8.5$ Hz, 1H, pyridine-H), 7.51 (d, $J = 8.7$ Hz, 1H, Ar–H), 7.50 (d, $J = 7.8$ Hz, 1H, Ar–H), 7.43 (d, $J = 7.6$ Hz, 1H, Ar–H), 7.41 (d, $J = 7.9$ Hz, 1H, Ar–H), 7.31 (t, $J = 7.4$ Hz, 1H, Ar–H), 6.58 (d, $J = 8.5$ Hz, 1H, pyridine-H), 4.50 (s, 2H, NH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.60, 146.43, 138.33, 136.57, 128.90, 127.43, 126.90, 126.30, 108.50; HRMS calcd for $C_{11}H_{10}N_2$ (M^++H), 171.0922. Found, 171.0933.

Compound **4i**: ^1H NMR (500 MHz, DMSO-d_6): δ 8.09 (d, $J = 5.5$ Hz, 1H, pyridine-H), 7.91 (d, $J = 8.5$ Hz, 1H, Ar–H), 7.91 (d, $J = 7.1$ Hz, 1H, Ar–H), 7.45–7.36 (m, 3H, Ar–H), 7.00 (d, $J = 2.1$ Hz, 1H, pyridine-H), 6.46 (dd, $J = 2.1$, 5.5 Hz, 1H, pyridine-H), 6.05 (s, 2H, NH_2); ^{13}C NMR (125 MHz, DMSO-d_6) δ 156.09, 155.01, 149.39, 139.68, 128.35, 128.26, 126.08, 107.76, 104.88; HRMS calcd for $C_{11}H_{10}N_2$ (M^++H), 171.0922. Found, 171.1002.

Compound **6**: crystallized from *i*-PrOAc/*n*-heptane. ^1H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, $J = 8.9$ Hz, 1H, Ar–H), 7.57 (d, $J = 7.7$, 8.8 Hz, 2H, Ar–H), 7.18–7.40 (m, 3H, Ar–H), 6.98 (d, $J = 1.9$ Hz, 1H, Ar–H), 6.93 (dd, $J = 1.9$, 8.9 Hz, 1H, Ar–H), 6.15 (s, 2H, NH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.57, 144.87, 138.93, 131.44, 128.98, 128.89, 127.17, 126.85, 116.55, 116.41; HRMS calcd for $C_{12}H_{10}N_2O_2$ (M^++H), 215.0821. Found, 215.0829.

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References and notes

1. (a) Criscione, L.; de Gasparo, M.; Buhlmayer, P.; Whitebread, S.; Ramjoue, H. P.; Wood, J. *Br. J. Pharmacol.* **1993**, *110*, 761–771; (b) Markham, A.; Goa, K. L. *Drugs* **1997**, *54*, 299; (c) Capdeville, R.; Buchdunger, E.; Zimmermann, J.; Matter, A. *Nat. Rev. Drug Discovery* **2002**, *1*, 493–502; (d) Boren, J.; Cascante, M.; Marin, S.; Comin-Anduix, B.; Centelles, J. J.; Lim, S.; Bassilian, S.; Ahmed, S.; Lee, W. N.; Boros, L. G. *J. Biol. Chem.* **2001**, *276*, 37747.
2. Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1470.
3. (a) Stille, J. K. *Angew. Chem., Int. Ed.* **1986**, *25*, 508–524; (b) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1997**, *50*, 1; (c) Mitchell, T. N. In *Metal-catalyzed Cross-coupling Reactions*; Diedrich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998, p 167.
4. (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483; (b) Suzuki, A. In *Metal-catalyzed Cross-coupling Reactions*; Diedrich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998, p 49; (c) Miyaura, N. *Adv. Organomet. Chem.* **1998**, *6*, 187.
5. (a) Thompson, A. E.; Hughes, G.; Batsanov, A. S.; Bryce, M. R.; Parry, P. R.; Tarbit, B. *J. Org. Chem.* **2005**, *70*, 388–390; (b) Gunda, P.; Russon, L. M.; Lakshman, M. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 6372–6377; (c) Agrofoglio, L. A.; Gillaizeau, I.; Saito, Y. *Chem. Rev.* **2003**, *103*, 1875–1916; (d) Thompson, W. J.; Jones, J. H.; Lyle, P. A.; Thies, J. E. *J. Org. Chem.* **1988**, *53*, 2052–2055; (e) Gronowitz, S.; Hoernfeldt, A. B.; Yang, Y. H. *Chem. Chem. Scr.* **1986**, *26*, 311–314.
6. Meier, P.; Legraverant, S.; Müller, S.; Schaub, J. *Synthesis* **2003**, *4*, 551–554.
7. Itoh, T.; Sato, K.; Mase, T. *Adv. Synth. Catal.* **2004**, *346*, 1859–1867.
8. Sielecki, T. M.; Johnson, T. L.; Liu, J.; Muckelbauer, J. K.; Grafstrom, R. H.; Cox, S.; Boylan, J.; Burton, C. R.; Chen, H.; Smallwood, A.; Chang, C.-H.; Boisclair, M.; Benfield, P. A.; Trainor, G. L.; Seitz, S. P. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 1157–1160.
9. Gautheron, C. V.; Ple, M.; Turck, A.; Queguiner, G. *Tetrahedron* **2000**, *56*, 5499–5507.

10. Caron, S.; Massett, S. S.; Bogle, D. E.; Castaldi, M. J.; Braish, T. F. *Org. Process Res. Dev.* **2001**, *5*, 254–256; Miller, J. A.; Farrell, R. P. *Tetrahedron Lett.* **1998**, *39*, 6441–6444.
11. The direct synthesis of 3-amino-2-phenylpyridine by using palladium charcoal was reported. Tagata, T.; Nishida, M. *J. Org. Chem.* **2003**, *68*, 9412–9415.
12. Recently, the coupling of 2-amino-5-bromopyridine with phenylboronic acid in the presence of a palladium–tetraphosphine catalyst has been reported. Feuerstein, M.; Doucet, H.; Santelli, M. *J. Organomet. Chem.* **2003**, *687*, 327–336.
13. Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 7240–7241.
14. Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 7369–7370.
15. Lakshman, M. K.; Hilmer, J. H.; Martin, J. Q.; Keeler, J. C.; Dinh, Y. Q. V.; Ngassa, F. N.; Russon, L. M. *J. Am. Chem. Soc.* **2001**, *123*, 7779–7787.
16. Western, E. C.; Daft, J. R.; Johnson, E. M., II; Gannett, P. M.; Shaughnessy, K. H. *J. Org. Chem.* **2003**, *68*, 6767–6774.
17. van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741–2769.
18. Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158–163.
19. Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **1998**, 155–157.
20. (a) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441–12453; (b) Morita, D. K.; Stille, J. K.; Norton, J. R. *J. Am. Chem. Soc.* **1995**, *117*, 8576–8581.