DOI: 10.1002/ejoc.201101409

Synthesis of Biaryls through a One-Pot Tandem Borylation/Suzuki–Miyaura Cross-Coupling Reaction Catalyzed by a Palladacycle

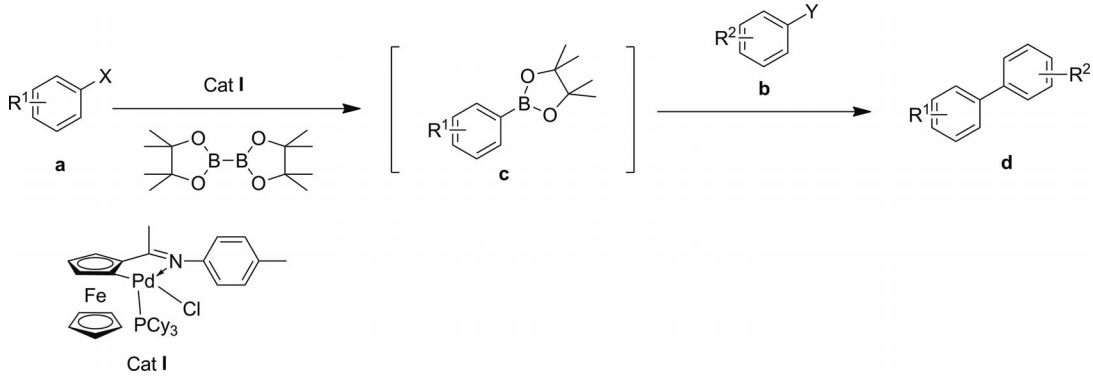
Lianhui Wang,[a,b] Xiuling Cui,*[a] Jingya Li,[b] Yusheng Wu,[b] Zhiwu Zhu,[a] and Yangjie Wu*[a]

Keywords: Cross-coupling / Halides / Borylation / Palladium / Biaryls

The tricyclohexylphosphane adduct of cyclopalladated ferrocenylimine **I** exhibited high catalytic activity in the one-pot borylation/Suzuki–Miyaura coupling (BSC) reaction with low catalyst loading (2 mol-%). Various biaryls were obtained in good to excellent yields for 37 examples. This process was applied to aryl and heteroaryl halides (Br and Cl) containing a variety of functional groups and did not require an excess amount of phosphane ligand and the addition of the palladium catalyst in the second step.

Introduction

Functionalized biaryls are important components of many medicinals and are employed as organic conductors or ligands for asymmetric catalysis.[1] The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of arylboronic acids or -boronates with aryl halides has shown to be the most common method to build such structures.[2] However, it is usually essential to prepare and isolate arylboronic acids or -boronate esters that are not commercially available prior to the coupling reaction, especially arylboronic acids or -boronate esters, which have complicated structures. Miyaura et al.[3] reported the first palladium-catalyzed one-pot borylation/Suzuki–Miyaura coupling (BSC) reaction for the synthesis of unsymmetrical biaryls, which involved converting an aryl triflate in situ into a boronate ester followed by the addition a second aryl triflate along with the palladium catalyst and base. Since then, the development of catalytic C–H[4] or C–X[5–7] borylation/Suzuki–Miyaura coupling processes in one pot has allowed for the preparation of unsymmetrical biaryls. This protocol has been applied to the syntheses of pharmaceuticals.[8] However, a high loading of catalyst (5–10 mol-%) and the addition of a second portion of the palladium catalyst are necessary.



Scheme 1. Palladium-catalyzed BSC coupling reaction.

Recently, Buchwald et al.[9] reported that $Pd_2(dba)_3$ and XPhos actively combine to catalyze efficiently the one-pot BSC reaction without adding a second portion of the catalyst prior to conducting the Suzuki–Miyaura reaction. In this process, an excess amount of the phosphane ligand (P/Pd, 4:1) was required.

In our laboratory, we found that cyclopalladated ferrocenylimine **I** was successfully employed in the borylation

[a] Department of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities Zhengzhou University, Zhengzhou 450052, P. R. China
E-mail: cuixl@zzu.edu.cn
wyj@zzu.edu.cn
[b] Tetranov Biopharm, Inc.
Zhengzhou 450052, P. R. China
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201101409.

of aryl halides and the one-pot BSC reaction to synthesize symmetrical biaryls.[10] Herein, we employ cyclopalladated ferrocenylimine **I** as a catalyst in the one-pot BSC reaction to synthesize unsymmetrical biaryls without an excess amount of phosphane ligand and the addition of catalyst in the second step. The results reveal that palladacycle **I** not only effected a highly efficient borylation reaction, but also maintained its catalytic activity in the subsequent Suzuki–Miyaura coupling by using only 2 mol-% of catalyst loading (Scheme 1).

Results and Discussion

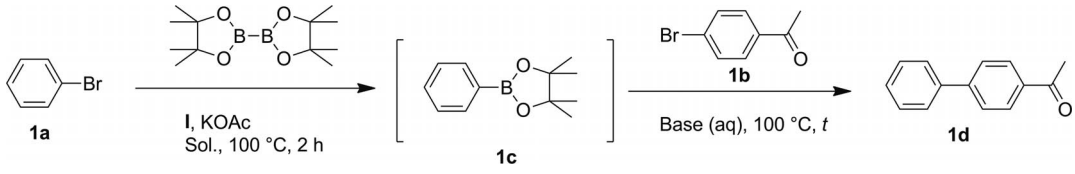
In our previous study,[10a] the efficient reaction conditions for the borylation of aryl halides catalyzed by palladacycle **I** were well developed. Under such optimized reaction conditions, the reaction of aryl bromides with bis(pinacolato)diboron quantitatively provided the arylboronate esters in only 2 h. In this endeavor, the one-pot borylation/Suzuki–Miyaura coupling reaction of bromobenzene (**1a**) with 1-(4-bromophenyl)ethanone (**1b**) was initially chosen as a model to screen the different reaction parameters for the second step, such as the base, solvent, and reaction time (see Table 1). After bromobenzene was completely consumed, a stronger base was required to promote the Suzuki–Miyaura coupling. Yields of 92%, 85%, 88%, and 90% were obtained when K_3PO_4, K_2CO_3, Cs_2CO_3, and NaO*t*Bu were used, respectively, as the base (Table 1, Entries 1–4). The solvent 1,4-dioxane was suitable for both the borylation and the Suzuki–Miyaura reactions (Table 1, Entries 1–5 and 10).[10a] The yield decreased to 68% from 92% when 1.0 equiv. of bromobenzene (**1a**) was used (Table 1, Entry 1 vs. 2). When the reaction time was prolonged from 3 h to 15 h, the yield did not improve significantly (Table 1, Entry 10 vs. 2).

Under the optimized reaction conditions (Table 1, Entry 2) and by using bromobenzene (**1a**) as the aryl halide, the scope of the substrates **b** was investigated. The total yields for the borylation/Suzuki–Miyaura reactions depend mainly on the Suzuki–Miyaura coupling, as bromobenzene (**1a**) can be quantitatively converted into the boronate ester. As illustrated in Table 2, **I** exhibited high catalytic activity for both aryl bromides and chlorides and tolerated a number of functionalities, such as nitro, cyano, acetyl, and amino groups. Electron-rich, electron-deficient, and relatively hindered aryl bromides afforded good to excellent yields in 3 h (Table 2, Entries 1–6). In addition, aryl chlorides with both electron-withdrawing and electron-donating groups provided unsymmetrical biaryls in moderate to excellent isolated yields when the reaction time was prolonged to 15 h (Table 2, Entries 7–10). It is worth noting that this protocol avoided the α-arylation reaction of ketones with arylboronate esters (Table 2, Entries 1, 3, and 7), and a 95% isolated yield was achieved with 3-chloroaniline (**10b**) without the additional amino group protection (Table 2, Entry 10).

Next, we evaluated heteroaryl halides as substrates for the BSC procedure with bromobenzene (**1a**) under the standard reaction conditions. The results (see Table 3) show that the heteroaryl halide could be employed as the substrate in both steps. For most cases, good yields were obtained when pyridyl bromide served as the second substrate (Table 3, Entries 1–8). Such a protocol was also applied to heteroaryl chlorides. 4-Chloropicolinonitrile (**18b**) and 2-chloro-6-phenylpyrazine (**19b**) provided the desired products in yields of 80% and 93%, respectively (Table 3, Entries 9 and 10).

When 3-bromopyridine (Table 3, Entry 1 vs. 11), 5-bromo-*N*,*N*-dimethylpyridin-2-amine (Table 3, Entry 2 vs. 12), and 5-bromopyridin-2-amine (Table 3, Entry 3 vs. 13) served as substrates in the first step and the reaction time

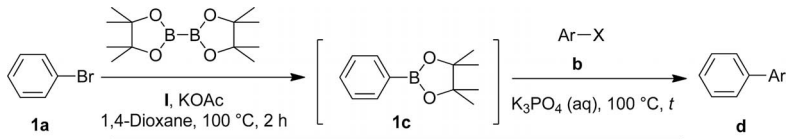
Table 1. Screening of bases and solvents for palladium-catalyzed BSC reaction.[a]

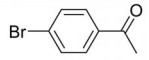
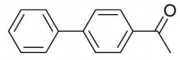
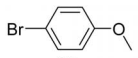
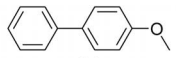
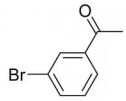
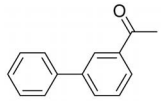
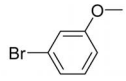
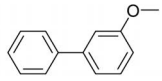
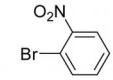
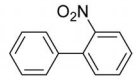
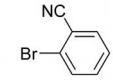
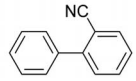
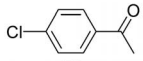
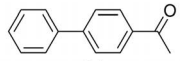
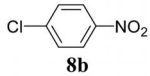
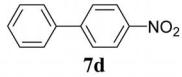
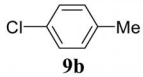
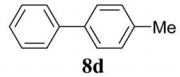
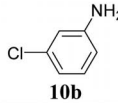
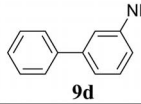


Entry	Base	Solvent	*t* [h]	Yield [%][b]
1	K_3PO_4	dioxane	3	68[c]
2	K_3PO_4	dioxane	3	92
3	K_2CO_3	dioxane	3	85
4	Cs_2CO_3	dioxane	3	88
5	NaO*t*Bu	dioxane	3	90
6	K_3PO_4	toluene	3	88
7	K_3PO_4	DMF[d]	3	84
8	K_3PO_4	THF[d]	3	32
9	K_3PO_4	DME[d]	3	82
10	K_3PO_4	dioxane	15	93

[a] Reagents and conditions: bromobenzene (**1a**, 1.2 equiv.), 1-(4-bromophenyl)ethanone (**1b**, 1.0 mmol), bis(pinacolato)diborane (1.44 equiv.), KOAc (2.4 equiv.), base (5 equiv.), solvent (2.5 mL), **I** [2 mol-% based on bromobenzene (**1a**)]. [b] Isolated yields based on 1-(4-bromophenyl)ethanone (**1b**). [c] The ratio of **1a**/**1b** is 1:1. [d] DMF = dimethylformamide, THF = tetrahydrofuran, DME = 1,2-dimethoxyethane.

Table 2. Palladium-catalyzed BSC reaction of aryl halides with bromobenzene (**1a**).[a]



Entry	Ar–X	*t* [h]	Ph–Ar	Yield [%][b]
1	 **1b**	3	 **1d**	92
2	 **2b**	3	 **2d**	86
3	 **3b**	3	 **3d**	77
4	 **4b**	3	 **4d**	85
5	 **5b**	3	 **5d**	84
6	 **6b**	3	 **6d**	82
7	 **7b**	15	 **1d**	70
8	 **8b**	15	 **7d**	87
9	 **9b**	15	 **8d**	76
10	 **10b**	15	 **9d**	95

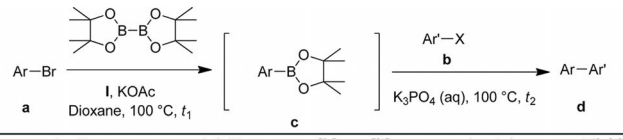
[a] Reagents and conditions: bromobenzene (**1a**, 1.2 equiv.), Ar–X (1.0 equiv.), bis(pinacolato)diborane (1.44 equiv.), KOAc (2.4 equiv.), K_3PO_4 (5 equiv.), 1,4-dioxane (2.5 mL), **I** [2 mol-% based on bromobenzene (**1a**)]. [b] Isolated yields based on Ar–X.

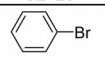
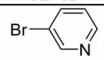
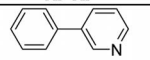
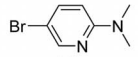
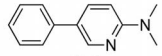
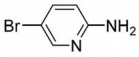
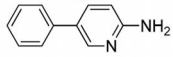
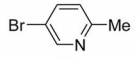
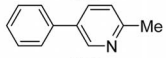
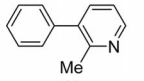
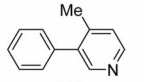
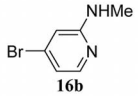
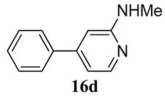
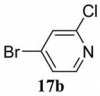
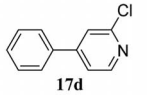
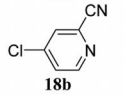
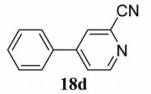
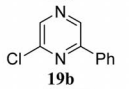
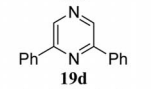
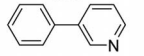
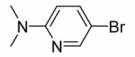
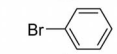
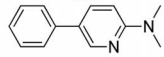
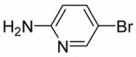
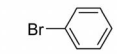
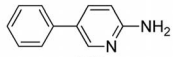
was prolonged from 2 h to 6 h, the yields improved. In contrast, when 5-bromo-2-methylpyridine (Table 3, Entry 4 vs. 14), 3-bromo-2-methylpyridine (Table 3, Entry 5 vs. 15), 3-bromo-4-methylpyridine (Table 3, Entry 6 vs. 16), and 4-bromo-*N*-methylpyridin-2-amine (Table 3, Entry 7 vs. 17) were used as substrates in the first step, the yields decreased dramatically, because of the low conversion in the borylation step.

Subsequently, we investigated the BSC coupling reaction between heteroaryl halides to synthesize unsymmetrical heteroaryls (Table 4). In all cases, the reaction of 3-bromopyridine (**2a**) and 4-bromo-2-methoxypyridine (**3a**) with pyridyl halides functionalized by electron-withdrawing (such as CN) and electron-donating groups (such as Me, MeO, and NHMe) gave good to excellent yields. Moreover, bulky functional groups on the pyridine ring did not significantly affect the yields. For example, 3-bromopyridine coupled with 3-bromo-2-methylpyridine (Table 4, Entry 2) and 3-bromo-4-methylpyridine (Table 4, Entry 3) gave the desired products in 81% and 82% yields, respectively. 2-Bromopyridine and its derivatives are generally considered as less active substrates in both the borylation and Suzuki–Miyaura reactions. To our delight, 73% and 78% isolated yields were achieved with 2-bromopyridine (**20b**, Table 4, Entry 8) and 2-bromo-6-methoxypyridine (**21b**, Table 4, Entry 10), respectively. However, low yields were obtained when indolyl, furyl, and thiophenyl bromides were utilized as the substrates.

To clarify the influence of the substituent in the substrates in the BSC reaction, control experiments were performed (Table 5). When 1-bromo-4-methoxybenzene (**2b**) and 1-bromo-4-(trifluoromethyl)benzene (**22b**) served as

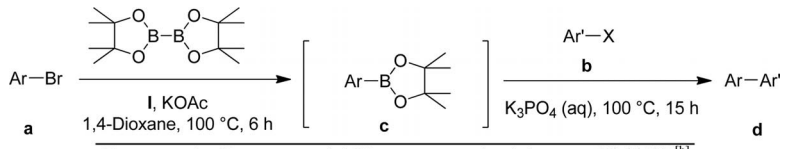
Table 3. Palladium-catalyzed BSC reaction of heteroaryl halides with aryl bromides.[a]



Entry	Ar–Br	Ar'–X	t_1 [h]	t_2 [h]	Ar–Ar'	Yield [%][b]
1	 **1a**	 **2a**	2	15	 **10d**	78
2	 **1a**	 **11b**	2	15	 **11d**	65
3	 **1a**	 **12b**	2	15	 **12d**	80
4	 **1a**	 **13b**	2	15	 **13d**	81
5	 **1a**	 **14b**	2	6	 **14d**	83
6	 **1a**	 **15b**	2	15	 **15d**	72
7	 **1a**	 **16b**	2	15	 **16d**	89
8	 **1a**	 **17b**	2	15	 **17d**	77
9	 **1a**	 **18b**	2	15	 **18d**	80
10	 **1a**	 **19b**	2	15	 **19d**	93
11	 **2a**	 **1a**	6	15	 **10d**	85
12	 **11b**	 **1a**	6	15	 **11d**	92
13	 **12b**	 **1a**	6	15	 **12d**	98
14	**13b**	**1a**	6	15	**13d**	39
15	**14b**	**1a**	6	15	**14d**	47
16	**15b**	**1a**	6	15	**15d**	32
17	**16b**	**1a**	6	15	**16d**	45
18	**17b**	**1a**	6	15	**17d**	70

[a] Reagents and conditions: Ar–Br (1.2 equiv.), Ar′–X (1.0 equiv.), bis(pinacolato)diborane (1.44 equiv.), KOAc (2.4 equiv.), K_3PO_4 (5 equiv.), 1,4-dioxane (2.5 mL), **I** (2 mol-% based on Ar–Br). [b] Isolated yield based on Ar′–X.

Table 4. Palladium-catalyzed one-pot BSC reaction of heteroaryl halides.[a]



Entry	Ar–Br	Ar'–X	Ar–Ar'	Yield [%][b]
1	**2a**	**11b**	**20d**	74
2	**2a**	**14b**	**21d**	81
3	**2a**	**15b**	**22d**	82
4	**2a**	**16b**	**23d**	90
5	**2a**	**17b**	**24d**	78
6	**2a**	**3a**	**25d**	92
7	**2a**	**18b**	**26d**	86
8	**2a**	**20b**	**27d**	73
9	**3a**	**16b**	**28d**	91
10	**3a**	**21b**	**29d**	78

[a] Reagents and conditions: Ar–Br (1.2 equiv.), Ar′–X (1.0 equiv.), bis(pinacolato)diborane (1.44 equiv.), KOAc (2.4 equiv.), K_3PO_4 (5 equiv.), 1,4-dioxane (2.5 mL), **I** (2 mol-% based on Ar–Br). [b] Isolated yield based on Ar′–X.

substrates for the first and the second step, respectively, a 95% yield was obtained (Table 5, Entry 2). In contrast, a lower yield of 87% was afforded (Table 5, Entry 1) when the experiment was changed to have **2b** and **22b** serve as substrates in the second and first step, respectively. These results suggest that the electron-donating group in substrate **a** and an electron-withdrawing group in substrate **b** would favor a BSC reaction catalyzed by **I**. Nevertheless, this reasoning did not apply to sterically hindered substrates such as **23b** and **6b**. Compound **6b** afforded the desired product in 91% yield, when it served as the substrate in the first step (Table 5, Entry 4), but the addition of **23b** as the substrate for the first step only gave a 47% yield (Table 5, Entry 3), because of the difficulty in forming the boronate from sterically hindered substrates.

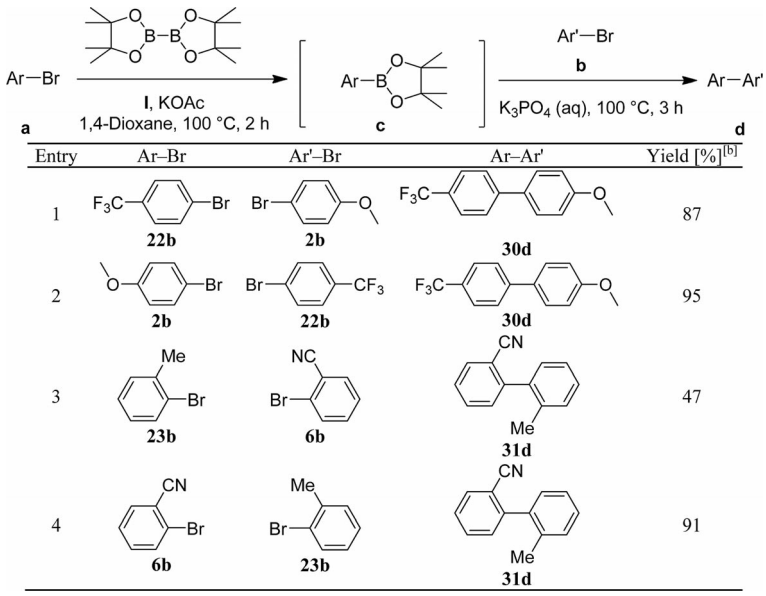
Conclusions

Cyclopalladated ferrocenylimine **I** was highly effective for catalyzing the BSC reaction. Various functionalized unsymmetrical biaryls have been obtained in good to excellent yields in one pot with 2 mol-% loading of complex **I** without an excess amount of ligand and the addition of catalyst in the second step. Such methodology tolerated not only a number of functional groups, such as primary amines, carbonyl groups, and nitriles, but also was applied to substrates such as aryl bromides and chlorides and heteroaryl halides.

Experimental Section

General Methods: ^1H and ^{13}C NMR spectroscopic data were recorded with a Bruker DPX 400 instrument by using $CDCl_3$ as the

Table 5. Control experiments to examine the influence of substituent in substrates on the palladium-catalyzed BSC reaction.[a]



[a] Reagents and conditions: Ar–Br (1.2 equiv.), Ar′–Br (1.0 equiv.), bis(pinacolato)diborane (1.44 equiv.), KOAc (2.4 equiv.), K_3PO_4 (5 equiv.), 1,4-dioxane (2.5 mL), **I** (2 mol-% based on Ar–Br). [b] Isolated yield based on Ar′–Br.

solvent and tetramethylsilane (TMS) as the internal standard. All coupling constants (*J*) are reported in Hertz (Hz). Melting points were measured with an XT4A microscopic apparatus. High-resolution mass spectra were recorded with a Waters Q-Tof micro spectrometer by using electrospray ionization (ESI). Preparative TLC was performed on silica gel plates and developed with ethyl acetate/petroleum ether. All solvents were dried according to standard methods. Aryl halides **a** and **b** and bis(pinacolato)diborane were obtained from commercial sources and were generally used without further purification. Cyclopalladated ferrocenylimine **I** was synthesized according to the reported procedure.[11,12]

General Procedure for Palladium-Catalyzed One-Pot Preparation of Unsymmetrical Biaryls: A Schlenk tube (10 mL) was charged with cyclopalladated ferrocenylimine **I** (8.9 mg, 0.012 mmol) in 1,4-dioxane (2.0 mL) followed by the addition of the first aryl halide **a** (0.60 mmol), KOAc (118 mg, 1.2 mmol), and bis(pinacolato)diborane (182 mg, 0.72 mmol). The reaction mixture under nitrogen was heated to reflux for 2 or 6 h. After the mixture had been cooled to room temperature, the second aryl halide **b** (0.50 mmol) in 1,4-dioxane (0.50 mL) and base (5 M aqueous solution, 0.50 mL) were added to the reaction mixture under nitrogen. The reaction mixture was heated to reflux for another 3 or 15 h, cooled to room temperature, and then diluted with diethyl ether. The mixture was washed with water (1×), and the organic layer was dried with Na_2SO_4. The solvent was removed under reduced pressure, and the crude material was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether).

1-(Biphenyl-4-yl)ethanone (1d): Table 2, Entry 1.[13] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) to afford a white solid (90 mg, 92%), m.p. 116–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–8.02 (m, 2 H, Ar), 7.70–7.68 (m, 2 H, Ar), 7.64–7.62 (m, 2 H, Ar), 7.49–7.45 (m, 2 H, Ar), 7.42–7.40 (m, 1 H, Ar), 2.64 (s, 3 H, CH_3) ppm.

4-Methoxybiphenyl (2d): Table 2, Entry 2.[14] Purified by flash chromatography on silica gel (petroleum ether) to afford a white solid (79 mg, 86%), m.p. 83–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.52 (m, 4 H, Ar), 7.43–7.40 (m, 2 H, Ar), 7.32–7.30 (m, 1 H, Ar), 6.99–6.97 (m, 2 H, Ar), 3.85 (s, 3 H, CH_3) ppm.

1-(Biphenyl-3-yl)ethanone (3d): Table 2, Entry 3.[15] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:40) to afford a colorless oil (76 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 1 H, Ar), 7.91 (d, *J* = 7.7 Hz, 1 H, Ar), 7.76 (d, *J* = 7.7 Hz, 1 H, Ar), 7.60 (d, *J* = 8.3 Hz, 2 H, Ar), 7.51 (t, *J* = 7.7 Hz, 1 H, Ar), 7.45 (t, *J* = 7.3 Hz, 2 H, Ar), 7.36 (t, *J* = 7.3 Hz, 1 H, Ar), 2.63 (s, 3 H, CH_3) ppm.

3-Methoxybiphenyl (4d): Table 2, Entry 4.[16] Purified by flash chromatography on silica gel (petroleum ether) to give a colorless oil (78 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.3 Hz, 2 H, Ar), 7.49 (t, *J* = 7.3 Hz, 2 H, Ar), 7.41–7.39 (m, 2 H, Ar), 7.25 (d, *J* = 8.0 Hz, 1 H, Ar), 7.19 (s, 1 H, Ar), 6.97 (dd, *J* = 8.2, 2.5 Hz, 1 H, Ar), 3.90 (s, 3 H, CH_3) ppm.

2-Nitrobiphenyl (5d): Table 2, Entry 5.[17] Purified by flash chromatography on silica gel (petroleum ether) to afford a yellow oil (85 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 7.6, 0.6 Hz, 1 H, Ar), 7.61 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1 H, Ar), 7.48–7.35 (m, 5 H, Ar), 7.35–7.33 (m, 2 H, Ar) ppm.

Biphenyl-2-carbonitrile (6d): Table 2, Entry 6.[18] Purified by flash chromatography on silica gel (petroleum ether) to afford a colorless oil (74 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (dd, *J* = 7.7, 1.2 Hz, 1 H, Ar), 7.56–7.54 (m, 1 H, Ar), 7.50–7.47 (m, 2 H, Ar), 7.46–7.41 (m, 5 H, Ar) ppm.

4-Nitrobiphenyl (7d): Table 2, Entry 8.[19] Purified by flash chromatography on silica gel (petroleum ether) to afford a yellow solid (87 mg, 87%), m.p. 109–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (dd, *J* = 6.6, 1.6 Hz, 2 H, Ar), 7.74 (dd, *J* = 8.8, 1.9 Hz, 2 H, Ar), 7.63 (dd, *J* = 7.0, 1.5 Hz, 2 H, Ar), 7.50–7.48 (m, 2 H, Ar), 7.46–7.44 (m, 1 H, Ar) ppm.

4-Methylbiphenyl (8d): Table 2, Entry 9.[20] Purified by flash chromatography on silica gel (petroleum ether) to afford a colorless solid (64 mg, 76%), m.p. 42–43 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (dd, *J* = 8.4, 1.3 Hz, 2 H, Ar), 7.49 (d, *J* = 8.1 Hz, 2 H,

Ar), 7.42 (t, J = 7.4 Hz, 2 H, Ar), 7.33–7.31 (m, 1 H, Ar), 7.24 (m, 2 H, Ar), 2.39 (s, 3 H, CH_3) ppm.

Biphenyl-3-amine (9d): Table 2, Entry 10.[21] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:7) to afford a colorless oil (80 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, J = 8.4 Hz, 2 H, Ar), 7.41 (t, J = 7.8 Hz, 2 H, Ar), 7.33 (d, J = 7.2 Hz, 1 H, Ar), 7.24–7.20 (m, 1 H), 6.98 (d, J = 7.6 Hz, 1 H, Ar), 6.66 (s, 1 H, Ar), 6.58 (dd, J = 7.8, 2.1 Hz, 1 H, Ar), 3.63 (br., 2 H, NH_2) ppm.

3-Phenylpyridine (10d): Table 3, Entry 11.[13] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) to afford a colorless oil (66 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (s, 1 H, pyridine-H), 7.58 (d, J = 3.7 Hz, 1 H, pyridine-H), 7.85 (d, J = 7.8 Hz, 1 H, pyridine-H), 7.57 (d, J = 7.3 Hz, 2 H, Ar), 7.46 (t, J = 7.2 Hz, 2 H, Ar), 7.39 (d, J = 7.2 Hz, 1 H, pyridine-H), 7.35 (m, 1 H) ppm.

***N*,*N*-Dimethyl-5-phenylpyridin-2-amine (11d):** Table 3, Entry 12.[22] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) to afford a white solid (92 mg, 92%), m.p. 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 2.2 Hz, 1 H, pyridine-H), 7.70 (dd, J = 8.8, 2.4 Hz, 1 H, pyridine-H), 7.51 (d, J = 7.4 Hz, 2 H, Ar), 7.40 (t, J = 7.4 Hz, 2 H, Ar), 7.30–7.25 (m, 1 H, Ar), 6.58 (d, J = 8.8 Hz, 1 H, pyridine-H), 3.13 (s, 6 H, NMe_2) ppm.

5-Phenyl-2-pyridinamine (12d): Table 3, Entry 13.[23] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:1) to afford a white solid (83 mg, 98%), m.p. 128–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, J = 2.1 Hz, 1 H, pyridine-H), 7.67 (dd, J = 8.5, 2.4 Hz, 1 H, pyridine-H), 7.51–7.49 (m, 2 H, Ar), 7.44–7.40 (m, 2 H, Ar), 7.33–7.31 (m, 1 H, Ar), 6.58 (d, J = 8.3 Hz, 1 H, pyridine-H), 4.08 (br., 2 H, NH_2) ppm.

2-Methyl-5-phenylpyridine (13d): Table 3, Entry 4.[24] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:20) to afford a colorless oil (69 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, J = 2.2 Hz, 1 H, pyridine-H), 7.78 (dd, J = 8.0, 2.4 Hz, 1 H, pyridine-H), 7.58–7.56 (m, 2 H, Ar), 7.47 (t, J = 7.8 Hz, 2 H, Ar), 7.41–7.39 (m, 1 H, Ar), 7.23 (d, J = 8.0 Hz, pyridine-H), 2.61 (s, 3 H, CH_3) ppm.

2-Methyl-3-phenylpyridine (14d): Table 3, Entry 5.[25] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) to afford a colorless oil (70 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (dd, J = 4.8, 1.6 Hz, pyridine-H), 7.50 (dd, J = 7.6, 1.6 Hz, 1 H, pyridine-H), 7.44–7.41 (m, 2 H, Ar), 7.37 (d, J = 7.2 Hz, pyridine-H), 7.30 (d, J = 8.3 Hz, Ar), 7.18–7.16 (m, 1 H, Ar), 2.50 (s, 3 H, CH_3) ppm.

4-Methyl-3-phenylpyridine (15d): Table 3, Entry 6.[26] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) to afford a colorless oil (61 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 4.5 Hz, 1 H, pyridine-H), 8.43 (s, 1 H, pyridine-H), 7.46–7.44 (m, 2 H, Ar), 7.43 (d, J = 6.3 Hz, 1 H, Ar), 7.32–7.30 (m, 2 H, Ar), 7.18 (d, J = 4.9 Hz, 1 H, pyridine-H), 2.28 (s, 3 H, CH_3) ppm.

***N*-Methyl-4-phenylpyridin-2-amine (16d):** Table 3, Entry 7. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 2:1) to afford a white solid (82 mg, 89%), m.p. 106–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 5.3 Hz, 1 H, pyridine-H), 7.61–7.55 (m, 2 H, Ar), 7.59–7.40 (m, 3 H, Ar), 6.81 (dd, J = 5.3, 1.4 Hz, 1 H, pyridine-H), 6.56 (s, 1 H, pyridine-H), 4.64 (br., 1 H, NH), 2.98 (d, J = 4.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 149.9, 148.5, 139.2, 128.8, 126.9, 111.5, 103.8, 29.2 ppm. HRMS (ESI): calcd. for $C_{12}H_{13}N_2$ [M + H]$^+$ 185.1079; found 185.1081.

2-Chloro-4-phenylpyridine (17d): Table 3, Entry 8.[27] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) to afford a white solid (73 mg, 77%), m.p. 58–59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 5.2 Hz, 1 H, pyridine-H), 7.61 (dd, J = 8.1, 1.9 Hz, 2 H, Ar), 7.54 (s, 1 H, pyridine-H), 7.50–7.48 (m, 3 H, Ar), 7.42 (m, 1 H, pyridine-H) ppm.

4-Phenyl-2-pyridinecarbonitrile (18d): Table 3, Entry 9. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) to afford a pale yellow solid (72 mg, 80%), m.p. 92–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, J = 4.9 Hz, 1 H, pyridine-H), 7.91 (s, 1 H, pyridine-H), 7.72 (dd, J = 5.2, 1.8 Hz, 1 H, pyridine-H), 7.64–7.62 (m, 2 H, Ar), 7.54–7.52 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 147.2, 133.3, 131.9, 127.6, 124.4, 123.8, 122.0, 114.7 ppm. HRMS (ESI): calcd. for $C_{12}H_{13}N_2$ [M + H]$^+$ 181.0766; found 181.0764.

2,6-Diphenylpyrazine (19d): Table 3, Entry 10.[28] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) to afford a white solid (108 mg, 93%), m.p. 85–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (s, 2 H, pyrazine-H), 8.07 (d, J = 3.4 Hz, 4 H, Ar), 7.48–7.41 (m, 6 H, Ar) ppm.

***N*,*N*-Dimethyl-3,3′-bipyridin-6-amine (20d):** Table 4, Entry 1. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:2) to afford a white solid (74 mg, 74%), m.p. 74–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 1 H, pyridine1-H), 8.53 (d, J = 3.9 Hz, pyridine1-H), 8.42 (s, 1 H, pyridine2-H), 7.81–7.78 (m, 1 H, pyridine1-H), 7.68 (dd, J = 8.8, 2.5 Hz, 1 H, pyridine1-H), 7.33 (dd, J = 7.8, 4.7 Hz, 1 H, pyridine2-H), 6.61 (d, J = 8.8 Hz, 1 H, pyridine2-H), 3.14 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 147.3, 147.0, 145.9, 135.4, 134.1, 132.9, 123.4, 120.6, 105.7, 37.9 ppm. HRMS (ESI): calcd. for $C_{12}H_{14}N_3$ [M + H]$^+$ 200.1188; found 200.1188.

2-Methyl-3,3′-bipyridine (21d): Table 4, Entry 2. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:1) to afford a colorless oil (69 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J = 7.2 Hz, 1 H, pyridine2-H), 8.60 (s, 1 H, pyridine 1-H), 8.55 (dd, J = 4.8, 1.3 Hz, 1 H, pyridine1-H), 6.67 (d, J = 7.8 Hz, pyridine1-H), 7.41 (d, J = 4.9 Hz, 1 H, pyridine2-H), 7.24 (dd, J = 7.8, 4.8 Hz, 1 H, pyridine1-H), 2.52 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 149.6, 148.7, 148.7, 137.2, 136.3, 135.5, 133.2, 123.2, 121.2, 23.2 ppm. HRMS (ESI): calcd. for $C_{11}H_{11}N_2$ [M + H]$^+$ 171.0922; found 171.0919.

4-Methyl-3,3′-bipyridine (22d): Table 4, Entry 3. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 3:1) to afford a colorless oil (70 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J = 4.8 Hz, 1 H, pyridine1-H), 8.60 (s, 1 H, pyridine1-H), 8.50 (d, J = 4.8 Hz, 1 H, pyridine2-H), 8.43 (s, 1 H, pyridine2-H), 7.69–7.66 (m, 1 H, pyridine1-H), 7.43–7.40 (m, 1 H, pyridine1-H), 7.24 (d, J = 4.8 Hz, 1 H, pyridine2-H), 2.30 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7, 149.0, 148.8, 144.8, 136.5, 134.0, 133.5, 125.3, 123.2, 19.6 ppm. HRMS (ESI): calcd. for $C_{11}H_{11}N_2$ [M + H]$^+$ 171.0922; found 171.0923.

***N*-Methyl-3,4′-bipyridin-2′-amine (23d):** Table 4, Entry 4. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:1) to afford a white solid (83 mg, 90%), m.p. 70–71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (s, 1 H, pyridine1-H), 8.64 (d, J = 4.7 Hz, 1 H, pyridine1-H), 8.17 (d, J = 5.1 Hz, 1 H, pyridine2-H), 7.88 (dd, J = 7.8, 5.1 Hz, 1 H, pyridine1-H), 7.39–7.37 (m, 1 H, pyridine1-H), 6.77 (d, J = 5.1 Hz, 1 H, pyridine-H), 6.54 (s, 1 H, pyridine2-H), 4.98 (br., 1 H, NH), 2.98 (d, J = 4.8 Hz, CH_3)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 151.0, 150.3, 149.4, 148.1, 136.3, 135.7, 125.0, 112.4, 105.1, 30.5 ppm. HRMS (ESI): calcd. for $C_{11}H_{12}N_3$ $[M + H]^+$ 186.1031; found 186.1034.

2′-Chloro-3,4′-bipyridine (24d): Table 4, Entry 5. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:2) to afford a white solid (74 mg, 78%), m.p. 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (s, pyridine1-H), 8.72 (dd, J = 4.8, 1.4 Hz, 1 H, pyridine2-H), 8.49 (d, J = 5.5 Hz, 1 H, pyridine2-H), 7.91 (d, J = 7.8 Hz, 1 H, pyridine1-H), 7.55 (s, 1 H, pyridine2-H), 7.45–7.43 (m, 2 H, pyridine1-H, pyridine2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 150.7, 150.3, 148.3, 148.0, 134.3, 132.6, 123.8, 122.0, 120.3 ppm. HRMS (ESI): calcd. for $C_{10}H_8ClN_2$ $[M + H]^+$ 191.0376; found 191.0374.

2′-Methoxy-3,4′-bipyridine (25d): Table 4, Entry 6. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) to afford a white solid (86 mg, 92%), m.p. 30–31 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (s, 1 H, pyridine1-H), 8.64 (d, J = 4.0 Hz, 1 H, pyridine1-H), 8.23 (d, J = 5.2 Hz, 1 H, pyridine1-H), 7.87 (d, J = 7.8 Hz, 1 H, pyridine2-H), 7.40–7.36 (m, 1 H, pyridine1-H), 7.07 (dd, J = 5.2, 0.7 Hz, 1 H, pyridine2-H), 6.92 (s, 1 H, pyridine2-H), 3.96 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 149.8, 147.9, 147.7, 147.5, 134.2, 133.8, 123.6, 114.9, 108.5, 53.5 ppm. HRMS (ESI): calcd for $C_{11}H_{11}N_2O$ $[M + H]^+$ 187.0871; found 187.0873.

3,4′-Bipyridine-2′-carbonitrile (26d): Table 4, Entry 7. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:1) to afford a white solid (78 mg, 86%), m.p. 177–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91 (s, 1 H, pyridine1-H), 8.82 (d, J = 4.8 Hz, 1 H, pyridine2-H), 7.77 (dd, J = 4.8, 1.5 Hz, 1 H, pyridine2-H), 7.93–9.72 (m, 2 H, pyridine1-H, pyridine2-H), 7.74 (dd, J = 5.2, 1.8 Hz, 1 H, pyridine1-H), 7.51–7.49 (m, 1 H, pyridine1-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2, 152.6, 149.4, 148.2, 136.3, 135.7, 133.2, 127.4, 125.9, 125.5, 118.4 ppm. HRMS (ESI): calcd. for $C_{11}H_8N_3$ $[M + H]^+$ 182.0718; found 182.0719.

2,3′-Bipyridine (27d): Table 4, Entry 8.[20] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) to afford a colorless oil (57 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (s, 1 H, pyridine1-H), 8.73 (d, J = 4.8 Hz, 1 H, pyridine1-H), 8.64 (d, J = 4.7 Hz, 1 H, pyridine1-H), 8.32 (d, J = 7.8 Hz, 1 H, pyridine2-H), 7.80–7.76 (m, 2 H, pyridine1-H, pyridine2-H), 7.41 (m, 1 H, pyridine2-H), 7.30–7.28 (m, 1 H, pyridine2-H) ppm.

2′-Methoxy-*N*-methyl-4,4′-bipyridin-2-amine (28d): Table 4, Entry 9. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) to afford a white solid (98 mg, 91%), m.p. 70–71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, J = 5.3 Hz, 1 H, pyridine2-H), 8.18 (d, J = 5.3 Hz, 1 H, pyridine2-H), 7.08 (dd, J = 5.3, 1.2 Hz, 1 H, pyridine1-H), 6.95 (s, 1 H, pyridine2-H), 6.78 (dd, J = 5.2, 1.2 Hz, 1 H, pyridine1-H), 6.55 (s, 1 H, pyridine1-H), 4.78 (br., 1 H, NH), 3.99 (s, 3 H, CH_3), 2.98 (d, J = 5.0 Hz, 3 H, NCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8, 159.1, 148.5, 147.9, 146.4, 146.2, 113.9, 109.9, 107.5, 102.6, 52.5, 28.1 ppm. HRMS (ESI): calcd. for $C_{12}H_{14}N_3O$ $[M + H]^+$ 216.1137; found 216.1137.

2′,6-Dimethoxy-2,4′-bipyridine (29d): Table 4, Entry 10. Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) to afford a white solid (84 mg, 78%), m.p. 56–57 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 5.4 Hz, 1 H, pyridine1-H), 7.58 (t, J = 8.2 Hz, 1 H, pyridine2-H), 7.42 (d, J = 5.4 Hz, 1 H, pyridine1-H), 7.34 (s, 1 H, pyridine1-H), 7.30 (d, J = 7.4 Hz, 1 H, pyridine2-H), 6.70 (d, J = 8.2 Hz, 1 H, pyridine2-H), 3.95 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 163.7, 151.7, 148.9, 147.1, 139.2, 114.3, 113.4, 111.3, 108.0, 53.5, 53.2 ppm. HRMS (ESI): calcd. for $C_{12}H_{13}N_2O_2$ $[M + H]^+$ 217.0977; found 217.0976.

4-Methoxy-4′-(trifluoromethyl)biphenyl (30d): Table 5, Entry 2.[29] Purified by flash chromatography on silica gel (petroleum ether) to afford a white solid (120 mg, 95%), m.p. 118–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.66 (m, 4 H, Ar), 7.57 (dd, J = 6.6, 2.1 Hz, 2 H, Ar), 7.03 (dd, J = 6.6, 2.1 Hz, Ar), 3.89 (s, 3 H, CH_3) ppm.

2′-Methylbiphenyl-2-carbonitrile (31d): Table 5, Entry 4.[30] Purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1:30) to afford a white solid (90 mg, 91%), m.p. 35–36 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.55 (m, 4 H, Ar), 7.47–7.45 (m, 2 H, Ar), 6.93–6.91 (m, 2 H, Ar) ppm.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of the products.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (NSFC) (20972139) and the National Science Foundation (NSF) of Henan (082300423201) for their financial support of this research.

[1] a) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609–679; b) S. L. Buchwald, D. S. Surry, *Angew. Chem.* **2008**, *120*, 6438–6461; *Angew. Chem. Int. Ed.* **2008**, *47*, 6338–6361; c) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931.

[2] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; b) J. Ma, X. L. Cui, B. Zhang, M. P. Song, Y. J. Wu, *Tetrahedron* **2007**, *63*, 5529–5538; c) A. F. Littke, G. C. Fu, *Angew. Chem.* **2002**, *114*, 4350–4386; *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211; d) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174–238.

[3] T. Ishiyama, Y. Itoh, T. Kitano, N. Miyaura, *Tetrahedron Lett.* **1997**, *38*, 3447–3450.

[4] a) A. Kondoh, T. F. Jamison, *Chem. Commun.* **2010**, *46*, 907–909; b) T. E. Hurst, T. K. Macklin, M. Becker, E. Hartmann, W. Kügel, J.-C. Parisienne-La Salle, A. S. Batsanov, T. B. Marder, V. Snieckus, *Chem. Eur. J.* **2010**, *16*, 8155–8161; c) M. Klečka, R. Pohl, B. Klepetářová, M. Hocek, *Org. Biomol. Chem.* **2009**, *7*, 866–868; d) P. Harrisson, J. Morris, T. B. Marder, P. G. Steel, *Org. Lett.* **2009**, *11*, 3586–3589; e) P. Harrisson, J. Morris, P. G. Steel, T. B. Marder, *Synlett* **2009**, 147–150; f) V. J. Olsson, K. J. Szabó, *Org. Lett.* **2008**, *10*, 3129–3131; g) A. D. Finke, J. S. Moore, *Org. Lett.* **2008**, *10*, 4851–4854.

[5] a) N. PraveenGanesh, P. Y. Chavant, *Eur. J. Org. Chem.* **2008**, 4690–4696; b) L. Zhu, M. Patel, M. Zhang, *Tetrahedron Lett.* **2008**, *49*, 2734–2737; c) O. Baudoin, M. Cesario, D. Guénard, F. Guéritte, *J. Org. Chem.* **2002**, *67*, 1199–1207; d) O. Baudoin, D. Gunard, F. Guritte, *J. Org. Chem.* **2000**, *65*, 9268–9271.

[6] a) M. Deodhar, D. StC. Black, D. S.-H. Chan, N. Kumar, *Heterocycles* **2010**, *80*, 1267–1274; b) T. Martin, C. Laguerre, C. Hoarau, F. Marsais, *Org. Lett.* **2009**, *11*, 3690–3693; c) H. A. Duong, S. Chua, P. B. Huleatt, C. L. L. Chai, *J. Org. Chem.* **2008**, *73*, 9177–9180; d) E. F. DiMauro, J. R. Vitullo, *J. Org. Chem.* **2006**, *71*, 3959–396; e) P.-E. Broutin, I. Čerňa, M. Campaniello, F. Leroux, F. Colobert, *Org. Lett.* **2004**, *6*, 4419–4422; f) I. C. F. R. Ferreira, M.-J. R. P. Queiroz, G. Kirsch, *Tetrahedron Lett.* **2003**, *44*, 4327–4329; g) A. S. Abreu, N. O. Silva, P. M. T. Ferreira, M.-J. R. P. Queiroz, *Tetrahedron Lett.* **2003**, *44*, 6007–6009; h) L. Zhu, J. Duquette, M. Zhang, *J. Org. Chem.* **2003**, *68*, 3729–3732.

[7] a) M. Miura, T. Koike, T. Ishihara, F. Hirayama, S. Sakamoto, M. Okada, M. Ohta, S. Tsukamoto, *Synth. Commun.* **2006**, *36*,

3809–3820; b) M. Penhoat, V. Levacher, G. Dupas, *J. Org. Chem.* **2003**, *68*, 9517–9520.

[8] a) G. Uray, A.-M. Kelterer, J. Hashim, T. N. Glasnov, C. O. Kappe, W. M. F. Fabian, *J. Mol. Struct.* **2009**, *929*, 85–96; b) M.-J. R. P. Queiroz, E. M. S. Castanheira, T. C. T. Lopes, Y. K. Cruz, G. Kirsch, *J. Photochem. Photobiol., A* **2007**, *190*, 45–52; c) E. F. DiMauro, J. R. Vitullo, *J. Org. Chem.* **2006**, *71*, 3959–3962; d) A. S. Abreu, P. M. T. Ferreira, M.-J. R. P. Queiroz, I. C. F. R. Ferreira, R. C. Calhelha, L. M. Estevinho, *Eur. J. Org. Chem.* **2005**, 2951–2957; e) M. Melucci, G. Barbarella, M. Zambianchi, P. D. Pietro, A. Bongini, *J. Org. Chem.* **2004**, *69*, 4821–4828; f) O. Skaff, K. A. Jolliffe, C. A. Hutton, *J. Org. Chem.* **2005**, *70*, 7353–7363; g) G. W. Kabalka, M.-L. Yao, *Tetrahedron Lett.* **2003**, *44*, 7885–7887.

[9] K. L. Billingsley, T. E. Barder, S. L. Buchwald, *Angew. Chem.* **2007**, *119*, 5455–5459; *Angew. Chem. Int. Ed.* **2007**, *46*, 5359–5363.

[10] a) L. H. Wang, J. Y. Li, X. L. Cui, Y. S. Wu, Z. W. Zhu, Y. J. Wu, *Adv. Synth. Catal.* **2010**, *352*, 2002–2010; b) C. Xu, J. F. Gong, M. P. Song, Y. J. Wu, *Transition Met. Chem.* **2009**, *34*, 175–179; c) N. Ma, Z. W. Zhu, Y. J. Wu, *Tetrahedron* **2007**, *63*, 4625–4629.

[11] S. Q. Huo, Y. J. Wu, C. X. Du, Y. Zhu, H. Z. Yuan, X. A. Mao, *J. Organomet. Chem.* **1994**, *483*, 139–146.

[12] J. F. Gong, G. Y. Liu, C. X. Du, Y. Zhu, Y. J. Wu, *J. Organomet. Chem.* **2005**, *690*, 3963–3969.

[13] E. Alacid, C. Nájera, *Org. Lett.* **2008**, *10*, 5011–5014.

[14] I. J. S. Fairlamb, A. R. Kapdi, A. F. Lee, *Org. Lett.* **2004**, *6*, 4435–4438.

[15] W. J. Zhou, K. H. Wang, J. X. Wang, *J. Org. Chem.* **2009**, *74*, 5599–5602.

[16] K. C. Y. Lau, H. S. He, P. Chiu, P. H. Toy, *J. Comb. Chem.* **2004**, *6*, 955–960.

[17] L. Caron, L. C. Campeau, K. Fagnou, *Org. Lett.* **2008**, *10*, 4533–4536.

[18] Q. Yang, S. M. Ma, J. X. Li, F. S. Xiao, H. Xiong, *Chem. Commun.* **2006**, 2495–2497.

[19] G. R. Rosa, C. H. Rosa, F. Rominger, J. Dupont, A. L. Monteiro, *Inorg. Chim. Acta* **2006**, *359*, 1947–1954.

[20] P. D. Stevens, J. Fan, H. M. R. Gardimalla, M. Yen, Y. Gao, *Org. Lett.* **2005**, *7*, 2085–2088.

[21] B. Tao, D. W. Boykin, *J. Org. Chem.* **2004**, *69*, 4330–4335.

[22] L. H. Heitman, J. P. D. van Veldhoven, A. M. Zweemer, K. Ye, J. Brussee, A. P. IJzerman, *J. Med. Chem.* **2008**, *51*, 4724–4729.

[23] T. Itoh, T. Mase, *Tetrahedron Lett.* **2005**, *46*, 3573–3577.

[24] B. W. Xin, *J. Chem. Res. (S)* **2008**, *7*, 412–415.

[25] D. Craig, F. Paina, S. C. Smith, *Chem. Commun.* **2008**, 3408–3410.

[26] P. T. F. McLoughlin, M. A. Clyne, F. Aldabbagh, *Tetrahedron* **2004**, *60*, 8065–8071.

[27] J. J. Hangeland, M. L. Quan, J. M. Smallheer, G. S. Bisacchi, J. R. Corte, T. J. Friends, Z. Sun, K. A. Rossi, C. L. Cavallaro, US Patent 7429604B2.20080930, **2008**.

[28] M. M. Marcial, *Synlett* **2006**, 3001–3004.

[29] L. Ackermann, A. Althammer, *Org. Lett.* **2006**, *8*, 3457–3460.

[30] Z. X. Xi, Y. B. Zhou, W. Z. Chen, *J. Org. Chem.* **2008**, *73*, 8497–8501.

Received: September 27, 2011
Published Online: November 29, 2011

