DOI: 10.1002/cjoc.201200775

Palladium-Catalyzed Suzuki-Miyaura Type Coupling Reaction of Aryl Halides with Triphenylborane-Pyridine

Yang, Minghua*(杨明华) Gu, Yongbing(顾勇冰) Wang, Yan(王艳)
Zhao, Xiyu(赵玺玉) Yan, Guobing*(严国兵)

Department of Chemistry, Lishui University, Lishui, Zhejiang 323000, China

The Suzuki-Miyaura type coupling reaction of aryl halides with triphenylborane-pyridine was described. The reaction can be catalyzed by $Pd(OAc)_2$ (5 mol%) in presence of Cs_2CO_3 at 50 ℃ or 80 ℃, and functionalized biaryls were obtained in good to excellent yields. This protocol is general and can tolerate a wide range of functional groups.

Keywords triphenylbroane-pyridine, Suzuki-Miyaura coupling, aryl halides, palladium catalysts

Introduction

Organoboron compounds have become one of the most popular organometallic reagents for transition metal-catalyzed formation of carbon-carbon bonds and carbon-heteroatom bonds in modern organic synthesis.[1] Commercially available organoboronic acids and boronate esters have been extensively used in cross-coupling reactions for decades.[2] Trialkylboranes used as partners in coupling reaction with aryl iodides and activated triflates have been documented sporadically.[3] In 2009, Lin and co-workers reported an efficient and chemoselective Suzuki-Miyaura coupling reaction of trialkylboranes with bromoarenes bearing unmasked acidic functions.[4] In contrast to these trivalent organoboranes, the tetracoordinated ate complex, potassium trifluoroborates $[RBF_3]K$ showed exceptional stability toward air and moisture, and established high reactivity in a large variety of reactions, especially palladium-catalyzed cross-coupling reactions.[5] Similarly, sodium trihydroxyborates $[RB(OH)_3]Na$ were also synthesized and used in cross-coupling in anhydrous solvents without the aid of an additional base.[6] Another tetravalent organoborane, sodium tetraphenylborate (Ph_4BNa), has also been applied to the Suzuki-Miyaura coupling reaction.[7] It is particularly noteworthy that its four phenyl groups can all be coupled with aryl halides to generate the product efficiently. In 2008, Miyaura and co-workers developed several novel cyclic triolborates (**A**, Figure 1), which are exceptionally stable in air and water and more soluble in organic solvents than potassium trifluoroborates.[8] Lithium and potassium triolborates showed the high transmetalation efficiency in palladium- and copper-catalyzed formation of C—C and C—N bonds. In 2009, Butke and co-workers synthesized a new air-stable *N*-methyliminodiacetic acid (MIDA) masked boronic acids (**B**, Figure 1), which can be liberated in controlled release fashion into the Suzuki-Miyaura coupling reaction.[9] Recently, this powerful methodology has been extended to enable the preparation of isoxazoles and triazoles MIDA boronates and their utility in Suzuki-Miyaura coupling reactions and [3＋2] cycloaddition reactions has been successfully demonstrated.[10] In 2010, Gras and co-workers reported the synthesis of dioxazaborocane (**C**, Figure 1) and their application in Suzuki-Miyaura coupling reaction with tetrafluoroborate diazonium salts without external activation.[11] They considered that dioxazaborocanes were able to self-activate by the way of an intramolecular N-B interaction. These masked organoboronic acids are more efficient than ordinarily unmasked boronic acids. So the development of new air- and moisture-stable organoboron compounds using coordination of nitrogen heteroatom to boron atom may be an interesting game.

Triphenylbronae-pyridine (TPBP, **D**, Figure 1), an air- and moisture-stable organoboron compound, is easy to prepare and known to be effective biocides and marine-fouling agents.[12] Recently, we have also developed a simple synthetic approach to this masked borane. Herein, we report the palladium-catalyzed Suzuki-Miyaura coupling reaction of TPBP with aryl halides under mild conditions as a complementary method for the synthsis of biaryls.

Results and Discussion

On the outset of this investigation, 4-methoxyiodobenzene **1a** was used as model substrate with triphenyl-

* E-mail: mhyang@lsu.edu.cn; gbyan@lsu.edu.cn; Tel: 0086-0578-2271113
Received July 27, 2012; accepted September 7, 2012.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201200775 or from the author.

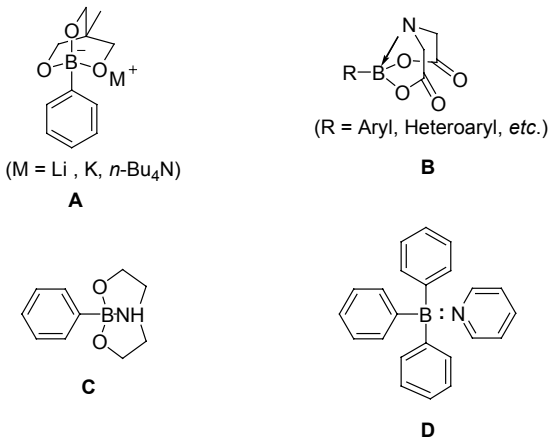
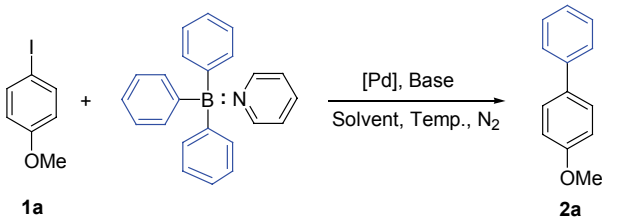


Figure 1 Several useful organoboron reagents.

borane-pyridine to screen suitable reaction conditions and the results were summarized in Table 1. When **1a** and triphenylborane-pyridine were catalyzed by $Pd(OAc)_2$ in the present of Na_2CO_3 in toluene at 40 ℃ under N_2, trace amounts of desired product **2a** was observed as shown by GC-MS analysis (Entry 1). Other solvents were further tested, and the similar results were obtained using MeCN, dioxane and THF as reaction media (Entries 2—4). To our delight, the desired product **2a** was obtained in excess of 70% yield in DMF, DMSO and EtOH (Entries 5—7). DMF was used for the transformation and gave the biaryls in best yield (Entry 5). Various palladium sources, such as $PdCl_2$, $PdCl_2(PPh_3)_2$, $Pd(dba)_3$, $Pd(PPh_4)_4$, were also tested in the reaction, but the yields could not increased (Entries 8—11). Switch of Na_2CO_3 to K_2CO_3 or Cs_2CO_3 could slightly improve the reaction (Entries 12—13), while other bases, such as KOH, Et_3N and *t*-BuONa dramatically decreased the yields (Entries 14—16). However, trace amounts of **2a** was observed without the aid of an additional base (Entry 17). The yield of the reaction was slightly improved by increasing reaction temperature (Entry 18). Further investigation revealed that there was no significant change when the amount of TPBP was decreased to 1.2 equivalents (Entry 19). Finally, for comparison the reaction was carried out in the absence of $Pd(OAc)_2$, no product could be detected (Entry 20).

Under the optimized conditions, the substrate scope of this reaction was investigated and the results were summarized in Table 2. The reaction of TPBP with *ortho*-, *meta*-, and *para*-substituted aryl iodides smoothly proceeded and afforded the corresponding asymmetric biaryls in excellent yields (Entries 1—11). It was observed that the reaction was slightly affected by electronic effects of the substituents on aryl iodides. The substituted aryl iodides bearing electron-deficient groups, showed slightly higher reactivity than those bearing electron-rich groups (Entries 1—3 vs. Entries 6, 9—10). It is particularly noteworthy that chloro substituent was tolerated in the reaction conditions, which is advantageous for further transformations (Entry 9).

Table 1 Optimization of reaction conditions[a]



Entry	[Pd]	Base	Solvent	Temp./℃	Yield[b]/%
1	$Pd(OAc)_2$	Na_2CO_3	Toluene	40	<5
2	$Pd(OAc)_2$	Na_2CO_3	MeCN	40	<5
3	$Pd(OAc)_2$	Na_2CO_3	Dioxane	40	<5
4	$Pd(OAc)_2$	Na_2CO_3	THF	40	10
5	$Pd(OAc)_2$	Na_2CO_3	DMF	40	78
6	$Pd(OAc)_2$	Na_2CO_3	DMSO	40	71
7	$Pd(OAc)_2$	Na_2CO_3	EtOH	40	74
8	$PdCl_2$	Na_2CO_3	DMF	40	70
9	$PdCl_2(PPh_3)_2$	Na_2CO_3	DMF	40	76
10	$Pd_2(dba)_3$	Na_2CO_3	DMF	40	30
11	$Pd(PPh_3)_4$	Na_2CO_3	DMF	40	45
12	$Pd(OAc)_2$	K_2CO_3	DMF	40	82
13	$Pd(OAc)_2$	Cs_2CO_3	DMF	40	86
14	$Pd(OAc)_2$	KOH	DMF	40	35
15	$Pd(OAc)_2$	Et_3N	DMF	40	28
16	$Pd(OAc)_2$	*t*-BuONa	DMF	40	10
17	$Pd(OAc)_2$	—	DMF	40	<5
18	$Pd(OAc)_2$	Cs_2CO_3	DMF	50	92
19[c]	**$Pd(OAc)_2$**	**Cs_2CO_3**	**DMF**	**50**	**91**
20	—	Cs_2CO_3	DMF	50	—

[a] Reaction conditions: 4-methoxyiodobenzene **1a** (0.5 mmol), TPBP (0.3 mmol), [Pd] (0.025 mmol), base (1.0 mmol), solvent (2 mL), under N_2, 12 h. [b] Yields determined by GC-MS method using mesitylene as the internal standard. [c] Using 0.2 mmol TPBP.

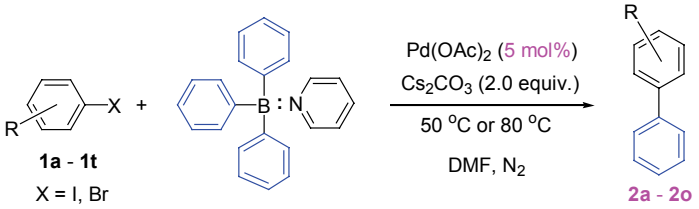
The reaction tolerated a wide range of functional groups, such as methyl, methoxy, nitro, trifluoromethyl, carbonyl, chloro and fluoro groups (Entries 1—3 and Entries 5—11). Next, we proceeded to apply aryl bromides as substrates, which are generally less reactive than aryl iodides in palladium-catalyzed reactions. The coupling reaction of aryl bromides indeed took place by increasing reaction temperature, but the reactions took longer time and gave moderate to good yields (Entries 12—20).

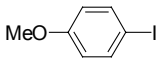
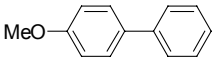
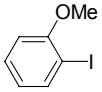
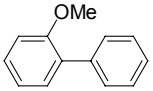
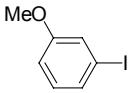
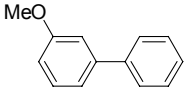
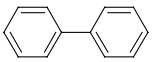
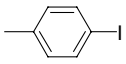
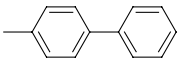
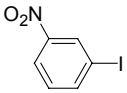
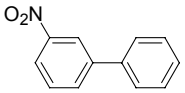
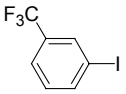
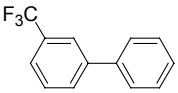
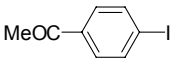
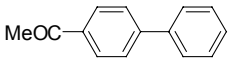
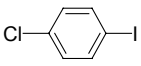
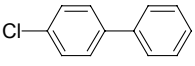
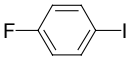
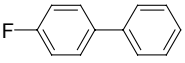
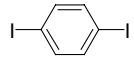
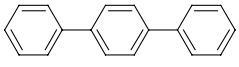
Conclusions

In summary, we have described that TPBP was used as a phenylation reagent for palladium-catalyzed Suzuki-Miyaura coupling reactions of aryl halides for synthesis of biaryls. This protocol is general and can be applied to a wide variety of substituted aryl halides. In most instances, the biaryls were obtained in good yields.

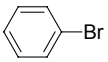
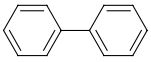
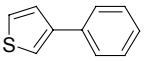
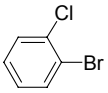
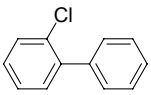
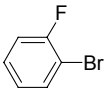
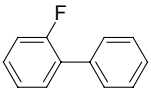
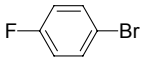
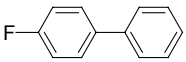
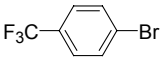
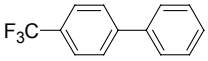
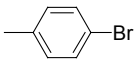
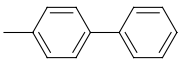
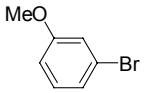
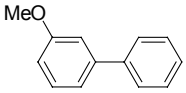
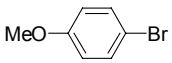
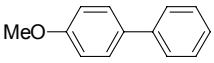
CHINESE JOURNAL OF CHEMISTRY

Table 2 Palladium-catalyzed coupling reaction of **1a**—**1t** with TPBP[a]



Entry	ArX	Time/h	Temp./℃	Product	Yield[b]/%
1	 **1a**	8	50	 **2a**	87
2	 **1b**	8	50	 **2b**	84
3	 **1c**	8	50	 **2c**	83
4	 **1d**	4	50	 **2d**	88
5	 **1e**	4	50	 **2e**	91
6	 **1f**	4	50	 **2f**	95
7	 **1g**	4	50	 **2g**	79
8	 **1h**	8	50	 **2h**	88
9	 **1i**	8	50	 **2i**	95
10	 **1j**	8	50	 **2j**	95
11[c]	 **1k**	8	50	 **2k**	87

Continued

Entry	ArX	Time/h	Temp./℃	Product	Yield[b]/%
12	 **1l**	12	80	 **2d**	87
13	 **1m**	12	80	 **2m**	70
14	 **1n**	12	80	 **2n**	71
15	 **1o**	12	80	 **2o**	77
16	 **1p**	12	80	 **2j**	87
17	 **1q**	12	80	 **2q**	80
18	 **1r**	12	80	 **2e**	73
19	 **1s**	12	80	 **2c**	65
20	 **1t**	12	80	 **2a**	82

[a] Reaction conditions: aryl halide **1** (0.5 mmol), TPBP (0.2 mmol), $Pd(OAc)_2$ (0.025 mmol), Cs_2CO_3 (1.0 mmol), DMF (2 mL), under N_2. [b] Isolated yield. [c] Using 0.4 mmol TPBP.

In addition, it was found that its three phenyl groups were transferred into the products, and this merit makes it an alternative for synthesis of biaryls. Further investigation toward its applications in transition metal-catalyzed coupling reactions is ongoing.

Experimental

NMR data were recorded on a Bruker AMX-300 spectrometer with chemical shifts referenced to $SiMe_4$ as internal standard. Mass spectra were taken using GC-MS spectrometer (Varian 431 GC-Varian 220 MS). All of ArI and ArBr were purchased from Acros and used without further purification.

Procedure for modified synthesis of triphenylborane-pyridine[13]

Mg turnings (2.4 g, 100 mmol) were taken into a three-necked flask fitted with reflux condenser, and then the flask was heated on an open flame and cooled under nitrogen. Next, BF_3•OEt_2 (4.3 g, 30 mmol) and dried THF (25 mL) were introduced into the reaction flask while maintaining the nitrogen atmosphere. The reaction was next initiated by a dropwise addition of PhBr (2 mL, 19.1 mmol) while stirring the reaction mixture and the remainder PhBr (8.5 mL, 81.2 mmol in 10 mL THF) was added slowly over a period of 30 min, so that the THF refluxed gently. Stirring was continued for an additional 3 h, and pyridine (2.8 g, 35 mmol) was added. A

solid precipitates instantly. The mixture was filtered after stirring for another 3 h at 40 ℃, and the resulting solid was washed with H_2O (50 mL) and THF (10 mL) and dried under vacuum. 7.2 g white power was obtained in 75% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.44 (s, 2H), 8.30 (s, 1H), 7.82 (s, 2H), 7.11 (s, 15H).

General procedure for coupling reaction of aryl halides with triphenylborane-pyridine

A mixture of aryl halides (0.5 mmol), triphenylborane-pyridine (0.2 mmol), Cs_2CO_3 (1.0 mmol), $Pd(OAC)_2$ (0.025 mmol), and DMF (2 mL) was stirred at the indicated temperature for the specified time until complete consumption of starting material as monitored by TLC. Ethyl acetate (5 mL) and water (5 mL) were then added to the reaction mixture. The organic phase was separated, and the aqueous phase was further extracted with ethyl acetate (5 mL×4). The combined organic phase was washed with brine, dried over $MgSO_4$, and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether) to give the corresponding biaryl compound.

4-Methoxybiphenyl (2a)[14] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.62—7.67 (m, 4H), 7.51 (t, J=7.5 Hz, 2H), 7.41 (d, J=7.2 Hz, 1H), 7.07 (d, J=8.6 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 159.0, 140.7, 133.6, 128.7, 128.1, 126.7, 126.6, 114.1, 55.2; MS (EI) *m/z* (%): 184.2 (100) [M^+], 169.2 (77), 141.2 (56), 115.2 (40).

2-Methoxybiphenyl (2b)[15] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.62 (d, J=7.2 Hz, 2H), 7.49 (t, J=7.2 Hz, 2H), 7.38—7.42 (m, 3H), 7.04—7.11 (m, 2H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 156.4, 138.5, 130.9, 130.6, 129.5, 128.6, 127.9, 126.9, 20.8, 111.1, 55.5; MS (EI) *m/z* (%): 184.2 (100) [M^+], 169.2 (52), 141.2 (52), 115.2 (47).

3-Methoxybiphenyl (2c)[15] ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 7.66 (d, J=7.5 Hz, 2H), 7.34—7.48 (m, 4H), 7.21 (d, J=9.0 Hz, 2H), 6.93 (dd, J=1.1, 8.1 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 160.2, 142.1, 140.5, 130.4, 129.3, 128.0, 127.2, 119.4, 113.4, 112.6, 55.5; MS (EI) *m/z* (%): 184.2 (100) [M^+], 154.2 (18), 141.2 (22), 115.2 (27).

Biphenyl (2d)[14] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.66—7.69 (m, 4H), 7.49—7.55 (m, 4H), 7.42—7.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 141.2, 128.7, 127.2, 127.1; MS (EI) *m/z* (%): 154.3 (100) [M^+], 76.5 (9).

4-Methylbiphenyl (2e)[14] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.66 (d, J=7.0 Hz, 2H), 7.58 (d, J=7.8 Hz, 2H), 7.51 (t, J=7.2 Hz, 2H), 7.41 (d, J=7.1 Hz, 1H), 7.33 (d, J=7.8 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 141.2, 137.0, 129.5, 28.8, 128.7, 127.2, 127.0, 127.0, 21.1; MS (EI) *m/z* (%): 168.0 (100) [M^+], 153.2 (26), 115.2 (10).

3-Nitrobiphenyl (2f)[14] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.45 (s, 1H), 8.20 (d, J=7.6 Hz, 1H), 7.92 (d, J=7.6 Hz, 1H), 7.62—7.64 (m, 3H), 7.44—7.53 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 148.5, 142.7, 138.5, 132.9, 129.6, 129.0, 128.4, 127.0, 121.9, 121.8; MS (EI) *m/z* (%): 199.2 (100) [M^+], 152.3 (38).

3-Trifluoromethylbiphenyl (2g)[16] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.91 (s, 1H), 7.81 (d, J=7.4 Hz, 1H), 7.57—7.65 (m, 4H), 7.45—7.55 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 142.0, 139.7, 131.2 (q, J= 31.7 Hz, 1C), 130.4, 129.2, 129.0, 128.7, 128.0, 127.2, 124.2 (q, J=270.6 Hz, 1C) 123.8 (q, J=3.6 Hz, 1C); MS (EI) *m/z* (%): 222.3 (100) [M^+], 201.3 (12), 152.3 (17).

4-Acetylbiphenyl (2h)[14] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.05 (d, J=8.0 Hz, 2H), 7.70 (d, J=8.0 Hz, 2H), 7.65 (d, J=7.7 Hz, 2H), 7.42—7.52 (m, 3H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 197.8, 145.7, 139.8, 135.8, 128.9, 128.9, 128.2, 127.2, 127.2, 26.7; MS (EI) *m/z* (%): 196.0 (42) [M^+], 181.1 (100), 152.2 (31).

4-Chlorobiphenyl (2i)[14] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.56—7.62 (m, 4H), 7.42—7.53 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 139.9, 139.6, 133.3, 128.9, 128.8, 128.3, 127.5, 126.9; MS (EI) *m/z* (%): 190.0 (32) [M^++2], 188.1 (100) [M^+], 152.2 (26), 115.2 (10), 76.0 (18).

4-Fluorobiphenyl (2j)[17] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.39—7.69 (m, 7H), 7.19 (t, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 162.9 (d, J=244.6 Hz, 1C), 141.2, 140.2, 137.3 , 128.6 (d, J=7.0 Hz, 1C), 127.2, 127.0, 115.6 (d, J=21.1 Hz, 1C); MS (EI) *m/z* (%): 172.3 (100) [M^+].

1,4-diphenylbenzene (2k)[18] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.68—7.72 (m, 8H), 7.50 (t, J=7.4 Hz, 4H), 7.41 (d, J=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 140.6, 140.1, 128.8, 127.5, 127.3, 127.0; MS (EI) *m/z* (%): 230.5 (100) [M^+], 152.4 (8), 115.5 (5), 77.3 (5).

3-Phenylthiophene (2m)[19] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.65 (d, J=7.2 Hz, 2H), 7.37—7.51 (m, 5H); MS (EI) *m/z* (%): 160.0 (100) [M^+], 128.1 (20), 115.0 (47).

2-Chlorobiphenyl (2n)[14] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.41—7.51 (m, 6H), 7.33—7.39 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 141.1, 139.8, 132.5, 131.3, 129.8, 129.4, 128.4, 128.0, 127.5, 126.8; MS (EI) *m/z* (%): 188.3 (100) [M^+], 152.5 (27).

2-Fluorobiphenyl (2o)[7] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.74 (s, 4H), 7.63—7.67 (m, 2H), 7.47—7.52 (m, 3H); MS (EI) *m/z* (%): 172.3 (100) [M^+], 152.3 (5).

4-Trifluoromethylbiphenyl (2g)[7] ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.74 (s, 4H), 7.63—7.67 (m, 2H), 7.47—7.52 (m, 3H); MS (EI) *m/z* (%): 222.3 (100) [M^+], 203.5 (5), 152.5 (10).

Acknowledgement

This work was supported by the Natural Science Foundation of Zhejiang Province (No. Y407081) and

the Research Foundation of Education Department of Zhejiang Province (No. YZ01018492).

References

[1] (a) Doe, I. S.; Smith, J.; Roe, P. *J. Am. Chem. Soc.* **1968**, *90*, 8234; (b) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev*. **2002**, *102*, 1359; (c) Hall, D. G. *Boronic Acids*: *Preparation, Applications in Organic Synthesis and Medicine*, Wiley-VCH, Weinheim, **2005**.

[2] (a) Miyaura, N.; Suzuki, A. *Chem. Rev*. **1995**, *95*, 2457; (b) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633.

[3] (a) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314; (b) Harada, T.; Yoshida, T.; Inoue, A.; Takeuchi, M.; Oku, A. *Synlett* **1995**, 283.

[4] (a) Wang, B.; Sun, H. X.; Sun, Z. H.; Lin, G. Q. *Adv*. *Synth. Catal.* **2009**, *351*, 415; (b) Sun, H. X.; Sun, Z. H.; Wang, B. *Tetrahedron Lett.* **2009**, *50*, 1596.

[5] (a) Molander, G. A.; Ellis, N. *Acc. Chem. Res.* **2007**, *40*, 275; (b) Darses, S.; Genet, J.-P. *Chem. Rev*. **2008**, *108*, 288; (c) Molander, G. A.; Canturk, B. *Angew. Chem.*, *Int. Ed*. **2009**, *48*, 9240.

[6] Cammidge, A. N.; Goddard, V. H. M.; Gopee, H.; Harrison, N. L.; Hughes, D. L.; Schubert, C. J.; Sutton, B. M.; Watts, G. L.; Whitehead, A. J. *Org. Lett.* **2006**, *8*, 4071.

[7] (a) Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1992**, *33*, 4815; (b) Bumagin, N. A.; Bykov, V. V. *Tetrahedron* **1997,** *53,* 14437; (c) Zhou, W. J.; Wang, K. H.; Wang, J. X.; Gao, Z. R. *Tetrahedron* **2010**, *66*, 7633.

[8] Yamamoto, Y.; Takizawa, M.; Yu, X. Q.; Miyaura, N. *Angew. Chem.*, *Int. Ed.* **2008**, *47*, 928.

[9] Knapp, D. M.; Gillis, E. P.; Burke, M. D. *J. Am. Chem. Soc.* **2009**, *131*, 6961.

[10] Grob, J. E.; Michael, J. N.; Hamann, L. G. *J. Org. Chem.* **2011**, *76*, 10241.

[11] (a) Bonin, H.; Delbrayelle, D.; Demonchaux, P.; Gras, E. *Chem. Commum.* **2010**, *46*, 2667; (b) Bonin, H.; Leuma-Yona, R.; Marchiori, B.; Demonchaux, P.; Gras, E. *Tetrahedron Lett.* **2011**, *52*, 1132.

[12] Ostermaier, J. *WO 100261A2*, **2009**.

[13] (a) Brown, H. C.; Racherla, U. S. *J. Org. Chem.* **1986**, *51*, 427; (b) Kokai, T. K. *JP 2003238572*, **2003**.

[14] Zhou, W. J.; Wang, K. H.; Wang, J. X.; Gao, Z. R. *Tetrahedron* **2010**, *66*, 7633.

[15] Bolliger, J. L.; Frech, C. M. *Chem. Eur. J.* **2010**, *16*, 4075.

[16] Zhang, Z. T.; Pitteloud, J. P.; Cabrera, L.; Liang, Y.; Toribio, M.; Wnuk, S. F. *Org. Lett*. **2010**, *12*, 816.

[17] Li, H.; Sun, C. L.; Yu, M.; Yu, D. G.; Li, B. J.; Shi, Z. J. *Chem. Eur. J.* **2011**, *17*, 3593.

[18] Liu, W.; Cao, H.; Xin, J.; Jin, L. Q.; Lei, A. W. *Chem. Eur. J.* **2011**, *17*, 3588 .

[19] Lee, D. H.; Choi, M.; Yu, B. W.; Ryoo, R.; Taher, A.; Hossain, S.; Jin, M. J. *Adv. Synth. Catal.* **2009**, *351*, 2912.

(Pan, B.; Fan, Y.)

