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Palladium-Catalyzed Suzuki−Miyaura Cross-Couplings of Aryl Tosylates with Potassium Aryltrifluoroborates

Liang Zhang,† Tianhao Meng,† and Jie Wu*,†,‡

Department of Chemistry, Fudan University, 220 Handan Road,
Shanghai 200433, China, and State Key Laboratory of
Organometallic Chemistry, Shanghai Institute of Organic
Chemistry, Chinese Academy of Sciences, 354 Fenglin Road,
Shanghai 200032, China

jie_wu@fudan.edu.cn

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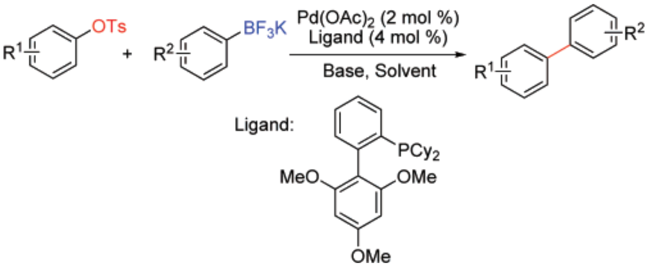

Pd-catalyzed Suzuki−Miyaura cross-coupling reaction of aryl tosylates with potassium aryl trifluoroborate in the presence of bulky and electron-rich phosphine ligand is described. In addition, a useful chemoselective coupling of an aryl chloride in the presence of a tosyloxy group was demonstrated.

Over the past several decades, the mild and selective Suzuki−Miyaura[1] coupling of arylboronic acids with aryl halides has become the method of choice for biaryl synthesis in laboratory and industrial applications. Largely due to the efforts of Molander, Buchwald, and others,[2,3] using trifluoroborates or boronate esters as alternatives to boronic acids in transition metal-catalyzed Suzuki−Miyaura cross-coupling reactions has been well developed since trifluoroborates or boronate esters can circumvent the drawbacks associated with the use of boronic acids, such as the structural ambiguity (the formation of the trimeric anhydride-boroxine). Although boronic acids could theoretically be purified to afford higher purity via recrystallization from water, a mixture of boronic acid and the corresponding boroxine was usually generated upon removal of the water. Thus, an excess amount of boronic acid has to be utilized in the reaction in order to obtain a respectable yield. However, the preparation of boronate esters and trifluoroborates can also be easily accomplished via a variety of different transformations.[4] Although couplings of tetrabutylammonium aryl trifluoroborates or potassium aryl trifluoroborates with aryl/vinyl halides, triflates, or alkenyl tosylates have been reported,[2,3] to our surprise, there are no reports for the couplings of trifluoroborates with aryl arenesulfonates.

On the other hand, as important alternatives to aryl/vinyl triflates and halides in transition metal catalyzed cross-coupling reactions, arenesulfonates are often more stable and easier to handle than the corresponding triflates both in the solid state and in solution. Among these, aryl tosylates are more attractive since they have several advantages compared with aryl triflates, which include easier preparation, increased stability, and less expense. Moreover, their reactivities are considered less active than that of aryl halides and triflates, which remains to be a challenge for organic chemists. Therefore, aryl arenesulfonates are becoming prominent substrates in cross-coupling reactions,[5,6] and it is of significant interest to develop general protocols to employ aryl tosylates in transition metal catalyzed Suzuki−Miyaura cross-coupling reactions of potassium aryl trifluoroborates.

Thus, we started to investigate the possibility of this transformation. Initial studies were performed by treatment of

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† Fudan University.

‡ Chinese Academy of Sciences.

(1) For recent reviews: (a) Miyaura, N. *Top. Curr. Chem.* **2002**, *219*, 11. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147. (c) Culkin, D. A.; Hartwig, J. F. *Acc. Chem. Res.* **2003**, *36*, 234. (d) Hassan, J.; Sevigon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (e) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, 9633.

(2) For recent selected examples, see: (a) Molander, G. A.; Ellis, N. *Acc. Chem. Res.* **2007**, *40*, 275. (b) Molander, G. A.; Sandrock, D. L. *Org. Lett.* **2007**, *9*, 1597. (c) Molander, G. A.; Brown, A. R. *J. Org. Chem.* **2006**, *71*, 9681. (d) Molander, G. A.; Vargas, F. *Org. Lett.* **2007**, *9*, 203. (e) Molander, G. A.; Ham, J.; Seapy, D. G. *Tetrahedron* **2007**, *63*, 768. (f) Molander, G. A.; Fumagalli, T. *J. Org. Chem.* **2006**, *71*, 5743. (g) Molander, G. A.; Elia, M. D. *J. Org. Chem.* **2006**, *71*, 9198. (h) Molander, G. A.; Yokoyama, Y. *J. Org. Chem.* **2006**, *71*, 2493. (i) Molander, G. A.; Sommers, E. M.; Baker, S. R. *J. Org. Chem.* **2006**, *71*, 1563. (j) Molander, G. A.; Petrillo, D. E.; Landzberg, N. R.; Rohanna, J. C.; Biolatto, B. *Synlett* **2005**, 1763. (k) Molander, G. A.; Figueroa, R. *Aldrichimica Acta* **2005**, *38*, 49. (l) Molander, G. A.; Felix, L. A. *J. Org. Chem.* **2005**, *70*, 3950. (m) Molander, G. A.; Biolatto, B. *Org. Lett.* **2002**, *4*, 1867.

(3) For selected examples, see: (a) Harker, R. L.; Crouch, R. D. *Synthesis* **2007**, 25. (b) Kabalka, G. W.; Zhou, L.-L.; Naravane, A. *Tetrahedron Lett.* **2006**, *47*, 6887. (c) Wu, J.; Zhang, L.; Luo, Y. *Tetrahedron Lett.* **2006**, *47*, 6747. (d) Wu, J.; Zhang, L.; Xia, H.-G. *Tetrahedron Lett.* **2006**, *47*, 1525. (e) Cella, R.; Cunha, R. L. O. R.; Reis, A. E. S.; Pimenta, D. C.; Klitzke, C. F.; Stefani, H. A. *J. Org. Chem.* **2006**, *71*, 244. (f) Kabalka, G. W.; Al-Masum, M. *Tetrahedron Lett.* **2005**, *46*, 6329. (g) Barder, T. E.; Buchwald, S. L. *Org. Lett.* **2004**, *6*, 2649. (h) Quach, T. D.; Batey, R. A. *Org. Lett.* **2003**, *5*, 4397. (i) Quach, T. D.; Batey, R. A. *Org. Lett.* **2003**, *5*, 1381. (j) Fang, G.-H.; Yan, Z.-J.; Deng, M.-Z. *Org. Lett.* **2004**, *6*, 357. (k) Darses, S.; Genet, J.-P. *Eur. J. Org. Chem.* **2003**, 4313. (l) Arvela, R. K.; Leadbeater, N. E.; Mack, T. L.; Kormos, C. M. *Tetrahedron Lett.* **2006**, *47*, 217.

(4) For selected examples, see: (a) Molander, G. A.; Cooper, D. J. *J. Org. Chem.* **2007**, *72*, 3558. (b) Molander, G. A.; Ham, J.; Canturk, B. *Org. Lett.* **2007**, *9*, 821. (c) Molander, G. A.; Ham, J. *Org. Lett.* **2006**, *8*, 2767. (d) Molander, G. A.; Ham, J. *Org. Lett.* **2006**, *8*, 2031. (d) Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, *60*, 3020. (e) Vedejs, E.; Fields, S. C.; Hayashi, R.; Hitchcock, S. R.; Powell, D. R.; Schrimpf, M. R. *J. Am. Chem. Soc.* **1999**, *121*, 2460.

(5) For examples of Suzuki−Miyaura reactions, see: (a) Tang, Z.-Y.; Hu, Q.-S. *J. Am. Chem. Soc.* **2004**, *126*, 3058. (b) Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818. (c) Percec, V.; Bae, J.-Y.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 1060. (d) Kobayashi, Y.; Mizojiri, R. *Tetrahedron Lett.* **1996**, *37*, 8531. (e) Zim, D.; Lando, V. R.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2001**, *3*, 3049. (f) Lakshman, M. K.; Thomson, P. F.; Nuqui, M. A.; Hilmer, J. H.; Sevova, N.; Boggess, B. *Org. Lett.* **2002**, *4*, 1479. (g) Huffman, M. A.; Yasuda, N. *Synlett* **1999**, 471. (h) Wu, J.; Wang, L.; Fathi, R.; Yang, Z. *Tetrahedron Lett.* **2002**, *43*, 4395. (i) Wu, J.; Zhu, Q.; Wang, L.; Fathi, R.; Yang, Z. *J. Org. Chem.* **2003**, *68*, 670. (j) Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold, O. *J. Org. Chem.* **2004**, *69*, 3447. (k) Baxter, J. M.; Steinhuebel, D.; Palucki, M.; Davies, I. W. *Org. Lett.* **2005**, *7*, 215. (l) Tang, Z. Y.; Hu, Q.-S. *Adv. Synth. Catal.* **2004**, *346*, 1635. (m) Steinhuebel, D.; Baxter, J. M.; Palucki, M.; Davies, I. W. *J. Org. Chem.* **2005**, *70*, 10124. (n) Netherton, M. R.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 3910.

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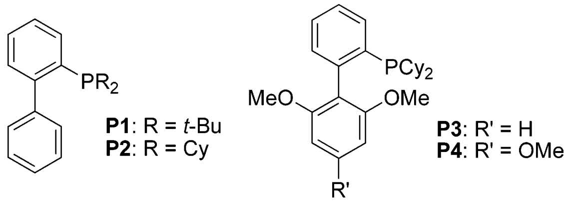
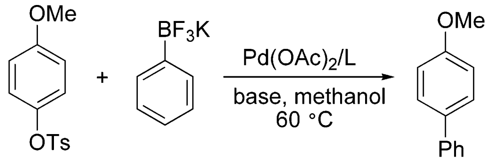
aryl tosylate **1a** and potassium phenyl trifluoroborate **2a** in methanol in the presence of $Pd(OAc)_2$ (2 mol %), phosphine ligand, and base, and the results are shown in Table 1. Inferior results were observed when PCy_3, PPh_3, DPPP, or DPPF were employed in the reaction (Table 1, entries 1−4). 15% of desired product **3a** was generated when ligand **P1** was utilized in the presence of K_2CO_3 as base (Table 1, entry 5).



However, only a trace amount of product was detected when ligand **P2** was added in the reaction (Table 1, entry 6). Using more bulky and electron-rich phosphines, such as **P3** or **P4**, improved the yield dramatically (**P3**: 51% yield, entry 7; **P4**: 67% yield, entry 8). These two electron-rich and bulky phosphines developed by Buchwald[3g,5b] were speculated to promote oxidative addition and tight binding to the metal, which prevents Pd black formation. Moreover, the steric bulk of the ligands also promoted reductive elimination. Further studies revealed that KOH was the best choice of base, and the yield of product **3a** could be increased to 98% (Table 1, entry 16). Decreasing the temperature retarded the reaction. No reaction occurred in the absence of phosphine ligand (Table 1, entry 23). A slightly lower yield was observed when 1.0 equiv of potassium phenyl trifluoroborate **2a** was employed in the reaction (84% yield, Table 1, entry 17). In the presence of 0.5 mol % of palladium catalyst, a prolonged reaction time was necessary for completion of the reaction with 68% yield (Table 1, entry 18).

TABLE 1. Conditions Screening for Reaction of Aryl Arenesulfonate 1a with Potassium Phenyltrifluoroborate 2a[a]



1a **2a** **3a**

entry	ligand	base	yield (%)[b]
1	PCy_3	K_2CO_3	trace
2	PPh_3	K_2CO_3	NR
3	DPPP	K_2CO_3	trace
4	DOOF	K_2CO_3	trace
5	**P1**	K_2CO_3	15
6	**P2**	K_2CO_3	trace
7	**P3**	K_2CO_3	51
8	**P4**	K_2CO_3	67
9	**P4**	Na_2CO_3	trace
10	**P4**	Cs_2CO_3	88
11	**P4**	KH_2PO_4	trace
12	**P4**	$K_2HOP_4 \cdot 3H_2O$	28
13	**P4**	K_3PO_4	43
14	**P4**	$LiOH \cdot H_2O$	49
15	**P4**	NaOH	53
16	**P4**	KOH	98
17	**P4**	KOH	84[c]
18	**P4**	KOH	69[d]
19	**P4**	CsOAc	trace
20	**P4**	CsF	trace
21	**P4**	$KF \cdot 2H_2O$	trace
22	**P4**	$NaHCO_3$	32
23	-	KOH	NR

[a] Reaction conditions: aryl tosylate **1a** (0.30 mmol), $PhBF_3K$ (1.1 equiv), $Pd(OAc)_2$ (2.0 mol %), ligand (4.0 mol %), base (3.0 equiv), methanol (2.0 mL), 60 °C, 24 h. [b]Isolated yield based on aryl tosylate **1a**. [c]1.0 equiv of $PhBF_3K$ was used in the reaction. [d]In the presence of 0.5 mol % of $Pd(OAc)_2$ and 1.0 mol % of **P4**.

The scope of this reaction was then investigated under optimized conditions [$Pd(OAc)_2$ (2 mol %), **P4** (4 mol %), KOH (3.0 equiv), 60 °C], and the results are summarized in Table 2. From Table 2, it was found that, for most cases, aryl tosylate **1** reacted with potassium aryltrifluoroborates leading to the corresponding products **3** in good to excellent yields. Better results were observed for the reaction of 4-methoxyphenyl 4-methylbenzenesulfonate **1a** with potassium aryltrifluoroborate with an electron-donating group attached on the aromatic ring. For instance, reaction of 4-methoxyphenyl 4-methylbenzenesulfonate **1a** with potassium 4-methylphenyltrifluoroborate **2b** proceeded smoothly to afford the desired product **3b** in 97% yield (Table 2, entry 2), while 76% or 37% yield of product **3c** or **3d** was obtained when potassium 4-fluorophenyltrifluoroborate **2c** or potassium 4-trifluoromethylphenyltrifluoroborate **2d** was employed in the reaction (Table 2, entries 3 and 4). *Ortho*-substituted aryltrifluoroborate **2e** was also a good partner for this kind of transformation (Table 2, entry 5). However, only a 32% yield of product **3n** was generated when highly hindered tosylate **1j** was utilized as substrate in the reaction (Table 2, entry 14). Although good results were displayed for the reactions of aryl tosylates with an electron-donating group attached on the aromatic ring, only a trace amount of product **3o** was detected for the reaction of 4-formylphenyl 4-methylbenzenesulfonate **1k** with potassium phenyl trifluoroborate **2a** (Table 2, entry 15). Meanwhile, a small amount of phenol from tosylate was observed, which was similar to that of Buchwald's report.[7] This result prompted us to re-examine the reaction conditions for this kind of substrate. After rescreening various solvents, bases, and temperatures, to our delight, we found that the corresponding product **3o** could be generated in 86% yield when the reaction was performed in EtOH, in the presence of triethylamine (3.0 equiv) as the base at 80 °C. With this promising result in hand, we started to examine the reactions of aryl tosylates with electron-withdrawing groups attached on the aromatic ring. The results were shown in Table 3.

The conditions shown in Table 3 have proven to be useful for coupling a range of aryl tosylates with electron-withdrawing

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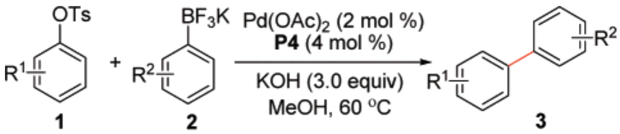
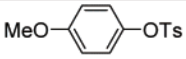
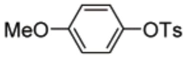
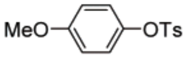
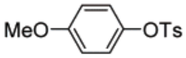
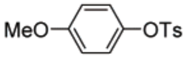
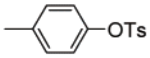
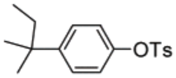
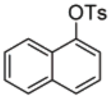
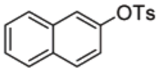
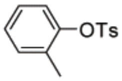
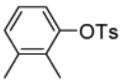
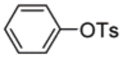
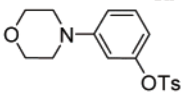
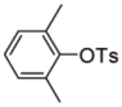
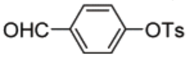
(6) For examples of Sonogashira coupling, see: (a) Fu, X.; Zhang, S.; Yin, J.; Schumacher, D. P. *Tetrahedron Lett.* **2002**, *43*, 6673. (b) Wu, J.; Liao, Y.; Yang, Z. *J. Org. Chem.* **2001**, *66*, 3642. Heck coupling: (c) Fu, X.; Zhang, S.; Yin, J.; McAllister, T. L.; Jiang, S. A.; Tann, C.-H.; Thiruvengadam, T. K.; Zhang, F. *Tetrahedron Lett.* **2002**, *43*, 573. Kumada coupling: (d) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 8704. (e) Iron-catalyzed coupling of alkyl Grignard reagents with ArOTs: Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856. Stille couplings: (f) Badone, D.; Cecchi, R.; Guzzi, U. *J. Org. Chem.* **1992**, *57*, 6321. (g) Nagatsugi, F.; Uemura, K.; Nakashima, S.; Minoru, M.; Sasaki, S. *Tetrahedron Lett.* **1995**, *36*, 421. (h) Schio, L.; Chatreaux, F.; Klich, M. *Tetrahedron Lett.* **2000**, *41*, 1543. Negishi-type reaction of arenesulfonates: (i) Wu, J.; Liao, Y.; Yang, Z. *J. Org. Chem.* **2001**, *66*, 3642. (j) Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 12527. For direct cross-coupling of 4-mesylcoumarins with aryl or vinyl halides, see: (k) Lei, J.-G.; Xu, M.-H.; Lin, G.-Q. *Synlett* **2004**, 2364.

(7) Anderson, K. W.; Ikawa, T.; Tundel, R. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 10694.

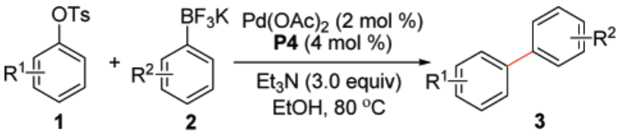
TABLE 2. Reaction of Aryl Tosylate 1 with Potassium Aryltrifluoroborate 2 Catalyzed by Pd(OAc)$_2$ (2 mol %)/P4 (4 mol %)[a]

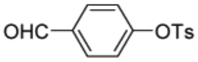
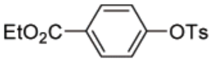
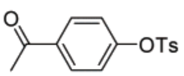
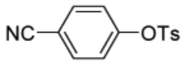
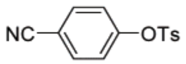
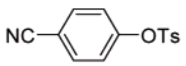
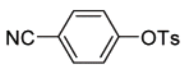
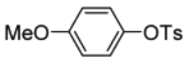


entry	aryl tosylate **1**	R^2	product	yield (%)[b]
1	 **1a**	H **2a**	**3a**	98
2	 **1a**	4-CH$_3$ **2b**	**3b**	97
3	 **1a**	4-F **2c**	**3c**	76
4	 **1a**	4-CF$_3$ **2d**	**3d**	37
5	 **1a**	2-OCH$_3$ **2e**	**3e**	53
6	 **1b**	H **2a**	**3f**	90
7	 **1c**	H **2a**	**3g**	75
8	 **1d**	H **2a**	**3h**	85
9	 **1e**	H **2a**	**3i**	85
10	 **1f**	H **2a**	**3j**	82
11	 **1g**	H **2a**	**3k**	80
12	 **1h**	H **2a**	**3l**	94
13	 **1i**	4-CH$_3$ **2b**	**3m**	88
14	 **1j**	4-CH$_3$ **2b**	**3n**	32
15	 **1k**	H **2a**	**3o**	trace

[a] Reaction conditions: aryl tosylate **1** (0.30 mmol), potassium aryltrifluoroborate **2** (1.1 equiv), Pd(OAc)$_2$ (2.0 mol %), **P4** (4 mol %), KOH (3.0 equiv), MeOH (2.0 mL), 60 °C, 0.5−6 h. [b]Isolated yield based on aryl tosylate **1**.

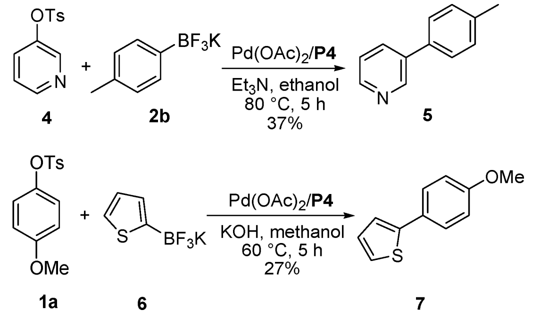
TABLE 3. Reaction of Aryl Tosylate 1 with Potassium Aryltrifluoroborate 2 Catalyzed by Pd(OAc)$_2$ (2 mol %)/P4 (4 mol %)[a]



entry	aryl tosylate **1**	R^2	product	yield (%)[b]
1	 **1k**	H **2a**	**3o**	86
2	 **1l**	H **2a**	**3p**	99
3	 **1m**	H **2a**	**3q**	81
4	 **1n**	H **2a**	**3r**	55
5	 **1o**	H **2a**	**3s**	77
6	 **1p**	H **2a**	**3t**	93
7	 **1p**	4-CH$_3$ **2b**	**3u**	98
8	 **1p**	4-F **2c**	**3v**	89
9	 **1p**	4-CF$_3$ **2d**	**3w**	47
10	 **1a**	H **2a**	**3a**	42

[a] Reaction conditions: aryl tosylate **1** (0.30 mmol), potassium aryltrifluoroborate **2** (1.1 equiv), Pd(OAc)$_2$ (2.0 mol %), **P4** (4 mol %), Et$_3$N (3.0 equiv), EtOH (2.0 mL), 80 °C, 0.5−6 h. [b]Isolated yield based on aryl tosylate **1**.

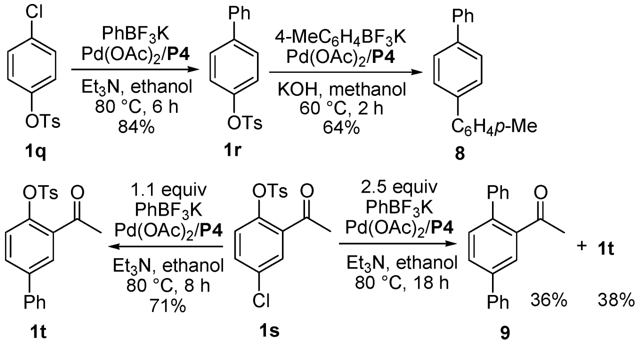
SCHEME 1. Reactions Using Heteroaryl Tosylate or Heteroaryl Trifluoroborate as Substrate



groups attached on the aromatic ring. For example, an almost quantitative yield of product **3o** was furnished in the reaction of ethyl 4-(tosyloxy)benzoate **1l** with potassium phenyl trifluoroborate **2a** (Table 3, entry 2). A whole range of substitutions in aryl tosylates were well tolerated in these conditions, although potassium aryl trifluoroborate **2** with an electron-donating group gave much better results. However, when these conditions were applied to the reaction of aryl tosylate **1a** and potassium phenyl trifluoroborate **2a**, only a moderate yield (Table 3, entry 10) was afforded compared with the result shown in Table 2 (entry 1).

Heteroaryl tosylate **4** or heteroaryl trifluoroborate **6** as substrate was examined in the coupling reactions, which was shown in Scheme 1. The yield was not as high as others described in Tables 2 and 3, which was possibly due to the catalyst deactivation by heteroatoms. We also tried the pal-

SCHEME 2. Chemoselective Cross-Coupling Reaction of Aryl Tosylate/Chloride with Potassium Aryltrifluoroborate



ladium-catalyzed reaction of 4-chlorophenyl 4-methylbenzenesulfonate **1q** with potassium aryl trifluoroborate (Scheme 2). As expected, the tosyloxy group in compound **1q** was retained during the transformation and the product **1r** was afforded in 84% yield. From this reaction, it was found that an aryl chloride is more active than an aryl tosylate under the conditions shown in Table 3. Compound **1r** could be further elaborated to furnish the triaryl compound **8**. Similarly, in the presence of 1.1 equiv of potassium phenyl trifluoroborate, reaction of compound **1s** proceeded smoothly to furnish the corresponding tosylate **1t** in 71% yield. When the amount of potassium phenyl trifluoroborate was increased to 2.5 equiv, compound **9** could be generated and the carbonyl group was tolerated during the transformations.

In summary, the palladium-catalyzed Suzuki−Miyaura cross-coupling reactions of aryl tosylates with potassium aryl trifluoroborates disclosed herein represent an efficient and practical synthesis of biaryl compounds. We believe that this method provides an excellent complement in palladium-catalyzed cross-coupling reactions, due to the attractive features and advantages of both substrates. Application of this method for the synthesis of natural productlike compounds is under investigation in our research group.

Experiment Section

General Procedure for the Pd-Catalyzed Cross-Coupling Reactions of Electron-Rich Aryl Tosylates with Potassium Aryltrifluoroborates: Under a nitrogen atmosphere, a mixture of electron-rich aryl tosylate **1** (0.30 mmol), potassium aryltrifluoroborate **2** (1.1 equiv), Pd(OAc)$_2$ (2 mol %), **P4** (4 mol %), and KOH (3.0 equiv) in MeOH (2.0 mL) was stirred at 60 °C for a period of time. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was diluted with EtOAc (5.0 mL) and washed with water (5.0 mL). Evaporation of the solvent followed by purification on silica gel afforded the corresponding product **3**. Data of selected example: 4-phenylanisole **3a**,[2m] 98% yield. ^{1}H NMR (400M Hz, CDCl$_3$): δ (ppm) 3.85 (s, 3H), 6.98 (d, $J = 8.7$ Hz, 2H), 7.29−7.42 (m, 3H), 7.52−7.57 (m, 4H). ^{13}C NMR (100M Hz): δ (ppm) 159.2, 140.9, 133.9, 128.8, 128.3, 126.8 (4), 126.7 (5), 114.3, 55.4.

General Procedure for the Pd-Catalyzed Cross-Coupling Reactions of Electron-Deficient Aryl Tosylates with Potassium Aryltrifluoroborates: Under a nitrogen atmosphere, a mixture of electron-deficient aryl tosylate **1** (0.30 mmol), potassium aryltrifluoroborate **2** (1.1 equiv), Pd(OAc)$_2$ (2 mol %), **P4** (4 mol %), and Et$_3$N (3.0 equiv) in EtOH (2.0 mL) was stirred at 80 °C for a period of time. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was diluted with EtOAc (5.0 mL) and washed with water (5.0 mL). Evaporation of the solvent followed by purification on silica gel afforded the corresponding product **3**. Data of selected example: 4-(4-formylphenyl)anisole **3o**,[8] 86% yield. ^{1}H NMR (400M Hz, CDCl$_3$): δ (ppm) 7.41 (t, $J = 7.3$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.64 (d, $J = 7.8$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.95 (d, $J = 7.8$ Hz, 2H), 10.06 (s, 1H). ^{13}C NMR (100M Hz): δ (ppm) 192.0, 147.3, 139.8, 135.3, 130.4, 129.1, 128.6, 127.8, 127.5.

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Supporting Information Available: Experimental procedures, characterization data, copies of ^{1}H and ^{13}C NMR spectra of product. This material is available free of charge via the Internet at http://pubs.acs.org.

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