Published in final edited form as:

Adv Synth Catal. 2016 June 30; 358(13): 2072–2076. doi:10.1002/adsc.201600205.

Electron-Poor, Fluoro-Containing Arylboronic Acids as Efficient Coupling Partners for Bis(1,5-cyclooctadiene)nickel(0)/Tricyclohexylphosphine-Catalyzed Cross-Coupling Reactions of Aryl Arenesulfonates

Dr. Wen-Bo Chen^{a,b,†}, Dr. Chun-Hui Xing^{a,‡}, Jie Dong^a, and Prof. Dr. Qiao-Sheng Hu^a

^aDepartment of Chemistry, College of Staten Island of the City University of New York, Staten Island, New York, 10314 and the Ph.D. Program in Chemistry, the Graduate Center of the City University of New York, New York, NY 10016, United States

Abstract

The use of electron-poor, fluoro-containing arylboronic acids as general coupling partners for nickel(0)/tricyclohexylphosphine-catalyzed cross-coupling of aryl arenesulfonates is described. Electron-poor fluoro-containing arylboronic acids were found to react, faster than electron-rich/neutral arylboronic acids, with (4-methoxyphenyl)(4-methylbenzenesulfonato- κO)bis(tricyclohexylphosphine)nickel. Bis(1,5-cyclooctadiene)nickel(0)/tricyclohexylphosphine, (4-methoxyphenyl)(4-methylbenzenesulfonato- κO)bis(tricyclohexylphosphine)nickel and bis(tricyclohexylphosphine)nickel (II) bromide were all found to be efficient catalysts/catalyst precursors.

Graphical abstract

Electron-poor, fluoro-containing arylboronic acids reacted, faster than electronrich/neutral arylboronic acids, with 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs and were excellent coupling partners for Ni(0)/PCy₃-catalyzed cross-coupling reactions of aryl arenesulfonates.

Keywords

Electron-Poor; Arylboronic Acids; Aryl Arenesulfonates; Ni(0); Cross-Coupling

Transition metal-catalyzed Suzuki cross-coupling reactions of arylboronic acids with aryl halides/sulfonates have become powerful transformations for organic synthesis.^[1,2] While

Correspondence to: Qiao-Sheng Hu.

^bCurrent Address: College of Environmental and Chemical Engineering, Shanghai University of Electric Power, No.2588 Changyang Road, Yangpu District, Shanghai 200090, China

[†]W.-B. Chen and C.-H. Xing contributed equally.

neutral and electron-rich arylboronic acids, even very sterically hindered ones, have proven to be excellent cross-coupling partners, electron-poor arylboronic acids have often been observed as problematic coupling reagents, especially with less reactive substrates such as aryl chlorides.^[3–5] The low coupling efficiency of electron-poor arylboronic acids has been attributed to their less nucleophilicity and slower transmetalation rate than electron-neutral/rich arylboronic acids, and/or faster decomposition via proto-deboration and/or homo-coupling.^[6] Over the past years, strategies to overcome the fast decomposition shortcoming of electron-poor arylboronic acids, *e.g.*, the use of more reactive aryl iodide/bromide substrates, more amounts of arylboronic acids, masked arylboronic acids^[7] or more robust catalysts,^[8] have been developed for crosscoupling reactions with electron-poor arylboronic acids as coupling partners. The disclosure of (XPhos)Pd(0) as catalyst for the cross-coupling reaction of fluorophenylboronic acids with aryl chlorides, reported by Buchwald,^[8a] represented probably the most notable advancement in this field. Despite these impressive developments, electron-poor arylboronic acids as general coupling partners for the cross-coupling reactions with aryl arenesulfonates, which are readily available from phenols but are less reactive coupling substrates than aryl chlorides, as substrates remained to be established.^[9]

Based on our experience in Pd(0)/Ni(0)-catalyzed cross-coupling reactions,^[10,11] we considered that the key to employ electron-poor arylboronic acids as coupling partners for aryl arenesulfonates might lie in whether the decomposition of electron-poor arylboronic acids could be effectively minimized under the reaction condition. We reasoned the decomposition could be minimized if the following issues could be addressed: (a) the cross-coupling reaction could occur via fast oxidative addition process under mild reaction conditions such as room temperature and (b) transmetalation of the oxidative addition adduct with electron-poor arylboronic acids could readily occur under non-aqueous conditions. We have previously established that Ni(0)/PCy₃ undergoes fast oxidative addition with aryl arenesulfonates^[11e] and Ni(0)/PCy₃-catalyzed cross-coupling reactions could take place at room temperature with the use of solid bases such as K₃PO₄, rather than aqueous bases.^[11] These results suggested that electron-poor arylboronic acids might be efficient cross-coupling reaction partners for Ni(0)/PCy₃-catalyzed cross-coupling reactions of aryl arenesulfonates if the issue of whether electron-poor arylboronic acids could efficiently undergo transmetalation with the oxidative addition adduct could be addressed. In this communication, we report our results on establishing that electron-poor arylboronic acids could readily undergo transmetalation, faster than electron-neutral/rich arylboronic acids, with 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs complex. We also reported for the first time the general use of electron-poor fluoro-containing arylboronic acids as efficient cross-coupling partners for Ni(0)/PCy₃-catalyzed Suzuki-coupling reactions of aryl arenesulfonates.^[12,13]

Our study began with the competition reactions of different arylboronic acids, namely, *p*-tolylboronic acid, phenylboronic acid, 4-acetylphenylboronic acid, 4-trifluoromethylphenylboronic acid, 2-fluorophenylboronic acid, 2-trifluoromethylphenylboronic acid, and 2,4-difluorophenylboronic acid, with 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs. Our results are listed in Table 1. We found that the reactions occurred smoothly and the coupling product of 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs with more electron-rich arylboronic acids was always the minor product (Table 1, entries 1–5). As the product ratio of the competition reaction would

likely be decided by the transmetalation step, our results suggested that phenylboronic acid reacted faster than *p*-tolylboronic acid with 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs (Table 1, entry 1), and 4-acetylphenylboronic acid, 4-trifluoromethylphenylboronic acid or 2-fluorophenylboronic acid, 2-trifluoromethylphenylboronic acid reacted faster than phenylboronic acid with 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs (Table 1, entries 2–5). We also found that 2,4-difluorophenylboronic acid exhibited higher reactivity than 2-fluorophenylboronic acid (Table 1, entry 6), suggesting that more electron-poor arylboronic acids possess higher reactivity. In addition, 2-fluorophenylboronic acid was found to exhibit higher reactivity than more sterically hindered 2-trifluoromethylphenylboronic acid (Table 1, entry 7). These results suggested that electron-poor arylboronic acids underwent transmetalation readily, faster than electron-neutral/rich phenylboronic acid, with 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs.

We next examined Ni(COD)₂/PCy₃-catalyzed competition cross-coupling reaction of 4-methoxyphenyl tosylate or 4-methoxyphenyl halides with phenylboronic acid and 2-fluorophenylboronic acid (Table 2), in which 4-MeOC₆H₄Ni(II)(PCy₃)₂X was believed to be the reaction intermediate. We found that different conversions were observed for 4-methoxyphenyl tosylate and 4-methoxyphenyl halides. As the reductive elimination step was the same for these cross-coupling reactions and our previous study showed the oxidative addition in Ni(0)/PCy₃-catalyzed cross-coupling reactions of arylboronic acids with aryl tosylates should not be the rate-determining step,^[11e] the observation of different conversions suggested that the transmetalation should be the rate-determining step. Significantly, the ratio of the cross-coupling products all showed that 2-fluoro-4'-methoxybiphenyl, the product generated from 2-fluorophenylboronic acid, was the major product, suggesting electron-poor 2-fluorophenylboronic acid underwent transmetalation (cross-coupling reaction) faster than phenylboronic acid.^[14]

Having established that fluoro-containing arylboronic acids could be excellent coupling partners for Ni(0)/PCy₃-catalyzed cross-coupling reactions of aryl tosylates, we next examined different fluoro-containing arylboronic acids for the cross-coupling reactions with aryl arenesulfonates. Our results are summarized in Table 3. As shown in Table 3, with Ni(COD)₂/PCy₃ as the catalyst, a number of fluoro-containing arylboronic acids reacted well with aryl arenesulfonates, including those with *ortho*-, *meta*- and *para*-substituents (entries 1–18). Complete conversions and excellent isolated yields were observed for all aryl arenesulfonates employed. *p*-Methoxyphenyl benzenesulfonate and *p*-tolyl mesylate were slightly less reactive than aryl tosylates, and reactions involving them as coupling partners required slightly heating to achieve complete conversions (Table 3, entries 19 and 20). The reaction of *p*-methoxyphenyl *p*-nitrobenzenesulfonate with 2-fluorophenylboronic acid was also tested and no reaction was observed (Table 3, entry 21).

As Ni(COD)₂/PCy₃, especially Ni(COD)₂, are air-sensitive, we next examined the use of air-stable 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs^[11a,e] and Ni(PCy₃)₂Br₂^[11a] complexes as catalysts for the cross-coupling reaction of fluoro-containing arylboronic acids with aryl tosylates. We found both 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs and Ni(PCy₃)₂Br₂ were efficient catalysts, with high yields being observed for all cases (Table 4). These results showed that Ni(PCy₃)₂Br₂ and 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs were operationally convenient substitutes for

Ni(COD)₂/PCy₃ catalyst system for the room temperature cross-coupling reactions of fluoro-containing arylboronic acids with aryl arenesulfonates.

To gain insights about why electron-deficient arylboronic acids reacted faster than electron-neutral/rich arylboronic acids, we carried out the following studies. We tested the reaction of 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs with phenylboronic acid in the presence of quinone and found that the reaction was not influenced by quinone. This result suggested that free-radicals were unlikely involved in the transmetalation process. The decreasing order of the conversions observed for 4-MeOC₆H₄OTs, 4-MeOC₆H₄Cl, 4-MeOC₆H₄Br and 4-MeOC₆H₄I (Table 2) suggested that the OTs or X group might interact directly with arylboronic acids during the transmetalation process. We thus carried out the reaction of 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs with 2-fluorophenylboronic acid in the absence of K₃PO₄. We found the reaction occurred to 80% conversion in 1 hour, which was slightly slower than the reaction in the presence of K₃PO₄, in which 100% conversion was observed. This observation, which showed the transmetalation occurred efficiently without the assistance of a base, suggested that the OTs group in 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs likely interacted with the arylboronic acid prior to transmetalation. Such an interaction would be more favorable for more electron-poor arylboronic acids than electron-rich or neutral arylboronic acids.

In summary, we have demonstrated that electron-poor fluoro-containing arylboronic acids reacted, faster than electron-rich/neutral arylboronic acids, with 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs and were excellent coupling partners for room temperature Ni(0)/PCy₃-catalyzed Suzuki-Miyaura cross-coupling reactions of readily available aryl arenesulfonates. Our study showed that Ni(COD)₂/PCy₃, 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs and Ni(PCy₃)₂Br₂ were all efficient catalysts/catalyst precursors for the cross-coupling reactions of electron-poor arylboronic acids with aryl arenesulfonates. Our study also suggested that the OTs group might coordinate with arylboronic acids during the transmetalation step and paved the road for the development of other transition metal catalysts for cross-coupling reactions with electron-poor arylboronic acids as coupling partners.

Experimental Section

General procedure: Ni(COD)₂-Catalyzed Suzuki-Miyaura Cross-Couplings of Fluoro-Containing Arylboronic Acids with Aryl Arenesulfonates

In a glovebox with N₂-atmosphere, to a vial containing phenylboronic acid (0.75 mmol, 1.5 equiv.), potassium phosphate (319 mg, 1.5 mmol, 3 equiv.) and THF (2 mL) were added bis(1,5-cyclopentadiene) nickel(0) (4.2 mg, 0.015 mmol, 0.03 equiv.) and tricyclohexylphosphine (16.8 mg, 0.06 mmol, 0.12 equiv.). After stirring for 5–10 minutes, aryl tosylate or aryl benzenesulfonate (0.5 mmol, 1.0 equiv.) was added. The mixture was allowed to react at the appointed temperature. After quenching with water, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine and then evaporated under vacuum. Flash chromatography on silica gel yielded the cross-coupling products.

General procedure: 4-CH₃OC₆H₄Ni(PCy₃)₂OTs or NiBr₂(PCy₃)₂-Catalyzed Cross-Coupling Reactions of Fluoro-Containing Arylboronic Acids with Aryl Tosylates

To a vial (5-mL) were added tosylate (0.5 mmol, 1.0 equiv.), phenylboronic acid (0.75 mmol, 1.5 equiv.) on the bench, then the vial was brought into glovebox, potassium phosphate (319 mg, 1.5 mmol, 3 equiv.) and 4-CH₃OC₆H₄Ni(PCy₃)₂OTs (22.4 mg, 0.025 mmol, 0.05 equiv.) or NiBr₂(PCy₃)₂ (19.6 mg, 0.025 mmol, 0.05 equiv.) and THF (2 mL) were added. After stirring for a 5 minutes, H₂O (18 µL, 1 mmol, 2 equiv.) was added. The resulting mixture was stirred at appointed temperature for 12 h. After quenching with water, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine and then evaporated under vacuum. Flash chromatography on silica gel yielded the cross-coupling products.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We gratefully thank the NSF (CHE0911533) and NIH (1R15 GM094709) for funding. Partial support from PSC-CUNY Research Award Program is also gratefully acknowledged..

References

1. For recent reviews on Suzuki cross-coupling reactions: Miyaura N. *Topics in Current Chem.* 2002; 219:11–59. Suzuki A. *J. Organomet. Chem.* 1999; 576:147–168. Littke AF, Fu GC. *Angew. Chem. Int. Ed.* 2002; 41:4176–4211. Diez-Gonzalez S, Marion N, Nolan SP. *Chem. Rev.* 2009; 109:3612–3676. [PubMed: 19588961] Darses S, Genet J–P. *Chem. Rev.* 2008; 108:288–325. [PubMed: 18095714] Yin L, Liebscher J. *Chem. Rev.* 2007; 107:133–173. [PubMed: 17212474]
2. For recent reviews on Suzuki cross-coupling polymerizations: Hu Q-S, Pu L, Itsuno S. *Polymeric Chiral Catalyst Design and Chiral Polymer Synthesis*. 2011 Wiley:323–364. Hu Q-S, Rogers M, Long T. *Synthetic Methods for Step-Growth Polymers*. 2003 Wiley:467–526. Schlüter AD. *J. Polym. Sci. Polym. Chem. Ed.* 2001; 39:1533–1556.
3. Korenaga T, Kosaki T, Fukumura R, Ema T, Sakai T. *Org. Lett.* 2005; 7:4915–4917. [PubMed: 16235921]
4. Raders SM, Moore JN, Parks JK, Miller AD, Leibing TM, Kelley SP, Rogers RD, Shaughnessy KH. *J. Org. Chem.* 2013; 78:4649–4664. [PubMed: 23638733]
5. Barder TE, Walker SD, Martinelli JR, Buchwald SL. *J. Am. Chem. Soc.* 2005; 127:4685–4696. [PubMed: 15796535]
6. a) Wong MS, Zhang XL. *Tetrahedron Lett.* 2001; 42:4087–4089. b) Kuivila HG, Reuwer JF, Mangravite JA. *J. Am. Chem. Soc.* 1964; 86:2666–2670. c) Kuivila HG, Reuwer JF, Mangravite JA. *Can. J. Chem.* 1963; 41:3081–3090.
7. For examples: Barder TE, Buchwald SL. *Org. Lett.* 2004; 6:2649–2652. [PubMed: 15281735] Sakashita S, Takizawa M, Sugai J, Ito H, Yamamoto Y. *Org. Lett.* 2013; 15:4308–4311. [PubMed: 23952320] Hodgson PB, Salingu FH. *Tetrahedron Lett.* 2004; 45:685–687. Molander GA, Ellis N. *Acc. Chem. Res.* 2007; 40:275–286. [PubMed: 17256882] Dick GR, Woerly EM, Burke MD. *Angew. Chem. Int. Ed.* 2012; 51:2667–2672. Yamamoto Y, Takizawa M, Yu X-Q, Miyaura N. *Angew. Chem. Int. Ed.* 2008; 47:928–931. Noguchi H, Hojo K, Sugimoto M. *J. Am. Chem. Soc.* 2007; 129:758–759. [PubMed: 17243801]
8. a) Kinzel T, Zhang Y, Buchwald SL. *J. Am. Chem. Soc.* 2010; 132:14073–14075. [PubMed: 20858009] b) Crowley BM, Potteiger CM, Deng JZ, Prier CK, Paone DV, Burgey CS. *Tetrahedron Lett.* 2011; 52:5055–5059.

9. For scattered reports of fluoro-containing arylboronic acids as coupling partners for aryl tosylates: Abe T, Mino T, Watanabe K, Yagishita F, Sakamoto M. *Eur. J. Org. Chem.* 2014;3909–3916. Hu F, Lei X. *Tetrahedron*. 2014; 70:3854–3858. Zhao F, Zhang Y-F, Wen J, Yu D-G, Wei J-B, Xi Z, Shi Z. *J. Org. Lett.* 2013; 15:3230–3233. [PubMed: 23789920] Wang Z-Y, Chen G-Q, Shao L-X. *J. Org. Chem.* 2012; 77:6608–6614. [PubMed: 22804630] Zhang L, Wu J. *Adv. Synth. & Catal.* 2008; 350:2409–2413. Zhang L, Meng T, Wu J. *J. Org. Chem.* 2007; 72:9346–9349. [PubMed: 17975932]
10. a) Zhang H-H, Xing C-H, Tsemo GB, Hu Q-S. *ACS MacroLett.* 2013; 2:10–13. b) Zhang H-H, Xing C-H, Hu Q-S. *J. Am. Chem. Soc.* 2012; 134:13156–13159. [PubMed: 22860802] c) Dong C-G, Hu Q-S. *J. Am. Chem. Soc.* 2005; 127:10006–10007. [PubMed: 16011357] d) Hu Q-S, Tang Z-Y, Lu Y, Yu H-B. *J. Am. Chem. Soc.* 2003; 125:2856–2857. [PubMed: 12617635]
11. a) Xing C-H, Lee J-R, Tang Z-Y, Zheng JR, Hu Q-S. *Adv. Synth. Catal.* 2011; 353:2051–2059. b) Tang Z-Y, Hu Q-S. *J. Org. Chem.* 2006; 71:2167–2169. [PubMed: 16497011] c) Tang Z-Y, Spinella S, Hu Q-S. *Tetrahedron Lett.* 2006; 47:2427–2730. d) Tang Z-Y, Hu Q-S. *Adv. Synth. Catal.* 2004; 346:1635–16367. e) Tang Z-Y, Hu Q-S. *J. Am. Chem. Soc.* 2004; 126:3058–3059. [PubMed: 15012129]
12. For fluoro-containing biaryls in medicine: Meyer EA, Castellano RK, Diederich F. *Angew. Chem., Int. Ed.* 2003; 42:1210–1250. Zahn A, Brotschi C, Leumann C. *J. Chem. Eur.* 2005; 11:2125–2129.
13. For fluoro-containing biaryls in materials chemistry: Montes VA, Li G, Pohl R, Shinar J, Anzenbacher P. *Adv. Mater.* 2004; 16:2001–2003. Tsuzuki T, Shirasawa N, Suzuki T, Tokito S. *Adv. Mater.* 2003; 15:1455–1458. Nitschke JR, Tilley TD. *J. Am. Chem. Soc.* 2001; 123:10183. [PubMed: 11603967] Sakamoto Y, Suzuki T, Miura A, Fujikawa H, Tokito S, Taga Y. *J. Am. Chem. Soc.* 2000; 122:1832–1833. Hwang DH, Song SY, Ahn T, Chu HY, Do LM, Kim SH, Shim HK, Zyung T. *Synth. Met.* 2000; 111:485–487. Kitamura T, Wada Y, Yanagida S. *J. Fluorine Chem.* 2000; 105:305–311. Weck M, Dunn AR, Matsumoto K, Coates GW, Lobkovsky EB, Grubbs RH. *Angew. Chem., Int. Ed.* 1999; 38:2741–2745.
14. For $\text{ArNi(II)(PPh}_3)_2\text{Cl/DPPF}$ -catalyzed competing reaction of 4-methoxyphenyl tosylate with phenylboronic acid and 4-(methoxycarbonyl)phenylboronic acid: see: Ref. 9b.

Table 1Competition Reactions of 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs with Different Arylboronic Acids^a

Entry	ArB(OH) ₂	Ar'B(OH) ₂	Ratio of A : B
1			46% : 54%
2			33% : 67%
3			36% : 64%
4			7% : 93%
5			26% : 74%
6			40% : 60%
7			11% : 89%

^a. Reaction conditions: 4-methoxyphenylNi(PCy₃)₂OTs (1.0 equiv.), phenylboronic acid (1.0 equiv.), 4-acetylphenylboronic acid or fluoro-containing phenylboronic acid (1.0 equiv.), K₃PO₄(3 equiv.), THF (2 ml), room temperature, 1 h.

^b. Based on GC-MS analysis.

Table 2

Ni(COD)₂/PCy₃-Catalyzed Competition Reaction of 4-MeOC₆H₄X with Phenylboronic Acid and 2-Fluorophenylboronic Acid ^a

Entry	X	Conversion (%) ^b	Ratio of A : B ^b
1	OTs	80	4 : 96
2	Cl	54	6 : 94
3	Br	40	4 : 96
4	I	35	9 : 91

^a. Reaction conditions: 4-methoxyphenyl tosylate or halide (1.0 equiv.), phenylboronic acid (1.0 equiv.), 2-fluorophenylboronic acid (1.0 equiv.), K₃PO₄(3 equiv.), THF (2 ml), room temperature, 4 h.

^b. Based on GC-MS analysis.

Table 3

Room Temperature Ni(COD)₂/PCy₃-Catalyzed Cross-Couplings of Aryl Arenesulfonates with Fluoro-Containing Arylboronic Acids ^a

Entry	ArF-B(OH) ₂	Ar'-OSO ₂ Ar'	Yield(%) ^b
1			90
2			98
3			99
4			99
5			91
6			92.5
7			94.5
8			91.5
9			83
10			89
11			91
12			97
13			90 ^c
14			94 ^d
15			97

Entry	Ar _F -B(OH) ₂	Ar-OSO ₂ Ar'	Yield(%) ^b
16	(1b)	(2e)	83
17	(1e)	(2f)	98
18	(1d)	(2f)	94
19	(1e)	(2g)	91 ^d
20	(1e)	(2h)	90 ^d
21	(1e)	(2i)	< 1 ^e

^a. Reaction conditions: aryl sulfonates (1.0 equiv.), arylboronic acids (1.5 equiv.), K₃PO₄ (3 equiv.), THF (2 ml), room temperature.

^b. Isolated yields (average of two runs).

^c. Reaction time: 80 °C, 8 h.

^d. Reaction time: 50 °C, 9 h.

^e. Reaction time: 12 h.

Table 4

Room Temperature 4-MeOC₆H₄Ni(II)(PCy₃)₂OTs or Ni(PCy₃)₂Br₂-Catalyzed Cross-Couplings of Aryl Tosylates with Arylboronic Acids ^a

Entry	ArF-B(OH) ₂	Ar-OSO ₂ Ar'	Yield(%) ^b
1			95 (93)
2			99 (98)
3			99
4			93 (87)
5			97 (92)
6			90 (86)
7			90 (89)
8			87 (84)
9			96
10			99 (97)
11			98
12			95
13			99

^a. Reaction conditions: aryl sulfonates (1.0 equiv.), arylboronic acids (1.5 equiv.), Ni(II) catalyst (5 mol%), K₃PO₄(3 equiv.), THF (2 ml), H₂O(2 eq.), room temperature.

^b. Isolated yields. In parenthesis: CH₃OC₆H₄Ni(II)(PCy₃)₂OTs as catalyst.