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Use of cheaper metal than Rh, $CHCl_3$-free Pd catalyst, in 1,2-addition of aromatic aldehydes with arylboronic acids

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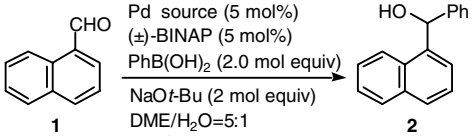
Abstract—$Pd(OAc)_2$-(±)-tol-BINAP-catalyzed arylation reaction of aromatic aldehydes with arylboronic acids in the absence of $CHCl_3$ is described.

Recently, Rh-catalyzed carbon–carbon bond forming reactions with arylboron reagents have been developed.[1] Arylboron reagents are nontoxic, air-stable, and practically useful. Miyaura found that Rh(I) complexes catalyze 1,2-addition to aldehyde with arylboronic acid.[2,3] From the viewpoint of cost, since the use of a cheaper metal than Rh is desirable, we were interested in using a Pd catalyst for arylation of aromatic aldehydes with arylboronic acids. However, unlike the Rh catalyst, the Pd catalyst showed rare activity for the 1,2-addition of arylboronic acids to aromatic aldehydes.[4–8] To date, only one successful example of Pd-catalyzed arylation of aromatic aldehydes with arylboronic acids has been reported by Ito and Ohta.[9,10] According to their report, it is described that the use of $CHCl_3$ is crucial for this Pd-catalyzed arylation, and in the absence of $CHCl_3$, the arylation does not proceed at all. Herein we would like to report our investigations on Pd-catalyzed arylation of aromatic aldehydes with arylboronic acids *in the absence of harmful $CHCl_3$*.

We considered that if arylboronic acid is activated by a strong base, this arylation in which a key step is transmetalation between the Pd catalyst and arylboronic acid, would smoothly proceed. We first screened Pd sources with (±)-BINAP as a ligand and NaO*t*-Bu as a base in $DME/H_2O = 5:1$ (from the viewpoint of easy handling, NaO*t*-Bu was used in place of NaOH. NaOH is produced in situ) as shown in Table 1. Among the Pd sources screened, only $Pd(OAc)_2$ catalyzed this arylation (entry 1). The use of KO*t*-Bu, LiO*t*-Bu, *i*-Pr_2NEt, and pyridine as a base gave less satisfactory results. The effect of ligands was then examined (Table 2). As shown in entries 3–5, the use of monodentate PPh_3, and bidentate dppp and dppb with smaller bite angle than (±)-BINAP resulted in no reaction. A (±)-BINAP derivative, (±)-tol-BINAP, was the best ligand (Table 2, entry 2).

Table 1. Effect of Pd sources[a]



Entry	Pd source	Yield[b] (%)
1	$Pd(OAc)_2$	63[c]
2	$Pd(OCOCF_3)_2$	NR[d]
3	$Pd(dba)_2$	NR[d]
4	$PdCl_2(MeCN)_2$	NR[d]

[a] The reactions were performed using 1-naphthaldehyde (**1**), 5 mol % of Pd and (±)-BINAP, and 2 mol equiv of $PhB(OH)_2$ and NaO*t*-Bu in $DME/H_2O = 5:1$ at 100 °C for 24 h.
[b] Isolated yield.
[c] Remainder of mass balance was the starting 1-naphthaldehyde (**1**).
[d] No reaction occurred.

Keywords: Arylation of aromatic aldehyde; 1,2-Addition; Arylboronic acid; Palladium; BINAP; Catalyst.
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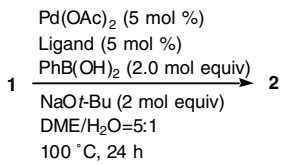
Table 2. Effect of ligands[a]

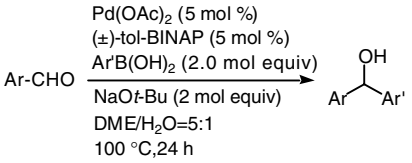


Entry	Ligand	Yield[b] (%)
1	(±)-BINAP	63[c]
2	(±)-Tol-BINAP	86
3[d]	PPh_3	NR[e]
4	dppp	NR[e]
5	dppb	NR[e]

[a] The reactions were performed using 1-naphthaldehyde (**1**), 5 mol % of $Pd(OAc)_2$ and ligand, and 2 mol equiv of $PhB(OH)_2$ and NaO*t*-Bu in DME/H_2O = 5:1 at 100 °C for 24 h.
[b] Isolated yield.
[c] Remainder of mass balance was the starting 1-naphthaldehyde (**1**).
[d] The use of 10 mol % of PPh_3 also resulted in no reaction.
[e] No reaction occurred.

Results of the arylation of aromatic aldehydes with arylboronic acids are shown in Table 3. As can be seen in entries 1–4, the electronic effect in the arylboronic acids was observed. Noteworthy is that electron-deficient arylboronic acids reacted smoothly with 1-naphthaldehyde (**1**), affording the corresponding products in good yields, because Ito and Ohta have reported that the arylation with electron-deficient arylboronic acids in the presence of Pd–$CHCl_3$ catalyst is sluggish.[9] Since 2-tolylboronic acid bears an *ortho*-substituent on the benzene ring (entry 5), and both electron-deficient and -rich aromatic aldehydes (entries 7–11) showed a somewhat low reactivity, their reactions were performed with 3 mol equiv of $Ar'B(OH)_2$. Electronic effects in the aldehydes were also observed. Compared with electron-rich aldehydes, the reaction with electron-deficient aldehydes resulted in better yields.

Table 3. $Pd(OAc)_2$-(±)-tol-BINAP catalyzed arylation of aromatic aldehydes with arylboronic acids[a]



Entry	Aromatic aldehyde	Arylboronic acid	Yield[b,c] (%)
1	1-Naphthaldehyde	4-F–C_6H_4–$B(OH)_2$	85
2	1-Naphthaldehyde	4-Cl–C_6H_4–$B(OH)_2$	85
3	1-Naphthaldehyde	4-Me–C_6H_4–$B(OH)_2$	81
4	1-Naphthaldehyde	4-MeO–C_6H_4–$B(OH)_2$	74
5[d]	1-Naphthaldehyde	2-Me–C_6H_4–$B(OH)_2$	72
6	2-Naphthaldehyde	Ph–$B(OH)_2$	92
7[d]	4-F–C_6H_4–CHO	Ph–$B(OH)_2$	76
8[d]	4-Cl–C_6H_4–CHO	Ph–$B(OH)_2$	77
9[d]	4-Me–C_6H_4–CHO	Ph–$B(OH)_2$	70
10[d]	2-MeO–C_6H_4–CHO	Ph–$B(OH)_2$	50
11[d]	2-Cl–C_6H_4–CHO	Ph–$B(OH)_2$	85

[a] The reactions were performed using aromatic aldehyde, 5 mol % of $Pd(OAc)_2$ and (±)-tol-BINAP, and 2 mol equiv of $Ar'B(OH)_2$ and NaO*t*-Bu in DME/H_2O = 5:1 at 100 °C for 24 h.
[b] Isolated yield.
[c] Remainder of mass balance was the starting aromatic aldehyde.
[d] 3 Mol equiv of $Ar'B(OH)_2$ was used.

In summary, $Pd(OAc)_2$-(±)-tol-BINAP catalyst[11] in the absence of $CHCl_3$ was found to proceed arylation reaction of aromatic aldehydes with arylboronic acids.[12] Mechanistic study[13] and development of an asymmetric version[14] are now in progress. Further, ongoing efforts are focused on using a much cheaper and more natural resources-abundant metal in this arylation.[15]

Acknowledgements

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12. *Representative procedure for the Pd-catalyzed arylation of 1-naphthaldehyde* (**1**) *with phenylboronic acid:* To a stirred solution of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) in DME/H_2O (5:1, 2.4 mL) were added (±)-tol-BINAP (17.0 mg, 0.025 mmol), NaO*t*-Bu (96.1 mg, 1.0 mmol), $PhB(OH)_2$ (122 mg, 1.0 mmol), and 1-naphthaldehyde (**1**) (76.1 mg, 0.5 mmol) at rt. The reaction mixture was stirred at 100 °C for 24 h under argon atmosphere, allowed to cool, diluted with H_2O and extracted with EtOAc. The combined extracts were washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column (EtOAc/hexane = 1:19 to 1:9) to give (1-naphthyl)phenylmethanol (**2**) (101 mg, yield 86%) as a colorless oil. The physical data as shown below were comparable to those reported.[2a] IR (neat): $\nu = 3381\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.42$ (s, 1H), 6.48 (s, 1H), 7.21–7.48 (m, 8H), 7.59 (d, $J = 7.1$ Hz, 1H), 7.74–7.86 (m, 2H), 7.98–8.02 (m, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 73.50$, 123.86, 124.48, 125.17, 125.44, 125.98, 126.90, 127.48, 128.29, 128.35, 128.60, 130.54, 133.75, 138.63, 142.94. EIMS: $m/z = 234$ (M^+), 217, 157, 129, 128, 105, 77. Anal. calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found C, 86.95; H, 5.99.

The physical data of other diarylmethanols are shown below.

4-Fluorophenyl-1-naphthylmethanol (Table 3, entry 1). IR (neat): $\nu = 3236\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.25$–2.40 (br, 1H), 6.52 (br s, 1H), 6.99 (d, $J = 8.7$ Hz, 1H), 7.02 (d, $J = 8.7$ Hz, 1H), 7.29–7.53 (m, 5H), 7.63 (d, $J = 6.8$ Hz, 1H), 7.79–7.91 (m, 2H), 7.95–8.02 (m, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 73.03$, 115.24 (d, $J = 21.2$ Hz), 123.73, 124.42, 125.21, 125.58, 126.11, 128.53, 128.62 (d, $J = 8.4$ Hz), 128.72, 130.40, 133.83, 138.44, 138.70 (d, $J = 3.4$ Hz), 162.00 (d, $J = 245.4$ Hz). FABMS: $m/z = 253$ (M^++1). Anal. calcd for $C_{17}H_{13}FO$: C, 80.93; H, 5.19. Found C, 81.11; H, 5.43.

4-Chlorophenyl-1-naphthylmethanol (entry 2). IR (Nujol): $\nu = 3295\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.31$–2.42 (br, 1H), 6.49 (br s, 1H), 7.28 (d, $J = 8.6$ Hz, 2H), 7.34 (d, $J = 8.6$ Hz, 2H), 7.38–7.52 (m, 3H), 7.58 (d, $J = 6.8$ Hz, 1H), 7.74–7.92 (m, 2H), 7.94–8.03 (m, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 72.84$, 123.66, 124.56, 125.13, 125.58, 126.12, 128.18, 128.41, 128.55, 128.66, 130.32, 133.10, 133.72, 138.10, 141.25. EIMS: $m/z = 270$ (M^+), 268 (M^+), 253, 251, 129, 128, 77. HRMS (M^+) calcd for $C_{17}H_{13}Cl^{37}O$ 270.0625, found 270.0631. HRMS (M^+) calcd for $C_{17}H_{13}Cl^{35}O$ 268.0654, found 268.0659. Anal. calcd for $C_{17}H_{13}ClO$: C, 75.98; H, 4.88. Found C, 76.10; H, 5.23.

1-Naphthyl-(4-tolyl)methanol (entry 3). IR (Nujol): $\nu = 3353\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.28$ (s, 3H), 2.55 (br s, 1H), 6.40 (br s, 1H), 7.07 (d, $J = 7.9$ Hz, 1 × 2H), 7.22 (d, $J = 7.9$ Hz, 1 × 2H), 7.34–7.48 (m, 3H), 7.59 (d, $J = 6.9$ Hz, 1H), 7.73–7.90 (m, 2H), 7.94–8.05 (m, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 21.18$, 73.38, 123.86, 124.23, 125.19, 125.40, 125.93, 126.90, 128.18, 128.59, 129.07, 130.50, 133.73, 137.20, 138.75, 140.06. FABMS: $m/z = 249$ (M^++1). Anal. calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found C, 87.10; H, 6.44.

4-Methoxyphenyl-1-naphthylmethanol (entry 4). IR (Nujol): $\nu = 3536\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.43$ (br s, 1H), 3.73 (s, 3H), 6.43 (s, 1H), 6.81 (d, $J = 8.7$ Hz, 2H), 7.26 (d, $J = 8.7$ Hz, 2H), 7.36–7.49 (m, 3H), 7.64 (d, $J = 7.1$ Hz, 1H), 7.74–7.87 (m, 2H), 7.90–7.99 (m, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 55.26$, 73.19, 113.87, 123.86, 124.08, 125.22, 125.43, 125.95, 128.21, 128.30, 128.63, 130.47, 133.76, 135.30, 138.81, 158.92. EIMS: $m/z = 264$ (M^+), 247, 135, 77. HRMS (M^+) calcd for $C_{18}H_{16}O_2$: 264.1150, found 264.1154. Anal. calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found C, 81.49; H, 6.18.

1-Naphthyl-(2-tolyl)methanol (entry 5). IR (Nujol): $\nu = 3218\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.19$ (br d, $J = 3.9$ Hz, 1H), 2.30 (s, 3H), 6.64–6.76 (d, $J = 3.9$ Hz, 1H), 7.10–7.28 (m, 3H), 7.31–7.54 (m, 5H), 7.76–7.92 (m, 2H), 8.00–8.08 (m, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 19.26$, 69.95, 123.45, 124.48, 125.24, 125.55, 126.05, 126.25, 126.60, 127.59, 128.39, 128.69, 130.42, 131.01, 133.75, 135.66, 138.10, 140.77. FABMS: $m/z = 249$ (M^++1). Anal. calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found C, 87.31; H, 6.59.

2-Naphthylphenylmethanol (entry 6). The physical data as shown below were comparable to those reported: Seebach, D.; Beck, A. K.; Roggo, S.; Wonnacotto, A. *Chem. Ber.* **1985**, *118*, 3673. IR (Nujol): $\nu = 3227\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.34$ (br s, 1H), 6.02 (s, 1H), 7.24–7.54 (m, 8H), 7.76–7.89 (m, 3H), 7.91 (s, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 76.33$, 124.64, 124.87, 125.86, 126.08, 126.58, 127.56, 127.94, 128.22, 128.43, 132.71, 133.08, 140.93, 143.45. EIMS: $m/z = 234$ (M^+), 155, 129, 105, 77. Anal. calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found C, 87.27; H, 6.38.

4-Fluorophenylphenylmethanol (entry 7). The spectral data as shown below were comparable to those reported: Wang, Z.; Chandler, W. D.; Lee, D. G. *Can. J. Chem.* **1998**, *76*, 919. IR (neat): $\nu = 3354\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.19$ (br d, $J = 3.3$ Hz, 1H), 5.83 (br d, $J = 3.3$ Hz, 1H), 6.99 (d, $J = 8.7$ Hz, 1H), 7.03 (d, $J = 8.7$ Hz, 1H), 7.22–7.40 (m, 7H). ^{13}C NMR ($CDCl_3$): $\delta = 75.63$ (br), 115.22 (d, $J = 21.0$ Hz), 126.38, 127.65, 128.14 (d, $J = 8.0$ Hz), 128.49, 139.46 (d, $J = 3.0$ Hz), 143.55, 162.04 (d, $J = 245$ Hz). EIMS: $m/z = 202$ (M^+), 183, 105, 77. Anal. calcd for $C_{13}H_{11}FO$: C, 77.21; H, 5.48. Found C, 77.39; H, 5.70.

4-Chlorophenylphenylmethanol (entry 8). The spectral data as shown below were comparable to those reported: Chen, D.-W.; Ochiai, M. *J. Org. Chem.* **1999**, *64*, 6804. IR (neat): $\nu = 3341\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.34$ (d, $J = 3.6$ Hz, 1H), 6.23 (d, $J = 3.6$ Hz, 1H), 7.18–7.45 (m, 8H), 7.61 (dd, $J = 7.7$, 1.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 72.55$, 126.78, 126.93, 127.61, 127.81, 128.31, 128.57, 129.35, 132.27, 140.74, 141.98. FABMS: $m/z = 221$ (M^++1), 219 (M^++1). Anal. calcd for $C_{13}H_{11}ClO$: C, 71.40; H, 5.07. Found C, 71.36; H, 5.05.

Phenyl-(4-tolyl)methanol (entry 9). The spectral data as shown below were comparable to those reported: Seebach, D.; Beck, A. K.; Roggo, S.; Wonnacotto, A. *Chem. Ber.* **1985**, *118*, 3673. IR (Nujol): $\nu = 3330\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.14$ (br d, $J = 3.3$ Hz, 1H), 2.33 (s, 3H), 5.82 (br d, $J = 3.3$ Hz, 1H), 7.14 (d, $J = 7.9$ Hz, 1H × 2), 7.26 (d, $J = 7.9$ Hz, 1H × 2), 7.28–7.42 (m, 5H). ^{13}C NMR ($CDCl_3$): $\delta = 21.16$, 76.10, 126.35, 126.42, 127.34, 128.32, 129.06, 137.15, 140.85, 143.84. EIMS: $m/z = 198$ (M^+), 183, 105, 77. Anal. calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found C, 84.69; H, 6.86.

2-Methoxyphenylphenylmethanol (entry 10). The physical data as shown below were comparable to those reported: Oi, S.; Moro, M.; Inoue, Y. *Organometallics* **2001**, *20*, 1036. IR (neat): $\nu = 3403\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 3.04$ (d, $J = 5.4$ Hz, 1H), 3.82 (s, 3H), 6.06 (d, $J = 5.4$ Hz, 1H), 6.90 (d, $J = 8.5$ Hz, 1H), 6.94 (dd, $J = 7.6$, 7.6 Hz, 1H), 7.19–7.43 (m, 7H). ^{13}C NMR ($CDCl_3$): $\delta = 55.32$, 72.06, 110.54, 120.61, 126.37, 126.96, 127.62, 127.98, 128.52, 131.72, 143.04. EIMS:

$m/z = 214$ (M^+), 196, 195, 135, 105, 77. Anal. calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found C, 78.79; H, 6.80.

2-Chlorophenylphenylmethanol (entry 11). The spectral data as shown below were comparable to those reported: Ohkuma, T.; Koizumi, M.; Ikehira, H.; Yokozawa, T.; Noyori, R. *Org. Lett*. **2000**, *2*, 659. IR (neat): $\nu = 3341\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 2.34$ (d, $J = 3.6$ Hz, 1H), 6.23 (d, $J = 3.6$ Hz, 1H), 7.18–7.45 (m, 8H), 7.61 (dd, $J = 7.7$, 1.7 Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 72.55$, 126.78, 126.93, 127.61, 127.81, 128.31, 128.57, 129.35, 132.27, 140.74, 141.98. FABMS: $m/z = 221$ (M^++1), 219 (M^++1). Anal. calcd for $C_{13}H_{11}ClO$: C, 71.40; H, 5.07. Found C, 71.23; H, 5.10.

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