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Recyclable and reusable $Pd(OAc)_2/P(1\text{-}Nap)_3/[bmim][PF_6]/H_2O$ system for the addition of arylboronic acids to aldehydes

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ABSTRACT

A stable and efficient $Pd(OAc)_2/P(1\text{-}Nap)_3$[tri(1-naphthyl)phosphine] catalytic system for the addition of arylboronic acids to aldehydes has been developed. In the presence of $Pd(OAc)_2$ and $P(1\text{-}Nap)_3$, the addition reaction of arylboronic acids with aldehydes was carried out smoothly at 65 °C to give a variety of carbinol derivatives in good to excellent yields using a mixture of $[bmim][PF_6]$ and water as the solvent. The isolation of the products was readily performed by the extraction with diethyl ether, and the $Pd(OAc)_2/P(1\text{-}Nap)_3/[bmim][PF_6]/H_2O$ system could be easily recycled and reused six times without significant loss of catalytic activity. Our system not only avoids the use of easily volatile THF or toluene as solvent but also solves the basic problem of palladium catalyst and these phosphine ligand reuse.

Introduction

Diarylmethanols are important intermediates for the preparation of a number of biologically active compounds [1–3]. For example, the 1,1-diarylalkyl structural moiety is present in some compounds with reported activity such as antimuscarinics [4], antidepressants [5], and endothelin antagonists [6]. Although the addition of strong organometallics (RLi, RMgX) to aldehydes provides one of the most versatile methods to prepare secondary alcohols, limitations as to their use arise from their high reactivity as nucleophile or base, which often gives rise to undesired side reactions in the preparation of multifunctional compounds. The addition of organozinc reagents to aldehydes has also been reported [7–9], but examples of aryl transfer are often limited to the introduction of a phenyl group [10–15]. Thus, there is still a need for practical synthetic methodologies for the synthesis of a variety of carbinol derivatives. In the past few years, the rhodium-catalyzed addition of organoboron reagents to aldehydes has received much attention [16–22] since organoboron reagents enjoy high prestige in the transition-metal-catalyzed C–C coupling reaction due to their advantages of low toxicity, stability to air or moisture, and good functional group tolerance [23–25]. Meanwhile the palladium-catalyzed addition of arylboronic acids to aldehydes has also emerged as a promising alternative for the synthesis of carbinol derivatives [26–30]. Generally, these rhodium- or palladium-catalyzed addition reactions of arylboronic acids with aldehydes are performed in easily volatile and toxic organic solvents such as toluene or THF using homogeneous rhodium or palladium complexes as catalysts, however, industrial applications of homogeneous rhodium or palladium complexes remain a challenge because they are expensive, cannot be separated from the product mixture and reused. These disadvantages have so far precluded their practical applications.

The development of environmentally friendly synthetic procedures has become a major concern throughout the chemical industry due to continuing depletion of natural resources and growing environmental awareness [31–34]. One of the prime concerns of industry and academia is the search for replacements to the environmentally damaging organic solvents used on a large scale, especially those which are volatile and difficult to contain. There are also significant economical and environmental reasons for developing recyclable catalytic reactions from both academic and industrial perspectives. To satisfy both recyclability and environmental concerns, a more facile method is to immobilize the catalyst in a liquid phase by dissolving it into a nonvolatile and non-

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mixing liquid, such as ionic liquids. Room temperature ionic liquids, especially those based upon the 1,3-dialkylimidazolium cation, have received much attention in the last decade [35–39]. They offer an alternative and ecologically sound medium compared to conventional organic solvents because they are non-volatile, recyclable, thermally robust and excellent solvents for a wide range of organic and inorganic reagents. Furthermore, their high compatibility with transition metal catalysts and limited miscibility with common solvents, enables easy product and catalyst separation with the retention of the stabilized catalyst in the ionic phase [40]. These and related ionic liquids have been successfully applied to palladium-catalyzed carbon–carbon bond formations such as Heck reaction [41,42], Suzuki reaction [43–46], Sonogashira reaction [47], Stille reaction [48,49], and carbon–heteroatom bond formation reactions [50,51]. Recently, the use of water as solvent in organic reactions has also attracted considerable interest due to the low cost, non-toxicity, safety, availability, and greater chemoselectivity compared with organic solvents [52–55]. We herein report the application of $Pd(OAc)_2/P(1\text{-}Nap)_3/[bmim][PF_6]/H_2O$ system as an extremely effective and reusable catalytic medium for the addition reaction of arylboronic acids with aldehydes. The developed methodology has important practical advantages deserving special note.

Experimental

General remarks

All chemicals were reagent grade and used as purchased. The products were purified by flash chromatography on silica gel. Mixture of EtOAc and hexane was generally used as eluent. All addition products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin–Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer in $CDCl_3$ as solvent. Melting points are uncorrected.

General procedure for the palladium-catalyzed addition of arylboronic acids to aldehydes in [bmim][PF_6]/H_2O

A Schlenk reaction tube was charged with [bmim][PF_6] (3 mL), distilled water (2 mL), $Pd(OAc)_2$ (0.05 mmol), $P(1\text{-}Nap)_3$ (0.05 mmol), aldehyde (1.0 mmol), aryl-boronic acid (2.0 mmol), and K_2CO_3 (3.0 mmol) under an argon atmosphere. The mixture was stirred at room temperature for 0.5 h, and then heated at 65 °C for 6–24 h. After being cooled to room temperature, the reaction mixture was extracted three times with diethyl ether (3 × 10 mL). The residue of the extraction was subjected to a second run of the addition reaction by charging with the same substrates (arylboronic acid, aldehyde, and K_2CO_3) under the same conditions without further addition of $Pd(OAc)_2$ or $P(1\text{-}Nap)_3$. The combined ether phase was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 10:1) to give the desired product.

(4-Nitrophenyl)phenylmethanol, ***3a*** *[30]*

Yellow solid, m.p. 68–69 °C. IR (KBr): ν_{max}/cm^{-1} 3449, 1601, 1514, 1340, 1048, 705. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.38–7.29 (m, 5H), 5.91 (s, 1H), 2.49 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.7, 142.9, 142.7, 129.1, 128.4, 127.1, 126.7, 123.7, 75.5.

(4-Chlorophenyl)phenylmethanol, ***3b*** *[19]*

White solid, m.p. 61–62 °C. IR (KBr): ν_{max}/cm^{-1} 3375, 3064, 1640, 1601, 1488, 1138, 1013, 848, 760, 700. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35–7.26 (m, 9H), 5.81 (s, 1H), 2.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.0, 141.7, 132.8, 128.2, 128.1, 127.4, 126.0, 75.1.

(4-Cyanophenyl)phenylmethanol, ***3c*** *[30]*

White solid, m.p. 65–66 °C. IR (KBr): ν_{max}/cm^{-1} 3406, 2197, 1629, 1487, 1067, 755, 699. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.61 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.39–7.32 (m, 5H), 5.86 (s, 1H), 2.52 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.9, 142.8, 132.3, 128.9, 128.4, 127.1, 126.6, 118.8, 111.2, 75.6.

(3-Nitrophenyl)phenylmethanol, ***3d*** *[17]*

Yellow solid, m.p. 43–44 °C. IR (KBr): ν_{max}/cm^{-1} 3435, 1639, 1619, 1530, 1351, 1138, 1122, 1068, 953. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.36–7.25 (m, 5H), 5.90 (s, 1H), 2.58 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.8, 142.8, 134.6, 132.5, 130.8, 129.0, 128.4, 126.7, 122.4, 121.3, 75.4.

(4-Methoxycarbonylphenyl)phenylmethanol, ***3e*** *[17]*

Colorless oil. IR (film): ν_{max}/cm^{-1} 3451, 1716, 1595, 1281, 1180, 1067, 751. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.36–7.24 (m, 5H), 5.86 (s, 1H), 3.88 (s, 3H), 2.54 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.0, 148.8, 143.2, 129.7, 128.8, 128.3, 127.9, 126.7, 126.3, 75.8, 52.2.

Phenyl(4-trifluoromethylphenyl)methanol, ***3f*** *[17]*

White solid, m.p. 95–97 °C. IR (KBr): ν_{max}/cm^{-1} 3302, 1318, 1164, 1107, 1056, 743. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.35–7.25 (m, 5H), 5.84 (s, 1H), 2.47 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 147.6, 143.2, 128.7, 128.2, 126.7, 126.6, 125.5, 125.4, 122.8, 75.8.

(Biphenyl-4-yl)phenylmethanol, ***3g*** *[30]*

White solid, m.p. 83–85 °C. IR (KBr): ν_{max}/cm^{-1} 3412, 3056, 1640, 1601, 1487, 1453, 1159, 1072, 759, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58–7.55 (m, 4H), 7.47–7.27 (m, 10H), 5.90 (s, 1H), 2.25 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.6, 142.8, 140.7, 140.5, 128.7, 128.4, 127.6, 127.3, 127.1, 127.0, 126.8, 126.5, 76.0.

(4-Methoxyphenyl)phenylmethanol, ***3h*** *[30]*

White solid, m.p. 66–67 °C. IR (KBr): ν_{max}/cm^{-1} 3412, 1612, 1587, 1517, 1494, 1178, 1034, 810, 727. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38–7.24 (m, 7H), 6.87 (d, J = 8.8 Hz, 2H), 5.81 (s, 1H), 3.79 (s, 3H), 2.17 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.9, 144.1, 136.2, 128.4, 127.9, 127.5, 126.4, 113.9, 75.8, 55.3.

(4-Methylphenyl)phenylmethanol, ***3i*** *[17]*

White solid, 54–55 °C. IR (KBr): ν_{max}/cm^{-1} 3307, 2936, 1623, 1501, 1165, 751. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39–7.28 (m, 5H), 7.26 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 5.99 (s, 1H), 2.36 (s, 3H), 2.18 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.9, 140.9, 137.4, 129.3, 128.4, 127.5, 126.6, 126.4, 76.2, 21.2.

(2-Chlorophenyl)phenylmethanol, ***3j***

Colorless oil. IR (film): ν_{max}/cm^{-1} 3433, 1638, 1066, 752, 699. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, J = 7.6 Hz, 1H), 7.33–7.12 (m, 8H), 6.15 (s, 1H), 2.32 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.2, 140.0, 131.5, 128.5, 127.7, 127.5, 127.0, 126.8, 126.1, 125.9, 71.7. Anal. Calcd for $C_{13}H_{11}OCl$: C, 71.39; H, 5.07. Found: C, 71.14; H, 4.86.

(2,5-Dichlorophenyl)phenylmethanol, ***3k***

Colorless oil. IR (film): ν_{max}/cm^{-1} 3339, 1590, 1562, 1381, 1020, 697. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58 (d, J = 8.4 Hz, 1H), 7.35–7.23 (m, 7H), 6.16 (s, 1H), 2.33 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.8, 139.7, 133.9, 133.1, 129.3, 129.0, 128.6, 128.0, 127.4, 126.9, 72.3. Anal. Calcd for $C_{13}H_{10}OCl_2$: C, 61.66; H, 3.98. Found: C, 61.43; H, 3.67.

4-Methylphenyl(4-nitrophenyl)methanol, ***3l*** *[29]*

Yellow solid, m.p. 105–106 °C. IR (KBr): ν_{max}/cm^{-1} 3423, 2920, 1639, 1509, 1344, 1178, 1063, 796. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.88 (s, 1H), 2.34 (s, 3H), 2.29 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.9, 147.2, 139.9, 138.3, 129.6, 127.0, 126.7, 123.6, 75.4, 21.1.

4-Chlorophenyl(4-nitrophenyl)methanol, ***3m*** *[30]*

Yellow solid, m.p. 130–131 °C. IR (KBr): ν_{max}/cm^{-1} 3421, 1638, 1512, 1346, 1067, 799. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.20 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 5.91 (s, 1H), 2.37 (br 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.3, 147.4, 141.2, 134.3, 129.2, 128.1, 127.2, 123.8, 74.7.

3-Methylphenyl(4-nitrophenyl)methanol, ***3n***

Yellow solid, m.p. 60–61 °C. IR (KBr): ν_{max}/cm^{-1} 3501, 2870, 1602, 1513, 1345, 1147, 1041, 857. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.27–7.13 (m, 4H), 5.88 (s, 1H), 2.41 (br, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.9, 147.5, 146.4, 127.2, 126.9, 125.9, 125.8, 124.1, 123.9, 74.9, 29.7. Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.13; H, 5.39; N, 5.76. Found: C, 68.87; H, 5.58, N, 5.47.

4-Methoxyphenyl(4-nitrophenyl)methanol, ***3o*** *[29]*

Yellow solid, m.p. 76–77 °C. IR (KBr): ν_{max}/cm^{-1} 3410, 2917, 2849, 1612, 1604, 1514, 1351, 1251, 1042, 800. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 5.88 (s, 1H), 3.79 (s, 3H), 2.41 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.7, 151.0, 147.2, 134.9, 128.2, 126.9, 123.6, 114.3, 75.1, 55.4.

4-Nitrophenyl(4-trifluoromethylphenyl)methanol, ***3p*** *[30]*

Yellow solid, m.p. 104–105 °C. IR (KBr): ν_{max}/cm^{-1} 3488, 2916, 1598, 1513, 1333, 1160, 1120, 1070, 804. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 5.99 (s, 1H), 2.51 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.9, 147.5, 146.4, 130.5, 127.2, 126.9, 126.6, 125.9, 123.9, 74.9.

4-Acetylphenyl(4-nitrophenyl)methanol, ***3q*** *[17]*

Yellow solid, m.p. 121–122 °C. IR (KBr): ν_{max}/cm^{-1} 3476, 2925, 1676, 1601, 1517, 1345, 1054, 961, 800. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.15 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 5.97 (d, J = 2.8 Hz, 1H), 3.38 (d, J = 3.2 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 198.1, 150.2, 147.7, 147.2, 136.5, 128.9, 127.2, 126.6, 123.8, 74.8, 26.6.

3-Nitrophenyl(4-nitrophenyl)methanol, ***3r*** *[30]*

Yellow solid, m.p. 117–118 °C. IR (KBr): ν_{max}/cm^{-1} 3457, 1603, 1517, 1345, 1082, 1047, 861, 736. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28–8.14 (m, 4H), 7.70 (d, J = 7.6 Hz, 1H), 7.61–7.52 (m, 3H), 6.02 (d, J = 2.4 Hz, 1H), 2.73 (d, J = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.3, 148.5, 147.5, 144.6, 132.4, 129.9, 127.2, 124.1, 123.1, 121.2, 74.5.

2-Methylphenyl(4-nitrophenyl)methanol, ***3s*** *[19]*

Yellow oil. IR (film): ν_{max}/cm^{-1} 3419, 2928, 1604, 1521, 1489, 1347, 1108, 1034, 758. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.19 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.34–7.18 (m, 4H), 6.11 (s, 1H), 2.32 (s, 3H), 2.28 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.2, 147.2, 140.5, 135.6, 131.1, 128.4, 127.5, 127.0, 126.6, 123.6, 72.8, 19.4.

2-Methoxyphenyl(4-nitrophenyl)methanol, ***3t***

Yellow oil. IR (film): ν_{max}/cm^{-1} 3421, 2940, 2839, 1601, 1521, 1490, 1347, 1245, 1028, 734. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.14 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.32–7.21 (m, 2H), 6.96 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.09 (d, J = 4.4 Hz, 1H), 3.80 (s, 3H), 3.23 (d, J = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.5, 151.0, 147.0, 130.8, 129.4, 127.7, 127.1, 123.4, 121.1, 111.0, 71.5, 55.4. Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.58; H, 5.27, N, 5.58.

1-Naphthyl(4-nitrophenyl)methanol, ***3u***

Yellow solid, m.p. 129–130 °C. IR (KBr): ν_{max}/cm^{-1} 3421, 1637, 1599, 1514, 1344, 1068, 954, 853, 783. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 7.6 Hz, 1H), 7.91–7.86 (m, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.50–7.45 (m, 4H), 6.58 (s, 1H), 2.53 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.3, 147.2, 137.8, 134.2, 130.5, 129.4, 129.0, 127.5, 126.6, 126.0, 125.6, 125.3, 123.7, 123.6, 73.3. Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.01. Found: C, 72.85; H, 4.52, N, 5.22.

4-Fluorophenyl(4-methoxyphenyl)methanol, ***3v*** *[17]*

White solid, m.p. 51–52 °C. IR (KBr): ν_{max}/cm^{-1} 3420, 2938, 1618, 1255, 1187, 1065, 750. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.34–7.32 (m, 2H), 7.27 (d, J = 8.8 Hz, 2H), 7.03–7.01 (m, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.79 (s, 1H), 3.80 (s, 3H), 2.04 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.9, 159.2, 136.1, 128.2, 128.1, 115.4, 115.2, 113.9, 75.3, 55.4.

4-Methoxyphenyl(4-trifluoromethylphenyl)methanol, ***3w*** *[19]*

White solid, m.p. 87–88 °C. IR (KBr): ν_{max}/cm^{-1} 3349, 2938, 2840, 1615, 1587, 1516, 1335, 1259, 1107, 1065, 814. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 5.78 (s, 1H), 3.77 (s, 3H), 2.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.4, 147.9, 135.5, 129.5, 128.1, 126.9, 126.6, 125.3, 114.1, 75.3, 55.3.

4-Cyanophenyl(4-methylphenyl)methanol, ***3x*** *[29]*

White solid, m.p. 69–71 °C. IR (KBr): ν_{max}/cm^{-1} 3406, 2962, 2198, 1605, 1496, 1165, 1067, 848, 746. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 5.80 (s, 1H), 2.53 (br, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 149.1, 139.9, 138.1, 132.2, 129.5, 126.9, 126.6, 118.8, 110.9, 75.4, 21.1.

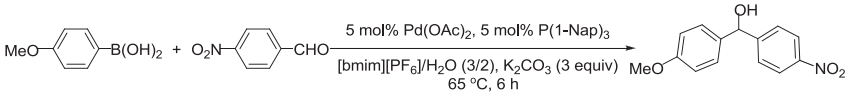
4-Methoxyphenyl(2-methylphenyl)methanol, ***3y*** *[17]*

Colorless oil. IR (film): ν_{max}/cm^{-1} 3403, 1607, 1295, 1252, 1065, 754. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 8.8 Hz, 2H), 7.28–7.17 (m, 2H), 7.12 (d, J = 7.4 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 5.95 (d, J = 4.0 Hz, 1H), 3.88 (s, 3H), 2.22 (s, 3H), 2.05 (d, J = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.7, 135.2, 135.1, 130.6, 127.5, 126.6, 126.1, 125.9, 113.7, 72.9, 55.3, 19.4.

2-Nitrophenyl(o-tolyl)methanol, ***4a*** *[30]*

Yellow solid, m.p. 92–93 °C. IR (KBr): ν_{max}/cm^{-1} 3308, 1610, 1522, 1493, 1343, 1037, 850, 791. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97 (d, J = 8.8 Hz, 1H), 7.60–7.45 (m, 3H), 7.25–7.17 (m, 4H), 6.54 (d, J = 4.4 Hz, 1H), 2.82 (d, J = 4.4 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR

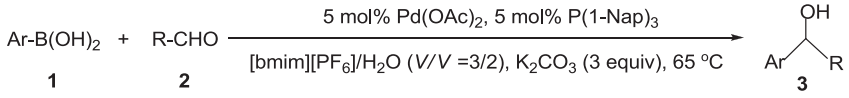
Table 1
Addition reaction of 4-methoxyphenylboronic acid with 4-nitrobenzaldehyde in different conditions.[a]



Entry	Solvent	Pd source	Base	Temp. (°C)	Yield (%)[b]
1	[bmim][PF_6]	$PdCl_2$	K_2CO_3	65	Trace
2	[bmim][PF_6]/H_2O (4/1)	$PdCl_2$	K_2CO_3	65	44
3	[bmim][PF_6]/H_2O (3/2)	$PdCl_2$	K_2CO_3	65	83
4	[bmim][PF_6]/H_2O (2/3)	$PdCl_2$	K_2CO_3	65	65
5	[bmim][PF_6]/H_2O (1/4)	$PdCl_2$	K_2CO_3	65	37
6	H_2O	$PdCl_2$	K_2CO_3	65	0
7	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	K_2CO_3	65	93
8	[bmim][PF_6]/H_2O (3/2)	$PdCl_2(PPh_3)_2$	K_2CO_3	65	84
9	[bmim][PF_6]/H_2O (3/2)	$PdCl_2(PhCN)_2$	K_2CO_3	65	79
10	[bmim][PF_6]/H_2O (3/2)	$Pd(PPh_3)_4$	K_2CO_3	65	83
11	[bmim][PF_6]/H_2O (3/2)	$Pd_2(dba)_3$	K_2CO_3	65	72
12	[bmim][PF_6]/H_2O (3/2)	Pd/C	K_2CO_3	65	14
13	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	Na_2CO_3	65	85
14	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	Cs_2CO_3	65	90
15	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	Et_3N	65	9
16	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	*n*-Bu_3N	65	11
17	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	DABCO	65	8
18	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	DMAP	65	7
19	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	DBU	65	10
20	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	K_2CO_3	80	90
21	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	K_2CO_3	95	89
22[c]	[bmim][PF_6]/H_2O (3/2)	$Pd(OAc)_2$	K_2CO_3	50	77

[a] Reaction conditions: 4-nitrobenzaldehyde (1.0 mmol), 4-methoxyphenylboronic acid (2.0 mmol), base (3.0 mmol), Pd source (5 mol%), P(1-Nap)$_3$ (5 mol%) in 5 mL of solvent for 6 h under Ar.
[b] Isolated yields.
[c] For 24 h.

Table 2
Addition of various arylboronic acids to aldehydes.[a]



Entry	Ar	R	Product	Time (h)	Yield (%)[b]
1	Ph	4-$O_2NC_6H_4$	**3a**	6	93
2	Ph	4-ClC_6H_4	**3b**	8	91
3	Ph	4-NCC_6H_4	**3c**	8	90
4	Ph	3-$O_2NC_6H_4$	**3d**	8	91
5	Ph	4-$MeOCOC_6H_4$	**3e**	8	92
6	Ph	4-$CF_3C_6H_4$	**3f**	6	93
7[c]	Ph	4-BrC_6H_4	**3g**	10	55
8	Ph	4-$MeOC_6H_4$	**3h**	15	77
9	Ph	4-MeC_6H_4	**3i**	12	83
10	Ph	2-ClC_6H_4	**3j**	20	79
11	Ph	2,5-$Cl_2C_6H_3$	**3k**	20	74
12	4-MeC_6H_4	4-$O_2NC_6H_4$	**3l**	6	92
13	4-ClC_6H_4	4-$O_2NC_6H_4$	**3m**	6	91
14	3-MeC_6H_4	4-$O_2NC_6H_4$	**3n**	6	96
15	4-$MeOC_6H_4$	4-$O_2NC_6H_4$	**3o**	6	93
16	4-$CF_3C_6H_4$	4-$O_2NC_6H_4$	**3p**	20	64
17	4-$MeCOC_6H_4$	4-$O_2NC_6H_4$	**3q**	20	68
18	3-$O_2NC_6H_4$	4-$O_2NC_6H_4$	**3r**	20	62
19	2-MeC_6H_4	4-$O_2NC_6H_4$	**3s**	10	95
20	2-$MeOC_6H_4$	4-$O_2NC_6H_4$	**3t**	10	96
21	1-Naphthyl	4-$O_2NC_6H_4$	**3u**	14	87
22	4-$MeOC_6H_4$	4-FC_6H_4	**3v**	10	86
23	4-$MeOC_6H_4$	4-$CF_3C_6H_4$	**3w**	6	92
24	4-MeC_6H_4	4-NCC_6H_4	**3x**	6	90
25	2-MeC_6H_4	4-$MeOC_6H_4$	**3y**	24	78

[a] Reaction conditions: aldehyde (1 mmol), arylboronic acid (2 mmol), K_2CO_3 (3 mmol), $Pd(OAc)_2$ (5 mol%), P(1-Nap)$_3$ (5 mol%), [bmim][PF_6] (3 mL), water (2 mL) at 65 °C under Ar.
[b] Isolated yields.
[c] Biphenyl-4-yl(phenyl)methanol was obtained.

(100 MHz, $CDCl_3$) δ (ppm): 148.6, 139.4, 138.1, 135.7, 133.3, 130.5, 129.3, 128.4, 128.1, 126.2, 126.0, 124.6, 68.6, 19.0.

2-Methoxyphenyl(2-nitrophenyl)methanol, ***4b*** *[19]*

Yellow solid, m.p. 80–81 °C. IR (KBr): ν_{max}/cm^{-1} 3498, 1596, 1518, 1340, 1110, 1032, 863. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88 (d, J = 8.4 Hz, 1H), 7.62–7.26 (m, 3H), 7.24–6.86 (m, 4H), 6.65 (d, J = 4.4 Hz, 1H), 3.75 (s, 3H), 3.22 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.4, 148.7, 137.8, 133.0, 130.2, 129.4, 129.2, 128.1, 126.7, 124.2, 120.6, 110.6, 66.7, 55.3.

2-Methoxyphenyl(2-trifluoromethylphenyl)methanol, ***4c*** *[30]*

Colorless oil. IR (film): ν_{max}/cm^{-1} 3475, 1603, 1492, 1314, 1126, 1042, 847. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70 (d, J = 7.6 Hz, 1H), 7.58–7.53 (m, 1H), 7.45–7.43 (m, 1H), 7.31–7.28 (m, 1H), 6.98 (d, J = 7.4 Hz, 1H), 6.94–6.88 (m, 3H), 6.55 (s, 1H), 3.84 (s, 3H), 3.18 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.6, 140.9, 131.9, 131.2, 129.3, 128.8, 127.7, 125.8, 122.5, 121.3, 120.4, 112.5, 110.4, 67.2, 55.3.

Bis(2-methoxyphenyl)methanol, ***4d*** *[56]*

Colorless oil. IR (film): ν_{max}/cm^{-1} 3446, 1598, 1487, 1128, 1056, 845. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36–7.30 (m, 4H), 7.05–6.92 (m, 4H), 6.47 (d, J = 4.8 Hz, 1H), 3.83 (s, 6H), 3.72 (d, J = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.6, 130.9, 128.3, 127.6, 120.4, 110.2, 67.0, 55.2.

Naphthalen-1-yl(2-nitrophenyl)methanol, ***4e*** *[30]*

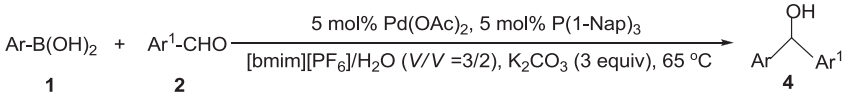
Yellow solid, m.p. 67–69 °C. IR (KBr): ν_{max}/cm^{-1} 3304, 1604, 1513, 1489, 1342, 803, 725. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (d, J = 8.4 Hz, 1H), 7.90–7.78 (m, 3H), 7.49–7.37 (m, 7H), 7.03 (d, J = 4.4 Hz, 1H), 3.47 (d, J = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.6, 138.2, 136.9, 134.0, 133.5, 130.9, 129.6, 129.1, 128.9, 128.7, 126.7, 125.9, 125.4, 124.9, 124.5, 123.4, 68.5.

Results and discussion

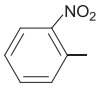
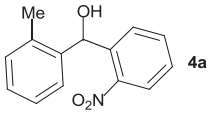
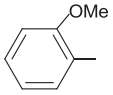
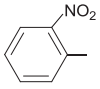
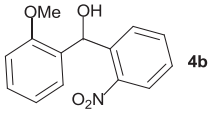
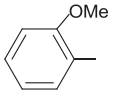
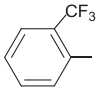
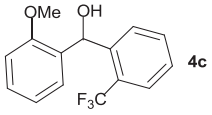
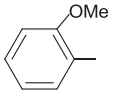
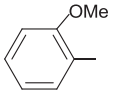
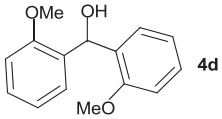
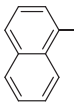
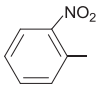
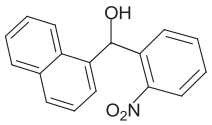
Optimization of reaction conditions

Initially, to determine the optimum conditions, the palladium-catalyzed addition of 4-methoxyphenylboronic acid to 4-nitrobenzaldehyde in the presence of $P(1\text{-Nap})_3$ as a ligand was chosen as a model reaction, the influences of various reaction parameters such as solvents, Pd sources, bases, and reaction temperatures on the reaction were examined and the results are summarized in Table 1. At first, the solvent effect was examined, and a significant solvent effect was observed. It is evident that the reaction proceeded very slowly and only trace of desired product was obtained when the moisture stable and commercially available 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) was used as solvent (Table 1, entry 1). However, a mixture of [bmim][PF_6] and H_2O was found to be effective (Table 1, entries 2–5). The reaction run in [bmim][PF_6]/H_2O (V/V = 3/2) gave 4-methoxyphenyl(4-nitrophenyl)methanol in 83% yield (Table 1, entry 3). It may be due to the fact that the ionic liquids and water dissolve the catalyst/reactants and the base, respectively, to make the reaction proceed smoothly. The reaction did not occur at all using neat water as solvent (Table 1, entry 6). Among the palladium sources tested [$PdCl_2$, $Pd(OAc)_2$, $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$, $Pd(PPh_3)_4$, $Pd_2(dba)_3$, and Pd/C], $Pd(OAc)_2$ exhibited the highest

Table 3
Addition of hindered arylboronic acids to hindered aromatic aldehydes.[a]



1 2 4

Entry	Ar	Ar^1	Product	Time (h)	Yield (%)[b]
1			 **4a**	20	83
2			 **4b**	20	85
3			 **4c**	24	78
4			 **4d**	24	72
5			 **4e**	20	82

[a] Reaction conditions: aldehyde (1 mmol), arylboronic acid (2 mmol), K_2CO_3 (3 mmol), $Pd(OAc)_2$ (5 mol%), $P(1\text{-Nap})_3$ (5 mol%), [bmim][PF_6] (3 mL), water (2 mL) at 65 °C under Ar.
[b] Isolated yields.

catalytic activity and afforded a 93% yield (Table 1, entry 7). Our next studies focused on the effect of base and reaction temperature on the model reaction. When Cs_2CO_3, K_2CO_3 and Na_2CO_3 were used as the base, good to excellent yields were obtained, whereas organic bases such as Et_3N, *n*-Bu_3N, DABCO, DMAP, and DBU afforded low yields (Table 1, entries 7, 13–19), so K_2CO_3 was finally selected as the base for the reaction. For the temperatures evaluated [50, 65, 80, and 95 °C], 65 °C gave the best result. It was found that the reaction was accomplished when it was carried out in [bmim][PF_6]/H_2O (V/V = 3/2) at 65 °C for 6 h. Reducing reaction temperature to 50 °C resulted in a decrease in yield and a longer reaction time was needed (Table 1, entry 22). Therefore, the optimal catalytic system involved the use of $Pd(OAc)_2$ (5 mol%), P(1-Nap)$_3$ (5 mol%), K_2CO_3 (3 equiv) in [bmim][PF_6]/H_2O (V/V = 3/2) at 65 °C under Ar for 6 h (Table 1, entry 7).

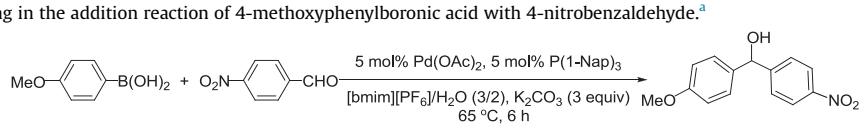
Scope of $Pd(OAc)_2$-catalyzed addition of various arylboronic acids to aldehydes in [bmim][PF_6]/H_2O

With this promising results in hand, we started to investigate the scope of this reaction under the optimized conditions. The scope of both aldehydes and arylboronic acids was explored, and the results are summarized in Table 2. At the beginning of the determination of the aldehydes substrate scope, phenylboronic acid was used as one of the model substrate. As shown in Table 2, the addition reaction of phenylboronic acid with various aldehydes proceeded smoothly under the optimized reaction conditions to afford the corresponding diarylmethanols in good to excellent yields and a wide range of functional groups including nitro, cyano, ester, methoxy, methyl, trifluoromethyl, and chloro groups on the benzene rings were well tolerated (Table 2, entries 1–11). Furthermore, electron-deficient aromatic aldehydes reacted with phenylboronic acid easily and furnished the desired products in excellent yields (Table 2, entries 1–6). Interestingly, the reaction of 4-chlorobenzaldehyde with phenylboronic acid afforded selectively (4-chlorophenyl)phenylmethanol **3b** in 91% yield and keep the chloro group untouched (Table 2, entry 2). However, the reaction of 4-bromobenzaldehyde with phenylboronic acid gave biphenyl-4-yl(phenyl)methanol **3g** in 55% yield due to the presence of Suzuki coupling of the aryl bromide (Table 2, entry 7). On the other hand, electron-rich aromatic aldehydes such as 4-methoxybenzaldehyde or 4-methylbenzaldehyde as less active substrates also gave the corresponding diarylmethanols **3h** and **3i** in good yields (Table 2, entries 8 and 9). Finally, it should be worth noting that the addition of phenylboronic acid to the sterically hindered aromatic aldehydes such as 2-chlorobenzaldehyde and 2,5-dichlorobenzaldehyde could also proceed effectively under the standard conditions to afford desired products **3j** and **3k** in 79% and 74% yields, respectively (Table 2, entries 10 and 11).

Encouraged by the above results, the scope and the generality of the reaction by varying the arylboronic acids were further investigated. We were pleased to find that the standard conditions were compatible with various arylboronic acids bearing methyl, chloro, methoxy, trifluoromethyl, acetyl and nitro groups. It was found that both electron-rich and electron-deficient arylboronic acids underwent the addition reaction efficiently and generated the corresponding diarylmethanols in moderate to excellent yields. For example, arylboronic acids with 4-methyl, 4-chloro, 4-methoxy and 3-methyl on the benzene rings underwent the reaction with 4-nitrobenzaldehyde smoothly and the desired products **3l**–**o** were isolated in 91–96% yields (Table 2, entries 12–15). Arylboronic acids bearing an electron-withdrawing substituent, which are less nucleophilic and, hence, transmetalate more slowly than the electro-neutral analogs, are prone to homocoupling and protodeboronation side reactions [57]. The reaction of arylboronic acids bearing 4-trifluoromethyl, 4-acetyl and 3-nitro groups also gave the corresponding diarylmethanols **3p**–**r** in 62–68% yields (Table 2, entries 16–18). The reaction of sterically hindered arylboronic acids such as 2-methylphenylboronic acid and 2-methoxyphenylboronic acid could proceed efficiently and the products **3s** and **3t** were isolated in 95% and 96% yield, respectively (Table 2, entries 19 and 20). The bulky 1-naphthylboronic acid also reacted with 4-nitrobenzaldehyde smoothly to give the desired product **3u** in 87% yield (Table 2, entry 21). In addition, the reactions of phenylboronic acids bearing substituents with various substituted benzaldehydes afforded the corresponding diarylmethanols **3v**–**y** also in good to high yields (Table 2, entries 22–25). We also tried to carry out the reaction of phenylboronic acid with aliphatic aldehydes such as 3-phenylpropanal or hexanal using this catalytic system, however, the addition reactions were very slow at standard condition and only traces of desired products were detected due to their lower electrophilicity than that of aromatic aldehydes.

In order to further show the usability of this palladium-catalyzed addition reaction of arylboronic acids with aromatic aldehydes in [bmim][PF_6]/H_2O as a practical method for the synthesis of hindered diarylmethanols, we next examined the addition reaction of hindered arylboronic acids with hindered aromatic aldehydes under the optimized conditions, and the results are summarized in Table 3. As shown in Table 3, a monosubstitution in the ortho position of both arylboronic acids and aromatic aldehydes could reduce their reactivity slightly. For instance, the reaction of 2-methylphenylboronic acid with 2-nitrobenzaldehyde gave 2-nitrophenyl(*o*-tolyl)methanol **4a** in 83% yield (Table 3, entry 1). 2-Methoxyphenylboronic acid could react with 2-nitrobenzaldehyde, 2-trifluoromethylbenzaldehyde, and 2-methoxybenzaldehyde to afford the corresponding desired products **4b**, **4c**, and **4d** in 85%, 78%, and 72% yield, respectively (Table 3,

Table 4
Ionic liquid and catalyst recycling in the addition reaction of 4-methoxyphenylboronic acid with 4-nitrobenzaldehyde.[a]



Cycle	Yield (%)[b]	Cycle	Yield (%)[b]
1	93	4	92
2	92	5	91
3	91	6	90

[a] Reaction conditions: 4-nitrobenzaldehyde (1 mmol), 4-methoxyphenylboronic acid (2 mmol), K_2CO_3 (3 mmol), $Pd(OAc)_2$ (5 mol%), P(1-Nap)$_3$ (5 mol%), [bmim][PF_6] (3 mL), water (2 mL) at 65 °C under Ar for 6 h.
[b] Isolated yields.

entries 2–4). The reaction of bulky 1-naphthylboronic acid with 2-nitrobenzaldehyde also furnished 1-naphthyl(2-nitrophenyl) methanol **4e** in 82% yield (Table 3, entry 5).

Recycling of the catalytic system

Isolation of the products **3** or **4** from the [bmim][PF_6]/H_2O reaction mixtures can be conveniently achieved by extraction with diethyl ether for three times. To evaluate the possibility of recycling the $Pd(OAc)_2$/P(1-Nap)$_3$/[bmim][PF_6]/H_2O catalytic system used in the reaction, 4-methoxyphenylboronic acid, 4-nitrobenzaldehyde and K_2CO_3 were allowed to react in this catalytic system at 65 °C for 6 h and then the product was extracted with diethyl ether for three times affording the cleaned catalytic solution. After removal of diethyl ether under the reduced pressure, a second amount of reactants were added to the solution and the process was repeated up to 3 times. After third cycle, the ionic liquid was washed with distilled water (2 × 5 mL) and mixed with distilled water (2 mL), and then recycled for another three times without addition of $Pd(OAc)_2$ and P(1-Nap)$_3$. The yield of the reaction by using of the recycling catalytic system was 92% for the first time, 91% for the second time, 92% for the third time, 91% for the fourth time, and 90% for the fifth time, respectively. It seems that there is no effect on the rate and yield of the reaction during each cycle (Table 4), the result is important from a practical point of view. Additionally, this ionic liquid/water catalytic system could be stored for several weeks with no special precautions to exclude air and still afford comparable results to the fresh ionic liquid/water catalytic system.

Conclusions

In summary, a highly efficient and reusable $Pd(OAc)_2$/P(1-Nap)$_3$/[bmim][PF_6]/H_2O system for the addition reaction of arylboronic acids with aromatic aldehydes has been developed. In the presence of $Pd(OAc)_2$ and P(1-Nap)$_3$, the addition reactions of a number of arylboronic acids with various aromatic aldehydes proceeded smoothly and efficiently at 65 °C using K_2CO_3 as base in a mixture of [bmim][PF_6] and water to afford a variety of diarylmethanols in good to excellent yields. Furthermore, the $Pd(OAc)_2$/P(1-Nap)$_3$/[bmim][PF_6]/H_2O system could be recycled and reused six times without significant loss of catalytic activity. This protocol will serve as an efficient and green way to prepare carbinol derivatives. Easy product isolation, the ionic liquid and catalyst recycling, and avoiding use of easily volatile THF or toluene as solvent are important advantages of the developed methodology.

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