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Anti-Markovnikov hydroaminations of styrene catalyzed by palladium(II) N-heterocyclic carbene complexes under conventional and microwave heating

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Abstract

Six palladium(II) complexes with benzimidazole-based N-heterocyclic carbene ligands were synthesized by transmetallation reactions between silver(I) N-heterocyclic carbene complexes and $PdCl_2(PhCN)_2$. The complexes were characterized by physicochemical and spectroscopic methods. The palladium complexes were tested as catalysts for intermolecular hydroamination reactions of styrene with various anilines in ionic liquids under both conventional and microwave heating. All of these complexes proved to be catalytically active in these reactions. The anti-Markovnikov addition products were selectively obtained by using 1 mol% of the palladium complex.

Introduction

The direct addition of N–H bonds across unactivated C–C multiple bonds, commonly known as hydroamination, is a simple and atom-economical route for constructing C–N bonds [1]. Hydroamination reactions can be applied to the synthesis of a broad range of nitrogen-containing molecules [2]. Nitrogen-containing organic compounds are widely found in nature and display a wide range of biological and pharmacological activities. They are also very important precursors in the synthesis of pharmaceuticals, agrochemicals, and various bulk and fine chemicals [3]. Therefore, much effort has been devoted to the synthesis and derivatization of amine-functionalized molecules [4]. Hydroamination is an attractive synthetic approach for efficient amine syntheses. Hydroamination reactions can be catalyzed by a variety of different metal-based catalysts, including complexes of main group metals, lanthanides, and both early and late transition metals [5–11]. Although the early transition metal as well as the lanthanide catalysts displays high activity for hydroamination reactions, catalysts based on late transition metals have more functional group tolerance and are less sensitive to air and moisture. Numerous catalytic systems including transition metal catalysts have been developed for the hydroamination of alkenes [12–15]. Generally, palladium-catalyzed intermolecular hydroamination of styrenes with amines gives the Markovnikov addition products [16–18]. Hartwig and co-workers have reported the addition of anilines to vinylarenes using palladium complexes in the presence of an acid cocatalyst such as TfOH. The Markovnikov addition products were obtained in 67–99% yields [19]. Unlike other palladium complexes, some palladium(II) N-heterocyclic carbene complexes catalyze anti-Markovnikov addition of amines to alkenes [20, 21]. For example, the anti-Markovnikov addition of secondary amines to activated olefins with good yields using palladium and nickel precatalysts with 1,2,4-triazole based N-heterocyclic carbene ligands has been reported by Ghosh [20]. While N-heterocyclic carbene (NHC) complexes have often been used as catalysts in the intramolecular hydroamination of alkenes and alkynes [22–24], their use in intermolecular hydroamination reactions is more limited [25, 26]. NHCs are a very important class of ligands which have been widely used in organometallic chemistry and catalysis in the last few decades, due to their versatile and tunable steric and electronic properties [27]. NHCs are strongly σ-donating and weakly π-accepting ligands, which form stable NHC complexes with a range of transition metals [28]. A variety of NHC complexes have been used as catalysts for various transformations [29, 30].

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Recently, ionic liquids have attracted much attention due to their valuable properties such as chemical and thermal stability, versatile structures and properties, negligible vapor pressure, non-flammability, good dissolving ability and recyclability. Moreover, ionic liquids have been used as solvents and/or catalysts in various chemical reactions. Reactions performed in ionic liquids often show rate enhancement, selectivity and higher yields with respect to traditional solvents [31]. In recent years, use of microwave heating in organic synthesis has attracted considerable attention because it often reduces reaction times, enhances reaction rates and improves product yields and purity [32]. The use of ionic liquids in microwave-assisted synthesis has great potential, and many research groups have begun to explore this approach in synthesis [33]. In this paper, we report a series of palladium(II) complexes of benzimidazole-based N-heterocyclic carbene ligands as effective catalysts for the intermolecular hydroamination of styrene with anilines.

Experimental

All preparative reactions for the palladium(II)–NHC complexes (**2a**–**f**) were carried out under argon in flame-dried glassware using standard Schlenk techniques. The solvents were purified by distillation over the drying agents indicated, and transferred under Ar; THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). All reagents were purchased from Sigma-Aldrich, Merck or Fluka. Microwave-assisted reactions were carried out in a microwave oven system manufactured by Milestone (Milestone Start S Microwave Labstation for Synthesis) under aerobic conditions. All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker AC300P FT spectrometer operating at 300.13 (^1H) or 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hertz. FTIR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a Mattson 1000 spectrophotometer. Gas chromatography was carried out by GC-FID on an Agilent 6890 N gas chromatograph equipped with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 µm film thickness. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were obtained with a LECO CHNS-932 elemental analyzer.

General procedure for preparation of the Ag(I)–NHC complexes 1

A mixture of the appropriate benzimidazolium chloride (1.0 mmol), Ag_2O (0.5 mmol) and activated 4 Å molecular sieves in dichloromethane (20 mL) was stirred for 24 h at room temperature in the dark. The mixture was then filtered through Celite, and the solvent was removed under reduced pressure. The crude product was recrystallized from dichloromethane/hexane (1:2) at room temperature. The resulting white solid was isolated by filtration and dried in vacuum.

Synthesis of Pd(II)–NHC complexes 2

A solution of the required silver(I) NHC complex (0.62 mmol) and $PdCl_2(PhCN)_2$ (0.31 mmol) in dichloromethane (20 mL) was stirred for 24 h at room temperature in the dark, whereupon an off-white AgCl precipitate was observed. The resulting mixture was filtered through Celite, and the solvent was removed under reduced pressure. The crude product was recrystallized from dichloromethane/diethyl ether (1:2) at room temperature. The white crystals were filtered off, washed with diethyl ether (3×10 mL) and dried under vacuum.

Bis[1-benzyl-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]-dichloropalladium(II) 2a Yield: 0.20 g, 77%, m.p.: 204–205 °C, IR: $\nu_{(NCN)}$ 1607 cm^{-1}. Anal. Calc. for $C_{50}H_{40}N_4PdCl_2$: C, 68.69; H, 4.61; N: 6.41. Found: C, 68.68; H, 4.62; N, 6.42%. ^1H NMR ($CDCl_3$) δ: 5.75 and 5.84 (s, 4H, $CH_2C_6H_5$), 6.10 and 6.21 (s, 4H, $CH_2C_{10}H_7$), 6.37–8.45 (m, 32H, Ar–H). ^{13}C NMR ($CDCl_3$) δ: 49.6 and 51.4 ($CH_2C_6H_5$), 52.4 and 53.2 ($CH_2C_{10}H_7$), 111.1, 111.2, 113.5, 113.8, 122.5, 122.8, 123.0, 125.2, 125.3, 125.5, 125.8, 126.3, 126.4, 126.5, 127.2, 127.5, 127. 7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.7, 128.8, 128.9, 129.2, 130.0, 130.3, 130.4, 130.8, 131.2, 131.3, 131.5, 132.8, 133.2, 133.5, 133.8, 134.3, 134.9, 135.3, 135.8 and 144.4 (Ar–C), 182.7 and 182.8 (C–Pd).

Bis[1-(4-methylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]-dichloropalladium(II) 2b Yield: 0.21 g, 75%, m.p.: 260–261 °C, IR: $\nu_{(NCN)}$ 1607 cm^{-1}. Anal. Calc. for $C_{52}H_{44}N_4PdCl_2$: C, 69.22; H, 4.92; N, 6.21. Found: C, 69.24; H, 4.93; N, 6.20%. ^1H NMR ($CDCl_3$) δ: 2.08 and 2.24 (s, 6H, $CH_2C_6H_4CH_3$-4), 5.85 and 6.12 (s, 4H, $CH_2C_6H_4CH_3$-4), 6.36 and 6.61 (s, 4H, $CH_2C_{10}H_7$);

6.66–8.44 (m, 28H, Ar–*H*). ^{13}C NMR (CDCl$_3$) δ: 21.1 and 21.2 (CH$_2$C$_6$H$_4$*C*H$_3$-4), 49.6 and 49.7 (*C*H$_2$C$_6$H$_4$CH$_3$-4), 51.1 and 51.3 (*C*H$_2$C$_{10}$H$_7$), 111.9, 112.1, 123.3, 123.7, 125.3, 125.4, 125.6, 125.8, 126.3, 126.6, 126.9, 127.9, 128.4, 128.6, 128.9, 129.1, 129.5, 130.5, 130.8, 131.3, 131.8, 133.1, 133.3, 133.5, 133.6, 133.9, 134.0, 134.4, 134.5, 136.9 and 137.5 (Ar–*C*), 182.3 (*C*–Pd).

Bis[1-(2-methylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]-dichloropalladium(II) 2c Yield: 0.18 g, 78%, m.p.: 253–254 °C, IR: $\nu_{(NCN)}$ 1607 cm^{-1}. Anal. Calc. for C$_{52}$H$_{44}$N$_4$PdCl$_2$: C, 69.22; H, 4.92; N, 6.21. Found: C, 69.22; H, 4.91; N, 6.22%. ^{1}H NMR (CDCl$_3$) δ: 1.85 and 2.18 (s, 6H, CH$_2$C$_6$H$_4$*C*H$_3$-2), 5.86 and 5.88 (s, 4H, *C*H$_2$C$_6$H$_4$CH$_3$-2), 6.35 and 6.38 (s, 4H, *C*H$_2$C$_{10}$H$_7$), 6.42–8.35 (m, 28H, Ar–*H*). ^{13}C NMR (CDCl$_3$) δ: 19.1 and 19.4 (CH$_2$C$_6$H$_4$*C*H$_3$-2), 49.6 and 49.8 (*C*H$_2$C$_6$H$_4$CH$_3$-2), 50.3 (*C*H$_2$C$_{10}$H$_7$), 111.9, 112.0, 123.6, 123.8, 125.4, 125.6, 125.9, 126.1, 126.2, 126.4, 126.6, 126.7, 126.9, 127.3, 127.5, 128.5, 128.6, 128.9, 130.1, 130.4, 130.7, 130.9, 131.5, 131.8, 133.4, 133.6, 134.0, 134.1, 134.2, 134.3, 134.4, 134.5, 135.1 and 135.5 (Ar–*C*), 183.3 and 183.4 (*C*–Pd).

Bis[1-(2,4,6-trimethylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]-dichloropalladium(II) 2d Yield: 0.28 g, 76%, m.p.: 270–271 °C, IR: $\nu_{(NCN)}$ 1607 cm^{-1}. Anal. Calc. for C$_{56}$H$_{52}$N$_4$PdCl$_2$: C, 70.18; H, 5.47; N, 5.85. Found: C, 70.19; H, 5.49; N, 5.85%. ^{1}H NMR (CDCl$_3$) δ: 2.06, 2.27, 2.28 and 2.2 (s, 18H, CH$_2$C$_6$H$_2$(*C*H$_3$)$_3$-2,4,6), 5.56 and 6.19 (s, 4H, *C*H$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 6.30 and 6.64 (s, 4H, *C*H$_2$C$_{10}$H$_7$), 6.73 (s, 4H, CH$_2$C$_6$*H*$_2$(CH$_3$)$_3$-2,4,6), 6.83-8.35 (m, 26H, Ar–*H*). ^{13}C NMR (CDCl$_3$) δ: 20.8, 20.9, 21.0 and 21.1 (CH$_2$C$_6$H$_2$(*C*H$_3$)$_3$-2,4,6), 49.2 and 49.4 (*C*H$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 49.5 and 65.8 (*C*H$_2$C$_{10}$H$_7$), 110.5, 110.9, 111.5, 111.7, 122.3, 122.6, 122.8, 125.1, 125.2, 125.3, 125.5, 125.6, 126.1, 126.5, 127.8, 127.9, 128.1, 138.3, 128.5, 129.3, 129.7, 130.1, 130.4, 130.5, 131.1, 133.1, 133.4, 134.2, 134.4, 134.9, 135.2, 137.6, 138.1 and 138.4 (Ar–*C*), 182.6 and 183.0 (*C*–Pd).

Bis[1-(3,4,5-trimethoxylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]-dichloropalladium(II) 2e Yield: 0.19 g, 83%, m.p.: 265–266 °C, IR: $\nu_{(NCN)}$ 1600 cm^{-1}. Anal. Calc. for C$_{56}$H$_{52}$N$_4$O$_6$PdCl$_2$: C, 63.79; H, 4.97; N, 5.31. Found: C, 63.79; H, 4.96; N, 5.31%. ^{1}H NMR (CDCl$_3$) δ: 3.72, 3.79, 3.83 and 3.84 (s, 18H, CH$_2$C$_6$H$_2$(OC*H*$_3$)$_3$-3,4,5), 5.70 and 6.06 (s, 4H, *C*H$_2$C$_6$H$_2$(OCH$_3$)$_3$-3,4,6), 6.23 and 6.54 (s, 4H, *C*H$_2$C$_{10}$H$_7$), 6.63 and 6.86 (s, 4H, CH$_2$C$_6$*H*$_2$(OCH$_3$)$_3$-3,4,5), 6.90–8.22 (m, 26H, Ar–*H*). ^{13}C NMR (CDCl$_3$) δ: 56.3, 56.4, 60.6 and 60.8 (CH$_2$C$_6$H$_2$(O*C*H$_3$)$_3$-3,4,5), 49.6 (*C*H$_2$C$_6$H$_2$(OCH$_3$)$_3$-3,4,5), 52.6 (*C*H$_2$C$_{10}$H$_7$), 104.0, 104.9, 111.0, 111.2, 111.4, 122.3, 122.4, 123.1, 123.3, 125.1, 125.3, 125.4, 125.5, 125.6, 126.3, 126.5, 128.3, 128.8, 130.3, 130.4, 130.5, 130.9, 131.3, 133.2, 133.4, 134. 1, 134.9, 135.1, 137.1, 153.1 and 153.5 (Ar–*C*), 182.4 and 182.9 (*C*–Pd).

Bis[1-(2-methoxylethyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]-dichloropalladium(II) 2f This known compound was synthesized and identified by comparison of its melting point and spectroscopic data with those reported in the literature [34].

General procedure for hydroamination of styrene by conventional heating

The NHC–Pd(II) catalyst **2** (1.0 mol%), *t*-BuOK (1.10 mmol), styrene (1.10 mmol), aromatic amine (1.00 mmol) and *N*-butylpyridinium hexafluorophosphate (1 mL) were added to a small Schlenk tube, and the mixture was heated at 160 °C for 1 h. At the end of reaction, the mixture was cooled to room temperature, and water (5 mL) was added. The mixture was extracted with EtOAc. The organic phase was dried over anhydrous Na$_2$SO$_4$ and filtered through a short silica column. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel (EtOAc/hexane: 1:5). The yields were calculated by GC analysis based on the aromatic amine.

General procedure for microwave-assisted hydroamination of styrene

The NHC–Pd(II) catalyst **2** (1.0 mol%), *t*-BuOK (1.10 mmol), styrene (1.10 mmol), aromatic amine (1.00 mmol) and *N*-butylpyridinium hexafluorophosphate (1 mL) were placed within the microwave apparatus, and the mixture was heated at 160 °C (300 W) for 5 min. At the end of the reaction, the mixture was cooled to room temperature, and water (5 mL) was added. The mixture was extracted with EtOAc, and the organic phase was processed as for the conventional heating experiments.

Results and discussion

Synthesis of the complexes

The silver complexes were prepared according to the literature method from the 1,3-dialkylbenzimidazolium chlorides, which were obtained by two-step N-alkylation of benzimidazole [35]. The palladium(II)–NHC complexes **2a**–**f** were prepared by treatment of the silver(I)–NHC complexes with PdCl$_2$(PhCN)$_2$ in dichloromethane at room temperature, in good yields (Scheme 1). The rapid precipitation of AgCl indicated successful carbene transfer onto palladium, giving the palladium(II)–NHC complexes **2a**–**f**. This useful synthetic method has been used to synthesize a variety of metal complexes [36]. The present complexes were obtained in high yields and proved to be stable both in solution and in the solid state against air, light and moisture. Single crystals of these complexes suitable for X-ray diffraction studies could not be obtained. Therefore, all of the Pd(II)–NHC complexes were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis, which all supported the proposed structures. NMR analyses of the complexes showed that the N-heterocyclic carbene ligands had been transferred from the silver complexes to palladium. The Pd(II)–NHC complexes all showed a characteristic $\upsilon_{(NCN)}$ band at 1600–1607 cm^{-1} in their IR spectra. The ^{13}C NMR spectrum of all of the complexes except **2b** showed two signals for the C2 carbons at 182.7 and 182.8 ppm (**2a**), 182.3 ppm (**2b**), 183.3 and 183.4 ppm (**2c**), 182.6 and 183.0 ppm (**2d**), 182.4 and 182.9 ppm (**2e**). This is consistent

with previously reported values for [PdCl$_2$(NHC)$_2$] complexes [37]. The elemental analyses of complexes **2a**–**e** are in agreement with the theoretical values, while the NMR data showed that all of these Pd-NHC complexes except **2b** were cis/trans-isomer mixtures.

Catalytic studies

The intermolecular hydroamination of styrene is a convenient method for the synthesis of phenethylamines [38], and many transition metal complexes have been used for this reaction. Based on our previous results, in this study, potassium *tert*-butoxide was selected as the base. According to previous studies, imidazolium-based ionic liquids which contain an acidic hydrogen are easily converted to N-heterocyclic carbenes by use of strong bases. Therefore, the *N*-butylpyridinium hexafluorophosphate was used as the ionic liquid. The catalytic reactions were performed at 160 °C by conventional heating for 1 h or microwave heating (300 W) for 5 min in the presence of complexes **2a**–**f**. In the absence of any Pd(II) complex, the reactions of styrene with aniline, *p*-chloroaniline, 2-aminopyridine or *p*-methoxyaniline resulted in very low yields under these reaction conditions. Using these systems, palladium-catalyzed hydroaminations of styrene with various aromatic amines bearing electron-withdrawing or donating groups at the *para* position were examined. In all cases, exclusively anti-Markovnikov products were formed. The reaction products were characterized by NMR. The conversions were screened by GC analysis, with the results presented in Table 1.
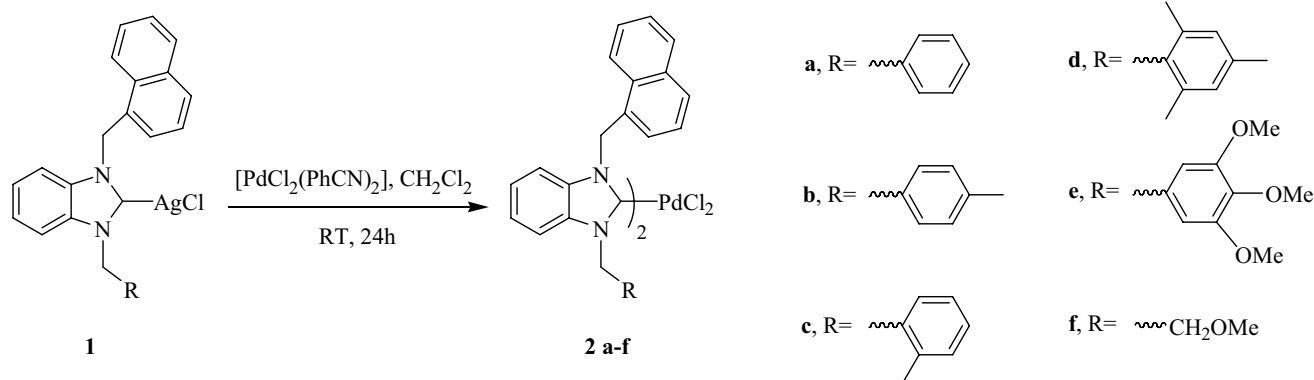
Scheme 1 Synthesis of the palladium(II) NHC complexes

Table 1 Intermolecular hydroamination of styrene with anilines in ionic liquid

Entry	ArNH$_2$	Catalyst	Yield (%)[a]	
			Microwave heating[b]	Thermal heating[c]
1	**4**	**2a**	96	99
2	**4**	**2b**	85	87
3	**4**	**2c**	91	89
4	**4**	**2d**	95	79
5	**4**	**2e**	99	96
6	**4**	**2f**	96	95
7	**5**	**2a**	88	89
8	**5**	**2b**	90	84
9	**5**	**2c**	93	90
10	**5**	**2d**	85	81
11	**5**	**2e**	92	92
12	**5**	**2f**	89	88
13	**6**	**2a**	83	85
14	**6**	**2b**	80	83
15	**6**	**2c**	89	89
16	**6**	**2d**	90	77
17	**6**	**2e**	95	98
18	**6**	**2f**	94	93
19	**7**	**2a**	86	97
20	**7**	**2b**	91	92
21	**7**	**2c**	87	90
22	**7**	**2d**	85	90
23	**7**	**2e**	94	96
24	**7**	**2f**	92	91
25	**4**	**None**	9[d]	7[d]
26	**5**	**None**	6[d]	5[d]
27	**6**	**None**	6[d]	Trace[d]
28	**7**	**None**	4[d]	Trace[d]

Reaction conditions: Pd-NHC (0.01 mmol), styrene (1.10 mmol), aromatic amine (1.00 mmol), t-BuOK (1.10 mmol), IL (1 mL)

[a]GC yields using dodecane as internal standard in an average of two runs. Products were characterized by NMR

[b]160 °C (300 W), 5 min

[c]160 °C, 1 h

[d]No catalyst

Initially, the reaction of styrene (**3**) with aniline (**4**) (Scheme 2) was examined in the presence of complexes **2a**–**f** as catalysts. From all of these reactions, only the anti-Markovnikov hydroamination product, N-(2-phenylethyl)aniline (**8**) was obtained, in high yields for all six catalysts (Table 1, entries 1–6). The best yields were achieved with catalysts **2a** and **2e**. No formation of the Markovnikov product was detected. Next, p-chloroaniline (**5**), p-methoxyaniline (**6**) and 2-aminopyridine (**7**) were reacted with styrene in the presence of complexes **2a**–**f** under the same reaction conditions (Table 1, entries 7–24). The treatment of styrene with p-chloroaniline (**5**) and 2-aminopyridine (**7**) (Table 1, entries 7–12, 19–24) gave the corresponding secondary amines with anti-Markovnikov selectivity in high yields. However, the reaction with p-methoxyaniline (**6**) gave slightly lower yields of the desired product (**10**) using both conventional and microwave-assisted heating (Table 1, entries 13–18). These results show that both electron-withdrawing (4-chloro) and electron-donating (4-methoxy) substituents on aniline gave slightly lower yields when compared to aniline itself. Similar observations have been documented by Zhou and Hartwig [39]. Both conventional and microwave-assisted heating provided similar results for the same substrates. However, reaction times were greatly reduced by employing microwave heating instead of conventional heating. Overall, complex (**2e**) with methoxy substituents on the phenyl group exhibited higher catalytic activities compared to the other five complexes.

Conclusion

The palladium(II)–NHC complexes **2a**–**f** have been readily prepared by reactions of the corresponding silver(I)–NHC complexes with PdCl$_2$(PhCN)$_2$ in dichloromethane at room temperature. These complexes all catalyze the hydroamination of styrene with aniline, p-chloroaniline, 2-aminopyridine and p-methoxyaniline, in good to excellent yields. Only the anti-Markovnikov addition products were obtained.
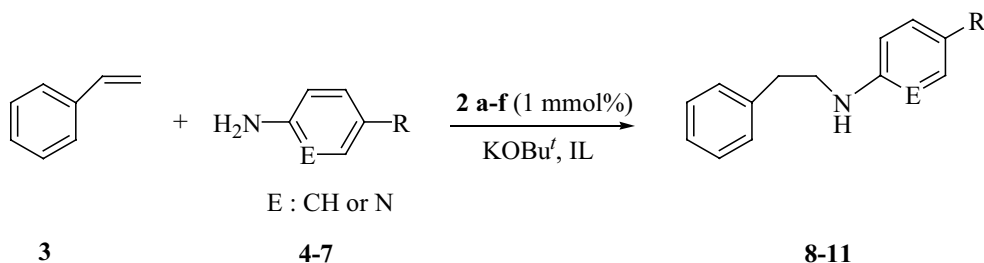
Scheme 2 Anti-Markovnikov hydroamination of styrene with aromatic amines

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