Supporting Information

Ru-catalyzed β-selective and enantioselective addition of amines to styrenes initiated by direct arene-exchange

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General NMR spectra were recorded with a JEOL AL-400 spectrometer at 400 MHz and 100 MHz respectively using CDCl$_3$ as a solvent. Chemical shift values for protons and carbons are reported in parts per million (ppm, $\delta$ scale) downfield from tetramethylsilane and are referenced to residual proton and carbon resources of CDCl$_3$ respectively ($\delta$ 7.26 and 77.0). ESI-MS spectra were measured with Accu TOF. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-GCMateII with FAB (Fast Atomic Bombardment) method. IR spectra were recorded by a IR Horiba FT730 spectrometer. Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates (Merck 60 GF254) prepared in our laboratory. All reactions were carried out under an atmosphere of argon in oven-dried glassware with a magnetic stirring bar. All reagents were purchased from Wako, Kanto, Aldrich and TCI and used without further purification.

Experimental procedure

General procedure for the nucleophilic addition of piperidine to styrene (Table 1, entry 6).
The mixture of [Ru(benzene)Cl$_2$]$_2$ (5.0 mg, 0.010 mmol) and AgOTf (10.8 mg, 0.042 mmol) in acetone was transferred to a Schlenk tube by a syringe filter under an atmosphere of argon. After acetone was excluded in vacuo and the container was backfilled with argon, a 1,4-dioxane solution (0.12 mL) of DPPPent (12.3 mg, 0.028 mmol), styrene (91.5 $\mu$L, 0.80 mmol) and piperidine (40 $\mu$L, 0.40 mmol) was added. The reaction mixture was stirred at 100 $^\circ$C for 72 h. Then, the solvent was removed in vacuo. The crude products were purified by thin-layer chromatography (hexane/AcOEt = 1/1) to give analytically pure 1 (78%).

General procedure for enantioselective nucleophilic addition of piperidine to $\alpha$-methylstyrene (Table 3, entry 6).
The mixture of [Ru(benzene)Cl$_2$]$_2$ (5.0 mg, 0.010 mmol) and AgOTf (10.8 mg, 0.042 mmol) in acetone was transferred to a Schlenk tube by a syringe filter under an atmosphere of argon. After acetone was excluded in vacuo and the container was backfilled with argon, a 1,4-dioxane solution (0.12 mL) of (S)-xyl-BINAP (20.6 mg, 0.028 mmol), $\alpha$-methylstyrene (78.2 $\mu$L, 0.60 mmol) and piperidine (40 $\mu$L, 0.40 mmol) was added. The reaction mixture was stirred at 100 $^\circ$C for 72 h. Then, the solvent was removed in vacuo. The crude products were purified by thin-layer chromatography (hexane/AcOEt = 1/1) to give analytically pure 4 (52%, 76% ee).

Compound data of the products

Known compounds:

$N$-(2-Phenethyl)piperidine (1),$^1$ $N$-(2-phenethyl)morpholine (2),$^1$ 1-phenyl-4-(2-phenylethyl)piperazine (3),$^1$ $N$-(2-phenethyl)tetrahydroisoquinoline (4),$^1$ $N$-1-(2-phenylpropyl)piperidine (8),$^2$ and $N$-1-(2-phenylpropyl)-morpholine (9).$^1$

$^1$H and $^{13}$C NMR spectra of these compounds were consistent with those in the literatures.
New compounds:

\[ \text{Me} \quad \text{N} \quad \text{Me} \quad \text{5} \]

\(N\text{-}[2-(4\text{-Methylphenyl})\text{ethyl}]\text{piperidine (5)}\)

Yellow oil, \(^1\text{H}\) NMR (CDCl\(_3\), 400 MHz) \(\delta 1.42-1.48 (m, 2H), 1.59-1.64 (m, 4H), 2.31 (s, 3H), 2.46 (br, 4H), 2.50-2.55 (m, 2H), 2.75-2.79 (m, 2H), 7.09 (br s, 4H); \(^{13}\text{C}\) NMR (CDCl\(_3\), 100 MHz) \(\delta 20.9, 24.3, 25.9, 33.1, 54.5, 61.6, 128.6, 129.0, 135.4, 137.6; \) IR (neat) 2910, 2873, 1652, 1599, 1512, 1360, 1288, 1253, 1032, 831, 654 cm\(^{-1}\); HRMS (FAB, positive) m/z Calcd. for: C\(_{14}\)H\(_{22}\)N \(204.1752 ([M+1]^+)\), Found: 204.1746 ([M+1]^+).

\((R)\text{-}N\text{-}1\text{-}(2\text{-Phenylpropyl})\text{piperidine}\)

\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of this compound was consistent with those in the literature.\(^1\) \([\alpha]^{26}_{D} = -6.2 (c 0.20, \text{CHCl}_3, 76\% \text{ ee}). \) Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak OD-3\(\times\)2.46 x 250mm, 254nm UV detector, rt, eluent: 0.5% isopropanol in hexane, flow rate: 0.2 mL/min, retention time: 38.7 min for minor isomer and 39.7 min for major isomer).

\(N\text{-}[2-(4\text{-Phenylpropyl})\text{morpholine (ent-9)}\)

\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of this compound was consistent with those in the literature.\(^1\) \([\alpha]^{26}_{D} = -12.4 (c 0.36, \text{CHCl}_3, 61\% \text{ ee}). \) Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak OD-3\(\times\)2.46 x 250mm, 254nm UV detector, rt, eluent: 2% isopropanol in hexane, flow rate: 0.5 mL/min, retention time: 13.1 min for minor isomer and 13.8 min for major isomer).

\(N\text{-}(2\text{-phenylpropyl})\text{tetrahydroisoquinoline (ent-10)}\)

Yellow oil, \(^1\text{H}\) NMR (CDCl\(_3\), 400 MHz) \(\delta 1.32 (d, J = 6.8 \text{ Hz}, 3H), 2.62-2.70 (m, 3H), 2.76-2.81 (m, 1H), 2.86 (s, br, 2H), 3.02-3.11 (m, 1H), 3.59 (d, J = 15.0 \text{ Hz}, 1H) 3.69 (d, J = 15.0 \text{ Hz}, 1H),\)
6.99-7.01 (m, 1H), 7.06-7.12 (m, 3H), 7.18-7.25 (m, 3H), 7.29-7.32 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 19.8, 29.0, 37.6, 51.0, 56.5, 65.9, 125.5, 126.0, 126.2, 126.6, 127.3, 128.4, 128.7, 134.6, 135.2, 146.3; IR (neat) 2894, 1681, 1269, 1288, 1053, 813, 684 cm$^{-1}$; HRMS (FAB, positive) m/z Calcd. for: C$_{18}$H$_{22}$N$_2$ 252.1752 ([M+1]$^+$), Found: 252.1756 ([M+1]$^+$). $[\alpha]_{26}^D = +7.54$ (c 0.26, CHCl$_3$, 64% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak OD-3×2:4.6 x 250mm, 254nm UV detector, rt, eluent: 0.5% isopropanol in hexane, flow rate: 0.2 mL/min, retention time: 66.6 min for minor isomer and 67.8 min for major isomer).

![ent-11](image)

**ent-11**

**N-(2-Phenylpropyl)-4-piperidone ethylene ketal (ent-11)**

Yellow oil, $^1$H NMR (CDCl$_3$, 400 MHz) δ 1.27 (d, $J = 7.2$ Hz, 3H) 1.69-1.75 (m, 4H), 2.43-2.48 (m, 4H), 2.52-2.59 (m, 2H), 2.88-2.95 (m, 1H), 3.94 (s, 4H), 7.17-7.22 (m, 3H), 7.26-7.31 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 19.8, 34.8, 37.8, 51.6, 64.1, 65.6, 107.4, 126.1, 127.2, 128.3, 146.4; IR (neat) 2905, 2873, 1648, 1346, 1213, 1032, 731, 673, 564 cm$^{-1}$; HRMS (FAB, positive) m/z Calcd. for: C$_{16}$H$_{24}$NO$_2$ 262.1807 ([M+1]$^+$), Found: 262.1806 ([M+1]$^+$). $[\alpha]_{26}^D = -9.65$ (c 0.26, CHCl$_3$, 75% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak OD-3×2:OD: 4.6 x 250mm, 254nm UV detector, rt, eluent: 0.5% isopropanol in hexane, flow rate: 0.5 mL/min, retention time: 51.3 min for minor isomer and 52.1 min for major isomer)
ESI-MS chart of complex B ([M]⁺):
[Ru((S)-xylyl-binap)(η⁶-α-methylstyrene)(OTf)]⁺
Observed isotope pattern of complex B ([M]*): [Ru((S)-xylyl-binap)(η\(^6\)-α-methylstyrene)(OTf)]*

Theoretical isotope pattern of complex B ([M]*): [Ru((S)-xylyl-binap)(η\(^6\)-α-methylstyrene)(OTf)]*
ESI-MS chart of complex E ([M-TfOH]+):
[Ru((S)-xylyl-binap)(η⁶-(1-methyl-2-piperidinoethyl)benzene)(OTf)]+

\begin{align*}
\text{(S)-xylyl-BINAP} & = P \quad \text{and} \\
\text{Ru} \quad \text{P} & = (S)-xylyl-BINAP
\end{align*}


References
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