

Supplementary Information for

Intramolecular Hydroamination of Unactivated Olefins with $\text{Ti}(\text{NMe})_4$ as a Precatalyst

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Experimental Procedures.

General. ^1H and ^{13}C NMR spectra were recorded on either a Bruker 300 MHz or 400 MHz Avance spectrometer at ambient temperature and chemical shifts are given relative to residual solvent. The assignment of N-benzoyl-pyrrolidine stereochemistry was based on NOE difference experiments. *Cis-trans* ratios were determined by GCMS analysis. GCMS spectra were recorded on an Agilent series 6890 GC system with a 5973 Mass Selective Detector. MS (ESI), HRMS and elemental analyses determinations were performed at the Department of Chemistry, University of British Columbia. All reactions were carried out using standard Schlenk line and glovebox techniques under an atmosphere of nitrogen, unless otherwise stated. $\text{Ti}(\text{NR}_2)_4$ ($\text{R} = \text{Me, Et}$) was purchased from Strem and used as received. d_6 -Benzene, d_8 -toluene and d_{10} -xylenes were degassed and dried over molecular sieves. Aminoalkenes 2,2-diphenyl-4-pentenylamine (**1**),¹ 2,2-diphenyl-5-hexenylamine,² 2,2,5-triphenyl-4-pentenylamine (**3**),^{2,3} 2,2-diphenyl-4-hexenylamine,² 2,2-dimethyl-4-pentenylamine,⁴ 2-methyl-4-pentenylamine,⁵ 2-phenyl-4-pentenylamine,² 2-methyl-2-phenyl-4-pentenylamine,² 4-pentenylamine,⁵ 2,2-diphenyl-6-heptenylamine,⁴ and *N*-methyl-2,2-diphenyl-4-pentenylamine (**2**)⁶ were prepared using modified literature procedures from commercially available starting materials purchased from Aldrich. Prior to use, all substrates were purified either by distillation or recrystallization. In addition liquid substrates were degassed and dried over molecular sieves prior to use. Heterocyclic products 2-methyl-4,4-diphenylpyrrolidine,¹ 2-methyl-5,5-diphenylpiperidine,⁷ 2-methyl-4,4-dimethylpyrrolidine,¹ 2-methyl-4-methylpyrrolidine,⁵ 2-methyl-4-phenylpyrrolidine⁸ are known compounds.

General procedure for NMR-tube scale intramolecular amino alkene hydroamination. All NMR-tube scale reactions were prepared in an N_2 -filled glove box. An NMR-tube equipped with a Teflon screw cap was charged with the internal standard (1,3,5-trimethoxybenzene) (0.5 mmol), the catalyst (0.025 mmol), and the amino alkene (0.5 mmol) and dissolved in either d_6 -benzene (~ 1 ml) or d_8 -toluene (~ 1 ml). The tube was then be heated to, and maintained at, the appropriate temperature for the stated duration of time. The NMR yields were determined by comparing the integration of the internal standard with a well-resolved signal for the heterocyclic product.

General procedure for scaled up intramolecular amino alkene hydroaminations. All isolation scale reactions were prepared in an N₂-filled glove box. A 15 mL Schlenk tube equipped with a magnetic stir bar was charged with the catalyst (0.05 mmol) and the amino alkene (1.0 mmol), dissolved in *d*₈-toluene (~ 2 ml). The Schlenk tube was then heated to the appropriate temperature, and stirred for the stated duration of time. Following this procedure the solution was concentrated under reduced pressure and the crude product was either directly subjected to flash column chromatography (hexanes/ether, SiO₂) to afford the purified pyrrolidine or piperidine product or converted to the N-benzoyl derivative according to literature procedures.¹

2,2-Diphenyl-6-heptenylamine. Prepared using modified literature procedures,⁴ with full characterization data presented here. ¹H NMR (CDCl₃, 300 MHz): δ 0.86 (2H, s, CH₂-NH₂), 1.05-1.17 (2H, m, CH₂-CH₂-CH₂), 1.97-2.05 (2H, m, CH₂=CH-CH₂), 2.07-2.14 (2H, m, CH₂-CH₂-CPh₂), 3.31 (2H, s, Ph₂C-CH₂-NH₂), 4.89-4.98 (2H, m, CH₂=CH), 5.65-5.75 (1H, m, CH₂=CH), 7.15-7.31 (10H, m, Ar-H); ¹³C NMR (CDCl₃, 75 MHz): δ 23.36, 34.18, 35.87, 49.06, 51.73, 114.63, 125.89, 127.96, 128.21, 138.57, 146.53; MS (ESI): *m/z* 266 (M+H⁺); Anal. Calcd for C₁₉H₂₃N: C, 85.99; H, 8.74; N, 5.28. Found: C, 85.64; H, 9.08; N, 5.24.

2-Benzyl-4,4-diphenyl-pyrrolidine. Yield 67%; ¹H NMR (CDCl₃, 300 MHz): δ 2.06 (1H, br s, NH), 2.17 (1H, dd, *J* = 9.0, 12.7 Hz, CHH-CH-Bn), 2.69-2.78 (2H, m, CHH-CH-Bn, Ph-CHH-CH), 2.88 (1H, dd, *J* = 7.0, 13.3 Hz, Ph-CHH-CH), 3.50-3.61 (2H, m, Bn-CH-NH, Ph₂C-CHH-NH), 3.73 (1H, d, *J* = 11.3 Hz, Ph₂C-CHH-NH), 7.17-7.29 (15H, m, Ar-H); ¹³C NMR (CDCl₃, 75 MHz): δ 43.53, 44.85, 56.56, 57.64, 59.12, 125.99, 126.08, 126.40, 126.90, 127.04, 128.28, 128.34, 129.04, 129.34, 139.83, 146.77, 147.67; MS (ESI): *m/z* 314 (M+H⁺), 336 (M+Na⁺); Anal. Calcd for C₂₃H₂₃N: C, 88.13; H, 7.40; N, 4.47. Found: C, 87.80; H, 7.80; N, 4.75.

N-Benzoyl-2-methyl-4,4-dimethylpyrrolidine. Yield 43%; ¹H NMR (CDCl₃, 300 MHz): δ 0.86 (3H, s, CH₂-C(CH₃)₂-CH₂), 1.00 (3H, s, CH₂-C(CH₃)₂-CH₂), 1.33-1.42 (4H, m, (CH₃)CH, (CH₃)₂C-CHH-CH(CH₃)), 1.90 (1H, dd, *J* = 6.0, 12.0 Hz, (CH₃)₂C-CHH-CH(CH₃)), 3.05 (1H, d, *J* = 10.0 Hz, (CH₃)₂C-CHH-NH), 3.25 (1H, d, *J* = 10.0 Hz, (CH₃)₂C-CHH-NH), 4.30 (1H, m, CH₂-CH-(CH₃)), 7.30-7.49 (5H, m, Ar-H); ¹³C NMR (CDCl₃, 75 MHz): δ 20.15, 25.39, 25.64, 38.18, 47.49, 52.83, 62.53, 127.42, 128.08, 129.83, 137.22, 170.00; HRMS Calcd for C₁₄H₁₉NO [M⁺]: 217.14666; Found: 217.14674.

N-Benzoyl-2-methyl-4-phenylpyrrolidine. A combined yield of 26% was obtained for the mixture of diastereomers. It was possible to separate a sufficient quantity of the major diastereomer by chromatography (hexane/ether, SiO₂) to provide ¹H NMR, ¹³C NMR, and GCMS (EI) data for this compound. A 2-D ¹H COSY NMR spectrum was used for peak assignment and selective NOE NMR spectroscopic experiments were used to assign the relative stereochemistry of the major diastereomer. This in turn facilitated the identification of the ¹H, ¹³C NMR and GCMS (EI) data for the minor diastereomer. This in turn facilitated the identification of the ¹H, ¹³C NMR and GCMS (EI) data for the minor diastereomer.¹ ¹H NMR (major diastereomer) (CDCl₃, 400 MHz): δ 1.50 (3H, d, *J* = 6.0 Hz, CH₃-CH-NBz), 1.76 – 1.87 (1H, m, PhCH-CHH-CH(CH₃)), 2.53 – 2.61 (1H, m, PhCH-CHH-CH(CH₃)), 3.15 – 3.22 (1H, m, CH₂-PhCH-CH₂), 3.50 - 3.56 (1H, m, PhCH-CHH-NBz), 3.75 – 3.79 (1H, m, PhCH-CHH-NBz), 4.36 – 4.42 (1H, m, CH₂-C(CH₃)H-

NBz), 7.15 – 7.58 (10H, m, Ar-H); ¹H NMR (minor diastereomer) (CDCl₃, 400 MHz): δ 1.44 (3H, d, J = 6.3 Hz, CH₃-CH-NBz), 1.98 – 2.04 (1H, m, PhCH-CHH-CH(CH₃)), 2.22 – 2.28 (1H, m, PhCH-CHH-CH(CH₃)), 3.33 - 3.40 (1H, m, PhCH-CHH-NBz), 3.83 - 3.87 (1H, m, PhCH-CHH-NBz), 4.05 – 4.20 (1H, m, CH₂-PhCH-CH₂), 4.50 – 4.65 (1H, m, CH₂-C(CH₃)H-NBz), 7.12 – 7.47 (10H, m, Ar-H); ¹³C NMR (major diastereomer) (CDCl₃, 75 MHz): δ 20.3, 40.8, 44.1, 54.0, 57.0, 127.0, 127.1, 127.7, 128.1, 128.6, 130.2, 136.9, 139.7, 169.8; ¹³C NMR (minor diastereomer) (CDCl₃, 75 MHz): δ 20.0, 39.4, 42.5, 53.1, 56.0, 126.7, 126.8, 128.3, 128.6, 129.5, 137.5, 141.3, 169.6; MS (EI) (major diastereomer): *m/z* 265 (M⁺), 250 (M⁺-CH₃); MS (EI) (minor diastereomer): *m/z* 265 (M⁺), 250 (M⁺-CH₃); Anal. Calcd for C₁₈H₁₉NO (mixture of diastereomers): C, 81.47; H, 7.22; N, 5.28. Found: C, 81.24; H, 7.29; N, 5.35.

N-Benzoyl-2,4-dimethyl-4-phenylpyrrolidine. A combined yield of 52% was obtained for the mixture of diastereomers. It was possible to separate a sufficient quantity of the major diastereomer by chromatography (hexane/ether, SiO₂) to provide ¹H NMR, ¹³C NMR, and GCMS (EI) data for this compound. Selective NOE NMR spectroscopic experiments were used to assign the relative stereochemistry of the major diastereomer. This in turn facilitated the identification of the ¹H, ¹³C NMR and GCMS (EI) data for the minor diastereomer. ¹H NMR (major diastereomer) (CDCl₃, 300 MHz): δ 0.86 (3H, s, PhC(CH₃)-CH₂), 1.44 (3H, d, J = 6.0 Hz, (CH₃)CH-NBz), 1.93 (1H, dd, J = 10.0, 12.1 Hz, (CH₃)CH-CHH-CPh(CH₃)), 2.41 (1H, dd, J = 7.2, 12.4 Hz, (CH₃)CH-CHH-CPh(CH₃)), 3.60 (1H, d, J = 10.4 Hz, Ph(CH₃)C-CHH-NBz), 3.72 (1H, d, J = 10.4, Ph(CH₃)C-CHH-NBz), 4.48–4.52 (1H, m, (CH₃)CH-NBz), 7.10-7.59 (10H, m, Ar-H); ¹H NMR (minor diastereomer) (CDCl₃, 300 MHz): δ 1.35 (3H, s, PhC(CH₃)-CH₂), 1.42 (3H, d, J = 5.8 Hz, (CH₃)CH-NBz), 1.74 (1H, dd, J = 9.7, 12.8 Hz, (CH₃)CH-CHH-CPh(CH₃)), 2.65 (1H, dd, J = 6.3, 13.1 Hz, (CH₃)CH-CHH-CPh(CH₃)), 3.47 (1H, d, J = 7.1 Hz, Ph(CH₃)C-CHH-NBz), 3.87 (1H, d, J = 7.1, Ph(CH₃)C-CHH-NBz), 4.0-4.1 (1H, m, (CH₃)CH-NBz), 7.10-7.59 (10H, m, Ar-H); ¹³C NMR (major diastereomer) (CDCl₃, 75 MHz): δ 20.12, 27.27, 45.34, 45.64, 52.51, 60.88, 125.55, 126.42, 127.56, 128.26, 128.49, 130.12, 136.97, 146.54, 170.29; ¹³C NMR (minor diastereomer) (CDCl₃, 75 MHz): δ 20.1, 27.3, 45.9, 47.4, 60.9, 125.3, 126.4, 127.2, 128.3, 128.5, 129.9, 137.2, 146.5, 169.8; MS (EI) (major diastereomer): *m/z* 279 (M⁺), 264 (M⁺-CH₃); MS (EI) (minor diastereomer): *m/z* 279 (M⁺), 264 (M⁺-CH₃); Anal. Calcd for C₁₉H₂₁NO (mixture of diastereomers): C, 81.68; H, 7.58; N, 5.01. Found: C, 81.37; H, 7.28; N, 5.31.

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