Enantioselective Imidazole-Directed Allylation of Aldimines and Ketimines

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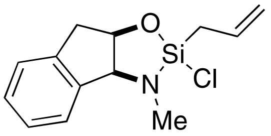
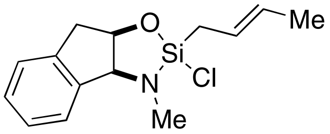
Supporting Information

General Information. All reactions were carried out in flame-dried glassware under an atmosphere of nitrogen with magnetic stirring unless otherwise indicated. Methylene chloride was obtained from Fisher and purified by degassing with argon followed by passage through an activated neutral alumina column. Benzene was purchased from Fisher and purified by degassing with argon followed by passage through both an activated neutral alumina column and Q5 reactant column. Toluene and triethylamine were purchased from Aldrich and purified by distillation from CaH_2 then stored under nitrogen. Pentane (HPLC grade) was purchased from Fisher and used as received. Anhydrous chloroform (stabilized with amylenes) and methanol were purchased from Aldrich and used as received. The Grubbs second generation and Hoveyda-Grubbs second generation catalysts were obtained from Materia Inc. and used without purification. Allylamine and all ketone reagents were purchased from Aldrich and used as received. ^1H NMR spectra were recorded on Bruker DPX-300 (300 MHz) or DPX-400 (400 MHz) spectrometers. ^1H NMR chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane internal standard (0 ppm) or CD_3OD internal standard (3.31 ppm). Data are reported as follows: (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, dq = doublet of quartets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet; integration; coupling constant in Hz; assignment). Proton decoupled ^{13}C NMR spectra were recorded on Bruker DPX-300 (75 MHz) or DPX-400 (100 MHz) spectrometers and are reported in ppm from $CDCl_3$ internal standard (77.1 ppm) or CD_3OD internal standard (49.0 ppm). ^{29}Si NMR spectra were recorded on a Bruker DPX-300 (60 MHz) spectrometer and are reported with tetramethylsilane (0 ppm) as an internal standard. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR or Nicolet Avatar 370 DTGS spectrometers. Optical rotations were recorded on a Jasco DIP-1000 digital polarimeter; the concentration *c* is reported in g/100mL. Low resolution mass spectra were obtained on a JEOL HX100 mass spectrometer in the Columbia University Mass Spectrometry Laboratory.

Preparation of Silane Reagents.

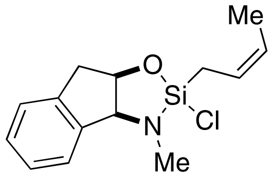


Preparation of reagent (1*S*,2*R*)-4: A 2-necked round-bottom flask was charged with allyltrichlorosilane (20.4 mL, 141 mmol) and methylene chloride (360 mL). After cooling the solution to 0 °C, triethylamine (34 mL, 244 mmol) was added dropwise via addition funnel over 10 minutes. N-methyl-(1*S*,2*R*)-1-amino-2-indanol[i] (20 g, 122 mmol) was then added portionwise over 15 minutes. The reaction solution was allowed to warm slowly to room temperature while stirring for 12 hours. Following removal of the solvent by distillation, 300 mL of pentane was added to the remaining residue. The heterogeneous mixture was stirred vigorously for 18 hours to ensure complete precipitation of the triethylamine salts. Filtration of the suspension and concentration of the filtrate by distillation afforded the unpurified product as a yellow oil. Purification by distillation under reduced pressure yielded the product as a colorless oil (20.6 g, 64%, b.p. 100 - 106°C @ 0.3 mm Hg, 2.4:1 mixture of diastereomers). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.34 (m, 1H, Ar-**H** (both diastereomers)), 7.28-7.20 (m, 3H, Ar-**H** (both diastereomers)), 5.88-5.74 (m, 1H, $SiCH_2C\mathbf{H}=CH_2$ (minor)), 5.61-5.50 (m, 1H, $SiCH_2C\mathbf{H}=CH_2$ (major)), 5.12-4.83 (m, 3H, $SiCH_2CH=C\mathbf{H_2}$ and $OC\mathbf{H}CH_2$ (both diastereomers)), 4.45 (d, 1H, J = 6.3 Hz, NC**H**Ar (minor)), 4.37 (d, 1H, J = 6.3 Hz, NC**H**Ar (major)), 3.32-3.00 (m, 2H, $OCHC\mathbf{H_2}Ar$ (both diastereomers)), 2.75 (s, 3H, $NC\mathbf{H_3}$ (major)), 2.73 (s, 3H, $NC\mathbf{H_3}$ (minor)), 2.04-2.01 (m, 2H, $SiC\mathbf{H_2}CH=CH_2$ (minor)), 1.88-1.85 (m, 2H, $SiC\mathbf{H_2}CH=CH_2$ (minor)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 141.6, 141.1, 140.9, 130.8, 130.4, 128.9, 128.8, 127.1, 126.9, 126.0, 125.9, 125.7, 125.7, 117.0, 80.7, 79.5, 68.8, 40.9, 40.7, 31.8, 30.6, 24.6, 24.6, 24.6; ^{29}Si NMR (60 MHz, $CDCl_3$) δ -5.98, -6.12; IR (neat) 3074, 2942, 2811, 1632, 1477, 1187, 1034, 1007 cm^{-1}; LRMS (FAB^+) calc'd for $C_{13}H_{16}ClNOSi$ 265.8, found 265.1.



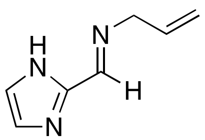
Preparation of *trans*-crotylsilane reagent (1*S*,2*R*)-11: A 2-necked round-bottom flask was charged with *trans*-crotyltrichlorosilane[ii] (4.1 g, 21.5 mmol) and methylene chloride (50 mL). After cooling the solution to 0 °C, triethylamine (5.0 mL, 35.8 mmol) was added dropwise via syringe over 10 minutes. N-methyl-(1*S*,2*R*)-1-amino-2-indanol (2.9 g, 17.7 mmol) was then added portionwise over

15 minutes. The reaction solution was allowed to warm slowly to room temperature while stirring for 12 hours. Following distillation of the solvent under nitrogen, 50 mL of pentane was added to the remaining residue. The heterogeneous mixture was stirred vigorously for 18 hours to ensure complete precipitation of the triethylamine salts. Filtration of the suspension and concentration of the filtrate by distillation afforded the unpurified product as a yellow oil. Purification by distillation under reduced pressure yielded the product **11** as a colorless oil (3.0 g, 60%, b.p. 92-97 °C @ 0.2 mm Hg, 2.8:1 mixture of diastereomers). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.20 (m, 4H, Ar-**H** (both diastereomers)), 5.57-5.27 (m, 3H, $SiCH_2$**CH**=**CH**Me and OC**H**CH_2 (both diastereomers)), 4.45 (d, 1H, J = 6.6 Hz, NC**H**Ar (minor)), 4.39 (d, 1H, J = 6.3 Hz, NC**H**Ar (major)), 3.34-2.99 (m, 2H, OCHC**H$_2$**Ar (both diastereomers)), 3.06 (s, 3H, NC**H$_3$** (major)), 2.72 (s, 3H, NC**H$_3$** (minor)), 1.94-1.91 (m, 2H, SiC**H$_2$**CH=CHCH_3 (minor)), 1.80-1.77 (m, 2H, SiC**H$_2$**CH=CHCH_3 (major)), 1.70-1.67 (m, 3H, CH=CHC**H$_3$** (minor)), 1.47 (dq, 3H, J = 6.3, 1.2 Hz, CH=CHC**H$_3$** (major)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 141.3, 140.8, 140.5, 128.5, 128.3, 127.2, 126.7, 126.5, 125.5, 125.5, 125.4, 125.2, 122.2, 121.9, 80.3, 79.1, 68.5, 40.5, 40.3, 31.4, 30.3, 22.5, 22.4, 18.2, 17.9, 17.9; ^{29}Si NMR (60 MHz, $CDCl_3$) δ -5.38, 5.38; IR (neat) 3022, 2933, 2810, 1477, 1187, 1169, 1033, 1007 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{14}H_{19}ClNOSi$ 279.8, found 280.1.

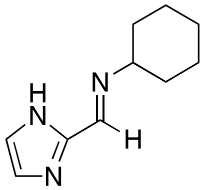


Preparation of *cis*-crotylsilane reagent (1*S*,2*R*)-13: A 2-necked round-bottom flask was charged with *cis*-crotyltrichlorosilane[iii] (5.57 g, 29.4 mmol) and methylene chloride (75 mL). After cooling the solution to 0 °C, triethylamine (6.8 mL, 49 mmol) was added dropwise via syringe over 10 minutes. N-methyl-(1*S*,2*R*)-1-amino-2-indanol (4.0 g, 24.5 mmol) was then added portionwise over 15 minutes. The reaction solution was allowed to warm slowly to room temperature while stirring for 12 hours. Following distillation of the solvent under nitrogen, 75 mL of pentane was added to the remaining residue. The heterogeneous mixture was stirred vigorously for 18 hours to ensure complete precipitation of the triethylamine salts. Filtration of the suspension and concentration of the filtrate by distillation afforded the unpurified product as a yellow oil. Purification by distillation under reduced pressure yielded the product **13** as a colorless oil (4.8 g, 70%, b.p. 86-95 °C @ 0.2 mm Hg, 2.7:1 mixture of diastereomers). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.34 (m, 1H, Ar-**H** (both diastereomers)), 7.27-7.19 (m, 3H, Ar-**H** (both diastereomers)), 5.34-5.20 (m, 2H, SiCH$_2$C**H**=C**H**Me (both diastereomers)), 5.11-5.06 (m, 1H, OC**H**CH$_2$ (both diastereomers)), 4.45 (d, 1H, J = 6.3 Hz, NC**H**Ar (minor)), 4.37 (d, 1H, J = 6.3 Hz, NC**H**Ar (major)), 3.34-3.01 (m, 2H, OCHC**H$_2$**Ar (both diastereomers)), 2.75 (s, 3H, NC**H$_3$** (major)), 2.72 (s, 3H, NC**H$_3$** (minor)), 1.99 (d, 2H, J = 8.1, SiC**H$_2$**CH=CHCH$_3$ (minor)), 1.99 (d, 2H, J = 8.1, SiC**H$_2$**CH=CHCH$_3$ (major)), 1.66 (d, 3H, J = 6.6 Hz, CH=CHC**H$_3$** (minor)), 1.47 (d, 3H, J = 6.6 Hz, CH=CHC**H$_3$** (major)); ^{13}C NMR (75 MHz, CDCl$_3$) δ 142.4, 141.2, 140.8, 140.6, 128.5, 128.4, 126.7, 126.5, 125.6, 125.6, 125.3, 125.3, 121.4, 121.1, 80.3, 79.1, 68.5, 68.3, 40.4, 40.3, 31.4, 30.2, 18.3, 18.2, 12.8, 12.7, 12.7; ^{29}Si NMR (60 MHz, CDCl$_3$) δ -5.91, -6.15; IR (neat) 3022, 2929, 2811, 1650, 1477, 1187, 1168, 1033, 1007, 743, 647 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{14}H_{19}ClNOSi$ 279.8, found 279.1.

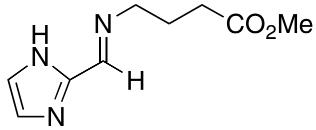
Preparation of Imines



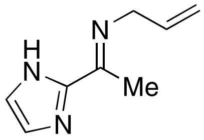
Preparation of allyl-(1*H*-imidazol-2-ylmethylene)-amine (2): To a solution of 2-formyl imidazole[iv] (3.0 g, 31 mmol) in methanol (50 mL) was added allylamine (2.6 mL, 34 mmol). The solution was stirred for 13 hours, after which the reaction mixture was concentrated. To ensure complete removal of water and methanol from the crude product, benzene (15 mL) was added and removed *in vacuo* to yield a yellow solid (4.1 g, 98%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 11.40 (br s, 1H, N**H**), 8.30 (s, 1H, N=C**H**), 7.16 (br d, 2H, J = 33.3 Hz, Ar-**H**), 5.99 (ddt, 1H, J = 17.1, 10.5, 5.7 Hz, C**H**=CH$_2$), 5.25-5.16 (m, 2H, CH=C**H$_2$**), 4.26 (dq, 2H, J = 5.4, 1.2 Hz, C=NC**H$_2$**); ^{13}C NMR (75 MHz, CDCl$_3$) δ 153.8, 144.9, 135.0, 130.8, 118.7, 117.1, 62.5; IR (neat) 3013, 2982, 2821, 2765, 2687, 1650, 1444, 1387, 1111, 915, 755 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_7H_9N_3$ 135.2, found (M+H)$^+$ 136.1.



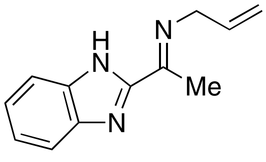
Preparation of cyclohexyl-(1*H*-imidazol-2-ylmethylene)-amine: To a solution of 2-formyl imidazole (300 mg, 3.12 mmol) in methanol (10 mL) was added cyclohexylamine (370 μL, 3.23 mmol). After concentration of the reaction mixture and recrystallization (pentane/methylene chloride) the product was obtained as a pale yellow solid (440 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.84 (br s, 1H, N-**H**), 8.31 (s, 1H, **H**C=N), 7.11 (br d, 2H, J = 54.9 Hz, Ar-**H**), 3.30-3.24 (m, 1H, C=NC**H**), 1.77-1.64 (m, 5H, Cy-**H**), 1.50-1.29 (m, 4H, Cy-**H**), 1.21-1.14 (m, 1H, Cy-**H**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.7, 145.1, 130.6, 118.3, 69.2, 34.3, 25.4, 24.6; IR (KBr) 3077, 2912, 1634, 1415, 1312, 1275, 745 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{10}H_{15}N_3$ 177.2, found $(M+H)^+$ 178.1.



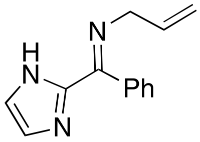
Synthesis of 4-[(1*H*-imidazol-2-ylmethylene)-amino]-butyric acid methyl ester: To a solution of 2-formyl imidazole (300 mg, 3.12 mmol) in methanol (5 mL) was added triethylamine (450 μL, 3.23 mmol) followed by methyl 4-aminobutyrate hydrochloride (450 mg, 2.92 mmol). After stirring for 7 hours, the reaction solution was concentrated *in vacuo*. Anhydrous ether (10 mL) was added to the crude product and the solution was stirred for 10 minutes, after which the triethylamine salts were filtered and the filtrate was concentrated. Benzene (5 mL) was added and removed *in vacuo* to yield a yellow solid (336 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 1H, **H**C=N), 7.16 (br d, 2H, J=24.6 Hz, Ar-**H**), 3.68-3.62 (m, 5H, C=NC**H$_2$** and OC**H$_3$** overlapping), 2.40 (t, 2H, J = 7.2 Hz, C**H$_2$**CO_2Me), 2.01 (quint, 2H, J = 6.9 Hz, C=NCH_2C**H$_2$**); ^{13}C NMR (75 MHz, CD_3OD) δ 175.5, 152.7, 145.9, 125.0, 60.9, 52.0, 32.3, 27.2; IR (neat) 3117, 2947, 2835, 2691, 1726, 1643, 1439, 1165, 760 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_9H_{13}N_3O_2$ 195.2, found $(M+H)^+$ 196.2.



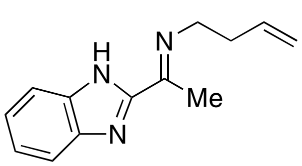
Synthesis of (*E*)-*N*-(1-(1*H*-imidazol-2-yl)ethylidene)prop-2-en-1-amine: To a solution of 2-acetylamidazole[4] (300 mg, 2.72 mmol) in chloroform (3 mL) was added allylamine (610 μL, 8.17 mmol). 4 Å molecular sieves were added, and the solution stirred for 14 hours. The reaction mixture was filtered through celite and concentrated *in vacuo* to give the product as a green oil (375 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.36 (br s, N-**H**), 7.14 (s, 1H, Ar-**H**), 7.00 (s, 1H, Ar-**H**), 5.98 (ddt, 1H, J = 17.1, 10.2, 5.4 Hz, **CH**CH_2), 5.21-5.09 (m, 2H, CH=C**H$_2$**), 4.18 (d, 2H, 5.4 Hz, C=N-C**H$_2$**), 2.41 (s, 3H, N=C-C**H$_3$**); ^{13}C NMR (75 MHz, $CDCl_3$.) δ 160.6, 147.4, 134.8, 129.6, 118.6, 115.8, 53.6, 14.6; IR (neat) 3013, 2986, 2848, 1634, 1442, 1383, 1302, 1103, 917 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_8H_{11}N_3$ 149.19, found $(M+H)^+$ 150.1.



Preparation of allyl-[1-(1*H*-benzoimidazol-2-yl)-ethylidene]-amine (15): To a solution of 2-acetyl benzimidazole[4] (300 mg, 1.87 mmol) in chloroform (6 mL) was added allylamine (420 µL, 5.60 mmol). 4 Å molecular sieves were added, and the solution stirred for 9 hours. After filtering through celite, the filtrate was concentrated *in vacuo*. Benzene (10 mL) was added and removed *in vacuo* to yield **15** as a white solid (320 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.68 (br s, 1H, N**H**), 7.84-7.82 (m, 1H, Ar-**H**), 7.40-7.37 (m, 1H, Ar-**H**), 7.31-7.23 (m, 2H, Ar-**H**), 6.06 (ddt, 1H, J = 17.4, 10.5, 5.4 Hz, C**H**=CH_2), 5.28-5.15 (m, 2H, CH=C**H_2**), 4.24 (d, 2H, 5.1 Hz, C=NC**H_2**), 2.49 (s, 3H, N=C**CH_3**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 151.6, 143.9, 135.0, 133.8, 124.5, 122.5, 120.7, 116.1, 111.2, 54.4, 14.5; IR (neat) 3057, 2980, 2889, 2755, 1647, 1634, 1420, 1312, 916, 743 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{12}H_{13}N_3$ 199.3, found $(M+H)^+$ 200.0.

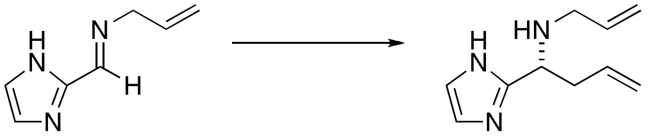


Preparation of (*E*)-*N*-((1*H*-imidazol-2-yl)(phenyl)methylene)prop-2-en-1-amine (9): To a solution of 2-benzoylimidazole[v] (2.0 g, 11.6 mmol) in methylene chloride (30 mL) was added allylamine (4.3 mL, 58 mmol). 4 Å molecular sieves were added, and the solution refluxed for 40 hours. After filtering through celite, the filtrate was concentrated *in vacuo*. Recrystallization (toluene/hexanes) provided the product **9** as a grey solid (1.75 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.43 (m, 3H, Ar-**H**), 7.34-7.31 (m, 2H, Ar-**H**), 7.17 (s, 1H, Imid-**H**), 7.09 (s, 1H, Imid-**H**), 6.01 (ddt, 1H, J = 17.1, 10.5, 5.4 Hz, C**H**=CH_2), 5.22-5.09 (m, 2H, CH=CH_2), 4.09 (dt, 2H, J = 5.4, 1.8 Hz, NC**H_2**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 147.1, 136.0, 133.7, 130.8, 129.3, 128.4, 128.0, 118.0, 115.7, 55.3; IR (KBr) 3014, 2900, 2755, 1613, 1437, 1385, 1308, 1107 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{13}H_{13}N_3$ 211.3, found $(M+H)^+$ 212.1.

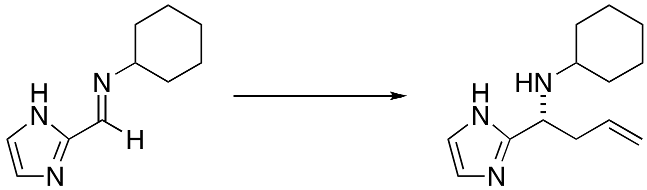


Preparation of [1-(1*H*-benzoimidazol-2-yl)-ethylidene]-but-3-enyl-amine (17): To a solution of 2-acetyl benzimidazole[4] (437 mg, 2.72 mmol) in anhydrous chloroform (6 mL) was added 3-buten-1-amine[vi] (386 mg, 5.44 mmol). 4 Å molecular sieves were added, and the solution was stirred for 24 hours. After filtering through celite, the filtrate was concentrated. Benzene (10 mL) was added and then removed *in vacuo* to yield **17** as a tan solid (507 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.81 (m, 1H, Ar-**H**), 7.38-7.36 (m, 1H, Ar-**H**), 7.27-7.24 (m, 2H, Ar-**H**), 5.88 (ddt, 1H, J = 17.2, 10.4, 6.4 Hz, C**H**=CH_2), 5.12-5.02 (m, 2H, CH=C**H_2**), 3.65 (t, 2H, J = 7.2 Hz, NC**H_2**), 2.51-2.45 (m, 5H, C**H_2**CH=CH_2 and N=CC**H_3**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 151.7, 143.8, 136.3, 133.9, 124.5, 122.5, 120.7, 116.3, 111.2, 51.6, 34.9, 14.6; IR (KBr) 3090, 2995, 2893, 1636, 1451, 1312, 1249, 746 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{13}H_{15}N_3$ 213.3, found $(M+H)^+$ 214.2.

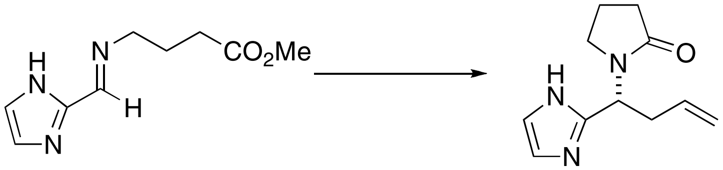
Preparation of Allylation Products.



Preparation of (*R*)-*N*-allyl-1-(1*H*-imidazol-2-yl)but-3-en-1-amine (3): To a solution of aldimine **2** (50 mg, 0.37 mmol) in toluene (3.7 mL) was added (1*S*,2*R*)-**4** (148 mg, 0.55 mmol). The reaction mixture was stirred for 1 hour, after which saturated sodium bicarbonate (2 mL) was added. After 15 minutes, a 30% solution of isopropyl alcohol in chloroform (15 mL) was added along with additional saturated sodium bicarbonate (10 mL). The aqueous layer was separated and extracted with additional 30% isopropanol/chloroform solution (4 x 5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography (5% methanol in methylene chloride) to afford amine **3** (53 mg, 80%). $[\alpha]_D$ = +34.9° (*c* 1.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 2H, Ar-**H**), 5.90-5.68 (m, 2H, C**H**=CH_2 x 2), 5.17-5.05 (m, 4H, CH=C**H_2** x 2), 3.99 (dd, 1H, J = 7.8, 5.5 Hz, ArC**H**), 3.21-3.09 (m, 2H, NC**H_2**CH=CH_2), 2.66-2.58 (m, 1H, one of CHC**H_2**CH=CH_2), 2.53-2.43 (m, 1H, one of CHC**H_2**CH=CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 136.2, 134.4, 121.6, 118.4, 116.3, 55.8, 50.4, 40.3; IR (neat) 2076, 2977, 2913, 2807, 1642, 1451, 1095, 917 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{10}H_{15}N_3$ 177.3, found $(M+H)^+$ 178.1.

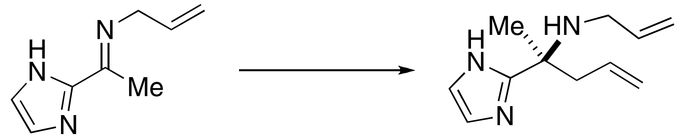


Preparation of (*R*)-*N*-(1-(1*H*-imidazol-2-yl)but-3-enyl)cyclohexanamine (5): To a solution of the aldimine (50 mg, 0.28 mmol) in toluene (2.8 mL) was added (1*S*,2*R*)-**4** (112 mg, 0.42 mmol) at room temperature. The reaction mixture was stirred for 12 hours, after which saturated sodium bicarbonate (2 mL) was added. After 15 minutes, a 30% solution of isopropyl alcohol in chloroform (15 mL) was added along with additional saturated sodium bicarbonate (10 mL). The aqueous layer was separated and extracted with additional 30% isopropanol/chloroform solution (2 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography (5% methanol in methylene chloride) to afford amine **5** (52 mg, 85%). $[\alpha]_D$ = +32.4° (*c* 2.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (s, 2H, Ar-**H**), 5.80-5.66 (m, 1H, **CH**=CH_2), 5.11-5.07 (m, 2H, CH=**CH₂**), 4.08 (dd, 1H, J = 7.8, 5.1 Hz, Ar-C**H**), 2.65-2.57 (m, 1H, one of **CH₂**CH=CH_2), 2.44-2.31 (m, 2H, overlapping one of **CH₂**CH=CH_2 and NC**H**(CH_2)$_2$), 1.93 (d, 1H, J = 12.6 Hz, Cy-**H**), 1.70-1.58 (m, 4H, Cy-**H**), 1.26-0.94 (m, 5H, Cy-**H**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 134.6, 121.4, 118.4, 55.2, 53.6, 40.9, 34.4, 33.3, 26.0, 25.1, 25.0; IR (neat) (3026, 2923, 2853, 1451, 1374, 1096, 992 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{13}H_{21}N_3$ 219.3, found $(M+H)^+$ 220.2.

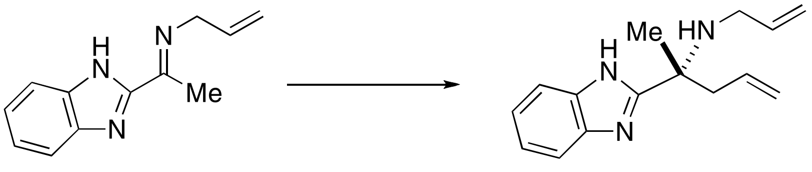


Preparation of (*R*)-1-(1-(1*H*-imidazol-2-yl)but-3-enyl)pyrrolidin-2-one (6): To a solution of the aldimine (50 mg, 0.26 mmol) in toluene (2.6 mL) was added (1*S*,2*R*)-**4** (102 mg, 0.38 mmol). The reaction mixture was stirred for one hour, after which the temperature was raised to 45 °C. After stirring the reaction mixture for another hour, the solution was cooled to room temperature and saturated sodium bicarbonate (2 mL) was added. The biphasic solution was stirred for an additional 15 minutes, after which a 30% solution of isopropyl alcohol in chloroform (15 mL) along with saturated sodium bicarbonate (10 mL) was added. The aqueous layer was separated and extracted with additional 30% isopropanol/chloroform solution (2 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash chromatography (4% methanol in methylene chloride) gave the product **6** as a white solid (38 mg, 71%). $[\alpha]_D$ = +93.0° (*c* 1.4, CH_2Cl_2);

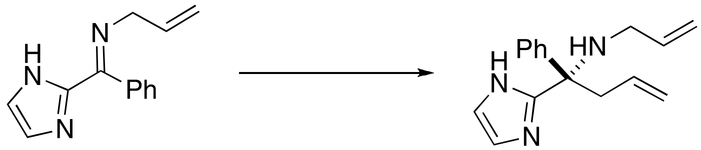
^{1}H NMR (400 MHz, CDCl$_3$) δ 11.45 (br s, 1H, N-**H**), 6.99 (s, 2H, Ar-H), 5.79-5.69 (m, 1H, C**H**=CH$_2$), 5.32 (dd, 1H, J = 10.0, 6.4 Hz, Ar-C**H**N), 5.16-5.06 (m, 2H, CH=C**H$_2$**), 3.51-3.44 (m, 1H, one of NC**H**$_2$CH$_2$), 3.30-3.24 (m, 1H, one of NC**H**$_2$CH$_2$), 2.93-2.80 (m, 2H, C**H$_2$**CH=CH$_2$), 2.47-2.29 (m, 2H, C**H$_2$**C=O), 2.02-1.93 (m, 2H, NCH$_2$C**H$_2$**); ^{13}C NMR (75 MHz, CD$_3$OD) δ 177.7, 146.5, 135.1, 122.9, 118.4, 49.9, 44.6, 35.4, 32.0, 18.8; IR (neat) 3152, 2978, 2913, 1656, 1435, 1287, 739 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{11}H_{15}N_3O$ 205.3, found $(M+H)^+$ 206.3.



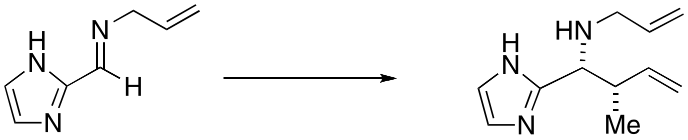
Preparation of (*S*)-*N*-allyl-2-(1*H*-imidazol-2-yl)pent-4-en-2-amine (7): To a stirred solution of of aldimine (50 mg, 0.34 mmol) in toluene (3.5 mL) was added (1*R*,2*S*)-**4** (132 mg, 0.5 mmol). After stirring for 30 minutes, aqueous saturatured sodium bicarbonate (2 mL) was added to the solution. The resulting biphasic solution was stirred for 15 minutes, after which a 30% solution of isopropanol in chloroform (15 mL) and additional saturated sodium bicarbonate (10 mL) was added. The aqueous layer was separated and extracted with additional 30% isopropanol/chloroform solution (2 x 10 mL). The combined organic layers were dried (MgSO$_4$), filtered, and concentrated. After column chromatography (5% methanol in methylene chloride), **7** was obtained as a white solid (55 mg, 85%). $[\alpha]_D$ = -14.2° (*c* 1.0, CH$_2$Cl$_2$); ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.98 (s, 2H, Ar-**H**), 5.88 (ddt, 1H, J = 17.1, 10.2, 5.7 Hz, C**H**=CH$_2$), 5.72 (ddt, 1H, J = 16.5, 10.5, 7.5 Hz, C**H**=CH$_2$), 5.23-5.05 (m, 4H, 2 x CH=C**H$_2$**), 3.13 (ddt, 1H, J = 14.1, 6.0, 1.5 Hz, one of N-C**H**$_2$), 3.02 (ddt, 1H, J = 14.1, 5.7, 1.5 Hz, one of N-C**H**$_2$), 2.61 (d, 2H, J = 7.2 Hz, CC**H$_2$**CH=CH$_2$), 1.51 (s, 3H, C**H$_3$**); ^{13}C NMR (75 MHz, CD$_3$OD) δ 153.4, 137.5, 134.4, 122.3, 119.1, 116.5, 57.8, 47.0, 46.8, 23.0; IR (neat) 3028, 2980, 2940, 2859, 2779, 2704, 1645, 1430, 1371, 1096, 916; LRMS (FAB$^+$) calc'd for $C_{11}H_{17}N_3$ 191.3, found $(M+H)^+$ 192.2.



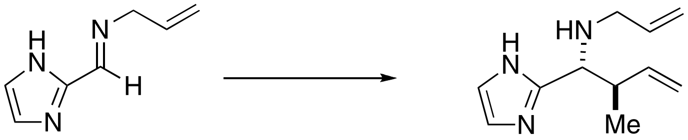
Preparation of (*R*)-*N*-allyl-2-(1*H*-benzo[*d*]imidazol-2-yl)pent-4-en-2-amine (8): To a solution of ketimine (50 mg, 0.25 mmol) in toluene (2.5 mL) was added (1*S*,2*R*)-**4**. After stirring for 1 hour at room temperature, aqueous saturated sodium bicarbonate (2 mL) was added to the solution. The resulting biphasic solution was stirred for 15 minutes, after which a 30% solution of isopropanol in chloroform (15 mL) and additional saturated sodium bicarbonate (10 mL) was added. The aqueous layer was separated and extracted with additional 30% isopropanol/chloroform solution (2 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. After column chromatography (4% methanol in methylene chloride), **8** was obtained as a white solid (52 mg, 86%). $[\alpha]_D$ = +20.3° (*c* 1.7, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (br s, 1H, N**H**), 7.73 (br s, 1H, Ar-**H**), 7.40 (br s, 1H, Ar-**H**), 7.24-7.18 (m, 2H, Ar-**H**), 5.95-5.70 (m, 2H, C**H**=CH_2 x 2), 5.25-5.06 (m, 4H, CH=C**H**$_2$ x 2), 3.19 (dd, 1H, J = 14.1, 5.7 Hz, one of NC**H**$_2$CH=CH_2), 3.09 (dd, 1H, J = 13.8, 5.4 Hz, one of NC**H**$_2$CH=CH_2), 2.73 (d, 2H, J = 7.5 Hz, CC**H**$_2$C=CH_2), 1.62 (s, 3H, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 323K) δ 159.6, 136.9, 133.1, 122.3, 119.4, 115.7, 110.8, 57.3, 45.8, 44.9, 24.6, 24.6; IR (KBr) 3076, 2977, 2885, 2843, 1641, 1452, 1411, 1275, 993, 918, 747 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{15}H_{19}N_3$ 241.3, found $(M+H)^+$ 242.1.



Preparation of (*S*)-*N*-allyl-1-(1*H*-imidazol-2-yl)-1-phenylbut-3-en-1-amine (10): To a cooled (10 °C) solution of ketimine **9** (50 mg, 0.24 mmol) in toluene (2.5 mL) was added (1*S*, 2*R*)-**4**. After 38 hours at 10 °C, the reaction mixture was quenched by the addition of aqueous saturated sodium bicarbonate (2 mL). The resulting biphasic mixture was stirred for 15 minutes, after which a 30% solution of isopropanol in chloroform (15 mL) and additional saturated sodium bicarbonate (10 mL) were added. The layers were separated and the aqueous layer was extracted with additional 30% isopropanol/chloroform solution (2 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. After column chromatography (30% ethyl acetate in hexanes), **10** was obtained as a white solid (41 mg, 69%). $[\alpha]_D$ = -25.3° (*c* 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.34 (br s, 1H, Imid N-**H**), 7.48-7.45 (m, 2H, Ar-**H**), 7.35-7.24 (m, 3H, Ar-**H**), 6.96 (s, 2H, Imid-**H**), 5.91 (ddt, 1H, J = 15.9, 10.5, 5.7 Hz, one **H**C=CH_2), 5.55 (ddt, 1H, J = 14.1, 10.2, 6.9 Hz, one **H**C=CH_2), 5.27-5.07 (m, 4H, 2 x CH=C**H$_2$**), 3.32 (dd, 1H, J = 14.4, 7.8 Hz, one C**H**$_2$CH=CH_2), 3.19 (dd, 1H, J = 14.4, 6.9 Hz, one C**H**$_2$CH=CH_2), 3.11 (dd, 1H, J = 14.1, 6.0 Hz, one C**H**$_2$CH=CH_2), 2.90 (dd, 1H, J = 13.8, 5.7 Hz, one C**H**$_2$CH=CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 145.0, 137.9, 134.4, 129.1, 128.1, 127.9, 122.2, 118.9, 115.9, 63.8, 46.6, 42.1; IR (KBr) 3069, 3026, 2950, 2793, 1641, 1434, 1377, 1099, 994 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{16}H_{19}N_3$ 253.3, found $(M+H)^+$ 254.1.

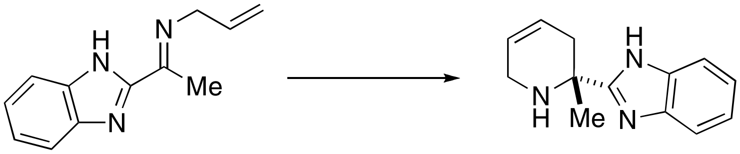


Preparation of (1*R*,2*S*)-*N*-allyl-1-(1*H*-imidazol-2-yl)-2-methylbut-3-en-1-amine (12): To a solution of aldimine **2** (50 mg, 0.37 mmol) in toluene (3.7 mL) was added (1*S*,2*R*)-**11** (155 mg, 0.55 mmol). After stirring for 1 hour at room temperature, aqueous saturated sodium bicarbonate (2 mL) was added to the solution. The resulting biphasic solution was stirred for 15 minutes, after which a 30% solution of isopropanol in chloroform (15 mL) and additional saturated sodium bicarbonate (10 mL) was added. The aqueous layer was separated and extracted with additional 30% isopropanol/chloroform solution (2 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. After column chromatography (5% methanol in methylene chloride), **12** was obtained as an oily solid (52 mg, 74%, >95:5 *dr*). $[\alpha]_D$ = +29.9° (*c* 1.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (s, 2H, Ar-**H**), 5.89-5.75 (m, 2H, C**H**=CH_2 x 2), 5.16-5.03 (m, 4H, CH=C**H**$_2$ x 2), 3.91 (d, 1H, J = 4.8 Hz, Ar-C**H**N), 3.20-3.05 (m, 2H, NC**H₂**CH=CH_2), 2.76-2.65 (m, 1H, C**H**CH_3), 0.98 (d, 3H, J = 6.9 Hz, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 140.2, 136.4, 121.5, 116.2, 115.8, 60.6, 50.9, 42.7, 14.8; IR (neat) 3148, 3034, 2967, 2886, 2812, 1452, 1095, 917, 737 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{11}H_{17}N_3$ 191.3, found $(M+H)^+$ 192.0.

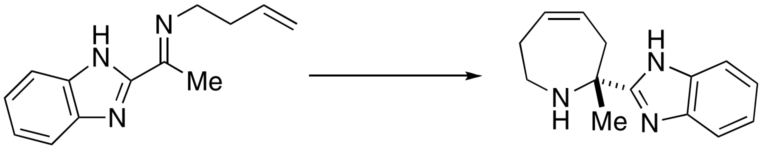


Preparation of (1*R*,2*R*)-*N*-allyl-1-(1*H*-imidazol-2-yl)-2-methylbut-3-en-1-amine (14): To a solution of aldimine **2** (50 mg, 0.37 mmol) in toluene (3.7 mL) was added (1*S*,2*R*)-**13** (155 mg, 0.55 mmol). After stirring for 1 hour at room temperature, aqueous saturated sodium bicarbonate (2 mL) was added to the solution. The resulting biphasic solution was stirred for 15 minutes, after which a 30% solution of isopropanol in chloroform (15 mL) and additional saturated sodium bicarbonate (10 mL) was added. The aqueous layer was separated and extracted with additional 30% isopropanol/chloroform solution (2 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. After column chromatography (5% methanol in methylene chloride), **14** was obtained as a clear oil (47 mg, 66%, >95:5 *dr*). $[\alpha]_D$ = +70.9° (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (s, 2H, Ar-**H**), 5.87-5.68 (m, 2H, C**H**=CH_2 x 2), 5.14-5.02 (m, 4H, CH=C**H**$_2$ x 2), 3.72 (d, 1H, J = 8.4 Hz, Ar-C**H**N), 3.16-3.01 (m, 2H, NC**H₂**CH=CH_2), 2.59-2.47 (m, 1H, C**H**CH_3), 0.922

(d, 3H, J = 6.6 Hz, C**H**$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 149.5, 141.2, 136.3, 121.5, 116.2, 116.0, 61.1, 50.5, 44.3, 17.3; IR (neat) 3076, 2973, 2878, 2810, 1640, 1456, 1097, 919, 736 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{11}H_{17}N_3$ 191.3, found $(M+H)^+$ 192.3.



Preparation of (*R*)-2-(2-methyl-1,2,3,6-tetrahydropyridin-2-yl)-1*H*-benzo[*d*]imidazole (16): To a solution of ketimine **15** (50 mg, 0.25 mmol) in toluene (2.5 mL) was added (1*S*,2*R*)-**4** (100 mg, 0.38 mmol). After 1 hour, Grubbs second generation catalyst (11 mg, 0.01 mmol) was added. The solution was heated at 45 °C for 14 hours, after which the reaction mixture was cooled to room temperature and quenched with saturated sodium bicarbonate (2 mL). After 15 minutes, the solution was diluted with a 30% isopropanol in chloroform mixture (15 mL). Additional saturated sodium bicarbonate (10 mL) was added, the layers were separated, and the aqueous layer was extracted with 30% isopropanol in chloroform (2 x 10 mL). The combined organic extracts were dried (MgSO$_4$), filtered and concentrated. The residue was purified by flash chromatography (5 – 7% methanol in methylene chloride) to give **16** as a tan solid (43 mg, 81%). $[\alpha]_D$ = -27.5° (*c* 1.1, CH$_2$Cl$_2$); ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.90 (br s, 1H, N**H**), 7.58 (br s, 2H, Ar-**H**), 7.26-7.21 (m, 2H, Ar-**H**), 5.91-5.87 (m, 1H, one C**H**=CH), 5.71-5.68 (m, 1H, one CH=C**H**), 3.43 (d, 1H, J = 18.0 Hz, one NC**H**$_2$), 3.30 (d, 1H, J = 18.3 Hz, one NC**H**$_2$), 3.00 (d, 1H, J = 17.1 Hz, one CC**H**$_2$CH=CH), 2.35 (d, 1H, J = 17.7 Hz, one CC**H**$_2$CH=CH), 2.00 (br s, 1H, N**H**), 1.57 (s, 3H, C**H**$_3$); ^{13}C NMR (75 MHz, CD$_3$OD, 325 K) δ 159.7, 138.5, 125.3, 123.9, 122.3, 114.7, 52.8, 41.8, 34.7, 27.6; IR (KBr) 3049, 2974, 2920, 1454, 1411, 1274, 1225, 745 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{13}H_{15}N_3$ 213.3, found $(M+H)^+$ 214.2.

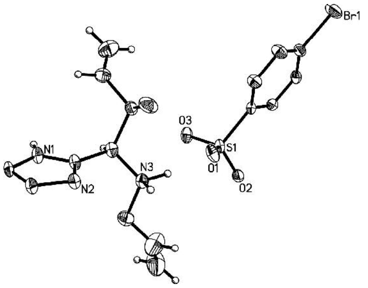


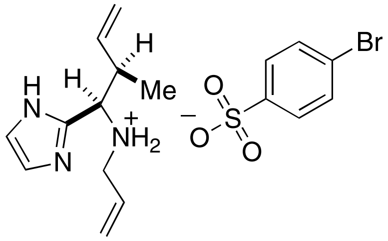
Synthesis of (*R*)-2-(2-methyl-2,3,6,7-tetrahydro-1*H*-azepin-2-yl)-1*H*-benzo[*d*]imidazole (18): To a solution of ketimine **17** (50 mg, 0.23 mmol) in toluene (2.3 mL) was added (1*S*,2*R*)-**4** (93mg, 0.35 mmol). After 1 hour, Grubbs second generation catalyst (11 mg, 0.01 mmol) was added. The solution was heated at 45 °C for 14 hours, after which the reaction mixture was cooled to room temperature and quenched with saturated sodium bicarbonate (2 mL). After 15 minutes, the solution was diluted with a

30% isopropanol in chloroform mixture (15 mL). Additional saturated sodium bicarbonate (10 mL) was added, the layers were separated, and the aqueous layer was extracted with 30% isopropanol in chloroform (2 x 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (5 – 6% methanol in methylene chloride) to give **18** as a tan solid (40 mg, 75%). $[\alpha]_D = +24.8°$ (*c* 1.2, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (br s, 2H, Ar-**H**), 7.21-7.19 (m, 2H, Ar-**H**), 5.74-5.67 (m, 2H, C**H**=C**H**), 3.16-3.10 (m, 1H, one of NC**H**$_2$), 3.01-2.90 (m, 2H, one NC**H**$_2$ and one CH_3CC**H**$_2$), 2.84-2.79 (m, 1H, one CH_3CC**H**$_2$), 2.38-2.28 (m, 2H, NCH_2C**H**$_2CH=CH$), 1.57 (s, 3H, C**H**$_3$); ^{13}C NMR (75 MHz, CD_3OD) δ 161.8, 139.4, 133.4, 128.2, 123.2, 115.6, 58.8, 43.5, 39.4, 32.6, 30.5; IR (KBr) 3062, 3022, 2967, 2926, 1453, 1411, 1273, 745 cm^{-1}; LRMS (FAB^+) calc'd for $C_{14}H_{17}N_3$ 227.3, found $(M+H)^+$ 228.2.

Determination of Absolute and Relative Configuration.

To a solution of allylamine **14** (51 mg, 0.27 mmol) in methanol (1 mL) was added *p*-bromobenzenesulfonic acid monohydrate (60 mg, 0.24 mmol). After 30 min, the solution was concentrated to a tan solid. A single crystal suitable for X-ray analysis was grown by slow-diffusion of pentane into a THF solution of the salt. The structure was solved and allowed the assignment of absolute and relative stereochemistry for amine **14**. The relative stereochemistry of amine **12** could therefore be assigned as *syn*, and by extension the relative stereochemistry of amines **15** and **16** was assigned as *syn* as well. The absolute configuration of all other products was assigned by analogy to the crystal structure assignment.

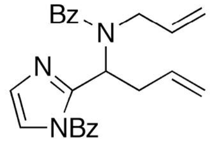




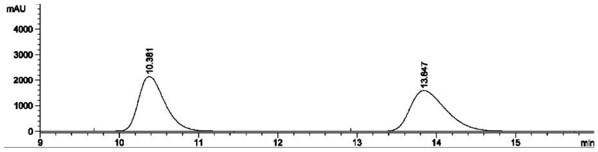
Determination of Enantiomeric Excess of Allylation Products.

The enantiomeric excess (ee) of the products reported in this study was in every case determined by chiral HPLC analysis. In every case the assay was performed on the derived mono- or bis-benzamide derivatives (except **7**, which was assayed as its *p*-NO_2-benzamide, and **8**, which was assayed as its bis-ethylcarbamate). Racemic samples were prepared by reacting the appropriate imine with *rac*-**1**, which was prepared by mixing equimolar amounts of (*S,S*)-**1** and (*R,R*)-**1**. Slight deviations from 50:50 in the racemic traces may therefore be attributed to the error inherent in this procedure.

Carbinamine **3**: Chiralpak AD-H column, 45.0% IPA/hexanes, 0.6 mL/min, 254 nm.



Racemic



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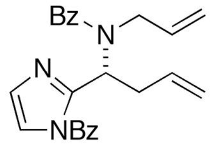
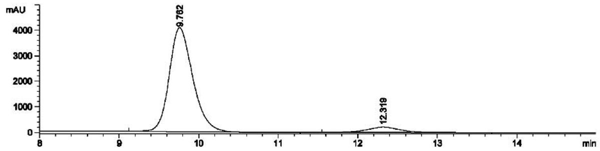
   2  13.847 VB    0.4846 4.98736e4  1580.80273  50.2311
```

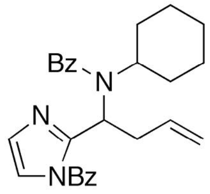


Enantioenriched Product

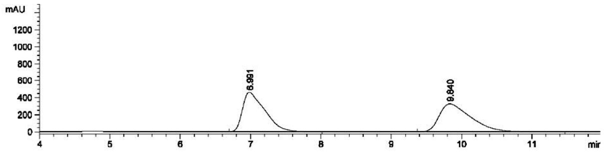


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1   9.762 VP    0.3217 8.35504e4  4057.86426  93.4364
   2  12.319 BP    0.4433 5869.16357  202.31509   6.5636
```

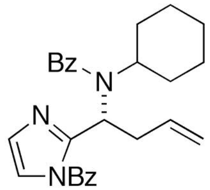
Carbinamine **5**: Chiralpak AD-H column, 25.0% IPA/hexanes, 1.0 mL/min, 254 nm.



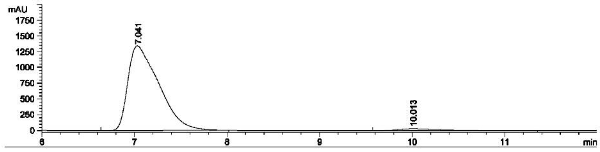
Racemic



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1   6.991 BBA   0.3194 1.01972e4   455.61020  49.9192
   2   9.840 BB    0.4722 1.02302e4   324.90442  50.0808
```

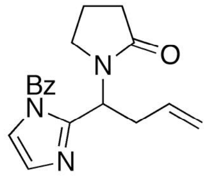


Enantioenriched Product

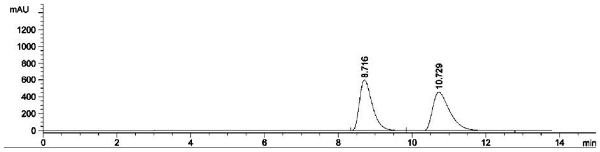


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1   7.041 VBA   0.3889 3.10838e4  1331.05994  97.3366
   2  10.013 PP    0.4532  850.53998   27.56359   2.6634
```

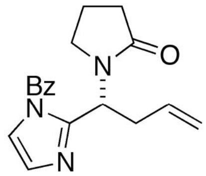
Carbinamine **6**: Chiralpak AD-H column, 20% IPA/hexanes, 1.0 mL/min, 254 nm.



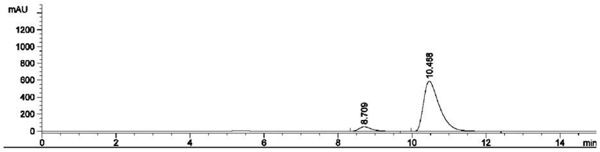
Racemic



```
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------|
   1   8.716 BV    0.3626 1.43267e4   594.73706  49.7331
   2  10.729 VB    0.4768 1.44805e4   454.20810  50.2669
```

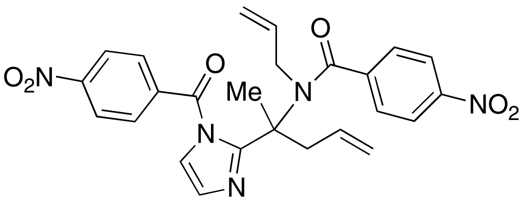


Enantioenriched Product



```
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------|
   1   8.709 BB    0.3482 1138.01819   49.78368   6.1939
   2  10.468 BB    0.4490 1.72352e4   584.24622  93.8061
```

Carbinamine **7**: Chiralpak AD-H column, 50% IPA/hexanes, 0.6 ml/min, 254 nm.



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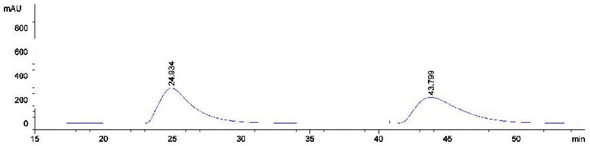
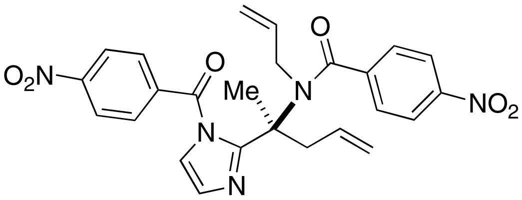
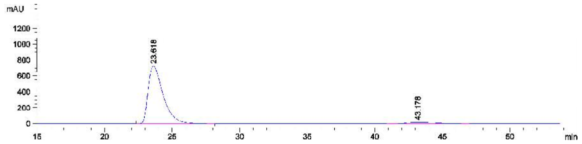


```
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------|
   1  24.934 PB    2.6642 5.17268e4   296.51297  50.0455
   2  43.799 PB    3.4956 5.16328e4   220.91139  49.9545
```

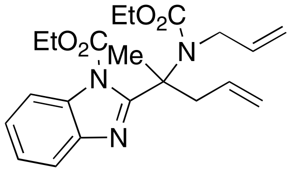


Enantioenriched Product



```
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------|
   1  23.618 PB    1.1637 5.58053e4   726.79633  95.7606
   2  43.178 PB    2.0980 2470.52588   17.53543   4.2394
```

Carbinamine **8**: Chiralpak AD-H column, 1% IPA/hexanes, 1.0 mL/min, 254 nm.



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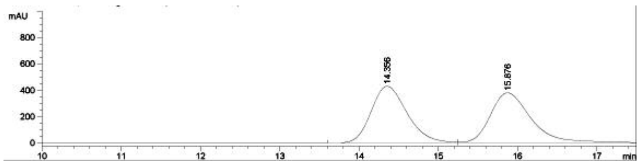
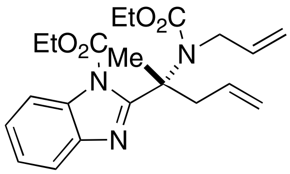
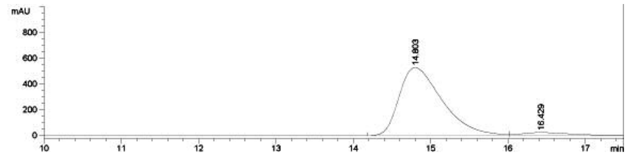


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.356 VV    0.4838 1.35189e4   429.35416  49.7020
   2  15.876 VBA   0.5488 1.36810e4   379.39035  50.2980
```

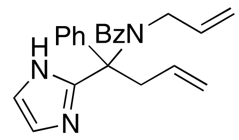


Enantioenriched Product

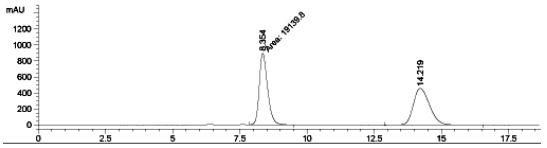


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.803 BV    0.5902 2.02913e4   525.62921  95.4597
   2  16.429 VB    0.6649  965.10583   21.92826   4.5403
```

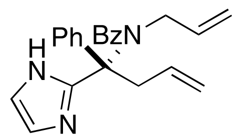
Carbinamine **10**: Chiralpak AD-H column, 8% EtOH/hexanes, 1.0 mL/min, 254 nm



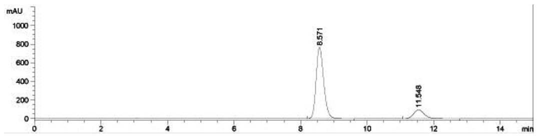
Racemic



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------
   1   8.354 MM    0.3563 1.91398e4   895.28076  50.1138
   2  14.219 VB    0.6498 1.90529e4   456.66595  49.8862
```

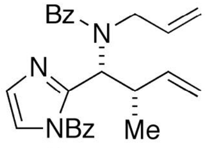


Enantioenriched Product

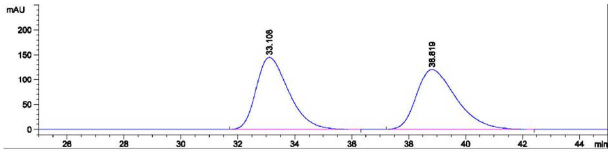


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   8.571 BB    0.2544 1.21032e4   765.10040  85.1044
   2  11.548 BB    0.3399 2118.40356   95.66491  14.8956
```

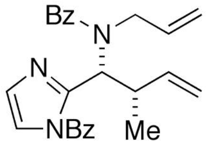
Carbinamine **12**: Chiralpak AD-H column, 12% IPA/hexanes, 1.0 mL/min, 254 nm.



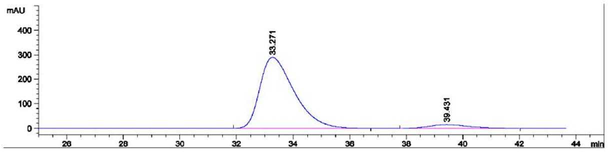
Racemate



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  33.108 BP     1.2010 1.14426e4   144.87794  49.6920
   2  38.819 BP     1.4621 1.15845e4   120.20523  50.3080
```

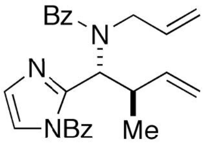


Enantioenriched Product

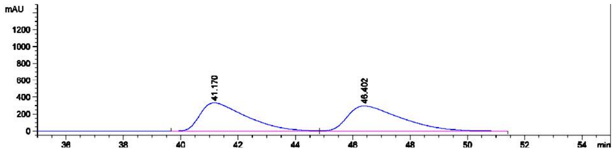


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------
   1  33.271 BB     1.2889 2.41745e4   289.44913  94.5450
   2  39.431 BB     1.4829 1394.81323   14.50562   5.4550
```

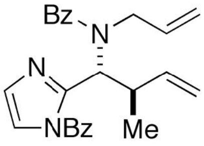
Carbinamine **14**: Chiralpak AD-H column, 12% IPA/hexanes, 1.0 mL/min, 254 nm.



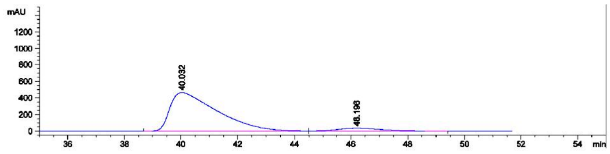
Racemate



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------
   1  41.170 BV     1.6518 3.68696e4   330.27353  49.2968
   2  46.402 VBA    1.8993 3.79215e4   294.29993  50.7032
```

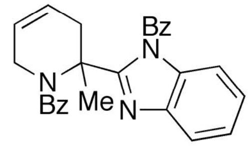


Enantioenriched Product

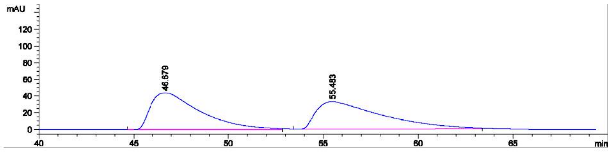


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------
   1  40.032 BV     1.6867 5.36439e4   463.97708  93.2013
   2  46.196 VB     1.6771 3913.12451   35.31684   6.7987
```

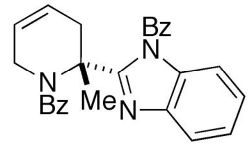
Carbinamine **16**: Chiralpak OD column, 1% IPA/hexanes, 1.0 mL/min, 254 nm.



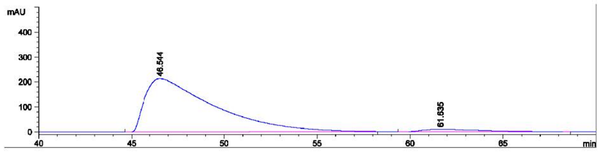
Racemic



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------
   1  46.679 PB     2.6461 7851.71680   43.40776  50.1071
   2  55.483 BB     3.3362 7818.16406   32.70720  49.8929
```

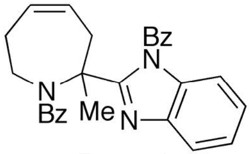


Enantioenriched Product

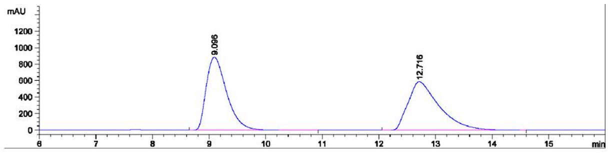


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------
   1  46.544 PB     3.5049 5.48674e4   212.26131  96.2526
   2  61.635 PB     3.2600 2136.16626    9.51453   3.7474
```

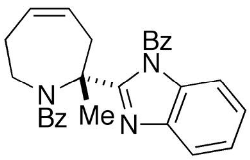
Carbinamine **18**: Chiralpak AD-H column, 10% IPA/hexanes, 1.0 mL/min, 254 nm.



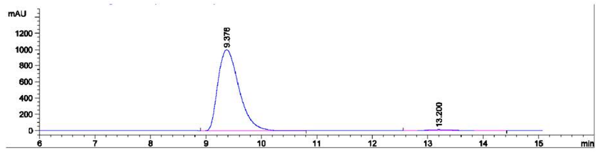
Racemic



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------
   1   9.096 PP     0.3859 2.21344e4   882.10376  49.6408
   2  12.716 BV     0.5544 2.24547e4   582.77460  50.3592
```

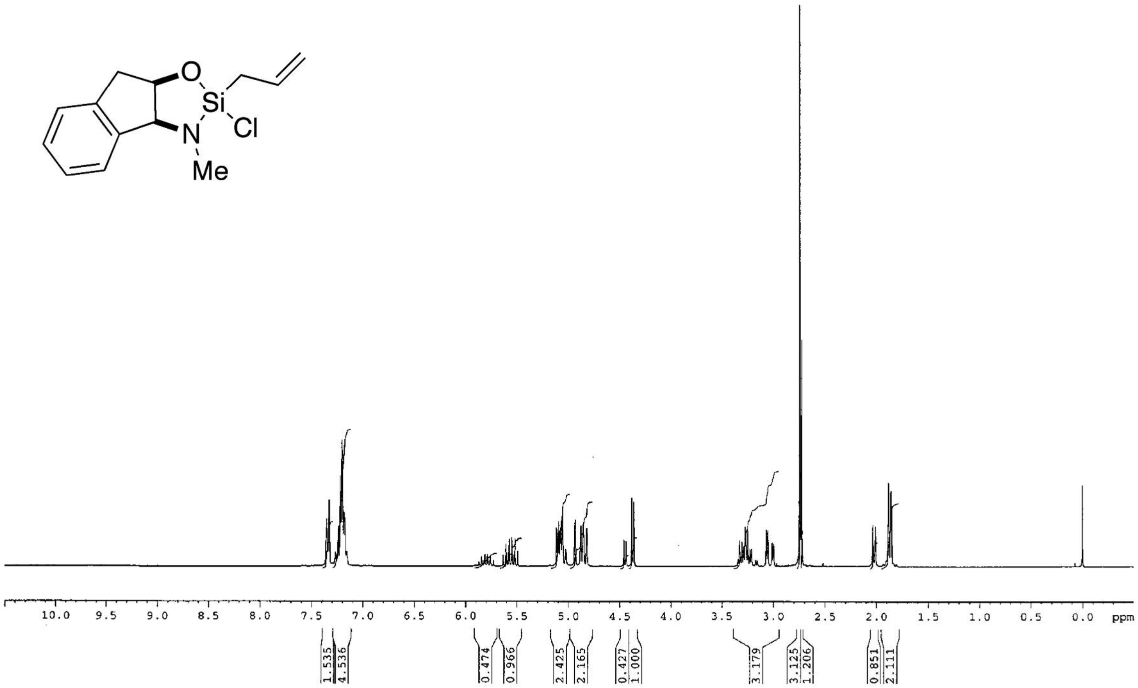


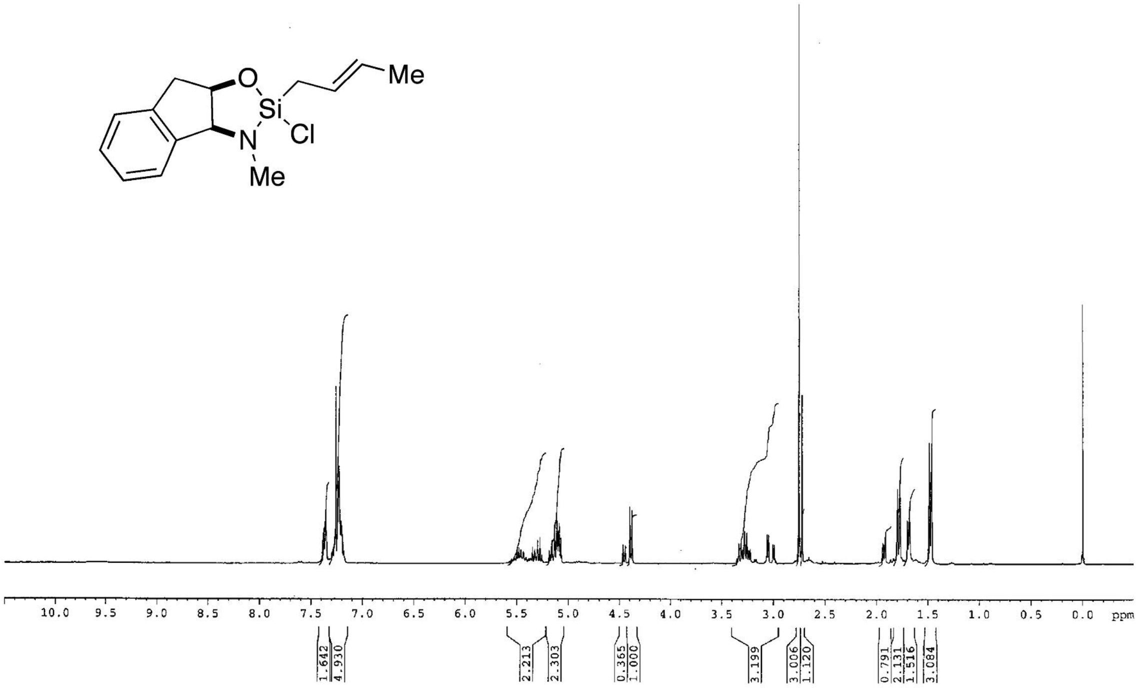
Enantioenriched Product

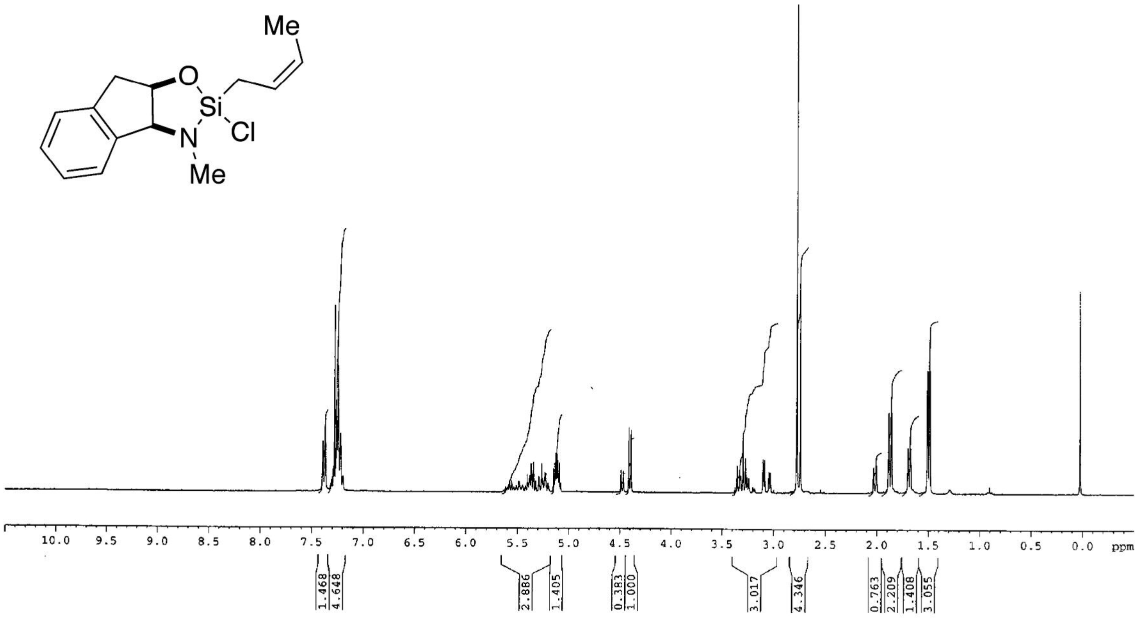


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------
   1   9.376 PB     0.4111 2.62428e4   999.55603  98.2047
   2  13.200 PB     0.5695  479.74521   13.38780   1.7953
```

^{1}H NMR Spectra.



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O
Si
Cl
N
Me
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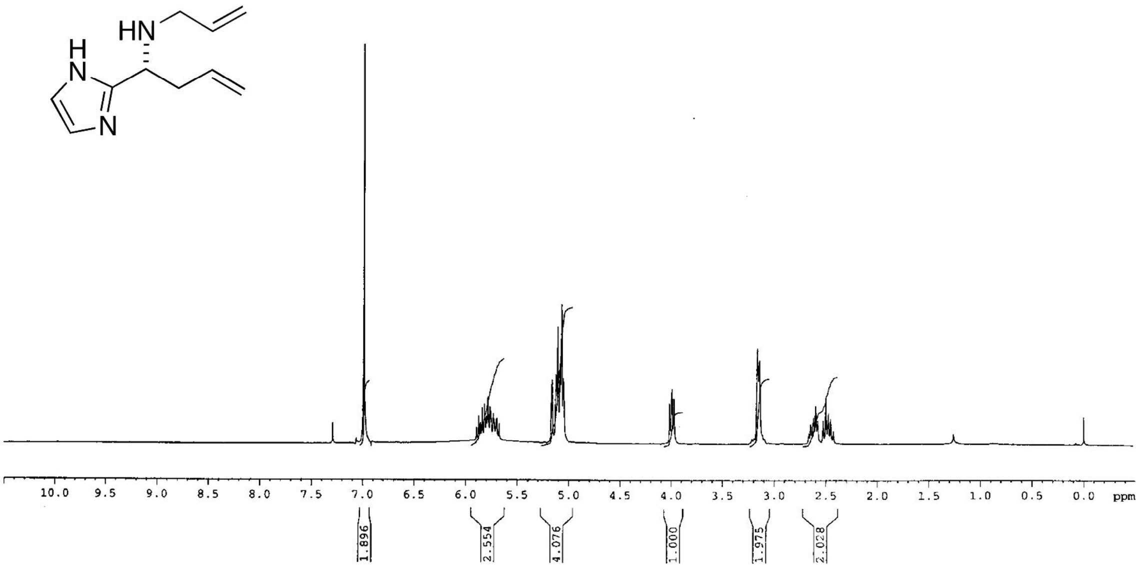
1.405
0.383
1.000
3.017
4.346
0.763
2.209
1.408
3.055


HN
H
N
N
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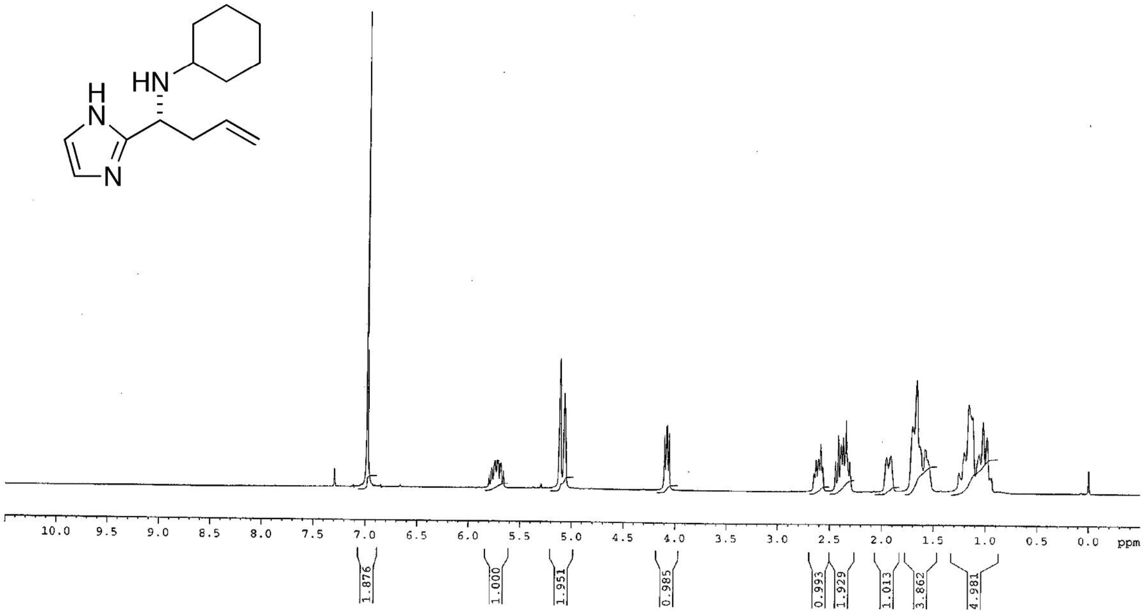
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N
N
HN
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4.0
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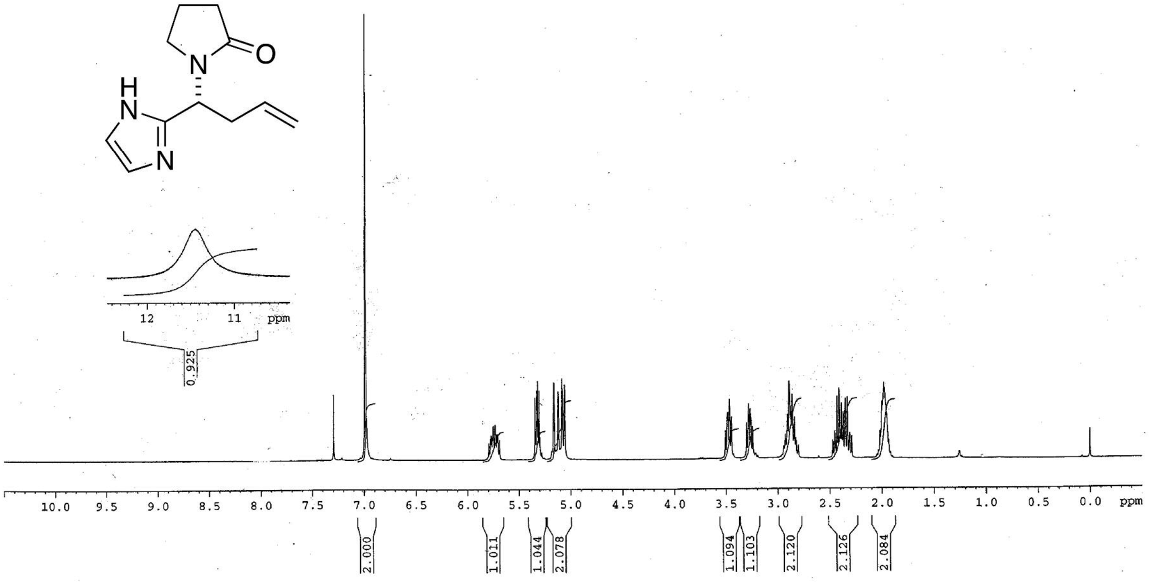
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3.0
2.5
2.0
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1.103
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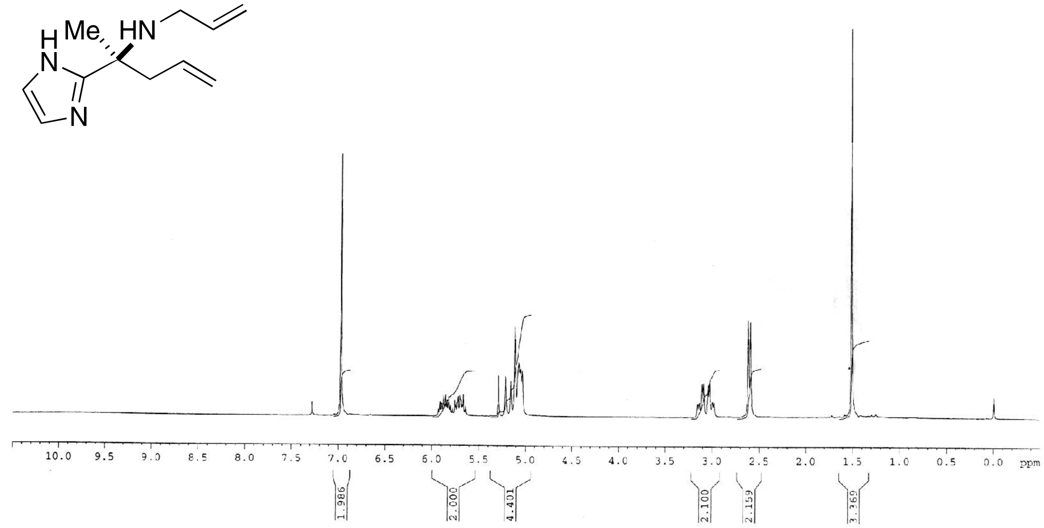
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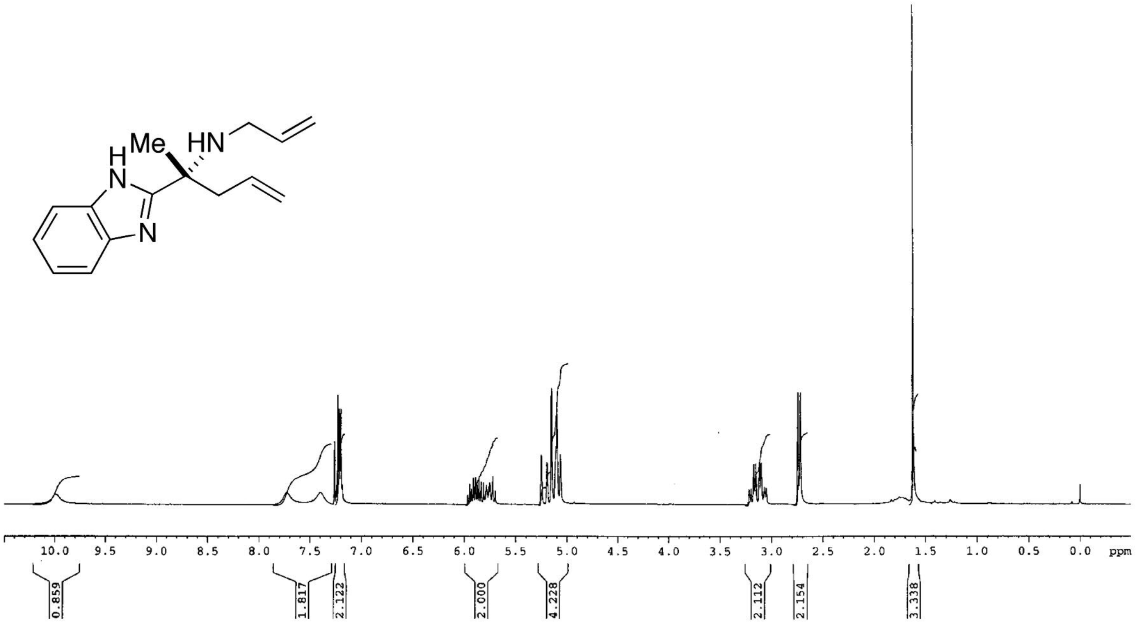
HN
H
N
N
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.986
2.000
4.401
2.100
2.159
3.369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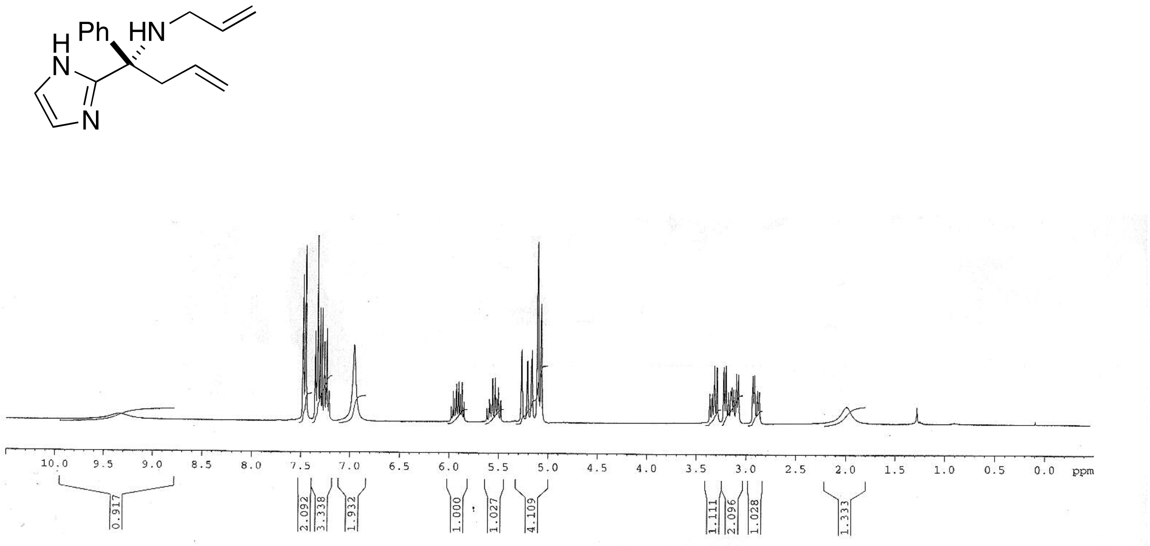
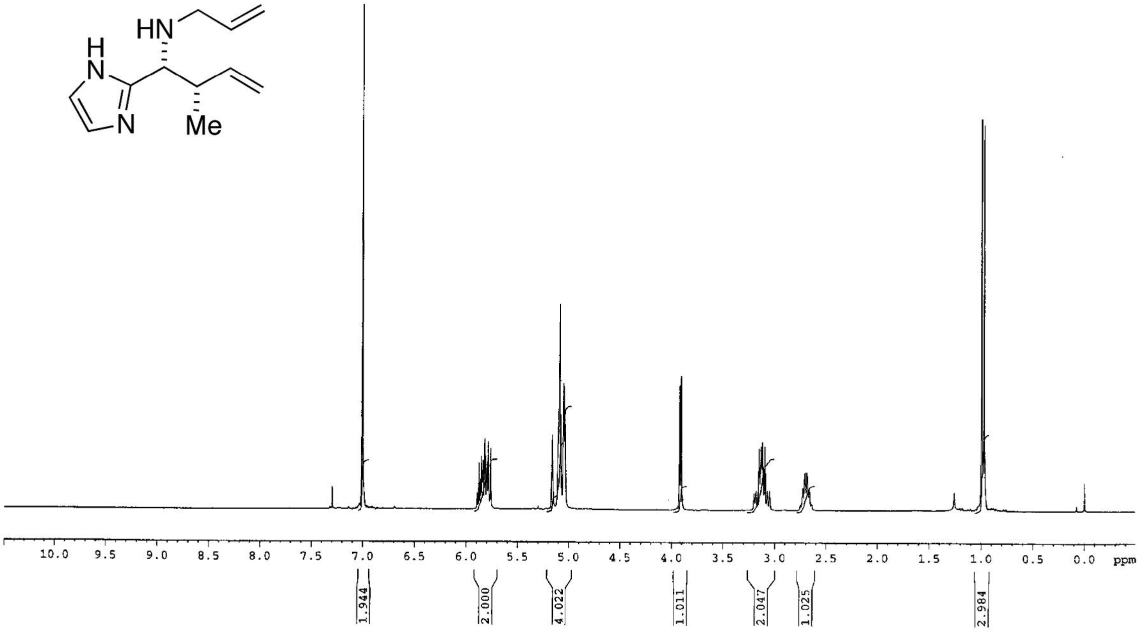
HN
H
N
N
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.859
1.817
2.122
2.000
4.228
2.112
2.154
3.338


H
N
N
Ph
HN
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.917
2.092
3.338
1.932
1.000
1.027
4.109
1.111
2.096
1.028
1.333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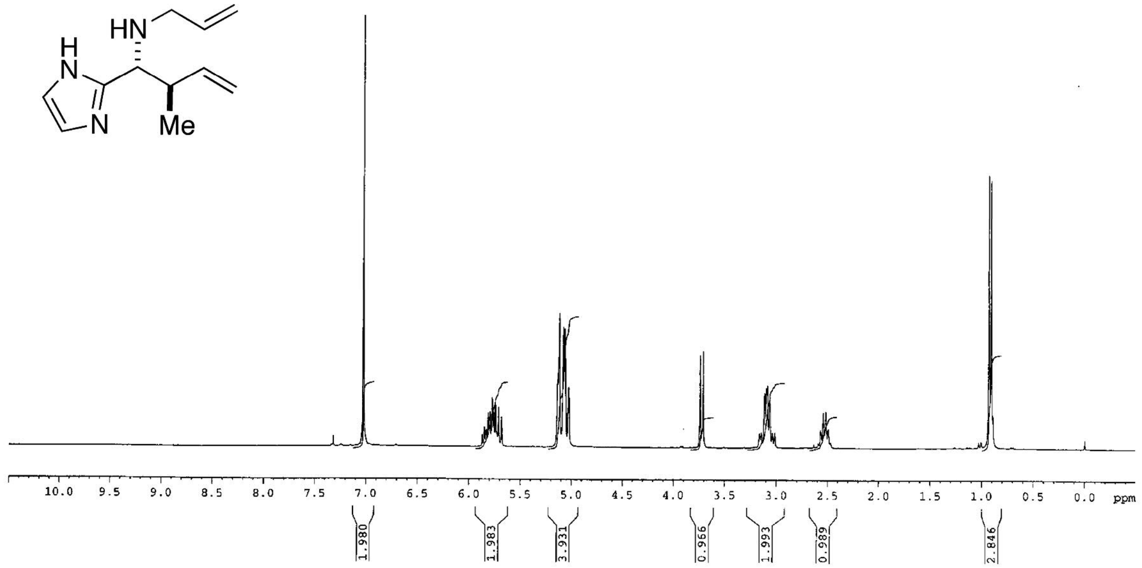
H
N
N
Me
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.944
2.000
4.022
1.011
2.047
1.025
2.984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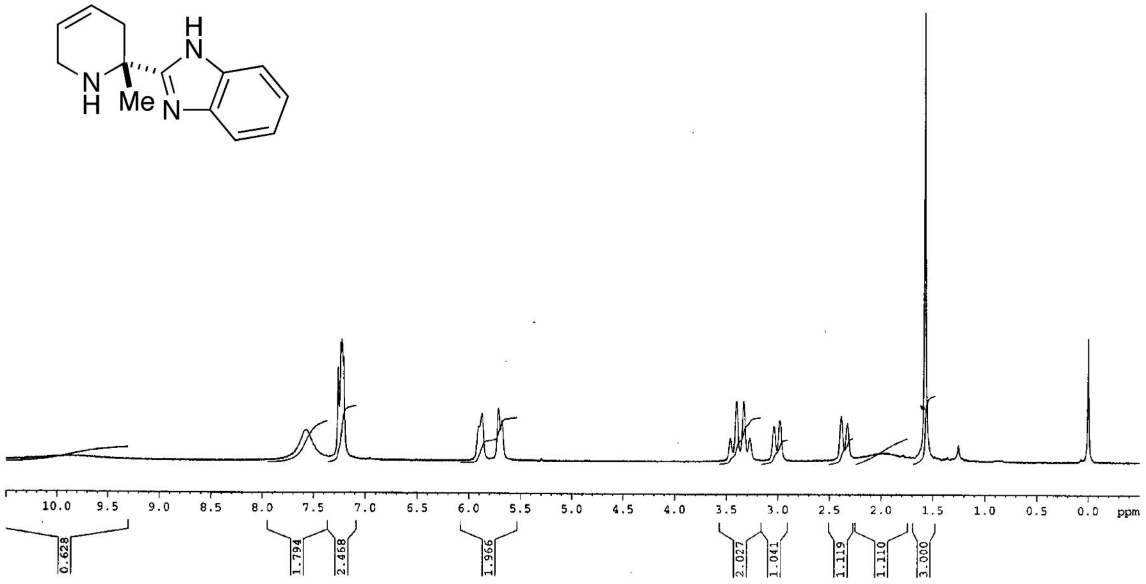
N
N
Me
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.980
1.983
3.931
0.966
1.993
0.989
2.846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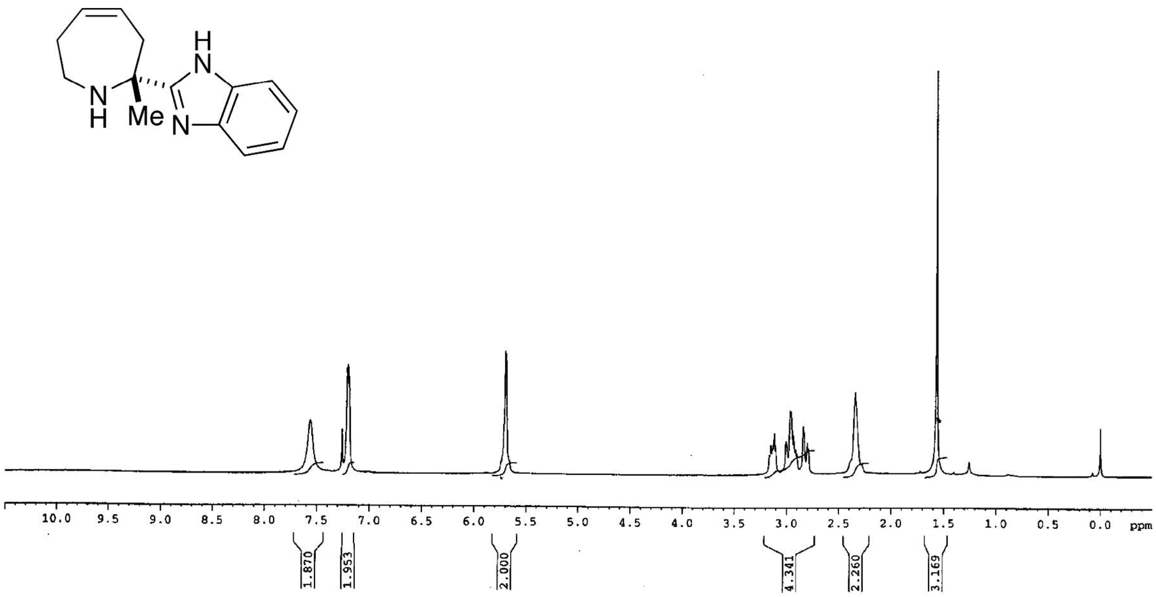
H
Me
H
N
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.628
1.794
2.468
1.966
2.027
1.041
1.119
1.110
3.000



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