Enantioselective Synthesis of Cyclic Secondary Amines through Mo-Catalyzed Asymmetric Ring-Closing Metathesis (ARCM)

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SUPPORTING INFORMATION

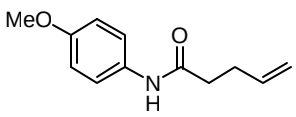
GENERAL

Infrared (IR) spectra were recorded on ThermoNicolet Avatar 360 spectrophotometer, ν_{max} in cm^{-1}. Bands were characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on Varian VXR 500 (500 MHz) or Unity 300 (300 MHz) spectrophotometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (C_6D_6: δ 7.16, $CDCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), integration, and assignment. ^{13}C NMR spectra were recorded on Varian VXR 500 (125 MHz) spectrophotometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (C_6D_6: δ 128.39, $CDCl_3$: δ 77.7). Enantiomer ratios were determined by chiral HPLC (Chiral Technologies Chiralpak AS (4.6 mm θ x 250 mm), Chiralcel OJ (4.6 mm θ x250 mm) or Chiralcel OD (4.6 mm θ x 250 mm)) in comparison with authentic racemic materials/ High-resolution mass spectrometry was performed at the Massachusetts Institute of Technology, Department of Chemistry Instrumentation Facility (Cambridge, MA).

All reactions were conduction in oven- (135 °C) or flame-dried glassware under an inert atmosphere of dry N_2. All metathesis substrates were dried by storing over molecular sieves under a N_2 atmosphere for a minimum of 12 hours prior to use. Handling of all Mo catalysts was performed in a drybox. Et_2O, toluene, and pentane were sparged with N_2 and then passed through an activated alumina column or distilled from sodium/benzophenone ketyl. Benzyl potassium was prepared by the literature method. All reagents were used as received from Aldrich Chemical Co., Lancaster Synthesis, or Strem Chemicals, Inc. unless otherwise stated. Mo complexes **3**, **4**, **5** and **9** were prepared according to published procedures.

EXPERIMENTALS FOR PRECURSORS

Pent-4-enoic acid (4-methoxy-phenyl)-amide: To a solution of p-anisidine, (10 g, 81 mmol) pyridine (8.3 mL, 89 mmol) and N,N-



dimethylaminopyridine (500 mg, 4 mmol) in dichloromethane at 0 °C was added drop-wise 4-pentenoyl chloride (9.9 mL, 89 mmol). After warming to room temperature, 10 % HCl in water (250 mL) was added to the solution. This mixture was extracted three times with dichloromethane (500 mL). All organic extracts were combined, washed with saturated $NaHCO_3$ solution, then NaCl solution, dried over $MgSO_4$ and concentrated *in vacuo* to a brown solid. The solid was recrystallized from a solution of ether and pentane to afford a white powder, 12.2 g, 59 mmol, 73 % yield. ^{1}H NMR (500 MHz, C_6D_6) δ 7.52 (d, 2H, J = 9 Hz, aryl C**H**) 6.76 (d, 2H, J = 9 Hz, aryl C**H**) 5.74 (m, 1H, C**H**=CH_2) 4.97 (m, 2H, CH=C**H$_2$**) 3.27 (s, 3H, C**H$_3$**O) 2.36 (m, 2H, C(O)C**H$_2$**CH_2) 1.97 (t, 2H, J = 7.5 Hz, C(O)CH_2C**H$_2$**). ^{13}C NMR (125 MHz, C_6D_6): δ 170.3 157.0 138.0 132.5 122.1 115.8 114.6 55.3 55.2 36.8 30.2. IR (KBr): 3308.5 (s) 3082.0 (w) 2952.4 (m) 1875.3 (w) 1652.9 (s) 1601.7 (m) 1542.1 (s) 1515.7 (s) 1410.3 (s) 1247.2 (s) 1173.5 (m) 1030.3 (s). HRMS (ESI) Calcd for $C_{12}H_{15}NO_2$ [M + Na]: 228.0995. Found: 228.0999.

Pent-4-enoic acid (4-bromo-phenyl)-amide: Analogous preparation as above: 8.45 g, 40 mmol, 98% yield. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.86 (br, 1H, N**H**) 7.41 (m, 4H, aryl C**H**) 5.86 (m, 1H, C**H**=CH_2) 5.09 (dd, 1H, J = 17.1 Hz, 0.9 Hz, CH=C**H$_a$**H_b) 5.02 (dd, 1H, J = 10.7 Hz, 0.9 Hz, CH=CH_a**H$_b$**) 2.43 (s, 4H, C**H$_2$**C**H$_2$**). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 171.5 137.9 137.8 132.3 122.0 116.9 116.0 37.1 29.8. IR (KBr): 3285.3 (s) 2978.9 (w) 1655.5 (s) 1589.1 (m) 1529.6 (s) 1488.2 (s) 1395.1 (m) 1298.6 (w) 1188.9 (w) 1072.3 (m). HRMS (ESI$^-$) Calcd for $C_{11}H_{12}NOBr$ [M + Na]: 275.9994. Found: 275.9997.

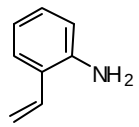
Pent-4-enoic acid (3-triflouromethyl-phenyl)-amide: Analogous preparation as above: 10 g, 41 mmol, 100% yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.87 (d, 1H, J = 8.2 Hz, aryl C**H**) 7.33 (br, 1H, aryl C**H**) 7.05 (d, 1H, J = 7.9 Hz, aryl C**H**) 6.89 (t, 1H, J = 7.9 Hz, aryl C**H**) 6.23 (br, 1H, N**H**) 5.71 (m, 1H, C**H**=CH_2) 4.98 (m, 1H, CH=C**H$_a$**H_b) 4.95 (m 1H, CH=CH_a**H$_b$**) 2.29 (m, 2H, C**H$_2$**) 1.83 (m, 2H, C**H$_2$**). ^{13}C NMR (125 MHz, C_6D_6): δ 139.5 137.5 130.1 127.1 123.3 120.8 116.6 116.1 36.8 29.8. IR (KBr): 3302.3 (s) 2981.9 (m) 1667.0 (s) 1558.2 (s) 1493.7 (s) 1447.6 (s) 1334.6 (s) 1282.0 (m) 1166.9 (s) 1071.1 (s). HRMS (ESI$^-$) Calcd for $C_{12}H_{12}NOF_3$ [M + Na]: 266.0763. Found: 266.0762.

Pent-4-enoic acid (2-methoxy-phenyl)-amide: Analogous preparation as above: 8.2 g, 40 mmol, 98% yield. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.31 (d, 1H, J = 7.9 Hz, aryl C**H**) 7.79 (br, 1H, N**H**) 7.02 (dt, 1H, J = 7.9 Hz, J = 1.2 Hz, aryl C**H**) 6.92 (dd, 1H, J = 7.9 Hz, 1.2 Hz, aryl C**H**) 6.89 (dd, 1H, J = 8.2 Hz, J = 1.2 Hz, aryl C**H**) 5.88 (m, 1H, C**H**=CH_2) 5.10 (d, 1H, J = 17.1 Hz, CH=C**H$_a$**H_b) 5.02 (d, 1H, J = 10.7 Hz, CH=CH_a**H$_b$**) 3.86 (s, 3H, C**H$_3$**O) 2.45 (m, 2H, C**H$_2$**). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 170.7 137.7 128.4 123.9 121.3 120.0 115.8 110.5 56.2 37.5 29.9. IR (KBr): 3324.8 (s) 2938.8 (m) 1678.9 (s) 1600.4 (s) 1524.0 (s) 1459.6 (s) 1434.1 (w) 1355.5 (s) 1253.4 (m) 1175.6 (m) 1047.3 (m). HRMS (ESI$^-$) Calcd for $C_{12}H_{15}NO_2$ [M + Na]: 228.0995. Found: 228.0996.

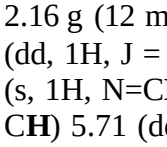
Pent-4-enoic acid (2-bromo-phenyl)-amide: Analogous preparation as above: 6.1 g, 24 mmol, 70% yield. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.29 (d, 1H, J =

7.9 Hz, aryl C**H**) 7.66 (br, 1H, N**H**) 7.55 (dd, 1H, J = 7.9 Hz, J = 1.5 Hz, aryl C**H**) 7.31 (dt, 1H, J = 7.8 Hz, 1.2 Hz, aryl C**H**) 6.99 (dt, 1H, J = 7.8 Hz, J = 1.5 Hz, aryl C**H**) 5.91 (m, 1H, C**H**=CH_2) 5.14 (d, 1H, J = 17.1 Hz, CH=C**H**$_a$H$_b$) 5.06 (d, 1H, J = 10.1 Hz, CH=CH$_a$**H$_b$**) 2.51 (m, 2H, C**H$_2$**). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 170.9 137.4 136.4 132.8 128.7 125.6 122.7 116.1 114.0 37.4 29.8. IR (KBr): 3273.7 (s) 1659.8 (s) 1579.6 (m) 1526.9 (s) 1438.3 (m) 1414.3 (m) 1374.5 (w) 1291.7 (m) 1186.3 (m) 1027.3 (m). HRMS (ESI$^-$) Calcd for $C_{11}H_{12}NOBr$ [M + Na]: 275.9994. Found: 275.9992.

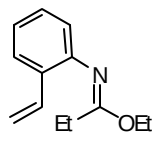
2-Vinyl-phenylamine: 2-Amino-phenethylalcohol (18 g, 131 mmol) and potassium hydroxide (7.36 g, 131 mmol) were combined in a distillation apparatus, then heated to 180 °C under vacuum. A clear, colorless oil was distilled over 4 hours at 55 - 60 °C at 0.25 Torr, 12.1 g 102 mmol, 78% yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.27 (dd, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 6.99 (dt, 1H, J = 1.5 Hz, 7.3 Hz, aryl C**H**) 6.71 (dt, 1H, J = 1.2 Hz, 7.3 Hz, aryl C**H**) 6.57 (dd, 1H, J = 11.2 Hz, 17.4 Hz, ArC**H**=CH_2) 6.31 (dd, 1H, J = 0.9 Hz, 7.9 Hz, aryl C**H**) 5.50 (dd, 1H, J = 1.5 Hz, 17.4 Hz, CH=C**H**$_a$H$_b$) 5.09 (dd, 1H, J = 1.5 Hz, 11.2 Hz, CH=CH$_a$**H$_b$**) 3.00 (br, 2H, N**H$_2$**). This spectrum matches published material[1-3] on this compound, therefore no further spectral data were obtained.



N-(2-Vinyl-phenyl)-formidic acid ethyl ester: 2-Vinyl-phenylamine, (2.15 g, 18 mmol) triethyl orthoformate (3.9 mL, 23 mmol) and *p*-toluenesulfonic acid (20 mg, 90 μmol) were heated to 130 °C to remove 2 equivalents of ethanol in a Dean-Stark condenser. After the mixture was cooled, residual orthoester was removed at room temperature under Schlenk vacuum. Subsequently, the crude material was distilled at reduced pressure with heating to afford 2.16 g (12 mmol) of a clear, colorless oil: 68 % yield. ^{1}H NMR (500 MHz, C_6D_6) δ 7.52 (dd, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 7.37 (dd, 1H, J = 11.0 Hz, 17.7 Hz, aryl C**H**) 7.27 (s, 1H, N=C**H**) 6.99 (m, 2H, aryl C**H** + C**H**=CH_2) 6.57 (dd, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 5.71 (dd, 1H, J = 17.7 Hz, 1.4 Hz, CH=C**H$_{cis}$**H$_{trans}$) 5.22 (dd, 1H, J = 11.1 Hz, 1.4 Hz, CH=CH$_{cis}$**H$_{trans}$**) 4.11 (q, 2H, J = 7.0 Hz, OC**H**$_2$CH$_3$) 1.06 (t, 3H, J = 7.0 Hz, OCH$_2$C**H**$_3$). ^{13}C NMR (125 MHz, C_6D_6) δ 154.8 146.6 134.4 131.8 129.2 126.2 125.0 120.9 114.1 62.6 14.6. IR (NEAT, NaCl plates): 3064.8 (m) 2931.5 (s) 1646.3 (s) 1594.3 (s) 1480.8 (s) 1389.8 (s) 1280.7 (s) 1200.9 (s) 1096.9 (s) 1054.27 (m). HRMS (EI$^+$) Calcd for $C_{11}H_{13}NO$: 175.0992. Found: 175.0997.



***N*-(2-Vinyl-phenyl)-propionimidic acid ethyl ester:** Analogous preparation as above, distilled at 65 °C at 100 mTorr, 7.6 g, 38 mmol, 76 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.52 (dd, 1H, J = 1.2 Hz, J = 7.6 Hz, aryl C**H**) 7.05 (m, 2H, aryl C**H** & C**H**=CH_2) 6.93 (td, 1H, J = 7.3 Hz, J = 0.6 Hz, aryl C**H**) 6.69 (dd, 1H, J = 1.2 Hz, 7.9 Hz, aryl C**H**) 5.65 (dd, 1H, J = 1.5 Hz, 17.7 Hz, CH=C**H**$_a$H$_b$) 5.15 (dd, 1H, J = 1.5 Hz, 11.0 Hz, CH=CH$_a$**H$_b$**) 4.21 (q, 2H, J = 7.1 Hz, OC**H$_2$**CH$_3$) 1.98 (q, 2H, J = 7.6 Hz, CC**H$_2$**CH$_3$) 1.14 (t, 3H, J = 7.1 Hz, OCH$_2$C**H$_3$**) 0.90 (t, 3H, J = 7.6 Hz, CCH$_2$C**H$_3$**). ^{13}C NMR (125 MHz, C_6D_6): δ 164.6 147.8 134.4 129.7 129.1 126.4 123.6 122.0 113.9 61.9 24.2 14.7 11.0. IR (NEAT, NaCl plates): 3085.8 (w) 2978.1 (s) 2896.5 (m) 1667.6 (s) 1625.5 (m) 1596.9 (m) 1478.9 (m) 1364.8 (m) 1282.5



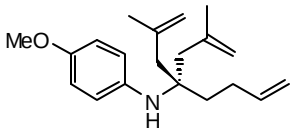
(s) 1231.0 (s) 1179.2 (m) 1086.6 (s) 1058.9 (s) 1016.0 (s). HRMS (ESI^+) Calcd for $C_{13}H_{17}NO$ [M + H]: 204.1383. Found: 204.1383.

***N*-(2-Vinyl-phenyl)-benzimidic acid ethyl ester:** Analogous preparation as above, distilled at 90 – 100 °C, at 100 mTorr, 4.5 g, 19 mmol, 56 % yield. ^1H NMR (500 MHz, C_6D_6): δ 7.50 (dd, 1H, J = 7.3 Hz, J = 1.2 Hz, aryl C**H**) 7.39 (dd, 1H, J = 7.9 Hz, J = 1.5 Hz, aryl C**H**) 7.25 (dd, 1H, J = 17.7, J = 11.0 Hz, C**H**=CH_2) 6.85 (m, 5H, aryl C**H**) 6.52 (dd, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 5.71 (dd, 1H, J = 1.5 Hz, 17.7 Hz, CH=C**H$_a$**H$_b$) 5.19 (dd, 1H, J = 2.2 Hz, 11.0 Hz, CH=CH$_a$**H$_b$**) 3.76 (s, 3H, OC**H$_3$**). ^{13}C NMR (125 MHz, C_6D_6): δ 147.2 134.4 132.2 130.5 130.0 129.8 129.1 126.4 123.6 122.2 114.2 54.1 13.0. IR (NEAT, NaCl plates): 3084.7 (m) 3014.1 (m) 2943.1 (m) 2836.7 (w) 1664.9 (s) 1624.5 (s) 1595.2 (s) 1492.9 (m) 1413.2 (w) 1270.2 (s) 1191.9 (m) 1119.3 (s) 1074.4 (m) 1029.1 (m). HRMS (ESI^+) Calcd for $C_{16}H_{15}NO$ [M+H]: 238.1226. Found: 238.1228.

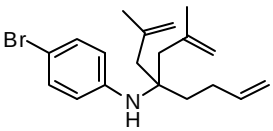
Pent-4-enoic acid (2-vinyl-phenyl)-amide: To a solution of 2-vinylaniline, (5 g, 42 mmol) pyridine (4.3 mL, 46 mmol) and N,N-dimethylaminopyridine (256 mg, 2.1 mmol) in dichloromethane at 0 °C was added drop-wise 4-pentenoyl chloride (5.1 mL, 46 mmol). After warming to room temperature, 10 % HCl in water (100 mL) was added to the solution. This mixture was extracted three times with dichloromethane (200 mL). All organic extracts were combined, washed with saturated $NaHCO_3$ solution, then NaCl solution, dried over $MgSO_4$ and concentrated *in vacuo* to an off-white solid. The solid was triterated in pentane for 1 hour, then filtered to afford a white powder, 6.94 g, 34 mmol, 82 % yield. ^1H NMR (500 MHz, C_6D_6) δ 7.95 (d, 1H, J = 7.9 Hz, aryl C**H**) 7.25 (d, 1H, J = 7.6 Hz, aryl C**H**) 7.08 (br, 1H, N**H**) 7.01 (m, 1H, aryl C**H**) 6.86 (t, 1H, J = 7.9 Hz, aryl C**H**) 6.64 (dd, 1H, J = 11.0 Hz, 17.4 Hz, ArC**H**=CH_2) 5.67 (m, 1H, CH_2C**H**=CH_2) 5.42 (dd, 1H, J = 1.5 Hz, 17.4 Hz, ArCH=C**H$_a$**H$_b$) 5.07 (d, 1H, J = 10.7 Hz, ArCH=CH$_a$**H$_b$**) 4.94 (d, 1H, J = 17.4 Hz, CH_2CH=C**H$_a$**H$_b$) 4.90 (d, 1H, J = 10.7 Hz, CH_2CH=CH$_a$**H$_b$**) 2.27 (m, 2H, C(O)C**H$_2$**CH_2) 1.94 (t, 2H, J = 7.5 Hz, C(O)CH_2C**H$_2$**). ^{13}C NMR (125 MHz, C_6D_6) δ 170.5 137.8 135.8 133.3 131.0 129.0 128.7 127.0 125.6 124.9 117.1 115.9 36.5 30.1. IR (KBr): 3271.5 (s) 3078.2 (w) 2977.3 (w) 1827.2 (w) 1651.5 (s) 1528.8 (s) 1449.8 (s) 1373.2 (m) 1291.3 (m) 1197.3 (m) 1022.1 (w). HRMS (ESI^-) Calcd for $C_{13}H_{15}NO$ [M + Na]: 224.1046. Found: 224.1050.

Pent-4-enoic acid (benzyl)-amide Prepared analogously to above: 9.35 g, 50 mmol, 90 % yield. ^1H NMR (500 MHz, C_6D_6) δ 7.09 (m, 5H, aryl C**H**) 5.73 (m, 1H, CH_2C**H**=CH_2) 5.10 (br, 1H, N**H**) 4.95 (m, 2H, CH=C**H$_2$**) 4.21 (s, 2H, C**H$_2$**Ar) 2.32 (m, 2H, C(O)C**H$_2$**CH_2) 1.86 (t, 2H, J = 7.6 Hz, C(O)CH_2C**H$_2$**). ^{13}C NMR (125 MHz, C_6D_6) δ 173.1 139.6 137.9 190.0 127.7 115.7 43.9 35.7 30.5. IR (NEAT, NaCl plates): 3288.5 (s) 3031.7 (m) 1727.5 (m) 1640.8 (s) 1546.4 (s) 1453.9 (m) 1380.1 (m) 1266.2 (m) 1079.7 (m) 1027.9 (m). HRMS (ESI) Calcd for $C_{12}H_{15}NO$ [M + Na]: 212.1046. Found: 212.1047.

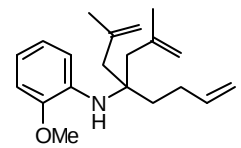
EXPERIMENTALS FOR SUBSTRATES AND PRODUCTS



[1,1-Bis-(2-methyl-allyl)-pent-4-enyl]-(4-methoxy-phenyl)-amine (1a) Phosphorous pentachloride (2 g, 9.7 mmol) was added to a solution of pent-4-enoic acid (4-methoxy-phenyl)-amide (2 g, 9.7 mmol) and dichloromethane (20 mL) in a Schlenk flask under vigorous N_2 flow, to produce a mild exotherm. After 20 minutes, the solvent was removed *in vacuo* to afford a green oil. ^{1}H NMR of the crude product indicated complete conversion to the imidoyl chloride. This material was diluted in THF (20 mL) and added to methallyl Grignard (73 mL, 0.4 M) at room temperature to afford an orange solution. The mixture was quenched on water (150 mL) then extracted three times with ether (200 mL). All organic extracts were combined, washed with saturated solutions of NH_4Cl, then NaCl, dried ($MgSO_4$) and concentrated *in vacuo* to a brown oil. The crude product was purified by column chromatography, eluting with 20 % ether in pentane, to afford 2.23 g (7.5 mmol, 77 %) of yellow oil. ^{1}H NMR (500 MHz, C_6D_6) δ 6.76 (d, 2H, J = 9 Hz, aryl C**H**) 6.55 (d, 2H, J = 9 Hz, aryl C**H**) 5.76 (m, 1H, C**H**=CH_2) 5.05 (dd, 1H, J = 1.5 Hz, 17.1 Hz, CH=C**H$_a$**H$_b$) 4.97 (dd, 1H, J = 1.2 Hz, 10.4 Hz, CH=CH$_a$**H$_b$**) 4.93 (m, 2H, CH_3C=C**H$_a$**H$_b$) 4.85 (m, 2H, CH_3C=CH$_a$**H$_b$**) 3.39 (s, 3H, C**H$_3$**O) 2.41 (d, 2H, J = 13.9 Hz, C(C**H$_a$**H$_b$)$_2$) 2.26 (d, 2H, J = 13.9 Hz, C(CH$_a$**H$_b$**)$_2$) 2.09 (m, 2H, C**H$_2$**) 1.74 (s, 6H, C**H$_3$**C=CH_2) 1.69 (m, 2H, C**H$_2$**). ^{13}C NMR (125 MHz, C_6D_6) δ 153.2 143.3 140.9 139.1 118.3 115.7 115.4 114.9 59.0 55.5 44.6 37.7 29.2 25.4. IR (NEAT, NaCl plates): 3406.1 (m) 3073.3 (m) 2945.4 (m) 1640.0 (m) 1510.3 (s) 1455.1 (m) 1373.5 (w) 1240.5 (s) 1179.4 (m) 1041.5 (m). HRMS (ESI) Calcd for $C_{20}H_{29}NO$ [M + H]: 300.2322. Found: 300.2318.



[1,1-Bis-(2-methyl-allyl)-pent-4-enyl]-(4-bromo-phenyl)-amine (1b) Analogous preparation as above: 2.2 g, 6.5 mmol, 82 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.15 (d, 2H, J = 8.9 Hz, aryl C**H**) 6.17 (d, 2H, J = 8.9 Hz, aryl C**H**) 5.70 (m, 1H, C**H**=CH_2) 5.00 (dd, 1H, J = 17.1 Hz, 0.6 Hz, CH=C**H$_a$**H$_b$) 4.95 (dd, 1H, J = 10.1 Hz, 0.9 Hz, CH=CH$_a$**H$_b$**) 4.86 (s, 2H, C(CH_3)=C**H$_a$**H$_b$) 4.72 (s, 2H, C(CH_3)=CH$_a$**H$_b$**) 3.29 (s, 3H, C**H$_3$**O) 2.29 (d, 2H, J = 14.3 Hz, C**H$_a$**H$_b$) 2.10 (d, 2H, J = 14.4 Hz, CH$_a$**H$_b$**) 1.97 (m, 2H, C**H$_2$**) 1.61 (s, 6H, C**H$_3$**C) 1.57 (m, 2H, C**H$_2$**). ^{13}C NMR (125 MHz, C_6D_6): δ 146.1 142.8 138.7 132.6 127.1 117.3 115.9 115.1 109.4 58.8 44.0 37.2 29.0 25.1. IR (NEAT, NaCl plates): 3416.5 (m) 3074.2 (s) 2945.3 (s) 1640.3 (s) 1591.5 (s) 1488.7 (s) 1452.3 (m) 1373.5 (m) 1318.9 (m) 1254.3 (m) 1180.8 (w) 1076.0 (s). HRMS (ESI^+) Calcd for $C_{19}H_{26}NBr$ [M + H]: 348.1321. Found: 348.1308.



[1,1-Bis-(2-methyl-allyl)-pent-4-enyl]-(2-methoxy-phenyl)-amine (1c) Analogous preparation as above: 0.72 g, 2.4 mmol, 25% yield. ^{1}H NMR (500 MHz, C_6D_6): δ 6.92 (m, 2H, aryl C**H**) 6.70 (m, 1H, aryl C**H**) 6.56 (d, 1H, J = 7.6 Hz, aryl C**H**) 5.76 (m, 1H, C**H**=CH_2) 5.02 (ddd, 1H, J = 17.1 Hz, 1.5 Hz, J = 3.66 Hz, CH=C**H$_a$**H$_b$) 4.94 (ddd, 1H, J = 10.4 Hz, 1.2 Hz, J = 2.1 Hz, CH=CH$_a$**H$_b$**) 4.91 (m, 2H, C(CH_3)=C**H$_a$**H$_b$) 4.84 (m, 2H, C(CH_3)=CH$_a$**H$_b$**) 4.63 (s, 1H, N**H**) 3.30 (s, 3H, C**H$_3$**O) 2.55 (d, 2H, J = 14.4 Hz, C**H$_a$**H$_b$) 2.35 (d, 2H, J = 14.4 Hz, CH$_a$**H$_b$**) 2.14 (m, 2H, C**H$_2$**) 1.85 (m, 2H, C**H$_2$**) 1.75 (s, 6H, C**H$_3$**C). ^{13}C NMR (125 MHz, C_6D_6): δ 147.9 143.2 139.1 137.3 127.1 121.8 116.6

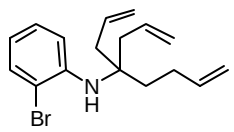
115.7 114.8 113.1 110.5 58.6 55.5 44.5 37.6 29.2 25.0. IR (NEAT, NaCl plates): 3427.7 (w) 3072.9 (m) 29.46.0 (s) 2834.0 (m) 1640.3 (s) 1602.1 (s) 1520.9 (s) 1457.5 (s) 1373.5 (m) 1351.6 (m) 1295.7 (w) 1251.1 (s) 1221.4 (s) 1177.0 (m) 1124.5 (m) 1088.3 (w) 1032.0 (s). HRMS (ESI^+) Calcd for $C_{20}H_{29}NO$ [M + Na]: 322.2141. Found: 322.2139.

[1,1-Bis-(2-methyl-allyl)-pent-4-enyl]-(2-bromo-phenyl)-amine (1d) Analogous preparation as above: 2.4 g, 6.8 mmol, 86% yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.38 (dd, 1H, J = 7.9 Hz, 1.5 Hz, aryl C**H**) 6.94 (dt, 1H, J = 7.8 Hz, 1.5 Hz, aryl C**H**) 6.82 (dd, 1H, J = 8.2 Hz, J = 1.2 Hz, aryl C**H**) 6.35 (dt, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 5.71 (m, 1H, C**H**=CH_2) 5.00 (dd, 1H, J = 17.1 Hz, 1.5 Hz, CH=C**H$_a$**H$_b$) 4.95 (dd, 1H, J = 10.1 Hz, 1.5 Hz, H=CH$_a$**H$_b$**) 4.94 (s, 2H, C(CH_3)=C**H$_a$**H$_b$) 4.89 (m, 2H, C(CH_3)=CH$_a$**H$_b$**) 4.64 (s, 1H, N**H**) 2.42 (d, 2H, J = 14.3 Hz, C**H$_a$**H$_b$) 2.29 (d, 2H, J = 14.3 Hz, CH$_a$**H$_b$**) 2.06 (m, 2H, C**H$_2$**) 1.80 (m, 2H, C**H$_2$**) 1.66 (s, 6H, C**H$_3$**C). ^{13}C NMR (125 MHz, C_6D_6): δ 144.1 142.6 138.7 133.7 127.1 118.0 116.4 115.0 114.2 112.0 59.3 44.6 37.5 29.1 25.0. IR (NEAT, NaCl plates): 3409.0 (m) 3073.8 (m) 2946.5 (m) 1640.4 (m)0 1593.4 (s) 1516.5 (s) 1463.1 (s) 1374.1 (w) 1318.8 (m) 1286.6 (m) 1261.1 (w) 1166.0 (w) 1087.7 (m) 1017.6 (s). HRMS (ESI^+) Calcd for $C_{19}H_{26}NBr$ [M + H]: 348.1321. Found: 348.1331.

[1,1-Bis-(2-methyl-allyl)-pent-4-enyl]-(3-triflouromethyl-phenyl)-amine (1e) Analogous preparation as above: 2.5 g, 7.4 mmol, 90 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 6.89 (m, 3H, aryl C**H**) 6.49 (m, 1H, aryl C**H**) 5.69 (m, 1H, C**H**=CH_2) 5.02 (ddd, 1H, J = 17.1 Hz, 1.5 Hz, J = 3.35 Hz, CH=C**H$_a$**H$_b$) 4.96 (ddd, 1H, J = 10.1 Hz, 1.2 Hz, J = 1.8 Hz, CH=CH$_a$**H$_b$**) 4.84 (m, 2H, C(CH_3)=C**H$_a$**H$_b$) 4.71 (m, 2H, C(CH_3)=CH$_a$**H$_b$**) 3.46 (s, 3H, C**H$_3$**O) 2.34 (d, 2H, J = 14.3 Hz, C**H$_a$**H$_b$) 2.13 (d, 2H, J = 14.3 Hz, CH$_a$**H$_b$**) 1.96 (m, 2H, C**H$_2$**) 1.62 (m, 2H, C**H$_2$**) 1.59 (s, 6H, C**H$_3$**C). ^{13}C NMR (125 MHz, C_6D_6): δ 147.5 142.6 138.6 130.2 118.1 116.1 115.2 113.9 (q, J = 4 Hz) 112.1 58.9 44.0 37.3 28.9 25.1. IR (NEAT, NaCl plates): 3422.5 (w) 3076.2 (m) 2946.7 (s) 1641.2 (m) 1613.3 (s) 1526.4 (s) 1492.2 (s) 1439.1 (s) 1349.5 (s) 1278.8 (w) 1164.4 (s) 1097.2 (m) 1071.1 (s). HRMS (ESI^+) Calcd for $C_{20}H_{26}NF_3$ [M + H]: 338.2090. Found: 338.2110.

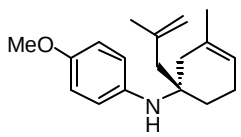
[1,1-Bis-(2-methyl-allyl)-pent-4-enyl]-(benzyl)-amine (1f) Analogous preparation as above: 1 g, 3.5 mmol, 33 % yield. ^{1}H NMR (500 MHz, C_6D_6) δ 7.38 (d, 2H, J = 7.5 Hz, aryl C**H**) 7.22 (t, 2H, J = 7.5 Hz, aryl C**H**) 7.12 (t, 1H, J = 7.5 Hz, aryl C**H**) 5.82 (m, 1H, C**H**=CH_2) 5.08 (dd, 1H, J = 1.5 Hz, 17.1 Hz, CH=C**H$_a$**H$_b$) 4.99 (dd, 1H, J = 1.2 Hz, 10.1 Hz, CH=CH$_a$**H$_b$**) 4.92 (m, 2H, CH_3C=C**H$_a$**H$_b$) 4.88 (m, 2H, CH_3C=CH$_a$**H$_b$**) 3.61 (s, 2H, PhC**H$_2$**N) 2.11 (s, 1H, N**H**) 2.10 – 2.06 (m, 6H, C**H$_2$**) 1.79 (s, 6H, C**H$_3$**) 1.55 (m, 2H, C**H$_2$**). ^{13}C NMR (125 MHz, C_6D_6) δ 143.4 142.0 139.6 129.0 128.8 127.5 115.2 114.6 58.7 46.7 43.9 36.7 29.1 25.8. IR (NEAT, NaCl plates): 3409.0 (br) 3073.6 (m) 2940.9 (s) 1639.8 (s) 1452.0 (s) 1373.2 (m) 1329.6 (m) 1241.9 (w) 1028.9 (m). HRMS (ESI^+) Calcd for $C_{20}H_{29}N$ [M + H]: 284.2373. Found: 284.2374.

(2-Bromo-phenyl)-(1,1-diallyl-pent-4-enyl)-amine Analogous preparation as above: 2 g, 6.3 mmol, 80 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.38 (dd, 1H, J = 7.9 Hz, J = 1.5



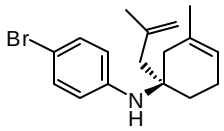
Hz, aryl C**H**) 7.11 (dt, 1H, J = 7.3 Hz, J = 1.2 Hz, aryl C**H**) 6.92 (dt, 1H, J = 1.2 Hz, J = 8.2 Hz, aryl C**H**) 6.79 (dd, 1H, J = 1.2 Hz, 7.6 Hz, aryl C**H**) 6.60 (dd, 1H, J = 1.2 Hz, 7.6 Hz, aryl C**H**) 6.37 (dt, 1H, J = 1.5 Hz, 7.5 Hz, aryl C**H**) 5.69 (m, 3H, C**H**=CH$_2$) 5.02 – 4.91 (m, 6H, CH=C**H$_2$**) 4.44 (br, 1H, N**H**) 2.31 – 2.18 (m, 4H, C**H$_2$**) 2.01 – 1.96 (m, 2H, C**H$_2$**) 1.69 – 1.61 (m, 2H, C**H$_2$**). ^{13}C NMR (125 MHz, C_6D_6): δ 139.0 134.5 134.0 133.6 129.8 128.8 119.2 118.7 116.9 115.0 114.6 112.6 58.9 41.6 36.6 29.4. IR (NEAT, NaCl plates): 3394.7 (br m) 3075.7 (m) 2936.2 (m) 2861.1 (w) 1639.9 (m) 1593.4 (s) 1515.2 (s) 1463.1 (s) 1327.9 (m) 1165.9 (w) 1018.6 (m).

(4-Methoxy-phenyl)-[3-methyl-1-(2-methyl-allyl)-cyclohex-3-enyl]-amine (2a)



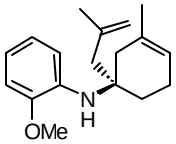
Catalyst **3** [(*R*)Pr$_2$Bnz$_2$Bitet] (5 mg, 7 μmol) was added to a solution of **1a** (68 mg, 230 μmol) in benzene-d_6 (1 mL), and the resultant mixture placed in a J. Young tube. The reaction was monitored by ^{1}H NMR analysis. After 1 hour, the reaction was complete. The mixture was exposed to air, stirred over charcoal, filtered through celite and concentrated *in vacuo*. The crude was purified by chromatography over silica gel, eluting with 1 % ether in pentanes to afford 50 mg of clear, colorless oil (186 μmol, 81 % yield.) ^{1}H NMR (500 MHz, C_6D_6): δ 6.75 (m, 2H, aryl C**H**) 6.60 (m, 2H, aryl C**H**) 5.35 (m, 1H, ArC**H**=C(CH$_3$)) 4.96 (m, 1H, CH$_3$C=C**H$_a$**H$_b$) 4.82 (m, 1H, CH$_3$C=CH$_a$**H$_b$**) 3.39 (s, 3H, C**H$_3$**O) 3.08 (br, 1H, N**H**) 2.54 (d, 1H, J = 13.7 Hz, CC**H$_a$**H$_b$C(CH$_3$)=) 2.23 (d, 1H, J = 13.7 Hz, CCH$_a$**H$_b$**C(CH$_3$)=)1.97 – 1.85 (m, 5H) 1.85 (s, 3H, C**H$_3$**) 1.56 (s, 3H, C**H$_3$**) 1.42 (m, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 153.8 143.6 141.1 131.5 128.7 121.3 119.5 115.2 115.1 55.5 46.4 42.9 31.7 25.4 24.2 23.3. IR (NEAT, NaCl plates): 3402.2 (w) 3069.7 (w) 2926.4 (s) 1640.5 (m) 1509.6 (s) 1441.5 (m) 1375.2 (w) 1239.0 (s) 1179.3 (m) 1040.7 (m). HRMS (ESI) Calcd for $C_{18}H_{25}NO$ [M + H]: 272.2009. Found: 272.2007. HPLC (Chiralpak AS, 0.1 % IPA in Hexane, 254 nm, 1.0 mL/min) 67% e.e.

(4-Bromo-phenyl)-[3-methyl-1-(2-methyl-allyl)-cyclohex-3-enyl]-amine (2b)



Analogous preparation as above, 57 mg, 178 μmol, 78% yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.17 (d, 2H, J = 6.7 Hz, aryl C**H**) 6.18 (d, 2H, J = 6.7 Hz, aryl C**H**) 5.30 (m, 1H, C**H**=C(CH$_3$)) 4.91 (m, 1H, C(CH$_3$)=C**H$_a$**H$_b$) 4.70 (m, 1H, C(CH$_3$)=CH$_a$**H$_b$**) 3.12 (br, 1H, N**H**) 2.45 (d, 1H, J = 13.7 Hz, C**H$_a$**H$_b$) 2.08 (d, 1H, J = 13.7 Hz, CH$_a$**H$_b$**) 1.92 (br d, 1H, J = 15.9 Hz, C**H$_a$**H$_b$) 1.83 – 1.77 (m, 3H, C**H$_2$**, C**H$_a$**H$_b$) 1.82 (br d, 1H, J = 17.8 Hz, CH$_a$**H$_b$**) 1.70 (s, 3H, C**H$_3$**) 1.53 (s, 3H, C**H$_3$**) 1.26 (m, 1H, CH$_a$**H$_b$**). ^{13}C NMR (125 MHz, C_6D_6): δ 146.5 143.0 132.5 130.8 121.7 117.4 115.3 109.6 55.2 45.3 43.3 31.1 25.0 24.1 23.0. IR (NEAT, NaCl): 3413.7 (m) 3071.8 (m) 2923.5 (s) 2849.6 (m) 1641.3 (m) 1591.1 (s) 1489.0 (s) 1444.4 (m) 1375.3 (m) 1317.1 (m) 1255.5 (m) 1180.0 (m) 1075.6 (m). HRMS (ESI$^-$) Calcd for $C_{17}H_{22}NBr$ [M + Na]: 342.0828. Found: 342.0832. HPLC (Chiralpak AS, 0.1 % IPA in Hexane, 254 nm, 1.0 mL/min) 67% e.e.

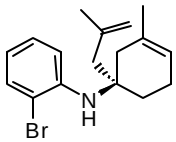
(2-Methoxy-phenyl)-[3-methyl-1-(2-methyl-allyl)-cyclohex-3-enyl]-amine (2c)



Analogous preparation as above, 62 mg, 230 μmol, 99 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 6.96 (m, 2H, aryl C**H**) 6.71 (dt, 1H, J = 1.8, J = 7.9 Hz, aryl C**H**) 6.57 (dd, 1H, J = 1.2 Hz, 7.9 Hz, aryl C**H**) 5.36 (m, 1H,

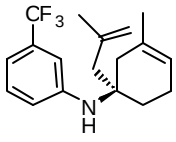
C**H**=C(CH_3)) 4.93 (m, 1H, C(CH_3)=C**H$_a$**H$_b$) 4.77 (m, 1H, C(CH_3)=CH$_a$**H$_b$**) 4.52 (br, 1H, N**H**) 3.28 (s, 3H, C**H$_3$**O) 2.70 (d, 1H, J = 13.7 Hz, C**H$_a$**H$_b$) 2.33 (d, 1H, J = 13.7 Hz, CH$_a$**H$_b$**) 2.18 – 1.84 (m, 5H, C**H$_2$**, C**H$_a$**H$_b$) 1.81 (s, 3H, C**H$_3$**) 1.54 (s, 3H, C**H$_3$**) 1.49 (m, 1H, CH$_a$**H$_b$**). ^{13}C NMR (125 MHz, C_6D_6): δ 148.0 143.5 137.6 131.3 121.8 121.5 116.6 115.1 113.1 110.5 55.5 55.0 45.2 43.5 31.7 24.9 24.2 23.3. IR (NEAT, NaCl): 3427.1 (w) 3069.8 (m) 2923.4 (s) 2834.6 (m) 1641.0 (m) 1601.6 (s) 1514.7 (s) 1457.2 (s) 1359.1 (m) 1252.0 (s) 1176.2 (m) 1115.2 (m) 1031.8 (s). HRMS (ESI$^+$) Calcd for $C_{18}H_{25}NO$ [M + H]: 272.2009. Found: 272.2012. HPLC (Chiralcel OD, 0.1 % IPA in Hexane, 254 nm, 1.0 mL/min) 79% e.e.

(2-Bromo-phenyl)-[3-methyl-1-(2-methyl-allyl)-cyclohex-3-enyl]-amine (2d)



Analogous preparation as above, 160 mg, 0.45 mmol, 91 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.39 (dt, 1H, J = 1.8 Hz, 7.9 Hz, aryl C**H**) 6.96 (dt, 1H, J = 1.5, J = 8.2 Hz, aryl C**H**) 6.85 (dd, 1H, J = 1.5 Hz, 8.2 Hz, aryl C**H**) 6.36 (dt, 1H, J = 1.5 Hz, 7.9 Hz, aryl C**H**) 5.33 (m, 1H, C**H**=C(CH_3)) 4.90 (m, 1H, C(CH_3)=C**H$_a$**H$_b$) 4.73 (m, 1H, C(CH_3)=CH$_a$**H$_b$**) 4.50 (br, 1H, N**H**) 2.55 (d, 1H, J = 13.7 Hz, C**H$_a$**H$_b$) 2.23 (d, 1H, J = 13.7 Hz, CH$_a$**H$_b$**) 2.09 (br d, 1H, J = 17.4 Hz, C**H$_a$**H$_b$) 2.02 – 1.78 (m, 5H, C**H$_2$**, C**H$_a$**H$_b$) 1.73 (s, 3H, C**H$_3$**) 1.54 (s, 3H, C**H$_3$**) 1.38 (m, 1H, CH$_a$**H$_b$**). ^{13}C NMR (125 MHz, C_6D_6): δ 144.5 142.8 133.6 130.9 121.6 118.0 115.6 114.2 112.2 55.7 45.2 43.0 31.2 24.8 24.1 23.2. IR (NEAT, NaCl): 3406.8 (m) 3071.1 (w) 2963.9 (m) 2923.6 (m) 2849.6 (m) 1641.6 (m) 1593.4 (s) 1515.2 (s) 1463.2 (s) 1375.4 (w) 1323.4 (m) 1286.6 (m) 1099.3 (m) 1018.1 (s). HRMS (ESI$^-$) Calcd for $C_{17}H_{22}NBr$ [M + Na]: 342.0828. Found: 342.0838. HPLC (Chiralcel OD, 0.1 % IPA in Hexane, 254 nm, 1.0 mL/min) 81% e.e.

(3-Triflouromethyl-phenyl)-[3-methyl-1-(2-methyl-allyl)-cyclohex-3-enyl]-amine (2e)



Analogous preparation as above, 60 mg, 191 μmol, 85 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 6.90 (m, 2H, aryl C**H**) 6.83 (s, 1H, aryl C**H**) 6.48 (m, 1H, aryl C**H**) 5.27 (m, 1H, C**H**=C(CH_3)) 4.88 (m, 1H, C(CH_3)=C**H$_a$**H$_b$) 4.68 (m, 1H, C(CH_3)=CH$_a$**H$_b$**) 3.31 (br, 1H, N**H**) 2.49 (d, 1H, J = 13.7 Hz, C**H$_a$**H$_b$) 2.11 (d, 1H, J = 13.7 Hz, CH$_a$**H$_b$**)1.93 (m, 1H, C**H$_a$**H$_b$) 1.85 – 1.7 (m, 4H, C**H$_2$**) 1.66 (s, 3H, C**H$_3$**) 1.52 (s, 3H, C**H$_3$**) 1.29 (m, 1H, CH$_a$**H$_b$**). ^{13}C NMR (125 MHz, C_6D_6): δ 147.9 142.8 130.7 130.1 121.7 118.0 115.5 113.9 112.0 55.3 45.2 43.3 31.1 25.0 24.0 23.0. IR (NEAT, NaCl plates): 3423.1 (m) 3073.9 (m) 2924.9 (s) 1642.6 (m) 1613.0 (s) 1524.2 (s) 1491.9 (s) 1439.9 (s) 1339.1 (s) 1263.8 (s) 1163.8 (s) 1124.4 (s) 1070.8 (s). HRMS (ESI$^+$) Calcd for $C_{18}H_{22}NF_3$ [M + H]: 310.1777. Found: 310.1769. HPLC (Chiralcel OD, 0.1 % IPA in Hexane, 254 nm, 1.0 mL/min) 64 % e.e.

Benzyl-[3-methyl-1-(2-methyl-allyl)-cyclohex-3-enyl]-amine (2f) Analogous preparation as above, catalyst **4** used, 25 mg, 96 μmol, 85 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.39 (d, 2H, J = 7.3 Hz, aryl C**H**) 7.20 (t, 2H, J = 7.3 Hz, aryl C**H**) 7.13 (t, 2H, J = 7.3 Hz, aryl C**H**) 5.33 (m, 1H, ArC**H**=CCH_3R) 4.95 (m, 1H, CH_3C=C**H$_a$**H$_b$) 4.81 (m, 1H, CH_3C=CH$_a$**H$_b$**) 3.63 (m, 2H, NC**H$_2$**Ph) 2.25 (d, 1H, J = 13.7 Hz, CC**H$_a$**H$_b$C(CH_3)=) 2.05 (d, 1H, J = 13.7 Hz, CCH$_a$**H$_b$**C(CH_3)=) 2.02 – 1.87 (m, 4H) 1.88 (s, 3H, C**H$_3$**) 1.61 (m, 1H) 1.57 (s, 3H, C**H$_3$**) 1.37 (m, 1H) 1.11 (t, 1H, J = 7.0 Hz,). ^{13}C

NMR (125 MHz, C_6D_6): δ 143.8 142.4 132.2 128.9 127.4 120.7 114.8 54.5 46.7 44.6 42.0 31.6 25.6 24.3 23.4. IR (NEAT, NaCl plates): 3404.7 (w) 3027.9 (m) 2923.8 (s) 1640.0 (m) 1451.4 (m) 1375.2 (m) 1114.3 (m) 1070.9 (w) 1028.7 (m). HRMS (ESI) Calcd for $C_{18}H_{25}N$ [M + H]: 256.2060. Found: 256.2056.

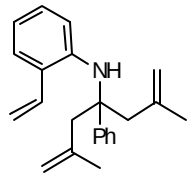
(1-Allyl-cyclohex-3-enyl)-(2-bromo-phenyl)-amine Analogous preparation as above, 50 mg, 170 μmol, 95 %. ^{1}H NMR (500 MHz, C_6D_6): δ 7.39 (dd, 1H, J = 1.2 Hz, 7.9 Hz, aryl C**H**) 6.94 (dt, 1H, J = 1.5, J = 7.8 Hz, aryl C**H**) 6.79 (dd, 1H, J = 1.5 Hz, 8.2 Hz, aryl C**H**) 6.38 (dt, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 5.76 (m, 1H, C**H**=CH) 5.59 (m, 1H, C**H$_a$**=CH$_b$) 5.43 (m, 1H, CH$_a$=C**H$_b$**) 4.98 (m, 2H, CH=C**H$_a$**H$_b$) 4.49 (br, 1H, N**H**) 2.43 (dd, 1H, J = 14.5 Hz, J = 7.3 Hz, C**H$_a$**H$_b$) 2.24 (dd, 1H, J = 14.5 Hz, J = 7.3 Hz, CH$_a$**H$_b$**) 2.15 (br d, 1H, J = 17.7 Hz, C**H$_a$**H$_b$) 2.00 – 1.70 (m, 4H, C**H$_2$**, C**H$_a$**H$_b$) 1.38 (m, 1H, C**H$_a$**H$_b$). ^{13}C NMR (125 MHz, C_6D_6): δ 134.3 133.6 129.7 127.5 118.4 116.9 114.5 55.0 42.2 37.9 31.1 23.2. IR (NEAT, NaCl): 3403.8 (m) 3072.9 (m) 2921.1 (m) 1638.9 (m) 1593.5 (s) 1513.4 (s) 1483.2 (s) 1326.2 (m) 1286.4 (m) 1131.0 (w) 1018.1 (m). HPLC (Chiralcel OD, 0.1 % IPA in Hexane, 254 nm, 1.0 mL/min) < 5 % e.e.

[3-Methyl-1-(2-methyl-allyl)-but-3-enyl]-(2-vinyl-phenyl)-amine (6a) Styrenyl imidate ester (1.62 g, 9.2 mmol) was added *via* syringe to methallyl Grignard (58 mL, 0.34 M) at -78 °C. After 1 minute, TLC of an aliquot indicated the reaction to be complete, and it was quenched by addition of 1 mL of methanol. After the mixture had warmed to room temperature, 10% HCl in water was added. The biphasic mixture was extracted three times with ether. All organic extracts were combined, washed with saturated $NaHCO_3$ solution (50 mL), then NaCl solution (50 mL), dried over $MgSO_4$ and concentrated *in vacuo* to a yellow oil. Purification by column chromatography over silica, eluting with 1 % ether in pentane afford 1.8 g of clear, bright yellow oil, 7.5 mmol, 82 % yield. ^{1}H NMR (500 MHz, C_6D_6) δ 7.32 (dd, 1H, J = 1.5 Hz, 7.3 Hz, aryl C**H**) 7.19 (m, 1H, aryl C**H**) 6.79 (dd, 1H, J = 11.0 Hz, 17.4 Hz, C**H**=CH$_2$) 6.73 (m, 1H, aryl C**H**) 5.56 (dd, 1H, J = 1.5 Hz, 17.4 Hz, CH=C**H$_a$**H$_b$) 5.17 (dd, 1H, J = 1.5 Hz, 11.0 Hz, CH=CH$_a$**H$_b$**) 4.79 (m, 2H, CH$_3$C=C**H$_a$**H$_b$) 4.75 (m, 2H, CH$_3$C=CH$_a$**H$_b$**) 3.76 (br, 1H, N**H**) 3.65 (pentet, 1H, J = 6.7 Hz, C**H**(CH$_2$R)$_2$) 2.15 (m, 4H, CH(C**H**$_2$R)$_2$) 1.56 (s, 6H, C**H**$_3$C=CH$_2$). ^{13}C NMR (125 MHz, C_6D_6) δ 145.4 143.6 134.0 129.8 128.7 125.3 117.9 116.3 113.6 111.3 49.6 43.7 22.7. IR (NEAT, NaCl plates) 3419.9 (m) 3074.2 (m) 2933.3 (m) 1647.4 (m) 1602.2 (s) 1508.9 (s) 1458.5 (s) 1374.7 (m) 1316.5 (s) 1260.1 (m) 1185.6 (m) HRMS (EI$^+$) Calcd for $C_{17}H_{23}N$: 241.1825. Found: 241.1822.

[1-Ethyl-3-methyl-1-(2-methyl-allyl)-but-3-enyl]-(2-vinyl-phenyl)-amine (6b) Analogous preparation as above, 400 mg, 1.6 mmol, 15 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.31 (dd, 1H, J = 7.6 Hz, J = 1.5 Hz, aryl C**H**) 7.13 (t, 1H, J = 8.2 Hz, aryl C**H**) 6.88 (d, 1H, J = 8.2 Hz, aryl C**H**) 6.73 (m, 2H, aryl C**H** & C**H**=CH$_2$) 5.50 (dd, 1H, J = 1.8 Hz, J = 17.4 Hz, CH=C**H$_a$**H$_b$) 5.12 (dd, 1H, J = 1.5 Hz, J = 11.0 Hz, CH=CH$_a$**H$_b$**) 4.89 (m, 2H, C=C**H$_a$**H$_b$) 4.79 (m, 2H, C=CH$_a$**H$_b$**) 3.90 (br s, 1H, N**H**) 2.50 (d, 2H, J = 14.4 Hz, C**H$_a$**H$_b$) 2.28 (d, 2H, J = 14.4 Hz, CH$_a$**H$_b$**) 1.68 (s, 6H, C**H$_3$**) 1.64 (q, 2H, J =

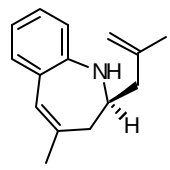
7.5 Hz, C**H**$_2$CH$_3$) 0.80 (t, 3H, J = 7.5 Hz, CH$_2$C**H**$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 143.2 134.5 129.3 129.0 117.5 116.9 115.9 114.2 43.9 30.8 25.1 9.2. IR (NEAT, NaCl plates): 3415.5 (m) 3072.7 (m) 2967.8 (s) 1639.6 (m) 1602.5 (s) 1514,3 (s) 1460.8 (s) 1373.67 (m) 1317.1 (s) 1282.7 (m) 1162.0 (m) 1027.0 (w). HRMS (ESI$^-$) Calcd for $C_{19}H_{27}N$ [M + Na]: 292.2036. Found: 292.2032.

[3-Methyl-1-(2-methyl-allyl)-1-phenyl-but-3-enyl]-(2-vinyl-phenyl)-amine (6c)

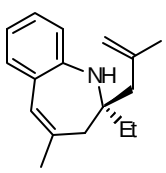


Prepared as above, 150 mg, 0.46 mmol, 11 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.33 (dd, 1H, J = 1.5 Hz, 7.3 Hz, aryl C**H**) 7.27 (m, 2H, aryl C**H**) 7.07 (m, 3H, aryl C**H**) 6.95 (dd, 1H, J = 17.4 Hz, J = 10.7 Hz, C**H**=CH$_2$) 6.81 (dt, 1H, J = 1.5 Hz, J = 7.8 Hz, aryl C**H**) 6.64 (d, 1H, J = 8.3 Hz, aryl C**H**) 6.34 (d, 1H, J = 8.3 Hz, aryl C**H**) 5.62 (dd, 1H, J = 1.7 Hz, 17.4 Hz, CH=C**H$_a$**H$_b$) 5.25 (dd, 1H, J = 1.7 Hz, 10.7 Hz, CH=CH$_a$**H$_b$**) 4.89 (m, 2H, C=C**H$_a$**H$_b$) 4.78 (m, 2H, C=CH$_a$**H$_b$**) 4.65 (s, 1H, N**H**) 2.82 (d, 2H, J = 13.4 Hz, C**H$_a$**H$_b$) 2.73 (d, 2H, J = 13.4 Hz, CH$_a$**H$_b$**) 1.36 (s, 6H, C**H$_3$**). ^{13}C NMR (125 MHz, C_6D_6): δ 144.8 143.7 143.1 134.4 128.8 127.9 125.9 117.6 116.9 116.7 116.1 61.1 47.7 24.8. IR (NEAT, NaCl plates): 3419.0 (m) 3069.9 (m) 2964.4 (s) 2279.8 (s) 1638.8 (m) 1602.3 (s) 1577.9 (m) 1511.2 (s) 1446.9 (s) 1374.5 (w) 1261.0 (s) 1185.9 (w) 1076.0 (s) 1025.3 (s). HRMS (ESI$^+$) Calcd for $C_{23}H_{27}N$ [M+H]: 318.2216. Found: 318.2217.

4-Methyl-2-(2-methyl-allyl)-2,3-1*H*-benzo[*b*]azepine (7a) [3-Methyl-1-(2-methyl-allyl)-but-3-enyl]-(2-vinyl-phenyl)-amine **6a** (300 mg, 1.2 mmol) and catalyst **5** [(*R*)iPr$_2$TRIP] (72 mg, 62 μmol) were dissolved in benzene (15 mL) and heated to 55 ºC under N_2 atmosphere for 5 hours. The reaction was cooled, then stirred over charcoal and filtered through celite and washed with ether. Solvents were removed *in vacuo* to afford a brown solid. This product was purified by column chromatography, eluting with 1% ether in pentane to afford 215 mg white solid. (240 μmol, 80 % yield) ^{1}H NMR (500 MHz, C_6D_6) δ 7.12 (dd, 1H, J = 1.2 Hz, 7.6 Hz, aryl C**H**) 6.93 (dt, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 6.80 (dt, 1H, J = 1.2 Hz, 7.3 Hz, aryl C**H**) 6.47 (d, 1H, J = 7.6 Hz, aryl C**H**) 6.27 (s, 1H, ArC**H**=CCH$_3$) 4.80 (s, 1H, CH$_3$C=C**H$_a$**H$_b$) 4.70 (s, 1H, CH$_3$C=CH$_a$**H$_b$**) 3.92 (br, 1H, N**H**) 3.18 (m, 1H, NHC**H**) 2.31 (dd, 1H, J = 9.2 Hz, 17.4 Hz, CH(C**H$_a$**H$_b$R)(CH$_2$R')) 1.98 (m, 3H, CH(CH$_a$**H$_b$**R)(C**H$_2$**R')) 1.78 (s, 3H, CH$_3$) 1.43 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, C_6D_6) δ 148.4 143.4 136.1 133.3 128.7 127.5 127.3 125.3 120.1 118.0 114.3 51.145.7 45.1 27.7 22.0. IR (KBr pellet): 3368.3 (s) 3055.2 (m) 2881.2 (m) 1646.4 (m) 1600.5 (s) 1580.1 (m) 1490.9 (s) 1442.2 (s) 1283.2 (s) 1199.26 (m) 1050.1 (m). HRMS (EI$^+$) Calcd for $C_{17}H_{23}N$ [M+H]: 242.1903. Found: 242.1906. (Chiralcel OJ, 0.1 % iPrOH in hexane, 1.0 mL/min, 254 nm) 93% e.e. $[\alpha]^D$ = - 22.5 ± 0.1 º(c = 1.0, $CHCl_3$).

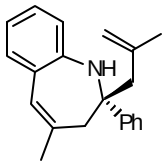


2-Ethyl-4-methyl-2-(2-methyl-allyl)- 2,3-dihydro-1*H*-benzo[*b*]azepine (7b) Analogous preparation as above, 9.3 mg catalyst **4** (9.3 μmol) and 50 mg **6b** (186 μmol) used; 32 mg isolated, 132 μmol, 71 % yield. ^{1}H NMR (500 MHz, C_6D_6) δ 7.07 (dd, 1H, J = 1.4 Hz, 7.6 Hz, aryl C**H**) 6.97 (dt, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 6.77 (dt, 1H, J = 1.2 Hz, 7.4 Hz, aryl C**H**) 6.34 (dd, 1H, J = 0.6 Hz, 8.1 Hz, aryl C**H**) 6.30 (s, 1H, ArC**H**=CR$_2$) 4.88 (m, 1H,



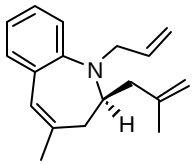
C=C**H$_a$**H$_b$) 4.73 4.74 (m, 1H, C=CH$_a$**H$_b$**) 3.81 (s, 1H, N**H**) 2.22 (m, 3H, C**H$_2$** & C**H$_a$**H$_b$) 2.04 (d, 1H, J = 13.6 Hz, C**H$_a$**H$_b$) 1.81 (s, 3H, C**H$_3$**) 1.64 (s, 3H, C**H$_3$**) 1.44 (m, 2H, C**H$_2$**CH$_3$) 0.72 (t, 3H, J = 7.5 Hz, CH$_2$C**H$_3$**). ^{13}C NMR (125 MHz, C_6D_6) δ 145.5 143.1 133.9 133.1 127.9 127.7 124.4 119.3 118.9 116.0 100.5 56.5 46.2 45.9 31.9 28.4 25.2. IR (NEAT, NaCl plate): 3378.8 (m) 3071.2 (m) 2966.7 (s) 1639.9 (m) 1601.9 (s) 1484.8 (s) 1447.5 (m) 1323.5 (m) 1275.6 (m) 1160.1 (w) 1059.9 (w). HRMS (EI$^+$) Calcd for $C_{17}H_{23}N$ [M=H]: 242.1903. Found: 242.1906. (Chiralcel OJ, 1 % iPrOH in hexane, 1.0 mL/min, 254 nm) 24 % e.e.

4-Methyl-2-(2-methyl-allyl)-2-phenyl-2,3-dihydro-1*H*-benzo[*b*]azepine (7c)



Analogous preparation as above, 10 mg catalyst **4** (10 μmol) and 60 mg **6c** (189 μmol) used; 55 mg isolated, 189 μmol, 99 % yield.^{1}H NMR (500 MHz, C_6D_6) δ 7.18 (m, 2H, aryl C**H**) 7.02 (m, 3H, aryl C**H**) 6.96 (m, 2H, aryl C**H**) 7.74 (dt, 1H, J = 1.2 Hz, 7.4 Hz, aryl C**H**) 6.66 (dd, 1H, J = 0.6 Hz, 8.1 Hz, aryl C**H**) 6.08 (s, 1H, ArC**H**=CR$_2$) 4.84 (m, 1H, C=C**H$_a$**H$_b$) 4.80 (s, 1H, N**H**) 4.74 (m, 1H, C=CH$_a$**H$_b$**) 2.54 (s, 2H, C**H$_2$**) 2.41 (d, 2H, J = 5.5 Hz, C**H$_2$**) 1.57 (s, 3H, C**H$_3$**) 1.11 (s, 3H, C**H$_3$**). ^{13}C NMR (125 MHz, C_6D_6) δ 146.2 145.6 143.2 134.3 132.9 128.7 127.9 127.1 126.7 123.9 118.7 118.4 116.8 100.5 63.5 53.9 47.9 27.8 24.2. IR (NEAT, NaCl plate): 3392.2 (m) 3057.1 (m) 2916.9 (m) 1639.2 (m) 1601.2 (s) 1486.7 (s) 1444.9 (s) 1374.6 (m) 1278.1 (m) 1186.0 (w) 1030.6 (w). HRMS (EI$^+$) Calcd for $C_{21}H_{23}N$ [M+H]: 290.1903. Found: 290.1905. (Chiralcel OJ, 1 % iPrOH in hexane, 1.0 mL/min, 254 nm) 80 % e.e.

1-Allyl-4-methyl-2-(2-methyl-allyl)-2,3-dihydro-1*H*-benzo[*b*]azepine Benzyl



potassium (80 mg, 610 μmol) was added to a solution of 4-Methyl-2-(2-methyl-allyl)-2,3-1*H*-benzo[*b*]azepine, **7a**, (100 mg, 470 μmol) in THF (7 mL) at –35 ºC. After warming to room temperature for 35 minutes, allyl bromide (74 mg, 610 μmol) was added to the solution. The reaction was stirred another 2 hours, then quenched on water (2 mL) and 10% HCl (1 mL). The mixture was extracted three times with ether (50 mL). All organic extracts were combined, washed with $NaHCO_3$, NaCl, then dried ($MgSO_4$) and concentrated *in vacuo*. The product was purified by column chromatography, eluting with 1% ether in pentane to obtain 65 mg of clear, colorless oil. (260 μmol, 55%) ^{1}H NMR (500 MHz, C_6D_6) δ 7.14 (dd, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 7.08 (dt, 1H, J = 1.8 Hz, 7.6 Hz, aryl C**H**) 6.87 (dt, 1H, J = 1.2 Hz, 7.3 Hz, aryl C**H**) 6.83 (d, 1H, J = 8.2 Hz, aryl C**H**) 6.37 (s, 1H, ArC**H**=CCH$_3$) 5.81 (m, 1H, CH$_2$C**H**=CH$_2$) 5.13 (m, 1H, CH$_2$CH=C**H$_a$**H$_b$) 5.02 (m, 1H, CH$_2$CH=CH$_a$**H$_b$**) 4.72 (m, 1H, CH$_3$C=C**H$_a$**H$_b$) 4.59 (m, 1H, CH$_3$C=CH$_a$**H$_b$**) 3.64 (m, 2H, NC**H$_2$**CH=CH$_2$) 3.49 (m, 1H, NC**H**) 2.27 (dd, 1H, J = 1.5 Hz, 17.4 Hz, CH(C**H$_a$**H$_b$R)(CH$_2$R')) 2.17 (dd, 1H, J = 3.5 Hz, 17.4 Hz, NCH(CH$_a$**H$_b$**R)(CH$_2$R')) 2.08 (m, 2H, NCH(CH$_2$R)(C**H$_2$**R')) 1.86 (s, 3H, CH$_3$) 1.56 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, C_6D_6) δ 147.9 143.9 137.1 134.9 133.1 129.2 128.7 127.5 120.4 120.3 117.0 113.5 58.3 54.2 40.1 40.0 28.0 22.8. IR (NEAT, NaCl plates): 3071.4 (m) 2965.7 (m) 1643.5 (m) 1595.3 (m) 1495.1 (s) 1439.1 (m) 1373.9 (m) 1232.3 (m) 1168.2 (m). HRMS (EI$^+$) Calcd for $C_{18}H_{23}N$: 253.1825. Found: 253.1821. [?]^D = -0.6 ± 0.1 º(c = 0.3, $CHCl_3$).

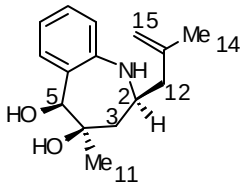
6,9-Dimethyl-7,7a,8,11-tetrahydro-11a-aza-dibenzo[*a,c*]cycloheptene (8) Schrock catalyst, **9**, (10 mg, 13 μmol) was added to a solution of 1-allyl-4-methyl-2-(2-methyl-allyl)-2,3-dihydro-1*H*-benzo[*b*]azepine (65 mg, 256 μmol) in benzene-d_6. After ten minutes, ^{1}H NMR indicated the reaction was complete. The solution was stirred over charcoal, filtered through celite and concentrated *in vacuo*. The product was purified by column chromatography eluting with 1 % ether in pentane to afford a white solid, 40 mg. (177 μmol, 69%) ^{1}H NMR (500 MHz, C_6D_6) δ 7.11 (m, 2H, aryl C**H**) 6.95 (m, 2H, aryl C**H**) 6.37 (s, 1H, ArC**H**=C) 5.24 (m, 1H, $NCH_2C\mathbf{H}=CCH_3$) 3.68 (m, 1H, $NC\mathbf{H_a}H_bCH$) 3.49 (m, 1H $C\mathbf{H}(CH_2R)(CH_2R')$) 3.36 (m, 1H, $NCH_a\mathbf{H_b}CH$) 2.21 (m, 2H, $CH(C\mathbf{H_2}R)(CH_2R')$) 1.82 (s, 3H, $C\mathbf{H_3}$) 1.81 (m, 2H, $CH(CH_2R)(C\mathbf{H_2}R')$) 1.59 (s, 3H, $C\mathbf{H_3}$). ^{13}C NMR (125 MHz, C_6D_6) δ 150.0 138.8 133.2 133.1 130.6 128.7 127.6 127.4 121.4 120.9 120.0 65.6 50.4 38.1 37.3 26.9 23.5. IR (NEAT, NaCl plates): 3060.6 (m) 2925.8 (s) 1593.4 (s) 1487.4 (s) 1442.4 (s) 1386.3 (m) 1257.0 (m) 1225.4 (s) 1178.9 (m) 1049.4 (m). HRMS (EI^+) Calcd for $C_{16}H_{19}N$: 225.1512. Found: 225.1513. HPLC (Chiralcel OJ, 100% hexane, 0 ºC, 1.0 mL/min, 254 nm) >90% e.e. (No baseline.) $[\alpha]^D$ = +6.5 ± 0.1 º(c = 1.0, $CHCl_3$).

[1,1-Bis-(2-methyl-allyl)-pent-4-enyl]-(2-vinyl-phenyl)-amine (10) Prepared analogously to **1a**, 0.64 g, 2.2 mmol, 22 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.30 (dd, 1H, J = 1.5 Hz, 7.3 Hz, aryl C**H**) 7.11 (dt, 1H, J = 1.8 Hz, 7.8 Hz, aryl C**H**) 6.88 (d, 1H, J = 8.2 Hz, aryl C**H**) 6.72 (m, 2H, aryl C**H** + ArC**H**=CH_2) 5.73 (m, 1H, $CH_2CH_2C\mathbf{H}=CH_2$) 5.49 (dd, 1H, J = 1.8 Hz, 17.1 Hz, ArCH=C$\mathbf{H_a}H_b$) 5.14 (dd, 1H, J = 1.8 Hz, 10.6 Hz, ArCH=$CH_a\mathbf{H_b}$) 5.01 (dd, 1H, J = 1.8 Hz, 17.1 Hz, $CH_2CH_2CH=C\mathbf{H_a}H_b$) 4.95 (dd, 1H, J = 1.2 Hz, 10.6 Hz, $CH_2CH_2CH=CH_a\mathbf{H_b}$) 4.89 (m, 2H, $CH_3C=C\mathbf{H_a}H_b$) 4.78 (m, 2H, $CH_3C=CH_a\mathbf{H_b}$) 3.94 (s, 1H, N**H**) 2.47 (d, 2H, J = 14.0 Hz, $C(C\mathbf{H_a}H_bR)_2$) 2.29 (d, 2H, J = 14.0 Hz, $C(CH_a\mathbf{H_b}R)_2$) 2.07 (m, 2H, $C\mathbf{H_2}$) 1.79 (m, 2H, $C\mathbf{H_2}$) 1.68 (s, 6H, $C\mathbf{H_3}$). ^{13}C NMR (125 MHz, C_6D_6): δ 144.4 143.0 138.9 134.5 129.4 129.1 126.4 117.6 117.0 116.1 115.0 114.0 58.9 44.7 37.7 29.2 25.1. IR (NEAT, NaCl plates): 3414.8 (m) 3074.0 (m) 29.46.0 (s) 1640.2 (s) 1602.4 (s) 1578.9 (s) 1513.9 (s) 1454.1 (s) 1373.8 (m) 1317.5 (s) 1260.0 (m) 1163.4 (m) 1058.8 (m). HRMS (ESI) Calcd for $C_{21}H_{29}N$ [M + H]: 296.2373. Found: 296.2381.

8,4'-Dimethyl-5,7-dihydrospiro[6H-benzo-5-aza-cycloheptene-6,1'-cyclohex-3'-ene] (12) Catalyst **3** [(*R*)Pr_2Bnz_2Bitet] (20 mg, 20 μmol) was added to a solution of **10** (110 mg, 370 μmol) in benzene (5 mL), and the resultant mixture placed in a Schlenk flask. The reaction was monitored by ^{1}H NMR analysis. After 1 hour, the ratio of (**10** : **11** : **12**) was (0 : 4 : 1); after 6 hours, only **12** was observable. The mixture was exposed to air, stirred over charcoal, filtered through celite and silica (eluting with ether in pentane) and concentrated *in vacuo* to 98 mg, 360 μmol, quantitiative yield. ^{1}H NMR (500 MHz, C_6D_6): δ 7.08 (dd, 1H, J = 1.5 Hz, 7.3 Hz, aryl C**H**) 6.94 (dt, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 6.79 (dt, 1H, J = 1.2 Hz, 7.3 Hz, aryl C**H**) 6.35 (dd, 1H, J = 1.2 Hz, 7.9 Hz, aryl C**H**) 6.32 (m, 1H, ArC**H**=CCH_3) 5.35 (m, 1H, $CH_2C\mathbf{H}=CCH_3$) 3.85 (s, 1H, N**H**) 2.43 (d, 1H, J = 17.1 Hz, C$\mathbf{H_a}H_b$) 2.04 (d, 1H, J = 17.1 Hz, $CH_a\mathbf{H_b}$) 1.88 – 1.71 (m, 5H, $C\mathbf{H_2}$) 1.81 (s,

3H, C**H**$_3$) 1.52 (s, 3H, C**H**$_3$) 1.24 (m, 1H, C**H**). ^{13}C NMR (125 MHz, C_6D_6): δ 145.7 134.0 132.9 131.4 128.7 127.6 127.4 125.3 121.9 119.6 119.5 52.2 49.0 43.9 30.4 28.4 24.1 23.0. IR (NEAT, NaCl plates): 3368.9 (m) 3051.2 (m) 2911.4 (s) 1601.3 (s) 1482.1 (s) 1446.6 (s) 1376.3 (m) 1278.0 (s) 1159.5 (m) 1082.5 (m) 1016.4 (m). HRMS (ESI) Calcd for $C_{17}H_{21}N$ [M + H]: 240.1747. Found: 240.1756. HPLC: (Chiralcel OJ, 1.0% Isopropanol in Hexane, 1.0 mL/min, 254 nm) 79% e.e.

4,5-Dihydroxy-4-methyl-2-(2-methyl-allyl)-2,3-1*H*-benzo[*b*]azepine



Solid **7a** (75 mg, 0.35 mmol) was added to a biphasic mixture of AD-mix-α (500 mg, 0.35 mmol) and methanesulfonamide (31 mg, 0.35 mmol) in *t*-butanol/water (2.5 mL each) at 0 °C. The mixture was vigorously stirred for 18 hours, then quenched by the addition of sodium sulfite and dichloromethane. The mixture was extracted three times with dichloromethane (20 mL) dried over $MgSO_4$ and concentrated in vacuo to a brown oil. The crude material was purified *via* preparative thin layer chromatography on silica gel, eluting with 40 % ethyl acetate in pentane. The clean material (10 mg, 39 μmol, 11 % yield) was removed at R_f ~ 0.6. ^{1}H NMR (500 MHz, C_6D_6): ? 7.09 (dd, 1H, J = 1.5 Hz, 7.3 Hz, aryl C**H**) 6.98 (dt, 1H, J = 1.5 Hz, 7.6 Hz, aryl C**H**) 6.81 (dt, 1H, J = 1.2 Hz, 7.5 Hz, aryl C**H**) 6.40 (dd, 1H, J = 1.2 Hz, 7.6 Hz, aryl C**H**) 4.79 (s, 1H, **H15**) 4.67 (s, 1H, **H15**) 4.38 (s, 1H, **H5**) 4.17 (br, 1H, O**H**) 3.43 (m, 1H, **H2**) 3.26 (s, 1H, N**H**) 1.76 (m, 2H, **H12**) 1.55 (dd, 1H, J = 2.7 Hz, 14.3 Hz, **H3-*cis***) 1.44 (s, 3H, **H14**) 1.35 (dd, 1H, J = 11.6 Hz, 14.3 Hz, **H3-*trans***) 1.23 (s, 3H, **H11**). ^{13}C NMR (125 MHz, C_6D_6): ? 143.3 131.1 130.4 121.7 (**C13**) 121.1 114.9 (**C15**) 81.3 (**C5**) 71.6 (**C4**) 48.6 (**C2**) 46.7 (**C12**) 46.6 (**C3**) 28.2 (**C11**) 21.9 (**C14**). (Assignments based on combination of HSQC, HMBC and nOe which follow.) IR (neat, NaCl plates): 3584.5 3397.5 3071/7 2963.9 2917.5 2849.1 1717.6 1646.4 1605.0 1374.4 1260.5. Nuclear Overhauser Effect (nOe) spectra are on the following pages. The absolute stereochemistry of the dihydroxylation is based on precendent;[4,5] assignment of stereochemistry at C2 based on nOe. There no significant nOe increase for H-2 when Me-11 is irradiated. However, based on the nOe arising from irradiation of Me-11 we assigned 1.55 ppm H-3 *cis* to Me-11. When H-3_{cis} is irradiated, H-2 experiences a significant nOe, whereas little to no increase is observed for irradiation of 1.22 ppm, H-3_{trans}. Based on these results, we assign the absolute stereochemistry at C-2 as (*S*).

(1) Cooper, M. K.; Yaniuk, D. W. *J. Organomet. Chem.* **1981**, *2*, 231.

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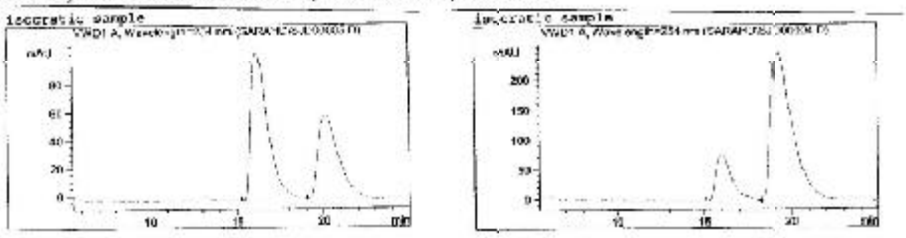
(3) Shirakawa, E.; Yamasaki, K.; Hiyama, T. *Synthesis* **1998**, *10*, 1544.

(4) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.

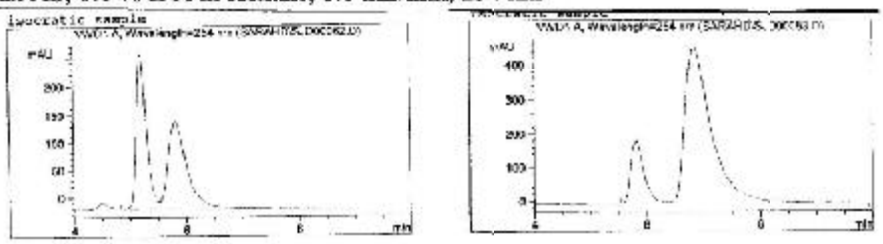
(5) Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. *J. Org. Chem.* **1992**, *57*, 2768.

HPLC traces:

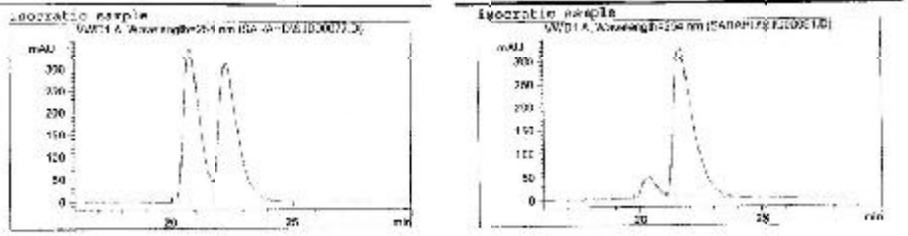
2a: Chiralpak AS, 0.1 % IPA in Hexane, 1.0 mL/min, 254 nm



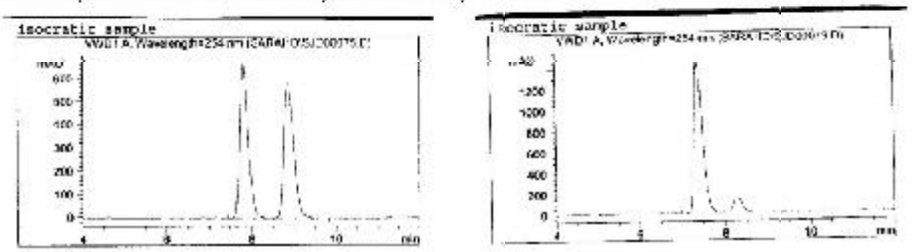
2b: Chiralpak AS, 0.1 % IPA in Hexane, 1.0 mL/min, 254 nm



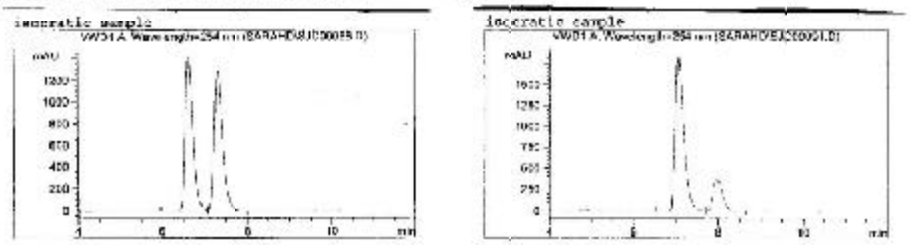
2c: Chiralcel OD, 0 % IPA in Hexane, 1.0 mL/min, 254 nm



2d: Chiralcel OD, 0.1 % IPA in Hexane, 1.0 mL/min, 254 nm

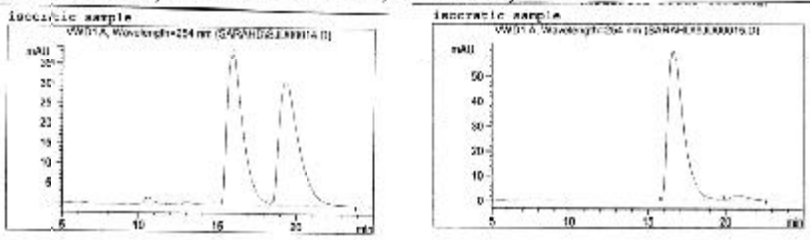


2e: Chiralcel OD, 0.1 % IPA in Hexane, 1.0 mL/min, 254 nm

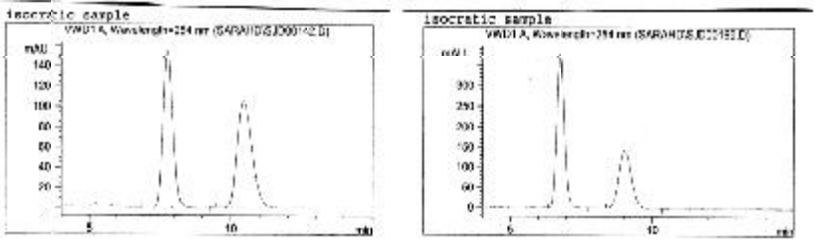


HPLC traces:

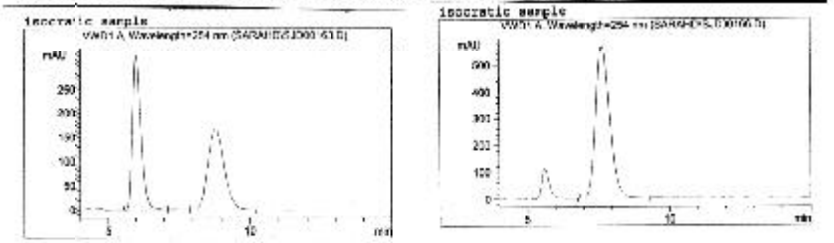
7a: Chiralcel OJ, 0.1 % IPA in Hexane, 1.0 mL/min, 254 nm



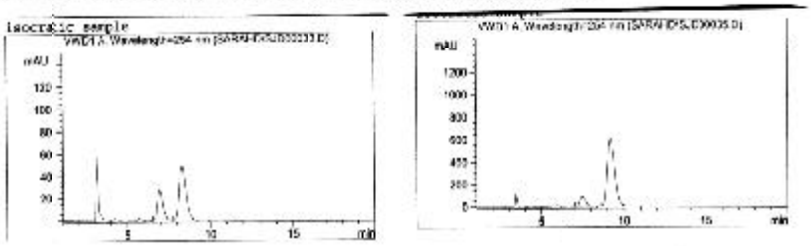
7b: Chiralcel OJ, 1.0 % IPA in Hexane, 1.0 mL/min, 254 nm



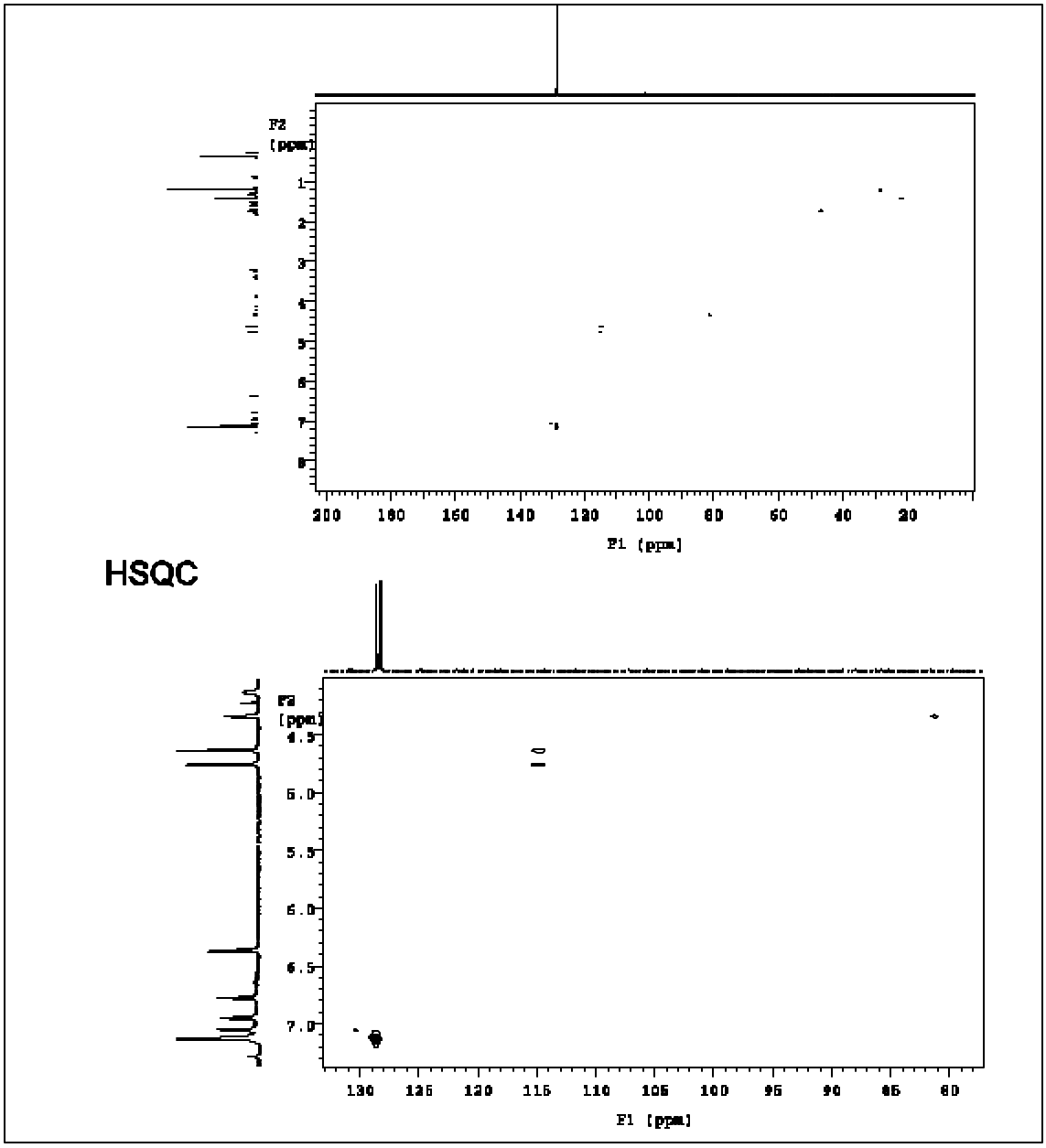
7c: Chiralcel OJ, 1.0 % IPA in Hexane, 1.0 mL/min, 254 nm

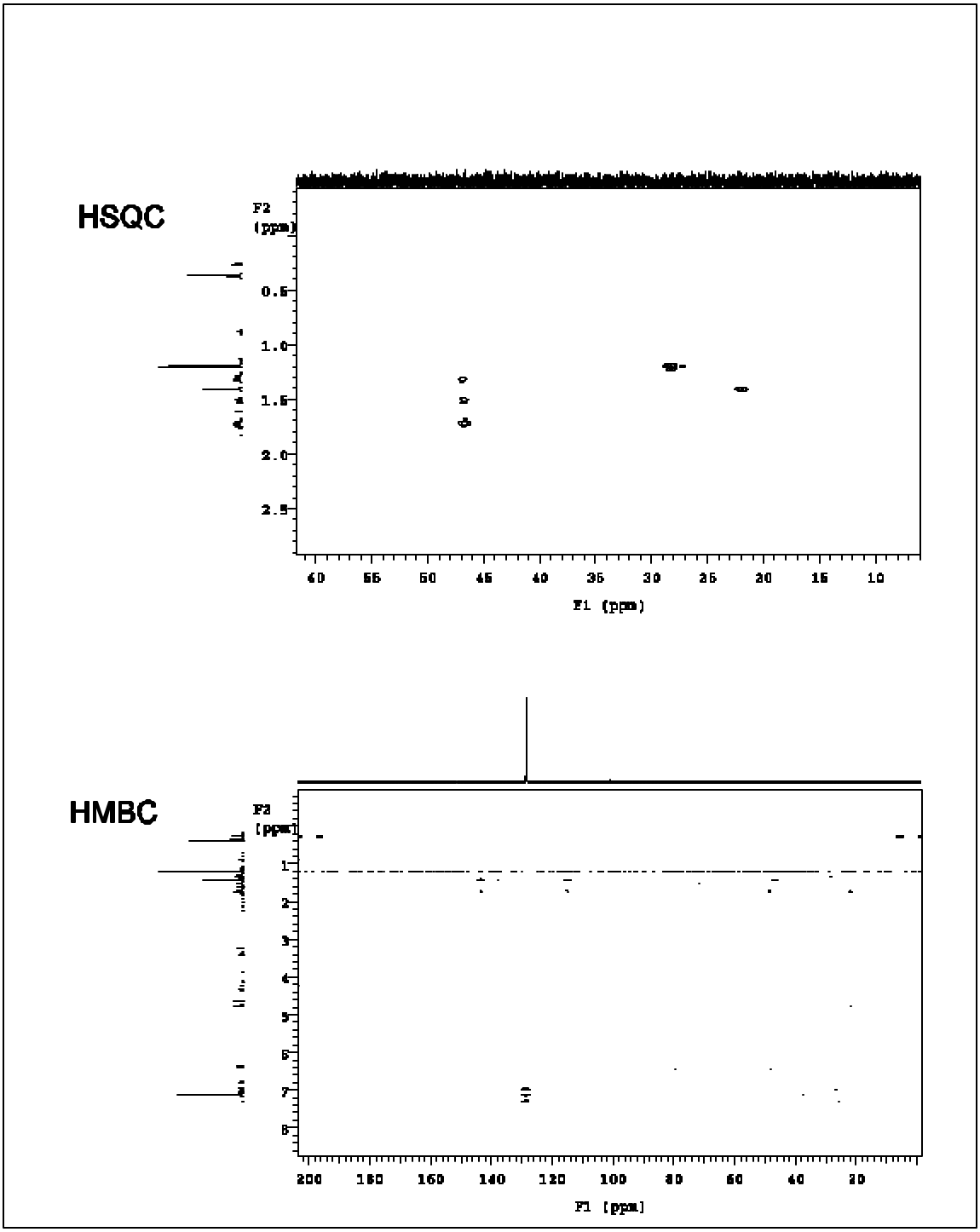


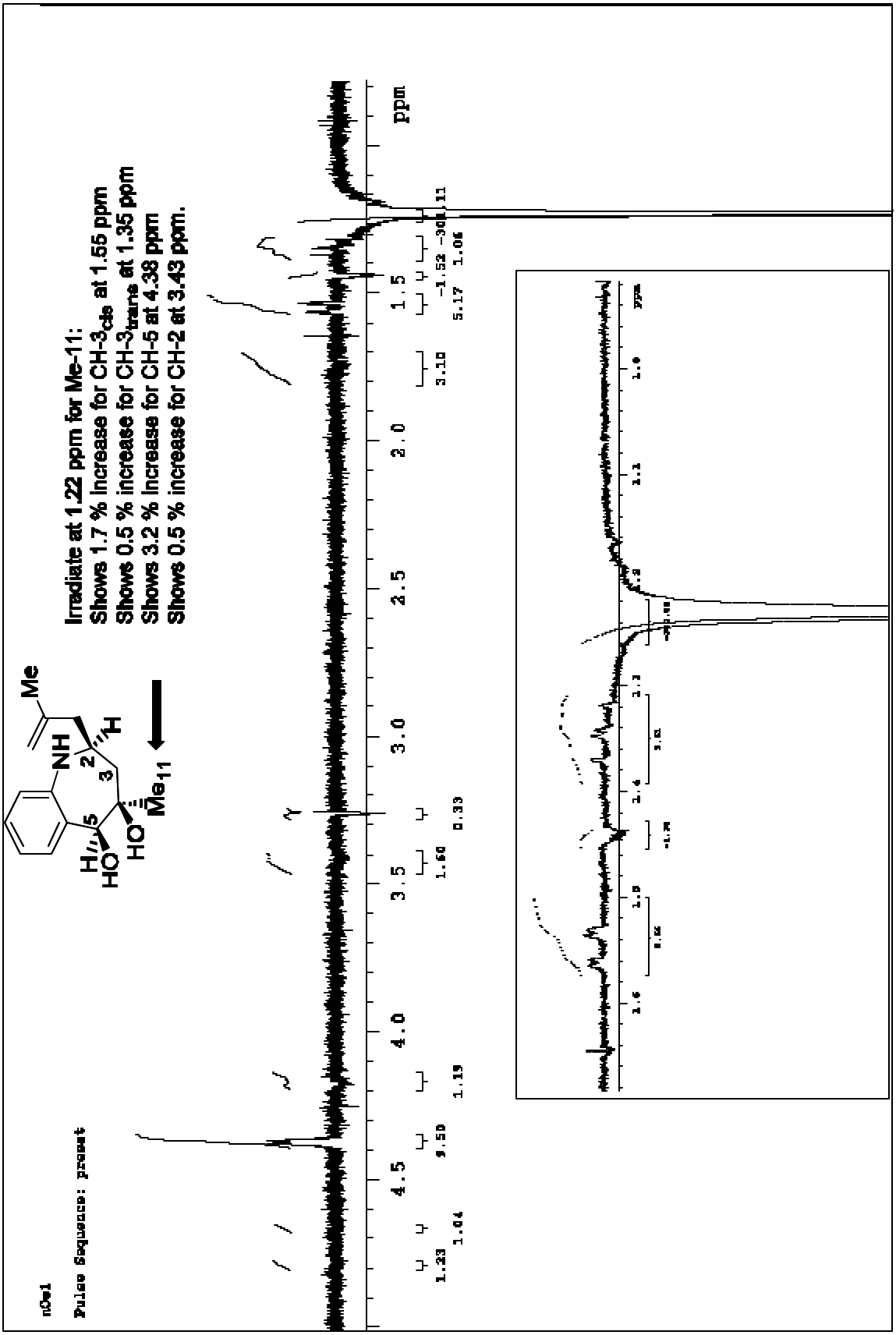
12: Chiralcel OJ, 1.0 % IPA in Hexane, 1.0 mL/min, 254 nm

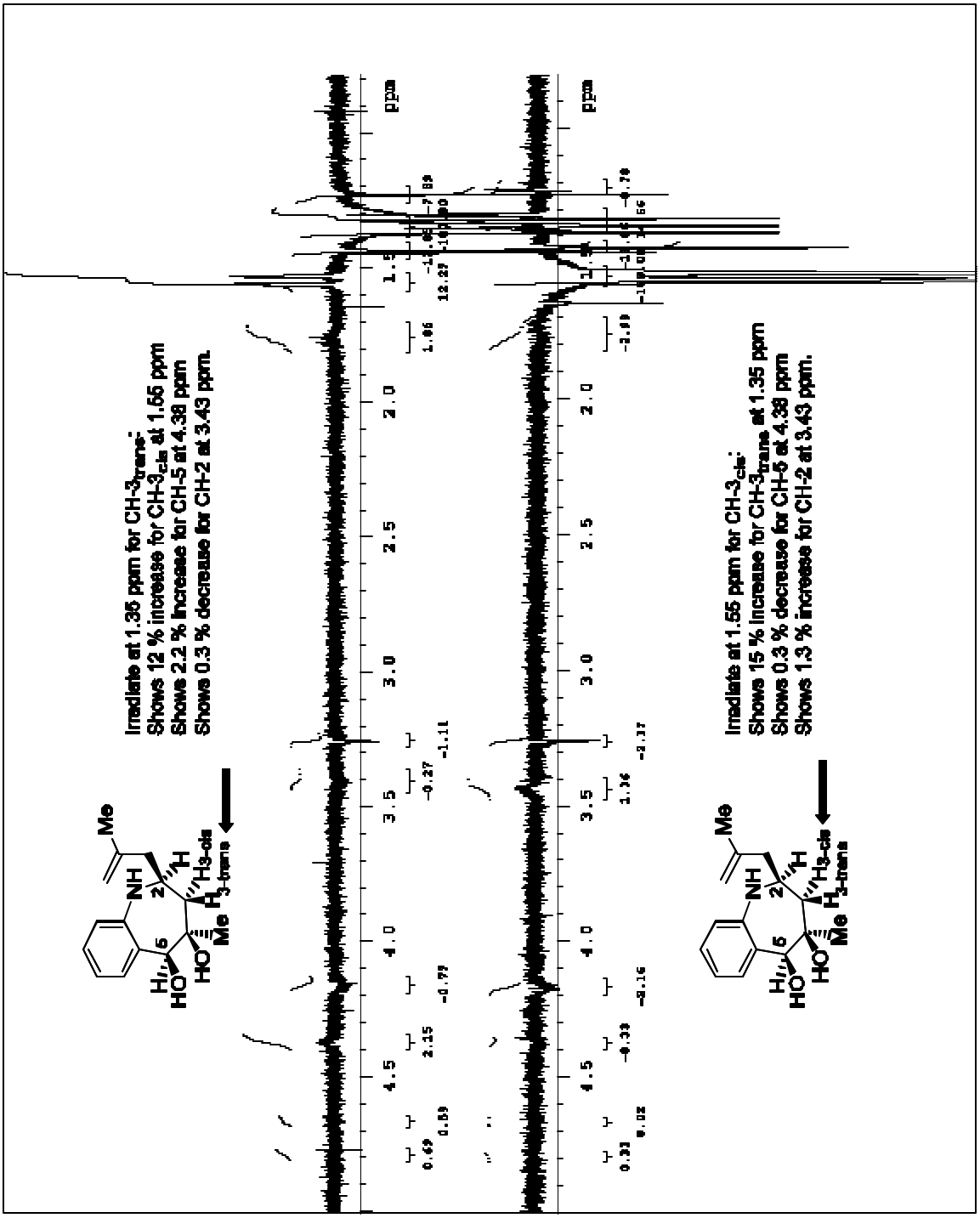


HSQC of 4,5-Dihydroxy-4-methyl-2-(2-methyl-allyl)-2,3-1*H*-benzo[*b*]azepine




HSQC
F2 (ppm)
0.5
1.0
1.5
2.0
2.5
60
55
50
45
40
35
30
25
20
15
10
F1 (ppm)
HMBC
F2 (ppm)
1
2
3
4
5
6
7
8
200
180
160
140
120
100
80
60
40
20
F1 (ppm)


Irradiate at 1.22 ppm for Me-11:
Shows 1.7 % increase for CH-3cis at 1.55 ppm
Shows 0.5 % increase for CH-3trans at 1.35 ppm
Shows 3.2 % increase for CH-5 at 4.38 ppm
Shows 0.5 % increase for CH-2 at 3.43 ppm.
Me
NH
H
HO
HO
Me11
ppm


Irradiate at 1.35 ppm for CH-3trans:
Shows 12 % increase for CH-3cis at 1.55 ppm
Shows 2.2 % increase for CH-5 at 4.38 ppm
Shows 0.3 % decrease for CH-2 at 3.43 ppm.
Irradiate at 1.55 ppm for CH-3cis:
Shows 15 % increase for CH-3trans at 1.35 ppm
Shows 0.3 % decrease for CH-5 at 4.38 ppm
Shows 1.3 % increase for CH-2 at 3.43 ppm.
ppm
ppm