

Experimental Section

General Methods: NMR spectra were recorded using Varian Unity Plus 500 MHz, Bruker AMX-400 MHz, and GE QE Plus 300MHz spectrometers and chemical shift values are reported in parts per million (ppm) downfield from tetramethylsilane. The infrared spectra were recorded using a Perkin Elmer Spectrum 1000 FT-IR spectrometer. The mass spectral data were obtained using a Finnigan SSQ700 DCI/MS and a Finnigan SSQ7000 APCI/MS and ESI/MS. All reactions were run under an atmosphere of N₂. All reagents and solvents were used as purchased from commercial suppliers. All reactions were monitored by TLC (250µm Merck Silica Gel 60 F₂₅₄) and HPLC (Hewlett-Packard 1100 series, Zorbax SB C8 4.6 mm x 7.5 mm column, Flow rate 1.5 mL/min., UV detection, gradient elution 0.1v/v% H₃PO₄ in H₂O:CH₃CN). Elemental analysis and optical rotations were performed by Robertson Microlit Laboratories, Inc., 29 Samson Avenue, PO Box 927, Madison, NJ 07940.

3S,4S)-4-[(*tert*-Butyloxycarbonyl)-amino]-6-methyl-1-hepten-3-ol (7) To a solution of *N*-Boc-L-leucinol, **5**, (2.00 Kg, 9.126 moles) and 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical (14.5 g, 92.7 mmol) in CH₂Cl₂ (36.6 Kg) and H₂O (5.54 Kg) at 0 °C was added 7% NaHCO₃ solution (28.9 Kg) and 12.6% NaOCl solution (6.62 Kg) over 2 h with vigorous stirring. The biphasic mixture was stirred for 20 min. then the layers were separated. The organic layer was washed sequentially with 10% NaHSO₄ solution (25.7 Kg) containing NaI (151 g), 10% Na₂S₂O₃ (28.7 Kg), 7% NaHCO₃ (28.5 Kg) and brine (21.7 Kg). The organic layer was dried over Na₂SO₄, filtered, and concentrated to 3.80 Kg of **6** in CH₂Cl₂ (a small portion was concentrated to dryness for characterization [α]_D²⁵ -32.4 (c 1.0, MeOH); IR (neat) 3346, 2955, 1731, 1713, 1694, 1515, 1363, 1249, 1166, 1054, 1017cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 9.43 (s, 1H), 7.22 (d, *J*=7.8 Hz, 1H), 3.86 (ddd, *J*=11.0, *J*=7.8, *J*=4.7 Hz, 1H), 1.65 (sept., *J*=6.8 Hz, 1H), 1.34-1.48 (m, 2H), 1.39 (s, 9H), 0.89 (d, *J*=6.8 Hz, 3H), 0.86 (d, *J*=6.8 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 202.0, 155.7, 78.2, 57.8, 36.5, 28.1, 24.0, 22.9, 21.3; Analytical calcd for C₁₁H₂₁NO₃: C, 61.37; H, 9.83; N, 6.51 Found: C, 61.16; H, 9.77; N, 6.43. The ee of **6** was determined see below in supplementary addendum.

To a solution of vinyl magnesium chloride in THF (17.5 wt%, 13.8 Kg, 27.9 moles) was added CH₂Cl₂ (18.8 Kg). The resulting solution was cooled to 10 °C and treated with *N*-Boc-L-leucinol **6** / CH₂Cl₂ (3.80 Kg) while maintaining an internal temperature < 30°C. The reaction was stirred for 25 min. then poured into a stirring solution of 15% NH₄Cl (51.9 Kg) and diluted with MTBE (25.6 Kg). Layers were separated and the organic layer washed with brine (26.9 Kg). The organic layer was concentrated to approximately 6 liters, whereupon heptane 20 Kg was added and concentrated to 3.65 kg, cooled to -20 °C (overnight), filtered and washed with cold heptane (1.2 Kg) to afford 1.48 Kg of off-white solid as a mixture of **7** (1.28 Kg 58 % overall) and the undesired isomer **13** (0.20 Kg, 9.0%). **(3S,4S)-4-[(*tert*-Butyloxycarbonyl)-amino]-6-methyl-1-hepten-3-ol (7)**. TLC: 2:1 heptane:EtOAc; R_f=0.42; [α]_D²⁵ -0.27.3 (c 1.01, MeOH); IR (neat) 3383, 2955, 2868, 1688, 1506, 1367, 1169, 919 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 5.89 (ddd, *J*=17.3, 10.7, 5.9 Hz, 1H), 5.29 (ddd, *J*=17.3, 1.5, 1.5 Hz, 1 H), 5.18 (ddd, *J*=10.7, 1.5, 1.5 Hz, 1H), 4.68 (br d, 1H), 4.06 (br s, 1H), 3.66 (br m, 1H), 2.60 (br s, 1H), 1.68 (hept, *J*=6.6 Hz, 1H), 1.43 (s, 9H), 1.71-1.35 (m, 2H), 0.92 (d, *J*=6.6 Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 156.3, 138.2, 116.1, 75.1, 52.9, 40.7, 28.3, 24.8, 23.3, 21.9; MS C₁₃H₂₅NO₃ m/z 243, DCI/NH₃⁺ [M+1] 244, ESI⁺ [M+1] 244, ESI⁻ [M-1] 242; Analytical calcd for C₁₃H₂₅NO₃: C, 64.16; H, 10.36; N, 5.76 Found: C,64.00; H,10.25; N,5.65. For the determination of the ee% of **7** see the supplementary material addendum.

(3R,4S)-4-[(*tert*-Butyloxycarbonyl)-amino]-6-methyl-1-hepten-3-ol (8). TLC: 2:1 heptane:EtOAc; R_f=0.33; [α]_D²⁵ -37.9 (c 9.54, MeOH); IR (neat) 3358, 2949, 1682, 1527 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 5.82 (ddd, *J*=17.3, 10.6, 5.5 Hz, 1H), 5.31 (ddd, *J*=17.3, 1.5,1.5 Hz, 1 H), 5.21 (ddd, *J*=10.6, 1.5, 1.5 Hz, 1H), 4.53-4.58 (br m, 1H), 4.17 (br s, 1H), 3.85-3.74 (br m, 1H), 3.14 (br s, 1H), 1.70-1.60 (m, 1H), 1.43 (s, 9H), 1.27-1.21 (m, 2H), 0.91 (d, *J*=5.5 Hz, 3H), 0.89 (d, *J*=5.5 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 156.8, 136.7, 116.5, 75.9, 53.5, 39.1, 28.3, 24.7, 23.4, 21.7; MS (APCI⁺) C₁₃H₂₅NO₃ m/z 243 (relative intensity), 244 (M+1, 85) 244, (100) 188, (47) 170, 144 (90); Analytical calcd for C₁₃H₂₅NO₃: C, 64.16; H, 10.36; N, 5.76 Found: C, 63.91; H, 10.36; N, 5.85.

(4S,5S)-3-(*tert*-Butyloxycarbonyl)-2,2-dimethyl-5-ethenyl-4-(2-methylpropyl)oxazolidine (9). To a solution of allylic alcohols **12** and **13** (20.5 g, 84.4 mmol, **7:8**, 6:1; Assay for **7**, 17.6 g, 72.3 mmol) in

CH₂Cl₂ (200 mL) was added pTSA (0.64 g, 3.4 mmol). The resulting mixture was cooled to -20 °C then added 2,2-dimethoxypropane (35.4 g, 340 mmol). The reaction was stirred at -20 °C for 4 h. While maintaining temperature at -20 °C, Et₃N (30.4 g, 300 mmol), succinic anhydride (25.1 g, 251 mmol), and DMAP (15.8 g, 129 mmol) were added to the reaction mixture. The reaction was then allowed to warm to ambient temperature. The reaction was quenched with MeOH (10.8 mL) and stirred for 30 min. The volatiles were removed by concentration and then diluted with heptane (210 mL), MTBE (55 mL), and a 5% NaH₂PO₄ solution (500 mL). The layers were separated and the organic layer was washed with a mixture of 5% NaHCO₃ solution (450 mL) and methanol (75 mL). The layers were separated and the remaining organic layer was washed with brine (50 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated to give **9** (18.6 g, 91% yield based on starting alcohol **7**) as a viscous oil. TLC: 2:1 heptane:EtOAc; **9**, R_f=0.56; [α]_D²⁵ +17.8 (c 6.09, MeOH); IR (neat) 2950, 1702, 1460, 1385, 1178 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 5.97 (ddd, *J*=17.3, 10.3, 7.4 Hz, 1H), 5.32 (dt, *J*=17.3, 1.1 Hz, 1H), 5.19 (dt, *J*=10.3, 1.1 Hz, 1H), 4.29 (dd, *J*=7.4, 3.6 Hz, 1H), 3.66 (br d, *J*=8.5 Hz, 1H), 1.68-1.53 (m, 2H), 1.50 (s, 3H), 1.42 (s, 3H), 1.41 (s, 9H), 1.40-1.35 (m, 1H), 0.88 (dd, *J*=9.7, 6.1 Hz, 6H); ¹³C NMR (DMSO-d₆, 75 MHz) δ 150.8, 138.8, 117.2, 93.7, 81.2, 79.3, 59.8, 28.3, 27.5, 24.8, 23.9, 21.4; MS (APCI⁺) C₁₆H₂₉NO₃ m/z (relative intensity) 284 (M+1, 11), 184 (100); Analytical calcd for C₁₆H₂₉NO₃: C, 67.90; H, 10.33; N, 4.95. Found: C, 67.66; H, 10.33; N, 4.83.

(4S,5R)-3-(tert-Butyloxycarbonyl)-2,2-dimethyl-4-(2-methylpropyl)-oxazolidine-5-carboxylic acid (4). To a suspension of RuO₂·xH₂O (0.42 g, 3.1 mmol), acetone (17 mL) and water (17 mL) at 0 °C was added NaIO₄ (2.90 g, 13.6 mmol) in H₂O (20 mL). After 5 min. the vinyl oxazolidine **9** (12.0 g, 41.6 mmol) in acetone (375 mL) was added. Next NaIO₄ (55.2 g, 256 mmol) in H₂O (355 mL) was added dropwise over 3 h keeping the temperature below 15 °C. After 1 h of additional stirring the reaction was cautiously quenched with *iso*-propanol (21 mL) and stirred for 30 minutes while the reaction warmed to ambient temperature. The reaction was then filtered through Celite and the resulting filter cake washed with a 1:1 acetone:water solution (300 mL). NaCl (20 g, 342 mmol) was added to the combined filtrates and then extracted with MTBE (500 mL). The organic extract was washed with a 1:1 mixture of 1 M NaHSO₄ and 1 M NaHSO₃ (190 mL total). The organic layer was then extracted with 0.5 M K₂CO₃ aq. solution (380 mL). The alkaline aqueous layer was pH adjusted to pH 5 with portion wise addition of a concentrated citric acid solution (47 g in 100 mL H₂O). The acidic aqueous layer was extracted with MTBE (360 mL) and the organic layer was washed with brine (90 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated to give **4** (10.6 g, 85%). TLC: 2:1 heptane:EtOAc; R_f=0.12; mp 91-93.5 °C, [α]_D²⁵ -7.4 (c 10.61, CHCl₃); IR (neat) 3500 (br), 1704, 1381 cm⁻¹; ¹H NMR (DMSO-d₆, 300 MHz) δ 13.0 (br s, 1H), 4.35 (d, *J*=1.5 Hz, 1H), 4.22-4.06 (br m, 1H), 1.80-1.55 (m, 2H), 1.51 (s, 3H), 1.47 (s, 3H), 1.41 (s, 9H), 1.40-1.32 (m, 1H), 0.96 (d, *J*=6.7 Hz, 6H); ¹³C NMR (DMSO-d₆, 75 MHz) δ 172.9, 150.3, 94.8, 79.2, 77.9, 58.2, 43.4, 28.1, 25.9, 25.0, 23.6, 21.1; MS (ESI⁺) C₁₅H₂₇NO₅ m/z 301 (relative intensity) 301 (M, 15), 300 (M-1, 100); Analytical calcd for C₁₅H₂₇NO₅: C, 59.77; H, 9.03; N, 4.65. Found: C, 59.46; H, 8.99; N, 4.66.

Iso-propyl (2R,3S)-3-amino-2-hydroxy-5-methylhexanoate (13). To a solution of the oxazolidine acid **16** (16.0 g, 53 mmol) in *iso*-propanol (95 mL) was added MeSO₃H (6.5 g, 68 mmol) and the resulting solution was heated to 73 °C for 4 h. The reaction was then cooled to ambient temperature and stirred for 1 h. Water (27 mL) was added to the reaction which was stirred for an additional 3 h. The reaction mixture was concentrated to a low volume then diluted with isopropyl acetate (350 mL). The isopropyl acetate solution was washed with 2 M K₂CO₃ solution (45 mL). The organic extract was dried over Na₂SO₄, filtered, and concentrated to give **13** (10.3 g, 96%). mp 54.6-55.8 °C; [α]_D²⁵ -13.6 (c 5.27, CHCl₃); IR (neat) 3085 (br), 1731, 1592, 1462, 1378, 1208; ¹H NMR (CDCl₃, 300 MHz) δ 5.20 (hept, *J*=6.3 Hz, 1H), 4.07 (d, *J*=2.6 Hz, 1H), 3.22 (td, *J*=7.0, 2.6 Hz, 1H), 2.33 (br s, 3H), 1.81 (hept, *J*=6.6 Hz, 1H), 1.46 (t, *J*=7.0 Hz, 2H), 1.37 (s, 3H), 1.35 (s, 3H), 1.02 (d, *J*=6.6 Hz, 3H), 0.99 (d, *J*=6.6 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 175.3, 75.1, 70.8, 52.9, 44.9, 26.1, 24.5, 23.5, 23.2; MS (APCI⁺) C₁₀H₂₁NO₅ m/z 245 (M+42, 32) 204 (M+1, 100); Analytical calcd for C₁₀H₂₁NO₅: C, 59.08; H, 10.41; N, 6.89. Found: C, 58.70; H, 10.32; N, 6.80.

(3R, 4S)-bis-N,O-triethylsilyl-4-(2-methylpropyl)-3-hydroxy-azetidin-2-one (15b). To a solution of isopropyl (2R,3S)-3-amino-2-hydroxy-5-methylhexanoate (**13**) (10.0 g, 49.3 mmol) in MTBE (200 mL) was added NEt₃ (13.3 g, 131 mmol). The mixture then was cooled to 0 °C and treated with TESCl (17.1

g, 113 mmol). The resulting white slurry was stirred at 23 °C for 1.5 h. The mixture was cooled to 0 °C and treated dropwise with *t*-butylmagnesium chloride (197 mL, 1 M solution in THF, 197 mmol). The reaction was stirred at 23 °C for 1 h during which it became thick slurry. The reaction mixture was poured into 15% NH₄Cl solution (735 mL) and diluted with MTBE (375 mL). The layers were separated and the organic layer washed with brine (212 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated to afford the crude bis-TES lactam **15b** as a brown oil (23.4 g, 78% pure by HPLC which indicates 18.3 g, 49.3 mmol). The crude **15b** was used directly in the next step. TLC: EtOAc/hexane (1:4), R_f=0.82; [α]_D²⁵+83.14 (c 10.021, CHCl₃); IR (neat) 2956, 1749, 1194, 1017 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.82 (d, *J*= 5.1 Hz, 1H), 3.62 (ddd, *J*= 10.5, 5.3, 3.3 Hz, 1 H), 1.77 (ddd, *J*= 13.2, 10.2, 4.5 Hz, 1H), 1.67-1.57 (m, 1H), 1.28 (ddd, *J*= 13.2, 9.0, 3.0 Hz, 1H), 0.98-0.91 (m, 18 H), 0.90 (d, *J*= 6.6 Hz, 3H), 0.88 (d, *J*= 6.6 Hz, 3H), 0.76-0.61 (m, 12 H); ¹³C NMR (CDCl₃, 75 MHz) δ 176.8, 79.0, 57.1, 41.8, 27.2, 25.6, 23.9, 8.64, 8.56, 6.7, 5.6; MS (ESI⁺) C₁₉H₄₁NO₂Si₂ m/z (relative intensity) 372 (MH⁺, 100), 342 (5); Analytical calcd for C₁₉H₄₁NO₂Si₂: C, 61.39, H, 11.12; Found: C, 61.27, H, 11.28.

(3R, 4S)-3-triethylsilyloxy-4-(2-methylpropyl)-azetidin-2-one (16b). To a solution of crude bis-TES lactam **15b** (23.4 g crude at 78% purity gives 18.3 g, 49.3 mmol) in EtOAc (250 mL) at -10 °C was added 0.7 % KF in EtOH (16 mL) then the reaction mixture was stirred at -10 °C for 4 h. The reaction mixture was diluted with 2% NaCl solution (100 mL) and the layers separated. The organic layer was diluted with hexane (130 mL) and washed sequentially with 5% NaH₂PO₄ (50 mL), 7% NaHCO₃ (50 mL) and brine (50 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated to afford 21.0 g of the crude mono-TES lactam **16b** (21.0 g, 60% pure by HPLC (contaminated with ethoxytriethylsilane) which indicates 12.7 g, 49.3 mmol). The crude **16b** was used directly in the next step. TLC EtOAc/hexane (1:4), R_f=0.15; [α]_D²⁵+33.60 (c 10.93, CHCl₃); IR (neat) 3228, 2957, 1760, 1182 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 6.77 (bs, 1H), 4.81 (dd, *J*= 4.8, 2.7 Hz, 1H), 3.71 (ddd, *J*=7.6, 5.7, 5.0 Hz, 1H), 1.70-1.57 (m, 1H), 1.37-1.34 (m, 2H), 0.95 (t, *J*= 7.8 Hz, 9H), 0.92 (d, *J*= 6.3 Hz, 3H), 0.89 (d, *J*= 6.6 Hz, 3H), 0.68-0.59 (m, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.3, 77.2, 54.1, 38.7, 25.3, 23.0, 22.3, 6.5, 4.6; MS (ESI⁻) C₁₃H₂₇NO₂Si m/z (relative intensity) 256 (M⁻ - H, 100); Analytical calcd for C₁₃H₂₇NO₂Si: C, 60.65, H, 10.57; Found: C, 60.45, H, 10.59.

(3R,4S)-1-(tert-Butyloxycarbonyl)-3-triethylsilyloxy-4-(2-methylpropyl)azetidin-2-one (2b). To a solution of mono-TES lactam **16b** (21.0 g, 60% pure by HPLC indicates 12.7 g, 49.3 mmol) in CH₂Cl₂ (80 mL) at 23 °C was added NEt₃ (14.6 g, 144 mmol), a solution of di-*tert*-butyl dicarbonate (16.1 g, 73.9 mmol) in CH₂Cl₂ (15 mL) and DMAP (3.31 g, 27.1 mmol). The reaction mixture was stirred at 23 °C for 1.5 h. The reaction was diluted with hexane (90 mL) and washed sequentially with 5% NaH₂PO₄ (3 x 255 mL), 7% NaHCO₃ (120 mL) and brine (180 mL). The organic layer was dried over Na₂SO₄ and concentrated to give the crude Boc lactam **2b** (22.0 g crude oil, 74% pure by HPLC indicates 16.3 g, 91% yield over 3 steps). The major impurity (~ 20 wt. %) is the by-product ethoxytriethylsilane carried over from the previous desilylation step. TLC EtOAc/hexane (1:4), R_f=0.67; [α]_D²⁵+79.19 (c 10.07, CHCl₃); IR (neat) 2957, 1805, 1731, 1330 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.83 (d, *J*= 5.7 Hz, 1H), 4.05 (q, *J*= 6.1 Hz, 1H), 1.78-1.64 (m, 3H), 1.49 (s, 9H), 0.96 (t, *J*= 7.8 Hz, 9H), 0.94 (d, *J*= 6.3 Hz, 3H), 0.93 (d, *J*= 5.9 Hz, 3H), 0.70-0.62 (m, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 166.4, 148.4, 83.1, 75.7, 57.0, 36.5, 28.3, 28.0, 25.1, 23.0, 6.5, 4.6; MS (ESI⁺) C₁₈H₃₅NO₄Si m/z (relative intensity) 375 (M⁺ + NH₄, 100); Analytical calcd for C₁₈H₃₅NO₄Si: C, 60.46, H, 9.87; Found: C, 60.57, H, 10.10.

SUPPLEMENTAL MATERIAL ADDENDUM:

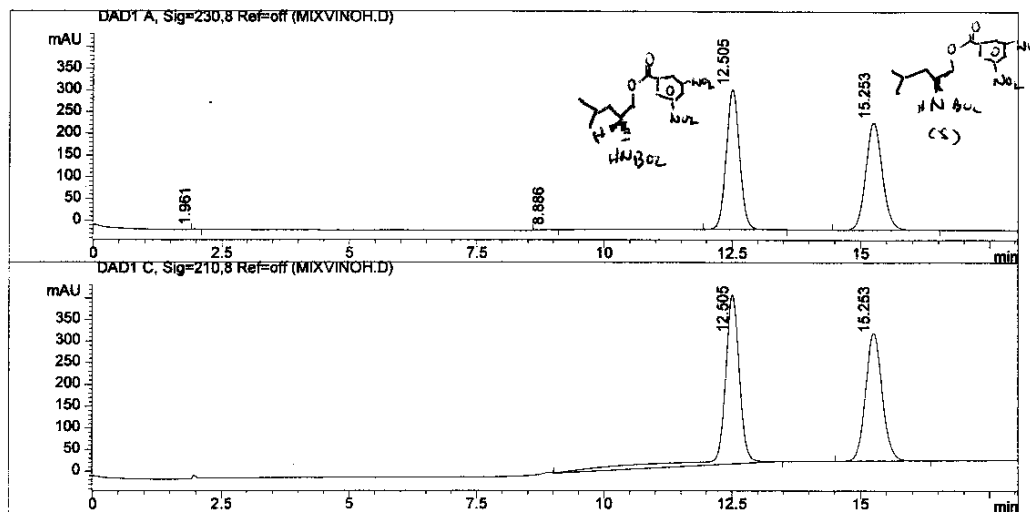
Determination of ee% of **6**. To a solution of aldehyde **6** (100 mg, 0.465 mmol) in THF (2 mL) at 0 °C was added dropwise a solution of lithium aluminum hydride in THF (1M, 0.51 mL, 0.51 mmol). The reaction mixture was stirred at room temperature for 1 h, then quenched slowly with MeOH followed by the addition of 15% NH₄Cl solution and the dilution with Et₂O. The layers were separated and the organic layer washed with brine and dried over Na₂SO₄. Concentration of the organic layer *in vacuo* gave 95 mg of the corresponding alcohol. The alcohol (95 mg, 0.438 mmol) was dissolved in CH₂Cl₂ (2 mL). Pyridine (0.071 mL, 0.876 mmol) was added followed by 3,5-dinitrobenzoyl chloride (121 mg, 0.525 mmol). The mixture was stirred at room temperature for 3 h, then quenched with unsym. dimethylethylenediamine (0.2 mL) and diluted with Et₂O (4 mL). The mixture was washed with 10% KHSO₄ (3 mL), 7% NaHCO₃ (3 mL) and brine (3 mL). The organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to give an oil

which was purified using column chromatography on silica gel eluting with EtOAc/hexane (1:9) solvent system to give 142 mg of pure 3,5-dinitrobenzoate. Chiral HPLC assay of the dinitrobenzoate indicates >99% ee.

Chiral HPLC assay: Pirkle Covalent D-naphthylalanine HiChrom HPLC Column, 25 cm x 4.6 mm; UV detection at 210 nm, 35 °C; Solvents: 90%hexane/10%IPA, 1.5 mL/min. run time: 17.5 min, Retention time: desired enantiomer 15.3 min, undesired enantiomer 12.5 min.

See 63176-142

Data file : D:\HPCHEM\1\DATA\MIXVINOH.D 1
 Sample Name: mixvinylalcohols
 mixture enantiomers of N-bocleucinol (as 3,5-dinitrobenzoates)
 Injection Date : Tue, 12. Jan. 1999 Inj. Vol. :
 Sample Name : mixvinylalcohols (modified after loading)
 Acq. Method : CHIRAL.M
 Analysis Method : D:\HPCHEM\1\METHODS\CHIRAL.M
 90/10 hex / ipa 1.5 ml min chiral assay



Customized Report:

Signal 1: DAD1 A, Sig=230,8 Ref=off

Compound	Peak	RT	Height	Width	Amount	Area	Area %
	1	1.961	1.222	0.066	0.000	5.410	0.048
	2	8.886	2.037	0.182	0.000	24.471	0.215
	3	12.505	323.739	0.275	0.000	5.754e3	50.516
	4	15.253	248.232	0.349	0.000	5.606e3	49.222

Signal 2: DAD1 C, Sig=210,8 Ref=off

Compound	Peak	RT	Height	Width	Amount	Area	Area %
	1	12.505	391.857	0.327	0.000	8.680e3	56.461
	2	15.253	296.463	0.347	0.000	6.694e3	43.539

*** End of Report ***

Column D-Naphtalamine Flow = 1.5 ml/min
 $\lambda = 210/230$
 Col Temp = 35.0°C 1 mg/ml injection @ 5 μ l injection
 90/10 hexane / ipa

Instrument 1

Tue, 12. Jan. 1999

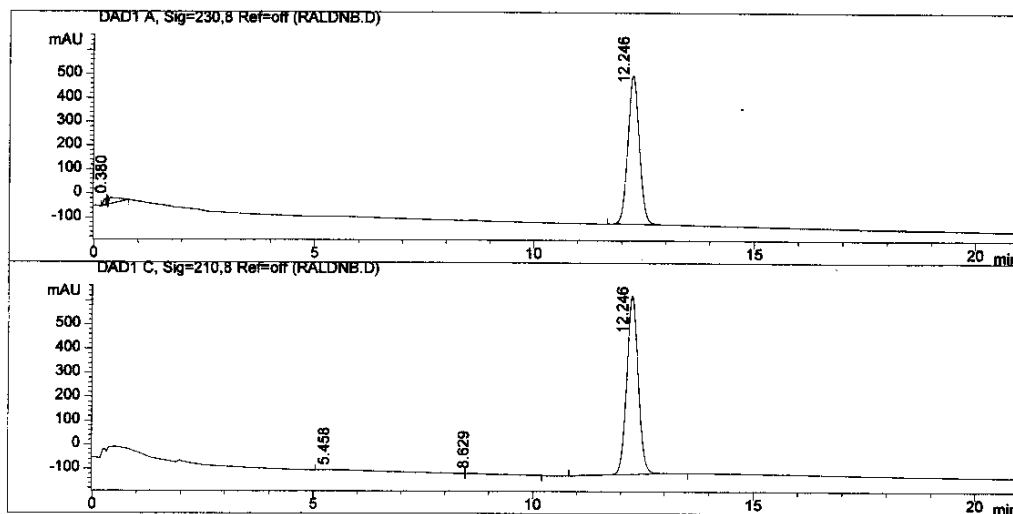
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Page 1 of 1

Data file : D:\HPCHEM\1\DATA\RALDNB.D
 Sample Name: ralcohol
 chiral chrom 1 mg/ml boc leu (r) dinitrobenzoate std

1

Injection Date : Mon, 11. Jan. 1999 Inj. Vol. :
 Sample Name : ralcohol (modified after loading)
 Acq. Method : CHIRAL.M
 Analysis Method : D:\HPCHEM\1\METHODS\CHIRAL.M
 90/10 hex / ipa 1.5 ml min chiral assay



Customized Report:

Signal 1: DAD1 A, Sig=230,8 Ref=off

Compound	Peak	RT	Height	Width	Amount	Area	Area %
	1	0.256	27.275	0.063	0.000	110.487	0.948
	2	0.291	22.248	0.036	0.000	48.651	0.418
	3	0.380	25.702	0.194	0.000	398.417	3.420
	4	12.246	623.701	0.276	0.000	1.109e4	95.215

Signal 2: DAD1 C, Sig=210,8 Ref=off

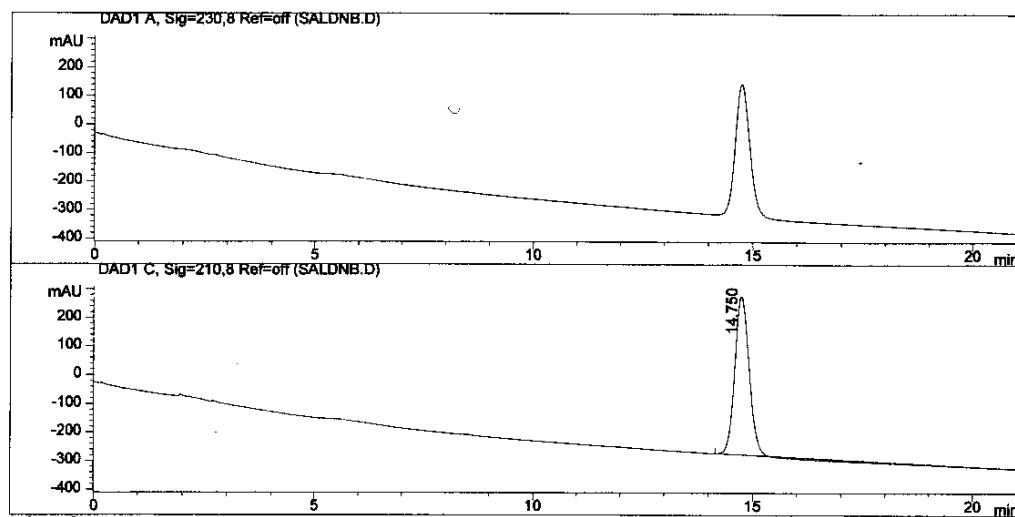
Compound	Peak	RT	Height	Width	Amount	Area	Area %
	1	5.458	3.557	0.927	0.000	271.864	1.972
	2	8.629	3.061	0.102	0.000	16.336	0.119
	3	12.246	745.066	0.279	0.000	1.350e4	97.909

*** End of Report ***

Data file : D:\HPCHEM\1\DATA\SALDNB.D
 Sample Name: salcohol
 chiral chrom 1 mg/ml boc leu (s) dinitrobenzoate std

1

Injection Date : Mon, 11. Jan. 1999 Inj. Vol. :
 Sample Name : salcohol (modified after loading)
 Acq. Method : CHIRAL.M
 Analysis Method : D:\HPCHEM\1\METHODS\CHIRAL.M
 90/10 hex / ipa 1.5 ml min chiral assay



Customized Report:

Signal 1: DAD1 A, Sig=230,8 Ref=off

Compound	Peak	RT	Height	Width	Amount	Area	Area %

Signal 2: DAD1 C, Sig=210,8 Ref=off

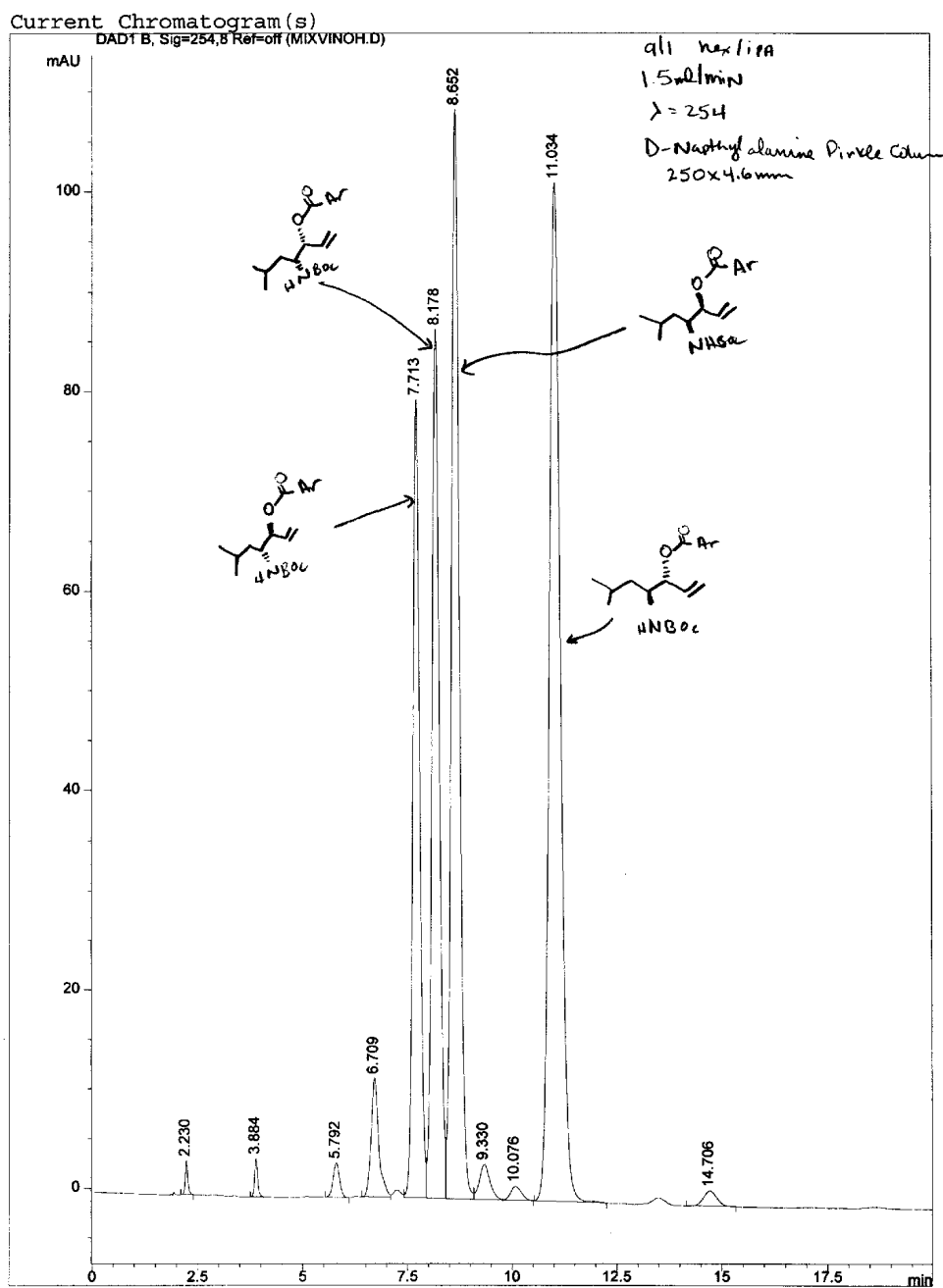
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	1	14.750	552.795	0.327	0.000	1.147e4	100.000

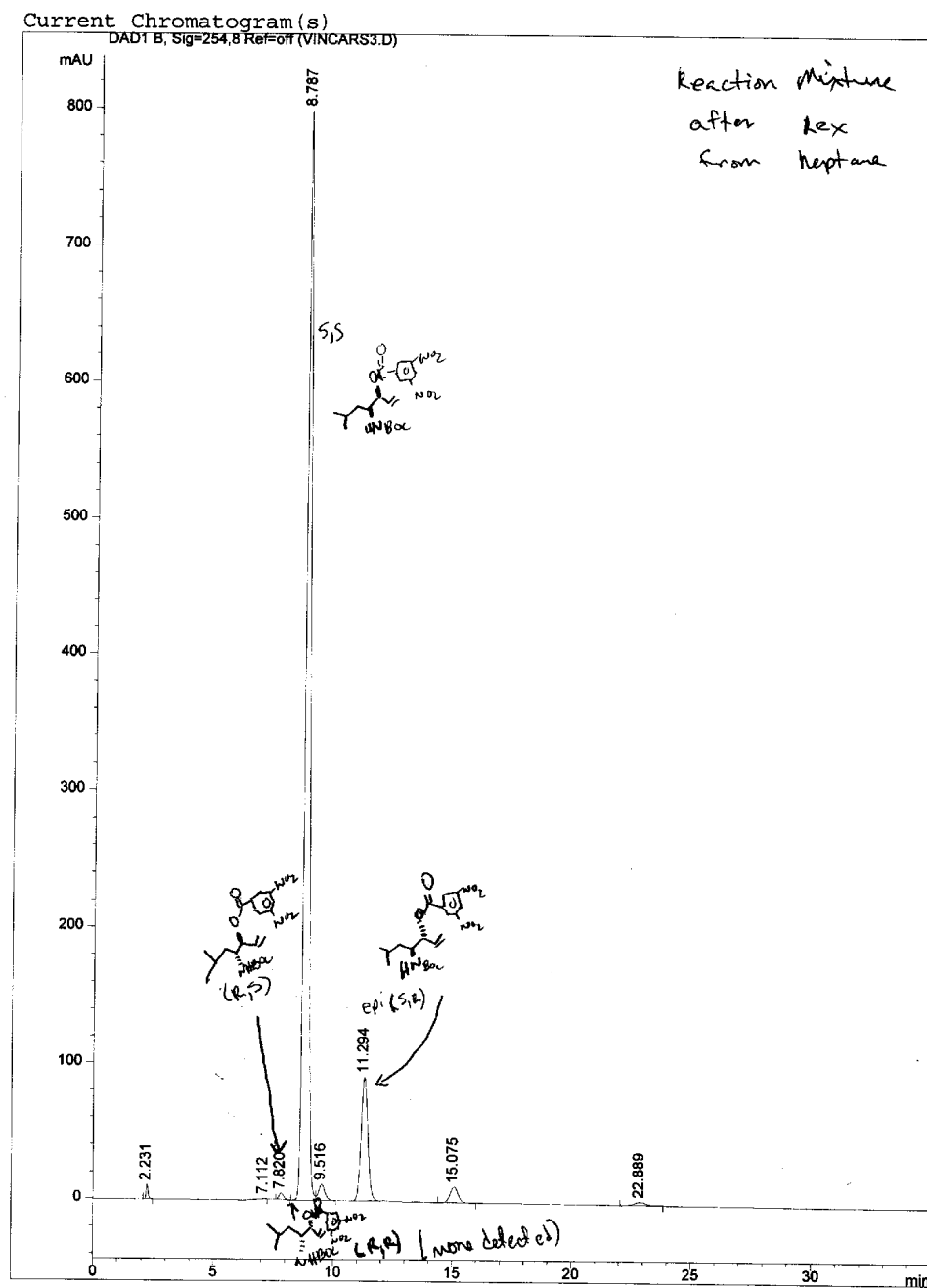
*** End of Report ***

Determination of ee% of **7**. To a solution of **7** (0.06 g, 0.25 mmol) in CH₂Cl₂ (2 mL) was added pyridine (0.05 mL, 0.62 mmol), followed by 3,5-dinitrobenzoyl chloride (0.085 g, 0.37 mmol). The mixture was stirred at room temperature for 1 h, then quenched with unsym. dimethylethylenediamine (0.1 mL) and diluted with Et₂O (4 mL). The mixture was washed with 10% KHSO₄ (5 mL), followed by 5% KH₂PO₄ (5 mL) and brine (5 mL). The organic layer was dried over Na₂SO₄ and concentrated to give 105 mg of 3,5-dinitrobenzoate of **12**. Chiral HPLC assay of the dinitrobenzoate indicates > 99% ee.

Chiral HPLC assay: Pirkle Covalent D-naphthylalanine HiChrom HPLC Column, 25 cm x 4.6 mm; UV detection at 235 nm, 35 °C; Solvents: 90% heptane/10% IPA, 1.5 mL/min. Retention time: 8.8 min.

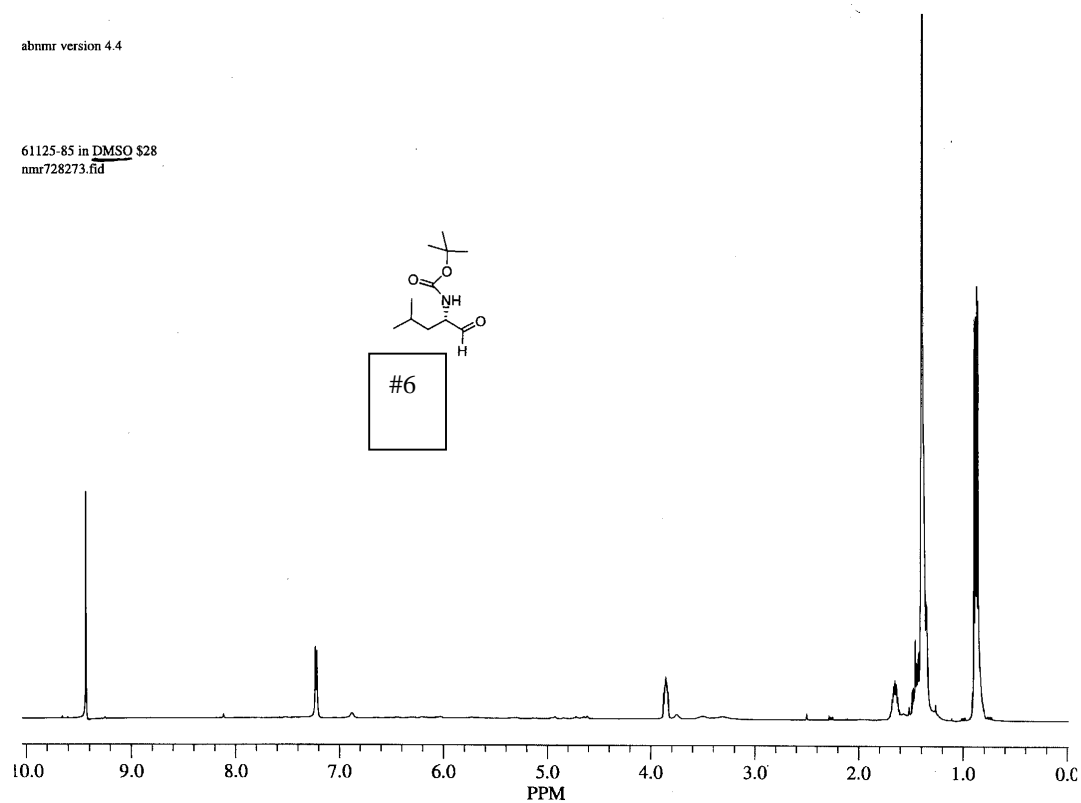
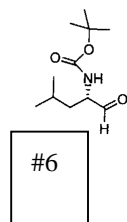
Print of window 38: Current Chromatogram(s)





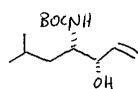
abnmr version 4.4

61125-85 in DMSO \$28
nmr728273.fid

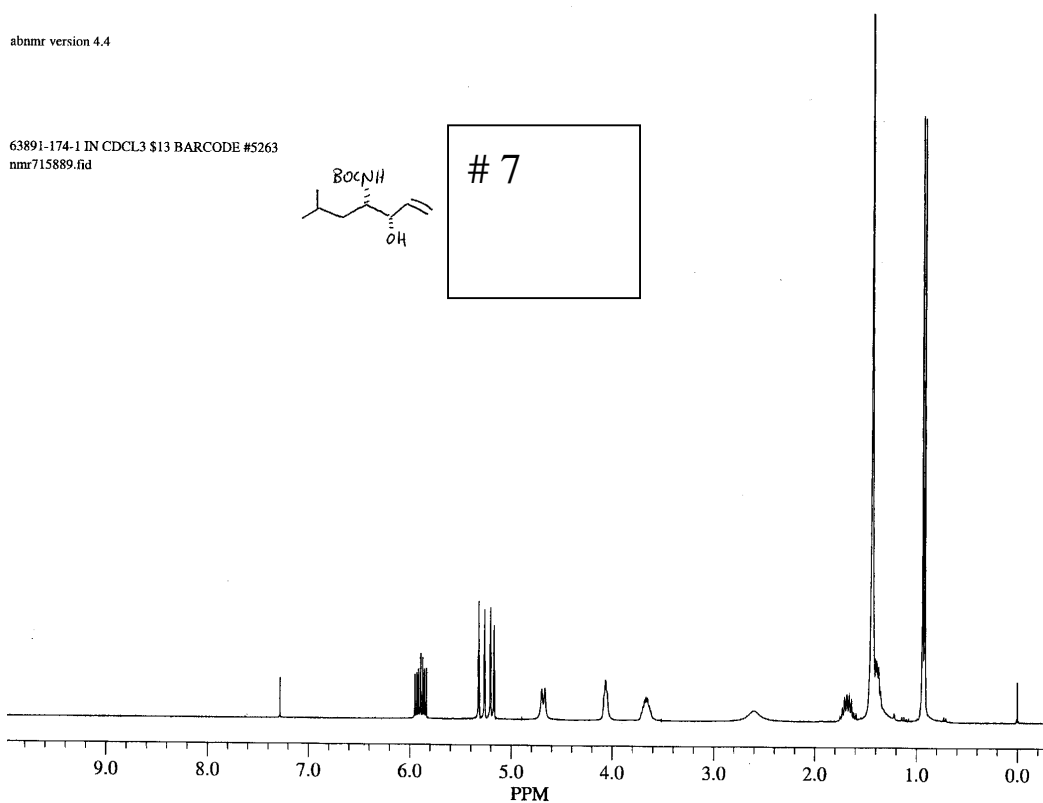


abnmr version 4.4

63891-174-1 IN CDCL3 \$13 BARCODE #5263
nmr715889.fid

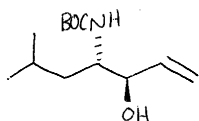


7

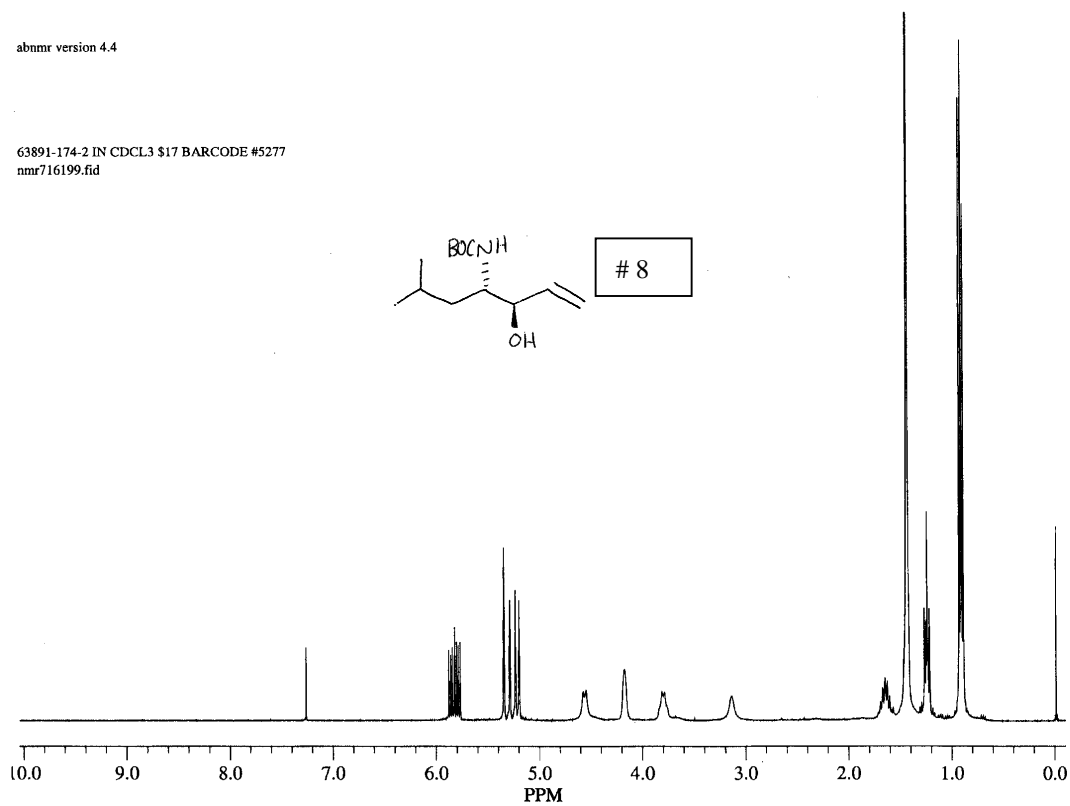


abnmr version 4.4

63891-174-2 IN CDCL3 \$17 BARCODE #5277
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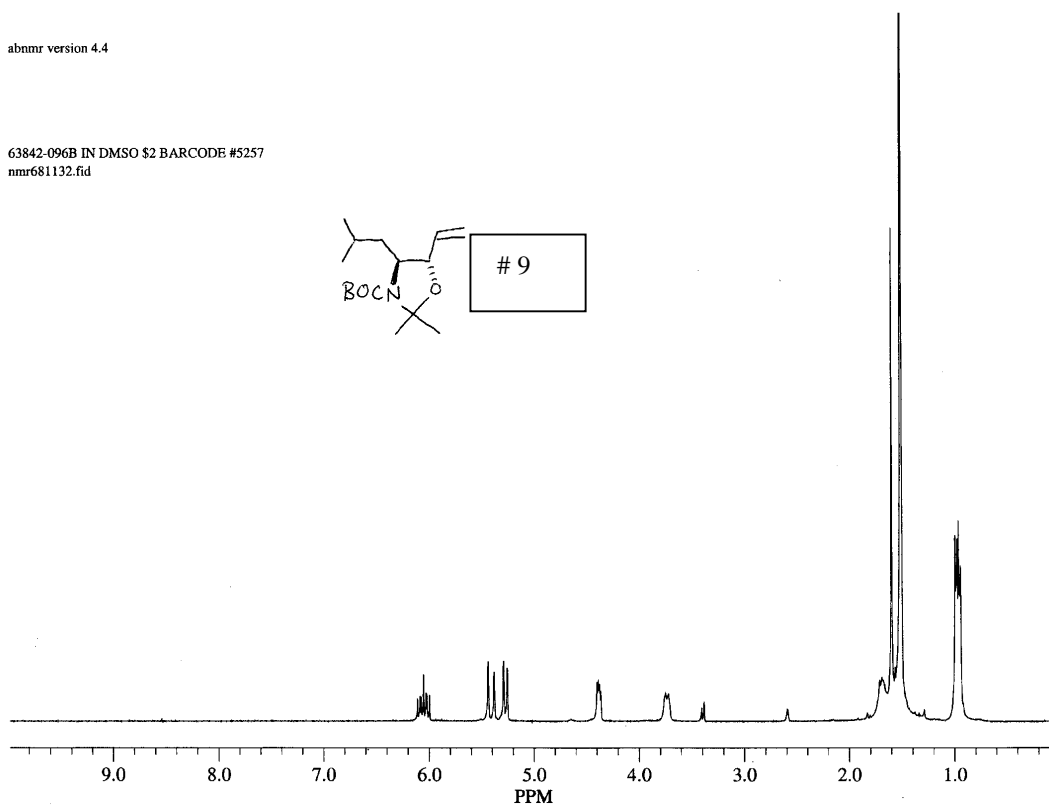
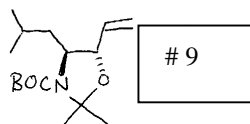


8



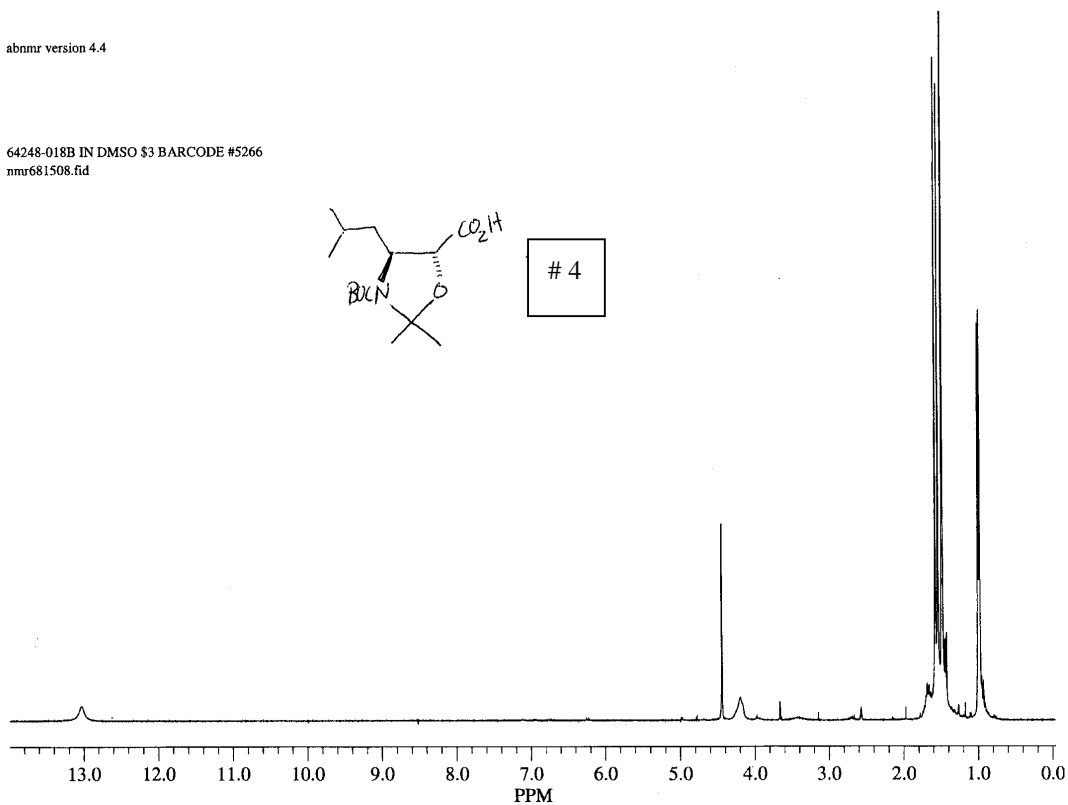
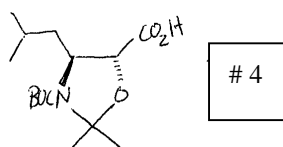
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63842-096B IN DMSO \$2 BARCODE #5257
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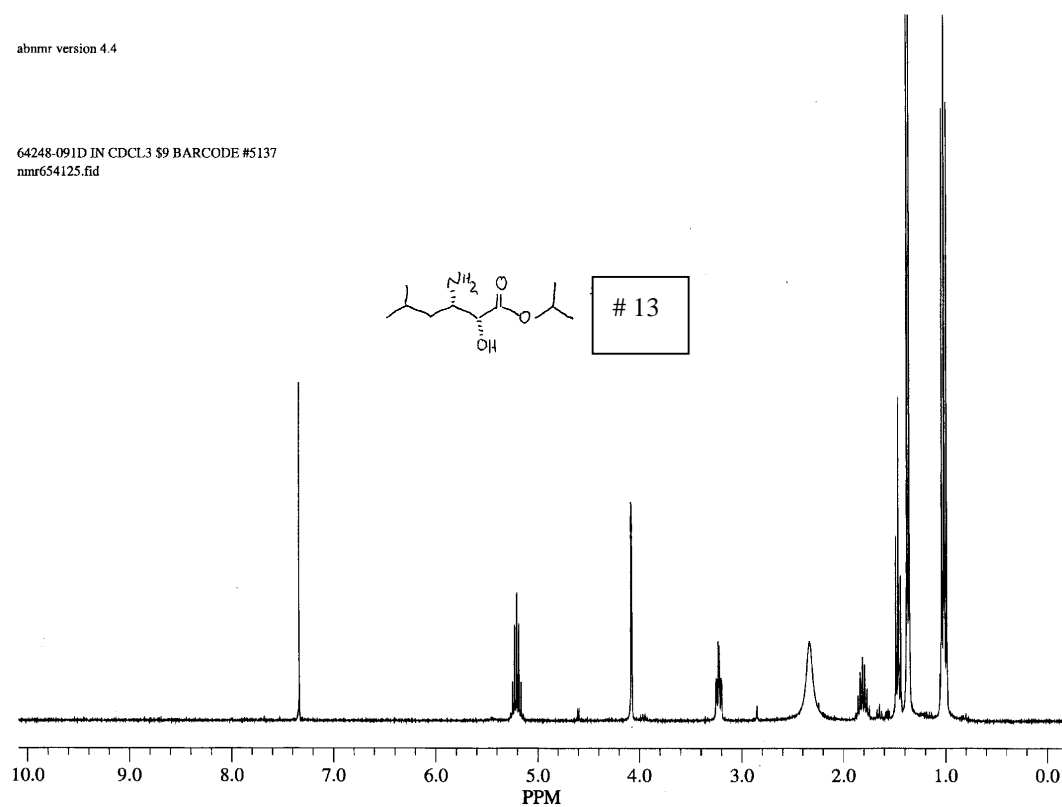
abnmr version 4.4

64248-018B IN DMSO \$3 BARCODE #5266
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
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nmr654125.fid

CC(C)OC(=O)[C@H](O)[C@@H](N)CC(C)C # 13

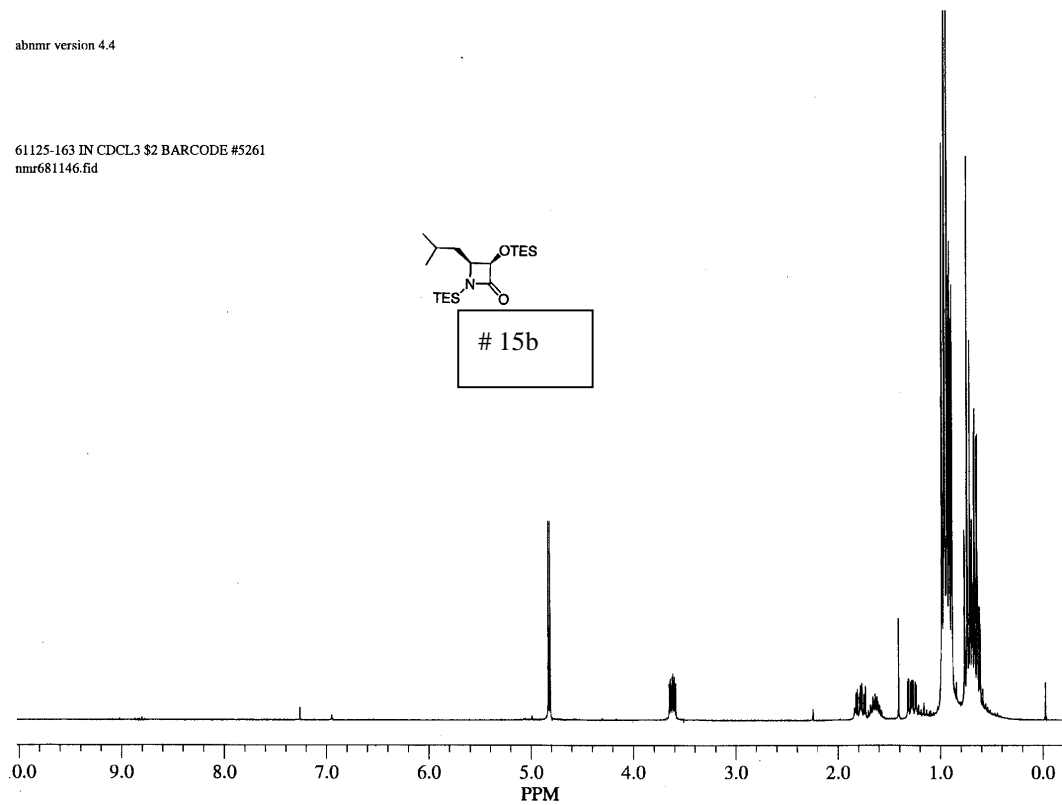


20

61125-163 IN CDCL3 \$2 BARCODE #5261
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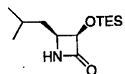


15b

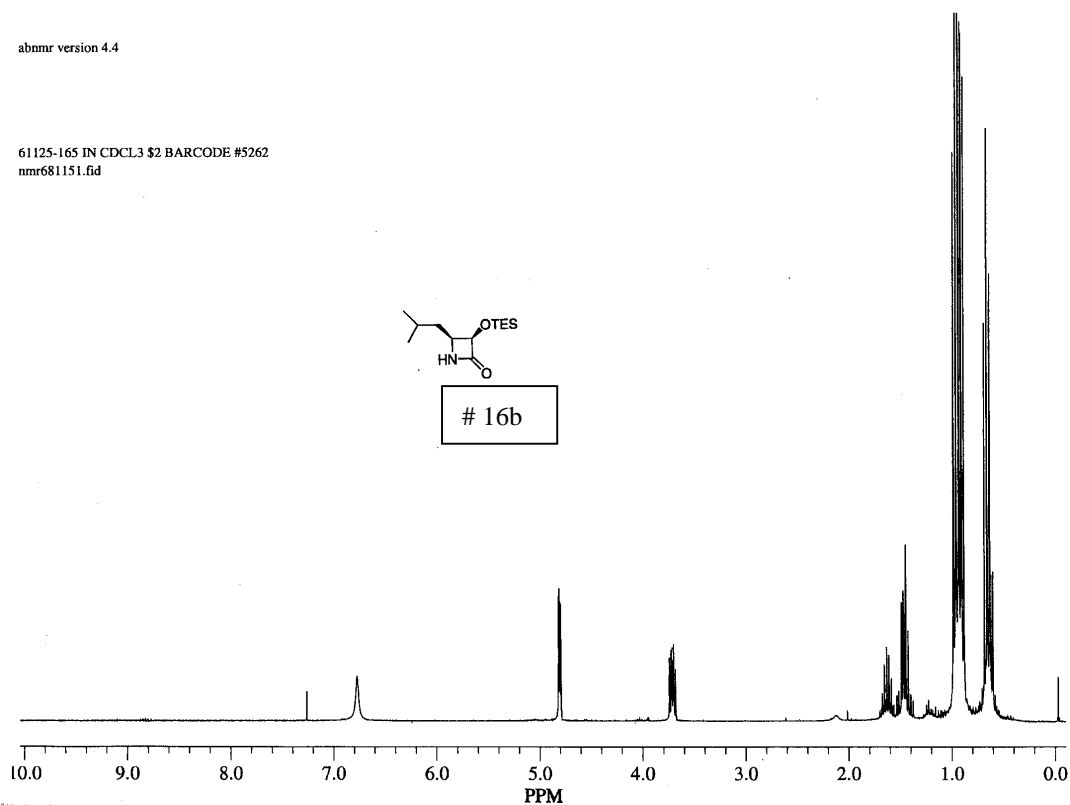


abnmr version 4.4

61125-165 IN CDCL3 \$2 BARCODE #5262
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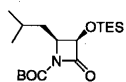


16b



abnmr version 4.4

61125-166 IN CDCL3 \$9 BARCODE #5205
nmr682869.fid



2b

