Experimental Section

Materials and Methods. Ether and tetrahydrofuran were distilled from benzophenone and sodium metal. Methylene chloride and triethylamine were distilled from calcium hydride. Unless otherwise noted, solvents were reagent grade and were used without purification. Air- and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven-dried glassware and standard syringe/septa techniques. Commercial reagents were used without purification unless otherwise noted. The ligands $(DHQ)_2PHAL$, $(DHQD)_2PHAL$, $(DHQ)_2AQN$, and $(DHQ)_2PYR$ were obtained from Aldrich Chemical Co. Fox Chlor (St. Paul, MN) brand aqueous sodium hypochlorite solutions (5.25 %) were used. *tert*-Butyl hypochlorite was freshly prepared according to the *Organic Synthesis* procedure and stored over anhydrous $CaCl_2$ at ~4 °C.[A] Furfural was freshly distilled. Furan **14** was synthesized from furfural and the corresponding Wittig reagent.

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Varian VXR-300 (300 MHz) or Varian VXR-500 (500 MHz) spectrometers. Chemicals shifts are reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^1H and $CDCl_3$ (δ 77.0 ppm) for ^{13}C. Infrared (IR) spectra were obtained on a Prospect MIDAC FT-IR spectrometer. Optical rotations were measured with a Jasco DIP-370 digital polarimeter in CH_2Cl_2. Flash column chromatography was performed on ICN reagent 60 (60-200 mesh) silica gel. Analytical thin-layer chromatography was performed with precoated glass-backed plates (Whatman K6F 60Å, F_{254}) and visualized by quenching of fluorescence and by charring after treatment with *p*-anisaldehyde stain. R_f values are obtained by elution in the stated sovent ratios (v/v). Combustion analysis was performed by M-H-W Laboratories, Phoenix, AZ.

(A) Mintz, M. J.; Walling, C. *Organic Synthesis*; Wiley: New York; 1983; Collect. Vol. V, p 183.

1-(2'-furyl)-2-trimethylsilylethan-1-ol (8a). Magnesium turnings (10.10 g, 415 mmol) were placed in a 1 L 3-neck round-bottomed flask. A condenser and a pressure equalizing addition funnel were attached. The apparatus was flame dried and then flushed with nitrogen gas (3 ×). Chloromethyltrimethylsilane (42.44 g, 346 mmol) and ether (200 mL) were slowly added to the dry magnesium. After the addition was complete, the solution was refluxed for 1 h. Freshly distilled furfural (25 mL, 302 mmol) and ether (300 mL) were slowly added to the Grignard reagent at 0 °C and the solution was stirred for 12 h. The reaction was quenched with saturated aqueous NH_4Cl (200 mL) and was extractedwith ether (3 × 100 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (2 × 50 mL), was dried (Na_2SO_4), and then concentrated under reduced pressure to give a yellow oil **8a** (not shown in the text, 50.05 g, 272 mmol, 90%). R_f = 0.58 (ether/hexane = 3:7); ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (dd, J = 1.8, 0.7, 1H), 6.24 (dd, J = 3.1, 1.8, 1H), 6.13 (d, J = 3.3, 1H), 4.77 (dd, J = 8.8, 6.9, 1H), 3.13 (bs, 1H), 1.28 (dd, J =

14.1, 8.8, 1H), 1.23 (dd, J = 14.1, 6.8, 1H), -0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 141.6, 110.1, 105.5, 65.6, 24.8, -1.4; IR (thin film) 3390, 2950, 2895, 1655, 1505, 1250, 1010, 860, 690 cm^{-1}; EI MS for $C_9H_{16}O_2Si$ (M^+): calcd, 184.0919; obsd 184.0905.

Vinylfuran (5). Furan **8a** (described above, 3.013 g, 16.34 mmol) and ether (8.4 mL) were added to a 50 mL round-bottomed flask followed by addition of aqueous HCl (1M, 16.4 mL) with vigorous stirring for 1 h, at which time the starting material had completely disappeared by TLC. The phases were separated and the aqueous layer was extracted with ether (2 x 50 mL) and combined with the organic layer.

(2*R*)-2-Amino-*N*-(benzyloxycarbonyl)-2-(2'-furyl)-ethanol (9a). A 250 mL round-bottomed flask was charged with benzyl carbamate (2.96 g, 19.6 mmol) and *t*-BuOH (64 mL). To this stirred solution was added a freshly prepared aqueous solution of NaOH (784 mg, 19.6 mmol in 64 mL water), followed by *tert*-butyl hypochlorite (2.13 g, 19.6 mmol). After 5 min a solution of $(DHQ)_2PHAL$ (153 mg, 0.19 mmol, 1.2 mol %) in *t*-BuOH was added; the reaction became homogeneous at this point. Vinylfuran (**5**) (16.34 mmol, dissolved in 8 mL of ether, from the above procedure) was then added, followed by OsO_4 (41 mg, 0.16 mmol, 1 mol %). The light green solution was stirred at 25 °C and became yellow after 1 h, indicating completion. The reaction was quenched by the addition of a saturated aqueous Na_2SO_3 solution (60 mL) and stirred for 15 min. The two phases were separated, and the aqueous phase was extracted with ethyl acetate (3 × 30 mL). The combined organic phases were washed with water (40 mL), brine (100 mL), dried over anhyd Na_2SO_4, and concentrated to afford the crude mixture of regioisomers (**a/b** = 34:66) and benzyl carbamate. Flash chromatography (SiO_2, 5-40% EtOAc/hexane gradient elution) provided regioisomer **9a** (598 mg, 14 %, 86 % ee) as a waxy solid (mp 84-86 °C). Material of higher % ee has been obtained from smaller scale reactions (3 mmol scale, 94 % ee, $[\alpha]^{25}_D$ = +32.1 ° (c = 3.82 CH_2Cl_2)). For **9a**: R_f = 0.15 (EtOAc/hexane = 3:7), $[\alpha]^{23}_D$ = +29.2 ° (c = 1.89, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.32 (m, 6H), 6.32 (dd, J = 3.3, 1.8 Hz, 1H), 6.25 (d, J = 3.3 Hz, 1 H), 5.57 (d, J = 8.4 Hz, 1 H, NH), 5.11 (s, 2 H), 4.94 (m, 1 H), 3.91 (dd, J = 11.2, 5.1 Hz, 1 H), 3.85 (dd, J = 11.2, 4.5 Hz, 1 H), 2.46 (br s, 1 H, OH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.2, 152.0, 136.1, 128.5, 128.2, 128.1, 110.4, 107.1, 67.7, 64.0, 51.1; IR (thin film) 3331, 3033, 2957, 1707, 1540, 1455, 1251, 1143, 1070, 739, 696 cm^{-1}; CI MS for $C_{14}H_{16}NO_4$, $(M+H)^+$: calcd, 262.1079; obsd 261.1065. Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.34; H, 5.79. Found: C, 64.12; H 5.70.

For **(1*R*)-2-Amino-*N*-(benzyloxycarbonyl)-1-(2'-furyl)-ethanol (9b):** a white crystaline solid (1.20 mg, 28 %, 14 % ee), mp 49.5-50.0 °C; R_f = 0.2 (EtOAc/hexane = 3:7), $[\alpha]^{23}_D$ = +2.9° (c = 2.85, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$)) δ 7.37-7.33 (m, 6H), 6.32 (dd, J = 3.3, 1.8 Hz, 1H), 6.28 (d, J = 3.3 Hz, 1 H), 5.60 (dd, J = 5.1, 5.1 Hz, 1 H), 5.09 (s, 2 H), 4.79 (m, 1 H), 3.98 (br s, 1 H, OH), 3.55 (ddd, J = 12.0, 7.2, 4.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.0,

154.0, 142.2, 137.3, 128.4, 128.1, 128.0, 110.2, 109.2, 67.0, 66.9, 45.4; IR (thin film) 3384, 3032, 2941, 1700, 1526, 1451, 1255, 1147, 735 cm^{-1}; CI MS for $C_{14}H_{16}NO_4$, $(M+H)^+$: calcd, 262.1079; obsd 262.1078. Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.34; H, 5.79. Found: C, 64.52; H 5.83.

Separation of **9a** and **9b** by conversion of **9a** to **(2*R*)-2-Amino-*N*-(benzyloxycarbonyl)-2-(2'-furyl)-*O*-*tert*-butyldimethylsilylethanol (10a).** A 50 mL round-bottomed flask was charged with a crude mixture of alcohols **9a** (2.60 g, 9.92 mmol) and **9b** (5.17 g, 19.83 mmol), methylene chloride (20 mL), triethylamine (4.15 mL, 29.76 mmol), DMAP (120 mg, 0.99 mmol, 10 mol %) and *t*-butyldimethylsilylchloride (2.24 g, 14.88 mmol). The reaction mixture was allowed to stir at rt for 3 h at which time the reaction was complete by TLC. Ether (20 mL) and saturated aqueous sodium bicarbonate (10 mL) were slowly added and the mixture was allowed to stir for 15 min, at which time the phases were separated and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo to yield a crude reaction mixture (8.25 g). Flash chromatography (SiO_2, 5-40% EtOAc/hexane gradient elution) provided furan **10a** as a colorless oil (2.43 g, 12 % from fufural). For **10a**: R_f = 0.33 (EtOAc/hexane = 1:19), $[\alpha]^{25}_D$ = +13.1 ° (c = 1.15, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.30 (m, 6H), 6.31 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.23 (d, *J* = 3.3 Hz, 1 H), 5.11 (s, 2 H), 5.04 (t, *J* = 3.9 Hz, 1 H), 4.82 (t, *J* = 6.0 Hz, 1 H), 3.51 (ddd, *J* = 27.2, 13.6, 6.0 Hz, 1 H), 0.87 (s, 9 H), 0.06 (s, 3 H), -0.06 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.3, 154.4, 131.9, 136.5, 128.5, 128.1, 110.1, 107.0, 67.3, 66.7, 46.1, 25.7, 18.1, -5.1, -5.2, missing 1 ipso carbon; IR (thin film) 3452, 3331, 2929, 2856, 1725, 1499, 1249, 1111, 837 cm^{-1}; CI MS for $C_{20}H_{30}NO_4Si$, $(M+H)^+$: calcd, 376.1944; obsd 376.1948. Anal. Calcd for $C_{20}H_{29}NO_4Si$: C, 63.97; H, 7.79. Found: C, 64.14; H 7.82.

(2*R*)-2-Amino-*N*-(benzyloxycarbonyl)-2-(2'-furyl)-*O*-*tert*-butyldimethylsilyl-ethanol (10a). A 5 mL round-bottomed flask was charged with pure **9a** (28.7 mg, 0.09 mmol), methylene chloride (0.5 mL), triethylamine (28 μL, 0.28 mmol), DMAP (1.1 mg, 0.01 mmol, 10 mol %) and *t*-butyldimethylsilylchloride (21.1 mg, 0.14 mmol). The reaction mixture was allowed to stir at rt for 3 h at which time the reaction was complete by TLC. Ether (3 mL) and saturated aqueous sodium bicarbonate (2 mL) were added and the mixture was allowed to stir for 15 min, at which time the phases were separated and the aqueous layer was extracted with ether (3 × 5 mL). The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo to yield a crude reaction mixture (39 mg). Flash chromatography (SiO_2, 5 % EtOAc/hexane) provided furan **10a** as a colorless oil (33.3 mg, 0.89 mmol, 95 %).

1-(*tert*-butyldimethylsilyl)-3-(2'-furyl)-2-propen-1-ol (12). A 50 mL flask was charged with a stirbar, 3-(2'-furyl)-2-propen-1-ol (500 mg, 4 mmol), 8 mL of dichloromethane, triethylamine (1.22 g, 12.1 mmol), DMAP (49 mg, 0.4 mmol), and*tert*-butyldimethylsilyl chloride

(728 mg, 4.8 mmol). The reaction mixture was allowed to stir for 12 h until all starting material had reacted, as monitored by TLC. The reaction was quenched with saturated aqueous $NaHCO_4$ (8 mL) and extracted with ether (3 × 10 mL). The organic phases were combined and dried (Na_2SO_4), then concentrated under reduced pressure to yield a colorless oil, furan **12** (866 mg, 3.6 mmol, 90%). R_f = 0.3 (ether/hexanes = 1:24); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 1.5, 1H), 6.45 (dt, J = 16, 9,1H), 6.36 (dd, J = 3.2, 1.7, 1H), 6.23 (dt, J = 16, 4.5, 1H), 6.21 (d, J = 3.2, 1H), 4.33 (dd, J = 4.6, 1.5, 2H), 0.94 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 141.7, 128.0, 117.7, 111.2, 107.3, 63.3, 26.0, 18.5, -5.19; IR (thin film) 2951, 2893, 1482, 1407 cm^{-1}; EI MS for $C_{13}H_{22}O_2Si$, $(M^{\cdot})^+$: calcd, 238.1389; obsd 238.1390.

(2*R*, 3*R*)-3-Amino-*N*-benzyloxycarbonyl-1-*tert*-butyldimethylsilyl-3-(2'-furyl)-propan-1,2-diol (13a). A 15 mL flask was charged with a stirbar, water (3 mL), *t*-BuOH (3 mL), and NaOH (90 mg, 2.25 mmol) and was allowed to stir until all of the NaOH dissolved. Benzyl carbamate (373 mg, 2.46 mmol) was then added followed by the slow addition of *tert*-butyl-hypochlorite (233 mg, 2.15 mmol). The reaction mixture was allowed to stir for five min before $(DHQ)_2PHAL$ (87.7 mg, 0.11 mmol) was added, followed by osmium tetroxide (26 mg, 0.10 mmol) and the reaction mixture was allowed to stir for another ten min. Once all of the ligand and osmium tetroxide had dissolved, 1-[(*tert*-butyldimethylsilyl)oxy]-3-(2'-furyl)-2-propene (**12**) was added and the mixture took a dark green color which faded slowly over time to a light yellow. The reaction mixture was allowed to stir for 2 d and was then extracted with ether (3 ×). The organic phases were combined and condensed under reduced pressure, and then flashed through a plug of silica gel to remove the starting material (151 mg, 0.638 mmol, 31.1 %), *N*-chlorobenzyl carbamate, and benzyl carbamate. Medium pressure liquid chromatography was used to separate the regioisomers yielding two colorless oils; **13a** (175 mg, 0.43 mmol, 21 %, 62 % ee) and **13b** (178 mg, 0.44 mmol, 21 %, 9 % ee). The reaction provided an overall yield of 43 % of both regioisomers, and 74 % based on recovered starting material. For **13a:** R_f = 0.25 (ether/hexanes = 4:6); $[\alpha]^{25}_D$ = +13.4 ° (c = 3.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 6H), 6.32 (dd, J = 3.0, 1.8 1H), 6.26 (d, J = 3.0, 1H), 5.57 (d, J = 8.5, 1H), 5.11 (s, 2H), 4.91 (dd, J = 8.7, 3.9, 1H), 3.64 (dd, J = 10, 4.5, 1H), 3.52 (dd, J = 9.9, 6.6, 1H), 2.65 (s, 1H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 152.9, 142.1, 136.4, 128.5, 128.2, 128.1, 110.4, 107.1, 72.4, 67.0, 63.8, 61.9, 50.6, 25.9, -5.5; IR (thin film) 3419, 3048, 2940, 2873, 1712, 1514, 1242 cm^{-1}; CI MS for $C_{21}H_{31}O_5SiN$, $(M^{\cdot})^+$: calcd, 405.1972; obsd 405.1971.

For **(1*R*, 2*R*)-2-Amino-*N*-benzyloxycarbonyl-3-*tert*-butyldimethylsilyl-1-(2'-furyl)-propan-1,3-diol (13b)**: R_f = 0.23 (ether/hexanes = 4:6); $[\alpha]^{23}_D$ = -9.85 ° (c = 3.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 6H), 6.31 (dd, J = 3.3, 1.8, 1H), 6.29 (dt, J = 3.0, 0.8, 1H), 5.51 (d, J = 8.4, 1H), 5.12 (d, J = 12.3, 1H), 5.09 (d, J = 12.3, 2H), 5.03 (dd, J = 3.8, 3.4, 1H), 4.07 (ddd, J = 8.4, 4.5, 3.0, 1H), 3.82 (dd, J = 10, 4.8, 1H), 3.75 (dd, J = 10, 3.3, 1H), 3.56 (s,

1H), 0.87 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 153.8, 146.9, 142.1, 136.4, 128.5, 128.2, 128.1, 125.6, 112.6, 110.3, 107.0, 69.1, 66.9, 65.8, 64.4, 54.6, 25.9, 18.2, -5.6; IR (thin film) 3426, 3049, 2940, 2873, 1708, 1516, 1241 cm^{-1}; CI MS for $C_{21}H_{31}O_5SiN$, $(M+H)^+$: calcd, 405.1972, obsd 406.2026.

Ethyl (2*R*, 3*R*)-3-amino-*N*-benzyloxycarboxy-3-(2'-furyl)-2-hydroxylpropionate (15a). A 100 mL round-bottomed flask was charged with benzyl carbamate (1.01 g, 6.68 mmol) and *t*-BuOH (24 mL). To this stirred solution was added freshly prepared aqueous solution of NaOH (267 mg, 6.68 mmol in 12 mL water), followed by *tert*-butyl hypochlorite (712 mg, 6.56 mmol). After 5 min a solution of $(DHQ)_2PHAL$ (280 mg, 0.36 mmol, 6 mol %) in *t*-BuOH was added; the reaction became homogeneous at this point. Ethyl 3-(2-furyl)-prop-2-enoate (**14**) (1.01 g, 6.06 mmol) was then added, followed by OsO_4 (61 mg, 0.24 mmol, 4 mol %). The light green solution was stirred at 25 °C and became brown after 1 h. The reaction was quenched by the addition of a saturated aqueous sodium sulfite solution (20 mL) and stirred for 15 min. The two phases were separated, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with water (20 mL), brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated to afford the crude mixture of regioisomers (**a/b** = 83:17), starting material (291 mg, 1.75 mmol, 29 %) and benzyl carbamate. Flash chromatography (SiO_2, 5-40% EtOAc/hexane gradient elution) provided regioisomer **15a** (798 mg, 2.4 mmol, 35 %, 87 % ee) as a colorless oil. The yield of **15a** at 71 % conversion is 50.3 %. For **15a**: R_f = 0.3 (EtOAc/hexane = 3:7), $[\alpha]^{23}_D$ = +26 ° (c = 0.84, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.25 (m, 6H), 6.30 (dd, *J* = 7.8, 2.1 Hz, 2H), 5.62 (d, *J* = 9.0 Hz, 1 H), 5.36 (d, *J* = 9.0 Hz, 1 H), 5.09 (s, 2 H), 4.58 (s, 1 H, NH), 4.23 (dd, *J* = 13.8, 6.9 Hz, 2 H), 3.40 (br s, 1H, OH), 1.26 (t, *J* = 6.9, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.4, 155.7, 151.6, 142.4, 136.2, 128.5, 128.2, 128.1, 110.5, 107.4, 71.7, 67.2, 62.6, 51.7, 14.0; IR (thin film) 3377, 2982, 1723, 1516, 1230 cm^{-1}; CI MS for $C_{17}H_{19}NO_6$, $(M+H)^+$: calcd, 334.1291; obsd 334.1277. Anal. Calcd for $C_{17}H_{19}NO_6$: C, 61.25; H, 5.75. Found: C, 61.40; H 5.83.

For **Ethyl (2*R*, 3*R*)-2-amino-*N*-benzyloxycarboxy-3-(2'-furyl)-3-hydroxylpropionate (15b):** (119 mg, 0.36 mmol, 6 %, 18 % ee) as a colorless oil. R_f = 0.3 (EtOAc/hexane = 3:7), $[\alpha]^{23}_D$ = +1.5 ° (c = 1.65, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.28 (m, 6H), 6.31 (d, *J* = 1.2 Hz, 2H), 5.62 (d, *J* = 8.7 Hz, 1 H), 5.20 (dd, *J* = 6.5, 3.6 Hz, 1 H), 5.09 (s, 2 H), 4.74 (dd, *J* = 9.0, 2.7 Hz, 1 H), 4.23 (dd, *J* = 14.4, 7.2 Hz, 2 H), 2.97 (d, *J* = 5.4 Hz), 1.26 (t, *J* = 7.2, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.2, 152.4, 142.6, 128.5, 128.2, 128.1, 110.4, 107.6, 68.5, 67.2, 62.1, 57.6, 14.1, missing 2 ipso carbons; IR (thin film) 3391, 2936, 2850, 1712, 1497, 1230, 1235 cm^{-1}; CI MS for $C_{17}H_{23}N_2O_6$, $(M+NH_4)^+$: calcd, 351.1556; obsd 351.1554. Anal. Calcd for $C_{17}H_{19}NO_6$: C, 61.25; H, 5.75. Found: C, 61.32; H 5.88.

(2*R*, 3*R*)-3-Amino-*N*-benzyloxycarbonyl-3-(2'-furyl)-propan-1,2-diol (16). An 18 mL plastic reagent tube was charged with a stirbar, **13a** (31 mg, 0.078 mmol), and 5 % HF in acetonitrile (w/w, 0.6 mL). The reaction was allowed to stir for 1 h, at which time the reaction was complete by TLC. The reaction was quenched with saturated aqueous sodium bicarbonate and washed with ether (3 × 10 mL). The organic phases were combined, dried over sodium sulfate, condensed under reduced pressure, and then flashed through a plug of silica gel to yield a yellow oil **16**, 23 mg (0.075 mmol, 96 %). R_f= 0.25 (ether/hexanes = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 6H), 6.33 (dd, *J* = 3.0, 1.8, 1H), 6.27 (d, *J* = 3.0, 1H), 5.58 (d, *J* = 8.7, 1H), 5.11 (s, 2H), 4.99 (dd, *J* = 8.7, 3.3, 1H), 4.10 (m, 1H), 3.56 (d, *J* = 6.0, 2H), 2.8 (s, 1H), 1.74 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 152.1, 143.3, 136.0, 128.6, 128.4, 128.2, 110.6, 107.4, 73.0, 67.4, 63.2, 50.8; IR (thin film) 3401, 2929, 1704, 1524 cm^{-1}; CI MS for $C_{15}H_{17}NO_5$, $(M+H)^+$: calcd, 292.1185; obsd 292.1197.

(1*R*, 2*R*)-2-Amino-*N*-benzyloxycarbonyl-1-(2'-furyl)-propan-1,3-diol (16b). An 18 mL plastic reagent tube was charged with a stirbar, **13b** (28 mg, 0.068 mmol), and 5 % HF in acetonitrile (w/w, 0.6 mL). The reaction was allowed to stir for 1 h, at which time the reaction was complete by TLC. The reaction was quenched with saturated aqueous sodium bicarbonate and washed with ether (3 × 10 mL). The organic phases were dried (Na_2SO_4), condensed under reduced pressure, and then flashed through a plug of silica gel to yield a yellow oil **16b**, 19 mg (0.067 mmol, 97%). R_f = 0.25 (ether/hexanes = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 6H), 6.32 (m, 2H), 5.50 (d, *J* = 7.2, 1H), 5.08 (s, 2H), 5.02 (dd, *J* = 3.6, 3.0, 1H), 4.06 (ddd, J = 8.7, 8.7, 4.2, 1H), 3.81 (s, 2H), 3.06 (s, 1H), 2.28 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 152.0, 142.4, 136.0, 128.6, 128.2, 128.1, 110.4, 107.3, 68.8, 67.1, 63.7, 55.3; IR (thin film) 3398, 3063, 2928, 2337, 1697, 1524 cm^{-1}; CI MS for $C_{15}H_{17}NO_5$, $(M+H)^+$: calcd, 292.1185; obsd 292.1184.

Conversion of 15a to 16: A 5 mL round-bottomed flask was charged with ester **15a** (22.5 mg, 0.077 mmol) and methylene chloride (0.8 mL). Dibal (0.30 mL, 0.30 mmol, 1 M in hexane) was added dropwise with stirring at -78 °C under a nitrogen atmosphere. The reaction was found to be complete after 4 h by TLC and was diluted with ether (4 mL) and was quenched by slow dropwise addition of methanol (1 mL) under nitrogen. The mixture was washed with aqueous HCl (1 M, 5 mL) and the phases were separated. The aqueous layer was extracted with ether (3 × 5 mL) and the combined organic phases were washed with saturated aqueous sodium bicarbonate. The phases were separated and the aqueous layer was extracted with ether (3 × 5 mL) and the combined organic phases were washed with brine. The organic layer was separated, dried (Na_2SO_4), and concentrated to produce crude diol **16** (20.5 mg, 0.070 mmol, 91 %) as a colorless oil.

(2*S*)-2-Amino-*N*-benzyloxycarbonyl-2-(2'-furyl)-acetaldehyde (17). A 5 mL round-bottomed flask was charged with diol **16** (20.5 mg,0.070 mmol), THF (0.5 mL) and water (1 mL). Sodium periodate (16.6 mg, 0.077 mmol) was allowed to stir for 3 h at which time the reaction

was complete by TLC. The reaction was diluted with ether (5 mL) and then with water. The phases were separated and the aqueous layer was extracted with ether (3 × 5 mL) and the combined organic layers were washed with brine. The organic layer was separated, dried (Na_2SO_4), and concentrated to produce crude aldehyde **17** (not pictured in text, 14.7 mg, 0.0567 mmol, 81 %) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.43 (dd, *J* = 1.8, 0.9, 1H), 6.42 (d, *J* = 3.0, 1H), 6.40 (dd, *J* = 3.0, 1.8, 1H), 5.78 (d, *J* = 7.2, 1H), 5.53 (d, *J* = 7.2, 1H), 5.13 (d, *J* = 3.0, 1H); CI MS for $C_{14}H_{14}NO_4$, $(M+H)^+$: calcd, 260.0923; obsd 260.0924.

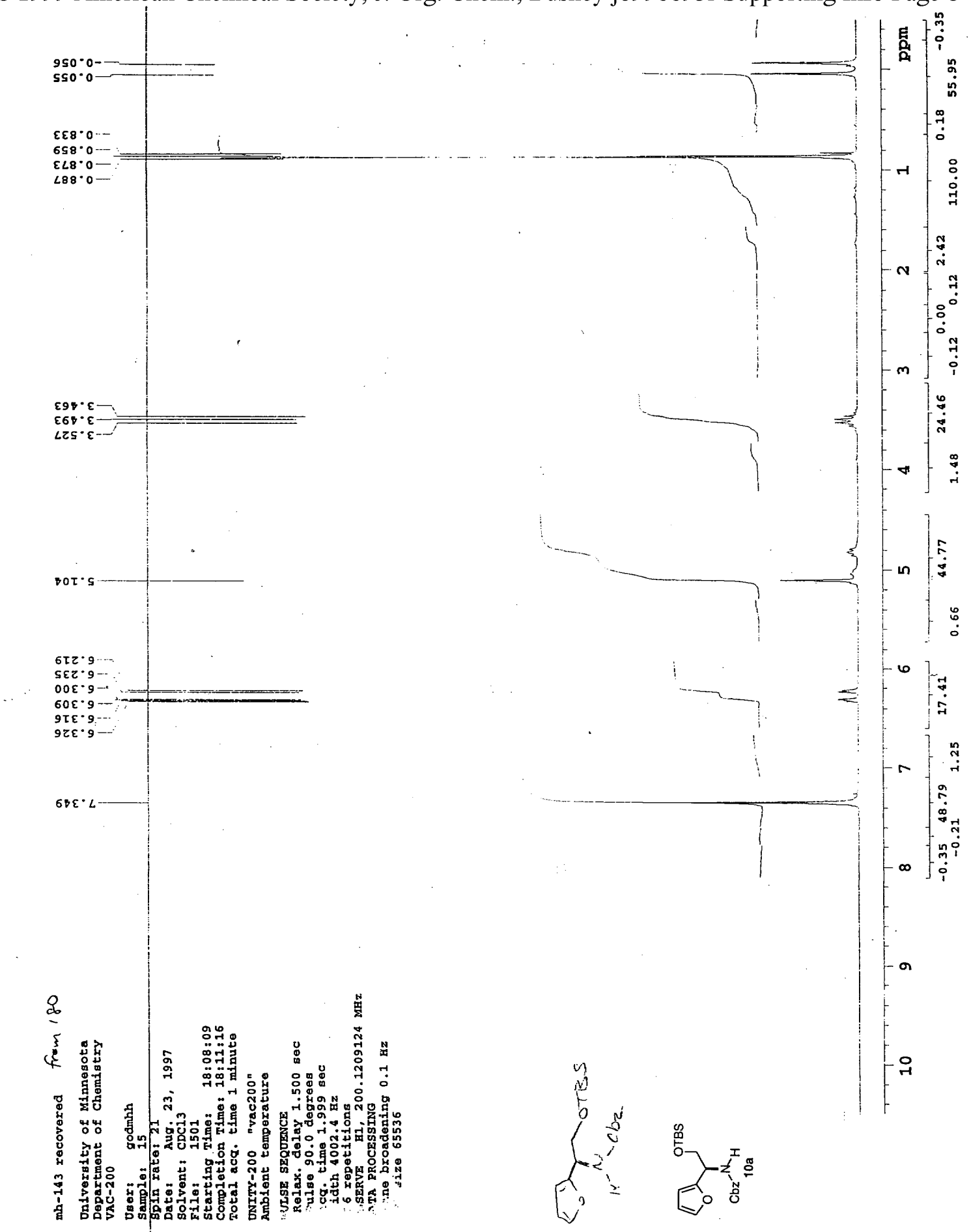
Conversion of aldehyde 17 to furan 9a: A 5 mL round-bottomed flask was charged with crude aldehyde **17a** (14.7 mg, 0.056 mmol), methanol (0.5 mL) and $NaBH_4$ (3.2 mg, 0.085 mmol) and was allowed to stir at rt for 2 h, at which time the reaction was complete by TLC. The reaction mixture was diluted with ether (4 mL) and was quenched with saturated aqueous sodium bicarbonate (5 mL). The phases were separated and the aqueous layer was extracted with ether (3 × 5 mL) and the combined organic phases were washed with brine. The organic layer was separated, dried (Na_2SO_4), and concentrated to produce crude alcohol **9a** (14.6 mg, 98 %) as a colorless oil. Flash chromatography produced pure alcohol **9a** (8.9 mg, 0.034 mmol, 60 %).

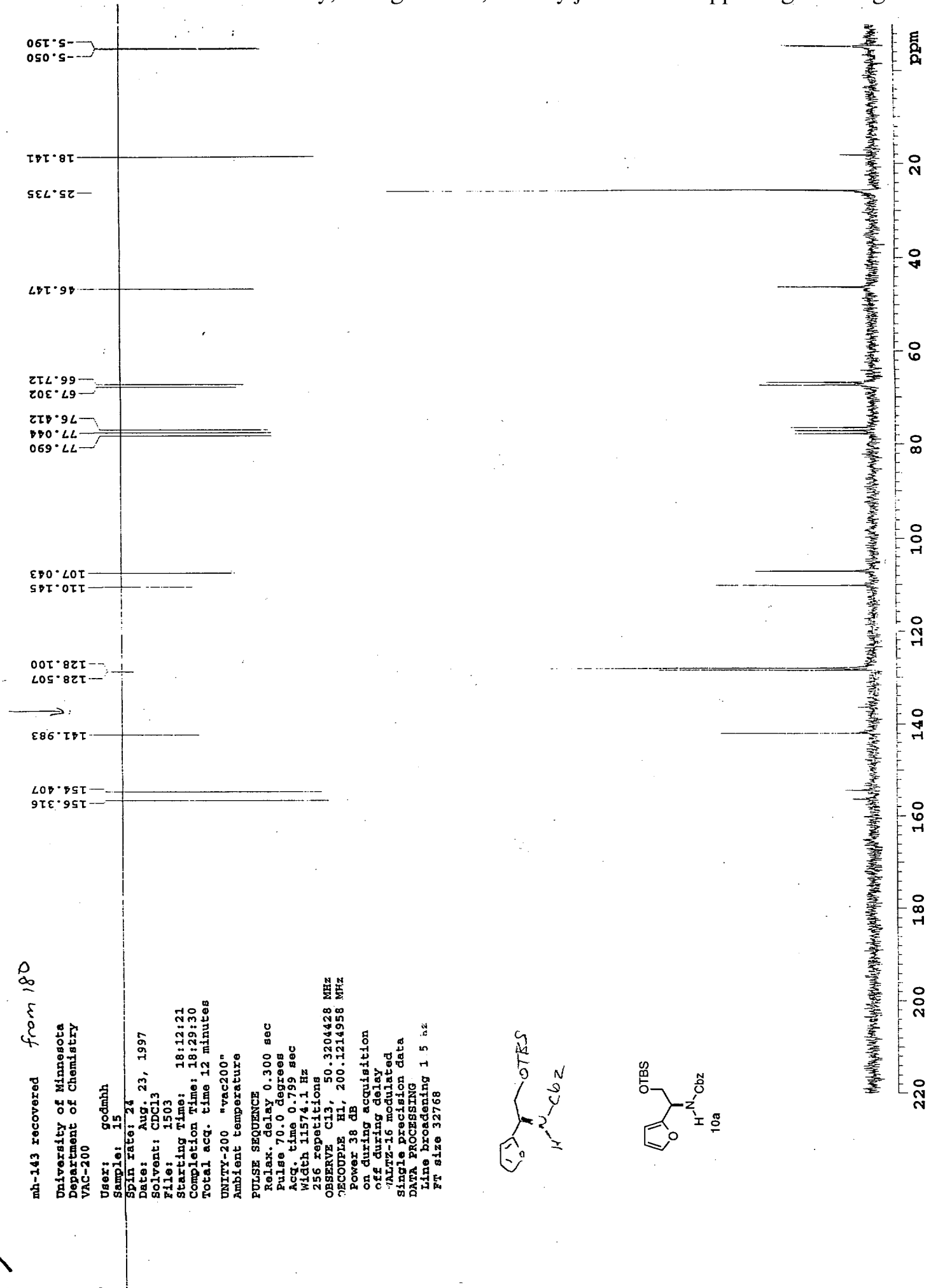
Mosher ester analysis. General procedure.

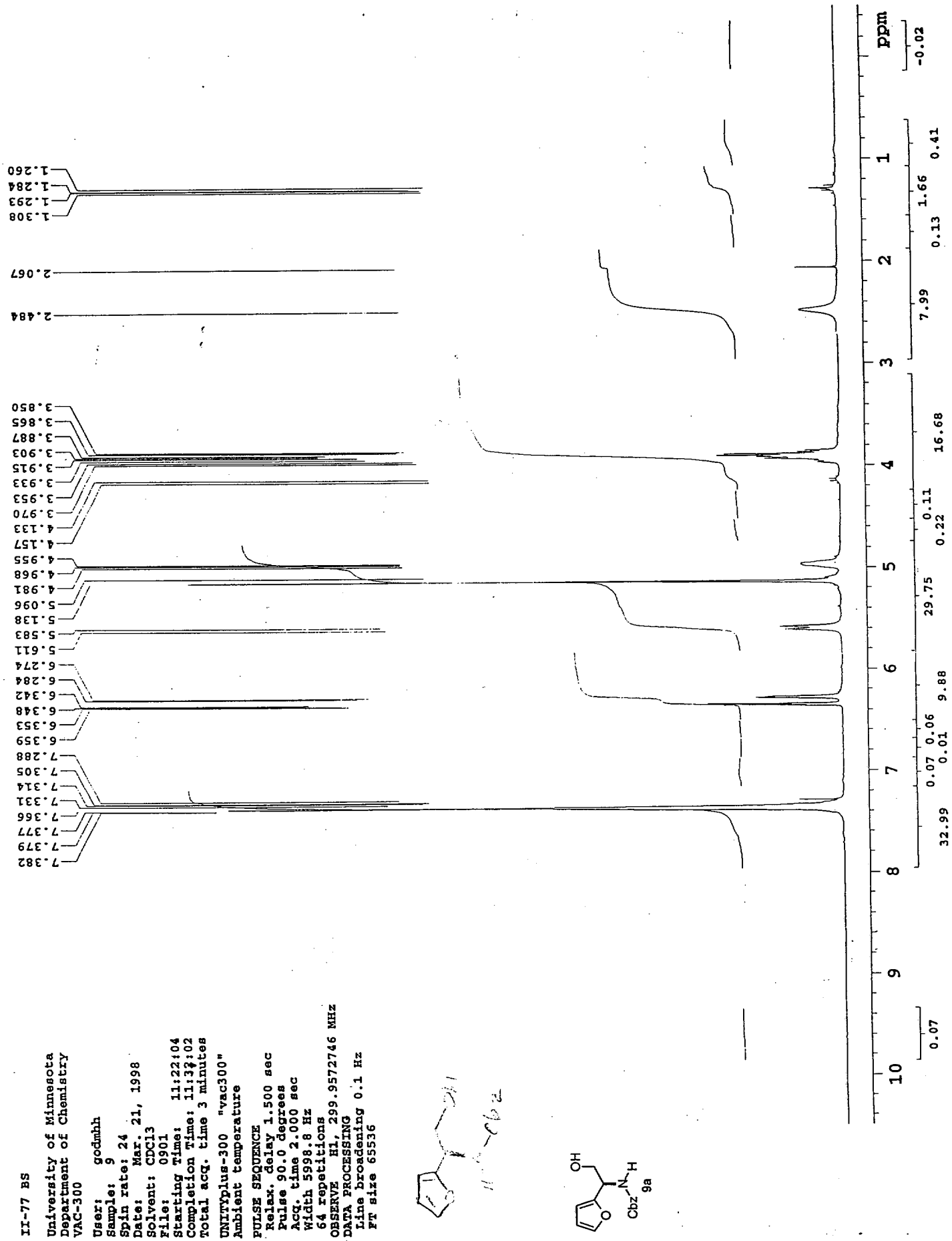
In a V-shaped 1 mL vial, 3 mg of compound is dissolved in methylene chloride (100 μL). A solution of 10 % DMAP in pyridine (1.4 molar eq) is added with stirring, followed by Mosher's acid chloride (1.2 molar eq for racemic acid chloride, 1.05 molar eq for enantiomerically pure acid chloride). The reaction is followed by TLC. Upon completion, the reaction of racemic material is chromatographed; the crude enantiomerically enriched reaction mixture is directly concentrated and ^1H and ^{19}F NMR spectra are recorded.

Peaks integrated for ^{19}F NMR spectra:

9a: δ = -81.92, -82.00.
9b: δ = -81.86, -82.09.
15a: δ = -81.83, -82.03.
15b: δ = -81.73, -82.02.







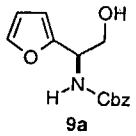
II-77 BS 49mg for C13

University of Minnesota
Department of Chemistry
VAC-300

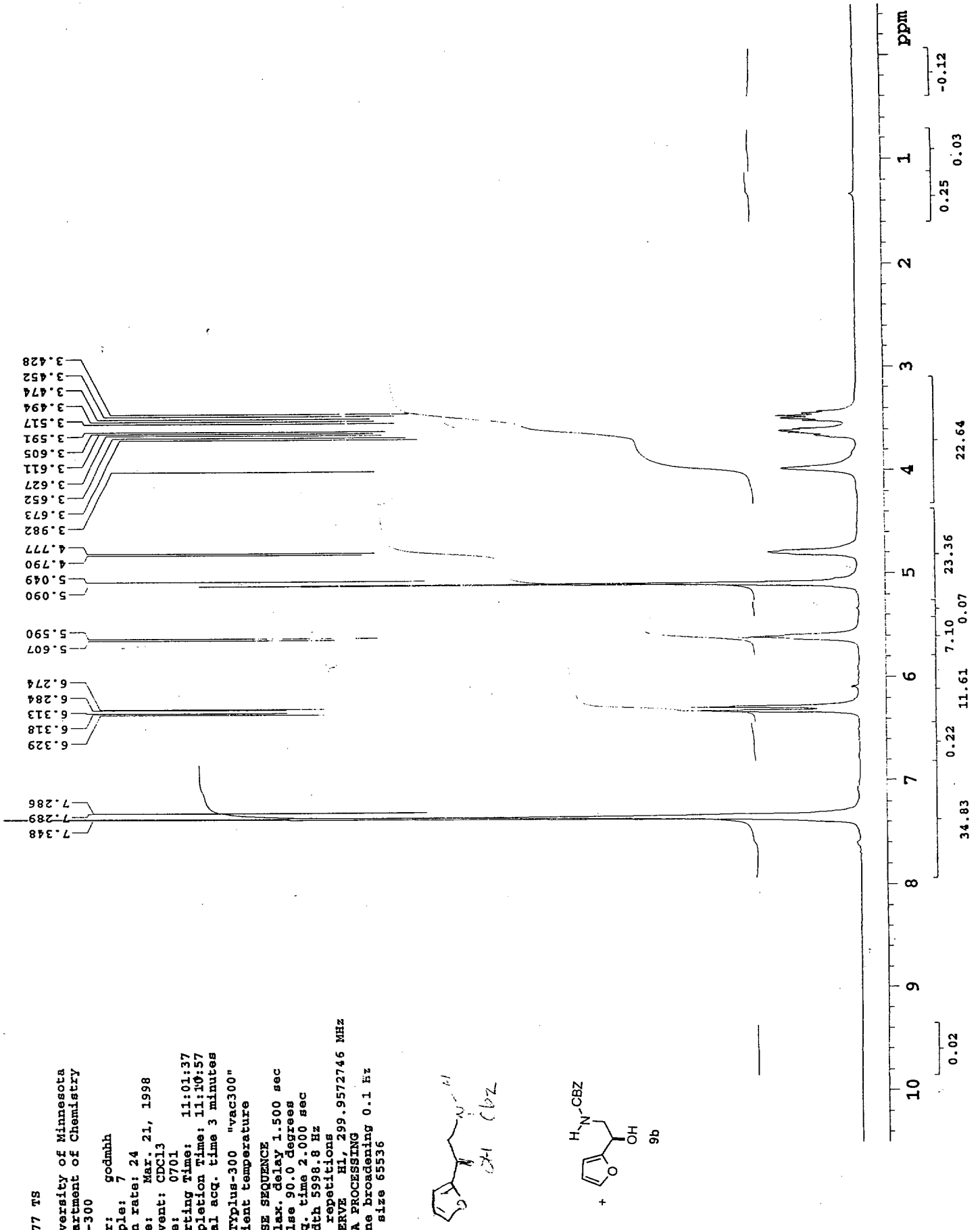
User: godmhh
Sample: 17
Spin rate: 24
Date: Mar. 23, 1998
Solvent: CDCl3
File: 1702
Starting Time: 01:31:41
Completion Time: 02:26:24
Total acq. time 54 minutes

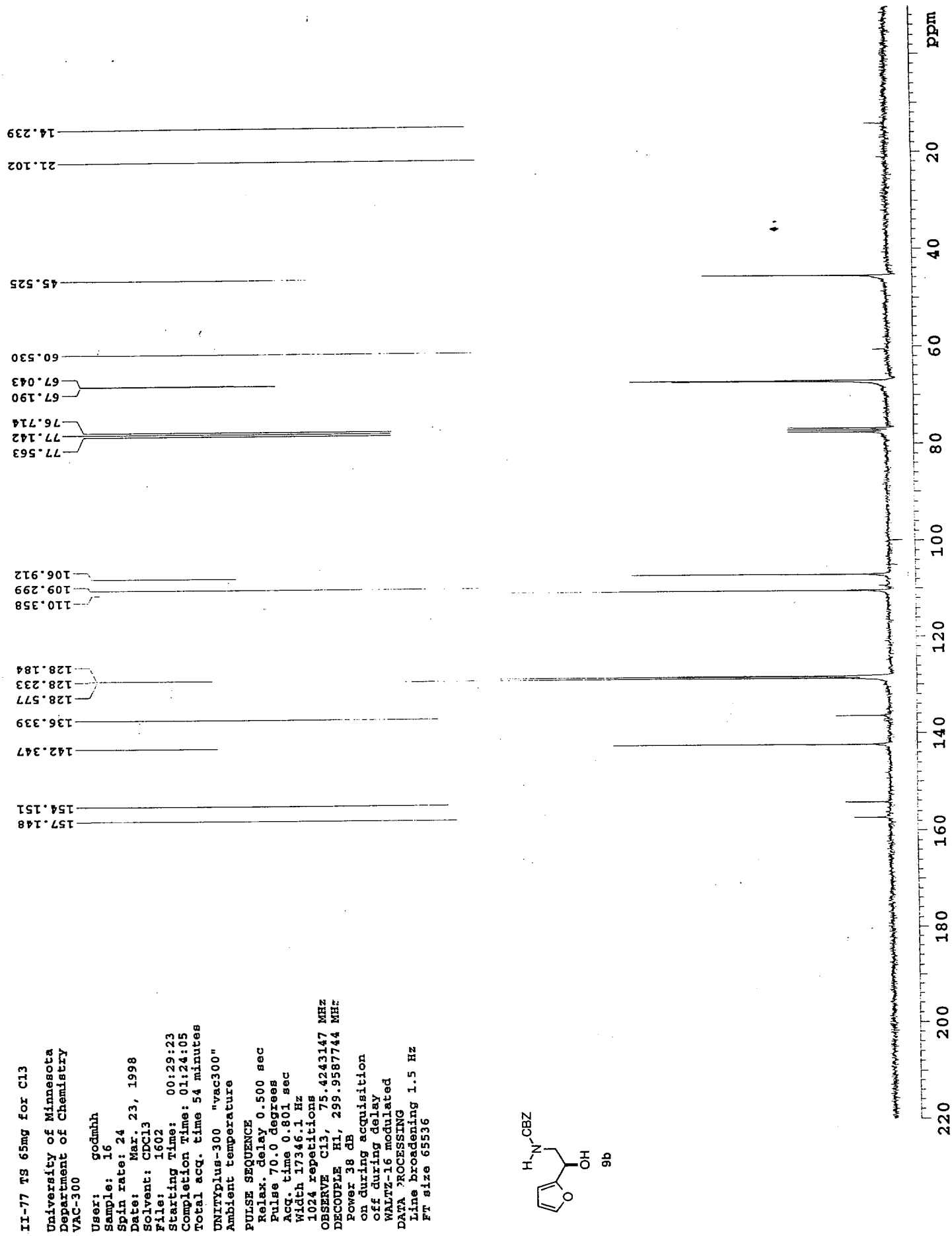
UNITYplus-300 "vac300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 70.0 degrees
Acq. time 0.801 sec
Width 17346.1 Hz
1024 repetitions
OBSERVE C13, 75.4243147 MHz
DECOUPLE H1, 299.9587744 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536



9a


II-77 TS
University of Minnesota
Department of Chemistry
VAC-300
User: godmhh
Sample: 7
Spin rate: 24
Date: Mar. 21, 1998
Solvent: CDCl3
File: 0701
Starting Time: 11:01:37
Completion Time: 11:10:57
Total acq. time 3 minutes
UNITYplus-300 "vac300"
Ambient temperature
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 5998.8 Hz
64 repetitions
OBSERVE H1, 299.9572746 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536
7.348
7.289
7.286
6.329
6.318
6.313
6.284
6.274
5.607
5.590
5.090
5.049
4.790
4.777
3.982
3.673
3.652
3.627
3.611
3.605
3.591
3.517
3.494
3.474
3.452
3.428
ppm
34.83
0.22
11.61
7.10
0.07
23.36
22.64
0.25
0.03
-0.12
0.02
CBZ
OH
9b



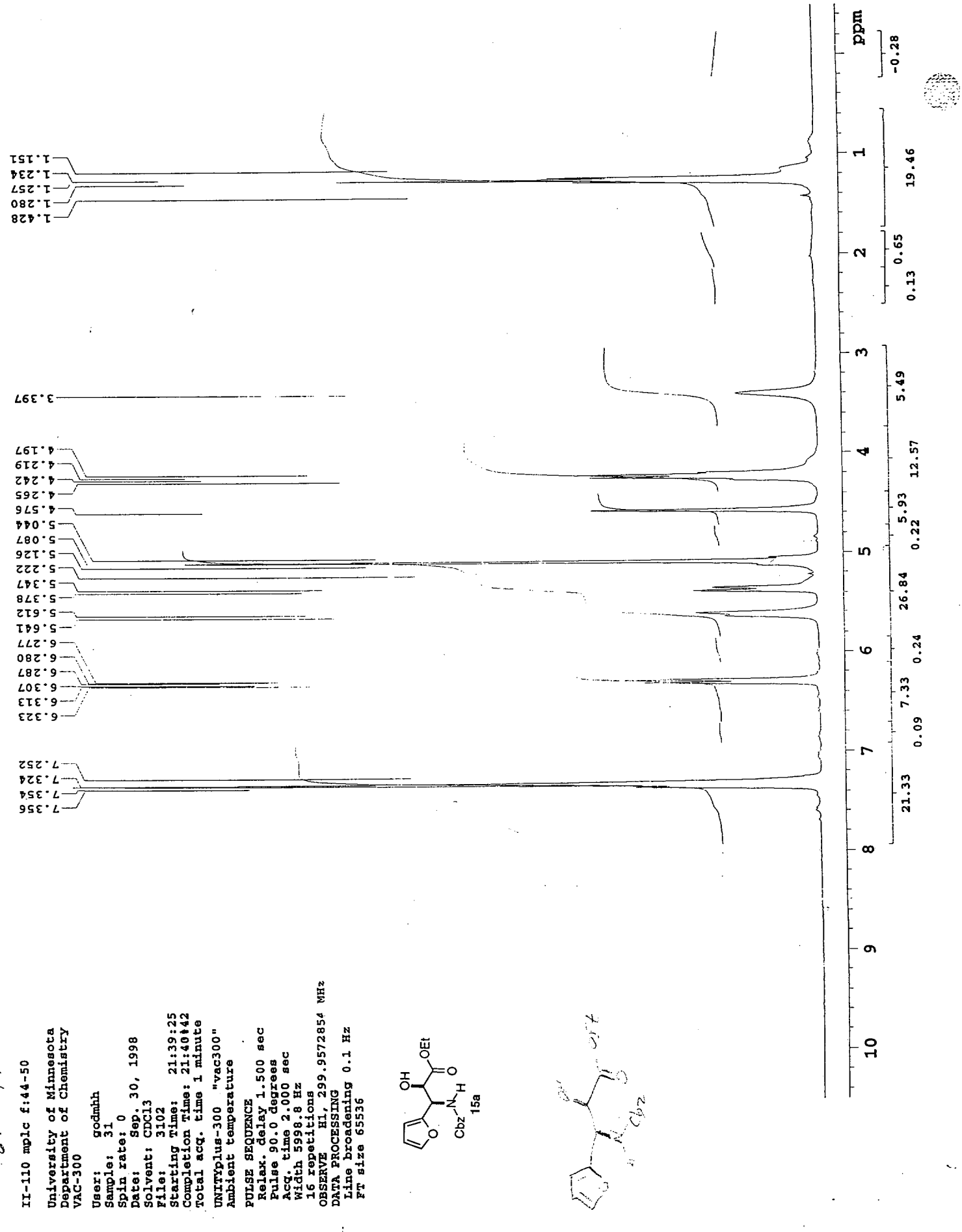
II-77 TS 65mg for C13

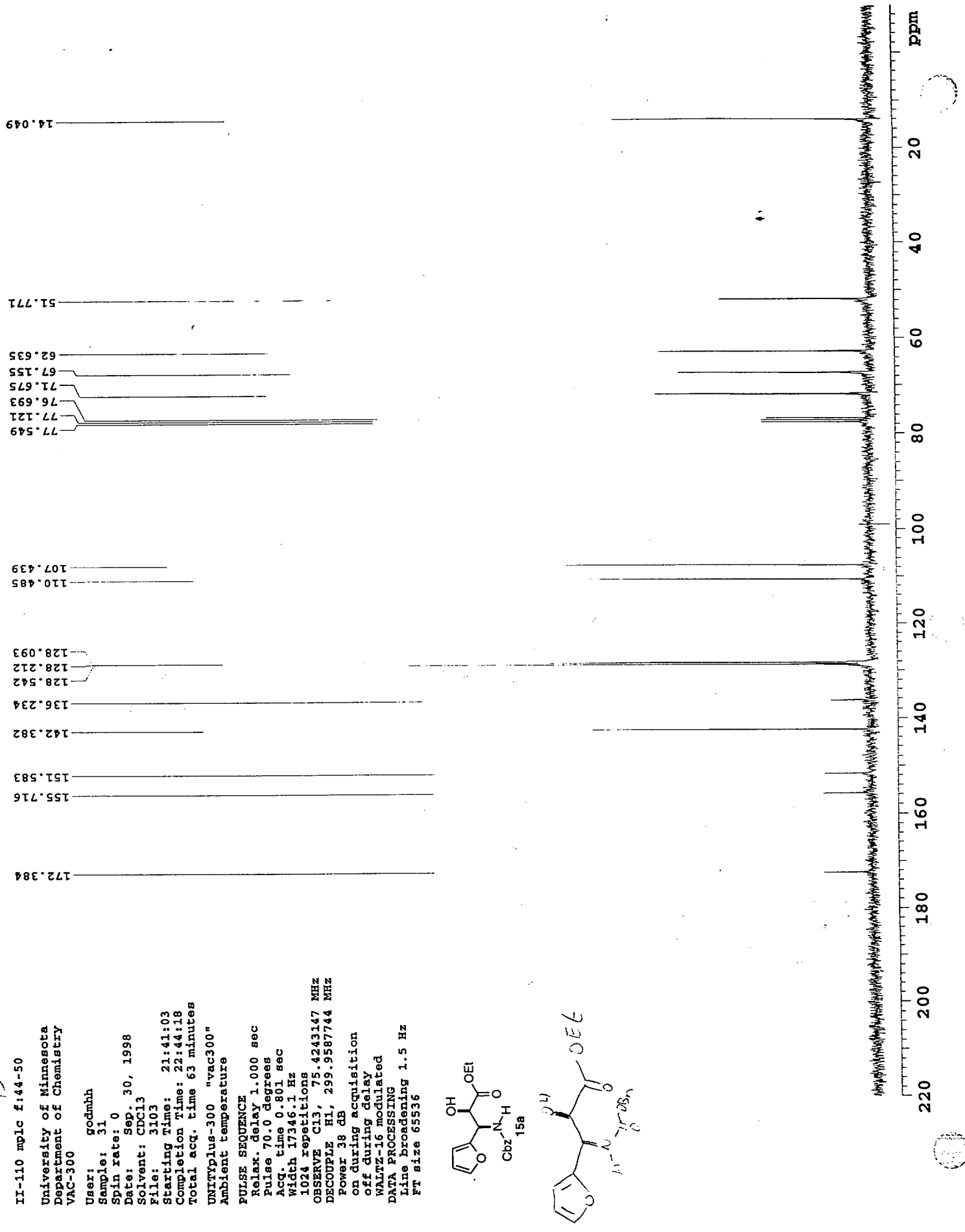
University of Minnesota
Department of Chemistry
VAC-300

User: godmhh
Sample: 16
Spin rate: 24
Date: Mar. 23, 1998
Solvent: CDCl3
File: 1602
Starting Time: 00:29:23
Completion Time: 01:24:05
Total acq. time 54 minutes

UNITYplus-300 "vac300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 0.500 sec
Pulse 70.0 degrees
Acq. time 0.801 sec
Width 17346.1 Hz
1024 repetitions
OBSERVE C13, 75.4243147 MHz
DECOUPLE H1, 299.9587744 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536





(6-10) 15

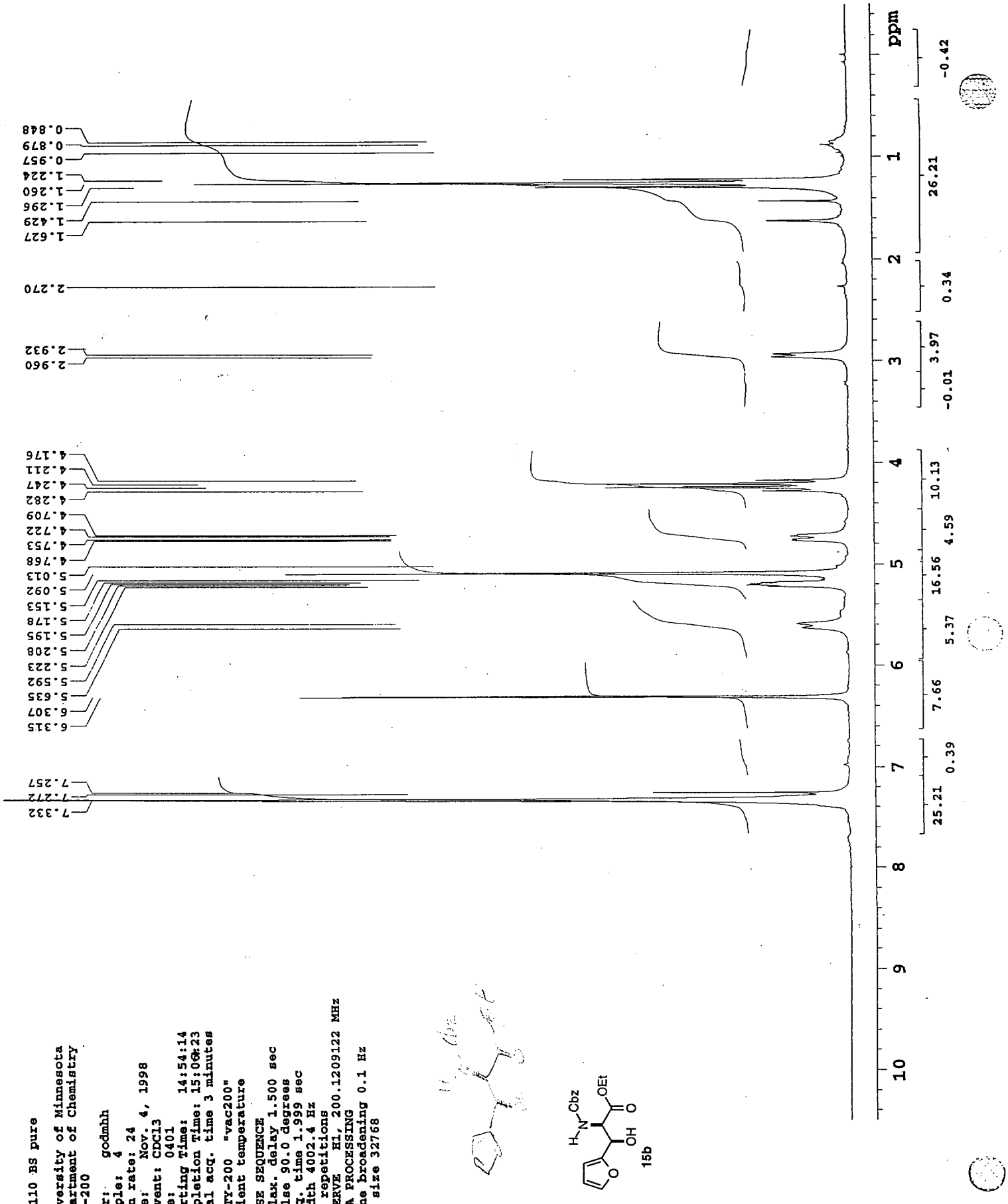
II-110 mplc f:44-50

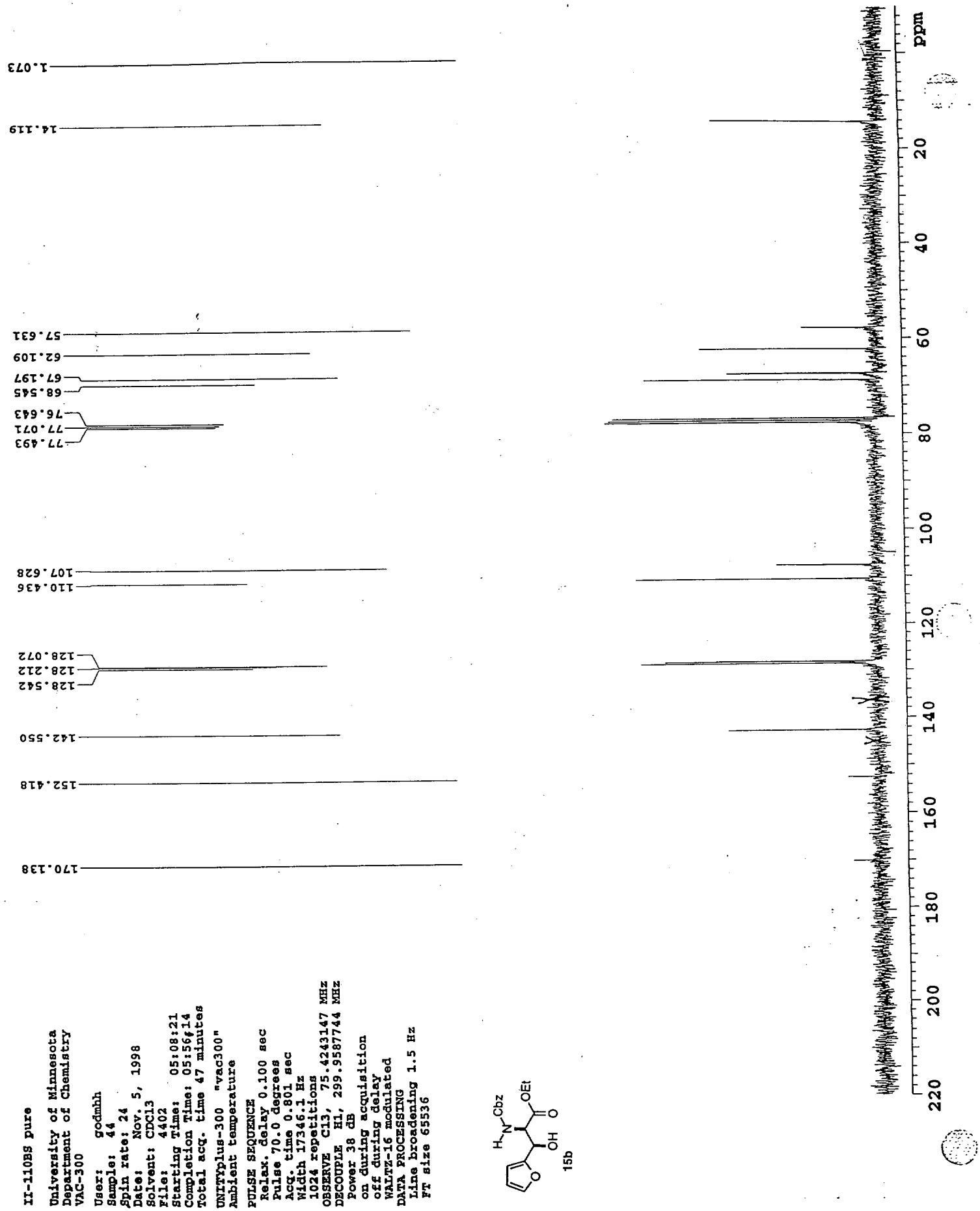
University of Minnesota
Department of Chemistry
VAC-300

User: godmhh
Sample: 31
Spin rate: 0
Date: Sep. 30, 1998
Solvent: CDCl3
File: 3103
Starting Time: 21:41:03
Completion Time: 22:44:18
Total acq. time 63 minutes

UNITYplus-300 "vac300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 70.0 degrees
Acq. time 0.801 sec
Width 17346.1 Hz
1024 repetitions
OBSERVE C13, 75.4243147 MHz
DECOUPLE H1, 299.9587744 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536





II-110BS pure

University of Minnesota
Department of Chemistry
VAC-300

User: godmbh
Sample: 44
Spin rate: 24
Date: Nov. 5, 1998
Solvent: CDCl3
File: 4402
Starting Time: 05:08:21
Completion Time: 05:56:14
Total acq. time 47 minutes

UNITYplus-300 "vac300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 0.100 sec
Pulse 70.0 degrees
Acq. time 0.801 sec
Width 17346.1 Hz
1024 repetitions
OBSERVE C13, 75.4243147 MHz
DECOUPLE H1, 299.9587744 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536

1,2-diol

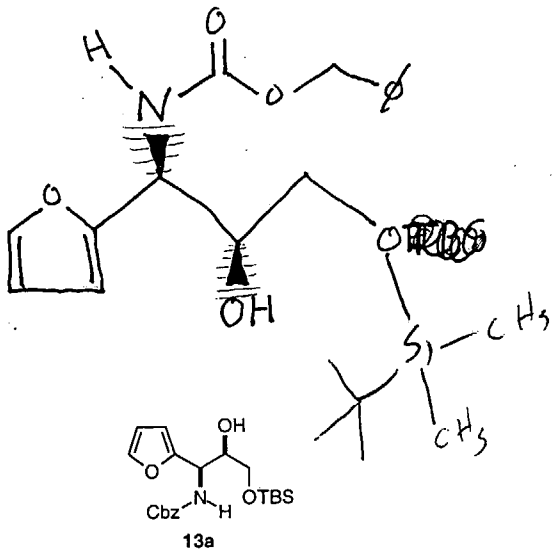
7-8

University of Minnesota
Department of Chemistry
VAC-200

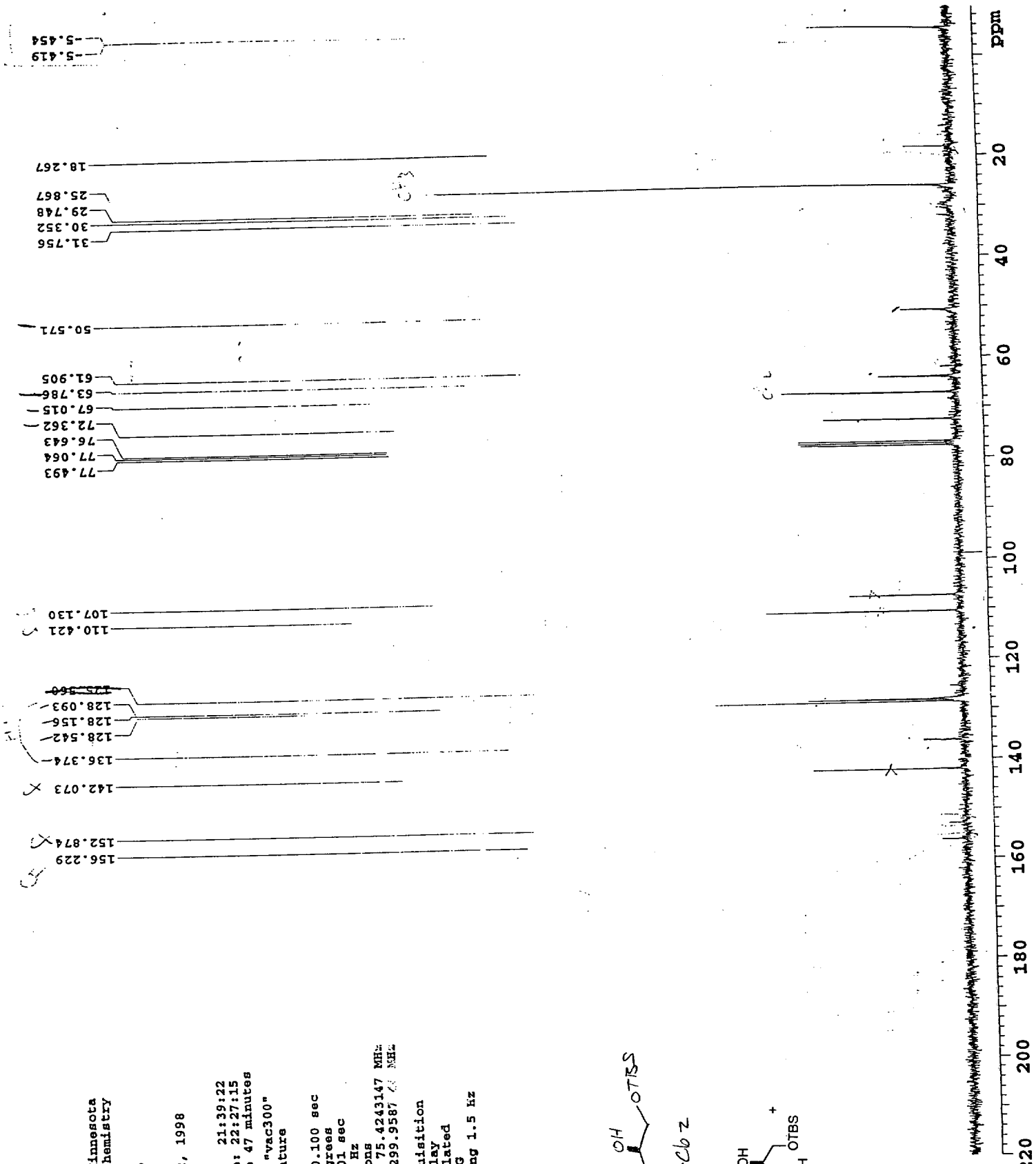
User: godmlb
Sample: 21
Spin rate: 23
Date: Aug. 31, 1998
Solvent: CDCl3
File: 2101
Starting Time: 20:45:46
Completion Time: 20:56:14
Total acq. time 1 minute

UNITY-200 "vac200"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.999 sec
Width 4002.4 Hz
16 repetitions
OBSERVE H1, 200.1209127 MH
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768



13a



1,2-diol

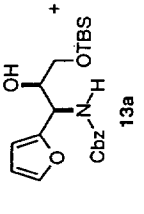
first

University of Minnesota
Department of Chemistry
VAC-300

User: godmlb
Sample: 8
Spin rate: 24
Date: Sep. 2, 1998
Solvent: CDCl3
File: 0803
Starting Time: 21:39:22
Completion Time: 22:27:15
Total acq. time 47 minutes

UNITYplus-300 "vac300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 0.100 sec
Pulse 70.0 degrees
Acq. time 0.801 sec
Width 17346.1 Hz
1024 repetitions
OBSERVE C13, 75.4243147 MHz
DECOUPLE H1, 299.9587 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536



13a