SUPPLEMENTARY INFORMATION

Synthesis of the Amino Sugar from C-1027

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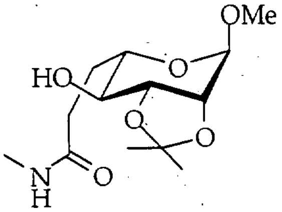
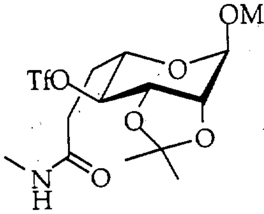
Experimental Part



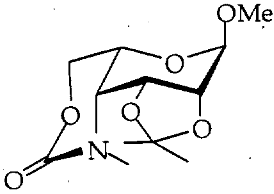
8 (MW=291)

A 25-mL RB flask was charged with **7** (0.264 g, 1.13 mmol), methyl isocyanate (0.066 g, 1.05 mol eq, 1.16 mmol), and triethylamine (5.6 mL, 20 mol-eq, 22.6 mol). The reaction mixture was stirred at 23 °C for 168 h, then quenched by the addition of 1.0 mL of water. The solvents were removed by rotary evaporation and the residue was purified by flash chromatography (SiO_2; 4:1 ethyl acetate:hexane) to give **8** as a thick oil in a yield of 0.325 g, 98.7%. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.9-4.7 (m, 2H), 4.69-4.74 (dd, J=2.93, 12.83 Hz, 1H), 4.07-4.17 (m, 3H), 3.8 (d, J=4.03 Hz, 1H), 3.49-3.61 (m, 2H), 3.4 (s, 3H, -OMe), 2.8 (d, J=4.76 Hz, 3H, -NMe), 1.51 (s, 3H, $-CH_3$), 1.35 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 157.9 (-CONH), 109.5, 77.7, 76.7, 75.6, 69.2, 68.5, 63.7, 55.2, 28.1, 27.8, 26.1 (13 out of 13 observed). IR (neat): 3581 (NH), 3370 (br, OH), 2986, 2938, 2910, 1702, 1538 cm^{-1}.



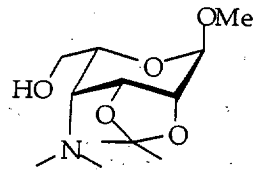
9 (MW=423)

To a solution of the carbamate **8** (0.365 g, 1.25 mmol) in 40 mL of freshly distilled dichloromethane in a 50-ml RB flask at 0 °C was added pyridine (0.052 mL , 4.0 mol-eq, 5.0 mmol) and triflic anhydride (0.318 mL, 1.50 mol-eq, 1.87 mmol), and the reaction mixture was allowed to stir at 0 °C for 1 h. A white precipitate formed after addition of the triflic anhydride and the reaction mixture slowly turned yellow-brown. Then the mixture was quenched by addition of 25 mL of water at 0 °C. The mixture was extracted with dichloromethane (3 x 20 mL) and the combined organic layer was washed with brine (25 mL), dried over $MgSO_4$, and then concentrated by rotary evaporation. Purification by flash chromatography (hexane:ethyl acetate 1:1)gave **9** as light yellow needles in a yield of 0.449 g, 85%, mp 67-71 °C. Compound **9** was quite sensitive to prolonged handling and should be stored at -20 °C under argon or used immediately.



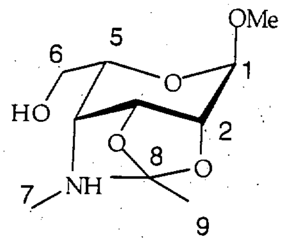
4 (MW=273)

A 50-mL RB flask was charged with a suspension of potassium hydride (0.188 g, 35 wt-%, 2.00 mol-eq, 2.50 mmol) and a catalytic amount (ca 10 mg) of 18-crown-6 in 10 mL of freshly distilled THF. The solution was cooled to -30 °C for 30 min and a solution of **9** (from above reaction without purification; ca 1.25 mmol) was added to the solution of KH dropwise over 5 min and the mixture was stirred for an additional 4 hr at -30 °C. The mixture was quenched with 3 mL of saturated ammonium chloride solution at 0 °C and then allowed slowly to warm to 23 °C. Water (10 mL) was added and the mixture was extracted with dichloromethane (3 x 20 mL); the combined organic layer was washed with brine (20 mL) and dried over $MgSO_4$. Concentration by rotary evaporation furnished a white solid, which was purified by flash chromatography (hexane:ethyl acetate 1:5). Compound **4** was obtained as white crystals in a yield of 0.266 g, 78% overall from **8**; mp 153-154 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ: 4.9 (dd, J=2.93, 7.69 Hz, 1H); 4.5-4.6 (m, 3H); 4.33-4.14 (m, 3H); 3.8 (dd, J=2.93, 8.05 Hz, 1H); 3.46 (s, 3H, -OMe); 3.05 (s, 3H, -NMe); 1.49 (s, 3H, $-CH_3$), 1.34 (s, 3H, $-CH_3$), ^{13}C NMR ($CDCl_3$, 75.5 kHz) δ: 154.0 (CONMe), 110.7, 99.3, 68.9, 66.7, 60.99, 56.3, 52.5, 34.3, 26.2, 24.5 (12 out of 12 observed). IR (neat): 2999, 2914, 2830, 1718, 1442, 1442, 1388 cm^{-1}. EIMS: 273 (M^+).



10 (MW=261)

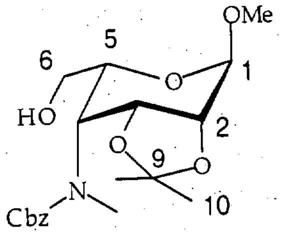
To a 100-ml RB-flask equipped with a reflux condensor was added a solution of of lithium aluminum hydride (83.5 mg, 5.0 mol-eq) in 15 mL of freshly distilled THF. A solution of **4** (0.12 g, 0.44 mmol) in 15 mL of freshly distilled THF was added dropwise at 23 °C. The reaction mixture was heated at reflux for 12 hr, then allowed to cool to 23 °C and the excess LAH was decomposed by sequential addition of 0.1 mL of cold water, 0.1 mL of 15% sodium hydroxide solution, and 0.3 mL of water. Stirring was continued for another 1 hr at 23 °C. The suspension was filtered, and the filtrate was washed with ether (3 x 10 mL). The filtrate washed with brine (10 mL) and dried over $MgSO_4$. Concentration by rotary evaporation provided a colorless oil, which was purified by chromatography (hexane:ethyl acetate 1:5) to give **10** as a colorless oil, 0.114 g, 99%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.5-4.6 (m, 2H); 4.1-4.2 (m, 2H); 3.9-4.1 (m, 3H); 3.44 (s, 3H, -OMe); 2.9 (dd, J=2.93, 6.96 Hz, 1H); 2.38 (s, 6H, -$N(CH_3)_2$); 1.53 (s, 3H, -CH_3), 1.34 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 110.3, 98.9, 75.5, 71.3, 70.6, 62.9, 59.96, 56.2, 44.3, 26.7, 24.7 (11 out of 11 expected peaks were observed). IR (neat): 3470 (br, -OH), 2988, 2937, 2904, 2828, 2776 cm^{-1}. EIMS: 261 (M$^+$)



15 (MW=247)

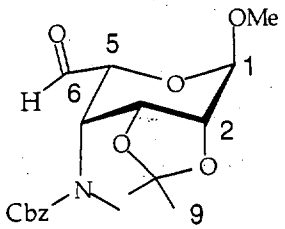
To a 50-ml RB-flask was introduced **4** (0.435 g 1.54 mmol) and 1N NaOH solution (8.0 mL, 8.0 mmol). The solution was heated at reflux for 20 min. During that time, the solid **4** dissolved to leave a light yellow solution. After an additional 4 h at reflux, the reaction mixture was allowed to cool to 23 °C and stir for 20-30 min. Then 1N HCl solution was added dropwise until pH 10 was reached (ca 6.5 mL). The aqueous solution was extracted with dichloromethane (3 x 15 mL). The combined organic extract was washed with cold brine (10 mL) quickly and dried over $MgSO_4$ for 10 min. Concentration under reduced pressure and drying under vacuum for 3 h provided a crude light yellow oil containing the amino sugar **15**. The yield was close to 100% according to the ^{1}H NMR spectrum of crude mixture. The crude mixture can be used directly to next step without purification but a pure sample was be obtained by flash chromatography (4:1 ethyl acetate:hexane with 1% triethylamine). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.75 (s, 1H, H_1); 4.56 (dd, J=4.5, 7.0 Hz, 1H, H_3); 4.08 (d, J=7.2 Hz, 1H, H_2); 3.8-3.9

(m, 3H, H_5&H_6); 3.45 (s, 3H, -OMe); 3.18 (t, J=4.5 Hz, 1H, H_4), 2.57 (s, 3H, H_7), 1.54 (s, 3H, -CH_3), 1.38 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 109.6, 99.1, 74.3, 71.4, 68.4, 64.1, 55.7, 35.4, 26.2, 24.8 (10 out of 10 observed). ^{1}H,^{1}H COSY (500 MHz, $CDCl_3$): H_2/H_3 coupling, H_5/H_6 coupling, H_4/H_7 coupling, H_3/H_4 coupling. IR (neat): 3434 (br), 2985, 2936, 2841, 1457, 1381 cm^{-1}. EIMS 247 (M^+).



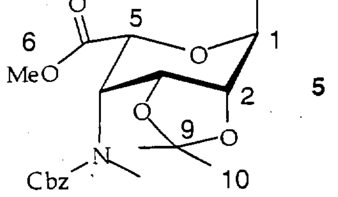
16 (MW=381)

To a 50-ml RB-flask was introduced **15** (0.388 g, 1.57 mmol), potassium carbonate (0.434 g, 3.14 mmol) and a mixture of 2.0 mL of H_2O and 6.0 mL of dioxane. The solution was stirred for 10 min to dissolve all solids and it became light yellow. To the reaction mixture was added carefully dropwise benzyl chloroformate (0.341 g, 2.00 mmol). The reaction mixture was allowed to cool to 23 °C and stir for an additional 10 h at 23 °C. Then an ice-cold 1N HCl solution was added dropwise until pH 8 was reached. The aqueous solution was extracted with dichloromethane (3 x 15 mL). The combined organic extracts were washed with cold brine (10 mL) quickly and dried over $MgSO_4$ for 10 min. Concentration under reduced pressure and drying *in vacuo* for 3 h provided a light yellow solid. The yield was 542 mg, 100%, and >95% pure according to the ^{1}H NMR. The crude mixture was used directly for the next step. A pure sample was obtained from chromatography (1:2 ethyl acetate:hexane with 1% triethylamine). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.3 (m, 5H, H_{arom}), 5.20 (s, 2H, H_8 of Cbz), 5.0-5.2 (m, 1H, H_3), 4.70 (m, 1H, J=4.0 Hz, H_1 two overlappings broad peaks, due to restricted rotation in the Cbz-N bond); 4.5 (dd, J=2.96, 7.25 Hz, 1H, H_4); 4.1 (m, 2H, H_5 and H_2); 3.6-3.8 (m, 2H, H_6); 3.4 (s, 3H, -OMe); 3.08 (s, 3H, -NCH_3), 1.55 (s, 3H, -CH_3), 1.36 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.2, 136.4, 128.4, 128.0, 127.7, 127.4, 126.8, 111.0, 110.6, 100.4, 100.2, 76.7, 76.2, 71.9, 70.3, 69.4, 67.5, 61.5, 61.4, 60.3, 55.9, 53.3, 50.0, 32.5, 26.3, 25.1, 24.9, 14.1 (17 out of 17 observed; every peak was doubled, due to two rigid conformations of **16**). ^{1}H,^{1}H COSY (500 MHz, $CDCl_3$): H_2/H_3 coupling, H_5/H_6 coupling, H_4/H_5 coupling, H_3/H_4 coupling, H_8/H_{arom} coupling. IR (neat): 3468 (br), 3063, 3033, 2986, 2938, 1698 cm^{-1}. EIMS: 381 (M^+)



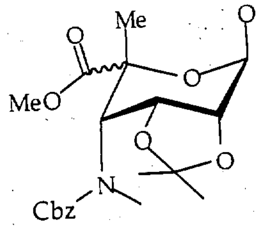
17 (MW=379)

All glassware was dried in an oven (150 °C) for 10 h before use. A solution of dry DMSO (0.224 mL, 2.96 mmol) in dichloromethane (6 mL) was added dropwise to a precooled(dry ice) solution of freshly distilled oxalyl chloride (0.920 mL, 2.0 M, 1.85 mmol) in 15 mL of CH_2Cl_2 at such rate that the reaction temperature remained between -61°C to -59 °C. After 20 min at -61°C to -59 °C, a solution of **16** (0.542 g, 1.42 mmol) in 5.0 mL of dichloromethane was added dropwise at such rate that the temperature remained at -61°C to -59 °C. After 5 min, triethylamine (0.576 g, 5.69 mmol) was added dropwise to maintain the reaction temperature at -61°C to -59 °C. The reaction mixture was warmed to 0 °C, and 20 mL of H_2O was added. The mixture was separated and the aqueous layer was washed with ether (3 x 70 mL). The combined organic extract was washed with brine (30 mL), dried over $MgSO_4$ for 10 min. and concentrated by rotary evaporation. The residue was diluted with 40 mL of ether, washed with 1% HCl (3 x 20 mL) and brine (30 mL). Crude product was purified by flash chromatography (4:1 hexane:ethyl acetate) to obtain 0.550 g of aldehyde **17** as a low mp solid, 93.1% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.8 (s, 1H, H_6), 7.3 (m, 5H, H_{arom}), 5.3 (d, 1H, J=7 Hz, H_1), 5.25 (d, J=3.5 Hz, 1H, H_5), 5.0-5.2 (m, 2H, $H_{7\ \text{from Cbz}}$), 4.6 (d, J=3.6 Hz, 1H, H_4); 4.5 (dd, J=2.0, 7.5 Hz, 1H, H_3); 4.25 (d, 1H, J=6 Hz, H_2); 3.5 (s, 3H, -OMe); 2.98 (s, 3H, $-NCH_3$),1.55 (s, 3H, $-CH_3$), 1.36 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 201.2, 200.4, 156.7, 155.7, 136.4, 136.1, 128.4, 127.9, 127.6, 111.4, 99.8, 76.4, 73.7, 73.0, 71.2, 71.0, 67.7, 67.5, 56.0, 55.7, 52.7, 32.5, 32.4, 26.6, 25.2 (17 out of 17 observed; every peak was doubled, due to two configurations of **17**). ^{1}H,^{1}H COSY (500 MHz, $CDCl_3$): H_2/H_3 coupling, H_5/H_6 coupling, H_4/H_5 coupling, H_3/H_4 coupling. IR (neat): 3065, 2938, 1773, 1701, 1450 cm^{-1}. EIMS: 379 (M^+)



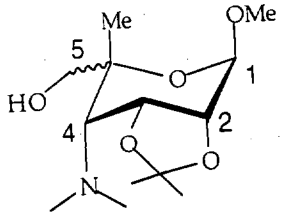
5 (MW=409)

The oxidation of aldehyde **17** to the ester **5** was carried out more than 10 times on scales ranging from 0.5 to 1.5 mmol according to the following procedure. The yields ranged from 62-84%, with an average of 72%. The aldehyde **17** (1 mmol) was dissolved in 15 mL of distilled methanol and ice-cold solutions of KOH (2.2 mmol) in MeOH (5 mL) and iodine (1.12 mmol) in methanol (5 mL) were successively added at 0 °C. KOH and iodine should be added separately and rapidly to give the active oxidant (HOI); the order of addition can be reversed without effect on the yield. After being stirred for an additional 45 min at 0 °C, the reaction mixture was warmed to 23 °C, and 20 mL of H_2O and 20 mL of ether were added. The mixture was poured into a separatory funnel and 10 mL of saturated $Na_2S_2O_3$ was added. The mixture was separated and the aqueous layer was washed with ether (3 x 70 mL). The combined organic extracts were washed with brine (30 mL), dried over $MgSO_4$ for 10 min and concentrated by rotary evaporation. The residue was diluted with 40 mL of ether, washed with 1% HCl (3 x 20 mL) and brine (30 mL). The crude product was purified by flash chromatography (4:1 hexane:ethyl acetate) to obtain the methyl ester sugar **5** as an oil (0.62-0.84 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.3 (m, 5H, H_{arom}), 5.17 (dd, 1H, J=3.5, 9.25 Hz, H_4), 5.1-5.2 (m, 2H, H_8 from Cbz), 4.94 (s, 1H, H_1); 4.65 (d, J=6 Hz, 1H, H_5); 4.5 (ddd, 1H, J=6, 4.5, 7.0 Hz, H_3); 3.696 (s, 3H, H_6, -OMe); 3.443 (s, 3H, H_{12}, -OMe); 3.01 (s, 3H, H_7, $-NCH_3$), 1.55 (s, 3H, $-CH_3$), 1.36 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.8, 169.6, 157.0, 156.3, 136.6, 136.5, 128.3, 128.2, 127.8, 127.6, 127.5, 110.5, 110.2, 99.5, 99.4, 99.4, 99.3, 74.5, 74.3, 70.9, 70.8, 67.3, 67.1, 67.1, 67.0, 66.7, 55.9, 55.8, 55.7, 52.1, 52.14, 52.0, 50.5, 50.3, 32.1, 32.0, 31.9, 25.7, 25.6, 24.9, 24.8, 24.7 (18 out of 18 expected peaks were observed, every peak was doubled, due to two conformations of **5**). ^{1}H,^{1}H COSY (500 MHz, $CDCl_3$): H_2/H_3 coupling, H_4/H_5 coupling, H_3/H_4 coupling, H_1/H_3 coupling. IR (neat): 3065, 2938, 1773, 1701, 1450 cm^{-1}. EIMS: 409 (M^+).



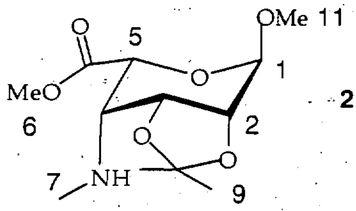
6a/b (MW=423)

All glassware was dried in an oven (150 $^{\circ}$C) over 10 h before use. A 25-ml RB-flask was charged with a solution of **5** (31 mg, 0.076 mmol) in 3 mL of THF and 0.01 ml HMPA under argon. The solution was cooled to -78 $^{\circ}$C and potassium bis(trimethylsilyl)amide (0.114 mL, 1.50 mol-eq, 0.114 mmol) was added dropwise to the cooled solution at a rate such that the reaction temperature remained near -70 $^{\circ}$C. After 2 min, a solution of methyl iodide (215 mg, 0.152 mmol) in 1.0 mL of THF was added dropwise at a rate such that the temperature remained near -70 $^{\circ}$C. After 35 min, 2 mL of saturated NH_4Cl was added dropwise. The reaction mixture was warmed to 0 $^{\circ}$C, and 10 mL of H_2O was added. The mixture was separated and the aqueous layer was washed with ether (3 x 10 mL). The combined organic extract was washed with brine (10 mL), dried over $MgSO_4$ for 10 min, and concentrated by rotary evaporation. The residue was diluted with 20 mL of ether, and the ether solution was washed with ice cold 1% HCl (3 x10 mL) and brine (10 mL). The crude product was purified by flash chromatography (4:1 hexane:ethyl acetate) to obtain **6a/b** as a low mp yellow solid with a yield of 24 mg, 77 %. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.3 (m, 5H, H_{arom}), 5.2 (m, 3H), 4.5 (m, 2H), 4.2 (m, 2H); 3.6 (s, 3H, $-OCH_3$); 3.4 (s, 3H, $-OCH_3$), 3.0 (s, 3H, $-NCH_3$), 1.5 (s, 3H, $-CH_3$), 1.32 (s, 3H, $-CH_3$), 1.2 (s, 3H, $-CH_3$). IR (neat): 2988, 2939, 1701, 1454, 1383 cm^{-1}. EIMS 423 (M^+)



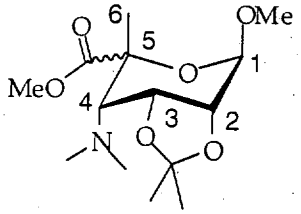
18a/b (MW=275)

The Cbz-methyl ester sugar **6a/b** (0.116 g, 0.284 mmol) was dissolved in 5.0 mL of freshly distilled THF, placed in a 25-ml RB-flask which was then immersed in a water bath at 25 $^{\circ}$C. A gentle stream of argon was passed over the reaction mixture and thorough agitation was provided by a Vitro stirrer. To the flask was added dropwise $LiAlH_4$ solution in ether (1.00 M, 0.464 mL, 0.464 mmol. After 4 h, the mixture was cooled to 0 $^{\circ}$C. To the mixture was added sequentially 0.5 mL of water, 0.5 mL of 3N NaOH and 1.5 mL of water. After 30 min, the mixture was filtered through a pad of Celite, rinsing with ether (3 x 10 mL) and the filtrate was concentrated by rotary evaporation. Flash chromatography of the residue (4:1 ethyl acetate:hexane) gave the product mixture (ca 1:1 **18a/b**) as a light yellow oil (0.068 g, 90 %). A sample of **18a** isomerically pure was obtained from reduction of **22a** (see text) and was characterized as follows. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 4.66 (s, 1H, H$_1$), 4.65 (m, 1H, H$_2$), 4.1 (m, 1H, H$_3$), 3.8 (dd, J=6.6, 93 Hz, H$_5$); 3.4 (s, 3H, -OCH$_3$), 2.9 (d, 1H, J=2.4 Hz, H$_4$); 2.5 (s, 3H, -NCH$_3$).1.539 (s, 3H, -CH$_3$), 1.42 (s, 3H, -CH$_3$), 1.36 (s, 3H, -CH$_3$). ^{13}C NMR (CDCl$_3$, 125 kHz) δ: 110.39, 101.88, 77.539, 76.068, 69.704, 67.17, 64.609, 56.129, 45.275, 26.833, 26.469, 24.917 (12 out of 12 expected peaks were observed). IR (neat): 3403(br), 2981, 2934, 1646, 1454, 1380 cm^{-1}. EIMS: 275 (M$^+$). Compound **18b** was not obtained in a pure state and the structure is inferred from the method of synthesis and the spectral data for the mixture of **18a/b**.



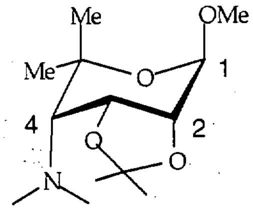
21 (MW=275)

The Cbz-methyl ester sugar **5** (0.116 g, 0.284 mmol) was dissolved in 5.0 mL of absolute ethanol in a 25-ml RB-flask which was immersed in a water bath at 25 °C. A gentle stream of argon was passed over the reaction mixture and thorough agitation was provided by a Vitro stirrer. The catalyst, 5% palladium-on-carbon (0.116 g), was added followed by 1,4-cyclohexadiene (0.135 ml, 1.42 mmol). After 4 h, the mixture was filtered through a pad of Celite, rinsed with ether (3 x 10 mL, and the filtrate was concentrated by rotary evaporation. The product **21** (68 mg, 86.8%) was obtained by flash chromatography (4:1 ethyl acetate:hexane). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.96 (d, 1H, J=2.2 Hz, H$_1$), 4.6 (dd, J=2.5, 3.75 Hz, 2H, H$_{3,5}$); 4.1 (dd, 1H, J=2.2, 6.59 Hz, H$_2$); 3.81 (s, 3H, H$_6$, -OMe); 3.488 (s, 3H, H$_{11}$, -OMe); 3.1 (br, 1H, H$_4$), 2.602 (s, 3H, H$_7$, -NCH$_3$).1.475 (s, 3H, -CH$_3$), 1.348 (s, 3H, -CH$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 170.8, 109.9, 99.1, 74.9, 72.8, 69.2, 56.2, 56.1, 51.9, 35.5, 25.7, 24.9 (12 out 12 expected peaks observed). IR (neat): 3367 (br), 2985, 2936, 1738, 1453 cm^{-1}.



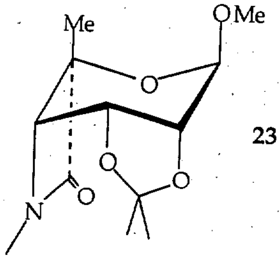
22a/b (MW=303)

The mixture **22a/b** was prepared as a 1:1 mixture of epimers from **21** exactly according to the experimental procedure for preparation of **6a/b** (above). An isomerically pure sample of **22a** was obtained by cleavage (NaOMe) of β-lactam **23**. Characterization of **22a**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.92 (d, J=2.92 Hz, 1H, H$_1$), 4.55 (dd, J=2.2, 5.86 Hz, 1H, H$_3$), 3.98 (dd, J=3.66, 5.86 Hz, 1H, H$_2$), 3.8 (s, 3H, -OCH$_3$); 3.52 (s, 3H, -OCH$_3$); 3.1 (d, J=2.2 Hz, 1H, H$_4$), 2.48 (s, 3H, -NCH$_3$).1.612 (s, 3H, -CH$_3$), 1.478 (s, 3H, -CH$_3$), 1.326 (s, 3H, -CH$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 173.5, 110.5, 100.3, 77.4, 69.5, 66.4, 56.6, 51.8, 45.4, 42.1, 26.4, 26.2, 25.4 (13 out 13 expected peaks observed). IR (neat): 2988, 2939, 1701, 1454, 1383 cm^{-1}. EIMS: 303 (M$^+$). Epimer **22b** could not be obtained in a pure state and the structure is inferred from the method of synthesis and the characteristic peaks in the ^{1}H NMR spectrum of the mixture **22a/b**.



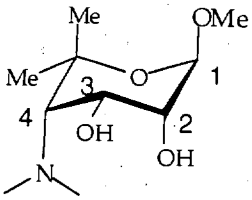
20 (MW=259)

(**a**) *Preparation of the mesylate from **22a/b**.* All glassware was dried in an oven (150 °C) over 10 h before use. A 25-ml RB-flask was charged with NaH (3.84 mg, 95%, 0.16 mmol) and 5 mL of freshly distilled ether under argon, and then immersed in an ice-water bath. A solution of **22a/b** (0.022 g, 0.080 mmol) in 0.5 mL of ether was introduced into the flask via syringe dropwise over 1 min. After 1 h at 0 °C, mesyl chloride (10.1 mg in 0.5 mL of ether) was added via syringe. After being stirred for 50 min at 0 °C, the mixture was carefully quenched with water (10 mL), the layers were separated, and the water layer was washed with ether (3 x 10 mL). The combined ether solution was dried over $MgSO_4$ and concentrated by rotary evaporation. The crude mesylate product **19a/b** (26 mg, 92.2%) was used in next step without chromatography. (**b**). *Preparation of **20**.* A 25-ml RB-flask was charged with $LiAlH_4$ (0.578 mL, 1.00 M, 0.578 mmol) and 5 mL of freshly distilled THF and then immersed in an ice-water bath. A solution of **19a/b** (0.051 g, 0.144 mmol) in 1 mL of THF was introduced into the flask via syringe dropwise over 5 min. After 4 h at 0 °C, to the solution was added sequentially 0.2 mL of water, 0.2 mL of 3N NaOH solution and 0.6 mL of water. After being stirred for 30 min at 0 °C, the mixture was filtered through a pad of Celite, washed with ether (3 x 10 mL) and the combined ether solutions were concentrated by rotary evaporation. The product **20** (0.027 g, 72%) was present in >95% purity without chromatography (^{1}H NMR analysis). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.86 (d, 1H, J=4.4 Hz, H_1), 4.58 (dd, J=2.93, 6.59 Hz, 1H, H_3); 4.05 (dd, 1H, J=5.13, 6.59 Hz, H_2); 3.56 (s, 3H, -OMe); 2.96 (d, J=2.93 Hz, 1H, H_4), 2.53 (s, 6H, -$N(CH_3)_2$).1.61 (s, 3H, -CH_3), 1.48 (s, 3H, -CH_3), 1.45 (s, 3H, -CH_3), 1.34 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 110.5, 100.3, 77.4, 69.6, 66.5, 57.7, 51.9, 45.6, 26.5, 26.3, 25.4, 24.2 (12 out of 12 expected peaks observed).



23 (MW=257)

Treatment of **21** exactly according to the procedure for the formation of **6a/b** from **5** (above) but with LiTMP as base produced two fractions on flash chromatography (4:1 hexane:ethyl acetate). The first fraction eluted as a mixture of **22a/b** (42%) and the second fraction was identified as β–lactam **23** (35 %). Characterization of **23**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.6 (d, J=7.21 Hz, 1H, H$_1$), 4.45 (dd, J=5.66, 8.62 Hz, 1H, H$_3$), 4.1 (dd, J=7.21, 8.65 Hz, 1H, H$_2$), 3.81 (d, J=5.66 Hz, H$_4$); 3.61 (s, 3H, OCH$_3$); 2.95 (s, 3H, -NCH$_3$),1.563 (s, 3H, -CH$_3$), 1.502 (s, 3H, -CH$_3$), 1.336 (s, 3H, -CH$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 169.0, 109.1, 101.1, 86.1, 73.9, 73.9, 60.2, 57.0, 29.1, 26.0, 23.4, 18.5 (12 out 12 expected peaks observed). IR (neat): 2981, 2935, 2361, 1760, 1382 cm^{-1}. EIMS: (M$^+$) 257. X-ray data: see below.

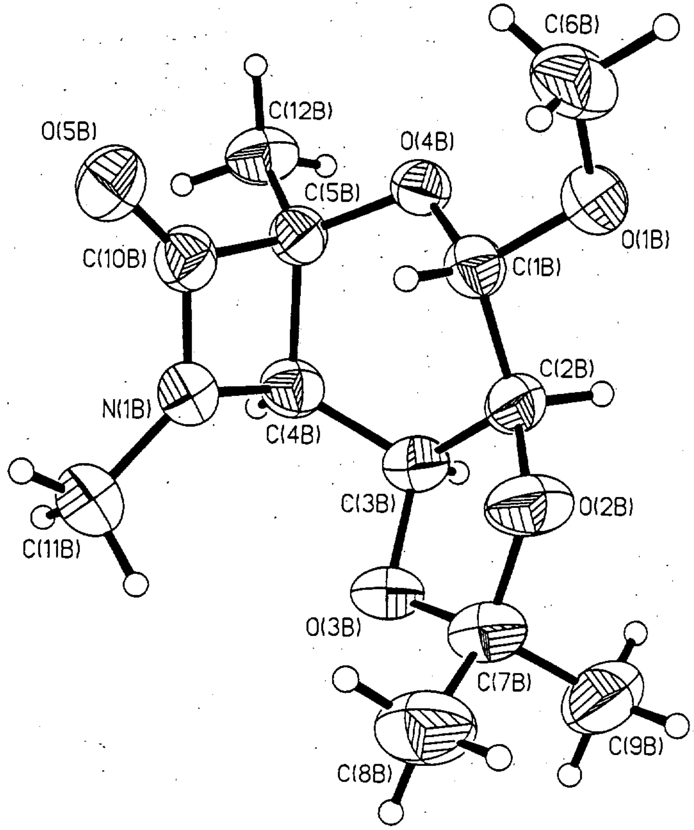


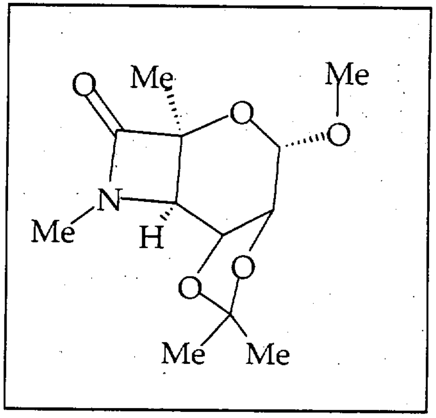
2 (MW=219)

The protected sugar **20** (0.015 g, 0.0579 mmol) was dissolved in 3.0 mL of dry acetonitrile in a 25-ml RB-flask and immersed in a water bath at 25 °C. A gentle stream of argon was passed over the reaction mixture and thorough agitation was provided by a Vitro stirrer. An HF solution (35 wt-%, 0.1 mL) was added and the reaction proceeded for an additional 40 min. The mixture was filtered through a pad of Celite, washed with ether (3 x 10 mL) and concentrated by rotary evaporation. The product **2** (6.8 mg, 53%) was obtained without chromatography, mp 118-119.5 °C, and was estimated at >95% purity by ^{1}H NMR. Recrystallization of samples collected from several runs gave the analytical sample of mp 123-123.5 °C. Literature:[1] mp 120-121 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.61 (d, 1H, J=7.84 Hz, H$_1$), 4.45 (dd, J=3.3, 2.95 Hz, 1H, H$_3$); 3.49 (s, 3H, -OMe); 3.25 (dd, 1H, J=3.1, 7.5 Hz, H$_2$); 2.45 (s, 6H, H$_7$, -N(CH$_3$)$_2$), 2.30 (d, J=2.95 Hz, 1H, H$_4$),1.55 (s, 3H, -CH$_3$), 1.30 (s, 3H, -CH$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 108.4, 78.7, 67.4, 64.3, 54.4, 49.7, 43.2, 19.1, 18.2 (9 out of 9 expected peaks observed). For comparison of these spectral data with those previously reported for **2** see the text, footnote 27.

(1) Iida, K-i.; Ishii, T.; Hirama, M. *Tetrahedron Lett.*, **1993**, *34*, 4079-4082.

X-ray Diffraction Data for Compound **23**:





ORTEP presentation of Compound **23**

A. Experimental: **pages 1-3**
B. Tables 1-6 of crystal data and structure refinement: **pages 1-13**

Experimental:

A colorless prism cut to 0.15 mm x 0.25 mm x 0.25 mm in size was mounted on a glass fiber with silicone grease and then transferred to a Nonius KappaCCD diffractometer equipped with an MSC X-stream cryosystem and Mo Kalpha radiation (lambda = 0.71073 Angstroms). Four hundred and sixty frames of data were collected at 200(2) K with an omega oscillation range of 1.0 deg/frame and an exposure time of 40 sec/deg.[REF1] A total of 28998 reflections (thetamax = 27.47 deg) were indexed, integrated and corrected for Lorentz and polarization effects using DENZO-SMN and SCALEPACK.[REF2] Data reduction yielded 6191 unique reflections (Rint = 0.052) of which 4062 had I > 2sigma(I). Postrefinement of the unit cell parameters gave a = 9.8961(2) Angstroms, b = 9.2301(2) Angstroms, c = 15.2748(3) Angstroms, alpha = 90 deg, beta = 104.301(1) deg, gamma = 90 deg, and V = 1351.99(5) cubic Angstroms. Axial photographs and systematic absences were consistent with the compound having crystallized in the monoclinic space group P2(1) or P2(1)/m. The former space group P2(1) (No. 4) was selected based on an observed mean |E*E-1| value of 0.786 (versus the expectation values of 0.968 and 0.736 for centric and noncentric data, respectively).

The structure was solved by direct methods and refined by full-matrix least-squares on F^2^ using SHELXTL.[REF3] All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(Cmethyl), and their coordinates were allowed to ride on their respective carbons. The weighting scheme employed was w = 1/[\s^2^(Fo^2^) + (0.0603P)^2^ + 0.3348P] where P = (Fo^2^ + 2Fc^2^)/3. The refinement converged to R(F) = 0.0477, wR(F^2^) = 0.1069, and S = 1.049 for 4062 reflections with I > 2sigma(I), and R(F) = 0.0922, wR(F^2^) = 0.1318, and S = 1.034 for 6191 unique reflections, 357 parameters, and 1 origin defining restraint.[REF4] The maximum |delta/sigma| in the final cycle of least-squares was less than 0.001, and the residual peaks on the final difference-Fourier map ranged from -0.214 to 0.184 electrons/cubic Angstroms. Scattering factors were taken from the International Tables for Crystallography, Volume C.[REF5,REF6].

The Flack absolute structure parameter refined to 0.1(10) (versus the expectation values of 0 for the correct hand and 1 for the wrong hand). Due to the large estimated standard deviation associated with the refined parameter, however, the hand of the molecule(s) cannot be reliably assigned with certainty.[REF7]

REF1 COLLECT Data Collection Software. Nonius B.V. Rontgenweg 1, P.O. Box 811, 2600 AV, Delft, The Netherlands, 1998.

REF2 Otwinowski, Z.; Minor, W., "Processing of X-ray Diffraction Data Collected in Oscillation Mode", Methods Enzymol. 1997, 276, 307-326.

REF3 Sheldrick, G. M. SHELXTL Version 5.04. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA, 1996.

REF4 R(F) = R1 = SIGMA(||Fo|-|Fc||) / SIGMA|Fo|, wR(F^2^) = wR2 = [SIGMA(w(Fo^2^-Fc^2^)^2^) / SIGMA(w(Fo^2^)^2^)]^1/2^, and S = Goodness-of-fit on F^2^ = [SIGMA(w(Fo^2^-Fc^2^)^2^) / (n-p)]^1/2^, where n is the number of reflections and p is the number of parameters refined.

REF5 Maslen, E. N.; Fox, A. G.; O'Keefe, M. A., International Tables for Crystallography: Mathematical, Physical and Chemical Tables, Vol C, Chapter 6, Wilson, A. J. C., Ed.; Kluwer, Dordrecht, The Netherlands, 1992; pp. 476-516.

REF6 Creagh, D. C.; McAuley, W. J., International Tables for Crystallography: Mathematical, Physical and Chemical tables, Vol C, Chapter 4, Wilson, A. J. C., Ed.; Kluwer, Dordrecht, The Netherlands, 1992; pp. 206-222.

REF7 Flack, H. D. Acta Crystallographica, Section A 1983, 39, 876-881.

Miscellaneous:

1. The compound examined crystallizes in the chiral space group P2(1) (No. 4) with 4 molecules in the unit cell, i.e., 2 molecules per asymmetric unit. An "A" or "B" has been appended to the nonhydrogen atom labels of those 2 molecules to aid in distinguishing one from the other.
2. The (1S,2S,3S,4R,5S) isomer is depicted in all of the plots included with this report. However, as indicated above, the absolute structure cannot be unequivocally assigned based on the intensity data. The enantiomer, i.e., (1R,2R,3R,4S,5R) gives an identically good fit of the data. One is therefore encouraged to restrict all discussions to matters of relative stereochemistry only.
3. The title compound is based on a (C3N-C3O2-C5O) fused-ring system. The C3N moiety corresponds to the beta-lactam part of the molecule, the C3O2 moiety corresponds to the 1,3-dioxolo portion of the molecule, and the C5O moiety is the pyran ring itself. A number of least-squares planes and interplanar angles of possible relevance may be computed and are tabulated below (angles in degrees):

Atoms defining Plane 1	Atoms defining Plane 2	Interplanar Angle

O(4A),C(3A),C(4A),C(5A)	N(1A),C(4A),C(5A),C(10A)	117.3(1)
O(4B),C(3B),C(4B),C(5B)	N(1B),C(4B),C(5B),C(10B)	117.2(1)
C(1A),C(2A),C(3A),C(4A)	O(2A),O(3A),C(2A),C(3A)	119.4(1)
C(1B),C(2B),C(3B),C(4B)	O(2B),O(3B),C(2B),C(3B)	119.4(2)
O(2A),O(3A),C(2A),C(3A)	O(2A),O(3A),C(7A)	144.9(2)
O(2B),O(3B),C(2B),C(3B)	O(2B),O(3B),C(7B)	149.0(2)

Please refer to the labelled plots included with this report to ascertain which portions of the molecule are being used to define the planes.

4. A number of pyranosyl compounds containing fused beta-lactam rings have been crystallographically characterized by others. For examples of beta-lactam fusion to the C(1) and C(2) positions of the pyran ring, please see: Journal of Chemical Crystallography, 1995, 25, 693-699, and Carbohydrate Research, 1990, 203, 183-194. All of these structurally characterized examples have nitrogen attached to the C(1) position and the C=O attached to the C(2) position. The molecule presented in this report, exhibits the alternate fusion mode, i.e., the nitrogen and C=O positions are swapped.
5. As indicated in Misc #3 above, the 5-membered dioxolo rings are not completely planar, but are folded along their O...O vectors. The dioxolo ring in Molecule B is slightly more planar than in Molecule A. The C(7B) atom is 0.449(4) Angstroms from the plane defined by [O(2B), O(3B), C(2B), C(3B)], while the C(7A) atom is 0.500(4) Angstroms from the [O(2A), O(3A), C(2A), C(3A)] plane.
6. The nitrogen atoms in the beta-lactam rings are not planar, but pyramidal. The N(1A) atom is displaced by 0.150(3) Angstroms off of the plane defined by [C(4A), C(10A), C(11A)]. The N(1B) atom is displaced by 0.130(3) Angstroms from [C(4B), C(10B), C(11B)]. The nitrogen atoms in the literature reference Journal of Chemical Crystallography, 1995, 25, 693-699 are significantly more planar, i.e., roughly 0.04 Angstroms from the planes defined by their 3 neighboring atoms.

Table 1. Crystal data and structure refinement for C12H19NO5.

Formula	C12 H19 N O5
Formula weight	257.28
Temperature	200(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1) (No. 4)
Unit cell dimensions	a = 9.8961(2) A alpha = 90 deg.
	b = 9.2301(2) A beta = 104.301(1) deg.
	c = 15.2748(3) A gamma = 90 deg.
Volume, Z	1351.99(5) A^3, 4
Density (calculated)	1.264 Mg/m^3
Absorption coefficient	0.098 mm^-1
F(000)	552
Crystal size	0.25 x 0.25 x 0.15 mm
Theta range for data collection	1.38 to 27.47 deg.
Limiting indices	-12<=h<=12, -11<=k<=11, -19<=l<=19
Reflections collected	28998
Independent reflections	6191 [R(int) = 0.0520]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6191 / 1 / 335
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1069
R indices (all data)	R1 = 0.0922, wR2 = 0.1318
Absolute structure parameter	0.1(10)
Largest diff. peak and hole	0.184 and -0.214 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for C12H19NO5. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1A)	7688(2)	8031(2)	5940(1)	47(1)
O(2A)	9048(2)	5101(2)	6086(1)	48(1)
O(3A)	7819(2)	3037(2)	5854(1)	44(1)

O(4A)	5687(2)	6779(2)	5882(1)	40(1)
O(5A)	5554(2)	5554(2)	7887(1)	53(1)
N(1A)	6006(2)	3780(2)	6901(1)	43(1)
C(1A)	7175(3)	6705(3)	6144(2)	39(1)
C(2A)	7688(3)	5543(3)	5609(2)	40(1)
C(3A)	6823(3)	4128(3)	5466(2)	39(1)
C(4A)	5611(3)	4064(3)	5925(2)	38(1)
C(5A)	5046(3)	5547(3)	6160(2)	38(1)
C(6A)	7434(4)	9190(3)	6492(2)	58(1)
C(7A)	9162(3)	3603(3)	5897(2)	43(1)
C(8A)	10187(3)	2920(4)	6691(2)	64(1)
C(9A)	9568(3)	3393(4)	5014(2)	55(1)
C(10A)	5573(3)	5065(3)	7150(2)	41(1)
C(11A)	6267(4)	2415(3)	7382(2)	61(1)
C(12A)	3498(3)	5769(4)	5894(2)	54(1)
O(1B)	6589(2)	7857(2)	533(1)	50(1)
O(2B)	8737(2)	5791(2)	274(2)	58(1)
O(3B)	8542(2)	3374(2)	385(1)	52(1)
O(4B)	5573(2)	5918(2)	1035(1)	38(1)
O(5B)	7099(2)	5046(2)	3125(1)	57(1)
N(1B)	7674(2)	3570(3)	2017(1)	45(1)
C(1B)	6847(3)	6470(3)	889(2)	41(1)
C(2B)	7291(3)	5550(3)	191(2)	42(1)
C(3B)	7163(3)	3908(3)	314(2)	43(1)
C(4B)	6671(3)	3442(3)	1132(2)	40(1)
C(5B)	5748(3)	4571(3)	1495(2)	37(1)
C(6B)	6613(4)	8954(3)	1188(2)	62(1)
C(7B)	9324(3)	4472(4)	69(2)	52(1)
C(8B)	10808(3)	4398(5)	590(2)	75(1)
C(9B)	9158(4)	4318(5)	-943(2)	75(1)
C(10B)	6923(3)	4517(3)	2375(2)	43(1)
C(11B)	8828(4)	2644(4)	2442(2)	64(1)
C(12B)	4350(3)	4058(3)	1575(2)	48(1)

Table 3. Selected bond lengths [A] and angles [deg] for C12H19NO5.

O(1A)-C(1A)	1.390(3)
O(1A)-C(6A)	1.423(3)

O(2A)-C(2A)	1.422(3)
O(2A)-C(7A)	1.423(3)
O(3A)-C(7A)	1.415(3)
O(3A)-C(3A)	1.432(3)
O(4A)-C(5A)	1.418(3)
O(4A)-C(1A)	1.429(3)
O(5A)-C(10A)	1.216(3)
N(1A)-C(10A)	1.348(3)
N(1A)-C(11A)	1.448(4)
N(1A)-C(4A)	1.469(3)
C(1A)-C(2A)	1.510(4)
C(2A)-C(3A)	1.547(4)
C(3A)-C(4A)	1.533(4)
C(4A)-C(5A)	1.554(4)
C(5A)-C(12A)	1.499(4)
C(5A)-C(10A)	1.538(4)
C(7A)-C(9A)	1.511(4)
C(7A)-C(8A)	1.514(4)
O(1B)-C(1B)	1.389(3)
O(1B)-C(6B)	1.420(4)
O(2B)-C(7B)	1.417(4)
O(2B)-C(2B)	1.422(3)
O(3B)-C(7B)	1.429(4)
O(3B)-C(3B)	1.430(3)
O(4B)-C(5B)	1.417(3)
O(4B)-C(1B)	1.428(3)
O(5B)-C(10B)	1.217(3)
N(1B)-C(10B)	1.348(4)
N(1B)-C(11B)	1.446(4)
N(1B)-C(4B)	1.470(4)
C(1B)-C(2B)	1.510(4)
C(2B)-C(3B)	1.536(4)
C(3B)-C(4B)	1.512(4)
C(4B)-C(5B)	1.574(4)
C(5B)-C(12B)	1.495(4)
C(5B)-C(10B)	1.545(4)
C(7B)-C(8B)	1.489(4)
C(7B)-C(9B)	1.520(4)

C(1A)-O(1A)-C(6A)	113.6(2)
C(2A)-O(2A)-C(7A)	106.7(2)
C(7A)-O(3A)-C(3A)	107.5(2)

C(5A)-O(4A)-C(1A)	112.6(2)
C(10A)-N(1A)-C(11A)	130.7(2)
C(10A)-N(1A)-C(4A)	96.1(2)
C(11A)-N(1A)-C(4A)	129.7(2)
O(1A)-C(1A)-O(4A)	107.6(2)
O(1A)-C(1A)-C(2A)	108.3(2)
O(4A)-C(1A)-C(2A)	110.0(2)
O(2A)-C(2A)-C(1A)	109.2(2)
O(2A)-C(2A)-C(3A)	104.5(2)
C(1A)-C(2A)-C(3A)	115.3(2)
O(3A)-C(3A)-C(4A)	108.6(2)
O(3A)-C(3A)-C(2A)	103.6(2)
C(4A)-C(3A)-C(2A)	115.8(2)
N(1A)-C(4A)-C(3A)	115.4(2)
N(1A)-C(4A)-C(5A)	86.7(2)
C(3A)-C(4A)-C(5A)	116.0(2)
O(4A)-C(5A)-C(12A)	108.1(2)
O(4A)-C(5A)-C(10A)	117.3(2)
C(12A)-C(5A)-C(10A)	112.5(2)
O(4A)-C(5A)-C(4A)	115.1(2)
C(12A)-C(5A)-C(4A)	117.4(2)
C(10A)-C(5A)-C(4A)	85.4(2)
O(3A)-C(7A)-O(2A)	104.3(2)
O(3A)-C(7A)-C(9A)	111.5(2)
O(2A)-C(7A)-C(9A)	111.0(2)
O(3A)-C(7A)-C(8A)	108.5(2)
O(2A)-C(7A)-C(8A)	108.3(2)
C(9A)-C(7A)-C(8A)	112.9(2)
O(5A)-C(10A)-N(1A)	131.8(3)
O(5A)-C(10A)-C(5A)	136.3(3)
N(1A)-C(10A)-C(5A)	91.8(2)
C(1B)-O(1B)-C(6B)	114.3(2)
C(7B)-O(2B)-C(2B)	107.8(2)
C(7B)-O(3B)-C(3B)	108.5(2)
C(5B)-O(4B)-C(1B)	112.7(2)
C(10B)-N(1B)-C(11B)	130.9(2)
C(10B)-N(1B)-C(4B)	96.3(2)
C(11B)-N(1B)-C(4B)	130.1(2)
O(1B)-C(1B)-O(4B)	107.8(2)
O(1B)-C(1B)-C(2B)	107.4(2)
O(4B)-C(1B)-C(2B)	109.4(2)
O(2B)-C(2B)-C(1B)	108.1(2)

O(2B)-C(2B)-C(3B)	104.7(2)
C(1B)-C(2B)-C(3B)	114.9(2)
O(3B)-C(3B)-C(4B)	109.6(2)
O(3B)-C(3B)-C(2B)	104.1(2)
C(4B)-C(3B)-C(2B)	115.8(2)
N(1B)-C(4B)-C(3B)	117.1(2)
N(1B)-C(4B)-C(5B)	86.7(2)
C(3B)-C(4B)-C(5B)	115.9(2)
O(4B)-C(5B)-C(12B)	108.4(2)
O(4B)-C(5B)-C(10B)	115.6(2)
C(12B)-C(5B)-C(10B)	115.6(2)
O(4B)-C(5B)-C(4B)	114.6(2)
C(12B)-C(5B)-C(4B)	116.6(2)
C(10B)-C(5B)-C(4B)	84.7(2)
O(2B)-C(7B)-O(3B)	104.4(2)
O(2B)-C(7B)-C(8B)	109.0(3)
O(3B)-C(7B)-C(8B)	109.4(3)
O(2B)-C(7B)-C(9B)	111.0(3)
O(3B)-C(7B)-C(9B)	110.2(3)
C(8B)-C(7B)-C(9B)	112.6(3)
O(5B)-C(10B)-N(1B)	132.6(3)
O(5B)-C(10B)-C(5B)	135.0(3)
N(1B)-C(10B)-C(5B)	92.3(2)

Table 4. Bond lengths [A] and angles [deg] for C12H19NO5.

O(1A)-C(1A)	1.390(3)
O(1A)-C(6A)	1.423(3)
O(2A)-C(2A)	1.422(3)
O(2A)-C(7A)	1.423(3)
O(3A)-C(7A)	1.415(3)
O(3A)-C(3A)	1.432(3)
O(4A)-C(5A)	1.418(3)
O(4A)-C(1A)	1.429(3)
O(5A)-C(10A)	1.216(3)
N(1A)-C(10A)	1.348(3)
N(1A)-C(11A)	1.448(4)
N(1A)-C(4A)	1.469(3)
C(1A)-C(2A)	1.510(4)
C(1A)-H(1A)	1.00

C(2A)-C(3A)	1.547(4)
C(2A)-H(2A)	1.00
C(3A)-C(4A)	1.533(4)
C(3A)-H(3A)	1.00
C(4A)-C(5A)	1.554(4)
C(4A)-H(4A)	1.00
C(5A)-C(12A)	1.499(4)
C(5A)-C(10A)	1.538(4)
C(6A)-H(6A)	0.98
C(6A)-H(6B)	0.98
C(6A)-H(6C)	0.98
C(7A)-C(9A)	1.511(4)
C(7A)-C(8A)	1.514(4)
C(8A)-H(8A)	0.98
C(8A)-H(8B)	0.98
C(8A)-H(8C)	0.98
C(9A)-H(9A)	0.98
C(9A)-H(9B)	0.98
C(9A)-H(9C)	0.98
C(11A)-H(11A)	0.98
C(11A)-H(11B)	0.98
C(11A)-H(11C)	0.98
C(12A)-H(12A)	0.98
C(12A)-H(12B)	0.98
C(12A)-H(12C)	0.98
O(1B)-C(1B)	1.389(3)
O(1B)-C(6B)	1.420(4)
O(2B)-C(7B)	1.417(4)
O(2B)-C(2B)	1.422(3)
O(3B)-C(7B)	1.429(4)
O(3B)-C(3B)	1.430(3)
O(4B)-C(5B)	1.417(3)
O(4B)-C(1B)	1.428(3)
O(5B)-C(10B)	1.217(3)
N(1B)-C(10B)	1.348(4)
N(1B)-C(11B)	1.446(4)
N(1B)-C(4B)	1.470(4)
C(1B)-C(2B)	1.510(4)
C(1B)-H(1B)	1.00
C(2B)-C(3B)	1.536(4)
C(2B)-H(2B)	1.00
C(3B)-C(4B)	1.512(4)

C(3B)-H(3B)	1.00
C(4B)-C(5B)	1.574(4)
C(4B)-H(4B)	1.00
C(5B)-C(12B)	1.495(4)
C(5B)-C(10B)	1.545(4)
C(6B)-H(6D)	0.98
C(6B)-H(6E)	0.98
C(6B)-H(6F)	0.98
C(7B)-C(8B)	1.489(4)
C(7B)-C(9B)	1.520(4)
C(8B)-H(8D)	0.98
C(8B)-H(8E)	0.98
C(8B)-H(8F)	0.98
C(9B)-H(9D)	0.98
C(9B)-H(9E)	0.98
C(9B)-H(9F)	0.98
C(11B)-H(11D)	0.98
C(11B)-H(11E)	0.98
C(11B)-H(11F)	0.98
C(12B)-H(12D)	0.98
C(12B)-H(12E)	0.98
C(12B)-H(12F)	0.98
C(1A)-O(1A)-C(6A)	113.6(2)
C(2A)-O(2A)-C(7A)	106.7(2)
C(7A)-O(3A)-C(3A)	107.5(2)
C(5A)-O(4A)-C(1A)	112.6(2)
C(10A)-N(1A)-C(11A)	130.7(2)
C(10A)-N(1A)-C(4A)	96.1(2)
C(11A)-N(1A)-C(4A)	129.7(2)
O(1A)-C(1A)-O(4A)	107.6(2)
O(1A)-C(1A)-C(2A)	108.3(2)
O(4A)-C(1A)-C(2A)	110.0(2)
O(1A)-C(1A)-H(1A)	110.28(13)
O(4A)-C(1A)-H(1A)	110.28(13)
C(2A)-C(1A)-H(1A)	110.28(14)
O(2A)-C(2A)-C(1A)	109.2(2)
O(2A)-C(2A)-C(3A)	104.5(2)
C(1A)-C(2A)-C(3A)	115.3(2)
O(2A)-C(2A)-H(2A)	109.19(13)
C(1A)-C(2A)-H(2A)	109.19(14)
C(3A)-C(2A)-H(2A)	109.19(13)

O(3A)-C(3A)-C(4A)	108.6(2)
O(3A)-C(3A)-C(2A)	103.6(2)
C(4A)-C(3A)-C(2A)	115.8(2)
O(3A)-C(3A)-H(3A)	109.51(13)
C(4A)-C(3A)-H(3A)	109.51(14)
C(2A)-C(3A)-H(3A)	109.51(14)
N(1A)-C(4A)-C(3A)	115.4(2)
N(1A)-C(4A)-C(5A)	86.7(2)
C(3A)-C(4A)-C(5A)	116.0(2)
N(1A)-C(4A)-H(4A)	112.14(13)
C(3A)-C(4A)-H(4A)	112.14(14)
C(5A)-C(4A)-H(4A)	112.14(13)
O(4A)-C(5A)-C(12A)	108.1(2)
O(4A)-C(5A)-C(10A)	117.3(2)
C(12A)-C(5A)-C(10A)	112.5(2)
O(4A)-C(5A)-C(4A)	115.1(2)
C(12A)-C(5A)-C(4A)	117.4(2)
C(10A)-C(5A)-C(4A)	85.4(2)
O(1A)-C(6A)-H(6A)	109.47(14)
O(1A)-C(6A)-H(6B)	109.5(2)
H(6A)-C(6A)-H(6B)	109.5
O(1A)-C(6A)-H(6C)	109.5(2)
H(6A)-C(6A)-H(6C)	109.5
H(6B)-C(6A)-H(6C)	109.5
O(3A)-C(7A)-O(2A)	104.3(2)
O(3A)-C(7A)-C(9A)	111.5(2)
O(2A)-C(7A)-C(9A)	111.0(2)
O(3A)-C(7A)-C(8A)	108.5(2)
O(2A)-C(7A)-C(8A)	108.3(2)
C(9A)-C(7A)-C(8A)	112.9(2)
C(7A)-C(8A)-H(8A)	109.5(2)
C(7A)-C(8A)-H(8B)	109.5(2)
H(8A)-C(8A)-H(8B)	109.5
C(7A)-C(8A)-H(8C)	109.5(2)
H(8A)-C(8A)-H(8C)	109.5
H(8B)-C(8A)-H(8C)	109.5
C(7A)-C(9A)-H(9A)	109.5(2)
C(7A)-C(9A)-H(9B)	109.5(2)
H(9A)-C(9A)-H(9B)	109.5
C(7A)-C(9A)-H(9C)	109.5(2)
H(9A)-C(9A)-H(9C)	109.5
H(9B)-C(9A)-H(9C)	109.5

O(5A)-C(10A)-N(1A)	131.8(3)
O(5A)-C(10A)-C(5A)	136.3(3)
N(1A)-C(10A)-C(5A)	91.8(2)
N(1A)-C(11A)-H(11A)	109.5(2)
N(1A)-C(11A)-H(11B)	109.5(2)
H(11A)-C(11A)-H(11B)	109.5
N(1A)-C(11A)-H(11C)	109.5(2)
H(11A)-C(11A)-H(11C)	109.5
H(11B)-C(11A)-H(11C)	109.5
C(5A)-C(12A)-H(12A)	109.5(2)
C(5A)-C(12A)-H(12B)	109.5(2)
H(12A)-C(12A)-H(12B)	109.5
C(5A)-C(12A)-H(12C)	109.5(2)
H(12A)-C(12A)-H(12C)	109.5
H(12B)-C(12A)-H(12C)	109.5
C(1B)-O(1B)-C(6B)	114.3(2)
C(7B)-O(2B)-C(2B)	107.8(2)
C(7B)-O(3B)-C(3B)	108.5(2)
C(5B)-O(4B)-C(1B)	112.7(2)
C(10B)-N(1B)-C(11B)	130.9(2)
C(10B)-N(1B)-C(4B)	96.3(2)
C(11B)-N(1B)-C(4B)	130.1(2)
O(1B)-C(1B)-O(4B)	107.8(2)
O(1B)-C(1B)-C(2B)	107.4(2)
O(4B)-C(1B)-C(2B)	109.4(2)
O(1B)-C(1B)-H(1B)	110.7(2)
O(4B)-C(1B)-H(1B)	110.70(13)
C(2B)-C(1B)-H(1B)	110.7(2)
O(2B)-C(2B)-C(1B)	108.1(2)
O(2B)-C(2B)-C(3B)	104.7(2)
C(1B)-C(2B)-C(3B)	114.9(2)
O(2B)-C(2B)-H(2B)	109.63(14)
C(1B)-C(2B)-H(2B)	109.6(2)
C(3B)-C(2B)-H(2B)	109.6(2)
O(3B)-C(3B)-C(4B)	109.6(2)
O(3B)-C(3B)-C(2B)	104.1(2)
C(4B)-C(3B)-C(2B)	115.8(2)
O(3B)-C(3B)-H(3B)	109.05(13)
C(4B)-C(3B)-H(3B)	109.1(2)
C(2B)-C(3B)-H(3B)	109.1(2)
N(1B)-C(4B)-C(3B)	117.1(2)
N(1B)-C(4B)-C(5B)	86.7(2)

C(3B)-C(4B)-C(5B)	115.9(2)
N(1B)-C(4B)-H(4B)	111.68(14)
C(3B)-C(4B)-H(4B)	111.7(2)
C(5B)-C(4B)-H(4B)	111.68(13)
O(4B)-C(5B)-C(12B)	108.4(2)
O(4B)-C(5B)-C(10B)	115.6(2)
C(12B)-C(5B)-C(10B)	115.6(2)
O(4B)-C(5B)-C(4B)	114.6(2)
C(12B)-C(5B)-C(4B)	116.6(2)
C(10B)-C(5B)-C(4B)	84.7(2)
O(1B)-C(6B)-H(6D)	109.5(2)
O(1B)-C(6B)-H(6E)	109.5(2)
H(6D)-C(6B)-H(6E)	109.5
O(1B)-C(6B)-H(6F)	109.5(2)
H(6D)-C(6B)-H(6F)	109.5
H(6E)-C(6B)-H(6F)	109.5
O(2B)-C(7B)-O(3B)	104.4(2)
O(2B)-C(7B)-C(8B)	109.0(3)
O(3B)-C(7B)-C(8B)	109.4(3)
O(2B)-C(7B)-C(9B)	111.0(3)
O(3B)-C(7B)-C(9B)	110.2(3)
C(8B)-C(7B)-C(9B)	112.6(3)
C(7B)-C(8B)-H(8D)	109.5(2)
C(7B)-C(8B)-H(8E)	109.5(2)
H(8D)-C(8B)-H(8E)	109.5
C(7B)-C(8B)-H(8F)	109.5(2)
H(8D)-C(8B)-H(8F)	109.5
H(8E)-C(8B)-H(8F)	109.5
C(7B)-C(9B)-H(9D)	109.5(2)
C(7B)-C(9B)-H(9E)	109.5(2)
H(9D)-C(9B)-H(9E)	109.5
C(7B)-C(9B)-H(9F)	109.5(2)
H(9D)-C(9B)-H(9F)	109.5
H(9E)-C(9B)-H(9F)	109.5
O(5B)-C(10B)-N(1B)	132.6(3)
O(5B)-C(10B)-C(5B)	135.0(3)
N(1B)-C(10B)-C(5B)	92.3(2)
N(1B)-C(11B)-H(11D)	109.5(2)
N(1B)-C(11B)-H(11E)	109.5(2)
H(11D)-C(11B)-H(11E)	109.5
N(1B)-C(11B)-H(11F)	109.5(2)
H(11D)-C(11B)-H(11F)	109.5

H(11E)-C(11B)-H(11F)	109.5
C(5B)-C(12B)-H(12D)	109.5(2)
C(5B)-C(12B)-H(12E)	109.5(2)
H(12D)-C(12B)-H(12E)	109.5
C(5B)-C(12B)-H(12F)	109.47(14)
H(12D)-C(12B)-H(12F)	109.5
H(12E)-C(12B)-H(12F)	109.5

Table 5. Anisotropic displacement parameters (A^2 x 10^3) for C12H19NO5. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1A)	60(1)	33(1)	54(1)	-4(1)	30(1)	-9(1)
O(2A)	38(1)	47(1)	56(1)	-11(1)	10(1)	-1(1)
O(3A)	40(1)	40(1)	53(1)	1(1)	14(1)	4(1)
O(4A)	44(1)	34(1)	46(1)	6(1)	18(1)	1(1)
O(5A)	79(1)	41(1)	46(1)	0(1)	30(1)	-2(1)
N(1A)	58(2)	31(1)	44(1)	2(1)	21(1)	1(1)
C(1A)	41(2)	35(1)	44(2)	2(1)	17(1)	-4(1)
C(2A)	39(1)	42(1)	41(1)	-1(1)	13(1)	-2(1)
C(3A)	42(2)	36(2)	40(1)	-3(1)	10(1)	1(1)
C(4A)	39(1)	36(1)	38(1)	-5(1)	10(1)	-3(1)
C(5A)	39(1)	35(1)	42(1)	0(1)	14(1)	-3(1)
C(6A)	77(2)	36(2)	68(2)	-13(1)	33(2)	-9(2)
C(7A)	40(2)	43(2)	48(2)	-5(1)	13(1)	5(1)
C(8A)	57(2)	76(2)	57(2)	3(2)	8(2)	9(2)
C(9A)	54(2)	63(2)	51(2)	-8(2)	19(2)	4(2)
C(10A)	48(2)	35(1)	44(2)	3(1)	19(1)	-3(1)
C(11A)	95(3)	31(2)	66(2)	11(1)	37(2)	7(2)
C(12A)	41(2)	55(2)	66(2)	-2(2)	14(1)	1(1)
O(1B)	60(1)	39(1)	54(1)	5(1)	20(1)	5(1)
O(2B)	48(1)	51(1)	84(2)	-9(1)	35(1)	-2(1)
O(3B)	42(1)	58(1)	60(1)	1(1)	21(1)	12(1)

O(4B)	39(1)	34(1)	42(1)	-1(1)	12(1)	3(1)
O(5B)	70(1)	61(1)	38(1)	-5(1)	10(1)	6(1)
N(1B)	48(1)	47(1)	41(1)	5(1)	12(1)	9(1)
C(1B)	43(2)	36(2)	46(2)	4(1)	14(1)	2(1)
C(2B)	37(1)	51(2)	38(1)	3(1)	12(1)	5(1)
C(3B)	39(2)	46(2)	45(2)	-7(1)	13(1)	3(1)
C(4B)	43(2)	32(1)	48(2)	-4(1)	13(1)	0(1)
C(5B)	40(2)	34(1)	38(1)	1(1)	11(1)	-1(1)
C(6B)	72(2)	37(2)	77(2)	-6(2)	20(2)	6(2)
C(7B)	42(2)	59(2)	58(2)	-7(2)	18(1)	4(2)
C(8B)	47(2)	98(3)	80(2)	-14(2)	14(2)	8(2)
C(9B)	71(2)	105(3)	57(2)	2(2)	31(2)	12(2)
C(10B)	49(2)	38(1)	42(2)	2(1)	12(1)	0(1)
C(11B)	64(2)	73(2)	56(2)	15(2)	14(2)	24(2)
C(12B)	44(2)	43(2)	61(2)	-10(1)	22(1)	-5(1)

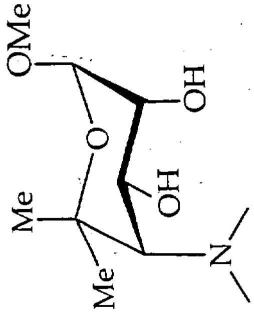
Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for C12H19NO5.

	x	y	z	U(eq)
H(1A)	7502(3)	6503(3)	6806(2)	47
H(2A)	7728(3)	5945(3)	5008(2)	48
H(3A)	6466(3)	3942(3)	4804(2)	47
H(4A)	4846(3)	3408(3)	5599(2)	45
H(6A)	7936(19)	10056(8)	6376(11)	86
H(6B)	7759(21)	8917(10)	7130(2)	86
H(6C)	6432(4)	9396(16)	6352(11)	86
H(8A)	9866(14)	3075(24)	7242(3)	96
H(8B)	11106(7)	3365(19)	6762(11)	96
H(8C)	10250(20)	1878(6)	6585(8)	96
H(9A)	8877(12)	3861(19)	4525(3)	82
H(9B)	9605(21)	2355(4)	4887(7)	82
H(9C)	10487(10)	3826(20)	5058(5)	82
H(11A)	6174(25)	2547(7)	8001(5)	92

H(11B)	7213(9)	2083(13)	7397(14)	92
H(11C)	5591(16)	1692(8)	7073(9)	92
H(12A)	3250(4)	6576(15)	6241(11)	81
H(12B)	3031(3)	4885(9)	6019(14)	81
H(12C)	3203(4)	5991(23)	5247(4)	81
H(1B)	7591(3)	6489(3)	1466(2)	49
H(2B)	6749(3)	5838(3)	-427(2)	50
H(3B)	6522(3)	3496(3)	-241(2)	51
H(4B)	6225(3)	2463(3)	1046(2)	49
H(6D)	6289(23)	9870(7)	883(2)	92
H(6E)	7567(6)	9073(18)	1559(11)	92
H(6F)	5998(19)	8677(12)	1574(10)	92
H(8D)	10862(4)	4514(31)	1236(3)	113
H(8E)	11339(7)	5173(19)	391(14)	113
H(8F)	11201(9)	3457(13)	487(15)	113
H(9D)	8170(5)	4404(31)	-1256(3)	113
H(9E)	9507(27)	3369(13)	-1072(3)	113
H(9F)	9690(24)	5082(19)	-1153(4)	113
H(11D)	9244(16)	2995(15)	3055(6)	97
H(11E)	9530(12)	2658(20)	2089(9)	97
H(11F)	8491(6)	1651(6)	2471(14)	97
H(12D)	3937(9)	4786(10)	1898(12)	72
H(12E)	4456(4)	3142(11)	1909(12)	72
H(12F)	3741(7)	3911(21)	970(2)	72

Spectra—^{1}H NMR and ^{13}C NMR

Compound **#2, 4, 5, 6a/b mix** (^{1}H only), **8, 10, 15, 16, 17, 18a, 20, 21, 22a, 23**



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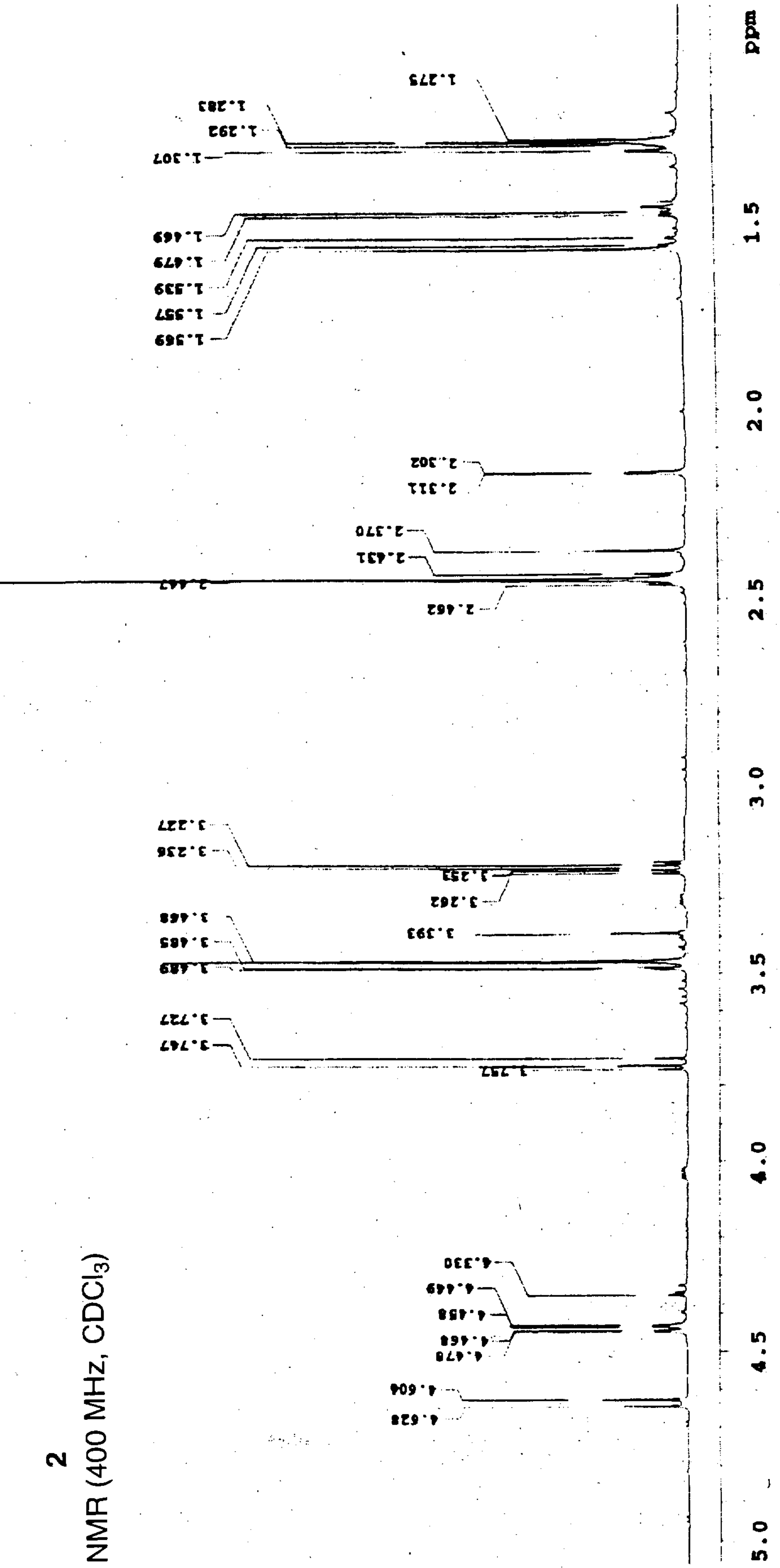
^{1}H NMR (400 MHz, $CDCl_3$)



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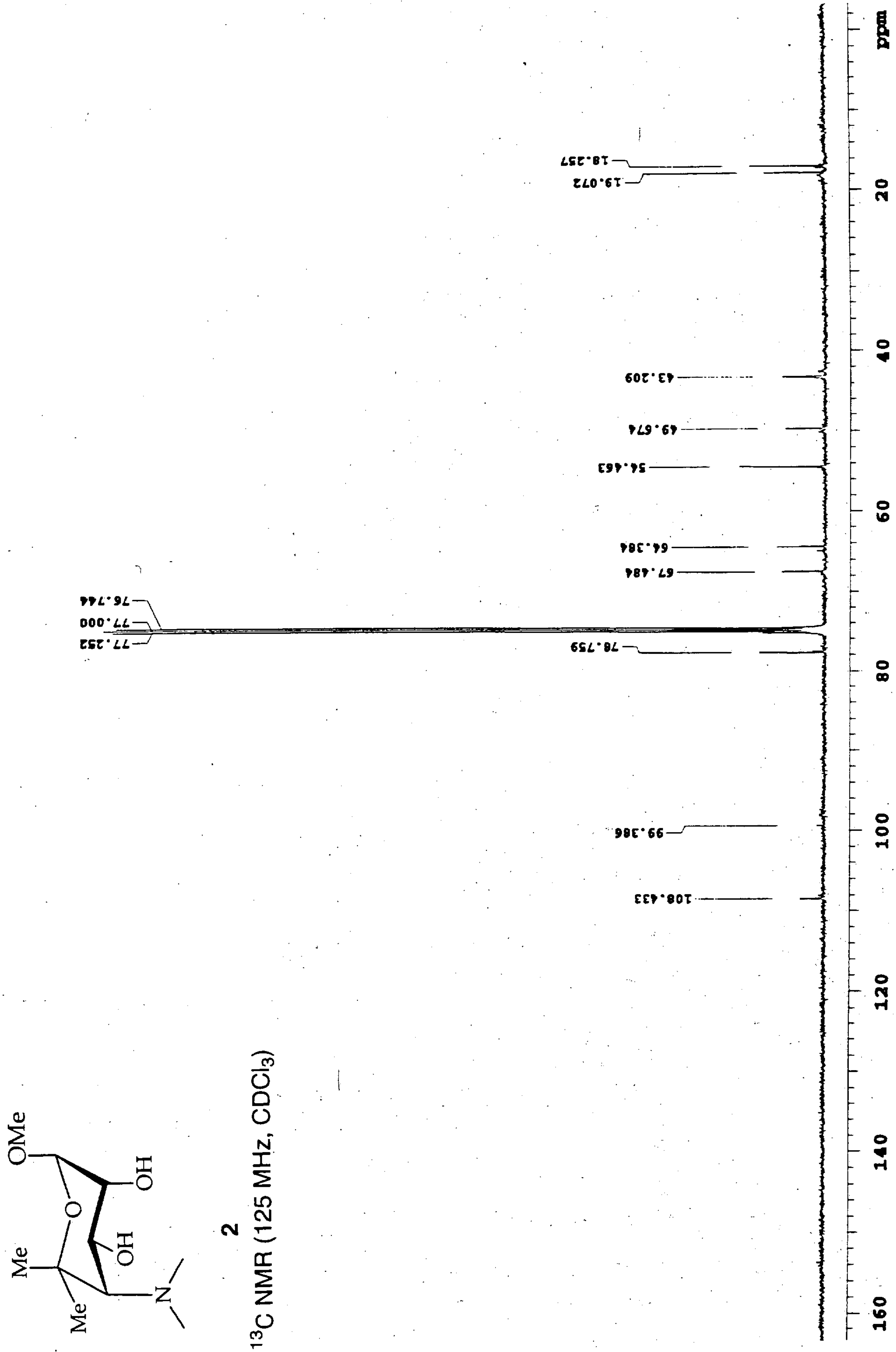

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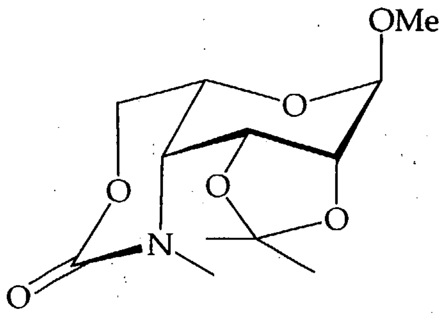
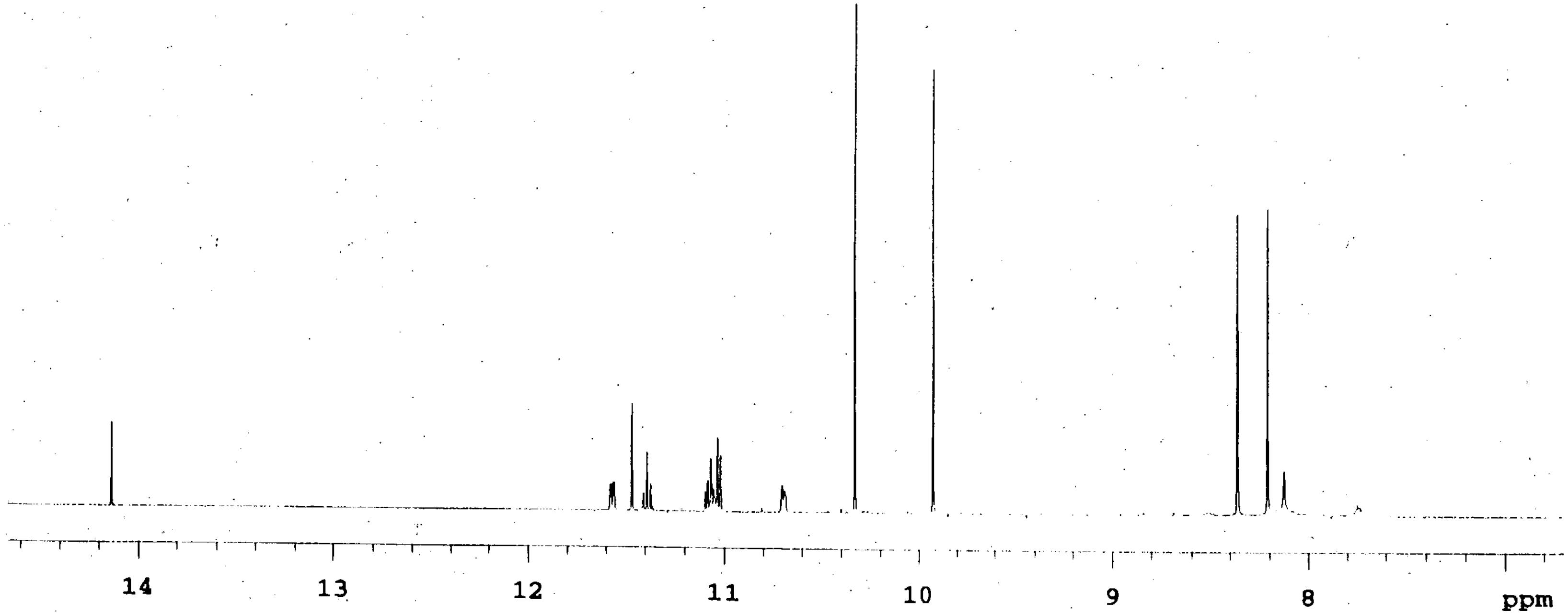
^{13}C NMR (125 MHz, CDCl$_3$)

3



4

^{1}H NMR ($CDCl_3$, 300 MHz)



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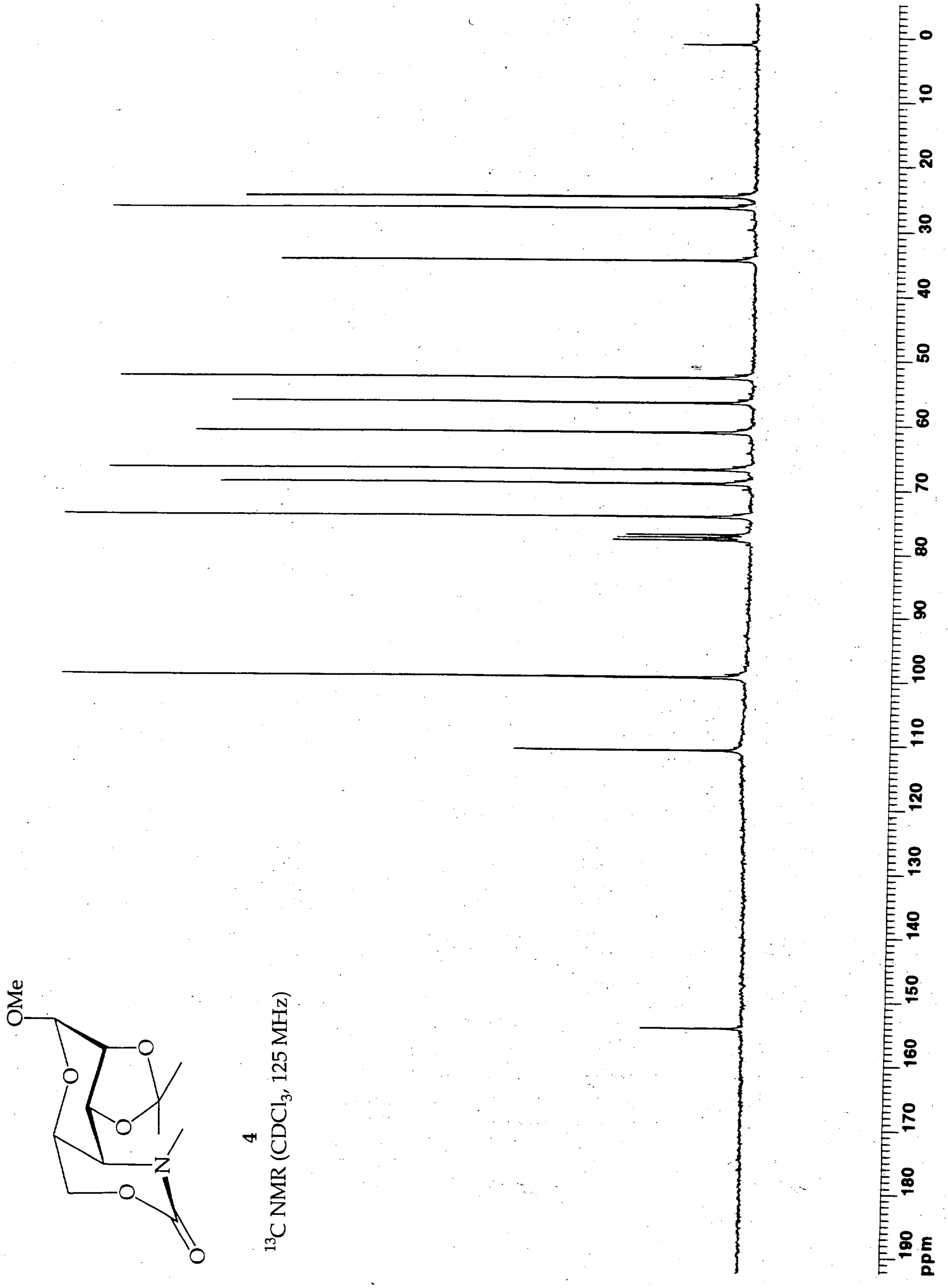
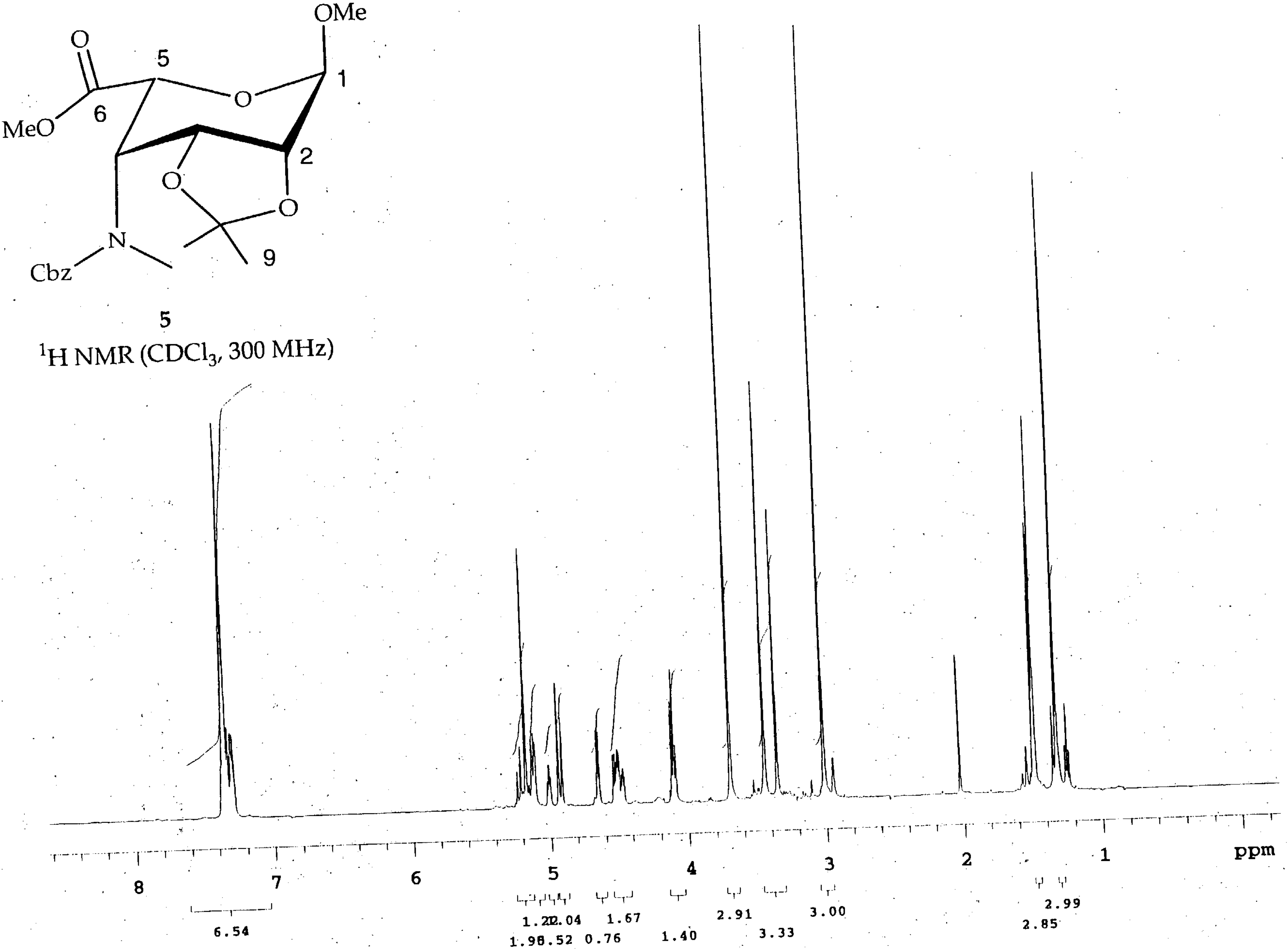


4

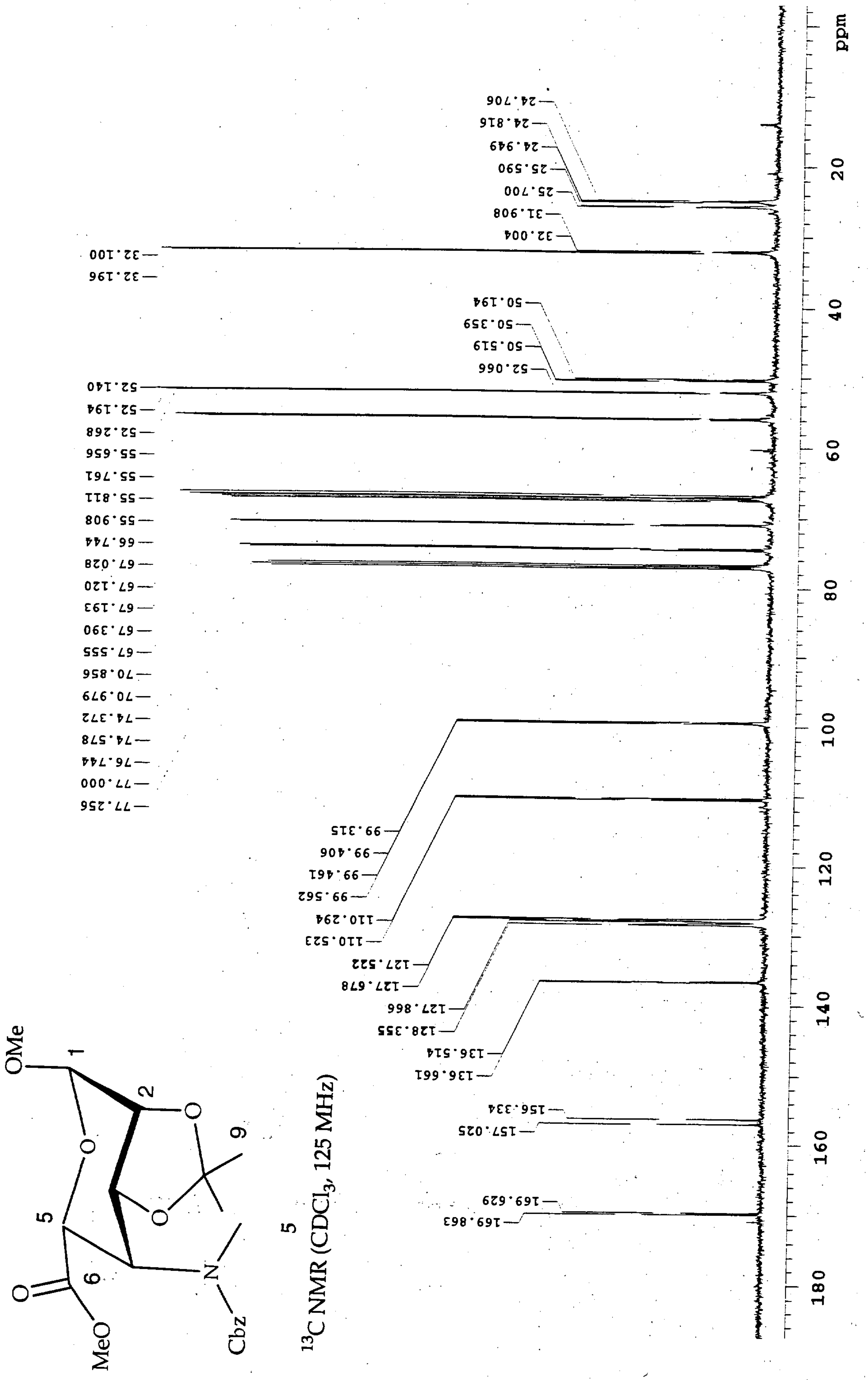
^{13}C NMR (CDCl$_3$, 125 MHz)



5

^{1}H NMR (CDCl$_3$, 300 MHz)

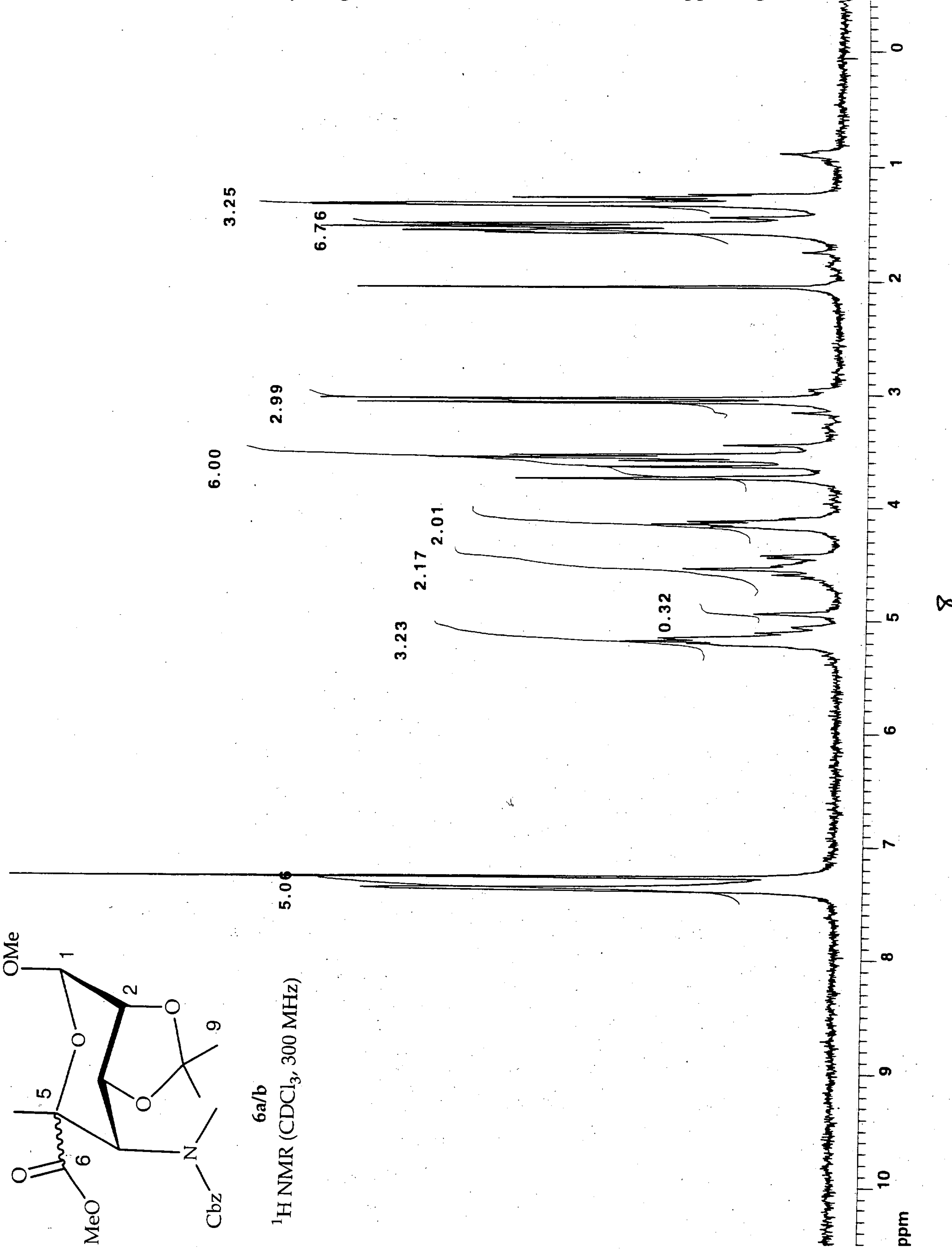
6



5

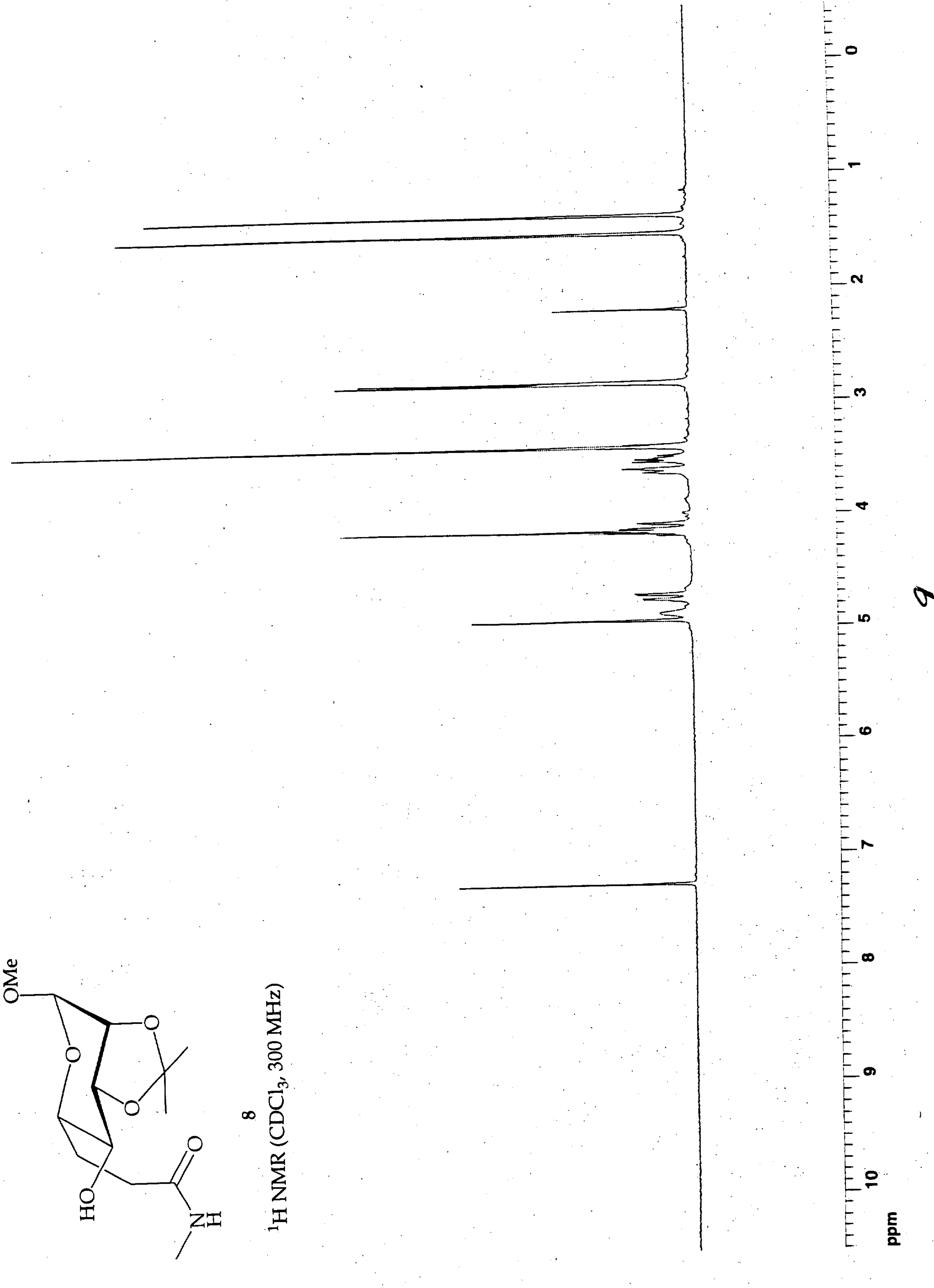
^{13}C NMR (CDCl$_3$, 125 MHz)

7



6a/b

^{1}H NMR (CDCl$_3$, 300 MHz)



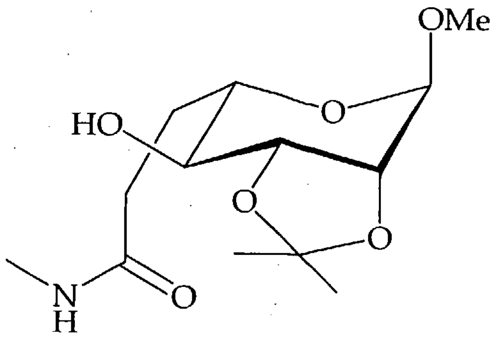
8

^{1}H NMR (CDCl$_3$, 300 MHz)

9

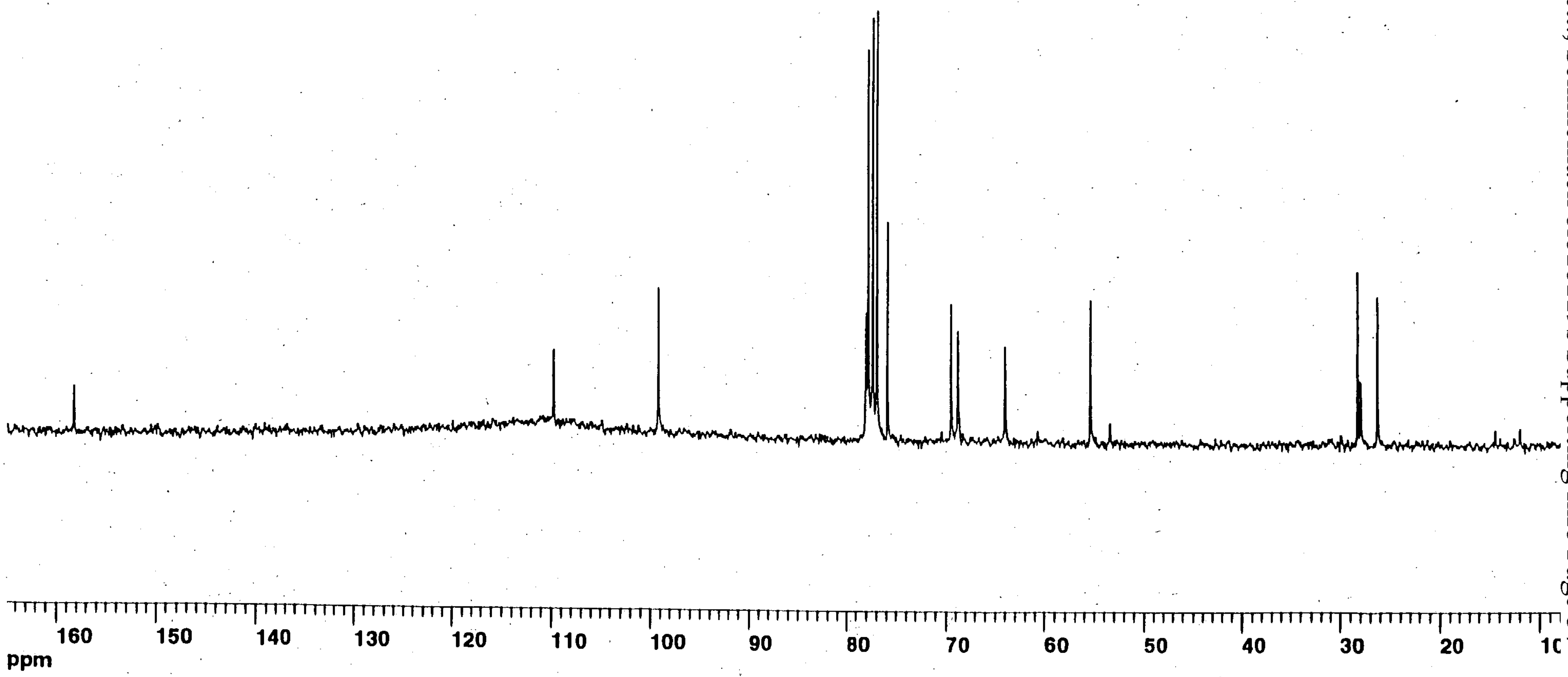
16 peaks found in carbamate 13C

peak	ppm	freq	amp
1	158.100	11932.28	173859.62
2	109.675	8277.49	317572.97
3	99.065	7476.71	532209.25
4	77.877	5877.59	454634.00
5	77.651	5860.50	1348185.12
6	77.456	5845.85	156960.45
7	77.230	5828.76	1457555.62
8	76.809	5797.02	1480603.25
9	75.774	5718.90	759412.19
10	69.369	5235.50	486359.31
11	68.625	5179.35	392494.41
12	63.838	4818.02	340776.25
13	55.298	4173.49	500304.62
14	28.223	2130.03	593812.81
15	27.931	2108.06	223896.61
16	26.282	1983.55	509988.12



8

^{13}C NMR ($CDCl_3$, 125 MHz)



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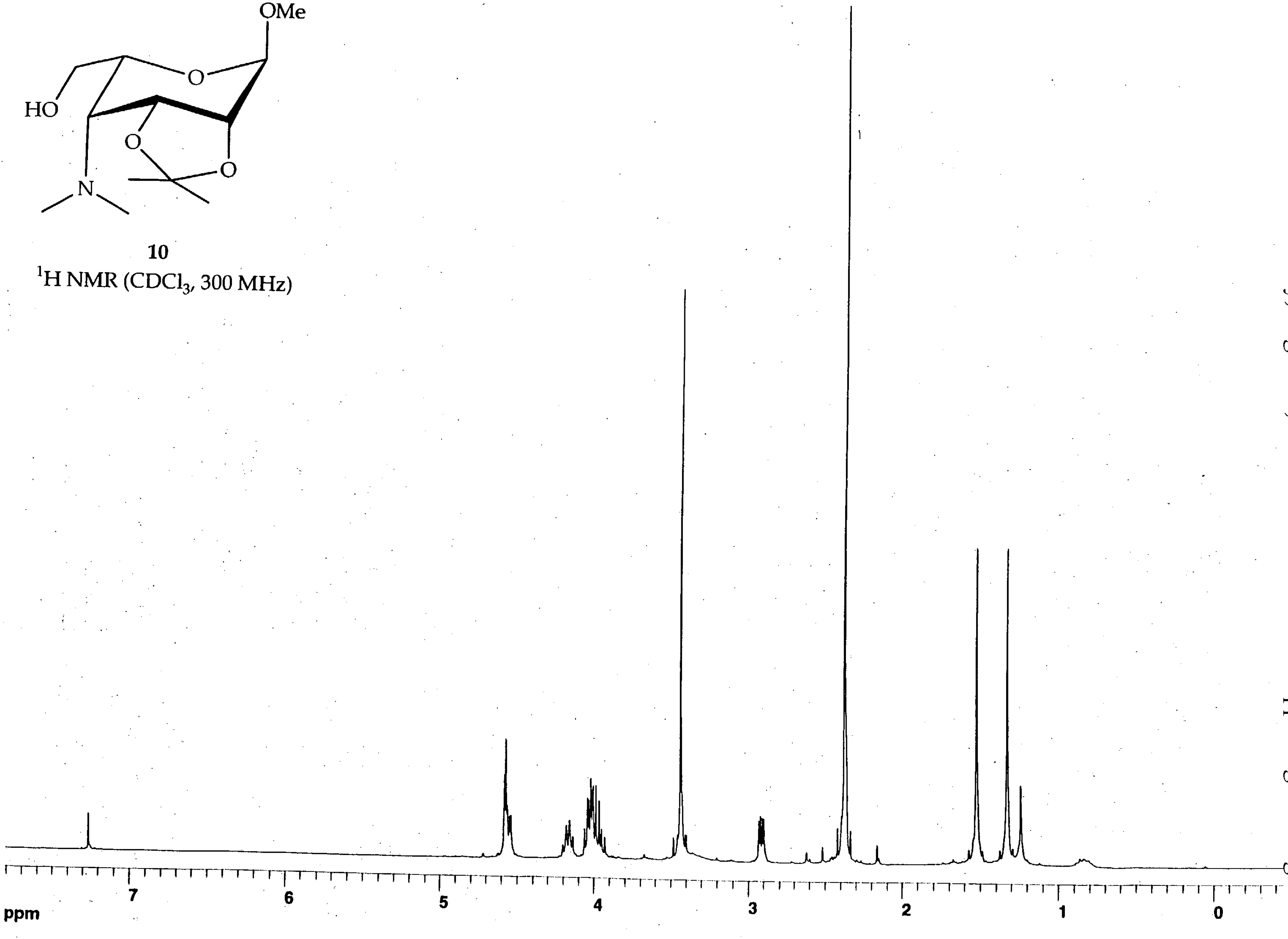
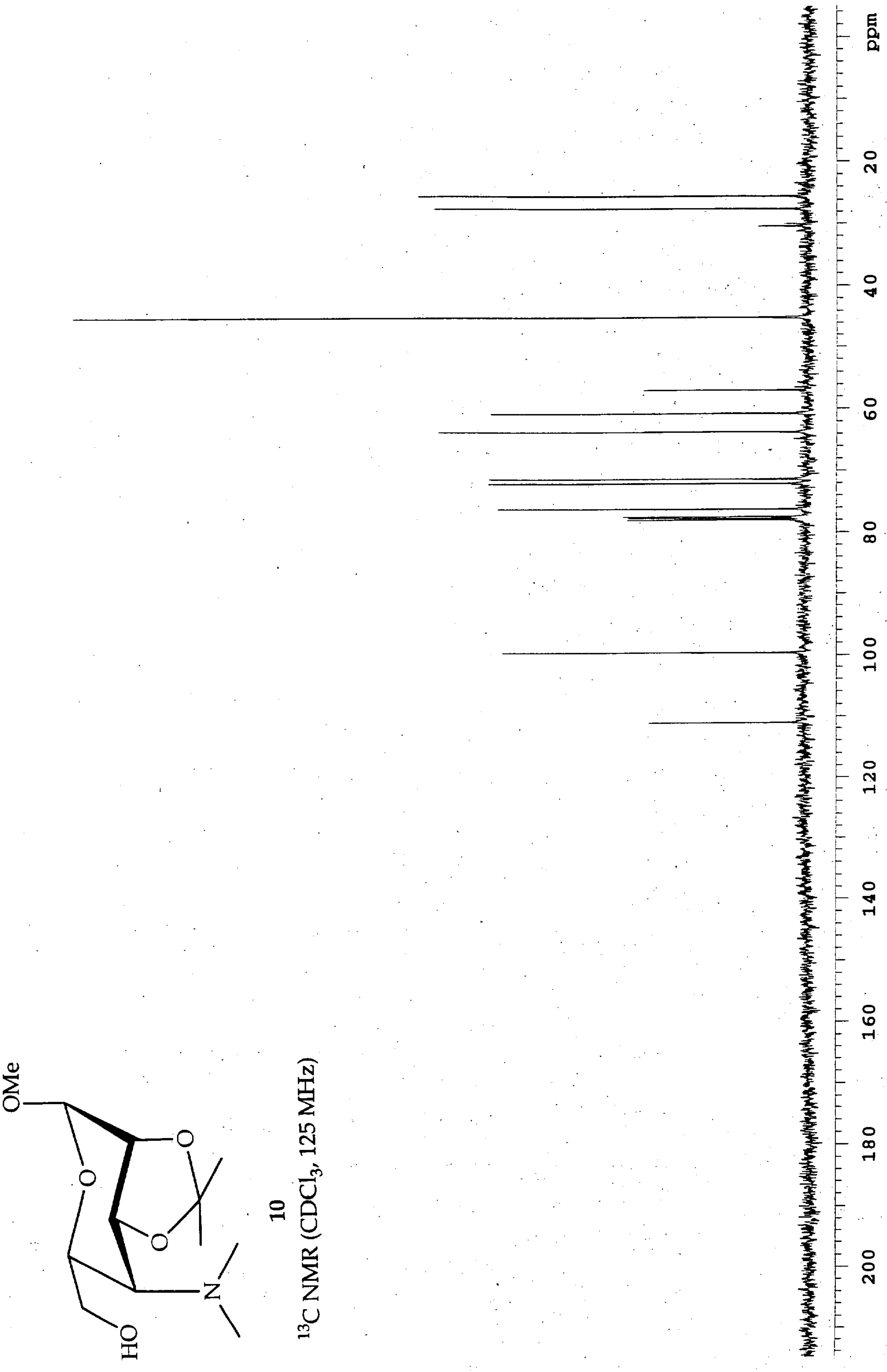


10

^{1}H NMR (CDCl$_3$, 300 MHz)

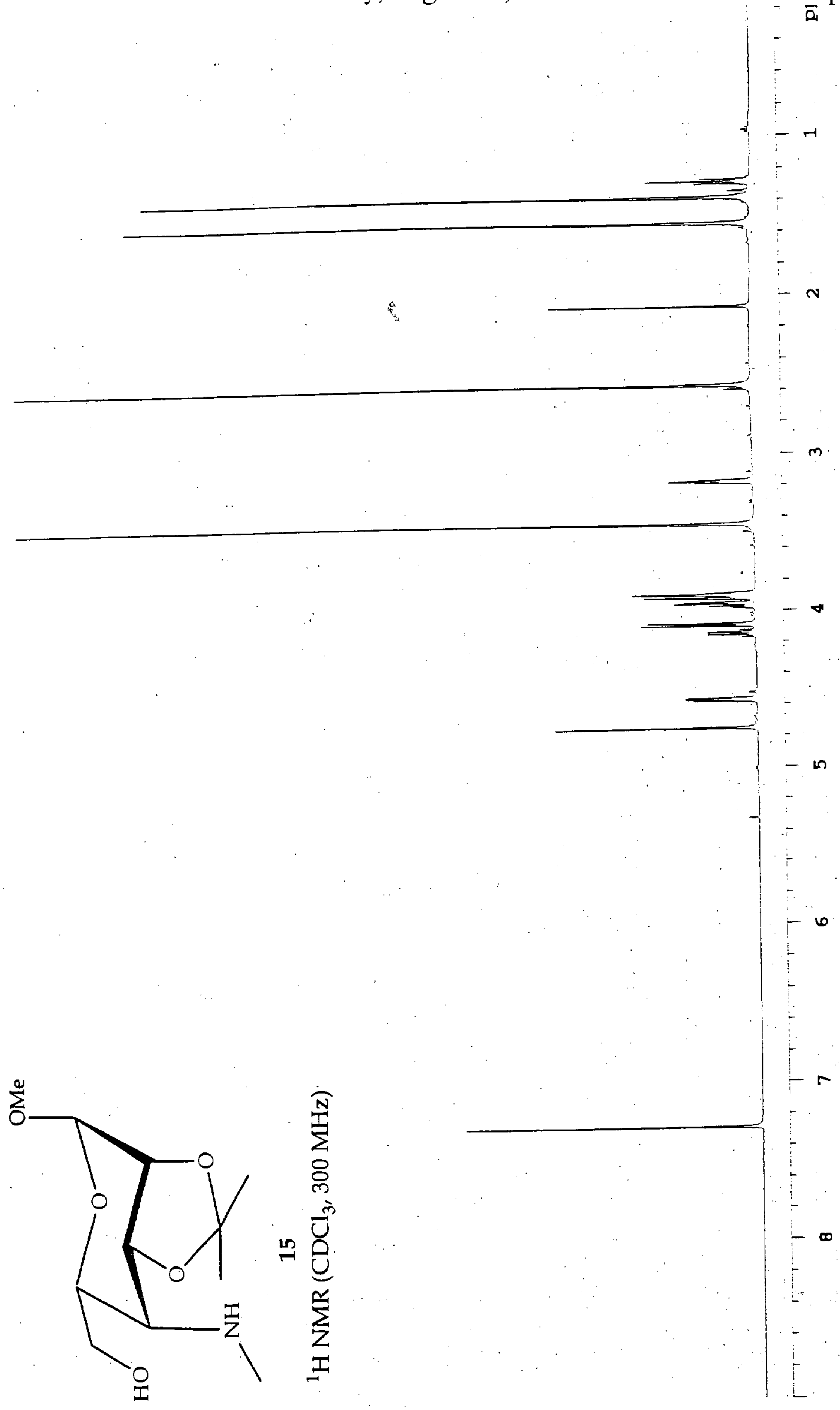
ll



10

^{13}C NMR (CDCl$_3$, 125 MHz)

21



15

^{1}H NMR (CDCl$_3$, 300 MHz)

13