Synthetic Studies Towards Mannopeptimycin-E: Synthesis of the *O*-Linked Tyrosine 1,4-α,α-*Manno,Manno*-Pyranosyl-Pyranoside.

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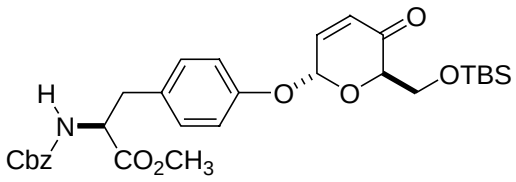
Supporting Information

Section A: General Information.

General Methods: Liquid chromatography was performed using the indicated solvent system on ICN reagent silica gel 60 (60-200 mesh). Ether, tetrahydrofuran, methylene chloride and methanol were dried by passing through activated alumina columns with argon gas pressure. Hexanes refer to the petroleum fraction bp 40-60 ^{o}C. Commercial reagents were used without purification unless otherwise noted. ^{1}H and ^{13}C spectra were recorded on Jeol 270 and 600 MHz spectrometers. Chemical shifts are reported relative to internal tetramethylsilane (δ 0.00) or $CHCl_3$ (δ 7.26) for ^{1}H and $CHCl_3$ (δ 77.0) for ^{13}C. Air- and/or moisture-sensitive reactions were carried out under an atmosphere of argon/nitrogen using oven-dried glassware and standard syringe/septa techniques. Melting points are uncorrected.

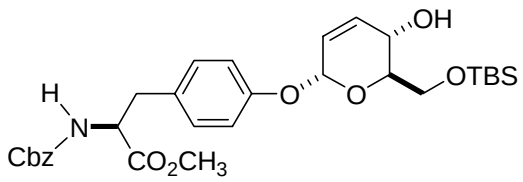
Section B: Experimental Procedures.

(2*S*,6*R*)-6-[(2'*S*)-2'- *N*-Carbobenzyloxy-D-tyrosine methoxycarbonyl)-2-*tert*-butyl-dimethyl-silanyloxymethyl-6*H*-pyran-3-one (8):



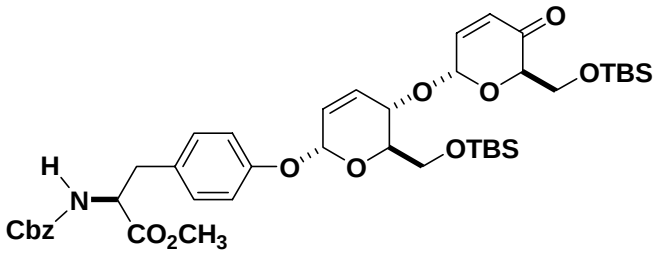
A CH_2Cl_2 (0.7 mL) solution of compound **6** (260 mg, 0.72 mmol) and Cbz-D-tyrosine methyl ester **5** (238 mg, 0.726 mmol) was cooled to 0 ^oC. A CH_2Cl_2 (0.7 mL) solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (18 mg, 2.5 mol%) and PPh_3 (16 mg, 10 mol%) was added to the reaction mixture at 0 ^oC. The reaction mixture was stirred at 0 ^oC for 3 hours. The reaction mixture was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 14% EtOAc/hexanes to give enone **8** (380 mg, 0.66 mmol, 92%) as viscous oil. R_f (30% EtOAc/hexanes) = 0.42; $[\alpha]_D^{26}$ = + 0.8 (*c* = 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3351, 2952, 1752, 1725, 1509, 1256, 1219, 1151, 995, 836; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.05 (m, 4H), 6.97 (dd, *J* = 10.2, 3.6 Hz, 1H), 6.22 (d, *J* = 10.8 Hz, 1H), 5.93 (d, *J* = 3.6 Hz, 1H), 5.30 (d, *J* = 7.8 Hz, 1H), 5.10 (d, *J* = 12.6 Hz, 1H), 5.07 (d, *J* = 12.6 Hz, 1H), 4.62 (dd, *J* = 13.8, 6.0 Hz, 1H), 4.54 (dd, *J* = 4.8, 3.0 Hz, 1H), 4.05 (dd, *J* = 11.4, 4.8 Hz, 1H), 4.02 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.71 (s, 3H), 3.10 (dd, *J* = 13.2, 5.4 Hz, 1H), 3.04 (dd, *J* = 14.4, 6.0 Hz, 1H), 0.84 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.2, 174.8, 156.1, 155.4, 151.6, 150.0, 142.6, 136.0, 130.3(2C), 130.0, 128.6, 128.4(2C), 128.0, 127.9, 117.0, 91.9, 76.6, 66.8, 62.5, 54.7, 52.2, 37.2, 25.7(3C), 18.1, -5.44, -5.48; CIHRMS Calcd for $[C_{30}H_{39}NO_8SiNa^+]$: 592.2337. Found 592.2290.

3-{4-[6-(*tert*-Butyl-dimethylsilanyloxymethyl)-5-hydroxy-5,6-dihydro-2*H*-pyran-2-yloxy]-phenyl}-2- *N*-carbobenzyloxy-D-tyrosine methyl ester (9):



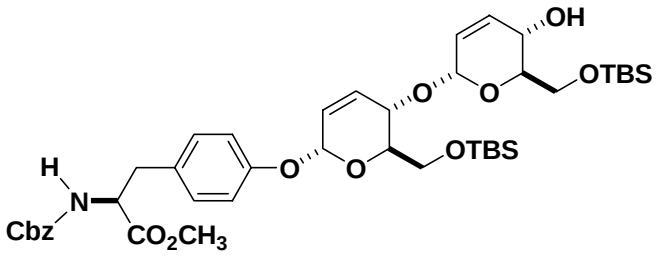
The enone compound **8** (320 mg, 0.562 mmol) was dissolved in 0.5 mL of CH_2Cl_2 and 0.5 mL MeOH in round bottom flask and cooled -78 ^oC then $NaBH_4$ (21 mg, 0.562 mmol) was added and the reaction mixture was stirred at -78 ^oC for 3 hours and on completion, monitored by TLC, reaction mixture was diluted with ether and was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 18% EtOAc/hexanes to give **9** (300 mg, 0.525 mmol, 87%) as viscous oil. R_f (30% EtOAc/hexanes) = 0.30; $[\alpha]_D^{26}$ = + 29.0 (*c* = 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3386, 2925, 1459, 1255, 1069, 1027, 838; ^1H NMR (600 MHz, $CDCl_3$) δ 7.32 (m, 5H), 6.98 (m, 4H), 6.08 (d, *J* = 10.2 Hz, 1H), 5.88 (ddd, *J* = 10.2, 2.4, 2.4 Hz, 1H), 5.57 (d, *J* = 1.8 Hz, 1H), 5.21 (d, *J* = 7.8 Hz, 1H), 5.11 (d, *J* = 13.2 Hz, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 4.62 (dd, *J* = 13.2, 5.4 Hz, 1H), 4.28 (dd, *J* = 9.0, 1.8 Hz, 1H), 3.89 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.84 (dqd, *J* = 12.0, 7.2, 4.8 Hz, 1H), 3.75 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.32 (s, 3H), 3.08 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.04 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.02 (d, *J* = 3.0 Hz, 1H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.9, 156.5, 133.3, 130.3, 130.2(2C), 128.5(2C), 128.4, 128.1, 128.0, 124.8, 116.9(2C), 115.5, 92.8, 70.7, 66.9, 66.5, 65.1, 54.8, 52.3, 52.2, 37.2, 25.7(3C), 18.1, -5.5, -5.6; CIHRMS Calcd for [$C_{30}H_{41}NO_8SiNa^+$]: 594.2493 Found 594.2467.

(1'*S*, 4'*S*, 5'*R*, 1*S*, 5*R*)-1-[1'-*N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5-(*tert*-butyl-dimethylsilanyloxymethyl)-1',4'-dihydro-5'H-pyran-4'-yloxy]-5-(*tert*-butyl-dimethylsilanyloxymethyl) -1H-pyran-4-one (4):



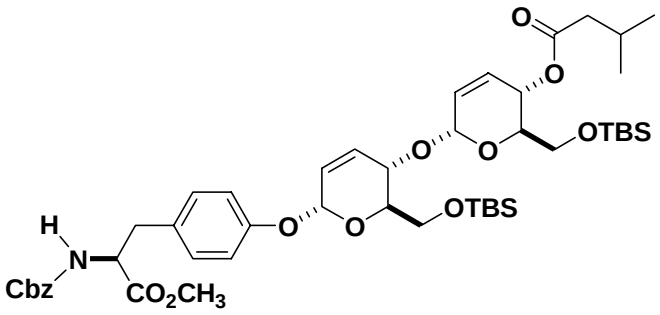
A CH_2Cl_2 (0.5 mL) solution of compound **6** (280 mg, 0.49 mmol) and alcohol **9** (175 mg, 0.49 mmol) was cooled to 0 ^oC. A CH_2Cl_2 (0.5 mL) solution of $Pd_2(dba)_3.CHCl_3$ (12 mg, 2.5 mol%) and PPh_3 (11 mg, 10 mol%) was added to the reaction mixture at 0 ^oC. The reaction mixture was stirred at 0 ^oC for 2 hours. The reaction mixture was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 16% EtOAc/hexanes to give dienone **4** (328 mg, 0.40 mmol, 82%) as viscous oil. R_f (30% EtOAc/hexanes) = 0.44; $[\alpha]_D^{26}$ = + 0.15 (*c* = 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3351, 2952, 1752, 1725, 1509, 1256, 1219, 1151, 995, 836; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.05 (m, 4H), 6.84 (dd, *J* = 10.2, 3.6 Hz, 1H), 6.23 (d, *J* = 10.8 Hz, 1H), 6.14 (d, *J* = 10.2 Hz, 1H), 5.95 (ddd, *J* = 10.2, 2.4, 1.8 Hz, 1H), 5.62 (d, *J* = 3.6 Hz, 1H), 5.60 (d, *J* = 1.8 Hz, 1H), 5.26 (d, *J* = 8.4 Hz, 1H), 5.10 (d, *J* = 13.2 Hz, 1H), 5.07 (d, *J* = 12.6 Hz, 1H), 4.62 (dd, *J* = 13.8, 6.0 Hz, 1H), 4.59 (d, *J* = 9.0 Hz, 1H), 4.44 (dd, *J* = 3.6, 2.4 Hz, 1H), 4.13 (d, *J* = 3.6 Hz, 1H), 4.10 (dd, *J* = 10.2, 4.2 Hz, 1H), 3.96 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.86 (dq, *J* = 9.6, 1.8 Hz, 1H), 3.81 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.70 (s, 3H), 3.08 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.03 (dd, *J* = 13.8, 6.0 Hz, 1H), 0.86 (s, 9H), 0.85 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.5, 171.8, 156.4, 155.5, 143.8, 136.1, 130.1(2C), 130.0, 129.0, 128.5, 128.4(2C), 128.0, 127.9(2C), 126.4, 116.9, 92.8, 89.7, 76.5, 71.1, 66.8, 66.3, 62.8, 62.4, 60.2, 54.7, 52.1, 37.2, 25.78(3C), 25.76(3C), 18.28, 18.23, -5.4, -5.3, -5.4, -5.2; CIHRMS Calcd for $[C_{42}H_{61}NO_{11}Si_2Na^+]$: 834.3675. Found 834.3638.

(1'*S*,4'*S*,5'*R*,1*S*,4*S*,5*R*)-1-[*N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5'-(*tert*-butyl-dimethylsilanyloxymethyl)-1',4'-dihydro-5'H-pyran-4'-yloxy]-5-(*tert*-butyl-dimethylsilanyloxymethyl)-1,4-dihydro-5H-pyran-4-ol (10) :



The enone compound **4** (200 mg, 0.246 mmol) was dissolved in 0.3 mL of CH_2Cl_2 and 0.3 mL MeOH were added to a round bottom flask and cooled to -78 ^oC then (9 mg, 0.246 mmol) $NaBH_4$ was added and the reaction mixture was stirred at -78^oC for 6 hours and on completion, as monitored by TLC, reaction mixture is diluted with ether and was quenched with 5 mL of satd aq $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 20% EtOAc/hexanes to give enol **10** (182 mg, 0.223 mmol, 91%) as viscous oil. R_f (40% EtOAc/hexanes) = 0.44; $[\alpha]_D^{26}$ = + 49 (*c* = 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3420, 2930, 2855, 1725, 1717, 1510, 1256, 1219, 1151, 995, 836; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.05 (m, 4H), 6.15 (d, *J* = 10.2 Hz, 1H), 5.96 (d, *J* = 10.2 Hz, 1H), 5.92 (dq, *J* = 10.2, 1.2 Hz, 1H), 5.68 (dd, *J* = 10.2, 2.4 Hz, 1H), 5.59 (d, *J* = 1.8 Hz, 1H), 5.25 (d, *J* = 7.8 Hz, 1H), 5.18 (d, *J* = 1.8 Hz, 1H), 5.10 (d, *J* = 12.6 Hz, 1H), 5.08 (d, *J* = 12.6 Hz, 1H), 4.62 (dd, *J* = 13.2, 5.4 Hz, 1H), 4.37 (d, *J* = 9.0 Hz, 1H), 4.24 (d, *J* = 8.4 Hz, 1H), 3.97 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.89 (ddd, *J* = 10.2, 5.4, 2.4 Hz, 1H), 3.85 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.81 (dd, *J* = 12.0, 5.4 Hz, 1H), 3.75 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.70 (s, 3H), 3.71 (m, 1H), 3.08 (d, *J* = 3.0 Hz, 1H), 3.05 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.02 (d, *J* = 6.0 Hz, 1H), 0.91 (s, 9H), 0.84 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.7, 171.8, 156.5, 155.5, 136.1, 133.1, 130.5, 130.0(2C), 128.4(2C), 128.0, 127.9(2C), 126.0, 125.3, 117.1(2C), 92.7, 91.0, 71.3, 70.1, 66.8, 66.6, 66.5, 65.1, 62.6, 54.8, 52.1, 37.2, 25.8(3C), 25.7(3C), 18.3, 18.1, -5.1, -5.2, -5.5, -5.6; CIHRMS Calcd for [$C_{42}H_{63}NO_{11}Si_2Na^+$]: 836.3831. Found 836.3818.

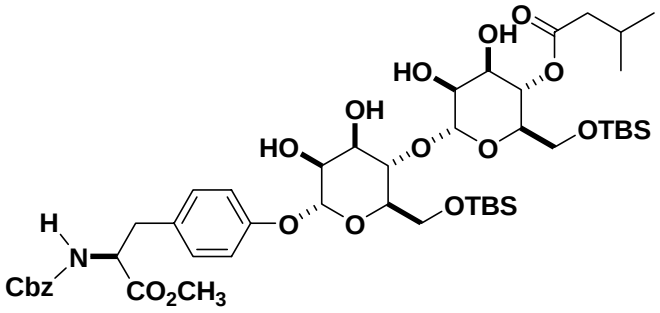
(1'*S*,4'*S*,5'*R*,1*S*,4*S*,5*R*)-1-[1'- *N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5'-(*tert*-butyl-dimethylsilanyloxymethyl)-1',4'-dihydro-5'H-pyran-4'-yloxy] -5-(*tert*-butyl-dimethylsilanyloxymethyl)-1,4-dihydro-5H-pyran-*O*-4'-isovalaric ester (11):



The alcohol compound **10** (140 mg, 0.171 mmol), isovaleric acid (21 mg, 0.206 mmol) and DCC (42 mg, 0.206 mmol) were dissolved in 0.3 mL of CH_2Cl_2 in a round bottom flask and cooled to 0 ^oC then DMAP (2 mg, 0.01 mmol) was added and the reaction mixture was stirred at 0 ^oC for 6 hours and on completion, as monitored by TLC, the reaction mixture was diluted with ether and was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 15% EtOAc/hexanes to give **11** (148 mg, 0.164 mmol, 96%) as viscous oil. R_f (30% EtOAc/hexanes) = 0.62; $[\alpha]_D^{26}$ = + 90 (*c* = 1, CH_2Cl_2); IR (thin film, cm^{-1}) 2956, 2928, 1738, 1733, 1510, 1253, 1219, 1123, 986, 835; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 5H), 7.00 (m, 4H), 6.20 (dd, *J* = 10.2, 2.4 Hz, 1H), 5.93 (m, 2H), 5.74 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 5.42 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.28 (d, *J* = 1.2 Hz, 1H), 5.24 (d, *J* = 8.4 Hz, 1H), 5.10 (d, *J* = 12.6 Hz, 1H), 5.08 (d, *J* = 12.6 Hz, 1H), 4.62 (dd, *J* = 13.2, 5.4 Hz, 1H), 4.42 (d, *J* = 9.0 Hz, 1H), 3.89 (ddd, *J* = 10.2, 5.4, 2.4 Hz, 1H), 3.85 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.81 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.78 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.75 (m, 1H), 3.70 (s, 3H), 3.71 (m, 1H), 3.08 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.04 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.20 (d, *J* = 1.2 Hz, 2H), 2.10 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 6H), 0.89 (s, 9H), 0.85 (s, 9H), 0.05 (s, 6H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 171.8, 156.6, 155.5, 136.2, 130.3, 130.0(2C), 129.8, 128.4(2C), 128.0(2C), 127.9, 127.2, 126.1, 117.2(2C), 92.9, 90.9, 71.4, 69.6, 66.8, 66.3, 64.6, 62.8, 62.1, 54.7, 52.1, 43.3, 37.2, 25.9,

25.8(6C), 25.6, 22.3, 22.2 18.38, 18.36, -5.1, -5.2, -5.41, -5.45; CIHRMS Calcd for [$C_{47}H_{71}NO_{12}Si_2Na^+$]: 920.4407. Found 920.4385.

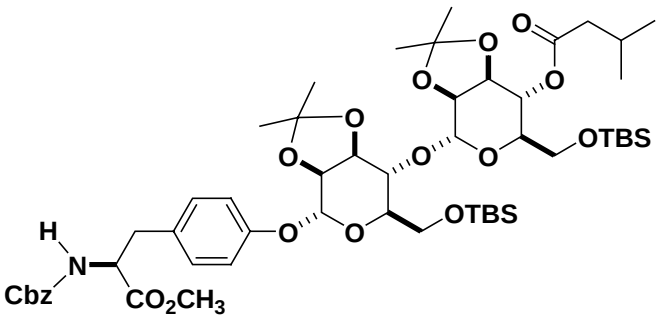
1'- *N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5',5-(*tert*-butyl-dimethylsilanyloxymethyl)-di-1,4-α-D-mannose -*O*-4' isovalaric ester (3a):



To a *t*-butanol-acetone (0.2 mL, 1:1) solution of diene ester **11** (100 mg, 0.11 mmol) at 0 ^oC was added a solution of (50% w/v) of *N*-methyl morpholine *N*-oxide / water (0.1 mL). Crystalline OsO_4 (1.4 mg, 5 mol %) was added and the reaction was stirred for 12 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with MeOH/ether (2:98 to 4:96). Pure fractions were combined and concentrated to afford bis-α-D-*manno*-tetrol **3a** (91 mg, 0.094 mmol, 85 %) as viscous oil. R_f (90% EtOAc/MeOH) = 0.56; $[\alpha]_D^{26}$ = + 61.9 (*c* = 2, CH_2Cl_2); IR (thin film, cm^{-1}) 2956, 2928, 1738, 1733, 1510, 1253, 1219, 1123, 986, 835; ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (m, 5H), 6.99 (m, 4H), 5.45 (d, *J* = 1.2 Hz, 1H), 5.36 (d, *J* = 1.8 Hz, 1H), 5.26 (d, *J* = 8.4 Hz, 1H), 5.10 (d, *J* = 12.6 Hz, 1H), 5.07 (d, *J* = 12.6 Hz, 1H), 5.02 (dd, *J* = 10.2, 9.0 Hz, 1H), 4.62 (dd, *J* = 6.0, 1.8 Hz, 1H), 4.22 (ddd, *J* = 10.2, 6.0, 3.6, Hz, 1H), 4.13 (dd, *J* = 10.2, 6.6 Hz, 1H), 4.03 (dd, *J* = 4.2, 1.8 Hz, 1H), 3.97 (ddd, *J* = 10.8, 7.2, 2.4 Hz, 1H), 3.93 (dd, *J* = 10.2, 4.2 Hz, 1H), 3.89 (dd, *J* = 10.2, 9.6 Hz, 1H), 3.86 (dd, *J* = 11.4, 10.2 Hz, 1H), 3.78 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.72 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.70 (s, 3H), 3.70 (m, 2H), 3.45 (d, *J* = 3.6 Hz, 1H), 3.25 (d, *J* = 7.2 Hz, 1H), 3.10 (d, *J* = 1.2 Hz, 1H), 3.06 (dd, *J* = 13.8, 6.0 Hz, 1H), 3.02 (dd, *J* = 15.0, 5.4 Hz, 1H), 2.24 (dd, *J* = 15.0, 7.2 Hz, 1H), 2.20 (dd, *J* = 13.8.0, 7.2 Hz, 1H), 2.16 (d, *J* = 1.8 Hz, 1H), 2.08 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 6H), 0.89 (s, 9H), 0.84 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.02 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 171.9, 155.6, 155.4, 136.1, 130.2(2C), 128.4(3C), 128.1(2C), 128.0, 116.8(2C), 98.3, 97.7, 73.7, 71.6, 71.2, 70.8, 70.1, 70.0, 69.8, 66.9, 62.8, 54.8,

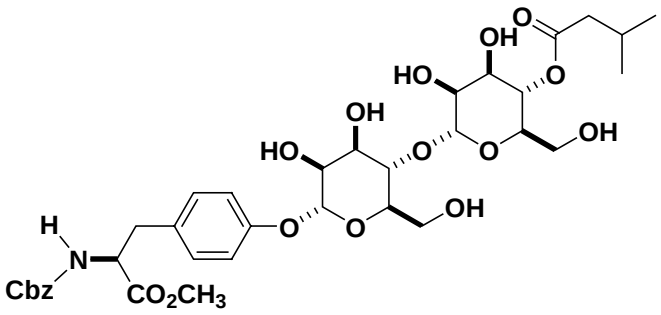
52.2, 43.4(2C), 37.2, 25.9, 25.9(3C), 25.8(3C), 25.7, 22.3, 22.2, 18.4, 18.3, -5.2, -5.3, -5.40, -5.47; CIHRMS Calcd for [$C_{47}H_{75}NO_{16}Si_2Na^+$]: 988.4516. Found 988.4459.

1'-*N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5',5-(*tert*-butyl-dimethylsilanyloxymethyl)-2,3,2',3'-di acetonide-bis-1,4-α-D-mannose-*O*-4'-isovalaric ester (3b) :



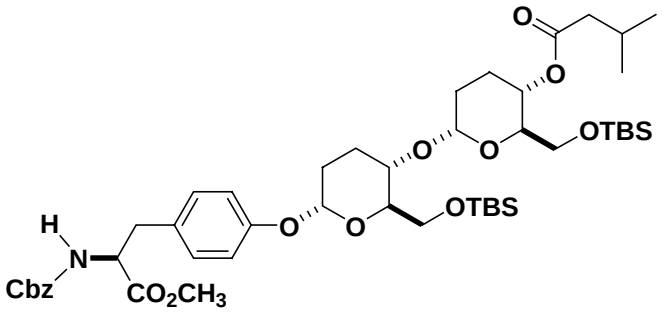
To a CH_2Cl_2 (0.1 mL, 1.0M) solution of D-*manno*-tetrol **3a** (20 mg, 0.02 mmol) and 2,2-dimethoxypropane (4.6 mg, 0.04 mmol) at 0 ^oC was added CSA (0.50 mg, 10 mol%) and the reaction was stirred for 6 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with EtOAc/Hexane (40:60). Pure fractions were combined and concentrated to afford **3b** (17 mg, 0.02 mmol, 80 %) as viscous oil. R_f (50% EtOAc/Hexane) = 0.45; $[\alpha]_D^{26}$ = +49 (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 2955, 2935, 1728, 1511, 1226, 1101, 1017, 833; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.29 (m, 4H), 5.97 (d, *J* = 10.2 Hz, 1H), 5.92 (ddd, *J* = 10.2, 3.0 1.8 Hz, 1H), 5.40 (br s, 1H), 5.04 (br s, 2H), 4.94 (dd, *J* = 9.6, 7.8 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.38 (ddd, *J* = 9.0, 4.2, 4.2 Hz, 1H), 4.26 (d, *J* = 6.0 Hz, 1H), 4.21 (dd, *J* = 13.2, 5.4 Hz, 1H), 4.09 (dd, *J* = 11.4, 5.4 Hz, 1H), 4.01 (m, 1H), 3.78 (d, *J* = 5.4 Hz, 1H), 3.74 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.72 (br s, 1H), 3.68 (d, *J* = 6.0 Hz, 1H), 3.67 (s, 3H), 3.61 (d, *J* = 10.2 Hz, 1H), 3.06 (dd, *J* = 7.2, 6.0 Hz, 1H), 2.95 (s, 1H), 2.88 (s, 1H), 2.26 (dd, *J* = 15.0, 6.6 Hz, 1H), 2.18 (dd, *J* = 15.0, 7.2 Hz, 1H), 1.93 (m, 3H), 1.85 (m, 3H), 1.63 (m, 3H), 1.50 (m, 3H), 0.97 (s, 6H), 0.95 (s, 9H), 0.90 (s, 9H), 0.10 (s, 3H), 0.09 (s, 6H), 0.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 172.6, 154.2, 137.5, 130.3, 128.7, 128.6(2C), 128.5, 128.4(2C), 128.1, 128.0(2C), 127.8, 116.7, 110.0, 92.9(2C), 75.1, 69.9(3C), 69.5(2C), 66.6, 62.8(2C), 58.8(2C), 53.2, 50.4, 40.1, 38.1, 29.3, 28.7(2C), 28.4, 26.0(3C), 25.9(3C), 22.3(2C), 18.6, 18.3(2C), -5.0, -5.2(2C), -5.3; CIHRMS Calcd for [$C_{53}H_{83}NO_{16}Si_2Na^+ - C_3H_6^{2+}$]: 1028.5142. Found 1028.4585.

1'- *N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5',5-(hydroxy methyl)-di-1,4-α-D-mannose –*O*-4' isovaleric ester (2a):



To a THF (0.5 mL, 0.1M) solution of D-*manno*-tetrol **3a** (50 mg, 0.05 mmol) at 0 ^{o}C was added a solution of TBAF in THF (50 µL, 1.0M) and the reaction was stirred for 1 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with MeOH/EtOAc/Hexane (10:40:50). Pure fractions were combined and concentrated to afford **2a** (31 mg, 0.04 mmol, 80 %) as viscous oil. R_f (10:50:40% MeOH/EtOAc/Hexane) = 0.20; $[\alpha]_D^{26}$ = + 71 (*c* 0.5, CH_3OH); IR (thin film, cm^{-1}) 3337, 2956, 2926, 1738, 1611, 1510, 1228, 1217, 1094, 976, 834; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (m, 5H), 7.17 (m, 4H), 5.48 (d, *J* = 1.8 Hz, 1H), 5.42 (d, *J* = 1.8 Hz, 1H), 5.09 (br s, 2H), 4.59 (br s, 1H), 4.45 (ddd, *J* = 7.8, 6.6, 1.8 Hz, 1H), 4.08 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.05 (m, 3H), 4.00 (br s, 1H), 3.89 (dd, *J* = 9.6, 2.4 Hz, 1H), 3.80 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.74 (m, 4H), 3.68 (m, 1H), 3.62 (m, 1H), 3.36 (m, 3H), 3.15 (ddd, *J* = 10.2, 4.8, 4.8 Hz, 1H), 2.93 (m, 2H), 2.29 (m, 1H), 2.13 (m, 1H), 1.34 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 6H); NMR (150 MHz, $CDCl_3$) δ 172.1, 155.8, 155.3, 136.4, 130.5(2C), 129.9, 128.4(2C), 128.2(2C), 116.6, 103.2, 102.4, 98.1, 71.8, 71.3, 67.1(2C), 61.1, 55.1, 52.5(2C), 43.6, 43.1, 37.5, 36.6, 31.6, 30.5, 29.8, 28.6, 25.9, 23.1, 22.5(2C); CIHRMS Calcd for $[C_{35}H_{47}NO_{16}Na^+]$: 760.2787. Found 760.2798.

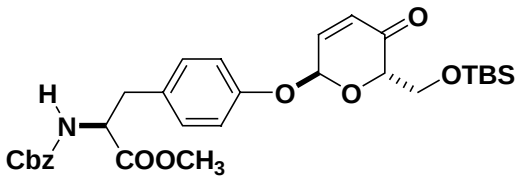
(1'*S*,4'*S*,5'*R*,1*S*,4*S*,5*R*)-1-[1'-*N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5'-(*tert*-butyl-dimethylsilanyloxymethyl)-tetrahydro-pyran-4'-yloxy]-5-(*tert*-butyl-dimethylsilanyloxymethyl) -tetrahydro-pyran-*O*-4'-isovalaric ester (16):



The dienone ester compound **11** (27 mg, 0.03 mmol) and *o*-$NO_2C_6H_4SO_2NHNH_2$ (20 mg, 0.02 mmol) were dissolved in 0.2 mL of CH_2Cl_2 in a round bottom flask and cooled 0 ^oC under nitrogen atmosphere then triethylamine (17 mg, 0.17 mmol) was added and the reaction mixture was stirred at 0 ^oC for 12 hours and on completion, as monitored by TLC. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. The crude product was purified using silica gel flash chromatography eluting with 15% EtOAc/hexanes to give **16** (18 mg, 0.02 mmol, 95 %) as viscous oil. R_f (30% EtOAc/Hexane) = 0.46; $[\alpha]_D^{26}$ = + 35 (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 2952, 2929, 1735, 1510, 1254, 1220, 1123, 996, 836; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 5H), 6.98 (m, 4H), 5.45 (br s, 1H), 5.24 (d, *J* = 7.8 Hz, 1H), 5.09 (br s, 2H), 5.08 (d, *J* = 2.4 Hz, 1H), 4.73 (ddd, *J* = 10.2, 9.6, 4.8 Hz, 1H), 4.60 (ddd, *J* = 7.8, 5.4, 5.4 Hz, 1H), 3.84 (d, *J* = 11.4 Hz, 1H), 3.79-3.67 (m, 6H), 3.70 (s, 3H), 3.05 (dd, *J* = 13.2, 6.0 Hz, 1H), 3.01 (dd, *J* = 13.2, 5.4 Hz, 1H), 2.15 (m, 3H), 2.06 (m, 1H), 2.00 (m, 2H), 1.80 (m, 3H), 1.71 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H), 0.86 (s, 9H), 0.84 (s, 9H), 0.03 (s, 6H), 0.01 (s, 6H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 172.0, 172.2, 156.4, 136.5, 130.2, 128.4(2C), 128.2(2C), 128.1, 128.0(2C), 116.7(2C), 94.8, 90.5, 75.1, 73.4, 71.5, 67.7, 66.8, 66.4, 63.1, 62.6, 54.6, 52.0, 43.6, 37.5,

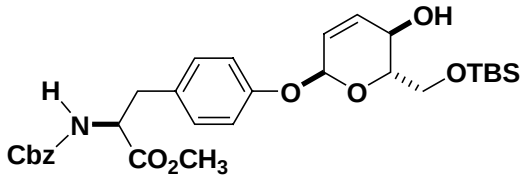
28.6, 25.8(3C), 25.7(3C), 25.7, 23.6, 22.2(3C), 22.0, 18.4, 18.2, -5.1, -5.3, -5.40, -5.44; CIHRMS Calcd for [$C_{47}H_{75}NO_{12}Si_2Na^+$]: 924.4720. Found 924.4702.

3-{4-[6-(*tert*-Butyl-dimethylsilanyloxymethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yloxy]-phenyl}-2-*N*-carbobenzyloxy-D-tyrosine methyl ester (A- structure was not shown in Scheme 6):



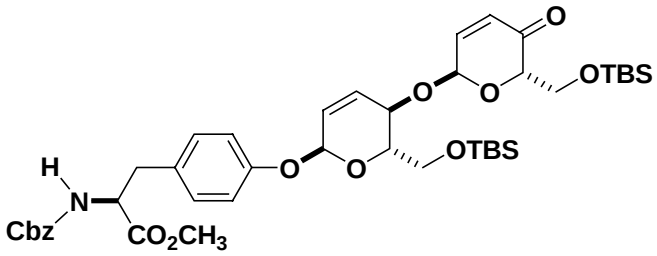
A CH_2Cl_2 (0.6 mL) solution of compound **(*ent*)-6** (200 mg, 0.55 mmol) and Cbz-D-tyrosine methyl ester **5** (220 mg, 0.67 mmol) was cooled to 0 ^oC. A CH_2Cl_2 (0.6 mL) solution of $Pd_2(dba)_3$-.$CHCl_3$ (14 mg, 2.5 mol%) and PPh_3 (14 mg, 10 mol%) was added to the reaction mixture at 0 ^oC. The reaction mixture was stirred at 0 ^oC for 3 hours. The reaction mixture was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 20% EtOAc/hexanes to give **12a** (278 mg, 0.50 mmol, 90%) as viscous oil. R_f (40% EtOAc/hexanes) = 0.40; $[\alpha]_D^{26}$ = (*c* 0.64, CH_2Cl_2); IR (thin film, cm^{-1}) 3351, 2952, 1752, 1725, 1509, 1256, 1219, 1151, 995, 836; ^1H NMR (270 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.05 (m, 4H), 6.97 (dd, *J* = 10.2, 3.5 Hz, 1H), 6.22 (d, *J* = 10.2 Hz, 1H), 5.94 (d, *J* = 3.3 Hz, 1H), 5.33 (dd, *J* = 8.5, 4.2 Hz, 1H), 5.09 (br s, 2H), 4.62 (dd, *J* = 13.2, 5.7 Hz, 1H), 4.53 (dd, *J* = 4.1, 3.1 Hz, 1H), 4.15-4.00 (m, 2H), 3.71 (s, 3H), 3.69 (m, 2H), 0.84 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 194.2, 177.7, 156.1, 155.4, 151.6, 150.0, 142.6, 136.0, 133.1, 130.2, 130.0, 128.5, 128.3, 128.0, 127.9, 121.2, 116.9, 91.8, 83.3, 66.8, 62.4, 54.7, 52.2, 37.1, 25.1(3C), 18.1, -5.46, -5.49; CIHRMS Calcd for [$C_{30}H_{39}NO_8SiNa^+$]: 592.2343. Found 592.2369.

3-{4-[6-(*tert*-Butyl-dimethylsilanyloxymethyl)-5-hydroxy-5,6-dihydro-2*H*-pyran-2-yloxy]-phenyl}-2- *N*-carbobenzyloxy-D-tyrosine methyl ester (B- structure was not shown in Scheme 6):



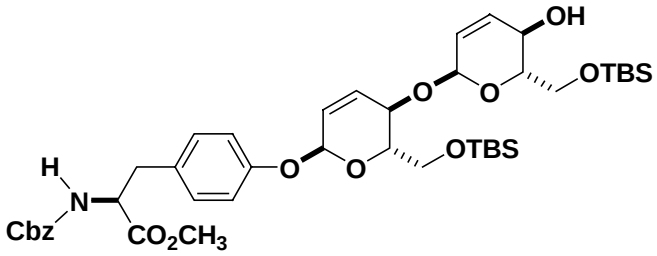
The enone compound **12a** (300 mg, 0.527 mmol), dissolved in 0.5 mL of CH_2Cl_2 and 0.5 mL MeOH, was added to a round bottom flask and cooled to -24 ^oC then (20 mg, 0.527 mmol) $NaBH_4$ was added and the reaction mixture was stirred at -24 ^oC for 1 hour and on completion, as monitored by TLC, the reaction mixture was diluted with ether and was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 25% EtOAc/hexanes to give **12b** (270 mg, 0.47 mmol, 89%) as viscous oil. R_f (30% EtOAc/hexanes) = 0.30; $[\alpha]_D^{26}$ = - 82 (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3357, 2928, 1722, 1611, 1439, 1225, 1054, 985, 835; ^1H NMR (600 MHz, $CDCl_3$) δ 7.33 (m, 5H), 6.97 (m, 4H), 6.07 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.85 (ddd, *J* = 10.2, 2.4, 2.4 Hz, 1H), 5.56 (dd, *J* = 2.4, 1.2 Hz, 1H), 5.20 (d, *J* = 7.8 Hz, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 4.61 (dd, *J* = 13.2, 5.4 Hz, 1H), 4.26 (dd, *J* = 9.0, 1.8 Hz, 1H), 3.89 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.83 (ddd, *J* = 9.0, 7.2, 4.8 Hz, 1H), 3.73 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.31 (s, 3H), 3.08 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.04 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.01 (d, *J* = 3.0 Hz, 1H), 0.87 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.9, 156.6, 136.2, 133.3, 130.2, 130.2(2C), 128.5(2C), 128.1, 128.0, 124.8, 116.9(2C), 116.6, 92.8, 70.7, 66.9, 66.8, 65.3, 54.8, 52.3, 52.2, 37.3, 25.7(3C), 18.1, -5.5, -5.6; CIHRMS Calcd for $[C_{30}H_{41}NO_8SiNa^+]$: 594.2493 Found 594.2500.

(1'*R*, 4'*R*, 5'*S*, 1*R*, 5*S*)-1-[1'-*N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5-(*tert*-butyl-dimethylsilanyloxymethyl)-1',4'-dihydro-5'H-pyran-4'-yloxy]-5-(*tert*-butyl-dimethylsilanyloxymethyl) -1H-pyran-4-one (12):



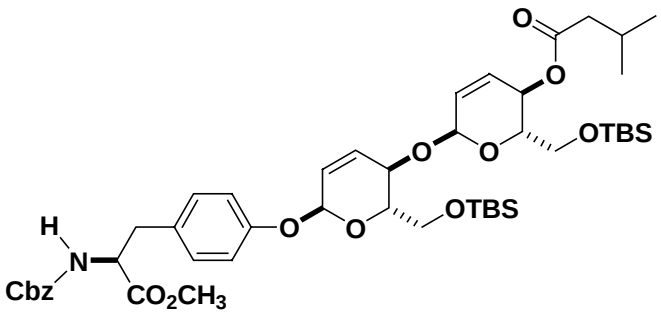
A CH_2Cl_2 (0.5 mL) solution of compound **(*ent*)-6** (163 mg, 0.45 mmol) and alcohol **12b** (260 mg, 0.45 mmol) was cooled to 0 ^oC. A CH_2Cl_2 (0.5 mL) solution of $Pd_2(dba)_3.CHCl_3$ (11.8 mg, 2.5 mol%) and PPh_3 (12 mg, 10 mol%) was added to the reaction mixture at 0 ^oC. The reaction mixture was stirred at 0 ^oC for 2 hours. The reaction mixture was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 16% EtOAc/hexanes to give dienone **12** (313 mg, 0.38 mmol, 85%) as viscous oil. R_f (30% EtOAc/hexanes) = 0.44; $[\alpha]_D^{26}$ = -63 (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3341, 2952, 1725, 1700, 1509, 1252, 1226, 1123, 984, 836; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 5H), 7.00 (m, 4H), 6.84 (dd, *J* = 10.2, 3.6 Hz, 1H), 6.23 (d, *J* = 10.2 Hz, 1H), 6.14 (d, *J* = 10.8 Hz, 1H), 5.95 (ddd, *J* = 10.2, 3.0, 1.2 Hz, 1H), 5.62 (d, *J* = 3.6 Hz, 1H), 5.61 (d, *J* = 1.8 Hz, 1H), 5.18 (d, *J* = 7.8 Hz, 1H), 5.10 (br s, 2H), 4.62 (dd, *J* = 13.8, 6.0 Hz, 1H), 4.59 (d, *J* = 9.0 Hz, 1H), 4.44 (dd, *J* = 3.6, 2.4 Hz, 1H), 4.13 (d, *J* = 3.6 Hz, 1H), 4.10 (dd, *J* = 10.2, 4.2 Hz, 1H), 3.96 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.86 (dq, *J* = 12.0, 3.6 Hz, 1H), 3.80 (dd, *J* = 12.0, 4.2 Hz, 1H), 3.72 (s, 3H), 3.07 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.03 (dd, *J* = 13.8, 6.0 Hz, 1H), 0.86 (s, 9H), 0.84 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.6, 171.9, 156.4, 155.6, 143.9, 136.2, 133.3, 130.2(2C), 130.1, 129.1, 128.6, 128.5(2C), 128.1, 128.0, 126.6(2C), 117.0, 92.9, 89.8, 76.7, 71.3, 66.9, 66.5, 62.9, 62.5, 54.8, 52.2, 37.3, 25.9(3C), 25.8(3C), 18.4, 18.3, -5.1, -5.3(2C), -5.4; CIHRMS Calcd for $[C_{42}H_{61}NO_{11}Si_2Na^+]$: 834.3675. Found 834.3648.

(1'*R*,4'*R*,5'*S*,1*R*,4*R*,5*S*)-1-[*N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5'-(*tert*-butyl-dimethylsilanyloxymethyl)-1',4'-dihydro-5'H-pyran-4'-yloxy]-5-(*tert*-butyl-dimethylsilanyloxymethyl)-1,4-dihydro-5H-pyran-4-ol (13a):



The dienone compound **12** (300 mg, 0.37 mmol), dissolved in 0.4 mL of CH_2Cl_2 and 0.4 mL MeOH, was added to a round bottom flask and cooled to -24 ^oC then $NaBH_4$ (14 mg, 0.37 mmol) was added and the reaction mixture was stirred at -24 ^oC for 1 hour and on completion, as monitored by TLC, the reaction mixture is diluted with ether and was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 25% EtOAc/hexanes to give **13a** (271 mg, 0.333 mmol, 90%) as viscous oil. R_f (30% EtOAc/hexanes) = 0.30; $[\alpha]_D^{26}$ = -72 (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3433, 2928, 2857, 1724, 1509, 1253, 1226, 1123, 1044, 981, 836; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 5H), 7.00 (m, 4H), 6.15 (d, *J* = 10.8 Hz, 1H), 5.97 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.92 (ddd, *J* = 10.2, 3.0, 1.8 Hz, 1H), 5.68 (ddd, *J* = 10.2, 2.4, 1.8 Hz, 1H), 5.59 (d, *J* = 1.8 Hz, 1H), 5.18 (br s, 2H), 5.09 (br s, 2H), 4.61 (dd, *J* = 13.2, 5.4 Hz, 1H), 4.36 (d, *J* = 8.4 Hz, 1H), 4.24 (d, *J* = 8.4 Hz, 1H), 3.97 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.89 (dddd, *J* = 5.4, 3.6, 1.8, 1.8 Hz, 1H), 3.85 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.80 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.73 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.72 (s, 3H), 3.69 (m, 1H), 3.06 (d, *J* = 6.0 Hz, 1H), 3.05 (d, *J* = 5.4 Hz, 1H), 3.02 (d, *J* = 2.4 Hz, 1H), 0.92 (s, 9H), 0.84 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.9, 156.7, 155.6, 136.2, 133.1, 130.5, 130.1(2C), 130.0, 129.0, 128.4(2C), 128.1, 128.0, 126.1, 125.4, 117.2, 116.9, 92.8, 91.1, 71.4, 70.0, 66.9, 66.9, 66.7, 65.3, 62.6, 54.8, 52.2, 37.3, 25.8(3C), 25.8(3C), 18.3, 18.2, -5.0, -5.1, -5.4, -5.6; CIHRMS Calcd for $[C_{42}H_{63}NO_{11}Si_2Na^+]$: 836.3831. Found 836.3844.

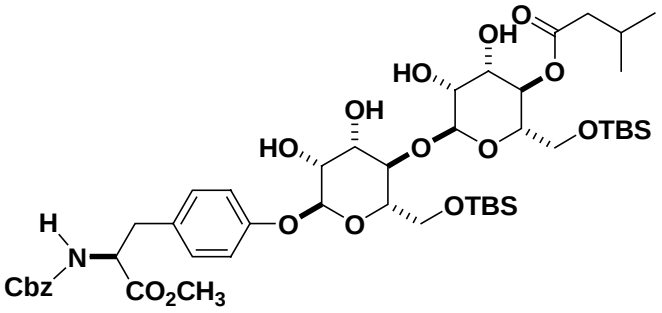
(1'*R*,4'*R*,5'*S*,1*R*,4*R*,5*S*)-1-[1'- *N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5'-(*tert*-butyl-dimethylsilanyloxymethyl)-1',4'-dihydro-5'H-pyran-4'-yloxy] -5-(*tert*-butyl-dimethylsilanyloxymethyl)-1,4-dihydro-5H-pyran-*O*-4'-isovalaric ester (13):



The alcohol compound **13a** (135 mg, 0.17 mmol), isovaleric acid (20 mg, 0.20 mmol) and DCC (41 mg, 0.20 mmol) were dissolved in 0.3 mL of CH_2Cl_2 in a round bottom flask and cooled to 0 ^oC then DMAP (2 mg, 0.016 mmol) was added and the reaction mixture was stirred at 0 ^oC for 6 hours and on completion, as monitored by TLC, the reaction mixture was diluted with ether and was quenched with 5 mL of satd. aq. $NaHCO_3$, extracted (3 x 5 mL) with Et_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 15% EtOAc/hexanes to give **13** (141.5mg, 0.16 mmol, 95%) as viscous oil. R_f (30% EtOAc/hexanes) = 0.60; $[\alpha]_D^{26}$ = - 99 (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 2956, 2929, 1737, 1509, 1253, 1219, 1123, 986, 835; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 5H), 7.00 (m, 4H), 6.20 (d, *J* = 10.2 Hz, 1H), 5.94 (dd, *J* = 2.4, 1.8 Hz, 1H)), 5.92 (dd, *J* = 2.4, 1.8 Hz, 1H)), 5.76 (dd, *J* = 3.0, 1.8 Hz, 1H), 5.74 (ddd, *J* = 10.2, 2.4, 2.4 Hz, 1H), 5.59 (d, *J* = 1.8 Hz, 1H), 5.41 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.28 (d, *J* = 1.8 Hz, 1H)), 5.17 (d, *J* = 7.8 Hz, 1H)) 5.10 (br s, 2H), 4.62 (dd, *J* = 13.2, 5.4 Hz, 1H), 4.41 (d, *J* = 9.0 Hz, 1H), 3.90 (dddd, *J* = 10.2, 5.4, 2.4, 2.4 Hz, 1H), 3.85 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.80 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.77 (dd, *J* = 6.0, 2.4 Hz, 1H), 3.75 (m, 1H), 3.72 (s, 3H), 3.06 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.04 (dd, *J* = 9.6, 5.4 Hz, 1H), 2.20 (d, *J* = 1.8 Hz, 2H), 2.10 (m, 1H), 0.96 (d, *J* = 7.6 Hz, 6H), 0.89 (s, 9H), 0.84 (s, 9H), 0.05 (s, 6H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.2, 171.9, 156.7, 136.2, 130.4, 130.1(2C), 129.9, 128.5(2C),

128.1(2C), 128.0, 127.3, 126.2, 117.3, 117.2(2C), 92.9, 91.0, 71.5, 69.7, 66.9, 66.4, 64.7, 62.9, 62.2, 54.8, 52.2, 43.4, 37.3, 25.94(3C), 25.92(3C), 25.7, 22.4, 22.3, 20.2, 18.45(2C), -5.1, -5.2, -5.4, -5.3; CIHRMS Calcd for [$C_{47}H_{71}NO_{12}Si_2Na^+$]: 920.4407. Found 920.4401.

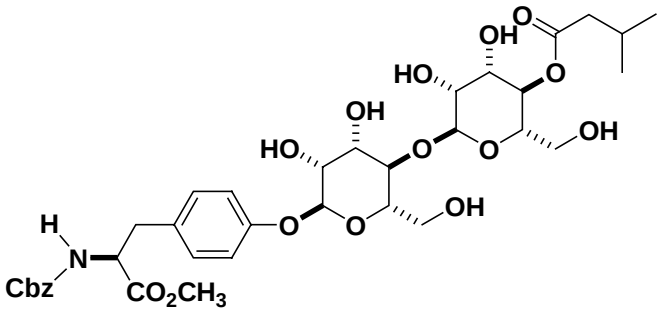
1'- *N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5',5-(*tert*-butyl-dimethylsilanyloxymethyl)-di-1,4-α-l-mannose–*O*-4'-isovalaric ester (14a):



To a CH_2Cl_2 (1.6 mL, 0.1M) solution of dienone **13** (148 mg, 0.16 mmol) at 0 ^oC was added a solution of (50% w/v) of *N*-methyl morpholine *N*-oxide / water (0.1 mL). Crystalline OsO_4 (4.2 mg, 10 mol %) was added and the reaction was stirred for 12 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with MeOH/EtOAc/Hexane (10:40:50). Pure fractions were combined and concentrated to afford *manno*-tetrol **14a** (137 mg, 0.142 mmol, 86 %) as viscous oil. R_f (60% EtOAc/Hexane) = 0.20; $[\alpha]_D^{26}$ = -20 (*c* 1, CH_3OH); IR (thin film, cm^{-1}) 3441, 2928, 2855, 1726, 1611, 1510, 1252, 1227, 1107, 1020, 835; ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 (m, 5H), 7.10 (m, 4H), 5.47 (d, *J* = 1.8 Hz, 1H), 5.44 (d, *J* = 1.8 Hz, 1H), 5.20 (dd, *J* = 10.2, 9.6 Hz, 1H), 5.10 (br s, 2H), 4.87 (br s, 4H), 4.59 (m, 1H), 4.45 (dd, *J* = 9.0, 5.4 Hz, 1H), 4.08 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.02 (dd, *J* = 3.0, 2.4 Hz, 1H), 4.00 (d, *J* = 1.8 Hz, 1H), 3.98 (dd, *J* = 9.0, 1.8 Hz, 1H), 3.90 (dd, *J* = 10.2, 9.0 Hz, 1H), 3.88 (ddd, *J* = 10.2, 6.6, 2.4 Hz, 1H), 3.87 (dd, *J* = 10.2, 9.6 Hz, 1H), 3.84 (dd, *J* = 4.8, 1.8 Hz, 1H), 3.83 (m, 1H), 3.75 (m, 3H), 3.74 (dd, *J* = 4.2, 1.8 Hz, 1H), 3.69 (ddd, *J* = 9.6, 6.6, 1.8 Hz, 1H), 3.13 (dd, *J* = 13.8, 5.4 Hz, 1H), 2.92 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.29 (dd, *J* = 15.0, 7.2 Hz, 1H), 2.24 (dd, *J* = 15.0, 7.2 Hz, 1H), 2.13 (m, 1H), 1.03 (d, *J* = 7.2 Hz, 6H), 0.95 (s, 9H), 0.89 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.8, 171.9, 155.6, 136.2, 130.3(2C), 128.5(3C), 128.2, 128.0, 116.6(2C), 97.5, 96.9,

73.9, 71.49, 71.40, 71.0, 70.8, 70.3(2C), 68.8, 66.9, 63.0, 62.9, 54.8, 52.3, 43.4(2C), 37.4, 25.9(3C), 25.8(3C), 25.8, 22.3(2C), 22.3, 18.4, 18.3, -5.2, -5.3, -5.40, -5.46; CIHRMS Calcd for $[C_{47}H_{75}NO_{16}Si_2Na^+]$: 988.4516. Found 988.4485.

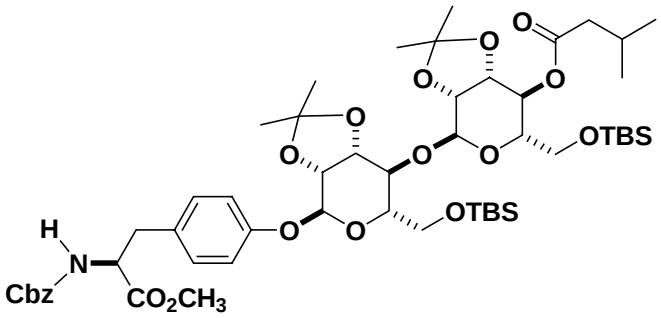
1'-*N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5',5-(hydroxy methyl)-di-1,4-α-l-mannose -*O*-4' isovaleric ester (14):



To a THF (0.8 mL, 0.1M) solution of *manno*-tetrol **14a** (67 mg, 0.16 mmol) at 0 ^oC was added a solution of TBAF in THF (138 µL, 1.0M) and the reaction was stirred for 1 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with MeOH/EtOAc/Hexane (10:40:50). Pure fractions were combined and concentrated to afford **14** (40 mg, 0.054 mmol, 78 %) as viscous oil. R_f (10:50:40% MeOH/EtOAc/Hexane) = 0.20; $[\alpha]_D^{26}$ = **-** 110 (*c* 0.5, CH_3OH); IR (thin film, cm^{-1}) 3337, 2956, 2926, 1738, 1611, 1510, 1228, 1217, 1094, 976, 834; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.10 (m, 4H), 5.48 (d, *J* = 1.8 Hz, 1H), 5.42 (d, *J* = 2.4 Hz, 1H), 5.12 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.07 (br s, 2H), 4.59 (s, 1H), 4.45 (ddd, *J* = 12.6, 9.6, 1.2 Hz, 1H), 4.10 (dd, *J* = 9.0, 3.6 Hz, 1H), 4.02-4.08 (m, 4H), 4.00 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.89 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.83 (dd, *J* = 5.4, 3.0 Hz, 1H), 3.80 (dd, *J* = 7.2, 5.4 Hz, 1H), 3.77-3.72 (m, 1H), 3.75 (s, 3H), 3.67 (s, 1H), 3.62 (dd, *J* = 6.0, 3.0 Hz, 1H), 3.35 (br s, 4H), 3.14 (dd, *J* = 13.8, 4.2 Hz, 1H), 2.92 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.31 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.30 (dd, *J* = 7.2, 2.4 Hz, 1H), 2.27 (dd, *J* =

14.4, 7.2 Hz, 1H), 2.14 (m, 1H), 1.02 (d, *J* = 6.6 Hz, 6H); NMR (150 MHz, $CDCl_3$) δ 173.6, 172.0, 155.7, 136.1, 130.3(2C), 128.4(3C), 128.1, 127.9, 116.3(2C), 101.6, 97.9, 73.9, 71.9, 71.6(2C), 71.1, 70.6, 69.3, 66.9, 60.9, 60.6, 60.4, 54.8, 52.2, 43.3, 42.9, 37.2, 29.5, 25.6, 22.23, 22.20; CIHRMS Calcd for [$C_{35}H_{47}NO_{16}Na^+$]: 760.2787. Found 760.2750.

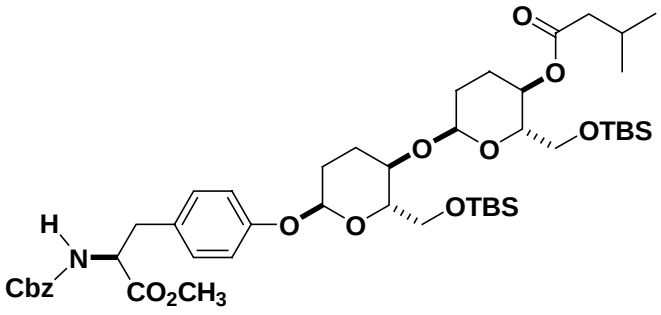
1'-*N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5',5-(*tert*-butyl-dimethylsilanyloxymethyl)-2,3,2',3'-bis acetonide-di-1,4-α-l-mannose-*O*-4'-isovalaric ester (15):



To a CH_2Cl_2 (0.1 mL, 1.0M) solution of *manno*-tetrol **14a** (25 mg, 0.02 mmol) and 2,2-dimethoxypropane (5.7 mg, 0.05 mmol) at 0 ^oC was added CSA (0.60 mg, 10 mol%) and the reaction was stirred for 6 h. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. Impurities were eluted with ether and the product was eluted with EtOAc/Hexane (40:60). Pure fractions were combined and concentrated to afford **15** (22 mg, 0.02 mmol, 81 %) as viscous oil. R_f (50% EtOAc/Hexane) = 0.44; $[\alpha]_D^{26}$ = -31 (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 2953, 2928, 1726, 1510, 1220, 1091, 1019, 833; ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (m, 5H), 6.96 (m, 4H), 5.51 (d, *J* = 1.2 Hz, 1H), 5.42 (d, *J* = 1.8 Hz, 1H), 5.06 (br s, 2H), 4.96 (dd, *J* = 10.2, 7.8 Hz, 2H), 4.62 (dd, *J* = 13.8, 5.4 Hz, 1H), 4.25 (dd, *J* = 9.6, 3.6, Hz, 1H), 4.16 (dd, *J* = 12.6, 5.4 Hz, 1H), 4.10 (d, *J* = 5.4 Hz, 1H), 4.00 (m, 1H), 3.91 (m, 1H), 3.89 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.86 (dd, *J* = 9.6, 4.8 Hz, 1H), 3.84 (d, *J* = 9.0 Hz, 1H), 3.75 (m, 2H), 3.69 (s, 3H), 3.64 (d, *J* = 5.4 Hz, 1H), 3.02 (m, 2H), 3.03 (d, *J* = 6.0 Hz, 1H), 2.73 (s, 1H), 2.56 (s, 1H), 2.24 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.20 (m, 1H), 2.16 (s, 1H), 2.12 (dd, *J* = 13.2, 6.0 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 6H), 0.87 (s, 9H), 0.81 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H), -0.08 (s, 3H), -0.01 (s, 3H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.0, 171.9, 155.5, 155.4, 130.3(2C), 128.4(3C), 128.1(2C), 128.0, 116.8(2C), 109.9 (2C), 97.7, 95.0, 76.0, 75.8, 73.8, 71.2, 70.8, 69.8, 69.1(2C), 66.9, 63.1, 62.9, 54.8, 54.7, 52.2, 43.3(2C), 37.2, 29.6, 27.4, 26.3, 25.85(3C), 25.81(3C), 25.6, 22.3, 22.2, 18.4, 18.3, -5.3(2C), -5.47, -5.57; CIHRMS Calcd for [$C_{53}H_{83}NO_{16}Si_2Na^+$ - $C_3H_6^{2+}$]: 1028.5142. Found 1028.4585.

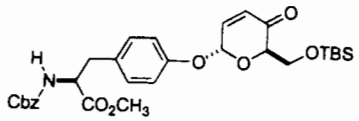
(1'*R*,4'*R*,5'*S*,1*R*,4*R*,5*S*)-1-[1'-*N*-carbobenzyloxy-D-tyrosine methoxycarbonyl -5'-(*tert*-butyl-dimethylsilanyloxymethyl)-tetrahydro-pyran-4'-yloxy]-5-(*tert*-butyl-dimethylsilanyloxymethyl)-tetrahydro-pyran-*O*-4'-isovalaric ester (17):



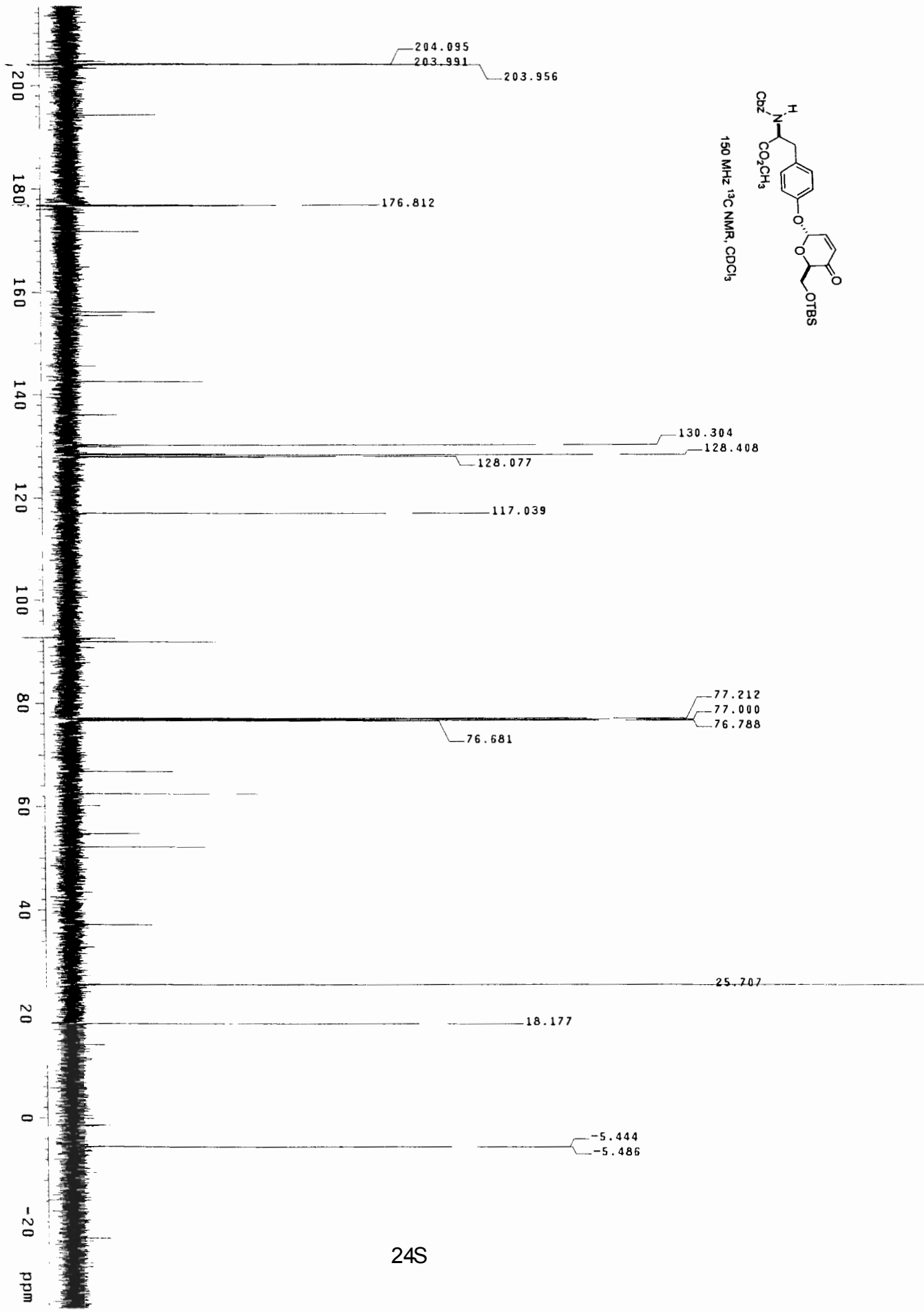
The diene ester **13** (27 mg, 0.03 mmol) and *o*-$NO_2C_6H_4SO_2NHNH_2$ (91.6 mg, 0.45 mmol) were dissolved in 0.3 mL of CH_2Cl_2 in a round bottom flask and cooled to 0 ^oC under nitrogen atmosphere then triethylamine (60.6 mg, 0.60 mmol) was added and the reaction mixture was stirred at 0 ^oC for 12 hours and on completion, as monitored by TLC. The reaction mixture was concentrated and was pipetted directly on to a silica gel column using CH_2Cl_2 (1 mL) in three portions. The crude product was purified using silica gel flash chromatography eluting with 15% EtOAc/hexanes to give **17** (26.2 mg, 0.03 mmol, 97 %) as viscous oil. R_f (30% EtOAc/Hexane) = 0.46; $[\alpha]_D^{26}$ = -59 (*c* 2, CH_2Cl_2); IR (thin film, cm^{-1}) 2955, 2928, 1738, 1510, 1252, 1219, 1122, 996, 835; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (m, 5H), 6.97 (m, 4H), 5.44 (br s, 1H), 5.24 (d, *J* = 7.8 Hz, 1H), 5.08 (br s, 2H), 5.07 (d, *J* = 2.4 Hz, 1H), 4.73 (ddd, *J* = 10.2, 9.6, 4.8 Hz, 1H), 4.60 (ddd, *J* = 7.8, 5.4, 5.4 Hz, 1H), 3.85 (d, *J* = 11.4 Hz, 1H), 3.78-3.64 (m, 6H), 3.70 (s, 3H), 3.05 (dd, *J* = 13.2, 6.0 Hz, 1H), 3.01

(dd, J = 13.2, 5.4 Hz, 1H), 2.13 (m, 3H), 2.06 (ddd, J = 13.2, 6.6, 6.6 Hz, 1H), 2.00 (m, 2H), 1.80 (m, 3H), 1.71 (m, 2H), 0.93 (d, J = 6.6 Hz, 6H), 0.88 (s, 9H), 0.84 (s, 9H), 0.02 (s, 6H), 0.018 (s, 3H), 0.004 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.1, 172.0, 156.2, 136.2, 130.1(2C), 128.6, 128.4(2C), 128.1, 128.0, 116.9(2C), 94.9, 90.5, 75.0, 73.3, 71.5, 67.5, 66.9, 66.3, 63.2, 62.6, 54.8, 52.2, 43.6, 37.3, 28.7, 25.92(3C), 25.91(3C), 25.7, 23.6, 22.3(2C), 22.2(2C), 22.0, 18.4, 18.3, -5.1, -5.3, -5.43, -5.46; CIHRMS Calcd for [$C_{47}H_{75}NO_{12}Si_2Na^+$]: 924.4720. Found 924.4717.

Section C: ^{1}H NMR and ^{13}C NMR Spectra.



600 MHz ^{1}H NMR, $CDCl_3$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203.991
203.956
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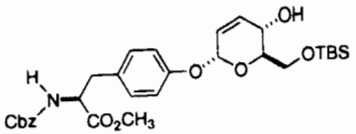
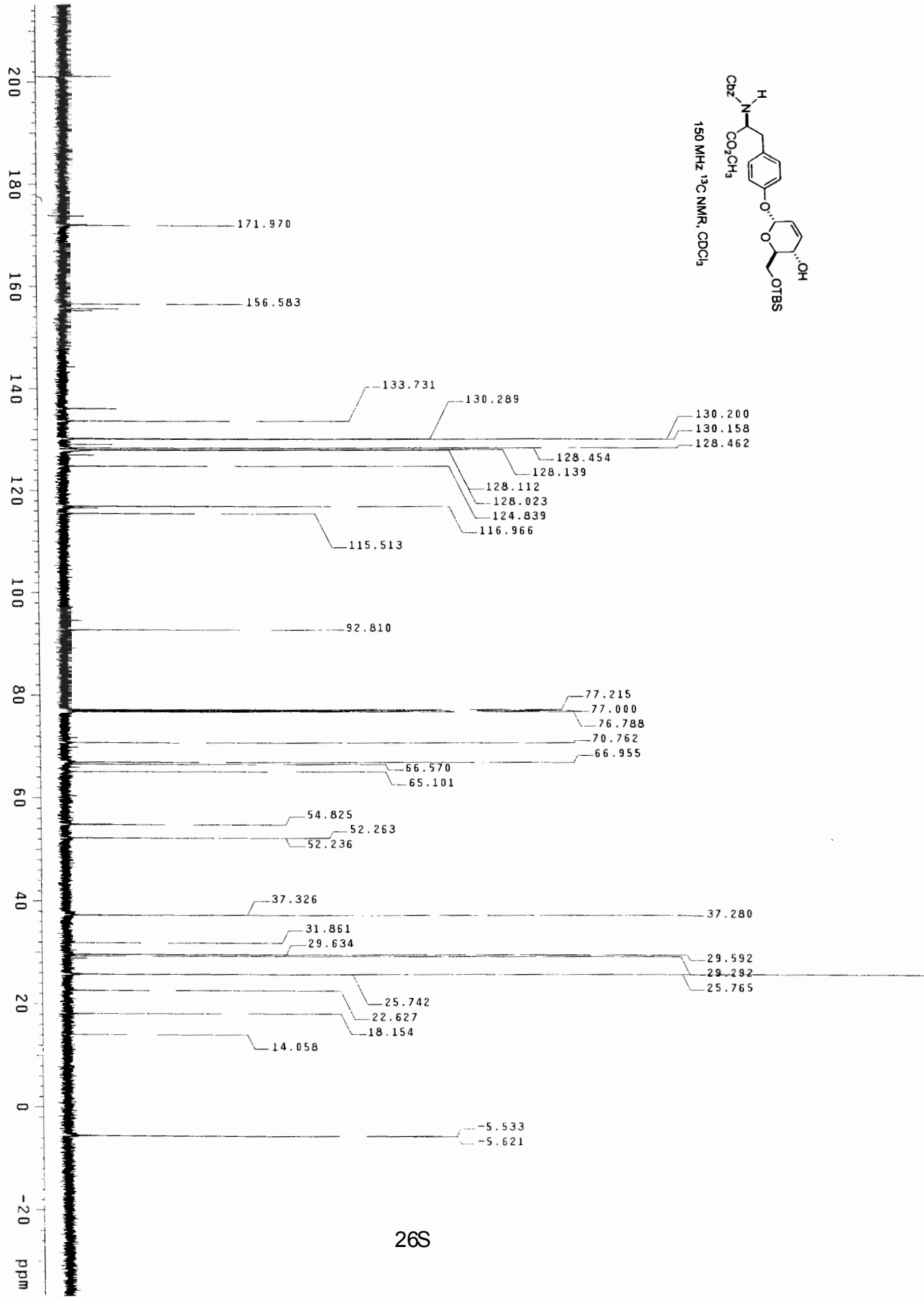
130.304
128.408
128.077
117.039
77.212
77.000
76.788
76.681
25.707
18.177
-5.444
-5.486
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
O
O
O
OTBS



600 MHz ^1H NMR, $CDCl_3$


150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
O
O
OH
OTBS
171.970
156.583
133.731
130.289
130.200
130.158
128.462
128.454
128.139
128.112
128.023
124.839
116.966
115.513
92.810
77.215
77.000
76.788
70.762
66.955
66.570
65.101
54.825
52.263
52.236
37.326
37.280
31.861
29.634
29.592
29.292
25.765
25.742
22.627
18.154
14.058
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-5.621
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180
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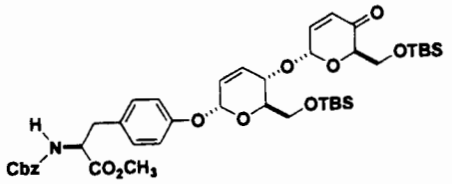
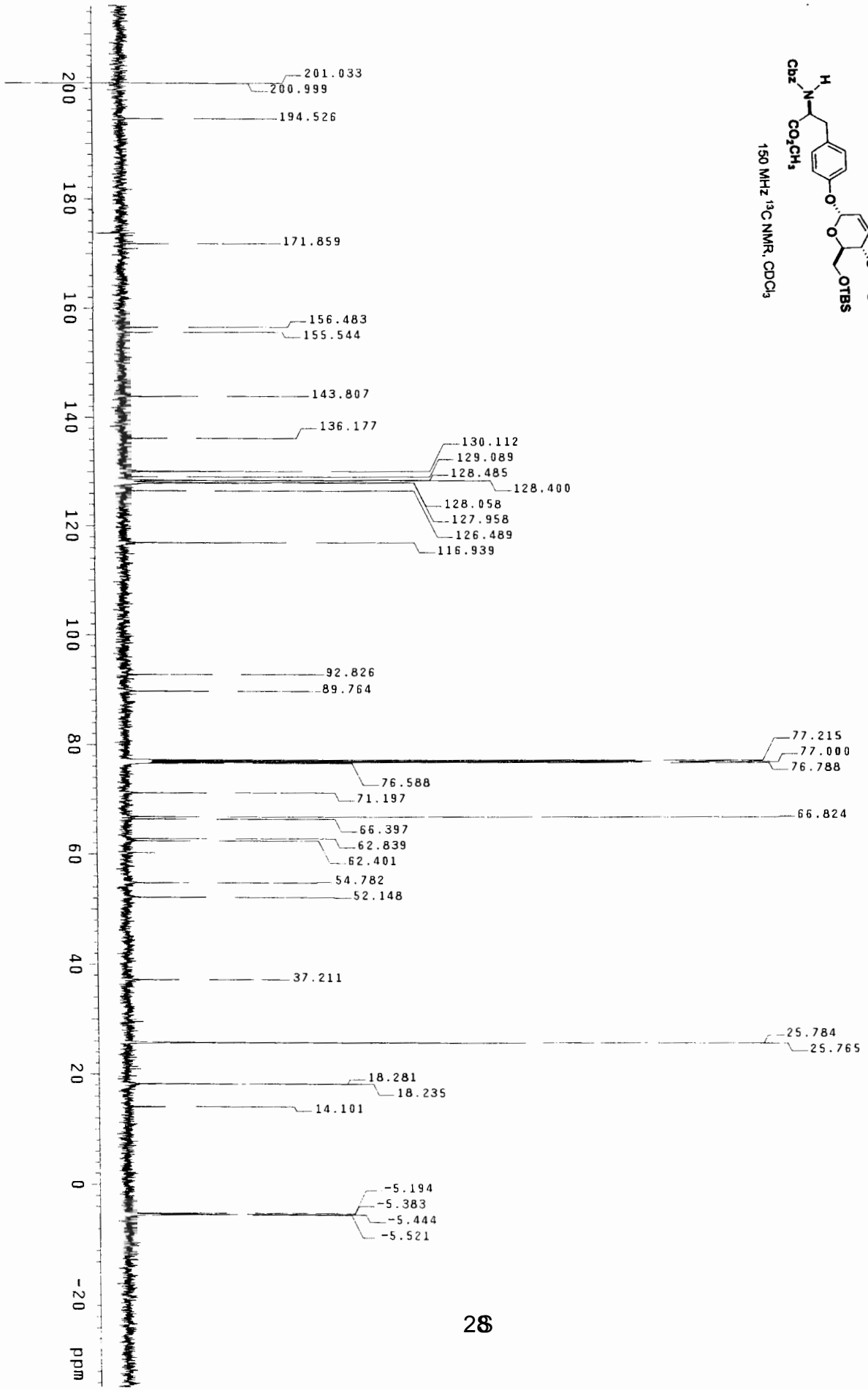
100
80
60
40
20
0
-20
ppm



600 MHz ^{1}H NMR, $CDCl_3$


150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
OTBS
OTBS
O
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200.999
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66.824
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14.101
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100
80
60
40
20
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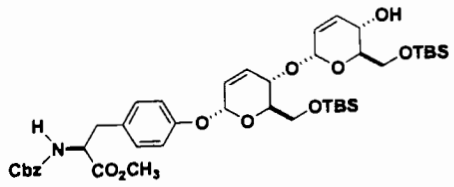
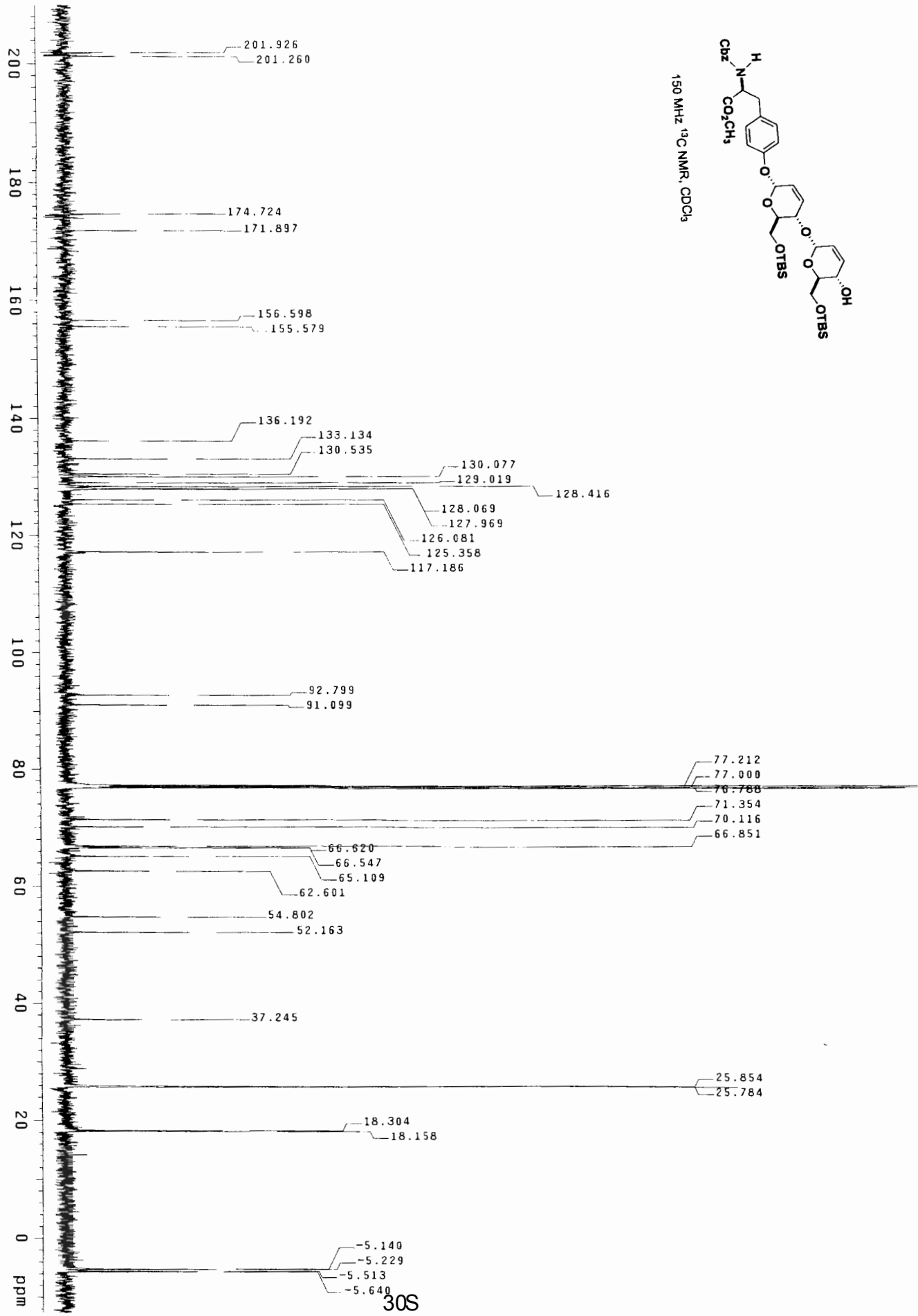
ppm



600 MHz ^{1}H NMR, $CDCl_3$


150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
O
OTBS
OTBS
OH
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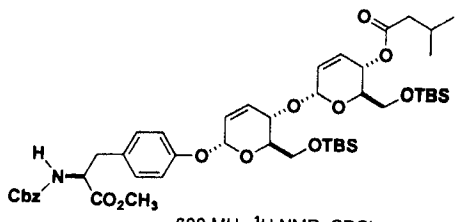
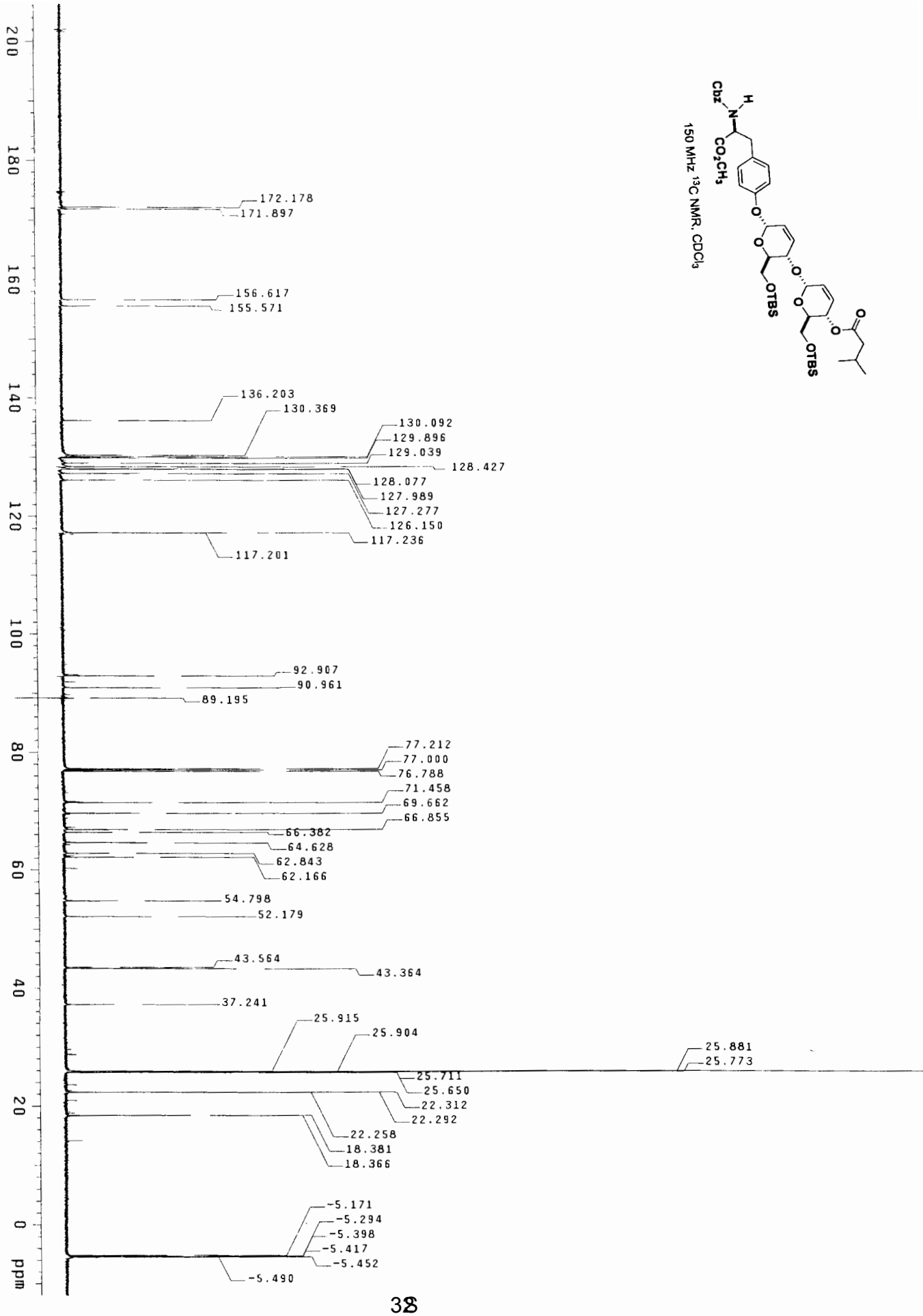
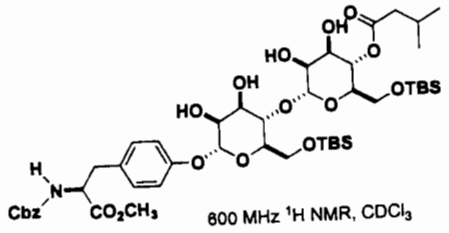
201.260
174.724
171.897
156.598
155.579
136.192
133.134
130.535
130.077
129.019
128.416
128.069
127.969
126.081
125.358
117.186
92.799
91.099
77.212
77.000
76.788
71.354
70.116
66.851
66.620
66.547
65.109
62.601
54.802
52.163
37.245
25.854
25.784
18.304
18.158
-5.140
-5.229
-5.513
-5.640
200
180
160
140
120
100
80
60
40
20
0
ppm

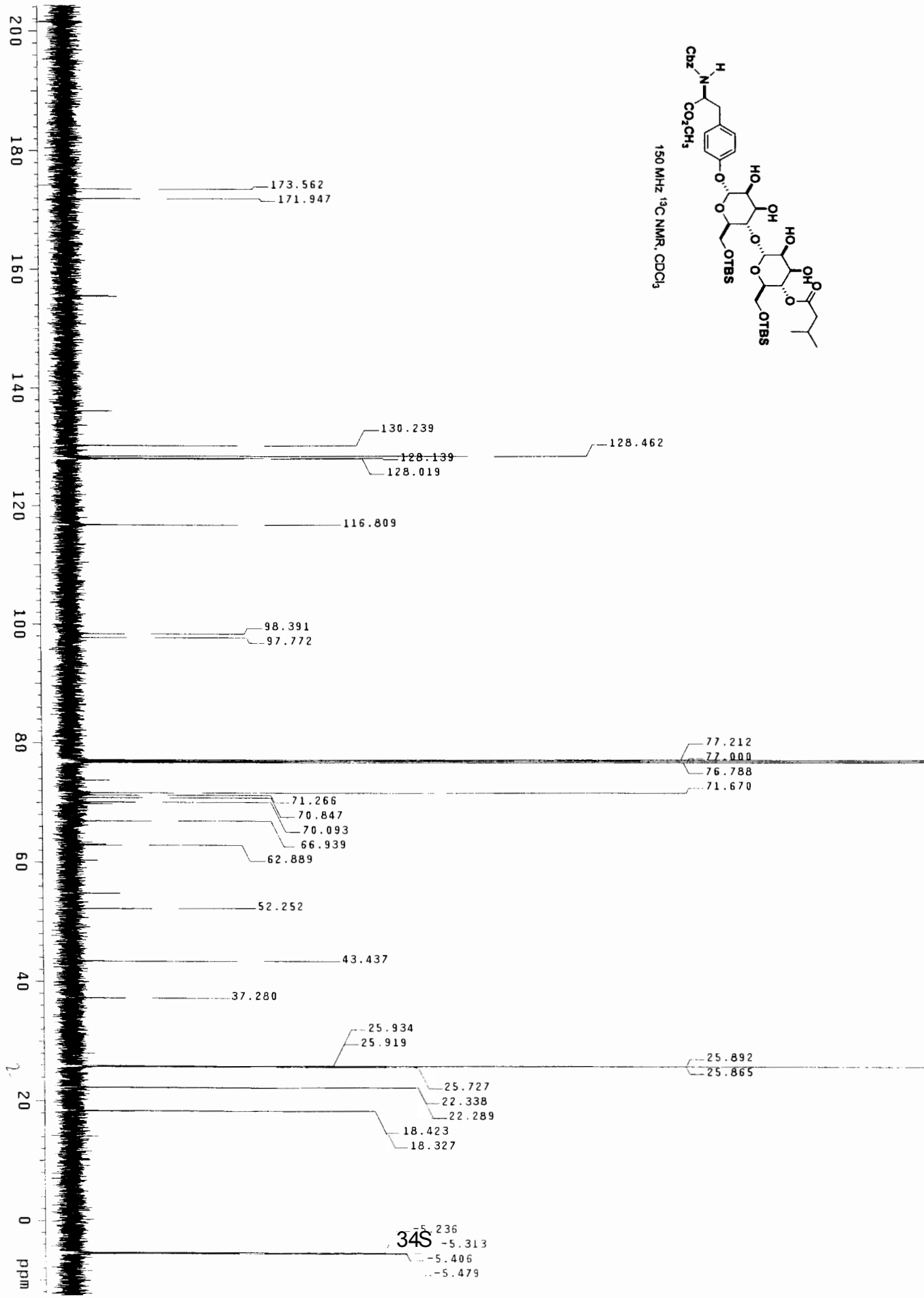


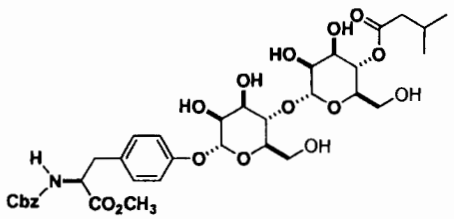
600 MHz ^{1}H NMR, $CDCl_3$


150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
OTBS
OTBS
172.178
171.897
156.617
155.571
136.203
130.369
130.092
129.896
129.039
128.427
128.077
127.989
127.277
126.150
117.236
117.201
92.907
90.961
89.195
77.212
77.000
76.788
71.458
69.662
66.855
66.382
64.628
62.843
62.166
54.798
52.179
43.564
43.364
37.241
25.915
25.904
25.881
25.773
25.711
25.650
22.312
22.292
22.258
18.381
18.366
-5.171
-5.294
-5.398
-5.417
-5.452
-5.490
ppm



600 MHz ^{1}H NMR, $CDCl_3$

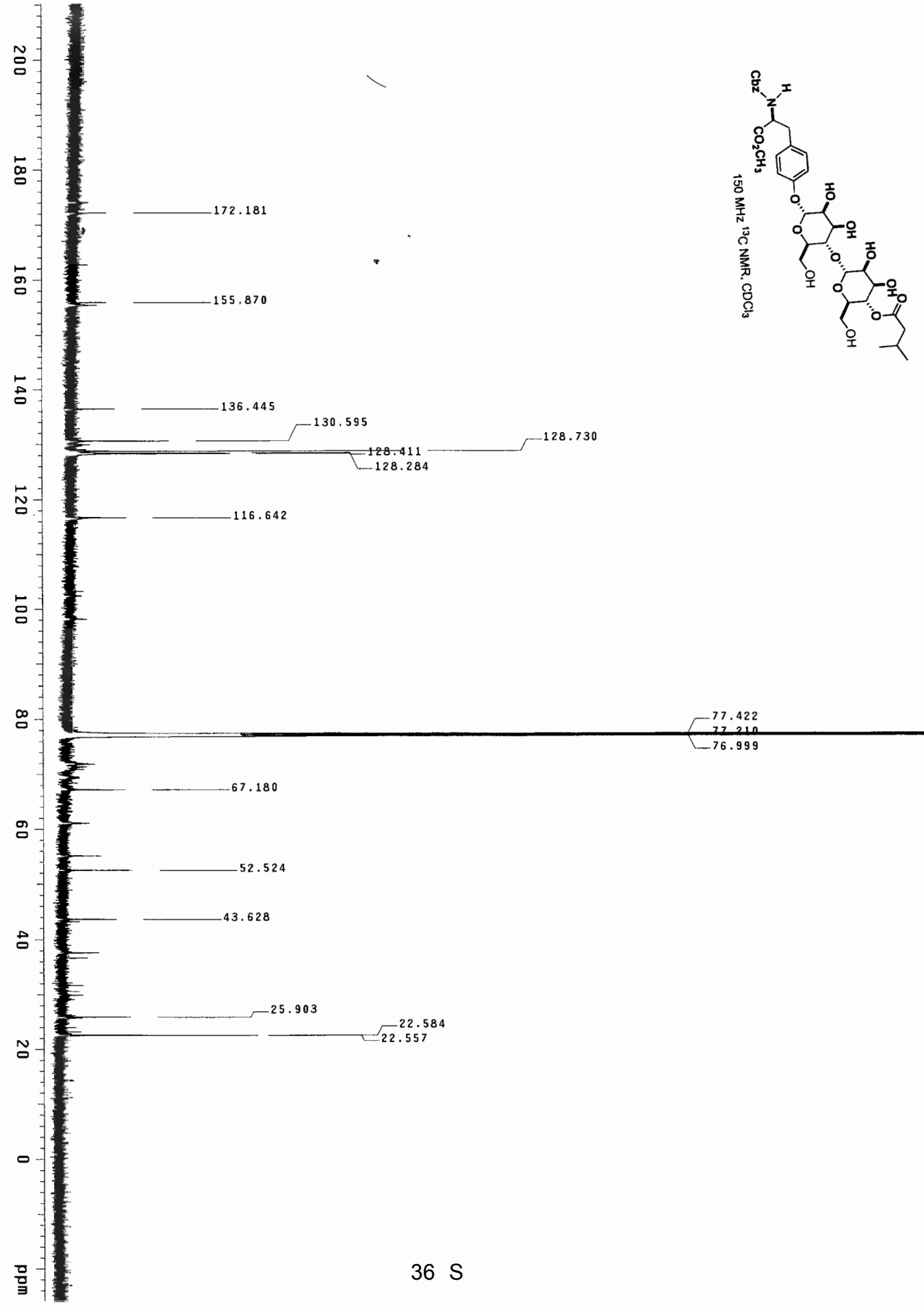

150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
HO
OH
HO
OH
O
OTBS
OTBS
173.562
171.947
130.239
128.462
128.139
128.019
116.809
98.391
97.772
77.212
77.000
76.788
71.670
71.266
70.847
70.093
66.939
62.889
52.252
43.437
37.280
25.934
25.919
25.892
25.865
25.727
22.338
22.289
18.423
18.327
-5.236
-5.313
-5.406
-5.479
200
180
160
140
120
100
80
60
40
20
0
ppm

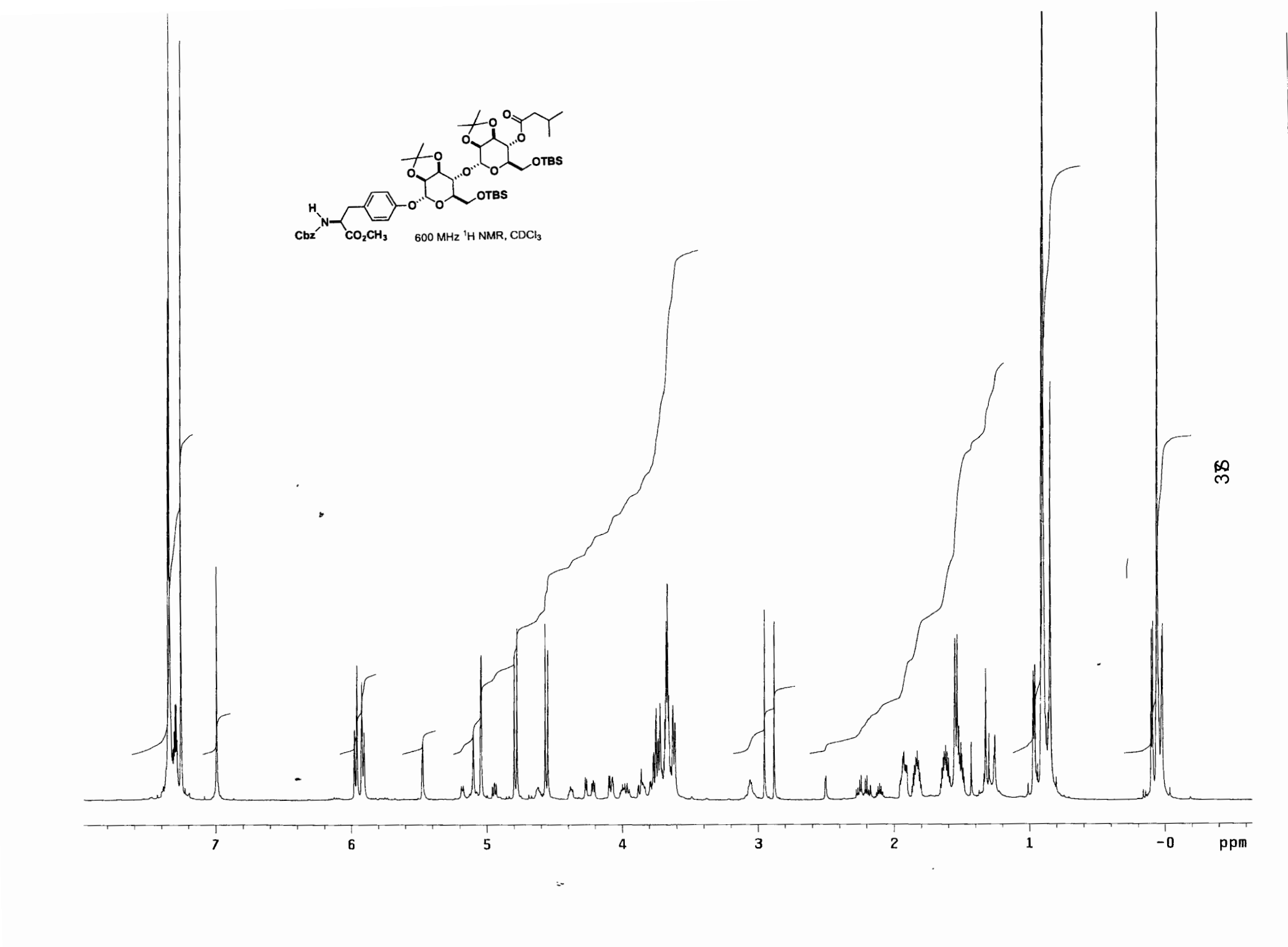


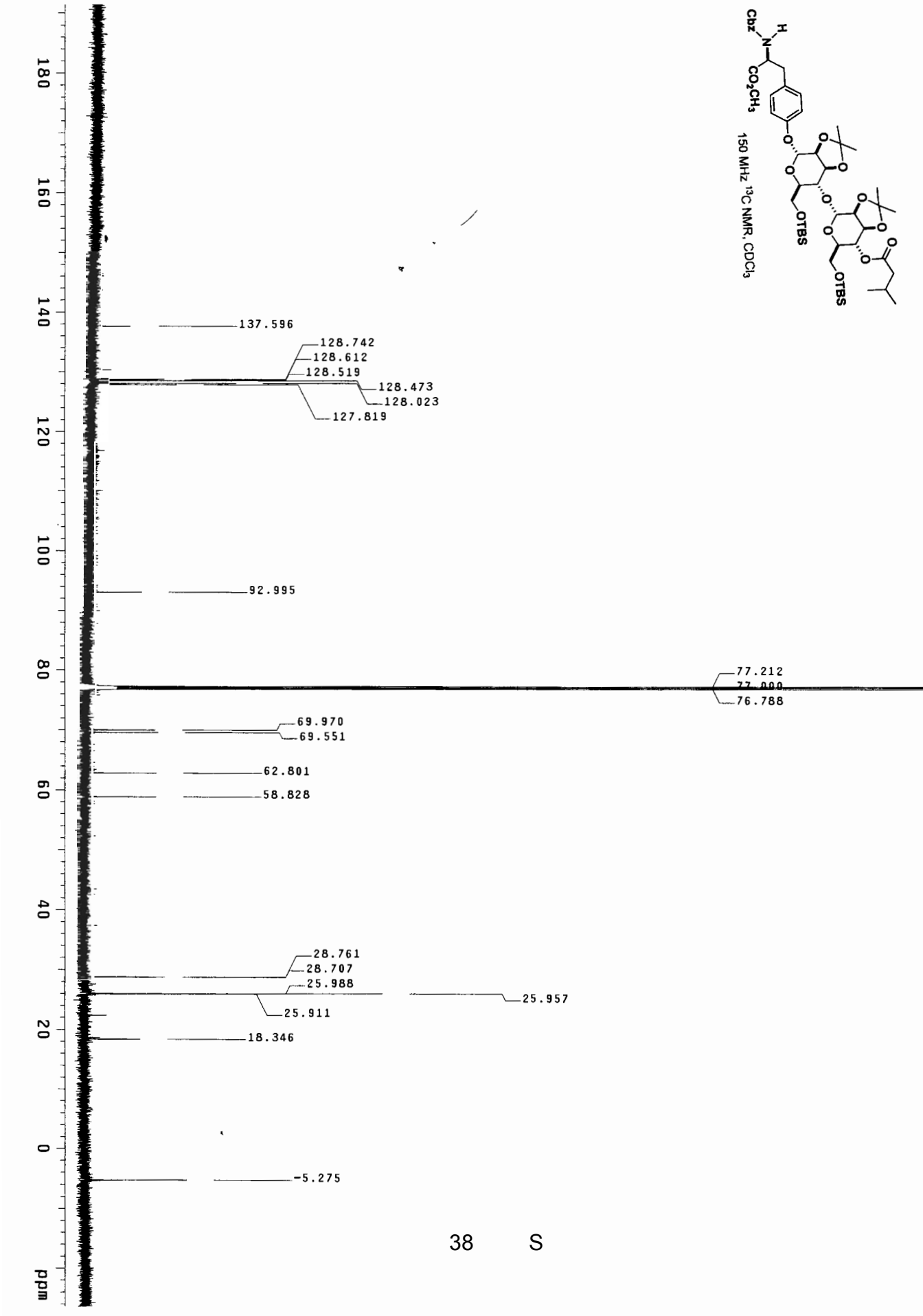
600 MHz ^1H NMR, CD_3OD

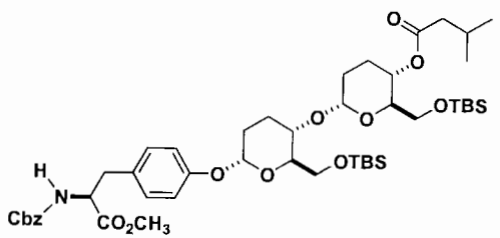
35 S

10 9 8 7 6 5 4 3 2 1 -0 ppm


150 MHz ^{13}C NMR, $CDCl_3$
172.181
155.870
136.445
130.595
128.730
128.411
128.284
116.642
77.422
77.210
76.999
67.180
52.524
43.628
25.903
22.584
22.557
ppm


OTBS
OTBS
H
N
Cbz
CO2CH3
600 MHz 1H NMR, CDCl3
7
6
5
4
3
2
1
-0
ppm

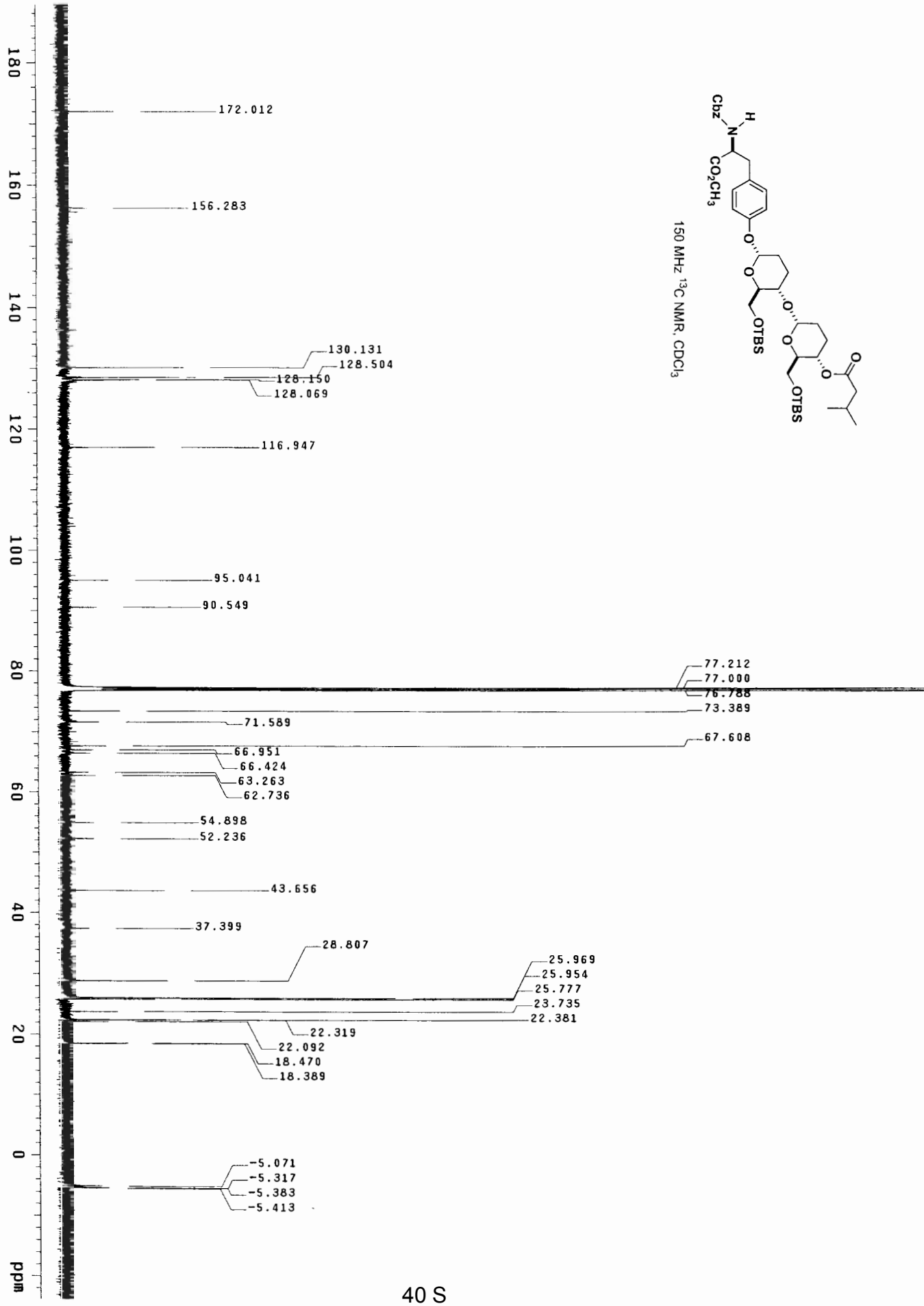

150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
OTBS
OTBS
137.596
128.742
128.612
128.519
128.473
128.023
127.819
92.995
77.212
77.000
76.788
69.970
69.551
62.801
58.828
28.761
28.707
25.988
25.957
25.911
18.346
-5.275
180
160
140
120
100
80
60
40
20
0
ppm

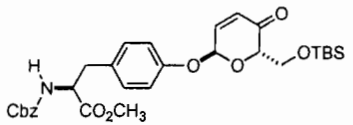


600 MHz ^{1}H NMR, CD_3OD

39 S

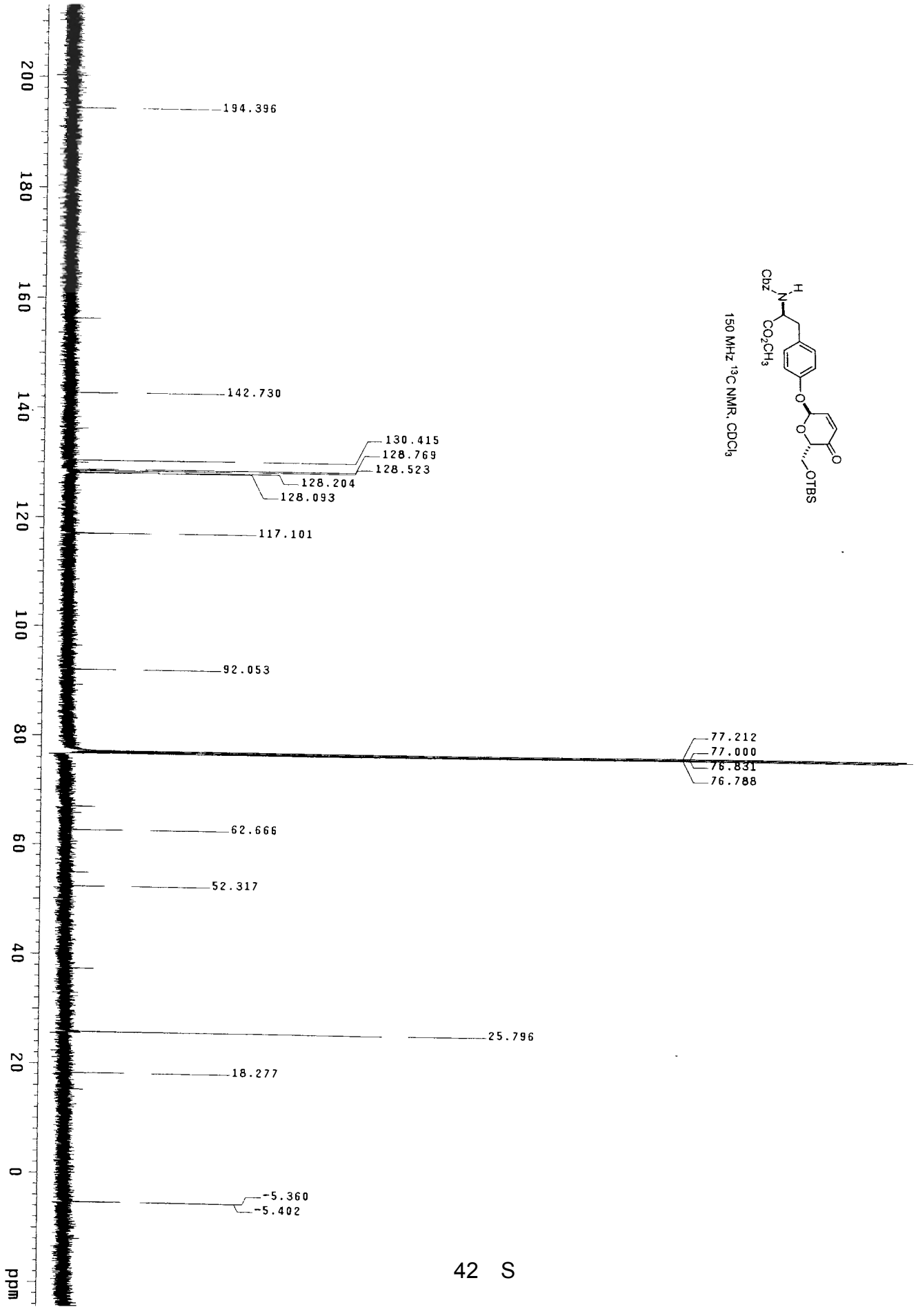
8 7 6 5 4 3 2 1 -0 ppm

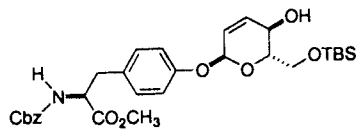

150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
OTBS
OTBS
O
172.012
156.283
130.131
128.504
128.150
128.069
116.947
95.041
90.549
77.212
77.000
76.788
73.389
71.589
67.608
66.951
66.424
63.263
62.736
54.898
52.236
43.656
37.399
28.807
25.969
25.954
25.777
23.735
22.381
22.319
22.092
18.470
18.389
-5.071
-5.317
-5.383
-5.413
180
160
140
120
100
80
60
40
20
0
ppm



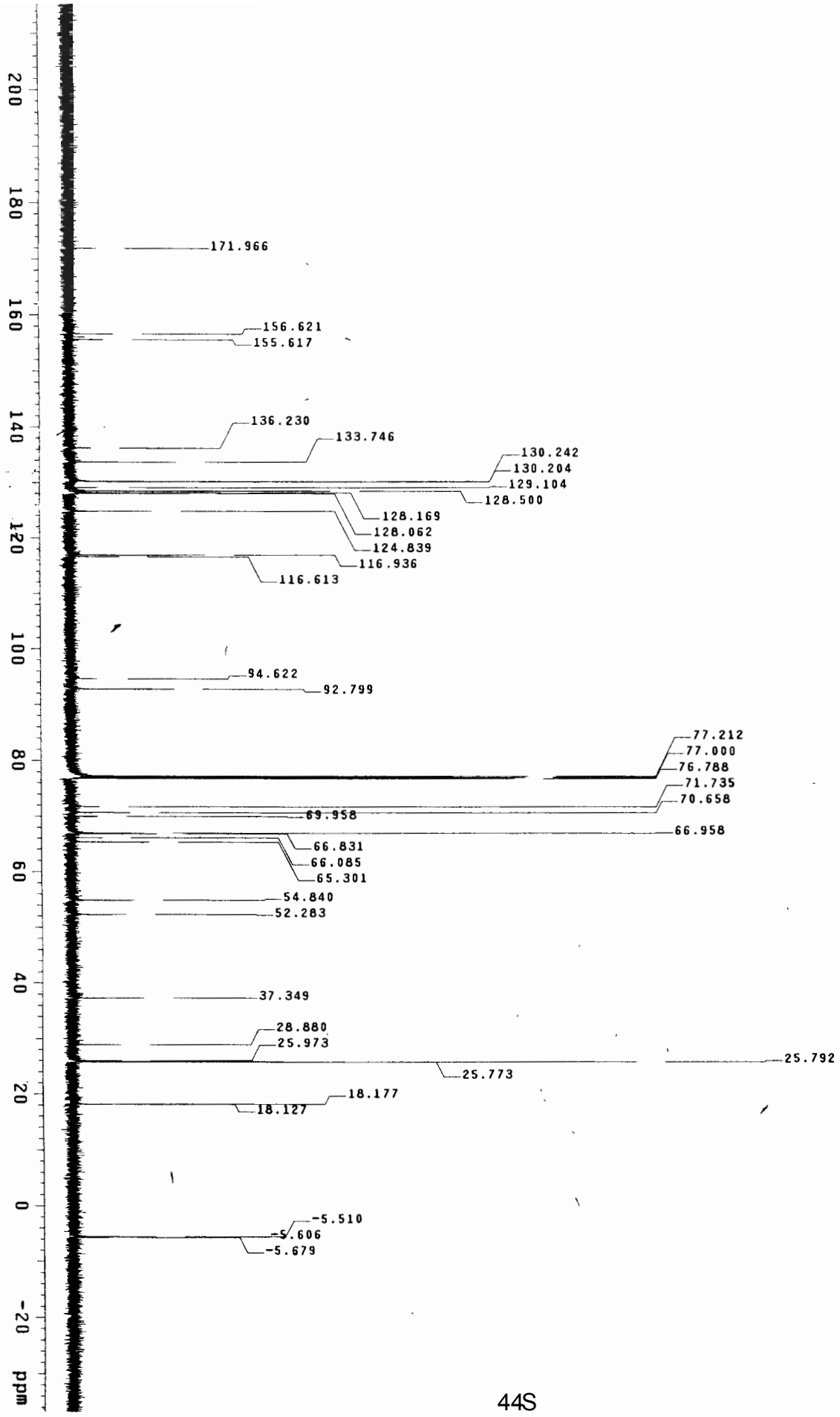
600 MHz ^{1}H NMR, $CDCl_3$

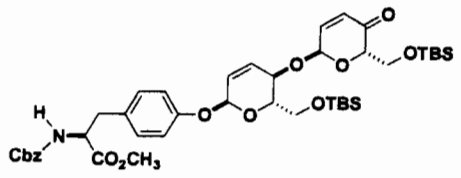
41 S


194.396
142.730
130.415
128.769
128.523
128.204
128.093
117.101
92.053
77.212
77.000
76.831
76.788
62.666
52.317
25.796
18.277
-5.360
-5.402
ppm
150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
O
O
O
OTBS

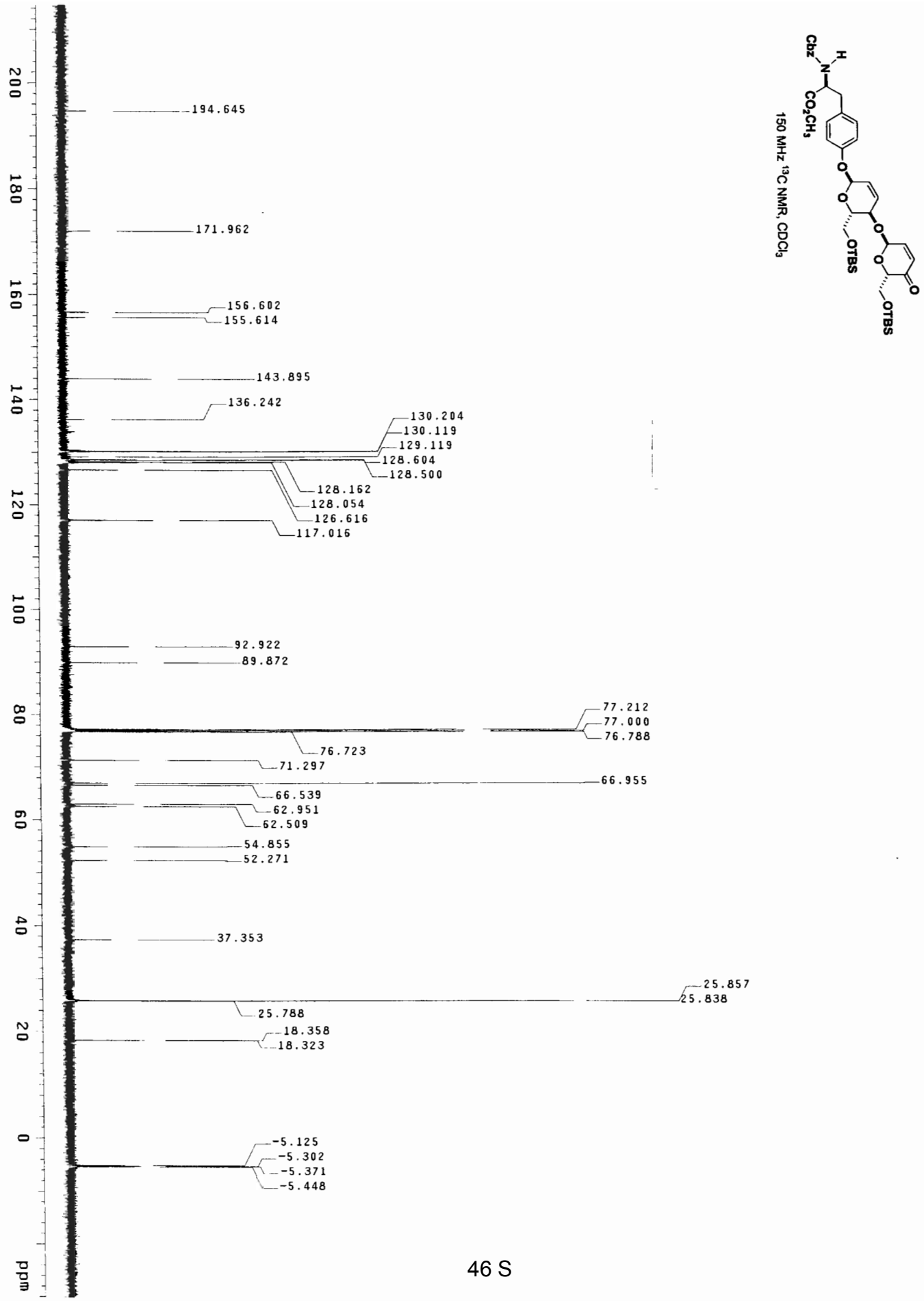


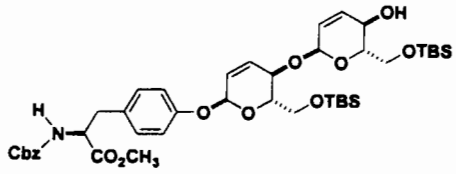
600 MHz ^{1}H NMR, $CDCl_3$


150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
O
O
OH
OTBS
171.966
156.621
155.617
136.230
133.746
130.242
130.204
129.104
128.500
128.169
128.062
124.839
116.936
116.613
94.622
92.799
77.212
77.000
76.788
71.735
70.658
69.958
66.958
66.831
66.085
65.301
54.840
52.283
37.349
28.880
25.973
25.792
25.773
18.177
18.127
-5.510
-5.606
-5.679
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

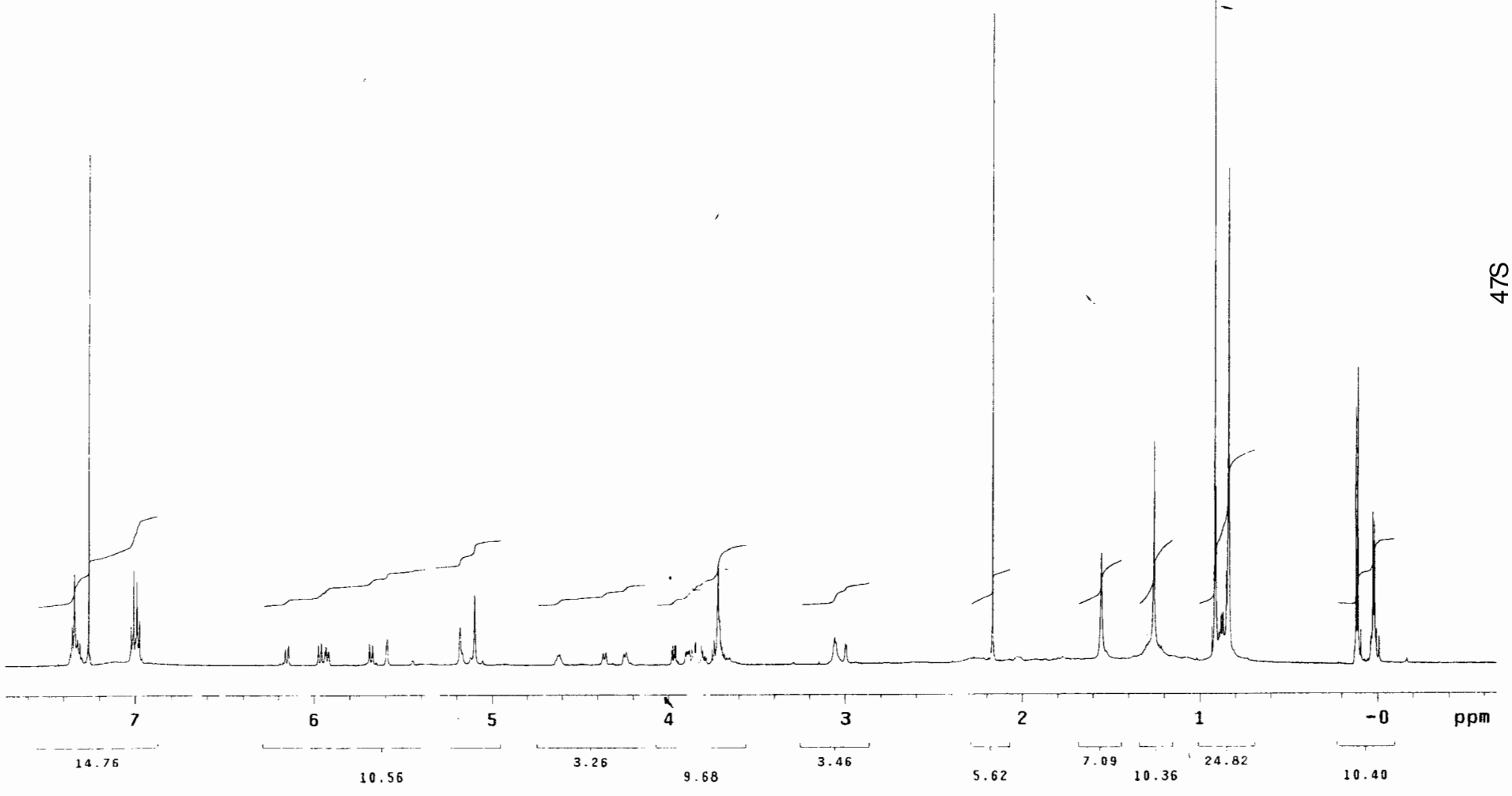


600 MHz ^{1}H NMR, $CDCl_3$

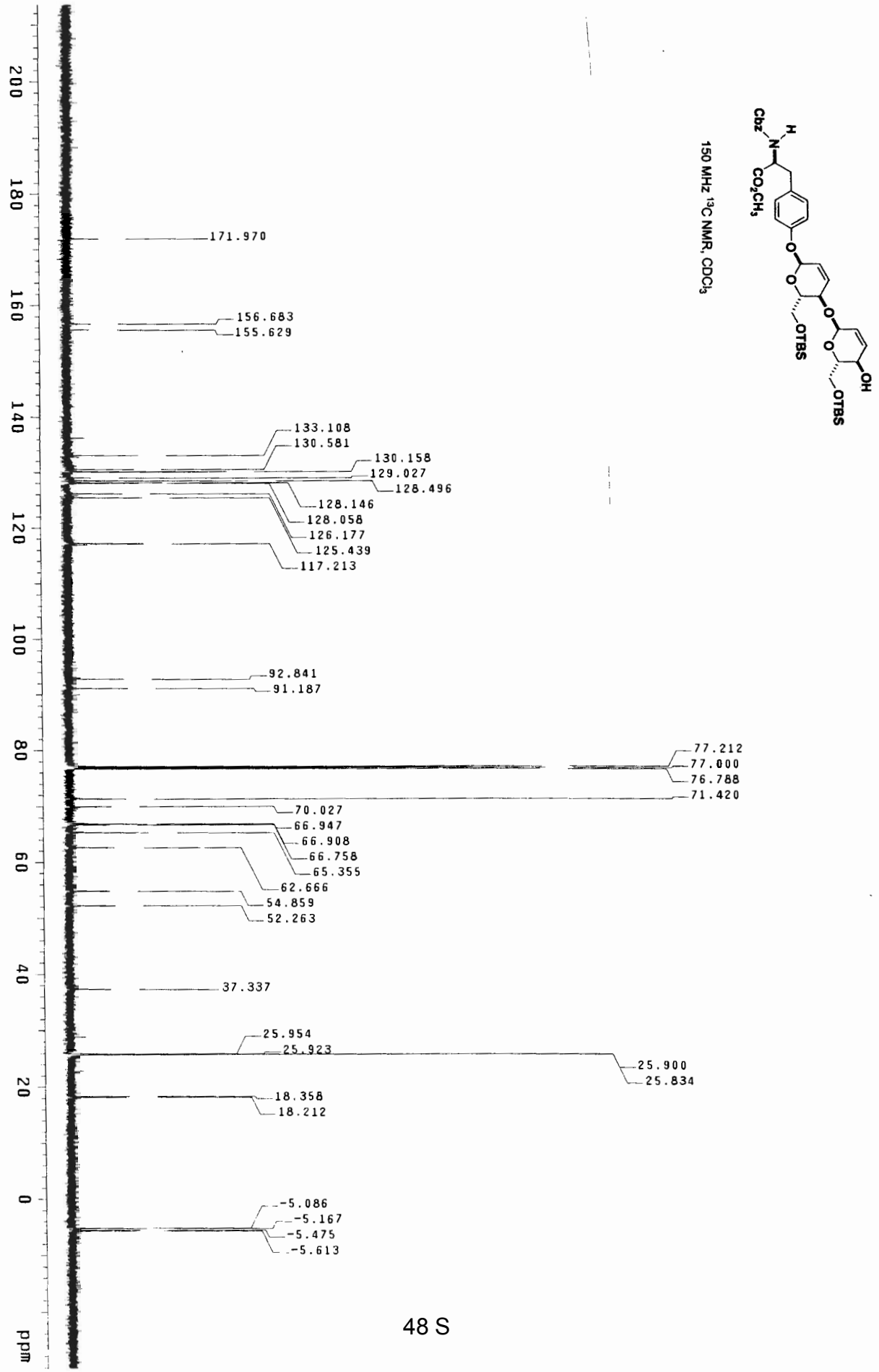

150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
OTBS
OTBS
O
194.645
171.962
156.602
155.614
143.895
136.242
130.204
130.119
129.119
128.604
128.500
128.162
128.054
126.616
117.016
92.922
89.872
77.212
77.000
76.788
76.723
71.297
66.955
66.539
62.951
62.509
54.855
52.271
37.353
25.857
25.838
25.788
18.358
18.323
-5.125
-5.302
-5.371
-5.448
200
180
160
140
120
100
80
60
40
20
0
ppm

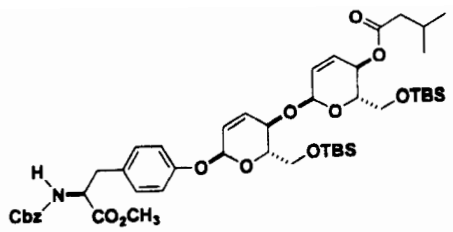


600 MHz ^1H NMR, $CDCl_3$

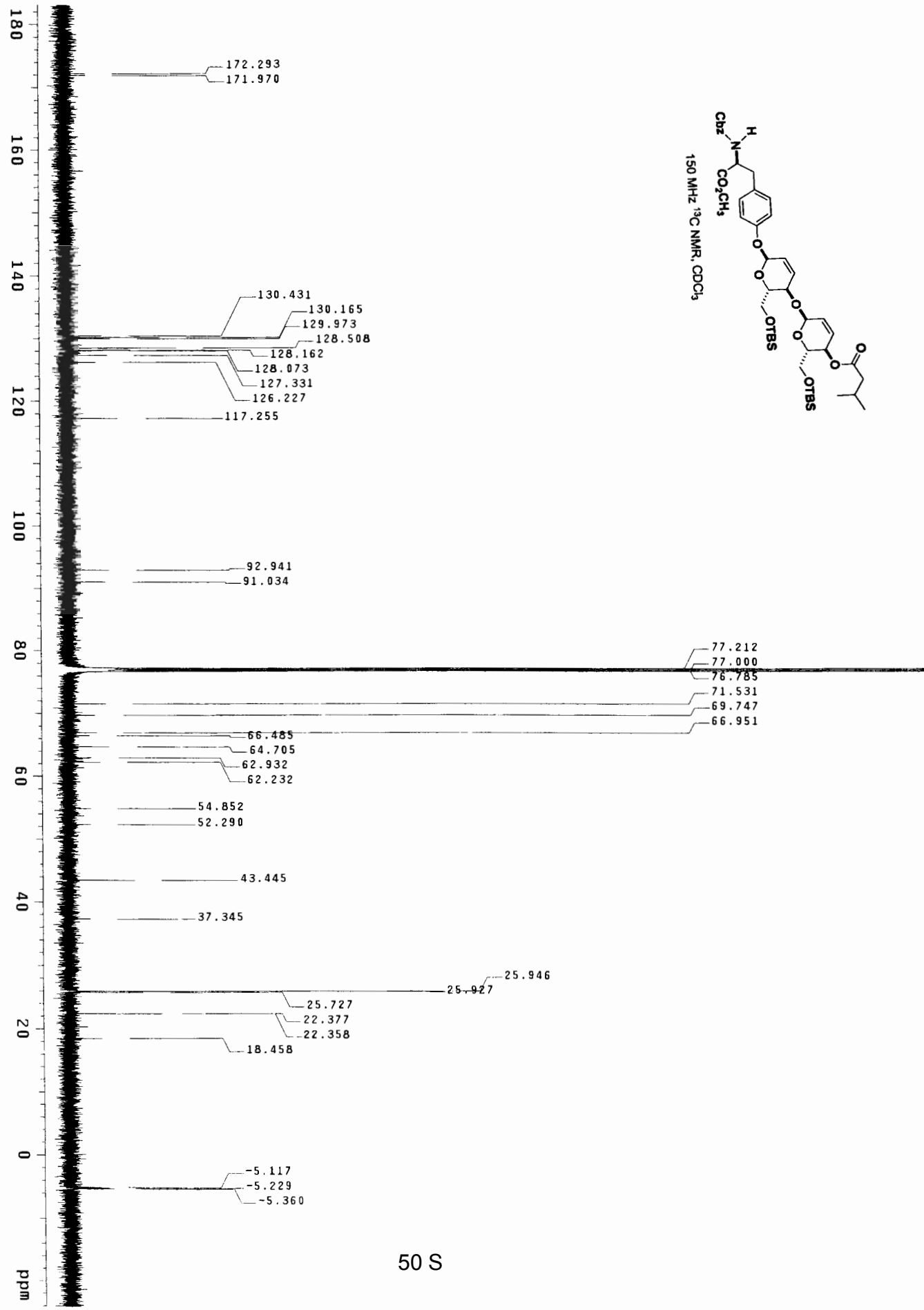


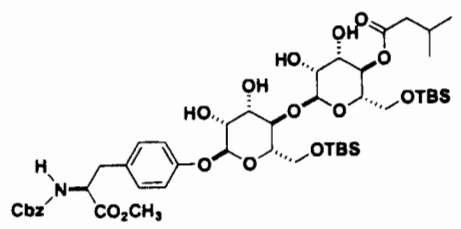
47S


150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
OTBS
OTBS
OH
171.970
156.683
155.629
133.108
130.581
130.158
129.027
128.496
128.146
128.058
126.177
125.439
117.213
92.841
91.187
77.212
77.000
76.788
71.420
70.027
66.947
66.908
66.758
65.355
62.666
54.859
52.263
37.337
25.954
25.923
25.900
25.834
18.358
18.212
-5.086
-5.167
-5.475
-5.613
ppm

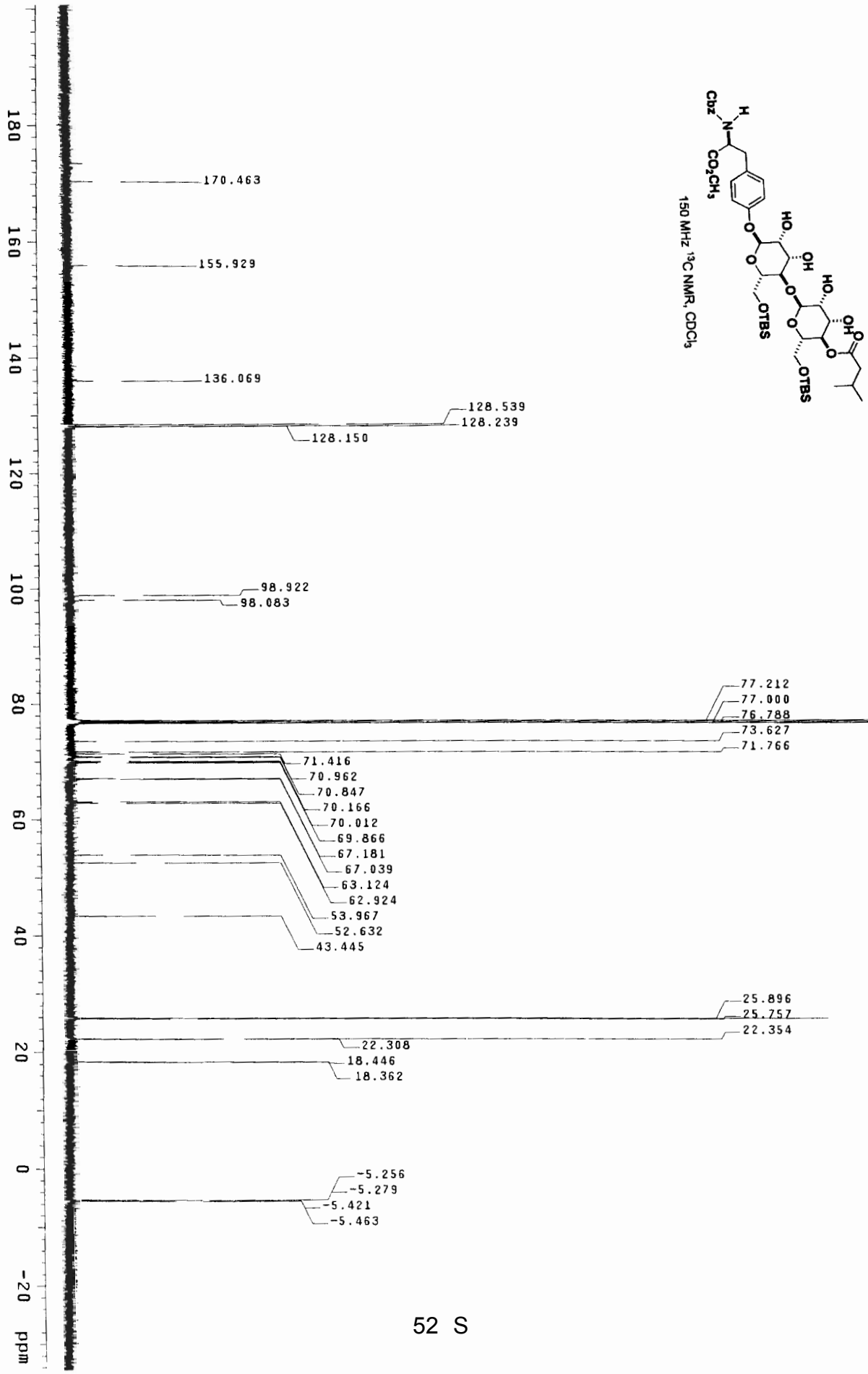


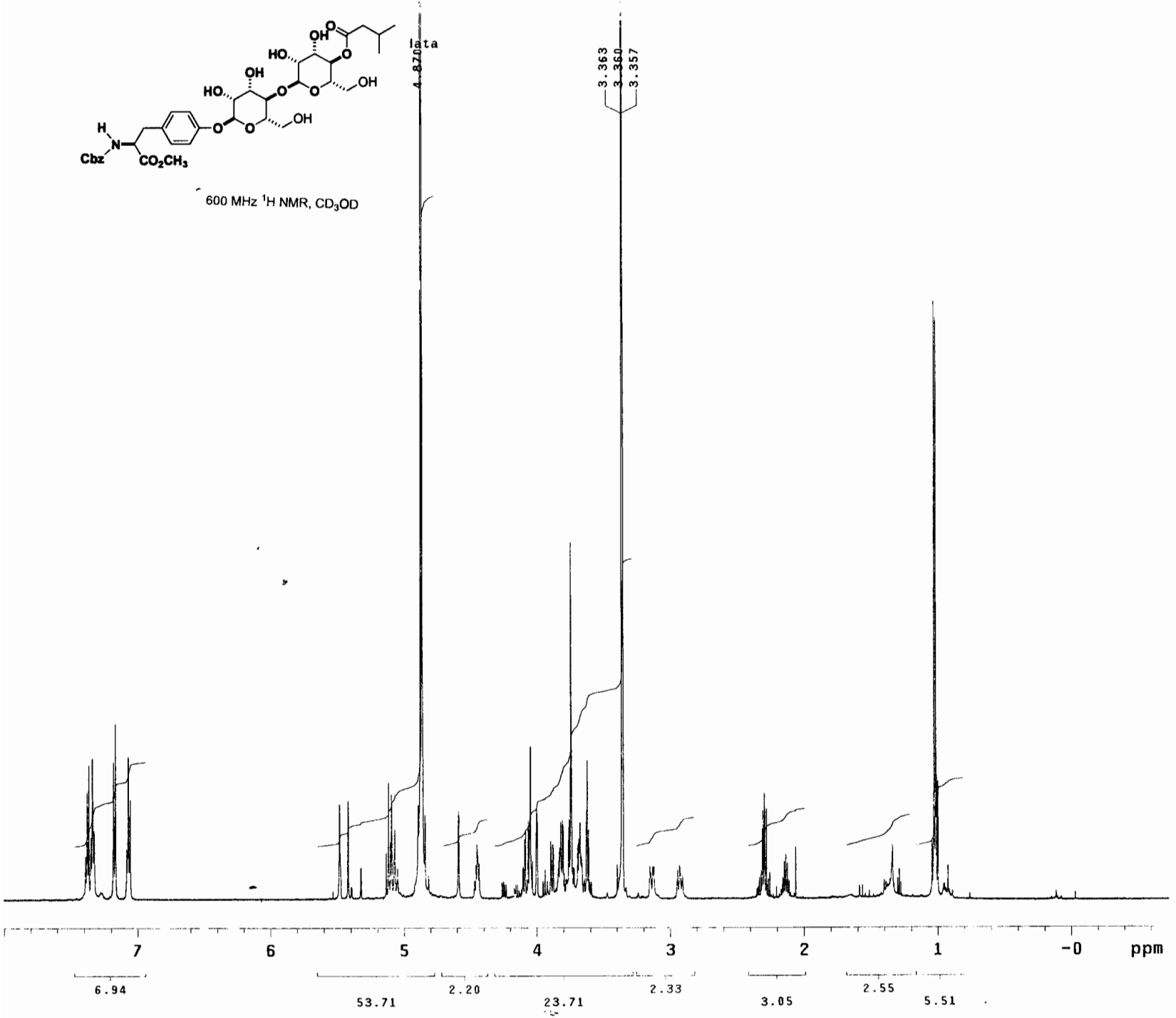
600 MHz ^{1}H NMR, $CDCl_3$

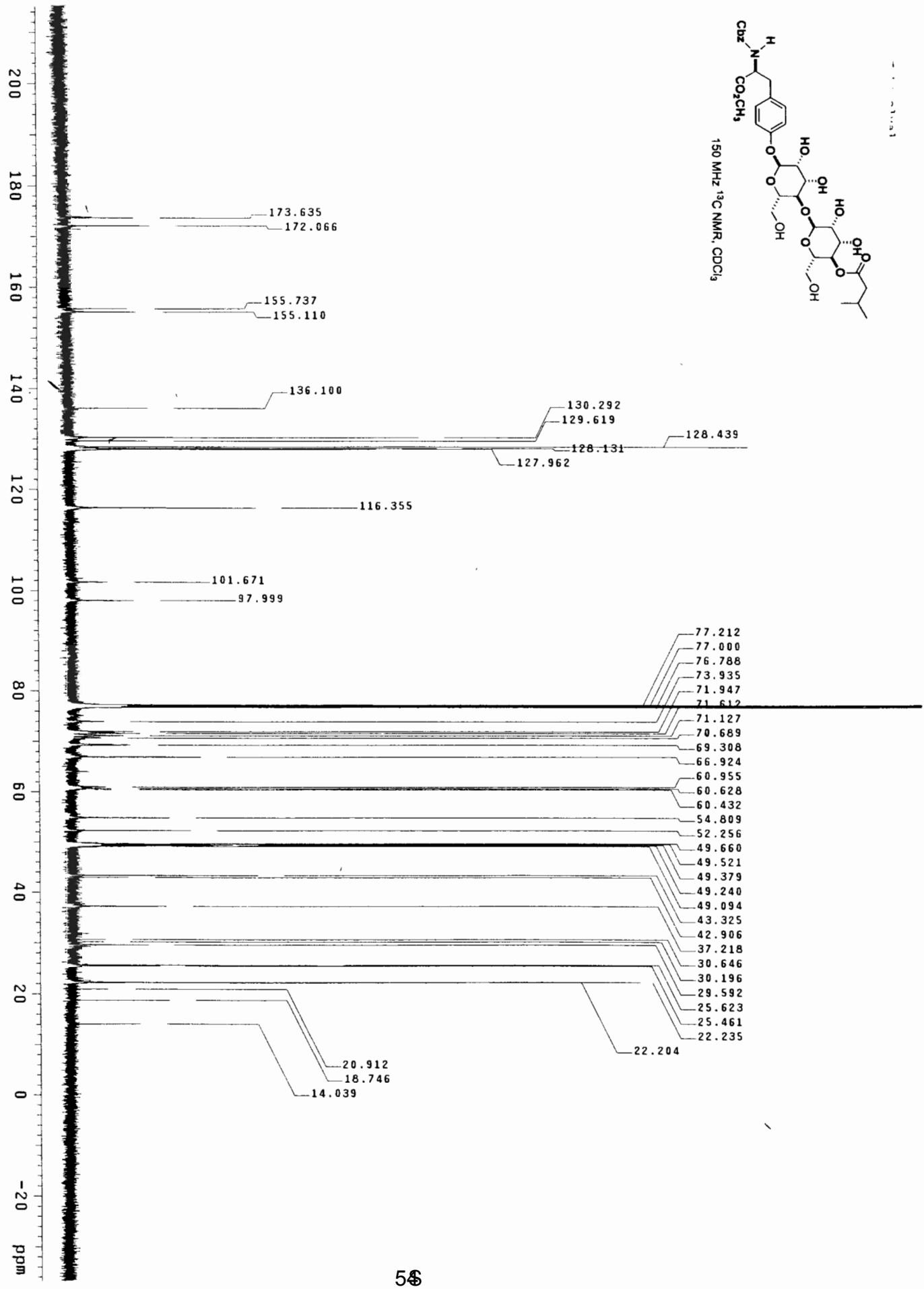

150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
OTBS
OTBS
O
172.293
171.970
130.431
130.165
129.973
128.508
128.162
128.073
127.331
126.227
117.255
92.941
91.034
77.212
77.000
76.785
71.531
69.747
66.951
66.485
64.705
62.932
62.232
54.852
52.290
43.445
37.345
25.946
25.927
25.727
22.377
22.358
18.458
-5.117
-5.229
-5.360
180
160
140
120
100
80
60
40
20
0
ppm

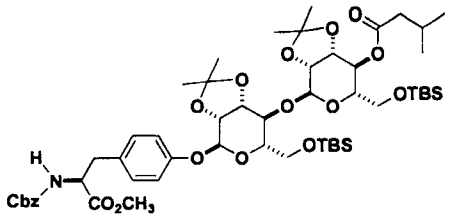


600 MHz ^{1}H NMR, $CDCl_3$

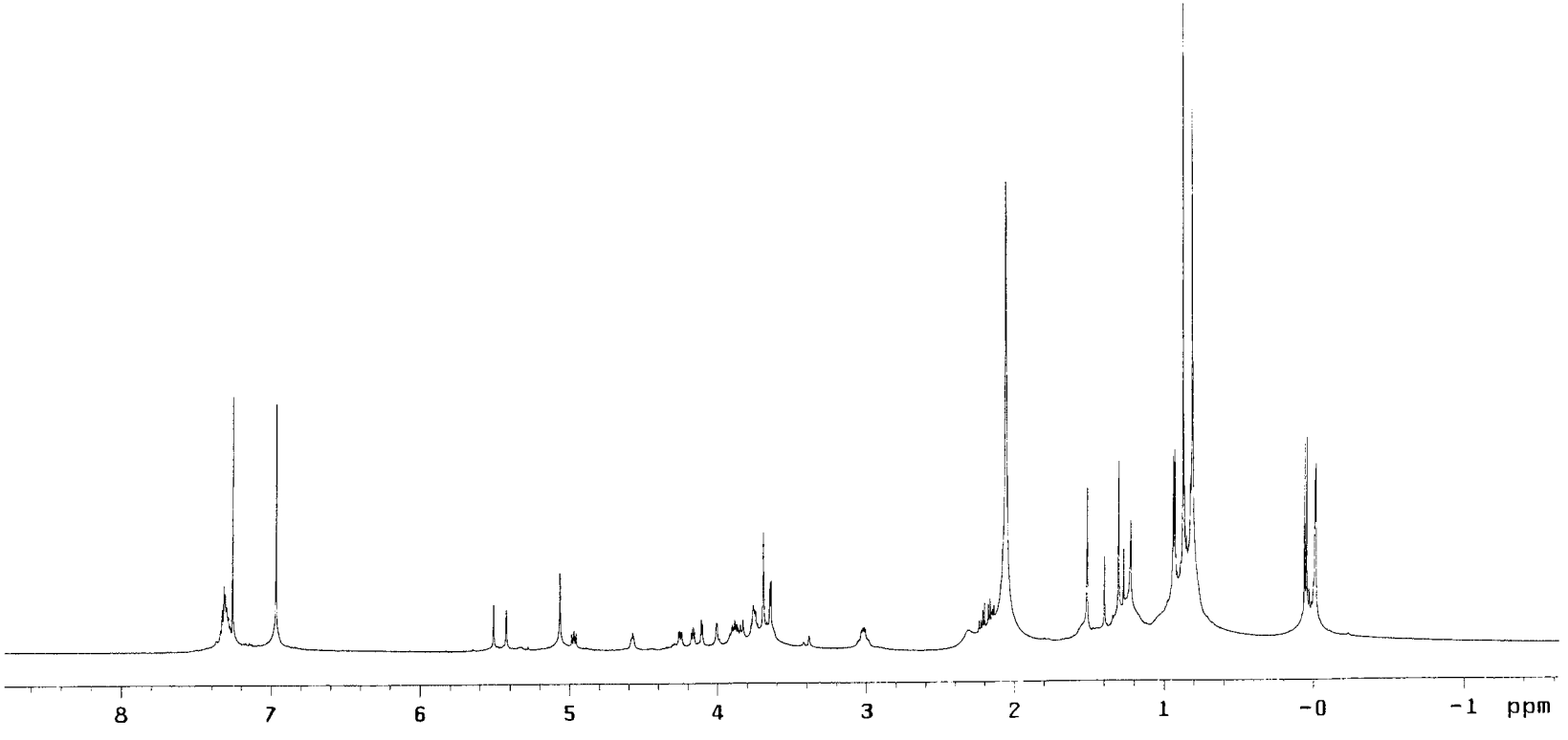

150 MHz ^{13}C NMR, CDCl$_3$
170.463
155.929
136.069
128.539
128.239
128.150
98.922
98.083
77.212
77.000
76.788
73.627
71.766
71.416
70.962
70.847
70.166
70.012
69.866
67.181
67.039
63.124
62.924
53.967
52.632
43.445
25.896
25.757
22.354
22.308
18.446
18.362
-5.256
-5.279
-5.421
-5.463
ppm

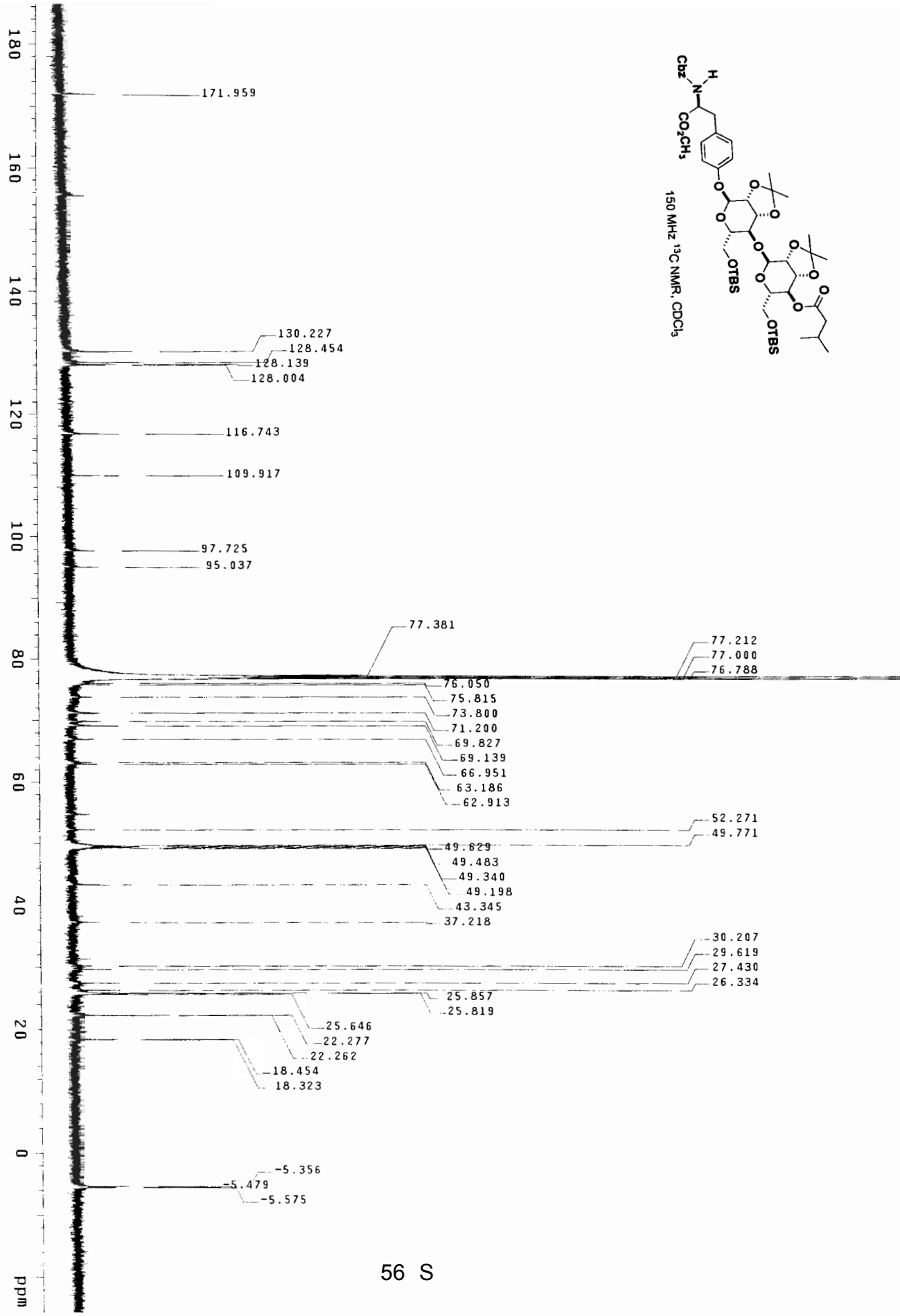

600 MHz ^{1}H NMR, CD_3OD
data
4.870
3.363
3.360
3.357
7
6
5
4
3
2
1
-0
ppm
6.94
53.71
2.20
23.71
2.33
3.05
2.55
5.51


150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
HO
OH
OH
OH
O
173.635
172.066
155.737
155.110
136.100
130.292
129.619
128.439
128.131
127.962
116.355
101.671
97.999
77.212
77.000
76.788
73.935
71.947
71.612
71.127
70.689
69.308
66.924
60.955
60.628
60.432
54.809
52.256
49.660
49.521
49.379
49.240
49.094
43.325
42.906
37.218
30.646
30.196
29.592
25.623
25.461
22.235
22.204
20.912
18.746
14.039
200
180
160
140
120
100
80
60
40
20
0
-20
ppm



600 MHz ^{1}H NMR, $CDCl_3$




150 MHz ^{13}C NMR, $CDCl_3$
Cbz
H
N
CO_2CH_3
OTBS
OTBS
171.959
130.227
128.454
128.139
128.004
116.743
109.917
97.725
95.037
77.381
77.212
77.000
76.788
76.050
75.815
73.800
71.200
69.827
69.139
66.951
63.186
62.913
52.271
49.771
49.629
49.483
49.340
49.198
43.345
37.218
30.207
29.619
27.430
26.334
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25.646
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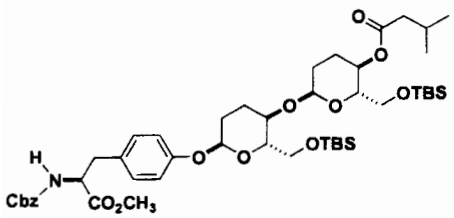
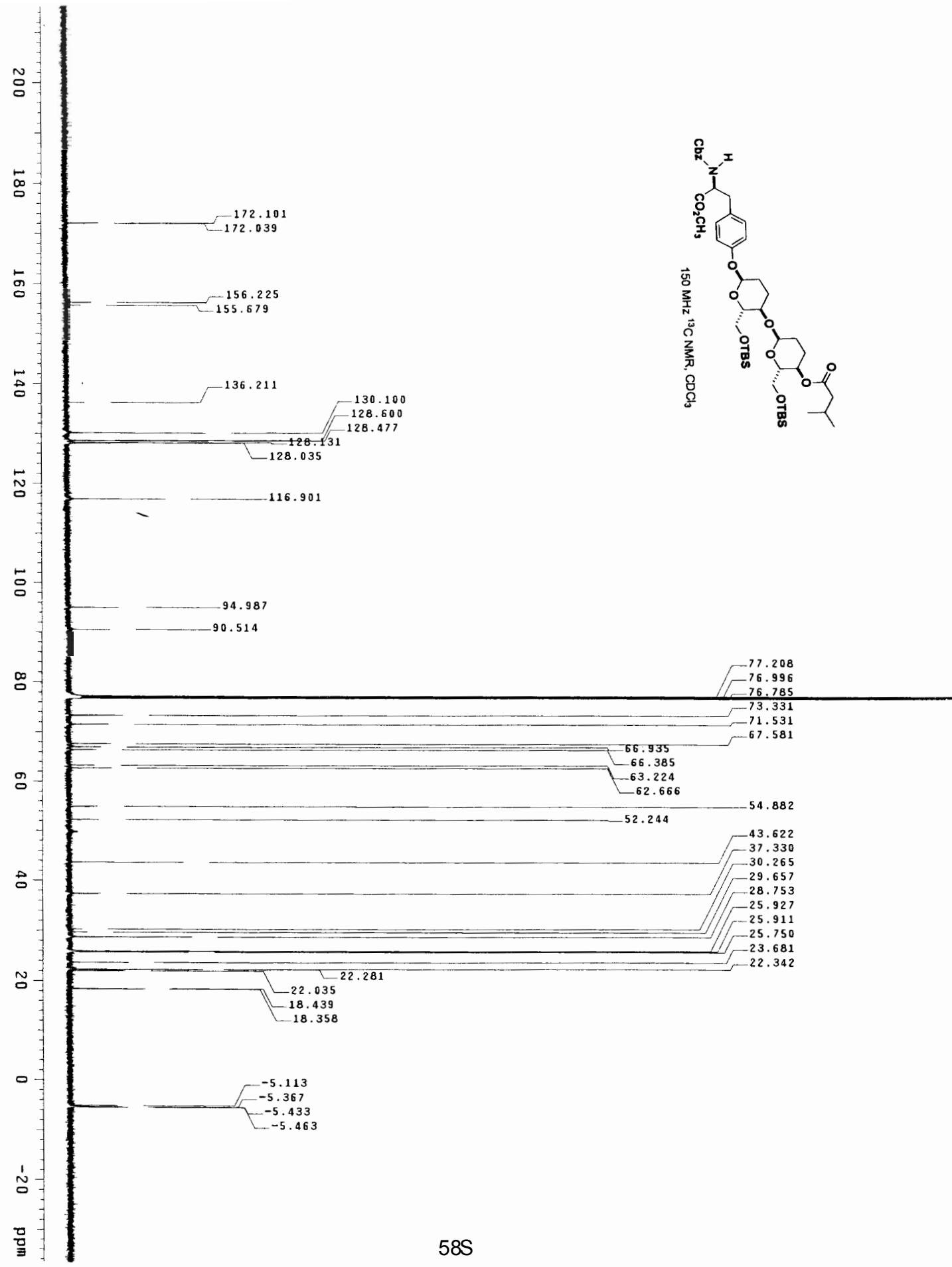
22.262
18.454
18.323
-5.356
-5.479
-5.575
ppm

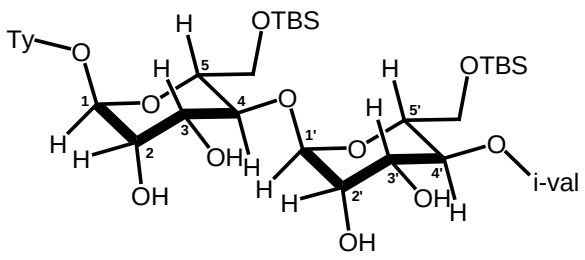


600 MHz ^{1}H NMR, $CDCl_3$

57S


150 MHz ^{13}C NMR, CDCl$_3$
Cbz
H
N
CO$_2$CH$_3$
OTBS
OTBS
O
172.101
172.039
156.225
155.679
136.211
130.100
128.600
128.477
128.131
128.035
116.901
94.987
90.514
77.208
76.996
76.785
73.331
71.531
67.581
66.935
66.385
63.224
62.666
54.882
52.244
43.622
37.330
30.265
29.657
28.753
25.927
25.911
25.750
23.681
22.342
22.281
22.035
18.439
18.358
-5.113
-5.367
-5.433
-5.463
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

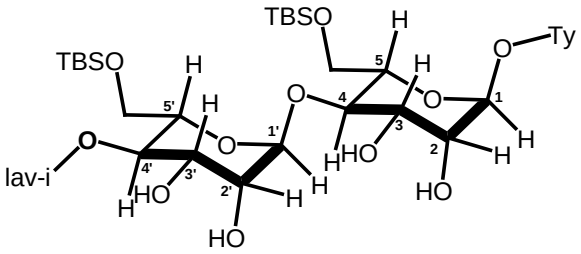
The relative stereochemistry of **3a** and **14a** was determined by various coupling constants from a series of ^{1}HNMR experiments



Compound-**3a**

H_1,H_2 J = 1.8 Hz
H_2,H_3 J = 4.2 Hz
H_3,H_4 J = 10.2 Hz
H_4,H_5 J = 10 Hz

$H_{1'}$,$H_{2'}$ J = 1.2 Hz
$H_{2'}$,$H_{3'}$ J = 6.0 Hz
$H_{3'}$,$H_{4'}$ J = 10.2 Hz
$H_{4'}$,$H_{5'}$ J = 10.8 Hz



Compound-**14a**

H_1,H_2 J = 1.8 Hz
H_2,H_3 J = 4.6 Hz
H_3,H_4 J = 9.0 Hz
H_4,H_5 J = 10.2 Hz

$H_{1'}$,$H_{2'}$ J = 1.8 Hz
$H_{2'}$,$H_{3'}$ J = 5.4 Hz
$H_{3'}$,$H_{4'}$ J = 9.6 Hz
$H_{4'}$,$H_{5'}$ J = 10.2 Hz