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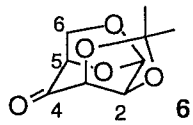
General. All reactions were carried out under argon with the exclusion of moisture. The reagents were purchased from Sigma-Aldrich Chemical Co. and Fluka Chemical Co. and were used without further purification. THF was distilled from sodium benzophenone ketyl; methylene chloride, pyridine and acetonitrile were distilled from calcium hydride. Flash column chromatography was carried out on 230-400 mesh silica gel. Analytical thin layer chromatography was done on GF-254 Merck silica gel.

Equation 3:

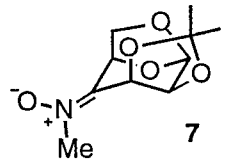
1,6-Anhydro-2,3-isopropylidene-4-oxo-*lyxo*-hexopyranose (6). A solution of 1,6-anhydro-2,3-isopropylidene-β-D-mannopyranose (1.5 g, 7.42 mmol) in CH_2Cl_2 (15 mL), was added dropwise to a well stirred suspension of PCC (6.4 g, 29.7 mmol) and molecular sieves (4 Å, 3.7 g) in methylene chloride (10 mL). After 17 h, the reaction mixture was diluted with Et_2O, and the solid residue was decanted and washed with more Et_2O. Filtration through silica gel (100% diethyl ether) gave **6** (1.25 g, 84%).



^{1}H NMR ($CDCl_3$, 300 MHz) δ:. 5.64 (d, $J_{1\text{-}2}$ = 3.2 Hz, 1H, H1), 4.59 (m, 1H, H5), 4.55-4.40 (m, 2H, H2, H3), 4.04 (d, $J_{6endo\text{-}6exo}$ = 7.9 Hz, 1H, H6endo), 3.90 (dd, $J_{6exo\text{-}6endo}$ = 7.9 Hz, $J_{6exo\text{-}5}$ = 5.7Hz, 1H, H6exo), 1.52 (s, 3H, CH_3), 1.36 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz)δ : 201.5 (C4),113.5 ($\underline{C}(CH_3)_2$), 99.8 (C1), 77.4, 76.8, 76.0 (C2, C3, C5), 67.5 (C6), 26.6, 25.9 (CH_3, CH_3).

Nitrone 7. MeNHOH.HCl (1.2 g, 14.36 mmol) was added to a solution of ketone **6** (954 mg, 4.78 mmol) in pyridine (15 mL) at 5 °C . After 5 h, the solvent was removed *in vacuo* and the crude residue was filtered through silica gel (EtOAc 100%). Final washing with hexane gave nitrone **7** as a white solid (1.06 g, 97%).

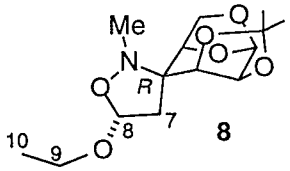


^{1}H NMR ($CDCl_3$, 500 MHz) δ : 5.79 (d, $J_{5\text{-}6exo}$ = 4.8 Hz, 1H, H5), 5.47 (d, $J_{1\text{-}2}$ = 2.9 Hz, 1H, H1), 4.96 (d, $J_{3\text{-}2}$ = 7.2 Hz, 1H, H3), 4.26 (dd, $J_{2\text{-}1}$ = 2.9 Hz, $J_{2\text{-}3}$ = 7.2 Hz, 1H, H2), 3.94 (d, $J_{6endo\text{-}6exo}$ = 7.4 Hz, 1H, H6endo), 3.86 (dd, $J_{6exo\text{-}6endo}$ = 7.4 Hz, $J_{6exo\text{-}5}$ = 4.8 Hz, 1H, H6exo), 3.81 (s, 3H, N-CH_3), 1.51 (s, 3H, CH_3), 1.38 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz,) δ : 141.5 (C4), 111.9 ($\underline{C}(CH_3)_2$), 98.5 (C1), 75.2 (C2), 69.3 (C5), 69.1 (C3), 68.2 (C6), 48.3 (CH_3-N), 26.2, 25.7 (CH_3, CH_3).

Ms *m/z* (%): 229 (36, M^+), 184 (100, M^+-($^-$O-N$^+$-Me)), 142, 126, 96, 85, 68.

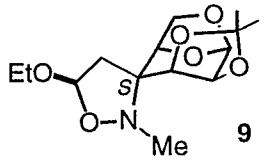
Cycloadducts 8 and 9. A solution of the nitrone **7** (120 mg, 0.53 mmol) in benzene (5 mL) was added to a suspension of molecular sieves (80 mg) in ethyl vinyl ether (1 mL, 5.26 mmol). After 38 h at rt and refluxing for 8 h, the reaction mixture was filtered. Column chromatography gave **8** (99 mg, 62%) and **9** (17 mg, 11%), and some starting ketone **6** (18 mg, 15%).



^{1}H NMR ($CDCl_3$, 500 MHz) δ : 5.43 (m, 1H, H8), 5.30 (d, $J_{1\text{-}2}$ = 2.7 Hz, 1H, H1), 4.57 (m, 1H, H5), 4.41 (d, $J_{6endo\text{-}6exo}$ = 7.2 Hz 1H, H6endo), 4.08 (d, $J_{3\text{-}2}$ = 5.4 Hz, 1H, H3), 4.00 (dd, $J_{2\text{-}1}$ = 2.7 Hz, $J_{2\text{-}3}$ = 5.4 Hz, 1H, H2), 3.80 (dq, 1H, H9'), 3.74 (dd, $J_{6exo\text{-}6endo}$~$J_{6exo\text{-}5}$= 7 Hz, 1H, H6exo), 3.50 (dq, 1H, H9), 2.86 (s, 3H, N-CH_3), 2.60 (dd, J_{gem} = 13.9 Hz, J = 2.8 Hz, 1H, H7'), 2.42 (dd, J_{gem} = 13.9 Hz, J = 6.6 Hz, 1H, H7), 1.59 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.21 (t, J = 7.1 Hz, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 111.2 ($\underline{C}(CH_3)_2$), 105.2 (C8), 99.5 (C1), 75.9 (C3), 74.4 (C2, C5), 69.2 (C4), 64.9 (C6), 64.3 (C9), 44.4 (C7), 41.8 ($\underline{C}H_3$-N), 25.9, 25.8 (CH_3, CH_3), 15.1 (C10).

MS *m/z* (%): 301 (68, M^+), 256 (53, (M-($^-$O-N$^+$-Me)$^+$), 214, 200, 159, 142, 85, 55.



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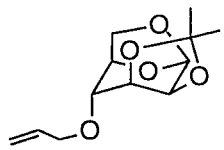
^{1}H NMR ($CDCl_3$), 300 MHz δ : 5.33 (dd, J = 6.6 Hz, J = 3.7 Hz, 1H, H8), 5.26 (m, 1H, H1), 4.42 (dd, $J_{6endo\text{-}6exo}$ = 7.2 Hz, $J_{6endo\text{-}5}$ = 0.9 Hz, 1H, H6endo), 4.31 (m, 1H, H3), 4.09 (d, 1H, H5), 3.96 (dd, $J_{2\text{-}1}$ = 2.7 Hz, $J_{2\text{-}3}$ = 5.3 Hz, 1H, H2), 3.82 (dq, J = 7.1 Hz, J = 9.5 Hz, 1H, H9), 3.66 (dd, $J_{6exo\text{-}6endo}$ = 7.2 Hz, $J_{6exo\text{-}5}$ = 5.9 Hz, 1H, H6exo), 3.50 (dq, J = 7.1 Hz, J = 9.5 Hz, 1H, H9'), 3.06 (s, 3H, CH_3-N), 3.00 (dd, J_{gem} = 13.8 Hz, J = 6.6 Hz, 1H, H7'), 2.20 (dd, J = 13.8 Hz, J = 3.7 Hz, 1H, H7), 1.57 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.21 (t, J = 7.1 Hz, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 111.3 ($\underline{C}(CH_3)_2$), 106.1 (C8), 99.6 (C1), 75.7, 75.2, 74.7 (C2, C3, C5), 69.5 (C4), 64.8 (C6), 64.1 (C9), 44.7 (C7), 41.7 (N-$\underline{C}H_3$), 25.9, 25.8 (CH_3, CH_3), 15.1 (C10).

ENTRY 1. TABLE 1:

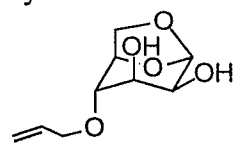
4-*O*-Allyl-1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose. A solution of 1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose (202 mg, 1 mmol) in dry THF (1.5 mL) was added dropwise to a suspension of sodium hydride (27 mg, 1.1 mmol) in dry THF (0.5 mL) at 0 °C (previously prepared by washing 60% sodium hydride (45 mg) with 0.5 mL of THF). After 30 min, the cooling bath was removed and the reaction was allowed to warm up to rt. Then, allyl bromide (89 μL, 1.03 mmol) and *n*-Bu_4NI (7 mg, 0.02 mmol) were added. After 16 h, a saturated NH_4Cl solution was added and the product was extracted with Et_2O. The ethereal extracts were dried over Na_2SO_4 and concentrated *in vacuo* to give the 4-*O*-allyl derivative (223 mg, 92%).



^{1}H NMR ($CDCl_3$, 300 MHz) δ : 5.93 (tdd, J_{trans} = 17.2 Hz, J_{cis} = 10.3 Hz, J = 5.7 Hz, 1H, -O-CH_2-C$\underline{H}$=CH_2), 5.36 (m, 1H, H1), 5.33 (m, J_{trans} = 17.2 Hz, J_{gem}~J_{al}~ 1.5 Hz, 1H, -O-CH_2-CH=C$\underline{H_2}$), 5.24 (m, J_{cis} = 10.3 Hz, $J_{gem} \approx J_{al}$ = 1.5 Hz, 1H, -O-CH_2-CH=C$\underline{H_2}$), 4.60 (m, 1H, H5), 4.22 (m, 1H, H3), 4.15 (m, 2H, -O-C$\underline{H_2}$-CH=CH_2), 4.09 (dd, $J_{4,3}$ = 6.4 Hz, $J_{4,5}$ = 3.0 Hz, 1H, H2), 3.94 (dd, J_{gem} = 7.3 Hz, $J_{6endo\text{-}5}$ = 1.3 Hz, 1H, H6endo), 3.76 (dd, J_{gem} = 7.3 Hz, $J_{6exo\text{-}5} \approx$ 7.3 Hz, 1H, H6exo), 3.64 (br s, 1H, H4), 1.53 (s, 3H, -CH_3), 1.33 (s, 3H, -CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 134.0 ($\underline{C}$H=CH_2), 118.0 (CH=$\underline{C}H_2$), 109.8 ($\underline{C}(CH_3)_2$), 99.2 (C1), 76.2, 73.8, 73.4 y 72.3 (C2, C3, C4, y C5), 70.7 (-O-$\underline{C}H_2$-CH=CH_2), 64.5 (C6), 26.0 y 25.8 ($C(\underline{C}H_3)_2$).

4-*O*-Allyl-1,6-anhydro-β-D-mannopyranose. A solution of 4-*O*-allyl-1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose (223 mg, 0.92 mmol) in 20% aqueous acetic acid (3 mL) and THF (2 mL) was stirred at 60 °C for 23 h. Evaporation of the solvent *in vacuo* and removal of the last traces of water by distillation with toluene (3 mL) gave the 2,3-diol (221 mg, quant.).

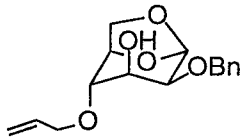


^{1}H NMR ($CDCl_3$, 300 MHz) δ : 5.92 (m, 1H, -O-CH_2-C$\underline{H}$=CH_2), 5.37 (s, 1H, H1), 5.30 (m, J_{trans} = 17.2 Hz, 1H, -O-CH_2-CH=C$\underline{H_2}$), 5.21 (m, J_{cis} = 10.4 Hz, 1H, -O-CH_2-CH=C$\underline{H_2}$), 4.56 (m, 1H, H5), 4.13 (m, 3H, -O-C$\underline{H_2}$-CH=CH_2, H6endo), 4.00 (m, 1H, H3), 3.72 (m, 2H, H2, H6exo), 3.57 (s, 1H, H4), 3.34 (br s, 2H, -OH, -OH).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 134.2 ($\underline{C}$H=CH_2), 117.9 (CH=$\underline{C}H_2$), 101.6 (C1), 78.5, 74.1 (C4, C5), 70.8 (C6), 68.8, 66.8 (C2, C3), 64.8 (C7).

4-*O*-Allyl-1,6-anhydro-2-*O*-benzyl-β-D-mannopyranose. A suspension of 4-*O*-allyl-1,6-anhydro-β-D-mannopyranose (221 mg, 1.09 mmol) and *n*-Bu_2SnO (280 mg, 1.12 mmol) in dry benzene (10 mL) was refluxed for 3 h, using a Dean-Stark trap to remove the generated water. The reaction mixture was diluted with benzene (8 mL) and allowed to warm up to rt. Benzyl bromide (175 mL, 1.47 mmol) and *n*-Bu_4NI (403 mg, 1.09 mmol) were added and stirring was continued at 90 °C for another 5

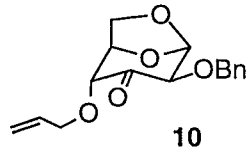
h. Flash chromatography (35%, 37%, 40% EtOAc-hexane mixtures) and bulb to bulb distillation (0.5 torr, 190°C) gave the benzyl derivative (119 mg, 40%).



^{1}H NMR ($CDCl_3$, 250 MHz) δ : 7.35 (m, 5H, ArH), 5.90 (tdd, J_{trans} = 17.4 Hz, J_{cis} = 10.3 Hz, J = 5.6 Hz, 1H, -O-CH_2-C<u>H</u>=CH_2), 5.41 (s, 1H, H1), 5.30 (m, J_{trans} = 17.4 Hz, $J_{gem} \sim J_{al}$ =1.6 Hz, 1H, -O-CH_2-CH=<u>C</u>H_2), 5.22 (m, J_{cis} = 10.3 Hz, $J_{gem} \sim J_{al}$ =1.6 Hz, 1H, -O-CH_2-CH=<u>C</u>H_2), 4.66 (AB_q, J = 11.7 Hz, $\Delta\delta$=0.11, 2H, ArCH_2), 4.56 (m, 1H, H5), 4.23 (dd, $J_{6endo-6exo}$ = 7.0 Hz, $J_{6endo-5} \sim$ 0.8 Hz, 1H, H6endo), 4.2-4.0 (m, 3H, H3, -O-<u>C</u>H_2-CH=CH_2), 3.73 (dd, $J_{6exo-6endo}$ = 7.0 Hz, J_{6exo-5} = 5.9 Hz, 1H, H6exo), 3.59 (m, 2H, H4 y H2), 3.11 (d, J = 2.5 Hz, 1H, OH).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 137.2 (Ar_{ipso}), 134.3 (-<u>C</u>H=CH_2), 128.6 (C_{meta}), 128.2 (C_{para}), 128.0 (C_{orto}), 117.8 (-CH=<u>C</u>H_2), 100.1 (C1), 78.1, 74.3, 73.4 (C2, C3, C4), 71.1 (Ph-<u>C</u>H_2-), 70.8 (-O-<u>C</u>H_2-), 67.3 (C5), 64.9 (C6).

4-*O*-Allyl-1,6-anhydro-2-*O*-benzyl-3-oxo-β-D-*arabino*-hexopyranose (10). Dess-Martin periodinane (126 mg, 0.3 mmol) and *tert*-butanol (30 µL, 0.32 mmol) were added to a solution of 4-*O*-allyl-1,6-anhydro-2-*O*-benzyl-β-D-mannopyranose (67 mg, 0.23 mmol) in CH_3CN (1.1 mL). After stirring at rt for 16 h, the reaction mixture was diluted with ethyl ether and a saturated aqueous solution of $NaHCO_3$:$Na_2S_2O_3$ (1:1). The organic layer was washed with brine, dried over $NaSO_4$ and concentrated *in vacuo* to give ketone **10** as an oil (62 mg, 92%).



10

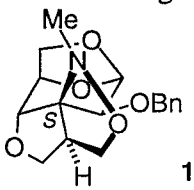
^{1}H NMR ($CDCl_3$, 300 MHz) δ : 7.5-7.2 (m, 5H, ArH), 5.85 (tdd, J_{trans} = 17.5 Hz, J_{cis} = 10.3 Hz, $J \sim$ 5.4 Hz, 1H, -O-CH_2-C<u>H</u>=CH_2), 5.58 (d, J_{1-2} = 2.2 Hz, 1H, H1), 5.4-5.2 (m, 2H, -O-CH_2-CH=<u>C</u>H_2), 4.93 (d, J_{gem} = 12.1 Hz, 1H, H10), 4.63 (d, J_{gem} = 12.1 Hz, 1H, H10'), 4.77 (m, 1H, H5), 4.21 (d, J = 2.2 Hz, 1H, H2*), 4.06 (tdd, J_{gem} = 12.7 Hz, J = 5.3 Hz, J = 1.2 Hz, 1H, -O-C<u>H</u>$_2$-CH=CH_2), 3.98 (tdd, J = 12.7 Hz, J = 6.1 Hz, J = 1.1 Hz, 1H, -O-C<u>H</u>$_2$-CH=CH_2), 3.83 (dd, J_{gem} = 8.3 Hz, J_{6exo-5} = 5.6 Hz, 1H, H6exo), 3.69 (m, 2H, H6endo, H4*).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 202.6 (C3), 137.0 (Ar_{ipso}), 133.0 (<u>C</u>H=CH_2), 128.5 (C_{meta}), 128.4 (C_{para}), 128.2 (C_{orto}), 119.0 (CH=<u>C</u>H_2), 102.5 (C1), 83.1, 81.2 (C4, C2), 76.4 (C5), 73.1, 71.0 (-O-<u>C</u>H_2-, Ph-<u>C</u>H_2), 65.4 (C6).

MS *m/z* (%): 290 (0.92, M^+), 261 (0.85, M-(CH_2-O-)$^+$), 203, 197, 157, 125, 91 (100, C_7H_7), 65.

IR : 2889 (O-CH_2-O), 1734 (C=O), 1454 (CH_2-C=C), 1105, 990, 742.

Cycloadduct 11. MeNHOH.HCl (250 mg, 2.9 mmol), pyridine (161 µL, 1.9 mmol), and molecular sieves (4 Å, 100 mg) were added to a solution of **10** (145 mg, 0.5 mmol) in ethanol (1 mL). After 36 h at rt and 6 h at 45 °C, the reaction mixture was filtered, diluted with water and extracted with CH_2Cl_2. The organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Column chromatography (15%, 40% EtOAc-hexane) of the crude residue gave **11** (124 mg, 78%).



11

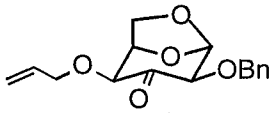
^{1}H NMR ($CDCl_3$, 500 MHz) δ : 7.36-7.29 (m, 5H, ArH), 5.46 (d, J = 2.2 Hz, 1H, H1), 4.72 (AB_q, Ar-C<u>H</u>$_2$), 4.63 (d, J_{5-6exo} = 5.5 Hz, 1H, H5), 4.24 (dd, J_{gem} = 9.2 Hz, J = 7.1 Hz, 1H, H7'), 4.19 (d, J_{gem} = 7.3 Hz, 1H, H6endo), 4.08 (dd, J_{gem} = 8.7 Hz, J = 7.0 Hz, 1H, H9'), 3.86 (d, $J_{1,2}$ = 2.2 Hz, 1H, H2), 3.69 (dd, J_{gem} = 9.2 Hz, J = 4.4 Hz, 1H, H7), 3.57 (dd, J_{gem} = 8.7 Hz, J = 2.1 Hz, 1H, H9), 2.88 (s, 3H, CH_3), 2.83 (m, 1H, H8).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 137.7 (Ar_{ipso}), 128.5 (C_{meta}), 128.0 (C_{para}), 127.8 (C_{orto}), 99.1 (C1), 79.9 (C4), 78.4 (C2), 75.6 (C5), 73.7 (C7), 73.4 (C10), 70.1 (C9), 66.0 (C6), 56.1 (C8), 40.6 (N-CH_3).

MS *m/z* (%): 319 (25, M^+), 228, 213, 183, 91 (100, C_7H_7), 68.

ENTRIES 2 AND 3. TABLE 1:

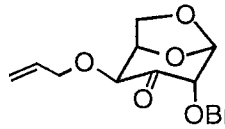
Ketones 12 and 14. A solution of **10** (261 mg) and DBU (147 μL) in toluene (30 mL) was left for 22 h at rt. DBU was removed by filtration through a short pad of silica gel and the solvents were evaporated. Column chromatography (15% EtOAc-hexane) gave ketone **12** (111 mg, 42%) and ketone **14** (67 mg, 26%).



12

Ketone 12: ^{1}H NMR ($CDCl_3$, 300 MHz) δ : 7.39-7.28 (m, 5H, ArH), 5.90 (tdd, J_{trans} = 16.4 Hz, J_{cis} = 10.3 Hz, J ~ 5.6 Hz, 1H, -O-CH_2-C<u>H</u>=CH_2), 5.52 (d, $J_{1\text{-}2}$ = 2.0 Hz, 1H, H1), 5.27 (m, 2H, -O-CH_2-CH=C<u>H</u>$_2$), 4.75 (m, 1H, H5), 4.63 (d, J_{gem} = 12.0 Hz, 1H, H10), 4.51 (d, J_{gem} = 12.0 Hz, 1H, H10'), 4.33 (d, $J_{4\text{-}5}$ = 4.5 Hz, 1H, H4), 4.32 (m, 1H, -O-C<u>H</u>$_2$-CH=CH_2), 4.05 (tdd, J = 12.7 Hz, J = 6.2 Hz, J = 1.2 Hz, 1H, -O-C<u>H</u>$_2$-CH=CH_2), 3.92 (m, $J_{6endo\text{-}6exo}$ = 7.9 Hz, 1H, H6endo), 3.69 (d, $J_{2\text{-}1}$ = 2.0 Hz, 1H, H2), 3.68 (m, $J_{6endo\text{-}6exo}$ = 7.9 Hz, $J_{6exo\text{-}5}$ = 4.8 Hz, 1H, H6exo).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 203.1 (C3), 136.6 (Ar_{ipso}), 133.6 (<u>C</u>H=CH_2), 128.3 (C_{meta}), 128.3 (C_{para}), 128.3 (C_{orto}), 118.4 (CH=<u>C</u>H$_2$), 101.6 (C1), 82.1, 79.1 (C4, C2), 75.1 (C5), 72.6, 72.5 (-O-<u>C</u>H$_2$-, Ph-<u>C</u>H$_2$), 65.1 (C6).

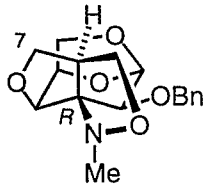


14

Ketone 14: ^{1}H NMR ($CDCl_3$, 300 MHz) δ : 7.39-7.27 (m, 5H, ArH), 5.91 (tdd, J_{trans} = 16.7 Hz, J_{cis} = 10.4 Hz, J ~ 5.4 Hz, 1H, -O-CH_2-C<u>H</u>=CH_2), 5.56 (d, $J_{1\text{-}2}$ = 2.3 Hz, 1H, H1), 5.34-5.22 (m, 2H, -O-CH_2-CH=C<u>H</u>$_2$), 4.97 (d, J_{gem} = 12.2 Hz, 1H, H10), 4.72 (m, 1H, H5), 4.62 (d, J_{gem} = 12.2 Hz, 1H, H10'), 4.40 (tdd, J_{gem} = 12.8 Hz, J = 5.3 Hz, J = 1.4 Hz, 1H, -O-C<u>H</u>$_2$-CH=CH_2), 4.14-4.04 (m, 3H, H_4, H_{6endo}, H7), 3.94 (m, $J_{2\text{-}1}$ = 2.3 Hz, $J_{2\text{-}4}$ = 3.8 Hz, 1H, H2), 3.80 (dd, J_{gem} = 8.0 Hz, $J_{6exo\text{-}5}$ = 5.0 Hz, 1H, H6exo).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 202.7 (C3), 137.2 (Ar_{ipso}), 133.7 (<u>C</u>H=CH_2), 128.5 (C_{meta}), 128.1 (C_{para}), 128.0 (C_{orto}), 118.4 (CH=<u>C</u>H$_2$), 102.4 (C1), 82.1, 80.2 (C4, C2), 75.5 (C5), 73.0, 72.4 (-O-<u>C</u>H$_2$-, Ph-<u>C</u>H$_2$), 66.6 (C6).

Cycloadduct 13. MeNHOH.HCl (582 mg, 6.97 mmol), pyridine (375 μL, 4.64 mmol), and molecular sieves (4 Å, 40 mg) were added to a solution of **12** (67 mg, 0.23 mmol) in EtOH (4 mL). After 24 h at rt and 6h at 55 °C, the reaction was worked-up as described for **11.** Chromatography (1% methanol-methylene chloride) gave **13** (48 mg, 65%).

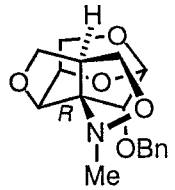


13

^{1}H NMR ($CDCl_3$, 500 MHz) δ : 7.41-7.26 (m, 5H, ArH), 5.28 (d, J = 2.5 Hz, 1H, H1), 4.79 (d, J = 11.7 Hz, 1H, Ar-C<u>H</u>$_2$), 4.69 (d, J = 11.7 Hz, 1H, Ar-C<u>H</u>$_2$), 4.47 (m, 1H, H5), 4.32 (m, 2H, H7, H4), 4.04 (d, J_{gem} = 8.3 Hz, 1H, H6endo), 3.98 (dd, J = 7.7 Hz, J = 5.4 Hz, 1H, H9), 3.81 (m, 1H, H7), 3.72 (m, 2H, H6exo, H9), 3.64 (m, 1H, H8), 3.55 (d, J = 1.9 Hz, 1H, H2), 2.72 (s, 3H, NCH_3).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 138.0 (Ar_{ipso}), 128.4 (C_{meta}), 127.9 (C_{para}), 127.8 (C_{orto}), 99.3 (C1), 78.4 (C3), 76.6, 76.0 (C2, C4, C5), 74.8, 71.9 (C9, C7), 73.2 (O<u>C</u>H$_2$Bn), 65.5 (C6), 50.5 (C8), 37.7 (NCH_3).

Cycloadduct 15. It was obtained (60 mg, 77%) from ketone **14** (70 mg, 0.24 mmol), MeNHOH.HCl (604 mg, 7.23 mmol), pyridine (390 μL, 4.82 mmol) and molecular sieves (40 mg) in EtOH (4 mL), following the procedure reported for **13**.



15

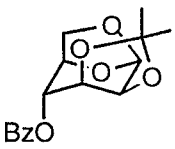
^{1}H NMR ($CDCl_3$, 500 MHz) δ : 7.41-7.26 (m, 5H, ArH), 5.27 (d, J = 1.5 Hz, 1H, H1, 4.94 (d, J = 11.8 Hz, 1H, Ar-C<u>H</u>$_2$), 4.68 (d, J = 11.8 Hz, 1H, Ar-C<u>H</u>$_2$), 4.61 (d, J = 6.1 Hz, 1H, H4), 4.50 (m, 1H, H5), 4.32 (dd, J_{gem} = $J_{7\text{-}8}$ = 9.0 Hz, 1H, H7), 3.93 (d, J_{gem} = 8.5 Hz, 1H, H6endo), 3.86 (dd,

J_{gem} = 8.9 Hz, J=3.5, 1H, H9'), 3.74 (d, J_{gem} = 8.9 Hz, 1H, H9), 3.64 (m, 2H, H6exo, H7), 3.49 (d, $J_{1,2}$ = 1.5 Hz, 1H, H2), 3.17 (m, 1H, H8), 2.83 (s, 3H, NCH_3).

^{13}C NMR ($CDCl_3$, 125 MHz) δ : 138.1 (Ar_{ipso}), 128.4 (C_{meta}), 128.2 (C_{para}), 127.8 (C_{orto}), 101.0 (C1), 79.5, 73.9 (C2, C4), 75.0 (C5), 74.9, 74.8 (C9, C7), 69.3 (C10), 64.7 (C6), 53.3 (C8), 40.1 (NCH_3).

ENTRY 4. TABLE 1:

1,6-Anhydro-4-*O*-benzoyl-2,3-isopropylidene-β-D-mannopyranose. To a cold (0°C) solution of 1,6-anhydro-2,3-isopropylidene-β-D-mannopyranose (2.0 g, 9.89 mmol) in dry Py (10 mL), BzCl (1.23 mL, 10.38 mmol, 105 mol%) and DMAP (cat.) were added and the reaction mixture was allowed to warm up slowly to rt. When no starting material was detected by TLC (EtOAc-hexane, 10:90, $Rf_{alcohol}$= 0.38), the reaction mixture was diluted with ethyl ether (30 mL) and washed with solutions of $NaHCO_{3(dil)}$ and $CuSO_4$ (5%; 100 mL). Drying over Na_2SO_4 and evaporation of the solvent, afforded the benzoate (3.0 g, 99%) as white crystals (EtOAc, mp= 134°C).



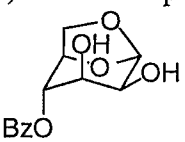
^1H NMR ($CDCl_3$, 300 MHz) δ : 8.09 (m, 2H; ArH_{orto}), 7.60 (m, 1H; ArH_{para}), 7.46 (m, 2H; ArH_{meta}), 5.43 (d, $J_{4,5}$ = 2.6 Hz, 1H; H4), 5.27 (s, 1H; H1), 4.70 (m, 1H; H3#), 4.30 (m, 1H; H5), 4.15 (m, 2H; H2#, H6endo), 3.83 (dd, $J_{6,6'} \approx J_{6exo,5} \approx$ 7 Hz, 1H; H6exo), 1.58 [s, 3H; $C(CH_3)_2$], 1.34 [s, 3H; $C(CH_3)_2$].(# This assignments could be interchanged).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 165.4 (PhCO), 133.5 (Ar, C_{para}), 129.8 (Ar, C_{orto}), 129.3 (Ar, C_{ipso}), 128.5 (Ar, C_{meta}), 110.3 [$\underline{C}(CH_3)_2$], 99.3 (C1), 74.1, 73.3, 72.2, 71.4 (C2, C3, C4, C5), 64.7 (C6), 25.9, 25.8 [$C(\underline{C}H_3)_2$].

IR (KBr): 1710 cm^{-1} (PhCOO-).

MS *m/z* (%): 291 [9, $(M-CH_3)^+$], 248, 184, 139, 127, 105 [100, $(PhCO)^+$], 77 (32, Ph^+), 43.

1,6-Anhydro-4-*O*-benzoyl-β-D-mannopyranose. A suspension of 1,6-anhydro-4-*O*-benzoyl-2,3-isopropylidene-β-D-mannopyranose (2.90 g, 9.6 mmol) in aqueous AcOH (30%, 125 mL) was refluxed in a 250 mL one-necked round-bottomed flask fitted with a reflux condenser. When no starting material was left (TLC, EtOAc-hexane, 10:90), the solvent was evaporated and the last traces of acid and water were removed by azeotropic distillation with toluene (3 x 50 mL) to give the diol (2.55 g, quant.) as a white powder (EtOAc, m.p.= 134°C).



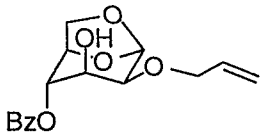
^1H NMR ($CDCl_3$, 250 MHz) δ : 8.06 (m, 2H; ArH_{orto}), 7.60 (m, 1H; ArH_{para}), 7.46 (m, 2H; ArH_{meta}), 5.48 (s, 1H; H4), 5.18 (s, 1H; H1), 4.70 (m, 1H; H5), 4.34 (d, $J_{6,6'}$ = 7.5 Hz 1H; H6endo), 4.13 (m, 1H; H3), 3.83 (m, 2H; H2, H6exo), 3.26 (d, $J_{OH,3}$ = 4.9 Hz, 1H; C_3OH), 3.06 (d, $J_{OH,2}$ = 7.1 Hz, 1H; C_2OH).

^{13}C NMR (CD_3Cl-CD_3OD, 4:1, 63 MHz) δ: 166.0 (Ph$\underline{C}$O), 133.4 (Ar, C_{para}), 129.6 (Ar, C_{orto}), 129.3 (Ar, C_{ipso}), 128.4 (Ar, C_{meta}), 101.7 (C1), 74.0, 73.6 (C4, C5), 68.1, 66.2 (C2, C3), 64.7 (C6).

MS *m/z* (%):123 [19, $(PhCO_2)^+$], 106, 105 [100, $(PhCO)^+$], 77 (29, Ph^+), 70, 60, 51.

Anal. calcd. for ($C_{13}H_{14}O_6$): 58.65 (%C), 5.31 (%H). Found: 58.42 (%C), 5.60 (%H).

2-*O*-Allyl-1,6-anhydro-4-*O*-benzoyl-β-D-mannopyranose. A mixture of 1,6-anhydro-4-*O*-benzoyl-β-D-mannopyranose (3.0 g, 11.27 mmol) and *n*-Bu_2SnO (3.0 g, 11.83 mmol, 105 mol%) in dry benzene (150 mL), was refluxed for 2h with azeotropic removal of water. The resulting homogeneous solution was cooled to rt, allyl bromide (3.23 mL, 36.63 mmol, 325 mol%) and *n*-Bu_4NI (3.19 g, 8.45 mmol, 75 mol%) were added, and the reaction mixture was warmed up again to reflux until no starting material was left (MeOH-CH_2Cl_2, 1:99). The solvent was removed under vacuum and the resulting oily residue was filtered through a path of silica using EtOAc-hexane mixtures as eluents. A further purification was done by dissolving the product in ethyl ether and stirring with a 10% solution of KF for 24h. The organic layer was dried and filtered. Elimination of the solvents afforded the 3-*O*-allyl derivative (2.92 g, 85%) as a slightly yellow oil.

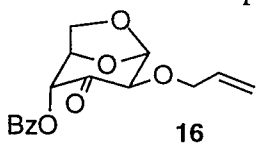


^{1}H NMR ($CDCl_3$, 250 MHz) δ : 8.07 (m, 2H; ArH_{orto}), 7.59 (m, 1H; ArH_{para}), 7.46 (m, 2H; Ar_{meta}), 5.95 (m, 1H; H8), 5.52 (br s, 1H; H1), 5.4-5.1 (m, 3H; H9cis, H9trans, H4), 4.70 (m, 1H; H5), 4.39 (d, $J_{6,6'}$ = 7.3 Hz, 1H; H6endo), 4.3-4.0 (m, 3H; H3, H7), 3.80 (dd, $J_{6,6'}$ = 7.3 Hz, $J_{6exo,5}$ = 5.8 Hz, 1H; H6exo), 3.63 (dd, $J_{2,3}$ = 5.1 Hz, $J_{2,1}$ = 1.8 Hz, 1H; H2), 3.19 (d, $J_{OH,3}$ = 2.3 Hz, 1H; OH).

^{13}C NMR ($CDCl_3$, 63 MHz) δ : 165.4 (PhCOO-), 133.8 (C8), 133.4 (Ar, C_{para}), 129.8 (Ar, C_{orto}), 129.3 (Ar, C_{ipso}), 128.5 (Ar, C_{meta}), 118.3 (C9), 100.2 (C1), 74.1 (C4), 73.3 (C3#), 73.2 (C5#), 70.3 (C7), 67.6 (C2), 65.2 (C6). (# This assignments could be interchanged).

MS *m/z* (%): 265 [6, $(M-C_3H_5)^+$], 218, 217, 105 [100, $(PhCO)^+$], 99, 77 (22, Ph^+), 71.

2-*O*-Allyl-1,6-anhydro-4-*O*-benzoyl-3-oxo-β-D-*arabino*-hexopyranose (16). To a solution of 2-*O*-allyl-1,6-anhydro-4-*O*-benzoyl-β-D-mannopyranose (1.07 g, 3.49 mmol) in dry acetonitrile (16 mL) magnetically stirred under Ar at rt, Dess-Martin periodinane (2.22 g, 5.23 mmol, 150 mol%) and *t*-BuOH (4.01 mmol, 0.37 mL, 115 mol%) were added. The consumption of the starting material was monitored by TLC (EtOAc-hexane, 25:75), the reaction mixture was diluted with ethyl ether and washed thoroughly with a 1/1 saturated solution of $NaHCO_3$-$Na_2S_2O_3$ and brine. Drying over Na_2SO_4, filtration and removal of the solvents under reduced pressure, afforded ketone **16** (1.02 g, 96%) which was used in the dipolar cycloadditions reactions without further purification.



16

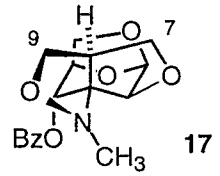
^{1}H NMR ($CDCl_3$, 250 MHz) δ : 8.04 (m, 2H; ArH_{orto}), 7.60 (m, 1H; ArH_{para}), 7.47 (m, 2H; ArH_{meta}), 5.95 (m, 1H; H8), 5.73 (d, $J_{1,2}$ = 2.3 Hz, 1H; H1), 5.4-5.2 (m, 3H; H9, H4), 5.02 (m, 1H; H5), 4.44 (ddt, 1H; H7), 4.27 (d, $J_{2,1}$ = 2.3 Hz, 1H; H2), 4.15 (ddt, 1H; H7'), 3.95 (dd, $J_{6,6'}$ = 8.5 Hz, $J_{6exo,5}$ = 5.3 Hz, 1H; H6exo), 3.88 (dd, $J_{6,6'}$ = 8.5 Hz, $J_{6endo,5}$ = 1.4 Hz, 1H; H6endo).

^{13}C NMR ($CDCl_3$, 63 MHz) δ : 199.2 (C3), 165.1 (PhCO), 133.9, 133.8 (Ar, C_{para}, C8), 130.0 (Ar, C_{orto}), 128.7 (Ar, C_{meta}), 118.5 (C9), 102.6 (C1), 81.9, 78.1, 75.6 (C2, C4, C5), 72.5 (C7), 65.7 (C6).

IR (film, NaCl): 3070, 2975, 2905, 2880, 1750 (PhCOO-), 1730 (CO, ketone), 1605, 1460, 1325, 1265, 1185, 1120, 1100, 1075 cm^{-1}.

MS *m/z* (%): 263 [5, $(M-C_3H_5)^+$], 217, 105 [100, $(PhCO)^+$], 77 (Ph^+; 16), 51.

Cycloaddition of ketone 16 and MeNHOH.HCl. A solution of ketone **16** (564 mg, 1.85 mmol), MeNHOH.HCl (474 mg, 5.56 mmol, 300 mol%) and dry Py (0.52 mL, 6.48 mmol, 350 mol%) in dry CH_2Cl_2 (16 mL), was heated to reflux in a 25 mL one-necked round-bottomed flask fitted with a reflux condenser and a $CaCl_2$ tube. After consumption of the starting material (28 h), as monitored by TLC (EtOAc-hexane, 25:75), the reaction mixture was poured into water (10 mL), the aqueous layer was decanted and further extracted with CH_2Cl_2. The combined organic extracts were concentrated and the resulting solid residue was dissolved in EtOAc. Washing with brine, drying over Na_2SO_4, filtration, elimination of the solvents and chromatographic purification afforded the isoxazolidine **17** (485 mg, 79%).



17

^{1}H NMR ($CDCl_3$, 500 MHz) δ : 8.07 (m, 2H; ArH_{orto}), 7.58 (m, 1H; ArH_{para}), 7.46 (m, 2H; ArH_{meta}), 5.55 (d, $J_{1,2}$ = 2.3 Hz, 1H; H1), 5.47 (s, 1H; H4), 4.65 (m, 1H; H5), 4.52 (dd, $J_{7,7'}$ = 8.3 Hz, 1H; H7endo#), 4.36 (br s, 1H; H2), 4.11 (d, $J_{6,6'}$ = 8.3 Hz, 1H; H6endo), 3.91 (dd, $J_{9,9'}$ = 8.9 Hz, $J_{9,8}$ = 3.5 Hz, 1H; H9exo^), 3.84-3.80 (m, 2H; H9'^, H6exo), 3.65 (dd, $J_{7,7'}$ = 7.6 Hz, $J_{7,8}$ = 4.5 Hz, 1H; H7exo#), 3.05 (m, 1H; H8), 2.73 (s, 3H; NCH_3). (# This assignments could be interchanged. ^ Idem).

^{13}C NMR ($CDCl_3$, 125 MHz) δ : 165.6 (PhCOO-), 132.7 (Ar, C_{orto}), 129.8 (Ar, C_{para}), 129.6 (Ar, C_{ipso}), 128.4 (Ar, C_{meta}), 101.9 (C1), 76.6 (C2), 75.8 (C5), 74.8 (C7), 73.9 (C4), 72.9 (C3), 70.5 (C9), 66.0 (C6), 54.7 (C8), 40.3 (NCH_3).

IR (film, NaCl): 1720 cm^{-1} (m, PhCO).

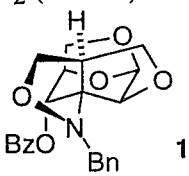
MS *m/z* (%): 334 [6, $(M+1)^+$], 333 (31, M^+), 228 [7, $(M-PhCO)^+$], 207, 149, 140, 105 [100, $(PhCO)^+$], 77 (31, Ph^+).

Anal. calcd. for ($C_{17}H_{19}NO_6$) : 61.26 (%C), 5.76 (%H), 4.20 (%N).

Found: 61.36 (%C), 6.00 (%H), 4.31 (%N).

Cycloadddition of ketone 16 and BnNHOH.HCl.

The isoxazolidine **18** (372 mg, 61%) was obtained starting from ketone **16** (456 mg, 1.5 mmol), BnNHOH.HCl (370 mg, 2.25 mmol, 150 mol%) and dry Py (0.24 mL, 3.0 mmol, 200 mol%) in dry CH_2Cl_2 (13 mL) following the procedure described for the preparation of its *N*-methylated analogue **17**.



18

^1H NMR ($CDCl_3$, 500 MHz) δ: 8.03 (m, 2H; ArHorto-PhCO), 7.50 (m, 1H; ArHpara-PhCO), 7.36 (m, 2H; ArH_{meta}-PhCO), 7.04 (m, 5H; H10), 5.60 (d, $J_{1,2}$ = 2.7 Hz, 1H; H1), 5.59 (d, $J_{4,5}$ = 1.2 Hz, 1H; H4), 4.69 (m, 1H; H5), 5.57 (dd, $J_{7,7'} = J_{7,8}$= 8.3 Hz, 1H; H7), 4.50 (d, $J_{2,1}$ = 2.7 Hz, 1H; H2), 4.15 (2 d, 2H; H6endo, H10), 3.95 (d, $J_{10,10'}$ = 13.7 Hz, 1H; H10'), 3.92 (dd, $J_{9,9'}$ = 8.9 Hz, $J_{9,8}$ = 3.8 Hz, 1H; H9), 3.83 (m, 2H; H6exo, H9'), 3.72 (dd, $J_{7,7'}$ = 7.8 Hz, $J_{7,8}$ = 4.5 Hz, 1H; H7'), 3.14 (m, 1H; H8).

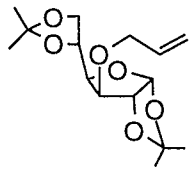
^{13}C NMR ($CDCl_3$, 125 MHz) δ: 165.7 (PhCOO-), 137.7 (Ar, C_{ipso}-NCH_2Ph), 133.2 (Ar, C_{para}-PhCOO-), 129.7 (Ar, C_{orto}-PhCOO-), 129.5 (Ar, C_{ipso}-PhCOO-), 128.4 (Ar, C_{meta}-PhCOO-), 127.9, 127.8, 126.7 (Ar-CH_2Ph), 101.9 (C1), 77.4 (C2)#, 76.0 (C5)#, 74.9 (C7), 73.9 (C4), 73.4 (C3), 70.8 (C9), 66.0 (C6), 57.2 (C10), 54.6 (C8). (# This assignments could be interchanged).

MS *m/z* (%): 410 [8, $(M+1)^+$], 409 (30, M^+), 333 [0.1, $(M+1-Ph)^+$], 304 [0.5, $(M-PhCO)^+$], 105 (100, $PhCO^+$), 91 [95, $(PhCH_2)^+$], 77 (77, Ph^+).

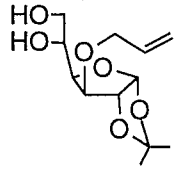
Anal. calcd. for ($C_{23}H_{23}NO_6$): 67.47 (%C), 5.67 (%H), 3.42 (%N). Found: 67.20 (%C), 5.80 (%H), 3.50 (%N).

ENTRY 5. TABLE 1:

3-*O*-Allyl-1,2-5,6-diisopropylidene-β-D-glucofuranose. It was prepared (1.13 g, 98%), according to the procedure reported above for 4-*O*-allyl-1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose (entry 1, Table 1), from 1,2-3,4-diisopropylidene-β-D-glucofuranose (1 g, 3.84 mmol), sodium hydride (100 mg, 4.22 mmol), allyl bromide (365 μL, 4.22 mmol) and *n*-Bu_4NI (28 mg, 0.07 mmol).

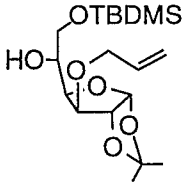


3-*O*-Allyl-1,2-isopropylidene-β-D-glucofuranose. A solution of 3-*O*-allyl-1,2-5,6-diisopropylidene-β-D-glucofuranose (892 mg, 2.97 mmol) in 9 mL of 33% acetic acid and 2 mL of THF was stirred at 60 °C for 7 h. Evaporation of the solvent *in vacuo* and removal of the last traces of water by distillation with toluene (3 mL) gave 3-*O*-allyl-1,2-isopropylidene-β-D-glucofuranose (867 mg, quantitative).



^1H NMR ($CDCl_3$, 250 MHz) δ : 5.91 (d, $J_{1\text{-}2}$ = 3.7 Hz, 1H, H1), 5.90 (m, 1H, -O-CH_2-C<u>H</u>=CH_2), 5.31 (m, J_{trans} ~ 17.1 Hz, 1H, -O-CH_2-CH=C<u>H</u>$_2$), 5.22 (m, J_{cis} ~ 10.3 Hz, 1H, -O-CH_2-CH=C<u>H</u>$_2$), 4.57 (d, J = 3.7 Hz, 1H, H2), 4.3-3.9 (m, 5H, H3, H4, H5, Hal), 3.83 (dd, $J_{6\text{-}6'}$ = 11.4 Hz, $J_{6\text{-}5}$ = 3.2 Hz, 1H, H6), 3.72 (dd, $J_{6\text{-}6'}$ = 11.4 Hz, $J_{6'\text{-}5}$ = 5.3 Hz, 1H, H6'), 2.73 (br, s, 2H, -OH, -OH), 1.48 (s, 3H,-CH_3), 1.31 (s, 3H, -CH_3).

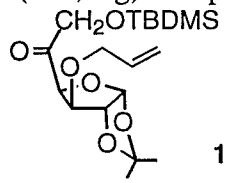
3-*O*-Allyl-6-*O*-(*tert*-butyldimethylsilyl)-1,2-isopropylidene-β-D-glucofuranose. Imidazole (241 mg, 3.54 mmol) and *tert*-butyldimethylsilyl chloride (534 mg, 3.54 mmol) were added to a solution of 3-*O*-allyl-1,2-isopropylidene-β-D-glucofuranose (838 mg, 3.22 mmol) in DMF (12 mL) at 0 °C . After 1 h., the reaction mixture was diluted with water and extracted with diethyl ether. The organic extracts were dried over Na_2SO_4. Purification through silica gel gave the silyl-ether (863 mg, 70%).



^{1}H NMR ($CDCl_3$, 300 MHz) δ : 6.00-5.85 (m, 1H, -O-CH_2-C<u>H</u>=CH_2), 5.89 (d, $J_{1\text{-}2}$ = 3.7 Hz, 1H, H1), 5.31 (m, 1H, -O-CH_2-CH=C<u>H</u>$_2$), 5.21 (m, 1H, -O-CH_2-CH=C<u>H</u>$_2$), 4.5 (d, $J_{1\text{-}2}$ = 3.7 Hz, 1H, H2), 4.15 (m, 2H, -O-C<u>H</u>$_2$-CH=CH_2), 4.09 (dd, $J_{4\text{-}5}$ = 8.4 Hz, $J_{3\text{-}4}$ = 2.9 Hz, 1H, H4), 4.02 (d, $J_{3\text{-}4}$ = 2.9 Hz, 1H, H3), 3.95 (m, 1H, H5), 3.82 (dd, $J_{6\text{-}6'}$ = 10.1 Hz, $J_{6\text{-}5}$ = 3.7 Hz, 1H, H6), 3.74 (dd, $J_{6\text{-}6'}$ = 10.1 Hz, $J_{6'\text{-}5}$ = 5.1 Hz, 1H, H6'), 2.70 (d, J = 6.3 Hz, 1H, -OH), 1.47 (s, 3H, -CH_3), 1.31 (s, 3H, -CH_3), 0.91 (s, 9H, -C(C<u>H</u>$_3$)$_3$), 0.08 (s, 6H, -CH_3).

^{13}C NMR ($CDCl_3$, 125 MHz) δ : 134.2 (<u>C</u>H=CH_2), 118.1 (<u>C</u>(CH_3)$_2$), 111.6 (CH=<u>C</u>H$_2$), 105.1 (C1), 82.5, 81.6, 79.5 (C2, C3, C4), 68.5 (C5), 71.4 (C6), 26.7, 26.3 (C(<u>C</u>H$_3$)$_2$), 25.8 (C(<u>C</u>H$_3$)$_3$), 18.3 (<u>C</u>(CH$_3$)$_3$), -5.5, -5.4 (Si-<u>C</u>H$_3$).

3-*O*-Allyl-6-*O*-(*tert*-butyldimethylsilyl)-5-oxo-1,2-isopropylidene-β-D-*xylo*-furanose (19). It was obtained (738 mg, 80%) from 3-*O*-allyl-6-*O*-(*tert*-butyldimethylsilyl)-1,2-isopropylidene-β-D-glucofuranose (941 mg, 2.51 mmol), PCC (2167 mg, 10.05 mmol) and molecular sieves (4 Å, 2 g) as reported for **6**. Total reaction time 2 h.



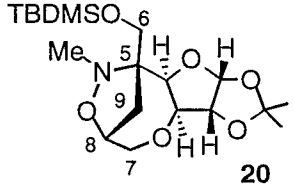
19

^{1}H NMR ($CDCl_3$, 300 MHz) δ : 6.02 (d, $J_{1\text{-}2}$ = 3.6 Hz, 1H, H1), 5.79 (m, J_{trans} = 17.2 Hz, J_{cis} = 10.3 Hz, J_{gem} = 5.6 Hz, 1H, -O-CH_2-C<u>H</u>=CH_2), 5.26-5.16 (m, 2H, -O-CH_2-CH=C<u>H</u>$_2$), 4.84 (d, $J_{3\text{-}4}$ = 3.6 Hz, 1H, H4),4.55 (d, $J_{1\text{-}2}$ = 3.6 Hz, 1H, H2), 4.54 (d, $J_{6\text{-}6'}$ = 19.0 Hz, 1H, H6), 4.46 (d, $J_{6\text{-}6'}$ = 19.0 Hz, 1H, H6'), 4.29 (d, $J_{3\text{-}4}$ = 3.6 Hz, 1H, H3), 4.04 (dd, J_{gem} = 12.8 Hz, J = 5.4 Hz, 1H, -O-C<u>H</u>$_2$-CH=CH_2), 3.94 (dd, J_{gem} = 12.8 Hz, J = 5.8 Hz, 1H, -O-C<u>H</u>$_2$-CH=CH_2), 1.47 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 0.92 (s, 9H, t-Bu), 0.08 (s, 3H, Si-CH_3), 0.06 (s, 3H, Si-CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 205.1 (C5), 133.5 (<u>C</u>H=CH_2), 118.1 (<u>C</u>(CH_3)$_2$), 112.3 (CH=<u>C</u>H$_2$), 105.7 (C1), 84.7, 83.2, 81.9 (C2, C3, C4), 71.3 (C6), 68.9 (-O-<u>C</u>H$_2$), 26.9, 26.3 ((<u>C</u>H$_3$)$_2$C-), 25.8 (<u>C</u>H$_3$-Si-), 18.4 ((CH$_3$)$_2$<u>C</u>-), -5.5, -5.4 (Si-CH_3). IR: 3470 (-OH), 2906 (=CH_2), 1738 (C=O), 1374 (-C(CH$_3$)$_3$), 1252, 845.

MS *m/z* (%): 357 (4, (M-CH_3)$^+$), 315, 257, 215, 199, 171 (100, (M-TBDMS)$^+$), 73 (45, (CH$_3$)$_4$C).

Cycloadduct 20. It was obtained (126 mg, 69%) from ketone **19** (169 mg, 0.45 mmol), MeNHOH.HCl (227 mg, 2.72 mmol), pyridine (146 μL, 1.81 mmol) and molecular sieves (100 mg) in EtOH (5 mL), following the procedure reported for **13**. Total reaction time 48 h. Mixtures of EtOAc-hexane of increasing polarity (15%, 20%, 50%, 70%) were used for the chromatography.



20

^{1}H NMR ($CDCl_3$, 500 MHz) δ : 5.82 (d, $J_{1\text{-}2}$ = 3.7 Hz, 1H, H1), 4.52 (m, 1H, H8), 4.37 (d, $J_{1\text{-}2}$ = 3.7 Hz, 1H, H2), 4.25 (br, s, 1H, H4), 4.13 (s, 1H, H3), 4.03 (d, $J_{6\text{-}6'}$ = 10.9 Hz, 1H, H6), 3.64 (d, $J_{6'\text{-}6}$ = 10.9 Hz, 1H, H6'), 3.57 (d, $J_{7\text{-}7'}$ = 12.6 Hz, 1H, H7), 3.52 (dd, $J_{7'\text{-}7}$ = 12.6 Hz, $J_{7'\text{-}8}$ = 2.5 Hz, 1H, H7'), 2.71 (s, 3H, N-CH_3), 2.35 (d, 1H, H9), 1.99 (m, 1H, H9'), 1.44 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 0.87 (s, 9H, C(CH$_3$)$_3$), 0.06 (s, 3H, CH_3), 0.06 (s, 3H, CH_3).

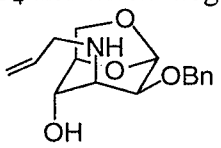
^{13}C NMR (C_6D_6, 125 MHz) δ : 111.5 (<u>C</u>(CH$_3$)$_2$), 104.5 (C1), 85.3 (C2), 82.9 (C4), 78.4 (C8), 77.7 (C3), 71.7 (C7), 71.0 (C5), 63.5 (C6), 40.2 (N-Me), 30.1 (C9), 27.0, 26.2 (CH_3, CH_3), 26.1 (C(<u>C</u>H$_3$)), 18.5 (<u>C</u>(CH$_3$)), -5.7, -5.2 (Si-CH_3, Si-CH_3).

MS *m/z* (%): 401 (17.86, M^+), 386 (10.05, $(M-H_2O)^+$), 344 (18.89, $(M-C_3H_5O)^+$), 286, 228, 213 (100), 172, 131 (19, $(M-OTBDMS)^+$), 84.

IR: 3416 (tertiary amine), 2930 (C-O-C), 2358, 1465 (CH_3-), 784 (Ph-) cm^{-1}.

ENTRY 6. TABLE 1:

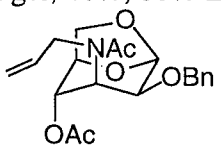
3-*N*-Allylamino-1,6-anhydro-2-*O*-benzyl-3-deoxy-β–D-mannopyranose. A solution of 1,6:3,4-dianhydro-2-*O*-benzyl-β-D-altropyranose (568 mg, 2.43 mmol) and allylamine (3.6 mL, 48.53 mmol) in 1 mL of DMF was heated in a sealed tube at 120 °C for 4 days. The solvent was evaporated *in vacuo* and the crude residue was partitioned between Et_2O and water. The organic extracts were dried over Na_2SO_4 and chromatographed to obtain the allylamine derivative (450 mg, 65%).



^1H NMR ($CDCl_3$, 300 MHz) δ : 7.4-7.27 (m, 5H, ArH), 5.84 (m, 1H, H8), 5.40 (s, 1H, H1), 5.24-5.0 (m, 2H, H9, H9'), 4.62 (d, $J_{6endo-5}$ = 7.0 Hz, 1H, H6endo), 4.55 (m, 2H, H10, H10), 4.43 (m, 1H, H5), 3.74-3.65 (m, 3H, H6exo, H4, H2), 3.29 (dd, 1H, H7), 3.12 (dd, 1H, H7).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 137.0 (C_{ipso}), 136.0 (C8), 128 (C_{meta}), 127 (C_{para}), 126 (C_{orto}), 115 (C9), 100 (C1), 76 (C5), 73, 70 (C2,C4), 71 (C10), 65 (C6), 59 (C3), 52 (C7).

4-*O*-Acetyl-3-(*N*-Acetyl-*N*-Allylamino)-1,6-anhydro-2-*O*-benzyl-3-deoxy-β–D-mannopyranose. A solution of 3-*N*-Allylamino-1,6-anhydro-2-*O*-benzyl-3-deoxy-β–D-mannopyranose (330 mg, 1.13 mmol), Et_3N (860 µL, 6.2 mmol), Ac_2O (530 µL, 5.6 mmol) and DMAP (14 mg, 0.11 mmol). in 1 mL of EtOAc was left for 3 days at rt. Removal of the solvent *in vacuo* and chromatography (silica gel, 40%, 80% EtOAc-hexane), gave the diacetyl derivative (398 mg, 91%).

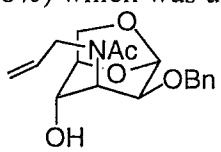


^1H NMR ($CDCl_3$, 300 MHz) δ : 7.37-7.25 (m, 5H, ArH), 5.67 (tdd, J_{trans} = 19.4 Hz, J_{cis} = 10.4 Hz, J_{vic} = 4.1 Hz, 1H, H8), 5.58 (m, $J_{1,2}$ = 5.0 Hz, 1H, H1), 5.13-5.03 (m, 3H, H9, H9', H4*), 4.67 (m, 2H, H3*, H6exo, H10), 4.45 (dd, J_{5-6exo} = 6.0 Hz, J = 1.6 Hz, 1H, H5), 4.34 (d, J_{gem} = 11.3 Hz, 1H, H10'), 4.12-3.88 (m, 5H, H6exo, H6endo, H2, H7, H7'), 2.06 (s, 3H, CH_3), 2.02 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 172.5 (-O-CO-CH_3), 170.9 (-N-CO-CH_3), 137.7 (C_{ipso}), 134.4 (C8), 128.5 (C_{meta}), 127.9 (C_{para}), 127.8 (C_{orto}), 115.3 (C9), 98.7 (C1), 76.7 (C5), 74.3, 73.7 (C2,C4), 72.9 (C10), 67.9 (C6), 50.2 (C3), 49.1 (C7), 22.0 (CH_3), 21.1 (CH_3).

IR: 3427, 2963, 1733 (-O-CO-CH_3), 1642 (-N-CO-CH_3), 1394, 1109, 1027 cm^{-1}.

3-(*N*-Acetyl-*N*-Allylamino)-1,6-anhydro-2-*O*-benzyl-3-deoxy-β–D-mannopyranose. K_2CO_3 (14 mg, 0.1 mmol) was added to a solution of 4-*O*-acetyl-3-(*N*-Acetyl-*N*-Allylamino)-1,6-anhydro-2-*O*-benzyl-3-deoxy-β–D-mannopyranose (35 mg, 0.09 mmol) in methanol (0.5 mL). After 45 min, the solvent was removed *in vacuo* and the crude residue was partitioned between water and CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to give the desired C4-alcohol derivative (30 mg, 98%) which was used without further purification.

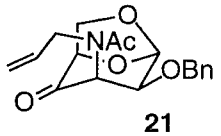


^1H NMR ($CDCl_3$, 300 MHz) δ : 7.31-7.26 (m, 5H, ArH), 5.88 (m, 1H, H8), 5.57 (d, J = 4.52 Hz 1H, H1), 5.14 (m, 2H, H9, H9'), 4.83 (m, 1H, H3), 4.63 (d, J_{gem} = 11.1 Hz, 1H, H10), 4.58 (d, J = 5.9 Hz, 1H, H5), 4.32 (d, J = 11.1 Hz, 1H, H10'), 4.15 (dd, J = 8.6 Hz, J = 2.4 Hz, 1H, H7), 3.98 (m, 2H, H2, H7'), 3.90-3.77 (m, 3H, H6endo, H6exo, OH), 3.73 (m, 1H, H4), 2.08 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 173.3 (-N-CO-CH_3), 137.9 (C_{ipso}), 135.4 (C8), 128.3 (C_{meta}), 127.7 (C_{para}), 127.7 (C_{orto}), 115.9 (C9), 98.7 (C1), 79.3 (C5), 74.5 (C4*), 72.8 (C10), 72.2 (C2*), 68.2 (C6), 54.5 (C3), 49.5 (C7), 22.2 (CH_3).

IR: 3417 (-OH), 2970, 2929, 1627 (-N-CO-) cm^{-1}.

3-(*N*-Acetyl-*N*-Allylamino)-1,6-anhydro-2-*O*-benzyl-3-keto-β–D-lyxopyranose (21). It was obtained from 3-(*N*-acetyl-*N*-Allylamino)-1,6-anhydro-2-*O*-benzyl-3-deoxy-β–D-mannopyranose (112 mg, 0.34 mmol), PCC (290 mg, 1.35 mmol) and molecular sieves (170 mg) as described for **6**. Final chromatography (silica gel, 50% ---> 70% EtOAc-hexane) gave ketone **21** (60 mg, 55%).



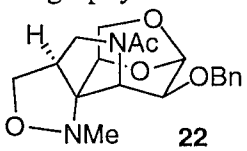
21

^{1}H NMR ($CDCl_3$, 300 MHz) δ : 7.40-7.29 (m, 5H, ArH), 5.76 (tdd, J_{trans} = 17.1 Hz, J_{cis} = 10.3 Hz, J_{vic} = 4.7 Hz, 1H, H8), 5.63 (d, $J_{1,2}$ = 1.8 Hz, 1H, H1), 5.33 (dd, J_{trans} = 17.1 Hz, J_{gem} = 1.3 Hz, 1H, H9), 5.18 (dd, J_{cis} = 10.3 Hz, J_{gem} = 1.3 Hz, 1H, H9'), 4.70 (d, J_{gem} = 11.9 Hz, 1H, H10), 4.64 (dd, $J_{5\text{-}6exo}$ = 4.0 Hz, J = 2.0 Hz, 1H, H5), 4.55 (d, J_{gem} = 11.9 Hz, 1H, H10'), 4.21 (d, $J_{6endo\text{-}6exo}$ = 8.1 Hz, 1H, H6endo), 4.0-3.89 (m, 4H, H2, H3, H7, H6exo), 3.73 (dd, J_{gem} = 17.1 Hz, $J_{7'\text{-}8}$ = 6.2 Hz, 1H, H7'), 1.98 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 197.0 (C4), (C=O), 137.5 (C_{ipso}), 132.7 (C8), 128.6 (C_{meta}), 128.2 (C_{para}), 128.2 (C_{orto}), 118.0 (C9), 100.1 (C1), 81.9 (C5), 78.5 (C2), 72.8 (C10), 67.6 (C6), 65.2 (C3), 53.7 (C7), 21.3 (CH_3).

IR: 3417, 2970, 2929, 1627 (-N-CO-) cm^{-1}.

Cycloadduct 22. It was obtained (43 mg, 52%) from ketone **21** (77 mg, 0.23 mmol), MeNHOH.HCl (388 mg, 4.63 mmol), pyridine (241 μL, 2.99 mmol) and molecular sieves (50 mg) in EtOH (0.7 mL), following the procedure reported for **13**. Total reaction time 15 h at room temperature and 15 h at 60°C. Mixtures of EtOAc-hexane of increasing polarity (25%, 50%, 70%), were used for chromatography.



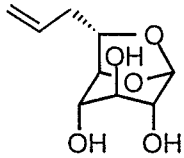
22

^{1}H NMR ($CDCl_3$, 300 MHz) δ : 7.36-7.27 (m, 5H, ArH), 5.39 (d, $J_{1\text{-}2}$ = 1.6 Hz, 1H, H1), 4.65 (d, J = 11.5 Hz, 1H, H10), 4.53 (d, J = 11.5 Hz, 1H, H10'), 4.25 (d, $J_{5\text{-}6exo}$ = 4.7 Hz, 1H, H5), 4.17 (dd, J_{gem} = 8.9 Hz, $J_{9\text{-}8}$ = 7.5 Hz, 1H, H9), 4.08 (d, J_{gem} = 8.1 Hz, 1H, H6endo), 4.02 (d, $J_{3\text{-}2}$ = 7.1 Hz, 1H, H3), 3.89 (dd, J_{gem} = 8.9 Hz, $J_{9'\text{-}8}$ = 4.6 Hz, 1H, H9'), 3.80 (dd, J_{gem} = 8.1 Hz, $J_{6exo\text{-}5}$ = 4.7 Hz, 1H, H6exo), 3.75 (dd, J_{gem} = 13.0 Hz, $J_{7\text{-}8}$ = 4.3 Hz, 1H, H7), 3.46 (dd, J_{gem} = 13.0 Hz, $J_{7'\text{-}8}$=9.5, 1H, H7'), 3.34 (dd, $J_{2\text{-}3}$ = 7.1 Hz, $J_{2\text{-}1}$ = 1.6 Hz, 1H, H2), 3.25 (m, 1H, H8), 2.59 (s, 3H, -N-C$\underline{H}_3$), 2.14 (s, 3H, -CO-C$\underline{H}_3$).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 168.7 (CO), 136.6 (C_{ipso}), 128.6 (C_{meta}), 128.3 (C_{para}), 128.2 (C_{orto}), 98.1 (C1), 80.8 (C2), 78.1 (C4), 75.8 (C5), 72.9 (C9#), 72.7 (C10#), 68.1 (C6), 60.2 (C8), 49.1 (C7), 47.9 (C3), 38.6 (-N-$\underline{C}H_3$), 22.2 (-CO-$\underline{C}H_3$).

ENTRY 7, TABLE 1.-

(6*S*)-1,6-Anhydro-6-(2-propenyl)-β-D-glucopyranose. A solution of (6*S*)-1,6-anhydro-2,3,4-tri-*O*-acetyl-6-(2-propenyl)-β-D-glucopyranose (700 mg, 2.13 mmol), and triethylamine (2.1 mL, 14.92 mmol, 700 mol%) in 5 mL of methanol was heated at 50°C for 24 h. Removal of the solvent and chromatographic purification through silica gel, (MeOH:CH_2Cl_2, 10:90), afforded the desired triol (391 mg, 91% yield) as a white solid.



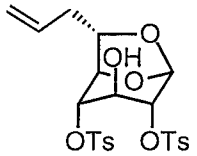
^{1}H NMR (CD_3OD, 250 MHz) δ : 5.86 (m, 1H, H8), 5.36 (s, 1H, H1), 5.18-5.10 (m, 2H, H9), 4.31 (t, $J_{6\text{-}7}$ = 6.7 Hz, 1H, H6), 4.18 (s, 1H, H5), 3.66, 3.51 and 3.37 (m each, 3H, H2, H3, H4) and 2.29 (m, 2H, H7).

^{13}C NMR (CD_3OD, 75 MHz) δ : 135.3 (C8), 117.9 (C9), 104.4 (C1), 81.3 (C6), 76.8 (C5), 75.0, 73.0 and 72.5 (C2, C3, C4), and 40.5 (C7).

MS *m/z* (%): 184 (1.6, $(M\text{-}H_2O)^+$), 167 (2.3, $(M\text{-}H_2O\text{-}OH)^+$), 161 (5.3, $(M\text{-}CH_2\text{-}CH\text{-}CH_2)^+$), 149 (9.5), 129 (12.8), 101 (16.5), 97 (28.0), 73 (100.0), 71 (27.3).

IR (film): 3600-3050 (strong, broad, OH), 1641 (sharp, strong, C=C) cm^{-1}.

(6*S*)-1,6-Anhydro-6-(2-propenyl)-2,4-*O*-paratoluensulphonyl-β-D-glucopyranose. A solution of (6*S*)-1,6-anhydro-6-(2-propenyl)-β-D-glucopyranose (380 mg, 1.88 mmol) in 4 mL of a 1:1 mixture of dry pyridine and dry acetone was treated with TsCl (860 mg, 4.51 mmol, 240 mol%) and *N,N'*-dimethylaminopyridine (69 mg, 0.56 mmol, 30 mol%). After three days at rt the mixture was diluted with ethyl ether and washed with a 5% aqueous solution of $CuSO_4$ and finally with water. The organic layer was dried with sodium sulfate, filtered and concentrated *in vacuo*. Purification of the residue by flash chromatography through silica gel (MeOH:CH_2Cl_2, 1:99--->2:98) afforded the ditosylated compound (652 mg, 68% yield) as a white solid and some of the tritosylated compound (137 mg, 12% yield).



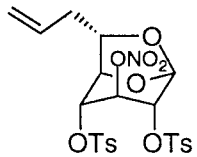
^{1}H NMR ($CDCl_3$, 300 MHz) δ : 7.79 (m, 4H, ArH), 7.35 (m, 4H, ArH), 5.64 (m, 1H, H8), 5.35 (s, 1H, H1), 5.08-5.02 (m, 2H, H9), 4.34 (d, J = 2.9 Hz, 1H, H4), 4.27 (s, 1H, H2), 4.14 (m, 2H, H5, H6), 3.94 (m, 1H, H3), 2.81 (d, J_{OH-3} = 5.3 Hz, 1H, OH), 2.45 (s, 3H, CH_3-Ar), 2.45 (s, 3H, CH_3-Ar), and 2.28-2.07 (m, 2H, H7).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 145.5 and 145.4 (Ar, C_{ipso}), 133.1 and 132.8 (Ar, C_{para}), 132.5 (C8), 130.0 (2C, Ar, C_{meta}), 127.94 and 127.89 (Ar, C_{orto}), 118.5 (C9), 100.4 (C1), 79.1, 78.0, 77.7 and 76.8 (C2, C4, C5, C6), 69.7 (C3), 38.5 (C7), and 21.7 (CH_3-Ar).

MS *m/z* (%): 469 (0.01, (M-CH_2-CH-CH_2)$^+$), 335 (9.1, (M-OTs)$^+$), 309 (4.1), 251 (2.8), 155 (60.7, (TsO)$^+$), 109 (20.9), 91 (100 (Ph-CH_3)$^+$).

IR (film): 3508 (medium, broad, OH) cm^{-1}.

(6*S*)-1,6-Anhydro-3-*O*-nitro-6-(2-propenyl)-2,4-*O*-paratoluensulphonyl-β-D-glucopyranose. Fuming nitric acid (0.52 mL, 8.16 mmol, 300 mol%) was added over 2 mL of acetic anhydride at 0°C. After 15 min, the nitrating mixture was added dropwise into a solution of (6*S*)-1,6-anhydro-6-(2-propenyl)-2,4-*O*-paratoluensulphonyl-β-D-glucopyranose (1390 mg, 2.72 mmol) in 9.3 mL of acetic anhydride, also kept at 0°C. After consumption of the starting material a cold saturated $NaHCO_3$ aqueous solution was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate and the organic extracts were washed with brine, dried over sodium sulfate, filtered and concentrated. Purification of the residual oil by flash chromatography, (EtOAc:Hexane, 25:75), afforded the nitrated as a white solid (1359 mg, 90% yield).

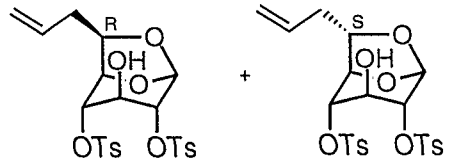


^{1}H NMR ($CDCl_3$, 300 MHz) δ : 7.75 (m, 4H, ArH), 7.35 (m, 4H, ArH), 5.66 (m, 1H, H8), 5.44 (s, 1H, H1), 5.13-5.01 (m, 3H, H9, H3), 4.35 (m, 2H, H2, H4), 4.16 (m, 1H, H5). 4.07 (t, J_{6-7} = 6.7 Hz, 1H, H6), 2.46 (s, CH_3-Ar), 2.45 (s, CH_3-Ar) and 2.33-2.06 (m, 2H, H7).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 145.8 (2C, Ar, Ci_{pso}), 132.7 and 132.4 (Ar, C_{para}), 132.1 (C8), 130.2 and 130.1 (Ar, C_{meta}), 127.9 and 127.8 (Ar, C_{orto}), 118.9 (C9), 99.9 (C1), 77.4 (C3), 76.8 and 76.6 (C4, C2), 74.8 and 73.7 (C5, C6), 38.4 (C7), and 21.7 (2C, CH_3-Ar).

MS *m/z* (%): 400 (7.9, (M-Ts)$^+$), 355 (3.2, (M-Ts-NO_2+H)$^+$), 325 (5.8), 297 (3.6), 227 (9.3), 183 (2.9, (M-2Ts-ONO_2)$^+$), 155 (97.4, Ts$^+$), 91 (100.0, (Ph-CH_3)$^+$).

(6*R*) and (6*S*)-1,6-Anhydro-6-(2-propenyl)-2,4-*O*-paratoluensulphonyl-β-D-glucopyranose. To a refluxing solution of (6*S*)-1,6-Anhydro-3-*O*-nitro-6-(2-propenyl)-2,4-*O*-paratoluensulphonyl-β-D-glucopyranose (970 mg, 1.75 mmol), in 75 mL of degassed benzene, a mixture of *n*-Bu_3SnH (4.5 mL, 26.59 mmol, 950 mol%) and AIBN (482 mg, 2.9 mmol, 165 mol%) in 13 mL of benzene, was slowly added (syringe pump, 5 h). Removal of the solvent, followed by flash chromatography on silica gel (EtOAc:Hexane, 30-70), afforded two compounds: the C6*R* (544 mg, 61% yield) and the C6*S* (271 mg, 30% yield) allylic derivatives.

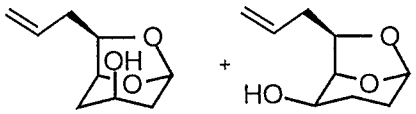


^{1}H NMR ($CDCl_3$, 300 MHz) δ : 7.79 (m, 4H, ArH), 7.35 (m, 4H, ArH), 5.71 (m, 1H, H8), 5.27 (s, 1H, H1), 5.17-5.08 (m, 2H, H9), 4.48 (m, 2H, H2, H4), 4.11 (m, 1H, H5), 3.92-3.85 (m, 2H, H6, H3), 2.85 (d, J_{OH-3} = 2.3 Hz, 1H, OH), 2.45 (s, 6H, CH_3-Ar), and 2.45-2.39 (m, 2H, H7).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 145.5 (2C, Ar, C_{ipso}), 132.7 (C8), 132.6 (2C, Ar, C_{para}), 130.0 y 129.97 (Ar, C_{meta}), 128.0 (2C, Ar, C_{orto}), 118.3 (C9), 100.5 (C1), 81.1, 77.75, 77.71 and 77.4 (C2, C4, C5, C6), 70.6 (C3), 33.5 (C7) and 21.7 ($\underline{C}H_3$-Ar).

IR (film): 3516 (strong, broad, OH) cm^{-1}.

(6*R*)-1,6-Anhydro-2,4-dideoxy-6-(2-propenyl)-β-D-*threo*-hexopyranose and (6*R*)-1,6-anhydro-2,3-dideoxy-6-(2-propenyl)-β-D-*threo*-hexopyranose. To a solution of (6*R*)-1,6-anhydro-6-(2-propenyl)-2,4-*O*-paratoluensulphonyl-β-D-glucopyranose (275 mg, 0.54 mmol), in 2.4 mL of dry THF, kept under argon at 0°C, lithium triethylborohydride (3.2 mL, 3.23 mol, 600 mol%) was slowly added *via* syringe. The reaction was maintained at 5°C for 12 h and at rt. for 24 h. After this period the mixture was cooled to 0°C, and treated cautiously with water (1.5 mL), followed by a mixture of hydrogen peroxide (1.44 mL of a 30% aqueous solution) and sodium hydroxide (1.84 mL of a 3M aqueous solution). After 1.5 h at rt the mixture was saturated with sodium chloride and the pH was adjusted to 10 by adding solid potassium carbonate. The mixture was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic extracts were dried with sodium sulfate, filtered and evaporated *in vacuo*. Purification of the residue by flash chromatography through silica gel (EtOAc:Hexane, 22-78), afforded the C3 alcohol derivative (51 mg, 55% yield) and its regioisomer at C4 (24 mg, 26% yield).



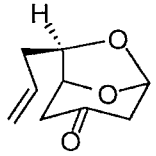
^{1}H NMR ($CDCl_3$, 300 MHz) δ : 5.79 (m, 1H, H8), 5.56 (d, J_{1-2} = 0.9 Hz, 1H, H1), 5.21-5.06 (m, 2H, H9), 4.26 (m, 1H, H5), 4.01 (dt, J_{6-5} = 3.5 Hz, J_{6-7} = 7.5 Hz, 1H, H6), 3.96 (m, 1H, H3), 2.87 (d, J_{OH-3} = 9.4 Hz, 1H, OH), 2.78 (m, 1H, H7), 2.60 (m, 1H, H7), 2.16 (m, 1H, $H4_{ax}$), 2.06 (m, 1H, $H2_{ax}$), 2.05-1.96 (m, 1H, $H2_{eq}$) and 1.92-1.84 (m, 1H, $H4_{eq}$).

^{13}C NMR ($CDCl_3$, 75 MHz) δ : 133.5 (C8), 117.4 (C9), 101.1 (C1), 79.2 (C6), 74.3 (C5), 63.1 (C3), 39.3 (C7), 34.4 and 32.4 (C2, C4).

MS *m/z* (%): 171 (0.1, $(M+1)^+$), 170 (0.2, M^+), 152 (9.26, $(M-H_2O)^+$), 139 (6.6), 129 (43.5, $(M-CH_2-CH-CH_2)^+$), 100 (100.0), 83 (90.8).

IR (film): 3439 (strong, broad, OH) cm^{-1}.

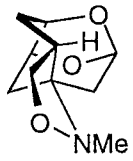
Ketone 23. To a solution of (6*R*)-1,6-anhydro-2,4-dideoxy-6-(2-propenyl)-β-D-*threo*-hexopyranose (50 mg, 0.29 mmol), in 2.5 mL of dry acetonitrile kept under argon at rt, Dess-Martin reagent (186 mg, 0.44 mmol, 150 mol%) and *t*-butanol (31 μL, 0.34 mmol, 115 mol%) were added. After 30 min, the reaction was diluted with ethyl ether, washed with a 1:1 mixture of saturated aqueous solutions of $NaHCO_3$ and $Na_2S_2O_3$ and finally with brine. The organic layer was dried with sodium sulfate, filtered and concentrated *in vacuo*. Ketone **23** was used in the next step without further purification.



23

^{1}H NMR ($CDCl_3$, 250 MHz) δ : 5.80-5.64 (m, 1H, H8), 5.75 (s, 1H, H5), 4.10 (m, 1H, H6), 2.70-2.50 (m, 4H, H2, H4), 2.44-2.35 (m, 1H, H7) and 2.19-2.08 (m, 1H, H7).

Isoxazolidine 24. To a solution of the ketone **23** (43 mg, 0.25 mmol) in 2.3 mL of dry CH_2Cl_2, MeNHOH.HCl (43 mg, 0.5 mmol, 200 mol%), and dry pyridine (41 μL, 0.5 mmol, 200 mol%) were added. After refluxing for 2 h additional amounts of MeNHOH.HCl (86 mg) and pyridine (82 mL) were needed to consume all the starting material. Then brine was added, and the aqueous layer was extracted with CH_2Cl_2. The organic extracts were dried with sodium sulfate, filtered and concentrated. Flash chromatography through silica gel (MeOH:CH_2Cl_2, 3:97) afforded the isoxazolidine **24** (25 mg, 49% yield) as a pale yellow oil.



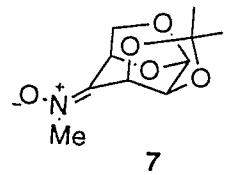
24

^{1}H NMR (C_6D_6, 500 MHz, 50°C) δ : 5.44 (s, 1H, H1), 4.18 (m, 1H, H5), 4.01 (m, 1H, H6), 3.96 (dd, $J_{9\text{-}9'}$ = 7.6 Hz, $J_{9\text{-}8}$ = 9.3 Hz, 1H, H9), 3.28 (dd, $J_{9'\text{-}9}$ = 7.6 Hz, $J_{9'\text{-}8}$ = 6.1 Hz, 1H, H9'), 2.61 (m, 1H, H8), 2.34 (s, 3H, CH_3-N), 2.04 (m, 1H, H7), 1.66-1.60 (m, 2H, H2, H4), 1.50 (d, $J_{4\text{-}4'}$ = 13.3 Hz, 1H, H4'), 1.36 (d, $J_{2\text{-}2'}$ = 12.6 Hz, 1H, H2'), 0.75 (dd, $J_{7'\text{-}7}$ = 9.4 Hz, $J_{7'\text{-}8}$ = 3.8 Hz, 1H, H7').

^{13}C NMR (C_6D_6, 125 MHz, 50°C) δ : 100.8 (C1), 73.8 (C5), 73.4 (C6), 71.1 (C9), 63.5 (C3), 44.9 (C8), 41.0 (C2), 36.9 ($\underline{C}H_3$-N), 30.1 (C4) and 28.7 (C7).

MS *m/z* (%): 198 (12.5, $(M+1)^+$), 197 (100.0, M^+), 196 (47.5, $(M-H)^+$), 182 (25.7, $(M-CH_3)^+$), 168 ($(M-CH_3-N)^+$), 152 (19.1, $(M-CH_3NO)^+$), 126 (10.7), 121 (15.3), 110 (17.4), 105 (14.9), 98 (18.6), 83 (23.4).

IR (film): 2952, 2876, 1646, 1459, 1441, 1314, 1118, 1093, 896 cm^{-1}.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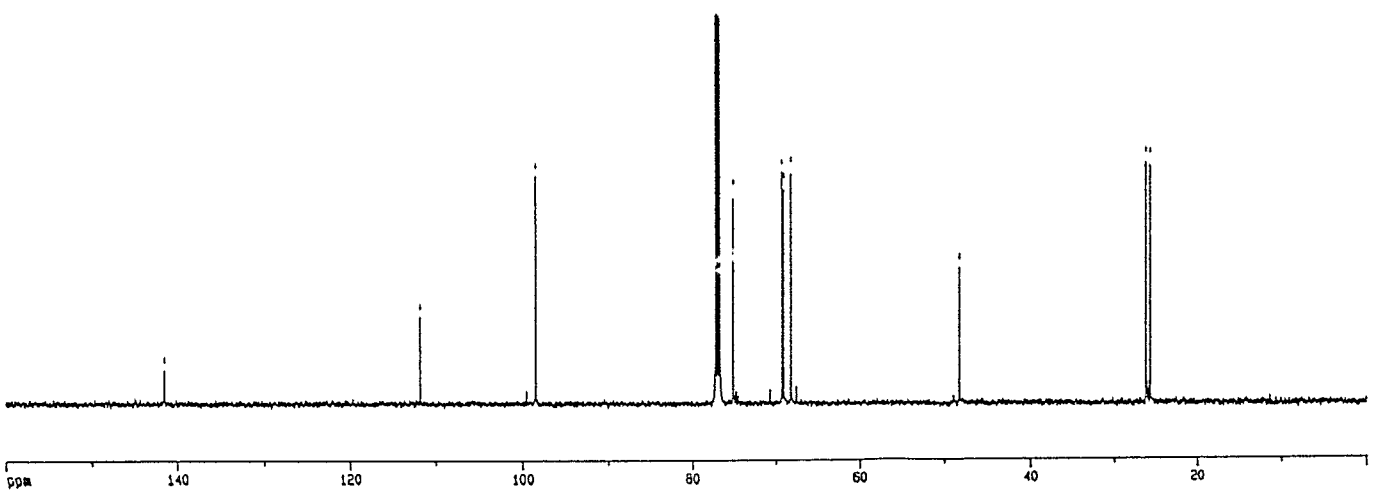
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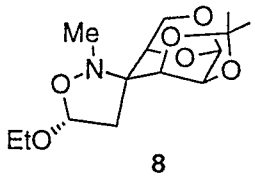
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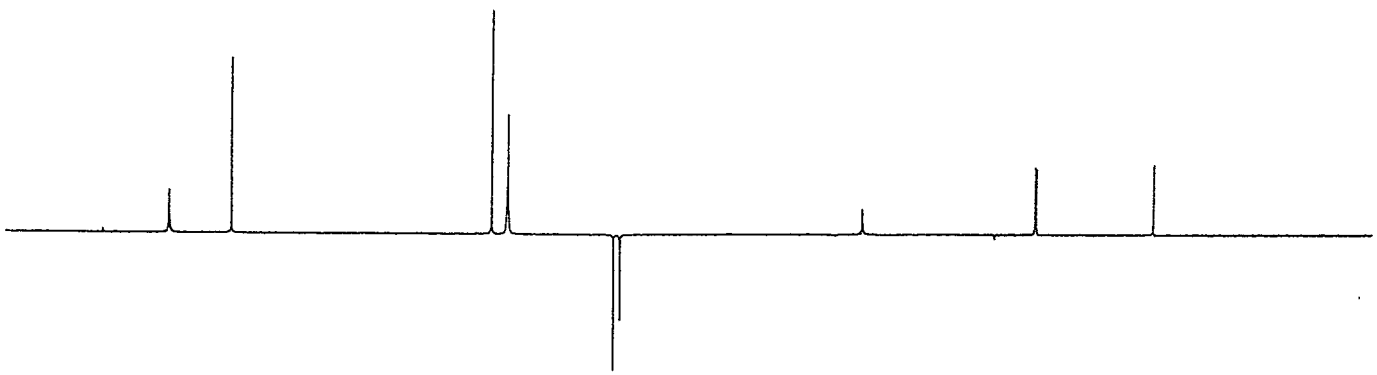

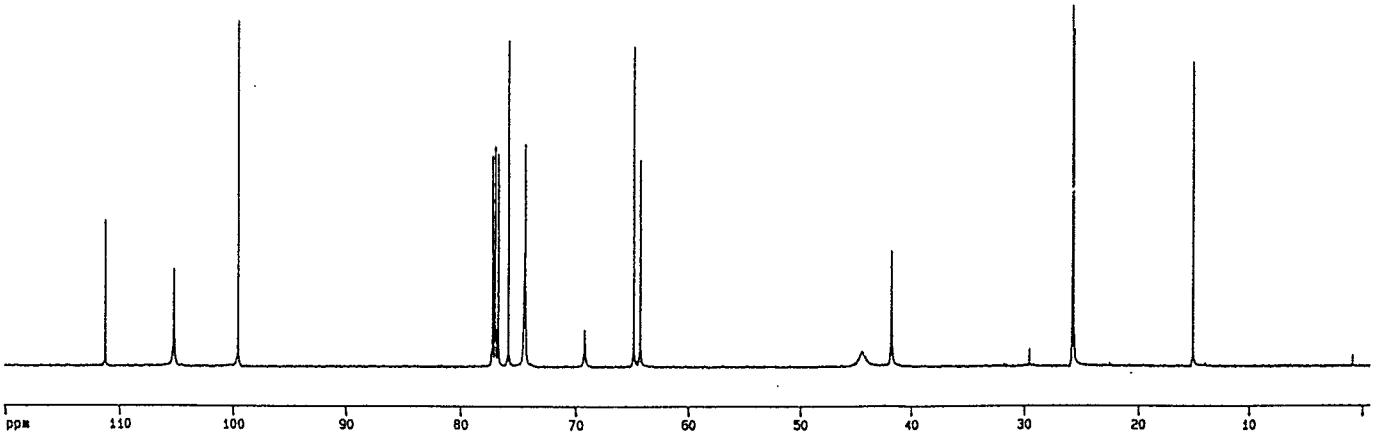
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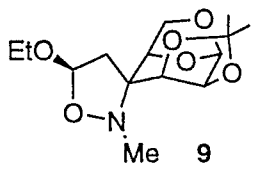
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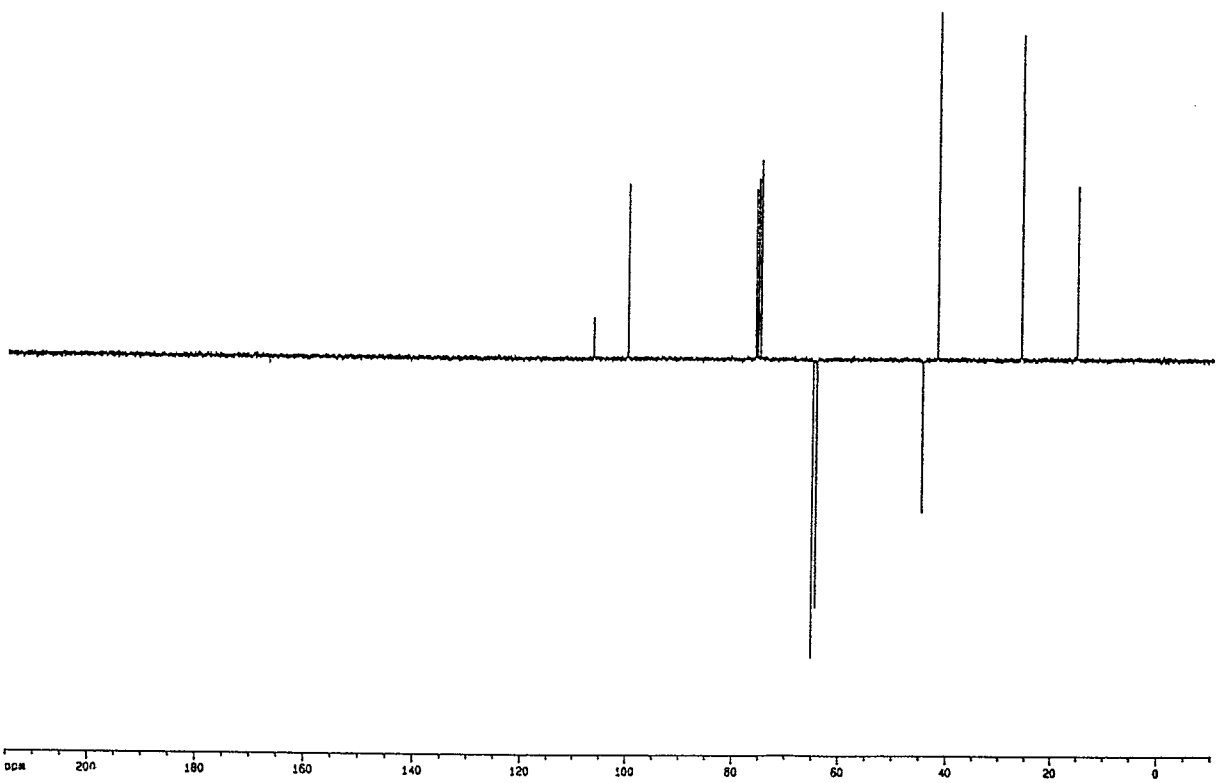
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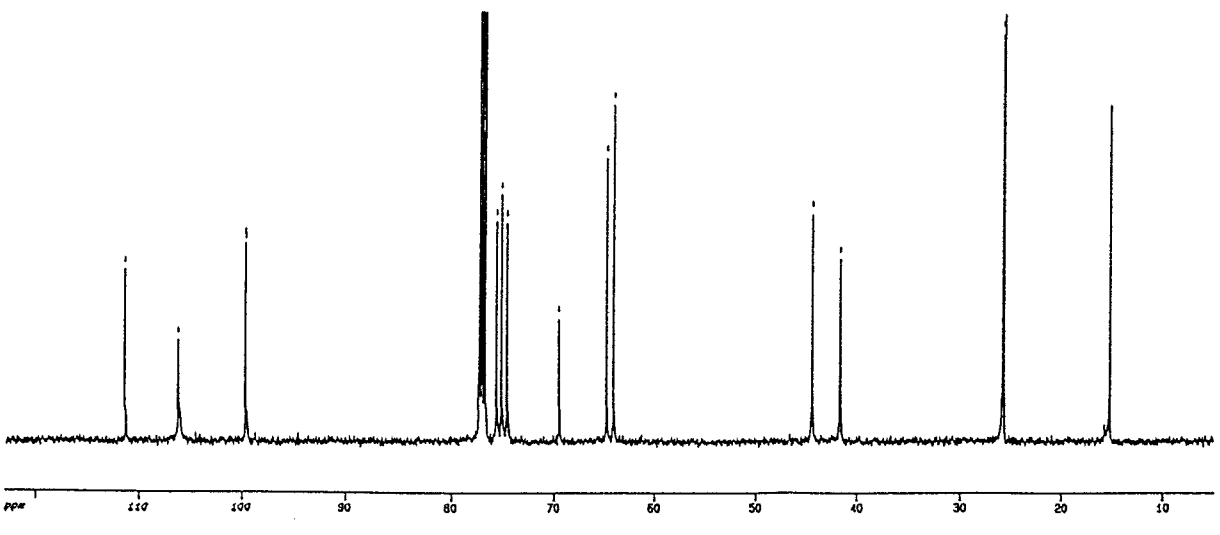
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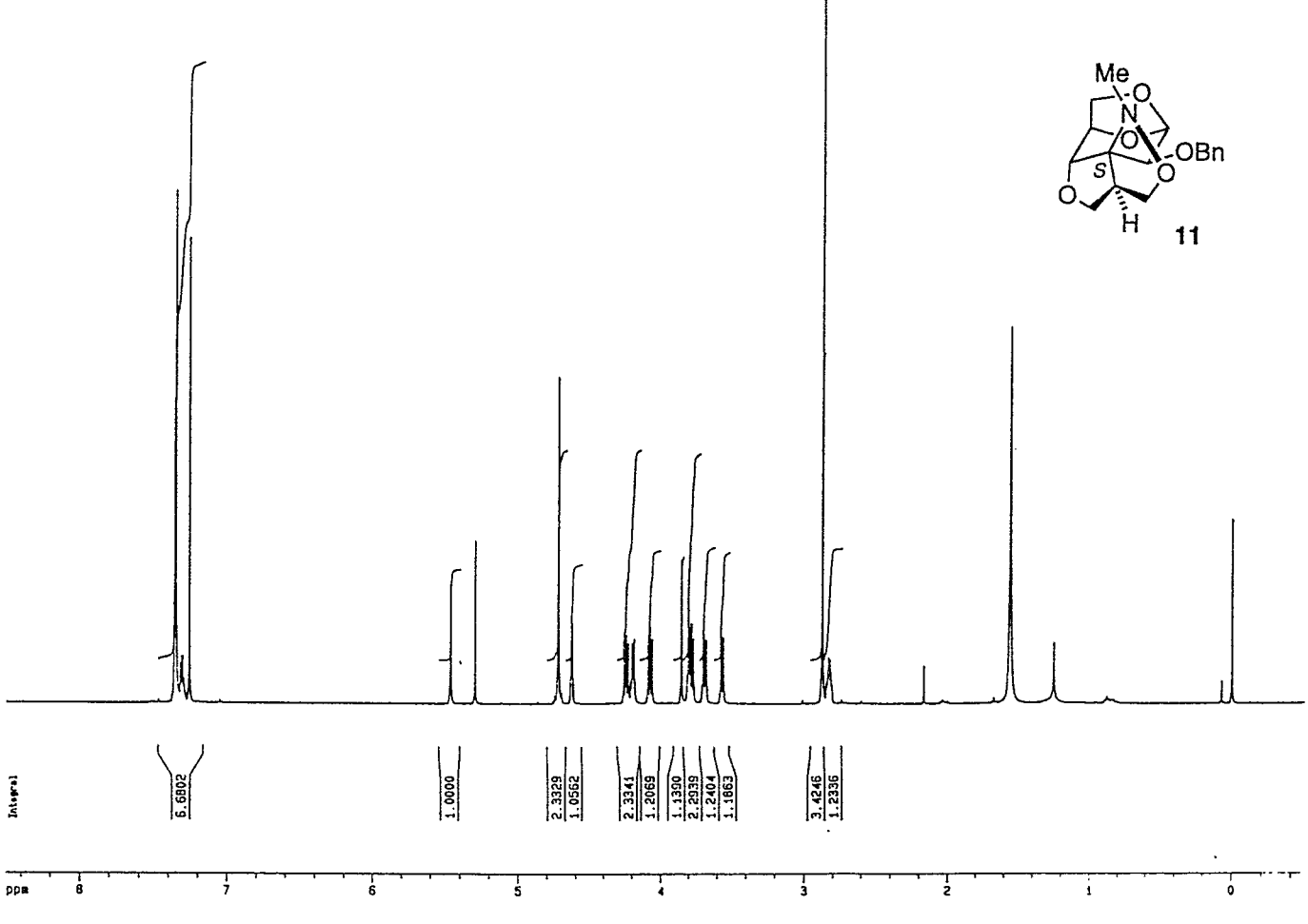
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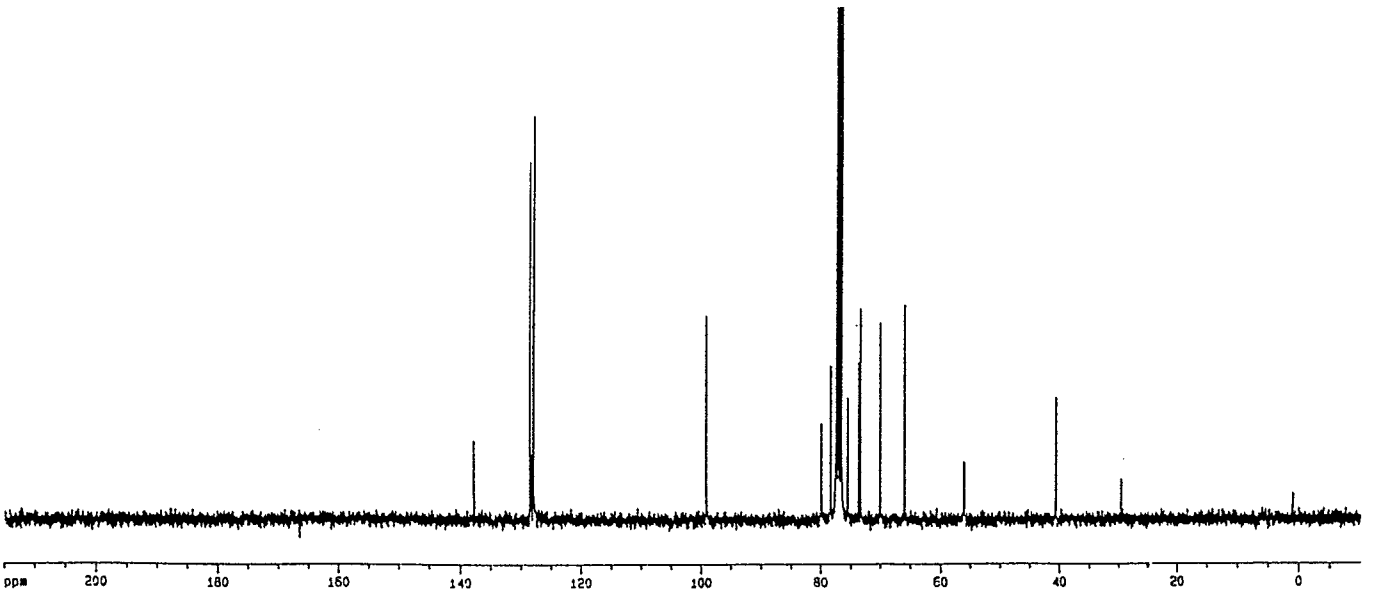
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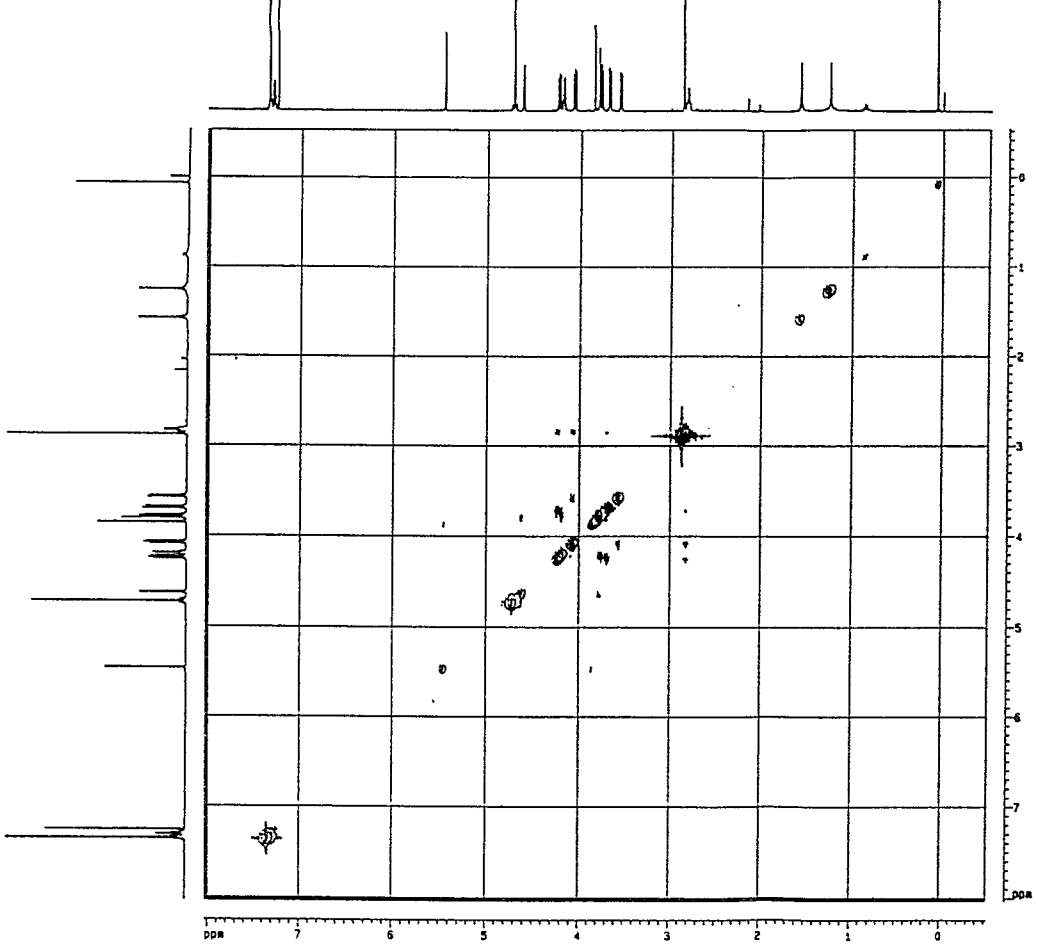
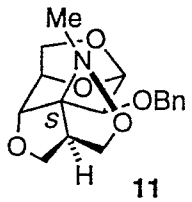
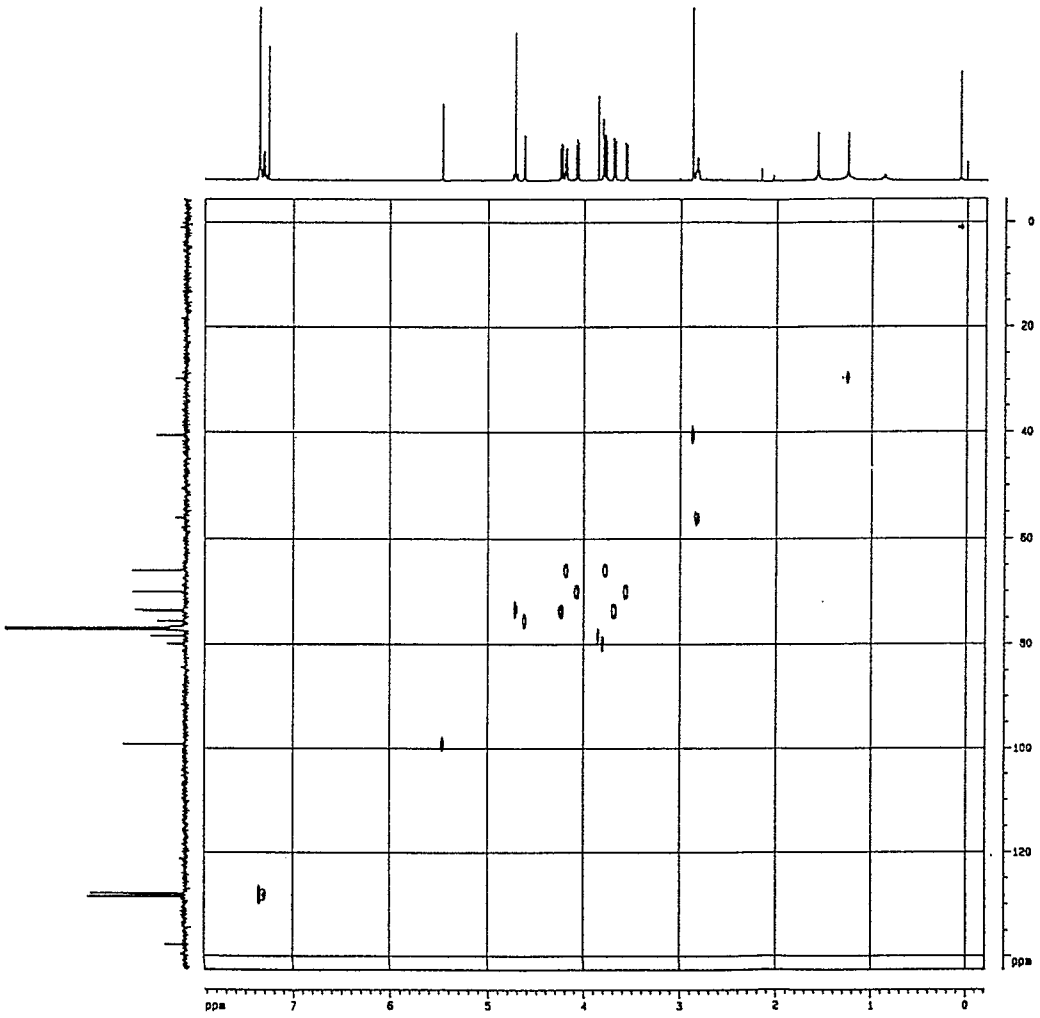


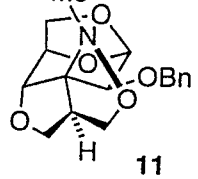


11

COSY



CORREL. C - H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11

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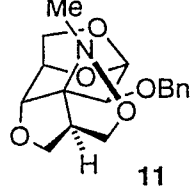

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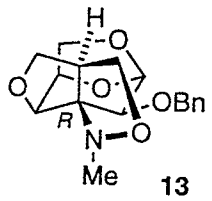
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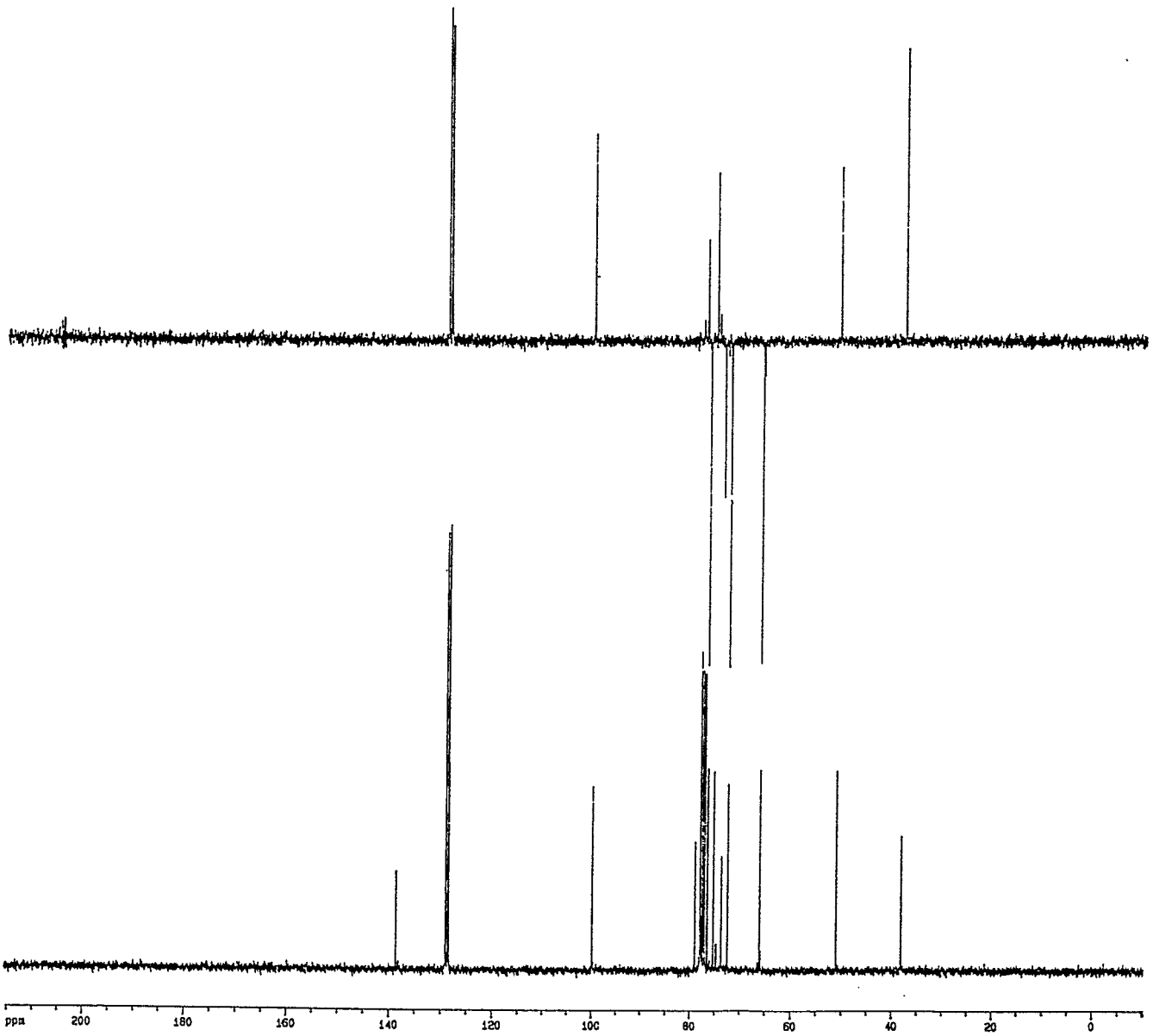
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20
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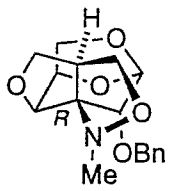
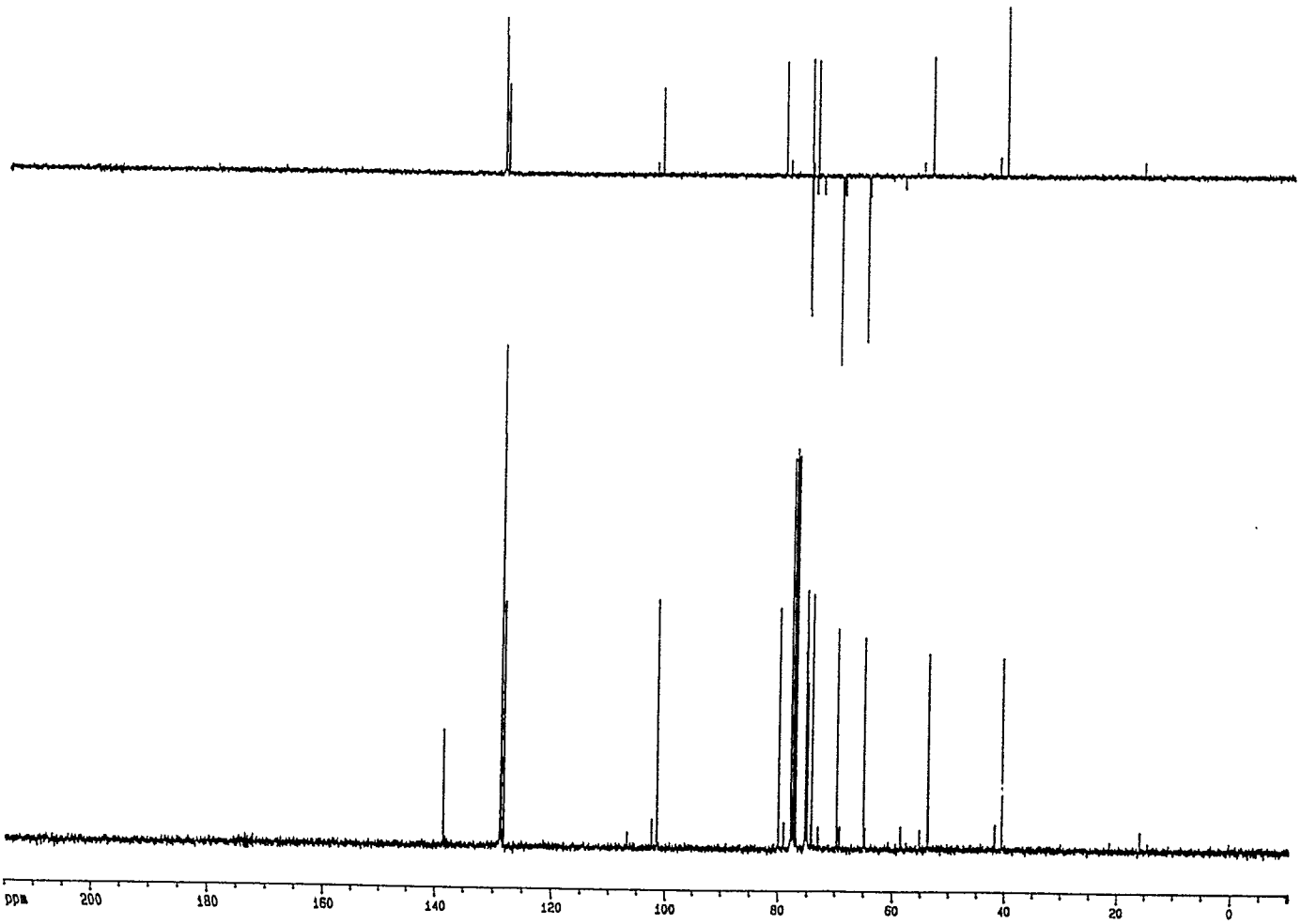
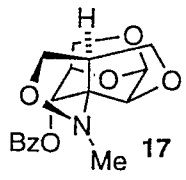

H
O
O
O
R
N
OBn
Me

15

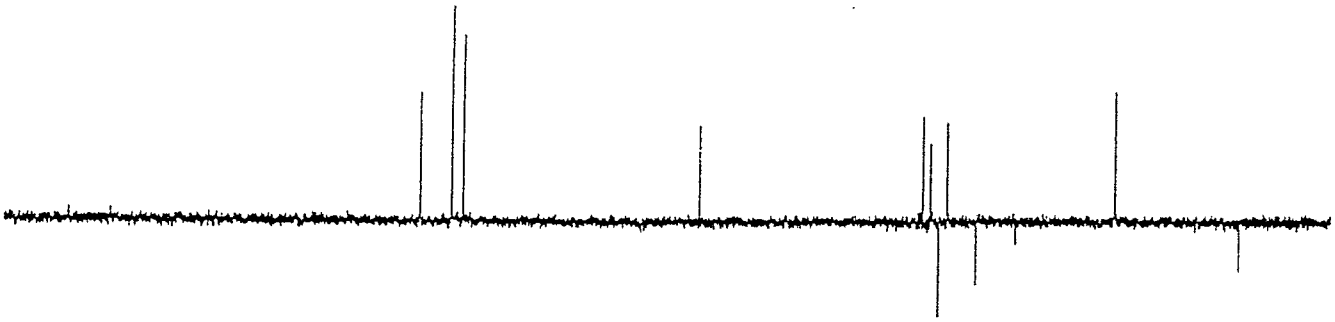
Integral
11.756
2.168
1.984
0.230
2.309
2.265
2.023
2.038
0.457
2.506
2.212
2.690
4.434
2.297
2.904
6.019
0.381
0.818
1.536
ppm
8
7
6
5
4
3
2
1
0

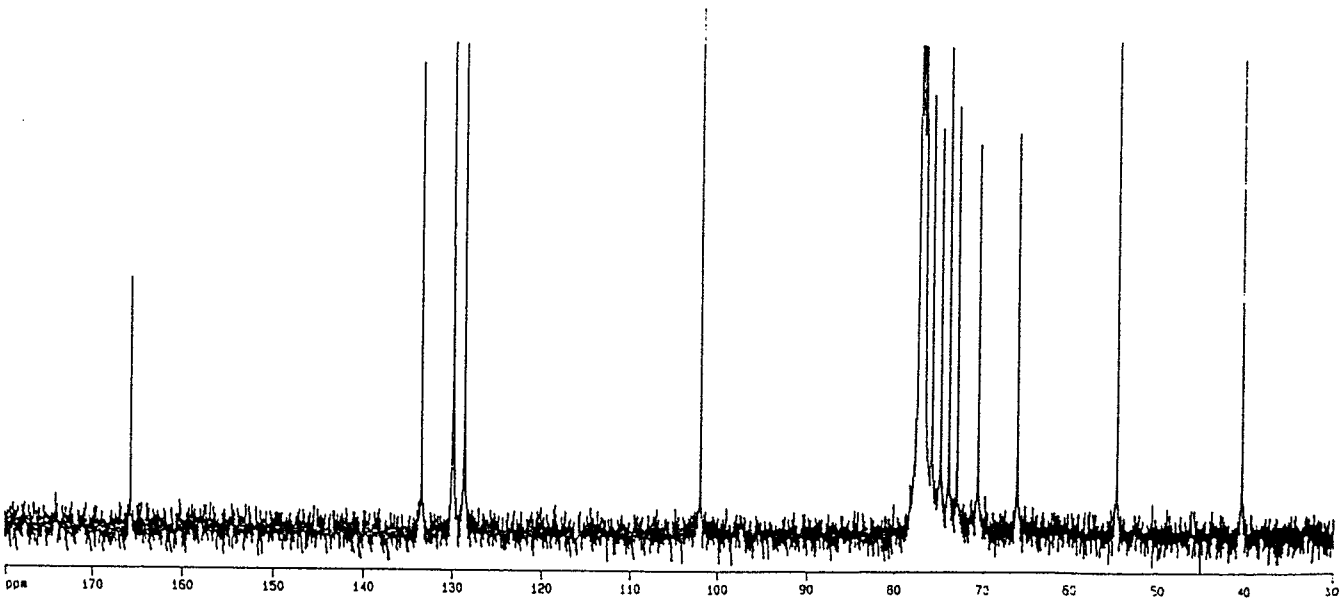

ppm
200
180
160
140
120
100
80
60
40
20
0

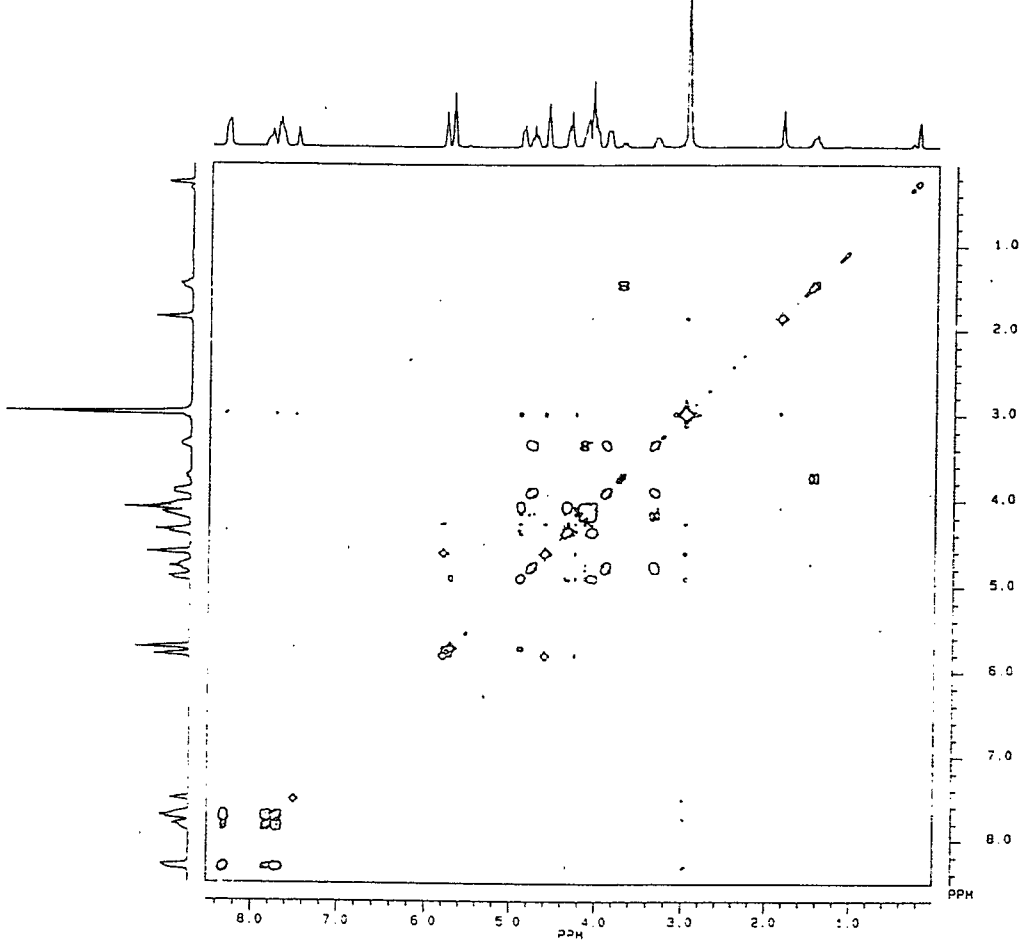

H
O
O
O
O
N
BzO
Me

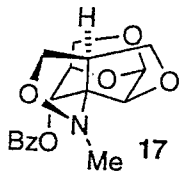
17

Integral
1.0603
0.5764
1.1237
0.5564
0.5560
0.5756
0.5971
0.5931
0.6081
0.5638
1.1372
0.5856
0.5589
1.5941
0.3135
ppm
8
7
6
5
4
3
2
1
0



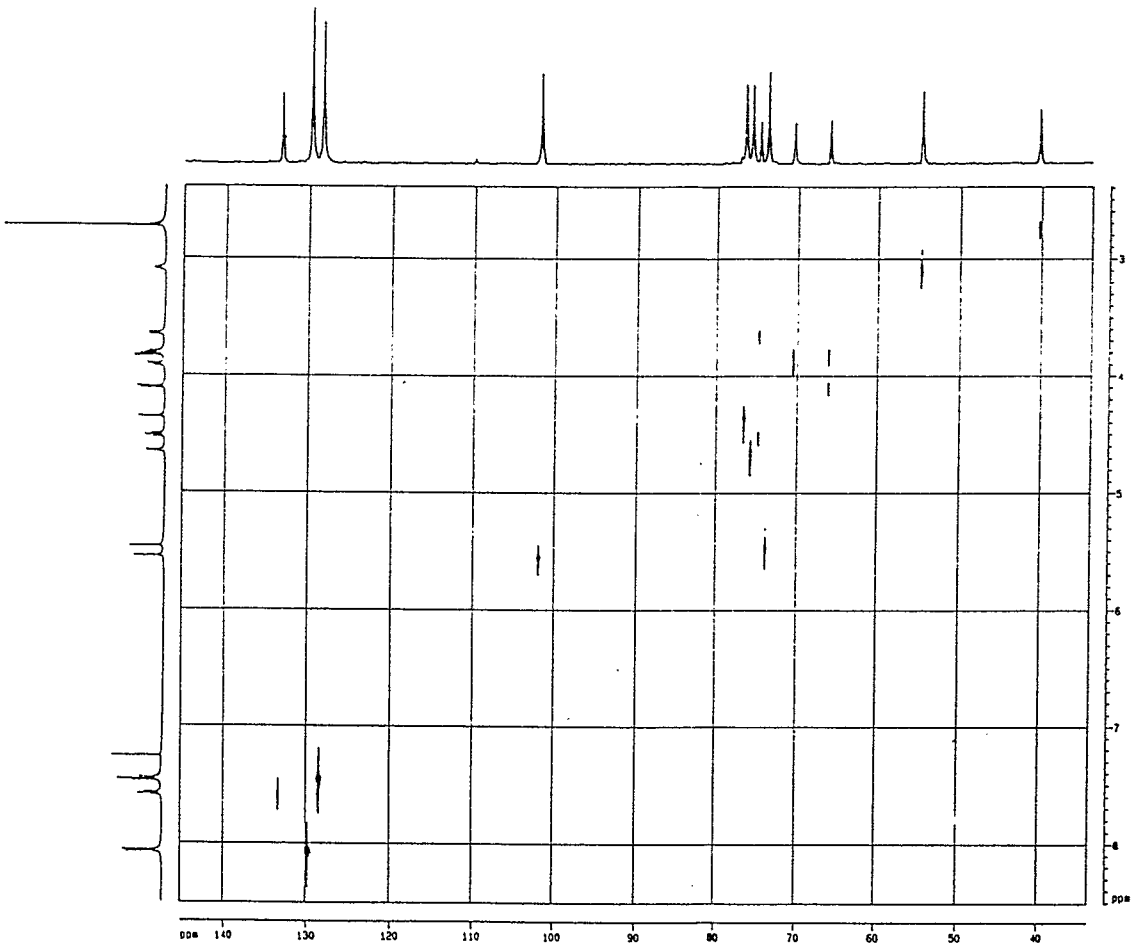

ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30



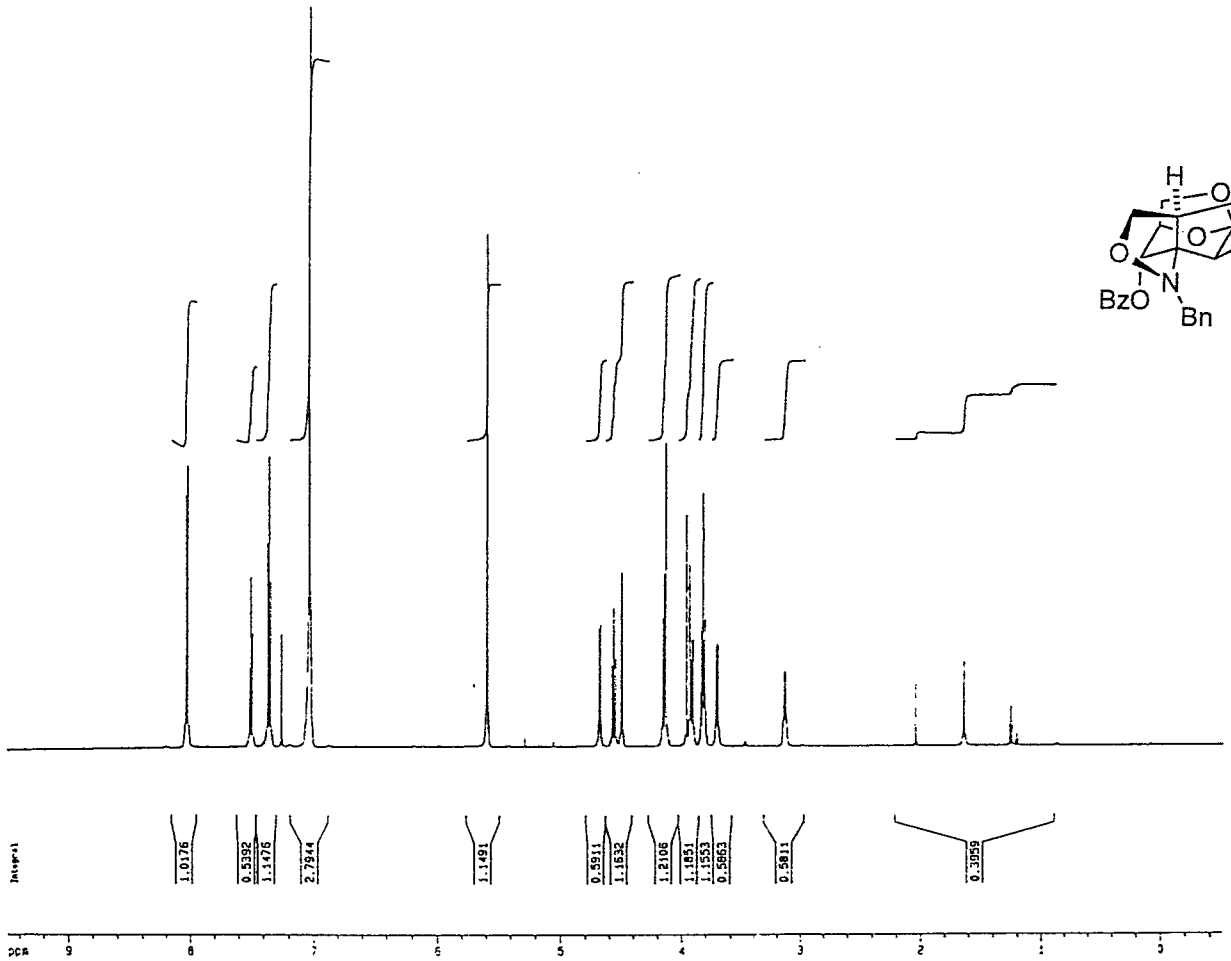


17

COSY

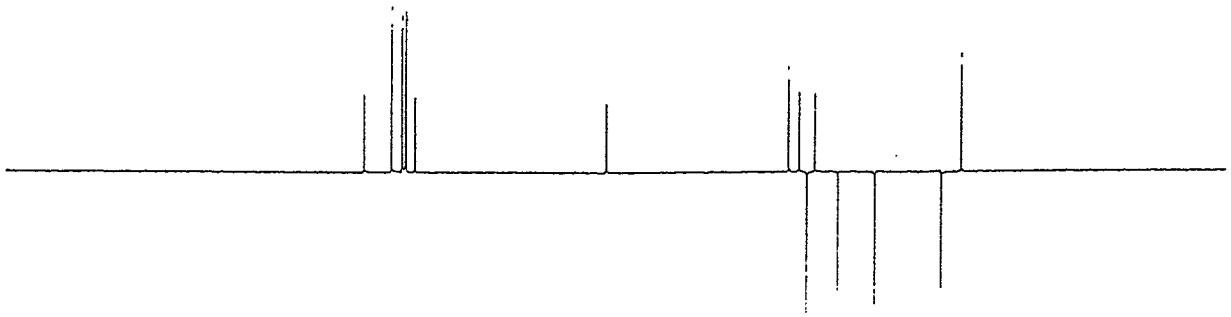


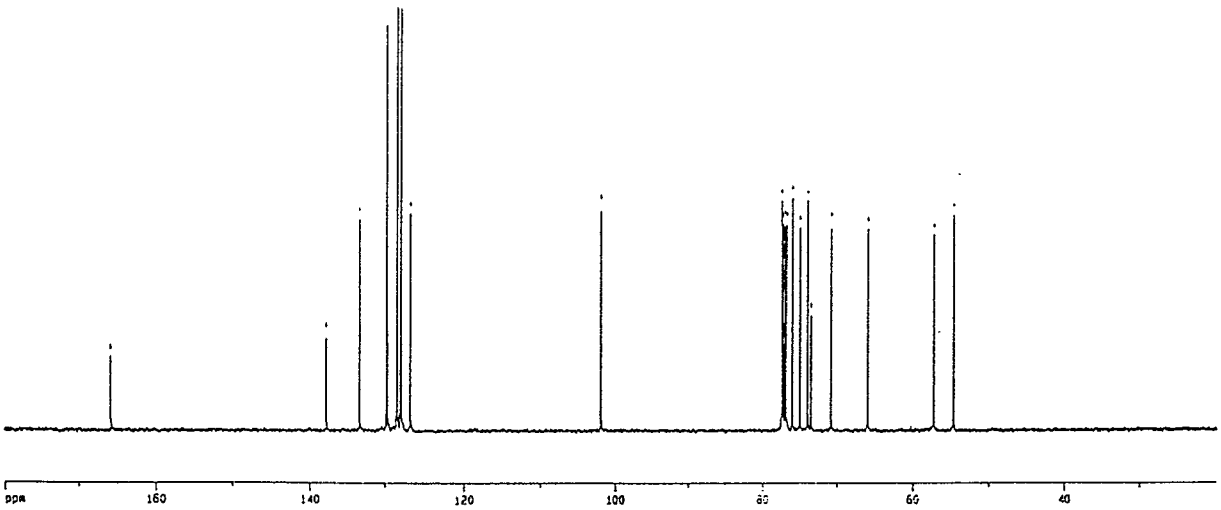
CORREL. C - H

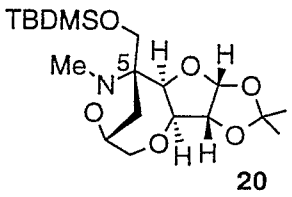

Integral
1.0176
0.5392
1.1476
2.7944
1.1491
0.5911
1.1632
1.2106
1.1851
1.1553
0.5863
0.5811
0.3959
ppm
9
8
7
6
5
4
3
2
1
0

H
O
O
O
O
BzO
N
Bn

18



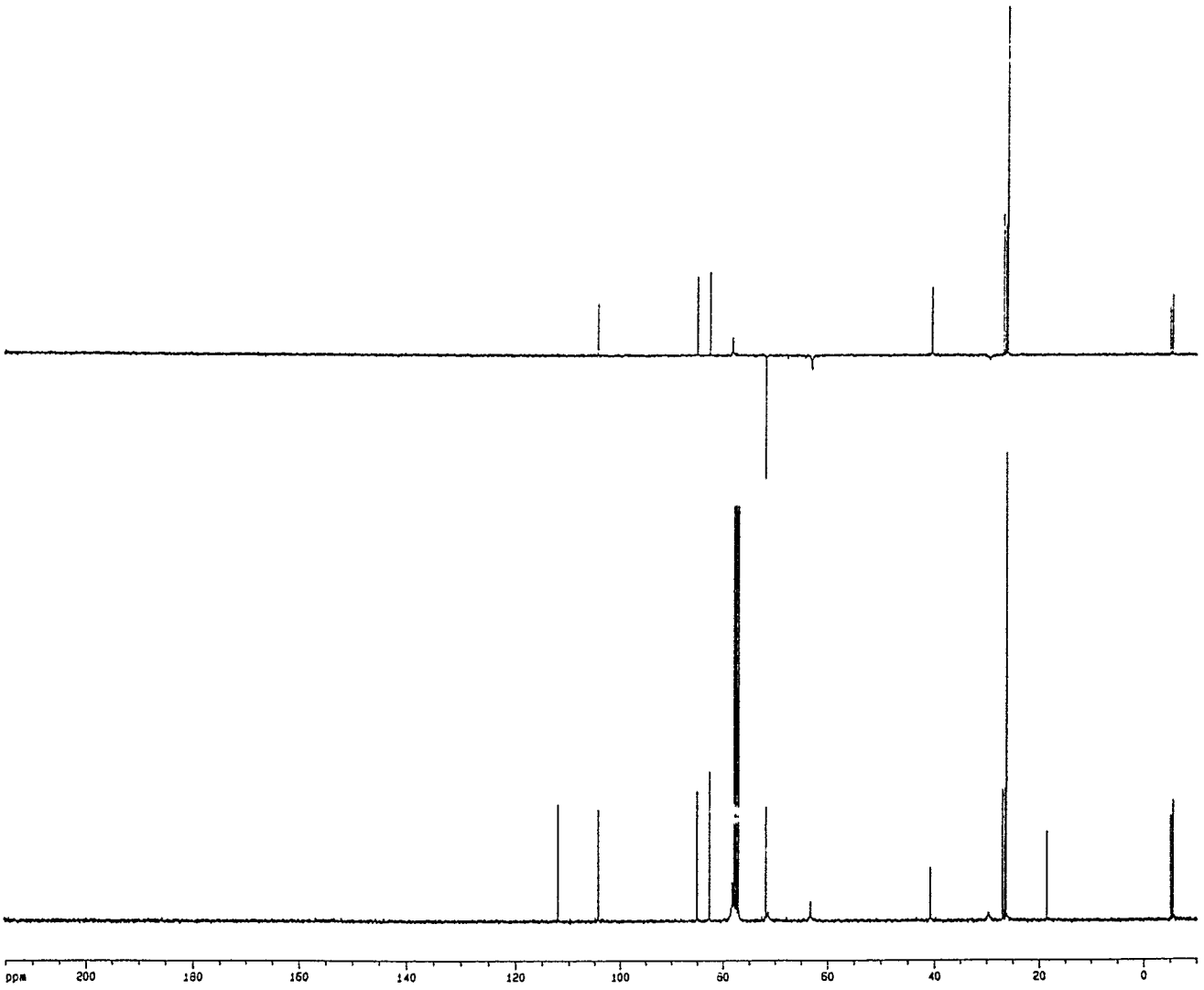

ppm
160
140
120
100
80
60
40

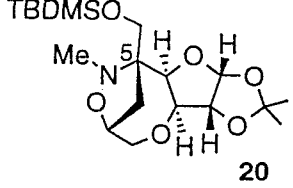

TBDMSO
Me
N
5
H
O
H
O
O
O
O
H
H

20

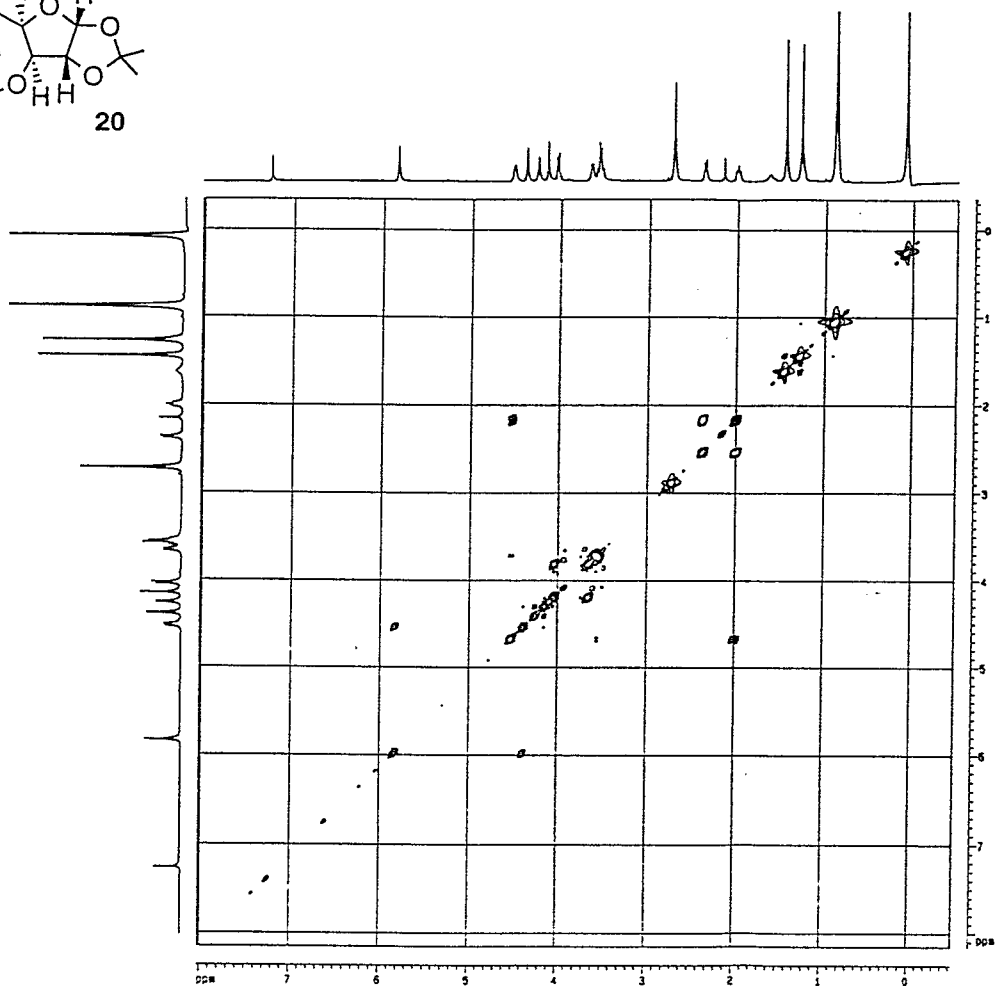
$CDCl_3$, r.t.

Integral
1.0000
1.0096
1.0163
0.9707
1.0431
1.0549
3.1377
3.0578
0.9976
1.0019
3.1864
3.9029
9.7652
6.4851
ppm
8
7
6
5
4
3
2
1
0


ppm
200
180
160
140
120
100
80
60
40
20
0

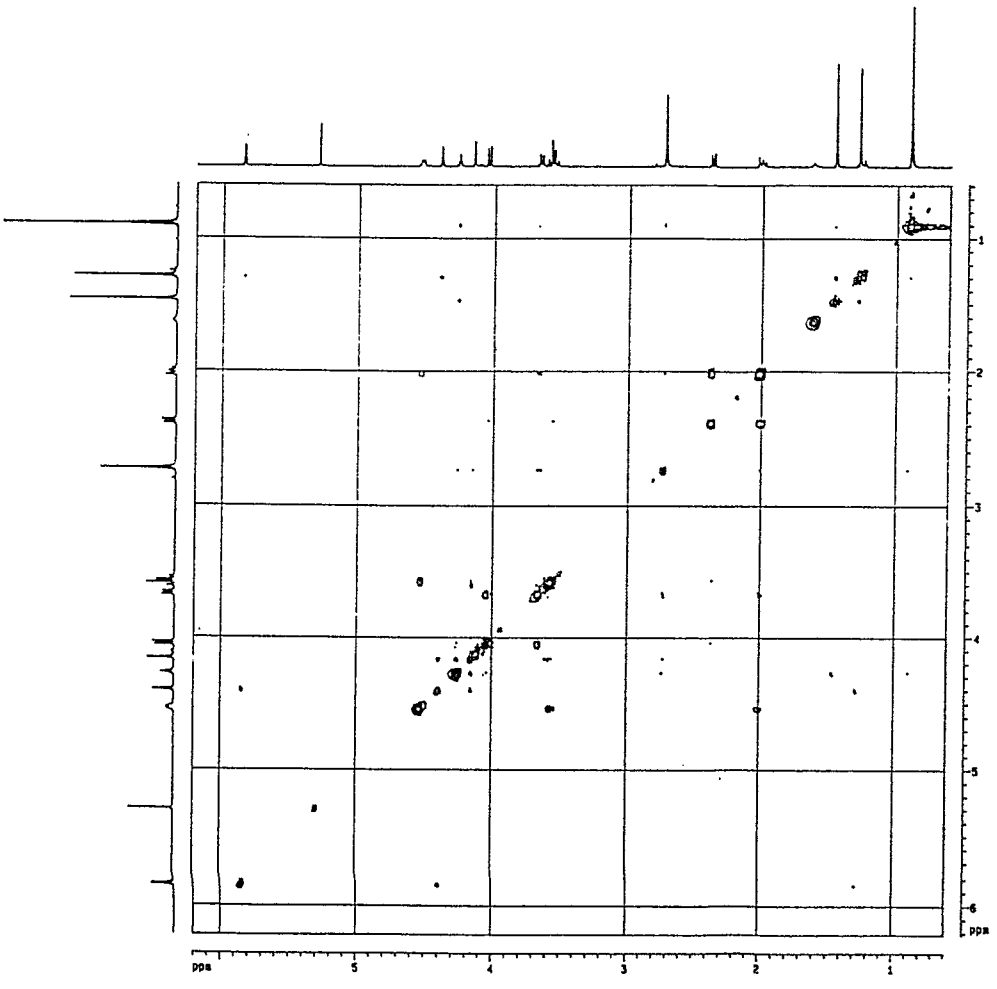


20



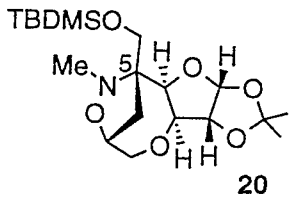
COSY

$CDCl_3$, r.t.



NOESY

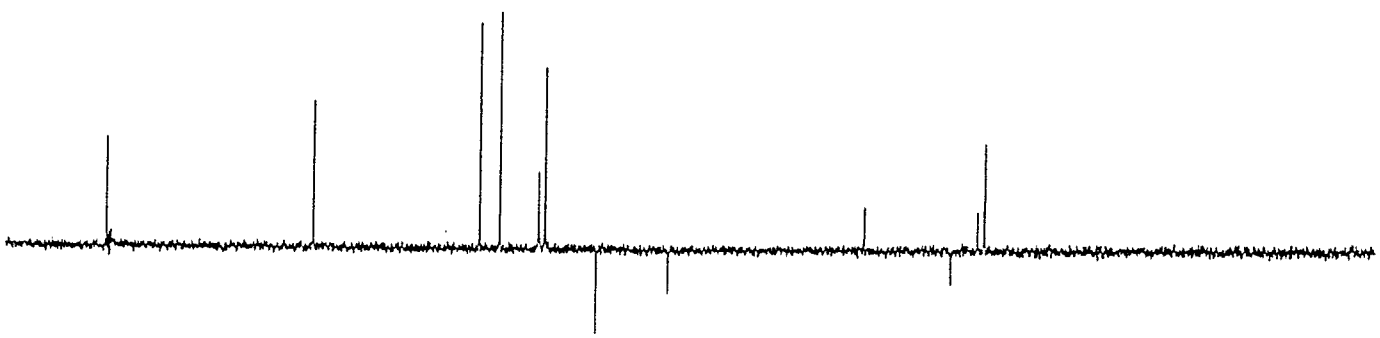
$CDCl_3$, r.t.

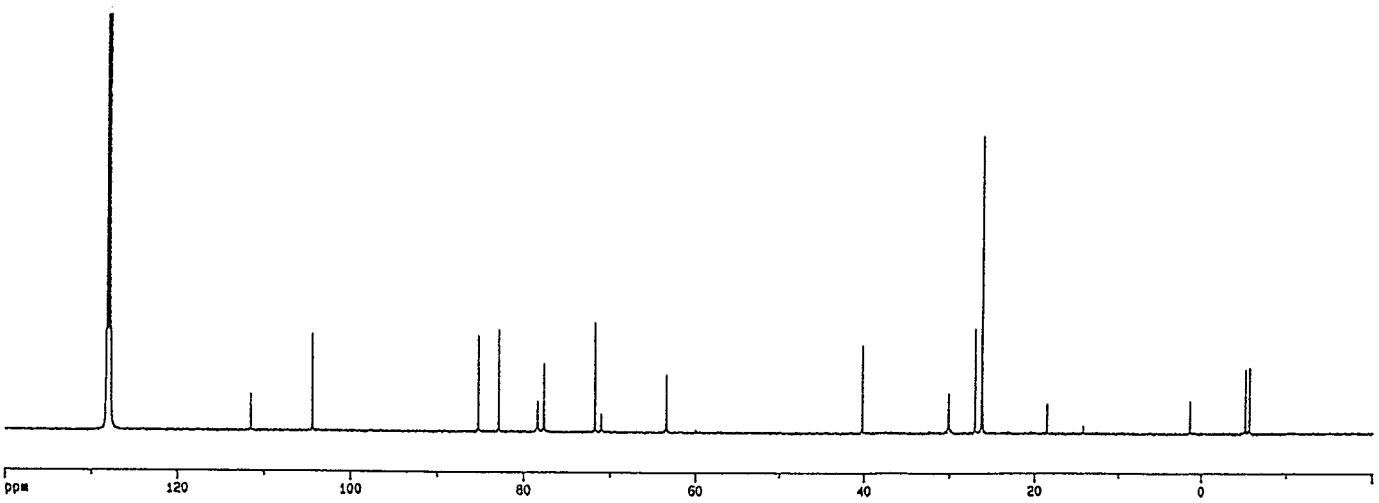

TBDMSO
Me
N
5
H
O
H
O
O
O
O
H
H

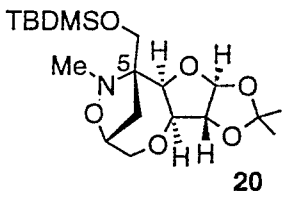
20

C_6D_6, 50ºC

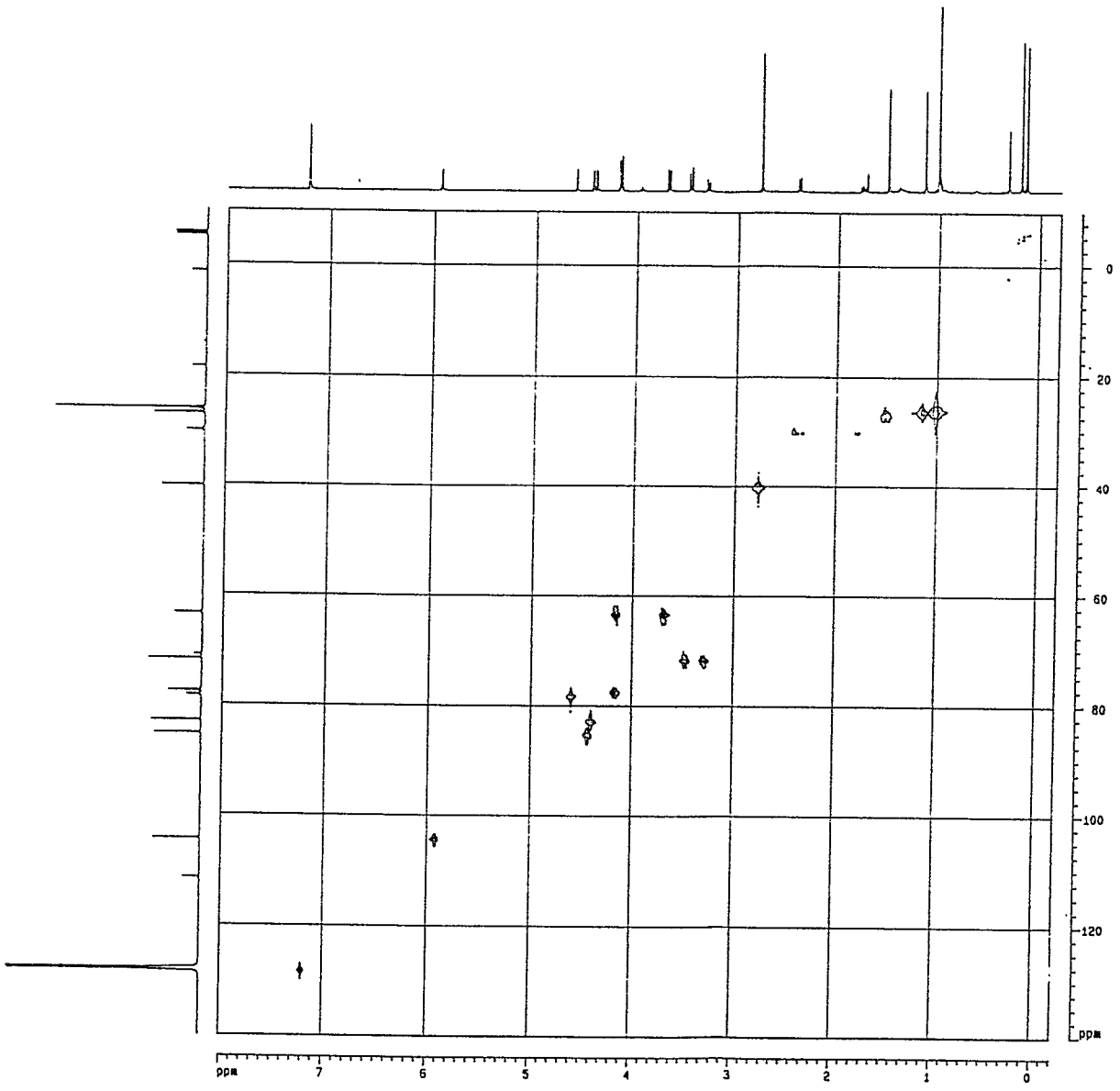
Integral
1.147
1.223
2.459
2.507
1.321
1.354
1.396
3.632
1.405
1.886
4.081
2.652
3.934
12.037
2.120
7.283
ppm
8
7
6
5
4
3
2
1
0




ppm
120
100
80
60
40
20
0

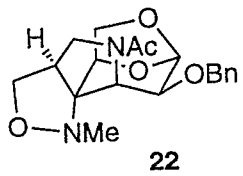


20



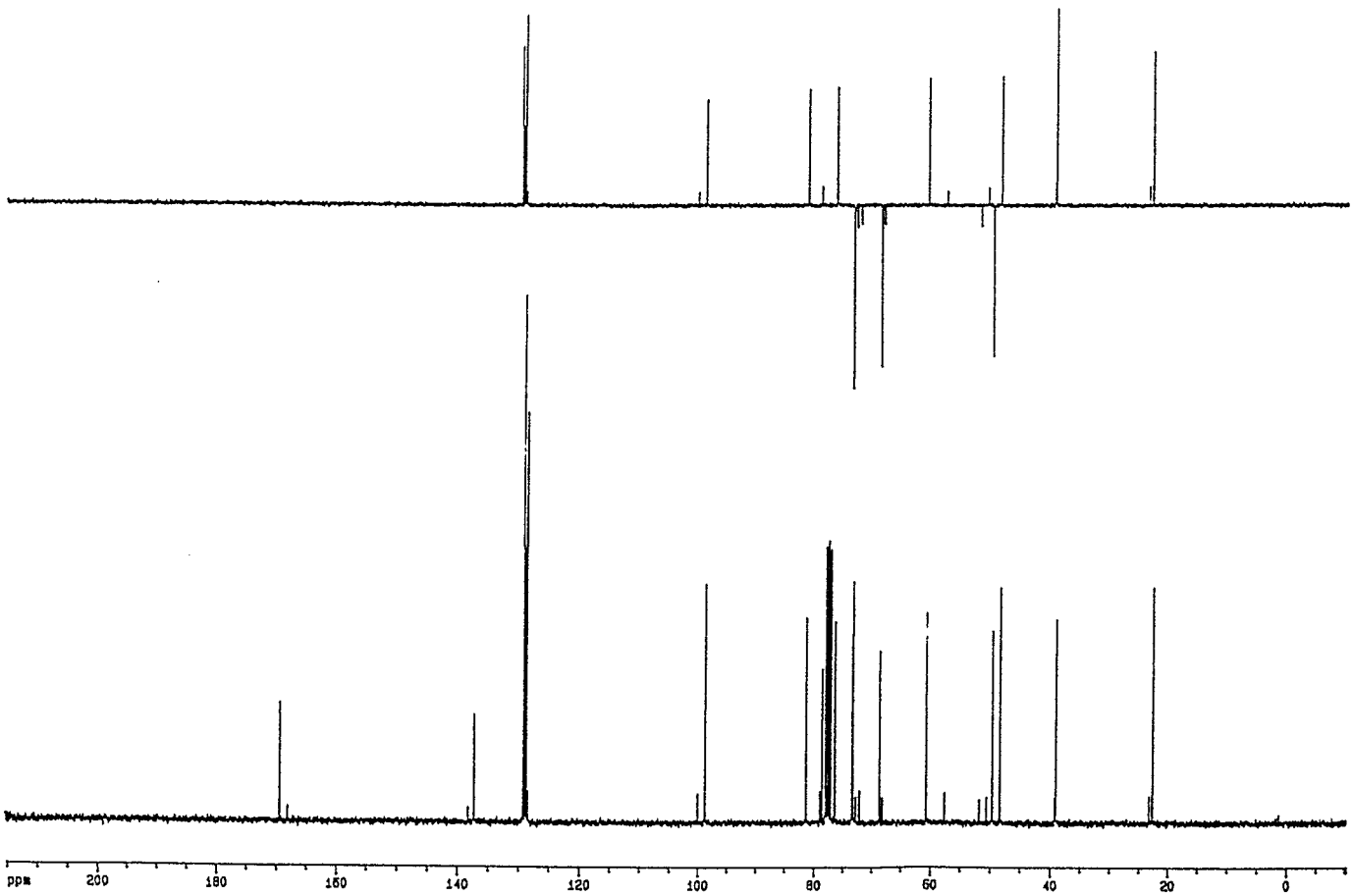
CORREL. C - H

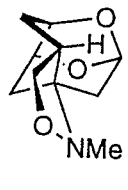
C_6D_6, 50ºC


H
O
NAc
O
OBn
O
NMe

22

Integral
20.172
3.801
76.027
ppm
10
9
8
7
6
5
4
3
2
1
0

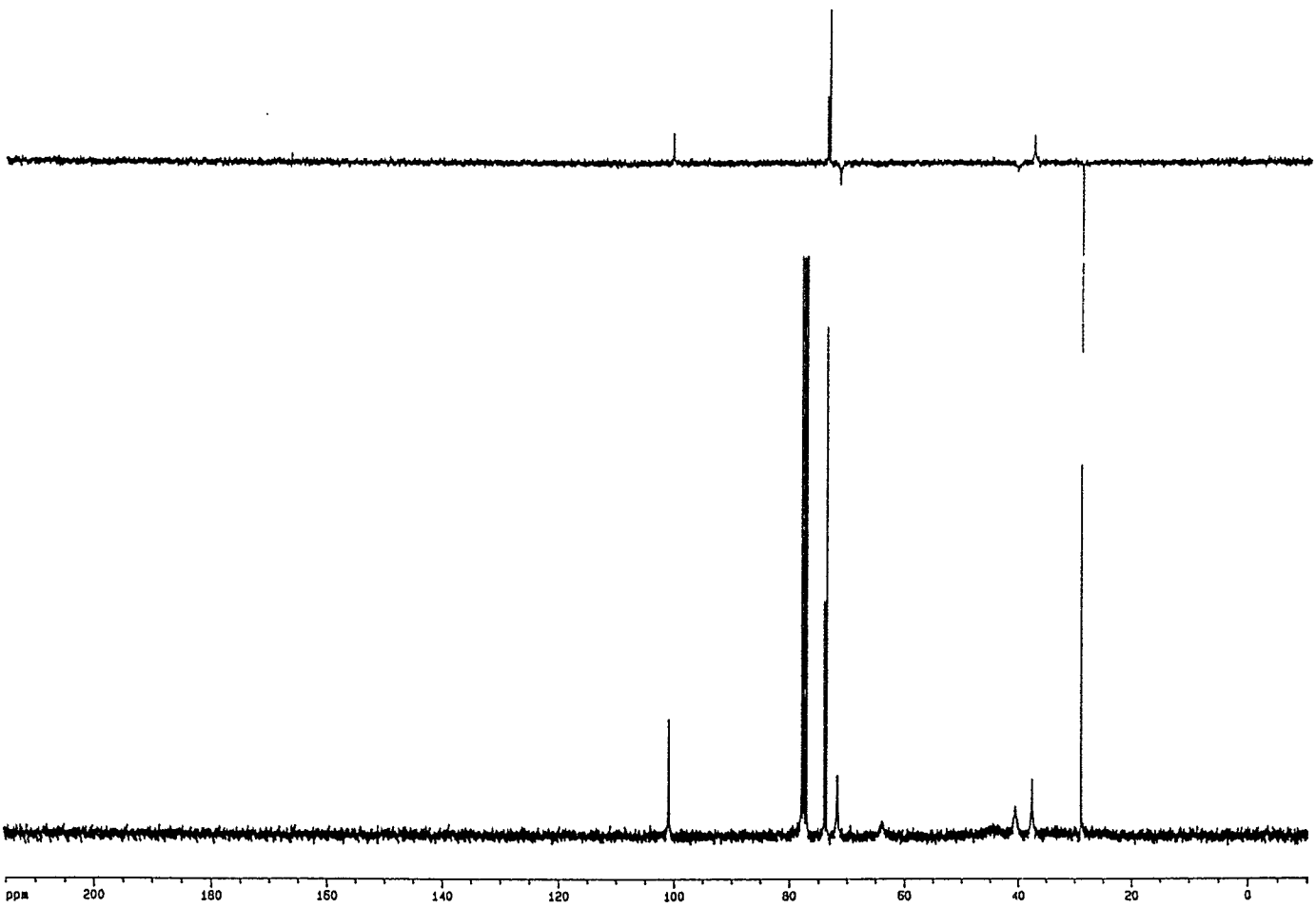

ppm
200
180
160
140
120
100
80
60
40
20
0


O
H
O
O
NMe

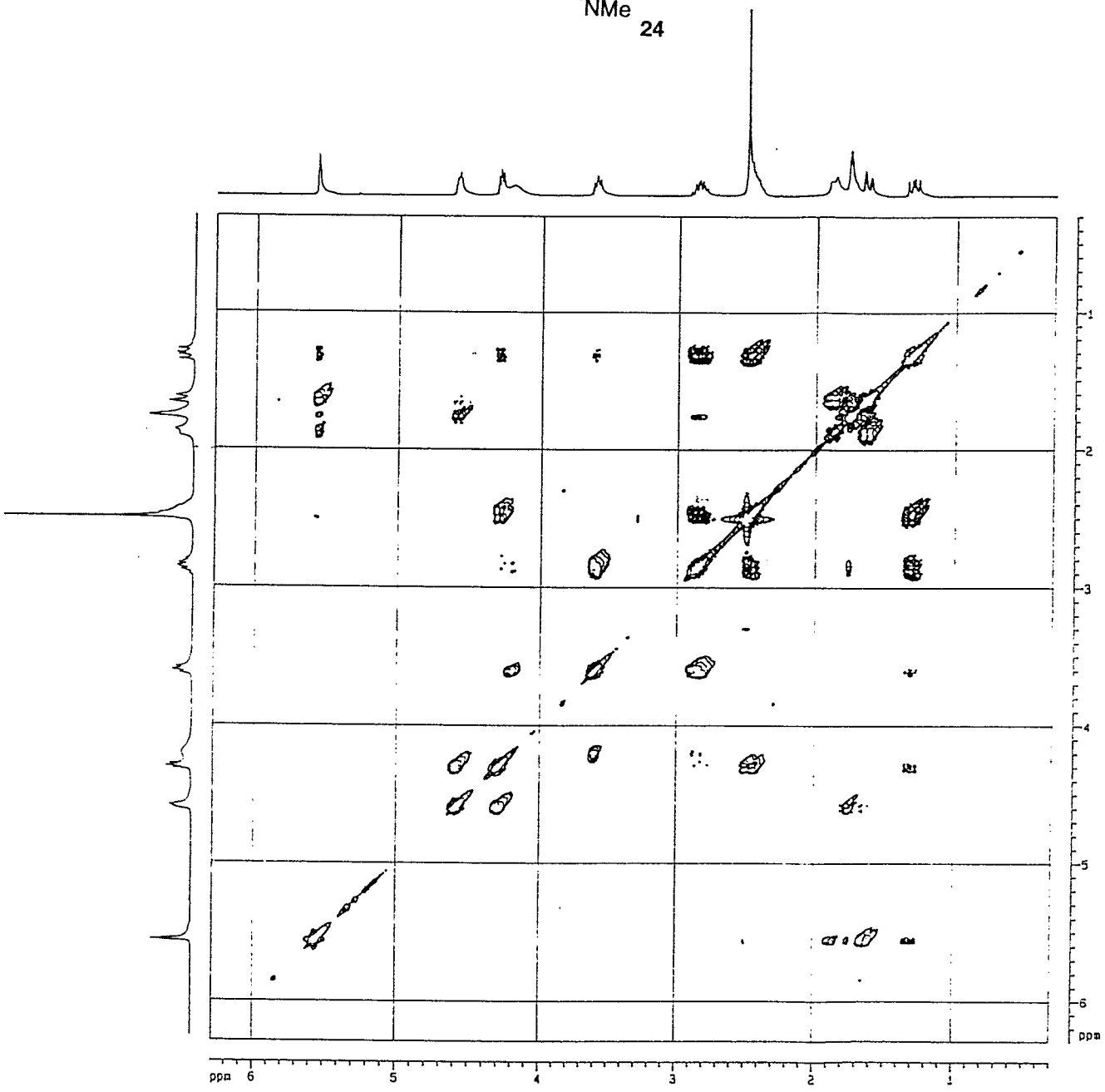
24

$CDCl_3$, r.t.

Integral
6.405
25.998
67.697
ppm
10
9
8
7
6
5
4
3
2
1
0

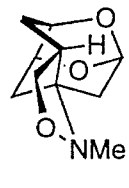

ppm
200
180
160
140
120
100
80
60
40
20
0

24



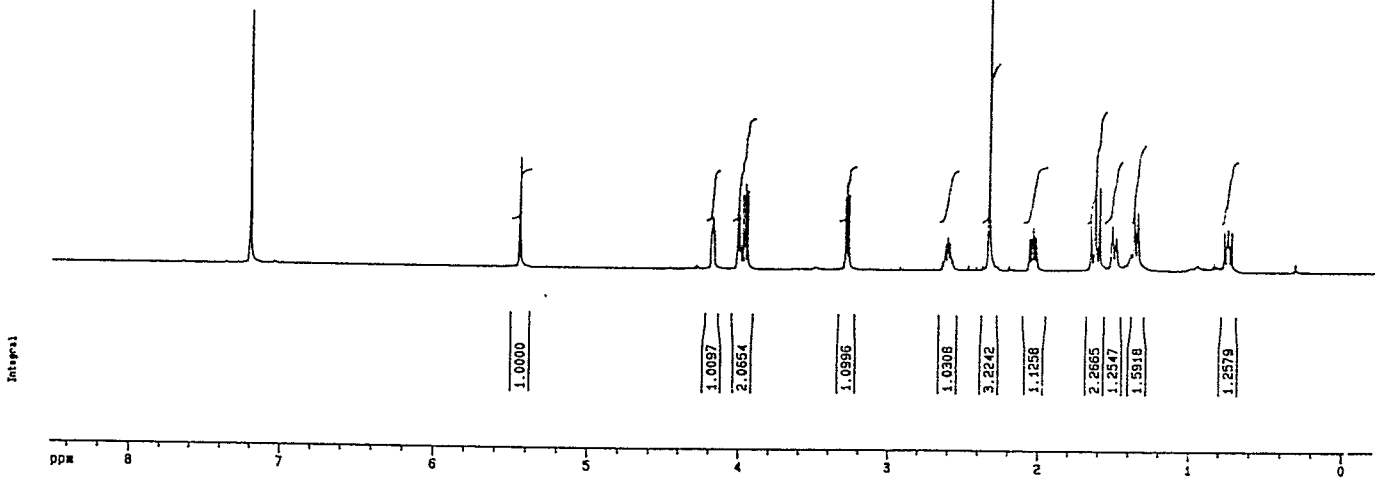
COSY

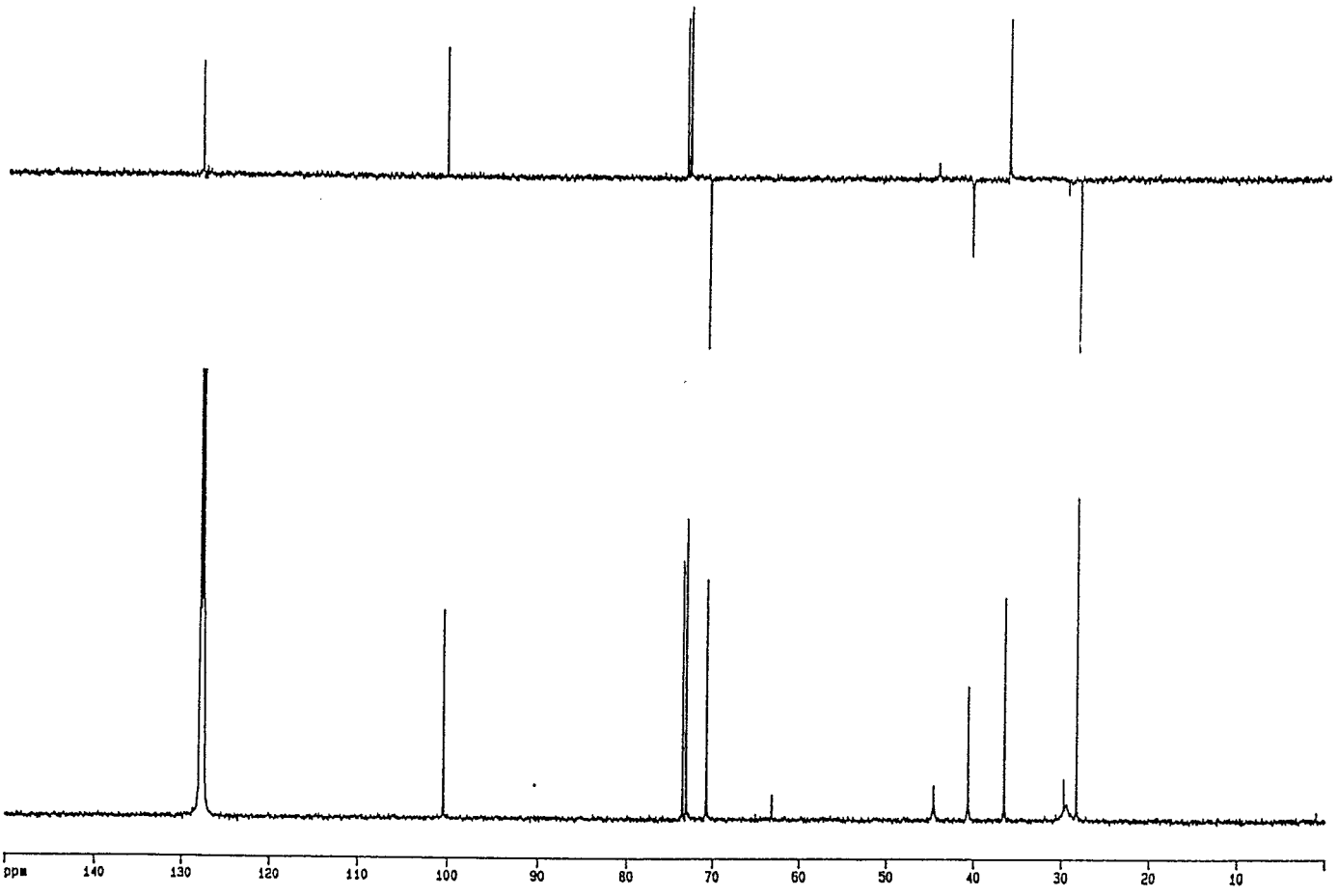
$CDCl_3$, r.t.

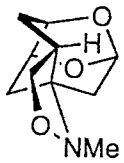

O
H
O
O
NMe

24

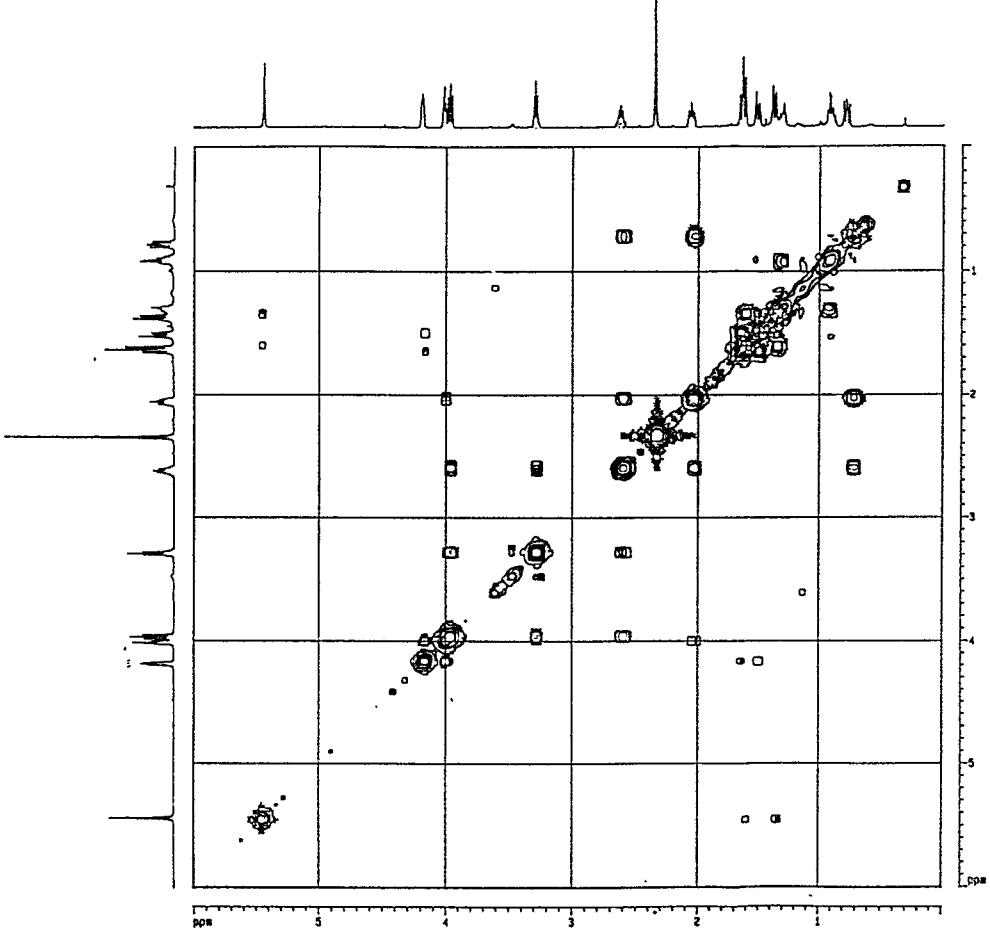
C_6D_6, 50ºC


Integral
1.0000
1.0097
2.0654
1.0996
1.0308
3.2242
1.1258
2.2665
1.2547
1.5918
1.2579
ppm
8
7
6
5
4
3
2
1
0


ppm
140
130
120
110
100
90
80
70
60
50
40
30
20
10

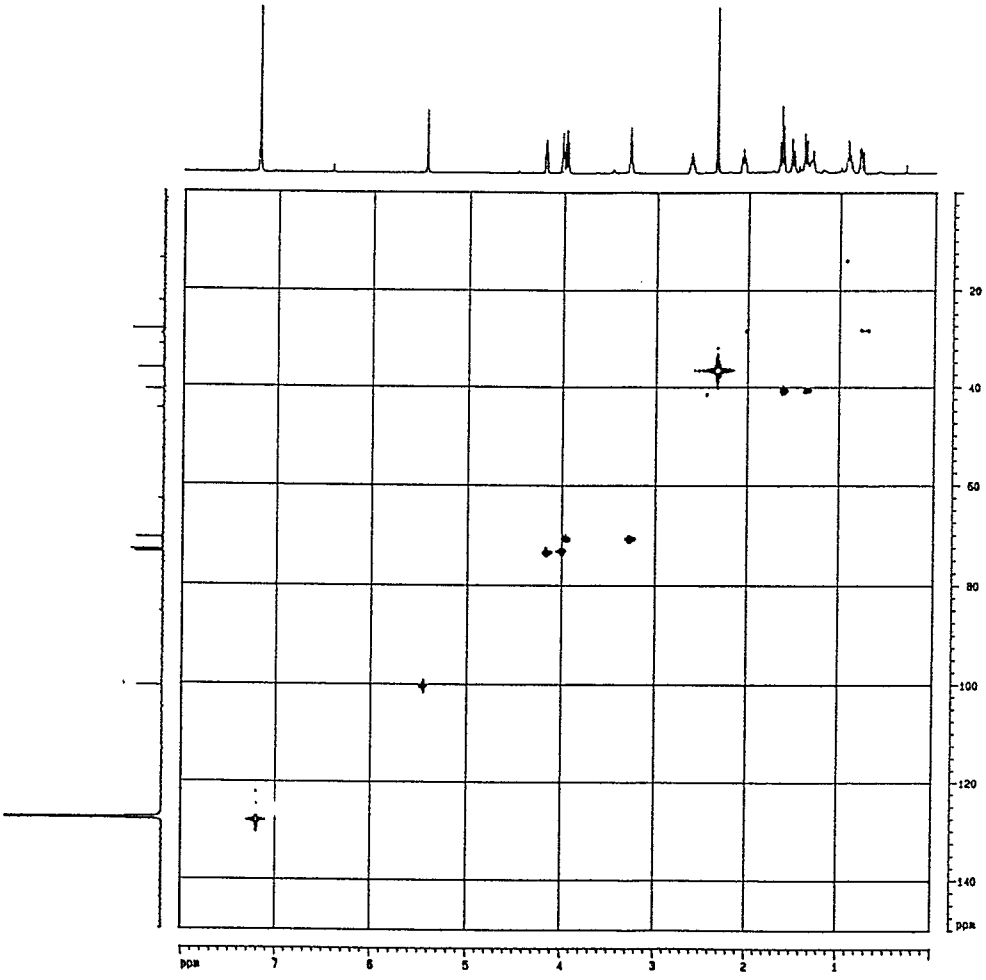


24



COSY

C_6D_6, 50ºC



CORREL. C - H

C_6D_6, 50ºC