Supplementary Information

Methyl 2,3,4 tri-O-acetyl 6-deoxy-α-D-xylohex-5-enopyranoside (3)
Triphenylphosphine (31.3 g, 0.123 mol), iodine (30.5 g,0.123 mol) and imidazole (24.5 g, 0.36 mol) were added to a solution of methyl α-D-glucopyranoside (20 g, 0.1 mol) in toluene (200 mL) at 70°C. The reaction mixture was stirred for 2 h after which time the starting material had been consumed (R_f = 0.6, 1:3 methanol:ethyl acetate) and then cooled to room temperature. Water (200 mL) was added and the mixture was stirred vigorously for 15 minutes. The layers were separated and the toluene phase was further extracted with H_2O until no product remained in the organic phase (checked by TLC). The combined H_2O extracts were concentrated under vaccum and toluene was evaporated from the residue. The residue was dissolved in pyridine (200 mL). The mixture was cooled to 0°C and chlorotrimethylsilane (80 mL, 0.4 mol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Water and diethyl ether were added and the layers separated. The aqueous layer was further washed with diethyl ether. The ether extracts were combined and washed with water, dried using anhydrous sodium sulfate and the solvent was removed under vaccum. The residue was dissoved in dry DMF (200 mL) and DBU (80 mL, 0.5 mol) was added and the mixture stirred under N_2 for 3 h at 75°C. Partial desilylation can occur (slower moving spots appear on the TLC using 1:10 ethyl acetate:petroleum spirits). The reaction mixture was cooled to room temperature. Acetic anhydride (100 mL) and pyridine (100 mL) were added to the reaction flask and the mixture left overnight. Water and ethyl acetate were added and layers separated and the aqueous layer was further extracted with ethyl acetate. The combined organic extracts were washed with $NaHCO_3$ and water, dried ($MgSO_4$) and concentrated. The residue was eluted from a column of silica gel with 1:4 ethyl acetate:petroleum spirits (b.p 40-60°) containing 0.1% of triethylamine to give the title compound as a white solid (22.9 g, 61%): $[\alpha]^{20}_D$ +109.8 (c 1.0, $CHCl_3$); m. pt. 98-99 °C (lit.,[7] m. pt. >100°C).

Methyl 2,3,4 tri-O-benzyl-6-deoxy-α-D-xylohex-5-enopyranoside (4)
A catalytic quantity of NaOMe solution (prepared by dissolving 0.3 g Na in 50 mL methanol) was added to a solution of **3** (22.9 g, 0.06 mol) in methanol (300 mL) and the mixture stirred at room temperature until a product (R_f = 0.4, 1:3 MeOH:EtOAc) had formed. The solvent was removed and the product dried under vaccum (0.5 mmHg, 10.7 g, 100%). The residue (5.0 g, 0.028 mol) was dissolved in DMF (50 mL) and sodium hydride (60% dispersion in mineral oil, 4.5 g, 0.113 mol) was added and the mixture was cooled to 0°C. Benzyl bromide (13.5 mL, 0.133 mol) was then added dropwise over 30 minutes to this mixture. The reaction was quenched after 1.5 h by addition of methanol and further diluted with H_2O. The product was extracted with EtOAc and the combined organic extracts washed with H_2O, dried ($MgSO_4$) and solvent removed. The product was purified by chromatography with (silica gel, 1:4 EtOAc:petroleum spirits (b.p 40-60°) as eluent to give the title compound (8.54 g, 68%): $[\alpha]^{20}_D$ –28.8 (c 1.0, $CHCl_3$); m. pt. 47.5-49 °C. The ^{1}H-NMR spectroscopic data is in good agreement with those previously reported.[7]

Spectroscopic data for 5:
Clear syrup; $[\alpha]^{20}_D$ +34.8 (c 0.046, $CHCl_3$); ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 5.46 (d, 1H, J_{1-2} = 2.0, H-1), 5.40 (appt, 1H J_{3-4} = J_{2-3} = 8.5, H-3), 5.14 (dd, 1H, J_{6a-4} = 2.0, J_{3-4} = 8.5, H-4), 4.60 (br s, OH), 4.91 (dd, 1H, J_{2-1} = 2.0, J_{2-3} = 8.5, H-2), 4.16 (d, 1H, J_{6a-6b} = 8.5, H-6b), 3.51 (dd, 1H, J_{4-6a} = 2.0, J_{6b-6a} = 8.5, H-6a, 2.04, 2.08 and 2.12 (each s, each 3H, OAc) ppm; ^{13}C NMR δ 173.1 (C=O), 170.9 (C=O), 170.6 (C=O), 103.1 (C-5), 99.0 (C-1), 74.7 (C-2), 74.6 (C-4), 74.5 (C-2), 70.7 (C-6), 21.4, 21.3 (2 signals) (each OAc); IR (liquid film) υ 3379, 2917, 1731, 1369, 1225 and 1041 cm^{-1}.

Spectroscopic data for 6:
White solid; $[\alpha]^{20}_D$ +34.5 (c 1.0, $CHCl_3$); m. pt. 98-99 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.22-7.34 (m,15H, phenyl), 5.26 (d, 1H, J_{1-2} = 2.0, H-1), 4.61-4.94 (m, 6H, CH_2, benzyl), 4.19 (d, 1H, J_{6a-6b} = 8.0 , H-6a), 3.79 (appt, 1H, J_{3-4} = J_{2-3} = 8.0, H-3), 3.68 (dd, 1H, J_{6a-4} = 2.0, J_{3-4}, 8.0, H-4), 3.53 (dd, 1H, J_{2-1} = 2.0, J_{2-3} = 8.0, H-2), 3.31 (dd, 1H, J_{6b-4} = 2.0, J_{6a-6b} = 8.0, H-6b); ^{13}C NMR δ 138.4, 138.2, 137.7 (each s), 128.8 -127.7 (18C aromatic, each d), 103.5(C-5), 98.4 (C-1), 82.6 (C-2), 82.0 (2s, C-3 and C-4), 75.6, 74.7 and 73.0 (each t), 68.5 (C-6); IR (solution in $CHCl_3$) υ 3356, 2323, 1453, 1344, 1208, 1067, 1003, 836 and 754 cm^{-1}. HRCI-MS Found: 466.2229. Calcd. for $C_{27}H_{32}O_6N$ (M+NH_4): 466.2291.

Spectroscopic data for 13a
Clear syrup; $[\alpha]^{20}_D$ +17.4 (c 0.26, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.18-7.28 (m, 15H, phenyl), 5.18 (d, 1H, J_{1-2} = 2.0, H-1), 4.83-4.56 (m, 6H, CH_2, benzyl), 3.93 (d, 1H, J_{6a-6b} = 8.0, H-6a), 3.71 (1H, appt, J_{3-4} = J_{2-3} = 8.0, H-3), 3.68 (1H, dd, J_{4-6b} = 2.0, J_{3-4} = 8.0, H-4), 3.56 (dd, 1H, J_{6b-4} = 2.0, J_{6a-6b} = 8.0, H-6b), 3.47 (dd, 1H, J_{1-2} = 2.0, $J_{2,3}$ = 8.0, H-2), 3.42 (s, 3H, OCH_3); ^{13}C NMR 138.5 (2 signals) and 137.9 (each s), 129.6-127.6 (18C, aromatic C, each d), 106.3 (C-5), 98.3 (C-1), 82.7 (C-2), 82.3 (C-3), 81.3 (C-4), 75.5, 74.4 and 73.0 (each t), 63.5 (C-6), 50.6 (q). IR (liquid film) υ 1651, 1453, 1365, 1260 and 1098 cm^{-1}. HRCI-MS: Found: 480.2386. Calcd. for $C_{28}H_{34}O_6N$ (M+NH_4): 480.2387.

Spectroscopic data for 13b
Clear syrup; $[\alpha]^{20}_D$ +12.8 (c 0.25, $CHCl_3$);
^{1}H NMR ($CDCl_3$, 300 MHz): 7.20-7.35 (m, 15H, phenyl), 5.39 (d,1H, J_{1-2} = 2.0, H-1), 4.60-4.94 (m, 6H, benzyl CH_2), 4.31 (d, 1H, J_{6a-6b} = 8.0, H-6b), 4.20 (dd, 1H, J_{6a-4} = 2.0, J_{3-4} = 8.0, H-4), 3.90 (dd, 1H, J_{6a-6b} = 8.0, J_{6a-4} = 2.0, H-6a), 3.75 (appt, 1H, J_{3-4} = 8.0 = J_{2-3}, H-3), 3.59 (dd, 1H, J_{1-2} = 2.0, J_{2-3} = 8.0, H-2), 3.15 (s, 3H, mesyl CH_3); ^{13}C NMR δ 138.5, 138.0 and 138.9 (each s), 128.9-128.0 (18C, aromatic C, each d), 108.1 (C-5), 100.4 (C-1), 82.9 (C-2), 82.5 (C-3), 82.3 (C-4), 75.9, 75.3 and 73.5 (each t), 68.4 (C-6), 42.15 (q); IR υ 2952, 1454, 1371, 1191, 1069, 787 cm^{-1}. HRCI-MS: Found: 544.2002. Calcd. for $C_{28}H_{34}O_8NS$ (M+NH_4): 544.2005.

Spectroscopic data for 13c
Clear syrup; $[\alpha]^{20}_D$ +27.9 (c 0.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.25-7.32 (m, 15H, phenyl), 5.42 (d, 1H, J_{1-2} = 2.0, H-1), 4.87-4.56 (m, 6H, benzyl CH_2), 4.37 (d, 1H, J_{6a-6b} = 8.0, H-6b), 4.08 (dd, 1H, J_{6a-4} = 2.0, J_{3-4} = 8.0, H-4), 3.94 (dd, 1H, J_{4-6a} = 2.0, J_{6b-6a} = 8.0, H-6a), 3.78 (appt, 1H, J_{3-4} = 8.0, H-3), 3.63 (dd, 1H, J_{1-2} = 2.0, J_{2-3} = 8.0, H-2); ^{13}C NMR δ137.8, 137.3 and 137.0 (each s), 128.7-127.8 (18C, aromatic C, each d), 111.0 (C-5), 100.1 (C-1), 82.1 (C-2), 82.0 (C-3), 81.5 (C-4), 75.6, 75.3 and

73.3 (each t), 67.5 (C-6); IR (liquid film) υ 2922, 1601, 1420, 1215, 1091, 799 cm^{-1}. HRCI-MS: Found: 598.1722 Calcd. for $C_{28}H_{31}F_3O_8NS$ (M + NH_4): 598.1728.

Spectroscopic data for 13d

Clear syrup $[\alpha]^{20}_D$ +15.4 (c1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz), δ 7.23-7.13 (m, 15H, phenyl), 5.23 (d, 1H, J_{1-2} = 2.0, H-1), 4.91-4.55 (m, 6H, benzyl CH_2), 4.10 (d, 1H, J_{6a-6b} = 8.0, H-6b), 3.65 (appt, 1H, J_{2-3} = J_{3-4} = 8.0, H-3), 3.53 (dd, 1H, J_{6a-4} = 2.0, J_{3-4} = 8.0, H-4), 3.45 (dd, 1H, J_{1-2} = 2.0, J_{2-3} = 8.0, H-2), 3.31 (dd, 1H, J_{6b-4} = 2.0, J_{6a-6b} = 8.0, H-6b), 0.82 (s, 9H, *t*-butyl), 0.09 (s, 6H, Si(CH_3)$_2$C(CH_3)$_3$); ^{13}C-NMR δ139.0 (2 signals) and 138.4 (each s), 128.9-128.0 (18C, aromatic C, each d), 105.1 (C-5), 98.8 (C-1), 84.9 (C-2), 82.9 (C-3), 82.4 (C-4), 76.0, 75.3, and 73.4 (each t), 73.3 (C-6), 26.2 (C(CH_3)$_3$), 18.3 (C(CH_3)$_3$), 1.44 and 0.43 (Si(CH_3)$_2$C(CH_3)$_3$); IR (liquid film) υ 2928, 1454, 1364, 1274, 1205, 1091, 859 cm^{-1}. HRCI-MS: Found: 580.3094. Calcd. for $C_{33}H_{46}O_6SiN$ (M + NH_4): 580.3101.

Spectroscopic data for 13e

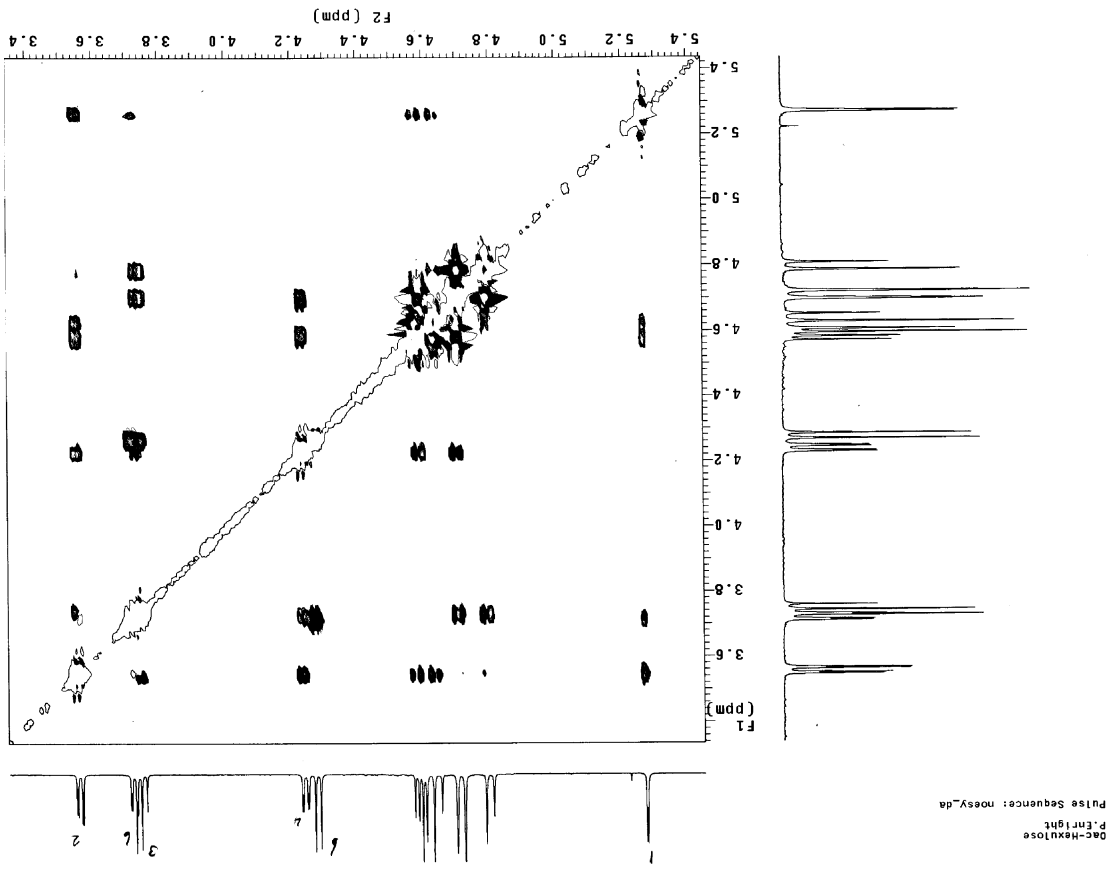
Clear syrup? $[\alpha]^{20}_D$ +42.3 (c.1.0 $CHCl_3$)

^{1}H NMR ($CDCl_3$, 270 MHz), δ 7.31-7.24 (m, 15H, phenyl), 5.35 (d, 1H, J_{1-2} = 2.0, H-1), 4.89-4.62 (m, 6H, benzyl CH_2), 4.35 (d, 1H, J_{6a-6b} = 8.0, H-6a), 4.31 (dd, 1H, J_{6a-4} = 2.0, J_{3-4} = 8.0, H-4), 3.83 (appt, 1H, J_{3-4} = J_{2-3} = 8.0, H-3), 3.80 (dd, 1H, J_{6b-4} = 2.0, J_{6a-6b} = 8.0, H-6b), 3.63 (dd, 1H, J_{1-2} = 2.0, J_{2-3} = 8.0, H-2), 2.00 (s, 3H, OAc); ^{13}C NMR 168.0 (C=O), 138.3, 138.0 and 137.7 (each s), 128.6-127.7 (18C, aromatic C, each d), 104.2 (C-5), 99.3 (C-1), 82.5 (C-2), 82.4 (C-3), 80.4 (C-4), 75.5, 74.9 and 73.1 (each t), 68.1 (C-6), 21.6 (q). IR (liquid film) υ 2923, 1761, 1454, 1363, 1219, 1074, 737 cm^{-1}. HRCI-MS: 508.2335. Calcd. for $C_{29}H_{34}O_7N$ (M + NH_4): 508.2346.

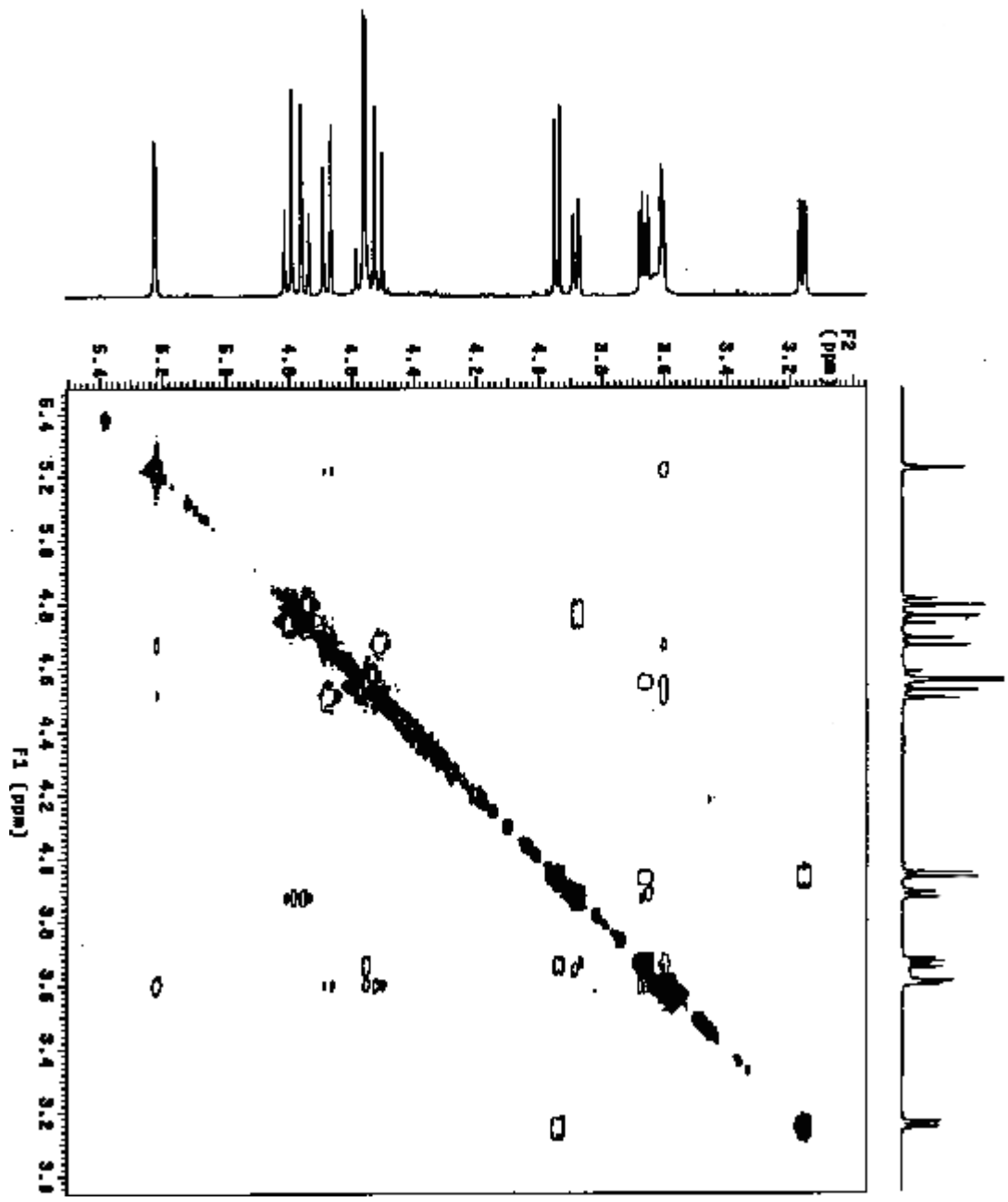
Spectroscopic data for 18

Clear syrup; $[\alpha]^{20}_D$ +14.2 (c 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.32-7.27 (m, 15, phenyl), 5.28 (d, 1H, J_{1-2} = 2.0, H-1), 4.72 (m, 6H, benzyl CH_2), 3.99 (d, 1H, dd, J_{6b-6a} = 9.0, H-6b), 3.99 (dd, 1H, J_{6a-4} = 1.0, J_{3-4} = 9.0, H-4), 3.73 (dd, 1H, J_{2-3} = 4.5, J_{3-4} = 9.0, H-3), 3.66 (dd, 1H, J_{1-2} = 2.0, J_{2-3} = 4.5, H-2), 3.24 (dd, 1H, J_{6a-4} = 1.0, J_{6b-6a} = 9.0, H-6a); ^{13}C-NMR: 138.5, 138.0 and 137.8 (each q), 128.8-127.5 (18 signals, aromatic C, each d), 102.6 (C-5), 99.4 (C-1), 81.4 (C-4), 78.5 (C-3), 75.0 (C-2), 75.2, 73.1 and 73.0 (each t), 66.9 (C-6); IR (liquid film) υ 3421, 2929, 1454, 1364, 1260, 1112, 799, 697 cm^{-1}. HRCI-MS: 466.2220. Calcd. for $C_{27}H_{32}O_6N$ (M + NH_4): 466.2230.

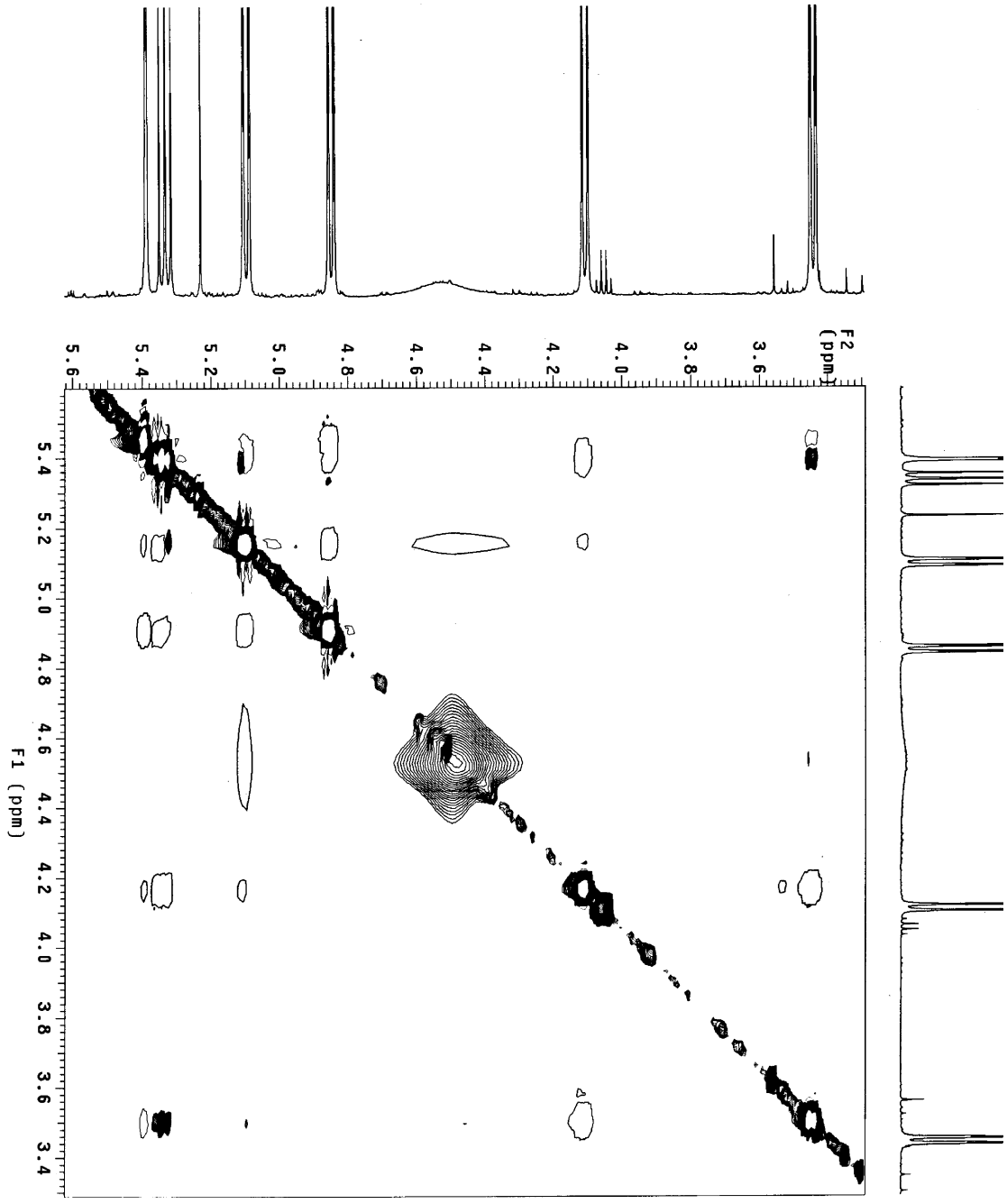
2D-NOESY for **13d**



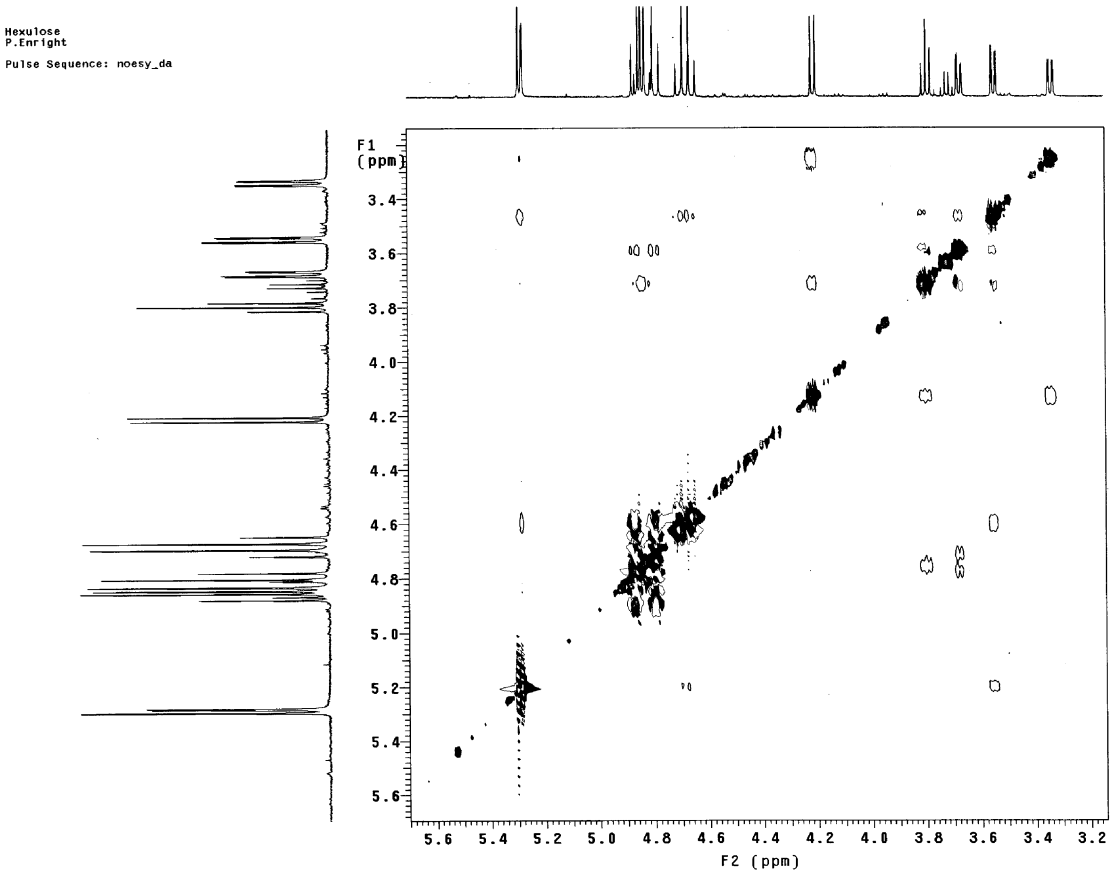
2D-NOESY of **18**



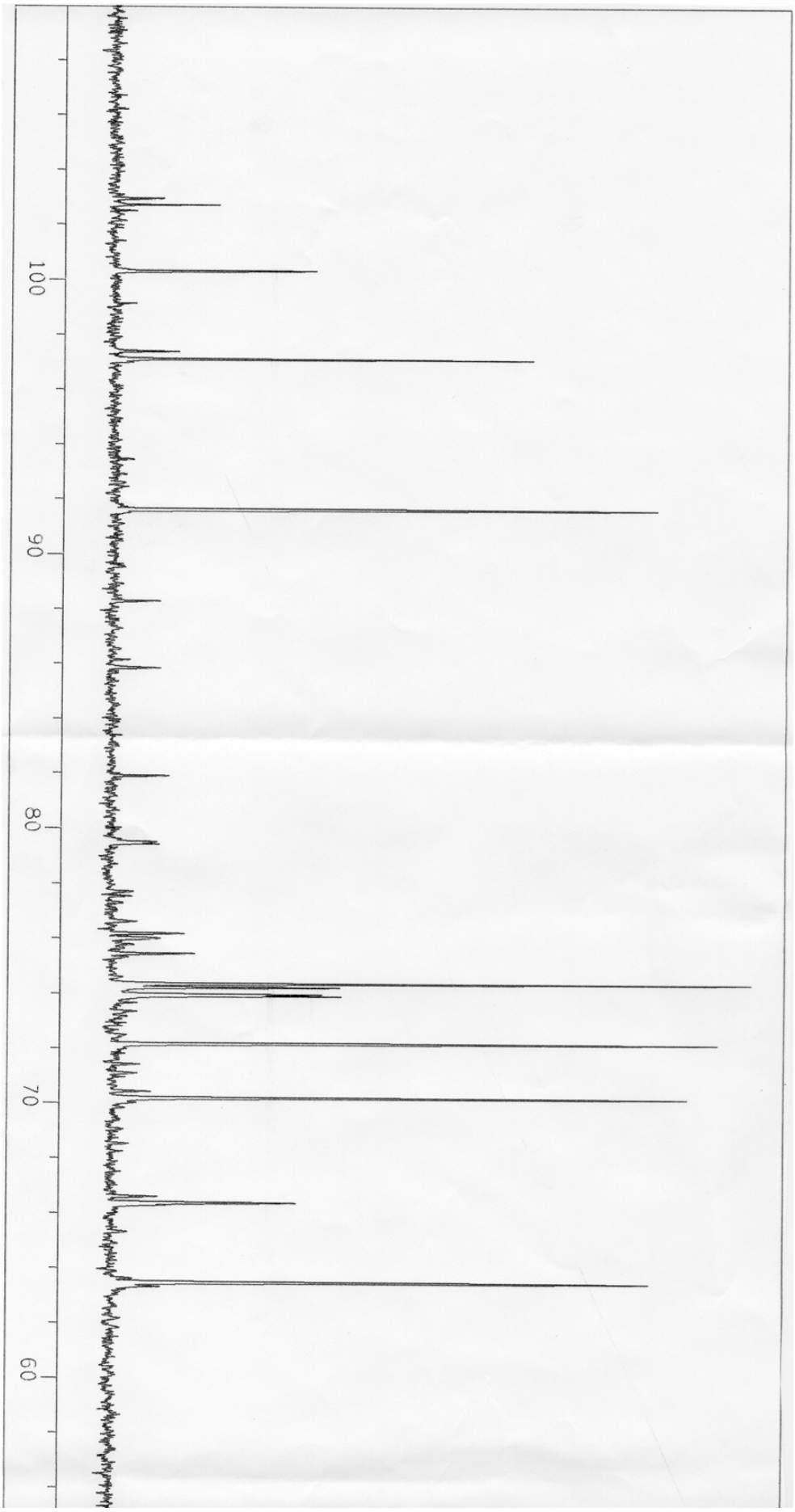
2D-NOESY for **5**



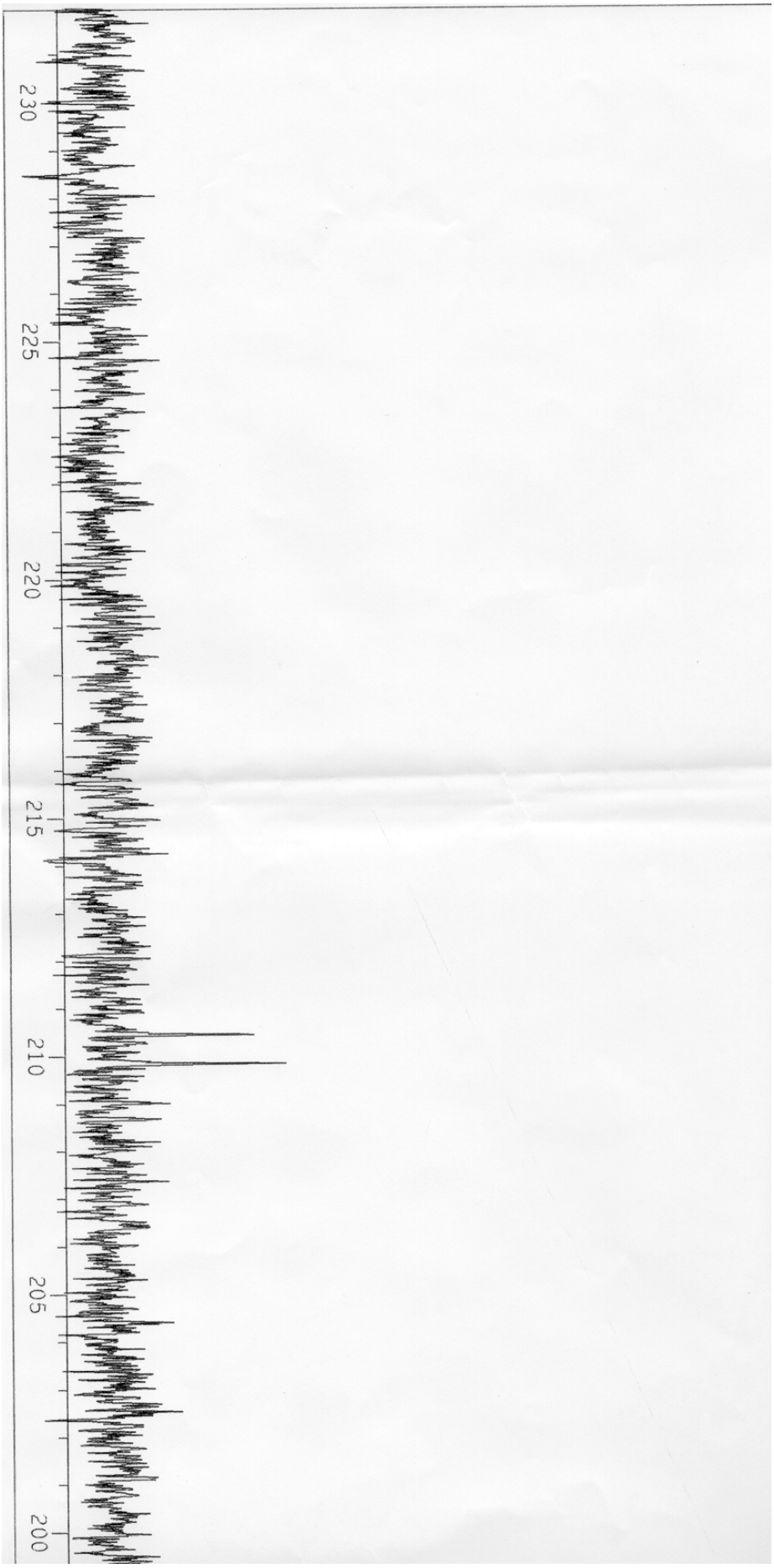
2D-NOESY for **6**



13C-NMR of **15** (60-110 ppm)



^{13}C-NMR **15** (200-230 ppm)



^{1}H-NMR spectrum for **15** (500MHz, D_2O)