Supporting Information

Synthesis and biological studies of different carbohydrate based prodrugs for their use in the ADEPT-concept

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General. All reactions were performed in flame-dried glassware under an atmosphere of argon. Solvents were dried and purified according to the method defined by Perrin and Armarego. Commercial reagents were used without further purification. Thin-layer chromatography (TLC) was carried out on precoated Alugram SIL G/UV$_{254}$ (0.25 mm) plates from Macherey-Nagel & Co. Column chromatography (CC) was carried out on silica gel 60 from Merck with particle size 0.063–0.200 mm for normal pressure and 0.020–0.063 mm for flash chromatography. IR spectra were determined on a Bruker Vektor 22, UV-VIS spectra on a Perkin-Elmer Lambda 2, and mass spectra on a Finnigan LCQ, Finnigan MAT 95 for EI-HRMS, and a Bruker APEX IV fourier transform ion cyclotron resonance mass spectrometer for ESI-HRMS.

^{1}H NMR spectra were recorded either on a Varian UNITY-300 MHz, Varian Inova 500 MHz, or Varian Inova 600 MHz. ^{13}C-NMR spectra were recorded at 75, 125 or 150 MHz. Spectra were taken at room temperature except otherwise stated in deuterated solvents as indicated using the solvent peak as internal standard.

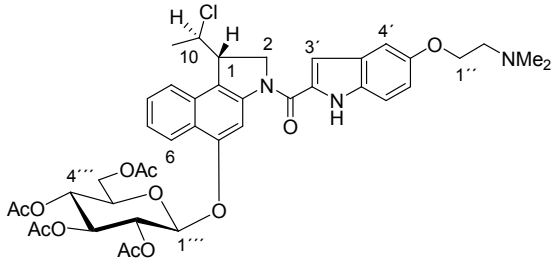
General procedure for the glycosylation, Boc-deprotection and DNA-binder coupling (GP 1): A solution of the phenol **5** (1.00 equiv.) in dry CH_2Cl_2 (45 mL/mmol) was suspended with freshly activated molecular sieves 4 Å (2.00 g/mmol) and stirred for 30 min at ambient temperature. After addition of the trichloroacetimidate (1.00-1.25 equiv.) and cooling to –20 to –18 °C the promoter $BF_3{\cdot}OEt_2$ (0.50 equiv.) in dry CH_2Cl_2 (0.5 mL) was added dropwise and stirred at the given temperature. The end of the reaction was controlled by TLC and subsequently excess $BF_3{\cdot}OEt_2$ (3.00 equiv.) in CH_2Cl_2 (2.0 mL) added, warmed to 25 °C and stirred for the given time. The reaction mixture was filtered through a small celite pad,, thoroughly washed with CH_2Cl_2, the solvent removed and the resulting foam dried under high vaccum for 1 h. The formed salt was dissolved in DMF (65 mL/mmol), the stirred solution cooled to 0 °C and EDC·HCl (3.0 equiv.) followed by DMAI-HCl (**12**) (1.5 equiv.) added. After stirring at 25 °C for 15-30 h the mixture was diluted with EtOAc (70 mL/mmol), Wasser (70 mL/mmol) and satd. $NaHCO_3$-solution (25 mL), the phases separated and water-layer extracted again with EtOAc (4 × 100 mL/mmol). The combined organic layers were washed with satd. NaCl-solution (4 × 60 mL/mmol), dried over $MgSO_4$ and the solvent concetrated in vacuo. The crude material was purified by column chromatography (CC) on silica gel (CH_2Cl_2/MeOH = 10:1) to yield the acetylated prodrugs.

General procedure for the *Zemplén* deactylation (GP 2): A solution of the acetylated prodrugs (1.0 equiv.) in MeOH (individual amounts) was treated at 0 °C with NaOMe-solution (30%-ig in MeOH, 0.15-3.0 equiv.) in MeOH (100 µl) and stirred at ambient

temperature till complete conversion (TLC-control). The mixture was neutralised with HCl (1 M in MeOH from acetylchloride-MeOH) or acetic acid, silica gel (1.5 mg/mg crude material) added and the solvents removed in vacuo. The crude materials were purified by column chromatography (CC) on silica gel (CH_2Cl_2/MeOH = 1:1) and filtered through a membrane-filter or purified by RP-HPLC if necessary.

General Procedure for the synthesis of trichloroacetimidates using polymer-supported DBU (GP 3): To a solution of the anomeric free sugar (1.0 equiv.) in CH_2Cl_2 (8-9 mL/mmol) was added polymer-supported 1,8-Diazabicyclo[5.4.0]undec-7ene (PS-DBU, 0.5 mmol/g, 0.5 equiv.) followed by trichloroacetonitrile (4.0 equiv.). The suspension was stirred at 25 °C for the given time, filtered over celite, and the solvents removed without heating under vaccum. Codestillation with benzol (3 × 50 mL/mmol) afforded the trichloroacetimidates as pure compounds. **7** and **8** are stable at 25 °C for several months without decomposition.

(+)-(1*S*,10*R*)-1-(10-Chloro-ethyl)-3-[(5-(2-(*N*,*N*-dimethylamino)-ethoxy)-indol-2-yl)carbonyl]-1,2-dihydro-3H-benz[*e*]indol-5-yl]-2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranoside ((+)-13):

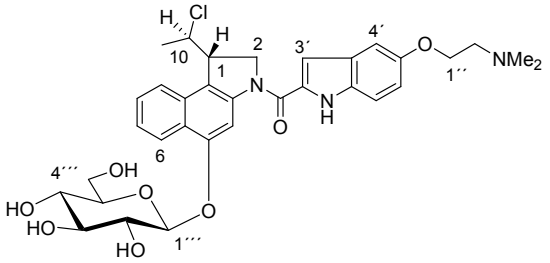


According to GP 1 the glucose trichloroacetimidate **6** (50.9 mg, 110 µmol, 1.1 equiv.) in CH_2Cl_2 (4.5 mL), phenol (+)-(1*S*,10*R*)-**5** (34.6 mg, 100 µmol, 1.0 equiv.) and molecular sieves 4 Å (200 mg) were allowed to react under $BF_3{\cdot}OEt_2$ (7.1 µl, 50.0 µmol, 0.5 equiv.) catalysis at -15 °C for 3.0 h. Additional $BF_3{\cdot}OEt_2$ (42.6 µl, 300 µmol, 3.0 equiv.), 2.5 h at 25 °C, work-up, subsequent reaction with DMAI·HCl (**12**) (42.7 mg, 150 µmol, 1.5 equiv.) and EDC·HCl (57.5 mg, 300 µmol, 3.0 equiv.) for 18 h gave crude material that was purified by CC to afford the title compound **(+)-13** (42.2 mg, 52.5 µmol, 53%) as colourless solid.

R_f = 0.36 (CH_2Cl_2/MeOH = 10:1); $[\alpha]_D^{20}$ = + 4.0 ° (c = 0.4, DMSO); **UV** (MeOH): λ_{max} (lg ε) = 206.5 nm (1.8065), 299.0 (1.6167), 334.5 (1.6077); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3458, 2946, 1750, 1627, 1520, 1463, 1414, 1231, 1040, 764; **^{1}H-NMR** (599.8 MHz, DMSO-d_6, 35 °C): δ = 1.64 (d, *J* = 6.6 Hz, 3 H, H_3-11), 2.01, 2.03, 2.05 (3 × s, 12 H, 4 × $COCH_3$), 2.26 (s, 6 H, NMe_2), 2.68 (t, *J* = 5.8 Hz, 2 H, H_2-2′′), 4.07 (m_c, 3 H, H_2-1′′, H-6_b′′′), 4.25 (m_c, 2 H, H-1, H-5′′′), 4.31 (dd, *J* = 11.8, 4.4 Hz, 1 H, H-6_a′′′), 4.63 (dd, *J* = 11.0, 1.7 Hz, 1 H, H-2_a), 4.76 (m_c, 1 H, H-2_b), 4.80 (dq, *J* = 12.8, 6.2, 2.4 Hz, 1 H, H-10), 5.10 (t, *J* = 9.6 Hz, 1 H, H-4′′′), 5.30 (dd, *J* = 9.7, 8.0 Hz, 1 H, H-2′′′), 5.51 (t, *J* = 9.5 Hz, 1 H, H-3′′′), 5.64 (d, *J* = 7.4 Hz, 1 H, H-1′′′), 6.93 (dd, *J* = 8.9, 2.4 Hz, 1 H, H-6′), 7.17 (s_{br}, 1 H, H-3′), 7.18 (d, *J* = 2.2 Hz, 1 H, H-4′), 7.42 (d, *J* = 8.9 Hz, 1 H, H-7′), 7.47 (t, *J* = 7.6 Hz, 1 H, H-7), 7.59 (t, *J* = 7.6 Hz, 1 H, H-8), 7.98, 8.00 (2 × d, *J* = 8.1 Hz, 2 H, H-6, H-9), 8.22 (s, 1 H, H-4), 11.58 (s, 1 H, NH); **^{13}C-NMR** (125.7 MHz, DMSO-d_6, 35 °C): δ = 20.21, 20.27, 20.32 (4 × $CO\underline{C}H_3$), 23.31 (11-CH_3), 45.41 ($N(CH_3)_2$), 45.87 (C-1), 52.20 (C-2), 57.72 (C-2''), 61.18 (C-10), 61.35 (C-6′′′), 66.17 (C-1′′), 67.93 (C-4′′′), 70.88 (C-2′′′, C-5′′′), 71.71 (C-3′′′), 98.62 (C-1′′′), 102.7 (C-4), 103.2 (C-4′), 105.5 (C-3′), 113.2 (C-7′), 115.9 (C-6′), 120.3 (C-5a), 122.0 (C-6), 122.6 (C-9b), 123.2 (C-9), 124.3 (C-7), 127.4, 127.5 (C-8, C-3a′), 129.4, 130.7, 131.8 (C-2′, C-7a′, C-9a), 141.8 (C-3a), 152.5, 153.0 (C-5, C-5′), 160.2 (NC=O), 169.2, 169.3, 169.4, 170.0 (4 × $\underline{C}OCH_3$); **MS** (ESI): *m/z* (%) = 809.3 (68) $[M + H]^+$, 1636.6 (75) $[2M + Na]^+$;

806.4 (78) $[M - H]^-$, 1614.2 (86) $[2M - H]^-$; **HRMS** $C_{41}H_{46}ClN_3O_{12}$: calcd. 808.28428; found 808.28419 $[M + H]^+$.

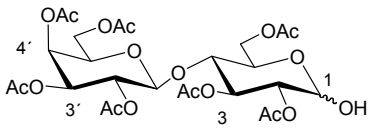
(–)-(1*S*,10*R*)-1-(10-Chloro-ethyl)-3-[(5-(2-(*N*,*N*-dimethylamino)-ethoxy)-indol-2-yl)carbonyl]-1,2-dihydro-3H-benz[*e*]indol-5-yl]-*β*-D-glucopyranoside ((–)-19):



Following GP 2 **(+)-13** (165 mg, 204 µmol, 1.0 equiv.) in MeOH (30.0 mL) was treated with NaOMe (5.51 mg, 19.4 µL, 18.6 µmol, 0.5 equiv.) and stirred for 3.0 h. Work-up and CC gave the title compound **(-)-19** as slightly ocher-couloured solid (106.5 mg, 166 µmol, 82%).

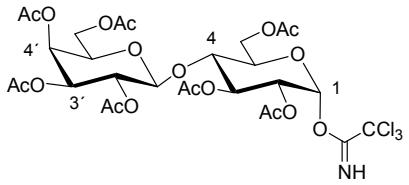
R_f = 0.26 (CH_2Cl_2/MeOH = 1:1); $[\alpha]_D^{20}$ = –24.0 ° (c = 0.4, DMSO); **UV** (MeOH): λ_{max} (lg ε) = 204.5 nm (1.6169), .299.0 (1.3426), 333.0 (1.3167); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3407, 2925, 1623, 1516, 1462, 1415, 1288, 1233, 1178, 1074, 760; ^{1}H-NMR (599.8 MHz, DMSO-d_6, 35 °C): δ = 1.65 (d, *J* = 6.5 Hz, 3 H, H_3-11), 2.24 (s, 6 H, NMe_2), 2.66 (t, *J* = 5.7 Hz, 2 H, H_2-2´´), 3.30 (m_c, 1 H, H-5´´´), 3.34 (t, *J* = 9.0 Hz, 1 H, H-3´´´), 3.39 (t, *J* = 9.0 Hz, 1 H, H-4´´´), 3.47 (m_c, 1 H, H-2´´´), 3.66 (dd, *J* = 11.3, 2.5 Hz, 1 H, H-6_b´´´), 3.75 (d, *J* = 11.0 Hz, 1 H, H-6_a´´´), 4.07 (t, *J* = 5.8 Hz, 1 H, H_2-1´´), 4.26 (d, *J* = 9.0 Hz, 1 H, H-1), 4.37 (s_{br}, 1 H, OH), 4.63 (d, *J* = 11.8 Hz, 1 H, H-2_b), 4.75 (t, *J* = 9.9 Hz, 1 H, H-2_a), 4.83 (m_c, 2 H, H-10), 4.99 (d, *J* = 7.3 Hz, 1 H, H-1´´´), 5.15, 5.40 (2 × s_{br}, 3 H, 3 × OH), 6.93 (dd, *J* = 8.8, 2.0 Hz, 1 H, H-6´), 7.18 (m_c, 2 H, H-3´, H-4´), 7.40 (d, *J* = 8.8 Hz, 1 H, H-7´), 7.43, 7.58 (t, *J* = 7.5 Hz, 2 H, H-7, H-8), 7.96, 8.35 (2 × d, *J* = 8.3 Hz, 2 H, H-6, H-9), 8.24 (s, 1 H, H-4), 11.60 (s, 1 H, NH); **^{13}C-NMR** (150.8 MHz, DMSO-d_6, 35 °C): δ = 23.36 (11-CH_3), 45.51 ($N(CH_3)_2$), 45.93 (C-1), 52.20 (C-2), 57.79 (C-2''), 60.72 (C-6´´´), 61.34 (C-10), 66.28 (C-1´´), 66.51 (C-4´´´), 70.07 (C-2´´´), 71.01 (C-3´´´), 75.38 (C-5´´´), 98.43 (C-1´´´), 100.9 (C-4), 103.3 (C-4´), 105.5 (C-3´), 113.1 (C-7´), 115.9 (C-6´), 118.7 (C-5a), 122.5 (C-9), 122.8 (C-9b), 123.2 (C-6), 123.9 (C-7), 127.3 (C-8), 127.5 (C-3a´), 129.6, 130.8, 131.7 (C-2´, C-7a´, C-9a), 142.0 (C-3a), 151.8, 153.0 (C-5, C-5´), 160.1 (NC=O); **MS** (ESI): *m/z* (%) = 640.3 (100) $[M + H]^+$, 662.2 (21) $[M + Na]^+$; **HRMS** $C_{33}H_{38}ClN_3O_8$: calcd. 640.24202; found 640.24194 $[M + H]^+$.

2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-*α/β*-D-glucopyranose (Lactose heptaacetate)



α-anomer: R_f = 0.11 (pentane/EtOAc = 1:1); **^{1}H-NMR** (300.5 MHz, $CDCl_3$): δ = 1.94, 2.01, 2.02, 2.03, 2.05, 2.10, 2.13 (7 × s, 21 H, 7 × COC*H*$_3$), 3.74 (t, *J* = 9.5 Hz, 1 H, H-4), 3.86 (t, *J* = 6.8 Hz, 1 H, H-5´), 3.95-4.23 (m, 4 H, H-5, H-6$_b$, H-6$_a$´, H-6$_b$´), 4.46 (m, 1 H, H-6$_a$), 4.48 (d, *J* = 7.9 Hz, 1 H, H-1´), 4.79 (dd, *J* = 10.2, 3.6 Hz, 1 H, H-2), 4.93 (dd, *J* = 10.4, 3.4 Hz, 1 H, H-3´), 5.09 (dd, *J* = 10.4, 7.9 Hz, 1 H, H-2´), 5.35 (m$_c$, 2 H, H-1, H-4´), 5.49 (t, *J* = 9.7 Hz, 1 H, H-3) ; **^{13}C-NMR** (75.7 MHz, $CDCl_3$): δ = 20.46, 20.58, 20.70, 20.82, 20.84 (7 × CO<u>C</u>H$_3$), 60.74 (C-6´), 61.82 (C-6), 66.55 (C-4´), 68.03 (C-3), 69.02 (C-2´), 69.51 (C-2), 70.51 (C-5´), 70.96 (C-5), 71.27 (C-3´), 76.25 (C-4), 89.93 (C-1), 100.90 (C-1´), 169.0, 169.6, 170.1, 170.2, 170.3, 170.4, 170.5 (7 × <u>C</u>OCH$_3$) ; **$C_{26}H_{36}O_{18}$** (636.55).

2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-*α*-D-glucopyranose trichloracetimidate (Lactose trichloroacetimidate) (7)

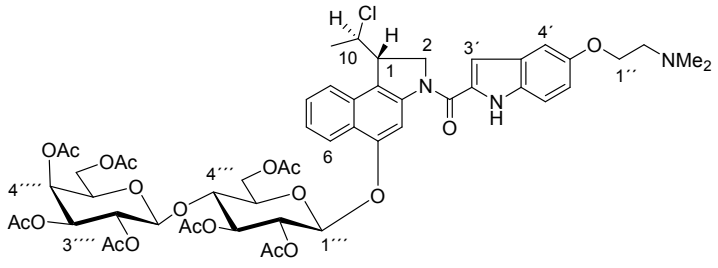


The anomeric free lactoside (2.02 g, 3.17 mmol, 1.00 equiv.) in CH_2Cl_2 (30.0 mL) was treated with PS-DBU (3.10 g, 1.55 mmol, 0.49 equiv.) and trichloroacetonitrile (1.83 g, 1.27 mL, 12.8 mmol, 4.00 equiv.) and stirred for 3 h according to GP 3 giving a colourless foam (2.44 g, 3.12 mmol, 99%).

***R*$_f$** = 0.32 (pentane/EtOAc = 1:1) ; **$[\alpha]_D^{20}$** = –11.8 ° (c = 0.5, MeOH) ; **UV** (CH_3CN): λ_{max} (lg ε) = 204.5 nm (0.5472), 299.0 (0.3436), 334.5 (0.3287) ; **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3417, 2943, 1756, 1626, 1593, 1518, 1461, 1411, 1371, 1231, 1173, 1042, 905, 762, 600 ; **^{1}H-NMR** (300.5 MHz, $CDCl_3$): δ = 1.94, 1.99, 2.02, 2.04, 2.09, 2.13 (6 × s, 21 H, 7 × COC*H*$_3$), 3.79-3.90 (m, 2 H, H-4, H-5´), 4.02-4.17 (m, 4 H, H-5, H-6$_b$, H-6$_a$´, H-6$_b$´), 4.46 (dd, *J* = 11.1, 3.5 Hz, 1 H, H-6$_a$), 4.50 (d, *J* = 7.9 Hz, 1 H, H-1´), 4.93 (dd, *J* = 10.4, 3.4 Hz, 1 H, H-3´), 5.03 (dd, *J* = 10.2, 3.8 Hz, 1 H, H-2), 5.10 (dd, *J* = 10.4, 7.9 Hz, 1 H, H-2´), 5.33 (dd, *J* = 3.4, 0.9 Hz, 1 H, H-4´), 5.54 (t, *J* = 9.8 Hz, 1 H, H-3), 6.46 (d, *J* = 3.8 Hz, 1 H, H-1), 8.65 (s$_{br}$,

1 H, NH) ; **^{13}C-NMR** (125.7 MHz, $CDCl_3$): δ = 20.39, 20.42, 20.55, 20.72, 20.79 (7 × CO<u>C</u>H$_3$), 60.73 (C-6′), 61.45 (C-6), 66.55 (C-4′), 69.08 (C-2′), 69.15 (C-3), 69.90 (C-2), 70.66 (C-5′), 70.86 (C-5), 71.05 (C-3′), 75.81 (C-4), 90.62 (CCl_3), 92.83 (C-1), 101.12 (C-1′), 160.9 (*C*=NH), 169.0, 169.3, 170.0, 170.1, 170.2, 170.3 (7 × <u>C</u>OCH$_3$); **MS** (ESI): *m/z* (%) = 802.0 (56) $[M + Na]^+$, 1582.3.0 (100) $[2M + Na]^+$; **$C_{28}H_{36}O_{18}NCl_3$** (780.96).

(+)-(1*S*,10*R*)-1-(10-Chloro-ethyl)-3-[(5-(2-(*N*,*N*-dimethylamino)-ethoxy)-indol-2-yl)carbonyl]-1,2-dihydro-3H-benz[*e*]indol-5-yl]-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-*β*-D-glucopyranoside ((+)-14):

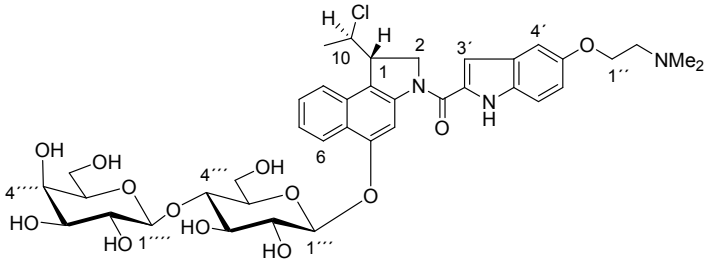


According to GP 1 the lactose trichloroacetimidate **7** (117 mg, 149 µmol, 1.15 equiv.) in CH_2Cl_2 (4.0 mL), phenol (+)-(1S,10R)-**5** (45.0 mg, 130 µmol, 1.0 equiv.) and molecular sieves 4 Å (200 mg) were allowed to react under $BF_3{\cdot}OEt_2$ (8.2 µl, 65.0 µmol, 0.5 equiv.) catalysis at -16 °C for 3.0 h. Additional $BF_3{\cdot}OEt_2$ (41.0 µl, 390 µmol, 3.0 equiv.), 2.0 h at 25 °C, work-up, subsequent reaction with DMAI·HCl (**12**) (59.2 mg, 208 µmol, 1.5 equiv.) and EDC·HCl (74.7 mg, 390 µmol, 3.0 equiv.) for 15 h gave crude material that was purified by CC to afford the title compound **(+)-14** (98.7 mg, 90.1 µmol, 69%) as colourless solid.

***R**$_f$* = 0.29 (CH_2Cl_2/MeOH = 10:1); $[\alpha]_D^{20}$ = +4.0 ° (c = 0.3, MeOH); **UV** (CH_3CN): λ_{max} (lg ε) = 206.0 nm (0.5228), 299.0 (0.3291), 335.5 (0.3143); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 2940, 1754, 1627, 1593, 1518, 1461, 1371, 1230, 1060, 762, 602; **^{1}H-NMR** (599.7 MHz, DMSO-d_6, 35 °C): δ = 1.64 (d, *J* = 6.6 Hz, 3 H, CH_3-11), 1.91, 2.03, 2.04, 2.06, 2.11 (5 × s, 21 H, 7 × COC*H*$_3$), 2.28 (s, 6 H, NMe_2), 2.71 (t, *J* = 5.7, 2 H, H-2′′), 4.00 (t, *J* = 9.4 Hz, 1 H, H-4′′′), 4.04-4.11 (m, 1 H, H-6_b′′′′), 4.09 (t, *J* = 5.8 Hz, 2 H, H-1′′), 4.14 (m, 1 H, H-5′′′), 4.19-4.27 (m, 3 H, H-1, H-6_a′′′, H-6_a′′′′), 4.35 (d, *J* = 11.3 Hz, 1 H, H-6_b′′′), 4.63 (dd, *J* = 10.9, 1.1 Hz, 1 H, H-2_a), 4.75 (d, *J* = 10.6 Hz, 1 H, H-2_b), 4.79 (m, 1 H, H-10), 4.81 (t, *J* = 8.0 Hz, 1 H, H-1′′′′), 4.89 (t, *J* = 10.2, 8.1 Hz, 1 H, H-2′′′′), 5.19 (dd, *J* = 10.3, 3.5 Hz, 1 H, H-3′′′′), 5.22 (dd, *J* = 9.7, 8.1 Hz, 1 H, H-2′′′), 5.26 (d, *J* = 3.4 Hz, 1 H, H-4′′′′), 5.40 (t, *J* = 9.4 Hz, 1 H, H-3′′′), 5.58 (d, *J* = 7.9 Hz, 1 H, H-1′′′), 6.94 (dd, *J* = 8.9, 2.3 Hz, 1 H,

H-6′), 7.17 (d, J = 1.2 Hz, 1 H, H-4′), 7.18 (d, J = 2.0 Hz, 1 H, H-4′), 7.42 (d, J = 8.9 Hz, 1 H, H-7′), 7.46 (t, J = 7.6 Hz, 1 H, H-7), 7.58 (t, J = 7.3Hz, 1 H, H-8), 7.96 (d, J = 8.5 Hz, 1 H, H-9), 7.99 (d, J = 8.4 Hz, 1 H, H-6), 8.19 (s_{br}, 1 H, H-4), 11.55 (s_{br}, 1 H, NH); **^{13}C-NMR** (150.8 MHz, DMSO-d_6, 35 °C): δ = 20.12, 20.17, 20.22, 20.31, 20.36, 20.40 (7 × CO<u>C</u>H$_3$), 23.33 (11-CH$_3$), 45.33 (N(CH$_3$)$_2$), 45.92 (C-1), 52.30 (C-2), 57.65 (C-2''), 60.80 (C-6′′′), 61.19 (C-10), 61.95 (C-6′′′′), 66.06 (C-1′′), 67.04 (C-4′′′′), 68.94 (C-2′′′′), 69.69 (C-5′′′′), 70.32 (C-3′′′′), 71.27 (C-2′′′), 71.96 (C-3′′′, C-5′′′), 75.92 (C-4′′′), 98.48 (C-1′′′), 99.87 (C-1′′′′), 102.9 (C-4), 103.3 (C-4′), 105.5 (C-3′), 113.2 (C-7′), 115.9 (C-6′), 120.3 (C-5a), 122.0 (C-9), 122.7 (C-9b), 123.2 (C-6), 124.3 (C-7), 127.4 (C-8, C-3a′), 129.4, 130.8, 131.8 (C-2′, C-7a′, C-9a), 141.8 (C-3a), 152.6, 152.9 (C-5, C-5′), 160.3 (NC=O), 169.0, 169.2, 169.4, 169.8, 170.4 (7 × <u>C</u>OCH$_3$); **MS** (ESI): *m/z* (%) = 1096.45 (100) $[M + H]^+$; **HRMS** $C_{53}H_{62}ClN_3O_{20}$: calcd. 1096.36880; found 1096.36907 $[M + H]^+$.

(1*S*,10*R*)-1-(10-Chloro-ethyl)-3-[(5-(2-(*N*,*N*-dimethylamino)-ethoxy)-indol-2-yl)carbonyl]-1,2-dihydro-3H-benz[*e*]indol-5-yl]-(D-galactopyranosyl)-(β1→4)-β-D-glucopyranoside (20):



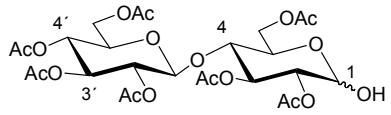
Following GP 2 **(+)-14** (67.0 mg, 61.1 µmol, 1.0 equiv.) in MeOH (8 mL) was treated with NaOMe (11.6 mg, 41 µL, 214 µmol, 3.5 equiv., in 1 mL MeOH) and stirred for 5.0 h. Work-up with acetic acid and RP-HPLC gave the title compound **20** as colourless solid (36.7 mg, 45.8 µmol, 75%).

***R**$_f$* = 0.22 (CH_2Cl_2/MeOH = 1:1.5); **UV** (CH_3CN): λ_{max} (lg ε) = 206.0 nm (0.5228), 299.0 (0.3291), 335.5 (0.3143); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 2940, 1754, 1627, 1593, 1518, 1461, 1371, 1230, 1060, 762, 602; **^{1}H-NMR** (599.7 MHz, DMSO-d_6, 35 °C): δ = 1.65 (d, J = 6.6 Hz, 3 H, CH$_3$-11), 2.27 (s, 6 H, NMe$_2$), 2.69 (t, J = 5.8 Hz, 2 H, H-2′′), 3.35 (dd, J = 9.5, 3.5 Hz, 1 H, H-3′′′′), 3.38 (dd, J = 9.5, 7.5 Hz, 1 H, H-2′′′′), 3.50 (t, J = 6.1 Hz, 1 H, H-5′′′′), 3.46-3.64 (m, 5 H, H-2′′′, H-3′′′, H-5′′′′, H-6$_{a,b}$′′′′), 3.66 (d, J = 2.7 Hz, 1 H, H-4′′′′), 3.82 (m_c, 1 H, H-6$_{a,b}$′′′′), 4.08 (t, J = 5.9 Hz 2 H, H-1′′), 4.25 (dt, J = 9.4, 2.4 Hz, 1 H, H-1), 4.39-4.61 (br,

6 H, 6 × OH), 4.31 (d, J = 7.5 Hz, 1 H, H-1′′′′), 4.63 (dd, J = 10.9, 1.6 Hz, 1 H, H-2_a), 4.76 (d, J = 9.7 Hz, 1 H, H-2_b), 4.82 (ddd, J = 8.9, 6.4, 1.9 Hz, 1 H, H-10), 5.03 (s_{br}, 1 H, H-1′′′), 5.60 (s_{br}, 1 H, OH), 6.92 (dd, J = 8.9, 2.3 Hz, 1 H, H-6′), 7.17 (s_{br}, 1 H, H-3′), 7.18 (d, J = 2.2 Hz, 1 H, H-4′), 7.40 (d, J = 8.9 Hz, 1 H, H-7′), 7.44 (t, J = 7.6 Hz, 1 H, H-7), 7.57 (t, J = 7.6Hz, 1 H, H-8), 7.97 (d, J = 8.4 Hz, 1 H, H-9), 8.24 (s_{br}, 1 H, H-4), 8.35 (d, J = 8.5 Hz, 1 H, H-6), 11.60 (s_{br}, 1 H, NH); **^{13}C-NMR** (150.8 MHz, DMSO-d_6, 35 °C): δ = 23.36 (11-CH_3), 45.40 (N(CH_3)$_2$), 45.91 (C-1), 52.03 (C-2), 57.69 (C-2′′), 59.79 (C-6′′′), 60.40 (C-6′′′′), 61.31 (C-10), 66.12 (C-1′′), 68.13 (C-4′′′′), 70.58 (C-2′′′′), 73.09 (C-5′′′′), 73.20 (C-3′′′′), 74.74, 74.94 (C-2′′′, C-3′′′), 75.51 (C-5′′′), 79.41 (C-4′′′), 101.2 (C-1′′′), 102.0 (C-4), 103.3 (C-4′), 103.7 (C-1′′′′), 105.4 (C-3′), 113.3 (C-7′), 115.9 (C-6′), 119.0 (C-5a), 122.9 (C-9), 122.9 (C-6), 123.3 (C-9b), 123.7 (C-7), 127.3 (C-3a′), 127.5 (C-8), 129.4, 130.8, 131.7 (C-2′, C-7a′, C-9a), 142.0 (C-3a), 152.9, 153.3 (C-5, C-5′), 160.1 (NC=O); **MS** (ESI): *m/z* (%) = 802.3 (100) $[M + H]^+$; **HRMS** $C_{39}H_{48}ClN_3O_{13}$: calcd. 802.29484; found 802.29496 $[M + H]^+$.

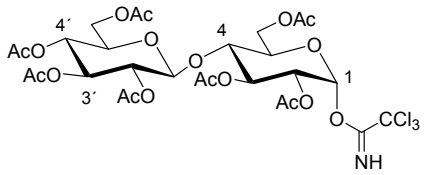
Chromatographic purification of crude 20: A solution of 60.0 mg of crude **20** in 3.00 mL CH_3CN/H_2O = 1:1 + 0.05% HOAc was separated (injection volume 0.50 mL) by semipreparative RP-HPLC (Kromasil 100 C18, 250 × 20 mm, particle size: 7 µm, isocratic CH_3CN/H_2O = 1:3 + 0.05% HOAc, flow: 12 mL·min^{-1}; UV-detector: λ = 299 nm, *Jasco*-module) to provide pure **20** (t_R = 5.6 min).

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α/β-D-glucopyranose (Cellobiose heptaacetate)



α-anomer: R_f = 0.15 (pentane/EtOAc = 1:1); **^{1}H-NMR** (300.5 MHz, $CDCl_3$): δ = 1.99, 2.01, 2.03, 2.04, 2.08, 2.10, 2.14 (7 × s, 21 H, 7 × COCH_3), 2.98 (s_{br}, 1 H, OH), 3.68 (ddd, J = 9.5, 4.0, 2.0 Hz, 1 H, H-5′), 3.75 (t, J = 9.5 Hz, 1 H, H-4), 4.01-4.21 (m, 3 H, H-5, H-6_a, H-6_a′), 4.39 (dd, J = 12.4, 4.1 Hz, 1 H, H-6_b′), 4.53 (m_c, 1 H, H-6_b), 4.54 (d, J = 7.9 Hz, 1 H, H-1′), 4.81 (dd, J = 10.2, 3.6 Hz, 1 H, H-2), 4.93 (dd, J = 10.4, 8.1 Hz, 1 H, H-2′), 5.08 (t, J = 9.4 Hz, 1 H, H-4′), 5.16 (t, J = 9.3 Hz, 1 H, H-3′), 5.36 (d, J = 3.6 Hz, 1 H, H-1), 5.50 (t, J = 9.0 Hz, 1 H, H-3) ; **^{13}C-NMR** (75.5 MHz, $CDCl_3$): δ = 20.43, 20.51, 20.55, 20.62, 20.64, 20.79 (7 × CO$\underline{C}$H$_3$), 61.45, 61.68 (C-6, C-6′), 67.67 (C-4′), 67.95 (C-5), 69.23 (C-3), 71.20 (C-2), 71.49 (C-2′), 71.73 (C-5′), 72.86 (C-3′), 76.43 (C-4), 89.82 (C-1), 100.5 (C-1′), 169.0, 169.2, 169.7, 170.2, 170.3, 170.4, 170.5 (7 × $\underline{C}$OCH$_3$) ; **$C_{26}H_{36}O_{18}$** (636.55).

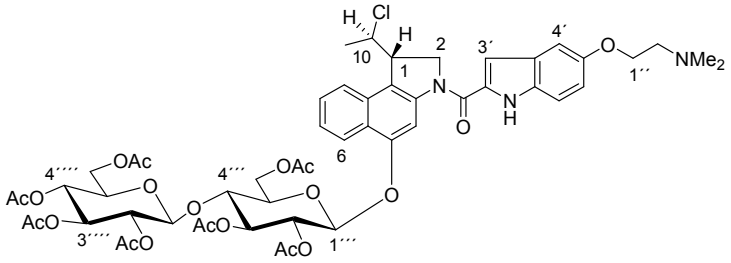
2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranose trichloracetimidate (Cellobiose trichloroacetimidate) (8):



The anomeric free lactoside (2.02 g, 3.17 mmol, 1.00 equiv.) in CH_2Cl_2 (30.0 mL) was treated with PS-DBU (3.00 g, 1.50 mmol, 0.47 equiv.) and trichloroacetonitrile (1.83 g, 1.27 mL, 12.8 mmol, 4.00 equiv.) and stirred for 3 h according to GP 3 giving a colourless solid (2.32 g, 2.97 mmol, 94%).

***R*$_f$** = 0.35 (pentane/EtOAc = 1:1); **^{1}H-NMR** (300.5 MHz, $CDCl_3$): δ = 1.99, 2.01, 2.02, 2.03, 2.05, 2.10, 2.12 (7 × s, 21 H, 7 × COC*H*$_3$), 3.68 (ddd, *J* = 9.1, 4.0, 2.0 Hz, 1 H, H-5´), 3.85 (t, *J* = 9.7 Hz, 1 H, H-4), 4.08 (dd, *J* = 12.6, 2.0 Hz, 1 H, H-6$_a$´), 4.15 (m$_c$, 1 H, H-5), 4.16 (dd, *J* = 12.8, 4.5 Hz, 1 H, H-6$_a$), 4.37 (dd, *J* = 12.6, 4.2 Hz, 1 H, H-6$_b$´), 4.52 (m$_c$, 1 H, H-6$_b$), 4.54 (d, *J* = 8.1 Hz, 1 H, H-1´), 4.94 (dd, *J* = 9.0, 8.2 Hz, 1 H, H-2´), 5.07 (dd, *J* = 10.2, 3.7 Hz, 1 H, H-2), 5.09 (t, *J* = 9.0 Hz, 1 H, H-4´), 5.15 (t, *J* = 9.1 Hz, 1 H, H-3´), 5.53 (t, *J* = 9.8 Hz, 1 H, H-3), 6.49 (d, *J* = 3.8 Hz, 1 H, H-1), 8.68 (s$_{br}$, 1 H, NH) ; **^{13}C-NMR** (75.5 MHz, $CDCl_3$): δ = 20.37, 20.45, 20.50, 20.58, 20.72 (7 × CO<u>C</u>H$_3$), 61.28 (C-6), 61.43 (C-6´), 67.58 (C-4´), 69.16 (C-3), 69.74 (C-2), 70.85 (C-5), 71.55 (C-2´), 71.89 (C-5´), 72.94 (C-3´), 76.00 (C-4), 90.56 (CCl_3), 92.73 (C-1), 100.8 (C-1´), 160.8 (*C*=NH), 169.0, 169.2, 169.3, 169.9, 170.0, 170.2, 170.4 (7 × <u>C</u>OCH$_3$) ; **MS** (ESI): *m/z* (%) = 802.0 (52) [M + Na]$^+$, 1582.3.0 (100) [2M + Na]$^+$; **$C_{28}H_{36}O_{18}NCl_3$** (780.94).

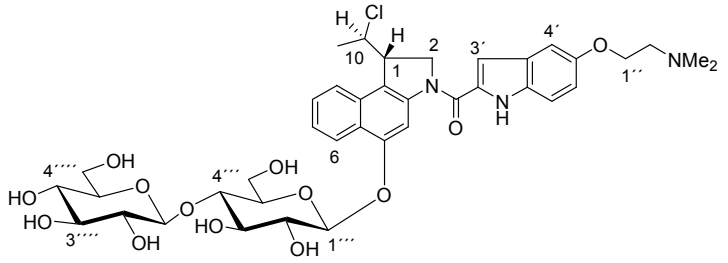
(+)-(1*S*,10*R*)-1-(10-Chloro-ethyl)-3-[(5-(2-(*N*,*N*-dimethylamino)-ethoxy)-indol-2-yl)carbonyl]-1,2-dihydro-3H-benz[*e*]indol-5-yl]-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-*β*-D-glucopyranoside ((+)-15):



A reaction identical to the procedure giving the lactose derivative **(+)-14** using the cellobiose trichloroacetimdiate **8** instead afforded the title compound **(+)-15** as colourless foam (95.7 mg, 87.3 µmol, 67%).

R_f = 0.42 (CH_2Cl_2/MeOH = 10:1); $[\alpha]_D^{20}$ = –11.8 ° (c = 0.5, MeOH); **UV** (CH_3CN): λ_{max} (lg ε) = 204.5 nm (0.5472), 299.0 (0.3436), 334.5 (0.3287); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3417, 2943, 1756, 1626, 1593, 1518, 1461, 1411, 1371, 1231, 1173, 1042, 905, 762, 600; **^{1}H-NMR** (599.7 MHz, $CDCl_3$): δ = 1.63 (d, *J* = 6.4 Hz, 3 H, CH_3-11), 1.92, 1.98, 2.00, 2.02, 2.03, 2.06 (6 × s, 21 H, 7 × COC*H*$_3$), 2.27 (s, 6 H, NMe_2), 2.70 (t, *J* = 5.5, 2 H, H-2´´), 3.96 (t, *J* = 9.4 Hz, 1 H, H-4´´´), 3.97-4.17 (m, 2 H, H-5´´´´, H-6_b´´´´), 4.08 (t, *J* = 5.7 Hz, 2 H, H-1´´), 4.14 (m, 1 H, H-5´´´), 4.20 (dd, *J* = 11.8, 6.0 Hz, 1 H, H-6_a´´´), 4.26 (m, 1 H, H-1), 4.27 (dd, *J* = 12.7, 4.2 Hz, 1 H, H-6_a´´´´), 4.36 (d, *J* = 11.6 Hz, 1 H, H-6_b´´´), 4.62 (d, *J* = 10.7 Hz, 1 H, H-2_a), 4.68 (t, *J* = 8.8 Hz, 1 H, H-3´´´´), 4.75 (d, *J* = 10.6 Hz, 1 H, H-2_b), 4.79 (m, 1 H, H-10), 4.87 (t, *J* = 8.4 Hz, 1 H, H-1´´´´), 4.91 (t, *J* = 9.8 Hz, 1 H, H-4´´´´), 5.20 (m, 1 H, H-2´´´), 5.27 (t, *J* = 9.0 Hz, 1 H, H-2´´´´), 5.39 (t, *J* = 9.4 Hz, 1 H, H-3´´´), 5.55 (d, *J* = 7.9 Hz, 1 H, H-1´´´), 6.93 (d, *J* = 8.6 Hz, 1 H, H-6´), 7.15, 7.17 (2 × s_{br}, 2 H, H-3´, H-4´), 7.41 (d, *J* = 8.9 Hz, 1 H, H-7´), 7.46 (t, *J* = 7.4 Hz, 1 H, H-7), 7.50 (t, *J* = 7.2 Hz, 1 H, H-8), 7.94 (d, *J* = 8.4 Hz, 1 H, H-9), 7.99 (d, *J* = 8.4 Hz, 1 H, H-6), 8.17 (s_{br}, 1 H, H-4), 11.53 (s_{br}, 1 H, NH); **^{13}C-NMR** (150.8 MHz, $CDCl_3$): δ = 20.12, 20.17, 20.22, 20.31, 20.36, 20.40 (7 × CO<u>C</u>H$_3$), 23.32 (11-CH_3), 45.38 (N(CH_3)$_2$), 45.90 (C-1), 52.28 (C-2), 57.69 (C-2´´), 61.18 (C-10), 61.45 (C-6´´), 61.89 (C-6´´´), 66.12 (C-1´´), 67.70 (C-4´´´´), 70.44 (C-5´´´´), 71.19 (C-2´´´, C-3´´´´), 71.69 (C-3´´´), 71.99 (C-5´´´), 72.23 (C-2´´´´), 76.11 (C-4´´´), 98.52 (C-1´´´), 99.49 (C-1´´´´), 102.9 (C-4), 103.2 (C-4´), 105.5 (C-3´), 113.2 (C-7´), 115.9 (C-6´), 120.3 (C-5a), 122.0 (C-9), 122.7 (C-9b), 123.2 (C-6), 124.3 (C-7), 127.4, 127.5 (C-8, C-3a´), 129.4, 130.7, 131.7 (C-2´, C-7a´, C-9a), 141.8 (C-3a), 152.5, 153.0 (C-5, C-5´), 160.3 (NC=O), 168.9, 169.1, 169.2, 169.4, 169.5, 169.9, 170.4 (7 × <u>C</u>OCH$_3$); **MS** (ESI): *m/z* (%) = 1096.45 (100) $[M + H]^+$; **HRMS** $C_{53}H_{62}ClN_3O_{20}$: calcd. 1096.36880; found 1096.36914 $[M + H]^+$.

(1*S*,10*R*)-1-(10-Chloro-ethyl)-3-[(5-(2-(*N*,*N*-dimethylamino)-ethoxy)-indol-2-yl)carbonyl]-1,2-dihydro-3H-benz[*e*]indol-5-yl]-(D-glucopyranosyl)-(β1→4)-β-D-glucopyranoside (21):

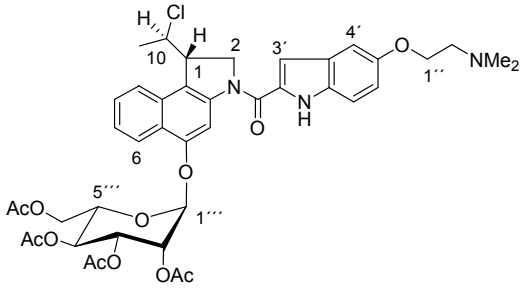


Following GP 2 **(+)-15** (65.9 mg, 60.1 µmol, 1.0 equiv.) in MeOH (8 mL) was treated with NaOMe (11.4 mg, 40 µL, 210 µmol, 3.5 equiv., in 1 mL MeOH) and stirred for 1.5 h. Work-up with acetic acid and RP-HPLC gave the title compound **21** as colourless cotton-like solid (24.1 mg, 30.1 µmol, 50%).

R_f = 0.25 (CH_2Cl_2/MeOH = 1:1.5); **UV** (MeOH): λ_{max} (lg ε) = 253.0 nm (1.1978), 297.0 (1.2604), 330.5 (1.2348); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3386, 2925, 1715, 1623, 1533, 1409, 1212, 1072, 759; **^{1}H-NMR** (599.7 MHz, DMSO-d_6, 35 °C): δ = 1.65 (d, *J* = 6.7 Hz, 3 H, CH_3-11), 2.51 (s_{br}, 6 H, NMe_2), 3.00-3.13 (m, 4 H, H-2´´, H-2´´´´, H-4´´´´), 3.17-3.27 (m, 2 H, H-5´´´, H-5´´´´), 3.45 (dd, *J* = 11.4, 6.4 Hz, 1 H, H-6_a´´´´), 3.48-3.55 (m, 3 H, H-2´´´, H-3´´´, H-3´´´´), 3.62 (t, *J* = 8.7 Hz, 1 H, H-4´´´), 3.73 (dd, *J* = 11.3, 1.5 Hz, 1 H, H-6_b´´´´), 3.78 (dd, *J* = 10.2, 1.6 Hz, 1 H, H-6_a´´´), 3.84 (d, *J* = 11.3 Hz, 1 H, H-6_b´´´), 4.20 (t, *J* = 5.4 Hz, 2 H, H-1´´), 4.26 (dt, *J* = 9.3, 2.3 Hz, 1 H, H-1), 4.37 (d, *J* = 7.9 Hz, 1 H, H-1´´´´), 4.59 (s_{br}, 2 H, 2 × OH), 4.62 (dd, *J* = 11.1, 1.8 Hz, 1 H, H-2_a), 4.75 (d, *J* = 10.1 Hz, 1 H, H-2_b), 4.78 (s_{br}, 1 H, OH), 4.82 (dq, *J* = 6.8, 2.5 Hz, 1 H, H-10), 4.96-5.03 (m_{br}, 4 H, H-1´´´, 3 × OH), 5.60 (s_{br}, 1 H, OH), 6.96 (dd, *J* = 8.9, 2.4 Hz, 1 H, H-6´), 7.18 (s_{br}, 1 H, H-3´), 7.21 (d, *J* = 2.2 Hz, 1 H, H-4´), 7.42 (d, *J* = 8.8 Hz, 1 H, H-7´), 7.44 (t, *J* = 8.0 Hz, 1 H, H-7), 7.57 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1 H, H-8), 7.97 (d, *J* = 8.4 Hz, 1 H, H-9), 8.22 (s_{br}, 1 H, H-4), 8.35 (d, *J* = 8.5 Hz, 1 H, H-6), 11.63 (s_{br}, 1 H, NH); **^{13}C-NMR** (150.8 MHz, DMSO-d_6, 35 °C): δ = 20.95 ($\underline{C}H_3CO_2H$), 23.37 (11-CH_3), 44.36 ($N(CH_3)_2$), 45.89 (C-1), 52.02 (C-2), 56.84 (C-2''), 59.66 (C-6´´´), 61.00 (C-6´´´´), 61.32 (C-10), 64.78 (C-1´´), 70.01 (C-4´´´´), 73.27 (C-2´´´´), 73.06, 74.82, 74.97 (C-2´´´, C-3´´´, C-3´´´´), 76.39, 76.76 (C-5´´´, C-5´´´´), 101.2 (C-1´´´), 103.0 (C-1´´´´), 103.6 (C-4´), 105.4 (C-3´), 113.2 (C-7´), 115.8 (C-6´), 119.0 (C-5a), 122.9 (C-9, C-9b), 123.3 (C-6), 123.7 (C-7), 127.3 (C-3a´), 127.4 (C-8), 129.4, 131.0, 131.8 (C-2´, C-7a´, C-9a), 141.9 (C-3a), 152.6, 153.3 (C-5, C-5´), 160.1 (NC=O), 171.9 (CO_2H); **MS** (ESI): *m/z* (%) = 802.3 (100) $[M + H]^+$; **HRMS** $C_{39}H_{48}ClN_3O_{13}$: calcd. 802.29484; found 802.29482 $[M + H]^+$.

Chromatographic purification of crude 21: the same conditions as described for **20** provided pure **21** (t_R = 4.7 min).

(+)-(1*S*,10*R*)-1-(10-Chloro-ethyl)-3-[(5-(2-(*N*,*N*-dimethylamino)-ethoxy)-indol-2-yl)carbonyl]-1,2-dihydro-3H-benz[*e*]indol-5-yl]-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside ((+)-16):

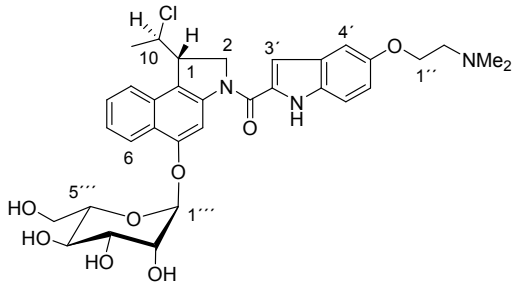


According to GP 1 mannose trichloroacetimidate **9** (77.6 mg, 168 µmol, 1.1 equiv.) in CH_2Cl_2 (7.0 mL), phenol (+)-(1*S*,10*R*)-**5** (52.8 mg, 152 µmol, 1.0 equiv.) and molecular sieves 4 Å (380 mg) were allowed to react under $BF_3{\cdot}OEt_2$ (9.6 µl, 76.0 µmol, 0.5 equiv.) catalysis at -20 °C for 100 min. Additional $BF_3{\cdot}OEt_2$ (57.8 µl, 456 µmol, 3.0 equiv.), 2.0 h at 25 °C, work-up, subsequent reaction with DMAI·HCl (**12**) (65.0 mg, 228 µmol, 1.5 equiv.) and EDC·HCl (87.3 mg, 456 µmol, 3.0 equiv.) for 15 h gave crude material that was purified by CC to afford the title compound **(+)-16** (80.0 mg, 99.0 µmol, 65%) as colourless solid.

R_f = 0.43 (CH_2Cl_2/MeOH = 9:1); $[\alpha]_D^{20}$ = +77.8 ° (c = 0.8, MeOH); ^{1}H-NMR (599.8 MHz, DMSO-d_6, 35 °C): δ = 1.65 (d, *J* = 6.7 Hz, 3 H, H_3-11), 1.87, 2.04, 2.19 (3 × s, 12 H, 4 × COCH_3), 2.24 (s, 6 H, NMe_2), 2.64 (t, *J* = 5.9 Hz, 2 H, H-2′′), 3.96 (dd, *J* = 12.2, 2.4 Hz, 1 H, H-6_b′′′), 4.07 (t, *J* = 5.9 Hz, 1 H, H-1′′), 4.09 (ddd, *J* = 10.0, 5.6, 2.3 Hz, 1 H, H-5′′′), 4.21 (dd, *J* = 12.3, 5.7 Hz, 1 H, H-6_a′′′), 4.28 (td, *J* = 9.3, 2.3 Hz, 1 H, H-1), 4.64 (dd, *J* = 11.0, 2.3 Hz, 1 H, H-2_a), 4.77(dd, *J* = 10.6, 9.9 Hz, 1 H, H-2_b), 4.81 (ddd, *J* = 13.4, 6.2, 2.4 Hz, 1 H, H-10), 5.27 (t, *J* = 10.1 Hz, 1 H, H-4′′′), 5.55 (dd, *J* = 3.5, 1.7 Hz, 1 H, H-2′′′), 5.58 (dd, *J* = 10.0, 3.5 Hz, 1 H, H-3′′′), 5.90 (d, *J* = 1.1 Hz, 1 H, H-1′′′), 6.93 (dd, *J* = 8.9, 2.4 Hz, 1 H, H-6′), 7.18 (2 × d, *J* = 2.2 Hz, 2 H, H-3′, H-4′), 7.40 (d, *J* = 8.9 Hz, 1 H, H-7′), 7.54 (ddd, *J* = 8.2, 6.8, 1.1 Hz, 1 H, H-7), 7.62 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1 H, H-8), 8.03 (d, *J* = 8.4 Hz, 1 H, H-9), 8.16 (d, *J* = 8.5 Hz, 1 H, H-6), 8.30 (s, 1 H, H-4), 11.56 (s, 1 H, NH); **^{13}C-NMR** (125.7 MHz, DMSO-d_6, 35 °C): δ = 20.09, 20.31, 20.37, 20.51 (4 × CO<u>C</u>H_3), 23.29 (11-CH_3), 45.49 ($N(CH_3)_2$), 45.91 (C-1), 51.99 (C-2), 57.77 (C-2′′), 61.24 (C-10),

61.66 (C-6′′′), 65.22 (C-4′′′), 66.28 (C-1′′), 68.58 (C-2′′′, C-3′′′), 68.97 (C-3′′′), 95.70 (C-1′′′), 101.8 (C-4), 103.3 (C-4′), 105.5 (C-3′), 113.1 (C-7′), 115.9 (C-6′), 119.9 (C-5a), 122.0 (C-6), 122.4 (C-9b), 123.3 (C-9), 124.4 (C-7), 127.5 (C-8, C-3a′), 129.6, 130.7, 131.7 (C-2′, C-7a′, C-9a), 141.8 (C-3a), 151.0, 153.0 (C-5, C-5′), 160.0 (NC=O), 169.4, 169.5, 169.7, 169.8 (4 × $\underline{C}OCH_3$); **MS** (ESI): *m/z* (%) = 808.3 (100) $[M + H]^+$; **HRMS** $C_{41}H_{46}ClN_3O_{12}$: calcd. 808.28456; found 808.28428 $[M + H]^+$.

(+)-(1*S*,10*R*)-1-(10-Chloro-ethyl)-3-[(5-(2-(*N*,*N*-dimethylamino)-ethoxy)-indol-2-yl)carb-onyl]-1,2-dihydro-3H-benz[*e*]indol-5-yl]-α-D-mannopyranoside ((+)-22):

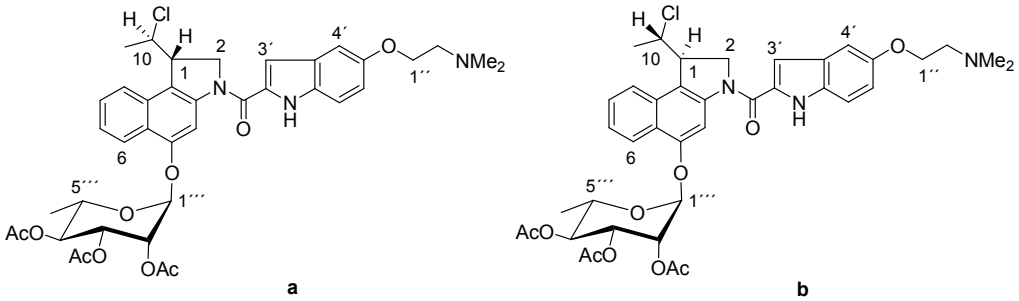


Following GP 2 **(+)-16** (28.1 mg, 34.8 µmol, 1.0 equiv.) in MeOH (30 mL) was treated with NaOMe (0.94 mg, 3.3 µL, 17.4 µmol, 0.5 equiv.) and stirred for 30 min. Work-up and CC gave the title compound **(+)-22** as colourless solid (18.3 mg, 28.6 µmol, 82%) which can be crystallised from a minimum amount methanol/ *n*-hexane.

R_f = 0.45 (CH_2Cl_2/MeOH = 1:1); $[\alpha]_D^{20}$ = +105.0 ° (c = 0.8, MeOH); **UV** (MeOH) λ_{max} (lg ε) = 201.5 nm (1.8119), 204.0 (1.7961), 300.0 (1.5398), 331.0 (1.4299); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3385, 2928, 1624, 1591, 1516, 1461, 1415, 1288, 1265, 1233, 1178, 1120, 1069, 841, 760, 690; **^{1}H-NMR** (599.8 MHz, DMSO-d_6, 35 °C): δ = 1.65 (d, *J* = 6.7 Hz, 3 H, H-11), 2.24 (s, 6 H, NMe_2), 2.65 (t, *J* = 5.8 Hz, 2 H, H-2′′), 3.43 (ddd, *J* = 9.2, 4.4, 2.3 Hz, 1 H, H-5′′′), 3.51 (dd, *J* = 11.8, 4.4 Hz, 1 H, H-6_a′′′), 3.56 (dd, *J* = 11.8, 2.2 Hz, 1 H, H-6_b′′′), 3.66 (t, *J* = 9.5 Hz, 1 H, H-4′′′), 3.94 (dd, *J* = 9.3, 3.0 Hz, 1 H, H-3′′′), 4.07 (m_c, 3 H, H-1′′, H-2′′′), 4.23 (dt, *J* = 9.2, 2.2 Hz, 1 H, H-1), 4.38 (s_{br}, 1 H, OH), 4.62 (dd, *J* = 11.0, 2.0 Hz, 1 H, H-2_a), 4.78 (m_c, 2 H, H-10, H-2_b), 4.88, 4.95, 5.20 (3 × s_{br}, 3 H, 3 × OH), 5.69 (s_{br}, 1 H, H-1′′′), 6.93 (dd, *J* = 8.8, 2.2 Hz, 1 H, H-6′), 7.18 (m_c, 2 H, H-3′, H-4′), 7.40 (d, *J* = 8.9 Hz, 1 H, H-7′), 7.46, 7.58 (t, *J* = 8.0 Hz, 2 H, H-7, H-8), 7.97, 8.15 (2 × d, *J* = 8.1 Hz, 2 H, H-6, H-9), 8.22 (s, 1 H, H-4), 11.60 (s, 1 H, NH); **^{13}C-NMR** (150.8 MHz, DMSO-d_6, 35 °C): δ = 23.36 (11-CH_3), 45.51 ($N(CH_3)_2$), 45.93 (C-1), 52.20 (C-2), 57.79 (C-2′′), 60.72 (C-6′′′), 61.34 (C-10), 66.28 (C-1′′), 66.51 (C-4′′′), 70.07 (C-2′′′), 71.01 (C-3′′′), 75.38 (C-5′′′), 98.43

(C-1´´´), 100.9 (C-4), 103.3 (C-4´), 105.5 (C-3´), 113.1 (C-7´), 115.9 (C-6´), 118.7 (C-5a), 122.5 (C-6), 122.8 (C-9b), 123.2 (C-9), 123.9 (C-7), 127.3 (C-8), 127.5 (C-3a´), 129.6, 130.8, 131.7 (C-2´, C-7a´, C-9a), 142.0 (C-3a), 151.8, 153.0 (C-5, C-5´), 160.1 (NC=O); **MS** (ESI): *m/z* (%) = 640.2 (100) $[M + H]^+$, 1280.9 (15) $[2M + H]^+$; **HRMS** $C_{33}H_{38}ClN_3O_8$: calcd. 640.24202; found 640.24211 $[M + H]^+$.

(1*SR*,10*RS*)-1-(10-Chloro-ethyl)-3-[(5-(2-(*N*,*N*-dimethylamino)-ethoxy)-indol-2-yl) carbonyl]-1,2-dihydro-3H-benz[*e*]indol-5-yl]-2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosides (17):

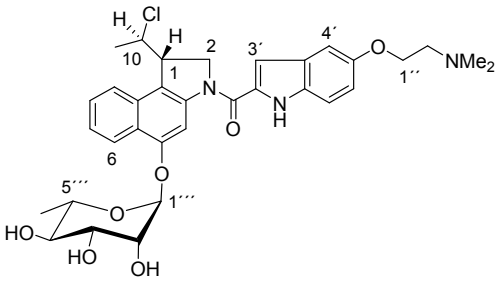


According to GP 1 the rhamnose trichloroacetimidate **10** (66.9 mg, 154 µmol, 1.05 equiv.) in CH_2Cl_2 (7.0 mL), phenol (+/–)-(1*RS,*10*SR*)-**5** (50.7 mg, 146 µmol, 1.0 equiv.) and molecular sieves 4 Å (350 mg) were allowed to react under $BF_3{\cdot}OEt_2$ (9.3 µl, 73.2 µmol, 0.5 equiv.) catalysis at –20 °C for 105 min. Additional $BF_3{\cdot}OEt_2$ (55.6 µl, 439 µmol, 3.0 equiv.), 1.5 h at 25 °C, work-up, subsequent reaction with DMAI·HCl (**12**) (62.3 mg, 219 µmol, 1.5 equiv.) and EDC·HCl (83.8 mg, 438 µmol, 3.0 equiv.) for 19.5 h gave crude material that was purified by CC to afford the title compound **17** (60.0 mg, 81.0 µmol, 54%) as colourless solids.

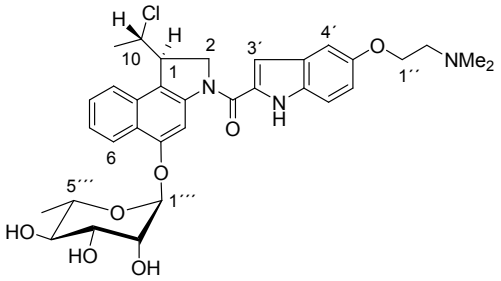
R_f = 0.45 (CH_2Cl_2/MeOH = 10:1); **^{1}H-NMR** (300.1 MHz, DMSO-d_6, 35 °C): δ = 1.16, 1.20 (2 × d, *J* = 6.2 Hz, 3 H, H_3-6), 1.66 (d, *J* = 6.6 Hz, 3 H, H_3-11), 2.04, 2.07, 2.08, 2.17, 2.19 (5 × s, 9 H, 3 × COCH_3), 2.26 (s, 6 H, NMe_2), 2.67 (t, *J* = 5.8 Hz, 2 H, H_2-2´´), 4.00 (dq, *J* = 9.8, 6.3 Hz, 1 H, H-5´´´), 4.07 (t, *J* = 5.7 Hz, 2 H, H_2-1´´), 4.28 (dd, *J* = 6.0, 2.5 Hz, 1 H, H-1), 4.65 (d, *J* = 10.9 Hz, 1 H, H-2_a), 4.75 (d, *J* = 10.0 Hz, 1 H, H-2_b), 4.68.4.78 (m, 1 H, H-10), 5.09, 5.10 (2 × t, *J* = 9.9 Hz, 1 H, H-4´´´), 5.51-5.58 (m, 2 H, H-2´´´, H-3´´´), 5.78, 5.83 (2 × s_{br}, 1 H, H-1´´´), 6.92, 6.95 (2 × s_{br}, 1 H, H-6´), 7.06-7.28 (s_{br}, 2 H, H-3´, H-4´), 7.41 (d, *J* = 8.9 Hz, 1 H, H-7´), 7.53 (t, *J* = 7.6 Hz, 1 H, H-7), 7.61 (t, *J* = 7.6 Hz, 1 H, H-8), 8.01 (d, *J* = 8.3 Hz, 1 H, H-9), 8.17 (d, *J* = 8.3 Hz, 1 H, H-6), 8.32, 8.36 (2 × s_{br}, 1 H, H-4), 11.60,

11.64 (2 × s_{br}, 1 H, NH); **^{13}C-NMR** (75.5 MHz, DMSO-d_6, 35 °C): δ = 17.19, 17.23 (C-6′′′), 20.39, 20.51 (3 × CO<u>C</u>H$_3$), 23.28, 23.35 (11-CH$_3$), 45.41 (N(<u>C</u>H$_3$)$_2$), 45.95 (C-1), 51.90, 52.04 (C-2), 57.72 (C-2''), 61.24 (C-10), 66.19 (C-1′′), 65.22 (C-4′′′), 68.58 (C-2′′′, C-3′′′), 68.97 (C-3′′′), 95.69, 96.08 (C-1′′′), 101.8, 102.0 (C-4), 103.3 (C-4′), 105.4, 105.5 (C-3′), 113.1 (C-7′), 115.9 (C-6′), 119.7, 119.8 (C-5a), 122.0 (C-6), 122.4, 122.5 (C-9b), 123.3 (C-9), 124.4 (C-7), 127.5 (C-8, C-3a′), 129.6, 130.7, 131.7 (C-2′, C-7a′, C-9a), 141.9 (C-3a), 151.2, 151.4, 152.9 (C-5, C-5′), 160.1, 162.2 (NC=O), 169.5, 169.6, 169.7 (3 × <u>C</u>OCH$_3$). **MS**: $C_{33}H_{38}ClN_3O_8$: calcd. 750.23.

(1*SR*,10*RS*)-1-(10-Chloro-ethyl)-3-[(5-(2-(*N*,*N*-dimethylamino)-ethoxy)-indol-2-yl) carbonyl]-1,2-dihydro-3H-benz[*e*]indol-5-yl]-α-L-rhamnopyranosides (23):



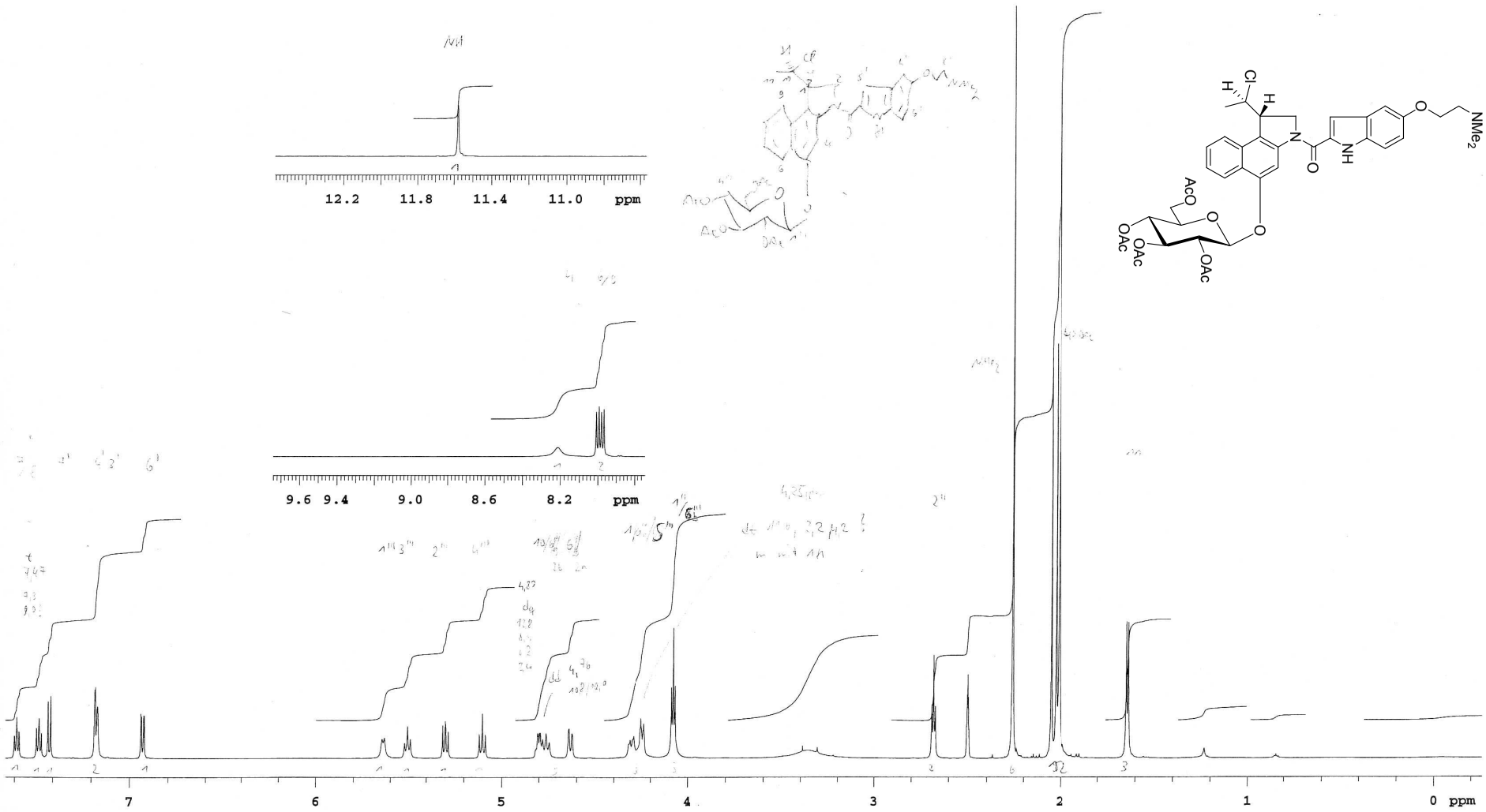
a



b

Following GP 2 (1*SR*,10*RS*)-**17** (30 mg, 40 µmol, 1.0 equiv.) in MeOH (30 mL) was treated with NaOMe (1.1 mg, 3.8 µL, 20 µmol, 0.94 mg, 0.5 equiv.) and stirred for 30 min. Work-up and CC gave the title compound **23** as slightly yellow solids (20 mg, 32 µmol, 80%). R_f = 0.42 (CH_2Cl_2/MeOH = 1:1); $[\alpha]_D^{20}$ = –53.3 ° (c = 0.6, MeOH); **UV** (MeOH): λ_{max} (lg ε) = 205.0 nm (1.6310), 242.5 (1.3344), 300.0 (1.4427), 336.0 (1.4121); **IR** (KBr): $\tilde{\nu}$ (cm^{-1}) = 3406, 2927, 1625, 1590, 1516, 1461, 1400, 1288, 1265, 1232, 1178, 1138, 1026, 971, 840, 760, 681; **^{1}H-NMR** (599.7 MHz, DMSO-d_6, 35 °C): δ = 1.12, 1.19 (2 × d, *J* = 6.2 Hz, 3 H, H_3-6), 1.65, 1.66 (2 × d, *J* = 6.5 Hz, 3 H, H_3-11), 2.24 (s, 6 H, NMe_2), 2.66 (t, *J* = 5.8 Hz, 2 H, H-2′′), 3.33-3.41 (m, 1 H, H-4′′′), 3.54, 3.65 (2 × dq, *J* = 9.7, 6.3 Hz, 1 H, H-5′′′), 3.86, 3.88 (2 × dd, *J* = 9.2, 3.3 Hz, 1 H, H-3′′′), 4.02-4.10 (m_c, 3 H, H-1′′, H-2′′′), 4.25 (dd, *J* = 9.3, 1.9 Hz, 1 H, H-1), 4.63 (2 × d, *J* = 10.8, 2.2 Hz, 1 H, H-2_a), 4.76-4.85 (m, 3 H, H-2_b, H-10, OH), 4.91, 5.15 (2 × s_{br}, 2 H, 2 × OH), 5.50, 5.59 (2 × s_{br}, 1 H, H-1′′′), 6.92 (2 × dd, *J* = 8.9, 1.9 Hz, 1 H, H-6′), 7.17 (s_{br}, 2 H, H-3′, H-4′), 7.29, 7.40 (2 × d, *J* = 8.9 Hz, 1 H, H-7′), 7.46 (t, *J* = 7.6 Hz, 1 H, H-7), 7.58 (t, *J* = 7.5 Hz, 1 H, H-8), 7.98 (d, *J* = 8.3 Hz, 1 H, H-9), 8.13 (d, *J* = 8.4 Hz, 1 H, H-6), 8.25, 8.32 (2 × s, 1 H, H-4), 11.59, 11.62 (2 × s, 1 H, NH); **^{13}C-NMR** (125.7 MHz, DMSO-d_6, 35 °C): δ = 17.34, 17.86 (C-6′′′), 23.35, 23.39 (11-CH$_3$), 45.52

($N(\underline{C}H_3)_2$), 45.92, 45.95 (C-1), 52.00 (C-2), 57.56, 57.79 (C-2''), 61.34 (C-10), 66.27 (C-1′′), 65.22 (C-4′′′), 68.58 (C-2′′′, C-3′′′), 68.97 (C-3′′′), 95.69, 96.08 (C-1′′′), 101.0, 101.6 (C-4), 103.3 (C-4′), 105.4, 105.5 (C-3′), 113.1 (C-7′), 115.9 (C-6′), 119.7, 119.8 (C-5a), 121.9, 122.0 (C-6), 122.4, 122.5 (C-9b), 122.8, 122.9 (C-9), 124.0 (C-7), 127.3, 127.5 (C-8, C-3a′), 129.6, 130.8, 131.7 (C-2′, C-7a′, C-9a), 142.0, 142.1 (C-3a), 151.8, 152.3, 153.0 (C-5, C-5′), 160.0, 160.1 (NC=O); **MS** (ESI): *m/z* (%) = 624.3 (100) $[M + H]^+$, 1247.5 (8) $[2M + H]^+$; **HRMS** $C_{33}H_{38}N_3O_7Cl$: calcd. 624.24710; found 624.24707 $[M + H]^+$.



Aquisition Parameters

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PULPROG s2pul	FIDRES	0.156 Hz
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SPECTRAL WIDTH 10000.0 Hz	PW	2.2 usec / 45 deg
NO. REPETITIONS 64		
TOTAL ACQ.TIME 3 minutes	TEMP	35.0 deg.C 308.1 K

Processing Parameters

FT SIZE	131072
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Plot Parameters

WP	4797.8 Hz, 8.0 ppm
WC	400.0 mm
VS	200.0 mm
F1P	7.741 ppm
F2P	-0.259 ppm
PPM/MM	0.020
HZ/MM	11.993

NAME	exp
DATE	Feb 1 2006
	recorded: INOVA-600
	processed: VNMR6.1C
	Univ. Goettingen OC

XY5103 dmso
Schuster / Tietze / CS

DATE: Feb 1 2006 FILE:nmrdast: tietze/xy5103_6h

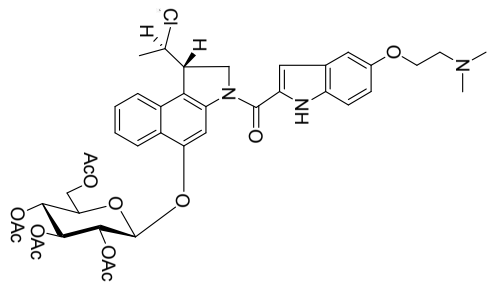
XY5103 dmso
Schuster / Tietze / CS
Feb 1 2006

INSTRUMENT: INOVA-500
OBSERVE C13
Frequency 125.707 MHz
Spectral width 28901.7 Hz
Acquisition time 2.214 sec
Relaxation delay 0.000 sec
Pulse 30.0 degrees
Temperature 35.0 deg. C /
4708 repetitions
DECOUPLE H1
Frequency 499.879 Mhz
Power 36 dB
Decoupler continuously on
WALTZ-16 modulated
Double precision acquisitio
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 2.9 h

XY5103 dmso
Schuster / Tietze / CS

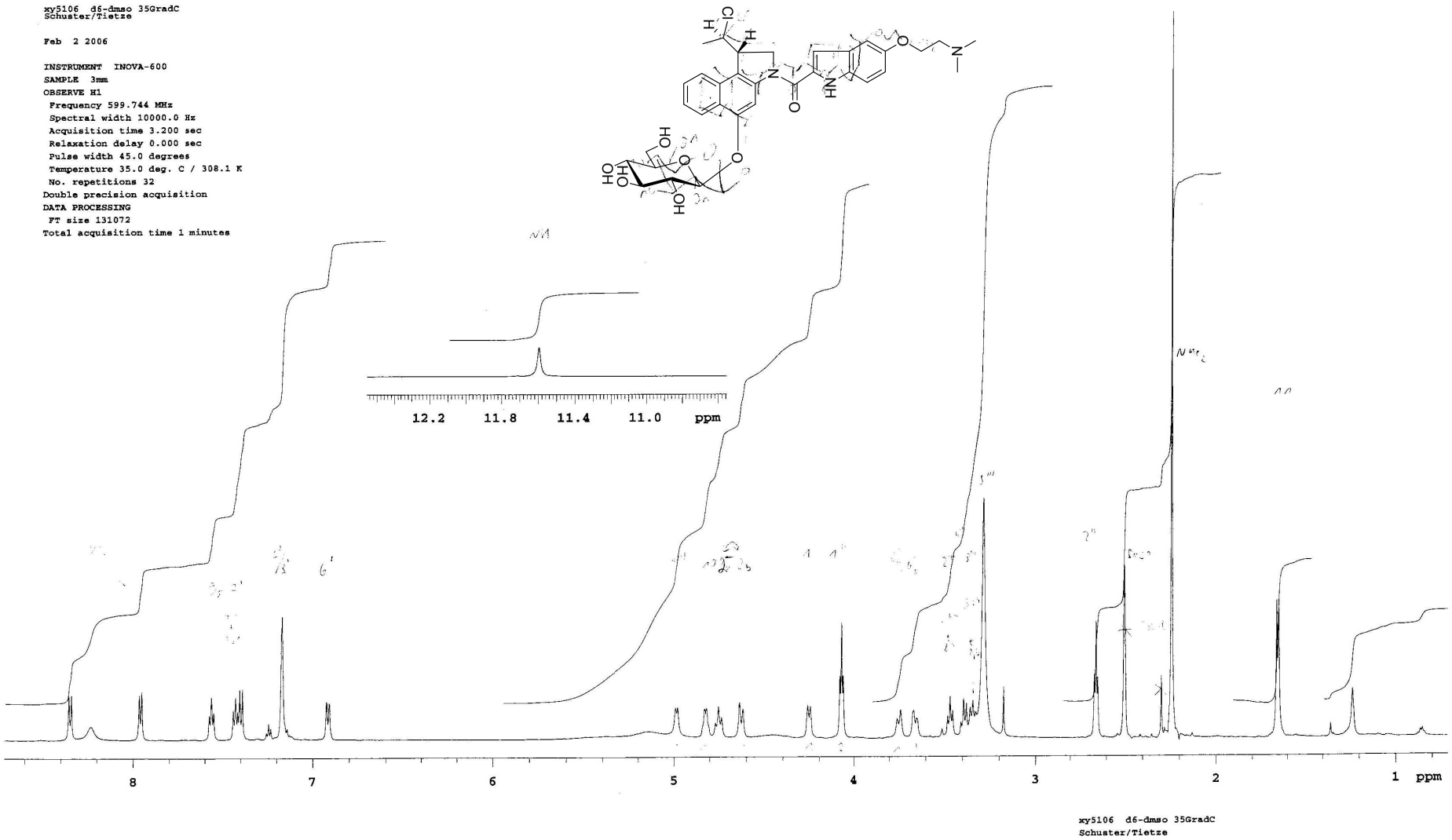
SPECTRAL LINES FOR TH= 5.2
FROM -9.6 PPM TO 220.4 PPM
RFL= 6168.3 RFP= 4964.9

INDEX	FREQ	PPM	HEIGHT
1	21374.7	170.05	24.0
2	21294.5	169.41	22.8
3	21279.9	169.30	23.6
4	21264.0	169.17	23.4
5	20140.4	160.23	22.1
6	19227.9	152.97	23.1
7	19166.2	152.48	20.7
8	17817.1	141.75	11.3
9	16558.5	131.74	21.4
10	16431.1	130.72	22.7
11	16269.2	129.43	17.9
12	16021.4	127.46	16.0
13	16014.8	127.41	21.5
14	15624.0	124.30	13.1
15	15489.5	123.23	15.0
16	15408.8	122.59	17.6
17	15329.0	121.95	12.7
18	15116.0	120.26	20.5
19	14564.7	115.87	15.1
20	14223.4	113.16	19.7
21	13255.8	105.46	17.0
22	12973.6	103.22	17.6
23	12911.4	102.72	7.1
24	12396.3	98.62	20.8
25	9012.9	71.71	22.5
26	8909.3	70.88	29.0
27	8537.9	67.93	15.2
28	8317.4	66.17	24.6
29	7711.1	61.35	12.1
30	7689.0	61.17	14.5
31	7254.6	57.72	39.2
32	6560.9	52.20	10.4
33	5765.8	45.87	13.8
34	5708.0	45.41	102.8
35	5028.0	40.00	56.3
36	5018.3	39.92	11.2
37	5006.8	39.83	33.9
38	4997.1	39.76	19.7
39	4986.1	39.67	30.7
40	4976.4	39.59	21.4
41	4964.9	39.50	100.0
42	4943.8	39.33	33.3
43	4923.0	39.17	19.9
44	4901.9	39.00	56.3
45	2930.1	23.31	28.4
46	2553.9	20.32	35.6
47	2547.8	20.27	63.9
48	2539.8	20.21	28.9



XY5103 dmso
Schuster / Tietze / CS

DATE: Feb 1 2006 FILE:nmrdast: tietze/xy5103_5c


xy5106 d6-dmso 35GradC
Schuster/Tietze
Feb 2 2006
INSTRUMENT INOVA-600
SAMPLE 3mm
OBSERVE H1
Frequency 599.744 MHz
Spectral width 10000.0 Hz
Acquisition time 3.200 sec
Relaxation delay 0.000 sec
Pulse width 45.0 degrees
Temperature 35.0 deg. C / 308.1 K
No. repetitions 32
Double precision acquisition
DATA PROCESSING
FT size 131072
Total acquisition time 1 minutes
12.2
11.8
11.4
11.0
ppm
8
7
6
5
4
3
2
1
ppm
xy5106 d6-dmso 35GradC
Schuster/Tietze

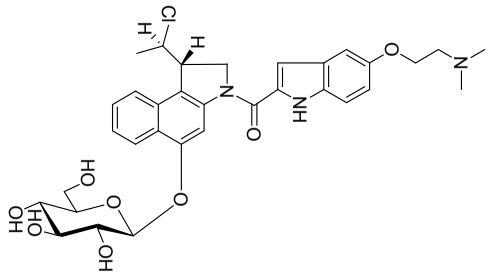
xy5106 d6-dmso 35GradC
Schuster/Tietze
Feb 2 2006

INSTRUMENT: INOVA-500
OBSERVE C13
Frequency 125.707 MHz
Spectral width 28901.7 Hz
Acquisition time 2.214 sec
Relaxation delay 0.000 sec
Pulse 30.0 degrees
Temperature 35.0 deg. C / 308.1 K
20480 repetitions
DECOUPLE H1
Frequency 499.879 Mhz
Power 36 dB
Decoupler continuously on
WALTZ-16 modulated
Double precision acquisition
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 12.6 hours

xy5106 d6-dmso 35GradC
Schuster/Tietze

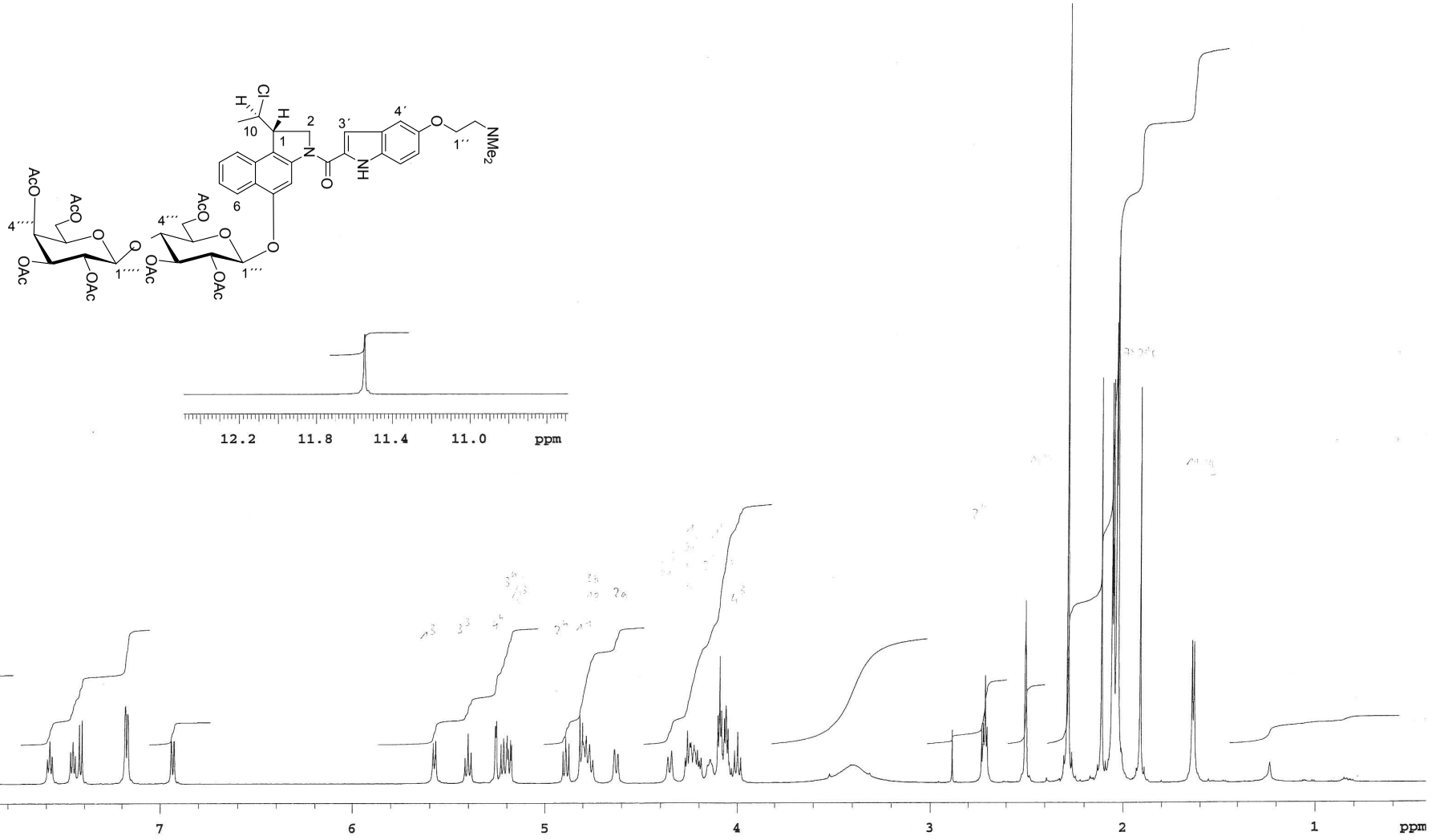
SPECTRAL LINES FOR TH= 4.6
FROM -2.5 PPM TO 197.5 PPM
RFL= 1203.9 RFP= 0.0

INDEX	FREQ	PPM	HEIGHT
1	20122.7	160.09	16.9
2	19277.3	153.37	19.0
3	19224.8	152.95	21.6
4	17844.9	141.97	11.4
5	16547.9	131.65	18.8
6	16441.6	130.81	17.9
7	16265.2	129.40	16.6
8	16186.3	128.78	16.3
9	16098.5	128.08	15.4
10	16022.2	127.47	18.9
11	15989.6	127.21	14.9
12	15735.6	125.19	9.0
13	15537.6	123.61	11.2
14	15495.7	123.28	11.7
15	15442.8	122.86	22.5
16	14929.4	118.78	19.5
17	14559.9	115.84	14.4
18	14216.3	113.10	17.0
19	13244.4	105.37	15.0
20	12973.1	103.21	18.0
21	12777.8	101.66	8.8
22	12752.6	101.46	16.7
23	9672.2	76.95	19.6
24	9620.6	76.54	21.8
25	9213.6	73.30	21.9
26	8682.6	69.08	20.1
27	8329.4	66.27	24.6
28	7703.1	61.28	13.2
29	7561.1	60.15	13.3
30	7263.4	57.79	38.5
31	6535.8	52.00	9.4
32	5770.2	45.91	12.5
33	5719.0	45.50	106.1
34	5039.0	40.09	9.9
35	5027.5	40.00	138.5
36	5017.8	39.92	23.5
37	5006.8	39.83	426.4
38	4997.1	39.76	42.7
39	4985.6	39.66	856.7
40	4976.4	39.59	48.0
41	4964.5	39.50	1000.0
42	4943.8	39.33	856.3
43	4922.6	39.16	429.5
44	4901.9	39.00	139.1
45	2932.8	23.33	25.7
46	2628.9	20.92	5.1



xy5106 d6-dmso 35GradC
Schuster/Tietze

DATE: Feb 2 2006 FILE:nmrdast: tietze/xy5106_5c



Aquisition Parameters

OBSERVE H1	ACQ.TIME	3.200 sec	
SOLVENT dmso	NP	64000	
PULPROG s2pul	FIDRES	0.156 Hz	
FREQUENCY 599.744 MHz	D1	0.000 sec	
SPECTRAL WIDTH 10000.0 Hz	PW	2.1 usec / 45 deg	
NO. REPETITIONS 64			
TOTAL ACQ.TIME 3 minutes	TEMP	35.0 deg.C	

Processing Parameters

FT SIZE	131072
DIGRES	0.153 Hz

Plot Parameters

WP	4797.8 Hz, 8.0 ppm
WC	400.0 mm
VS	200.0 mm
F1P	8.389 ppm
F2P	0.389 ppm
PPM/MM	0.020
HZ/MM	11.993

NAME exp
DATE Feb 14 2007

recorded: INOVA-600
processed: VNMRJ_1.1C

Univ. Goettingen OC

XY5113a dmso
Schuster / Tietze / CS

DATE: Feb 14 2007

FILE:nmrdast: tietze/xy5113a_6h

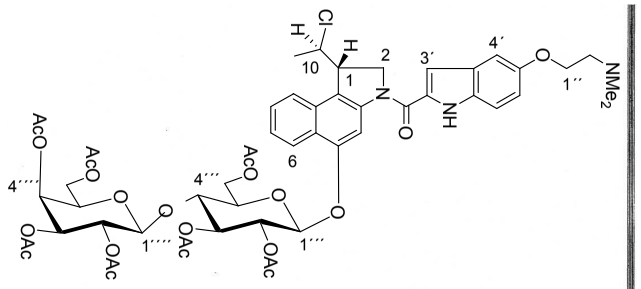
XY5113a dmso-d6
Schuster / Tietze
Feb 14 2007

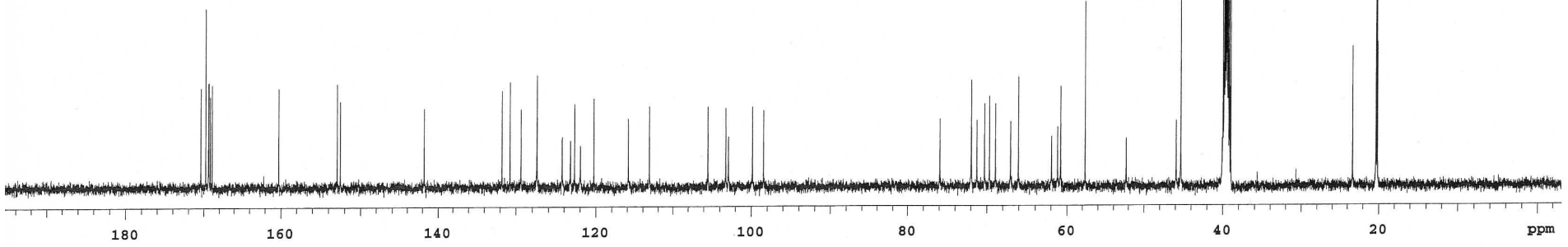
INSTRUMENT INOVA-500
SAMPLE 3mm
OBSERVE C13
Frequency 125.707 MHz
Spectral width 28901.7 Hz
Acquisition time 2.214 sec
Relaxation delay 0.000 sec
Pulse width 30.0 degrees
Temperature 35.0 deg. C / 308.1
No. repetitions 5120
DECOUPLE H1
Frequency 499.879 Mhz
Power 36 dB
Decoupler continuously on
WALTZ-16 modulated
Double precision acquisition
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 3:08 hour

XY5113a dmso-d6
Schuster / Tietze

SPECTRAL LINES FOR TH= 4.0
FROM -3.1 PPM TO 196.9 PPM
RFL= 6166.6 RFP= 4964.9

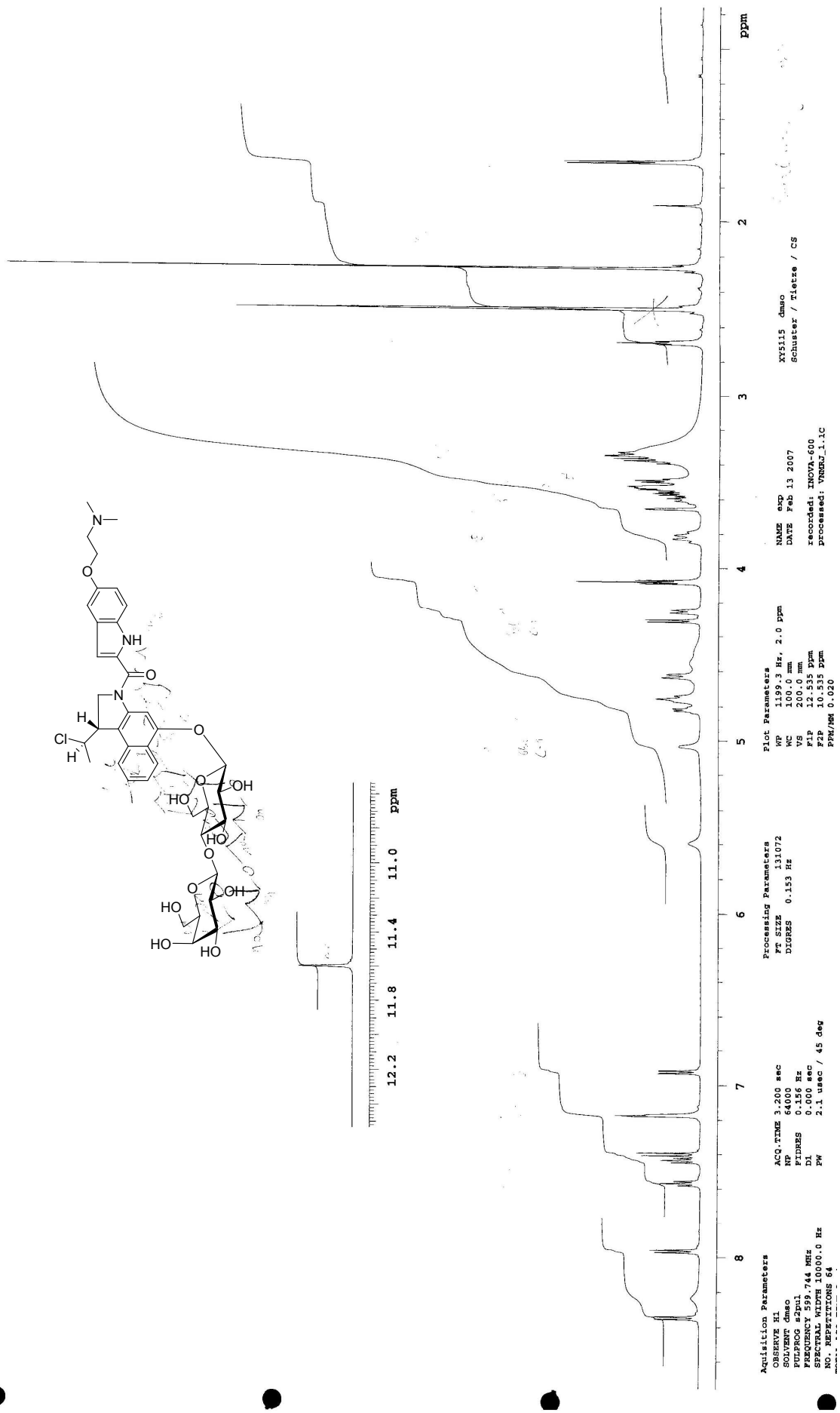
INDEX	FREQ	PPM	HEIGHT	INDEX	FREQ	PPM	HEIGHT
1	21419.3	170.41	24.9	30	8838.7	70.32	20.5
2	21339.9	169.78	45.0	31	8760.2	69.69	22.4
3	21295.8	169.43	26.1	32	8665.4	68.94	20.4
4	21288.7	169.37	26.3	33	8425.9	67.04	16.0
5	21265.8	169.19	22.7	34	8303.8	66.06	27.1
6	21235.8	168.95	25.6	35	7787.4	61.95	12.3
7	20146.1	160.28	24.7	36	7690.8	61.19	14.6
8	19223.9	152.94	25.9	37	7642.7	60.80	24.8
9	19175.4	152.56	21.5	38	7246.2	57.65	46.1
10	17824.6	141.81	19.6	39	6573.7	52.30	11.8
11	16562.0	131.76	24.0	40	5772.0	45.92	16.2
12	16435.0	130.75	26.2	41	5697.9	45.33	115.0
13	16266.6	129.41	19.4	42	5039.0	40.09	11.8
14	16016.5	127.42	28.0	43	5027.5	40.00	72.6
15	15621.4	124.28	12.4	44	5017.8	39.92	24.3
16	15488.6	123.22	11.5	45	5006.8	39.83	215.8
17	15422.0	122.69	20.7	46	4996.7	39.75	39.0
18	15332.1	121.98	10.2	47	4985.6	39.66	430.6
19	15119.1	120.28	22.1	48	4975.9	39.59	36.2
20	14565.2	115.88	17.0	49	4964.5	39.50	500.0
21	14225.6	113.18	20.0	50	4943.8	39.33	428.1
22	13262.0	105.51	20.0	51	4922.6	39.16	212.7
23	12979.3	103.26	19.6	52	4901.9	39.00	69.0
24	12935.7	102.91	12.4	53	2931.9	23.33	34.7
25	12552.9	99.87	19.9	54	2561.4	20.38	54.2
26	12378.7	98.48	19.0	55	2560.1	20.37	49.1
27	9543.0	75.92	16.7	56	2556.6	20.34	48.5
28	9045.5	71.96	26.4	57	2543.8	20.24	52.1
29	8957.8	71.27	16.3	58	2535.9	20.17	35.7





XY5113a dmso-d6
Schuster / Tietze

DATE: Feb 14 2007 FILE:nmrdast: tietze/xy5113a_5c


N
O
NH
O
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H
Cl
H
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OH
HO
HO
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O
OH
HO
HO
HO
12.2
11.8
11.4
11.0
ppm
Acquisition Parameters
OBSERVE H1
SOLVENT dmso
PULPROG s2pul
FIDRES 0.156 Hz
SPECTRAL SW 744 MHz
SPECTRAL WIDTH 10000.0 Hz
NO. REPETITIONS 64
ACQ.TIME 3.200 sec
NP 64000
D1 0.000 sec
PW 2.1 usec / 45 deg
Processing Parameters
FT SIZE 131072
DIGRES 0.153 Hz
Plot Parameters
WP 1199.3 Hz, 2.0 ppm
WC 100.0 mm
VS 200.0 mm
F1P 12.535 ppm
F2P 10.535 ppm
PPM/MM 0.020
NAME exp
DATE Feb 13 2007
recorded: INOVA-600
processed: VNMRJ_1.1C
XY5115 dmso
Schuster / Tietze / CS
ppm

XY5115 dmso
Schuster / Tietze / CS

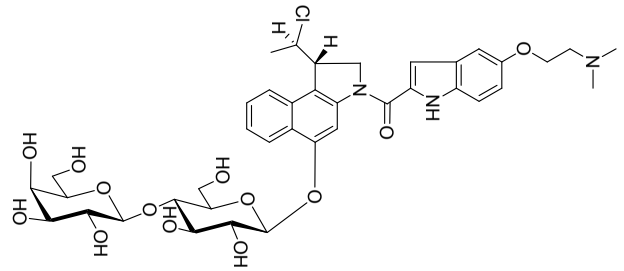
Feb 12 2007

INSTRUMENT INOVA-600
SAMPLE 3mm
OBSERVE C13
Frequency 150.821 MHz
Spectral width 34965.0 Hz
Acquisition time 1.829 se
Relaxation delay 0.000 se
Pulse width 33.6 degrees
Temperature 35.0 deg. C /
No. repetitions 2020
DECOUPLE H1
Frequency 599.743 Mhz
Power 48 dB
Decoupler continuously on
WALTZ-16 modulated
Double precision acquisiti
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 1:01

XY5115 dmso
Schuster / Tietze / CS

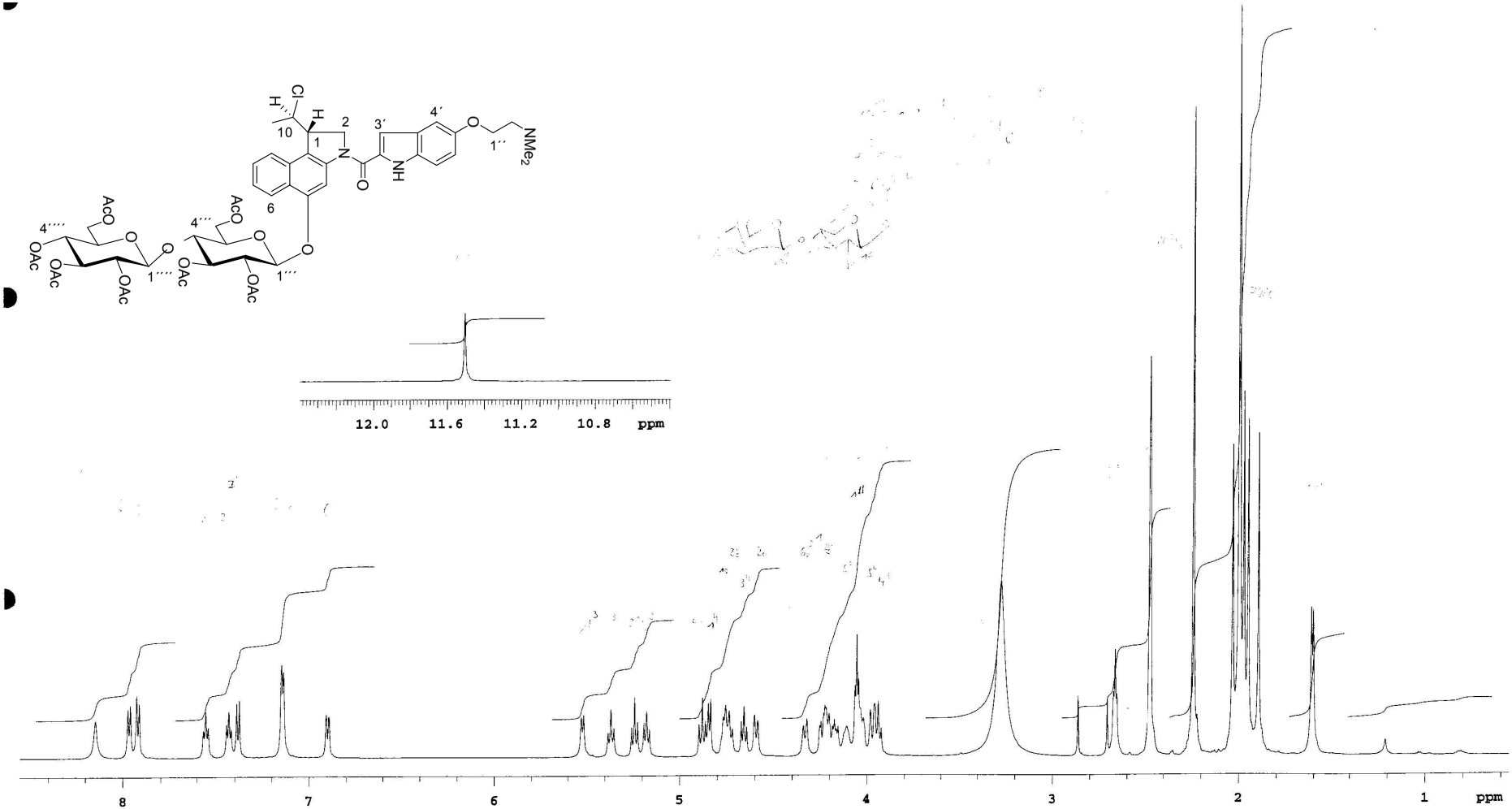
SPECTRAL LINES FOR TH= 9.5
FROM -2.5 PPM TO 197.5 PPM
RFL= 7659.3 RFP= 5956.8

INDEX	FREQ	PPM	HEIGHT
1	24145.2	160.11	27.9
2	23116.5	153.29	27.0
3	23062.1	152.93	27.4
4	21407.7	141.96	11.6
5	19859.4	131.69	28.9
6	19729.7	130.83	31.6
7	19515.8	129.41	20.2
8	19223.9	127.48	26.1
9	19192.5	127.27	19.1
10	18655.2	123.70	18.0
11	18586.9	123.25	18.1
12	18537.8	122.93	17.0
13	18531.4	122.88	29.4
14	17949.3	119.02	28.4
15	17471.8	115.86	23.8
16	17063.2	113.15	27.3
17	15893.1	105.39	23.9
18	15631.7	103.66	38.4
19	15570.9	103.25	29.0
20	15383.6	102.01	9.7
21	15261.5	101.20	22.8
22	11974.9	79.41	26.2
23	11429.7	75.79	13.9
24	11387.0	75.51	37.5
25	11301.1	74.94	26.2
26	11271.8	74.74	30.3
27	11039.1	73.20	35.0
28	11022.6	73.09	28.4
29	10643.8	70.58	38.1
30	10274.1	68.13	27.3
31	9971.0	66.12	34.7
32	9246.0	61.31	21.3
33	9108.3	60.40	43.1
34	9017.1	59.79	18.1
35	8700.2	57.69	57.1
36	7846.5	52.03	14.9
37	6923.0	45.91	17.3
38	6846.7	45.40	145.7
39	6037.9	40.04	20.5
40	6019.7	39.92	148.0
41	5998.9	39.78	434.6
42	5977.6	39.64	842.3
43	5956.8	39.50	1000.0
44	5936.0	39.36	848.2
45	5914.6	39.22	422.9
46	5893.8	39.08	141.4
47	3522.3	23.36	47.2



XY5115 dmso
Schuster / Tietze / CS

DATE: Feb 12 2007 FILE:nmrdast: tietze/xy5115_6c



Aquisition Parameters
OBSERVE H1
SOLVENT dmso
PULPROG s2pul
FREQUENCY 599.744 MHz
SPECTRAL WIDTH 10000.0 Hz
NO. REPETITIONS 64
TOTAL ACQ.TIME 3 minutes

ACQ.TIME 3.200 sec
NP 64000
FIDRES 0.156 Hz
D1 0.000 sec
PW 2.1 usec / 45 deg

TEMP 35.0 deg.C
308.1 K

Processing Parameters
FT SIZE 131072
DIGRES 0.153 Hz

Plot Parameters
WP 4797.8 Hz, 8.0 ppm
WC 400.0 mm
VS 200.0 mm
F1P 8.555 ppm
F2P 0.555 ppm
PPM/MM 0.020
HZ/MM 11.993

NAME exp
DATE Feb 13 2007

recorded: INOVA-600
processed: VNMRJ_1.1C

Univ. Goettingen OC

XY5112a dmso
Schuster / Tietze / CS

DATE: Feb 13 2007

FILE:nmrdast: tietze/xy5112a_6h

XY5112a dmso
Schuster / Tietze /

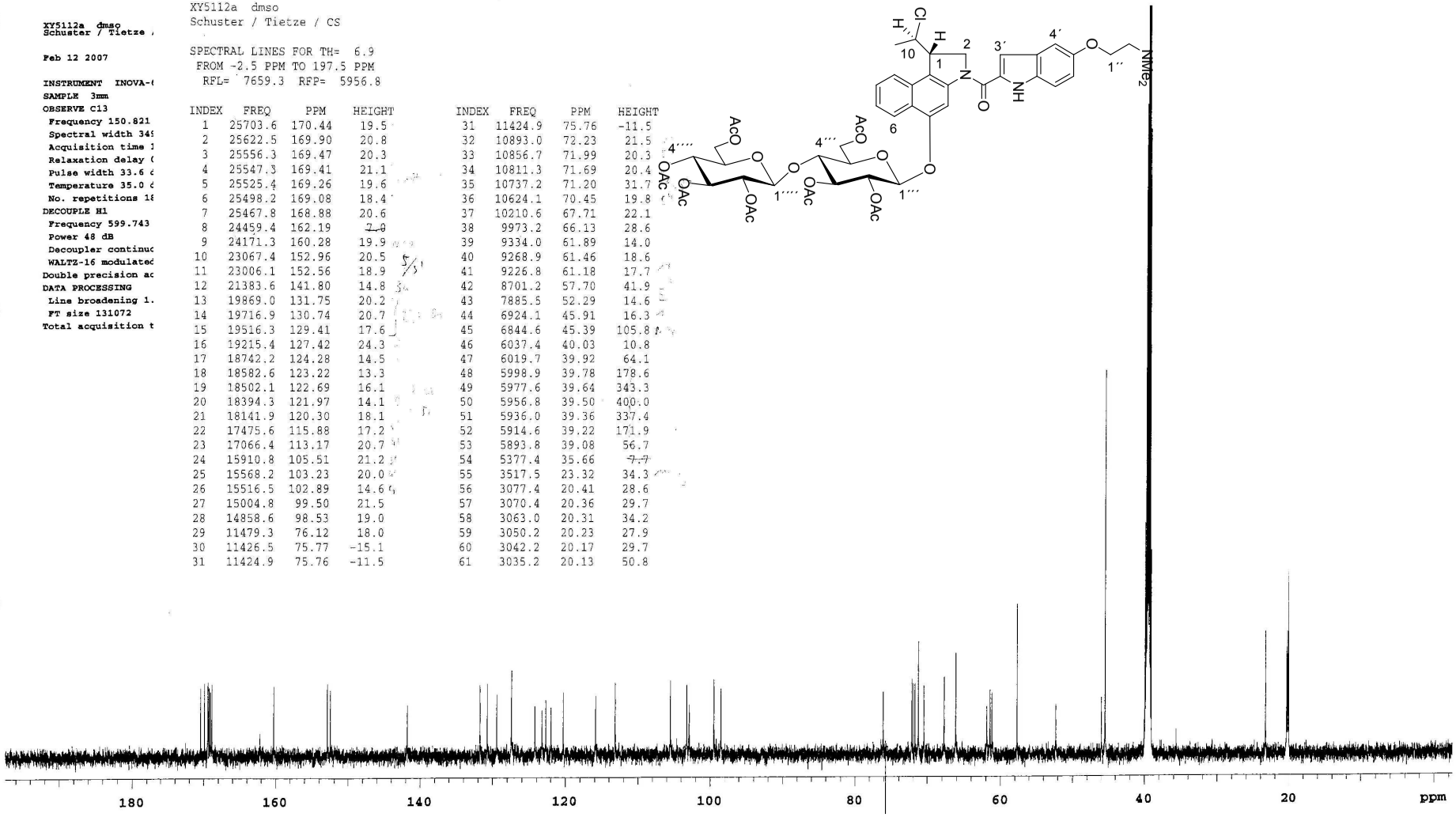
Feb 12 2007

INSTRUMENT INOVA-(
SAMPLE 3mm
OBSERVE C13
Frequency 150.821
Spectral width 34
Acquisition time 1
Relaxation delay (
Pulse width 33.6 d
Temperature 35.0 d
No. repetitions 18
DECOUPLE H1
Frequency 599.743
Power 48 dB
Decoupler continuc
WALTZ-16 modulated
Double precision ac
DATA PROCESSING
Line broadening 1.
FT size 131072
Total acquisition t

XY5112a dmso
Schuster / Tietze / CS

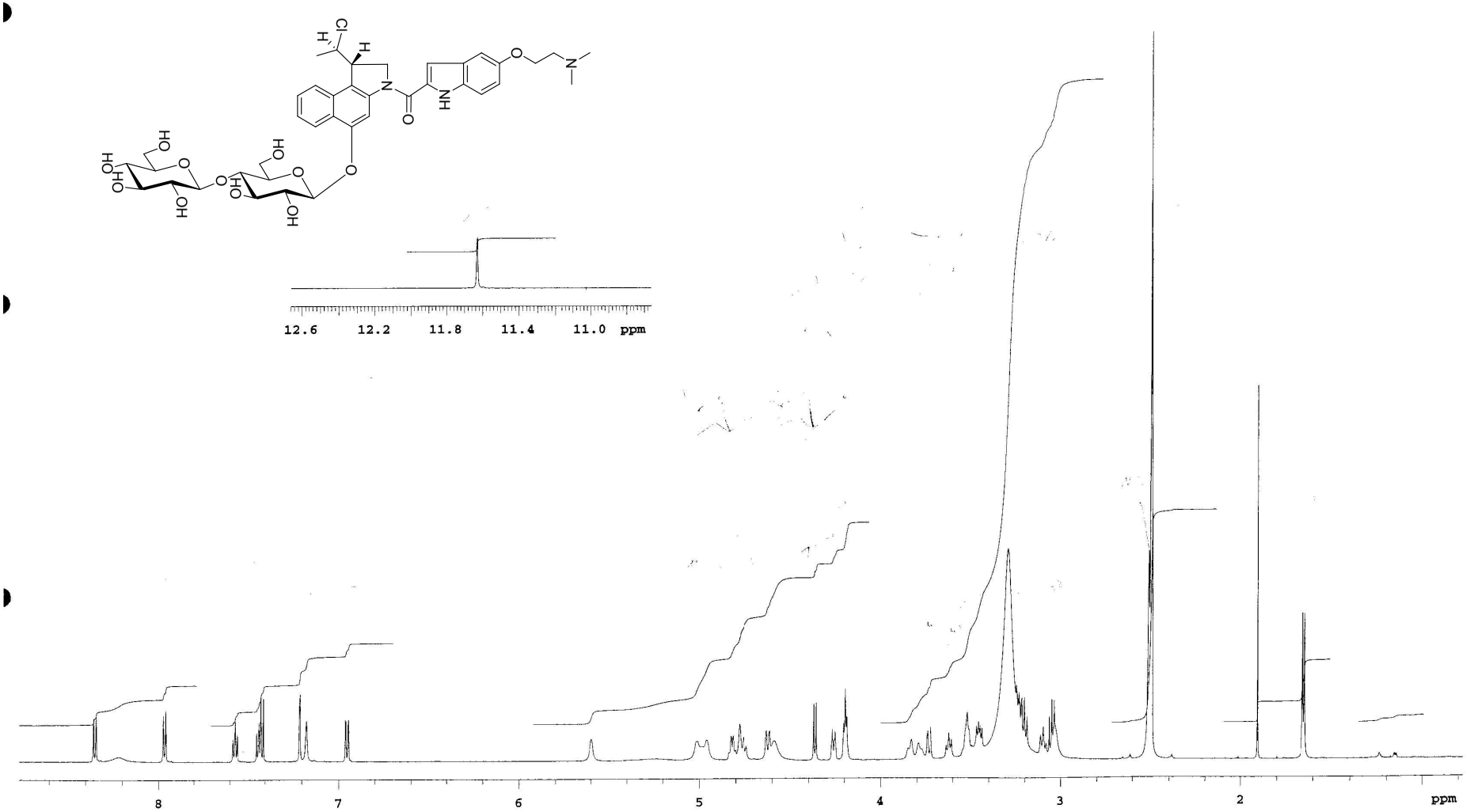
SPECTRAL LINES FOR TH= 6.9
FROM -2.5 PPM TO 197.5 PPM
RFL= 7659.3 RFP= 5956.8

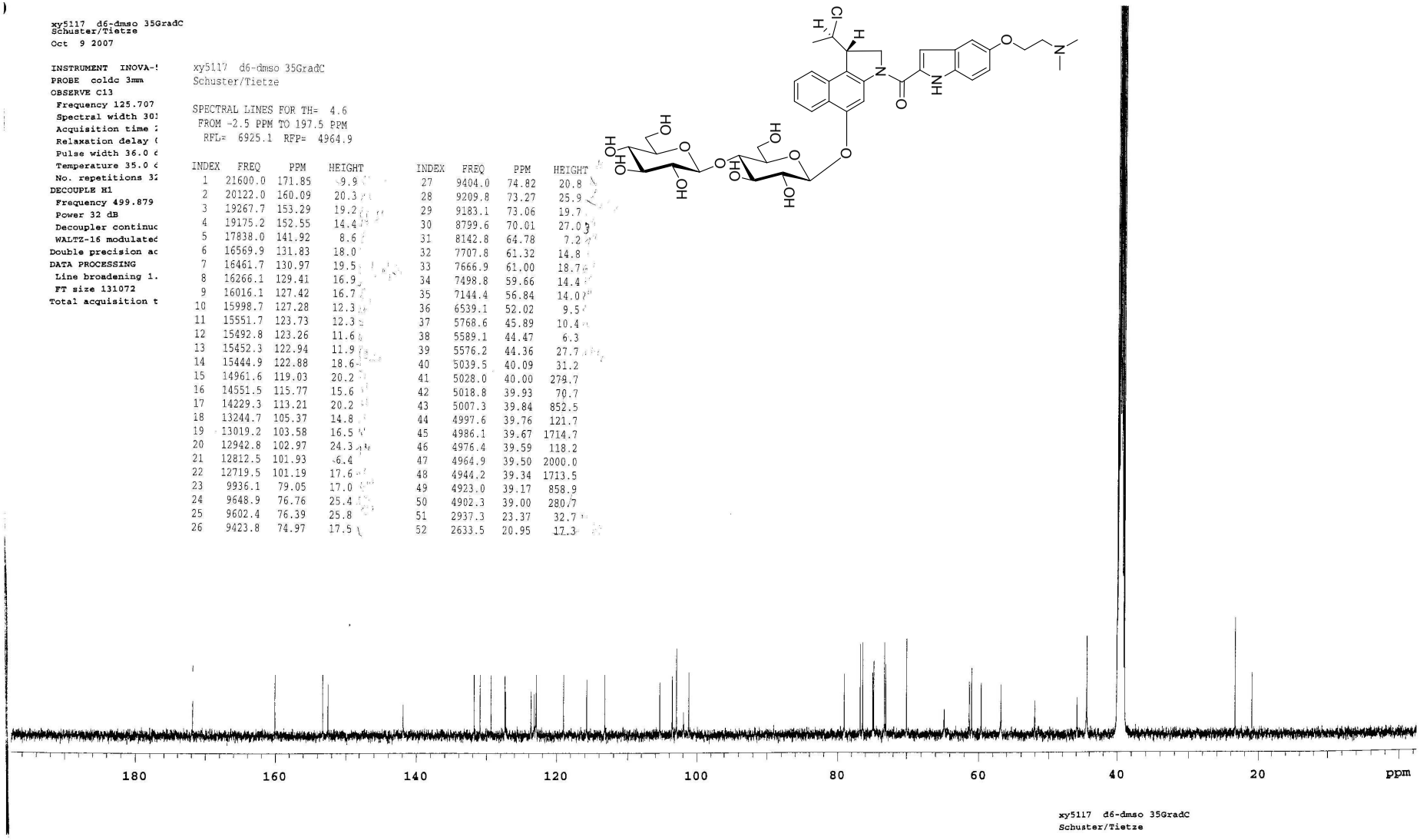
INDEX	FREQ	PPM	HEIGHT	INDEX	FREQ	PPM	HEIGHT
1	25703.6	170.44	19.5	31	11424.9	75.76	-11.5
2	25622.5	169.90	20.8	32	10893.0	72.23	21.5
3	25556.3	169.47	20.3	33	10856.7	71.99	20.3
4	25547.3	169.41	21.1	34	10811.3	71.69	20.4
5	25525.4	169.26	19.6	35	10737.2	71.20	31.7
6	25498.2	169.08	18.4	36	10624.1	70.45	19.8
7	25467.8	168.88	20.6	37	10210.6	67.71	22.1
8	24459.4	162.19	7.0	38	9973.2	66.13	28.6
9	24171.3	160.28	19.9	39	9334.0	61.89	14.0
10	23067.4	152.96	20.5	40	9268.9	61.46	18.6
11	23006.1	152.56	18.9	41	9226.8	61.18	17.7
12	21383.6	141.80	14.8	42	8701.2	57.70	41.9
13	19869.0	131.75	20.2	43	7885.5	52.29	14.6
14	19716.9	130.74	20.7	44	6924.1	45.91	16.3
15	19516.3	129.41	17.6	45	6844.6	45.39	105.8
16	19215.4	127.42	24.3	46	6037.4	40.03	10.8
17	18742.2	124.28	14.5	47	6019.7	39.92	64.1
18	18582.6	123.22	13.3	48	5998.9	39.78	178.6
19	18502.1	122.69	16.1	49	5977.6	39.64	343.3
20	18394.3	121.97	14.1	50	5956.8	39.50	400.0
21	18141.9	120.30	18.1	51	5936.0	39.36	337.4
22	17475.6	115.88	17.2	52	5914.6	39.22	171.9
23	17066.4	113.17	20.7	53	5893.8	39.08	56.7
24	15910.8	105.51	21.2	54	5377.4	35.66	7.7
25	15568.2	103.23	20.0	55	3517.5	23.32	34.3
26	15516.5	102.89	14.6	56	3077.4	20.41	28.6
27	15004.8	99.50	21.5	57	3070.4	20.36	29.7
28	14858.6	98.53	19.0	58	3063.0	20.31	34.2
29	11479.3	76.12	18.0	59	3050.2	20.23	27.9
30	11426.5	75.77	-15.1	60	3042.2	20.17	29.7
31	11424.9	75.76	-11.5	61	3035.2	20.13	50.8

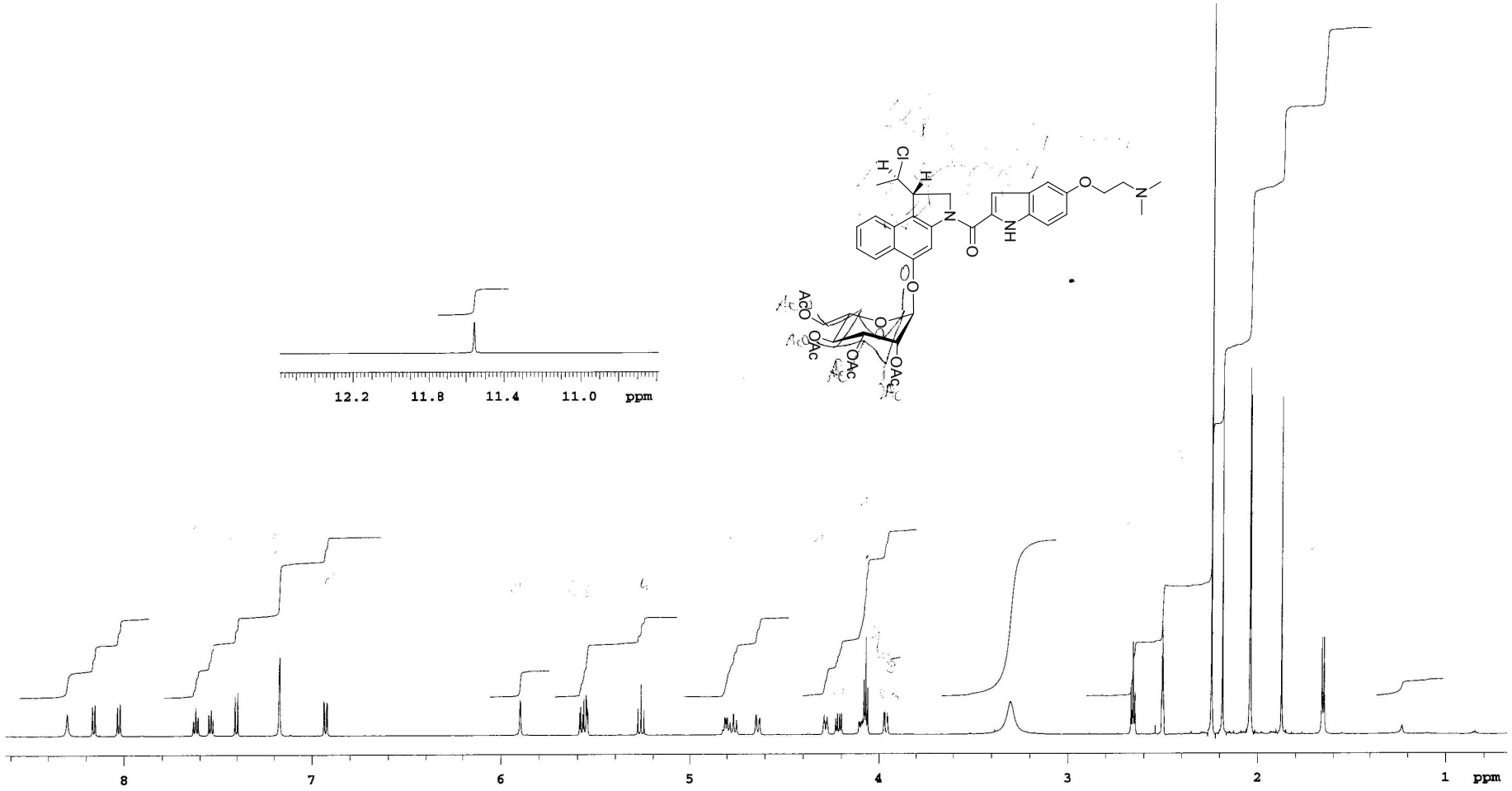


XY5112a dmso
Schuster / Tietze / CS

DATE: Feb 12 2007 FILE:nmrdast: tietze/xy5112a_6c


12.6
12.2
11.8
11.4
11.0 ppm
8
7
6
5
4
3
2
ppm
Aquisition Parameters
OBSERVE H1
SOLVENT dmso
PULPROG s2pul
FREQUENCY 599.744 MHz
SPECTRAL WIDTH 10000.0 Hz
NO. REPETITIONS 64
TOTAL ACQ.TIME 3 minutes
ACQ.TIME 3.200 sec
NP 64000
FIDRES 0.156 Hz
D1 0.000 sec
PW 2.0 usec / 45 deg
TEMP 35.0 deg.C
308.1 K
Processing Parameters
FT SIZE 131072
DIGRES 0.153 Hz
Plot Parameters
WP 4797.8 Hz, 8.0 ppm
WC 400.0 mm
VS 200.0 mm
F1P 8.773 ppm
F2P 0.773 ppm
PPM/MM 0.020
HZ/MM 11.993
NAME exp
DATE Oct 9 2007
recorded: INOVA-600
processed: VNMRJ_1.1C
Univ. Goettingen OC
xy5117 d6-dmso 35GradC
Schuster/Tietze
DATE: Oct 9 2007
FILE:nmrdast: tietze/xy5117_6h


xy5117 d6-dmso 35GradC
Schuster/Tietze
Oct 9 2007
INSTRUMENT INOVA-5
PROBE coldc 3mm
OBSERVE C13
Frequency 125.707
Spectral width 30
Acquisition time
Relaxation delay
Pulse width 36.0
Temperature 35.0
No. repetitions 3
DECOUPLE H1
Frequency 499.879
Power 32 dB
Decoupler continuc
WALTZ-16 modulated
Double precision ac
DATA PROCESSING
Line broadening 1.
FT size 131072
Total acquisition t
xy5117 d6-dmso 35GradC
Schuster/Tietze
SPECTRAL LINES FOR TH= 4.6
FROM -2.5 PPM TO 197.5 PPM
RFL= 6925.1 RFP= 4964.9
INDEX FREQ PPM HEIGHT
1 21600.0 171.85 9.9
2 20122.0 160.09 20.3
3 19267.7 153.29 19.2
4 19175.2 152.55 14.4
5 17838.0 141.92 8.6
6 16569.9 131.83 18.0
7 16461.7 130.97 19.5
8 16266.1 129.41 16.9
9 16016.1 127.42 16.7
10 15998.7 127.28 12.3
11 15551.7 123.73 12.3
12 15492.8 123.26 11.6
13 15452.3 122.94 11.9
14 15444.9 122.88 18.6
15 14961.6 119.03 20.2
16 14551.5 115.77 15.6
17 14229.3 113.21 20.2
18 13244.7 105.37 14.8
19 13019.2 103.58 16.5
20 12942.8 102.97 24.3
21 12812.5 101.93 6.4
22 12719.5 101.19 17.6
23 9936.1 79.05 17.0
24 9648.9 76.76 25.4
25 9602.4 76.39 25.8
26 9423.8 74.97 17.5
INDEX FREQ PPM HEIGHT
27 9404.0 74.82 20.8
28 9209.8 73.27 25.9
29 9183.1 73.06 19.7
30 8799.6 70.01 27.0
31 8142.8 64.78 7.2
32 7707.8 61.32 14.8
33 7666.9 61.00 18.7
34 7498.8 59.66 14.4
35 7144.4 56.84 14.0
36 6539.1 52.02 9.5
37 5768.6 45.89 10.4
38 5589.1 44.47 6.3
39 5576.2 44.36 27.7
40 5039.5 40.09 31.2
41 5028.0 40.00 279.7
42 5018.8 39.93 70.7
43 5007.3 39.84 852.5
44 4997.6 39.76 121.7
45 4986.1 39.67 1714.7
46 4976.4 39.59 118.2
47 4964.9 39.50 2000.0
48 4944.2 39.34 1713.5
49 4923.0 39.17 858.9
50 4902.3 39.00 280.7
51 2937.3 23.37 32.7
52 2633.5 20.95 17.3
180
160
140
120
100
80
60
40
20
ppm
xy5117 d6-dmso 35GradC
Schuster/Tietze
DATE: Oct 9 2007
FILE:nmrdast: tietze/xy5117_5c



Aquisition Parameters
OBSERVE H1
SOLVENT dmso
PULPROG s2pul
FREQUENCY 599.744 MHz
SPECTRAL WIDTH 10000.0 Hz
NO. REPETITIONS 64
TOTAL ACQ.TIME 3 minutes

ACQ.TIME 3.200 sec
NP 64000
FIDRES 0.156 Hz
D1 0.000 sec
PW 2.2 usec / 45 deg

TEMP 35.0 deg.C
308.1 K

Processing Parameters
FT SIZE 131072
DIGRES 0.153 Hz

Plot Parameters
WP 4797.8 Hz, 8.0 ppm
WC 400.0 mm
VS 200.0 mm
F1P 8.680 ppm
F2P 0.680 ppm
PPM/MM 0.020
HZ/MM 11.993

NAME exp
DATE Feb 7 2006

recorded: INOVA-600
processed: VNMR6.1C

Univ. Goettingen OC

XY5104 dmso
Schuster / Tietze / CS

DATE: Feb 7 2006 FILE:nmrdast: tietze/xy5104_6h

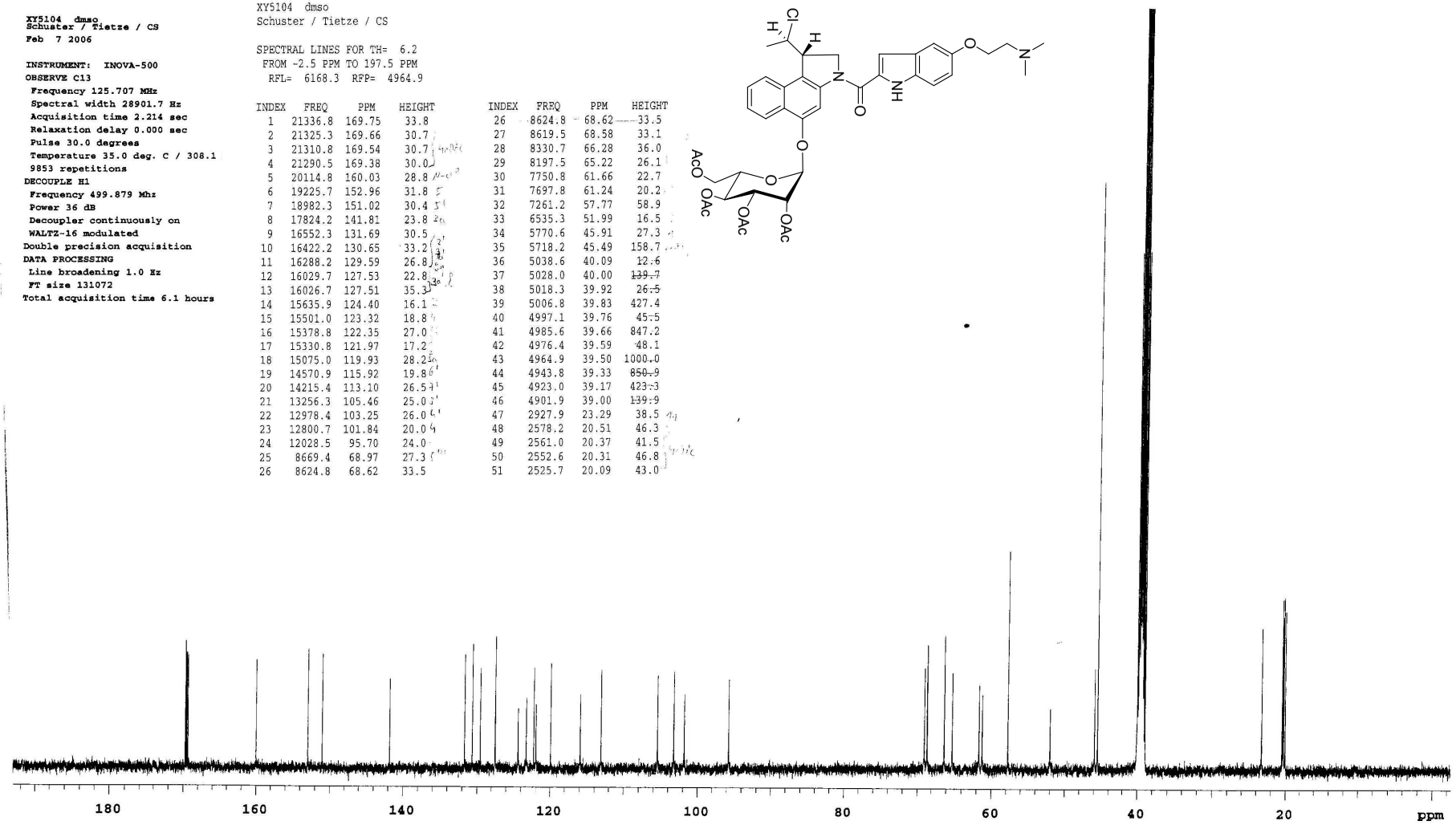
XY5104 dmso
Schuster / Tietze / CS
Feb 7 2006

INSTRUMENT: INOVA-500
OBSERVE C13
Frequency 125.707 MHz
Spectral width 28901.7 Hz
Acquisition time 2.214 sec
Relaxation delay 0.000 sec
Pulse 30.0 degrees
Temperature 35.0 deg. C / 308.1
9853 repetitions
DECOUPLE H1
Frequency 499.879 Mhz
Power 36 dB
Decoupler continuously on
WALTZ-16 modulated
Double precision acquisition
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 6.1 hours

XY5104 dmso
Schuster / Tietze / CS

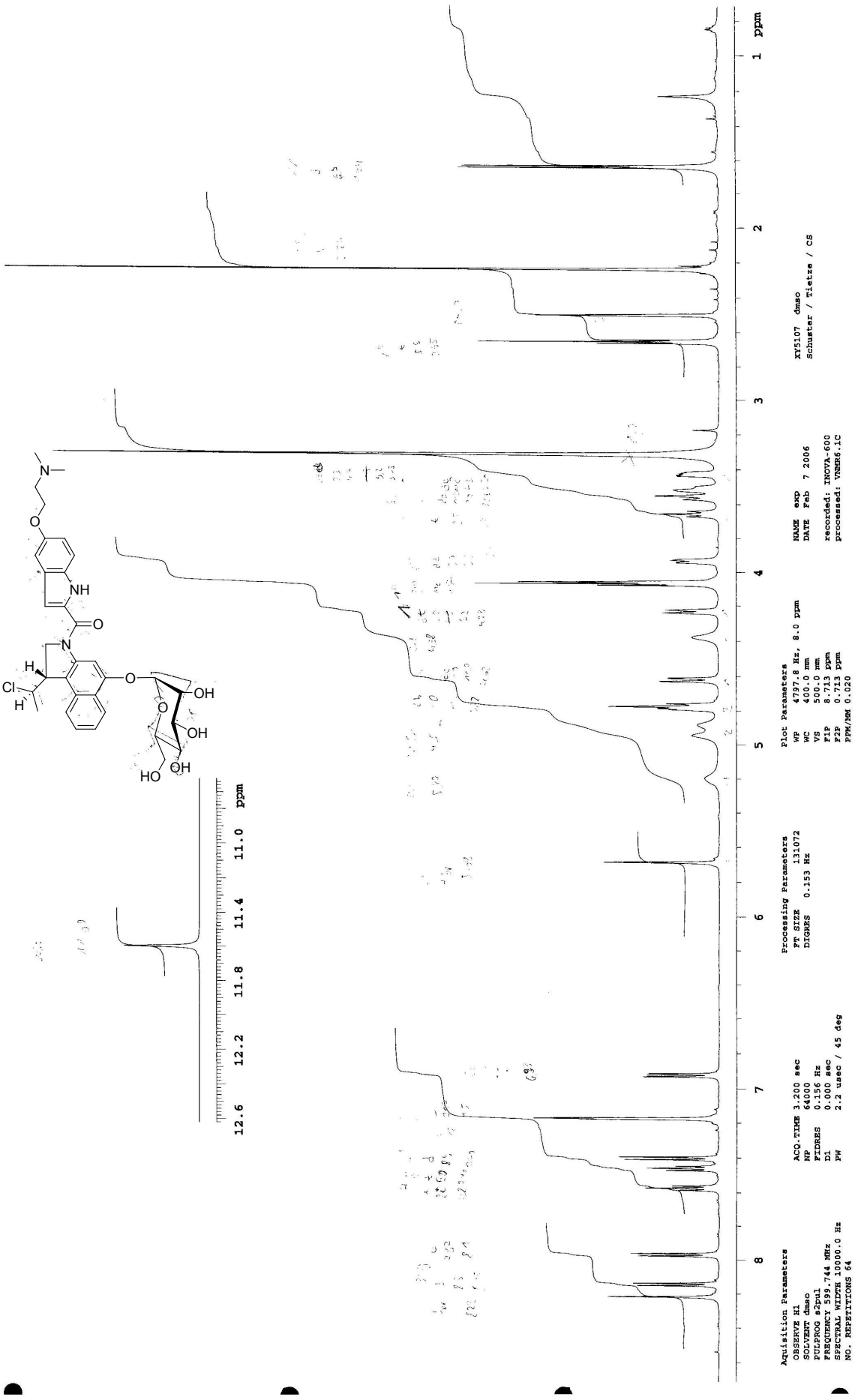
SPECTRAL LINES FOR TH= 6.2
FROM -2.5 PPM TO 197.5 PPM
RFL= 6168.3 RFP= 4964.9

INDEX	FREQ	PPM	HEIGHT	INDEX	FREQ	PPM	HEIGHT
1	21336.8	169.75	33.8	26	8624.8	68.62	33.5
2	21325.3	169.66	30.7	27	8619.5	68.58	33.1
3	21310.8	169.54	30.7	28	8330.7	66.28	36.0
4	21290.5	169.38	30.0	29	8197.5	65.22	26.1
5	20114.8	160.03	28.8	30	7750.8	61.66	22.7
6	19225.7	152.96	31.8	31	7697.8	61.24	20.2
7	18982.3	151.02	30.4	32	7261.2	57.77	58.9
8	17824.2	141.81	23.8	33	6535.3	51.99	16.5
9	16552.3	131.69	30.5	34	5770.6	45.91	27.3
10	16422.2	130.65	33.2	35	5718.2	45.49	158.7
11	16288.2	129.59	26.8	36	5038.6	40.09	12.6
12	16029.7	127.53	22.8	37	5028.0	40.00	139.7
13	16026.7	127.51	35.3	38	5018.3	39.92	26.5
14	15635.9	124.40	16.1	39	5006.8	39.83	427.4
15	15501.0	123.32	18.8	40	4997.1	39.76	45.5
16	15378.8	122.35	27.0	41	4985.6	39.66	847.2
17	15330.8	121.97	17.2	42	4976.4	39.59	48.1
18	15075.0	119.93	28.2	43	4964.9	39.50	1000.0
19	14570.9	115.92	19.8	44	4943.8	39.33	850.9
20	14215.4	113.10	26.5	45	4923.0	39.17	423.3
21	13256.3	105.46	25.0	46	4901.9	39.00	139.9
22	12978.4	103.25	26.0	47	2927.9	23.29	38.5
23	12800.7	101.84	20.0	48	2578.2	20.51	46.3
24	12028.5	95.70	24.0	49	2561.0	20.37	41.5
25	8669.4	68.97	27.3	50	2552.6	20.31	46.8
26	8624.8	68.62	33.5	51	2525.7	20.09	43.0



XY5104 dmso
Schuster / Tietze / CS

DATE: Feb 7 2006 FILE:nmrdast: tietze/xy5104_5c


Acquisition Parameters
OBSERVE H1
SOLVENT dmso
PULPROG s2pul
FREQUENCY 599.744 MHz
SPECTRAL WIDTH 10000.0 Hz
NO. REPETITIONS 64
ACQ.TIME 3.200 sec
NP 64000
FIDRES 0.156 Hz
D1 0.000 sec
PW 2.2 usec / 45 deg
Processing Parameters
FT SIZE 131072
DIGRES 0.153 Hz
Plot Parameters
WP 4797.8 Hz, 8.0 ppm
WC 400.0 mm
VS 500.0 mm
F1P 8.713 ppm
F2P 0.713 ppm
PPM/MM 0.020
NAME exp
DATE Feb 7 2006
recorded: INOVA-600
processed: VNMR6.1C
xr5107 dmso
Schuster / Tietze / CS
ppm
12.6
12.2
11.8
11.4
11.0
NH
N
O
Cl
H
OH
HO

XY5107 dmso
Schuster / Tietze / CS

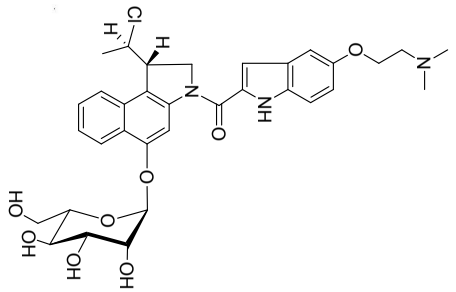
Feb 6 2006

INSTRUMENT INOVA-600
SAMPLE 3mm
OBSERVE C13
Frequency 150.821 MHz
Spectral width 34965.0 Hz
Acquisition time 1.829 sec
Relaxation delay 0.000 sec
Pulse width 35.0 degrees
Temperature 35.0 deg. C / 30
No. repetitions 23504
DECOUPLE H1
Frequency 599.743 Mhz
Power 48 dB
Decoupler continuously on
WALTZ-16 modulated
Double precision acquisition
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 11:56

XY5107 dmso
Schuster / Tietze / CS

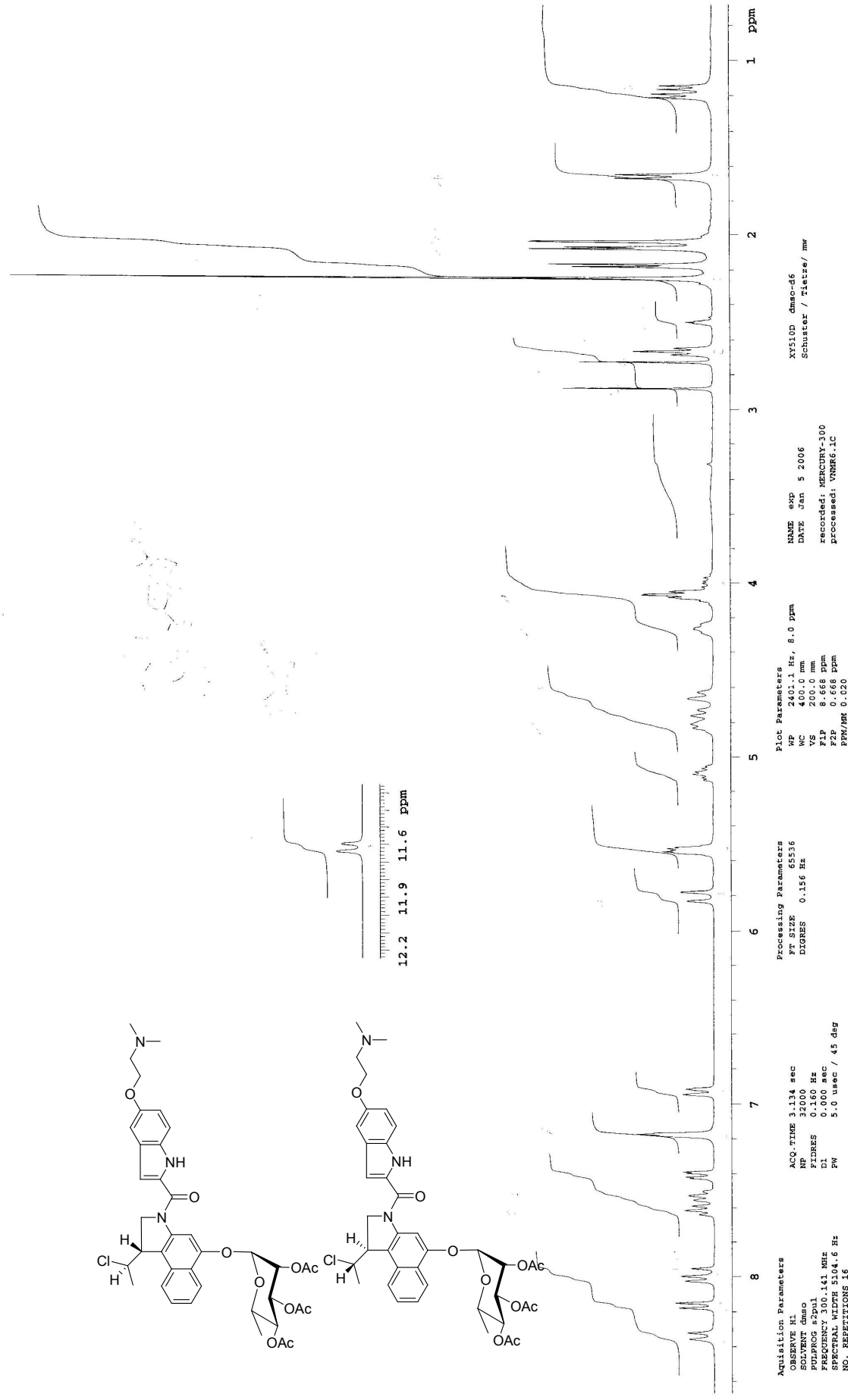
SPECTRAL LINES FOR TH= 7.2
FROM -2.5 PPM TO 197.5 PPM
RFL= 1703.0 RFP= 0.0

INDEX	FREQ	PPM	HEIGHT
1	24146.2	160.12	34.6
2	23067.4	152.96	38.2
3	22887.6	151.77	34.9
4	21410.9	141.98	29.7
5	19858.3	131.68	35.5
6	19729.2	130.83	38.4
7	19546.7	129.62	31.9
8	19229.8	127.51	36.6
9	19196.2	127.29	31.9
10	18689.3	123.93	26.0
11	18574.1	123.17	29.7
12	18513.8	122.77	33.1
13	18470.1	122.48	27.8
14	17905.1	118.73	33.6
15	17475.0	115.88	34.9
16	17055.7	113.10	43.3
17	15905.4	105.47	42.7
18	15573.0	103.27	42.5
19	15216.1	100.90	33.4
20	14843.2	98.43	44.8
21	11367.3	75.38	45.3
22	10708.9	71.01	46.5
23	10567.5	70.07	48.8
24	10030.8	66.51	46.6
25	9995.6	66.28	64.4
26	9250.8	61.34	35.8
27	9156.3	60.72	41.6
28	8715.1	57.79	91.0
29	7871.6	52.20	30.8
30	6926.7	45.93	42.1
31	6863.8	45.51	223.0
32	6037.4	40.03	12.8
33	6019.7	39.92	117.1
34	5998.4	39.78	341.4
35	5977.6	39.64	681.0
36	5956.8	39.50	800.0
37	5935.5	39.36	675.7
38	5914.6	39.22	345.2
39	5893.8	39.08	116.8
40	4353.6	28.87	8.3
41	3523.4	23.36	66.0



XY5107 dmso
Schuster / Tietze / CS

DATE: Feb 6 2006 FILE:nmrdast: tietze/xy5107_6c


12.2 11.9 11.6 ppm
1 ppm
2
3
4
5
6
7
8
Acquisition Parameters
OBSERVE H1
SOLVENT dmso
PULPROG s2pul
FREQUENCY 300.141 MHz
SPECTRAL WIDTH 5104.6 Hz
NO. REPETITIONS 16
ACQ.TIME 3.134 sec
NP 32000
FIDRES 0.160 Hz
D1 0.000 sec
PW 5.0 usec / 45 deg
Processing Parameters
FT SIZE 65536
DIGRES 0.156 Hz
Plot Parameters
WP 2401.1 Hz, 8.0 ppm
WC 400.0 mm
VS 200.0 mm
F1P 8.668 ppm
F2P 0.668 ppm
PPM/MM 0.020
NAME exp
DATE Jan 5 2006
recorded: MERCURY-300
processed: VNMR6.1C
XY510D dmso-d6
Schuster / Tietze/ mw
N
O
NH
O
N
H
Cl
H
O
OAc
O
OAc
OAc

XY510D dmso-d6
Schuster / Tietze/ mw

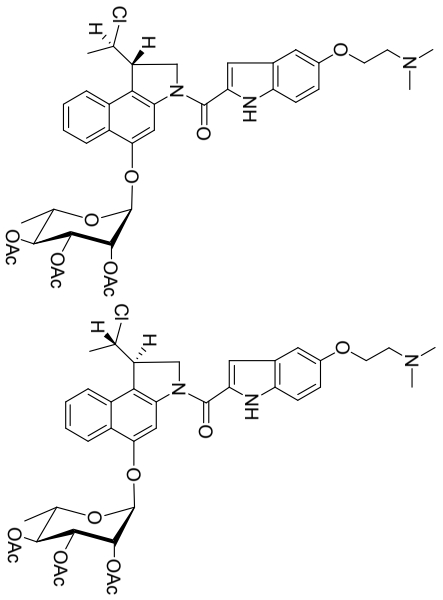
Jan 5 2006

INSTRUMENT MERCURY-300
OBSERVE C13
Frequency 75.478 MHz
Spectral width 18761.7 Hz
Acquisition time 1.706 sec
Relaxation delay 0.000 sec
Pulse width 35.0 degrees
Temperature 35.0 deg. C / 3
No. repetitions 937
DECOUPLE H1
Frequency 300.141 Mhz
Power 40 dB
Decoupler continuously on
WALTZ-16 modulated
Double precision acquisition
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 26 mir

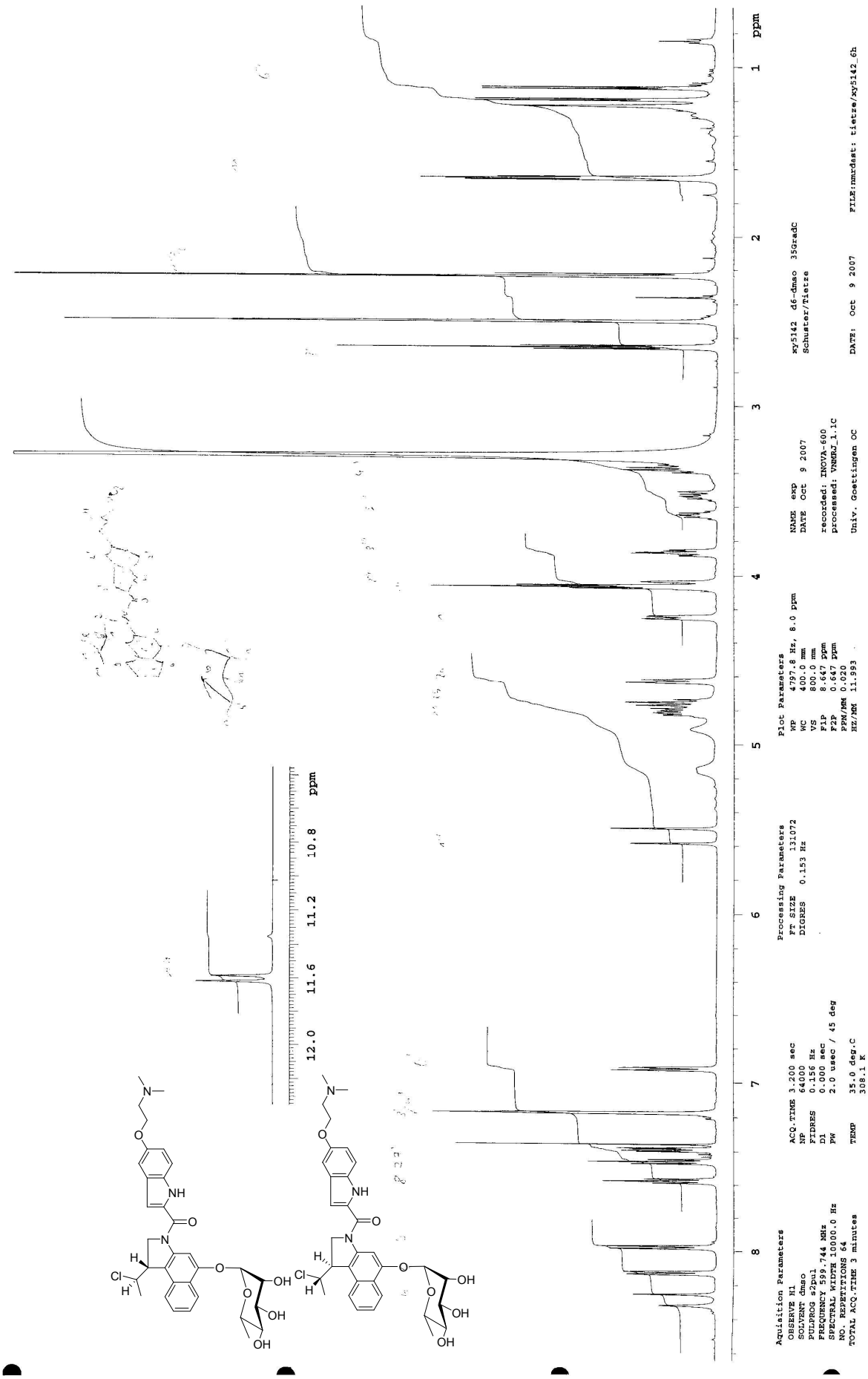
XY510D dmso-d6
Schuster / Tietze/ mw

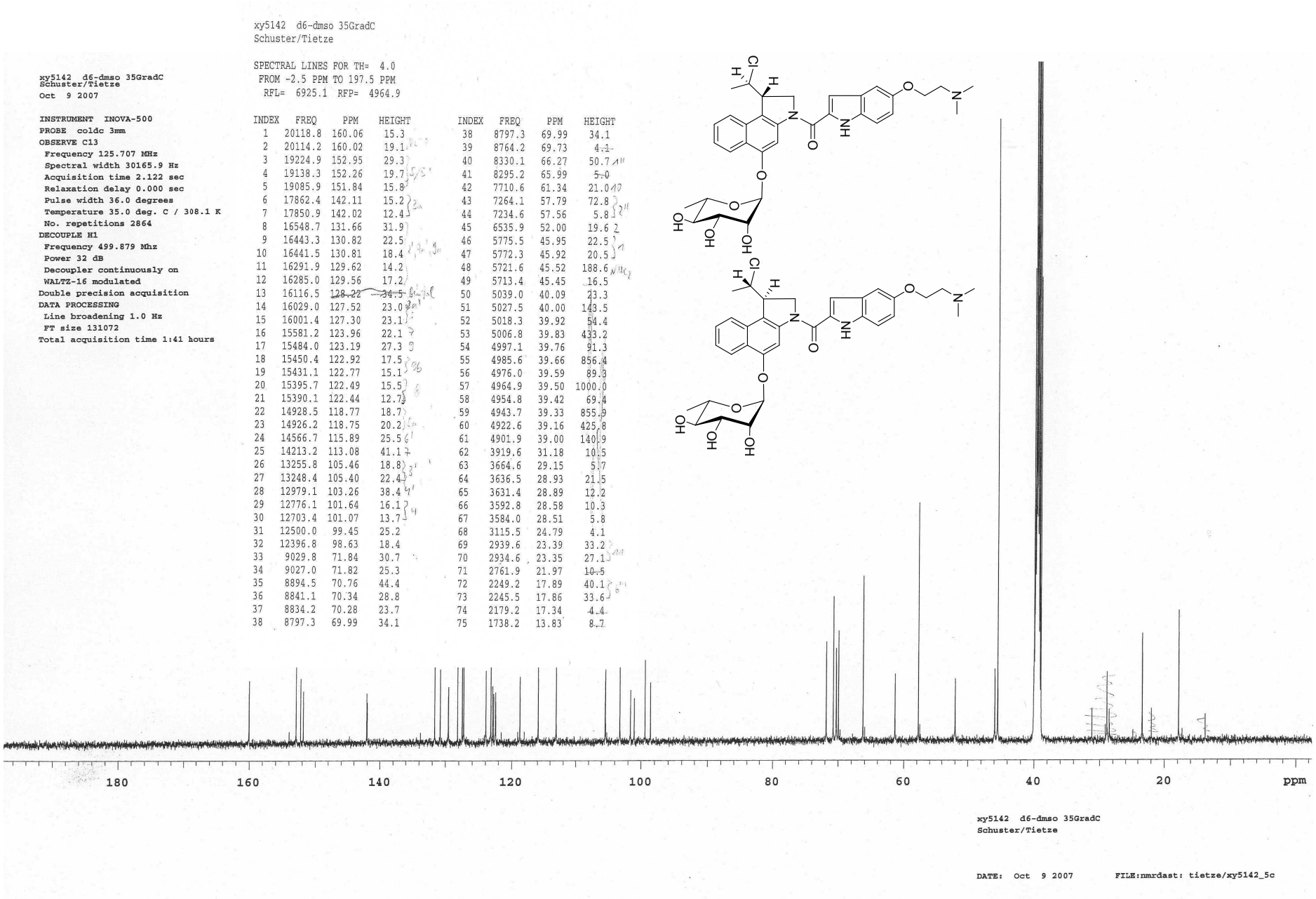
SPECTRAL LINES FOR TH= 7.5
FROM -2.5 PPM TO 197.5 PPM
RFL= 4120.4 RFP= 2981.1

INDEX	FREQ	PPM	HEIGHT	INDEX	FREQ	PPM	HEIGHT
1	12807.4	169.70	38.8	31	7694.1	101.95	12.3
2	12799.4	169.60	66.7	32	7682.4	101.79	9.7
3	12796.8	169.56	26.6	33	7251.2	96.08	17.0
4	12238.0	162.16	12.6	34	7222.0	95.69	14.2
5	12080.2	160.07	25.6	35	5268.5	69.81	26.8
6	11542.3	152.94	42.2	36	5197.7	68.87	23.8
7	11423.5	151.36	21.1	37	5176.6	68.59	22.7
8	11407.5	151.15	16.9	38	5078.1	67.29	27.5
9	10709.8	141.91	18.0	39	4995.1	66.19	39.8
10	10706.1	141.86	15.6	40	4621.5	61.24	23.2
11	9940.3	131.71	25.6	41	4355.8	57.72	54.7
12	9864.1	130.70	29.2	42	3927.5	52.04	9.1
13	9863.0	130.69	26.3	43	3916.6	51.90	9.5
14	9781.7	129.61	16.6	44	3467.7	45.95	22.3
15	9778.2	129.56	18.0	45	3427.4	45.41	145.0
16	9624.8	127.53	27.1	46	3044.1	40.33	29.1
17	9622.2	127.50	47.5	47	3023.2	40.06	85.3
18	9384.3	124.34	15.3	48	3002.0	39.78	170.1
19	9305.3	123.30	18.2	49	2981.1	39.50	200.0
20	9246.9	122.52	19.5	50	2960.2	39.22	167.7
21	9240.6	122.44	15.4	51	2948.4	39.07	7.7
22	9210.3	122.04	10.9	52	2939.0	38.94	83.1
23	9204.8	121.97	10.7	53	2918.1	38.67	27.4
24	9043.4	119.83	15.8	54	2689.1	35.63	14.7
25	9035.1	119.72	19.2	55	2313.7	30.66	10.0
26	8748.2	115.92	21.1	56	1762.1	23.35	22.9
27	8534.4	113.08	27.6	57	1757.2	23.28	18.3
28	7962.4	105.50	13.2	58	1547.7	20.51	40.0
29	7957.8	105.44	17.3	59	1538.5	20.39	58.4
30	7792.6	103.25	27.1	60	1300.3	17.23	29.5
31	7694.1	101.95	12.3	61	1297.4	17.19	23.4



XY510D dmso-d6
Schuster / Tietze/ mw


ppm
12.0
11.6
11.2
10.8
Cl
OH
NH
O
N


xy5142 d6-dmso 35GradC
Schuster/Tietze
Oct 9 2007
INSTRUMENT INOVA-500
PROBE coldc 3mm
OBSERVE C13
Frequency 125.707 MHz
Spectral width 30165.9 Hz
Acquisition time 2.122 sec
Relaxation delay 0.000 sec
Pulse width 36.0 degrees
Temperature 35.0 deg. C / 308.1 K
No. repetitions 2864
DECOUPLE H1
Frequency 499.879 Mhz
Power 32 dB
Decoupler continuously on
WALTZ-16 modulated
Double precision acquisition
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 1:41 hours
xy5142 d6-dmso 35GradC
Schuster/Tietze
SPECTRAL LINES FOR TH= 4.0
FROM -2.5 PPM TO 197.5 PPM
RFL= 6925.1 RFP= 4964.9
INDEX FREQ PPM HEIGHT
1 20118.8 160.06 15.3
2 20114.2 160.02 19.1
3 19224.9 152.95 29.3
4 19138.3 152.26 19.7
5 19085.9 151.84 15.8
6 17862.4 142.11 15.2
7 17850.9 142.02 12.4
8 16548.7 131.66 31.9
9 16443.3 130.82 22.5
10 16441.5 130.81 18.4
11 16291.9 129.62 14.2
12 16285.0 129.56 17.2
13 16116.5 128.22 34.5
14 16029.0 127.52 23.0
15 16001.4 127.30 23.1
16 15581.2 123.96 22.1
17 15484.0 123.19 27.3
18 15450.4 122.92 17.5
19 15431.1 122.77 15.1
20 15395.7 122.49 15.5
21 15390.1 122.44 12.7
22 14928.5 118.77 18.7
23 14926.2 118.75 20.2
24 14566.7 115.89 25.5
25 14213.2 113.08 41.1
26 13255.8 105.46 18.8
27 13248.4 105.40 22.4
28 12979.1 103.26 38.4
29 12776.1 101.64 16.1
30 12703.4 101.07 13.7
31 12500.0 99.45 25.2
32 12396.8 98.63 18.4
33 9029.8 71.84 30.7
34 9027.0 71.82 25.3
35 8894.5 70.76 44.4
36 8841.1 70.34 28.8
37 8834.2 70.28 23.7
38 8797.3 69.99 34.1
INDEX FREQ PPM HEIGHT
38 8797.3 69.99 34.1
39 8764.2 69.73 4.1
40 8330.1 66.27 50.7
41 8295.2 65.99 5.0
42 7710.6 61.34 21.0
43 7264.1 57.79 72.8
44 7234.6 57.56 5.8
45 6535.9 52.00 19.6
46 5775.5 45.95 22.5
47 5772.3 45.92 20.5
48 5721.6 45.52 188.6
49 5713.4 45.45 16.5
50 5039.0 40.09 23.3
51 5027.5 40.00 143.5
52 5018.3 39.92 54.4
53 5006.8 39.83 433.2
54 4997.1 39.76 91.3
55 4985.6 39.66 856.4
56 4976.0 39.59 89.3
57 4964.9 39.50 1000.0
58 4954.8 39.42 69.4
59 4943.7 39.33 855.9
60 4922.6 39.16 425.8
61 4901.9 39.00 140.9
62 3919.6 31.18 10.5
63 3664.6 29.15 5.7
64 3636.5 28.93 21.5
65 3631.4 28.89 12.2
66 3592.8 28.58 10.3
67 3584.0 28.51 5.8
68 3115.5 24.79 4.1
69 2939.6 23.39 33.2
70 2934.6 23.35 27.1
71 2761.9 21.97 10.5
72 2249.2 17.89 40.1
73 2245.5 17.86 33.6
74 2179.2 17.34 4.4
75 1738.2 13.83 8.7
180
160
140
120
100
80
60
40
20
ppm
xy5142 d6-dmso 35GradC
Schuster/Tietze
DATE: Oct 9 2007
FILE:nmrdast: tietze/xy5142_5c

Results for β-D-Glucoside 19:

with β-D-Glucosidase (10 U/ml)		with Cellulase (0.17 U/ml)		without β-D-Glucosidase	
concentration [nM]	Clone formation rate [%] pH = 7.4	concentration [nM]	Clone formation rate [%] pH = 7.4	concentration [nM]	Clone formation rate [%] pH = 7.4
0	100			0	100
0.16	95.97			781	90.78
0.78	93.96	0	100	1172	90.63
1.56	95.3	0.78	83.09	1562	65.39
3.91	112.75	1.56	62.91	2343	39.67
7.81	100.67	3.91	14.87	3906	23.32
15.62	107.38	7.81	3.99	7811	1.47
39.06	95.97	15.62	0.107	11717	0.12
78.1	83.22			15622	0.0023
152.2	98.66			23433	0.0018

The effective dose (IC_{50}) of prodrug **19** ist 2000 nM without addition of β-D-Glucosidase and >150 nM in the presence of β-D-Glucosidase. In presence of Cellulase results IC_{50} = 1.9 nM.

Results for α-D-Mannoside 22:

without α-D-Mannosidase		with α-D-Mannosidase (0.4 U/ml)	
concentration [nM]	Clone formation rate [%] pH = 7.4	concentration [nM]	Clone formation rate [%] pH = 7.4
0	100	0	100
1172	84.55	0.16	101.84
1562	75.77	0.39	77.08
2343	61.67	0.78	35.63
3124	40.60	1.17	12.55
3906	28.68	1.56	7.13
5468	13.52	2.34	2.3
7811	2.15	3.91	0.26
11717	0.206		

The effective dose (IC_{50}) of prodrug **22** ist 3300 nM without addition of α-D-Mannosidase and 2.1 nM in the presence of α-D-Mannosidase.

Results for α-L-Rhamnoside 23:

concentration [nM]	Clone formation rate [%] pH = 7.4
0	100
801	93.95
1602	98.87
2403	69.63
4006	43.14
5608	15.17
8011	2.73
12017	0.373
16022	0.043

The effective dose (IC_{50}) of prodrugs **23** is 3500 nM.

Results for β-D-Cellobioside 21:

without Cellulase		with Cellulase (0.17 U/ml)	
concentration [nM]	Clone formation rate [%] pH = 7.4	concentration [nM]	Clone formation rate [%] pH = 7.4
0	100	0	100
125	98.82	0.62	102.69
623	94.08	1.25	93.46
1870	73.58	3.12	41.19
3116	31.25	6.23	4.03
6230	2.86	12.46	0.55
9349	0.56	31.2	0.004
12465	0.127		

The effective dose (IC_{50}) of the prodrug **21** is 2400 nM without Cellulase and 2.6 nM in the presence of Cellulase.

Results for β-D-Lactoside 20:

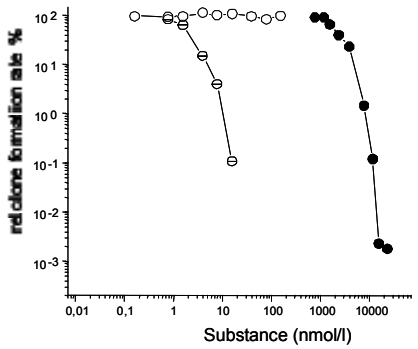
Without enzyme		with Cellulase (0.17 U/ml)	
concentration [nM]	Clone formation rate [%] pH = 7.4	concentration [nM]	Clone formation rate [%] pH = 7.4
0	100	0	100
125	101.45	1.25	100.53
623	100.11	6.23	93.61
1870	85.59	12.46	62.49
3116	39.49	31.16	8.01
6230	3.83	62.23	1.07
9349	0.84	93.49	0.27
12465	0.44		

with Cellulase (0.17 U/ml) and β-D-Galactosidase (4 U/ml)		with β-D-Galactosidase (4 U/ml)	
concentration [nM]	Clone formation rate [%] pH = 7.4	concentration [nM]	Clone formation rate [%] pH = 7.4
0	100	0	100
0.62	90.59	0.62	101.64
1.25	79.6	1.25	102.22
3.12	29.67	3.12	93.46
6.23	3.67	6.23	101.05
9.35	0.51	9.35	94.63
12.46	0.36	12.46	91.71
31.16	0.018	31.16	100.47

The effective dose (IC_{50}) of prodrug **20** ist 2700 nM without addition of any enzyme and 14.5 nM in the presence of Cellulase, 2.1 nM in presence of Cellulase and β-D-Galactosidase and 31 nM in presence of only β-D-Galactosidase

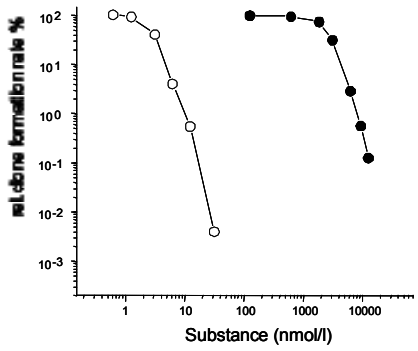
Graphs of HTCFA *in vitro* results of all tested compounds

β-D-Glucoside (–)-(1*S*,10*R*)-**19**



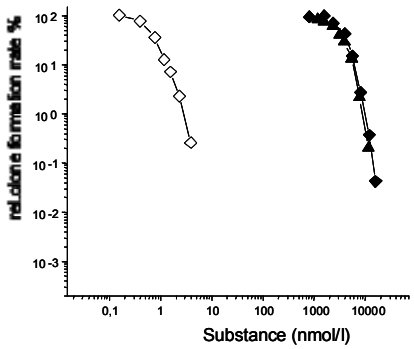
Glucoside without enzyme	IC_{50}	2000 nmol/l
Glucoside with 10 U/ml β-D-Glucosidase	IC_{50}	>150 nmol/l
	QIC_{50}	**= <10**
Glucoside with 0.17 U/ml Cellulase	IC_{50}	1.9 nmol/l
	QIC_{50}	**= 1100**

β-D-Cellobioside (1*S*,10*R*)-**21**



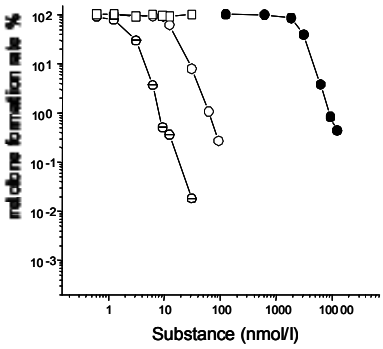
Cellobioside without enzyme	IC_{50}	2400 nmol/l
Cellobioside with 0.17 U/ml Cellulase	IC_{50}	2.6 nmol/l
	QIC_{50}	**= 920**

α-L-Rhamnosides (1*SR*,10*RS*)-**23** and
α-D-Mannoside (+)-(1*S*,10*R*)-**22**



Rhamnosides without enzyme	IC_{50}	3500 nmol/l
Mannoside without enzyme	IC_{50}	2700 nmol/l
Mannoside with 0.4 U/ml α-Mannosidase	IC_{50}	0.6 nmol/l
	QIC_{50}	**= 4500**

β-D-Lactoside (1*S*,10*R*)-**20**



Lactoside without enzyme	IC_{50}	2700 nmol/l
Lactoside with 0.17 U/ml Cellulase	IC_{50}	14.5 nmol/l
	QIC_{50}	**= 190**
Lactoside with 0.17 U/ml Cellulase and 4 U/ml β-D-Galactosidase	IC_{50}	2.1 nmol/l
	QIC_{50}	**= 1300**
Lactosid with 4 U/ml β-D-Galactosidase	IC_{50}	> 31 nmol/l
	QIC_{50}	**= < 90**

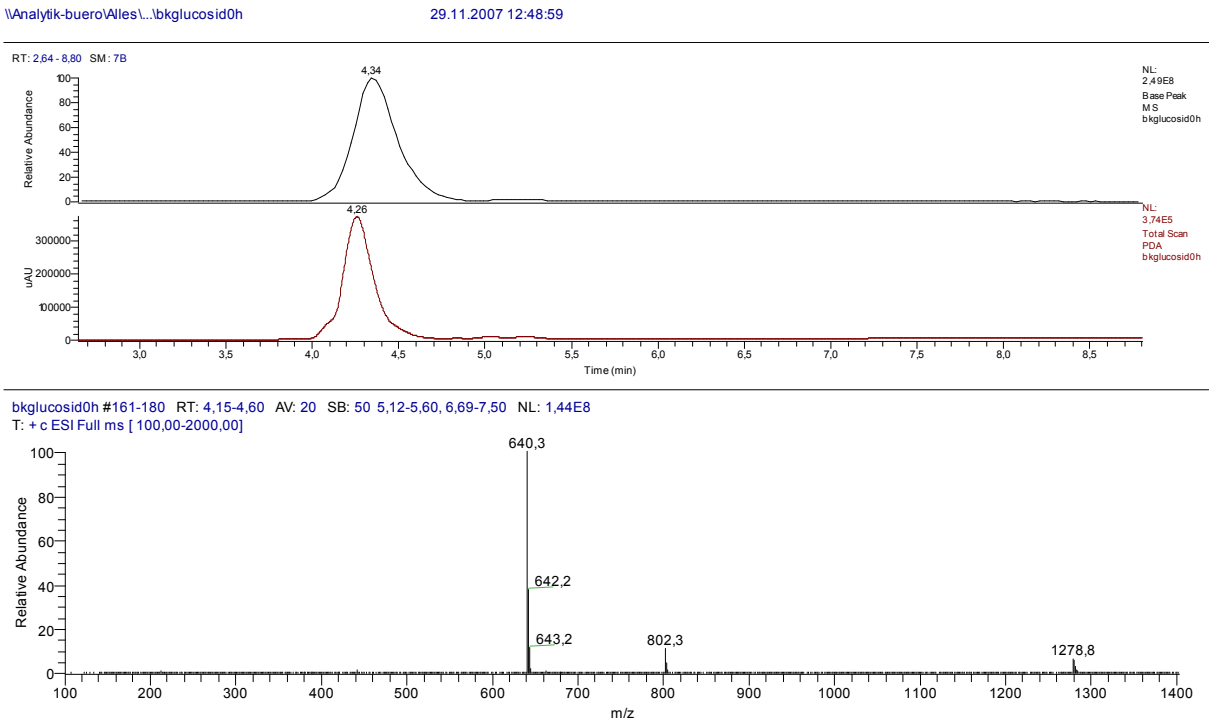
HPLC-MS: The analytical separation were realized using a Rheos 4000 solvent pump, a ERC-3415α degaser (*Flux Instruments*), a Jasco 851-AS autosampler and a *Thermo* diodearray-detector. The used column was a *phenomenex* Synergi Max-RP C12 (150 × 2 mm, particle size 4 µm) and the injestion volume 5 µL. For han
dling, data collection and data evaluation we used the computer programs Janeiro and Xcalibur. The eluents were H_2O (solvent A) and Methanol (solvent B) of *VWR*. To enhance the peak shape 0.05% of formic acid (*Roth*) was added. The flow rate was 300 µL/min using the following gradients

Time [min]	A/B
0	70/30
0 – 15	70/30 → 0/100
15 – 22	0/100
22 – 23	0/100 → 70/30
23 – 29	70/30

The subsequent online analysis of the analytical separations was realized using ESI mass spectroscopy with an ion-trap-masspectrometer LCQ (*Finnigan*), the UV detection done between 200-800 nm and mass-detection between 100-2000 m/z. The temperature of the capillary was 220 °C, the spray-current 4.5 kV and the sheath-gas flow 80 (random unit).

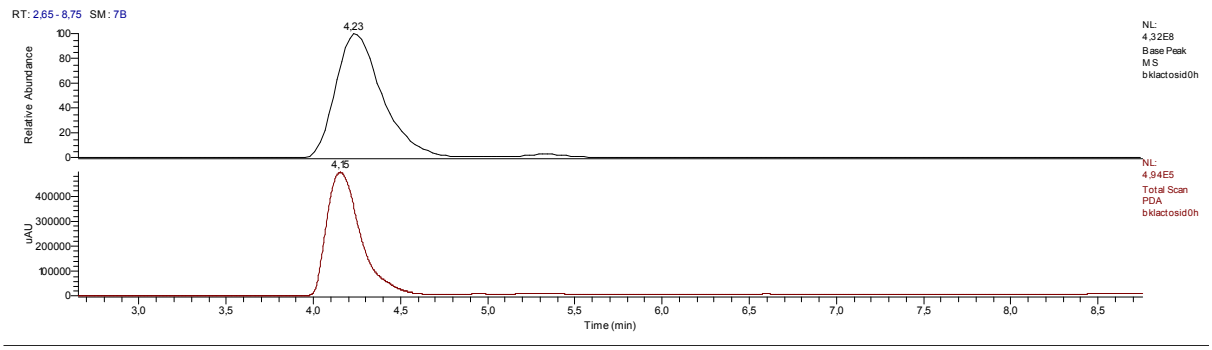
HPLC-MS chromatograms

Glucose Prodrug (**19**):

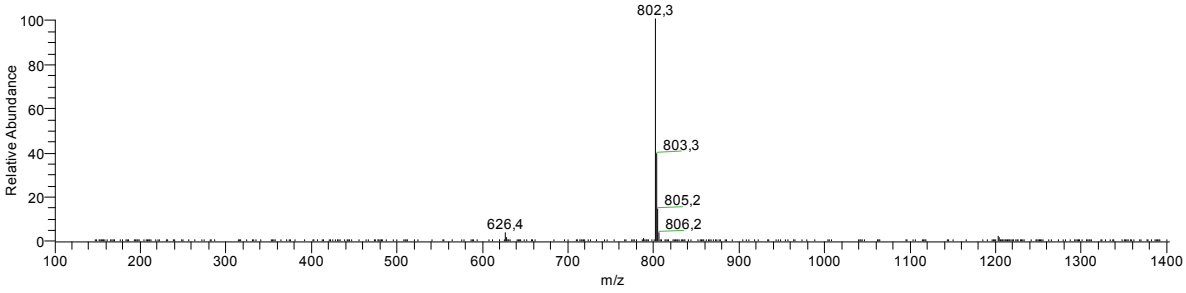


Lactose Prodrug (**20**):

\\Analytik-buero\Alles\...\bklactosid0h 29.11.2007 10:31:19

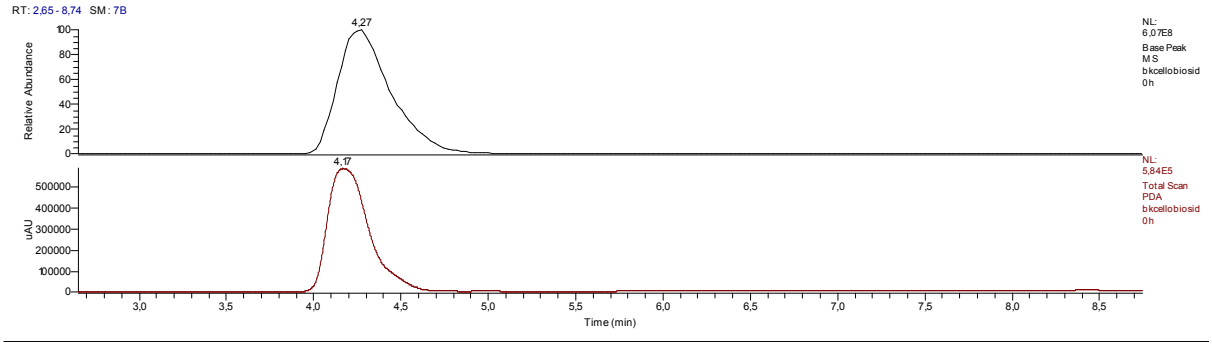


bklactosid0h #154-166 RT: 4,11-4,39 AV: 13 SB: 50 5,13-5,61, 6,68-7,50 NL: 3,58E8
T: + c ESI Full ms [100,00-2000,00]

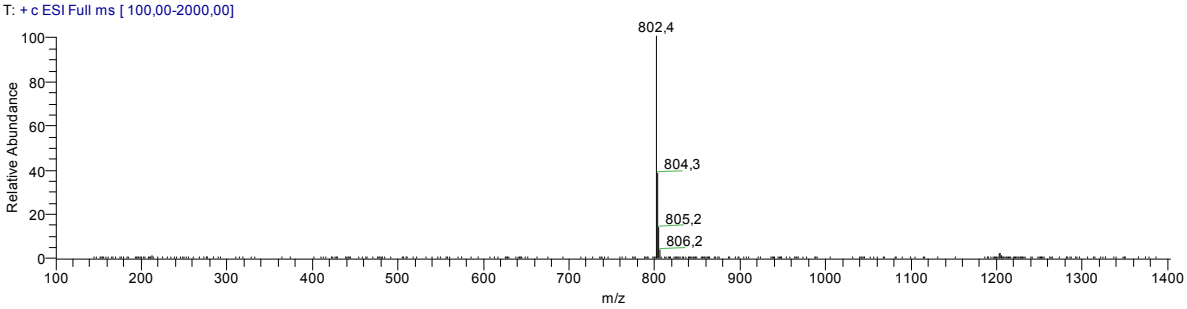


Cellobiose Prodrug (**21**):

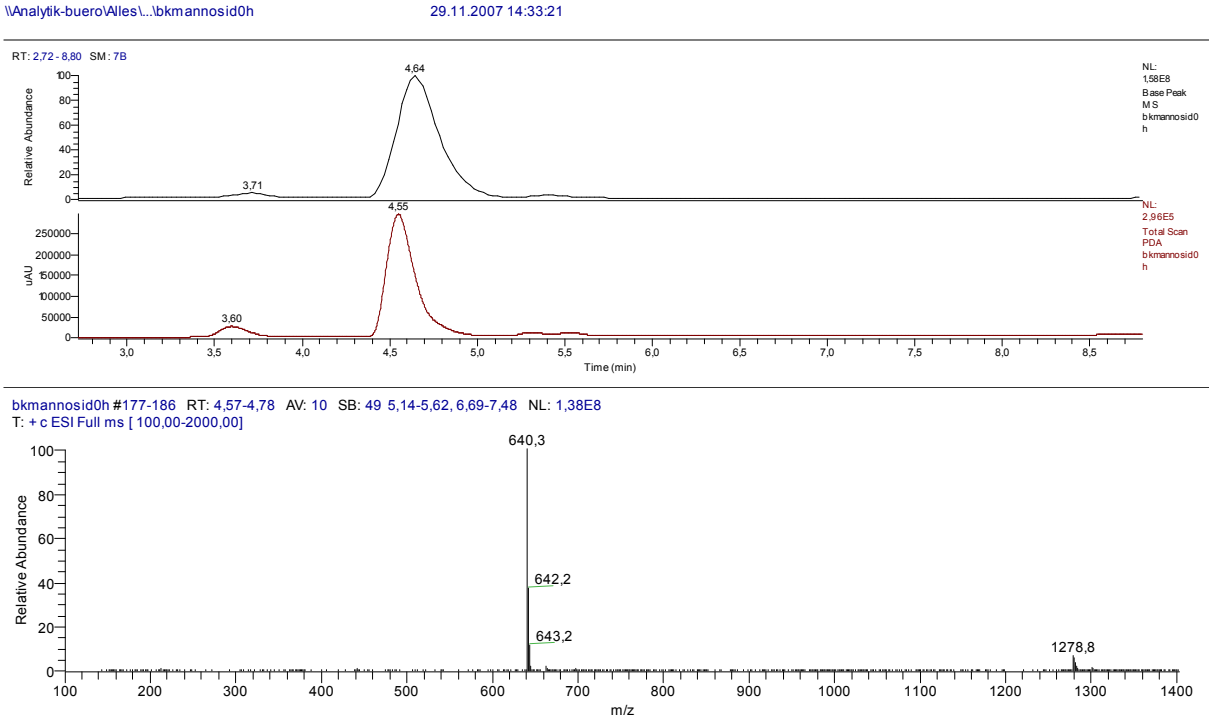
bkcellobiosid0h 29.11.2007 11:39:09



bkcellobiosid0h #160-173 RT: 4,13-4,43 AV: 14 SB: 50 5,14-5,62, 6,68-7,50 NL: 5,12E8
T: + c ESI Full ms [100,00-2000,00]



Mannose Prodrug (**22**):



Rhamnose Prodrugs (**23**):

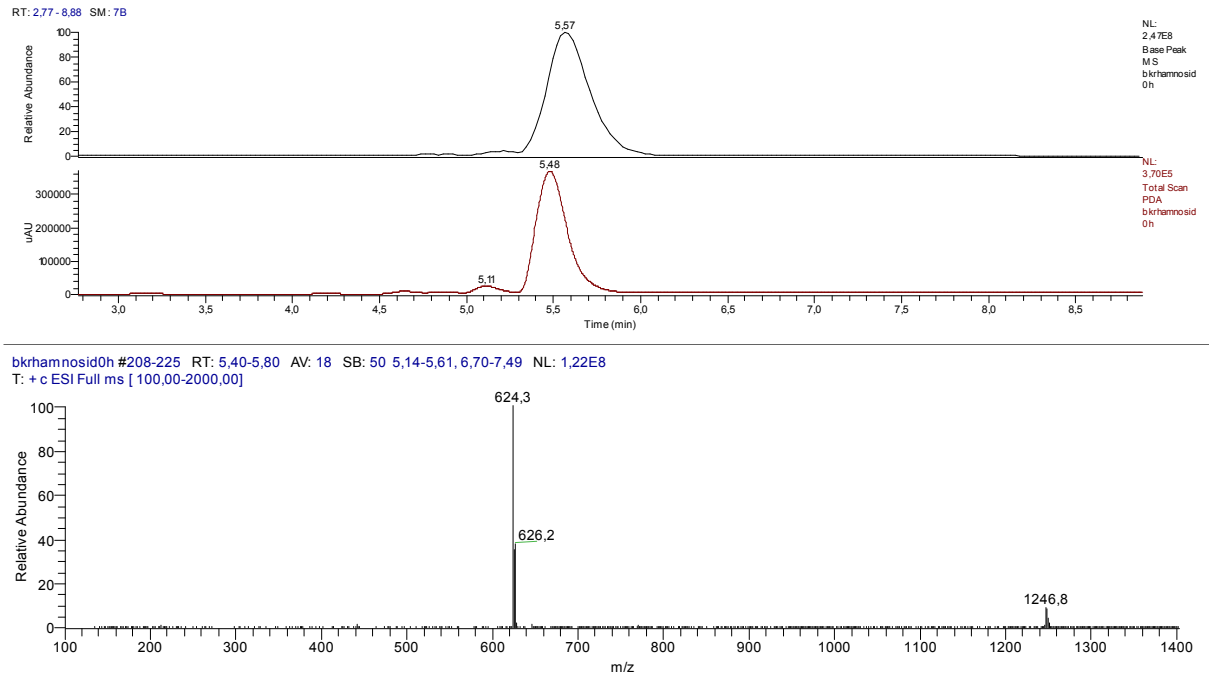


Table of analytical data and purity criteria of target and other compounds

Compound or structure number	Known [citation given]	R_f	Optical rotation	^1H NMR	^{13}C NMR	IR	UV-vis	MS	Copy of $^1H/^{13}C$ NMR for SI	HR-MS	LC Purity
Acetylated Glucose Prodrug **13**	–	X	X	X	X	X	X	X	X	X	–
Glucose Prodrug **19**	–	X	X	X	X	X	X	X	X	X	98
Lactose Heptaacetate	X	X	–	X	X	–	–	–	–	–	–
Lactose trichloroacetimidate **7**	X	X	X	X	X	X	X	X	–	–	–
Acetylated Lactose Prodrug **14**	–	X	X	X	X	X	X	X	X	X	–
Lactose Prodrug **20**	–	X	–	X	X	X	X	X	X	X	99
Cellobiose Heptaacetate	X	X	–	X	X	–	–	–	–	–	X
Cellobiose trichloroacetimidate **8**	X	X	–	X	X	–	–	X	–	–	X
Acetylated Cellobiose Prodrug **15**	–	X	X	X	X	X	X	X	X	X	X
Cellobiose Prodrug **21**	–	X	–	X	X	X	X	X	X	X	100
Acetylated Mannose Prodrug **16**	–	X	X	X	X	–	–	X	X	X	X
Mannose Prodrug **22**	–	X	X	X	X	X	X	X	X	X	98
Acetylated Rhamnose Prodrug rac**17**	–	X	–	X	X	–	–	-	X	X	X
Rhamnose Prodrug rac**23**	–	X	X	X	X	X	X	X	X	X	96

Purity and Peak attributes of target prodrugs

Compound	HRMS $[M+H]^+$		HPLC	
	Calculated	Found	Purity (%)[a]	Retention time (min.)
19	640.24202	640.24194	98.1	4.26
20	802.29484	802.29496	99.0	4.15
21	802.29484	802.29482	99.8	4.17
22	640.24202	640.24211	98.4	4.55
23	624.24710	624.24707	96.4	5.48

[a] Purity was assessed by integration of relevant peak areas from UV trace from 200-800 nm.