

Supporting Information

for

Stereo- and Chemoselective Amidoglycosylation of Glucal 3-Carbamates

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General: NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz for ^1H spectra and 75 MHz for ^{13}C spectra. ^1H chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS, δ 0.00), using as a reference either added TMS or an appropriate signal for residual solvent protons. ^{13}C NMR chemical shifts are reported in parts per million, using the center peak of the solvent signal as a reference. ^{13}C NMR peak multiplicities, where reported, were inferred using either DEPT 135 or edited HSQC experiments. The designation “o” (for odd number of attached hydrogens) denotes a CH or CH_3 carbon. Where ^1H and ^{13}C NMR peak assignments are given, these were made unambiguously by a combination of $^1\text{H}/^1\text{H}$ COSY, $^1\text{H}/^{13}\text{C}$ HSQC, and $^1\text{H}/^{13}\text{C}$ HMBC experiments. The NMR simulations applied in some of the $J_{\text{H4,H5}}$ determinations used gNMR from Adept Scientific. Infrared spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrometer. Melting points were obtained using a Thomas Hoover capillary melting point apparatus and are uncorrected. High resolution mass spectra were measured at the Columbia University Mass Spectroscopy Laboratory.

Iodosobenzene (PhIO) was prepared according to the literature procedure¹ and was stored in the dark at $-20\text{ }^\circ\text{C}$ under dry argon or nitrogen. Oven-dried ($135\text{ }^\circ\text{C}$) 4 Å molecular sieves were further activated by flame-drying under vacuum (0.5 mmHg) just prior to use. Benzene and toluene used as reaction solvents were distilled from CaH_2 , while methylene chloride was either distilled from CaH_2 or purchased from Sigma-Aldrich (anhydrous, Sure Seal). Anhydrous tetrahydrofuran (inhibitor-free, Sure Seal) and dimethylformamide (anhydrous, Sure Seal) were purchased from Sigma-Aldrich. Trichloroacetyl isocyanate ampoules (Sigma-Aldrich) were opened just prior to use. Other reagents were obtained commercially and were used as received. Reactions were carried out in oven- or flame-dried glassware under an atmosphere of dry argon or nitrogen. The amidoglycosylation products were sometimes difficult to visualize on TLC. A useful system to char the TLC plates involved preheating the eluted TLC plate, dipping the plate in a basic solution of permanganate [KMnO_4 (3 g), K_2CO_3 (20 g), 5% NaOH (5 mL), H_2O (300 mL)], and then *gently* warming the TLC plate.

¹ Saltzman, H.; Sharefkin, J. G. In *Organic Syntheses*; Baumgarten, H. E., Ed.; John Wiley & Sons: New York, 1973; Coll. Vol. 5, pp 658–659.

Experimental Procedures and Characterization Data

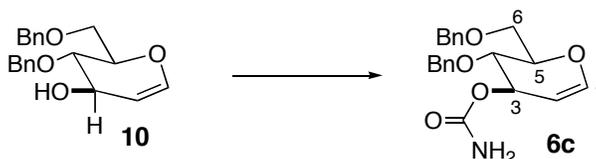
Part 1. Amidoglycosylation of benzylidene-protected allal 3-carbamate **4**.



4-Pentenyl 2-amino-4,6-O-benzylidene-2-N,3-O-carbonyl- β -D-allopyranoside (5**).** Freshly activated 4Å molecular sieves (253 mg), carbamate **4**² (101.3 mg, 0.366 mmol), Rh₂(OAc)₄ (17.0 mg, 0.0385 mmol), and iodosobenzene (133.7 mg, 0.608 mmol) were combined and 4-penten-1-ol (190 μ L, 1.83 mmol) was added, followed by benzene (4.0 mL). The greenish, heterogeneous mixture was well-stirred at room temperature for 3 h. The now translucent reaction mixture was filtered through a pad of Celite, rinsing with EtOAc and the filtrate was concentrated (rotovap then overnight at 0.5 mmHg). The crude was analyzed by ¹H NMR, showing a single anomer and no dihydropyranone byproduct, then chromatographed (45% EtOAc/hexanes, 30 mL SiO₂). Oxazolidinone **5** was a colorless glass (109.4 mg, 83%). Under identical conditions but with CH₂Cl₂ as the solvent the yield was 80%, and in toluene the yield was 79%. *R*_f = 0.3 (50% EtOAc/hexanes), IR (thin film) 3297, 3070, 3037, 1762 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.57-7.44 (m, 2H), 7.42-7.29 (m, 3H), 6.64 (br s, 1H), 5.82 (dddd, *J* = 17.0, 10.3, 6.7, 6.7 Hz, 1H), 5.56 (s, 1H), 5.12-4.97 (m, 2H), 4.96 (dd, *J* = 7.7, 3.3 Hz, 1H), 4.59 (d, *J* = 4.1 Hz, 1H), 4.38 (dd, *J* = 10.4, 5.0 Hz, 1H), 4.18 (dd, *J* = 10.0, 3.4 Hz, 1H), 4.00 (ddd, *J* = 10.0, 10.0, 5.0 Hz, 1H), 3.91-3.78 (m, 2H), 3.70 (dd, *J* = 10.2, 10.2 Hz, 1H), 3.46 (ddd, *J* = 9.5, 6.5, 6.5 Hz, 1H), 2.13 (apparent q, *J* = 7.1 Hz, 2H), 1.70 (apparent quintet, *J* = 7.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 159.2, 137.7, 136.7, 129.3, 128.3, 126.3, 115.1, 102.6, 100.4, 74.8, 73.0, 69.6, 68.8, 62.4, 55.5, 30.1, 28.6; HRMS (FAB) *m/z* calcd for C₁₉H₂₄NO₆ (M+H)⁺ 362.1604, found 362.1602.

Part 2. Synthesis of glucal 3-carbamates **6c–6i**

2.1. Preparation of dibenzyl-protected glucal 3-carbamate **6c**



3-O-Carbamoyl-4,6-di-O-benzyl-D-glucal (6c**).** Following the general method of Kocovsky,³ a solution of 4*O*,6*O*-dibenzyl-D-glucal (**10**⁴) (431.1 mg, 1.322 mmol) in CH₂Cl₂ (5.0 mL) was cooled to 0

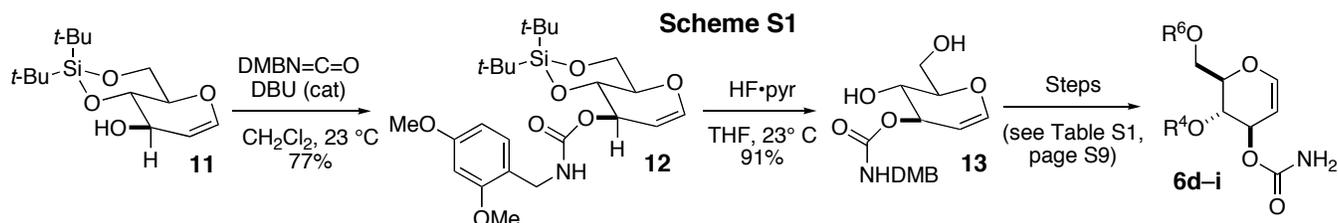
² Levites-Agababa, E.; Menhaji, E.; Perlson, L. N.; Rojas, C. M. *Org. Lett.* **2002**, *4*, 863–865.

³ Kocovsky, P. *Tetrahedron Lett.* **1986**, *27*, 5521–5524.

⁴ Prepared from D-glucal according to Franck et al. (a) Dios, A.; Geer, A.; Marzabadi, C. H.; Franck, R. W. *J. Org. Chem.* **1998**, *63*, 6673–6679. (b) Franck, R. W.; Marzabadi, C. H. *J. Org. Chem.* **1998**, *63*, 2197–2208. We had difficulty separating pure 4,6-di-O-benzyl-D-glucal (**10**) from a second dibenzylated D-glucal byproduct via column chromatography on

°C and trichloroacetyl isocyanate (240 μ L, 2.02 mmol, freshly opened ampoule) was added. The mixture was stirred 10 min at 0 °C, 20 min at room temperature, and recooled to 0 °C. MeOH (6 mL) was added, followed by K_2CO_3 (533 mg, 3.86 mmol), and the mixture was well-stirred as the ice bath melted and the mixture warmed to room temperature. TLC showed complete imide methanolysis 3 h after addition of the methanol and K_2CO_3 . The reaction mixture was poured into satd aq NH_4Cl (30 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The organic layers was dried ($MgSO_4$), filtered, and concentrated. The crude was chromatographed, affording carbamate **6c** as a white solid (464.7 mg, 95%). The carbamate **6c** could also be recrystallized from hot hexanes with a few drops EtOAc added to dissolve all solids. mp 113-114 °C; R_f = 0.3 (40% EtOAc/hexanes); IR (thin film) 3420, 3351, 3297, 3203, 3088, 3064, 3032, 1725, 1693, 1651, 1645 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.21 (m, 10H), 6.43 (dd, J = 6.0, 1.1 Hz, 1H, H1), 5.35 (ddd, J = 6.2, 2.5, 1.3 Hz, 1H, H3), 4.80 (dd, J = 6.1, 2.8 Hz, 1H, H2), 4.66 (AB, J_{AB} = 11.4 Hz, $\Delta\nu_{AB}$ = 27.1 Hz, 2H, OCH_2Ph), 4.59 (AB, J_{AB} = 11.9 Hz, $\Delta\nu_{AB}$ = 13.9 Hz, 2H, OCH_2Ph), 4.54 (br s, 2H, NH_2), 4.09 (m, 1H, H5), 3.90 (dd, J = 8.8, 6.4 Hz, 1H, H4), 3.79 (AB of ABX, J_{AB} = 10.7 Hz, J_{AX} = 4.6 Hz, J_{BX} = 2.8 Hz, $\Delta\nu_{AB}$ = 19.9 Hz, 2H, H6a and H6b); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3 (s, $OCONH_2$), 145.6 (o, C1), 137.9 (s, Ph), 137.8 (s, Ph), 128.4 (o, Ph), 128.3 (o, Ph), 128.0 (o, Ph), 127.8 (o, Ph), 127.7 (o, Ph), 99.5 (o, C1), 76.8 (o, C5), 73.5 (t, CH_2Ph), 73.4 (t, CH_2Ph), 73.2 (o, C4), 71.6 (o, C3), 68.0 (t, C6); HRMS (FAB) m/z calcd for $C_{21}H_{23}NO_5$ (M)⁺ 369.1576, found 369.1591. Anal. calcd for $C_{21}H_{23}NO_5$: C, 68.28; H, 6.28; N, 3.79. Found: C, 67.96; H, 6.20; N, 3.84.

2.2. Preparation of glucal 3-carbamates **6d-i**



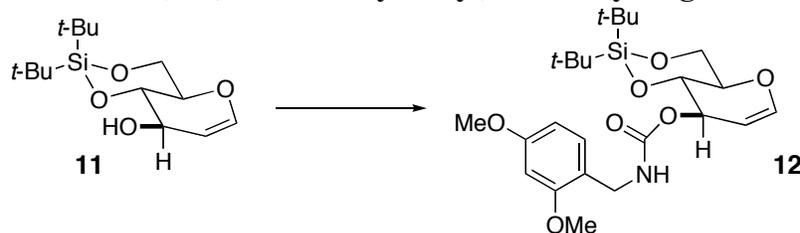
We used the versatile synthesis of differentially 4*O*,6*O*-diprotected glucal 3-carbamates shown in Scheme S1 above. Formation of the 2,4-dimethoxybenzyl carbamate **12** from known silylene-protected glucal **11**,⁵ followed by desilylation, provided diol **13**.⁶ Protection of the hydroxyls and mild oxidative cleavage of the *N*-dimethoxybenzyl group provided a range of glucal 3-carbamate amidoglycosylation substrates **6d-i** for comparison with the acetonide-, silylene-, and dibenzyl-protected carbamates **6a**, **6b**, and **6c**.

silica gel. However, after initial chromatography, the impure material solidified on storage at -20 °C, and we recrystallized **10** by suspending the impure material in warm hexanes, adding EtOAc dropwise to obtain a homogenous solution, and allowing the solution to cool. After cooling further in an ice bath, filtration provided pure 4,6-di-*O*-benzyl-D-glucal (**10**) as white needles or flakes.

⁵ Hoberg, J. O. *Carbohydr. Res.* **1997**, *300*, 365–367.

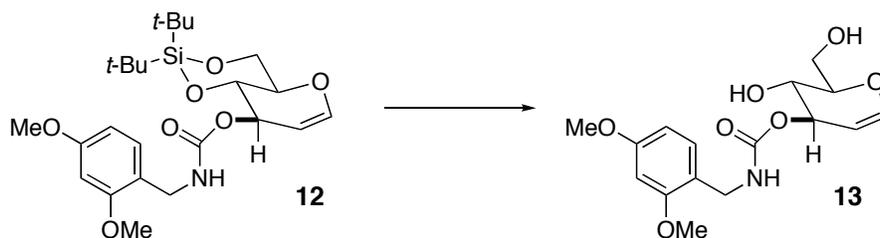
⁶ Our approach closely follows a route developed by Nicolaou but incorporates a different carbamate group. See: Nicolaou, K. C.; Baran, P. S.; Zhong, Y.-L.; Barluenga, S.; Hunt, K. W.; Kranich, R.; Vega, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 2233–2244.

2.2.1. Conversion of **11** to 3-*O*-(*N*-2,4-dimethoxybenzyl)carbamoyl-D-glucal **13**.



4,6-*O*-Di-*tert*-butylsilylene-3-*O*-(*N*-2,4-dimethoxybenzyl)carbamoyl-D-glucal (**12**).

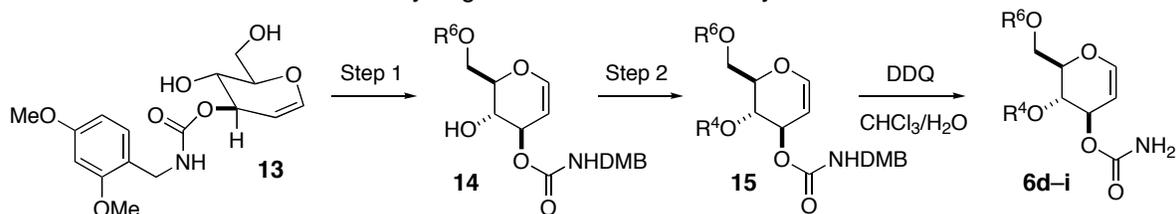
Di-*tert*-butylsilylene-protected glucal **11**⁵ (2.090 g, 7.29 mmol) was dissolved in CH₂Cl₂ (6.0 mL) and 2,4-dimethoxybenzyl isocyanate (1.5 mL, 9.0 mmol) and DBU (310 μL, 2.0 mmol) were added. The solution was stirred 2 h at 25 °C, diluted with CH₂Cl₂ and washed with 10% aq NaHCO₃ (40 mL). The aq layer was back-extracted with CH₂Cl₂ (3 x 25 mL) and the combined organic layers were washed with water (2 x 50 mL) and brine (40 mL), dried (MgSO₄), filtered, and concentrated. The crude product was chromatographed (20% EtOAc/hexanes, 200 mL SiO₂), providing dimethoxybenzyl carbamate **12** as a white crystalline solid (2.691 g, 77%). mp 125-126 °C; *R*_f = 0.4 (20% EtOAc/hexanes); IR (thin film) 3367, 1723, 1648, 1615, 1590 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.19 (d, *J* = 7.9 Hz, 1H), 6.43 (m, 2H), 6.28 (d, *J* = 5.8 Hz, 1H), 5.29 (ddd, *J* = 7.5, 1.6, 1.6 Hz, 1H), 5.19 (br t, *J* = 5.2 Hz, 1H), 4.80 (dd, *J* = 5.8, 1.2 Hz, 1H), 4.30 (m, 2H), 4.22-3.86 (m, 4H), 3.82 (s, 3H), 3.79 (s, 3H), 1.03 (s, 9H), 0.98 (s, 9H), N-H resonance of minor rotamer was noted as br peak at δ 4.99; ¹³C NMR (75 MHz, CDCl₃) δ 160.5, 158.5, 156.2, 144.4, 130.1, 119.2, 103.8, 101.5, 98.5, 73.9, 72.9, 72.6, 65.7, 55.4, 55.3, 40.5, 27.4, 26.8, 22.7, 19.8; HRMS (FAB) *m/z* calcd for C₂₄H₃₈NO₇Si (M+H)⁺ 480.2418, found 480.2414.



3-*O*-(*N*-2,4-dimethoxybenzyl)carbamoyl-D-glucal (13**).** Di-*tert*-butylsilylene-protected **12** (0.5070 g, 1.06 mmol) was dissolved in THF (10 mL) in a 25 mL plastic vial and cooled to 0 °C. HF•pyr (5 drops, dispensed with a plastic dropper) was added and the mixture was stirred at 0 °C for 5 min then at 25 °C for 1 h 15 min. The mixture was recooled to 0 °C, neutralized with satd aq NaHCO₃ (15 mL), and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with water (2 x 10 mL) and brine (10 mL). The combined water and brine washings were back-extracted with a single portion of EtOAc (10 mL). The combined EtOAc extracts were dried (MgSO₄), filtered, and concentrated. The crude product was chromatographed (90% EtOAc/hexanes, 100 mL SiO₂), providing diol **13** as a white solid (0.3267 g, 91%). mp 108-109 °C; *R*_f = 0.4 (90% EtOAc/hexanes); IR (thin film) 3371, 1694, 1651, 1614, 1590 cm⁻¹; ¹H NMR (300 MHz, acetone-*d*₆) δ 7.16 (d, *J* = 8.3 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 1H), 6.51 (br, 1H), 6.46 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.41 (dd, *J* = 6.0, 1.4 Hz, 1H), 5.12 (m, 1H), 4.84 (br d, *J* =

2.6 Hz, 1H), 4.68 (dd, $J = 6.1, 2.4$ Hz, 1H), 4.24 (m, 2H), 3.91-3.78 (m, 4H), 3.83 (s, 3H), 3.78 (s, 3H), 3.74 (br, 1 H), the resonances at δ 4.84 and δ 3.74 disappeared upon addition of D₂O; ¹³C NMR (75 MHz, acetone-*d*₆) δ 161.4, 159.2, 158.0, 146.2, 130.1, 120.3, 105.0, 101.0, 99.0, 80.3, 74.0, 68.1, 61.8, 55.8, 55.7, 40.4; HRMS (FAB) m/z calcd for C₁₆H₂₁NO₇ (M)⁺ 339.1318, found 339.1333.

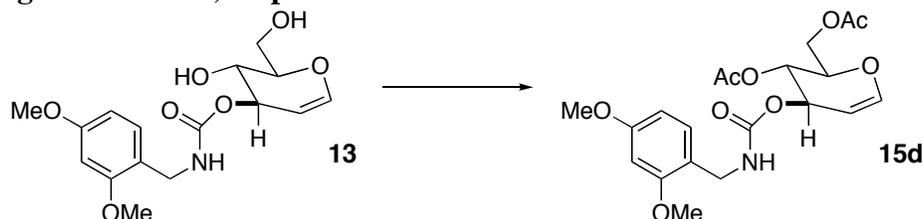
Table S1. Summary of glucal 3-carbamate **6d-i** synthesis from diol **13**



Entry	Step 1 Conditions	14 (% Yield) ^a	Step 2 Conditions	15 (% Yield) ^a	R ⁶	R ⁴	6 (% Yield) ^a
1	Ac ₂ O, pyr, DMAP, CH ₂ Cl ₂ , 25 °C	---	---	15d (85)	Ac	Ac	6d (72)
2	TsCl, pyr, DMAP, 25 °C	14e (73)	Ac ₂ O, pyr, DMAP, CH ₂ Cl ₂ , 25 °C	15e (95)	Ts	Ac	6e (72)
3	Triphosgene, pyr, CH ₂ Cl ₂ , 25 °C	---	---	15f (79)	-CO-		6f (53)
4	TBSCl, imid, DMF, 25 °C	14g (76)	Ac ₂ O, pyr, DMAP, CH ₂ Cl ₂ , 25 °C	15g (96)	TBS	Ac	6g (92)
5	See entry 2 above	14e	TBSCl, imid, DMF, 25 °C	15h (86)	Ts	TBS	6h (77)
6	TBSCl, imid, DMF, 25 °C	---	---	15i (90)	TBS	TBS	6i (56)

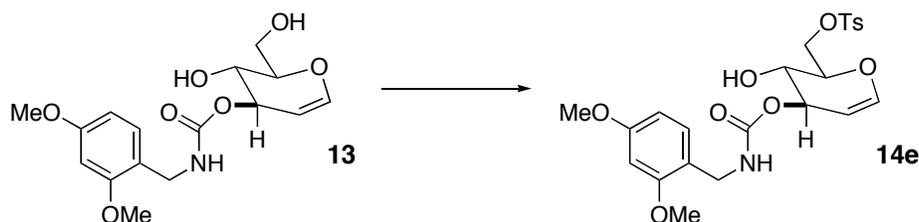
^aIsolated yield after silica gel chromatography.

2.2.2. Advancing diol **13** to 4*O*,6*O*-protected derivatives **15**.

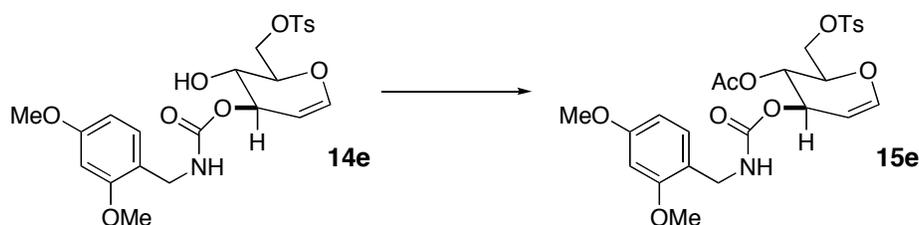


4,6-Di-*O*-acetyl-3-*O*-(*N*-2,4-dimethoxybenzyl)carbamoyl-D-glucal (15d**).** Diol **13** (0.230 g, 0.678 mmol) was suspended in CH₂Cl₂ (6 mL) and pyridine (438 μ L, 5.42 mmol), acetic anhydride (256 μ L, 2.71 mmol), and *N,N*-dimethyl-4-aminopyridine (0.021 g, 0.172 mmol) were added. After 2 h at 25 °C, the reaction mixture was diluted with CH₂Cl₂ (5 mL) and washed with saturated aq NaHCO₃ (x1) and CuSO₄ (x1). The combined aqueous layers were back-extracted with CH₂Cl₂ and the combined organic extracts were dried (MgSO₄), filtered, and concentrated. The crude material was chromatographed (40% EtOAc/hex, 40 mL SiO₂), providing diacetate **15d** as a white, lustrous solid (0.244 g, 85%). mp 100-101 °C; $R_f = 0.5$ (80% EtOAc/hexanes); IR (thin film) 3368, 1743, 1736 (sh), 1720, 1648, 1612, 1589 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.16 (d, $J = 8.0$ Hz, 1H), 6.43 (m, 3H), 5.32-5.14 (m, 3H), 4.88 (dd, $J = 6.1, 3.1$ Hz, 1H), 4.36 (dd, $J = 11.6, 5.4$ Hz, 1H), 4.29-4.14 (m, 4H), 3.82 (s, 3H), 3.80 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.7 (s), 169.6 (s), 160.6 (s), 158.5 (s), 155.3 (s), 145.1 (o), 130.2 (o), 118.8 (s), 103.7 (o), 99.8 (o), 98.5 (o), 73.8 (o), 67.6 (o), 67.3 (o), 61.4 (t), 55.4 (o),

55.3 (o), 40.6 (t), 20.8 (o), 20.7 (o); HRMS (FAB) m/z calcd for $C_{20}H_{25}NO_9$, (M)⁺ 423.1529, found 423.1520.

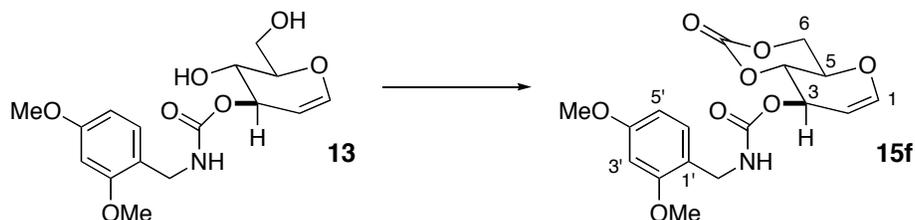


3-*O*-(*N*-2,4-Dimethoxybenzyl)carbamoyl-6-*O*-*p*-toluenesulfonyl-D-glucal (14e). Diol **13** (1.889 g, 3.504 mmol) was dissolved in pyridine (3 mL) at 25 °C. Tosyl chloride (1.050 g, 5.505 mmol) and *N,N*-dimethyl-4-aminopyridine (0.0475 g, 0.3854 mmol) were added. After 5.5 h, the reaction mixture was diluted with CH_2Cl_2 and washed with saturated aq $NaHCO_3$ (x1), H_2O (x2), and brine (x1). The combined aqueous layers were back-extracted with CH_2Cl_2 and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The crude material was chromatographed (40% EtOAc/hex, 200 mL SiO_2), providing monotosylate **14e** as a sticky, yellow-white solid (1.266 g, 73%). R_f = 0.35 (50% EtOAc/hexanes); IR (thin film) 3386, 1693, 1651, 1614, 1590 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.80 (apparent d, J = 8.3 Hz, 2H), 7.33 (apparent d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.9 Hz, 1H), 6.48-6.41 (m, 2H), 6.34 (dd, J = 6.1, 1.3 Hz, 1H), 5.42 (br t, J = 5.9 Hz, 1H), 5.08 (ddd, J = 6.5, 2.0, 2.0 Hz, 1H), 4.66 (br s, 1H), 4.63 (dd, J = 6.1, 2.4 Hz, 1H), 4.39 (dd, J = 10.8, 2.3 Hz, 1H), 4.35-4.17 (m, 3H), 3.91 (ddd, J = 10.0, 4.9, 2.3 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.77 (m, 1H), 2.44 (s, 3H), signals for a minor rotamer appeared at δ 7.08 (d, J = 7.7 Hz), 6.39, 5.21 (br t, J = 5.7 Hz) and just downfield of the signals at δ 5.08 and 5.36; ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7 (s), 158.5 (s), 157.6 (s), 145.7 (o), 144.8 (s), 132.7 (s), 130.3 (o), 129.8 (o), 128.0 (o), 118.4 (s), 103.8 (o), 99.4 (o), 98.6 (o), 75.7 (o), 74.1 (o), 68.3 (t), 67.5 (o), 55.4 (o), 55.3 (o), 40.9 (t), 21.6 (o); HRMS (FAB) m/z calcd for $C_{23}H_{28}NO_9S$ (M+H)⁺ 494.1485, found 494.1483.



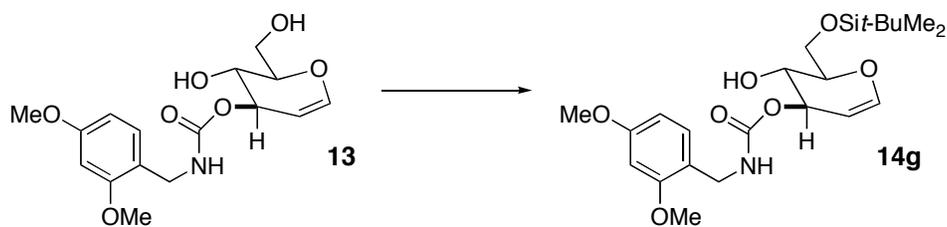
4-*O*-Acetyl-3-*O*-(*N*-2,4-dimethoxybenzyl)carbamoyl-6-*O*-*p*-toluenesulfonyl-D-glucal (15e). The 6-*O*-tosyl glucal 3-carbamate **14e** (1.239 g, 2.511 mmol) was dissolved in CH_2Cl_2 (5 mL) at 25 °C. Pyridine (0.850 mL, 10.523 mmol), acetic anhydride (0.475 mL, 5.029 mmol), and *N,N*-dimethyl-4-aminopyridine (0.0369 g, 0.3025 mmol) were added. After 2 h, the reaction mixture was diluted with CH_2Cl_2 and washed with saturated aq $NaHCO_3$ (x1), H_2O (x2), and brine (x1). The combined aqueous layers were back-extracted with CH_2Cl_2 and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The crude material was chromatographed (45% EtOAc/hex, 150 mL SiO_2), providing

acetate ester **15e** as a white, crystalline solid (1.279 g, 95%). mp 108-110 °C; $R_f = 0.44$ (50% EtOAc/hexanes); IR (thin film) 3401, 1753, 1722, 1650, 1614, 1591 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.77 (apparent d, $J = 8.1$ Hz, 2H), 7.32 (apparent d, $J = 8.0$ Hz, 2H), 7.16 (s, $J = 7.9$ Hz, 1H), 6.49-6.35 (m, 2H), 6.30 (d, $J = 6.1$ Hz, 1H), 5.37 (br t, $J = 5.6$ Hz, 1H), 5.24-5.03 (m, 2H), 4.87 (dd, $J = 5.9$, 3.5 Hz, 1H), 4.31-4.02 (m, 5H), 3.81 (s, 3H), 3.79 (s, 3H), 2.43 (s, 3H), 2.00 (s, 3H), a signal for a minor rotamer appeared at δ 7.08; ^{13}C NMR (75 MHz, CDCl_3) δ 169.3 (s), 160.5 (s), 158.4 (s), 155.1 (s), 145.0 (s), 144.6 (o), 132.5 (s), 130.0 (o), 129.8 (o), 127.9 (o), 118.8 (s), 103.8 (o), 99.5 (o), 98.4 (o), 72.8 (o), 67.0 (o), 66.3 (o), 66.1 (t), 55.3 (o), 55.2 (o), 40.5 (t), 21.5 (o), 20.6 (o).

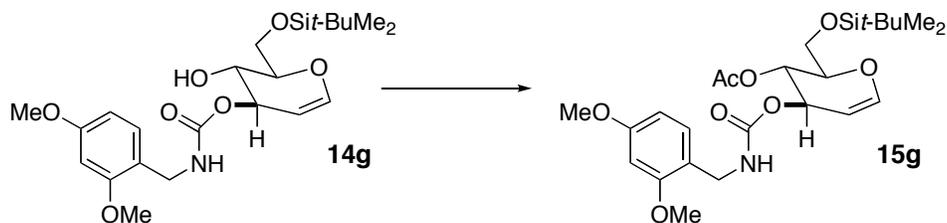


4-O,6-O-Carbonyl-3-O-(N-2,4-dimethoxybenzyl)carbamoyl-D-glucal (15f). Diol **13** (306.4 mg, 0.904 mmol) was dissolved in CH_2Cl_2 (28 mL) and pyridine (300 μL , 3.71 mmol) was added, followed by triphosgene (137.2 mg, 0.462 mmol). There was a mild exotherm, and TLC showed the reaction was complete within 5 min. The reaction mixture was poured into satd aq NaHCO_3 (30 mL), rinsing with an approximately equal volume CH_2Cl_2 . After extraction, the organic layer was washed with additional satd aq NaHCO_3 (30 mL) and brine (30 mL), dried (MgSO_4), filtered, and concentrated. ^1H NMR of the crude material showed that it was quite pure, and it may be possible to use the crude cyclic carbonate without further purification or after trituration with a non-polar solvent. Nevertheless, the crude was chromatographed (60 \rightarrow 65 \rightarrow 70% EtOAc/hexanes, 100 mL SiO_2), eluting quickly because there was TLC evidence of product decomposition on SiO_2 .⁷ Cyclic carbonate **15f** was isolated as a white solid (261.0 mg, 79%). mp 133-135 °C; $R_f = 0.54$ (80% EtOAc/hexanes); IR (thin film) 3343, 1767, 1716, 1644, 1614, 1589 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.18 (d, $J = 7.9$ Hz, 1H, H6'), 6.48-6.40 (m, 2H, H3', H5'), 6.37 (dd, $J = 6.1$, 1.3 Hz, 1H, H1), 5.47 (ddd, $J = 7.9$, 1.8, 1.8 Hz, 1H, H3), 5.24 (br t, $J = 5.8$ Hz 1H, NH), 4.97 (dd, $J = 6.1$, 2.1 Hz, 1H, H2), 4.59 (dd, $J = 10.2$, 5.9 Hz, 1H, H6_{eq}), 4.48 (dd, $J = 10.5$, 8.0 Hz, 1H, H4), 4.34 (dd, $J = 10.1$, 10.1 Hz, 1H, H6_{ax}), 4.32-4.17 (m, 3H, H5, ArCH₂N), 3.83 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃); ^{13}C NMR (75 MHz, CDCl_3) δ 160.6 (s), 158.5 (s), 155.0 (s), 146.7 (s), 144.2 (o, C1), 130.3 (o, C6'), 118.6 (s), 103.8 (o, C3' or C5'), 101.7 (o, C2), 98.6 (o, C3' or C5'), 75.7 (o, C4), 68.4 (o, C3), 68.3 (t, C6), 65.6 (o, C5), 55.4 (o, OCH₃), 55.3 (o, OCH₃), 40.7 (t, ArCH₂N); HRMS (FAB) m/z calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_8$ (M)⁺ 365.1111, found 365.1132.

⁷ Trans-fused 4,6-cyclic carbonate sugar derivatives are known to be unstable: (a) Trimmell, D.; Doane, W. M.; Russell, C. R.; Rist, C. E. *Carbohydr. Res.* **1970**, *13*, 301–305. (b) Allainmat, M.; Plusquellec, D. *Tetrahedron Lett.* **1991**, *32*, 2751–2754.



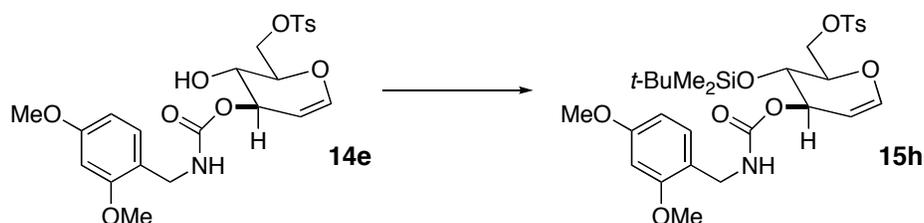
6-*O*-*tert*-Butyldimethylsilyl-3-*O*-(*N*-2,4-dimethoxybenzyl)carbamoyl-D-glucal (14g). To a solution of diol **13** (372.2 mg, 1.098 mmol) in DMF (2.5 mL) was added imidazole (157.8 mg, 2.32 mmol), followed by *tert*-butyldimethylsilyl chloride (168.4 mg, 1.11 mmol). Additional portions of imidazole (4 x ~35 mg, 4 x ~0.51 mmol) and *tert*-butyldimethylsilyl chloride (4 x ~35 mg, 4 x ~0.23 mmol) were added over 48 h to consume most of the starting material while minimizing formation of bis silylated material (TLC). The reaction mixture was poured into satd aq NaHCO₃ (15 mL) and extracted with CH₂Cl₂ (40 mL). The organic layer was washed with satd aq NaHCO₃ (15 mL) and the combined aq layers were back extracted with CH₂Cl₂ (20 mL). The combined organic layers were dried (MgSO₄), filtered, and concentrated (rotovap then overnight on the vacuum line (0.5 mmHg) to remove most residual DMF). The crude was chromatographed (25→30% EtOAc/hexanes, 150 mL SiO₂), providing the mono silylated **14g** (379.4 mg, 76%) as a clear, colorless oil. *R*_f = 0.47 (50% EtOAc/hexanes); IR (thin film) 3380, 1696, 1651, 1615, 1590 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.17 (d, *J* = 7.9 Hz, 1H), 6.49-6.35 (m, 3H), 5.38 (br t, *J* = 5.8 Hz, 1H), 5.16 (ddd, *J* = 6.5, 1.8, 1.8 Hz, 1H), 4.64 (dd, *J* = 6.1, 2.3 Hz, 1H), 4.39 (d, *J* = 1.6 Hz, 1H), 4.28 (m, 2H), 3.95 (m, 2H), 3.93-3.72 (m, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 0.90 (s, 9H), 0.09 (apparent s, 6H); a minor rotamer (~10%) was apparent in the ¹H NMR at δ 7.10 (d, *J* = 8.1 Hz), as downfield shoulders on the signals at δ 5.16, 4.64, and 4.39, and as an upfield shoulder to the resonance at δ 4.28; ¹³C NMR (75 MHz, CDCl₃) δ 160.6 (s), 158.5 (s), 157.5 (s), 146.1 (o), 130.3 (o), 118.6 (s), 103.8 (o), 99.0 (o), 98.5 (o), 78.3 (o), 74.5 (o), 68.4 (o), 62.5 (t), 55.3 (o), 55.2 (o), 40.8 (t), 25.9 (o), 18.4 (s), -5.4 (o) (the ¹³C resonance at δ -5.4 was resolved into two signals at δ -5.35, -5.38 upon reprocessing the FID using line broadening = 0); LRMS (FAB) *m/z* calcd for C₂₂H₃₆NO₇Si (M+H)⁺ 454.2, found 454.2.



4-*O*-Acetyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-(*N*-2,4-dimethoxybenzyl)carbamoyl-D-glucal (15g).

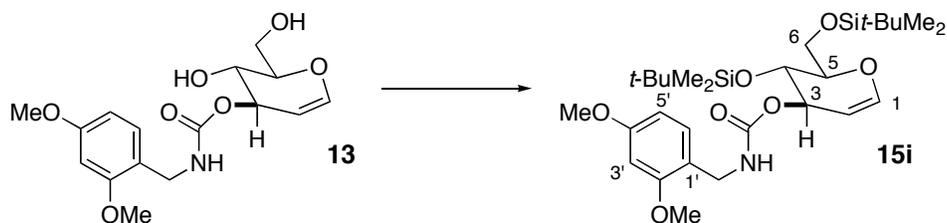
Alcohol **14g** (376 mg, 0.830 mmol) was dissolved in CH₂Cl₂ (6.0 mL), and pyridine (270 μL, 3.34 mmol) was added, followed by acetic anhydride (160 μL, 1.69 mmol) and *N,N*-dimethyl-4-amino pyridine (10.7 mg, 0.087 mmol). After 1.75 h the mixture was poured into satd aq NaHCO₃ (25 mL) and extracted with CH₂Cl₂ (75 mL). The organic layer was washed with satd aq CuSO₄ (2 x 25 mL), satd aq NaHCO₃ (25 mL), and brine (25 mL), dried (MgSO₄), filtered, and concentrated. The crude was

chromatographed (30% EtOAc/hexanes, 16 cm x 4 cm column of 150 mL SiO₂, 20 mL fractions), providing the acetate ester **15g** (392.6 mg, 96%) as a clear, colorless oil. $R_f = 0.35$ (30% EtOAc/hexanes); IR (thin film) 3372, 1752, 1723, 1651, 1614, 1590 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.16 (d, $J = 7.9$ Hz, 1H), 6.49-6.35 (m, 3H), 5.30-5.13 (m, 3H), 4.80 (dd, $J = 6.1, 2.9$ Hz, 1H), 4.25 (m, 2H), 4.06 (ddd, $J = 7.6, 3.9, 3.9$ Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.78 (m, 2H), 2.02 (s, 3H), 0.88 (s, 9H), 0.04 (apparent s, 6H); a minor rotamer (~10-15%) was apparent in the ¹H NMR at δ 7.11 (d, $J = 8.1$ Hz), just downfield of the multiplet at δ 5.30-5.13, as broadened signals at δ 5.00 and 4.86, and just upfield of the resonance at δ 4.25; ¹³C NMR (75 MHz, CDCl₃) δ 169.4 (s), 160.5 (s), 158.5 (s), 155.6 (s), 145.4 (o), 130.1 (o), 118.9 (s), 103.7 (o), 99.3 (o), 98.5 (o), 76.8 (o), 68.4 (o), 67.7 (o), 61.4 (t), 55.3 (o), 55.2 (o), 40.6 (t), 25.8 (o), 20.9 (o), 18.2 (s), -5.5 (o, two overlapping SiCH₃ resonances); HRMS (FAB) m/z calcd for C₂₄H₃₇NO₈Si (M)⁺ 495.2288, found 495.2293.



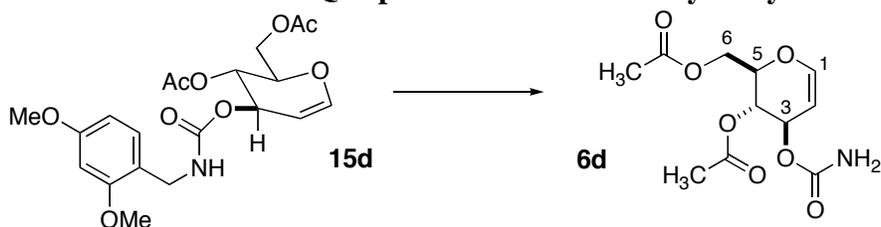
4-*O*-*tert*-Butyldimethylsilyl-3-*O*-(*N*-2,4-dimethoxybenzyl)carbamoyl-6-*O*-*p*-toluenesulfonyl-*D*-glucal (15h**).**

To a solution of alcohol **14e** (170 mg, 0.345 mmol) in DMF (0.6 mL) were added imidazole (48.3 mg, 0.710 mmol) and *tert*-butyldimethylsilyl chloride (82.9 mg, 0.549 mmol), followed by more DMF (0.4 mL) to rinse the inside of the flask. Additional portions of imidazole (52.9 mg, 0.778 mmol; 34.7 mg, 0.510 mmol; and 35.1 mg, 0.516 mmol) and *tert*-butyldimethylsilyl chloride (83.4 mg, 0.552 mmol; 49.0 mg, 0.325 mmol; and 54.6 mg, 0.362 mmol) were added over 48 h to gradually consume all starting material (TLC). The mixture was poured into satd aq NaHCO₃ (15 mL) and extracted with CH₂Cl₂ (2 x 25 mL). The combined organic layers were washed with brine, dried (MgSO₄), filtered, and concentrated. The residue was chromatographed (25→30→35→40% EtOAc/hexanes, 100 mL SiO₂), affording silyl ether **15h** (181.1 mg, 86%) as a clear oil. $R_f = 0.55$ (50% EtOAc/hexanes); IR (thin film) 3378, 1722, 1652, 1614, 1590 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.78 (apparent d, $J = 8.3$ Hz, 2H), 7.32 (apparent d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 1H), 6.47-6.38 (m, 2H), 6.22 (dd, $J = 6.0, 0.5$ Hz, 1H), 5.18 (br t, $J = 5.9$ Hz, 1H), 5.04 (m, 1H), 4.76 (dd, $J = 6.1, 2.8$ Hz, 1H), 4.26 (AB of ABX, $J_{AB} = 10.6$ Hz, $J_{AX} = 5.2$ Hz, $J_{BX} = 2.7$ Hz, $\Delta\nu_{AB} = 26.7$ Hz, 2H), 4.26 (apparent d, $J = 6.0$ Hz, 2H), 3.98-3.83 (m, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 2.44 (s, 3H), 0.78 (s, 9H), 0.04 (s, 3H), -0.01 (s, 3H); a minor rotamer (~5-10%) was apparent in the ¹H NMR at δ 7.08 (d, $J = 7.8$ Hz) and just upfield of the resonances at δ 5.18, 5.04, and 4.76; ¹³C NMR (75 MHz, CDCl₃) δ 160.5 (s), 158.4 (s), 155.4 (s), 144.9 (s), 144.5 (o), 132.7 (s), 130.2 (o), 129.8 (o), 128.0 (o), 118.9 (s), 103.7 (o), 100.2 (o), 98.4 (o), 75.9 (o), 71.8 (o), 67.8 (t), 67.0 (o), 55.4 (o), 55.2 (o), 40.7 (t), 25.6 (o), 21.6 (o), 17.9 (s), -4.6 (o), -5.1 (o); HRMS (FAB) m/z calcd for C₂₉H₄₀NO₉SiS (M-H)⁺ 606.2193, found 606.2214.



4,6-Di-*O*-*tert*-butyldimethylsilyl-3-*O*-(*N*-2,4-dimethoxybenzyl)carbamoyl-D-glucal (15i**).** Imidazole (129.6 mg, 1.91 mmol) was added to a solution of diol **13** (185.5 mg, 0.547 mmol) in DMF (1.0 mL). Once all the imidazole had dissolved, *tert*-butyldimethylsilyl chloride (208.7 mg, 1.38 mmol) was added and the solution was stirred 23 h. The reaction mixture was poured into satd aq NaHCO₃ (15 mL) and extracted with CH₂Cl₂ (30 mL). The organic layer was washed with brine, dried (MgSO₄), filtered, and concentrated. The crude was chromatographed (15% EtOAc/hexanes, 200 mL SiO₂), affording bis silyl ether **15i** (277.9 mg, 90%). *R_f* = 0.39 (20% EtOAc/hexanes); IR (thin film) 3457, 3361, 1720, 1652, 1615, 1590 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.17 (d, *J* = 7.8 Hz, 1H, H6'), 6.46-6.38 (m, 2H, H3', H5'), 6.34 (d, *J* = 5.9 Hz, 1H, H1), 5.16-5.08 (m, 2H, H3, NH), 4.72 (dd, *J* = 6.0, 2.3 Hz, 1H, H2), 4.27 (apparent d, *J* = 6.0 Hz, 2H, ArCH₂N), 3.97 (dd, *J* = 9.2, 7.0 Hz, 1H, H4), 3.86 (m, 2H, H6a, H6b), 3.80 (s, 3H, OCH₃), 3.79 (s, 3H, OCH₃), 3.75 (m, 1H, H5), 0.89 (s, 9H, SiC(CH₃)₃), 0.82 (s, 9H, SiC(CH₃)₃), 0.08 (s, 3H, SiCH₃), 0.06 (s, 3H, SiCH₃), 0.05 (s, 3H, SiCH₃), 0.01 (s, 3H, SiCH₃); a minor rotamer (~10%) was apparent in the ¹H NMR as a shoulder upfield of the δ 7.17 signal, a shoulder downfield of the δ 5.16-5.08 signal, and as a broad signal centered at δ 4.93; ¹³C NMR (75 MHz, CDCl₃) δ 160.5 (s), 158.4 (s), 155.9 (s), 145.1 (o, C1), 130.3 (o, C6'), 119.1 (s), 103.7 (o, C3' or C5'), 99.8 (o, C2), 98.5 (o, C3' or C5'), 79.3 (o, C5), 73.4 (o, C3), 66.9 (o, C4), 61.6 (t, C6), 55.4 (o, OCH₃), 55.2 (o, OCH₃), 40.7 (t, ArCH₂N), 25.9 (o, SiC(CH₃)₃), 25.7 (o, SiC(CH₃)₃), 18.4 (s, SiC(CH₃)₃), 18.0 (s, SiC(CH₃)₃), -4.7 (o, SiCH₃), -5.0 (o, SiCH₃), -5.1 (o, SiCH₃), -5.4 (o, SiCH₃); HRMS (FAB) *m/z* calcd for C₂₈H₄₈NO₇Si₂ (M-H)⁺ 566.2969, found 566.2938.

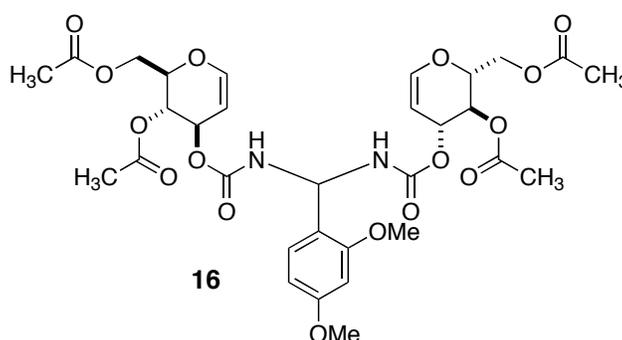
2.2.3. Primary carbamates **6d-i** via DDQ deprotection of dimethoxybenzyl carbamates **15d-i**.



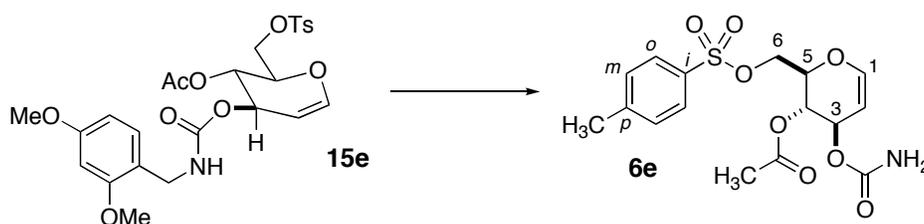
Representative deprotection procedure:

3*O*-carbamoyl-4,6-di-*O*-acetyl-D-glucal (6d**).** The 4*O*,6*O* diacetylated carbamate **15d** (0.189 g, 0.447 mmol) was dissolved in CHCl₃ (3.2 mL total) at 23 °C and water (330 μL) was added, followed by 2,3-dichloro-5,6-dicyano benzoquinone (0.310 g, 1.36 mmol). The vigorously stirred reaction mixture was monitored closely by TLC, showing very near complete consumption of starting material within 1 h. At this point, however, TLC also indicated an approximately 1:1 mixture of the desired carbamate **6d** and bisamide benzylidene **16**. Stirring was continued as TLC showed gradual conversion of **16** to the carbamate **6d** over a total reaction time of 3 h 20 min. The reaction mixture was poured into satd aq

NaHCO₃ (30 mL), rinsing with CH₂Cl₂. The organic layer from this initial extraction was washed with additional satd aq NaHCO₃ (2 x 30 mL), dried (MgSO₄), filtered, and concentrated. The crude product was chromatographed (40→50→60→70→80% EtOAc/hexanes, 150 mL SiO₂), providing carbamate **6d** as a white solid (88 mg, 72%). mp 131–132°C; *R_f* = 0.3 (70% EtOAc/hexanes); IR (thin film) 3471, 3368, 3200, 1739, 1731, 1650, 1605 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.46 (d, *J* = 6.0 Hz, 1H, H1), 5.30–5.16 (m, 2H, H3 and H4, H3 part of the multiplet is downfield of H4 part), 5.00 (br s, 2H, NH₂), 4.90 (dd, *J* = 6.1, 3.0 Hz, 1H, H2), 4.45–4.32 (m, 1H, H6a), 4.31–4.16 (m, 2H, H5 and H6b), 2.101 (s, 3H, C(O)CH₃), 2.097 (s, 3H, C(O)CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.7 (s), 169.6 (s), 156.0 (s), 145.3 (C1), 99.3 (C2), 73.8 (C5), 68.0 (C3), 67.1 (C4), 61.3 (C6), 20.8 (C(O)CH₃), 20.7 (C(O)CH₃); HRMS (FAB) *m/z* calcd for C₁₁H₁₆NO₇ (M+H)⁺ 274.0927, found 274.0917.

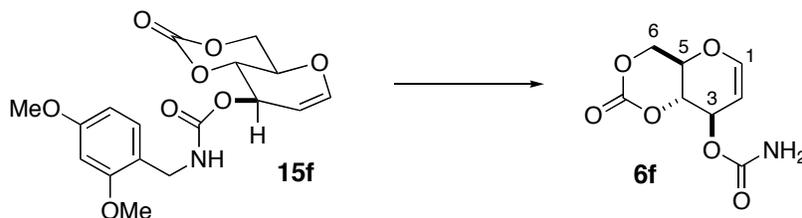


Bisamide benzylidene **16** was isolated from a reaction stopped before complete hydrolysis to the primary carbamate **6d**. While it could be converted to **6d** upon stirring in MeOH/CH₂Cl₂ with added PPTs, **16** was stable to chromatography on silica gel and was amenable to full characterization. Data for **16**: *R_f* = 0.29 (60% EtOAc/hexanes; **16** is best distinguished by TLC from the slightly less polar **6d** by eluting twice with 50% EtOAc/hexanes); IR (thin film) 3352, 1744, 1650, 1614, 1590 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.24 (d, *J* = 8.2 Hz, 1H), 6.54–6.27 (m, 5H), 5.94 (apparent d, *J* = 8.9 Hz, 2H), 5.40–5.10 (m, 4H), 4.94 (m, 1H), 4.81 (m, 1H), 4.44–4.13 (m, 6H), 3.90 (s, 3H), 3.80 (s, 3H), 2.10 (two overlapping s, 6H), 2.03 (s, 3H), 1.96 (s, 3H); ¹H NMR signals for minor rotamer(s) δ 6.22, 5.77, 4.90, 2.05, 1.93; ¹³C NMR (75 MHz, CDCl₃) δ 170.6 (s), 169.8 (s), 169.5 (s), 161.1 (s), 157.4 (s), 155.7 (s), 154.0 (s), 153.9 (s), 145.2 (o), 129.4 (o), 119.1 (s), 104.0 (o), 99.5 (o), 99.3 (o), 99.2 (o), 73.8 (o), 68.2 (o), 68.1 (o), 67.9 (o), 67.2 (o), 67.1 (o), 61.3 (t), 61.1 (o), 55.5 (o), 55.4 (o), 20.8 (o), 20.7 (o); HRMS (FAB) *m/z* calcd for C₃₁H₃₈N₂O₁₆ (M)⁺ 694.2221, found 694.2234.



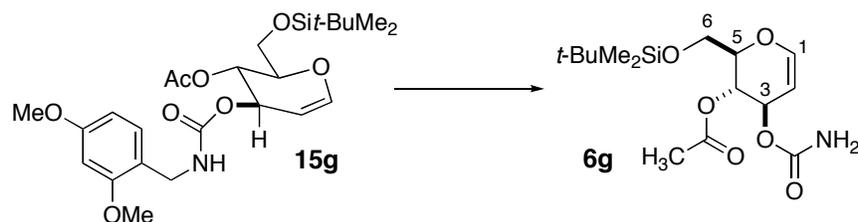
4-*O*-Acetyl-3-*O*-carbamoyl-6-*O*-*p*-toluenesulfonyl-D-glucal (6e**).** Prepared from **15e** (1.2550 g, 2.3513 mmol) using the general procedure outlined for **6d** above. Primary carbamate **6e** was purified by

chromatography (50% EtOAc/hexanes, 200 mL SiO₂), yielding a white crystalline solid (654.3 mg, 72%). mp 102-103 °C; *R_f* = 0.2 (50% EtOAc/hexanes); IR (thin film) 3486, 3383, 3196, 3067, 1754, 1747, 1738, 1731, 1715, 1651, 1598 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.80 (apparent d, *J* = 8.3 Hz, 2H), 7.36 (apparent d, *J* = 8.0 Hz, 2H), 6.35 (d, *J* = 6.1 Hz, 1H), 5.22-5.13 (m, 2H), 5.04-4.80 (m, 3H), 4.35-4.24 (m, 2H), 4.23-4.13 (m, 1H), 2.46 (s, 3H), 2.06 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.5, 155.7, 145.2, 145.0, 132.4, 129.9, 128.0, 99.2, 72.8, 66.9 (two overlapping resonances), 66.1, 21.7, 20.8. In C₆D₆, the C3 and C4 resonances were resolved in the ¹³C NMR spectrum. Using C₆D₆ as the NMR solvent, ¹H and ¹³C resonances were assigned with the aid of ¹³C DEPT, ¹H/¹³C HSQC, and ¹H/¹³C HMBC experiments: ¹H NMR (300 MHz, C₆D₆) δ 7.76 (apparent d, *J* = 8.3 Hz, 2H, H_o), 6.70 (apparent d, *J* = 8.0 Hz, 2H, H_m), 5.95 (d, *J* = 6.1 Hz, 1H, H1), 5.37-5.28 (m, 2H, H3 and H4), 4.74 (ddd, *J* = 6.2, 2.5, 1.4 Hz, 1H, H2), 4.45 (br s, 2H, NH₂), 4.21 (AB of ABX, *J*_{AB} = 10.8 Hz, *J*_{AX} = 5.5 Hz, *J*_{BX} = 4.1 Hz, Δ*v*_{AB} = 8.2 Hz, 2H, H6a and H6b), 3.98 (m, 1H, H5), 1.81 (s, 3H, Ar-CH₃), 1.63 (s, 3H, C(O)CH₃). ¹³C NMR (75 MHz, C₆D₆) δ 169.5 (s, C(O)CH₃), 156.3 (s, C(O)NH₂), 145.5 (o, C1), 145.0 (s, C_p), 134.0 (s, C_i), 130.2 (o, C_m), 128.7 (o, C_o, this resonance was visible in the DEPT 135 spectrum but was obscured by solvent peaks in the regular, proton-decoupled ¹³C NMR spectrum), 100.2 (o, C2), 73.8 (o, C5), 67.8 (o, C3), 67.7 (o, C4), 66.6 (t, C6), 21.5 (o, Ar-CH₃), 20.7 (o, C(O)CH₃); HRMS (FAB) *m/z* calcd for C₁₆H₂₀NO₈S (M+H)⁺ 386.0910, found 386.0920.

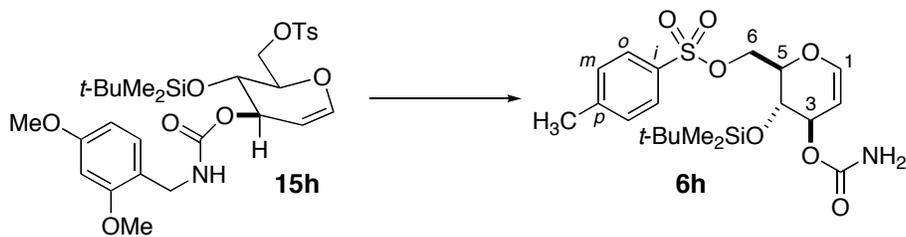


3-*O*-Carbamoyl-4-*O*,6-*O*-carbonyl-D-glucal (6f). Dimethoxybenzyl carbamate **15f** (198.3 mg, 0.543 mmol) was stirred in CHCl₃ (10 mL) for several min until it completely dissolved. Water (1.0 mL) was added, followed by DDQ (371.5 mg, 1.637 mmol), and the well-stirred mixture was monitored closely by TLC. Two initial product spots (*R_f* = 0.41 and 0.27, 80% EtOAc/hexanes) converged to the less polar of the two over 4 h 15 min. The reaction mixture was transferred to a separatory funnel with satd aq NaHCO₃ (30 mL) and EtOAc (80 mL). After extraction, the aq layer was back extracted with EtOAc (3 x 15 mL) and the combined organic layers were dried (MgSO₄), filtered, and concentrated to a red residue. The crude material was chromatographed immediately and quickly (70→75% EtOAc/hexanes, 75 mL SiO₂), as the cyclic carbonate **6f** is not completely stable on silica gel.⁷ The product **6f** (61.8 mg, 53%) was a white solid. mp 193-194 °C (dec); *R_f* = 0.4 (80% EtOAc/hexanes); IR (thin film) 3465, 3344, 3285, 3191, 1754, 1726, 1674, 1642, 1626, 1607 cm⁻¹; ¹H NMR (300 MHz, acetone-*d*₆) δ 6.53 (dd, *J* = 6.1, 1.7 Hz, 1H, H1), 6.08 (br s, 2H, NH₂), 5.45 (ddd, *J* = 8.0, 1.9, 1.9 Hz, 1H, H3), 4.89 (dd, *J* = 6.1, 2.1 Hz, 1H, H2), 4.69 (dd, *J* = 10.4, 8.0 Hz, 1H, H4), 4.65-4.56 (m, 1H, H6a), 4.55-4.42 (m, 2H, H5, H6b); ¹³C NMR (75 MHz, acetone-*d*₆) δ 156.8 (s), 147.3 (s), 145.5 (o, C1), 102.4 (o, C2), 76.5 (o,

C4), 69.1 (o, C3), 68.9 (t, C6), 66.4 (o, C5); HRMS (FAB) m/z calcd for $C_8H_{10}NO_6$ (M+H)⁺ 216.0508, found 216.0500.

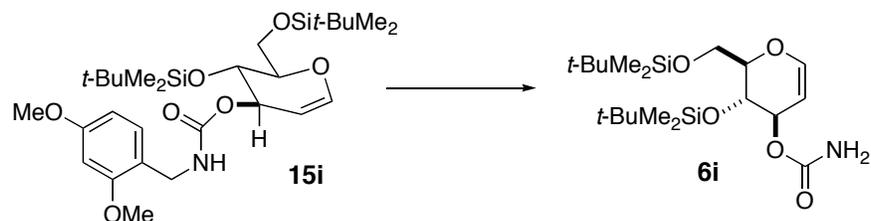


4-*O*-Acetyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-carbamoyl-D-glucal (6g). Prepared from **15g** (381 mg, 0.770 mmol) following the general debenzylation procedure as for **6d** and purified by chromatography (40% EtOAc/hexanes, 200 mL SiO₂, 24 cm x 4 cm, 8 mL fractions). Primary carbamate **6g** (246.0 mg, 92%) was a clear, colorless oil. R_f = 0.26 (40% EtOAc/hexanes); IR (thin film) 3471, 3364, 3286 (shoulder), 3196, 1732, 1651, 1601 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.45 (d, J = 6.0 Hz, 1H, H1), 5.27 (m, 2H, H3, H4), 4.88 (br s, 2H, NH₂), 4.81 (ddd, J = 6.1, 2.3, 0.7 Hz, 1H, H2), 4.06 (m, 1H, H5), 3.80 (m, 2H, H6a, H6b), 2.08 (s, 3H, C(O)CH₃), 0.89 (s, 9H, SiC(CH₃)₃), 0.060 (s, 3H, SiCH₃), 0.058 (s, 3H, SiCH₃); ¹³C NMR (75 MHz, CDCl₃) δ 169.5 (s, C(O)CH₃), 156.2 (s, C(O)NH₂), 145.7 (o, C1), 98.9 (o, C2), 76.8 (o, C5), 69.2 (o, C3), 67.6 (o, C4), 61.3 (t, C6), 25.8 (o, SiC(CH₃)₃), 20.9 (o, C(O)CH₃), 18.3 (s, SiC(CH₃)₃), -5.5 (o, two overlapping SiCH₃); HRMS (FAB) m/z calcd for C₁₅H₂₇NO₆SiK (M+K)⁺ 384.1245, found 384.1263.



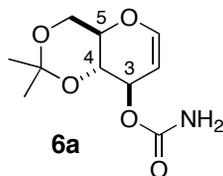
4-*O*-*tert*-Butyldimethylsilyl-3-*O*-carbamoyl-6-*O*-*p*-toluenesulfonyl-D-glucal (6h). DDQ cleavage of the dimethoxybenzyl protecting group from **15h** (178.6 mg, 0.294 mmol) was accomplished according to the general procedure given for **6d**. Chromatography (30→35→40→45→50→55% EtOAc/hexanes, 200 mL SiO₂) completely removed the 2,4-dimethoxybenzaldehyde byproduct but did not separate a small amount of material with R_f just above the desired material. Rechromatography (50% EtOAc/hexanes, 200 mL SiO₂) provided pure **6h** (103.2 mg, 77%) as a clear glass. Redissolving the product in a small amount of CH₂Cl₂ (~1 mL), adding *n*-pentane (~10 mL), and removal of solvent gave a white solid. mp 92-98 °C; R_f = 0.37 (50% EtOAc/hexanes); IR (thin film) 3491, 3392, 3278, 3192, 1723, 1652, 1598 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.80 (apparent d, J = 8.3 Hz, 2H, H_o), 7.35 (apparent d, J = 8.0 Hz, 2H, H_m), 6.26 (dd, J = 6.1, 1.2 Hz, 1H, H1), 5.05 (dddd, J = 5.3, 2.7, 1.4, 1.4 Hz, 1H, H3), 4.84 (br s, 2H, NH₂), 4.79 (dd, J = 6.1, 2.8 Hz, 1H, H2), 4.34 (dd, J = 10.6, 2.7 Hz, 1H, H6a), 4.22 (dd, J = 10.6, 4.8 Hz, 1H, H6b), 4.00-3.89 (m, 2H, H4 and H5), 2.45 (s, 3H, Ar-CH₃), 0.83 (s, 9H, SiC(CH₃)₃), 0.09 (s, 3H, SiCH₃), 0.08 (s, 3H, SiCH₃); ¹³C NMR (75 MHz, CDCl₃) δ 156.0 (s, C(O)NH₂),

145.0 (s, C_i), 144.8 (o, C1), 132.6 (s, C_p), 129.8 (o, C_m), 128.0 (o, C_o), 99.7 (o, C2), 75.8 (o, C5), 72.4 (o, C3), 67.7 (t, C6), 66.7 (o, C4), 25.6 (o, SiC(CH₃)₃), 21.6 (o, Ar-CH₃), 17.9 (s, SiC(CH₃)₃), -4.5 (o, SiCH₃), -5.1 (o, SiCH₃); HRMS (FAB) *m/z* calcd for C₂₀H₃₁NO₇SiNa (M+Na)⁺ 480.1488, found 480.1508.



3-O-Carbamoyl-4,6-di-O-tert-butyl dimethylsilyl-D-glucal (6i). Prepared from **15i** (170.3 mg, 0.300 mmol) following the general debenzoylation procedure as for **6d** and purified by chromatography (30% EtOAc/hexanes, 200 mL SiO₂). Primary carbamate **6i** (70.1 mg, 56% yield) was initially an oil then yielded a white solid on storage at -20 °C. mp 72.5-74.0 °C; *R_f* = 0.30 (30% EtOAc/hexanes); IR (thin film) 3510, 3346, 3275, 3196, 1716, 1651, 1600 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.37 (dd, *J* = 6.0, 1.0 Hz, 1H), 5.13 (ddd, *J* = 6.8, 1.8, 1.8 Hz, 1H), 4.75 (br s, 2H), 4.74 (dd, *J* = 6.1, 2.4 Hz, 1H), 4.02 (dd, *J* = 9.4, 6.9 Hz, 1H), 3.89 (AB of ABX, *J*_{AB} = 11.4 Hz, *J*_{AX} = 3.9 Hz, *J*_{BX} = 2.0 Hz, Δ*v*_{AB} = 8.9 Hz, 2H), 3.77 (apparent ddd, *J* = 9.3, 3.1, 3.1 Hz, 1H), 0.90 (s, 9H), 0.88 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.07 (apparent s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 156.3 (s), 145.5 (o), 99.3 (o), 79.3 (o), 74.2 (o), 66.7 (o), 61.5 (t), 25.9 (o), 25.7 (o), 18.4 (s), 18.1 (s), -4.6 (o), -5.0 (o), -5.1 (o), -5.3 (o); HRMS (FAB) *m/z* calcd for C₁₉H₃₈NO₅Si₂ (M-H)⁺ 416.2289, found 416.2307.

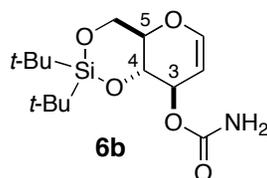
Part 3. Determination of *J*_{H4,H5} values for glucal 3-carbamates **6**



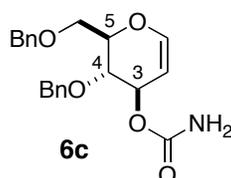
3-O-Carbamoyl-4,6-O-isopropylidene-D-glucal (6a).⁸ Because of extensive overlap of signals in the ¹H NMR and limited solubility in CDCl₃, complete NMR analysis of **6a** was completed in DMSO-*d*₆. ¹H/¹H COSY, ¹H/¹³C HSQC, and ¹H/¹³C HMBC experiments permitted conclusive proton and carbon signal assignments. The H4 signal (δ 3.98) appeared as a doublet of doublets (*J* = 9.8, 8.1 Hz). Upon homonuclear decoupling at H3 (δ 5.06), the H4 resonance collapsed to a doublet (*J*_{H4,H5} = 9.9 Hz). Complete NMR data for **6a**, including peak assignments based on the 2D experiments: ¹H NMR (300 MHz, DMSO-*d*₆) δ 6.88-6.35 (br, 2H, NH₂), 6.45 (dd, *J* = 6.1, 1.3 Hz, 1H, H1), 5.06 (ddd, *J* = 7.9, 1.6, 1.6 Hz, 1H, H3), 4.69 (dd, *J* = 6.1, 1.8 Hz, 1H, H2), 3.98 (dd, *J* = 9.8, 8.1 Hz, 1H, H4), 3.93-3.78 (m,

⁸ Bodner, R.; Marcellino, B. K.; Severino, A.; Smenton, A. L.; Rojas, C. M. *J. Org. Chem.* **2005**, *70*, 3988–3996. We have now made full ¹H and ¹³C NMR assignments based on 2-D experiments and they are included in the data listed above.

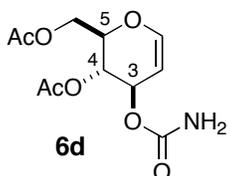
2H, H6), 3.82-3.69 (m, 1H, H5), 1.47 (s, 3H, CH₃), 1.32 (s, 3H, CH₃); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 156.3 (s, C(O)NH₂), 144.7 (o, C1), 101.9 (o, C2), 99.3 (s, C(CH₃)₂), 69.5 (o, C5), 69.3 (o, C4), 68.4 (o, C3), 60.6 (t, C6), 28.8 (o, CH₃), 19.1 (o, CH₃).



3-O-Carbamoyl-4,6-O-di-tert-butylsilylene-D-glucal (6b).⁸ Conclusive NMR assignments were made using ¹H/¹H COSY, ¹H/¹³C HSQC, and ¹H/¹³C HMBC in CDCl₃. The H4 resonance (δ 4.13) was a doublet of doublets ($J = 10.0, 7.6$ Hz) that collapsed to a doublet ($J_{H4,H5} = 10.0$ Hz) upon irradiation of the H3 signal (δ 5.26). Complete NMR data for **6b**, including peak assignments based on the 2D experiments: ¹H NMR (300 MHz, CDCl₃) δ 6.31 (dd, $J = 6.0, 1.4$ Hz, 1H, H1), 5.26 (ddd, $J = 7.6, 1.8, 1.8$ Hz, 1H, H3), 4.90 (br s, 2H, NH₂), 4.81 (dd, $J = 6.1, 2.0$ Hz, 1H, H2), 4.19 (m, 1H, H6a), 4.13 (dd, $J = 10.0, 7.6$ Hz, 1H, H4), 4.03-3.95 (m, 1H, H6b), 3.95-3.85 (m, 1H, H5), 1.06 (s, 9H, C(CH₃)₃), 0.99 (s, 9H, C(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 156.8 (s, C(O)NH₂), 144.7 (o, C1), 100.1 (o, C2), 73.7 (o, C4), 73.1 (o, C3), 72.9 (o, C5), 65.7 (t, C6), 27.4 (o, C(CH₃)₃), 26.9 (o, C(CH₃)₃), 22.7 (s, C(CH₃)₃), 19.8 (s, C(CH₃)₃).



3-O-Carbamoyl-4,6-di-O-benzyl-D-glucal (6c). In CDCl₃, ¹H/¹H COSY and ¹H/¹³C HSQC data provided unambiguous NMR assignments. The H4 resonance (δ 3.90) was a doublet of doublets ($J = 8.8, 6.4$ Hz) that collapsed to a doublet ($J_{H4,H5} = 8.8$ Hz) when the H3 resonance (δ 5.35) was irradiated.



3-O-Carbamoyl-4,6-di-O-acetyl-D-glucal (6d). Determining $J_{H4,H5}$ in **6d** posed a challenge because the H3 and H4 resonances overlapped, rendering the spin system second-order. To determine the $J_{H4,H5}$ values, we began by unambiguously assigning all proton and carbon resonances using ¹H/¹H COSY, ¹H/¹³C HSQC, and ¹H/¹³C HMBC experiments in CDCl₃. We next used coupled HSQC experiments to lift the second-order behavior.⁹ In the case of **6d**, H4 appeared as a doublet of doublets in the trace through C4 in the coupled HSQC (Figure S1 and Figure S2, top). To simplify the system further, we

⁹ Simova, S. *Magn. Reson. Chem.* **1998**, *36*, 505–510.

performed a three-channel experiment, measuring the coupled HSQC spectrum with homonuclear decoupling at H5 (Figure S3). This reduced the H4 resonance to a doublet ($J_{H_3,H_4} = 6.0$ Hz) in the trace through C4 (Figure S4). Finally, fixing $J_{H_3,H_4} = 6.0$ Hz, we simulated the H4 doublet of doublets, varying J_{H_4,H_5} to best fit the coupled HSQC data (Figure S2, bottom). This gave $J_{H_4,H_5} = 7.5 \pm 0.3$ Hz.

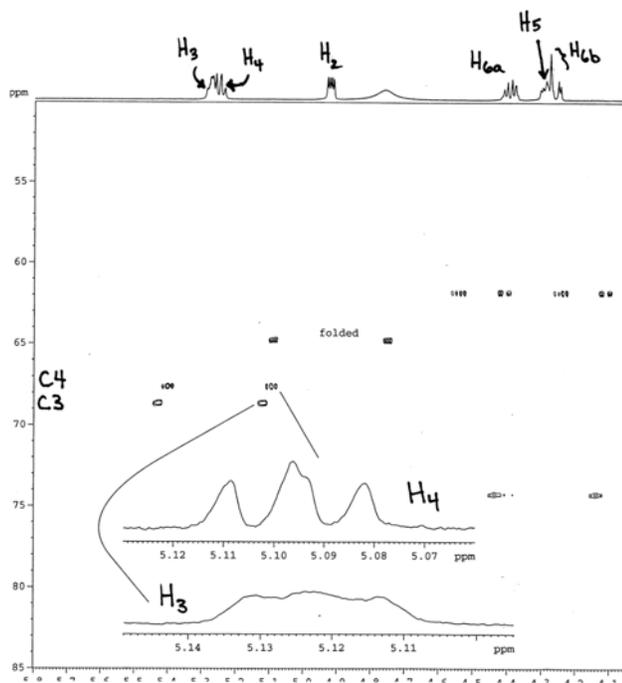


Figure S1. Coupled HSQC spectrum of **6d**. The trace through C4 is shown in the top panel of Figure S2. The external 1-D ^1H NMR projection (top) shows the overlap of H3 and H4 resonances, even at 500 MHz.

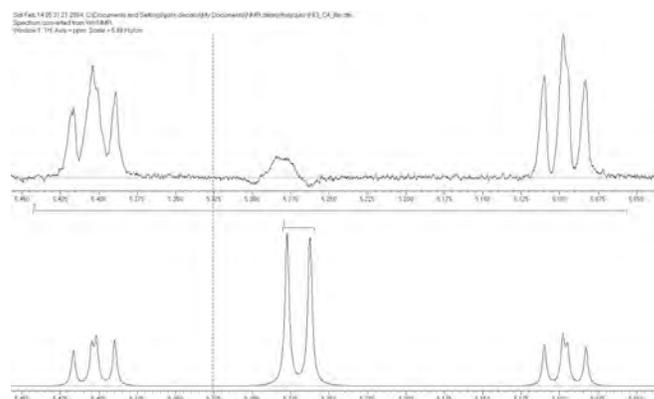


Figure S2. At top is the trace through C4 from the coupled HSQC spectrum of **6d** without any third-channel homonuclear decoupling. H4 appears as a doublet of doublets. At bottom is the best-fit simulated spectrum (gNMR, Adept Scientific), obtained setting $J_{H_3,H_4} = 6.0$ Hz and varying J_{H_4,H_5} . We found the best fit with $J_{H_4,H_5} = 7.5 \pm 0.3$ Hz.

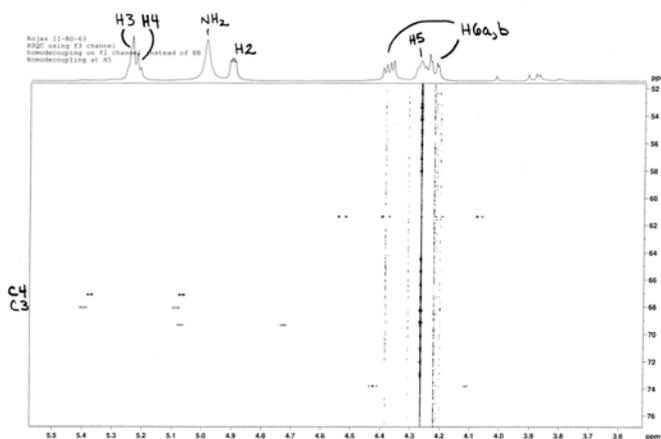


Figure S3. Coupled HSQC spectrum of **6d** with third-channel homonuclear decoupling at H5.

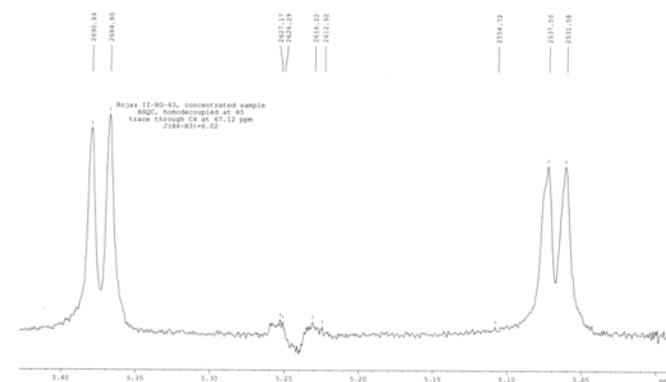
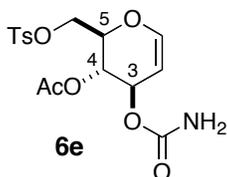
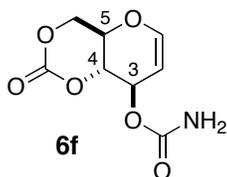


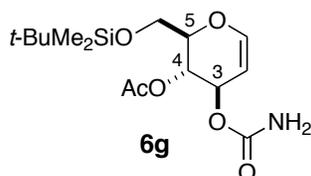
Figure S4. Trace through C4 of the 2-D spectrum from Figure S3, showing $J_{H_3,H_4} = 6.0$ Hz.



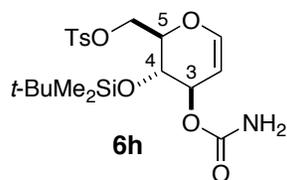
4-*O*-Acetyl-3-*O*-carbamoyl-6-*O*-*p*-toluenesulfonyl-D-glucal (6e). Proton and carbon assignments were made by $^1\text{H}/^1\text{H}$ COSY, $^1\text{H}/^{13}\text{C}$ HSQC, and HMBC. We conducted NMR experiments in C_6D_6 to resolve the C3 and C4 resonances, which coincided in CDCl_3 , even at 125 MHz. Resolution of those carbon signals was necessary for the coupled HSQC procedure, as described above for **6d**. In the case of **6e**, the H3 and H4 resonances overlapped in the 1-D ^1H NMR, but we were able to determine $J_{\text{H}_3,\text{H}_4}$ from the C3 trace of the three-channel coupled HSQC experiment, using homonuclear decoupling at H2. Alternatively, we determined $J_{\text{H}_3,\text{H}_4}$ from the C4 trace of the three-channel coupled HSQC experiment, using homonuclear decoupling at H5. The coupling constant determined in this way was $J_{\text{H}_3,\text{H}_4} = 5.5$ Hz. Using this value for $J_{\text{H}_3,\text{H}_4}$ we simulated the C4 trace from the coupled HSQC experiment, varying $J_{\text{H}_4,\text{H}_5}$ and obtaining the best fit with $J_{\text{H}_4,\text{H}_5} = 6.7 \pm 0.4$ Hz.



3-*O*-Carbamoyl-4-*O*,6-*O*-carbonyl-D-glucal (6f). For sufficient solubility, we measured NMR data for **6f** in acetone- d_6 . Assignment of ^1H and ^{13}C resonances was made using $^1\text{H}/^1\text{H}$ COSY and $^1\text{H}/^{13}\text{C}$ HSQC experiments. The system was amenable to direct first-order analysis. The H4 signal (δ 4.69) was a doublet of doublets ($J = 10.4, 8.0$ Hz). Meanwhile, examination of the H3 signal (δ 5.45, ddd, $J = 8.0, 1.9, 1.9$ Hz) provided $J_{\text{H}_3,\text{H}_4} = 8.0$ Hz. Consequently, we determined $J_{\text{H}_4,\text{H}_5} = 10.4$ Hz.



4-*O*-Acetyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-carbamoyl-D-glucal (6g). Conclusive ^1H and ^{13}C assignments were made through $^1\text{H}/^1\text{H}$ COSY, $^1\text{H}/^{13}\text{C}$ HSQC, and HMBC experiments in CDCl_3 . The H3 and H4 resonances overlapped (δ 5.47), necessitating the coupled HSQC technique to lift the second-order behavior. In the coupled HSQC experiment, the trace through C4 appeared as a doublet of doublets. Third-channel decoupling at H2 (δ 4.81) sharpened this doublet of doublets, apparently by removing a small long-range coupling. We also conducted a coupled HSQC experiment with third-channel decoupling at H5 (δ 4.06). The trace through C4 showed H4 as a doublet, giving $J_{\text{H}_3,\text{H}_4} = 6.5$ Hz. Finally, we simulated the H4 doublet of doublets, fixing $J_{\text{H}_3,\text{H}_4} = 6.5$ Hz and varying $J_{\text{H}_4,\text{H}_5}$ to visually match the C4 trace of the coupled HSQC spectrum taken with third-channel decoupling at H2. This procedure gave $J_{\text{H}_4,\text{H}_5} = 7.9 \pm 0.3$ Hz.



4O-*tert*-Butyldimethylsilyl-3-O-carbamoyl-6-O-*p*-toluenesulfonyl-D-glucal (6h). Proton and carbon resonances were assigned using $^1\text{H}/^1\text{H}$ COSY, $^1\text{H}/^{13}\text{C}$ HSQC, and $^1\text{H}/^{13}\text{C}$ HMBC experiments in CDCl_3 . The resonances for H4 and H5 overlapped, so we used coupled HSQC to enable determination of $J_{\text{H4,H5}}$. In the coupled HSQC with third-channel decoupling at H3 (Figure S5), the H4 signal as observed through the C4 trace was a doublet (Figure S6), showing $J_{\text{H4,H5}} = 9.0$ Hz.

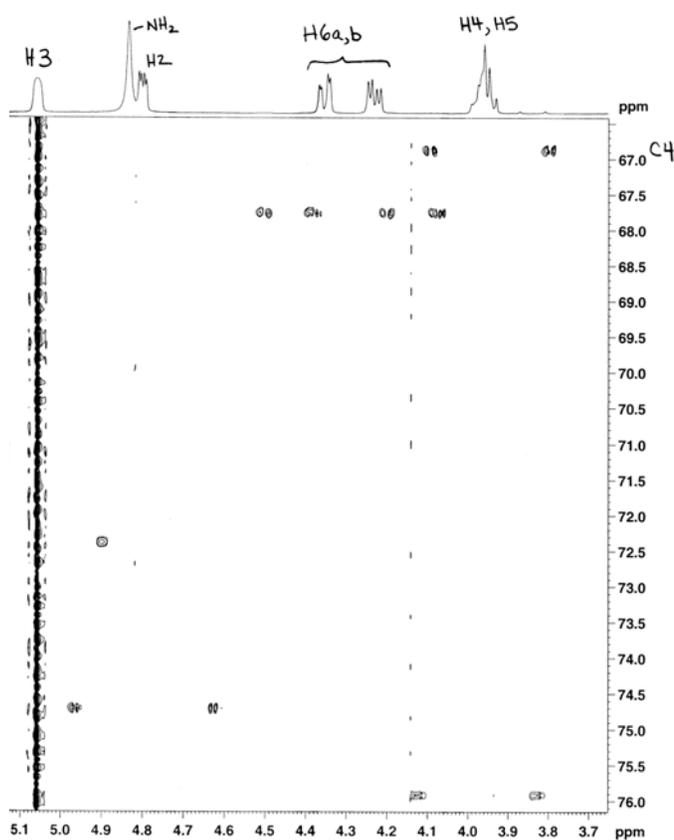


Figure S5. Coupled HSQC spectrum of **6h** with third-channel homonuclear decoupling at H3. The external 1-D ^1H projection at the top shows the overlap of the H4 and H5 resonances at 500 MHz.

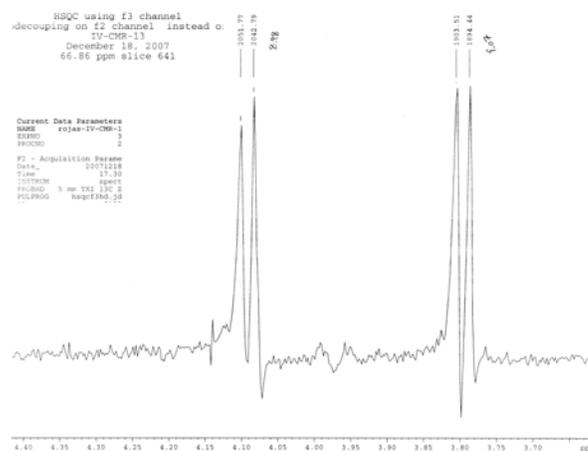
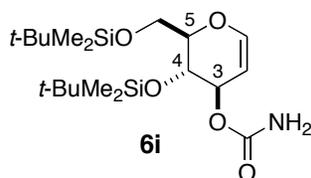
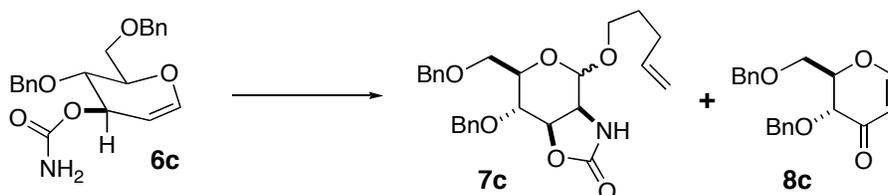


Figure S6. Trace through C4 of the 2-D spectrum of **6h** shown in Figure S5.



3-*O*-Carbamoyl-4,6-di-*O*-*tert*-butyldimethylsilyl-D-glucal (6i). The $J_{H4,H5}$ value was available by straightforward first-order analysis of the 1-D ^1H NMR spectrum in CDCl_3 . The H4 resonance (δ 4.02) appeared as a doublet of doublets ($J = 9.4, 6.9$ Hz), while H3 was a ddd (δ 5.13, $J = 6.8, 1.8, 1.8$ Hz), leading to the conclusion that $J_{H4,H5} = 9.4$ Hz.

Part 4. Amidoglycosylation of glucal 3-carbamates 6c–i using 4-penten-1-ol as the acceptor and determination of the α : β ratio in 7 and the ratio of 7 to byproduct 8.



General procedure for glucal 3-carbamate amidoglycosylation:

4-Pentenyl 2-amino-2-*N*-3-*O*-carbonyl-2-deoxy-4,6-di-*O*-benzyl-D-mannopyranosides (7c) and 1,2-Dideoxy-4,6-di-*O*-benzyl-D-erythro-hex-1-enopyran-3-ulose (8c¹⁰). The glucal carbamate **6c** (50.4 mg, 0.137 mmol), activated 4Å molecular sieves (152 mg), $\text{Rh}_2(\text{OAc})_4$ (6.6 mg, 0.0149 mmol), PhIO (55.6 mg, 0.253 mmol), and 4-penten-1-ol (70 μL , 0.69 mmol) were combined and CH_2Cl_2 (2.0 mL) was added. The reaction mixture was well stirred during 2 h and filtered through a pad of Celite, washing with EtOAc . The filtrate was concentrated on the rotovap and the residue placed under vacuum (0.5 mmHg) overnight. The crude material was analyzed by ^1H and ^{13}C NMR to determine the ratio of amidoglycosylation to C3–H oxidation (i.e., **7c**:**8c**) and the anomeric composition of amidoglycosylation product **7c** (see discussion below). The crude material was then chromatographed (30→35→40→45% EtOAc /hexanes, 35 mL SiO_2), providing **7c- α** (37.9 mg, 61%), **7c- β** (7.1 mg of material containing inseparable impurities, <10%), and dihydropyranone **8c** (10.4 mg, 23%).

The **7c**:**8c** composition was readily determined by integration of the ^1H NMR spectrum of the crude material, but the ratio of anomers **7c- α** :**7c- β** could not be measured by ^1H NMR of the crude material (CDCl_3 , 300 MHz) because of almost complete signal overlap. The anomeric ratio for reaction in CH_2Cl_2 based on the weights of isolated products (5.4:1) was a significant underestimate because, while the major α anomer was obtained in high purity, the minor β diastereomer could not be completely separated from unidentified byproducts by silica gel chromatography. Using crude product as well as chromatographed samples of **7c- α** and **7c- β** , we investigated a number of solvents for ^1H NMR analysis

¹⁰ Kirschning, A. *J. Org. Chem.* **1995**, *60*, 1228–1232.

(CD_2Cl_2 , C_6D_6 , bromobenzene- d_5) but found that the anomers could not be distinguished cleanly. However, in the ^{13}C NMR, C1 and C2 resonances for the anomers of **7c** were clearly resolved. The C1 resonances, though separated, were quite close (δ 96.32 for **7c- α** and δ 96.67 for **7c- β**), so the C2 peaks (δ 56.31 for **7c- α** and δ 53.80 for **7c- β**) were used for analysis. The ^{13}C NMR data for is shown in the first panel of Figure S7. The largest contribution to the T_1 relaxation time of C2 is the dipolar coupling of the CH pair. Because this should be very similar for both anomers, any difference in T_1 for the C2 carbons would be small, making integration of the ^{13}C NMR peaks a reasonable measure of the anomeric ratio. Additionally, this was confirmed in our study of **7i** (see pp S30–S32) by comparing integration results from an inverse-gated ^{13}C pulse sequence experiment using a longer delay time. Overall, the combination of ^1H and ^{13}C NMR analysis showed that **7c:8c** was 2.9:1 and **7c- α :7c- β** was 12:1 for the reaction run in CH_2Cl_2 .

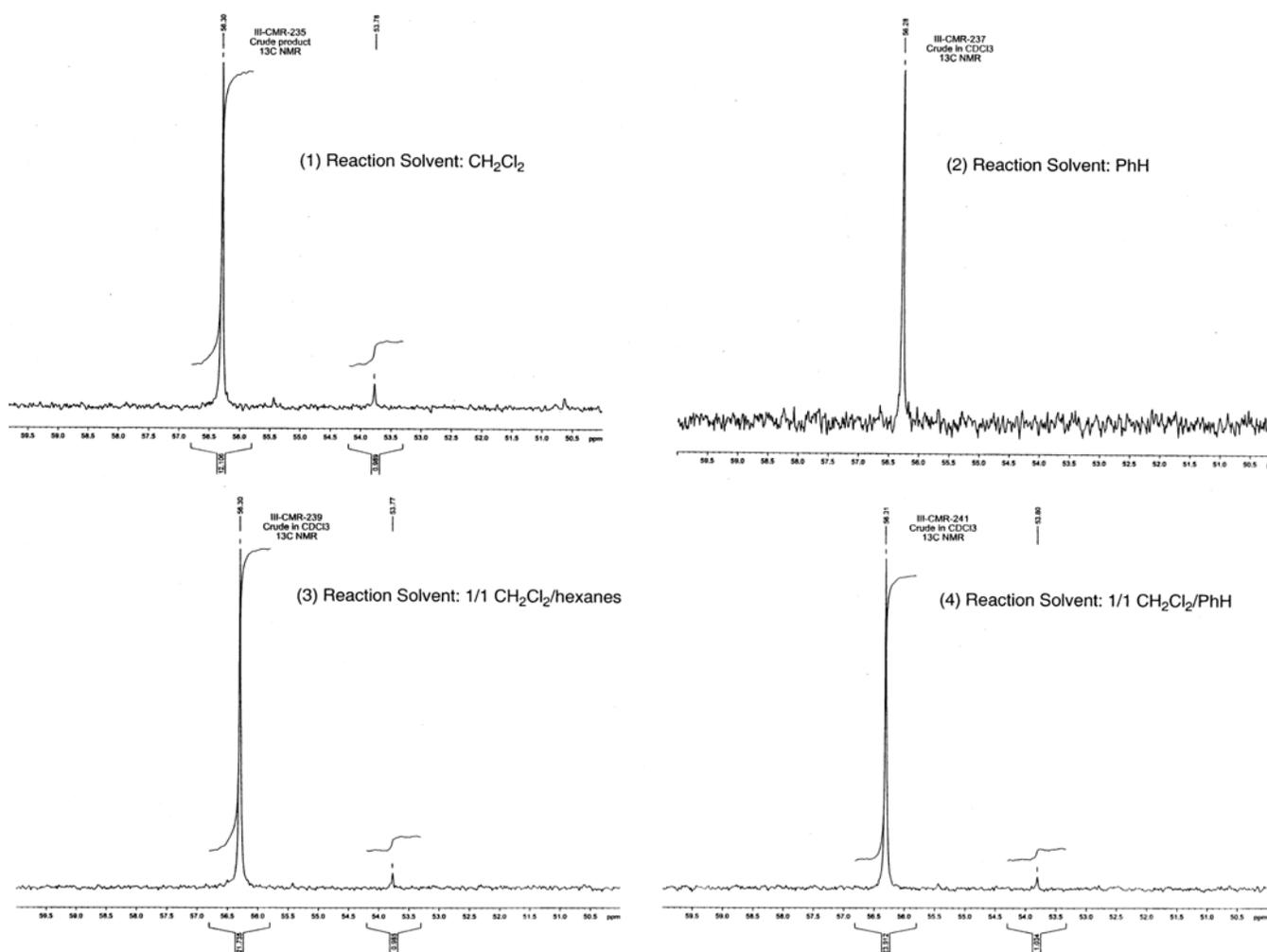


Figure S7. Measurement of **7c- α :7c- β** from C2 resonances of the anomers for reactions conducted using different solvents.

Anomers **7c- α** and **7c- β** were distinguished by their $J_{\text{H}_1,\text{H}_2}$ values, since we have found that 2-mannosamine oxazolidinones have $J_{\text{H}_1,\text{H}_2} \approx 0$ Hz for the α anomers and $J_{\text{H}_1,\text{H}_2} = 2\text{--}3$ Hz for the

β anomers.⁸ These findings are in accord with ¹H NMR coupling constants in conformationally similar 2,3-*O*-carbonates of manno- and rhamnopyranosides.¹¹

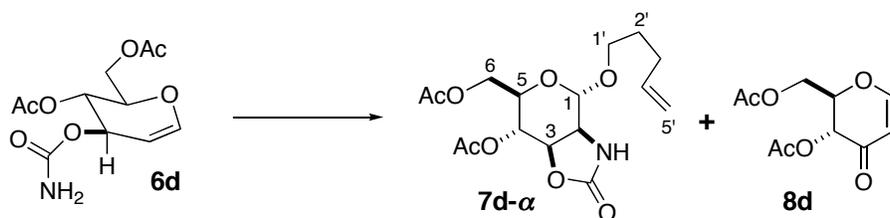
The amidoglycosylation reaction of **6c** was also conducted in solvents of varying polarity, but otherwise under the same conditions described above. In benzene, **7c:8c** was 2.3:1, only **7c- α** was detected, and the isolated yield of **7c- α** was 47%. In 1/1 CH₂Cl₂/hexanes, **7c:8c** was 3.0:1, **7c- α :7c- β** was 22:1, and the isolated yield of **7c- α** was 54%. In 1/1 CH₂Cl₂/benzene, **7c:8c** was 3.0:1, **7c- α :7c- β** was 23:1, and the isolated yield of **7c- α** was 56%. Use of ¹³C NMR for anomer ratio determination in these cases is illustrated in panels 2–4 of Figure S7.

Data for **7c- α** : $R_f = 0.26$ (45% EtOAc/hexanes); IR (thin film) 3305, 3064, 3031, 1769, 1640 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.37–7.18 (m, 10H), 6.16 (br s 1H), 5.77 (dddd, $J = 17.0, 10.3, 6.7, 6.7$ Hz, 1H), 5.06–4.92 (m, 2H), 4.90 (s, 1H), 4.84 (d, $J = 11.1$ Hz, 1H), 4.77 (dd, $J = 7.8, 6.3$ Hz, 1H), 4.57 (AB, $J_{AB} = 12.2$ Hz, $\Delta\nu_{AB} = 30.7$ Hz, 2H), 4.52 (d, $J = 11.1$ Hz, 1H), 4.04 (d, $J = 8.0$ Hz, 1H), 3.88–3.63 (m, 5H), 3.39 (ddd, $J = 9.6, 6.5, 6.5$ Hz, 1H), 2.08 (apparent q, $J = 7.2$ Hz, 2H), 1.65 (apparent quintet, $J = 7.0$ Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 159.0 (s), 137.8 (s), 137.7 (o), 137.5 (s), 128.4 (o), 127.9 (o), 127.8 (o), 127.7 (o), 115.0 (t), 96.4 (o), 79.7 (o), 74.9 (o), 73.53 (t), 73.50 (t), 68.5 (t), 67.3 (o), 67.1 (t), 56.3 (o), 30.1 (t), 28.4 (t); HRMS (FAB) m/z calcd for C₂₆H₃₂NO₆ (M+H)⁺ 454.2230, found 454.2242.

Data for **7c- β** : $R_f = 0.24$ (45% EtOAc/hexanes); IR (thin film) 3288, 3064, 3027, 1760, 1641 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.38–7.18 (m, 10H), 5.79 (dddd, $J = 17.1, 10.3, 6.7, 6.7$ Hz, 1H), 5.14 (br s 1H), 5.07–4.93 (m, 2H), 4.77 (dd, $J = 8.2, 5.1$ Hz, 1H), 4.72 (d, $J = 2.2$ Hz, 1H), 4.64 (AB, $J_{AB} = 11.8$ Hz, $\Delta\nu_{AB} = 36.3$ Hz, 2H), 4.56 (AB, $J_{AB} = 12.4$ Hz, $\Delta\nu_{AB} = 8.5$ Hz, 2H), 4.02 (dd, $J = 8.3, 2.2$ Hz, 1H), 3.98–3.86 (m, 2H), 3.80 (m, 1H), 3.70–3.62 (m, 2H), 3.48 (ddd, $J = 9.4, 6.7, 6.7$ Hz, 1H), 2.09 (apparent q, $J = 7.2$ Hz, 2H), 1.68 (apparent quintet, $J = 7.1$ Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 158.3, 138.0, 137.9, 137.3, 128.5, 128.4, 128.01, 127.97, 127.8, 127.7, 115.0, 96.8, 78.1, 75.2, 73.54, 73.46, 72.7, 69.8, 68.9, 53.7, 30.1, 28.6.

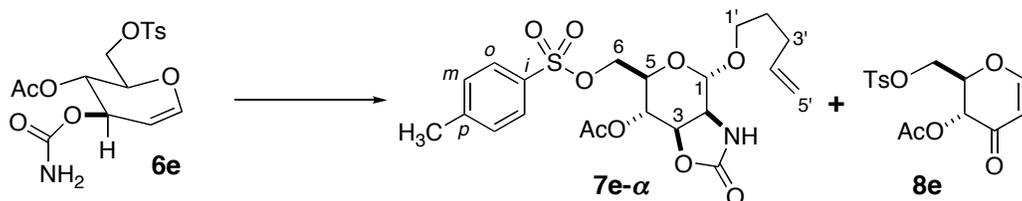
Data for **8**:¹⁰ $R_f = 0.5$ (45% EtOAc/hexanes); IR (thin film) 3087, 3063, 3030, 1686, 1599 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.40–7.25 (m, 11H), 5.39 (d, $J = 5.9$ Hz, 1H), 5.08 (d, $J = 11.1$ Hz, 1H), 4.61 (d, $J = 11.1$ Hz, 1H), 4.55 (AB, $J_{AB} = 12.1$ Hz, $\Delta\nu_{AB} = 14.1$ Hz, 2H), 4.43 (ddd, $J = 11.6, 3.1, 3.1$ Hz, 1H), 4.24 (d, $J = 11.6$ Hz, 1H), 3.80 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 193.6 (s), 162.3 (o), 137.5 (s), 137.4 (s), 128.5 (o), 128.39 (o), 128.35 (o), 128.0 (o), 127.9 (o), 127.8 (o), 105.2 (o), 81.0 (o) 74.6 (t), 74.1 (o), 73.6 (t), 67.8 (t); HRMS (FAB) m/z calcd for C₂₀H₂₁O₄ (M+H)⁺ 325.1440, found 325.1453.

¹¹ (a) Günther, W.; Kunz, H. *Carbohydr. Res.* **1992**, 228, 217–241. (b) Crich, D.; Cai, W.; Dai, Z. *J. Org. Chem.* **2000**, 65, 1291–1297. (c) Crich, D.; Vinod, A. U.; Picione, J. *J. Org. Chem.* **2003**, 68, 8453–8458.



4-Pentenyl 2-amino-2-*N*-3-*O*-carbonyl-2-deoxy-4,6-di-*O*-acetyl- α -D-mannopyranoside (7d- α) and 1,2-Dideoxy-4,6-di-*O*-acetyl-D-erythro-hex-1-enopyran-3-ulose (8d¹²). Reaction of glucal carbamate **6d** (47.0 mg, 0.172 mmol) under the general amidoglycosylation conditions as described for **6c** led to complete consumption of starting material within 2 h. Analysis of the crude reaction product by ¹H and ¹³C NMR indicated a single anomer **7d- α** and a **7d:8d** ratio of 15:1. Chromatography (45→50→55→60% EtOAc/hex, 35 mL SiO₂), provided **7d- α** (42.4 mg, 69%) and a small quantity of **8d** (1.3 mg, 3.3%). Data for **7d- α** : *R*_f = 0.4 (70% EtOAc/hexanes); IR (thin film) 3339, 1768, 1747, 1641 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.60 (br s, 1H, NH), 5.80 (dddd, *J* = 17.0, 10.3, 6.7, 6.7 Hz, 1H, H4'), 5.16 (dd, *J* = 9.9, 7.2 Hz, 1H, H4), 5.09-4.95 (m, 2H, H5'a,b), 4.92 (s, 1H, H1), 4.70 (dd, *J* = 7.4, 7.4 Hz, 1H, H3), 4.26 (dd, *J* = 12.2, 5.4 Hz, 1H, 6a), 4.17-4.03 (m, 2H, H6b and H2), 3.91 (ddd, *J* = 9.8, 5.4, 2.7 Hz, 1H, H5), 3.70 (ddd, *J* = 9.6, 6.6, 6.6 Hz, 1H, H1'a), 3.44 (ddd, *J* = 9.6, 6.4, 6.4 Hz, 1H, H1'b), 2.18-2.06 (m, 2H, H3'a,b), 2.11 (s, 3H, C(O)CH₃), 2.10 (s, 3H, C(O)CH₃), 1.69 (apparent quintet, *J* = 7.0 Hz, 2H, H2'a,b); ¹³C NMR (75 MHz, CDCl₃) δ 170.7 (s), 169.4 (s), 158.9 (s), 137.6 (o, C4'), 115.2 (t, C5'), 96.3 (o, C1), 76.2 (o, C3), 68.2 (o, C4), 67.4 (t, C1'), 65.5 (o, C5), 62.3 (t, C6), 55.9 (o, C2), 30.1 (t, C3'), 28.3 (t, C2'), 20.7 (o, two overlapping signals, C(O)CH₃); HRMS (FAB) *m/z* calcd for C₁₆H₂₄NO₈ (M+H)⁺ 358.1502, found 358.1516.

Data for **8d**: *R*_f = 0.5 (70% EtOAc/hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.37 (d, *J* = 5.9 Hz, 1H), 5.55 (d, *J* = 13.1 Hz, 1H), 5.50 (d, *J* = 5.9 Hz, 1H), 4.66-4.56 (m, 1H), 4.41 (AB of ABX, *J*_{AB} = 12.7 Hz, *J*_{AX} = 4.3 Hz, *J*_{BX} = 2.1 Hz, $\Delta\nu_{AB}$ = 16.1 Hz, 2H), 2.20 (s, 3H), 2.12 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.8, 170.3, 169.2, 162.3, 105.4, 78.3, 68.1, 61.4, 20.6, 20.4.



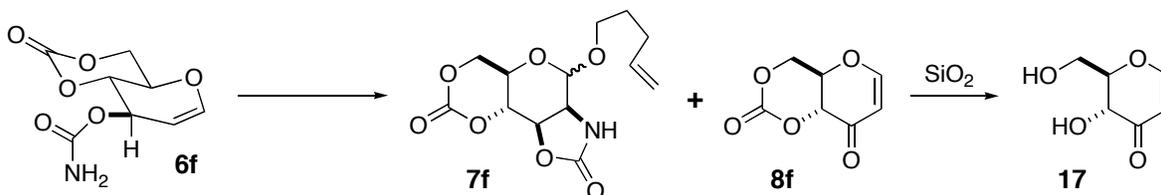
4-Pentenyl 4-*O*-acetyl-2-amino-2-*N*-3-*O*-carbonyl-2-deoxy-6-*O*-*p*-toluenesulfonyl- α -D-mannopyranoside (7e- α) and 1,2-Dideoxy-4-*O*-acetyl-6-*O*-*p*-toluenesulfonyl-D-erythro-hex-1-enopyran-3-ulose (8e¹³). Following the general procedure described for **6c**, amidoglycosylation of glucal carbamate **6e** (53.5 mg, 0.139 mmol) was complete within 2 h. The crude material was analyzed

¹² (a) Fétizon, M.; Do Khac, D.; Nguyen Dinh, T. *Tetrahedron Lett.* **1986**, 26, 1777–1780. (b) Czernecki, S.; Vijayakumaran, K.; Ville, G. *J. Org. Chem.* **1986**, 51, 5472–5475. (c) Bouillot, A.; Do Khac, D.; Fétizon, M.; Guir, F.; Memoria, Y. *Synth. Commun.* **1993**, 23, 2071–2081.

¹³ Sridhar, P. R.; Prabhu, K. R.; Chandrasekaran, S. *Eur. J. Org. Chem.* **2004**, 4809–4815.

by ^1H and ^{13}C NMR to determine the anomeric composition of amidoglycosylation product **7e** (only the α anomer was observed) and the ratio **7e**:**8e** (14:1). Chromatography (45 \rightarrow 50 \rightarrow 55 \rightarrow 60% EtOAc/hexanes, 35 mL SiO₂) provided **7e- α** (45.2 mg, 69%) and **8e** (2.0 mg, 4%). Data for **7e- α** : $R_f = 0.34$ (60% EtOAc/hexanes); IR (thin film) 3368, 1770, 1741 (shoulder), 1640, 1598 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 7.77 (apparent d, $J = 8.3$ Hz, 2H, H_o), 7.35 (apparent d, $J = 8.4$ Hz, 2H, H_m), 6.45 (br s, 1H, NH), 5.79 (dddd, $J = 17.0, 10.3, 6.7, 6.7$ Hz, 1H, H4'), 5.08-4.95 (m, 2H, H5'a,b), 4.95 (dd, $J = 9.9, 7.1$ Hz, 1H, H4), 4.82 (s, 1H, H1), 4.67 (dd, $J = 7.4, 7.4$ Hz, 1H, H3), 4.14-3.98 (m, 3H, H2 and H6a,b), 3.95 (m, 1H, H5), 3.66 (ddd, $J = 9.6, 6.6, 6.6$ Hz, 1H, H1'a), 3.36 (ddd, $J = 9.6, 6.4, 6.4$ Hz, 1H, H1'b), 2.45 (s, 3H, Ar-CH₃), 2.15-2.02 (m, 2H, H3'a,b), 2.08 (s, 3H, C(O)CH₃), 1.65 (apparent quintet, $J = 7.0$ Hz, 2H, H2'a,b); ^{13}C NMR (75 MHz, CDCl₃) δ 169.6 (s), 158.6 (s), 145.1 (s), 137.7 (o, C4'), 132.4 (s), 129.9 (o, C_m), 128.0 (o, C_o), 115.1 (t, C5'), 96.0 (o, C1), 75.8 (o, C3), 68.5 (o, C4), 68.3 (t, C6), 67.4 (t, C1'), 65.5 (o, C5), 55.8 (o, C2), 30.1 (t, C3'), 28.3 (t, C2'), 21.6 (o, Ar-CH₃), 20.7 (o, C(O)CH₃); HRMS (FAB) m/z calcd for C₂₁H₂₈NO₉S (M+H)⁺ 470.1485, found 470.1470.

Data for **8e**:¹³ $R_f = 0.45$ (60% EtOAc/hexanes); IR (thin film) 1759, 1697, 1598 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 7.81 (apparent d, $J = 8.3$ Hz, 2H), 7.38 (apparent d, $J = 8.2$ Hz, 2H), 7.28 (d, overlaps with residual CHCl₃ peak from NMR solvent, 1H), 5.46 (d, $J = 13.2$ Hz, 1H), 5.46 (d, $J = 5.9$ Hz, 1H), 4.59 (m, 1H), 4.33 (AB of ABX, $J_{AB} = 11.5$ Hz, $J_{AX} = 4.2$ Hz, $J_{BX} = 2.0$ Hz, $\Delta\nu_{AB} = 33.1$ Hz, 2H), 2.47 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, CDCl₃) δ 187.3 (s), 168.8 (s), 162.0 (o), 145.4 (s), 132.2 (s), 130.0 (o), 128.1 (o), 105.5 (o), 77.5 (o, signal was obscured by the solvent peak but was detected in the DEPT 135 experiment), 67.8 (o), 66.3 (t), 21.7 (o), 20.3 (o); HRMS (FAB) m/z calcd for C₁₅H₁₇O₇S (M+H)⁺ 341.0695, found 341.0694.

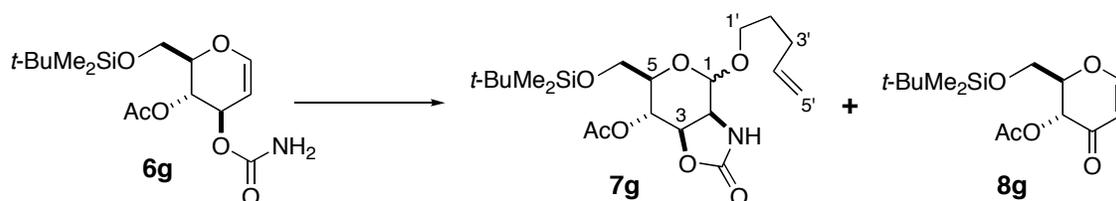


4-Pentenyl 2-amino-2-*N*-3-*O*-carbonyl-4,6-*O*-carbonyl-2-deoxy-D-mannopyranosides (7f) and 1,2-Dideoxy-D-erythro-hex-1-enopyran-3-ulose (17^{12b}). The general amidoglycosylation procedure described for **6c** was used. The reaction time for amidoglycosylation of carbonate-protected glucal 3-carbamate **6f** (30.1 mg, 0.140 mmol) was 2.25 h. ^1H and ^{13}C NMR analysis of the crude product was used to determine the anomeric composition of **7f** (α : $\beta = 2.9$:1) and the ratio **7f**:**8f** (2.4:1). Although **8f** was present in the crude product, during chromatography (70 \rightarrow 75 \rightarrow 80% EtOAc/hexanes, 35 mL SiO₂), **8f** was converted to the corresponding diol **17**^{12b} by hydrolysis of the cyclic carbonate. Sugar 4,6-carbonates having the trans ring fusion are recognized to be labile.⁷ Data for **7f- α** : $R_f = 0.41$ (80% EtOAc/hexanes); IR (thin film) 3329, 1770, 1640 cm⁻¹; ^1H NMR (300 MHz, acetone-*d*₆) δ 6.91 (br s, 1H), 5.84 (dddd, $J = 17.1, 10.3, 6.7, 6.7$ Hz, 1H), 5.08 (s, 1H), 5.03 (dddd, $J = 17.2, 1.8, 1.8, 1.8$ Hz, 1H), 4.95 (dddd, $J = 10.2, 2.2, 1.1, 1.1$ Hz, 1H), 4.83 (dd, $J = 7.7, 7.7$ Hz, 1H), 4.59 (dd, $J = 10.2, 7.8$ Hz, 1H), 4.58 (dd, $J = 9.5, 5.9$ Hz, 1H), 4.42 (dd, $J = 9.9, 9.9$ Hz, 1H), 4.33-4.20 (m, 2H), 3.80 (ddd, $J =$

9.7, 6.5, 6.5 Hz, 1H), 3.50 (ddd, $J = 9.7, 6.4, 6.4$ Hz, 1H), 2.15 (m, 2H), 1.70 (m, 2H); ^{13}C NMR (75 MHz, acetone- d_6) δ 158.3 (s), 147.4 (s), 139.1 (o), 115.4 (t), 98.3 (o), 78.4 (o), 74.8 (o), 69.7 (t), 68.2 (t), 57.6 (o), 57.1 (o), 30.9 (t), 29.3 (t); HRMS (FAB) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_7$ ($\text{M}+\text{H}$) $^+$ 300.1083, found 300.1082.

Data for **7f- β** : $R_f = 0.26$ (80% EtOAc/hexanes); IR (thin film) 3328, 1766, 1640, 1597 cm^{-1} ; ^1H NMR (300 MHz, acetone- d_6) δ 6.89 (br s, 1H), 5.82 (dddd, $J = 17.1, 10.3, 6.7, 6.7$ Hz, 1H), 5.06-4.97 (m, 3H), 4.94 (dddd, $J = 10.2, 2.1, 1.1, 1.1$ Hz, 1H), 4.87 (dd, $J = 8.2, 7.2$ Hz, 1H), 4.54 (dd, $J = 9.6, 5.8$ Hz, 1H), 4.42-4.31 (m, 2H), 4.13 (ddd, $J = 10.4, 10.4, 5.8$ Hz, 1H), 3.88 (ddd, $J = 9.5, 6.3, 6.3$ Hz, 1H), 3.53 (ddd, $J = 9.5, 6.4, 6.4$ Hz, 1H), 2.14 (m, 2H), 1.68 (apparent quintet, $J = 7.0$ Hz, 2H); ^{13}C NMR (75 MHz, acetone- d_6) δ 158.8 (s), 147.3 (s), 139.2 (o), 115.3 (t), 98.6 (o), 88.0 (o), 75.6 (o), 70.3 (t), 69.3 (t), 62.0 (o), 54.5 (o), 30.9 (t), 29.6 (t, obscured by solvent peak but visible in the DEPT 135 experiment); HRMS (FAB) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_7$ ($\text{M}+\text{H}$) $^+$ 300.1083, found 300.1084.

Dihydropyranone **8f** was detected in the crude reaction product: $R_f = 0.21$ (80% EtOAc/hexanes); ^1H NMR (300 MHz, acetone- d_6) δ 7.63 (dd, $J = 6.0, 0.6$ Hz), 5.50 (d, $J = 6.0$ Hz), 5.30 (d, $J = 13.0$ Hz), other signals overlapped with those from other components of the crude mixture; ^{13}C NMR (75 MHz, acetone- d_6) δ 185.7, 162.9, 147.0 and 146.9 (we do not know which of these carbonate carbonyl signals is from **8f**), 106.6, we could not assign other carbon signals for **8f** conclusively in the crude sample. Upon silica gel chromatography, UV-active dihydropyranone material emerged from the column with lower R_f than that observed for carbonate **8f**. Characterization data for this lower- R_f UV-active material was consistent with the corresponding diol **17**.^{12b} Data for isolated diol **17**: IR (thin film) 3386, 1754 (we attribute this IR band to an impurity), 1678, 1596 cm^{-1} ; ^1H NMR (300 MHz, acetone- d_6) δ 7.55 (d, $J = 5.8$ Hz, 1H), 5.35 (d, $J = 5.8$ Hz, 1H), 4.39 (d, $J = 3.1$ Hz, 1H), 4.30 (dd, $J = 13.0, 3.1$ Hz, 1H), 4.13 (dddd, $J = 12.9, 4.2, 2.2, 0.6$ Hz, 1H), 4.12 (dd, $J = 6.7, 5.4$ Hz, 1H), 4.00 (ddd, $J = 12.4, 5.4, 2.2$ Hz, 1H), 3.89 (ddd, $J = 12.4, 6.8, 4.3$ Hz, 1H); ^{13}C NMR (75 MHz, acetone- d_6) δ 194.9 (s), 164.7 (o), 104.2 (o), 84.9 (o), 68.6 (o), 61.6 (t).

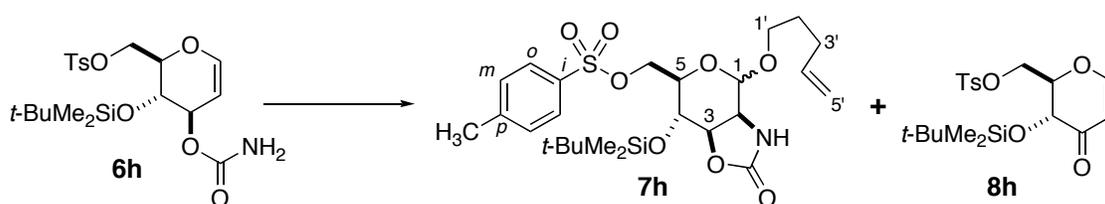


4-Pentenyl 4-O-acetyl-2-amino-6-O-tert-butyl dimethylsilyl-2-N-3-O-carbonyl-2-deoxy-D-mannopyranosides (7g) and 1,2-Dideoxy-4-O-acetyl-6-O-tert-butyl dimethylsilyl-D-erythro-hex-1-enopyran-3-ulose (8g)^{12c}. Using the general procedure as described for **6c**, amidoglycosylation with **6g** (50.1 mg, 0.145 mmol) was complete within 2 h 10 min. Analysis of the crude product by ^1H and ^{13}C NMR, provided the ratio **7g**:**8g** (6.6:1) and the anomeric distribution for **7g** (α : $\beta = 25$:1). Chromatography (20% (75 mL)→30% (50 mL)→40% (50 mL)→60% (50 mL) EtOAc/hexanes, 35 mL SiO_2 (15 cm x 2 cm), 5 mL fractions) gave **7g- α** (42.3 mg, 68%), **7g- β** (2.1 mg, 3.4%), and **8g** (1 mg). Data for **7g- α** : $R_f = 0.38$ (50% EtOAc/hexanes); IR (thin film) 3326, 1770, 1641 cm^{-1} ; ^1H NMR (300

MHz, CDCl₃) δ 6.50 (br s, 1H, NH), 5.81 (dddd, $J = 17.0, 10.3, 6.7, 6.7$ Hz, 1H, H4'), 5.10-4.94 (m, 3H, H4 and H5'), 4.87 (s, 1H, H1), 4.70 (dd, $J = 7.5, 7.5$ Hz, 1H, H3), 4.04 (d, $J = 7.9$ Hz, 1H, H2), 3.77 (ddd, $J = 9.7, 6.5, 6.5$ Hz, 1H, H1'a), 3.75 (m, 1H, H5), 3.67 (m, 2H, H6), 3.40 (ddd, $J = 9.6, 6.5, 6.5$ Hz, 1H, H1'b), 2.12 (m, 2H, H3'), 2.10 (s, 3H, C(O)CH₃), 1.68 (apparent quintet, $J = 7.0$ Hz, 2H, H2'), 0.89 (s, 9H, SiC(CH₃)₃), 0.06 (two overlapping s, 6H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 169.4 (s), 159.0 (s), 137.8 (o, C4'), 115.0 (t, C5'), 96.1 (o, C1), 76.3 (o, C3), 68.8 (o, C4 or C5), 68.7 (o, C4 or C5), 67.0 (t, C1'), 62.9 (t, C6), 58.9 (o, C2), 30.2 (t, C3'), 28.4 (t, C2'), 25.8 (o, SiC(CH₃)₃), 20.8 (o, C(O)CH₃), 18.3 (s), -5.4 (o, SiCH₃), -5.5 (o, SiCH₃); HRMS (FAB) m/z calcd for C₂₀H₃₆NO₇Si (M+H)⁺ 430.2261, found 430.2256.

Data for **7g- β** : $R_f = 0.35$ (50% EtOAc/hexanes); IR (thin film) 3308, 1767, 1640 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.80 (dddd, $J = 17.0, 10.3, 6.7, 6.7$ Hz, 1H), 5.19 (br s, 1H), 5.17 (dd, $J = 7.6, 3.7$ Hz, 1H), 5.10-4.94 (m, 2H), 4.74 (dd, $J = 8.4, 4.2$ Hz, 1H), 4.70 (d, $J = 2.1$ Hz, 1H), 3.95 (dd, $J = 8.4, 2.1$ Hz, 1H), 3.91 (ddd, $J = 9.4, 6.5, 6.5$ Hz, 1H), 3.84-3.63 (m, 3H), 3.51 (ddd, $J = 9.4, 6.7, 6.7$ Hz, 1H), 2.12 (m, 2H), 2.10 (s, 3H), 1.71 (apparent quintet, $J = 7.0$ Hz, 2H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.0 (s), 158.0 (s), 137.8 (o), 115.1 (t), 96.4 (o), 78.2 (o), 74.7 (o), 68.9 (t), 66.4 (o), 63.4 (t), 52.7 (o), 30.1 (t), 28.6 (t), 25.8 (o), 20.9 (o), 18.2 (s), -5.36 (o), -5.44 (o); HRMS (FAB) m/z calcd for C₂₀H₃₆NO₇Si (M+H)⁺ 430.2261, found 430.2281.

Data for **8g**:^{12c} $R_f = 0.59$ (50% EtOAc/hexanes); IR (thin film) 1760, 1699, 1600 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.36 (d, $J = 5.9$ Hz, 1H), 5.63 (d, $J = 12.9$ Hz, 1H), 5.43 (d, $J = 5.9$ Hz, 1H), 4.45 (ddd, $J = 12.9, 2.8, 2.0$ Hz, 1H), 3.92 (AB of ABX, $J_{AB} = 12.0$ Hz, $J_{AX} = 3.5$ Hz, $J_{BX} = 1.8$ Hz, $\Delta\nu_{AB} = 31.2$ Hz, 2H), 2.19 (s, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 189.9, 169.0, 162.7, 104.8, 81.1, 68.4, 61.4, 25.8, 20.6, 18.3, -5.5, -5.6; LRMS (FAB) m/z calcd for C₁₄H₂₅O₄Si (M+H)⁺ 285.15, found 285.2.



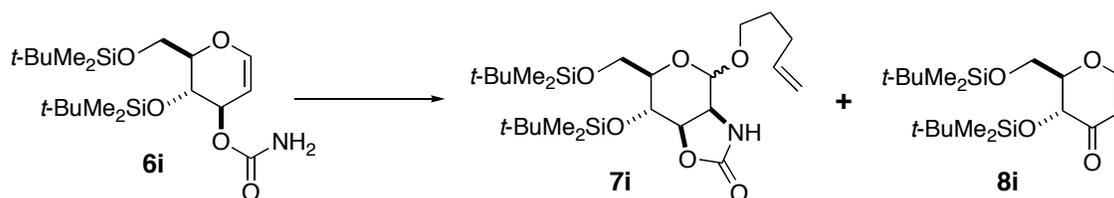
4-Pentenyl 2-amino-4-O-tert-butyl dimethylsilyl-2-N-3-O-carbonyl-2-deoxy-6-O-p-toluenesulfonyl-D-mannopyranosides (7h) and 1,2-Dideoxy-4-O-tert-butyl dimethylsilyl-6-O-p-toluenesulfonyl-D-erythro-hex-1-enopyran-3-ulose (8h¹⁴). Using the standard amidoglycosylation procedure as described for **6c** with a 3 h reaction time, **6h** (64.8 mg, 0.141 mmol) gave **7h- α** (51.6 mg, 67%), **7h- β** (3.8 mg, 5.0%), and dihydropyranone **8h** (4.5 mg), all as clear oils, after chromatography (40% (200 mL)→50% EtOAc/hexanes, 40 mL SiO₂ (16 cm x 2 cm), 5 mL fractions). The anomeric selectivity for **7h** (α : β = 12:1) and the ratio **7h**:**8h** (8.1:1) were determined from ¹H and ¹³C NMR spectra of the crude product.

¹⁴ (a) Kirschning, A.; Hary, U.; Plumeier, C.; Ries, M.; Rose, L. *J. Chem. Soc., Perkin Trans 1* **1999**, 519–528. (b) Kirschning, A. *Liebigs Ann.* **1995**, 2053–2056.

Data for **7h- α** : $R_f = 0.40$ (50% EtOAc/hexanes); IR (thin film) 3303, 1768, 1640, 1598 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.79 (apparent d, $J = 8.3$ Hz, 2H, H_o), 7.34 (apparent d, $J = 8.1$ Hz, 2H, H_m), 6.44 (br s, 1H, NH), 5.79 (dddd, $J = 17.0, 10.3, 6.7, 6.7$ Hz, 1H, $\text{H4}'$), 5.08-4.93 (m, 2H, $\text{H5}'$), 4.78 (s, 1H, H1), 4.47 (dd, $J = 7.2, 7.2$ Hz, 1H, H3), 4.31 (dd, $J = 10.5, 1.8$ Hz, 1H, H6), 4.10 (dd, $J = 10.5, 6.1$ Hz, 1H, H6), 3.99 (d, $J = 7.8$ Hz, 1H, H2), 3.77 (ddd, $J = 10.1, 6.0, 1.8$ Hz, 1H, H5), 3.66 (dd, $J = 9.7, 7.1$ Hz, 1H, H4), 3.64 (ddd, $J = 9.2, 6.8, 6.8$ Hz, 1H, $\text{H1}'$), 3.32 (ddd, $J = 9.6, 6.5, 6.5$ Hz, 1H, $\text{H1}'$), 2.45 (s, 3H, Ar- CH_3), 2.08 (apparent q, $J = 7.2$ Hz, 2H, $\text{H3}'$), 1.64 (apparent quintet, $J = 7.0$ Hz, 2H, $\text{H2}'$), 0.83 (s, 9H, $\text{SiC}(\text{CH}_3)_3$), 0.15 (s, 3H, SiCH_3), 0.05 (s, 3H, SiCH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 159.2 (s), 144.9 (s), 137.8 (o, $\text{C4}'$), 132.7 (s), 129.8 (o, C_m), 127.9 (o, C_o), 115.0 (t, $\text{C5}'$), 96.0 (o, C1), 79.6 (o, C3), 69.2 (o, C4), 68.8 (t, C6), 67.2 (two overlapping resonances; o, C5 ; t, $\text{C1}'$), 56.3 (o, C2), 30.1 (t, $\text{C3}'$), 28.3 (t, $\text{C2}'$), 25.7 (o, $\text{SiC}(\text{CH}_3)_3$), 21.6 (o, Ar- CH_3), 17.9 (s), -4.4 (o, SiCH_3), -5.4 (o, SiCH_3); HRMS (FAB) m/z calcd for $\text{C}_{25}\text{H}_{40}\text{NO}_8\text{SiS}$ ($\text{M}+\text{H}$) $^+$ 542.2244, found 542.2233.

Data for **7h- β** : $R_f = 0.35$ (50% EtOAc/hexanes); IR (thin film) 3299, 1766, 1640, 1598 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.79 (apparent d, $J = 8.3$ Hz, 2H), 7.35 (apparent d, $J = 8.0$ Hz, 2H), 5.80 (dddd, $J = 17.0, 10.3, 6.7, 6.7$ Hz, 1H), 5.11-4.94 (m, 2H), 5.06 (br s, 1H), 4.71 (d, $J = 2.3$ Hz, 1H), 4.52 (dd, $J = 8.1, 5.3$ Hz, 1H), 4.13 (AB of ABX, $J_{\text{AB}} = 10.5$ Hz, $J_{\text{AX}} = 6.0$ Hz, $J_{\text{BX}} = 4.7$ Hz, $\Delta\nu_{\text{AB}} = 32.7$ Hz, 2H), 3.95 (dd, $J = 8.2, 2.3$ Hz, 1H), 3.93 (dd, $J = 6.2, 5.4$ Hz, 1H), 3.84 (ddd, $J = 9.5, 6.5, 6.5$ Hz, 1H), 3.75 (apparent q, $J = 5.6$ Hz, 1H), 3.46 (ddd, $J = 9.5, 6.6, 6.6$ Hz, 1H), 2.45 (s, 3H), 2.10 (apparent q, $J = 7.2$ Hz, 2H), 1.66 (apparent quintet, $J = 7.0$ Hz, 2H), 0.85 (s, 9H), 0.14 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 158.0, 145.1, 137.8, 132.6, 129.9, 128.0, 115.1, 96.4, 78.4, 75.4, 69.0, 68.8, 67.2, 53.5, 30.1, 28.6, 25.6, 21.7, 17.8, -4.7, -5.2; HRMS (FAB) m/z calcd for $\text{C}_{25}\text{H}_{40}\text{NO}_8\text{SiS}$ ($\text{M}+\text{H}$) $^+$ 542.2244, found 542.2267.

Data for **8h**: $R_f = 0.61$ (50% EtOAc/hexanes); IR (thin film) 1698, 1601 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.82 (apparent d, $J = 8.3$ Hz, 2H), 7.37 (apparent d, $J = 8.1$ Hz, 2H), 7.21 (d, $J = 5.8$ Hz, 1H), 5.34 (d, $J = 5.8$ Hz, 1H), 4.47-4.24 (m, 4H), 2.47 (s, 3H), 0.84 (s, 9H), 0.20 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 192.4 (s), 161.5 (o), 145.2 (s), 132.5 (s), 129.9 (o), 128.1 (o), 105.1 (o), 80.1 (o), 69.5 (o), 67.6 (t), 25.8 (o), 21.7 (o), 18.4 (s), -4.0 (o), -5.6 (o); HRMS (FAB) m/z calcd for $\text{C}_{19}\text{H}_{29}\text{O}_6\text{SiS}$ ($\text{M}+\text{H}$) $^+$ 413.1454, found 413.1447.

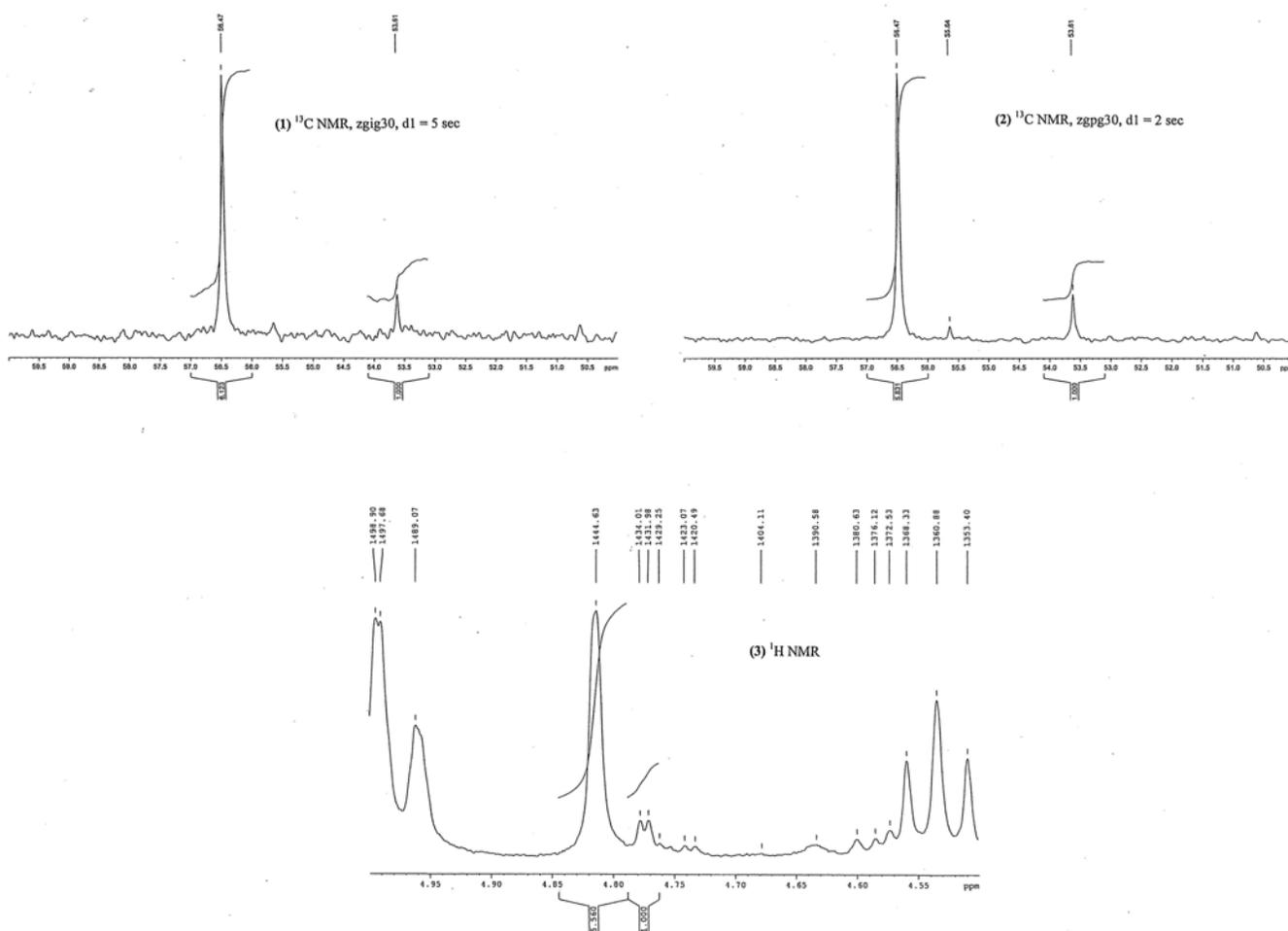


4-Pentenyl 2-amino-2-N-3-O-carbonyl-2-deoxy-4,6-di-O-tert-butyl dimethylsilyl-D-mannopyranosides (7i) and 1,2-Dideoxy-4,6-di-O-tert-butyl dimethylsilyl-D-erythro-hex-1-enopyran-3-ulose (8i)¹⁵. Amidoglycosylation with glucal carbamate **6i** (52.9 mg, 0.127 mmol) was

¹⁵ (a) Ganguly, D.; Tang, H.; Rodriguez, M. J. *Synth. Commun.* **2007**, *37*, 4219–4226. (b) Fujiwara, T.; Hayashi, M. *J. Org. Chem.* **2008**, *73*, 9161–9163.

carried out using the general procedure, as described for **6c**. The reaction was monitored carefully by TLC. Starting material clearly remained after 30 min, but by 90 min was nearly gone. It was difficult to detect complete conversion by TLC because the starting material and product had similar R_f , but using 20% EtOAc/hexanes as the eluent and eluting four times prior to staining was helpful. Reaction time was 4 h.

The anomeric composition of amidoglycosylation product **7i** was determined using ^1H and ^{13}C NMR. Two ^{13}C NMR determinations were made independently, one using an inverse-gated pulse sequence (zgif30) with a 5-sec d1 delay and the other with our standard proton-gated pulse sequence (zpgp30) with a 2-sec d1 delay. Integration of the C2 resonances for the **7i** anomers in the two ^{13}C NMR experiments (Figure S8, panels 1 and 2) and integration of the H1 resonances for the anomers in the ^1H NMR experiment (Figure S8, panel 3) gave results consistent to within $\pm 6\%$ of the average value.



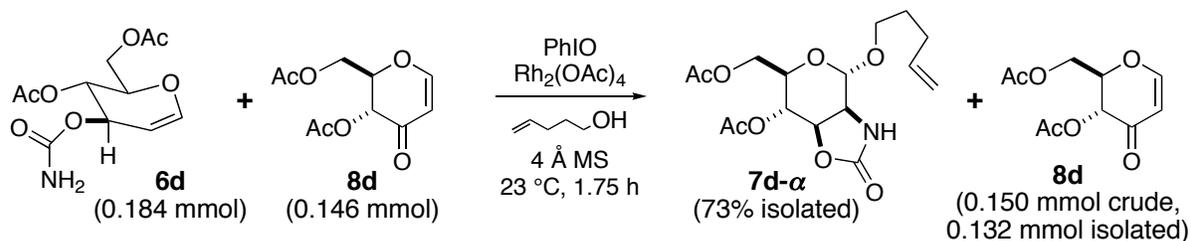
of the manuscript. These results support our general method of using the shorter zgpg30 experiment with 2 sec d1 delay for ^{13}C NMR determination of the anomeric ratios of our amidoglycosylation products.

The ratio **7i:8i** (2.4:1), meanwhile, was determined from integration of the ^1H NMR signals in the crude product.

The crude material was chromatographed (10→20%→30%→40% EtOAc/hexanes, 35 mL SiO_2), providing **7i** (34.2 mg, 54%, inseparable 6:1 $\alpha:\beta$ mixture of anomers) as an oil and dihydropyranone **8i** (9.8 mg, 21%) as a white solid. Data for **7i**: $R_f = 0.33$ (30% EtOAc/hexanes); IR (thin film) 3300, 1769, 1642 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) signals for major (α) anomer δ 6.23 (br s, 1H), 5.80 (dddd, $J = 17.0, 10.3, 6.7, 6.7$ Hz, 1H), 5.07-4.93 (m, 2H), 4.83 (s, 1H), 4.52 (dd, $J = 7.4, 7.4$ Hz, 1H), 4.00 (d, $J = 7.9$ Hz, 1H), 3.89 (dd, $J = 11.1, 1.7$ Hz, 1H), 3.82-3.68 (m, 3H), 3.56 (ddd, $J = 9.9, 5.5, 1.8$ Hz, 1H), 3.36 (ddd, $J = 9.6, 6.6, 6.6$ Hz, 1H), 2.11 (apparent q, $J = 7.2$ Hz, 2H), 1.67 (apparent quintet, $J = 7.1$ Hz, 2H), 0.90 (two overlapping s, 18H), 0.17 (s, 3H), 0.11 (s, 3H), 0.07 (two overlapping s, 6H); distinguishable ^1H NMR signals for minor (β) anomer δ 5.48 (br s), 4.78 (d, $J = 2.1$ Hz), 4.57 (dd, $J = 8.2, 4.8$ Hz), 4.05 (dd, $J = 4.7, 4.7$ Hz), 3.94 (dd, $J = 8.2, 2.2$ Hz), 3.62 (m), 3.49 (ddd, $J = 9.5, 6.6, 6.6$ Hz), 0.14 (s), 0.12 (s), 0.08 (s); the $\alpha:\beta$ ratio of this purified sample was 6.1:1 by integration of the H1 resonances for the α (δ 4.83) and β (δ 4.78) anomers; ^{13}C NMR (75 MHz, CDCl_3) signals for major (α) anomer δ 159.4 (s), 137.87 (o), 115.0 (t), 96.2 (o), 80.3 (o), 70.3 (o), 69.1 (o), 66.8 (t), 62.5 (t), 56.5 (o), 30.2 (t), 28.4 (t), 25.9 (o), 25.8 (o), 18.4 (s), 18.0 (s), -4.5 (o), -5.23 (o), -5.24 (o), -5.41 (o); distinguishable ^{13}C NMR signals for the minor (β) anomer δ 158.8 (s), 137.92 (o), 96.3 (o), 79.4 (o), 78.4 (o), 68.7 (t), 66.4 (o), 62.9 (t), 53.6 (o), 30.1 (t), 28.6 (t), 25.7 (o), 17.8 (s), -4.8 (o), -5.0 (o), -5.3 (o), -5.39 (o); HRMS (FAB) m/z calcd for $\text{C}_{24}\text{H}_{48}\text{NO}_6\text{Si}_2$ ($\text{M}+\text{H}$) $^+$ 502.3020, found 502.3016.

Data for **8i**: mp 63.5-65.5 $^\circ\text{C}$; $R_f = 0.62$ (30% EtOAc/hexanes); IR (thin film) 1682, 1595 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.29 (d, $J = 5.8$ Hz, 1H), 5.31 (d, $J = 5.8$ Hz, 1H), 4.43 (d, $J = 12.2$ Hz, 1H), 4.18 (ddd, $J = 12.2, 2.6, 2.6$ Hz, 1H), 3.99 (apparent d, $J = 2.7$ Hz, 2H), 0.914 (s, 9H), 0.908 (s, 9H), 0.23 (s, 3H), 0.09 (three overlapping s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 194.1 (s), 162.1 (o), 104.5 (o), 83.6 (o), 69.4 (o), 61.5 (t), 25.9 (o, two overlapping resonances), 18.5 (s), 18.4 (s), -4.0 (o), -5.2 (o), -5.3 (o), -5.7 (o); HRMS (FAB) m/z calcd for $\text{C}_{18}\text{H}_{37}\text{O}_4\text{Si}_2$ ($\text{M}+\text{H}$) $^+$ 373.2230, found 373.2211.

Part 5. Control experiment to check dihydropyranone stability under the reaction conditions



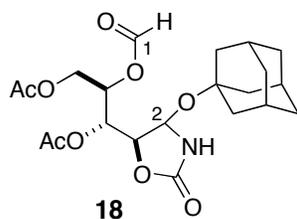
The stability of dihydropyranone **8d** under the amidoglycosylation reaction conditions was assessed in the following control experiment. Dihydropyranone **8d** (33.3 mg, 0.146 mmol), prepared

independently according to a literature procedure,^{12b} was included in the reaction mixture with glucal 3-carbamate **6d** (50.2 mg, 0.184 mmol), Rh₂(OAc)₄ (8.4 mg, 0.0190 mmol), PhIO (73.2 mg, 0.333 mmol), 4-penten-1-ol (93 μ L, 0.91 mmol), and activated 4Å molecular sieves (153 mg) in CH₂Cl₂ (2.0 mL). After 1 h 45 min all starting **6d** had reacted, and the reaction mixture was filtered and concentrated as usual. The crude product was analyzed by ¹H NMR, using mesitylene as an internal standard, showing 0.150 mmol of dihydropyranone **8d** in the crude product. A separate ¹H NMR calibration experiment was done using weighed amounts of dihydropyranone **8d** and mesitylene, confirming the reliability of the ¹H NMR integration procedure for gauging the amount of **8d**. The crude was chromatographed (50% (100 mL)→60% (100 mL)→70% (100 mL)→80% (50 mL) EtOAc/hexanes, 40 mL SiO₂ (16 cm x 2 cm), 5 mL fractions), providing amidoglycosylation product **7d- α** (47.2 mg, 72%) and dihydropyranone **8d** (30.2 mg, 0.132 mmol). The control experiment indicated the stability of **8d** under the reaction conditions.

Part 6. Experimentals and characterization data for glycosylation of other acceptors using **6d** and **6e**



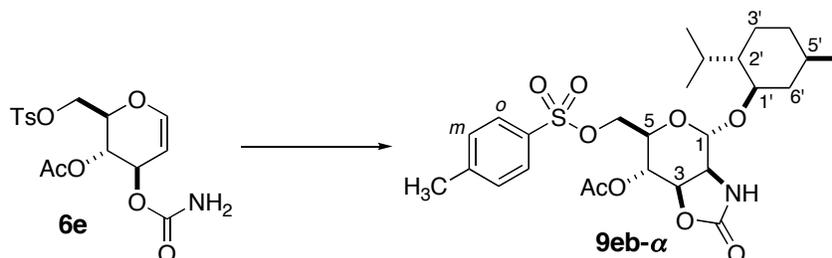
1-Adamantyl 2-amino-2-N,3-O-carbonyl-2-deoxy-4,6-di-O-acetyl-D-mannopyranosides (9da). The standard amidoglycosylation conditions described for **6c**, but using either 5.0 equiv or 2.0 equiv 1-adamantanol as the glycosyl acceptor and in one case 3.0 equiv of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) as an additive (Table 2, entries 1–4 in the manuscript), gave **9da- α** as the major product, with small amounts of the C1 diastereomer **9da- β** . Reaction times varied, depending on the initial carbamate concentration and the addition of HFIP. Times for consumption of **6d** (TLC analysis) for the reactions shown in Table 2 of the manuscript were as follows: entry 1, 2.5 h; entry 2, 5.5 h; entry 3, <1 h; entry 4, <2.5 h. The anomeric selectivities were determined from ¹H NMR (CDCl₃) analysis of the crude product by integration of the α anomer H3 resonance at δ 4.71 and the β anomer H1 signal at δ 4.96. The anomers were separated by chromatography on silica gel and characterized independently (chromatography conditions on a 0.180 mmol scale: 50% (100 mL)→60% (100 mL)→70% (100 mL)→80% (50 mL) EtOAc/Hexanes, 40 mL SiO₂ (16 cm x 2 cm), 5 mL fractions).



Limited amounts of a formate ester byproduct **18** were formed by oxidative cleavage of the C1–C2 bond. We noted this type of oxidative cleavage process in a previous study with allal 3-carbamates.² We were unable to separate the formate ester from the main product **9da- α** , so the reported yields in Table 2 are corrected for the presence of **9da- α :18** mixtures in the isolated products. Extent of C1–C2 oxidative cleavage in the reactions shown in Table 2 was as follows: entry 1, **9da- α :18** = 14:1; entry 2, **9da- α :18** = 8.6:1; entry 3, **9da- α :18** = 19:1; entry 4, **9da- α :18** = 7.4:1. Formate ester **18** had the formyl hydrogen resonance in the ¹H NMR at δ 8.08 (CDCl₃).

Data for **9da- α** : R_f = 0.43 (70% EtOAc/hexanes); IR (thin film) 3351, 1771, 1748 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.54 (br s, 1H, NH), 5.33 (s, 1H, H1), 5.17 (dd, J = 9.6, 7.3 Hz, 1H, H4), 4.72 (dd, J = 7.4, 7.4 Hz, 1H, H3), 4.24 (m, 1H, H6a), 4.18-4.04 (m, 2H, H5 and H6b), 3.97 (d, J = 7.7 Hz, 1H, H2), 2.17 (m, 3H, H3'), 2.11 (s, 3H, C(O)CH₃), 2.09 (s, 3H, C(O)CH₃), 1.87-1.72 (m, 6H, H2' or H4'), 1.72-1.53 (m, 6H, H2' or H4'); ¹³C NMR (75 MHz, CDCl₃) δ 170.8 (s), 169.4 (s), 159.0 (s), 89.8 (o, C1), 76.4 (o, C3), 75.8 (s), 68.4 (o, C4), 65.5 (o, C5), 62.5 (t, C6), 57.4 (o, C2), 42.2 (t, C2' or C4'), 36.0 (t, C2' or C4'), 30.5 (o, C3'), 20.7 (two overlapping resonances, o, C(O)CH₃); HRMS (FAB) m/z calcd for C₂₁H₃₀NO₈ (M+H)⁺ 424.1971, found 424.1963.

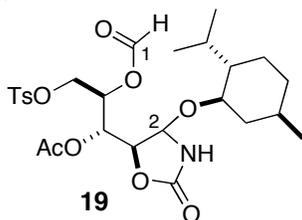
Data for **9da- β** : R_f = 0.24 (70% EtOAc/hexanes); IR (thin film) 3354, 1759 (shoulder), 1747 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.26 (br s, 1H), 5.13 (dd, J = 5.2, 5.2 Hz, 1H), 4.96 (d, J = 2.3 Hz, 1H), 4.73 (dd, J = 8.2, 4.8 Hz, 1H), 4.23 (AB of ABX, J_{AB} = 11.7 Hz, J_{AX} = 6.9 Hz, J_{BX} = 4.4 Hz, $\Delta\nu_{AB}$ = 37.6 Hz, 2H), 3.90 (dd, J = 8.2, 2.3 Hz, 1H), 3.85 (m, 1H), 2.17 (m, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 1.88-1.71 (m, 6H), 1.71-1.55 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 169.2, 157.8, 90.1, 76.0, 75.4, 73.8, 67.3, 63.4, 54.2, 42.4, 36.1, 30.6, 20.9, 20.8; HRMS (FAB) m/z calcd for C₂₁H₃₀NO₈ (M+H)⁺ 424.1971, found 424.1946.



(-)-Menthyl 4-*O*-acetyl-2-amino-2-*N*,3-*O*-carbonyl-2-deoxy-6-*O*-*p*-toluenesulfonyl-

D-mannopyranosides (9eb). The standard amidoglycosylation procedure as described for **6c**, but with 5.0 equiv or 2.1 equiv menthol as the acceptor (Table 2, entries 5–6 of the manuscript), gave **9eb- α** as the major product, with small amounts of the C1 diastereomer **9eb- β** . Time to consumption of **6e** (TLC

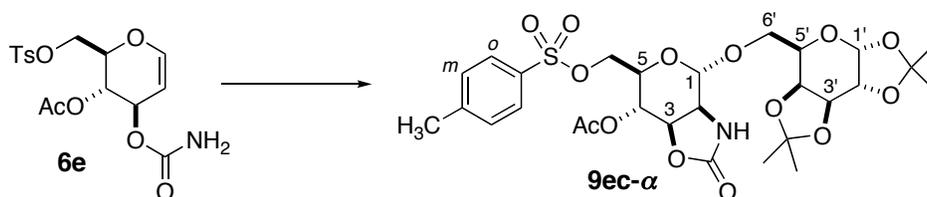
analysis) was 3.5 h for the experiment described in entry 5 and 4.3 h for entry 6. The anomeric selectivities were determined from ^1H NMR (CDCl_3) analysis of the crude product by integration of the α anomer H3 resonance at δ 4.66 and the β anomer H1 signal at δ 4.79. The anomers were separated by chromatography and characterized independently (chromatography conditions on a 0.178 mmol scale: 40% (100 mL) \rightarrow 45% (50 mL) \rightarrow 50% (100 mL) \rightarrow 60% (100 mL) \rightarrow 70% (100 mL) EtOAc/Hexanes, 40 mL SiO_2 (16 cm x 2 cm), 5 mL fractions).



A byproduct **19** from C1–C2 oxidative cleavage also formed and was inseparable from **9eb- α** . The reported yields (Table 2, entries 5–6) are corrected for the presence of this byproduct: entry 5, **9eb- α** :**19** = 21:1; entry 6, **9eb- α** :**19** = 8.1:1. Formate ester **19** had the formyl hydrogen resonance in the ^1H NMR at δ 7.95 (CDCl_3).

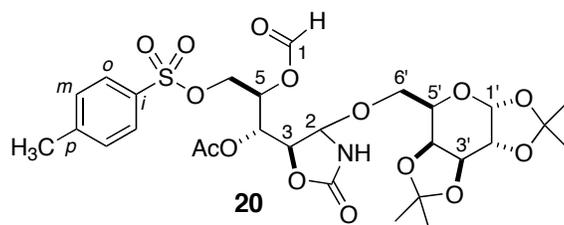
Data for **9eb- α** : R_f = 0.45 (60% EtOAc/hexanes); IR (thin film) 3359, 1771, 1598 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.77 (apparent d, J = 8.3 Hz, 2H, H_o), 7.35 (apparent d, J = 8.1 Hz, 2H, H_m), 6.37 (br s, 1H, NH), 4.97 (dd, J = 9.8, 7.3 Hz, 1H, H_4), 4.90 (s, 1H, H_1), 4.66 (dd, J = 7.4, 7.4 Hz, 1H, H_3), 4.13 (m, 1H, H_5), 4.10–3.98 (m, 3H, H_2 and H_6), 3.34 (ddd, J = 10.6, 10.6, 4.3 Hz, 1H, H_1'), 2.45 (s, 3H, Ar- CH_3), 2.12 (m, 1H, $\text{H}_6'a$), 2.06 (s, 3H, $\text{C}(\text{O})\text{CH}_3$), 1.96 (septet of d, J = 6.9, 2.3 Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 1.62 (m, 2H, $\text{H}_3'a$ and $\text{H}_4'a$), 1.35 (m, 1H, H_5'), 1.19 (m, 1H, H_2'), 1.05–0.77 (m, 3H, $\text{H}_3'b$, $\text{H}_4'b$, and $\text{H}_6'b$), 0.90 (d, J = 6.3 Hz, 3H, $\text{C}_5'\text{CH}_3$), 0.89 (d, J = 6.9 Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.73 (d, J = 7.0 Hz, 3H, $\text{CH}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 169.5 (s), 158.5 (s), 145.0 (s), 132.3 (s), 129.8 (o, C_m), 128.0 (o, C_o), 97.7 (o, C1), 82.1 (o, C_1'), 75.8 (o, C3), 68.6 (o, C4), 68.3 (t, C6), 65.6 (o, C5), 56.3 (o, C2), 48.5 (o, C_2'), 42.4 (t, C_6'), 34.0 (t, C_3' or C_4'), 31.5 (o, C_5'), 25.7 (o, $\text{CH}(\text{CH}_3)_2$), 29.2 (t, C_3' or C_4'), 22.0 (o, $\text{C}_5'\text{CH}_3$), 21.6 (o, Ar- CH_3), 21.0 (o, $\text{CH}(\text{CH}_3)_2$), 20.6 (o, $\text{C}(\text{O})\text{CH}_3$), 16.0 (o, $\text{CH}(\text{CH}_3)_2$); HRMS (FAB) m/z calcd for $\text{C}_{26}\text{H}_{38}\text{NO}_9\text{S}$ ($\text{M}+\text{H}$) $^+$ 540.2267, found 540.2283.

Data for **9eb- β** : R_f = 0.33 (60% EtOAc/hexanes); IR (thin film) 3370, 1768, 1598 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.77 (apparent d, J = 8.4 Hz, 2H), 7.35 (apparent d, J = 8.0 Hz, 2H), 5.16 (br s, 1H), 4.95 (dd, J = 5.3, 5.3 Hz, 1H), 4.79 (d, J = 2.2 Hz, 1H), 4.70 (dd, J = 8.1, 4.9 Hz, 1H), 4.17–4.00 (m, 2H), 3.98–3.89 (m, 2H), 3.53 (ddd, J = 10.7, 10.7, 4.3 Hz, 1H), 2.46 (s, 3H), 2.12 (s, 3H), 2.07 (m, 1H), 1.96 (m, 1H), 1.66 (m, 2H), 1.38 (m, 1H), 1.21 (m, 1H), 0.98–0.72 (m, 3H), 0.94 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 7.1 Hz, 3H), 0.69 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 169.3 (s), 157.5 (s), 145.2 (s), 132.3 (s), 130.0 (o), 128.0 (o), 93.1 (o), 76.9 (o, resonance obscured by solvent signal but detected in DEPT 135 experiment), 75.1 (o), 74.0 (o), 68.8 (t), 67.2 (o), 53.7 (o), 47.8 (o), 40.2 (t), 34.2 (t), 31.3 (o), 25.4 (o), 23.0 (t), 22.2 (o), 21.7 (o), 20.9 (o), 20.8 (o), 15.7 (o); HRMS (FAB) m/z calcd for $\text{C}_{26}\text{H}_{38}\text{NO}_9\text{S}$ ($\text{M}+\text{H}$) $^+$ 540.2267, found 540.2244.



6-O-(4-O-Acetyl-2-amino-2-N,3-O-carbonyl-2-deoxy-6-O-*p*-toluenesulfonyl- α -D-mannopyranosyl)-1,2:3,4-di-O-isopropylidene- α -D-galactopyranoside (9ec- α**). Using the standard amidoglycosylation procedure as described for **6c**, but with 2.0 equiv of the acceptor and in one case 1.0 equiv of HFIP as an additive (see Table 2, entries 7–8 of the manuscript), gave **9ec- α** . For the reaction in entry 7, starting carbamate **6e** remained (15% vs mesitylene as an internal standard) even after 21 h reaction time. For entry 8, where the HFIP was included, TLC showed most **6e** was consumed after 6 h, although stirring was continued for a total of 21 h. Analysis of the crude reaction mixture from entry 8 by ^1H NMR revealed only about 5% remaining **6e** vs the mesitylene internal standard. We were unable to identify the β anomer in the crude ^1H NMR spectrum or isolate it from chromatography on silica gel. Chromatography conditions on a 0.207 mmol scale: 60% (150 mL) \rightarrow 65% (60 mL) \rightarrow 70% (60 mL) \rightarrow 75% (50 mL) \rightarrow 80% (50 mL) EtOAc/Hexanes, 40 mL SiO₂ (17 cm x 2 cm), 5 mL fractions.**

Data for **9ec- α** : R_f = 0.18 (70% EtOAc/hexanes); IR (thin film) 3365, 1771, 1598 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 7.79 (apparent d, J = 8.3 Hz, 2H, H_{*o*}), 7.35 (apparent d, J = 8.1 Hz, 2H, H_{*m*}), 6.40 (br s, 1H, NH), 5.52 (d, J = 5.0 Hz, 1H, H1'), 5.02 (dd, J = 9.3, 7.3 Hz, 1H, H4), 4.89 (s, 1H, H1), 4.68 (dd, J = 7.5, 7.5 Hz, 1H, H3), 4.62 (dd, J = 7.9, 2.4 Hz, 1H, H3'), 4.33 (dd, J = 5.0, 2.4 Hz, 1H, H2'), 4.19 (dd, J = 7.9, 1.8 Hz, 1H, H4'), 4.15–3.99 (m, 4H, H2, H5, and H6), 3.96 (ddd, J = 7.0, 4.8, 1.4 Hz, 1H, H5'), 3.78 (dd, J = 10.7, 7.6 Hz, 1H, H6'a), 3.61 (dd, J = 10.8, 4.9 Hz, 1H, H6'b), 2.45 (s, 3H, Ar-CH₃), 2.06 (s, 3H, C(O)CH₃), 1.52 (s, 3H, acetonide CH₃), 1.45 (s, 3H, acetonide CH₃), 1.34 (two overlapping s, 6H, acetonide CH₃); ^{13}C NMR (75 MHz, CDCl₃) δ 169.4 (s), 158.4 (s), 145.0 (s), 132.3 (s), 129.8 (o, C_{*m*}), 128.0 (o, C_{*o*}), 109.5, (s), 108.7 (s), 96.2 (o, C1'), 95.9 (o, C1), 75.8 (o, C3), 70.9 (o, C4'), 70.6 (o, C3'), 70.3 (o, C2'), 68.1 (o, C4), 67.9 (t, C6), 66.5 (t, C6'), 65.7 (o, C5'), 65.6 (o, C5), 55.7 (o, C2), 25.93 (o, acetonide CH₃), 25.90 (o, acetonide CH₃), 24.8 (o, acetonide CH₃), 24.5 (o, acetonide CH₃), 21.6 (o, Ar-CH₃), 20.6 (o, C(O)CH₃), the signals at δ 25.93 and 25.90 were best resolved by processing with line broadening = 0; HRMS (FAB) m/z calcd for C₂₈H₃₈NO₁₄S (M+H)⁺ 644.2013, found 644.2027.



In the experiment given in Table 2, entry 8 of the manuscript, in addition to the product **9ec- α** (44%), we were able to isolate the C1–C2 oxidative cleavage byproduct **20** (8%) separately as one diastereomer (stereochemistry at C2 not determined). Data for **20**: R_f = 0.32 (70% EtOAc/hexanes); IR (thin film) 3335, 1772, 1759, 1733, 1598 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 7.96 (s, 1H, H1), 7.78

(apparent d, $J = 8.3$ Hz, 2H, H_o), 7.37 (apparent d, $J = 8.1$ Hz, 2H, H_m), 6.14 (s, 1H, NH), 5.59 (d, $J = 5.1$ Hz, 1H, $H1'$), 5.49 (m, 1H, $H4$), 5.44 (m, 1H, $H5$), 4.97 (s, 1H, $H2$), 4.65 (slightly broadened s, 1H, $H3$), 4.61 (dd, $J = 7.9, 2.5$ Hz, 1H, $H3'$), 4.38 (dd, $J = 11.8, 2.3$ Hz, 1H, $H6a$), 4.34 (dd, $J = 5.1, 2.4$ Hz, 1H, $H2'$), 4.20 (m, 1H, $H6b$), 4.18 (m, 1H, $H4'$), 3.87 (m, 1H, $H5'$), 3.80-3.70 (m, 2H, $H6'$), 2.46 (s, 3H, $ArCH_3$), 2.06 (s, 3H, $C(O)CH_3$), 1.53 (s, 3H, acetonide CH_3), 1.45 (s, 3H, acetonide CH_3), 1.34 (two overlapping s, 6H, acetonide CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 (s, $C(O)CH_3$), 159.1 (o, $C1$), 157.2 (s, $OC(O)N$), 145.3 (s, C_p), 132.3 (s, C_i), 130.0 (o, C_m), 128.0 (o, C_o), 109.7 (s, $OC(CH_3)_2O$), 108.9 (s, $OC(CH_3)_2O$), 96.4 (o, $C1'$), 86.2 (o, $C2$), 80.9 ($C3$), 70.8 (o, $C4'$), 70.6 (o, $C3'$), 70.2 (o, $C2'$), 68.9 (o, $C5$), 68.8 (o, $C4$), 68.5 (t, $C6'$), 67.1 (o, $C5'$), 66.4 (t, $C6$), 25.9 (o, acetonide CH_3), 25.8 (o, acetonide CH_3), 24.7 (o, acetonide CH_3), 24.4 (o, acetonide CH_3), 21.7 (o, $ArCH_3$), 20.4 ($C(O)CH_3$); HRMS (FAB) m/z calcd for $C_{28}H_{38}NO_{15}S$ ($M+H$) $^+$ 660.1962, found 660.1980.

III-CMR-203
Chromatographed product

Current Data Parameters
NAME III-CMR-203
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050812
Time 10.21

INSTRUM spect
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PULPROG zg30

TD 65536
SOLVENT CDCl3
NS 32

DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz

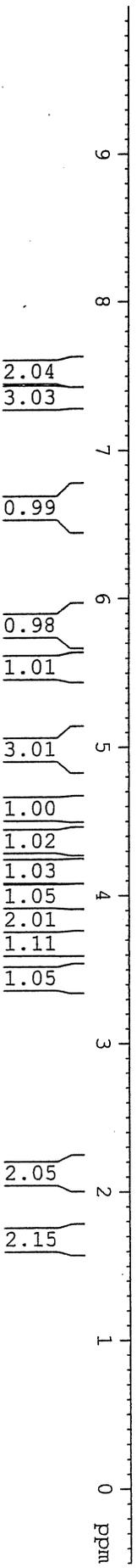
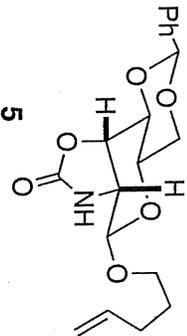
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RG 181
DW 81.000 usec
DE 6.00 usec

TE 294.3 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 6.80 usec
PL1 3.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300067 MHz

WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
 NAME III-CMR-203
 EXPNO 4
 PROCNO 1

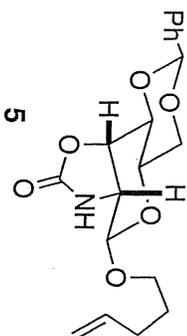
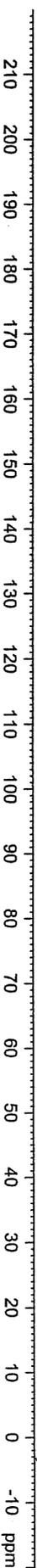
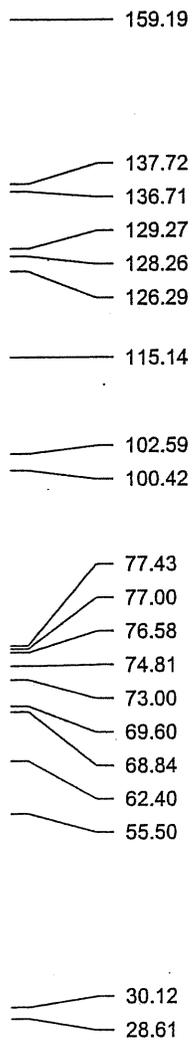
III-CMR-203
 Chromatographed product

F2 - Acquisition Parameters
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 Time 11.09
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 TD 65536
 SOLVENT CDCl3
 NS 750
 DS 4
 SWH 18518.518 Hz
 FIDRES 0.282570 Hz
 AQC 1.7695220 sec
 RG 1625.5
 DW 27.000 usec
 DE 6.00 usec
 TE 295.1 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 5.50 usec
 PL1 2.00 dB
 SFO1 75.4752653 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 3.00 dB
 PL12 24.41 dB
 PL13 24.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677551 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



5
 63

IV-CMR-23

Current Data Parameters
 NAME IV-CMR-23
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080108
 Time 15.07

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30

TD 65536
 SOLVENT DMSO
 NS 16

DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz

AQ 5.3084660 sec
 RG 161.3

DW 81.000 usec
 DE 6.00 usec

TE 294.2 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====

P1 6.65 usec
 NUC1 1H

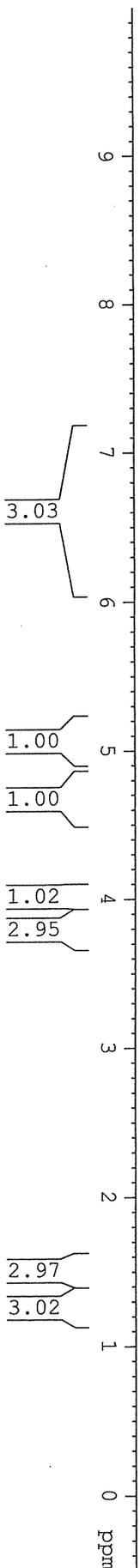
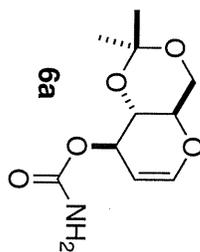
PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300007 MHz

WDW EM
 SSB 0

LB 0.30 Hz
 GB 0

PC 1.00



Current Data Parameters
NAME IV-CMR-23
EXPNO 2
PROCNO 1

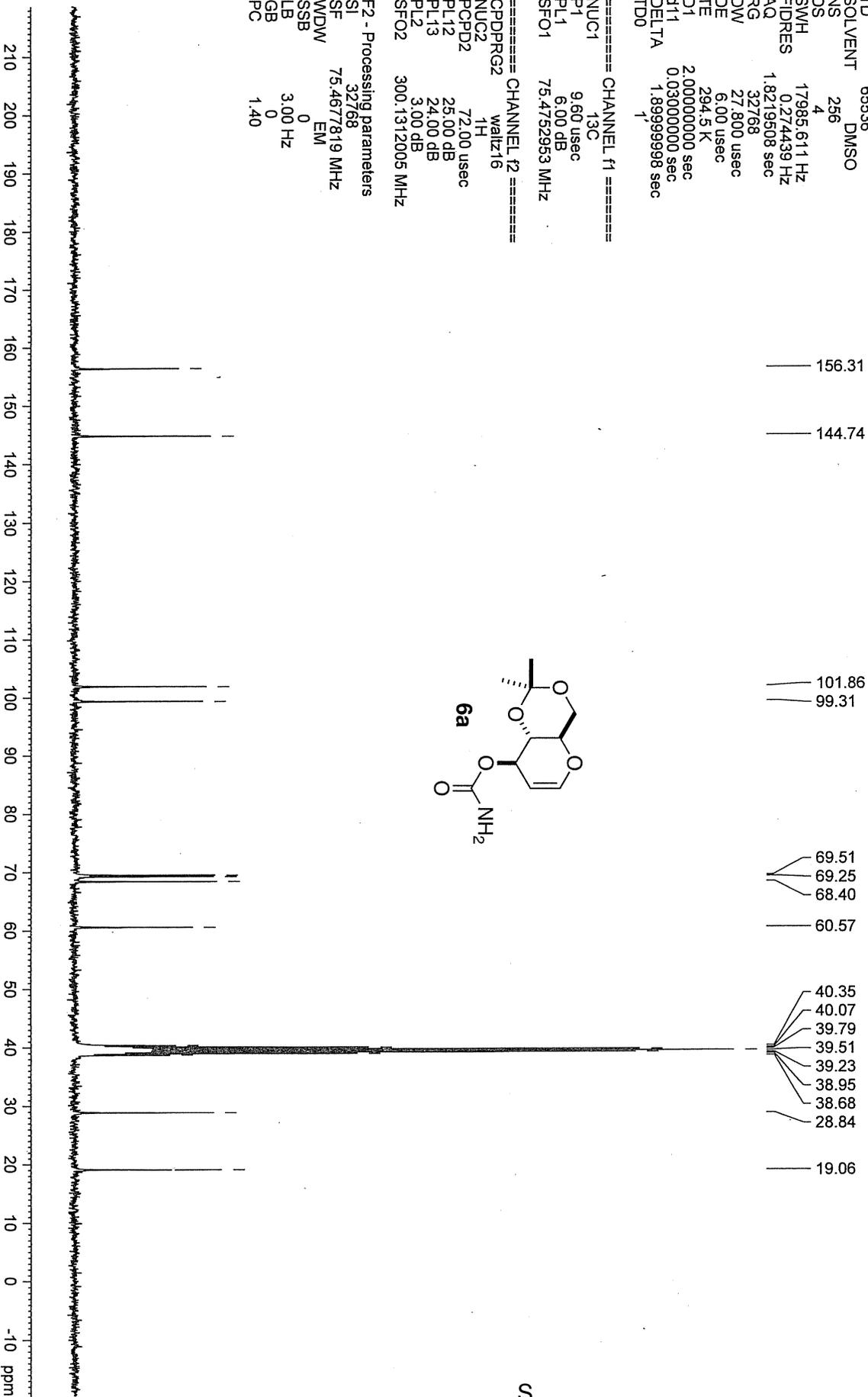
IV-CMR-23
13C NMR

F2 - Acquisition Parameters
Date_ 20080108
Time 15:20
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PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 256
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 294.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

==== CHANNEL f1 =====
NUC1 13C
P1 9.60 usec
PL1 6.00 dB
SFO1 75.4752953 MHz

==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 72.00 usec
PL12 25.00 dB
PL13 24.00 dB
PL2 3.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677819 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40



Current Data Parameters
 NAME I-AS-3
 EXPNO 1
 PROCNO 1

I-AS-3
 Di-t-butyl silylene-protected carbamate
 By CNMR on 12/21/2007

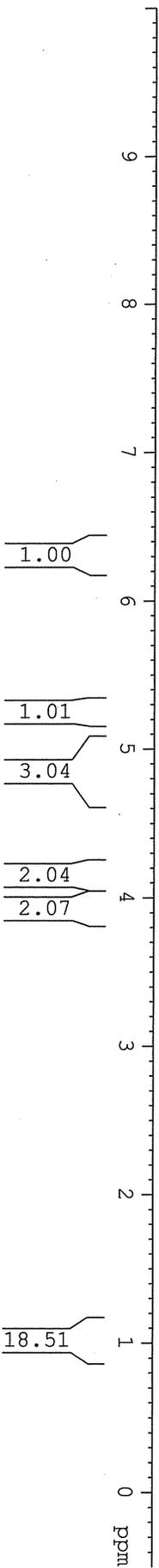
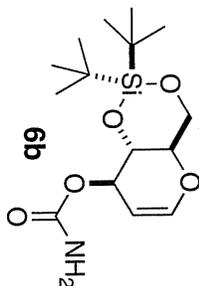
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 Date_ 20071221
 Time 15.52

INSTRUM spect
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 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2

SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 128
 DW 81.000 usec
 DE 6.00 usec
 TE 293.8 K
 D1 1.00000000 sec
 TDD 1

===== CHANNEL f1 =====
 P1 6.65 usec
 NUC1 1H
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300027 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
NAME I-AS-3
EXPNO 2
PROCNO 1

I-AS-3
Di-*t*-butyl silylene-protected carbamate
By CMR on 12/21/2007

F2 - Acquisition Parameters
Date_ 20071221
Time 16:14

INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30

TD 65536
SOLVENT CDCl3

DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz

AQ 1.8219508 sec
RG 32768

DW 27.800 usec
DE 6.00 usec

TE 294.0 K
D1 2.00000000 sec

d11 0.03000000 sec
DELTA 1.89999998 sec

TD0 1

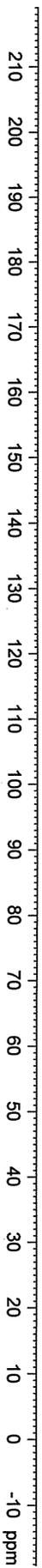
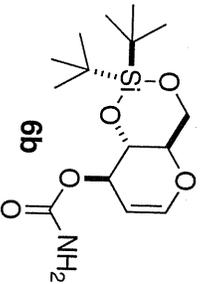
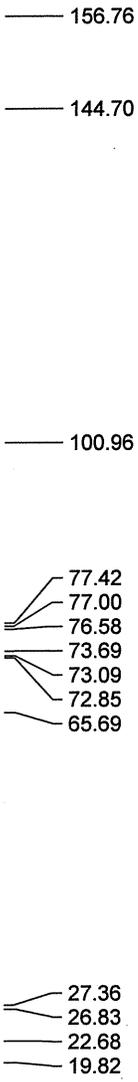
===== CHANNEL f1 =====
NUC1 13C

P1 9.60 usec
PL1 6.00 dB
SFO1 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16

NUC2 1H
PCPD2 72.00 usec
PL12 25.00 dB
PL13 24.00 dB
PL2 3.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677514 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40



Current Data Parameters

NAME III-CMR-229
 EXPNO 1
 PROCNO 1

III-CMR-229

F2 - Acquisition Parameters

Date 20060804
 Time 15:33
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 32
 DS 2

SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec

DW 81.000 usec
 DE 6.00 usec
 TE 294.5 K

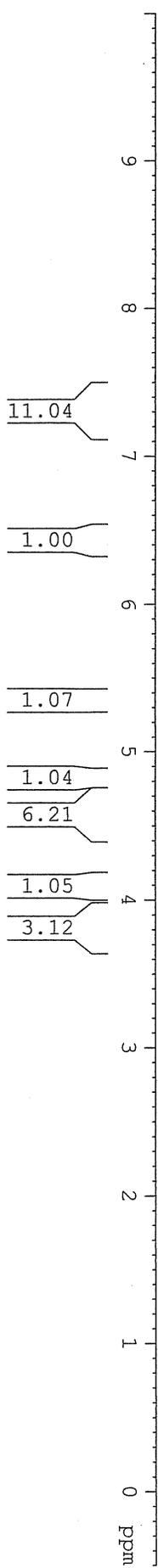
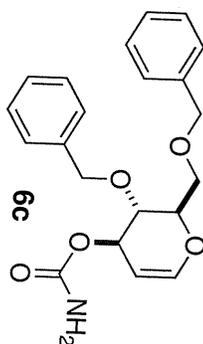
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==== CHANNEL f1 =====

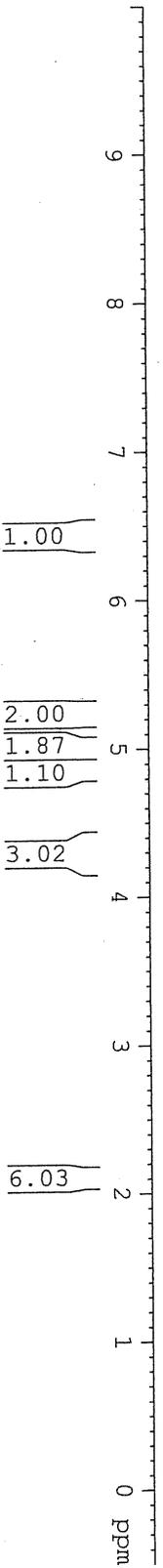
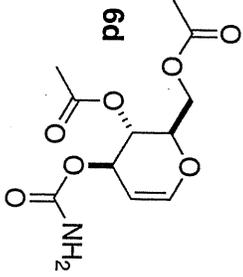
NUC1 1H
 P1 6.80 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters

SI 32768
 SF 300.1300065 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



II-RG-77
 di-acylated carbamate (-NH2)
 1H NMR



Current Data Parameters
 NAME II-RG-77
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date 20061128
 Time 10.10

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30

TD 65536
 SOLVENT CDCl3
 NS 16

DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz

AQ 5.3084660 sec
 RG 114
 DW 81.000 usec
 DE 6.00 usec
 TE 295.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 6.80 usec
 PL1 3.00 dB

SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1299965 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

II-RG-77
 di-acylated carbamate (-NH2)
 13 C NMR

Current Data Parameters
 NAME II-RG-77
 EXPNO 2
 PROCNO 1

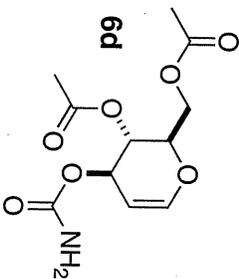
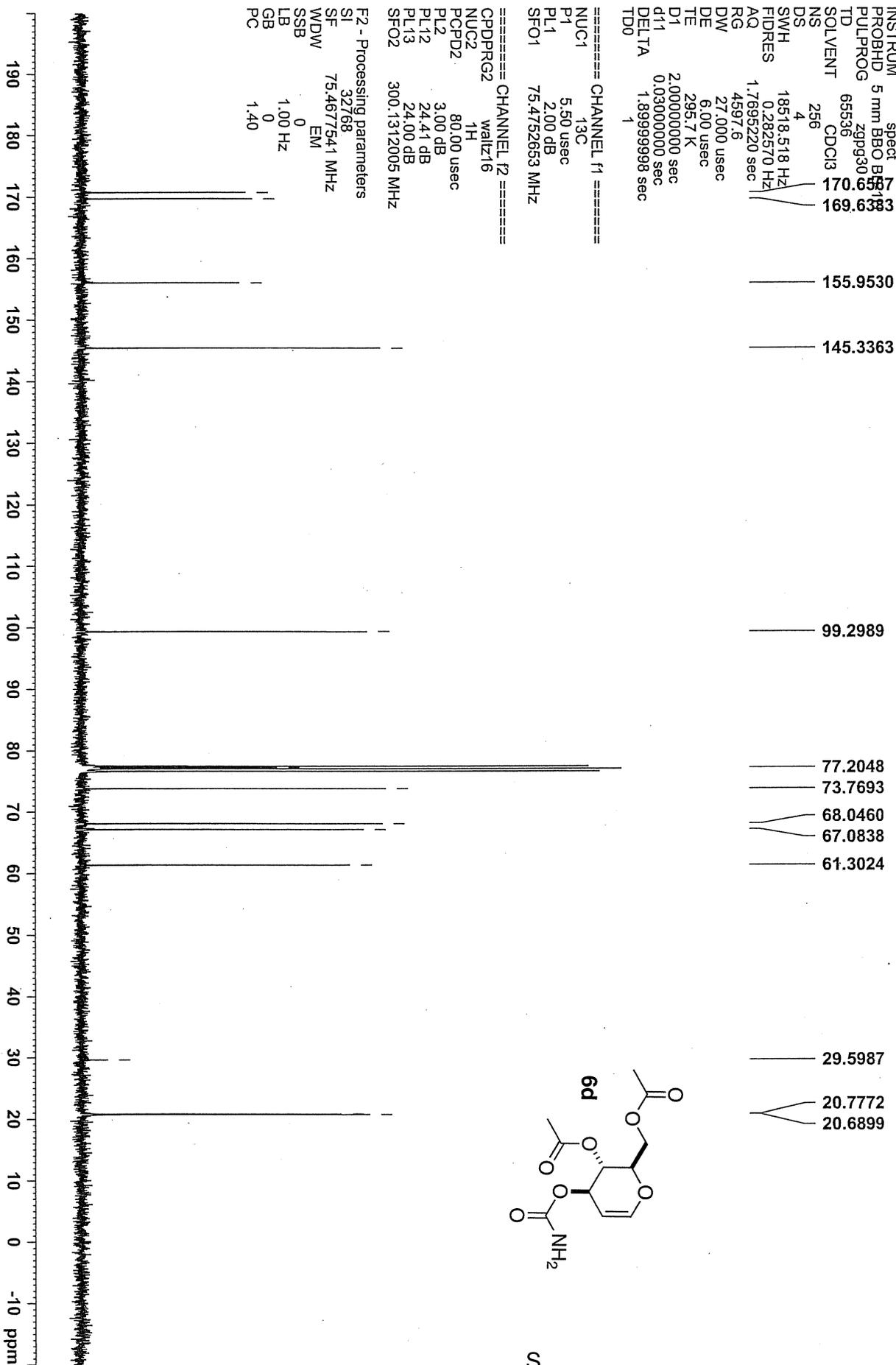
F2 - Acquisition Parameters
 Date_ 20061128
 Time 10.45

INSTRUM spect
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 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 256
 DS 4
 SWH 18518.518 Hz
 FIDRES 0.282570 Hz
 AQC 1.7695220 sec
 RG 4597.6
 DW 27.000 usec
 DE 6.00 usec
 TE 295.7 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 5.50 usec
 PL1 2.00 dB
 SFO1 75.4752653 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 3.00 dB
 PL12 24.41 dB
 PL13 24.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677541 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



Current Data Parameters
 NAME II-RG-87
 EXPNO 1
 PROCNO 1

II-RG-87
 C6D6

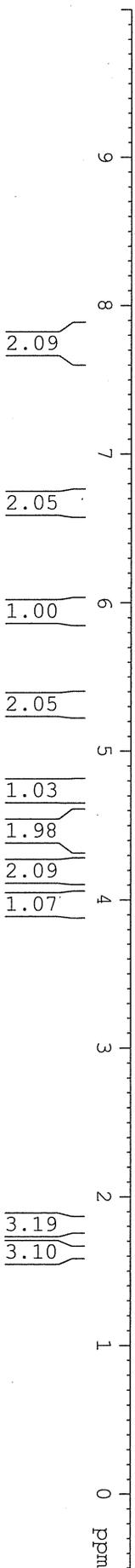
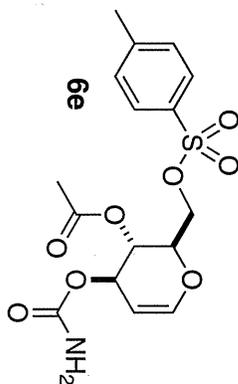
F2 - Acquisition Parameters
 Date_ 20070302
 Time 17.09

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT C6D6
 NS 16
 DS 2

SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 228.1
 DW 81.000 usec
 DE 6.00 usec
 TE 295.2 K
 D1 1.0000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 6.80 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing Parameters
 SI 32768
 SF 300.1300323 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME IL-RG-87
 EXPNO 2
 PROCNO 1

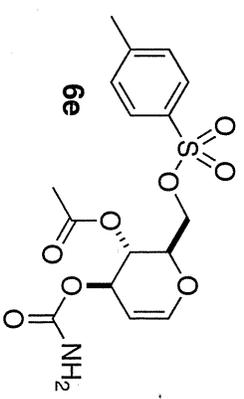
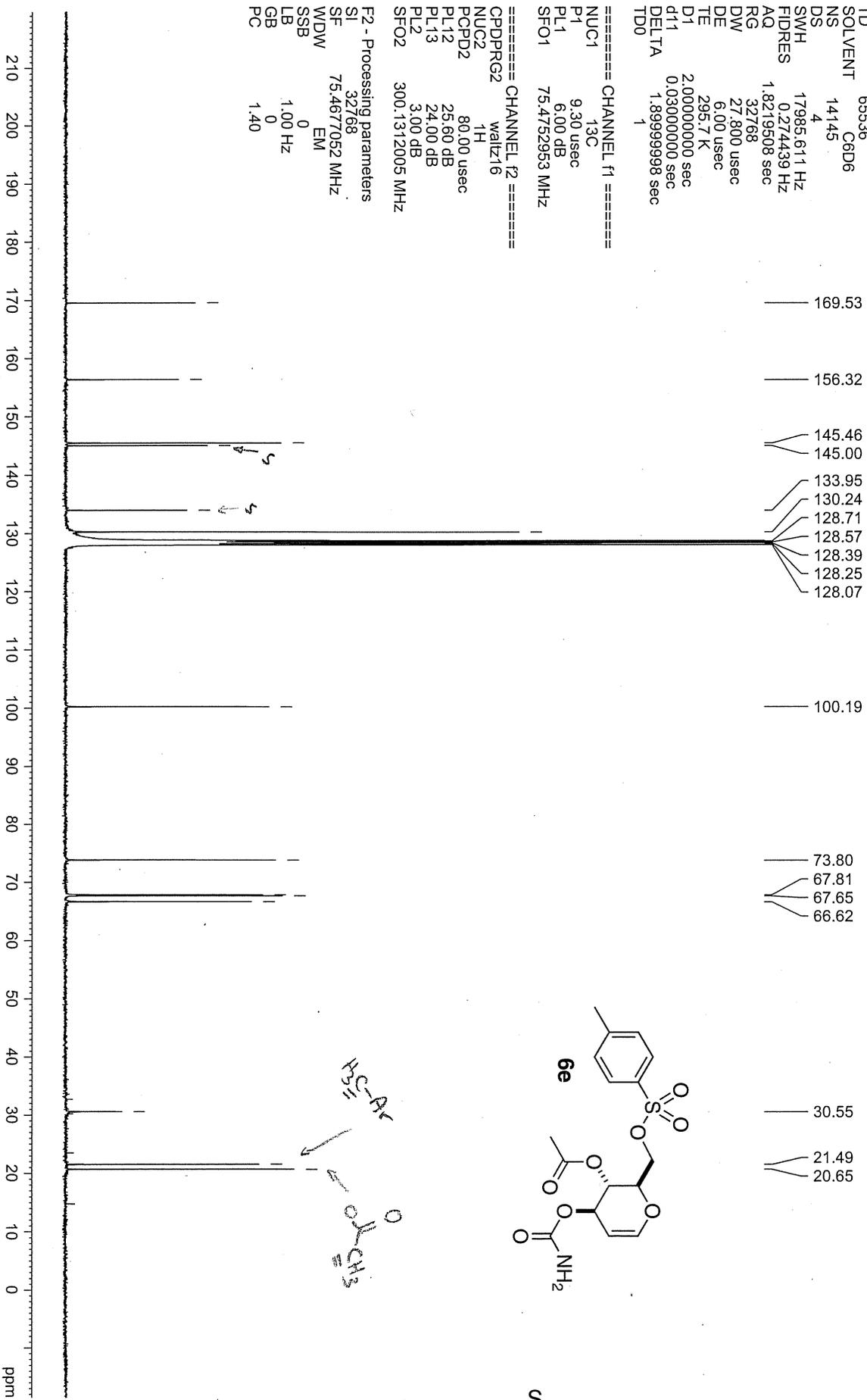
IL-RG-87
 C6D6

F2 - Acquisition Parameters
 Date_ 20070302
 Time 17:28
 INSTRUM spect
 PROBHHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT C6D6
 NS 14145
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 32768
 DW 27.800 usec
 DE 6.00 usec
 TE 295.7 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 9.30 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL12 25.60 dB
 PL13 24.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677052 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



Current Data Parameters

NAME IV-CMR-1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20071106
Time 16.57
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 456.1
DW 81.000 usec
DE 6.00 usec
TE 294.6 K
D1 1.00000000 sec
TD0 1

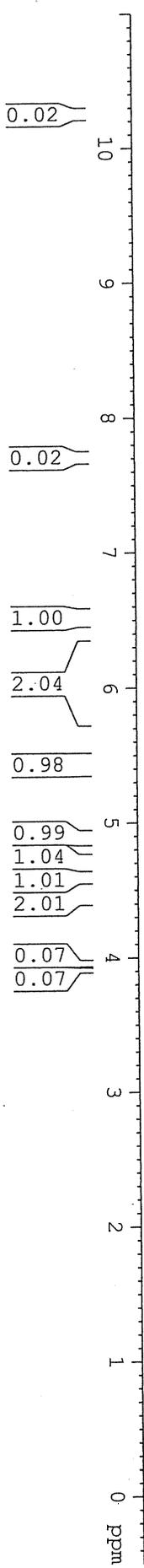
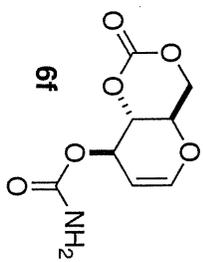
==== CHANNEL f1 =====

NUC1 1H
P1 6.65 usec
PL1 3.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters

SI 32768
SF 300.1300040 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

IV-CMR-1



Current Data Parameters
 NAME IV-CMR-1
 EXPNO 2
 PROCNO 1

IV-CMR-1

F2 - Acquisition Parameters
 Date_ 20071107
 Time 1.58

INSTRUM spect
 PROBD 5 mm BBO BB-1H
 PULPROG zgpg30

TD 65536
 SOLVENT Acetone
 NS 98192
 DS 4

SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQC 18219508 sec
 RG 32768
 DW 27.800 usec
 DE 6.00 usec
 TE 295.2 K

D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.60 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 72.00 usec
 PL12 25.00 dB
 PL13 24.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

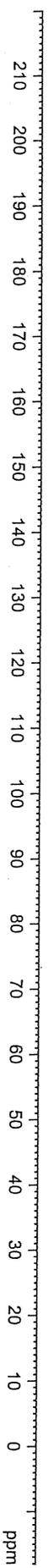
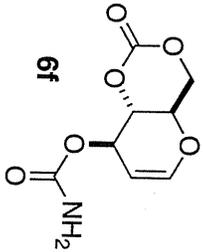
F2 - Processing parameters
 SI 82768
 SF 75.4676762 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

156.82
 147.28
 145.46

102.43

76.50
 69.12
 68.87
 66.42

30.69
 30.43
 30.18
 29.92
 29.66
 29.41
 29.15



Current Data Parameters

NAME IV-CMR-21
EXPNO 1
PROCNO 1

IV-CMR-21

F2 - Acquisition Parameters

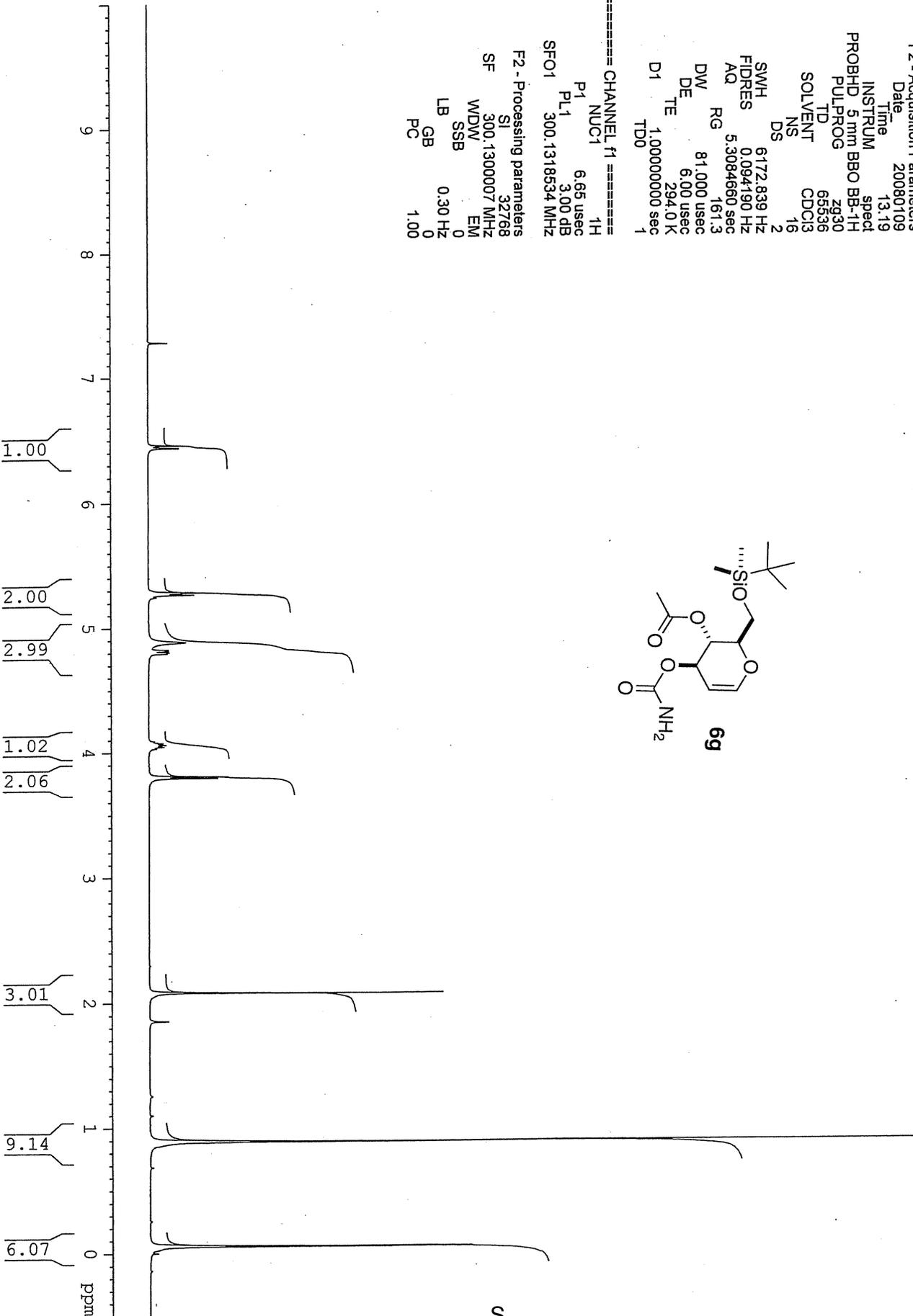
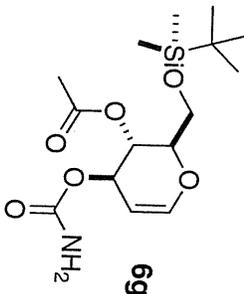
Date_ 20080109
Time 13.19
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 161.3
DW 81.000 usec
DE 6.00 usec
TE 294.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====

NUC1 1H
P1 6.65 usec
PL1 3.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters

SI 32768
SF 300.1300007 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
 NAME IV-CMR-21
 EXPNO 3
 PROCNO 1

IV-CMR-21
 13C NMR

F2 - Acquisition Parameters
 Date_ 20080109
 Time 14.29

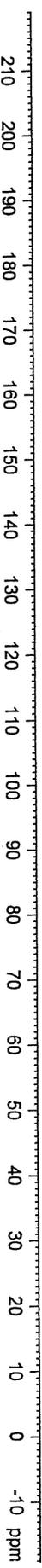
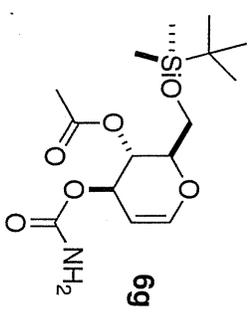
INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 512
 DS 4
 SSWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 32768
 DW 27.800 usec
 DE 6.00 usec
 TE 294.8 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.60 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 72.00 usec
 PL12 25.00 dB
 PL13 24.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677522 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

- 169.49
- 156.23
- 145.72
- 98.94
- 77.42
- 77.00
- 76.81
- 76.58
- 69.17
- 67.57
- 61.34
- 25.76
- 20.90
- 18.25
- 5.45



Current Data Parameters
 NAME IV-CMR-13
 EXPNO 6
 PROCNO 1

IV-CMR-13
 1H NMR after rechromatography

F2 - Acquisition Parameters
 Date 20071217
 Time 11.38

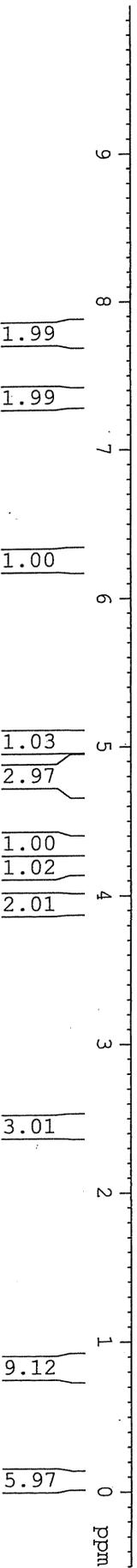
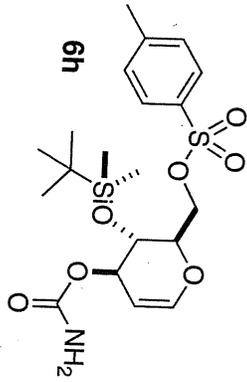
INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2

SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec

DW 81.000 usec
 DE 6.00 usec
 TE 293.6 K
 D1 1.00000000 sec
 TDO 1

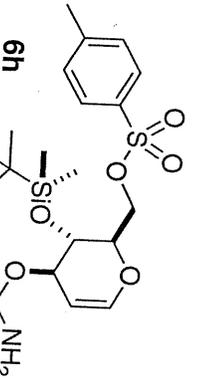
===== CHANNEL f1 =====
 P1 6.65 usec
 NUC1 1H
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300024 MHz
 W/DW EM 0
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME IV-CMR-13
 EXPNO 2
 PROCNO 1

IV-CMR-13
 13C NMR

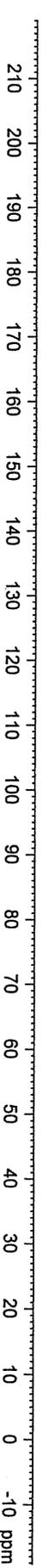
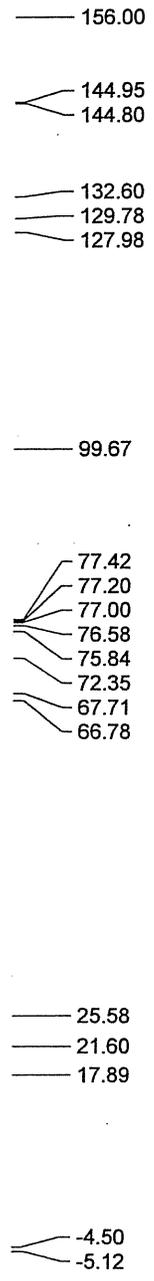


F2 - Acquisition Parameters
 Date_ 20071211
 Time 14.19
 INSTRUM spect
 PROBHID 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 3169
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 32768
 DW 27.800 usec
 DE 6.00 usec
 TE 294.5 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 9.60 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 72.00 usec
 PL12 25.00 dB
 PL13 24.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677540 MHz
 WIDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40



Current Data Parameters

NAME III-CMR-283
EXPNO 1
PROCNO 1

III-CMR-283

F2 - Acquisition Parameters

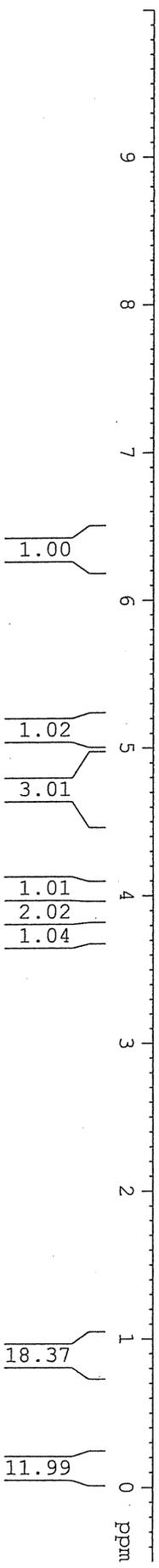
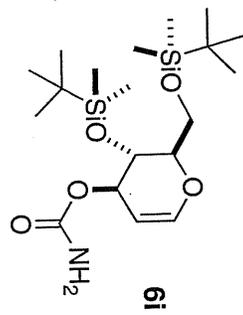
Date_ 20071003
Time 15.28
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 90.5
DW 81.000 usec
DE 6.00 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====

NUC1 1H
P1 6.65 usec
PL1 3.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters

SI 32768
SF 300.1300038 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
 NAME III-CMR-279
 EXPNO 4
 PROCNO 1

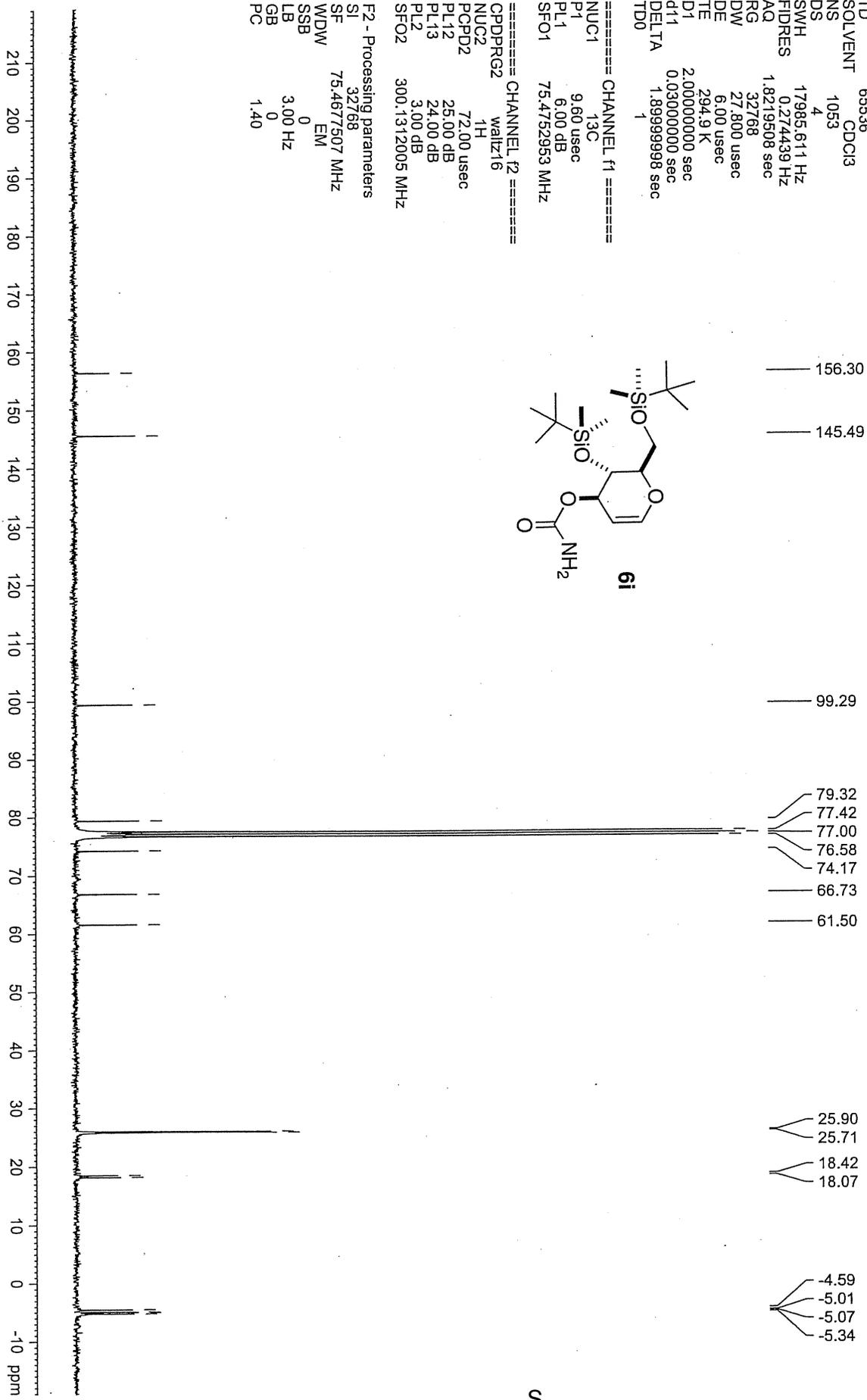
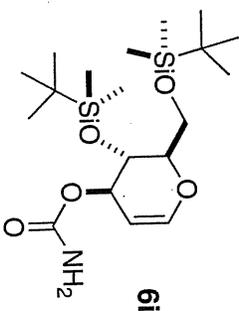
III-CMR-279
 F29-32
 13C NMR

F2 - Acquisition Parameters
 Date_ 20070928
 Time 16:55
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1053
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 32768
 DW 27.800 usec
 DE 6.00 usec
 TE 294.9 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.60 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 72.00 usec
 PL12 25.00 dB
 PL13 24.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677507 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40



Current Data Parameters
NAME IIL-CMR-241
EXPNO 3
PROCNO 1

IIL-CMR-241
F28-35

F2 - Acquisition Parameters
Date 20060914
Time 14.47

INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30

TD 65536
SOLVENT CDCl3
NS 32

DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz

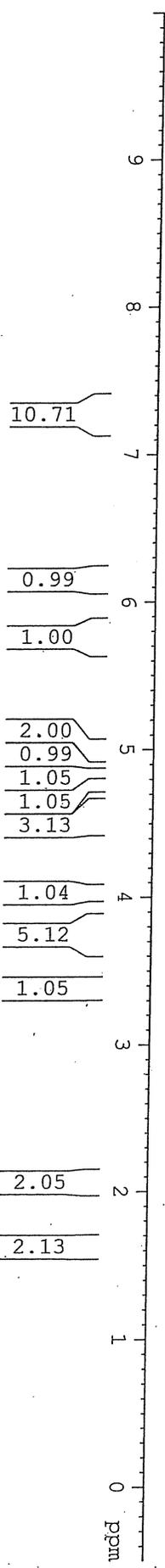
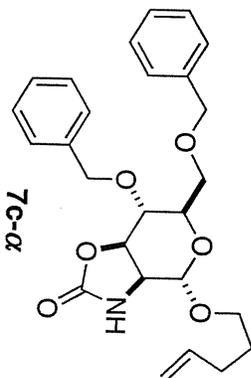
AQ 5.3084660 sec
RG 161.3
DE 81.000 usec
TE 294.4 K

D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
P1 NUC1 1H
PL1 6.80 usec
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300080 MHz
WDW EM
SSB 0

LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
 NAME III-CMR-241
 EXPNO 4
 PROCNO 1

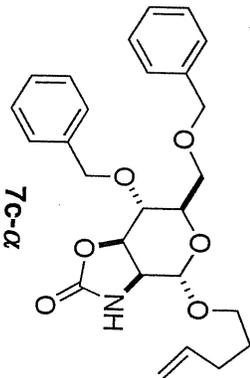
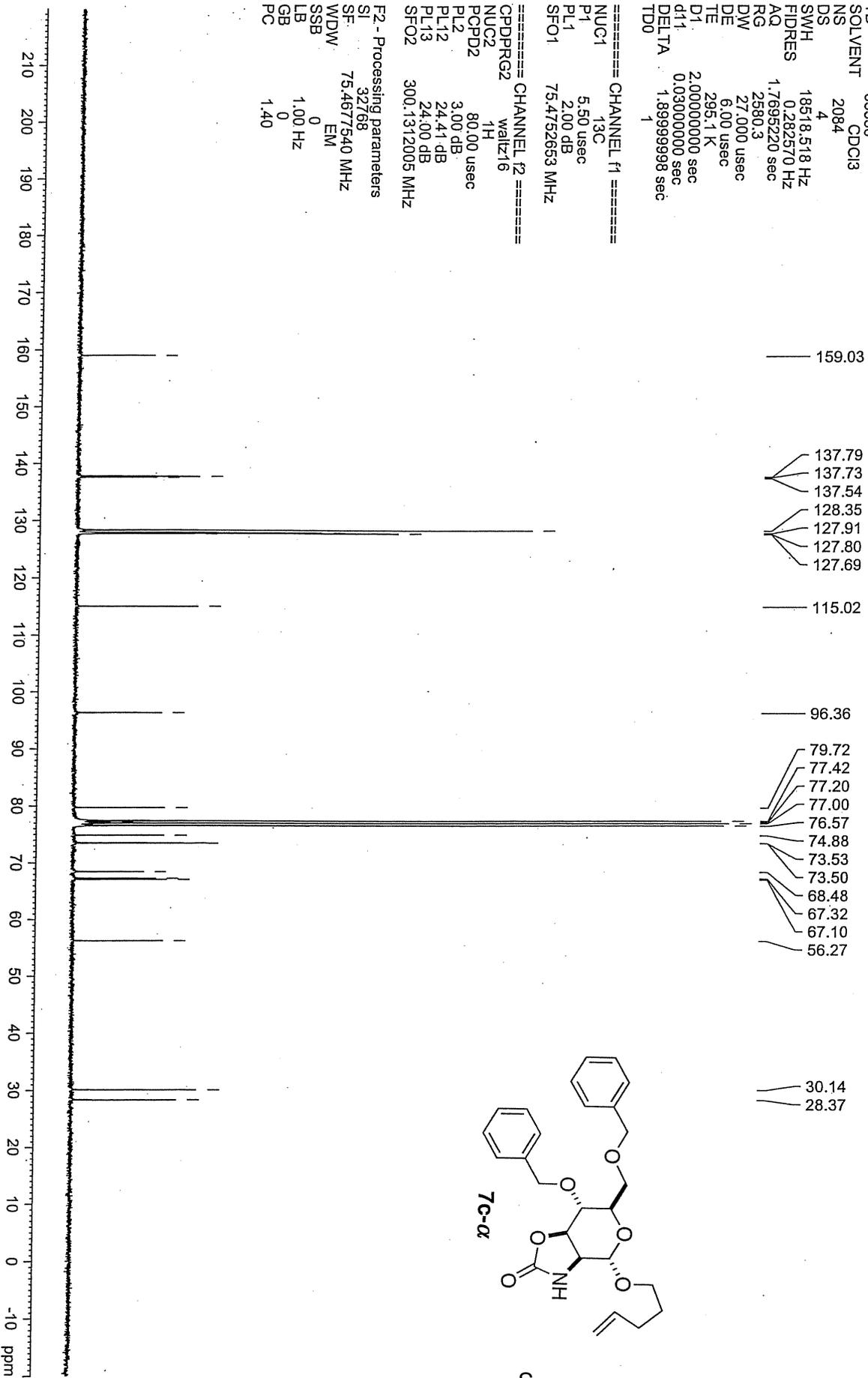
III-CMR-241
 F28-35
 13C NMR

F2 - Acquisition Parameters
 Date_ 20060914
 Time 15.20
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2084
 DS 4
 SWH 18518.518 Hz
 FIDRES 0.282570 Hz
 RG 1.7695220 sec
 AQ 2580.3
 DW 27.000 usec
 DE 6.00 usec
 TE 295.1 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TDO 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 5.50 usec
 PL1 2.00 dB
 SFO1 75.4752653 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 3.00 dB
 PL12 24.41 dB
 PL13 24.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677540 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



5

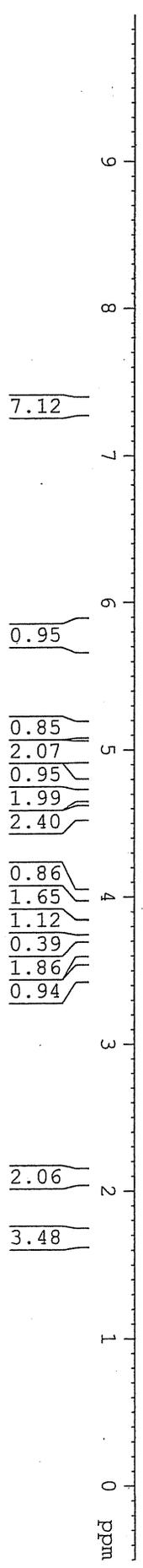
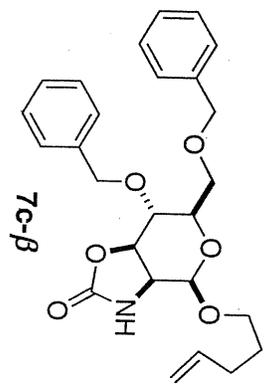
Current Data Parameters
 NAME III-CMR-235
 EXPNO 13
 PROCNO 1

III-CMR-235
 F38-42
 1H NMR CDCl3

F2 - Acquisition Parameters
 Date 20060814
 Time 15.46
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 362
 DW 81.000 usec
 DE 6.00 usec
 TE 294.4 K
 D1 1.00000000 sec
 TDO 1

==== CHANNEL f1 =====
 P1 1H
 NUC1 13
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300056 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME III-CMR-235
 EXPNO 14
 PROCNO 1

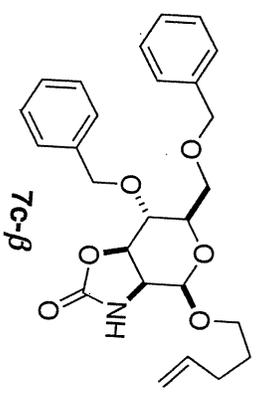
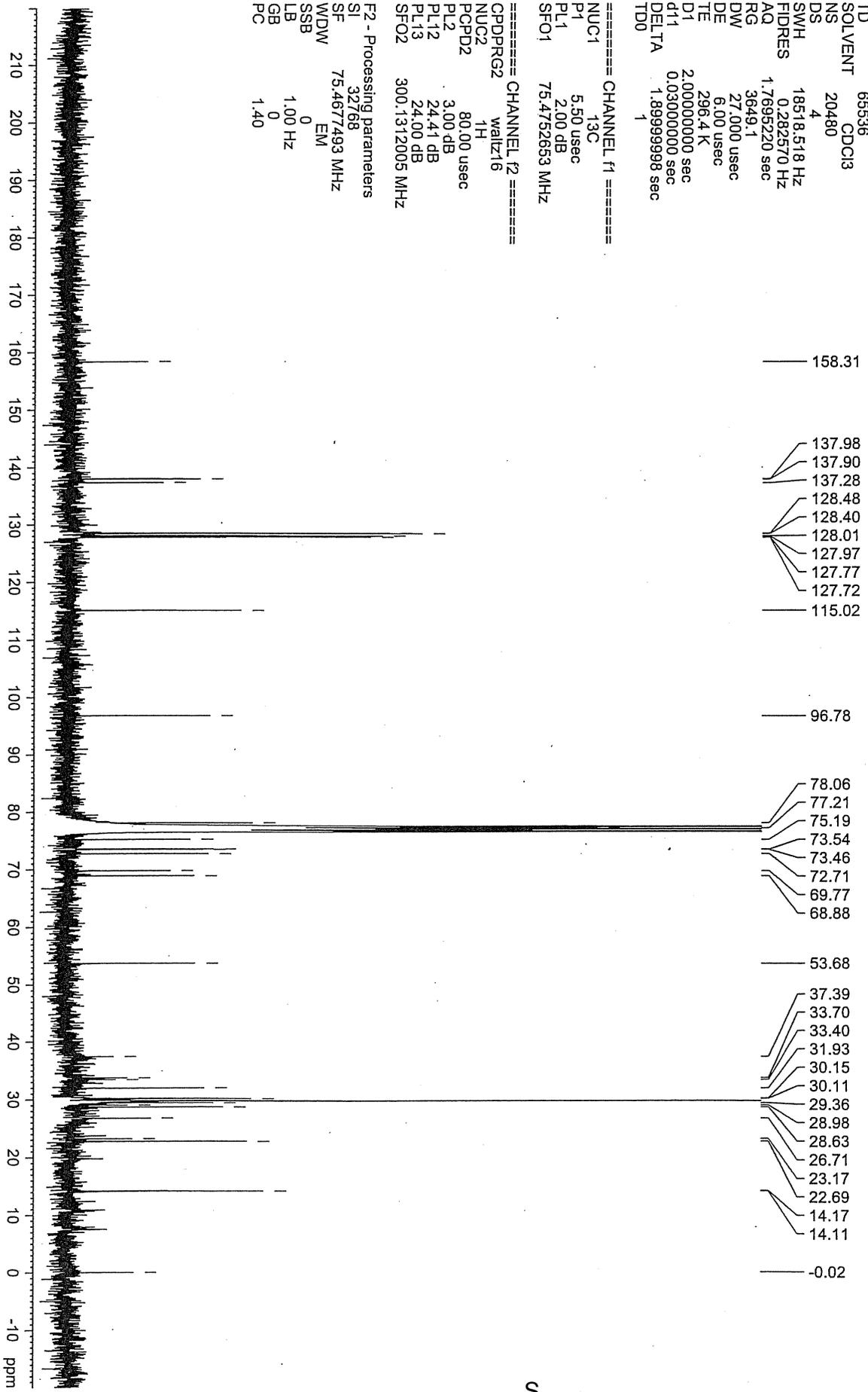
III-CMR-235
 F38-42
 13C NMR

F2 - Acquisition Parameters
 Date_ 20060815
 Time 10.53
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 20480
 DS 4
 SWH 18518.518 Hz
 FIDRES 0.282570 Hz
 AQ 1.7695220 sec
 RG 3649.1
 DW 27.000 usec
 DE 6.00 usec
 TE 296.4 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

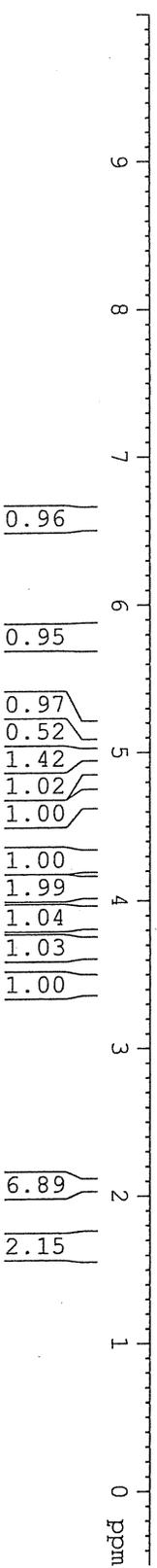
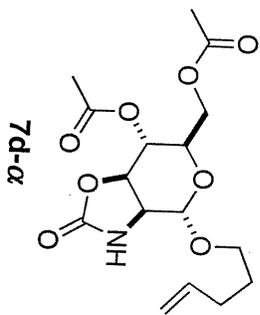
==== CHANNEL f1 =====
 NUC1 13C
 P1 5.50 usec
 PL1 2.00 dB
 SFO1 75.4752653 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 3.00 dB
 PL12 24.41 dB
 PL13 24.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677493 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



II-RG-71
 di-acylated carbamate, amidoglycosylation
 1H NMR- alpha product



Current Data Parameters
 NAME II-RG-71
 EXPNO 5
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20061016
 Time 10.45
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 114
 DW 81.000 usec
 DE 6.00 usec
 TE 294.8 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 6.80 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1299995 MHz
 W/DW 0
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

III-CMR-245
F23-29

Current Data Parameters
NAME III-CMR-245
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070803
Time 10.43

INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30

TD 65536
SOLVENT CDCl3

NS 4
DS 4

SWH 17985.611 Hz
FIDRES 0.274439 Hz

AQ 1.8219508 sec
RG 32768

DW 27.800 usec
DE 6.00 usec

TE 295.5 K
D1 2.00000000 sec

d11 0.03000000 sec
DELTA 1.89999998 sec

TD0 1

===== CHANNEL f1 =====

NUC1 13C
P1 9.60 usec

PL1 6.00 dB
SFO1 75.4752953 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
NUC2 1H

PCPD2 72.00 usec
PL12 25.00 dB

PL13 24.00 dB
PL2 3.00 dB

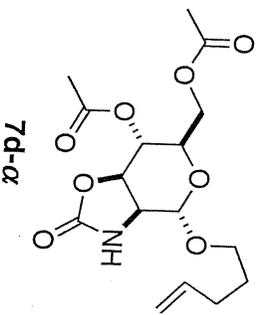
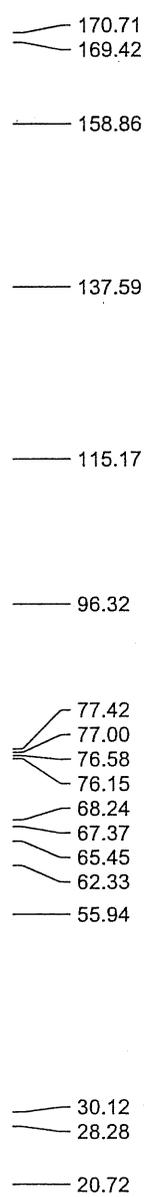
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768

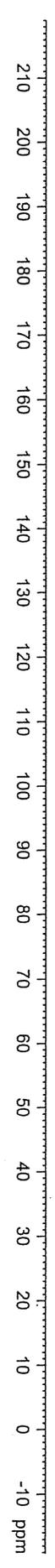
SF 75.4677540 MHz
WIDW EM

SSB 0
LB 3.00 Hz

GB 0
PC 1.40



7d-α



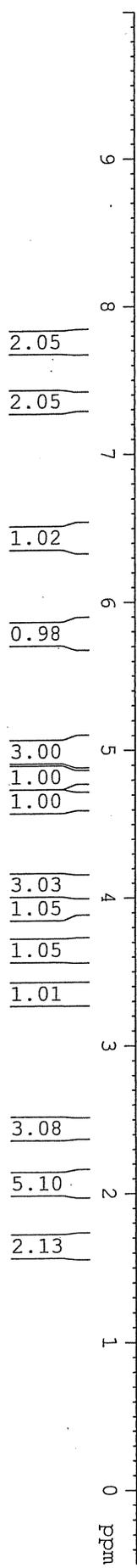
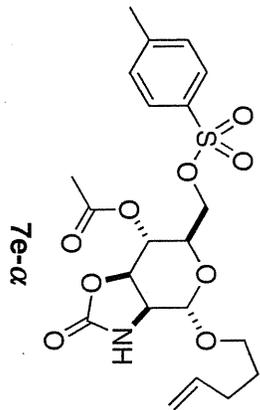
Current Data Parameters
 NAME III-CMR-249
 EXPNO 4
 PROCNO 1

III-CMR-249
 F23-30

F2 - Acquisition Parameters
 Date_ 20070809
 Time 14.11
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 161.3
 DW 81.000 usec
 DE 6.00 usec
 TE 294.5 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 6.65 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300017 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



III-CMR-249
F23-30

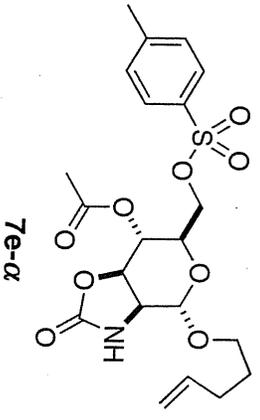
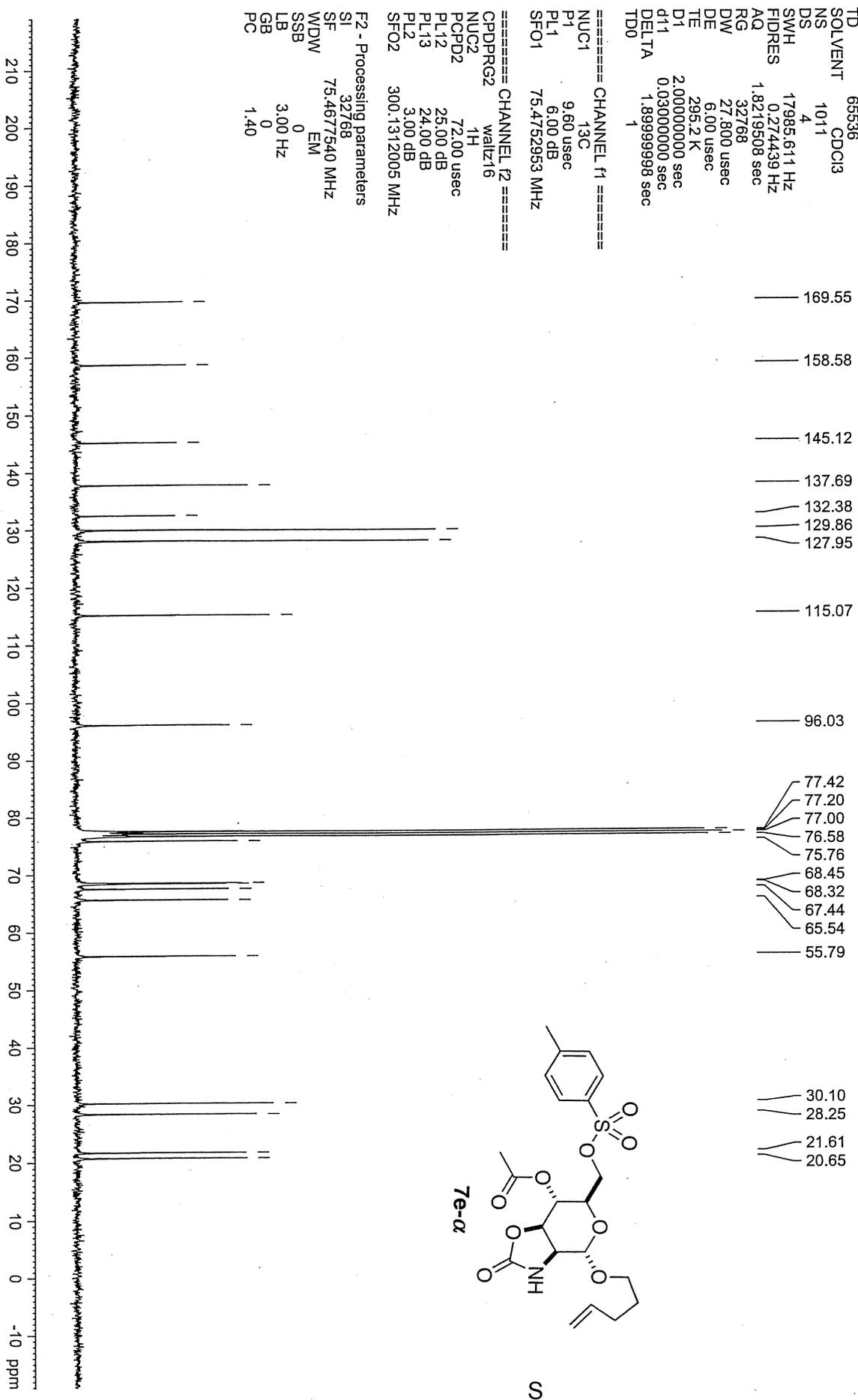
Current Data Parameters
NAME III-CMR-249
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070809
Time 15:17
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1011
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

==== CHANNEL f1 =====
NUC1 13C
P1 9.60 usec
PL1 6.00 dB
SFO1 75.4752953 MHz

==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 72.00 usec
PL12 25.00 dB
PL13 24.00 dB
PL2 3.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677540 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40



Current Data Parameters
 NAME IV-CMR-7
 EXPNO 5
 PROCNO 1

IV-CMR-7
 F8-15
 13C NMR

F2 - Acquisition Parameters
 Date_ 20071119
 Time 4.30

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30

TD 65536
 SOLVENT Acetone
 NS 9216
 DS 4

SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec

RG 32768
 DW 27.800 usec
 DE 6.00 usec

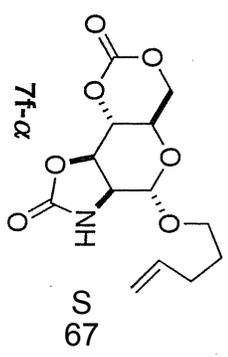
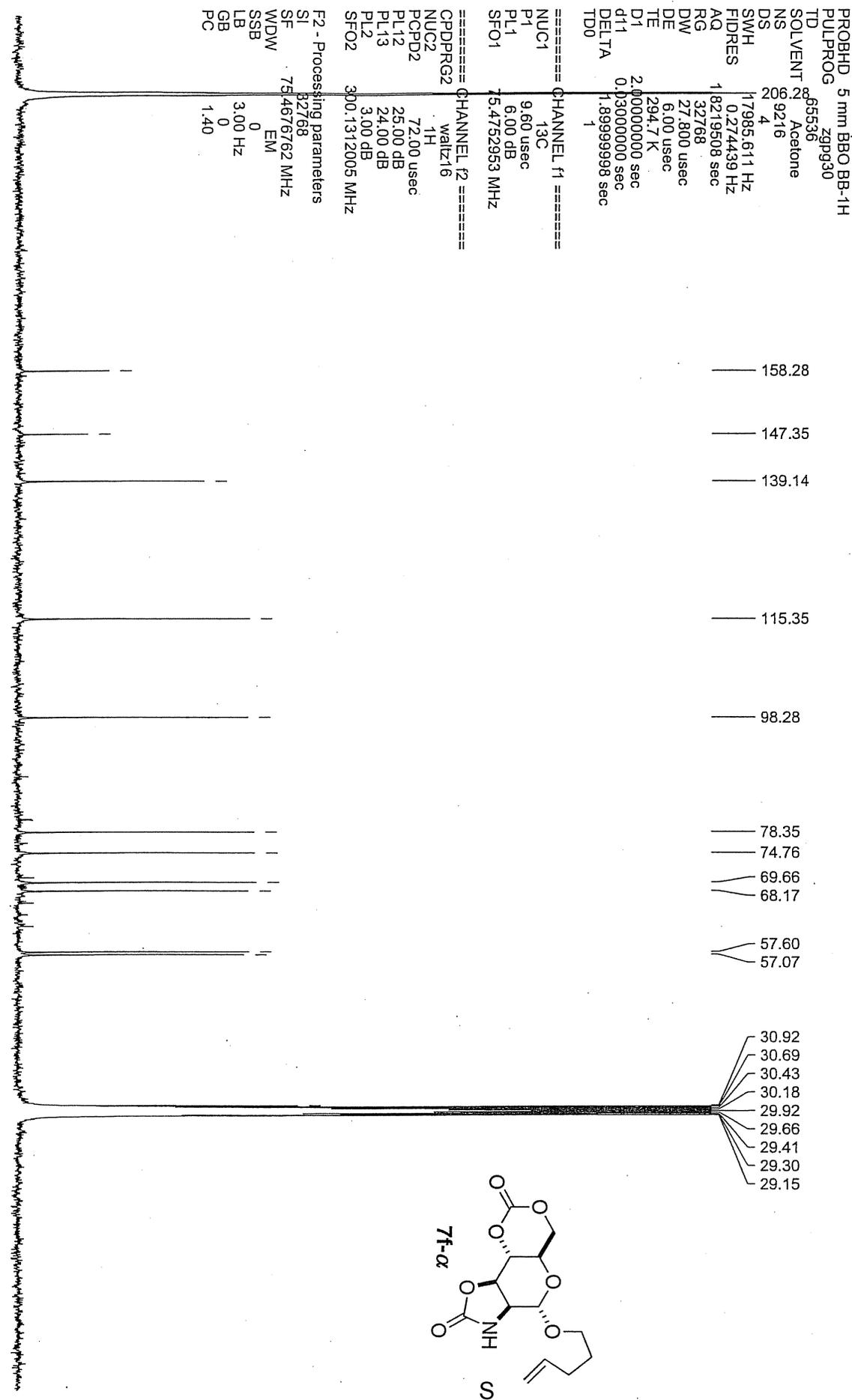
TE 294.7 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.60 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 72.00 usec
 PL12 25.00 dB
 PL13 24.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 82768
 SF 75.4676762 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



Current Data Parameters
NAME IV-CMR-7
EXPNO 9
PROCNO 1

IV-CMR-7
F23-28

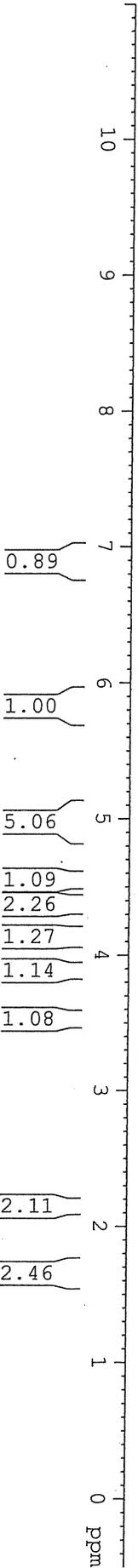
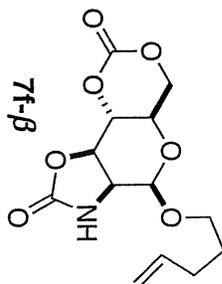
F2 - Acquisition Parameters
Date_ 20071119
Time 10.37

INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 48
DS 2

SW/H 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 574.7
DW 81.000 usec
DE 6.00 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 6.65 usec
PL1 3.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300040 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
 NAME IV-CMR-7
 EXPNO 10
 PROCNO 1

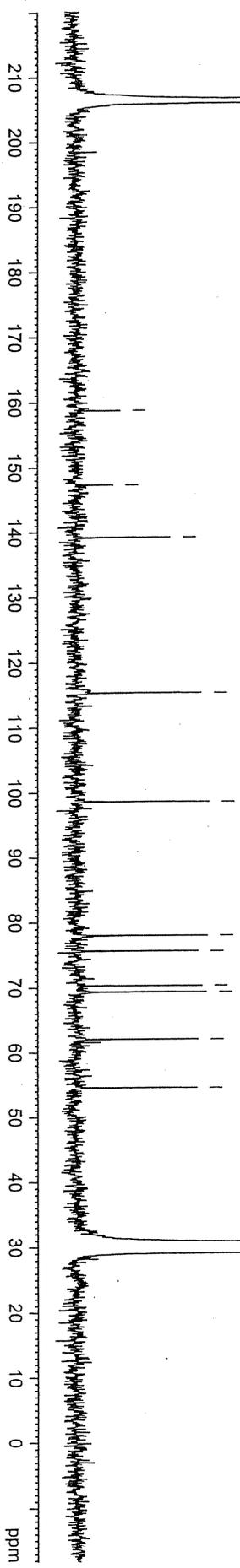
IV-CMR-7
 F23-28
 13C NMR

F2 - Acquisition Parameters
 Date_ 20071120
 Time 4.06
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT Acetone
 NS 99216
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQC 1.8219508 sec
 RG 32768
 DW 27.800 usec
 DE 6.00 usec
 TE 295.1 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

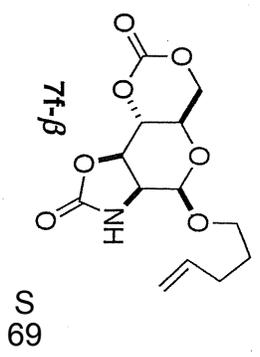
==== CHANNEL f1 =====
 NUC1 13C
 P1 9.60 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 72.00 usec
 PL12 25.00 dB
 PL13 24.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 754676753 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40



- 158.75
- 147.29
- 139.20
- 115.33
- 98.60
- 77.99
- 75.61
- 70.27
- 69.30
- 62.03
- 54.51
- 30.85
- 30.69
- 30.43
- 30.18
- 29.92
- 29.66
- 29.41
- 29.15



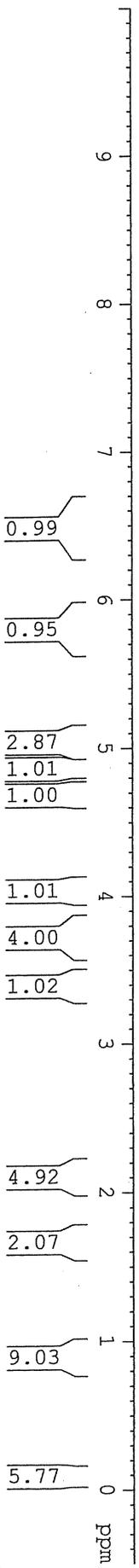
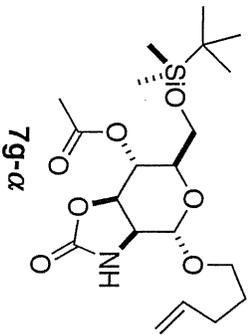
Current Data Parameters
 NAME IV-CMR-27
 EXPNO 4
 PROCNO 1

IV-CMR-27
 F29-36

F2 - Acquisition Parameters
 Date_ 20080117
 Time 17.20
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 16
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 114
 DW 81.000 usec
 DE 6.00 usec
 TE 294.3 K
 D1 1.000000000 sec
 TD0 1

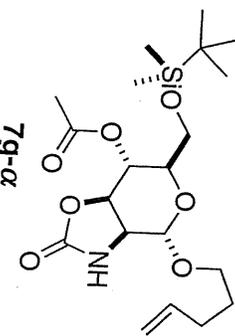
===== CHANNEL f1 =====
 NUC1 1H
 P1 6.65 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300012 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME IV-CMR-27
 EXPNO 5
 PROCNO 1

IV-CMR-27
 F29-36
 13C NMR

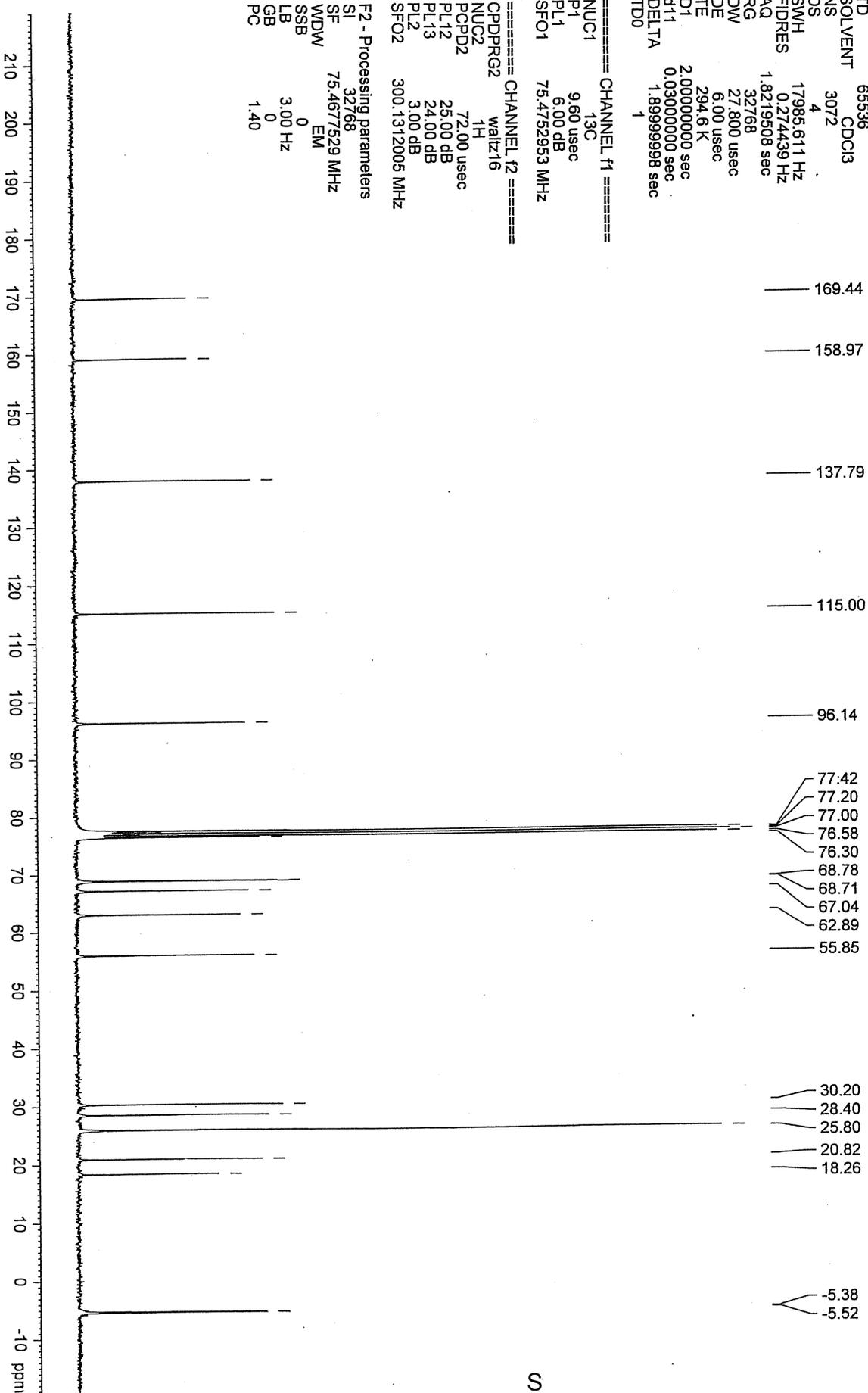


F2 - Acquisition Parameters
 Date_ 20080117
 Time 20.41
 INSTRUM spect
 PROBHID 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 3072
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 32768
 DW 27.800 usec
 DE 6.00 usec
 TE 294.6 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.60 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 72.00 usec
 PL12 25.00 dB
 PL13 24.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677529 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40



Current Data Parameters
 NAME IV-CMR-27
 EXPNO 10
 PROCNO 1

IV-CMR-27
 F38-42

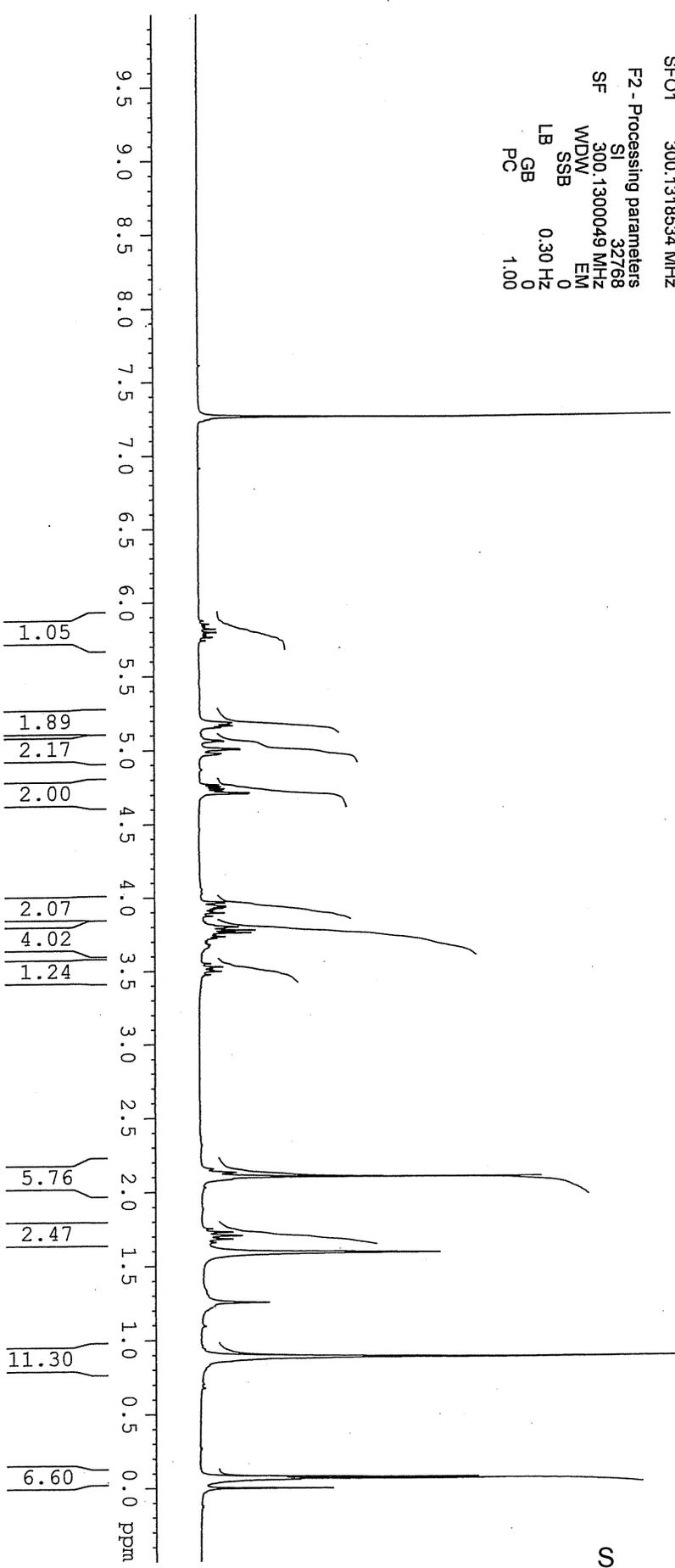
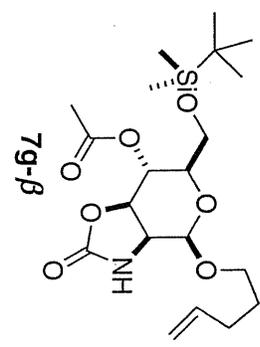
F2 - Acquisition Parameters
 Date 20080118
 Time 15.15

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 64

DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 574.7
 DW 81.000 usec
 DE 6.00 usec
 TE 293.6 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 P1 6.65 usec 1H
 NUC1 1H
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300049 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME IV-CMR-27
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080118
 Time 16:12

INSTRUM spect
 PROBHID 5 mm BBO BB-1H
 PULPROG zgpg30

TD 65536
 SOLVENT CDCl3

NS 15419
 DS 4

SWH 17985.611 Hz
 FIDRES 0.274439 Hz

AQ 1.8219508 sec
 RG 32768

DW 27.800 usec
 DE 6.00 usec

TE 293.7 K
 D1 2.00000000 sec

dt1 0.03000000 sec
 DELTA 1.89999986 sec

TD0 1

===== CHANNEL f1 =====
 NUC1 13C

P1 9.60 usec
 PL1 6.00 dB

SFO1 75.4752953 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16

NUC2 1H

PCPD2 72.00 usec

PL12 25.00 dB
 PL13 24.00 dB
 PL2 3.00 dB

SFO2 300.1312005 MHz

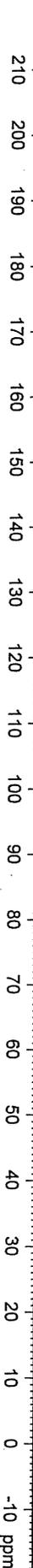
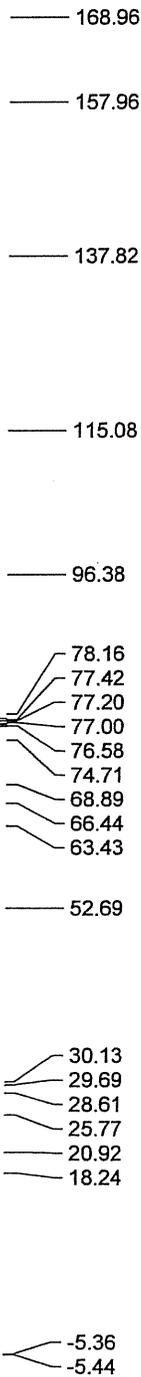
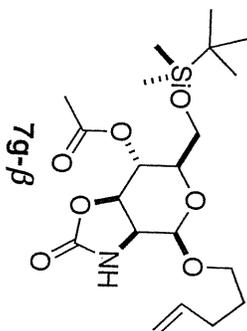
F2 - Processing parameters

SI 32768

SF 75.4677507 MHz

WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

IV-CMR-27
 F38-42
 13C NMR



Current Data Parameters
 NAME IV-CMR-31
 EXPNO 14
 PROCNO 1

IV-CMR-31
 F22-33

F2 - Acquisition Parameters
 Date 20080201
 Time 10.33

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16

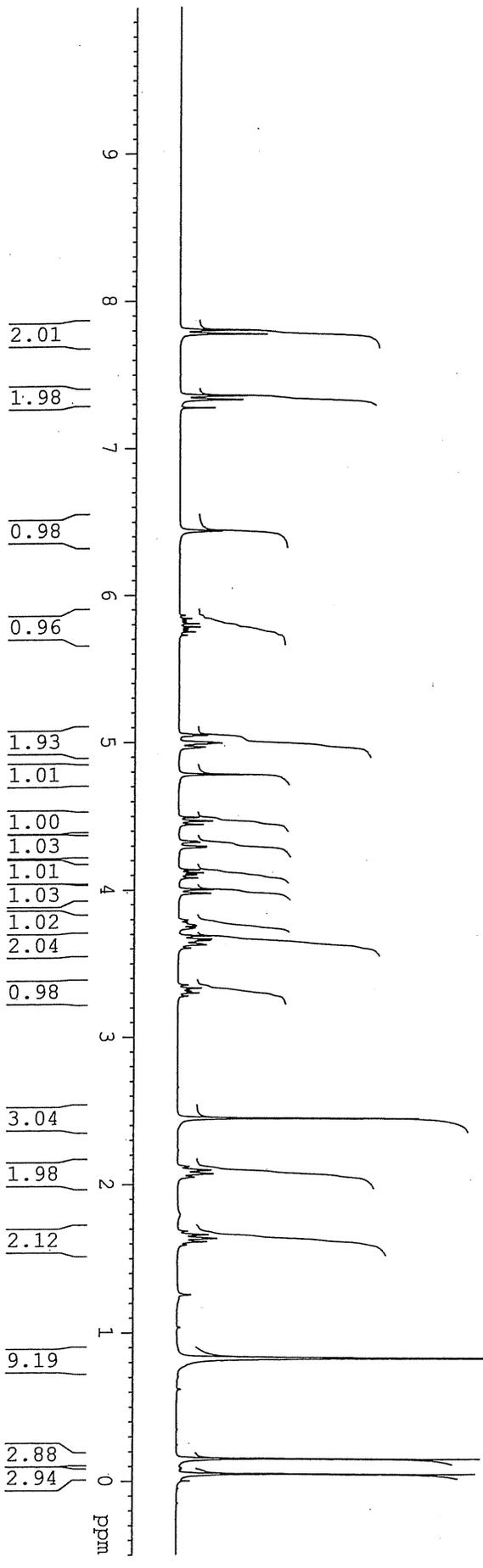
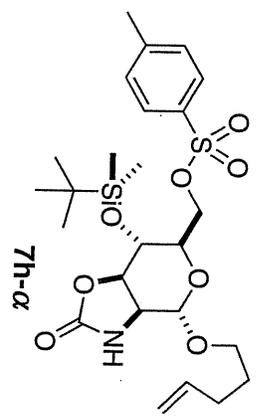
DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec

RG 71.8
 DW 81.000 usec
 DE 6.00 usec
 TE 294.4 K

D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 P1 6.65 usec
 NUC1 1H
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300024 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME IV-CMR-31
 EXPNO 16
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080201
 Time 12.11

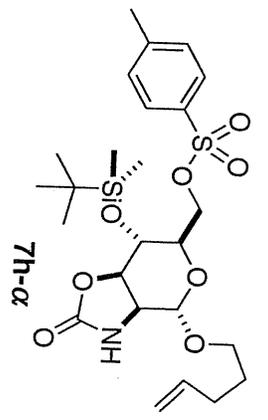
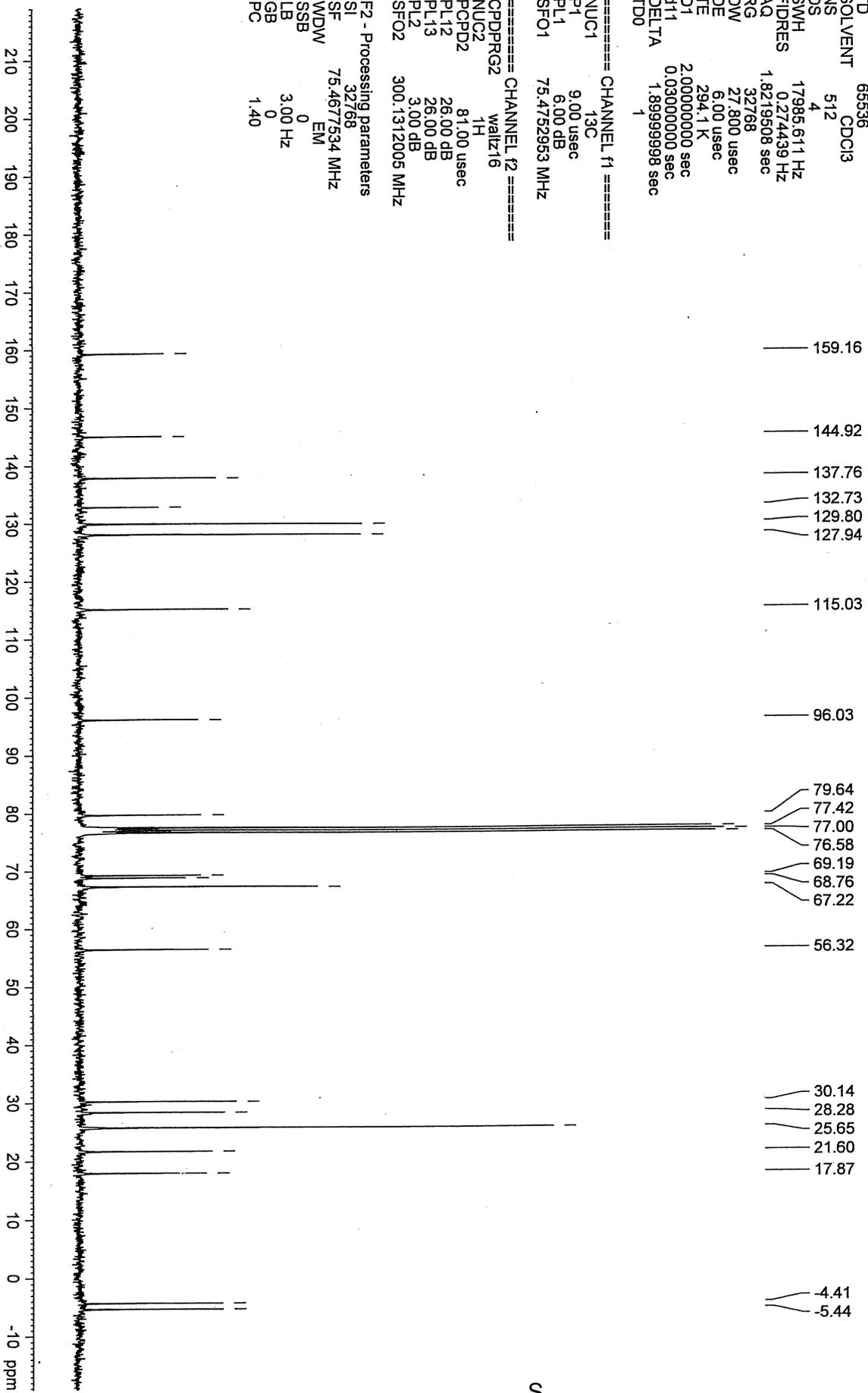
INSTRUM spect
 PROBD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 512
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 32768
 DW 27.800 usec
 DE 6.00 usec
 TE 294.1 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 9.00 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 81.00 usec
 PL12 26.00 dB
 PL13 26.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677534 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

IV-CMR-31
 F22-33
 13C NMR



Current Data Parameters
 NAME IV-CMR-31
 EXPNO 11
 PROCNO 1

IV-CMR-31
 F36-45

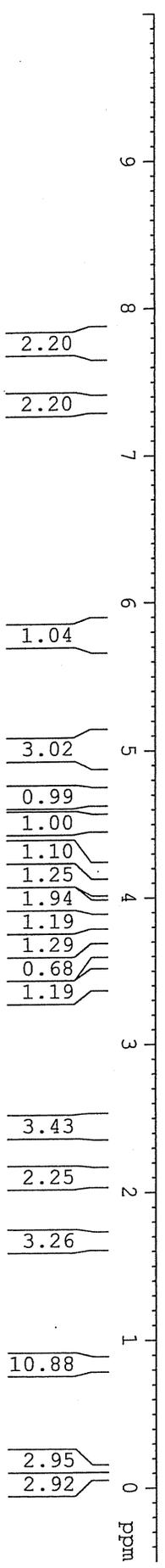
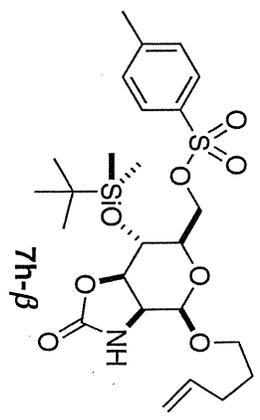
F2 - Acquisition Parameters
 Date_ 20080129
 Time 16.43

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 64
 DS 2

SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 574.7
 DW 81.000 usec
 DE 6.00 usec
 TE 293.8 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 6.65 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300051 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME IV-CMR-31
 EXPNO 12
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080129
 Time 16.56

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30

TD 65536
 SOLVENT CDCl3
 NS 17746
 DS 4

SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec

RG 32768
 DW 27.800 usec
 DE 6.00 usec
 TE 294.1 K

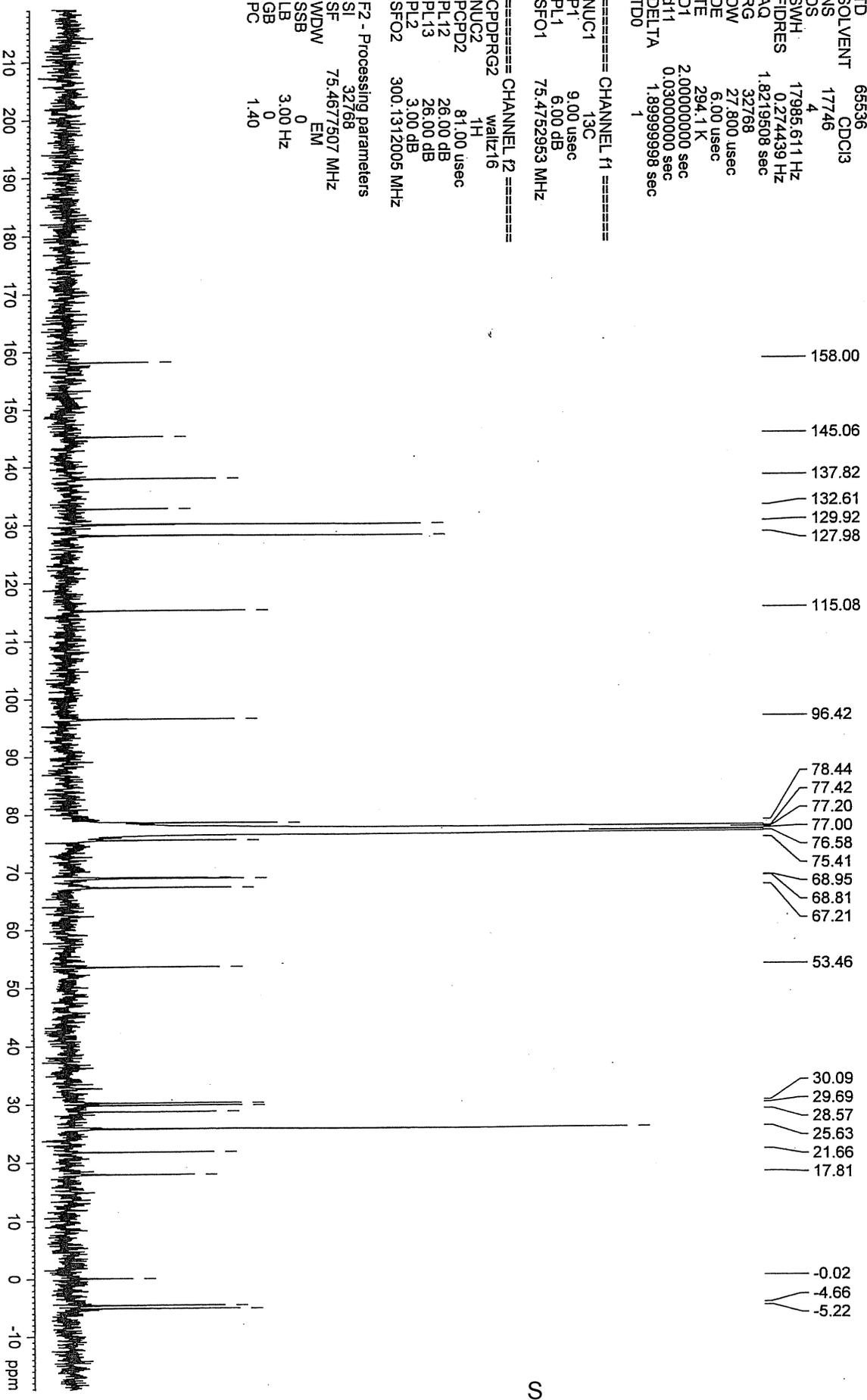
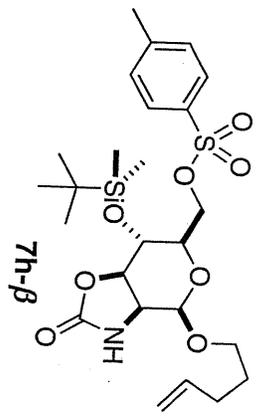
D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 9.00 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 81.00 usec
 PL12 26.00 dB
 PL13 26.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677507 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

IV-CMR-31
 F36-45
 13C NMR



Current Data Parameters
 NAME III-CMR-287
 EXPNO 7
 PROCNO 1

III-CMR-287
 F29-34

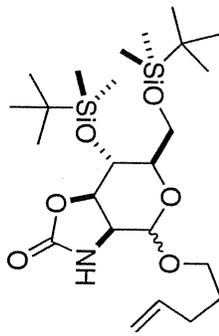
F2 - Acquisition Parameters
 Date_ 20071011
 Time 11.20

INSTRUM spect
 PROBHD 5mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2

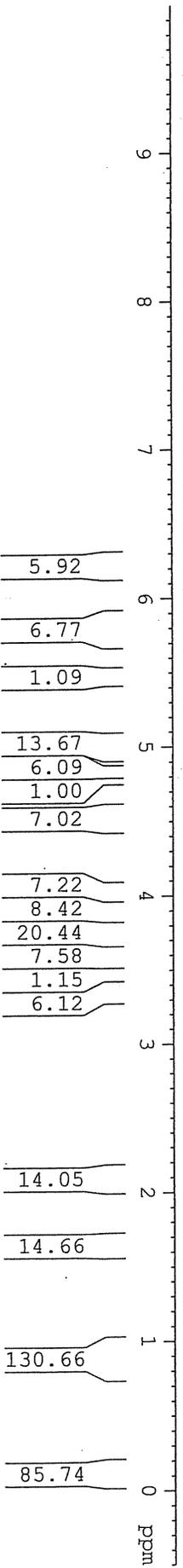
SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 114
 DW 81.000 usec
 DE 6.00 usec
 TE 294.3 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 6.65 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300029 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



α : β = 6 : 1



Current Data Parameters
 NAME III-CMR-287
 EXPNO 8
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20071011
 Time 11.35

INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30

TD 65536
 SOLVENT CDCl3
 NS 4

DS 4
 SMH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 32768

DW 27.800 usec
 DE 6.00 usec
 TE 294.7 K

D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C

P1 9.60 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

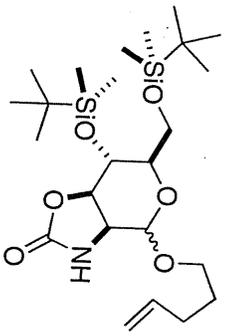
===== CHANNEL f2 =====
 CPDPRG2 waltz16

NUC2 1H
 PGPD2 72.00 usec
 PL12 25.00 dB
 PL13 24.00 dB
 PL2 3.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768

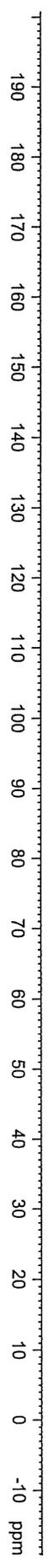
SF 75.4677515 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

III-CMR-287
 F29-34
 13C NMR (lb = 1)



7i- α : 7i- β = 6 : 1

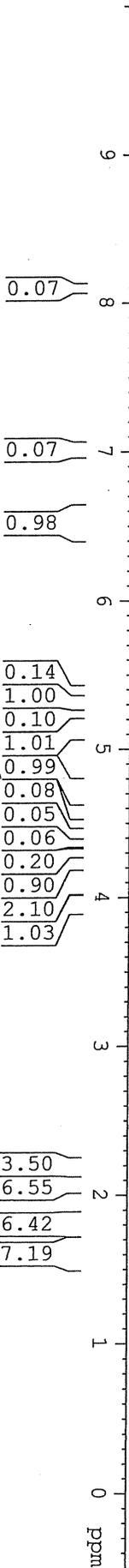
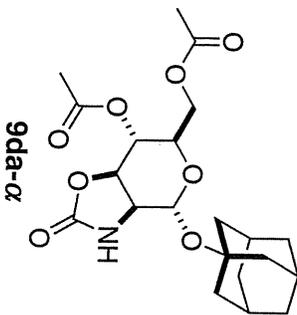
- 159.41
- 158.77
- 137.92
- 137.87
- 114.96
- 96.29
- 96.22
- 80.31
- 79.42
- 78.42
- 77.42
- 77.20
- 77.00
- 76.57
- 70.31
- 69.09
- 68.72
- 66.81
- 66.38
- 62.94
- 62.45
- 56.46
- 53.55
- 30.24
- 30.12
- 28.64
- 28.42
- 25.87
- 25.75
- 25.66
- 18.36
- 18.01
- 17.83
- 4.46
- 4.83
- 4.96
- 5.23
- 5.24
- 5.33
- 5.41



IV-CMR-41
F21-28

NAME IV-CMR-41
EXPNO 4
PROCNO 1
Date_ 20080328
Time 10.59
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.00 usec
TE 293.8 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 6.65 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1299985 MHz
WDWV EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME IV-CMR-41
 EXPNO 7
 PROCNO 1
 Date_ 20080620
 Time 16.23
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 526
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 32768
 DW 27.800 usec
 DE 6.00 usec
 TE 294.7 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

IV-CMR-41
 F21-28
 13C NMR on June 20, 2008

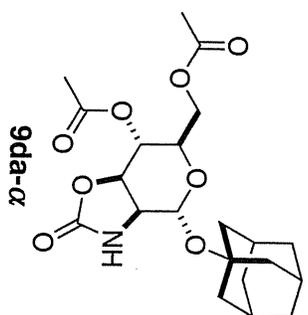
==== CHANNEL f1 =====

NUC1 13C
 P1 9.00 usec
 PL1 6.00 dB
 SFO1 75.4752953 MHz

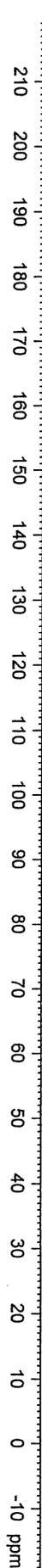
==== CHANNEL f2 =====

CPDPRG2 waltz16
 NUC2 1H
 PCPD2 81.00 usec
 PL2 3.00 dB
 PL12 26.00 dB
 PL13 26.00 dB
 SFO2 300.1312005 MHz
 SI 32768
 SF 75.4677544 MHz
 W/DW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

170.77
 169.38
 158.99



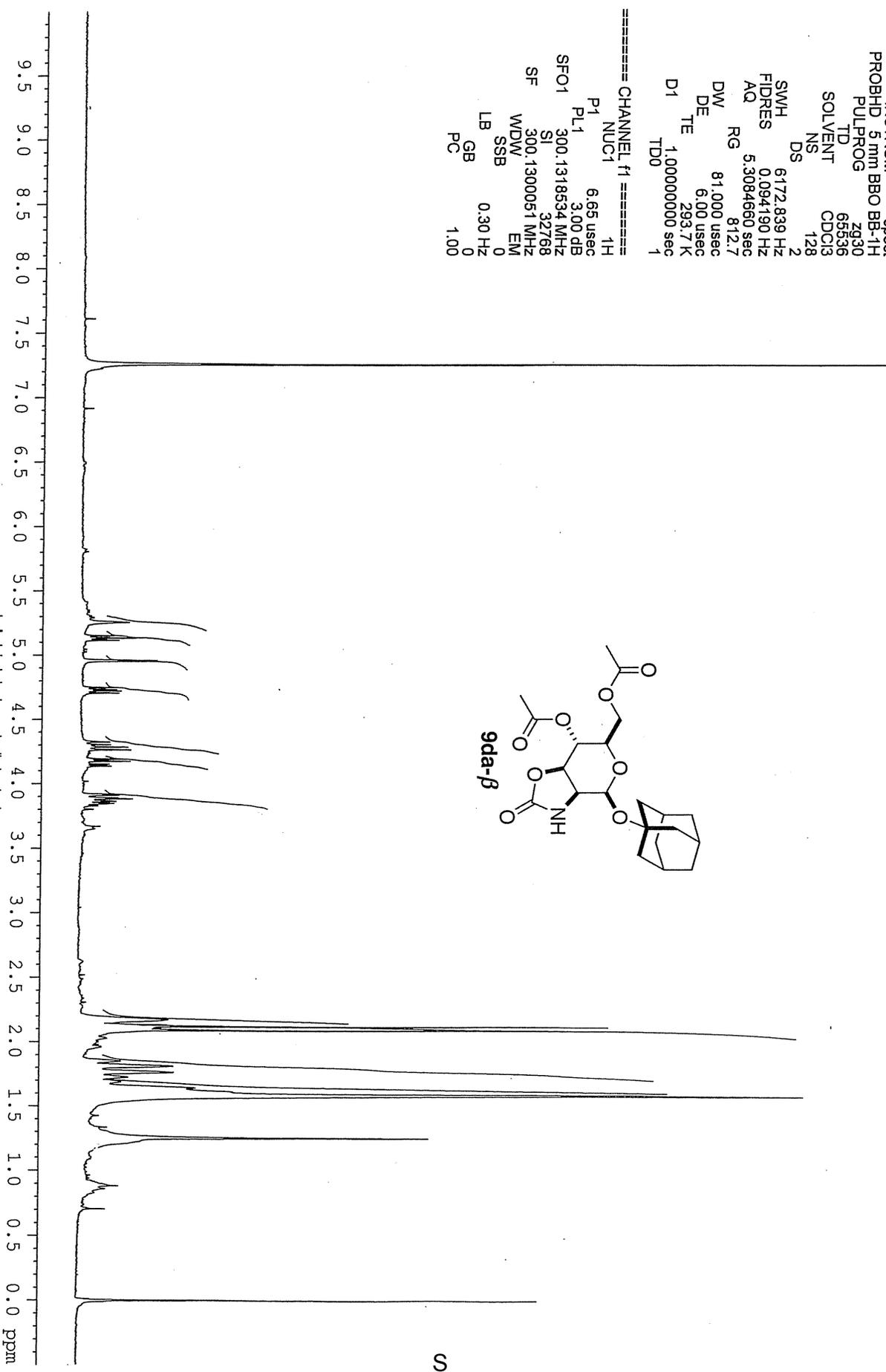
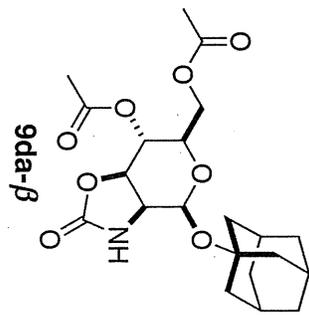
89.78
 77.42
 77.00
 76.58
 76.38
 75.75
 68.36
 65.53
 62.51
 57.37
 45.20
 42.24
 35.98
 30.50
 20.74



IV-CMR-41
F36-40

NAME IV-CMR-41
EXPNO 5
PROCNO 1
Date_ 20080328
Time 17.01
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 812.7
DW 81.000 usec
DE 6.00 usec
TE 293.7 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 6.65 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300051 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



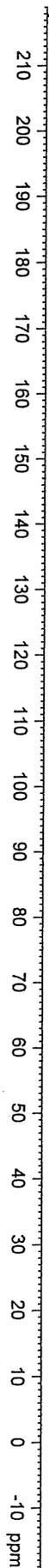
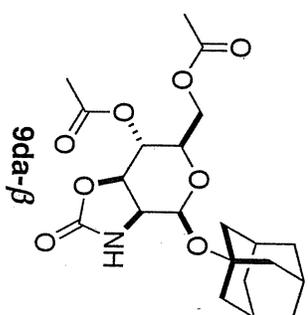
IV-CMR-41
F36-40
June 25, 2008

NAME IV-CMR-41
EXPNO 11
PROCNO 1
Date 20080625
Time 17.54
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 15166
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 294.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 6.00 dB
SFO1 75.4752963 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 81.00 usec
PL2 3.00 dB
PL12 26.00 dB
PL13 26.00 dB
SFO2 300.1312005 MHz
SF 32768
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

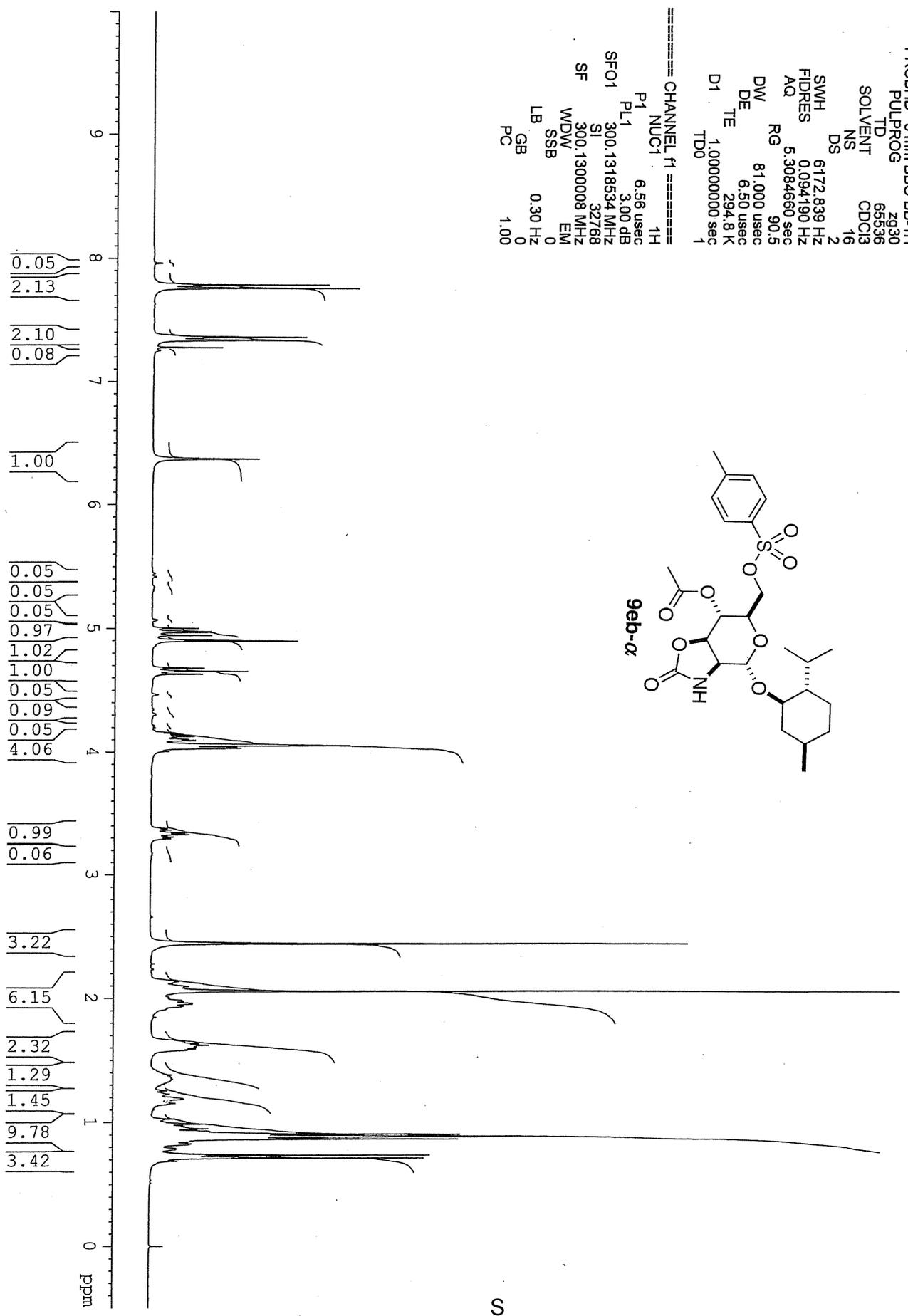
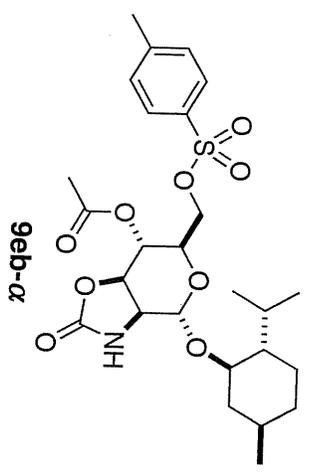
- 170.78
- 169.16
- 157.75
- 90.08
- 77.42
- 77.00
- 76.58
- 76.01
- 75.42
- 73.76
- 67.34
- 63.44
- 54.20
- 42.39
- 36.06
- 30.61
- 29.70
- 20.88
- 20.79
- 0.01



IV-CMR-51
 F22-26
 June 27, 2008

NAME IV-CMR-51
 EXPNO 4
 PROCNO 1
 Date 20080627
 Time 9:52
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 90.5
 DW 81.000 usec
 DE 6.50 usec
 TE 294.8 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 6.56 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz
 SI 32768
 SF 300.1300008 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



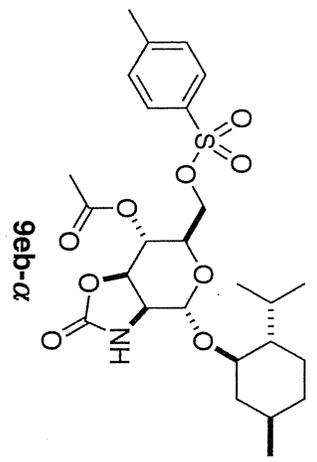
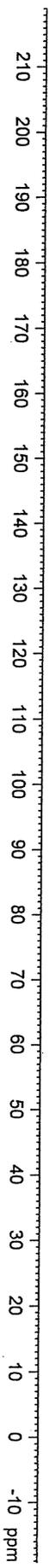
IV-CMR-51
F22-26
June 27, 2008

NAME IV-CMR-51
EXPNO 5
PROCNO 1
Date_ 20080627
Time 10.21
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCI3
NS 512
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 295.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 6.00 dB
SFO1 75.4752953 MHz

==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 81.00 usec
PL2 3.00 dB
PL12 26.00 dB
PL13 26.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677547 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

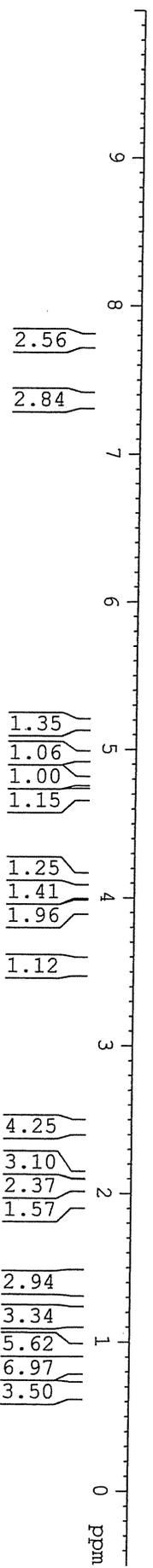
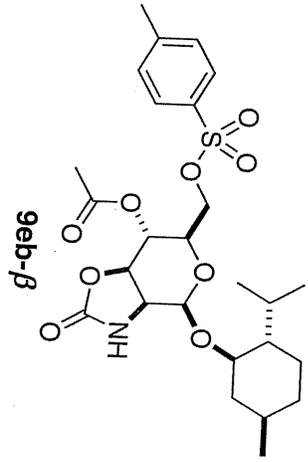
- 169.49
- 158.51
- 145.04
- 132.34
- 129.83
- 127.99
- 97.69
- 82.08
- 77.42
- 77.00
- 76.58
- 75.84
- 68.58
- 68.27
- 65.62
- 56.29
- 48.51
- 42.41
- 34.02
- 31.53
- 25.66
- 22.94
- 22.01
- 21.59
- 21.00
- 20.64
- 16.01



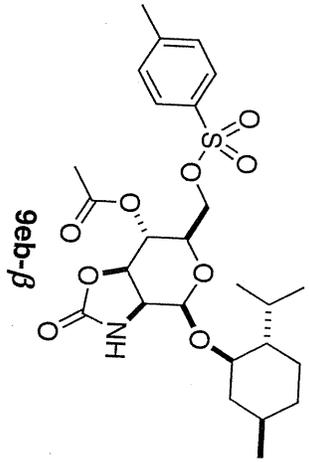
NAME IV-CMR-51
 EXPNO 9
 PROCNO 1
 Date 20080630
 Time 18.46
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 64
 DS 2
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 574.7
 DW 81.000 usec
 DE 6.50 usec
 TE 294.5 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 6.56 usec
 PL1 3.00 dB
 SFO1 300.1318534 MHz
 SI 32768
 SF 300.1300049 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

IV-CMR-51
 F41-48
 June 30, 2008



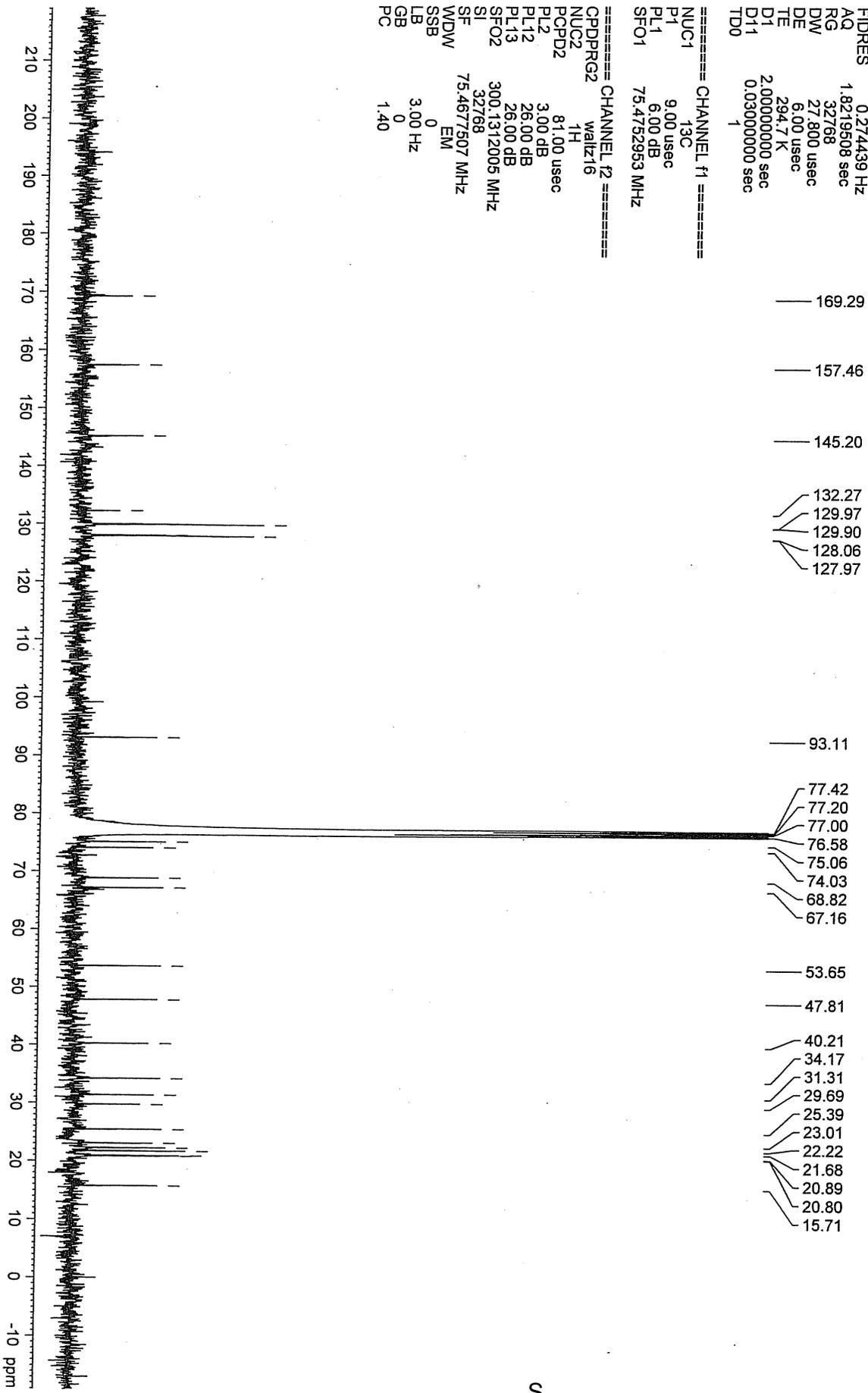
IV-CMR-51
F41-48
June 30, 2008



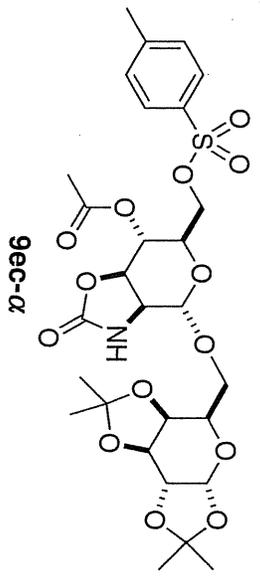
NAME IV-CMR-51
EXPNO 10
PROCNO 1
Date_ 20080630
Time 19.06
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 13790
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 294.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 6.00 dB
SFO1 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 81.00 usec
PL2 3.00 dB
PL12 26.00 dB
PL13 26.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677507 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

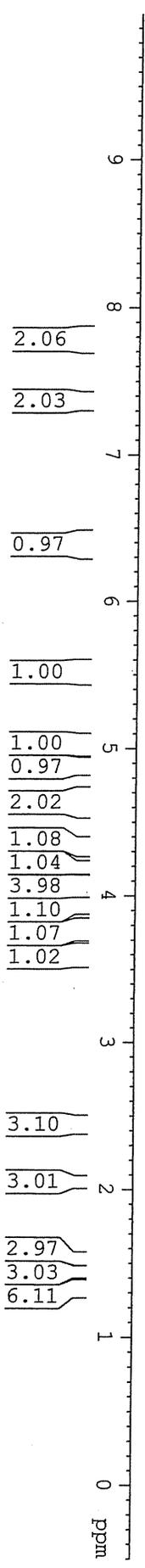


IV-CMR-55
 F22-29
 June 27, 2008

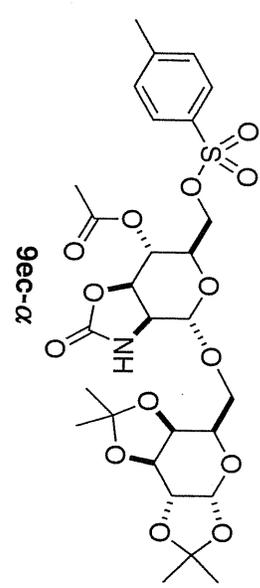


```

NAME IV-CMR-55
EXPNO 2
PROCNO 1
Date_ 20080627
Time 13.27
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.50 usec
TE 294.7 K
D1 1.00000000 sec
TDO 1
===== CHANNEL f1 =====
NUC1 1H
P1 6.56 usec
PL1 3.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1299994 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
  
```



IV-CMR-55
F22-29
June 27, 2008



NAME IV-CMR-55
EXPNO 3
PROCNO 1
Date_ 20080627
Time 14.03
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 294.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 6.00 dB
SFO1 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 81.00 usec
PL2 3.00 dB
PL12 26.00 dB
PL13 26.00 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677548 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

- 169.39
- 158.44
- 145.00
- 132.34
- 129.82
- 128.02
- 109.52
- 108.65
- 96.24
- 95.92
- 77.42
- 77.00
- 76.58
- 75.76
- 70.90
- 70.58
- 70.31
- 68.10
- 67.94
- 66.52
- 65.73
- 65.64
- 55.65
- 25.93
- 24.81
- 24.45
- 21.60
- 20.63

