# *N*-glycosylation of sulfoxides donors for the synthesis of peptidonucleosides

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## Supplementary Information



# Experimental procedures

**General**

All non-aqueous reactions were run under an inert atmosphere (argon), by using standard techniques for manipulating air-sensitive compounds and the glassware was stored in the oven prior to use. All reagents and solvents were commercially available and were used without further purification. Molecular sieves 4 Å were used as a powder and were activated overnight at 250 °C and under reduced pressure, in a Kugelrohr apparatus or with a micro-wave for 45 seconds. Reactions were monitored with analytical Merck TLC silica gel 60 F254 plates and visualized under UV (254 nm) and stained with $KMNO_4$ or vanillin. Column chromatography was done with Merck Geduran silical gel Si 60 (40-63 µm) and Redisep Rf columns (silica gel Si 60 , 40-63 µm) on an Interchim puriFlash® apparatus and on a Teledyne Isco combiflash Rf. Preparative thin-layer chromatography was performed on silica gel 60 F254 0.5 mm 20×20 cm plates and visualised under UV (254 nm). Deuterated chloroform used for NMR analyses was generally neutralized by addition of anhydrous and granular $K_2CO_3$. NMR spectra were recorded with AM 300, AVANCE 300 and AVANCE 500 Brüker spectrometers. Chemical shifts are given in parts per million, referenced to the solvent peak of $CDCl_3$, defined at 77.2 ppm ($^{13}$C NMR) and 7.26 ppm ($^{1}$H NMR) or to the solvent peak of $CD_3OD$, defined at 49.9 ppm ($^{13}$C NMR) and 3.34 ppm ($^{1}$H NMR) or to the solvent peak of $D_2O$, defined at 4.79 ppm ($^{1}$H NMR) or to the solvent peak of DMSO-$d_6$, defined at 39.5 ppm ($^{13}$C NMR) and 2.50 ppm ($^{1}$H NMR). Data are reported as follow: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, bs = broad singlet), coupling constant (in Hz) and integration. IR spectra were recorded on a Perkin-Elmer Spectrum BX instrument with an FT-IR system. Optical rotation were measured on an Anton Paar MCP300 polarimeter using a cell of 1-dm-length path. Mass spectra were recorded with Waters Micromass LCT Premier mass spectrometer.

**Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-galactopyranoside 2a**. According to the procedure of Ferro *et al*,[1] a suspension of methyl α-D-galactopyranoside (5.0 g, 25.75 mmol, 1.0 eq.), camphor-10-sulfonic acid (119.6 mg, 0.52 mmol, 0.02 eq.) and benzaldehyde dimethyl acetal (5.4 mL, 36.05 mmol, 1.4 eq.) in dry chloroform (400 mL) under argon atmosphere was stirred for 24 h at 80 °C. Solvent was then removed and the residue was diluted in EtOAc (75 mL), neutralized with triethylamine then washed with water (75 mL). Aqueous phase was extracted with EtOAc (10 x 50 mL). The organic layers were combined, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to afford the pure 4,6-*O*-benzylidene acetal intermediate (6.52 g, 23.12 mmol, 90%) as a white powder. 1H-NMR ($CDCl_3$, 500 MHz) δ 7.53-7.46 (m, 2H, $H_{Ar}$), 7.41-7.34 (m, 3H, $H_{Ar}$), 5.56 (s, 1H, PhC*H*), 4.94 (d, 1H, *J* = 1.0 , 3.0 Hz, *H*1), 4.34-4.25 (m, 2H, *H*6, *H*4), 4.09 (dd, 1H, *J* = 2.0 and 12.6 Hz, Hz, H6a), 3.95-3.87 (m, 2H, *H*2, *H*3), 3.73-3.70 (m, 1H, *H*5), 3.48 (s, 3H, OC$H_3$), 2.37 (bs, 1H, O*H*), 2.11 (bs, 1H, O*H*).[2] To a stirred

[1] V. Ferro, M. Mocerino, R. V. Stick and D. M. G. Tilbrook, *Austr. J. Chem.*, 1988, **41**, 813.
[2] Experimental data are in agreement with those reported in the literature : A. H. Viuff, L. M. Besenbacher, A. Kamori, M. T. Jensen, M. Kilian, A. Kato and H. H. Jensen, *Org. Biomol. Chem.*, 2015, **13**, 9637.

solution of the 4,6-*O*-benzylidene acetal (2.47 g, 8.76 mmol, 1 eq.) in pyridine (14 mL) was added acetic anhydride (6.62 mL, 70.1 mmol, 8 eq.). The resulting mixture was stirred at room temperature for 12 h. Solvent was then removed and the residue was co-evaporated with toluene (3 x 20 mL). The crude product was purified by flash chromatography on silica gel (Heptane/EtOAc 70:30 to 60:40) to afford product **2a** (3.20 g, 8.74 mmol, quantitative) as a white powder. $[\alpha]_D^{25}$ + 202.3 ($c$ = 0.6, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.53-7.46 (m, 2H, $H_{Ar}$), 7.41-7.31 (m, 3H, $H_{Ar}$), 5.50 (s, 1H, *H*7), 5.35 (dd, 1H, $J_{2,1}$= 3.0 Hz, $J_{2,3}$= 10.5 Hz, *H*2), 5.30 (dd, 1H, $J_{3,4}$= 2.5 Hz, $J_{3,2}$= 10.5 Hz, *H*3), 5.07 (d, 1H, $J_{1,2}$= 3.0 Hz, *H*1), 4.45 (d, 1H, $J_{4,3}$= 2.5 Hz, *H*4), 4.27 (dd, 1H, $J_{6,5}$= 1.5 Hz, $J_{6,6'}$= 12.5 Hz, *H*6), 4.05 (dd, 1H, $J_{6',5}$= 1.5 Hz, $J_{6',6}$= 12.5 Hz, *H*6'), 3.74 (m, 1H, *H*5), 3.40 (s, 3H, OC$H_3$), 2.07 (s, 3H, OCOC$H_3$), 2.06 (s, 3H, OCOC$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.9 (*C*=O), 170.4 (*C*=O), 137.7 (*C*$q_{Ar}$) 129.2 (*C*$H_{Ar}$), 128.4 (*C*$H_{Ar}$), 126.4 (*C*$H_{Ar}$), 101.1 (*C*7), 98.0 (*C*1), 74.1 (*C*4), 69.3 (*C*6), 68.8 (*C*3), 68.3 (*C*2), 62.2 (*C*5), 55.7 (O*C*$H_3$), 21.2 (OCO*C*$H_3$), 21.1 (OCO*C*$H_3$). IR ν (film, $cm^{-1}$) 2914 (=C-H), 2866 ($CH_3$), 1746 (C=O); ESIHRMS *m/z* = 389.1214 $[M+Na]^+$. $C_{18}H_{22}O_8Na$ requires 389.1212.

**Methyl 2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-galactopyranoside 3a**. A solution of **2a** (2.72 g, 7.4 mmol, 1 eq.) and 4Å molecular sieves (5 g) in dry $CH_2Cl_2$ (50 mL) was stirred for 1 h at room temperature under argon atmosphere. The mixture was cooled to –78 °C and $Et_3SiH$ (1.18 mL, 7.4 mmol, 1 eq.) and TfOH (330 µL, 3.7 mmol, 0.5 eq.) were added successively. After being stirred for 15 min at –78 °C, $Et_3SiH$ (1eq.) and TfOH (0.5 eq) were added again. After 15 min on same conditions, new additions of $Et_3SiH$ (0.5 eq.) and TfOH (0.5 eq.) were done. Finally, after again 15 min, a final addition of TfOH (0.5 eq.) was realized. The resulting mixture was stirred at –78°C for 30 min then diluted with $CHCl_3$ (20 mL) and poured in saturated aqueous solution of sodium bicarbonate (40 mL). The organic layer was extract with $CHCl_3$ (3 x 25 mL), dried over $Na_2SO_4$, filtered and concentrated under vacuum. The crude mixture was directly dissolved in MeCN (25 mL) and treated with a diluted aqueous solution of $HBF_4$ (0.25 M, 25 mL). The resulting solution was stirred at room temperature for 1h30 and then quenched with saturated solution of $NaHCO_3$ until neutralization. Aqueous layer was extracted with EtOAc (3 x 15 mL). Organic layers were dried over $Na_2SO_4$, filtered and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (Heptane/EtOAc 90:10 to 60:40) to afford the clean product **3a** (1.52 g, 4.1 mmol, 63%) as a colorless oil. $[\alpha]_D^{25}$ +119.6 ($c$ = 0.9, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.36-7.26 (m, 5H, $H_{Ar}$), 5.30 (dd, 1H, $J_{2,1}$ = 3.0 Hz, $J_{2,3}$= 10.5 Hz, *H*2), 5.24 (dd, 1H, $J_{3,4}$ = 2.5 Hz, $J_{3,2}$ = 10.5 Hz, *H*3), 5.00 (d, 1H, $J_{1,2}$ = 3.0 Hz, *H*1), 4.60 (d, 1H, $J_{H,H}$ = 12.0 Hz, C$H_2$Ph) 4.54 (d, 1H, $J_{H,H}$ = 12.0 Hz, C$H_2$Ph), 4.24 (m, 1H, *H*4), 3.97 (t, 1H, $J_{5,4}$ = $J_{5,6}$ = 4.5 Hz, *H*5), 3.78 (dd, 1H, $J_{6,5}$ = 4.5 Hz, $J_{6,6}$ = 10.0 Hz, *H*6), 3.73 (dd, 1H, $J_{6',5}$ = 4.5 Hz, $J_{6',6}$ = 10.0 Hz, *H*6'), 3.38 (s, 3H, OC$H_3$), 3.01 (bs, 1H, O*H*), 2.08 (s, 3H, OCOC$H_3$), 2.06 (s, 3H, OCOC$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.6 (*C*=O), 170.3 (*C*=O), 137.5 (*C*$q_{Ar}$), 128.7 (*C*$H_{Ar}$), 128.1 (*C*$H_{Ar}$), 127.9 (*C*$H_{Ar}$), 97.6 (*C*1), 74.1 (*C*$H_2$Ph), 70.4 (*C*2), 70.4 (*C*6), 69.4 (*C*4), 68.5 (*C*3), 68.1 (*C*5), 55.6 (O*C*$H_3$), 21.2 (OCO*C*$H_3$), 21.1 (OCO*C*$H_3$); IR ν (film, $cm^{-1}$) 3466 (O-H), 2934 (=C-H), 1738 (C=O); ESIHRMS *m/z* = 391.1369 $[M+Na]^+$. $C_{18}H_{24}O_8Na$ requires 391.1369.

**Methyl 2,3-di-*O*-acetyl-4-azido-6-*O*-benzyl-α-D-glucopyranoside 4a**. Galactopyranose **3a** (77 mg, 0.209 mmol, 1 eq.) was co-evaporated 2 times with toluene (5 mL) and then diluted in dry $CH_2Cl_2$ (C = 0.1 M, 2 mL) under argon atmosphere. Pyridine (0.18 mL, 2.29 mmol, 11 eq.) was added and the mixture was cooled to 0 °C. Triflic anhydride (70 µL, 0.418 mmol, 2 eq.) was added and the mixture stirred for 90 min at 0 °C. The mixture was quenched by addition of 10% aqueous $NaHCO_3$ solution (20 mL), the phases were separated and the organic layer was extracted with 3% hydrochloric acid (3 x 10 mL), with water (10 mL), dried over $Na_2SO_4$ and was concentrated under vacuum. The resulting crude product was co-evaporated with toluene (3 x) to remove all traces of pyridine and dried for 1 h under vacuum. The yellow residue was dissolved in dry DMF (2.4 mL), sodium azide (332 mg, 5.12 mmol, 12 eq.) was added, and the reaction mixture was stirred overnight. The mixture was diluted with water and EtOAc (15 mL) and the phases were separated. The organic phase was washed with brine (3 x 15 mL), dried over $Na_2SO_4$ and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (Heptane/EtOAc 90:10 to 80:20) to afford **4a** (69 mg, 0.175 mmol, 84%) as a colorless oil. $[\alpha]_D^{25}$ + 136.2 ($c$ = 0.6, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.39-7.26 (m, 5H, $H_{Ar}$), 5.41 (t, 1H, $J_{3,2}$ = 10.0 Hz, *H*3), 4.91 (d, 1H, $J_{1,2}$ = 4.0 Hz, *H*1), 4.85 (dd, 1H, $J_{2,1}$ = 4.0 Hz, $J_{2,3}$ = 10.0 Hz, *H*2), 4.65 (d, 1H, $J_{H,H}$= 12.0 Hz, C$H_2$Ph) 4.54 (d, 1H, $J_{H,H}$= 12.0 Hz, C$H_2$Ph), 3.79 (t, 1H, $J_{4,3}$ = $J_{4,5}$ = 10.0 Hz, *H*4), 3.74-3.41 (m, 3H, *H*5, *H*6, *H*6'), 3.36 (s, 3H, OC$H_3$), 2.08 (s, 3H, OCOC$H_3$), 2.05 (s, 3H, OCOC$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.5 (*C*=O), 170.0 (*C*=O), 137.8 (*C*$q_{Ar}$), 128.7 (*C*$H_{Ar}$), 128.0 (*C*$H_{Ar}$), 128.0 (*C*$H_{Ar}$), 97.3 (*C*1), 73.8 (*C*$H_2$Ph), 71.2 (*C*2), 70.9 (*C*3), 69.3 (*C*5), 68.5 (*C*6), 60.2 (*C*4), 55.6 (O-*C*$H_3$), 21.0 (OCO*C*$H_3$), 21.0 (OCO*C*$H_3$); IR ν (film, $cm^{-1}$) 2935 ($CH_2$), 2106 ($N_3$), 1746 (C=O); ESIHRMS *m/z* = 457.1712 $[M+ CH_3CN +Na]^+$. $C_{20}H_{26}N_4O_7Na$ requires 457.1699.

**1,2,3,6-Tetra-*O*-acetyl-4-azido-α-D-glucopyranose 5**. To a stirred solution of **4a** (57 mg, 0.16 mmol, 1 eq.) in acetic anhydride (0.5 mL) was added dropwise at 0 °C $H_2SO_4$ (10 µL). The resulting mixture was stirred overnight at room temperature and then diluted by cold water. After being stirred for 1 h, the phases were separated and the

aqueous phase was extracted with EtOAc (3 x 2 mL). Organic layers were combined, neutralized with aqueous $NaHCO_3$ (4 mL), then washed with brine (2 x 3 mL), dried over $Na_2SO_4$ and evaporated under vacuum. The residue was then purified by flash chromatography on silica gel (Heptane/EtOAc 70:30 to 60:40) to afford clean product **5** (α/β 8:2) (43 mg, 0.12 mmol, 73%) as a colorless oil. For the major α anomer: $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 6.31 (d, $J$ = 3.5 Hz, 1H, $H1$), 5.49 (t, $J$ = 10.0 Hz, 1H, $H4$), 5.07 (dd, $J$ = 10.5 and 3.5 Hz,1H, $H2$), 4.37 (dd, $J$ = 12.0 and 4.5 Hz, 1H, $H6$), 4.29 (dd, $J$ = 12.0 and 4.0 Hz, 1H, $H6$), 3.95-3.85 (m, $H5$), 3.71 (t, $J$ = 10.5 Hz, 1H, $H3$), 2.19−2.04 (4s,12H, $COCH_3$).[3]

**2,3,6-Tri-*O*-acetyl-4-azido-D-glucopyranose 5-OH**. To a stirred solution of **5** (1 eq., 50 mg, 0.13 mmol) in THF (1.3 mL) was added benzylamine (1.5 eq., 22 µL, 0.20 mmol) and the resulting mixture was stirred at room temperature for 14 h under inert atmosphere. After addition of 1 N HCl (0.1 mL), the reaction mixture was stirred for one more hour. The reaction mixture was diluted with 1 N HCl (6 mL) and extracted with $CH_2Cl_2$ (3 x 8 mL). The combined extracts were dried over anhydrous $Na_2SO_4$ and concentrated under reduce pressure. The residue was purified by flash chromatography on silica gel (Heptane/EtOAc 70:30 to 40:60) to give the corresponding hemiacetal **5-OH** (28 mg, 0.085 mmol, 63%, α/β = 70:30) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.51 (t, 0.7H, $J_{3,2} = J_{3,4} = 10.0$ Hz, $H3\alpha$), 5,38 (bs, 0.7H, $H1\alpha$), 5.19 (t, 0.3H, $J_{3,2} = J_{3,4} = 9.5$ Hz, $H3\beta$), 4.82 (dd, 0.7H, $J_{2,3} = 10.0$ Hz, $J_{2,1} = 3.5$ Hz, $H2\alpha$), 4.80 (dd, 0.3H, $J_{2,3} = 9.5$ Hz, $J_{2,1} = 8.0$ Hz, $H2\beta$), 4.70 (t, 0.3H, $J_{1,2} = 7.0$ Hz, $H1\beta$), 4.39 (dd, 0.3H, $J_{6,6'} = 12.0$ Hz, $J_{6,5} = 2.5$ Hz, $H6\beta$), 4.37 (dd, 0.7H, $J_{6,6'} = 12.0$ Hz, $J_{6,5} = 2.5$ Hz, $H6\alpha$), 4.22 (dd, 1H, $J_{6',6} = 12.0$ Hz, $J_{6',5} = 4.0$ Hz, $H6'\beta$, $H6'\alpha$), 4.02 (ddd, 0.7H, $J_{5,4} = 10.0$ Hz, $J_{5,6'} = 4.0$ Hz, $J_{5,6} = 2.5$ Hz, $H5\alpha$), 3.63 (t, 0.3H, $J_{4,3} = J_{4,5} = 10$ Hz, $H4\beta$), 3.58 (t, 0.7H, $J_{4,3} = J_{4,5} = 10.0$ Hz, $H4\alpha$), 3.48 (ddd, 0.3H, $J_{5,4} = 10.0$ Hz, $J_{5,6'} = 4.0$ Hz, $J_{5,6} = 2.5$ Hz, $H5\beta$), 2.10 (s, 3H, $OCOCH_3$), 2.09 (s, 3H, $OCOCH_3$), 2.06 (s, 3H, $OCOCH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.9 ($C$=O), 170.8 ($C$=O), 170.7 ($C$=O), 170.4 ($C$=O), 169.9 ($C$=O), 95.5 ($C1\beta$), 90.6 ($C1\alpha$), 73.5 ($C2\beta$), 73.2 ($C3\beta$), 72.5 ($C5\beta$), 71.5 ($C2\alpha$), 70.6 (C3α), 67.8 ($C5\alpha$), 63.0 ($C6\beta$), 62.8 ($C6\alpha$), 60.4 ($C4\beta$), 60.3 ($C4\alpha$), 21.0 ($COCH_3$) 20.9 ($COCH_3$), 20.8 ($COCH_3$); IR ν (film, cm$^{-1}$) 3458 (O-H), 2960 ($CH_3$), 2108 ($N_3$), 1739 (C=O); ESIHRMS $m/z$ = 354.0903 $[M+Na]^+$. $C_{12}H_{17}N_3O_8Na$ requires 354.0913.

**1-*O*-(*ortho*-Hexynylbenzoyl)-2,3,4-tri-*O*-acetyl-4-azido-D-glucopyranose 6**. To a stirred solution of **5-OH** (1 eq., 28 mg, 0.08 mmol) and *ortho*-(hex-1-yn-1-yl)benzoic acid (1.2 eq., 20 mg, 0.10 mmol), in $CH_2Cl_2$ (0.3 mL) were added DCC (1.5 eq., 26 mg, 0.13 mmol) and DMAP (1.5 eq., 15 mg, 0.13 mmol) under inert atmosphere. After being stirred for 3 h at room temperature, the reaction mixture was diluted with $CH_2Cl_2$ (1 mL) and washed with saturated aqueous $NaHCO_3$ (1 mL) and brine (1 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Heptane/EtOAc 90:10 to 70:30) to provide **6** (36 mg, 84%; α/β = 3:6) as a white solid. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.93-7.79 (m, 1H, $H_{Ar}\alpha$, $H_{Ar}\beta$), 7.53-7.21 (m, 3H, $H_{Ar}\alpha$, $H_{Ar}\beta$), 6.51 (d, 0.4H, $J_{1,2} = 3.5$ Hz, $H1\alpha$), 5.86 (d, 0.6H, $J_{1,2} = 8.0$ Hz, $H1\beta$), 5.55 (t, 0.4H, $J_{3,2} = J_{3,4} = 10.0$ Hz, $H3\alpha$), 5.23 (t, 0.6H, $J_{3,2} = J_{3,4} = 9.0$ Hz, $H3\beta$), 5.16 (dd, 0.6H, $J_{2,1} = 8.0$ Hz, $J_{2,3} = 9.0$ Hz, $H2\beta$), 5.09 (dd, 0.4H, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.0$ Hz, $H2\alpha$), 4.37-4.20 (m, 2H, $H6\alpha$, $H6'\alpha$, $H6\beta$, $H6'\beta$), 4.03-3.94 (m, 0.4H, $H5\alpha$), 3.72 (t, 0.6H, $J_{4,3} = J_{4,5} = 9.0$ Hz, $H4\beta$), 3.69 (t, 0.4H, $J_{4,3} = J_{4,5} = 10.0$ Hz, $H4\alpha$), 3.65-3.58 (m, 0.6H, $H5\beta$), 2.50-2.36 (m, 2H, $H7$), 2.07 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 1.93 (s, 1.2H, $COCH_3\alpha$), 1.92 (s, 1.8H, $COCH_3\beta$), 1.64-1.49 (m, 2H, $H8$), 1.49-1.34 (m, 2H, $H9$), 0.88 (t, 3H, $J_{CH3,9} = 7.0$ Hz, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.7 ($C$=O), 170.2 ($C$=O), 170.0 ($C$=O), 169.9 ($C$=O), 164.2 ($C$q), 163.3 ($C$q), 135.4 ($CH_{Ar}$), 135.0 ($CH_{Ar}$), 132.8 ($CH_{Ar}$), 132.7 ($CH_{Ar}$), 130.9 ($CH_{Ar}$), 129.8 ($Cq_{Ar}$), 129.2 ($Cq_{Ar}$), 127.6 ($CH_{Ar}$), 127.4 ($CH_{Ar}$), 126.1 ($Cq_{Ar}$), 125.5 ($Cq_{Ar}$), 97.7 ($Cq_{alkyne}$), 97.5 ($Cq_{alkyne}$), 92.1 ($C1\beta$), 90.1 ($C1\alpha$), 79.8 ($Cq_{alkyne}$), 79.1 ($Cq_{alkyne}$), 73.7 ($C3\beta$), 73.1 ($C5\beta$), 70.8 ($C3\alpha$), 70.6 ($C2\beta$, C5α), 69.7 ($C2\alpha$), 62.7 ($C6\beta$), 62.5 ($C6\alpha$), 60.2 ($C4\beta$), 60.0 ($C4\alpha$), 30.9 ($C8\beta$), 30.8 ($C8\alpha$), 22.3 ($C9\beta$, $C9\alpha$), 20.9 ($COCH_3$), 20.9 ($COCH_3$), 20.8 ($COCH_3$), 20.7 ($COCH_3$), 20.7 ($COCH_3$), 19.8 ($C7\beta$), 19.7 ($C7\alpha$), 13.9 ($CH_3\beta$), 13.8 ($CH_3\alpha$); IR ν (film, cm$^{-1}$) 2959 ($CH_3$), 2935 ($CH_2$), 2229 (alkyne), 2110 ($N_3$), 1745 (C=O); ESIHRMS $m/z$ = 538.1804 $[M+Na]^+$. $C_{25}H_{29}N_3O_9Na$ requires 538.1801.

**Phenyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-thio-β-D-galactopyranoside 2b**. To a stirred solution of Na (52 mg, 20 mol%) in dry MeOH (113 mL) was added phenyl 2,3,4,6-tetra-*O*-acetyl-thio-β-D-galactoside (5 g, 11.35 mmol, 1 eq.) under argon atmosphere. The resulting mixture was stirred at room temperature for 2 h and then neutralized with Dowex® $H^+$, filtered on celite®, concentrated under reduced pressure and co-evaporated with toluene to afford the deprotected adduct **1b**. This latter (3.03 g, 11.3 mmol, 1 eq.) was then dissolved in dry MeCN (24 mL) then benzaldehyde dimethyl acetal (2.7 mL, 17.8 mmol, 1.6 eq.) and *p*-TsOH (15 mol%, 300 mg) were added. The mixture was stirred at room temperature for 2 h under argon atmosphere and then neutralized with $Et_3N$ (2 mL).

[3] Experimental data agree with those reported in the literature : Z. Lei, J. Wang, G. Mao, Y. Wen, Y. Tian, H. Wu, Y. Li and H. Xu, *J Agric Food Chem*, 2014, **62**, 6065.

Water (30 mL) and EtOAc (50 mL) were added and the aqueous layer was extracted with EtOAc (2 x 50 mL). Organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The crude product was recrystallized with heptane/EtOAc 70:30 to afford the desired compound (3.3 g, 82%) as a white solid.[4] The obtained product (3.27 g, 11.1 mmol, 1 eq.) was dissolved in pyridine (12 mL). $Ac_2O$ (6 mL) was added and the mixture was stirred at room temperature overnight. Pyridine was co-evaporated with toluene. The crude product was recrystallized with Heptane/EtOAc 55/45 to afford **2b** (3.61 g, 73%) as a white solid. 1H NMR ($CDCl_3$) $\delta$ 7.70–7.19 (m, $10H_{Ar}$), 5.49 (s, 1H, PhC*H*), 5.36 (t, $J$ = 10.0 Hz, 1H, *H*2), 5.02 (dd, $J$ = 10.0 and 3.5 Hz, 1H, *H*3), 4.73 (d, $J$ = 10.0 Hz,1H, *H*1), 4.44-4.36 (m, 2H, *H*4 and *H*6), 4.04 (dd, $J$ =12.5 and 1.5 Hz, 1H, *H*6), 3.64–3.60 (m, 1H, *H*5), 2.08, 2.02 (2s, 6H, 2 $COCH_3$).[5]

**Phenyl 2,3-di-*O*-acetyl-6-*O*-benzyl-thio-β-D-galactopyranoside 3b.** A solution of **2b** (5.0 g, 11.2 mmol, 1 eq.) in dry MeCN (110 mL) was cooled to 0 °C and $Et_3SiH$ (10.8 mL, 67.4 mmol, 1 eq.) was added, followed by the addition of $Cu(OTf)_2$ (200 mg, 0.56 mmol, 0.05 eq.). The resulting mixture was stirred at 0 °C for 1 h and then hydrolysed with a saturated solution of $NaHCO_3$ (60 mL). The phases were separated and organic layer was dried over $Na_2SO_4$, filtered and concentrated under vacuum. The desired product was obtained in mixture with the silylated one (6.28 g, ratio 30:70). The crude mixture was directly dissolved in MeCN (20 mL) and treated with a diluted aqueous solution of $HBF_4$ (C = 0.25 M, 20 mL). The resulting solution was stirred at room temperature for 1.5 h and then quenched with saturated solution of $NaHCO_3$ until neutralization. Aqueous layer was extracted with EtOAc (3 x 15 mL). Organic layers were dried over $Na_2SO_4$, filtered and concentrated under vacuum. The crude product was purified by flash chromatography (Heptane/EtOAc 90:10 to 40:60) to afford product **3b** (4.43 g, 9.93 mmol, 88%) as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) $\delta$ 7.54 (dd, $J$ = 6.5, 3.0 Hz, 2H), 7.41 – 7.11 (m, 8H), 5.33 (t, $J$ = 10.0 Hz, 1H), 4.98 (dd, $J$ = 10.0 and 3.0 Hz, 1H), 4.71 (d, $J$ = 10.0 Hz, 1H), 4.64 – 4.22 (m, 2H), 4.25 – 4.16 (m, 1H), 3.84 – 3.72 (m, 2H), 2.64 (d, $J$ = 4.0 Hz, 1H), 2.10 (s, 6H).[6]

**Phenyl 2,3-di-*O*-acetyl-4-azido-6-*O*-benzyl-thio-β-D-glucopyranoside 4b**. **3b** (500 mg, 1.12 mmol, 1 eq.) was co-evaporated 2 times with toluene (5 mL) and then diluted in dry $CH_2Cl_2$ (C = 0.1 M, 11.2 mL) under argon atmosphere. Pyridine (1.0 mL, 12.32 mmol, 11 eq.) was added and the mixture was cooled to 0 °C. Triflic anhydride (280 µL, 1.68 mmol, 2 eq.) was added and the mixture stirred for 90 min at 0 °C. The mixture was quenched by addition of 10% aqueous $NaHCO_3$ solution (50 mL), the phases were separated and the organic layer was extracted with 3% hydrochloric acid (3 x 20 mL), with water (20 mL), dried over $Na_2SO_4$ and was concentrated under vacuum. The resulting crude product was co-evaporated with toluene (3 x) to remove all traces of pyridine and dried for 1 h under vacuum. The yellow residue was dissolved in dry DMF (10 mL), sodium azide (1.6 g, 25.0 mmol, 12 eq.) was added, and the reaction mixture was stirred overnight. The mixture was diluted with water and EtOAc (20 mL) and the phases were separated. The organic phase was washed with brine (3 x 30 mL), dried over $Na_2SO_4$ and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (Heptane/EtOAc 90:10 to 80:20) to afford product **4b** (347 mg, 0.736 mmol, 66%) as a colorless oil. $[\alpha]_D^{25}$ – 4.4 ($c$ =1.1, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.42-7.34 (m, 2H, $H_{Ar}$), 7.30-7.09 (m, 8H, $H_{Ar}$), 5.04 (dd, 1H, $J_{3,2}$ = 9.5 Hz and $J_{3,4}$ = 10.0 Hz, *H*3), 4.79 (dd, 1H, $J_{2,1}$ = 10.0 Hz and $J_{2,3}$ = 9.5 Hz, *H*2), 4.56 (d, 1H, $J_{1,2}$ = 10.0 Hz, *H*1), 4.52 (d, 1H, $J_{H,H}$ = 12.0 Hz, C$H_2$Ph), 4.45 (d, 1H, $J_{H,H}$ = 12.0 Hz, C$H_2$Ph), 3.69 (dd, 1H, $J_{6,6'}$ = 11.0 Hz and $J_{6,5}$ = 2.0 Hz, *H*6), 3.64 (t, 1H, $J_{4,3}$ = $J_{4,5}$ = 10.0 Hz, *H*4) 3.62 (dd, 1H, $J_{6',6}$ = 11.0 Hz, $J_{6',5}$ = 4.0 Hz, *H*6'), 3.31 (ddd, 1H, $J_{5,4}$ = 10.0 Hz, $J_{5,6'}$ = 4.0 Hz and $J_{5,6}$ = 2.0 Hz, *H*5), 1.96 (s, 6H, C$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.2 (*C*=O), 169.7 (*C*=O), 138.0 ($Cq_{Ar}$), 133.3 ($CH_{Ar}$), 132.0 ($Cq_{Ar}$), 129.2 ($CH_{Ar}$), 128.6 ($CH_{Ar}$), 128.5 ($CH_{Ar}$), 128.0 ($CH_{Ar}$), 127.9 ($CH_{Ar}$), 85.9 (*C*1), 78.4 (*C*5) 75.0 (*C*3), 73.8 (*C*$H_2$Ph), 70.4 (*C*2), 69.0 (*C*6), 60.0 (*C*4), 21.0 (CO*C*$H_3$), 20.9 (CO*C*$H_3$); IR ν (film, $cm^{-1}$) 3122 (=C-H), 2926 (-$CH_2$), 2110 ($N_3$), 1752 (C=O); ESIHRMS *m/z* = 494.1360 $[M+Na]^+$. $C_{23}H_{25}N_3O_6SNa$ requires 494.1362.

**Phenyl 2,3,6-tri-*O*-acetyl-4-azido-thio-β-D-glucopyranoside**. To a stirred solution of **4b** (1.48g, 3.14 mmol, 1 eq.) in dry acetic anhydride (5.6 mL) at 0 °C was added dropwise a solution of NaI (471 mg, 3.14 mmol, 1 eq) in MeCN (1.9 mL) followed by $BF_3$•$OEt_2$ (1.16 mL, 4.71 mmol, 1.5 eq). After completion of the reaction, the reaction mixture was quenched with aqueous $Na_2S_2O_3$ until neutralization and extracted with EtOAc (15 mL). The organic layer was washed with water (3 x 15 mL), brine (3 x 15 mL), dried over $Na_2SO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography (Heptane/EtOAc 90:10 to 75:25) to afford the desired

[4] Experimental data agree with those reported in the literature: M. C. Andersen, S. K. Kracun, M. G. Rydahl, W. G. Willats and M. H. Clausen, *Chem. Eur. J.*, 2016, **22**, 11543.
[5] Experimental data agree with those reported in the literature: P. Tiwari and A. K. Misra, *Carbohydr. Res.*, 2006, **341**, 339.
[6] Experimental data agree with those reported in the literature: S. Dara, V. Saikam, M. Yadav, P. P. Singh and R. A. Vishwakarma, *Carbohydr Res*, 2014, **391**, 93.

clean product (0.8242 g, 62%) as a colorless oil. $[\alpha]_D^{25}$ – 2.80 (*c*=1, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) : 7.56-7.44 (m, 2H, $H_{Ar}$), 7.37-7.28 (m, 3H, $H_{Ar}$), 5.21 (t, 1H, $J_{2,3}$=$J_{3,4}$=10.5 Hz, $H_3$), 4.91 (t, 1H, $J_{1,2}$=$J_{2,3}$= 10.5 Hz, $H_2$), 4.68 (d, 1H, $J_{1,2}$= 10.5 Hz, $H_1$), 4.52-4.45 (dd, 1H, $J_{6,6'}$=12.5 Hz and $J_{6,5}$= 2.0 Hz, $H_6$), 4.30-4.21 (dd, 1H, $J_{6,6'}$=12.5 Hz and $J_{6',5}$= 5.0 Hz, $H_{6'}$) 3.64 (t, 1H, $J_{4,5}$=$J_{3,4}$=10.0 Hz, $H_4$), 3.54-3.46 (ddd, 1H, $J_{4,5}$=10.2 Hz, $J_{6',5}$=5.0 Hz and $J_{6,5}$=2.0 Hz, $H_5$), 2.13 (s, 3H, C$H_3$), 2.12 (s, 3H, C$H_3$), 2.11 (s, 3H, C$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) : 170.38 (*C*=O), 169.87 (*C*=O), 169.48 (*C*=O), 133.4 (2**C*$H_{Ar}$), 128.9 (2**C*$H_{Ar}$), 128.5 ($Cq_{Ar}$), 85.6 (*C*1), 75.9 (*C*5), 74.7 (*C*3), 69.8 (*C*2), 62.8 (*C*6), 59.9 (*C*4), 20.8 (CO*C*$H_3$), 20.6 (CO*C*$H_3$); IR ν (film, $cm^{-1}$) : 2952 (-CH2), 2109 (N3), 1745 (C=O); ESIHRMS *m/z* = 446.1004 $[M+Na]^+$. $C_{18}H_{21}N_3O_7SNa$ requires 446.0998.

**2,3,6-Tri-*O*-acetyl-4-azido-β-D-glucopyranosyl phenyl sulfoxide 7**. To a stirred solution the previous described sulfide compound (1.4 g, 3.27 mmol, 1 eq.) in $CH_2Cl_2$ (31 mL) was added *m*-CPBA (75%, 0.85 g, 3.92 mmol, 1.2 eq.) at -78 °C under argon atmosphere. The resulting mixture was stirred at -30 °C overnight and a solution of aqueous $Na_2S_2O_3$/$NaHCO_3$ 50:50 (20/20 mL) was then added. The solution was allowed to warm at room temperature, extracted with EtOAc (2 x 30 mL). Organics layers were dried over $Na_2SO_4$, filtered and concentrated under vacuum. The crude product was purified by flash chromatography (Heptane/EtOAc 80:20 to 50:50) to afford the clean product **7** as a mixture of two diastereoisomers (dr = 1:1, 1.2 g, 84%) as a colorless oil. $^1$H NMR (300 MHz, $CDCl_3$) : 7.71-7.50 (m, 10H, $H_{Ar}$), 5.40-5.14 (m, 4H, $H_2$, $H_3$), 4.51-4.44 (m, 2H, $H_6$), 4.31 (dd, 1H, $J_{6,6}$=12.0 Hz and $J_{6,5}$=1.5 Hz, $H_6$), 4.24 (d, 1H, $J_{2,1}$=9.5 Hz, $H_1$), 4.22-4.09 (m, 2H, $H_1$, $H_6$), 3.70-3.56 (m, 2H, $H_4$), 3.52-3.47 (m, 1H, $H_5$), 3.43-3.33 (m, 1H, $H_5$), 2.14 (s, 3H, C$H_3$), 2.12 (s, 3H, C$H_3$), 2.11 (s, 3H, C$H_3$), 2.08 (s, 3H, C$H_3$), 2.02 (s, 3H, C$H_3$), 1.86 (s, 3H, C$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) : 170.2 (*C*=O), 170.1 (*C*=O), 169.9 (*C*=O), 169.5 (*C*=O), 169.2 (*C*=O), 131.7 ($C_{Ar}$), 131.5 ($C_{Ar}$), 129.0 ($C_{Ar}$), 128.9 ($C_{Ar}$), 125.7 ($C_{Ar}$), 125.4 ($C_{Ar}$), 92.4 (*C*1), 90.1 (*C*1), 77.5 (*C*5), 77.0 (*C*5), 74.9 (*C*3), 74.6 (*C*3), 67.5 (*C*2), 67.1 (*C*2), 62.4 (*C*6), 62.2 (*C*6), 59.6 (*C*4), 59.3 (*C*4), 20.7 (CO*C*$H_3$), 20.6 (CO*C*$H_3$), 20.5 (CO*C*$H_3$); IR ν (film, $cm^{-1}$) : 2942 (-CH2), 2110 (N3), 1741 (C=O); ESIHRMS *m/z* = 901.2006 $[2M+Na]^+$. $C_{36}H_{42}N_6O_{16}S_2Na$ requires 901.2006.

**2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-β-D-glucopyranosyl phenyl sulfoxide 8**. To a stirred solution of **4b** (1.0 g, 2.12 mmol, 1 eq.) in $CH_2Cl_2$ (21 mL) was added *m*-CPBA (above 75%, 550 mg, 3.18 mmol, 1.5 eq.) at –78 °C under argon atmosphere. The resulting mixture was stirred at –30 °C overnight and dimethylsulfide (0.2 mL) was then added. The solution was allowed to warm at room temperature, diluted with $CH_2Cl_2$ (10 mL), washed with water (8 mL), with a saturated aqueous solution of $NaHCO_3$ (8 mL), with water again (8 mL) and finally with brine (8 mL). The organic phase was dried with $Na_2SO_4$, filtered and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (Heptane/EtOAc 80:20 to 60:40) to afford product **8** (914 mg, 1.875 mmol, 89%) as a colorless oil and as a mixture of two diastereoisomers (dr = 2:3). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.71-7.59 (m, 2H, $H_{Ar}$), 7.55-7.42 (m, 3H, $H_{Ar}$), 7.42-7.21 (m, 5H, $H_{Ar}$), 5.29 (t, 0.4H, $J_{2x,1x}$ = $J_{2x,3x}$ = 9.5 Hz, *H*2x), 5.24 (t, 0.6H, $J_{2y,1y}$ = $J_{2y,3y}$ = 9.0 Hz *H*2y), 5.19 (t, 0.4H, $J_{3x,2x}$ = $J_{3x,4x}$ = 9.5 Hz, *H*3x), 5.16 (t, 0.6H, $J_{3y,2y}$ = $J_{3y,4y}$ = 9.0 Hz, *H*3y), 4.56-4.36 (m, 2.6H, C$H_2$Ph, *H*1y), 4.25 (d, 0.4H, $J_{1x,2x}$ = 9.5 Hz, *H*1x), 3.82-3.69 (m, 2.2H, *H*6, *H*6'), 3.69-3.56 (m, 1H, *H*4), 3.48-3.38 (dt, 0.6H, $Jb_{5y,4y}$ = 10.0 Hz, $J_{5y,6'y}$ = 5.0 Hz and $J_{5y,6y}$ = 2.5 Hz, *H*5y), 3.36-3.24 (ddd, 0.4H, $Jb_{5x,4x}$ = 10.0 Hz, $J_{5x,6'x}$ = 6.0 Hz and $J_{5x,6x}$ = 4.0 Hz, *H*5x), 2.10 (s, 1.2H, OCOC$H_3$x), 2.08 (s, 1.8H, OCOC$H_3$y), 2.06 (s, 1.2H, OCOC$H_3$x), 1.83 (s, 1.8H, OCOC$H_3$y); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.4 (*C*=O), 170.3 (*C*=O), 169.7 (*C*=O), 169.4 (*C*=O), 139.6 ($Cq_{Ar}$), 139.0 ($Cq_{Ar}$), 137.8 ($Cq_{Ar}$), 137.7 ($Cq_{Ar}$), 131.8 (*C*$H_{Ar}$), 131.7 (*C*$H_{Ar}$), 129.2 (*C*$H_{Ar}$), 129.1 (*C*$H_{Ar}$), 128.6 (*C*$H_{Ar}$), 128.5 (*C*$H_{Ar}$), 128.1 (*C*$H_{Ar}$), 128.0 (*C*$H_{Ar}$), 127.9 (*C*$H_{Ar}$), 127.9 (*C*$H_{Ar}$), 125.8 (*C*$H_{Ar}$), 125.6 (*C*$H_{Ar}$), 93.0 (*C*1y), 90.5 (*C*1x), 79.3 (*C*5x), 79.0 (*C*5y), 75.1 (*C*2y), 74.8 (*C*3y), 73.8 (*C*$H_2$Ph), 68.6 (*C*6x), 68.4 (*C*6y), 67.8 (*C*2x), 67.4 (*C*3x), 59.4 (*C*4y), 59.2 (*C*4x), 20.9 (CO*C*$H_3$), 20.8 (CO*C*$H_3$), 20.7 (CO*C*$H_3$); IR ν (film, $cm^{-1}$) 2988 (=C-H), 2901 (-$CH_2$), 2110 ($N_3$), 1755 (C=O); ESIHRMS *m/z* = 510.1312 $[M+Na]^+$. $C_{23}H_{25}N_3O_7SNa$ requires 510.1311.

***N*-Acetyl-cytosine 9**. To a stirred solution of cytosine (500 mg, 4.5 mmol, 1eq.) in pyridine (2.5 mL) was added acetic anhydride (2.1 mL, 22.05 mmol, 5 eq.). The resulting mixture was stirred overnight at room temperature then diluted with EtOAc (2.0 mL) and stirred again for 30 min at room temperature. The resulting white solid was filtered, washed with EtOAc, co-evaporated with toluene and dried under vacuum to afford clean product **9** (0.6521 g, 95%) as a white solid. $^1$H NMR (DMSO-$d_6$) $\delta$ 11.50 (bs, 1H, N*H*), 10.75 (bs, 1H, NH), 7.80 (d, *J* = 7 Hz, C*H*-cytosine), 7.09, (d, *J* = 7 Hz, 1H, CH-cytosine), 2.08 (s, 3H, $CH_3$).[7]

***N*-Benzoyl-5-methyl-cytosine 10**.[8] To a suspension of 5-methyl-cytosine (1.5 g, 12 mmol, 1eq.) in dry MeCN (40 mL) was added benzoic anhydride (3.25 g, 14.4 mmol, 1.2 eq.) followed by DMAP (293 mg, 2.4 mmol, 0.2 eq.) under argon atmosphere. The resulting mixture was refluxed for 24 h then EtOH (25 mL) was added to the hot

[7] Prepared following H. Pelissier, J. Rodriguez and K. P. C. Vollhardt, *Chem. Eur. J.*, 1999, **5**, 3549.
[8] Prepared following S. Buchini and C. J. Leumann, *Eur. J. Org. Chem.*, 2006, **2006**, 3152.

solution. The solution was cooled to room temperature and the resulting solid was filtered, washed with EtOH (15 mL) and $Et_2O$ (15 mL) and dried under vacuum to afford clean product **10** (1.913 g, 70%) as a white solid.

***N*-Benzoyl-5-fluoro-cytosine 13**. To a suspension of 5-fluoro-cytosine (1.5 g, 11.6 mmol, 1 eq.) in dry MeCN (15 mL) was added benzoic anhydride (3.15g, 13.9 mmol, 1.2 eq.) followed by DMAP (283 mg, 2.32 mmol, 0.2 eq.) under argon atmosphere. The resulting mixture was refluxed for 24 h then EtOH (2 mL) was added to the hot solution. The solution was cooled to room temperature and the resulting solid was filtered, washed with EtOH (15 mL) and $Et_2O$ (15 mL) and dried under vacuum to afford clean product **13** (1.9 g, 70%) as a white solid. 1H NMR (DMSO-d6, 300 MHz) $\delta$ 8.01 (bd, J= 7.4, 3H), 7.60 (t, $J$ = 7.4 Hz, 1H), 7.49 (t, $J$ = 7.7 Hz, 2H).[9]

**2,3,6-Tri-*O*-acetyl-4-azido-1-*N*-thymine-β-D-glucopyranoside 16**. The general procedure was followed using **7** (70 mg, 0.16 mmol), **10** (32 mg, 0.256 mmol), BSA (0.16 mL, 0.64 mmol), TMSOTf (43 µL, 0.24 mmol, 1.5 eq.), 4 Å molecular sieves (150 mg) in dry MeCN (3mL). The residue was purified by preparative TLC (Hept/EtOAc 20:80) to afford product **16** (63 mg, 89%) as a white powder. $[\alpha]_D^{25}$ + 8.7 ($c$ = 0.9, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.68 (s, 1H, N*H*), 7.05 (d, 1H, $J_{HAr,CH3}$= 1.3 Hz, $H_{Ar}$), 5.82 (d, 1H, $J_{1,2}$= 9.5 Hz, *H*1), 5.35 (t, 1H, $J_{3,2}$ = $J_{3,4}$= 9.5 Hz, *H*3), 5.10 (t, 1H, $J_{2,1}$ = $J_{2,3}$= 9.5 Hz, *H*2), 4.37 (dd, 1H, $J_{6,6'}$= 12.5 Hz and $J_{6,5}$= 1.5 Hz, *H*6), 4.25 (dd, 1H, $J_{6',6}$= 12.5 Hz, $J_{6',5}$ = 4.5 Hz, *H*6'), 3.71-3.64 (m, 2H, *H*4, *H*5), 2.11 (s, 3H, C(O)C$H_3$), 2.10 (s, 3H, C(O)C$H_3$), 1.97 (s, 3H, C(O)C$H_3$), 1.92 (d, 3H, $J_{CH3,HAr}$= 1.0 Hz, $C_{Ar}CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.4 (*C*=O), 169.7 (*C*=O), 169.4 (*C*=O), 162.9 (*C*$q_{Ar}$), 150.2 (*C*$q_{Ar}$), 134.3 (*C*$H_{Ar}$), 112.3 (*C*$q_{Ar}$, 80.2 (*C*1), 75.1 (*C*5), 73.5 (*C*3), 69.3 (*C*2), 62.6 (*C*6), 59.9 (*C*4), 20.8 (C(O)*C*$H_3$), 20.6 (C(O)*C*$H_3$), 20.4 (C(O)*C*$H_3$), 12.6 (CAr*C*$H_3$); IR ν (film, $cm^{-1}$) 3220 (N-H), 3075 (=C-H), 2931 ($CH_3$), 2111 ($N_3$), 1748 (C=O), 1690 (NH-C=O); ESIHRMS *m/z* = 440.1418 $[M+H]^+$. $C_{17}H_{22}N_5O_9$ requires 440.1409.

**2,3,6-Tri-*O*-acetyl-4-azido-1-*N*-(5-fluoro-uracil)-β-D-glucopyranoside 17**. The general procedure was followed using **7** (70 mg, 0.16 mmol), **11** (33 mg, 0.256 mmol), BSA (0.16 mL, 0.64 mmol), TMSOTf (43 µL, 0.24 mmol, 1.5 eq.), 4 Å molecular sieves (150 mg) in dry MeCN (3 mL). The residue was purified by preparative TLC (Hept/EtOAc 30:70) to afford product **17** (49 mg, 68%) as a yellow powder. $[\alpha]_D^{25}$ + 23.0 ($c$ =1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.48 (d, 1H, $J_{NH,F}$= 4.5 Hz, N*H*), 7.34 (d, 1H, $J_{HAr,F}$= 5.5 Hz, $H_{Ar}$), 5.84 (d, 1H, $J_{1,2}$= 9.5 Hz, *H*1), 5.39 (t, 1H, $J_{3,2}$= $J_{3,4}$= 9.5 Hz, *H*3), 5.03 (t, 1H, $J_{2,3}$ = $J_{2,1}$= 9.5 Hz, *H*2), 4.39 (dd, 1H, $J_{6,6}$ = 12.5 Hz and $J_{6,5}$= 1.5 Hz, *H*6), 4.25 (dd, 1H, $J_{6',6}$ = 12.5 Hz and $J_{6',5}$ = 4.5 Hz, *H*6'), 3.80-3.71 (m, 1H, *H*5), 3.66 (dd, 1H, $J_{4,5}$ = 10.5 Hz and $J_{4,3}$ = 9.5 Hz, *H*4), 2.11 (s, 3H, C$H_3$), 2.10 (s, 3H, C$H_3$), 1.98 (s, 3H, C$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.4 (*C*=O), 169.9 (*C*=O), 169.5 (*C*=O), 156.4 (d, $J_{C\text{-}F}$ = 27 Hz, *C*$q_{Ar}$), 142.4 (*C*$q_{Ar}$), 139.3 (*C*$q_{Ar}$), 123.3 (d, $J_{C\text{-}F}$ = 34 Hz, *C*$H_{Ar}$), 80.5 (*C*1), 75.0 (*C*5), 73.1 (*C*3), 69.5 (*C*2), 62.4 (*C*6), 59.7 (*C*4), 20.8 (C(O)*C*$H_3$), 20.6 (C(O)*C*$H_3$), 20.4 (C(O)*C*$H_3$); IR ν (film, $cm^{-1}$) 3222 (N-H), 3096 (=C-H), 2116 ($N_3$), 1712 (C=O), 1673 (NH-C=O); ESIHRMS *m/z* = 444.1167 $[M+H]^+$. $C_{16}H_{19}N_5O_9F$ requires 444.1180.

**2,3,6-Tri-*O*-acetyl-4-azido-1-*N*-(4-*N*-benzoyl-5-methyl-cytosine)-β-D-glucopyranoside 18**. The general procedure was followed using **7** (70 mg, 0.16 mmol), **12** (59 mg, 0.256 mmol), BSA (0.16 mL, 0.64 mmol), TMSOTf (43 µL, 0.24 mmol, 1.5 eq.), 4 Å molecular sieves (150 mg) in dry MeCN (3 mL). The residue was purified by preparative TLC (Hept/EtOAc 30:70) to afford product **18** (76 mg, 88%) as a white powder. $[\alpha]_D^{25}$ + 4.1 ($c$ = 1.2, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.39-8.19 (m, 2H, $H_{Ar}$), 7.59-7.36 (m, 3H, $H_{Ar}$), 7.20 (d, 1H, $J_{HAr,CH3}$ = 1.5 Hz, $H_{Ar}$), 5.85 (d, 1H, $J_{1,2}$ = 9.5 Hz, *H*1), 5.35 (m, 1H, *H*3), 5.12 (t, 1H, $J_{2,1}$ = $J_{2,3}$ = 9.5 Hz, *H*2), 4.38 (d, 1H, $J_{6,6'}$ = 12.5 Hz, *H*6), 4.27 (dd, 1H, $J_{6',6}$ = 12.5 Hz and $J_{6',5}$ = 3.5 Hz, *H*6'), 3.79-3,61 (m, 2H, *H*4, *H*5), 2.12 (s, 3H, C$H_3$), 2.11 (s, 3H, COC$H_3$), 1.98 (s, 3H, COC$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 180.0 (*C*=O), 170.5 (*C*=O), 170.0 (*C*=O), 169.6 (*C*=O), 159.0 (*C*$q_{Ar}$), 148.2 (*C*$q_{Ar}$), 136.9 (C$q_{Ar}$), 135.5 (*C*$H_{Ar}$), 133.0 (*C*$H_{Ar}$), 130.2 (*C*$H_{Ar}$), 128.4 (*C*$H_{Ar}$), 113.3 (*C*$q_{Ar}$), 80.6 (*C*1), 75.4 (*C*5), 73.8 (*C*3), 69.8 (*C*2), 62.9 (*C*6), 60.1 (*C*4), 20.8 (C(O)*C*$H_3$), 20.6 (C(O)*C*$H_3$), 14.0 (*C*$H_3$); IR ν (film, $cm^{-1}$) 3072 (=C-H), 2959 (C-H), 2110 ($N_3$), 1740 (C=O), 1707 (C=O), 1656 (NH-C=O); ESIHRMS *m/z* = 543.1835 $[M+H]^+$. $C_{24}H_{27}N_6O_9$ requires 543.1840.

**2,3,6-Tri-*O*-acetyl-4-azido-1-*N*-(4-*N*-benzoyl-5-fluoro-cytosine)-β-D-glucopyranoside 19**. The general procedure was followed using **7** (70 mg, 0.16 mmol), **13** (56 mg, 0.256 mmol), BSA (0.16 mL, 0.64 mmol), TMSOTf (43 µL, 0.24 mmol, 1.5 eq.), 4 Å molecular sieves (150 mg) in dry MeCN (3 mL). The residue was purified by preparative TLC (Hept/EtOAc 20:80) to afford product **19** (75 mg, 75%) as a white powder. $[\alpha]_D^{20}$ = + 37.4 (c = 0.5, MeOH); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.26 (d, 2H, $J_{HAr,HAr}$ = 7.5 Hz, $H_{Ar}$), 7.55 (t, 1H, $J_{HAr,HAr}$ = 7.5 Hz $H_{Ar}$), 7.47-7.39 (m, 3H, $H_{Ar}$), 5.82 (d, 1H, $J_{1,2}$= 9.5 Hz, *H*1), 5.37 (t, 1H, $J_{3,2}$= $J_{3,4}$= 9.5 Hz, *H*3), 5.03 (t, 1H, $J_{2,3}$ = $J_{2,1}$= 9.5 Hz, *H*2), 4.39 (d, 1H, $J_{H6,H6'}$ = 12.5 Hz, *H*6), 4.27 (dd, 1H, $J_{H6',H6}$ = 12.5 Hz and $J_{H6',H5}$ = 4.0 Hz, H6'), 3.72-3.63 (m, 2H, *H*4,

[9] Prepared following M. F. Caso, D. D'Alonzo, S. D'Errico, G. Palumbo and A. Guaragna, *Org. Lett.*, 2015, **17**, 2626.

*H*5), 2.12 (s, 3H, C*H*$_3$), 2.11 (s, 3H, C*H*$_3$), 1.99 (s, 3H, C*H*$_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.5 (*C*=O), 170.1 (*C*=O), 169.5 (*C*=O), 151.8 (d, $J_{C\text{-}F}$ = 19 Hz, *C*q$_{Ar}$), 146.8 (*C*q$_{Ar}$), 141.8 (*C*q$_{Ar}$), 138.7 (*C*H$_{Ar}$), 135.7 (*C*H$_{Ar}$), 133.7 (*C*H$_{Ar}$), 130.4 (*C*H$_{Ar}$), 128.6 (*C*H$_{Ar}$), 124.0 (d, $J_{C\text{-}F}$ = 35 Hz, *C*H$_{Ar}$), 81.1 (*C*1), 75.5 (*C*5), 73.4 (*C*3), 69.8 (*C*2), 62.7 (*C*6), 60.0 (*C*4), 21.0 (C(O)*C*H$_3$), 20.7 (C(O)*C*H$_3$), 20.6 (C(O)*C*H$_3$); IR ν (film, cm$^{-1}$) 3100 (=C-H), 2113 (N$_3$), 1754 (C=O), 1674 (NH-C=O) ESIHRMS *m/z* = 547.1589 [M+H]$^+$. $C_{23}H_{24}N_6O_9F$ requires 547.1589.

**2,3,6-Tri-*O*-acetyl-4-azido-1-*N*-uracil-β-D-glucopyranoside 20**. The general procedure was followed using **7** (70 mg, 0.16 mmol), **14** (29 mg, 0.256 mmol), BSA (0.16 mL, 0.64 mmol), TMSOTf (43 µL, 0.24 mmol, 1.5 eq.), 4 Å molecular sieves (150 mg) in dry MeCN (3 mL). The residue was purified by preparative TLC (Hept/EtOAc 20:80) to afford product **20** (63 mg, 94%) as a white powder. $[\alpha]_D^{25}$ + 24.1 (*c* =1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 9.13 (bs, 1H, N*H*), 7.21 (d, 1H, $J_{HAr,HAr}$ = 8.5 Hz, *H*$_{Ar}$), 5.77 (d, 1H, $J_{1,2}$ = 9.5 Hz, *H*1), 5.74 (d, 1H, $J_{HAr,HAr}$ = 8.5 Hz, *H*$_{Ar}$), 5.32 (t, 1H, $J_{3,2} = J_{3,4}$ = 9.0 Hz, *H*3), 5.03 (dd, 1H, $J_{2,1}$ = 9.5 Hz, $J_{2,3}$ = 9.0 Hz, *H*2), 4.33 (d, 1H, $J_{6,6'}$ = 12.5 Hz, *H*6), 4.20 (dd, 1H, $J_{6',6}$ = 12.5 Hz and $J_{6',5}$ = 3.0 Hz, *H*6'), 3.72-3.53 (m, 2H, *H*4, *H*5), 2.05 (s, 6H, 2 C*H*$_3$), 1.93 (s, 3H, C*H*$_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.5 (*C*=O), 169.9 (*C*=O), 169.6 (*C*=O), 162.4 (*C*q$_{Ar}$), 150.3 (*C*q$_{Ar}$), 139.1 (*C*H$_{Ar}$), 104.0 (*C*H$_{Ar}$), 80.5 (*C*1), 75.4 (*C*5), 73.6 (*C*3), 69.6 (*C*2), 62.7 (*C*6), 60.1 (*C*4), 21.0 (*C*H$_3$), 20.8 (*C*H$_3$), 20.5 (*C*H$_3$); IR ν (film, cm$^{-1}$) 2960 (=C-H), 2111 (N$_3$), 1748 (C=O), 1689 (NH-C=O); ESIHRMS *m/z* = 426.1260 [M+H]$^+$. $C_{16}H_{19}N_5O_9F$ requires 426.1261.

**2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-1-*N*-(*N*-acetyl-cytosine)-β-D-glucopyranoside 21**. The General Procedure was followed using **8** (50 mg, 0.10 mmol), **9** (25 mg, 0.16 mmol), BSA (0.1 mL, 0.41 mmol), TMSOTf (22 µL, 0.12 mmol), 4 Å molecular sieves (50 mg) in dry MeCN (1 mL). The residue was purified by preparative TLC (Heptane/EtOAc 1:1) to afford product **21** (28 mg, 0.05 mmol, 54%) as a colorless oil. $[\alpha]_D^{25}$ + 47.5 (*c* = 1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7,67 (d, 1H, $J_{HAr,HAr}$ = 7.5 Hz, *H*$_{Ar}$), 7.47 (d, 1H, $J_{HAr,HAr}$ = 7.5 Hz, *H*$_{Ar}$) 7.36-7.27 (m, 5H, *H*$_{Ar}$), 5.99 (d, 1H, $J_{1,2}$ = 9.5 Hz, *H*1), 5.32 (dd, 1H, $J_{3,2}$ = 9.5 Hz and $J_{3,4}$ = 10.0 Hz, *H*3), 5.03 (t, 1H, $J_{2,3} = J_{2,1}$ = 9.5 Hz, *H*2), 4.57 (d, 1H, $J_{H,H}$ = 12.0 Hz, C*H*$_2$Ph), 4.52 (d, 1H, $J_{H,H}$ = 12.0 Hz, C*H*$_2$Ph), 3.94 (t, 1H, $J_{4,3} = J_{4,5}$ = 10.0 Hz, *H*6), 3.80-3.67 (m, 2H, *H*6), 3.60 (ddd, 1H, $J_{5,4}$ = 10.0 Hz and $J_{5,6}$ = 3.5 Hz, $J_{5,6'}$ = 2.0 Hz, *H*5), 2.23 (s, 3H, NHCOC*H*$_3$), 2.08 (s, 3H, OCOC*H*$_3$), 1.92 (s, 3H, OCOC*H*$_3$); $^{13}$C NMR (75 MHz, MeOD) $\delta$ 170.0 (*C*=O), 169.7 (*C*=O), 163.1 (*C*q$_{Ar}$), 155.3 (*C*q$_{Ar}$), 144.5 (*C*H$_{Ar}$), 137.6 (*C*q$_{Ar}$), 128.7 (*C*H$_{Ar}$), 128.2 (*C*H$_{Ar}$), 128.1 (*C*H$_{Ar}$), 98.0 (*C*H$_{Ar}$), 81.5 (*C*1), 77.3 (*C*5), 73.9 (*C*H$_2$Ph), 73.5 (*C*2), 71.0 (*C*3), 68.2 (*C*6), 59.7 (*C*4), 25.2 (CO*C*H$_3$), 20.8 (CO*C*H$_3$), 20.6 (CO*C*H$_3$); IR ν (film, cm$^{-1}$) 3148 (=C-H), 2110 (N$_3$), 1754 (C=O), 1667 (NH-C=O); ESIHRMS *m/z* = 515.1878 [M+H]$^+$. $C_{23}H_{27}N_6O_8$ requires 515.1890.

**2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-1-*N*-thymine-β-D-glucopyranoside 22**. The General Procedure was followed using **8** (581 mg, 1.2 mmol), Thymine **10** (267 mg, 2.1 mmol), BSA (1.3 mL, 5.29 mmol), TMSOTf (1.6 mL, 1.9 mmol) in dry MeCN (25 mL). The residue was purified by flash chromatography on silica gel (Heptane/EtOAc 70:30 to 60:40) to afford product **22** (496 mg, 77%) as a white powder. $[\alpha]_D^{25}$ + 11.1 (*c* = 1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.42-7.25 (m, 5H, *H*$_{Ar}$), 7.11 (d, 1H, $J_{HAr,CH3}$= 1.0 Hz, *H*$_{Ar}$), 5.79 (d, 1H, $J_{1,2}$= 9.5 Hz, *H*1), 5.29 (dd, 1H, $J_{3,2}$= 9.5 Hz and $J_{3,4}$= 10.0 Hz, *H*3), 5.07 (t, 1H, $J_{2,1} = J_{2,3}$= 9.5 Hz, *H*2), 4.59 (d, 1H, $J_{H,H}$ = 12.0 Hz, C*H*$_2$Ph), 4.52 (d, 1H, $J_{H,H}$ = 12.0 Hz, C*H*$_2$Ph), 3.90 (t, 1H, $J_{4,3} = J_{4,5}$ = 10.0 Hz, *H*4), 3.79-3.66 (m, 2H, *H*6, *H*6'), 2.08 (s, 3H, C(O)C*H*$_3$), 1.95 (s, 3H, C(O)C*H*$_3$), 1.91 (d, 3H, $J_{CH3,HAr}$= 1.0 Hz, C$_{Ar}$C*H*$_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.9 (*C*=O), 169.8 (*C*=O), 163.5 (*C*q$_{Ar}$), 150.6 (*C*q$_{Ar}$), 137.6 (*C*q$_{Ar}$), 134.6 (*C*H$_{Ar}$), 128.7 (*C*H$_{Ar}$), 128.2 (*C*H$_{Ar}$), 128.0 (*C*H$_{Ar}$), 112.3 (*C*q$_{Ar}$), 80.2 (*C*1), 76.9 (*C*5), 73.8 (*C*H$_2$Ph), 73.7 (*C*3), 69.8 (*C*2), 68.2 (*C*6), 59.7 (*C*4), 20.8 (C(O)*C*H$_3$), 20.6 (C(O)*C*H$_3$), 12.6 (CAr*C*H$_3$); IR ν (film, cm$^{-1}$) 3675 (N-H), 2988 (=C-H), 2901 (CH$_2$), 2111 (N$_3$), 1754 (C=O), 1697 (NH-C=O); ESIHRMS *m/z* = 487.1783 [M+H]$^+$. $C_{22}H_{26}N_5O_8$ requires 487.1781.

**2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-1-*N*-(5-fluoro-uracil)-β-D-glucopyranoside 23**. A mixture of 5-fluoro-uracil **11** (42 mg, 0.31 mmol, 1.5 eq.), hexamethyldisilazane (77 µL, 0.37 mmol, 1.8 eq.) and saccharine (3 mg, 0.01 mmol, 6.5 mol%) in anhydrous MeCN (1.5 mL) was refluxed for 30 min under inert atmosphere. **8** (100 mg, 0.21 mmol, 1 eq.) and TMSOTf (56 µL, 0.37 mmol, 1.5 eq.) were then added and the resulting mixture was refluxed for 6 h, cooled to room temperature, neutralized with saturated aqueous sodium bicarbonate (3 mL) and extracted with $CH_2Cl_2$ (8 mL). The organic extract was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (Heptane/EtOAc 90:10 to 50:50) to afford the clean product **23** (80 mg, 0.16 mmol, 76%) as a yellow powder. $[\alpha]_D^{25}$ + 25.6 (c = 1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.41-7.26 (m, 6H, *H*$_{Ar}$), 5.75 (dd, 1H, $J_{1,2}$= 9.5 Hz and $J_{1,HAr}$ = 1.5 Hz, *H*1), 5.30 (t, 1H, $J_{3,2} = J_{3,4}$ = 9.5 Hz, *H*3), 4.97 (t, 1H, $J_{2,3}$= $J_{2,1}$= 9.5 Hz, *H*2), 4.58 (d, 1H, $J_{H,H}$ = 12.0 Hz, C*H*$_2$Ph), 4.53 (d, 1H, $J_{H,H}$ = 12.0 Hz, C*H*$_2$Ph), 3.89 (t, 1H, $J_{4,3}$= $J_{4,5}$ = 10.0 Hz, *H*4), 3.80-3.66 (m, 2H, *H*6, *H*6'), 3.59 (dt, 1H, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 5.0 Hz, $J_{5,6'}$ = 2.0 Hz, *H*5), 2.09 (s, 3H, C*H*$_3$), 1.97 (s, 3H, C*H*$_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.0 (*C*=O), 169.7 (*C*=O), 156.5 (d, $J_{C\text{-}F}$ = 27 Hz, *C*q$_{Ar}$), 149.1 (*C*q$_{Ar}$), 142.6 (*C*q$_{Ar}$), 139.4 (*C*q$_{Ar}$), 137.4 (*C*q$_{Ar}$), 128.7 (*C*H$_{Ar}$), 128.3 (*C*H$_{Ar}$),

123.5 (d, $J_{C\text{-}F}$ = 34 Hz, $C$H$_{Ar}$), 80.9 (*C*1), 77.0 (*C*5), 73.8 ($C$H$_2$Ph), 73.3 (*C*3), 69.9 (*C*2), 68.1 (*C*6), 59.5 (*C*4), 20.8 (C(O)$C$H$_3$), 20.5 (C(O)$C$H$_3$); IR ν (film, cm$^{-1}$) 3089 (NH), 2112 (N$_3$), 1710 (C=O), 1670 (NH-C=O); ESIHRMS *m/z* = 514.1348 [M+Na]$^+$. $C_{21}H_{22}N_5O_8FNa$ requires 514.1350.

**2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-1-*N*-(4-*N*-benzoyl5-methyl-cytosine)-β-D-glucopyranoside 24**. The General Procedure was followed using **8** (45 mg, 0.092 mmol), **12** (34 mg, 0.148 mmol), BSA (90 µL, 0.37 mmol), TMSOTf (20 µL, 0.11 mmol), 4 Å molecular sieves (50 mg) in dry MeCN (0.9 mL). The residue was purified by preparative TLC (Heptane/EtOAc 1:1) to afford product **24** (36 mg, 66%) as a yellow powder. $[\alpha]_D^{25}$ – 12.7 (*c* =1.2, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.33-8.25 (m, 2H, $H_{Ar}$), 7.57-7.26 (m, 9H, $H_{Ar}$), 5.82 (d, 1H, $J_{1,2}$ = 9.5 Hz, *H*1), 5.30 (dd, 1H, $J_{3,2}$ = 9.5 Hz, $J_{3,4}$ = 10.0 Hz, *H*3), 5.10 (t, 1H, $J_{2,1} = J_{2,3}$ = 9.5 Hz, *H*2), 4.60 (d, 1H, $J_{H,H}$ = 12.0 Hz, C$H_2$Ph), 4.53 (d, 1H, $J_{H,H}$ = 12.0 Hz, C$H_2$Ph), 3.95 (t, 1H, $J_{4,3} = J_{4,5}$ = 10.0 Hz, *H*4), 3.81-3.68 (m, 2H, *H*6, *H*6'), 3.50 (ddd, 1H, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 4.5 Hz, $J_{5,6'}$ = 2.0 Hz, *H*5), 2.10 (s, 3H, C$H_3$), 2.09 (s, 3H, COC$H_3$), 1.96 (s, 3H, COC$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 180.0 (*C*=O), 170.0 (*C*=O), 169.7 (*C*=O), 159.2 ($C$q$_{Ar}$), 148.2 ($C$q$_{Ar}$), 137.6 ($C$q$_{Ar}$), 137.0 ($C$q$_{Ar}$), 135.9 ($C$H$_{Ar}$), 132.9 ($C$H$_{Ar}$), 130.2 ($C$H$_{Ar}$), 128.7 ($C$H$_{Ar}$), 128.4 ($C$H$_{Ar}$), 128.2 ($C$H$_{Ar}$), 128.0 ($C$H$_{Ar}$), 113.1 ($C$qAr), 80.7 (*C*1), 77.0 (*C*5), 73.8 ($C$H$_2$Ph), 73.7 (*C*3), 69.9 (*C*2), 68.2 (*C*6), 59.6 (*C*4), 20.8 (C(O)$C$H$_3$), 20.6 (C(O)$C$H$_3$), 13.9 ($C$H$_3$); IR ν (film, cm$^{-1}$) 2109 (N$_3$), 1753 (C=O), 1709 (C=O) 1656 (NH-C=O); ESIHRMS *m/z* = 591.2208 [M+H]$^+$. $C_{29}H_{31}N_6O_8$ requires 591.2203.

**2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-1-*N*-(4-*N*-benzoyl-5-fluoro-cytosine)-β-D-glucopyranoside 25**. The General Procedure was followed using **8** (1.49 g, 3.05 mmol), **13** (1.14 g, 4.89 mmol), BSA (2.27 mL, 9.16 mmol), TMSOTf (0.66 mL, 3.66 mmol) in dry MeCN (30 mL). The residue was purified by preparative HPLC, gradient from 30 to 100% MeCN in 15 min, to afford product **25** (918 mg, 1.54 mmol, 50%) as a yellow powder. $[\alpha]_D^{20}$ + 22.9 (*c* =0.84, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.29 (d, 2H, $J_{HAr,HAr}$ = 7.0 Hz, $H_{Ar}$), 7.57-7.43 (m, 4H, $H_{Ar}$), 7.42-7.30 (m, 5H, $H_{Ar}$), 5.79 (d, 1H, $J_{1,2}$= 9.0 Hz, *H*1), 5.32 (t, 1H, $J_{3,2} = J_{3,4}$= 9.5 Hz, *H*3), 5.00 (t, 1H, $J_{2,3} = J_{2,1}$= 9.5 Hz, *H*2), 4.61 (d, 1H, $J_{H,H}$ = 12.0 Hz, C$H_2$Ph), 4.56 (d, 1H, $J_{H,H}$ = 12.0 Hz, C$H_2$Ph), 3.94 (t, 1H, $J_{4,3} = J_{4,5}$= 10.0 Hz, *H*4), 3.81-3.71 (m, 2H, *H*6, *H*6'), 3.59 (d, 1H, $J_{5,4}$ = 10.0 Hz, *H*5), 2.12 (s, 3H, C$H_3$), 2.00 (s, 3H, C$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.1 (*C*=O), 169.7 (*C*=O), 152.2 ($C$q$_{Ar}$), 147.0 ($C$q$_{Ar}$), 141.5 ($C$q$_{Ar}$), 139.5 ($C$q$_{Ar}$), 137.5 ($C$q$_{Ar}$), 133.5 ($C$H$_{Ar}$), 130.4 ($C$H$_{Ar}$), 128.8 ($C$H$_{Ar}$), 128.6 ($C$H$_{Ar}$), 128.3 ($C$H$_{Ar}$), 128.1 ($C$H$_{Ar}$), 81.1 (*C*1), 77.1 (*C*5), 73.9 ($C$H$_2$Ph), 73.3 (*C*3), 70.1 (*C*2), 68.1 (*C*6), 59.5 (*C*4), 20.8 (C(O)$C$H$_3$), 20.6 (C(O)$C$H$_3$); IR ν (film, cm$^{-1}$) 3089 (=C-H), 2111 (N$_3$), 1753 (C=O), 1672 (NH-C=O); ESIHRMS *m/z* = 595.1951 [M+H]$^+$. $C_{28}H_{28}N_6O_8F$ requires 595.1953.

**2,3-Di-*O*-acetyl-4-azido-6-*O*-benzyl-1-*N*-uracil-β-D-glucopyranoside 26**. The General Procedure was followed using **8** (400 mg, 0.82 mmol), **14** (147 mg, 1.31 mmol), BSA (0.80 mL, 3.28 mmol), TMSOTf (0.18 mL, 0.98 mmol) in dry MeCN (8.2 mL). The residue was purified by flash chromatography (Heptane/EtOAc 90:10 to 50:50) to afford product **26** (314 mg, 0.66 mmol, 81%) as a yellow powder. $[\alpha]_D^{25}$ + 20.6 (*c* = 1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.78 (bs, 1H, N*H*), 7.43-7.29 (m, 6H, $H_{Ar}$), 5.81 (d, 1H, $J_{1,2}$ = 9.0 Hz, *H*1), 5.80 (d, 1H, $J_{HAr,HAr}$ = 8.0 Hz, $H_{Ar}$), 5.33 (t, 1H, $J_{3,2} = J_{3,4}$ = 9.5 Hz, *H*3), 5.07 (dd, 1H, $J_{2,1}$ = 9.0 Hz, $J_{2,3}$ = 9.5 Hz, *H*2), 4.62 (d, 1H, $J_{H,H}$ = 12.0 Hz, C$H_2$Ph), 4.55 (d, 1H, $J_{H,H}$ = 12.0 Hz, C$H_2$Ph), 3.94 (dd, 1H, $J_{4,3}$ = 9.5 Hz, $J_{4,5}$ = 10.0 Hz, *H*4), 3.82-3.70 (m, 2H, *H*6, *H*6'), 3.61 (ddd, 1H, $J_{5,4}$ = 10.0 Hz, $J_{5,6}$ = 3.0 Hz, $J_{5,6'}$ = 2.0 Hz, *H*5), 2.13 (s, 3H, C$H_3$), 1.99 (s, 3H, C$H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.9 (*C*=O), 169.7 (*C*=O), 162.5 ($C$q$_{Ar}$), 150.3 ($C$q$_{Ar}$), 139.4 ($C$H$_{Ar}$), 137.5 ($C$q$_{Ar}$), 128.7 ($C$H$_{Ar}$), 128.3 ($C$H$_{Ar}$), 128.0 ($C$H$_{Ar}$), 103.8 ($C$H$_{Ar}$), 80.6 (*C*1), 77.0 (*C*5), 73.9 ($C$H$_2$Ph), 73.5 (*C*3), 69.8 (*C*2), 68.2 (*C*6), 59.6 (*C*4), 20.8 ($C$H$_3$), 20.6 ($C$H$_3$); IR ν (film, cm$^{-1}$) 2109 (N$_3$), 1752 (C=O), 1688 (NH-C=O); ESIHRMS *m/z* = 474.1626 [M+H]$^+$. $C_{21}H_{24}N_5O_8$ requires 474.1625.

**Boc-sarcosinyl-*O-tert*-butyl-L-serine methyl ester 29-L**. To a stirred solution of *O-tert*-butyl-L-serine methyl ester hydrochloride (250 mg, 1.18 mmol, 1 eq.) and Boc-sarcosine (290 mg, 1,55 mmol, 1.3 eq.) in dry $CH_2Cl_2$ (10 mL) were added 4Å molecular sieves (335 mg), hydroxybenzotriazole (240 mg, 1.77 mmol, 1.5 eq.) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (453 mg, 0.47 mmol, 2 eq.). The resulting mixture was cooled to 0 °C and $Et_3N$ (0.5 mL, 2.36 mmol, 3 eq.) was added. After being stirred overnight at room temperature, the mixture was diluted with aqueous saturated $NaHCO_3$ (6 mL). Aqueous phase was then extracted with EtOAc (3 x 5 mL). Organic layers were combined, dried over $Na_2SO_4$, filtered and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (Heptane/EtOAc 50:50 to 30:70) to afford product **29-L** (400 g, 1.16 mmol, 98%) as a colorless oil. $[\alpha]_D^{25}$ + 32.9 (*c* = 0.82, $CHCl_3$).

**Boc-sarcosinyl-*O-tert*-butyl-L-serine 30-L**. To a stirred solution of **29-L** (320 mg, 0.92 mmol, 1 eq.) in THF/$H_2O$ mixture (7.7 mL/1.5 mL 5:1) was added lithium hydroxide (29 mg, 1.20 mmol, 1.3 eq.). The resulting mixture was stirred for 1 h at room temperature and then concentrated under vacuum until THF was evaporated. HCl 1 N was then added until pH 2. The aqueous layer was extracted with EtOAc (3 x 10 mL). The organic layers were

combined, dried over $Na_2SO_4$ and concentrated under vacuum to afford the clean product **30-L** (305 mg, 0.92 mmol, quantitative). The product is used without further purification. $[\alpha]_D^{25}$ + 27.3 (*c* = 1.0, $CHCl_3$).

**Peptidonucleoside 31-L**. The **solution 1** was prepared with Na (10 mg) in dry MeOH (2 mL, C = 0.22 M). To a stirred solution of the protected nucleoside **27** (503 mg, 0.96 mmol) in dry MeOH (16 mL) was added the **solution 1** (0.88 mL, 20 mol%). The resulting mixture was stirred at room temperature for 1 h and then neutralized with Dowex® $H^+$, filtered on celite and concentrated under reduce pressure to afford clean product without further purification. The obtained product (355 mg) was then hydrogenolysed at atmospheric pressure in the presence of $Pd(OH)_2$-C (40%w/w, 142 mg) in MeOH (8.9 mL) for 12 h. The resulting mixture was then filtered on celite® and concentrated under reduced pressure to afford the clean corresponding amine (318 mg). To a stirred solution of the latter (150 mg, 0.40 mmol) in DMF (6 mL) was added the dipeptide (174 mg, 0.52 mmol, 1.3 eq.) and DIPEA (0.28 mL, 1.61 mmol, 4 eq.). After 1 min, HATU (184 mg, 0.48 mmol, 1.5 eq.) was added and the resulting mixture was stirred at room temperature for 18 h. Solvent was removed and the crude product was purified by flash chromatography on silica gel (EtOAc/EtOH 99:1 to 92:8) to afford product **31-L** (158 mg, 0.23 mmol, 57%) as a yellow powder. $[\alpha]_D^{20}$ – 99.0 (*c* = 0.34, $H_2O$/MeOH 1:1); $^1$H NMR (500 MHz, $CD_3OD$)[10] $\delta$ 8.15 (d, 1H, $J_{HAr,HAr}$ = 7.5 Hz, $H_{Ar}$), 7.37 (d, 1H, $J_{HAr,HAr}$ = 7.5 Hz, $H_{Ar}$), 5.81 (d, 1H, $J_{1,2}$ = 9.0 Hz, *H*1), 4.60-4.49 (m, 1H, *H*7), 4.10-3.97 (m, 2H, H9), 3.95 (t, 1H, $J_{4,3} = J_{4,5}$= 10.0 Hz, *H*4), 3.87-3.71 (m, 2H, *H*3, *H*6), 3.71-3.58 (m, 5H, *H*2, *H*5, *H*6', *H*8), 3.03-2.91 (bs, 3H, $NCH_3$), 1.58 (s, 9H, $CO_2C(CH_3)_3$), 1.55-1.47 (m, 9H, $OC(CH_3)_3$), 1.25 (s, 9H, $CO_2C(CH_3)_3$); $^{13}$C NMR (75 MHz, $CD_3OD$)[11] $\delta$ 173.4 (*C*=O), 171.9 (*C*=O), 165.3 (*C*q), 158.6 (*C*q), 153.6 (*C*=O), 146.5 ($CH_{Ar}$), 97.7 ($CH_{Ar}$), 85.3 (*C*1), 83.4 ($C(CH_3)_3$), 81.8 ($C(CH_3)_3$), 80.2 (*C*5), 75.8 (*C*3), 75.0 ($C(CH_3)_3$), 74.5 (*C*2), 62.8 (*C*6), 58.6 (*C*8), 55.7 (*C*7), 53.2 (*C*4), 52.9 (*C*9), 36.4 ($NCH_3$), 28.8 ($C(CH_3)_3$), 28.5 ($C(CH_3)_3$), 27.8 ($C(CH_3)_3$); IR ν (film, $cm^{-1}$) 3310 (O-H), 3282 (N-H), 2976 ($CH_3$), 2933 ($CH_2$), 1744 (C=O), 1653 (NH-C=O); ESIHRMS *m/z* = 687.3566 $[M+H]^+$. $C_{30}H_{51}N_6O_{12}$ requires 687.3565.

**Analogue 32-L**. To a stirred solution of **31-L** (90 mg, 0.131 mmol, 1 eq.) in $CH_2Cl_2$/MeOH (2:1 v/v, 1.3 mL) was added a solution of 4M HCl in dioxane (0.23 mL, 0.92 mmol, 7 eq.). The resulting mixture was stirred at room temperature for 2 days and then diluted with $H_2O$ and then neutralized with DOWEX® MONOSPHERE® 550A (OH) anion exchange resin. The mixture was filtered on celite and then concentrated under vaccum. The crude product was purified by preparative TLC ($H_2O$/EtOH/EtOAc 4:4:2, pH 9) to afford clean product **32-L** as a white powder (10.3 mg, 0.024 mmol, 28%). $[\alpha]_D^{25}$ + 278.3 (*c* = 1.0, $H_2O$); $^1$H NMR (500 MHz, $D_2O$) $\delta$ 7.80 (d, 1H, $J_{HAr,HAr}$ = 7.5 Hz, $H_{Ar}$), 6.14 (d, 1H, $J_{HAr,HAr}$ = 7.5 Hz, $H_{Ar}$), 5.71 (d, 1H, $J_{1,2}$ = 9.0 Hz, *H*1), 4.52 (t, 1H, $J_{7,8} = J_{7,8'}$ = 5.5 Hz, *H*7), 3.99 (t, 1H, $J_{4,3} = J_{4,5}$= 10.0 Hz, *H*4), 3.92 (d, 2H, $J_{8,7}$ = 5.5 Hz, *H*8), 3.85 (dd, 1H, $J_{3,2}$= 9.0 Hz and $J_{3,4}$ = 10.0 Hz, *H*3), 3.82 (t, 1H, $J_{2,3} = J_{2,1}$= 9.0 Hz, *H*2), 3.80-3.70 (m, 2H, *H*5, *H*6), 3.66-3.60 (m, 3H, *H*6, *H*9), 2.54 (s, 3H, $NCH_3$); $^{13}$C NMR (75 MHz, $D_2O$) $\delta$ 172.2 (*C*=O), 171.1 (*C*=O), 166.1 (*C*=O), 158.0 ($Cq_{Ar}$), 141.8 ($CH_{Ar}$), 97.1 ($CH_{Ar}$), 83.1 (*C*1), 77.5 (*C*5), 73.8 (*C*3), 71.7 (*C*2), 61.2 (*C*8), 60.7 (*C*6), 55.8 (*C*7), 51.4 (*C*4), 51.3 (*C*9), 33.8 ($NCH_3$); IR ν (film, $cm^{-1}$) 3310 (O-H), 3282 (N-H), 2976 ($CH_3$), 2933 ($CH_2$), 1744 (C=O), 1653 (NH-C=O); ESIHRMS *m/z* = 431.1890 $[M+H]^+$. $C_{16}H_{27}N_6O_8$ requires 431.1901.

**Peptidonucleoside 33**. The same Procedure as described for **31-D** was followed using **16** (315 mg, 0.72 mmol), **solution 1** (0.65 mL, C = 0.44 M, 40 mol%) in MeOH (10 mL) to obtain the deacetylated compound (227 mg). The obtained product was hydrogenolysed with $Pd(OH)_2$-C (68 mg) in MeOH (3.8 mL) to give the corresponding amine (110 mg, 0.38 mmol). Then, the peptide coupling was carried out with the amine (110 mg), **30-D** (195 mg, 0.59 mmol), DIPEA (0.3 mL, 1.8 mmol) and HATU (206 mg, 0.54 mmol) in DMF (7.5 mL). The residue was purified by flash chromatography on silica gel (EtOAc/EtOH 99:1 to 92:8) to afford clean product **33** (204 mg, 0.34 mmol, 47%) as a yellow powder. $[\alpha]_D^{25}$ +24.4 (*c* = 0.55, MeOH). $^1$H NMR (500 MHz, $CD_3OD$)[10] $\delta$ 7.60 (s, 1H, $H_{Ar}$), 5.55 (d, 1H, $J_{1,2}$ = 9.0 Hz, *H*1), 4. 45 (t, 1H, $J_{7,8} = J_{7,8'}$ = 5.0 Hz, *H*7), 4.01-3.91 (m, 2H, *H*9), 3.89-3.55 (m, 7H, *H*2, *H*3, *H*4, *H*5, *H*6, *H*8), 2.99-2.88 (m, 3H, $NCH_3$), 1.91 (s, 3H, $CH_3$), 1.57-1.35 (m, 9H, $OC(CH_3)_3$), 1.21 (s, 9H, $CO_2C(CH_3)_3$); $^{13}$C NMR (75 MHz, $CD_3OD$)[11] $\delta$ 172.0 (*C*=O), 170.6 (*C*=O), 170.5 (*C*=O), 164.7 (*C*=O), 151.5 (*C*=O), 136.7 ($CH_{Ar}$), 110.5 ($Cq_{Ar}$), 85.5 (*C*1), 80.3 ($C(CH_3)_3$), 78.3 (*C*H), 74.0 (*C*H), 73.5 ($C(CH_3)_3$), 71.9 (*C*H), 61.4 ($CH_2$), 54.3 (*C*7), 51.7 (*C*H), 51.5 ($CH_2$), 35.1 ($NCH_3$), 27.2 ($C(CH_3)_3$), 26.2 ($C(CH_3)_3$), 10.8 ($CH_3$); IR ν (film, $cm^{-1}$) 3295 (N-H), 2974 (CH), 1654 (NH-C=O); ESIHRMS *m/z* = 602.4783 $[M+H]^+$. $C_{26}H_{44}N_5O_{11}$ requires 602.3037.

**Peptidonucleoside 35**. To a stirred solution of **33** (30 mg, 0.05 mmol, 1 eq.) in $CH_2Cl_2$/MeOH (2:1 v/v, 0.6 mL) was added a solution of 4M HCl in dioxane (0.3 mL, 1.2 mmol, 25 eq.). The resulting mixture was stirred at room

[10] Peaks in $^1$H-NMR spectrum broad and split due to the presence of *N*-Boc rotamers.
[11] Peaks in $^{13}$C-NMR spectrum broad and split due to the presence of *N*-Boc rotamers.

temperature for 2 days and then diluted with $H_2O$ and then neutralized with $NEt_3$ (0.2 mL). The mixture was concentrated under vaccum and the crude product was purified by preparative TLC ($H_2O$/EtOH/EtOAc 2:2:1, with 1% of $NH_4OH$) to afford clean product **35** as a white powder (10 mg, 0.022 mmol, 45%); $[\alpha]_D^{20}$ + 8.9 (*c* = 1.0, MeOH); $^1$H NMR (300 MHz, $D_2O$) $\delta$ 7.62 (s, 1H, $H_{Ar}$), 5.61-5.54 (m, 1H, *H*1), 4.44 (t, 1H, $J_{7,8} = J_{7,8'} = 5.5$ Hz, *H*7), 3.92-3.79 (m, 4H, 1 x C*H and* $CH_2$), 3.79-3.64 (m, 5H, 3 x C*H and* $CH_2$), 3.63-3.54 (m, 1H, $CH_2$), 2.67 (s, 3H, $NCH_3$), 1.86 (s, 3H, $CH_3$); $^{13}$C NMR (75 MHz, $D_2O$) $\delta$ 172.1 (*C*=O), 167.8 (*C*=O), 166.3 (*C*=O), 152.2 (*C*=O), 137.3 ($CH_{Ar}$), 111.1 ($Cq_{Ar}$), 82.5 (*C*1), 77.5 (*C*H), 73.6 (*C*H), 71.6 (*C*H), 61.1 ($CH_2$), 60.7 ($CH_2$), 56.0 (*C*7), 51.4 (*C*H), 49.4 ($CH_2$), 33.1 ($NCH_3$), 11.4 ($CH_3$); IR ν (film, cm$^{-1}$) 3288 (N-H), 2923 (CH), 2854 (CH), 1664 (NH-C=O); ESIHRMS *m/z* = 446.1867 $[M+H]^+$. $C_{18}H_{27}N_5O_9$ requires 446.1887.

**Peptidonucleoside 36**. The same Procedure as described for **31-D** was followed using **17** (194 mg, 0.72 mmol), **solution 1** (1.2 mL, C=0.22 M, 40 mol% of Na) in MeOH (7 mL). The obtained product (125 mg) was hydrogenolysed with $Pd(OH)_2$-C (50 mg) in MeOH (4 mL) to give the corresponding amine (107 mg). Then, the peptide coupling was carried out using the amine (107 mg, 0.37 mmol), **30-D** (158 mg, 0.48 mmol), DIPEA (0.25 mL, 1.48 mmol) and HATU (167 mg, 0.44 mmol) in DMF (6 mL). The residue was purified by chromatography on silica gel (DCM/MeOH 96:4 to 92:8) to afford **34** (124 mg, 0.20 mmol, 56% over three steps). ESIHRMS *m/z* = 606.2786 $[M+H]^+$. $C_{25}H_{41}N_5O_{11}F$ requires 606.2787. As **34** was not very clean, it was not fully characterized and then engaged in the next step. To a stirred solution of **34** (124 mg, 0.2 mmol, 1 eq.) in $CH_2Cl_2$/MeOH (2:1 v/v, 2.3 mL) was added a solution of 4M HCl in dioxane (0.35 mL, 1.4 mmol, 6.8 eq.). The resulting mixture was stirred at room temperature for 3 days and then diluted with $H_2O$ and then neutralized with $NEt_3$ (0.2 mL). The mixture was concentrated under vaccum and the crude product was purified by preparative TLC ($H_2O$/EtOH/EtOAc 3:1:1, with 1% of $NH_4OH$) to afford clean product **36** as a white powder (54 mg, 0.013 mmol, 63%). $[\alpha]_D^{20}$ – 73.3 (*c* = 0.15, $H_2O$/MeOH: 1:1); $^1$H NMR (300 MHz, $D_2O$) $\delta$ 7.94 (d, 1H, $J_{HAr,F}$ = 6.0 Hz, $H_{Ar}$), 5.59 (d, 1H, $J_{1,2}$ = 9.0 Hz, *H*1), 4.51-4.38 (m, 1H, *H*7), 3.99-3.46 (m, 10H, *H*2, *H*3, *H*4, *H*5, *H*6, *H*8, *H*9), 2.72 (s, 3H, $NCH_3$), 2.72 (s, 9H, $C(CH_3)_3$); $^{13}$C NMR (75 MHz, $D_2O$) $\delta$ 181.4 (*C*=O), 172.3 (*C*=O), 166.7 (*C*=O), 161.2 (d, *J* = 23.6 Hz, $CH_{Ar}$), 152.2 (CO), 125.3 (d, *J* = 23.6 Hz, *C*qAr), 125.2 (*C*H), 82.9 (*C*1), 77.5 (*C*H), 75.0 ($C(CH_3)_3$), 73.3 (*C*H), 71.7 (*C*H), 61.0 ($CH_2$), 60.7 ($CH_2$), 56.0 (*C*7), 51.3 (*C*H), 49.4 ($CH_2$), 32.8 ($NCH_3$), 26.4 ($C(CH_3)_3$); IR ν (film, cm$^{-1}$) 3288 (N-H), 2923 (CH), 2854 (CH), 1664 (NH-C=O); ESIHRMS *m/z* = 506.2249 $[M+H]^+$. $C_{20}H_{33}N_5O_9F$ requires 506.2262.

***tert*-butyl (*R*)-(2-((1-(*tert*-butoxy)-3-hydroxypropan-2-yl)amino)-2-oxoethyl)(methyl)carbamate 37**. To a stirred solution of **29-D** (193 mg, 0.557 mmol, 1 eq.) in THF (2 mL) was added at 0 °C $LiBH_4$ (21 mg, 0.95 mmol, 1.7 eq.). The resulting mixture was stirred at room temperature for 4 h and then hydrolyzed with a saturated aqueous solution of $NH_4Cl$ (10 mL). Water (10 mL) was added and the aqueous phase was extracted with EtOAc (3 x 15 mL). The organic phase was dried with $Na_2SO_4$, filtered and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (Heptane/EtOAc 30:70 to 0:100) to afford product **37** (160 mg, 0.5 mmol, 90%) as a colorless oil. $[\alpha]_D^{20}$ – 5.4 (*c* = 0.24, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$)[10] $\delta$ 6.81-6.58 (bs, 1H, N*H*), 4.03-3.93 (m, 1H, C*H*N), 3.91-3.81 (m, 2H, $COCH_2N$), 3.80 (dd, 1H, *J* = 11.5 and 3.5 Hz, $CH_2$), 3.69-3.58 (m, 1H, $CH_2$), 3.57-3.50 (m, 2H, $CH_2$), 3.25-3.09 (m, 1H, O*H*), 2.91 (s, 3H, $NCH_3$), 1.43 (s, 9H, $C(CH_3)_3$), 1.15 (s, 9H, $C(CH_3)_3$); $^{13}$C NMR (75 MHz, $CDCl_3$)[11] $\delta$ 169.5 (*C*=O), 80.7 ($C(CH_3)_3$), 73.8 ($C(CH_3)_3$), 64.4 ($CH_2$), 63.0 ($CH_2$), 53.1 ($COCH_2N$), 50.5 (*C*HN), 35.6 ($NCH_3$), 28.3 ($C(CH_3)_3$), 27.3 ($C(CH_3)_3$); IR ν (film, cm$^{-1}$) 3217 (N-H), 2974 (CH), 2875 (CH), 1662 (NH-C=O); ESIHRMS *m/z* = 419.2219 $[M+H]^+$. $C_{15}H_{31}N_2O_5$ requires 419.2233.

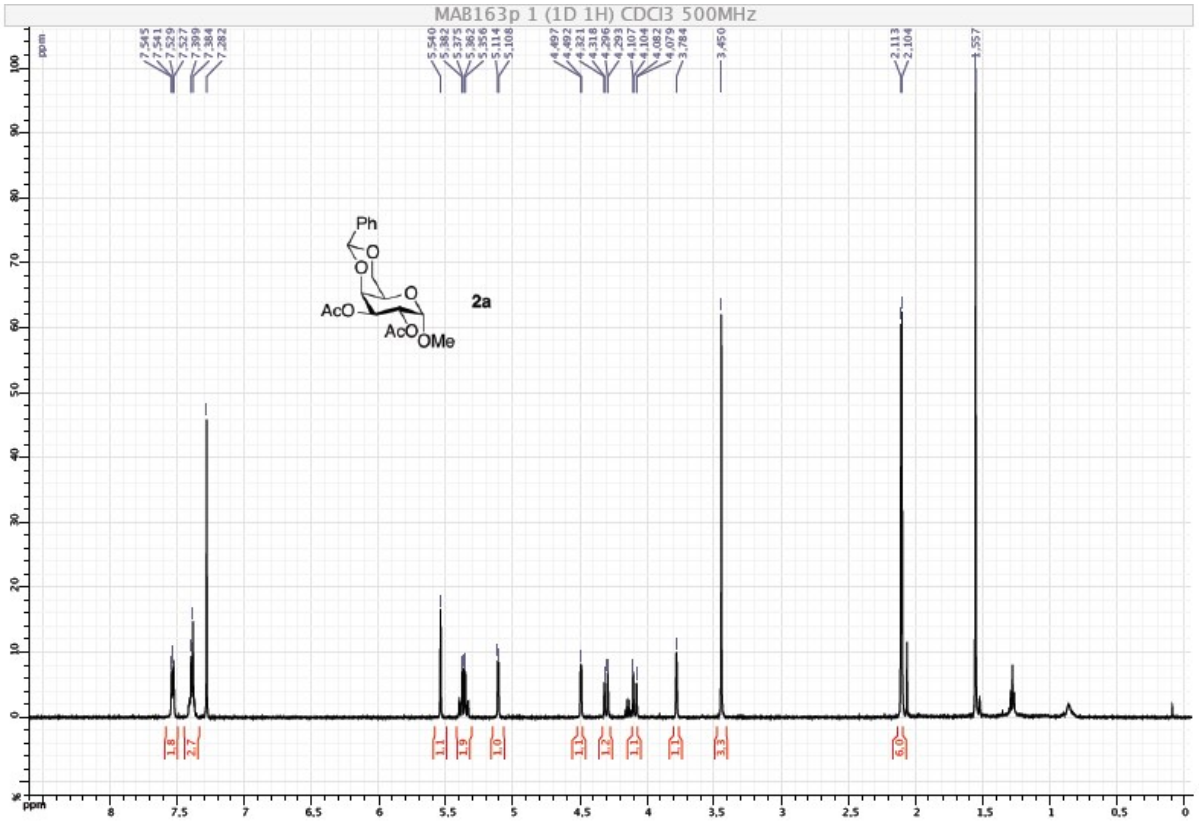
***tert*-butyl (*R*)-(2-((1-(*tert*-butoxy)but-3-yn-2-yl)amino)-2-oxoethyl)(methyl)carbamate 38**. To a stirred solution of alcohol **37** (0.130 g, 0.408 mmol, 1.0 eq.) in $CH_2Cl_2$ (8 mL) at 0 °C was added saturated aqueous $NaHCO_3$ (4 mL), KBr (49 mg, 0.408 mmol, 1.0 eq.) and TEMPO (3 mg, 0.02 mmol, 0.05 eq.). NaOCl (0.5 M, 1.6 mL, 2.0 eq.) was then added with a syringe pump over 30 min. Saturated aqueous $Na_2S_2O_3$ (4 mL) was added, the phases were separated and the aqueous layer was extracted with DCM (3 x 15 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to afford the corresponding crude α-amino aldehyde (95 mg) which was used directly in the next step. To the latter (90 mg, 0.284 mmol, 1 eq.) and dimethyl (1-diazo-2-oxopropyl)phosphonate (96 mg, 0.498 mmol, 1.75 eq.) in MeOH (2 mL) at 0 °C was added $K_2CO_3$ (83 mg, 0.597 mmol, 2.1 eq.). The resulting mixture was stirred at 0 °C for 3 h and was hydrolyzed with a sat. aq. solution of $NH_4Cl$ (10 mL). Water (10 mL) was added and the aqueous phase was extracted with EtOAc (3 x 15 mL). The organic phase was dried with $Na_2SO_4$, filtered and concentrated under vacuum pressure. The crude product was purified by flash chromatography on silica gel (Heptane/EtOAc 70:30 to 50:50) to afford product **38** (51 mg, 0.163 mmol, 42% over the two steps) as a colorless oil. $[\alpha]_D^{20}$ + 2.5 (*c* = 0.32, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$)[10] $\delta$ 6.65-6.26 (bs, 1H, N*H*), 4.83-4.69 (m, 1H, C*H*N), 3.90-3.67 (m, 2H, $COCH_2N$), 3.50-3.37 (m, 2H, $CH_2$), 2.86 (s, 3H, $CH_3$), 2.17 (d, 1H, *J* = 2.5 Hz, $CH_{Alkyne}$), 1.41 (s, 9H, $C(CH_3)_3$), 1.09 s, 9H, $(C(CH_3)_3)$; $^{13}$C NMR (75 MHz, $CDCl_3$)[11] $\delta$ 168.5 (*C*=O), 81.4 ($Cq_{Alkyne}$), 80.7 ($C(CH_3)_3$), 73.6 ($C(CH_3)_3$), 70.8 ($CH_{Alkyne}$), 63.5 ($CH_2$), 53.1 ($CH_2$),

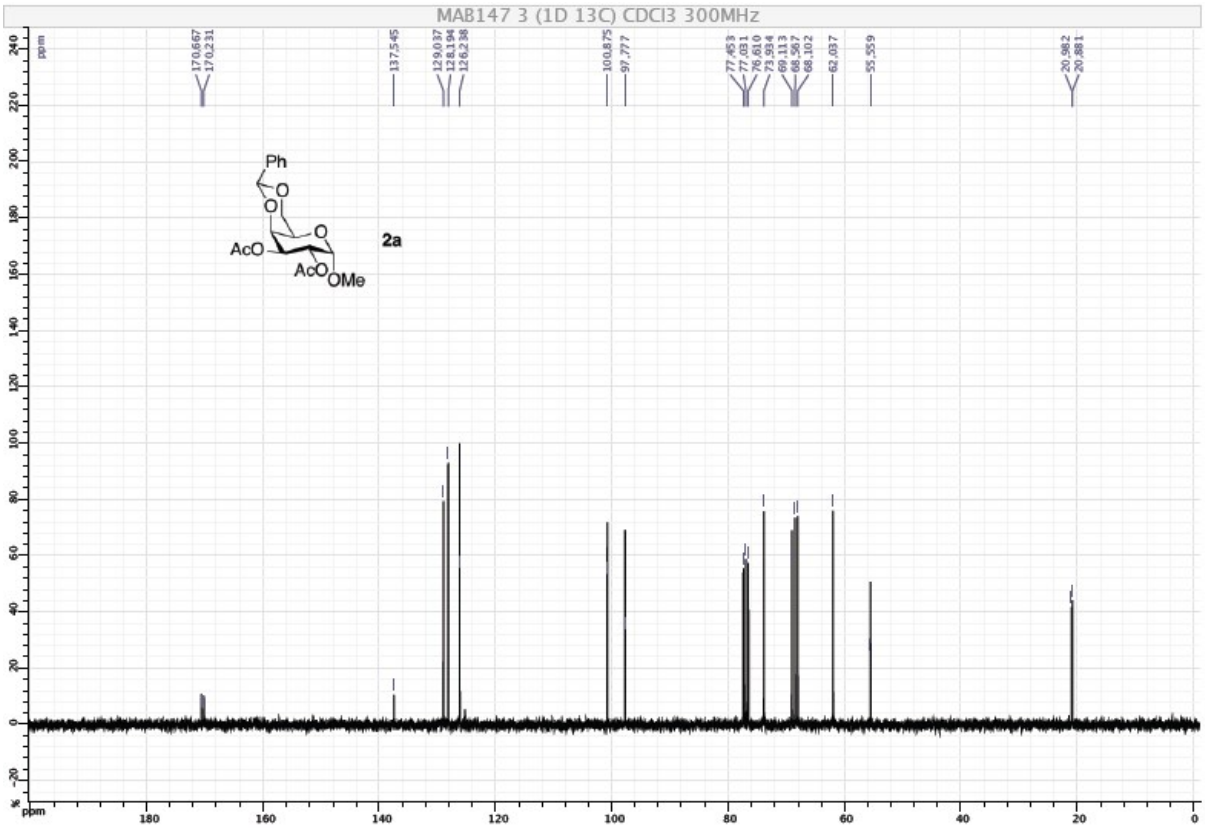
41.6 (CO*C*H$_2$N), 35.6 (N*C*H$_3$), 28.3 (C(CH$_3$)$_3$), 27.4 (C(*C*H$_3$)$_3$); IR ν (film, cm$^{-1}$) 3310 (N-H), 2975 (CH), 2873 (CH), 1666 (NH-C=O); ESIHRMS *m/z* = 335.1947 [M+Na]$^+$. $C_{16}H_{28}N_2O_4$ requires 335.1947.

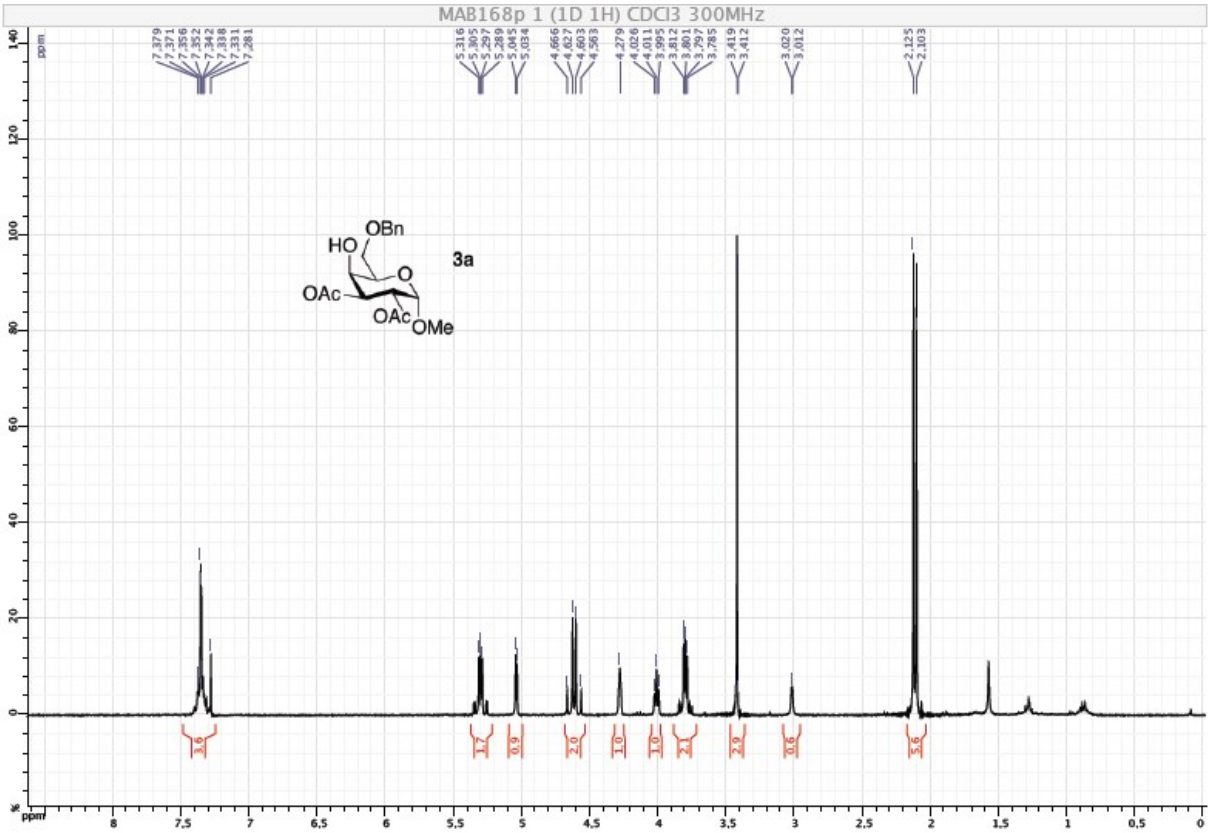
**Peptidonucleoside 39**. To a stirred solution of azid **18** (78 mg, 0.144 mmol, 1.0 eq.) and alkyne **38** (45 mg, 0.144 mmol, 1.0 eq.) in $CH_2Cl_2$ (2 mL) at r.t. was added $CuSO_4$•5$H_2O$ (4 mg, 0.014 mmol, 0.1 eq.) in water (1 mL) followed by sodium ascorbate (3 mg, 0.014 mmol, 0.1 eq.) in water (1 mL). After stirring for 18 h, water (10 mL) and EtOAc (15 mL) were added. The phases were separated and the aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (Heptane/EtOAc 50:50 to 0:100) to afford product **39** (94 mg, 0.163 mmol, 76%) as a colorless oil. $[\alpha]_D^{20}$ – 26.9 (*c* = 0.58, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$)[10] $\delta$ 8.28 (d, 2H, *J* = 7.5 Hz, *H*$_{Ar}$), 7.57 (s, 1H, *H*$_{triazole}$), 7.54-7.46 (m, 1H, *H*$_{Ar}$), 7.42(t, 2H, *J* = 7.5 Hz, *H*$_{Ar}$), 7.27 (s, 1H, *H*$_{Ar}$), 6.94-6.77 (bs, 1H, N*H*), 6.09 (d, 1H, $J_{1,2}$ = 9.5 Hz, *H*1), 5.79 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, *H*3), 5.27 (t, 1H, $J_{2,3} = J_{2,1}$ = 9.5 Hz, *H*2), 5.23-5.12 (m, 1H, C*H*N), 4.73 (t, 1H, $J_{4,5} = J_{4,3}$ = 9.5 Hz, *H*4), 4.62-4.61 (m, 1H, *H*5), 4.08 (dd, 1H, *J* = 2.0 and 12.0 Hz, C*H*$_2$), 3.94-3.73 (m, 4H, C*H*$_2$), 3.62-3.49 (m, 1H, C*H*$_2$), 2.92 (s, 3H, NC*H*$_3$), 2.12 (s, 3H, C*H*$_3$), 2.04 (s, 3H, COC*H*$_3$), 1.97 (s, 3H, COC*H*$_3$), 1.85 (s, 3H, COC*H*$_3$), 1.45 (s, 9H, C(C*H*$_3$)$_3$), 1.09 (s, 9H, C(C*H*$_3$)$_3$); $^{13}$C NMR (75 MHz, $CDCl_3$)[11] $\delta$ 179.9 (*C*=O), 169.9 (*C*=O), 169.7 (*C*=O), 169.0 (*C*=O), 168.5 (*C*=O), 158.8 (*C*=O), 148.0 (*C*q), 136.7 (*C*q), 135.1 (*C*H$_{Ar}$), 132.8 (*C*H$_{Ar}$), 130.0 (*C*H$_{Ar}$), 128.1 (*C*H$_{Ar}$), 122.6 (*C*H$_{Triazole}$), 113.2 (*C*H$_{Ar}$), 80.6 (*C*1), 77.2 (*C*q), 74.9 (*C*5), 73.5 (*C*q), 72.2 (*C*3), 69.7 (*C*2), 62.8 (CH$_2$), 61.8 (CH$_2$), 59.9 (*C*4), 53.0 (*C*H$_2$), 46.5 (*C*HN), 35.8 (N*C*H$_3$), 28.3 (C(CH$_3$)$_3$), 27.4 (C(*C*H$_3$)$_3$), 20.6 (CO*C*H$_3$), 20.4 (CO*C*H$_3$), 20.1 (CO*C*H$_3$), 13.7 (*C*H$_3$); IR ν (film, cm$^{-1}$) 2973 (CH), 2854 (CH), 1750 (CO), 1704 (CO), 1659 (NH-C=O); ESIHRMS *m/z* = 855.3889 [M+H]$^+$. $C_{40}H_{55}N_8O_{13}$ requires 855.13889.

**Peptidonucleoside 40**. The solution **1** was prepared with Na (20 mg) in dry MeOH (2 mL). To a stirred solution of the protected nucleoside **39** (70 mg, 0.028 mmol) in dry MeOH (0.2 mL) was added the solution **1** (0.4 mL, 1 eq.). The resulting mixture was stirred at room temperature for 5 h and a solution of 4M HCl in dioxane (0.6 mL, 2.4 mmol, 30 eq.) was added. The resulting mixture was stirred at room temperature for 8 h and neutralized with $NEt_3$ (0.35 mL). The mixture was concentrated under vaccum and the crude product was purified by preparative TLC ($H_2O$/EtOH/EtOAc 1:2:2, with 1% of $NH_4OH$) to afford product **40** as a white powder, which was washed several times with $CHCl_3$ (25 mg, 0.047 mmol, 58%). $[\alpha]_D^{20}$ – 43.4 (*c* = 0.35, $H_2O$/MeOH: 1/1); $^1$H NMR (300 MHz, $CD_3OD$) $\delta$ 8.15 (s, 1H, *H*$_{triazole}$), 7.91 (s, 1H, *H*$_{Ar}$), 7.62-7.24 (bs, 1H, N*H*), 5.89 (d, 1H, $J_{1,2}$ = 9.5 Hz, *H*1), 5.31 (t, 1H, *J* = 5.5 Hz, C*H*N), 4.74 (t, 1H, $J_{3,4} = J_{3,2}$ = 9.5 Hz, *H*3), 5.34-4.24 (m, 2H, *H*4 and *H*5), 3.97-3.88 (m, 2H, C*H*$_2$), 3.85 (t, 1H, $J_{2,1} = J_{2,3}$ = 9.5 Hz, *H*2), 3.82-3.71 (m, 2H, C*H*$_2$), 3.52 (dd, 1H, *J* = 1.5 and 12.0 Hz, *H*6), 3.52 (dd, 1H, *J* = 4.0 and 12.0 Hz, *H*6'), 2.78 (s, 3H, NC*H*$_3$), 2.10 (s, 3H, C*H*$_3$), 1.21 (s, 9H, C(C*H*$_3$)$_3$), 1.09 (C(C*H*$_3$)$_3$); $^{13}$C NMR (75 MHz, $CD_3OD$) $\delta$ 164.9 (*C*=O), 163.4 (*C*=O), 153.5 (*C*q), 145.8 (*C*q), 140.6 (*C*H$_{Ar}$), 124.0 (*C*H$_{Triazole}$), 100.7 (*C*q), 83.7 (*C*1), 77.5 and 74.4 (*C*4 and *C*5), 73.4 (*C*q), 72.4 (*C*2), 63.0 (*C*H$_2$), 61.7 (*C*3), 60.0 (*C*6), 49.4 (*C*H$_2$), 47.2 (*C*HN), 32.4 (N*C*H$_3$), 26.3 (C(CH$_3$)$_3$), 11.7 (*C*H$_3$); IR ν (film, cm$^{-1}$) 3056 (NH), 2921 (CH), 1666 (NH-C=O); ESIHRMS *m/z* = 525.2787 [M+H]$^+$. $C_{22}H_{37}N_8O_7$ requires 525.2785.

# $^{1}$H-NMR and $^{13}$C-NMR spectra

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4.279
4.026
4.011
3.995
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3.801
3.797
3.785
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3.012
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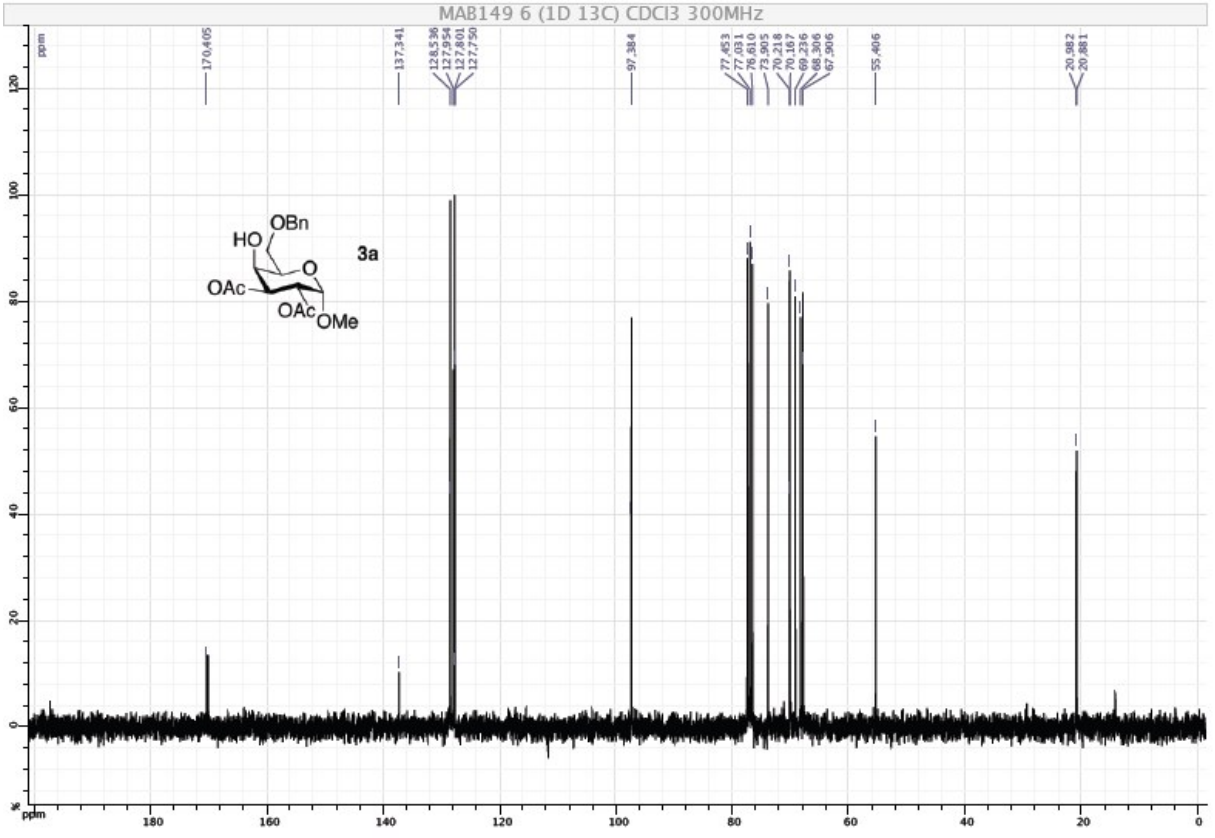
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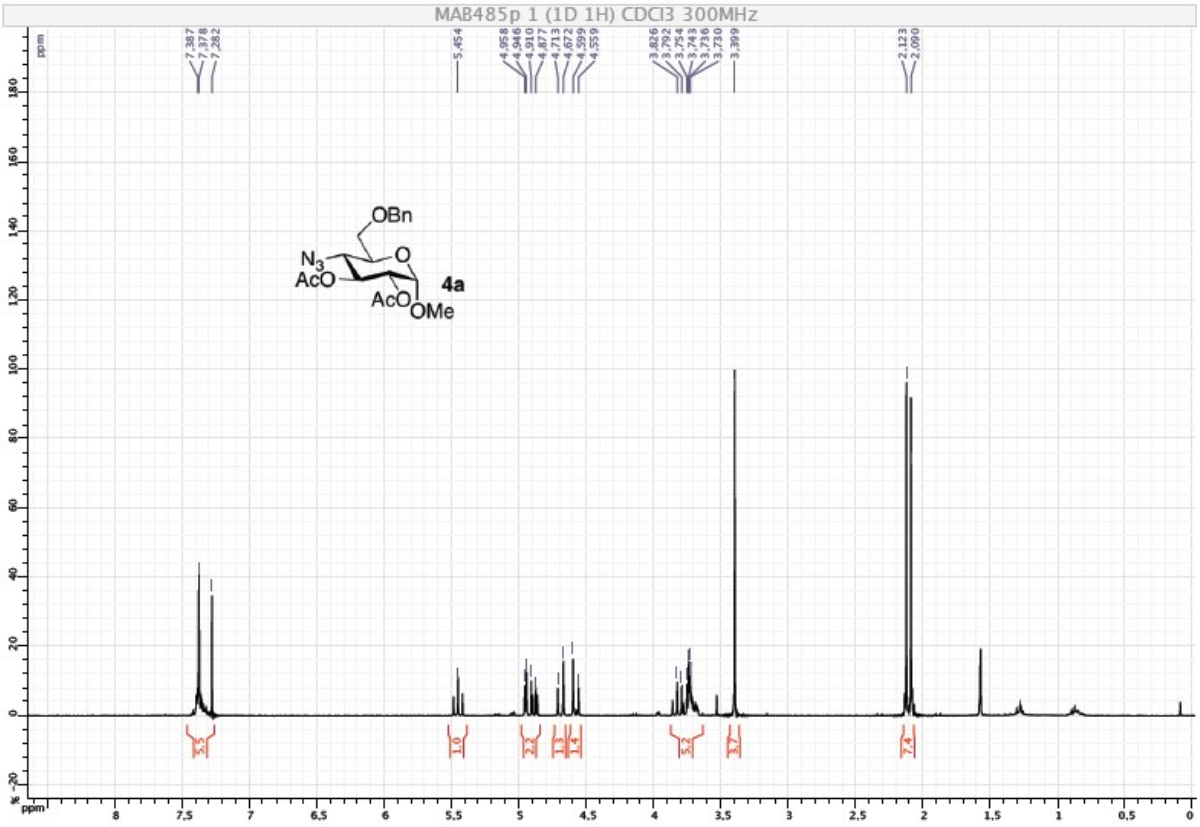
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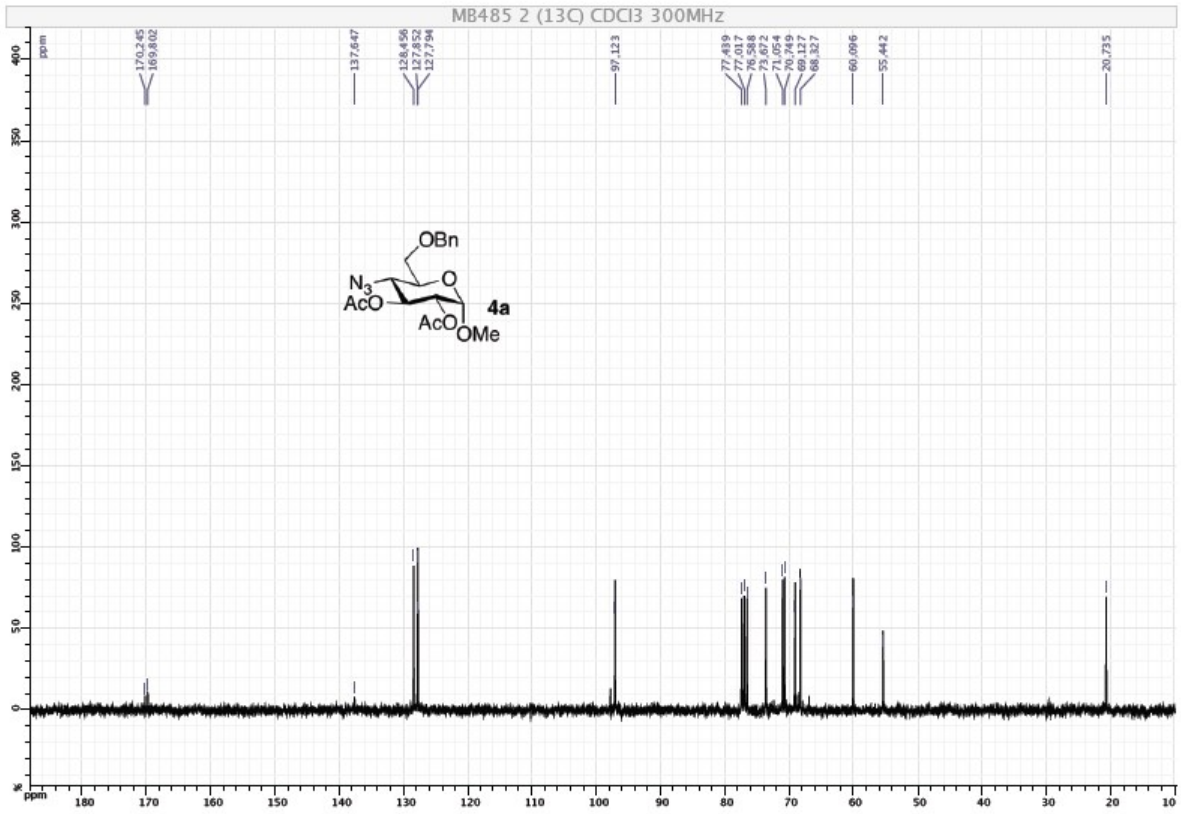
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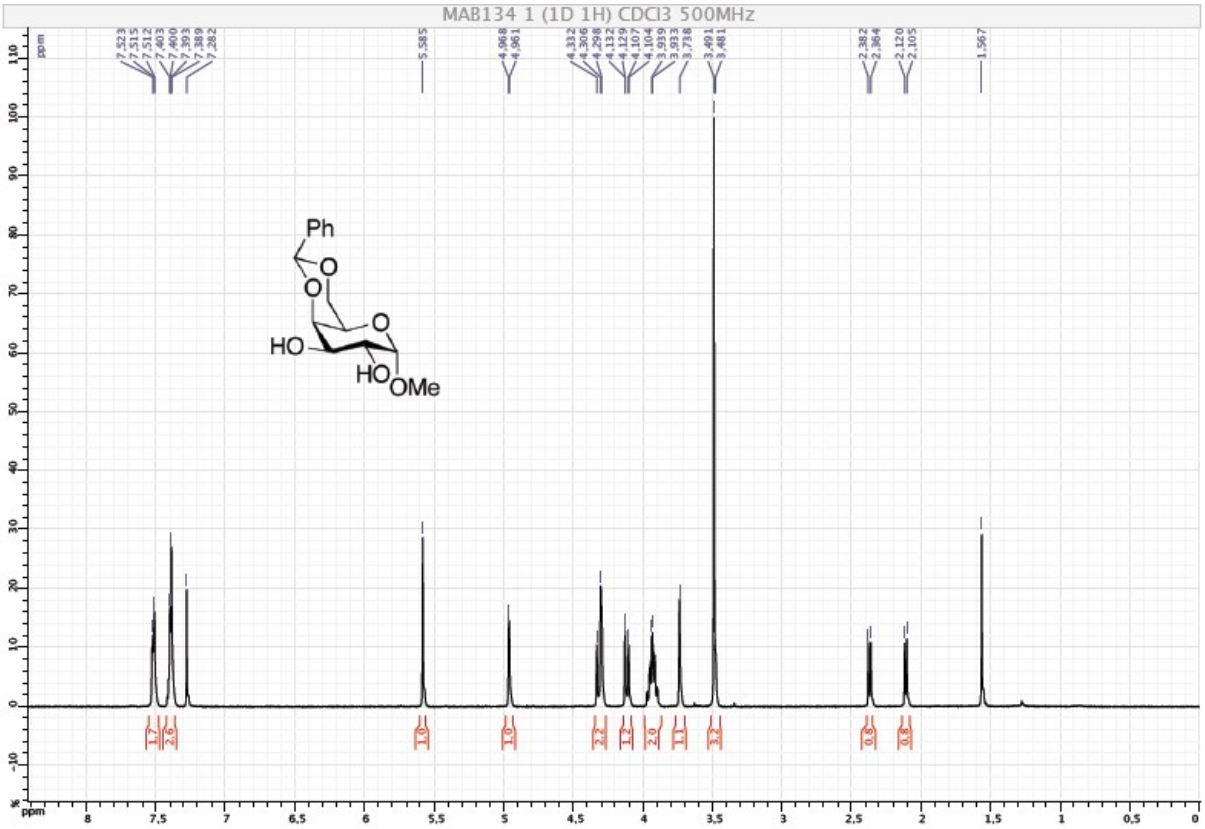
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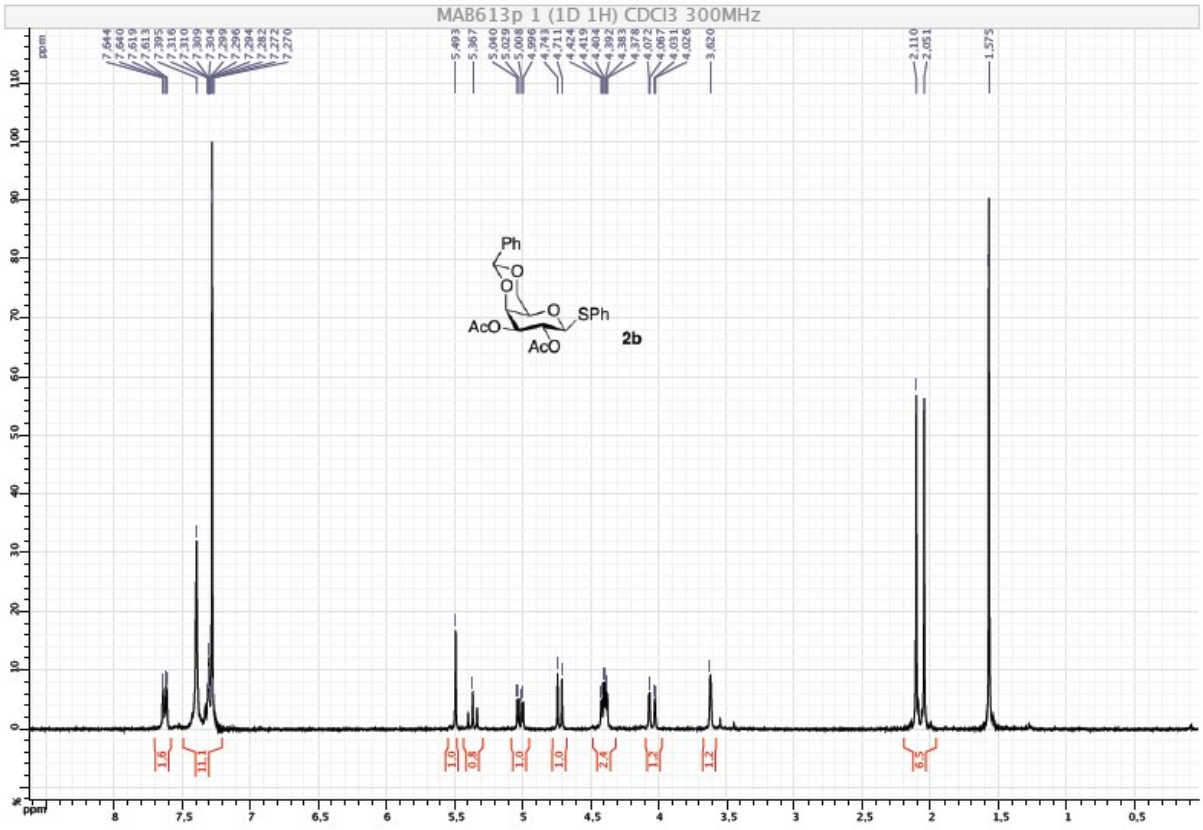
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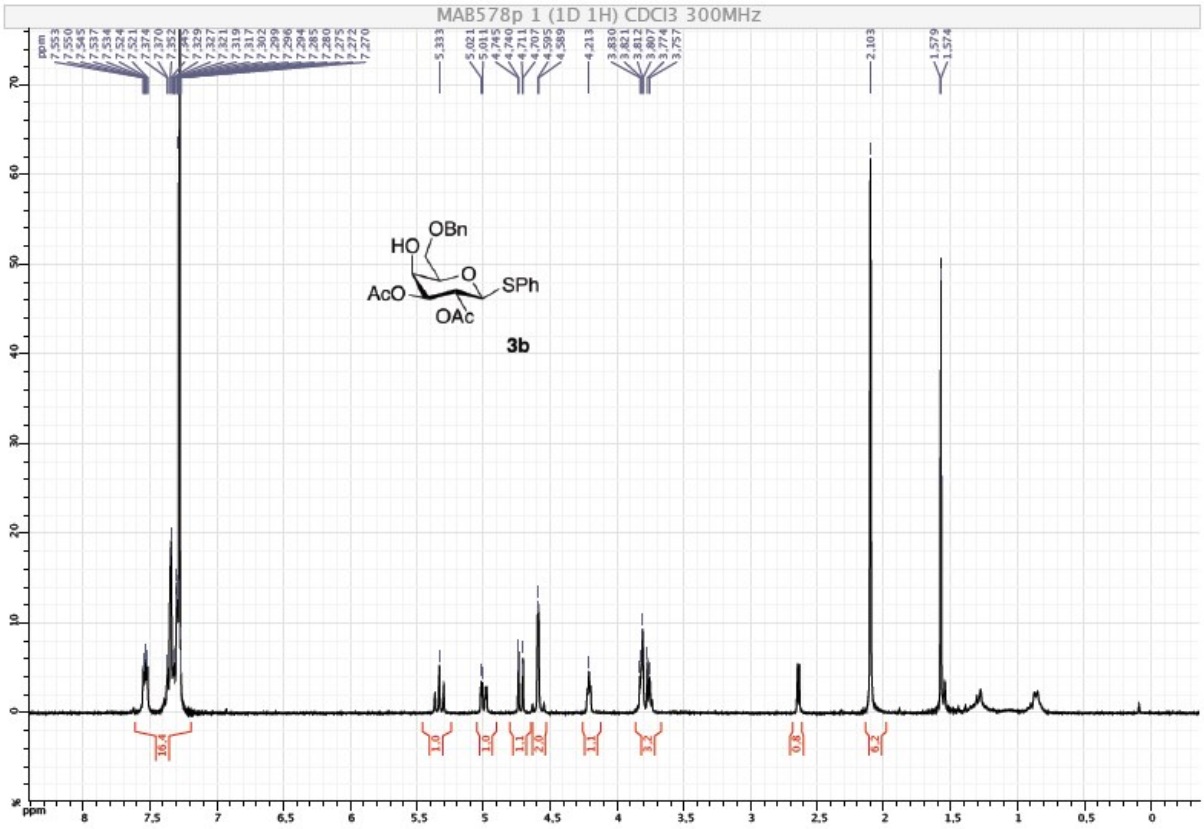
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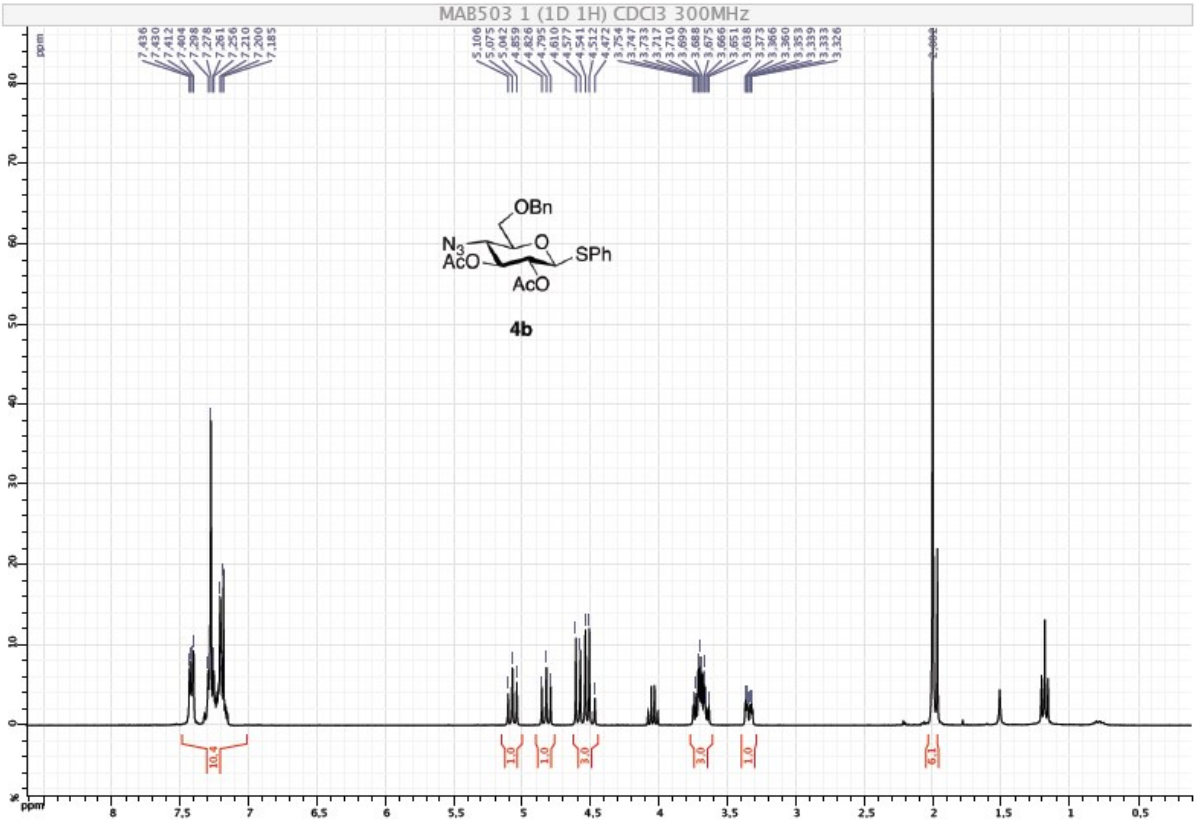
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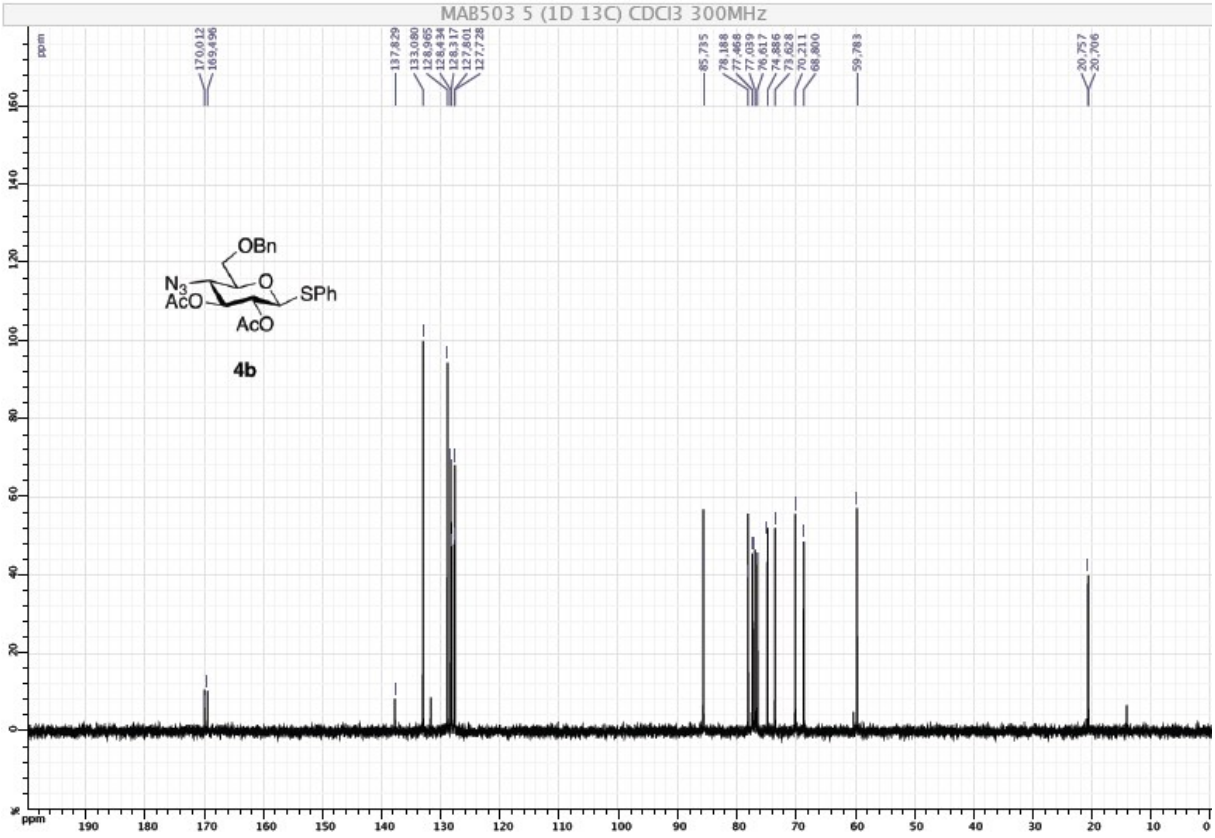
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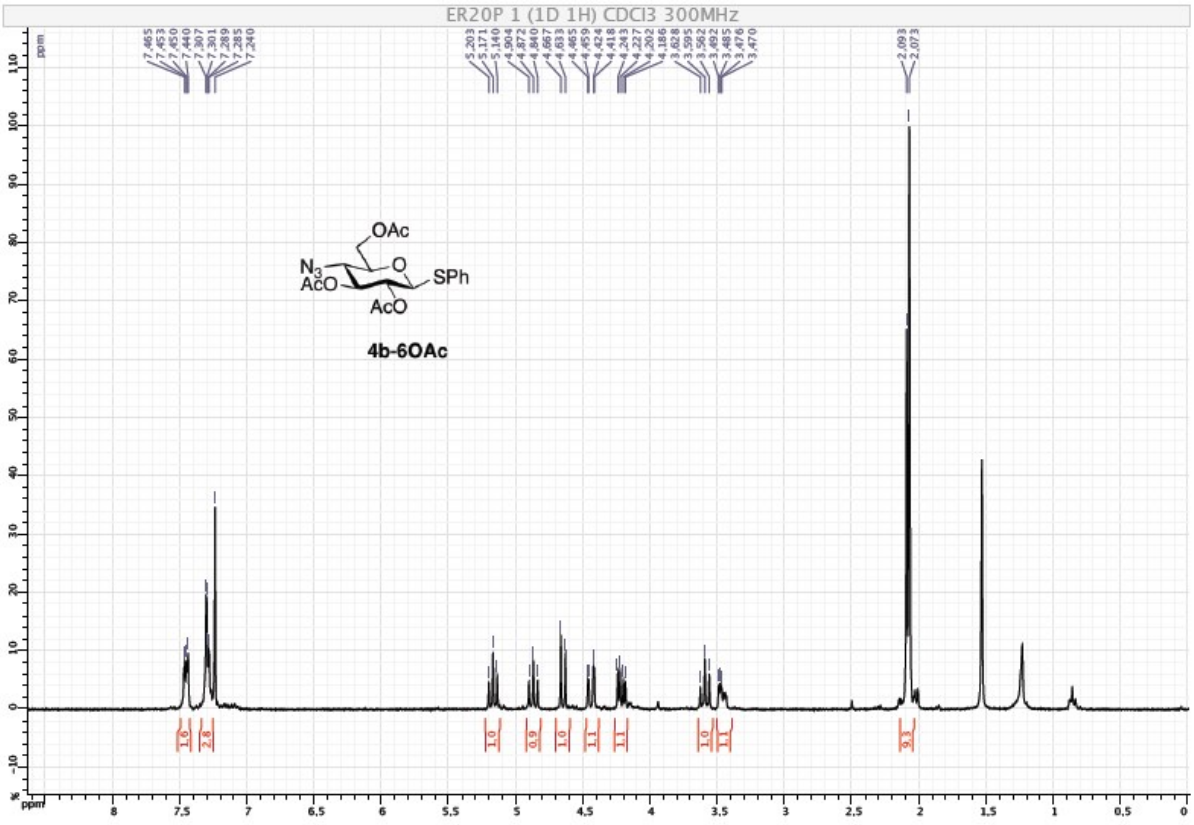
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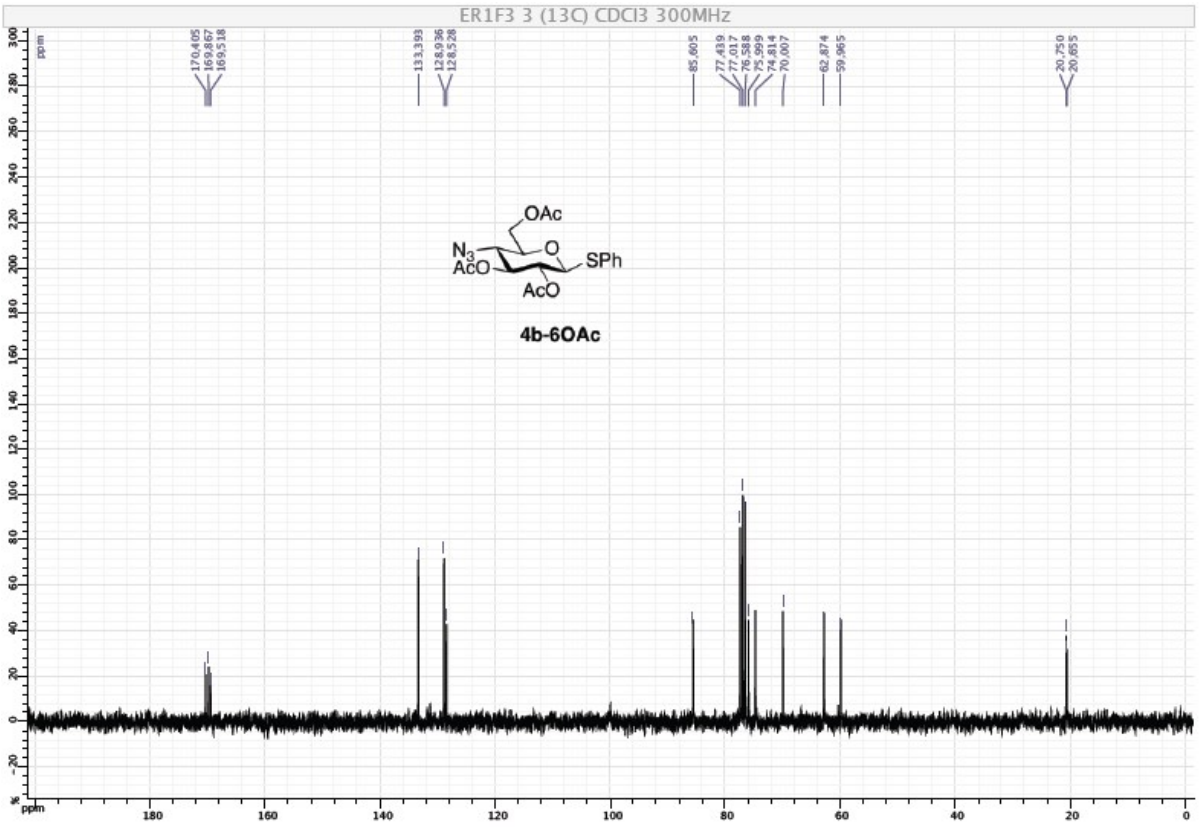
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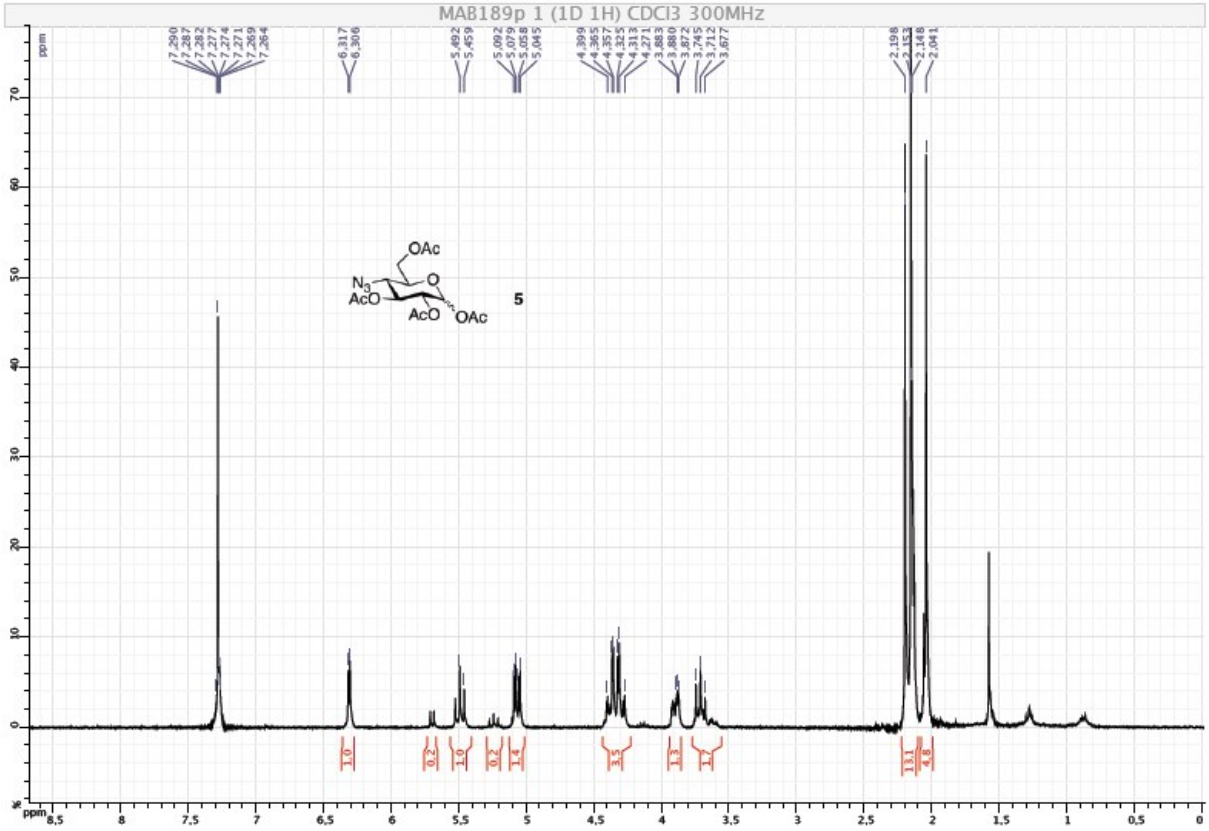
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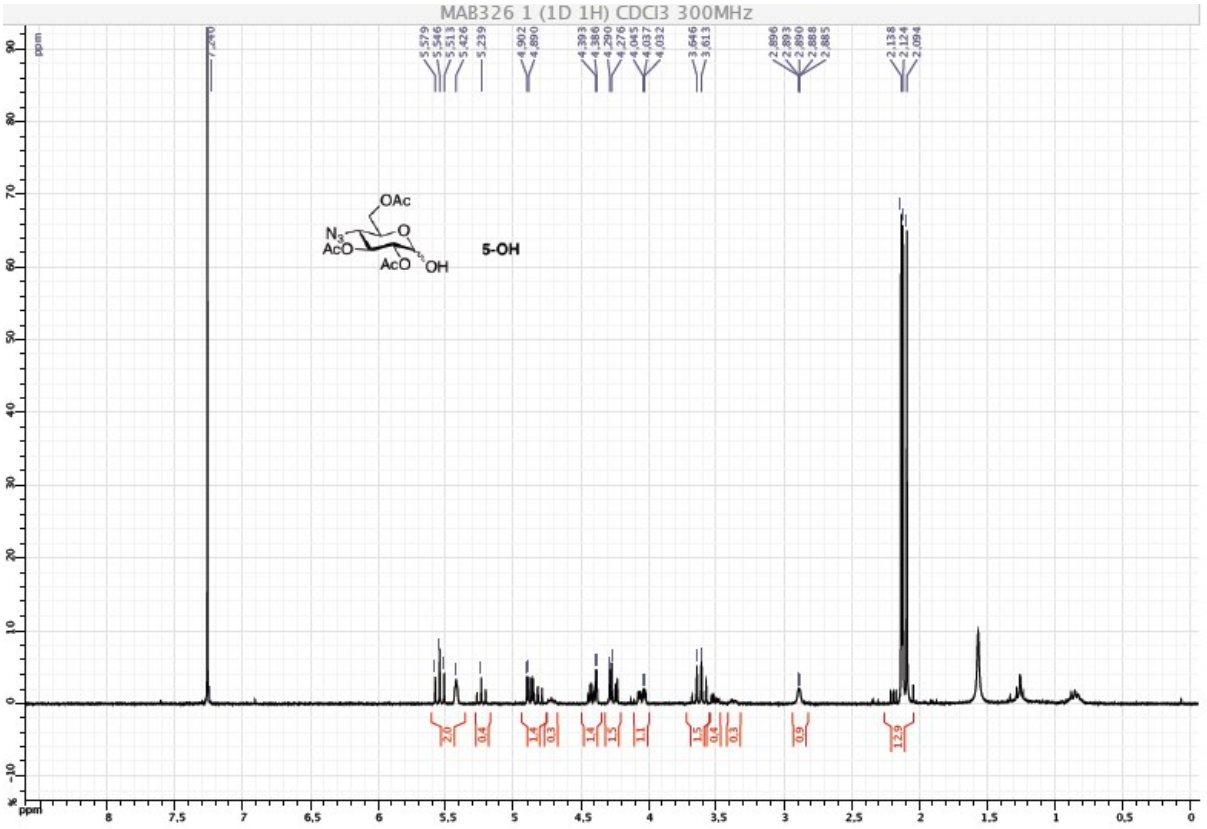
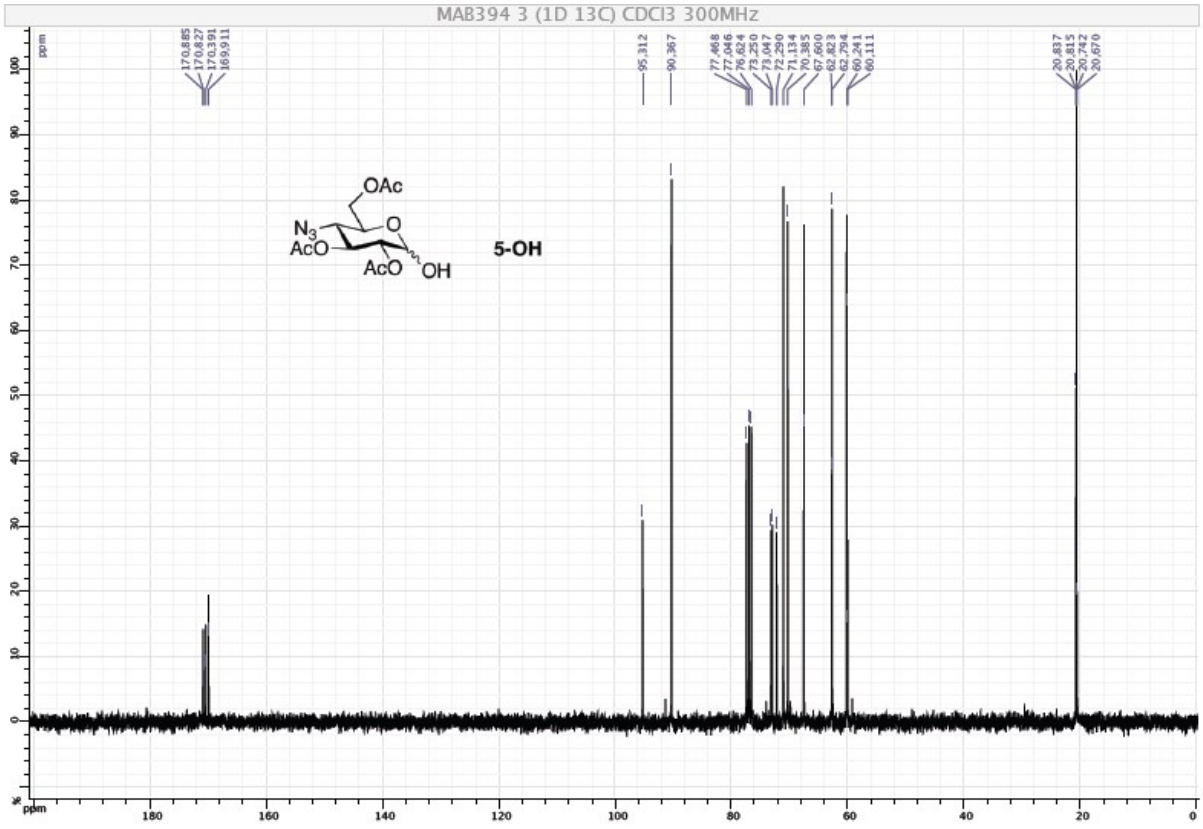
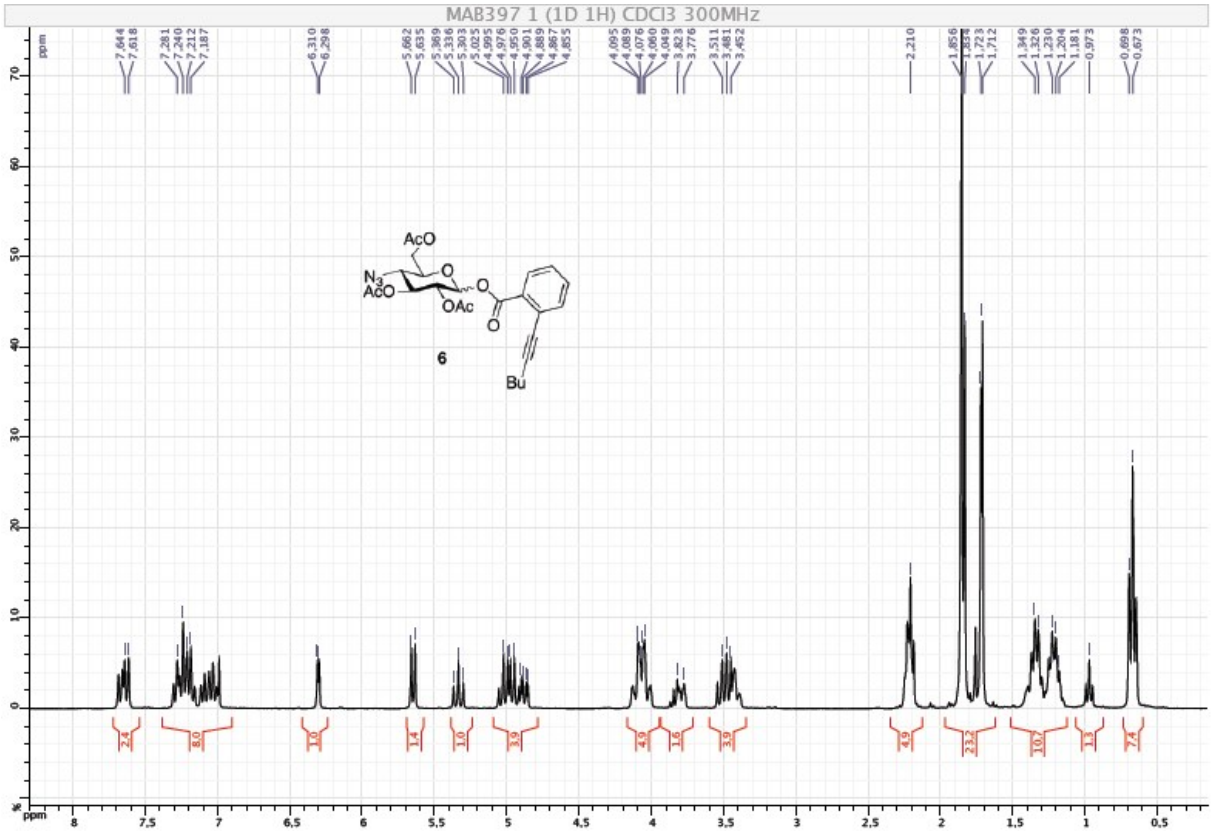
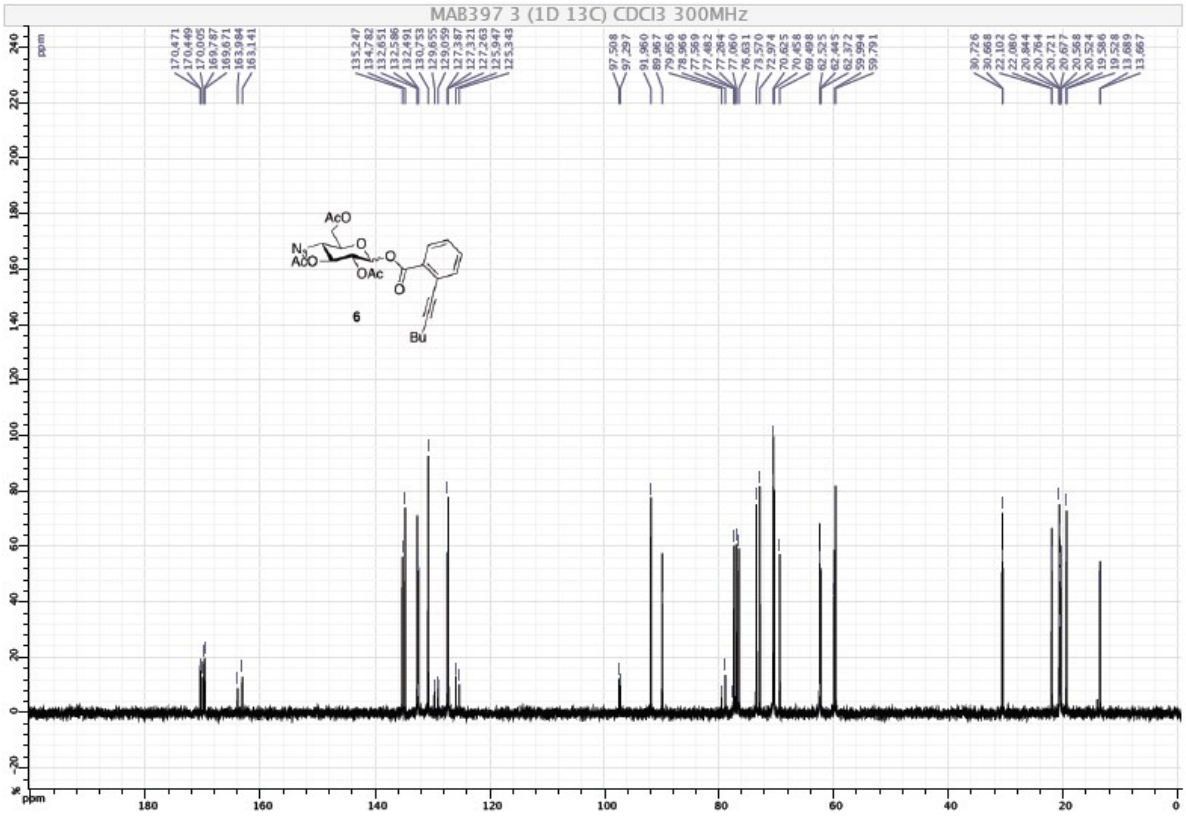
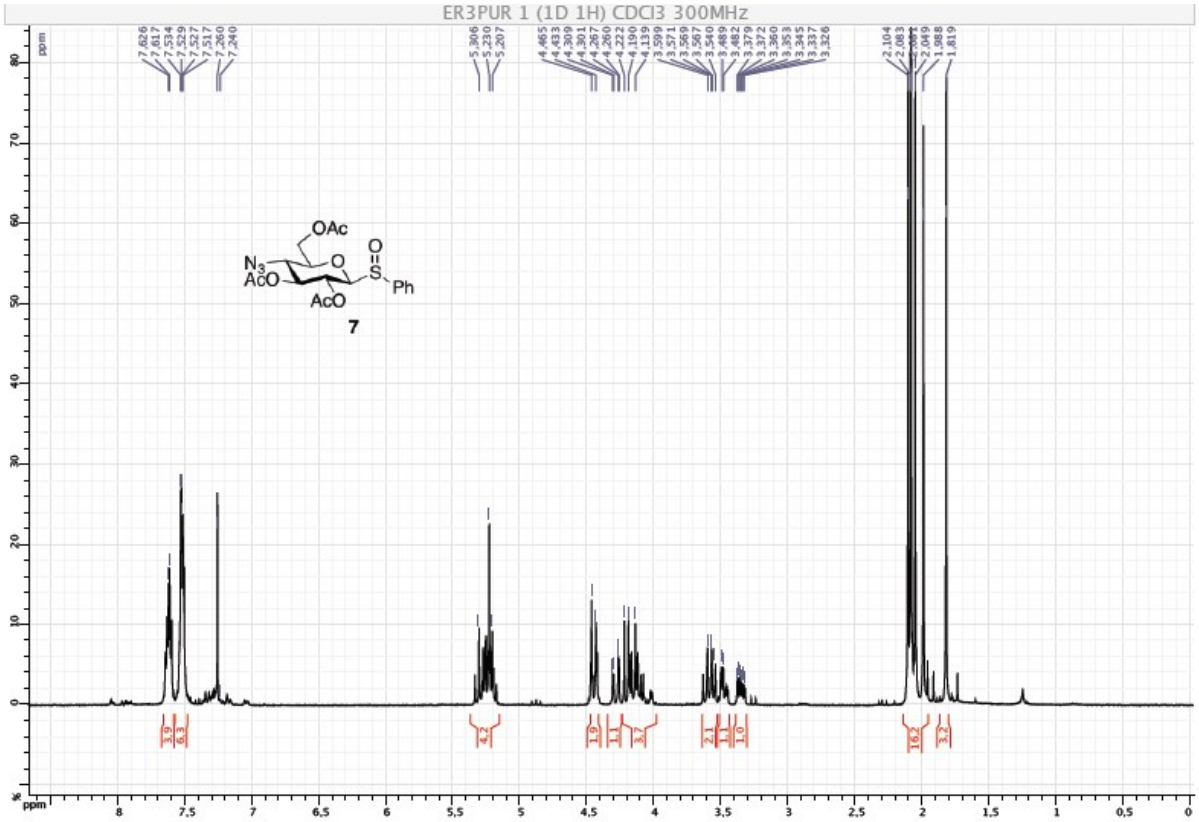
13,1
4,8

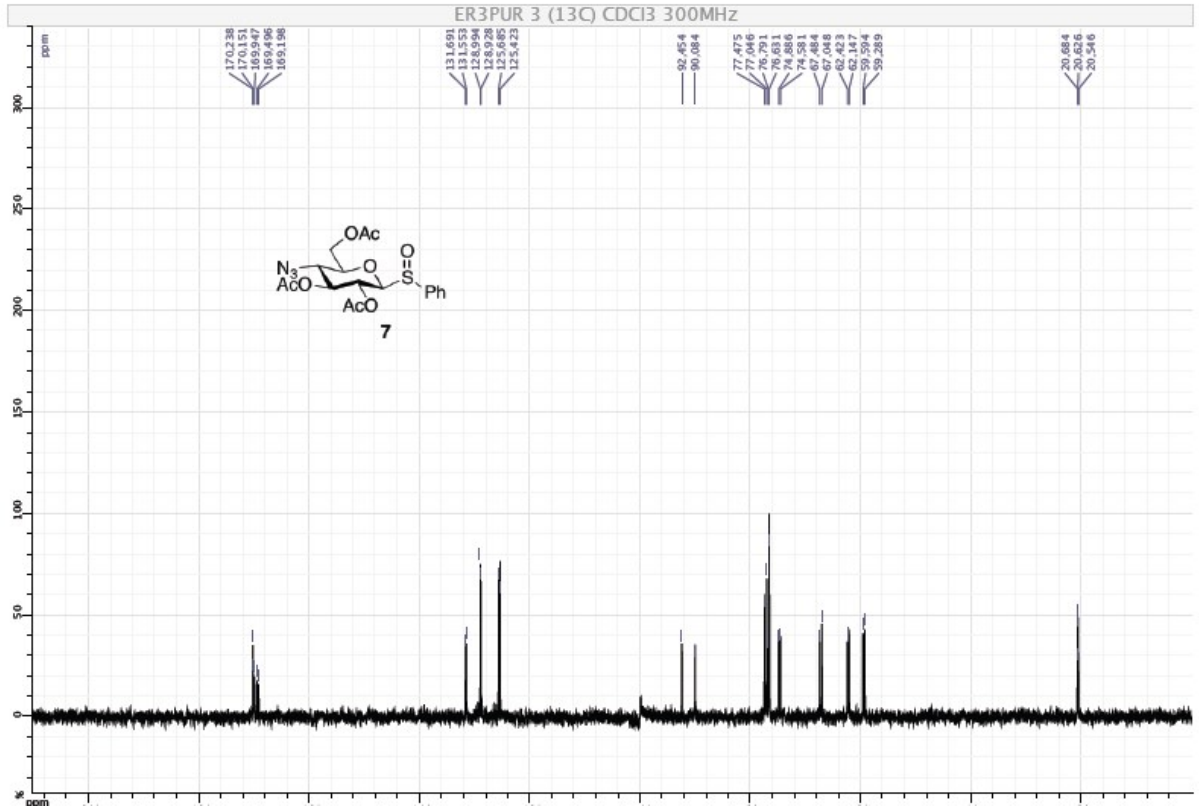

MAB326 1 (1D 1H) CDCl3 300MHz
5-OH

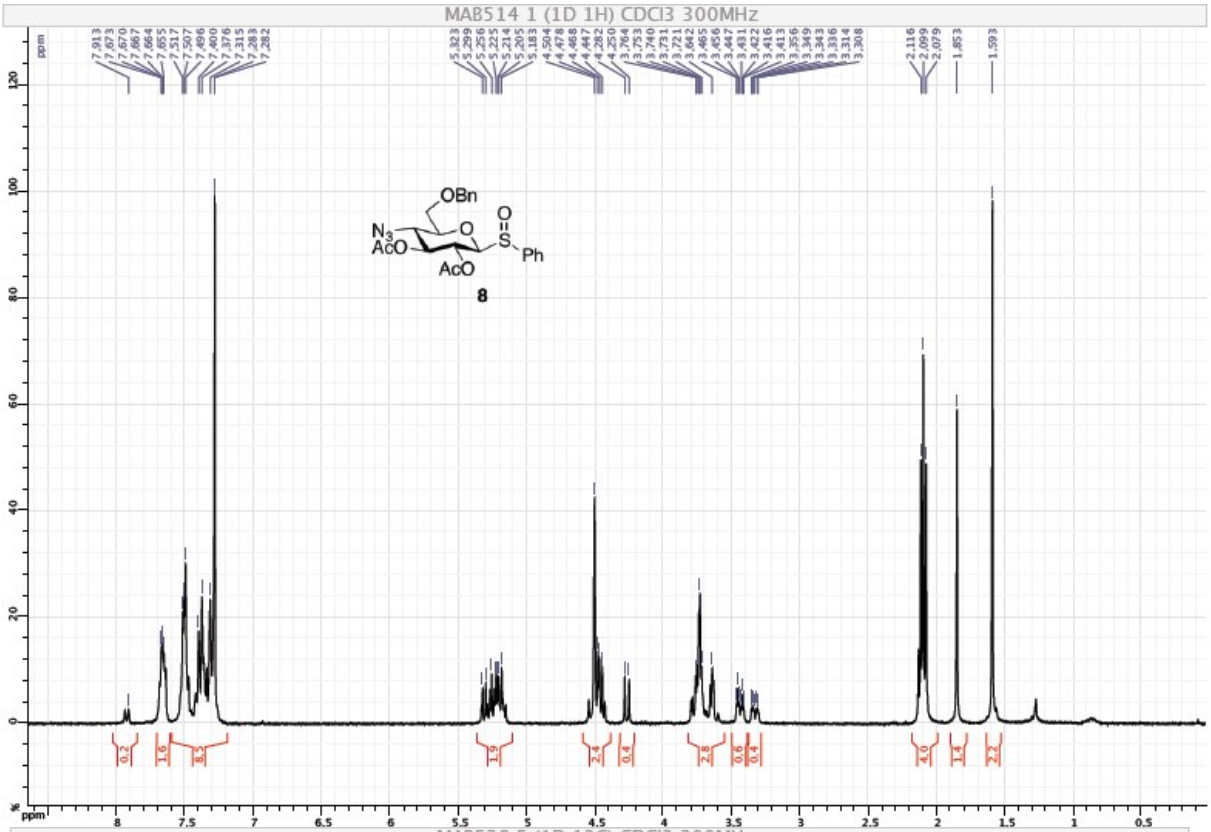

MAB394 3 (1D 13C) CDCl3 300MHz
5-OH

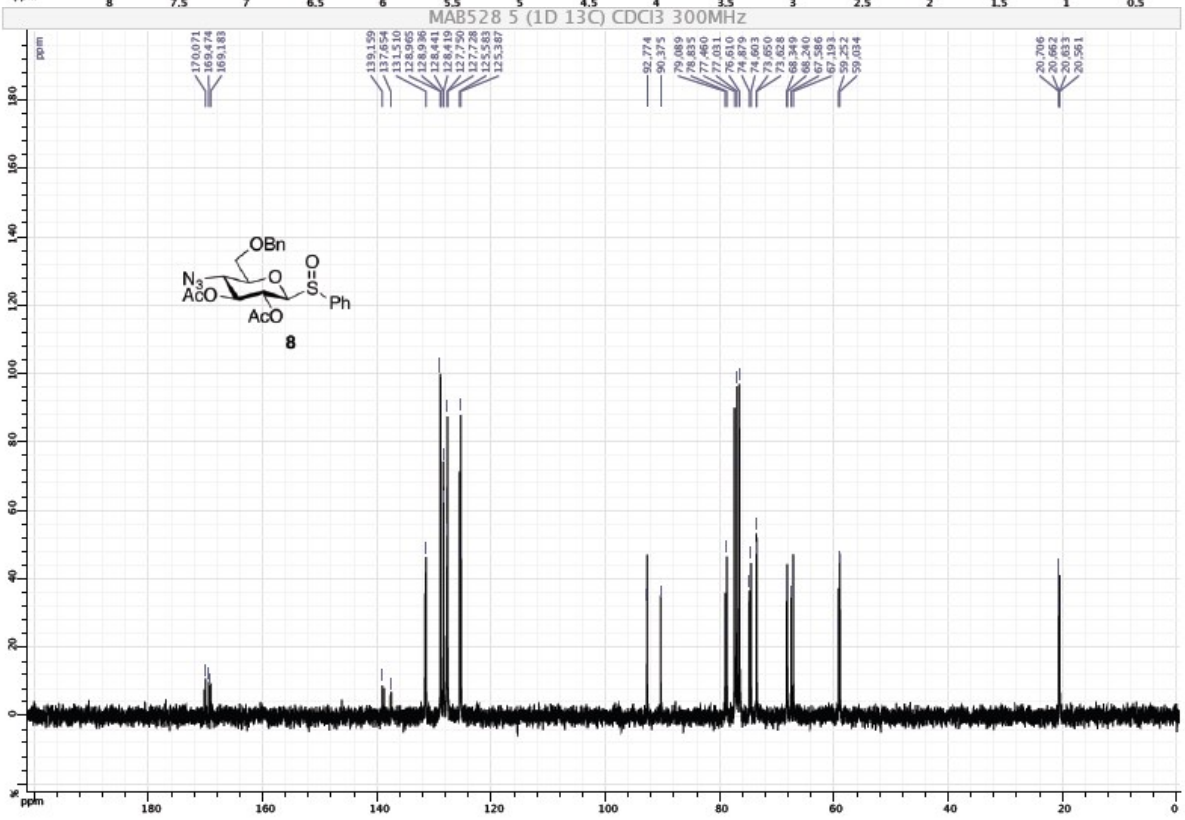

MAB397 1 (1D 1H) CDCl3 300MHz
AcO
N3
AcO
OAc
O
O
6
Bu

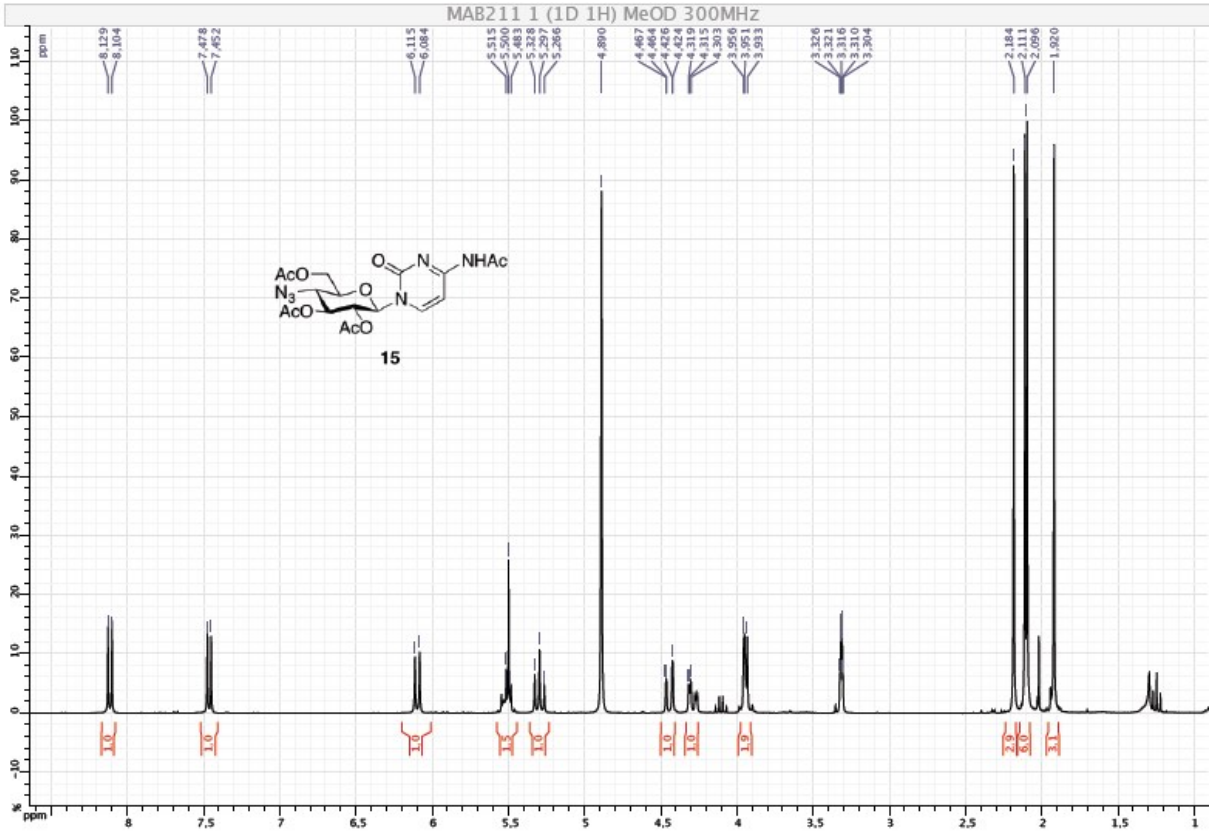

MAB397 3 (1D 13C) CDCl3 300MHz
AcO
N3
AcO
OAc
O
O
6
Bu

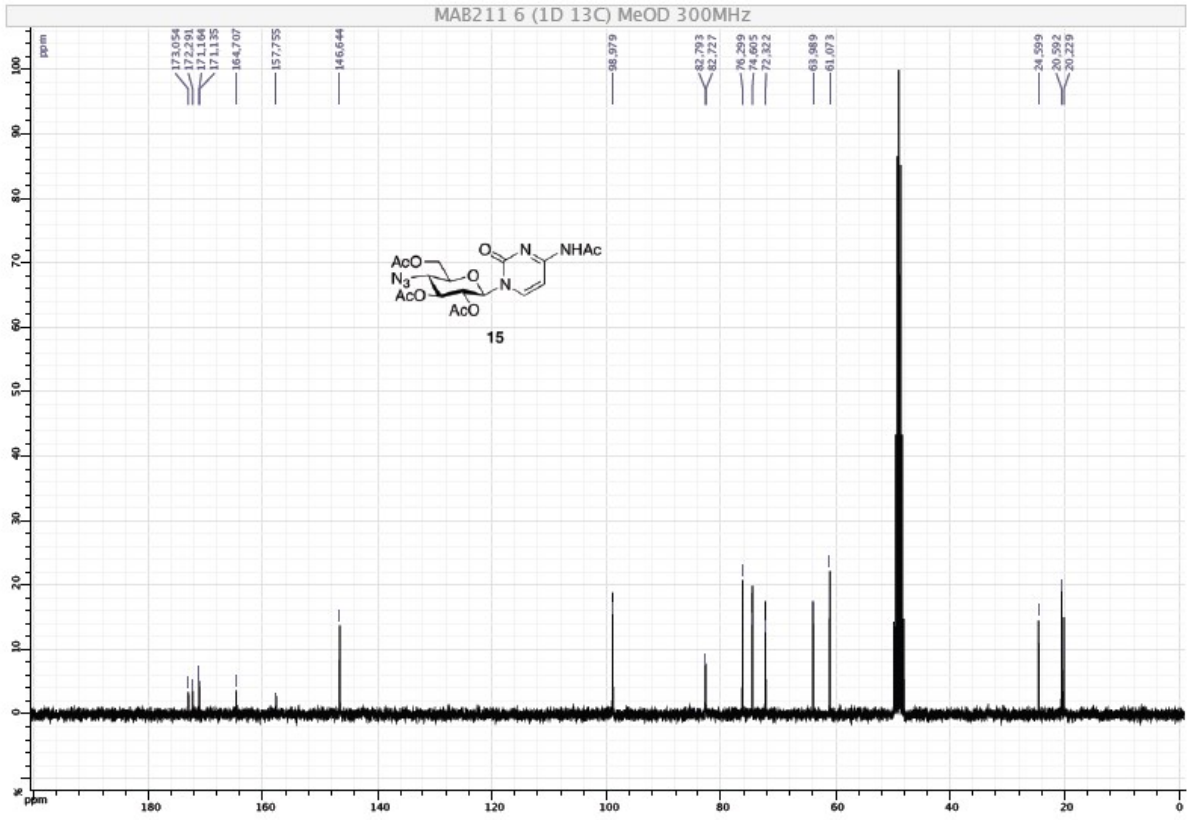

ER3PUR 1 (1D 1H) CDCl3 300MHz
OAc
N3
AcO
O
S
Ph
AcO
7

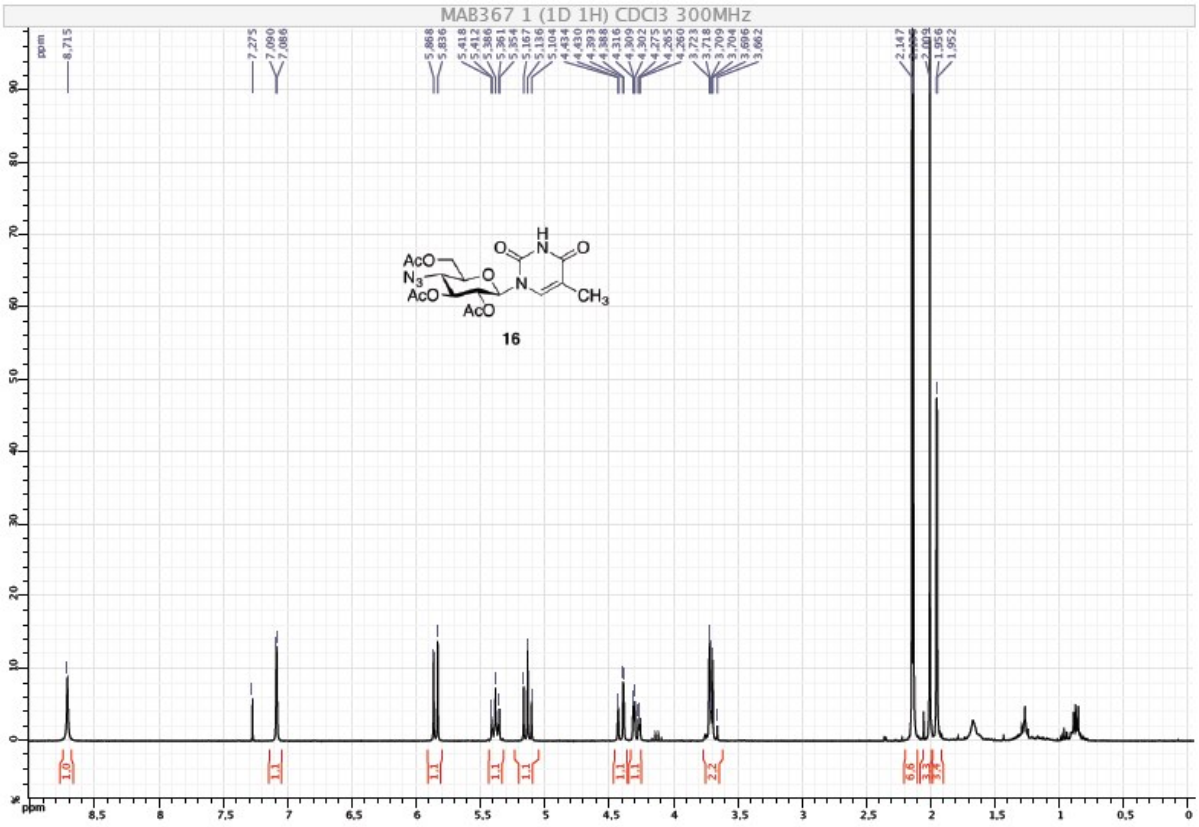

ER3PUR 3 (13C) CDCl3 300MHz
OAc
N3
AcO
O
S
Ph
AcO
7

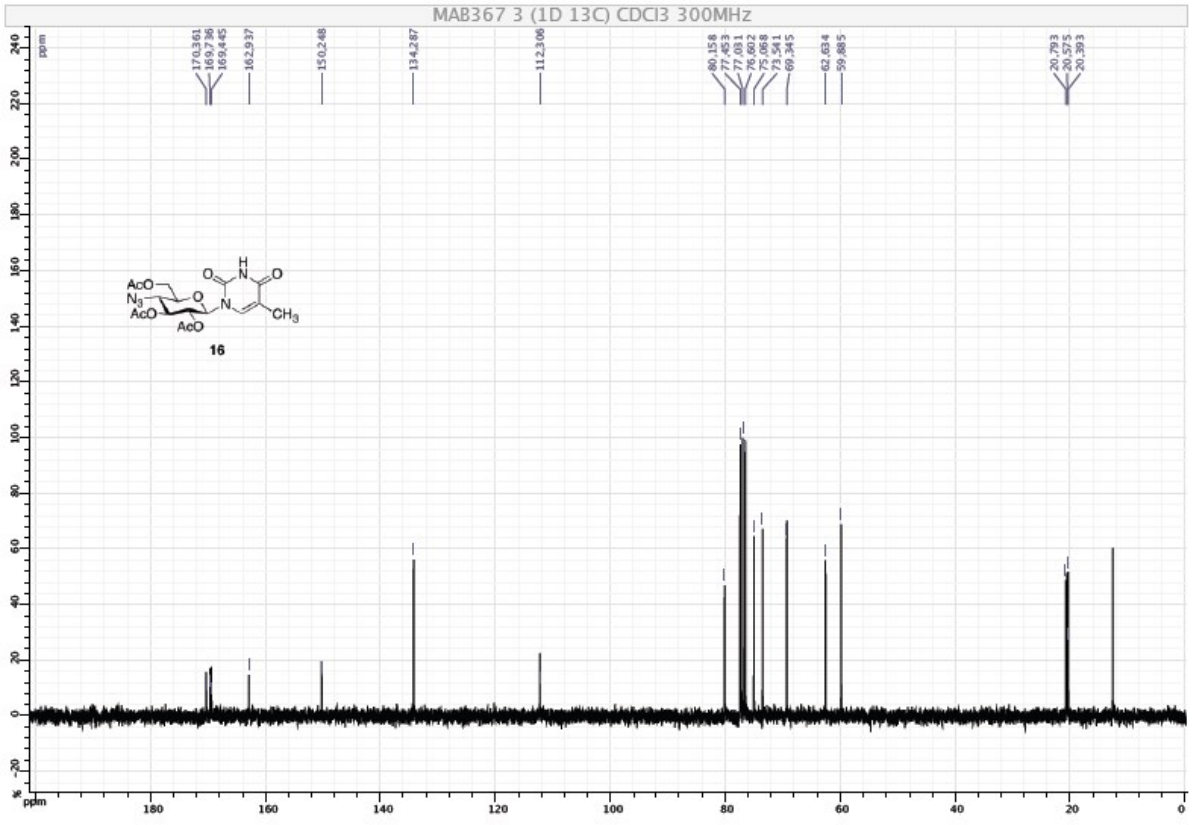

MAB514 1 (1D 1H) CDCl3 300MHz
OBn
N3
AcO
O
O
S
Ph
AcO
8

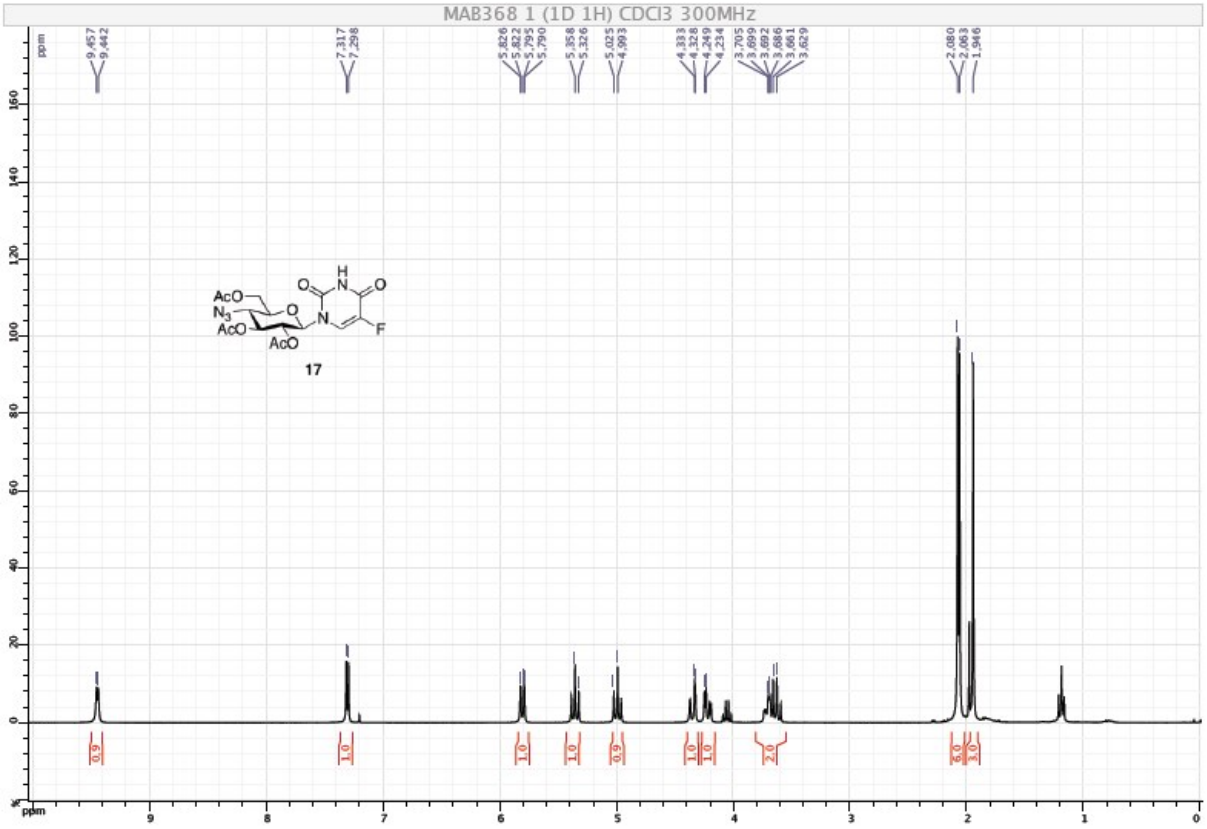

MAB528 5 (1D 13C) CDCl3 300MHz
OBn
N3
AcO
O
O
S
Ph
AcO
8

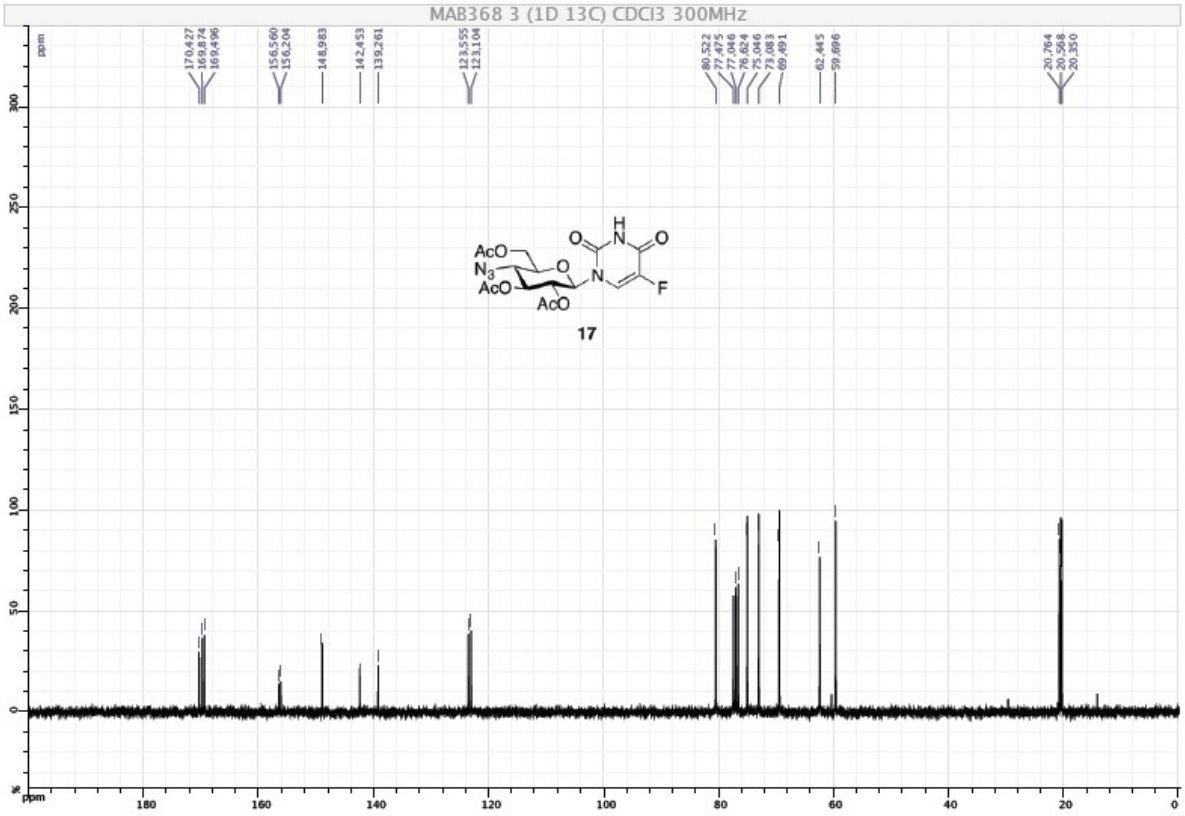

MAB211 1 (1D 1H) MeOD 300MHz
8.129
8.104
7.478
7.452
6.115
6.084
5.515
5.500
5.483
5.328
5.297
5.266
4.890
4.467
4.464
4.426
4.424
4.319
4.315
4.303
3.956
3.951
3.933
3.326
3.321
3.316
3.310
3.304
2.184
2.111
2.096
1.920
AcO
N3
AcO
AcO
O
N
NHAc
15
ppm

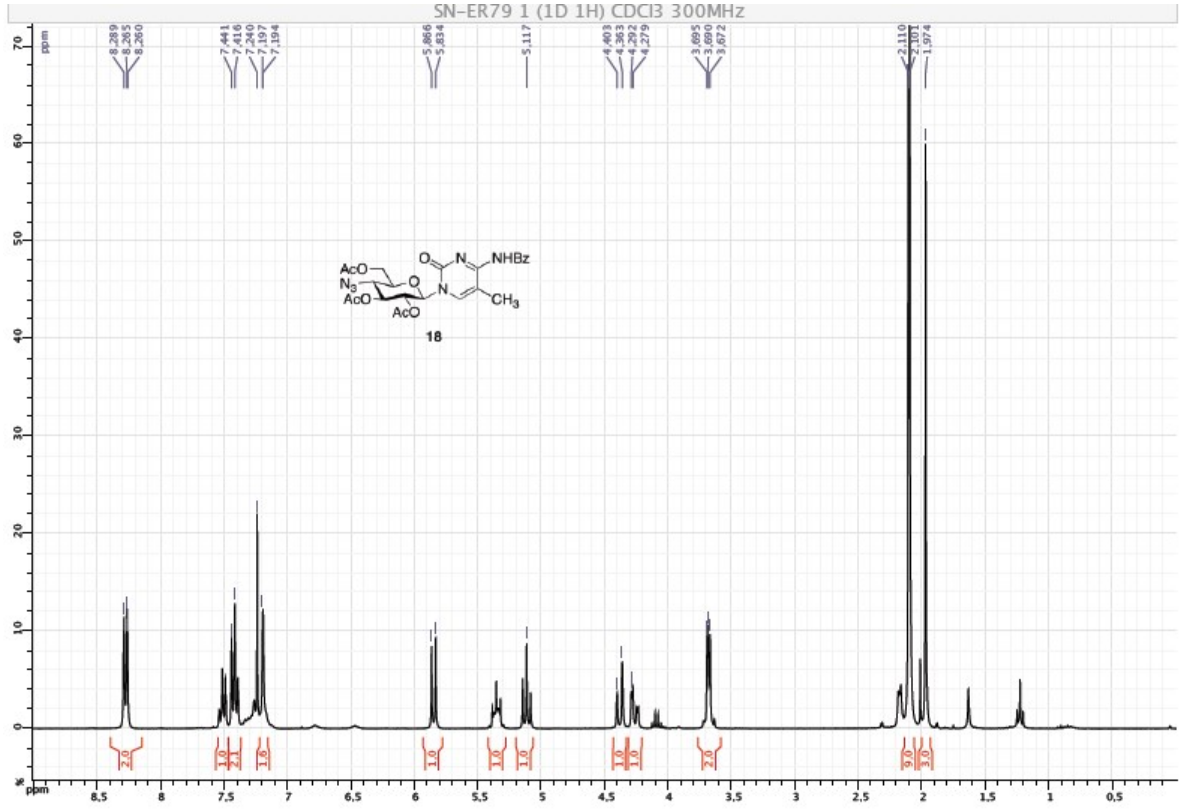

MAB211 6 (1D 13C) MeOD 300MHz
173.054
172.291
171.164
171.135
164.707
157.755
146.644
98.979
82.793
82.727
76.299
74.605
72.322
63.989
61.073
24.599
20.592
20.229
AcO
N3
AcO
AcO
O
N
NHAc
15
ppm

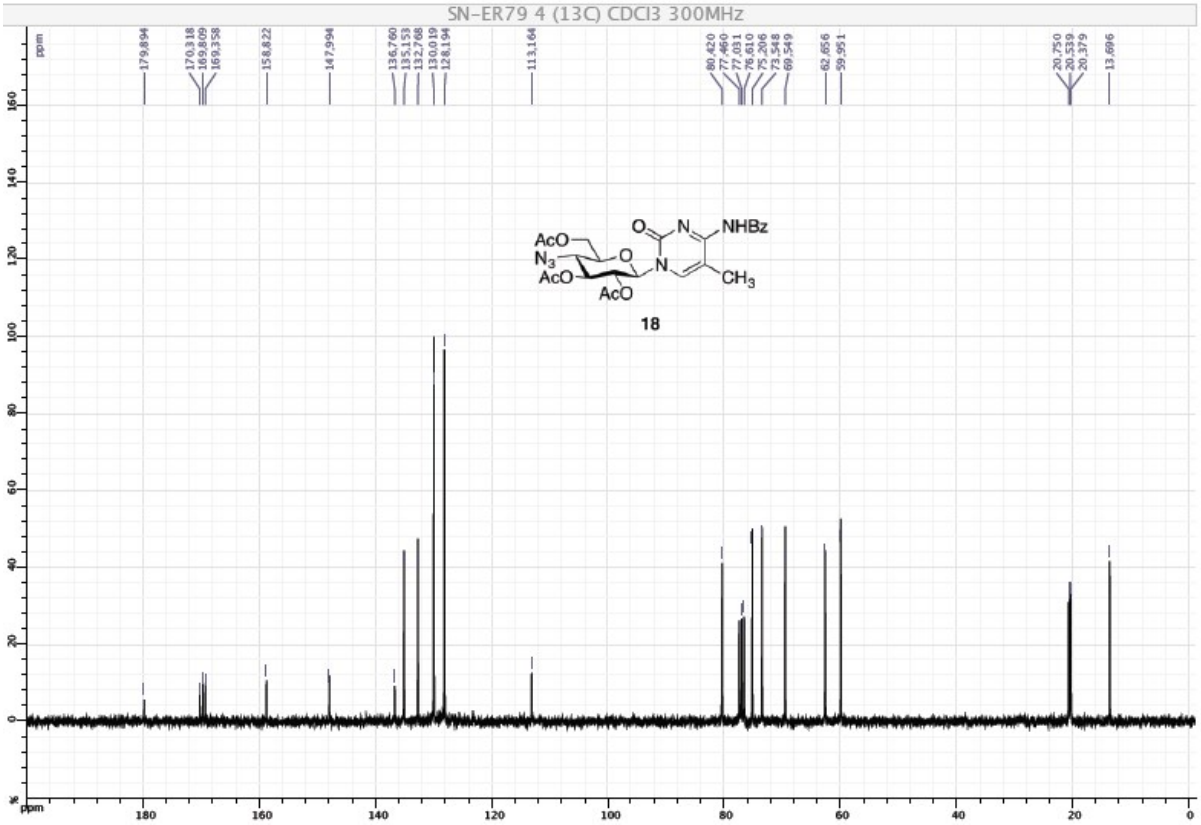

MAB367 1 (1D 1H) CDCl3 300MHz
ppm
8.715
7.275
7.090
7.086
5.868
5.836
5.418
5.412
5.386
5.361
5.354
5.167
5.138
5.104
4.434
4.430
4.393
4.388
4.316
4.309
4.302
4.275
4.265
4.260
3.718
3.709
3.704
3.696
3.662
2.147
2.019
1.956
1.952
AcO
N3
AcO
AcO
O
N
H
O
O
N
CH3
16

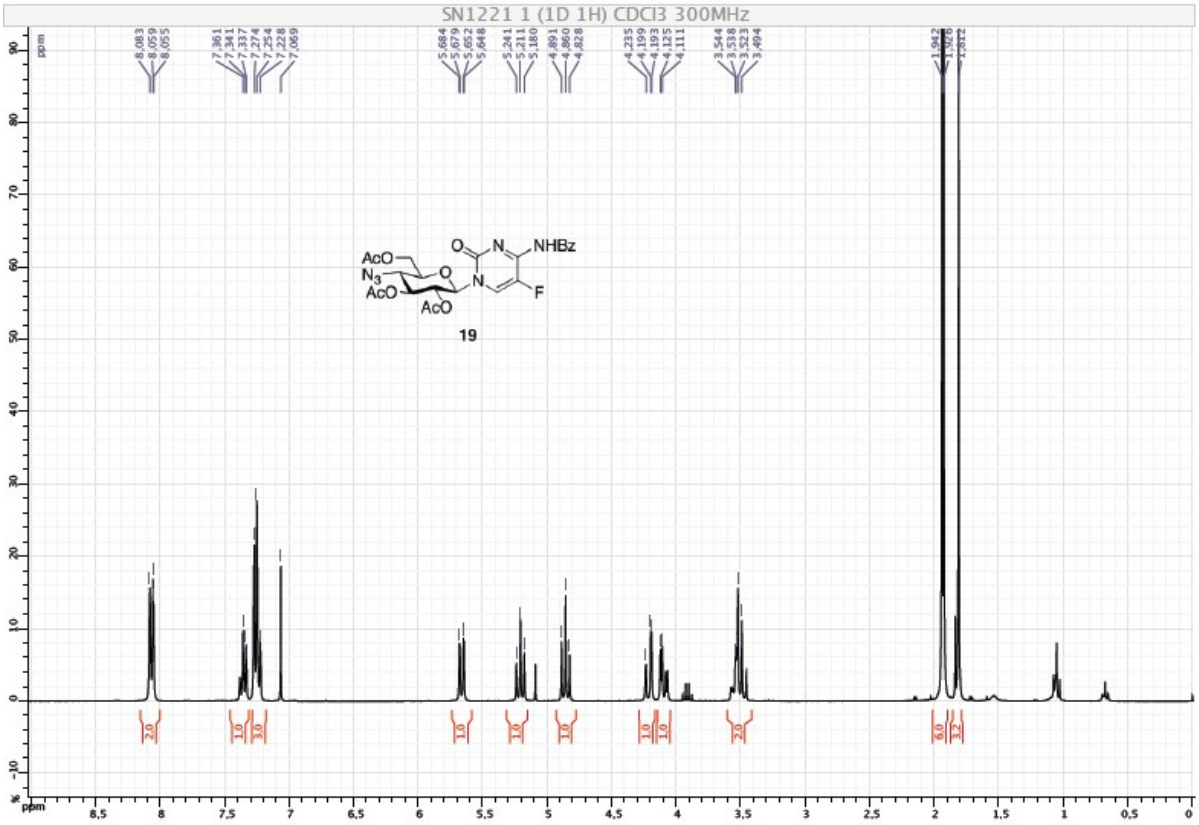

MAB367 3 (1D 13C) CDCl3 300MHz
ppm
170.361
169.736
169.445
162.937
150.248
134.287
112.306
80.158
77.453
77.031
76.602
75.668
73.341
69.345
62.634
59.885
20.793
20.575
20.393
AcO
N3
AcO
AcO
O
N
H
O
O
N
CH3
16

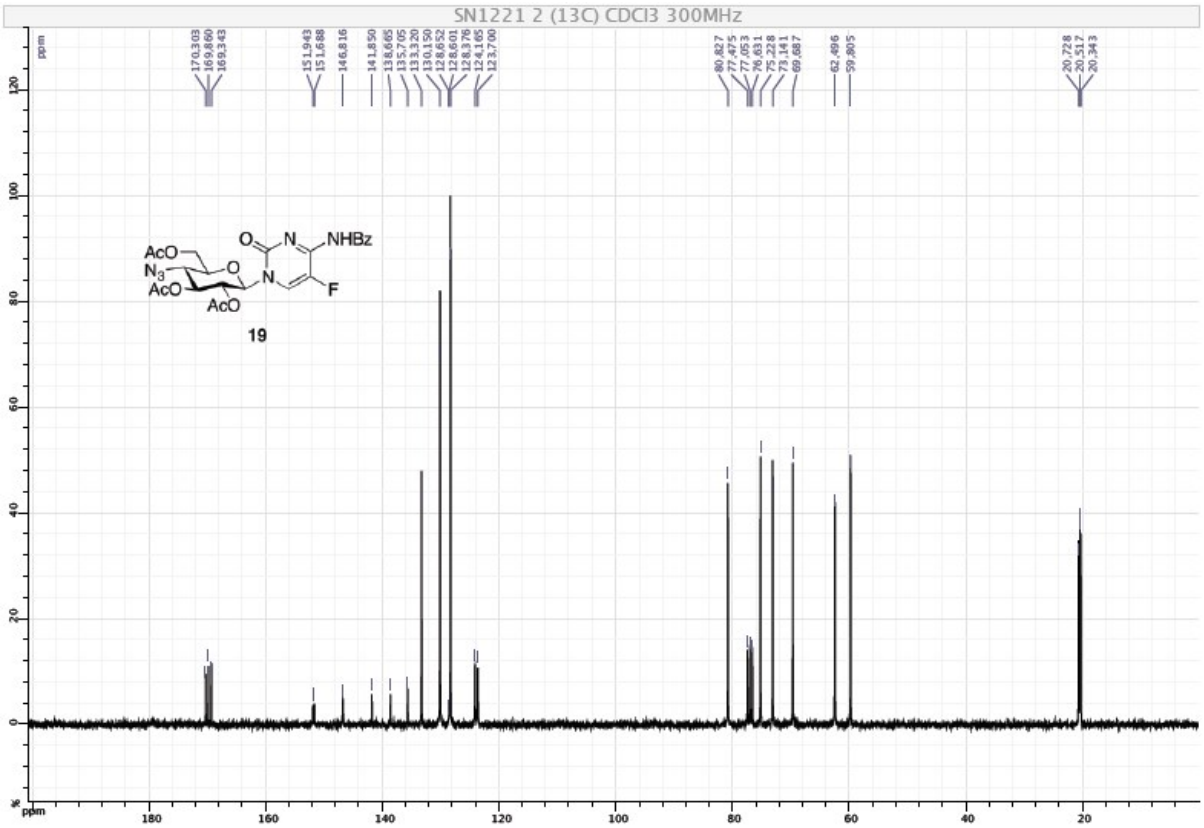

MAB368 1 (1D 1H) CDCl3 300MHz
9.457
9.442
7.317
7.298
5.826
5.822
5.795
5.790
5.358
5.326
5.025
4.993
4.333
4.318
4.249
4.234
3.705
3.699
3.692
3.686
3.681
3.629
2.080
2.063
1.946
AcO
N3
AcO
AcO
O
N
H
O
O
N
F
17
ppm

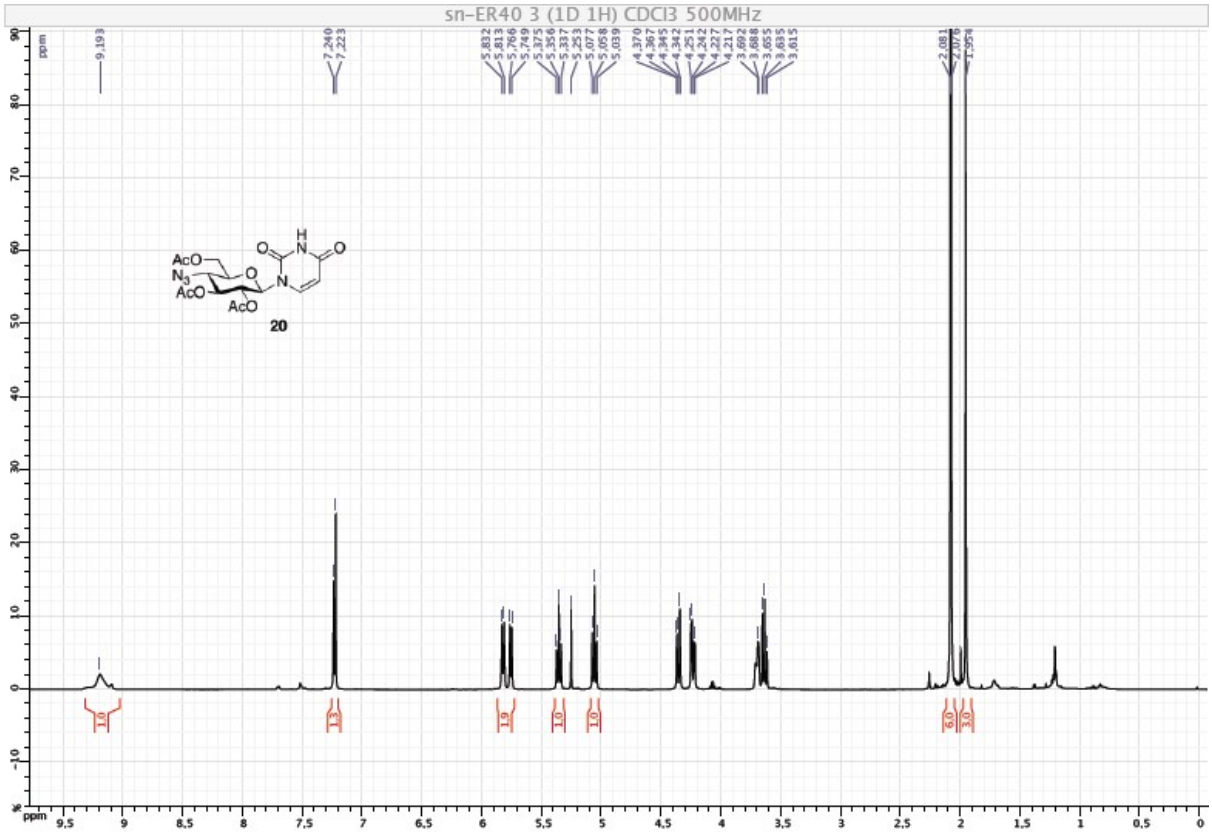

MAB368 3 (1D 13C) CDCl3 300MHz
170.427
169.874
169.496
156.560
156.204
148.983
142.453
139.261
123.555
123.104
80.522
77.475
77.046
76.824
75.446
73.088
69.491
62.445
59.896
20.764
20.568
20.350
AcO
N3
AcO
AcO
O
N
H
O
O
N
F
17
ppm

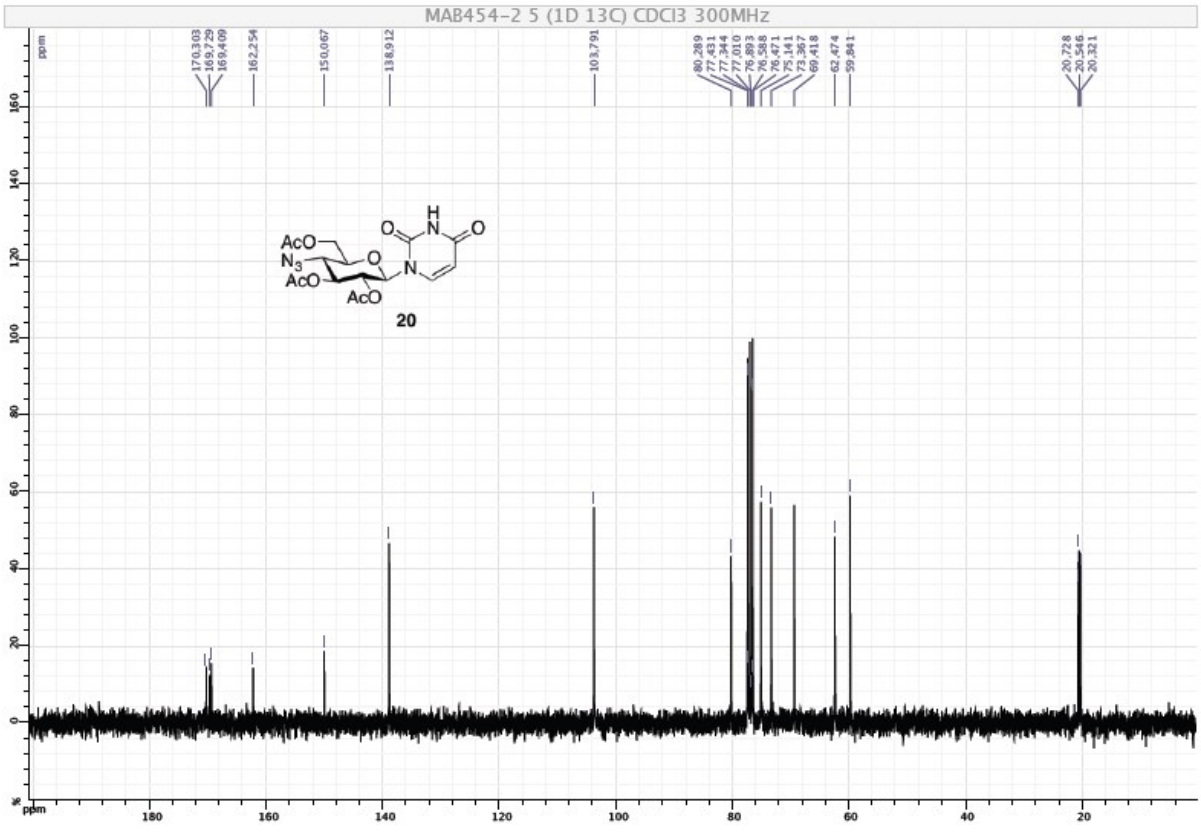

SN-ER79 1 (1D 1H) CDCl3 300MHz
AcO
N3
AcO
O
N
NHBz
CH3
AcO
18

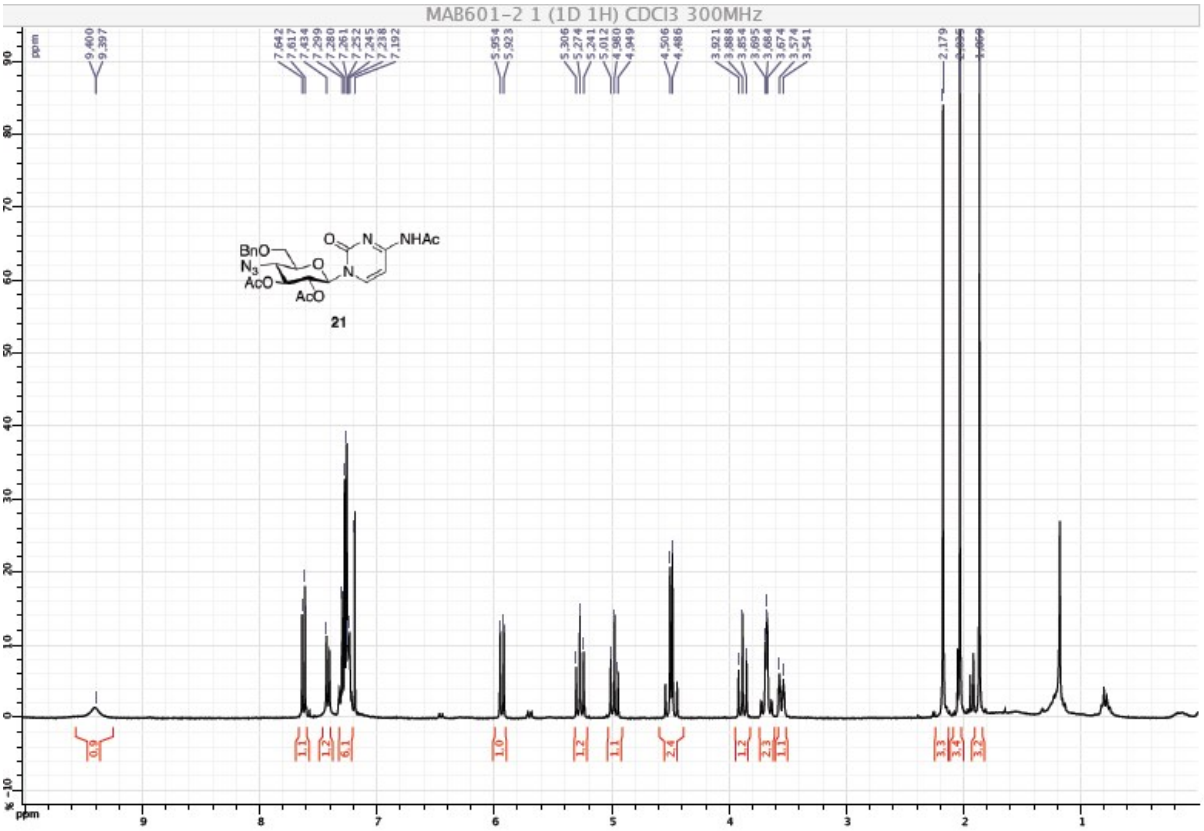

SN-ER79 4 (13C) CDCl3 300MHz
AcO
N3
AcO
O
N
NHBz
CH3
AcO
18

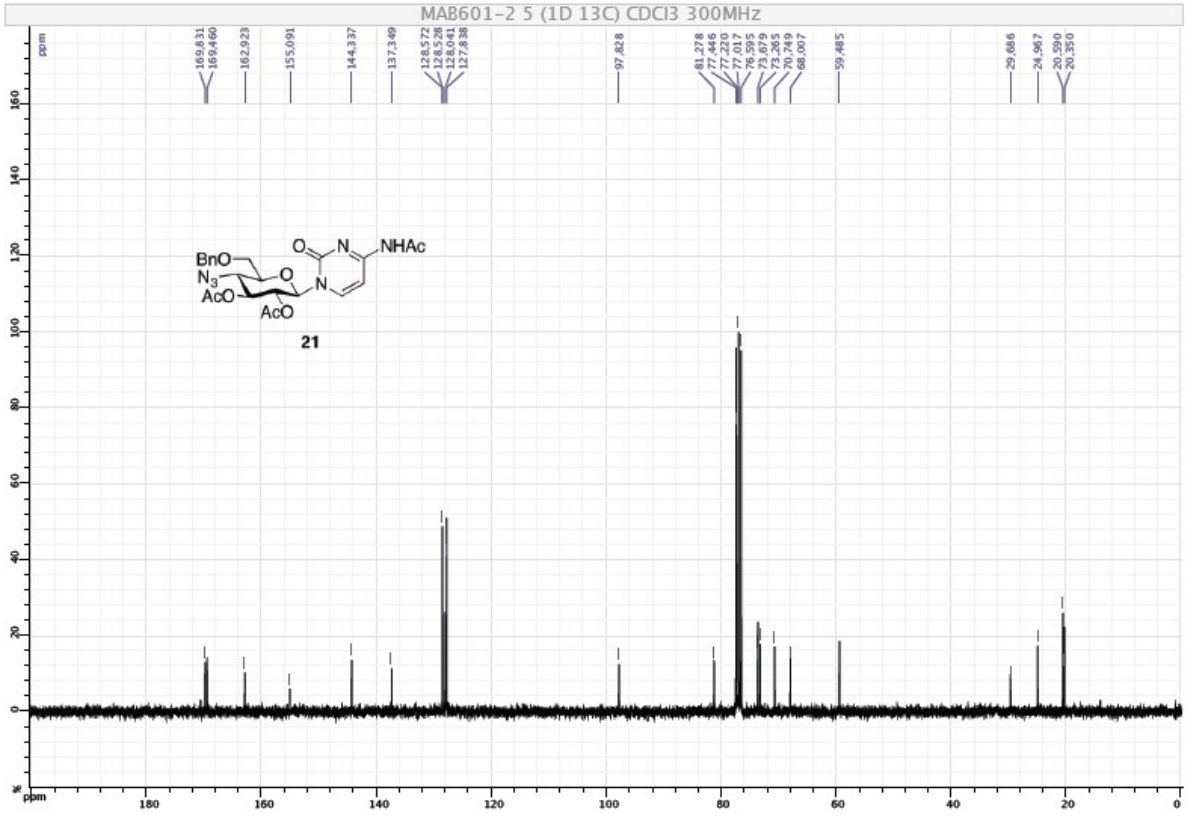

SN1221 1 (1D 1H) CDCl3 300MHz
AcO
N3
AcO
O
N
NHBz
N
F
AcO
19

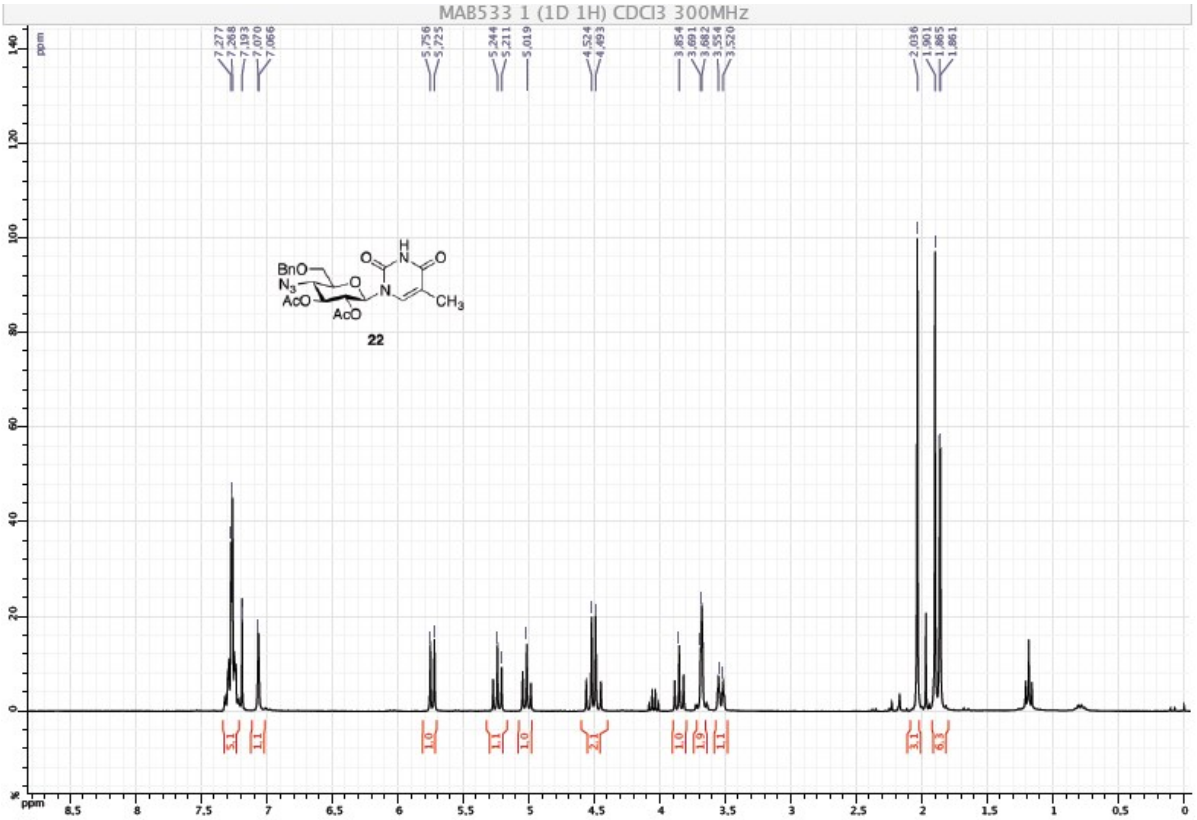

SN1221 2 (13C) CDCl3 300MHz
AcO
N3
AcO
O
N
NHBz
N
F
AcO
19

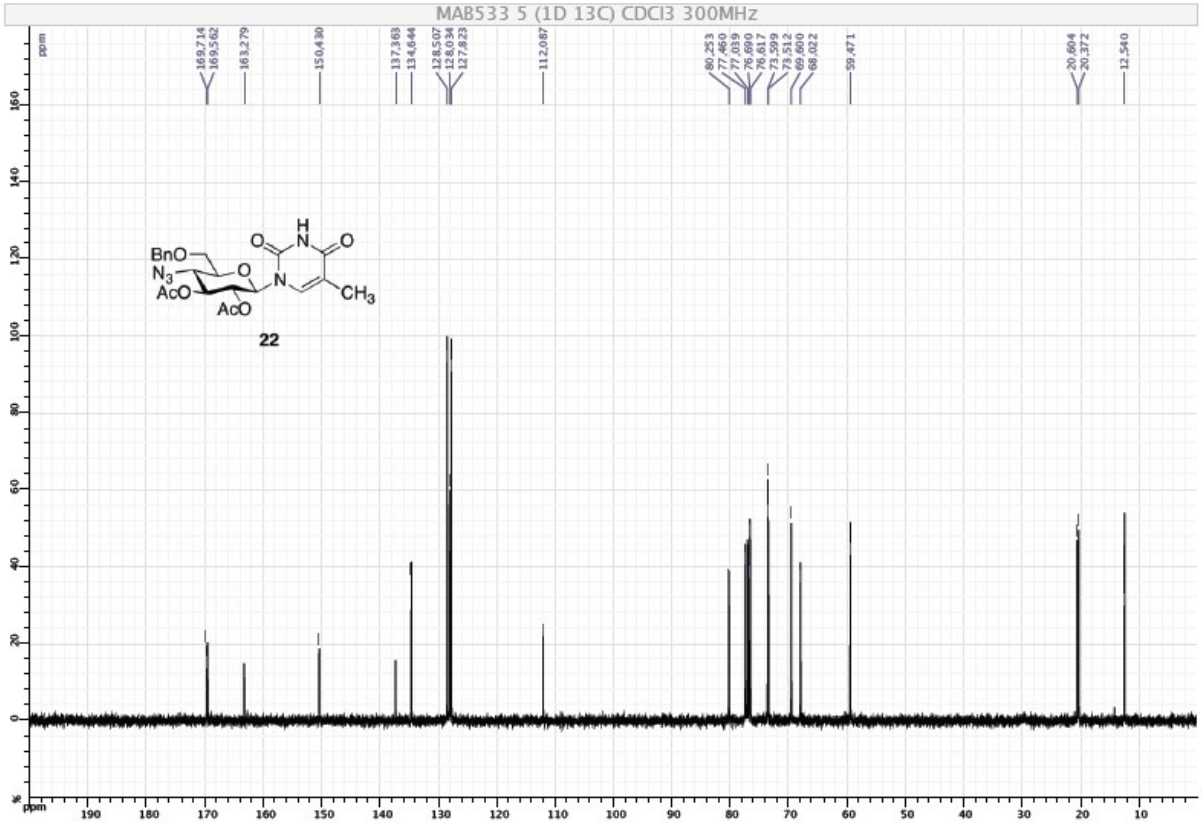

sn-ER40 3 (1D 1H) CDCl3 500MHz
20

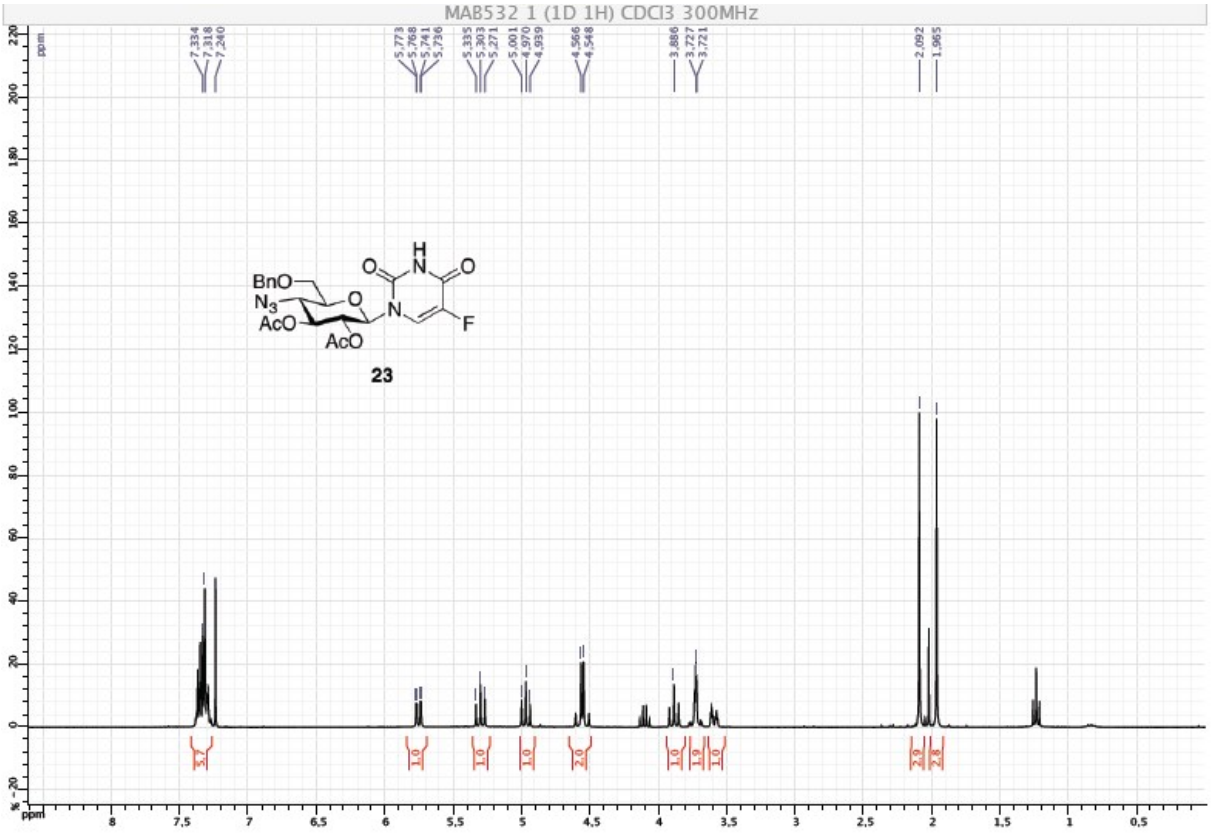

MAB454-2 5 (1D 13C) CDCl3 300MHz
20

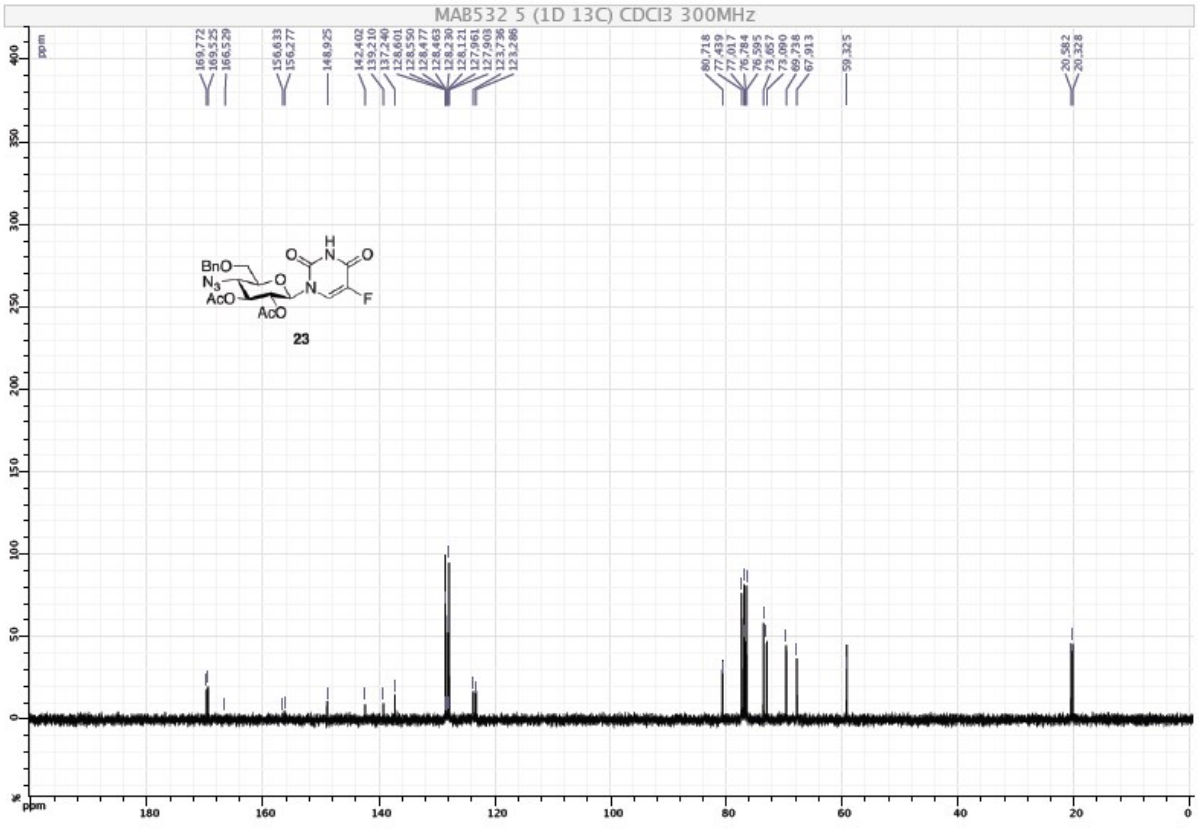

MAB601-2 1 (1D 1H) CDCl3 300MHz
ppm
9.400
9.397
7.642
7.617
7.464
7.299
7.280
7.261
7.252
7.245
7.238
7.192
5.954
5.923
5.306
5.274
5.241
5.012
4.980
4.949
4.506
4.486
3.921
3.888
3.854
3.695
3.684
3.674
3.574
3.541
2.179
BnO
N3
AcO
AcO
O
N
NHAc
21

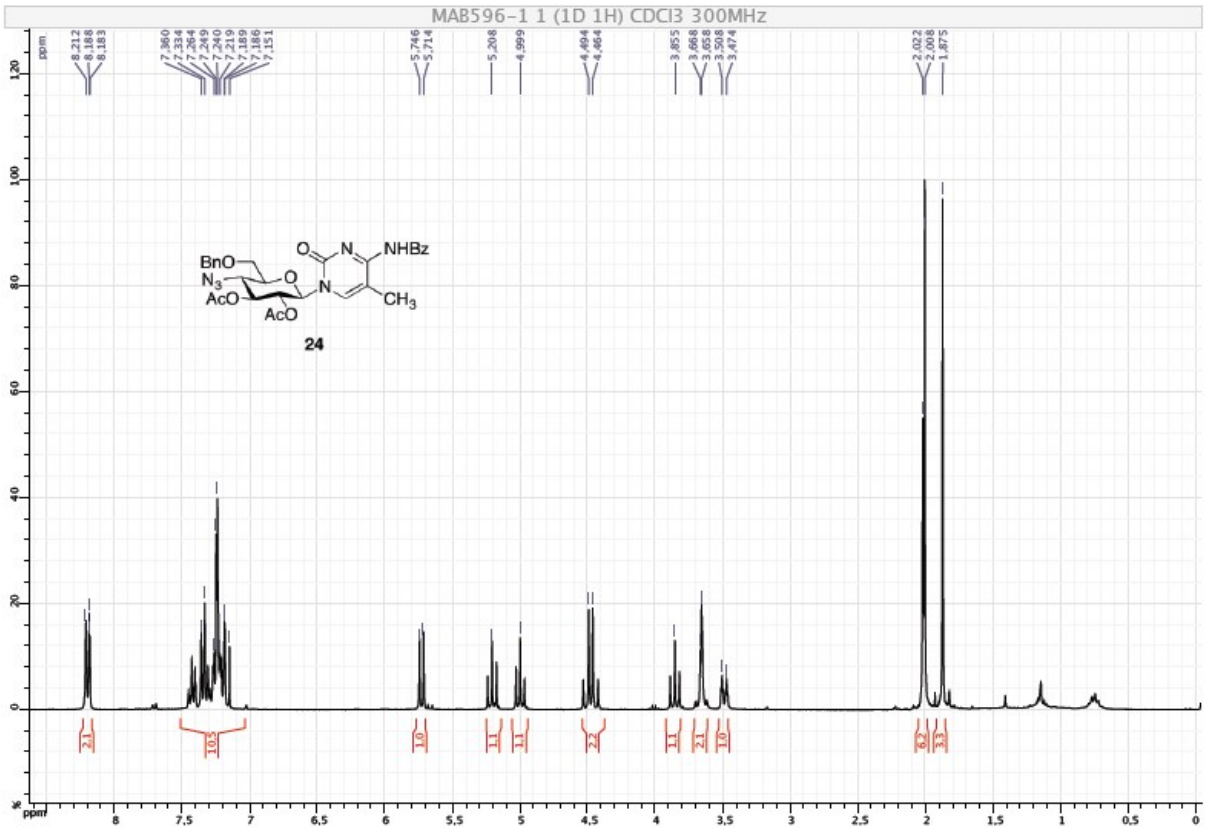

MAB601-2 5 (1D 13C) CDCl3 300MHz
ppm
169.831
169.460
162.923
155.091
144.337
137.349
128.572
128.528
128.041
127.838
97.828
81.278
77.446
77.231
77.017
76.595
73.679
73.265
70.749
68.007
59.485
29.686
24.567
20.590
20.350
BnO
N3
AcO
AcO
O
N
NHAc
21

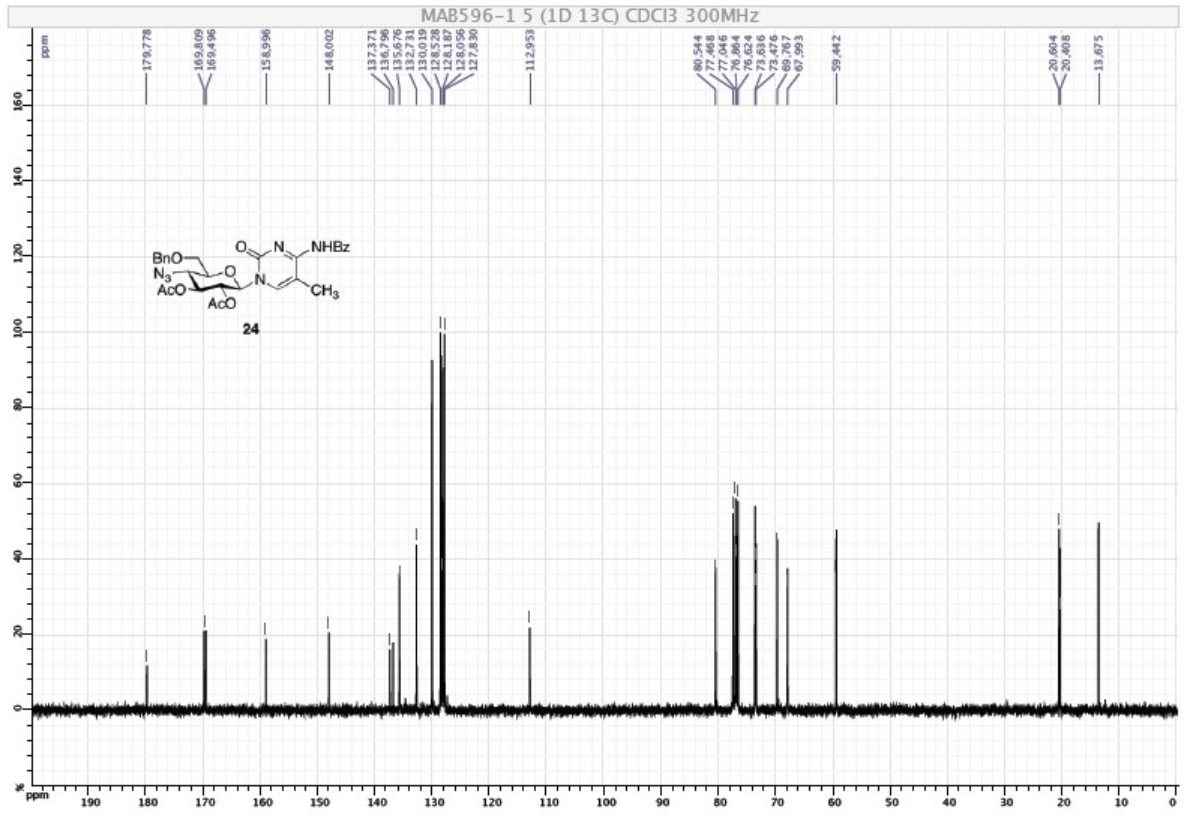

MAB533 1 (1D 1H) CDCl3 300MHz
7.277
7.268
7.193
7.070
7.066
5.756
5.725
5.244
5.211
5.019
4.524
4.493
3.854
3.691
3.682
3.554
3.520
2.036
1.901
1.885
1.861
BnO
N3
AcO
AcO
O
N
H
O
O
CH3
22

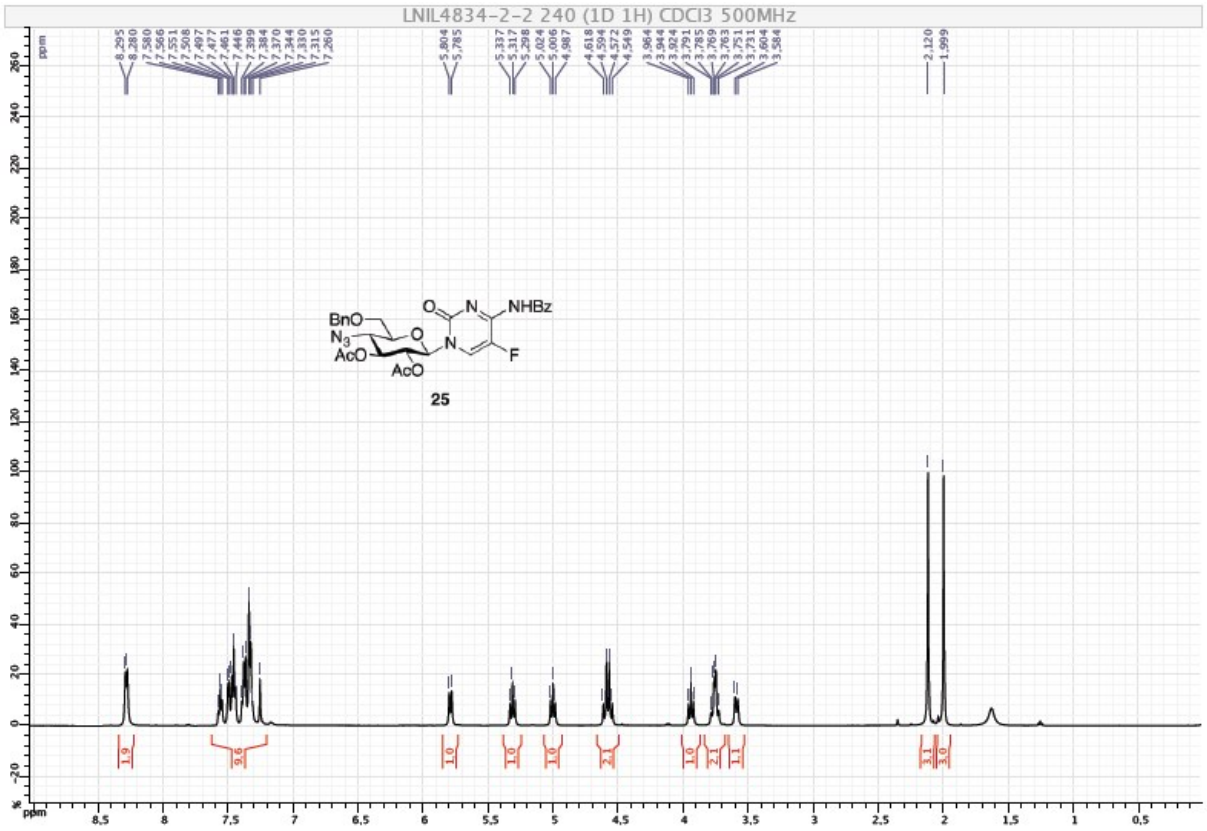

MAB533 5 (1D 13C) CDCl3 300MHz
169.714
169.562
163.279
150.430
137.363
134.644
128.507
128.034
127.823
112.087
80.253
77.460
77.039
76.690
76.617
73.599
73.512
69.600
68.022
59.471
20.694
20.372
12.540
BnO
N3
AcO
AcO
O
N
H
O
O
CH3
22

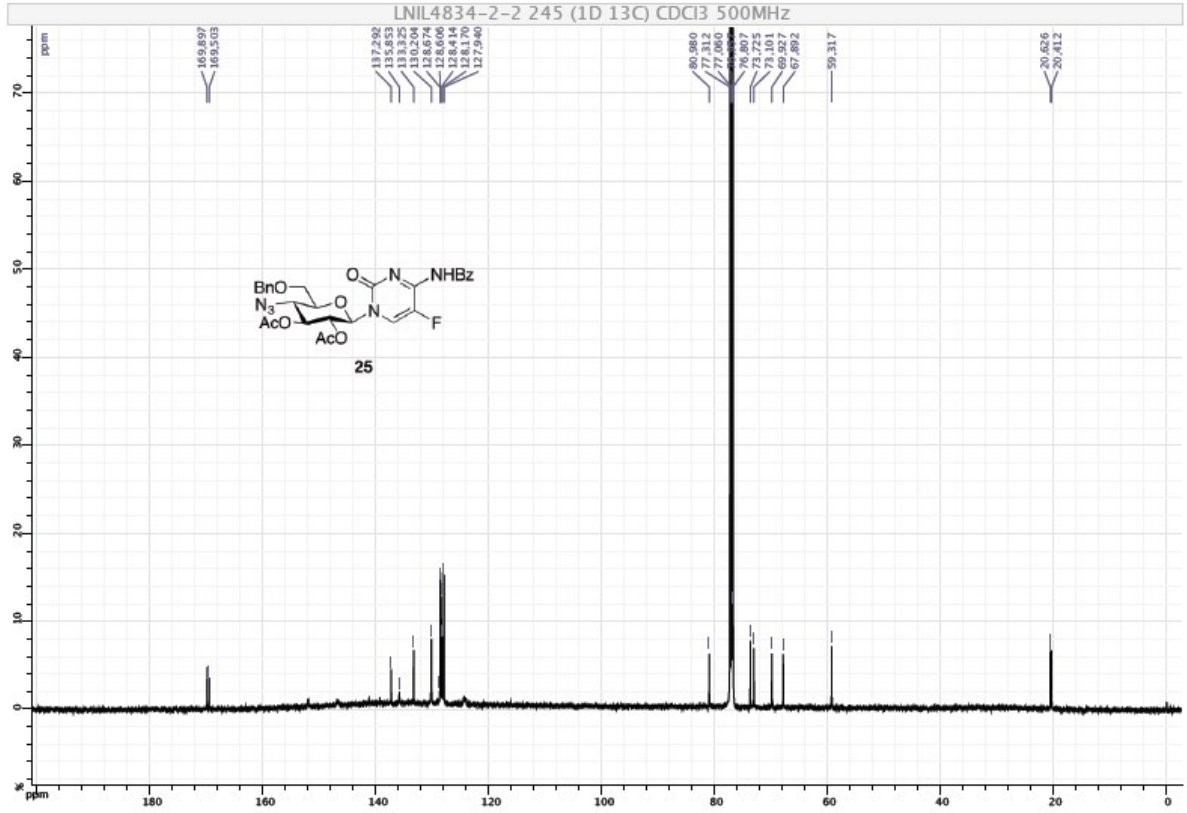

MAB532 1 (1D 1H) CDCl3 300MHz
ppm
7.334
7.318
7.240
5.773
5.768
5.741
5.736
5.335
5.303
5.271
5.001
4.970
4.939
4.566
4.548
3.886
3.727
3.721
2.092
1.965
BnO
N3
AcO
AcO
O
N
H
F
23

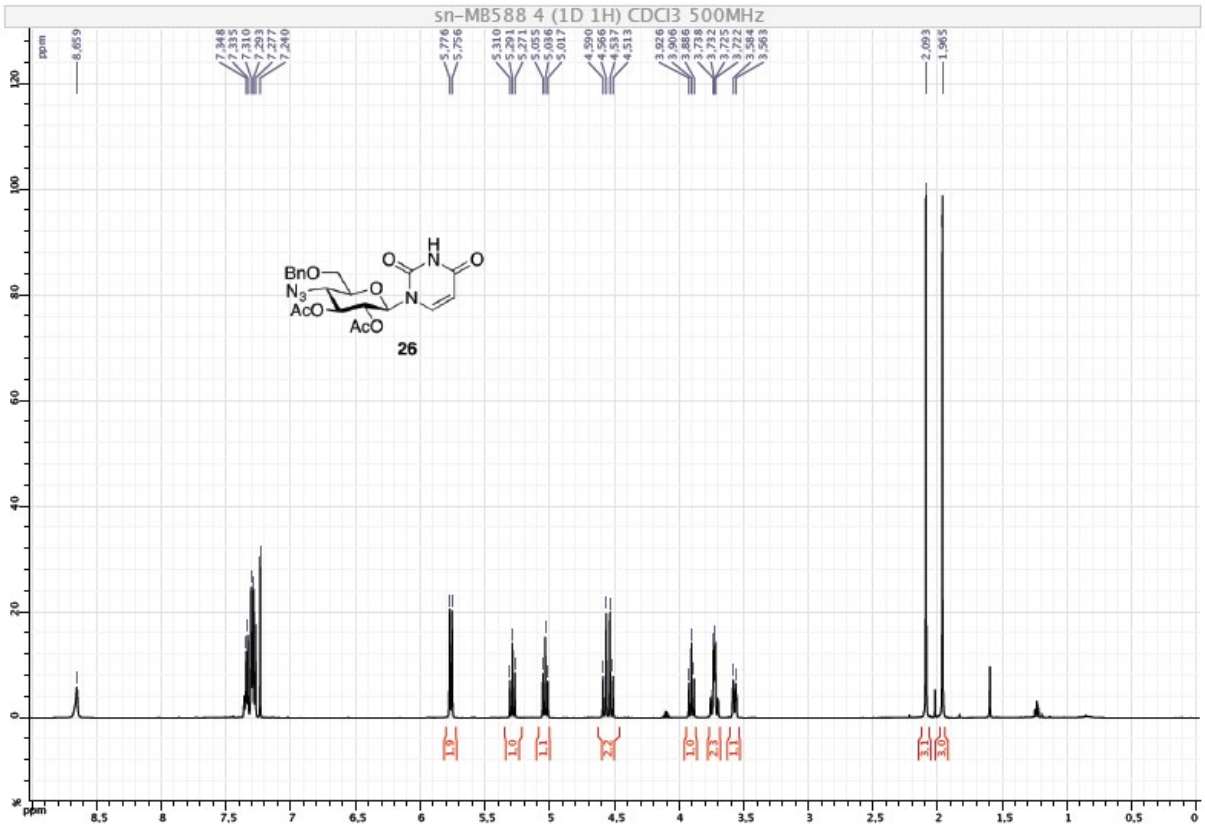

MAB532 5 (1D 13C) CDCl3 300MHz
ppm
169.772
169.525
166.529
156.633
156.277
148.925
142.402
139.210
137.240
128.601
128.550
128.477
128.468
128.211
127.961
127.903
123.736
123.286
80.718
77.439
77.017
76.784
75.855
73.090
69.738
67.913
59.325
20.582
20.328
BnO
N3
AcO
AcO
O
N
H
F
23

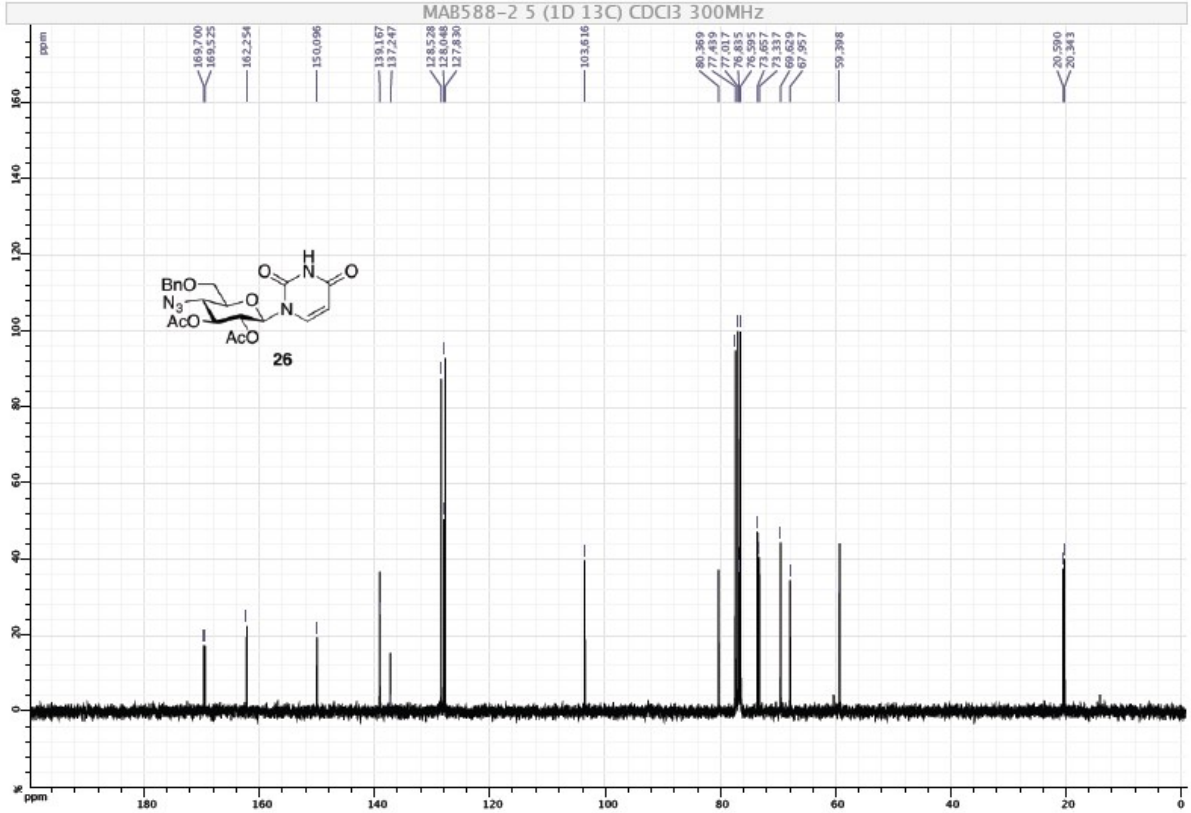

MAB596-1 1 (1D 1H) CDCl3 300MHz
8.212
8.188
8.183
7.360
7.334
7.264
7.249
7.240
7.219
7.189
7.186
7.151
5.746
5.714
5.208
4.999
4.494
4.464
3.855
3.668
3.658
3.508
3.474
2.022
2.008
1.875
BnO
N3
AcO
AcO
O
N
NHBz
CH3
24
2.1
10.5
1.0
1.1
1.1
2.2
1.1
2.1
1.0
6.2
3.3
ppm

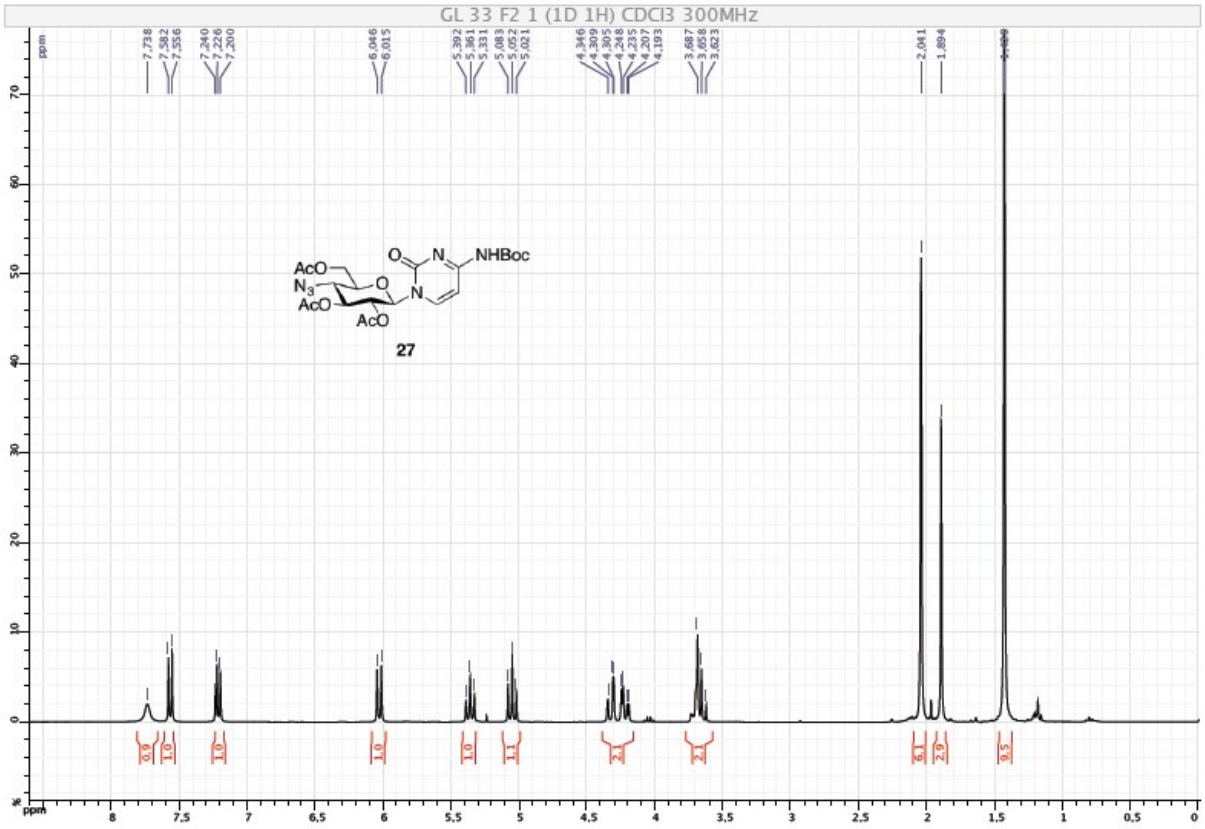

MAB596-1 5 (1D 13C) CDCl3 300MHz
179.778
169.809
169.496
158.996
148.002
137.371
134.796
135.678
132.731
130.019
128.528
128.187
128.056
127.830
112.953
80.544
77.468
77.046
76.884
76.624
73.836
73.476
69.767
67.993
59.442
20.604
20.408
13.675
BnO
N3
AcO
AcO
O
N
NHBz
CH3
24
ppm

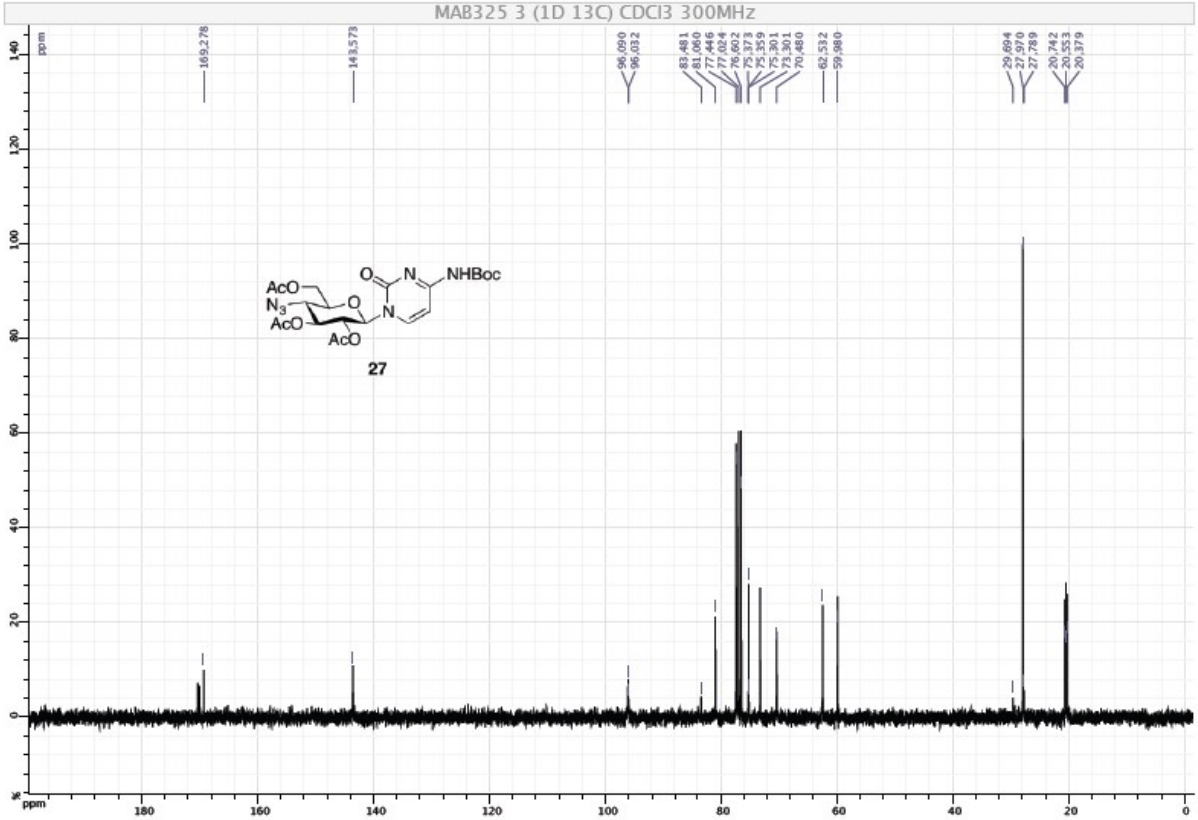

LNIL4834-2-2 240 (1D 1H) CDCl3 500MHz
8.295
8.280
7.580
7.566
7.551
7.508
7.497
7.477
7.461
7.446
7.399
7.384
7.370
7.344
7.330
7.315
7.260
5.804
5.785
5.337
5.317
5.298
5.024
5.006
4.987
4.618
4.594
4.572
4.549
3.964
3.944
3.924
3.791
3.785
3.769
3.763
3.751
3.731
3.604
3.584
2.120
1.999
BnO
N3
AcO
AcO
O
N
NHBz
N
F
25
1.9
9.6
1.0
1.0
1.0
2.1
1.0
2.1
1.1
3.1
3.0
ppm

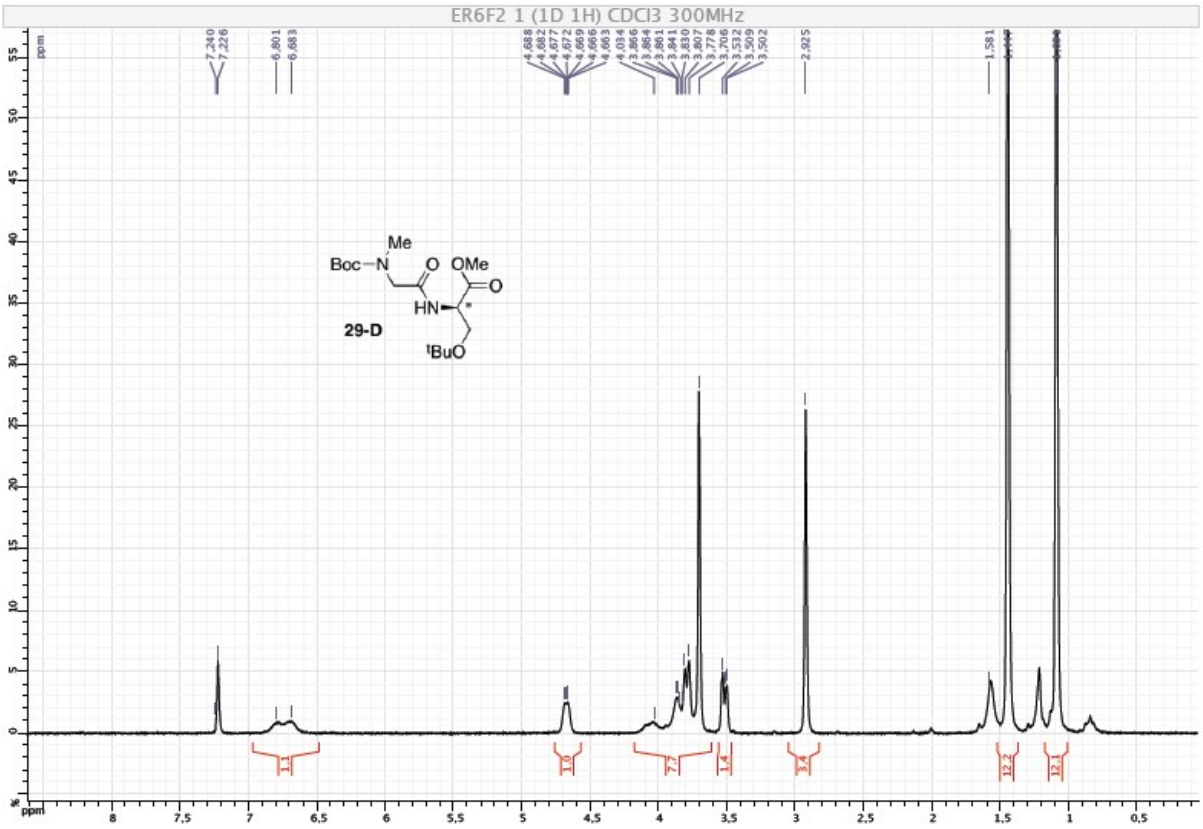

LNIL4834-2-2 245 (1D 13C) CDCl3 500MHz
169.897
169.503
137.292
133.535
133.338
130.204
128.674
128.606
128.414
128.170
127.940
80.980
77.312
77.060
76.807
73.725
73.101
69.927
67.892
59.317
20.626
20.412
BnO
N3
AcO
AcO
O
N
NHBz
N
F
25
ppm

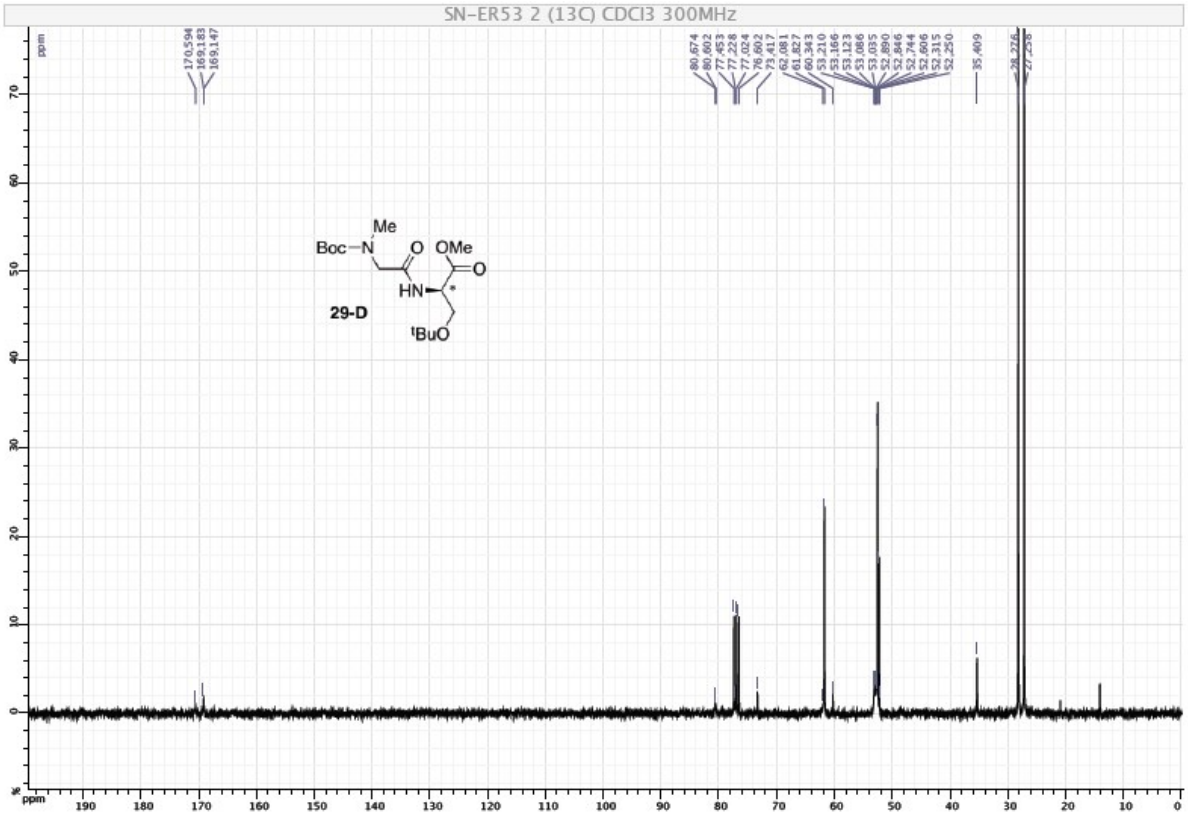

sn-MB588 4 (1D 1H) CDCl3 500MHz
BnO
N3
AcO
AcO
26

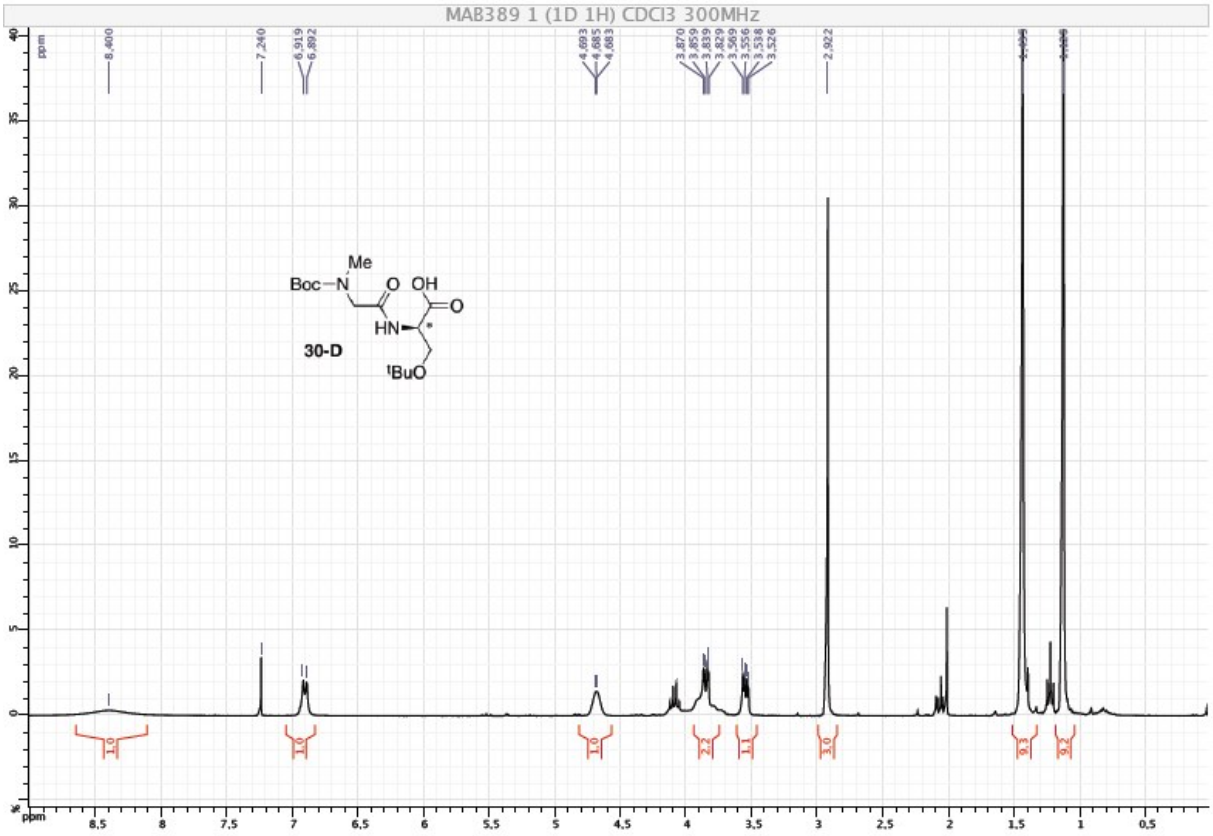

MAB588-2 5 (1D 13C) CDCl3 300MHz
BnO
N3
AcO
AcO
26

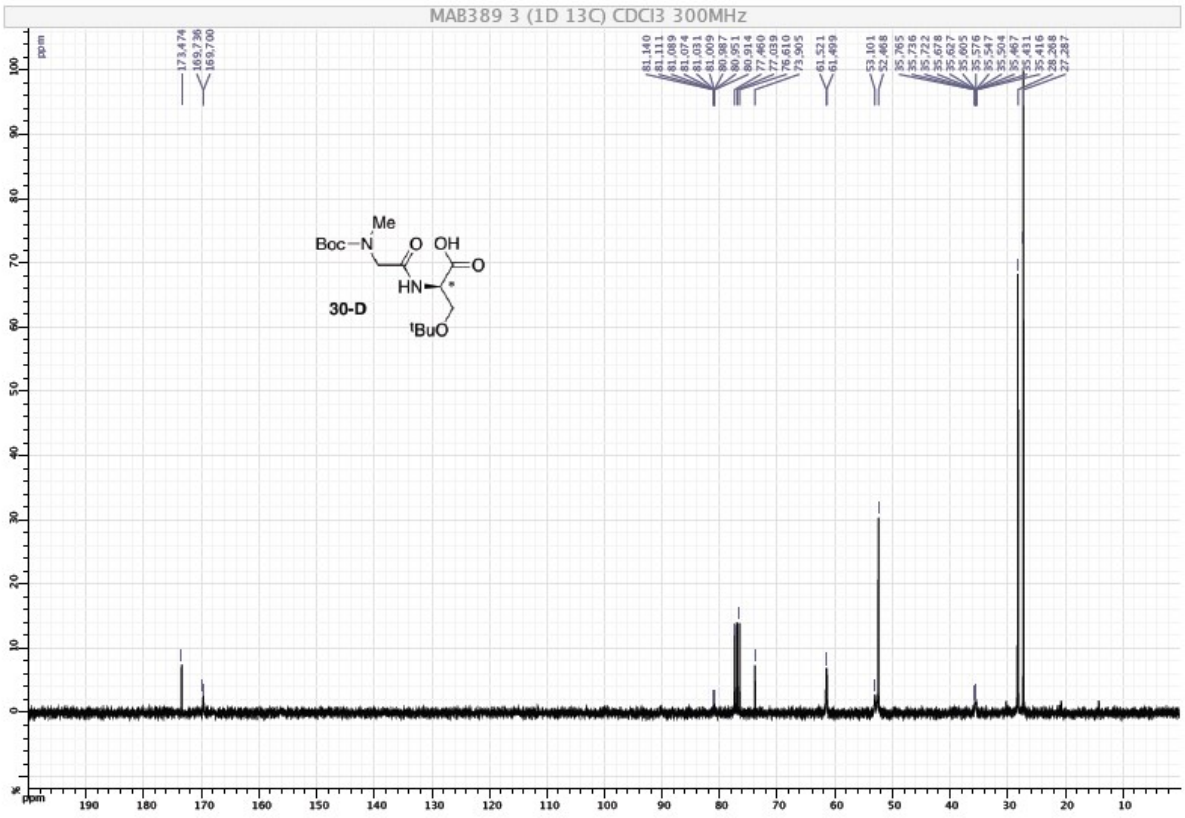

GL 33 F2 1 (1D 1H) CDCl3 300MHz
7.738
7.582
7.556
7.240
7.226
7.200
6.046
6.015
5.392
5.361
5.331
5.083
5.052
5.021
4.346
4.309
4.305
4.248
4.235
4.207
4.193
3.687
3.658
3.623
2.041
1.894
AcO
N3
AcO
AcO
O
N
NHBoc
27

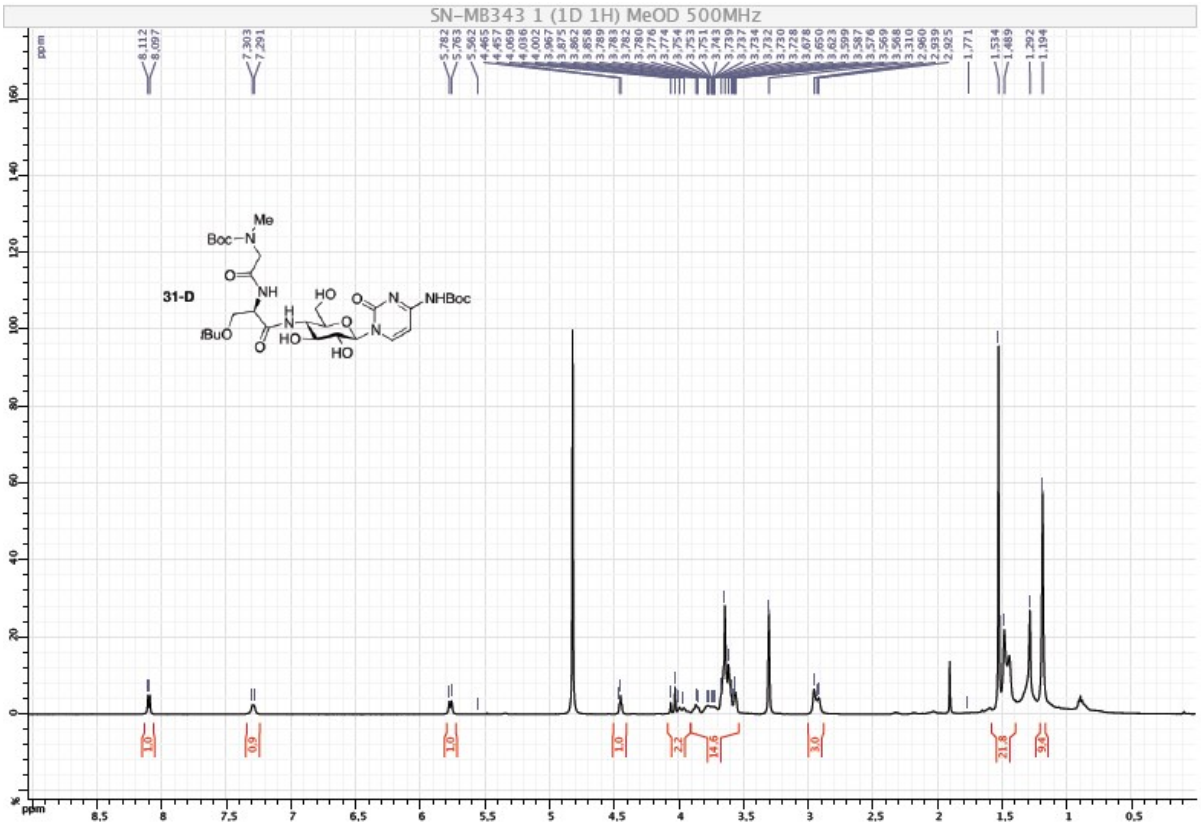

MAB325 3 (1D 13C) CDCl3 300MHz
169.278
148.573
96.090
96.032
83.481
81.060
77.446
77.024
76.602
75.373
75.359
75.301
73.301
70.480
62.532
59.980
29.694
27.970
27.789
20.742
20.553
20.379
AcO
N3
AcO
AcO
O
N
NHBoc
27

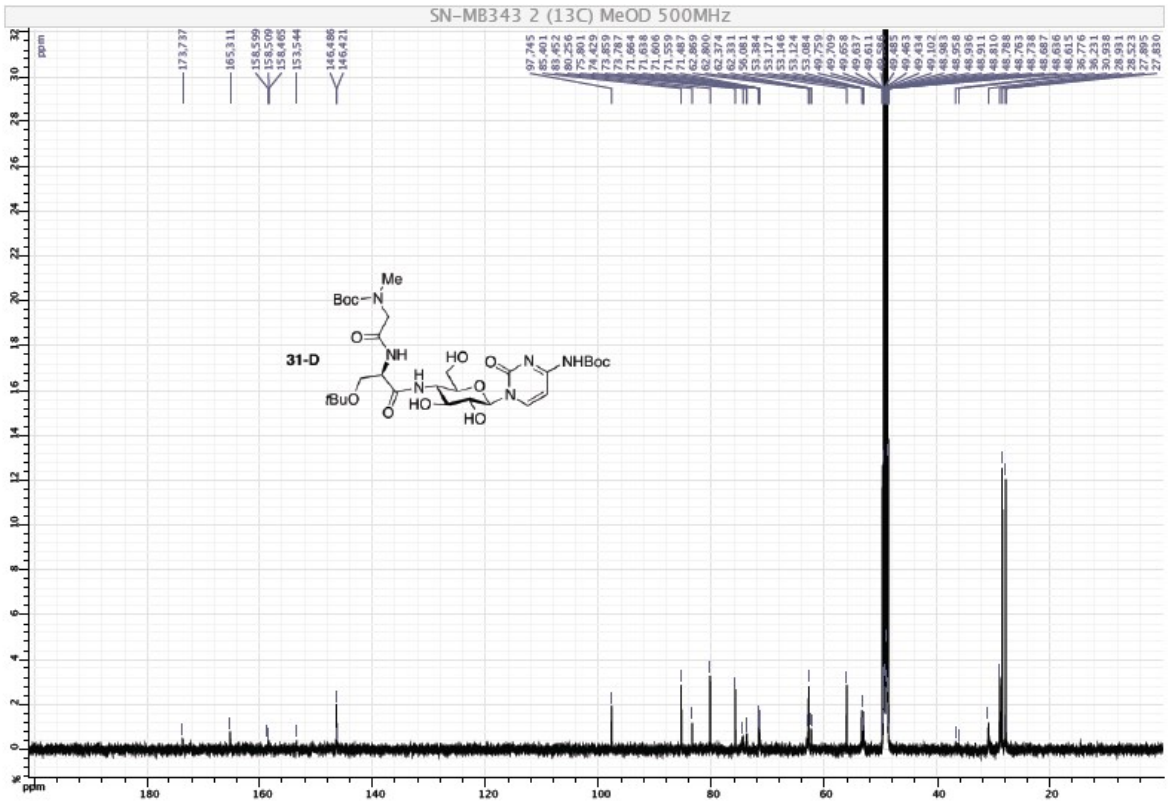

ER6F2 1 (1D 1H) CDCl3 300MHz
ppm
7.240
7.226
6.801
6.683
4.688
4.682
4.677
4.672
4.669
4.666
4.663
4.034
3.866
3.864
3.861
3.841
3.830
3.807
3.778
3.706
3.532
3.509
3.502
2.925
1.581
Me
Boc–N
O
OMe
O
HN
*
29-D
tBuO
1.1
1.0
7.7
1.4
3.4
12.2
12.1

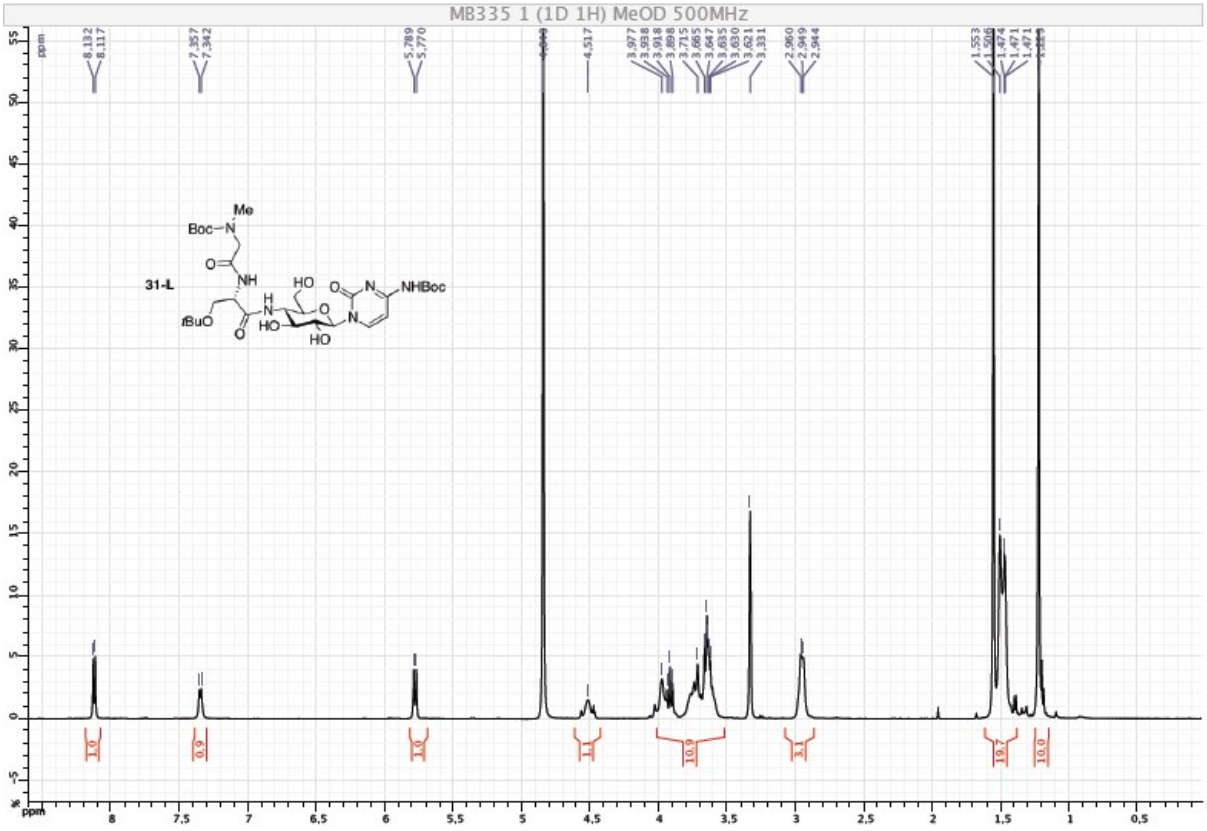

SN-ER53 2 (13C) CDCl3 300MHz
ppm
170.594
169.183
169.147
80.674
80.602
77.453
77.228
77.024
76.602
76.417
63.081
61.827
60.343
53.210
53.166
53.123
53.086
53.035
52.890
52.846
52.744
52.696
52.315
52.250
35.409
28.226
27.258
Me
Boc–N
O
OMe
O
HN
*
29-D
tBuO

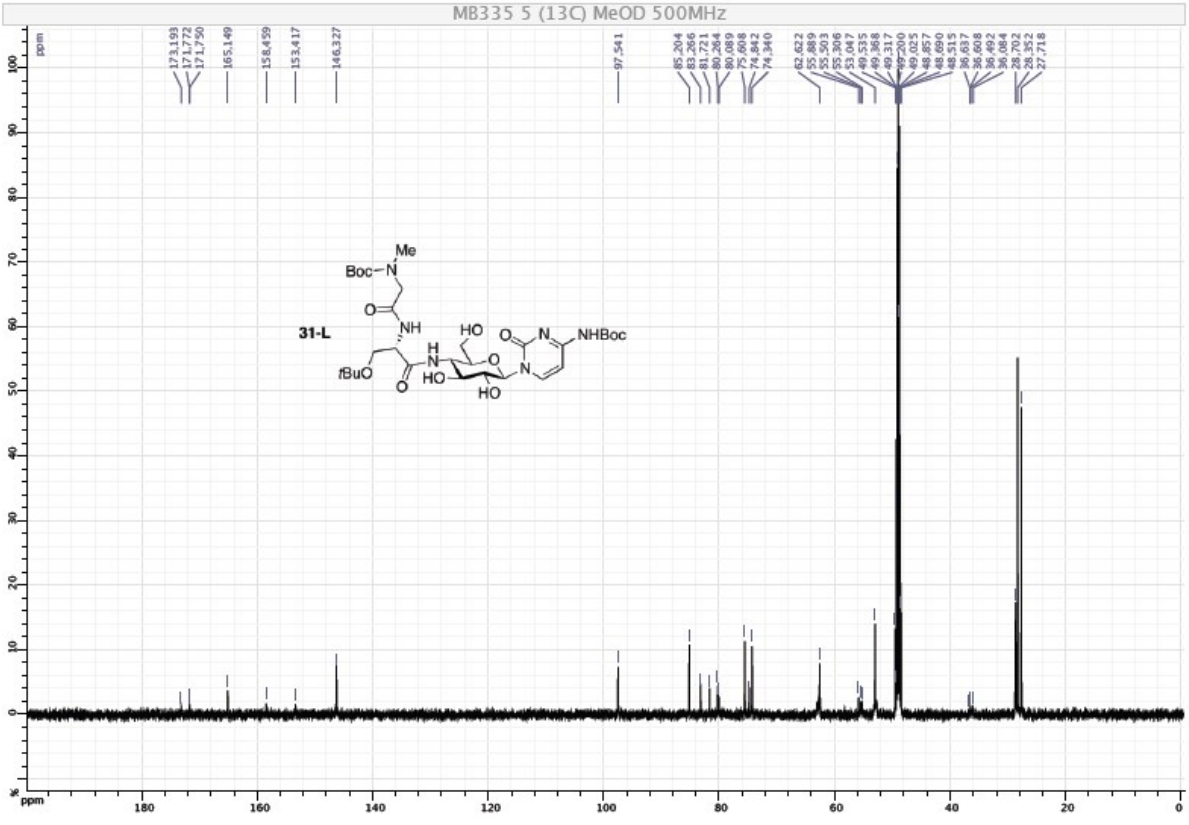

MAB389 1 (1D 1H) CDCl3 300MHz
ppm
8,400
7,240
6,919
6,892
4,693
4,685
4,683
3,870
3,859
3,839
3,829
3,569
3,556
3,538
3,526
2,922
1,469
1,439
Boc
N
Me
O
OH
HN
*
tBuO
30-D
1,0
1,0
1,0
2,2
1,1
3,0
9,3
9,2

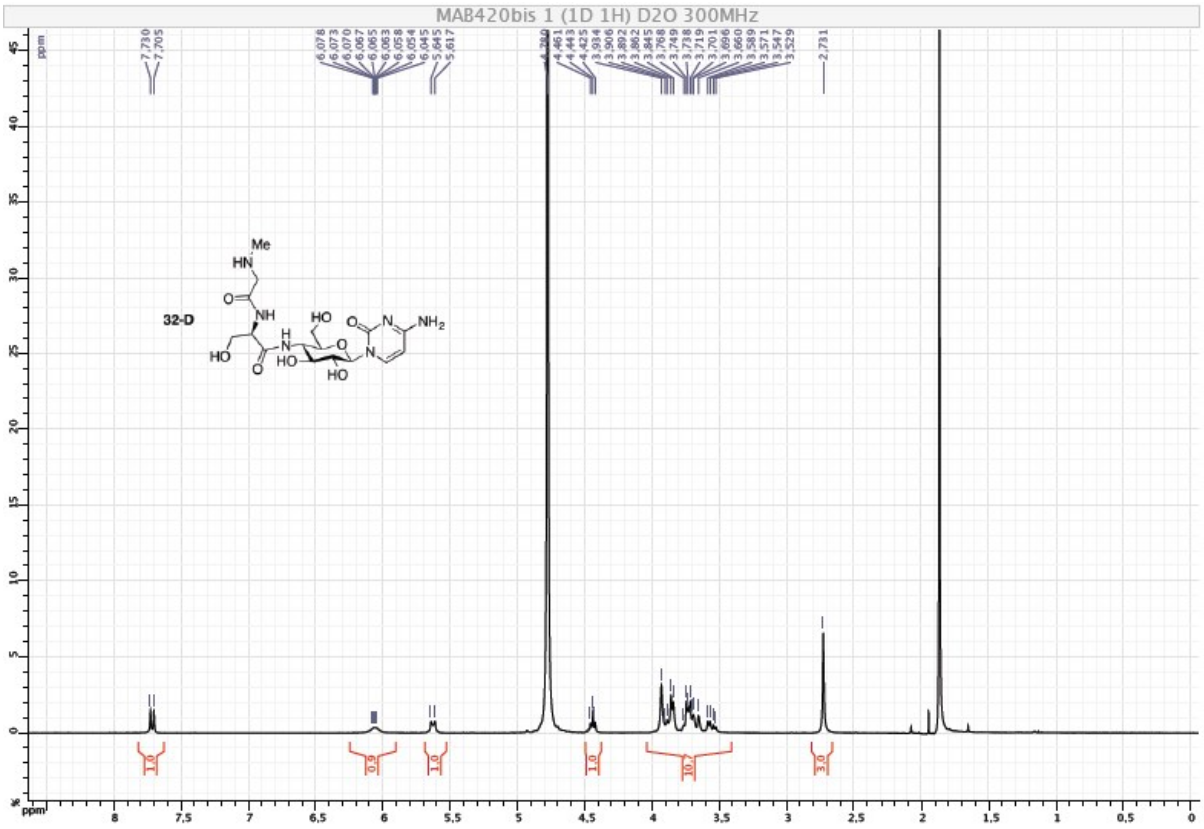

MAB389 3 (1D 13C) CDCl3 300MHz
ppm
173,474
169,736
169,700
81,140
81,111
81,089
81,074
81,038
81,009
80,987
80,951
80,914
77,460
77,039
76,610
73,905
61,521
61,499
53,101
52,468
35,765
35,736
35,722
35,678
35,627
35,605
35,576
35,547
35,504
35,467
35,431
35,416
28,268
27,287
Boc
N
Me
O
OH
HN
*
tBuO
30-D

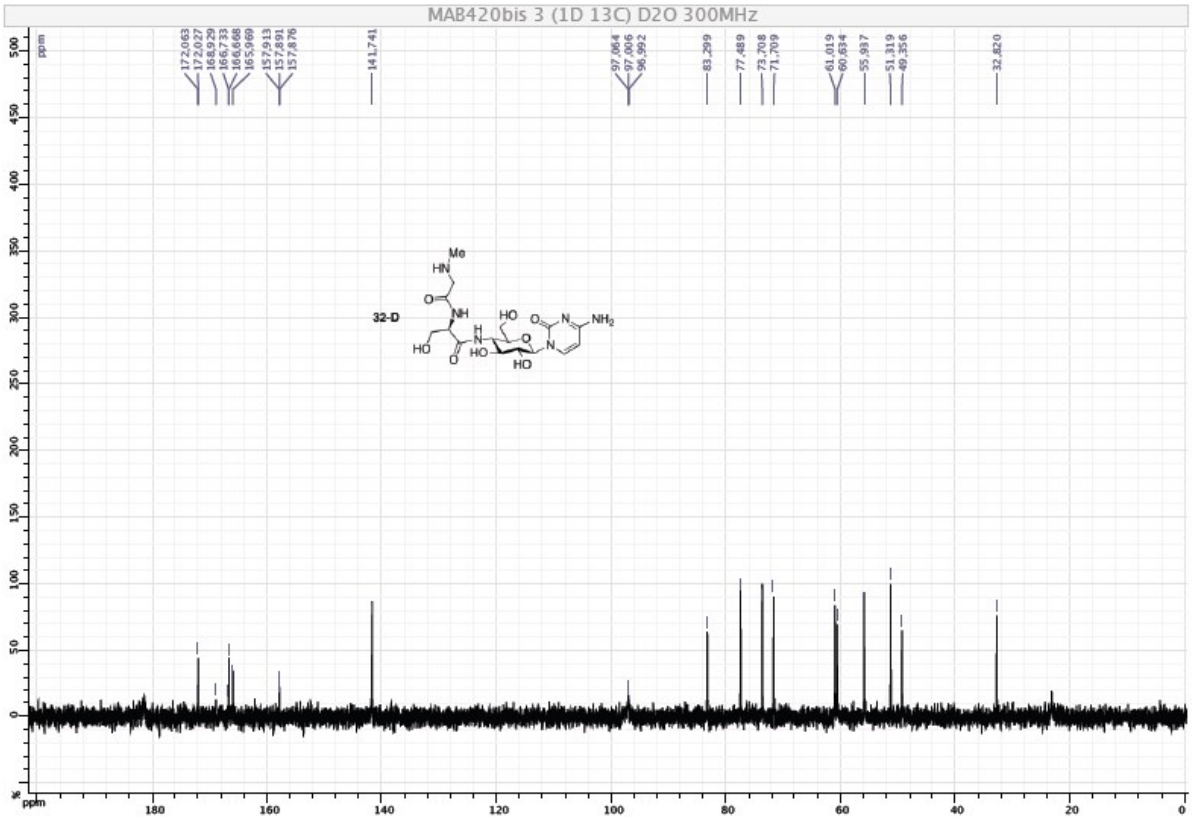

SN-MB343 1 (1D 1H) MeOD 500MHz
31-D

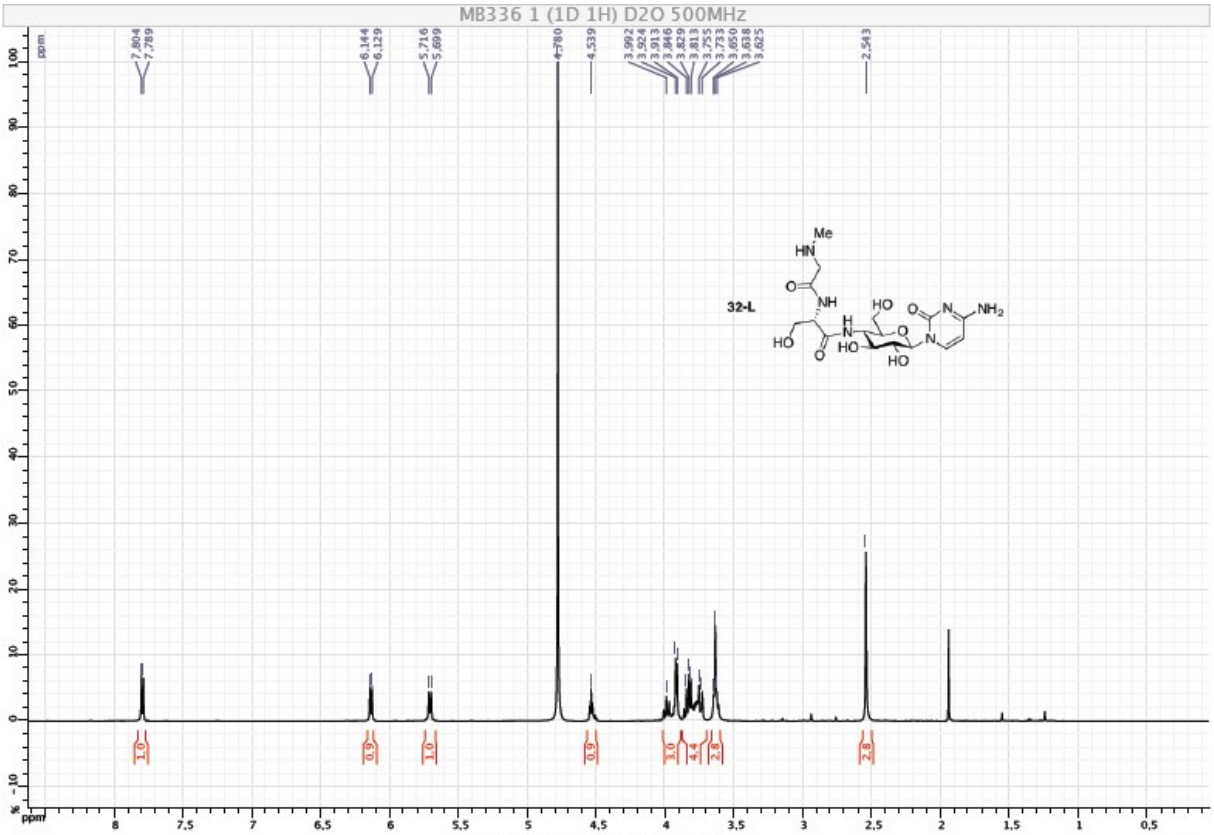

SN-MB343 2 (13C) MeOD 500MHz
31-D

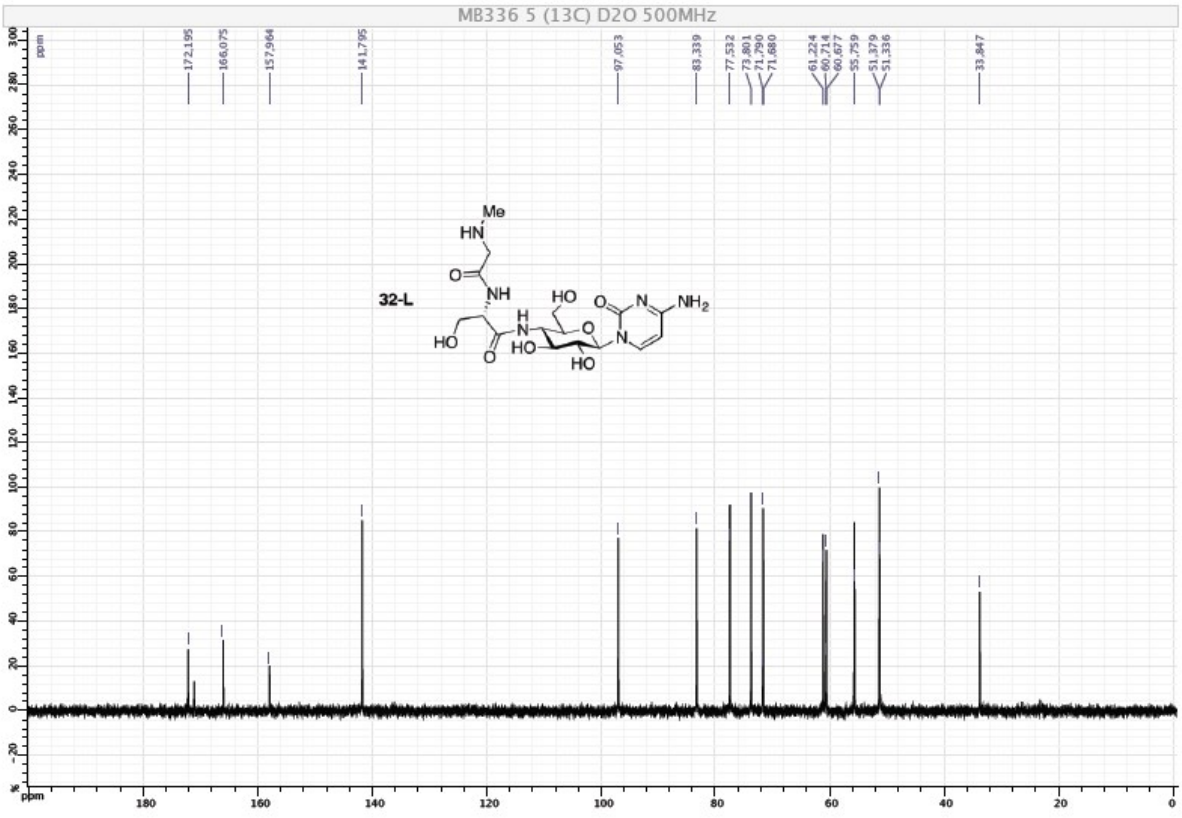

MB335 1 (1D 1H) MeOD 500MHz
31-L

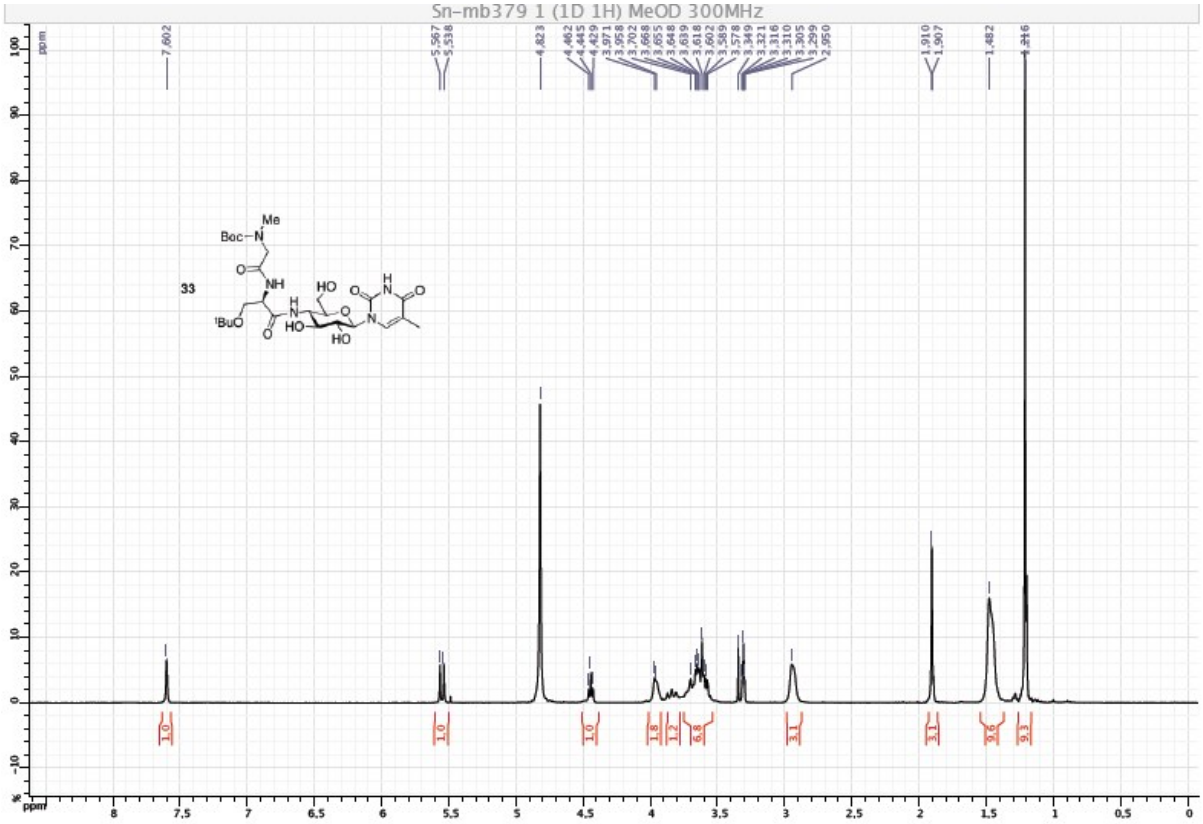

MB335 5 (13C) MeOD 500MHz
31-L

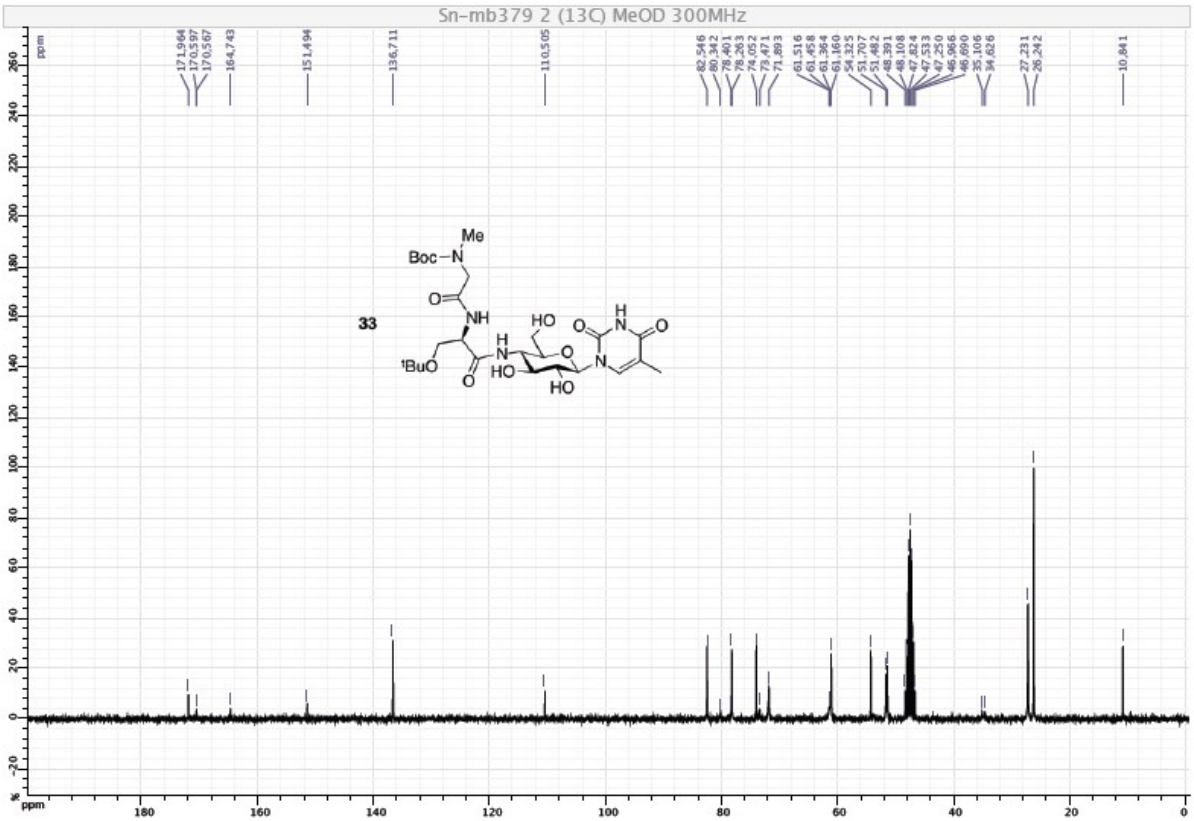

MAB420bis 1 (1D 1H) D2O 300MHz
ppm
7,730
7,705
6,078
6,073
6,070
6,067
6,065
6,063
6,058
6,054
6,045
5,645
5,617
4,461
4,443
4,425
3,934
3,906
3,892
3,862
3,845
3,768
3,749
3,738
3,719
3,701
3,666
3,589
3,571
3,547
3,529
2,731
Me
HN
O
NH
HO
HO
O
H
N
HO
HO
O
N
O
N
NH2
32-D
1,0
0,9
1,0
1,0
10,7
3,0

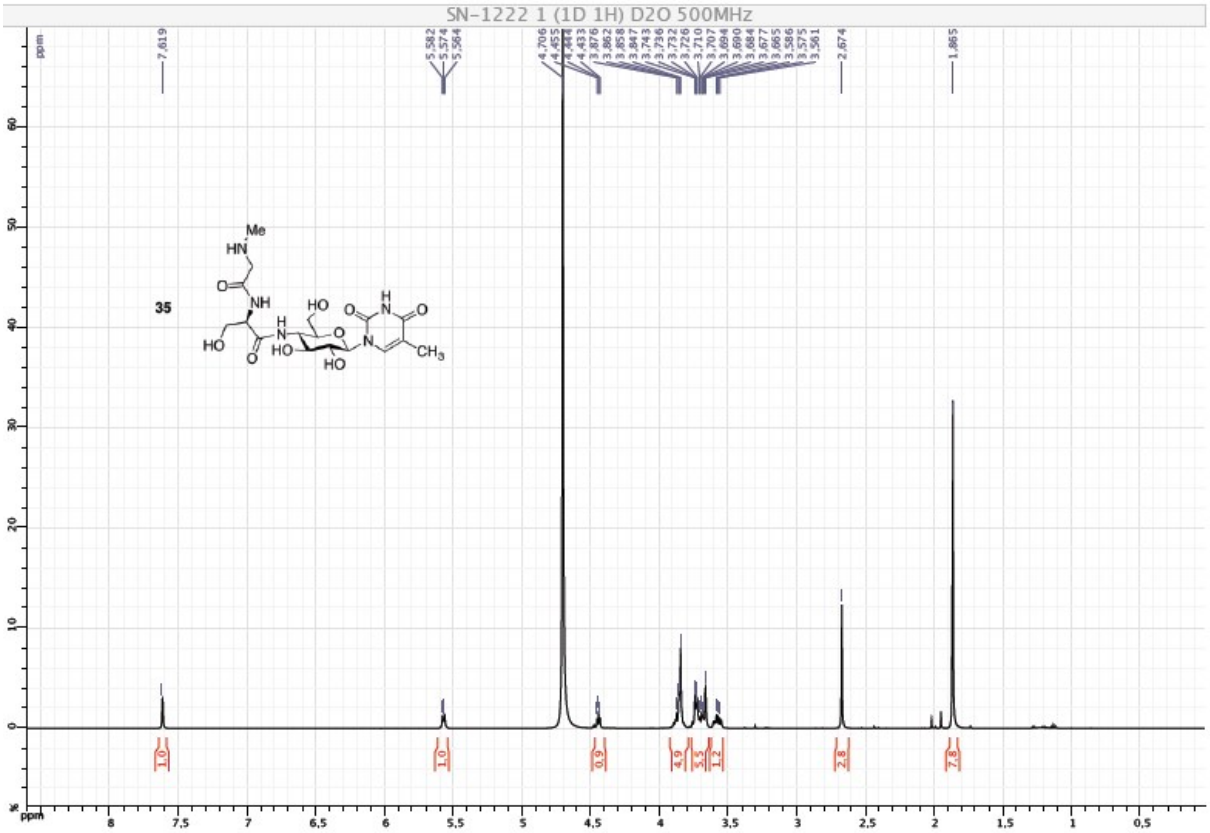

MAB420bis 3 (1D 13C) D2O 300MHz
ppm
172,063
172,027
168,929
166,733
166,688
165,969
157,913
157,891
157,876
141,741
97,084
97,066
96,992
83,299
77,489
73,708
71,709
61,019
60,834
55,937
51,319
49,356
32,820
Me
HN
O
NH
HO
HO
O
H
N
HO
HO
O
N
O
N
NH2
32-D

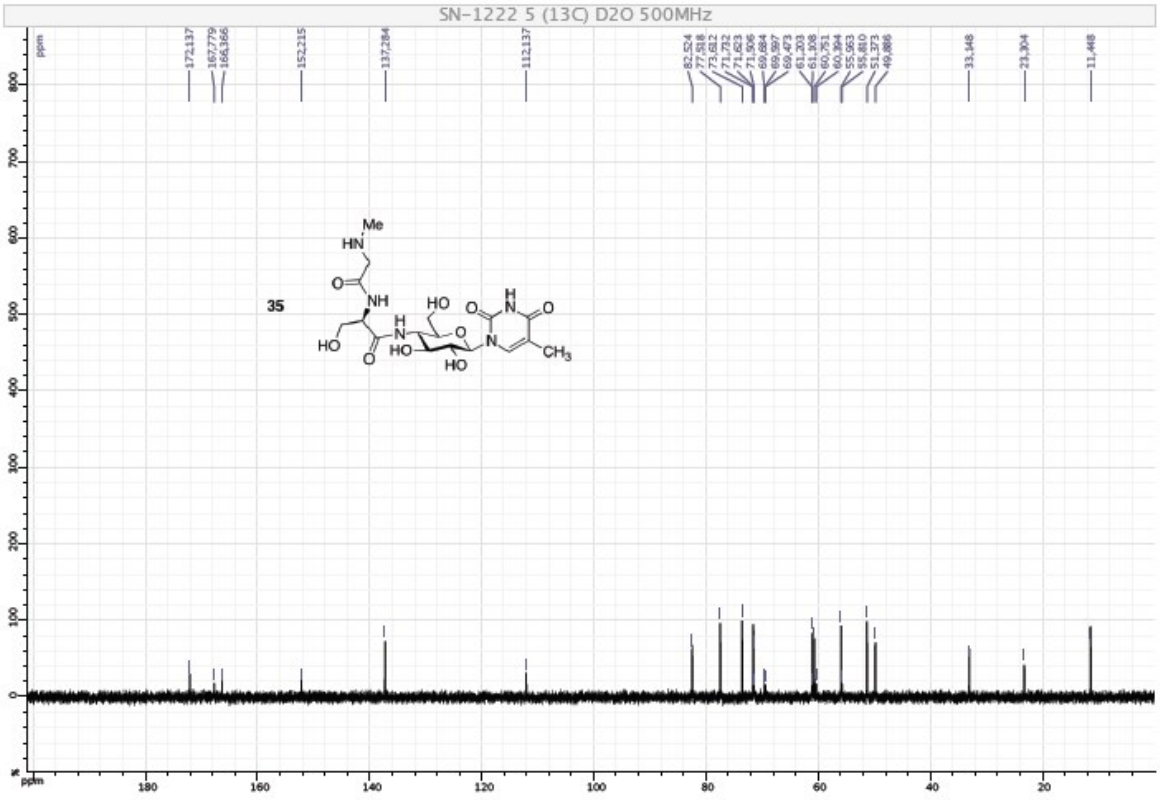

MB336 1 (1D 1H) D2O 500MHz
ppm
7.804
7.789
6.144
6.129
5.716
5.699
4.780
4.539
3.992
3.924
3.913
3.846
3.819
3.811
3.755
3.733
3.650
3.638
3.625
2.543
1.0
0.9
1.0
0.9
3.0
4.1
2.8
2.8
32-L
Me
HN
O
NH
HO
HO
H
N
O
HO
HO
O
N
NH2

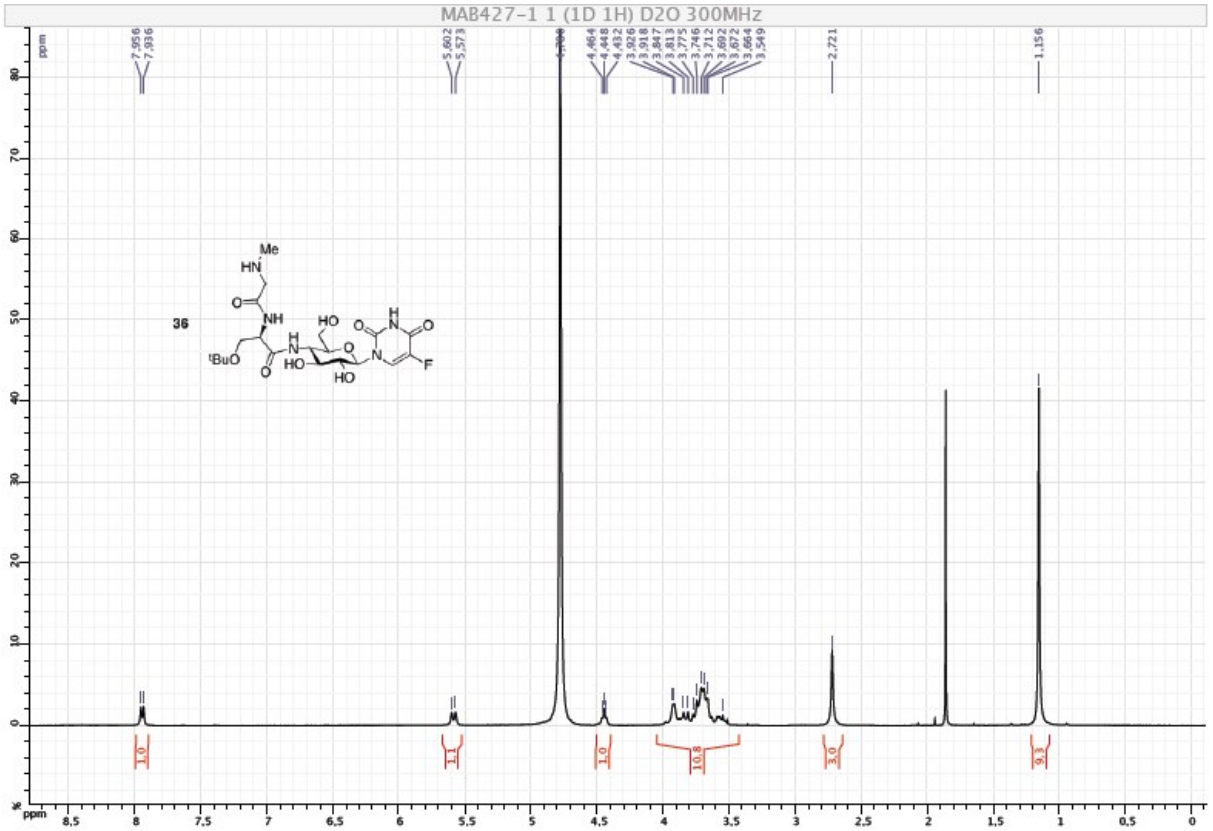

MB336 5 (13C) D2O 500MHz
ppm
172.195
166.075
157.964
141.795
97.053
83.339
77.532
73.801
71.790
71.680
61.224
60.714
60.677
55.759
51.379
51.336
33.847
32-L
Me
HN
O
NH
HO
HO
H
N
O
HO
HO
O
N
NH2

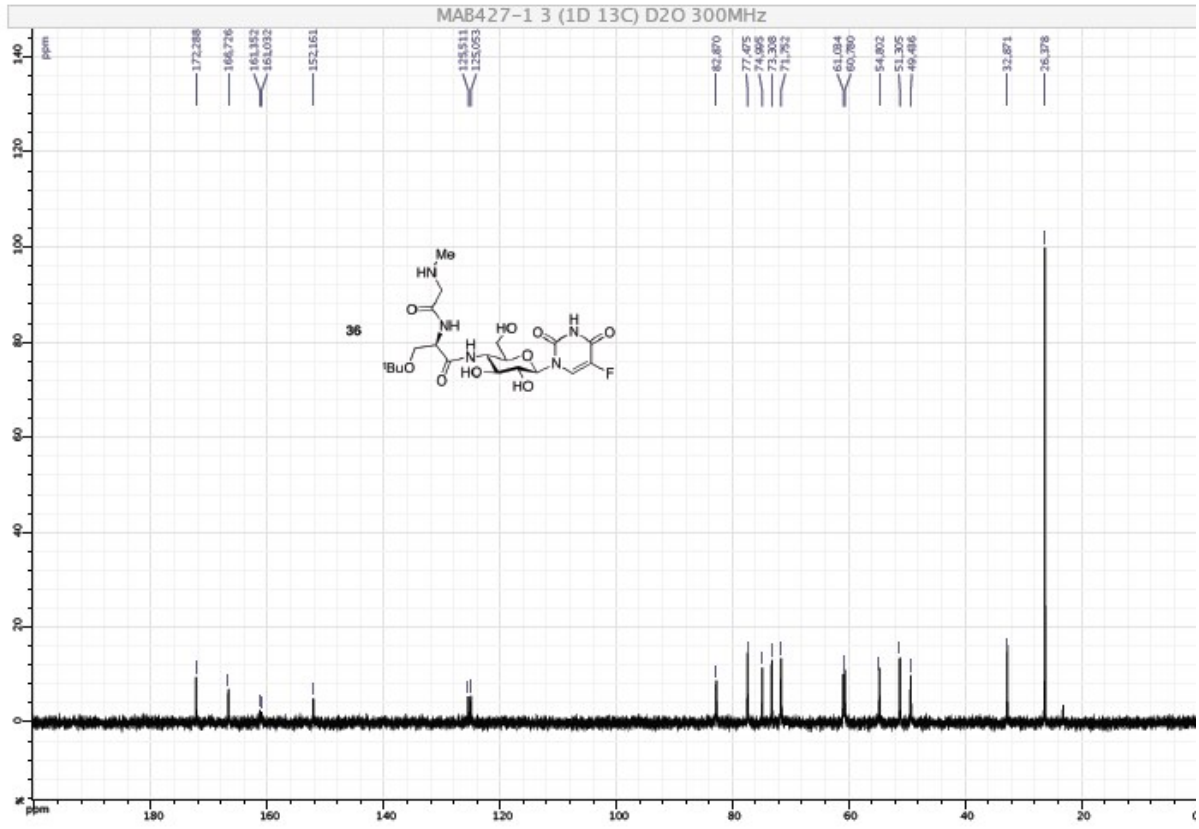

Sn-mb379 1 (1D 1H) MeOD 300MHz
ppm
33
Boc–N
Me
NH
HO
HO
HO
tBuO
7.602
5.567
5.538
4.823
4.462
4.445
4.429
3.971
3.958
3.702
3.668
3.655
3.648
3.639
3.618
3.602
3.578
3.349
3.321
3.316
3.310
3.305
3.299
2.950
1.910
1.907
1.482
1.216
1.0
1.0
1.0
1.8
1.2
6.8
3.1
3.1
10.6
9.3

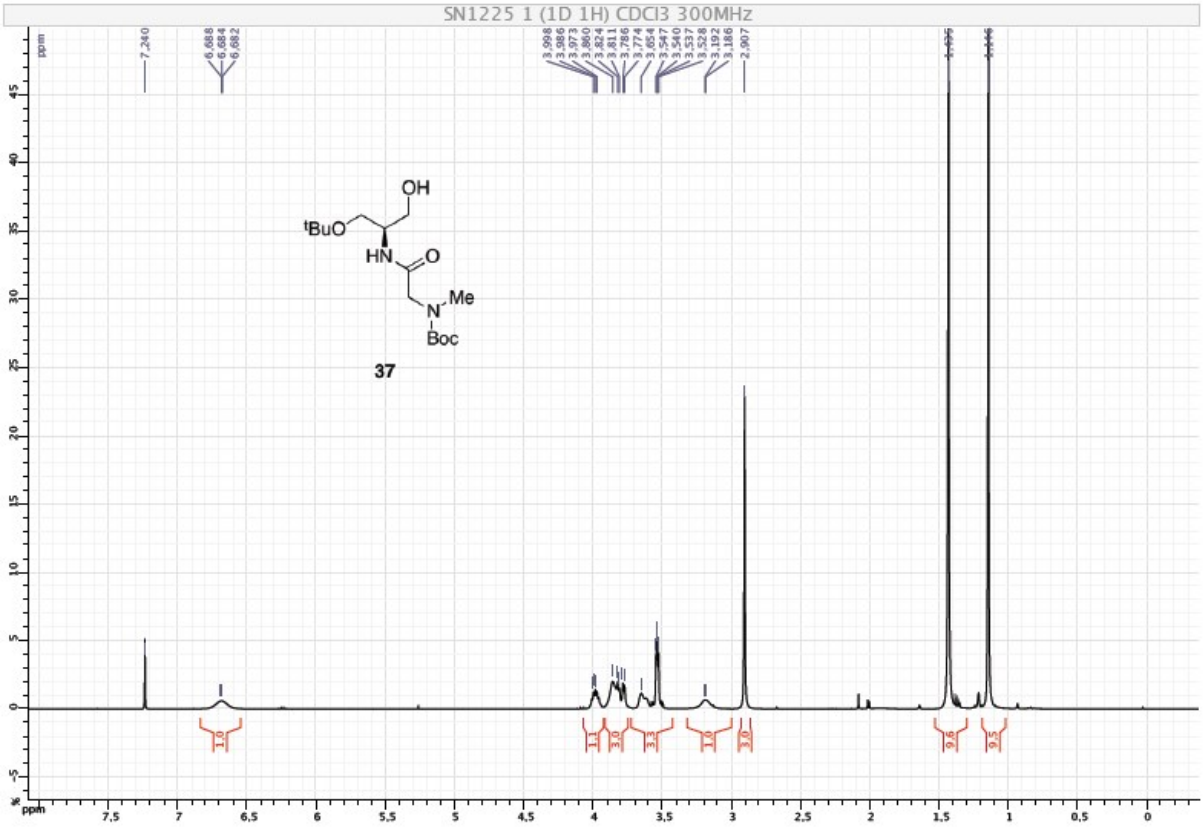

Sn-mb379 2 (13C) MeOD 300MHz
ppm
33
Boc–N
Me
NH
HO
HO
HO
tBuO
171.964
171.597
170.567
164.743
151.494
136.711
110.505
82.546
80.342
78.401
78.263
78.051
73.471
71.893
61.516
61.458
61.364
61.160
54.325
51.707
51.482
48.391
48.108
47.824
47.533
47.250
46.966
46.690
35.106
34.626
27.231
26.242
10.841

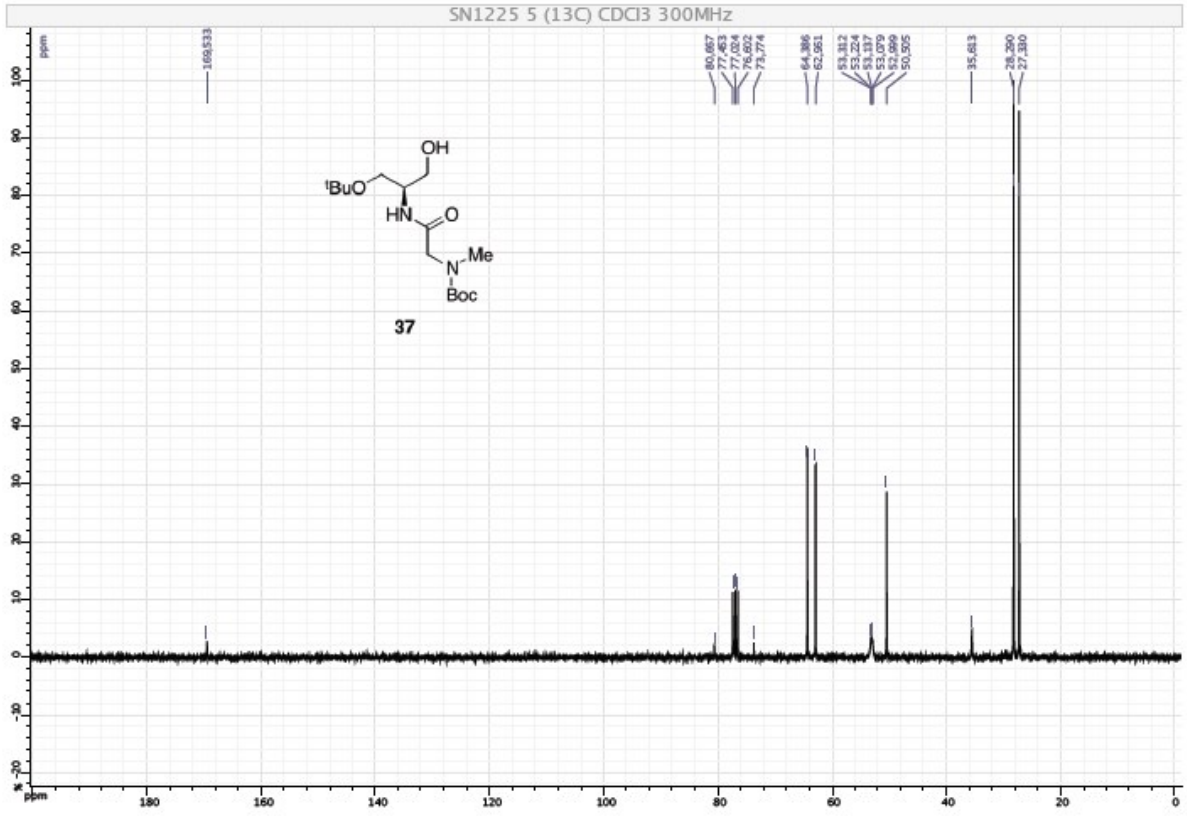

SN-1222 1 (1D 1H) D2O 500MHz
35

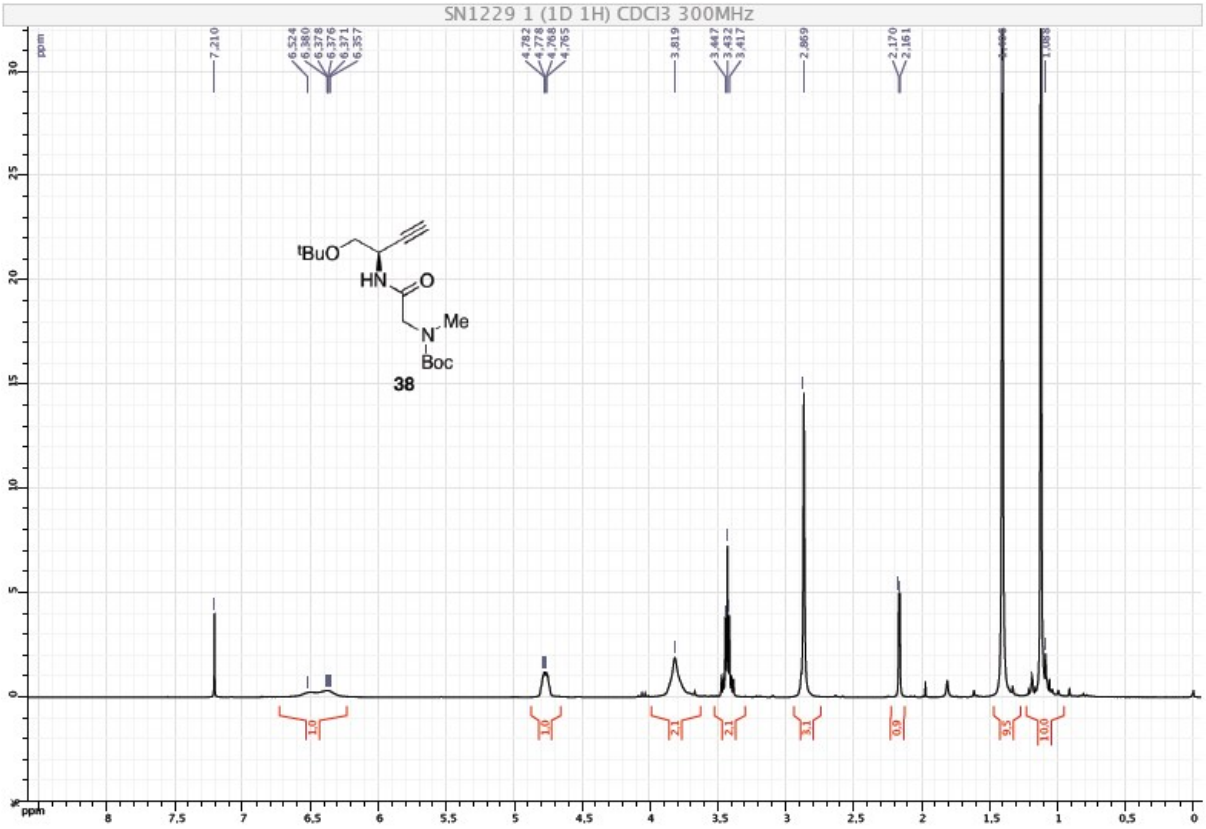

SN-1222 5 (13C) D2O 500MHz
35

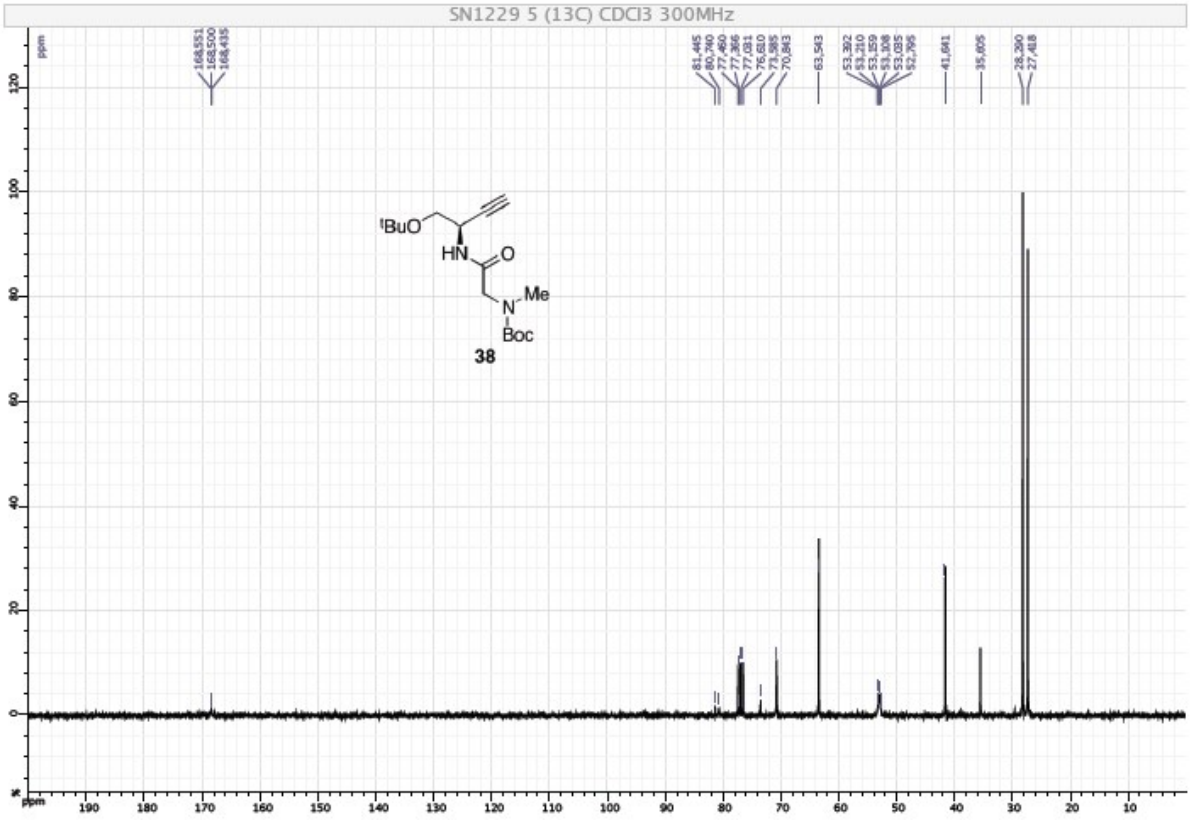

MAB427-1 1 (1D 1H) D2O 300MHz
ppm
7,956
7,936
5,602
5,573
4,464
4,448
4,432
3,926
3,918
3,847
3,813
3,775
3,746
3,732
3,693
3,672
3,664
3,549
2,721
1,156
Me
HN
O
NH
O
35
tBuO
HO
HO
O
N
H
O
O
N
F
1,0
1,1
1,0
10,8
3,0
9,3
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

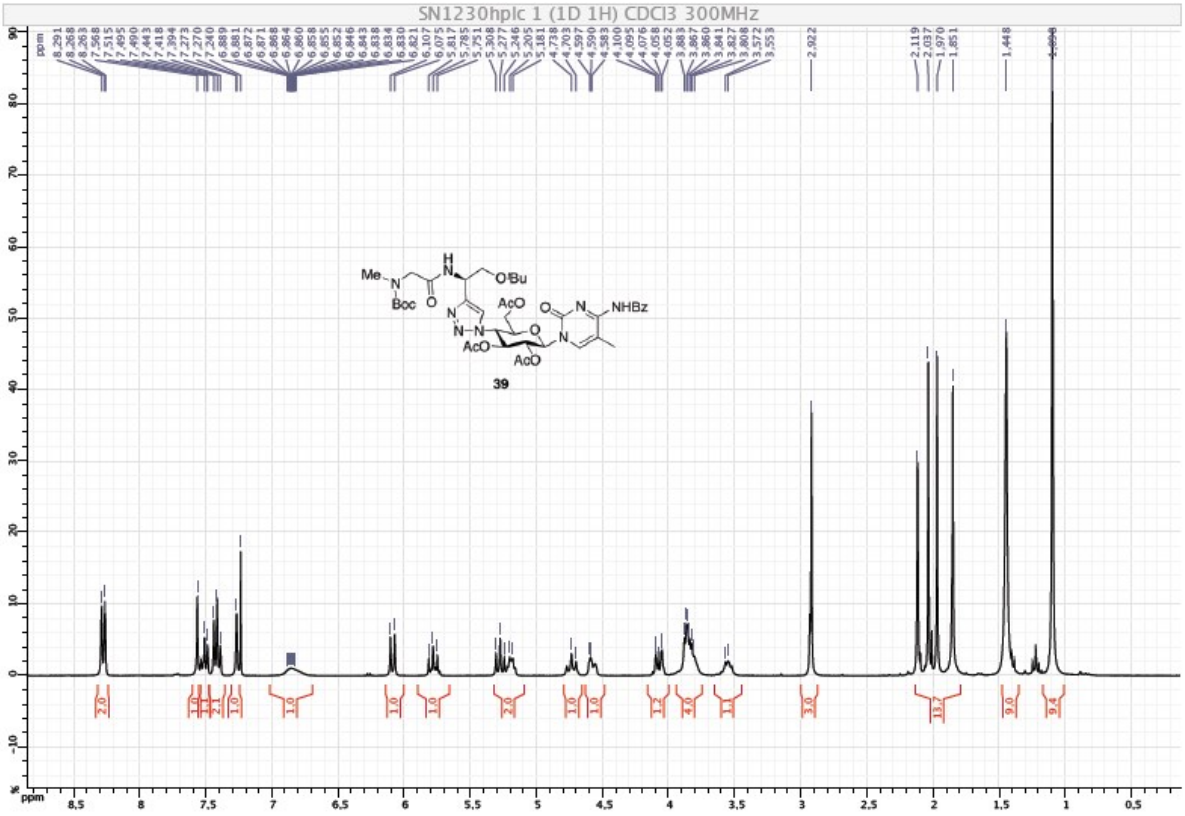

MAB427-1 3 (1D 13C) D2O 300MHz
ppm
172,288
166,726
161,352
161,032
152,161
125,511
125,053
82,870
77,475
74,995
73,308
71,752
61,034
60,780
54,802
51,305
49,486
32,871
26,378
Me
HN
O
NH
O
36
tBuO
HO
HO
O
N
H
O
O
N
F
ppm
180
160
140
120
100
80
60
40
20

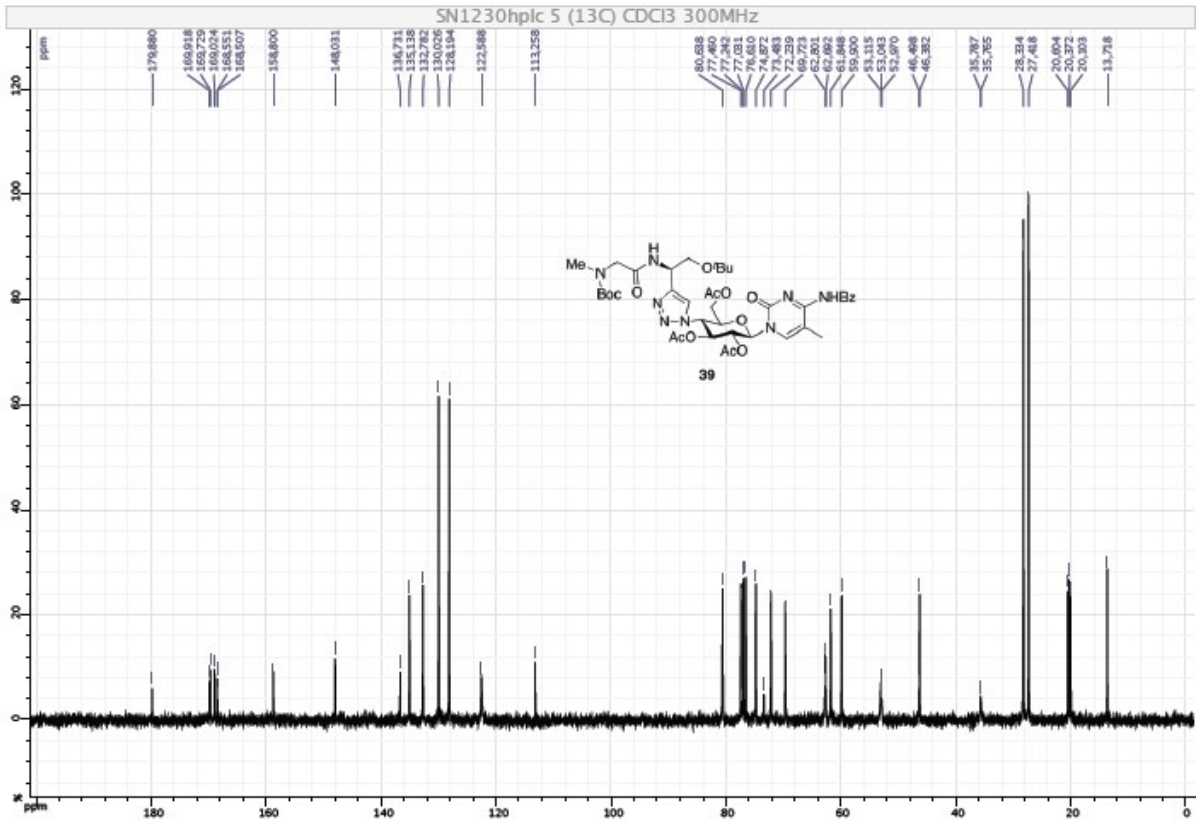

SN1225 1 (1D 1H) CDCl3 300MHz
OH
tBuO
HN
O
N
Me
Boc
37

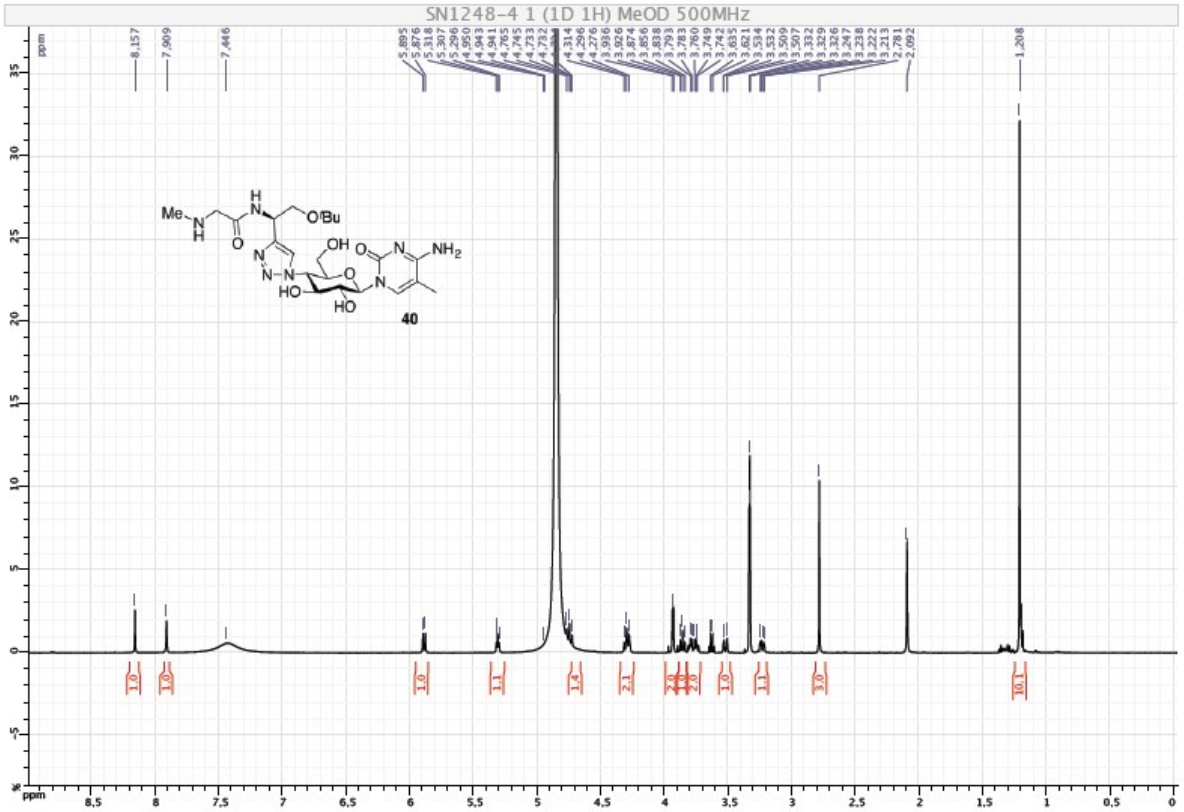

SN1225 5 (13C) CDCl3 300MHz
OH
tBuO
HN
O
N
Me
Boc
37

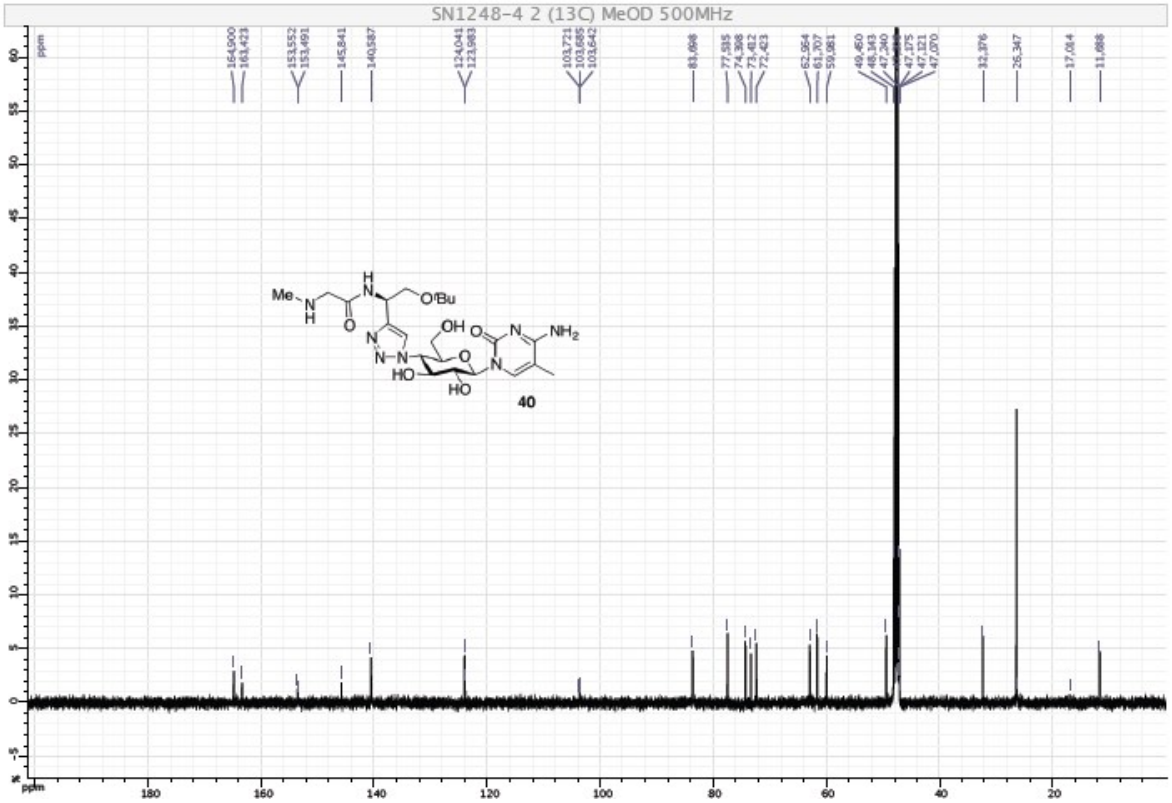

SN1229 1 (1D 1H) CDCl3 300MHz
7.210
6.524
6.380
6.378
6.376
6.371
6.357
4.782
4.778
4.768
4.765
3.819
3.447
3.432
3.417
2.869
2.170
2.161
1.088
tBuO
HN
O
N
Me
Boc
38


SN1229 5 (13C) CDCl3 300MHz
168.551
168.500
168.435
81.445
80.740
77.460
77.366
77.031
76.610
73.385
70.843
63.543
53.392
53.210
53.159
53.108
52.955
52.795
41.641
35.605
28.260
27.418
tBuO
HN
O
N
Me
Boc
38


SN1230hplc 1 (1D 1H) CDCl3 300MHz
Me
N
Boc
O
H
N
O'Bu
AcO
AcO
AcO
N
N
N
O
O
N
NHBz
39


SN1230hplc 5 (13C) CDCl3 300MHz
Me
N
Boc
O
H
N
O'Bu
AcO
AcO
AcO
N
N
N
O
O
N
NHBz
39


SN1248-4 1 (1D 1H) MeOD 500MHz
40


SN1248-4 2 (13C) MeOD 500MHz
40