Electronic Supplementary Material (ESI) for Chemical Communications

Iron (III) Chloride as an Efficient Catalyst for Stereoselective Synthesis of Glycosyl Azides and a Cocatalyst with Cu(0) for the Subsequent Click Chemistry

Santosh B. Salunke,[b,c] N.Seshu Babu[a,c] and Chien-Tien Chen[a*]

[a]Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan

[b]National Taiwan Normal University, Taipei, Taiwan

[c]Santosh B.Salunke and N.Seshu Babu made equal contributions to this work

e-mail: ctchen@mx.nthu.edu.tw

SUPPORTING INFORMATION

Detailed procedures for $FeCl_3$ catalyzed azido glycosylation and analytical data of azido glycosides **1-10**; Detailed procedures for $FeCl_3$:Cu catalyzed dipolar cycloaddition and analytical data for glycosyl 1,2,3-triazole conjugates **11-16**; procedure for one pot synthesis of **17**; ^1H and ^{13}C NMR spectra for **1-17** (63 pages).

Table of Content

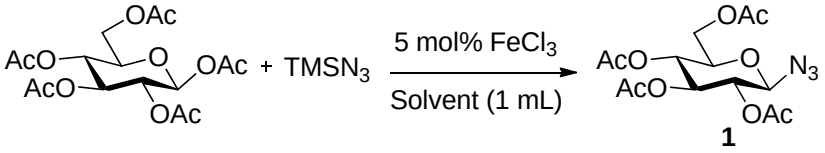
General. ^1H NMR and ^{13}C NMR spectra were recorded on 400 MHz ^1H (100 MHz ^{13}C) spectrometers in deuterochloroform with chloroform as an internal reference unless otherwise stated. Chemical shifts are reported in ppm (δ). Coupling constants, *J*, are reported in Hz. Electrospray ionization (ESI) mass spectra were recorded with data reported in the form m/e (intensity relative to base peak). Analytical TLC was performed on silica gel glass plates. Visualization was accomplished with UV light or with phosphomolybdic acid (PMA) and $KMnO_4$ staining agents. Column (flash) chromatography was performed using 32-63 μm silica gels. THF and toluene were dried over Na with benzophenone-ketyl intermediate under nitrogen atmosphere and distilled before use. DMF, CH_2Cl_2 and $CHCl_3$ were dried over CaH and distilled before use. MeOH was dried over magnesium turnings under nitrogen atmosphere and distilled before use. Oxygen was purged in $CHCl_3$ before use. All reaction products were isolated as chromatographically pure materials. All reagents and catalysts used for azido glycosylation reaction were purchased from Across Organics. The acetate

derivatives of glucose[1], glactose[2], mannose[3], ribose, xylose[4], maltose, lactose[5], maltotriose[6] were synthesized by using 2 equiv of acetic anhydride (for each hydroxyl group) in the presence of 10 mol% of Sodium acetate under reflux condition. *N*-protected glucosamine derived substrates and propargyl-*O*-linked glucose peracetate[7] were synthesized by using literature methods.

Caution: Organic azides (e.g. $TMSN_3$) are potentially explosive and corrosive compounds and should be handled with great care,[8] despite we did not sense any adverse effects during our studies at small scale reactions.

Attention: It has been documented in the literatures that, ionic azides react with CH_2Cl_2 to form explosive azidochloromethane and/or diazidomethane.[9] It has been noted that, if these azides were formed, they would be converted to stable triazole derivatives in the subsequent azide-alkyne cycloaddition reactions. However, we did not observe these side products under our catalytic conditions.

Table S1. Effect of solvents on the azido glycosylation of glucose β-peracetate.[a]

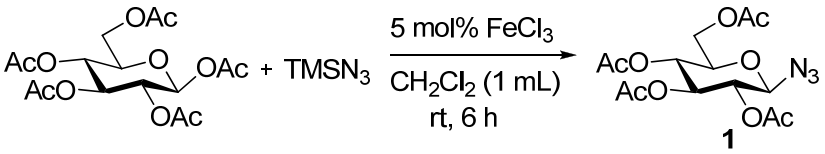


Entry	Solvent	Time (h)	Conversion (%)[b]	Yield (%)[c]
1	CH_3CN	36	5	n.d.
2	CH_3COCH_3	36	0	--
3	CH_3NO_2	36	decomposed	--
4	THF	36	0	--
5	TBME	40	55	47
6	toluene	40	95	86
7[d]	toluene	7	quantitative	91
8	CH_2Cl_2	6	quantitative	96

[a]Carried out by using $TMSN_3$ (0.38 mmol, 1.5 equiv), 5 mol% $FeCl_3$ catalyst in 1 mL of solvent. [b]Conversion of β-D-glucose peracetate was determined by ^1H NMR analysis of the crude reaction mixture. [c]Isolated, purified yield. [d]Reaction was conducted at 70 °C .

(A) Detailed procedures for $FeCl_3$ catalyzed azido glycosylation and analytical data of azido glycosides 1-10.

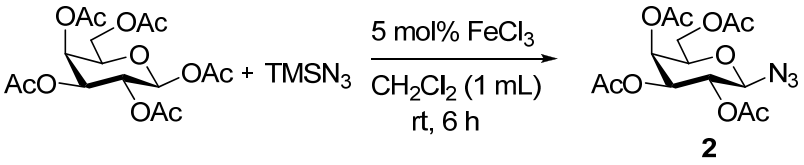
2,3,4,6-tetra-*O*-acetyl-6-deoxy-β-D-glucopyranosyl azide (1).[10]



To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (2 mg, 0.0125 mmol, 0.05 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of (2*S*,3*R*,4*S*,5*R*,6*R*)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2,3,4,5-tetrayl tetraacetate (97.5 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been

stirred for 5 min at ambient temperature, a solution of trimethyl silyl azide i.e. $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 6 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). Two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude reside was purified by column chromatography (EtOAc/hexanes, 1/2) on silica gel to afford 89 mg (96%) of 2,3,4,6-tetra-*O*-acetyl-6-deoxy-β-D-glucopyranosyl azide **1** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (t, J = 9.2, 1H), 5.07 (t, J = 10, 1H), 4.92 (t, J = 9.2, 1H), 4.63 (d, J = 8.8, 1H), 4.25 (dd, J = 12.4, 4.8, 1H), 4.14 (dd, J = 12.4, 2, 1H), 3.80-3.76 (m, 1H), 2.07 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.00 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.0, 169.2, 169.1, 87.8, 74.0, 72.5, 70.6, 67.9, 61.6, 20.6, 20.4; MS ESI ($C_{14}H_{19}O_9N_3$, 373): 396 ($M+Na^+$, 100); TLC R_f 0.34 (EtOAc/hexanes, 1/2); m.p. 124-125 °C (lit.[11] m.p. 127 °C); $[\alpha]_D^{25}$ -30.2 (*c* 1.0, $CHCl_3$) (lit.[10] $[\alpha]_D^{23}$ -31 (*c* 1.0, $CHCl_3$)).

2,3,4,6-tetra-*O*-acetyl-6-deoxy-β-D-galactopyranosyl azide (2).[10]

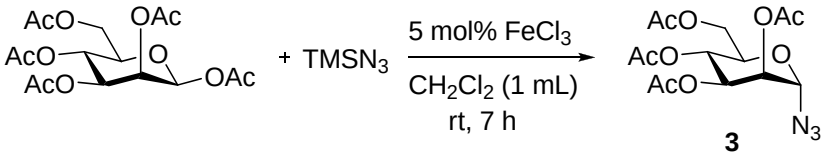


2

To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (2 mg, 0.0125 mmol, 0.05 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of (2*S*,3*S*,4*S*,5*R*,6*R*)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2,3,4,5-tetrayl tetraacetate (97.5 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been stirred for 5 min at ambient temperature, a solution of $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 6 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). Two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude reside was purified by column chromatography (EtOAc/hexanes, 1/2) on silica gel to afford 89 mg (96%) of 2,3,4,6-tetra-*O*-acetyl-6-deoxy-β-D-galactopyranosyl azide **2** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (d, *J* = 2.4, 1H), 5.15 (dd, *J* = 10, 8.8, 1H), 5.02 (dd, *J* = 10.4, 3.6, 1H), 4.59 (d, *J* = 8.8, 1H), 4.18-4.14 (m, 2H), 4.00 (td, *J* = 6.8, 0.6, 1H),

2.16 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.0, 169.9, 169.2, 88.1, 72.7, 70.6, 67.95, 66.8, 61.2, 20.5, 20.4, 20.35; MS ESI ($C_{14}H_{19}O_9N_3$, 373): 396 ($M+Na^+$, 100); TLC R_f 0.35 (EtOAc/hexanes, 1/2); m.p. 95-97 °C (lit.[11] m.p. 94-95 °C); $[\alpha]_D^{25}$ -15.4 (*c* 1.0, $CHCl_3$) (lit.[10] $[\alpha]_D^{23}$ -14 (*c* 1.0, $CHCl_3$)).

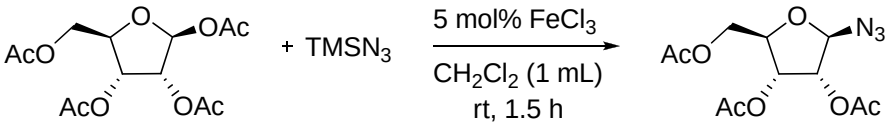
2,3,4,6-tetra-*O*-acetyl-6-deoxy-α-D-mannopyranosyl azide (3).[12]



To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (2 mg, 0.0125 mmol, 0.05 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of (3*S*,4*S*,5*S*,6*R*)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2,3,4,5-tetrayl tetraacetate (97.5 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been stirred for 5 min at ambient temperature, a solution of $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 7 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). Two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL).

The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude reside was purified by column chromatography (EtOAc/hexanes, 1/2) on silica gel to afford 83 mg (89%) of 2,3,4,6-tetra-*O*-acetyl-6-deoxy-α-D-mannopyranosyl azide **3** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (d, *J* = 1.5, 1H), 5.28-5.20 (m, 2H), 5.13 (t, *J* =2.3, 1H), 4.28 (dd, *J* = 12.4, 5.5, 1H), 4.16-4.11 (m, 2H), 2.18 (s, 3H, $COCH_3$), 2.14 (s, 3H, $COCH_3$), 2.1 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.8, 169.7, 169.6, 87.4, 70.6, 69.1 68.2, 65.6, 62.1, 20.7, 20.61, 20.6, 20.5; MS ESI ($C_{14}H_{19}O_9N_3$, 373): 396 ($M+Na^+$, 100); TLC R_f 0.32 (EtOAc/hexanes, 1/2). m.p. 103-105 °C (lit.[13] m.p. 104.1-104.9 °C); $[\alpha]_D^{25}$ +181.1 (*c* 1.0, $CHCl_3$) (lit.[13] $[\alpha]_D^{23}$ +184 (*c* 1.0, $CHCl_3$)).

2,3,5-tri-*O*-acetyl-β-D-ribofurunosyl azide (4).[14]

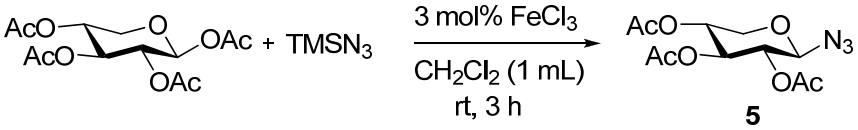


4

To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (1.2 mg, 0.0075 mmol, 0.03 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of (2*S*,3*R*,4*R*,5*R*)-5-(acetoxymethyl)tetrahydrofuran-2,3,4-triyl triacetate (79.5 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been stirred for 5 min at

ambient temperature, a solution of $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 1.5 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). Two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude reside was purified by column chromatography (EtOAc/hexanes, 1/2) on silica gel to afford 72 mg (96%) of 2,3,5-tri-*O*-acetyl-β-D-ribofurunosyl azide **4** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (d, *J* = 1.4, 1H), 5.30 (dd, *J* = 6.6, 5.0, 1H), 5.10 (dd, *J* = 4.8, 1.6, 1H), 4.38 (dd, *J* = 12, 3.2, 1H), 4.34-4.30 (m, 1H), 4.12 (dd, *J* = 12.2, 4.2, 1H), 2.092 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.5, 169.3, 92.6, 79.3, 74.4, 70.4, 62.9, 20.6, 20.4, 20.3; MS ESI ($C_{11}H_{15}O_7N_3$, 301): 324 ($M+Na^+$, 100); TLC R_f 0.34 (EtOAc/hexanes, 1/2); $[\alpha]_D^{25}$ +111.3 (*c* 1.0, $CHCl_3$) (lit.[14] $[\alpha]_D^{23}$ +116 (*c* 1.0, $CHCl_3$)).

2,3,5-tri-*O*-acetyl-β-D-xylopyranosyl azide (5).[10]

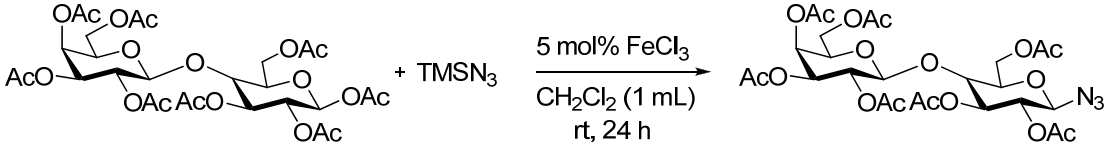


5

To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (1.2 mg, 0.0075 mmol, 0.03 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of (2*S*,3*S*,4*S*)-tetrahydro-2*H*-pyran-2,3,4,5-tetrayl tetraacetate (79.5 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been stirred for 5 min at ambient temperature, a solution of $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). Two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude reside was purified by column chromatography (EtOAc/hexanes, 1/2) on silica gel to afford 69 mg (92%) of 2,3,5-tri-*O*-acetyl-β-D-xylopyranosyl azide **5** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (t, *J* = 8.8, 1H), 5.00-4.95 (m, 1H), 4.87 (t, *J* = 8.4, 1H), 4.63 (d, *J* = 8.0, 1H), 4.21 (dd, *J* = 12, 5.6, 1H), 3.44 (dd, *J* = 11.6, 9.2, 1H), 2.07 (s, 3H, $COCH_3$), 2.042 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.7, 169.3, 88.3, 71.5,

70.4, 68.4, 64.3, 20.6, 20.6; MS ESI ($C_{11}H_{15}O_7N_3$, 301): 324 ($M+Na^+$, 100); TLC R_f 0.34 (EtOAc/hexanes, 1/2); m.p. 84-85 °C (lit.[15] m.p. 87 °C); $[\alpha]_D^{25}$ +88.4 (*c* 1.0, $CHCl_3$) (lit.[15] $[\alpha]_D^{25}$ +86 (*c* 1.0, $CHCl_3$)).

2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)-β-D-glucopyranosylazide (6).[10]

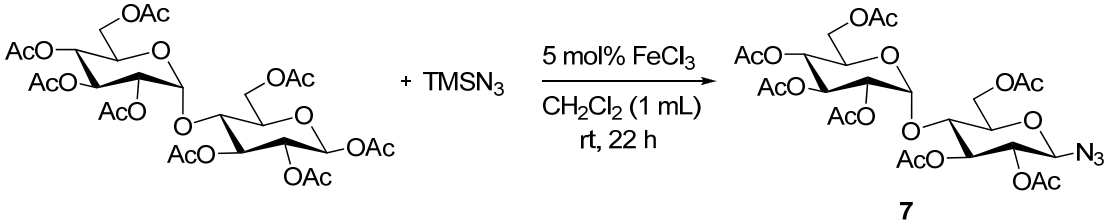


6

To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (2 mg, 0.0125 mmol, 0.05 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of (2*S*,3*S*,4*S*,6*R*)-6-(acetoxymethyl)-5-((2*S*,3*S*,4*S*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl) tetrahydro-2*H*-pyran-2-yloxy)tetrahydro-2*H*-pyran-2,3,4-triyl triacetate (169.5 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been stirred for 5 min at ambient temperature, a solution of $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 24 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). Two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and

evaporated under reduced pressure. The crude reside was purified by column chromatography (EtOAc/hexanes, 3/2) on silica gel to afford 149 mg (90%) of 2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-glucopyr -anosyl azide **6** as a amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (d, *J* = 3.6, 1H), 5.20 (t, *J* = 9.4, 1H), 5.09 (dd, *J* = 10.4, 8, 1H), 4.94 (dd, *J* = 10.4, 3.6, 1H), 4.85 (t, *J* = 9.6, 1H), 4.62 (d, *J* = 8.8, 1H), 4.52-4.46 (m, 2H), 4.14-4.05 (m, 3H), 3.87 (t, *J* = 6.8, 1H), 3.81 (t, *J* = 9.6, 1H), 3.70-3.71 (m, 1H), 2.14 (s, 3H, $COCH_3$), 2.13 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 1.95 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.1, 170.0, 169.6, 169.5, 169.1, 101.1, 87.7, 75.7, 74.8, 72.5, 71.0, 70.9, 70.7, 69.0, 66.6, 61.7, 60.8, 20.8, 20.7, 20.6, 20.5; MS ESI ($C_{26}H_{35}O_{17}N_3$, 661): 684 ($M+Na^+$, 100); TLC R_f 0.20 (EtOAc/hexanes, 1/1); $[\alpha]_D^{25}$ -21.2 (*c* 1.0, $CHCl_3$) (lit.[10] $[\alpha]_D^{23}$ -20.4 (*c* 1.0, $CHCl_3$)).

2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucop yranosylazide (7).[10]



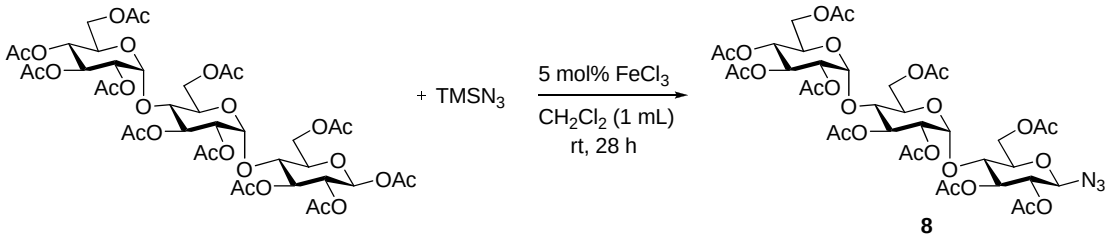
7

To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (2 mg, 0.0125 mmol, 0.05 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of

(2*S*,3*S*,4*S*,5*R*,6*R*)-6-(acetoxymethyl)-5-((3*S*,4*S*,5*S*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yloxy)tetrahydro-2*H*-pyran-2,3,4-triyl triacetate (169.5 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been stirred for 5 min at ambient temperature, a solution of $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 22 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). Two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude reside was purified by column chromatography (EtOAc/hexanes, 3/2) on silica gel to afford 152 mg (92%) of 2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl azide **7** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (d, *J* = 4, 1H), 5.35 (t, *J* = 10, 1H), 5.26 (t, *J* = 9.0, 1H), 5.05 (t, *J* = 9.8, 1H), 4.85 (dd, *J* = 10.8, 4.0, 1H), 4.78 (t, *J* = 8.8, 1H), 4.70 (d, *J* = 8.8, 1H), 4.51 (dd, *J* = 12, 2.4, 1H), 4.26-4.24 (m, 12.4, 2H), 4.07-4.03 (m, 2H), 4.01-3.99 (m, 1H), 3.79-3.70 (m, 1H), 2.15 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 2.00 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 170.4, 170.3, 169.9, 169.8, 169.3, 169.3, 95.6, 77.3, 77.0, 76.7, 74.9, 72.3, 71.4, 69.9, 69.1, 68.5, 67.9, 62.4, 61.4, 20.7, 20.6, 20.5, 20.4; MS ESI ($C_{26}H_{35}O_{17}N_3$, 661): 684 ($M+Na^+$, 100); TLC R_f 0.15 (EtOAc/hexanes, 1/1); m.p. 181-183 °C (lit.[16a] m.p. 180-182 °C); $[\alpha]_D^{25}$ -32.1 (*c* 1.0, $CHCl_3$) (lit.[16b] $[\alpha]_D^{24}$ -31 (*c* 1.0, $CHCl_3$)).

2,3,4,6-tetra-*O*-acetyl-6-deoxy-α-D-glucopyranosyl-(1-4)-2,3,6-tri-*O*-acetyl-6-deoxy-α-D-glucopyranosyl-(1-4)-2,3,6-tri-*O*-acetyl-6-deoxy-β-D-glucopyranosyl azide (8).[17]



8

To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (2 mg, 0.0125 mmol, 0.05 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of (2*S*,3*R*,4*S*,5*R*,6*R*)-6-(acetoxymethyl)-5-((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4-diacetoxy-6-(acetoxymethyl)-5-((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2-yloxy)tetrahydro-2*H*-pyran-2-yloxy)tetrahydro-2*H*-pyran-2,3,4-triyl triacetate (241.5 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been stirred for 5 min at ambient temperature, a solution of $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 28 h, the reaction mixture was

quenched with saturated aqueous $NaHCO_3$ solution (5 mL). Two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude reside was purified by column chromatography (EtOAc/hexanes, 3/2) on silica gel to afford 206 mg (87%) of 2,3,4,6-tetra-*O*-acetyl-6-deoxy-α-D-glucopyranosyl-(1-4)-2,3,6-tri-*O*-acetyl-6-deoxy-α-D-glucopyranosyl-(1-4)-2,3,6-tri-*O*-acetyl-6-deoxy-β-D-glucopyranosyl azide **8** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37-5.32 (m, 2H), 5.32 (d, *J* = 6.4, 1H), 5.25-5.21 (m, 2H), 5.03 (t, *J* = 9.8, 1H), 4.82 (dd, *J* = 10.4, 4.0, 1H), 4.76-4.67 (m, 3H), 4.49-4.41 (m, 2H), 4.29 (dd, *J* = 12.2, 4.4, 1H), 4.21 (dd, *J* = 12.4, 3.6, 1H), 4.15 (dd, *J* = 12.4, 3.2, 1H), 4.02 (dd, *J* = 12.4, 2.0, 1H), 3.96 (d, *J* = 9.2, 1H), 3.93-3.87 (m, 3H), 3.81-3.79 (m, 1H), 2.15 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 2.0 (s, 6H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.97 (s, 6H, 2 × $COCH_3$), 1.96 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.4, 170.3, 170.4, 170.2, 169.7, 169.6, 169.4, 169.3, 95.8, 95.6, 87.3, 74.8, 74.0, 73.4, 72.4, 71.6, 71.4, 70.3, 70.0, 69.2, 69.0, 68.4, 67.8, 62.6, 62.2, 61.3, 20.8, 20.7, 20.5, 20.5, 20.4; MS ESI ($C_{38}H_{51}O_{25}N_3$, 949): 972 ($M+Na^+$, 100); TLC R_f 0.10 (EtOAc/hexanes, 1/1); m.p. 95-96 °C; $[\alpha]_D^{25}$ +69.2 (*c* 1.0, $CHCl_3$) (lit.[17b] $[\alpha]_D^{25}$ +65 (*c* 1.2, $CHCl_3$)).

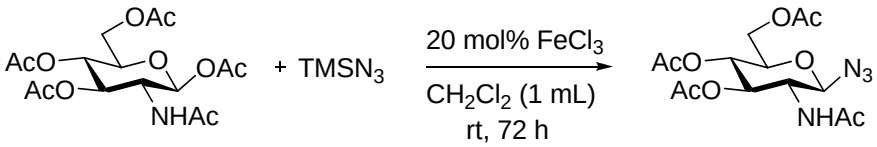
3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (9).[18]

9

To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (2 mg, 0.0125 mmol, 0.05 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of (2*S*,3*R*,4*R*,5*S*,6*R*)-6-(acetoxymethyl)-3-(1,3-dioxoisoindolin-2-yl)tetrahydro-2*H*-pyra n-2,4,5-triyl triacetate (119 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been stirred for 5 min at ambient temperature, a solution of $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 22 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). Two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude reside was purified by column chromatography (EtOAc/hexanes, 3/2) on silica gel to afford 105 mg (91%) of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide **9** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 5.4, 3.0, 2H), 7.76 (dd, J =

5.5, 3.0, 2H), 5.80 (dd, *J* = 10.5, 9.2, 1H), 5.65 (d, *J* = 9.4, 1H), 5.19 (t, *J* = 9.7, 1H), 4.35 (dd, *J* = 4.7, 12.4, 1H), 4.24 (dd, *J* = 12.5, 2.3, 1H), 4.24 (dd, *J* = 10.6, 9.2, 1H), 3.99-3.96 (m, 1H), 2.12 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 1.86 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.9, 169.3, 134.5, 131.2, 123.7, 73.9, 85.5, 70.4, 68.4, 61.7, 53.1, 20.6, 20.5, 20.3; MS ESI ($C_{20}H_{20}O_9N_4$, 460): 483 ($M+Na^+$, 100); TLC R_f 0.28 (EtOAc/hexanes, 1/1); m.p. 135-137 °C (lit.[18a] m.p. 135-138 °C); $[\alpha]_D^{25}$ +39.6 (*c* 1.0, $CHCl_3$) (lit.[18b] $[\alpha]_D^{25}$ +38 (*c* 1.0, $CHCl_3$)).

3,4,6-tri-*O*-acetyl-2-*N*-acetyl-2-deoxy-β-D-glucopyranosyl azide (10).[10]

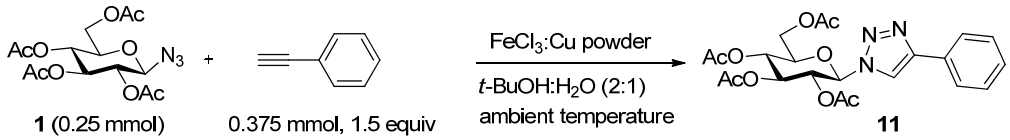


10

To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (8 mg, 0.05 mmol, 0.2 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of (2*S*,3*R*,4*R*,5*S*,6*R*)-3-acetamido-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2,4,5-triyl triacetate (97 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been stirred for 5 min at ambient temperature, a solution of $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 72 h, the

reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). Two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude reside was purified by column chromatography (EtOAc/hexanes, 3/2) on silica gel to afford 86 mg (93%) of 3,4,6-tri-*O*-acetyl-2-*N*-acetyl-2-deoxy-β-D-glucopyranosyl azide **10** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (d, *J* = 8.8, 1H, NH), 5.25 (t, *J* = 10, 1H), 5.08 (t, *J* = 9.6, 1H), 4.78 (d, *J* = 9.2, 1H), 4.25 (dd, *J* = 4.8, 12.4, 1H), 4.16-4.13 (m, 1H), 3.91 (dd, *J* = 19.4, 9.3, 1H), 3.81 (m, 1H), 2.09 (s, 3H, $COCH_3$), 2.024 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.7, 170.6, 169.3, 88.3, 76.7, 73.9, 72.1, 68.1, 61.9, 54.0, 23.1, 20.7, 20.6, 20.5; MS ESI ($C_{14}H_{20}O_8N_4$, 372): 395 ($M+Na^+$, 100); TLC R_f 0.20 (EtOAc/hexanes, 1/1); m.p. 161-162 °C (lit.[19] m.p. 158-161 °C); $[\alpha]_D^{25}$ -45.9 (*c* 1.0, $CHCl_3$) (lit.[10] $[\alpha]_D^{23}$ -47.7 (*c* 1.0, $CHCl_3$)).

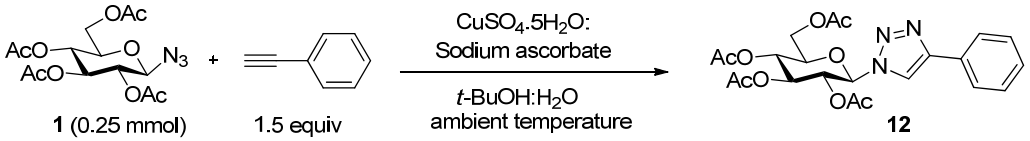
Table S2: Optimization of $FeCl_3$/Cu(0) ratio for cycloaddition reactions (i. e. click chemistry) between β-azido glucose and 2-phenylethyne.[a]



Entry	$FeCl_3$ mol%	Cu powder mol%	$FeCl_3$:Cu ratio	Time, h	Yield (%)
1	20	0	1:0	48	No reaction
2	0	100	0:1	48	No reaction
3	20	20	1:1	48	No reaction
4	20	30	1:1.5	48	Sluggish reaction
5	20	40	1:2	40	92
6	20	100	1:5	10	94

[a]Reaction details: β-azido glucose (0.25 mmol, 1 equiv), 2-phenylethyne (0.375 mmol, 1.5 equiv) in *t*-BuOH:H_2O (2 mL:1 mL). [b]Isolated yield after purification by silica gel column chromatography .

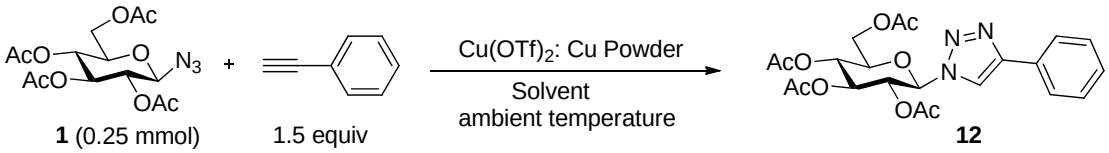
Table S3: Control experiments for cycloaddition reactions between β-azido glucose and 2-phenylethyne[a] by using Sharpless and Fokin's reagents.[20]



Entry	$CuSO_4$ (mol%)	sodium ascorbate (mol%)	$CuSO_4$: sodium ascorbate ratio	Time (h)	Conversion (%)[b]	Yield (%)[c]
1	3	30	1:10	48	8	n.d.
2	20	40	1:2	20	7	n.d.
3	20	40	1:2	70	30	24[d]
4	20	100	1:5	20	15	n.d.
5	20	100	1:5	70	45	40

[a]Reaction details: β-azido glucose (0.25 mmol, 1 equiv), 2-phenylethyne (0.375 mmol, 1.5 equiv) in *t*-BuOH:H_2O (2 mL:1 mL). [b]Conversion of β-azido glucose **1** was determined by ^1H NMR analysis of the crude reaction mixture. [c]Isolated yield after purification by silica gel column chromatography. n.d. = not determined. [d]Remaining starting material was recovered.

Table S4: Control experiments for cyclo-addition reaction between β-azido glucose and 2-phenylethyne[a] by using bimetallic catalyst $Cu(OTf)_2$:Cu system.[21]

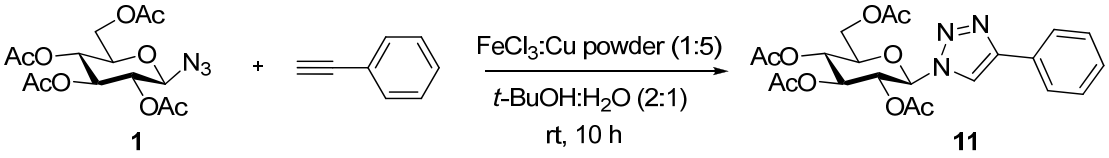


Entry	$Cu(OTf)_2$ (mol%)	Cu Powder (mol%)	$Cu(OTf)_2$: Cu(0) ratio	Solvent	Time (h)	Conv. (%)[b]	Yield (%)[c]
1	10	10	1:1	CH_3CN	40	21	16[d]
2	10	50	1:5	CH_3CN	12	quant.	92
3	10	10	1:1	*t*-BuOH:H_2O	35	0	n.d.
4	10	50	1:5	*t*-BuOH:H_2O	35	9	n.d.

[a]Reaction details: β-azido glucose (0.25 mmol, 1 equiv), 2-phenylethyne (0.375 mmol, 1.5 equiv) in CH_3CN (6 mL) or *t*-BuOH:H_2O (2 mL:1 mL). [b]Conversion of β-azido glucose **1** was determined by ^1H NMR analysis of the crude reaction mixture. [c]Isolated yield after purification by silica gel column chromatography. n.d. = not determined. [d]Remaining starting material was recovered.

(B) Detailed procedures for $FeCl_3$:Cu catalyzed 1,3-dipolar cycloaddition and analytical data for glycosyl 1,2,3-triazole conjugates 11-16.

Phenyl 2,3,4,6-tetra-*O*-acetyl-6-deoxy-β-D-glucopyranosyl 1,2,3-triazole (11).[22]

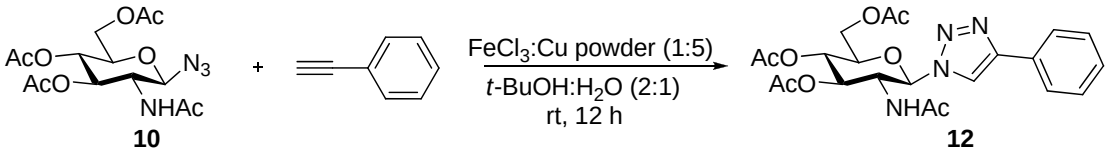


In a 10 mL, round bottomed flask were placed 20 mol% of $FeCl_3$ (8.1 mg, 0.05 mmol, 0.2 equiv) and $Cu_{(s)}$ powder (16 mg, 0.25 mmol, 1.0 equiv) in 1:1 mixture of *t*-BuOH:H_2O (1 mL : 1 mL). The resulting mixture was stirred at ambient temperature for 5 min and a solution of 2,3,4,6-tetra-*O*-acetyl-6-deoxy-β-D-gluco-pyranosyl azide

1 (93 mg, 0.25 mmol, 1 equiv) in *t*-BuOH (1 mL) was added followed by addition of ethynylbenzene (41 μL, 38 mg, 0.375 mmol, 1.5 equiv). The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 10 h, the organic volatiles were removed under reduced pressure and the resulting mixture was partitioned between H_2O and CH_2Cl_2 (5 mL each). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered, passed through Celite bed to remove inorganic salts and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (EtOAc/hexanes, 1/1) on silica gel to afford 109 mg (92%) of phenyl 2,3,4,6-tetra-*O*-acetyl-6-deoxy-β-D-glucopyranosyl 1,2,3-triazole **11** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0 (s, 1H), 7.83 (d, *J* = 7.2, 2H), 7.43 (t, *J* = 7.2, 2H,), 7.36 (d, *J* = 7.6, 1H), 5.93 (d, *J* = 9.2, 1H), 5.52 (t, *J* = 9.4, 1H), 5.44 (t, *J* = 9.4, 1H), 5.27 (t, *J* = 9.6, 1H), 4.33 (dd, *J* = 12.6, 5.0, 1H), 4.16 (dd, *J* = 12.6, 1.8, 1H), 4.05-4.02 (m, 1H), 2.084 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 1.88 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.9, 169.4, 169.0, 148.5, 129.9, 128.9, 128.6, 125.9, 117.7, 85.8, 75.3, 72.7, 70.2, 67.7, 61.6, 20.7, 20.6, 20.5, 20.2; MS ESI ($C_{22}H_{25}O_9N_3$, 475): 498 ($M+Na^+$, 100); TLC R_f 0.42 (EtOAc/hexanes, 1/1); m.p. 211-213 °C (lit.[22b] m.p.

213-215 °C); $[\alpha]_D^{25}$ -54.5 (*c* 1.0, $CHCl_3$) (lit.[22c] $[\alpha]_D^{20}$ -56.2 (*c* 1.0, $CHCl_3$)).

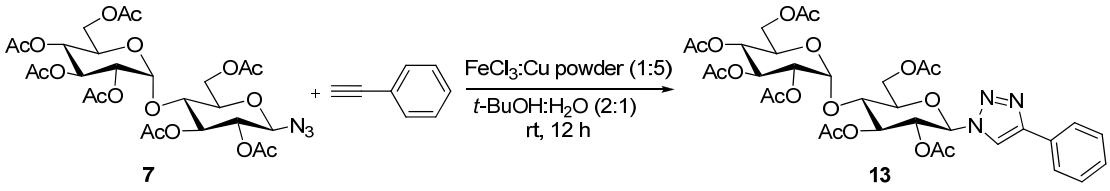
Phenyl 3,4,6-tri-*O*-acetyl-2-*N*-acetyl-6-deoxy-β-D-glucopyranosyl 1,2,3-triazole (12).



In a 10 mL, round bottomed flask were placed 20 mol% of $FeCl_3$ (8.1 mg, 0.05 mmol, 0.2 equiv) and $Cu_{(s)}$ powder (16 mg, 0.25 mmol, 1.0 equiv) in 1:1 mixture of *t*-BuOH:H_2O (1 mL : 1 mL). The resulting mixture was stirred at ambient temperature for 5 min and a solution of 3,4,6-tri-*O*-acetyl-2-*N*-acetyl-2-deoxy-β-D-glucopyranosyl azide **10** (93 mg, 0.25 mmol, 1 equiv) in *t*-BuOH (1 mL) was added followed by addition of ethynylbenzene (41 μL, 38 mg, 0.375 mmol, 1.5 equiv). The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 12 h, the organic volatiles were removed under reduced pressure and the resulting mixture was partitioned between H_2O and CH_2Cl_2 (5 mL each). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered, passed through Celite bed to remove inorganic salts and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (EtOAc/hexanes, 1/1)

on silica gel to afford 105 mg (89%) of phenyl 3,4,6-tri-*O*-acetyl-2-*N*-acetyl-6-deoxy-β-D-glucopyranosyl 1,2,3-triazole **13** as a off white solid. ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$) δ 8.04 (s, 1H), 7.52 (d, *J* = 7.3, 2H), 7.13 (t, *J* = 7.4, 2H), 7.05 (d, *J* = 7.2, 1H), 5.81 (d, *J* = 10, 1H), 5.19 (t, *J* = 10, 1H), 4.99 (t, *J* = 9.6, 1H), 4.36 (t, *J* = 10.2, 1H), 4.05 (dd, *J* = 12.4, 4.8, 1H), 3.89-3.82 (m, 2H), 1.79 (s, 3H), 1.787 (s, 3H, $COCH_3$), 1.76 (s, 3H, $COCH_3$), 1.46 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3/CD_3OD$) δ 171.5, 170.6, 170.1, 169.4, 147.6, 129.2, 128.3, 128.0, 125.2, 118.7, 85.4, 74.2, 72.0, 67.8, 61.4, 52.6, 21.4, 19.7, 19.7, 19.6; MS ESI ($C_{22}H_{26}O_8N_4$, 474): 497 ($M+Na^+$, 100); TLC R_f 0.40 (EtOAc/hexanes, 1/1); m.p. 228-229 °C; $[\alpha]_D^{25}$ -62.4 (*c* 1.0, $CHCl_3$).

Phenyl 2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl 1,2,3-triazole (13).[22]

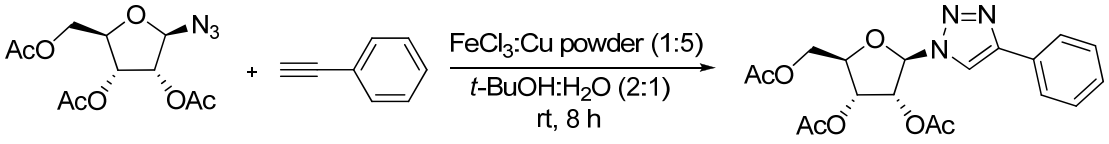


In a 10 mL, round bottomed flask were placed 20 mol% of $FeCl_3$ (8.1 mg, 0.05 mmol, 0.2 equiv) and $Cu_{(s)}$ powder (16 mg, 0.25 mmol, 1.0 equiv) in 1:1 mixture of *t*-BuOH:H_2O (1 mL : 1 mL). The resulting mixture was stirred at ambient temperature for 5 min and a solution of 2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosylazide **7** (165 mg, 0.25 mmol, 1 equiv)

in *t*-BuOH (1 mL) was added followed by addition of ethynylbenzene (41 μL, 38 mg, 0.375 mmol, 1.5 equiv). The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 12 h, the organic volatiles were removed under reduced pressure and the resulting mixture was partitioned between H_2O and CH_2Cl_2 (5 mL each). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered, passed through Celite bed to remove inorganic salts and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (EtOAc/hexanes, 3/2) on silica gel to afford 166 mg (87%) of phenyl 2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyran-osyl)-β-D-glucopyranosyl 1,2,3-triazole **13** as a off white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.81 (d, *J* = 7.6, 2H), 7.42 (t, *J* = 7.4, 2H), 7.34 (d, *J* = 7.4, 1H), 5.94 (d, *J* = 9.2, 1H), 5.51-5.36 (m, 4H), 5.07 (t, *J* = 9.8, 1H), 4.88 (dd, *J* = 10.8, 4, 1H), 4.49 (dd, *J* = 12.4, 2.0, 1H), 4.29-4.23 (m, 2H), 4.17 (t, *J* = 8.8, 1H), 4.08 (dd, *J* = 12.6, 1.8, 1H), 4.02-3.99 (m, 2H), 2.12 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 1.85 (s, 3H, $COCH_3$); 1.72 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.5, 170.3, 169.9, 169.4, 169.3, 148.4, 129.9, 128.9, 128.6, 125.9, 95.9, 85.3, 75.4, 75.2, 72.5,

70.8, 70.0, 69.2, 68.8, 67.9, 62.5, 61.5, 20.8, 20.7, 20.6, 20.6, 20.2; MS ESI ($C_{34}H_{41}O_{17}N_3$, 763): 786 ($M+Na^+$, 100); TLC R_f 0.21 (EtOAc/hexanes, 1/1); m.p. 170-171 °C; $[\alpha]_D^{25}$ -38.5 (*c* 1.0, $CHCl_3$).

Phenyl 2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl 1,2,3-triazole (14).[22]

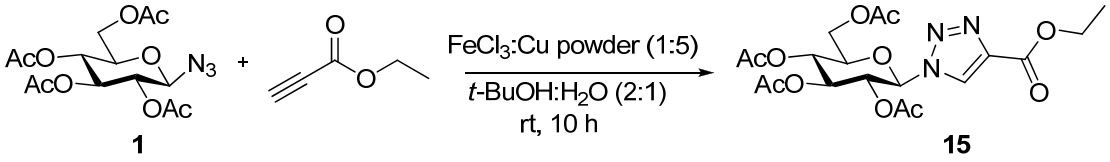


4 **14**

In a 10 mL, round bottomed flask were placed 20 mol% of $FeCl_3$ (8.1 mg, 0.05 mmol, 0.2 equiv) and $Cu_{(s)}$ powder (16 mg, 0.25 mmol, 1.0 equiv) in 1:1 mixture of *t*-BuOH:H_2O (1 mL : 1 mL). The resulting mixture was stirred at ambient temperature for 5 min and a solution of 2,3,5-tri-*O*-acetyl-β-D-ribofurunosyl azide **4** (75 mg, 0.25 mmol, 1 equiv) in *t*-BuOH (1 mL) was added followed by addition of ethynylbenzene (41 μL, 38 mg, 0.375 mmol, 1.5 equiv). The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 8 h, the organic volatiles were removed under reduced pressure and the resulting mixture was partitioned between H_2O and CH_2Cl_2 (5 mL each). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered, passed through Celite bed to remove

inorganic salts and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (EtOAc/hexanes, 1/1) on silica gel to afford 97 mg (96%) of phenyl 2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl 1,2,3-triazole **14** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.80 (d, *J* = 7.2, 2H), 7.40 (t, *J* = 7.6, 2H), 7.32 (d, *J* = 7.2, 1H), 6.18 (d, *J* = 3.6, 1H), 5.9 (dd, *J* = 4.8, 4.0, 1H), 5.63 (t, *J* = 5.4, 1H), 4.48 (dd, 8.2, 4.2, 1H), 4.40 (dd, *J* = 12.4, 2.8, 1H), 4.23 (dd, *J* = 12.4, 4, 1H), 2.10 (s, 6H, 2 × $COCH_3$), 2.02 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.3, 169.2, 148.0, 129.9, 128.8, 125.7, 118.8, 89.9, 80.0, 74.1, 70.6, 62.7, 20.5, 20.3, 20.2; MS ESI ($C_{19}H_{21}O_7N_3$, 403): 426 ($M+Na^+$, 100); TLC R_f 0.43 (EtOAc/hexanes, 1/1); $[\alpha]_D^{25}$ +87.2 (*c* 1.0, $CHCl_3$).

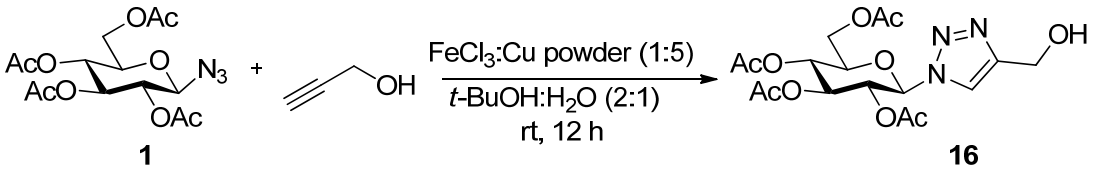
2,3,4,6-tetra-*O*-acetyl-(4'-ethylcarboxylate)-β-*D*-glucopyranosyl 1,2,3-triazole (15).[22]



In a 10 mL, round bottomed flask, 20 mol% of $FeCl_3$ (8.1 mg, 0.05 mmol, 0.2 equiv) and $Cu_{(s)}$ powder (16 mg, 0.25 mmol, 1.0 equiv) were placed in 1:1 mixture of *t*-BuOH:H_2O (1 mL : 1 mL). The resulting mixture was stirred at ambient temperature for 5 min and a solution of 2,3,4,6-tetra-*O*-acetyl-6-deoxy-β-D-gluco-pyranosyl azide **1** (93 mg, 0.25 mmol, 1 equiv) in *t*-BuOH (1 mL) was added followed by addition of

ethyl propiolate (38 μL, 37 mg, 0.375 mmol, 1.5 equiv). The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 10 h, the organic volatiles were removed under reduced pressure and the resulting mixture was partitioned between H_2O and CH_2Cl_2 (5 mL each). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered, passed through Celite bed to remove inorganic salts and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (EtOAc/hexanes, 1/1) on silica gel to afford 112 mg (95%) of 2,3,4,6-tetra-*O*-acetyl-(4'-ethyl carboxylate)-β-D-glucopyranosyl 1,2,3-triazole **15** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 5.92 (d, J = 8.8, 1H), 5.46-5.37 (m, 2H), 5.24 (t, J = 9.6, 1H), 4.42 (q, J = 7.1, 2H), 4.31 (dd, J = 12.6, 5.0, 1H), 4.15 (dd, J = 12.8, 1.4, 1H), 4.03-4.0 (m, 1H), 2.08 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 1.89 (s, 3H, $COCH_3$), 1.41 (t, J = 7, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.8, 169.3, 168.8, 160.1, 140.9, 126.0, 85.8, 75.3, 72.3, 70.4, 67.5, 61.5, 61.4, 20.6, 20.4, 20.0, 14.2; MS ESI ($C_{19}H_{25}O_{11}N_3$, 494): 517 ($M+Na^+$, 100); TLC R_f 0.39 (EtOAc/hexanes, 1/1); m.p. 170-171 °C (lit.[22d] m.p. 172-174 °C); $[\alpha]_D^{25}$ -46.3 (*c* 1.0, $CHCl_3$) (lit.[22d] $[\alpha]_D^{25}$ -62 (*c* 0.2, $CHCl_3$)).

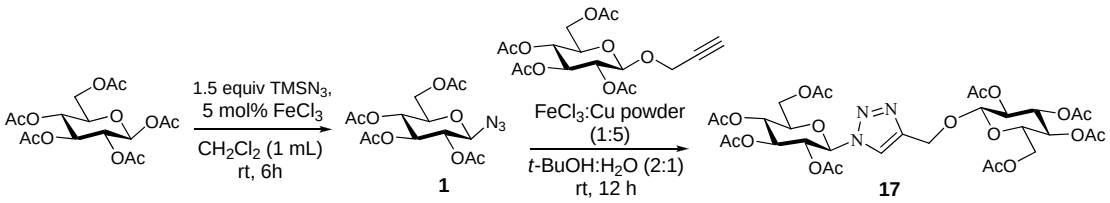
2,3,4,6-tetra-*O*-acetyl-(4'-hydroxymethyl)-6-deoxy-β-D-glucopyranosyl 1,2,3-triazole (16).[22]



In a 10 mL, round bottomed flask were placed 20 mol% of $FeCl_3$ (8.1 mg, 0.05 mmol, 0.2 equiv) and $Cu_{(s)}$ powder (16 mg, 0.25 mmol, 1.0 equiv) in 1:1 mixture of *t*-BuOH:H_2O (1 mL : 1 mL). The resulting mixture was stirred at ambient temperature for 5 min and a solution of 2,3,4,6-tetra-*O*-acetyl-6-deoxy-β-D-gluco-pyranosyl azide **1** (93 mg, 0.25 mmol, 1 equiv) in *t*-BuOH (1 mL) was added followed by addition of prop-2-yn-1-ol (22 μL, 21 mg, 0.375 mmol, 1.5 equiv). The resulting reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 12 h, the organic volatiles were removed under reduced pressure and the resulting mixture was partitioned between H_2O and CH_2Cl_2 (5 mL each). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered, passed through Celite bed to remove inorganic salts and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (EtOAc/hexanes, 1/1) on silica

gel to afford 100 mg (93%) of 2,3,4,6-tetra-*O*-acetyl-(4'-hydroxymethyl) -6-deoxy-β-D-glucopyranosyl 1,2,3-triazole **16** as a off white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 5.89 (d, *J* = 8.4, 1H), 5.46-5.37 (m, 2H), 5.23 (t, *J* = 9.4, 1H), 4.74 (brs, 2H), 4.25 (dd, *J* = 12.6, 5, 1H), 4.10 (d, *J* = 12.4, 1H), 4.01-3.99 (m, 1H), 3.42 (brs, 1H), 2.021 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.82 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.9, 169.4, 169.0, 148.5, 120.2, 85.6, 75.0, 72.6, 70.3, 67.7, 61.5, 56.3, 20.6, 20.5, 20.4, 20.1; MS ESI ($C_{17}H_{23}O_{10}N_3$, 429): 452 ($M+Na^+$, 100); TLC R_f 0.40 (EtOAc/hexanes, 1/1); m.p. 149-151 °C (lit.[22d] m.p. 152-154 °C); $[\alpha]_D^{25}$ -9.1 (*c* 1.0, $CHCl_3$) (lit.[22c] $[\alpha]_D^{20}$ -6 (*c* 1.0, $CHCl_3$)).

(C) Procedure for one pot synthesis of 2,3,4,6-tetra-*O*-acetyl-4'-*O*-(2,3,4,6-tetra -*O*- acetyl-6-deoxy-glucopyranose)-6-deoxy-β-D-glucopyranosyl triazole (17).[22]



To a 10 mL, round bottomed flask was placed 5 mol% of $FeCl_3$ (2 mg, 0.0125 mmol, 0.05 equiv) in anhydrous CH_2Cl_2 (0.5 mL) under nitrogen atmosphere. A solution of (2*S*,3*S*,4*S*,5*R*)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-2,3,4,5-tetrayl tetraacetate (98 mg, 0.25 mmol, 1 equiv) in CH_2Cl_2 (0.25 mL) was added. After having been stirred for 5 min, a solution of $TMSN_3$ (50 μL, 44 mg, 0.38 mmol, 1.5 equiv) in CH_2Cl_2 (0.25 mL) was added slowly. The resulting reaction mixture was stirred at ambient

temperature and the progress of the reaction was monitored by TLC. After complete consumption of starting material in 6 h as judged by TLC, the reaction mixture was concentrated under reduced pressure and the resulting residue was dried in *vacuo*. The residue was then suspended in a mixture of *t*-BuOH:H_2O (1 mL: 1 mL). After having been stirred for 5 min, a solution of 15 mol% of $FeCl_3$ (6.0 mg, 0.0375 mmol, 0.15 equiv) and (3*R*,4*S*,5*S*,6*R*)-2-(acetoxymethyl)-6-(prop-2-ynyloxy)tetrahydro-2*H*-pyran -3,4,5-triyl triacetate (145 mg, 0.375 mmol, 1.5 equiv) in *t*-BuOH (1 mL) was added followed by addition of $Cu_{(s)}$ powder (16 mg, 0.25 mmol, 1.0 equiv). After having been stirred for 12 h at ambient temperature, the organic volatiles were removed under reduced pressure and the resulting mixture was partitioned between H_2O and CH_2Cl_2 (5 mL each). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and passed through Celite bed to remove inorganic salts. The organic layer was then concentrated under reduced pressure and the resulting crude residue was purified by column chromatography (EtOAc/hexanes, 1/1) on silica gel to afford 171 mg (90%) of **17** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 5.86 (d, *J* = 8.8, 1H), 5.42-5.39 (m, 2H), 5.23 (t, *J* = 9.6, 1H), 5.16 (t, *J* = 9.4, 1H), 5.08 (t, *J* = 9.6, 1H), 4.97 (td, *J* = 8.2, 1.2, 1H), 4.90 (d, *J* = 12.8, 1H), 4.79 (d, *J* = 12.8, 1H), 4.53 (d, *J* = 8.0, 1H), 4.31-4.25 (m, 2H), 4.19-4.10 (m,

1H), 4.02-3.98 (m, 1H), 3.76-3.72 (m, 1H), 2.10 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 2.00 (s, 3H, $COCH_3$), 1.96 (s, 3H, $COCH_3$), 1.94 (s, 3H, $COCH_3$), 1.88 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.4, 170.2, 169.8, 169.4, 169.3, 169.0, 144.2, 121.9, 98.7, 75.2, 72.6, 72.4, 71.7, 71.0, 70.4, 68.3, 67.6, 61.8, 61.7, 61.4, 20.7, 20.6, 20.5, 20.5, 20.0; MS ESI ($C_{30}H_{39}O_{19}N_3$, 745): 768 ($M+Na^+$, 100); TLC R_f 0.33 (EtOAc/hexanes, 1/1); m.p. 198-200 °C (lit.[23] m.p. 199-199.5 °C); $[\alpha]_D^{25}$ -41.6 (*c* 1.0, $CHCl_3$).

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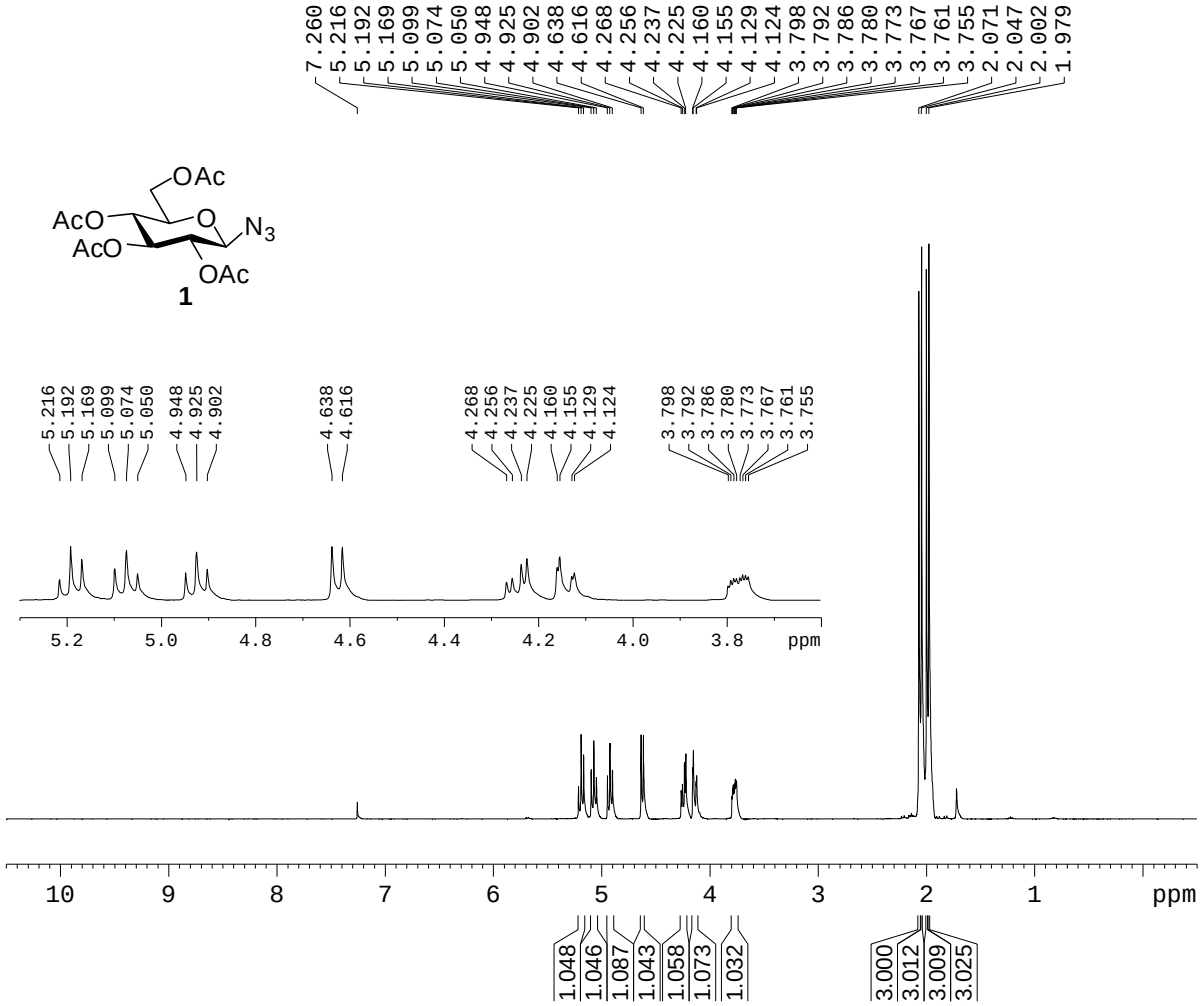


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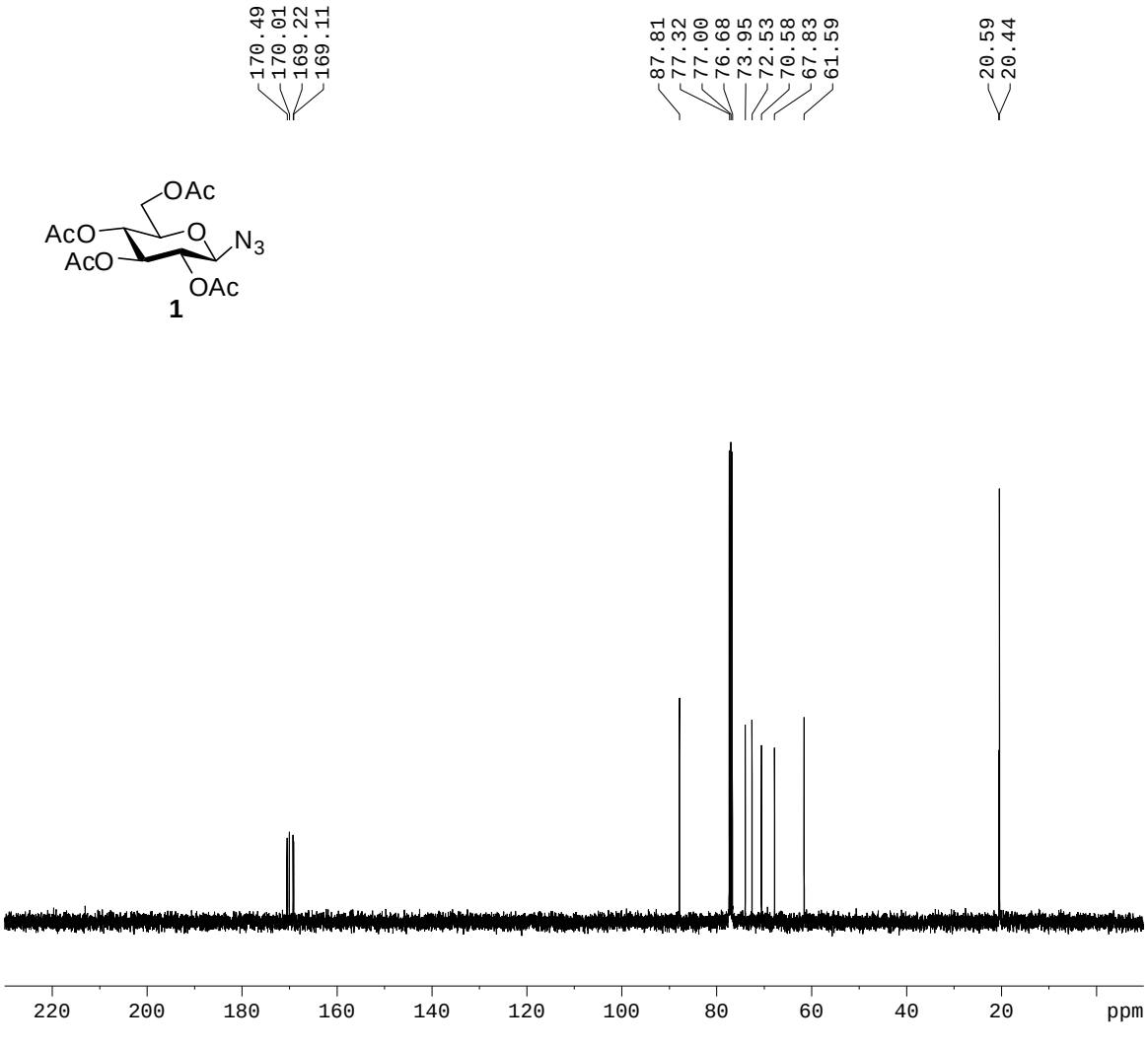


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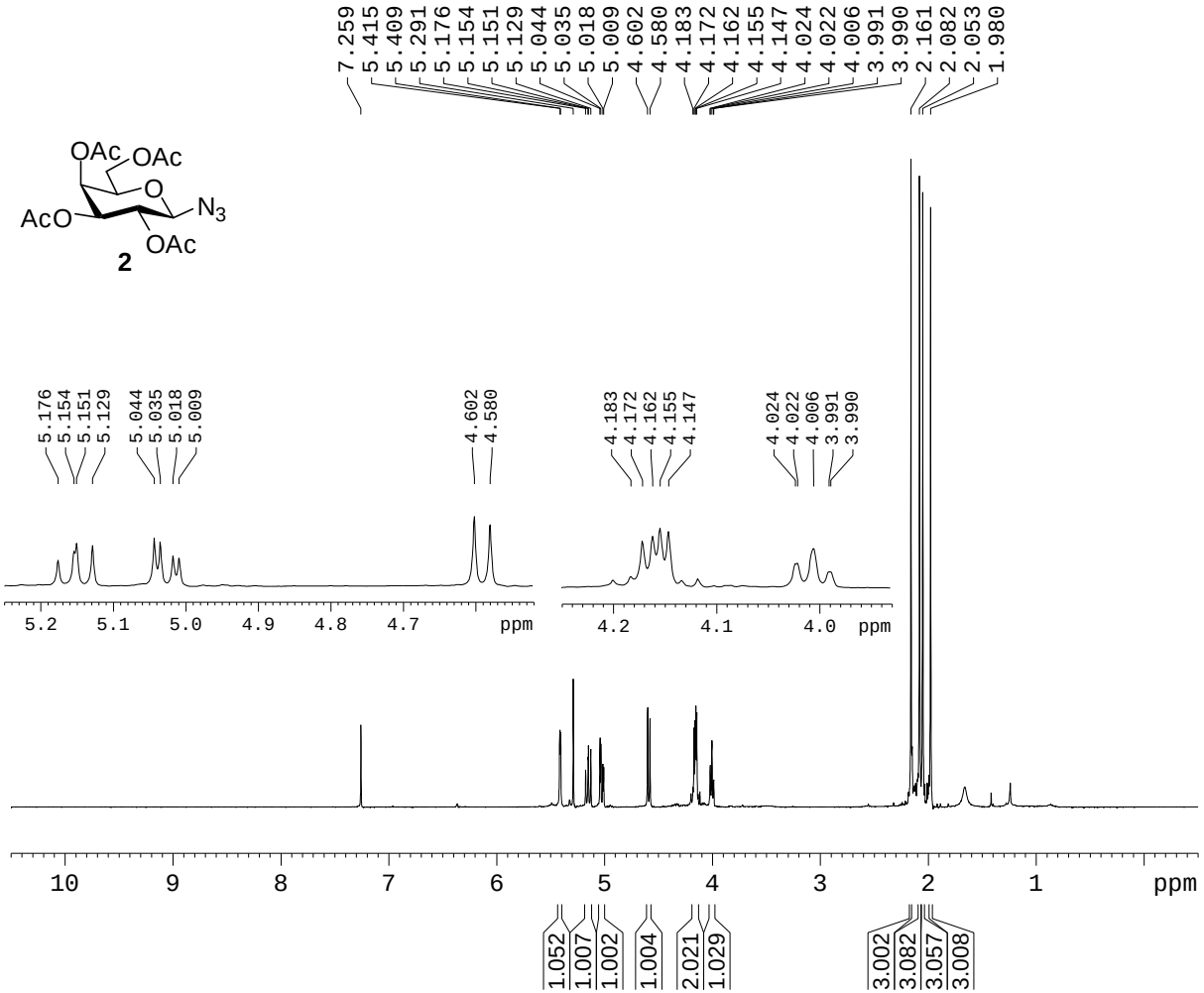


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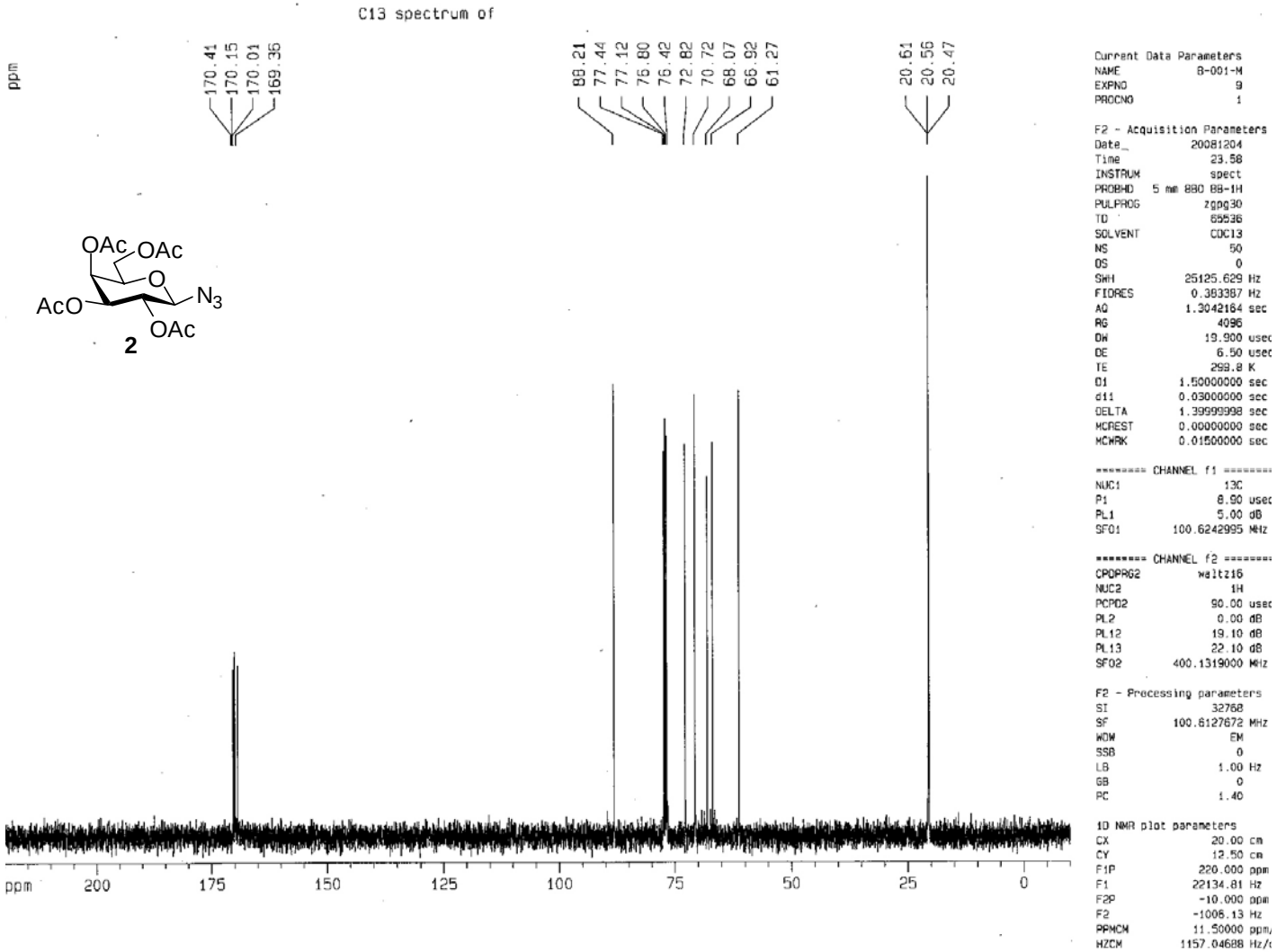

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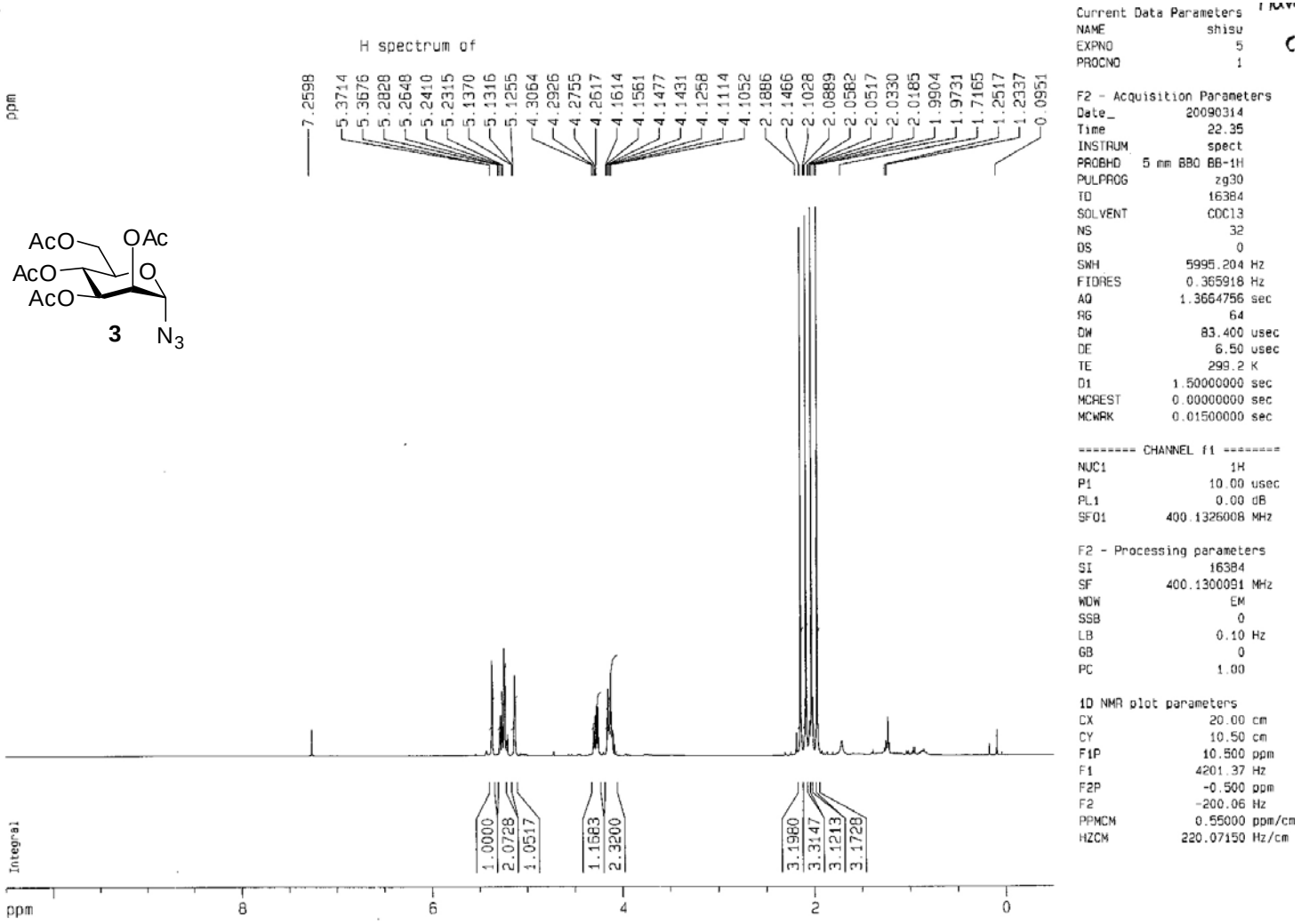


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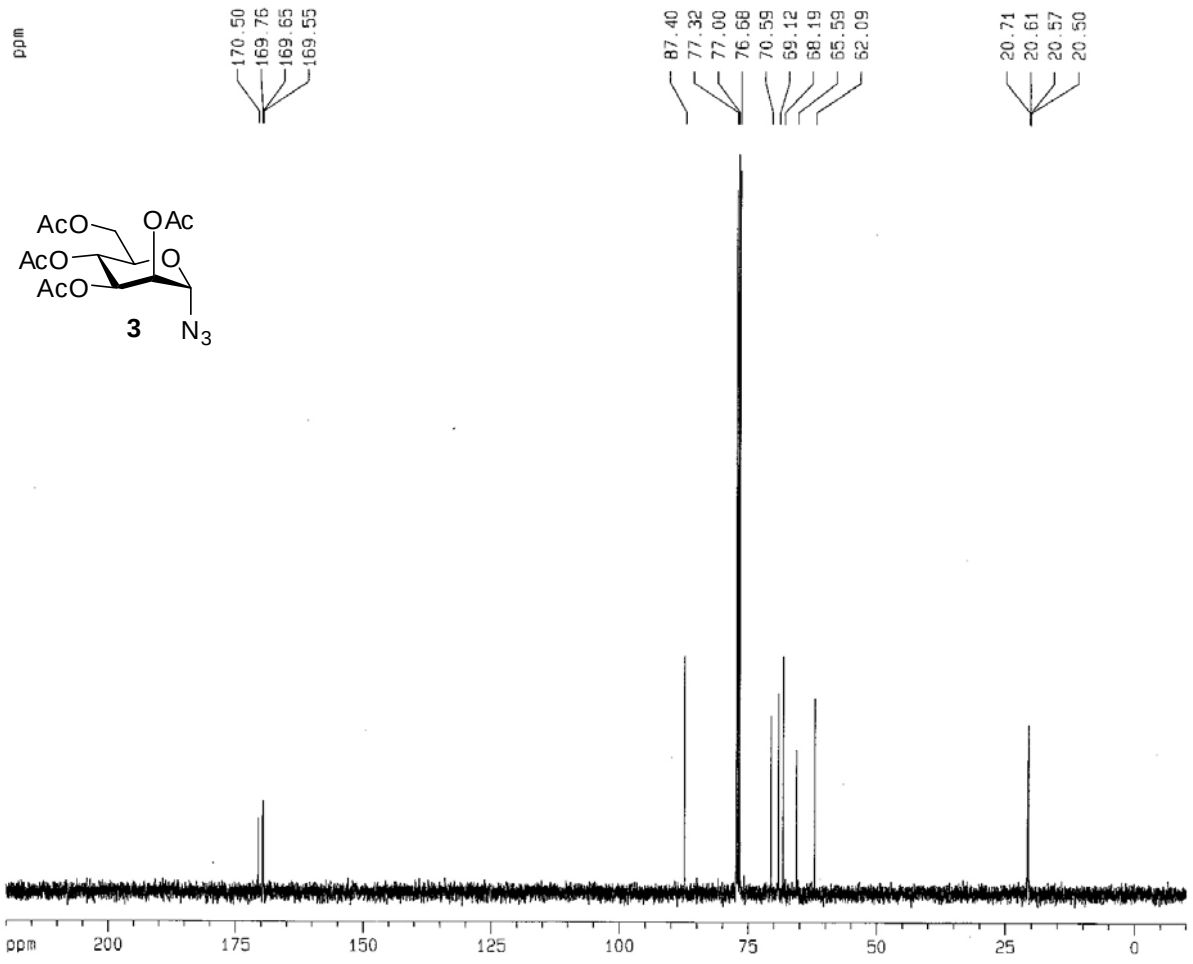
SFO1              400.1326008 MHz

F2 - Processing parameters
SI                        16384
SF                400.1300091 MHz
WDW                          EM
SSB                       0
LB                     0.10 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    20.00 cm
CY                    10.50 cm
F1P                  10.500 ppm
F1                  4201.37 Hz
F2P                  -0.500 ppm
F2                  -200.06 Hz
PPMCM                0.55000 ppm/cm
HZCM               220.07150 Hz/cm
```

C13 spectrum of




```
Current Data Parameters
NAME                  shisu
EXPNO                     6
PROCNO                    1

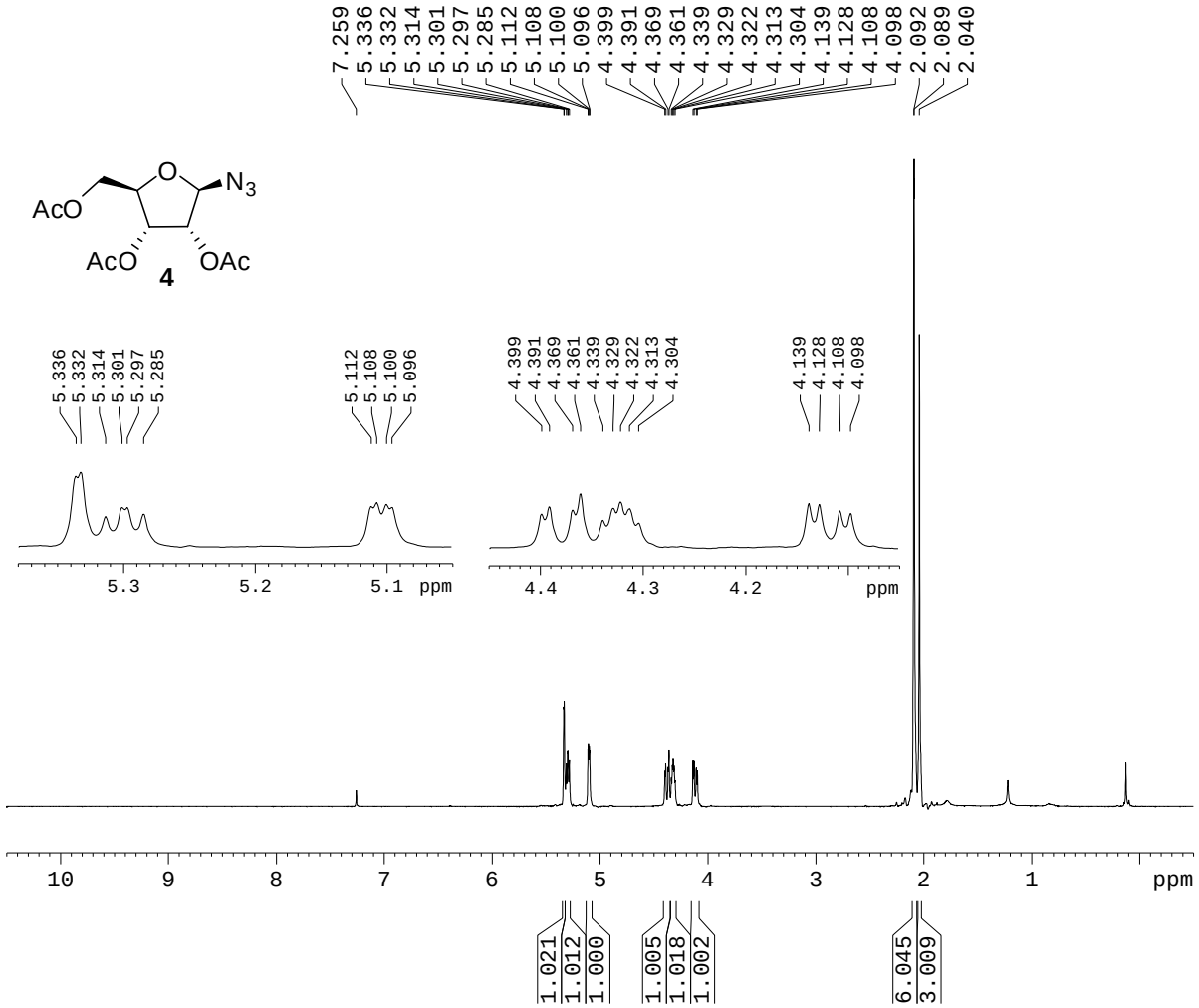
F2 - Acquisition Parameters
Date_              20090314
Time                  22.36
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG               zgpg30
TD                     65536
SOLVENT               CDCl3
NS                      102
DS                        0
SWH               25125.629 Hz
FIDRES             0.383387 Hz
AQ                 1.3042164 sec
RG                     8192
DW                   19.900 usec
DE                    6.50 usec
TE                   299.2 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                     8.90 usec
PL1                    5.00 dB
SFO1             100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 90.00 usec
PL2                    0.00 dB
PL12                  19.10 dB
PL13                  22.10 dB
SFO2             400.1319000 MHz

F2 - Processing parameters
SI                       32768
SF               100.6127736 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
CY                       12.50 cm
F1P                     220.000 ppm
F1                    22134.91 Hz
F2P                     -10.000 ppm
F2                    -1006.13 Hz
PPMCM                 11.50000 ppm/cm
HZCM                  1157.04688 Hz/cm
```



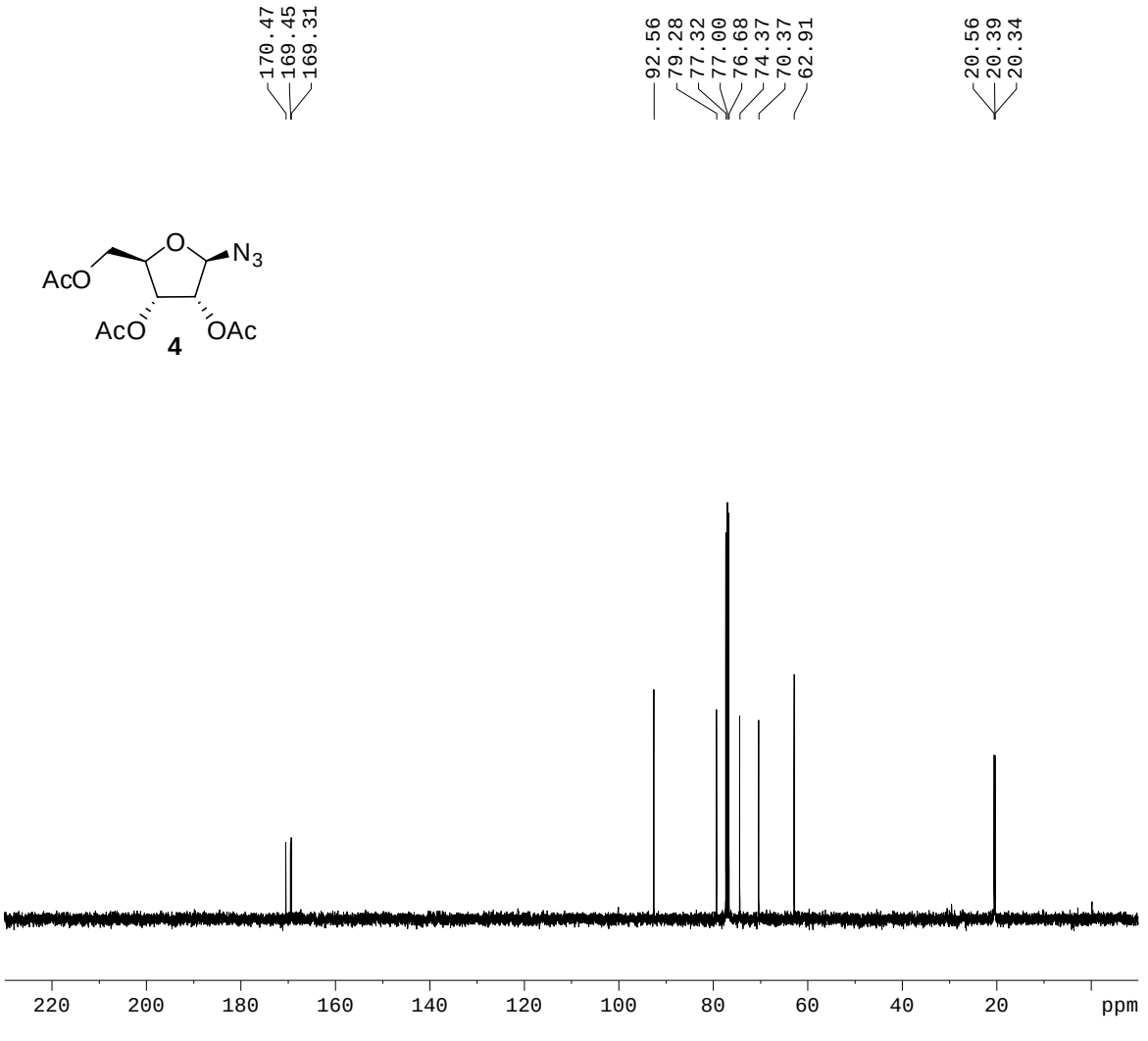

```
Current Data Parameters
NAME       ribose-azide
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20090121
Time              13.56
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                16384
SOLVENT           CDCl3
NS                    1
DS                    0
SWH            5995.204 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                   57
DW                83.400 usec
DE                 6.50 usec
TE                297.8 K
D1           1.50000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                10.00 usec
PL1                0.00 dB
SFO1        400.1326008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300088 MHz
WDW                  EM
SSB                   0
LB                 0.10 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                21.22 cm
F1P               2.133 ppm
F1              853.54 Hz
```



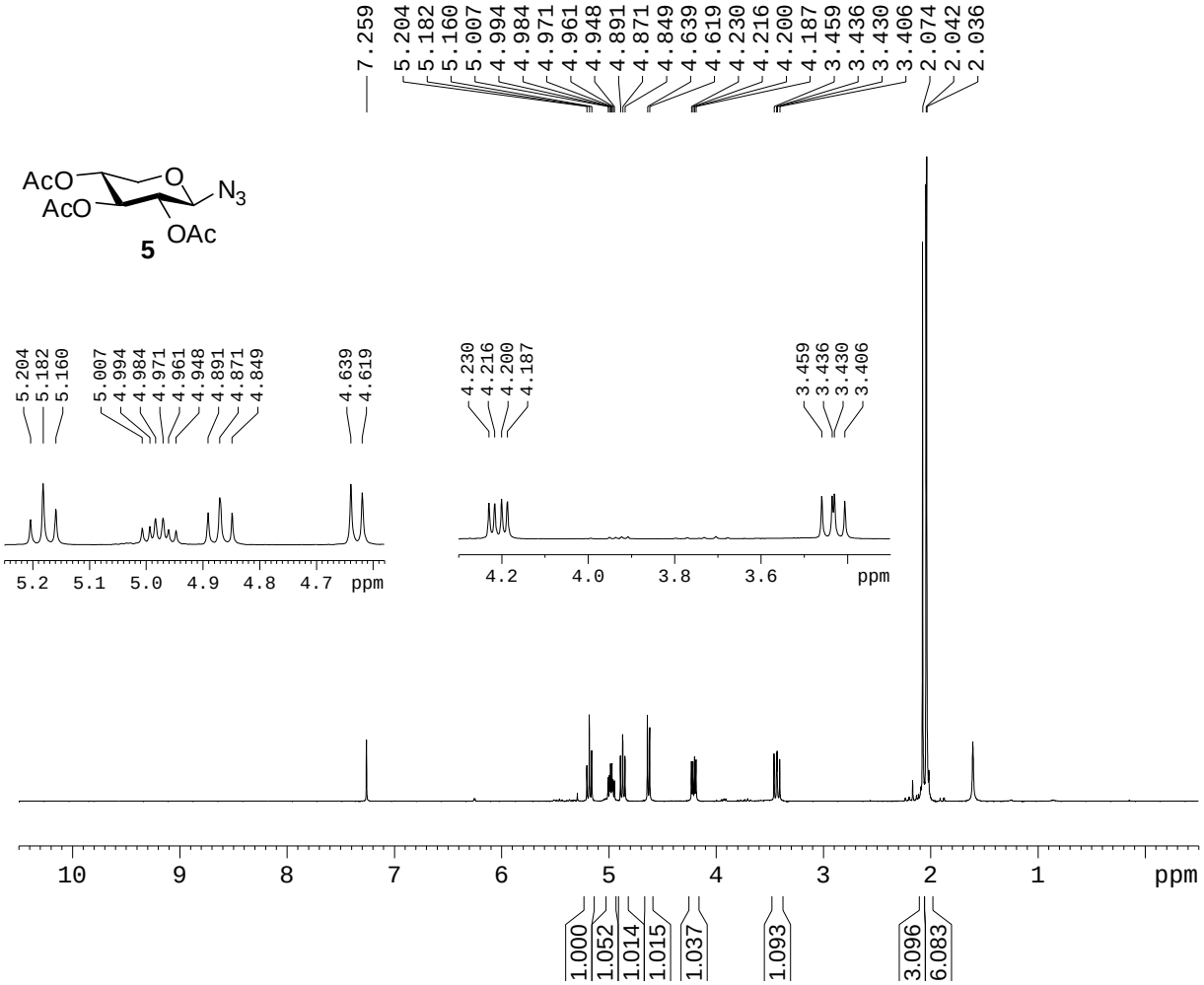

```
Current Data Parameters
NAME       ribose-azide
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20090121
Time              14.00
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   62
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                 4096
DW               19.900 usec
DE                6.50 usec
TE                297.8 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.90 usec
PL1                 5.00 dB
SFO1        100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2        400.1319000 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127535 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



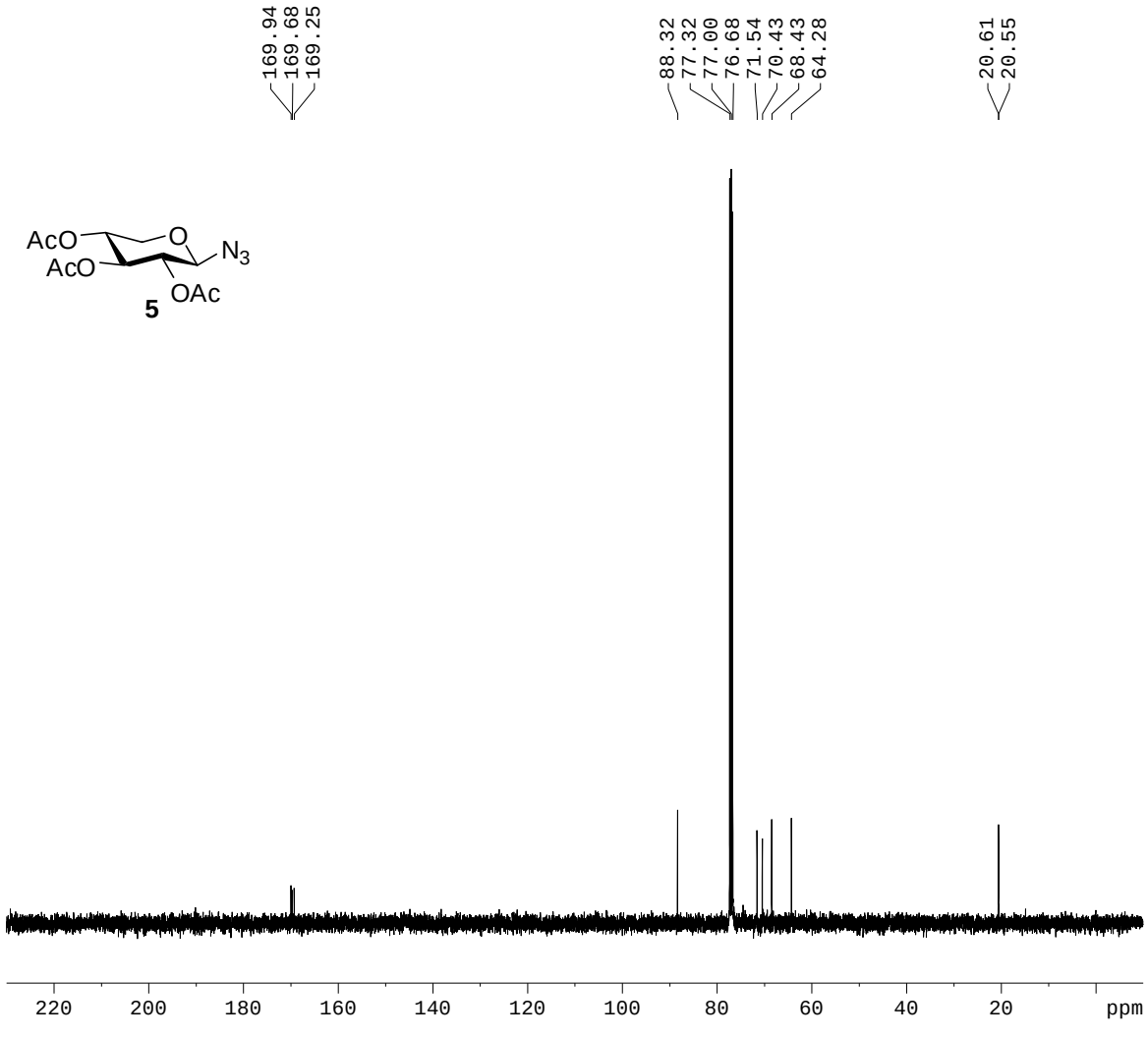

```
Current Data Parameters
NAME       xylose azide
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20081212
Time              20.32
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                16384
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            5995.204 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                203.2
DW               83.400 usec
DE                6.50 usec
TE                298.9 K
D1           1.50000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1                0.00 dB
SFO1        400.1326008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300091 MHz
WDW                  EM
SSB                   0
LB                 0.10 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                10.50 cm
F1P               5.373 ppm
F1              2150.09 Hz
```



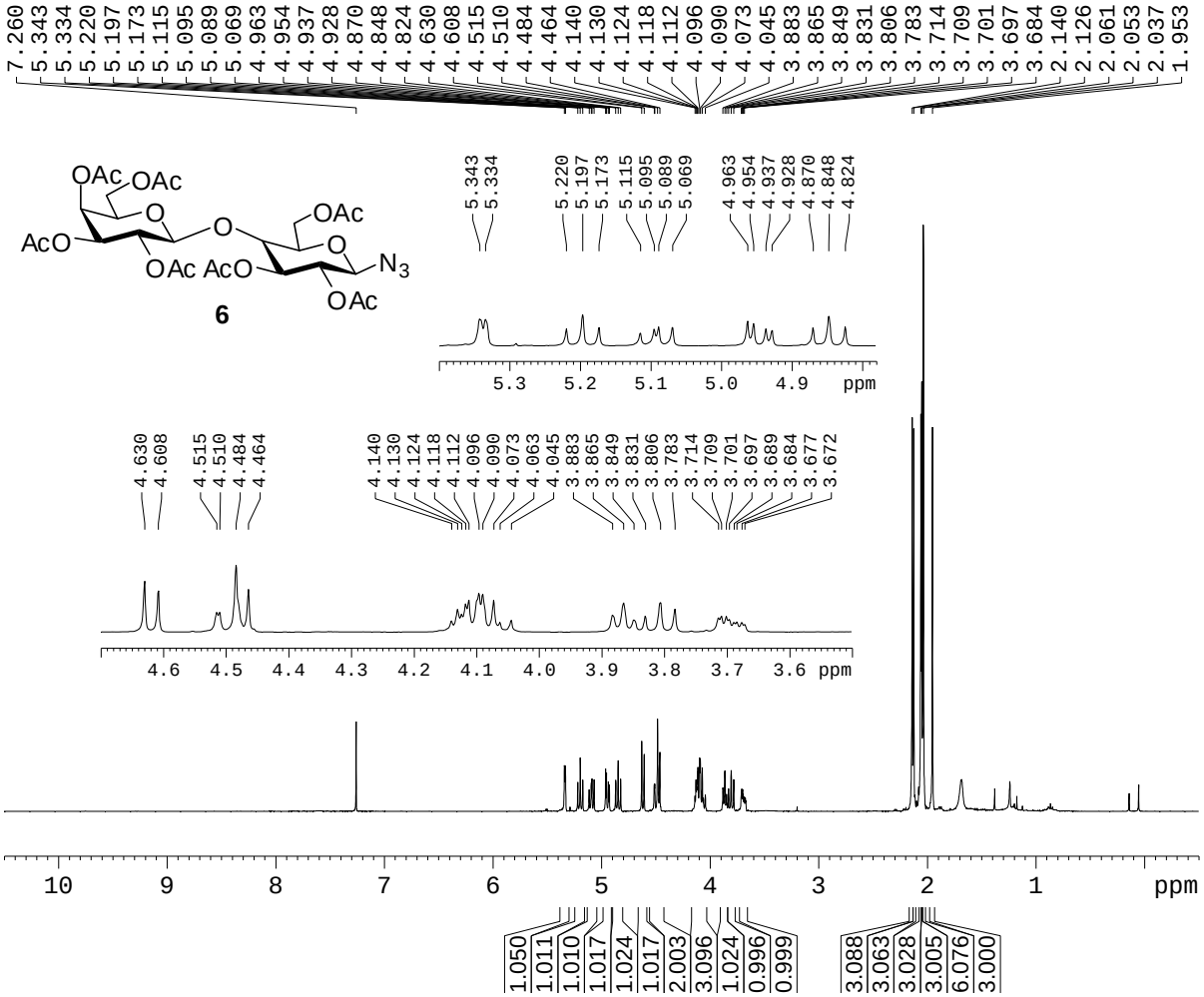

```
Current Data Parameters
NAME     nsp-triazole-clcl
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_          20081227
Time              22.21
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  182
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                 4096
DW               19.900 usec
DE                6.50 usec
TE                302.9 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.90 usec
PL1                 5.00 dB
SFO1        100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2        400.1319000 MHz

F2 - Processing parameters
SI                  32768
SF          100.6127466 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



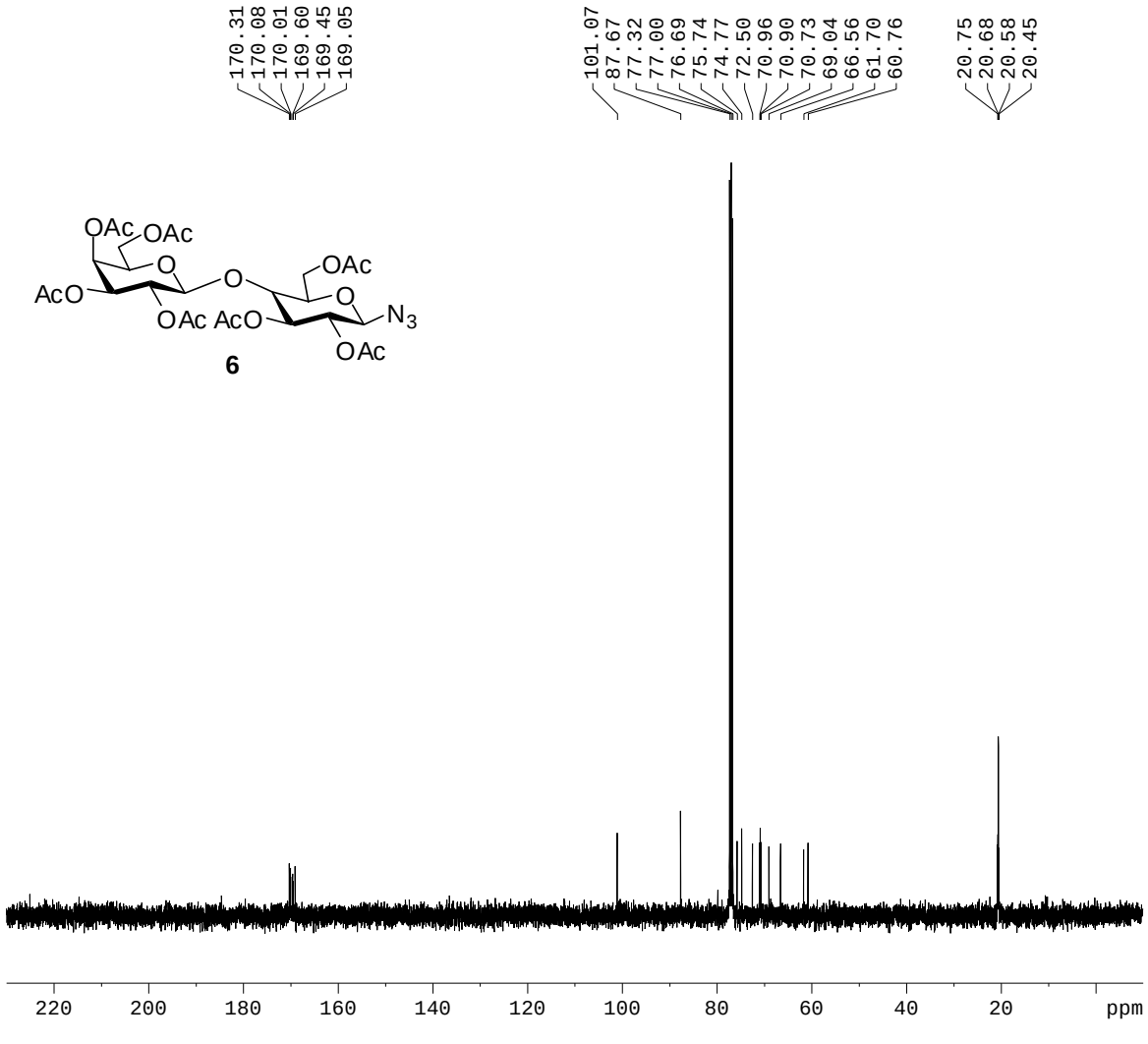

```
Current Data Parameters
NAME      Lact azide-pure
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20100428
Time               15.46
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             5995.204 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                   114
DW                83.400 usec
DE                 8.00 usec
TE                673.2 K
D1            1.50000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.00 usec
PL1                 0.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300091 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 11.96 cm
F1P                2.194 ppm
F1                877.95 Hz
```



6

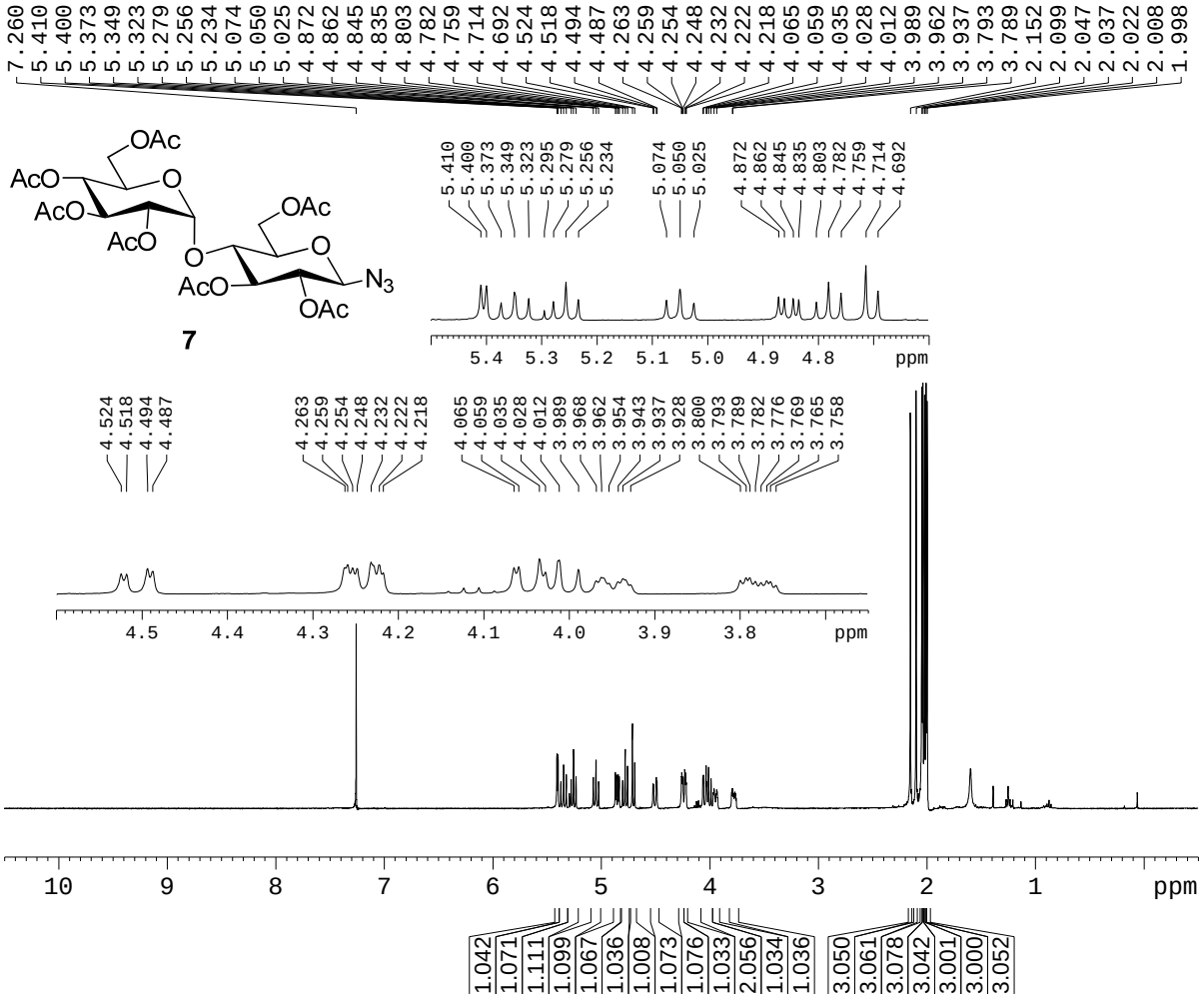
```
Current Data Parameters
NAME      Lact azide-pure
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20100428
Time               15.47
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    97
DS                     0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ             1.3042164 sec
RG                  8192
DW                19.900 usec
DE                 8.00 usec
TE                673.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.90 usec
PL1                 5.00 dB
SFO1         100.6243390 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2         400.1319000 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



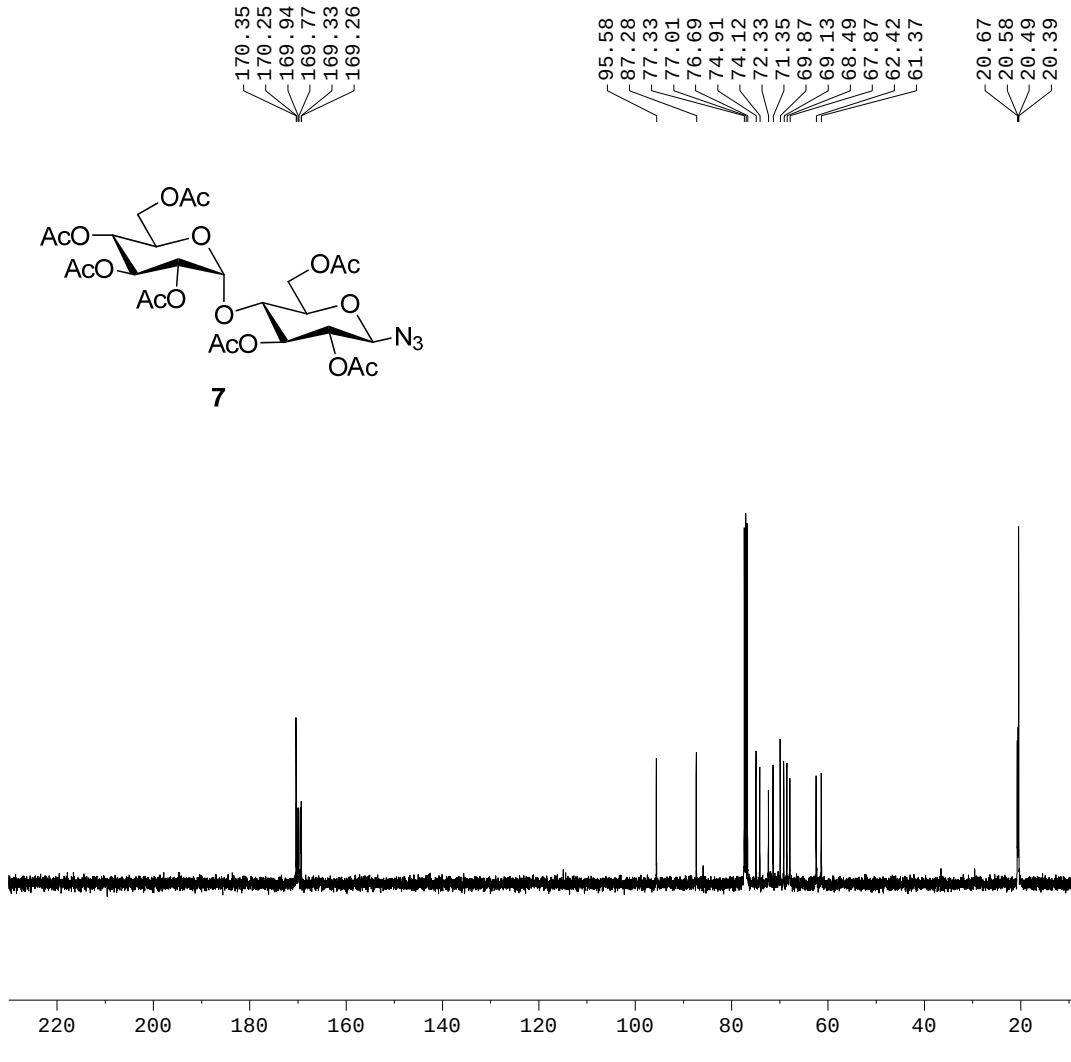

```
Current Data Parameters
NAME      Maltose azide-pure
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20100331
Time               16.24
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             5995.204 Hz
FIDRES          0.365918 Hz
AQ              1.3664756 sec
RG                 322.5
DW                83.400 usec
DE                 6.50 usec
TE                297.8 K
D1             1.50000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  9.70 usec
PL1                 3.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300095 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 10.42 cm
F1P                5.482 ppm
F1               2193.37 Hz
```



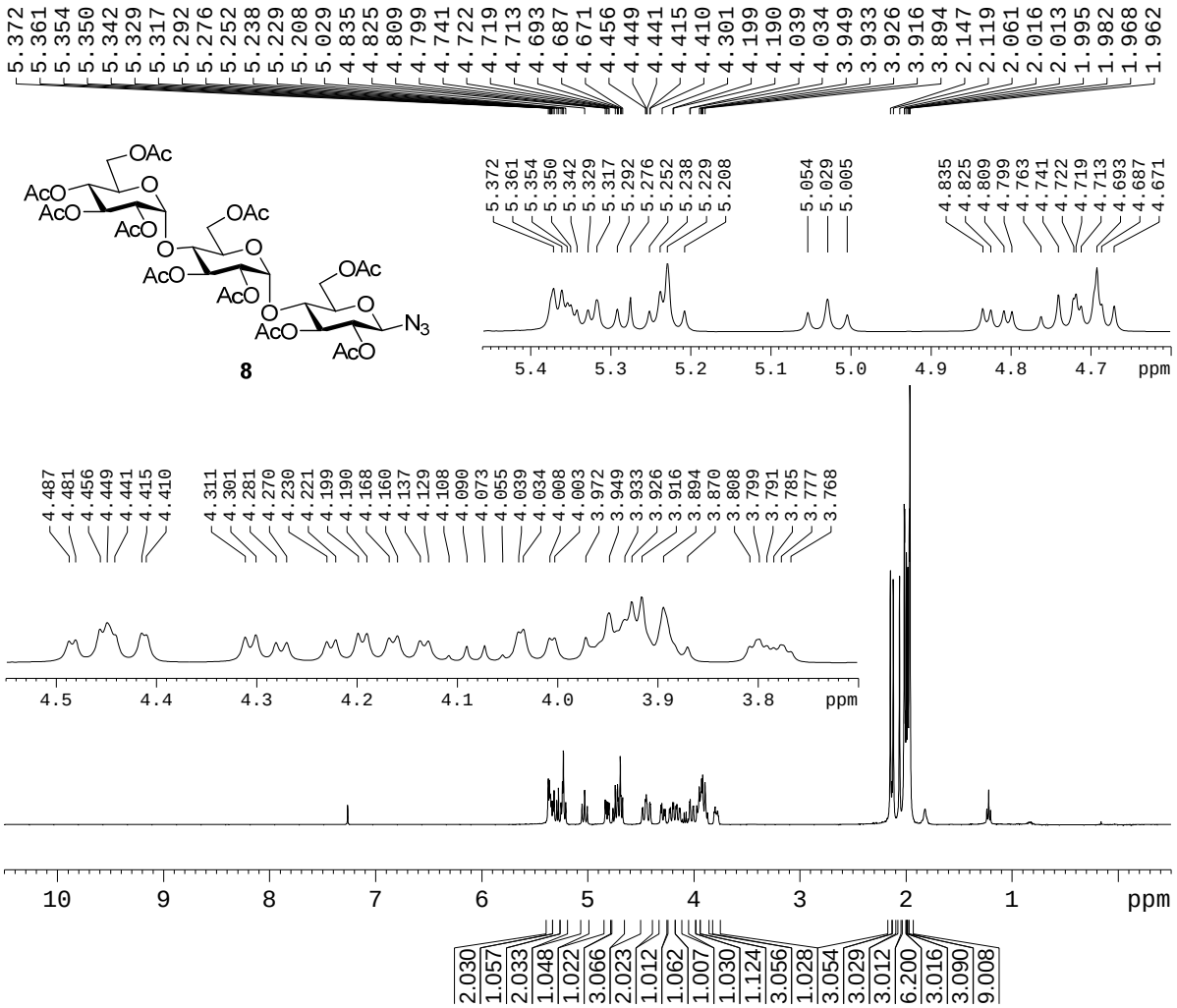

```
Current Data Parameters
NAME                 pure
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20100410
Time               15.39
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   93
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ             1.3042164 sec
RG                  181
DW                19.900 usec
DE                 8.00 usec
TE                673.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.90 usec
PL1                 5.00 dB
SFO1         100.6243390 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                 0.00 dB
PL12                19.10 dB
PL13                22.10 dB
SFO2         400.1319000 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127533 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



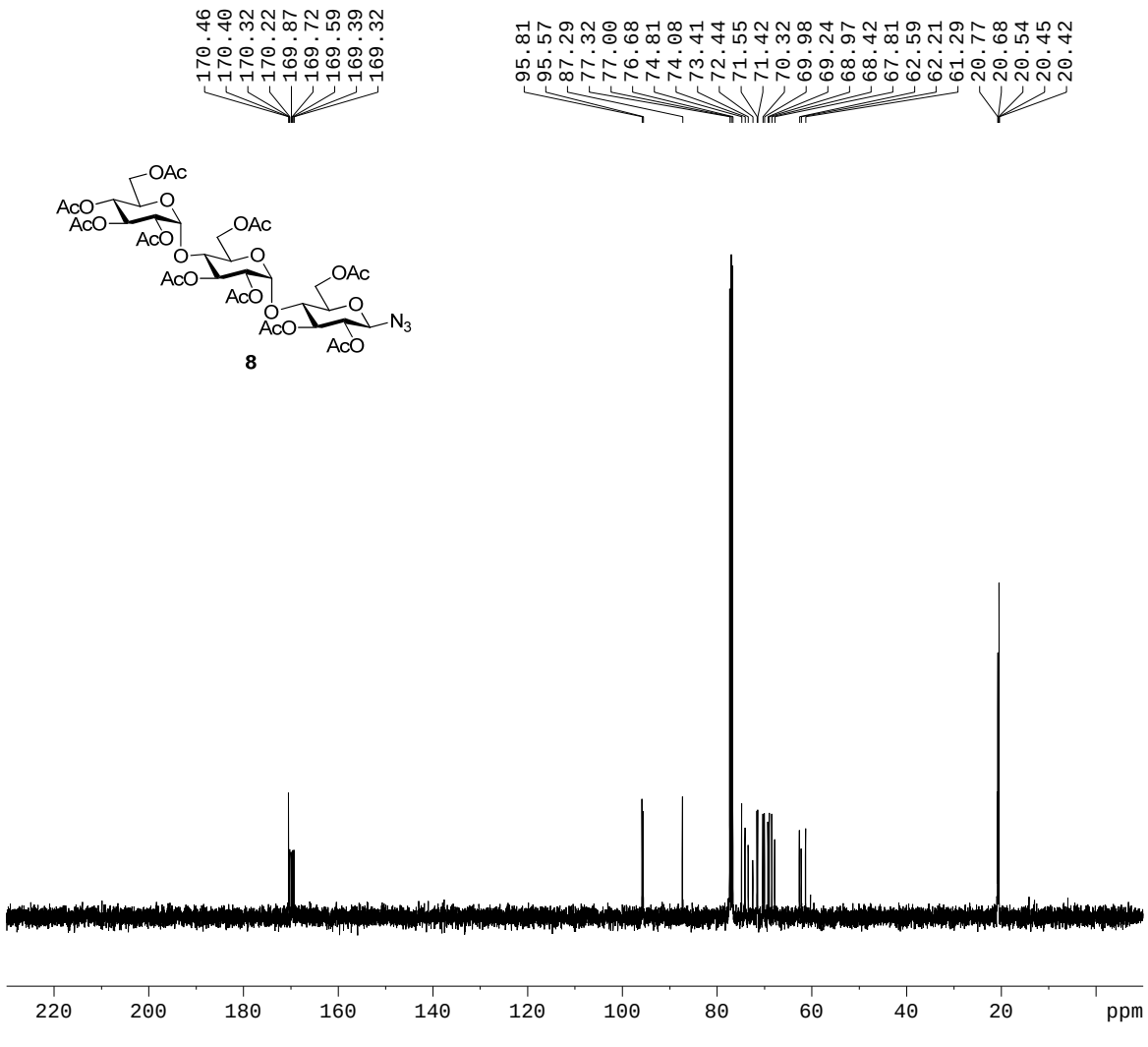

```
Current Data Parameters
NAME      PTHALIC-12PH-INDOL
EXPNO                     6
PROCNO                    1

F2 - Acquisition Parameters
Date_           20090321
Time                21.25
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     32
DS                      0
SWH              5995.204 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   40.3
DW                 83.400 usec
DE                  6.50 usec
TE                 299.9 K
D1              1.50000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.00 usec
PL1                  0.00 dB
SFO1          400.1326008 MHz

F2 - Processing parameters
SI                  16384
SF            400.1300091 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
CY                  10.50 cm
F1P                 2.281 ppm
F1                912.69 Hz
```



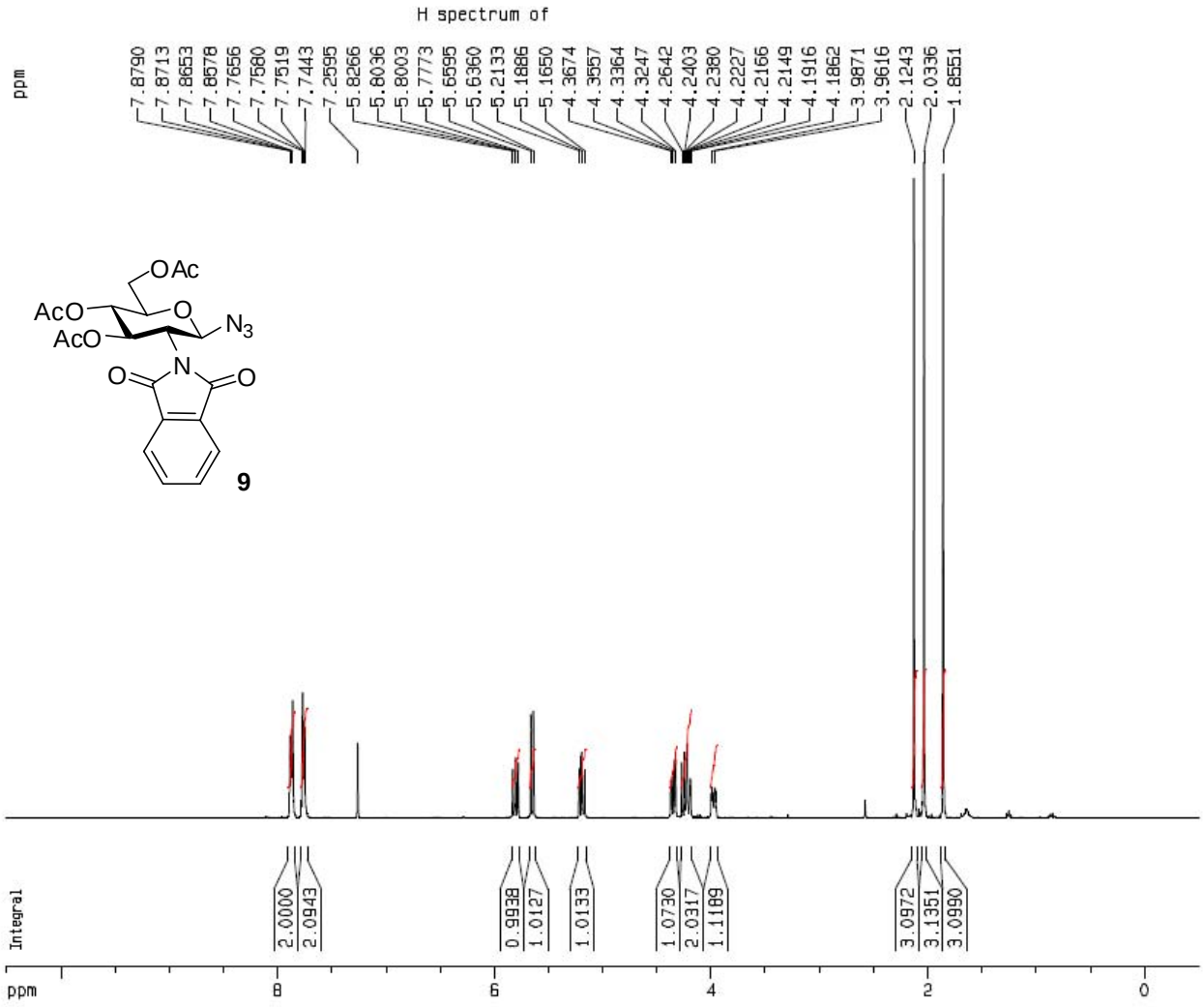

```
Current Data Parameters
NAME      maltose azide
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20090323
Time              19.35
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   75
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                 8192
DW               19.900 usec
DE                6.50 usec
TE                298.5 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.90 usec
PL1                 5.00 dB
SFO1        100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2        400.1319000 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127528 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



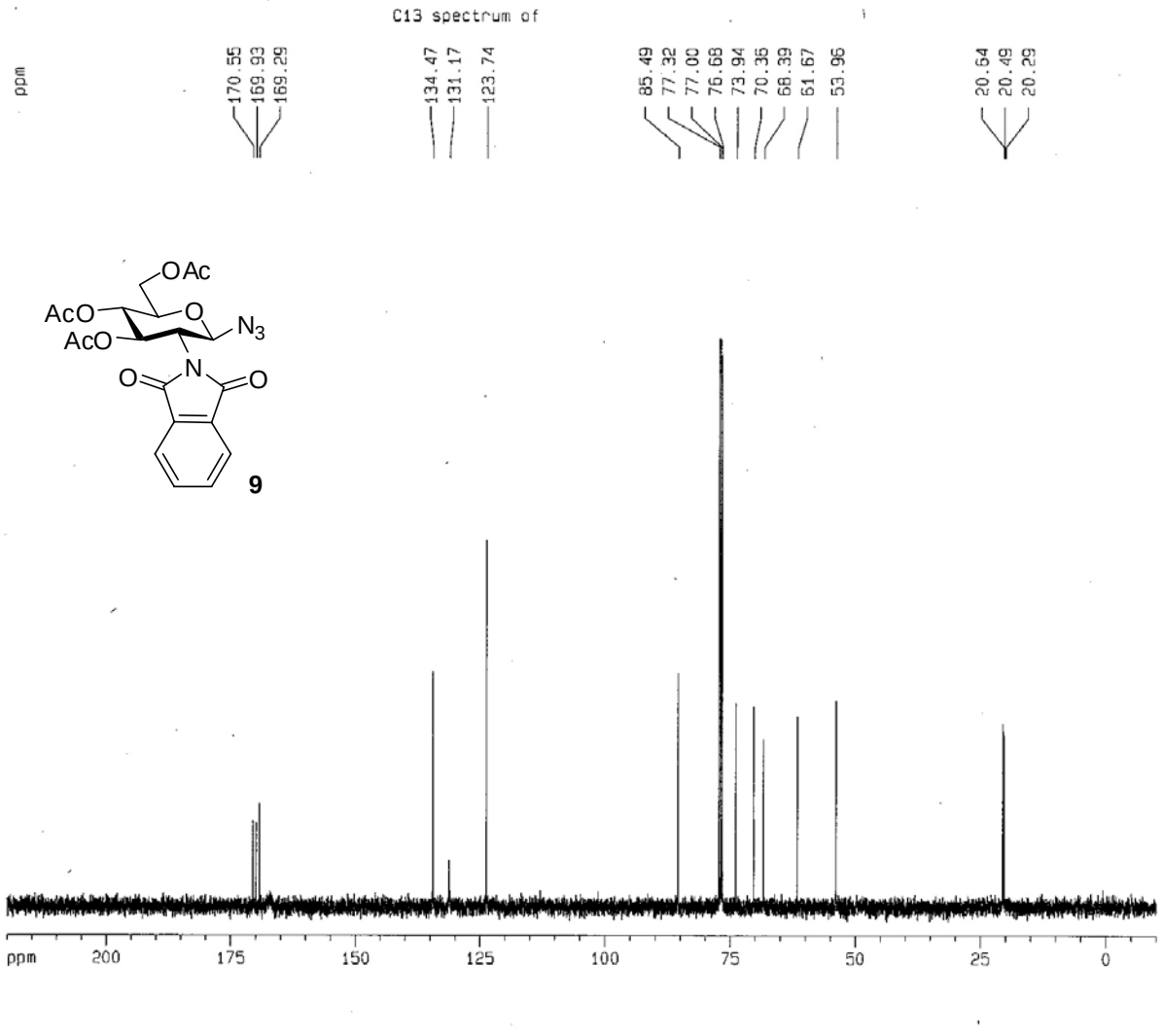

```
Current Data Parameters
NAME        naphta azide
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20081205
Time               20.50
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     0
SWH           5995.204 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 sec
RG                   181
DW                83.400 usec
DE                 6.50 usec
TE                300.8 K
D1           1.50000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

====== CHANNEL f1 =======
NUC1                  1H
P1                10.00 usec
PL1                0.00 dB
SFO1        400.1326008 MHz

F2 - Processing parameters
SI                 16384
SF          400.1300091 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                20.00 cm
CY                11.09 cm
F1P              10.500 ppm
F1              4201.37 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM            0.55000 ppm/cm
HZCM           220.07150 Hz/cm
```



Current Data Parameters
NAME naphtaazide
EXPNO 2
PROCNO 1

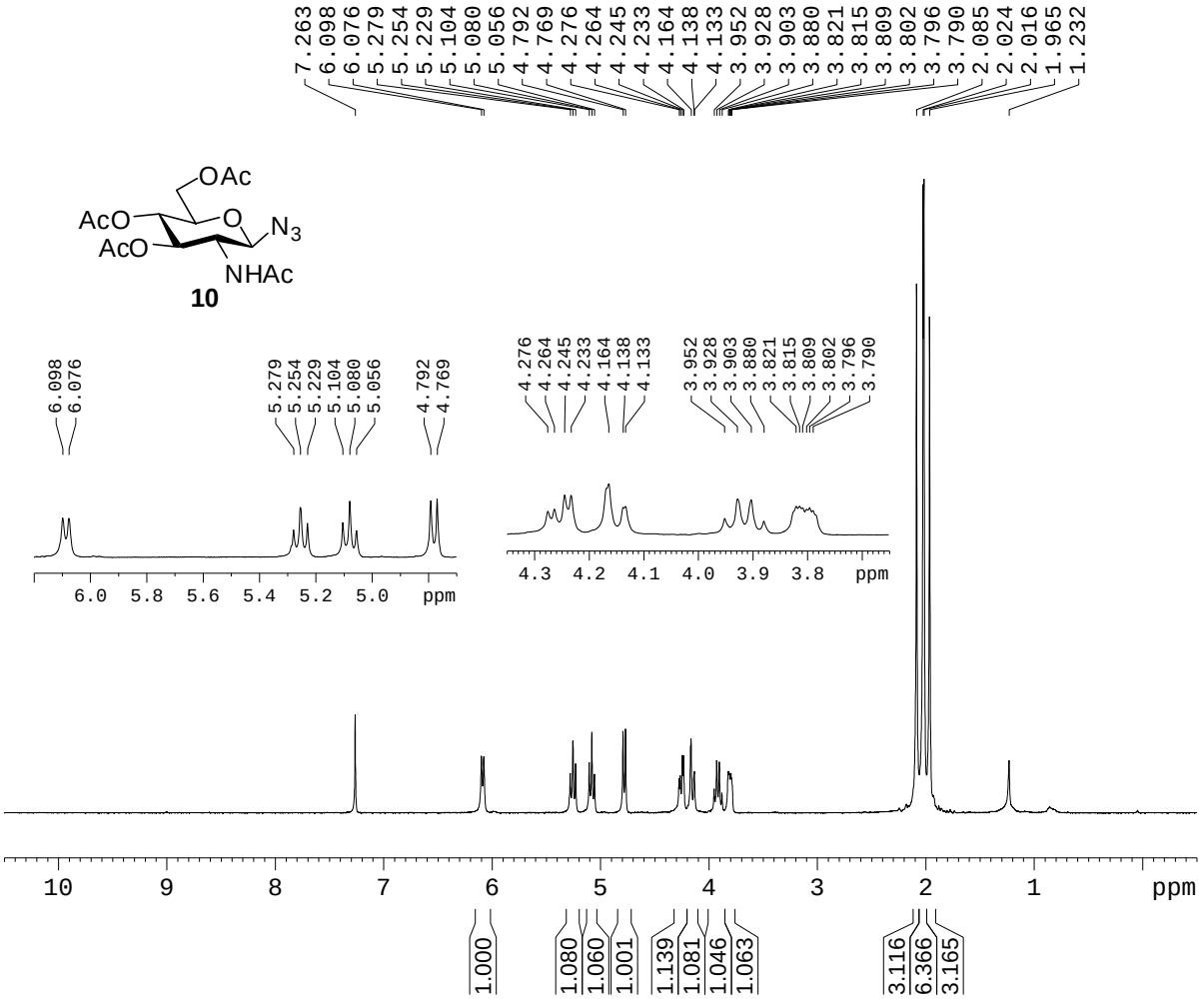
F2 - Acquisition Parameters
Date_ 20081207
Time 17.15
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 59
DS 0
SWH 25125.629 Hz
FIDRES 0.383397 Hz
AQ 1.3042164 sec
RG 8192
DW 19.900 usec
DE 6.50 usec
TE 299.4 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 8.90 usec
PL1 5.00 dB
SFO1 100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.10 dB
PL13 22.10 dB
SFO2 400.1319000 MHz

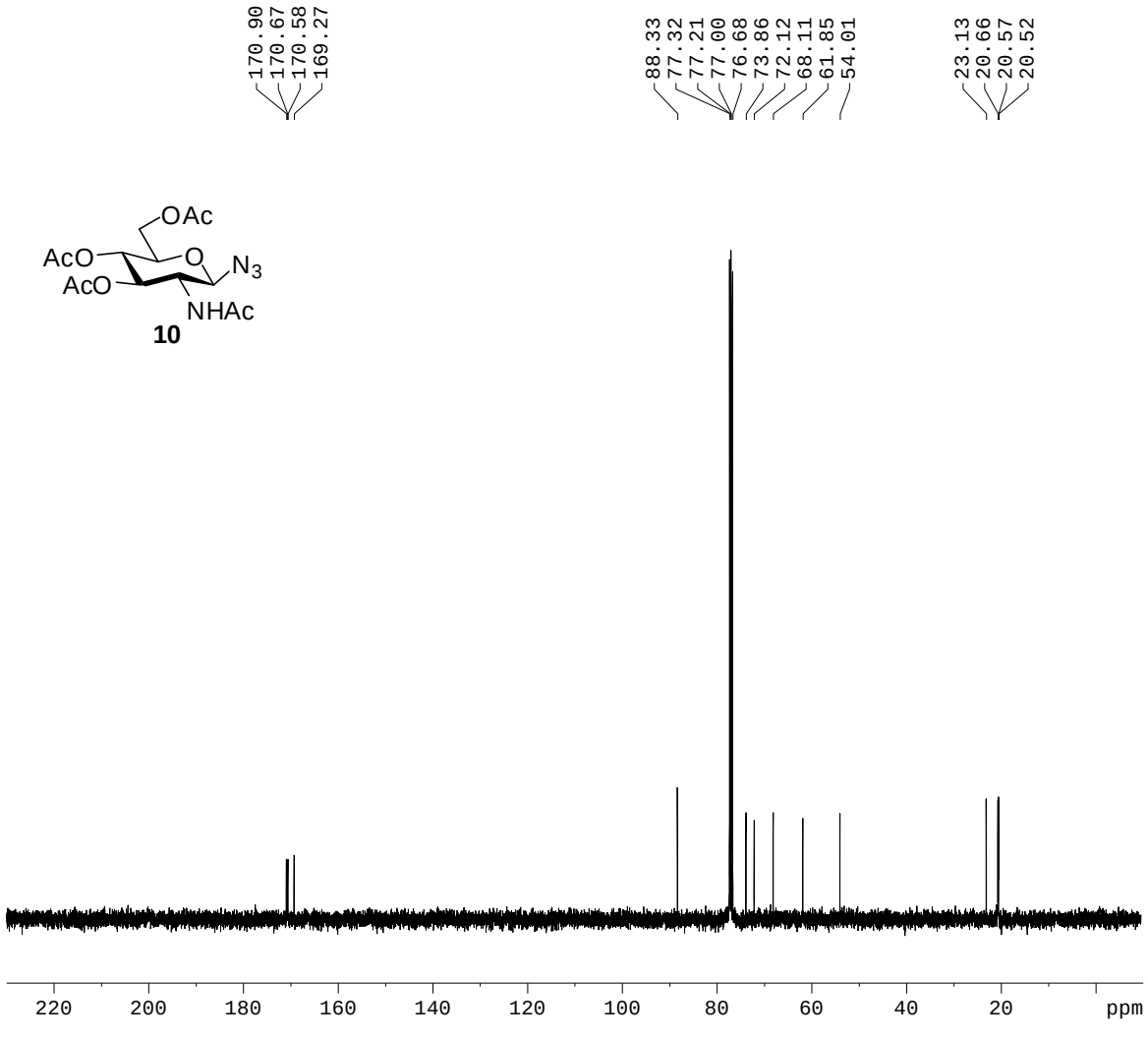
F2 - Processing parameters
SI 32768
SF 100.6127759 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 10.04 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 11.50000 ppm/cm
HZCM 1157.04688 Hz/cm




```
NAME      NH AC azide C13
EXPNO                   1
PROCNO                  1
Date_            20091218
Time                21.49
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                      1
DS                      0
SWH              5995.204 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   90.5
DW                 83.400 usec
DE                   6.50 usec
TE                  297.2 K
D1             1.50000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.00 usec
PL1                  0.00 dB
SFO1          400.1326008 MHz
SI                  16384
SF            400.1300074 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00
```



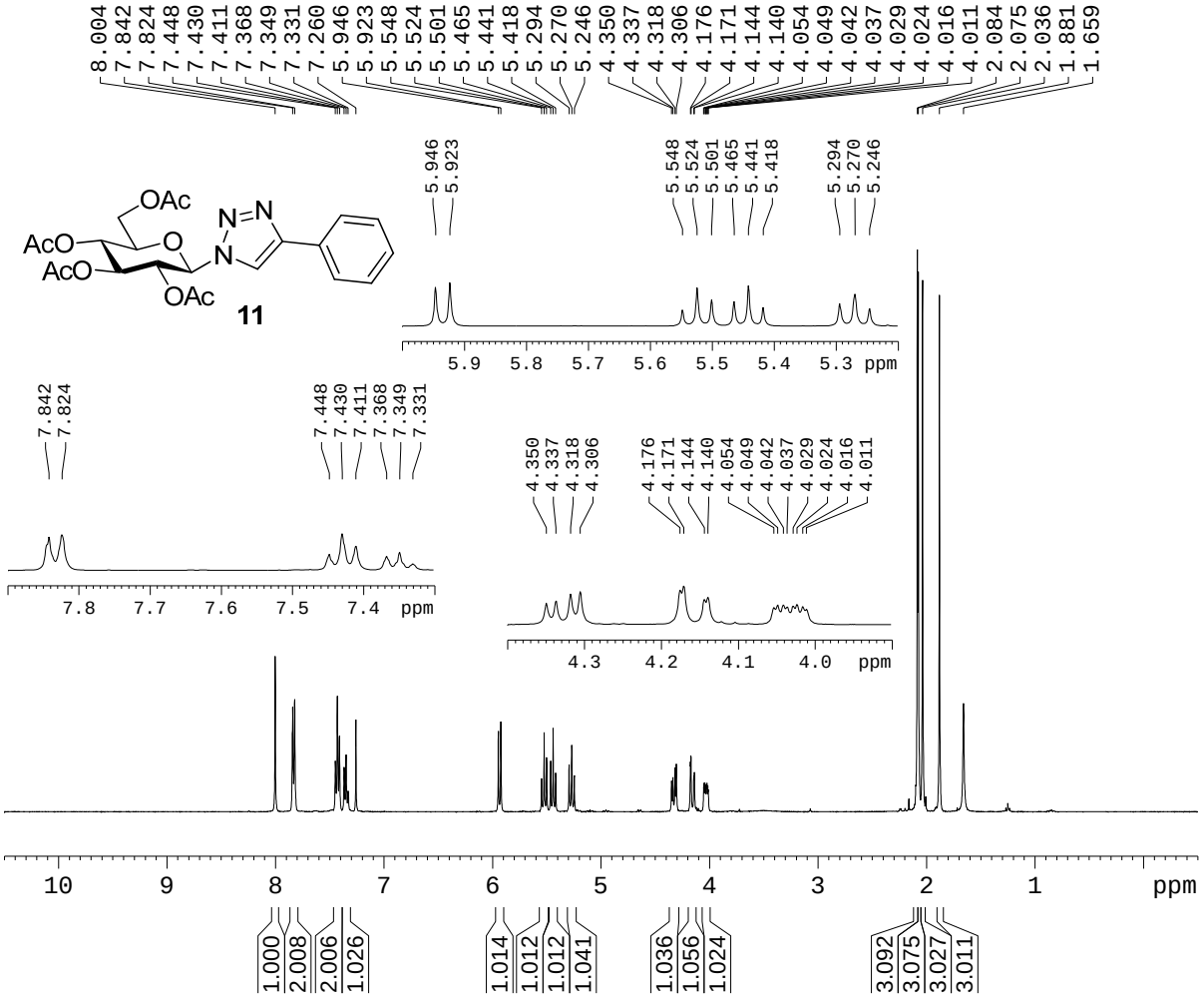

```
Current Data Parameters
NAME      NH AC azide C13
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20091218
Time               21.50
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    98
DS                     0
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ             1.3074932 sec
RG                  8192
DW                19.950 usec
DE                 6.50 usec
TE                297.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.90 usec
PL1                 5.00 dB
SFO1         100.6243390 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2         400.1319000 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127513 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



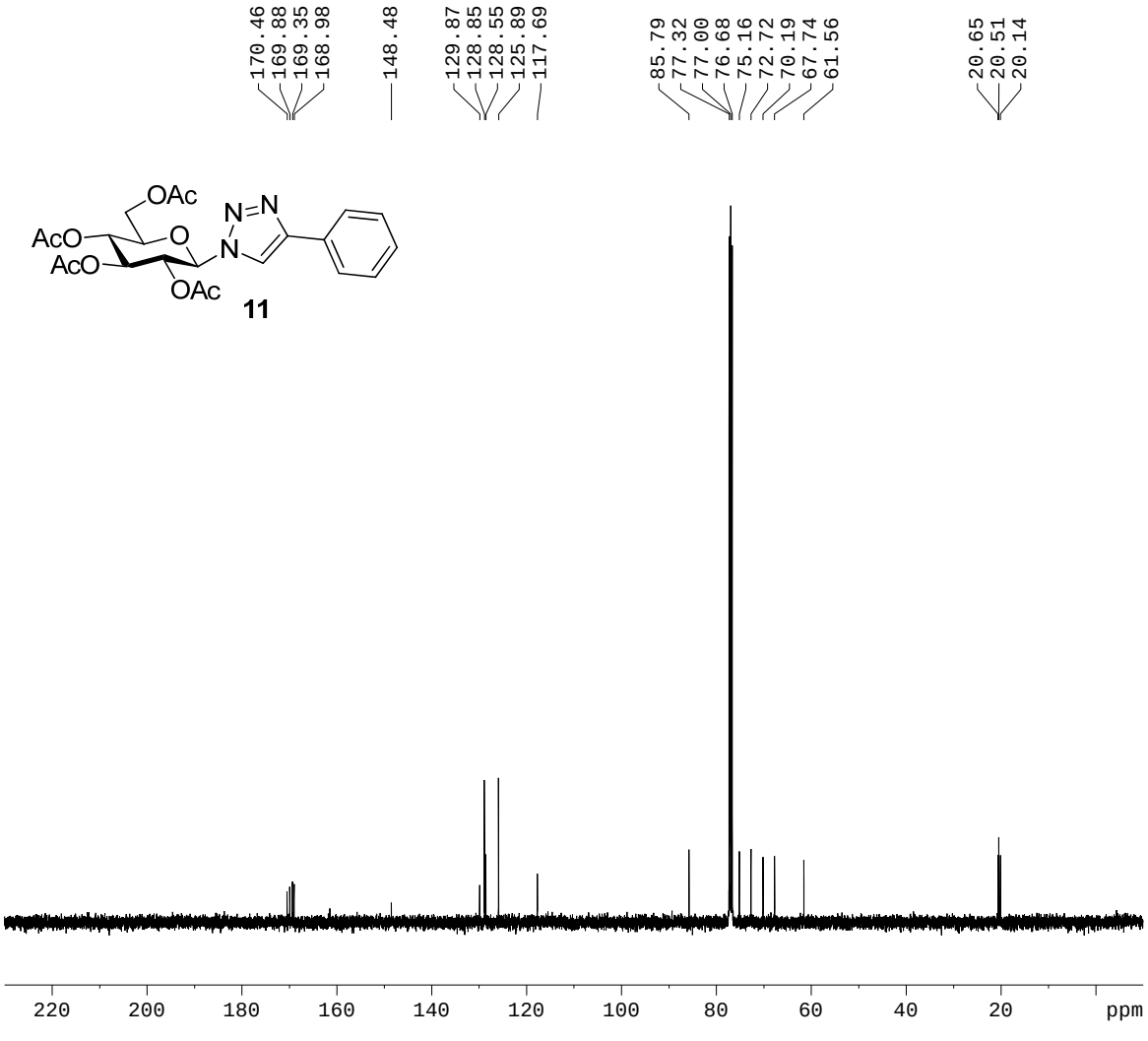

```
Current Data Parameters
NAME      glucose triazole pu
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090411
Time               20.58
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             5995.204 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 161.3
DW                83.400 usec
DE                 6.50 usec
TE                297.6 K
D1             1.50000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                 0.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300095 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 10.50 cm
F1P                2.155 ppm
F1               862.43 Hz
```



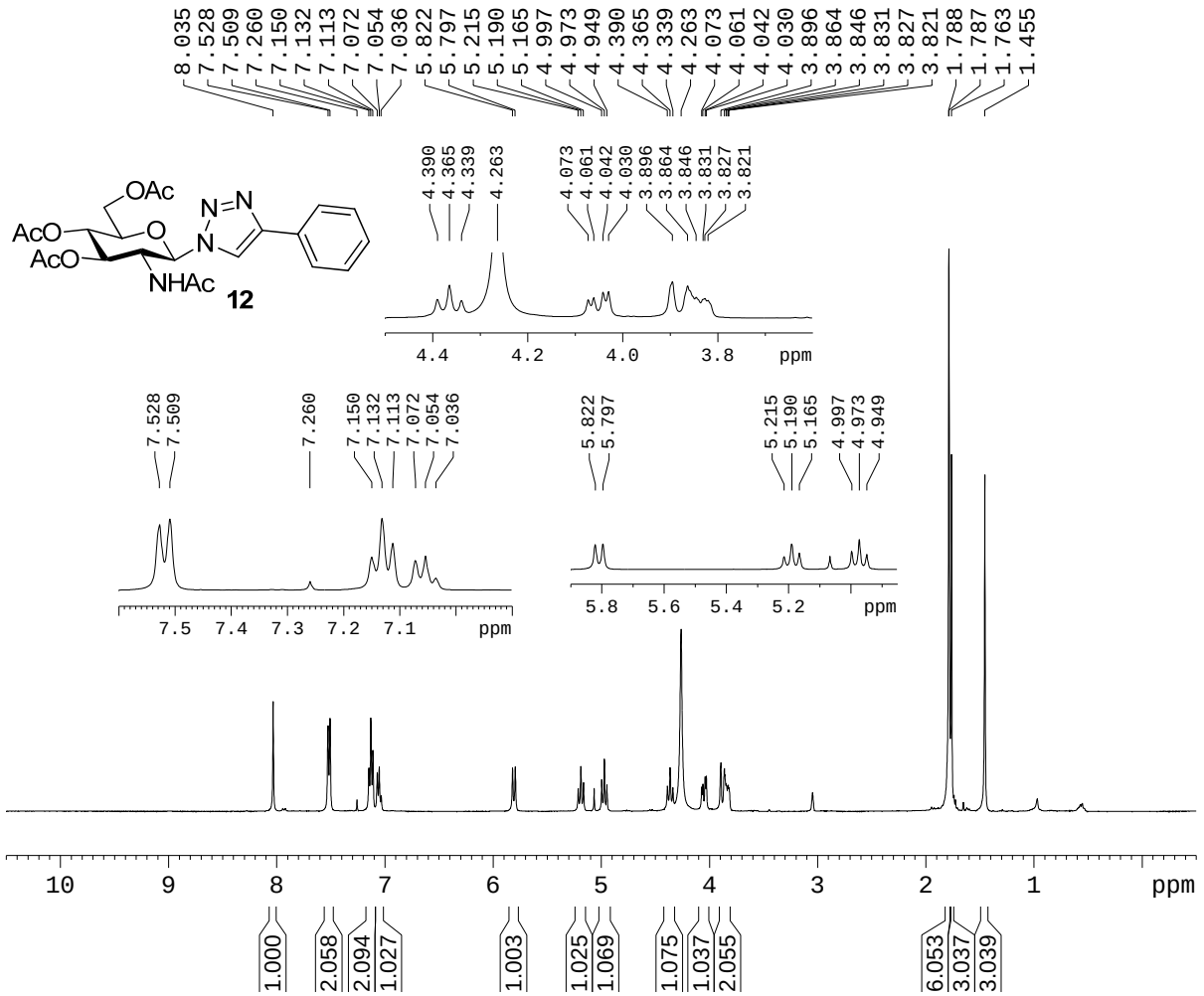

```
Current Data Parameters
NAME                 dr-12
EXPNO                    9
PROCNO                   1

F2 - Acquisition Parameters
Date_           20090307
Time                21.22
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   151
DS                     0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ             1.3042164 sec
RG                  4096
DW                19.900 usec
DE                 6.50 usec
TE                299.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.90 usec
PL1                 5.00 dB
SFO1         100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2         400.1319000 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127672 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



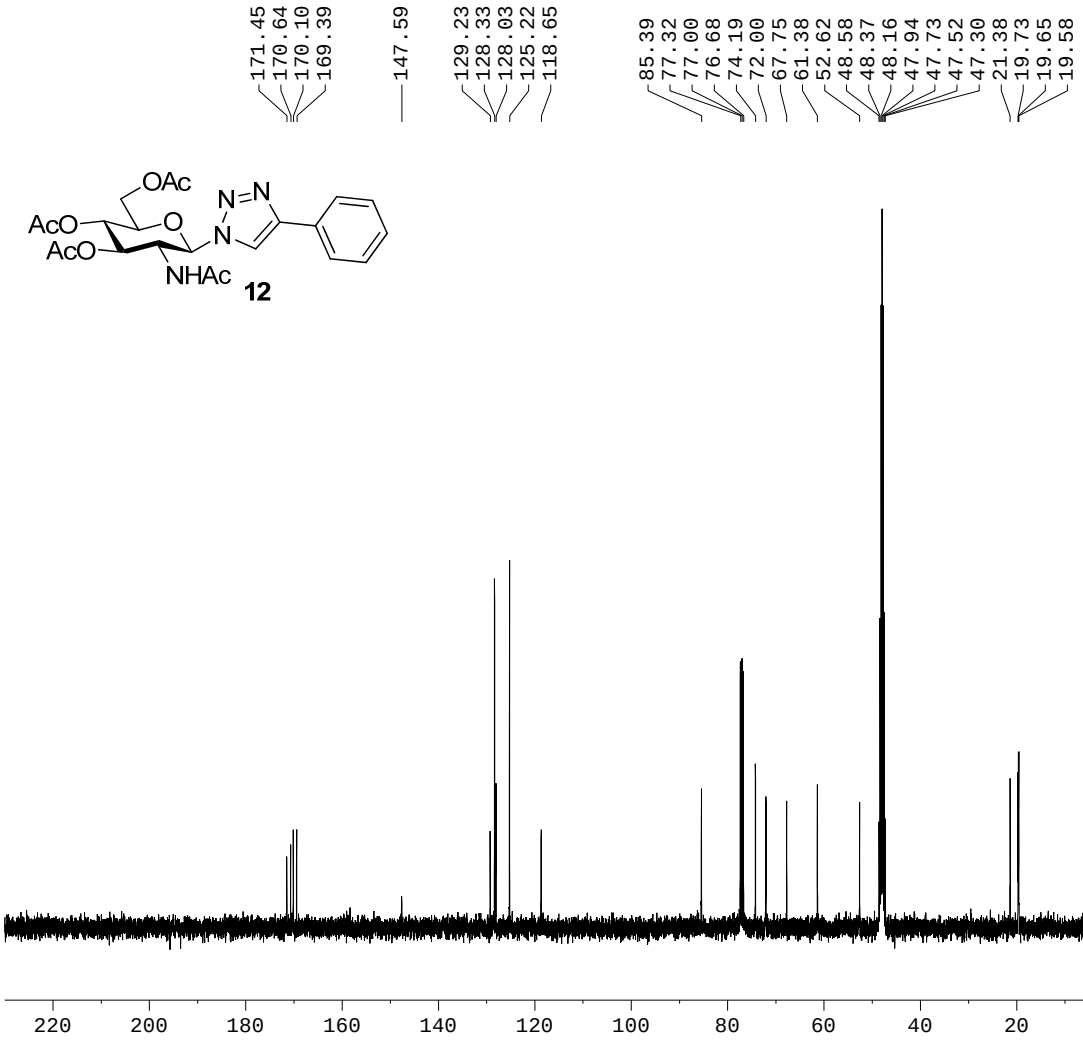

```
Current Data Parameters
NAME                  NHac
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20090405
Time                17.49
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT              MeOD
NS                     16
DS                      0
SWH              5995.204 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                     57
DW                 83.400 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.50000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.00 usec
PL1                  0.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                  16384
SF           400.1301123 MHz
WDW                    EM
SSB                     0
LB                   0.10 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
CY                  10.50 cm
F1P                 5.882 ppm
F1                2353.48 Hz
```



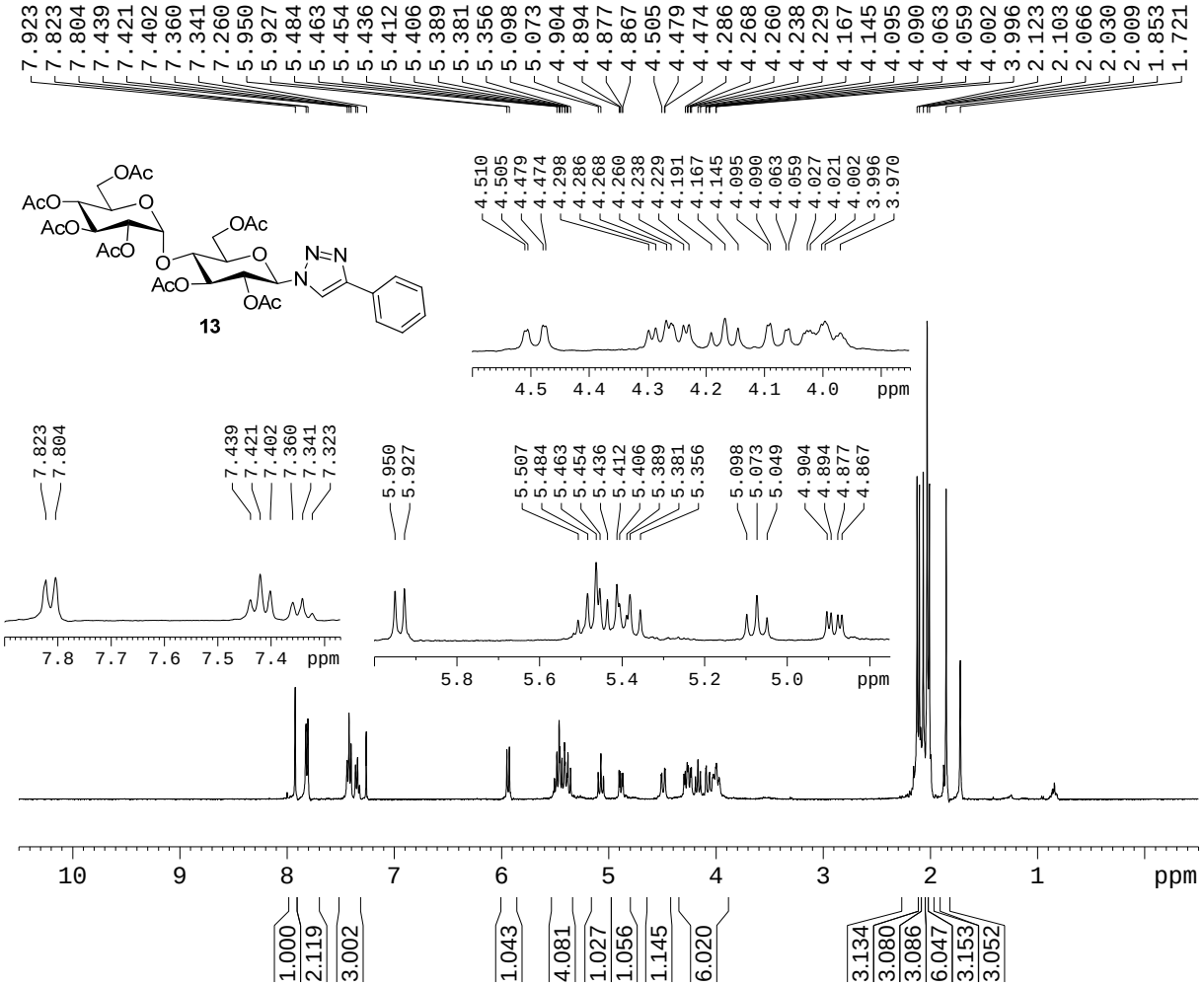

```
Current Data Parameters
NAME            NHAc C13
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090405
Time               18.28
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  108
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                 8192
DW               19.900 usec
DE                6.50 usec
TE                298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.90 usec
PL1                5.00 dB
SFO1        100.6242995 MHz

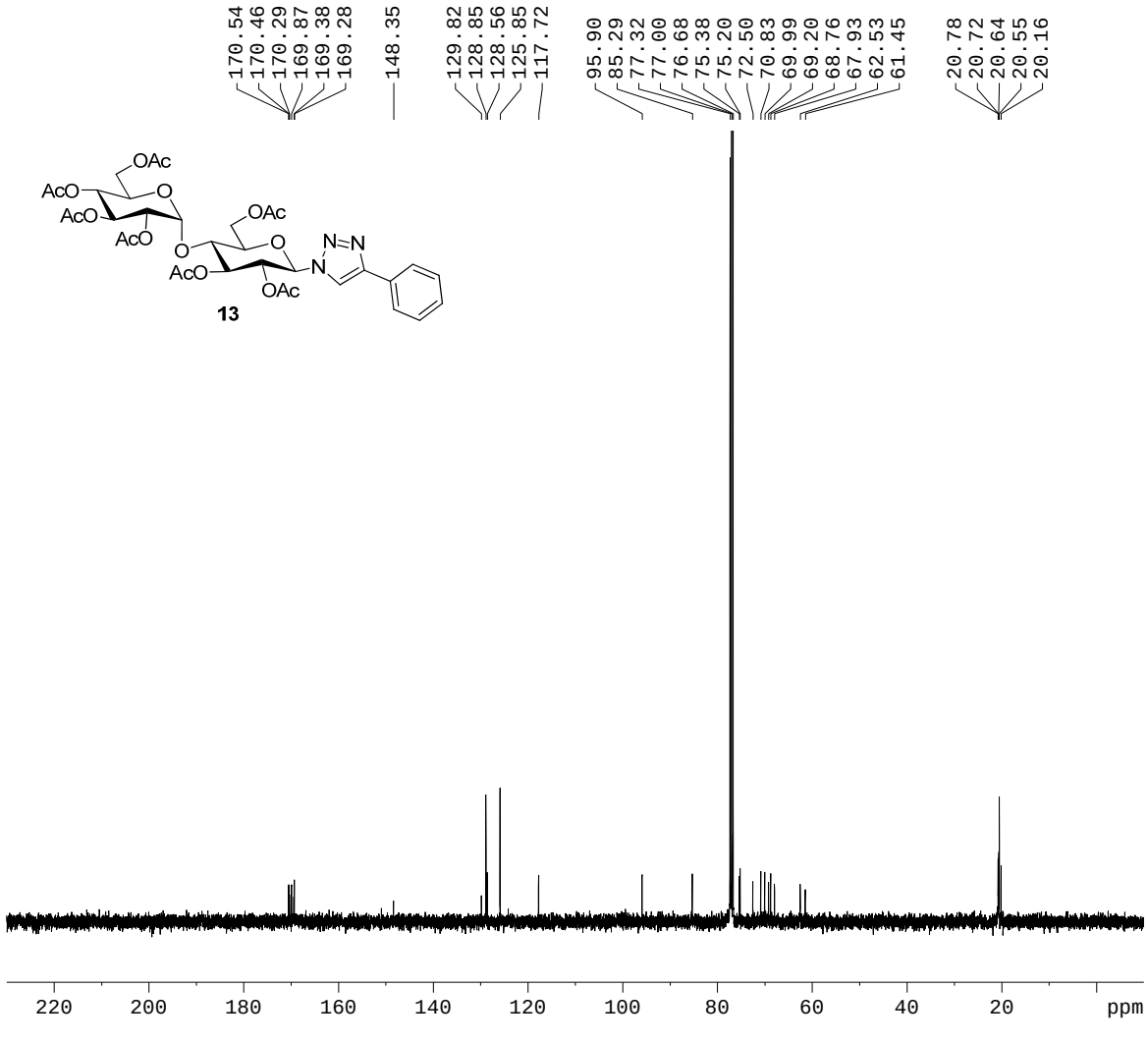
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             90.00 usec
PL2                0.00 dB
PL12              19.10 dB
PL13              22.10 dB
SFO2        400.1319000 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127934 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```




```
NAME      maltose triazole c13
EXPNO                    9
PROCNO                   1
Date_             20090307
Time                 21.56
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   16384
SOLVENT              CDCl3
NS                       1
DS                       0
SWH               5995.204 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                     114
DW                  83.400 usec
DE                   6.50 usec
TE                  299.1 K
D1              1.50000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  10.00 usec
PL1                  0.00 dB
SFO1          400.1326008 MHz
SI                   16384
SF            400.1300089 MHz
WDW                     EM
SSB                      0
LB                    0.10 Hz
GB                       0
PC                    1.00
```



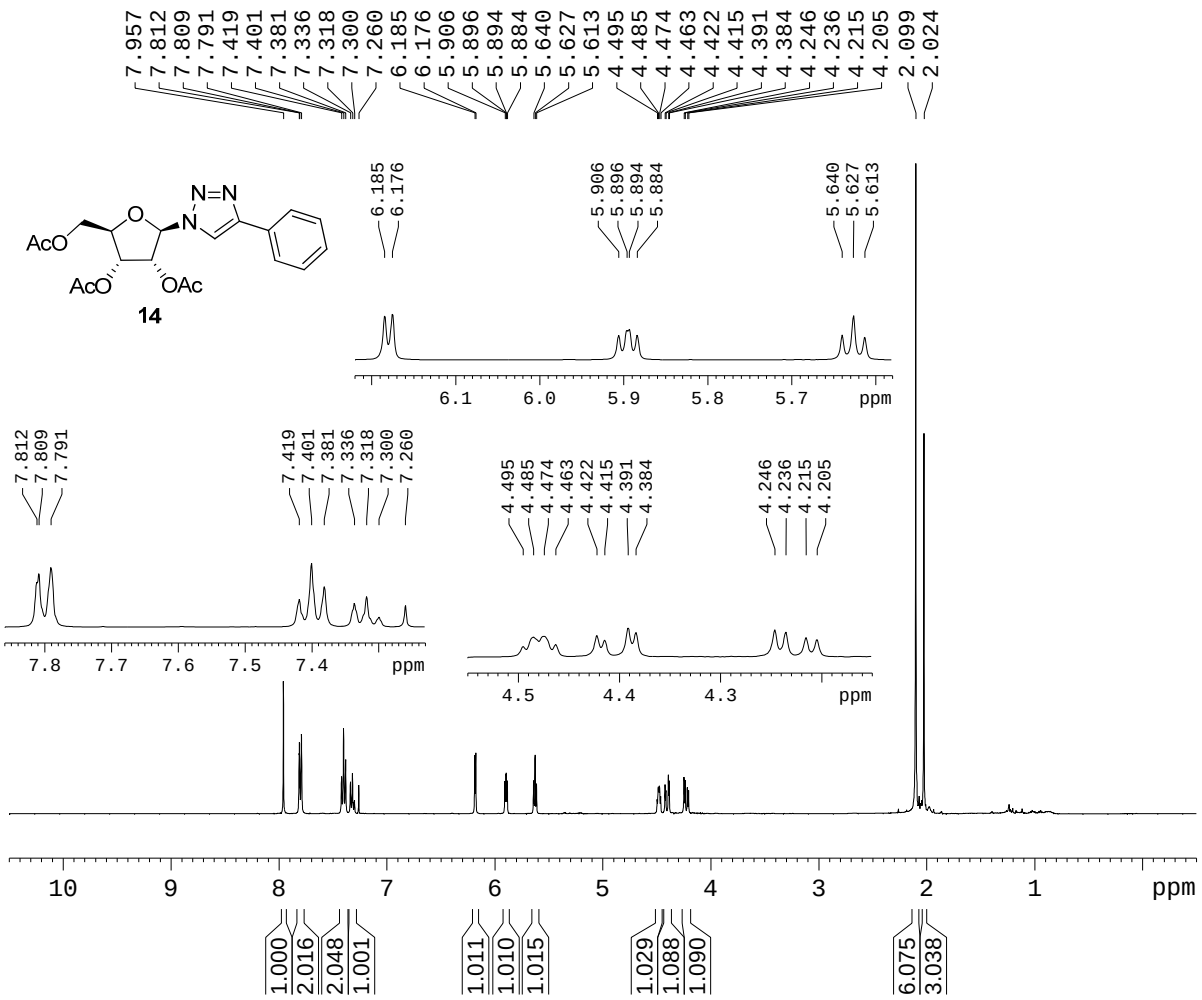

```
Current Data Parameters
NAME     maltose triazole c13
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_          20090307
Time              21.58
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  158
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                 8192
DW                19.900 usec
DE                 6.50 usec
TE                299.1 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.90 usec
PL1                5.00 dB
SFO1        100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2        400.1319000 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127497 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



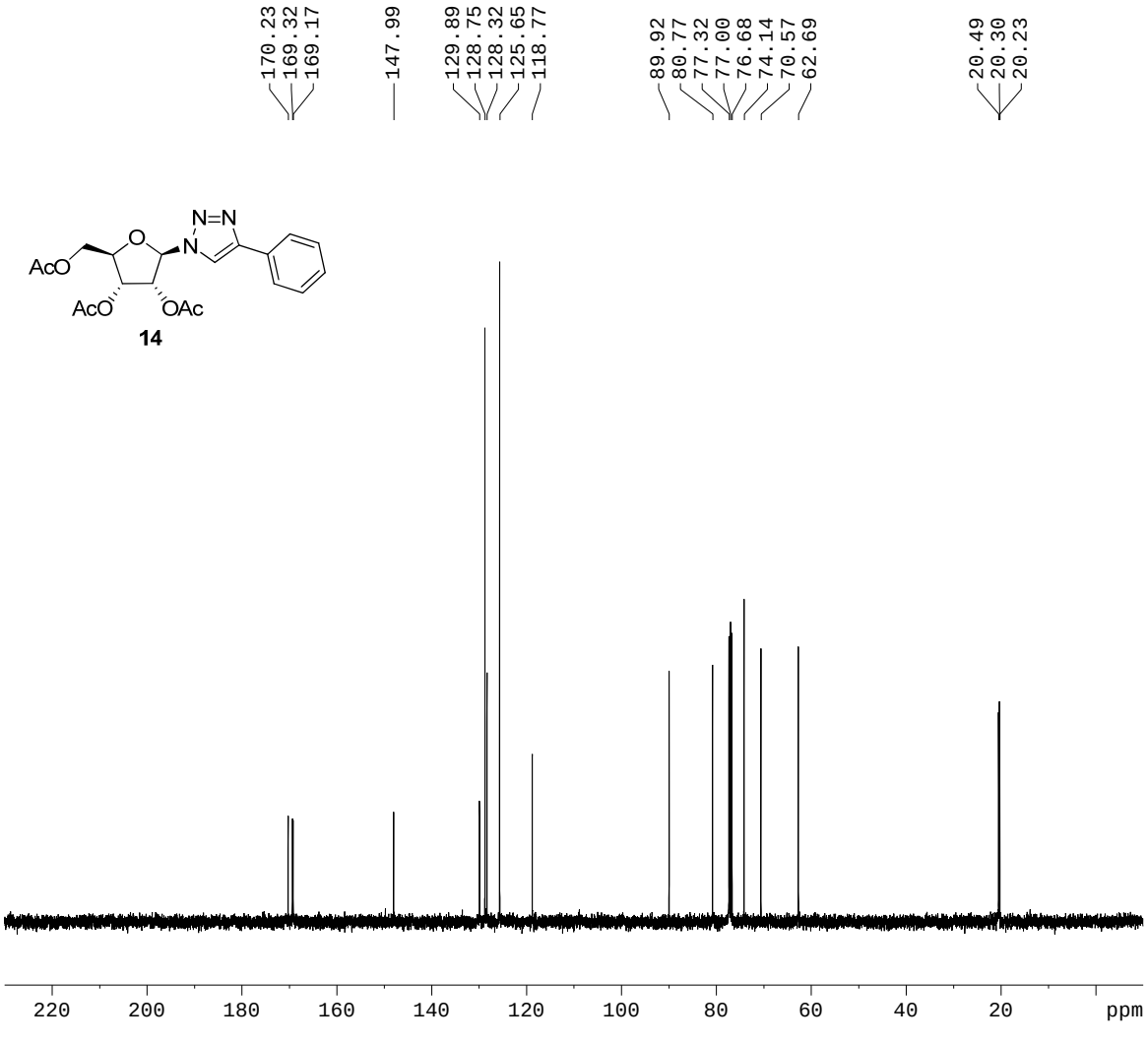

```
Current Data Parameters
NAME      ribose triazole
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090314
Time               16.19
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             5995.204 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                  40.3
DW                83.400 usec
DE                 6.50 usec
TE                299.9 K
D1           1.50000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                 0.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300088 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 10.50 cm
F1P                8.128 ppm
F1               3252.12 Hz
```



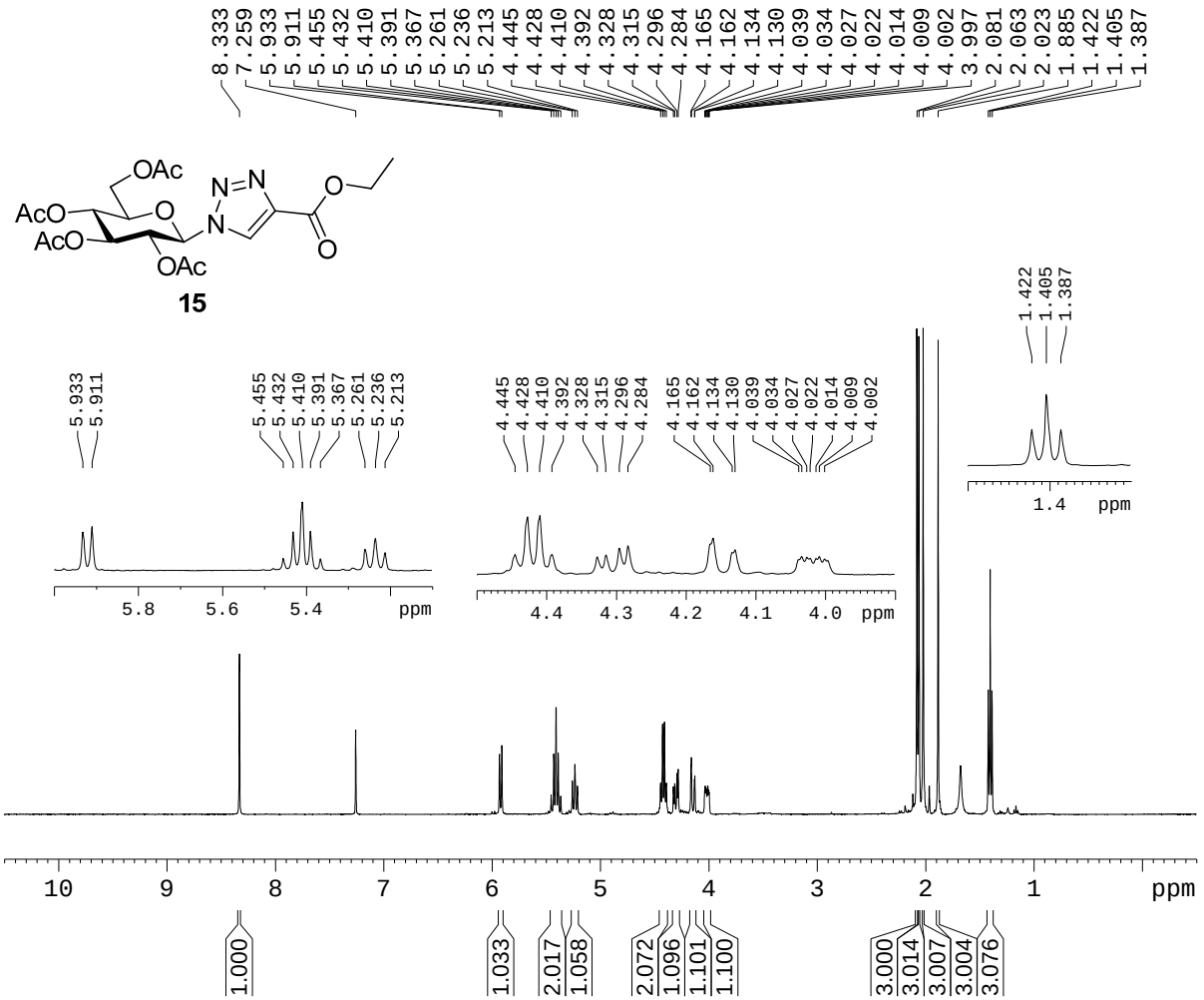

```
Current Data Parameters
NAME      PTHALIC-12PH-INDOL
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_           20090321
Time               20.57
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   68
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ             1.3042164 sec
RG                 4096
DW                19.900 usec
DE                 6.50 usec
TE                300.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.90 usec
PL1                 5.00 dB
SFO1         100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2         400.1319000 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127604 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



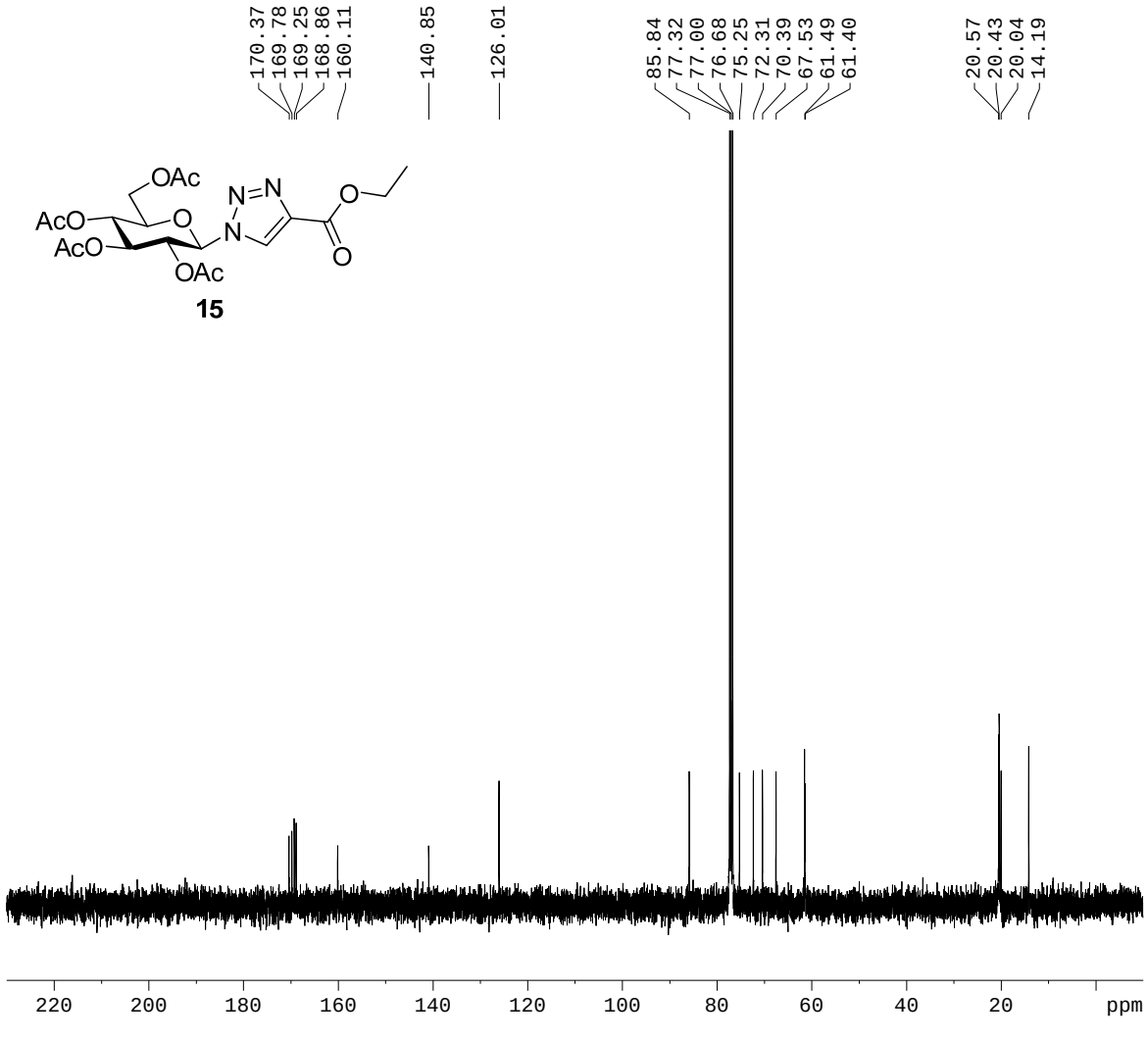

```
Current Data Parameters
NAME                 NHac
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20090405
Time               18.17
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     0
SWH              5995.204 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                 161.3
DW                83.400 usec
DE                 6.50 usec
TE                298.0 K
D1             1.50000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                10.00 usec
PL1                0.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300095 MHz
WDW                   EM
SSB                    0
LB                 0.10 Hz
GB                     0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                10.50 cm
F1P                2.215 ppm
F1               886.46 Hz
```



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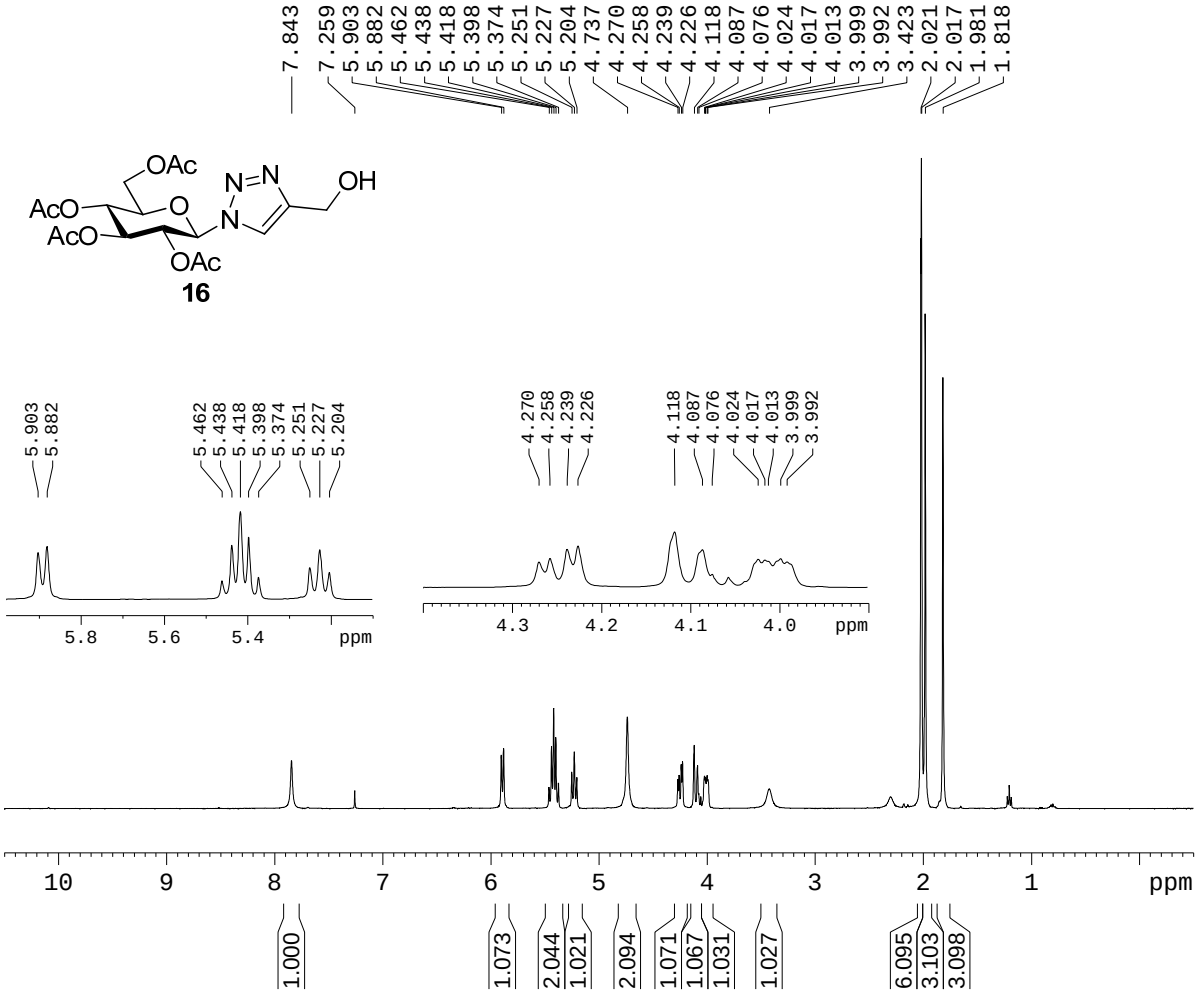
```
Current Data Parameters
NAME     propargy ester triazol
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20090404
Time              20.39
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   83
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                 8192
DW                19.900 usec
DE                 6.50 usec
TE                297.8 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.90 usec
PL1                5.00 dB
SFO1        100.6242995 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2        400.1319000 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127520 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



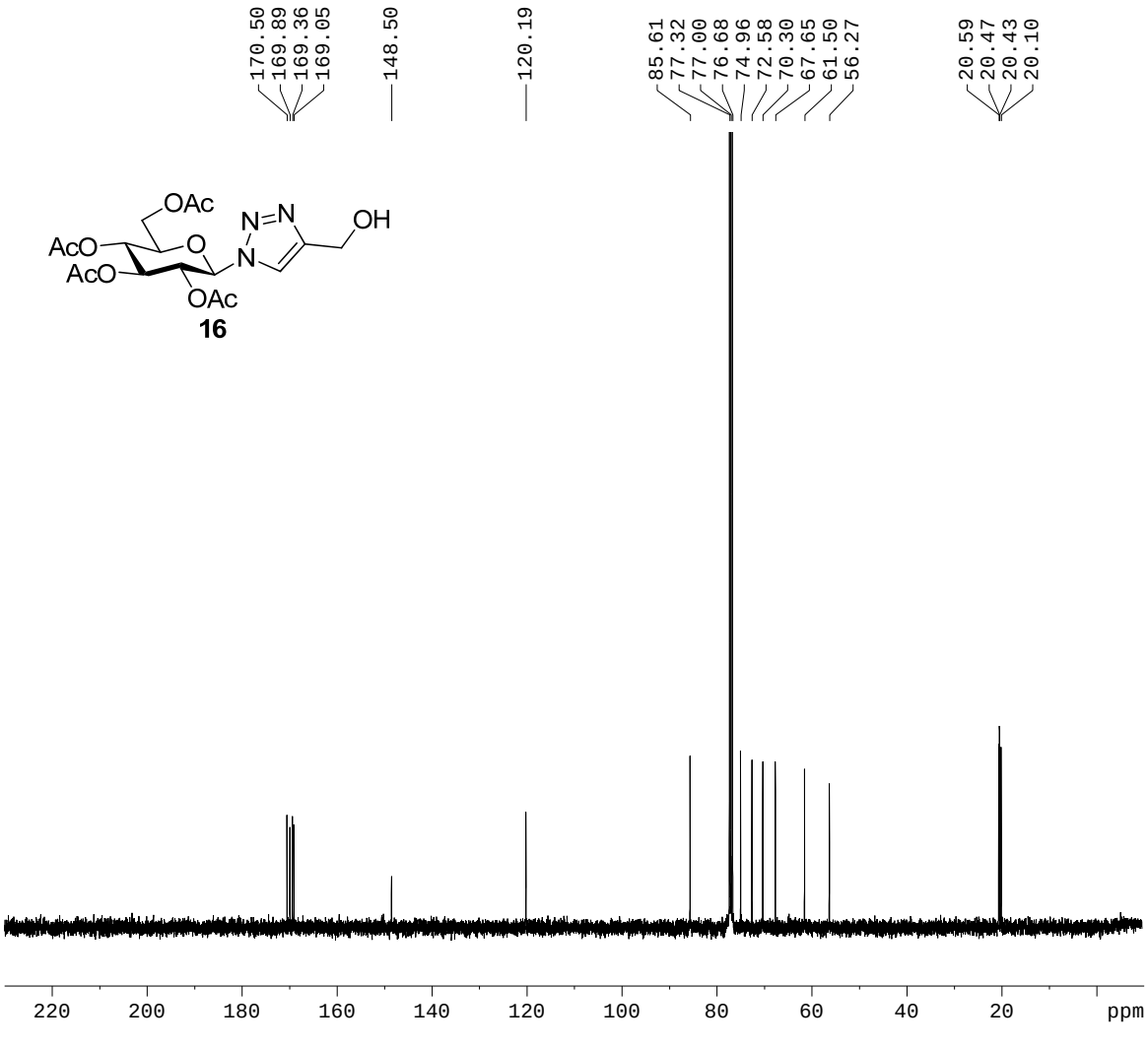

```
Current Data Parameters
NAME      -propargy triazole
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20090326
Time               20.50
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             5995.204 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                  45.3
DW                83.400 usec
DE                 6.50 usec
TE                298.7 K
D1            1.50000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                 0.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300095 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 10.50 cm
F1P                 6.065 ppm
F1               2426.88 Hz
```



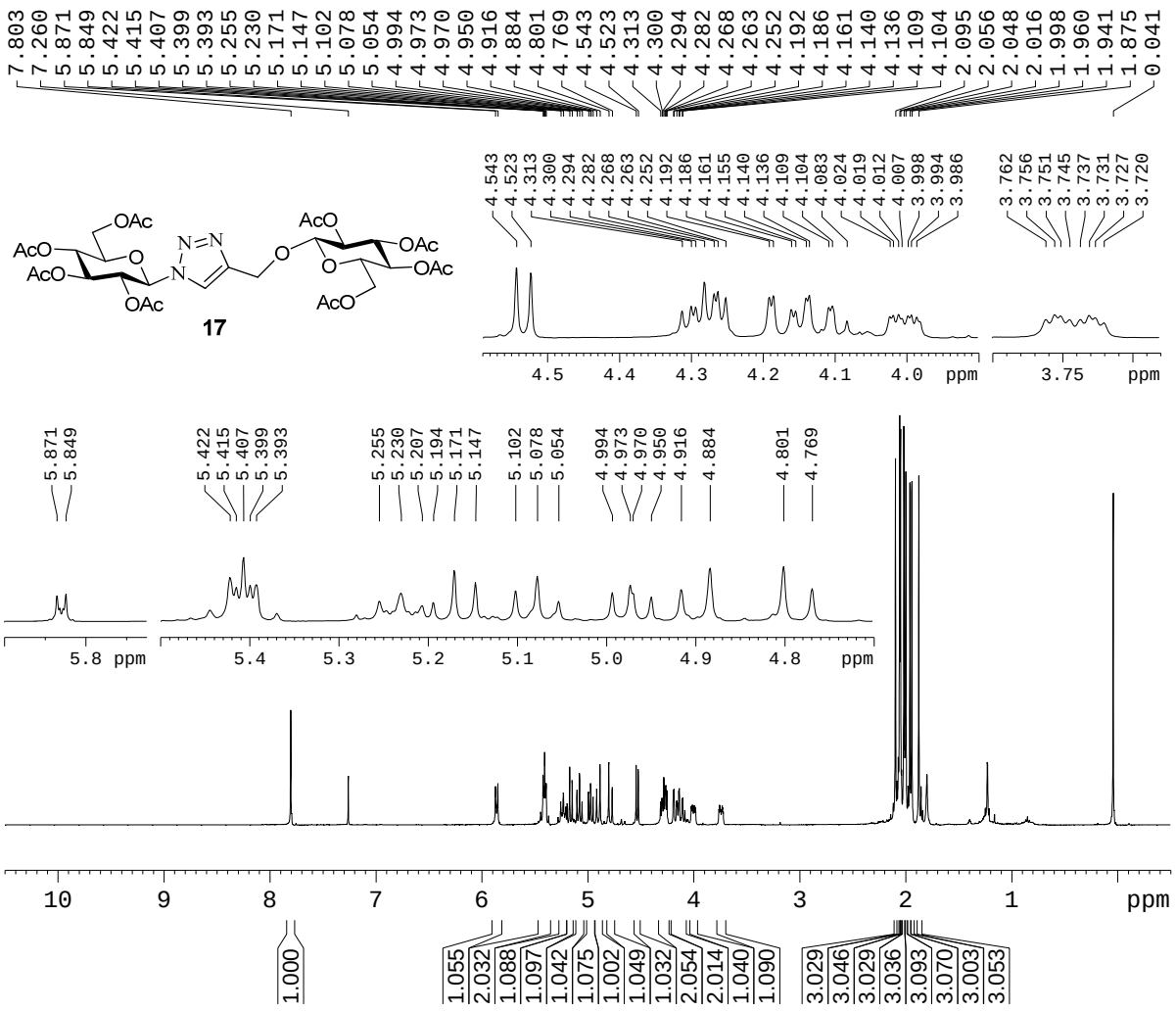

```
Current Data Parameters
NAME     prp-alcohol-sug
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20100107
Time              21.48
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  207
DS                    0
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ            1.3074932 sec
RG                 4096
DW               19.950 usec
DE                6.50 usec
TE               297.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.90 usec
PL1                 5.00 dB
SFO1         100.6243390 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2         400.1319000 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127528 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



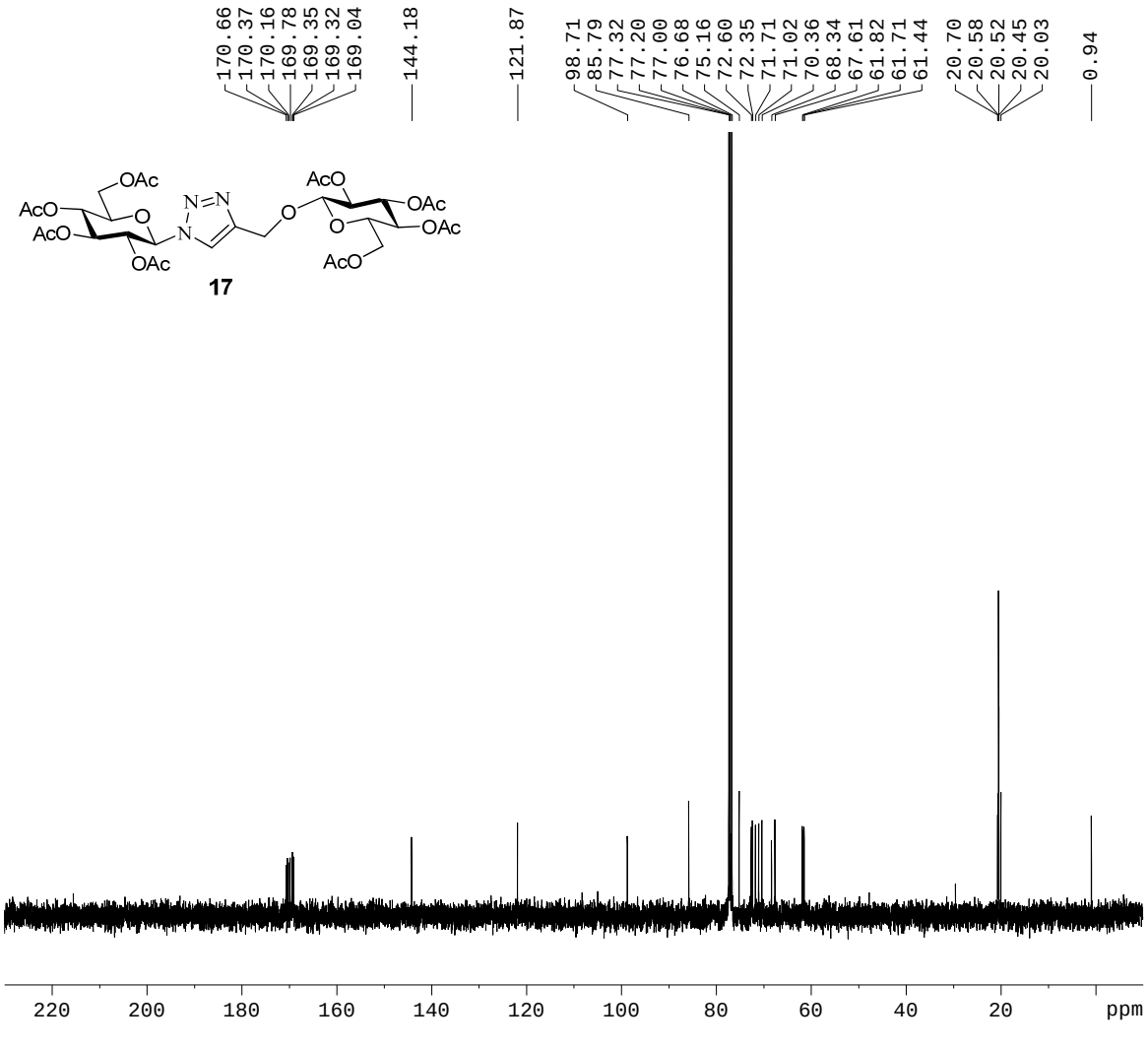

```
Current Data Parameters
NAME          prp-triaz
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20100428
Time              16.36
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                16384
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            5995.204 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 sec
RG                   22
DW               83.400 usec
DE                8.00 usec
TE               673.2 K
D1           1.50000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1               10.00 usec
PL1               0.00 dB
SFO1        400.1326008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300091 MHz
WDW                  EM
SSB                   0
LB                0.10 Hz
GB                    0
PC                1.00

1D NMR plot parameters
CX               20.00 cm
CY               12.80 cm
F1P               2.164 ppm
F1              865.96 Hz
```




```
Current Data Parameters
NAME          prp-triaz
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20100428
Time              16.39
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   84
DS                    0
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                 4096
DW               19.900 usec
DE                8.00 usec
TE               673.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.90 usec
PL1                 5.00 dB
SFO1        100.6243390 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               19.10 dB
PL13               22.10 dB
SFO2        400.1319000 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127509 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```