Application of the Synthetic Aminosugars for Glycodiversification: Synthesis and Antimicrobial Studies of Pyranmycin

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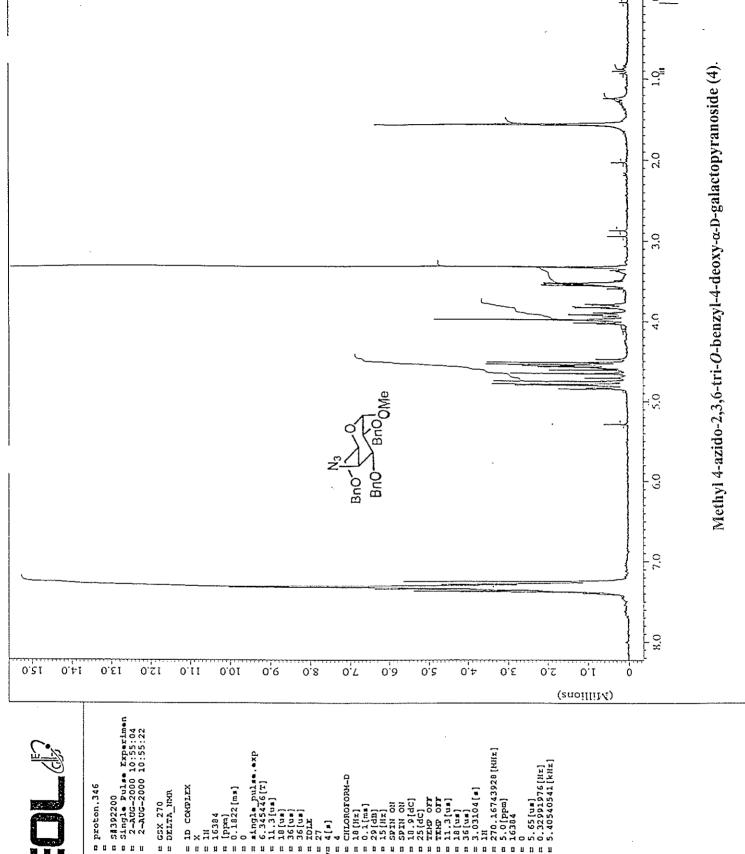
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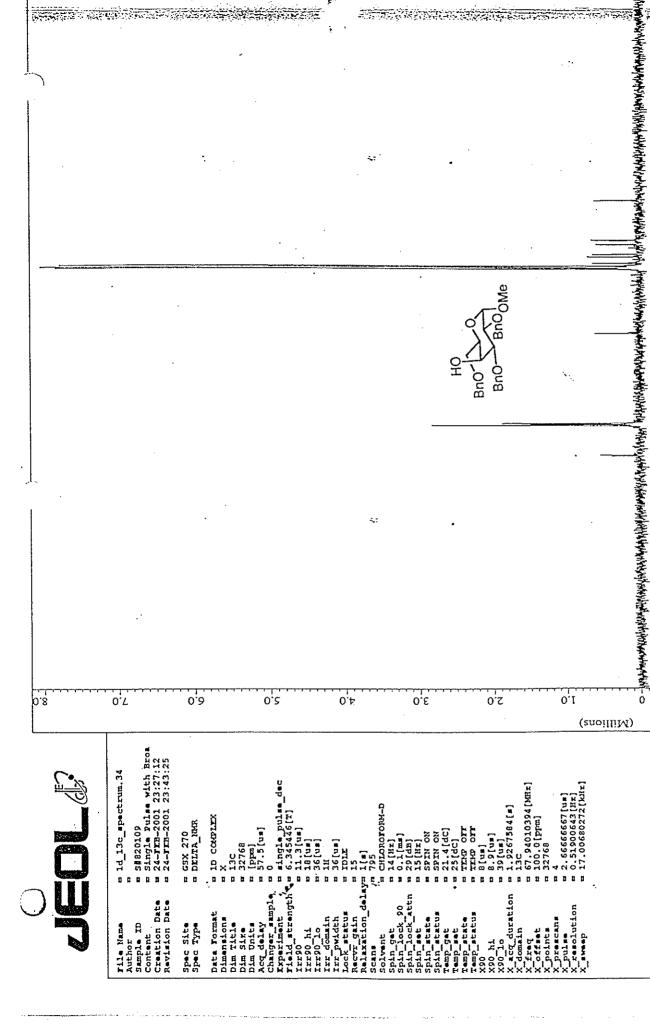
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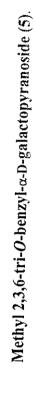
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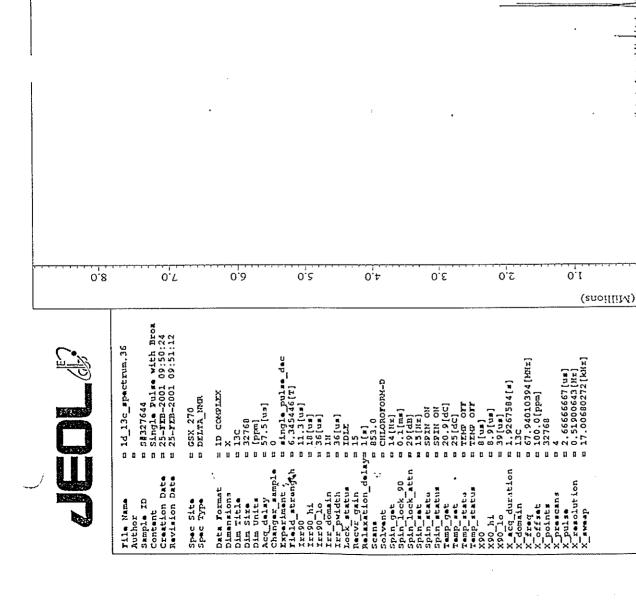
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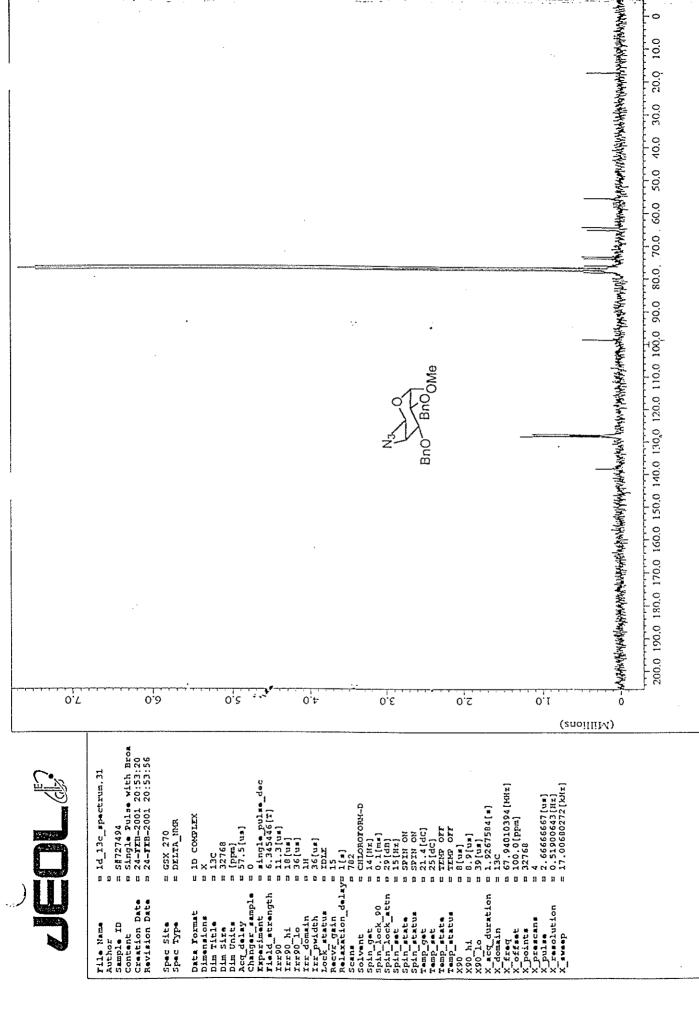
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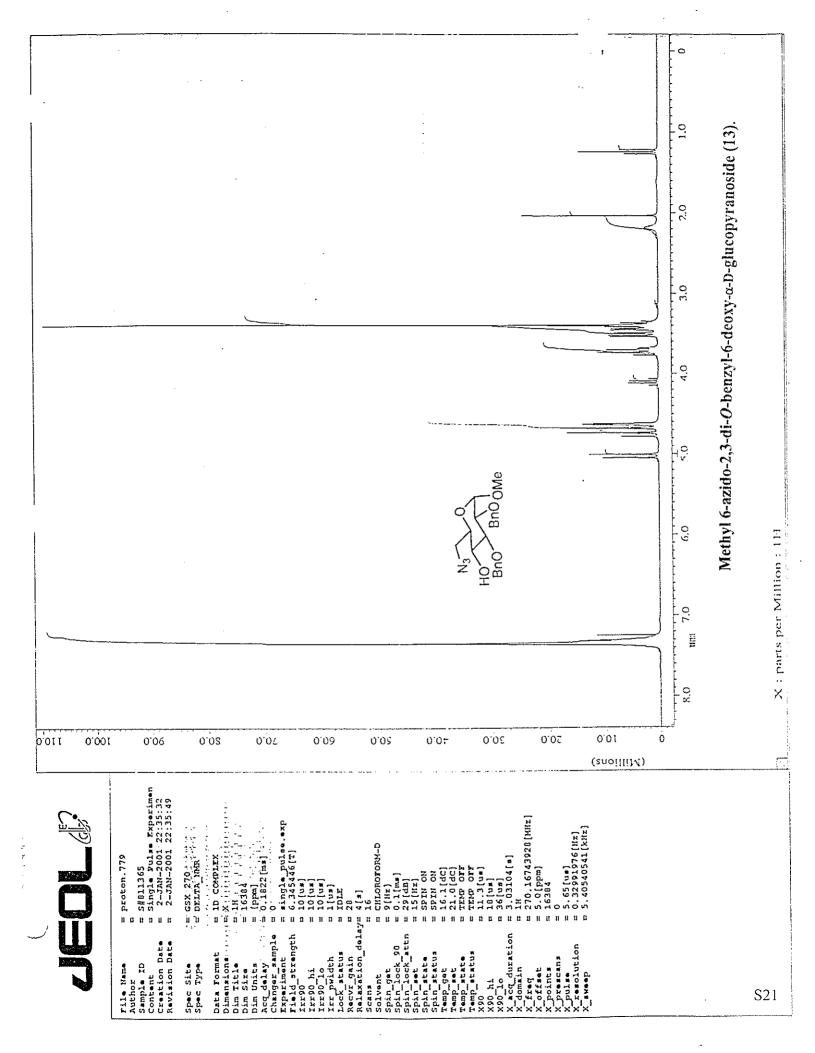
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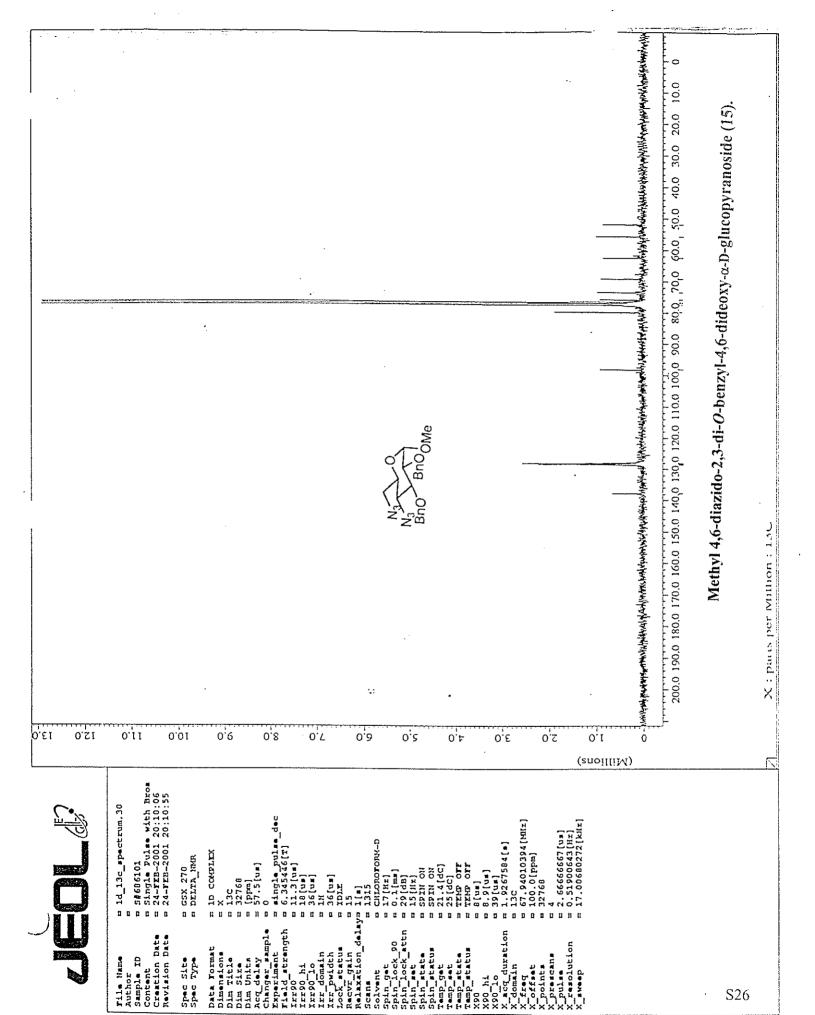
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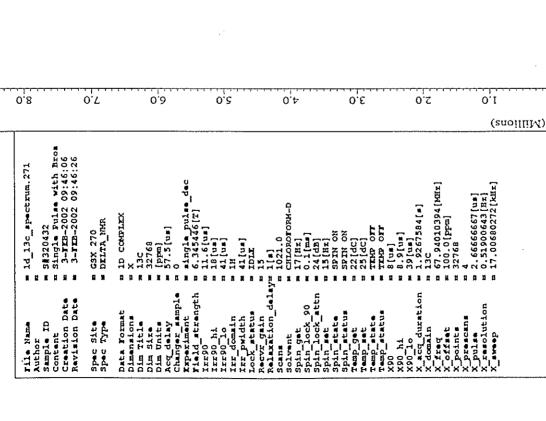
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				Aco			200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0, 60.0 50.0 40.0 30.0 20.0 10.0 0	Acetyl 4-azido-2,3,6-tri-O-acetyl-4-deoxy-α-D-galactopyranoside (16).	X:pn
-	0'9	0.2	0.4	0,5	0.2	0,1	onoilliliM)		×
			Spec Type DELTA, NGR Spec Type DELTA, NGR Dimensions N X Dim Title N 13C Dim Sire 22768 Dim Units Dippuls Dippuls Acq delay D 57.5[us] Changer, sample 0 Experiment Single pulse dec Tield strength H 5.34446[T]			X90 lo X acq duration		\$2	

بر .					
5		0.08	0.08		
rile Name Author Sample ID Content Creation Date Revision Date	m proton.2211 m 3#454216 m 5#454216 m 5#391e Pulse Experimen m 2-FEB-2002 12:39:06 m 2-FEB-2002 12:39:24	0.0 <i>T</i>	0.07		
Spec Site Spec Type Data Format	m GSX 270 m DELTA_MMR m 1D COMPLEX	0	0		
Dimensions Dim Title Dim Sire Dim Gire Acc delay	n X n 1H n 16394 n [Ppn]	.09	.09		
] , , , , , , , , ,	m single pulse.exp m 6.345446[T] m 11.6[us] m 18[us]	0.02	0.02		
Tracks Tr	# 41[us] # 1Dix # 1Dix # 29 # 4[s] # 8 # CLOROYONM-D # 14[HE]	40.0	0.01		
Spin lock attn Spin set Spin state Spin status Temp get Temp set	12 24 (db) 12 15 (hr) 12 5 DIN ON 12 19 18 (dc) 13 15 16 (dc) 14 15 16 OIF	0.08	AcO AcO AcO AcO		- (A)
X90 hi X90 hi X90 hi X90 ho X acq duration X domain X freq X offeet	11.6[us] 11.6[us] 14.[us] 13.03104[s] 11.8 12.03104[s] 13.0[ppm] 16.1310	20.0	20.0		
X prescans X pulse X resolution X awap			10.0	. –	.
makka akka akka akka ka ka ka ka ka ka ka		ioilliM)			- 1 - 1 - 1 - 1
Name		0	8.0	1.0	0
			Acetyl 4-azido-2,3,6-tri-O-acetyl-4-deoxy-α-D-glucopyranoside (17).		
S29			$X: parts \ per \ Million: 1H$		

0.6

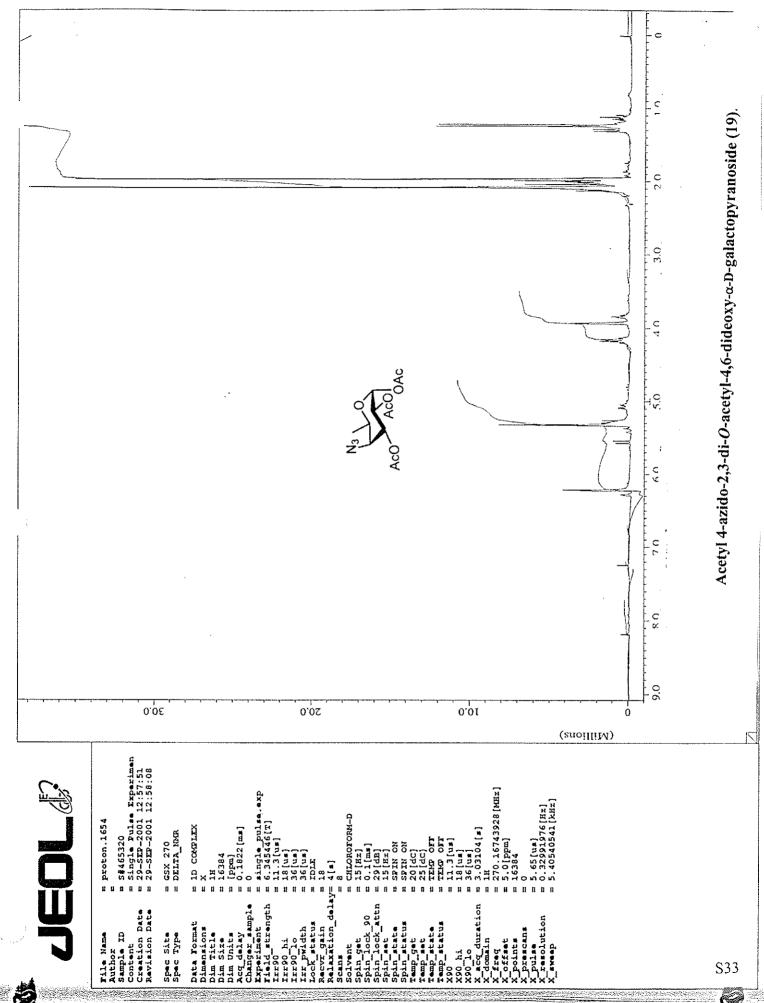


200,0 190,0 180,0 170,0 160,0 150,0 140,0 130,0 120,0 110,0 100,0 80,0, 70,0 60,0 50,0 40,0 30,0 20,0 10.0 6 0 大学の大学ではないないというないないないないないないないないないないないないないないない

Acetyl 4-azido-2,3,6-tri-O-acetyl-4-deoxy- α -D-glucopyranoside (17).

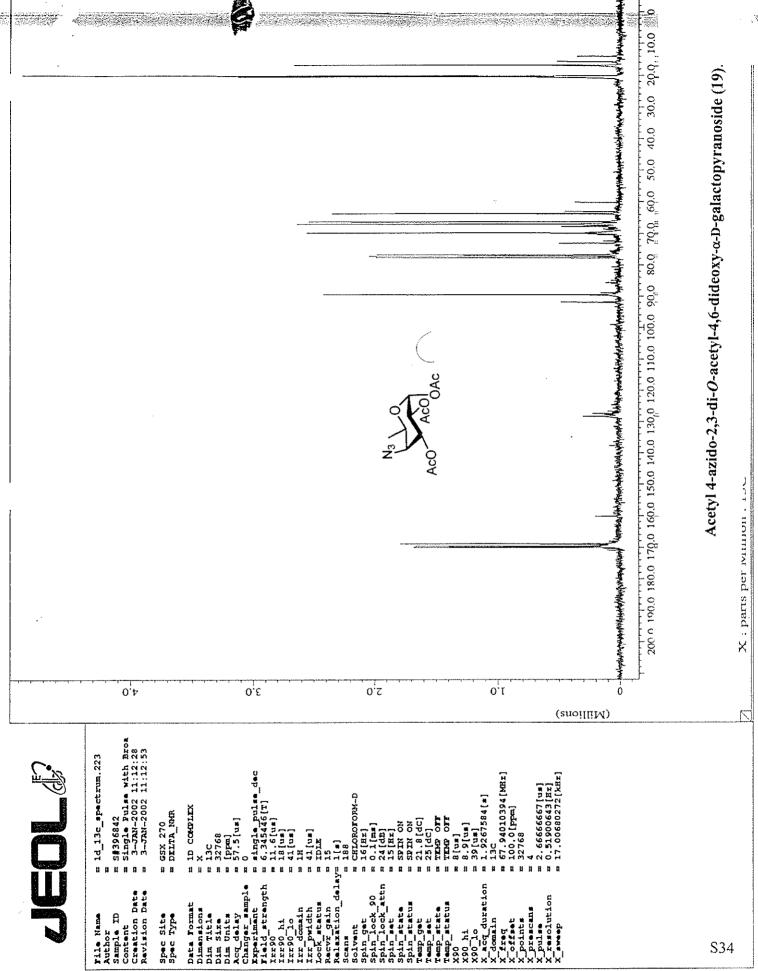
X : parts per Million : 13C

	Aco		8.0 7.0 6.0 7.0 7.0 6.0 7.0 7.0 6.0 7.0 7.0 6.0 7.0 7.0 7.0 7.0 7.0 7.0 7.0 7.0 7.0 7	Acetyl 4,0-dlazld0-2,3-dl-U-acetyl-4,6-dldeoxy-α-D-galactopyranoside (18). Χ : parts per Million : 114
30.0	0.05	0.01	0.6	X
	ttp de gtp. ttp de gtp. ttp de la	Temp get = 20 [dC] Temp_state = 72 [dC] Temp_status = 72 [dC] Temp_status = 11.3 [dx] Temp_status = 11.3 [dx] X90 hi = 11.3 [dx] X90 hi = 36 [dx] X domain = 36 [dx] X domain = 13 03104 [x] X freq = 270,16743928 [HHx] X freq = 16384 X prescans = 6 0 [ppm] X prescans = 6 0 [ppm]	ıtion	\$32









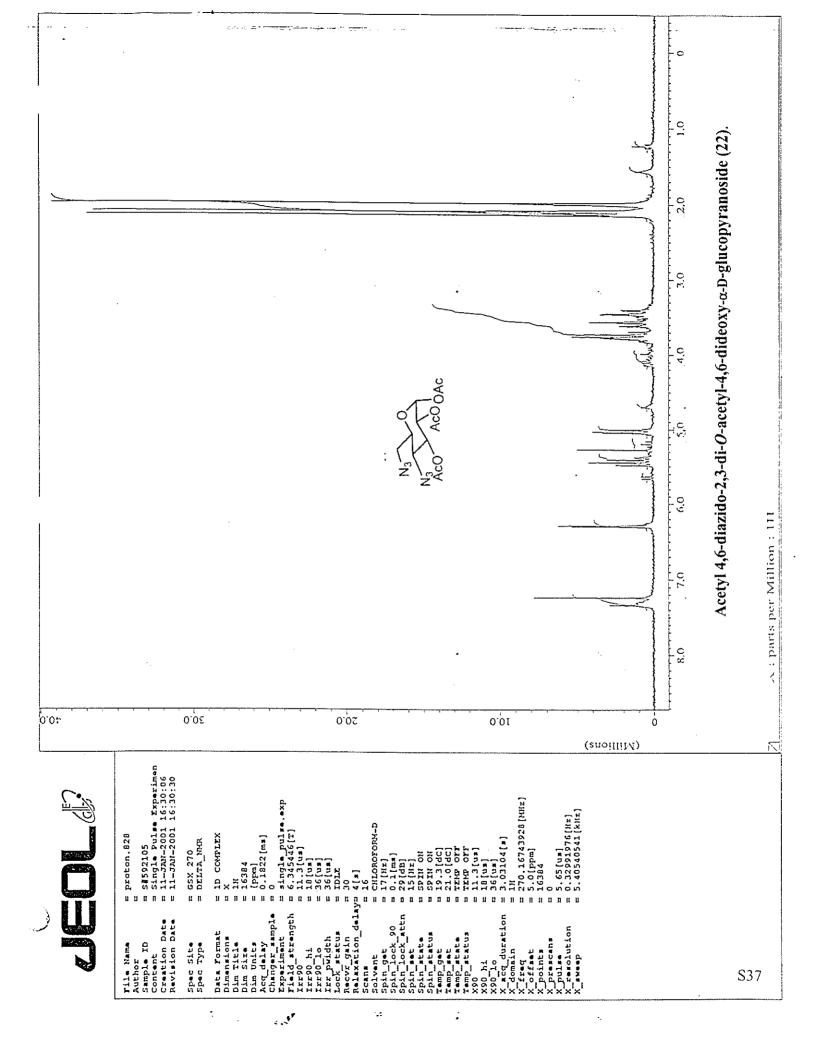
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52 0.22 0.	15 0.05 0.01 0.81 0.71 0.81 0.21 0.81 0.81 0.11 0.01 0.0 0.8, 0.7 0.8 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2
	(snoilli)
	1d_13c_spectrum.29 2d_11525 2d_11525 2d_11D_2001 19:01:05 2d_10D_2001 19:01:05 2d_10D_2001 19:01:05 2d_10D_2001 19:01:05 2d_10D_2001 19:01 2d_10D_20D_2001 19:01 2d_10D_2001 19:01
	rile Name Author Sample ID Content Creation Date Spec Site Spec Site Spec Type Data Tornat Dim Title Dim T

Acetyl 4,6-diazido-2,3-di-O-acetyl-4,6-dideoxy-α-D-glucopyranoside (20). 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90,0 80.0, 70,0 60.0 50.0 40.0 30.0

20.0 10.0

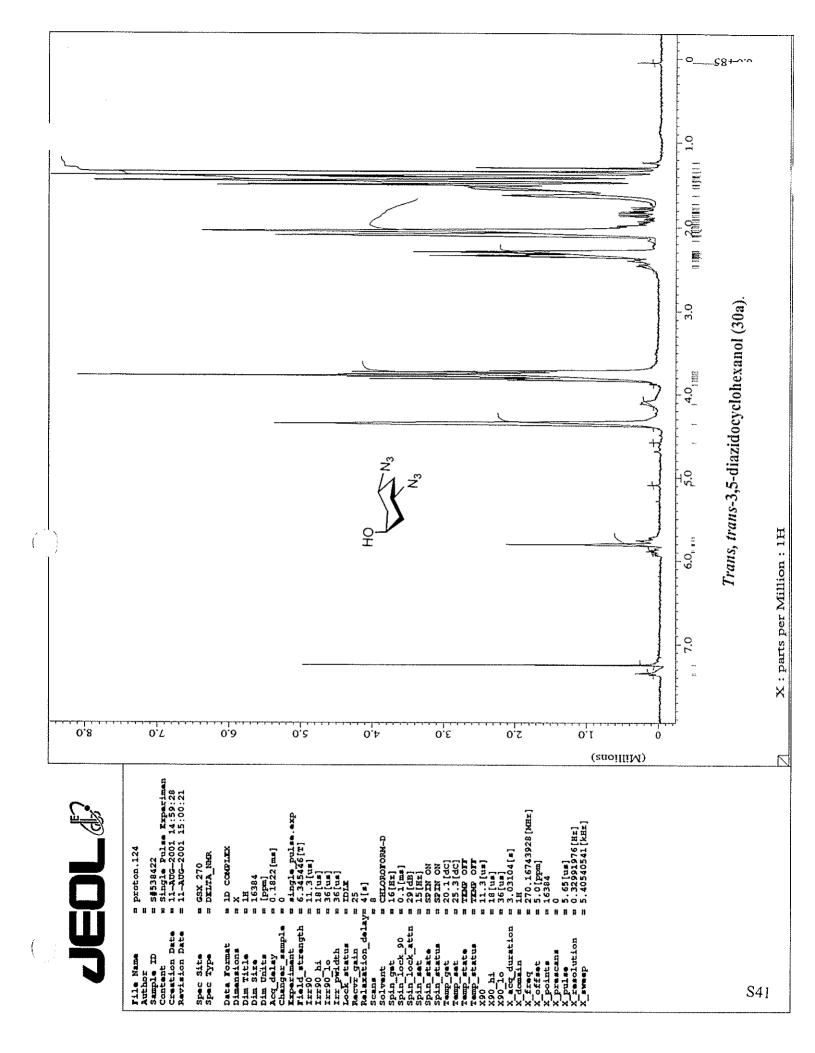
X : parts per Million : 13C



14 THE RESERVE TO THE RESERVE			N3 Aco Aco OAc	
	0.71 0.91	### ### ##############################	### ### ### ##########################	2.6666667[u*] 0.51900643[iix] 17.00690272[xiix] 17.00f00272[xiix] 0.00f0010010010010010010010010010010010010

The second secon				E Z Z			40 30 30 30 30 30 30 30 30 30 30 30 30 30	X : parts per Million : 1H
	0.9	o's	0 ['] t	ο.ε	0,2	1,0	(anoilliM)	
		Author) hi) lo) lo midth status status cation_delay statin lock 90 lock 90		n = 14 = 270.16743928[MHz] tt = 5.0[ppm] :s = 16384 .ans = 5.8[us] .ution = 0.3293976[Hz] = 5.40540541[NHz]		S39

The property of the property o	The column of th		X : parts per Million : 13C
	ig (anoilliM)		
Source	File Name	S40	



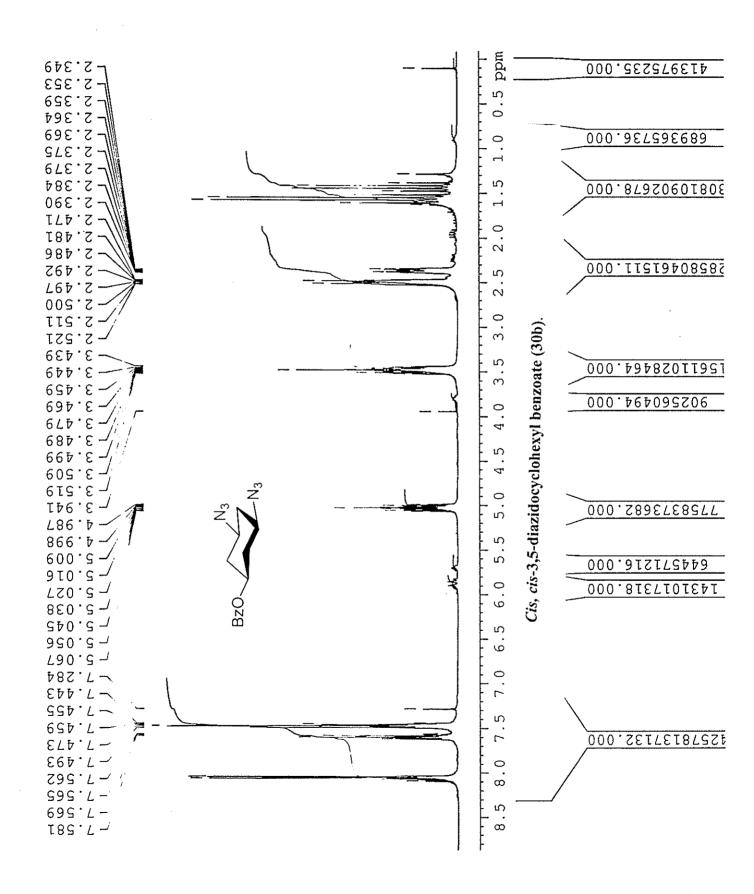
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CX 20.00 cm
F1P 180.000 ppm
F1 18110.31 Hz
F2 0.000 ppm
F2 0.00 ppm
F2 9.00000 ppm/Cn
HZCM 905.51538 Hz/cm
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SF 100.6128220 MH2
WDK EN 6
SSB 0
LB 1.00 H2
GB 0 0
PC 1.40
Current Data Parameters
NAME 090301
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DE
SF01
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D11
                       EXPNO
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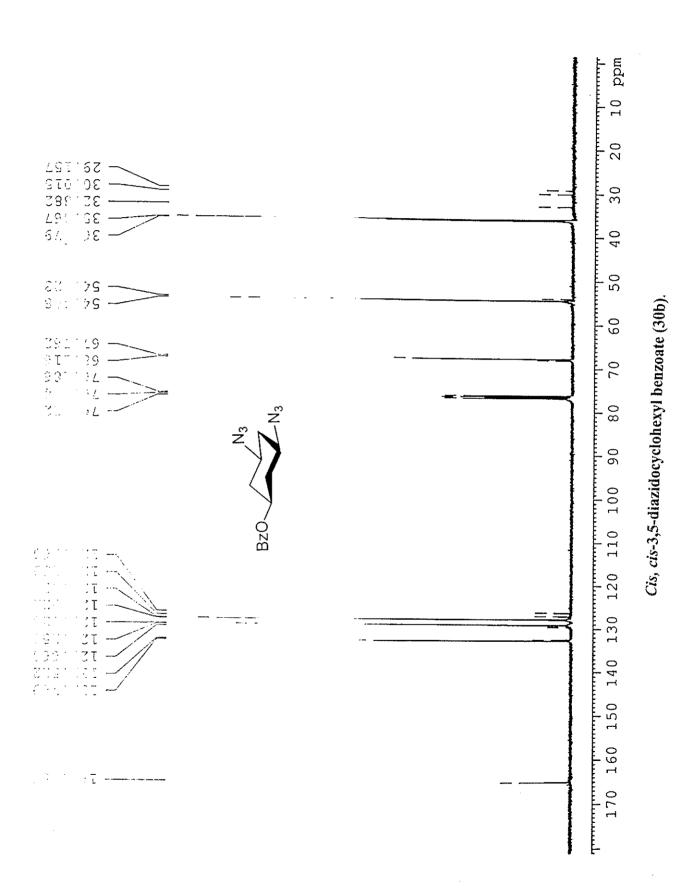
Trans, trans-3,5-diazidocyclohexanol (30a).

-09 -ස -00 -82 -82 140 mdd.

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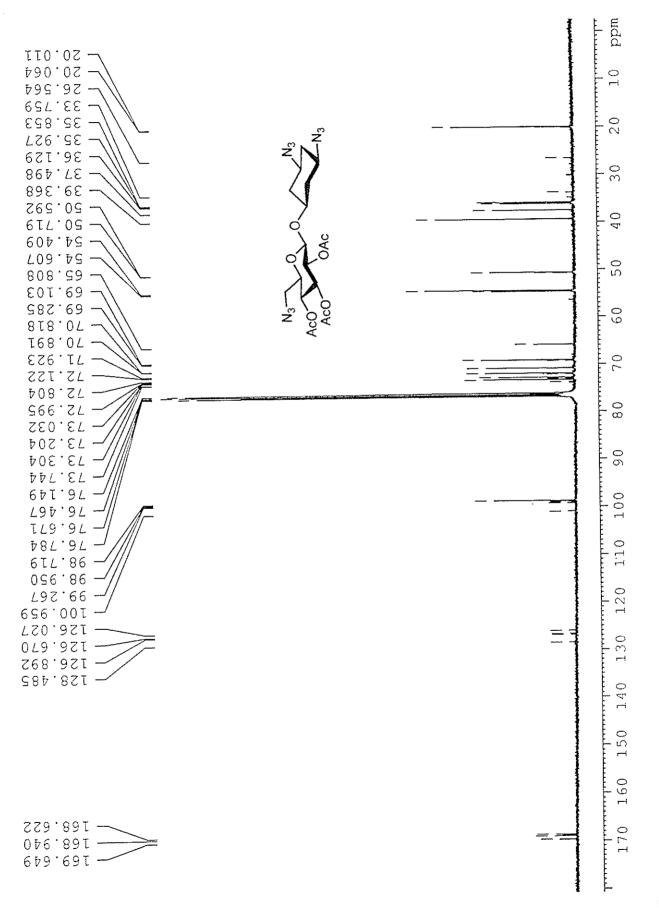
-6



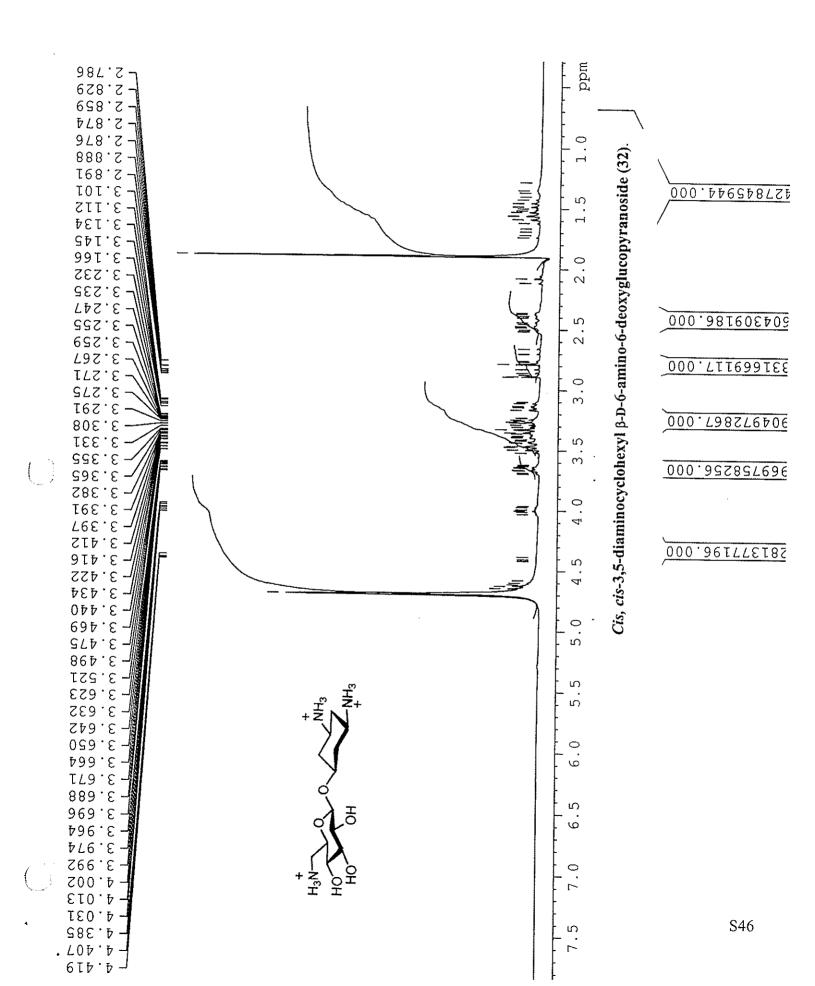


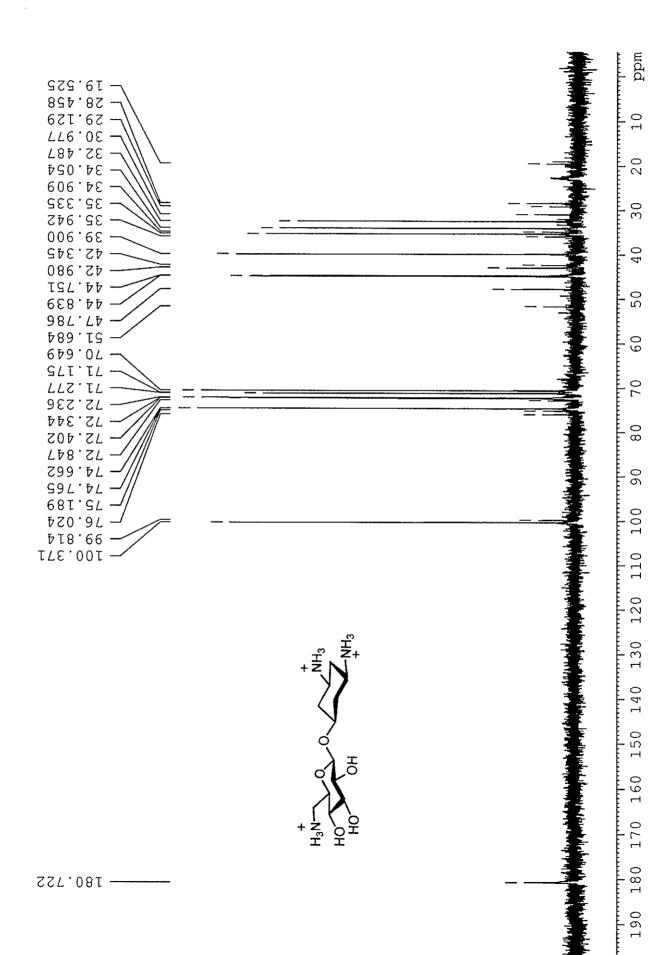
S44





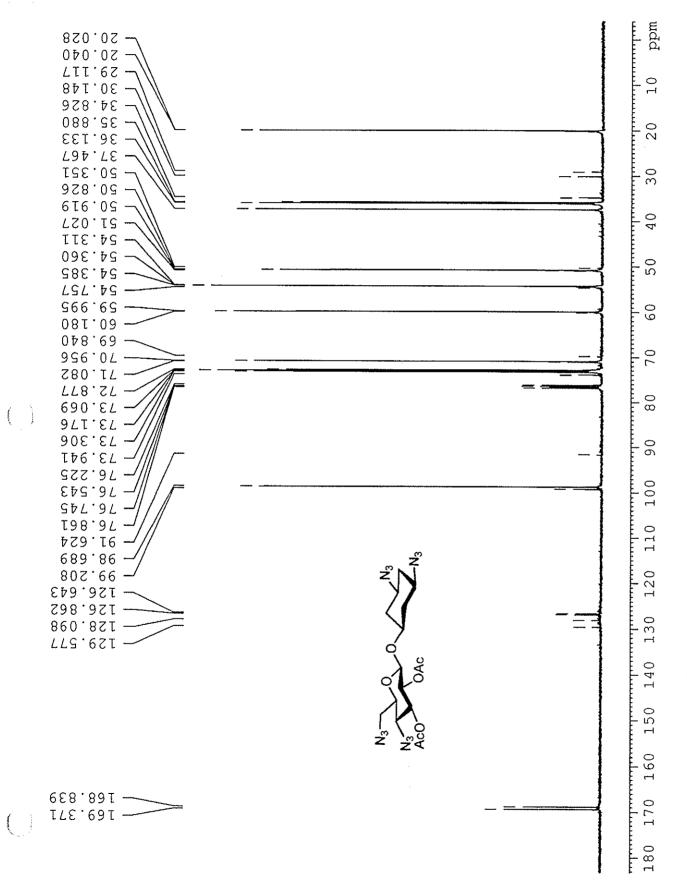
Cis, cis-3,5-diazidocyclohexyl \(\beta\text{-D-2,3,4-tri-}O\)-acetyl-6-azido-6-deoxyglucopyranoside (31).





Cis, cis-3,5-diaminocyclohexyl \(\beta \)-6-amino-6-deoxyglucopyranoside (32).

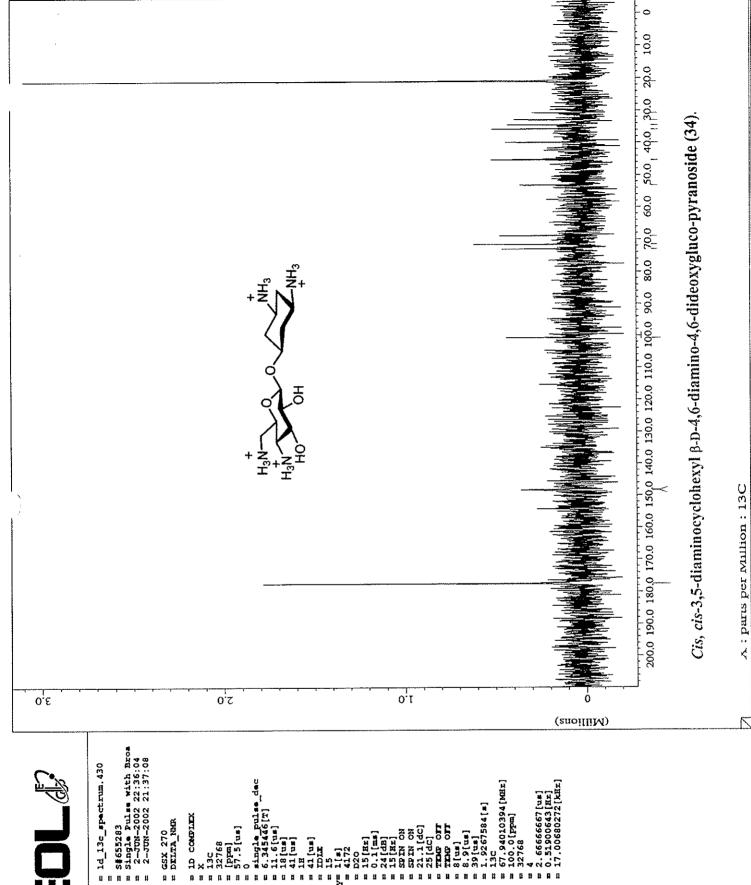
		eoxyglucopyranoside (33).
		tyl-4,6-diazido-4,6-dideoxy
Angular de la companya de la company	N ₃ N ₃ N ₃ A _{CO} O O N ₃ A _{CO} O O O O O O O O O O O O O O O O O O	Cis, cis-3,5-diazidocyclohexyl β-D-2,3-di-O-acetyl-4,6-diazido-4,6-dideoxyglucopyranoside (33). X: parts per Million: 1.H
	Tile Nume	S48

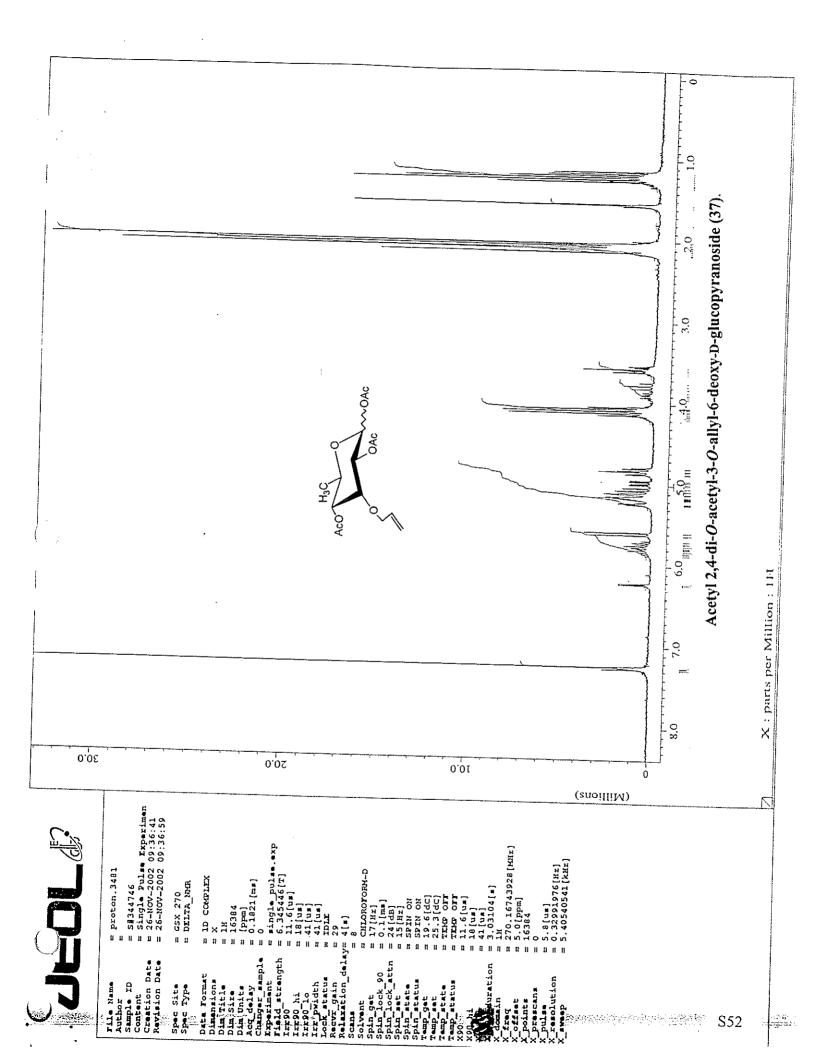


Cis, cis-3,5-diazidocyclohexyl \(\beta\text{-D-2,3-di-}O\)-acetyl-4,6-diazido-4,6-dideoxyglucopyranoside (33).

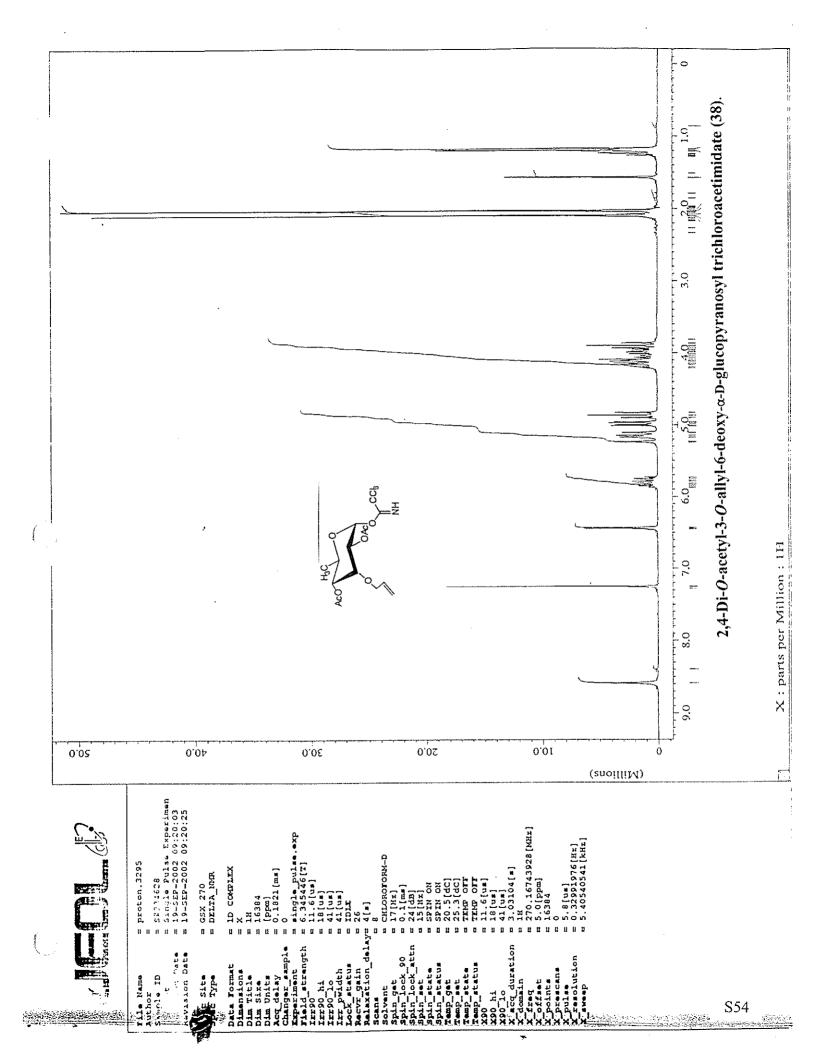
**************************************		HO OH	Significates per Million: 11H X: parts per Million: 11H
	0.2	0,6 0.1	(snoilliM)
1		Author A	·

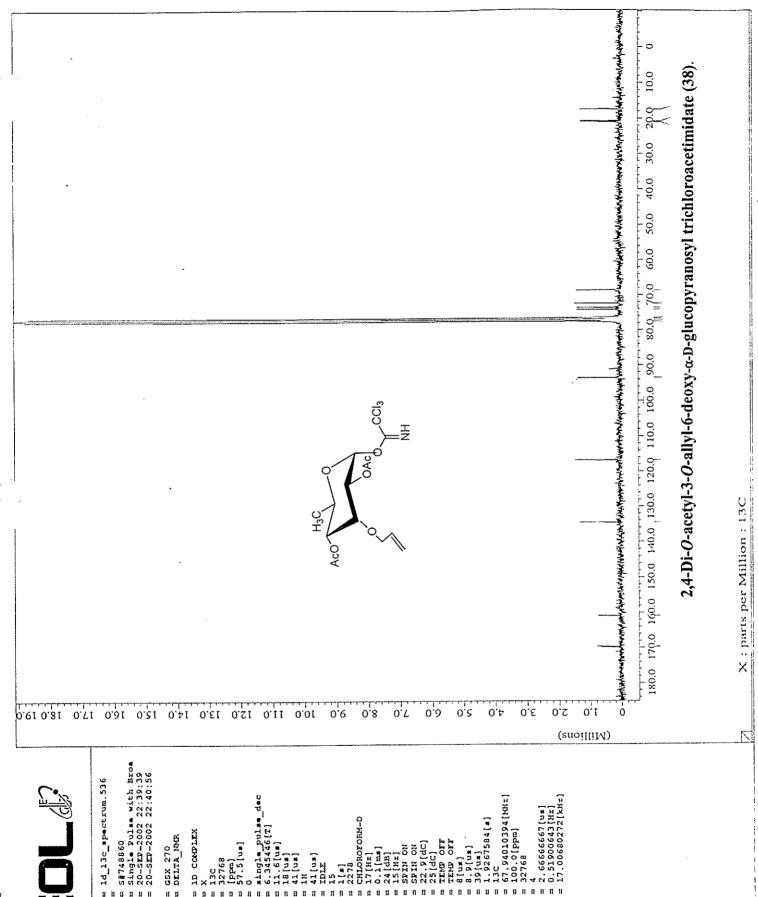






									****	30.0 20.0 10.0	
									· Tana	70.0 60.0 50.0 40.0	lucopyranoside (37).
						OAc			-	0.00 80.00 100.0 110.0 1	3-0-allyl-6-deoxy-D-g
,						27	, o v		:	140.0 130.0 120.0	Acetyl 2,4-di-O-acetyl-3-O-allyl-6-deoxy-D-glucopyranoside (37).
	0.00									180.0 170.0 160.0	Acetyl 2,4 X: parts per Million: 13C
	0.08	0.08	0.07	0.09	0.08	0.04	ο.οε	0.0Z	(znoilliM 0.01	0	
		# 1d_13c_spectrum.651 = 5#770679 = 5ingle Pulse with Bros = 20-JUN-2003 07:10:16 # 20-JUN-2003 08:39:37		# 34768 # 57.5[us] # 57.5[us] # 50.345446[T] # 6.345446[T] # 11.6[us]			= 27.10 On = 23.3[dC] = 40.3[dC] = TEMP OFF = ELMP OFF = 8.9[ux]	= 19[um] = 1.9265584[m] = 13C = 67.94010394[MHz] = 32768 = 4 66666667[um]	= 0.51900643[Hz] = 17.00680272[kHz]		
	5	File Name Author Sample ID Content Creation Date Revision Date	Spec Site Spec Type Data Format Dimensions	Dim Units Acq delay Changer sample Experiment Tield strength Trengo				X X90 Lo X Acq duration X Acmain X Fraq X Offset X Point* X Point* X Point* X Pulae	N X X		S53





5'-0-(2,4-Di-O-acetyl-3-O-allyl-6-deoxy-β-D-glucopyranosyl)-6,3'4'-tri-O-benzyl-1,3,2'6'-40 0.9 X : parts per Million : 114 tetraazidoneamine (39). 8.0 10 20 30 40 80 60 10 80 80 80 100110120130140120120120180180180051025025023024028050 (Millions) S#379693 Single Pulme Experimen 5-0cr-2002 10:34:55 5-0cr-2002 10:35:16 270.16743928 [MHz] 5.0 [ppm] proton,3336 1D COMPLEX

*trength

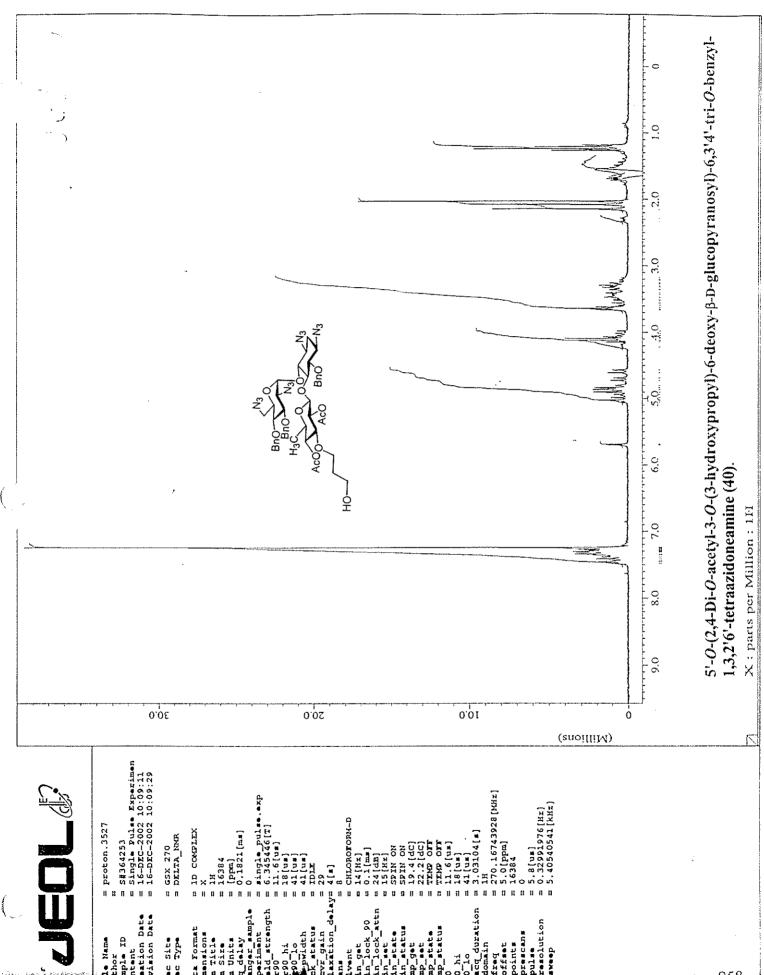
Creation Date Revision Date

Spec Site

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. . . 190.0 180.0 179.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 10.0 60.0 50.0 40.0 30.0 20.0 10.0 5'-O-(2,4-Di-O-acetyl-3-O-allyl-6-deoxy-β-D-glucopyranosyl)-6,3'4'-tri-O-benzyl-1,3,2'6'-X : parts per Million : 13C tetraazidoneamine (39). Acon 0.02 30.0 10.0 (knoilliM)



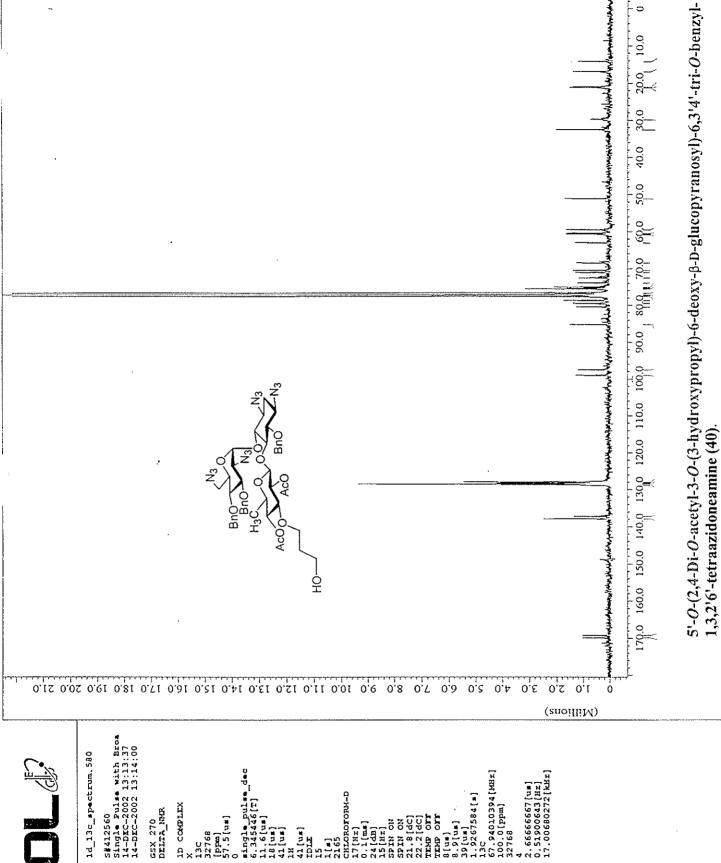
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			è

Creation Date Revision Date

Spec Site

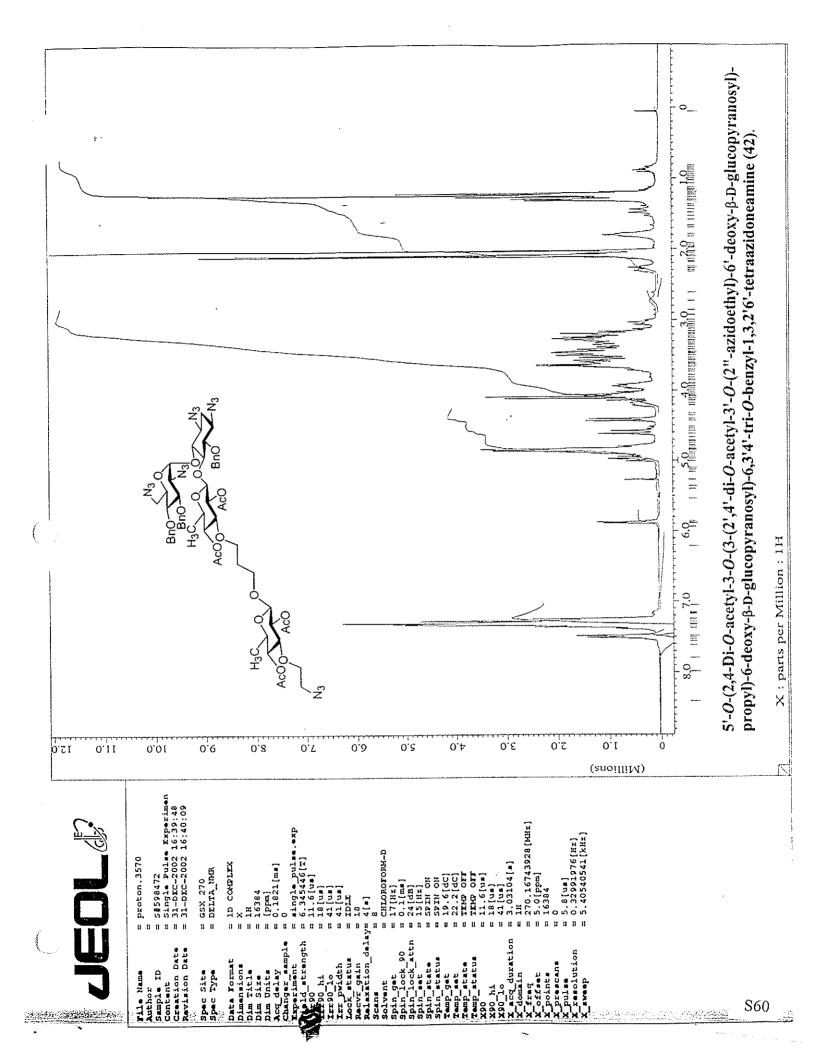
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S59

X: parts per Million: 13C



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ID COMPLEX GSX 270 DELTA_NMR

Data Format Spec Site

Dimensions Dim Title Dim Sixe Dim Units

5#600602

Tile Name

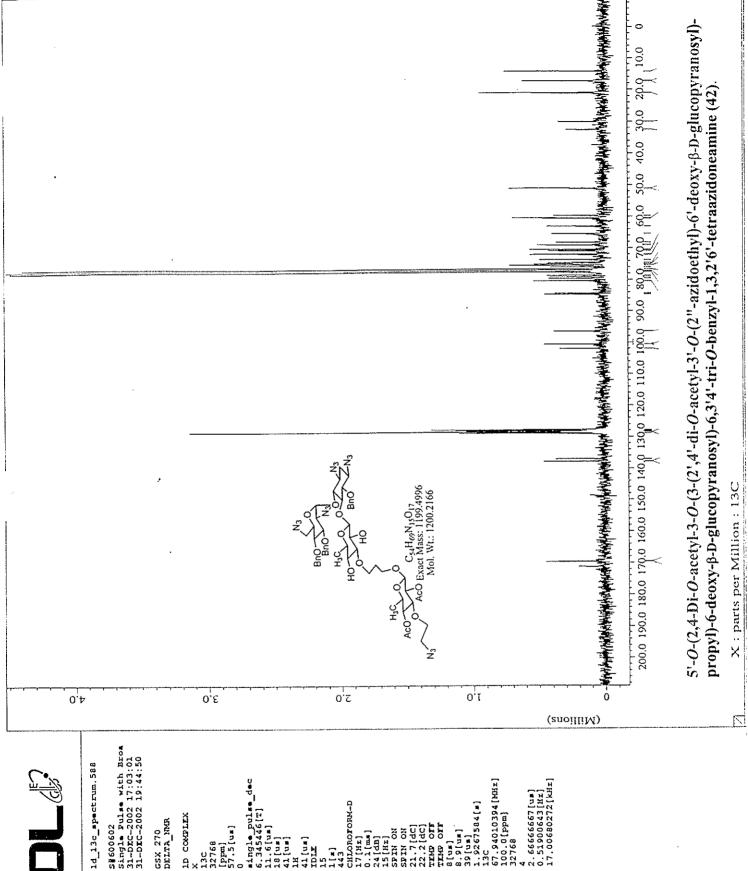
Creation Date

[ppm] 57.5[um]

Changer sample strength Mecvr gain Malaxation delay

#ttn

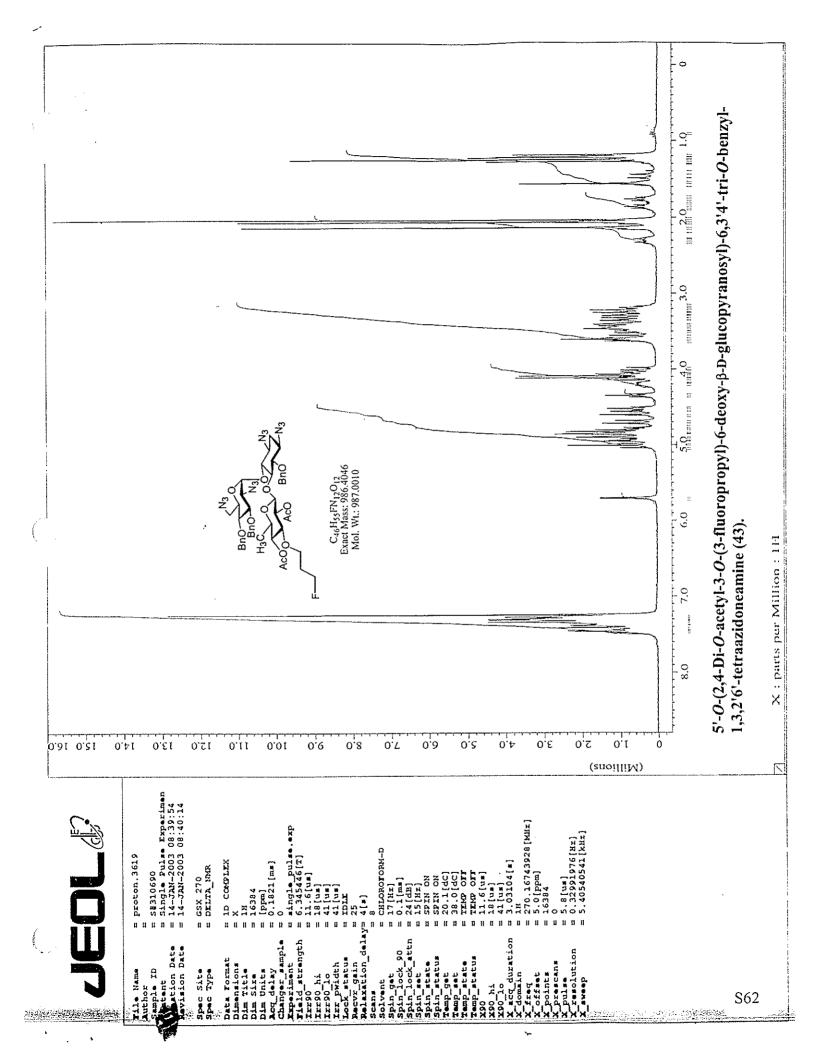
lock 20



[mm] 6

emp state

resolution



Author

Switchest

Switchest

Content

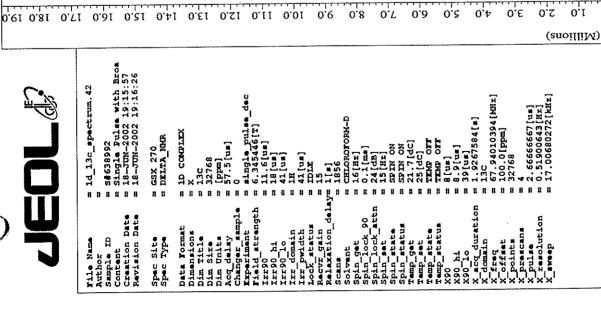
Conte

·					4	-0.0265	
						loroacetimidate (46).	
						2,3,4-Tri-O-acetyl-6-deoxy-6-fluoro-α-D-glucopyranosyl trichloroacetimidate (46).	
	0.04	ο,οε	20.0	10.0		8.0 7.0,	X: parts per Million: 1H
					(anoilliM)		
-	### ##################################		th the state of th	Temp state	Total [KRE]	AcO AcO NiH AcO NiH AcO OAce OAce OAce OAce OAce OAce OAce	4

								170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 3.2 4 Tri O ocetyl & deoxy-6-fluoro & D. chiconyranosyl trichlorocetimidate (46)
								170.0 160.0 150.0 140.0
I.I	6°0		9.0	<i>5</i> .0	+ 0	£.0	2.0	17

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		(1)-6,3'4'-tri-0-benzyl-1,3,2'6'-
		0 1 6.0 1 1 1 1 1 1 1 1 1
O'ST O	proton.223 s#581203 s#581203 s#581203 s#581203 s#581203 s#581203 s#581203 single Pulse Experimen 17—UNR-2002 16:10:145 GSX 270 DELLA NOR X X X X X X X X X X X X X	S'-O-(2,3,4-T tetraazidone
9		Aco O O O O O O O O O O O O O O O O O O O



5'-O-(2,3,4-Tri-O-acetyl-6-deoxy-6-fluoro-β-D-glucopyranosyl)-6,3'4'-tri-O-benzyl-1,3,2'6'tetraazidoneamine (47).

40.0

90.07 BOOM 70.06

100.0

110.0

120.0

1300

140.0

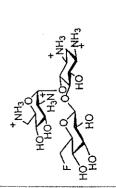
160.0 150.0

X : parts per Million : 13C

											8.0 7.0 6.0	5'-O-(6-Deoxy-6-fluoro-β-D-glucopyranosyl)neamine (TC033).	X: parts per Million: 1H
ļ-	4,2 E,2 <u>\$</u> .	2 1.2 0.2 6.	I 8.I	7.I	1 1.2 1,3 1	1.1 0.1 9.0	8.0 7.0 8.0	2.0 4.0 €.0 <u>2</u>		oilliM) I.0-2.0-	0.6		
أكد		#11e Name = proton.3005 Author = \$\frac{8}{2}\$ Sample ID = \$\frac{8}{2}\$\$ \$\frac{1}{2}\$\$ Total = \$\frac{1}{2}\$\$ \$\frac{1}{2}\$\$ Total = \$\frac{1}{2}\$\$\$ \$\frac{1}{2}\$\$\$ Total = \$\frac{1}{2}\$\$\$\$ Total = \$\frac{1}{2}\$\$\$\$\$\$\$\$ Pulse Experiment of \$2\$	Spec Site = GSX 270 Spec Type = DELTA_NOR	Format sions itle ixe iixe elay er sample		Relaxation delaym 4[s] Scans	Table to the state of the state	# 4 % H 5 % 9 C	X_pulse = 5.8[us] X_resolution = 0.32991976[Er] X_sweep = 5.40540541[kHz]	+ NH ³	F + 10 00 0 NH3	() ()	668

0.2

	0 t		ο ε	2.0	0,1	Ó
						(snoilliM)
= 1d_13c_spectrum.44 = 5#630161 = Single Fulse with Broa = 1_JUL_2002_22:47:52 = 1_JUL_2002_22:47:52		= 1D COMPLEX = X = 13C = 32768 = [ppm]		-	H	0.51900643[Hz] 17.00680272[KHz]
File Name Author Sample ID Content Creation Date Revision Date	Spec Site	a Format busions Title Size Units	Acq. calay changer ample = Experiment = Experiment = Experiment = Experiment = Experiment = Exponent = Exponen		etatus ii lo C duration gd sat nuts secans	X resolution u



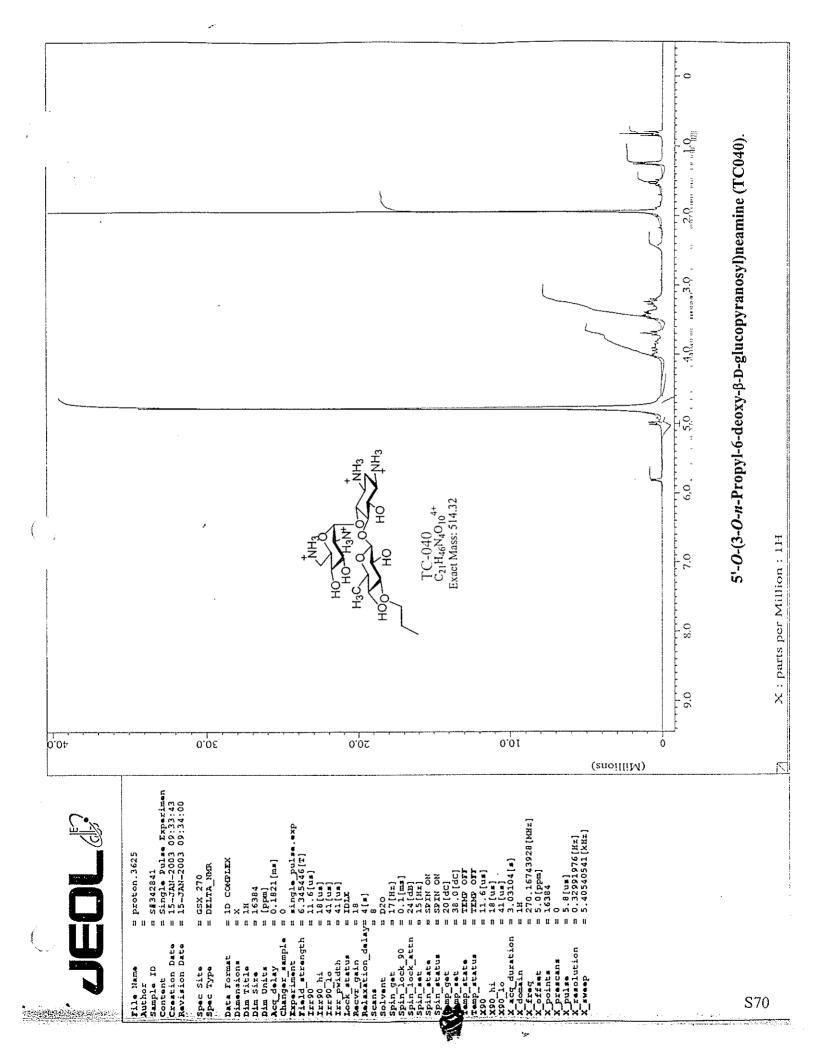
5'-O-(6-Deoxy-6-fluoro-β-D-glucopyranosyl)neamine (TC033).

X : parts per Million : 13C

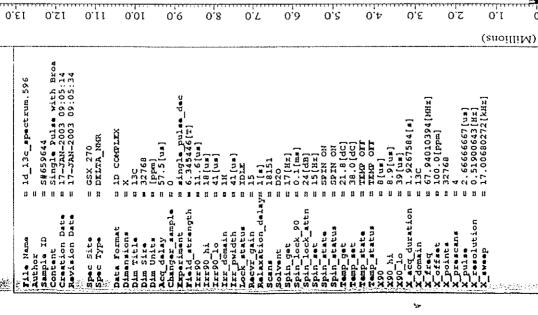
-0

70,0 60.0 50,0 40.0 30,0 20.0 10.0

200.0 190.0 180,0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0



14.0

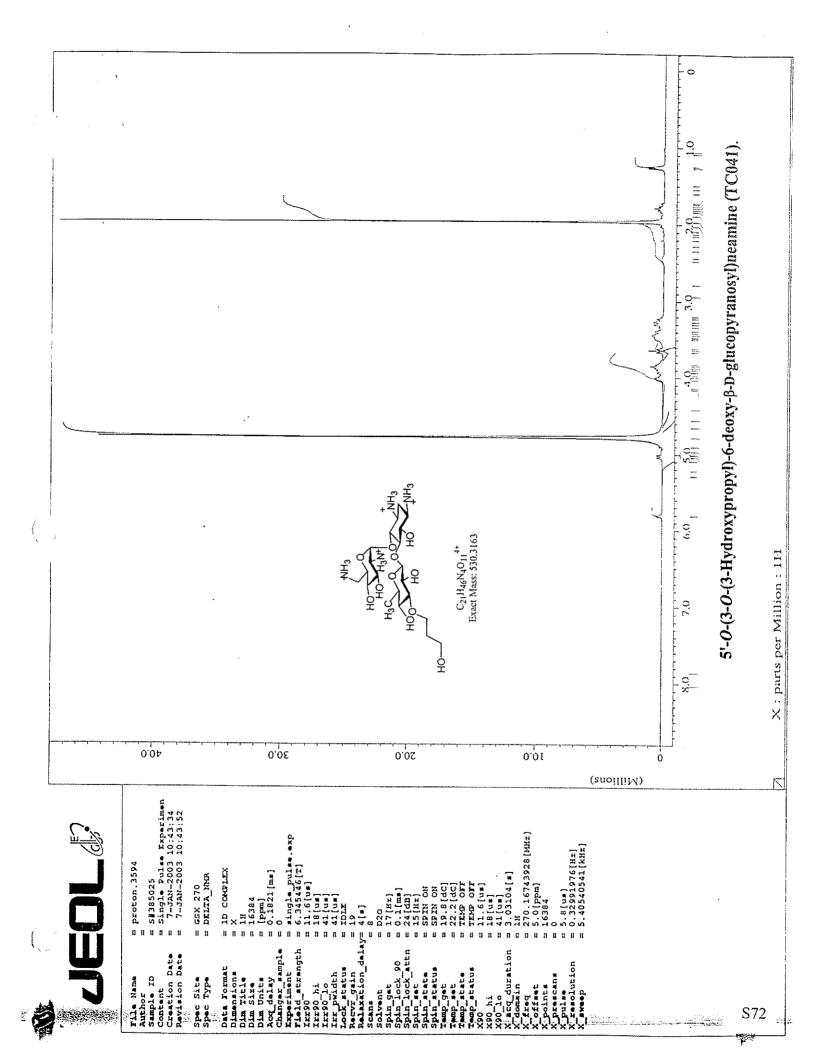


0,E 0.8 0.4 0,8 0.9 0,1 0.7 0,2

5'-O-(3-O-n-Propyl-6-deoxy-\bar{\theta}\-D-glucopyranosyl)neamine (TC040).

220.0210.0200.0190.0180,0170.0160.0150.0140.0130.0120.0110.0100.0 90.0 80.0 700 60.0 500 40.0 30.0 20.0 10.0

X : parts per Million : 13C



HOO HO HO HO WH

(Ailillions)

0.65 0.45 0.45 0.60 0.81 0.71 0.81 0.81 0.81 0.81 0.81 0.81 0.81 0.91 0.92 0.8 0.7 0.8 0.8 0.8 0.8 0.8 0.5 0.5

0'01--

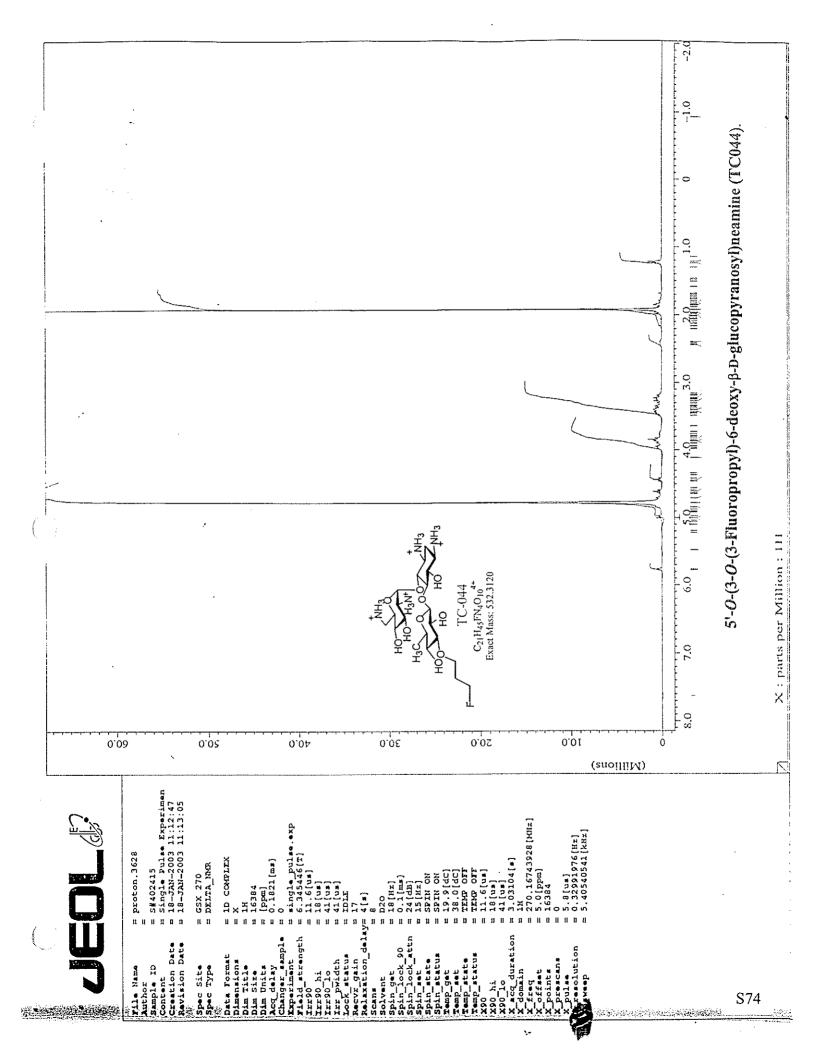
70,0 60,0 50,0 40.0 30,0 20.0 10.0

220,0210,0200,0190,0180,0170,0160,0150,0140,0130,0120,0110,01,00,0 90.0 ,80.0 ,

5'-O-(3-O-(3-Hydroxypropyl)-6-deoxy-\bar{b}-D-glucopyranosyl)neamine (TC041).

X : parts per Million : 13C

S73



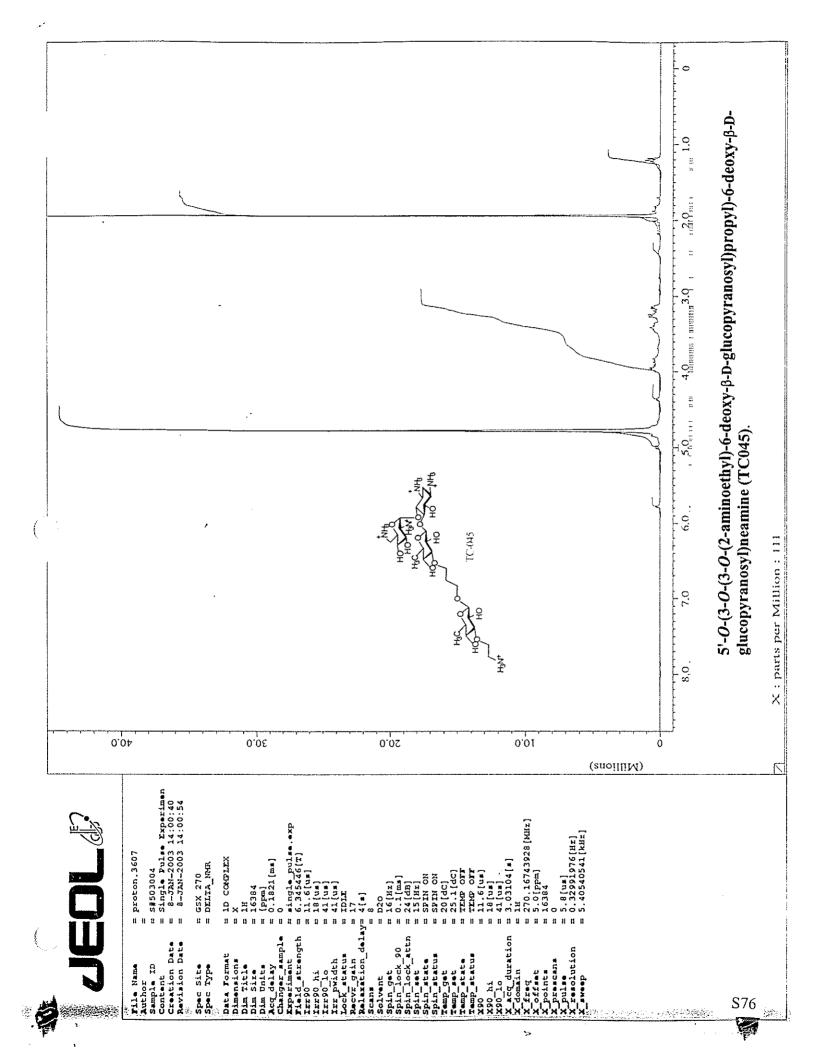


= Single Pulse with Bross = 19-JAN-2003 09:09:48 = 19-JAN-2003 09:10:07 = 1d_13c_spectrum.598 2.6666667[u#] 0.51900643[Hz] 17.00680272[kHz] = 67.94010394[MHz] = 100.0[ppm] = 32768 = 39[u#] = 1.9267584[#] 1D COMPLEX GSX 270 DELTA NAGR . 5 [u.s.] File Name Author Sample ID Content Creation Date Revision Date Data Format Spec Site Spec Type ٠,-

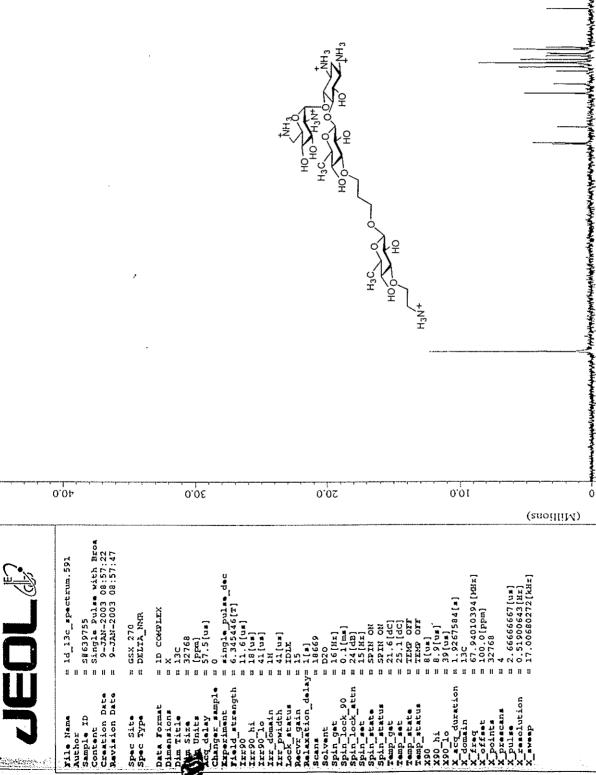
S75

X: parts per Million: 13C

Z







5'-O-(3-O-(3-O-(2-aminoethyl)-6-deoxy-b-D-glucopyranosyl)propyl)-6-deoxy-b-Dglucopyranosyl)neamine (TC045).

X : parts per Million : 13C

220.0210.0200.0190.0180,0170.0160.0150.0140.0130.0120.0110.0100.0 90.0 180.0 170.0 60.0 50.0 40.0 30.0 20.0 10.0

-10.0

Proton magnetic resonance spectra were recorded using spectrometers at 270 or 400 MHz. Chemical shifts were reported as parts per million (ppm) downfield from tetramethylsilane in δ unit, and coupling constants were given in cycles per second (Hz). Splitting patterns were designed as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. 13 C spectra were obtained using spectrometers at 68 MHz or 100 MHz. Routine 13 C NMR spectra were fully decoupled by broadband waltz decoupling. All NMR spectra were recorded at ambient temperature unless otherwise noted. Purchased chemical reagents and starting materials were used without purification unless otherwise noted. Dichloromethane was distilled over CaH₂. Other solvents were used without purification.

Methyl 4-azido-2,3,6-tri-*O*-benzyl-4-deoxy-a-D-glucopyranoside (6). Please refer to the procedure for the preparation of 4. 1 H NMR (270 MHz, CDCl₃) δ 7.2 - 7.4 (m, 15H), 4.95 (d, J = 11.6 Hz, 1H), 4.80 (d, J = 11.6 Hz, 1H), 4.78 (d, J = 12.2 Hz, 1H), 4.63 (d, J = 12.2 Hz, 1H), 4.62 (d, J = 12.2 Hz, 1H), 4.60 (d, J = 3.3 Hz, 1H), 4.49 (d, J = 12.2 Hz, 1H), 3.84 (dd, J = 9.2 Hz, J = 9.6 Hz, 1H), 3.5 - 3.7 (m, 5H), 3.33 (s, 3H); 13 C NMR (68 MHz, CDCl₃) δ 138.10 (s), 137.95 (s), 137.81 (s), 128.6 (s), 128.5 (s), 128.4 (s), 128.2 (s), 128.1 (s), 127.9 (s), 127.8 (s), 98.4 (s), 80.2 (s), 79.7 (s), 75.8 (s), 73.6 (s), 73.4 (s), 69.3 (s), 68.7 (s), 61.8 (s), 55.5 (s); LRFAB m/e 507 [M+NH₄]⁺; HRFAB Calcd for C₂₈H₃₅N₄O₅ [M+NH₄]⁺ m/e 507.2607; measure m/e 507.2611.

Methyl 4,6-diazido-2,3-di-*O***-benzyl-4,6-dideoxy-a-D-galactopyranoside (8)**. Please refer to the procedure for the preparation of **4**. 1 H NMR (270 MHz, CDCl₃) δ 7.2-7.4 (m, 10H), 4.85 (d, J =11.7 Hz, 1H), 4.84 (d, J =12.1 Hz, 1H), 4.75 (d, J =11.7 Hz, 1H), 4.65 (d, J =12.1 Hz, 1H), 4.61 (d, J = 3.8 Hz, 1H), 4.04 (dd, J = 9.7 Hz, J = 3.8 Hz, 1H), 3.85 (dd, J = 9.7 Hz, J = 3.8 Hz, 1H),

3.8 - 3.9 (m, 2H), 3.53 (dd, J = 12.6 Hz, J = 7.9 Hz, 1H), 3.38 (s, 3H), 3.19 (dd, J = 12.6 Hz, J = 5.1 Hz, 1H); 13 C NMR (68 MHz, CDCl₃) δ 137.9 (s), 137.8 (s), 128.4 (s), 128.3 (s), 127.9 (s), 127.8 (s), 127.7 (s), 127.6 (s), 98.5 (s), 77.5 (s), 75.7 (s), 73.7 (s), 73.2 (s), 67.4 (s), 61.4 (s), 55.4 (s), 51.5 (s); LRCI m/e 442.4 [M+NH₄]⁺; HRCI Calcd for $C_{21}H_{28}N_7O_5$ [M+NH₄]⁺ m/e 442.2203; measure m/e 442.2198.

Methyl 4-azido-2,3-di-*O*-benzyl-4,6-dideoxy-a-D-galactopyranoside (10). Please refer to the procedure for the preparation of 4. ¹H NMR (270 MHz, CDCl₃) δ 7.2 - 7.4 (m, 10H), 4.84 (d, J = 11.9 Hz, 1H), 4.82 (d, J = 12.2 Hz, 1H), 4.73 (d, J = 11.9 Hz, 1H), 4.64 (d, J = 12.2 Hz, 1H), 4.54 (d, J = 3.6 Hz, 1H), 4.01 (dd, J = 9.8 Hz, J = 3.6 Hz, 1H), 3.89 (dq, J = 6.3 Hz, J = 1.3 Hz, 1H), 3.82 (dd, J = 9.8 Hz, J = 3.6 Hz, 1H), 3.69 (dd, J = 3.6 Hz, J = 1.3 Hz, 1H), 3.33 (s, 3H), 1.21 (d, J = 6.3 Hz, 3H); ¹³C NMR (68 MHz, CDCl₃) δ 138.34 (s), 138.29 (s), 128.54 (s), 128.48 (s), 128.2 (s), 127.90 (s), 127.84 (s), 127.8 (s), 98.8 (s), 78.1 (s), 76.0 (s), 73.8 (s), 73.3 (s), 65.1 (s), 64.3 (s), 55.5 (s), 17.4 (s); LRFAB m/e 401 [M+NH₄]⁺; HRFAB Calcd for C₂₁H₂₉N₄O₄ [M+NH₄]⁺ m/e 401.2189; measure m/e 401.2204.

Methyl 2,3-di-*O*-benzyl-6-deoxy-a-D-galactopyranoside (11). Please refer to the procedure for the preparation of 5. 1 H NMR (270 MHz, CDCl₃) δ 7.2 - 7.4 (m, 10H), 4.79 (d, J = 11.9 Hz, 2H), 4.69 (d, J = 11.6 Hz, 1H), 4.65 (d, J = 11.9 Hz, 1H), 4.60 (d, J = 3.3 Hz, 1H), 3.7 - 3.9 (m, 4H), 3.36 (s, 3H), 2.42 (broad, 1H, 4-OH), 1.25 (d, J = 6.6 Hz, 3H); 13 C NMR (68 MHz, CDCl₃) δ 138.4 (s), 138.2 (s), 128.6 (s), 128.5 (s), 128.1 (s), 127.95 (s), 127.88 (s), 98.6 (s), 78.0 (s), 75.5 (s), 73.5 (s), 72.9 (s), 70.4 (s), 65.1 (s), 55.4 (s), 16.2 (s); LRFAB m/e 376 [M+NH₄]⁺; HRFAB Calcd for C₂₁H₃₀N₁O₅ [M+NH₄]⁺ m/e 376.2124; measure m/e 376.2131.

Methyl 4-azido-2,3-di-*O*-benzyl-4,6-dideoxy-a-D-glucopyranoside (12). Please refer to the procedure for the preparation of 4. 1 H NMR (270 MHz, CDCl₃) δ 7.2 - 7.4 (m, 10H), 4.94 (d, J = 10.5 Hz, 1H), 4.78 (d, J = 10.5 Hz, 1H), 4.76 (d, J = 12.0 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 3.7 Hz, 1H), 3.81 (dd, J = 9.6 Hz, J = 9.6 Hz, 1H), 3.50 (dd, J = 9.6 Hz, J = 3.7 Hz, 1H), 3.4 - 3.5 (m, 1H), 3.35 (s, 3H), 3.06 (dd, J = 9.6 Hz, J = 9.9 Hz, 1H), 1.25 (d, J = 5.9 Hz, 3H); 13 C NMR (68 MHz, CDCl₃) δ 138.1 (s), 138.0 (s), 128.6 (s), 128.5 (s), 128.4 (s), 128.2 (s), 128.1 (s), 127.9 (s), 98.1 (s), 80.7 (s), 79.9 (s), 75.8 (s), 73.4 (s), 68.1 (s), 65.9 (s), 55.4 (s), 18.5 (s); LRFAB m/e 401 [M+NH₄]⁺; HRFAB Calcd for C₂₁H₂₉N₄O₄ [M+NH₄]⁺ m/e 401.2189; measure m/e 401.2203.

Methyl 6-azido-2,3-di-*O*-benzyl-6-deoxy-a-D-galactopyranoside (14). Please refer to the procedure for the preparation of 5. 1 H NMR (270 MHz, CDCl₃) δ 7.2 - 7.4 (m, 10H), 4.80 (d, J = 11.5 Hz, 1H), 4.75 (d, J = 11.5 Hz, 1H), 4.69 (d, J = 8.6 Hz, 1H), 4.66 (d, J = 3.6 Hz, 1H), 4.64 (d, J = 8.6 Hz, 1H), 3.8 - 3.9 (m, 3H), 3.83 (dd, J = 8.2 Hz, J = 3.6 Hz, 1H), 3.59 (dd, J = 12.8 Hz, J = 8.4 Hz, 1H), 3.40 (s, 3H), 3.26 (dd, J = 12.8 Hz, J = 4.3 Hz, 1H), 2.48 (s, 1H, 4-OH); 13 C NMR (68 MHz, CDCl₃) δ 138.3 (s), 138.0 (s), 128.7 (s), 128.5 (s), 128.1 (s), 127.99 (s), 127.96 (s), 98.6 (s), 77.3 (s), 75.6 (s), 73.6 (s), 73.2 (s), 69.8 (s), 68.3 (s), 55.6 (s), 51.3 (s); LRFAB m/e 417 [M+NH₄]⁺; HRFAB Calcd for C₂₁H₂₉N₄O₅ [M+NH₄]⁺ m/e 417.2138; measure m/e 417.2122.

Methyl 4,6-diazido-2,3-di-*O***-benzyl-4,6-dideoxy-a-D-glucopyranoside** (**15**). Please refer to the procedure for the preparation of **4**. 1 H NMR (270 MHz, CDCl₃) δ 7.2 - 7.4 (m, 10H), 4.97 (d, J = 10.6 Hz, 1H), 4.79 (d, J = 12.0 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H), 4.60

(d, J = 2.6 Hz, 1H), 3.87 (dd, J = 9.6 Hz, J = 9.0 Hz, 1H), 3.5 - 3.6 (m, 3H), 3.4 - 3.5 (m, 2H), 3.36 (s, 3H); ¹³C NMR (68 MHz, CDCl₃) δ 137.9(s), 137.8 (s), 128.6 (s), 128.5 (s), 128.4 (s), 128.20 (s), 128.16 (s), 128.0 (s), 98.2 (s), 79.86 (s), 79.85 (s), 75.8 (s), 73.5 (s), 69.2 (s), 62.5 (s), 55.7 (s), 51.8 (s); LRFAB m/e 442 [M+NH₄]⁺; HRFAB Calcd for C₂₁H₂₈N₇O₅ [M+NH₄]⁺ m/e 442.2203; measure m/e 442.2216.

Acetyl 4-azido-2,3,6-tri-*O*-acetyl-4-deoxy-a-D-galactopyranoside (16). ¹H NMR (270 MHz, CDCl₃) (α anomer) δ 6.23 (d, J = 2.6 Hz, 1H), 5.32 (m, 2H), 4.0 - 4.2 (m, 4H), 2.072 (s, 3H), 2.070 (s, 3H), 2.01 (s, 3H), 1.95 (s, 3H); ¹³C NMR (68 MHz, CDCl₃) (α anomer) δ 170.4 (s), 170.1 (s), 169.7 (s), 168.8 (s), 89.5 (s), 69.5 (s), 68.5 (s), 66.5 (s), 62.5 (s), 60.4 (s), 20.8 (s), 20.7 (s), 20.5 (s, 2 carbons); LRFAB m/e 380.1 [M+Li]⁺; HRFAB Calcd for $C_{14}H_{19}N_3O_9Li$ [M+Li]⁺ m/e 380.1281; measure m/e 380.1274.

Acetyl 4-azido-2,3,6-tri-*O*-acetyl-4-deoxy-a-D-glucopyranoside (17). ¹H NMR (270 MHz, CDCl₃) (α anomer) δ 6.27 (d, J = 4.0 Hz, 1H), 5.45 (dd, J = 10.2 Hz, J = 9.9 Hz, 1H), 5.03 (dd, J = 10.2 Hz, J = 4.0 Hz, 1H), 4.35 (dd, J = 12.5 Hz, J = 2.5 Hz, 1H), 4.26 (dd, J = 12.5 Hz, J = 3.6 Hz, 1H), 3.87 (ddd, J = 10.2 Hz, J = 3.6 Hz, J = 2.5 Hz, 1H), 3.67 (dd, J = 10.2 Hz, J = 9.9 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 6H), 2.00 (s, 3H); ¹³C NMR (68 MHz, CDCl₃) (α anomer) δ 170.5 (s), 169.90 (s), 169.84 (s), 168.4 (s), 89.2 (s), 70.5 (s), 70.2 (s), 69.3 (s), 62.4 (s), 59.9 (s, C-4), 21.0 (s), 20.82 (s), 20.77 (s), 20.5 (s); LRFAB m/e 380.1 [M+Li]⁺; HRFAB Calcd for C₁₄H₁₉N₃O₉Li [M+Li]⁺ m/e 380.1281; measure m/e 380.1272.

Acetyl 4,6-diazido-2,3-di-*O*-acetyl-4,6-dideoxy-a-D-galactopyranoside (18). ¹H NMR (270 MHz, CDCl₃) (α anomer) δ 6.30 (d, J = 2.6 Hz, 1H), 5.38 (m, 2H), 4.14 (m, 1H), 4.09 (ddd, J = 6.6 Hz, J = 6.9 Hz, J = 1.3 Hz, 1H), 3.54 (dd, J = 12.5 Hz, J = 6.6 Hz, 1H), 3.37 (dd, J = 12.5 Hz, J = 6.9 Hz, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.01 (s, 3H); ¹³C NMR (68 MHz, CDCl₃) (α anomer) δ 170.2 (s), 169.8 (s), 168.8 (s), 89.5 (s), 69.7 (s), 69.5 (s), 66.5 (s), 60.4 (s), 50.8 (s), 20.9 (s), 20.60 (s), 20.56 (s); LRFAB m/e 363.1 [M+Li]⁺; HRFAB Calcd for $C_{12}H_{16}N_6O_7Li$ [M+Li]⁺ m/e 363.1241; measure m/e 363.1234.

Acetyl 4azido-2,3-di-*O*-acetyl-4,6-dideoxy-a-D-galactopyranoside (19). ¹H NMR (270 MHz, CDCl₃) (α anomer) δ 6.22 (d, J = 2.6 Hz, 1H), 5.30 (m, 2H), 4.16 (qd, J = 6.3 Hz, J = 1.0 Hz, 1H), 3.92 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 1.97 (s, 3H), 1.24 (d, J = 6.3 Hz, 3H); ¹³C NMR (68 MHz, CDCl₃) (α anomer) δ 170.0 (s), 169.6 (s), 168.9 (s), 89.6 (s), 69.9 (s), 67.1 (s), 66.4 (s), 63.8 (s. C-4), 20.7 (s), 20.5 (s, 2 carbons), 17.0 (s); LRFAB m/e 322.1 [M+Li]⁺; HRFAB Calcd for $C_{12}H_{17}N_3O_7Li$ [M+Li]⁺ m/e 322.1227; measure m/e 322.1235.

Acetyl 4-azido-2,3-di-*O*-acetyl-4,6-dideoxy-a-D-glucopyranoside (20). ¹H NMR (270 MHz, CDCl₃) (α anomer) δ 6.22 (d, J = 2.6 Hz, 1H), 5.3 (m, 2H), 4.16 (qd, J = 6.3 Hz, J = 1.0 Hz, 1H), 3.92 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 1.97 (s, 3H), 1.24 (d, J = 6.3 Hz, 3H); ¹³C NMR (68 MHz, CDCl₃) (α anomer) δ 170.0 (s), 169.1 (s), 89.2 (s), 70.4 (s), 69.7 (s), 68.6 (s), 65.7 (s), 20.1 (s), 20.8 (s), 20.6 (s), 18.3 (s); LRFAB m/e 363.1 [M+Li]⁺; HRFAB Calcd for $C_{12}H_{16}N_6O_7Li$ [M+Li]⁺ m/e 363.1241; measure m/e 363.1231.

Acetyl 4,6-diazido-2,3-di-O-acetyl-4,6-dideoxy-a-D-glucopyranoside (22). ¹H NMR (270 MHz, CDCl₃) (α anomer) δ 6.29 (d, J = 3.6 Hz, 1H), 5.45 (dd, J = 10.1 Hz, J = 9.6 Hz, 1H), 5.02 (dd, J = 10.1 Hz, J = 3.6 Hz, 1H), 3.77 (dd, J = 10.2 Hz, J = 9.6 Hz, 1H), 3.58 (dd, J = 13.6 Hz, J = 2.0 Hz, 1H), 3.50 (ddd, J = 10.2 Hz, J = 3.4 Hz, J = 2.0 Hz, 1H), 3.43 (dd, J = 13.6 Hz, J = 3.4 Hz, 1H), 2.15 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H); ¹³C NMR (68 MHz, CDCl₃) (α anomer) δ 169.9 (s), 169.8 (s), 168.8 (s), 89.2 (s), 71.4 (s), 69.3 (s), 69.3(s), 60.0 (s), 51.0 (s), 21.0 (s), 20.8 (s), 20.5 (s); LRFAB m/e 363.1 [M+Li]⁺; HRFAB Calcd for $C_{12}H_{16}N_6O_7Li$ [M+Li]⁺ m/e 363.1241; measure m/e 363.1231.

For the synthesis of 23 - 29, please refer to reference 28.

2,4-Di-*O*-acetyl-3-*O*-allyl-6-deoxy-a-D-glucopyranosyl trichloroacetimidate (38). Please refer the general procedure for the preparation of glycosyl trichloroacetimidate. 1 H NMR (270 M Hz, CDCl₃) δ 8.58 (s, N*H*CCl₃), 6.44 (d, J = 3.6 Hz, 1H), 5.80 (dddd, J = 17.4 Hz, J = 10.2 Hz, J = 5.3 Hz, J = 5.6 Hz, 1H), 5.21 (dd, J = 17.4 Hz, J = 1.6 Hz, 1H), 5.12 (dd, J = 10.2 Hz, J = 1.6 Hz, 1H), 4.98 (dd, J = 9.9 Hz, J = 3.6 Hz, 1H), 4.87 (dd, J = 9.9 Hz, J = 9.6 Hz, 1H), 4.17 (dd, J = 12.9 Hz, J = 5.3 Hz, 1H), 4.07 (dd, J = 12.9 Hz, J = 5.6 Hz, 1H), 3.97(dq, J = 9.9 Hz, J = 6.3 Hz, 1H), 3.90 (dd, J = 9.9 Hz, J = 9.6 Hz, 1H), 2.10 (s, 3H), 2.03 (s, 3H), 1.19 (d, J = 6.3 Hz, 3H); 13 C NMR (68MHz, CDCl₃) δ 169.9 (s), 169.6 (s), 160.9 (s), 134.5 (s), 116.8 (s), 93.6 (s), 76.5 (s), 74.2 (s), 73.6 (s), 72.4 (s), 68.7 (s), 21.0 (s), 20.7 (s), 17.4 (s).

2,3,4-Tri-*O***-acetyl-6-deoxy-6-fluoro-a-D-glucopyranosyl trichloroacetimidate** (**46**). Please refer the general procedure for the preparation of glycosyl trichloroacetimidate. ¹H NMR (270

MHz, CDCl₅) δ 8.67 (s, 1H), 6.54 (d, J = 5.4 Hz, 1H), 5.55 (t, J = 10.8 Hz, 1H), 5.15 (t, J = 10.8 Hz, 1H), 5.05 (dd, J = 8.1 Hz, J = 5.4 Hz, 1H), 4.6 – 4.5 (m, 1H), 4.4 – 4.3 (m, 1H), 4.2 – 4.1 (m, 1H), 2.03 (s, 3H), 2.0 (s, 3H), 1.9 (s, 3H); ¹³C NMR (68 MHz, CDCl₅) δ 170.1 (s), 169.8 (s), 169.5 (s), 160.8 (s), 92.9 (s), 90.7 (s), 80.7 (d, J_{CF} = 177 Hz), 70.7 (d, J_{CF} = 19 Hz), 69.7 (d, J_{CF} = 8.8 Hz), 67.6 (s), 67.4 (s), 20.8 (s), 20.6 (s), 20.5 (s).

Cis, cis-3,5-diazidocyclohexyl b-D-2,3,4-tri-O-acetyl-6-azido-6-deoxyglucopyranoside (31). Please refer to the general procedure for glycosylation. The compound is mixed with inseparable impurities, and characterized only by 1 H and 13 C NMR. 1 H NMR (270 MHz, CDCl₃) δ 5.19 (t, J = 9.6 Hz, 1H), 4.94 (dd, J = 9.6 Hz, J = 7.9 Hz, 1H), 4.93 (t, J = 9.6 Hz, 1H), 4.63 (d, J = 7.9 Hz, 1H), 3.67 (ddd, J = 9.6 Hz, J = 4.7 Hz, J = 2.3 Hz, 1H), 3.60-3.78 (m, 1H), 3.30-3.51 (m, 1H), 3.32 (tt, J = 11.9 Hz, J = 4.1 Hz, 2H), 3.11 (dd, J = 13.2 Hz, J = 2.3 Hz), 2.16-2.38 (m, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99(s, 3H), 1.18-1.46(m, 3H); 13 C NMR (68 MHz, CDCl₃) δ 169.6 (s), 168.9 (s), 168.6 (s), 98.7 (s), 73.7 (s), 73.3 (s), 71.9 (s), 70.8 (s), 69.1 (s), 54.6 (s), 54.4 (s), 50.6 (s), 37.5 (s), 36.1 (s), 35.9 (s), 35.8 (s), 20.1 (s), 20.0 (s).

Cis, cis-3,5-diazidocyclohexyl b-D-2,3,4-tri-O-acetyl-6-azido-6-deoxyglucopyranoside (31). Please refer to the general procedure for glycosylation. The compound is mixed with inseparable impurities, and characterized only by 1 H and 13 C NMR. 1 H NMR (270 MHz, CDCl₃) δ 5.19 (t, J = 9.6 Hz, 1H), 4.94 (dd, J = 9.6 Hz, J = 7.9 Hz, 1H), 4.93 (t, J = 9.6 Hz, 1H), 4.63 (d, J = 7.9 Hz, 1H), 3.67 (ddd, J = 9.6 Hz, J = 4.7 Hz, J = 2.3 Hz, 1H), 3.60-3.78 (m, 1H), 3.30-3.51 (m, 1H), 3.32 (tt, J = 11.9 Hz, J = 4.1 Hz, 2H), 3.11 (dd, J = 13.2 Hz, J = 2.3 Hz), 2.16-2.38 (m, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99(s, 3H), 1.18-1.46(m, 3H); 13 C NMR (68 MHz, CDCl₃) δ 169.6 (s), 168.9 (s), 168.6 (s),

98.7 (s), 73.7 (s), 73.3 (s), 71.9 (s), 70.8 (s), 69.1 (s), 54.6 (s), 54.4 (s), 50.6 (s), 37.5 (s), 36.1 (s), 35.9 (s), 35.8 (s), 20.1 (s), 20.0 (s).

Cis, cis-3,5-diazidocyclohexyl b-D-2,3-di-O-acetyl-4,6-diazido-4,6-dideoxyglucopyranoside (33). Please refer to the general procedure for glycosylation. 1 H NMR (270 MHz, CDCl₃) δ 5.11 (t, J = 9.6 Hz, 1H), 4.85 (dd, J = 9.6 Hz, J = 7.9 Hz, 1H), 4.58 (d, J = 7.9 Hz, 1H), 3.64 (tt, J = 12.0 Hz, J = 4.3 Hz, 1H), 3.57 (t, J = 9.6 Hz, 1H), 3.45 (d, J = 4.3 Hz, 1H), 3.40 (dt, J = 9.6 Hz, J = 4.3 Hz, 1H), 3.25 (tt, J = 12.0 Hz, J = 4.3 Hz, 2H), 2.27-2.38 (m, 1H), 2.15-2.26 (m, 2H), 2.06 (s, 3H), 2.00 (s, 3H), 1.27 (q, J = 12.0 Hz, 2H), 1.15-1.45 (m, 1H); 13 C NMR (68 MHz, CDCl₃) δ 169.4 (s), 168.8 (s), 98.7 (s), 73.3 (s), 73.1 (s), 72.9 (s), 71.0 (s), 60.0 (s), 54.4 (s), 54.3 (s), 50.8 (s), 37.5 (s), 36.1 (s), 35.9 (s), 20.1 (s), 20.0 (s); LRFAB m/e 501 [M+Na]⁺; HRFAB Calcd for $C_{12}H_{22}N_{12}O_6Na$ [M+Na]⁺ m/e 501.1683; measure m/e 501.1692.

5-O-(2,4-Di-O-acetyl-3-O-allyl-6-deoxy-b-D-glucopyranosyl)-6,3'4'-tri-O-benzyl-1,3,2'6'-

tetra-azidoneamine (39). Please refer to the general procedure for glycosylation. ¹H NMR (270 M Hz, CDCl₃) δ 7.2 – 7.5 (m, 15H), 5.76 (dddd, J = 17.1 Hz, J = 10.2 Hz, J = 5.6 Hz, J = 5.6 Hz, 1H), 5.71 (d, J = 3.6 Hz, 1H), 5.20 (dd, J = 17.1 Hz, J = 1.6 Hz, 1H), 5.14 (dd, J = 10.2 Hz, J = 1.6 Hz, 1H), 5.03 (d, J = 11.2 Hz, 1H), 5.00 (d, J = 11.9 Hz, 1H), 4.8 - 4.9 (m, 5H), 4.70 (d, J = 9.9 Hz, 1H), 4.59 (d, J = 11.2 Hz, 1H), 4.20 (m, 1H), 4.0 - 4.1 (m, 4H), 3.2 - 3.6 (m, 10H), 2.30 (ddd, J = 13.5 Hz, J = 4.6 Hz, J = 4.6 Hz, 1H), 2.13 (s, 3H), 2.06 (s, 3H), 1.46 (ddd, J = 13.5 Hz, J = 12.5 Hz, J = 12.5 Hz, 1H), 1.20 (d, J = 6.3 Hz, 3H); ¹³C NMR (68 MHz, CDCl₃) δ 169.5(s), 168.8(s), 137.9 (s, 2C), 137.2 (s), 134.5 (s), 128.7 (s), 128.7 (s), 128.5 (s), 128.4 (s), 128.2 (s), 127.9 (s), 117.0 (s), 99.0 (s), 97.5 (s), 85.2 (s), 79.7 (s), 79.5 (s), 78.7 (s), 77.3 (s), 75.5 (s, 2 carbons), 75.3

(s), 75.0 (s), 74.4 (s), 72.9 (s), 72.3 (s), 71.1 (s), 70.6 (s), 63.0 (s), 60.7 (s), 59.5 (s), 51.2 (s), 32.6 (s), 21.2 (s), 21.1 (s), 17.0 (s); MALDI Calcd for $C_{46}H_{54}N_{17}O_{12}K$ [M+K]⁺ m/e 1005.3616; measure m/e 1005.3566.

5-*O*-(3-*O*-(3-(2,4-Di-*O*-acetyl-3-*O*-(2-azidoethyl)-6-deoxy-b-D-glucopyranosyl)-*n*-propyl)-6-deoxy-b-D-glucopyranosyl)-6,3'4'-tri-*O*-benzyl-1,3,2'6'-tetraazidoneamine (42). Please refer to the general procedure for glycosylation. ¹H NMR (270 MHz, CDCl₃) δ 7.3-7.5 (m, 15H), 5.88 (d, *J* = 3.9 Hz, 1H), 4.8 - 5.0 (m, 8H), 4.60 (d, *J* = 11.2 Hz, 1H), 4.32 (d, *J* = 7.9 Hz, 1H), 3.9 - 4.2 (m, 4H), 3.0 - 3.7 (m, 21H), 2.28 (ddd, *J* = 13.3 Hz, *J* = 4.3 Hz, *J* = 4.0 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 1.80 (m, 2H), 1.46 (ddd, *J* = 13.3 Hz, *J* = 12.5 Hz, *J* = 12.5 Hz, 1H), 1.30 (d, *J* = 5.3 Hz, 3H), 1.23 (d, *J* = 5.9Hz, 3H); ¹³C NMR (68 MHz, CDCl₃) δ 169.7 (s), 169.5 (s), 137.9 (s), 137.8 (s), 137.1 (s), 128.9 (s), 128.6 (s), 128.5 (s), 128.2 (s), 128.0 (s), 127.8 (s), 102.0 (s), 100.6 (s), 96.5 (s), 84.7 (s), 84.3 (s), 80.4 (s), 79.6 (s), 79.1 (s), 78.7 (s), 76.0 (s), 75.5 (s), 75.1 (s), 75.0 (s), 74.6 (s), 73.7 (s), 72.1 (s), 72.0 (s), 70.9 (s), 70.5 (s), 69.1 (s), 68.3 (s), 65.5 (s), 63.2 (s), 60.7 (s), 60.5 (s), 59.8 (s), 51.2 (s), 51.1 (s), 32.6 (s), 30.1 (s), 21.1 (s), 21.0 (s), 17.4 (s), 17.2 (s); MALDI Calcd for $C_{54}H_{69}N_{15}O_{17}Na$ [M+Na]⁺ m/e 1222.4888; measure m/e 1222.4854.

5-O-(2,3,4-Tri-O-acetyl-6-deoxy-6-fluoro-b-D-glucopyranosyl)-6,3'4'-tri-O-benzyl-1,3,2'6'-tetraazidoneamine (47). Please refer to the general procedure for glycosylation. ¹H NMR (270 MHz, CDCl₃) δ 7.2 - 7.5 (m, 15H), 5.66 (d, J = 2.7 Hz, 1H), 5.20 (d, J = 7.6 Hz, 1H), 5.0 - 5.1 (m, 3H), 4.8 - 5.0 (m, 3H), 4.5 - 4.7 (m, 2H), 4.21 (ddd, J = 9.9 Hz, J = 4.9 Hz, J = 2.6 Hz, 1H), 4.09 (dd, J = 8.9 Hz, J = 9.2 Hz, 1H), 4.03 (dd, J = 8.9 Hz, J = 8.6 Hz, 1H), 3.2 - 3.6 (m, 10H), 2.32 (ddd, J = 13.2 Hz, J = 4.3 Hz, J = 4.3 Hz, 1H), 2.10 (s, 3H), 2.015 (s, 3H), 2.010 (s, 3H), 1.48 (ddd, J = 13.2 Hz, J = 4.3 Hz, J = 4.3 Hz, 1H), 2.10 (s, 3H), 2.015 (s, 3H), 2.010 (s, 3H), 1.48 (ddd, J = 13.2 Hz, J = 4.3 Hz, J = 4.3 Hz, 1H), 2.10 (s, 3H), 2.015 (s, 3H), 2.010 (s, 3H), 1.48 (ddd, J = 13.2 Hz, J = 4.3 Hz,

J = 13.2 Hz, J = 12.5 Hz, J = 12.5 Hz, 1H; ¹³C NMR (68 MHz, CDCl₃) δ 170.3 (s), 169.4 (s), 168.9 (s), 137.9 (s), 136.8 (s), 129.0 (s), 128.8 (s), 128.7 (s), 128.5 (s), 128.2 (s), 128.0 (s), 98.9 (s), 97.6 (s), 85.0 (s), 80.9 (d, J = 213 Hz), 79.4 (s), 78.7 (s), 78.0 (s), 77.3 (s), 75.8 (s), 75.7 (s), 75.3 (s), 75.0 (s), 72.8 (s), 71.6 (s), 71.1 (s), 68.2 (d, J = 7.5 Hz), 62.9 (s), 60.7 (s), 59.5 (s), 51.2 (s), 32.5 (s), 21.0 (s), 20.7 (s), 20.6 (s); MALDI Calcd for C₄₅H₅₁O₁₃N₁₂FNa [M+Na]⁺ m/e 1009.3575; measure m/e 1009.3602.

Cis, *cis*-3,5-diaminocyclohexyl b-D-4,6-diamino-4,6-dideoxygluco-pyranoside (34). Please refer to the procedure for the synthesis of 32. 1 H NMR (270 MHz, D₂O) (acetate salt) δ 4.66 (d, J = 7.9 Hz, 1H), 4.0 (m, 2H), 3.66 (dd, J = 9.9 Hz, J = 9.9 Hz, 1H), 3.48 (d, J = 13.2 Hz, 1H), 3.3 - 3.4 (m, 3H), 3.1 - 3.2 (m, 2H), 2.3 - 2.5 (m, 3H), 2.00 (s, 12H), 1.3 - 1.6 (m, 3H); 13 C NMR (68 MHz, D₂O) (acetate salt) δ 177.6 (s), 100.8 (s), 73.04 (s), 73.00 (s), 71.6 (s), 68.9 (s), 53.3 (s), 45.4 (s), 45.3 (s), 40.0 (s), 35.8 (s), 34.6 (s), 33.0 (s), 21.0 (s). LRFAB m/e 291 [MH]⁺; HRFAB Calcd for $C_{12}H_{27}N_4O_4$ [MH]⁺ m/e 291.2032; measure m/e 291.2025.

5-*O*-(6-Deoxy-6-fluoro-b-D-glucopyranosyl)neamine (TC033). Please refer to the procedure for the final synthesis. 1 H NMR (270 MHz, D₂O) (chloride salt) δ 5.83 (d, J = 2.7 Hz, 1H), 5.08 (d, J = 8.1 Hz, 1H), 4.55 (d, J = 8.1 Hz, 1H), 4.0 - 3.8 (m, 8H), 3.6 - 3.3 (m, 8H), 2.4 (m, 2H); 13 C NMR (68 MHz, D₂O) (acetate salt) δ 178.2 (s), 102.6 (s), 96.1 (s), 81.4 (d, $J_{CF} = 163$ Hz), 80.1 (s), 75.5 (s), 75.4 (s), 74.9 (d, $J_{CF} = 13.6$ Hz), 73.3 (s), 73.0 (s), 70.7 (s), 69.6 (s), 68.1 (s, 2 carbons), 53.4 (s), 49.8 (s), 48.6 (s), 40.0 (s), 28.2 (s), 21.4 (s). LRFAB m/e 487 [MH]⁺; HRFAB Calcd for C₁₈H₃₆O₁₀N₄F [MH]⁺ m/e 487.2415; measure m/e 487.2427.

5-*O*-(3-*O*-*n*-Propyl-6-deoxy-b-D-glucopyranosyl)neamine (TC040). Please refer to the procedure for the final synthesis. 1 H NMR (270 M Hz, 1 DO) (acetate salt) δ 5.81 (d, J = 3.6 Hz, 1H), 5.00 (d, J = 7.9 Hz, 1H), 3.8 - 4.0 (m, 5H), 3.70 (dd, J = 6.6 Hz, J = 6.9 Hz, 2H), 3.1 - 3.5 (m, 10H), 2.45 (m, 1H), 1.94 (s, 12H), 1.83 (m, 1H), 1.53 (m, 2H), 1.25 (d, J = 5.9 Hz, 3H), 0.82 (t, J = 7.5 Hz, 3H); 13 C NMR (68 MHz, 1 DO) (acetate salt) δ 178.7 (s), 102.7 (s), 96.3 (s), 83.7 (s), 80.7 (s), 76.0 (s), 75.1 (s), 74.5 (s), 73.3 (s), 73.1 (s), 72.9 (s), 70.8 (s), 69.6 (s), 68.2 (s), 53.5 (s), 49.8 (s), 48.8 (s), 40.1 (s), 28.2 (s), 22.8 (s), 21.7 (s), 16.6 (s), 9.8 (s); MALDI Calcd for $C_{21}H_{46}N_{4}O_{10}N_{8}$ [M+Na] $^{+}$ m/e 533.2793; measure m/e 533.2817.

5-*O*-(3-*O*-(3-Hydroxypropyl)-6-deoxy-b-D-glucopyranosyl)neamine (TC041). Please refer to the procedure for the final synthesis. 1 H NMR (270 M Hz, D₂O) (acetate salt) δ 5.80 (d, J = 3.6 Hz, 1H), 5.02 (d, J = 7.9 Hz, 1H), 3.8 - 4.0 (m, 7H), 3.64 (dd, J = 6.3 Hz, J = 6.3 Hz, 2H), 3.2 - 3.5 (m, 10H), 2.45 (m, 1H), 1.92 (s, 12H), 1.7 - 2.0 (m, 3H), 1.26 (d, J = 6.0 Hz, 3H); 13 C NMR (68 MHz, D₂O) (acetate salt) δ 178.2 (s), 102.6 (s), 96.4 (s), 84.1 (s), 80.7 (s), 76.1 (s), 74.4 (s), 73.2 (s), 73.1 (s), 72.9 (s), 70.6 (s), 70.3 (s), 69.6 (s), 68.3 (s), 59.0 (s), 53.4 (s), 49.7 (s), 48.7 (s), 40.0 (s), 31.9 (s), 28.2 (s), 21.4 (s), 16.6 (s); MALDI Calcd for C₂₁H₄₆N₄O₁₁Na [M+Na]⁺ m/e 549.2742; measure m/e 549.2738.

δ 178.5 (s), 102.6 (s), 96.3 (s), 84.1 (s), 82.4 (d, $J_{CF} = 157.8$ Hz), 80.7 (s), 76.1 (s), 74.4 (s), 73.2 (s), 73.1 (s), 72.9 (s), 70.6 (s), 69.6 (s), 69.1 (d, $J_{CF} = 5.2$ Hz), 68.3 (s), 53.4 (s), 49.7 (s), 48.7 (s), 40.0 (s), 30.5 (d, $J_{CF} = 19.2$ Hz), 28.2 (s), 21.6 (s), 16.6 (s); MALDI Calcd for $C_{21}H_{45}FN_4O_{10}Na$ [M+Na]⁺ m/e 551.2699; measure m/e 551.2719.

5-O-(3-O-(2-aminoethyl)-6-deoxy-b-D-glucopyranosyl)-n-propyl)-6-deoxy-b-D-gluco-

pyranosyl)neamine (**TC045**). Please refer to the procedure for the final synthesis. 1 H NMR (270 MHz, D_{2} O) (acetate salt) δ 5.78 (d, J = 3.6 Hz, 1H), 4.99 (d, J = 7.9 Hz, 1H), 4.35 (m, 1H), 3.6 - 4.0 (m, 10H), 3.1 - 3.5 (m, 17H), 2.43 (m, 1H), 1.94 (s, 15H), 1.8 - 2.0 (m, 3H), 1.24 (d, J = 5.9 Hz, 3H), 1.20 (d, J = 5.9Hz, 3H); 13 C NMR (68 MHz, D_{2} O) (acetate salt) δ 178.2 (s), 102.6 (s), 102.1 (s), 96.4 (s), 84.2 (s), 84.1 (s), 80.8 (s), 76.1 (s), 74.6 (s), 74.4 (s), 73.3 (s), 73.1 (s, 2 carbons), 72.9 (s), 71.9 (s), 70.6 (s), 70.0 (s), 69.6 (s), 68.3 (s), 68.2 (s), 67.5 (s), 53.4 (s), 49.7 (s), 48.7 (s), 40.0 (s), 39.7 (s), 29.7 (s), 28.2 (s), 21.4 (s), 16.7 (s), 16.6 (s); MALDI Calcd for $C_{29}H_{57}N_{5}O_{15}Na$ [M+Na]⁺ m/e 738.3743; measure m/e 738.3786.