

Supporting Information

A short route for the synthesis of “sweet” macrocycles via a click dimerization/ring-closing metathesis approach

Simon Dörner and Bernhard Westermann

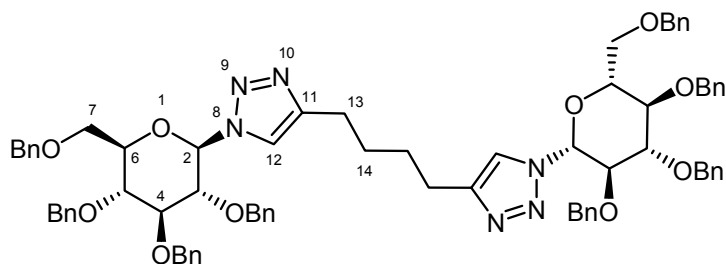
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1 Experimental data and spectra for dimers 4–6

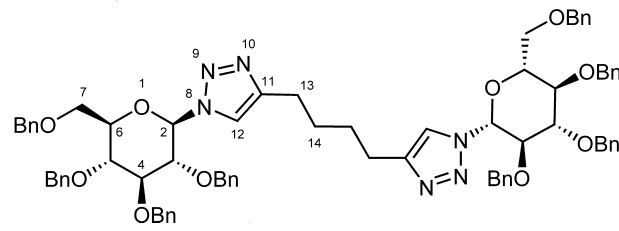
11,17-Butane-13,16-diylbis(8-{(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-[(benzyloxy)-methyl]tetrahydro-2*H*-pyran-2-yl}-1*H*-8,9,10-triazole) (4)



¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 1.75 (bs, 4H, 10-H), 2.75 (bs, 4H, 9-H), 3.70–3.74 (m, 4H), 3.76–3.86 (m, 4H), 4.00–4.07 (m, 4H), 4.43–4.62 (m, 8H), 4.82–4.96 (m, 6H), 5.52 (d, *J* = 9.0 Hz, 2H, 2-H), 6.90–6.96 (m, 4H), 7.14–7.22 (m, 10H, CH arom.), 7.26–7.36 (m, 30H, CH arom.).–

¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 25.36, 28.86 (t, C-13, C-14), 68.34 (t, C-7), 73.47, 74.85, 75.18, 75.74 (t, CH_{2(Bn)}), 77.23, 77.95, 80.79, 85.44 (d, C-3, C-4, C-5, C-6), 87.38 (d, C-2), 120.20 (d, C-12), 127.68–128.46 (d, CH arom.), 137.00, 137.68, 137.75, 138.14 (s, C arom), 148.05 (s, C-11).–

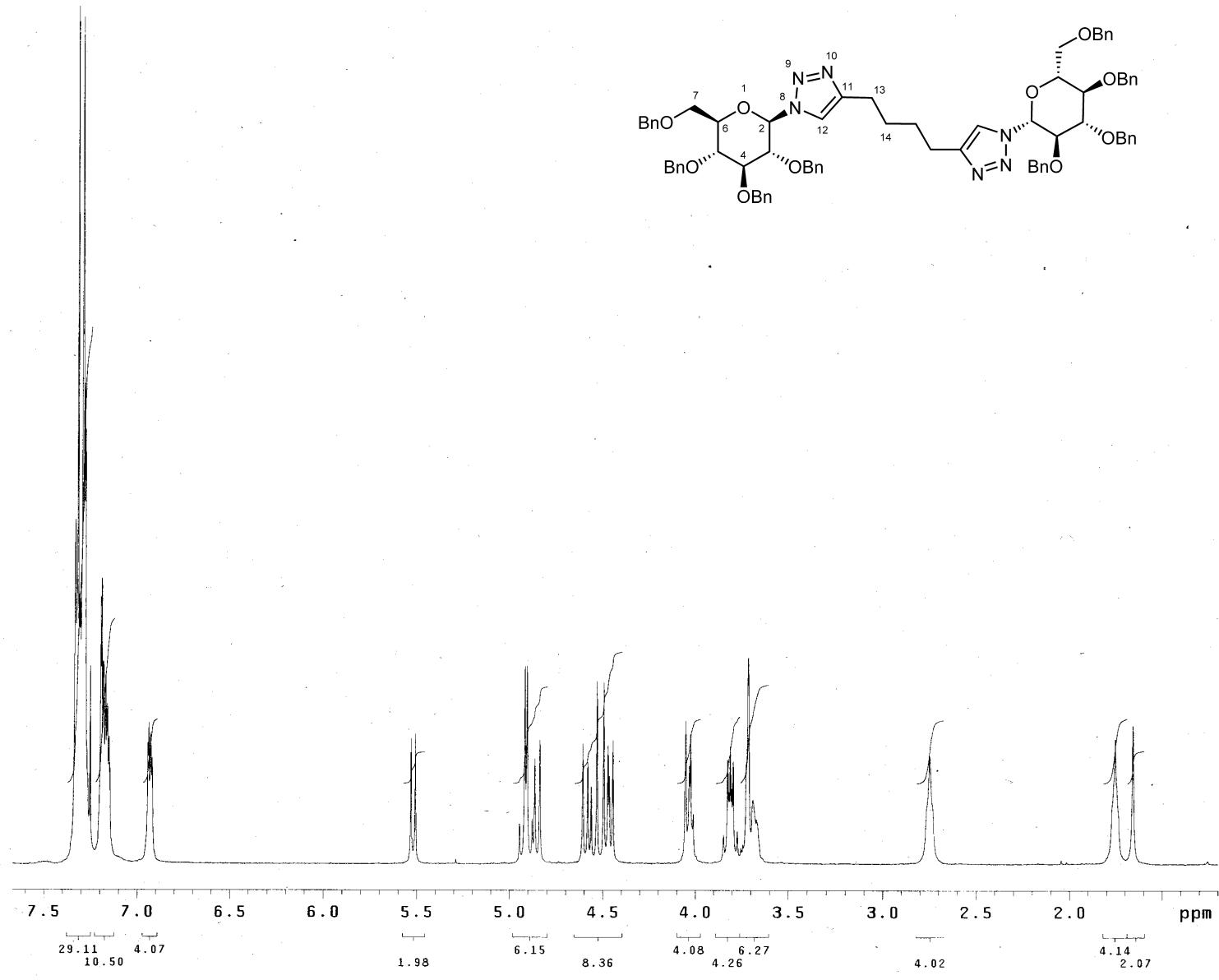
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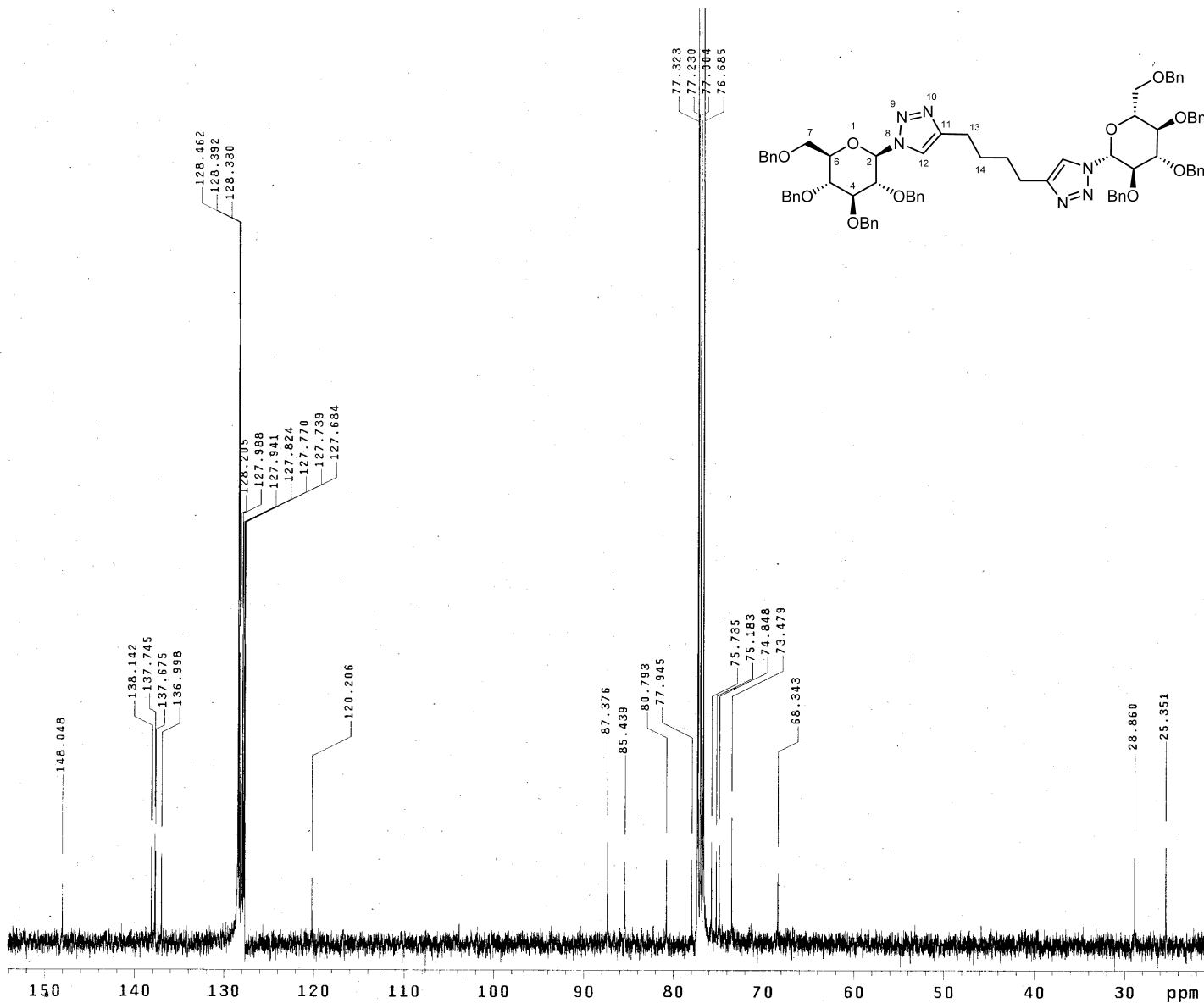


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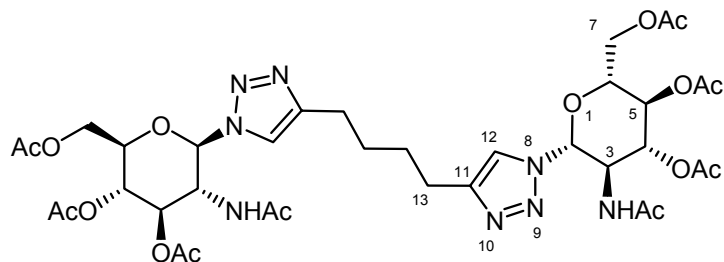
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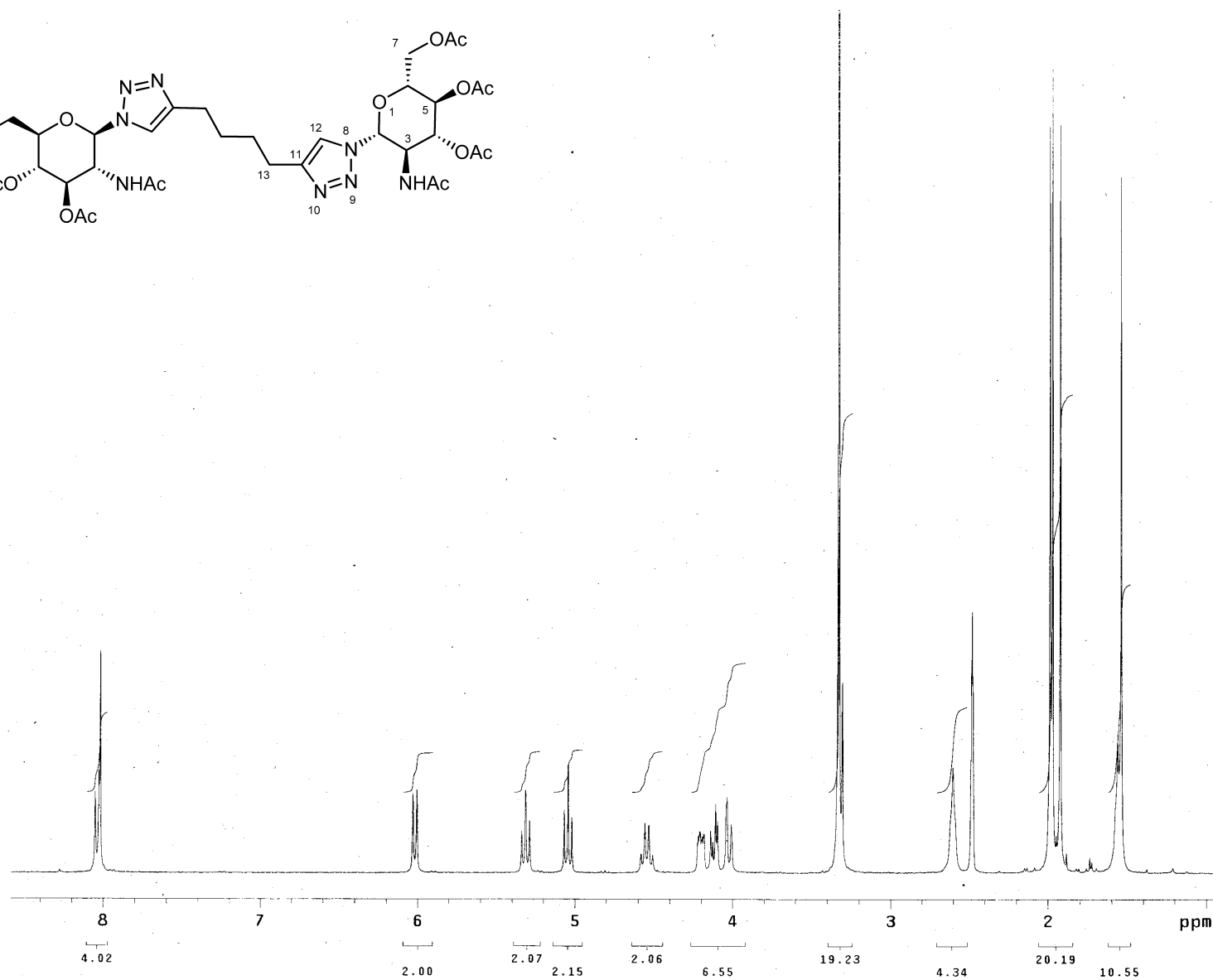
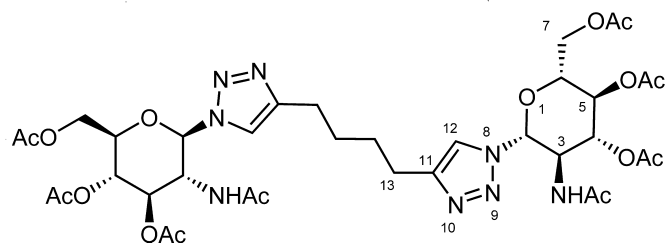
Butane-13,16-diylbis{1*H*-8,9,10-triazole-11,17-diyl(2*R*,3*R*,4*R*,5*S*,6*R*)-3-(acetylamino)-6-[(acetyloxy)methyl]tetrahydro-2*H*-pyran-2,4,5-triyl} tetraacetate (5)



¹H-NMR (400 MHz, DMSO-*d*₆): δ [ppm] = 1.54 (bs, 6H, CH_{3(NHAc)}), 1.56 (bs, 4H, 13-H), 1.92, 1.97, 1.99 (s, 6H, CH_{3(Ac)}), 2.60 (bs, 4H, 12-H), 4.00 (dd, *J* = 12.5, 2.3 Hz, 2H, 7^a-H), 4.12 (dd, *J* = 12.5, 5.1 Hz, 2H, 7^b-H), 4.20 (ddd, *J* = 10.2, 5.1, 2.3 Hz, 2H, 6-H), 4.55 (ddd, *J* = 9.8, 9.8, 9.4 Hz, 2H, 3-H), 5.05 (dd, *J* = 10.2, 9.8 Hz, 2H, 5-H), 5.32 (dd, *J* = 9.8, 9.8 Hz, 2H, 4-H), 6.02 (d, *J* = 9.8 Hz, 2H, 2-H), 8.02 (s, 2H, 12-H), 8.04 (d, *J* = 9.4 Hz 2H, NH).–

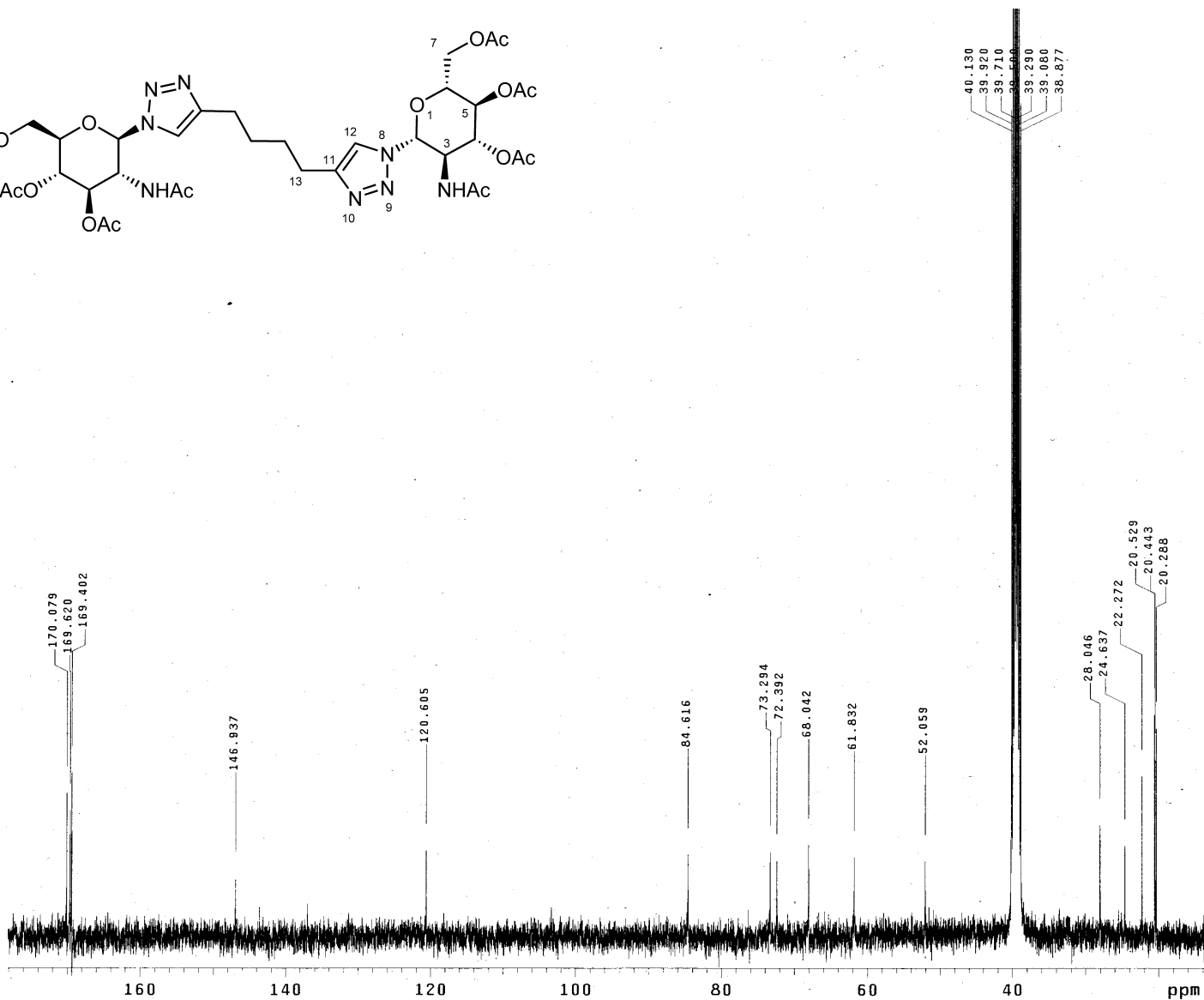
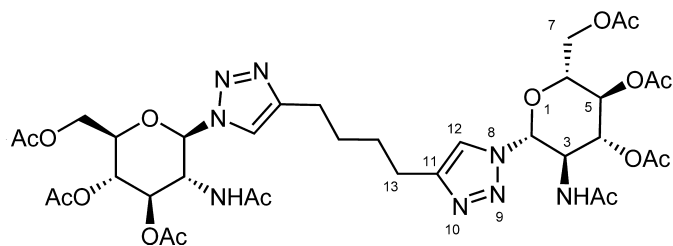
¹³C-NMR (100 MHz, DMSO-*d*₆): δ [ppm] = 20.95, 21.11, 21.20 (q, CH_{3(Ac)}), 22.94 (q, CH_{3(NHAc)}), 25.31, 28.72 (t, C-13, C-14), 52.73 (d, C-3), 62.49 (t, C-7), 68.71, 73.05, 73.96 (d, C-4, C-5, C-6), 85.28 (d, C-2), 120.61 (d, C-12), 146.94 (s, C-11), 169.40, 169.62, 170.08 (s, CO).–

HRMS (ESI)	C ₃₆ H ₅₀ N ₈ O ₁₆ Na	[M+Na ⁺]	calcd	873.3237
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pw 2.8
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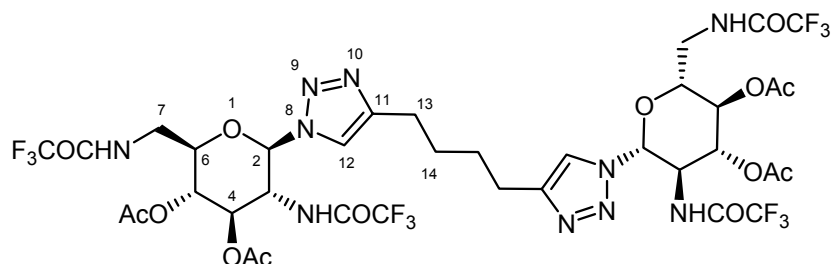


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bs 16
tpwr 61
pw 4.0
d1 1.689
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ct 1000
alock n
gain not used
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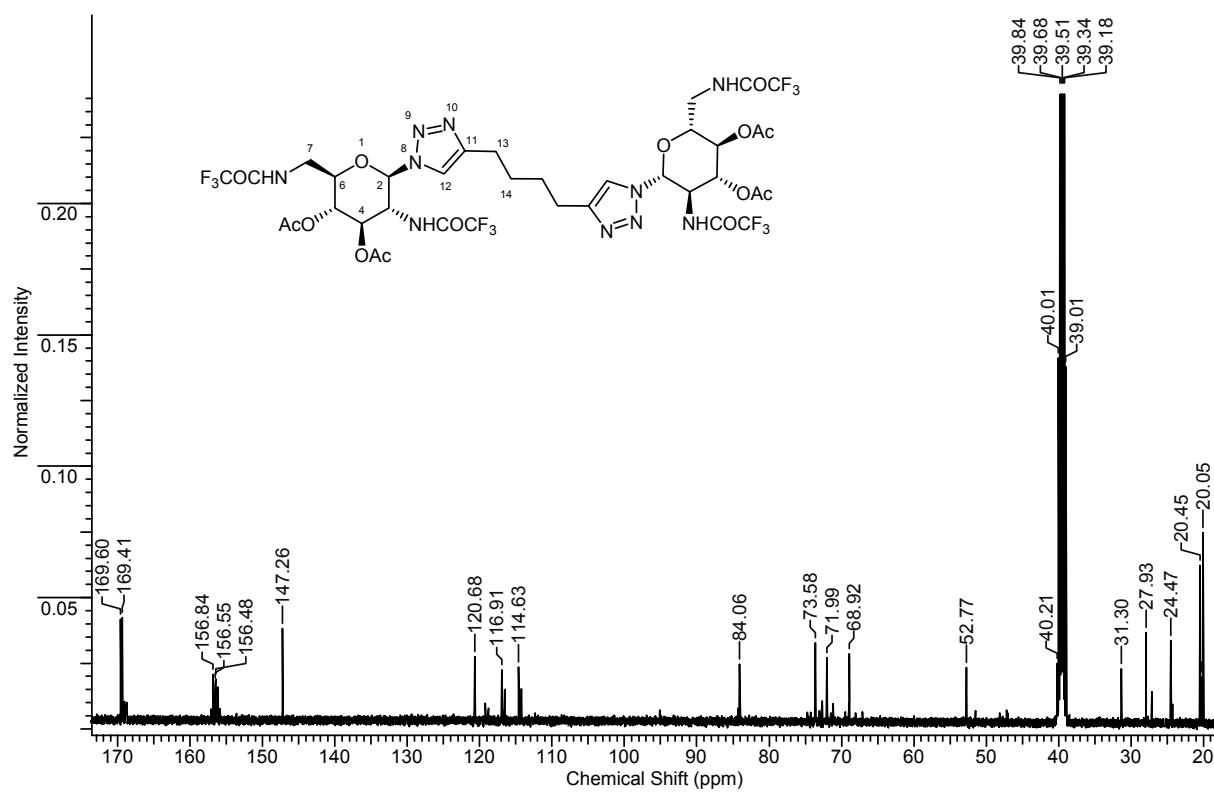
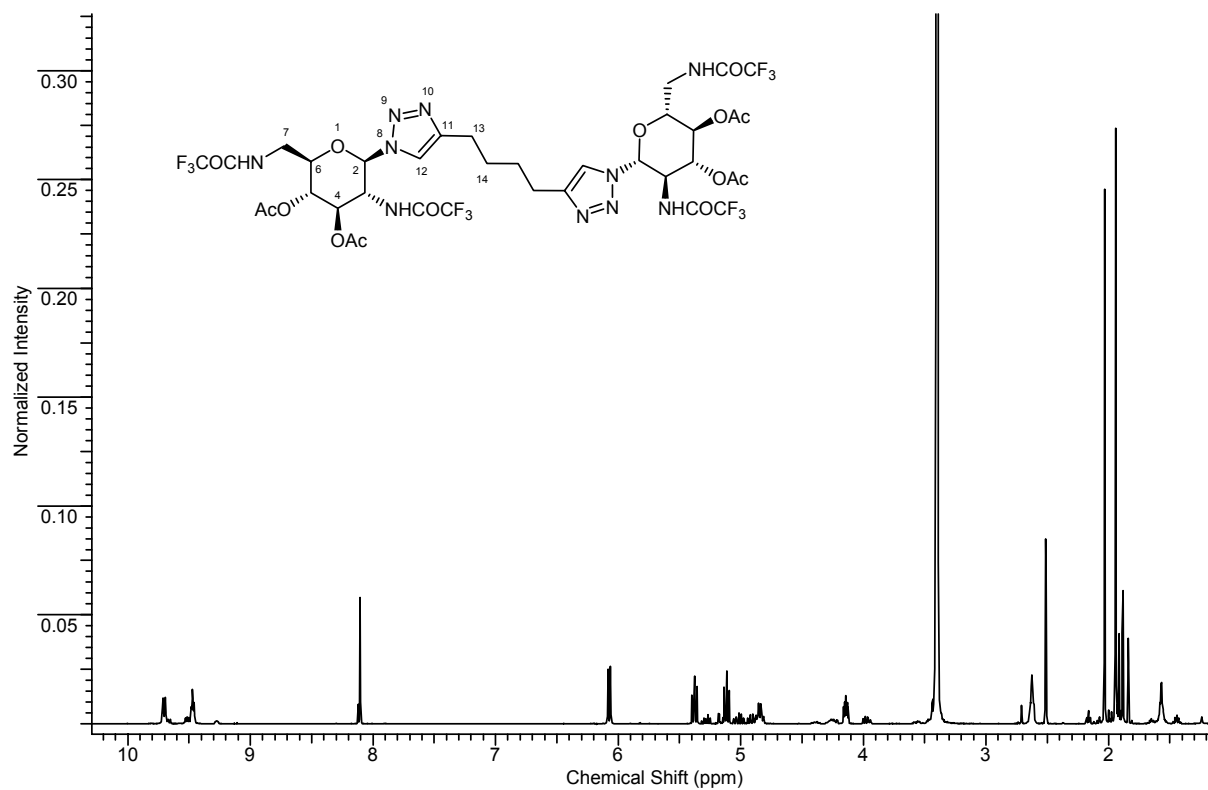

Butane-13,16-diylbis(1*H*-8,9,10-triazole-11,8-diyl(2*R*,3*R*,4*R*,5*R*,6*R*)-3-[(trifluoroacetyl)-amino]-6-[[trifluoroacetyl]amino]methyl}tetrahydro-2*H*-pyran-2,4,5-triyl) tetraacetate (6)



¹H-NMR (500 MHz, DMSO-*d*₆): δ [ppm] = 1.56 (bs, 4H, 16-H), 1.93, 2.03 (s, 6H, CH_{3(Ac)}), 2.61 (bs, 4H, 13-H), 3.40–3.44 (m, 4H, 7-H), 4.13 (ddd, *J* = 10.0, 6.2, 3.3 Hz, 2H, 6-H), 4.84 (ddd, *J* = 10.4, 9.8, 8.8 Hz, 2H, 3-H), 5.11 (dd, *J* = 10.0, 9.5 Hz, 2H, 5-H), 5.38 (dd, *J* = 10.4, 9.5 Hz, 2H, 4-H), 6.07 (d, *J* = 9.8 Hz, 2H, 2-H), 8.11 (s, 2H, 12-H), 9.47 (bt, *J* = 5.5 Hz, 2H, 7-NH) 9.70 (bd, *J* = 8.8 Hz, 2H, 3-NH).

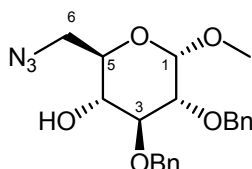
¹³C-NMR (125 MHz, DMSO-*d*₆): δ [ppm] = 20.05, 20.45 (q, CH_{3(Ac)}), 24.47 (t, C-13), 27.93 (t, C-14), 40.21 (t, C-7), 52.77 (d, C-3), 68.92 (d, C-5), 71.99 (d, C-4), 73.58 (d, C-6), 84.06 (d, C-2), 115.77 (q, ¹*J*(¹³C, ¹⁹F) = 287.7 Hz, CF₃), 115.36 (q, ¹*J*(¹³C, ¹⁹F) = 288.2 Hz, CF₃), 120.68 (d, C-12), 147.26 (s, C-11), 156.33 (q, ²*J*(¹³C, ¹⁹F) = 37.2 Hz, C(O)CF₃), 156.70 (q, ²*J*(¹³C, ¹⁹F) = 36.4 Hz, C(O)CF₃), 169.41, 169.61 (s, CO).–

HRMS (ESI)	C ₃₆ H ₁₄ F ₁₂ N ₁₀ O ₁₄ Na [M+Na ⁺]	calcd	1087.2426
		found	1087.2440



2 Experimental data and spectra for bifunctional building blocks 9–13

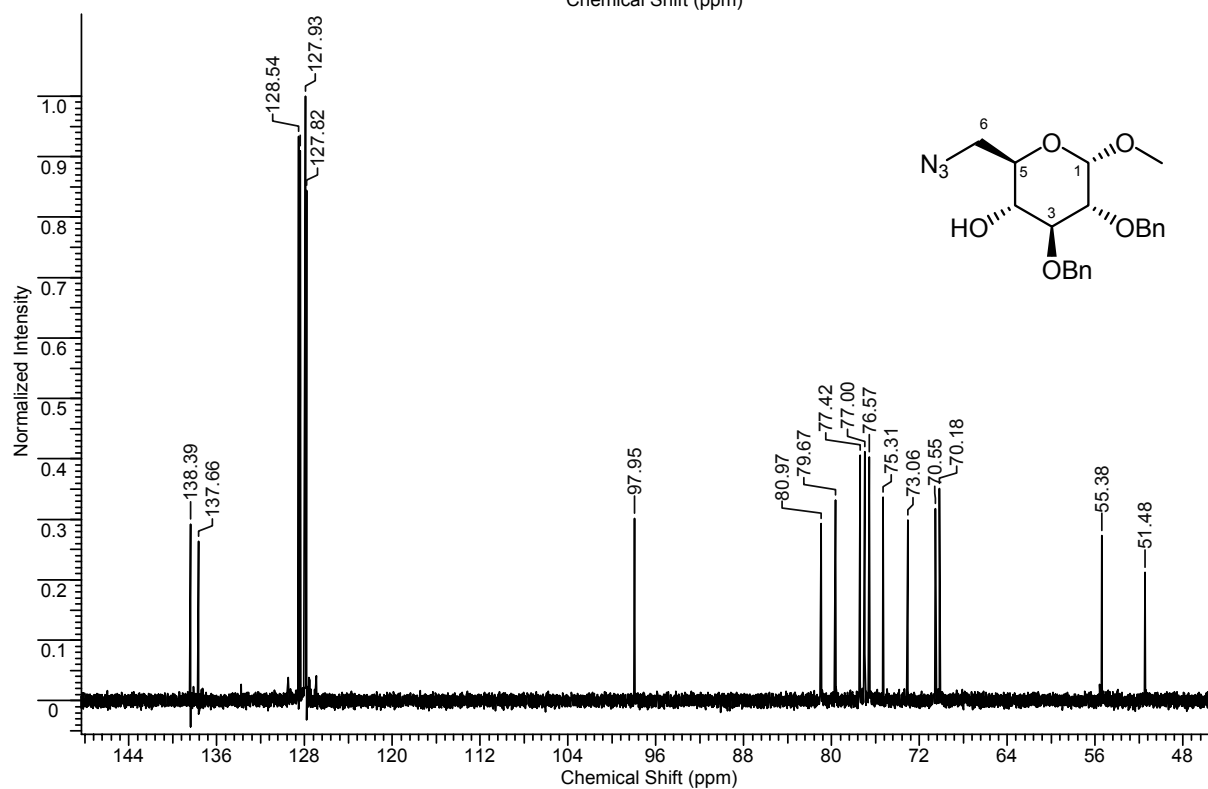
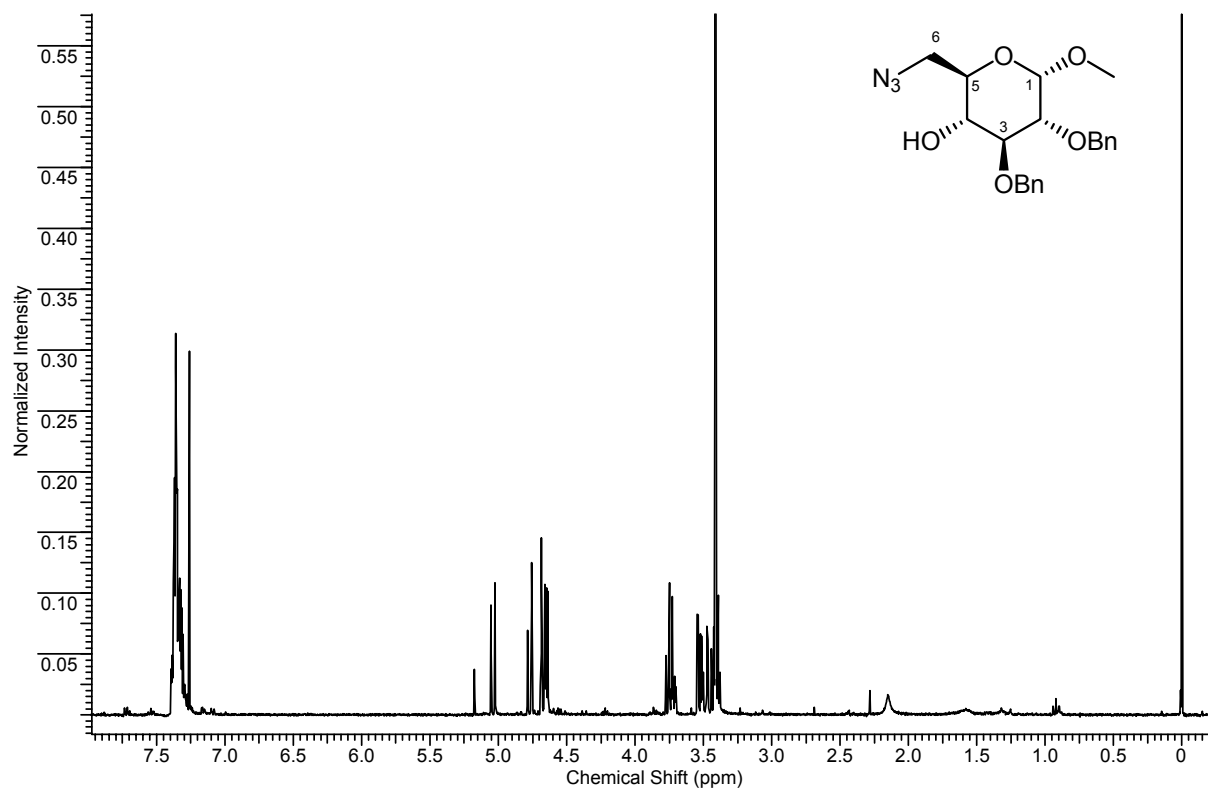
Methyl 6-azido-2,3-di-*O*-benzyl-6-deoxy- α -D-glucopyranoside (9)^[1]



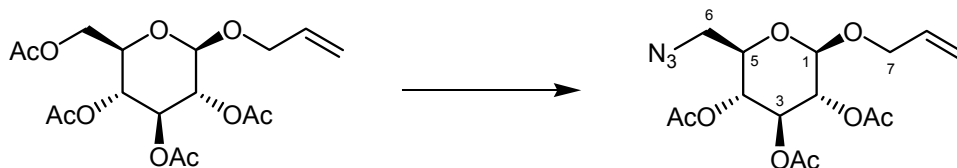
¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 2.15 (bs, 1H, OH), 3.37–3.45 (m, 5H), 3.46–3.51 (m, 1H), 3.53 (dd, J = 9.4, 3.5 Hz, 1H), 3.70–3.78 (m, 2H), 4.64 (d, J = 3.5 Hz, 1H), 4.67 (d, J = 11.3 Hz, 1H), 4.67 (d, J = 12.1 Hz, 1H), 5.04 4.67 (d, J = 11.3 Hz, 1H), 4.77 4.67 (d, J = 12.1 Hz, 1H), 7.28–7.41 (m, 10H, CH arom.)–

¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 51.48 (t, C-6), 55.38, 70.17, 70.55 (d, CH), 73.06, 75.31 (t, CH₂ benzyl.), 79.66, 80.97 (d, CH), 97.94 (d, C-1), 127.82, 127.85, 127.89, 127.92, 128.37, 128.53 (d, CH arom.), 137.66, 138.38 (s, C arom.)–

HRMS (ESI)	C ₂₁ H ₂₅ N ₃ O ₅ Na	[M+Na ⁺]	calcd	422.1686
			found	422.1683



Allyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy- β -D-glucopyranoside (10)



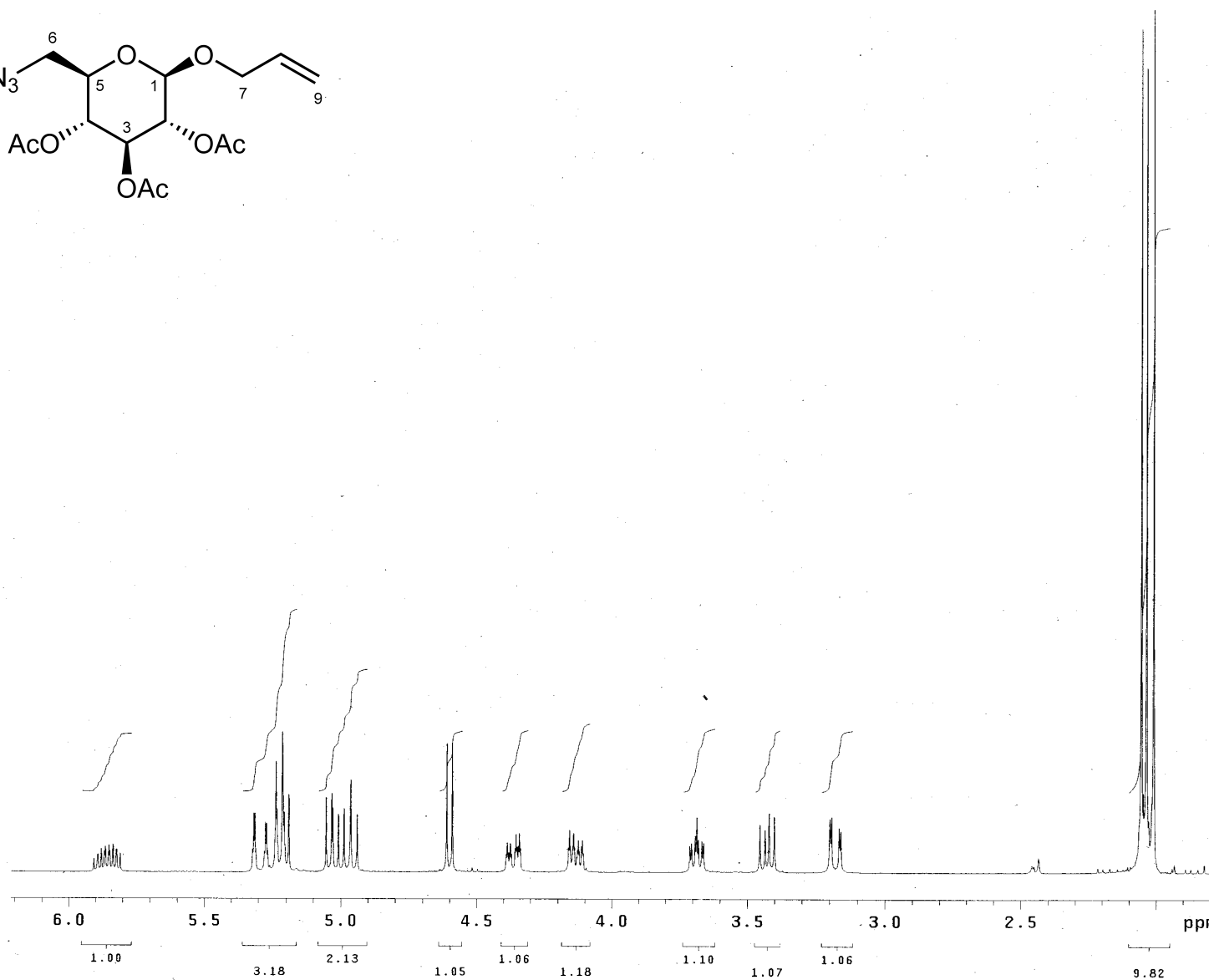
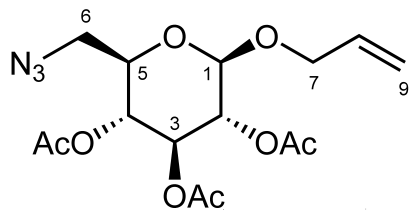
Allyl 2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside (1.0 g, 2.57 mmol) was dissolved in methanol (20 ml) and treated with a catalytic amount of NaOMe (1 M). The reaction was stirred for 30 min neutralized with Lewatit S1080 resin and filtered. The residue was dried, dissolved in dry pyridine (10 ml) and cooled in an ice bath. Then TsCl (736 mg, 2.57 mmol) was slowly added and the mixture was allowed to stir over night. Acetic anhydride (1.1 ml, 11.6 mmol) was added and the mixture was stirred for 60 min. The solution was diluted with ethyl acetate and extracted with diluted HCl to remove the pyridine. The organic phase was dried and concentrated. The residue was diluted with dry DMF (15 ml) and treated with sodium azide (0.5 g, 7.72 mmol). After heating the reaction mixture for 4 h at 90°C DMF was evaporated and the residue was diluted with ethyl acetate, extracted with water and brine, concentrated and dried. The product was purified by flash chromatography (silica, eluent: hexanes/ethyl acetate = 1/1, R_f =0.59) to yield 666 mg (1.79 mmol, 70%) of a colourless solid.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ [ppm] = 2.01, 2.04, 2.06 (s, 3H, $\text{CH}_{3(\text{Ac})}$), 3.18 (dd, J = 13.3, 2.3 Hz, 1H, 6^{a}-H), 3.43 (dd, J = 13.3, 7.6 Hz, 1H, 6^{b}-H), 3.69 (ddd, J = 10.0, 7.6, 2.3 Hz, 1H, 5-H), 4.13 (dddd, J = 13.3, 6.3, 1.4, 1.4 Hz, 1H, 7^{a}-H), 4.37 (dddd, J = 13.3, 4.9, 1.6, 1.6 Hz, 1H, 7^{b}-H), 4.60 (d, J = 7.8 Hz, 1H, 1-H), 4.97 (dd, J = 9.8, 9.4 Hz, 1H, 3-H), 5.03 (dd, J = 9.8, 7.8 Hz, 1H, 2-H), 5.21 (dd, J = 9.4, 9.4 Hz, 1H, 4-H), 5.22 (dddd, J = 10.5, 2.9, 1.4, 1.4 Hz, 1H, 9^{a}-H), 5.30 (dddd, J = 17.2, 3.3, 1.6, 1.6 Hz, 1H, 9^{b}-H), 5.86 (dddd, J = 17.2, 10.5, 6.3, 4.9 Hz, 1H, 8-H).–

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ [ppm] = 20.58, 20.64 (s, 3H, $\text{CH}_{3(\text{Ac})}$), 51.13 (t, C-6), 69.70 (d, CH), 69.85 (t, C-7), 71.22, 72.53, 73.64 (d, CH), 99.25 (d, C-1), 117.82 (t, C-9), 133.10 (d, C-8), 169.30, 169.53, 170.24 (s, CO).–

HRMS (ESI) $\text{C}_{15}\text{H}_{21}\text{N}_3\text{O}_8\text{Na}$ $[\text{M}+\text{Na}^+]$ calcd 394.1221
found 394.1221

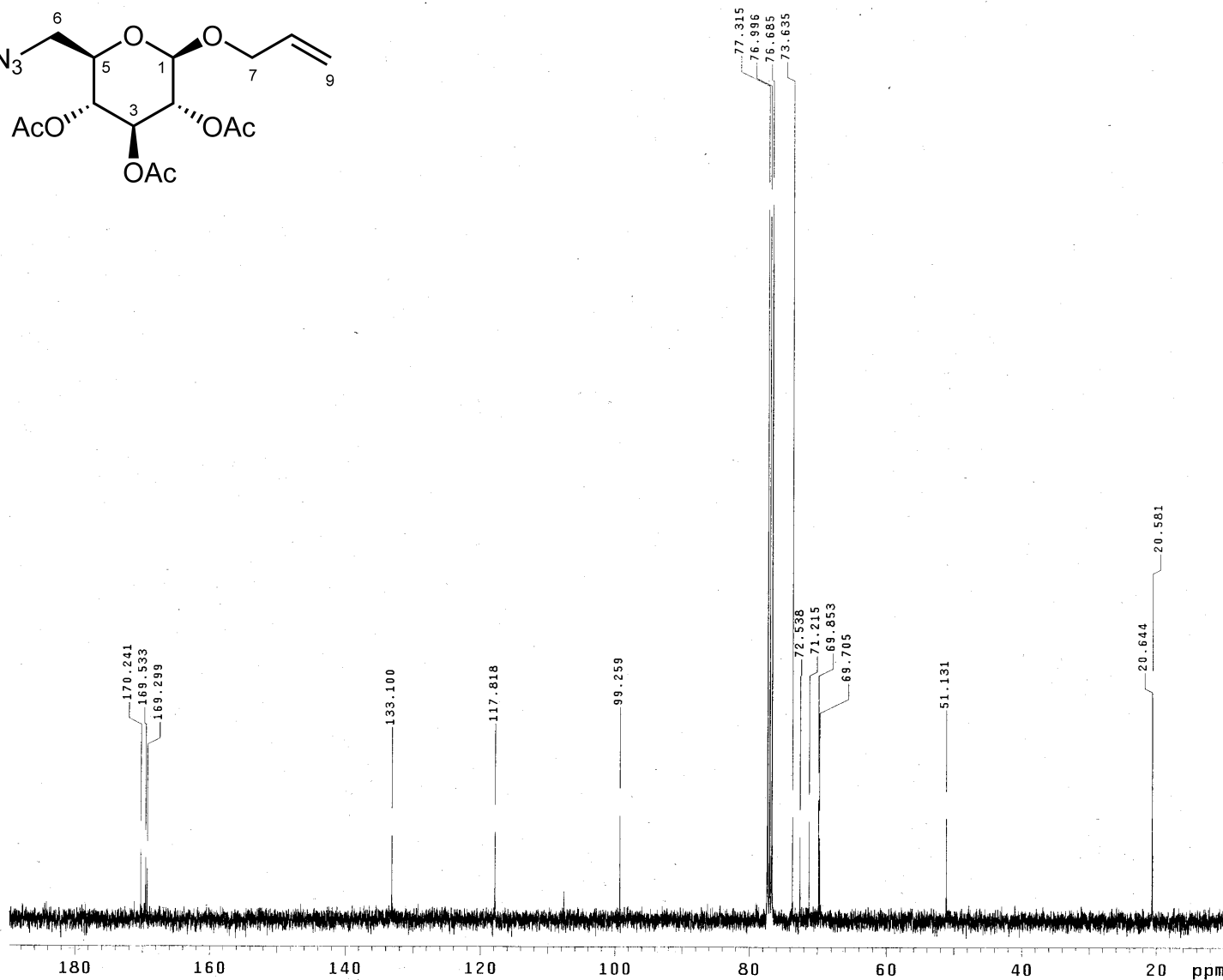
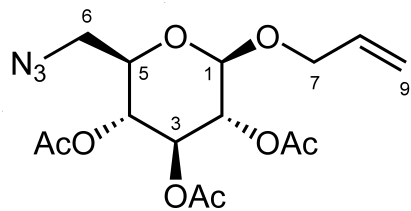
$\text{C}_{15}\text{H}_{21}\text{N}_3\text{O}_8$ (371.34) Calcd C 48.52 H 5.70
Found C 48.70 H 5.89



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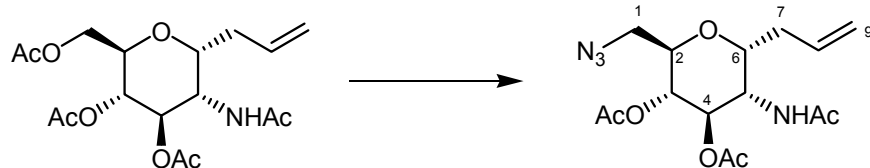
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Thu Oct 21 16:37 2004

exp3 std13c

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sw 25641.0
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tpwr 61
pw 4.0
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nm no ph

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3,4-Di-*O*-acetyl-5-(acetylamino)-2,6-anhydro-1-azido-1,5,7,8,9-pentadeoxy-D-*glycero*-L-*gulo*-non-8-enitol (11)

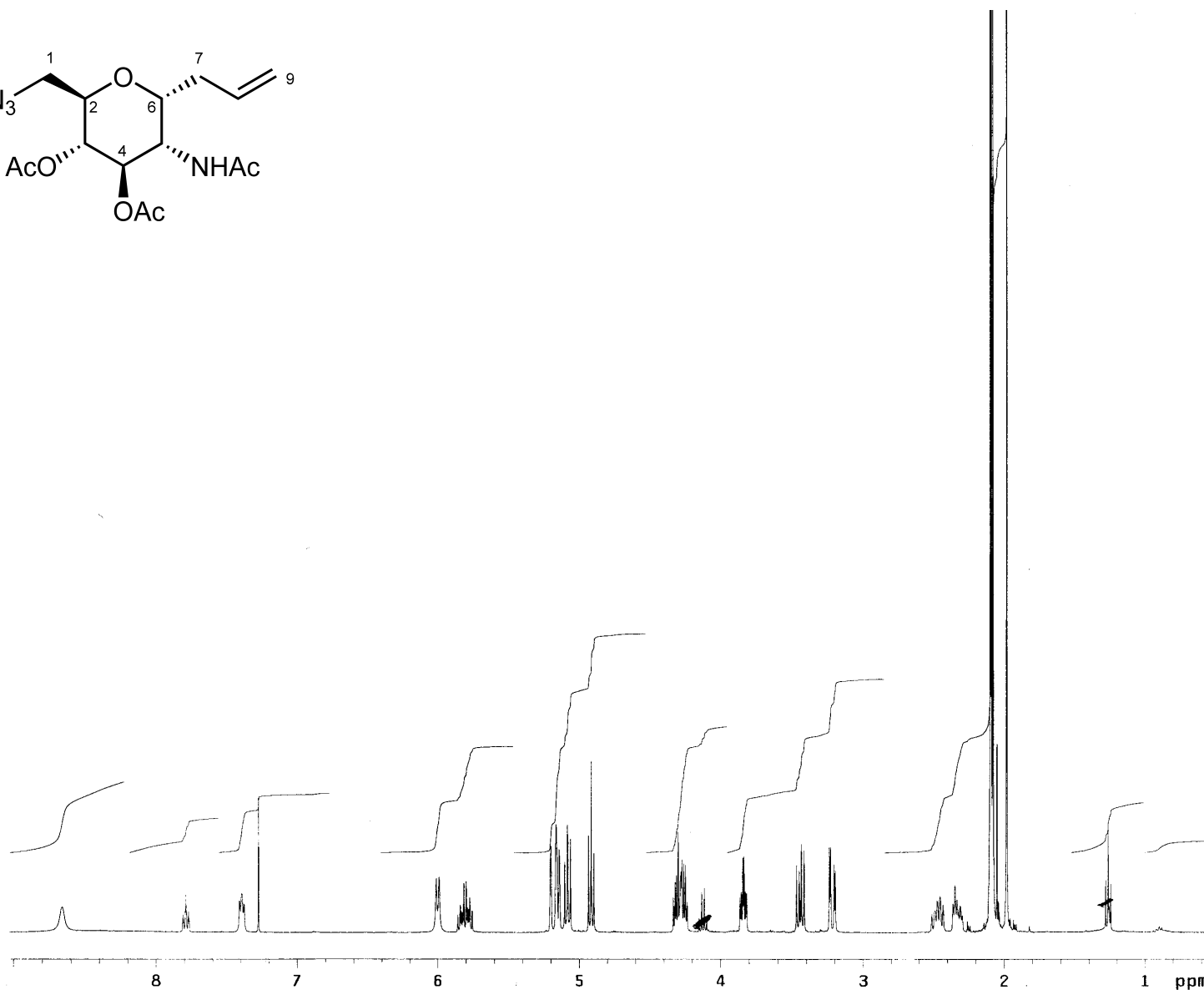
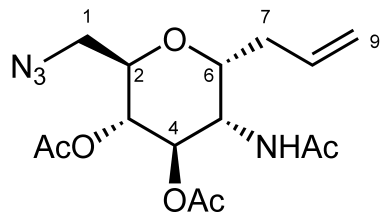


The product was prepared in analogy to (10).

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 1.96 (s, 3H, CH₃(NHAc)), 2.08, 2.09 (s, 3H, CH₃(Ac)), 2.29–2.37 (m, 1H, 7^a-H), 2.43–2.52 (m, 1H, 7^b-H), 3.22 (dd, *J* = 13.4, 3.5 Hz, 1H, 1^a-H), 3.44 (dd, *J* = 13.4, 7.6 Hz, 1H, 1^b-H), 3.84 (ddd, *J* = 7.6, 7.6, 3.5 Hz, 1H, 2-H), 4.23–4.33 (m, 2H, 5-H, 6-H), 4.92 (dd, *J* = 7.6, 7.6 Hz, 1H, 3-H), 5.08 (dd, *J* = 8.6, 7.6 Hz, 1H, 3-H), 5.13–5.21 (m, 2H, 9-H), 5.75–5.86 (m, 1H, 8-H), 5.90 (bd, *J* = 8.2 Hz, 1H, NH).–

¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 20.73, 20.83 (q, CH₃(Ac)), 23.17 (q, CH₃(NHAc)), 31.62 (t, C-7), 50.59 (t, C-1), 50.91 (d, C-5), 69.00, 70.14, 71.22, 71.39 (d, C-2, C-3, C-4, C-6), 117.92 (t, C-9), 132.97 (d, C-8), 169.16, 169.81, 171.30 (s, CO).–

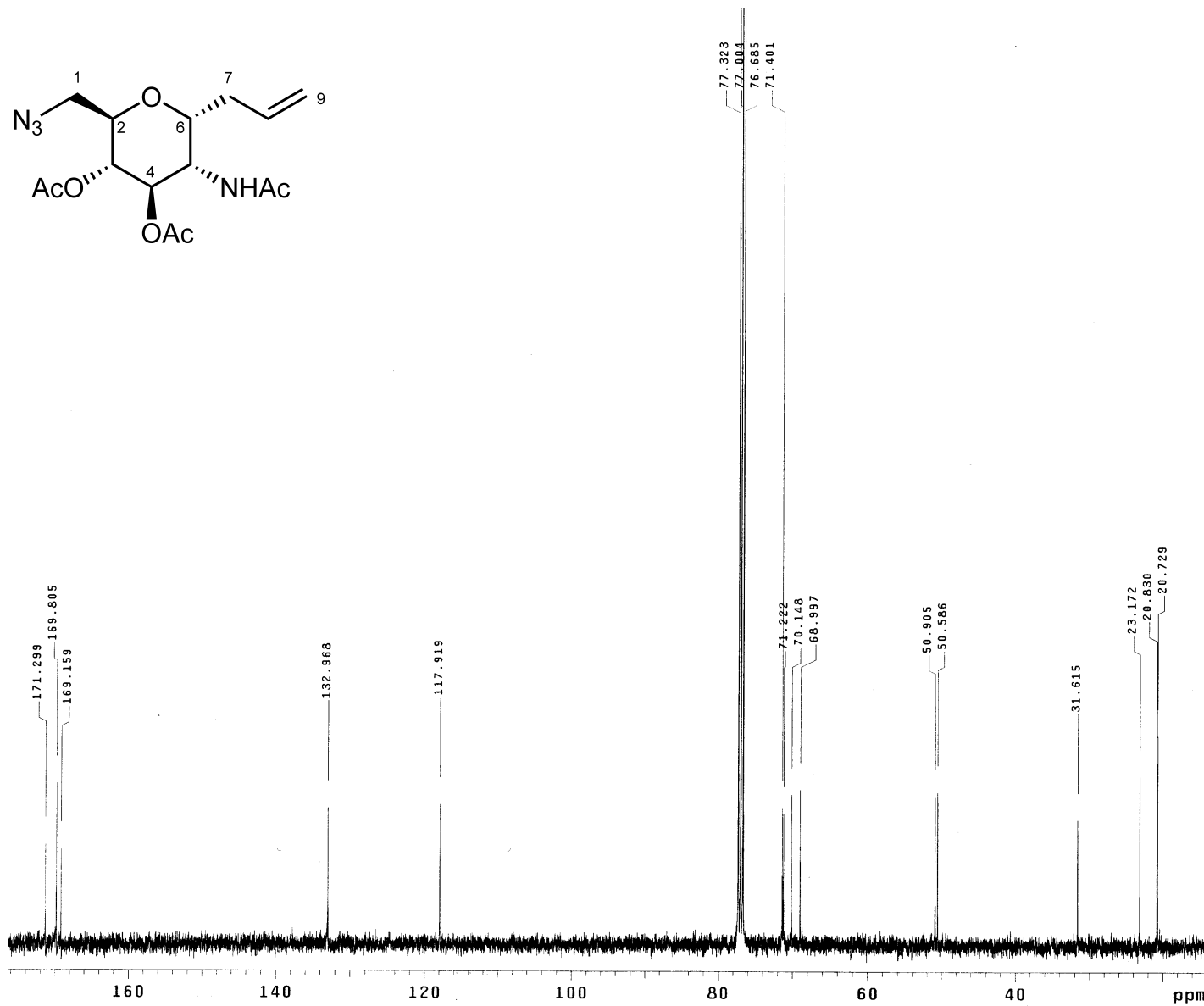
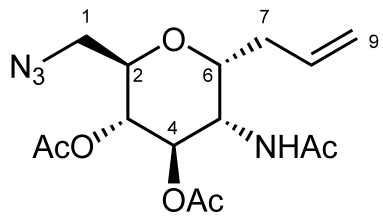
HRMS (ESI)	C ₁₅ H ₂₂ N ₄ O ₆ Na	[M+Na ⁺]	calcd	377.1432
			found	377.1433



```

dos305.1H.cdc13
Mon Nov 29 09:27 2004
exp7 std1h
SAMPLE
date Nov 29 2004
solvent CDC13
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used
FLAGS
fl n
fn nw
dp y
DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.40
wtfile
proc ft
fn 65536
DISPLAY
sp 205.3
wp 3405.0
vs 377
sc 65
wc 225
hzmm 15.13
ls 1203.57
rfl 3540.8
rfp 0
th 2.9
ins 100.000
rp 3.4
lp -183.8
nm ph

```

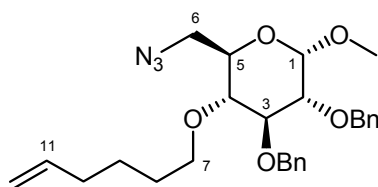


dos305.nFiltr.13C.cd13
 Mon Nov 29 11:18 2004

exp2 std13c

SAMPLE
 date Nov 29 2004
 solvent CDC13
 file exp
 ACQUISITION
 instrum m400
 probe asw5
 seqfil s2pu1
 sfrq 100.574
 tn C13
 at 1.311
 np 67216
 sw 25641.0
 bs 16
 tpwr 61
 pw 4.0
 d1 1.689
 d2 0
 tof 1327.2
 nt 800
 ct 800
 alock n
 gain not used
 FLAGS
 il n
 in n
 dp y
 DEC. & VT
 dn H1
 dfrq 399.936
 homo n
 dpwr 40
 dof 0
 dm yyy
 dmm w
 dmf 9350
 pp 17.5
 PROCESSING
 lb 1.00
 wtfile ft
 proc
 fn 65536
 DISPLAY
 sp 1340.4
 wp 16397.8
 vs 269
 sc 65
 wc 225
 hzmm 72.88
 rfl 9742.1
 rfp 7743.4
 th 11.5
 rp 27.4
 lp -264.7
 nm no ph

Methyl 6-azido-2,3-di-*O*-benzyl-6-deoxy-4-*O*-hex-11-ene-7-yl- α -D-glucopyranoside (12)



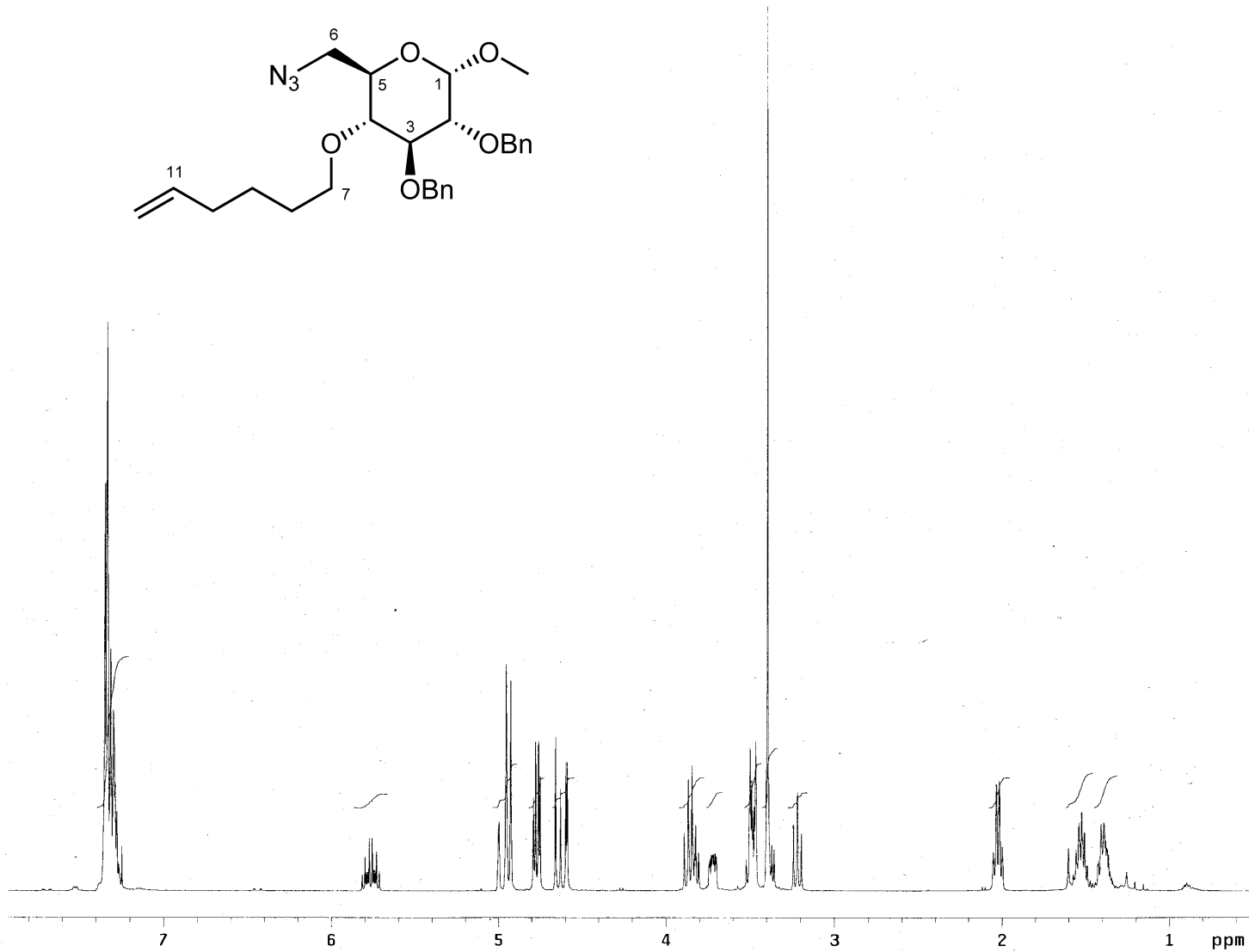
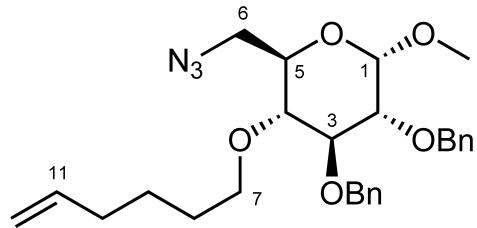
Methyl 6-azido-2,3-di-*O*-benzyl-6-deoxy- α -D-glucopyranoside (1.0 g, 2.50 mmol) was dissolved in dry THF and treated with NaH (150 mg, 3.76 mmol). 6-Bromo-1-hexene (0.39 ml, 2.88 mmol) was added dropwise and the mixture was refluxed for 3 h. Excess NaH was quenched by adding methanol and the solution was diluted with water, extracted with ethyl acetate, dried and concentrated. The product was purified by flash chromatography (silica, eluent: hexanes/ethyl acetate = 4/1, R_f =0.43) to yield 521 mg (1.10 mmol, 43%) of (12).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ [ppm] = 1.34–1.43 (m, 2H), 1.48–1.58 (m, 2H), 2.03 (q, J = 7.0 Hz, 2H), 3.22 (dd, J = 9.8, 9.4 Hz, 1H), 3.40 (s, 3H, OCH_3), 3.45–3.51 (m, 3H), 3.72 (ddd, J = 9.9, 5.6, 2.5 Hz, 1H, 5-H), 3.80–3.90 (m, 2H), 4.59 (d, J = 3.5 Hz, 1H), 4.64 (d, J = 12.1 Hz, 1H), 4.77 (d, J = 10.9 Hz, 1H), 4.78 (d, J = 12.1 Hz, 1H), 4.94 (d, J = 10.9 Hz, 1H), 5.72–5.82 (m, 1H, 11-H), 7.26–7.37 (m, 10H, CH arom.).–

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ [ppm] = 25.46, 29.83, 33.56 (t, C-8, C-9, C-10), 51.41 (t, C-6), 55.31, 70.04 (d, CH), 73.17, 73.38, 75.63 (t, C-7, CH_2 benzyl.) 78.68, 79.72, 81.62 (d, CH), 97.97 (d, C-1), 114.55 (t, C-12). 127.49–128.33 (d, CH arom.), 137.88, 138.36 (s, C arom.), 138.49 (d, C-11).–

HRMS (ESI)	$\text{C}_{27}\text{H}_{35}\text{N}_3\text{O}_5\text{Na}$	$[\text{M}+\text{Na}^+]$	calcd	504.2469
			found	504.2464

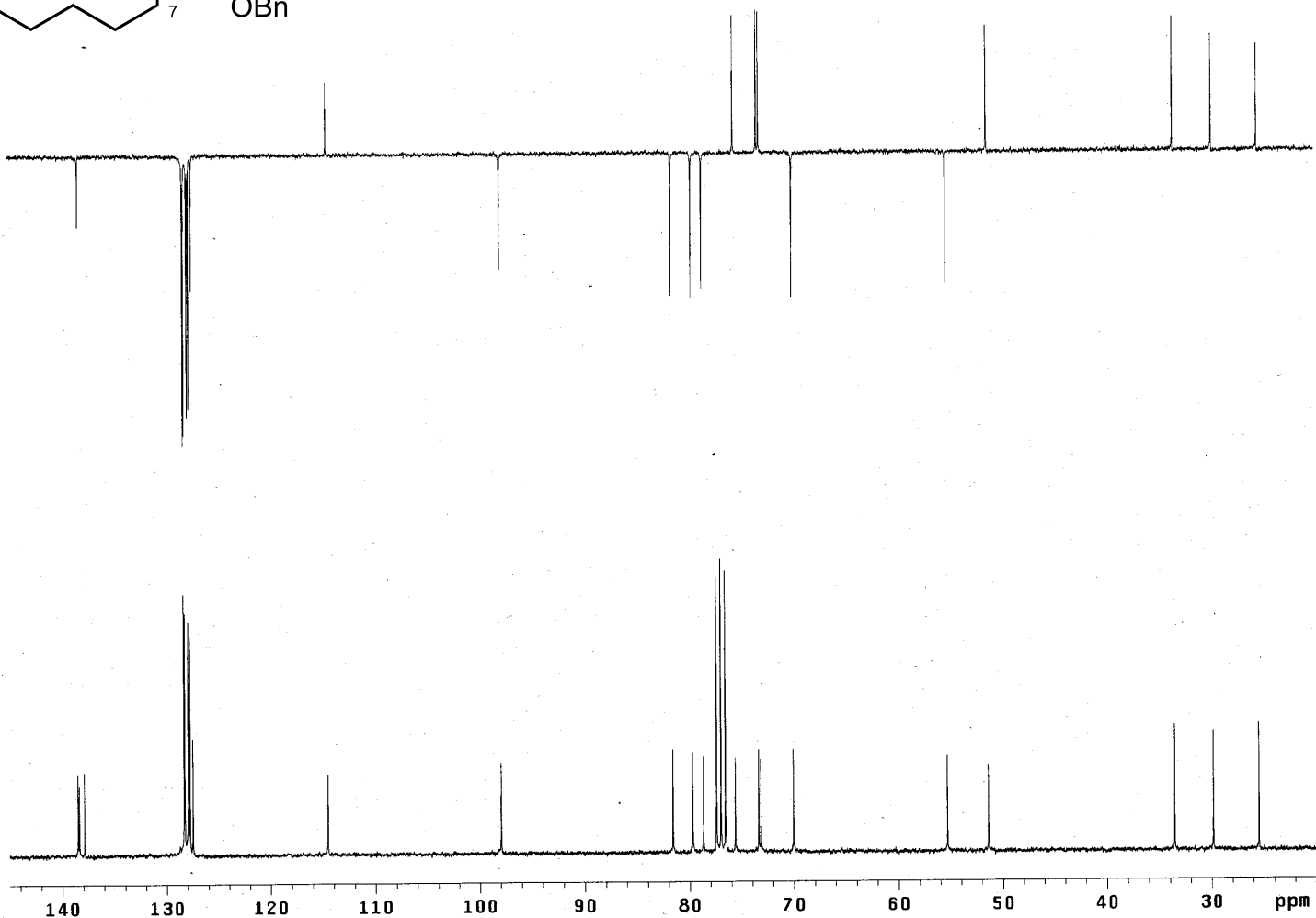
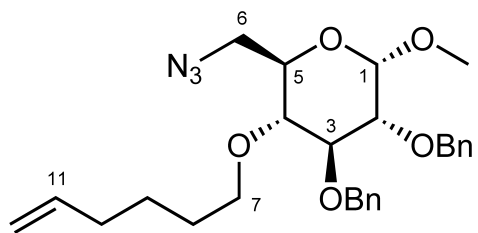
$\text{C}_{27}\text{H}_{35}\text{N}_3\text{O}_5$ (481.58)	Calcd	C 67.34	H 7.33	N 8.73
	Found	C 67.53	H 7.40	N 8.34



```

dos287.1H.cdcl3
Tue Nov 2 15:56 2004
exp1 std1h
SAMPLE
date Nov 2 2004
solvent CDCl3
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.40
wtfile
proc ft
fn 65536
DISPLAY
sp 203.5
wp 2965.6
vs 162
sc 65
wc 225
hzmm 13.18
is 346.29
rfl 3551.6
rfp 0
th 2.1
ins 2.000
rp 2.1
lp -193.8
nm ph

```



DOS287/CDC13/136
 Doerner 021104_03
 DEPT-135
 Tue Nov 2 17:42 2004

exp7 dept

SAMPLE
 date Nov 2 2004
 solvent CDCl3
 file exp

ACQUISITION
 instrum g300
 probe atb5
 seqfil dept
 sfrq 75.500
 tn C13
 at 1.747
 np 65906
 sw 18867.9
 bs 16
 tpwr 56
 pw 9.6
 d1 2.000
 d2 0
 tof 767.8
 nt 500
 ct 500
 alock n
 gain not used
 pp 16.2
 pplvl 56
 J 140.0
 mult 1.5
 satdly 0

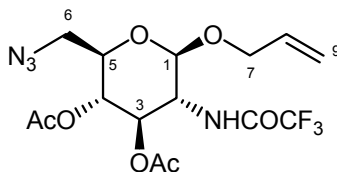
FLAGS
 il n
 in n

DEC. & VT
 dn H1
 dfrq 300.225
 homo n
 dpwr 37
 dof 0
 dm nny
 dmm ccw
 dmf 7900
 pplvl 56
 pp 16.2
 J 140.0

PROCESSING
 lb 1.00
 wtfile ft
 proc fn 65536

wexp procplot
 DISPLAY
 sp 1509.7
 wp 9437.1
 vs 50
 sc 65
 wc 225
 hzmm 41.94
 rfl 1137.9
 rfp 0
 th 5.0
 rp 248.4
 lp -280.7
 nm no ph

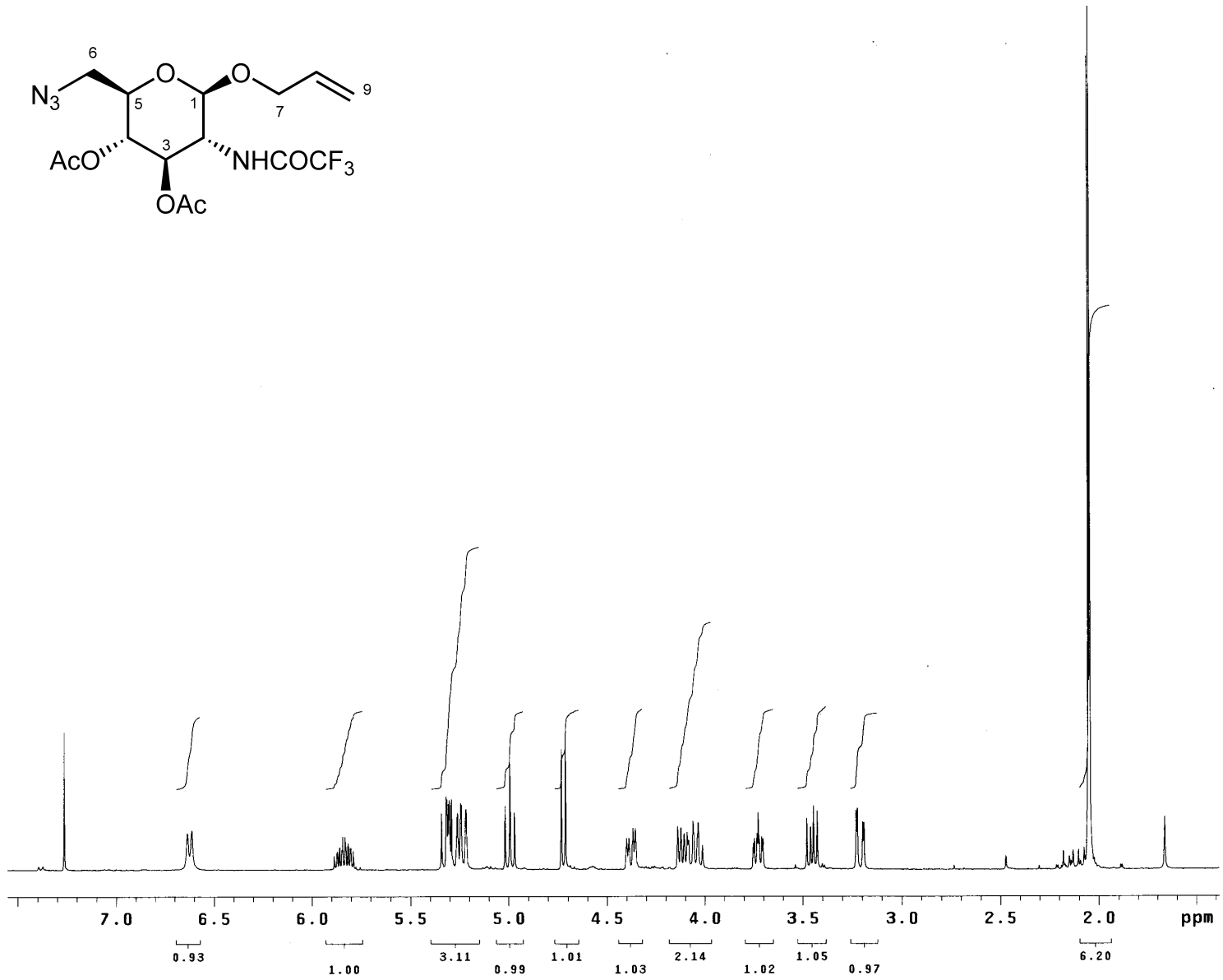
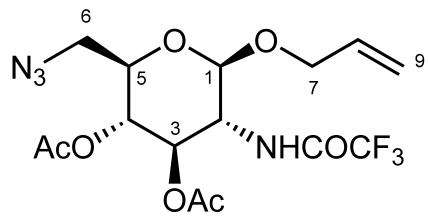
Allyl 3,4-di-*O*-acetyl-6-azido-2,6-dideoxy-2-[(trifluoroacetyl)amino]- β -D-glucopyranoside (13)^[2]



¹H-NMR (500 MHz, CDCl₃): δ [ppm] = 2.04, 2.05 (s, 3H, CH_{3(Ac)}), 3.22 (dd, J = 13.4, 2.4 Hz, 1H, 6^a-H), 3.46 (dd, J = 13.4, 7.6 Hz, 1H, 6^b-H), 3.75 (ddd, J = 10.0, 7.6, 2.4 Hz, 1H, 5-H), 4.05–4.09 (m, 1H, 2-H), 4.12 (dddd, J = 13.2, 6.4, 1.3, 1.3 Hz, 1H, 7^a-H), 4.37 (dddd, J = 13.2, 4.9, 1.5, 1.5 Hz, 1H, 7^b-H), 4.73 (d, J = 8.3 Hz, 1H, 1-H), 5.00 (dd, J = 10.0, 9.3 Hz, 1H, 4-H), 5.22 (ddd, J = 10.4, 2.6, 1.3 Hz, 1H, 9^a-H), 5.28 (ddd, J = 17.2, 3.2, 1.6 Hz, 1H, 9^a-H), 5.34 (dd, J = 10.7, 9.3 Hz, 1H, 3-H), 5.84 (dddd, J = 17.2, 10.4, 6.4, 4.9 Hz, 1H, 8-H), 6.91 (bd, J = 9.0 Hz, 1H, NH)

¹³C-NMR (125 MHz, CDCl₃): δ [ppm] = 20.49, 20.68 (q, CH_{3(Ac)}), 51.14 (t, C-6), 54.80 (d, C-2), 69.67 (d, C-4), 69.97 (t, C-7), 77.52 (d, C-3), 73.70 (d, C-5), 98.71 (d, C-1), 115.45 (q, $^1J(^{13}\text{C}, ^{19}\text{F}) = 287.3$ Hz, CF₃), 118.21 (t, C-9), 132.74 (d, C-8), 157.23 (q, $^2J(^{13}\text{C}, ^{19}\text{F}) = 37.4$ Hz, C(O)CF₃), 169.30, 171.04 (s, CO).–

HRMS (ESI)	C ₁₅ H ₁₉ F ₃ N ₄ O ₇ Na	[M+Na ⁺]	calcd	447.1098
			found	447.1095

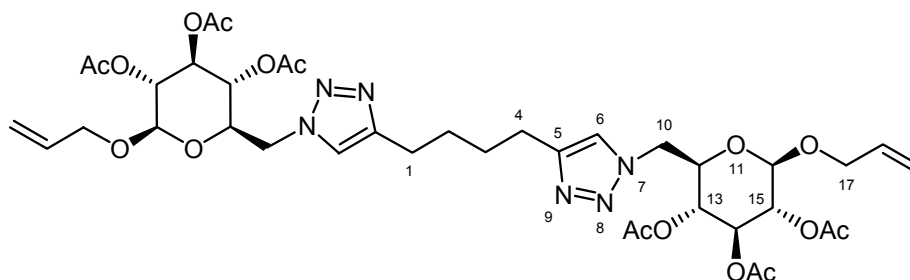


```

1H Standard-Parameter
Mon Jan 10 17:41 2005
exp7 std1h
SAMPLE
date Jan 10 2005
solvent CDC13
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 0
alock
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.40
wtfile
proc ft
fn 65536
DISPLAY
sp 553.0
wp 2467.6
vs 162
sc 65
wc 225
hzmm 10.97
is 977.74
rf1 3544.8
rfp 0
th 2.1
ins 1.000
rp -2.4
lp -189.1
nm ph
  
```

3 Experimental data and spectra for dimerized molecules 14–17

Butane-1,4-diylbis[1*H*-7,8,9-triazole-5,7-diylmethylene(12*S*,13*S*,14*R*,15*S*,16*S*)-16-(allyloxy)tetrahydro-2*H*-pyran-12,13,14,15-tetrayl] hexaacetate (14)



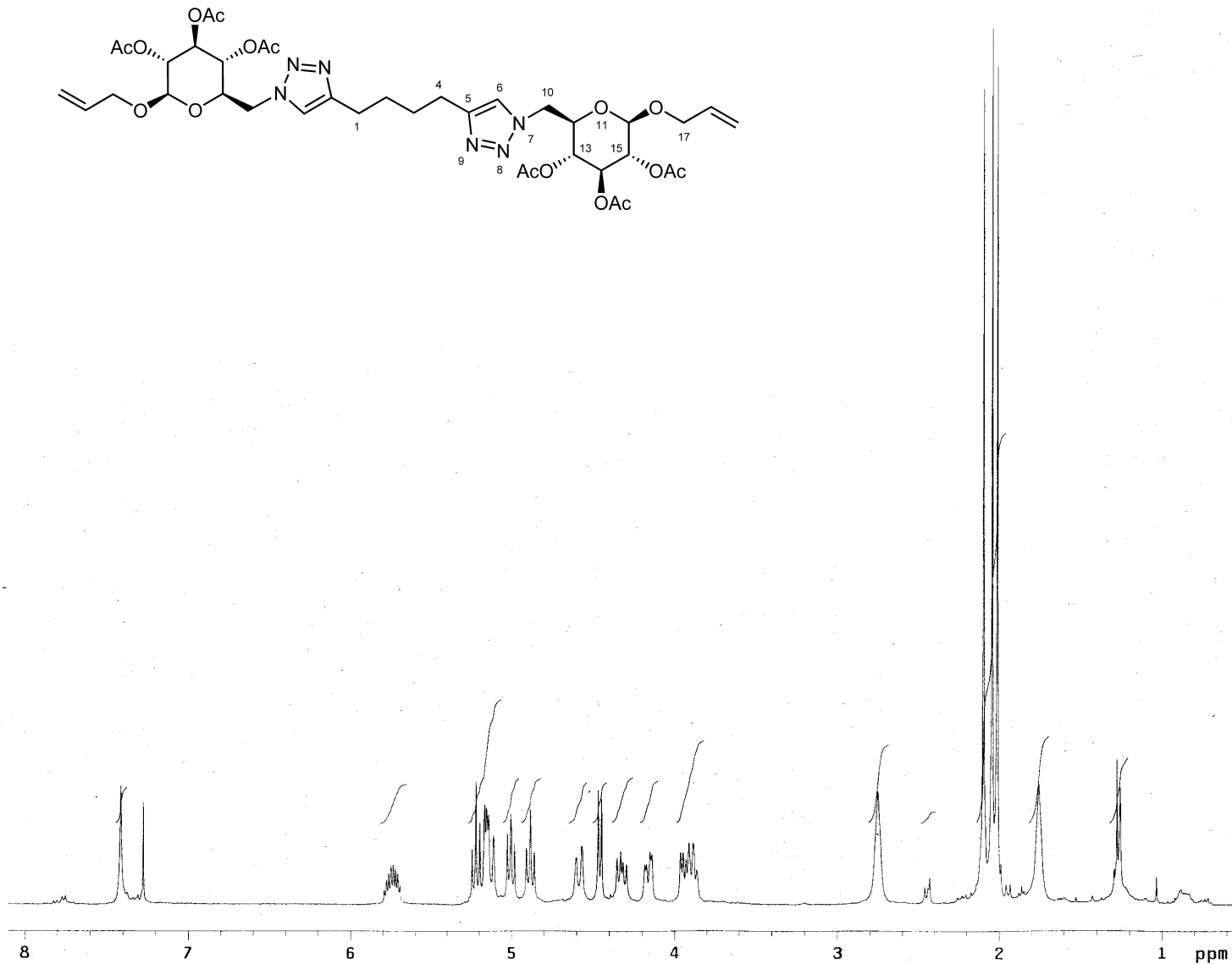
$$[\alpha]_{\text{D}}^{23} = -21.5 \quad (c = 0.265, \text{CHCl}_3)$$

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 1.75 (bs, 4H), 2.01, 2.04, 2.10 (s, 3H, CH_{3(Ac)}), 2.75 (bs, 4H), 3.85–3.98 (m, 4H), 4.16 (dd, *J* = 13.3, 4.7 Hz, 2H), 4.33 (dd, *J* = 14.4, 8.6 Hz, 2H), 4.46 (d, *J* = 8.2 Hz, 2H), 4.58 (dd, *J* = 14.4, 1.2 Hz, 2H), 4.88 (t, *J* = 9.8 Hz, 2H), 5.00 (dd, *J* = 9.6, 8.0 Hz, 2H), 5.10–5.18 (m, 4H), 5.22 (t, *J* = 9.6 Hz, 2H), 5.69–5.80 (m, 2H), 7.42 (bs, 2H).–

¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 20.65, 20.71, 20.75 (q, CH_{3(Ac)}), 25.38, 29.08, (t, C-4, C-3), 50.80 (t, C-10), 69.93 (t, C-17), 70.13, 71.08, 72.39 (d, C-12, C-13, C-14, C-15), 99.29 (d, C-16), 117.86 (t, C-18), 122.50 (d, C-6), 132.63 (d, C-18), 147.65 (s, C-5), 169.14, 169.54, 169.90 (s, CO).–

HRMS (ESI)	C ₃₈ H ₅₂ N ₆ O ₁₆ Na	[M+Na ⁺]	calcd	871.3332
			found	871.3318

C₃₈H₅₂N₆O₁₆ (848.85)	Calcd	C 53.77	H 6.17
	Found	C 53.99	H 6.46



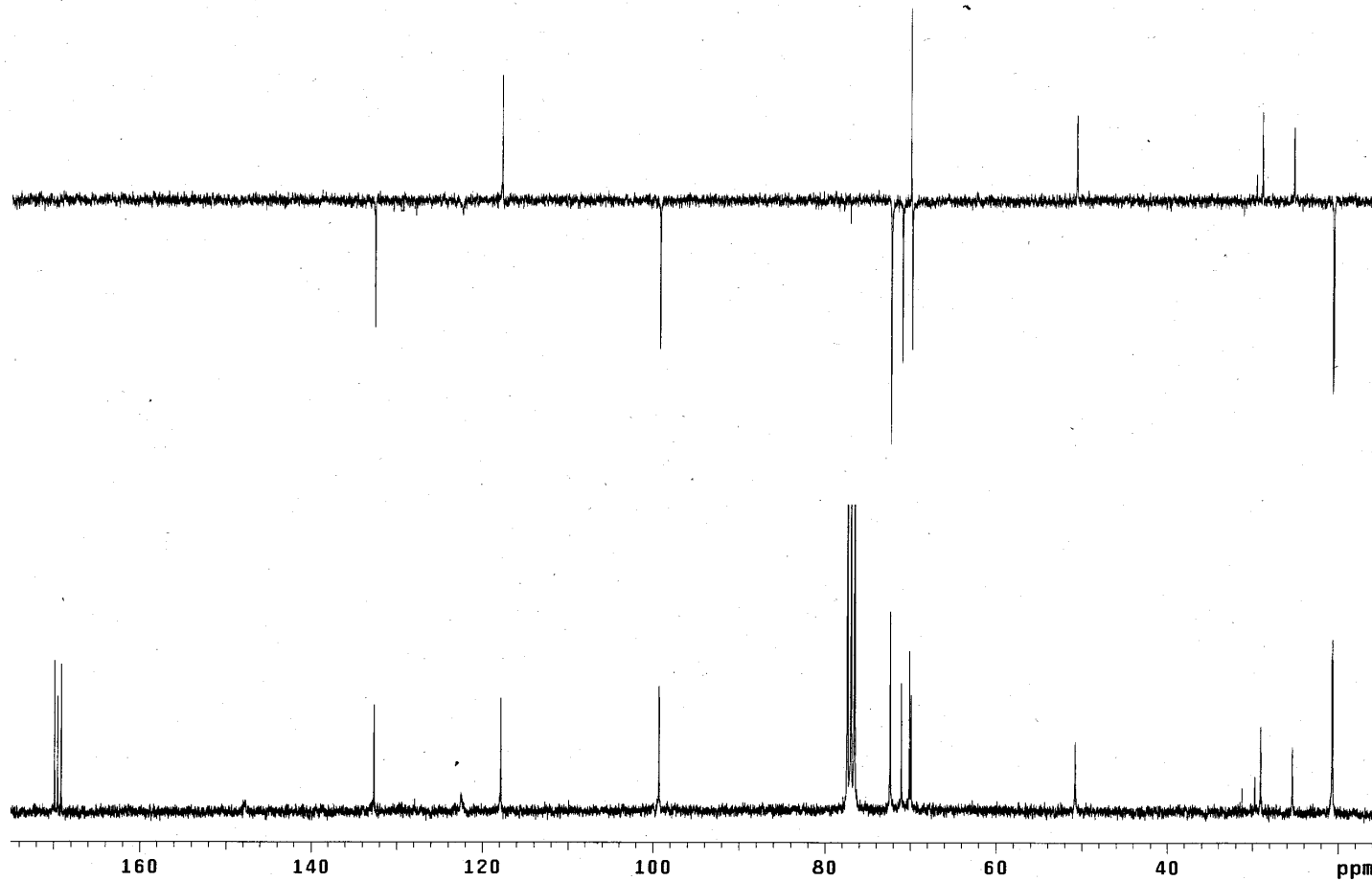
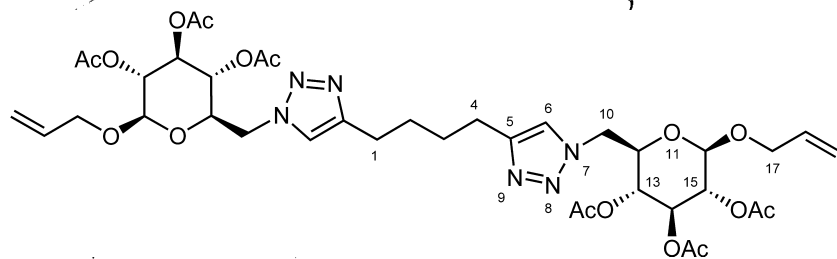
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dos283.1H.cdc13
Fri Oct 22 15:25 2004
exp6 std1h

SAMPLE
date Oct 22 2004
solvent CDC13
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 20
ct 20
alock n
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm hnn
dmm c
dmf 200
PROCESSING
lb 0.40
wtfile
proc ft
fn 65536

DISPLAY
sp 221.3
wp 3018.3
vs 162
sc 65
wc 225
hzmm 13.41
is 929.56
rf1 3540.5
rfp 0
th 2.1
ins 100.000
rp 18.8
lp -238.8
nm ph

```



DOS283/CDC13/13C
Doerner 251004_01
DEPT-135
Mon Oct 25 16:21 2004

exp9 dept

SAMPLE
date Oct 25 2004
solvent CDC13
file exp

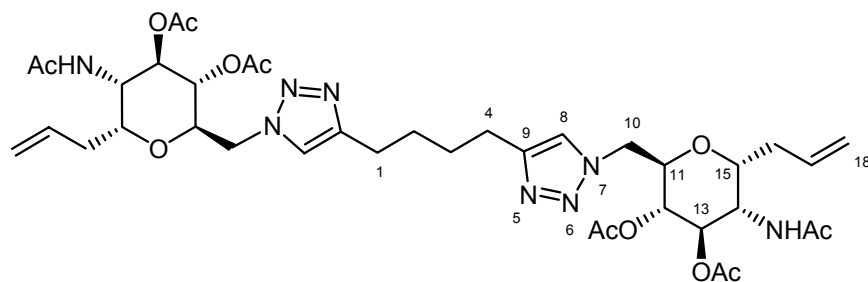
ACQUISITION
instrum g300
probe atb5
seqfil dept
sfrq 75.500
tn C13
at 1.747
np 65906
sw 18867.9
bs 16
tpwr 56
pw 9.6
d1 2.000
d2 0
tof 767.8
nt 1000
ct 1000
alock n
gain not used
pp 16.2
pplvl 56
J 140.0
mult 1.5
satdly 0

FLAGS
f1 n
f2 n
DEC. & VT
dn H1
dfrq 300.225
homo n
dpwr 37
dof 0
dm nny
dmm ccw
dmf 7900
pplvl 56
pp 16.2
J 140.0

PROCESSING
lb 1.00
wtfile
proc ft
fn 65536

wexp procplot
DISPLAY
sp 1132.4
wp 12079.6
vs 40
sc 65
wc 225
hzmm 53.69
rfl 1135.7
rfp 0
th 20.0
rp 217.1
lp -224.7
nm no ph

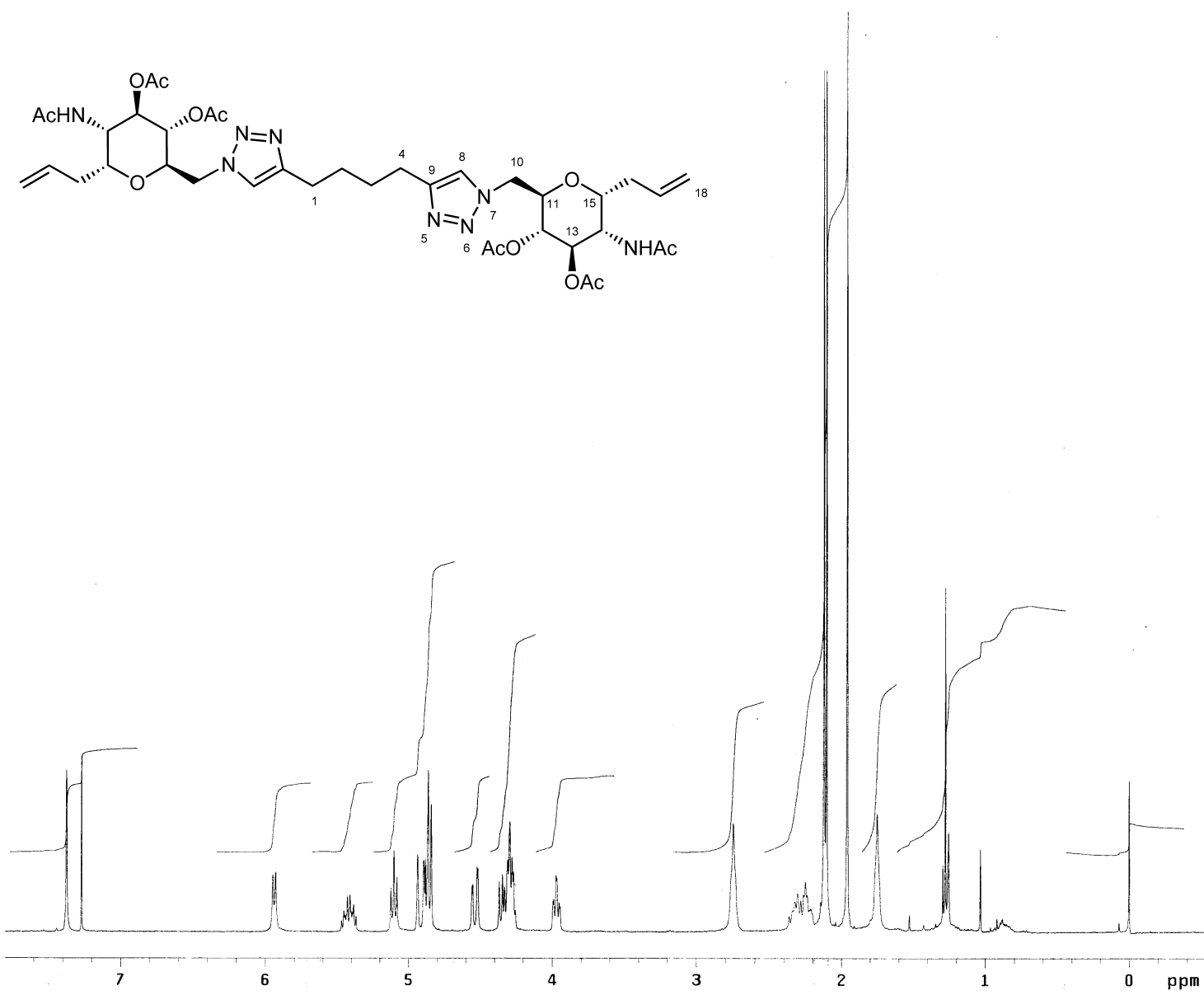
Butane-1,4-diylbis[1*H*-5,6,7-triazol-9,7-diylmethylene(11*S*,12*S*,13*S*,14*R*,15*S*)-14-(acetyl-amino)-15-allyltetrahydro-2*H*-pyran-11,12,13-triyl] tetraacetate (15)



¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 1.69–1.83 (bs, 4H, 3-H), 1.96 (s, 6H, CH_{3(NHAc)}), 2.10, 2.12 (s, 6H, CH_{3(Ac)}), 2.18–2.40 (m, 4H, 16-H), 2.70–2.80 (bs, 4H, 4-H), 3.97 (dt, *J* = 8.6, 2.7 Hz, 1H, 11-H), 4.25–4.38 (m, 6H), 4.54 (dd, *J* = 14.2, 2.5 Hz, 2H), 4.84–4.95 (m, 6H), 5.10 (t, *J* = 8.4 Hz, 2H), 5.36–5.48 (m, 2H, 17-H), 5.94 (d, *J* = 7.8 Hz, 2H, NH), 7.38 (s, 2H, 8-H).–

¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 20.75, 20.80 (q, CH_{3(Ac)}), 23.10 (q, CH_{3(NHAc)}), 25.17, 28.90, 30.93 (t, C-3, C-4, C-16), 50.42 (t, C-10), 51.30 (d, C-14), 69.39, 70.15, 70.57, 71.79 (d, C-11, C-12, C-13, C-15), 117.85 (t, C-18), 122.36 (d, C-8), 132.81 (d, C-17), 147.81 (s, C-9), 169.42, 169.93, 171.44 (s, CO).–

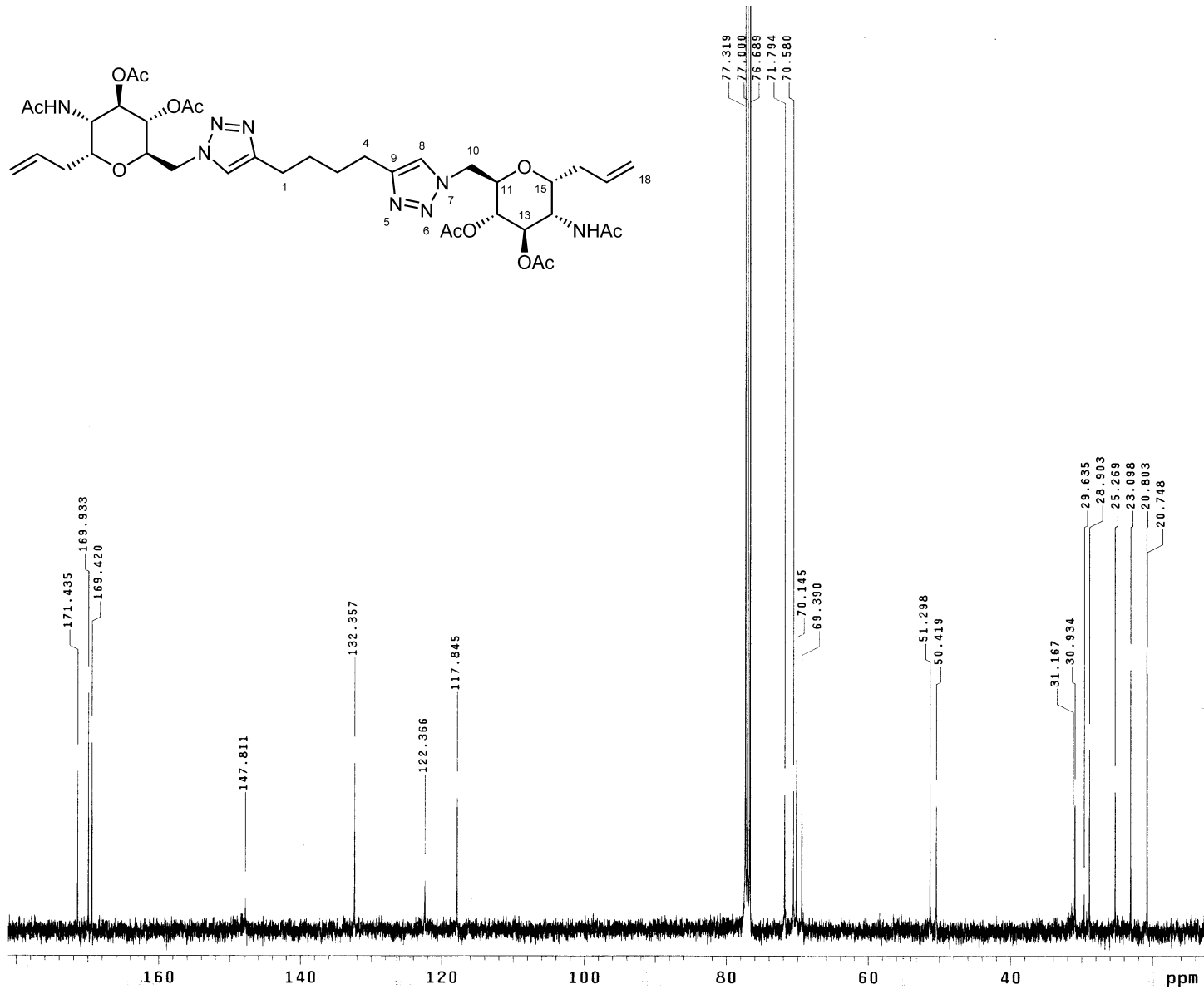
HRMS (ESI)	C ₃₈ H ₅₄ N ₈ O ₁₂ Na	[M+Na ⁺]	calcd	837.3753
			found	837.3745



```

dos306.1H.cd13
Tue Nov 30 10:24 2004
exp7 std1h
SAMPLE
date Nov 30 2004
solvent CDCl3
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.40
wtfile ft
proc ft
fn 65536
DISPLAY
sp -211.9
wp 3330.5
vs 162
sc 65
wc 225
hzmm 14.80
is 1904.45
rfl 3542.4
rfp 0
th 2.1
ins 100.000
rp 18.6
lp -221.1
nm ph

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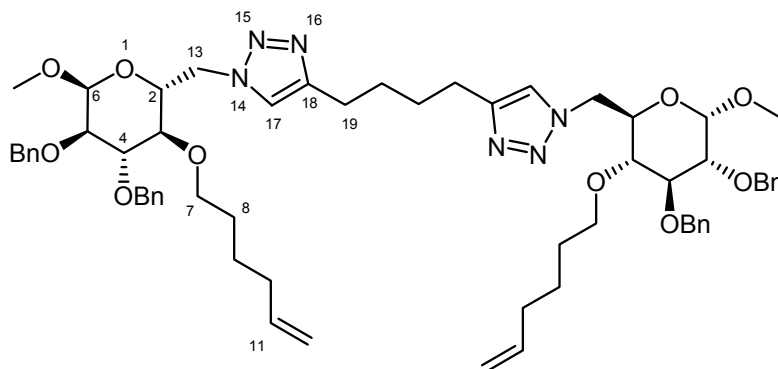


dos306.13C.cdc13
Tue Nov 30 10:38 2004

exp8 std13c

SAMPLE
date Nov 30 2004
solvent CDC13
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 100.574
tn C13
at 1.311
np 67216
sw 25641.0
bs 16
tpwr 61
pw 4.0
d1 1.689
d2 0
tof 1327.2
nt 1000
ct 1000
alock n
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 40
dof 0
dm yyy
dmm w
dmf 9350
pp 17.5
PROCESSING
lb 1.00
wtfile ft
proc
fn 65536
DISPLAY
sp 1278.9
wp 16934.6
vs 379
sc 65
wc 225
hzmm 75.27
rfl 9744.0
rfp 7743.4
th 5.2
rp 57.5
lp -329.5
nm no ph

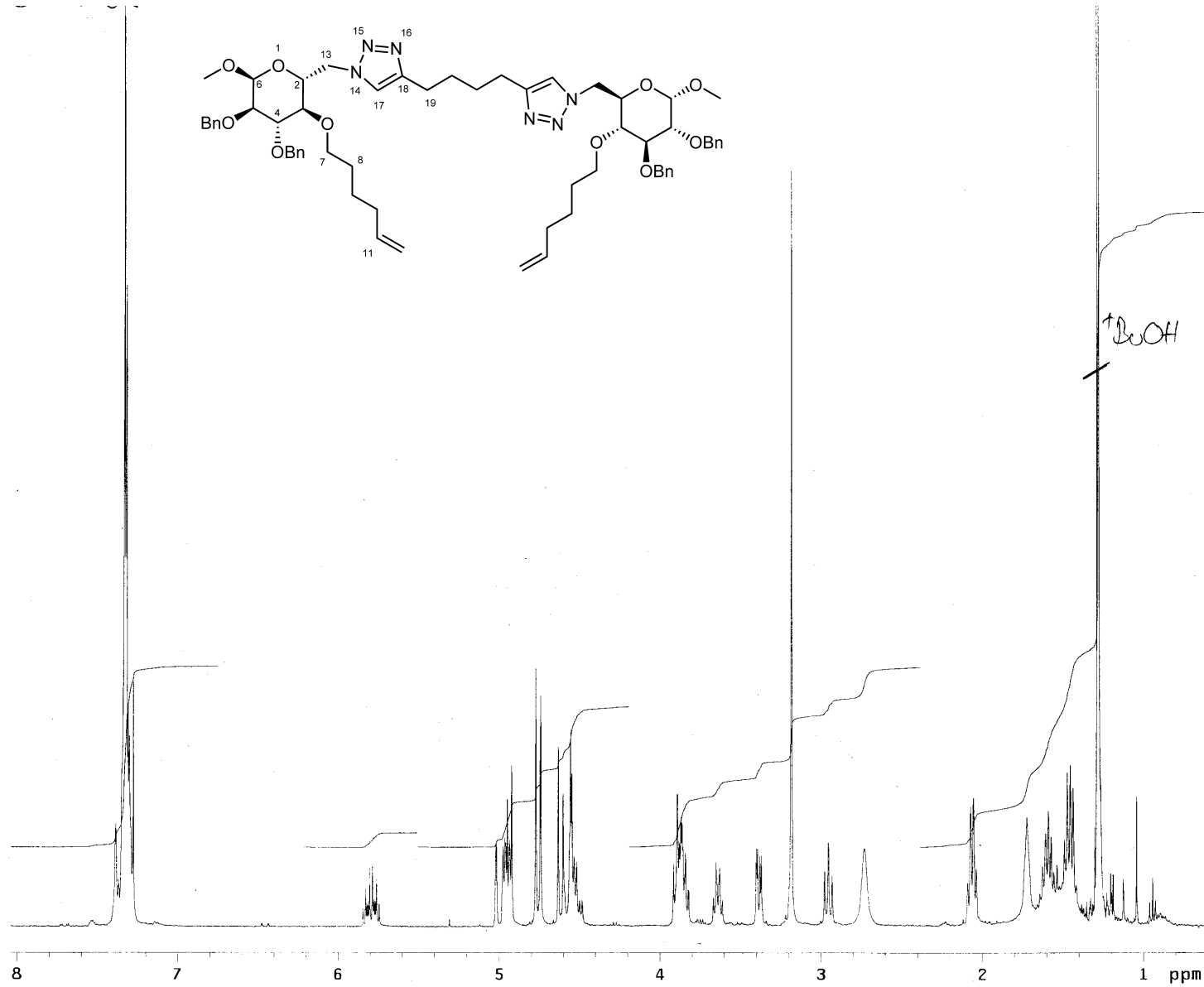
18,23-Butane-19,22-diylbis(14-{[(2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-bis(benzyloxy)-3-(hex-11-ene-7-yloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl]methyl}-1*H*-14,15,16-triazole) (16)



¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 1.41–1.65 (m, 12H), 1.73 (bs, 4H, 16-H), 2.03–2.10 (m, 4H), 2.73 (bs, 4H, 15-H), 2.95 (t, *J* = 9.0 Hz, 2H), 3.18 (s, 6H, 17-H), 3.38 (dd, *J* = 9.8, 3.5 Hz, 2H), 3.60–3.67 (m, 2H), 3.82–3.93 (m, 6H), 4.48–4.57 (m, 4H), 4.62 (d, *J* = 12.5 Hz, 2H), 4.76 (d, *J* = 11.7 Hz, 4H), 4.92–5.01 (m, 6H), 5.74–5.85 (m, 2H, 11-H), 7.29–7.36 (m, 20H, CH arom.).–

¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 25.31, 25.40, 28.90, 29.86, 33.57, 50.59 (t, CH₂), 55.20 (d, CH), 69.39 (d, CH), 73.18, 73.39, 75.70 (t, CH₂ benzyl, C-7), 78.61, 79.68, 81.66 (d, CH), 97.97 (d, C-1), 114.61 (t, C-12), 122.14 (d, C-13), 127.68–128.45 (d, CH arom.), 137.96, 138.43 (s, C arom.), 138.56 (d, C-11), 147.83 (s, C-14).–

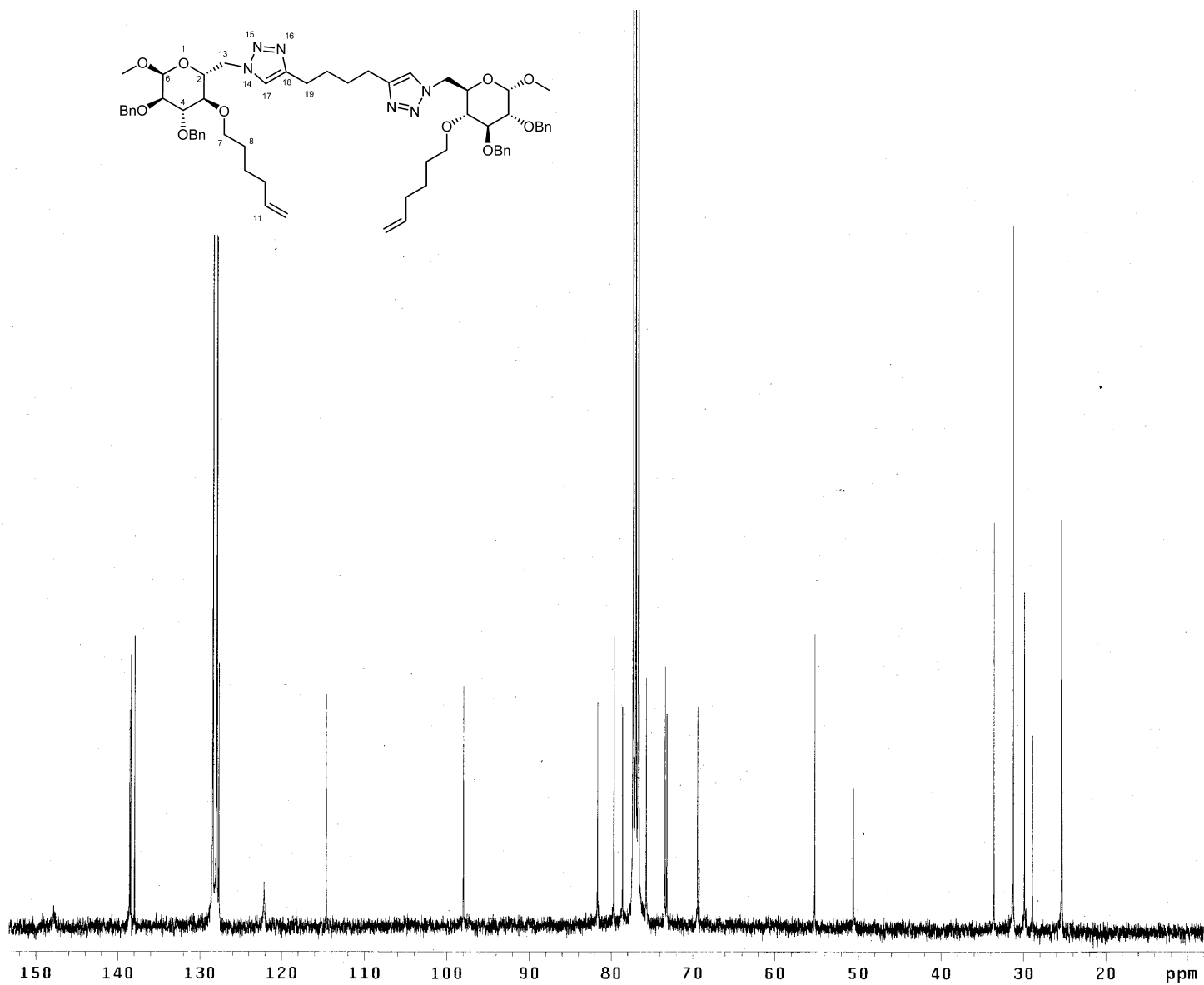
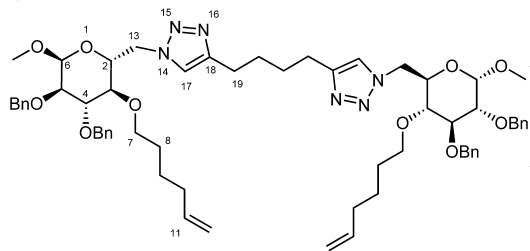
HRMS (ESI)	C ₆₂ H ₈₀ N ₆ O ₁₀ Na	[M+Na ⁺]	calcd	1091.5828
			found	1091.5816



```

dos288.1H.cdc13
Fri Nov 5 18:08 2004
expl std1h
SAMPLE
date Nov 5 2004
solvent CDCl3
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.40
wtfile
proc ft
fn 65536
DISPLAY
sp 241.1
wp 2973.0
vs 2249
sc 65
wc 225
hzmm 13.21
is 704.99
rf1 3539.8
rfp 0
th 2.9
ins 100.000
rp -0.2
lp -186.6
nm ph

```



dos288,13C.cdc13
Fri Nov 5 19:19 2004

exp2 std13c

SAMPLE
date Nov 5 2004
solvent CDC13
file exp

ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 100.574
tn C13
at 1.311
np 67216
sw 25641.0
bs 16
tpwr 61
pw 4.0
d1 1.689
d2 0
tof 1327.2
nt 12000
ct 12000
alock n
gain not used

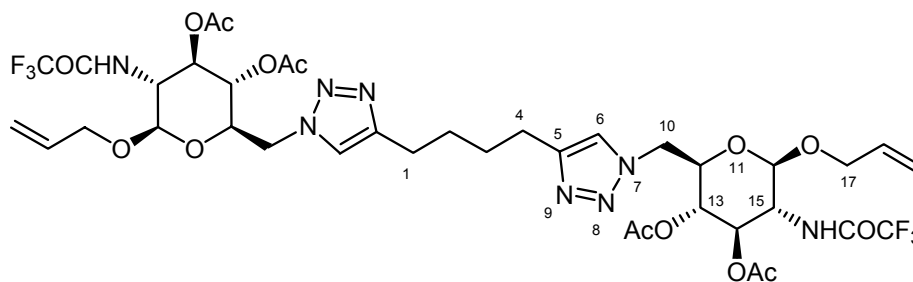
FLAGS
il n
in n
dp y

DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 40
dof 0
dm yyy
dmm w
dmf 9350
pp 17.5

PROCESSING
lb 1.00
wtfile
proc ft
fn 65536

DISPLAY
sp 803.5
wp 14609.0
vs 1091
sc 65
wc 225
hzmm 64.93
rfl 9742.1
rfp 7743.4
th 20.0
rp 48.6
lp -339.8
nm no ph

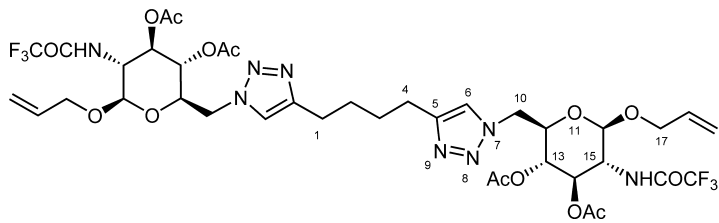
Butane-1,4-diylbis{1*H*-7,8,9-triazole-5,7-diylmethylene(12*S*,13*S*,14*S*,15*S*,16*S*)-16-(allyloxy)-15-[(trifluoroacetyl)amino]tetrahydro-2*H*-pyran-12,13,14-triyl} tetraacetate (17)



¹H-NMR (400 MHz, DMSO-*d*₆): δ [ppm] = 1.60 (bs, 4H), 1.90, 2.01 (s, 3H, CH_{3(Ac)}), 2.61 (bs, 4H), 3.79–3.90 (m, 4H), 3.93–4.06 (m, 4H), 4.43 (dd, *J* = 14.6, 8.4 Hz, 2H), 4.58 (dd, *J* = 14.4, 2.7 Hz, 2H), 4.62 (d, *J* = 8.6 Hz, 2H), 4.80 (t, *J* = 9.6 Hz, 2H), 5.00–5.07 (m, 4H), 5.17 (dd, *J* = 10.3, 9.6 Hz, 2H), 5.63–5.74 (m, 2H), 7.80 (s, 2H), 9.63 (d, *J* = 9.0 Hz, 2H).–

¹³C-NMR (100 MHz, DMSO-*d*₆): δ [ppm] = 20.16, 20.60 (q, CH_{3(Ac)}), 24.71, 28.57, (t, C-4, C-3), 49.83 (t, C-10), 53.69 (d, C-15), 69.09 (t, C-17), 69.88, 71.39, 71.78 (d, C-14, C-13, C-12), 98.42 (d, C-16), 115.70 (m, CF₃), 116.76 (t, C-19), 122.83 (d, C-6), 133.59 (d, C-18), 146.36 (s, C-5), 156.47 (m, C(O)CF₃), 169.20, 169.39 (s, CO).–

HRMS (ESI)	C ₃₈ H ₅₂ N ₆ O ₁₆ Na	[M+Na ⁺]	calcd	871.3332
			found	871.3318

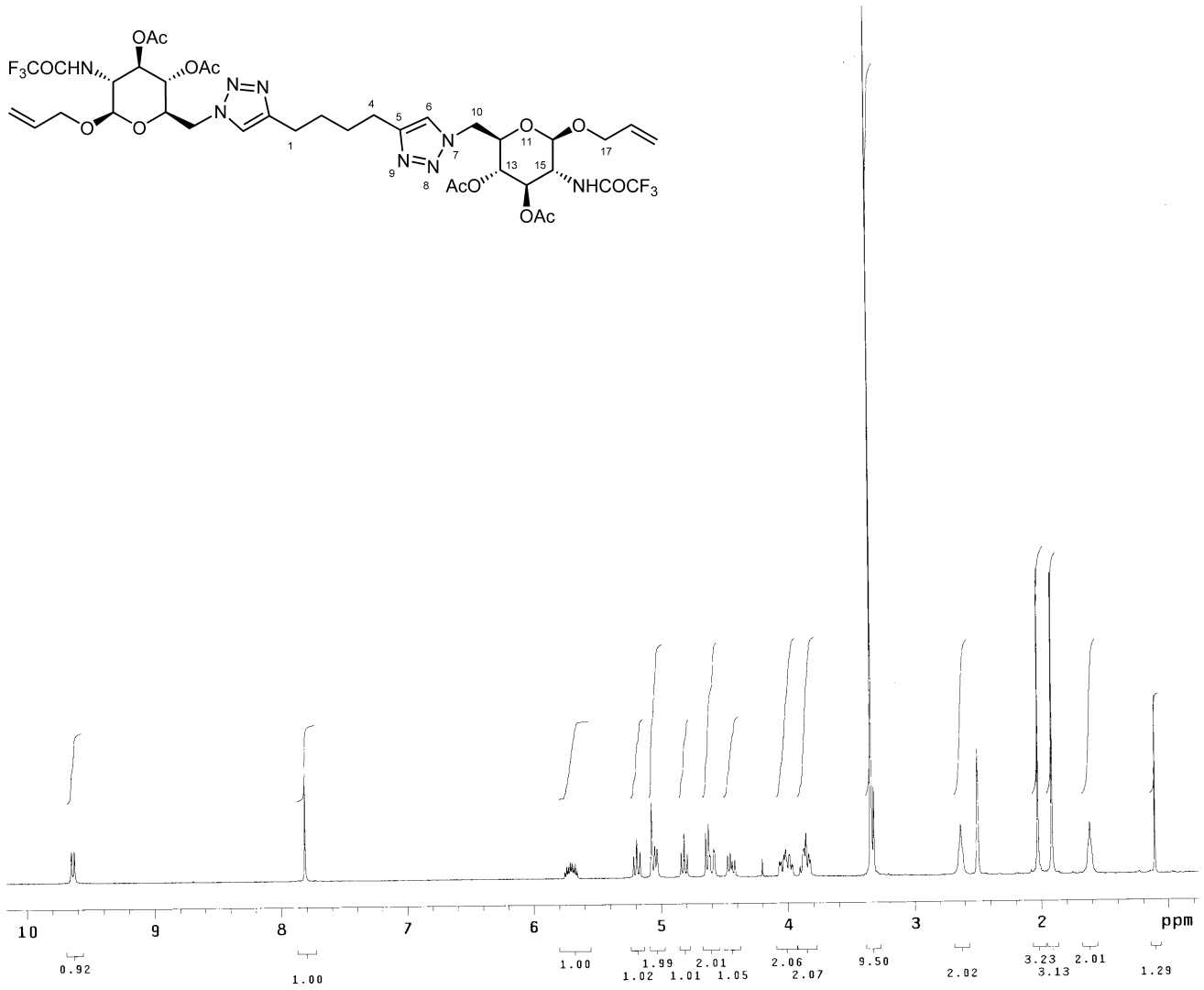


```

dos272.1H.dms0.110195
Tue Jan 11 12:40 2005

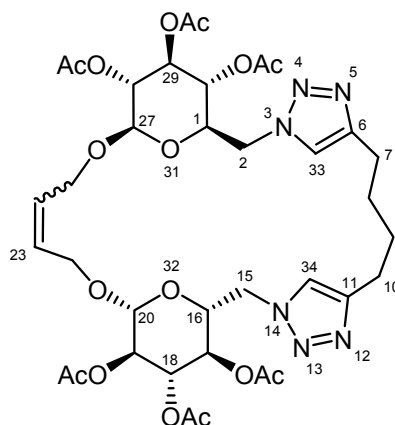
exp7 std1h

SAMPLE
date Jan 11 2005
solvent DMSO
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pu1
sfrq 399.939
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 0
alock n
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.938
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.40
wtfile ft
proc ft
fn 65536
DISPLAY
sp 304.3
wp 3761.7
vs 198
sc 85
wc 225
hzmm 16.72
is 2415.53
rfl 4532.2
rfp 1000.2
th 2.9
ins 1.000
rp 5.1
dp -194.8
nm ph
  
```



4 Experimental data and spectra for cyclic molecules 18–25

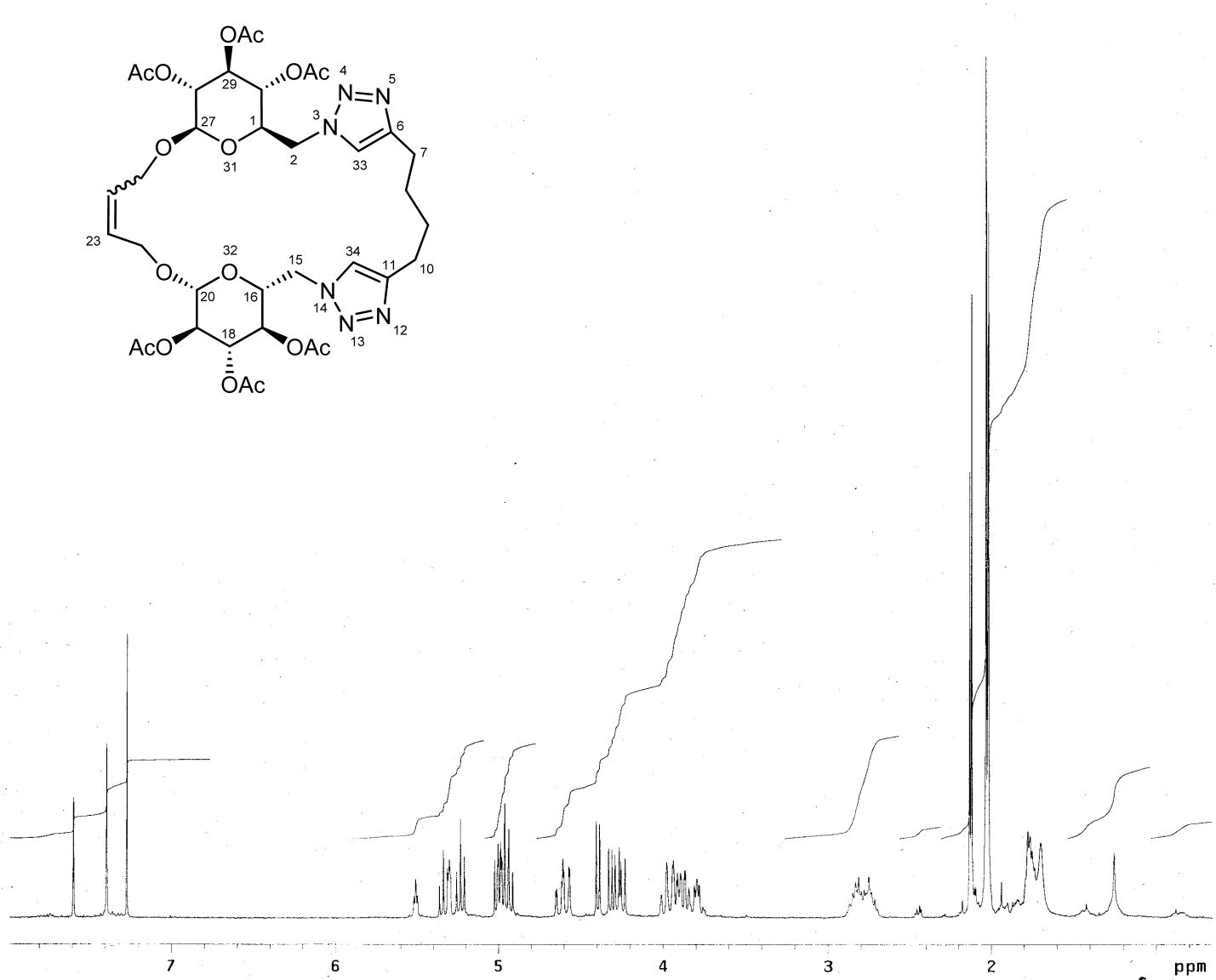
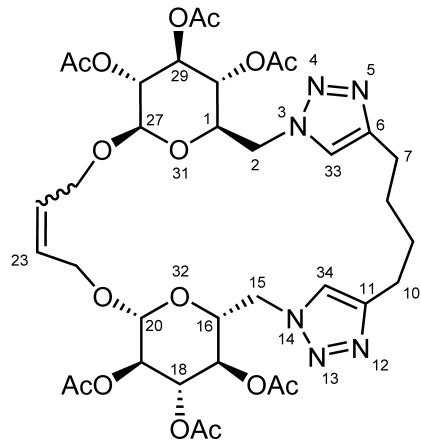
(1*R*,16*R*,17*R*,18*S*,19*R*,20*R*,23(*E*;Z),27*R*,28*R*,29*S*,30*R*)-21,26,31,32-tetraoxa-3,4,5,12,13,14-hexaazapentacyclo[25.3.1.1^{3,6}.1^{11,14}.1^{16,20}]tetratriaconta-4,6(34),11(33),12,23-pentaene-17,18,19,28,29,30-hexayl hexaacetate (18)



¹H-NMR (400 MHz, CDCl₃): isomer mixture: δ [ppm] = 1.66–1.82 (m, 4H, 8-H), 2.02, 2.02, 2.03, 2.12, 2.13 (s, 6H, CH_{3(Ac)}), 2.70–2.88 (m, 4H, 7-H), 3.77–4.03 (m, 6H), 4.22–4.44 (m, 4H), 4.55–4.66 (m, 2H), 4.90–5.04 (m, 4H), 5.20–5.54 (m, 4H), 7.39, 7.59 (s, 2H, 33-H).–

¹³C-NMR (100 MHz, CDCl₃) major isomer: δ [ppm] = 20.56, 20.59, 20.61 (q, CH_{3(Ac)}), 25.32, 28.29 (t, C-7, C-8), 50.67 (t, C-2), 68.32 (t, C-22), 70.09, 71.22, 72.39, 72.56 (d, C-16–C-19), 99.67 (d, C-20), 122.61 (d, C-33), 128.34 (d, C-23), 147.53 (s, C-6), 169.87, 169.96, 170.04 (s, CO).–

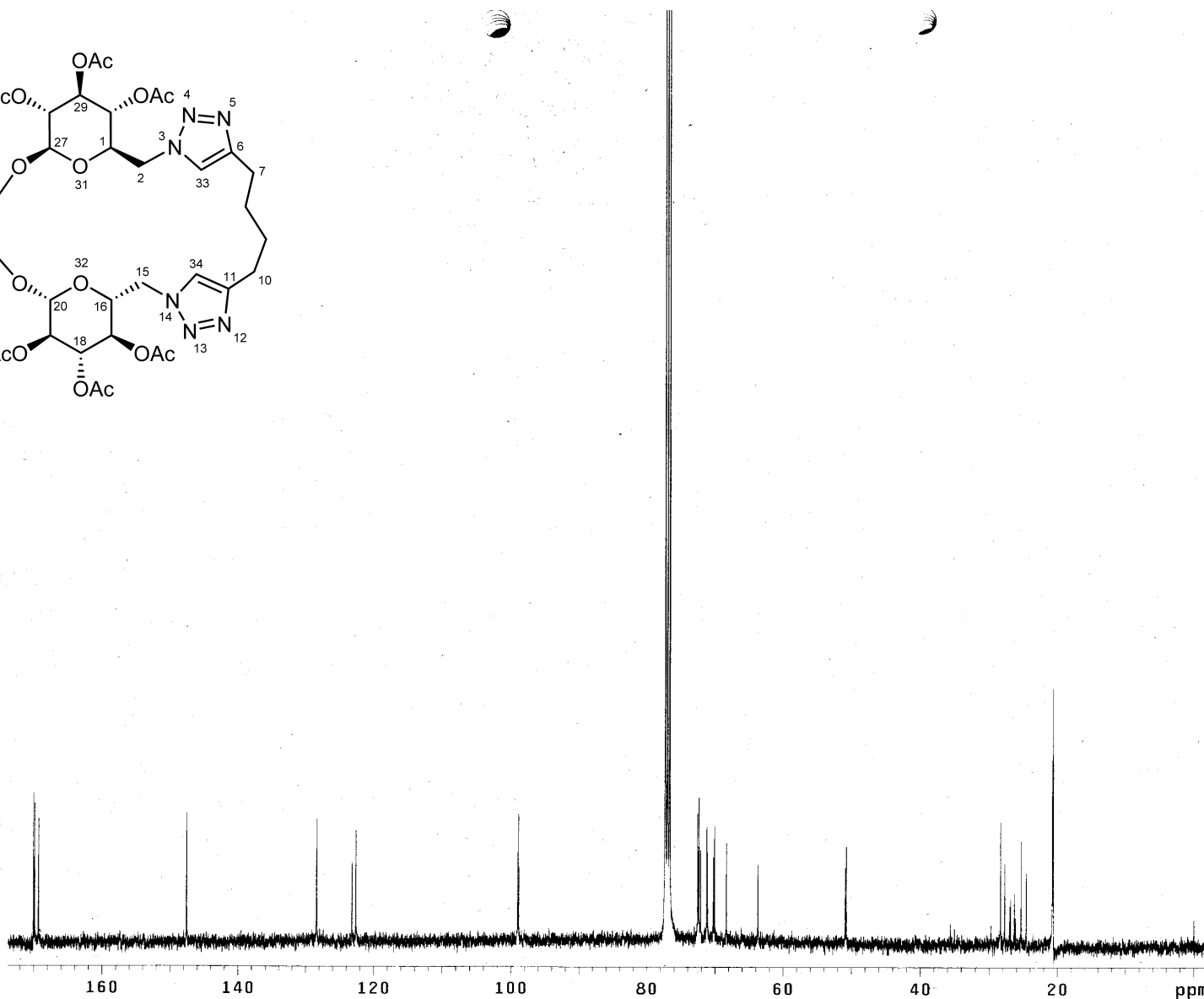
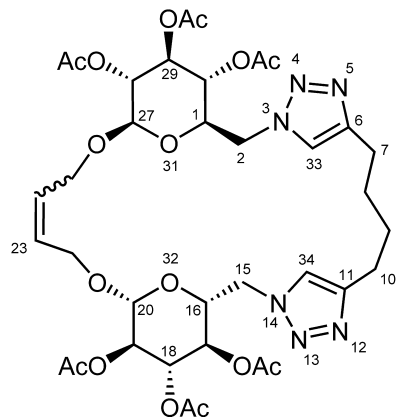
HRMS (ESI) C₃₆H₄₈N₆O₁₆Na [M+Na⁺] calcd 843.3019
found 843.3017



```

dos285.1H.cdc13
Fri Oct 29 13:22 2004
exp2 std1h
SAMPLE
date Oct 29 2004
solvent CDC13
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.40
wtfile
proc ft
fn 65536
DISPLAY
sp 263.0
wp 2928.9
vs 162
sc 65
wc 225
hzmm 13.02
is 680.76
rfl 3543.2
rfp 0
th 2.1
ins 100.000
rp 2.2
lp -188.0
nm ph

```



dos285.13C.cdc13
 Fri Oct 29 18:07 2004

exp2 std13c

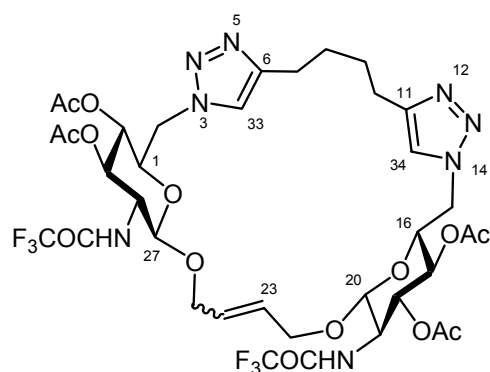
SAMPLE
 date Oct 29 2004
 solvent CDC13
 file exp

ACQUISITION
 instrum m400
 probe asw5
 seqfil s2pul
 sfrq 100.574
 tn C13
 at 1.311
 np 67216
 sw 25641.0
 bs 16
 tpwr 61
 pw 4.0
 d1 1.689
 d2 0
 tof 1327.2
 nt 15000
 ct 15000
 alock n
 gain not used

FLAGS
 il n
 in n
 dp y
 DEC. & VT
 dn H1
 dfrq 399.936
 homo n
 dpwr 40
 dof 0
 dm yyy
 dmm w
 dmf 9350
 pp 17.5
 PROCESSING
 lb 1.00
 wtfile
 proc ft
 fn 65536

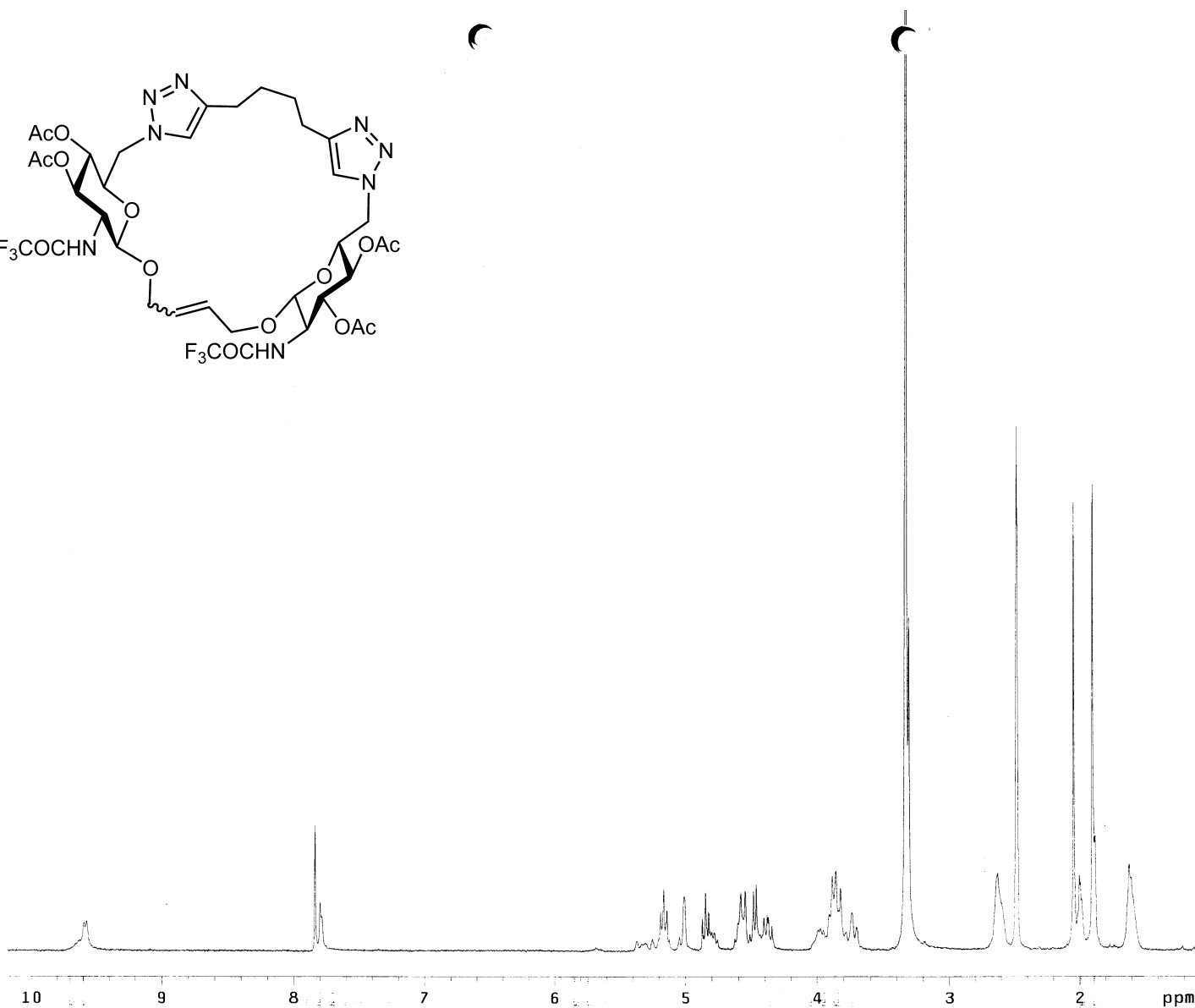
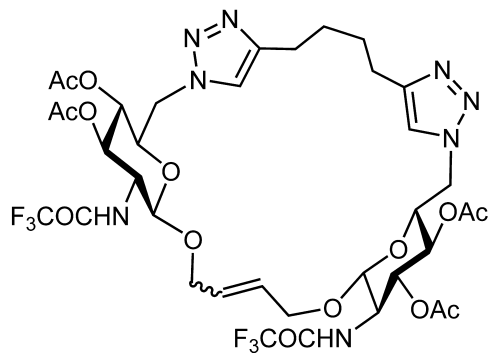
DISPLAY
 sp -298.5
 wp 17769.6
 vs 926
 sc 65
 wc 225
 hzmm 78.98
 rfl 9740.8
 rfp 7743.4
 th 6.3
 rp 68.0
 lp -372.4
 nm no ph

(1*R*,16*R*,17*R*,18*R*,19*R*,20*R*,23(*E*,*Z*),27*R*,28*R*,29*R*,30*R*)-19,28-Bis[(trifluoroacetyl)amino]-21,26,31,32-tetraoxa-3,4,5,12,13,14-hexaazapentacyclo[25.3.1.1^{3,6}.1^{11,14}.1^{16,20}]tetratriaconta-4,6(34),11(33),12,23-pentaene-17,18,29,30-tetrayl tetraacetate (19)



¹H-NMR (400 MHz, CDCl₃) isomer mixture: δ [ppm] = 1.56–1.68 (m, 4H), 1.88–1.95 (m, 6H), 1.98–2.09 (m, 6H), 2.57–2.69 (m, 4H), 3.70–4.06 (m, 8H), 4.34–4.66 (m, 6H), 4.76–4.90 (m, 2H), 5.00–5.40 (m, 4H), 7.78–7.87 (m, 2H), 9.55–9.69 (m, 2H).–

HRMS (ESI)	C ₃₆ H ₄₄ F ₆ N ₈ O ₁₄ Na	[M+Na ⁺]	calcd	949.2773
			found	949.2773



```

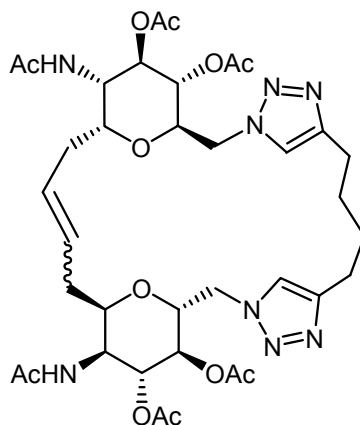
dos276.1H.dms0.dezember
Fri Dec 3 12:51 2004
exp7 std1h

SAMPLE
date Dec 3 2004
solvent DMSO
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.939
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.938
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.40
wtfile
proc ft
fn 65536

DISPLAY
sp 430.4
wp 3642.7
vs 590
sc 65
wc 225
hzmm 16.19
rfl 3539.8
rfp 0
th 2.1
rp 23.3
lp -229.9
nm ph

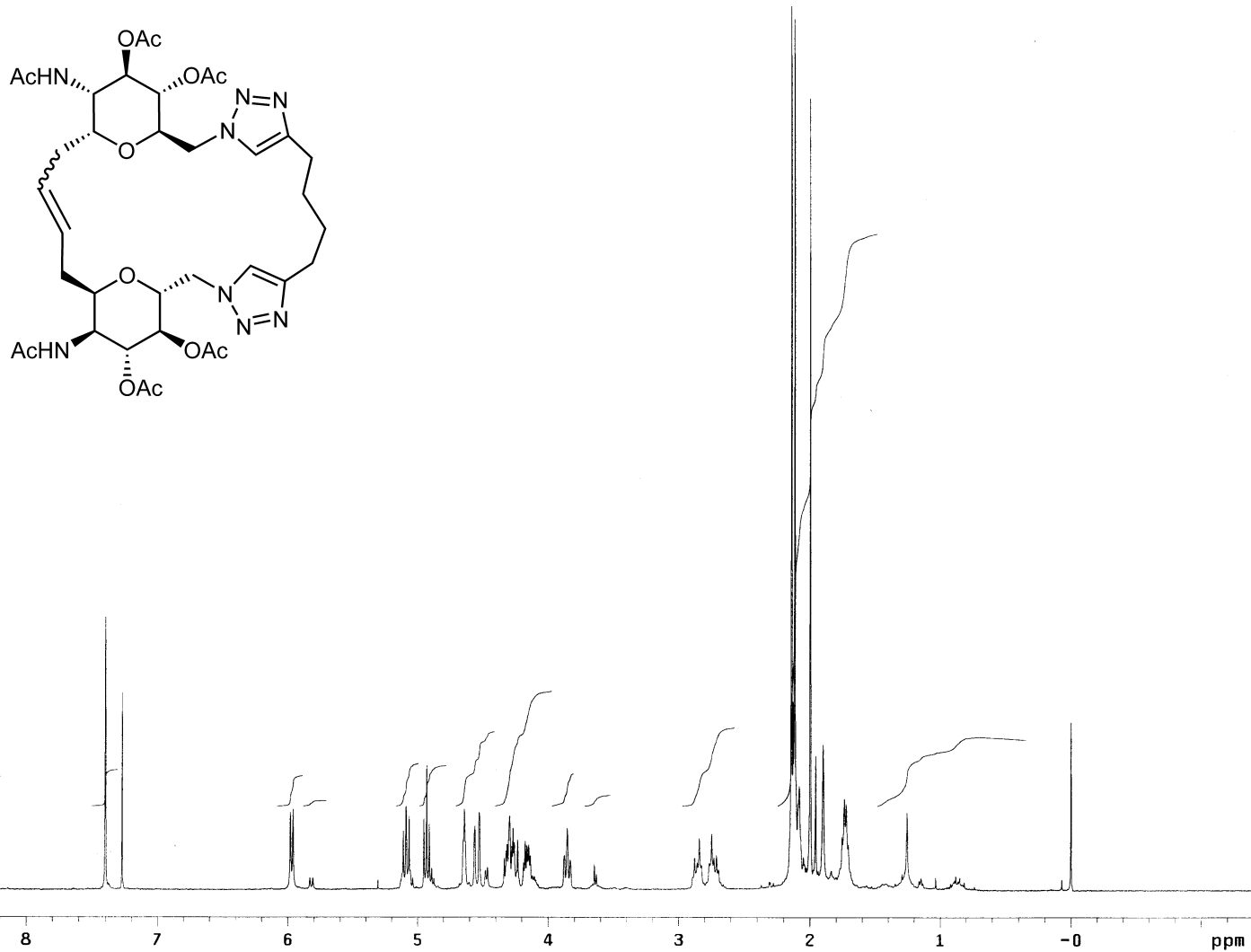
```

(1*R*,16*R*,17*R*,18*R*,19*S*,20*R*,22(*E*; *Z*),25*R*,26*S*,27*R*,28*R*)-19,26-Bis(acetylamino)-29,30-dioxo-3,4,5,12,13,14-hexaazapentacyclo[23.3.1.1^{3,6}.1^{11,14}.1^{16,20}]dotriaconta-4,6(32),11(31),12,22-pentaene-17,18,27,28-tetrayl tetraacetate (20)



¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 1.66–1.79 (m, 4H), 1.85–1.98 (m, 4H), 1.98–2.18 (m, 18H), 2.67–2.90 (m, 4H), 3.62–3.89 (m, 2H), 4.07–4.35 (m, 6H), 4.45–4.67 (m, 4H), 4.86–4.96 (m, 2H), 5.03–5.13 (m, 2H), 5.80–5.99 (m, 2H), 7.40 (s, 2H).–

HRMS (ESI)	C ₃₆ H ₅₀ N ₈ O ₁₂ Na	[M+Na ⁺]	calcd	809.3440
			found	809.3452



```

dos307.1H.cdc13
Mon Dec 6 17:17 2004
exp7 std1h

SAMPLE
date Dec 6 2004
solvent CDC13
file exp

ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used

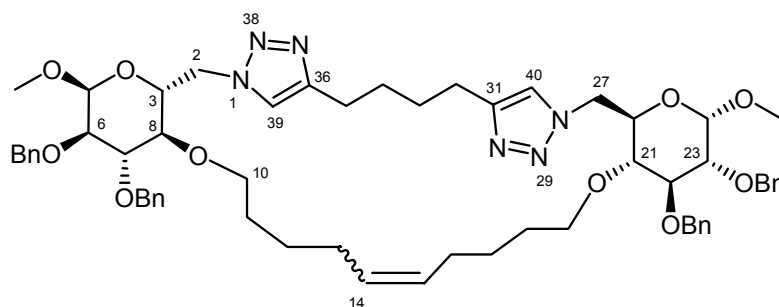
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200

PROCESSING
lb 0.40
wtfile
proc ft
fn 65536

DISPLAY
sp -553.4
wp 3836.3
vs 162
sc 65
wc 225
hzmm 17.05
is 913.12
rf1 3542.0
rfp 0
th 2.1
ins 100.000
rp 5.7
lp -193.3
nm ph

```

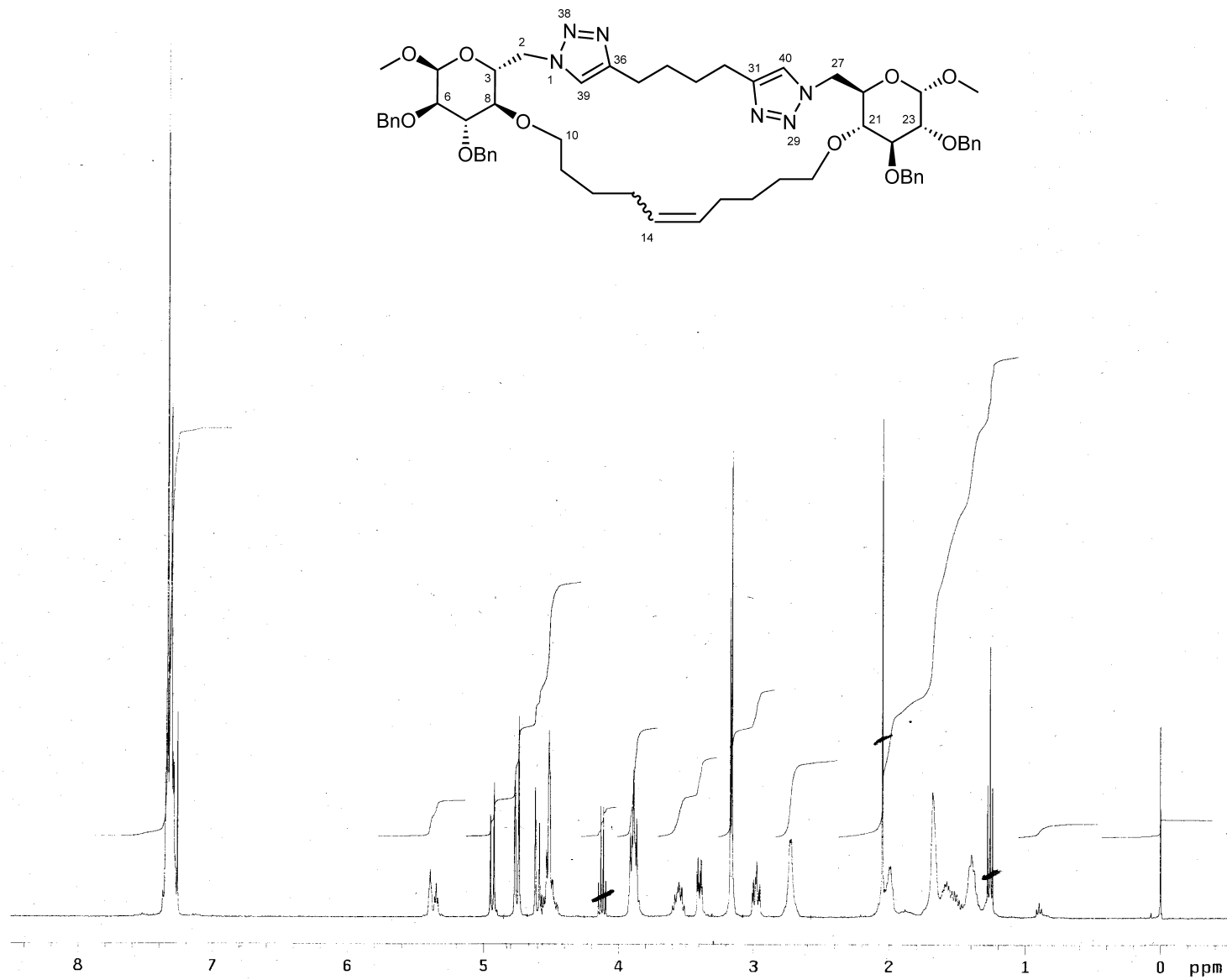
(3*R*,5*S*,6*R*,7*S*,8*R*,14(*E*;Z),21*R*,22*S*,23*R*,24*S*,26*R*)-6,7,22,23-Retrakis(benzyloxy)-5,24-dimethoxy-4,9,20,25-tetraoxa-1,28,29,30,37,38-hexaazapentacyclo[34.2.1.1^{28,31}.0^{3,8}.0^{21,26}]-tetraconta-14,29,31(40),36(39),37-pentaene (21)



¹H-NMR (400 MHz, CD₃OD) isomer mixture: δ [ppm] = 1.33–1.74 (m, 16H), 1.96–2.03 (bs, 4H), 2.67–2.76 (m, 4H), 2.95–3.02 (m, 2H), 3.16 (s, 6H, CH₃), 3.37–3.43 (m, 2H), 3.50–3.61 (m, 2H), 3.85–3.94 (m, 6H), 4.48–4.55 (m, 4H), 4.60 (d, *J* = 12.1 Hz, 2H), 4.75 (d, *J* = 10.2 Hz, 2H), 4.94 (d, *J* = 10.9 Hz, 2H), 5.39 (bt, *J* = 3.5 Hz, 2H, 14-H), 7.28–7.36 (m, 20H, CH arom.).–

¹³C-NMR (100 MHz, CD₃OD) major isomer: δ [ppm] = 25.12, 26.14, 28.43, 29.96, 32.46 (t, C-11–C-13, C-32, C-33), 50.78 (t, C-2), 55.12 (q, CH₃), 69.36 (d, CH), 73.44 (t, C-10), 75.69, 75.71 (t, CH_{2(Bn)}), 78.85, 79.64, 81.79, 97.88 (d, CH), 121.61 (d, C-39), 127.59, 127.85, 127.93, 128.31, 128.35 (d, CH arom.), 130.10 (d, C-14), 137.81, 138.31 (s, C arom.), 147.53 (s, C-31).–

HRMS (ESI) C₆₀H₇₆N₆O₁₀Na [M+Na⁺] calcd 1063.5515
found 1063.5509



```

dos293.1H.cdc13
Wed Nov 10 14:12 2004
exp3 std1h

SAMPLE
date Nov 10 2004
solvent CDC13
file exp

ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used

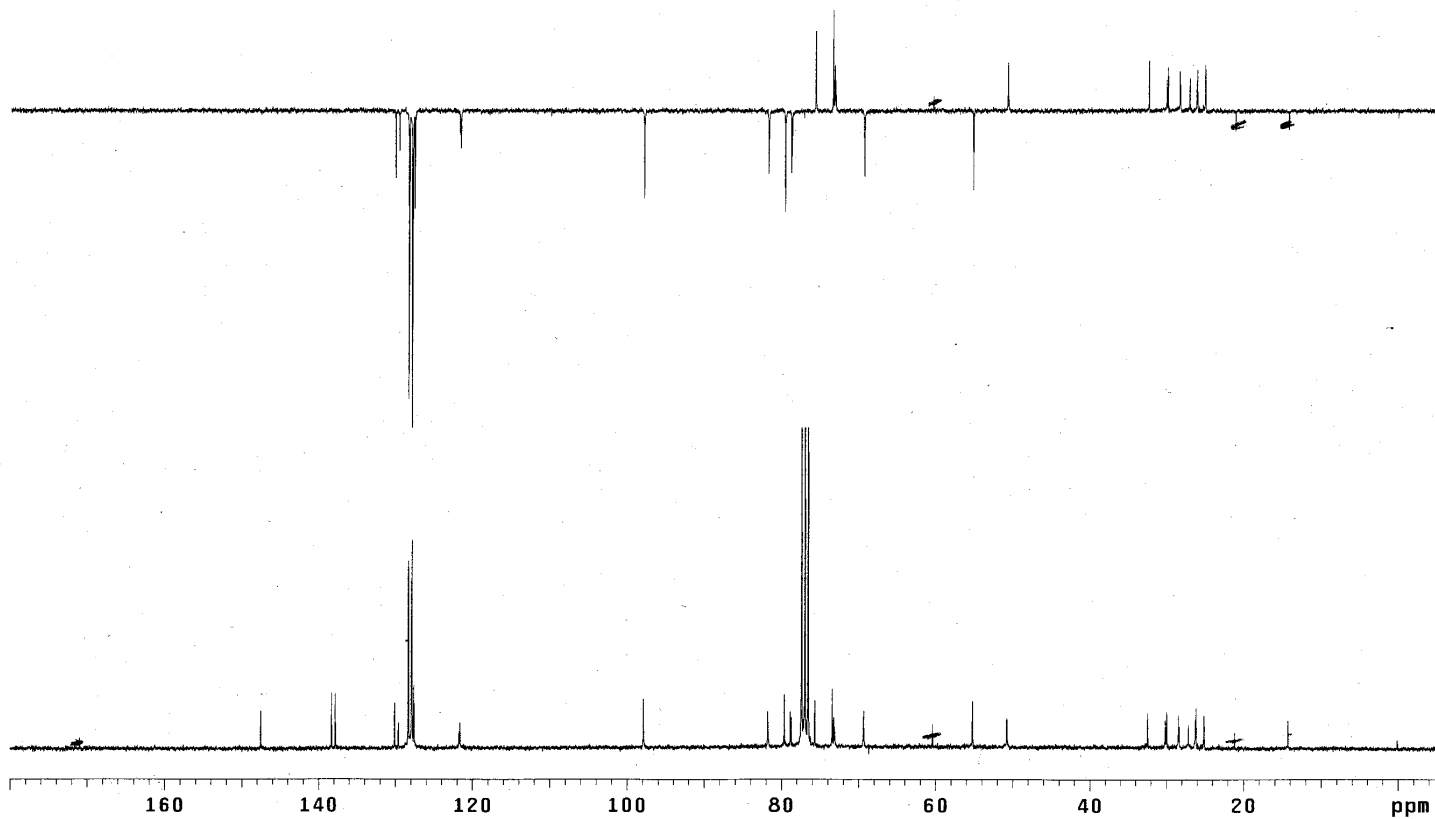
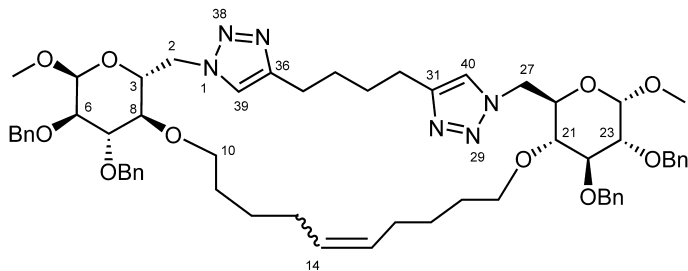
FLAGS
il n
in nw
dp y

DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200

PROCESSING
lb 0.40
wtfile
proc ft
fn 65536

DISPLAY
sp -200.2
wp 3599.4
vs 162
sc 65
wc 225
hzmm 16.00
is 1007.15
rf1 3545.5
rfp 0
th 2.1
ins 100.000
rp -1.6
lp -185.3
nm ph

```



DOS293/CDC13/13C
 Doerner 101104_05
 DEPT-135
 Thu Nov 11 02:49 2004

exp7 dept

SAMPLE
 date Nov 10 2004
 solvent CDC13
 file exp

ACQUISITION
 instrum g300
 probe atb5
 seqfil dept
 sfrq 75.500
 tn C13
 at 1.747
 np 65906
 sw 18867.9
 bs 16
 tpwr 56
 pw 9.6
 d1 2.000
 d2 0
 tof 767.8
 nt 600
 ct 600
 alock n
 gain not used
 pp 16.2
 pp1v1 56
 J 140.0
 mult 1.5
 satdly 0

FLAGS

il n
 in n

DEC. & VT

dn H1
 dfrq 300.225
 homo n
 dpwr 37
 dof 0
 dm nny
 dmm ccw
 dmf 7900
 pp1v1 56
 pp 16.2
 J 140.0

PROCESSING

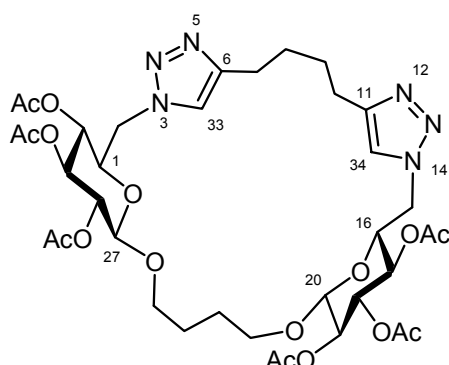
lb 1.00
 wtfile
 proc ft
 fn 65536

wexp procplot

DISPLAY

sp -377.8
 wp 13967.1
 vs 50
 sc 65
 wc 225
 hzmm 62.08
 rfl 1135.6
 rfp 0
 th 2.0
 rp 241.3
 lp -274.9
 nm no ph

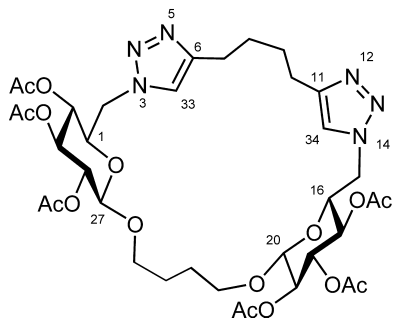
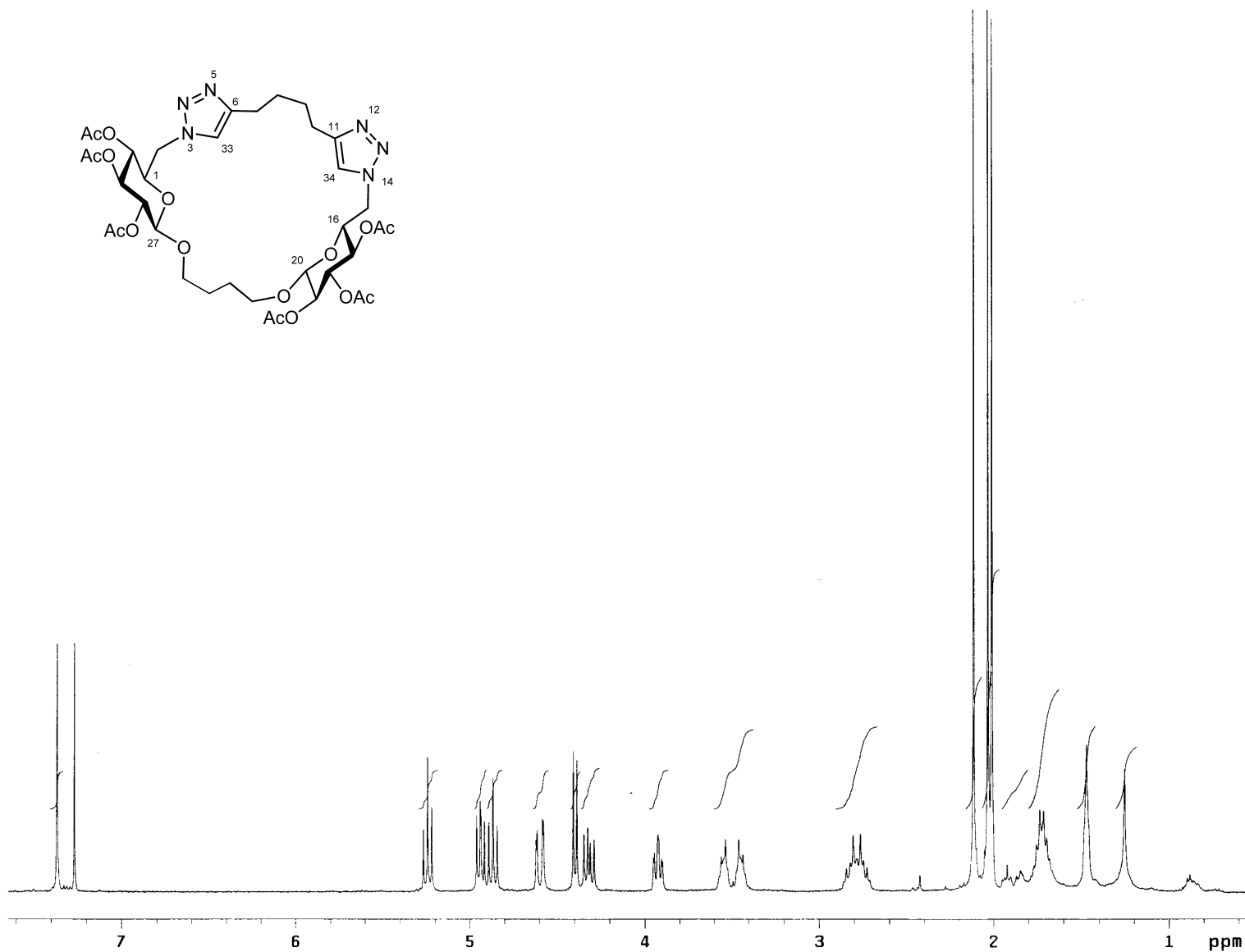
(1*R*,16*R*,17*R*,18*S*,19*R*,20*R*,27*R*,28*R*,29*S*,30*R*)-21,26,31,32-Tetraoxa-3,4,5,12,13,14-hexaazapentacyclo[25.3.1.1^{3,6}.1^{11,14}.1^{16,20}]tetratriaconta-4,6(34),11(33),12-tetraene-17,18,19,28,29,30-hexayl hexaacetate (18 reduced)



¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 1.47 (bs, 4H, 23-H) 1.64–1.80 (m, 4H, 8-H) 2.01 (s, 3H, 18-CH_{3(Ac)}), 2.03 (s, 3H, 19-CH_{3(Ac)}), 2.12 (s, 3H, 17-CH_{3(Ac)}), 2.71–2.78 (m, 2H, 7-H^a), 2.78–2.86 (m, 2H, 7-H^b), 3.42–3.48 (m, 2H, 22-H^a), 3.52–3.58 (m, 2H, 22-H^b), 3.93 (ddd, *J* = 9.6, 8.8, 2.8 Hz, 2H, 1-H), 4.32 (dd, *J* = 14.5, 8.8 Hz, 2H, 2-H^a), 4.40 (d, *J* = 8.2 Hz, 2H, 20-H), 4.60 (dd, *J* = 14.5, 2.8 Hz, 2H, 2-H^b), 4.87 (dd, *J* = 9.6, 9.2 Hz, 2H, 17-H), 4.94 (dd, *J* = 9.8, 8.2 Hz, 2H, 19-H), 5.24 (dd, *J* = 9.8, 9.2 Hz, 2H, 18-H), 7.37 (s, 2H, 33-H).–

¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 20.58 (q, CH_{3(Ac)}-18), 20.63 (q, CH_{3(Ac)}-19), 20.69 (q, CH_{3(Ac)}-17), 25.21 (t, C-7), 26.03 (t, C-23), 28.16 (t, C-8), 50.51 (t, C-2), 69.65 (t, C-22), 69.86 (d, C-17), 71.13 (d, C-19), 72.12 (d, C-16), 72.38 (d, 18), 100.59 (d, C-20), 122.32 (d, C-33), 147.77 (s, C-6), 169.34 (s, CO-19), 169.74 (s, CO-17), 170.10 (s, CO-18).–

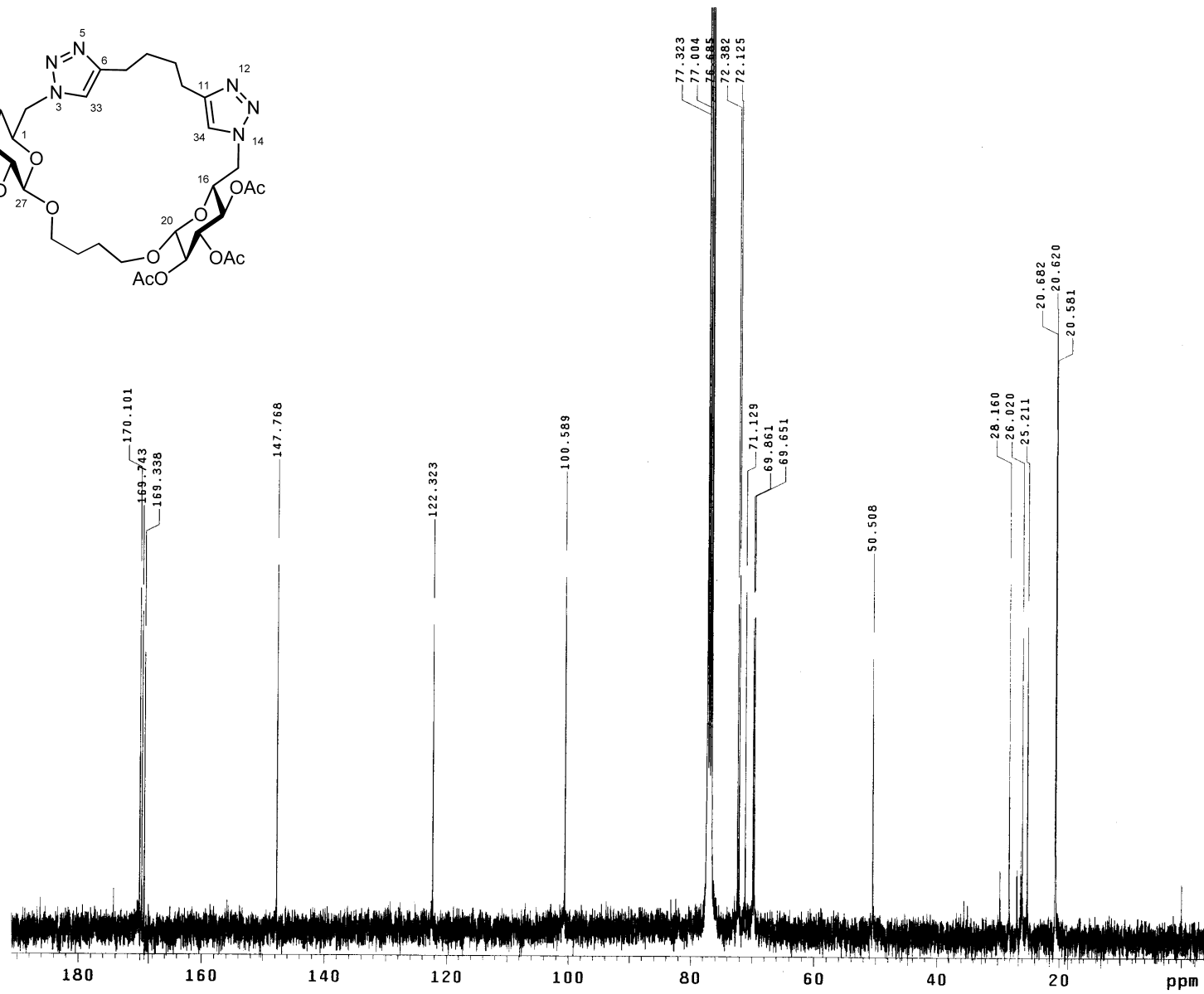
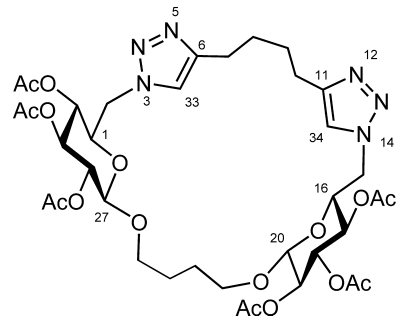
HRMS (ESI)	C ₃₆ H ₅₀ N ₆ O ₁₆ Na	[M+Na ⁺]	calcd	845.3176
			found	845.3175



```

dos294II.1H.cdc13
Wed Nov 24 20:03 2004
exp1 stdih
SAMPLE
date Nov 24 2004
solvent CDC13
file exp
ACQUISITION
instrum m400
probe .asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
DISPLAY
sp 218.3
wp 2839.9
vs 162
sc 65
wc 225
hzmm 12.62
is 640.99
rf1 3543.6
rfp 0
th 2.1
ins 1.000
rp 11.3
lp -202.9
nm ph

```



dos294.13C.cdc13
Wed Nov 24 20:22 200

exp2 std13c

SAMPLE
date Nov 24 2004
solvent CDC13
file exp

ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 100.574
tn C13
at 1.311
np 67216
sw 25641.0
bs 16
tpwr 61
pw 4.0
d1 1.689
d2 0
tof 1327.2
nt 9000
ct 9000
alock n
gain not used

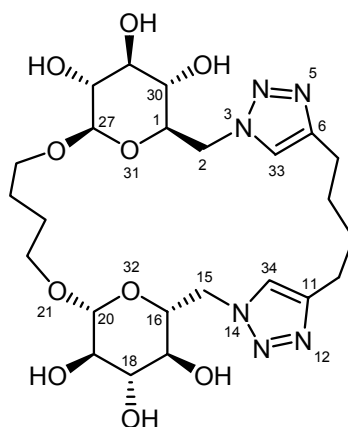
FLAGS
il n
in n
dp y

DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 40
dof 0
dm yyy
dmm w
dmf 9350
pp 17.5

PROCESSING
lb 1.00
wtfile
proc ft
fn 65536

DISPLAY
sp -388.2
wp 19588.2
vs 1800
sc 65
wc 225
h2mm 87.06
rf1 9741.3
rfp 7743.4
th 20.0
rp 30.6
lp -282.9
nm no ph

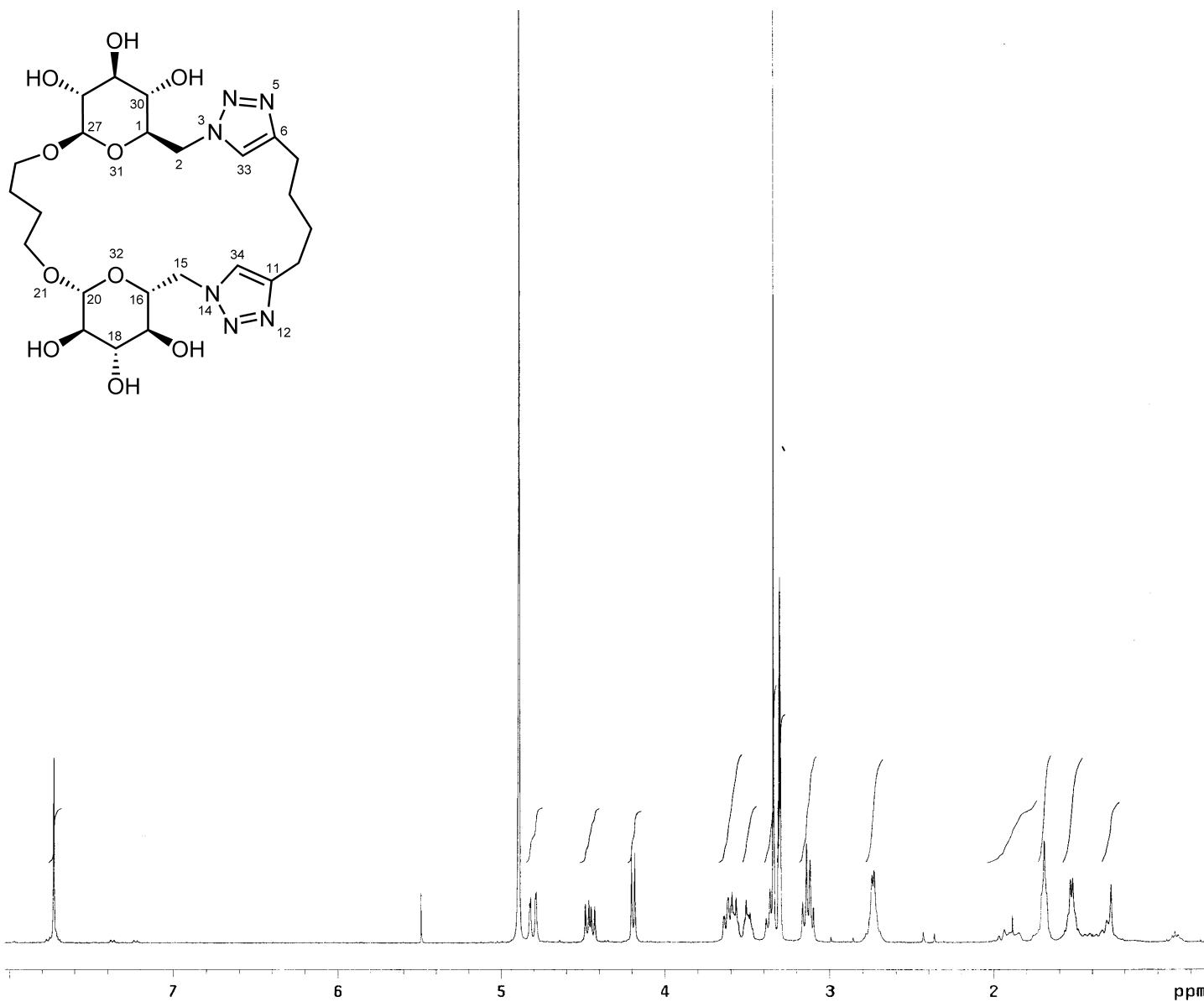
(1*R*,16*R*,17*S*,18*S*,19*R*,20*R*,27*R*,28*R*,29*S*,30*S*)-21,26,31,32-Tetraoxa-3,4,5,12,13,14-hexaazapentacyclo[25.3.1.1^{3,6}.1^{11,14}.1^{16,20}]tetratriaconta-4,6(34),11(33),12-tetraene-17,18,19,28,29,30-hexol (22)



¹H-NMR (400 MHz, CD₃OD): δ [ppm] = 1.47–1.59 (bs, 4H), 1.65–1.74 (bs, 4H), 2.69–2.79 (bs, 4H), 3.13 (q, *J* = 9.2 Hz, 4H) 3.35–3.39 (m, 2H), 3.46–3.53 (m, 2H), 3.55–3.65 (m, 4H), 4.19 (d, *J* = 7.8 Hz, 2H), 4.46 (dd, *J* = 14.1, 8.6 Hz, 2H), 4.81 (dd, *J* = 14.1, 2.3 Hz, 2H), 7.73 (s, 2H).–

¹³C-NMR (100 MHz, CD₃OD): δ [ppm] = 25.85, 27.62, 29.47 (t, C-7, C-8, C-24), 52.41 (t, C-2), 70.79 (t, C-25), 72.95, 74.95, 75.39, 77.74 (d, C-1, C-28–C-30), 104.39 (d, C-27), 124.20 (d, C-33), 148.28 (s, C-6).–

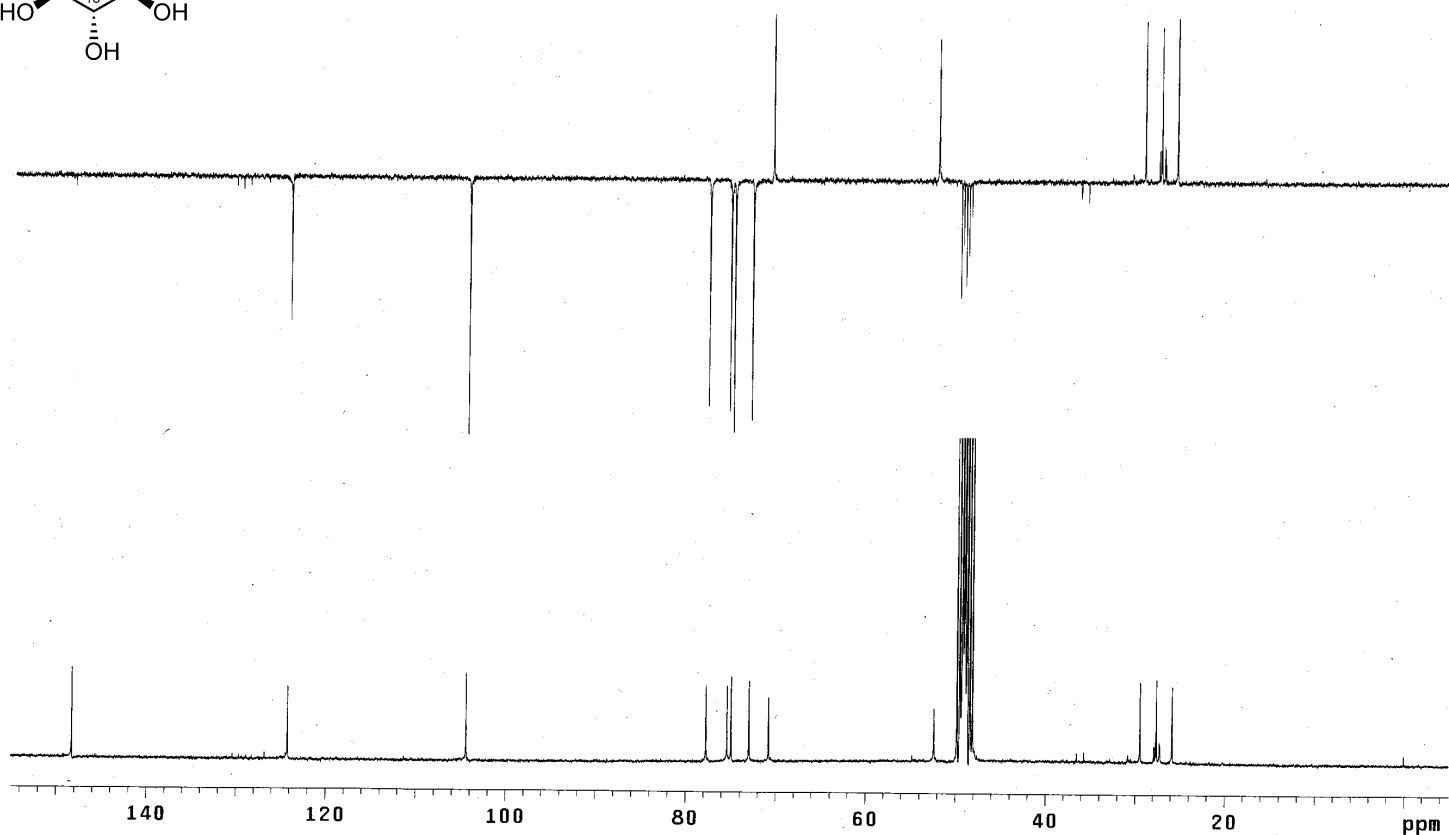
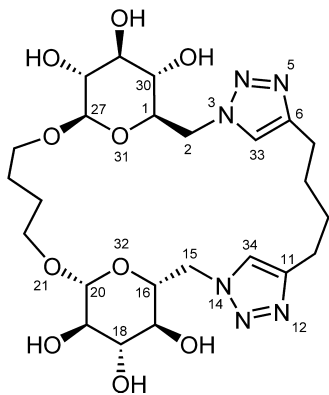
HRMS (ESI)	C ₂₄ H ₃₈ N ₆ O ₁₀ Na	[M+Na ⁺]	calcd	593.2542
			found	593.2546



```

dos304.1H.meod
Thu Nov 25 18:34 2004
exp7 std1h
SAMPLE
date Nov 25 2004
solvent CD30D
file exp
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.939
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.938
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.40
wtfile
proc ft
fn 65536
DISPLAY
sp 267.3
wp 2944.1
vs 341
sc 65
wc 225
hzmm 13.09
is 1269.21
rfl 3538.9
rfp 0
th 2.9
ins 100.000
rp 6.3
lp -187.9
nm ph

```



DOS304/CD300/13C
 Doerner 261104_01
 DEPT-135
 Sun Nov 28 07:08 2004

exp9 dept

SAMPLE
 date Nov 26 2004
 solvent CD30D
 file exp

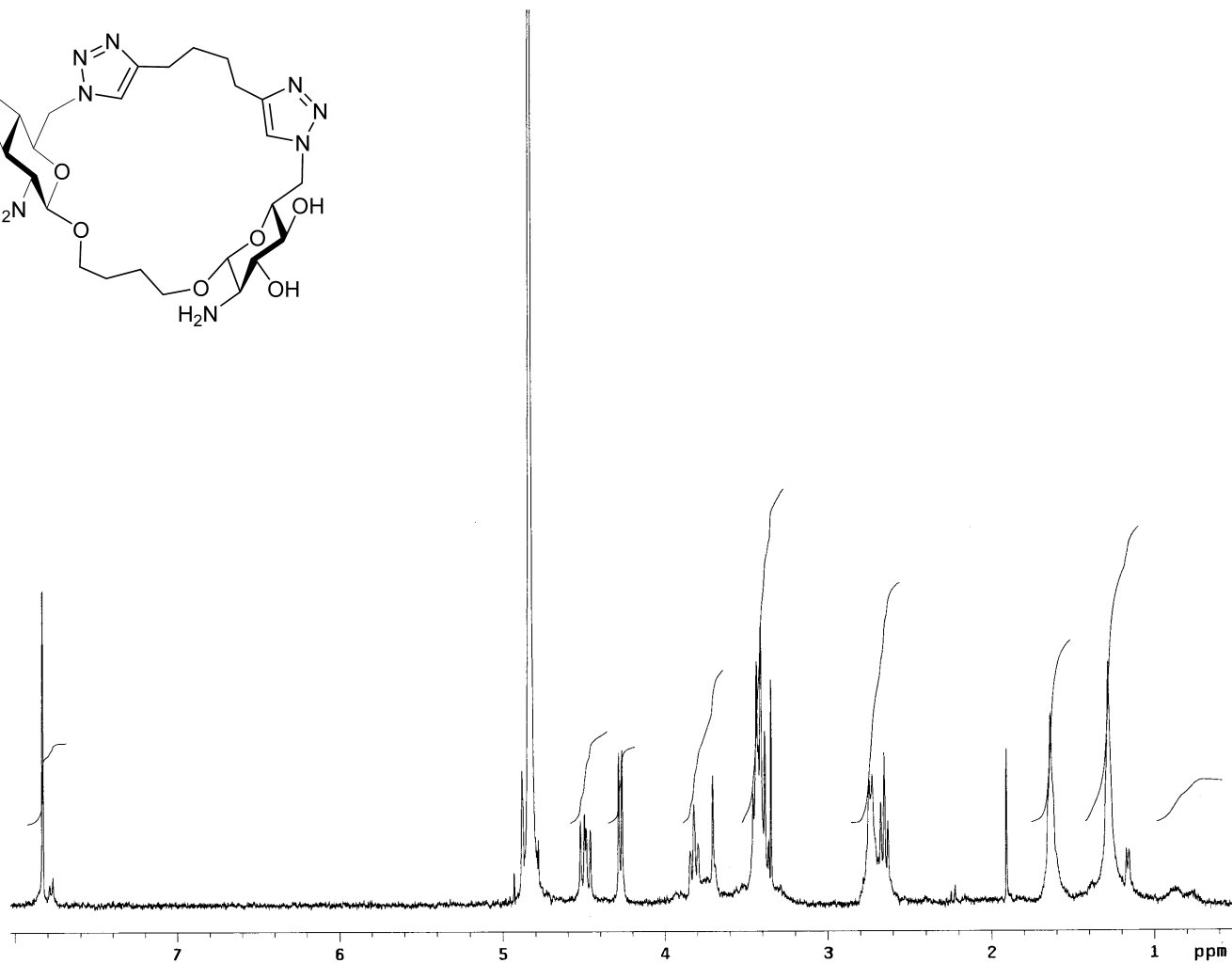
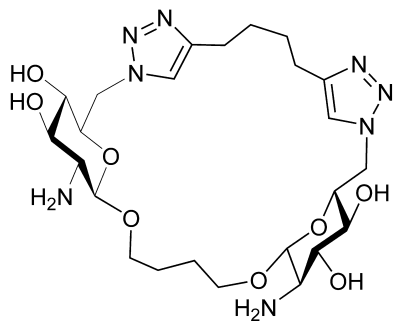
ACQUISITION
 instrum g300
 probe_ atb5
 seqfil dept
 sfrq 75.500
 tn C13
 at 1.747
 np 65906
 sw 18867.9
 bs 16
 tpwr 56
 pw 9.6
 d1 2.000
 d2 0
 tof 767.8
 nt 25000
 ct 25000
 alock n
 gain not used
 pp 16.2
 pplvl 56
 J 140.0
 mult 1.5
 satdly 0

FLAGS
 il n
 in n

DEC. & VT
 dn H1
 dfrq 300.226
 homo n
 dpwr 37
 dof 0
 dm nny
 dmm ccw
 dmf 790
 pplvl 56
 pp 16.2
 J 140.0

PROCESSING
 lb 1.00
 wtfile
 proc ft
 fn 65536

wexp procplot
 DISPLAY
 sp -378.0
 wp 12079.6
 vs 40
 sc 65
 wc 225
 hzmm 53.69
 rfl 1030.4
 rfp 0
 th 3.0
 rp 311.5
 lp -219.2
 nm no ph



1H Standard-Parameter

Tue Feb 15 15:50 2005

expB stdih

SAMPLE
date Feb 15 2005
solvent D2O
file exp

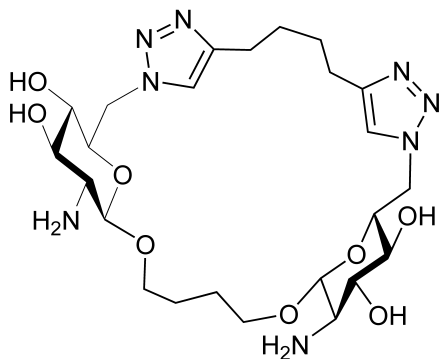
ACQUISITION
instrum m400
probe asw5
seqf11 s2pu1
sfrq 399.938
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 40
ct 40
alock n
gain not used

FLAGS
f1 n
f2 nw
dp y

DEC. & VT
dn H1
dfrq 399.937
homo n
dpwr 30
dof 0.0
dm hnn
dmm c
dmf 200

PROCESSING
lb 0.40
wtfile
proc ft
fn 65536

DISPLAY
sp 206.7
wp 3003.5
vs 5048
sc 65
wc 225
hzmm 13.35
fs 5849.41
rf1 5397.0
rfp 1931.7
th 2.1
ins 1.000
rp -25.7
lp -115.8
nm ph



dos330.13C.d2o
 Mon Feb 7 19:32 2005

exp9 std13c

SAMPLE
 date Feb 7 2005
 solvent D2O
 file exp

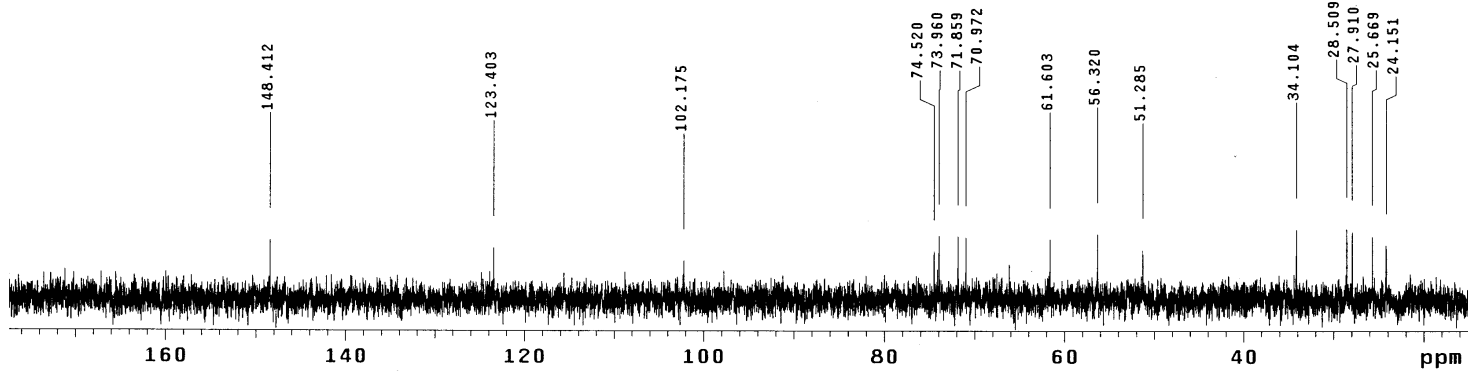
ACQUISITION
 instrum m400
 probe asw5
 seqfil s2pul
 sfrq 100.575
 tn C13
 at 1.311
 np 67216
 sw 25641.0
 bs 16
 tpwr 61
 pw 4.0
 d1 1.689
 d2 0
 tof 1327.2
 nt 18000
 ct 16064
 alock n
 gain not used

FLAGS
 il n
 in nw
 dp y

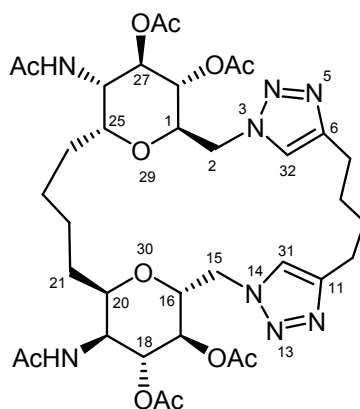
DEC. & VT
 dn H1
 dfrq 399.937
 homo n
 dpwr 40
 dof 0
 dm yyy
 dmm w
 dmf 9350
 pp 17.5

PROCESSING
 lb 1.00
 wtfile
 proc ft
 fn 65536

DISPLAY
 sp 1496.0
 wp 17512.1
 vs 11
 sc 65
 wc 225
 hzmm 77.83
 rfl 1970.6
 rfp 0
 th 5.8
 rp -136.9
 lp -288.0
 nm no ph



(1*R*,16*R*,17*R*,18*R*,19*S*,20*R*,25*R*,26*S*,27*R*,28*R*)-19,26-Bis(acetylamino)-29,30-dioxo-3,4,5,12,13,14-hexaazapentacyclo[23.3.1.1^{3,6}.1^{11,14}.1^{16,20}]dotriaconta-4,6(32),11(31),12-tetraene-17,18,27,28-tetrayl tetraacetate (20 reduced)



$$[\alpha]_{\text{D}}^{22} = +41.8 \quad (c = 0.225, \text{CHCl}_3)$$

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 0.80–0.91 (m, 4H), 1.22–1.34 (m, 4H), 1.68–1.76 (m, 4H), 1.99 (s, 6H, CH₃(NHAc)), 2.11, 2.15 (s, 6H, CH₃(OAc)), 1.66–1.88 (m, 4H), 3.89 (ddd, *J* = 10.5, 8.4, 2.5 Hz, 2H), 4.00–4.07 (m, 2H), 4.24–4.34 (m, 4H), 4.53 (dd, *J* = 14.2, 2.2 Hz, 2H), 4.92 (t, *J* = 8.2 Hz, 2H), 5.05 (dd, *J* = 9.6, 8.0 Hz, 2H), 5.84 (d, *J* = 7.8 Hz, 2H), 7.40 (s, 2H).–

¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 20.80, 20.85, 23.08, 23.32, 25.12, 28.26, 29.67, 50.58, 51.72, 69.56, 70.31, 70.62, 72.35 (d, C-1, C-25), 122.32 (d, C-32), 147.66 (s, C-6), 169.62, 169.87, 171.72 (s, CO).–

HRMS (ESI)	C ₃₆ H ₅₂ N ₈ O ₁₂ Na	[M+Na ⁺]	calcd	811.3597
			found	811.3613

dos308.1H.nS.cdc13

Wed Dec 15 21:06 2004

exp2 std1h

SAMPLE
date Dec 15 2004
solvent CDC13
file exp

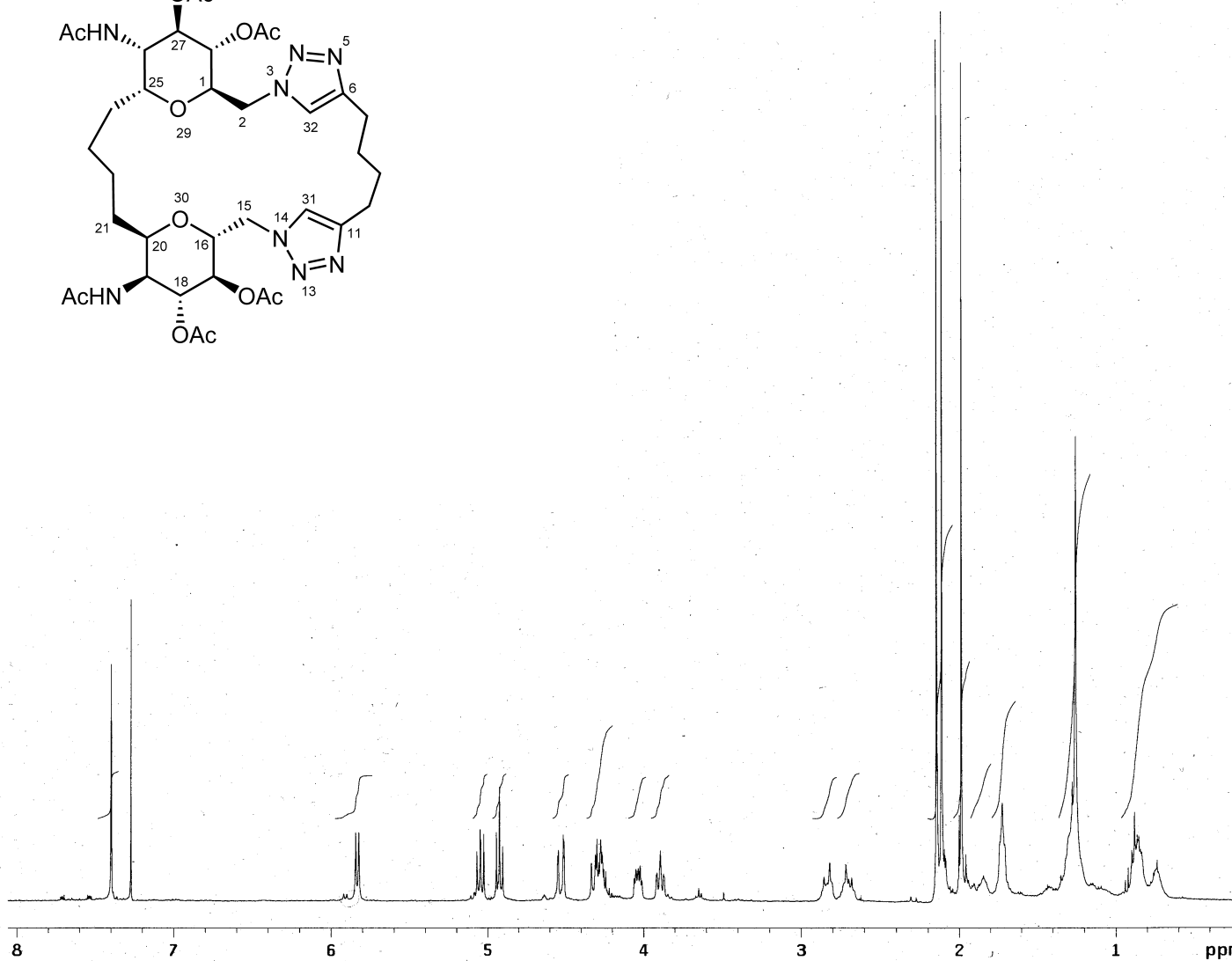
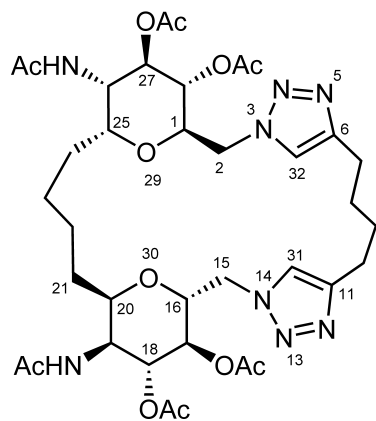
ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.937
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used

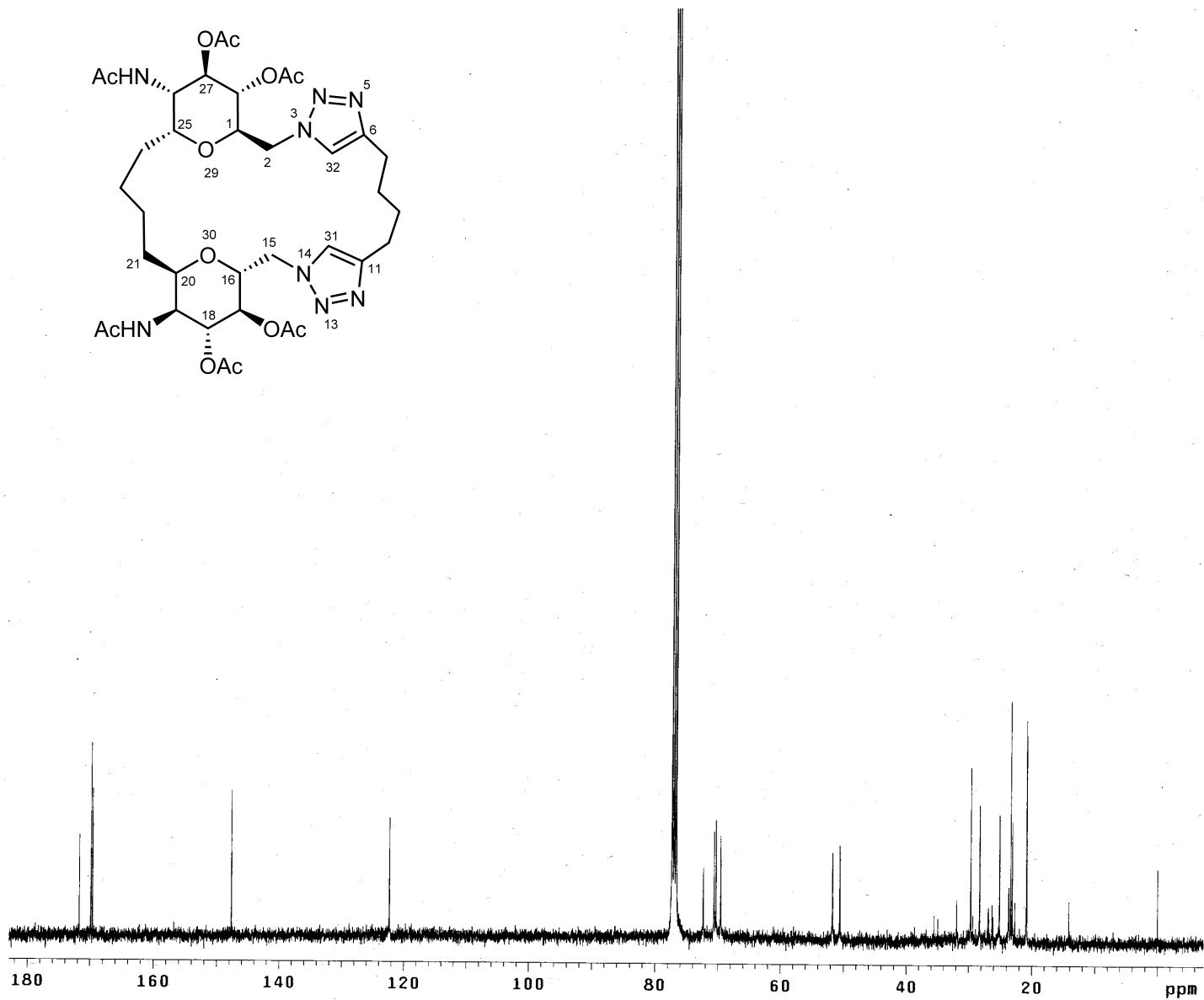
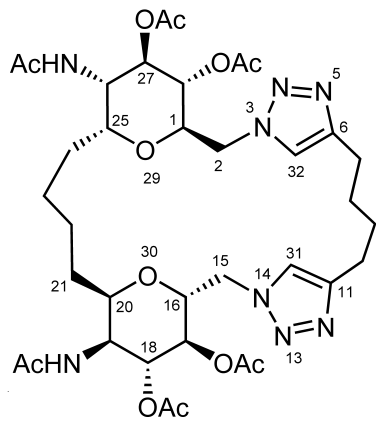
FLAGS
il n
in nw
dp y

DEC. & VT
dn H1
dfrq 399.936
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200

PROCESSING
lb 0.40
wtfile
proc ft
fn 65536

DISPLAY
sp 70.6
wp 3152.1
vs 162
sc 65
wc 225
hzmm 14.01
is 1287.36
rfl 3542.4
rfp 0
th 2.9
ins 100.000
rp -16.7
lp -137.8
nm ph





```

dos308.13C.nS.cdc13
Wed Dec 15 21:08 2004

exp3 std13c

SAMPLE
date Dec 15 2004
solvent CDC13
file exp

ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 100.574
tn C13
at 1.311
np 67216
sw 25641.0
bs 16
tpwr 61
pw 4.0
d1 1.689
d2 0
tof 1327.2
nt 8000
ct 8000
alock n
gain not used
FLAGS

il n
in n
dp y
DEC. & VT

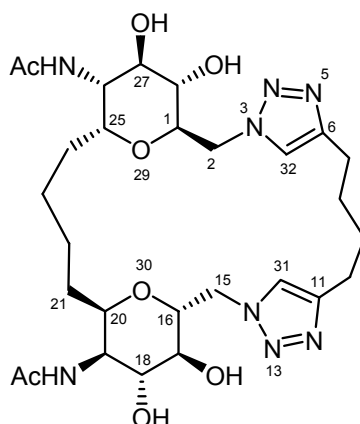
dn H1
dfrq 399.936
homo n
dpwr 40
dof 0
dm yyy
dmm w
dmf 9350
pp 17.5

PROCESSING
lb 1.00
wtfile
proc ft
fn 65536

DISPLAY
sp -746.2
wp 19140.6
vs 657
sc 65
wc 225
hzmm 85.07
rfl 9741.6
rfp 7743.4
th 20.0
rp 62.4
lp -327.8
nm no ph

```

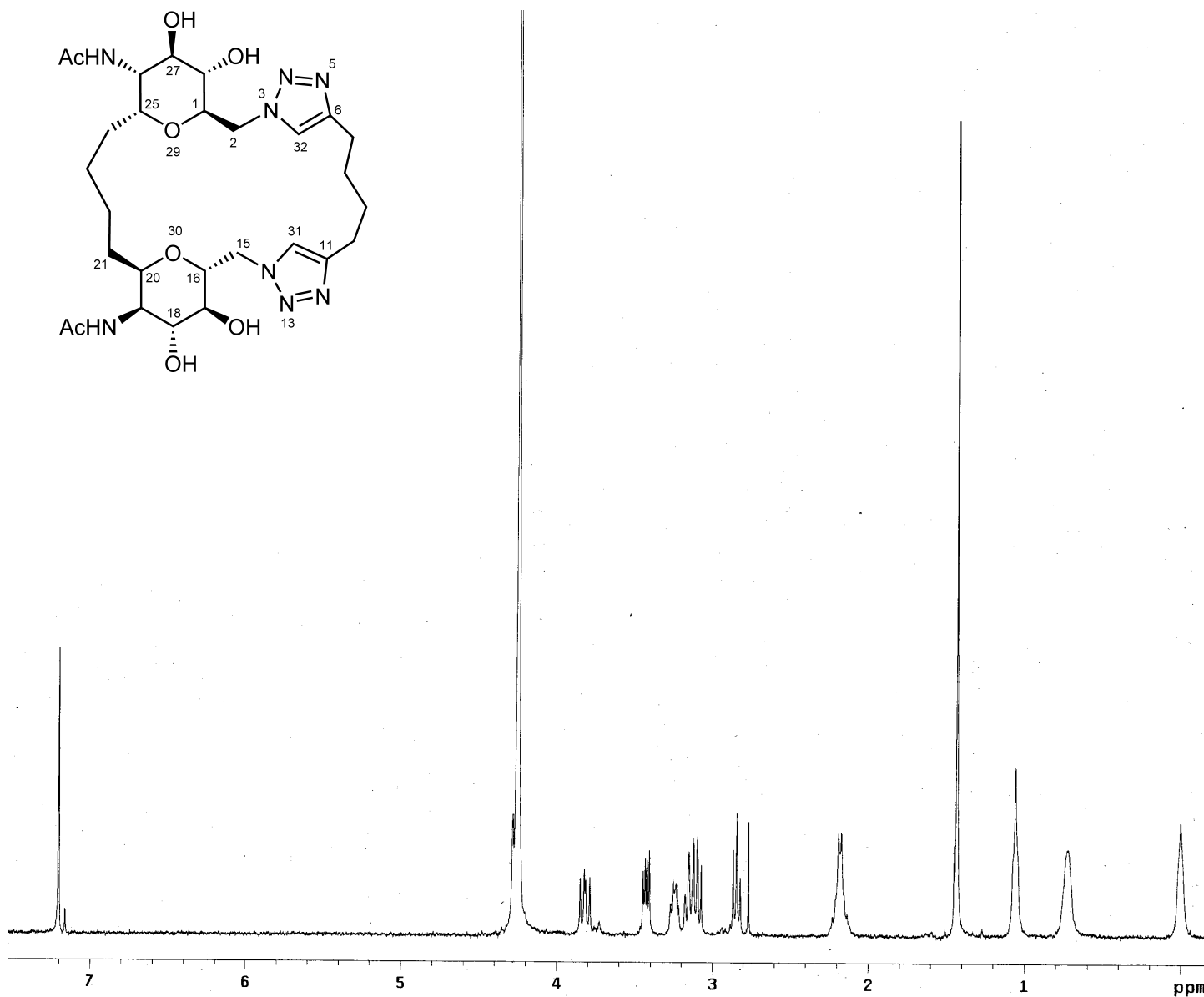

N,N'-[(1*R*,16*R*,17*S*,18*R*,19*R*,20*R*,25*R*,26*R*,27*R*,28*S*)-17,18,27,28-Tetrahydroxy-29,30-dioxo-3,4,5,12,13,14-hexaazapentacyclo[23.3.1.1^{3,6}.1^{11,14}.1^{16,20}]dotriaconta-4,6(32),11(31),12-tetraene-19,26-diyl]diacetamide (24)



¹H-NMR (400 MHz, D₂O): δ [ppm] = 0.50 (bs, 4H), 1.22 (bs, 4H), 1.56 (bs, 4H), 1.93 (s, 6H, CH₃(_{NHAc})), 2.60–2.75 (m, 4H), 3.34 (t, *J* = 8.9 Hz, 2H), 3.56–3.69 (m, 4H), 3.70–3.78 (m, 2H), 3.93 (dd, *J* = 10.7, 5.7 Hz, 2H), 4.32 (dd, *J* = 14.1, 10.5 Hz, 2H), 4.75–4.79 (m, 2H), 7.70 (s, 2H).–

¹³C-NMR (100 MHz, D₂O): δ [ppm] = 21.97, 22.20, 24.03, 27.86 (t, C-7, C-8, C-21, C-22), 51.57 (t, C-2), 53.39 (d, C-19), 70.66, 71.70, 72.63, 73.81 (d, C-16, C-17, C-18, C-20), 123.82 (d, C-31), 148.35 (s, C-6), 174.27 (s, CO).–

HRMS (ESI)	C ₂₈ H ₄₄ N ₈ O ₈ Na	[M+Na ⁺]	calcd	643.3174
			found	643.3159



1H Standard-Parameter
 Mon Dec 20 12:06 2004
 exp8 std1h

SAMPLE
 date Dec 20 2004
 solvent D2O
 file exp

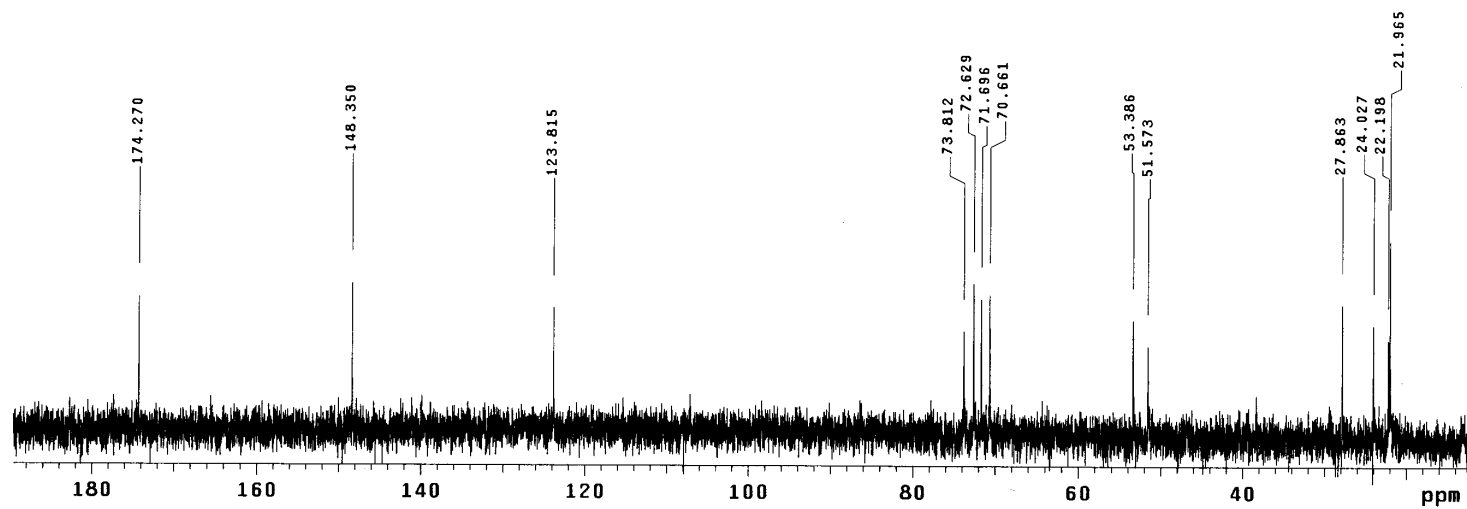
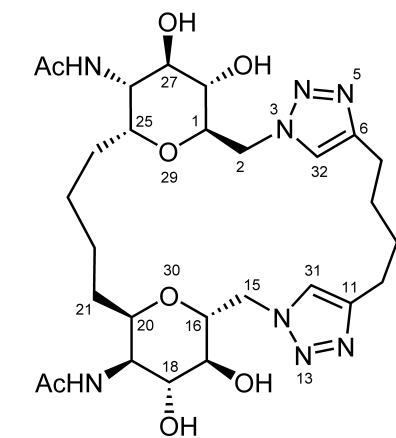
ACQUISITION
 instrum m400
 probe asw5
 seqfil s2pul
 sfrq 399.938
 tn H1
 at 2.562
 np 65536
 sw 12787.7
 bs 8
 tpwr 58
 pw 2.8
 d1 1.000
 d2 0
 tof 828.3
 nt 16
 ct 16
 alock n
 gain not used

FLAGS
 il n
 in nw
 dp y

DEC. & VT
 dn H1
 dfrq 399.937
 homo n
 dpwr 30
 dof 0.0
 dm nnn
 dmm c
 dmf 200

PROCESSING
 lb 0.40
 wtfile
 proc ft
 fn 65536

DISPLAY
 sp -82.0
 wp 3090.9
 vs 1755
 sc 65
 wc 225
 hzmm 13.74
 rfl 3696.2
 rfp 0
 th 2.9
 rp -7.5
 lp -150.4
 nm ph



dos309.13C.d2o
 Fri Jan 7 19:26 2005

exp3 std13c

SAMPLE
 date Jan 7 2005
 solvent D2O
 file exp

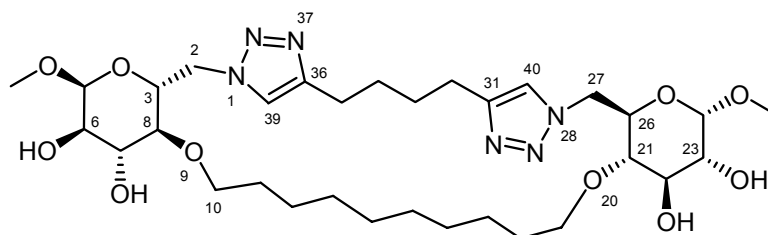
ACQUISITION

instrum m400
 probe asw5
 seqfil s2pu1
 sfrq 100.575
 tn C13
 at 1.311
 np 67216
 sw 25641.0
 bs 16
 tpwr 61
 pw 4.0
 d1 1.689
 d2 0
 tof 1327.2
 nt 15000
 ct 0
 alock n
 gain not used
 FLAGS

PROCESSING
 lb 1.00
 wtfile ft
 proc
 fn 65536

DISPLAY
 sp 1256.5
 vp 17811.1
 vs 30
 sc 65
 wc 225
 hzmm 79.16
 rfl 1970.6
 rfp 0
 th 10.2
 rp 193.0
 lp -295.0
 nm no ph

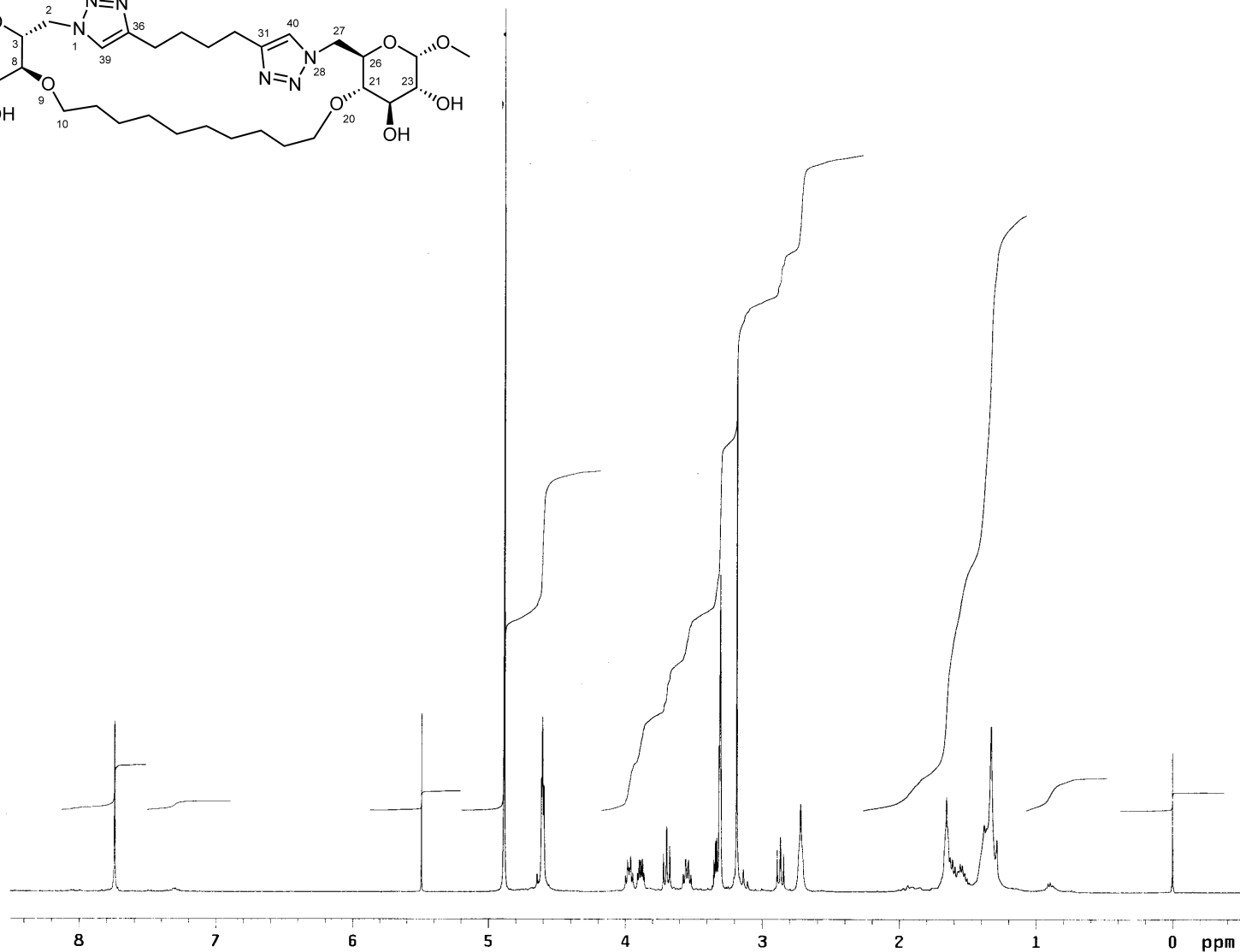
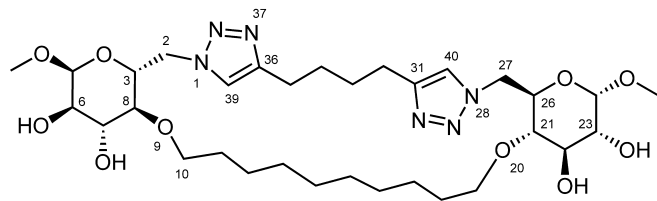
(3*R*,5*S*,6*R*,7*R*,8*S*,21*S*,22*R*,23*R*,24*S*,26*R*)-5,24-Dimethoxy-4,9,20,25-tetraoxa-1,28,29,30,37,38-hexaazapentacyclo[34.2.1.1^{28,31}.0^{3,8}.0^{21,26}]tetraconta-29,31(40),36(39),37-tetraen-6,7,22,23-tetrol (25)



¹H-NMR (400 MHz, CD₃OD): δ [ppm] = 1.27–1.69 (m, 24H), 2.72 (bs, 4H), 2.87 (dd, *J* = 10.0, 8.8 Hz, 2H), 3.19 (s, 6H), 3.33–3.35 (m, 2H), 3.51–3.58 (m, 2H), 3.70 (dd, *J* = 9.8, 9.0 Hz, 2H), 3.68–3.92 (m, 2H), 3.97 (ddd, *J* = 9.0, 6.1, 6.1 Hz, 2H), 4.59–4.62 (m, 6H), 7.74 (s, 2H).–

¹³C-NMR (100 MHz, CD₃OD): δ [ppm] = 25.64, 27.08, 29.45, 30.36, 30.43, 31.28 (t, C-11–C-14, C-37, C-38), 52.22 (t, C-2), 55.54 (q, CH₃), 70.64, 73.49 (d, CH), 73.96 (t, C-10), 75.47, 80.76, 101.14 (d, CH), 124.52 (d, C-39), 148.52 (s, C-36).–

HRMS (ESI)	C ₃₂ H ₅₄ N ₆ O ₁₀ Na	[M+Na ⁺]	calcd	705.3794
			found	705.3788



dos297.1H.meod

Thu Nov 18 14:36 2004

exp7 stdih

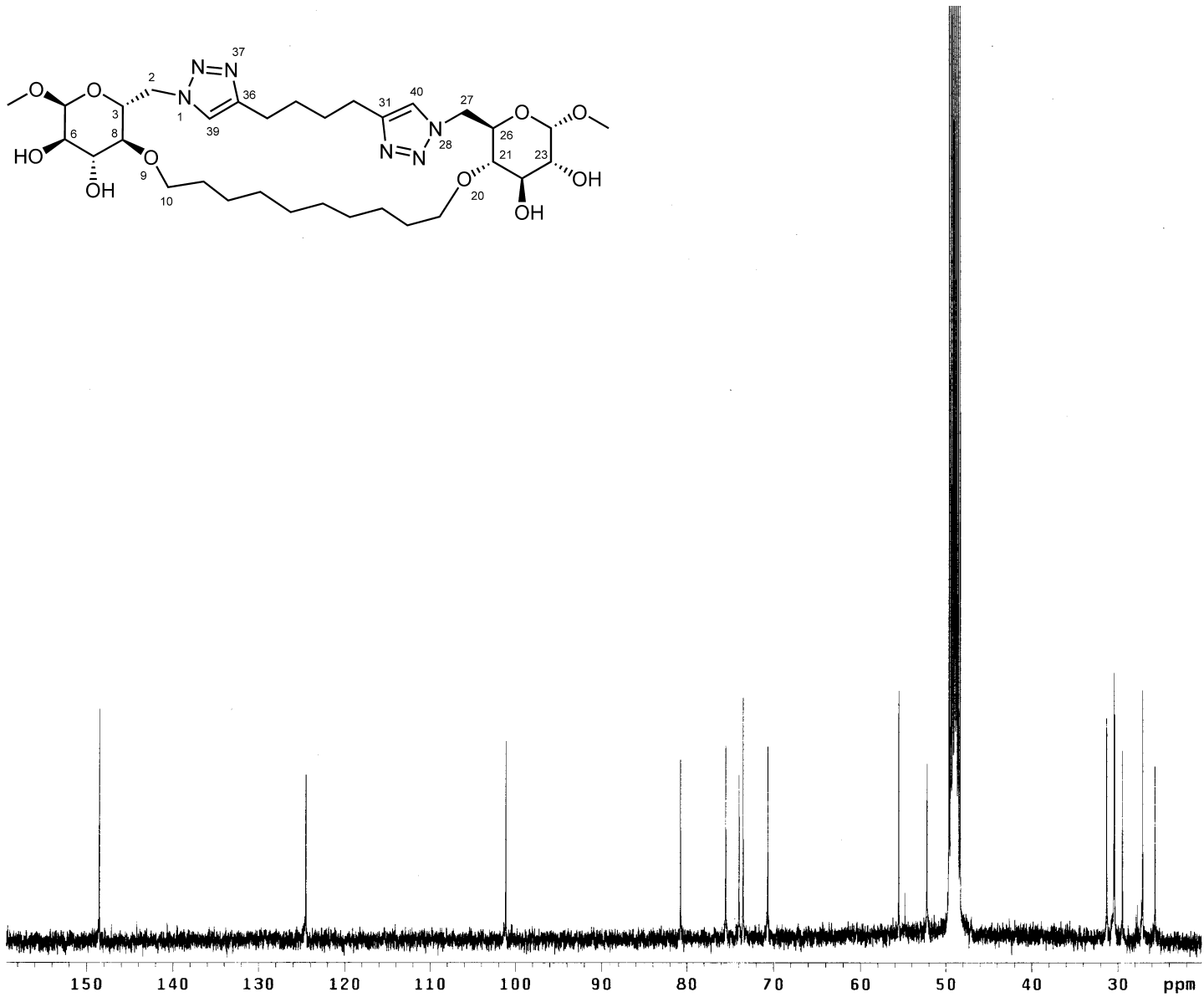
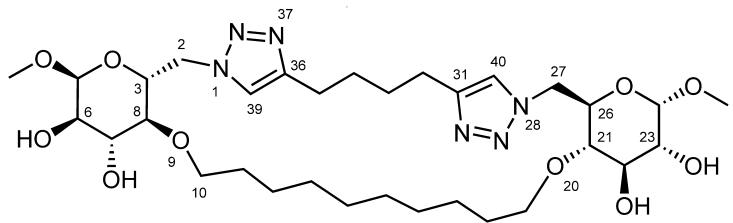
SAMPLE
date Nov 18 2004
solvent CD3OD
file exp

ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 399.939
tn H1
at 2.562
np 65536
sw 12787.7
bs 8
tpwr 58
pw 2.8
d1 1.000
d2 0
tof 828.3
nt 16
ct 16
alock n
gain not used

FLAGS
il n
in nw
dp y
DEC. & VT
dn H1
dfrq 399.938
homo n
dpwr 30
dof 0.0
dm nnn
dmm c
dmf 200

PROCESSING
lb 0.40
wtfile
proc ft
fn 65536

DISPLAY
sp -200.2
wp 3599.4
vs 162
sc 65
vc 225
hzmm 16.00
is 948.34
rfl 3538.9
rfp 0
th 2.1
ins 100.000
rp -2.3
lp -172.5
nm ph



```

dos297.13C.m
Thu Nov 18 18:5
exp8 std13c

SAMPLE
date Nov 18 2004
solvent CD300
file exp

ACQUISITION
instrum m400
probe asw5
seqfil s2pul
sfrq 100.575
tn C13
at 1.311
np 67216
sw 25641.0
bs 16
tpwr 61
pw 4.0
d1 1.689
d2 0
tof 1327.2
nt 10000
ct 10000
alock n
gain not used

FLAGS
il n
in nw
dp y

DEC. & VT
dn H1
dfrq 399.938
homo n
dpwr 40
dof 0
dm yyy
dmm w
dmf 9350
pp 17.5

PROCESSING
lb 1.00
wtfile
proc ft
fn 65536

DISPLAY
sp 2033.1
wp 13985.3
vs 3533
sc 65
wc 225
hzmm 62.16
rfl 6779.0
rfp 4927.6
th 20.0
rp 186.3
lp -316.4
nm no ph

```

Reference List

- [1.] B. Elchert, J. Li, J. H. Wang, Y. Hui, R. Rai, R. Ptak, P. Ward, J. Y. Takemoto, M. Bensaci, C. W. T. Chang, *J.Org.Chem.* **2004**, *69* 1513-1523.
- [2.] C. Rosenbohm, D. Vanden Berghe, A. Vlietinck, J. Wengel, *Tetrahedron* **2001**, *57* 6277-6287.