Supporting Information

Heptosides from Galactose based Oxepanes via Stereoselective Addition Reactions

*Rhys Batchelor,† Joanne E. Harvey,† Peter T. Northcote,† Paul Teesdale-Spittle† and John O. Hoberg**

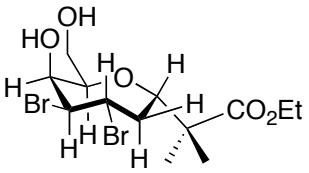
School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand and Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

hoberg@uwyo.edu

Page #:

General. General: All reagents were of commercial quality and solvents were dried using standard procedures. Standard syring techniques were used and all reactions were carried out under argon unless otherwise noted. Reaction progress was monitored using aluminium backed TLC plates pre-coated with silica UV254 and visualised by either UV radiation (254 nm) or ceric ammonium molybdate dip. Flash chromatography was performed using silica gel 60 (220-240 mesh) with the solvent systems as indicated. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova at 300 and 75 MHz, respectively; and referenced to solvent peaks (^{1}H - residual $CHCl_3$; ^{13}C - $CDCl_3$). Accurate masses were recorded on a Mariner time of flight spectrometer. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quarted; m, multiplet; b, broad and coupling constant are reported in hertz.

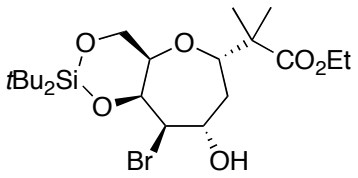
Deprotection of 3.1 to give 3.3.



3.3

To a solution of dibromide **3.1** (32 mg, 0.057 mmol) in THF (1 mL) at ambient temperature was added TBAF (1 M in hexanes, 171 μL, 0.17 mmol, 3 eq) and the reaction stirred for 2 h. The resulting mixture was poured into Et_2O (20 mL) and washed with H_2O (3 x 20 mL). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. Flash chromatography on silica with 9:1 hexanes: ethyl acetate gave 14 mg of **3.3** as a colorless oil (58%). ^{1}H NMR: δ_H = 4.51 (dt, *J*=11.0, 3.7 Hz, 1H, H-3), 4,43 (t, *J*=1.7 Hz, 1H, H-5), 4.34 (dd, *J*=10.5, 1.0 Hz, 1H, H-1), 4.25 (dd, *J*=10.7, 1.9 Hz, 1H, H-4), 4.18 (t, *J*=7.3 Hz, 2H, -O$\underline{CH_2}$Me), 3.84 (td, *J*=4.1, 1.7 Hz, 1H, H-6), 3.78 (dd, *J*=11.7, 4.1 Hz, 1H, H-7), 3.71 (dd, *J*=11.7, 4.1 Hz, 1H, H-7), 2.50 (ddd, *J*=15, 3.7, 1.2 Hz, 1H, H-2), 2.23 (ddd, *J*=15.1, 12.2, 10.5 Hz, 1H, H2), 1.28 (t, J7.1 Hz, 3H, H-Et-me), 1.18, (s, 3H, H-9), 1.15 9s, 3H, H-10). ^{13}C NMR: δ_C = 177.2 (C-11), 78.9 (C-1), 76.0 (C-5), 74.9 (C-6), 65.4 (C-7), 63.5 (C-4), 61.2 (-O$\underline{CH_2}$Me), 53.7 (C-3), 47.8 (C-8), 39.7 (C-2), 22.4 (C-9), 18.8 (C-10), 14.1 (-OCH$_2\underline{Me}$). IR (neat): 3440, 2930, 2860, 1718 cm^{-1}.

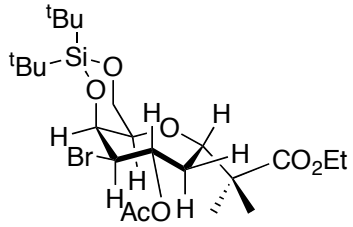
(1*R*,7*R*)-3-(ethyl-2-methyl-2-propanoate)-9,9-di-(*t*-butyl)-2,8,10-trioxa-9-silabicyclo [5.4.0]-6(*S*)-bromo-5(*R*)-undecanol (3.4).



3.4

To a solution of oxepine **2** (103 mg, 0.258 mmol) in a mixture of 1:1 THF:H_2O (2 mL) at ambient temperature was added NBS (55 mg, 0.31 mmol, 1.2 eq) with vigorous stirring. After 1 h, H_2O (2 mL) was added and the mixture stirred an additional five minutes. The resulting mixture was poured into Et_2O (20 mL) and washed with H_2O (2 x 20 mL). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. Flash chromatography on silica with 9:1 hexanes:EtOAc gave 99 mg of a colorless oil (77%) as a 5:1 mixture of isomers. ^{1}H NMR major isomer: δ_H = 4.50 (s, 1H, H-5), 4.25-4.0 (m, 7H, H-1, H-3, H-4, H-7, -O$\underline{CH_2}$Me), 3.80 (s, 1H, H-6), 2.39 (s, 1H, OH), 2.18 (dd, *J*=15.6, 3.2 Hz, 1H, H-2), 1.83 (m, 1H, H-2), 1.25 (t, *J*=7.1 Hz, 3H, -OCH$_2\underline{Me}$), 1.18 (s, 3H, H-9), 1.15 (s, 3H, H-10), 1.07 (s, 9H, *t*Bu), 1.05 (s, 9H, *t*Bu). ^{13}C NMR: δ_C = 176.1 (C-8), 77.7 (C-1), 74.5 (C-5), 71.3 (C-6), 70.7 (C-7), 69.8 (C-3), 67.6 (C-4), 60.7 (-O$\underline{CH_2}$Me), 48.0 (C-8), 33.2 (C-2), 27.6 (*t*Bu), 27.5 (*t*Bu), 21.8 (C-9), 21.5 (C-10), 20.7 (Si-C), 14.1 (-OCH$_2\underline{Me}$). IR (neat): 3446, 2859, 1718 cm^{-1}.

(1*R*,7*R*)-3-(ethyl-2-methyl-2-propanoate)-9,9-di-(*t*-butyl)-2,8,10-trioxa-9-silabicyclo [5.4.0]-6(*S*)-bromo-5-(*R*)-O-acetyl-undecanol (3.5).

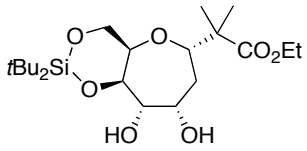


3.5

Bromohydrin **3.4** was acetylated using the general procedure (see manuscript) to give **3.5** as a clear oil in an 85% yield. ^{1}H NMR: δ_H = 5.14 (td, *J*=10.4, 1.6 Hz, 1H, H-3), 4.53 (d, 1H, *J*=3.3 Hz, 1H, H-5), 4.2-4.0 (m, 6H, H-1, H-4, H-7, -O$\underline{CH_2}$Me), 3.80 (s, 1H, H-6), 2.09 (s, 3H, Ac), 1.96 (m, 2H, H-2), 1.24 (t, 3H, *J*=7.0 Hz, 3H, -OCH$_2\underline{Me}$), 1.15 (s, 3H,

H-9), 1.12 (s, 3H, H-10), 1.06 (s, 18H, *t*Bu). ^{13}C NMR: δ_C = 176.0 (C-11), 169.6 (Ac), 78.0 (C-1), 74.3 (C-5), 72.1 (C-3), 70.5 (C-7), 60.8 (-O<u>CH$_2$</u>Me), 58.7 (C-4), 47.8 (C-8), 33.3 (C-2), 27.6 (*t*Bu), 23.7 (Si-C), 21.7 (C-9), 21.0 (C-10), 20.7 (Ac), 14.1 (-OCH$_2$<u>Me</u>). IR (neat): 2935, 2860, 2254, 1725, 1474, 1387, 1366, 1237, 1157, 1126 cm^{-1}. HRMS *m/z*: calculated for $C_{23}H_{42}O_7BrSi$ + Na = 559.1703. Found 559.1710.

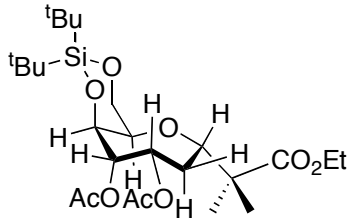
(1*R*,7*R*)-3-(ethyl-2-methyl-2-propanoate)-9,9-di-(*t*-butyl)-2,8,10-trioxa-9-silabicyclo [5.4.0]-5(*R*),6(*R*)-di-undecanol (3.9).



3.9

To a solution of oxepine **2** in a 1:1 mix of Et_2O:H_2O (2 mL) at ambient temperature was added a 2.5% solution of OsO_4 in water (126 μL, 3.2 mg, 0.026 mmol, 5%) and NMO (118 mg, 0.27 mmol, 1.1 eq). After 1 h, the mixture was poured into Et_2O (20 mL), washed with H_2O (20 mL) and dried over $MgSO_4$. Concentration *in vacuo* followed by flash chromatography on silica in 9:1 hexanes:EtOAc gave 64 mg of a colorless oil (59%). ^{1}H NMR: δ_H = 4.15-3.95 (m, 8H, H-1, H-3, H-4, H-5, H-7, -O<u>CH$_2$</u>Me), 3.80 (s, 1H, H-6), 2.7 (bs, 2H, OH), 2.34 (q, *J*=12.9 Hz, 1H, H-2a), 1.51 (dd, *J*=14.4, 1.3 Hz, 1H, H-2b), 1.19 (t, *J*=7.1 Hz, 3H, -OCH$_2$<u>Me</u>), 1.12 (s, 3H, H-9), 1.07 (s, 3H, H-10), 0.96 (s, 9H, *t*Bu), 0.95 (s, 9H, *t*Bu). ^{13}C NMR: δ_C = 176.6 (C-8), 78.3 (C-1), 75.5 (C-3), 75.0 (C-4), 70.1 (C-7), 70.0 (C-5), 68.2 (C-6), 60.7 (-O<u>CH$_2$</u>Me), 47.9 (C-8), 28.3 (C-2), 27.6 (*t*Bu), 27.5 (*t*Bu), 21.9 (C-9), 21.2 (C-10), 20.7 (Si-C), 14.1 (-OCH$_2$<u>Me</u>). IR (neat): 3433, 2933, 2859, 1713, 1473, 1387, 1364, 1262, 1131, 1081, 1022, 930, 910, 825, 756, 738 cm^{-1}.

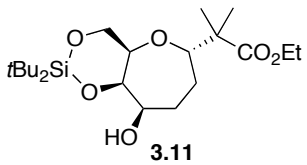
(1*R*,7*R*)-3-(ethyl-2-methyl-2-propanoate)-9,9-di-(*t*-butyl)-2,8,10-trioxa-9-silabicyclo [5.4.0]-5(*R*),6(*R*)-O-acetyl--di-undecanol (3.10).



3.10

Diol **3.9** was acetylated using the general procedure to give **3.10** in a 79% yield. ^{1}H NMR: δ_H = 5.24 (d, *J*=1.7 Hz, 1H, H-4), 5.19 (d, *J*=10.5 Hz, 1H, H-3), 4.2-4.05 (m, 5H, H-1, H-7, -O<u>CH$_2$</u>Me), 3.99 (d, *J*=3.7 Hz, 1H, H-5), 3.81 (s, 1H, H-6), 2.49 (td, J=12.5, 10.5 Hz, 1H, H-2), 2.14 (s, 3H, Ac), 2.02 (s, 3H, Ac), 1.67 (dd, *J*=13.4, 3.0 Hz, H-2), 1.27 (t, *J*=7.1 Hz, 3H, H-Et-Me), 1.19 (s, 3H, H-9), 1.17 (s, 3H, H-10), 1.03 (s, 9H, *t*Bu), 1.01 (s, 9H, *t*Bu). ^{13}C NMR: δ_C = 176.1 (C-11), 169.9 (Ac), 167.7 (Ac), 78.5 (C-1), 74.0 (C-4), 73.5 (C-5), 70.6 (C-3), 70.4 (C-7), 68.6 (C-6), 60.7 (-O<u>CH$_2$</u>Me), 47.7 (C-8), 27.5 (*t*Bu), 27.4 (*t*Bu), 27.0 (C-2), 23.5 (Si-C), 22.4 (Si-C), 21.5 (C-9), 21.2 (C-10), 21.1 (Ac), 20.8 (Ac), 14.1 (-OCH$_2$<u>Me</u>). IR (neat): 2933, 2860, 1739, 1474, 1369, 1244, 1223, 1132, 1097, 1027, 916, 826, 731 cm^{-1}. HRMS *m/z*: calculated for $C_{23}H_{44}O_9Si$ + Na 539.2652. Found 539.2652.

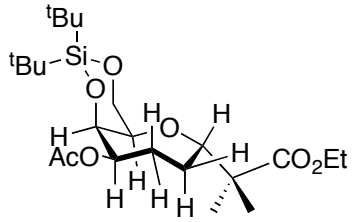
(1*R*,7*R*)-3-(ethyl-2-methyl-2-propanoate)-9,9-di-(*t*-butyl)-2,8,10-trioxa-9-silabicyclo [5.4.0]-6(*S*)-undecanol (3.11).



3.11

To a solution of oxepine **2** (78 mg, 0.20 mmol) in THF (1 mL) at 0 ^{o}C was added 2 M BH_3-DMS complex (198 μL, 0.39 mmol). After stirring 1 h at 0 ^{o}C the reaction was quenched by the addition of H_2O (100 μL) and stirred for 5 min. To the mixture was added 3 M NaOH (0.2 mL) and 3 M H_2O_2 (0.2 mL). This was warmed to ambient temperature and stirred overnight. The mixture was poured into Et_2O (20 mL), washed with H_2O (2 x 20 mL) and dried over $MgSO_4$. Concentration *in vacuo* followed by flash chromatography on silica with 9:1 hexanes:EtOAc gave 32 mg of a colorless oil (40%) and 20 mg recovered starting material (26%). ^{1}H NMR: δ_H = 4.2-3.95 (m, 7H, H-4, H-5, H-6, H-7, -O$\underline{CH_2}$Me), 3.89 (dd, *J*=12.5, 4.0 Hz, 1H, H-1), 2.05-1.8 (m, 3H, H-2, H-3), 1.48 (m, 1H, H-3), 1.25 (t, *J*=7.1 Hz, 3H, H-Et-Me), 1.18 (s, 3H, H-9), 1.12 (s, 3H, H-10), 1.03 (s, 9H, *t*Bu), 1.02 (s, 9H, *t*Bu). ^{13}C NMR: δ_C = 176.7 (C-11), 81.7 (C-1), 78.6 (C-6), 70.9 (C-5), 69.7 (C-7), 68.8 (C-4), 60.5 (-O$\underline{CH_2}$Me), 48.1 (C-8), 28.0 (C-2), 27.5 (*t*Bu), 23.2 (*t*Bu), 21.7(C-9), 21.4 (C-10), 20.9 (Si-C), 19.3 (Si-C), 14.1 (-OCH$_2\underline{Me}$). IR (neat): 3450, 2934, 2859, 1712, 1473 cm^{-1}.

(1*R*,7*R*)-3-(ethyl-2-methyl-2-propanoate)-9,9-di-(*tert*-butyl)-2,8,10-trioxa-9-silabicyclo [5.4.0]-6(*S*)-O-acetyl-undecanol (3.12).

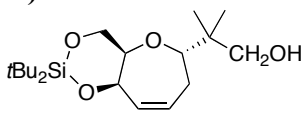


3.12

Alcohol **3.11** was acetylated using the general procedure to give **3.12** in a 68% yield. ^{1}H NMR: δ_H = 4.96 (t, *J*=3.4 Hz, 1H, H-4), 4.2-4.0 (m, 5H, H-5, H-7, -O$\underline{CH_2}$Me), 3.89 (dd, *J*=12.5, 4.4 Hz, 1H, H-1), 3.82 (t, *J*=2.0 Hz, 1H, H-6), 2.08 (s, 3H, Ac), 2.00 (m, 1H, H-

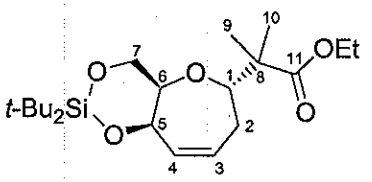
2), 1.92 (m, 2H, H-3), 1.51 (m, 1H, H-2), 1.26 (t, *J*=7.0 Hz, 3H, -OCH$_2$Me), 1.19 (s, 3H, H-9), 1.15 (s, 3H, H-10), 1.03 (s, 9H, H-*t*Bu), 1.02 (s, 9H, H-*t*Bu). ^{13}C NMR: δ_C = 176.6 (C-11), 169.7 (C-Ac), 82.4 (C-1), 75.7 (C-5), 73.3 (C-4), 70.6 (C-7), 68.9 (C-6), 60.5 (-OCH$_2$Me), 48.0 (C-8), 27.6 (*t*Bu), 27.4 (*t*Bu), 25.5 (C-3), 22.0 (Si-C), 21.7 (C-9), 21.3 (C-10), 20.8 (Ac), 19.7 (C-2), 14.1 (-OCH$_2$Me). IR (neat): 2935, 2859, 1728, 1474 cm^{-1}. HRMS *m/z*: calculated for $C_{23}H_{42}O_7Si$ + Na 481.2598. Found 481.2602.

(1*R*,7*R*)-3-(12,12-dimethyl-13-ethanol)-9,9-di-(*t*-butyl)-2,8,10-trioxa-9-silabicyclo [5.4.0]undec-5-ene (3.13).



3.13

To a solution of the oxepine **2** (65 mg, 0.163 mmol) in 1 mL CH_2Cl_2 at –78 ^{o}C was added DIBAL 1 M in CH_2Cl_2 (163 μL, 0.163 mmol). After stirring for 2h, H_2O (500 μL) was added and the reaction warmed to ambient temperature. The mixture was poured into Et_2O (20 mL), washed with H_2O (2 x 20 mL) and dried over $MgSO_4$. Concentration *in vacuo* followed by flash chromatography on silica in 9:1 hexanes:EtOAc gave 31 mg of the alcohol as a colorless oil (54%) and 15mg recovered starting material (23%). ^{1}H NMR: δ_H = 5.87 (tdd, *J*=9.0, 3.1, 1.2 Hz, 1H, H-3), 5.74 (ddd, *J*=11.2, 4.4, 2.6 Hz, 1H, H-4), 4.85 (m, 1H, H-5), 4.26 (s, 2H, H-11), 4.06 (s, 1H, H-6), 4.01 (dd, *J*=11.5, 1.7 Hz, 1H, H-1), 3.46 (dd, *J*=56.4, 9.0 Hz, 2H, H-7), 2.52 (ddd, *J*=16.8, 11.5, 2.7 Hz, 1H, H-2), 2.14 (qd, *J*=9.0, 2.0 Hz, 1H, H-2), 1.08 (s, 9H, *t*Bu), 1.07 (s, 9H, *t*Bu), 0.97 (s, 3H, H-9), 0.82 (s, 3H, H-10). ^{13}C NMR: δ_C = 132.1 (C-4), 128.0 (C-3), 86.1 (C-1), 75.0 (C-5), 72.8 (C-7), 72.2 (C-6), 68.7 (C-11), 39.0 (C-8), 27.7 (*t*Bu), 27.2 (*t*Bu), 25.7 (C-2), 22.7 (C-9), 20.6 (C-10), 18.2 (Si-C). IR (neat): 3420, 2934, 2859, 1716, 1472, 1364, 1097, 826, 737 cm^{-1}.


t-Bu2Si
O
O
O
O
OEt
1
2
3
4
5
6
7
8
9
10
11

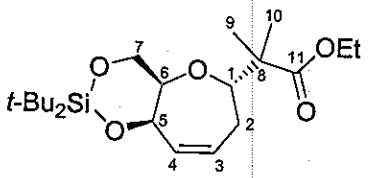
2

9
8
7
6
5
4
3
2
1
ppm
4.97
2.49
15.69
2.59
2.61
71.65

RB061206a

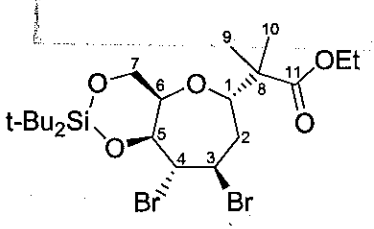
exp2 Carbon

SAMPLE		SPECIAL	
date	Jun 12 2006	temp	not used
solvent	cdcl3	gain	30
file	/export/home/~	spin	20
everyone/Rhys/RB06~		hst	0.008
1206aCarboncdcl350~		pw90	7.600
	0	alfa	10.000
ACQUISITION		FLAGS	
sw	30165.9	il	n
at	2.000	in	n
np	120664	dp	y
fb	not used	hs	nn
bs	64	PROCESSING	
d1	0	lb	1.00
nt	1792	fn	not used
ct	1792	DISPLAY	
TRANSMITTER		sp	-1891.4
tn	C13	wp	30165.9
sfrq	125.682	rfl	1891.4
tof	1285.2	rfp	0
tpwr	56	rp	50.4
pw	3.800	lp	-60.6
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	43295
dmm	w	th	6
dpwr	46	ai cdc ph	
dmf	12107		



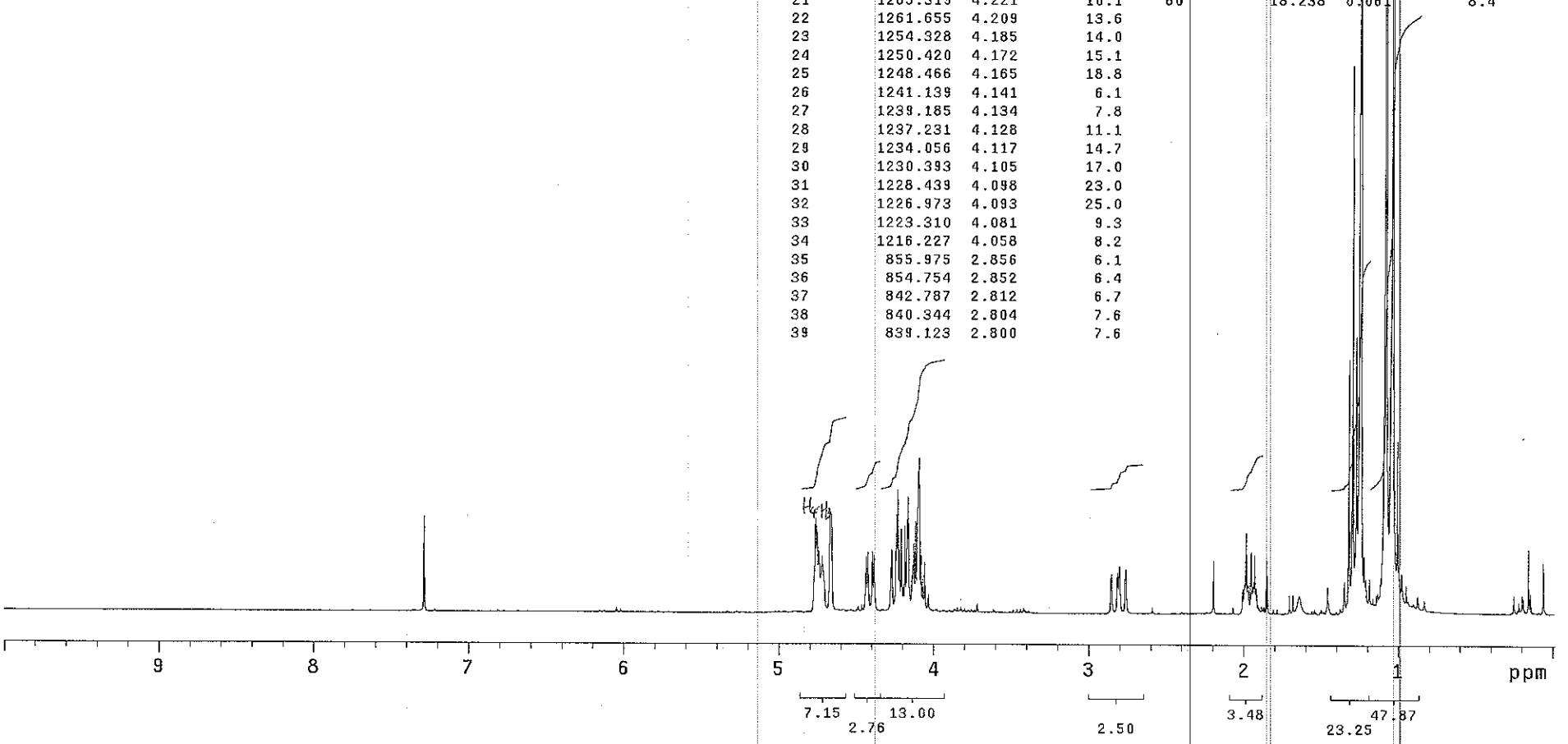
2

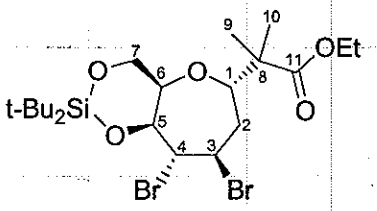
10



3.2

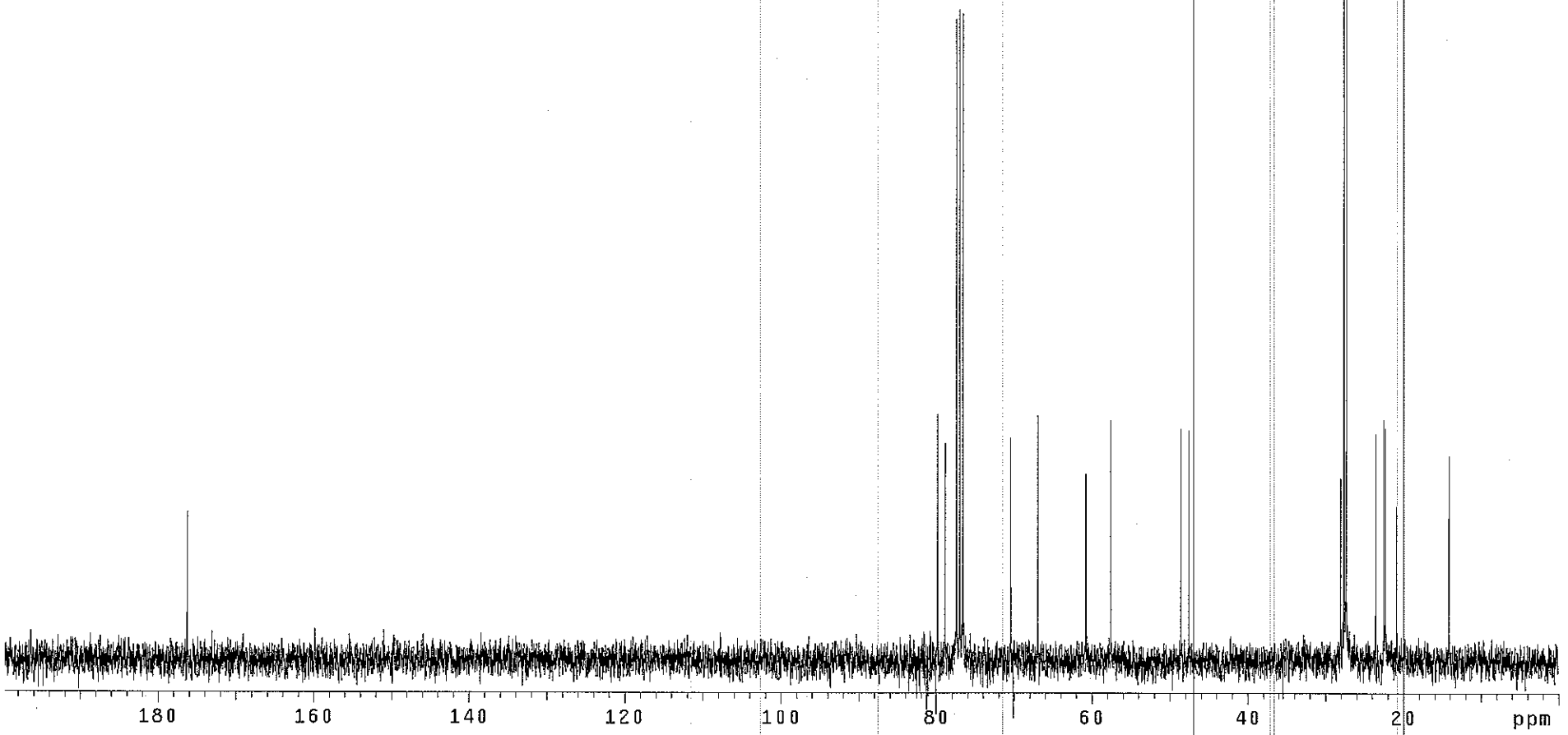
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2184.388	7.288	15.4	40	828.132	2.763	6.6
2	1430.424	4.772	6.6	41	827.155	2.760	7.1
3	1427.737	4.763	15.3	42	658.142	2.196	8.6
4	1425.295	4.755	13.5	43	595.129	1.985	13.1
5	1424.562	4.753	12.7	44	585.115	1.952	10.0
6	1421.631	4.743	10.0	45	578.521	1.930	9.6
7	1417.968	4.731	6.0	46	555.074	1.852	8.7
8	1415.037	4.721	9.2	47	395.830	1.321	40.9
9	1411.618	4.709	6.1	48	388.748	1.297	88.6
10	1399.406	4.669	16.3	49	384.107	1.281	10.0
11	1398.429	4.665	16.4	50	381.665	1.273	44.7
12	1329.798	4.437	9.1	51	375.803	1.254	122.8
13	1326.134	4.424	9.8	52	373.605	1.246	128.6
14	1317.830	4.397	9.9	53	366.278	1.222	9.4
15	1314.167	4.384	9.4	54	325.978	1.088	400.7
16	1281.683	4.276	7.3	55	312.789	1.044	373.5
17	1279.729	4.269	10.3	56	302.043	1.008	27.8
18	1272.402	4.245	10.1	57	299.112	0.998	7.2
19	1270.448	4.239	15.8	58	293.250	0.978	6.6
20	1268.494	4.232	19.8	59	47.547	0.159	10.5
21	1265.319	4.221	10.1	60	18.238	0.061	8.4
22	1261.655	4.209	13.6				
23	1254.328	4.185	14.0				
24	1250.420	4.172	15.1				
25	1248.466	4.165	18.8				
26	1241.139	4.141	6.1				
27	1239.185	4.134	7.8				
28	1237.231	4.128	11.1				
29	1234.056	4.117	14.7				
30	1230.393	4.105	17.0				
31	1228.439	4.098	23.0				
32	1226.973	4.093	25.0				
33	1223.310	4.081	9.3				
34	1216.227	4.058	8.2				
35	855.975	2.856	6.1				
36	854.754	2.852	6.4				
37	842.787	2.812	6.7				
38	840.344	2.804	7.6				
39	839.123	2.800	7.6				

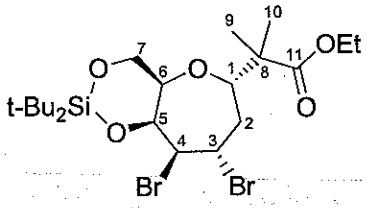




3.2

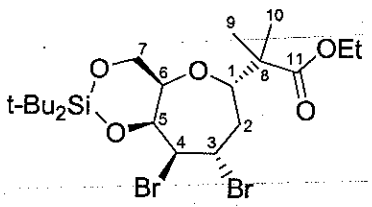
INDEX	FREQUENCY	PPM	HEIGHT
1	13283.987	176.251	24.3
2	6016.506	79.827	39.9
3	5945.027	78.878	35.3
4	5835.445	77.424	103.8
5	5803.460	77.000	105.3
6	5771.475	76.576	104.7
7	5308.392	70.431	36.2
8	5045.562	66.944	39.7
9	4577.194	60.730	30.3
10	4338.839	57.567	38.9
11	3661.041	48.575	37.6
12	3584.834	47.563	37.4
13	2114.650	28.057	29.6
14	2081.275	27.614	113.2
15	2059.581	27.326	133.4
16	1773.109	23.526	36.7
17	1695.790	22.500	38.9
18	1680.493	22.297	37.6
19	1572.857	20.869	25.1
20	1064.996	14.130	33.2





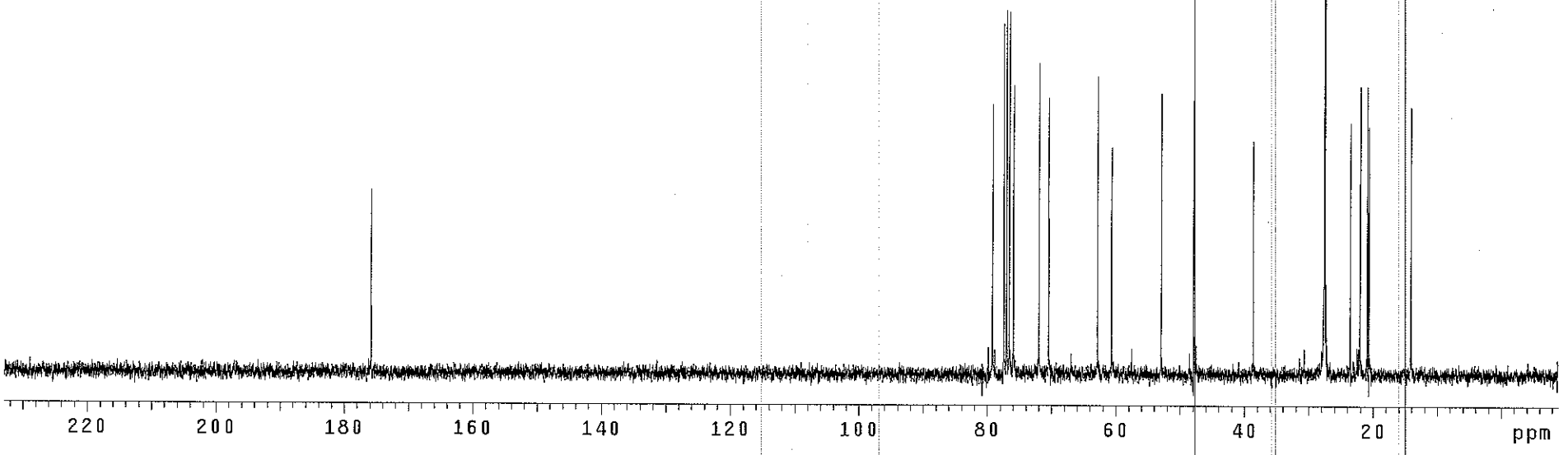
3.1

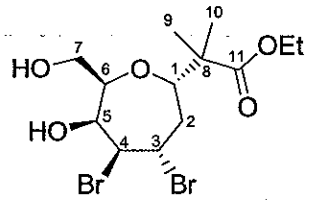
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	1392.811	4.647	17.2	40	306.439	1.022	9.8
2	1389.636	4.636	18.0				
3	1336.148	4.458	11.3				
4	1334.438	4.452	11.7				
5	1269.227	4.234	9.3				
6	1262.144	4.211	10.4				
7	1258.480	4.199	26.3				
8	1255.305	4.188	17.3				
9	1251.397	4.175	15.2				
10	1249.688	4.169	15.3				
11	1247.489	4.162	13.9				
12	1244.070	4.151	17.3				
13	1241.139	4.141	41.5				
14	1238.941	4.133	43.4				
15	1235.033	4.120	8.6				
16	1229.904	4.103	13.2				
17	1227.706	4.096	24.6				
18	1220.623	4.072	14.3				
19	1218.181	4.064	14.2				
20	1216.715	4.059	14.0				
21	1215.739	4.056	13.3				
22	1209.633	4.036	8.0				
23	1153.702	3.849	19.5				
24	766.096	2.556	7.6				
25	763.898	2.549	11.2				
26	707.967	2.362	9.9				
27	440.038	1.468	10.1				
28	388.015	1.295	42.8				
29	380.932	1.271	80.9				
30	373.849	1.247	47.1				
31	360.416	1.202	7.5				
32	355.775	1.187	108.7				
33	344.052	1.148	111.9				
34	338.190	1.128	8.4				
35	331.352	1.105	23.7				
36	326.467	1.089	378.4				
37	324.269	1.082	463.5				
38	314.255	1.048	10.9				
39	310.103	1.035	36.7				



3.1

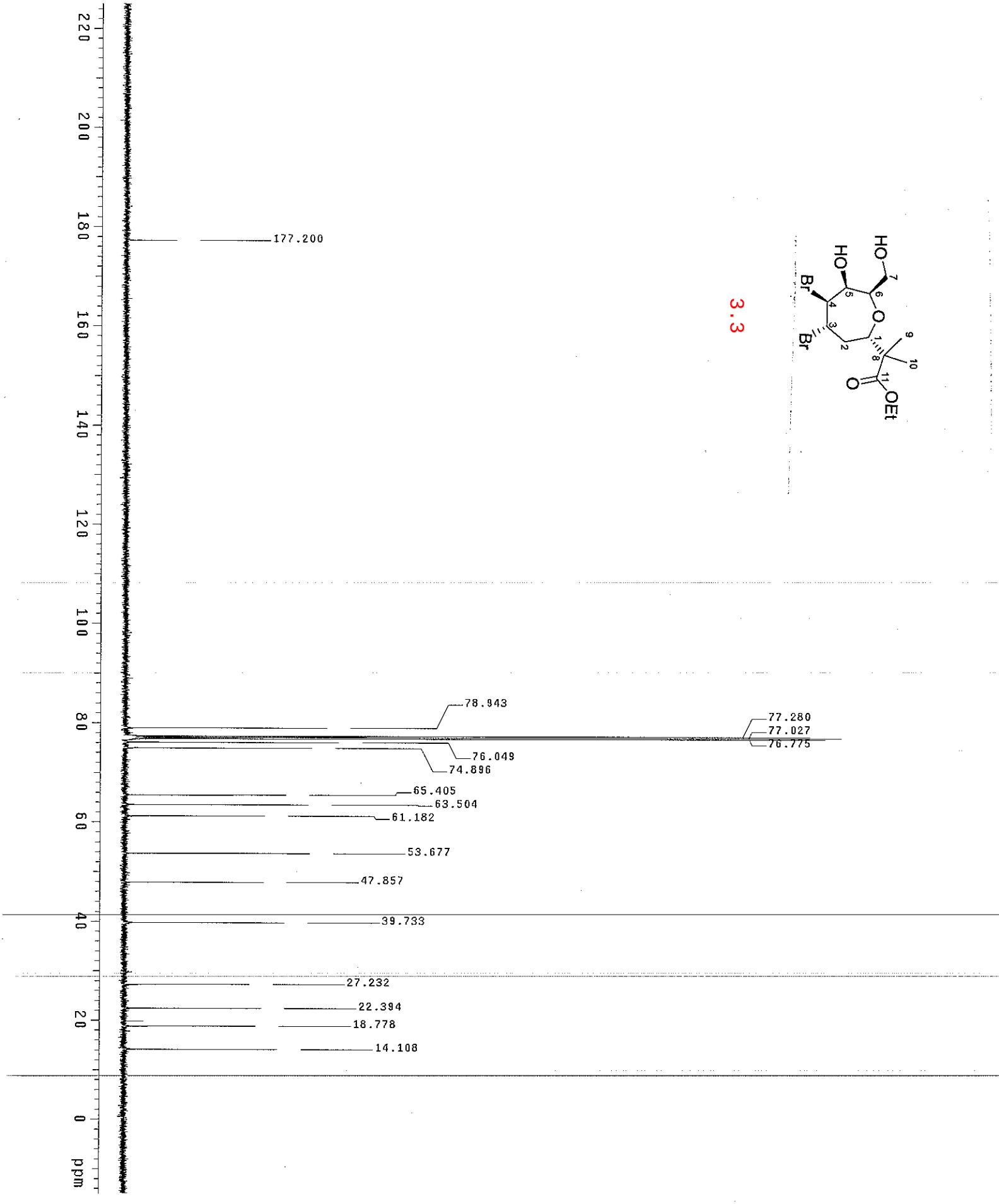
INDEX	FREQUENCY	PPM	HEIGHT
1	13251.446	175.819	29.5
2	5968.946	79.196	43.4
3	5835.167	77.421	56.4
4	5803.460	77.000	58.5
5	5771.475	76.576	58.3
6	5722.525	75.926	46.4
7	5424.094	71.967	50.0
8	5309.227	70.443	44.4
9	4736.005	62.837	47.9
10	4573.022	60.675	36.5
11	3980.345	52.944	45.2
12	3612.091	47.925	44.0
13	2912.043	38.637	37.5
14	2084.613	27.659	172.1
15	2080.162	27.599	25.1
16	2074.878	27.529	148.0
17	1775.334	23.555	40.5
18	1661.580	22.046	46.3
19	1576.195	20.913	46.3
20	1557.004	20.658	39.9
21	1063.883	14.116	43.0

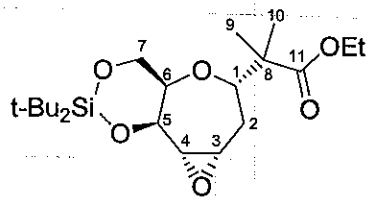



HO
7
6
O
1
8
9
10
11
OEt
O
HO
5
4
3
2
Br
Br

3.3

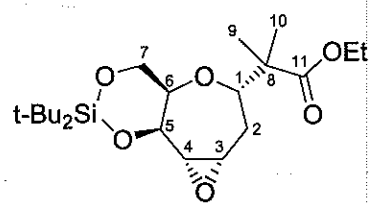
9
8
7
6
5
4
3
2
1
ppm
24.28
13.13
6.04
6.27
15.04
10.82
24.43


177.200
78.943
77.280
77.027
76.775
76.049
74.896
65.405
63.504
61.182
53.677
47.857
39.733
27.232
22.394
18.778
14.108
220
200
180
160
140
120
100
80
60
40
20
0
ppm
3.3
HO
HO
Br
Br
O
OEt
O
1
2
3
4
5
6
7
8
9
10
11


t-Bu2Si
O
OEt
1
2
3
4
5
6
7
8
9
10
11

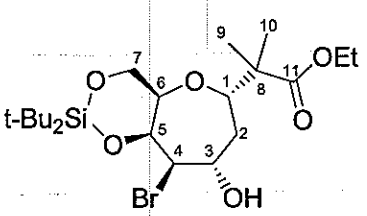
3.6

9
8
7
6
5
4
3
2
1
ppm
2.23
12.33
2.47
2.56
2.21
2.89
2.96
72.35



3.6

INDEX	FREQUENCY	PPM	HEIGHT
1	22147.957	176.241	47.5
2	9844.264	78.335	52.7
3	9713.080	77.291	152.8
4	9680.859	77.035	155.6
5	9649.099	76.782	154.3
6	9320.448	74.167	49.7
7	9314.004	74.115	50.9
8	8693.525	69.178	65.9
9	8551.755	68.050	41.3
10	8543.930	67.988	41.8
11	7603.086	60.501	48.1
12	7110.110	56.578	70.2
13	6992.274	55.640	56.5
14	5998.497	47.733	76.7
15	3472.856	27.635	112.0
16	3470.555	27.617	117.7
17	3435.112	27.335	118.9
18	3432.811	27.316	126.0
19	3408.875	27.126	71.0
20	2934.311	23.350	70.5
21	2824.300	22.474	35.0
22	2821.078	22.448	35.9
23	2585.867	20.577	57.4
24	2511.299	19.983	36.0
25	2508.077	19.958	36.5
26	1783.112	14.189	38.2
27	1779.890	14.163	37.6


t-Bu2Si
O
O
O
O
OEt
Br
OH
1
2
3
4
5
6
7
8
9
10
11

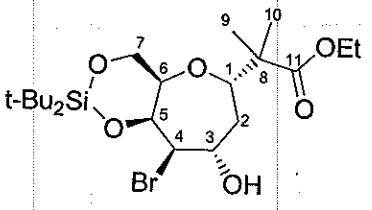
3.4

9
8
7
6
5
4
3
2
1
ppm
1.92
18.03
2.30
0.44
2.36
2.99
3.23
12.62
22.30

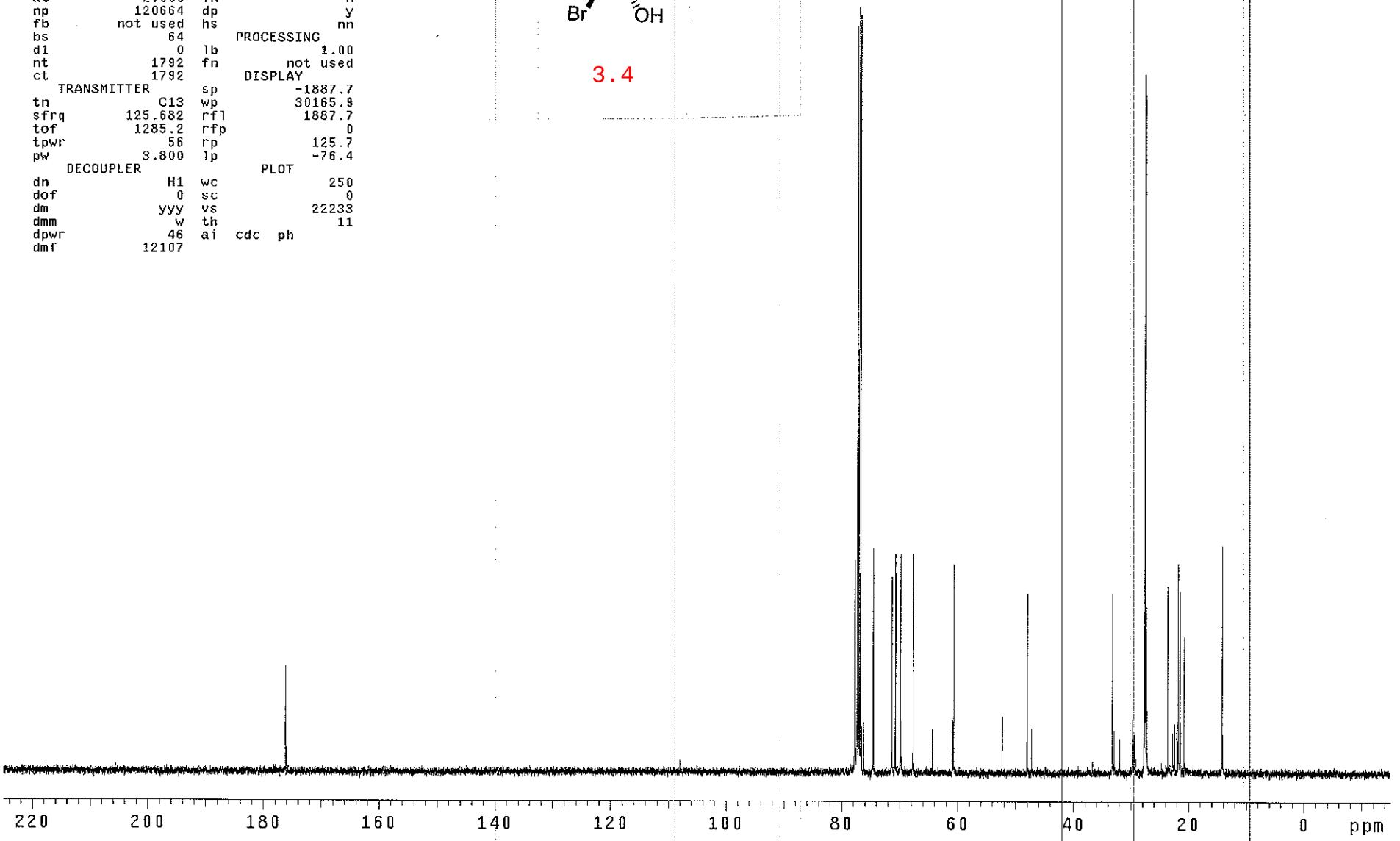
RB062006b

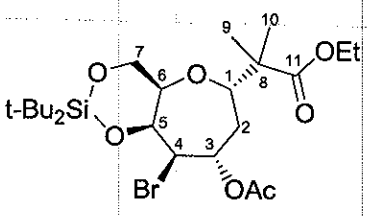
exp2 Carbon

SAMPLE		SPECIAL	
date	Jun 21 2006	temp	not used
solvent	cdcl3	gain	30
file	/export/home/~	spin	20
everyone/Rhys/RB06~		hst	0.008
2006bCarboncdcl350~		pw90	7.600
	0	alfa	10.000
ACQUISITION		FLAGS	
sw	30165.9	il	n
at	2.000	in	n
np	120664	dp	y
fb	not used	hs	nn
bs	64	PROCESSING	
d1	0	lb	1.00
nt	1792	fn	not used
ct	1792	DISPLAY	
TRANSMITTER		sp	-1887.7
tn	C13	wp	30165.9
sfrq	125.682	rfl	1887.7
tof	1285.2	rfp	0
tpwr	56	rp	125.7
pw	3.800	lp	-76.4
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	22233
dmm	w	th	11
dpwr	46	ai cdc ph	
dmf	12107		



3.4



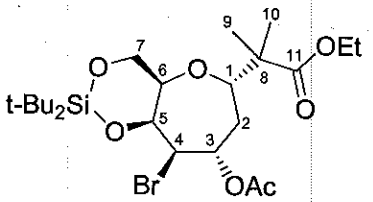


3.5

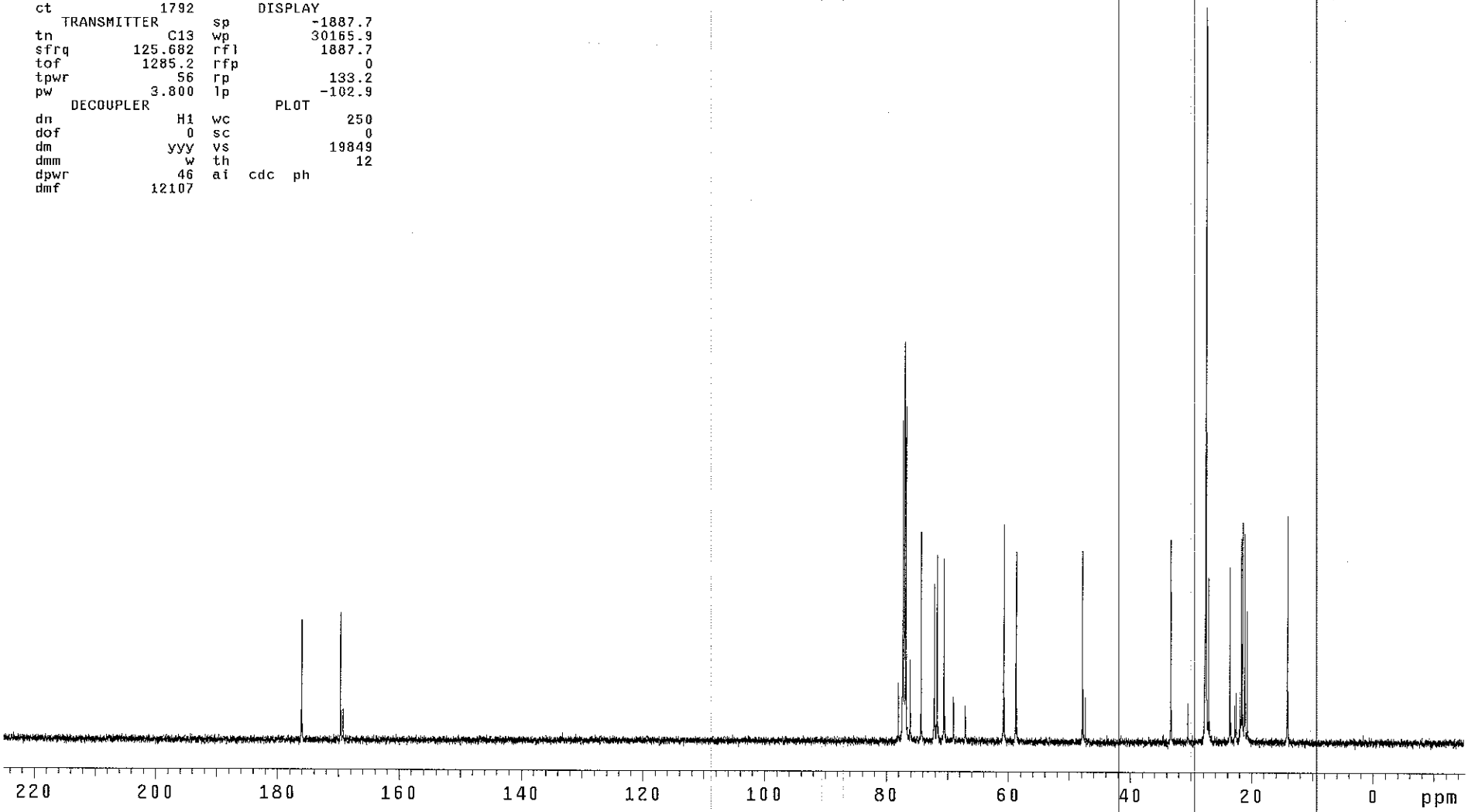
RB062806a

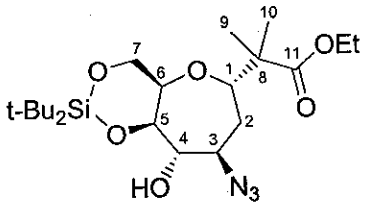
exp2 Carbon

SAMPLE		SPECIAL	
date	Jul 3 2006	temp	not used
solvent	cdcl3	gain	30
file	/export/home/~	spin	20
everyone/Rhys/RB06~		hst	0.008
2806aCarboncdcl350~		pw90	7.600
	0	alfa	10.000
ACQUISITION		FLAGS	
sw	30165.9	il	n
at	2.000	in	n
np	120664	dp	y
fb	not used	hs	nn
bs	64	PROCESSING	
d1	0	lb	1.00
nt	1792	fn	not used
ct	1792	DISPLAY	
TRANSMITTER		sp	-1887.7
tn	C13	wp	30165.9
sfrq	125.682	rfl	1887.7
tof	1285.2	rfp	0
tpwr	56	rp	133.2
pw	3.800	lp	-102.9
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	19849
dmm	w	th	12
dpwr	46	ai cdc ph	
dmf	12107		



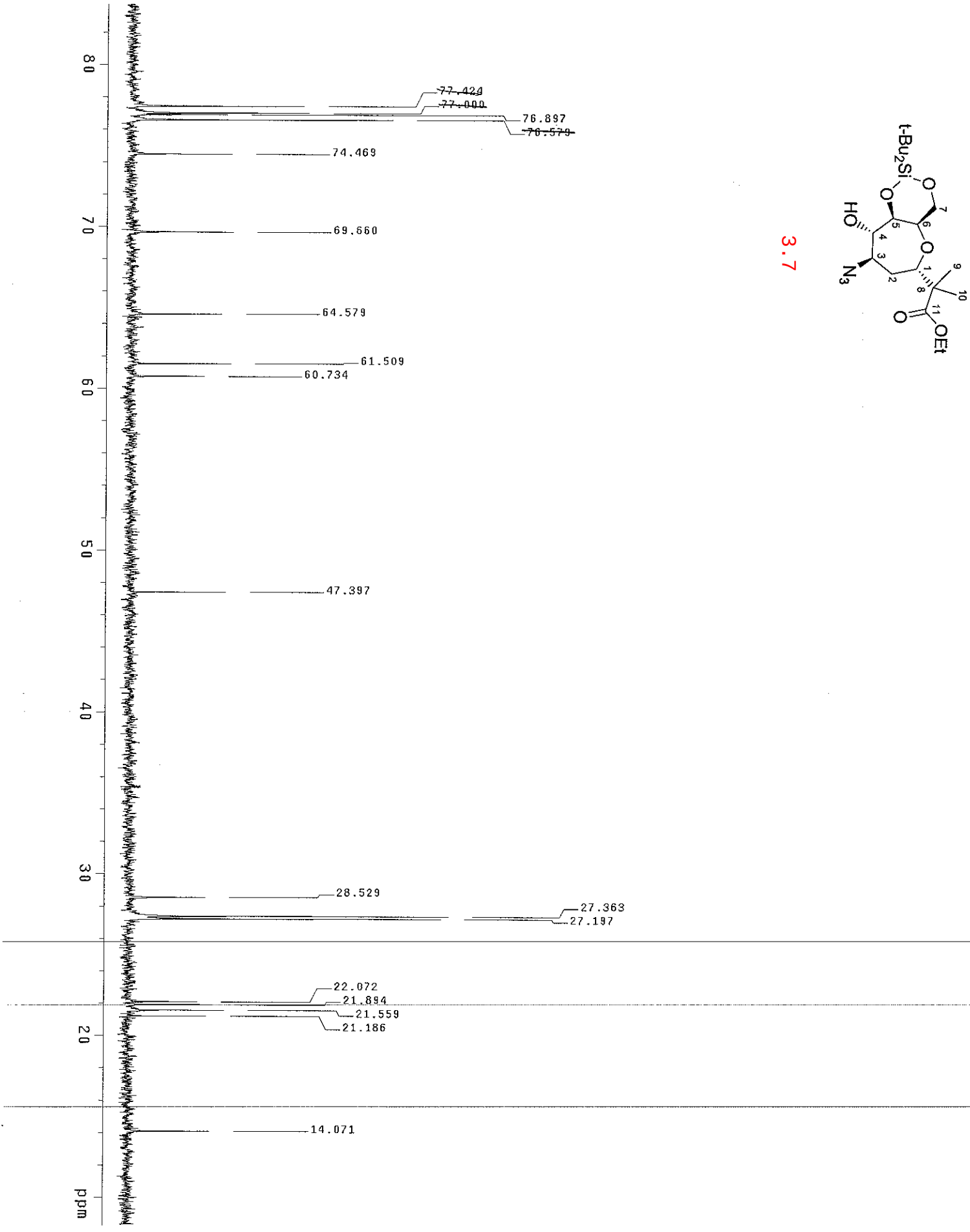
3.5




t-Bu2Si
O
O
O
O
HO
N3
OEt
1
2
3
4
5
6
7
8
9
10
11

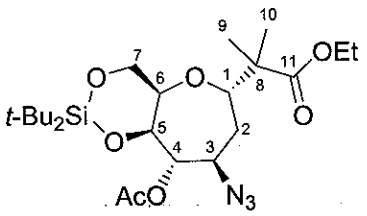
3.7

9
8
7
6
5
4
3
2
1
ppm
20.25
2.80
2.40
2.88
3.19
68.47


77.429
77.000
76.897
76.579
74.469
69.660
64.579
61.509
60.734
47.397
28.529
27.363
27.197
22.072
21.894
21.559
21.186
14.071
80
70
60
50
40
30
20
ppm

3.7

t-Bu2Si
HO
N3
OEt
O


9
10
7
6
1
8
11
OEt
O
O
O
t-Bu2Si
5
4
3
2
O
AcO
N3

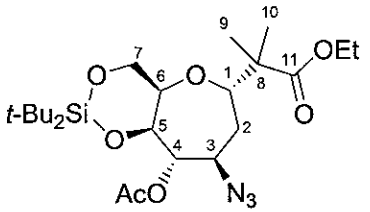
3.8

9
8
7
6
5
4
3
2
1
ppm
2.32
7.04
7.50 4.77
9.50
2.54
7.64 44.07
14.62

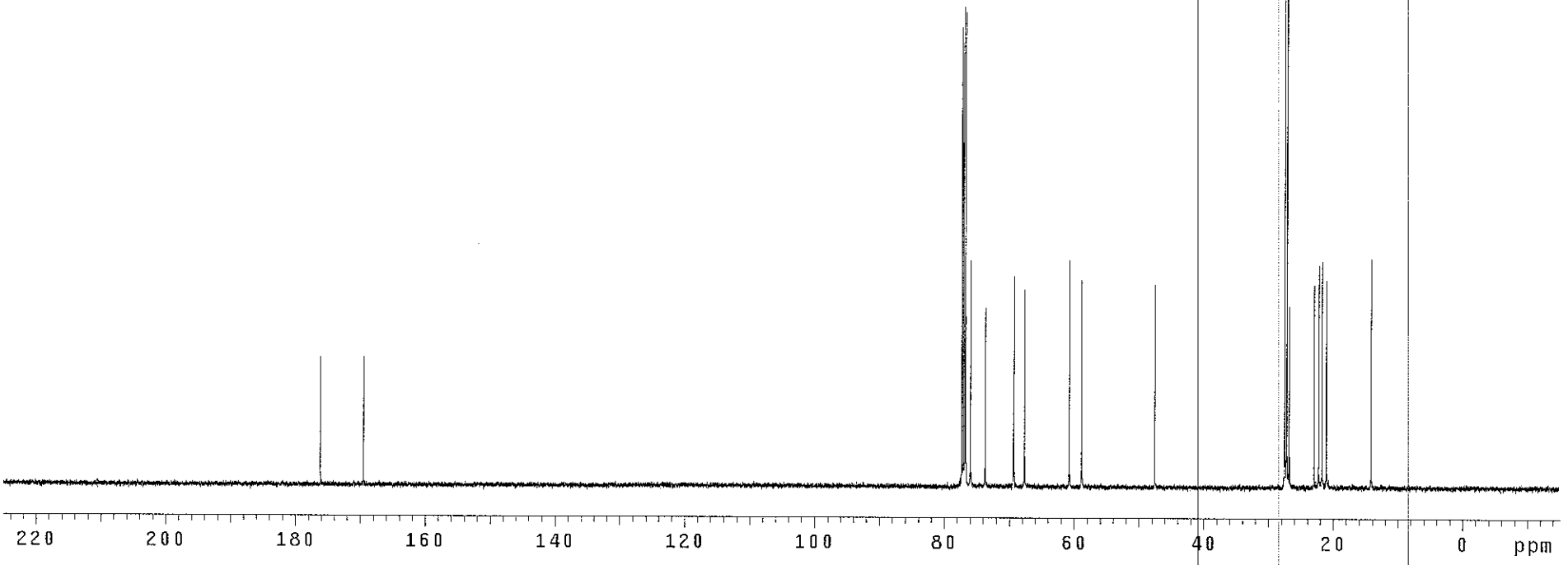
RB062906a

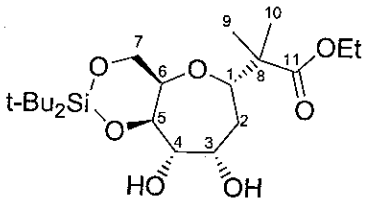
exp2 Carbon

SAMPLE		SPECIAL	
date	Jul 3 2006	temp	not used
solvent	cdcl3	gain	30
file	/export/home/~	spin	20
everyone/Rhys/RB06~		hst	0.008
2906aCarboncdcl350~		pw90	7.600
	0	alfa	10.000
ACQUISITION		FLAGS	
sw	30165.9	il	n
at	2.000	in	n
np	120664	dp	y
fb	not used	hs	nn
bs	64	PROCESSING	
d1	0	lb	1.00
nt	1792	fn	not used
ct	1792	DISPLAY	
TRANSMITTER		sp	-1887.7
tn	C13	wp	30165.9
sfrq	125.682	rfl	1887.7
tof	1285.2	rfp	0
tpwr	56	rp	155.3
pw	3.800	lp	-100.9
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	12293
dmm	w	th	2
dpwr	46	ai cdc ph	
dmf	12107		



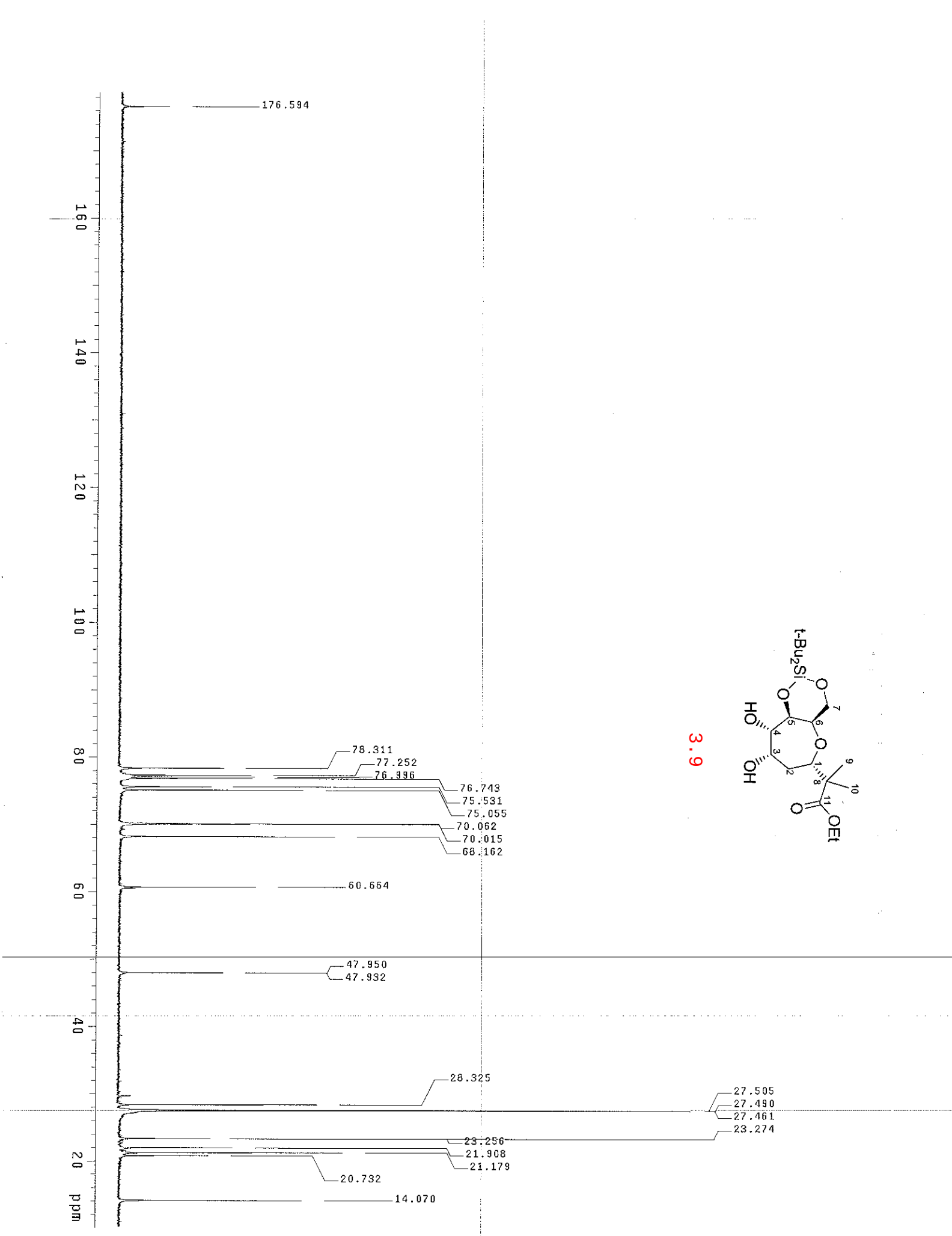
3.8




t-Bu2Si
O
O
O
O
O
OEt
HO
OH
1
2
3
4
5
6
7
8
9
10
11

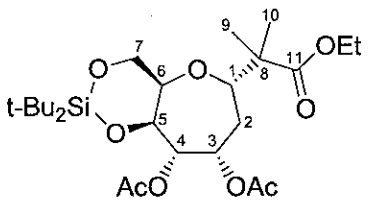
3.9

9
8
7
6
5
4
3
2
1
ppm
21.85
4.05
2.67
2.50
68.93


176.594
78.311
77.252
76.996
76.748
75.531
75.055
70.062
70.015
68.162
60.664
47.950
47.932
28.325
27.505
27.490
27.461
23.274
23.256
21.908
21.179
20.732
14.070
160
140
120
100
80
60
40
20
ppm

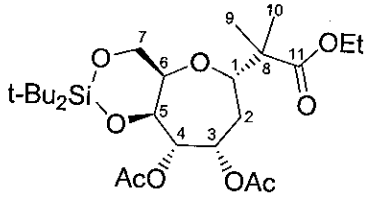
t-Bu2Si
HO
OH
O
OEt
1
2
3
4
5
6
7
8
9
10
11

3.9


t-Bu2Si
O
O
O
O
OEt
AcO
OAc
1
2
3
4
5
6
7
8
9
10
11

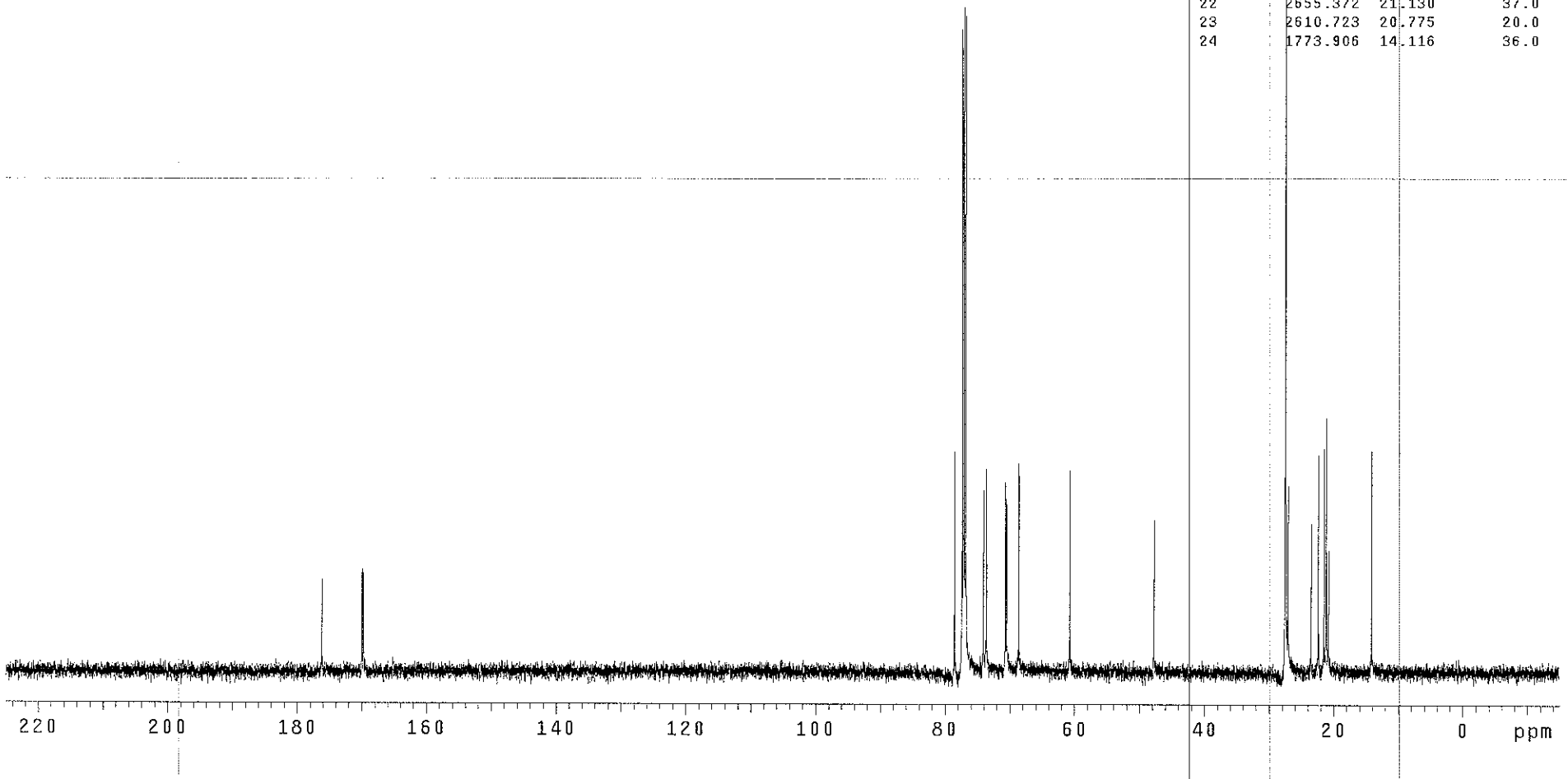
3.10

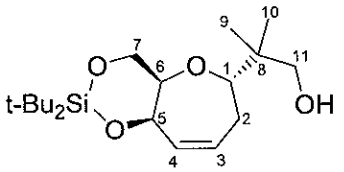
9
8
7
6
5
4
3
2
1
ppm
4.19
13.02
2.58
2.19
6.59
6.61
4.02
20.95
39.85



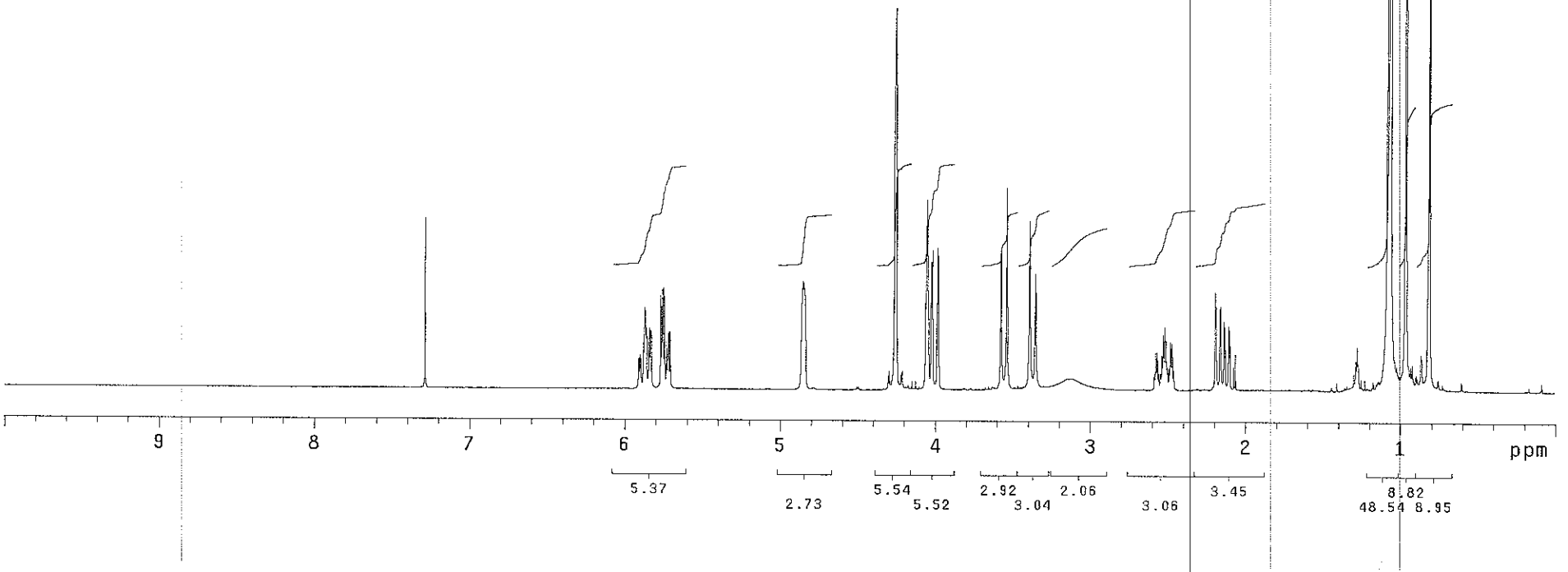
3.10

INDEX	FREQUENCY	PPM	HEIGHT
1	22135.069	176.138	15.2
2	21352.567	169.911	16.9
3	21324.028	169.684	16.2
4	9861.295	78.470	35.8
5	9712.619	77.287	103.8
6	9680.399	77.031	107.5
7	9648.638	76.778	106.0
8	9301.576	74.017	29.7
9	9243.578	73.555	33.1
10	8873.961	70.614	31.0
11	8846.344	70.394	27.4
12	8618.037	68.577	33.9
13	7628.402	60.702	32.8
14	5997.576	47.725	24.9
15	3457.206	27.510	126.0
16	3445.239	27.415	123.6
17	3399.209	27.049	30.4
18	2949.040	23.467	24.4
19	2811.412	22.372	35.3
20	2700.941	21.493	36.3
21	2658.594	21.156	41.2
22	2655.372	21.130	37.0
23	2610.723	20.775	20.0
24	1773.906	14.116	36.0




t-Bu2Si
O
O
O
OH
1
2
3
4
5
6
7
8
9
10
11

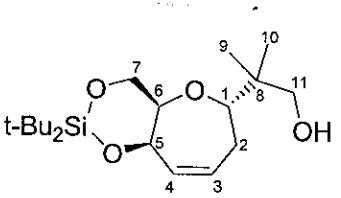
3.13


9
8
7
6
5
4
3
2
1
ppm
5.37
2.73
5.54
5.52
2.92
3.04
2.06
3.06
3.45
8.82
48.54
8.95

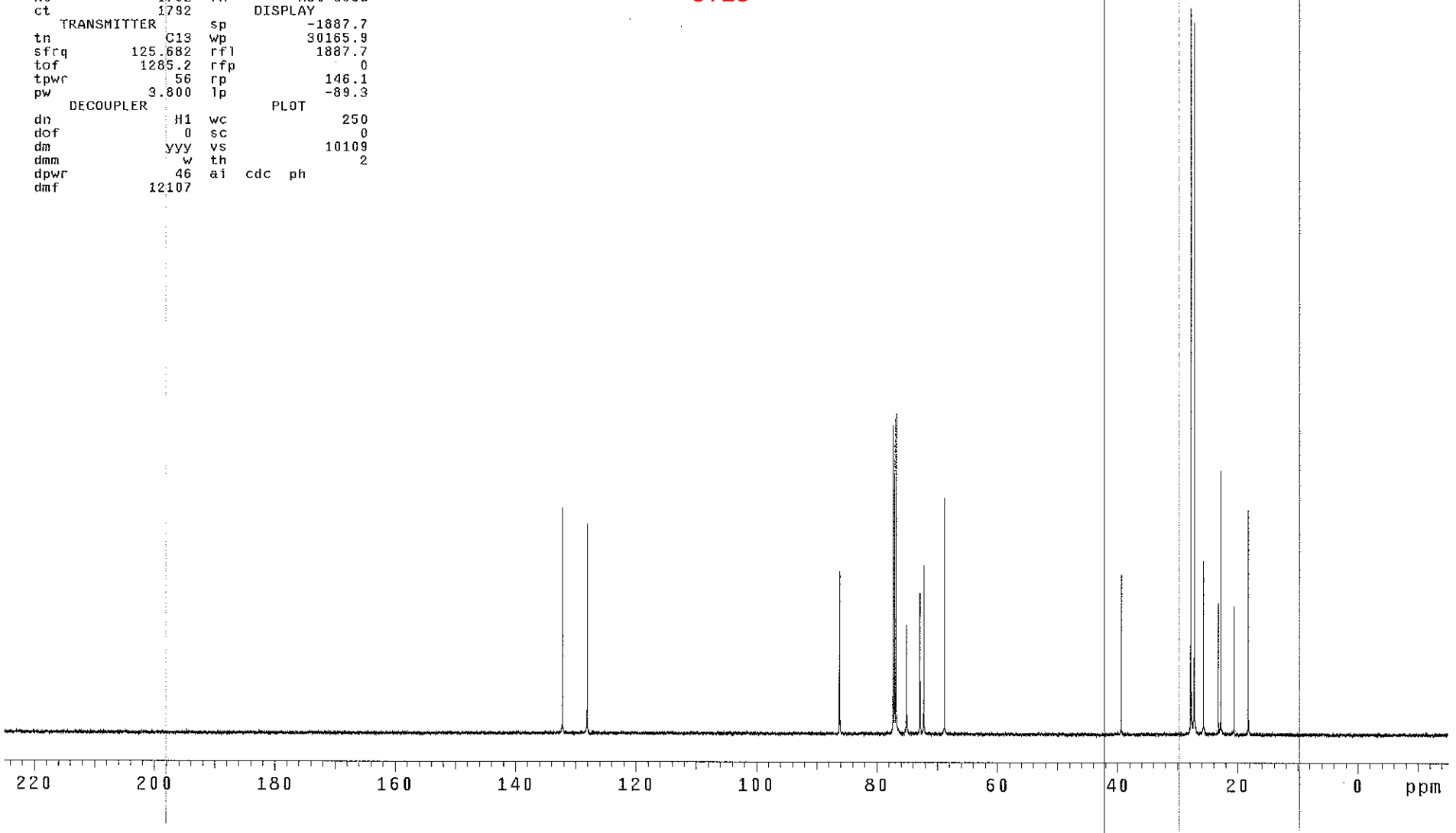
RB070506b

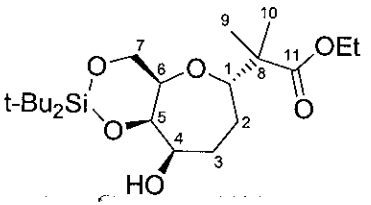
exp2 Carbon

SAMPLE		SPECIAL	
date	Jul 6 2006	temp	not used
solvent	cdcl3	gain	30
file	/export/home/~	spin	20
everyone/Rhys/RB07~		hst	0.008
0506bCarboncdcl350~		pw90	7.600
	0	alfa	10.000
ACQUISITION		FLAGS	
sw	30165.9	il	n
at	2.000	in	n
np	120664	dp	y
fb	not used	hs	nn
bs	64	PROCESSING	
d1	0	lb	1.00
nt	1792	fn	not used
ct	1792	DISPLAY	
TRANSMITTER		sp	-1887.7
tn	C13	wp	30165.9
sfrq	125.682	rfl	1887.7
tof	1285.2	rfp	0
tpwr	56	rp	146.1
pw	3.800	lp	-89.3
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	10109
dmm	w	th	2
dpwr	46	ai cdc ph	
dmf	12107		



3.13




t-Bu2Si
O
O
O
O
HO
OEt
1
2
3
4
5
6
7
8
9
10
11

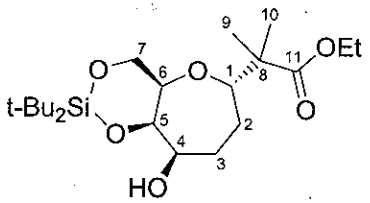
3.11

9
8
7
6
5
4
3
2
1
ppm
19.63
10.44
2.98
22.86
44.09

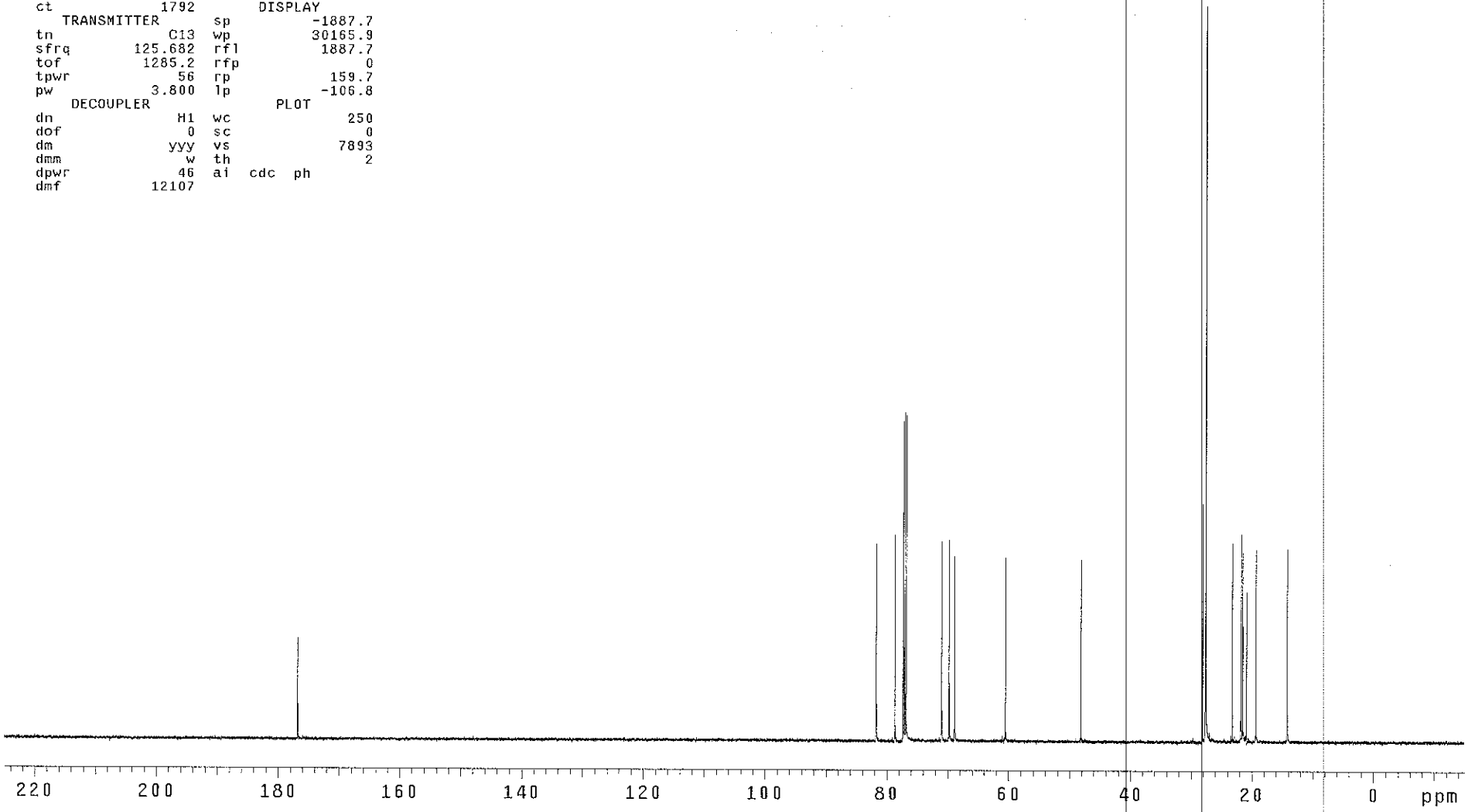
RB070806b

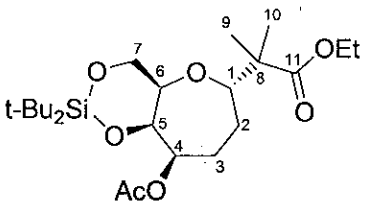
exp2 Carbon

SAMPLE		SPECIAL	
date	Jul 10 2006	temp	not used
solvent	cdcl3	gain	30
file	/export/home/~	spin	20
everyone/Rhys/RB07~		hst	0.008
0806bCarboncdcl350~		pw90	7.600
	0	alfa	10.000
ACQUISITION		FLAGS	
sw	30165.9	il	n
at	2.000	in	n
np	120664	dp	y
fb	not used	hs	nn
bs	64	PROCESSING	
d1	0	lb	1.00
nt	1792	fn	not used
ct	1792	DISPLAY	
TRANSMITTER		sp	-1887.7
tn	C13	wp	30165.9
sfrq	125.682	rfl	1887.7
tof	1285.2	rfp	0
tpwr	56	rp	159.7
pw	3.800	lp	-106.8
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	7893
dmm	w	th	2
dpwr	46	ai cdc ph	
dmf	12107		



3.11




t-Bu2Si
AcO
OEt
O
1
2
3
4
5
6
7
8
9
10
11

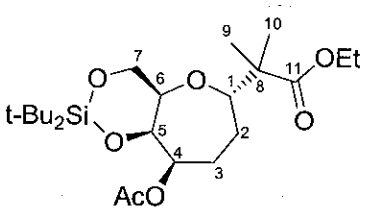
3.12

9
8
7
6
5
4
3
2
1
ppm
2.52
11.82
5.22
6.98
7.15
2.62
21.20
42.49

Rb071006a

exp2 Carbon

SAMPLE		SPECIAL	
date	Jul 11 2006	temp	not used
solvent	cdcl3	gain	30
file	/export/home/~	spin	20
everyone/Rhys/RB07~		hst	0.008
1006aCarboncdcl350~		pw90	7.600
	0	alfa	10.000
ACQUISITION		FLAGS	
sw	30165.9	il	n
at	2.000	in	n
np	120664	dp	y
fb	not used	hs	nn
bs	64	PROCESSING	
d1	0	lb	1.00
nt	1792	fn	not used
ct	1792	DISPLAY	
TRANSMITTER		sp	-1887.7
tn	C13	wp	30165.9
sfrq	125.682	rfl	1887.7
tof	1285.2	rfp	0
tpwr	56	rp	-161.1
pw	3.800	lp	-217.2
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	19445
dmm	w	th	4
dpwr	46	ai	cdc ph
dmf	12107		

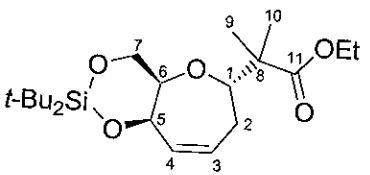


3.12

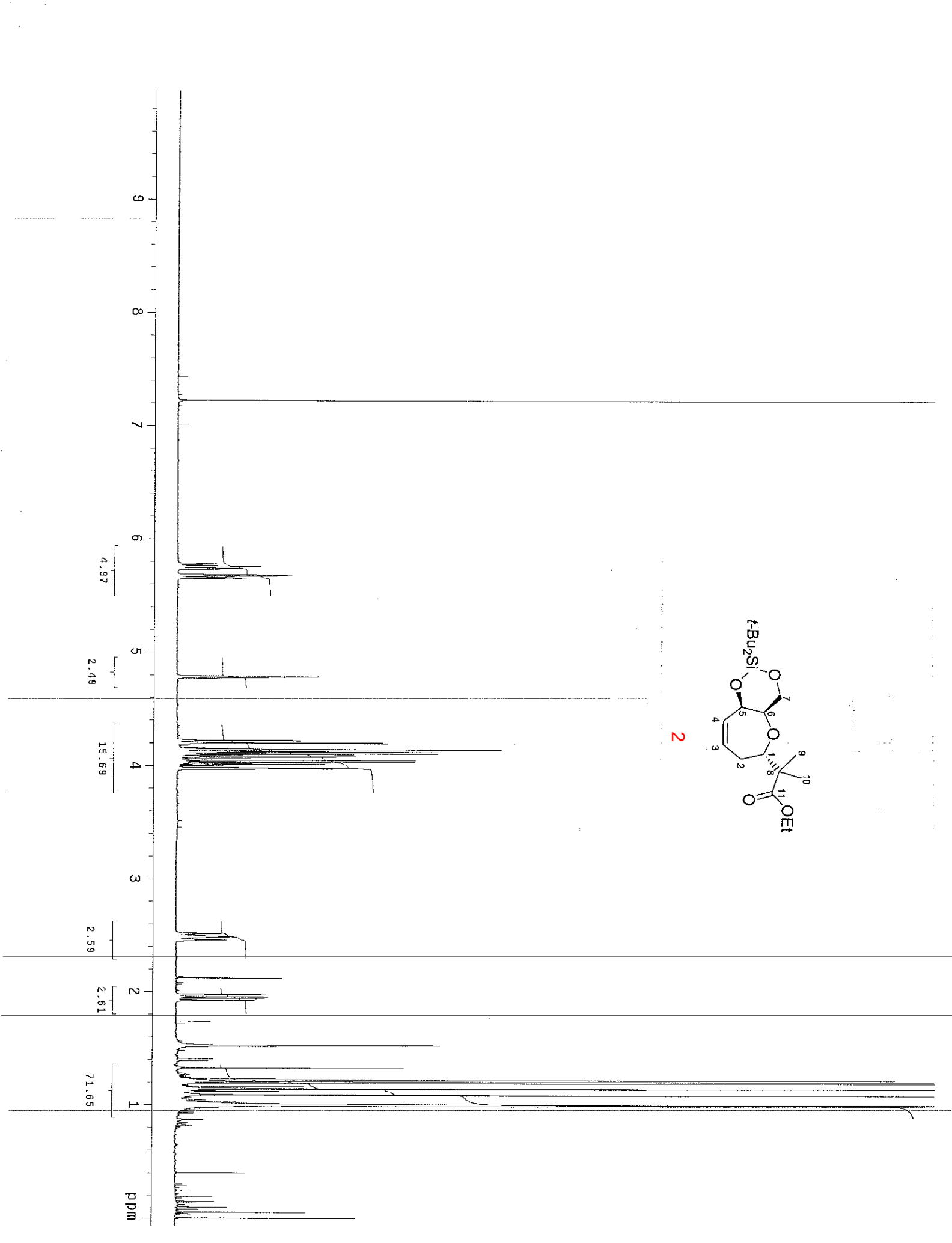
RB061206a

exp2 Carbon

SAMPLE		SPECIAL	
date	Jun 12 2006	temp	not used
solvent	cdcl3	gain	30
file	/export/home/~	spin	20
	everyone/Rhys/RB06~	hst	0.008
	1206aCarboncdcl350~	pw90	7.600
	0	alfa	10.000
ACQUISITION		**FLAGS**	
sw	30165.9	il	n
at	2.000	in	n
np	120664	dp	y
fb	not used	hs	nn
bs	64	**PROCESSING**	
d1	0	lb	1.00
nt	1792	fn	not used
ct	1792	**DISPLAY**	
TRANSMITTER		sp	-1891.4
tn	C13	wp	30165.9
sfrq	125.682	rfl	1891.4
tof	1285.2	rfp	0
tpwr	56	rp	50.4
pw	3.800	lp	-60.6
DECOUPLER		**PLOT**	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	43295
dmm	w	th	6
dpwr	46	ai cdc ph	
dmf	12107		



2


9
8
7
6
5
4
3
2
1
ppm
4.97
2.49
15.69
2.59
2.61
71.65
t-Bu2Si
O
O
O
O
OEt
1
2
3
4
5
6
7
8
9
10
11