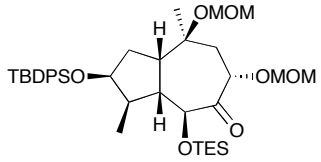
Design and Total Synthesis of Unnatural Analogues of the Sub-Nanomolar SERCA Inhibitor, Thapsigargin

Stephen P. Andrews, Malcolm M. Tait, Matthew Ball, and Steven V. Ley*

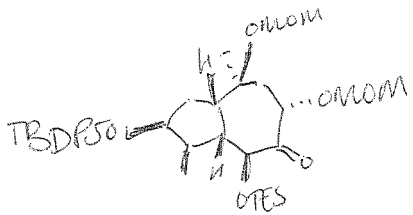
Supplementary Information

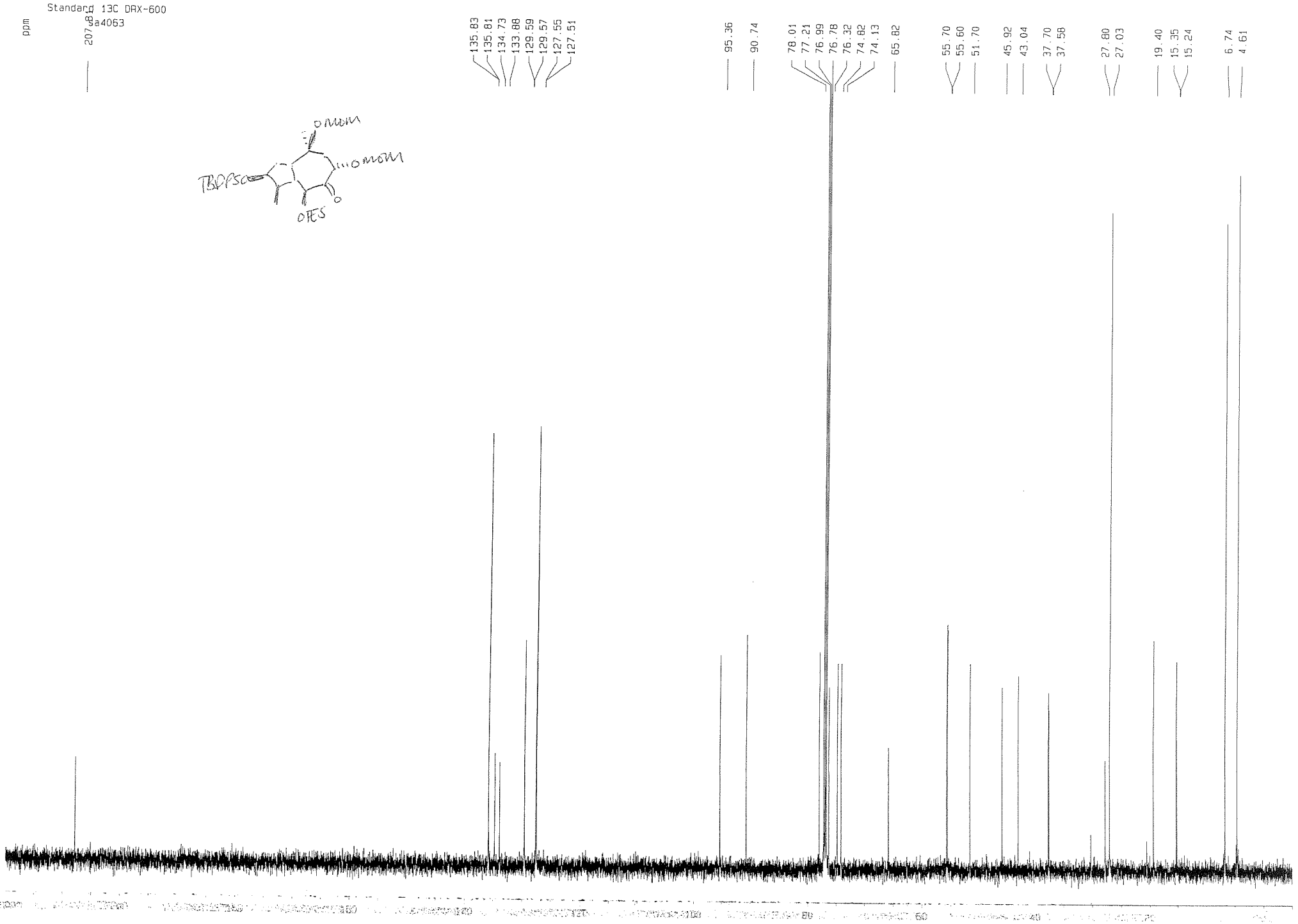


13

MOM acetal 13: A solution of hydroxy ketone **12** (605 mg, 944 μmol) was treated with Hünig's base (1.64 mL, 9.44 mmol), DMAP (11 mg, 94 μmol) and then MOM-Cl (480 μL, 6.32 mmol) and stirred at room temperature for 16 hours. The reaction was quenched with saturated ammonium chloride solution (50 mL), diluted with H_2O (30 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine (100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The pale yellow oil was used without further purification, 746 mg; δ_H (600 MHz; $CDCl_3$) 7.67 (4H, m, *o*-Ph), 7.43 (2H, m, *p*-Ph), 7.37 (4H, m, *m*-Ph), 4.72 (1H, d, *J* 7.4, O-10-CH_2O), 4.66 (1H, d, *J* 7.4, O-8-10-CH_2O), 4.62 (1H, d, *J* 6.7, O-8-CH_2O), 4.55-4.52 (2H, m, H-8 and O-8-CH_2O), 4.25 (1H, m, H-3), 4.17 (1H, d, *J* 7.6, H-6), 3.34 (6H, s, 2 × OCH_3), 2.90 (1H, ddd, *J* 11.9, 7.8, 7.7, H-1), 2.13 (2H, m, H-4 and H-9), 1.95 (1H, dd, *J* 13.9, 7.6, H-5), 1.68 (1H, dd, *J* 14.3, 10.1, H-9'), 1.49 (1H, ddd, *J* 11.5, 7.2, 1.0, H-2), 1.31 (1H, ddd, *J* 12.8, 12.6, 5.2, H-2'), 1.14 (3H, d, *J* 7.1, H-15), 1.12 (3H, s, H-14), 1.08 (9H, s, $C(CH_3)_3$), 0.93 (9H, t, *J* 8.0, $Si(CH_2C\underline{H}_3)_3$), 0.56 (6H, m, $Si(CH_2)_3$); δ_C (150 MHz; $CDCl_3$) 207.8 (C-7), 135.83 (*o*-Ph), 135.81 (*o*-Ph), 134.7 (*ipso*-Ph), 133.8 (*ipso*-Ph), 129.59 (*p*-Ph), 129.57 (*p*-Ph), 127.6 (*m*-Ph), 127.5 (*m*-Ph), 95.3 (O-8-CH_2O), 90.7 (O-10-CH_2O), 78.0 (C-10), 76.3 (C-6), 74.8 (C-8), 74.1 (C-3), 55.7 and 55.6 (2 × OCH_3), 51.7 (C-5), 45.9 (C-1), 43.0 (C-4), 37.7 (C-2), 37.6 (C-9), 27.8 (C–14), 27.0 ($C(\underline{C}H_3)_3$), 19.4 ($\underline{C}(CH_3)_3$), 15.3 (C-15), 6.7 ($Si(CH_2\underline{C}H_3)_3$), 4.6 ($Si(CH_2)_3$); ν_{max} (film; cm^{-1}) 2955 (C-H), 2933 (C-H), 2879 (C-H), 1727 (C=O), 1590 (Ar), 1541 (Ar); $[\alpha]_D$ +7.70 (*c*. 1.0, $CHCl_3$); found (ESI+) $[MNa]^+$ 707.3803; $C_{38}H_{60}O_7Si_2Na$ requires *M,* 707.3775.

sa4063
Standard 1H DRX-600

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76.99
76.78
76.32
74.82
74.13
65.82
55.70
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45.92
43.04
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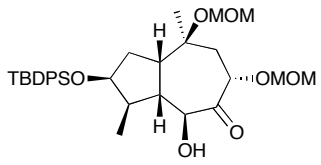
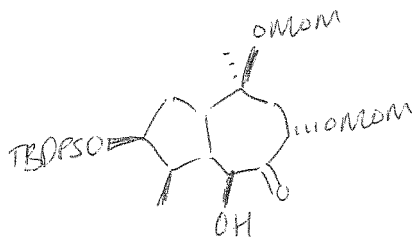
TBDPSO
OMOM
OTES



14

Alcohol 14: A stock solution of HF.pyridine (3.5 mL) and pyridine (2.6 mL) in THF (6.0 mL) was added to a stirring solution of crude triethylsilylether **13** (87% by mass from previous step, assume 822 μmol) in pyridine (6.0 mL) and THF (10 mL). The resulting mixture was stirred at room temperature for 25 minutes then quenched by drop-wise addition of saturated sodium bicarbonate solution (250 mL) and extracted with Et_2O (3 × 100 mL). The combined organic phases were washed with saturated ammonium chloride solution (100 mL) and brine (100 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography (SiO_2, Et_2O/petrol ether, 1:4 then 2:3) afforded the hydroxy ketone as a colourless oil, 449 mg, 96% over two steps; δ_H (600 MHz; $CDCl_3$) 7.66 (4H, m, *o*–Ph), 7.43 (2H, m, *p*-Ph), 7.37 (4H, m, *m*–Ph), 5.05 (1H, d, *J* 10.6, OH), 4.98 (1H, dd, *J* 11.1, 6.5, H-8), 4.86 (2H, s, O-10-CH_2O), 4.62 (1H, d, *J* 6.9, O-8-CH_2O), 4.59 (1H, d, *J* 6.9, O-8-CH_2O), 4.19 (1H, m, H-3), 4.03 (1H, dd, *J* 10.6, 5.0, H-6), 3.47 (3H, s, O-10-$CH_2OC\underline{H}_3$), 3.36 (3H, s, O-8-$CH_2OC\underline{H}_3$), 2.95 (1H, m, H-1), 2.22 (1H, m, H-5), 2.11 (1H, dd, *J* 14.4, 6.5, H-9), 1.93 (1H, m, H-4), 1.58 (1H, dd, *J* 14.4, 11.1, H-9'), 1.39 (1H, dd, *J* 12.7, 6.6, H-2), 1.15 (3H, s, H-14), 1.13 (3H, d, *J* 6.8, H-15), 1.09 (9H, s, $C(CH_3)_3$), 1.09 (1H, m, H–2'); δ_C (150 MHz; $CDCl_3$) 210.6 (C-7), 135.8 (*o*-Ph), 135.7 (*o*-Ph), 134.8 (*ipso*-Ph), 133.7 (*ipso*-Ph), 129.7 (*p*-Ph), 127.6 (*m*-Ph), 127.5 (*m*-Ph), 95.7 (O-8-CH_2O), 91.0 (O-10-CH_2O), 79.9 (C-10), 77.2 (C-6), 74.9 (C-3), 73.5 (C-8), 56.3 (O-10-$CH_2O\underline{C}H_3$), 55.7 (O-8-$CH_2O\underline{C}H_3$), 49.9 (C-5), 47.6 (C-1), 43.0 (C-4), 38.1 (C-2), 37.3 (C-9), 27.3 (C-14), 27.0 ($C(\underline{C}H_3)_3$), 19.4 ($\underline{C}(CH)_3$), 14.5 (C-15); ν_{max} (film; cm^{-1}) 3424 (br OH), 2931 (C-H), 2858 (C-H), 1721 (C=O), 1590 (w Ar); $[\alpha]_D$ +19.0 (*c*. 0.675, $CHCl_3$); found (ESI+) $[MNa]^+$ 593.2919; $C_{32}H_{46}O_7SiNa$ requires *M,* 593.2911.

sa4064, Standard 1H DRX-600



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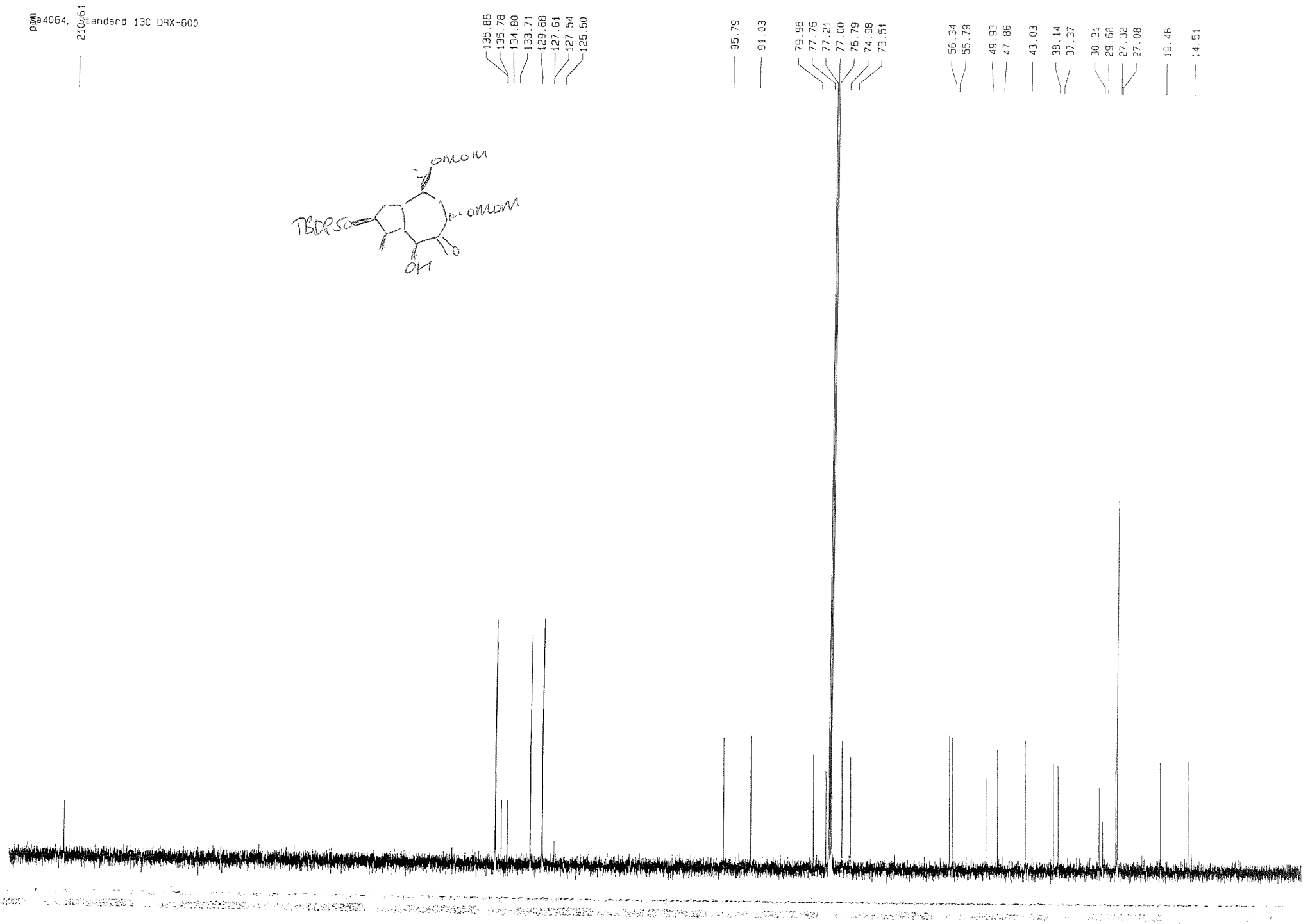
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76.79
74.98
73.51
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43.03
38.14
37.37
30.31
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27.08
19.48
14.51
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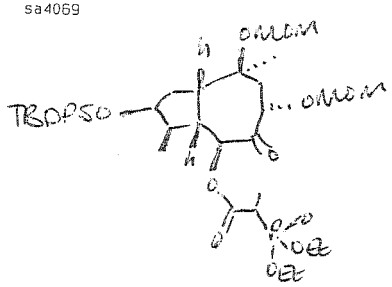
TBDPSO
OMOM
O
OH

Standard 1H DRX-600
sa4069



Standard 13C DRX-600
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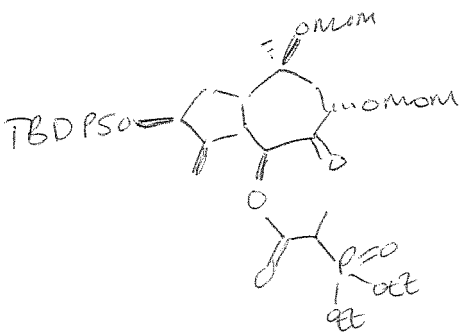
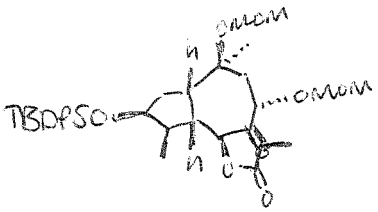


Standard 1H DRX-600

Sa4071



ppm Standard 13C DRX-600

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126.21
94.79
90.60
82.61
77.33
77.21
77.00
76.79
73.33
66.94
55.83
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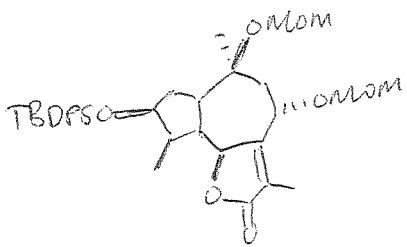

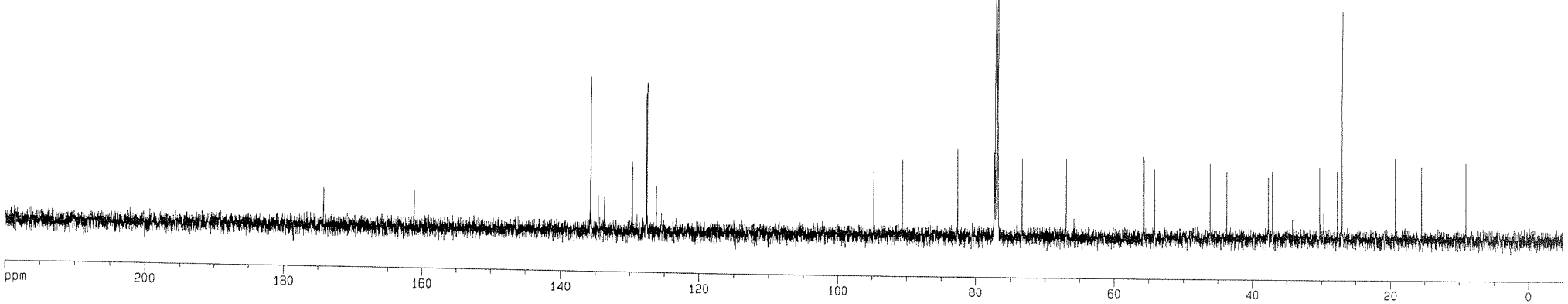

sa4090, cdcl3
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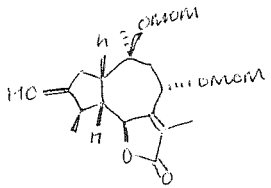

Standard 13C DRX-600
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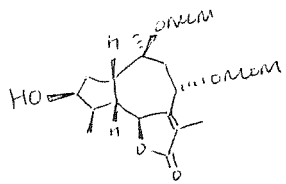

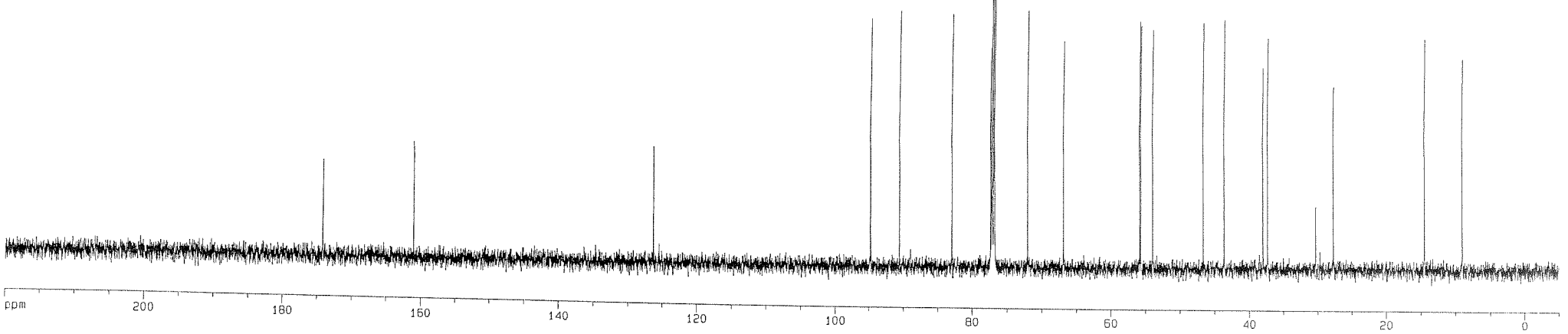

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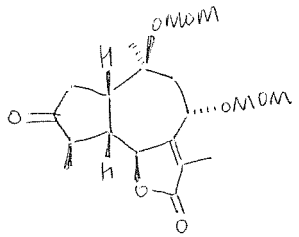

Standard 13C DRX-600
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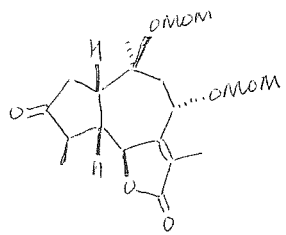

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56.01
55.96
51.69
48.49
45.18
39.47
37.17
30.32
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1.01

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Standard 1H Qtx-600
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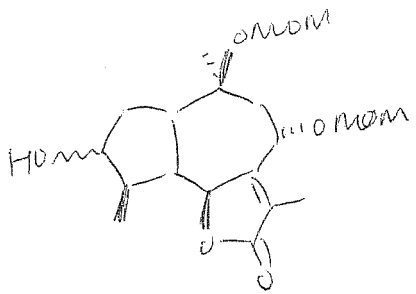

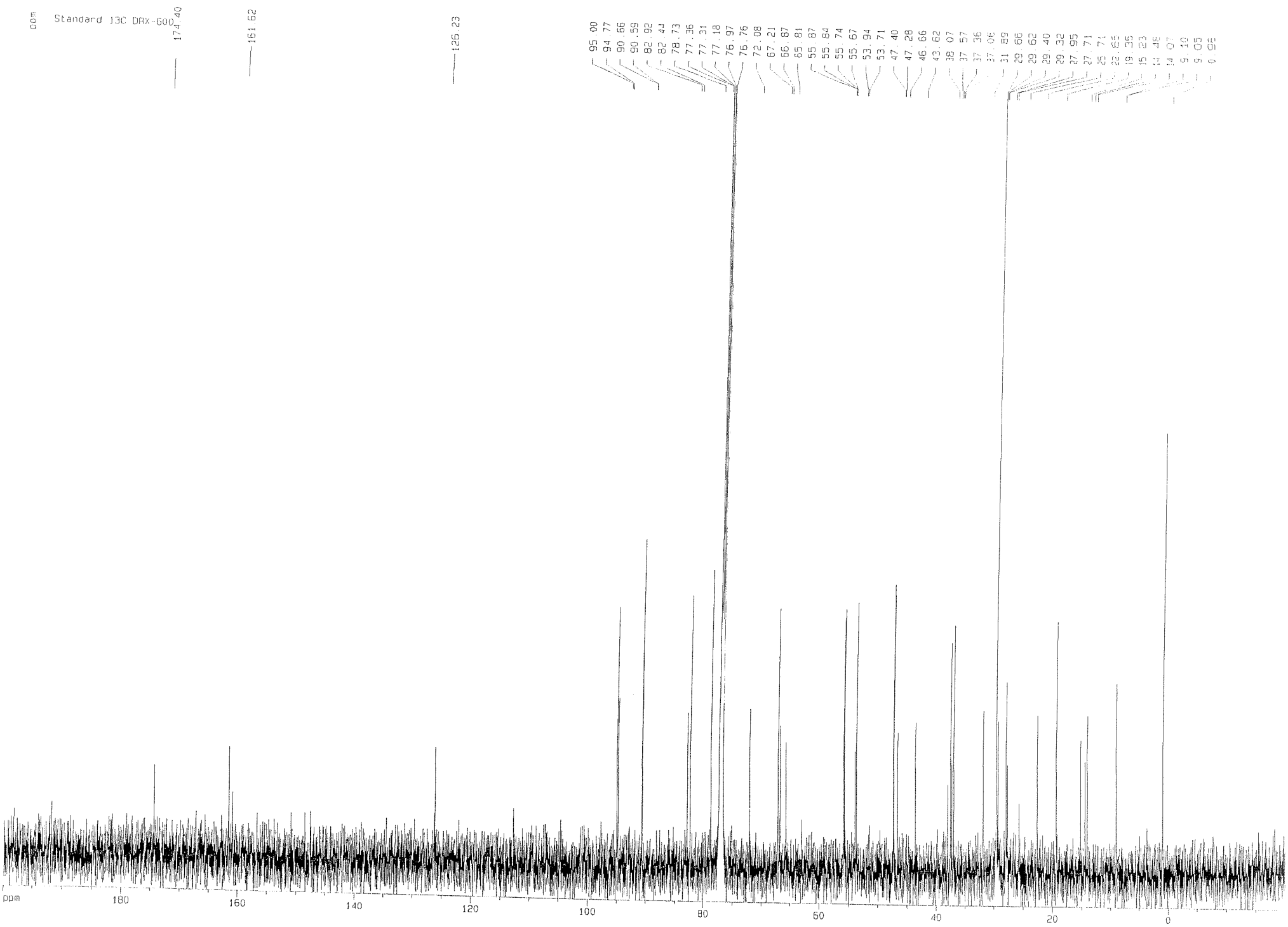
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19.35
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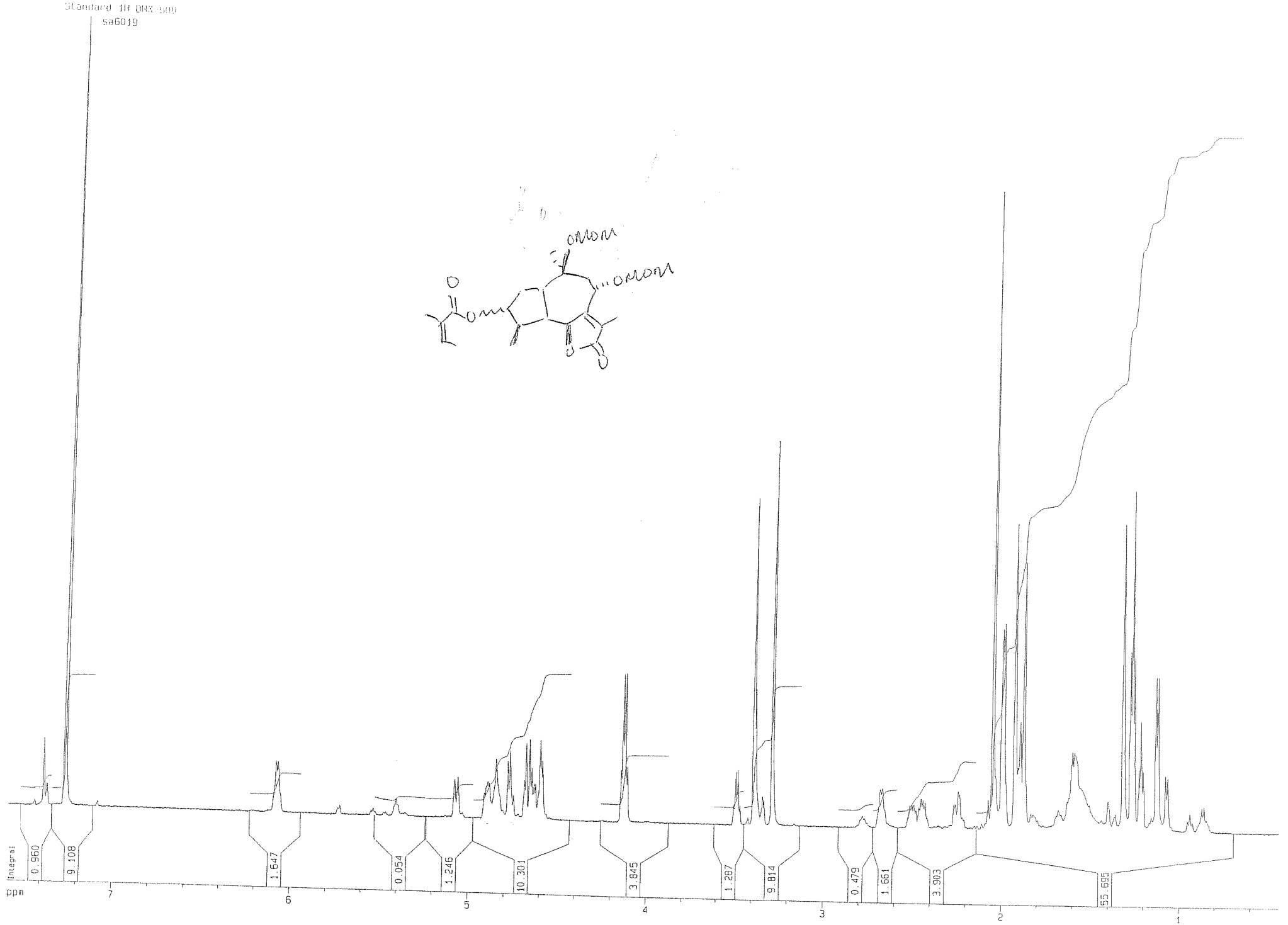
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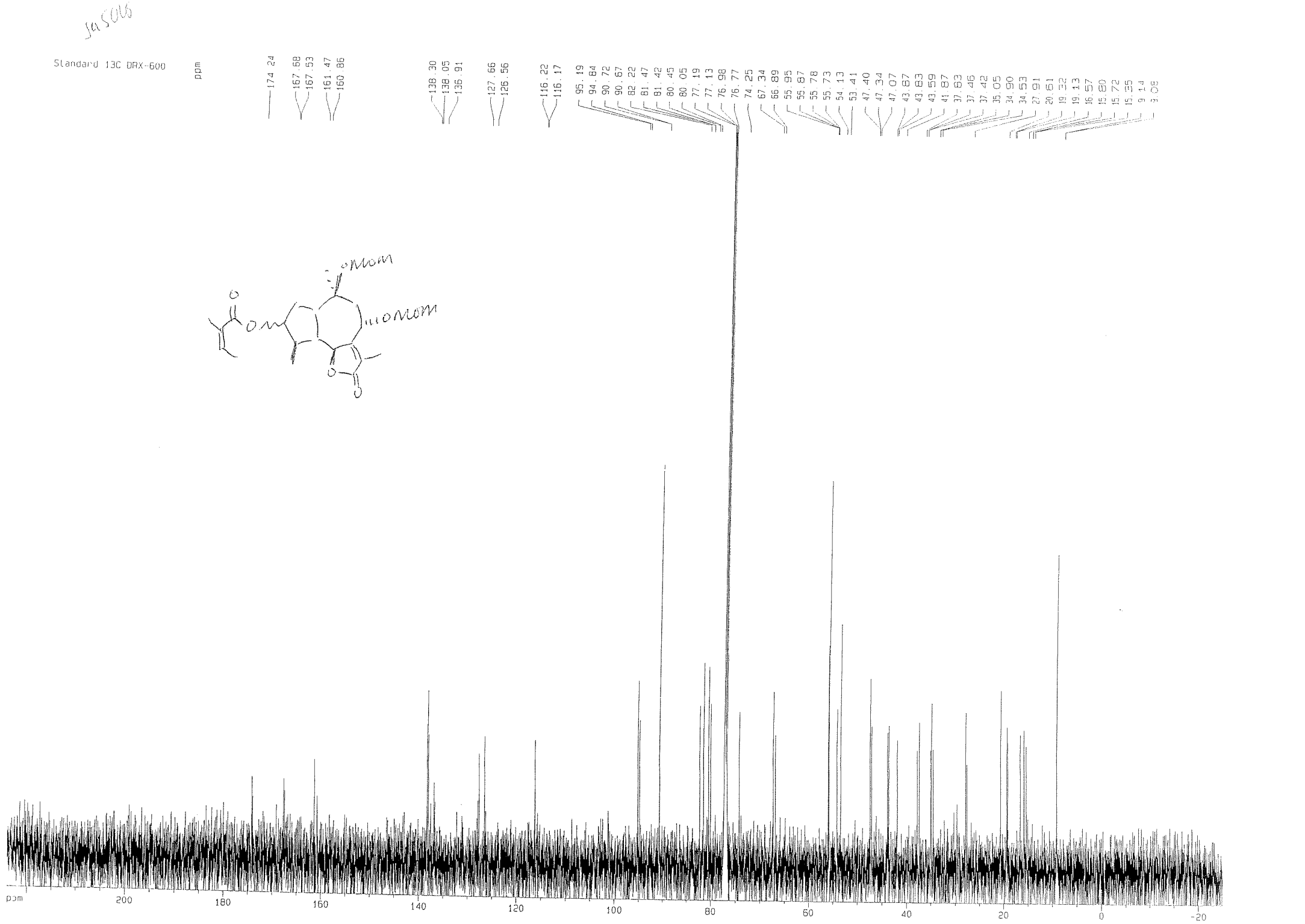
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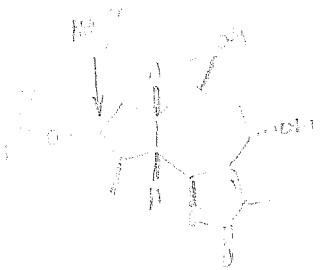

Standard 13C DRX-600
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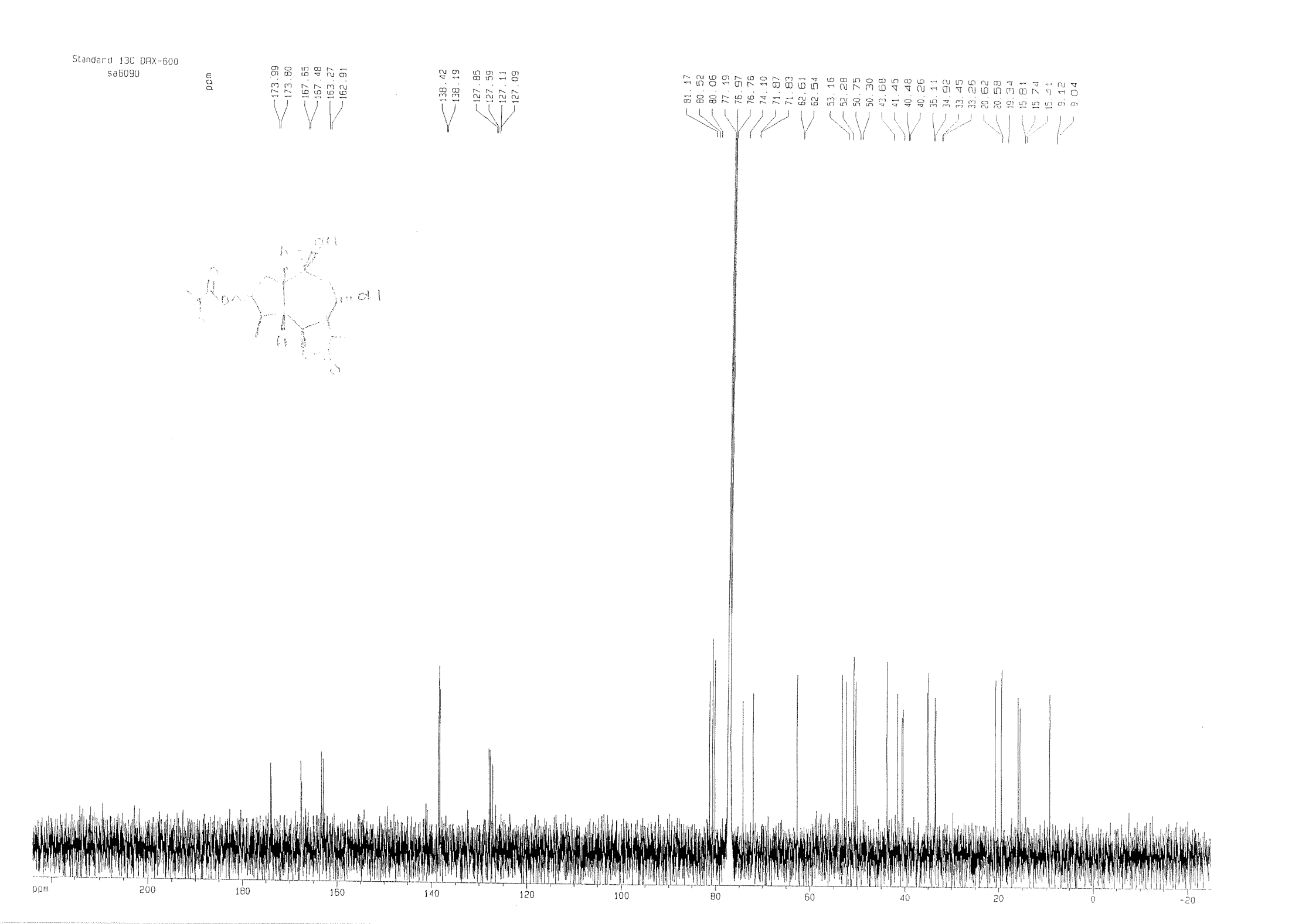

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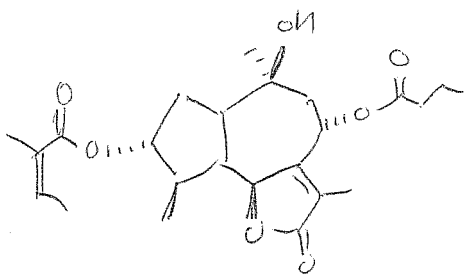

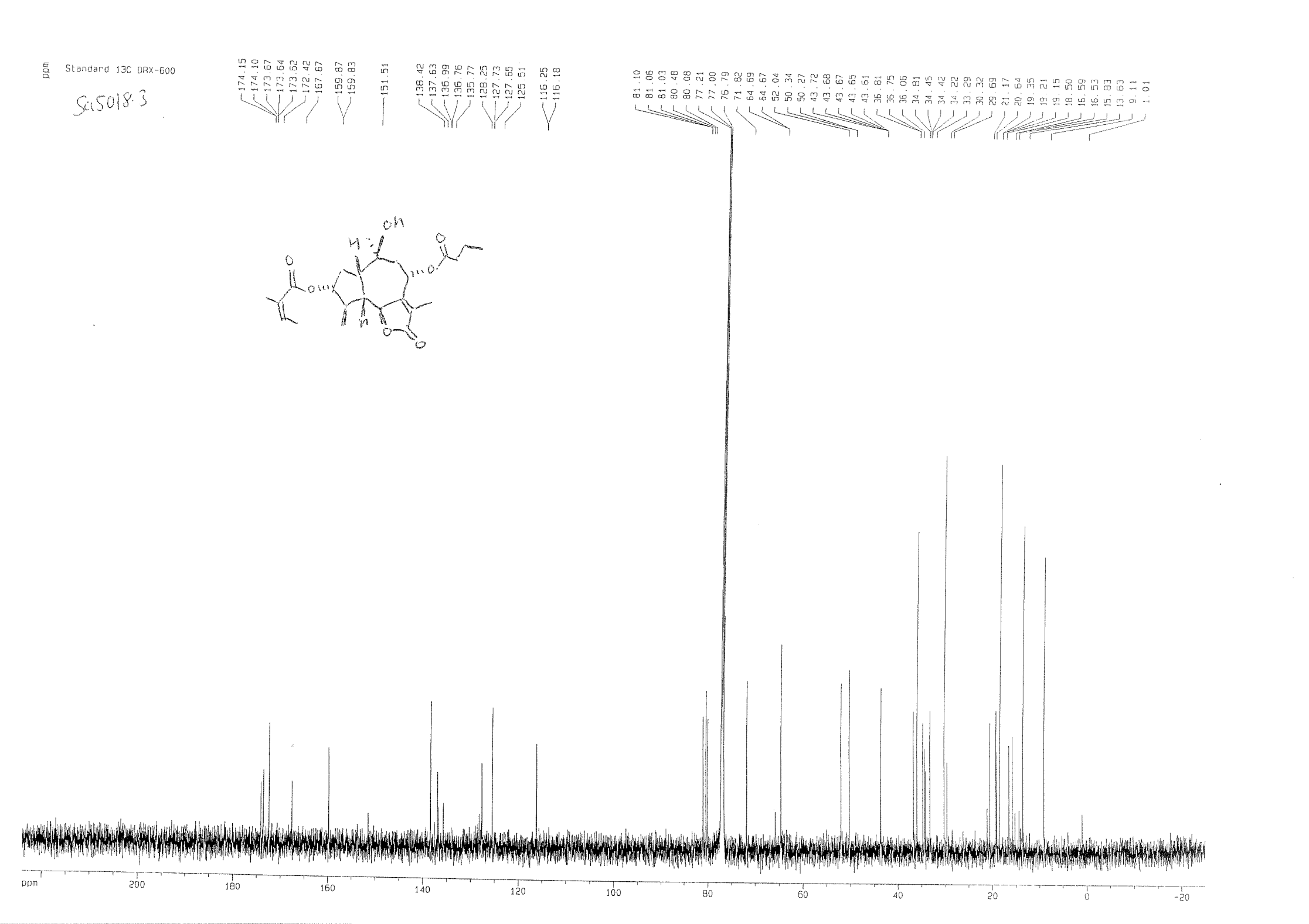
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135.77
128.25
127.73
127.65
125.51
116.25
116.18
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81.03
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80.08
77.21
77.00
76.79
71.82
64.69
64.67
52.04
50.34
50.27
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43.67
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43.61
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36.06
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34.45
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19.35
19.21
19.15
18.50
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16.53
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13.63
9.11
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OH
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O
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ppm
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-20

Standard 1H (25-Jun
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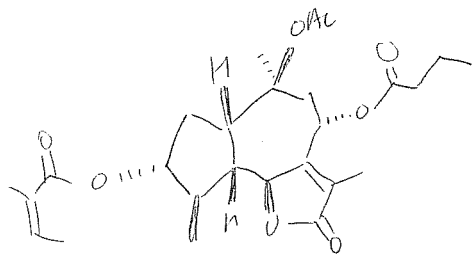

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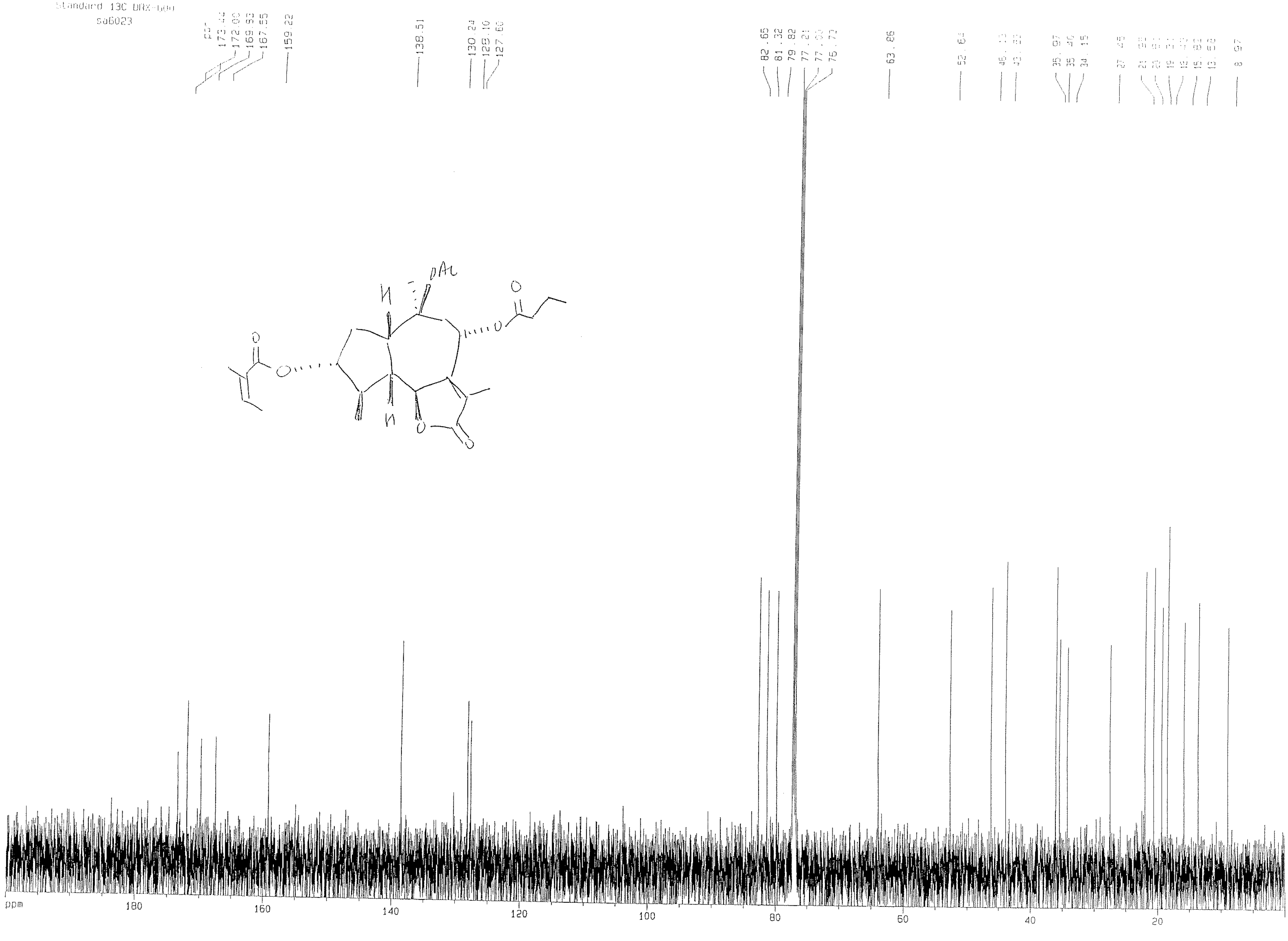
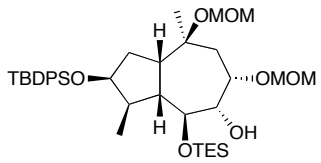
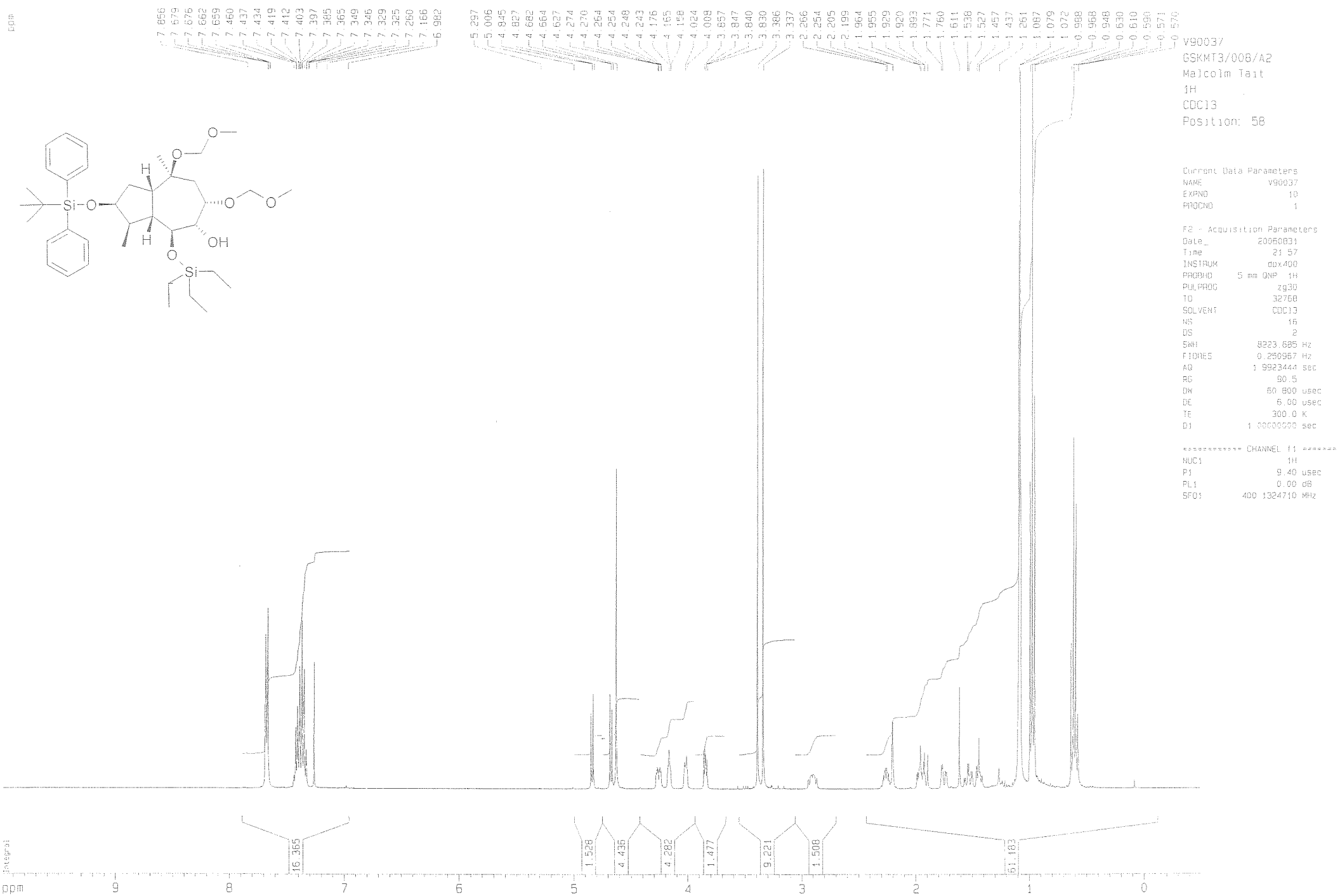




23

Alcohol 23: Sodium borohydride (17.0 mg, 0.446 mmol) was added in 2 batches to a solution of ketone **13** (30.6 mg, 0.045 mmol) in THF (0.1 mL) at 0 °C. After stirring for 3.5 hours at this temperature and addition of a further 17 mg sodium borohydride (0.446 mmol) the reaction was incomplete by TLC analysis. The suspension was therefore quenched at 0 °C with aqueous ammonium chloride (3 mL), warmed to room temperature over 30 minutes, diluted with water (3 mL) and extracted with Et_2O (4 × 5 mL). The combined organics were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was flushed through a short pad of silica with Et_2O and the resulting oil was dissolved in THF (0.1 mL) at 0 °C and re-treated with sodium borohydride (17 mg, 0.446 mmol). After stirring for 2 hours at this temperature the reaction was complete so the mixture was quenched and worked-up in the same way as previously. The residue obtained was purified by flash chromatography (SiO_2, Et_2O/petrol ether, 1:10 then 1:4) to yield the title compound as a clear oil, 27.8 mg, 91%, *S:R* ratio >19:1; δ_H (400 MHz; $CDCl_3$) 7.68 – 7.66 (4H, m, *o*-Ph), 7.44 – 7.33 (6H, m, *m*-Ph, *p*-Ph), 4.84 (1H, d, *J* 7.3, O-10-CH_2O), 4.67 (1H, d, *J* 7.3, O-10-CH_2O), 4.64 (1H, d, *J* 6.6, O-8-CH_2O), 4.62 (1H, d, *J* 6.6, O-8-CH_2O), 4.26 (1H, ddd, *J* 2.4, 4.2, 10.5, H-8), 4.17 – 4.16 (1H, m (br), H-3), 4.02, (1H, d (br), *J* 6.5, H-7), 3.84 (1H, dd, *J* 4.1, 6.6, H-6), 3.39 (3H, s, O-10-$CH_2OC\underline{H}_3$), 3.34 (3H, s, O-8-$CH_2OC\underline{H}_3$), 2.94 – 2.87 (1H, m, H-1), 2.30 – 2.24 (1H, m, H-4), 2.20 (1H, d, *J* 2.2, OH), 1.98 – 1.92 (1H, m, H-5), 1.92 (1H, dd, *J* 10.6, 14.2, H-9), 1.75 (1H, dd, *J* 4.3, 14.2, H-9'), 1.53 (1H, ddd, *J* 4.2, 12.6, 12.6, H-2), 1.46 – 1.41 (1H, m, H-2'), 1.09 – 1.07 (15H, m, H-11, H-12, $C(CH_3)_3$), 0.97 (9H, t, *J* 8.0, $SiCH_2C\underline{H}_3$), 0.60 (6H, q, *J* 8.0, $SiC\underline{H}_2CH_3$) [selected NOE contacts: H-7 to H-5, 2.9%; H-7 to H-6, 6.2%; H-7 to H-8, 8.7% enhancement]; δ_C (100 MHz; $CDCl_3$) 135.9 (*o*-Ph), 135.9 (*o*-Ph), 135.0 (*ipso*-Ph), 134.3 (*ipso*-Ph), 129.4 (*p*-Ph), 127.5 (*m*-Ph), 127.4 (*m*-Ph), 95.6 (O-8-CH_2O), 91.0 (O-10-CH_2O), 77.7 (C-10), 76.8 (C-7), 75.0 (C-3), 73.6 (C-8), 72.1 (C-6), 55.4, 55.3 (O-10-$CH_2O\underline{C}H_3$ and O-8-$CH_2O\underline{C}H_3$), 51.9 (C-5), 45.6 (C-1), 44.2 (C-4), 38.6 (C-2), 36.8 (C-9), 29.3 (C-11), 27.1 ($C(\underline{C}H_3)_3$), 19.5 ($\underline{C}(CH_3)_3$), 15.5 (C-12), 6.9 ($SiCH_2\underline{C}H_3$), 4.9 ($Si\underline{C}H_2CH_3$); υ_{max} (film; cm^{-1}) 3462w (br), 2952m, 2931m, 2877m, 2325w, 1730w, 1461m, 1428m, 1372m, 1292w, 1239m, 1191m, 1148m, 1128m, 1103s, 1076s, 1039s, 968m, 917m, 878w, 824m, 740m, 701s; $[\alpha]_D$ +16.2 (*c*. 0.34, $CHCl_3$); found (ESI+) $[MNa]^+$ 709.3951; $C_{38}H_{62}O_7NaSi_2$ requires *M*, 709.3932.


V90037/
GSKMT3/008/A2
Malcolm Tait
1H
CDCl3
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EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060831
Time 21.57
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PROBHD 5 mm QNP 1H
PULPROG zg30
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SOLVENT CDCl3
NS 16
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SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 90.5
DW 60.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
ppm
Integral
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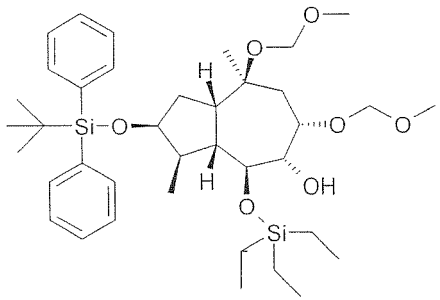
9.221
1.508
51.163

V90037
GSKMT3/008/A2
Malcolm Tait
13C
CDCl3
Position: 58



ppm

135.9 135.9 135.0 134.3 129.4 127.5 127.4 95.6 91.0 77.7 77.3 77.0 76.9 76.7 75.0 73.6 72.1 55.4 55.3 51.9 45.6 44.2 38.6 36.8 29.3 27.1 19.5 15.5 6.9 4.9

Current Data Parameters

NAME	V90037
EXPNO	12
PROCNO	1

F2 - Acquisition Parameters

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Time	23.17
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FIDRES	0.399445 Hz
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RG	574.7
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TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec

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PL1	-2.00 dB
SFO1	100.6248025 MHz

========== CHANNEL f2 ========

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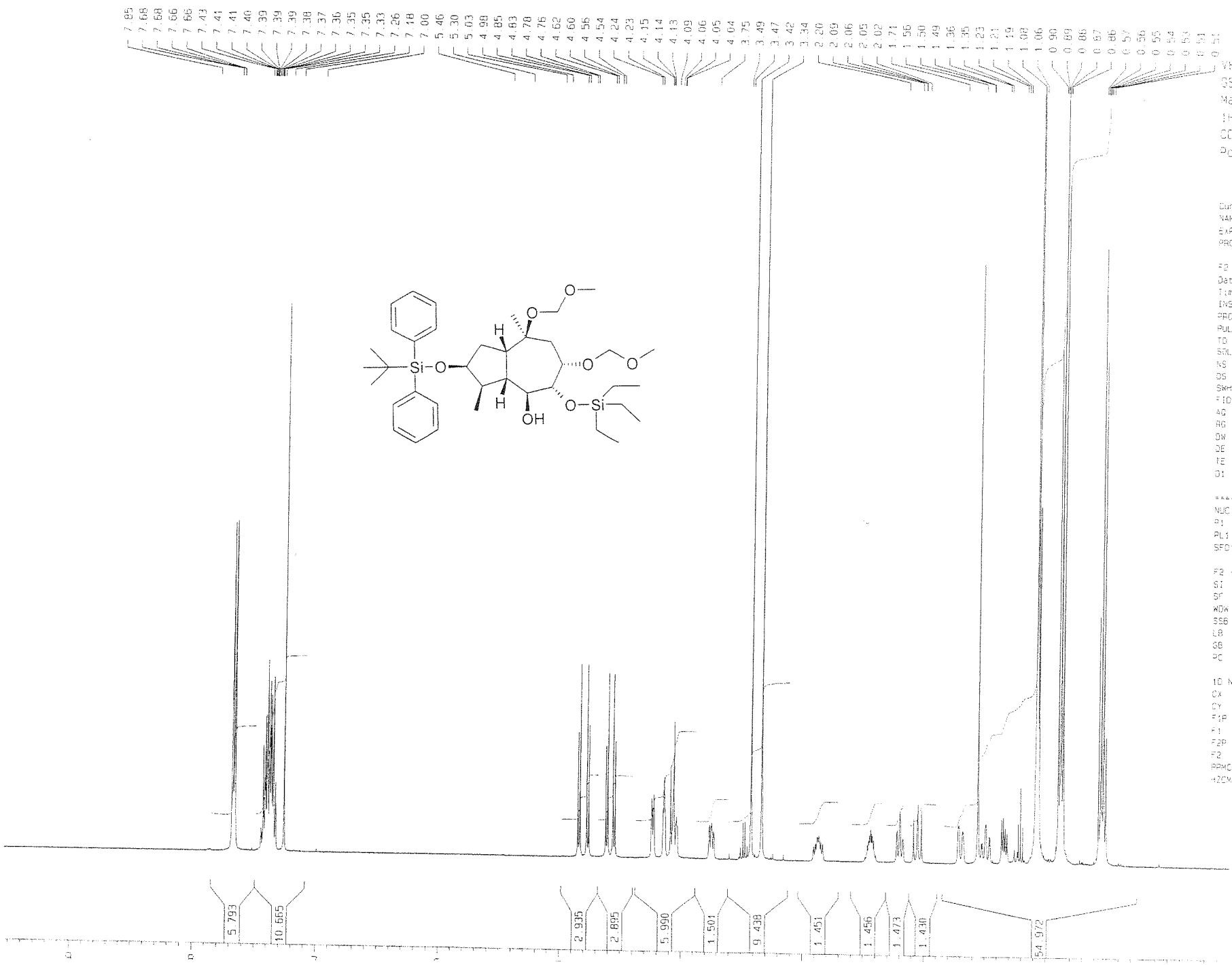
PCPD2	110.00 usec
PL2	0.00 dB
PL12	21.00 dB
SFO2	400.1320007 MHz


VB6471
GSKMT2/051/A3
Malcolm Tait,
1H
CDCl3
Position: 51
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EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
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Time 18.21
INSTRUM dpx400
PROBHD 5 mm GNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 362
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DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
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GB 0
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CY -1.00 cm
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F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
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HZCM 120.03900 Hz/cm
7.85 7.68 7.68 7.66 7.66 7.43 7.41 7.41 7.40 7.39 7.39 7.39 7.38 7.37 7.36 7.35 7.35 7.33 7.26 7.18 7.00
5.46 5.30 5.03 4.98 4.85 4.83 4.78 4.76 4.62 4.60 4.56 4.54 4.24 4.23 4.15 4.14 4.13 4.09 4.06 4.05 4.04 3.75 3.49 3.47 3.42 3.34
2.20 2.09 2.06 2.05 2.02 1.71 1.56 1.50 1.49 1.36 1.35 1.23 1.21 1.19 1.08 1.06 0.90 0.89 0.86 0.87 0.86 0.57 0.56 0.55 0.54 0.53 0.51
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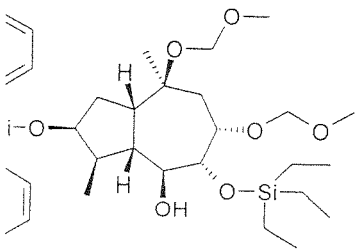

V8547.1
OSKMT2/051/A3
Malcolm Tait
13C
CDCl3
Position: 51

Current Data Parameters
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EXPNO 12
PROCNO 1

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Time 19.40
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TD 65536
SOLVENT CDCl3
NS 1536
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 2580.3
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec

========== CHANNEL f1 ==========
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P1 9.30 usec
PL1 -2.00 dB
SFO1 100.6248025 MHz

========== CHANNEL f2 ==========
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NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 400.1320007 MHz

F2 - Processing parameters
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SF 100.6127697 MHz
WDW EM
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GB 0
PC 1.40

1D NMR plot parameters
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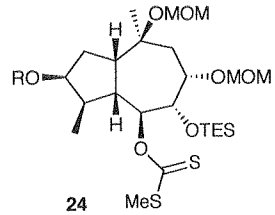
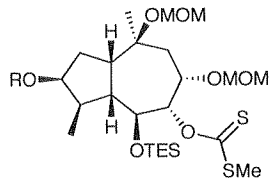


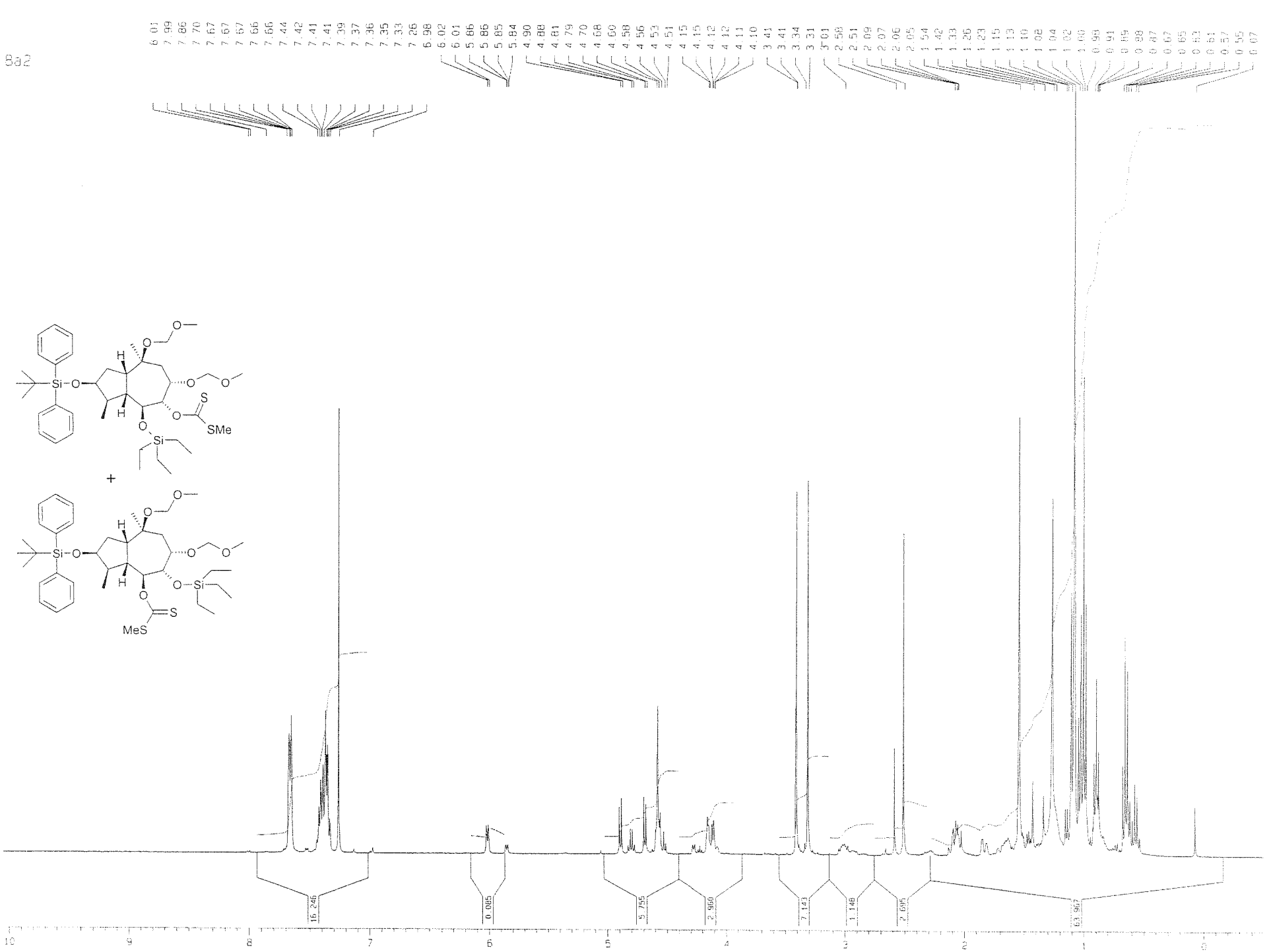
24



25

Xanthates 24 and 25: Carbon disulfide (1.8 μL, 0.0312 mmol) was added to a solution of alcohol **23** (7.2 mg, 0.0104 mmol) in THF (0.3 mL) at –78 °C. After stirring at this temperature for 30 minutes the mixture was treated dropwise with NaHMDS (11.4 μL of a 1 M solution in THF, 0.0114 mmol). The resulting yellow solution was stirred for 50 minutes then treated with MeI (3.2 μL, 0.0520 mmol) and stirred for a further 2 hours. After this time the reaction mixture was quenched at -78 °C with aqueous ammonium chloride (0.5 mL) then allowed to warm to room temperature over 40 minutes. After diluting with water (5 mL) the mixture was extracted with EtOAc (3 × 5 mL). The combined organics were dried ($MgSO_4$) and concentrated *in vacuo* to a yellow oil. This was purified by flash chromatography (SiO_2, Et_2O/petrol ether, 1:4) to yield a mixture of the title compounds as a clear oil, 7.8 mg, 96%, 3.1:1 ratio of 2 components by ^1H NMR. This was used crude in the next step.

The xanthates were tentatively assigned as **24** and **25**. Key signals: δ_H (400 MHz; $CDCl_3$) 6.02 (major component, 1H, d, *J* 4.0, H-6 or H-7), 5.86 (minor component, 1H, d, *J* 4.0, H-6 or H-7), 2.58 (minor component, 3H, s, $OC(S)SCH_3$), 2.51 (major component, 3H, s, $OC(S)SCH_3$).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SMe
MeS
+
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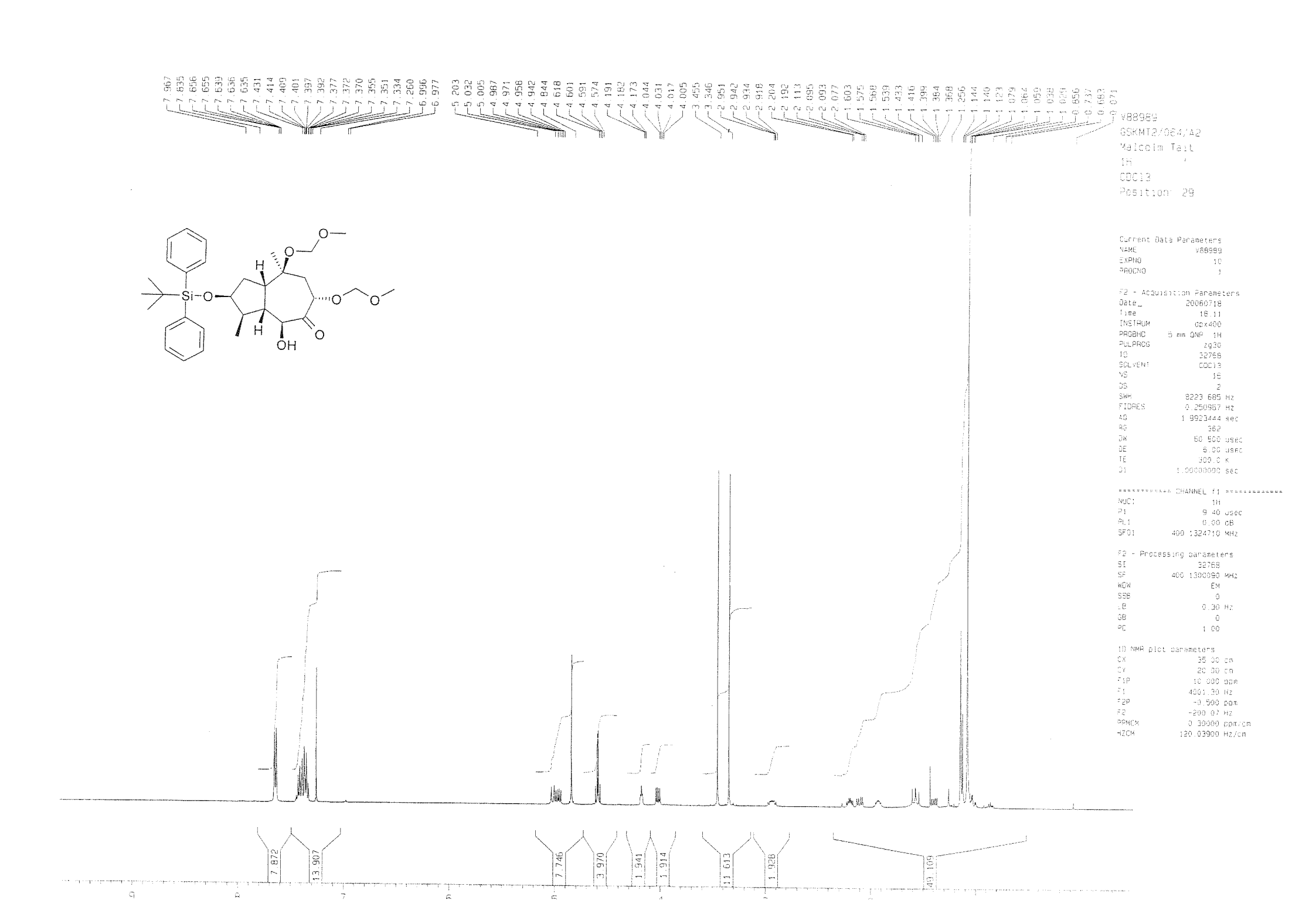
2.960
7.143
1.148
2.696
63.967


7.967
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7.656
7.655
7.639
7.636
7.635
7.431
7.414
7.409
7.401
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7.377
7.372
7.370
7.355
7.351
7.334
7.260
6.996
6.977
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5.032
5.005
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4.971
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4.844
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4.191
4.182
4.173
4.044
4.031
4.017
4.005
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3.346
2.951
2.942
2.934
2.918
2.204
2.192
2.113
2.095
2.093
2.077
1.603
1.575
1.568
1.539
1.433
1.416
1.394
1.364
1.358
1.256
1.144
1.140
1.123
1.079
1.064
1.059
1.038
1.026
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0.732
0.683
0.071
V88989
GSKMT2/084/A2
Malcolm Tait
1H
CDCl3
Position 29
Si
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H
OH
Current Data Parameters
NAME V88989
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060718
Time 18.11
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PULPROG zg30
TD 32768
SOLVENT CDCl3
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DS 2
SWH 8223.685 Hz
FIDRES 0.250957 Hz
AQ 1.9923444 sec
RG 362
DW 60.900 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
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PL1 0.00 dB
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F2 - Processing parameters
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LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
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CY 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.30000 ppm/cm
HZCM 120.03900 Hz/cm
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13.907
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3.970
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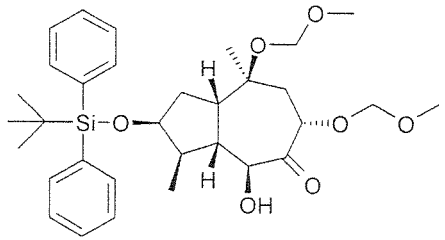
11.613
1.928
49.109

V88989
GSKMT2/084/42
Malcolm Tait
13C
CDCl3
Position 29



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129.7
127.6
127.5
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86.0
77.8
77.3
77.0
76.7
75.0
73.5
56.3
55.8
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47.9
43.0
38.1
37.4
27.3
27.1
19.5
14.5

Current Data Parameters
NAME V88989
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
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Time 19.50
INSTRUM dpx400
PROBHD 5 mm QNP 1H
PULPROG zgpg30
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SOLVENT CDCl3
NS 1536
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 812.7
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec

========== CHANNEL f1 ==========
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P1 9.30 usec
PL1 -2.00 dB
SFO1 100.6248025 MHz

========== CHANNEL f2 ==========
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NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 400.1320007 MHz

F2 - Processing parameters
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WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
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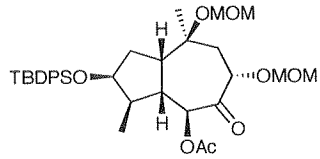
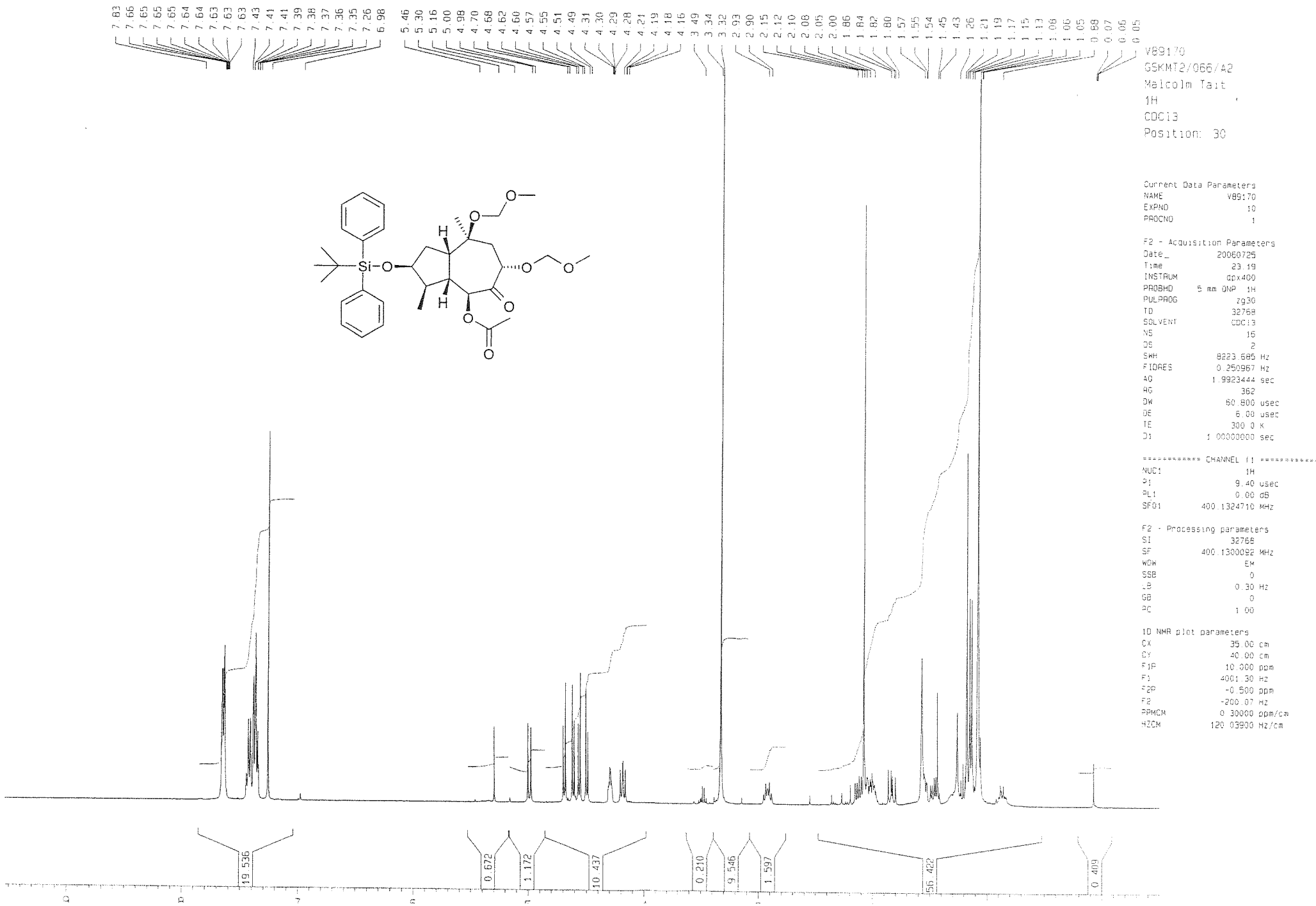
CY 10.00 cm
F1P 220.000 ppm
F1 22134.61 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 6.42857 ppm/cm
HZCM 646.79633 Hz/cm

200
180
160
140
120



O-6 Acetoyl derivative of 14: A solution of alcohol **14** (10.3 mg, 0.018 mmol) in CH_2Cl_2 (1 mL) was treated with acetic anhydride (20 μL, 0.207 mmol), pyridine (20 μL, 0.252 mmol) and DMAP (1 granule). The solution was stirred at room temperature for 37.5 hours to leave a yellow solution which was quenched with aqueous ammonium chloride (5 mL). This mixture was extracted with CH_2Cl_2 (3 x 10 mL) then the combined organics were washed with brine (5 mL), dried ($MgSO_4$) and concentrated *in vacuo* to a yellow oil. This was purified by flash chromatography (SiO_2, Et_2O/petrol ether, 1:2) to yield the title compound as a clear oil, 10.1 mg, 91%; δ_H (400 MHz; $CDCl_3$) 7.66 – 7.63 (4H, m, *o*-Ph), 7.45 – 7.34 (6H, m, *m*-Ph, *p*-Ph), 4.99 (1H, d, *J* 10.3, H-6), 4.69 (1H, d, *J* 7.3, O-10-CH_2O), 4.61 (1H, d, *J* 7.3, O-10-CH_2O), 4.56 (1H, d, *J* 6.8, O-8-CH_2O), 4.51 (1H, d, *J* 6.8, O-8-CH_2O), 4.31 – 4.28 (1H, m (br), H-3), 4.19 (1H, dd, *J* 7.5, 10.1, H-8), 3.32 (6H, s, $OCH_2OC\underline{H}_3$), 2.92 (1H, ddd, *J* 7.6, 7.6, 12.9, H-1), 2.13 (1H, dd, *J* 7.4, 14.6, H-9), 2.08 (3H, s, $C(O)CH_3$), 2.08 – 1.95 (2H, m, H-4, H-5), 1.83 (1H, dd, *J* 10.1, 14.6, H-9'), 1.57 – 1.52 (1H, m, H-2), 1.45 (1H, ddd, *J* 5.5, 12.8, 12.8, H-2'), 1.17 (3H, s, H-13), 1.14 (3H, d, *J* 7.1, H-14), 1.08 (9H, s, $C(CH_3)_3$); δ_C (100 MHz; $CDCl_3$) 202.4 (C-7), 170.0 (C-12), 135.9 (*o*-Ph), 135.8 (*o*-Ph), 134.5 (*ipso*-Ph), 133.8 (*ipso*-Ph), 129.7 (*p*-Ph), 127.6 (*m*-Ph), 94.8 (O-8-CH_2O), 90.6 (O-10-CH_2O), 77.8 (C-10), 76.9 (C-6), 74.2 (C-8), 73.8 (C-3), 56.0, 55.8 (O-8-$CH_2O\underline{C}H_3$/O-10-$CH_2O\underline{C}H_3$), 47.9 (C-5), 46.3 (C-1), 43.9 (C-4), 37.1 (C-2), 36.5 (C-9), 27.8 (C-13), 27.1 ($C(\underline{C}H_3)_3$), 20.6 ($C(O)\underline{C}H_3$), 19.4 ($\underline{C}(CH_3)_3$), 15.6 (C-14); υ_{max} (film; cm^{-1}) 2932m, 2857m, 1748m, 1733m, 1460m, 1429m, 1377m, 1253m, 1227m, 1147m, 1104m, 1021s, 943m, 920m, 823w, 742m, 703s; $[\alpha]_D$ -8.4 (*c.* 0.49, $CHCl_3$); found (ESI+) $[MNa]^+$ 635.3013; $C_{34}H_{48}O_8NaSi$ requires *M*, 635.3016.



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EXPNO	10
PROCNO	1

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FIDRES	0.250967 Hz
AQ	1.9923444 sec
RG	362
DW	60.800 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 ==========

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F2 - Processing parameters

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1D NMR plot parameters

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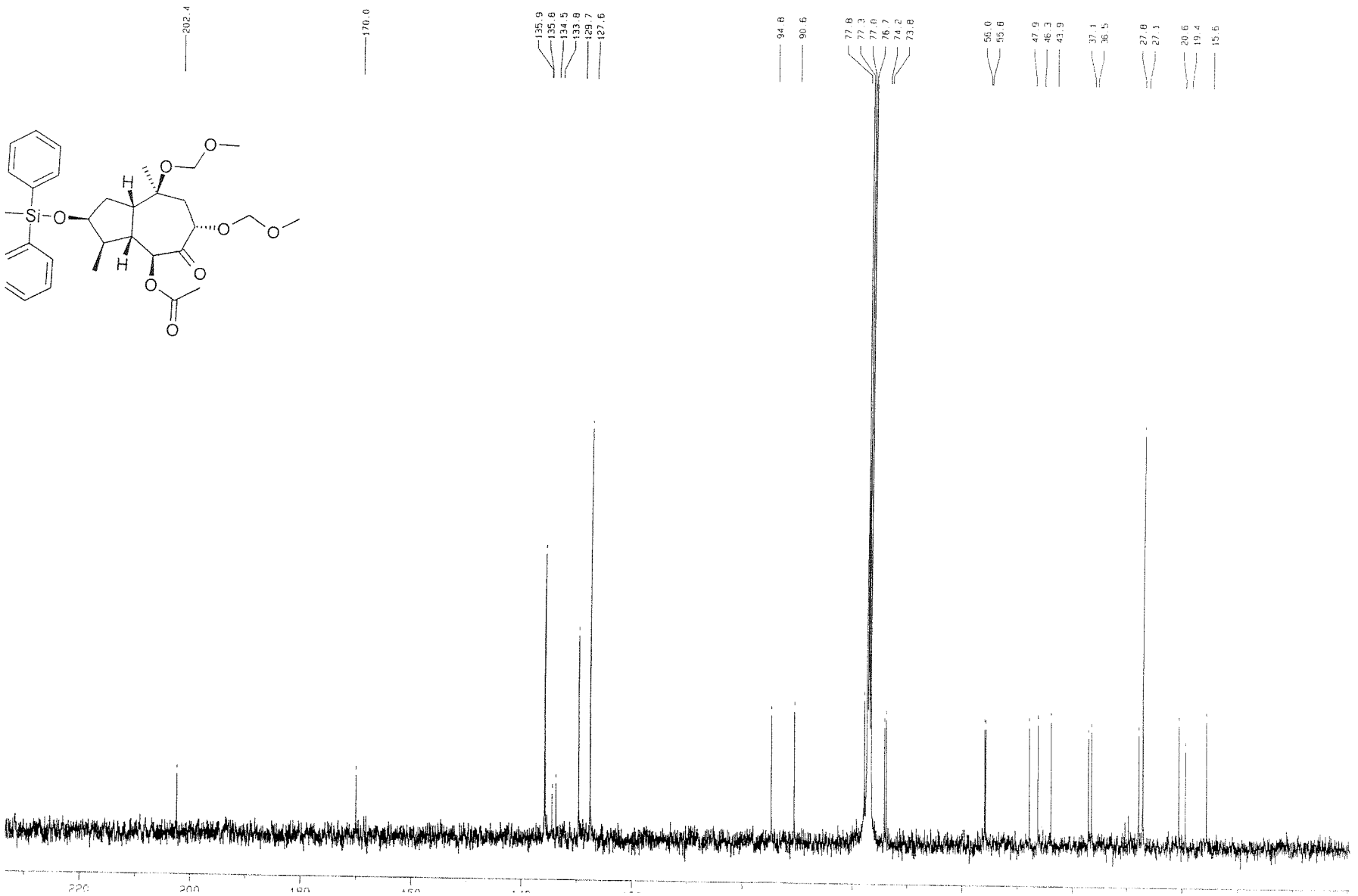

VB91/0
GSKMT2/066/A2
Malcolm Tait
13C
CDCl3
Position: 30

Current Data Parameters
NAME VB9170
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
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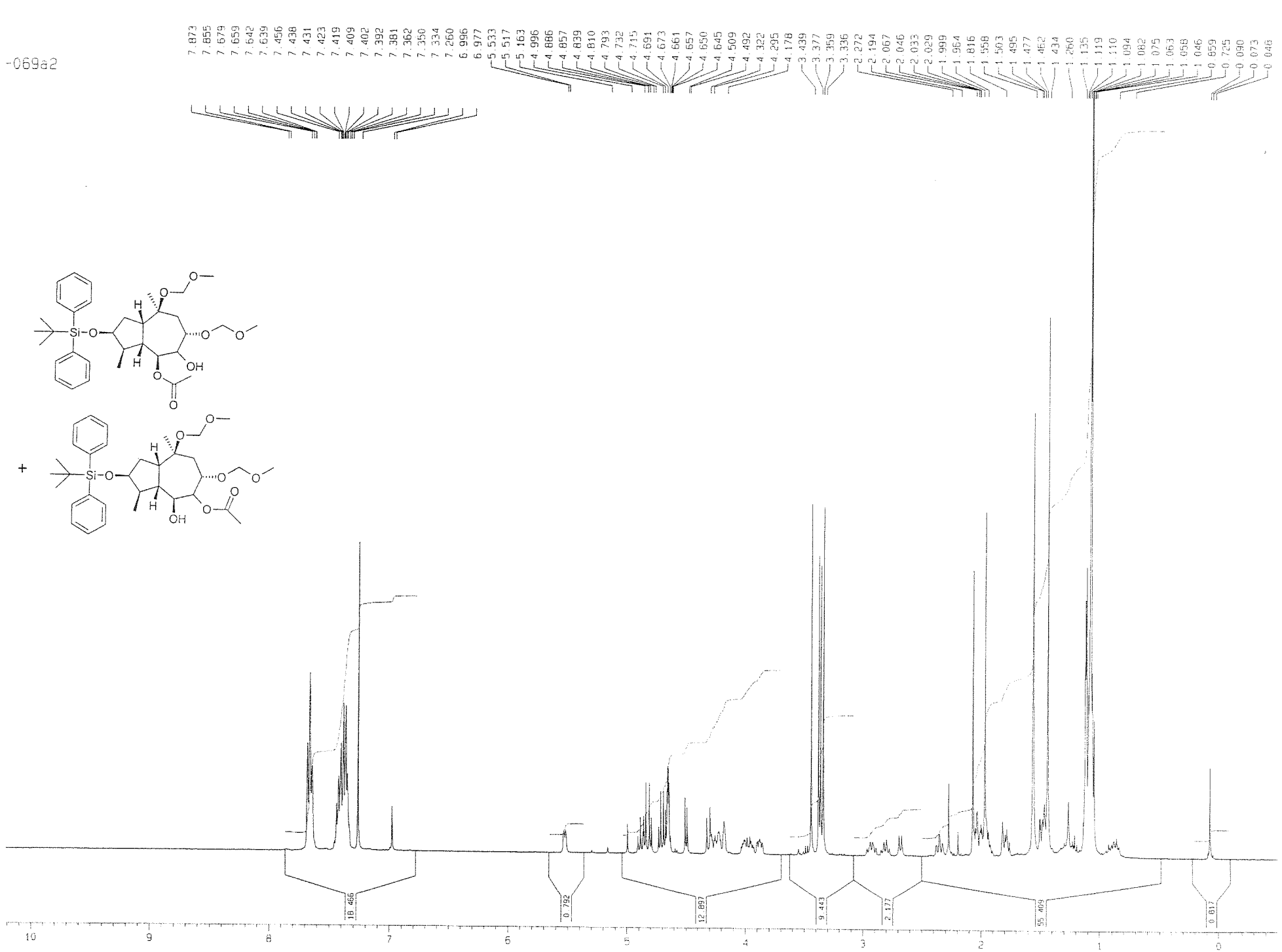
Time 0.38
INSTRUM dpx400
PROBHD 5 mm QNP 1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1536
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 574.7
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec

========== CHANNEL f1 ==========
NUC1 13C
P1 9.30 usec
PL1 -2.00 dB
SF01 100.6248025 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 21.00 dB
SF02 400.1320007 MHz

F2 - Processing parameters
SI 65536
SF 100.6127701 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 35.00 cm
CY 10.00 cm
F1P 249.664 ppm
F1 25121.43 Hz
F2P -10.501 ppm
F2 -1056.58 Hz
PPMCM 7.43368 ppm/cm
HZCM 747.94324 Hz/cm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7.642
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7.409
7.402
7.392
7.381
7.362
7.350
7.334
7.260
6.996
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5.533
5.517
5.163
4.996
4.886
4.857
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4.715
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4.673
4.661
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2.029
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1.503
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1.119
1.110
1.094
1.082
1.075
1.063
1.058
1.046
0.859
0.725
0.090
0.073
0.048
Si-O
OH
+
18.456
0.792
12.897
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2.177
55.469
0.817
10
9
8
7
6
5
4
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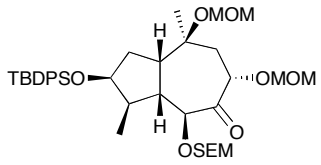
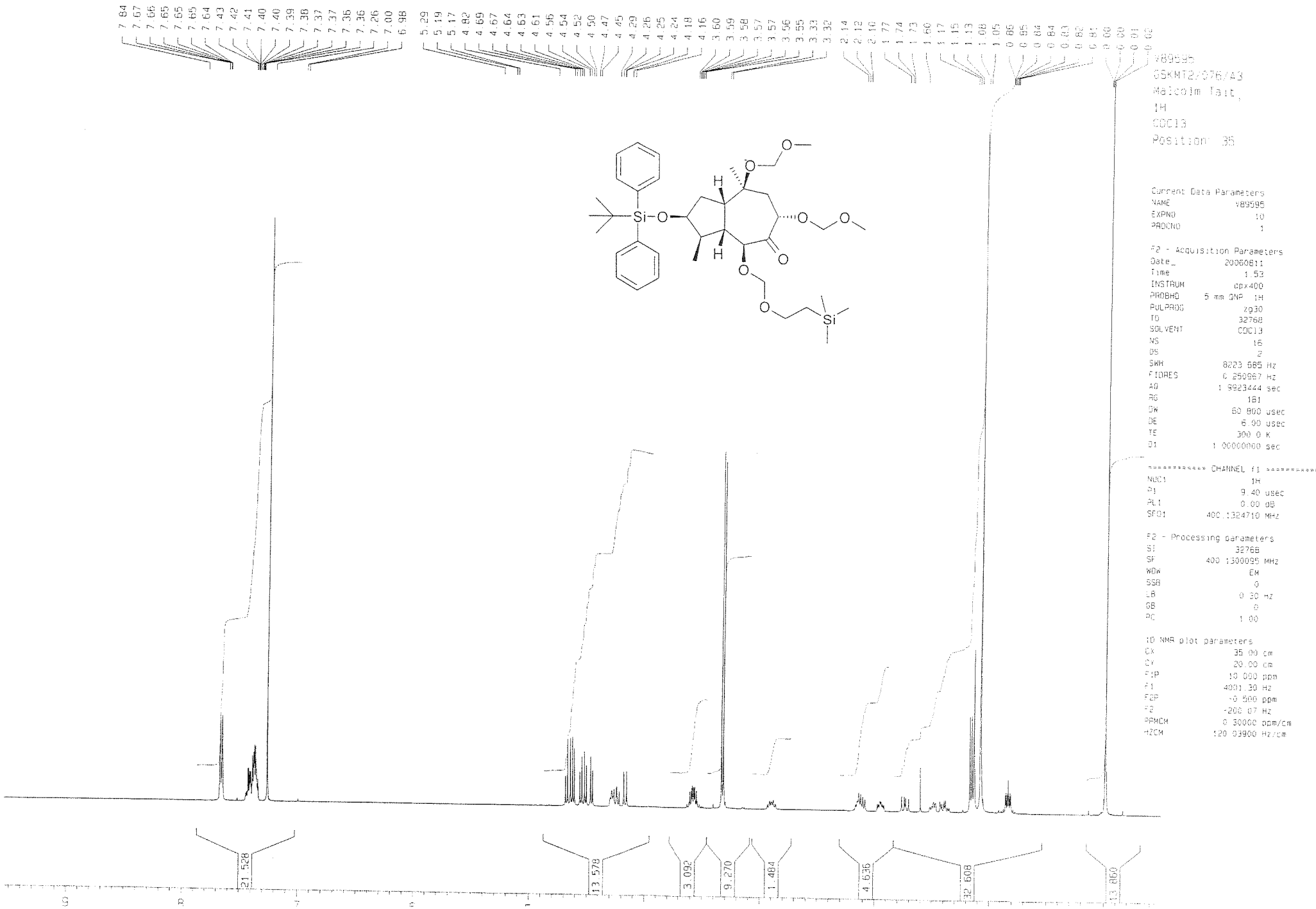


26

SEM acetal 26: A solution of alcohol **14** (901 mg, 1.58 mmol) in CH_2Cl_2 (16 mL) at 0 ^oC was treated with DIPEA (4.33 mL, 24.85 mmol) then SEM-Cl (2.51 mL, 14.20 mmol). The mixture was warmed to room temperature then DMAP (10 granules) was added and the mixture stirred for 15 hours. After this time the reaction mixture was partitioned between water (30 mL) and EtOAc (50 mL). The aqueous layer was extracted with EtOAc (3 × 50 mL) then the combined organics were washed with brine (50 mL), dried ($MgSO_4$) and concentrated *in vacuo* to a yellow oil. This was purified by flash chromatography (SiO_2, Et_2O/petrol ether, neat petrol then 1:19 to 1:1) to yield the title compound as a clear oil, 883 mg, 80%; δ_H (400 MHz; $CDCl_3$) 7.67 – 7.64 (4H, m, *o*-Ph), 7.45 – 7.34 (6H, m, *m*-Ph, *p*-Ph), 4.68 (1H, d, *J* 7.3, O-10-CH_2O), 4.64 (1H, d, *J* 7.4, O-10-CH_2O), 4.62 (1H, d, *J* 6.8, O-8-CH_2O), 4.55 (1H, d, *J* 7.1, O-6-CH_2O), 4.51 (1H, d, *J* 6.7, O-8-CH_2O), 4.46 (1H, d, *J* 7.1, O-6-CH_2O), 4.30 – 4.26 (1H, m, H-3), 4.24 (1H, dd, *J* 7.5, 10.0, H-8), 4.17 (1H, d, *J* 9.7, H-6), 3.63 – 3.52 (2H, m, $SiCH_2C\underline{H}_2$), 3.33 (3H, s, O-10-$CH_2OC\underline{H}_3$), 3.32 (3H, s, O-8-$CH_2OC\underline{H}_3$), 2.90 (1H, ddd (br), *J* 7.4, 7.4, 12.8, H-1), 2.18 – 2.08 (2H, m, H-4, H-9), 1.95 (1H, ddd, *J* 4.4, 9.3, 9.3, H-5), 1.74 (1H, dd, *J* 10.4, 14.4, H-9'), 1.49 (1H, ddd, *J* 1.6, 6.7, 12.9, H-2), 1.39 (1H, ddd, *J* 5.1, 12.9, 12.9, H-2'), 1.16 (3H, d, *J* 7.1, H-12), 1.13 (3H, s, H-11), 1.08 (9H, s, $C(CH_3)_3$), 0.86 – 0.81 (2H, m, $SiC\underline{H}_2CH_2$), -0.01 (9H, s, $Si(CH_3)_3$); δ_C (100 MHz; $CDCl_3$) 205.8 (C-7), 135.9 (*o*-Ph), 135.8 (*o*-Ph), 134.7 (*ipso*-Ph), 133.8 (*ipso*-Ph), 129.6 (*p*-Ph), 127.6 (*m*-Ph), 127.5 (*m*-Ph), 95.3 (O-8-CH_2O), 94.4 (O-6-CH_2O), 90.6 (O-10-CH_2O), 80.0 (C-6), 78.1 (C-10), 75.4 (C-8), 74.1 (C-3), 65.7 ($SiCH_2\underline{C}H_2$), 56.1 (O-10-$CH_2O\underline{C}H_3$), 55.7 (O-8-$CH_2O\underline{C}H_3$), 49.4 (C-5), 46.3 (C-1), 44.2 (C-4), 37.6 (C-2), 36.8 (C-9), 27.9 (C-11), 27.0 ($C(\underline{C}H_3)_3$), 19.4 ($\underline{C}(CH_3)_3$), 18.0 ($Si\underline{C}H_2CH_2$), 15.8 (C-12), –1.5 ($Si(CH_3)_3$); υ_{max} (film; cm^{-1}) 2948m, 2931m, 2983, 1731m, 1473, 1428m, 1376m, 1249m, 1193m, 1148m, 1106s, 1027s, 939m, 920m, 860m, 836m, 741m, 702m; $[\alpha]_D$ – 4.5 (*c*. 0.33, $CHCl_3$); found (ESI+) $[MNa]^+$ 723.3688; $C_{38}H_{60}O_8NaSi_2$ requires *M*, 723.3724.



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EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
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INSTRUM cpx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 181
DW 60.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

========== CHANNEL f1 ==========
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P1 9.40 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
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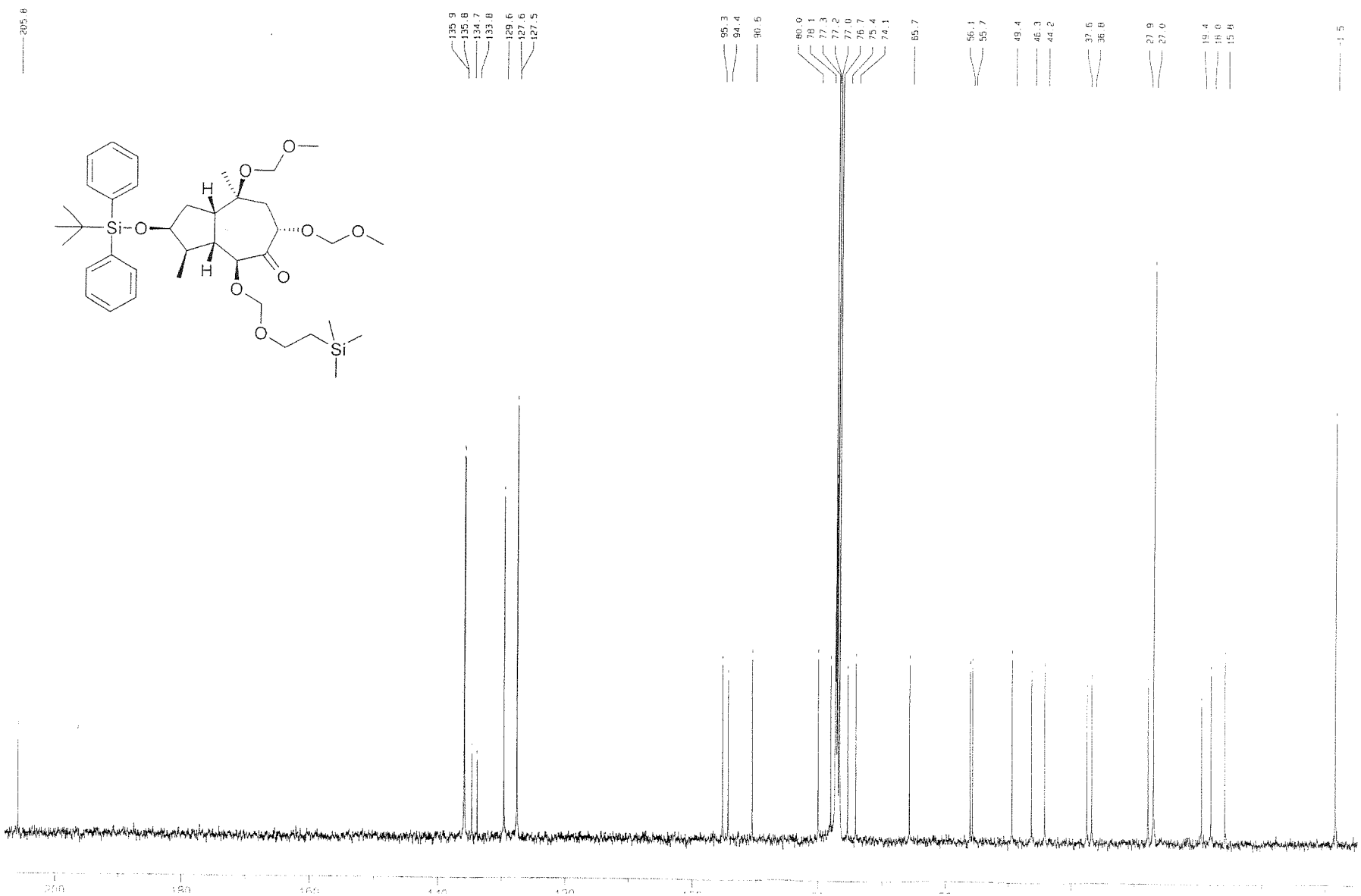
CY 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.30000 ppm/cm
HZCM 120.03900 Hz/cm



V89595
GSKMT2/076/A3
Malcolm Tait
13C
CDCl3
Position: 35

Current Data Parameters
NAME V89595
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060811
Time 3.12
INSTRUM dpx400
PROBHD 5 mm QNP 1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1536
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517675 sec
RG 5160.6
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec

========== CHANNEL f1 ==========
NUC1 13C
P1 9.30 usec
PL1 -2.00 dB
SFO1 100.6248025 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 65536
SF 100.6127709 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 35.00 cm
CY 14.00 cm
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F2P -5.000 ppm
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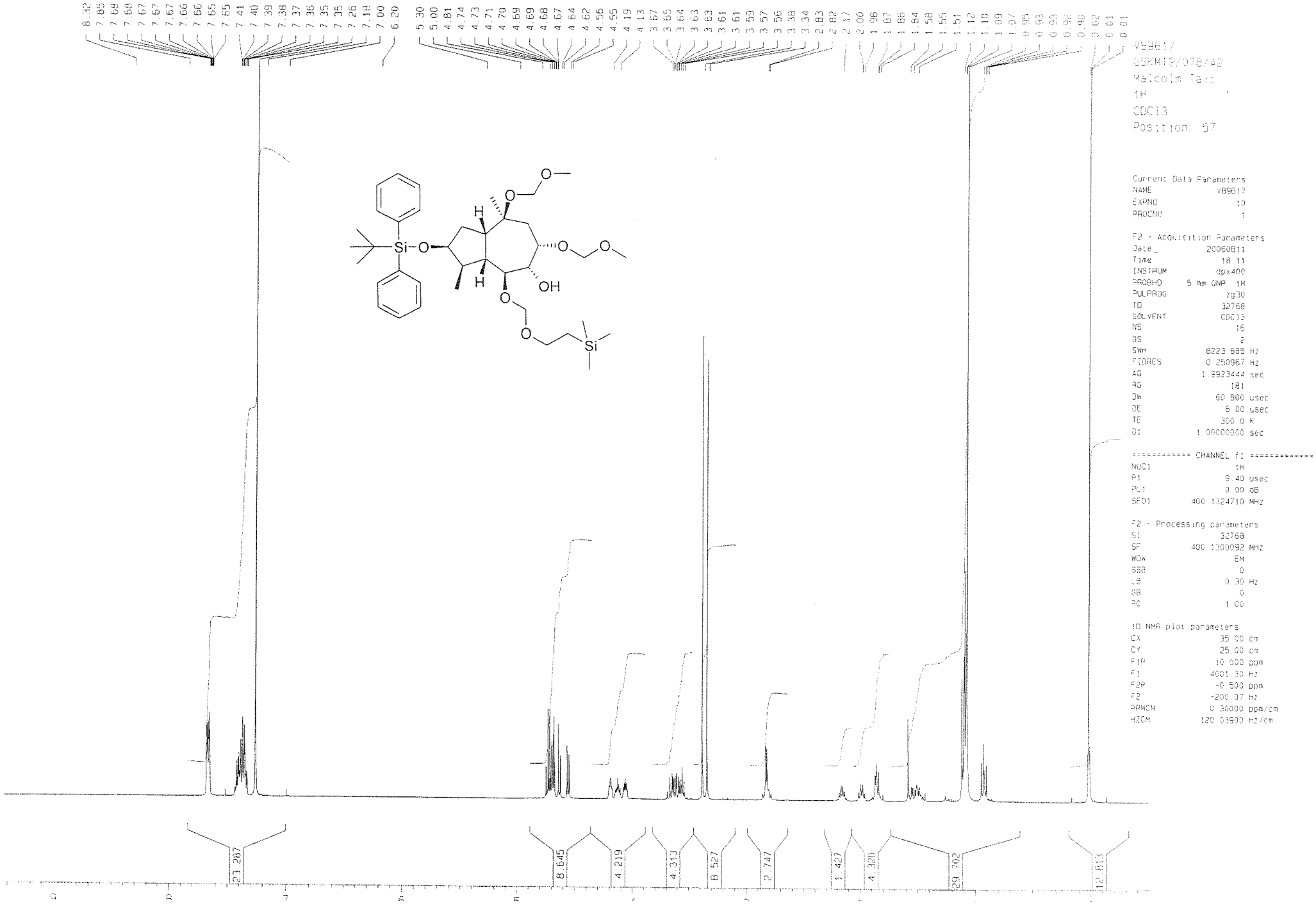
HZCM 1648.79633 Hz/cm


8.32 7.85 7.68 7.68 7.67 7.67 7.67 7.66 7.66 7.65 7.65 7.41 7.40 7.39 7.38 7.37 7.36 7.35 7.35 7.26 7.18 7.00 6.20
5.30 5.00 4.81 4.74 4.73 4.71 4.70 4.69 4.69 4.68 4.67 4.64 4.62 4.56 4.55 4.19 4.13 3.67 3.65 3.64 3.63 3.63 3.61 3.61 3.59 3.57 3.56 3.38 3.34 2.83 2.82 2.17 2.00 1.98 1.87 1.86 1.84 1.58 1.55 1.51 1.12 1.10 1.09 1.07 0.95 0.93 0.89 0.82 0.90 0.02 0.01 0.01
V89617
GSKMTP/078/AB
Malcolm Tait
1H
CDCl3
Position: 57
Si
O
H
OH
Current Data Parameters
NAME V89617
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060811
Time 18.11
INSTRUM dpx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 181
DW 60.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
========== CHANNEL f1 ==========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
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WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 35.00 cm
CY 25.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.30000 ppm/cm
HZCM 120.03900 Hz/cm
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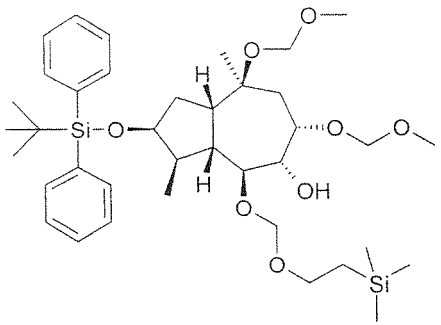
29.702
12.613

V89617
GSKMT2/078/A2
Malcolm Tait
13C
CDCl3
Position: 57



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134.9
134.2
129.5
127.5
127.5
96.2
95.8
90.8
79.6
78.0
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77.2
77.0
76.7
74.6
74.5
74.4
65.7
55.6
55.5
50.0
46.1
44.1
38.0
37.5
28.0
27.1
19.5
16.1
15.5
-1.4

Current Data Parameters
NAME V89617
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060811
Time 19.30
INSTRUM dpx400
PROBHD 5 mm QNP 1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1536
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 1149.4
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec

========== CHANNEL f1 ==========
NUC1 13C
P1 9.30 usec
PL1 -2.00 dB
SFO1 100.6248025 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 65536
SF 100.6127701 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 35.00 cm
CY 14.00 cm
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F1 22134.61 Hz
F2P -5.000 ppm
F2 -503.06 Hz
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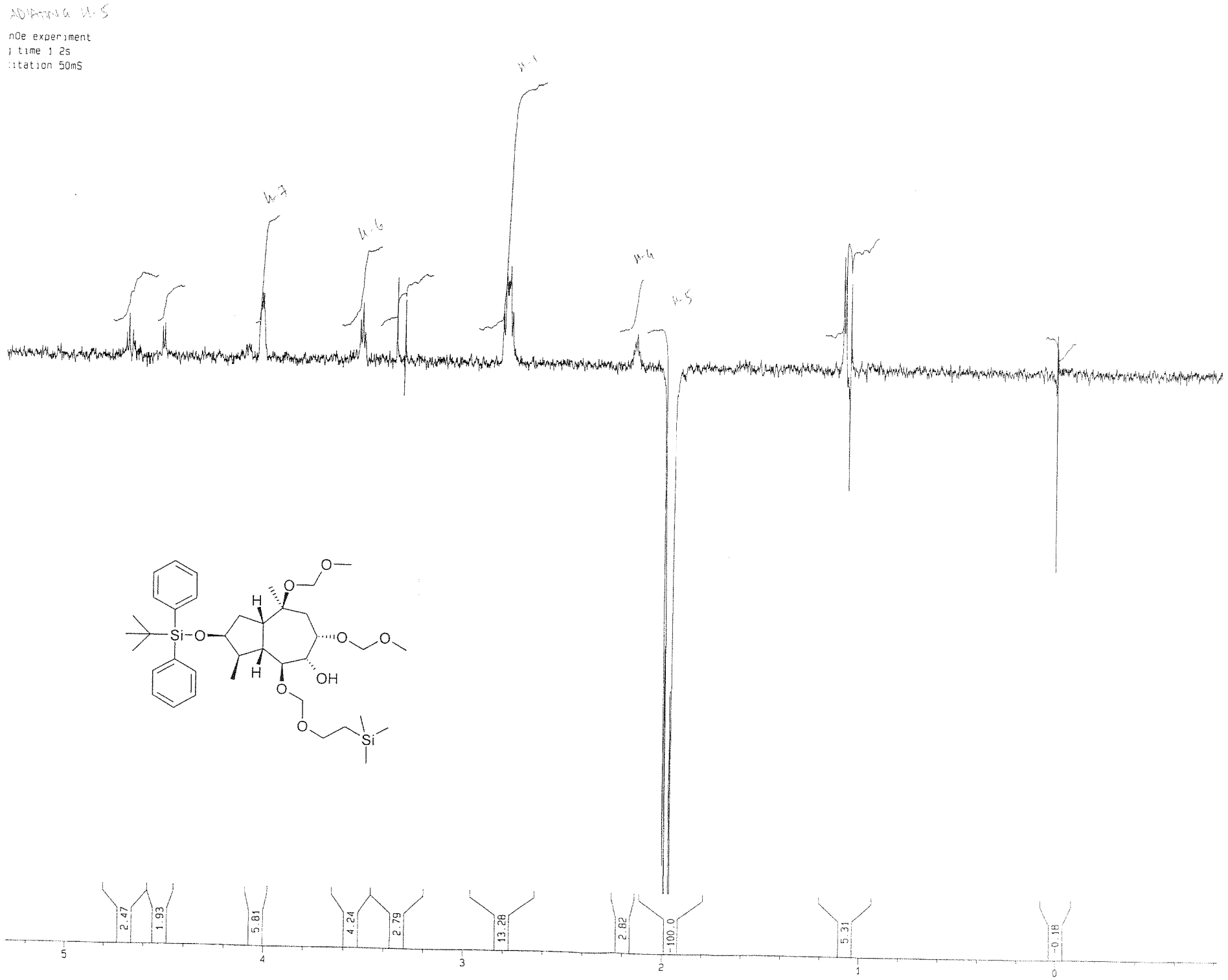
HZCM 646.79633 Hz/cm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time 1 2s
itation 50mS
H-7
H-6
H-1
H-4
H-5
Si
O
H
OH
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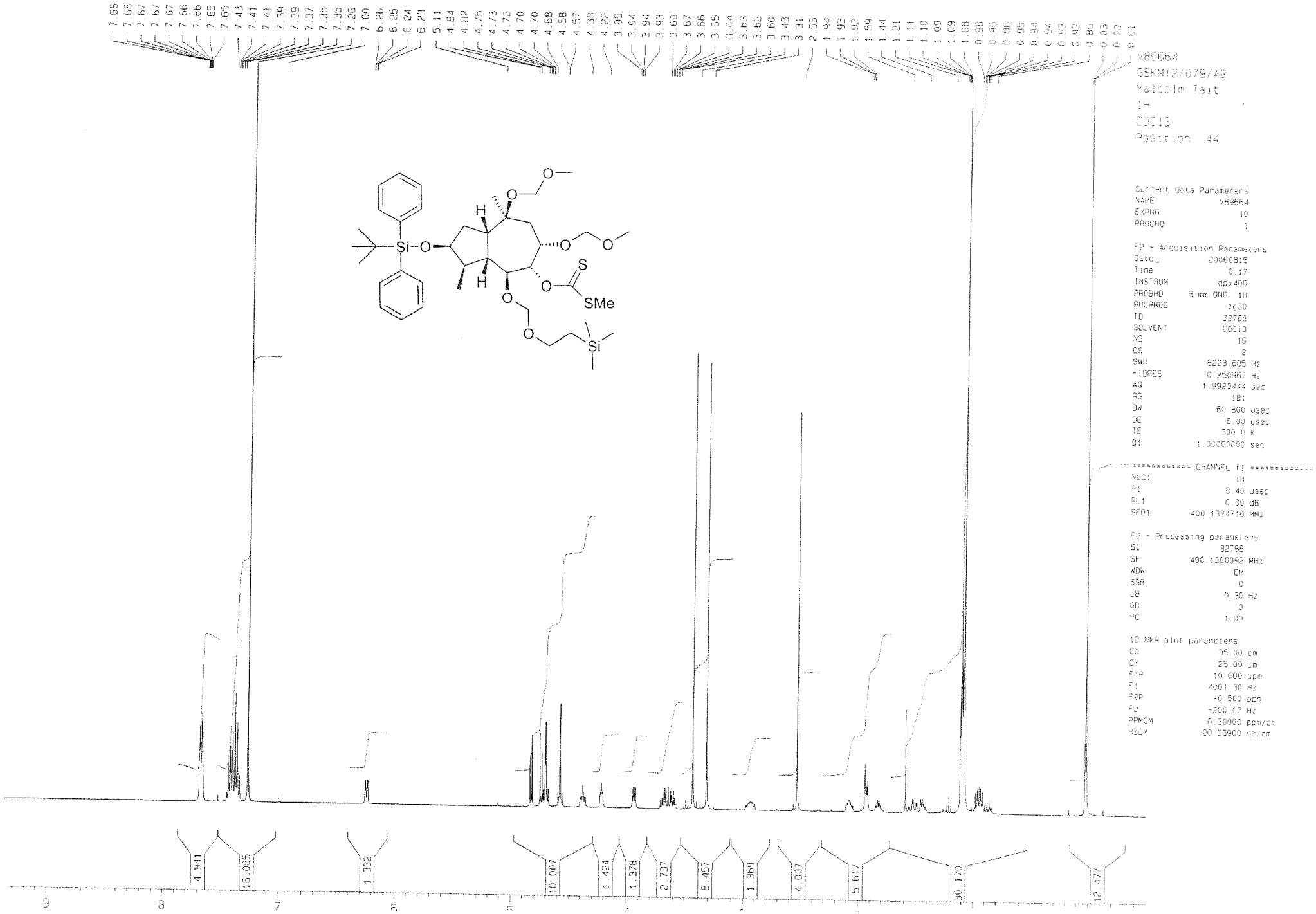
5.81
4.24
2.79
13.28
2.82
100.0
5.31
0.18
5
4
3
2
1
0



Current Data Parameters
NAME V89664
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060615
Time 0.17
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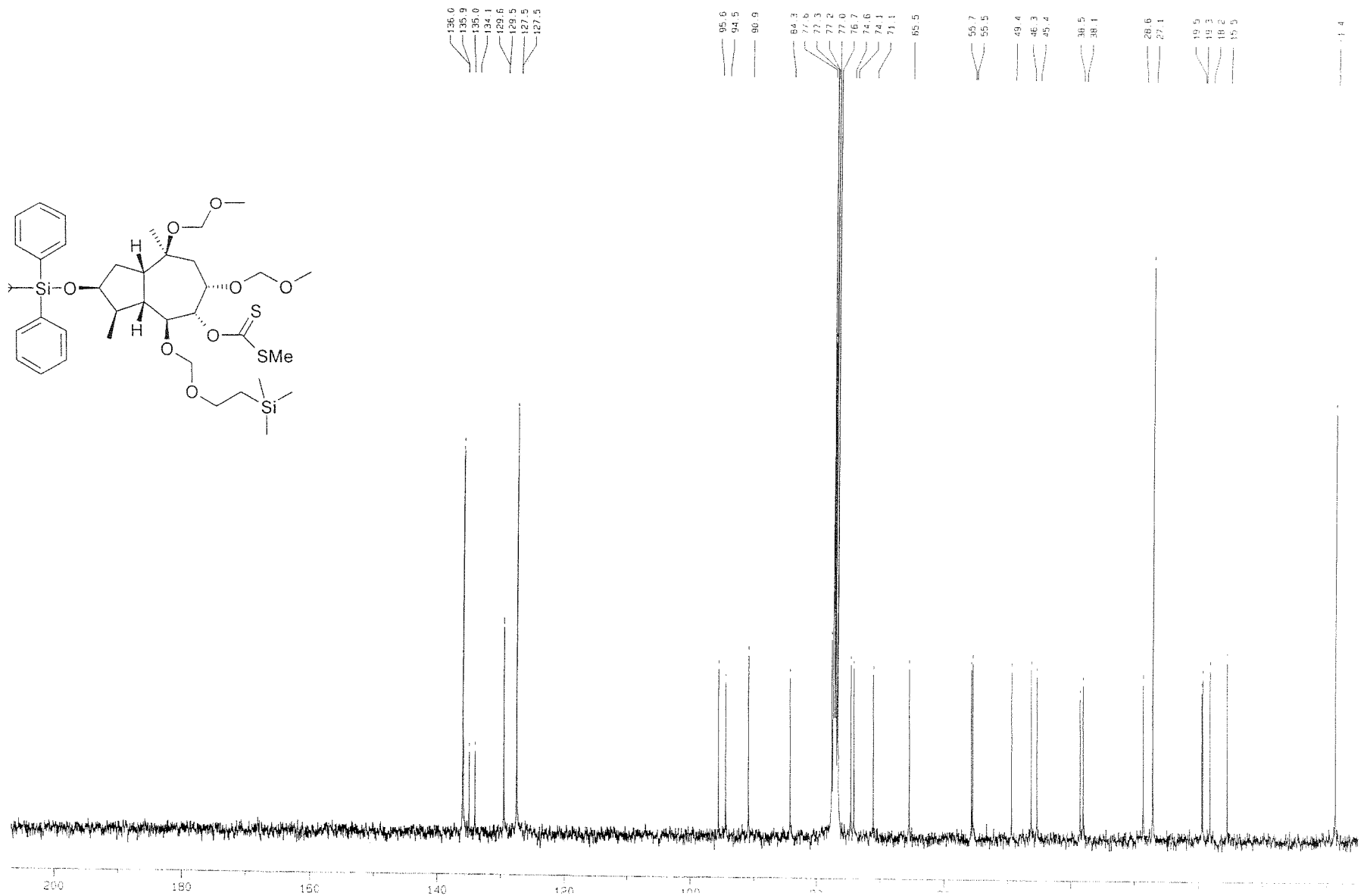
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 181
DW 60.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

========== CHANNEL f1 ==========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 35.00 cm
CY 25.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.30000 ppm/cm
HZCM 120.03900 Hz/cm



V89664
GSKM12/079/A2
Malcolm Tait
13C
CDCl3
Position: 44

Current Data Parameters
NAME V89664
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060815
Time 1 36
INSTRUM dpx400
PROBHD 5 mm DNP 1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1536
DS 4
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517675 sec
RG 574.7
DW 19.100 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec

========== CHANNEL f1 ==========
NUC1 13C
P1 9.30 usec
PL1 -2.00 dB
SF01 100.6248025 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 21.00 dB
SF02 400.1320007 MHz

F2 - Processing parameters
SI 65536
SF 100.6127705 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 35.00 cm
CY 14.00 cm
F1P 220.000 ppm
F1 22134.81 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 6.42857 ppm/cm
HZCM 646.79633 Hz/cm


tandard 1H DRX-600
ppm
7.674 7.662 7.420 7.408 7.396 7.380 7.367 7.354 7.341 7.260
4.735 4.652 4.641 4.626 4.615 4.573 4.569 4.562 4.557 4.224 4.218 3.639 3.629 3.622 3.581 3.571 3.515 3.501 3.404 3.322
2.171 1.942 1.930 1.887 1.877 1.817 1.808 1.671 1.584 1.568 1.560 1.543 1.356 1.349 1.133 1.122 1.079 1.074 0.920 0.910 0.902 0.892 0.883 0.873 0.030 0.006
Current Data Parameters
NAME - MT2-080A4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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Time 11.56
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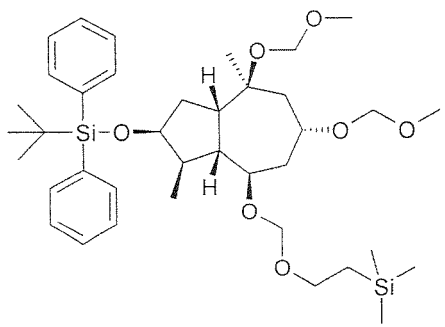
Standard 13C DRX-600



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76.79
74.79
74.47
70.55
65.22
55.64
55.19
52.09
46.12
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28.67
27.09
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18.10
15.79
-1.44

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140
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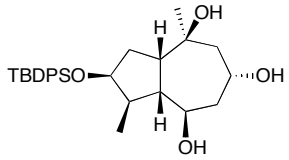
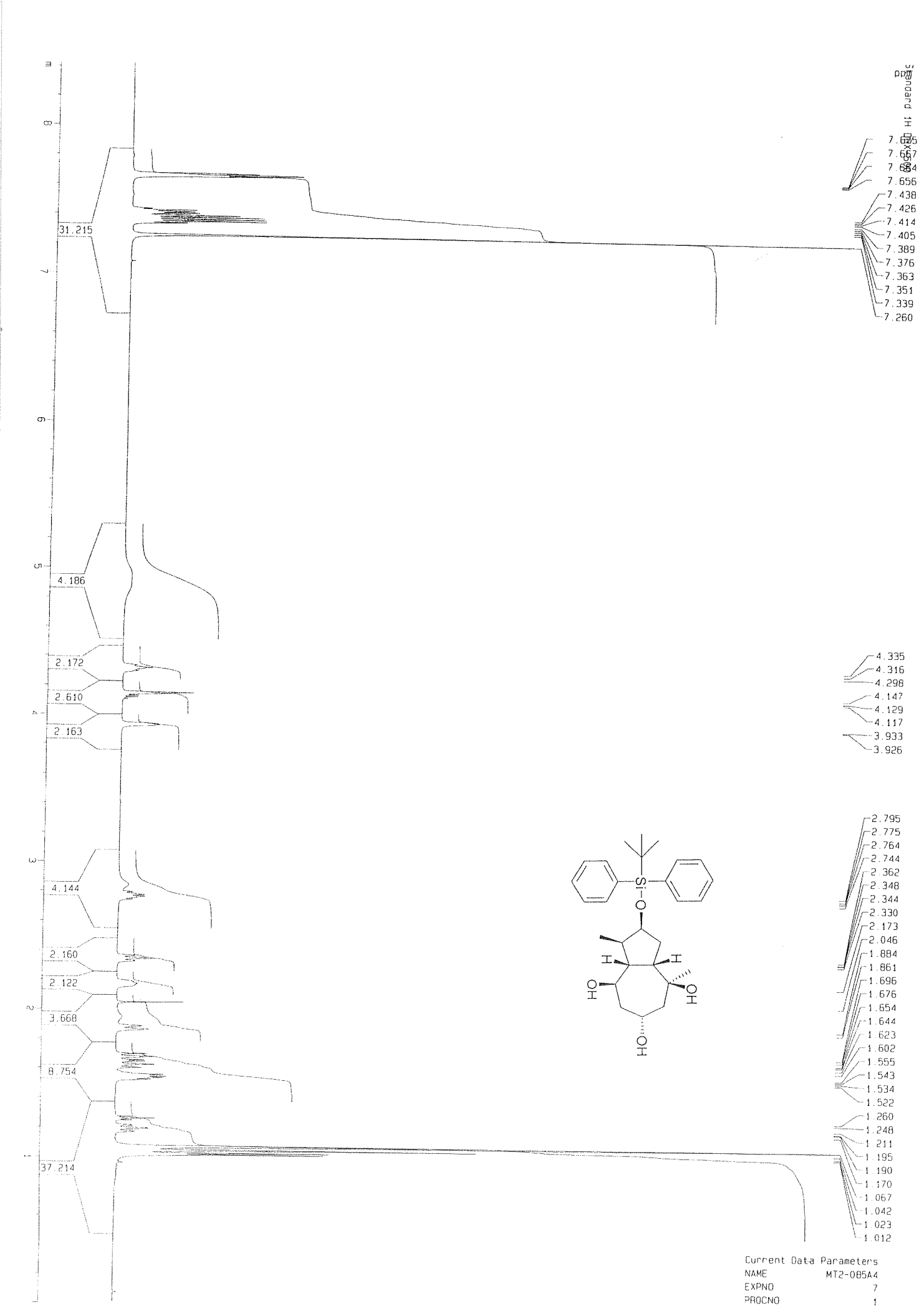
60
40
20
0



30

Triol 30: A solution of **29** (199.4 mg, 0.29 mmol) in MeOH (3 mL) and HCl (Specific Gravity 1.16 - 32%, 6 drops) was heated to 40 ^{o}C for 2 hours. After cooling to room temperature the reaction mixture was quenched with aqueous sodium bicarbonate (10 mL) and extracted with EtOAc (4 × 10 mL). The combined organics were dried ($MgSO_4$) and concentrated *in vacuo* to a clear oil. This was purified by flash chromatography (SiO_2, ethyl acetate) to yield the title compound as a cream foam, 124.6 mg, 92%; δ_H (600 MHz; $CDCl_3$) 7.68 – 7.66 (4H, m, *o*-Ph), 7.43 – 7.34 (6H, m, *m*-Ph, *p*-Ph), 4.95 (2H, br, OH), 4.34 – 4.30 (1H, m, H-8), 4.16 – 4.13 (1H, m (br), H-3), 3.96 – 3.89 (1H, m (br), H-6), 2.84 (1H, br, OH), 2.77 (1H, ddd, *J* 7.0, 11.8, 11.8, H-1), 2.35 (1H, ddd, *J* 2.4, 10.9, 10.9, H-5), 2.21 – 2.12 (1H, m (br), H-7), 1.87 (1H, d (br), *J* 13.6, H-9), 1.68 (1H, dd, *J* 11.6, 13.5, H-9'), 1.62 (1H, dd, *J* 12.6, 12.6, H-7'), 1.58 – 1.50 (2H, m, H-2, H-4), 1.19 (1H, ddd, *J* 2.4, 11.1, 11.1, H-2'), 1.07 (9H, s, $C(CH_3)_3$), 1.04 (3H, s, H-11), 1.02 (3H, d, *J* 6.6, H-12); δ_C (150 MHz; $CDCl_3$) 136.0 (*o*-Ph), 135.9 (*o*-Ph), 134.8 (*ipso*-Ph), 133.9 (*ipso*-Ph), 129.6 (*p*-Ph), 129.6 (*p*-Ph), 127.6 (*m*-Ph), 127.5 (*m*-Ph), 76.1 (C-3), 73.4 (C-10), 69.0 (C-6), 64.4 (C-8), 50.4 (C-5), 49.7 (C-1), 45.9 (C-9), 44.7 (C-4), 39.5 (C-7), 39.1 (C-2), 32.1 (C-11), 27.1 ($C(\underline{C}H_3)_3$), 19.5 ($\underline{C}(CH_3)_3$), 14.3 (C-12); υ_{max} (film; cm^{-1}) 3271m (br), 3071w, 2960m, 2930m, 2857m, 1473m, 1459m, 1428m, 1375m, 1290w, 1259w, 1233w, 1190m, 1111s, 1074m, 1040m, 1019m, 934w, 905m, 858w, 822m, 741m, 702s, 667m; $[\alpha]_D$ +35.2 (*c*. 1.23, $CHCl_3$); mp 159 – 160 ^{o}C; found (ESI+) $[MNa]^+$ 491.2592, $C_{28}H_{40}O_4NaSi$ requires *M*, 491.2594.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3.926
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EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
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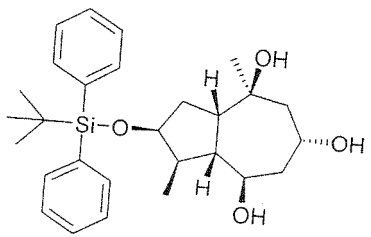
Time 13.42

Standard 13C DRX-600



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Current Data Parameters

NAME	MT2-085A4
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PROCNO	1

F2 - Acquisition Parameters

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========== CHANNEL f1 ==========

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PL1	0.00 dB
SFO1	150.9178393 MHz

========== CHANNEL f2 ==========

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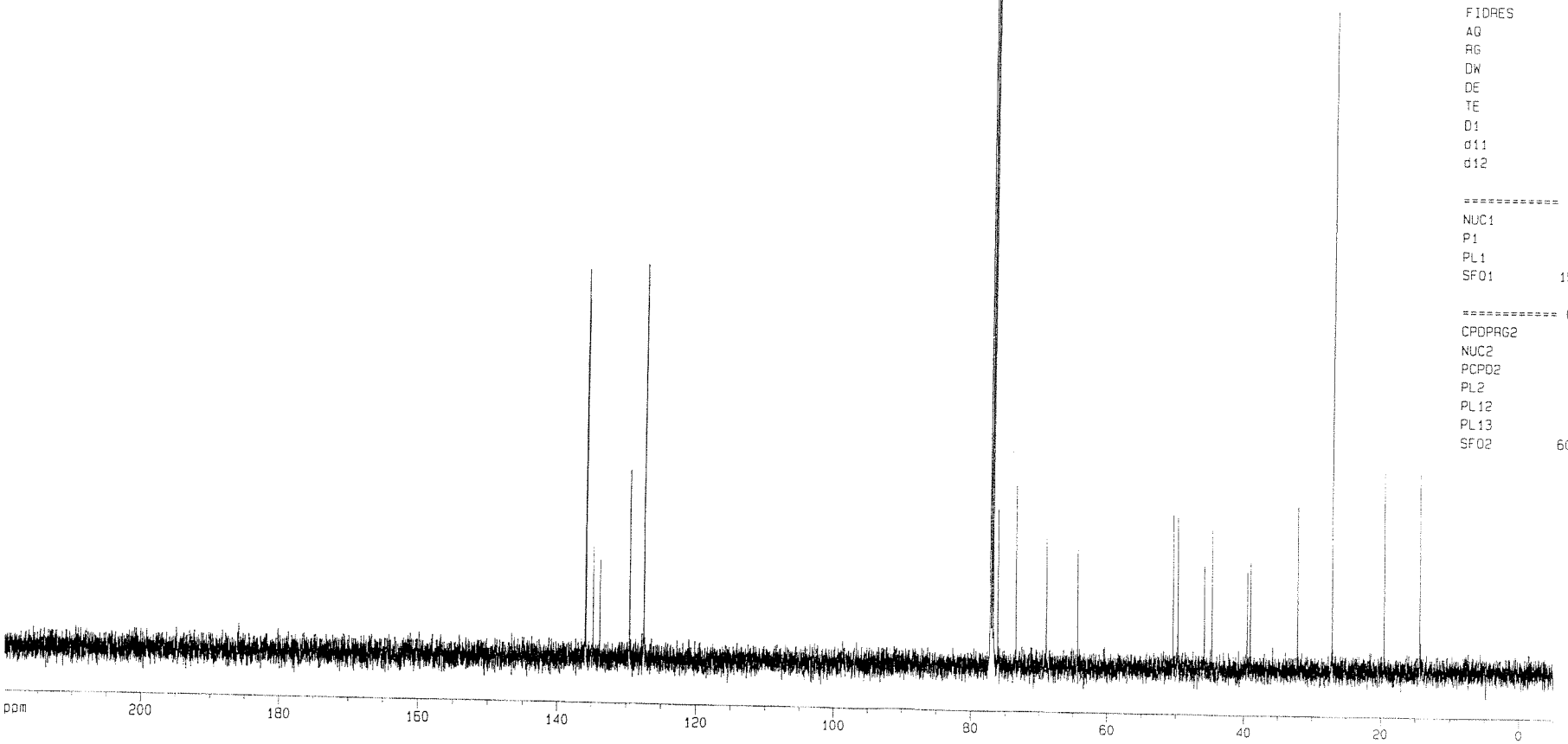
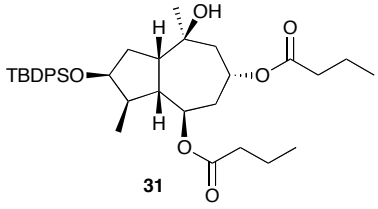
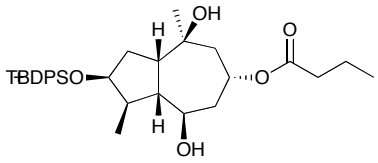




31



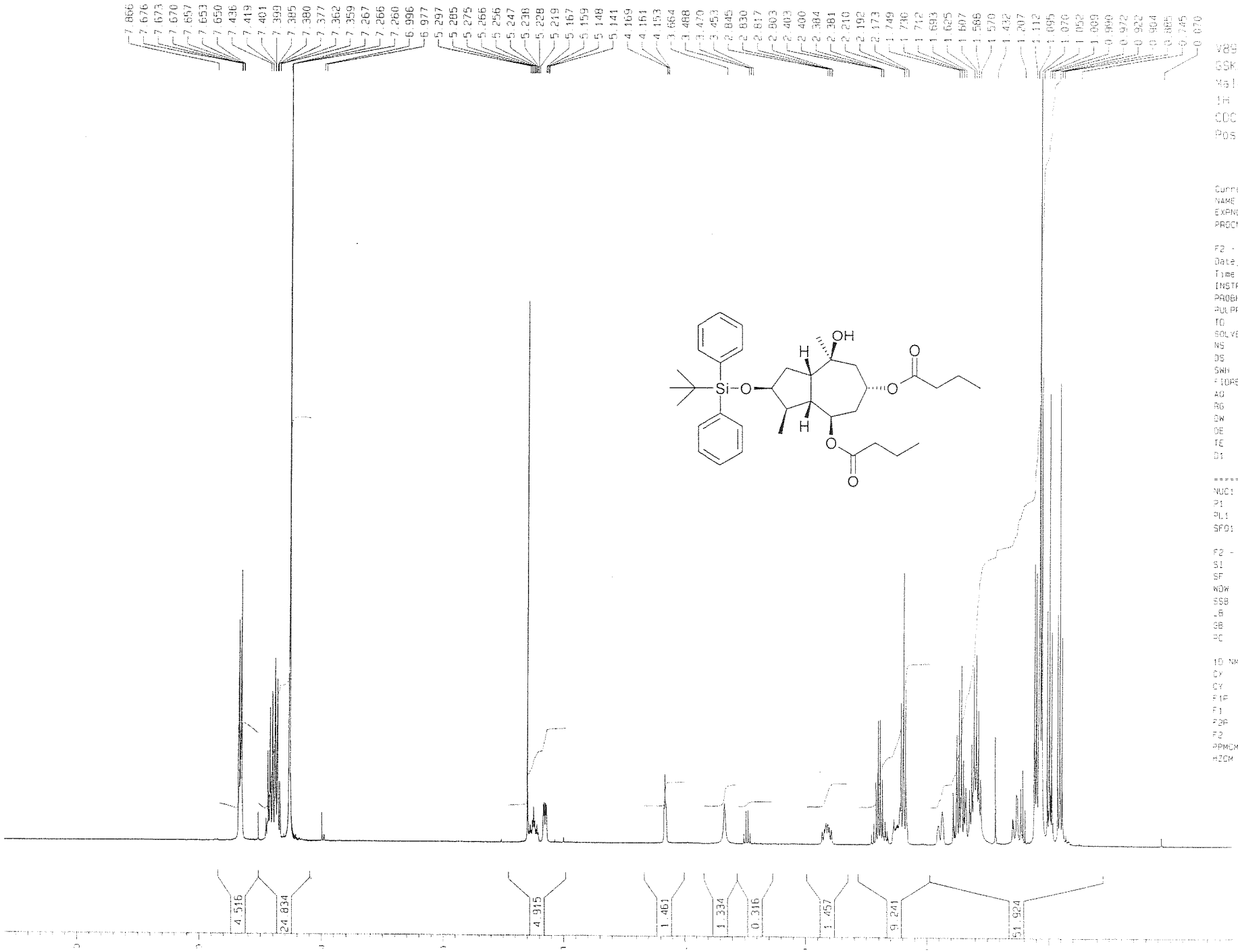
32

Butyrates 31 and 32: To a solution of triol **30** (124.6 mg, 0.266 mmol) and DMAP (3 granules) in CH_2Cl_2 (5 mL) was added butyric anhydride (48 μL, 0.292 mmol) as a solution in CH_2Cl_2 (5 mL) in one portion. The solution was stirred for 1 hour at which point another aliquot of butyric anhydride (9 μL, 0.053 mmol) was added and the mixture stirred for a further 2 hours. The solution was quenched with aqueous ammonium chloride (20 mL) and extracted with EtOAc (4 × 20 mL). The combined organics were washed with aqueous sodium bicarbonate (2 × 10 mL), brine (10 mL) then dried ($MgSO_4$) and concentrated *in vacuo* to a clear oil. This was purified by flash chromatography (SiO_2, Et_2O/petrol ether, 1:10 to 1:1) to yield mono-acylated **32** (81 mg, 57%) and bis-acylated **31** (48 mg, 30%) as clear oils, 87% overall yield.

32: δ_H (600 MHz; $CDCl_3$) 7.67 (4H, d (br), *J* 6.9, *o*-Ph), 7.43 – 7.35 (6H, m, *m*-Ph, *p*-Ph), 5.43 – 5.39 (1H, m (br), H-8), 4.28 (1H, br, OH), 4.17 – 4.14 (1H, m (br), H-3), 3.99 (1H, br, OH), 3.95 – 3.94 (1H, m (br), H-6), 2.81 (1H, ddd, *J* 7.4, 11.8, 11.8, H-1), 2.40 (1H, ddd, *J* 1.6, 10.8, 10.8, H-5), 2.21 (2H, t, *J* 7.4, $C\underline{H}_2CH_2CH_3$), 2.20 – 2.16 (1H, m, H-7), 1.91 – 1.87 (1H, m, H-9), 1.71 (1H, dd, *J* 12.5, 12.5, H-9'), 1.67 (1H, dd, *J* 12.6, 12.6, H-7'), 1.65 – 1.57 (2H, m, $CH_2C\underline{H}_2CH_3$), 1.56 – 1.54 (2H, m, H-2, H-4), 1.19 (1H, ddd, *J* 2.6, 13.8, 13.8, H-2'), 1.07 (9H, s, $C(CH_3)_3$), 1.07 (3H, s, H-11), 1.04 (3H, d, *J* 6.6, H-12), 0.91 (3H, t, *J* 7.4, $CH_2CH_2C\underline{H}_3$); δ_C (150 MHz; $CDCl_3$) 172.9 ($\underline{C}(O)CH_2$), 136.0 (*o*-Ph), 135.9 (*o*-Ph), 134.8 (*ipso*-Ph), 133.9 (*ipso*-Ph), 129.6 (*p*-Ph), 129.6 (*p*-Ph), 127.5 (*m*-Ph), 127.5 (*m*-Ph), 76.0 (C-3), 73.3 (C-10), 68.9 (C-6), 68.2 (C-8), 50.4 (C-5), 49.6 (C-1), 44.9 (C-4), 42.2 (C-9), 39.1 (C-2), 36.6 ($\underline{C}H_2CH_2CH_3$), 36.2 (C-7), 32.2 (C-11), 27.1 ($C(\underline{C}H_3)_3$), 19.5 ($\underline{C}(CH_3)_3$), 18.5 ($CH_2\underline{C}H_2CH_3$), 14.3 (C-12), 13.6 ($CH_2CH_2\underline{C}H_3$); υ_{max} (film; cm^{-1}) 3274m (br), 3071w, 2962m, 2931m, 2857m, 1733m, 1460m, 1428m, 1362m, 1306m, 1287m, 1260m, 1230m, 1184s, 1140m, 1128m, 1105s, 1074m, 1054m, 1033m, 1024m, 971m, 951m, 934m, 906, 864w, 822m, 741m, 704s, 672m; $[\alpha]_D$ +37.7 (*c*. 0.62, $CHCl_3$); found (ESI+) $[MNa]^+$ 561.3027; $C_{32}H_{46}O_5NaSi$ requires *M*, 561.3012.

31: δ_H (400 MHz; $CDCl_3$) 7.68 – 7.65 (4H, m, *o*-Ph), 7.46 – 7.34 (6H, m, *m*-Ph, *p*-Ph), 5.29 – 5.21 (1H, m, H-8), 5.15 (1H, dd (br), *J* 3.1, 7.2, H-6), 4.17 – 4.15 (1H, m (br), H-3), 3.66 (1H, br, OH), 2.82 (1H, ddd, *J* 6.8, 10.8, 12.6, H-1), 2.46 – 2.32 (2H, m, O-8-$C(O)C\underline{H}_2CH_2CH_3$), 2.27 – 2.16 (2H, m, H-5, H-7), 2.19 (2H, t, *J* 7.4, O-6-$C(O)C\underline{H}_2CH_2CH_3$), 1.90 – 1.87 (1H, m (br), H-9), 1.78 – 1.67 (4H, m, H-7', H-9', O-8-$C(O)CH_2C\underline{H}_2CH_3$), 1.64 – 1.55 (4H, m, H-2, H-4, O-6-$C(O)CH_2C\underline{H}_2CH_3$), 1.29 – 1.23 (1H, m, H-2'), 1.10 (3H, d, *J* 6.7, H-14), 1.07 (9H, s, $C(CH_3)_3$), 1.05 (3H, s, H-13), 0.99 (3H, t, *J* 7.4, O-8-$C(O)CH_2CH_2C\underline{H}_3$), 0.90 (3H, t, *J* 7.4, O-6-$C(O)CH_2CH_2C\underline{H}_3$); δ_C (100 MHz; $CDCl_3$) 172.4 (O-6-C(O)), 171.5 (O-8-C(O)), 136.0 (*o*-Ph), 135.9 (*o*-Ph), 134.7 (*ipso*-Ph), 133.7 (*ipso*-Ph), 129.6 (*p*-Ph), 127.6 (*m*-Ph), 127.5 (*m*-Ph), 75.5 (C-3), 72.5 (C-10), 71.8 (C-6), 67.3 (C-8), 49.9 (C-1), 48.3 (C-5), 45.0 (C-4), 42.7 (C-9), 39.4 (C-2), 36.5, 36.4 (O-6-$C(O)\underline{C}H_2CH_2CH_3$ and O-8-$C(O)\underline{C}H_2CH_2CH_3$), 33.8 (C-7), 31.4 (C-13), 27.1 ($C(\underline{C}H_3)_3$), 19.5 ($\underline{C}(CH_3)_3$), 18.4, 18.3 (O-6-$C(O)CH_2\underline{C}H_2CH_3$ and O-8-$C(O)CH_2\underline{C}H_2CH_3$), 14.3 (C-14), 13.6, 13.6 (O-6-$C(O)CH_2CH_2\underline{C}H_3$ and O-8-$C(O)CH_2CH_2\underline{C}H_3$); υ_{max} (film; cm^{-1}) 3557w (br), 2965s, 2933s, 1733s, 1458m, 1428m, 1382m, 1362m, 1258m, 1184s, 1105s, 1077s, 1037m, 1015m, 951w, 922w, 823m,

742m, 703s; $[\alpha]_D$ +35.4 (*c*. 0.42, $CHCl_3$); found (ESI+) $[MNa]^+$ 631.3411; $C_{36}H_{52}O_6NaSi$ requires *M*, 631.3431.



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Malcolm Tait
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PROCNO 1

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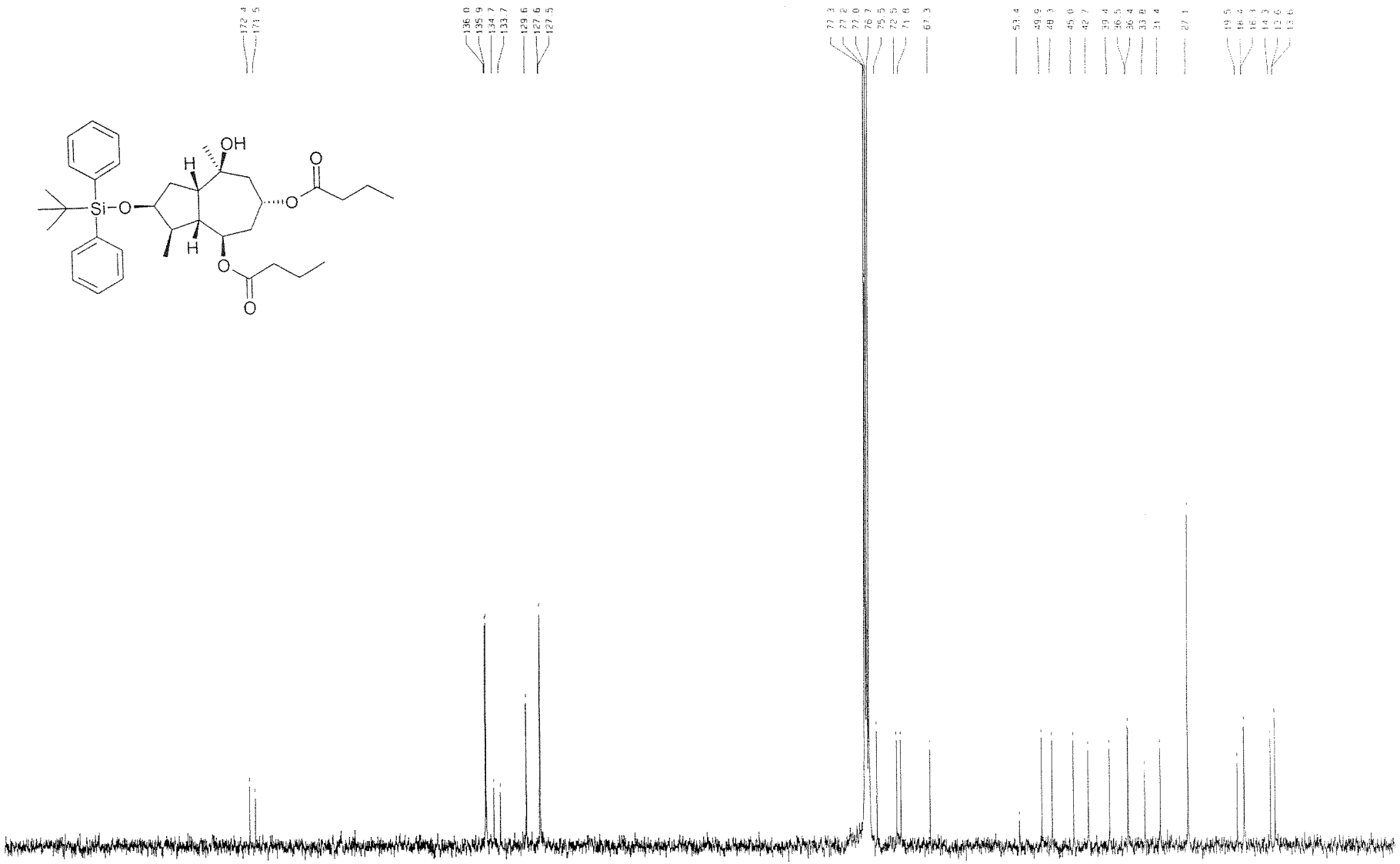

989806
GSKMT2/086/A2
Malcolm Teit
13C
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Position 6

Current Data Parameters
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EXPNO 12
PROCNO 1

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PL12 21.00 dB
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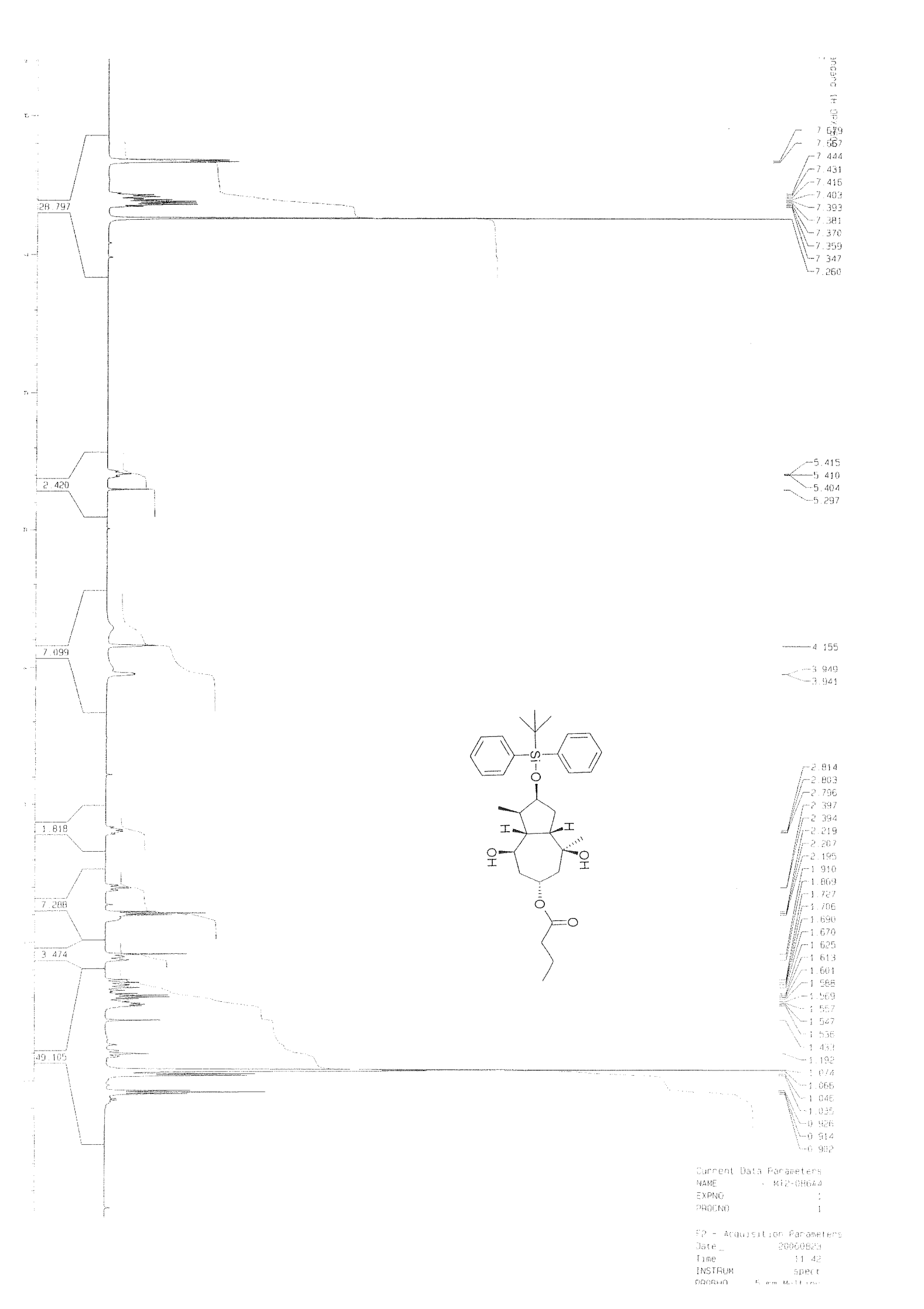
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PROCNO 1
F2 - Acquisition Parameters
Date_ 20060823
Time 11.42
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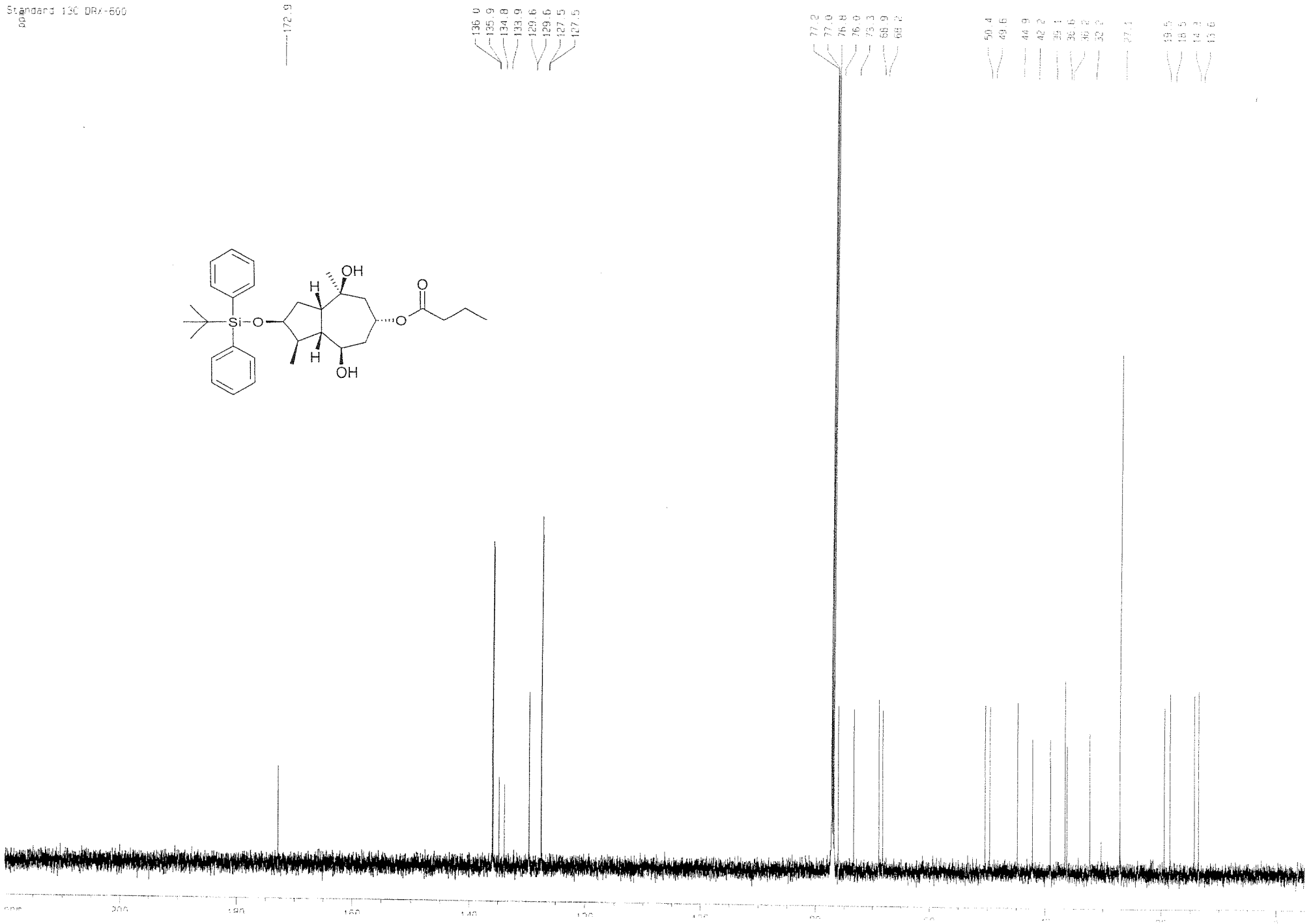
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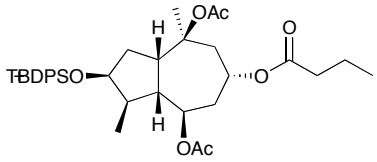
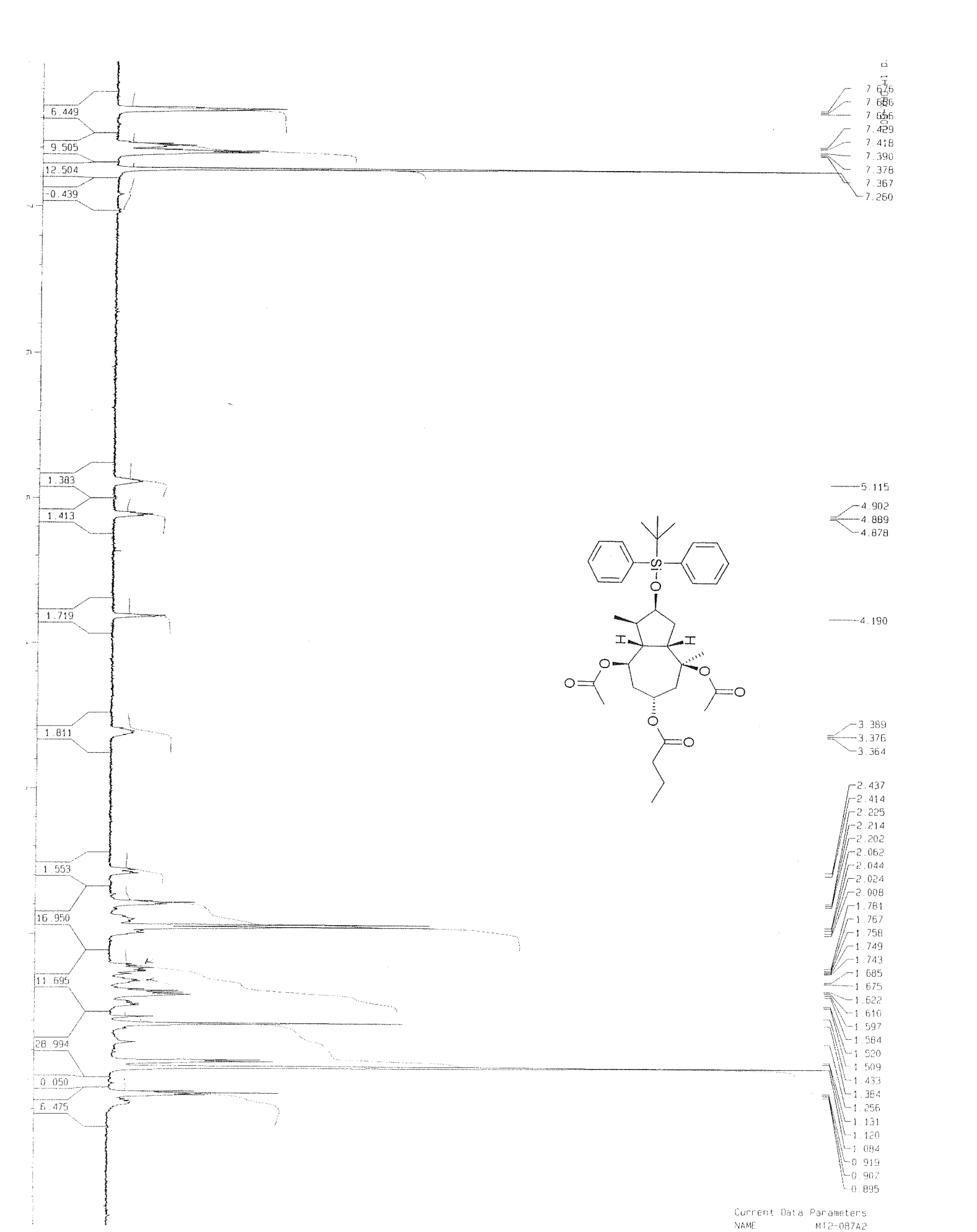


33

***Bis*-acetate 33:** *p*-Toluenesulfonic acid (2 granules) was added to a solution of diol **32** (63.9 mg, 0.119 mmol) in neat isopropenyl acetate (1.6 mL) and the mixture stirred for 16 hours at room temperature. After this time the solution was quenched with aqueous ammonium chloride (10 mL) and extracted with EtOAc (4 × 20 mL). The combined organics were dried ($MgSO_4$) and concentrated *in vacuo* to a yellow oil. This was purified by flash chromatography (SiO_2, Et_2O/petrol ether, 1:4) to yield the title compound as a clear oil, 64.1 mg, 87%; δ_H (600 MHz; $CDCl_3$) 7.68 – 7.66 (4H, m, *o*-Ph), 7.43 – 7.37 (6H, m, *m*-Ph, *p*-Ph), 5.14 – 5.09 (1H, m (br), H-8), 4.90 – 4.88 (1H, m (br), H-6), 4.20 – 4.17 (1H, m (br), H-3), 3.41 – 3.36 (1H, m (br), H-1), 2.43 (1H, dd, *J* 4.4, 13.8, H-9), 2.21 (2H, t (br), *J* 6.9, $C\underline{H}_2CH_2CH_3$), 2.12 – 2.06 (1H, m, H-7), 2.06, 2.04 (6H, 2 × s, O-6-C(O)CH_3 and O-10-C(O)CH_3), 2.04 – 2.01 (1H, m, H-5), 1.79 – 1.73 (2H, m, H-7', H-9'), 1.70 – 1.65 (1H, m, H-4), 1.64 – 1.58 (2H, m, $CH_2C\underline{H}_2CH_3$), 1.53 (1H, dd, *J* 6.8, 11.8, H-2), 1.41 – 1.34 (1H, m, H-2'), 1.38 (3H, s, H-13), 1.13 (3H, d, *J* 6.7, H-14), 1.09 (9H, s, $C(CH_3)_3$), 0.91 (3H, t, *J* 7.3, $CH_2CH_2C\underline{H}_3$); δ_C (150 MHz; $CDCl_3$) δ 172.7 (O-8-C(O)), 170.1 (O-6-C(O), O-10-C(O)), 136.0 (*o*-Ph), 135.9 (*o*-Ph), 134.7 (*ipso*-Ph), 133.7 (*ipso*-Ph), 129.6 (*p*-Ph), 127.6 (*m*-Ph), 127.5 (*m*-Ph), 83.8 (C-10), 74.3 (C-3), 71.8 (C-6), 67.3 (C-8), 50.1 (C-5), 45.7 (C-1), 45.1 (C-4), 39.2 (C-9), 37.8 (C-2), 36.7 (C-7), 36.4 ($\underline{C}H_2CH_2CH_3$), 27.5 (C-13), 27.1 ($C(\underline{C}H_3)_3$), 22.6, 21.4 (O-6-C(O)$\underline{C}H_3$ and O-10-C(O)$\underline{C}H_3$), 19.4 ($\underline{C}(CH_3)_3$), 18.3 ($CH_2\underline{C}H_2CH_3$), 15.2 (C-14), 13.6 ($CH_2CH_2\underline{C}H_3$); υ_{max} (film; cm^{-1}) 3663w, 2965m, 2933m, 1733s, 1457m, 1428m, 1367m, 1249s, 1181m, 1111m, 1074m, 1028m, 940w, 823w, 742w, 703m; $[\alpha]_D$ +21.1 (*c*. 0.55, $CHCl_3$); found (ESI+) $[MNa]^+$ 645.3243; $C_{36}H_{50}O_7NaSi$ requires *M*, 645.3224.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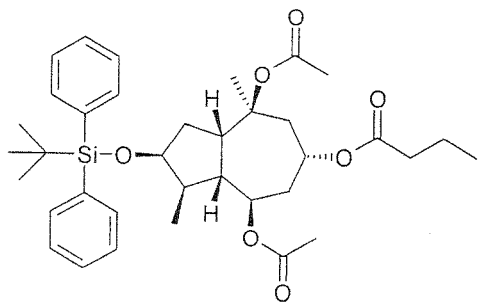
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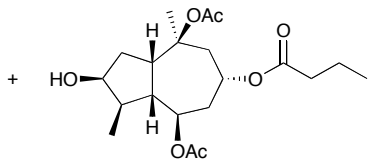
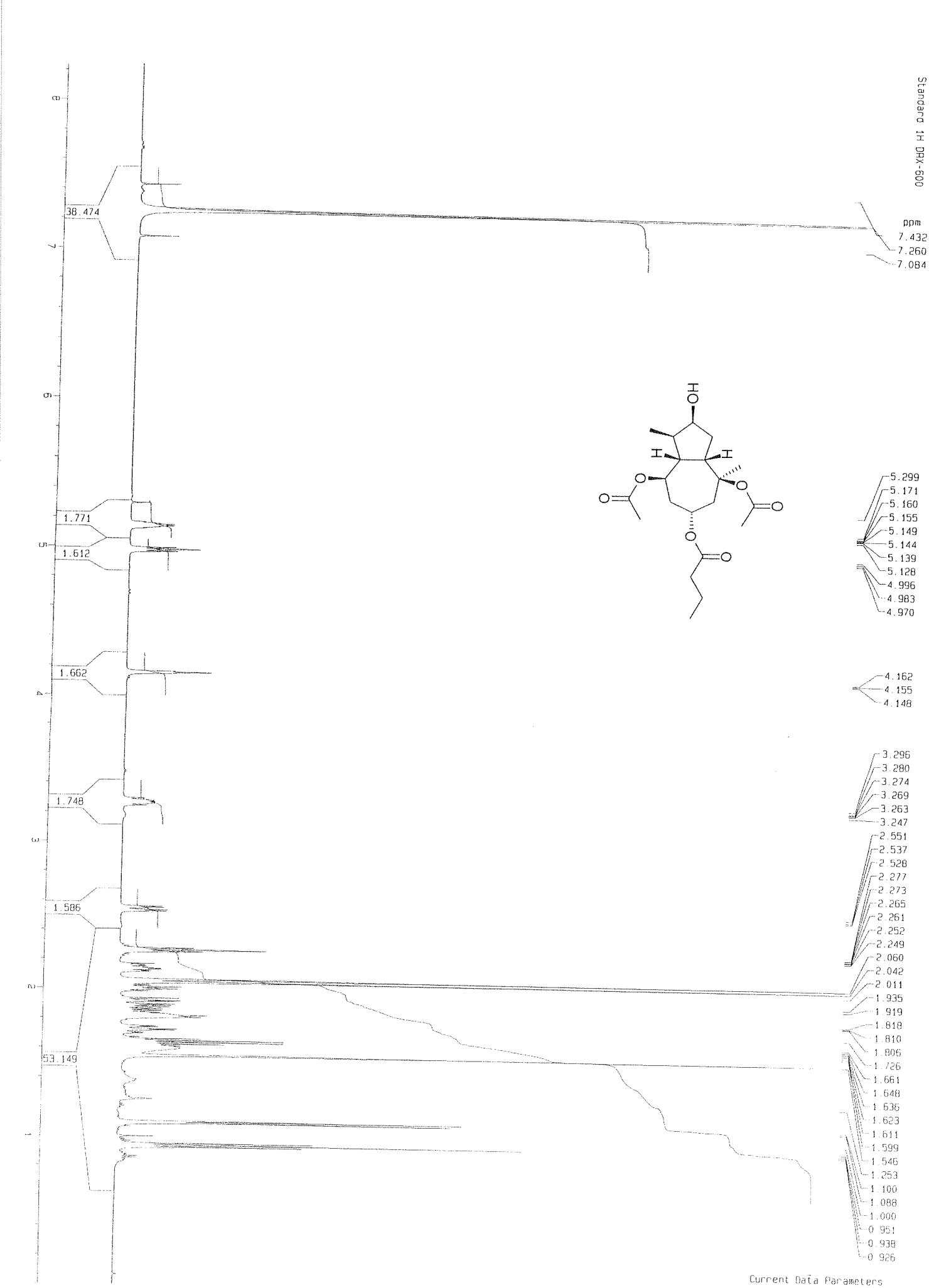
H
Si
O
O
H
O
O



34

Alcohol 34: 33 (7.6 mg, 0.0122 mmol) was dissolved in a 1 M solution of TBAF in THF (0.7 mL) and stirred at room temperature for 15.5 hours. The reaction mixture was quenched with water (5 mL) and extracted with EtOAc (4 × 5 mL). The combined organics were washed with brine (5 mL), dried ($MgSO_4$) and concentrated *in vacuo* to a brown oil. This was purified by flash chromatography (SiO_2, EtOAc/petrol ether, 1:3 to 1:1) to yield the title compound as a clear oil, 3.5 mg, 75%; δ_H (600 MHz; $CDCl_3$) 5.17 – 5.13 (1H, m, H-8), 4.98 (1H, dd, *J* 7.9, 7.9 H-6), 4.16 – 4.15 (1H, m (br), H-3), 3.27 (1H, ddd, *J* 3.8, 9.1, 16.0, H-1), 2.54 (1H, dd, *J* 5.3, 14.2, H-9), 2.26 (2H, ddd, *J* 2.2, 7.5, 7.5, C$\underline{H}_2CH_2CH_3$), 2.17 – 2.12 (1H, m, H-7), 2.06, 2.04 (6H, two s, O-6-C(O)CH_3/O-10-C(O)CH_3), 1.99 (1H, dd (br), *J* 7.2, 16.4, H-5), 1.92 (1H, dd, *J* 9.9, 14.2, H-9'), 1.87 (1H, dd, *J* 6.8, 14.6, H-7'), 1.83 – 1.81 (2H, m, H-2, H-4), 1.72 (1H, ddd, *J* 4.4, 13.0, 13.0, H-2'), 1.66 – 1.60 (2H, m, $CH_2C\underline{H}_2CH_3$), 1.55 (3H, s, H-13), 1.09 (3H, d, *J* 7.0, H-14), 0.94 (3H, t, *J* 7.4, $CH_2CH_2C\underline{H}_3$); δ_C (150 MHz; $CDCl_3$) 172.7 (O-8-$\underline{C}$(O)CH_2), 170.2, 170.1 (O-6-$\underline{C}$(O)CH_3 and O-10-$\underline{C}$(O)CH_3), 83.9 (C-10), 73.0 (C-3), 71.9 (C-6), 67.3 (C-8), 49.7 (C-5), 46.1 (C-1), 44.5 (C-4), 39.1 (C-9), 37.8 (C-2), 37.0 (C-7), 36.5 ($\underline{C}H_2CH_2CH_3$), 27.4 (C-13), 22.5, 21.8 (O-6-C(O)$\underline{C}H_3$ and O-10-C(O)$\underline{C}H_3$), 18.3 ($CH_2\underline{C}H_2CH_3$), 14.2 (C-14), 13.7 ($CH_2CH_2\underline{C}H_3$); υ_{max} (film; cm^{-1}) 3483w (br), 2966m, 2932m, 2873w, 1730s, 1457m, 1371m, 1249s, 1185m, 1121m, 1088w, 1064w, 1028m, 991m, 937w; $[\alpha]_D$ +1.8 (*c*. 0.83, $CHCl_3$); found (ESI+) $[MNa]^+$ 407.2036; $C_{20}H_{32}O_7Na$ requires *M*, 407.2046.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4.983
4.970
4.162
4.155
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3.274
3.269
3.263
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2.537
2.528
2.277
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2.265
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2.252
2.249
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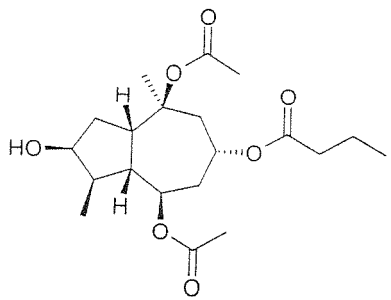
Time 20.04

Standard 13C DRX-600



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77.00
76.79
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67.34

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46.10
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39.14
37.80
36.97
36.46

27.40

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18.34

14.15
13.67

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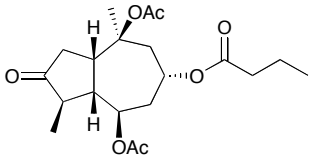
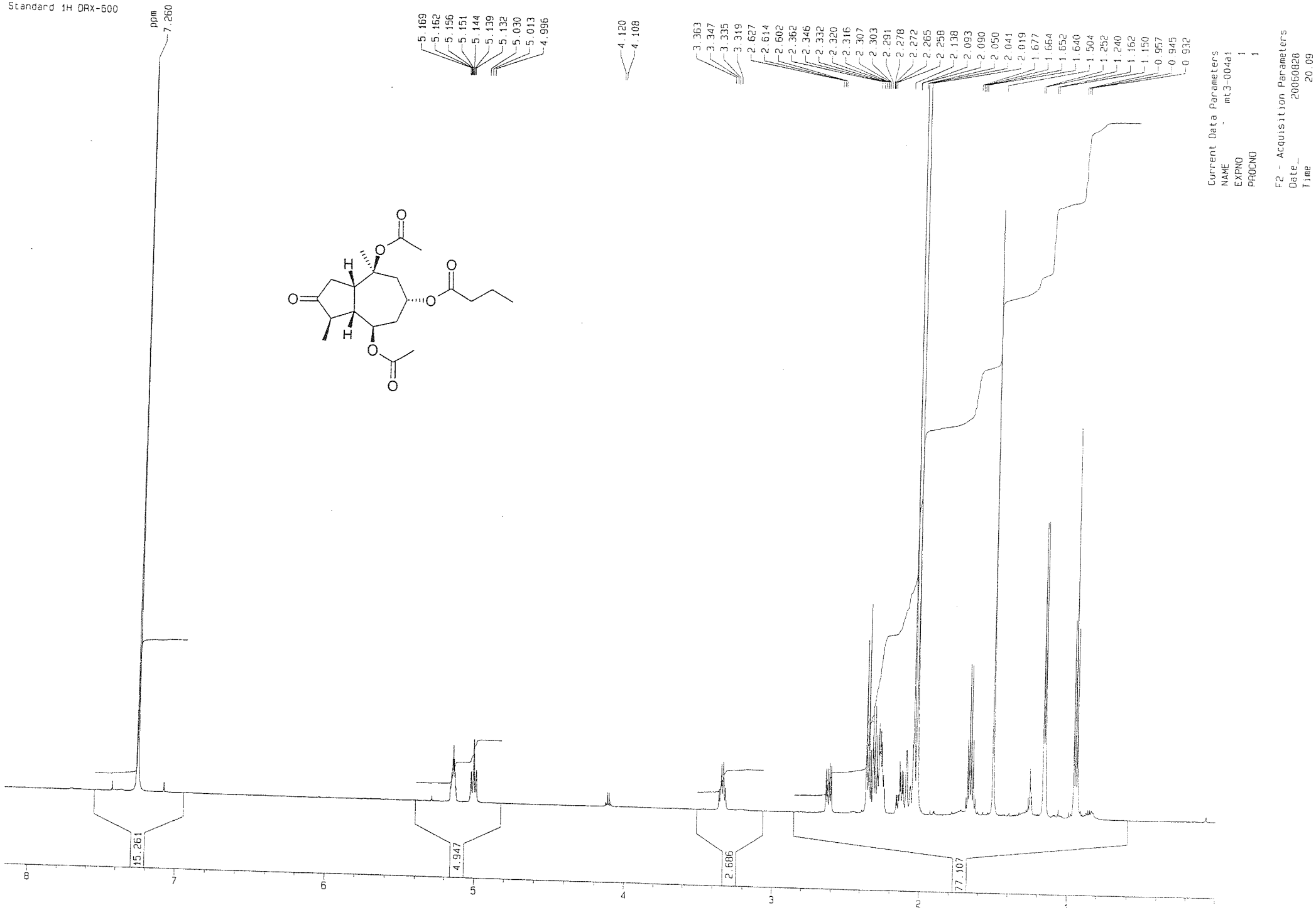


35

Ketone 35: A solution of alcohol **34** (11.4 mg, 0.0296 mmol) in CH_2Cl_2 (0.33 mL) was treated with NMO (5.2 mg, 0.0444 mmol) and pre-dried 4 Å molecular sieves (20 mg). TPAP (1.0 mg, 0.0029 mmol) was added and the dark mixture stirred for 30 minutes. After this time the solution was directly applied to a pad of silica and eluted with 1:1 ethyl acetate/petrol to yield the title compound as a clear oil, 10.5 mg, 93%; δ_H (600 MHz; $CDCl_3$) 5.17 – 5.13 (1H, m, H-8), 5.01 (1H, dd (br), *J* 10.1, 10.1, H-6), 3.34 (1H, dd (br), *J* 9.5, 16.7, H-1), 2.62 (1H, dd, *J* 6.9, 14.9, H-9), 2.36 – 2.25 (6H, m, H-2, H-4, H-5, C$\underline{H}_2$CH$_2$CH$_3$), 2.16 – 2.11 (2H, m, H-7), 2.09 – 2.02 (1H, m, H-9'), 2.04, 2.02 (6H, two s, O-6-C(O)CH$_3$/O-10-C(O)CH$_3$), 1.66 (2H, ddd, *J* 7.4, 14.9, 14.9, CH$_2$C$\underline{H}_2$CH$_3$), 1.50 (3H, s, H-13), 1.16 (3H, d, *J* 7.3, H-14), 0.94 (3H, t, *J* 7.4, CH$_2$CH$_2$C$\underline{H}_3$); δ_C (150 MHz; $CDCl_3$) 218.0 (C-3), 172.9 (O-8-$\underline{C}$(O)CH$_2$), 170.0, 169.8 (O-6-$\underline{C}$(O)CH$_3$/O-10-$\underline{C}$(O)CH$_3$), 83.9 (C-10), 70.2 (C-6), 67.2 (C-8), 50.5 (C-4), 47.5 (C-5), 42.7 (C-1), 39.5 (C-2), 38.5 (C-7), 37.9 (C-9), 36.4 ($\underline{C}$H$_2$CH$_2$CH$_3$), 26.5 (C-13), 22.3, 21.2 (O-6-C(O)$\underline{C}$H$_3$/O-10-C(O)$\underline{C}$H$_3$), 18.3 (CH$_2\underline{C}$H$_2$CH$_3$), 16.7 (C-14), 13.7 (CH$_2$CH$_2\underline{C}$H$_3$); υ_{max} (film; cm^{-1}) 2966m, 2936m, 2877w, 1733s, 1455m, 1370m, 1233s, 1172m, 1129m, 1071m, 1028m, 973w, 950w; $[\alpha]_D$ -5.9 (*c*. 0.51, $CHCl_3$); found (ESI+) $[MNa]^+$ 405.1900; $C_{20}H_{30}O_7Na$ requires *M*, 405.1889.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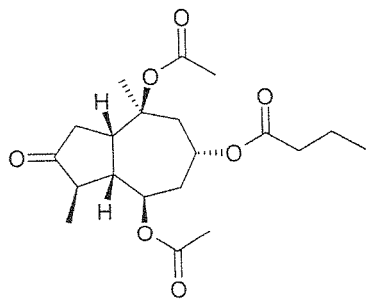
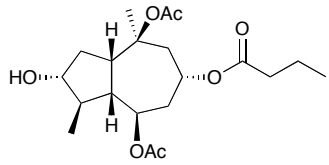
Time 20.09

Standard 13C DRX-600

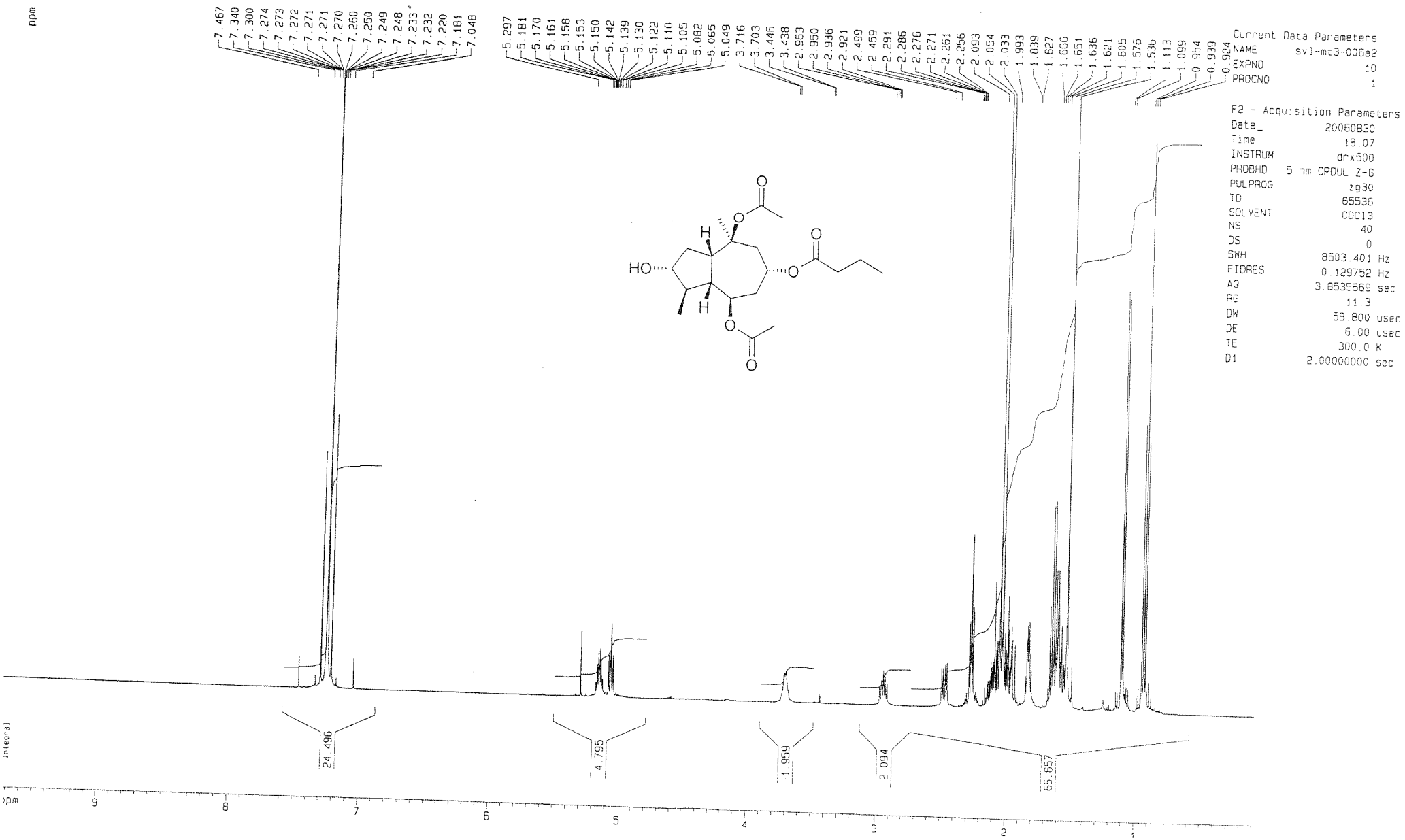




36

Alcohol 36: A solution of ketone **35** (9.5 mg, 0.0248 mmol) in MeOH (0.3 mL) at -30 ^{o}C was treated portionwise with sodium borohydride (9.4 mg, 0.248 mmol). The mixture was stirred for one hour then quenched with aqueous ammonium chloride (3 mL). After warming to room temperature the resulting solution was extracted with EtOAc (4 x 5 mL). The combined organics were washed with brine (5 mL), ($MgSO_4$) and concentrated *in vacuo* to a clear oil. This was purified by flash chromatography (SiO_2, EtOAc/petrol ether, 1:1) to yield the title compound as a clear oil, 8.4 mg, 88%, *R*:*S* ratio > 19:1; δ_H (500 MHz; $CDCl_3$) 5.18 – 5.13 (1H, m, H-8), 5.07 (1H, dd (br), *J* 8.2, 8.2, H-6), 3.76 – 3.65 (1H, m (br), H-3), 2.98 – 2.92 (1H, m, H-1), 2.48 (1H, dd, *J* 6.0, 14.3, H-9), 2.27 (2H, ddd, *J* 2.5, 7.5, 7.5, C$\underline{H}_2CH_2CH_3$), 2.17 – 1.93 (4H, m, H-2, H-7, H-9'), 2.05, 2.03 (6H, two s, O-6-C(O)CH_3/O-10-C(O)CH_3), 1.86 – 1.80 (1H, m, H-5), 1.69 – 1.54 (4H, m, H-2', H-4, $CH_2C\underline{H}_2CH_3$), 1.54 (3H, s, H-13), 1.11 (3H, d, *J* 6.9, H-14), 0.94 (3H, t, *J* 7.4, $CH_2CH_2C\underline{H}_3$); δ_C (125 MHz; $CDCl_3$) 172.9 (O-8-$\underline{C}$(O)CH_2), 170.3, 170.2 (O-6-$\underline{C}$(O)CH_3/O-10-$\underline{C}$(O)CH_3), 83.7 (C-10), 77.7 (C-3), 71.9 (C-6), 67.3 (C-8), 50.9 (C-5), 46.9 (C-4), 44.4 (C-1), 38.8 (C-9), 37.5, 37.5 (C-2/C-7), 36.4 ($\underline{C}H_2CH_2CH_3$), 27.7 (C-13), 22.5, 21.4 (O-6-C(O)$\underline{C}H_3$/O-10-C(O)$\underline{C}H_3$), 18.7 (C-14), 18.3 ($CH_2\underline{C}H_2CH_3$), 13.7 ($CH_2CH_2\underline{C}H_3$); υ_{max} (film; cm^{-1}) 3455w (br), 2966m, 2881m, 1728s, 1457w, 1371m, 1240s, 1180m, 1124w, 1067m, 1045m,1027m, 941w; $[\alpha]_D$ –23.5 (*c*. 0.38, $CHCl_3$); found (ESI+) $[MNa]^+$ 407.2043; $C_{20}H_{32}O_7Na$ requires *M*, 407.2046.

Avance 500 1H Cryo
MT3-006A2
M. Tait - SVL



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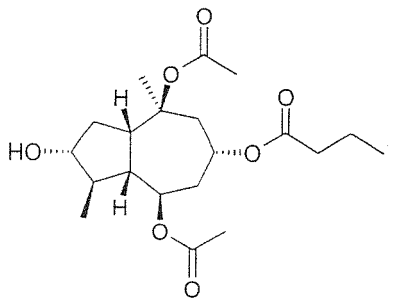
MT3-006A2
M. Tait - SVL



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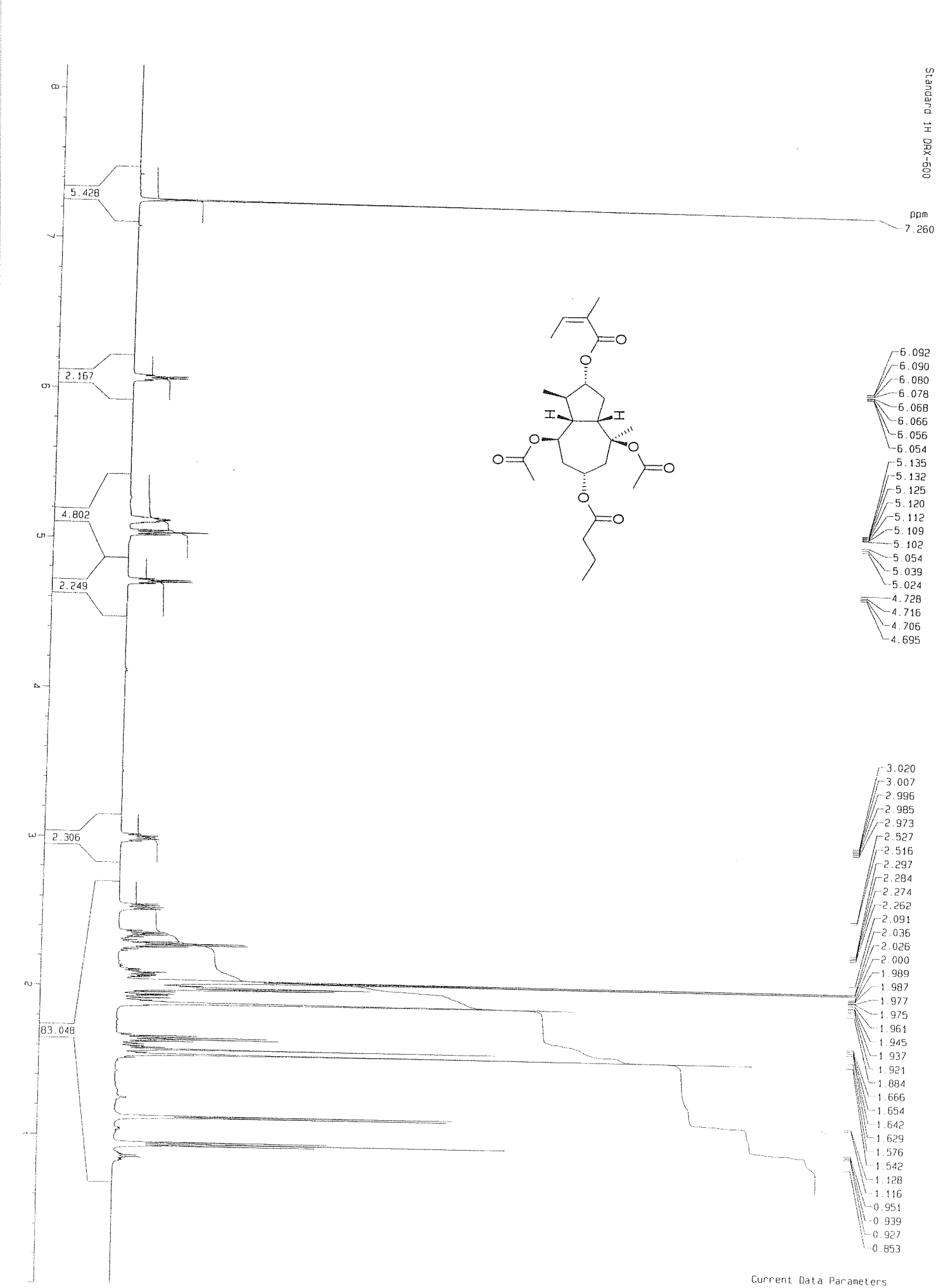
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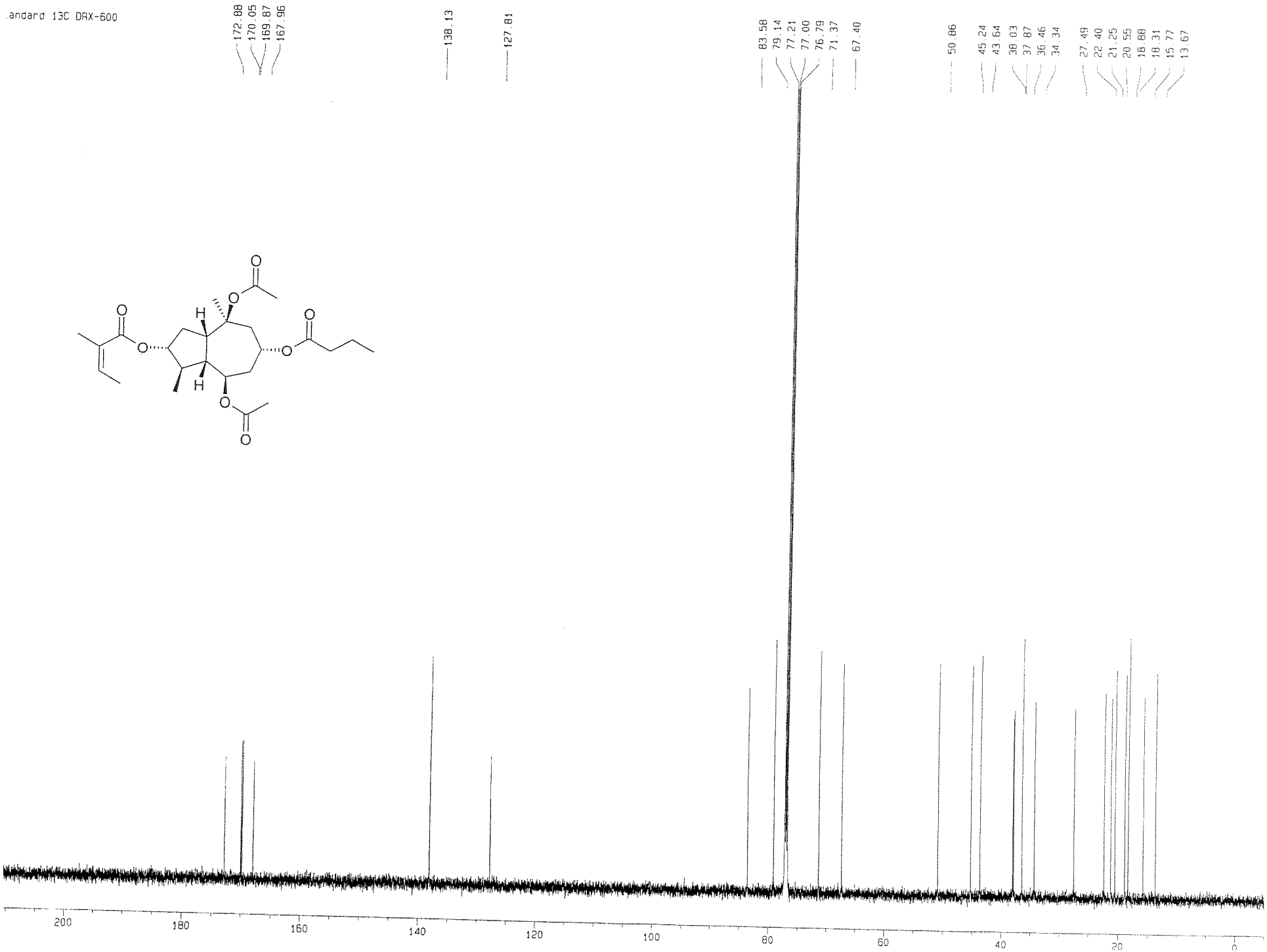
Time 18.03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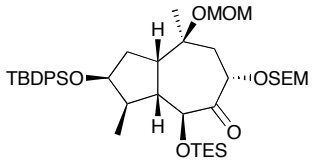
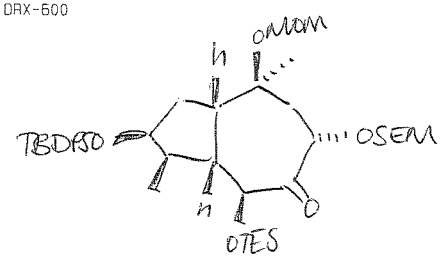
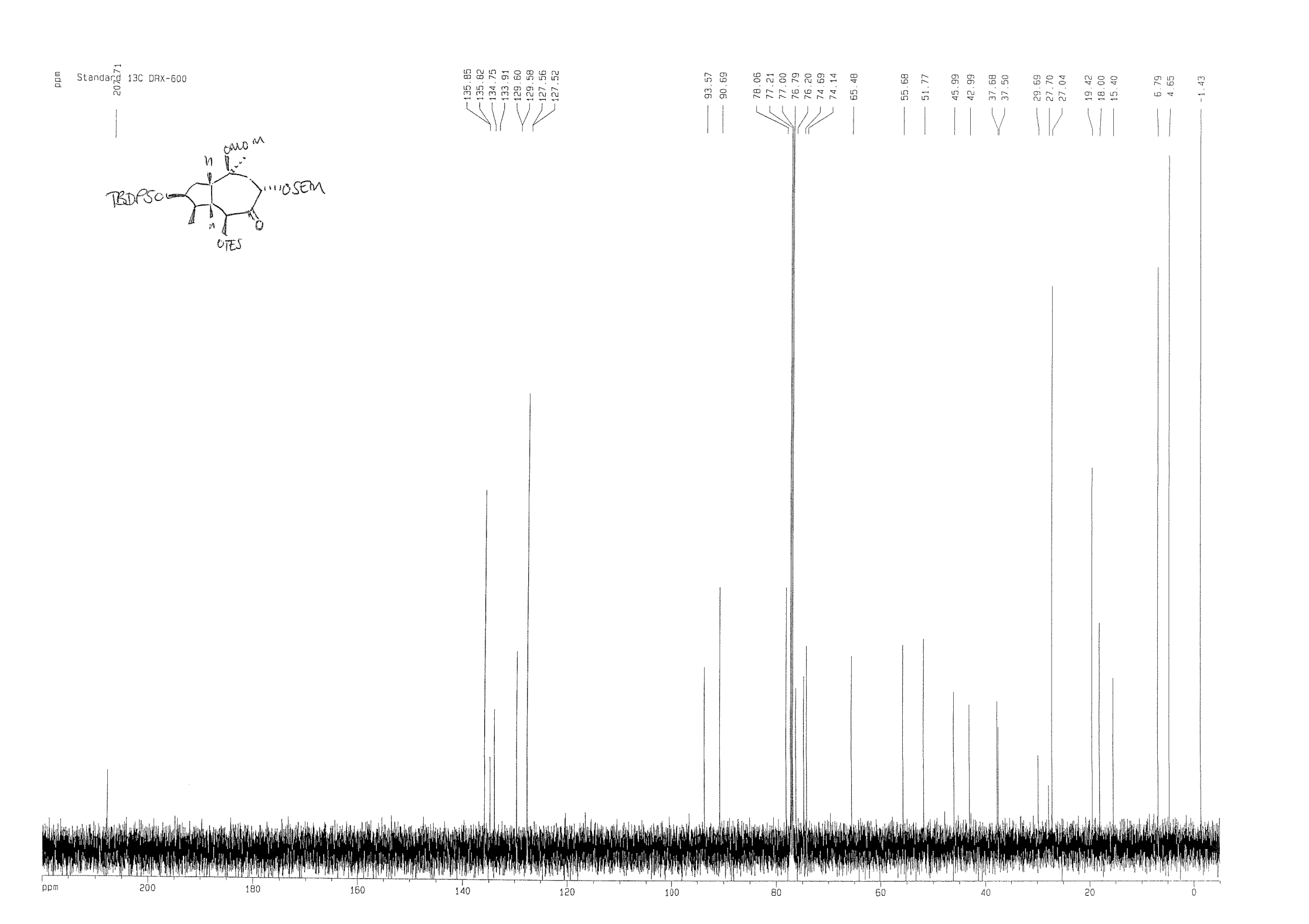


38

SEM acetal 38: Hünig's base (1.01 mL, 5.80 mmol), SEM-Cl (515 μL, 2.91 mmol) and DMAP (18.0 mg, 145 μmol) were added sequentially to a stirring solution of alcohol **12** (932 mg, 1.45 mmol) in CH_2Cl_2 (5.0 mL) at room temperature. The resulting mixture was stirred at room temperature for 18 hours, then quenched with water (100 mL) and diluted with CH_2Cl_2 (100 mL). The separated aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL) and the combined organic phases washed with brine (200 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (SiO_2, Et_2O/petrol ether, 1:19 to 1:9) afforded the diol as a colourless oil, 1.11 g, quantitative; δ_H (600 MHz; $CDCl_3$) 7.66 (4H, m, *o*-Ph), 7.41 (2H, m, *p*-Ph), 7.37 (4H, m, *m*-Ph), 4.71 (1H, d, *J* 7.3, O-10-CH_2O), 4.65 (1H, d, *J* 7.3, O-10-CH_2O), 4.63 (1H, d, *J* 6.8, O-10-CH_2O), 4.61 (1H, d, *J* 6.8, O-10-CH_2O), 4.52 (1H, dd, *J* 9.8, 7.0, H-8), 4.26 (1H, m, H-3), 4.17 (1H, d, *J* 7.8, H-6), 3.66 (1H, ddd, *J* 16.6, 9.8, 6.8, $SiCH_2C\underline{H}_2$), 3.53 (1H, ddd, *J* 16.6, 9.8, 6.6, $SiCH_2C\underline{H}_2$), 3.34 (3H, s, OCH_3), 2.88 (1H, ddd, *J* 12.7, 7.8, 7.5, H-1), 2.12 (2H, m, H-4 and H-9), 1.96 (1H, dd, *J* 12.7, 7.8, H-5), 1.67 (1H, dd, *J* 14.3, 9.8, H-9'), 1.48 (1H, m, H-2), 1.33 (1H, ddd, *J* 12.5, 12.5, 5.4, H-2'), 1.27 (3H, s, H-14), 1.14 (3H, d, *J* 7.0, H-15), 1.08 (9H, s, $C(CH_3)_3$), 0.92 (11H, m, H-17 and $Si(CH_2C\underline{H}_3)_3$), 0.55 (6H, m, $Si(C\underline{H}_2)_3$ 0.02 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 207.7 (C-7), 135.85 (*o*-Ph), 135.82 (*o*-Ph), 134.7 (*ipso*-Ph), 133. (*ipso*-Ph), 129.60 (*p*-Ph), 129.58 (*p*–Ph), 127.56 (*m*-Ph), 127.52 (*m*-Ph), 93.5 (O-8-CH_2O), 90.6 (O-10-CH_2O), 78.0 (C-10), 76.2 (C-6), 74.6 (C-8), 74.1 (C-3), 65.4 ($SiCH_2\underline{C}H_2$), 55.6 (OCH_3), 51.7 (C-5), 45.9 (C-1), 42.9 (C-4), 37.6 (C-2), 37.5 (C-9), 29.6 (C-14), 27.0 ($C(\underline{C}H_3)_3$), 19.4 ($\underline{C}(CH_3)_3$), 18.0 ($Si\underline{C}H_2CH_2$), 15.4 (C-12), 6.7 ($Si(CH_2\underline{C}H_3)_3$) 4.6 ($Si(\underline{C}H_2)_3$), –1.4 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 2954 (C-H), 2878 (C-H), 1726 (C=O), 1460 (Ar), 1428 (Ar), 835 ($Si(CH_3)_3$); $[\alpha]_D$ +4.06 (*c*. 1.33, $CHCl_3$); found (ESI+) $[MNa]^+$ 793.4297; $C_{42}H_{70}O_7Si_3Na$ requires *M*, 793.4327.

sa4031
Standard 1H DRX-600

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20
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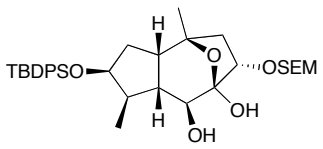
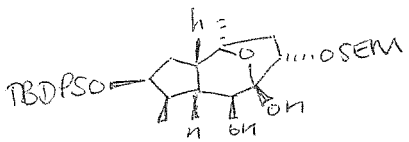


39

Lactol 39: Amberlyst 15 (10 mg) was added to a stirring suspension of the MOM ether **38** (50.9 mg, 66.0 μmol) and 4 Å molecular sieves (100 mg) in MeOH (1.0 mL). After stirring at room temperature for 4 hours, the reaction was quenched with sodium bicarbonate solution (5 mL) and filtered then the solid was washed with H_2O (10 mL) and Et_2O (20 mL). The separated aqueous phase was extracted with Et_2O (2 × 20 mL) and the combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (SiO_2, Et_2O/petrol ether, 1:4) afforded the acetal as a colourless oil, 23 mg, 57%; δ_H (600 MHz; $CDCl_3$) 7.67 (4H, m, *o*-Ph), 7.44 (2H, *p*-Ph), 7.38 (4H, *m*-Ph), 4.71 (1H, d, *J* 6.6, O-8-CH_2O), 4.64 (1H, d, *J* 6.6, O-8-CH_2O), 4.55 (1H, br s, OH), 4.21 (1H, dd, *J* 4.0, 3.9, H-3), 4.18 (1H, dd, *J* 11.7, 4.8, H-8), 3.79 (1H, d, *J* 8.1, H-6), 3.56 (2H, t, *J* 8.4, Si$CH_2C\underline{H}_2$), 2.44-2.37 (2H, m, H-1 and H-5), 2.25 (1H, d, *J* 8.1, OH), 2.10 (1H, m, H-4), 1.87 (1H, dd, *J* 13.9, 11.7, H-9), 1.73 (1H, dd, *J* 14.6, 8.7, H-2), 1.65 (1H, dd, *J* 13.9, 4.8, H-9'), 1.12 (3H, s, H-11), 1.09 (9H, s, $C(CH_3)_3$), 1.08 (1H, m, H-2') 1.07 (3H, d, *J* 7.0, H-15), 0.87 (2H, m, Si$C\underline{H}_2CH_2$), 0.00 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 135.9 (*o*-Ph), 135.8 (*o*-Ph), 134.95 (*ipso*-Ph), 133.91 (*ipso*-Ph), 129.58 (*p*-Ph), 129.54 (*p*-Ph), 127.5 (*m*-Ph), 127.4 (*m*-Ph), 102.8 (C-7), 94.8 (OCH_2O), 82.2 (C-10), 79.5 (C-8), 77.4 (C-3), 68.6 (C-6), 65.6 ($SiCH_2\underline{C}H_2$), 50.4 (C-5), 42.4 (C-1), 42.3 (C-4), 36.3 (C-2), 36.2 (C-9), 27.1 (C-14), 27.0 ($C(\underline{C}H_3)_3$), 19.5 ($\underline{C}(CH_3)_3$), 18.0 ($Si\underline{C}H_2CH_2$), 13.0 (C-15), –1.5 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 3426 (br OH), 2929 (C-H), 2857 (C-H), 1589 (w Ar), 834 ($Si(CH_3)_3$); $[\alpha]_D$ +27.8 (*c*. 1.19, $CHCl_3$); found (ESI+) $[MNa]^+$ 635.3185; $C_{34}H_{52}O_6Si_2Na$ requires *M*, 635.3200.

Standard 1H DRX-600
sa4054



Standard 13C DRX-600
sa4054

ppm

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133.91
129.58
129.54
127.55
127.47
102.89
94.85
82.27
79.50
77.43
77.21
77.00
76.79
68.60
65.56
50.44
42.49
42.36
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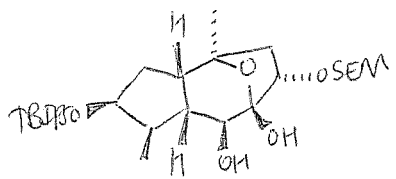
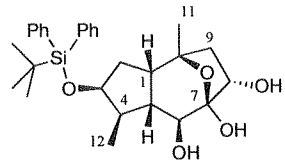
27.04
19.52
18.03
13.05
-1.47

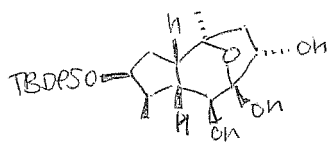


ppm 200 180 160 140 120 100 80 60 40 20 0



The hydroxy ketone **12** (39.2 mg, 61.2 μmol) was stirred in MeOH (300 μL) with 4 Å molecular sieves (50 mg) for 5 minutes. Amberlyst 15 (15 mg) was added and the resulting mixture was stirred at room temperature for 16 hours, quenched with sodium bicarbonate (3 mL) and filtered. The solid was washed with H_2O (15 mL) and Et_2O (20 mL) and the separated aqueous phase was back-extracted with Et_2O (2 × 20 mL). Combined organic phases were washed with brine (50 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford the title compound, 30.9 mg. (This compound was also formed during the formation of **39** if the reaction was left for more than 4 hours.) δ_H (600 MHz; $CDCl_3$) 7.67 (4H, m, *o*-Ph), 7.44 (2H, m, *p*-Ph), 7.38 (4H, m, *m*-Ph), 4.81 (1H, br s, OH), 4.33 (1H, dd, *J* 12.0, 4.9, H-8), 4.23 (1H, m, H-3), 3.85 (1H, d, *J* 4.6, H-6), 2.54 (1H, br s, OH), 2.44-2.39 (2H, m, OH and H-1), 2.36 (1H, dd, *J* 12.9, 10.4, H–5), 2.14 (1H, m, H-4), 1.88 (1H, dd, *J* 14.4, 12.0, H-9), 1.72 (1H, dd, *J* 14.7, 7.0, H-2), 1.62 (1H, dd, *J* 14.4, 4.9, H-9'), 1.11 (3H, s, H-11), 1.09 (9H, s, $C(CH_3)_3$), 1.08 (1H, m, H-2'), 1.07 (3H, d, *J* 7.1, H-12); δ_C (150 MHz; $CDCl_3$) 135.9 (*o*-Ph), 135.8 (*o*–Ph), 134.9 (*ipso*-Ph), 133.9 (*ipso*-Ph), 129.58 (*p*-Ph), 129.53 (*p*-Ph), 127.5 (*m*-Ph), 127.4 (*m*-Ph), 103.3 (C-7), 82.1 (C-10), 77.3 (C-3), 74.6 (C-8), 68.2 (C-6), 50.5 (C-5), 42.6 (C-1), 42.4 (C-4), 37.1 (C-9), 36.3 (C-2), 27.1 (C-11), 27.0 ($C(\underline{C}H_3)_3$), 19.5 ($\underline{C}(CH_3)_3$), 13.0 (C-12); ν_{max} (film; cm^{-1}) 3411 (br OH), 2960 (C-H), 2930 (C-H), 2857 (C-H), 1589 (w Ar); $[\alpha]_D$ +44.9 (*c*. 0.63, $CHCl_3$); found (ESI+) $[MNa]^+$ 505.2389; $C_{28}H_{38}O_5SiNa$ requires *M,* 505.2386.

Standard 1H ORX-600
sa4043



Standard 13C DRX-600
sa4043

ppm

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134.96
133.92
129.58
129.53
127.55
127.47
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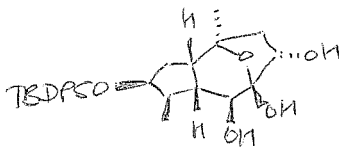
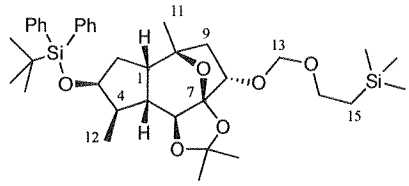
37.15
36.35
27.10
27.04
19.51
11.09

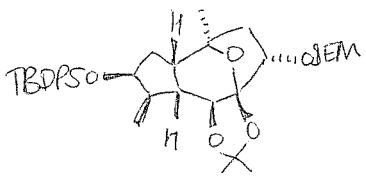


ppm 200 180 160 140 120 100 80 60 40 20 0



Amberlyst 15 (10 mg) was added to a stirring suspension of the MOM ether **13** (45.3 mg, 58.7 μmol) and 4 Å molecular sieves (100 mg) in acetone (1.0 mL). The mixture was stirred at room temperature for 50 minutes then quenched with sodium bicarbonate solution (5 mL) and filtered. The solid was washed with H_2O (10 mL) and Et_2O (20 mL). The separated aqueous phase was extracted with Et_2O (2 × 20 mL) and the combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (SiO_2, Et_2O/petrol ether, 1:19) afforded the acetal as a colourless oil, 28 mg, 78%; δ_H (600 MHz; $CDCl_3$) 7.67 (4H, m, *o*-Ph), 7.43 (2H, *p*-Ph), 7.38 (4H, m, *m*-Ph), 4.72 (1H, d, *J* 6.7, H-13), 4.65 (1H, d, *J* 6.7, H–13'), 4.17 (2H, m, H-3 and H-8), 4.09 (1H, s, H-6), 3.57 (2H, t, *J* 8.5, H–14), 2.61 (1H, m, H-1), 2.43 (1H, dd, *J* 12.0, 11.8, H-5), 1.81 (1H, dd, *J* 13.5, 10.7, H-9), 1.66 (2H, m, H-2 and H-4), 1.47 (3H, s, $C(C\underline{H}_3)(CH_3)$), 1.35 (3H, s, $(CH_3)(C\underline{H}_3)$) 1.34 (1H, m, H-9'), 1.14 (3H, s, H–11), 1.13 (3H, d, *J* 6.6, H-12), 1.08 (10H, m, H-2' and $C(CH_3)_3$), 0.89 (2H, m, H-15), 0.02 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 136.0 (*o*-Ph), 135.8 (*o*-Ph), 134.8 (*ipso*-Ph), 133.9 (*ipso*-Ph), 129.55 (*p*-Ph), 129.52 (*p*-Ph), 127.5 (*m*-Ph), 127.4 (*m*-Ph), 109.2 ($\underline{C}(CH_3)_2$), 107.1 (C-7), 94.2 (C-13), 78.9 (C-10), 76.7 (C-3), 76.2 (C-6), 73.8 (C-8), 65.2 (C–14), 45.4 (C-4), 45.1 (C-5), 43.8 (C-1), 35.8 (C-2), 35.3 (C-9), 27.8 and 27.7 (C-11 and $C(\underline{C}H_3)(CH_3)$), 27.0 ($C(\underline{C}H_3)_3$), 25.8 ($C(CH_3)(\underline{C}H_3)$), 19.4 ($\underline{C}(CH_3)_3$), 18.0 (C-15), 13.2 (C-12), -1.4 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 2955 (C-H), 2928 (C-H), 2856 (C-H), 1590 (w Ar), 835 ($Si(CH_3)_3$); $[\alpha]_D$ +29.2 (*c*. 0.73, $CHCl_3$); found (ESI+) $[MNa]^+$ 675.3469; $C_{37}H_{56}O_6Si_2Na$ requires 675.3513.

Standard 1H DRX-600
sa4053



Standard 13C DRX-600
sa4053

ppm

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76.29
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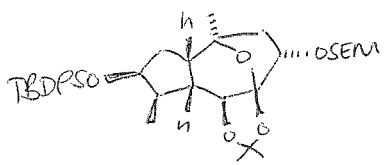
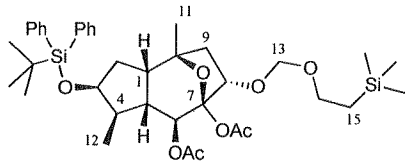
18.03
13.24
-1.47

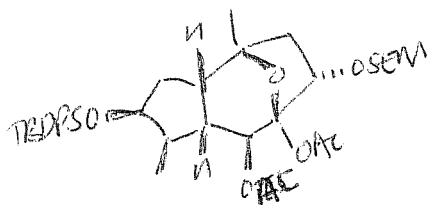


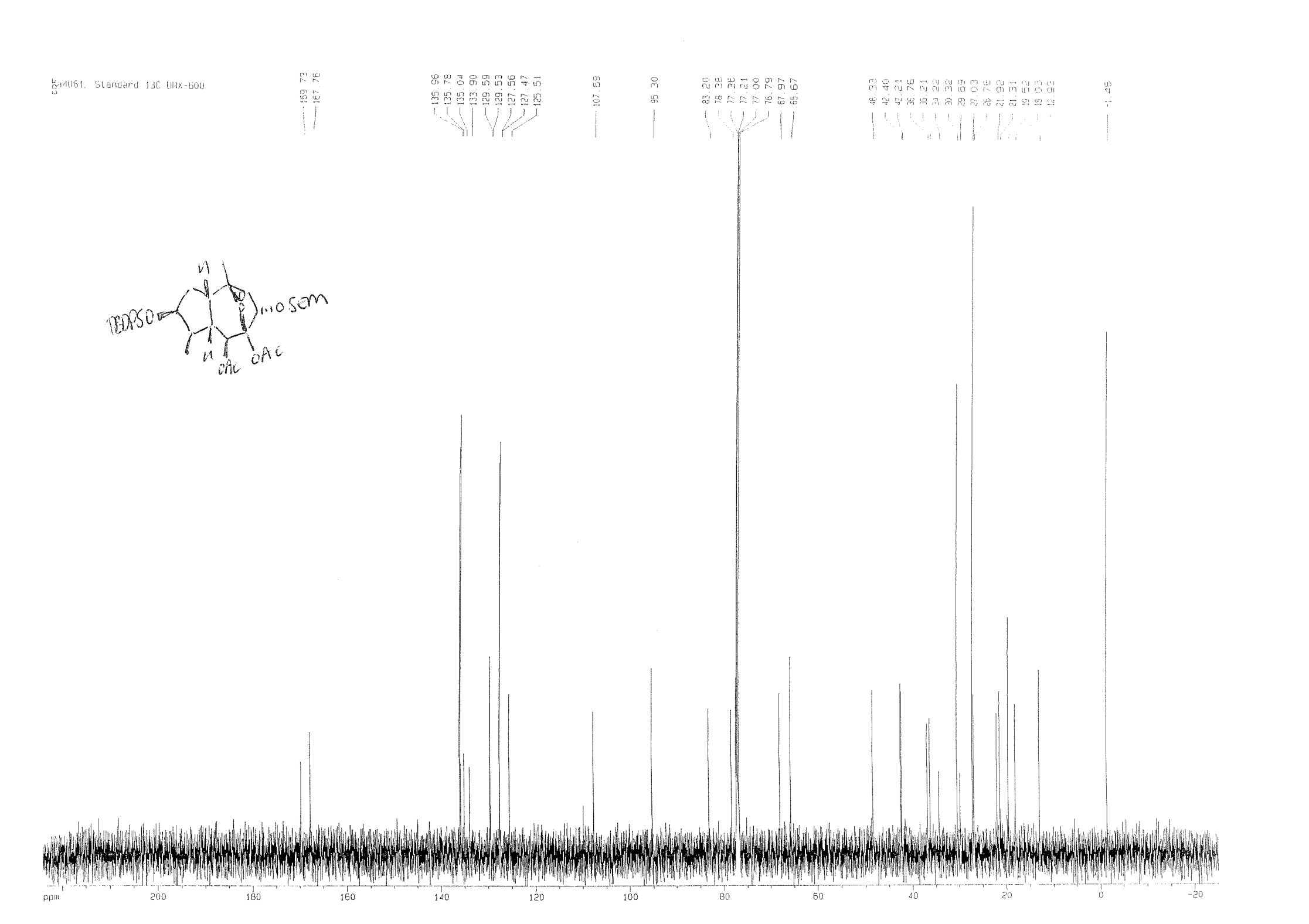
ppm 200 180 160 140 120 100 80 60 40 20 0 -20



Acetyl chloride (42.2 μL, 594 μmol) was added to a stirring solution of lactol **39** (36.4 mg, 59.4 μmol) and Et_3N (164.9 μL, 1.19 mmol) in CH_2Cl_2 (200 μL). The resulting mixture was stirred at room temperature for 1 hour then quenched with saturated ammonium chloride solution (15 mL), diluted with H_2O (5 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with brine (50 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography (SiO_2, Et_2O/petrol ether, 1:4) afforded the *bis*-acetate as a colourless oil, 21 mg, 51%; δ_H (600 MHz; $CDCl_3$) 7.67 (4H, m, *o*-Ph), 7.44 (2H, m, *p*-Ph), 7.38 (4H, m, *m*-Ph), 5.58 (1H, s, H-6), 4.79 (1H, m, H-8), 4.63 (2H, m, H-13), 4.21 (1H, br s, H-3), 3.57 (2H, m, H-14), 2.58 (1H, m, H-1), 2.22 (2H, m, H-4 and H-5), 2.16 (3H, s, CH_3C=O), 2.13 (3H, s, CH_3'C=O), 2.12 (1H, m, H-9), 1.76 (2H, m, H-2 and H-9'), 1.17 (3H, s, H-11), 1.13 (3H, d, *J* 7.0, H-12), 1.09 (10H, s, $C(CH_3)_3$ and H-2' underneath), 0.87 (2H, m, H-15), 0.02 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 169.7 (C=O), 167.7 (C'=O), 135.9 (*o*–Ph), 135.7 (*o*-Ph), 135.0 (*ipso*-Ph), 133.9 (*ipso*-Ph), 129.59 (*p*-Ph), 129.53 (*p*-Ph), 127.5(*m*–Ph), 127.4 (*m*-Ph), 107.6 (C-7), 95.3 (C-13), 83.2 (C-10), 78.3 (C-8), 77.3 (C-3), 67.9 (C-6), 65.6 (C-14), 48.3 (C-5), 42.4 (C-1), 42.3 (C-4), 36.7 (C-9), 36.2 (C-2), 27.0 ($C(\underline{C}H_3)_3$), 26.8 (C-11), 21.9 ($\underline{C}H_3C$=O), 21.3 ($\underline{C}'H_3C$=O), 19.5 ($\underline{C}(CH_3)_3$), 18.0 (C-15), 12.9 (C-12), –1.5 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 2954 (C-H), 1746 (C=O), 836 ($Si(CH_3)_3$); $[\alpha]_D$ +31.2 (*c*. 1.05, $CHCl_3$); found (ESI+) $[MNa]^+$ 719.3416; $C_{38}H_{56}O_8Si_2Na$ requires 719.3411.

sa4061, Standard 1H UNX-600

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129.59
129.53
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107.59
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1.45
TBDPSO
H
H
OAc
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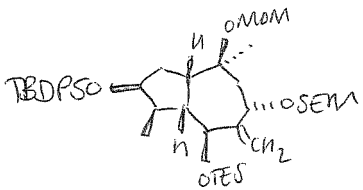
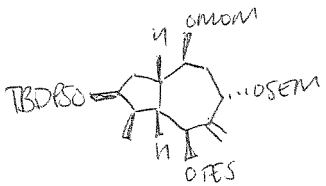
SA4033, Standard 1H DRX-600



SA40033, scan : 8k, d1 : 4 sec, Standard 13C DRX-600



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72.74
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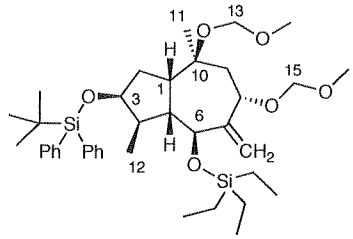
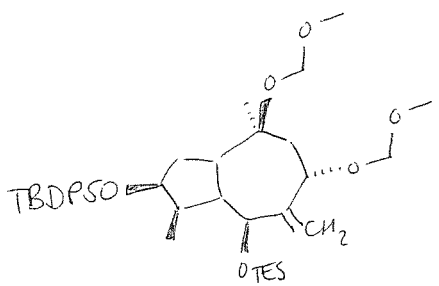
5.80
4.77
-1.42

ppm 200 180 160 140 120 100 80 60 40 20 0



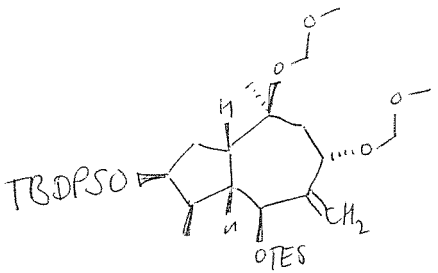
KHMDS (131 μL, 65.4 μmol, 0.5 M in PhMe) was added drop-wise to a stirring suspension of methyltriphenylphosphonium bromide (24.3 mg, 68.1 μmol) in THF (200 μL). The resulting yellow mixture was stirred at rt for 1 hour then cooled to –78 °C. The ketone **13** (30 mg, 38.9 μmol) was added drop-wise as a solution of THF (200 μL) and the mixture warmed to room temperature with stirring for 1 hour. The reaction was quenched with saturated ammonium chloride solution (20 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography (SiO_2, Et_2O/petrol ether, 1:19) afforded the title compound as a colourless oil, 9.8 mg, 33%; δ_H (600 MHz; $CDCl_3$) 7.67 (4H, m, *o*-Ph), 7.42 (2H, m, *p*-Ph), 7.37 (4H, m, *m*-Ph), 5.14 (1H, s, =CH), 5.02 (1H, s, =CH'), 4.71 (1H, d, *J* 7.2, H-13), 4.67 (1H, d, *J* 7.2, H-13'), 4.66 (1H, d, *J* 6.6, H-15), 4.44 (1H, d, *J* 6.6, H-15'), 4.43 (1H, m, H-8), 4.22 (1H, m, H-3), 3.95 (1H, d, *J* 7.7, H-6), 3.36 (3H, s, H–14), 3.35 (3H, s, H–16), 2.82 (1H, ddd, *J* 12.3, 7.7, 7.6, H-1), 2.07 (1H, m, H-4), 2.02 (1H, dd, *J* 14.2, 6.2, H-9), 1.85 (1H, m, H–5), 1.63 (1H, dd, *J* 14.2, 10.2, H-9'), 1.44 (1H, m, H-2), 1.34 (1H, m, H-2'), 1.27 (3H, s, H–11), 1.13 (3H, d, *J* 7.1, H-12), 1.08 (9H, s, $SiC(CH_3)_3$), 0.91 (9H, t, *J* 7.9, $Si(CH_2\underline{C}H_3)_3$), 0.50 (6H, q, *J* 7.9, $Si(\underline{C}H_2CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 150.1 (C–7), 135.88 (*o*–Ph), 135.84 (*o*–Ph), 134.9 (*ipso*-Ph), 134.1 (*ipso*-Ph), 129.49 (*p*-Ph), 129.46 (*p*-Ph), 127.48 (*m*-Ph), 127.44 (*m*-Ph), 108.1 ($=CH_2$), 92.9 (C-15), 90.8 (C-13), 74.2 (C-3), 72.8 and 72.7 (C-6 and C-8), 55.6 (C-14 and C-5), 55.2 (C-16), 45.4 (C-1), 43.6 (C-4), 39.8 (C–9), 38.1 (C-2), 29.6 (C-11), 27.0 ($C(\underline{C}H_3)_3$), 19.4 ($\underline{C}(CH_3)_3$), 15.7 (C-12), 6.6 ($Si(CH_2\underline{C}H_3)_3$), 4.7 ($Si(\underline{C}H_2CH_3)_3$); ν_{max} (film; cm^{-1}) 2929 (C-H), 823 ($Si(CH_3)_3$); $[\alpha]_D$ –17.1 (*c*. 0.48, $CHCl_3$); found (ESI+) $[MNa]^+$ 705.4009; $C_{39}H_{62}O_6Si_2Na$ requires *M*, 705.3983.

sa4084
Standard 1H DRX-600



ppm Standard 13C DRX-600

Sa4084



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134.16
129.49
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127.48
127.44
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90.89
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29.67
28.71
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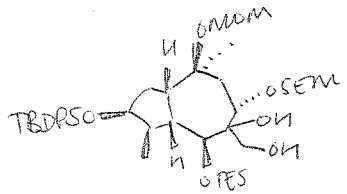
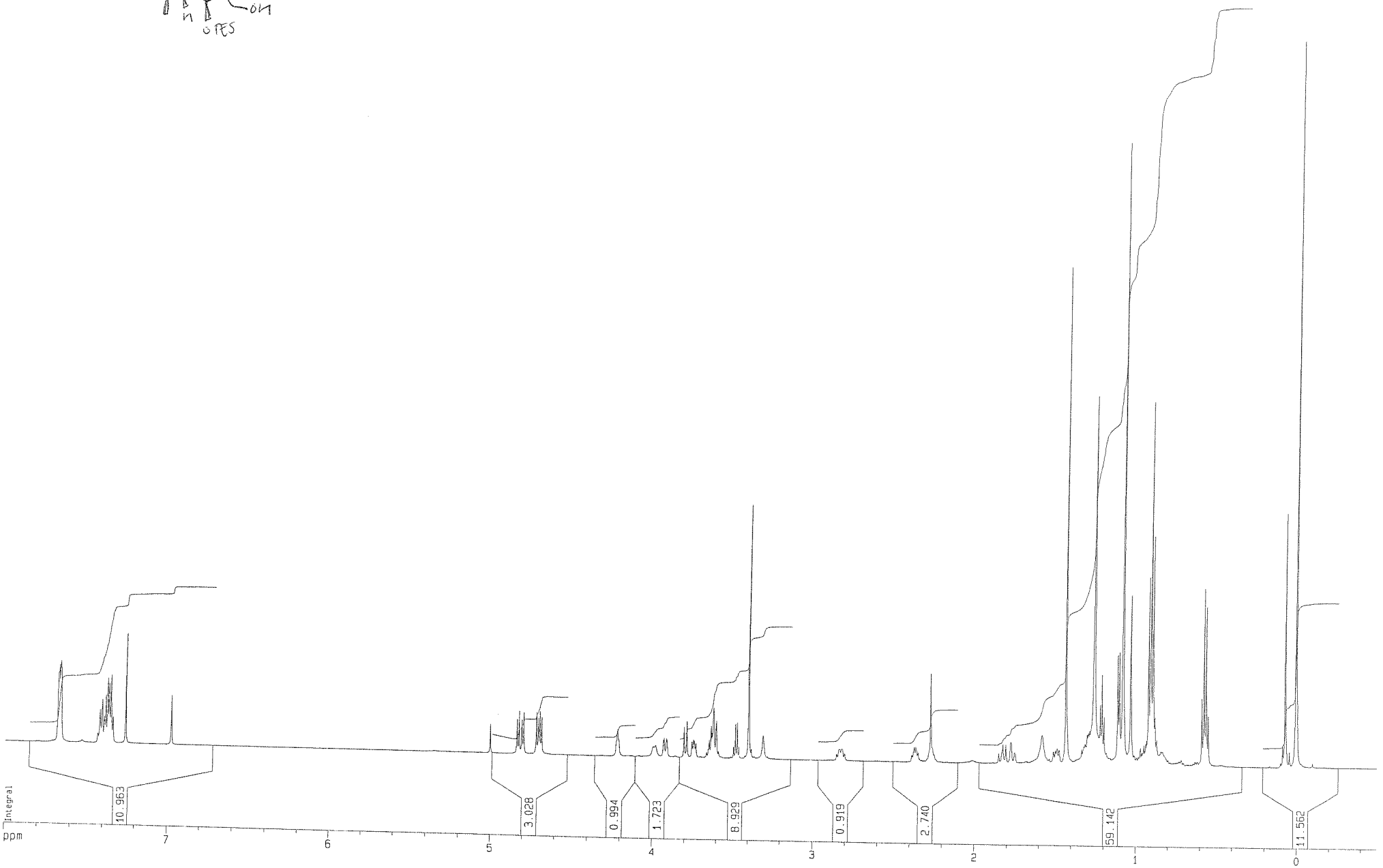
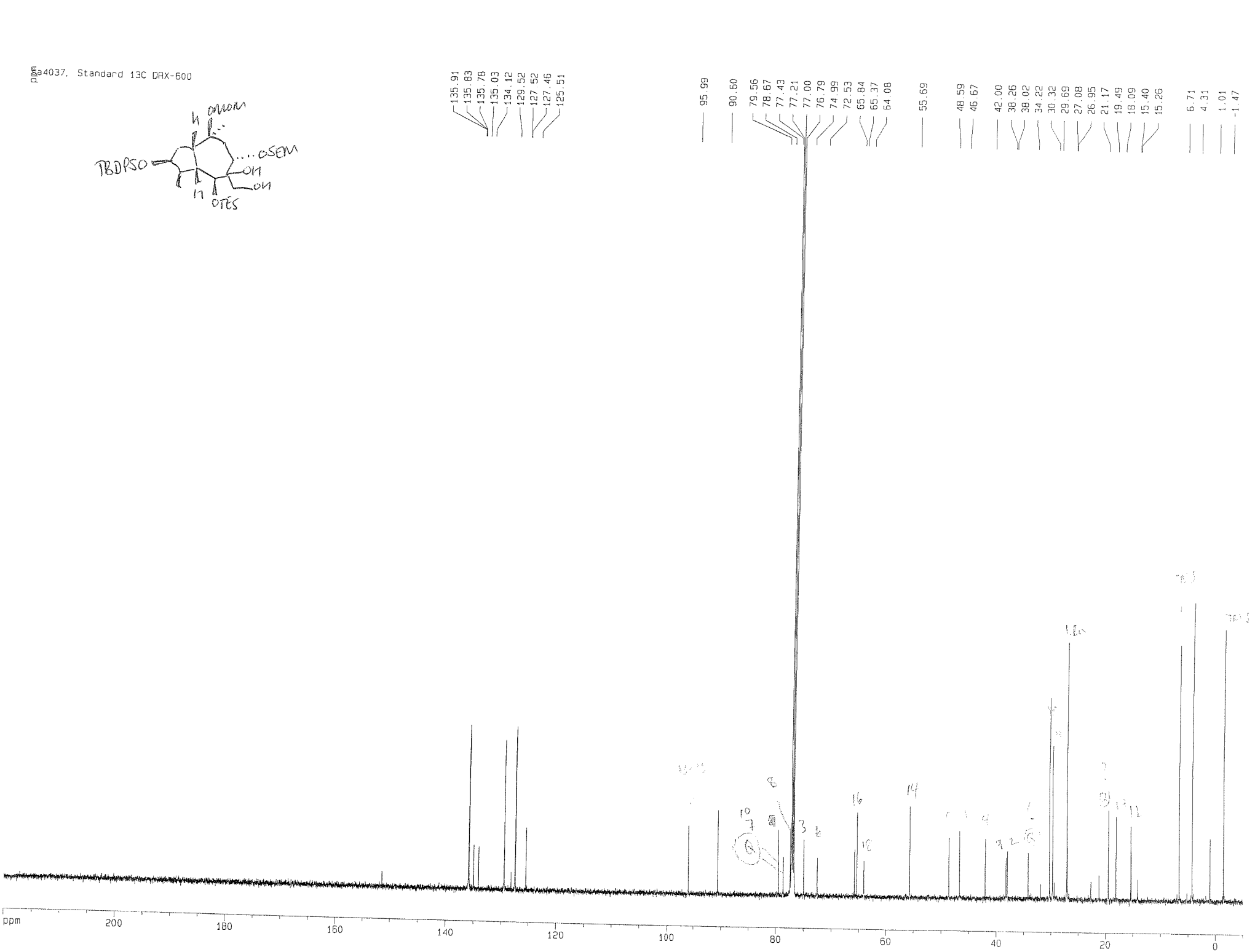
6.62
4.74
-16.73
-21.69

sa4037
Standard 1H DRX-600



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OSEM
OH
OH
H
17
OTES
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135.83
135.78
135.03
134.12
129.52
127.52
127.46
125.51
95.99
90.60
79.56
78.67
77.43
77.21
77.00
76.79
74.99
72.53
65.84
65.37
64.08
55.69
48.59
46.67
42.00
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15.40
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6.71
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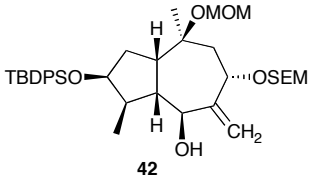
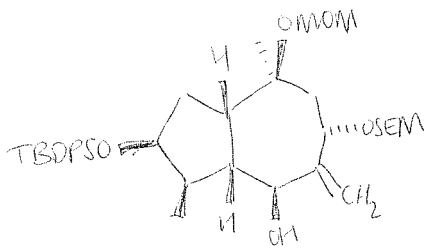


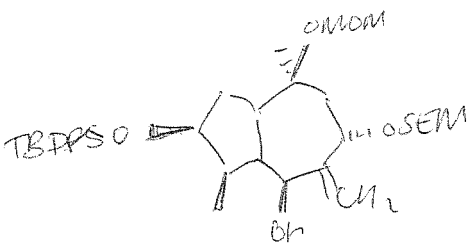
42

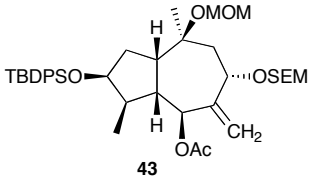
Alcohol 42: 4 Å molecular sieves (400 mg) were added to a solution of triethylsilyl ether **40** (108 mg, 141 μmol) in methanol (4.0 mL) and the resulting mixture stirred at room temperature for 5 minutes. The mixture was then treated with Amberlyst-15 resin (80 mg, 640 μmol) and stirred at room temperature for a further 16 hours. The suspension was filtered through a pad of silica, concentrated *in vacuo* and combined with an identical batch from a reaction with 111 mg of silyl ether. The crude oil was purified by column chromatography (SiO_2, Et_2O/petrol ether 1:9 to 1:4) to afford recovered starting material (36 mg, 16%) and the alcohol 141 mg, 76%; δ_H (600 MHz; $CDCl_3$) 7.67 (4H, m, *o*-Ph), 7.44 (2H, *p*-Ph), 7.38 (4H, *m*-Ph), 5.08 (2H, m, =CH and OH), 4.90 (1H, d, *J* 7.2, O-10-CH_2O), 4.85 (1H, d, *J* 7.2, O-10-CH_2O), 4.80 (1H, s, =CH'), 4.67 (1H, d, *J* 6.7, O-8-CH_2O), 4.63 (1H, d, *J* 6.7, O-8-CH_2O), 4.58 (1H, dd, *J* 9.9, 2.5, H-8), 4.13 (2H, m, H-3 and H-6), 3.74 (1H, ddd, *J* 16.1, 6.0, 5.9, SiCH_2C$\underline{H}_2$), 3.55 (1H, ddd, *J* 16.1, 6.1, 6.1, SiCH_2C$\underline{H}_2$), 3.47 (3H, s, OCH_3), 2.86 (1H, m, H-1), 2.36 (1H, ddd, *J* 10.4, 8.4, 2.4, H-5), 2.07 (1H, dd, *J* 13.7, 2.5, H-9), 1.66 (1H, m, H-4), 1.54 (1H, dd, *J* 13.7, 9.9, H-9'), 1.42 (1H, m, H-2), 1.27 (3H, s, H-14), 1.09 (9H, s, Si$C(CH_3)_3$), 1.08 (3H, d, *J* 7.0, H-15), 1.07 (1H, m, H-2'), 0.93 (2H, m, Si$C\underline{H}_2CH_2$), 0.19 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 149.0 (C-7) 135.9 (*o*-Ph), 135.8 (*o*-Ph), 134.9 (*ipso*–Ph), 133.9 (*ipso*-Ph), 129.59 (*p*-Ph), 129.57 (*p*-Ph), 127.5 (*m*-Ph), 127.4 (*m*-Ph), 109.8 (=CH_2), 93.6 (O-8-CH_2O), 90.7 (O-10-CH_2O), 80.6 (C-10), 75.9 and 75.8 (C-3 and C 6), 70.5 (C-8), 65.1 (Si$CH_2\underline{C}H_2$), 56.1 (OCH_3), 50.8 (C-5), 47.9 (C-1), 43.9 (C-4), 42.1 (C-9), 38.7 (C-2), 29.6 (C-14), 27.0 (C($\underline{C}H_3)_3$), 19.5 ($\underline{C}(CH_3)_3$), 18.0 (Si$\underline{C}H_2CH_2$), 14.0 (C-15), -1.4 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 3438 (br OH), 2928 (C-H), 2857 (C-H), 1645 (w C=C), 835 ($Si(CH_3)_3$); $[\alpha]_D$ +20.8 (*c*. 0.355, $CHCl_3$); found (ESI+) $[MNa]^+$ 677.3660; $C_{37}H_{58}O_6Si_2Na$ requires *M*, 677.3670.

Standard 1H ORX-600
sa6043



Standard 13C DRx-600
sa4070

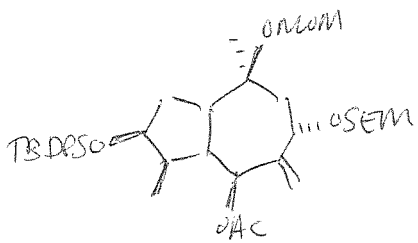




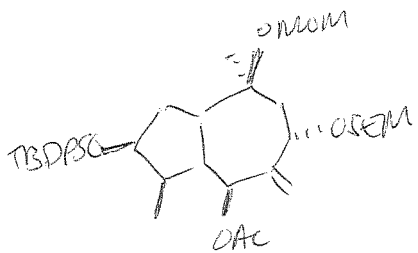
43

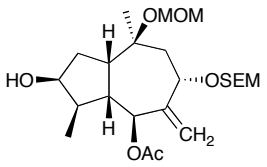
Acetate 43: Catalytic DMAP was added to a solution of alcohol **42** (173 mg, 265 μmol), acetic anhydride (249 μL, 2.65 mmol) and pyridine (257 μL, 3.18 mmol) in CH_2Cl_2 (4.0 mL). The resulting mixture was stirred at room temperature for 18 hours then quenched with ammonium chloride solution (50 mL) and extracted with Et_2O (3 × 50 mL). The combined organic phases were washed with brine (100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (SiO_2, Et_2O/petrol ether, 15:85) afforded the acetate as a pale yellow oil, 167 mg, 91%; δ_H (600 MHz; $CDCl_3$) 7.65 (4H, m, *o*-Ph), 7.43 (2H, m, *p*-Ph), 7.37 (4H, m, *m*–Ph), 5.12 (1H, s, =CH), 5.04-5.03 (2H, m, H-6 and =CH'), 4.72 (1H, d, *J* 7.1 O-10-CH_2O), 4.66 (1H, d, *J* 7.1, O-10-CH_2O), 4.59 (1H, d, *J* 7.1, O-8-CH_2O), 4.53 (1H, d, *J* 7.1, O-8-CH_2O), 4.38 (1H, dd, *J* 9.7, 6.5, H–8), 4.20 (1H, m, H-3), 3.72 (1H, ddd, *J* 16.5, 6.6, 6.1, $SiCH_2C\underline{H}_2$), 3.48 (1H, m, $SiCH_2C\underline{H}_2$), 3.37 (3H, s, OCH_3), 2.84 (1H, ddd, *J* 12.0, 7.7, 4.9, H-1), 2.04 (2H, m, H-5 and H-9), 2.03 (3H, s, $C(O)CH_3$), 1.83 (1H, m, H-4), 1.72 (1H, dd, *J* 14.4, 9.7, H-9'), 1.44 (1H, dd, *J* 13.2, 7.7, H-2), 1.39 (1H, ddd, *J* 13.2, 12.7, 4.9, H-2'), 1.13 (3H, d, *J* 6.6, H-15), 1.12 (3H, s, H-14), 1.08 (9H, s, $C(CH_3)_3$), 0.90 (2H, m, $SiC\underline{H}_2CH_2$), 0.02 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 169.8 (C=O), 146.1 (C-7), 135.9 (*o*-Ph), 135.8 (*o*-Ph), 134.6 (*ipso*-Ph), 133.9 (*ipso*-Ph), 129.6 (*p*-Ph), 127.5 (*m*-Ph), 127.4 (*m*-Ph), 113.2 ($=CH_2$), 91.0 (O-8-CH_2O), 90.7 (O-10-CH_2O), 77.9 (C-10), 74.8 (C-6), 74.2 (C–3), 71.9 (C-8), 64.9 ($SiCH_2\underline{C}H_2$), 55.6 (OCH_3), 51.5 (C-5), 46.0 (C-1), 44.1 (C-4), 37.7 (C-9), 30.2 (C-2), 29.0 (C-14), 27.0 ($C(\underline{C}H_3)_3$), 21.3 ($C(O)\underline{C}H_3$), 19.4 ($\underline{C}(CH_3)_3$), 18.0 ($Si\underline{C}H_2CH_2$), 15.3 (C-15), -1.4 ($Si(CH)_3)_3$); ν_{max} (film; cm^{-1}) 2930 (C-H), 2848 (C-H), 1740 (C=O), 1647 (w C=C), 1588 (w Ar), 835 ($Si(CH_3)_3$); $[\alpha]_D$ –23.5 (*c*. 0.345, $CHCl_3$); found (ESI+) $[MNa]^+$ 719.3799; $C_{39}H_{60}O_7Si_2Na$ requires *M*, 719.3775.

Standard 1H DRX-600
sa4076



Standard 13C DRX-600
sa4076



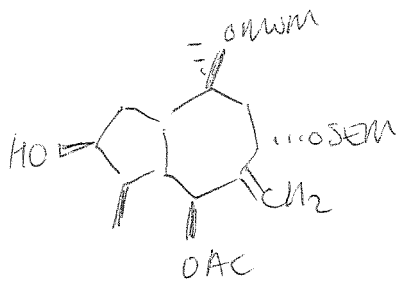


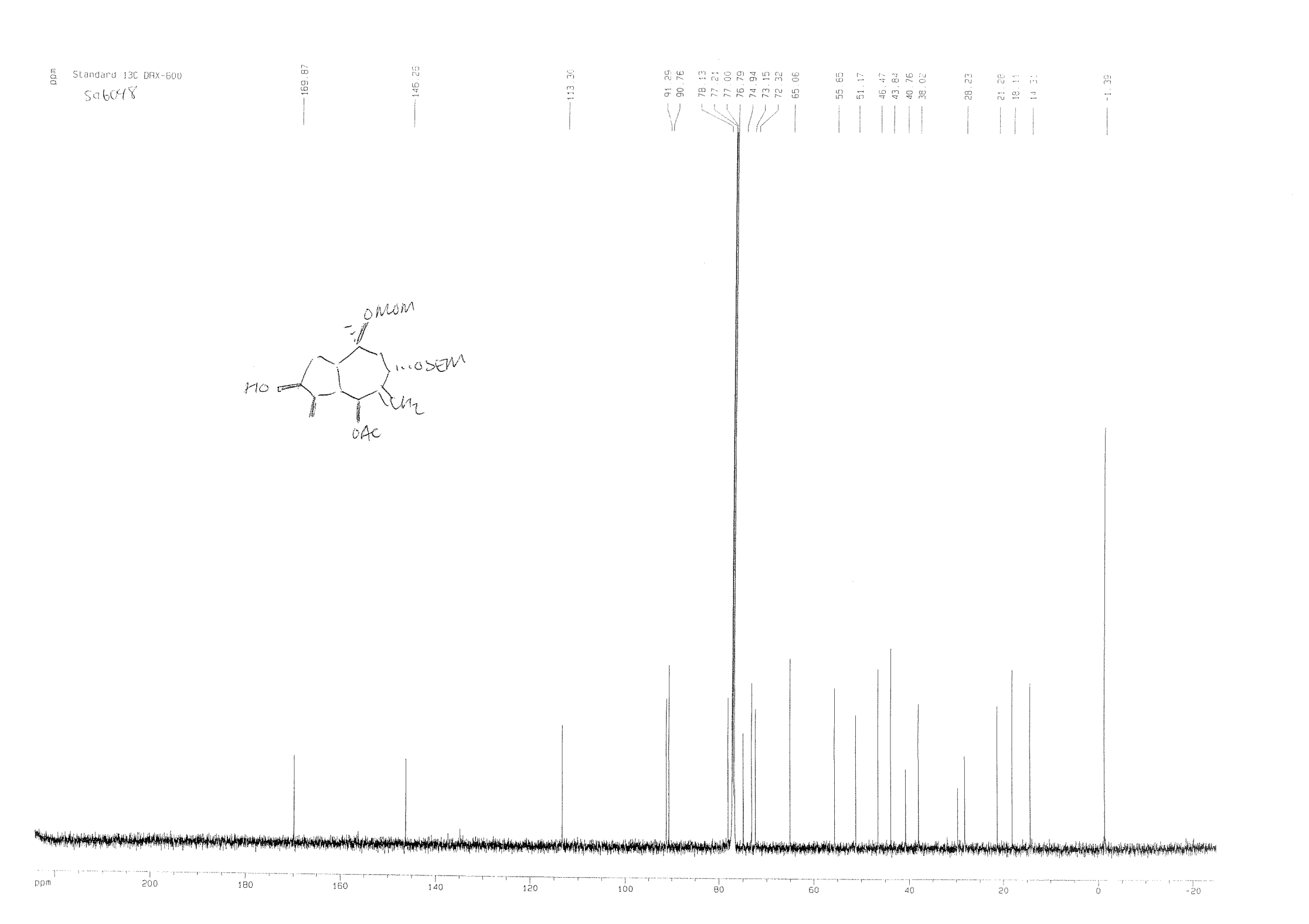
44

Alcohol 44: TBAF solution (4.0 mL, 4.0 mmol, 1.0 M in THF) was added to the silyl ether **43** (165 mg, 237 μmol) and the resulting mixture was stirred at room temperature for 12 hours. The mixture was poured into water (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organics were washed with brine (50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (SiO_2, Et_2O/petrol ether, 3:2) afforded the alcohol as a colourless oil, 95.8 mg, 88%; δ_H (600 MHz; $CDCl_3$) 5.19 (1H, d, *J* 8.4, H-6), 5.18 (1H, s, =CH), 5.08 (1H, s, =CH'), 4.74 (1H, d, *J* 7.2, O-10-CH_2O), 4.67 (1H, d, *J* 7.2, O-10-CH_2O), 4.63 (1H, d, *J* 7.1, O-8-CH_2O), 4.58 (1H, d, *J* 7.1, O-8-CH_2O), 4.43 (1H, dd, *J* 9.2, 6.3, H-8), 4.14 (1H, m, H-3), 3.74 (1H, ddd, *J* 16.5, 6.8, 6.6, $SiCH_2C\underline{H}_2$), 3.52 (1H, ddd, *J* 16.5, 6.6, 6.4, $SiCH_2C\underline{H}_2$), 3.36 (3H, s, OCH_3), 2.76 (1H, m, H-1), 2.12 (1H, dd, *J* 14.4, 6.3, H-9), 2.07 (3H, s, $C(O)CH_3$), 2.01 (1H, m, H-5), 1.94 (1H, m, H-4), 1.88 (1H, dd, *J* 14.4, 9.2, H–9'), 1.71, (2H, m, H-2), 1.29 (3H, s, H-14), 1.12 (3H, d, *J* 7.0, H-15), 0.94 (1H, ddd, *J* 12.9, 6.8, 6.6, $SiC\underline{H}_2CH_2$), 0.93 (1H, ddd, *J* 12.9, 6.6, 6.4, $SiC\underline{H}_2CH_2$) 0.02 (9H, s, $Si(CH_3)_3$), (OH not observed); δ_C (150 MHz; $CDCl_3$) 169.9 (C=O), 146.3 (C-7), 113.3 (=CH_2), 91.3 (O-8-CH_2O), 90.8 (O-10-CH_2O), 78.1 (C-10), 74.9 (C-6), 73.2 (C-3), 72.3 (C-8), 65.1 ($SiCH_2\underline{C}H_2$), 55.6 (OCH_3), 51.2 (C–5), 46.5 (C-1), 43.8 (C-4), 40.8 (C-9), 38.0 (C-2), 28.2 (C-14), 21.3 ($C(O)\underline{C}H_3$), 18.1 ($Si\underline{C}H_2CH_2$), 14.3 (C–15), –1.4 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 3453 (br OH), 1740 (C=O), 835 ($Si(CH_3)_3$); $[\alpha]_D$ –59.7 (*c*. 0.64, $CHCl_3$); found (ESI+) $[MNa]^+$ 481.2590; $C_{23}H_{42}O_7SiNa$ requires *M*, 481.2598.

Standard 1H DRX-600

Xa6c4f

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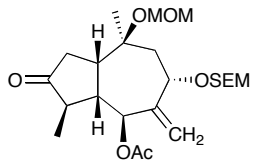


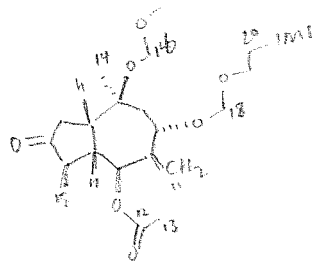
45

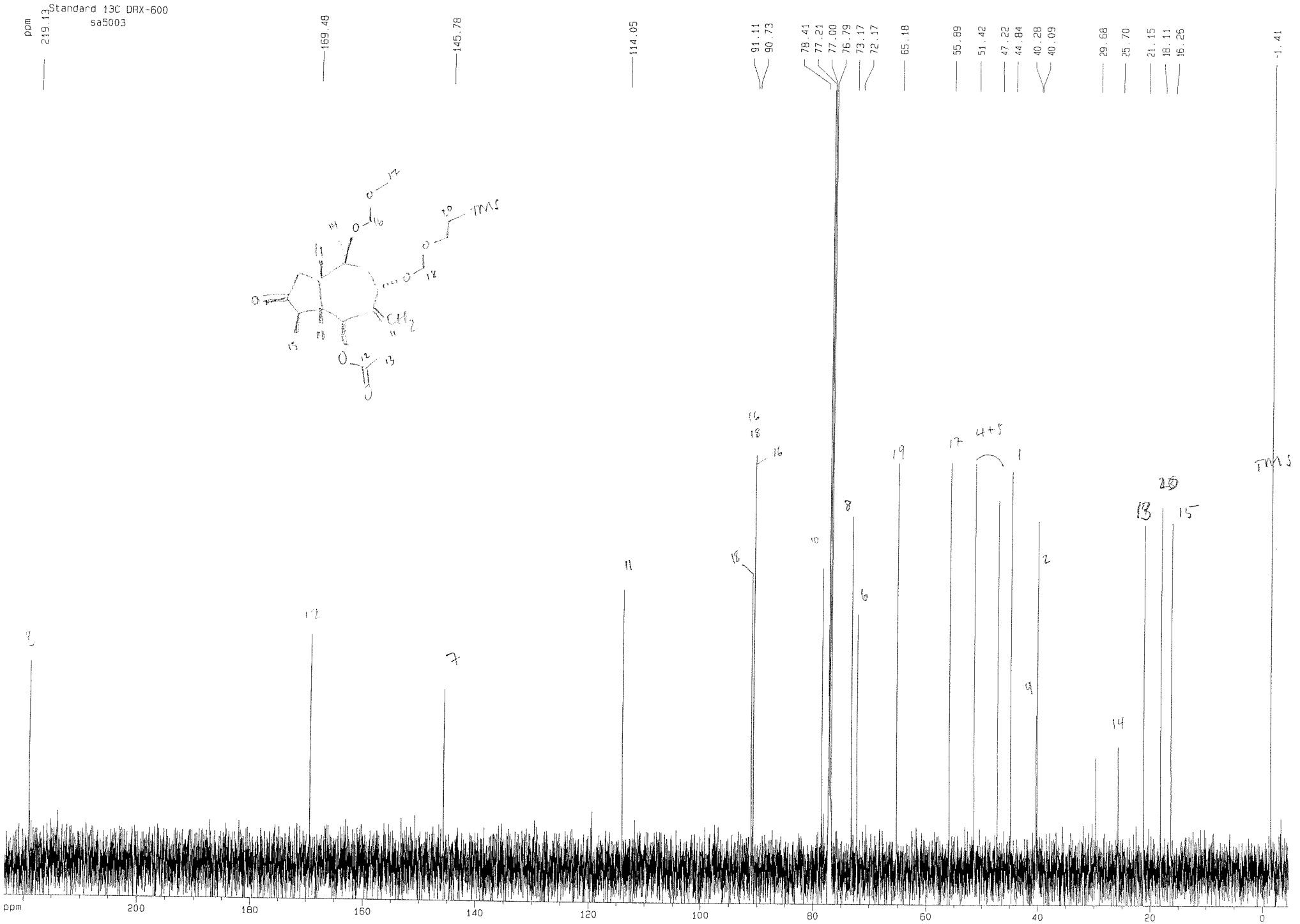
Ketone 45: *Procedure A:* A stirring mixture of alcohol **45** (12.5 mg, 27.3 μmol), NMO (20 mg, 93.9 μmol), 4 Å MS (60 mg) and CH_2Cl_2 was treated with TPAP (2.0 mg, 5.6 μmol). After 1 hour at room temperature, the reaction was quenched with saturated sodium sulfite solution (20 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic extracts were washed with copper sulfate solution (30 mL), brine (30 mL), then dried ($MgSO_4$) and evaporated under reduced pressure. The crude black material was purified by column chromatography (SiO_2, Et_2O/petrol ether, 1:1) to afford the ketone as a colourless oil, 8.4, 67%.

Procedure B: Dess-Martin periodinane (132 mg, 311 μmol) was added in two batches over 10 minutes to a suspension of alcohol **81** (93 mg, 202 μmol) and sodium bicarbonate (52 mg, 621 μmol) in CH_2Cl_2 (1.0 mL). The resulting mixture was stirred at room temperature for 30 minutes then quenched by stirring with sodium thiosulfate solution (20 mL) and sodium bicarbonate solution (20 mL) for 30 minutes. The reaction was then extracted with Et_2O (3 × 30 mL) and the combined organic phases were washed with sodium bicarbonate solution (30 mL) then brine (30 mL). The ethereal layer was then dried ($MgSO_4$), concentrated under reduced pressure and purified by column chromatography (SiO_2, Et_2O/petrol ether 2:3) to afford the ketone, 73.8 mg, 80%.

δ_H (600 MHz; $CDCl_3$) 5.30 (1H, d, *J* 9.3, H-6), 5.27 (1H, s, =CH), 5.12 (1H, s, =CH'), 4.78 (1H, d, *J* 7.4, O-10-CH_2O), 4.66 (1H, d, *J* 7.2, O-8-CH_2O), 4.61 (1H, d, *J* 7.4, O-10-CH_2O'), 4.60 (1H, d, *J* 7.2, O-8-CH_2O), 4.41 (1H, dd, *J* 6.8, 6.8, H-8), 3.76 (1H, ddd, *J* 16.5, 6.6, 6.5, $SiCH_2C\underline{H}_2$), 3.51 (1H, ddd, *J* 16.5, 6.4, 6.2, $SiCH_2C\underline{H}_2$), 3.36 (3H, s, OCH_3), 2.69 (1H, m, H-1), 2.47 (1H, dd, *J* 18.6, 9.6, H-2), 2.31 (2H, m, H-4 and H-5), 2.28 (1H, dd, *J* 18.6, 8.3, H-2'), 2.18 (1H, dd, *J* 15.1, 6.8, H-9), 2.08 (3H, s, $C(O)CH_3$), 2.08 (1H, m, H-9'), 1.26 (3H, s, H-14), 1.17 (3H, d, *J* 7.0, H-15), 0.95 (2H, m, $SiC\underline{H}_2CH_2$), 0.03 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 219.1 (C-3), 169.4 ($\underline{C}(O)CH_3$), 145.8 (C-7), 114.0 (=CH_2), 91.1 (O-8-CH_2O), 90.7 (O-10-CH_2O), 78.4 (C-10), 73.1 (C-8), 72.1 (C-6), 65.1 ($SiCH_2\underline{C}H_2$), 55.9 (OCH_3), 51.4 (C-5), 47.2 (C-4), 44.8 (C-1), 40.2 (C-9), 40.0 (C-2), 25.7 (C-14), 21.1 ($C(O)\underline{C}H_3$), 18.1 ($Si\underline{C}H_2CH_2$), 16.2 (C-15), -1.4 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 2953 (C-H), 2920 (C-H), 1742 (C=O), 1647 (w C=C), 836 ($Si(CH_3)_3$); $[\alpha]_D$ –65.5 (*c*. 0.42, $CHCl_3$); found (ESI+) $[MNa]^+$ 479.2463; $C_{23}H_{40}O_7Na$ requires *M*, 479.2441.

Standard 1H DRX-600
sa5003

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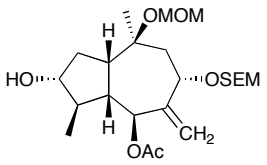
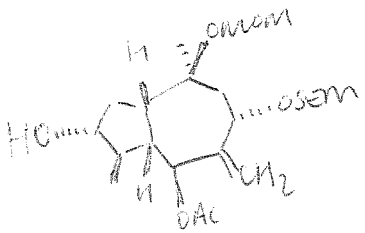
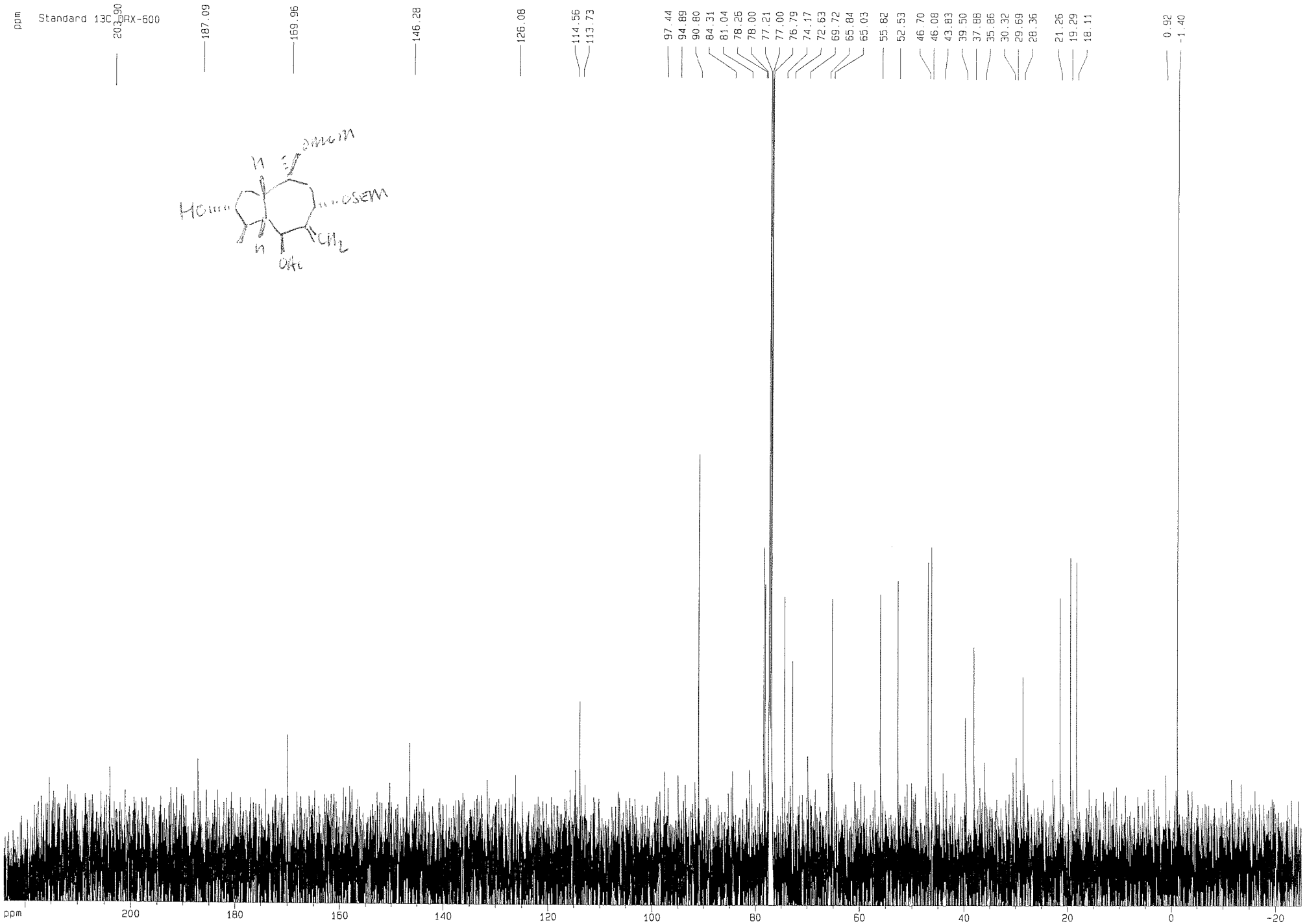


46

Alcohol 46: Sodium borohydride (21.0 mg, 560 μmol) was added to a solution of ketone **45** (85.3 mg, 187 μmol) in MeOH (1.0 mL) at 0 ˚C. The resulting mixture was stirred at 0 ˚C for 2 hours then quenched with saturated ammonium chloride solution (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine (50 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography (SiO_2, Et_2O /petrol ether, 2:3 increasing to neat Et_2O) afforded the alcohol as a single C-3 isomer; 63.7 mg, 74%; δ_H (600 MHz; $CDCl_3$) 5.29 (1H, d, *J* 9.7, H-6), 5.24 (1H, s, =CH), 5.05 (1H, s, =CH'), 4.73 (1H, d, *J* 7.3, O-10-CH_2O), 4.65 (1H, d, *J* 7.2, O-8-CH_2O), 4.58 (1H, d, *J* 7.3, O-10-CH_2O), 4.56 (1H, d, *J* 7.2, O-8-CH_2O), 4.37 (1H, dd, *J* 9.4, 6.4, H-8), 3.73 (2H, m, H-3 and $SiCH_2C\underline{H}_2$), 3.50 (1H, m, $SiCH_2C\underline{H}_2$), 3.34 (3H, s, OCH_3), 2.33 (1H, m, H-1), 2.11 (1H, dd, *J* 14.4, 6.4, H-9), 2.07 (3H, s, $C(O)CH_3$), 2.02 (1H, m, H-2), 1.96 (1H, dd, *J* 14.4, 9.4, H-9'), 1.89 (1H, m, H-5), 1.72, (1H, m, H-4), 1.54 (1H, m, H-2'), 1.27 (3H, s, H-14), 1.13 (3H, d, *J* 7.0, H-15), 0.93 (2H, m, $SiC\underline{H}_2CH_2$), 0.02 (9H, s, $Si(CH_3)_3$) (OH signal not observed); δ_C (150 MHz; $CDCl_3$) 169.9 ($\underline{C}(O)CH_3$), 146.2 (C-7), 113.7 ($=CH_2$), 90.8 (O-10-CH_2O), 90.7 (O-8-CH_2O), 78.2 (C-3), 78.0 (C-10), 74.1 (C-6), 72.6 (C-8), 65.0 ($SiCH_2\underline{C}H_2$), 55.8 (OCH_3), 52.5 (C-5), 46.7 (C-4), 46.0 (C-1), 39.5 (C-9), 37.8 (C-2), 28.3 (C-14), 21.2 ($C(O)\underline{C}H_3$), 19.2 (C–15), 18.1 ($Si\underline{C}H_2CH_2$), -1.4 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 3449 (br OH), 1742 (C=O), 1647 (w C=C), 836 ($Si(CH_3)_3$); $[\alpha]_D$ –97.0 (*c*. 0.635, $CHCl_3$); found (ESI+) $[MNa]^+$ 481.2615; $C_{23}H_{42}O_7SiNa$ requires *M*, 481.2598.

Standard 1H DRX-600
sa5006

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46.70
46.08
43.83
39.50
37.88
35.86
30.32
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28.36
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20
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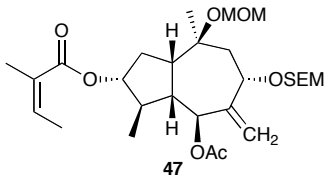
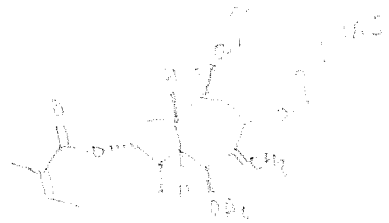
-20

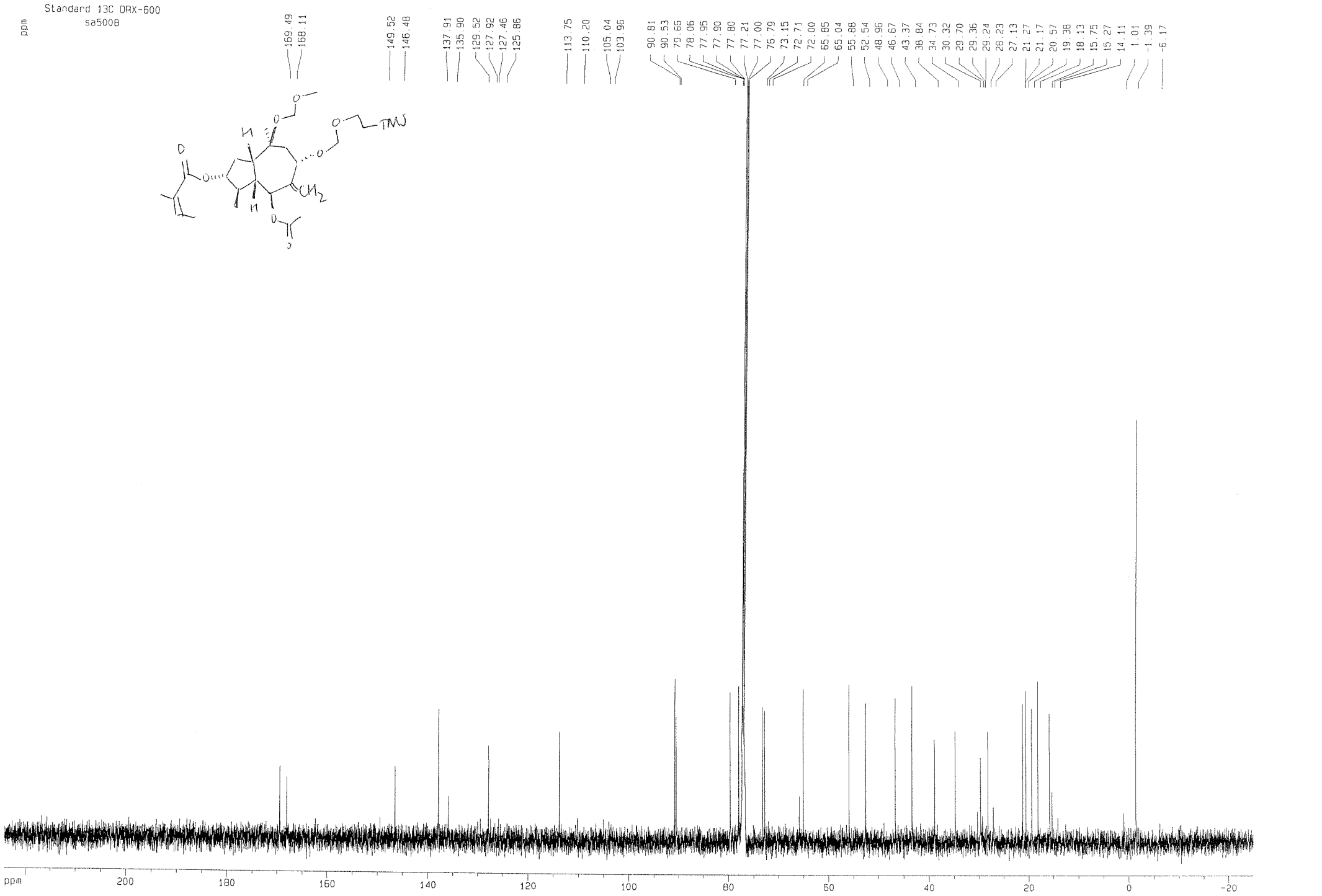


47

Angelate 47: *Procedure A:* A toluene solution (600 μL) of preformed anhydride **37** (27.7 mg, 90.3 μmol) was added to a mixture of sodium bicarbonate (12.6 mg, 151 μmol) and alcohol **46** (13.8 mg, 30.1 μmol) in PhMe (300 μL). The resulting mixture was heated at 80 ˚C for 22 hours then cooled, quenched with sodium bicarbonate solution (20 mL) and extracted with Et_2O (3 × 20 mL). The combined extracts were washed with brine (40 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was then purified by column chromatography (SiO_2, Et_2O/petrol ether, 1:9 then 1:4) to afford a colourless gum, 15.5 mg, 96%.
Procedure B: 2,4,6-Trichlorobenzoyl chloride (172 μL, 1.10 mmol) was added to a solution of angelic acid (110 mg, 1.10 mmol) in toluene (1.0 mL) followed by Et_3N (154 μL, 1.10 mmol). The mixture was stirred at room temperature for 2 hours then treated with a solution of alcohol **46** (46.9 mg, 102 μmol, previously azeotroped three times with toluene) in toluene (2.0 mL). The resulting mixture was stirred at 75 ˚C for 2 days, at this time a number of components were identified by TLC. The mixture was cooled, quenched with saturated ammonium chloride solution (20 mL) and extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with brine (30 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (SiO_2, Et_2O/petrol ether, 3:7 increasing gradually to 4:1) was used to fractionate the complex mixture into two mixtures, each containing two esters. Mixture A (49 mg) contained angelate **47** with loss of MOM, and the tiglate isomer. (The mixture was further separated by preparative HPLC to afford the angelate, 4.6 mg, 9.1% and tiglate, 2.1 mg, 4.2%, see supplementary information.) Mixture B (8.1 mg) contained desired angelate ester **47** and the isomeric tiglate ester. The mixture was further separated by preparative HPLC to afford the title compound, 1.6 mg, 2.9% and the tiglate, 2.0 mg, 3.6% (see supplementary information). [HPLC conditions (Agilent HP1100): *Column*: Berger Cyano 250mm x 10 mm. *Eluent*: 2% *i*PrOH/hexanes (95% n–hexane). *Flow rate*: 0 to 5 mins: 1 to 5 ml min^{-1} and 5 ml min^{-1} thereafter. *Detection*: diode array.]
δ_H (600 MHz; $CDCl_3$) 6.05 (1H, q, *J* 7.2, C=C(H)CH_3), 5.25 (1H, s, =CH), 5.21 (1H, d, *J* 10.3, H-6), 5.03 (1H, s, =CH'), 4.76 (1H, d, *J* 7.3, O-10-CH_2O), 4.71 (1H, m, H-3), 4.67 (1H, d, *J* 7.2, O-8-CH_2O), 4.57 (1H, d, *J* 7.3, O-10-CH_2O), 4.55 (1H, d, *J* 7.2, O-8-CH_2O), 4.37 (1H, dd, *J* 8.7, 7.6, H-8), 3.75 (1H, ddd, *J* 16.5, 6.7, 6.5, $SiCH_2CH_2$), 3.50 (1H, ddd, *J* 16.5, 7.2, 6.8, $SiCH_2CH_2$), 3.34 (3H, s, OCH_3), 2.44 (1H, m, H-1), 2.29 (1H, m, H-2), 2.13 (2H, m, H-4 and H-9), 2.06 (3H, s, C(O)CH_3), 1.1.97 (5H, m, H-5, H-9' and C=C(H)CH_3), 1.86 (3H, s, C(O)CCH_3), 1.57 (1H, m, H–2'), 1.26 (3H, s, H-14), 1.15 (3H, d, *J* 7.2, H-15), 0.93 (2H, m, $SiCH_2CH_2$), 0.03 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 169.4 (C(O)CH_3), 168.1 (C(O)CCH_3), 146.4 (C-7), 137.9 (C=C(H)CH_3), 129.5 (C=C(H)CH_3), 113.7 (=CH_2), 90.8 (O-10-CH_2O), 90.5 (O-8-CH_2O), 79.6 (C-3), 78.0 (C-10), 73.1 (C–6), 72.7 (C-8), 65.0 ($SiCH_2CH_2$), 55.8 (OCH_3), 52.5 (C-5), 46.6 (C-1), 43.3 (C-4), 38.8 (C-9), 34.7 (C-2), 28.2 (C–14), 21.1 (C(O)CH_3), 20.5 (C(O)CCH_3), 19.3 (C–15), 18.1 ($SiCH_2CH_2$), 15.7 (C=C(H)CH_3), -1.4 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 2953 (C-H), 2928 (C-H), 1745 (acetate C=O), 1714 (angelate C=O), 1649 (w C=C), 836 ($Si(CH_3)_3$); $[\alpha]_D$ –101.7 (*c*. 0.155, $CHCl_3$); found (ESI+) $[MNa]^+$ 563.3010; $C_{28}H_{48}O_8Na$ requires *M*, 563.3016.

Standard 1H DRX-600
sa500B

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90.53
79.65
78.06
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77.90
77.80
77.21
77.00
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52.54
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46.67
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38.84
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30.32
29.70
29.36
29.24
28.23
27.13
21.27
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19.38
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14.11
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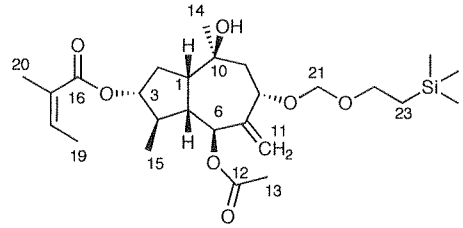
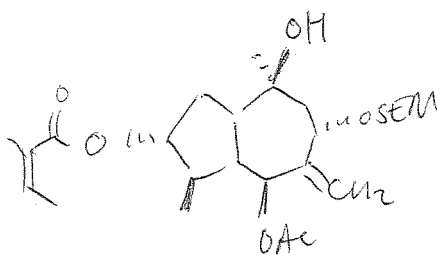


This molecule was formed as an undesired side-product during the formation of angelate ester **47**. δ_H (600 MHz; $CDCl_3$) 6.05 (1H, q, *J* 7.2, H-18), 5.35 (1H, d, *J* 7.3, H-6), 5.29 (1H, s, H-11), 5.26 (1H, s, H-11'), 4.69 (1H, dd, *J* 8.0, 6.9, H-3), 4.60 (2H, s, H-21), 4.44 (1H, dd, *J* 10.0, 6.3, H-8), 3.73 (1H, ddd, *J* 16.6, 7.0, 6.9, H-22), 3.51 (1H, ddd, *J* 16.6, 6.9, 6.8, H-22'), 2.78 (1H, s, OH), 2.35-2.28 (2H, m, H-1 and H-2), 2.07 (3H, s, H-13), 2.04 (2H, m, H-4 and H–9), 1.99 (1H, m, H-5) 1.98 (3H, s, H-19), 1.89 (1H, dd, *J* 14.1, 10.0, H-9'), 1.86 (3H, s, H–20), 1.47 (1H, m, H-2'), 1.24 (3H, s, H-14), 1.14 (3H, d, *J* 6.9, H-15), 0.91 (4H, m, H-23), 0.03 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 168.8 (C-12), 168.0 (C-16), 146.3 (C-7), 138.0 (C-18), 127.8 (C-17), 115.1 (C-11), 91.6 (C-21), 78.9 (C-3), 78.1 (C-10), 72.6 (C-6), 71.3 (C–8), 65.2 (C-22), 48.8 (C-5), 42.9 (C-1), 41.2 (C-4), 35.2 (C-2), 31.91 (C-9), 30.2 (C-14), 21.1 (C-13), 20.5 (C–20), 18.1 (C-15 and C-23), 15.7 (C-19), –1.4 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 2926 (C-H), 2854 (C-H), 1745 (acetate C=O), 1717 (angelate C=O), 1651 (w C=C); $[\alpha]_D$ –41.7 (*c*. 0.06, $CHCl_3$); found (ESI+) $[MNa]^+$ 519.2749; $C_{26}H_{44}O_7Na$ requires *M*, 519.2754.

Standard 1H DRX-600
sa6054 prep2 fr2



Standard 13C DRX-600
sa6054 prep2 fr2

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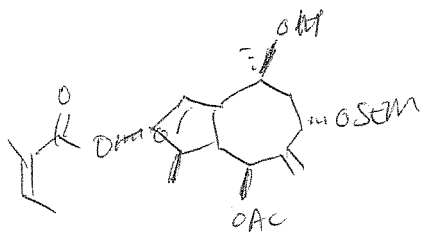
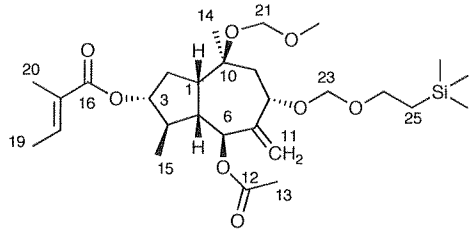
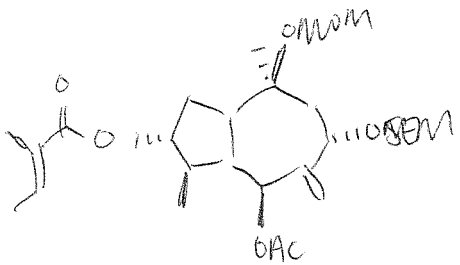




This compound was formed as an undesired side product during the formation of angelate ester **47**. δ_H (600 MHz; $CDCl_3$) 6.82 (1H, q, *J* 7.0, H-18), 5.26 (1H, s, H-11), 5.23 (1H, d, *J* 10.5, H-6), 5.03 (1H, s, H-11'), 4.76 (1H, d, *J* 7.3, H-21), 4.71 (1H, m, H-3), 4.69 (1H, d, *J* 7.3, H-23), 4.56 (2H, d, *J* 7.3, H-21' and H-23'), 4.37 (1H, dd, *J* 8.4, 7.9, H-8), 3.76 (1H, ddd, *J* 16.6, 6.8, 6.5, H-24), 3.49 (1H, ddd, *J* 16.6, 6.9, 6.4, H-24'), 3.34 (3H, s, H-22), 2.46 (1H, ddd, *J* 13.0, 7.1, 6.6, H-1), 2.28 (1H, ddd, *J* 13.7, 7.1, 6.8, H-2), 2.15 (2H, m, H-4 and H–9), 2.07 (3H, s, H–13), 1.96 (2H, m, H-5 and H-9'), 1.81 (3H, s, H-20), 1.78 (3H, d, *J* 7.0, H-19), 1.58 (1H, m, H-2'), 1.27 (3H, s, H-14), 1.13 (3H, d, *J* 7.2, H-15), 0.94 (2H, m, H-25), 0.03 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 169.5 (C-12), 168.1 (C-16), 146.7 (C-7), 137.5 (C-18), 128.5 (C-17), 113.8 (C-11), 90.8 (C-21), 90.4 (C-23), 79.8 (C-3), 77.9 (C-10), 73.0 (C–6), 72.7 (C-8), 65.8 (C-24), 55.9 (C-22), 52.7 (C-5), 46.6 (C-1), 43.3 (C-4), 38.6 (C-9), 34.6 (C-2), 29.7 (C-14), 21.2 (C-13), 19.3 (C-20), 18.1 and 18.0 (C-15 and C-25), 14.3 (C-19), –1.4 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 2921 (C-H), 1744 (acetate C=O), 1709 (tiglate C=O); $[\alpha]_D$ –50.0 (*c*. 0.10, $CHCl_3$); found (ESI+) $[MNa]^+$ 563.3011; $C_{28}H_{48}O_8SiNa$ requires *M*, 563.3016.

Standard 1H DAX-600

Sa6054 pmp3 hr3 (sa.6054-3-3)



Standard 13C DRX-600
sa6054 prep3 fr3

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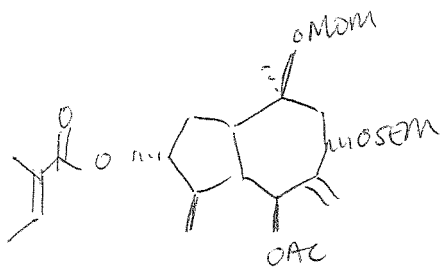

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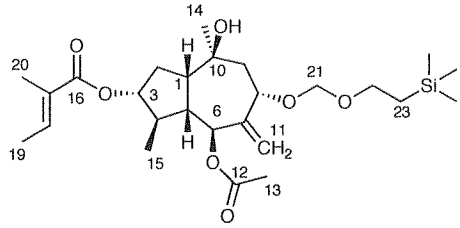
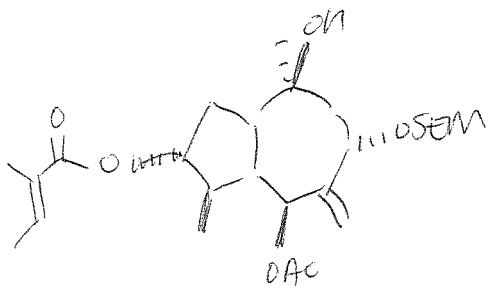
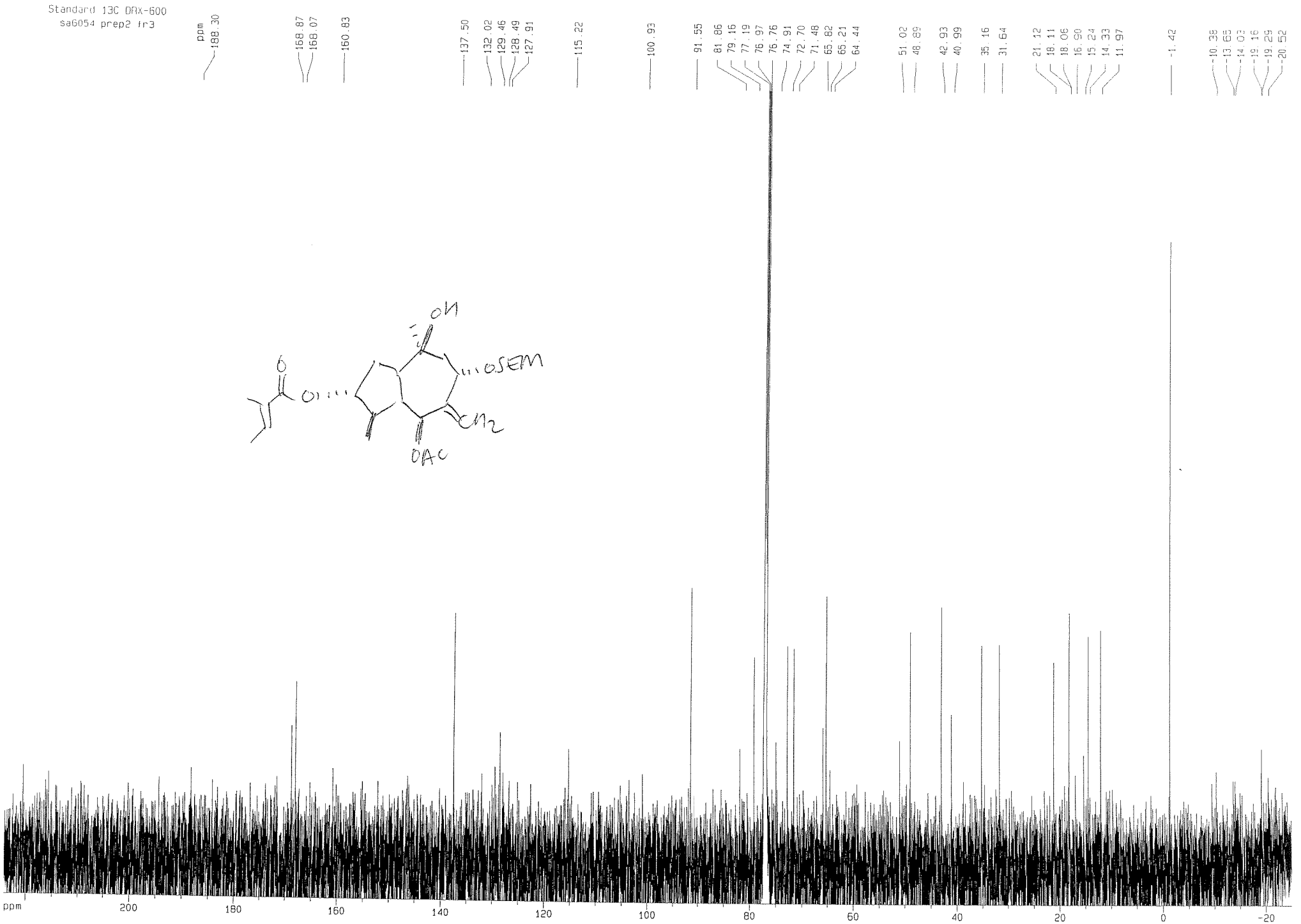


This compound was formed as an undesired side product during the formation of angelate ester **47**. δ_H (600 MHz; $CDCl_3$) 6.82 (1H, q, *J* 7.1, H-18), 5.36 (1H, d, *J* 7.6, H-6), 5.31 (1H, s, H-11), 5.29 (1H, s, H-11'), 4.68 (1H, m, H-3), 4.63 (1H, d, *J* 7.2, H-21), 4.61 (1H, d, *J* 7.2, H–21'), 4.45 (1H, dd, *J* 10.0, 6.5, H-8), 3.76 (1H, ddd, *J* 16.5, 7.0, 6.7, H-22), 3.53 (1H, ddd, *J* 16.5, 7.0, 6.8, H-22'), 2.34 (1H, m, H-1), 2.26 (1H, ddd, *J* 12.8, 6.8, 4.8, H-2), 2.08 (5H, m, H-4, H-9 and H-13), 1.98 (1H, m, H-5), 1.93 (1H, dd, 14.1, 10.0, H-9'), 1.83 (3H, s, H-20), 1.79 (3H, d, *J* 7.1, H-19), 1.46 (1H, ddd, *J* 12.4, 12.0, 8.1, H-2'), 1.23 (3H, s, H-14), 1.13 (1H, d, *J* 6.9, H-15), 0.94 (2H, m, H-23), 0.03 (9H, s, $Si(CH_3)_3$); δ_C (150 MHz; $CDCl_3$) 168.9 (C–16), 168.1 (C-12), 160.8 (C-7), 137.5 (C-18), 128.5 (C-17), 115.2 (C-11), 100.9 (C-21), 79.16 (C-3), 74.9 (C-6), 72.7 (C-10), 71.5 (C-8), 65.8 (C-22), 51.0 (C-5), 48.9 (C-1), 42.9 (C–4), 41.0 (C-9), 35.2 (C-2), 31.6 (C-14), 21.1 (C-13), 18.1 (C-15 and C-23), 14.3 (C-19), 12.0 (C-20), –1.4 ($Si(CH_3)_3$); ν_{max} (film; cm^{-1}) 3501 (br OH), 2958 (C-H), 1744 (acetate C=O), 1709 (tiglate C=O), 1649 (w C=C), 836 ($Si(CH_3)_3$); $[\alpha]_D$ –90.4 (*c*. 0.115, $CHCl_3$); found (ESI+) $[MNa]^+$ 519.2765; $C_{26}H_{44}O_7SiNa$ requires *M*, 519.2754.

Standard 1H ORX-600
sa6054 prep 2 fr3

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sa6054 prep2 fr3
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-19.16
-19.29
-20.52
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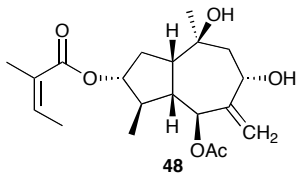
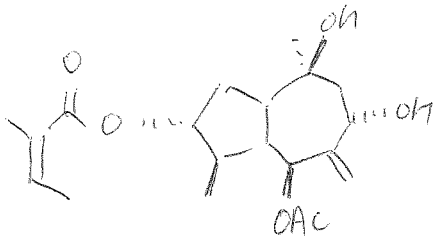
40
20
0
-20



48

Diol 48: A methanolic solution (1.0 mL) of methoxymethyl ether **47** (15.5 mg, 28.7 μmol) was treated with 2 drops of concentrated HCl at 40 ˚C for 45 minutes. The mixture was then quenched with sodium bicarbonate solution (20 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The crude gum was purified by column chromatography (SiO_2, Et_2O/petrol ether, 4:1 then 9:1) to afford the title compound which was used without further purification; δ_H (600 MHz; $CDCl_3$) 6.07 (1H, q, *J* 7.1, C=C(H)CH_3), 5.37 (1H, s, =CH), 5.33 (1H, d, *J* 6.6, H-6), 5.21 (1H, s, =CH'), 4.73 (1H, m, H-3), 4.54 (1H, dd, *J* 9.5, 6.5, H-8), 2.75 (1H, br s, OH), 2.36 (2H, m, H-1 and H-2), 2.17 (2H, m, H-4 and H-9), 2.05 (3H, s, C(O)CH_3), 2.02 (1H, m, H-5), 1.98 (3H, d, *J* 7.1, C=C(H)CH_3), 1.89 (1H, dd, *J* 14.3, 9.5, H-9'), 1.87 (3H, s, C(O)CCH_3), 1.45 (1H, m, H-2'), 1.44 (3H, s, H-14), 1.15 (3H, d, *J* 6.9, H-15) (one OH signal not observed); δ_C (125 MHz; $CDCl_3$) 169.6 (C(O)CH_3), 167.9 (C(O)CCH_3), 143.0 (C-7), 138.1 (C=C(H)CH_3), 127.1 (C=C(H)CH_3), 113.6 (=CH_2), 84.1 (C-10), 79.0 (C-3), 72.8 (C-6), 69.0 (C-8), 50.7 (C-5), 48.9 (C-1), 42.6 and 42.5 (C-4 and C-9), 35.2 (C-2), 29.3 (C-14), 21.8 (C(O)CH_3), 21.2 (C(O)CCH_3), 17.9 (C-15), 15.8 (C=C(H)CH_3); found (ESI+) $[MNa]^+$ 389.1923; $C_{20}H_{30}O_6Na$ requires *M*, 389.1940.

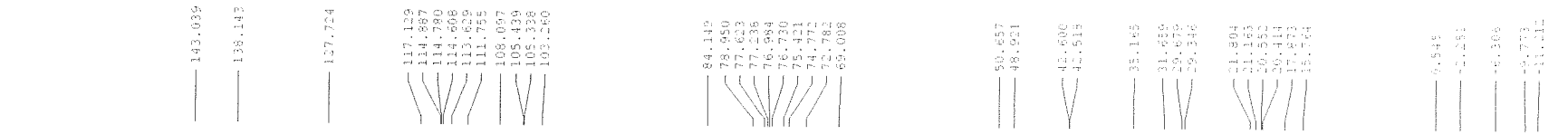
Standard 1H DRX-600
sa6058

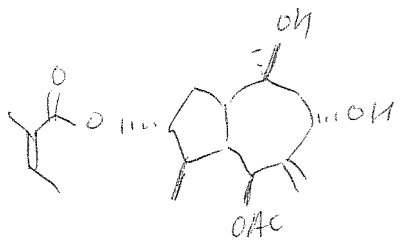


Avance 500 13C Cryo

~~sa5068~~ Sa6058

S. Andrews -- SVL



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PROCNO                         1

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TD                       65536
SOLVENT                  CDCl3
NS                         800
DS                           8
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FIDRES              0.519006 Hz
AQ                  0.9634439 sec
RG                        4096
DW                      14.700 usec
DE                       6.00 usec
TE                      300.0 K
D1                  3.00000000 sec
d11                 0.03000000 sec
DELTA               2.90000010 sec
TD0                          1

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P1                        9.10 usec
PL1                      -6.00 dB
SFO1             125.7520828 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   100.00 usec
PL2                      -6.00 dB
PL12                     12.00 dB
PL13                    120.00 dB
SFO2             500.0517480 MHz

F2 - Processing parameters
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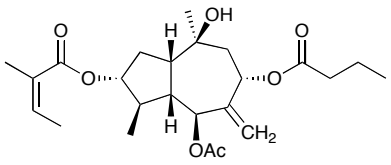
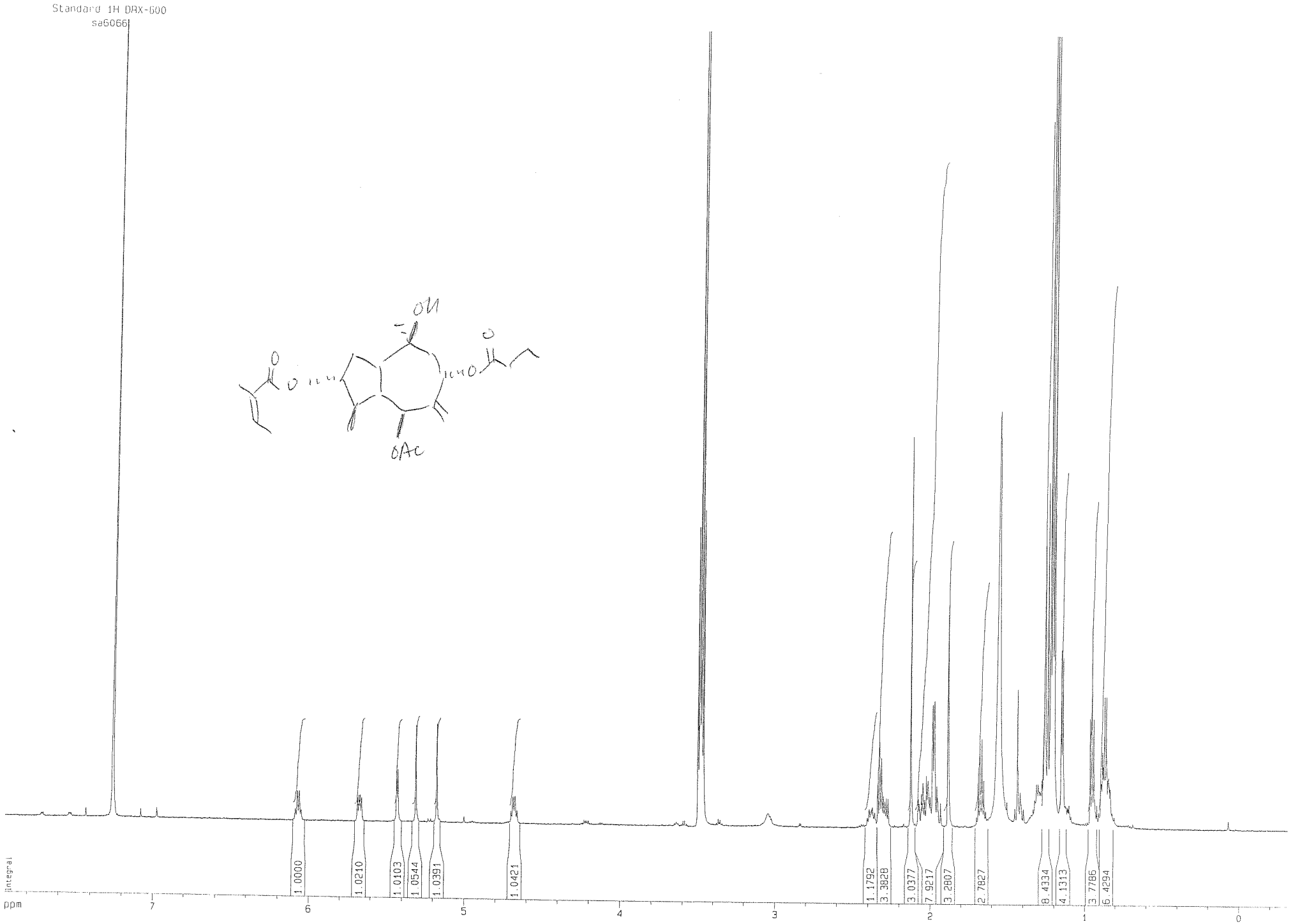


49

Butyrate 49: Butyric anhydride (50 μL, 306 μmol) and catalytic DMAP were added to a solution of diol **48** (assume 28.7 μmol) in CH_2Cl_2 (1.0 mL). The mixture was stirred at room temperature for 1 hour, quenched with saturated sodium bicarbonate solution (20 mL) and extracted with Et_2O (3 × 20 mL). The combined extracts were then washed with saturated ammonium chloride solution (40 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The crude gum was purified by column chromatography (SiO_2, Et_2O/petrol ether, 2:3 then 3:2) to afford the title compound as a colourless oil, used without further purification; δ_H (600 MHz; $CDCl_3$) 6.08 (1H, q, *J* 7.1, C=C(H)CH_3), 5.68 (1H, dd, *J* 10.8, 5.8, H-8), 5.44 (1H, d, *J* 5.4, H-6), 5.32 (1H, s, =CH), 5.18 (1H, s, =CH'), 4.69 (1H, dd, *J* 5.2, 7.2, H-3), 3.06 (1H, br s, OH), 2.40 (1H, m, H-1), 2.33 (2H, t, *J* 7.4, C$H_2$$CH_2CH_3$), 2.30 (1H, dd, *J* 12.5, 6.6, H-2), 2.13 (3H, s, C(O)CH_3), 2.05 (3H, m, H-4, H-5 and H–9), 2.00 (3H, d, *J* 7.1, C=C(H)CH_3), 1.97 (1H, dd, *J* 13.8, 10.8, H-9'), 1.89 (3H, s, C(O)CCH_3), 1.68 (2H, tq, *J* 7.4, 7.4, $CH_2C$$H_2CH_3$), 1.42 (1H, ddd, *J* 12.5, 12.5, 8.9, H-2'), 1.24 (3H, s, H-14), 1.14 (3H, d, *J* 7.1, H-15), 0.96 (3H, t, *J* 7.4, $CH_2CH_2C$$H_3$); δ_C (150 MHz; $CDCl_3$) 172.2 (C(O)CH_2), 168.6 (C(O)CH_3), 168.0 (C(O)CCH_3), 144.7 (C-7), 138.0 (C=C(H)CH_3), 127.8 (C=C(H)CH_3), 114.8 (=CH_2), 78.6 (C-3), 75.7 (C-6), 72.6 (C–10), 69.3 (C-8), 49.8 (C-5), 48.6 (C-1), 42.7 (C-4), 40.8 (C-9), 36.4 ($CH_2CH_2CH_3$), 35.3 (C-2), 31.5 (C-14), 21.1 (C(O)CH_3), 20.6 (C(O)CCH_3), 18.3 ($CH_2CH_2CH_3$), 17.5 (C-15), 15.8 (C=C(H)CH_3), 13.7 ($CH_2CH_2CH_3$); ν_{max} (film; cm^{-1}) 3530 (br OH), 2967 (C-H), 1743 (acetate C=O), 1716 (angelate C=O) 1649 (w C=C); $[\alpha]_D$ –59.5 (*c*. 0.205, $CHCl_3$); found (ESI+) $[MNa]^+$ 459.2343; $C_{24}H_{36}O_7Na$ requires *M*, 459.2359.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2
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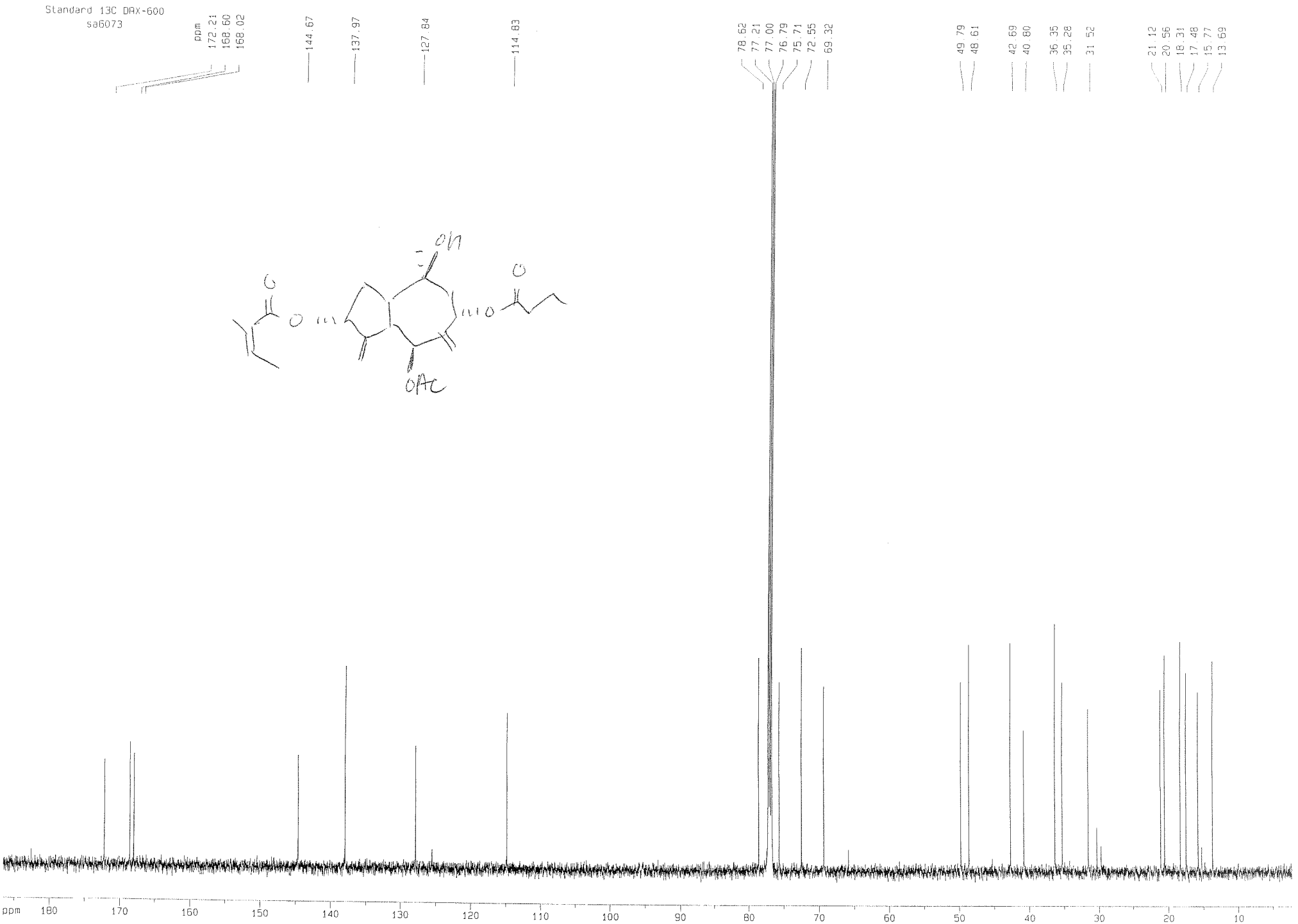
0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O
O
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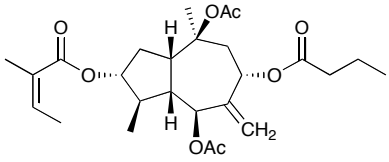
10



11

Olefin 11: Catalytic *p*-toluenesulfonic acid was added to a solution of tertiary alcohol **49** (assume 28.7 μmol) and *iso*-propenyl acetate (200 μL, 1.82 mmol) in CH_2Cl_2 (500 μL). The mixture was stirred at room temperature for 18 hours, quenched with aqueous sodium bicarbonate solution (20 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with brine (50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography (SiO_2, Et_2O/petrol ether, 1:9 to 3:7) afforded the title compound as a colourless gum, 5.5 mg, 42% over 3 steps; δ_H (600 MHz; $CDCl_3$) 6.08 (1H, q, *J* 7.2, C=C(H)CH_3), 5.52 (1H, dd, *J* 9.4, 7.5, H-8), 5.30 (1H, d, *J* 9.8, H-6), 5.25 (1H, s, =CH), 5.23 (1H, s, =CH'), 4.75 (1H, m, H-3), 2.89 (1H, ddd, *J* 14.0, 7.4, 6.6, H-1), 2.65 (1H, dd, *J* 14.4, 7.5, H-9), 2.38 (1H, ddd, *J* 13.0, 7.0, 6.6, H-2), 2.30 (2H, t, *J* 7.4, C$H_2$$CH_2CH_3$), 2.18 (1H, m, H-4), 2.06 (3H, s, O-6-C(O)CH_3), 2.04 (1H, dd, *J* 14.4, 9.4, H-9'), 2.00 (3H, d, *J* 7.2, C=C(H)CH_3), 1.95 (3H, s, O-10-C(O)CH_3), 1.90 (1H, m, H-5), 1.88 (3H, s, C(O)CCH_3), 1.64 (2H, tq, *J* 7.4, 7.4, CH_2CH_2CH_3), 1.62 (1H, m, H-2'), 1.54 (3H, s, H-14), 1.15 (3H, d, *J* 7.1, H-15), 0.93 (3H, t, *J* 7.4, CH_2CH_2CH_3); δ_C (150 MHz; $CDCl_3$) 172.6 (C(O)CH_2), 170.1 (O-10-C(O)CH_3), 169.3 (O-6-C(O)CH_3), 167.9 (C(O)CCH_3), 146.4 (C-7), 138.2 (C=C(H)CH_3), 127.8 (C=C(H)CH_3), 115.1 (C-11), 83.0 (C-10), 79.4 (C-3), 73.1 (C-6), 71.1 (C–8), 52.4 (C-5), 45.9 (C-1), 43.5 (C-4), 36.5 (C-9 and C$H_2CH_2CH_3$), 34.1 (C-2), 27.5 (C-14), 22.2 (O-10-C(O)CH_3), 21.1 (O-6-C(O)CH_3), 20.5 (C(O)CCH_3), 19.1 (C-15), 18.2 (CH_2CH_2CH_3), 15.8 (C(O)CCH_3), 13.7 (CH_2CH_2CH_3); ν_{max} (film; cm^{-1}) 2930 (C-H), 1736 (acetate C=O), 1716 (angelate C=O), 1647 (w C=C); $[\alpha]_D$ –168 (*c*. 0.100, $CHCl_3$); found (ESI+) $[MNa]^+$ 501.2479; $C_{26}H_{38}O_8Na$ requires *M*, 501.2464.

Standard 1H DRX-600
sa6074

Hz
3321.54
3313.99
3312.34
3304.79
3186.79
3177.00
3148.87
3138.84

2859.78
2852.91
2847.92
2840.97

2096.58
2089.51

1746.35
1739.75
1733.14
1599.90
1592.59
1585.47
1578.23
1408.46
1390.82
1383.17
1380.88
1375.65
1373.27
1365.71
1236.55
1228.53
1204.37
1200.78
1199.36
1193.64
1192.20
1170.86
1135.87
1134.46
999.25
991.78
984.33
976.96
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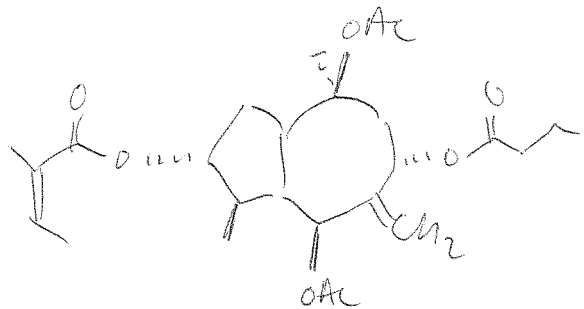
560.92
553.57



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PROCNO 1

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Time 19.09

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9.351
3.412
3.506

ppm
6
5
4
3
2
1

Standard 13C DRX-600
sa6074

ppm

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170.11
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167.93
146.36
138.21
127.79
115.06
82.99
79.38
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77.00
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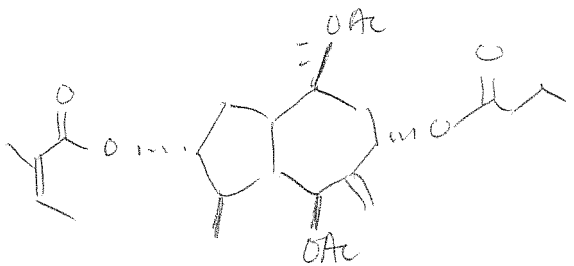
15.77
15.26
13.66



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