

SUPPLEMENTARY MATERIAL

Synthetic Mimic of Carbohydrated-Based Anticancer Vaccines: Preparation of Carbohydrate Polymers Bearing Unimolecular Trivalent Carbohydrates Ligand by Controlled Living Radical Polymerization

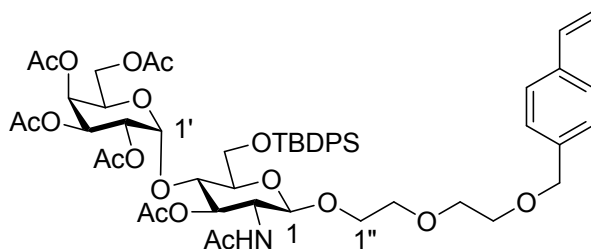
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Taipei City, 24205 Taiwan, R.O.C.; E-mail:080686@mail.fju.edu.tw*

This supplementary material includes:

1. Experimental procedures and characterization data of “acetylated” **10a** and “acetylated” **10b**....2.
2. NMR spectra (^1H , $^{13}\text{C}/\text{DEPT}$, COSY) of compound **1**, **3**, **5**, **7**, **8**, **10a**, and **10b**.....5.
3. NMR spectra (^1H , $^{13}\text{C}/\text{DEPT}$, COSY, HSQC, NOESY, ROESY) of “acetylated” **10a** and
“acetylated” **10b**.....23.

2-[2-(4-Vinylbenzyloxy)ethoxy]ethyl-*O*-(2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl)-(1 \rightarrow 4)-3-*O*-acetyl-2-acetamido-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy- β -D-glucopyranoside [acetylated **10a]**



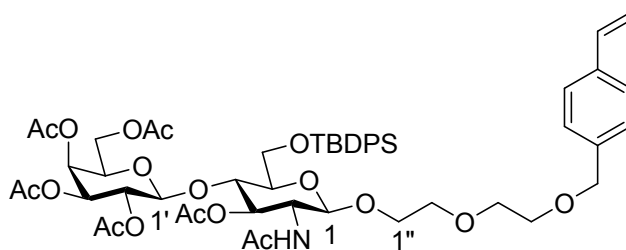
To a solution of 2-[2-(4-vinylbenzyloxy)ethoxy]ethyl *O*-(2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl)-(1 \rightarrow 4)-2-acetamido-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy- β -D-glucopyranoside (50mg, 0.05 mmol), and DMAP (10 mg, 0.082 mmol) in pyridine (2.5 mL) was added Ac₂O (2.5 mL) at room temperature. The reaction mixture was stirred at same temperature for 36 h, then diluted with DCM (100 mL). The resulting mixture was washed with 2 M HCl (20 mL) and 50% NaHCO₃ (20 mL). The organic layers were dried over MgSO₄ and concentrated in vacuum to give a crude product, which was purified by silica gel chromatography (EtOAc:hexane = 8:2) to afford the acetylated disaccharide as a white solid (0.05 g, 83%):

α -isomer

mp 98.1–103.2 °C; $[\alpha]_D^{25} +39.22$ (c = 1.75, CHCl₃); IR (neat) 3276, 3072, 2933, 2859, 1748 (C=O), 1654 (NHCO), 1513, 1485, 1428, 1373, 1258, 1234, 1159, 1108, 1065, 1045, 960, 945, 905, 848, 825, 801, 780, 739, 703, 676 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.68–7.60 (m, 4H, Ph), 7.41–7.31 (m, 8H, Ph), 7.28 (d, *J* = 8.1 Hz, 2H, *para*-), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H, ArCH=CH₂), 6.24 (d, *J* = 7.8 Hz, 1H, NHAc), 5.71 (d, *J* = 17.6 Hz, 1H, ArCH=CH₂), 5.39 (d, *J* = 2.2 Hz, 1H, H_{4'}), 5.24–5.20 (two overlapping d at 5.22, *J* = 11.0 Hz, 1H, H_{3'}, and at 5.22, *J* = 10.8 Hz, 1H, RCH=CH₂), 5.18 (d, *J* = 3.8 Hz, 1H, H_{1'}, α -form), 5.06 (dd, *J* = 11.0, 3.9 Hz, 1H, H_{2'}), 4.93 (d, *J* = 8.2 Hz, 1H, H₁, β -form), 4.89 (dd, *J* = 9.6, 9.1 Hz, 1H, H₄), 4.57 (d, *J* = 12.3 Hz, 1H,

ArCH₂O, AB), 4.54 (d, $J = 12.3$ Hz, 1H, ArCH₂O, AB), 4.33–4.24 (m, 2H, H_{5'}, H₃), 4.13 (dd, $J = 11.0, 8.4$ Hz, 1H, H_{6'a}), 3.95 (dd, $J = 11.0, 5.9$ Hz, 1H, H_{6'b}), 3.90 (dt, $J = 11.8, 3.8$ Hz, 1H, H_{1'a}), 3.73–3.69 (m, 1H, H_{1'b}), 3.67–3.58 (m, 7H, CH₂×3, H_{6a}), 3.56 (dd, $J = 11.5, 2.2$ Hz, 1H, H_{6b}), 3.42 (ddd, $J = 9.3, 6.7, 2.6$ Hz, 1H, H₅), 3.41–3.35 (m, 1H, H₂), 2.09 (s, 3H, Ac), 2.003 (s, 3H, Ac), 1.998 (s, 3H, Ac), 1.94 (s, 3H, Ac), 1.93 (s, 3H, Ac), 1.01 (s, 9H, *t*-Bu); ¹³C NMR (125 MHz, CDCl₃) δ 171.0 (s), 170.9 (s), 170.3 (s), 170.1 (s), 169.7 (s), 169.5 (s), 137.5 (s), 137.1 (s), 136.4 (d), 135.6 (d×2), 135.6 (d×2), 133.3 (s), 133.2 (s), 129.6 (d), 129.6 (d), 127.9 (d×2), 127.6 (d×2), 127.6 (d×2), 126.3 (d×2), 113.9 (t), 99.6 (d), 96.0 (d), 75.8 (d), 74.7 (d), 72.9 (d×2), 72.6 (d×2), 72.3 (d), 70.7 (t), 70.4 (t), 69.4 (t), 68.3 (t), 67.5 (d), 67.4 (d), 67.1 (d), 66.2 (d), 63.2 (t), 60.9 (t), 56.9 (d), 26.7 (q×3), 23.4 (q), 20.8 (q), 20.7 (q), 20.6 (q), 20.6 (q×2), 19.2 (s); HRMS (ESI⁺): m/z calcd for C₅₃H₆₉NO₁₈Si [M+H]⁺: 1036.4362; found: 1036.4368.

2-[2-(4-Vinylbenzyloxy)ethoxy]ethyl *O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-(1→4)-3-*O*-acetyl-2-acetamido-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy- β -D-glucopyranoside [acetylated 10b]



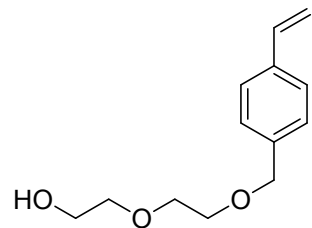
To a solution of 2-[2-(4-vinylbenzyloxy)ethoxy]ethyl *O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-(1→4)-2-acetamido-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy- β -D-glucopyranoside (30.1 mg, 0.0302 mmol), and DMAP (6.2 mg, 0.0513 mmol) in pyridine (1.5 mL) was added Ac₂O (1.5 mL) at room temperature. The reaction mixture was stirred at same temperature for 36 h, then diluted with DCM (100 mL). The resulting

mixture was washed with 2 M HCl (20 mL) and 50% NaHCO₃ (20 mL). The organic layers were dried over MgSO₄ and concentrated in vacuum to give a crude product, which was purified by silica gel chromatography (EtOAc:hexane = 9:1) to afford the acetylated disaccharide as a white solid (0.03 g, 85%):

β-isomer

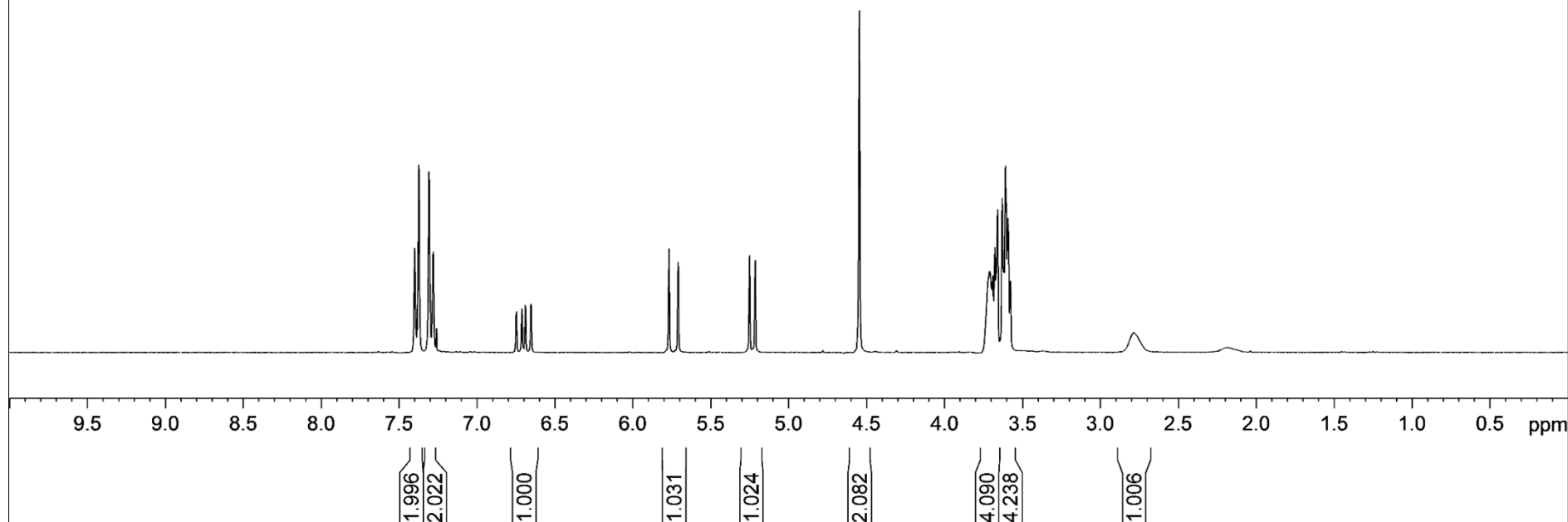
$[\alpha]_D^{25} -123.33$ (c = 0.21, CHCl₃); IR (neat) 3072, 2934, 2859, 1750 (C=O), 1672 (NHCO), 1589, 1472, 1462, 1429, 1369, 1222, 1165, 1135, 1112, 1046, 998, 960, 915, 824, 797, 740, 705, 675, 605 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 7.6 Hz, 2H, Ph), 7.71 (d, *J* = 7.6 Hz, 2H, Ph), 7.47–7.32 (m, 8H, overlapped with one d at 7.37, *J* = 7.9 Hz, Ph, *para*-), 7.29 (d, *J* = 7.9 Hz, *para*-), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H, ArCH=CH₂), 6.34 (d, *J* = 9.6 Hz, 1H, NHAc), 5.72 (d, *J* = 17.6 Hz, ArCH=CH₂), 5.29 (d, *J* = 3.4 Hz, 1H, H_{4'}), 5.21 (d, *J* = 10.9 Hz, 1H, ArCH=CH₂), 5.05 (dd, *J* = 10.2, 8.2 Hz, 1H, H_{2'}), 4.96 (t, *J* = 9.7 Hz, 1H, H₃), 4.91 (dd, *J* = 10.2, 3.4 Hz, 1H, H_{3'}), 4.77 (d, *J* = 8.2 Hz, 1H, H_{1'}, β-form), 4.68 (d, *J* = 12.4 Hz, 1H, ArCH₂O, AB), 4.59–4.53 (two overlapping d at 4.57, *J* = 8.0 Hz, 1H, H₁, β-form, and at 4.56, *J* = 12.4 Hz, 1H, ArCH₂O, AB), 4.15–4.03 (m, 4H, H₆, H₄, H₂), 3.96–3.81 (m, 3H, H₆, H_{1''a}), 3.78–3.69 (m, 2H, H_{1''b}, H_{5'}), 3.65–3.49 (m, 6H, CH₂×3), 3.27 (d, *J* = 9.3 Hz, 1H, H₅), 2.11 (s, 3H, Ac), 2.04 (s, 3H, Ac), 2.04 (s, 3H, Ac), 1.96 (s, 3H, Ac), 1.92 (s, 3H, Ac), 1.78 (s, 3H, Ac), 1.06 (s, 9H, *t*-Bu); ¹³C NMR (125 MHz, CDCl₃) δ 170.9 (s), 170.4 (s), 170.3 (s), 170.2 (s), 169.9 (s), 168.9 (s), 137.3 (s), 137.2 (s), 136.4 (d), 136.0 (d×2), 135.4 (d×2), 133.4 (s), 132.2 (s), 129.9 (d), 129.8 (d), 128.4 (d×2), 127.9 (d×2), 127.6 (d×2), 126.3 (d×2), 114.0 (t), 101.9 (d), 100.3 (d), 75.2 (d), 74.3 (d), 73.4 (d), 73.0 (t), 71.6 (t), 71.1 (d), 70.7 (t), 70.6 (d), 69.4 (d), 69.1 (t), 67.9 (t), 67.0 (d), 61.3 (t), 61.1 (t), 53.6 (d), 26.8 (q×3), 23.1 (q), 20.9 (q), 20.6 (q), 20.6 (q), 20.5 (q), 20.5 (q), 19.3 (s); HRMS (ESI⁺): *m/z* calcd for C₅₃H₆₉NO₁₈Si [M+H]⁺: 1036.4362; found: 1036.4385.

TYK2038-B-20130419



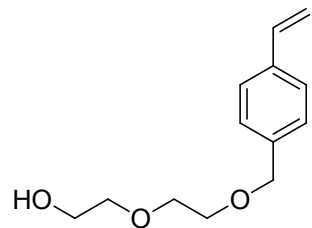
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6.748
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5.215
4.547
3.710
3.694
3.690
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3.605
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2.787



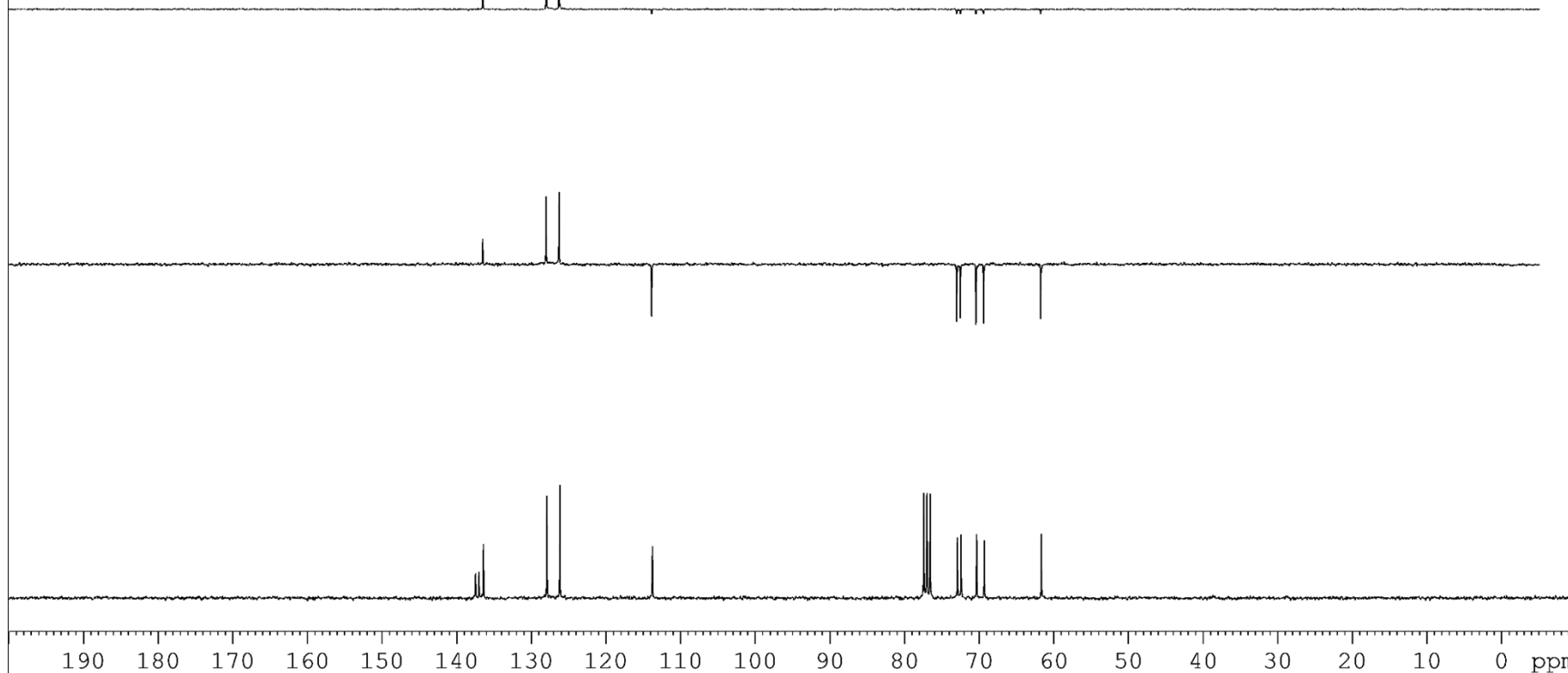
¹H NMR (300 MHz, CDCl₃) of 1

TYK-Styrene



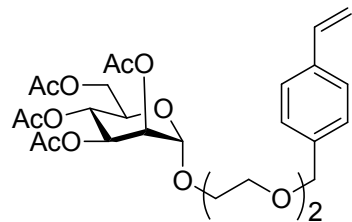
1

- 137.4745
- 137.0069
- 136.4089
- 127.9093
- 126.1770
- 113.7714
- 77.4219
- 76.9982
- 76.5740
- 72.9139
- 72.4273
- 70.3401
- 69.3221
- 61.6692



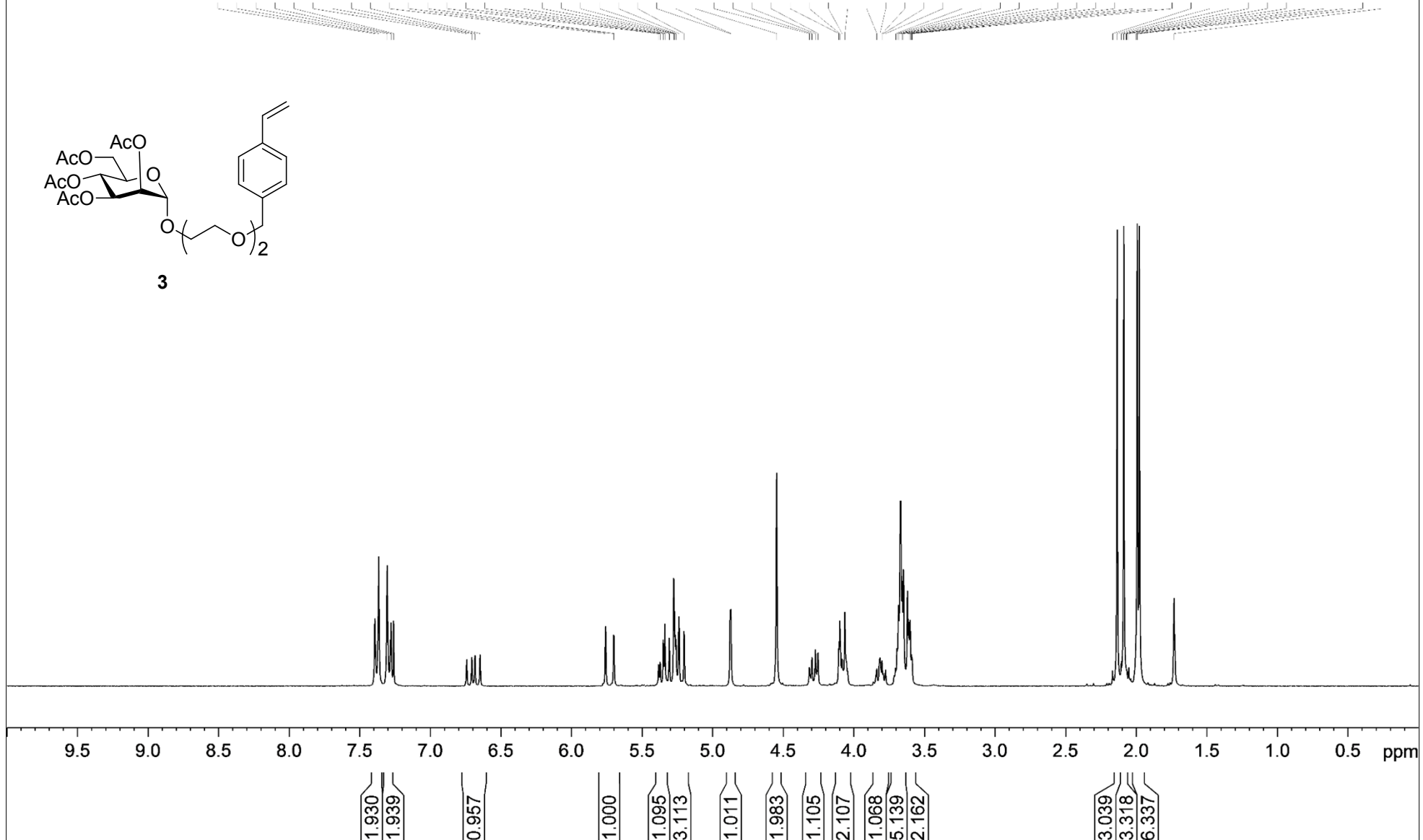
¹³C/DEPT NMR (75 MHz, CDCl₃) of **1**

YCC1005-B-20130725



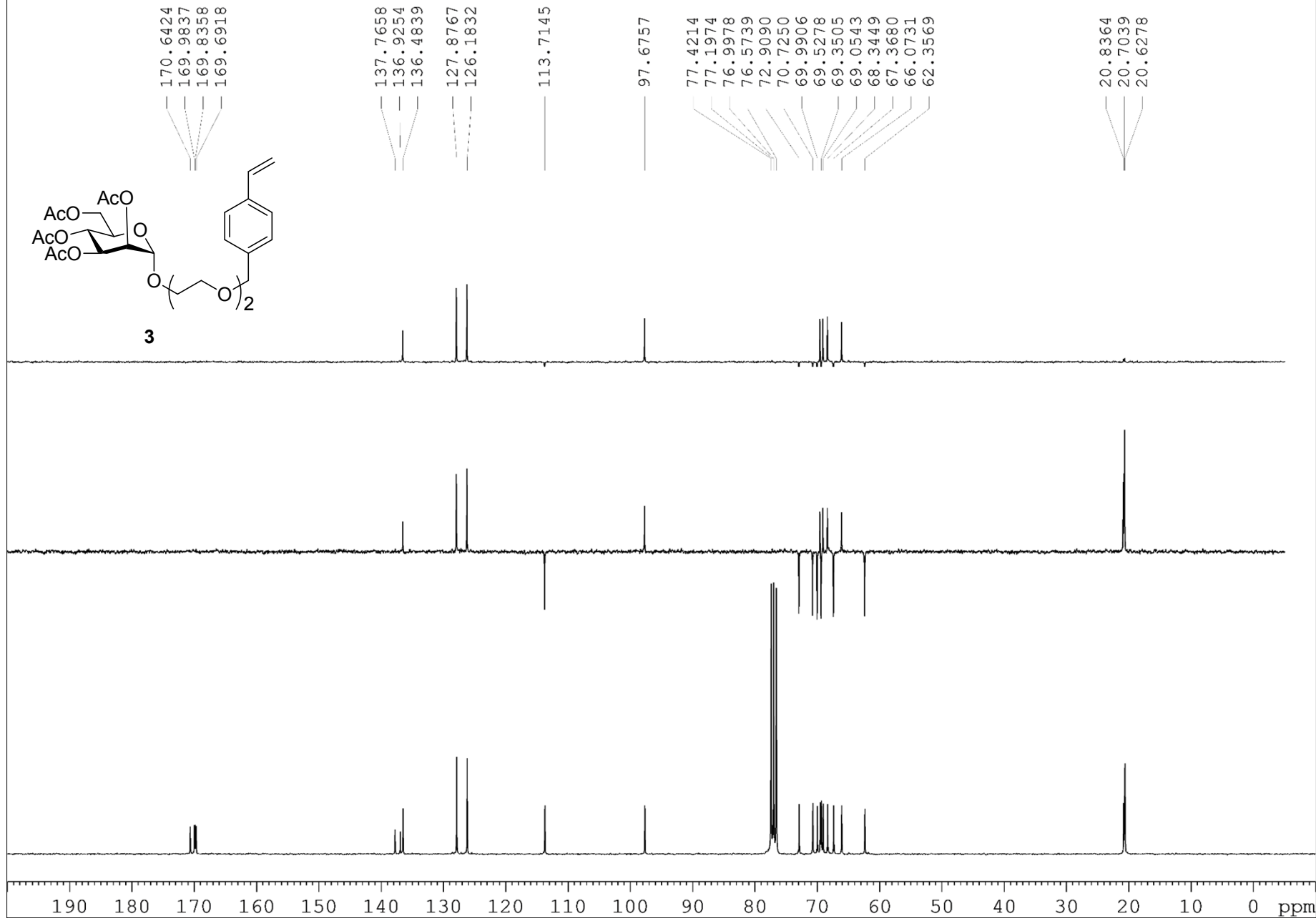
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5.699
5.383
5.372
5.350
5.339
5.307
5.276
5.272
5.265
5.260
5.239
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4.876
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3.837
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3.684
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3.668
3.657
3.648
3.620
3.611
3.601
3.591
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2.002
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1.977
1.732



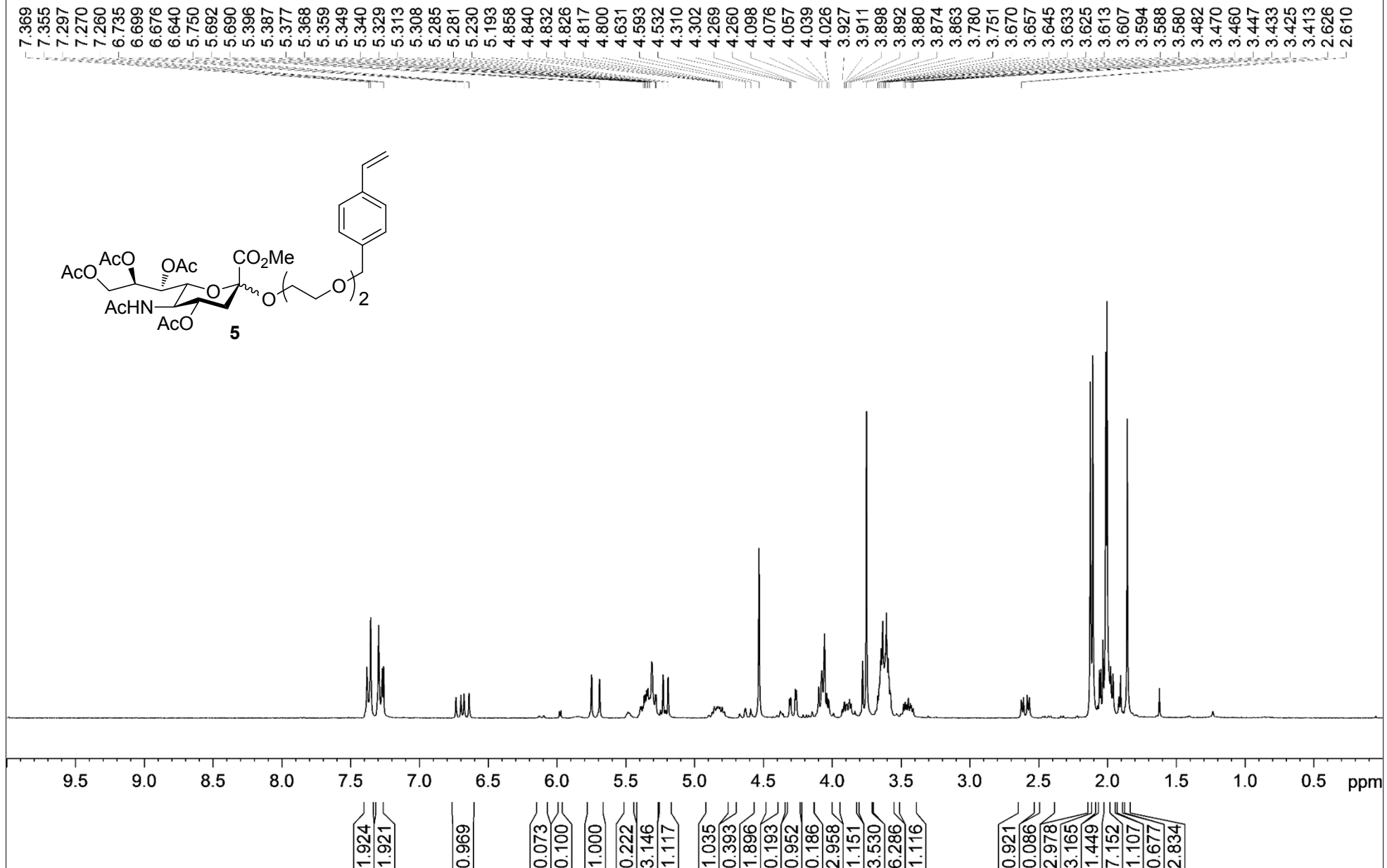
¹H NMR (300 MHz, CDCl₃) of **3**

YCC1005-B-20130725



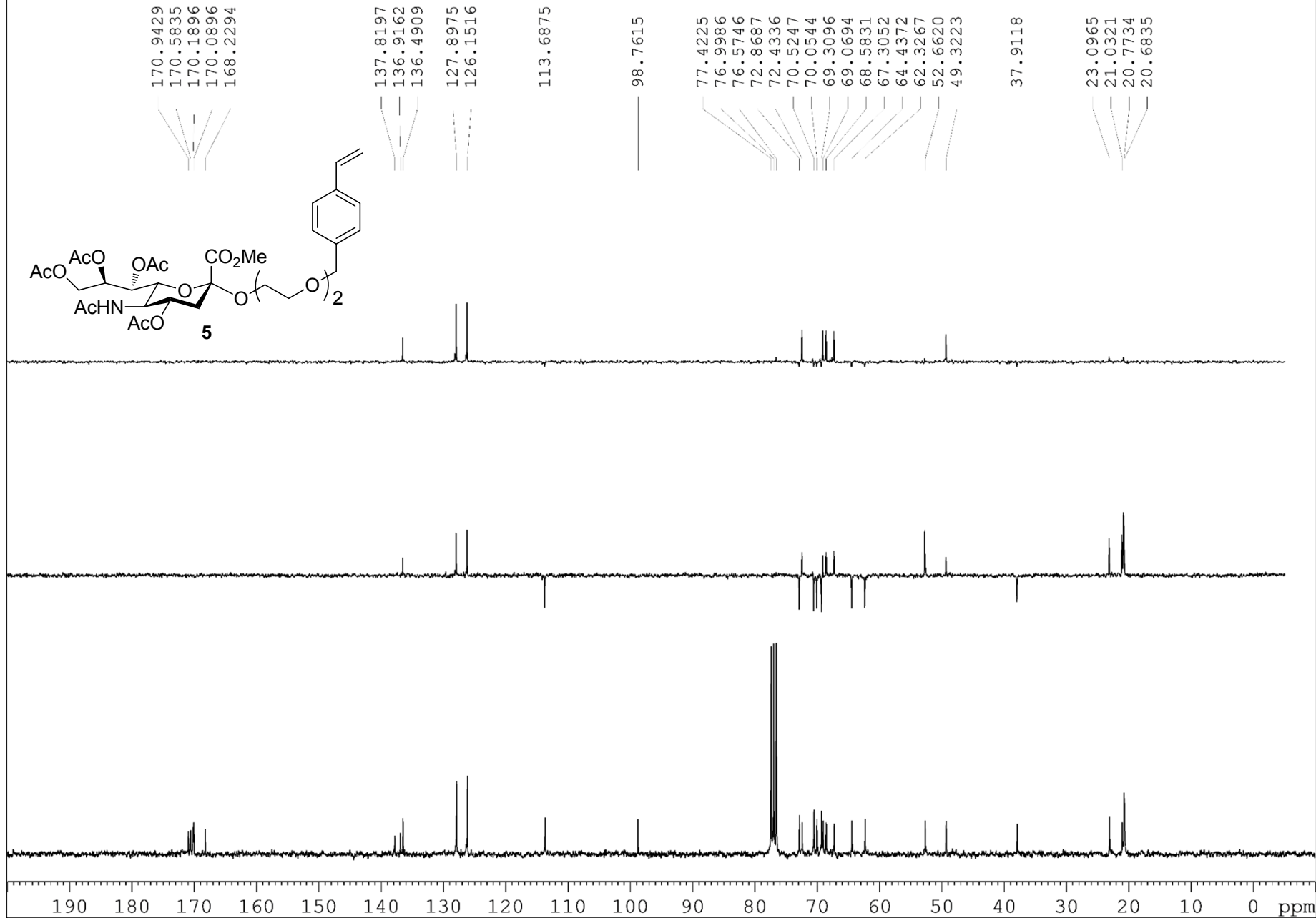
¹³C/DEPT NMR (75 MHz, CDCl₃) of **3**

TYK2101-C-20131103

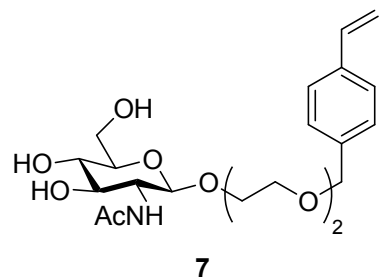


¹H NMR (300 MHz, CDCl₃) of **5**, α and β mixtures ($\alpha/\beta = 91/9$)

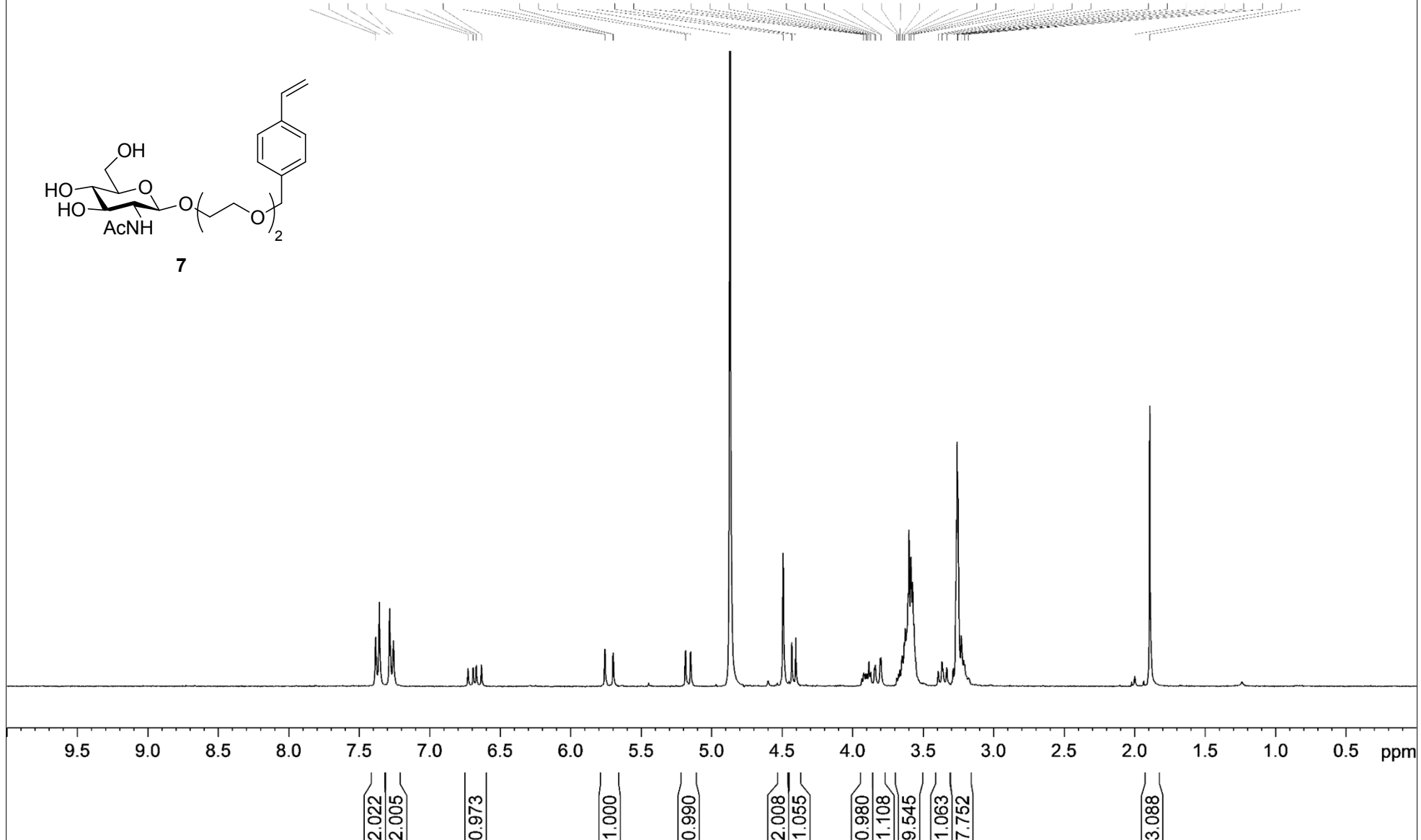
TYK2101-C-20131103



¹³C/DEPT NMR (75 MHz, CDCl₃) of **5** (only α-isomer)

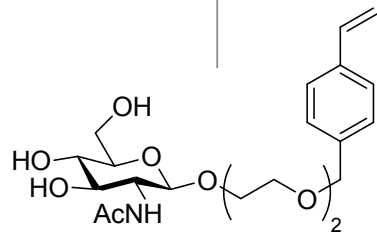


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3.872
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3.839
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3.634
3.627
3.607
3.600
3.587
3.575
3.565
3.393
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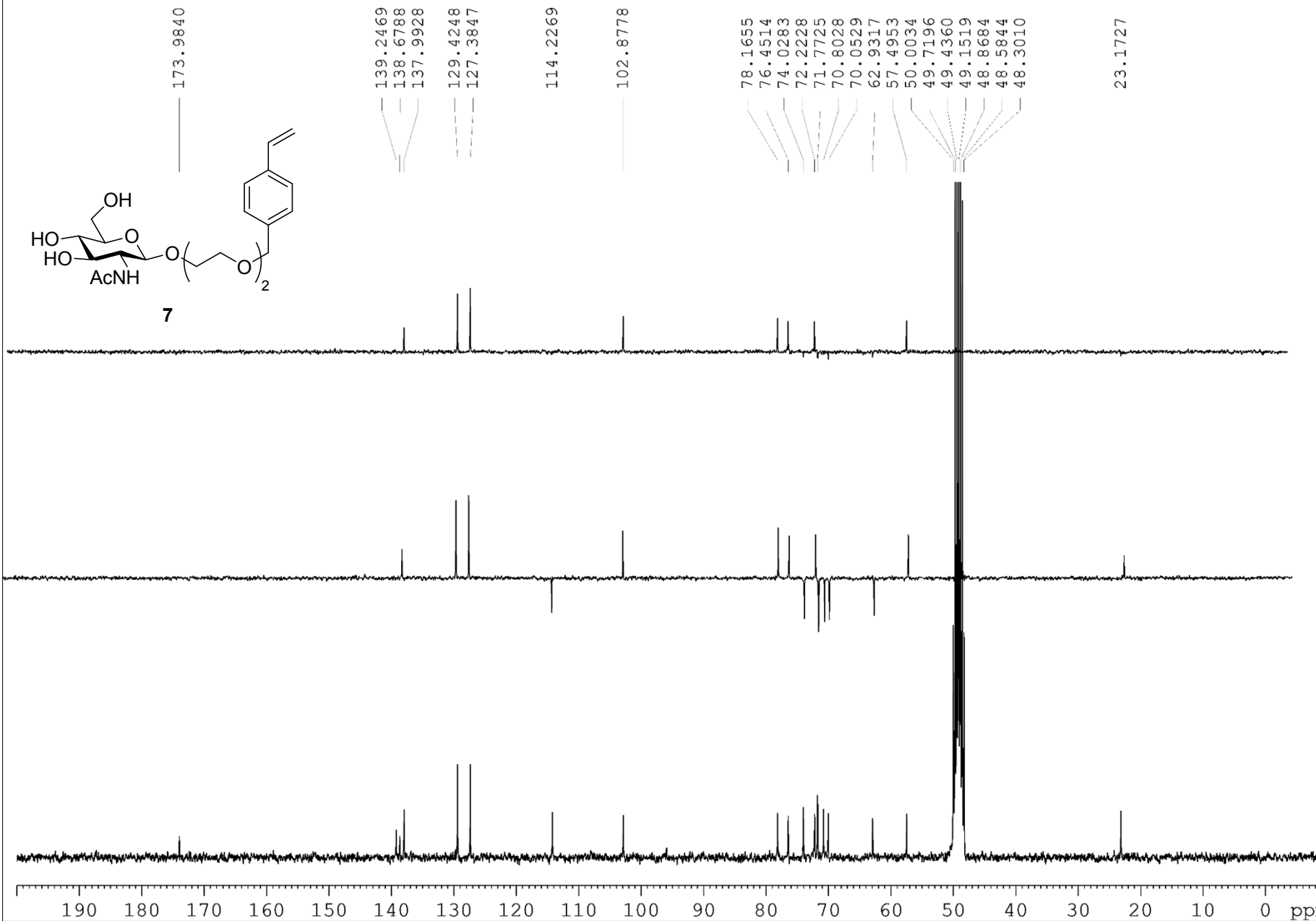


¹H NMR (300 MHz, CD₃OD) of 7

TYK2026-B-20130523

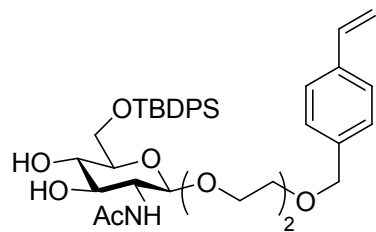


7

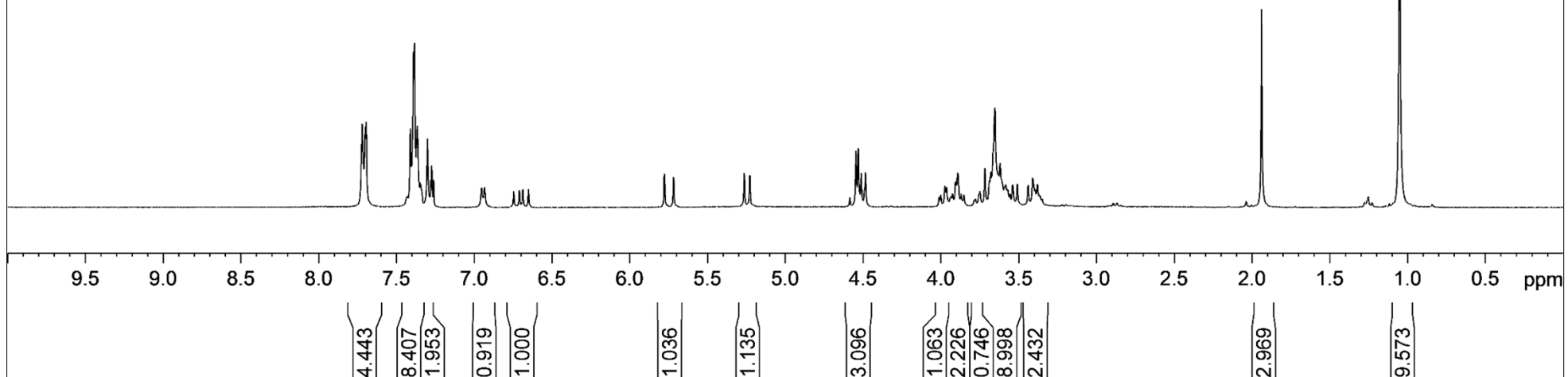


TYK2046-B-20130530

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7.339
7.301
7.274
7.260
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6.934
6.746
6.710
6.687
6.651
5.778
5.776
5.719
5.718
5.265
5.228
5.227
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4.545
4.531
4.512
4.484
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4.000
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3.964
3.934
3.925
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3.870
3.852
3.785
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3.756
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3.631
3.619
3.591
3.584
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3.556
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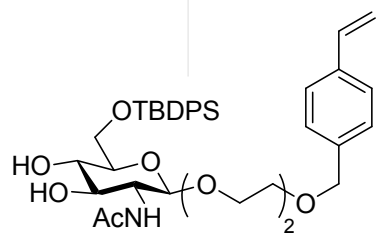


8



^1H NMR (300 MHz, CDCl_3) of **8**

TYK2046-B-20130530



8

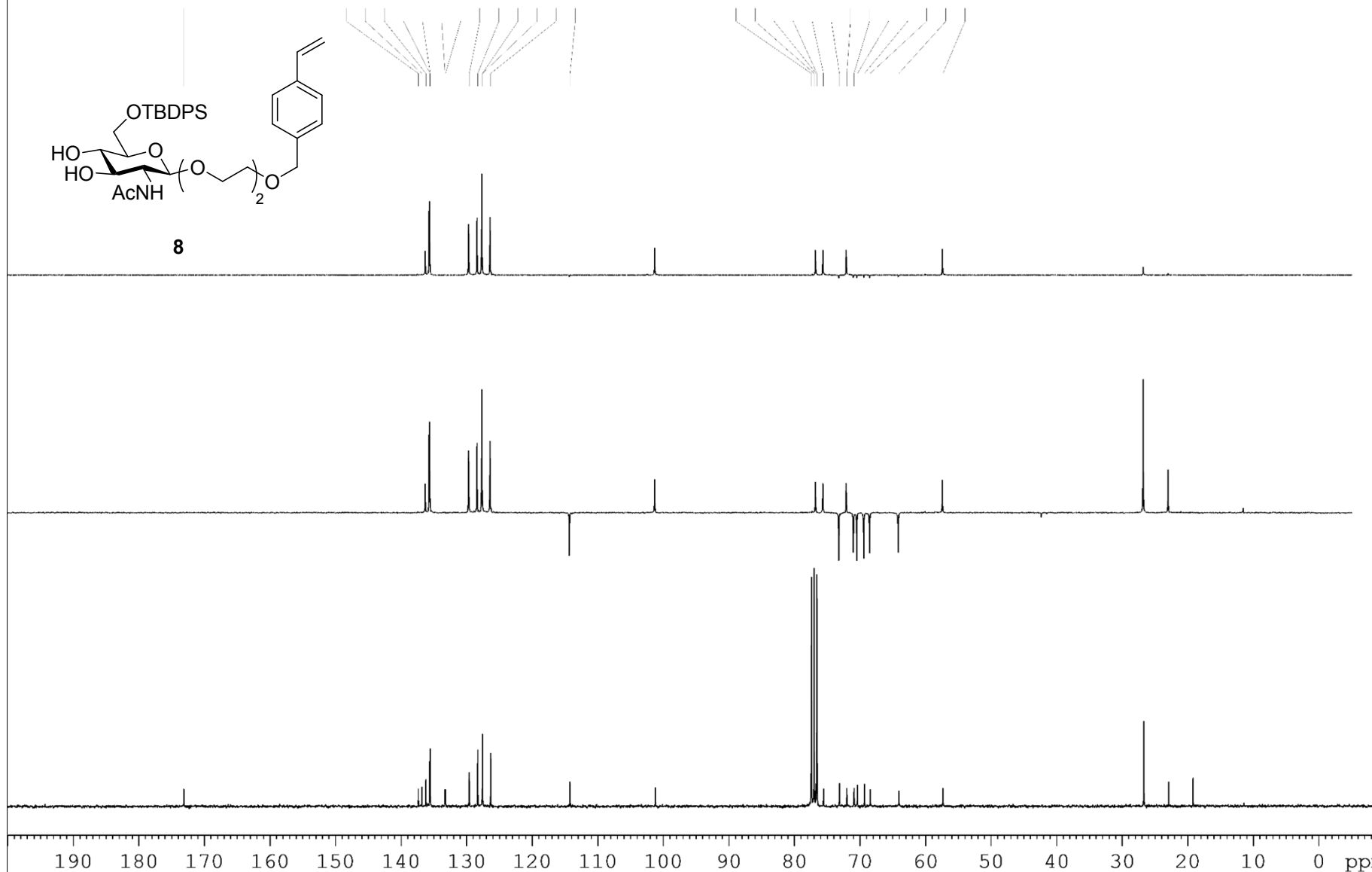
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136.2177
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126.3389
114.2278

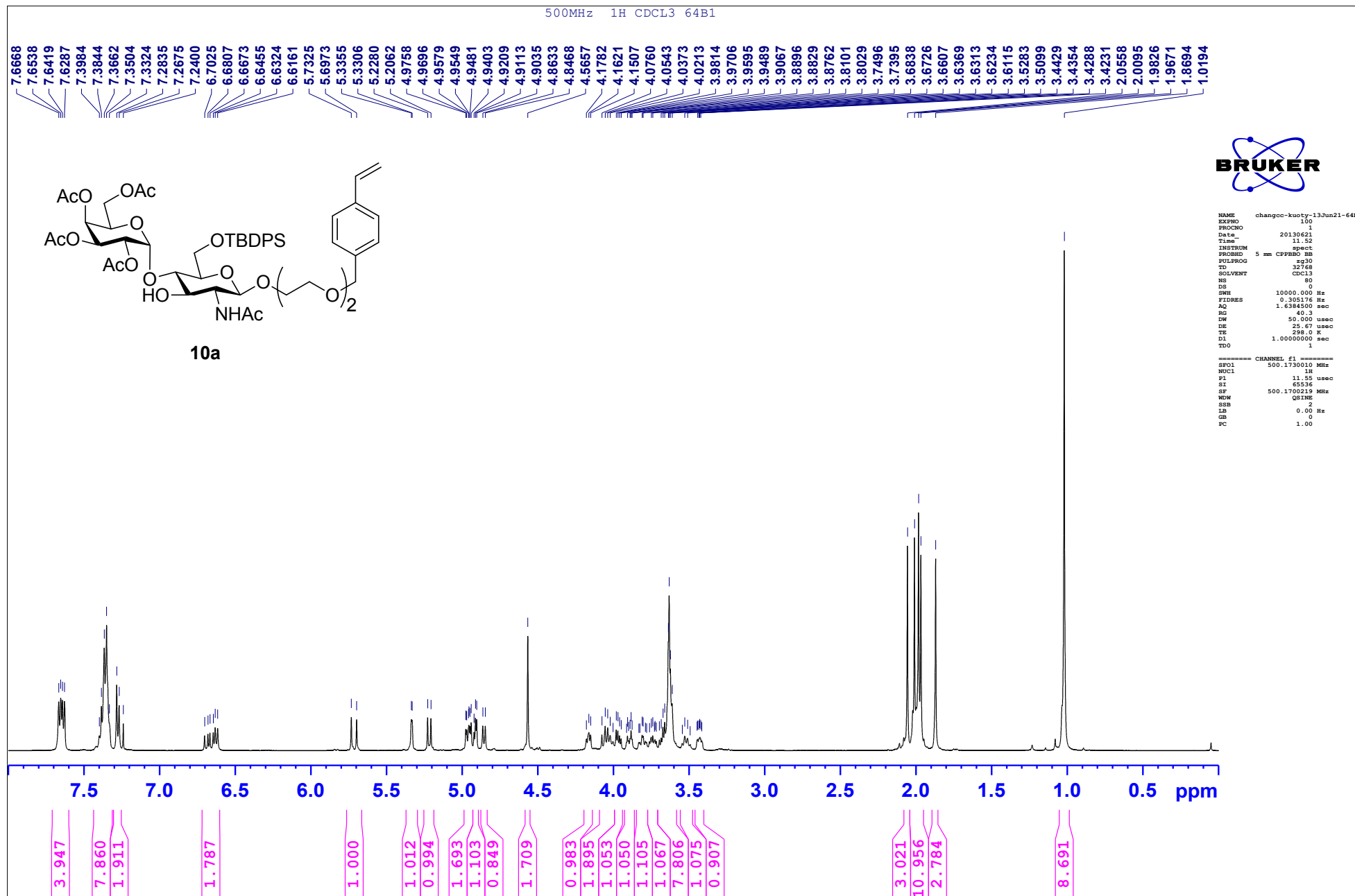
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57.3527

26.7074
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19.2057



¹³C/DEPT NMR (75 MHz, CDCl₃) of **8**

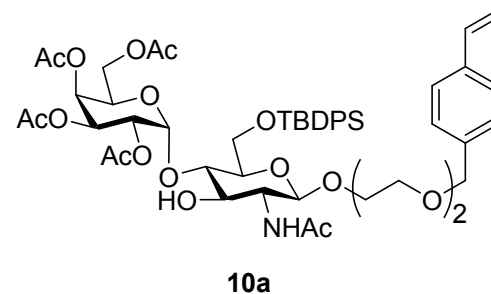


¹H NMR (500 MHz, CDCl₃) of **10a** (α-isomer)

Dept135

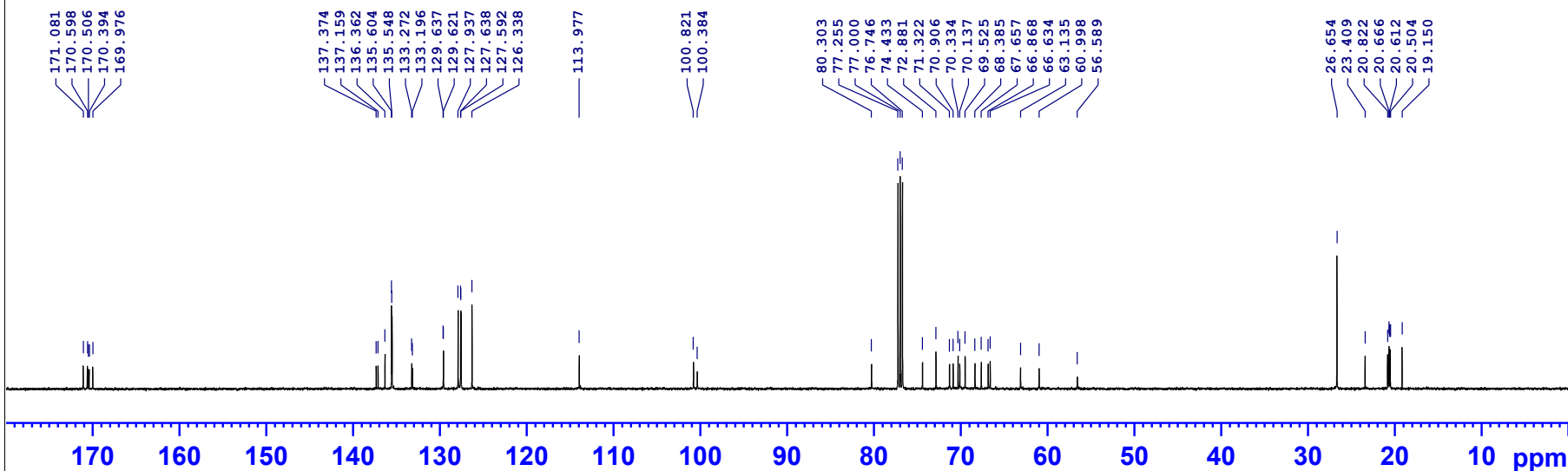


Dept90



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PROCNO    1
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PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        100
DS        4
SWH       34090.910 Hz
FIDRES    0.520186 Hz
AQ        0.9612446 sec
RG        2050
DW        14.667 usec
DE        24.00 usec
TE        298.0 K
D1        2.0000000 sec
D11       0.0300000 sec
TDO       100
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NUC1     13C
P1       10.00 usec
SI       65536
SF       125.7678558 MHz
WWSW    RM
SSB      0
LB       1.00 Hz
GB       0
PC       1.00
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500MHz 13C CDCL3 64B1



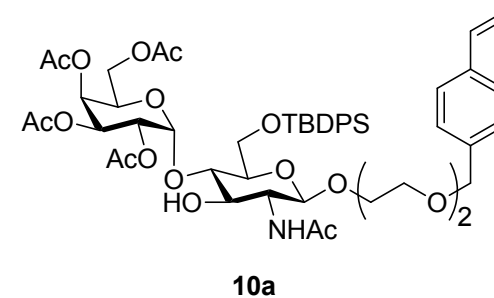
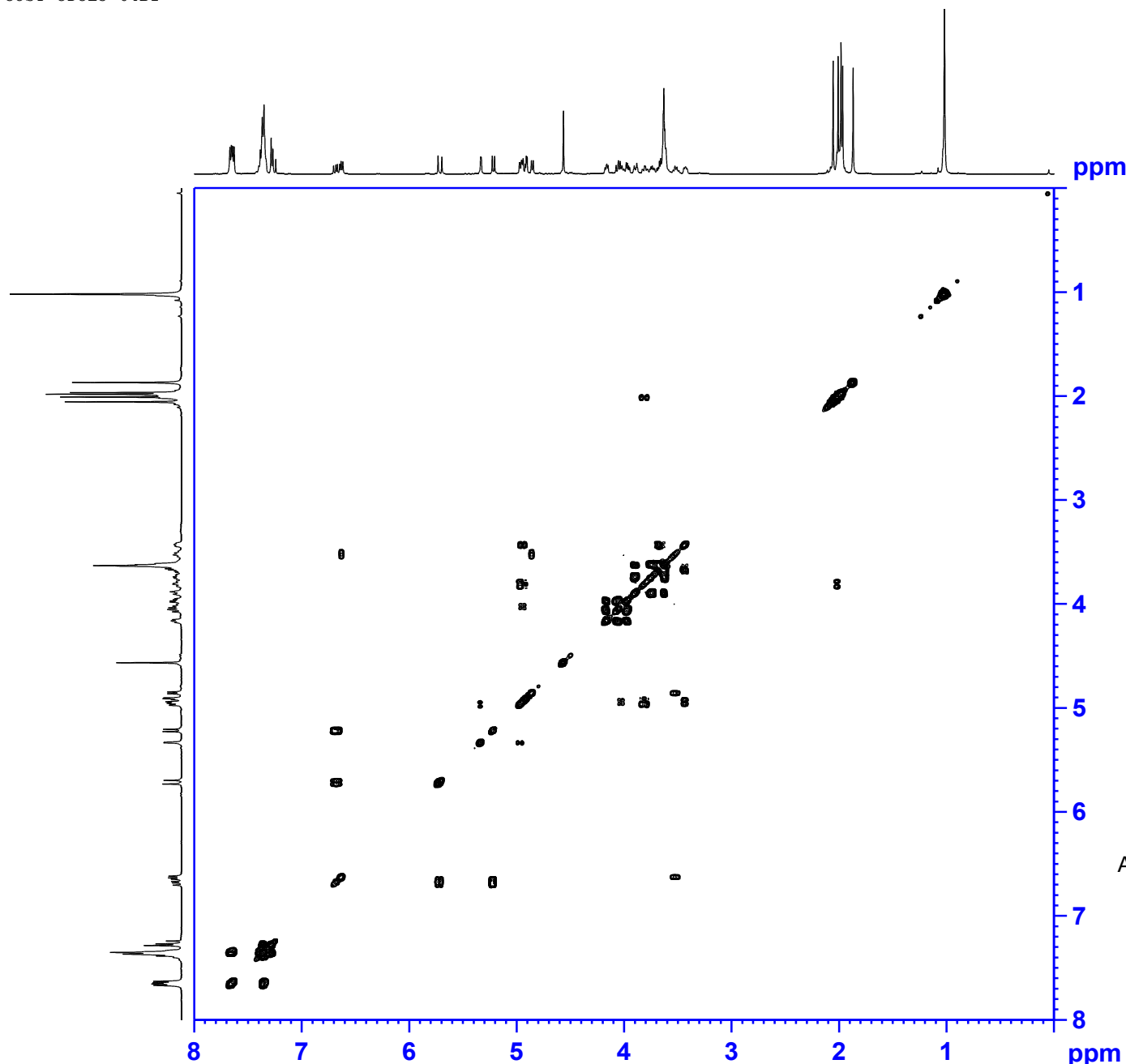
¹³C/DEPT NMR (125 MHz, CDCl₃) of **10a** (α-isomer)

500MHz COSY CDCL3 64B1

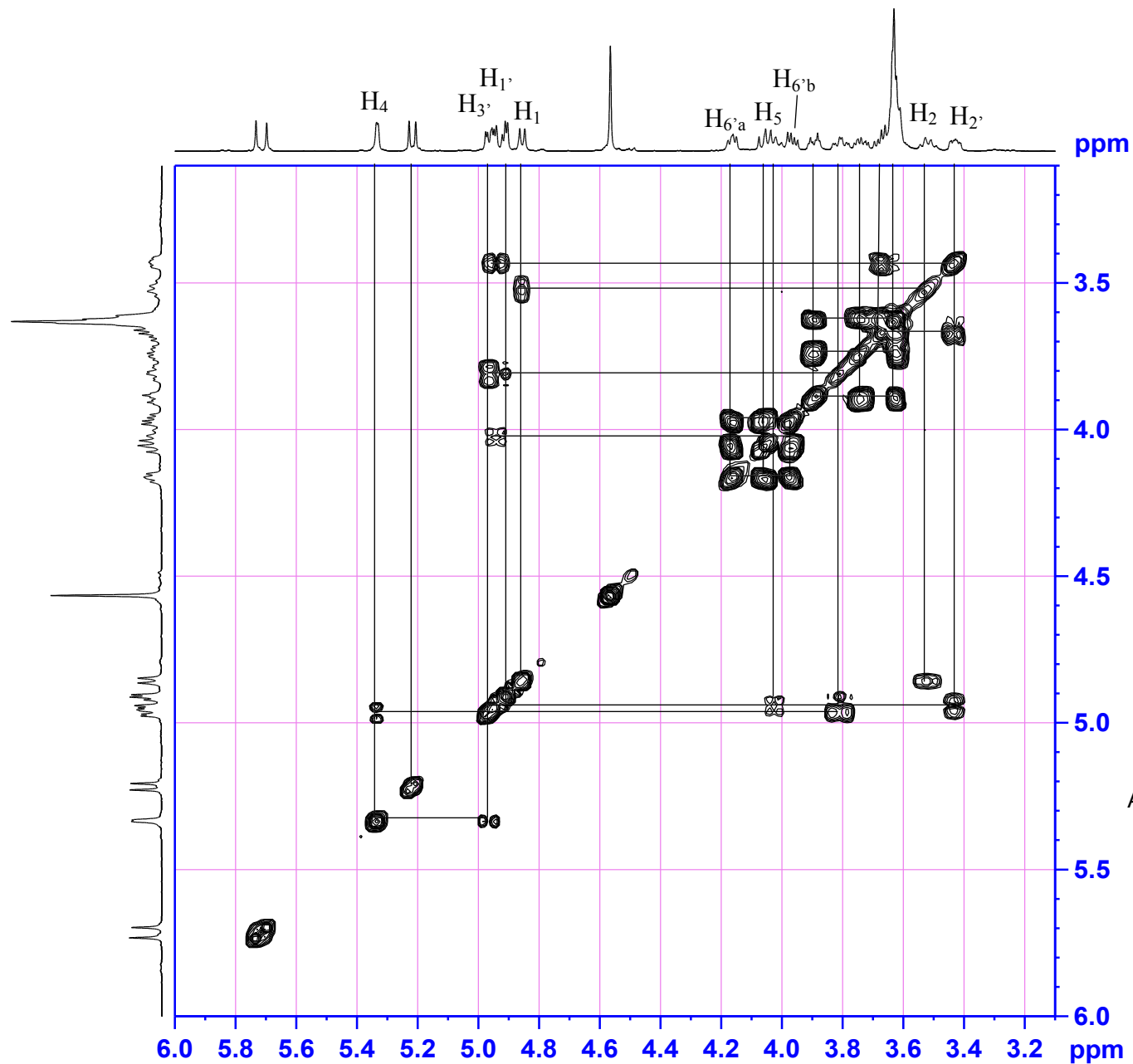


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PROCNO    1
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TD         2048
SOLVENT   CDCL3
NS         4
DS         16
SWH        6510.417 Hz
FIDRES     3.178914 Hz
AQ         0.1373364 sec
RG         203
DW         76.800 usec
DE         22.00 usec
TE         298.0 K
DO         0.0000000 sec
D1         1.0000000 sec
D11        0.0300000 sec
D12        0.0002000 sec
D13        0.0000400 sec
D16        0.0002000 sec
INO        0.00015360 sec

===== CHANNEL f1 =====
SFO1      500.135010 MHz
NUC1       1H
FO         5.78 usec
F1         11.55 usec
PC         2500.00 usec
WDW        3
SSB        0
TD         512
SFO1      500.135 MHz
FIDRES     12.715657 Hz
SW         13.014 Ppm
FHM0DE     QF
SI         1024
SF         500.135010 MHz
WDW        Q8INE
SSB        0
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PC         1.00
SI         1024
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SSB        0
GB         0.00 Hz
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¹H NMR COSY (500 MHz, CDCl₃) of **10a** (α-isomer)

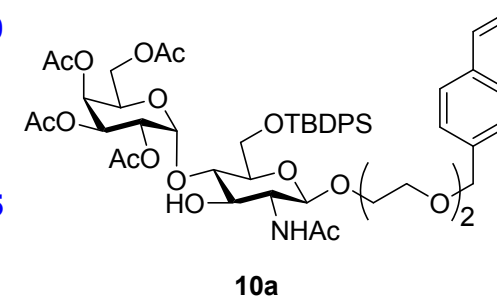


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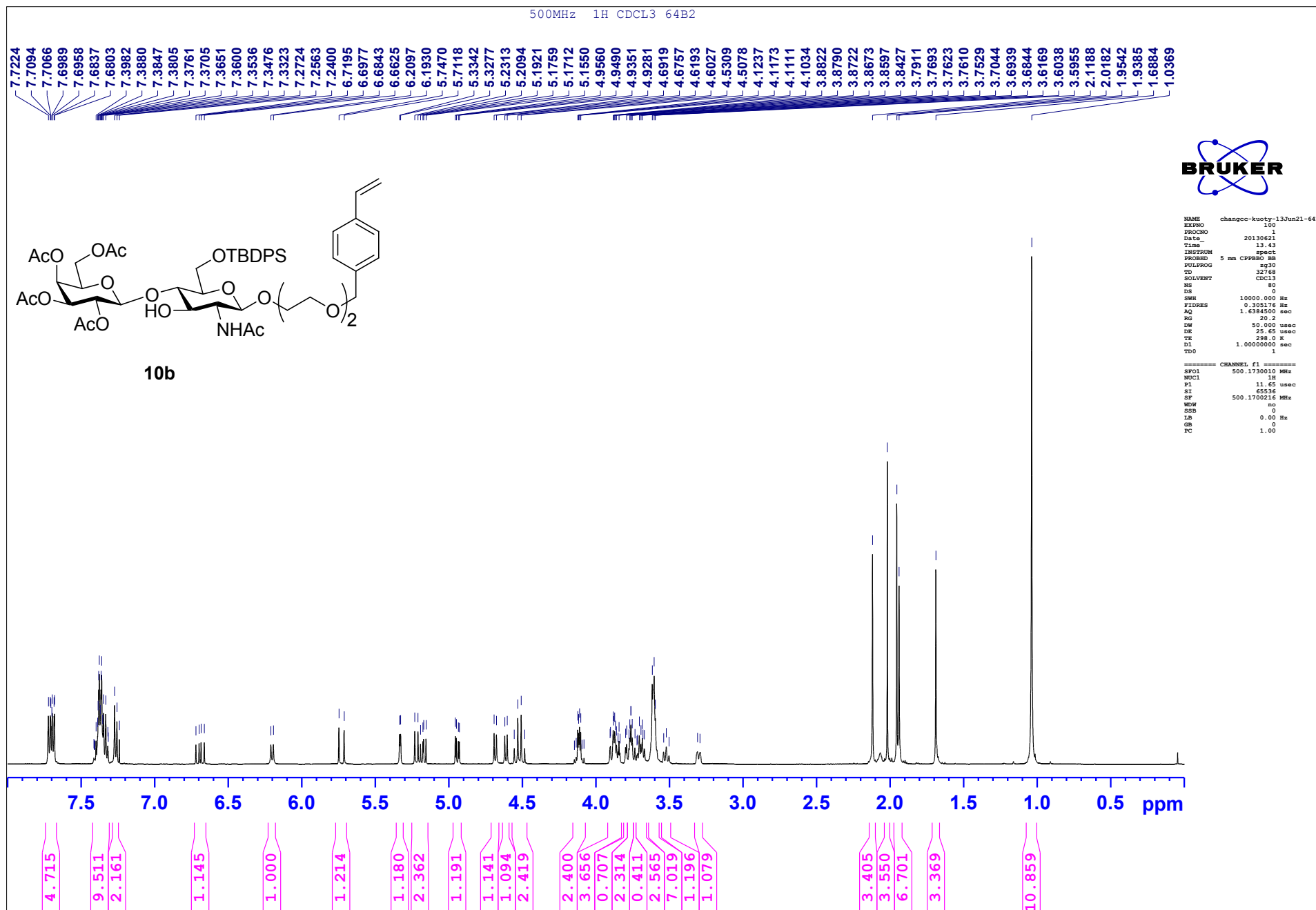
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DW         76.900 usec
DE         22.00 usec
TE         298.0 K
DO         0.0000300 sec
D1         1.0000000 sec
D11        0.0300000 sec
D12        0.0002000 sec
D13        0.0000400 sec
D14        0.0002000 sec
INV        0.00015360 sec

===== CHANNEL f1 =====
SF01      500.130010 MHz
NUC1       1H
P0         5.78 usec
P1         11.55 usec
P17        2500.00 usec
NUC0       1
TD         812
SF01      500.1313 MHz
FIDRES     12.715657 Hz
SW         13.016 ppm
PRMODE     QF
SI         1024
SF         500.1700181 MHz
WDM        QSIGN
SSB         0
LB          0.00 Hz
GB          0
PC          1.00
SI         1024
MC2        QF
SF         500.1700179 MHz
WDM        QSIGN
SSB         0
LB          0.00 Hz
GB          0

```



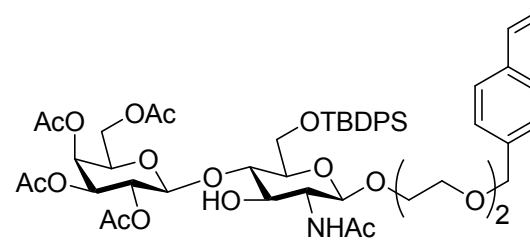
^1H NMR COSY (500 MHz, CDCl_3) of **10a** (α -isomer)



Dept135



Dept90

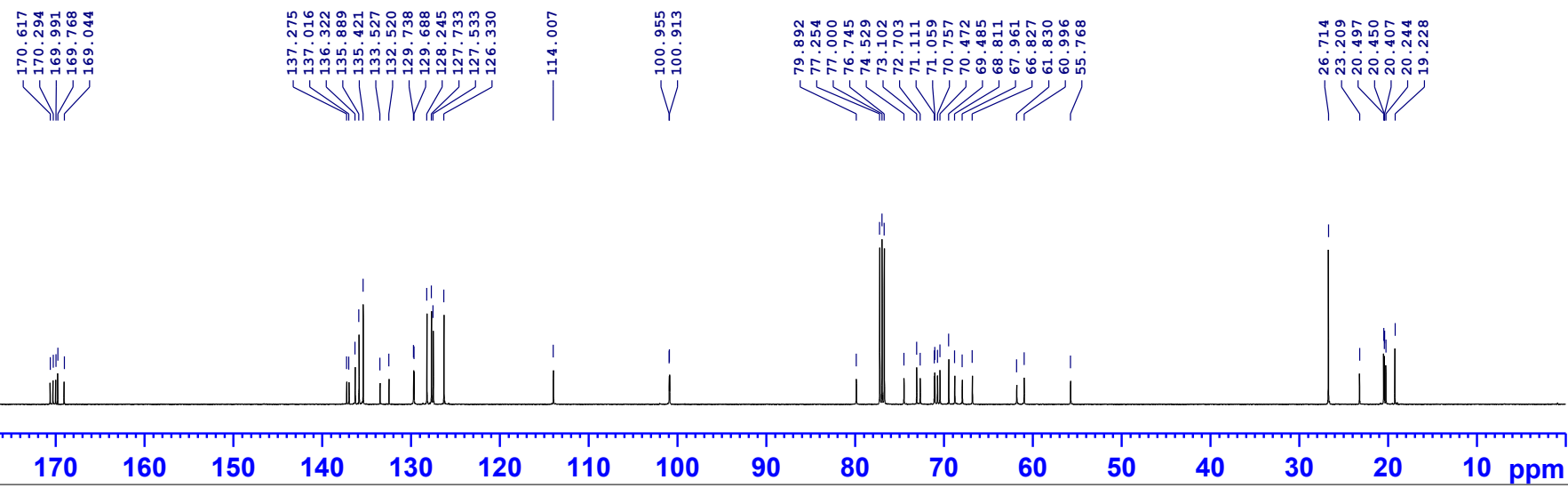


10b

```
NAME      changcc-kuoty-13Jun21-64B2
EXPNO     400
PROCNO    1
Date_     20130621
Time      14.52
INSTRUM   spect
PROBHD    5 mm CPBBO BB
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         165
DS         4
SWH       34090.910 Hz
FIDRES    0.520186 Hz
AQ         0.9612446 sec
RG         2050
DW         14.667 usec
DE         24.00 usec
TE         298.0 K
D1         2.0000000 sec
D11        0.0300000 sec
TDO        100

----- CHANNEL f1 -----
SFO1      125.7623103 MHz
NUC1      13C
P1         10.00 usec
SI         65536
SF         125.7678616 MHz
WDEW      BW
SSB        0
LB         1.00 Hz
GB         0
PC         1.00
```

500MHz 13C CDCL3 64B2



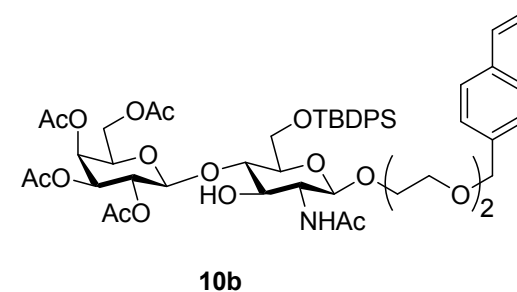
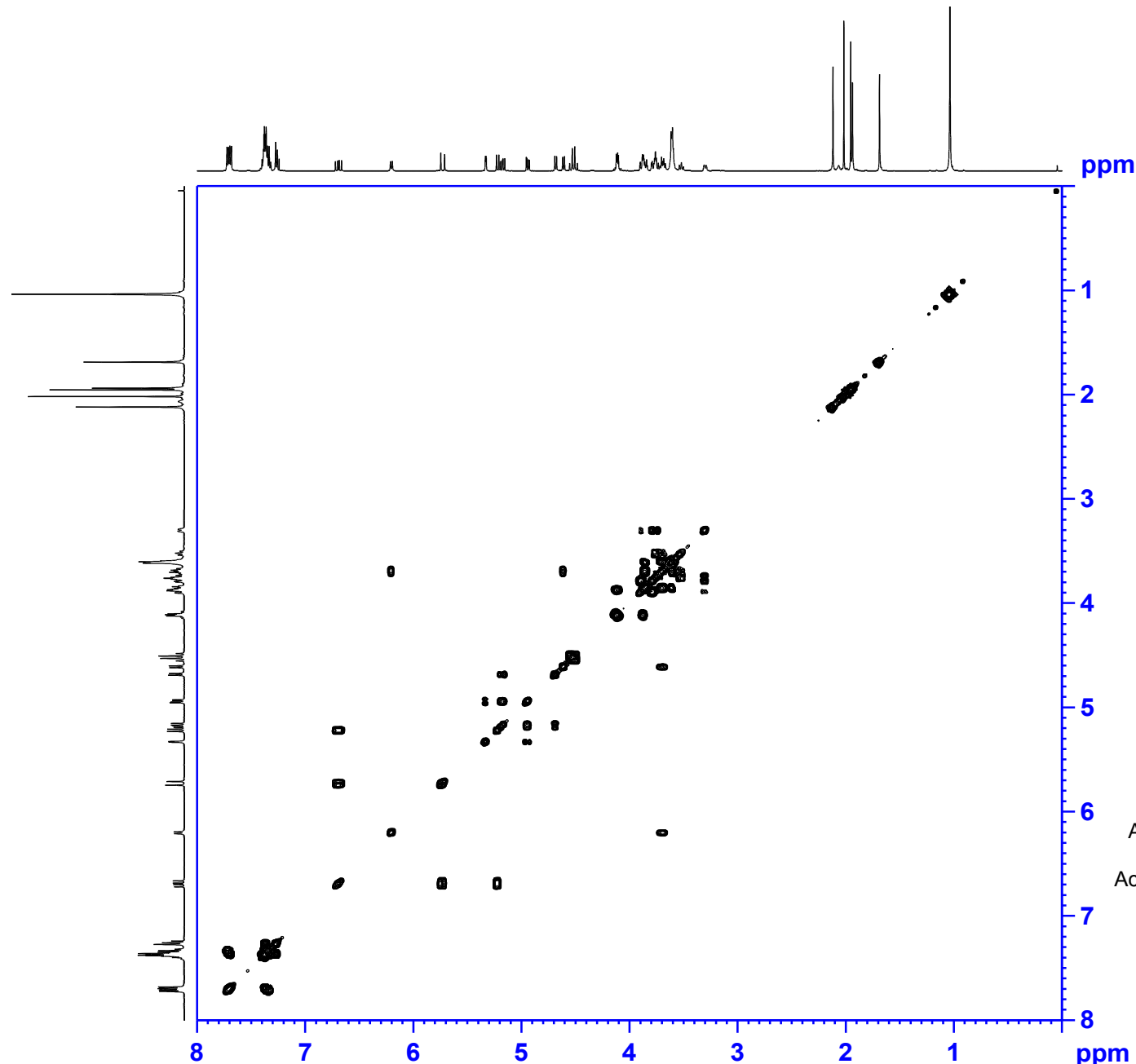
¹³C/DEPT NMR (125 MHz, CDCl₃) of 10b (β-isomer)

500MHz COSY CDCl3 64B2



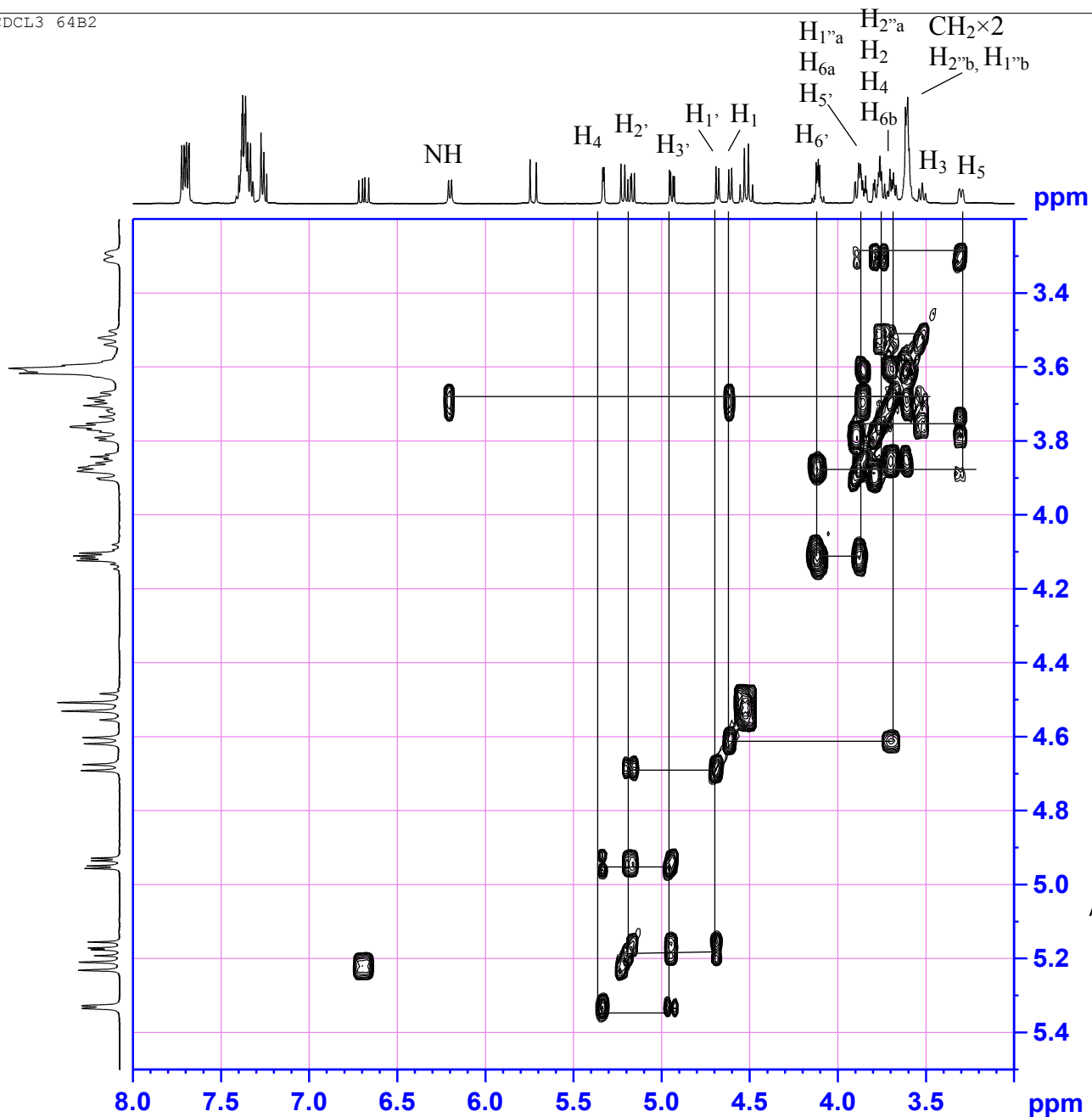
```
NAME changoc-kuoxy-13Jun21-64B2
EXPNO 1
PROCNO 1
Date_ 20130621
Time 13.44
INSTRUM spect
PROBHD 5 mm CP1HMQ BB
PULPROG cosypppgp45
TD 2048
SOLVENT CDCl3
NS 4
DS 16
SWH 6510.417 Hz
FIDRES 3.178914 Hz
AQ 0.1573164 sec
RG 90.5
DW 76.800 usec
DE 22.00 usec
TE 298.0 K
DO 0.0000000 sec
D1 1.0000000 sec
D11 0.0300000 sec
D12 0.0002000 sec
D13 0.0000000 sec
D14 0.0002000 sec
D16 0.00015360 sec
INO 0.00015360 sec

===== CHANNEL f1 =====
NUC1 500.170010 MHz
PO 5.92 usec
P1 11.65 usec
P17 2500.00 usec
ND0 1
TD 612
SFO1 500.170 MHz
FIDRES 12.715657 Hz
SF 13.016 ppm
P1MODE QF
SI 1024
SF 500.1700178 MHz
WWSW 0
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
SI 1024
MC2 QF
SF 500.1700176 MHz
WWSW 0
SSB 0
LB 0.00 Hz
GB 0
```



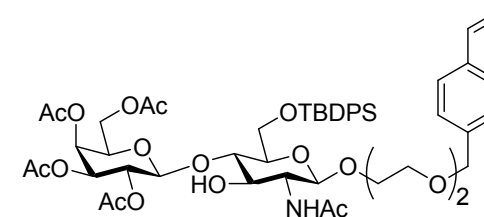
¹H NMR COSY (500 MHz, CDCl₃) of **10b** (β-isomer)

500MHZ COSY CDCL3 64B2



```

NAME      changoc-kuoty-13Jun21-64B2
EXPNO    1
PROCNO   1
Date_    20130621
Time     13.44
INSTRUM  spect
PROBHD   5 mm CPBPRB 1H
PULPROG  cosygpppg45
TD       2048
SOLVENT  CDCL3
NS       4
DS       16
SWH      6510.417 Hz
FIDRES   3.178914 Hz
AQ       0.1573364 sec
RG       90.5
DW       76.800 usec
DE       22.00 usec
TE       298.0 K
D0       0.0000000 sec
D1       1.0000000 sec
D11      0.0300000 sec
D12      0.0000200 sec
D13      0.0000400 sec
D14      0.0000200 sec
D15      0.00015360 sec
===== CHANNEL f1 =====
NUC1     500.170010 MHz
P0       5.82 usec
P1       11.65 usec
P17      2500.00 usec
RG       1
TD       512
SFO1     500.173 MHz
FIDRES   12.715657 Hz
SF       13.016 ppm
F2MODE   OF
SI       1024
SF       500.1700178 MHz
WDW      Q8INE
SSB      0
LB       0.00 Hz
GB       0
PC       1.00
FT       1024
MC2      OF
SF       500.1700176 MHz
WDW      Q8INE
SSB      0
LB       0.00 Hz
GB       0
    
```

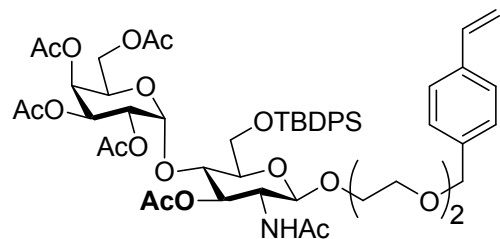


10b

¹H NMR COSY (500 MHz, CDCl₃) of **10b** (β-isomer)

800MHz 1H CDCL3 2070

7.6476
7.6391
7.6372
7.6349
7.6264
7.6251
7.3881
7.3789
7.3697
7.3646
7.3545
7.3482
7.3466
7.3387
7.3370
7.3301
7.2816
7.2716
7.2399
6.6789
6.6705
6.6569
6.2530
6.2433
5.7257
5.7037
5.3900
5.3872
5.2282
5.2225
5.2144
5.2090
5.1862
5.1814
5.0686
5.0637
5.0548
5.0499
4.9272
4.8932
4.8819
4.8813
4.8698
4.5590
4.5493
4.3086
4.2997
4.1382
4.1277
4.1244
4.1140
3.9571
3.9497
3.9433
3.6532
3.6467
3.6385
3.6334
3.6266
3.6175
3.6145
3.6102
3.6050
3.5668
3.5639
3.5523
3.5496
2.0867
2.0038
1.9980
1.9417
1.9290
1.8100
1.0085

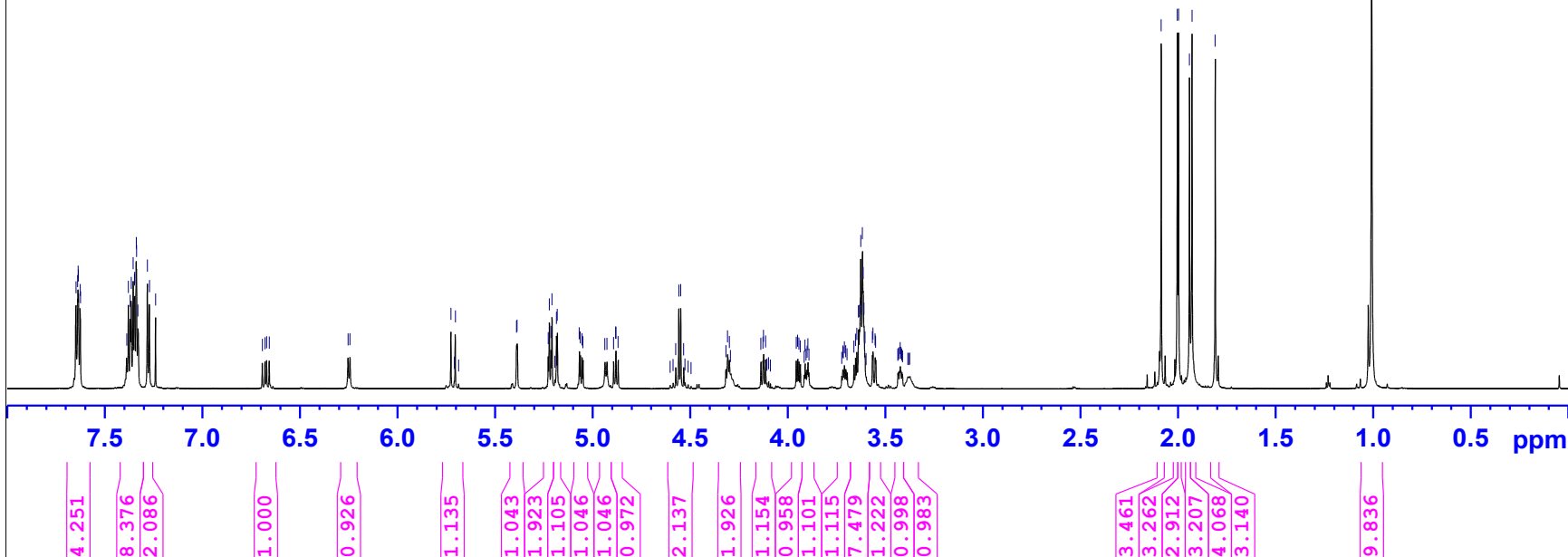


acetylated 10a

```

NAME      changcc-kuoty-13Jul07-2070
EXPNO     100
PROCNO    1
Date_     20130707
Time      20.08
INSTRUM   spect
PROBHD    5 mm CPACI 1H-
PULPROG   zg30
TD         32768
SOLVENT   CDCL3
NS         40
DS         0
SWH        12019.230 Hz
FIDRES     0.366798 Hz
AQ          1.3631988 sec
RG          14.2
DW          41.600 usec
DE          25.00 usec
TE          298.0 K
D1          1.0000000 sec
TDO         1

===== CHANNEL f1 =====
SFO1      800.2040010 MHz
NUC1       1H
P1         8.75 usec
SI         32768
SE         800.2000062 MHz
WDW        QSINE
SSB         2
LB          0.00 Hz
GB          0
PC          1.00
    
```

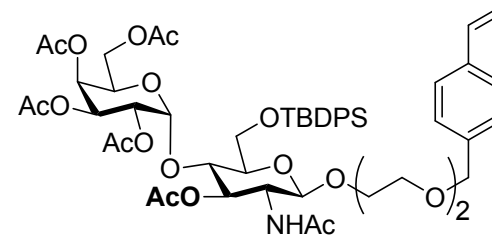


¹H NMR (800 MHz, CDCl₃) of acetylated 10a (α-isomer)

DEPT135



800MHz DEPT90

acetylated **10a**

```

NAME      changcc-kuoty-13Jul07-2070
EXPNO     40099
PROCNO    1
Date_     20130708
Time      10.43
INSTRUM   spect
PROBHD    5 mm CPTCI 1H-
PULPROG   zgpg30
TD         130936
SOLVENT   CDCl3
NS         902
DS         0
SWH       50000.000 Hz
FIDRES    0.381866 Hz
AQ         1.3094100 sec
RG         512
DW         10.000 usec
DE         25.00 usec
TE         298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TDO        2
----- CHANNEL f1 -----
SFO1      201.2325833 MHz
NUC1       13C
P1         12.00 usec
SI         65536
SF         201.2104629 MHz
WOW        6M
SSB        0
LB         1.00 Hz
GB         0
PC         1.00

```

800MHz 13C CDCl3 2070

171.000
170.899
170.292
170.101
169.715
169.474

137.456
137.114
136.386
135.591
135.552
133.288
133.239
129.632
129.623
127.919
127.680
127.627
127.603
126.301

113.949

99.551
95.966

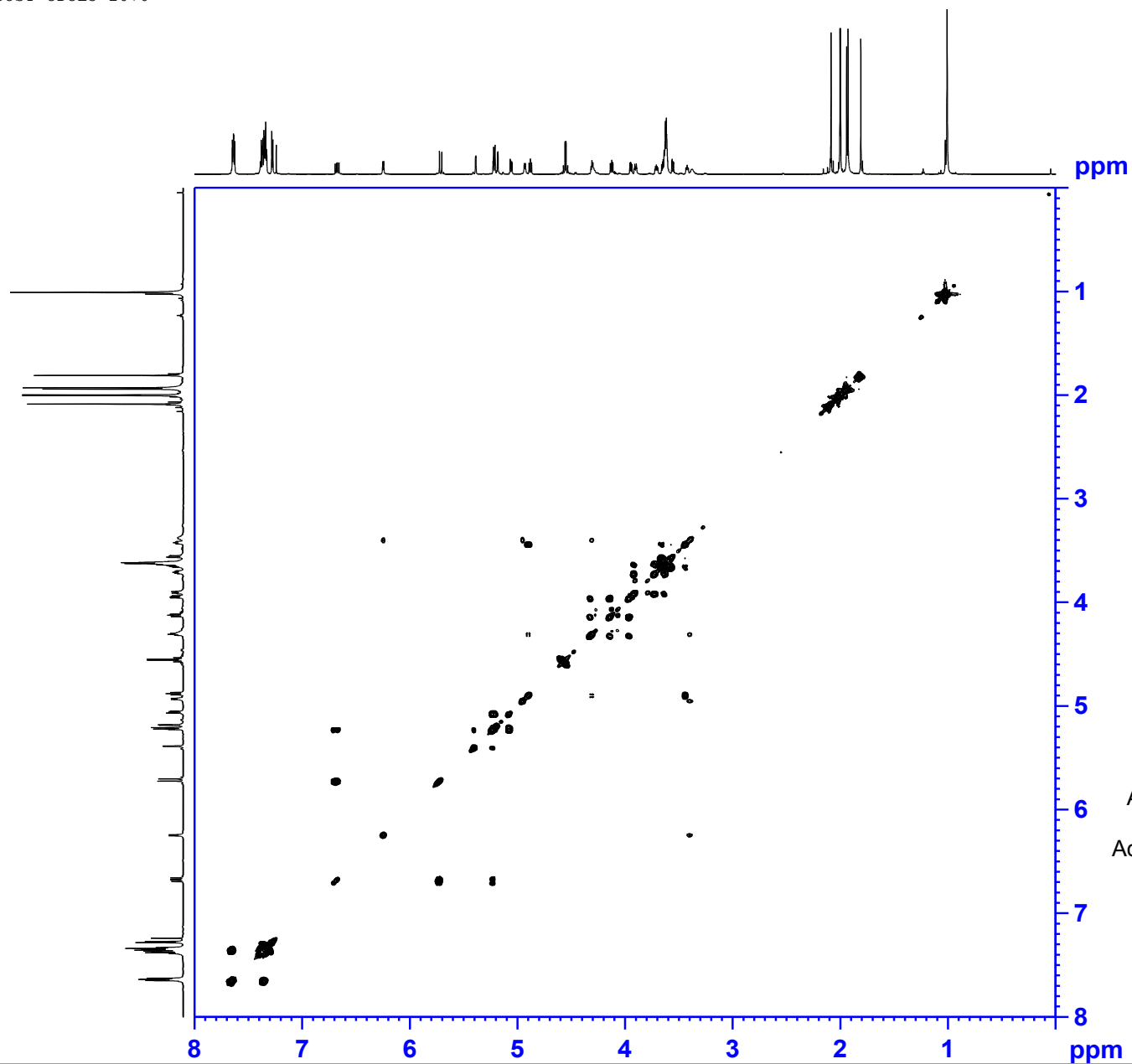
77.158
76.999
76.840
75.765
74.686
72.886
72.325
70.700
70.391
69.432
68.306
67.474
67.423
67.117
66.225
63.158
60.878
56.914

26.670
23.411
20.780
20.724
20.621
20.560
19.162

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

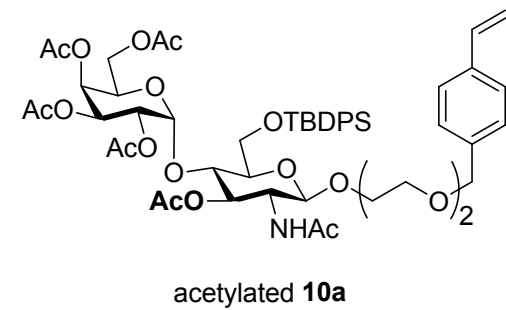
¹³C/DEPT NMR (200 MHz, CDCl₃) of acetylated **10a** (α-isomer)

800MHz COSY CDCl3 2070

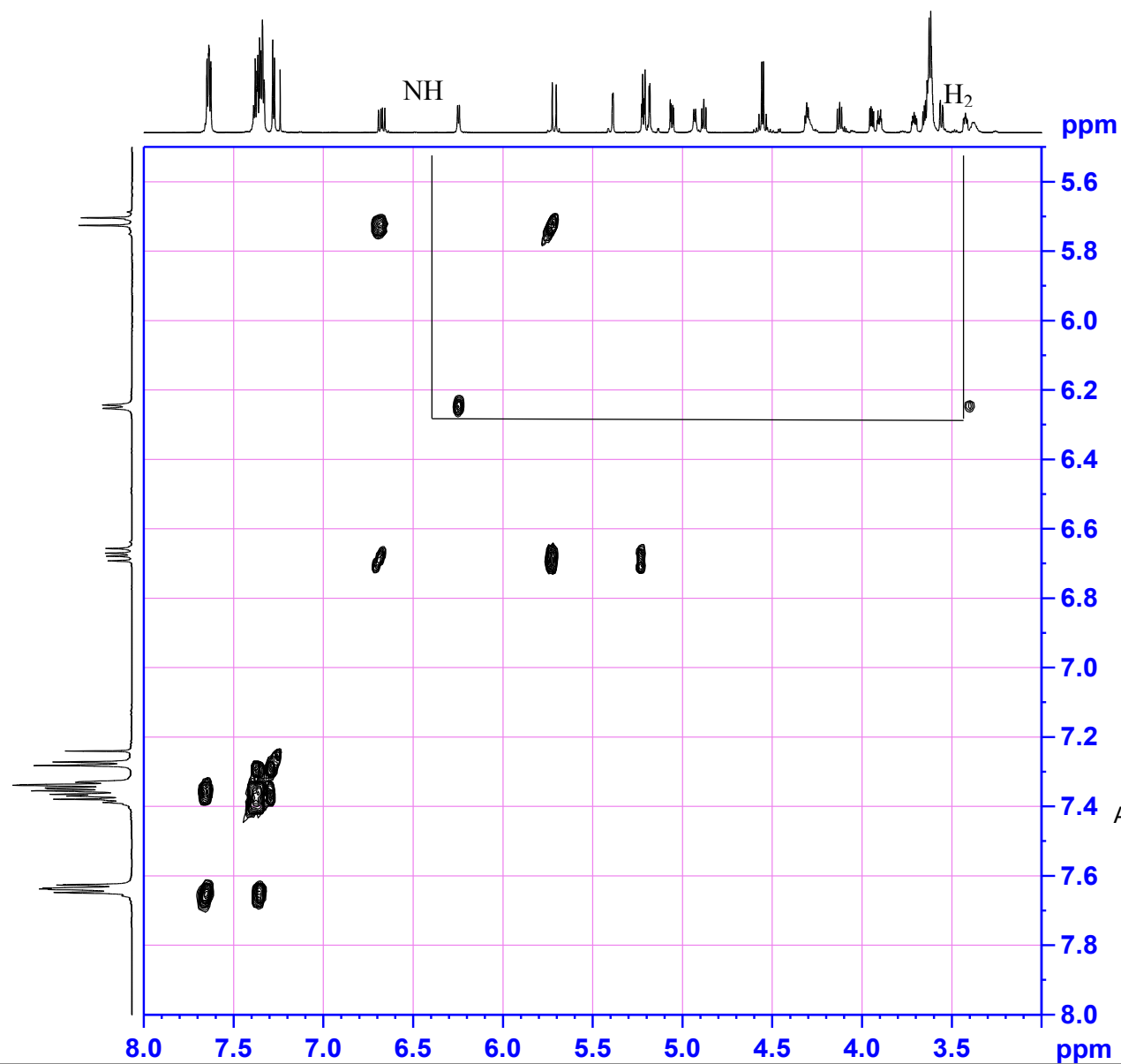


```
NAME      changoc-kucy-13Jul07-2070
EXPNO     81
PROCNO    1
Date_     20130708
Time      9.32
INSTRUM   spect
PROBHD    5 mm CPYCI 1H-
PULPROG   coasygpgp
TD        2048
SOLVENT   CDCl3
NS        2
DS        4
SWH       9615.385 Hz
FIDRES    4.695012 Hz
AQ        0.1065460 sec
RG         80.6
DW        52.000 usec
DE        25.00 usec
TE        298.0 K
DQ        0.0000330 sec
D1        1.0000000 sec
D13       0.0000400 sec
D16       0.0002000 sec
TD0       0.0001400 sec

===== CHANNEL f1 =====
SFO1      800.2040010 MHz
NUC1      13C
PC        4.38 usec
P2        8.75 usec
ND0
TD        312
SFO1      800.204 MHz
FIDRES    18.780048 Hz
SI        32.016 ppm
FVMODE    GP
SI        1024
SF        800.2000204 MHz
WWSW     SINE
SSB       0
GB        0.00 Hz
PC        1.00
P2        1024
MC2
SF        800.2000377 MHz
WWSW     SINE
SSB       0
GB        0.00 Hz
```



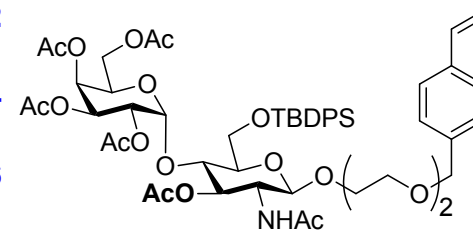
¹H NMR COSY (800 MHz, CDCl₃) of acetylated **10a** (α-isomer)

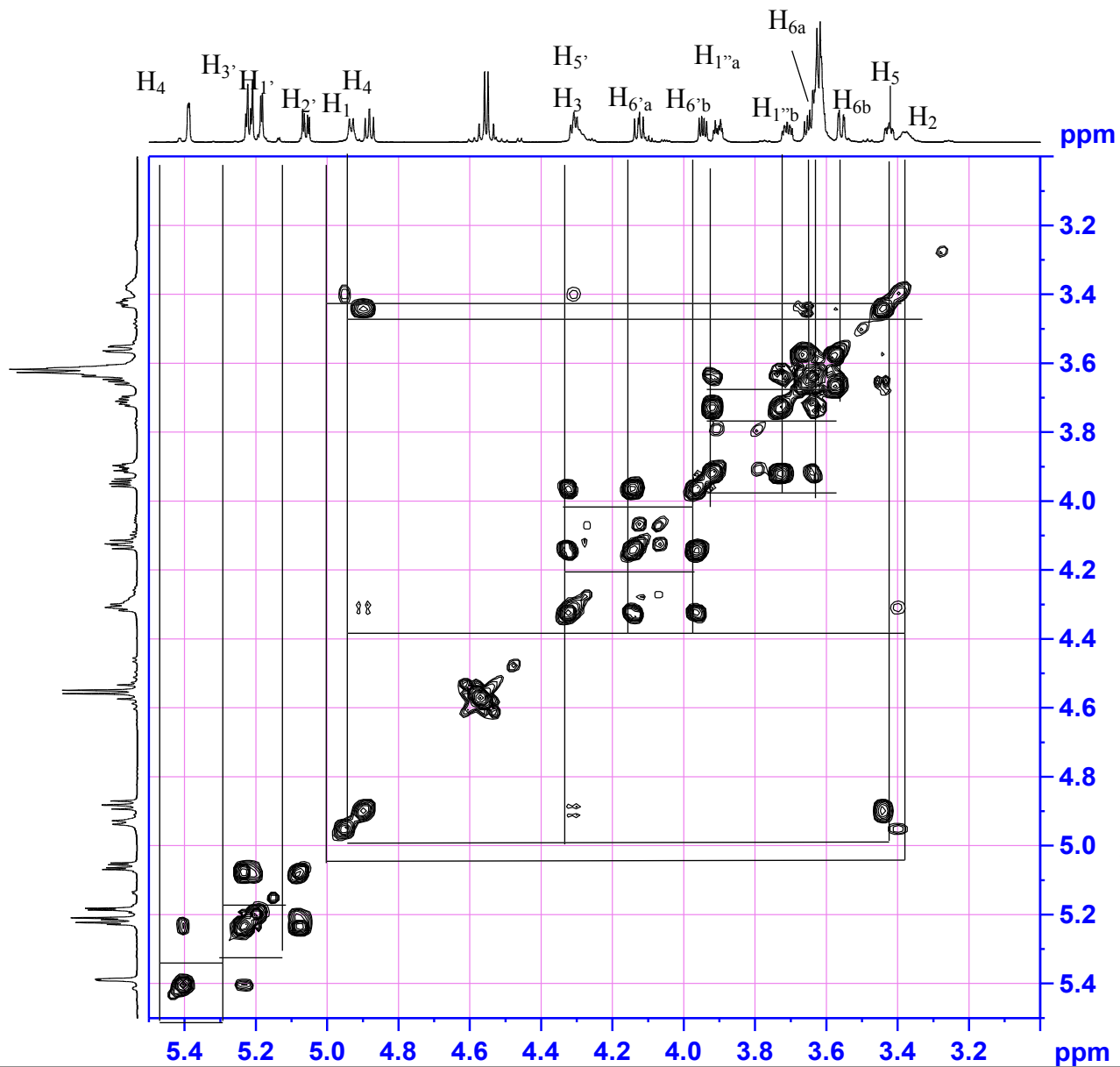


```

NAME      changoc-kuoty-13Jul07-2070
EXPNO     53
PROCNO    1
Date_     20130708
Time      9.32
INSTRUM   spect
PROBHD    5 mm CPYCI 1H-
PULPROG   cosyppmgp
TD         2048
SOLVENT   CDCl3
NS         4
DS         2
SB         9615.385 Hz
FIDRES    4.695012 Hz
AQ         0.1065460 sec
RG         80.6
DE         52.000 usec
DW         25.00 usec
TE         298.0 K
DD         0.00000300 sec
DI         1.00000000 sec
D13        0.00000400 sec
D16        0.00020000 sec
IRI        0.00010400 sec
===== CHANNEL f1 =====
NUC1      800.2040010 MHz
NUC1      1H
PD         4.38 usec
PI         8.75 usec
NDO        1
TD         512
SF01      800.204 MHz
FIDRES    18.780048 Hz
SW         12.016 ppm
F2MODE    QF
SI         1024
SF         800.20020204 MHz
SINE
SBB        0
LB         0.00 Hz
GB         0
PC         1.00
SI         1024
MC2        QF
SF         800.2000197 MHz
SINE
SBB        0
LB         0.00 Hz
GB         0

```

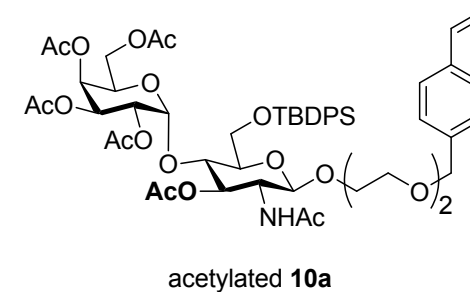
acetylated **10a**¹H NMR COSY (800 MHz, CDCl₃) of acetylated **10a** (α-isomer)



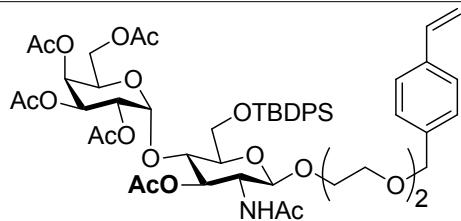
```

NAME          changoc-kuoty-13Jul07-2070
EXPNO         5
PROCNO        1
Date_         20130708
Time          9.32
INSTRUM       spect
PROBHD        5 mm CPXI 1H-
PULPROG       zgpg30
TD            2048
SOLVENT       CDCl3
NS            2
DS            4
SWH           9615.385 Hz
FIDRES        4.695012 Hz
AQ            0.1065460 sec
RG            80.6
AQ            52.000 usec
DE            25.00 usec
TE            298.0 K
DD            0.0000300 sec
DI            1.0000000 sec
D13           0.0000400 sec
D16           0.0002000 sec
TBO           0.0001000 sec

===== CHANNEL f1 =====
RF01          800.2040010 MHz
NUC1          1H
PD            4.38 usec
PI            8.75 usec
NDO           1
TD            512
SF01          800.204 MHz
FIDRES        18.780048 Hz
SW            12.016 ppm
F2MODE        QF
SI            1024
SF            800.2000204 MHz
WDW           SINE
SSB           0
GB            0
PC            1.00
SI            1024
MC2           SF
SF            800.2000197 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0
  
```



^1H NMR COSY (800 MHz, CDCl_3) of acetylated **10a** (α -isomer)

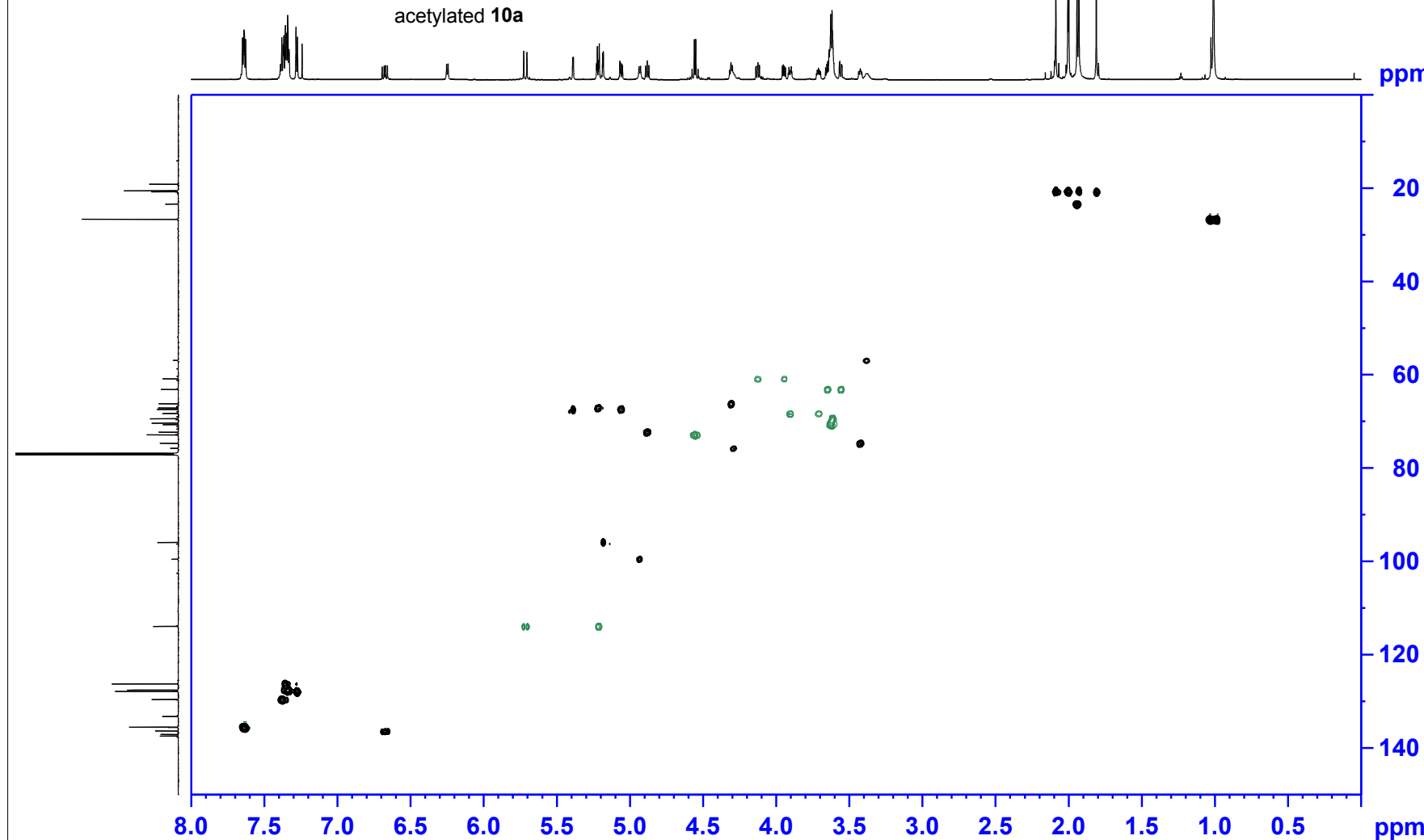


acetylated 10a



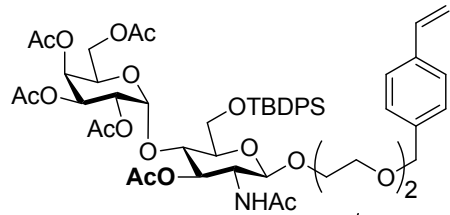
```

NAME      changco-kuoty-13Jul07-2070
EXPNO     82
PROCNO    20130708
Date_     7.46
INSTRUM   spect
PROBHD    5 mm CPTCI 1H-
PULPROG   hsqcetayps1sp2.4
TD        2048
SOLVENT   CDCl3
NS        4
DS        4
SWH       9615.385 Hz
FIDRES    4.69512 Hz
AQ        0.1065460 sec
RG        2050
RW        52.000 usec
DE        25.00 usec
TE        298.0 K
CNPRT2    145.0000000
CNPRT17   -0.5000000
D0        0.0000000 sec
D1        2.0000000 sec
D2        0.00344828 sec
D4        0.00172414 sec
D11       0.03000000 sec
D16       0.00020000 sec
D21       0.00060000 sec
D24       0.00089000 sec
TMO       0.00000000 sec
LQ        0
TD0       2
===== CHANNEL f1 =====
SF01      800.2037628 MHz
NUC1      13C
P1        8.75 usec
P2        17.50 usec
P22       0.00 usec
MDO       2
TD        512
SF01      201.2286 MHz
FIDRES    98.64677 Hz
SW        250.584 ppm
F2NAME2   Echo-AntiEcho
SF        800.2000149 MHz
MORF      QSNMR
SFB       2
GB        0.00 Hz
GB        0
PC        1.00
ST        1024
MC2       echo-anti-echo
SF        201.2104316 MHz
MORF      QSNMR
SFB       2
GB        0.00 Hz
    
```

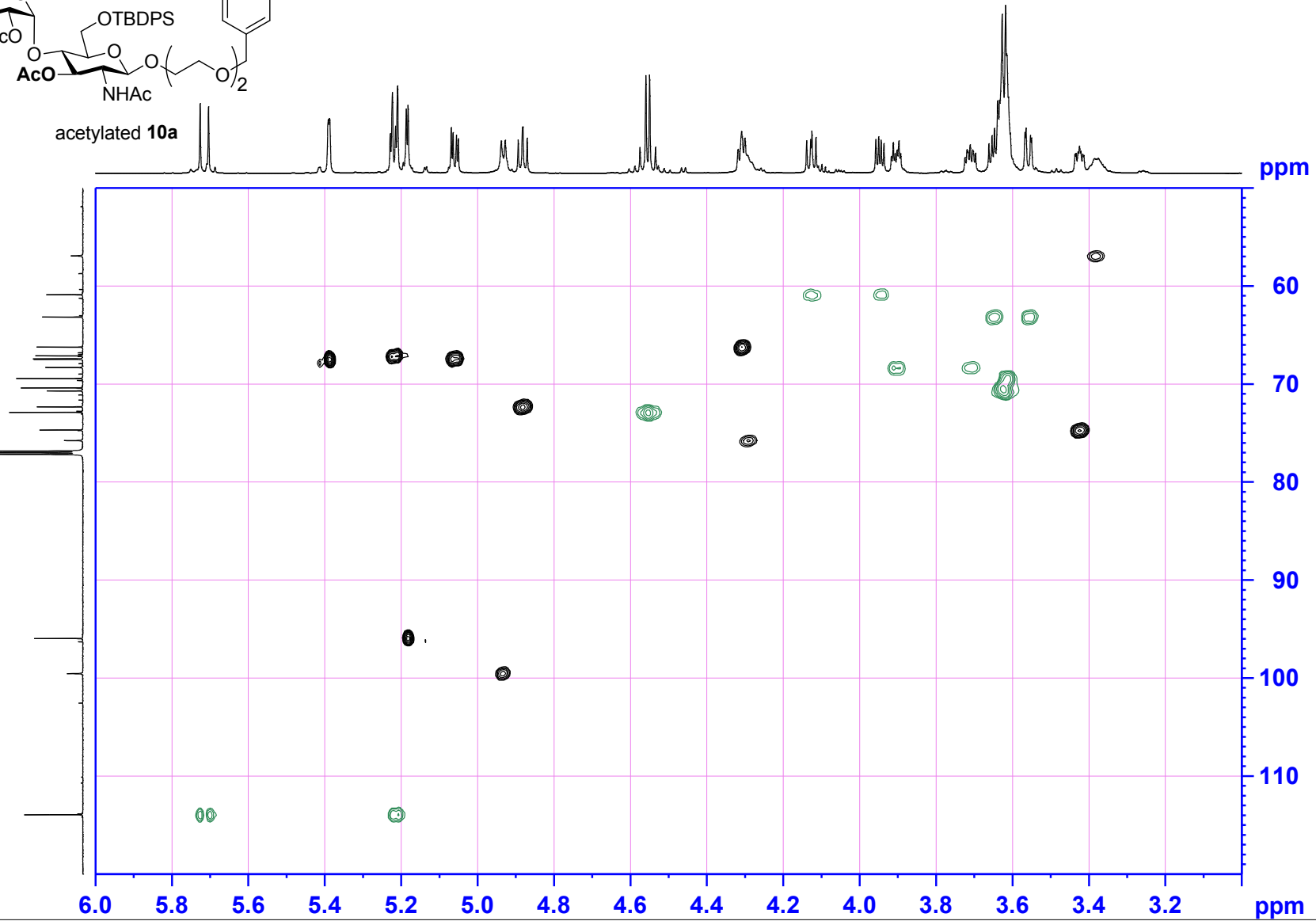


¹H-¹³C NMR HSQC (800 MHz, CDCl₃) of acetylated 10a (α-isomer)

800MHz HSQC CDCl3 2070

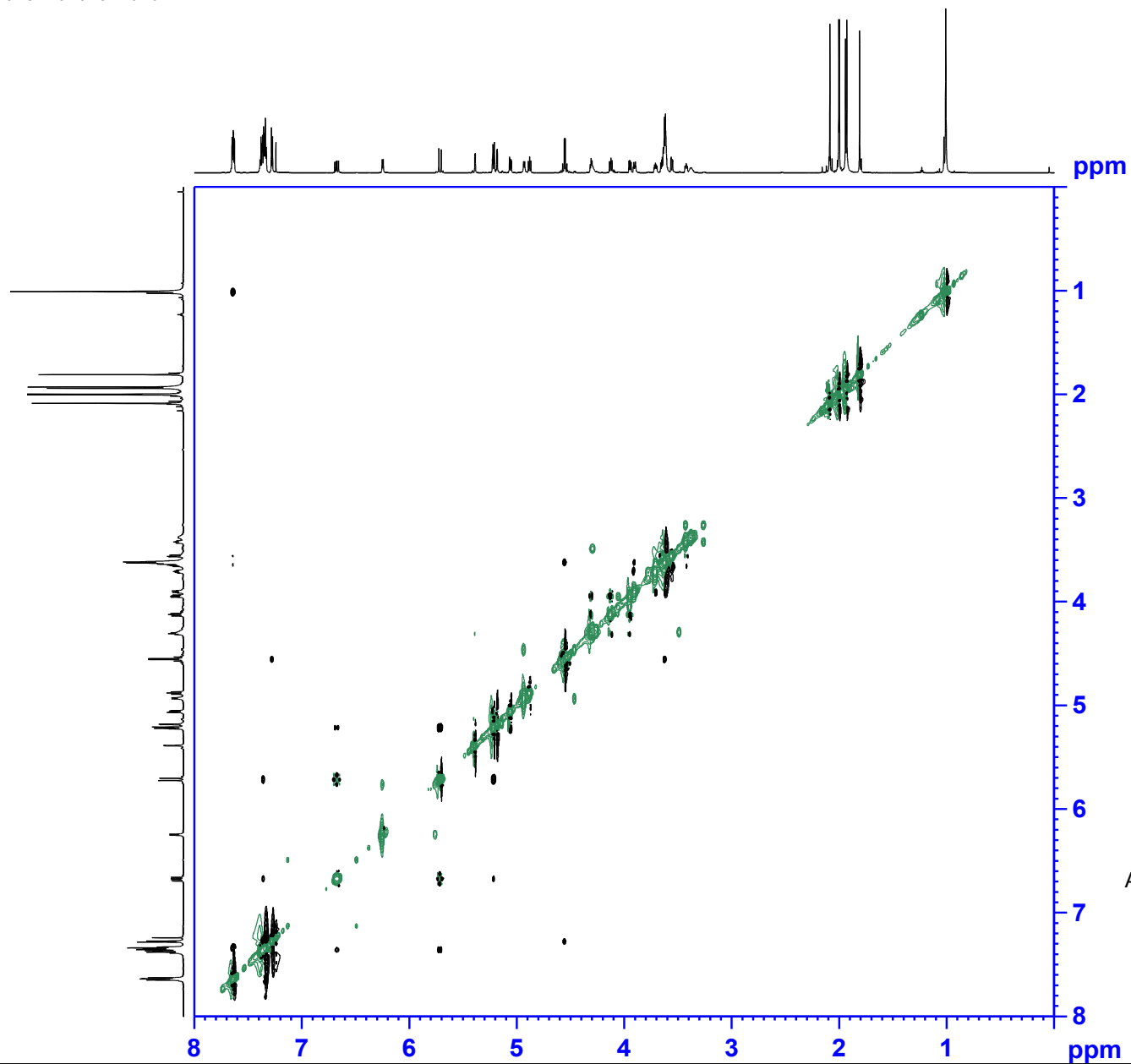


acetylated 10a



```
NAME change-kuoty-13Jul07-2070
EXPNO 82
PROCNO 1
Date_ 20130708
Time 7.46
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG hsgpdelatgpusp2.4
TD 2048
SOLVENT CDCl3
NS 4
DS 16
SWH 9615.385 Hz
FIDRES 4.69012 Hz
AQ 0.1065460 sec
RG 2050
RW 52.000 usec
DE 25.00 usec
TE 298.0 K
CNPX2 145.0000000
CNPX17 -0.5000000
D0 0.0000000 sec
D1 2.0000000 sec
D2 0.00344828 sec
D4 0.00172414 sec
D11 0.03000000 sec
D16 0.00200000 sec
D21 0.00360000 sec
D24 0.00089000 sec
TMO 0.0000000 sec
L0 0
TDO 2
===== CHANNEL f1 =====
SFO1 800.2037628 MHz
NUC1 13C
P1 8.75 usec
P2 17.50 usec
P2B 0.00 usec
MDO 2
TD 512
SFO1 201.2286 MHz
FIDRES 98.442677 Hz
SW 250.584 ppm
F2MODE Echo-Antiecho
SF 800.2000349 MHz
SFO 201.2286 MHz
SFB 0.00 Hz
GB 0
PC 1.00
ST 1024
MC2 echo-antiecho
SF 201.2104316 MHz
SFB 0.00 Hz
GB 0
```

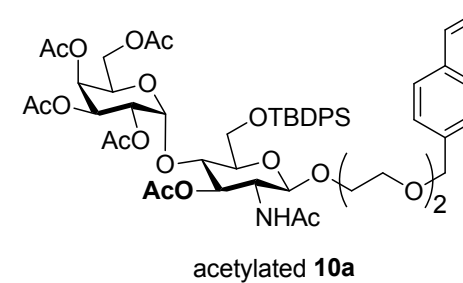
^1H - ^{13}C NMR HSQC (800 MHz, CDCl_3) of acetylated 10a (α -isomer)



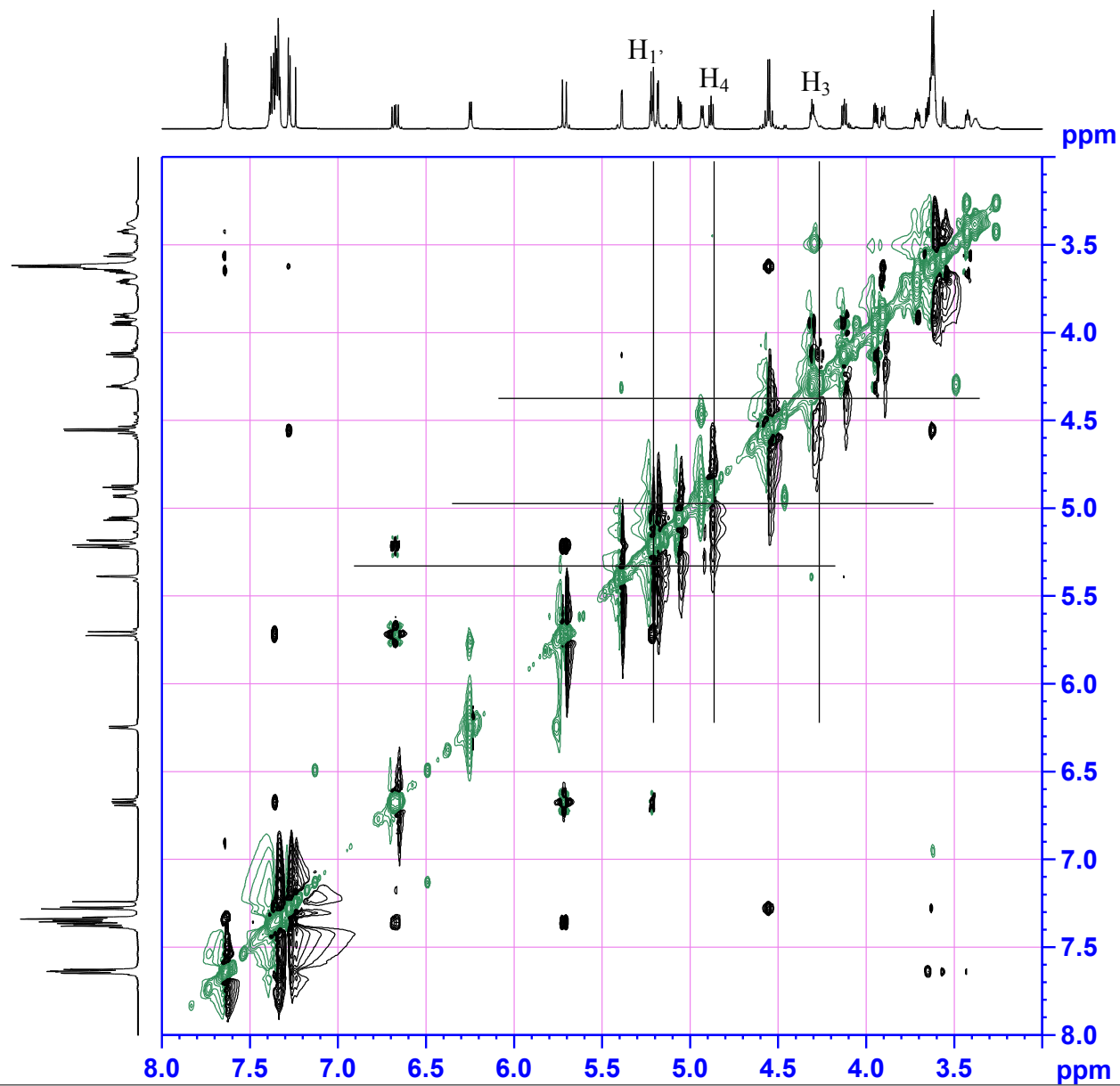
```

NAME      changec-kuoty-13Jul107-2070
EXPNO     1
PROCNO    1
Date_     20130707
Time      20.18
INSTRUM   spect
PROBHD    5 mm CPXI 1H-
PULPROG   noesygph
TD         2048
SOLVENT   CDCL3
NS         32
DS         4
SWH        9615.385 Hz
FIDRES     4.695012 Hz
AQ         0.1065460 sec
RG         4
DE         52.000 usec
TE         300.0 K
DE         25.00 usec
DQ         398.0 K
DD         0.00004086 sec
DI         2.00000000 sec
DS         0.40000001 sec
D16        0.00020000 sec
D10        0.00010000 sec
===== CHANNEL f1 =====
SFO1      800.2036009 MHz
NUC1       1H
P1         8.75 usec
P2         17.50 usec
ND0        1
TD         512
SFO1      800.2036 MHz
FIDRES     10.780048 Hz
SW         12.016 ppm
FMODE     States-TPPI
SI         2048
SF         800.2000350 MHz
WDW        QSSINE
SSB        2
LB         0.00 Hz
GB         0
PC         1.00
SI         2048
MC2       States-TPPI
SF         800.2000350 MHz
WDW        QSSINE
SSB        2
LB         0.00 Hz
GB         0

```



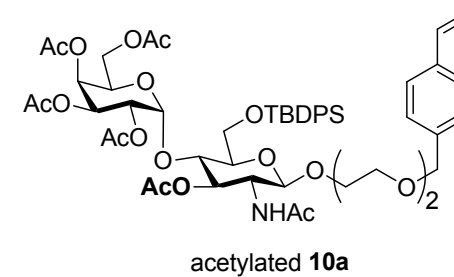
^1H NMR NOESY (800 MHz, CDCl_3) of acetylated **10a** (α -isomer)



```

NAME      changoc-kuoty-133u107-2070
EXPNO     1
PROCNO    1
Date_     20130707
Time      20.18
INSTRUM   spect
PROBHD    5 mm CPXI 1H-
PULPROG   noesygpgp
TD        2048
SOLVENT   CDCl3
NS        32
DS        4
SWH        9615.385 Hz
FIDRES    4.695012 Hz
AQ         0.1065460 sec
RG         4
DE         52.000 usec
TE         298.0 K
DO         0.0004086 sec
D1         2.0000000 sec
D8         0.4000001 sec
D16        0.0002000 sec
TD0        0.0001000 sec

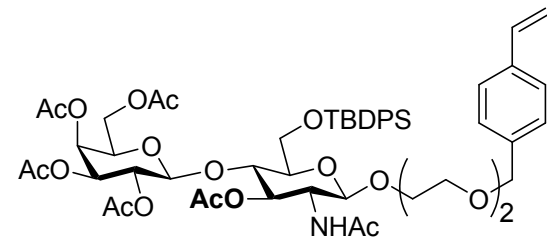
===== CHANNEL f1 =====
SFO1      800.2036009 MHz
NUC1      1H
P1         8.75 usec
PC        17.50 usec
ND0        1
TD         32
SFO1      800.2036 MHz
FIDRES    18.780048 Hz
SF        12.016 ppm
PRACMODE   States-TFPT
SI         2048
SF        800.2000350 MHz
WOW        Q5INE
SFB        2
LB         0.00 Hz
GB         1.00
SI         2048
MC2       States-TFPT
SF        800.2000333 MHz
WOW        Q5INE
SFB        2
LB         0.00 Hz
GB         0
  
```



^1H NMR NOESY (800 MHz, CDCl_3) of acetylated **10a** (α -isomer)

500MHz 1H CDCL3 2071

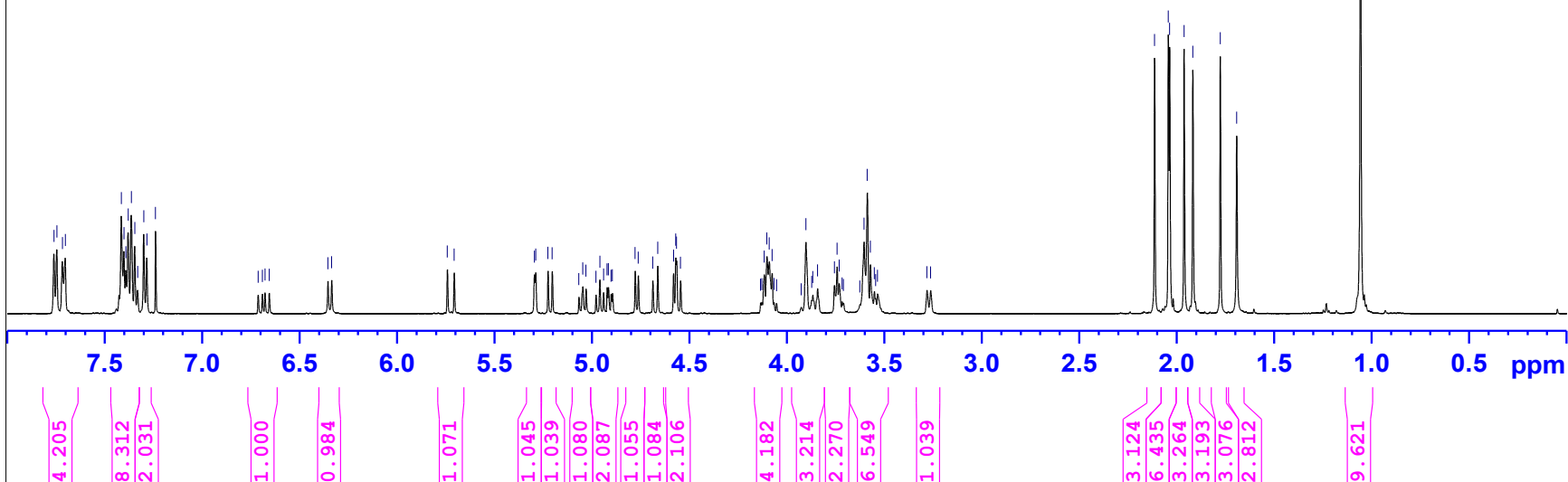
7.7604
7.7453
7.7173
7.7022
7.4146
7.4011
7.3916
7.3794
7.3638
7.3457
7.3304
7.2996
7.2837
7.2399
7.2399
6.7133
6.6916
6.6782
6.6564
6.3550
6.3359
5.7423
5.7071
5.2958
5.2891
5.2258
5.2040
5.0672
5.0473
5.0308
4.9799
4.9600
4.9410
4.9225
4.9157
4.9019
4.8951
4.7786
4.7626
4.6880
4.6631
4.5820
4.5704
4.5661
4.5457
4.1289
4.1160
4.1027
4.0763
4.0669
4.0669
3.9030
3.8733
3.8674
3.8428
3.7566
3.7428
3.7321
3.7168
3.6045
3.5877
3.5718
3.5513
3.5451
3.5348
3.2814
3.2628
2.1141
2.0437
2.0367
1.9628
1.9177
1.7771
1.6926
1.0580



acetylated **10b**

```

NAME      changcc-kuoty-13Jul06-2071
EXPNO     100
PROCNO    1
Date_     20130706
Time      0.25
INSTRUM   spect
PROBHD    5 mm CPMAS BB
PULPROG   zgpg
TD         32768
SOLVENT   CDCL3
NS         80
DS         0
SWH        10000.000 Hz
FIDRES     0.305176 Hz
AQ         1.6384500 sec
RG         80.6
DW         50.000 usec
DE         23.66 usec
TE         298.0 K
D1         1.0000000 sec
TDO        1
===== CHANNEL f1 =====
SFO1      500.1730010 MHz
NUC1       1H
P1         11.60 usec
SI         65536
SE         500.1700222 MHz
WDW        QSINE
SSB        2
LB         0.00 Hz
GB         0
PC         1.00
    
```



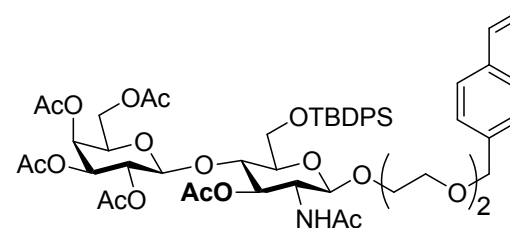
¹H NMR (500 MHz, CDCl₃) of acetylated **10b** (β-isomer)

Dept135



NAME changccc-kuoty-13Jul06-2071
EXPNO 40099
PROCNO 1
Date 20130706
Time 16.04
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zgpg30
TD 65400
SOLVENT CDCl3
NS 3072
DS 4
SWH 34099.910 Hz
FIDRES 0.521268 Hz
AQ 0.9592500 sec
RG 2050
DW 14.667 usec
DE 24.00 usec
TE 298.0 K
D1 2.0000000 sec
D11 0.0300000 sec
D12 3
----- CHANNEL f1 -----
SF01 125.7823103 MHz
NUC1 13C
P1 10.00 usec
SI 65536
SF 125.7678506 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

Dept90



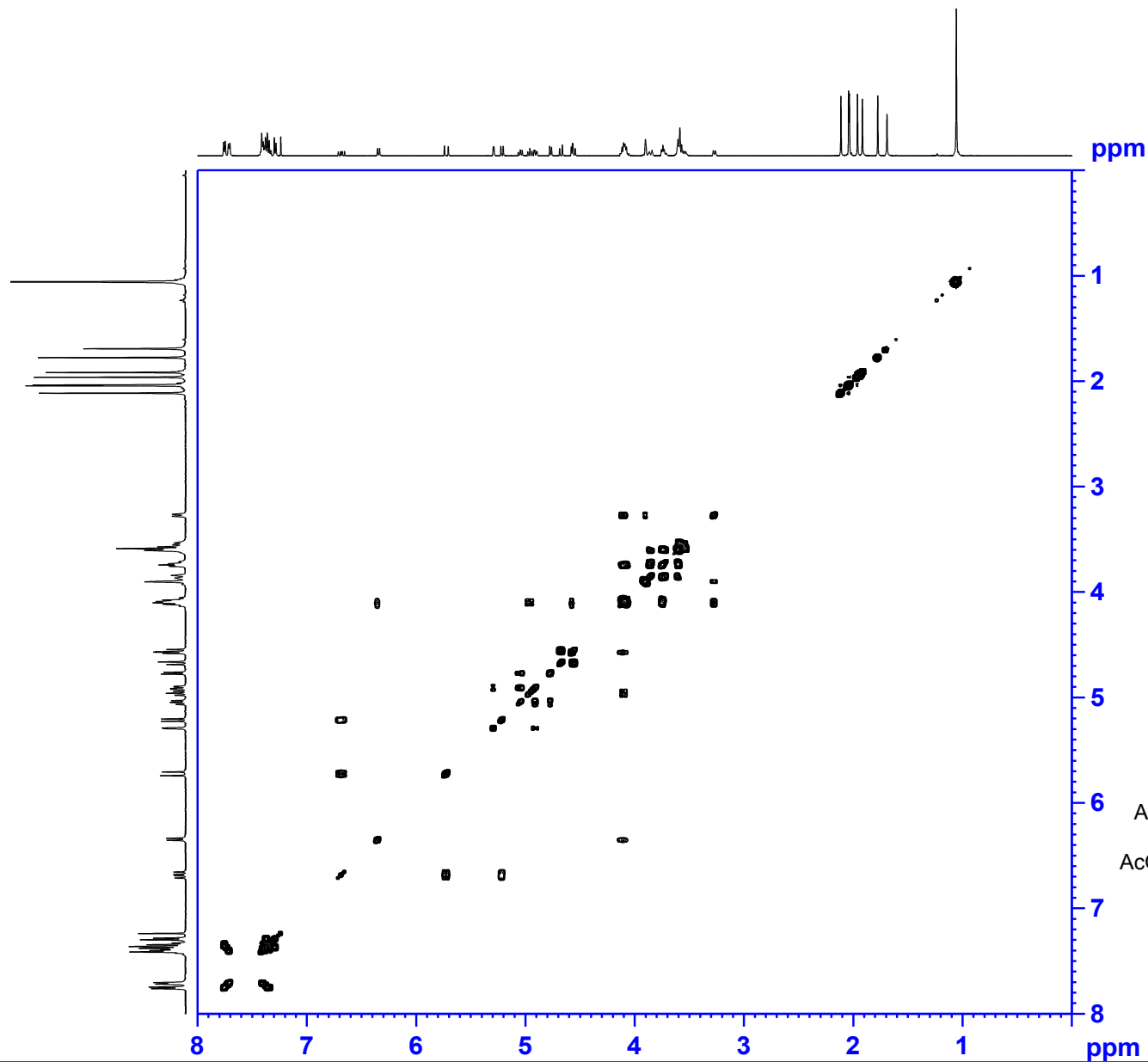
500MHz 13C CDCl3 2071



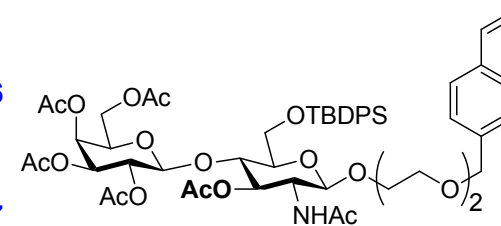
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

¹³C/DEPT NMR (125 MHz, CDCl₃) of acetylated 10b (β-isomer)

500MHz COSY CDCL3 2071

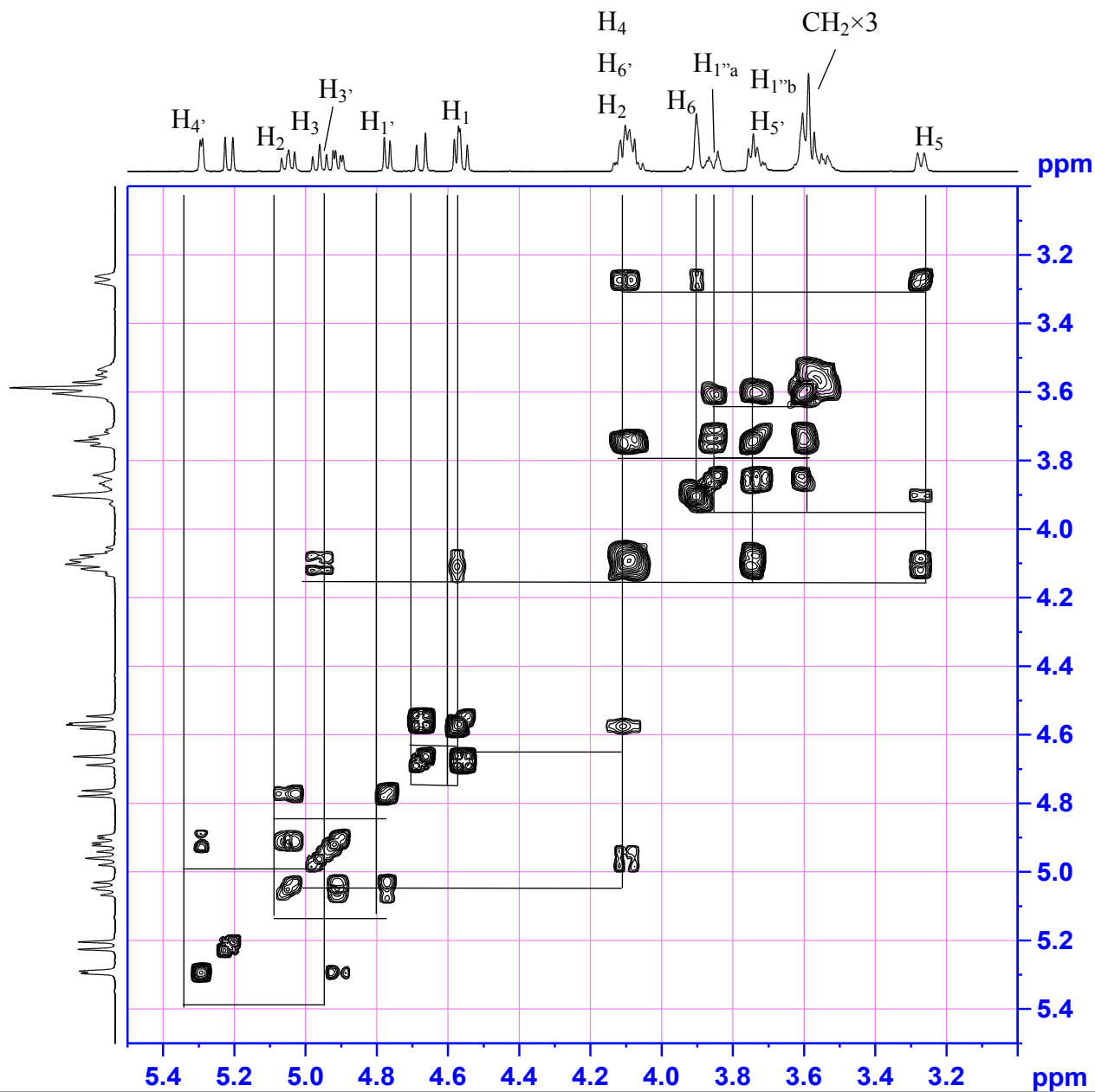


```
NAME change-kusty-13Jul06-2071
EXPNO 1
PROCNO 1
Date_ 20130706
Time 13.38
INSTRUM spect
PROBHD 5 mm CPYPRBO BB
PULPROG cosypppgr45
TD 2048
SOLVENT CDCL3
SI 4
DS 16
SB 6510.417 Hz
FIDRES 0.1373364 sec
AQ 0.1373364 sec
RG 512
SW 76.800 usec
DE 22.00 usec
TE 298.0 K
DO 0.0000300 sec
D1 1.0000000 sec
D11 0.0300000 sec
D12 0.0002000 sec
D13 0.0000400 sec
D16 0.0002000 sec
TD 0.0015360 sec
===== CHANNEL f1 =====
SF01 500.170010 MHz
NUC1 13
PC 5.80 usec
PI 11.60 usec
PT 2500.00 usec
ND0 1
TD 512
SF01 500.173 MHz
FIDRES 12.715607 Hz
SW 13.016 ppm
FREQDE 0
SI 2048
SF 500.1700203 MHz
WDW 0
SSB 0
GB 0
PC 1.00
SI 2048
MCZ 0
SF 500.1700201 MHz
WDW 0
SSB 0
LB 0.00 Hz
GB 0
```



acetylated 10b

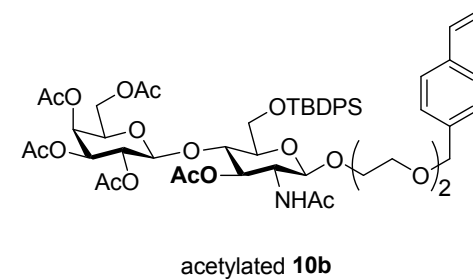
¹H NMR COSY (500 MHz, CDCl₃) of acetylated 10b (β-isomer)



```

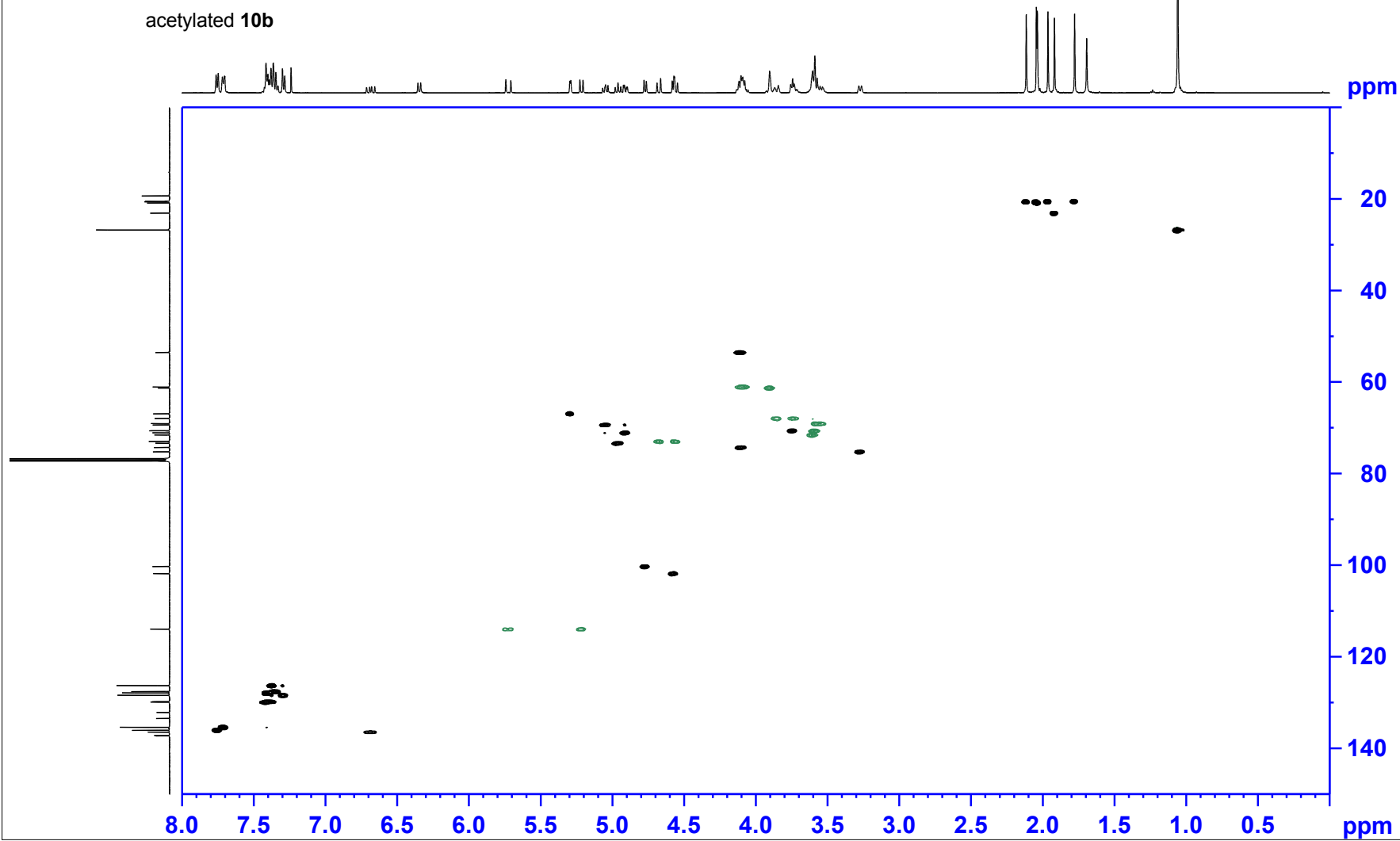
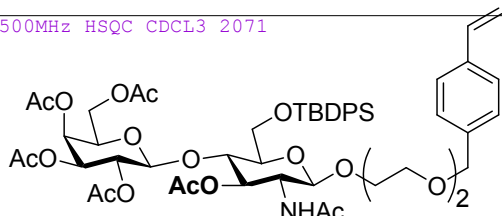
NAME          changoc-kucby-13Jul06-2071
EXPNO         73
PROCNO        20130706
Date_         13.38
INSTRUM       spect
PROBHD        5 mm CPBPRBO BB
PULPROG       coesypppgp45
TD            2048
SOLVENT       CDCL3
NS            4
DS            16
SWH           6510.417 Hz
FIDRES       3.178914 Hz
AQ           0.157366 sec
RG            512
AW           76.800 usec
DE           22.00 usec
TE           298.0 K
DO           0.0000300 sec
D1           1.0000000 sec
D11          0.0300000 sec
D12          0.0002000 sec
D13          0.0000400 sec
D16          0.0002000 sec
TD0          0.0001360 sec

===== CHANNEL f1 =====
SFO1          500.170010 MHz
NUC1          1H
P1            5.80 usec
PL            11.60 usec
P17          2500.00 usec
NUC0          13C
TD            512
SFO0          500.173 MHz
FIDRES       12.71607 Hz
SW           13.016 ppm
FNAME0       0
SI            2048
SF           500.1700201 MHz
WDW          QFHM
SSB          0
LB           0.00 Hz
GB           0
PC           1.00
SI            2048
WDW          QFHM
SF           500.1700201 MHz
WDW          QFHM
SSB          0
LB           0.00 Hz
GB           0
    
```



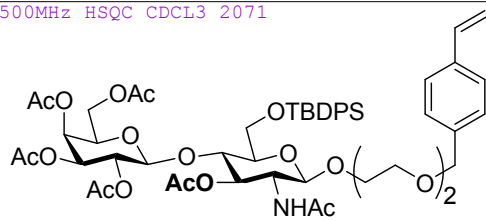
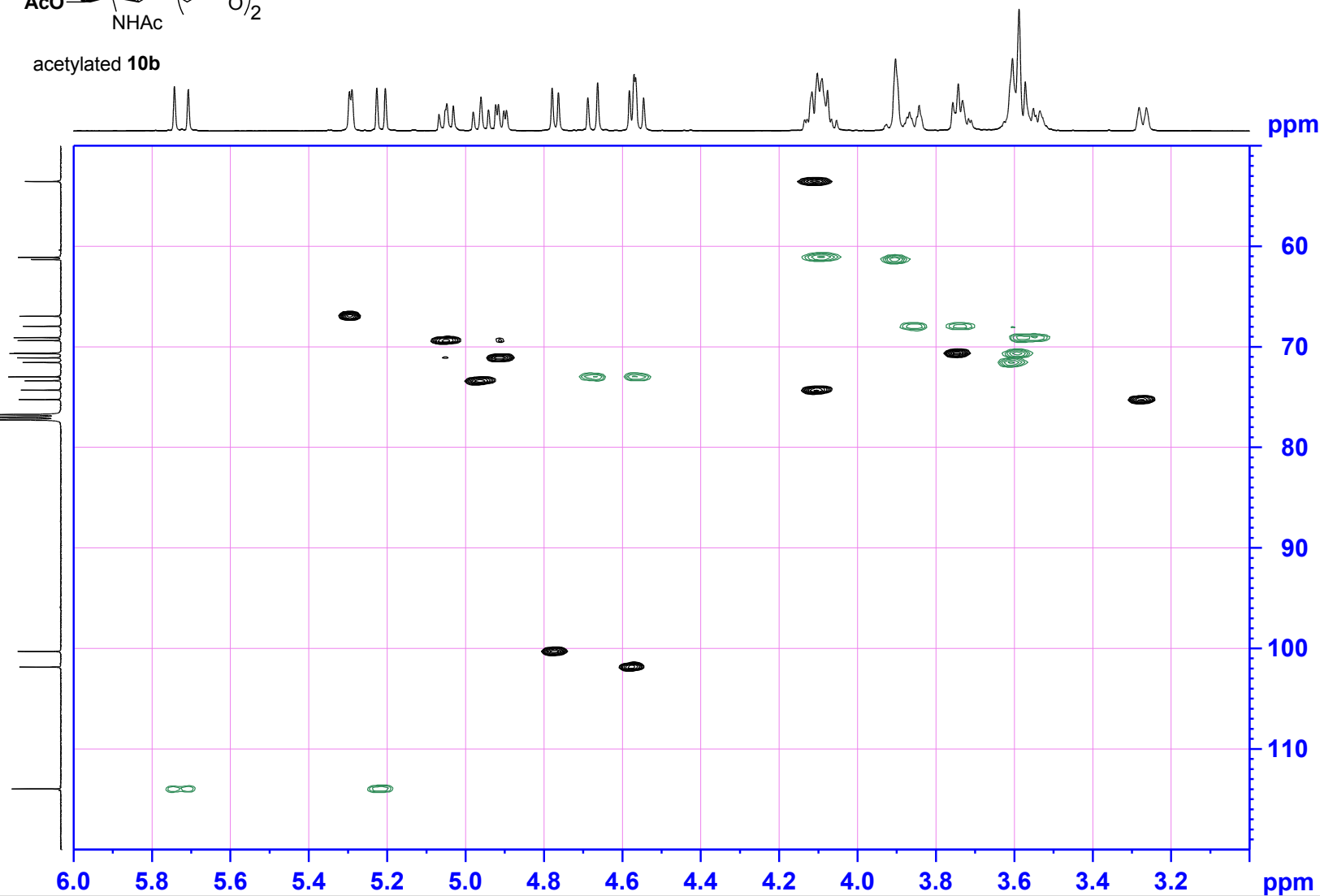
¹H NMR COSY (500 MHz, CDCl₃) of acetylated **10b** (β-isomer)

500MHz HSQC CDCl3 2071



```
NAME changco-kuoty-13Jul06-2071
EXPNO 72
PROCNO 1
Date_ 20130706
Time 12.21
INSTRUM spect
PROBHD 5 mm CP98BO BB
PULPROG hugedatgpg1asp.3
TD 1024
SOLVENT CDCl3
NS 8
DS 4
SWH 6009.615 Hz
FIDRES 3.868745 Hz
AQ 0.082468 sec
RG 32
RW 83.200 usec
DE 35.00 usec
TE 298.0 K
CNPX2 155.000000
CNPX1 -0.500000
D0 0.0000300 sec
D1 1.0000000 sec
D4 0.00161290 sec
D11 0.0300000 sec
D16 0.0002000 sec
D21 0.0032581 sec
D24 0.0000045 sec
INO 0.00001660 sec
===== CHANNEL f1 =====
SFO1 500.132509 MHz
NUC1 13
P1 11.60 usec
P2 23.20 usec
P2B 0.00 usec
NUC2 1
SFO2 125.7779 MHz
FIDRES 58.829607 Hz
SW 239.474 ppm
F1M2ODE Echo-Anti1ecb0
SI 2048
SF 500.1700188 MHz
QSDONE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 1024
MC2 echo-anti1ecb0
SF 125.7678371 MHz
QSDONE
SSB 2
LB 0.00 Hz
GB 0
```

^1H - ^{13}C NMR HSQC(500 MHz, CDCl_3) of acetylated 10b (β -isomer)

acetylated **10b**

```

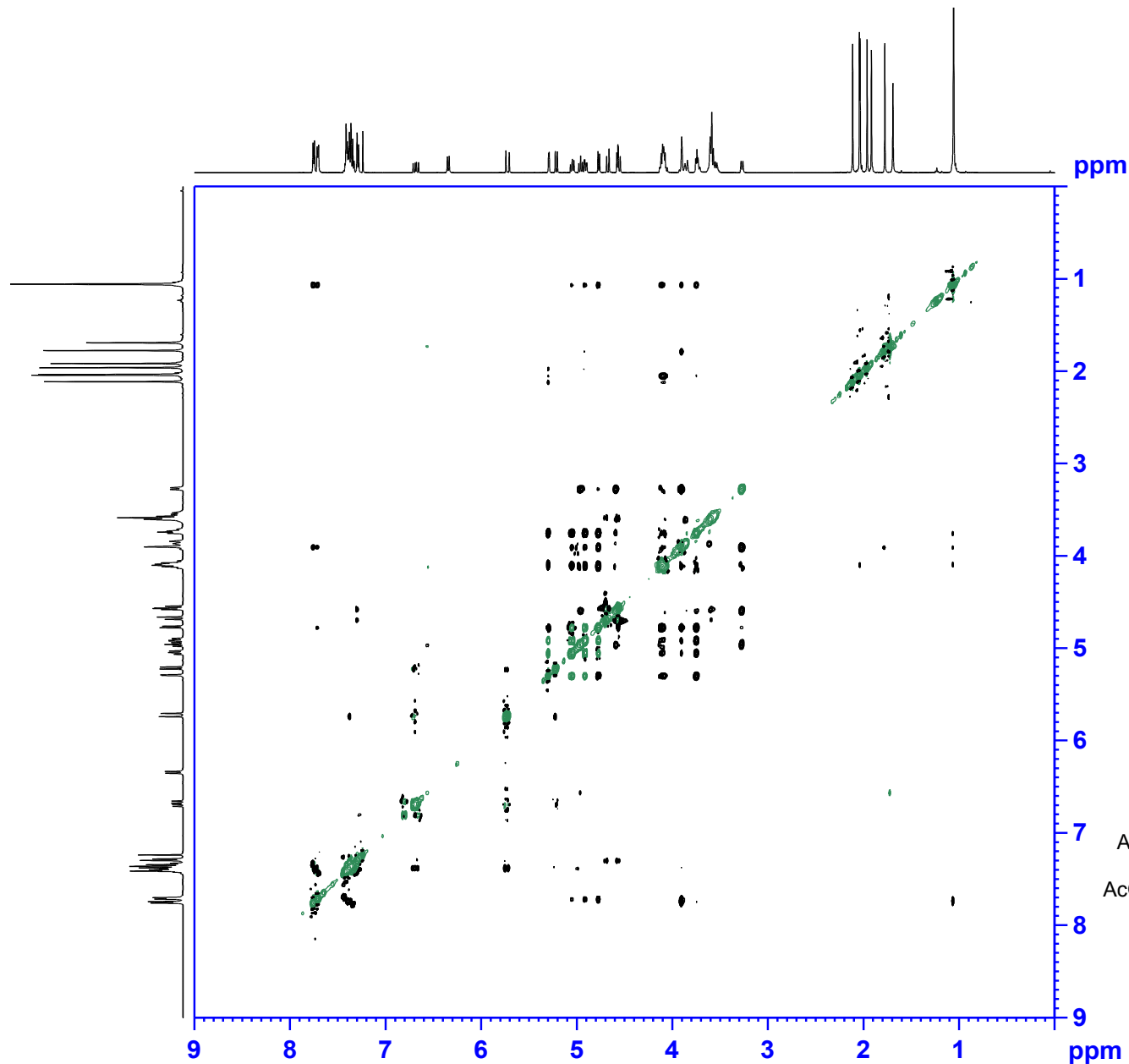
NAME      changco-kuoty-13Jul06-2071
EXPNO     72
PROCNO    1
Date_     20130706
Time      12.21
INSTRUM   spect
PROBHD    5 mm CP98BO BB
PULPROG   hsqcetqpsisp.3
TD        1024
SOLVENT   CDCl3
NS        8
DS        8
SWH       6009.615 Hz
FIDRES    3.868765 Hz
AQ        0.082468 sec
RG        32
RW        83.200 usec
DE        35.00 usec
TE        298.0 K
CNPFTZ    155.0000000
CHFT17    -0.5000000
D0         0.0000300 sec
D1         1.0000000 sec
D4         0.00161290 sec
D11        0.0300000 sec
D16        0.0002000 sec
D21        0.0032581 sec
D24        0.0008045 sec
INO        0.00001660 sec

===== CHANNEL f1 =====
SFO1      500.1325009 MHz
NUC1      13
P1        18
P2        11.60 usec
P3        23.20 usec
P3B       0.00 usec
ND0       2
SD        812
SFO1      125.7779 MHz
FIDRES    58.82967 Hz
SW        239.474 ppm
F2MODE    Echo-AntiEcho
SI        2048
SF        500.1700188 MHz
QSBINE
SSB       2
LB        0.00 Hz
GB        0
PC        1.00
SI        1024
MC2       Echo-AntiEcho
SFO2      125.7678371 MHz
SF        125.7678371 MHz
QSBINE
SSB       2
LB        0.00 Hz
GB        0

```

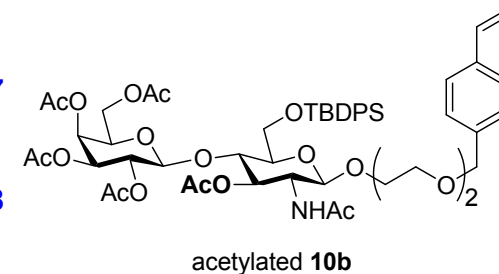
 ^1H - ^{13}C NMR HSQC (500 MHz, CDCl_3) of acetylated **10b** (β -isomer)

500MHz ROESY CDCL3 2071

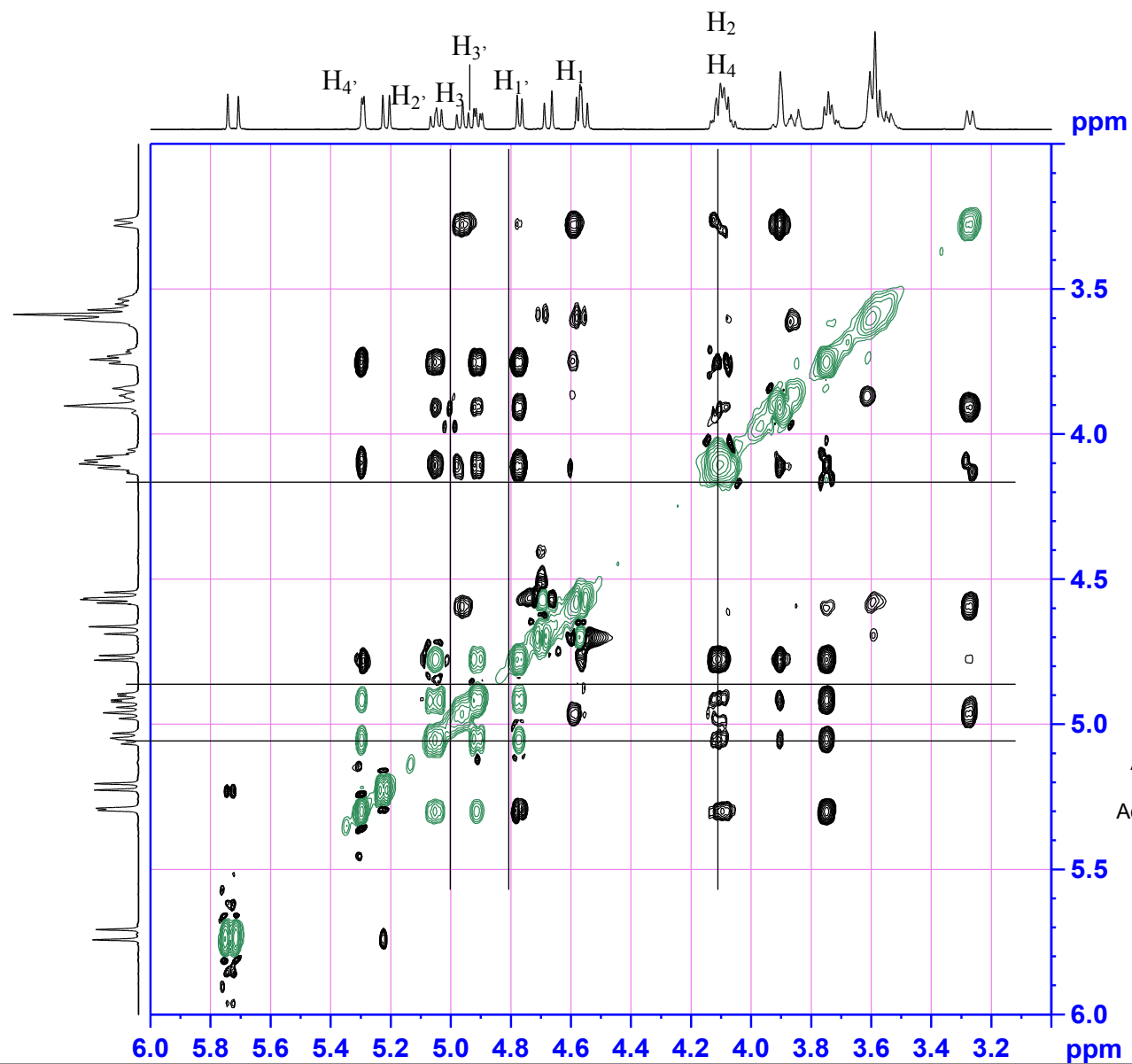


```
NAME changoc-kuoty-13Jul06-2071
EXPNO 1
PROCNO 1
Date_ 20130710
Time 12.40
INSTRUM spect
PROBHD 5 mm CPBPRB0 BB
PULPROG roesyph
TD 2048
SOLVENT CDCL3
NS 8
DS 16
SWH 6009.615 Hz
FIDRES 2.934982 Hz
AQ 0.1704616 sec
RG 40.3
OW 81.200 usec
DE 22.00 usec
TE 300.0 K
DD 0.00007182 sec
D1 2.00000000 sec
D12 0.00002000 sec
IM0 0.00016640 sec

===== CHANNEL f1 =====
SFO1 500.1707509 MHz
NUC1 13
P1 11.60 usec
P15 200000.00 usec
RG 1
TD 512
SFO2 500.1708 MHz
FIDRES 11.737530 Hz
SW 12.015 ppm
PULPROG States-TPPI
SF 500.1700198 MHz
WDW QSIWE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 2048
MC2 States-TPPI
SF 500.1700179 MHz
WDW QSIWE
SSB 2
LB 0.00 Hz
GB 0
```



¹H NMR ROESY (500 MHz, CDCl₃) of acetylated **10b** (β-isomer)



```

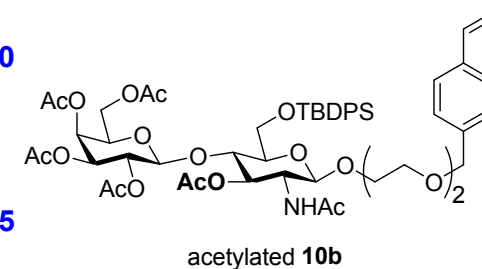
NAME      changoc-kuoty-13Jul06-2071
EXPNO     1
PROCNO    1
Date_     20130710
Time      12.40
INSTRUM   spect
PROBHD    5 mm CPMAS BB
PULPROG   roesyph
TD         2048
SOLVENT   CDCL3
NS         8
DS         16
SWH        6009.615 Hz
FIDRES     2.934982 Hz
AQ         0.1704616 sec
RG         40.3
DE         81.200 usec
QE         298.0 K
DE         22.00 usec
TE         300.2
DD         0.00007182 sec
DI         2.00000000 sec
D12        0.00002000 sec
INO        0.00016640 sec

```

```

===== CHANNEL f1 =====
SFO1      500.1707509 MHz
NUC1       13
P1         11.60 usec
P15        200000.00 usec
RG         1
TD         512
SFO2      500.1708 MHz
FIDRES     11.737530 Hz
SW         12.015 ppm
PULPROG   States-TPPI
SF         500.1700198 MHz
WDW        QSINE
SSB        2
LB         0.00 Hz
GB         0
PC         1.00
SI         2048
MC2        States-TPPI
SF         500.1700179 MHz
WDW        QSINE
SSB        2
LB         0.00 Hz
GB         0

```



^1H NMR ROESY (500 MHz, CDCl_3) of acetylated **10b** (β -isomer)