Orthoesters Formation Leading to Mismatched Helferich Glycosylations at O-3 of *N*-trichloroacetylated Glucosamine Residues.

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Supplementary Material

Table of Contents

	Page
1. ^1H - and ^{13}C - NMR spectra for compounds 9-24, 26-28	2-78
2. Scheme describing the synthesis of diol acceptors 3 and 25 <i>via</i> intermediates 30, 31	79
3. Experimental procedures for the synthesis of compounds 3, 25, 30, 31	80-83
4. ^1H - and ^{13}C - NMR spectra for compounds 3, 25, 30, 31	84-100

1. NMR data for compounds 9-24, 26-28

Compound **9**, 400 MHz, CDCl₃

NAME AF.3.13.4.40A
 EXPNO 1
 PROCNO 1
 Date_ 20130920
 Time 13.38
 INSTRUM spect
 PROBHD 5 mm CPPBBO BE
 PULPROG zg30
 TD 44774
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 5597.015
 FIDRES 0.125006
 AQ 3.9998608
 RG 181
 DW 89.333
 DE 10.00
 TE 296.0
 D1 2.0000000
 TD0 1

===== CHANNEL f1 =====
 SF01 400.1324708
 NUC1 1H
 P1 11.00
 SI 65536
 SF 400.1300181
 WDW FM

Compound **9**, COSY, 600 MHz, CDCl₃

```

NAME      AF.3.12.3.40A
EXPNO     2
PROCNO    1
Date_     20131202
Time      17.11
INSTRUM   Spect
PROBHD    5 mm PATXO 19F
PULPROG   cosygpf45.al
TD        2048
SOLVENT   CDCl3
NS         2
DS        16
SWH       6009.615 Hz
FIDRES    2.934382 Hz
AQ        0.1704436 sec
RG         203
DW        83.200 usec
DE         6.50 usec
TE        297.1 K
D0         0.00000300 sec
D1        1.48689198 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00016640 sec
  
```

```

===== CHANNEL f1 =====
SFO1      600.1330006 MHz
NUC1       1H
P0         5.50 usec
P1        11.00 usec
ND0         1
TD        256
SFO1      600.133 MHz
FIDRES    23.475060 Hz
SW        10.014 ppm
FnMODE     QF
SI         1024
SF        600.1300295 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
PC         5.00
SI         1024
MC2        QF
SF        600.1300295 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
  
```


Compound **9**, 151 MHz, CDCl₃

Compound **9**, edited HSQC (CH and CH₃ blue, CH₂ black),
600 MHz, CDCl₃

NAME	AF.3.12.3.40A
EXPNO	3
PROCNO	1
Date_	20131202
Time	17.28
INSTRUM	Spect

Compound **10**, 400 MHz, CDCl₃

```

NAME      AF.3.7.1.45A
EXPNO     1
PROCNO    1
Date_     20130905
Time_     11.07
INSTRUM   spect
PROBHD    5 mm CFPBBO BE
PULPROG   zg30
TD        44774
SOLVENT   CDCl3
NS         16
DS         0
SWH        5597.015
FIDRES     0.125006
AQ         3.9998608
RG         101
DW         89.333
DE         10.00
TE         296.0
D1         2.00000000
TD0        1
  
```

```

===== CHANNEL f1 =====
SFO1      400.1324708
NUC1       1H
P1         11.00
SI         65536
SF         400.1300177
WDW        RM
  
```

Compound **10**, COSY, 400 MHz, CDCl₃

```

NAME      AF.3.7.1.45A
EXPNO     2
PROCNO    1
Date_     20130905
Time      11.08
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   cosygpf45.al
TD        2048
SOLVENT   CDCl3
NS        2
DS        16
SWH       4000.000 Hz
FIDRES    1.953125 Hz
AQ        0.2560500 sec
RG        203
DW        125.000 usec
DE        10.00 usec
TE        296.0 K
D0        0.00000300 sec
D1        1.48689198 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00025000 sec
  
```

```

===== CHANNEL f1 =====
SFO1      400.1319206 MHz
NUC1      1H
P0        5.50 usec
P1        11.00 usec
ND0       1
TD        128
SFO1      400.1319 MHz
FIDRES    31.250000 Hz
SW        9.997 ppm
FnMODE    QF
SI        1024
SF        400.1300177 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
PC        1.40
SI        512
MC2       QF
SF        400.1300177 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
  
```

Compound **10**, 101 MHz, CDCl₃

Compound **10**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.3.7.1.45A
EXPNO 3
PROCNO 1
Date_ 20130905
Time_ 11.18
INSTRUM spect

Compound **11**, 400 MHz, CDCl₃

```

NAME      AF.2.67.3.30A-
EXPNO     1
PROCNO    1
Date_     20130527
Time      17.40
INSTRUM   spect
PROBHD    5 mm CFPBBO BE
PULPROG   zg30
TD         44774
SOLVENT   CDCl3
NS         32
DS         C
SWH        5597.015
FIDRES     0.125006
AQ         3.9998608
RG         101
DW         89.333
DE         10.00
TE         295.9
D1         2.0000000
TD0        1
  
```

```

===== CHANNEL f1 =====
SFO1      400.1324708
NUC1       1F
P1         11.00
SI         65536
SF         400.1300180
WDW        FM
  
```

Compound **11**, 400 MHz, CDCl₃

```

NAME      AF.2.67.3.30A-3
EXPNO     2
PROCNO    1
Date_     20130528
Time      13.36
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   cosygpgf
TD        2048
SOLVENT   CDCl3
NS        4
DS        0
SWH       4000.000 Hz
FIDRES    1.953125 Hz
AQ        0.2560500 sec
RG        203
DW        125.000 usec
DE        10.00 usec
TE        296.1 K
D0        0.00000300 sec
D1        1.48689198 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00025000 sec
  
```

```

===== CHANNEL f1 =====
SFO1      400.1319206 MHz
NUC1      1H
P0        11.00 usec
P1        11.00 usec
ND0       1
TD        128
SFO1      400.1319 MHz
FIDRES    31.250000 Hz
SW        9.997 ppm
FnMODE    QF
SI        1024
SF        400.1300180 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
PC        1.00
SI        512
MC2       QF
SF        400.1300180 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
  
```


Compound **11**, 101 MHz, CDCl₃

```

NAME      AF.2.67.3.30A-JMOD
EXPNO     4
PROCNO    1
Date_     20131204
Time      17.58
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   jmod
TD        65536
SOLVENT   CDCl3
NS        247
DS        0
SWH       22058.824 Hz
FIDRES    0.336591 Hz
AQ        1.4855326 sec
RG        203
DW        22.667 usec
DE        18.00 usec
TE        296.1 K
CNST2     145.0000000
CNST11    1.0000000
D1        5.00000000 sec
D20       0.00689655 sec
TD0       1

===== CHANNEL f1 =====
SFO1     100.623333 MHz
NUC1     13C
P1       10.00 usec
P2       20.00 usec
SI       32768
SF       100.6127739 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
    
```

Compound **11**, HSQC, 400 MHz, CDCl₃

Current Data Parameters
NAME AF.2.67.3.30A
EXPNO 3
PROCNO 1

Compound **12**, 400 MHz, CDCl₃

Compound **12**, COSY, 400 MHz, CDCl₃

```

NAME      AF.2.76.3.33A
EXPNO     2
PROCNO    1
Date_     20130626
Time      16.08
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   cosygpgf
TD        2048
SOLVENT   CDCl3
NS        2
DS        0
SWH       4000.000 Hz
FIDRES    1.953125 Hz
AQ        0.2560500 sec
RG        203
DW        125.000 usec
DE        10.00 usec
TE        296.1 K
D0        0.00000300 sec
D1        1.48689198 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00025000 sec
  
```

```

===== CHANNEL f1 =====
SFO1     400.1319206 MHz
NUC1      1H
P0        11.00 usec
P1        11.00 usec
ND0       1
TD        128
SFO1     400.1319 MHz
FIDRES    31.250000 Hz
SW        9.997 ppm
FnMODE    QF
SI        1024
SF        400.1300178 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
PC        1.00
SI        512
MC2       QF
SF        400.1300178 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
  
```

Compound **12** ~80% pure (see text, 20% suspected orthoester), 101 MHz, CDCl₃

Compound **12**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.2.76.3.33A
EXPNO 3
PROCNO 1
Date_ 20130626
Time_ 16.18
INSTRUM spect

Compound **13**, 400 MHz, CDCl₃

NAME AF.2.76.3.33E
 EXPNO 1
 PROCNO 1
 Date_ 20130627
 Time_ 15.12
 INSTRUM spect
 PROBHD 5 mm CPPBBO BE
 PULPROG zg30
 TD 44774
 SOLVENT CDCl₃
 NS 32
 DS C
 SWH 5597.015
 FIDRES 0.125006
 AQ 3.9998608
 RG 101
 DW 89.333
 DE 10.00
 TE 295.5
 D1 2.0000000
 TD0 1

===== CHANNEL f1 =====
 SFO1 400.1324708
 NUC1 ¹H
 P1 11.00
 SI 65536
 SF 400.1300179
 WDW RM

Compound **13**, COSY, 400 MHz, CDCl₃

```

NAME      AF.2.76.3.33B
EXPNO     2
PROCNO    1
Date_     20130627
Time      15.12
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   cosygpgf
TD        2048
SOLVENT   CDCl3
NS         2
DS         0
SWH        4000.000 Hz
FIDRES     1.953125 Hz
AQ         0.2560500 sec
RG         203
DW         125.000 usec
DE         10.00 usec
TE         295.9 K
D0         0.00000300 sec
D1         1.48689198 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00025000 sec
  
```

```

===== CHANNEL f1 =====
SFO1      400.1319206 MHz
NUC1       1H
P0         11.00 usec
P1         11.00 usec
ND0        1
TD         128
SFO1      400.1319 MHz
FIDRES     31.250000 Hz
SW         9.997 ppm
FnMODE     QF
SI         1024
SF         400.1300179 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0
PC         1.00
SI         512
MC2        QF
SF         400.1300179 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0
  
```


Compound 13, 151 MHz, CDCl₃

Compound **13**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.2.76.3.33B
EXPNO 4
PROCNO 1
Date_ 20130627
Time_ 17.03
INSTRUM spect

Compound **14**, 400 MHz, CDCl₃

Current Data Parameters
 NAME AF.2.73.1.35A-
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20130626
 Time_ 13.37
 INSTRUM spect
 PROBHD 5 mm CFPBBO BE
 PULPROG zg30
 TD 44774
 SOLVENT CDCl₃
 NS 32
 DS C
 SWH 5597.015
 FIDRES 0.125006
 AQ 3.9998107
 RG 101
 DW 89.333
 DE 10.00
 TE 296.0
 D1 2.0000000
 TD0 1

===== CHANNEL f1 =====
 SFO1 400.1324708
 NUC1 ¹H

Compound **14**, COSY, 400 MHz, CDCl₃

```

NAME      AF.2.73.1.35A-3
EXPNO     2
PROCNO    1
Date_     20130626
Time      13.38
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   cosygpgf
TD        2048
SOLVENT   CDCl3
NS        2
DS        0
SWH       4000.000 Hz
FIDRES    1.953125 Hz
AQ        0.2560500 sec
RG        203
DW        125.000 usec
DE        10.00 usec
TE        296.0 K
D0        0.00000300 sec
D1        1.48689198 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00025000 sec
  
```

```

===== CHANNEL f1 =====
SFO1     400.1319206 MHz
NUC1      1H
P0        11.00 usec
P1        11.00 usec
ND0       1
TD        128
SFO1     400.1319 MHz
FIDRES    31.250000 Hz
SW        9.997 ppm
FnMODE    QF
SI        1024
SF        400.1300179 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
PC        1.00
SI        512
MC2       QF
SF        400.1300179 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
  
```

Compound **14**, 101 MHz, CDCl₃

```

NAME      AF.2.73.1.35A-JMOD
EXPNO     4
PROCNO    1
Date_     20131208
Time      15.12
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   jmod
TD        65536
SOLVENT   CDCl3
NS        543
DS        0
SWH       22058.824 Hz
FIDRES    0.336591 Hz
AQ        1.4855326 sec
RG        203
DW        22.667 usec
DE        18.00 usec
TE        295.9 K
CNST2     145.0000000
CNST11    1.0000000
D1        5.00000000 sec
D20       0.00689655 sec
TD0       1

===== CHANNEL f1 =====
SFO1      100.623333 MHz
NUC1      13C
P1        10.00 usec
P2        20.00 usec
SI        32768
SF        100.6127732 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.00
    
```

Compound **14**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.2.73.1.35A-3
EXPNO 3
PROCNO 1
Date_ 20130626
Time_ 13.47
INSTRUM spect

Compound **15**, 400 MHz, CDCl₃

```

NAME      AF.2.90.1.417
EXPNO     1
PROCNO    1
Date_     20130820
Time_     14.04
INSTRUM   spect
PROBHD    5 mm CPPBBO BE
PULPROG   zg30
TD        44774
SOLVENT   CDCl3
NS        8
DS        0
SWH       5597.015
FIDRES    0.125006
AQ        3.9998608
RG        203
DW        89.333
DE        10.00
TE        296.1
D1        2.0000000
D10       1
TD0       1
    
```

```

===== CHANNEL f1 =====
SFO1      400.1324708
NUC1      1H
P1        11.00
SI        65536
SF        400.1300177
WDW       FM
    
```

Compound **15**, COSY, 400 MHz, CDCl₃

```

NAME      AF.2.90.1.41A
EXPNO     2
PROCNO    1
Date_     20130820
Time      14.05
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   cosygpgf45.al
TD        2048
SOLVENT   CDCl3
NS         2
DS        16
SWH       4000.000 Hz
FIDRES    1.953125 Hz
AQ        0.2560500 sec
RG         203
DW        125.000 usec
DE         10.00 usec
TE        296.1 K
D0         0.00000300 sec
D1         1.48689198 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00025000 sec
  
```

```

===== CHANNEL f1 =====
SFO1      400.1319206 MHz
NUC1       1H
P0         5.50 usec
P1        11.00 usec
ND0         1
TD         128
SFO1      400.1319 MHz
FIDRES    31.250000 Hz
SW         9.997 ppm
FnMODE     QF
SI         1024
SF        400.1300177 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
PC         1.00
SI         512
MC2        QF
SF        400.1300177 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
  
```


Compound **15**, 101 MHz, CDCl₃

```

NAME      AF.2.90.1.41A-JMOD
EXPNO     4
PROCNO    1
Date_     20131126
Time_     16.54
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   jmod
TD        65536
SOLVENT   CDCl3
NS        162
DS        0
SWH       22058.824 Hz
FIDRES    0.336591 Hz
AQ        1.4855326 sec
RG        203
DW        22.667 usec
DE        18.00 usec
TE        291.9 K
CNST2     145.0000000
CNST11    1.0000000
D1        5.0000000 sec
D20       0.00689655 sec
TD0       1

===== CHANNEL f1 =====
SFO1     100.6233333 MHz
NUC1     13C
P1       10.00 usec
P2       20.00 usec
SI       32768
SF       100.6127761 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.00
    
```

Compound **15**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.2.90.1.41A
EXPNO 3
PROCNO 1
Date_ 20130820
Time_ 14.14
INSTRUM spect

Compound **16**, 400 MHz, CDCl₃

NAME AF.2.73.1.35E
EXPNO 1
PROCNO 1
Date 20130619
Time 14.41
INSTRUM spect
PROBHD 5 mm CPPBBO BE
PULPROG zg30
TD 44774
SOLVENT CDCl3
NS 32
DS 0
SWH 5597.015
FIDRES 0.125006
AQ 3.9998608
RG 101
DW 89.333
DE 10.00
TE 292.2
D1 2.00000000
TD0 1

===== CHANNEL f1 =====
SFO1 400.1324708
NUC1 1H
P1 11.00
SI 65536
SF 400.1300184
WDW RM

Compound **16**, COSY, 400 MHz, CDCl₃

Compound **16**, 101 MHz, CDCl₃

Compound **16**, HSQC, 400 MHz, CDCl₃

NAME AF.2.73.1.35B
EXPNO 3
PROCNO 1
Date_ 20130619
Time_ 14.51
INSTRUM spect

Compound **17**, 400 MHz, CDCl₃

NAME AF.2.73.1.35C
 EXPNO 1
 PROCNO 1
 Date_ 20130618
 Time_ 14.53
 INSTRUM spect
 PROBHD 5 mm CPPBBO BE
 PULPROG zg30
 TD 44774
 SOLVENT CDCl₃
 NS 16
 DS 0
 SWH 5597.015
 FIDRES 0.125006
 AQ 3.9998608
 RG 101
 DW 89.333
 DE 10.00
 TE 292.2
 D1 2.0000000
 TD0 1

===== CHANNEL f1 =====
 SFO1 400.1324708
 NUC1 ¹H
 P1 11.00
 SI 65536
 SF 400.1300185
 WDW FM

Compound **17**, COSY, 400 MHz, CDCl₃

```

NAME      AF.2.73.1.35C
EXPNO     2
PROCNO    1
Date_     20130618
Time      14.54
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   cosygpgf
TD        2048
SOLVENT   CDCl3
NS        2
DS        0
SWH       4000.000 Hz
FIDRES    1.953125 Hz
AQ        0.2560500 sec
RG        203
DW        125.000 usec
DE        10.00 usec
TE        292.2 K
D0        0.00000300 sec
D1        1.48689198 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00025000 sec
  
```

```

===== CHANNEL f1 =====
SFO1     400.1319206 MHz
NUC1      1H
P0       11.00 usec
P1       11.00 usec
ND0       1
TD       128
SFO1     400.1319 MHz
FIDRES    31.250000 Hz
SW        9.997 ppm
FnMODE    QF
SI       1024
SF       400.1300185 MHz
WDW       SINE
SSB       0
LB       0.00 Hz
GB       0
PC       1.00
SI       512
MC2       QF
SF       400.1300185 MHz
WDW       SINE
SSB       0
LB       0.00 Hz
GB       0
  
```


Compound **17**, 101 MHz, CDCl₃

```

NAME      AF.2.73.1.35C-JMOD
EXPNO     4
PROCNO    1
Date_     20131206
Time      12.26
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   jmod
TD        65536
SOLVENT   CDCl3
NS        512
DS        0
SWH       22058.824 Hz
FIDRES    0.336591 Hz
AQ        1.4855326 sec
RG        203
DW        22.667 usec
DE        18.00 usec
TE        296.0 K
CNST2     145.0000000
CNST11    1.0000000
D1        5.00000000 sec
D20       0.00689655 sec
TD0       1

===== CHANNEL f1 =====
SFO1     100.623333 MHz
NUC1     13C
P1       10.00 usec
P2       20.00 usec
SI       32768
SF       100.6127734 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.00
    
```

Compound **17**, HSQC, 400 MHz, CDCl₃

NAME AF.2.73.1.35C
EXPNO 3
PROCNO 1
Date_ 20130618
Time_ 15.03
INSTRUM spect

Compound **18**, 600 MHz, CDCl₃

C₆₂H₈₁O₂₇N₂Cl₃
1392.66 g/mol

```
NAME      AF.2.81.1.39A-
EXPNO     5
PROCNO    1
Date_     20131126
Time      17.04
INSTRUM   Spect
PROBHD    5 mm PATXO 19F
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         0
SWH        7812.500
FIDRES     0.119209
AQ         4.1943541
RG         203
DW         64.000
DE         6.50
TE         297.1
D1         2.0000000
TD0        1
```

```
===== CHANNEL f1 =====
SFO1      600.1336008
NUC1       1F
P1         11.00
SI         65536
SF         600.1300294
WDW        EM
```

Compound **18**, COSY, 400 MHz, CDCl₃

```

NAME      AF.2.81.1.39A
EXPNO     2
PROCNO    1
Date_     20130712
Time      10.13
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   cosygpqf45.al
TD        2048
SOLVENT   CDCl3
NS         2
DS        16
SWH        4000.000 Hz
FIDRES     1.953125 Hz
AQ         0.2560500 sec
RG         203
DW         125.000 usec
DE         10.00 usec
TE         292.7 K
D0         0.00000300 sec
D1         1.48689198 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00025000 sec
  
```

```

===== CHANNEL f1 =====
SFO1      400.1319206 MHz
NUC1       1H
P0         5.50 usec
P1        11.00 usec
ND0        1
TD         128
SFO1      400.1319 MHz
FIDRES     31.250000 Hz
SW         9.997 ppm
FnMODE     QF
SI         1024
SF         400.1300173 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
PC         1.00
SI         512
MC2        QF
SF         400.1300173 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
  
```

Compound **18**, 101 MHz, CDCl₃

Compound **18**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.2.81.1.39A
EXPNO 3
PROCNO 1
Date_ 20130712
Time_ 10.23
INSTRUM spect

Compound **19**, 600 MHz, CDCl₃

NAME AF.2.94.1.43F
 EXPNO 1
 PROCNO 1
 Date_ 20130822
 Time_ 16.03
 INSTRUM Spect
 PROBHD 5 mm PATXO 19F
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 16
 DS 0
 SWH 7812.500
 FIDRES 0.119209
 AQ 4.1943541
 RG 203
 DW 64.000
 DE 6.50
 TE 297.0
 D1 2.0000000
 TD0 1

===== CHANNEL f1 =====
 SFO1 600.1336008
 NUC1 1F
 P1 11.00
 SI 65536
 SF 600.1300299
 WDW nc

Compound **19**, COSY, 600 MHz, CDCl₃

```

NAME      AF.2.94.1.43A
EXPNO     2
PROCNO    1
Date_     20130822
Time      16.04
INSTRUM   Spect
PROBHD    5 mm PATXO 19F
PULPROG   cosygpgqf45.al
TD        2048
SOLVENT   CDCl3
NS         2
DS         16
SWH        6009.615 Hz
FIDRES     2.934382 Hz
AQ         0.1704436 sec
RG         203
DW         83.200 usec
DE         6.50 usec
TE         297.0 K
D0         0.00000300 sec
D1         1.48689198 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00016640 sec
  
```

```

===== CHANNEL f1 =====
SFO1      600.1330006 MHz
NUC1       1H
P0         5.50 usec
P1        11.00 usec
ND0         1
TD         256
SFO1      600.133 MHz
FIDRES     23.475060 Hz
SW         10.014 ppm
FnMODE     QF
SI         1024
SF        600.1300299 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
PC         5.00
SI         1024
MC2        QF
SF        600.1300299 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
  
```


Compound **19**, 101 MHz, CDCl₃

Compound **19**, edited HSQC (CH and CH₃ blue, CH₂ black),
600 MHz, CDCl₃

NAME AF.2.94.1.43A
EXPNO 3
PROCNO 1
Date_ 20130822
Time_ 16.20
INSTRUM Spect

Compound **20**, 600 MHz, CDCl₃

NAME AF.2.94.1-43B-
EXPNO 100
PROCNO 1
Date 20150602
Time 10.01
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl₃
NS 2
DS 0
SWH 8417.509
FIDRES 0.128441
AQ 3.8928883
RG 16
DW 59.400
DE 20.00
TE 295.0
D1 1.0000000
TD0 1

===== CHANNEL f1 ===
NUC1 1H
P1 8.60
PL1 5.30
PL1W 7.41310215
SFO1 600.0037054
ST 32768

Compound **20**, COSY, 600 MHz, CDCl₃

```

NAME      AF.2.94.1-43B-FI
EXPNO     19
PROCNO    1
Date_     20150601
Time      17.54
INSTRUM   spect
PROBHD    5 mm CPTCI 1H-
PULPROG   cosygpgf45.al
TD        2048
SOLVENT   CDCl3
NS        1
DS        16
SWH       6009.615 Hz
FIDRES    2.934382 Hz
AQ        0.1704436 sec
RG        181
DW        83.200 usec
DE        20.00 usec
TE        298.0 K
D0        0.00000300 sec
D1        1.48689198 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00016640 sec

===== CHANNEL f1 =====
NUC1      1H
P0        4.00 usec
P1        8.00 usec
PL1       5.30 dB
PL1W      7.41310215 W
SFO1      600.0027001 MHz

===== GRADIENT CHANNEL =====
GPNAM1    SINE.100
GPZ1      10.00 %
P16       1000.00 usec
ND0       1
TD        256
SFO1      600.0027 MHz
FIDRES    23.475060 Hz
SW        10.016 ppm
FnMODE     QF
SI        2048
SF        600.0000275 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
PC        1.00
SI        2048
MC2       QF
SF        600.0000275 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
    
```

Compound **20**, 151 MHz, CDCl₃

Compound **20**, edited HSQC (CH and CH₃ blue, CH₂ black)
600 MHz, CDCl₃

NAME AF.2.94.1-43B-FI
EXPNO 2
PROCNO 1
Date_ 20150601
Time_ 17.37
INSTRUM spect

Compound **21**, 400 MHz, CDCl₃

```

NAME      AF.2.79.1.38A
EXPNO     1
PROCNO    1
Date_     20130705
Time      9.58
INSTRUM   spect
PROBHD    5 mm CPPBBO BE
PULPROG   zg30
TD        44774
SOLVENT   CDCl3
NS        16
DS        0
SWH       5597.015
FIDRES    0.125006
AQ        3.9998608
RG        203
DW        89.333
DE        10.00
TE        296.0
D1        2.00000000
TD0       1
  
```

```

===== CHANNEL f1 =====
SFO1      400.1324708
NUC1      1H
P1        11.00
SI        65536
SF        400.1300178
WDW       RM
  
```

Compound **21**, COSY, 400 MHz, CDCl₃

```

NAME      AF.2.79.1.38A
EXPNO     2
PROCNO    1
Date_     20130705
Time      10.00
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   cosygpgf
TD        2048
SOLVENT   CDCl3
NS        2
DS        0
SWH       4000.000 Hz
FIDRES    1.953125 Hz
AQ        0.2560500 sec
RG        203
DW        125.000 usec
DE        10.00 usec
TE        295.9 K
D0        0.00000300 sec
D1        1.48689198 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00025000 sec
  
```

```

===== CHANNEL f1 =====
SFO1     400.1319206 MHz
NUC1      1H
P0        11.00 usec
P1        11.00 usec
ND0       1
TD        128
SFO1     400.1319 MHz
FIDRES    31.250000 Hz
SW        9.997 ppm
FnMODE    QF
SI        1024
SF        400.1300178 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
PC        1.40
SI        512
MC2       QF
SF        400.1300178 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
  
```


Compound **21**, 101 MHz, CDCl₃

Compound **21**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.2.79.1.38A
EXPNO 3
PROCNO 1
Date_ 20130705
Time_ 10.09
INSTRUM spect

Compound **22**, 600 MHz, CDCl₃

Current Data Parameters
 NAME AF.2.92.1.422
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20130822
 Time_ 15.22
 INSTRUM Spect
 PROBHD 5 mm PATXO 19F
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 7812.500
 FIDRES 0.119209
 AQ 4.1943040
 RG 203
 DW 64.000
 DE 6.50
 TE 297.1
 D1 2.0000000
 TD0 1

===== CHANNEL f1 =====
 SFO1 600.1336008
 NUC1 1F

Compound **22**, COSY, 600 MHz, CDCl₃

```

NAME      AF.2.92.1.42A
EXPNO     2
PROCNO    1
Date_     20130822
Time      15.23
INSTRUM   Spect
PROBHD    5 mm PATXO 19F
PULPROG   cosygpf45.al
TD        2048
SOLVENT   CDCl3
NS         2
DS         16
SWH        6009.615 Hz
FIDRES     2.934382 Hz
AQ         0.1704436 sec
RG         203
DW         83.200 usec
DE         6.50 usec
TE         297.1 K
D0         0.00000300 sec
D1         1.48689198 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00016640 sec

===== CHANNEL f1 =====
SFO1      600.1330006 MHz
NUC1       1H
P0         5.50 usec
P1        11.00 usec
ND0         1
TD         256
SFO1      600.133 MHz
FIDRES     23.475060 Hz
SW         10.014 ppm
FnMODE     QF
SI         1024
SF         600.1300298 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
PC         5.00
SI         1024
MC2        QF
SF         600.1300298 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
    
```

Compound **22**, 101 MHz, CDCl₃

Compound **22**, edited HSQC (CH and CH₃ blue, CH₂ black), 600 MHz, CDCl₃

NAME AF.2.92.1.42A
EXPNO 3
PROCNO 1
Date_ 20130822
Time_ 15.40
INSTRUM Spect

Compound **23**, 400 MHz, CDCl₃, ~80% pure (see text, 20% suspected orthoester)

NAME AF.2.79.1.38E
 EXPNO 1
 PROCNO 1
 Date_ 20130705
 Time_ 10.31
 INSTRUM spect
 PROBHD 5 mm CPPBBO BE
 PULPROG zg30
 TD 44774
 SOLVENT CDCl₃
 NS 16
 DS 0
 SWH 5597.015
 FIDRES 0.125006
 AQ 3.9998608
 RG 203
 DW 89.333
 DE 10.00
 TE 296.0
 D1 2.0000000
 TD0 1

===== CHANNEL f1 ===
 SFO1 400.1324708
 NUC1 1F
 P1 11.00
 SI 65536
 SF 400.1300179
 WDW FM

Compound **23**, COSY, 400 MHz, CDCl₃, ~80% pure (see text, 20% suspected orthoester)

Compound **23**, 101 MHz, CDCl₃ , ~80% pure (see text, 20% suspected orthoester, quat 123.57 ppm)

Compound **23**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃, ~80% pure (see text, 20% suspected
orthoester)

NAME AF.2.79.1.38B
EXPNO 3
PROCNO 1
Date_ 20130705
Time 10.43
INSTRUM spect

Compound **24**, 600 MHz, CDCl₃

Current Data Parameters
 NAME AF.2.92.1.42E
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20130823
 Time_ 10.49
 INSTRUM Spect
 PROBHD 5 mm PATXO 19F
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 7812.500
 FIDRES 0.119209
 AQ 4.1943040
 RG 203
 DW 64.000
 DE 6.50
 TE 297.0
 D1 2.0000000
 TD0 1

===== CHANNEL f1 =====
 SFO1 600.1336008
 NUC1 1F

Compound **24**, COSY, 600 MHz, CDCl₃

```

NAME      AF.2.92.1.42B
EXPNO     2
PROCNO    1
Date_     20130823
Time      10.50
INSTRUM   Spect
PROBHD    5 mm PATXO 19F
PULPROG   cosygpcqf45.al
TD        2048
SOLVENT   CDCl3
NS         2
DS         16
SWH        6009.615 Hz
FIDRES     2.934382 Hz
AQ         0.1704436 sec
RG         203
DW         83.200 usec
DE         6.50 usec
TE         297.0 K
D0         0.00000300 sec
D1         1.48689198 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00016640 sec
  
```

```

===== CHANNEL f1 =====
SFO1      600.1330006 MHz
NUC1       1H
P0         5.50 usec
P1        11.00 usec
ND0        1
TD         256
SFO1      600.133 MHz
FIDRES     23.475060 Hz
SW         10.014 ppm
FnMODE     QF
SI         1024
SF         600.1300298 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0
PC         5.00
SI         1024
MC2        QF
SF         600.1300298 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0
  
```

Compound **24**, 101 MHz, CDCl₃

Compound **24**, edited HSQC (CH and CH₃ blue, CH₂ black),
600 MHz, CDCl₃

NAME AF.2.92.1.42B
EXPNO 3
PROCNO 1
Date_ 20130823
Time_ 11.12
INSTRUM Spect

Compound **26**, 400 MHz, CDCl₃

```

NAME      AF.3.16.1.462
EXPNO     1
PROCNO    1
Date_     20131009
Time      16.25
INSTRUM   spect
PROBHD    5 mm CPPBBO BE
PULPROG   zg30
TD         44774
SOLVENT   CDCl3
NS         16
DS         0
SWH        5597.015
FIDRES     0.125006
AQ         3.9998608
RG         101
DW         89.333
DE         10.00
TE         296.0
D1         2.00000000
TD0        1
  
```

```

===== CHANNEL f1 =====
SFO1      400.1324708
NUC1      1H
P1        11.00
SI        65536
SF        400.1300184
WDW       EM
  
```

Compound **26**, COSY, 400 MHz, CDCl₃

```

NAME          AF.3.16.1.46A
EXPNO         2
PROCNO        1
Date_         20131009
Time_         16.26
INSTRUM       spect
PROBHD        5 mm CPPBBO BB
PULPROG       cosygpgf45.al
TD            2048
SOLVENT       CDCl3
NS            2
DS            16
SWH           4000.000 Hz
FIDRES        1.953125 Hz
AQ            0.2560500 sec
RG            203
DW            125.000 usec
DE            10.00 usec
TE            296.0 K
D0            0.00000300 sec
D1            1.48689198 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00025000 sec

===== CHANNEL f1 =====
SFO1          400.1319206 MHz
NUC1           1H
P0             5.50 usec
P1            11.00 usec
ND0            1
TD            128
SFO1          400.1319 MHz
FIDRES        31.250000 Hz
SW             9.997 ppm
FnMODE        QF
SI            1024
SF            400.1300184 MHz
WDW           SINE
SSB            0
LB             0.00 Hz
GB            0
PC             1.40
SI            512
MC2           QF
SF            400.1300184 MHz
WDW           SINE
SSB            0
LB             0.00 Hz
GB            0
    
```


Compound **26**, 101 MHz, CDCl₃

Compound **26**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.3.16.1.46A
EXPNO 3
PROCNO 1
Date_ 20131009
Time_ 16.37
INSTRUM spect

Compound **27**, 600 MHz, CDCl₃

Current Data Parameters
 NAME AF.3.20.1.30E
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20131108
 Time_ 11.17
 INSTRUM Spect
 PROBHD 5 mm PATXO 19E
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 32
 DS 1
 SWH 7812.500
 FIDRES 0.119209
 AQ 4.1943040
 RG 203
 DW 64.000
 DE 6.50
 TE 297.0
 D1 2.00000000
 TD0 1

===== CHANNEL f1 =====
 SFO1 600.1336008
 NUC1 ¹H

Compound **27**, 600 MHz, CDCl₃

```

NAME      AF.3.20.1.30B
EXPNO     2
PROCNO    1
Date_     20131108
Time      11.18
INSTRUM   Spect
PROBHD    5 mm PATXO 19F
PULPROG   cosygpgf45.al
TD        2048
SOLVENT   CDCl3
NS         4
DS        16
SWH        6009.615 Hz
FIDRES     2.934382 Hz
AQ         0.1704436 sec
RG         203
DW         83.200 usec
DE         6.50 usec
TE         297.0 K
D0         0.00000300 sec
D1         1.48689198 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00016640 sec
  
```

```

===== CHANNEL f1 =====
SFO1      600.1330006 MHz
NUC1       1H
P0         5.50 usec
P1        11.00 usec
ND0         1
TD        129
SFO1      600.133 MHz
FIDRES     46.586166 Hz
SW         10.014 ppm
FnMODE     QF
SI         1024
SF        600.1300296 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
PC         5.00
SI         1024
MC2        QF
SF        600.1300296 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
  
```

Compound **27**, 101 MHz, CDCl₃

Compound **27**, HSQC, 600 MHz, CDCl₃

NAME AF.3.20.1.30B-HSQC
EXPNO 5
PROCNO 1
Date_ 20131128
Time_ 12.12
INSTRUM spect

Compound **28** (major in a 75/25 mixture with compound **28**),
600 MHz, CDCl₃

NAME AF.3.20.1.30C
EXPNO 1
PROCNO 1
Date_ 20131108
Time_ 12.02
INSTRUM Spect
PROBHD 5 mm PATXO 19F
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS C
SWH 7812.500
FIDRES 0.119209
AQ 4.1943541
RG 203
DW 64.000
DE 6.50
TE 297.0
D1 2.00000000
TD0 1

===== CHANNEL f1 =====
SFO1 600.1336008
NUC1 1F
P1 9.85
SI 65536
SF 600.1300294
WDW RM

Compound **28** (major in a 75/25 mixture with compound **28**),
 COSY, 600 MHz, CDCl₃

```

NAME      AF.3.20.1.30C
EXPNO     2
PROCNO    1
Date_     20131108
Time      12.03
INSTRUM   Spect
PROBHD    5 mm PATXO 19F
PULPROG   cosygpgf45.al
TD        2048
SOLVENT   CDCl3
NS        4
DS        16
SWH       6009.615 Hz
FIDRES    2.934382 Hz
AQ        0.1704436 sec
RG        203
DW        83.200 usec
DE        6.50 usec
TE        297.0 K
D0        0.00000300 sec
D1        1.48689198 sec
D13       0.00000400 sec
D16       0.00020000 sec
IN0       0.00016640 sec
  
```

```

===== CHANNEL f1 =====
SFO1      600.1330006 MHz
NUC1      1H
P0        5.50 usec
P1        11.00 usec
ND0       1
TD        131
SFO1      600.133 MHz
FIDRES    45.874928 Hz
SW        10.014 ppm
FnMODE    QF
SI        1024
SF        600.1300294 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
PC        5.00
SI        1024
MC2       QF
SF        600.1300294 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
  
```


Compound **28** (major in a 75/25 mixture with compound **28**),
151 MHz, CDCl₃

Compound **28** (major in a 75/25 mixture with compound **28**),
HSQC, 600 MHz, CDCl₃

NAME AF3.20.1.30C-FI
EXPNO 2
PROCNO 1
Date_ 20150513
Time_ 16.32
INSTRUM spect

2. Scheme describing the synthesis of diol acceptors **3** and **25** via intermediate **29-31**

Synthesis of acceptor **3** and **25** from chloroacetylated analogue **29**.¹¹

3. Experimental procedures for the synthesis of diol acceptors **3** and **25**

3.1. *Pentyl O-[3-O-(chloro)acetyl-2-deoxy-2-(trichloro)acetamido-β-D-glucopyranosyl]-(1→3)-O-(2,4-di-O-acetyl-6-O-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-6-O-benzoyl-3-O-(chloro)acetyl-2-deoxy-β-D-glucopyranoside (30)*

Trisaccharide **29**¹¹ (300 mg, 0.24 mmol) was dissolved in 90% aq AcOH (30 mL), the solution was stirred at 80 °C for 2 h, then co-concentrated with toluene (2 × 100 mL). Pure diol **30** (279 mg, quant) was obtained as a brownish powder. $[\alpha]_D -2.0$ (c 1.0, MeOH). ¹H NMR (CD₃OD, 400 MHz): δ_H 8.23 (d, $J = 9.3$ Hz, 1 H, NH), 8.03–7.52 (3 m, 5 H, Ar), 5.43 (d, $J = 3.3$ Hz, 1 H, H-4'), 5.25 (dd, $J = 9.0, 10.7$ Hz, 1 H, H-3''), 5.18 (dd, $J = 8.5, 10.6$ Hz, 1 H, H-3), 4.97 (dd, $J = 8.0, 10.1$ Hz, 1 H, H-2'), 4.84 (d, $J = 8.2$ Hz, 1 H, H-1''), 4.63 (dd, $J = 1.8, 12.2$ Hz, 1 H, H-6a), 4.55 (d, $J = 8.4$ Hz, 1 H, H-1), 4.48 (d, $J = 8.0$ Hz, 1 H, H-1'), 4.40 (dd, $J = 4.5, 12.2$ Hz, 1 H, H-6b), 4.25–4.18 (m, 3 H, COCH₂Cl, COCHHCl), 4.13–4.06 (m, 3 H, H-6ab', COCHHCl), 4.02 (dd, $J = 3.5, 10.2$ Hz, 1 H, H-3'), 3.90–3.83 (m, 3 H, H-2, H-5', H-6a''), 3.82–3.76 (m, 3 H, H-4, H-5, OCHHCH₂), 3.67–3.60 (m, 2 H, H-2'', H-6b''), 3.50 (dd, $J = 9.8, 18.8$ Hz, 1 H, H-4''), 3.46 (m, 1 H, OCHHCH₂), 3.36 (m, 1 H, H-5''), 2.14, 2.09, 1.89 (3 s, 9 H, 3 × COCH₃), 1.52 (m, 2 H, OCH₂CH₂), 1.30–1.25 (m, 4 H, CH₂CH₂CH₃), 1.23 (s, 9 H, C(CH₃)₃), 0.85 (t, $J = 6.9$ Hz, 3 H, CH₂CH₃). ¹³C NMR (CD₃OD, 101 MHz): δ_C 179.3, 173.4, 172.5, 171.0, 168.6, 168.5, 167.3, 164.0 (C=O), 134.7, 131.0, 130.6, 129.9 (Ar), 102.3 (C-1'), 102.2 (C-1), 100.9 (C-1''), 77.8 (C-5''), 77.5 (C-3'), 77.4 (C-3''), 77.1 (C-4), 75.8 (C-3), 73.8 (C-5), 72.6 (C-5'), 71.8 (C-2'), 71.0 (OCH₂CH₂), 70.8 (C-4'), 69.3 (C-4''), 63.8 (C-6), 63.1 (C-6'), 62.1 (C-6''), 57.6 (C-2''), 55.1 (C-2), 41.9, 41.7 (2 COCH₂Cl), 39.8 (C(CH₃)₃), 30.3, 29.3, 27.7 (CH₂CH₂CH₂CH₃), 27.7 (C(CH₃)₃), 22.7, 21.4, 20.9 (COCH₃), 14.4 (CH₂CH₃). HRESIMS (m/z): $[M + H]^+$ calcd for C₄₇H₆₄O₂₂N₂Cl₅ 1183.2351, found 1183.2271.

2.2. Pentyl O-[4,6-di-O-acetyl-3-O-(chloro)acetyl-2-deoxy-2-(trichloro)acetamido-β-D-glucopyranosyl]-(1→3)-O-(2,4-di-O-acetyl-6-O-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-6-O-benzoyl-3-O-(chloro)acetyl-2-deoxy-β-D-glucopyranoside (31)

Diol **30** (224 mg, 0.19 mmol) was dissolved in a 1:1 mixture of pyridine/Ac₂O (20 mL). The solution was stirred at rt for 1 h, co-concentrated with toluene (2 × 100 mL) and the residue dissolved in CH₂Cl₂ (100 mL) was washed with 2 M HCl (100 mL). The aq layer was re-extracted with CH₂Cl₂ (3 × 20 mL), and the combined organic layers were dried and concentrated giving pure diacetate **31** (237 mg, 99%) as a yellow amorphous solid. $[\alpha]_D^{+9.8}$ (*c* 1.0, CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ_H 7.99–7.47 (3 m, 5 H, Ar), 6.87 (d, *J* = 8.0 Hz, 1 H, NH”), 5.71 (d, *J* = 9.1 Hz, 1 H, NH), 5.46 (dd, *J* = 9.2, 10.7 Hz, 1 H, H-3”), 5.30 (d, *J* = 3.4 Hz, 1 H, H-4’), 5.18 (dd, *J* = 8.1, 9.6 Hz, 1 H, H-3), 5.07 (t, *J* = 10.0 Hz, 1 H, H-4”), 5.00 (dd, *J* = 8.0, 9.9 Hz, 1 H, H-2’), 4.94 (d, *J* = 8.0 Hz, 1 H, H-1”), 4.67 (dd, *J* = 2.6, 12.0 Hz, 1 H, H-6a), 4.53 (d, *J* = 7.4 Hz, 1 H, H-1), 4.36 (dd, *J* = 4.7, 11.9 Hz, 1 H, H-6b), 4.33 (d, *J* = 8.0 Hz, 1 H, H-1’), 4.23 (dd, *J* = 2.4, 12.4 Hz, 1 H, H-6a”), 4.16–3.91 (m, 8 H, H-2, H-6ab’, H-6b”), 2 × COCH₂Cl, 3.84–3.76 (m, 3 H, H-4, H-3’, OCHHCH₂), 3.75–3.57 (m, 4 H, H-5, H-5’, H-2”, H-5”), 3.40 (m, 1 H, OCHHCH₂), 2.10, 2.06, 2.05, 2.00, 1.94 (5 s, 15 H, 5 × COCH₃), 1.52 (m, 2 H, OCH₂CH₂), 1.27–1.20 (m, 4 H, CH₂CH₂CH₃), 1.17 (s, 9 H, C(CH₃)₃), 0.83 (t, *J* = 6.8 Hz, 3 H, CH₂CH₃). ¹³C NMR (CDCl₃, 101 MHz): δ_C 177.9, 170.7, 170.1, 169.8, 169.4, 169.2, 167.3, 167.0, 166.0, 161.9 (C=O), 133.6, 129.5, 129.4, 128.7 (Ar), 100.8 (C-1, C-1’), 99.0 (C-1”), 91.9 (CCl₃), 75.8 (C-3’), 75.0 (C-4), 73.6 (C-3), 72.5 (C-5), 72.3 (C-5”), 71.8 (C-3”), 71.4 (C-5’), 70.7 (C-2’), 70.0 (OCH₂CH₂), 68.6 (C-4’), 68.0 (C-4”), 62.6 (C-6), 61.7 (C-6’), 61.0 (C-6”), 56.7 (C-2”), 53.1 (C-2), 40.7, 40.3 (COCH₂Cl), 38.7 (C(CH₃)₃), 29.0, 28.0, 22.3 (CH₂CH₂CH₂CH₃), 27.1 (C(CH₃)₃), 23.3, 21.1, 20.7, 20.6 (COCH₃), 14.0 (CH₂CH₃). HRESIMS (*m/z*): [M + H]⁺ calcd for C₅₁H₆₈O₂₄N₂Cl₅H 1267.2605, found 1267.2572.

2.3. Pentyl O-[4,6-di-O-acetyl-2-deoxy-2-(trichloro)acetamido-β-D-glucopyranosyl]-(1→3)-O-(2,4-di-O-acetyl-6-O-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-6-O-benzoyl-2-deoxy-β-D-glucopyranoside (3)

Diacetate **31** (236 mg, 0.19 mmol) and thiourea (142 mg, 1.86 mmol, 10 equiv) were dissolved in a mixture of 1:1 pyridine/EtOH (24 mL). The solution was stirred at 70 °C for 18 h, cooled to rt, diluted with CHCl₃ (100 mL), and successively washed with 2 M HCl (100 mL) and satd aq NaHCO₃ (100 mL). The aq layers were re-extracted with CHCl₃ (3 × 20 mL each), and the combined organic layers were dried and concentrated. Column chromatography (CH₂Cl₂/MeOH, 20:1) gave diacetate acceptor **3** (248 mg, 89%) pure as a yellow amorphous solid. $[\alpha]_D^{+15.6}$ (c 0.50, CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ_H 8.00–7.45 (3 m, 5 H, Ar), 7.19 (d, *J* = 7.0 Hz, 1 H, N-H”), 5.61 (d, *J* = 7.9 Hz, 1 H, NH), 5.35 (br d, *J* = 3.3 Hz, 1 H, H-4’), 5.14 (dd, *J* = 8.1, 10.1 Hz, 1 H, H-2’), 5.03 (d, *J* = 8.0 Hz, 1 H, H-1”), 4.83 (t, *J* = 9.2 Hz, 1 H, H-4”), 4.76 (d, *J* = 8.2 Hz, 1 H, H-1), 4.51 (dd, *J* = 1.9, 11.7 Hz, 1 H, H-6a), 4.47 (d, *J* = 8.0 Hz, 1 H, H-1’), 4.30–4.08 (m, 6 H, H-6b, H-6a’, H-3”, H-6ab”, OH-3), 4.04–3.93 (m, 2 H, H-3, H-6b’), 3.90–3.82 (m, 2 H, H-3’, H-5’), 3.79 (m, 1 H, OCHHCH₂), 3.70 (m, 1 H, H-5), 3.60 (m, 1 H, H-5”), 3.50 (t, *J* = 9.4 Hz, 1 H, H-4), 3.47–3.38 (m, 2 H, H-2, OCHHCH₂), 3.27 (m, 1 H, H-2”), 3.21 (s, 1 H, OH-3”), 2.10, 2.08, 2.07, 2.06, 1.96 (5 s, 15 H, 5 × COCH₃), 1.52 (m, 2 H, OCH₂CH₂), 1.28–1.22 (m, 4 H, CH₂CH₂CH₃), 1.16 (s, 9 H, C(CH₃)₃), 0.83 (t, *J* = 6.8 Hz, 3 H, CH₂CH₃). ¹³C NMR (CDCl₃, 101 MHz): δ_C 178.1, 170.9, 170.8, 170.4, 169.9, 169.4, 166.2, 162.4 (C=O), 133.3, 129.6, 128.5 (Ar), 101.5 (C-1’), 100.1 (C-1), 98.7 (C-1”), 92.1 (CCl₃), 82.1 (C-4), 75.7 (C-3’), 72.0 (C-5), 71.9 (C-5”), 71.8 (C-5’), 71.5 (C-3), 71.3 (C-4”), 70.3 (C-2’), 70.0 (C-3”), 69.9 (OCH₂CH₂), 69.0 (C-4’), 63.2 (C-6), 62.5 (C-6’), 61.4 (C-6”), 59.8 (C-2”), 56.7 (C-2), 38.7 (C(CH₃)₃), 29.1, 28.0, 22.3 (CH₂CH₂CH₂CH₃), 26.9 (C(CH₃)₃), 23.5, 21.1, 20.8, 20.7 (COCH₃), 14.0 (CH₂CH₃). HRESIMS (*m/z*): [M + H]⁺ calcd for C₄₇H₆₆O₂₂N₂Cl₃ 1115.3173, found 1115.3164.

2.4. Pentyl O-[2-acetamido-4,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl]-(1→3)-O-(2,4-di-O-acetyl-6-O-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-6-O-benzoyl-2-deoxy-β-D-glucopyranoside (25)

Trisaccharide diol acceptor **3** (190 mg, 0.17 mmol) was dissolved in AcOH (19 mL). Activated Zn dust (3×1.11 g, 3×100 equiv) was added in portion wise every 4 h while the reaction mixture was sonicated at 50 °C for 12 h. The mixture was cooled to rt, filtered over celite and the filtrate was washed successively with CH₂Cl₂ (2×100 mL) and satd aq NaHCO₃ (200 mL). The aq layers were re-extracted with CH₂Cl₂ (5×50 mL), and the combined organic layers were dried and concentrated giving acetamido acceptor **25** (154 mg, 89%) as a colorless solid. $[\alpha]_D^{+7.4}$ (c 0.61, MeOH). ¹H NMR (CDCl₃, 600 MHz): δ_H 8.01–7.45 (3 m, 5 H, Ar), 5.96 (s, 1 H, NH”), 5.59 (d, J = 7.4 Hz, 1 H, NH), 5.34 (d, J = 3.5 Hz, 1 H, H-4’), 5.13 (dd, J = 8.1, 9.9 Hz, 1 H, H-2’), 4.87 (t, J = 9.5 Hz, 1 H, H-4”), 4.84 (d, J = 8.3 Hz, 1 H, H-1), 4.68 (d, J = 8.1 Hz, 1 H, H-1”), 4.56 (dd, J = 1.2, 10.3 Hz, 1 H, H-6a), 4.51 (d, J = 8.0 Hz, 1 H, H-1’), 4.28 (dd, J = 5.5, 11.7 Hz, 1 H, H-6b), 4.24 (dd, J = 1.5, 10.4 Hz, 1 H, H-6a”), 4.20 (br s, 1 H, OH-3), 4.16 (dd, J = 4.4, 11.8 Hz, 1 H, H-6a’), 4.08 (t, J = 9.1 Hz, 2 H, H-3), 4.05 (dd, J = 4.1, 12.4 Hz, 1 H, H-6b”), 4.02–3.95 (m, 2 H, H-6b’, H-3”), 3.86 (m, 1 H, H-5’), 3.81 (m, 1 H, OCHHCH₂), 3.77 (dd, J = 3.7, 14.9 Hz, 1 H, H-3’), 3.73 (m, 1 H, H-5), 3.55 (m, 1 H, H-5”), 3.51 (dd, J = 8.3, 9.3 Hz, 1 H, H-4), 3.46 (m, 1 H, OCHHCH₂), 3.34 (m, 1 H, H-2), 3.06 (m, 1 H, H-2”), 2.12, 2.10, 2.07, 2.05, 1.99, 1.97 (6 s, 18 H, $6 \times$ COCH₃), 1.53 (m, 2 H, OCH₂CH₂), 1.28–1.22 (m, 4 H, CH₂CH₂CH₃), 1.17 (s, 9 H, C(CH₃)₃), 0.83 (t, J = 6.9 Hz, 3 H, CH₂CH₃). ¹³C NMR (CDCl₃, 151 MHz): δ_C 178.1, 172.4, 170.9, 170.5, 170.4, 169.5, 166.2 (C=O), 133.4, 129.6, 128.5 (Ar), 101.3 (C-1’), 99.9 (C-1, C-1”), 82.4 (C-4), 76.2 (C-3’), 72.0 (C-5’, C-5”), 71.8 (C-5), 71.4 (C-3), 71.3 (C-3”), 71.0 (C-2’, C-4”), 69.1 (OCH₂CH₂), 69.1 (C-4’), 63.3 (C-6), 62.3 (C-6’), 61.5 (C-6”), 59.4 (C-2”), 57.1 (C-2), 38.7 (C(CH₃)₃), 29.1, 28.0, 22.3 (CH₂CH₂CH₂CH₃), 26.9 (C(CH₃)₃), 23.6, 23.4, 21.0, 20.9, 20.8, 20.7 (COCH₃), 14.0 (CH₂CH₃). HRESIMS (m/z): $[M - H]^-$ calcd for C₄₇H₆₇O₂₂N₂ 1011.4190, found 1011.4158.

4. NMR data for compounds 3, 25, 30, 31

Compound 3, 400 MHz, CDCl₃

Current Data Parameters
NAME AF.2.87.3.322
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130723
Time_ 12.08
INSTRUM spect
PROBHD 5 mm CPPBBO BE
PULPROG zg30
TD 44774
SOLVENT CDCl₃
NS 8
DS 0
SWH 5597.015
FIDRES 0.125006
AQ 3.9998107
RG 203
DW 89.333
DE 10.00
TE 296.0
D1 2.00000000
TD0 1

===== CHANNEL f1 =====
SFO1 400.1324708
NUC1 1H

Compound 3, COSY, 400 MHz, CDCl₃

```

NAME      AF.2.87.3.32A
EXPNO     2
PROCNO    1
Date_     20130723
Time      12.10
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   cosygpqf45.al
TD        2048
SOLVENT   CDCl3
NS         2
DS        16
SWH       4000.000 Hz
FIDRES    1.953125 Hz
AQ        0.2560500 sec
RG         203
DW        125.000 usec
DE         10.00 usec
TE        296.0 K
D0         0.00000300 sec
D1         1.48689198 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00025000 sec
  
```

```

===== CHANNEL f1 =====
SFO1      400.1319206 MHz
NUC1       1H
P0         5.50 usec
P1         11.00 usec
ND0         1
TD         128
SFO1      400.1319 MHz
FIDRES     31.250000 Hz
SW         9.997 ppm
FnMODE     QF
SI         1024
SF         400.1300177 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
PC         1.00
SI         512
MC2        QF
SF         400.1300177 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
  
```

Compound 3, 101 MHz, CDCl₃

```

NAME      AF.2.87.3.32A
EXPNO     4
PROCNO    1
Date_     20130723
Time      12.51
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   jmod
TD         65536
SOLVENT   CDCl3
NS         256
DS         0
SWH        22058.824 Hz
FIDRES     0.336591 Hz
AQ         1.4855326 sec
RG         203
DW         22.667 usec
DE         18.00 usec
TE         296.0 K
CNST2     145.0000000
CNST11    1.0000000
D1         5.00000000 sec
D20        0.00689655 sec
TD0        1

===== CHANNEL f1 =====
SFO1      100.6233333 MHz
NUC1       13C
P1         10.00 usec
P2         20.00 usec
SI         32768
SF         100.6127741 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

Compound **3**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.2.87.3.32A
EXPNO 3
PROCNO 1
Date_ 20130723
Time_ 12.19
INSTRUM spect

Compound **25**, 600 MHz, CDCl₃

Current Data Parameters
NAME AF.3.6.1.44P
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130830
Time_ 10.33
INSTRUM Spect
PROBHD 5 mm PATXO 19F
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS C
SWH 7812.500
FIDRES 0.119209
AQ 4.1943040
RG 203
DW 64.000
DE 6.50
TE 297.0
D1 2.0000000
TD0 1

===== CHANNEL f1 =====
SFO1 600.1336008
NUC1 1F

Compound **25**, COSY, 600 MHz, CDCl₃

```

NAME      AF.3.6.1.44A
EXPNO     2
PROCNO    1
Date_     20130830
Time      10.34
INSTRUM   Spect
PROBHD    5 mm PATXO 19F
PULPROG   cosygpcqf45.al
TD        2048
SOLVENT   CDCl3
NS         2
DS        16
SWH        6009.615 Hz
FIDRES     2.934382 Hz
AQ         0.1704436 sec
RG         203
DW         83.200 usec
DE         6.50 usec
TE         297.0 K
D0         0.00000300 sec
D1         1.48689198 sec
D13        0.00000400 sec
D16        0.00020000 sec
IN0        0.00016640 sec
  
```

```

===== CHANNEL f1 =====
SFO1      600.1330006 MHz
NUC1       1H
P0         5.50 usec
P1        11.00 usec
ND0         1
TD         139
SFO1      600.133 MHz
FIDRES     43.234642 Hz
SW         10.014 ppm
FnMODE     QF
SI         1024
SF         600.1300297 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
PC         5.00
SI         1024
MC2        QF
SF         600.1300297 MHz
WDW        SINE
SSB         0
LB         0.00 Hz
GB         0
  
```

Compound **25**, 101 MHz, CDCl₃

```

NAME      AF.3.6.1.44A
EXPNO     4
PROCNO    1
Date_     20130901
Time      13.53
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   jmod
TD        65536
SOLVENT   CDCl3
NS        256
DS        0
SWH       22058.824 Hz
FIDRES    0.336591 Hz
AQ        1.4855326 sec
RG        203
DW        22.667 usec
DE        18.00 usec
TE        296.0 K
CNST2     145.0000000
CNST11    1.0000000
D1        5.0000000 sec
D20       0.00689655 sec
TD0       1
  
```

```

===== CHANNEL f1 =====
SF01    100.6233333 MHz
NUC1     13C
P1       10.00 usec
P2       20.00 usec
SI       32768
SF       100.6127735 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
  
```

Compound **25**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.3.6.1.44A
EXPNO 3
PROCNO 1
Date_ 20130830
Time_ 10.44
INSTRUM Spect.

Compound **30**, 400 MHz, CD₃OD

C₄₇H₆₃O₂₂N₂Cl₅
1185.27 g/mol

Current Data Parameters
NAME AF.2.83.3.29A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130716
Time_ 10.53
INSTRUM spect
PROBHD 5 mm CPPBBO BE
PULPROG zg30
TD 44774
SOLVENT MeOH
NS 8
DS C
SWH 5597.015
FIDRES 0.125006
AQ 3.9998107
RG 203
DW 89.333
DE 10.00
TE 296.0
D1 2.0000000
TD0 1

===== CHANNEL f1 =====
SF01 400.1324708
NUC1 1F

Compound **30**, COSY, 400 MHz, CD₃OD

Compound **30**, 101 MHz, CD₃OD

```

NAME      AF.2.83.3.29A
EXPNO     4
PROCNO    1
Date_     20130716
Time_     11.33
INSTRUM   spect
PROBHD    5 mm CPPBBO BB
PULPROG   jmod
TD        65536
SOLVENT   MeOD
NS        257
DS        0
SWH       22058.824 Hz
FIDRES    0.336591 Hz
AQ        1.4855326 sec
RG        203
DW        22.667 usec
DE        18.00 usec
TE        296.0 K
CNST2     145.0000000
CNST11    1.0000000
D1        5.0000000 sec
D20       0.00689655 sec
TD0       1

===== CHANNEL f1 =====
SFO1      100.6233333 MHz
NUC1      13C
P1        10.00 usec
P2        20.00 usec
SI        32768
SF        100.6126281 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
    
```

Compound **30**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CD₃OD

NAME AF.2.83.3.29A
EXPNO 3
PROCNO 1
Date_ 20130716
Time_ 11.04
INSTRUM spect

Compound **31**, 400 MHz, CDCl₃

C₅₁H₆₇O₂₄N₂Cl₅
1269.34 g/mol

Current Data Parameters
NAME AF.2.84.4.31F
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130717
Time_ 16.53
INSTRUM spect
PROBHD 5 mm CPPBBO BE
PULPROG zg30
TD 44774
SOLVENT CDCl₃
NS 8
DS 0
SWH 5597.015
FIDRES 0.125006
AQ 3.9998107
RG 181
DW 89.333
DE 10.00
TE 296.0
D1 2.0000000
TD0 1

===== CHANNEL f1 =====
SFO1 400.1324708
NUC1 1H

Compound **31**, COSY, 400 MHz, CDCl₃

Compound **31**, 101 MHz, CDCl₃

Compound **31**, edited HSQC (CH and CH₃ blue, CH₂ black),
400 MHz, CDCl₃

NAME AF.2.84.4.31A
EXPNO 3
PROCNO 1
Date_ 20130717
Time_ 17.03
INSTRUM spect