Supporting Information

Stereoselective Glycosylation of *exo*-Glycals Accelerated by Ferrier-type Rearrangement

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Typical glycosylation procedure. To a stirred solution of a glycosyl acceptor (1.0–2.0 equiv.) and *exo*-glycal **2** or **3** (1.0 equiv.) in anhydrous CH₂Cl₂ at 0 °C was added dropwise BF₃·OEt₂ (1.0 equiv.) in the presence of 4 Å molecular sieves. The reaction was usually complete within an hour. The reaction mixture was quenched by addition of saturated NaHCO₃ and extracted with CH₂Cl₂ for three times. The collected organic layers were washed with brine, dried over MgSO₄, and evaporated *in vacuo*. The resulting residue was subjected to silica gel chromatography (with hexanes and EtOAc) to afford the product.

037

337AT24/CDC13/10-H
0730-337at24/1/1/u/1ch

Current Data Parameters
NAME 0730-337at24
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020730
Time 10.24
INSTRUM spect
PROBHD 5 mm Dual 13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860212 sec
RG 812.7
DE 48.400 usec
TE 300.0 K
D1 1.00000000 sec
P1 13.70 usec
SF01 500.133085 MHz
NUC1 1H
PL1 -4.00 dB

F2 - Processing parameters
SI 16384
SF 500.1300231 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

10 NMR plot parameters
CX 20.00 cm
FIP 10.000 ppm
F1 5001.30 Hz
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56927 Hz/cm

340A C12-C22

PPM

7.29581
7.25024
7.24849
7.23191
7.22791

340A/CDC13/NOESY
0813-340a/11/1/u/1ch

Current Data Parameters

NAME 0813-340a

EXPNO 11

PROCNO 1

F2 - Acquisition Parameters

Date_ 20080814

Time 17.12

INSTRUM spect

PROBHD 5 mm

PULPROG zgpg30

TD 65536

SF 200.13

WDW EM

SSB 0

LB 0.00 Hz

GB 0

PC 1.00

RG 128

DE 6.50 uSec

TE 300.2 K

DELTA 0.0000000 sec

DELTA2 0.0000000 sec

DELTA3 0.0000000 sec

DELTA4 0.0000000 sec

DELTA5 0.0000000 sec

DELTA6 0.0000000 sec

DELTA7 0.0000000 sec

DELTA8 0.0000000 sec

DELTA9 0.0000000 sec

DELTA10 0.0000000 sec

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DELTA18 0.0000000 sec

DELTA19 0.0000000 sec

DELTA20 0.0000000 sec

DELTA21 0.0000000 sec

DELTA22 0.0000000 sec

DELTA23 0.0000000 sec

DELTA24 0.0000000 sec

DELTA25 0.0000000 sec

DELTA26 0.0000000 sec

DELTA27 0.0000000 sec

DELTA28 0.0000000 sec

F1 - Processing parameters

SI 1024

MF 128

WDW EM

SSB 0

LB 0.00 Hz

GB 0

F1 - Acquisition parameters

WDW EM

SSB 0

LB 0.00 Hz

GB 0

PC 1.00

RG 128

DE 6.50 uSec

TE 300.2 K

DELTA 0.0000000 sec

DELTA2 0.0000000 sec

DELTA3 0.0000000 sec

DELTA4 0.0000000 sec

DELTA5 0.0000000 sec

DELTA6 0.0000000 sec

DELTA7 0.0000000 sec

DELTA8 0.0000000 sec

DELTA9 0.0000000 sec

DELTA10 0.0000000 sec

DELTA11 0.0000000 sec

DELTA12 0.0000000 sec

DELTA13 0.0000000 sec

DELTA14 0.0000000 sec

DELTA15 0.0000000 sec

DELTA16 0.0000000 sec

DELTA17 0.0000000 sec

351A/CDC13/1D-H
0902-351a/1/1/u/1ch

Current Data Parameters
NAME 0902-351a
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020902
Time 13.02
INSTRUM spect
PROBHD 5 mm Duai 13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860212 sec
RG 362
DM 48.400 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
P1 13.90 usec
SF01 500.130085 MHz
NUC1 1H
PL1 -4.00 dB

F2 - Processing parameters
SI 16384
SF 500.1300231 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 262.56827 Hz/cm

351A/CDCl3/NOESY
0902-351a/11/1/u/1ch

Current Data Parameters

NAME 0902-351a
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters

Date_ 20000903
Time 18.50
INSTRUM spect
PROBHD 5 mm WALT
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 05
SWH 5000.000 Hz
FIDRES 0.200000 Hz
AQ 0.204550 sec
RG 128
DE 100.000 uS
TE 300.0 K
D1 0.000000 sec
d11 0.000000 sec
P16 0.2487999 sec
d12 0.000000 sec
P1 5.90 uS
PC 500.130000 MHz
N1 1
PC1 -2.00 dB
DO 0.0000000 sec
GR1 0.00 %
GR2 0.00 %
GR3 40.00 %
PR1 100
PR2 10.00 uS
GR2 0.00 %
GR2 40.00 %
PR2 100
RG 0.0000000 sec

F1 - Acquisition Parameters

NO 2
DS 05
SWH 500.130000 MHz
FIDRES 19.536125 Hz
AQ 10.000 uS

F2 - Processing parameters

SI 500.130000 MHz
SF 500.130000 MHz
WDW SSB
SSB 2
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters

SI 1024
MC 1991
SF 500.130000 MHz
WDW SSB
SSB 0
LB 0.00 Hz
GB 0

2D NMR Plot Parameters

CPD 0
C1 15.00 cm
F2P0 7.506 ppm
F2P1 3754.12 Hz
F2P2 0.994 ppm
F2P3 497.29 Hz
F2P4 3754.46 Hz
F2P5 0.993 ppm
F2P6 496.81 Hz
F2P7 0.43413 ppm/cm
F2P8 217.2230 Hz/cm
F2P9 444.50 Hz/cm
F2P10 217.17688 Hz/cm

345A C14-16

Ser-sugar/CDC13/COSY
 0530-ser-sugar/11/1/u/1ch

Current Data Parameters
 NAME 0530-ser-sugar
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080530
 Time 14.32
 INSTRUM spect
 PROBHD 5 mm Multinu
 PULPROG zgpg30
 TO 2048
 SCALEN 1
 SOLVENT CDC13
 DS 8
 SH 16
 SFO 600.615 Hz
 FIDRES 2.934002 Hz
 AQ 0.170446 sec
 RG 320
 DE 3.200 usec
 TE 300.2 K
 P1 1.4888198 sec
 P2 10.25 usec
 P3 10.25 usec
 P4 10.25 usec
 P5 10.25 usec
 P6 10.25 usec
 P7 10.25 usec
 P8 10.25 usec
 P9 10.25 usec
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 P99 10.25 usec
 P100 10.25 usec

F1 - Processing Parameters
 SI 1024
 SF 500.1300770 MHz
 SFO 500.1300770 MHz
 SF2 500.1300770 MHz
 SF3 500.1300770 MHz
 SF4 500.1300770 MHz
 SF5 500.1300770 MHz
 SF6 500.1300770 MHz
 SF7 500.1300770 MHz
 SF8 500.1300770 MHz
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 SF10 500.1300770 MHz
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 SF15 500.1300770 MHz
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 SF99 500.1300770 MHz
 SF100 500.1300770 MHz

2D NMR plot parameters
 SI 1024
 SF 500.1300770 MHz
 SFO 500.1300770 MHz
 SF2 500.1300770 MHz
 SF3 500.1300770 MHz
 SF4 500.1300770 MHz
 SF5 500.1300770 MHz
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