Supporting Information

for

Metal-free glycosylation with glycosyl fluorides in liquid SO₂

Krista Gulbe, Jevgeņija Lugojina, Edijs Jansons, Artis Kinens and Māris Turks

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Copies of NMR spectra
1. Glycosyl donors .................................................................................................................. S2-2
2. Intermediates isolated in the synthesis of 2-deoxy glucosyl fluoride $\alpha$-19 ........ S2-19
3. Target glycosides .............................................................................................................. S2-24
4. Side-products .................................................................................................................... S2-88
1. GLYCOSYL DONORS
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\beta_9$

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\alpha$-11

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\alpha$-12

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

S2-10
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
$1^H$ NMR (500 MHz, CDCl$_3$)

$1^C$ NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\beta$-S11

$^1$H NMR (500 MHz, CDCl$_3$)

$^13$C NMR (126 MHz, CDCl$_3$)
\^{1}H NMR (500 MHz, CDCl\textsubscript{3})

\[^{13}C\text{NMR (126 MHz, CDCl}\textsubscript{3})\]
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2. INTERMEDIATES ISOLATED IN THE SYNTHESIS OF
2-DEOXY GLUCOSYL FLUORIDE \( \alpha \)-19
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$\alpha, \beta = 81.19$

$^{13}$C NMR (126 MHz, CDCl$_3$)

$\alpha, \beta = 81.19$
$\alpha\beta = 77.23$
3. TARGET GLYCOSIDES
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
$\beta$-3d

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\alpha$-3e

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
$^{1}$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
\[
\alpha-3f
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\))

\[^{13}\)C NMR (126 MHz, CDCl\(_3\))

S2-34
$^{1}$H NMR (500 MHz, CDCl₃)

$^{13}$C NMR (126 MHz, CDCl₃)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
$\alpha$-3i

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\beta$-3j

$^1$H NMR (500 MHz, CDCl$_3$)

$\beta$-3j

$\alpha$-2-adamantanol (2j)
$\beta$-3k

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

S2-43
$\alpha$-3l

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\beta$-3m

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
$\alpha$-3n

$^1$H NMR (300 MHz, CDCl$_3$)

$^13$C NMR (75.5 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl$_3$)

$^{13}C$ NMR (75.5 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
α-8b

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75.5 MHz, CDCl$_3$)
\( ^1H \text{NMR} \ (500 \text{ MHz, CDCl}_3) \)

\( ^{13}C \text{NMR} \ (126 \text{ MHz, CDCl}_3) \)
$\beta$-10a

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\alpha$-10b

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}\text{H NMR (500 MHz, CDCl}_3\text{)}$

\[\text{Compound } \alpha-13a\]

$^{13}\text{C NMR (126 MHz, CDCl}_3\text{)}$
$^\beta$-13a

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

S2-63
\( ^1H \text{NMR (500 MHz, CDCl}_3) \)

\( ^{13}C \text{NMR (126 MHz, CDCl}_3) \)
$\beta$-13b

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)

\[ \alpha-14b \]

$^{13}$C NMR (126 MHz, CDCl$_3$)
\( \alpha-17a \)

\(^1\)H NMR (500 MHz, CDCl\(_3\))

\(^{13}\)C NMR (126 MHz, CDCl\(_3\))
\[^{1}H\text{ NMR (500 MHz, CDCl}_3\text{)}\]

\[^{13}C\text{ NMR (126 MHz, CDCl}_3\text{)}\]

\[\alpha\text{-17b}\]
$\alpha$-17c

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\beta$-17c

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\alpha$-17d

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\alpha$-17e

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
\[1^H\text{NMR (500 MHz, CDCl}_3\text{)}\]

\[13C\text{NMR (126 MHz, CDCl}_3\text{)}\]
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
\( ^1H \text{ NMR} \ (500 \text{ MHz, CDCl}_3) \)

\( ^13C \text{ NMR} \ (126 \text{ MHz, CDCl}_3) \)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
4. SIDE-PRODUCTS
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (75.5 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H-$^{13}$C HMBC (CDCl$_3$)

$\alpha,\alpha$-S14
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}H\text{-}^{13}C$ HMBC (CDCl$_3$)

A = H-C4 ↔ Piv
B = H-C2 ↔ Piv
C = H-C6 ↔ Piv
D = H-C1' ↔ C1

$\alpha$-S15
$^{1}$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
S17

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

$\alpha: \beta = 69:31$
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

S2-97
$^{1}H-^{13}C$ HMBC (CDCl$_3$)

A = H- C3 ↔ Piv
B = H- C4 ↔ Piv
C = H- C6 ↔ Piv
$\alpha$-S19 & $\beta$-S20 (66:34)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$\alpha$-S21

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
\[ \alpha^{21}S2 \]

\[ \text{H}^{13}\text{C} \text{HMBC (CDCl}_{3}\text{)} \]

- A = H-C3 ↔ Piv
- B = H-C4 ↔ Piv
- C = H-C6 ↔ Piv
- D = H-C1 ↔ C1

\[ \text{A} = (5.17, 78.66), \quad \text{B} = (4.95, 176.35), \quad \text{C} = (3.86, 179.17), \quad \text{D} = (3.34, 87.81) \]

\[ \text{O} \quad \text{PivO} \quad \text{PivO} \quad \text{HO} \quad \text{O} \]

\[ \text{Q Piv} \]

\[ \text{Diagram showing molecular structure with HMBC peaks.} \]
$\alpha$-S22

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{1}\text{H NMR (500 MHz, CDCl}_3\text{)}$

$^{13}\text{C NMR (126 MHz, CDCl}_3\text{)}$
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
H NMR (500 MHz, CDCl₃)

\[
\begin{align*}
\alpha : \beta &= 72:28
\end{align*}
\]

C NMR (126 MHz, CDCl₃)

\[
\begin{align*}
\alpha : \beta &= 72:28
\end{align*}
\]
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
**S28**

**$^1$H NMR (500 MHz, CDCl$_3$)**

![NMR Spectrum](image)

**$^{13}$C NMR (126 MHz, CDCl$_3$)**

![NMR Spectrum](image)

α:β = 63:37
S29

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

\[ \alpha : \beta = 50:50 \]
$^1$H-$^{13}$C HMBC (CDCl$_3$)

A = $\beta$-H-C3 ↔ Piv
B = $\alpha$-H-C(3,4); $\beta$-H-C4 ↔ Piv
C = $\beta$-H-C6 ↔ Piv
D = $\alpha$-H-C8 ↔ Piv
E = H-C'1 ↔ C1
$\alpha$-S30

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

$\alpha, \beta = 34.66$