Supplementary Material

Studies in glycopeptide synthesis

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1H, 13C NMR spectra, Mass data, and HPLC profiles of compounds .................................................................S2
Synthesis of Auxiliary group

1. TrCl, pyridine, 50 °C, 2 days → 92%
2. KSAc, DMF, 40 °C, 16 h → 72%
3. NH₂NH₂·H₂O, MeOH, r.t., 1 h → 84%
4. HCOOH/EtOH, r.t., 30 min → 78%
5. Dess-Martin periodinane, Na₂CO₃, DCM, r.t., 5 min → 70%
$^1$HNMR
$^{13}$CNMR

![NMR Spectrum](image)

ESI-MS

- $[M+Na]^+$
  - Calcd. 403.2
  - Obsd. 403.3
- $[M+K]^+$
$^1$HNMR

![HNMR spectrum with peaks labeled a, b, and c.](image)
$^1$HNMR
$^1$HNMR

![NMR Spectrum Image]

Chemical shifts and peak assignments:
- Peak a
- Peak b
- Peak c
$^{13}$CNMR

![NMR spectrum with peaks labeled](image)

**ESI-MS**

- $[\text{M+Na}]^+$
  - Calcd. 419.2
  - Obsd. 419.3

- $[\text{M+K}]^+$

![Mass spectrum with peaks labeled](image)
$^1$HNMR

[Chemical structure image]

(a)  
(b)
Incorporation of Auxiliary Group to N-glycan
Incorporation of Auxiliary Group to N-glycan

HPLC

ESI-MS

Calcd. 2716.0
Obsd. 2715.8

yield 55%
HSQC NMR (700MHz)
Protection of sialic acids

10

adjusted to pH 4.0 by Cs$_2$CO$_3$
phenacyl bromide (6 eq)
DMF, r.t., 6 h

11

M. Murakami, et al., Angew. Chem. Int.Ed. 2012, 51, 3567-3572
Protection of sialic acids
Protection of sialic acids

HPLC

ABS. at 220 nm

Time/min

0 15

Calcd. 2951.1
Obsd. 2952.0

ESI-MS

Intensity

m/z

400 1800

yield 43%
Coupling Reaction

\[
\begin{align*}
\text{11} & \quad \text{PyBOP} & \quad \text{DIEA} \\
& \quad \text{DMF:DMSO} & \quad 1:1, \\
& \quad -20^\circ C
\end{align*}
\]
Coupling Reaction

HPLC (Crude)

ESI-MS

Calcd. 3209.2
Obsd. 3209.3

HPLC area yield. 52%
De-protection

Deprotection

Calcd. 2811.0
Obsd. 2810.9

TFA/TIPS = 95:5 in ice

ESI-MS

600 1200 1800

m/z

3+