Supporting Information

Synthesis of α-C-Glycosides by Samarium Diiodide-Mediated Coupling of Glycosyl Pyridyl Sulfones with Alkenes

Gen Li, De-Cai Xiong, Xin-Shan Ye*

State Key Laboratory of Natural and Biomimetic Drugs, Peking University, and School of Pharmaceutical Sciences, Peking University, Xue Yuan Rd No. 38,
Beijing 100191, China
xinshan@bjmu.edu.cn

Contents

Experimental ...........................................................................................................................................S-1

1H and 13C NMR spectra of compound 3.................................................................S-7

1H and 13C NMR spectra of compound 4.................................................................S-9

1H and 13C NMR spectra of compound 5.................................................................S-11

1H and 13C NMR spectra of compound 6.................................................................S-13

1H and 13C NMR spectra of compound 8.................................................................S-15

1H and 13C NMR spectra of compound 9.................................................................S-17

1H and 13C NMR spectra of compound 10.............................................................S-19

1H and 13C NMR spectra of compound 11.............................................................S-21

1H and 13C NMR spectra of compound 12.............................................................S-23

1H and 13C NMR spectra of compound 13.............................................................S-25

1H and 13C NMR spectra of compound 14.............................................................S-27

1H and 13C NMR spectra of compound 16.............................................................S-29
Experimental Section

All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. All reactions were carried out under argon unless otherwise indicated. THF was dried and freshly distilled over sodium potassium alloy. SmI$_2$ was prepared according to the literature. Glycosyl 2-pyridyl sulfones were prepared according to the literature. N-Phenylacrylamide and ethyl 2-acrylamidoacetate were prepared according to the literature. Analytical TLC was performed on silica gel 60-F$_{254}$ precoated on aluminium plates (E. Merck), with detection by fluorescence and/or by staining with acidic ceric ammonium molybdate. Column chromatography was performed employing silica gel 200-300 mesh. $^1$H-NMR spectra were recorded on a AVANCE III 400 spectrometer at 25 °C. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in deuterated chloroform. $^{13}$C NMR spectra were obtained by using the same NMR spectrometer and were calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). High-resolution mass spectrometry was performed on a LTQ Orbitrap Discovery or a Bruker APEX. SmI$_2$ solution was added by a LP215 syringe pump.

General Procedure. Samarium diiodide (0.10 M in THF with 1% NiI$_2$) was added by a syringe pump to a stirred solution of glycosyl 2-pyridyl sulfone (0.05 mmol), alkene (0.06 mmol) and i-ProOH (8 $\mu$L, 0.1 mmol) in THF (1.0 mL) under an argon atmosphere until a persistent dark blue color was obtained. The mixture was stirred at 20 °C for 10 min and then quenched by the addition of saturated aqueous NH$_4$Cl. The mixture was diluted with ethylacetate and the aqueous phase was extracted twice with ethyl acetate. The combined organic phases were dried (Na$_2$SO$_4$) and concentrated in vacuo. The residue was purified by column chromatography on silica gel to yield the product.

Methyl-3-(2, 3, 4, 6-tetra-O-benzyl-$\alpha$-D-glucopyranosyl)propanoate (2)

Compound 2 was prepared according to the General Procedure by the coupling of glucosyl 2-pyridyl sulfone and methyl acrylate. Flash column chromatography (EtOAc: petroleum ether, 1:10 to 1:8) gave the desired product as a colorless oil (26 mg, 84% yield). The spectroscopic data coincide with those reported in the literature.$^4$

$t$-Butyl-3-(2, 3, 4, 6-tetra-O-benzyl-$\alpha$-D-glucopyranosyl)propanoate (3)

Compound 3 was prepared according to the General Procedure by the coupling of glucosyl 2-pyridyl sulfone and $t$-Butyl acrylate. Flash column chromatography (EtOAc: petroleum ether, 1:10 to 1:8) gave the desired product as a colorless oil (26 mg, 80% yield).$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-7.11 (m, 20H, Ph), 4.92 (d, $J = 10.8$ Hz, 1H, CH$_2$-Ph), 4.80 (d, $J = 11.2$, 1H, CH$_2$-Ph), 4.78 (d, $J = 11.2$, 1H, CH$_2$-Ph), 4.66 (s, 2H, CH$_2$-Ph), 4.61 (d, $J = 12.0$ Hz, 1H, CH$_2$-Ph), 4.47 (d, $J = 12.0$ Hz, CH$_2$-Ph), 4.46 (d, $J = 10.8$ Hz, CH$_2$-Ph), 4.06 (dt, $J = 4.8$, 10.0 Hz, 1H, H1), 3.82-3.5 6 (m, 6H, H2, H3, H4, H5, H6), 2.35-

---

2.23 (m, 2H), 2.03-1.97 (m, 2H), 1.44 (s, 9H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 172.6, 138.8, 138.4, 138.3, 138.1, 128.4, 128.3, 127.84, 127.80, 127.8, 127.6, 127.57, 127.5, 82.4, 80.2, 80.0, 78.2, 75.4, 74.9, 73.5, 73.4, 72.9, 71.3, 69.2, 31.4, 28.2 (3C), 20.4. HRMS (ESI): calcd for C₄₁H₅₂O₇N [M+NH₄]+ 670.3738, found 670.3738.

3-(2, 3, 4, 6-Tetra-O-benzyl-α-D-glucopyranosyl) propionamide (4)

Compound 4 was prepared according to the General Procedure by the coupling of glucosyl 2-pyridyl sulfone and acrylamide. Flash column chromatography (EtOAc: petroleum ether, 1:6) gave the desired product as a colorless oil (25 mg, 80% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.31-7.25 (m, 18H, Ph), 7.15 (d, J = 2.0 Hz, 1H, Ph), 7.14 (d, J = 5.6 Hz, 1H, Ph), 5.58 (s, 1H, NH), 5.26 (s, 1H, NH), 4.90 (d, J = 11.2 Hz, CH₂-Ph), 4.81 (d, J = 10.8 Hz, 1H, CH₂-Ph), 4.77 (d, J = 10.8 Hz, 1H, CH₂-Ph), 4.66 (d, J = 11.6 Hz, 1H, CH₂-Ph), 4.63 (d, J = 11.6 Hz, 1H, CH₂-Ph), 4.56 (d, J = 12.0 Hz, 1H, CH₂-Ph), 4.46 (d, J = 12.0 Hz, 2H, CH₂-Ph), 4.10 (dt, J = 4.8, 5.6, 12.4 Hz, 1H, H1), 3.74 (dd, J = 5.6, 9.6 Hz, 1H, H2), 3.68-3.63 (m, 2H, H₅, H₆a), 3.56 (dd, J = 6.0, 10.0 Hz, 1H, H6b), 3.44 (t, J = 9.2 Hz, 1H, H4), 2.42 (t, J = 7.2 Hz, 2H, CH₂), 2.19-2.04 (m, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 170.9, 138.6, 138.1, 137.8, 128.8, 128.4, 128.4, 128.3, 128.3, 128.2, 127.8, 127.7, 127.6, 124.0, 119.8, 82.3, 79.9, 78.3, 75.5, 74.9, 73.5, 73.9, 72.4, 71.3, 69.6, 33.2, 21.4. HRMS (ESI): calcd for C₃₇H₄₂NO₆ [M+H]+ 596.3006, found 596.3006.

1-N-Phenyl-3-(2, 3, 4, 6-tetra-O-benzyl-α-D-glucopyranosyl) propionamide (5)

Compound 5 was prepared according to the General Procedure by the coupling of glucosyl 2-pyridyl sulfone and N-phenylacrylamide. Flash column chromatography (EtOAc: petroleum ether, 1:2) gave the desired product as a colorless oil (23 mg, 68% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.30-7.25 (m, 18H, Ph), 7.15 (d, J = 2.0 Hz, 1H, Ph), 7.14 (d, J = 5.6 Hz, 1H, Ph), 5.58 (s, 1H, NH), 5.26 (s, 1H, NH), 4.90 (d, J = 11.2 Hz, CH₂-Ph), 4.81 (d, J = 10.8 Hz, 1H, CH₂-Ph), 4.77 (d, J = 10.8 Hz, 1H, CH₂-Ph), 4.66 (d, J = 11.6 Hz, 1H, CH₂-Ph), 4.63 (d, J = 11.6 Hz, 1H, CH₂-Ph), 4.56 (d, J = 12.0 Hz, 1H, CH₂-Ph), 4.46 (d, J = 12.0 Hz, 2H, CH₂-Ph), 4.10 (dt, J = 4.8, 5.6, 12.4 Hz, 1H, H1), 3.74 (dd, J = 5.6, 9.6 Hz, 1H, H2), 3.68-3.63 (m, 2H, H₅, H₆a), 3.56 (dd, J = 6.0, 10.0 Hz, 1H, H6b), 3.44 (t, J = 9.2 Hz, 1H, H4), 2.42 (t, J = 7.2 Hz, 2H, CH₂), 2.19-2.04 (m, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 170.9, 138.6, 138.1, 137.8, 128.8, 128.4, 128.3, 128.3, 128.2, 127.8, 127.7, 127.6, 124.0, 119.8, 82.3, 79.9, 78.3, 75.5, 74.9, 73.5, 73.9, 72.4, 71.3, 69.6, 33.2, 21.4. HRMS (ESI): calcd for C₃₇H₄₂NO₆ [M+H]+ 596.3006, found 596.3006.
Compound 6 was prepared according to the General Procedure by the coupling of glucosyl 2-pyridyl sulfone and ethyl 2-acrylamidoacetate. Flash column chromatography (EtOAc: petroleum ether, 1:2) gave the desired product as a colorless oil (18 mg, 51% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32-7.26 (m, 18H, Ph), 7.15 (d, $J = 2.4$ Hz, 1H, Ph), 7.13 (d, $J = 5.2$ Hz, 1H, Ph), 6.12 (t, $J = 5.2$ Hz, 1H, NH), 4.90 (d, $J = 11.2$ Hz, 1H, CH$_2$-Ph), 4.80 (d, $J = 11.6$ Hz, 1H, CH$_2$-Ph), 4.76 (d, $J = 11.2$ Hz, 1H, CH$_2$-Ph), 4.65 (s, 2H, CH$_2$), 4.57 (d, $J = 12.0$ Hz, 1H, CH$_2$-Ph), 4.48 (d, $J = 12.0$ Hz, 1H, CH$_2$-Ph), 4.46 (d, $J = 10.8$ Hz, 1H, CH$_2$-Ph), 4.19 (q, $J = 7.2$ Hz, 2H, CH$_2$), 4.08 (dt, $J = 4.4$, 5.6, 10.0 Hz, 1H, H1), 3.96 (dd, $J = 5.2$, 19.6 Hz, 1H, CH$_2$), 3.90 (dd, $J = 5.2$, 19.6 Hz, 1H, CH$_2$), 3.79 (dd, $J = 8.4$, 9.2 Hz, 1H, H3), 3.75 (dd, $J = 5.6$, 9.2 Hz, 1H, H2), 2.62-2.59 (m, 3H, H5, H6), 3.51 (t, $J = 8.4$ Hz, 1H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 172.6, 169.9, 138.7, 138.2, 138.1, 138.0, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 82.3, 78.2, 75.4, 74.9, 73.5, 72.9, 72.7, 71.2, 69.4, 61.4, 41.3, 31.8, 21.0, 14.1. HRMS (ESI): calcd for C$_{41}$H$_{51}$N$_2$O$_8$ [M+NH$_4$]$^+$ 699.3639, found 699.3634.

3-(2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl)propanoic acid (7)

Compound 7 was prepared according to the General Procedure by the coupling of glucosyl 2-pyridyl sulfone and acrylic acid. Flash column chromatography (DCM: MeOH, 200:1) gave the desired product as a colorless oil (14 mg, 47% yield). The spectroscopic data coincide with those reported in the literature.$^5$

1-(2-(2, 3, 4, 6-tetra-O-benzyl-α-D-glucopyranosyl)ethylsulfonyl)benzene (8)

Compound 8 was prepared according to the General Procedure by the coupling of glucosyl 2-pyridyl sulfone and 1-(vinylsulfonyl)benzene. Flash column chromatography (EtOAc: petroleum ether, 1:3) gave the desired product as a colorless oil (22 mg, 62% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J = 7.6$ Hz, 2H, Ph), 7.63 (t, $J = 7.6$ Hz, 1H, Ph), 7.52 (t, $J = 7.8$ Hz, 2H, Ph), 7.29-7.23 (m, 17H, Ph), 7.13 (t, $J = 3.6$ Hz, 2H, Ph), 4.86 (d, $J = 11.2$ Hz, 1H, CH$_2$-Ph), 4.78 (d, $J = 10.8$ Hz, 1H, CH$_2$-Ph), 4.75 (d, $J = 10.8$ Hz, 1H, CH$_2$-Ph), 4.67 (d, $J = 11.6$ Hz, 1H, CH$_2$-Ph), 4.54 (d, $J = 10.4$ Hz, 2H, CH$_2$-Ph), 4.45 (d, $J = 12.0$ Hz, 2H, CH$_2$-Ph), 3.93 (m, 1H, H1), 3.72-3.67 (m, 2H, H2, H3), 3.63-3.57 (m, 2H, H6), 3.53-3.43 (m, 2H, H4, H5), 3.26-3.18 (m, 1H, CH$_3$), 3.08-3.00 (m, 1H, CH$_3$), 2.12 (dd, $J = 8.0$, 15.6 Hz, 2H, CH$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.3, 138.6, 138.1, 137.9, 133.6, 129.3, 129.2, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 82.0, 79.5, 77.8, 75.4, 74.9, 73.5, 73.4, 72.5, 71.5, 69.0, 52.7, 19.0. HRMS (ESI): calcd for C$_{42}$H$_{45}$O$_7$S [M+H]$^+$ 693.2880, found 693.2884.

Methyl 2-methyl-3-(2, 3, 4, 6-tetra-O-benzyl-α-D-glucopyranosyl)propanoate (9)

Compound 9 was prepared according to the General Procedure by the coupling of glucosyl 2-pyridyl sulfone and methyl methacrylate. Flash column chromatography (EtOAc: petroleum ether, 1:8 to 1:6) gave the desired product as a colorless oil (29 mg, 91% yield, dr = 3.2:1). Signals were assigned according to the major component indicated in the sequence. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.35-7.11 (m, 20H, Ph), 4.93 (d, \(J = 11.2\) Hz, 1H, CH\(_2\)-Ph), 4.81 (d, \(J = 10.8\) Hz, 1H, CH\(_2\)-Ph), 4.77 (d, \(J = 10.8\) Hz, 1H, CH\(_2\)-Ph), 4.63 (d, \(J = 11.2\) Hz, 1H, CH\(_2\)-Ph), 4.63 (d, \(J = 12.0\) Hz, 2H, CH\(_2\)-Ph), 4.47 (d, \(J = 12.0\) Hz, 1H, CH\(_2\)-Ph), 4.46 (d, \(J = 10.4\) Hz, 1H, CH\(_2\)-Ph), 4.17 (ddd, \(J = 2.8, 5.2, 12.0\) Hz, 1H, H1), 3.76-3.53 (m, 6H, H2, H3, H4, H5, H6), 3.66 (s, 3H, CH\(_3\)), 2.68 (m, 1H, CH), 2.12 (ddd, \(J = 2.8, 10.4, 14.8\) Hz, 1H, CH\(_2\)), 1.79 (ddd, \(J = 3.2, 12.0, 14.8\) Hz, 1H, CH\(_2\)), 1.21 (d, \(J = 7.2\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 176.6, 138.8, 138.2, 138.14, 138.07, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 82.2, 79.7, 78.0, 75.4, 75.1, 73.5, 72.7, 72.1, 71.4, 69.0, 51.6, 35.4, 28.4, 18.4. HRMS (ESI): calcd for C\(_{39}\)H\(_{45}\)O\(_7\) [M+H]+ 625.3159, found 625.3159.

Methyl 2-acetamido-3-(2, 3, 4, 6-tetra-O-benzyl-α-D-glucopyranosyl)propanoate (10)

Compound 10 was prepared according to the General Procedure by the coupling of glucosyl 2-pyridyl sulfone and methyl 2-acetamidoacrylate. Flash column chromatography (EtOAc: petroleum ether, 1:2) gave the desired product as a colorless oil (20 mg, 59% yield, dr = 1.3:1). Signals were assigned according to the major component indicated in the sequence. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.34-7.26 (m, 18H, Ph), 7.14 (t, \(J = 3.6\) Hz, 2H, Ph), 6.79 (d, \(J = 8.8, 1H, NH\)), 4.92 (m, 1H, CH), 4.87 (d, \(J = 11.2\) Hz, 1H, CH\(_2\)-Ph), 4.79 (d, \(J = 10.8\) Hz, 1H, CH\(_2\)-Ph), 4.76 (d, \(J = 10.8\) Hz, 1H, CH\(_2\)-Ph), 4.65 (d, \(J = 11.6\) Hz, 1H, CH\(_2\)-Ph), 4.67 (d, \(J = 11.6\) Hz, 1H, CH\(_2\)-Ph), 4.57 (m, 3H, CH\(_2\)-Ph), 4.44 (d, \(J = 11.2\) Hz, 1H, CH\(_2\)-Ph), 4.12 (m, 1H, H1), 3.75-3.53 (m, 5H, H2, H3, H4, H5, H6), 3.72 (s, 3H, CH\(_3\)), 3.33 (dd, \(J = 8.8, 9.2\) Hz, 1H), 2.26 (m, 2H, CH\(_2\)), 1.78 (s, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 172.2, 170.34, 138.45, 138.1, 137.8, 137.5, 128.5, 128.4, 128.0, 127.9, 127.7, 127.6, 82.2, 79.7, 75.4, 75.0, 52.3, 50.2, 26.0, 22.6. HRMS (ESI): calcd for C\(_{40}\)H\(_{46}\)NO\(_8\) [M+H]+ 668.3217, found 668.3218.

2-Methyl-3-(2, 3, 4, 6-tetra-O-benzyl-α-D-glucopyranosyl) propionamide (11)

Compound 11 was prepared according to the General Procedure by the coupling of glucosyl 2-pyridyl sulfone and methacrylamide. Flash column chromatography (EtOAc: petroleum ether, 1:6) gave the desired product as a colorless oil (21 mg, 68% yield, dr = 2.5:1). Signals were assigned according to the major component indicated in the sequence. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.31-7.25 (m, 18H, Ph), 7.17 (dd, \(J = 1.8, 2.4\) Hz, 1H), 5.90 (s, 1H, NH), 5.18 (s, 1H, NH), 4.92 (d, \(J = 10.8\) Hz, 1H, CH\(_2\)-Ph), 4.83 (d, \(J = 10.8\) Hz, 1H, CH\(_2\)-Ph), 4.83 (d, \(J = 10.8\) Hz, 1H, CH\(_2\)-Ph), 4.63 (d, \(J = 10.8\) Hz, 1H, CH\(_2\)-Ph), 4.62 (d, \(J = 11.6\) Hz, 1H, CH\(_2\)-Ph), 4.57 (d, \(J = 11.6\) Hz, 1H, CH\(_2\)-Ph), 4.47 (d, \(J = 11.6\) Hz, 1H, CH\(_2\)-Ph), 4.46 (d, \(J = 10.8\) Hz, 1H, CH\(_2\)-Ph), 4.14 (dt, \(J = 4.4, 6.0, 11.6\) Hz, 1H, H1), 3.79 (dd, \(J = 8.8, 9.2\) Hz, 1H, H3), 3.72 (dd, \(J = 6.0, 9.2\) Hz, 1H,
H2), 3.66-3.52 (m, 3H, H5, H6), 3.41 (t, J = 8.8 Hz, 1H, H4), 2.48 (m, 1H, CH), 1.88 (m, 2H, CH2), 1.15 (d, J = 6.8 Hz, 3H, CH3). 13C NMR (100 MHz, CDCl3): δ 178.0, 138.5, 138.0, 137.9, 137.7, 128.5, 128.4, 128.3, 128.3, 128.0, 127.9, 127.8, 127.8, 127.6, 82.1, 79.6, 78.3, 75.4, 75.0, 73.5, 72.8, 71.23, 70.9, 69.8, 35.4, 30.3, 18.2. HRMS (ESI): calcd for C38H44NO6 [M+H]+ 610.3163, found 610.3161.

Methyl 3-(2, 3, 4, 6-tetra-O-benzyl-α-D- galactopyranosyl)propanoate (12)

Compound 12 was prepared according to the General Procedure by the coupling of galactosyl 2-pyridyl sulfone and methyl acrylate. Flash column chromatography (EtOAc: petroleum ether, 1:8 to 1:6) gave the desired product as a colorless oil (23 mg, 74% yield). 1H NMR (400 MHz, CDCl3): δ 7.34-7.25 (m, 20H, Ph), 4.77 (d, J = 12.0 Hz, 1H, CH2-Ph), 4.70 (d, J = 12.0 Hz, 1H, CH2-Ph), 4.65 (d, J = 12.0 Hz, 1H, CH2-Ph), 4.64 (d, J = 12.0 Hz, 1H, CH2-Ph), 4.56 (d, J = 11.6 Hz, 1H, CH2-Ph), 4.54 (d, J = 11.6 Hz, 1H, CH2-Ph), 4.50 (d, J = 12.0 Hz, 1H, CH2-Ph), 4.44 (d, J = 12.0 Hz, 1H, CH2-Ph), 3.99-3.86 (m, 4H), 3.72-3.59 (m, 3H), 3.62 (s, 3H, OCH3), 2.47-2.27 (m, 2H), 2.03-1.92 (m, 2H). 13C NMR (100 MHz, CDCl3): δ 174.0, 138.6, 138.5, 138.3, 128.4, 128.3, 127.9, 127.8, 127.6, 82.1, 79.6, 78.3, 75.4, 75.0, 73.5, 72.8, 71.23, 70.9, 69.8, 35.4, 30.5, 22.2. HRMS (ESI): calcd for C38H43O7 [M+H]+ 611.3003, found 611.3019.

Methyl 3-(2, 3, 4, 6-tetra-O-benzyl-α-D- mannopyranosyl)propanoate (13)

Compound 13 was prepared according to the General Procedure by the coupling of mannosyl 2-pyridyl sulfone and methyl acrylate. Flash column chromatography (EtOAc: petroleum ether, 1:8 to 1:6) gave the desired product as a colorless oil (20 mg, 65% yield). 1H NMR (400 MHz, CDCl3): δ 7.35-7.17 (m, 20H, Ph), 4.67 (d, J = 11.2 Hz, 1H, CH2-Ph), 4.60 (d, J = 12.0 Hz, 1H, CH2-Ph), 4.57 (d, J = 12.4 Hz, 1H, CH2-Ph), 4.56 (d, J = 12.4 Hz, 1H, CH2-Ph), 4.53 (s, 2H, CH2-Ph), 4.52 (d, J = 12.0 Hz, 1H, CH2-Ph), 4.50 (d, J = 11.6 Hz, 1H, CH2-Ph), 3.97 (dt, J = 4.8, 5.2, 10.0 Hz, 1H, H1), 3.85 (dd, J = 6.4, 12.8 Hz, 1H, H6a), 3.81-3.73 (m, 3H, H3, H5, H6b), 3.69 (dd, J = 3.6, 9.6 Hz, 1H, H4), 3.64 (s, 2H, OCH3), 3.57 (dd, J = 2.8, 4.8 Hz, 1H, H2), 2.51-3.30 (m, 2H, CH2), 1.91-1.81 (m, 2H, CH2). 13C NMR (100 MHz, CDCl3): δ 173.8, 138.4, 138.3, 138.2, 128.4, 128.32, 128.28, 127.94, 127.87, 127.8, 127.7, 127.65, 127.62, 127.5, 76.1, 74.9, 73.6, 73.5, 73.3, 73.2, 73.0, 71.9, 71.3, 67.9, 51.4, 30.5, 22.2. HRMS (ESI): calcd for C38H43O7 [M+H]+ 611.3003, found 611.3019.

Methyl 3-(3-O-tert-butyldimethylsilyl-4, 6-O-benzylidene-2-deoxy-2-acetamido-α-D-glucopyranosyl) propanoate (14)
Compound 14 was prepared according to the General Procedure by the coupling of 2-acetamido-glucopyranosyl 2-pyridyl sulfone and methyl acrylate. Flash column chromatography (EtOAc: petroleum ether, 1:2) gave the desired product as a colorless oil (14 mg, 55% yield). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.47 (2d, \( J = 5.2 \) Hz, 2H, Ph), 7.37-7.35 (m, 3H, Ph), 5.50 (s, 1H, CH-Ph), 5.44 (d, \( J = 6.8 \) Hz, 1H, NH), 4.24 (dt, \( J = 3.6 \), 6.0, 9.2 Hz, 1H, H1), 4.22-4.17 (m, 2H, H2, H6a), 3.81 (dd, \( J = 8.4 \), 9.2 Hz, 1H, H3), 3.69 (s, 3H, OCH\(_3\)), 3.69 (dd, \( J = 9.6 \), 10.0 Hz, 1H, H6b), 3.54 (td, \( J = 4.8 \), 9.2, 9.6 Hz, 1H, H5), 3.50 (dd, \( J = 8.4 \), 9.2 Hz, 1H, H4), 2.46-2.41 (m, 1H, CH2), 2.36-2.32 (m, 1H, CH2), 2.06-2.00(m, 1H, CH2), 2.00 (s, 3H, COCH\(_3\)), 1.84-1.81 (m, 1H, CH2), 0.83 (s, 9H, t-Bu), 0.04 (s, 3H, CH3), -0.04 (s, 3H, CH3). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 173.7, 170.1, 137.1, 129.0, 128.1, 126.3, 102.0, 83.1, 74.2, 70.1, 69.3, 63.8, 51.8, 30.1, 25.7, 23.3, 20.9, 18.1, -3.9, -4.9. HRMS (ESI): calcd for C\(_{25}\)H\(_{40}\)NO\(_7\)Si [M+H]+ 494.2568, found 494.2568.

Methyl 3-(2, 3, 4, 6-tetra-O-acetyl-α-D-galactopyranosyl)propanoate (15)

To the solution of 12 (15 mg, 0.02 mmol) in MeOH (2.0 mL) was added Pd-C (10%, 5 mg), and the mixture was stirred under a H\(_2\) atmosphere for 8 h. The reaction was then filtered through Celite, the solvent was removed in vacuo. The crude product was dissolved in pyridine (2.0 mL) and Ac\(_2\)O (1.0 mL) and stirred for 8 h. The solution was evaporated to dryness in vacuo. The residue was purified by flash column chromatography on silica gel (EtOAc: petroleum ether, 1:2) to provide 15 (9 mg, 85% yield). The spectroscopic data coincide with those reported in the literature.\(^6\)

Methyl 3-(3, 4, 6-tri-O-acetyl-2-deoxy-2-acetamido-α-D-glucopyranosyl)propanoate (16)

To the solution of 14 (20.0 mg, 0.04 mmol) in MeOH (2.0 mL) was added CSA (7.5 mg, 0.03 mmol). The solution was stirred overnight. Triethylamine was added to the solution and the mixture was evaporated to dryness in vacuo. The residue was dissolved in pyridine (2.0 mL) and Ac\(_2\)O (1.0 mL) and stirred for 8 h. The solution was evaporated to dryness in vacuo. The residue was purified by flash column chromatography on silica gel (EtOAc: petroleum ether, 1:2) to provide 16 (13.0 mg, 80% yield). \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 5.88 (d, \( J = 8.4 \) Hz, 1H, NH), 5.04 (t, \( J = 7.6 \), 8.4 Hz, 1H, H3), 4.97 (t, \( J = 7.2 \), 7.2 Hz, 1H, H4), 4.32 (dd, \( J = 6.0 \), 12.0 Hz, 1H, H6a), 4.28 (td, \( J = 3.6 \), 8.0, 8.4 Hz, 1H, H2), 4.16 (dt, \( J = 3.6 \), 4.4, 11.6 Hz, 1H, H1), 4.08 (dd, \( J = 3.2 \), 12.0 Hz, 1H, H6b), 3.86 (m, 1H, H5), 3.69 (s, 3H), 2.44-2.39 (m, 2H), 2.10 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 1.98 (s, 3H), 2.05-1.82 (m, 1H), 1.81-1.79 (m, 1H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 173.4, 171.1, 170.6, 169.8, 169.0, 71.1, 70.3, 70.1, 67.8, 61.6, 51.8, 50.8, 29.8, 23.2, 22.1, 20.8, 20.7, 20.6. HRMS (ESI): calcd for C\(_{18}\)H\(_{28}\)NO\(_{10}\)Si[M+H]+ 418.1708, found 418.1719.

---
