Supporting Information

Convergent Synthesis of N-Linked Glycopeptide via Aminolysis of ω-Asp p-Nitrophenyl Thioesters in Solution

Jing-Jing Du,† Xiao-Fei Gao,‡ Ling-Ming Xin, Ze Lei, Zheng Liu*, and Jun Guo*

Key Laboratory of Pesticide & Chemical Biology of Ministry of Education, CCNU-\n\nOttawa Joint Research Centre, College of Chemistry, Central China Normal\nUniversity, 152 Luoyu Road, Wuhan, Hubei 430079, P.R. China

E-mail: jguo@mail.ccnu.edu.cn, liuz1118@mail.ccnu.edu.cn

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1. General Materials and Methods

**General:** 2-chlorotrityl chloride resin, protected amino acids and beznotriazole-1-yl-oxy-tris-pyrrolidino-phosphonium hexafluorophosphate (PyBOP), N-methylmorpholine (NMM), N,N-diisopropylethylamine (DIPEA), trifluoroacetic acid (TFA), triisopropylsilane (TIPS), acetic acid (AcOH), trifluoroethanol (TFE), 1-hydroxybenzotriazole (HOBt), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI), N,N-dicyclohexylcarbodiimide (DCC), diisopropylcarbodiimide (DIC), 4-dimethylaminopyridine (DMAP) and tris (2-carboxyethyl) phosphine hydrochloride (TCEP-HCl) were obtained from InnoChem Science & Technology Co., Ltd. N-methyl-2 pyrrolidone (NMP), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), DCM and THF were purchased from Aldrich and dried before use. The glycosylamines (1a, 1b)\(^1\) or sialyloligosaccharide (1c)\(^2\) were synthesized according to the reported procedure.

**NMR Spectrometry:** NMR spectra (\(^1\)H and \(^13\)C) were recorded on a Varian Mercury Plus 400 MHz or 600 MHz, referenced to TMS (tetramethylsilane).

**Mass Spectrometry:** electrospray ionization mass (ESI-MS) was performed on TSQ Quantum Access MAX (ThermoFisher Scientific).

**High Performance Liquid Chromatography (HPLC):** analytical reversed-phase HPLC was performed on an Agilent (1100 series HPLC system) instrument using an analytical column (Agilent 250 × 4.6 mm, 5 \(\mu\)m). Semi-preparative reversed-phase HPLC was performed on an Agilent (1100 series HPLC system) instrument using a semi-preparative column (Agilent 250 × 9.2 mm, 5 \(\mu\)m). Linear gradients of acetonitrile B (0.1% TFA) in water A (0.1% TFA) were used for all systems to elute peptides. The flow rates were 1.0 mL/min (analytical) and 4.0 mL/min (semi-preparative).
2. Optimal Reaction Conditions and generation of product 3

Table S1. Optimization of Reaction Conditions

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$^a$Reaction conditions: 1a (0.1 M), 2a (0.05 M), base, rt, 4 h. $^b$Yield determined by HPLC. PB = phosphate buffer (pH = 7.4, 200 mM). NMP = N-methyl-2-pyrrolidone. DMF = N, N-dimethylformamide. NMM = 4-methylmorpholine. TEA = trimethylamine.
**N-linked glycosylamino acid 3**

The glycosylamine (1a) (0.1 M) was dissolved in DMSO (0.5 mL) in a round bottom flask, added DIPEA (0.1 M), then, the purified p-nitrophenyl thioester (2a) (0.05 M) was added to the solution, the resulting mixture was stirred at room temperature for 4 h, the reaction process was monitored by HPLC. After the completion of the reaction, it was purified by semi-preparative HPLC to give N-linked glycosylamino acid 3 as a white solid (9.1 mg, 73%).

**Figure S1.** Analytical HPLC (35-90% B in A over 20 min, λ = 254 nm) profiles of the ligation reaction: (a) t = 0 h, (b) t = 3 h (asterisk is the hydrolyzed 2a segment, D is the p-nitrophenol), (c) purified product 3.
3. Synthesis of Oxoesters and Thioesters 2a-2i

**General procedure for synthesis of oxoesters and thioesters:** (a) Fmoc-Gly-OH (1.0 mmol) was dissolved in dry THF (5.0 mL) in a round bottom flask thoroughly flushed with the argon, added DCC (1.0 mmol), DMAP (0.25 mmol) to the solution at 0 °C. Then, phenols or thiophenols (1.0 mmol) was added. The resulting mixture was stirred at room temperature. The progress of the reaction was analyzed by TLC. After 2 h, it was cooled in ice bath and filtered under vacuum to remove dicyclohexyl urea. The filtrate was concentrated under vacuum and the residue was purified by flash chromatography to give the Fmoc-Gly-oxoester or Fmoc-Gly-thioester as a white solid; yield 75-84%.

(b) Thioaldehydes derived esters: (b) Fmoc-Gly-OH (1.0 mmol) was dissolved in dry THF (5.0 mL) in a round bottom flask thoroughly flushed with the argon, added DCC (1.0 mmol) to the solution at 0 °C. Then, 2, 2'-dithiodibenzaldehyde3 or 4, 4'-dithiodibenzaldehyde3,4 (0.5 mmol), TCEP-HCl (0.6 mmol), DIPEA (0.6 mmol) and 2 drops of water were added. The resulting reaction mixture was stirred at room temperature. The progress of the reaction was analyzed by TLC. After 0.5 h, it was cooled in ice bath and filtered under vacuum to remove dicyclohexyl urea. The filtrate was concentrated under...
vacuum and the residue was purified by flash chromatography to give the Fmoc-Gly-thio-benzaldehyde ester as a white solid; yield 72-81%.

\[ \text{p-nitrophenyl thioester 2a} \]

2a was prepared according to the general procedure (a) and purified by column chromatography (EtOAc/petroleum ether 1/3, v/v), to afford the desired product as a white solid (0.32 g, 75%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.28 - 8.22 (m, \(J = 9.2\) Hz, 2H), 7.77 (d, \(J = 7.5\) Hz, 2H), 7.62 (d, \(J = 7.5\) Hz, 2H), 7.59 - 7.56 (m, \(J = 9.2\) Hz, 2H), 7.40 (t, \(J = 7.5\) Hz, 2H), 7.32 (t, \(J = 7.1\) Hz, 2H), 5.50 (s, 1H), 4.51 (d, \(J = 6.7\) Hz, 2H), 4.30 - 4.18 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 194.4, 156.2, 148.3, 143.6, 141.3, 135.1, 135.0, 127.8, 127.1, 125.0, 124.0, 120.0, 67.4, 50.7, 47.1; HPLC: 35-90% B in A over 20 min, flow rate = 1.0 mL/min. Retention time (R\(_t\)) = 18.5 min; ESI-MS calcd for 2a \(\text{C}_{23}\text{H}_{18}\text{N}_{2}\text{O}_{5}\text{S} \ [\text{M + Na}]^+ m/z = 457.56\), \([\text{M + H}]^+ m/z = 435.56\), found: 457.60, 435.72.

\[ \text{benzaldehyde thioester 2b} \]

2b\(^5\) was prepared according to the general procedure (b) and purified by column chromatography (EtOAc/petroleum ether 1/3, v/v), to afford the desired product as a white solid (0.33 g, 81%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 10.17 (s, 1H), 8.05 (d, \(J = 7.4\) Hz, 1H), 7.76 (d, \(J = 7.4\) Hz, 2H), 7.63 - 7.57 (m, 4H), 7.48 (d, \(J = 7.4\) Hz, 1H), 7.40 - 7.37 (m, 2H), 7.32 - 7.28 (m, 2H), 5.70 (s, 1H), 4.50 (d, \(J = 6.4\) Hz, 2H), 4.33 - 4.17 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 195.9, 190.8, 156.5, 143.4, 141.0, 136.6, 136.4, 134.2, 130.2, 129.1, 127.5, 126.8, 124.8, 119.7, 67.1, 50.5, 47.0; HPLC:
35-90% B in A over 20 min, flow rate = 1.0 mL/min. Retention time (R<sub>t</sub>) = 17.6 min; ESI-MS calcd for \(\text{C}_{24}\text{H}_{19}\text{NO}_{4}\text{S}\) [M + Na]<sup>+</sup> m/z = 440.10, [M + H]<sup>+</sup> m/z = 418.10, found: 440.24, 418.28.

**p-hydroxybenzaldehyde thioester 2c**

![p-hydroxybenzaldehyde thioester 2c](image)

2c was prepared according to the general procedure (b) and purified by column chromatography (EtOAc/petroleum ether 1/3, v/v), to afford the desired product as a white solid (0.29 g, 72%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.99 (s, 1H), 7.92 (d, \(J = 8.3\) Hz, 2H), 7.77 (d, \(J = 7.4\) Hz, 2H), 7.60 (d, \(J = 7.4\) Hz, 2H), 7.40 (t, \(J = 7.8\) Hz, 2H), 7.33 - 7.29 (m, 4H), 5.48 (s, 1H), 4.45 (d, \(J = 6.4\) Hz, 2H), 4.29 - 4.23 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 195.2, 191.5, 156.4, 143.3, 141.0, 136.2, 134.6, 134.2, 129.8, 127.5, 126.9, 124.8, 119.8, 67.1, 50.5, 47.0; HPLC: 35-90% B in A over 20 min, flow rate = 1.0 mL/min. Retention time (R<sub>t</sub>) = 17.2 min; ESI-MS calcd for \(\text{C}_{24}\text{H}_{19}\text{NO}_{4}\text{S}\) [M + Na]<sup>+</sup> m/z = 440.20, [M + H]<sup>+</sup> m/z = 418.20, found: 440.31, 418.37.

**phenyl thioester 2d**

![phenyl thioester 2d](image)

2d<sup>5</sup> was prepared according to the general procedure (a) and purified by column chromatography (EtOAc/petroleum ether 1/3, v/v), to afford the desired product as a white solid (0.30 g, 78%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.79 (d, \(J = 7.5\) Hz, 2H), 7.64 (d, \(J = 7.5\) Hz, 2H), 7.46 - 7.39 (m, 7H), 7.35 - 7.32 (m, 2H), 5.57 (s, 1H), 4.49 (d, \(J = 7.5\) Hz, 2H), 4.30 - 4.26 (m, 1H), 4.22 (d, \(J = 5.9\) Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.2, 156.2, 143.7, 141.3, 134.7, 129.7, 129.4, 127.8, 127.1, 126.3, 125.1, 120.0, 67.3, 50.5, 47.1; HPLC: 35-90% B in A over 20 min, flow rate = 1.0
mL/min. Retention time (Rt) = 18.7 min; ESI-MS calcd for 2d C_{23}H_{19}NO_{3}S [M + Na]^+ m/z = 412.21, [M + H]^+ m/z = 390.21, found: 412.29, 390.32.

**benzyl thioester 2e**

![Benzyl thioester 2e](image)

2e was prepared according to the general procedure (a) and purified by column chromatography (EtOAc/petroleum ether 1/3, v/v), to afford the desired product as a white solid (0.33 g, 84%). ¹H NMR (600 MHz, CDCl₃) δ 7.76 (d, J = 7.3 Hz, 2H), 7.60 (d, J = 7.3 Hz, 2H), 7.41 - 7.37 (m, 2H), 7.32 - 7.27 (m, 7H), 5.36 (s, 1H), 4.46 (d, J = 6.7 Hz, 2H), 4.25 (t, J = 7.0 Hz, 1H), 4.18 - 4.14 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 197.0, 155.9, 143.3, 140.8, 136.5, 128.5, 128.3, 127.4, 127.1, 126.7, 124.7, 119.7, 66.9, 50.3, 46.9, 32.8; HPLC: 35-90% B in A over 20 min, flow rate = 1.0 mL/min. Retention time (Rt) = 19.2 min; ESI-MS calcd for 2e C_{24}H_{21}NO_{3}S [M + Na]^+ m/z = 426.22, [M + H]^+ m/z = 404.22, found: 426.36, 404.29.

**p-nitrophenyl oxoester 2f**

![p-nitrophenyl oxoester 2f](image)

2f was prepared according to the general procedure (a) and purified by column chromatography (EtOAc/petroleum ether 1/3, v/v), to afford the desired product as a white solid (0.34 g, 83%). ¹H NMR (600 MHz, CDCl₃) δ 8.24 (d, J = 9.2 Hz, 2H), 7.76 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.33 - 7.24 (m, 4H), 5.63 (s, 1H), 4.45 (d, J = 6.7 Hz, 2H), 4.31 - 4.14 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 156.5, 154.8, 145.4, 143.6, 141.3, 127.8, 127.1, 125.2, 125.0, 122.2, 120.0, 67.3, 47.0, 42.9; HPLC: 35-90% B in A over 20 min, flow rate = 1.0
mL/min. Retention time (R_t) = 17.5 min; ESI-MS calcd for 2f C_{23}H_{18}N_{2}O_{6} [M + Na]^+ m/z = 441.32, [M + H]^+ m/z = 419.32, found: 441.40, 419.31.

**salicylaldehyde oxoester 2g**

![Diagram](attachment:diagram.png)

2g was prepared according to the general procedure (a) and purified by column chromatography (EtOAc/petroleum ether 1/3, v/v), to afford the desired product as a white solid (0.30 g, 76%). ^1^H NMR (600 MHz, CDCl₃) δ 10.03 (s, 1H), 7.85 (d, J = 7.4 Hz, 1H), 7.76 (d, J = 7.4 Hz, 2H), 7.61 (d, J = 7.4 Hz, 3H), 7.42 - 7.37 (m, 3H), 7.32 - 7.28 (m, 2H), 7.20 (d, J = 8.3 Hz, 1H), 5.75 (s, 1H), 4.44 (d, J = 7.4 Hz, 2H), 4.36 (d, J = 5.5 Hz, 2H), 4.25 - 4.21 (m, 1H); ^13^C NMR (100 MHz, CDCl₃) δ 189.3, 168.9, 156.6, 143.8, 141.3, 135.5, 132.5, 127.8, 127.1, 126.9, 125.2, 123.5, 120.0, 67.3, 47.1, 43.0; HPLC: 35-90% B in A over 20 min, flow rate = 1.0 mL/min. Retention time (R_t) = 15.9 min; ESI-MS calcd for 2g C_{24}H_{19}NO_{5} [M + Na]^+ m/z = 424.23, [M + H]^+ m/z = 402.23, found: 424.30, 402.41.

**p-hydroxybenzaldehyde oxoester 2h**

![Diagram](attachment:diagram.png)

2h was prepared according to the general procedure (a) and purified by column chromatography (EtOAc/petroleum ether 1/3, v/v), to afford the desired product as a white solid (0.29 g, 75%). ^1^H NMR (600 MHz, CDCl₃) δ 9.99 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 7.4 Hz, 2H), 7.60 (d, J = 7.4 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.33 - 7.29 (m, 4H), 5.48 (s, 1H), 4.45 (d, J = 6.4 Hz, 2H), 4.31 - 4.22 (m, 3H); ^13^C NMR (100 MHz, CDCl₃) δ 190.9, 168.2, 156.4, 154.8, 143.7, 141.3, 134.3, 131.3, 127.8, 127.1, 125.0, 122.1, 120.1, 67.4, 47.1, 43.0; HPLC: 35-90% B in A over 20
min, flow rate = 1.0 mL/min. Retention time (R_t) = 14.9 min; ESI-MS calcd for 2h C_{24}H_{19}NO_{5} [M + Na]^+ m/z = 424.13, [M + H]^+ m/z = 402.13, found: 424.22, 402.26.

phenyl oxoester 2i

2i was prepared according to the general procedure (a) and purified by column chromatography (EtOAc/petroleum ether 1/3, v/v), to afford the desired product as a white solid (0.29 g, 81%). ^1H NMR (600 MHz, CDCl$_3$) δ 7.79 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.44 - 7.39 (m, 4H), 7.35 - 7.31 (m, 2H), 7.29 - 7.25 (m, 1H), 7.17 - 7.09 (m, J = 7.4 Hz, 2H), 5.48 (s, 1H), 4.46 (d, J = 7.4 Hz, 2H), 4.27 (m., 3H); ^13C NMR (100 MHz, CDCl$_3$) δ 168.8, 156.7, 150.0, 143.5, 141.0, 129.3, 127.5, 126.9, 125.9, 124.9, 121.1, 119.8, 67.1, 47.0, 42.7; HPLC: 35-90% B in A over 20 min, flow rate = 1.0 mL/min. Retention time (R_t) = 16.5 min; ESI-MS calcd for 2i C_{35}H_{53}N_{11}O_{13}S [M + Na]^+ m/z = 396.23, [M + H]^+ m/z = 374.23, found: 396.40, 374.28.

4. General procedure for Solid-Phase Peptide Synthesis (SPPS)

Preloading 2-chlorotrityl chloride resin: 2-chlorotrityl chloride resin (1.06 mmol/g) was swollen in dry DCM for 30 min then washed with DCM (3 × 3 mL) and DMF (3 × 3 mL). Followed by a solution of Fmoc-AA-OH (3.0 equiv) and DIPEA (6.0 equiv) in DMF (final concentration 0.1 M) was added to the resin bubbling with N$_2$ and shaken at room temperature for 10 h. The resin was washed with DMF (3 × 3 mL), DCM (3 × 3 mL) and DMF (3 × 3 mL) and subsequently submitted to iterative peptide assembly.
Manual solid-phase peptide synthesis: peptides were synthesized manually according to the general procedure for iterative peptide assembly. The general procedures are as follows:

**Deprotection:** the resin was treated with 20% piperidine/DMF (3 mL, 3 × 5 min), then washed with DMF (3 × 3 mL), DCM (3 × 3 mL) and DMF (3 × 3 mL).

**Amino acid coupling:** a solution of PyBOP (3.0 equiv), DIPEA (6.0 equiv) and Fmoc-AA-OH (3.0 equiv) in DMF (final concentration 0.1 M) were added to the resin bubbling with N\textsubscript{2} and shaken at room temperature for 2 h, the resin was washed with DMF (3 × 3 mL), DCM (3 × 3 mL) and DMF (3 × 3 mL).

**Cleavage:** a mixture of DCM, TFE and AcOH (3/1/1, v/v/v) were added to the resin. After 2 h, the resin was washed with DCM (3 × 3 mL).

**Work-up:** the combined solution was removed azeotropically with toluene under vaccum and the residue was precipitated with Et\textsubscript{2}O, the resulting solid was ready for purificaiton by semi-preparative HPLC and analysis by ESI-MS spectrometry.

5. Synthesis of \(\rho\)-Nitrophenyl Thioester of Peptides

![Chemical structure of p-Nitrophenyl Thioester of Peptides]

Reaction conditions: \(^a\)Pd(PPh\textsubscript{3})\textsubscript{4}, PhSiH\textsubscript{3}, DCM. \(^b\)DIC, DMAP, \(\rho\)-nitrophenol, DMF. \(^c\)DCM/TFE/AcOH (3/1/1, v/v/v).

**Removal of allylic group:** the allyl protected peptides were synthesized manually on 2-chlorotrityl chloride resin as the general procedure, followed by removal of allylic
group under neutral conditions with catalytic amounts of Pd(PPh\(_3\))\(_4\) (0.2 equiv) in the presence of PhSiH\(_3\) (10.0 equiv)\(^6\) were dissolved in dry DCM bubbling with N\(_2\) and shaken for 30 min. Next, the resin was washed with dry DCM and the process was repeated once. After 1 h, the resin was washed with DMF (3 × 3 mL), DCM (3 × 3 mL) and DMF (3 × 3 mL).

**Synthesis of p-nitrophenyl thioester peptides:** add a solution of DIC (5.0 equiv relative to resin loading) in dry DCM to the resin, dissolve DMAP (0.25 equiv relative to resin loading) in dry DCM to the resin, then, dissolve p-nitrothiophenol (3.0 equiv relative to resin loading) in dry DCM and dry DMF to the resin. After 5 h, the resin was washed with DMF (3 × 3 mL), DCM (3 × 3 mL) and DMF (3 × 3 mL).

**Cleavage:** a mixture of DCM, TFE and AcOH (3/1/1, v/v/v) was added to the resin. After 2 h, the resin was washed with DCM (3 × 3 mL). The resin was removed by filtration and the resulting solution was concentrated in vacuo and precipitated by Et\(_2\)O to get crude peptide. The crude peptide was analyzed by analytical HPLC and ESI-MS spectrometry.

![Figure S2](image)

**Figure S2.** Analytical HPLC of the crude product 4a: 35-90% B in A over 15 min, \(\lambda = 254\) nm. The total yield of 4a by SPPS is about 85%.
**Figure S3.** Analytical HPLC of the crude product 5a: 35-80% B in A over 15 min, $\lambda = 280$ nm. The total yield of 5a by SPPS is about 75%.

[Image: Figure S3 spectrum]

**Figure S4.** Analytical HPLC of the crude product 6a: 35-85% B in A over 15 min, $\lambda = 280$ nm. The total yield of 6a by SPPS is about 80%.

[Image: Figure S4 spectrum]

**Figure S5.** Analytical HPLC of the crude product 7a: 35-90% B in A over 20 min, $\lambda = 280$ nm (asterisk is the unreacted peptide with a free carboxyl group on the side chain). The total yield of 7a by SPPS is about 70%.

[Image: Figure S5 spectrum]

**Figure S6.** Analytical HPLC of the crude product 8a: 55-90% B in A over 15 min, $\lambda = 280$ nm (asterisk is the unreacted peptide with a free carboxyl group on the side chain). The total yield of 8a by SPPS is about 70%.

[Image: Figure S6 spectrum]

**Figure S7.** Analytical HPLC of the crude product 9a: 35-90% B in A over 20 min, $\lambda = 254$ nm. The total yield of 9a by SPPS is about 75%.

[Image: Figure S7 spectrum]
Figure S8. Analytical HPLC of the crude product 10a: 40-90% B in A over 20 min, λ = 280 nm. The total yield of 10a by SPPS is about 80%.

6. General Procedure for N-Linked Glycosylation

The glycosylamines (1a, 1b) (0.1 M) were dissolved in DMSO (0.5 mL) in a round bottom flask and added DIPEA (0.1 M), then, the purified p-nitrophenyl thioester peptides (4a-10a) (0.05 M) were added to the solution, the resulting mixture was stirred at room temperature for 4 h. However, for product 8d or 9d, the sialyloligosaccharide (1c, 2.7 mM) was dissolved in DMSO (0.25 mL), 4 Å MS (2.0 mg), the p-nitrophenyl thioester peptide (1.8 mM), DIPEA (3.6 mM), rt, 10 h, the reaction process was monitored by HPLC. After the completion of the reaction, it was purified by semi-preparative HPLC to give N-linked glycopeptide (4b-10b, 4c, 8c, 9c, 8d, 9d) as a white solid.
N-linked glycopeptide 4b was prepared following the general procedure of N-linked glycosylation, the reaction process was monitored by HPLC.

**Figure S9.** Analytical HPLC (35-82% B in A over 15 min, $\lambda = 254$ nm) profiles of the ligation reaction: (a) $t = 0$ h, (b) $t = 3$ h (D is the $p$-nitrophenol), (c) $t = 4$ h, (d) purified product 4b (the hydrolyzed 4a segment was not detected during the reaction).

N-linked glycopeptide 4c was prepared following the general procedure of N-linked glycosylation, the reaction process was monitored by HPLC.

**Figure S10.** Analytical HPLC (35-80% B in A over 15 min, $\lambda = 254$ nm) profiles of the ligation reaction: (a) $t = 0$ h, (b) $t = 3$ h (D is the $p$-nitrophenol), (c) $t = 4$ h, (d) purified product 4c (the hydrolyzed 4a segment was not detected during the reaction).
*N*-linked glycopeptide 5b was prepared following the general procedure of *N*-linked glycosylation, the reaction process was monitored by HPLC.

**Figure S11.** Analytical HPLC (35-80% B in A over 15 min, λ = 280 nm) profiles of the ligation reaction: (a) t = 0 h, (b) t = 3 h (c) t = 4 h, (d) purified product 5b (the hydrolyzed 5a segment was not detected during the reaction).

*N*-linked glycopeptide 6b was prepared following the general procedure of *N*-linked glycosylation, the reaction process was monitored by HPLC.

**Figure S12.** Analytical HPLC (35-90% B in A over 20 min, λ = 280 nm) profiles of the ligation reaction: (a) t = 0 h, (b) t = 3 h (D is the p-nitrophenol), (c) t = 4 h, (d) purified product 6b (asterisk is the hydrolyzed 6a segment, D is the p-nitrophenol).
*N*-linked glycopeptide 7b was prepared following the general procedure of *N*-linked glycosylation, the reaction process was monitored by HPLC.

**Figure S13.** Analytical HPLC (35-93% B in A over 20 min, \( \lambda = 280 \) nm) profiles of the ligation reaction: (a) \( t = 0 \) h, (b) \( t = 3 \) h (D is the p-nitrophenol), (c) \( t = 4 \) h, (d) purified product 7b (the hydrolyzed 7a segment was not detected during the reaction).

*N*-linked glycopeptide 8b was prepared following the general procedure of *N*-linked glycosylation, the reaction process was monitored by HPLC.

**Figure S14.** Analytical HPLC (50-90% B in A over 20 min, \( \lambda = 254 \) nm) profiles of the ligation reaction: (a) \( t = 0 \) h, (b) \( t = 3 \) h (D is the p-nitrophenol), (c) \( t = 4 \) h, (d) purified product 8b (the hydrolyzed 8a segment was not detected during the reaction).
$N$-linked glycopeptide 8c was prepared following the general procedure of $N$-linked glycosylation, the reaction process was monitored by HPLC.

**Figure S15.** Analytical HPLC (50-90% B in A over 20 min, $\lambda = 254$ nm) profiles of the ligation reaction: (a) $t = 0$ h, (b) $t = 3$ h (D is the $p$-nitrophenol), (c) $t = 4$ h, (d) purified product 8c (the hydrolyzed 8a segment was not detected during the reaction).

$N$-linked glycopeptide 8d was prepared following the general procedure of $N$-linked glycosylation, the reaction process was monitored by HPLC.

**Figure S16.** Analytical HPLC (35-90% B in A over 20 min, $\lambda = 254$ nm) profiles of the ligation reaction: (a) $t = 0$ h, (b) $t = 5$ h (D is the $p$-nitrophenol), (c) $t = 10$ h, (d) purified product 8d (the hydrolyzed 8a segment was not detected during the reaction).
N-linked glycopeptide 9b was prepared following the general procedure of N-linked glycosylation, the reaction process was monitored by HPLC.

Figure S17. Analytical HPLC (35-75% B in A over 15 min, λ = 254 nm) profiles of the ligation reaction: (a) t = 0 h, (b) t = 3 h (D is the p-nitrophenol), (c) t = 4 h, (d) purified product 9b (the hydrolyzed 9a segment was not detected during the reaction).

N-linked glycopeptide 9c was prepared following the general procedure of N-linked glycosylation, the reaction process was monitored by HPLC.

Figure S18. Analytical HPLC (35-75% B in A over 15 min, λ = 254 nm) profiles of the ligation reaction: (a) t = 0 h, (b) t = 3 h (D is the p-nitrophenol), (c) t = 4 h, (d) purified product 9c (the hydrolyzed 9a segment was not detected during the reaction).
N-linked glycopeptide 9d was prepared following the general procedure of N-linked glycosylation, the reaction process was monitored by HPLC.

![Figure S19](image)

**Figure S19.** Analytical HPLC (5-90% B in A over 20 min, λ = 254 nm) profiles of the ligation reaction: (a) t = 0 h, (b) t = 5 h (D is the p-nitrophenol), (c) t = 10 h, (d) purified product 9d (the hydrolyzed 9a segment was not detected during the reaction).

N-linked glycopeptide 10b was prepared following the general procedure of N-linked glycosylation, the reaction process was monitored by HPLC.

![Figure S20](image)

**Figure S20.** Analytical HPLC (35-80% B in A over 15 min, λ = 254 nm) profiles of the ligation reaction: (a) t = 0 h, (b) t = 3 h (c) t = 4 h, (d) purified product 10b (the hydrolyzed 10a segment was not detected during the reaction).
7. **N-Linked Glycopeptide’s Ligation/Desulfurization**

*N-linked glycopeptide 6b₁*: the side-chain protected *N*-linked glycopeptide 6b (33.5 mg, 20.0 μmol) was treated with a mixture of TFA, TIPS and water (95/2.5/2.5, v/v/v), stirred at room temperature for 2 h. The majority of the solvents were removed under vacuum and the remaining residue was purified by semi-preparative HPLC and analyzed by ESI-MS spectrometry (21.6 mg, 91%).

*N-linked glycopeptide 7b₁*: the crude *N*-linked glycopeptide 7b (30.0 mg, 24.2 μmol) was dissolved in dried DMF (0.5 mL), EDCI (23.0 mg, 0.12 mmol), HOBt (16.0 mg, 0.12 mmol) and benzyl mercaptan (BnSH) (28.0 μL, 0.24 mmol) were added, the reaction mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo, the residue was purified by flash chromatography (MeOH/DCM 1/15, v/v) to give the side-chain protected thioester *N*-glycopeptide (26.9 mg, 83%). Then, the side-chain protected thioester *N*-glycopeptide was treated with a mixture of TFA, TIPS and water (95/2.5/2.5, v/v/v), stirred at room temperature for 2 h. The majority of the solvents were removed under vacuum and the remaining residue was purified by semi-preparative HPLC and analyzed by ESI-MS spectrometry (24.2 mg, 92%).

**Peptide 11**: ligation conditions: 6b₁ (1.0 mM), 7b₁ (2.0 mM), TCEP-HCl (20.0 equiv), Gn·HCl (6.0 M), sodium 2-mercaptoethanesulfonate (MESNa) (10.0 equiv), PB (phosphate buffer, pH = 7.4, 200 mM) 2.0 mL, stirred at room temperature for 5 h. The majority of the solvents were removed under vacuum and the remaining residue was purified by semi-preparative HPLC and analyzed by ESI-MS spectrometry (3.5 mg, 83%) (see Figure S21).
Figure S21. HPLC profiles of the ligation reaction: (a) $t = 0$ h, (b) $t = 3$ h, (c) purified ligation product 11. Analytical HPLC: 5-90% B in A over 20 min, $\lambda = 254$ nm. ESI-MS calcd for $\text{6b}_1$ C$_{33}$H$_{60}$N$_{12}$O$_{17}$S [M + K]$^+$ m/z = 1229.56, [M + H]$^+$ m/z = 1191.56, found: 1229.69, 1191.73. ESI-MS calcd for $\text{7b}_1$ C$_{48}$H$_{60}$N$_{9}$O$_{16}$S$_2$ [M + Na]$^+$ m/z = 1114.63, [M + H]$^+$ m/z = 1092.63, found: 1114.73, 1092.74. ESI-MS calcd for $\text{11}$ C$_{94}$H$_{143}$N$_{21}$O$_{33}$S$_2$ [M + H + 2 K]$^{3+}$ m/z = 745.38, [M + H + K]$^{2+}$ m/z = 1099.38, found: 745.61, 1099.03.

Desulfurization of peptide 11: to a solution of purified peptide 11 (1.0 mM) in PB (phosphate buffer, pH = 7.4, 200 mM) 2.0 mL, Gn-HCl (200 mM), 3,3',3''-phosphinidynetris(benzenesulfonic acid) trisodium salt (TPPTS) (50.0 mM), Ru(bpy)$_3$Cl$_2$ (5 mol %) and tert-butyl mercaptan (TBM) (80 mM) were added, the resulting solution was degased with an argon balloon for 15 min and sealed. The reaction solution was stirred and irradiated with 36 W household bulb for 5 h, then, it was purified by semi-preparative HPLC and analyzed by ESI-MS spectrometry (3.0 mg, 72%) (see Figure S22).
Figure S22. HPLC profiles of the desulfurization reaction: (a) $t = 0$ h, (b) $t = 3$ h, (c) purified desulfurization product 12. Analytical HPLC: 5-90% B in A over 20 min, $\lambda = 254$ nm, ESI-MS calcd for 12 $C_{92}H_{143}N_{21}O_{23}S$ $[M + H + 2 K]^{3+}$ m/z = 735.11, $[M + H + K]^{2+}$ m/z = 1083.16, found: 735.06, 1083.20.
8. HPLC and ESI-MS Spectra of Peptides

**Figure S23.** Analytical HPLC (left) and ESI-MS (right) analysis of the purified 4a. Analytical HPLC: 35-80% B in A over 15 min, λ = 254 nm, ESI-MS calcd for 4a C_{76}H_{104}N_{10}O_{18}S_{2} [M + Na]^+ m/z = 1531.80, [M + H]^+ m/z = 1509.80, found: 1531.81, 1509.95.
Figure S24. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 4b (31.0 mg, 81%). Analytical HPLC: 35-80% B in A over 15 min, \( \lambda = 254 \) nm, ESI-MS calcd for \( 4b \) C\(_{78}H_{115}N_{11}O_{21}S \) [M + Na]\(^+\) m/z = 1597.47, [M + H]\(^+\) m/z = 1575.47, found: 1597.22, 1575.68.
Figure S25. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 4c (33.8 mg, 77%). Analytical HPLC: 35-70% B in A over 15 min, $\lambda = 254$ nm, ESI-MS calcd for 4c C$_{36}$H$_{128}$N$_{12}$O$_{36}$S [M + Na]$^+$ m/z = 1800.38, [M + H]$^+$ m/z = 1778.38, found: 1800.45, 1778.38.
Figure S26. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 5a. Analytical HPLC: 35-90% B in A over 20 min, \( \lambda = 280 \text{ nm} \), ESI-MS calcd for 5a \( \text{C}_{62}\text{H}_{92}\text{N}_{10}\text{O}_{19}\text{S} \) \([\text{M} + \text{Na}]^+\) m/z = 1335.63, \([\text{M} + \text{H}]^+\) m/z = 1313.63, found: 1335.83, 1313.70.
Figure S27. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 5b (26.8 mg, 79%). Analytical HPLC: 35-80% B in A over 15 min, λ = 280 nm, ESI-MS calcd for 5b C_{64}H_{103}N_{11}O_{22} [M + K]^+ m/z = 1417.26 [M + Na]^+ m/z = 1401.26, [M + H]^+ m/z = 1379.26, found: 1417.10, 1401.15, 1379.11.
Figure S28. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 6a. Analytical HPLC: 35-95% B in A over 15 min, λ = 280 nm, ESI-MS calcd for 6a C_{83}H_{105}N_{11}O_{18}S_{2} [M + K]^+ m/z = 1647.21, [M + H]^+ m/z = 1609.21, found: 1647.32, 1609.02.
Figure S29. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 6b (30 mg, 72%). Analytical HPLC: 35-90% B in A over 20 min, λ = 280 nm, ESI-MS calcd for 6b \( \text{C}_{85}\text{H}_{110}\text{N}_{12}\text{O}_{21}\text{S} \) \([\text{M + Na}]+ m/z = 1696.36, [\text{M + H}]+ m/z = 1674.36, \) found: 1696.44, 1674.18.
Figure S30. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 7a. Analytical HPLC: 35-90% B in A over 20 min, $\lambda$ = 280 nm, ESI-MS calcd for 7a C$_{55}$H$_{89}$N$_{10}$O$_{16}$S$_{2}$ $[M + K]^+$ m/z = 1211.51, $[M + H]^+$ m/z = 1173.51, found: 1211.81, 1173.13.
**Figure S31.** Analytical HPLC (left) and ESI-MS (right) analysis of the purified 7b (23.8 mg, 78%). Analytical HPLC: 35-90% B in A over 20 min, $\lambda = 280$ nm, ESI-MS calcd for $7b \, C_{57}H_{91}N_9O_{19}S \, [M + Na]^+ \, m/z = 1260.82, [M + H]^+ \, m/z = 1238.82$, found: 1260.90, 1238.89.
Figure S32. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 8a. Analytical HPLC: 50-90% B in A over 20 min, $\lambda = 280$ nm, ESI-MS calcd for $8a$ $C_{75}H_{91}N_{11}O_{18}S$ [M + Na]$^+$ m/z = 1489.85, [M + H]$^+$ m/z = 1467.85, found: 1489.92, 1467.91.
Figure S33. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 8b (28.8 mg, 76%). Analytical HPLC: 35-85% B in A over 15 min, λ = 280 nm, ESI-MS caleed for 8b C_{77}H_{102}N_{12}O_{21} [M + Na]^+ m/z = 1554.50, [M + H]^+ m/z = 1532.50, found: 1554.06, 1532.77.
Figure S34. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 8c (31.3 mg, 73%). Analytical HPLC: 35-70% B in A over 15 min, \( \lambda = 280 \) nm, ESI-MS calcd for 8c \( C_{85}H_{115}N_{13}O_{26} \) [M + Na]\(^+\) m/z = 1757.49, [M + H]\(^+\) m/z = 1735.49, found: 1757.55, 1735.42.
Figure S35. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 8d (0.9 mg, 62%). Analytical HPLC: 35-90% B in A over 20 min, λ = 254 nm, ESI-MS calcd for 8d C_{38}H_{57}N_{15}O_{15} [M + 4 H]^{4+} m/z = 884.63, [M + 3 H]^{3+} m/z = 1179.17, [M + 2 H]^{2+} m/z = 1768.26, found: 884.75, 1179.15, 1768.43.
Figure S36. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 9a. Analytical HPLC: 35-85% B in A over 15 min, $\lambda = 254$ nm, ESI-MS calcd for 9a $C_{78}H_{105}N_{11}O_{10}S$ [M + Na]$^+$ m/z = 1555.30, [M + H]$^+$ m/z = 1533.30, found: 1555.35, 1533.11.
Figure S37. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 9b (29.6 mg, 74%). Analytical HPLC: 35-75% B in A over 15 min, λ = 254 nm, ESI-MS calcd for 9b C₈₀H₁₁₆N₁₂O₂₂ [M + Na]⁺ m/z = 1620.34, [M + H]⁺ m/z = 1598.34, found: 1620.25, 1598.35.
Figure S38. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 9c (31.9 mg, 71%). Analytical HPLC: 35-70% B in A over 15 min, $\lambda = 254$ nm, ESI-MS calcd for 9c $C_{88}H_{129}N_{13}O_{27}$ [M + Na]$^+$ m/z = 1823.50, [M + H]$^+$ m/z = 1801.50, found: 1823.48, 1801.74.
Figure S39. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 9d (1.0 mg, 67%). Analytical HPLC: 5-90% B in A over 20 min, $\lambda = 254$ nm, ESI-MS calcd for 9d $C_{38}H_{57}N_7O_{15}$ $[M + 3 H]^+ m/z = 1200.51$, $[M + 2 H + Na]^{3+} m/z = 1207.84$, $[M + 2 H]^2+ m/z = 1800.27$, found: 1200.39, 1207.26, 1800.25.
Figure S40. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 10a. Analytical HPLC: 35-90% B in A over 20 min, $\lambda = 280$ nm, ESI-MS calcd for 10a $C_{36}H_{46}N_6O_{12}S$ [M + Na]$^+$ m/z = 809.29, [M + H]$^+$ m/z = 787.29, found: 809.21, 787.24.
Figure S41. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 10b (18.0 mg, 86%). Analytical HPLC: 35-50% B in A over 15 min, λ = 280 nm, ESI-MS calcd for 10b C_{38}H_{57}N_{15}O_{15} [M + Na]^+ m/z = 874.39, [M + H]^+ m/z = 852.39, found: 874.48, 852.51.
Figure S42. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 11 (3.5 mg, 83%). Analytical HPLC: 5-90% B in A over 20 min, $\lambda = 254$ nm, ESI-MS calcd for 11 $C_{93}H_{143}N_{23}O_{33}S_{2}$ $[M + H + 2 K]^{3+} m/z = 745.38$, $[M + H + K]^{2+} m/z = 1099.38$, found: 745.61, 1099.03.
Figure S43. Analytical HPLC (left) and ESI-MS (right) analysis of the purified 12 (3.0 mg, 72%). Analytical HPLC: 5-90% B in A over 20 min, $\lambda = 254$ nm, ESI-MS calcd for $12\text{C}_{94}\text{H}_{143}\text{N}_{23}\text{O}_{33}\text{S}$ [M + H + 2 K]$^{3+}$ m/z = 735.11, [M + H + K]$^{2+}$ m/z = 1083.16, found: 735.06, 1083.20.
9. **1H NMR and 13C NMR Spectra**

Conversion of free sugar N-acetyl-D-glucosamine into their corresponding glycosylamine 1a by using methanolic ammonia and ammonium bicarbonate.

**Figure S44.** Glycosylamine 1a, 1H NMR (400 MHz, D₂O) δ 4.18 (d, J = 9.2 Hz, 1H), 3.92 (d, J = 12.1 Hz, 1H), 3.74 (dd, J = 12.2, 4.3 Hz, 1H), 3.64 (t, J = 9.6 Hz, 1H), 3.59-3.50 (m, 1H), 3.45 (d, J = 5.6 Hz, 2H), 3.38 (s, 2H). (only the signal of H1 from β anomer (δ = 4.14, J = 9.2 Hz) was detected, and no that of H1 from α anomer was observed in the region of 4-5.5 ppm), which of that were consistent with the reported works (SI ref. 7: *J. Am. Chem. Soc.* 2010, 132, 3211-3216; *Org. Lett.* 2013, 15, 732-735).
Figure S45. N-linked glycosylamino acid 3. $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.01 (d, $J = 8.7$ Hz, 1H), 7.89 (d, $J = 7.9$ Hz, 3H), 7.71 (dd, $J = 16.2, 7.6$ Hz, 2H), 7.57 (t, $J = 6.3$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 2H), 5.03 (dd, $J = 22.0, 4.8$ Hz, 2H), 4.74 (t, $J = 9.2$ Hz, 1H), 4.27 (d, $J = 4.6$ Hz, 2H), 3.64 (dd, $J = 11.8, 5.3$ Hz, 1H), 3.58 (d, $J = 5.7$ Hz, 1H), 3.36 - 3.30 (m, 2H), 3.10 (s, 2H), 1.81 (s, 3H) (only the signal of H1 from β anomer ($δ = 4.74$, $J = 9.2$ Hz) was detected, and no that of H1 from α anomer was observed in the region of 4-5.5 ppm), which of that were consistent with the reported works.\(^7\)
Figure S46. N-linked glycopeptide 4b as a model of glycosylation reaction, $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.58 (d, $J = 8.0$ Hz, 1H), 8.38 (d, $J = 7.9$ Hz, 1H), 8.19 - 8.08 (m, 2H), 7.83 (d, $J = 8.9$ Hz, 1H), 7.75(d, $J = 8.6$ Hz, 1H), 7.47 (s, 1H), 7.31 - 7.23 (m, 15H), 6.84 (s, 1H), 4.97 (s, 2H), 4.76 (t, $J = 9.2$ Hz, 1H), 4.59 - 4.45(m, 2H), 4.32 (q, $J = 7.2$ Hz, 2H), 4.25 - 3.83 (m, 8H), 3.77 (s, 1H), 3.60 (d, $J = 11.8$ Hz, 2H), 3.06 (s, 2H), 2.34 (s, 5H), 2.16 (s, 1H), 1.85 (s, 1H), 1.73 (s, 3H), 1.48 (d, $J = 6.9$ Hz, 5H), 1.34 (t, $J = 5.8$ Hz, 26H), 1.22 - 1.17(m, 5H), 1.09 (d, $J = 6.8$ Hz, 3H), 0.86 - 0.77 (m, 14H), 0.69 (d, $J = 6.3$ Hz, 6H) (only the signal of H1 from $\beta$ anomer ($\delta = 4.76$, $J = 9.2$ Hz) was detected, and no that of H1 from $\alpha$ anomer was observed in the region of 4-5.5 ppm), which of that were consistent with the reported works. $^7$
$^1$H NMR and $^{13}$C NMR Spectra of 2a, 2c, 2e, 2f, 2h
10. Reference


