Highly Faciallyselective Synthesis of Pyranose 1,3-Oxazines and Their Ring-opening with Nucleophiles: A Novel Entry to 2-C-Branched Glycosides

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General experimental details

All reactions were performed under a nitrogen atmosphere. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. IR spectra were recorded with FT-IR as a thin film or using KBr pellets and were expressed in cm^{-1} . ^1H (400 or 600 MHz) and ^{13}C (100 or 150 MHz) NMR spectra were recorded using CDCl_3 as a solvent, and the ratio of the compounds were determined by ^1H NMR. Chemical shifts were reported in ppm downfield to tetramethylsilane. Coupling constants were reported and expressed in Hz; splitting patterns were designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), dt (double triplet). Optical rotations were measured using polarimeter at 20 or 25 °C. Analytical thin layer chromatography (TLC) was performed over silica gel (100-200 Mesh) using petroleum ether and ethyl acetate as eluent. Mass spectra were obtained from high resolution ESI mass spectrometer. X-ray crystallographic data was collected by using a Bruker X8Apex diffractometer with Mo K α radiation (graphite monochromator).

General procedure for the addition of 7 to enol ether 1:

To the mixture of *N*-acyl, *N*, *O*-acetal **7** (1 equiv), enol ethers **1** (1 equiv) in anhydrous dichloromethane (10 ml) under nitrogen was added at -78 °C TMSOTf (1 equiv). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with dichloromethane. The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel to provide desired **8**.

Characterization of the 8

The synthesis of 8aa

(4*S*, 6*S*, 7*S*, 4*aS*, 8*aR*)- Acetic acid 7-acetoxymethyl-2,4-diphenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*] [1,3]oxazin-6-yl ester (8aa)

To the mixture of 4,6-di-*O*-acetyl-3-deoxyglucal (**1a**, 107 mg, 0.5 mmol), *N*-(methoxy-phenyl-methyl)-benzamide (**7a**, 120.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to provide desired **8aa** (173 mg, 82%) as colorless oil. $[\alpha]_D^{20} = -12.1$ (*c* 1.25 g/mL, CH₃COCH₃); IR (neat) ν : 2948, 1740, 1653, 1367, 1235, 1124, 1032, 917, 703 cm⁻¹; ¹H NMR (400MHz, CDCl₃) δ 8.15–8.13 (m, 2H), 7.50–7.35 (m, 7H), 7.29–7.26 (m, 1H), 5.85 (d, *J* = 3.2 Hz, 1H), 5.05 (d, *J* = 4.4 Hz, 1H), 4.83–4.76 (m, 1H), 4.33 (dd, *J* = 12.4 Hz, 4.4 Hz, 1H), 4.19 (dd, *J* = 12.4 Hz, 2.0 Hz, 1H), 4.04–4.00 (m, 1H), 2.56–2.49 (m, 1H), 2.11 (s, 3H), 1.92 (s, 3H), 1.45–1.40 (m, 1H), 1.32–1.28 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 169.6, 154.9, 140.0, 132.4, 131.1, 128.5, 128.2, 127.4, 127.1, 126.8, 95.7, 70.1, 66.2, 62.3, 58.2, 36.2, 23.6, 20.9, 20.8; HRMS (ESI) *m/z* calcd for C₂₄H₂₆NO₆ [*M* + *H*]⁺ 424.1760, Found: 424.1578.

The synthesis of **8ad**

(4*S*, 6*S*, 7*S*, 4*aS*, 8*aR*)-Acetic acid 7-acetoxymethyl-4-(4-chloro-phenyl)-2-phenyl-4*a*,6,7,8*a*-tetrahydro-4*H*, 5*H*-pyrano[3,2-*e*][1,3]oxazin-6-yl ester (**8ad**)

To the mixture of 4,6-di-*O*-acetyl-3-deoxyglucal (**1a**, 107 mg, 0.5 mmol), *N*-[(4-chloro-phenyl)-methoxy-methyl]-benzamide (**7d**, 137.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to provide desired **8ad** (193 mg, 85%) as colorless oil. $[\alpha]_{\text{D}}^{20} = -12.8$ (*c* 0.87 g/mL, CH₃COCH₃); IR (neat) ν : 2944, 1739, 1655, 1367, 1235, 1099, 1027, 917, 696 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 6.4 Hz, 2H), 7.51-7.43 (m, 3H), 7.35 (m, 4H), 5.83 (d, *J* = 2.8 Hz, 1H), 5.02 (d, *J* = 4.4 Hz, 1H), 4.79 (dt, *J* = 10.8 Hz, 4.8 Hz, 1H), 4.33 (dd, *J* = 12.0 Hz, 4.4 Hz, 1H), 4.18 (d, *J* = 12.0 Hz, 1H), 4.02 (d, *J* = 10.0 Hz, 1H), 2.52–2.48 (m, 1H), 2.11 (s, 3H), 1.93 (s, 3H), 1.43–1.40 (m, 1H), 1.28–1.22 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 169.6, 155.1, 138.6, 132.9, 132.2, 131.2, 128.7, 128.3, 127.1, 127.4, 95.5, 70.1, 66.1, 62.2, 57.6, 36.0, 23.5, 20.9, 20.8; HRMS (ESI) *m/z* calcd for C₂₄H₂₅ClNO₆ [M + H]⁺ 458.1370, Found: 458.1371.

The synthesis of **8ae**

(4*S*, 6*S*, 7*S*, 4*aS*, 8*aR*)-Acetic acid 7-acetoxymethyl-4-(4-nitro-phenyl)-2-phenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H* -pyrano[3,2-*e*][1,3]oxazin-6-yl ester (**8ae**)

To the mixture of 4,6-di-*O*-acetyl-3-deoxyglucal (**1a**, 107 mg, 0.5 mmol), *N*-[(4-nitro-phenyl)-methoxy-methyl]-benzamide (**7e**, 143 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to provide desired **8ae** (122 mg, 52%) as a white solid. mp 202.5-204.5 °C; $[\alpha]_{\text{D}}^{25} = -18.5$ (*c* 0.27 g/mL, CH₃COCH₃); IR (KBr) ν : 2944, 1733, 1652, 1519, 1355, 1234, 1109, 1030, 917, 704 cm⁻¹, ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.4 Hz, 2H), 8.14 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.56-7.45 (m, 3H), 5.88 (d, *J* = 2.4 Hz, 1H), 5.15 (d, *J* = 4.4 Hz, 1H), 4.78 (dt, *J* = 10.8 Hz, 5.2 Hz, 1H), 4.33 (dd, *J* = 12.4 Hz, 4.4 Hz, 1H), 4.20 (d, *J* = 12.4 Hz, 1H), 4.04 (d, *J* = 10.0 Hz, 1H), 2.61–2.57 (m, 1H), 2.12 (s, 3H), 1.93 (s, 3H), 1.38-1.22 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 169.6, 155.6, 147.7, 147.2, 132.0, 131.5, 128.4, 127.7, 127.4, 123.8, 95.4, 70.1, 65.9, 62.1, 57.9, 35.7, 23.5, 20.8, 20.8; HRMS (ESI) *m/z* calcd for C₂₄H₂₅N₂O₈ [M + H]⁺ 469.1611, Found: 469.1607.

The synthesis of **8ag**

(4*S*, 6*S*, 7*S*, 4a*S*, 8a*R*)-Acetic acid 7-acetoxymethyl-4-naphthalen-1-yl-2-phenyl-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*][1,3]oxazin-6-yl ester (**8ag**)

To the mixture of 4,6-di-*O*-acetyl-3-deoxyglucal (**1a**, 107 mg, 0.5 mmol), *N*-(methoxy-naphthalen-1-yl-methyl)-benzamide (**7g**, 145.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to provide desired **8ae** (196 mg, 83%) as a colorless oil. $[\alpha]_{\text{D}}^{25} = -103.6$ (c 0.45 g/mL, CH₃COCH₃); IR (neat) ν : 2959, 1740, 1658, 1366, 1226, 1116, 1028, 913, 696 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 7.2 Hz, 2H), 7.92-7.89 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 6.8 Hz, 1H), 7.58-7.45 (m, 6H), 6.00 (d, *J* = 2.4 Hz, 1H), 5.79 (d, *J* = 4.4 Hz, 1H), 4.70 (dt, *J* = 11.2 Hz, 4.8 Hz, 1H), 4.32 (dd, *J* = 12.0 Hz, 4.4 Hz, 1H), 4.18-4.11 (m, 1H), 4.05-4.02 (m, 1H), 2.79-2.75 (m, 1H), 2.08 (s, 3H), 1.88 (s, 3H), 1.38-1.32 (m, 1H), 1.18-1.15 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 169.5, 155.2, 135.2, 133.9, 132.5, 131.1, 130.1, 129.3, 128.3, 127.9, 127.5, 126.3, 125.6, 125.5, 121.9, 95.6, 70.1, 66.1, 62.2, 55.2, 32.6, 24.1, 20.8, 20.8; HRMS (ESI) *m/z* calcd for C₂₈H₂₈NO₆ [M + H]⁺ 474.1917, Found: 474.1910.

The synthesis of **8ah**

(4*S*, 6*S*, 7*S*, 4*aS*, 8*aR*)-Acetic acid 7-acetoxymethyl-2-oxo-4-phenyl-hexahydro-pyrano[3,2-*e*][1,3]oxazin -6-yl ester (**8ah**)

To the mixture of 4,6-di-*O*-acetyl-3-deoxyglucal (**1a**, 107 mg, 0.5 mmol), methoxy-phenyl-methyl)-carbamic acid tert-butyl ester (**7h**, 118.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 1:1) to provide desired **8ah** as a colorless oil (143 mg, 79%). $[\alpha]_D^{25} = +0.9$ (c 0.34 g/mL, CH₃COCH₃); IR (neat) ν : 3340, 2945, 1738, 1620, 1351, 1230, 1110, 1045, 920, 704 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.23 (m, 5H), 6.51–6.39 (m, 1H), 5.76 (s, 1H), 4.87 (d, $J = 3.6$ Hz, 1H), 4.74 (dt, $J = 10.8$ Hz, 4.4 Hz, 1H), 4.33 (dd, $J = 12.0$ Hz, 4.0 Hz, 1H), 4.11–4.08 (m, 1H), 2.39–2.35 (m, 1H), 2.05 (s, 3H), 1.99 (s, 3H), 1.64–1.45 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 169.7, 153.3, 153.3, 135.9, 129.1, 128.7, 126.0, 96.7, 70.2, 65.8, 62.0, 54.1, 36.7, 23.0, 20.9, 20.7; HRMS (ESI) m/z calcd for C₁₈H₂₂NO₇ [M + H]⁺ 364.1396, Found: 364.1388.

The synthesis of **8am**

(4*S*, 6*S*, 7*S*, 4*aS*, 8*aR*)- Acetic acid 7-acetoxymethyl-4-(3-nitro-phenyl)-2-phenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*][1,3]oxazin-6-yl ester (**8am**)

To the mixture of 4,6-di-*O*-acetyl-3-deoxyglucal (**1a**, 107 mg, 0.5 mmol), *N*-[methoxy-(3-nitro-phenyl)-methyl]-benzamide (**7m**, 143 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8ah** as a white solid (115 mg, 49%). mp 172.5-174.5 °C; $[\alpha]_D^{25} = -15.64$ (c 0.18 g/mL, CH₃COCH₃); IR (neat) ν : 3335, 2937, 1734, 1635, 1334, 1134, 1027, 908, 715 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 1H), 8.18-8.14 (m, 3H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.59–7.46 (m, 5H), 5.88 (d, *J* = 2.0 Hz, 1H), 5.15 (d, *J* = 4.0 Hz, 1H), 4.82–4.75 (m, 1H), 4.33 (dd, *J* = 12.4 Hz, 4.4 Hz, 1H), 4.20 (d, *J* = 12.4 Hz, 1H), 4.04 (d, *J* = 10.0 Hz, 1H), 2.61–2.57 (m, 1H), 2.12 (s, 3H), 1.93 (s, 3H), 1.40–1.24 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 169.6, 155.8, 148.6, 142.5, 132.9, 131.9, 131.5, 129.5, 128.4, 127.5, 122.4, 122.0, 94.4, 70.1, 65.9, 62.1, 57.7, 35.7, 23.4, 20.8; HRMS (ESI) *m/z* calcd for C₂₄H₂₅N₂O₈ [M + H]⁺ 469.1611, Found: 469.1628.

The synthesis of 8ba

(4*S*, 6*R*, 7*S*, 4*aS*, 8*aR*)-Acetic acid 7-acetoxymethyl-2,4-diphenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*] [1,3]oxazin-6-yl ester (**8ba**)

To the mixture of 4,6-di-*O*-acetyl-3-deoxygalactal (**1b**, 107 mg, 0.5 mmol), *N*-(methoxy-phenyl-methyl)-benzamide (**7a**, 143 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8ba** as a colorless oil (169 mg, 80%). [α]_D²⁵ = - 89.7 (c 0.60 g/mL, CH₃COCH₃); IR (neat) ν : 2960, 1739, 1656, 1440, 1366, 1223, 1114, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 7.2 Hz, 2H), 7.49–7.25 (m, 8H), 5.93 (s, 1H), 5.03–4.98 (m, 2H), 4.23–4.13 (m, 3H), 2.63 (d, *J* = 13.2 Hz, 1H), 2.07 (s, 3H), 2.04 (s, 3H), 1.49 (t, *J* = 14.0 Hz, 1H), 1.25 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 167.0, 155.0, 140.2, 132.4, 131.1, 128.5, 128.2, 127.4, 127.0, 126.7, 96.2, 68.5, 65.5, 62.7, 58.2, 31.2, 22.4, 21.0, 20.8; HRMS (ESI) *m/z* calcd for C₂₄H₂₆NO₆ [M + H]⁺ 424.1760, Found: 424.1754.

The synthesis of **8bg**

(4*S*, 6*R*, 7*S*, 4*aS*, 8*aR*)- Acetic acid 6-acetoxy-4-naphthalen-1-yl-2-phenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*] [1,3]oxazin-7-ylmethyl ester (**8bg**)

To the mixture of 4,6-di-*O*-acetyl-3-deoxygalactal (**1b**, 107 mg, 0.5 mmol), *N*-(methoxy-naphthalen-1-yl-methyl)-benzamide (**7g**, 145.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8bg** as a colorless oil (208 mg, 88%). $[\alpha]_{\text{D}}^{25} = -98.5$ (c 0.72 g/mL, CH₃COCH₃); IR (neat) ν : 2948, 1735, 1630, 1429, 1357, 1218, 1107, 705 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 7.6 Hz, 2H), 7.97 (s, 1H), 7.88–7.84 (m, 3H), 7.55–7.44 (m, 6H), 5.90 (d, *J* = 2.4 Hz, 1H), 5.22 (d, *J* = 4.0 Hz, 1H), 4.80 (dt, *J* = 10.8 Hz, 4.8 Hz, 1H), 4.33 (dd, *J* = 12.0 Hz, 4.4 Hz, 1H), 4.19 (d, *J* = 12.4 Hz, 1H), 4.04 (d, *J* = 10.0 Hz, 1H), 2.67–2.63 (m, 1H), 2.11 (s, 3H), 1.87 (s, 3H), 1.38–1.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 169.5, 155.0, 137.5, 133.4, 132.7, 132.5, 131.2, 128.3, 28.0, 127.7, 127.5, 126.1, 125.7, 125.7, 124.7, 95.7, 70.2, 66.1, 62.3, 58.2, 36.1, 23.7, 20.8; HRMS (ESI) *m/z* calcd for C₂₈H₂₈NO₆ [M + H]⁺ 474.1917, Found: 474.1924.

The synthesis of **8bl**

(4*S*, 6*R*, 7*S*, 4*aS*, 8*aR*)- Acetic acid 6-acetoxy-2-phenyl-4-*p*-tolyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*] [1,3]oxazin -7-ylmethyl ester (**8bl**)

To the mixture of 4,6-di-*O*-acetyl-3-deoxygalactal (**1b**, 107 mg, 0.5 mmol), *N*-(methoxy-*p*-tolyl-methyl)-benzamide (**7l**, 127.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8bl** as a colorless oil (194 mg, 89%). $[\alpha]_{\text{D}}^{25} = -161.4$ (c 0.74 g/mL, CH₂Cl₂); IR (neat) ν : 2933, 1738, 1658, 1441, 1366, 1217, 1113, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 7.2 Hz, 2H), 7.50–7.41 (m, 3H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 5.91 (d, *J* = 4.0 Hz, 1H), 4.98 (m, 2H), 4.23–4.10 (m, 3H), 2.61–2.56 (m, 1H), 2.35 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.47 (dt, *J* = 15.6 Hz, 2.8 Hz, 1H), 1.29 (dt, *J* = 14.8 Hz, 3.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 170.0, 154.9, 137.1, 136.5, 132.5, 131.0, 129.2, 128.2, 127.4, 126.6, 96.2, 68.6, 65.6, 62.8, 58.1, 31.3, 22.4, 21.1, 21.0, 20.8; HRMS (ESI) *m/z* calcd for C₂₅H₂₈NO₆ [M + H]⁺ 438.1917, Found: 474.1935.

The synthesis of **8da**

(4*S*, 5*R*, 6*S*, 7*S*, 4*aS*, 8*aR*)-5,6- Dimethoxy-7-methoxymethyl-2,4-diphenyl -4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*][1,3]oxazine (**8da**)

To the mixture of 3,4,6-tri-*O*-methyl-D-glucal (**1d**, 94 mg, 0.5 mmol), *N*-(methoxy-phenyl-methyl)-benzamide (**7a**, 120.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to provide desired **8da** as a colorless oil (149 mg, 75%). $[\alpha]_{\text{D}}^{25} = +33.3$ (c, 0.62 g/mL, CH₃COCH₃); IR (neat) ν : 2933, 1658, 1441, 1366, 1217, 1113, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.49-7.21 (m, 5H), 7.25-7.21 (m, 1H), 5.91 (s, 1H), 5.04 (s, 1H), 3.78 (d, *J* = 10.0 Hz, 1H), 3.65 (s, 2H), 3.45 (s, 3H), 3.41 (s, 3H), 3.30 (t, *J* = 9.6 Hz, 1H), 3.19 (t, *J* = 9.6 Hz, 1H), 2.75 (s, 3H), 2.69-2.66 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 155.3, 126.2, 97.5, 80.9, 78.3, 72.0, 70.7, 60.4, 59.7, 58.2, 57.2, 43.3; HRMS (ESI) *m/z* calcd for C₂₃H₂₈NO₅ [M + H]⁺ 398.1967, Found: 398.1966.

The synthesis of 8fa

(4*S*, 5*R*, 6*S*, 7*S*, 4*aS*, 8*aR*)- 5,6-Bis-allyloxy-7-allyloxymethyl-2,4-diphenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*][1,3]oxazine (8fa)

To the mixture of 3,4,6-tri-*O*-2-propenyl-D-glucal (**1f**, 133 mg, 0.5 mmol), *N*-(methoxy-phenyl-methyl)-benzamide (**7a**, 120.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8fa** as a colorless syrup (150 mg, 63%). $[\alpha]_D^{25} = +46.7$ (c, 0.59 g/mL, CH₃COCH₃); IR (neat) ν : 2914, 1720, 1651, 1437, 1366, 1205, 1124, 687 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 7.2 Hz, 1.2H), 8.07 (d, *J* = 8.0 Hz, 0.8H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.51–7.32 (m, 6H), 7.26–7.21 (m, 1H), 5.99–5.76 (m, 3H), 5.34–5.02 (m, 6H), 4.84–4.71 (m, 2H), 4.15–4.01 (m, 3H), 3.97–3.70 (m, 6H), 3.58–3.52 (m, 1H), 3.42–3.35 (m, 1H), 3.23 (dd, *J* = 10.8 Hz, 4.0 Hz, 1H), 2.82–2.77 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 155.3, 141.8, 140.4, 134.8, 134.6, 134.5, 133.9, 133.8, 132.0, 131.0, 130.4, 128.7, 128.2, 128.0, 127.9, 127.5, 127.4, 127.2, 127.0, 126.6, 126.2, 126.0, 117.4, 117.3, 117.0, 116.8, 116.6, 97.8, 84.8, 78.8, 77.5, 77.2, 76.9, 76.8, 76.2, 73.8, 73.6, 72.5, 72.3, 72.2, 70.5, 68.3, 57.1, 43.1, 29.7; HRMS (ESI) *m/z* calcd for C₂₉H₃₄NO₅ [M + H]⁺ 476.2437, Found: 476.2451.

The synthesis of **8ia**

(4*S*, 5*R*, 6*S*, 7*S*, 4*aS*, 8*aR*)- Acetic acid 5,6-bis-allyloxy-2,4-diphenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*] [1,3] oxazin-7-yl-methyl ester (**8ia**)

To the mixture of 3,4-di-*O*-(2-propenyl)-6-*O*-acetyl-D-glucal (**1i**, 134 mg, 0.5 mmol), *N*-(methoxy-phenyl-methyl)-benzamide (**7a**, 120.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8ia** as a colorless syrup (188 mg, 79%). $[\alpha]_D^{25} = +7.8$ (c, 1.0 g/mL, CH₂Cl₂); IR (neat) ν : 2921, 1735, 1647, 1445, 1339, 1211, 1108, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 7.6 Hz, 1.34H), 8.07 (d, *J* = 7.6 Hz, 1.34H), 7.69 (d, *J* = 7.6 Hz, 1.34H), 7.51–7.22 (m, 6.66 H), 5.91–5.73 (m, 2H), 5.19–4.72 (m, 6H), 4.42 (dd, *J* = 11.6 Hz, 1.6 Hz, 1H), 4.28 (dd, *J* = 12.4 Hz, 4.0 Hz, 1H), 4.13 (dd, *J* = 12.0 Hz, 5.6 Hz, 1H), 3.98 – 3.94 (m, 2H), 3.77 (dd, *J* = 10.0 Hz, 5.2 Hz, 1H), 3.46–3.37 (m, 2H), 3.23 (dd, *J* = 10.0 Hz, 2.4 Hz, 1H), 2.86–2.78 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 155.5, 140.6, 134.1, 133.9, 133.8, 132.1, 131.3, 131.0, 130.8, 128.3, 128.2, 128.1, 127.4, 127.3, 120.1, 120.0, 117.5, 116.9, 97.4, 94.8, 78.8, 75.9, 74.0, 73.4, 70.9, 70.8, 62.6, 56.6, 42.9, 21.0; HRMS (ESI) *m/z* calcd for C₂₈H₃₂NO₆ [M + H]⁺ 478.2230, Found: 476.2217.

The synthesis of **9ie**

(4*S*, 5*R*, 6*S*, 7*S*, 4*aS*, 8*aR*)- Acetic acid 3,4-bis-allyloxy-5-[benzoylamino -(4-nitro-phenyl)-methyl]-6-methoxy- tetrahydro-pyran-2-ylmethyl ester (**9ie**)

To the mixture of 3,4-di-*O*-(2-propenyl)-6-*O*-acetyl-D-glucal (**1i**, 134 mg, 0.5 mmol), *N*-[methoxy-(4-nitro-phenyl)-methyl]-benzamide (**7e**, 143 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to provide desired **9ie** as a colorless syrup (166 mg, 60%). $[\alpha]_{\text{D}}^{25} = +35.3$ (c, 0.27 g/mL, CH₂Cl₂); IR (neat) ν : 2931, 1738, 1657, 1435, 1347, 1206, 1114, 703 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H) 7.56 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.63 (d, *J* = 9.6 Hz, 1H), 6.05 (d, *J* = 10.0 Hz, 1H), 6.03–5.95 (m, 1H), 5.92–5.83 (m, 1H), 5.78 (dt, *J* = 10.4 Hz, 2.0 Hz, 1H), 5.38 (dd, *J* = 13.2 Hz, 1.2 Hz, 1H), 5.30–5.18 (m, 3H), 4.88 (d, *J* = 2.4 Hz, 1H), 4.36–4.23 (m, 4H), 4.12 (dd, *J* = 12.8 Hz, 5.6 Hz, 1H), 4.00–3.92 (m, 3H), 3.46 (s, 0.33H), 3.43 (s, 2.67H), 2.11 (s, 2.67H), 2.09 (s, 0.33H); ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 169.3, 147.9, 146.6, 134.3, 133.6, 133.1, 132.4, 130.4, 128.8, 127.1, 126.5, 123.8, 118.0, 117.7, 95.5, 79.0, 77.3, 70.1, 69.9, 69.7, 67.7, 63.7, 55.8, 29.7, 21.0; HRMS (ESI) *m/z* calcd for C₂₉H₃₅N₂O₆ [M + H]⁺ 555.2343, Found: 555.2359.

The synthesis of **8ig**

(4*S*, 5*R*, 6*S*, 7*S*, 4*aS*, 8*aR*)-Acetic acid 5,6-bis-allyloxy-4-naphthalen-1-yl-2-phenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*][1,3]oxazin-7-ylmethyl ester (**8ig**)

To the mixture of 3,4-di-*O*-(2-propenyl)-6-*O*-acetyl-D-glucal (**1i**, 134 mg, 0.5 mmol), *N*-(methoxy-naphthalen-1-yl-methyl)-benzamide (**7g**, 145.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8ig** as a colorless syrup (182 mg, 69%). $[\alpha]_D^{25} = -156.3^\circ$ (c, 0.38 g/mL, CH₂Cl₂); IR (neat) ν : 2927, 1736, 1649, 1422, 1356, 1214, 1108, 708 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.23–8.18 (m, 2H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.78–7.75 (m, 1H), 7.55–7.45 (m, 6H), 6.11 (d, *J* = 4.2 Hz, 0.09H), 6.05 (d, *J* = 4.2 Hz, 0.91H), 5.76–5.68 (m, 1H), 5.68 (d, *J* = 3.6 Hz, 1H), 5.11 (dd, *J* = 1.8 Hz, 17.4 Hz, 1H), 5.05 (dd, *J* = 16.8 Hz, 1.8 Hz, 1H), 4.59–4.51 (m, 2H), 4.48–4.42 (m, 2H), 4.26 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 4.01–3.97 (m, 2H), 3.88 (dd, *J* = 12.0 Hz, 5.4 Hz, 1H), 3.75 (dd, *J* = 11.4 Hz, 6.6 Hz, 1H), 3.43–3.36 (m, 2H), 3.23 (dd, *J* = 12.0 Hz, 2.4 Hz, 1H), 3.07 (dt, *J* = 10.2 Hz, 4.2 Hz, 1H), 2.12 (s, 2.7H), 1.90 (s, 0.3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 155.4, 137.6, 134.2, 134.0, 133.7, 132.4, 131.2, 130.7, 129.2, 128.3, 127.6, 127.5, 126.1, 125.6, 125.2, 124.3, 122.4, 117.3, 115.7, 97.1, 79.3, 75.4, 73.7, 72.5, 70.6, 62.6, 55.0, 42.6, 21.0; HRMS (ESI) *m/z* calcd for C₃₂H₃₄NO₆ [M + H]⁺ 528.2386, Found: 528.2374.

The synthesis of **8il**

(4*S*, 5*R*, 6*S*, 7*S*, 4*aS*, 8*aR*)- Acetic acid 5,6-bis-allyloxy-2-phenyl-4-*p*-tolyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano [3,2-*e*][1,3]oxazin-7-ylmethyl ester (**8il**)

To the mixture of 3,4-di-*O*-(2-propenyl)-6-*O*-acetyl-D-glucal (**1i**, 134 mg, 0.5 mmol), *N*-(methoxy-*p*-tolyl-methyl)-benzamide (**7l**, 127.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8il** as a colorless syrup (179 mg, 73%). $[\alpha]_D^{25} = +72.3$ (c, 0.21 g/mL, CH₂Cl₂); IR (neat) ν : 2918, 1739, 1642, 1437, 1348, 1226, 1117, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 7.2 Hz, 1.4H), 8.06 (d, *J* = 7.2 Hz, 0.6H), 7.58–7.33 (m, 5H), 7.17 (d, *J* = 7.6 Hz, 2H), 5.89 (d, *J* = 3.6 Hz, 1H), 5.83–5.74 (m, 1H), 5.19–4.70 (m, 6H), 4.41 (dd, *J* = 12.0 Hz, 2.0 Hz, 1H), 4.28 (dd, *J* = 12.4 Hz, 4.0 Hz, 1H), 4.14 (dd, *J* = 12.0 Hz, 6.0 Hz, 1H), 3.99–3.93 (m, 2H), 3.77 (dd, *J* = 12.4 Hz, 6.4 Hz, 1H), 3.45–3.35 (m, 2H), 3.22 (dd, *J* = 10.4 Hz, 4.4 Hz, 1H), 2.83–2.75 (m, 1H), 2.35 (s, 3H), 2.16 (s, 0.9H), 2.14 (s, 2.1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 155.1, 138.5, 135.7, 134.3, 134.2, 134.1, 132.3, 131.1, 128.9, 128.2, 128.0, 127.4, 127.3, 126.4, 117.7, 117.3, 116.7, 97.5, 95.0, 78.8, 76.1, 73.9, 73.6, 70.9, 70.7, 62.7, 56.8, 43.1, 30.9, 21.2, 21.0, 20.9, 20.8; HRMS (ESI) *m/z* calcd for C₂₉H₃₄NO₆ [M + H]⁺ 492.2386, Found: 492.2391.

The synthesis of **8ja**

(4*S*, 5*R*, 6*S*, 7*S*, 4*aS*, 8*aR*)-Acetic acid 5,6-bis-allyloxy-2,4-diphenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*] [1,3]oxazin-7-ylmethyl ester (**8ja**):

To the mixture of 3,4-di-*O*-(2-propenyl)-6-*O*-acetyl-D-galactal (**1j**, 134 mg, 0.5 mmol), *N*-(methoxy-phenyl-methyl)-benzamide (**7a**, 120.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8ja** as a colorless syrup (188 mg, 79%). $[\alpha]_{\text{D}}^{25} = +0.8$ (c, 1.0 g/mL, CH₂Cl₂); IR (neat) ν : 2922, 1735, 1639, 1431, 1335, 1237, 1124, 704 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.52–7.44 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.02 (d, *J* = 3.6 Hz, 1H), 5.90–5.80 (m, 1H), 5.17 (d, *J* = 18.0 Hz, 1H), 5.13 (d, *J* = 11.2 Hz, 1H), 4.77–5.12 (m, 2H), 5.09–6.00 (m, 2H), 4.77 (d, *J* = 9.6 Hz, 1H), 4.70 (d, *J* = 17.2 Hz, 1H), 4.30–4.24 (m, 3H), 4.06 (t, *J* = 6.4 Hz, 1H), 3.92 (dd, *J* = 12.4 Hz, 6.8 Hz, 1H), 3.64 (d, *J* = 2.0 Hz, 1H), 3.59 (dd, *J* = 11.6 Hz, 6.4 Hz, 1H), 3.41 (dd, *J* = 12.6 Hz, 2.8 Hz, 1H), 3.27 (*J* = 11.6 Hz, 4.4 Hz, 1H), 3.14 (dt, *J* = 11.2 Hz, 4.0 Hz, 1H), 2.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 155.3, 142.5, 135.1, 133.8, 132.5, 131.0, 128.2, 127.4, 126.4, 126.0, 117.6, 116.1, 98.0, 73.7, 70.9, 70.3, 69.7, 63.6, 57.4, 37.9, 20.9; HRMS (ESI) *m/z* calcd for C₂₈H₃₂NO₆ [M + H]⁺ 478.2230, Found: 492.2247.

The synthesis of **8jd**

(4*S*, 5*R*, 6*R*, 7*S*, 4*aS*, 8*aR*)- Acetic acid 5,6-bis-allyloxy-4-(4-chloro-phenyl)-2-phenyl-4*a*,6,7,8*a*-tetrahydro-4*H*, 5*H*-pyrano[3,2-*e*][1,3]oxazin-7-ylmethyl ester (**8jd**)

To the mixture of 3,4-di-*O*-(2-propenyl)-6-*O*-acetyl-D-galactal (**1j**, 134 mg, 0.5 mmol), *N*-[(4-chloro-phenyl)-methoxy-methyl]-benzamide (**7k**, 137.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8kj** as a colorless syrup (217 mg, 85%). $[\alpha]_{\text{D}}^{25} = -0.69$ (c, 0.87 g/mL CH₂Cl₂); IR (neat) ν : 2931, 1739, 1640, 1423, 1331, 1240, 1132, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 6.8 Hz, 2H), 7.54–7.43 (m, 5H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.00 (d, *J* = 3.2 Hz, 1H), 5.90–5.80 (m, 1H), 5.20–5.10 (m, 3H), 4.98 (d, *J* = 3.6 Hz, 1H), 4.85 (dd, *J* = 10.8 Hz, 1.2 Hz, 1H), 4.71 (dd, *J* = 17.2 Hz, 1.6 Hz, 1H), 4.30–4.23 (m, 3H), 4.05 (t, *J* = 6.4 Hz, 1H), 3.92 (dd, *J* = 12.8 Hz, 6.8 Hz, 1H), 3.66–3.62 (m, 2H), 3.38 (dd, *J* = 11.2 Hz, 2.4 Hz, 1H), 3.27–3.23 (m, 1H), 3.11 (dt, *J* = 11.2 Hz, 4.0 Hz, 1H), 2.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 155.6, 141.2, 134.9, 133.3, 132.3, 131.7, 131.1, 128.3, 128.0, 127.7, 127.4, 117.6, 116.1, 97.9, 73.8, 73.6, 70.8, 70.3, 69.4, 63.5, 56.9, 37.7, 20.9; HRMS (ESI) *m/z* calcd for C₂₈H₃₁ClNO₆ [M + H]⁺ 512.1840, Found: 512.1851.

The synthesis of **8ke**

(4*S*, 5*R*, 6*R*, 7*S*, 4*aS*, 8*aR*)- 5,6-Bis-allyloxy-7-allyloxymethyl-4-(4-nitro-phenyl)-2-phenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*][1,3]oxazine (**8ke**)

To the mixture of 3,4,6-tri-*O*-2-propenyl-D-galactal (**1k**, 133 mg, 0.5 mmol), *N*-[(4-nitro-phenyl)-methoxy-methyl]-benzamide (**7e**, 143 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8ke** as a colorless syrup (179 mg, 69%). [α]_D²⁵ = +12.5 (c, 0.60 g/mL, CH₂Cl₂); IR (neat) ν : 2876, 1647, 1341, 1099, 921, 746, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.53–7.50 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.02 (d, *J* = 3.6 Hz, 1H), 5.97–5.81 (m, 1H), 5.29 (dd, *J* = 17.2 Hz, 2.8 Hz, 1H), 5.22–5.04 (m, 5H), 4.71 (dd, *J* = 10.4 Hz, 1.6 Hz, 1H), 4.60 (d, *J* = 17.2 Hz, 1.6 Hz, 1H), 4.19 (dd, *J* = 12.4 Hz, 2.4 Hz, 1H), 4.09–3.93 (m, 5H), 3.74–3.61 (m, 4H), 3.39 (dd, *J* = 11.2 Hz, 2.4 Hz, 1H), 3.23–3.15 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 150.8, 146.4, 135.1, 134.3, 133.0, 132.1, 131.3, 128.3, 127.5, 127.2, 123.2, 117.6, 117.3, 115.8, 97.8, 73.9, 73.5, 72.5, 71.1, 70.6, 68.8, 68.4, 57.3, 38.0; HRMS (ESI) *m/z* calcd for C₂₉H₃₃N₂O₇ [M + H]⁺ 521.2288, Found: 521.2276.

The synthesis of **8kj**

(4*S*, 5*R*, 6*R*, 7*S*, 4*aS*, 8*aR*)- 5,6-Bis-allyloxy-7-allyloxymethyl-4-(4-fluoro-phenyl)-2-phenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*][1,3]oxazine (**8kj**)

To the mixture of 3,4,6-tri-*O*-2-propenyl-D-galactal (**1k**, 133 mg, 0.5 mmol), *N*-[(4-fluoro-phenyl)-methoxy-methyl]-benzamide (**7j**, 129.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8kj** as a colorless syrup (180 mg, 73%). $[\alpha]_{\text{D}}^{25} = +6.6$ (c, 0.27 g/mL CH₂Cl₂); IR (neat) ν : 2865, 1640, 1338, 1087, 935, 741, 705 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.49–7.34 (m, 5H), 6.94 (t, *J* = 8.8 Hz, 2H), 5.91 (d, *J* = 4.0 Hz, 1H), 5.90 – 5.75 (m, 2H), 5.22 (dd, *J* = 15.6 Hz, 1.6 Hz, 1H), 5.15–5.03 (m, 4H), 4.90 (d, *J* = 3.2 Hz, 1H), 4.75 (dd, *J* = 10.4 Hz, 1.6 Hz, 1H), 4.64 (dd, *J* = 13.2 Hz, 1.6 Hz, 1H), 4.16 (dd, *J* = 12.4 Hz, 5.6 Hz, 1H), 4.02–3.87 (m, 4H), 3.64–3.55 (m, 4H), 3.21 (dd, *J* = 11.2 Hz, 2.8 Hz, 1H), 3.21–3.17 (m, 1H), 3.01 (dt, *J* = 11.2 Hz, 3.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 162.7, 160.3, 155.6, 138.4, 135.3, 134.4, 133.6, 132.4, 131.0, 128.2, 127.8, 127.7, 127.4, 117.5, 117.2, 116.0, 114.6, 114.4, 98.0, 73.9, 73.6, 72.5, 71.0, 70.9, 69.3, 68.6, 56.9, 38.0; HRMS (ESI) *m/z* calcd for C₂₉H₃₃FNO₅ [M + H]⁺ 494.2343, Found: 494.2331.

The synthesis of 8kk

4*S*, 5*R*, 6*R*, 7*S*, 4*aS*, 8*aR*)- 5,6-Bis-allyloxy-7-allyloxymethyl-4-(4-bromo-phenyl)-2-phenyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*][1,3]oxazine (8kk):

To the mixture of 3,4,6-tri-*O*-2-propenyl-*D*-galactal (**1k**, 133 mg, 0.5 mmol), *N*-[(4-bromo-phenyl)-methoxy-methyl]-benzamide (**7k**, 159.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8kk** as a colorless syrup (232 mg, 84%). $[\alpha]_{\text{D}}^{25} = +4.7$ (c, 0.68 g/mL, CH₂Cl₂); IR (neat) ν : 2867, 1654, 1486, 1341, 1098, 1059, 1007, 922, 839, 749, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, $J = 7.2$ Hz, 2H), 7.49–7.40 (m, 7H), 5.96 (d, $J = 3.6$ Hz, 1H), 5.93–5.81 (m, 2H), 5.28 (dd, $J = 17.2$ Hz, 1.6 Hz, 1H), 5.22–5.10 (m, 4H), 4.91 (d, $J = 3.6$ Hz, 1H), 4.84 (dd, $J = 17.2$ Hz, 1.6 Hz, 1H), 4.69 (dd, $J = 17.2$ Hz, 1.6 Hz, 1H), 4.22 (dd, $J = 12.8$ Hz, 5.6 Hz, 1H), 4.11–3.93 (m, 4H), 3.70–3.62 (m, 4H), 3.36 (dd, $J = 11.2$ Hz, 2.8 Hz, 1H), 3.23 (ddd, $J = 12.0$ Hz, 3.2 Hz, 1.6 Hz, 1H), 3.06 (dt, $J = 11.2$ Hz, 4.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 155.7, 141.9, 135.3, 134.4, 133.4, 132.4, 131.1, 130.9, 128.2, 127.5, 119.7, 117.5, 117.2, 116.0, 98.0, 73.8, 73.6, 72.5, 71.0, 70.8, 69.2, 68.6, 57.0, 37.9; HRMS (ESI) m/z calcd for C₂₉H₃₃BrNO₅ [M + H]⁺ 554.1542, Found: 554.1557.

The synthesis of **8kl**

(4*S*, 5*R*, 6*R*, 7*S*, 4*aS*, 8*aR*)- 5,6-Bis-allyloxy-7-allyloxymethyl-2-phenyl-4-*p*-tolyl-4*a*,6,7,8*a*-tetrahydro-4*H*,5*H*-pyrano[3,2-*e*][1,3]oxazine (**8kl**)

To a mixture of 3,4,6-tri-*O*-2-propenyl-D-galactal (**1k**, 133 mg, 0.5 mmol), *N*-(methoxy-*p*-tolyl-methyl)-benzamide (**7l**, 127.5 mg, 0.5 mmol) and anhydrous DCM (10 ml) under nitrogen was added at -78 °C TMSOTf (111 mg, 0.5 mmol). After 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, and then extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 6:1 to 3:1) to provide desired **8kl** as a colorless syrup (215 mg, 88%). $[\alpha]_D^{25} = +0.73$ (c, 0.78 g/mL, CH₂Cl₂); IR (neat) ν : 2860, 1654, 1479, 1350, 1087, 1044, 1011, 935, 844, 752, 687 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.14–8.12 (m, 2H), 7.48–7.45 (m, 3H), 7.42–7.40 (m, 3H), 7.11 (d, *J* = 5.2 Hz, 1H), 5.96 (d, *J* = 2.8 Hz, 1H), 5.95–5.83 (m, 1H), 5.30–5.26 (m, 1H), 5.21–5.16 (m, 2H), 5.12–5.07 (m, 2H), 4.96 (d, 2.4 Hz, 1H), 4.78–4.76 (m, 1H), 4.70–4.68 (m, 1H), 4.26–4.22 (m, 1H), 4.07–3.93 (m, 4H), 3.69 (d, *J* = 2.4 Hz, 1H), 3.66–3.59 (m, 3H), 3.38 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 3.27–3.25 (m, 1H), 3.07 (dt, *J* = 7.6 Hz, 2.4 Hz, 1H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.3, 139.7, 135.4, 135.2, 134.5, 134.0, 132.6, 130.9, 128.5, 128.2, 127.5, 126.3, 117.4, 117.1, 115.8, 98.1, 73.9, 73.8, 72.5, 71.1, 71.0, 69.6, 68.7, 57.3, 38.1, 21.1; HRMS (ESI) *m/z* calcd for C₃₀H₃₆NO₅ [M + H]⁺ 490.2593, Found: 490.2580.

General procedure for the conversion of 8 to 9:

For **9aaa**, **9aab**, **9iga**, **9igb**, **9igc**, **9jaa**, **9klb**, **9kle**, the procedure was following:

A mixture of **8** (0.5 mmol) and nucleophiles (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8** according to the TLC. After cooling to the room temperature, the reaction mixture was evaporated under reduced pressure providing the residue which was purified by column chromatography on silica gel to give **9**.

For **9igd**, **9klf**, **9klg**, **9klh**, **9kli**, **9klj**, the procedure was following:

A mixture of **8** (0.5 mmol) and nucleophiles (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8** according to the TLC. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (10 mL). The resulting mixture was washed with H₂O (3 × 10 mL), dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel to give **9**.

The synthesis of **9aaa**

(2'S, 2R, 3S, 5S, 6S)- Acetic acid 2-acetoxymethyl-5-(benzoylamino-phenyl-methyl)-6-methoxy-tetrahydro -pyran-3-yl ester (**9aaa**)

A mixture of **8aa** (212 mg, 0.5 mmol) and MeOH (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8aa** according to the TLC. After cooling to the room temperature, the reaction mixture was evaporated under reduced pressure providing the residue which was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to give **9aaa** as colorless syrup (202 mg, 89%). $[\alpha]_{\text{D}}^{25} = +71.1$ (c 0.54 g/mL, CH₃COCH₃); IR (neat) ν : 3412, 2944, 1741, 1654, 1523, 1373, 1238, 1036, 708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.6 Hz, 2H), 7.52-7.24 (m, 8H), 5.09 (d, J = 8.0 Hz, 1H), 4.79 (dt, J = 10.4 Hz, 4.4 Hz, 1H), 4.20 (dd, J = 11.6 Hz, 5.2 Hz, 1H), 4.12-4.06 (m, 2H), 3.64 (s, 3H), 3.40-3.36 (m, 1H), 2.33-2.22 (m, 2H), 2.05 (s, 3H), 2.03 (s, 3H), 1.35 (q, J = 12.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 169.8, 165.6, 138.3, 134.4, 131.5, 128.6, 128.5, 127.7, 127.4, 126.9, 104.0, 74.8, 67.3, 62.7, 56.4, 55.4, 43.8, 31.6, 21.0, 20.8; HRMS (ESI) m/z calcd for C₂₅H₃₀NO₇ [M + H]⁺ 456.2022, Found: 456.2033.

The synthesis of **9aab**

(2'S, 2R, 3S, 5S, 6S)- Acetic acid 2-acetoxymethyl-5-(benzoylamino-phenyl-methyl)-6-ethoxy-tetrahydro- pyran-3-yl ester (**9aab**)

A mixture of **8aa** (212 mg, 0.5 mmol) and EtOH (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8aa** according to the TLC. After cooling to the room temperature, the reaction mixture was evaporated under reduced pressure providing the residue which was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to give **9aab** as colorless syrup (206 mg, 88%). $[\alpha]_{\text{D}}^{25} = +47.9$ (c 0.63 g/mL, CH₃COCH₃); IR (neat) ν : 3405, 2968, 1739, 1653, 1524, 1367, 1222, 1035, 708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.6 Hz, 2H), 7.50-7.24 (m, 8H), 5.08 (d, J = 8.0 Hz, 1H), 4.78 (dt, J = 10.4 Hz, 4.4 Hz, 1H), 4.20-4.08 (m, 4H), 3.63-3.56 (m, 1H), 3.41-3.36 (m, 1H), 2.33-2.24 (m, 2H), 2.05 (s, 3H), 2.03 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H), 1.34 (q, J = 12.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 169.8, 165.5, 138.3, 134.4, 131.5, 128.5, 128.4, 127.7, 127.4, 126.8, 103.0, 74.8, 67.4, 64.8, 62.7, 55.5, 43.7, 31.7, 21.0, 20.8, 15.5; HRMS (ESI) m/z calcd for C₂₆H₃₂NO₇ [M + H]⁺ 470.2179, Found: 470.2164.

The synthesis of **9iga**

(2'S, 2R, 3S, 4R, 5S, 6S)-Acetic acid 3,4-bis-allyloxy-5-(benzoylamino-naphthalen-1-yl-methyl)-6-methoxy- tetrahydro-pyran-2-ylmethyl ester (**9iga**)

A mixture of **8ig** (263 mg, 0.5 mmol) and MeOH (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8ig** according to the TLC. After cooling to the room temperature, the reaction mixture was evaporated under reduced pressure providing the residue which was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to give **9iga** as colorless syrup (238 mg, 85%). $[\alpha]_{\text{D}}^{25} = +98.7$ (c 0.45 g/mL, CH₂Cl₂); IR (neat) ν : 3435, 2861, 1741, 1655, 1522, 1475, 1369, 1231, 1082, 931, 777, 705 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.86–7.78 (m, 4H), 7.57–7.40 (m, 7H), 6.57 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 5.90–5.78 (m, 2H), 5.23 (ddd, J = 17.2 Hz, 10.4 Hz, 1.6 Hz, 2H), 5.15 (ddd, J = 10.0 Hz, 5.2 Hz, 1.2 Hz, 2H), 4.48 (d, J = 8.4 Hz, 1H), 4.30 (dd, J = 12.0 Hz, 3.2 Hz, 1H), 4.21–4.14 (m, 2H), 4.10–4.00 (m, 2H), 3.81–3.77 (m, 1H), 3.66 (s, 3H), 3.51 (t, J = 8.0 Hz, 1H), 3.42–3.38 (m, 1H), 3.29 (dd, J = 9.2 Hz, 7.6 Hz, 1H), 2.55 (dt, J = 8.8 Hz, 2.4 Hz, 1H), 2.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 166.1, 136.1, 134.6, 134.4, 133.8, 131.7, 131.5, 128.7, 128.6, 128.4, 127.0, 126.5, 125.9, 124.9, 123.8, 117.7, 116.2, 102.7, 78.5, 73.2, 72.8, 70.7, 63.4, 56.8, 50.5, 47.0, 20.9; HRMS (ESI) m/z calcd for C₃₃H₃₈NO₇ [M + H]⁺ 560.2648, Found: 560.2657.

The synthesis of **9igb**

(2'S, 2R, 3S, 4R, 5S, 6S)-Acetic acid 3,4-bis-allyloxy-5-(benzoylamino-naphthalen-1-yl-methyl)-6-ethoxy-tetrahydro-pyran-2-ylmethyl ester (**9igb**)

A mixture of **8ig** (263 mg, 0.5 mmol) and EtOH (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8ig** according to the TLC. After cooling to the room temperature, the reaction mixture was evaporated under reduced pressure providing the residue which was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to give **9igb** as colorless syrup (263 mg, 92%). $[\alpha]_D^{25} = +111.0$ (c 0.31 g/mL, CH₂Cl₂); IR (neat) ν : 3439, 2868, 1741, 1659, 1516, 1481, 1374, 1235, 1079, 925, 781, 711 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.86–7.77 (m, 4H), 7.56–7.39 (m, 7H), 6.60 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 5.95–5.78 (m, 2H), 5.31 (d, J = 17.2 Hz, 8.4 Hz, 1H), 5.29 (d, J = 8.4 Hz, 17.2 Hz, 1H), 5.23–5.13 (m, 3H), 4.56 (d, J = 8.8 Hz, 1H), 4.28 (dd, J = 12.0 Hz, 2.8 Hz, 1H), 4.18–4.09 (m, 4H), 4.02 (dd, J = 12.8 Hz, 6.4 Hz, 1H), 3.84–3.79 (m, 1H), 3.73–3.69 (m, 1H), 3.50 (t, J = 8.4 Hz, 1H), 3.36–3.31 (m, 1H), 3.25 (dd, J = 10.0 Hz, 8.0 Hz, 1H), 2.53 (dt, J = 10.0 Hz, 2.8 Hz, 1H), 2.07 (s, 3H), 1.40 (t, J = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 165.9, 136.2, 134.7, 134.4, 134.0, 133.8, 131.8, 131.5, 128.7, 128.5, 128.4, 127.0, 126.4, 125.9, 125.0, 124.9, 124.0, 117.7, 116.1, 101.7, 78.7, 77.8, 73.1, 72.8, 70.6, 65.2, 63.3, 50.6, 47.8, 20.9, 15.4; HRMS (ESI) m/z calcd for C₃₄H₄₀NO₇ [M + H]⁺ 574.2805, Found: 574.2814.

The synthesis of **9igc**

(2'S, 2R, 3S, 4R, 5S, 6S)-Acetic acid 3,4,6-tris-allyloxy-5-(benzoylamino-naphthalen-1-yl-methyl)-tetrahydro-pyran-2-ylmethyl ester (**9igc**)

A mixture of **8ig** (263 mg, 0.5 mmol) and allyl alcohol (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8ig** according to the TLC. After cooling to the room temperature, the reaction mixture was evaporated under reduced pressure providing the residue which was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to give **9igc** as colorless syrup (257 mg, 88%). $[\alpha]_{\text{D}}^{25} = +78.9$ (c 0.75 g/mL, CH₂Cl₂); IR (neat) ν : 3444, 2871, 1744, 1652, 1520, 1474, 1368, 1241, 1085, 936, 785, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, $J = 8.0$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.86 – 7.78 (m, 4H), 7.58–7.38 (m, 7H), 6.58 (dd, $J = 2.8$ Hz, 8.4 Hz, 1H), 8.15–8.05 (m, 1H), 5.91–5.77 (m, 2H), 5.43–5.13 (m, 6H), 4.63 (d, $J = 8.4$ Hz, 1H), 4.52 (dd, $J = 12.0$ Hz, 5.6 Hz, 1H), 4.29 (dd, $J = 12.0$ Hz, 2.8 Hz, 1H), 4.20–4.13 (m, 3H), 4.09–4.00 (m, 2H), 3.77 (dd, $J = 13.2$ Hz, 4.8 Hz, 1H), 3.51 (t, $J = 8.0$ Hz, 1H), 3.41–3.37 (m, 1H), 3.29 (t, $J = 8.0$ Hz, 1H), 2.58 (dt, $J = 13.2$ Hz, 2.8 Hz, 1H), 2.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 166.0, 136.1, 134.6, 134.4, 134.0, 133.8, 133.5, 131.7, 131.5, 128.7, 128.5, 128.4, 127.1, 126.4, 125.9, 124.9, 124.8, 123.9, 118.8, 117.7, 116.1, 100.9, 78.4, 77.6, 73.3, 72.8, 70.6, 70.3, 63.4, 50.5, 47.0, 20.9; HRMS (ESI) m/z calcd for C₃₅H₄₀NO₇ [M + H]⁺ 586.2805, Found: 586.2823.

The synthesis of **9igd**

(2'S, 2R, 3S, 4R, 5S, 6S)- Acetic acid 3,4-bis-allyloxy-5-(benzoylamino-naphthalen-1-yl-methyl)-6-(2-hydroxy-propoxy)-tetrahydro-pyran-2-ylmethyl ester (**9igd**)

A mixture of **8ig** (263 mg, 0.5 mmol) and (*R*)-1,2-propanediol (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8** according to the TLC. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (10 mL). The resulting mixture was washed with H₂O (3 × 10 mL), dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 1:1) to give **9igd** as colorless syrup (244 mg, 81%). $[\alpha]_D^{25} = +67.4$ (c 0.83 g/mL, CH₂Cl₂); IR (neat) ν : 3437, 3356, 2864, 1740, 1646, 1524, 1467, 1359, 1238, 1077, 925, 776, 698 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.40 (d, *J* = 8.4 Hz, 0.67H), 8.35 (d, *J* = 8.4 Hz, 0.33H), 7.87 – 7.77 (m, 4H), 7.69 (d, *J* = 7.2 Hz, 0.33H), 7.65 (d, *J* = 7.2 Hz, 0.67H), 7.56–7.35 (m, 4H), 6.59 (d, *J* = 6.4 Hz, 0.67H), 6.51 (d, *J* = 6.4 Hz, 0.33H), 5.88 – 5.81 (m, 1H), 5.75 – 5.63 (m, 1H), 5.28 – 5.00 (m, 4H), 4.91 (d, *J* = 6.4 Hz, 0.33H), 4.74 (d, *J* = 6.4 Hz, 0.67H), 4.39 – 4.31 (m, 1H), 4.18 – 4.11 (m, 2H), 4.09 – 4.03 (m, 2H), 3.97 – 3.88 (m, 2H), 3.74 – 3.64 (m, 2H), 3.58 – 3.40 (m, 4H), 2.69 – 2.65 (m, 1H), 1.34 (d, *J* = 6.6 Hz, 1H), 1.20 (d, *J* = 6.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.8, 166.7, 136.4, 134.4, 134.1, 134.0, 133.7, 133.6, 131.7, 131.3, 128.8, 128.6, 128.4, 127.1, 127.0, 126.6, 125.9, 124.9, 124.8, 123.6, 123.5, 118.2, 118.0, 116.4, 102.3, 102.0, 80.8, 78.3, 78.2, 78.0, 73.8, 73.6, 73.0, 72.9, 71.1, 70.8, 67.0, 64.5, 63.6, 64.4, 50.6, 47.6, 47.3, 20.9, 20.8, 18.8, 17.6; HRMS (ESI) *m/z* calcd for C₃₅H₄₂NO₈ [M + H]⁺ 604.2910, Found: 604.2926.

The synthesis of **9jaa**

(2'S, 2R, 3R, 4R, 5S, 6S)- Acetic acid 3,4-bis-allyloxy-5-(benzoylamino-phenyl-methyl)-6-methoxy-tetrahydro -pyran-2-ylmethyl ester (**9jaa**)

A mixture of **8ja** (238.5 mg, 0.5 mmol) and MeOH (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8ja** according to the TLC. After cooling to the room temperature, the reaction mixture was evaporated under reduced pressure providing the residue which was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to give **9jaa** as colorless syrup (239 mg, 94%). $[\alpha]_{\text{D}}^{25} = +65.7$ (c 0.23 g/mL, CH₂Cl₂); IR (neat) ν : 3429, 2865, 1743, 1639, 1535, 1478, 1342, 1235, 1080, 928, 774, 687 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 7.6 Hz, 2H), 7.50–7.40 (m, 3H), 7.33 (m, 4H), 6.13–6.04 (m, 1H), 5.98–5.86 (m, 1H), 5.75 (dd, J = 8.0 Hz, 2.8 Hz, 1H), 5.49 (dd, J = 17.6 Hz, 1.2 Hz, 1H), 5.30 (dd, J = 10.4 Hz, 1.2 Hz, 1H), 5.25 (dd, J = 17.2 Hz, 1.6 Hz, 1H), 5.17 (d, J = 10.4 Hz, 2H), 4.39–4.28 (m, 2H), 4.26–4.18 (m, 2H), 4.13–4.06 (m, 1H), 4.03–3.99 (m, 2H), 3.63 (s, 1H), 3.31 (t, J = 6.4 Hz, 1H), 3.05 (dd, J = 11.6 Hz, 2.4 Hz, 1H), 2.68 (dt, J = 11.2 Hz, 2.4 Hz, 1H), 2.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 165.6, 138.9, 135.1, 134.7, 133.6, 131.3, 128.5, 128.4, 127.5, 127.4, 126.9, 117.6, 117.3, 102.6, 78.0, 77.4, 77.3, 77.1, 76.7, 73.5, 72.2, 69.7, 69.5, 63.2, 56.4, 50.7, 45.6, 20.8; HRMS (ESI) m/z calcd for C₂₉H₃₆NO₇ [M + H]⁺ 510.2492, Found: 510.2478.

The synthesis of **9klb**

(2'S, 2R, 3R, 4R, 5S, 6S)-N-[(4,5-bis-allyloxy-6-allyloxymethyl-2-ethoxy-tetrahydro-pyran-3-yl)-p-tolyl-methyl]-benzamide (**9klb**)

A mixture of **8kl** (244.5 mg, 0.5 mmol) and EtOH (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8kl** according to the TLC. After cooling to the room temperature, the reaction mixture was evaporated under reduced pressure providing the residue which was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to give **9klb** as colorless syrup (243 mg, 91%). $[\alpha]_{\text{D}}^{25} = +108.9$ (c 0.58 g/mL, CH₂Cl₂); IR (neat) ν : 3437, 2857, 1644, 1539, 1469, 1338, 1232, 1075, 931, 767, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 2H), 7.47–37 (m, 3H), 7.16–7.10 (m, 4H), 6.13 – 6.04 (m, 1H), 5.98–5.81 (m, 2H), 5.72 (dd, $J = 2.8$ Hz, 8.0 Hz, 1H), 5.47 (dd, $J = 17.2$ Hz, 1.2 Hz, 1H), 5.30–5.12 (m, 5H), 4.34–4.38 (m, 2H), 4.16–4.08 (m, 3H), 4.00–3.95 (m, 3H), 3.79 (m, 1H), 3.64 (dd, $J = 9.2$ Hz, 7.2 Hz, 1H), 3.54–3.49 (m, 2H), 3.26 (t, $J = 6.4$ Hz, 1H), 3.03 (dd, $J = 11.2$ Hz, 2.0 Hz, 1H), 2.65 (dt, $J = 11.2$ Hz, 2.8 Hz, 1H), 2.31 (s, 3H), 1.41 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.4, 136.9, 136.0, 135.5, 134.9, 134.55, 133.9, 131.1, 129.0, 128.4, 127.4, 126.9, 117.1, 101.7, 78.0, 77.4, 77.1, 76.8, 73.6, 73.4, 72.3, 69.7, 69.5, 68.6, 64.7, 50.5, 45.7, 21.1, 15.4; HRMS (ESI) m/z calcd for C₃₂H₄₂NO₆ [M + H]⁺ 536.3012, Found: 536.3027.

The synthesis of **9kle**

(2'S, 2R, 3R, 4R, 5S, 6S)-N-[(4,5-Bis-allyloxy-6-allyloxymethyl-2-propoxy- tetrahydro-pyran-3-yl)-p-tolyl-methyl]-benzamide (**9kle**)

A mixture of **8kl** (244.5 mg, 0.5 mmol) and 1-propanol (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8kl** according to the TLC. After cooling to the room temperature, the reaction mixture was evaporated under reduced pressure providing the residue which was purified by column chromatography on silica gel (eluted with PE/EA = 4:1 to 2:1) to give **9kle** as colorless syrup (239 mg, 87%). $[\alpha]_{\text{D}}^{25} = +116.4$ (c 0.64 g/mL, CH₂Cl₂); IR (neat) ν : 3446, 2849, 1640, 1534, 1456, 1342, 1228, 1064, 946, 754, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 6.8 Hz, 2H), 7.47–7.37 (m, 3H), 7.17–7.10 (m, 4H), 6.12–6.04 (m, 1H), 5.97–5.82 (m, 2H), 5.72 (dd, J = 8.0 Hz, 2.4 Hz, 1H), 5.47 (dd, J = 17.2 Hz, 1.2 Hz, 1H), 5.29–5.13 (m, 5H), 4.35–4.28 (m, 2H), 4.15–4.11 (m, 2H), 4.03–3.95 (m, 4H), 3.79 (d, J = 1.6 Hz, 1H), 3.64 (dd, J = 9.6 Hz, 7.6 Hz, 1H), 3.52 (dd, J = 9.6 Hz, 5.6 Hz, 1H), 3.43–3.37 (m, 1H), 3.26 (t, J = 6.4 Hz, 1H), 3.02 (dd, J = 11.2 Hz, 2.0 Hz, 1H), 2.68–2.62 (m, 1H), 2.31 (s, 3H), 1.84–1.78 (m, 2H), 1.00 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 136.9, 136.0, 135.5, 134.9, 133.9, 131.1, 129.0, 128.4, 127.5, 126.9, 117.1, 101.9, 78.1, 73.6, 73.4, 72.3, 71.0, 69.7, 69.6, 68.6, 50.6, 45.7, 23.2, 21.1, 10.9; HRMS (ESI) m/z calcd for C₃₃H₄₄NO₆ [M + H]⁺ 550.3169, Found: 550.3148.

The synthesis of **9klf**

(2'S, 2R, 3R, 4R, 5S, 6S)-N-[[4,5-Bis-allyloxy-6-allyloxymethyl-2-(2-methoxyethoxy)-tetrahydro-pyran-3-yl]-p-tolyl-methyl}-benzamide (**9klf**)

A mixture of **8kl** (244.5 mg, 0.5 mmol) and 2-methoxy-ethanol (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8kl** according to the TLC. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (10 mL). The resulting mixture was washed with H₂O (3 × 10 mL), dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 2:1) to give **9klf** as colorless syrup (223 mg, 79%). $[\alpha]_D^{25} = +101.2$ (c 0.79 g/mL, CH₂Cl₂); IR (neat) ν : 3441, 2843, 1643, 1530, 1450, 1335, 1233, 1064, 941, 750, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 6.8 Hz, 2H), 7.45–7.36 (m, 3H), 7.28–7.26 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.13–6.06 (m, 1H), 5.96–5.79 (m, 3H), 5.49 (dd, J = 17.2 Hz, 1.2 Hz, 1H), 5.30–5.13 (m, 5H), 5.35–5.29 (m, 2H), 4.13–4.08 (m, 3H), 4.01–3.96 (m, 3H), 3.78–3.73 (m, 2H), 3.66–3.61 (m, 2H), 3.54–3.48 (m, 2H), 3.25 (t, J = 6.8 Hz, 1H), 3.03 (dd, J = 11.6 Hz, 2.4 Hz, 1H), 2.64 (dt, J = 8.8 Hz, 2.4 Hz, 1H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 136.7, 135.9, 135.5, 135.3, 134.4, 133.9, 130.8, 129.0, 128.2, 127.8, 127.2, 117.1, 101.8, 78.1, 73.6, 73.4, 72.3, 71.2, 69.7, 69.6, 68.7, 68.4, 58.8, 50.3, 45.7, 21.7; HRMS (ESI) m/z calcd for C₃₃H₄₄NO₇ [M + H]⁺ 566.3118, Found: 566.3130.

The synthesis of **9klg**

(2'S, 2R, 3R, 4R, 5S, 6S)-N-{[4,5-Bis-allyloxy-6-allyloxymethyl-2-(2-cyano-ethoxy)-tetrahydro-pyran-3-yl]-p-tolyl-methyl}-benzamide (**9klg**)

A mixture of **8kl** (244.5 mg, 0.5 mmol) and 3-hydroxy-propionitrile (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8kl** according to the TLC. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (10 mL). The resulting mixture was washed with H₂O (3 × 10 mL), dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 2:1) to give **9klg** as colorless syrup (235 mg, 84%). $[\alpha]_D^{25} = +86.7$ (c 0.43 g/mL, CH₂Cl₂); IR (neat) ν : 3435, 2837, 1635, 1528, 1444, 1331, 1228, 1057, 935, 744, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, $J = 4.4$ Hz, 1H), 7.75 (d, $J = 7.2$ Hz, 2H), 7.44 (t, $J = 7.2$ Hz, 1H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.03–5.84 (m, 2H), 5.69–5.60 (m, 1H), 5.32–5.17 (m, 4H), 5.10–4.97 (m, 3H), 4.37 (dd, $J = 12.8$ Hz, 6.0 Hz, 1H), 4.16–4.11 (m, 3H), 4.01–3.88 (m, 5H), 3.83 (m, 1H), 3.64–3.58 (m, 2H), 3.50 (dd, $J = 9.6$ Hz, 6.4 Hz, 1H), 3.36–3.31 (m, 1H), 2.73 (dt, $J = 10.4$ Hz, 3.2 Hz, 2H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 138.2, 137.0, 135.2, 134.4, 133.2, 131.2, 129.1, 128.3, 127.5, 127.2, 118.4, 117.7, 117.4, 117.2, 98.7, 78.9, 74.2, 72.4, 71.6, 70.1, 69.7, 68.8, 62.6, 56.3, 43.6, 21.2, 18.8; HRMS (ESI) m/z calcd for C₃₃H₄₁N₂O₆ [M + H]⁺ 561.2956, Found: 561.2948.

The synthesis of **9klh**

(2'S, 2R, 3R, 4R, 5S, 6S)-N-[(4,5-Bis-allyloxy-6-allyloxymethyl-2-prop-2-ynyloxy-tetrahydro-pyran-3-yl)-p-tolyl-methyl]-benzamide (**9klh**)

A mixture of **8kl** (244.5 mg, 0.5 mmol) and prop-2-yn-1-ol (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8kl** according to the TLC. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (10 mL). The resulting mixture was washed with H₂O (3 × 10 mL), dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 2:1) to give **9klh** as colorless syrup (213 mg, 78%). $[\alpha]_D^{25} = +65.4$ (c 0.55 g/mL, CH₂Cl₂); IR (neat) ν : 3447, 2838, 2104, 1640, 1531, 1443, 1335, 1231, 1063, 930, 741, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, J = 8.0 Hz, 0.81H), 7.98 (d, J = 4.0 Hz, 0.19H), 7.85 (d, J = 7.2 Hz, 1.62H), 7.76 (d, J = 7.2 Hz, 0.38H), 7.47–7.33 (m, 3H), 7.27–7.25 (m, 2H), 7.12–7.07 (m, 2H), 6.13–5.81 (m, 2.81 H), 5.75 (dd, J = 8.4 Hz, 2.8 Hz, 0.82H), 5.69–5.60 (m, 0.19H), 5.48 (dd, J = 17.2 Hz, 1.6 Hz, 0.82 H), 5.32–5.05 (m, 5.19H), 4.97 (dd, J = 10.0 Hz, 0.8 Hz, 0.19H), 4.61 (dd, J = 15.6 Hz, 2.4 Hz, 0.81H), 4.38–4.28 (m, 3.38H), 4.20 (d, J = 3.2 Hz, 0.19H), 4.16–4.05 (m, 1.38 H), 4.02–3.87 (m, 3.62H), 3.84–3.83 (m, 0.19H), 3.79 (d, J = 1.6 Hz, 0.81H), 3.65–3.59 (m, 1H), 3.53–3.47 (m, 1H), 3.28 (t, J = 6.4 Hz, 0.81H), 3.03 (dd, J = 11.2 Hz, 2.4 Hz, 0.81H), 2.72–2.64 (m, 1H), 2.56 (t, J = 2.4 Hz, 0.81H), 2.36 (t, J = 2.4 Hz, 0.19H), 2.31 (s, 2.43H), 2.78 (s, 0.57H); ¹³C NMR δ 166.5, 165.4, 138.3, 136.9, 135.7, 135.3, 134.7, 134.6, 134.4, 134.3, 133.8, 133.3, 131.1, 129.0, 128.9, 128.3, 128.2, 127.8, 127.7, 127.2, 127.1, 118.2, 117.2, 100.2, 97.8, 79.0, 78.6, 77.9, 75.7, 74.4, 74.2, 73.6, 73.5, 72.3, 71.5, 70.0, 69.6, 69.5, 69.4, 68.5, 68.4, 56.3, 55.8, 55.0, 50.5, 45.5, 43.8, 30.9, 21.1; HRMS (ESI) m/z calcd for C₃₃H₄₀NO₆ [M + H]⁺ 546.2856, Found: 546.2842.

The synthesis of **9kli**

(2'S, 2R, 3R, 4R, 5S, 6S)-N-[(4,5-Bis-allyloxy-6-allyloxymethyl-2-isopropyl-sulfanyl-tetrahydro-pyran-3-yl)-p-tolyl-methyl]-benzamide (**9kli**)

A mixture of **8kl** (244.5 mg, 0.5 mmol), isopropyl mercaptan (152 mg, 2 mmol) and 2-propanol (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8kl** according to the TLC. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (10 mL). The resulting mixture was washed with H₂O (3 × 10 mL), dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 2:1) to give **9kli** as colorless syrup (226 mg, 80%). $[\alpha]_{\text{D}}^{25} = +123.5$ (c 0.89 g/mL, CH₂Cl₂); IR (neat) ν : 3438, 2835, 1645, 1537, 1434, 1342, 1235, 1067, 938, 737, 705 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, $J = 7.8$ Hz, 1 H), 7.83–7.81 (m, 2H), 7.49–7.46 (m, 1H), 7.43–7.40 (m, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.13–6.06 (m, 1H), 5.98–5.85 (m, 2H), 5.73 (dd, $J = 7.8$ Hz, 3.0 Hz, 1H), 5.51–5.47 (m, 1H), 5.31–5.28 (m, 1H), 5.28–5.27 (m, 1H), 5.25–5.24 (m, 1H), 5.25–5.24 (m, 1H), 4.35–4.33 (m, 1H), 4.32–4.30 (m, 2H), 4.00–3.94 (m, 3H), 3.80 (d, $J = 2.8$ Hz, 1H), 3.65 (dd, $J = 9.6$ Hz, 7.2 Hz, 1H), 3.52 (dd, $J = 9.6$ Hz, 6.0 Hz, 1H), 3.29 (dt, $J = 5.4$ Hz, 0.6 Hz, 1H), 3.04 (dd, $J = 11.4$ Hz, 2.4 Hz, 1H), 2.67 (dt, $J = 9.0$ Hz, 3.0 Hz, 1H), 2.32 (s, 3H), 1.39 (d, $J = 6.0$ Hz, 3H), 1.30 (d, $J = 6.0$ Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 165.5, 136.8, 136.0, 135.5, 134.9, 134.5, 133.8, 131.1, 128.9, 128.3, 127.6, 127.0, 117.2, 117.1, 99.4, 78.2, 73.6, 73.3, 72.3, 70.5, 69.6, 69.4, 68.7, 50.6, 45.8, 24.0, 21.5, 21.1; HRMS (ESI) m/z calcd for C₃₃H₄₄NO₅S [M + H]⁺ 566.2940, Found: 566.2928.

The synthesis of **9klj**

(2'S, 2R, 3R, 4R, 5S, 6S)-N-[(4,5-Bis-allyloxy-6-allyloxymethyl-2-formylamino-tetrahydro-pyran-3-yl)-p-tolyl-methyl]-benzamide (**9klj**)

A mixture of **8kl** (244.5 mg, 0.5 mmol), formamide (1 mL) was heated in a Schlenk tube at 80 °C for 24-48 h until the disappearance of **8kl** according to the TLC. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (10 mL). The resulting mixture was washed with H₂O (3 × 10 mL), dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluted with PE/EA = 1:1) to give **9klj** as colorless syrup (186 mg, 68%).

$[\alpha]_D^{25} = +126.5$ (c 0.74 g/mL, CH₂Cl₂); IR (neat) ν : 3428, 2830, 1689, 1534, 1427, 1325, 1239, 1074, 945, 742, 695 cm⁻¹; H NMR (400 MHz, CDCl₃) δ 8.54 (d, J = 7.6 Hz, 0.65 H), 7.86 (d, J = 4.8 Hz, 0.35 H), 7.44–7.23 (m, 5H), 7.05 (t, J = 8.0 Hz, 2H), 6.10–5.79 (m, 2.65H), 5.71 (dd, J = 8.0 Hz, 2.8 Hz, 0.65H), 5.69–5.62 (m, 0.35H), 5.45 (dd, J = 17.2 Hz, 1.2 Hz, 0.65H), 5.31–4.97 (m, 6.70H), 4.72 (t, J = 3.2 Hz, 0.35 H), 4.55 (dd, J = 8.8 Hz, 3.6 Hz, 0.65H), 4.39–4.25 (m, 1.65H), 4.18–4.06 (m, 2.35H), 4.02–3.89 (m, 3.35H), 3.86–3.83 (m, 0.7 H), 3.73 (br, 0.65H), 3.70–3.47 (m, 4.35H), 3.30 (t, J = 6.4 Hz, 0.65H), 2.97 (dd, J = 11.6 Hz, 2.0 Hz, 0.65H), 2.74 (dt, J = 11.6 Hz, 2.8 Hz, 0.35H), 2.61 (dt, J = 11.2 Hz, 2.8 Hz, 0.65H), 2.28 (s, 1.95H), 2.25 (s, 1.05H); ¹³C NMR δ 166.6, 165.8, 136.6, 136.8, 136.0, 135.4, 134.7, 134.4, 134.3, 133.9, 133.4, 131.3, 131.1, 129.0, 128.4, 128.3, 127.9, 127.7, 127.2, 127.1, 118.0, 117.5, 117.3, 117.2, 117.1, 117.0, 96.1, 92.8, 78.4, 78.1, 74.1, 73.5, 73.3, 72.4, 72.3, 71.8, 69.9, 69.8, 69.6, 69.0, 68.9, 60.5, 56.1, 50.8, 46.0, 44.2, 21.2, 21.1; HRMS (ESI) m/z calcd for C₃₁H₃₉N₂O₆ [M + H]⁺ 535.2808, Found: 535.2827.

ORTEP drawing and details of the crystallographic data of 8am

Figure S1. ORTEP Drawing of Compound 8am.

Table 1. Crystal data and structure refinement for 8am.

Identification code	8am
Empirical formula	C ₂₄ H ₂₄ N ₂ O ₈
Formula weight	468.45
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21
Unit cell dimensions	a = 11.367(2) Å alpha = 90 deg. b = 9.0168(18) Å beta = 94.36(3) deg. c = 11.449(2) Å gamma = 90 deg.
Volume	1170.1(4) Å ³
Z, Calculated density	2, 1.330 Mg/m ³
Absorption coefficient	0.101 mm ⁻¹
F(000)	492
Crystal size	0.32 x 0.25 x 0.25 mm
Theta range for data collection	3.32 to 27.47 deg.
Limiting indices	-14 ≤ h ≤ 14, -11 ≤ k ≤ 11, -14 ≤ l ≤ 14
Reflections collected / unique	10989 / 4872 [R(int) = 0.0656]
Completeness to theta = 27.47	98.6 %
Max. and min. transmission	0.9752 and 0.9684
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4872 / 1 / 308
Goodness-of-fit on F ²	1.012
Final R indices [I > 2sigma(I)]	R1 = 0.0525, wR2 = 0.1203
R indices (all data)	R1 = 0.1312, wR2 = 0.1860
Absolute structure parameter	-1.7(17)
Extinction coefficient	0.016(4)
Largest diff. peak and hole	0.208 and -0.223 e.Å ⁻³

¹H NMR (400 MHz) Spectrum of Compound **8aa**

¹³C NMR (100 MHz) Spectrum of Compound **8aa**

¹H NMR (400 MHz) Spectrum of Compound **8ad**

¹³C NMR (100 MHz) Spectrum of Compound **8ad**

¹H NMR (400 MHz) Spectrum of Compound **8ae**

¹³C NMR (100 MHz) Spectrum of Compound **8ae**

¹H NMR (400 MHz) Spectrum of Compound **8ag**

¹³C NMR (100 MHz) Spectrum of Compound **8ag**

¹H NMR (400 MHz) Spectrum of Compound **8am**

¹³C NMR (100 MHz) Spectrum of Compound **8am**

¹H NMR (400 MHz) Spectrum of Compound **8ba**

¹³C NMR (100 MHz) Spectrum of Compound **8ba**

¹H NMR (400 MHz) Spectrum of Compound **8bg**

¹³C NMR (100 MHz) Spectrum of Compound **8bg**

¹H NMR (400 MHz) Spectrum of Compound **8da**

¹³C NMR (100 MHz) Spectrum of Compound **8da**

¹H NMR (400 MHz) Spectrum of Compound **8ia**

¹³C NMR (100 MHz) Spectrum of Compound **8ia**

¹H NMR (400 MHz) Spectrum of Compound **9ie**

¹³C NMR (100 MHz) Spectrum of Compound **9ie**

¹H NMR (400 MHz) Spectrum of Compound **8ig**

¹³C NMR (100 MHz) Spectrum of Compound **8ig**

¹H NMR (400 MHz) Spectrum of Compound 8jd

¹³C NMR (100 MHz) Spectrum of Compound 8jd

¹H NMR (400 MHz) Spectrum of Compound **8ke**

¹³C NMR (100 MHz) Spectrum of Compound **8ke**

¹H NMR (400 MHz) Spectrum of Compound **9aa**

¹³C NMR (100 MHz) Spectrum of Compound **9aa**

¹H NMR (400 MHz) Spectrum of Compound **9aab**

¹³C NMR (100 MHz) Spectrum of Compound **9aab**

¹H NMR (400 MHz) Spectrum of Compound 9eib

¹³C NMR (100 MHz) Spectrum of Compound 9eib

¹³C NMR (100 MHz) Spectrum of Compound 9klb

^1H NMR (400 MHz) Spectrum of Compound 9kle

^{13}C NMR (100 MHz) Spectrum of Compound 9kle

¹H NMR (400 MHz) Spectrum of Compound 9klg

¹³C NMR (100 MHz) Spectrum of Compound 9klg

¹H NMR (400 MHz) Spectrum of Compound 9klh

¹³C NMR (100 MHz) Spectrum of Compound 9klh