Supporting Information

Catalytic Anomeric Aminoalkynylation of Unprotected Aldoses

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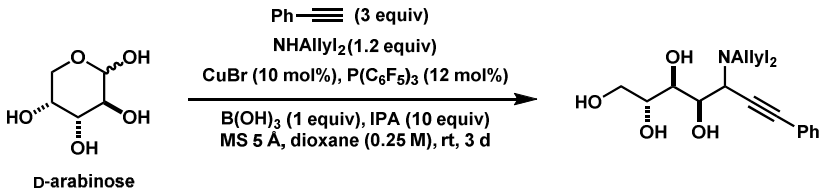
1. General Methods

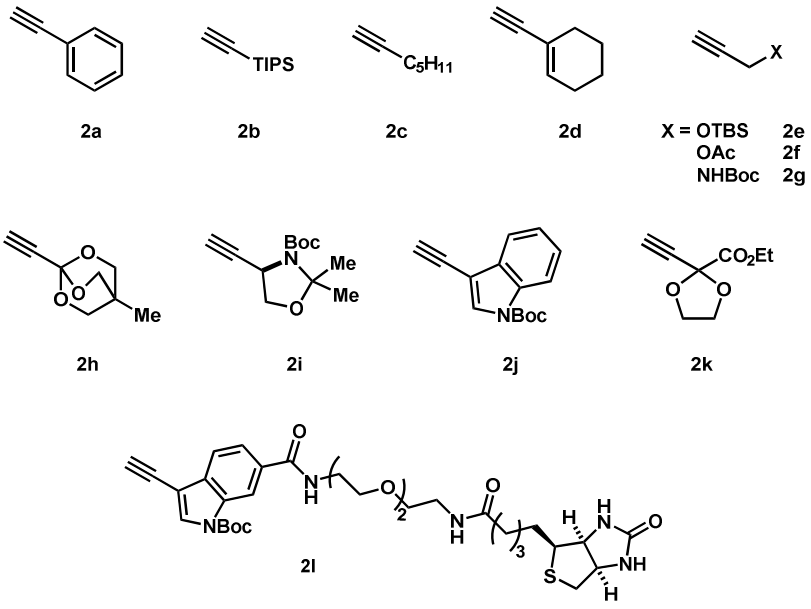
NMR spectra were recorded on JEOL JNM-LA500, JEOL ECX500 (500 MHz for ^{1}H NMR and 125.65 MHz for ^{13}C NMR), and JEOL ECS400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}CNMR) spectrometer. Chemical shifts were reported in ppm on the δ scale relative to residual $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR), CHD_2OD (δ = 3.31 for ^{1}H NMR and δ = 49.0 for ^{13}C NMR), CHD_2CN (δ = 1.94 for ^{1}H NMR and δ = 118.2 for ^{13}C NMR), or CHD_2COCD_3 (δ = 2.05 for ^{1}H NMR and δ = 29.8 for ^{13}C NMR) as an internal reference, respectively. Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. Optical rotations were measured on a JASCO P-1010 polarimeter. ESI-mass spectra were measured on a Waters ZQ4000 spectrometer (for LRMS), and a JEOL JMS-T100LC AccuTOF spectrometer (for HRMS). Normal phase column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM) or neutral silica gel 60 N KANTO CHEMICAL, spherical, neutral, 40-100 μm). For reversed phase column chromatographies, Wakosil® 40C18 (from Wako Pure Chemical Industries) was used. Reactions were carried out in dry solvents under an argon atmosphere, unless otherwise stated. 2-Propanol, ethynylbenzene and diallylamine were distilled prior to use. Other reagents were used as received from commercial sources, unless otherwise stated.

2. General Procedures for Catalytic Aminoalkynylation Reaction of Unprotected Aldoses



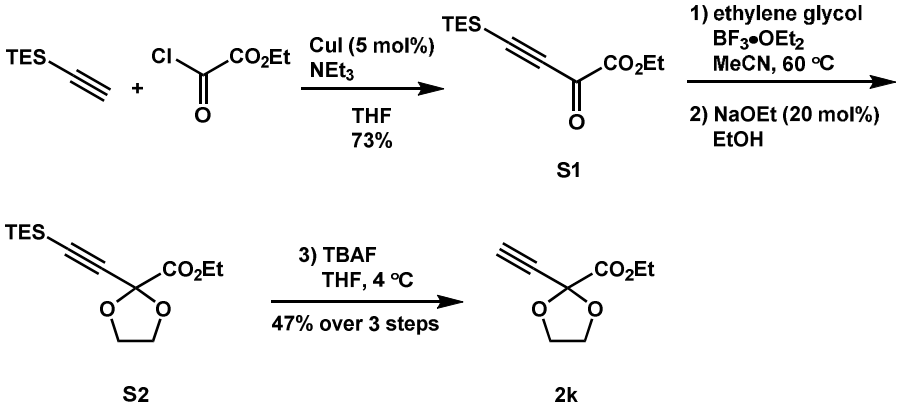
A dry and argon-flushed tube equipped with a magnetic stirrer bar and activated MS 5 Å (336 mg) was charged with D-arabinose (42.0 mg, 280 μmol), CuBr (4.00 mg, 28.0 μmol), $P(C_6F_5)_3$ (17.9 mg, 33.6 μmol) and $B(OH)_3$ (17.3 mg, 280 μmol). After anhydrous 1,4-dioxane (1.12 ml, 0.25 M), ethynylbenzene (92.2 μl, 840 μmol), $NHAllyl_2$ (41.3 μl, 336 μmol), and 2-propanol (214 μl, 2.80 mmol) were added, the mixture was degassed (3 x freeze/pump/thaw). The reaction mixture was then stirred at room temperature for 3 h, and quenched with MeOH. The molecular sieves were removed by filtration and washed with MeOH. The filtrate was concentrated *in vacuo* and the crude product was purified by chromatography on silica gel (CH_2Cl_2/MeOH = 80/1 to 10/1), yielding the target propargylamine **3aa** (77.9 mg, 235 μmol, y. 84%, *dr*: 1:1)

3. Preparation of Substrates



Alkynes **2e**[1], **2g**[2], **2h**[3], **2i**[4] and **2j**[5] were prepared following the reported procedures. **2k** and **2l** were synthesized by the procedure described below. Other alkynes were from commercial sources.

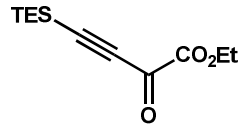
3-1. Synthesis of 2k



S1 was prepared following the reported procedure for a similar substrate.[6] To a stirred solution of **S1** (12.0 g, 50.0 mmol) in MeCN (100ml, 0.5 M) were added ethylene glycol (5.49 ml, 100 mmol) and $BF_3 \cdot OEt_2$ (12.3 ml, 100 mmol). The resulting mixture was stirred at 60 °C for 2.5 h. Ethylene glycol (2.25 ml, 50 mmol) and $BF_3 \cdot OEt_2$ (6.25 ml, 50 mmol) were added further and the whole was stirred at the same temperature for 30 min. The reaction was quenched with saturated $NaHCO_3$ aqueous solution. The aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated. The resulting mixture was dissolved in EtOH (100ml, 0.5 M), to which NaOEt (680 mg, 10.0 mmol) was added (for converting all the various esters in the mixture to an ethyl ester). The reaction mixture was stirred for 5 min at the same temperature. Saturated NH_4Cl aqueous solution was added to the reaction mixture at 4 °C. The aqueous layer was extracted with Et_2O and combined organic layers were washed with H_2O and brine, dried over Na_2SO_4 and

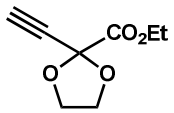
concentrated to give crude **S2** (10.6 g), which was used in the next reaction without further purification.

To a stirred solution of crude **S2** (10.6 g) in THF (107 ml), TBAF solution (1M in THF, 64.2 ml) was added at 4 °C dropwise and the resulting reaction mixture was stirred at the same temperature for 5 min. After confirming the complete consumption of **S2** by TLC analysis, saturated aqueous solution of NH_4Cl was added at 4 °C and the aqueous layer was extracted with a mixture of hexane and Et_2O solvents (hexane/Et_2O = 1/3). The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4 and concentrated to give crude **2k** (9.6 g), which was purified with column chromatography (eluent; hexane/Et_2O = 50 to 10) to give isolated **2k** (4.00 g, 23.5 mmol, 47 % over 3 steps).



ethyl 2-oxo-4-(triethylsilyl)but-3-ynoate (S1)

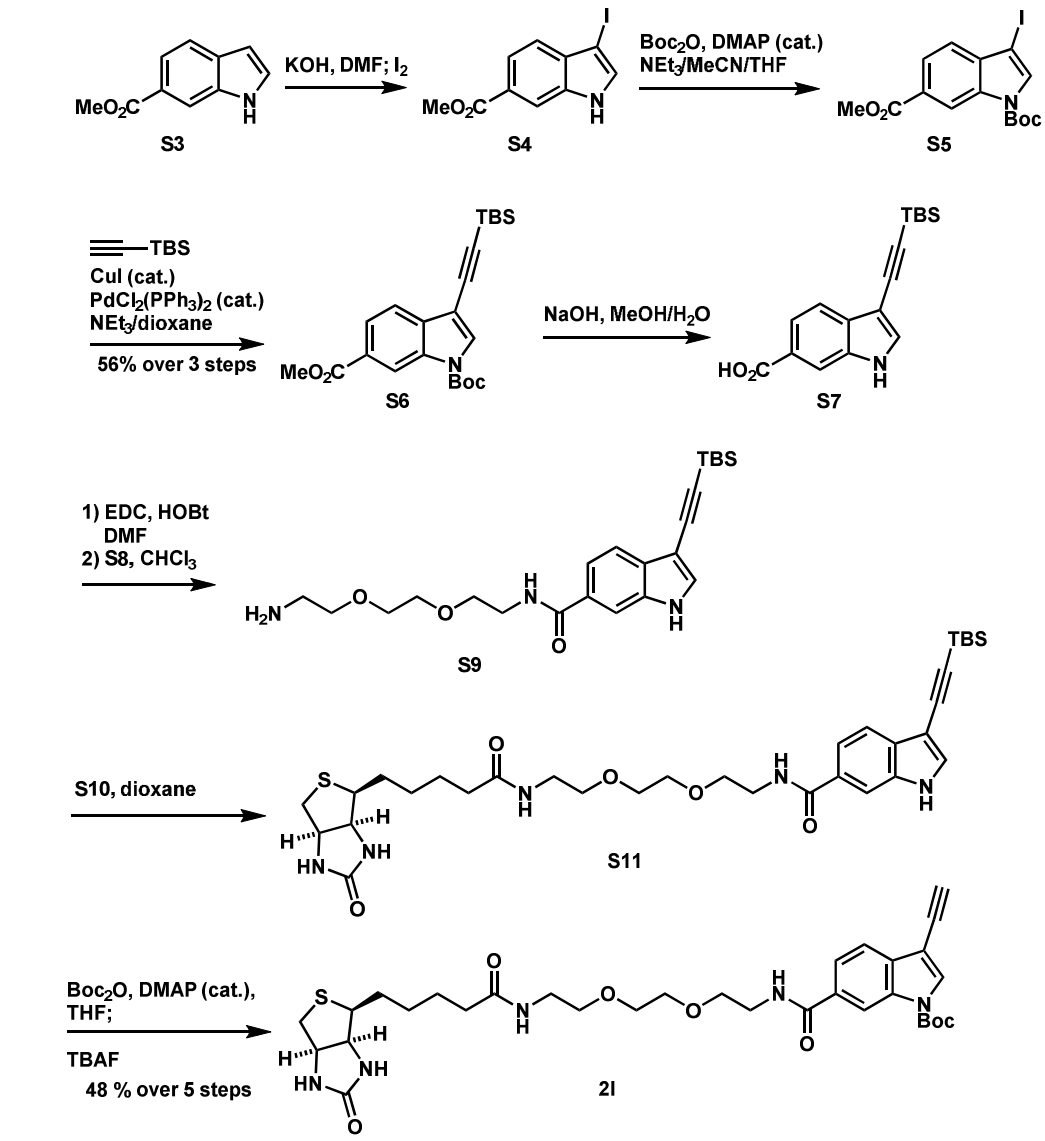
^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.32 (q, *J* = 7.3 Hz, 2H), 1.34 (t, *J* = 7.3 Hz, 3H), 1.00 (t, *J* = 7.8 Hz, 9H), 0.68 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 158.7, 105.4, 101.4, 63.1, 13.8,
7.2, 3.6; IR (neat, cm^{-1}) 2959, 2877, 2147, 1744, 1684, 1457, 1259, 1096, 732; ESI-MS: *m*/*z* 262.6 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{12}H_{20}O_3Si$ $[M+Na]^+$: 263.1073. Found: 263.1075.

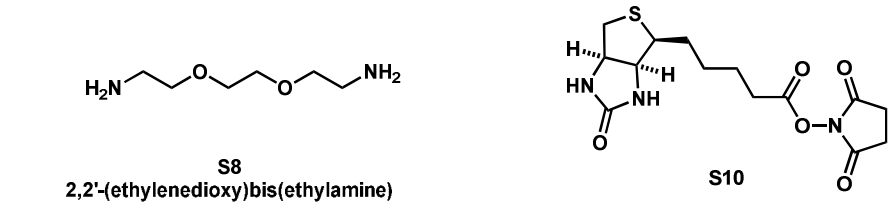


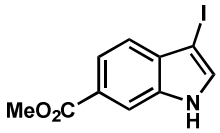
ethyl 2-ethynyl-1,3-dioxolane-2-carboxylate (2k)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.25 (q, *J* = 7.4 Hz, 2H), 4.16 – 4.06 (m, 4H), 2.64 (s, 1H), 1.29 (q, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.5, 97.5, 77.9, 74.4, 66.1, 62.7, 13.8; IR (neat, cm^{-1}) 3272, 2985, 2904, 2122, 1752, 1278, 1174, 1068, 680; ESI-MS: *m*/*z* 192.7 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_8H_{10}O_4$ $[M+Na]^+$: 193.0471. Found: 193.0467.

3-2. Synthesis of 2l

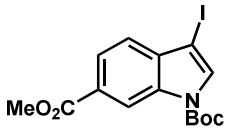






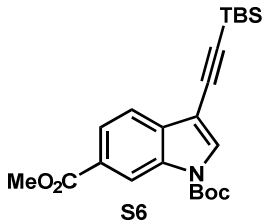
methyl 3-iodo-1*H*-indole-6-carboxylate (S4): A solution of I_2 (7.82 g, 30.8 mmol) in DMF (36 ml) was added dropwise to a solution of **S3** (5.4 g, 30.8 mmol) and KOH (3.10 g, 55.5 mmol) in DMF (36 ml) and the mixture

was stirred for 1 h. Then, the reaction mixture was poured into aqueous solution of sodium thiosulfate (NaS_2O_3 2 g in H_2O 350 ml, containing ice). The precipitate formed was collected by filtration and washed with cold water. The resulting crude solid was dried under vacuum to afford crude **S4** (8.10 g, 26.9 mmol, ca. 87%), which was used for the next reaction without further purification.



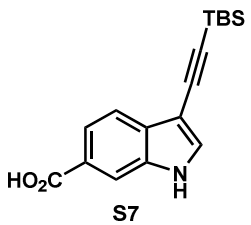
S5

1-(*tert*-butyl) 6-methyl 3-iodo-1*H*-indole-1,6-dicarboxylate (S5): To a stirred solution of crude **S4** (8.10 g, 26.9 mmol) in a mixed solvent of Et_3N (12 ml), MeCN (20 ml) and THF (20 ml), Boc_2O (6.8 ml, 29.6 mmol) was added and the mixture was stirred at room temperature for 14 h. Then, DMAP (0.33 g, 2.7mmol) was added and the reaction mixture was further stirred for 1 h. The reaction mixture was concentrated under vacuum to give a residue, which was washed with MeCN. The obtained crude **S5** (7.55 g, 18.8 mmol, ca. 70% yield) was used for the next reaction without further purification.



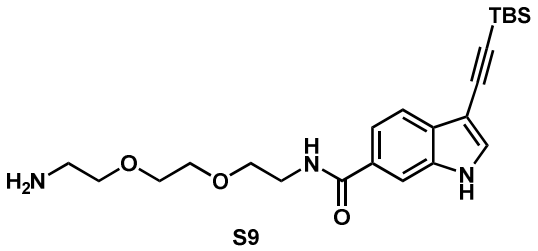
S6

1-(*tert*-butyl) 6-methyl 3-((*tert*-butyldimethylsilyl)ethynyl)-1*H*-indole-1,6-dicarboxylate (S6): A solution of **S5** (7.20 g, 17.9 mmol), *tert*-butyl(ethynyl)dimethylsilane (3.02 g, 21.5 mmol), CuI (0.68 g, 3.58 mmol) and $PdCl_2(PPh_3)_2$ (2.51 g, 3.58 mmol) in Et_3N (150 ml) and dioxane (75 ml) was stirred under argon for 1 h. The reaction mixture was concentrated under vacuum to give a residue, to which CH_2Cl_2 and water were added. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The obtained crude **S6** was purified by silica gel chromatography (eluent: AcOEt/hexane=1/10) to give **S6** as white solid in ca. 93% yield (6.88 g, 16.6 mmol, 56% yield over 3 steps). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.85 (s, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.89 (s, 1H), 7.67 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H), 1.68 (s, 9H), 1.03 (s, 9H), 0.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.5, 148.7, 134.4, 134.1, 132.0, 127.1, 124.5, 120.0, 117.3, 103.7, 97.3, 96.6, 85.1, 52.2, 28.2, 26.3, 16.7, -4.37; IR (neat, cm^{-1}) 2951, 2929, 2856, 2156, 1748, 1719, 1616, 1437, 1371, 1298, 1239, 1158, 1091, 828, 772; ESI-MS: *m*/*z* 436.2 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_{23}H_{31}NO_4Si$ $[M+Na]^+$: 436.1914. Found: 436.1908.



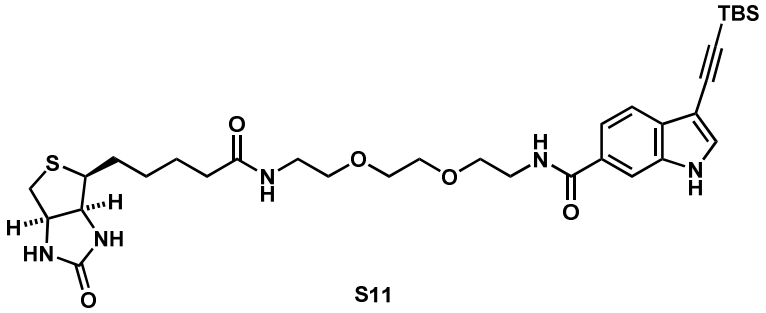
S7

3-((*tert*-butyldimethylsilyl)ethynyl)-1*H*-indole-6-carboxylic acid (S7): A solution of **S6** (5.50 g, 13.3 mmol) in MeOH (700 ml) and 2 M NaOH aq.(140 ml) was stirred at 60 ºC. After 3 h, 1 M HCl aqueous solution was added to adjust pH to 6 ~ 7. After removing the volatiles under reduced pressure, water was added and the mixture was diluted with Et_2O. 1 M HCl was then added to adjust pH to 1 ~ 2, and the organic layer was separated. The aqueous phase was further extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$, and concentrated *in vacuo* to afford crude **S7** (3.88 g, 12.9 mmol, ca. 97% yield) as white solid. The obtained crude **S7** was used for the next reaction without further purification.



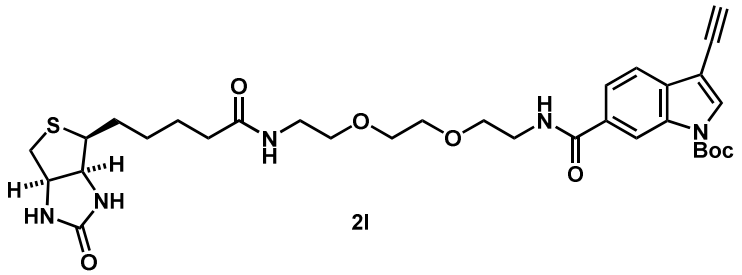
S9

***N*-(2-(2-(2-aminoethoxy)ethoxy)ethyl)-3-((*tert*-butyldimethylsilyl)ethynyl)-1*H*-indole-6-carboxamide (S9)**: A solution of **S7** (3.88 g, 12.9 mmol), EDC (2.72 g, 14.2 mmol) and HOBt (2.17 g, 14.2 mmol) in DMF (50 ml) was stirred at room temperature for 12 h. The volatiles were removed under vacuum and the concentrated mixture was dissolved in $CHCl_3$ (200 ml). The resulting solution was added dropwise to a stirred solution of 2,2'-(ethylenedioxy)bis(ethylamine) (**S8**, 11.4 ml, 78 mmol) in $CHCl_3$ (300 ml). The mixture was stirred at room temperature for 22 h, and the organic layer was washed with brine (500 ml) and 1 M NaOH aqueous solution (200 ml), again with brine (500ml x 5). The organic layer was dried over $MgSO_4$ and concentrated under vacuum to afford crude **S9** (4.66 g, 10.9 mmol, ca. 84% yield over 2 steps), which was used for the next reaction without further purification.



S11

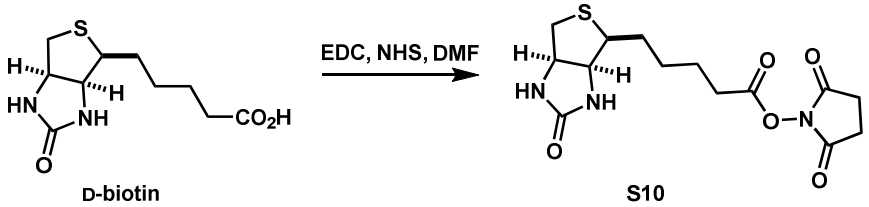
3-((*tert*-butyldimethylsilyl)ethynyl)-*N*-(2-(2-(2-(5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)pentanamido)ethoxy)ethoxy)ethyl)-1*H*-indole-6-carboxamide (S11): A solution of **S10** (3.52 g, ca. 10.4 mmol) and **S9** (4.66 g, 10.9 mmol) in dioxane (150 ml) was stirred at room temperature for 17 h. Then, the volatiles were removed under reduced pressure and the resulting crude was dissolved in CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ aqueous solution and brine, dried over $MgSO_4$ and concentrated to give a residue, which was only partially purified by silica gel chromatography (CH_2Cl_2/MeOH = 10/1) to afford partially isolated **S11** in ca. 73% yield (5.20 g, 7.93 mmol).



2l

***tert*-butyl**

3-ethynyl-6-((2-(2-(2-(5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)pentanamido)ethoxy) ethoxy)ethyl)carbamoyl)-1*H*-indole-1-carboxylate (2l): To a solution of crude **S11** (5.20 g, 7.93 mmol) in Et_3N (60 ml) and THF (290 ml), Boc_2O (2 ml, 8.72 mmol) and DMAP (50 mg, 0.4 mmol) were added. The mixture was stirred at room temperature for 20 h. Boc_2O (0.19 ml, 0.87 mmol) was then added and the mixture was stirred for 1 h. The reaction mixture was cooled to 0 ºC, and TBAF (1 M in THF, 16 ml) was added. The mixture was stirred at 0 ºC for 2 h. Then, saturated NH_4Cl aqueous solution was added to quench the reaction, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The resulting crude was purified by silica gel chromatography (CH_2Cl_2/MeOH = 10/1) to give **2l** as white solid in ca. 80% yield (4.1 g, 6.4 mmol, 48% yield over 5 steps). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.61 (s, 1H), 7.85 (s, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.16 (br, 1H), 6.80 – 6.65 (m, 2H), 5.89 (br, 1H), 4.50 – 4.35 (m, 1H), 4.25 – 4.10 (m, 1H), 3. 80 – 3.45 (m, 10H), 3.45 – 3.35 (m, 2H), 3.27 (s, 1H), 3.09 – 2.98 (m, 1H), 2.81 (dd, *J* = 12.6 Hz, 4.6 Hz), 2.67 (d, *J* = 12.6 Hz, 1H), 2.13 (t, *J* = 7.4 Hz, 2H), 1.68 – 1.50 (m, 13H), 1.38 – 1. 26 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.5, 167.8, 164.3, 148.7, 134.2, 132.9, 131.9, 131.7, 122.2, 120.0, 114.7, 102.3, 85.1, 81.4, 75.2, 70.2, 70.1, 70.0, 69.9, 61.8, 60.2, 55.7, 40.5, 40.0, 39.1, 36.0, 28.3, 28.2, 28.1, 25.6; IR (neat, cm^{-1}) 3274, 2928, 1739, 1697, 1636, 1540, 1473, 1433, 1367, 1323, 1251, 1226, 1153, 1082, 835, 765; ESI-MS: *m*/*z* 664.3 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_{32}H_{43}N_5O_7S$ $[M+Na]^+$: 664.2775. Found: 664.2803. $[\alpha]_D^{25}$ 29.9 (c = 1.17, CH_3OH)



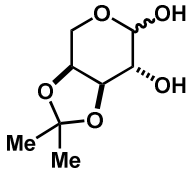
D-biotin **S10**

2,5-dioxopyrrolidin-1-yl

5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)pentanoate (S10):

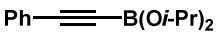
Prepared following the procedure reported by S. Q. Yao.[7] A solution of D-biotin (3.00 g, 12.3 mmol), EDC (2.82 g, 14.7 mmol) and NHS (1.70 g, 14.7 mmol) in DMF (100 ml) was stirred at room temperature overnight. The reaction mixture was then concentrated under reduced pressure and the residue was filtered and washed with EtOH/AcOH/H_2O (95:1:4). The obtained **S10** (3.96 g, 11.6 mmol, ca. 94% yield) was used for the next reaction without further purification.

3-3. Synthesis of other substrates



3,4-*O*-Isopropylidene-L-arabinopyranose (1h)

This arabinose derivative was prepared following the reported procedures.[8]



diisopropyl (phenylethynyl)boronate (2m)

Prepared following the reported procedures.

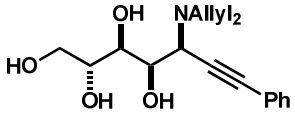
4. Analytical Data for Products of Catalytic Aminoalkynylation Reactions

Diastereoselectivity of the reactions was ca. 1:1, unless otherwise stated. Stereochemical assignment of the products from each aldose and ethynylbenzene[10] was performed through derivatization to the corresponding cyclic compounds and NOE analysis (section 5). For other products, stereochemistry was tentatively assigned based on ^{1}H NMR analysis.

4-1. Products from D-arabinose (3aa ~ 3ak)

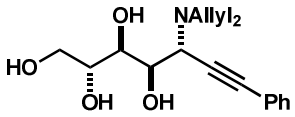
The reactions were performed with D-arabinose (42.0 mg, 280 μmol) and the corresponding alkyne following the general procedures in section 2 unless otherwise stated. Purification of the products was performed by chromatography on silica gel (CH_2Cl_2/MeOH = 80/1 to 5/1). Separation of diastereomers was performed with additional chromatography (CH_2Cl_2/MeOH = 80/1 to 5/1) on silica gel or preparative TLC method (CH_2Cl_2/MeOH = 20/1 ~ 10/1).

3aa: 77.9 mg of **3aa** (235 μmol, y. 84%) was obtained using 92.2 μl of **2a** (840 μmol, 3 equiv) as alkyne substrate.



(2*R*,3*S*,4*R*,5*S*)-5-(diallylamino)-7-phenylhept-6-yne-1,2,3,4-tetraol (3aa-LP)

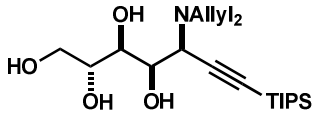
^{1}H NMR (CD_3OD, 400 MHz) δ 7.46 – 7.40 (m, 2H), 7.35 – 7.30 (m, 3H), 5.99 – 5.85 (m, 2H), 5.27 (d, J = 17.4 Hz, 2H), 5.18 (d, J = 10.1 Hz, 2H), 4.07 (d, J = 10.1 Hz, 1H), 4.00 (d, J = 10.1 Hz, 1H), 3.83 (dd, J = 11.4, 2.3 Hz, 1H), 3.76 – 3.70 (m, 2H), 3.64 (dd, J = 11.4, 5.0 Hz, 1H), 3.54 – 3.42 (m, 2H), 3.09 (dd, J = 14.6, 8.7 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ 136.9, 132.7, 129.4, 124.0,
118.5, 88.6, 84.7, 72.8, 71.9, 70.0, 65.0, 56.4, 55.3; IR (neat, cm^{-1}) 3373, 2926, 1419, 1088, 755; ESI-MS: *m*/*z* 332.0 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{19}H_{25}NO_4$ $[M+H]^+$: 332.1856. Found: 332.1863. $[\alpha]_D^{28}$ 106.1 (c = 0.81, CH_3OH)



(2*R*,3*S*,4*R*,5*R*)-5-(diallylamino)-7-phenylhept-6-yne-1,2,3,4-tetraol (3aa-MP)

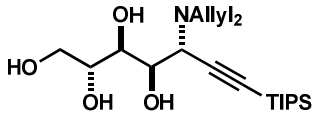
^{1}H NMR (CD_3OD, 400 MHz) δ 7.49 – 7.41, (m, 2H), 7.35 – 7.26 (m, 3H), 5.97 – 5.82 (m, 2H), 5.23 (d, *J* = 17.4 Hz, 2H), 5.12 (d, *J* = 10.5 Hz, 2H), 4.08 – 3.97 (m, 2H), 3.91 (d, *J* = 8.7 Hz, 1H), 3.82 (dd, *J* = 11.5, 2.8 Hz, 1H), 3.76 – 3.68 (m, 1H), 3.63 (dd, *J* = 11.5, 6.4 Hz, 1H), 3.37 (dd, *J* = 14.2, 4.6 Hz, 2H), 3.02 (dd, *J* = 14.2, 8.2 Hz, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ 137.5, 132.7, 129.3, 129.0, 124.8, 117.8, 87.4, 87.0, 73.0, 71.5, 70.9, 65.2, 56.7, 55.8; IR (neat, cm^{-1}) 3329, 2926, 1084, 1025, 906, 748; ESI-MS: *m*/*z* 332.2 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{19}H_{25}NO_4$ $[M+H]^+$: 332.1856. Found: 332.1861. $[\alpha]_D^{28}$ -112.4 (c = 0.62, CH_3OH).

3ab: 97.6 mg of **3ab** (237 μmol, y. 85%) was obtained using 187 μl of **2b** (840 μmol, 3 equiv) as alkyne substrate.



(2*R*,3*S*,4*R*,5*S*)-5-(diallylamino)-7-(triisopropylsilyl)hept-6-yne-1,2,3,4-tetraol (3ab-LP)

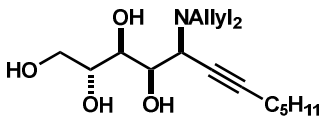
^{1}H NMR (CD_3OD, 400 MHz) δ 5.96 – 5.82 (m, 2H), 5.20 (d, *J* = 17.4 Hz, 2H), 5.15 (d, *J* = 10.1 Hz, 2H), 3.90 (brs, 2H), 3.81 (dd, *J* = 11.5, 3.2 Hz, 1H), 3.76 – 3.66 (m, 2H), 3.56 (dd, *J* = 11.5, 6.0 Hz, 1H), 3.41 (dd, *J* = 14.2, 6.0 Hz, 2H), 3.03 (dd, *J* = 14.2, 8.7 Hz, 2H), 1.10 (brs, 21H); ^{13}C NMR (CD_3OD, 100 MHz) δ 136.9, 118.3, 103.8, 89.1, 73.0, 72.2, 70.0, 65.3, 56.7, 55.4, 19.1, 12.4; IR (neat, cm^{-1}) 3391, 2941, 2864, 2360, 2162, 1457, 1086, 1010, 919, 882; ESI-MS: *m*/*z* 412.0 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{41}NO_4Si$ $[M+H]^+$: 412.2878. Found: 412.2868. $[\alpha]_D^{29}$ 40.5 (c = 1.03, CH_3OH)



(2*R*,3*S*,4*R*,5*R*)-5-(diallylamino)-7-(triisopropylsilyl)hept-6-yne-1,2,3,4-tetraol (3ab-MP)

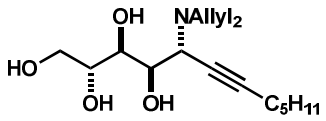
^{1}H NMR (CD_3OD, 400 MHz) δ 5.93 – 5.79 (m, 2H), 5.16 (d, *J* = 16.5 Hz, 2H), 5.09 (d, *J* = 10.0 Hz, 2H), 3.95 (dd, *J* = 9.6, 0.88 Hz, 1H), 3.86 – 3.77 (m, 3H), 3.71 – 3.62 (m, 1H), 3.60 (dd, *J* = 11.0, 5.9 Hz, 1H), 3.34 – 3.31 (m, 2H), 2.96 (dd, *J* = 14.2, 8.7 Hz, 2H), 1.12 (brs, 21H); ^{13}C NMR (CD_3OD, 100 MHz) δ 137.6, 117.7, 106.4, 86.6, 72.9, 71.4, 70.9, 65.2, 56.8, 55.8, 19.1, 12.5; IR (neat, cm^{-1}) 3375, 2941, 2864, 2165,1459, 1079, 918, 883; ESI-MS: *m*/*z* 412.0 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{41}NO_4Si$ $[M+H]^+$: 412.2878. Found: 412.2868. $[\alpha]_D^{26}$ -60.8 (c = 0.58, CH_3OH)

3ac: 71.5 mg of **3ac** (237 μmol, y. 79%) was obtained using 43.7 μl of **2c** (336 μmol, 1.2 equiv) as alkyne substrate.



(2*R*,3*S*,4*R*,5*S*)-5-(diallylamino)dodec-6-yne-1,2,3,4-tetraol (3ac-LP)

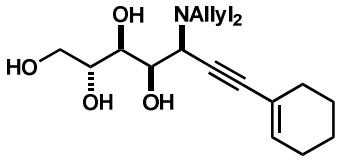
^{1}H NMR (CD_3OD, 500 MHz) δ 5.84 – 5.72 (m, 2H), 5.12 (d, *J* = 16.6 Hz, 2H), 5.05 (d, *J* = 10.3 Hz, 2H), 3.78 – 3.68 (m, 3H), 3.68 – 3.58 (m, 1H), 3.55 – 3.46 (m, 2H), 3.32 – 3.24 (m, 2H), 2.88 (dd, *J* = 14.3, 8.6 Hz, 2H), 2.14 (dd, *J* = 6.9, 1.7 Hz, 2H), 1.47 – 1.40 (m, 2H), 1.38 – 1.30 (m, 2H), 1.30 – 1.21 (m, 2H), 0.83 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 1137.1, 118.1, 88.9, 75.1, 73.0, 71.9, 70.1, 65.2, 56.0, 55.2, 32.1, 29.6, 23.2, 19.3, 14.3; IR (neat, cm^{-1}) 2929, 2361, 2339, 1087, 918; ESI-MS: *m*/*z* 326.2 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{18}H_{31}NO_4$ $[M+H]^+$: 326.2326. Found: 326.2336. $[\alpha]_D^{28}$ 48.9 (c = 0.92, CH_3OH)



(2*R*,3*S*,4*R*,5*R*)-5-(diallylamino)dodec-6-yne-1,2,3,4-tetraol (3ac-MP)

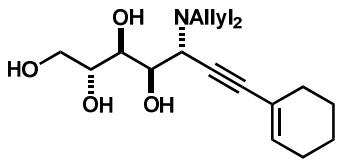
^{1}H NMR (CD_3CN, 500 MHz) δ 5.86 – 5.76 (m, 2H), 5.18 (d, *J* = 16.1 Hz, 2H), 5.09 (d, *J* = 9.8 Hz, 2H), 3.77 (d, *J* = 9.1 Hz, 1H), 3.71 (d, *J* = 6.9 Hz, 1H), 3.68 – 3.60 (m, 2H), 3.58 – 3.48 (m, 2H), 3.29 – 3.20 (m, 2H), 3.10 (brs, 2H), 2.89 (dd, *J* = 13.7, 8.0 Hz, 2H), 2.81 (brs, 1H), 2.22 (td, *J* = 4.6, 2.3 Hz, 2H), 2.10 (brs, 1H), 1.57 – 1.48 (m, 2H), 1.46 – 1.36 (m, 2H), 1.38 – 1.30 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 137.8, 117.5, 87.2, 77.1, 73.2, 71.7, 71.1, 65.2, 56.3, 55.7, 32.2, 29.8, 23.2, 19.4, 14.4; IR (neat, cm^{-1}) 3331, 2929, 1651, 1085, 904; ESI-MS: *m*/*z* 326.2 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{18}H_{31}NO_4$ $[M+H]^+$: 326.2326. Found: 326.2340. $[\alpha]_D^{26}$ -63.9 (c = 0.44, CH_3OH)

3ad: 71.0 mg of **3ad** (212 μmol, y. 76%) was obtained using 39.5 μl of **2d** (336 μmol, 1.2 equiv) as alkyne substrate.



(2*R*,3*S*,4*R*,5*S*)-7-(cyclohex-1-en-1-yl)-5-(diallylamino)hept-6-yne-1,2,3,4-tetraol (3ad-LP)

^{1}H NMR (CD_3OD, 500 MHz) δ 6.09 – 6.04 (m, 1H), 5.92 – 5.86 (m, 2H), 5.22 (d, *J* = 15.5 Hz, 2H), 5.14 (d, *J* = 10.5 Hz, 2H), 3.92 (d, *J* = 9.5 Hz, 1H), 3.87 (d, *J* = 9.5 Hz, 1H), 3.81 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.75 – 3.69 (m, 1H), 3.64 – 3.58 (m, 2H), 3.42 – 3.36 (m, 2H), 2.98 (dd, *J* = 14.0, 8.0 Hz, 2H), 2.14 – 2.06 (m, 4H), 1.68 – 1.56 (m, 4H); ^{13}C NMR (CD_3OD, 125 MHz) δ 137.3, 135.7, 121.9, 118.5, 90.7, 82.0, 73.2, 72.2, 70.4, 65.4, 56.7, 55.5, 30.8, 26.7, 23.7, 22.9; IR (neat, cm^{-1}) 3421, 2948, 2361, 1646, 1017; ESI-MS: *m*/*z* 335.9 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{19}H_{29}NO_4$ $[M+H]^+$: 336.2169 .Found: 336.2164. $[\alpha]_D^{29}$ 25.0 (c = 0.26, CH_3OH)

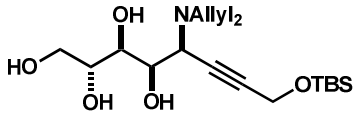


(2*R*,3*S*,4*R*,5*R*)-7-(cyclohex-1-en-1-yl)-5-(diallylamino)hept-6-yne-1,2,3,4-tetraol (3ad-MP)

^{1}H NMR (CD_3OD, 400 MHz) δ 6.08 – 6.04 (m, 1H), 5.92 – 5.79 (m, 2H), 5.18 (d, *J* = 17.4 Hz, 2H), 5.09 (d, *J* = 10.6 Hz, 2H), 3.91 (d, *J* = 9.6 Hz, 1H), 3.89 – 3.82 (m, 2H), 3.79 (dd, *J* = 11.0, 3.7 Hz, 1H), 3.72 – 3.62 (m, 1H), 3.60 (dd, *J* = 11.4, 5.9 Hz, 1H), 3.32 – 3.22 (m, 2H), 2.91 (dd, *J* = 14.2, 8.2 Hz, 2H), 2.18 – 2.05 (m, 4H), 1.69 –

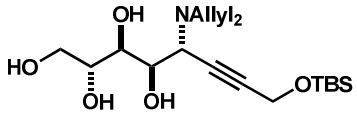
1.56 (m, 4H); ^{13}C NMR (CD_3OD, 100 MHz) δ 137.7, 134.6, 122.1, 117.6, 88.9, 84.1, 73.1, 71.6, 71.0, 65.2, 56.6, 55.7, 30.7, 26.5, 23.5, 22.7; IR (neat, cm^{-1}) 3357, 2930, 1418, 1082, 1027, 916; ESI-MS: *m/z* 336.0 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{19}H_{29}NO_4$ $[M+H]^+$: 336.2169. Found: 336.2170. $[\alpha]_D^{29}$ -78.3 (c = 0.26, CH_3OH)

3ae: 91.3 mg of **3ae** (228 μmol, y. 81%) was obtained using 68.1 μl of **2e** (336 μmol, 1.2 equiv) as alkyne substrate.



(2*R*,3*S*,4*R*,5*S*)-8-((*tert*-butyldimethylsilyl)oxy)-5-(diallylamino)oct-6-yne-1,2,3,4-tetraol (3ae-LP)

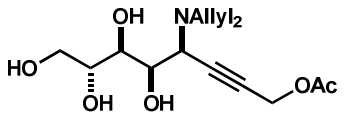
^{1}H NMR (CD_3OD, 400 MHz) δ 5.94 – 5.80 (m, 2H), 5.22 (d, *J* = 17.4 Hz, 2H), 5.15 (d, *J* = 10.1 Hz, 2H), 4.38 (s, 2H), 3.88 (brs, 2H), 3.81 (dd, *J* = 11.0, 3.7 Hz, 1H), 3.75 – 3.65 (m, 1H), 3.65 – 3.55 (m, 2H), 3.44 – 3.36 (m, 2H), 3.00 (dd, *J* = 14.2, 8.7 Hz, 2H), 0.92 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (CD_3OD, 100 MHz) δ 137.0, 118.3, 87.2, 80.2, 72.9, 72.0, 69.8, 65.2, 55.8, 55.3, 52.5, 26.2, 19.1, -4.9; IR (neat, cm^{-1}) 3365, 2928, 1255, 1080, 920, 835, 778; ESI-MS: *m/z* 399.8 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{20}H_{37}NO_5Si$ $[M+Na]^+$: 422.2333. Found: 422.2318. $[\alpha]_D^{28}$ 36.5 (c = 0.44, CH_3OH)



(2*R*,3*S*,4*R*,5*R*)-8-((*tert*-butyldimethylsilyl)oxy)-5-(diallylamino)oct-6-yne-1,2,3,4-tetraol (3ae-MP)

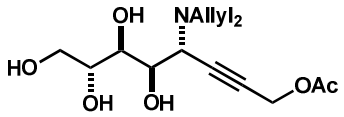
^{1}H NMR (CD_3CN, 400 MHz) δ 5.87 – 5.73 (m, 2H), 5.19 (d, *J* = 16.5 Hz, 2H), 5.10 (d, *J* = 10.5 Hz, 2H), 4.37 (d, *J* = 1.8 Hz, 2H), 3.82 (d, *J* = 9.6 Hz, 1H), 3.74 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.68 (dt, *J* = 9.6, 1.8 Hz, 1H), 3.64 (brs, 1H), 3.58 – 3.49 (m, 2H), 3.29 – 3.20 (m, 2H), 3.15 (brs, 2H) 2.90 (dd, *J* = 14.7, 8.7 Hz, 2H), 2.80 (brs, 1H), 0.90 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (CD_3OD, 125 MHz) δ 137.7, 117.7, 85.4, 82.6, 73.1, 71.4, 70.9, 65.2, 56.2, 55.7, 52.7, 26.2, 19.1, -4.9; IR (neat, cm^{-1}) 3375, 2929, 2857, 1255, 1079, 918, 836; ESI-MS: *m/z* 340.0 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{20}H_{37}NO_5Si$ $[M+Na]^+$: 422.2333. Found: 422.2351. $[\alpha]_D^{29}$ -54.3 (c = 0.47, CH_3OH)

3af: 66.0 mg of **3af** (201 μmol, y. 72%) was obtained using 33.3 μl of **2f** (336 μmol, 1.2 equiv) as alkyne substrate.



(4*S*,5*R*,6*S*,7*R*)-4-(diallylamino)-5,6,7,8-tetrahydroxyoct-2-yn-1-yl acetate (3af-LP)

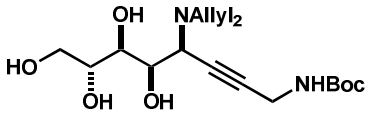
^{1}H NMR (CD_3CN, 500 MHz) δ 5.92 – 5.82 (m, 2H), 5.22 (d, *J* = 17.1 Hz, 2H), 5.14 (d, *J* = 10.2 Hz, 2H), 4.68 (d, *J* = 1.15 Hz, 2H), 3.78 – 3.72 (m, 2H), 3.70 – 3.61 (m, 1H), 3.59 – 3.49 (m, 3H), 3.45 (d, *J* = 8.0 Hz, 1H), 3.38 – 3.30 (m, 2H), 2.99 – 2.91 (m, 3H), 2.03 (s, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 172.0, 137.0, 118.5, 83.0, 82.2, 72.9, 71.9, 69.9, 65.2, 56.1, 55.3, 53.2, 20.6; IR (neat, cm^{-1}) 3390, 2928, 1743, 1225, 1087, 1026, 923; ESI-MS: *m/z* 328.1 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{16}H_{25}NO_6$ $[M+H]^+$: 328.1755. Found: 328.1745. $[\alpha]_D^{25}$ 51.2 (c = 1.23, CH_3OH)



(4*R*,5*R*,6*S*,7*R*)-4-(diallylamino)-5,6,7,8-tetrahydroxyoct-2-yn-1-yl acetate (3af-MP)

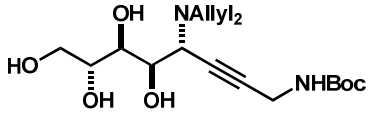
^{1}H NMR (CD_3CN, 400 MHz) δ 5.93 – 5.78 (m, 2H), 5.21 (d, *J* = 17.9 Hz, 2H), 5.11 (d, *J* = 10.1 Hz, 2H), 4.72 (d, *J* = 1.8 Hz, 2H) 3.86 (d, *J* = 9.2 Hz, 1H), 3.79 (d, *J* = 6.0 Hz, 1H), 3.74 (dd, *J* = 9.2, 1.8 Hz, 1H), 3.73 – 3.65 (m, 1H), 3.65 – 3.54 (m, 2H), 3.34 – 3.23 (m, 2H), 3.19 – 2.91 (m, 5H), 2.7 (brs, 1H), 2.04 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ 172.0, 137.5, 117.7, 84.5, 81.0, 73.0, 71.2, 70.8, 65.2, 56.2, 55.6, 53.4, 20.6; IR (neat, cm^{-1}) 3357, 2935, 1746, 1378, 1227, 1082, 1026, 921; ESI-MS: *m/z* 328.1 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{16}H_{25}NO_6$ $[M+H]^+$: 328.1755. Found: 328.1753. $[\alpha]_D^{28}$ -79.0 (c = 0.53, CH_3OH)

3ag: 87.4 mg of **3ag** (227 μmol, y. 81%) was obtained using 52.1 mg of **2g** (336 μmol, 1.2 equiv) as alkyne substrate.



***tert*-butyl ((4*S*,5*R*,6*S*,7*R*)-4-(diallylamino)-5,6,7,8-tetrahydroxyoct-2-yn-1-yl)carbamate (3ag-LP)**

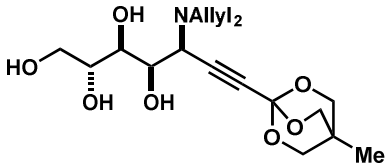
^{1}H NMR (CD_3OD, 400 MHz) δ 5.90 – 5.76 (m, 2H), 5.20 (d, *J* = 17.4 Hz, 2H), 5.10 (d, *J* = 10.5 Hz, 2H), 3.86 – 3.76 (m, 5H), 3.70 – 3.64 (m, 1H), 3.60 – 3.51 (m, 2H), 3.40 – 3.33 (m, 2H), 2.96 (dd, *J* = 14.2, 8.2 Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (CD_3OD, 100 MHz) δ 158.0, 137.0, 118.3, 85.4, 80.5, 77.6, 72.9, 71.9, 69.9, 65.1, 55.9, 55.2, 30.9, 28.7; IR (neat, cm^{-1}) 3336, 2929, 2360, 1968, 1540, 1165, 1085, 919; ESI-MS: *m/z* 385.2 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{19}H_{32}N_2O_6$ $[M+H]^+$: 385.2333. Found: 385.2335. $[\alpha]_D^{27}$ 46.9 (c = 1.24, CH_3OH)



***tert*-butyl ((4*R*,5*R*,6*S*,7*R*)-4-(diallylamino)-5,6,7,8-tetrahydroxyoct-2-yn-1-yl)carbamate (3ag-MP)**

^{1}H NMR (CD_3CN, 400 MHz, 60 ºC) δ 5.90 – 5.76 (m, 2H), 5.20 (d, *J* = 17.4 Hz, 2H), 5.10 (d, *J* = 10.5 Hz, 2H), 3.89 – 3.80 (m, 3H), 3.76 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.72 – 3.64 (m, 2H), 3.64 – 3.52 (m, 2H), 3.32 – 3.21 (m, 2H), 2.95 (dd, *J* = 14.7, 7.8 Hz, 2H), 1.43 (s, 9H); ^{13}C NMR (CD_3OD, 100 MHz, 60 °C) δ 156.7, 137.5, 117.8, 84.5, 80.1, 79.7, 73.3, 71.7, 71.5, 65.0, 56.8, 55.6, 31.4, 28.8; IR (neat, cm^{-1}) 3357, 2938, 2362, 1716, 1697, 1168, 1081, 918; ESI-MS: *m/z* 385.1 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{19}H_{32}N_2O_6$ $[M+H]^+$: 385.2333. Found: 385.2335. $[\alpha]_D^{27}$ -58.6 (c = 0.44,
CH_3OH)

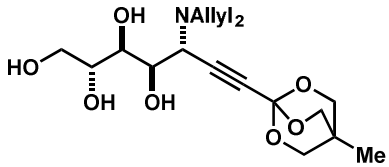
3ah: 83.1 mg of **3ah** (217 μmol, y. 78%) was obtained using 51.8 mg of **2h** (336 μmol, 1.2 equiv) as alkyne substrate.



(2*R*,3*S*,4*R*,5*S*)-5-(diallylamino)-7-(4-methyl-2,6,7-trioxabicyclo[2.2.2]octan-1-yl)hept-6-yne-1,2,3,4-tetraol (3ah-LP)

^{1}H NMR (CD_3OD, 400 MHz) δ 5.91 – 5.77 (m, 2H), 5.24 (d, *J* = 17.0 Hz, 2H), 5.15 (d, *J* = 10.1 Hz, 2H), 3.94 (s, 6H), 3.89 (d, *J* = 4.1 Hz, 2H), 3.80 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.75 – 3.65 (m, 1H), 3.65 – 3.52 (m, 2H), 3.38 (dd, *J* = 14.3, 4.6 Hz, 2H), 2.97 (dd, *J* = 14.3, 8.2 Hz, 2H), 0.80 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ 136.8, 118.6, 103.0, 82.9, 77.8, 74.0, 72.9, 71.9, 69.6, 65.1, 55.5, 55.2, 31.0, 14.1; IR (neat, cm^{-1}) 3373, 2882, 1313, 1044, 988; ESI-MS: *m*/*z* 384.0 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{19}H_{29}NO_7$ $[M+H]^+$: 384.2017. Found: 384.2016. $[\alpha]_D^{29}$ 18.5 (c = 0.50, CH_3OH)

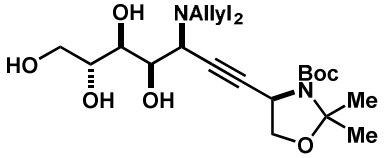
(2*R*,3*S*,4*R*,5*R*)-5-(diallylamino)-7-(4-methyl-2,6,7-trioxabicyclo[2.2.2]octan-1-yl)hept-6-yne-1,2,3,4-tetraol



(3ah-MP)

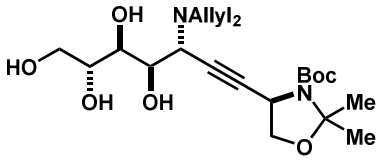
^{1}H NMR (CD_3OD, 400 MHz) δ 5.88 – 5.75 (m, 2H), 5.19 (d, *J* = 17.4 Hz, 2H), 5.09 (d, *J* = 10.1 Hz, 2H), 3.96 (s, 6H), 3.94 (d, *J* = 3.2 Hz, 1H), 3.84 – 3.75 (m, 3H), 3.68 – 3.61 (m, 1H), 3.59 (dd, *J* = 11.5, 6.4 Hz, 1H), 3.30 – 3.22 (m, 2H), 2.89 (dd, *J* = 14.2, 8.7 Hz, 2H), 0.81 (s, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ 137.5, 117.9, 103.1, 80.9, 80.8, 74.0, 72.9, 70.9, 70.7, 65.2, 55.9, 55.6, 31.0, 14.2; IR (neat, cm^{-1}) 3365, 2930, 1313, 1043, 979, 930; ESI-MS: *m*/*z* 384.0 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{19}H_{29}NO_7$ $[M+H]^+$: 384.2017. Found: 384.2018. $[\alpha]_D^{29}$ -117.1(c = 0.26, CH_3OH)

3ai: 53.3 mg of **3ai** (118 μmol, y. 84%) was obtained from 21.0 mg of D-arabinose (140 μmol) using **2i** (168 μmol in 168 μl of dioxane, 1.2 equiv) as alkyne substrate.



(*R*)-*tert*-butyl 4-((3*S*,4*R*,5*S*,6*R*)-3-(diallylamino)-4,5,6,7-tetrahydroxyhept-1-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (3ai-LP) (Diastereoselectivity: **3ai -LP**/**3ai -MP** = 1.9)

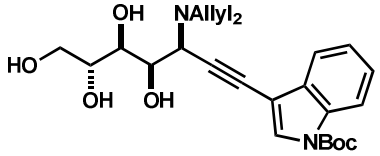
^{1}H NMR (CD_3OD, 400 MHz, 60 ºC) δ 5.96 – 5.80 (m, 2H), 5.20 (d, *J* = 17.8 Hz, 2H), 5.13 (d, *J* = 10.6 Hz, 2H), 4.61 (d, *J* = 4.9 Hz, 1H), 4.07 (dd, *J* = 9.0, 5.9 Hz, 1H), 3.97 (dd, *J* = 9.0, 1.8 Hz, 1H), 3.85 (brs, 2H), 3.80 (dd, *J* = 11.4, 3.7 Hz, 1H), 3.76 – 3.65 (m, 1H), 3.64 – 3.56 (m, 2H), 3.38 (dd, *J* = 14.2, 4.6 Hz, 2H), 3.03 (dd, *J* = 14.2, 8.2 Hz, 2H), 1.61 (s, 3H), 1.50 (s, 9H), 1.48 (s, 3H); ^{13}C NMR (CD_3CN, 100 MHz, 75 ºC) δ 152.6, 137.1, 118.3, 95.1, 88.5, 81.2, 77.6, 73.4, 72.4, 70.2, 65.2, 56.3, 55.3, 49.8, 29.0, 27.3, 25.3; IR (neat, cm^{-1}) 3375, 2979, 1455, 1384, 1172, 1087, 1054, 920; ESI-MS: *m*/*z* 455.1 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{23}H_{38}N_2O_7$ $[M+H]^+$: 455.2752. Found: 455.2741. $[\alpha]_D^{27}$ -15.5 (c = 1.40, CH_3OH)



(*R*)-*tert*-butyl 4-((3*R*,4*R*,5*S*,6*R*)-3-(diallylamino)-4,5,6,7-tetrahydroxyhept-1-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (3ai-MP)

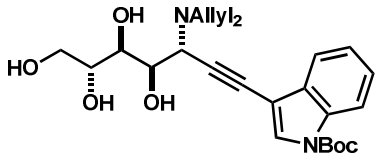
^{1}H NMR (CD_3CN, 400 MHz, 75 ºC) δ 5.94 – 5.80 (m, 2H), 5.20 (d, *J* = 16.5 Hz, 2H), 5.11 (d, *J* = 10.5 Hz, 2H), 4.62 (d, *J* = 6.0 Hz, 1H), 4.08 (dd, *J* = 8.7, 6.0 Hz, 1H), 3.96 (dt, *J* = 8.7, 2.3 Hz, 1H), 3.85 (d, *J* = 8.7 Hz, 1H), 3.81 – 3.66 (m, 3H), 3.65 – 3.54 (m, 2H), 3.30 (dd, *J* = 14.6, 5.0 Hz, 2H), 3.12 (brs, 2H), 3.00 (dd, *J* = 14.6, 7.8 Hz, 2H), 2.70 (brs. 1H), 1.62 (s, 3H), 1.50 (s, 9H), 1.49 (s, 3H); NMR (CD_3CN, 100 MHz, 70 ºC) δ 152.8, 137.7, 117.8, 95.2, 87.3, 73.6, 72.0, 71.9, 70.3, 68.8, 65.2, 57.2, 55.8, 50.0, 29.0, 27.3, 25.4; IR (neat, cm^{-1}) 3383, 2978, 1700, 1383, 1171, 1086, 1055, 918; ESI-MS: *m*/*z* 455.1 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{23}H_{38}N_2O_7$ $[M+H]^+$: 455.2752. Found: 455.2745. $[\alpha]_D^{27}$ -61.0 (c = 0.442, CH_3OH)

3aj: 126 mg of **3aj** (268 μmol, y. 96%) was obtained using **2j** (336 μmol in 448 μl of dioxane, 1.2 equiv) as alkyne substrate.



***tert*-butyl 3-((3*S*,4*R*,5*S*,6*R*)-3-(diallylamino)-4,5,6,7-tetrahydroxyhept-1-yn-1-yl)-1*H*-indole-1-carboxylate (3aj-LP)**

^{1}H NMR (CD_3OD, 400 MHz) δ 8.12 (d, *J* = 8.2Hz, 1H), 7.77 (s, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.39 – 7.26 (m, 2H), 6.03 – 5.86 (m, 2H), 5.29 (d, *J* = 17.0 Hz, 2H), 5.19 (d, *J* = 10.6 Hz, 2H), 4.16 (d, *J* = 9.8 Hz, 1H), 4.06 (d, *J* = 9.8 Hz, 1H), 3.85 (dd, *J* = 11.3, 2.7 Hz, 1H), 3.82 – 3.74 (m, 2H), 3.66 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.52 (dd, *J* = 14.6, 4.6 Hz, 2H), 3.14 (dd, *J* = 14.6, 8.7 Hz, 2H), 1.66 (s, 9H); ^{13}C NMR (CD_3OD, 100 MHz) δ 1503., 137.0, 135.9, 131.8, 129.89, 126.2, 124.3, 120.8, 118.5, 116.2, 104.1, 88.5, 85.7, 80.1, 72.9, 72.0, 70.2, 65.1, 56.8, 55.4, 28.3; IR (neat, cm^{-1}) 3367, 2977, 1737, 1452, 1371, 1231, 1156, 1098, 1047, 921; ESI-MS: *m*/*z* 471.1 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{26}H_{34}N_2O_6$ $[M+H]^+$: 471.2490. Found: 471.2478. $[\alpha]_D^{27}$ 76.1 (c = 0.80, CH_3OH)

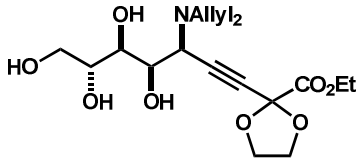


***tert*-butyl 3-((3*R*,4*R*,5*S*,6*R*)-3-(diallylamino)-4,5,6,7-tetrahydroxyhept-1-yn-1-yl)-1*H*-indole-1-carboxylate (3aj-MP)**

^{1}H NMR (CD_3OD, 400 MHz) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.76 (s, 1H), 7.68 (d, *J* = 6.9 Hz, 1H), 7.37 – 7.27 (m, 2H), 5.99 – 5.84 (m, 2H), 5.25 (d, *J* = 17.4 Hz, 2H), 5.13 (d, *J* = 10.1 Hz, 2H), 4.08 (brs, 2H), 3.93 (d, *J* = 8.7 Hz, 1H), 3.83 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.78 – 3.69 (m, 1H), 3.64 (dd, *J* = 11.4, 6.4 Hz, 1H), 3.41 (dd, *J* = 14.2 4.6 Hz, 2H), 3.08 (dd, *J* = 14.2, 8.7 Hz, 2H), 1.67 (s, 9H); ^{13}C NMR (CD_3OD, 100 MHz) δ 150.1, 137.6, 135.9, 132.1,

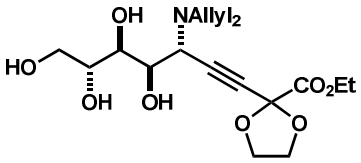
129.4, 126.1, 124.2, 120.9, 117.5, 116.2, 104.9, 91.1, 85.5, 78.2, 73.1, 71.6, 71.0, 65.2, 57.0, 55.9, 28.3; IR (neat, cm^{-1}) 3347, 2978, 1736, 1452, 1371, 1231, 1156, 1098; ESI-MS: *m/z* 471.0 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{26}H_{34}N_2O_6$ $[M+H]^+$: 471.2490. Found: 471.2476. $[\alpha]_D^{25}$ -91.3 (c = 0.24, CH_3OH)

3ak: 109 mg of **3ak** (273 μmol, y. 96%) was obtained using **2k** (336 μmol in 336 μl of dioxane, 1.2 equiv) as alkyne substrate.



ethyl 2-((3*S*,4*R*,5*S*,6*R*)-3-(diallylamino)-4,5,6,7-tetrahydroxyhept-1-yn-1-yl)-1,3-dioxolane-2-carboxylate (3ak-LP)

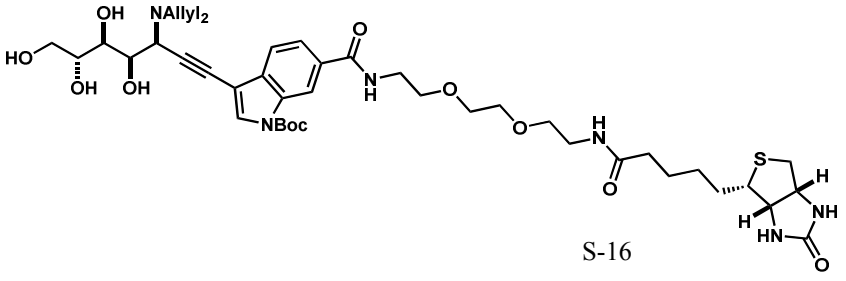
^1H NMR (CD_3OD, 400 MHz) δ 5.96 – 5.80 (m, 2H), 5.24 (d, *J* = 16.5 Hz, 2H), 5.16 (d, *J* = 9.6 Hz, 2H), 4.26 (q, *J* = 7.3 Hz, 2H), 4.18 – 4.03 (m, 4H), 3.92 (brs, 2H), 3.80 (dd, *J* = 11.5, 3.2 Hz, 1H), 3.75 – 3.68 (m, 1H), 3.64 – 3.54 (m, 2H), 3.45 – 3.35 (m, 2H), 3.02 (dd, *J* = 14.2, 8.2 Hz, 2H), 1.31 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ 167.8, 136.8, 118.5, 99.3, 83.4, 82.8, 72.8, 72.0, 69.7, 67.1, 65.1, 63.6, 55.9, 55.3, 14.4; IR (neat, cm^{-1}) 3392, 2903, 1749, 1558, 1088, 1026, 945; ESI-MS: *m/z* 399.9 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{19}H_{29}NO_8$ $[M+H]^+$: 400.1966. Found: 400.1973. $[\alpha]_D^{26}$ 48.2 (c = 1.65, CH_3OH)



ethyl 2-((3*R*,4*R*,5*S*,6*R*)-3-(diallylamino)-4,5,6,7-tetrahydroxyhept-1-yn-1-yl)-1,3-dioxolane-2-carboxylate (3ak-MP)

^1H NMR (CD_3CN, 400 MHz, 60 ºC) δ 5.96 – 5.80 (m, 2H), 5.24 (d, *J* = 16.5 Hz, 2H), 5.16 (d, *J* = 9.6 Hz, 2H), 4.26 (q, *J* = 7.3 Hz, 2H), 4.18 – 4.03 (m, 4H), 3.92 (brs, 2H), 3.80 (dd, *J* = 11.5, 3.2 Hz, 1H), 3.75 – 3.68 (m, 1H), 3.64 – 3.54 (m, 2H), 3.45 – 3.35 (m, 2H), 3.18 (brs, 1H), 3.12 – 2.90 (m, 4H), 2.74 (brs, 1H), 1.31 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ 167.8, 136.8, 118.5, 99.3, 83.4, 82.8, 72.8, 72.0, 69.7, 67.1, 65.1, 63.6, 55.9, 55.3, 14.4; IR (neat, cm^{-1}) 3392, 2903, 1749, 1558, 1088, 1026, 945; ESI-MS: *m/z* 399.9 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{19}H_{29}NO_8$ $[M+H]^+$: 400.1966. Found: 400.1973. $[\alpha]_D^{26}$ -64.7 (c = 0.73, CH_3OH)

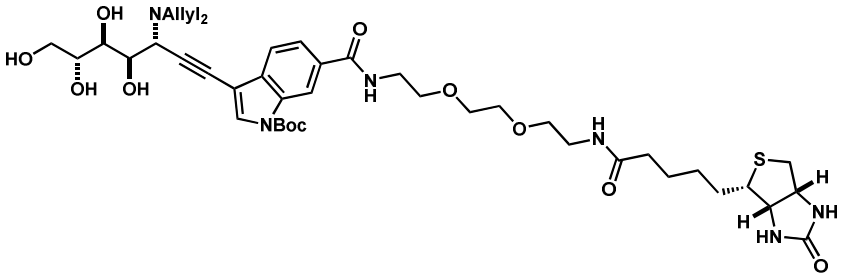
3al: 76.8 mg of **3al** (88.1 μmol, y. 66%) was obtained from 20.0 mg of **1a** (133 μmol) using **2l** (103 mg, 160 μmol, 1.2 equiv) and 17.0 mg of $P(C_6F_5)_3$ (32.0 mmol, 24 mol%) at 40 °C for 30 h under otherwise standard conditions described in section 2. Purification was performed by column chromatography on silica gel. (DCM/MeOH = 6.5 to 5.5).



***tert*-butyl**

3-((3*S*,4*R*,5*S*,6*R*)-3-(diallylamino)-4,5,6,7-tetrahydroxyhept-1-yn-1-yl)-6-((2-(2-(2-(5-((3a*S*,4*R*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-d]imidazol-4-yl)pentanamido)ethoxy)ethoxy)ethyl)carbamoyl)-1*H*-indole-1-carboxylate (3al-LP)

^{1}H NMR (CD_3OD, 500 MHz) δ 8.69 (s, 1H), 7.94 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 6.02 – 5.90 (m, 2H), 5.30 (d, *J* = 17.1 Hz, 2H), 5.20 (d, *J* = 10.3 Hz, 2H), 4.45 (dd, *J* = 7.7 Hz, 5.0 Hz, 1H), 4.23 (dd, *J* = 7.7 Hz, 4.2 Hz, 1H), 4.17 (d, *J* = 9.7 Hz, 1H), 4.07 (d, *J* = 9.7 Hz, 1H), 3.85 (dd, *J* = 11.4 Hz, 2.9 Hz, 1H), 3.83 – 3.75 (m, 1H), 3.74 – 3.59 (m, 10H), 3.58 – 3.50 (m, 4H), 3.33 (t, *J* = 5.1 Hz, 1H), 3.19 – 3.06 (m, 3H), 2.88 (dd, *J* = 12.6 Hz, 5.0 Hz, 1H), 2.68 (d, *J* = 12.6 Hz, 1H), 2.13 (t, *J* = 7.1 Hz, 2H), 1.75 – 1.49 (m, 13 H), 1.40 – 1.30 (m, 2H); ^{13}C NMR (CD_3OD, 125 MHz) δ 176.0, 170.6, 166.0, 150.0, 137.0, 135.5, 134.3, 132.9, 132.2, 123.2, 120.8, 118.5, 116.1, 104.0, 89.1, 86.3, 79.6, 72.9, 72.0, 71.3, 70.6, 70.1, 65.1, 63.3, 61.5, 56.9, 56.8, 55.4, 41.0, 40.3, 36.6, 29.7, 29.4, 28.3, 26.7; IR (neat, cm^{-1}) 3397, 2935, 2222, 1738, 1644, 1548, 1475, 1434, 1372, 1324, 1255, 1233, 1154, 1102, 1026, 926, 887, 837, 766; ESI-MS: *m*/*z* 893.5 [M +Na]$^+$; ESI-HRMS: *m*/*z* calcd for $C_{43}H_{62}N_6O_{11}S$ [M+Na]$^+$: 893.4089. Found: 893.4052. $[\alpha]_D^{25}$ 59.8 (c = 0.77, CH_3OH)



***tert*-butyl**

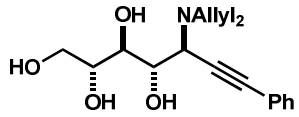
3-((3*R*,4*R*,5*S*,6*R*)-3-(diallylamino)-4,5,6,7-tetrahydroxyhept-1-yn-1-yl)-6-((2-(2-(2-(5-((3a*S*,4*R*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)pentanamido)ethoxy)ethoxy)ethyl)carbamoyl)-1*H*-indole-1-carboxylate (3al-MP)

^{1}H NMR (CD_3OD, 500 MHz) δ 8.68 (s, 1H), 7.92 (s, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 6.00 – 5.88 (m, 2H), 5.26 (d, *J* = 16.6 Hz, 2H), 5.14 (d, *J* = 9.7 Hz, 2H), 4.45 (dd, *J* = 8.0 Hz, 4.3 Hz, 1H), 4.24 (dd, *J* = 8.0 Hz, 4.5 Hz, 1H), 4.10 (s, 2H), 3.94 (d, *J* = 8.6, 1H), 3.84 (dd, *J* = 10.9 Hz, 3.4 Hz, 1H), 3.79 – 3.60 (m, 10H), 3.54 (t, *J* = 5.4 Hz, 2H), 3.46 – 3.39 (m, 2H), 3.33 (t, *J* = 5.4 Hz, 2H), 3.14 – 3.04 (m, 3H), 2.88 (dd, *J* = 12.6 Hz, 4.3 Hz, 1H), 2.69 (d, *J* = 12.6 Hz, 1H), 2.13 (t, *J* = 7.1 Hz, 2H), 1.80 – 1.45 (m, 13H), 1.40 – 1.30 (m, 2H); ^{13}C NMR (CD_3OD, 125 MHz) δ 176.2, 170.8, 166.2, 150.2, 137.8, 135.7, 134.7, 132.9, 132.0, 123.3, 121.1, 118.0, 116.2, 104.9, 91.9, 86.3, 77.8, 73.2, 71.8, 71.5, 71.1, 70.7, 65.4, 63.4, 61.7, 57.2, 57.1, 56.1, 41.2, 40.4, 36.8, 29.8, 29.6, 28.4, 26.9; IR (neat, cm^{-1}) 3304, 2932, 1738, 1691, 1642, 1548, 1474, 1434, 1372, 1323, 1255, 1232, 1155, 1102, 1030, 922, 887, 850, 766; ESI-MS: *m*/*z* 893.2 [M+Na]$^+$; ESI-HRMS: *m*/*z* calcd for $C_{43}H_{62}N_6O_{11}S$ [M+Na]$^+$: 893.4089. Found: 893.4058. $[\alpha]_D^{24}$ -27.8 (c = 1.16, CH_3OH).

4-2. Products from D-ribose (3ba, 3bj)

Reactions were performed with D-ribose (42.0 mg, 280 μmol), diallylamine (104 μl, 840 μmol, 3 equiv) and the corresponding alkyne following the general procedures in section 2. Purification of the products was performed by chromatography on silica gel (CH_2Cl_2/MeOH = 80/1 to 5/1).

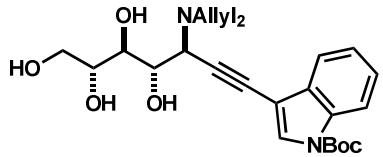
3ba: 44.0 mg of **3ba** (132 μmol, y. 47%) was obtained using 92.2 μl of **2a** (840 μmol, 3 equiv) as alkyne substrate.



(2*R*,3*S*,4*S*,5*S*)-5-(diallylamino)-7-phenylhept-6-yne-1,2,3,4-tetraol (3ba)

^{1}H NMR (CD_3OD, 500 MHz, 55 ºC) δ 7.50 – 7.45 (m, 2H), 7.35 – 7.30 (m, 3H), 5.94 – 5.87 (m, 2H), 5.28 (d, *J* = 17.2 Hz, 2H), 5.22 (d, *J* = 10.3 Hz, 2H), 4.14 (d, *J* = 8.0 Hz, 1H), 3.85 (t, *J* = 5.7 Hz, 1H), 3.86 – 3.82 (m, 1H), 3.80 – 3.72 (m, 2H), 3.68 (dd, *J* = 12.0, 6.3 Hz, 1H), 3.52 (dd, *J* = 14.0, 4.6 Hz, 2H), 3.10 (dd, *J* = 14.0, 8.6 Hz, 2H); ^{13}C NMR (CD_3OD, 125 MHz) δ 136.1, 132.8, 129.4, 129.3, 124.3,119.3, 88.0, 84.9, 76.5, 74.8, 72.6, 64.0, 59.2, 55.9; IR (neat, cm^{-1}) 3346, 2912, 1597, 1489, 1418, 1057, 922, 755, 691; ESI-MS: *m*/*z* 332.1 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{19}H_{25}NO_4$ $[M+H]^+$: 332.1856. Found: 332.1862. $[\alpha]_D^{27}$ 85.9 (c = 0.73, CH_3OH)

3bj: 67.1 mg of **3bj** (143 μmol, y. 51%) was obtained using **2j** (840 μmol in 1.12 ml of dioxane, 3 equiv) as alkyne substrate.



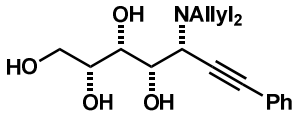
***tert*-butyl 3-((3*S*,4*S*,5*S*,6*R*)-3-(diallylamino)-4,5,6,7-tetrahydroxyhept-1-yn-1-yl)-1*H*-indole-1-carboxylate (3bj)**

^{1}H NMR (CD_3OD, 400 MHz) δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.80 (s, 1H), 7.67 (d, *J* = 6.8 Hz, 1H), 7.37 – 7.26 (m, 2H), 5.99 -5.86 (m, 2H), 5.29 (d, *J* = 17.0 Hz, 2H), 5.22 (d, *J* = 10.6 Hz, 2H), 4.22 (d, *J* = 7.8 Hz, 1H), 3.91 (t, *J* = 7.8 Hz, 1H), 3.89 – 3.83 (m, 1H), 3.82 – 3.74 (m, 2H), 3.70 (dd, *J* = 11.9, 6.4 Hz, 1H), 3.56 (dd, *J* = 14.2, 5.0 Hz, 2H), 3.13 (dd, *J* = 14.2, 8.7 Hz, 2H), 1.66 (s, 9H); ^{13}C NMR (CD_3OD, 100 MHz) δ 150.3, 136.2, 135.8, 131.8, 129.9, 126.1, 124.2, 120.9, 119.3, 116.1, 104.3, 88.5, 85.5, 79.5, 76.5, 74.8, 72.7, 64.0, 59.3, 55.9, 28.2; IR (neat, cm^{-1}) 3359, 2977, 1737, 1452, 1371, 1306, 1231, 1156, 1049, 923, 746, 600; ESI-MS: *m*/*z* 470.9 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{26}H_{34}N_2O_6$ $[M+H]^+$: 471.2490. Found: 471.2474. $[\alpha]_D^{27}$ 41.4 (c = 0.84, CH_3OH)

4-3. Products from D-xylose (3ca)

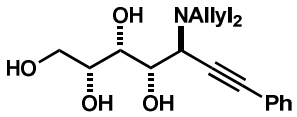
Reactions were performed with D-xylose (42.0 mg, 280 μmol), diallylamine (36.5 μl, 336 μmol, 1.2 equiv) and **2a** (92.2 μl, 840 μmol) following the general procedures in section 2. Purification of the products was performed by chromatography on silica gel (CH_2Cl_2/MeOH = 80/1 to 5/1). Separation of diastereomers was performed with additional chromatography on silica gel (CH_2Cl_2/MeOH = 80/1 to 5/1).

3ca: 38.4 mg of **3ca** (116 μmol, y. 41%) was obtained.



(2*R*,3*R*,4*S*,5*R*)-5-(diallylamino)-7-phenylhept-6-yne-1,2,3,4-tetraol (3ca-LP)

(dr: **3ca-LP**/**3ca-MP** = 2.3); ^{1}H NMR (CD_3OD, 500 MHz) δ 7.45 – 7.39 (m, 2H), 7.34 – 7.28 (m, 3H), 5.94 – 5.86 (m, 2H), 5.26 (d, *J* = 17.0 Hz, 2H), 5.17 (d, *J* = 10.1 Hz, 2H), 4.09 (d, *J* = 9.4 Hz, 1H), 3.90 (d, *J* = 4.9 Hz, 1H), 3.85 -3.78 (m, 2H), 3.70 (dd, *J* = 11.8, 4.5 Hz, 1H), 3.65 – 3.59 (m, 1H), 3.47 (d, *J* = 14.0, Hz, 2H), 3.07 (dd, *J* = 14.0, 8.6 Hz, 2H); ^{13}C NMR (CD_3OD, 125 MHz) δ 137.0, 132.7, 129.4, 124.1, 118.4, 88.6, 84.8, 75.3, 72.4, 71.6, 63.9, 56.7, 55.4; IR (neat, cm^{-1}) 3393, 1698, 1558, 1507, 1068, 920, 755; ESI-MS: *m*/*z* 332.1 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{19}H_{25}NO_4$ $[M+H]^+$: 332.1856. Found: 332.1863. $[\alpha]_D^{27}$ -66.2 (c = 0.87, CH_3OH)



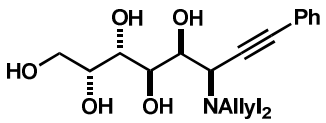
(2*R*,3*R*,4*S*,5*S*)-5-(diallylamino)-7-phenylhept-6-yne-1,2,3,4-tetraol (3ca-MP)

^{1}H NMR (CD_3OD, 500 MHz) δ 7.44 – 7.36 (m, 2H), 7.30 – 7.23 (m, 3H), 5.91 – 5.82 (m, 2H), 5.18 (d, *J* = 17.0 Hz, 2H), 5.08 (d, *J* = 10.0 Hz, 2H), 4.01 (d, *J* = 8.9 Hz, 1H), 3.99 – 3.94 (m, 1H), 3.85 (d, *J* = 8.9 Hz, 1H), 3.78 – 3.71 (m, 1H), 3.65 (dd, *J* = 11.1, 4.6 Hz, 1H), 3.58 (dd, *J* = 11.1, 5.8 Hz, 1H), 3.35 (dd, *J* = 14.2, 4.2 Hz, 2H), 3.02 (dd, *J* = 14.2, 8.0 Hz, 2H); ^{13}C NMR (CD_3OD, 125 MHz) δ 137.3, 132.6, 129.3, 129.0, 124.7, 117.7, 87.2, 87.0, 74.7, 73.1, 71.0, 64.2, 57.2, 55.9 ; IR (neat, cm^{-1}) 3364, 2926, 1683, 1558, 1071, 920, 757, 691; ESI-MS: *m*/*z* 332.0 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{19}H_{25}NO_4$ $[M+H]^+$: 332.1856. Found: 332.1863. $[\alpha]_D^{27}$ 53.6 (c = 1.36, CH_3OH)

4-4. Products from D-galactose (3ea, 3ee)

Reactions were performed with D-galactose (50.4 mg, 280 μmol), diallylamine (104 μl, 840 μmol, 3 equiv) and the corresponding alkyne following the general procedures in section 2 unless otherwise stated. Purification of the products was performed by chromatography on silica gel (CH_2Cl_2/MeOH = 80/1 to 5/1). Separation of diastereomers was performed with additional chromatography on silica gel (CH_2Cl_2/MeOH = 80/1 to 5/1) or preparative TLC method (CH_2Cl_2/MeOH = 20/1 ~10/1).

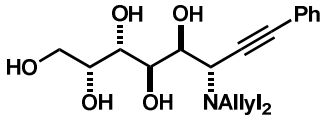
3ea: 56.0 mg of **3ea** (137 μmol, y. 50%) was obtained using **2a** (840 μmol, 3 equiv) as alkyne substrate.



(2*R*,3*S*,4*R*,5*S*,6*R*)-6-(diallylamino)-8-phenyloct-7-yne-1,2,3,4,5-pentaol (3ea-LP)

^{1}H NMR (CD_3OD, 500 MHz) δ 7.46 – 7.40 (m, 2H), 7.34 – 7.28 (m, 3H), 5.98 – 5.82 (m, 2H), 5.26 (d, *J* = 17.1 Hz, 2H), 5.17 (d, *J* = 10.1 Hz, 2H), 4.09 (d, *J* = 9.8 Hz, 1H), 4.03 (d, *J* = 9.8 Hz, 1H), 3.95 (t, *J* = 6.3 Hz, 1H),

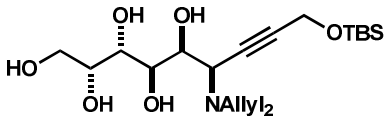
3.90 (d, *J* = 9.3 Hz, 1H), 3.73 (d, *J* = 6.3 Hz, 1H), 3.66 (d, *J* = 9.3 Hz, 2H), 3.49 (dd, *J* = 14.1, 4.6 Hz, 2H), 3.10 (dd, *J* = 14.1, 8.3 Hz, 2H); ^{13}C NMR (CD_3OD, 125 MHz) δ 137.0, 132.7, 129.4, 129.3, 124.1, 118.3, 88.6, 85.0, 71.7, 71.5, 71.1, 70.1, 65.1, 56.7, 55.3 IR (neat, cm^{-1}) 3853, 3648, 1652, 1540, 1507, 1339, 1080, 600; ESI-MS: *m*/*z* 362.0 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{20}H_{27}NO_5$ $[M+H]^+$: 362.1962. Found: 362.1965. $[\alpha]_D^{27}$ -88.4 (c = 0.64, CH_3OH)



(2*R*,3*S*,4*R*,5*S*,6*S*)-6-(diallylamino)-8-phenyloct-7-yne-1,2,3,4,5-pentaol (3ea-MP)

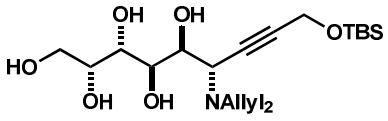
^{1}H NMR (CD_3OD, 500 MHz) δ 7.49 – 7.41 (m, 2H), 7.34 – 7.28 (m, 3H), 5.97 – 5.86 (m, 2H), 5.23 (d, *J* = 17.1 Hz, 2H), 5.12 (d, *J* = 10.1 Hz, 2H), 4.10 – 4.00 (m, 3H), 3.93 (t, *J* = 6.3 Hz, 1H), 3.69 (d, *J* = 6.1 Hz, 1H), 3.66 (d, *J* = 6.3 Hz, 2H), 3.37 (dd, *J* = 14.1, 4.2 Hz, 2H), 3.05 (dd, *J* = 14.1, 8.3 Hz, 2H); ^{13}C NMR (CD_3OD, 125 MHz) δ 137.6, 132.7, 129.3, 128.9, 124.9, 117.7, 87.6, 87.0, 71.9, 71.6, 70.2, 65.0, 57.0, 55.8; IR (neat, cm^{-1}) 3347, 2921, 1418, 1087, 918, 754, 690; ESI-MS: *m*/*z* 362.0 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{20}H_{27}NO_5$ $[M+H]^+$: 362.1962. Found: 362.1969. $[\alpha]_D^{27}$ 64.7 (c = 0.49, CH_3OH)

3ee: 56.2 mg of **3ee** (131 μmol, y. 47%) was obtained using **2e** (840 μmol, 3 equiv) as alkyne substrate.



(2*R*,3*S*,4*R*,5*S*,6*R*)-9-((*tert*-butyldimethylsilyl)oxy)-6-(diallylamino)non-7-yne-1,2,3,4,5-pentaol (3ee-LP)

^{1}H NMR (CD_3OD, 400 MHz) δ 5.78 – 5.64 (m, 2H), 5.07 (d, *J* = 17.9 Hz, 2H), 5.01 (d, *J* = 10.5 Hz, 2H), 4.24 (d, *J* = 1.6 Hz, 2H), 3.83 – 3.75 (m, 3H), 3.63 (d, *J* = 9.6 Hz, 1H), 3.54 (dd, *J* = 9.6, 1.6 Hz, 1H), 3.52 – 3.46 (m, 2H), 3.30 – 3.22 (m, 2H), 2.87 (dd, *J* = 14.2, 8.7 Hz, 2H), 0.77 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (CD_3OD, 100 MHz) δ 137.0, 118.3, 87.2, 80.3, 71.2, 71.4, 71.0, 69.9, 65.1, 56.0, 55.3, 52.5, 26.2, 19.1, -4.9; IR (neat, cm^{-1}) 3335, 2928, 1636, 1540, 1507, 1256, 1081, 918, 836, 777; ESI-MS: *m*/*z* 430.1 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{21}H_{39}NO_6Si$ $[M+H]^+$: 430.2619. Found: 430.2612. $[\alpha]_D^{27}$ -34.8 (c = 0.38, CH_3OH)



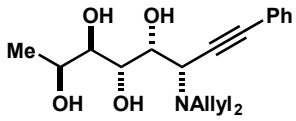
(2*R*,3*S*,4*R*,5*S*,6*S*)-9-((*tert*-butyldimethylsilyl)oxy)-6-(diallylamino)non-7-yne-1,2,3,4,5-pentaol (3ee-MP)

^{1}H NMR (CD_3CN, 400 MHz) δ 5.87 – 5.78 (m, 2H), 5.20 (d, *J* = 17.2 Hz, 2H), 5.11 (d, *J* = 10.3 Hz, 2H), 4.38 (d, *J* = 1.7 Hz, 2H), 3.85 (d, *J* = 9.1 Hz, 1H), 3.83 (d, *J* = 8.6 Hz, 1H) 3.80 – 3.70(m, 1H), 3.69 (dt, *J* = 9.7, 1.7 Hz, 1H), 3.58 – 3.50 (m, 3H), 3.30 – 3.22 (m, 2H), 3.16 (brs, 2H), 3.05 (brs, 1H), 2.96 – 2.88 (m, 3H), 0.91 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (CD_3OD, 100 MHz, 55 ºC) δ 137.6, 117.6, 85.7, 82.7, 72.2, 72.0, 71.7, 70.5, 65.1, 56.8, 55.8, 52.7, 26.3, 19.1, -4.9; IR (neat, cm^{-1}) 3365, 2928, 1652, 1540, 1507, 1255, 1078, 918, 836, 777; ESI-MS: *m*/*z* 430.4 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{21}H_{39}NO_6Si$ $[M+H]^+$: 430.2619. Found: 430.2612. $[\alpha]_D^{27}$ 36.3 (c = 0.51, CH_3OH)

4-5. Products from L-fucose (3fa, 3fg, 3fi)

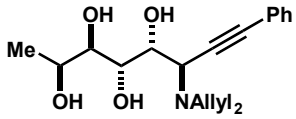
Reactions were performed with L-fucose (46.0 mg, 280 μmol), diallylamine (36.5 μl, 336 μmol, 1.2 equiv) and the corresponding alkyne following the general procedures in section 2 unless otherwise stated. Purification of the products was performed by chromatography on silica gel (CH_2Cl_2/MeOH = 80/1 to 5/1). Separation of diastereomers was performed with additional chromatography on silica gel (CH_2Cl_2/MeOH = 80/1 to 5/1) or preparative TLC method (CH_2Cl_2/MeOH = 20/1 ~ 5/1).

3fa: 48.5 mg of **3fa** (140 μmol, y. 50%) was obtained using **2a** (840 μmol, 3 equiv) as alkyne substrate.



(2*S*,3*R*,4*S*,5*R*,6*S*)-6-(diallylamino)-8-phenyloct-7-yne-2,3,4,5-tetraol (3fa-LP)

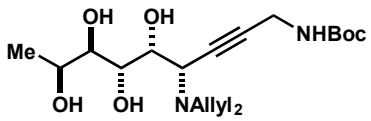
^{1}H NMR (CD_3OD, 500 MHz) δ 7.48 – 7.40 (m, 2H), 7.35 – 7.28 (m, 3H), 5.96 – 5.84 (m, 2H), 5.26 (d, *J* = 17.4 Hz, 2H), 5.17 (d, *J* = 10.1 Hz, 2H), 4.12 – 4.06 (m, 2H), 4.02 (d, *J* = 9.4 Hz, 1H), 3.86 (d, *J* = 9.1 Hz, 1H), 3.52 – 3.43 (m, 3H), 3.10 (dd, *J* = 14.3, 8.2 Hz, 2H), 1.24 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 137.0, 132.7, 129.4, 129.3, 124.1, 118.3, 88.6, 85.0, 74.8, 71.4, 70.3, 67.3, 56.6, 55.3, 20.1; IR (neat, cm^{-1}) 3374, 3078, 2975, 2929, 2852, 1489, 1444, 1418, 1300, 1101, 994, 921, 756; ESI-MS: *m*/*z* 345.9 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{20}H_{27}NO_4$ $[M+H]^+$: 346.2013. Found: 346.2016. $[\alpha]_D^{27}$ 105.8 (c = 0.85, CH_3OH)



(2*S*,3*R*,4*S*,5*R*,6*S*)-6-(diallylamino)-8-phenyloct-7-yne-2,3,4,5-tetraol (3fa-MP)

^{1}H NMR (CD_3OD, 500 MHz) δ 7.48 -7.41 (m, 2H), 7.33 – 7.27 (m, 3H), 5.97 – 5.83 (m, 2H), 5.23 (d, *J* = 17.0 Hz, 2H), 5.11 (d, *J* = 10.1 Hz, 2H), 4.10 – 3.98 (m, 4H), 3.45 (dd, *J* = 8.9, 1.8 Hz, 1H) 3.37 (dd, *J* = 14.0, 4.3 Hz, 2H), 3.04 (dd, *J* = 14.0, 8.2 Hz, 2H), 1.24 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 137.4, 132.6, 129.3, 128.9, 124.8, 117.6, 87.5, 87.0, 75.1, 71.8, 70.4, 67.5, 56.9, 55.8, 20.0; IR (neat, cm^{-1}) 3365, 2817, 2360, 1509, 1403, 1095, 1030, 913, 755; ESI-MS: *m*/*z* 345.9 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{20}H_{27}NO_4$ $[M+H]^+$: 346.2013. Found: 346.2017. $[\alpha]_D^{27}$ -97.3 (c = 0.48, CH_3OH)

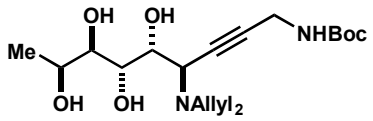
3fg: 69.7 mg of **3fg** (179 μmol, y. 64%) was obtained using 130 mg of **2g** (840 μmol, 3 equiv) as alkyne substrate.



***tert*-butyl ((4*S*,5*R*,6*S*,7*R*,8*S*)-4-(diallylamino)-5,6,7,8-tetrahydroxynon-2-yn-1-yl)carbamate (3fg-LP)**

^{1}H NMR (CD_3OD, 400 MHz, 55 ºC) δ 5.84 – 5.72 (m, 2H), 5.12 (d, *J* = 17.6 Hz, 2H), 5.04 (d, *J* = 10.5 Hz, 2H), 3.95 (qd, *J* = 6.9, 2.3 Hz, 1H), 3.81 – 3.71 (m, 4H), 3.64 (d, *J* = 9.2 Hz, 1H), 3.36 (dd, *J* = 9.2, 2.3 Hz, 1H), 3.28 (dd, *J* = 14.2, 5.0 Hz, 2H), 2.94 (dd, *J* = 14.2, 7.8 Hz, 2H), 1.35 (s, 9H), 1.14 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (CD_3CN, 100 MHz, 75 ºC) δ 157.9, 137.1, 118.3, 85.3, 80.4, 77.6, 74.7, 71.3, 70.1, 67.3, 56.0, 55.2, 30.9, 28.7,

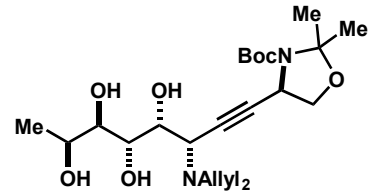
20.0; IR (neat, cm^{-1}) 3336, 2976, 2931, 1716, 1698, 1507, 1281, 1107, 1041, 994, 921, 860; ESI-MS: *m/z* 399.0 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{20}H_{34}N_2O_6$ $[M+H]^+$: 399.2490. Found: 399.2487. $[\alpha]_D^{27}$ 43.2 (c = 1.16, CH_3OH)



***tert*-butyl ((4*R*,5*R*,6*S*,7*R*,8*S*)-4-(diallylamino)-5,6,7,8-tetrahydroxynon-2-yn-1-yl)carbamate (3fg-MP)**

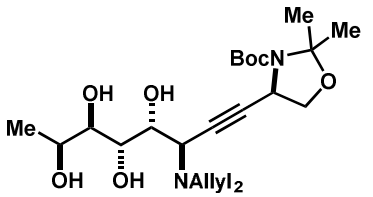
^1H NMR (CD_3CN, 400 MHz, 75 ºC) δ 5.91 – 5.79 (m, 2H), 5.33 (brs, 1H), 5.21 (d, *J* = 17.9 Hz, 2H), 5.11 (d, *J* = 10.6 Hz, 2H), 4.00 – 3.90 (m, 1H), 3.89 – 3.80 (m, 4H), 3.71 (dt, *J* = 9.2, 1.8 Hz, 1H), 3.35 (dd, *J* = 8.2, 2.7 Hz, 1H), 3.32 – 3.24 (m, 2H), 3.12 – 2.94 (m, 5H), 1.44 (s, 9H), 1.18 (d, *J* = 6.4 Hz, 3H), ; ^{13}C NMR (CD_3CN, 100 MHz, 75 ºC) δ 156.9, 137.7 117.8, 84.8, 80.3 80.0, 76.1, 72.1, 71.2, 68.0, 57.2, 55.8, 31.6, 28.9, 20.4; IR (neat, cm^{-1}) 3336, 2976, 2930, 2376, 2310, 1715, 1697, 1520, 1507, 1366, 1251, 1168, 1047, 918; ESI-MS: *m/z* 399.0 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{20}H_{34}N_2O_6$ $[M+H]^+$: 399.2490. Found: 399.2490. $[\alpha]_D^{27}$ -55.0 (c = 0.52, CH_3OH)

3fi: 55.4 mg of **3fi** (118 μmol, y. 84%) was obtained from 23.0 mg of L-fucose (140 μmol) using **2i** (420 μmol in 420 μl of dioxane, 3 equiv) as alkyne substrate.



(*R*)-*tert*-butyl 4-((3*S*,4*R*,5*S*,6*R*,7*S*)-3-(diallylamino)-4,5,6,7-tetrahydroxyoct-1-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (3fi-LP) (*dr*: **3fi-LP**/**3fi-MP** = 1.9)

^1H NMR (CD_3OD, 400 MHz, 55 ºC) δ 5.94 – 5.80 (m, 2H), 5.20 (d, *J* = 17.8 Hz, 2H), 5.13 (d, *J* = 10.1 Hz, 2H), 4.61 (d, *J* = 6.0 Hz, 1H), 4.12 – 4.00 (m, 2H), 3.97 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.91 – 3.83 (m, 2H), 3.72 (d, *J* = 8.7 Hz, 1H), 3.45 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.39 (d, *J* = 14.4 Hz, 2H), 3.04 (dd, *J* = 14.4, 10.2 Hz, 2H), 1.61 (s, 3H), 1.50 (s, 9H), 1.47 (s, 3H), 1.23 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (CD_3CN, 125 MHz, 75 ºC) δ 152.7, 137.2, 118.3, 95.2, 88.5, 81.3, 77.8, 76.1, 71.9, 70.6, 70.3, 68.0, 56.5, 55.8, 55.4, 49.9, 29.1, 27.4, 25.3, 20.5; IR (neat, cm^{-1}) 3749, 3648, 2978, 2933, 1698, 1558, 1375, 1172, 1087, 1054, 918; ESI-MS: *m/z* 469.3 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{24}H_{40}N_2O_7$ $[M+H]^+$: 469.2908. Found: 469.2896. $[\alpha]_D^{27}$ -10.6 (c = 1.63, CH_3OH)



(*R*)-*tert*-butyl 4-((3*R*,4*R*,5*S*,6*R*,7*S*)-3-(diallylamino)-4,5,6,7-tetrahydroxyoct-1-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (3fi-MP)

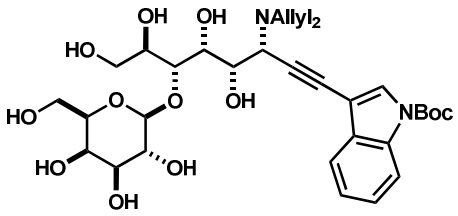
^1H NMR (CD_3CN, 400 MHz, 75 ºC) δ 5.86 – 5.74 (m, 2H), 5.15 (d, *J* = 16.9 Hz, 2H), 5.06 (d, *J* = 10.1 Hz, 2H),

4.56 (d, *J* = 6.0 Hz, 1H), 4.06 – 3.98 (m, 1H), 3.94 – 3.86 (m, 2H), 3.84 – 3.75 (m, 2H), 3.69 (d, *J* = 8.7 Hz, 1H), 3.31 (dd, *J* = 8.2, 2.8 Hz, 1H), 3.28 – 3.20 (m, 2H), 3.02 – 2.80 (m, 5H), 1.57 (s, 3H), 1.45 (s ,9H), 1.44 (s, 3H), 1.14 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (CD_3CN, 100 MHz, 75 ºC) δ 152.8, 137.6, 117.9, 95.2, 87.3, 81.3, 76.14, 76.10, 72.2, 71.3, 70.3, 68.0, 57.2, 55.8, 50.0, 29.0, 27.3, 25.5, 20.4; IR (neat, cm^{-1}) 3749, 3628, 3545, 2977, 2926, 2365, 2304, 1698, 1540, 1507, 1375, 1171, 1056, 918; ESI-MS: *m*/*z* 469.2 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{24}H_{40}N_2O_7$ $[M+H]^+$: 469.2908. Found: 469.2894. $[\alpha]_D^{27}$ -68.3 (c = 0.87, CH_3OH).

4-6. Products from β-D-lactose (3gj)

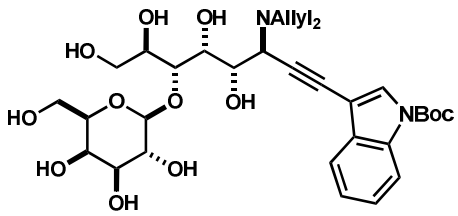
Reactions were performed with β-D-lactose (47.9 mg, 140 μmol), diallylamine (17.3 μl, 140 μmol, 1 equiv), alkyne **2j** (420 μmol in 420 μl of dioxane, 3 equiv), CuBr (6.03 mg, 42.0 μmol, 30 mol %), and $P(C_6F_5)_3$ (26.8 mg, 50.4 μmol, 36 mol %) at 70 °C for 36 h with otherwise the standard procedures in section 2. Purification of the products was performed by chromatography on silica gel (CH_2Cl_2/MeOH = 6/1 to 5/1). Separation of diastereomers was performed with additional chromatography on silica gel (CH_2Cl_2/MeOH = 6/1 to 5/1).

3gi: 68.3 mg of **3gj** (103 μmol, y. 74%) was obtained.



***tert*-butyl 3-((3*R*,4*S*,5*R*,6*R*,7*R*)-3-(diallylamino)-4,5,7,8-tetrahydroxy-6-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)oct-1-yn-1-yl)-1*H*-indole-1-carboxylate (3gj-LP)** (*dr*: **3gj-LP**/**3gj-MP** = 1.5)

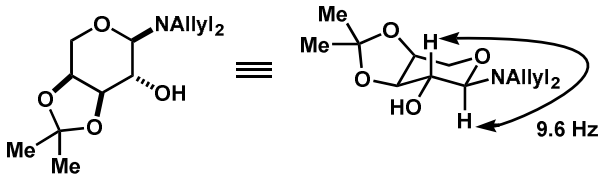
^{1}H NMR (CD_3OD, 400 MHz) δ 8.10 (d, *J* = 8.2 Hz, 1H), 7.79 (s, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.33 (m, 2H), 6.01 – 5.89 (m, 2H), 5.30 (d, *J* = 17.4 Hz, 2H), 5.20 (d, *J* = 9.8 Hz, 2H), 4.51 (d, *J* = 6.6 Hz, 1H), 4.26 (d, *J* = 9.2 Hz, 1H), 4.15 (d, *J* = 6.4 Hz, 1H), 4.04 (t, *J* = 6.4 Hz, 1H), 4.00 – 3.91 (m, 2H), 3.85 – 3.67 (m, 5H), 3.64 – 3.46 (m, 5H), 3.20 – 3.08 (m, 2H), 1,65 (s, 9H); ^{13}C NMR (CD_3OD, 100 MHz) δ 150.2, 136.6, 135.8, 131.7, 129.9, 126.2, 124.3, 12.8, 118.8, 116.1, 106.0, 103.9, 88.1, 85.6, 85.4, 80.3, 77.0, 74.7, 73.2, 72.9, 71.5, 71.4, 70.2, 63.5, 62.4, 57.0, 55.5, 28.2; IR (neat, cm^{-1}) 3347, 2930, 1736, 1451, 1370, 1231, 1155, 1049, 930, 746, 613; ESI-MS: *m*/*z* 662.9 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{33}H_{46}N_2O_{12}$ $[M+H]^+$: 663.3124. Found: 663.3139. $[\alpha]_D^{23}$ -37.8 (c = 0.67, CH_3OH)



***tert*-butyl 3-((3*S*,4*S*,5*R*,6*R*,7*R*)-3-(diallylamino)-4,5,7,8-tetrahydroxy-6-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)oct-1-yn-1-yl)-1*H*-indole-1-carboxylate (3gj-MP)**

^{1}H NMR (CD_3OD, 400 MHz) δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.76 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.26 (m, 2H), 6.00 – 5.85 (m, 2H), 5.25 (d, *J* = 17.4 Hz, 2H), 5.13 (d, *J* = 10.1 Hz, 2H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.26 (d, *J* = 5.5 Hz, 1H), 4.15 (d, *J* = 9.2 Hz, 1H), 4.02 – 3.92 (m, 2H), 3.89 (q, *J* = 8.2 Hz, 1H), 3.85 – 3.70 (m, 5H), 3.63 – 3.53 (m, 2H), 3.50 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.48 – 3.36 (m, 2H), 3.08 (dd, *J* = 14.2, 8.2 Hz, 2H), 1.66 (s, 9H); ^{13}C NMR (CD_3OD, 100 MH) δ 150.4, 137.6, 135.9, 132.0, 129.4, 1626.1, 124.2, 121.0, 117.7, 116.1, 105.9, 104.9, 90.9, 85.5, 84.8, 78.2, 77.1, 74.8, 73.3, 72.9, 72.7, 70.2, 70.1, 63.6, 62.4, 57.2, 55.9, 28.3; IR (neat, cm^{-1}) 3358, 2934, 2217, 1739, 1644, 1452, 1371, 1231, 1156, 1030, 921, 854, 748; ESI-MS: *m*/*z* 663.0 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{33}H_{46}N_2O_{12}$ $[M+H]^+$: 663.3124. Found: 663.3091. $[\alpha]_D^{25}$ 45.4 (c = 1.85, CH_3OH)

4-7 Product in Control Reaction



(3a*S*,6*R*,7*R*,7a*R*)-6-(diallylamino)-2,2-dimethyltetrahydro-4*H*-[1,3]dioxolo[4,5-*c*]pyran-7-ol (7h)

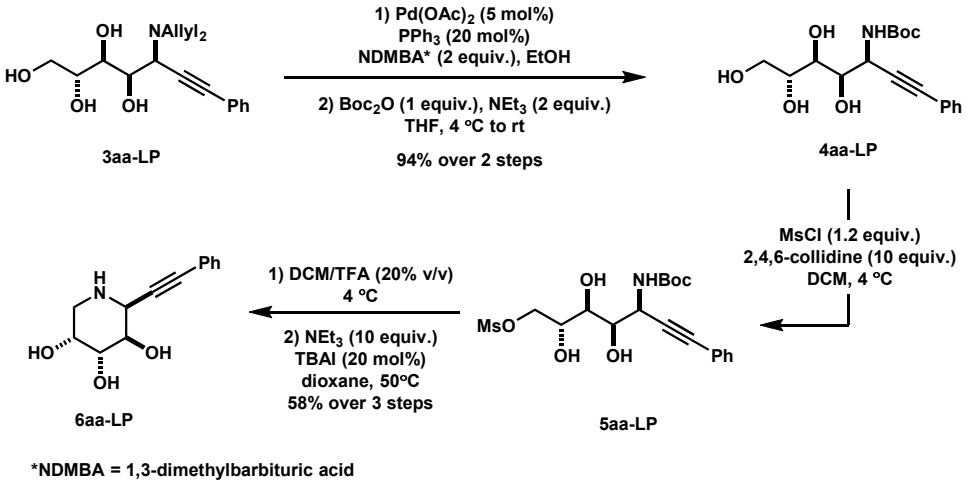
The reaction was performed by following the general procedures in section 2 using **1h** as aldose substrate. Isolation of **7h** was performed by column chromatography on silica gel (DCM/MeOH = 80/1 to 40/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.80 – 5.66 (m, 2H), 5.09 (d, *J* = 19.2 Hz, 2H), 5.05 (d, *J* = 10.5 Hz, 2H), 4.18 (d, *J* = 13.7 Hz, 1H), 4.05 (dd, *J* = 5.8, 2.3 Hz, 1H), 3.97 (t, *J* = 5.8 Hz, 1H), 3.71 (d, *J* = 9.6 Hz, 1H), 3.65 – 3.55 (m, 2H), 3.35 (dd, *J* = 15.1, 5.5 Hz, 2H), 3.11 (dd, *J* = 15.1, 7.8 Hz, 2H), 1.48 (s, 3H), 1.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.1, 117.3, 109.5, 90.9, 79.3, 73.7, 69.7, 65.0, 51.9, 28.2, 26.1; IR (neat, cm^{-1}) 3477, 3075, 2983, 2934, 1643, 1447, 1379, 1242, 1218, 1119, 1079, 993, 921, 849; ESI-MS: *m*/*z* 269.8 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{14}H_{23}NO_4$ $[M+H]^+$: 270.1699. Found 270.1697. $[\alpha]_D^{24}$ 26.3 (c = 1.44, $CHCl_3$)

5. Conversion of Products and Analytical Data for Derivatives

5-1. Synthesis of Iminosugars and Their Analytical Data

In order to assign the stereochemistry of the products (**3aa-LP** and **3aa-MP**) from arabinose, both compounds were converted to the corresponding iminosugars[11] **6aa-LP** and **6aa-MP**.

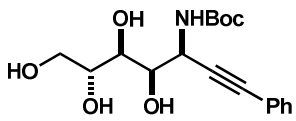


A dry tube equipped with a magnetic stirrer bar was charged with propargylamine **3aa-LP** (100 mg, 302 μmol), $Pd(OAc)_2$ (3.40 mg, 15.1 μmol), PPh_3 (15.8 mg, 60.4 μmol), 1,3-dimethylbarbituric acid (94.3 mg, 604 μmol) and EtOH (604 μl). The resulting mixture was stirred for 3 h and the volatiles were removed under reduced pressure. The resulting crude aminoalcohol was partially purified with reversed-phase column chromatography. (H_2O/MeCN = 3).

To a tube containing the partially isolated aminoalcohol and THF (3.02 ml), NEt_3 (84.2 μl, 604 μmol), Boc_2O (69.3 μl, 302 μmol) were added at 4 °C and the mixture was stirred for 5 h at room temperature. The reaction mixture was concentrated under reduced pressure to afford crude **4aa-LP**, which was purified with silica gel column chromatography (DCM/MeOH = 15 with 0.5% NEt_3) and the purified **4aa-LP** (100 mg, 284 μmol, 94% over 2 steps) was obtained.

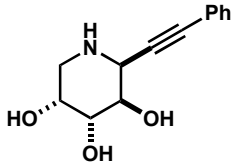
To a stirred solution of **4aa-LP** (154 mg, 438 μmol) in DCM (8.76 ml), 2,4,6-collidine (579 μl, 4.38 mmol) and MsCl (37.3 μl, 482 μmol) were added at 4 °C.[12] The resulting mixture was stirred for 12 h at the same temperature and additional MsCl (3.39 μl, 43.8 μmol) was added. After stirring the mixture at 4 °C for 3 h, MeOH was added to the mixture at the same temperature and the volatiles were removed under reduced pressure affording crude **5aa-LP**, which was purified with silica gel column chromatography (DCM/MeOH = 80 to 35) to give partially isolated **5aa-LP** (243μmol, ca. 58% yield).

To a stirred solution of partially isolated **5aa-LP** (102 μmol) in DCM (325 μl) was added TFA (81.8 μl) at 4 °C and the solution was stirred for 4 h. The volatiles were removed under reduced pressure giving oily crude amine-TFA salt, which was solved in dioxane (204 μl). To the solution, NEt_3 (142 μl, 1.02 mmol) and TBAI (3.77 mg, 10.2 μmol) were added and the reaction mixture was stirred at 50 °C for 12 h. The volatiles were removed under reduced pressure giving crude **6aa-LP**, which was isolated with reversed phase column chromatography (H_2O/MeCN = 8) to afford **6aa-LP** (23.7 mg, 101 μmol, 99% yield)



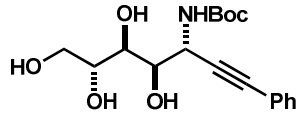
***tert*-butyl ((3*S*,4*R*,5*S*,6*R*)-4,5,6,7-tetrahydroxy-1-phenylhept-1-yn-3-yl)carbamate (4aa-LP)**

^{1}H NMR (CD_3OD, 400 MHz) δ 7.35 – 7.30 (m, 2H), 7.26 – 7.18 (m, 3H), 4.64 (d, *J* = 9.2 Hz, 1H), 3.88 – 3.80 (m, 2H), 3.73 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.65 – 3.59 (m, 1H), 3.55 (dd, *J* = 11.2, 5.9 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (CD_3OD, 100 MHz) δ 158.2, 13.27, 129.36, 124.26, 88.0, 85.0, 80.5, 73.3, 72.8, 72.0, 65.0, 47.7, 28.7; IR (neat, cm^{-1}) 3369, 2976, 2930, 1691, 1514, 1166, 1051, 756, 691; ESI-MS: *m*/*z* 373.7 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_{18}H_{25}NO_6$ $[M+Na]^+$: 374.1574. Found: 374.1581 $[\alpha]_D^{23}$ 71.9 (c = 0.45, CH_3OH)



(2*S*,3*R*,4*R*,5*R*)-2-(phenylethynyl)piperidine-3,4,5-triol (6aa-LP)

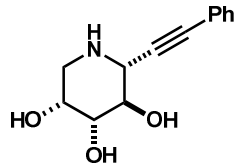
^{1}H NMR (CD_3OD, 400 MHz) δ 7.46 – 7.41 (m, 2H), 7.34 – 7.26 (m, 3H), 4.17 (d, *J* = 3.2 Hz, 1H), 3.95 – 3.88 (m, 2H), 3.86 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.07 (d, *J* = 13.7 Hz, 1H), 2.90 (dd, *J* = 13.7, 6.9 Hz, 1H); ^{13}C NMR (CD_3OD, 100 MHz) δ 132.7, 129.4, 129.3, 124.2, 87.0, 86.4, 72.5, 71.6, 68.2, 51.1, 46.6; IR (neat, cm^{-1}) 3325, 2915, 1682, 1489, 1339, 1076, 1024, 836, 755, 691; ESI-MS: *m*/*z* 233.9 $[M+H]^+$; ESI-HRMS: *m*/*z* calcd for $C_{13}H_{15}NO_3$ $[M+H]^+$: 234.1125. Found: 234.1119. $[\alpha]_D^{29}$ -58.3 (c = 0.53, CH_3OH)



***tert*-butyl ((3*R*,4*R*,5*S*,6*R*)-4,5,6,7-tetrahydroxy-1-phenylhept-1-yn-3-yl)carbamate (4aa-MP)**

4aa-MP (36.3 mg, 103 μmol, y. 85%) was obtained from **3aa-MP** (40 mg, 121 μmol) following the procedures identical to those for **4aa-LP**.

^{1}H NMR (CD_3OD, 400 MHz) ^{1}H NMR (CD_3OD, 500 MHz) δ 7.46 – 7.42 (m, 2H), 7.32 – 7.28 (m, 3H), 4.74 (d, *J* = 7.4 Hz, 1H), 3.93 (d, *J* = 7.4 Hz, 2H), 3.79 (dd, *J* = 11.2, 2.9 Hz, 1H), 3.75 – 3.69 (m, 2H), 3.63 (dd, *J* = 11.2, 5.2 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR (CD_3OD, 125 MHz) δ 154.7, 131.0, 128.1, 157.8, 122.6, 89.5, 82.0, 78.1, 71.2, 70.2, 70.0, 63.2, 46.4, 27.9; IR (neat, cm^{-1}) 3392, 2976, 2931, 1689, 1490, 1367, 1249, 1166, 1047, 756, 692; ESI-MS: *m*/*z* 373.8 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_{18}H_{25}NO_6$ $[M+Na]^+$: 374.1574. Found: 374.1555. $[\alpha]_D^{24}$ -89.8 (c = 0.47, CH_3OH)



(2*R*,3*R*,4*R*,5*R*)-2-(phenylethynyl)piperidine-3,4,5-triol (6aa-MP)

6aa-MP (13.3 mg, 57.7 mmol, y. 27% over 3 steps) was obtained from **4aa-MP** (73.8 mg, 210 μmol) following the procedures identical to those for **6aa-LP**.

^{1}H NMR (CD_3OD, 400 MHz) δ 7.48 – 7.42 (m, 2H), 7.36 – 7.28 (m, 3H), 3.87 (brs, 1H), 3.67 (t, *J* = 9.6 Hz, 1H), 3.44 – 3.36 (m, 2H), 2.96 (dd, *J* = 14.4, 2.8 Hz, 1H), 2.75 (dd, *J* = 14.4, 1.4 Hz, 1H); ^{13}C NMR (CD_3CN, 100 MHz, 65 °C) δ 132.7, 129.6, 129.4, 124.3, 90.1, 84.0, 76.1, 74.4, 70.2, 55.1, 50.4; IR (neat, cm^{-1}) 3311, 2920, 1682,

1489, 1442, 1203, 1069, 858, 756, 691; ESI-MS: *m/z* 233.9 $[M+H]^+$; ESI-HRMS: *m/z* calcd for $C_{13}H_{15}NO_3$ $[M+H]^+$: 234.1125. Found: 234.1126. $[\alpha]_D^{28}$ -1.10 (c = 0.72, CH_3OH)

5-2 Determination of Stereochemistry of Iminosugars (6aa-LP and 6aa-MP)

Theoretically, there would be four stereo- and conformational-isomers for the iminosugars, because each of two diastereomeric isomers possibly has two conformational isomers (Figure S5-1, from **6A** to **6D**). If NOE correlations between protons at 1-, 3-, and 5-positions (i.e. H_a, H_c and H_e) are concerned, these four isomers would show different NOE correlation patterns, because the number of 1,3-diaxial protons are different for each isomer (Figure S5-1 (a)).[13] The iminosugar **6aa-LP** showed NOE correlation between protons at 1 and 5 positions, suggesting that its structure and conformation corresponds to **6B** (Figure S5-1 (b)). As for the **3aa-MP**-derived product **6aa-MP**, NOE correlations were observed for protons at 1,3,5-positions, which means **6aa-MP** corresponds to **6D**. Based on these results, the stereochemistry of the original products (**3aa-LP** and **3aa-MP**) was successfully assigned. In both cases, the alkynyl group (R in the figure) was confirmed to be in equatorial position.

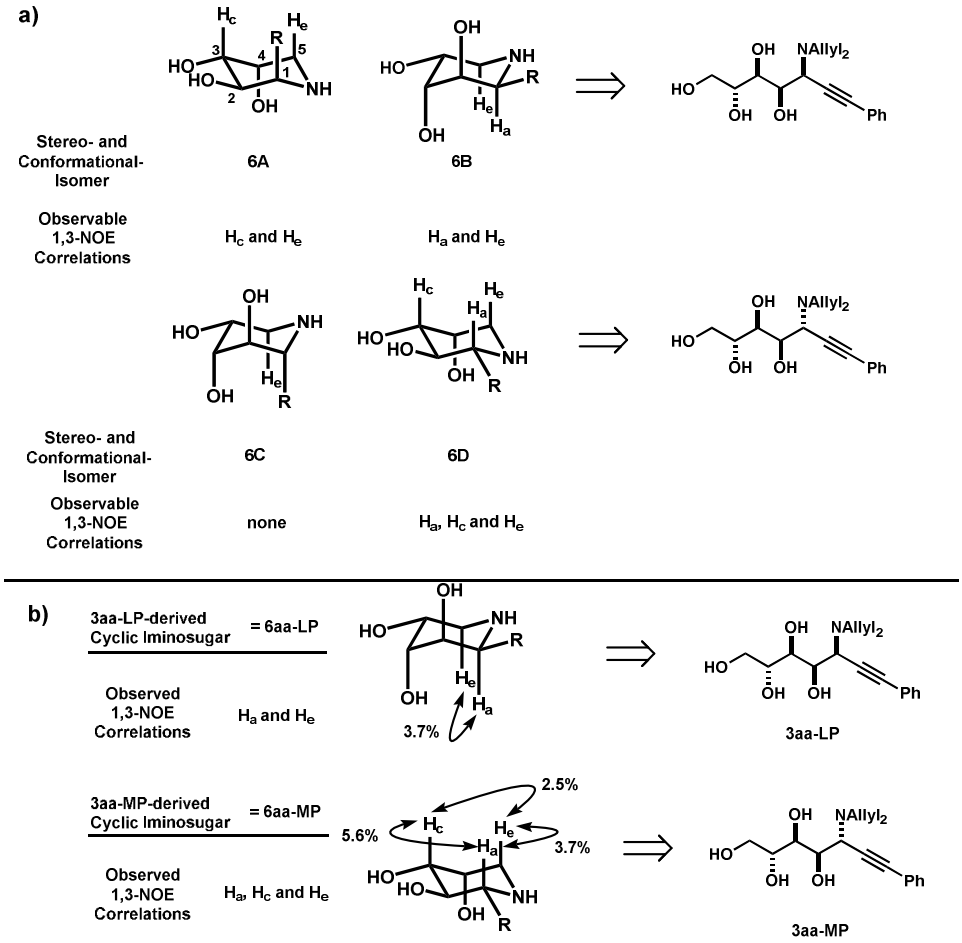
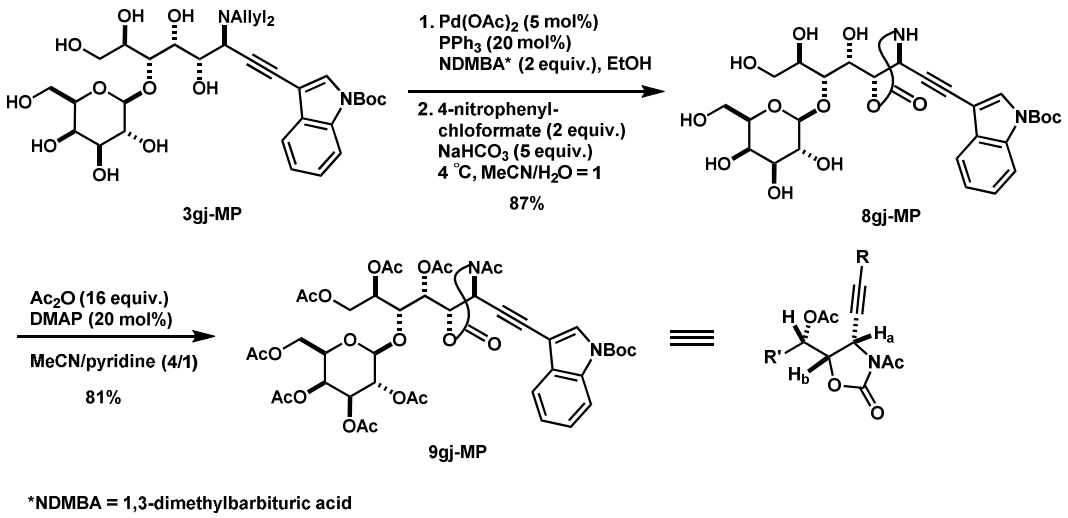


Figure S5-1. **a**) Possible four stereo- and conformational-isomers of iminosugars; **b)** Assignment of the stereochemistry of the products based on observed NOE correlations

5-3 Conversion and Stereochemical Determination of Products from Other Aldoses

5-3-1 Lactose-Derived Products

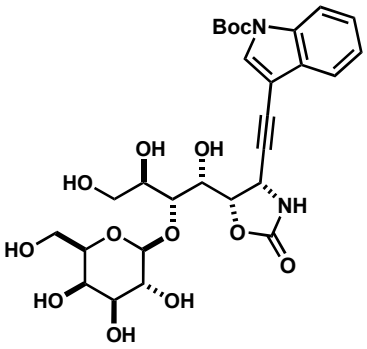
In the cases of the aldoses other than arabinose, the products were converted to the cyclic carbamates to assign the stereochemistry. A representative example with a lactose-derived product (**3fj-MP**) is described in Scheme S5-1. Determination of the stereochemistry was based on the coupling constant and NOE correlation between the two protons of the cyclic carbamate moiety (i.e. H_a and H_b in Scheme S5-1).



Scheme S5-1 Synthetic route to cyclic carbamate

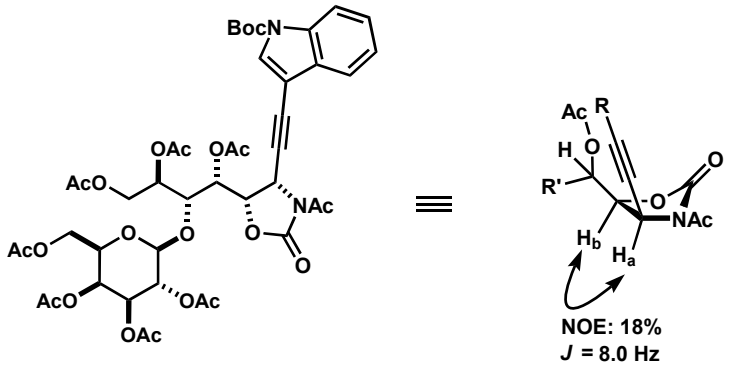
To a tube containing **3gj-MP** (20 mg, 30.2 μmol), $Pd(OAc)_2$ (0.34 mg, 1.51 μmol), PPh_3 (1.58 mg, 6.04 μmol), 1,3-dimethylbarbituric acid (9.43 mg, 60.4 μmol) and EtOH (300 μl) were added and the resulting suspension was stirred for 4 h. The volatiles were removed under reduced pressure and crude amine salt was partially isolated by reversed phase column chromatography. To a solution of the amine salt in H_2O/MeCN = 1 (604 μl), sodium bicarbonate (12.6 mg, 151 μmol) and 4-nitrophenyl chloroformate (15.2 mg, 75.5 μmol) were added at 4 °C and the reaction mixture was stirred at the same temperature for 4 h. The reaction was quenched with MeOH and the volatiles were removed under reduced pressure to give crude **8gj-Mp**, which was purified by silica gel column chromatography (DCM/MeOH = 3) to afford pure **8gj-MP** (16.3 mg, 26.7 μmol, 87 % over 2 steps).

To a solution of **8gj-MP** (10.0 mg, 16.4 μmol) in MeCN/pyridine = 4/1 (328 μl), Ac_2O (24.9 μl, 263 μmol) and DMAP (0.400 mg, 3.28 μmol) were added. The reaction mixture was stirred for 3 h and the volatiles were removed under reduced pressure to give crude **9gj-MP**, which was purified by silica gel column chromatography (DCM/MeOH = 40/1) to give **9gj-MP** (12.6 mg, 13.3 μmol, 81%).



***tert*-butyl 3-(((4*S*,5*S*)-2-oxo-5-((1*R*,2*R*,3*R*)-1,3,4-trihydroxy-2-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)butyl)oxazolidin-4-yl)ethynyl)-1*H*-indole-1-carboxylate (8gj-MP)**

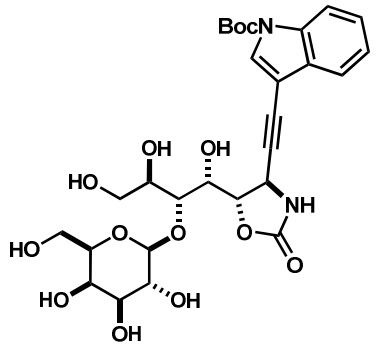
^{1}H NMR (CD_3OD, 500 MHz) δ 8.10 (d, *J* = 7.7 Hz, 1H), 7.88 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 5.32 (d, *J* = 7.4 Hz, 1H), 5.01 (t, *J* = 7.4 Hz, 1H), 4.53 (d, *J* = 9.1 Hz, 1H), 4.45 (d, *J* = 7.4 Hz, 1H), 4.01 (d, *J* = 7.4 Hz, 1H), 3.99 – 3.92 (m, 1H), 3.84 – 3.74 (m, 5H), 3.61 – 3.48 (m, 3H), 1.67 (s, 9H); ^{13}C NMR (CD_3OD, 125 MHz) δ 161.5, 150.3, 135.8, 131.5, 130.9, 126.3, 1024.4, 121.0, 116.1, 104.6, 103.4, 88.6, 85.8, 80.7, 80.6, 77.8, 76.9, 74.6, 72.6, 72.3, 71.6, 70.4, 63.6, 62.8, 47.7, 28.2; IR (neat, cm^{-1}) 3353, 1740, 1372, 1233, 1154, 1075, 748; ESI-MS: *m*/*z* 630.9 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_{28}H_{36}N_2O_{13}$ $[M+Na]^+$: 631.2110. Found: 631.2132. $[\alpha]_D^{24}$ -39.7 (c = 0.53, CH_3OH)



(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((1*R*,2*R*,3*R*)-1,3,4-triacetoxy-1-((4*S*,5*S*)-3-acetyl-4-((1-(*tert*-butoxycarbonyl)-1*H*-indol-3-yl)ethynyl)-2-oxooxazolidin-5-yl)butan-2-yl)oxy) tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (9gj-MP)

^{1}H NMR (acetone-d_6, 500 MHz) δ 8.18 (d, *J* = 8.0 Hz, 1H), 8.01 (s, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.38 (m, 1H), 7.38 – 7.32 (m, 1H), 5.94 (dd, *J* = 9.7, 1.7 Hz, 1H), 5.83 (d, *J* = 8.0 Hz, 1H), 5.38 (d, *J* = 3.4 Hz, 1H), 5.25 – 5.10 (m, 3H), 5.10 – 5.06 (m, 1H), 5.04 (d, *J* = 8.0 Hz, 1H), 4.75 (dd, *J* = 8.6, 1.7 Hz, 1H), 4.61 (dd, *J* = 12.6, 3.3 Hz, 1H), 4.45 – 4.32 (m, 2H), 4.15 (dd, *J* = 12.6, 5.2 Hz, 1H), 4.07 (dd, *J* = 11.5, 6.9 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), 1.75 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 170.7, 170.69, 170.65, 170.2, 170.1, 169.9, 169.6, 169.4, 152.5, 149.5, 135.4, 131.0, 130.8, 126.3, 124.3, 120.7, 116.1, 102.1, 101.5, 86.1, 85.5, 80.6, 74.8, 74.2, 72.6, 71.6, 70.6, 69.7, 69.6, 68.4, 62.8,

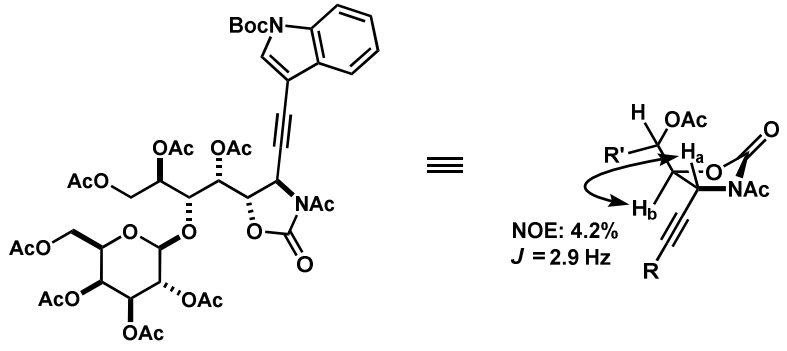
62.4, 48.8, 28.1, 23.5, 20.8, 20.7, 20.6, 20.58, 20.55, 20.4; IR (neat, cm^{-1}) 2359, 1800, 1750, 1372, 1232, 1147, 1069, 633; ESI-MS: *m/z* 967.0 $[M+Na]^+$; ESI-HRMS: *m/z* calcd for $C_{44}H_{52}N_2O_{21}$ $[M+Na]^+$: 967.2955. Found: 967.2911. $[\alpha]_D^{27}$ 67.6 (c = 0.52, CH_3OH)



***tert*-butyl 3-(((4*R*,5*S*)-2-oxo-5-((1*R*,2*R*,3*R*)-1,3,4-trihydroxy-2-(((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)butyl)oxazolidin-4-yl)ethynyl)-1*H*-indole-1-carboxylate (8gj-LP)**

8gj-LP (12.6 mg, 20.1 μmol, y. 89%) was obtained from **3gj-LP** (15 mg, 22.6 μmol) following the procedures identical to those for **3gj-MP**.

^{1}H NMR (CD_3OD, 400 MHz) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.85 (s, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.26 (m, 2H), 5.03 (dd, *J* = 6.0, 3.7 Hz, 1H), 4.98 (d, *J* = 6.0 Hz, 1H), 4.46 (d, *J* = 7.8 Hz, 1H), 4.09 – 4.02 (m, 1H), 4.01 – 3.94 (t, *J* = 3.7 Hz, 1H), 3.95 – 3.90 (m, 1H), 3.80 – 3.75 (m, 4H), 3.70 (dd, *J* = 11.4, 5.5 Hz, 1H), 3.58 – 3.50 (m, 2H), 3.43 (dd, *J* = 10.1, 3.6 Hz, 1H), 1.67 (s, 9H); ^{13}C NMR (CD_3OD, 100 MHz) δ 160.8, 150.2, 135.9, 131.4, 130.6, 126.3, 124.5, 120.8, 116.2, 106.0, 103.4, 91.1, 85.8, 83.5, 81.8, 77.8, 76.9, 74.9, 73.3, 72.9, 72.3, 70.1, 63.8, 62.2, 47.5, 28.2; IR (neat, cm^{-1}) 3357, 1740, 1455, 1372, 1233, 1155, 1054, 748; ESI-MS: *m/z* 630.8 $[M+Na]^+$; ESI-HRMS: *m/z* calcd for $C_{28}H_{36}N_2O_{13}$ $[M+Na]^+$: 631.2110. Found: 631.2102. $[\alpha]_D^{29}$ 32.0 (c = 1.24, CH_3OH)



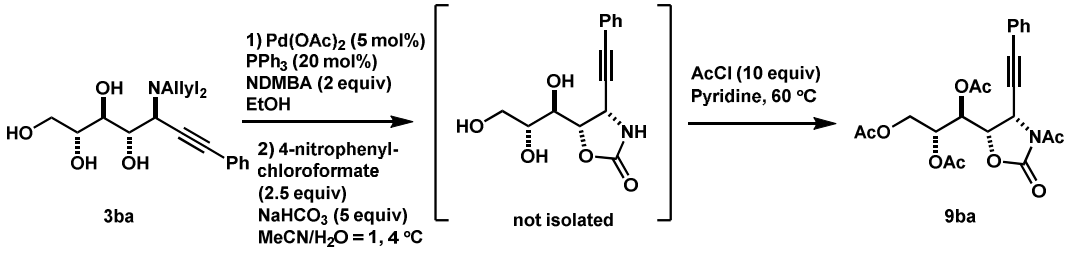
(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((1*R*,2*R*,3*R*)-1,3,4-triacetoxy-1-((4*R*,5*S*)-3-acetyl-4-((1-(*tert*-butoxycarbonyl)-1*H*-indol-3-yl)ethynyl)-2-oxooxazolidin-5-yl)butan-2-yl)oxy) tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (9gj-LP)

9gj-LP (10.5 g, 11.1 μmol, y. 68%) was obtained from **8gj-LP** (10 mg, 16.4 μmol) following the procedures identical to those for **9gj-MP**.

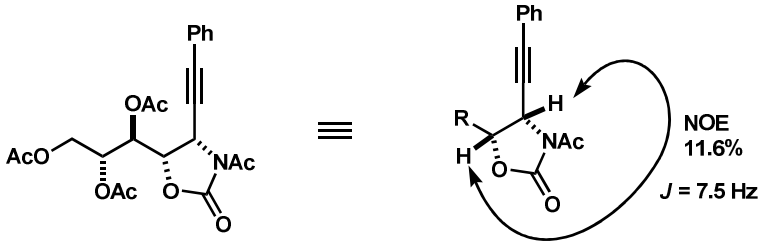
^{1}H NMR (acetone-d_6, 500 MHz) δ 8.15 (d, J = 8.3 Hz, 1H), 7.93 (s, 1H), 7.66 (d, J = 8.3 Hz, 1H), 7.38 (t, J = 8.3 Hz, 1H), 7.33 (t, J = 8.3 Hz, 1H), 5.52 (t, J = 5.4 Hz, 1H), 5.44 (d, J = 2.9 Hz, 1H), 5.36 – 5.30 (m, 2H), 5.17 (dd, J = 5.4, 2.9 Hz, 1H), 5.14 (d, J = 2.9 Hz, 1H) 5.02 (d, J = 8.0 Hz, 1H), 4.54 (dd, J = 12.0, 2.9 Hz, 1H), 4.48 (t, J = 4.5 Hz, 1H), 4.26 (t, J = 6.9 Hz, 1H), 4.18 – 4.11 (m, 3H), 2.47 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.99 (brs, 6H), 1.88 (brs, 6H), 1.67 (s, 9H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 170.8, 170.7, 170.6, 170.3, 170.2, 170.1, 169.8 ,169.3, 152.6, 149.5, 135.4, 131.06, 131.03, 126.1, 124.2, 120.6, 116.0, 102.3, 102.2, 89.2, 85.3, 78.2, 77.6, 77.0, 72.0, 71.5, 71.3, 71.2, 69.8, 68.1, 62.7, 62.3, 49.3, 28.1, 23.5, 20.9, 20.7, 20.65, 20.60, 20.4, 20.2; IR (neat, cm^{-1}) 2360, 1794, 1749, 1455, 1372, 1221, 1155, 1048; ESI-MS: m/z 967.1 $[M+Na]^+$; ESI-HRMS: m/z calcd for $C_{44}H_{52}N_2O_{21}$ $[M+Na]^+$: 967.2955. Found: 967.2921. $[\alpha]_D$ ^{27} 7.39 (c = 0.62, CH_3OH)

For the other products, **3ba** (from D-ribose), **3ca** (from D-xylose), **3ea** (from D-galactose), **3fa** (from L-fucose) were derivatized to the corresponding cyclic carbamates by the same or identical procedures (i.e. removal of the allyl groups, cyclic carbamate formation, and overall acetylation). In
the case of the conversion of **3ba** and **3ca**, any intermediates were not isolated.

5-3-2 Ribose-Derived Product



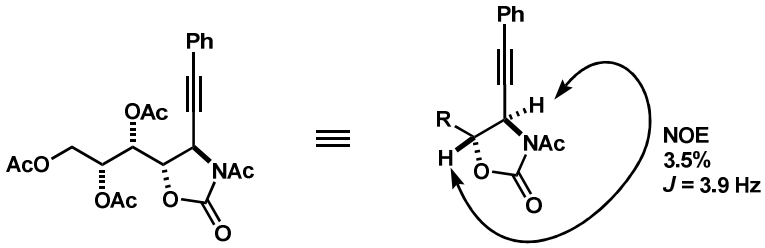
To a tube containing **3ba** (20 mg, 60 μmol), $Pd(OAc)_2$ (0.68 mg, 3.02 μmol), PPh_3 (3.16 mg, 12 μmol), 1,3-dimethylbarbituric acid (18.7 mg, 121 μmol) and EtOH (120 μl) were added and the resulting suspension was stirred for 13 h. The volatiles were removed under reduced pressure and the crude amine salt was partially isolated by reversed phase column chromatography (H_2O/MeCN = 8 to 1). To a solution of the crude amine salt in H_2O/MeCN = 1 (1.2 ml), sodium bicarbonate (25.2 mg, 300 μmol) and 4-nitrophenyl chloroformate (30.3 mg, 150 μmol) were added at 4 °C and the reaction mixture was stirred at the same temperature for 24 h. The reaction was quenched with MeOH and the volatiles were removed under reduced pressure to give crude cyclic carbamate**.**
To a solution of crude cyclic carbamate in pyridine (600 μl), AcCl (42.8 μl, 600 μmol) was added. The reaction mixture was stirred for 12 h at 60 °C and 1 M HCl aqueous solution was added. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with saturated $NaHCO_3$ aqueous solution and brine, dried with Na_2SO_4 and concentrated under reduced pressure to give crude **9ba**, which was purified by silica gel column chromatography (Hexane/EtOAc = 5 to 2) to give isolated **9ba** (15.2 mg, 33.7 μmol, y. 56%).



(1*S*,2*R*)-1-((4*S*,5*S*)-3-acetyl-2-oxo-4-(phenylethynyl)oxazolidin-5-yl)propane-1,2,3-triyl triacetate (9ba)

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38 – 7.32 (m, 2H), 7.27 – 7.21 (m, 3H), 5.51 (dd, *J* = 10.3, 2.9 Hz, 1H), 5.46 (dt, *J* = 5.9, 2.9 Hz, 1H), 5.31 (d, *J* = 7.5 Hz, 1H), 4.74 (dd, *J* = 10.3, 7.5 Hz, 1H), 4.28 (d, *J* = 5.9 Hz, 2H), 2.49 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.3, 169.8, 168.9, 168.7, 151.2, 132.0, 129.2, 128.3, 120.8, 87.9, 79.5, 72.4, 70.4, 69.9, 61.7, 49.4, 23.6, 20.8, 20.6, 20.5; IR (neat, cm^{-1}) 1797, 1748, 1716, 1507, 1217, 1046, 756; ESI-MS: *m*/*z* 467.8 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{23}NO_9$ $[M+Na]^+$: 468.1265. Found: 468.1268 $[\alpha]_D^{28}$ 51.1 (c = 0.17, CH_3OH)

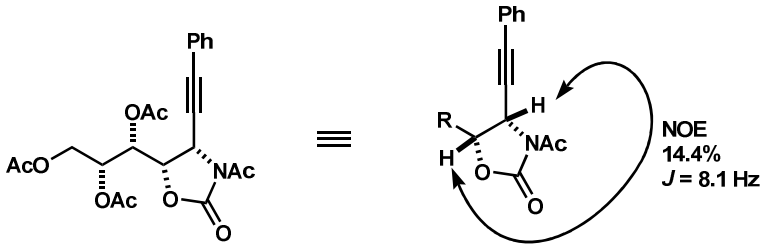
5-3-3 Xylose-Derived Products



(1*R*,2*R*)-1-((4*R*,5*S*)-3-acetyl-2-oxo-4-(phenylethynyl)oxazolidin-5-yl)propane-1,2,3-triyl triacetate (9ca-LP)

45.2 mg of **9ca-LP** (101 μmol, y. 52%) was obtained from 65.2 mg of **3ca-LP** (196 μmol) following the procedures identical to those for **9ba**.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40 – 7.32 (m, 2H), 7.32 – 7.22 (m, 3H), 5.35 – 5.28 (m, 1H), 5.31 (t, *J* = 3.9 Hz, 1H), 5.03 (d, *J* = 3.9 Hz, 1H), 4.77 (t, *J* = 3.9 Hz, 1H), 4.33 (dd, *J* = 12.2, 4.6 Hz, 1H), 4.05 (dd, *J* = 12.2, 5.5 Hz, 1H), 2.48 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.1, 169.5, 169.4, 168.9, 151.3, 131.8, 129.2, 128.2, 120.9, 85.9, 82.9, 77.5, 69.8, 68.7, 61.4, 47.8, 23.4, 20.6, 20.5, 20.2; IR (neat, cm^{-1}) 1793, 1749, 1716, 1372, 1211, 1046, 757; ESI-MS: *m*/*z* 467.8 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_{22}H_{23}NO_9$ $[M+Na]^+$: 468.1265. Found: 468.1255 $[\alpha]_D^{26}$ 22.8 (c = 1.25, CH_3OH)



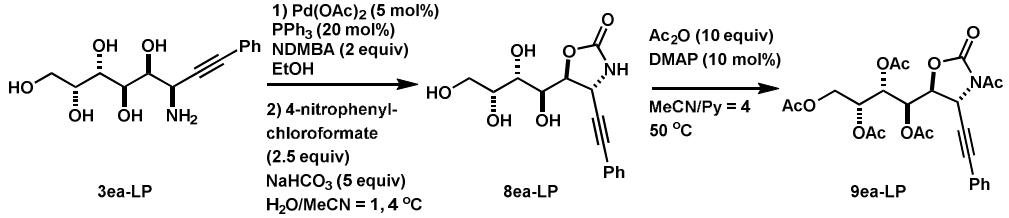
(1*R*,2*R*)-1-((4*S*,5*S*)-3-acetyl-2-oxo-4-(phenylethynyl)oxazolidin-5-yl)propane-1,2,3-triyl triacetate (9ca-MP)

35.3 mg of **9ca-MP** (79.2 μmol, y. 33%) was obtained from 80.0 mg of **3ca-MP** (241 μmol) following the procedures identical to those for **9ba**.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 – 7.44 (m, 2H), 7.38 – 7.27 (m, 3H), 5.81 (d, *J* = 8.1 Hz, 1H), 5.49 (t, *J* = 6.6 Hz, 1H), 5.43 (d, *J* = 8.1 Hz, 1H), 4.57 (t, *J* = 8.1 Hz, 1H), 4.19 (dd, *J* = 12.0, 6.6 Hz, 1H), 4.04 (dd, *J* = 12.0, 6.6 Hz, 1H), 2.52 (s, 3H), 2.14 (s, 3H), 2.13 (s, 3H), 1.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.5, 169.4, 168.7,

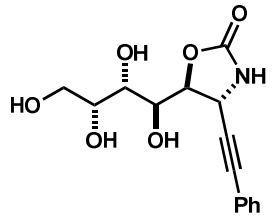
168.2, 150.8, 131.4, 128.8, 127.7, 120.2, 88.1, 79.1, 73.1, 68.7, 67.7, 60.6, 47.7, 22.9, 20.0, 19.9, 19.6; IR (neat, cm^{-1}) 1793, 1749, 1716, 1373, 1213, 1047, 757; ESI-MS: *m/z* 467.7 $[M+Na]^+$; ESI-HRMS: *m/z* calcd for $C_{22}H_{23}NO_9$ $[M+Na]^+$: 468.1265. Found: 468.1258 $[\alpha]_D^{27}$ 132.3 (c = 1.51, CH_3OH)

5-3-4 Galactose-Derived Products



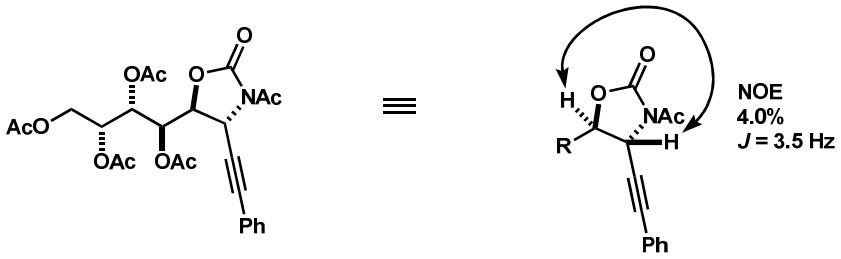
To a tube containing **3ea-LP** (75 mg, 208 μmol), $Pd(OAc)_2$ (2.33 mg, 10.3 μmol), PPh_3 (10.9 mg, 41.5μmol), 1,3-dimethylbarbituric acid (64.8 mg, 415 μmol) and EtOH (415 μl) were added and the resulting suspension was stirred for 13 h. The volatiles were removed under reduced pressure and the crude amine salt was partially isolated by reversed phase column chromatography (H_2O/MeCN = 8 to 1). To a solution of the crude amine salt in H_2O/MeCN = 1 (4.16 ml), sodium bicarbonate (87.4 mg, 1.04 mmol) and 4-nitrophenyl chloroformate (105 mg, 520 μmol) were added at 4 °C and the reaction mixture was stirred at the same temperature for 7 h. The reaction was quenched with MeOH and the volatiles were removed under reduced pressure to give crude cyclic carbamate **8ea-LP**, which was purified with reversed phase column chromatography (H_2O/MeCN = 3) to give isolated **8ea-LP** (46.1 mg, 150 μmol, y. 72%).

To a solution of **8ea-LP** (7.7 mg, 25.1 μmol) in MeCN/pyridine = 4 (500 μl), Ac_2O (23.7 μl, 251 μmol) and DMAP (0.306 mg, 2.51 μmol) were added. The reaction mixture was stirred for 30 min at 50 °C and the volatiles were removed under reduced pressure to give crude **9ea-LP,** which was purified by silica gel column chromatography (Hexane/EtOAc = 2) to give isolated **9ea-LP** (8.8 mg, 17.0 μmol, y. 68%).



(4*R*,5*S*)-4-(phenylethynyl)-5-((1*S*,2*S*,3*R*)-1,2,3,4-tetrahydroxybutyl)oxazolidin-2-one (8ea-LP)

^1H NMR (CD_3OD, 500 MHz) δ 7.46 – 7.40 (m, 2H), 7.38 – 7.30 (m, 3H), 4.97 (dd, *J* = 6.9, 1.1 Hz, 1H), 4.86 (d, *J* = 6.9 Hz, 1H), 3.97 – 3.90 (m, 1H), 3.78 – 3.72 (m, 1H), 3.72 – 3.65 (m, 1H), 3.65 (d, *J* = 6.3 Hz, 2H); ^{13}C NMR (CD_3OD, 125 MHz) δ 160.8, 132.7, 129.9, 129.5, 123.3, 87.0, 85.7, 83.7, 71.4, 70.9, 70.8, 64.8, 46.9; IR (neat, cm^{-1}) 3343, 1740, 1419, 1090, 755; ESI-MS: *m/z* 329.9 $[M+Na]^+$; ESI-HRMS: *m/z* calcd for $C_{15}H_{17}NO_6$ $[M+Na]^+$: 330.0948. Found: 330.0937. $[\alpha]_D^{27}$ 101.8 (c = 0.73, CH_3OH)

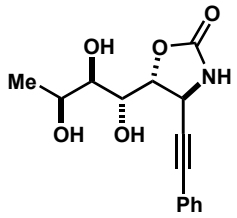


(1*R*,2*S*,3*R*)-1-((4*R*,5*S*)-3-acetyl-2-oxo-4-(phenylethynyl)oxazolidin-5-yl)butane-1,2,3,4-tetrayl tetraacetate (9ea-LP)

^{1}H NMR ($CDCl_3$ 500 MHz) δ 7.44 – 7.38 (m, 2H), 7.38 – 7.26 (m, 3H), 5.53 (dd, *J* = 9.1, 2.3 Hz, 1H), 5.34 – 5.27 (m, 2H), 5.06 (d, *J* = 3.5Hz, 1H), 4.61 (t, *J* = 3.5 Hz, 1H), 4.23 (dd, *J* = 11.5, 5.7 Hz, 1H), 3.90 (dd, *J* = 11.5, 6.9 Hz, 2H), 2.52 (s, 3H), 2.18 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 170.0, 169.6, 169.3, 168.9, 151.6, 131.9,
129.3, 128.4, 121.0, 85.9, 83.2, 77.2, 68.4, 68.1, 67.6, 61.3, 48.0, 23.5, 20.7, 20.6, 20.2; IR (neat, cm^{-1}) 3392, 2965, 2233, 1796, 1752, 1715, 1491, 1443, 1372, 1208, 1047, 757, 693; ESI-MS: *m*/*z* 539.7 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_{25}H_{27}NO_{11}$ $[M+Na]^+$: 540.1476. Found: 540.1450. $[\alpha]_D^{24}$ 51.2 (c = 0.52, $CHCl_3$)

In the case of the conversion from **3ea-MP**, formation of cyclic carbamate did not occur even under heated and more basic conditions. Based on the above structural analysis of **9ea-LP,** cyclic carbamate derived from **3ea-MP** (i.e. **9ea-MP**) would have two large substituents in 1,2-*cis* stereochemical relationships, if it was formed. In light of this consideration, the failure of the cyclic carbamate formation is due to too large steric repulsion.

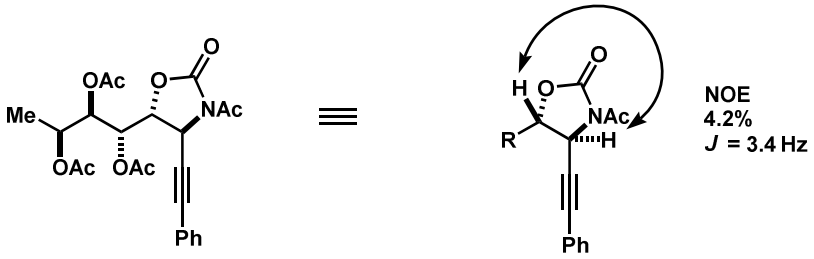
5-3-5 Fucose-Derived Products



(4*S*,5*R*)-4-(phenylethynyl)-5-((1*R*,2*R*,3*S*)-1,2,3-trihydroxybutyl)oxazolidin-2-one (8fa-LP)

63.8 mg of **8fa-LP** (219 μmol, y. 76%) was obtained from **3fa-LP** (100 mg, 289 μmol) following the procedures identical to those for **8ea-LP**.

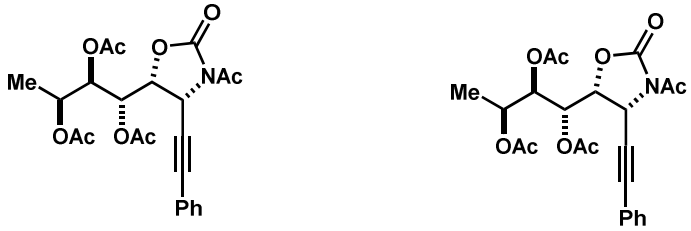
^{1}H NMR (CD_3OD, 500 MHz) δ 7.48 – 7.40 (m, 2H), 7.37 – 7.30 (m, 3H), 4.97 (d, *J* = 6.7 Hz, 1H), 4.85 (d, *J* = 6.7 Hz, 1H), 4.08 (q, *J* = 6.6 Hz, 1H), 3.72 (d, *J* = 9.5 Hz, 1H), 3.44 (d, *J* = 9.5 Hz, 1H), 1.25 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 160.8, 132.7, 129.9, 129.5, 123.3, 87.0, 85.7, 83.9, 74.1, 71.3, 66.9, 46.9, 19.9; IR (neat, cm^{-1}) 3347, 1747, 1397, 1102, 1027, 757, 691; ESI-MS: *m*/*z* 314.2 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_{15}H_{17}NO_5$ $[M+Na]^+$: 314.0999. Found: 314.0993. $[\alpha]_D^{30}$ -123.3 (c = 0.90, CH_3OH)



(1*S*,2*R*,3*S*)-1-((4*S*,5*R*)-3-acetyl-2-oxo-4-(phenylethynyl)oxazolidin-5-yl)butane-1,2,3-triyl triacetate (9fa-LP)

15.3 mg of **9fa-LP** (33.3 μmol, y. 81%) was obtained from **8fa-LP** (12.0 mg, 41.2 μmol) following the procedures identical to those for **9ea-LP**.

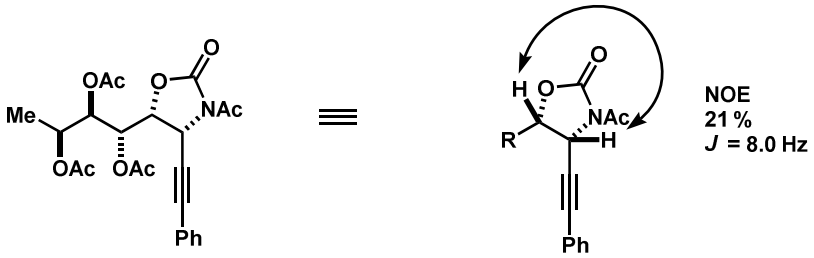
^{1}H NMR δ 7.45 – 7.38 (m, 2H), 7.35 – 7.27 (m, 3H), 5.35 (dd, *J* = 9.1, 2.3 Hz, 1H), 5.31 (dd, *J* = 9.1, 3.4 Hz, 1H), 5.10 (m, 1H), 5.06 (d, *J* = 3.4 Hz, 1H), 4.62 (t, *J* = 3.4 Hz, 1H), 2.52 (s, 3H), 2.20 (s, 3H), 2.02 (s, 3H), 1.15 (d, *J* = 6.9 Hz) ;^{13}C NMR ($CDCl_3$) δ 170.2, 169.5, 168.9, 151.6, 131.9, 129.2, 128.3, 121.1, 85.8, 83.4, 77.5, 71.1, 69.0, 67.1, 48.0, 23.5, 20.9, 20.7, 20.2, 16.1; IR (neat, cm^{-1}) 2989, 2238, 1795, 1751, 1715, 1443, 1372, 1207, 1127, 1042, 756, 692; ESI-MS: *m/z* 481.6 $[M+Na]^+$; ESI-HRMS: *m/z* calcd for $C_{23}H_{25}NO_9$ $[M+Na]^+$: 482.1421. Found: 482.1410. $[\alpha]_D^{24}$ -28.3 (c = 0.47, $CHCl_3$)



(4*R*,5*R*)-4-(phenylethynyl)-5-((1*R*,2*R*,3*S*)-1,2,3-trihydroxybutyl)oxazolidin-2-one (8fa-MP)

39.4 mg of **8fa-MP** (135 μmol, y. 80%) was obtained from **3fa-MP** (58.7 mg, 170 μmol) following the procedures identical to those for **8ea-LP**.

^{1}H NMR (CD_3OD, 500 MHz) δ 7.50 – 7.44 (m, 2H), 7.36 – 7.29 (m, 3H), 5.09 (d, *J* = 8.6 Hz, 1H), 4.99 (dd, *J* = 8.6, 3.3 Hz, 1H), 4.19 (dd, *J* = 9.2, 3.3 Hz, 1H), 4.09 (q, *J* = 6.7 Hz, 1H), 3.38 (d, *J* = 9.2 Hz, 1H), 1.24 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (CD_3OD, 125 MHz) δ 161.2, 132.9, 129.9, 129.5, 123.7, 88.0, 85.2, 79.8, 75.0, 71.8, 66.8, 48.6, 20.1; IR (neat, cm^{-1}) 3360, 2932, 1748, 1396, 1337, 1071, 1029, 758, 692; ESI-MS: *m/z* 313.9 $[M+Na]^+$; ESI-HRMS: *m/z* calcd for $C_{15}H_{17}NO_5$ $[M+Na]^+$: 314.0999. Found: 314.0996. $[\alpha]_D^{38}$ 4.23 (c = 0.90, CH_3OH)



(1*S*,2*R*,3*S*)-1-((4*R*,5*R*)-3-acetyl-2-oxo-4-(phenylethynyl)oxazolidin-5-yl)butane-1,2,3-triyl triacetate (9fa-MP)

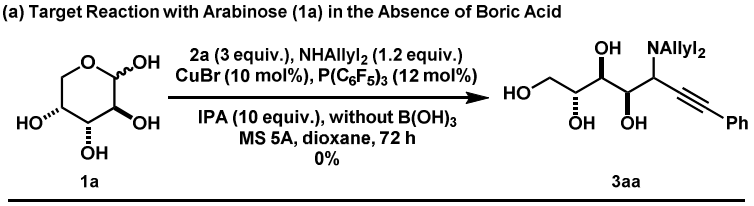
18.8 mg of **9fa-MP** (41.1 μmol, y. 75%) was prepared from **8fa-MP** (16.0 mg, 54.9 μmol) following the

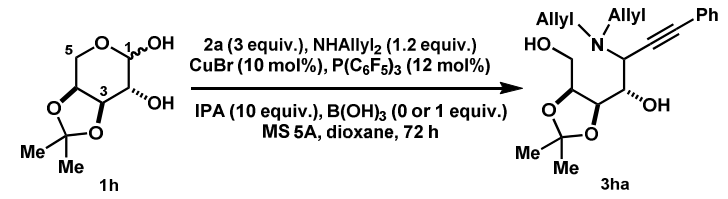
procedures identical to those for **9ea-LP**.

^{1}H NMR ($CDCl_3$ 500 MHz) δ 7.51 – 7.48 (m, 2H), 7.36 – 7.28 (m, 3H), 5.77 (dd, *J* = 7.5, 5.2 Hz, 1H), 5.28 (d, *J* = 8.0 Hz, 1H), 5.27 (dd, *J* = 7.5, 2.9 Hz, 1H), 5.10 – 5.05 (m, 1H), 4.70 (dd, *J* = 8.0, 5.2 Hz, 1H), 2.52 (s, 3H) 2.18 (s, 3H), 2.03 (s, 3H), 1.95 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 170.2, 169.8, 169.1, 169.0, 151.4, 132.0, 129.2, 128.3, 121.1, 88.6, 79.6, 77.2, 74.1, 72.3, 68.3, 67.3, 48.8, 23.7, 20.9, 20.7, 16.3; IR (neat, cm^{-1}) 2988, 2235, 1795, 1747, 1490, 1373, 1214, 1041, 757, 693 ;MS: *m*/*z* 481.7 $[M+Na]^+$; ESI-HRMS: *m*/*z* calcd for $C_{23}H_{25}NO_9$ $[M+Na]^+$: 482.1421. Found: 482.1409. $[\alpha]_D^{24}$ -94. 3(c = 0.55, $CHCl_3$)

6. Control Experiments

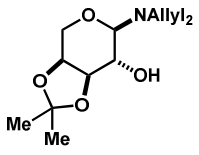
To gain mechanistic insight into the developed reaction, especially the role of boric acid, we performed several control experiments. The reaction with **1a** in the absence of boric acid was examined under otherwise optimized conditions (Scheme S6-1 (a)). The target compound **3aa** was not obtained at all, confirming that boric acid is essential. Next, the reactions with 3,4-*O*-protected arabinose **1h** were examined (Scheme S6-1 (b)). The corresponding aminoalkynylation product **3ha** was not obtained in either the absence or presence of boric acid[14]. Instead, hemiaminal **7h** was obtained as the major product in the presence of boric acid (entry 2).





Entry	$B(OH)_3$	Yield	
		3ha	7h
1	0 equiv.	0%	0%
2	1 equiv.	0%	44% (76%[a])

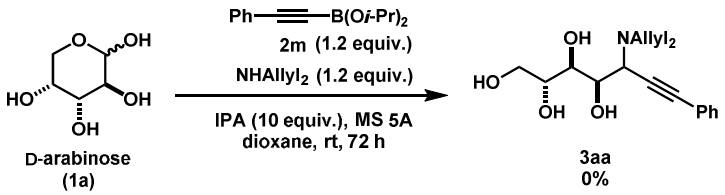
[a] The yield is based on ^{1}H NMR analysis of crude 7h, which was partially decomposed during purification by column chromatography.



Scheme S6-1 Control reactions with arabinose and 3,4-*O*-protected arabinose (a) Target reaction in the absence of boric acid; (b) Reactions with 3,4-*O*-protected arabinose in the absence and presence of boric acid

These results suggest that complexation of boric acid with arabinose at the 3,4-*cis* diol moiety[15] is essential and that this particular complexation accelerates the desired reaction by suppressing the formation of the unreactive hemiaminal species. The importance of the 3,4-*cis* diol moiety is also consistent with the aldose scope (Tables 2 and 3 in the main text), where aldoses with this structural motif (i.e., arabinose, galactose, and fucose) exhibited higher reactivity than did other aldoses.

Next, we examined another control reaction using phenylethynylboronic acid ester **2m** as a nucleophile without the copper catalyst and boric acid (Scheme S6-2).



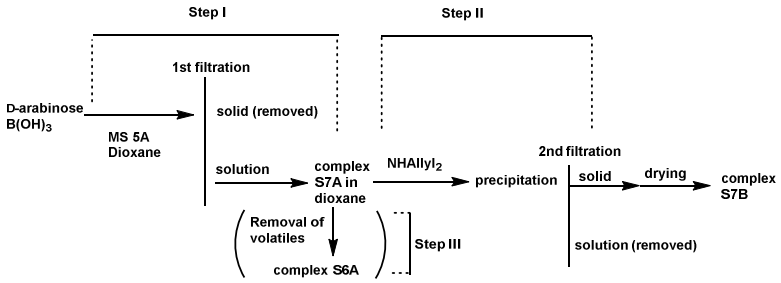
Scheme S6-2 Control reaction with phenylethynylboronic acid ester

As expected, target product **3aa** was not obtained. This result indicates that the developed reaction proceeds through nucleophilic addition of the copper alkynylide to the iminium intermediate, and not through a Petasis' boronic acid Mannich reaction[16].

7 Preliminary Mechanistic Study

In order to gain insights into structural feature and reactivity of an arabinose-boron complex, we prepared and analyzed complex **S7B** derived from arabinose, boric acid and diallylamine (in section 7-1), and performed control experiments with **S7B** (in sections 7-2 and 7-3).

7-1. Preparation and analysis of arabinose-boron-diallylamine complex (complex S7B)



(Step I) To a flask containing D-arabinose (1.00 g, 6.66 mmol), $B(OH)_3$ (412 mg, 6.66 mmol) and activated molecular sieve 5A (1.33 g), dioxane (26.6 ml) were added and the reaction mixture was stirred for 17 h. The insoluble compounds and molecular sieves were removed by filtration to afford dioxane solution of arabinose-boron complex (complex **S7A**).

(Step II) To the solution of arabinose-boron **S7A**, $NHAllyl_2$ (822 μl, 6.66 mmol) was added to afford white precipitation, which was collected by filtration[17] and dried under reduced pressure to give complex **S7B** (725 mg, 1.91 mmol as arabinose-derived species in total, 29% yield, based on ^{1}H NMR using internal standard).[18]

(Analysis of complex S7B) Complex **S7B** was analyzed based on ^{1}H, ^{13}C, ^{11}B NMR and HMBC measurements. **S7B** were not very soluble in dioxane-d_8 and the NMR measurements were performed using DMSO-d_6 as solvent instead. Although the full characterization of this complex was not successful, several structural features were speculated in light of these spectroscopic data. Based on ^{1}H NMR, there existed two arabinose-derived species (ca.

1:1 in molar ratio) and the ratio of the arabinose-derived compounds in total and $NHAllyl_2$ was 1:1. The protons connected to carbons of arabinose-derived species showed downfield shift by ca. 0.2 ~ 0.8 ppm compared with pure arabinose in DMSO-d_6. This result suggested that arabinose-derived species form complexes with boron species. In HMBC analysis, the correlations between the anomeric carbon (C1) and protons connected to C5 was observed for both of the arabinose-derived species, which suggested that both of them existed in pyranose form (Figure S7-1 (a), (b)).

S7B was speculated to be a hemiacetal, not a hemiaminal based on HMBC analysis (no correlations were observed which should have been observed if hemiaminal was formed, see Figure S7-1 (c)). ^{11}B NMR analysis suggested this complex includes several borate ester species.

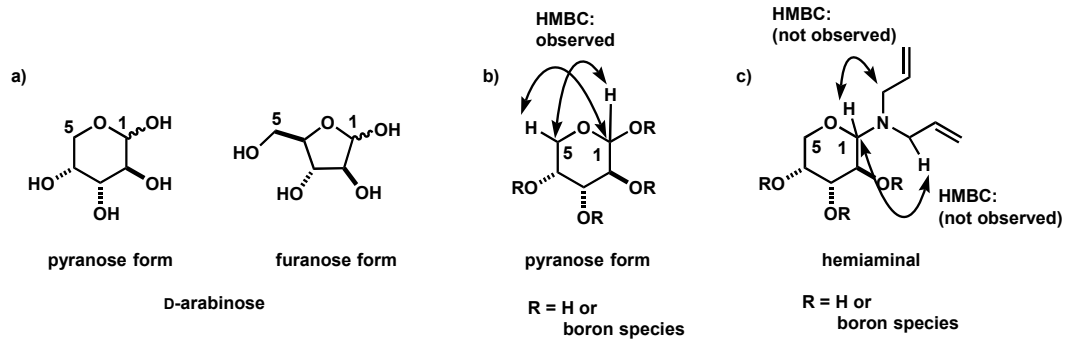
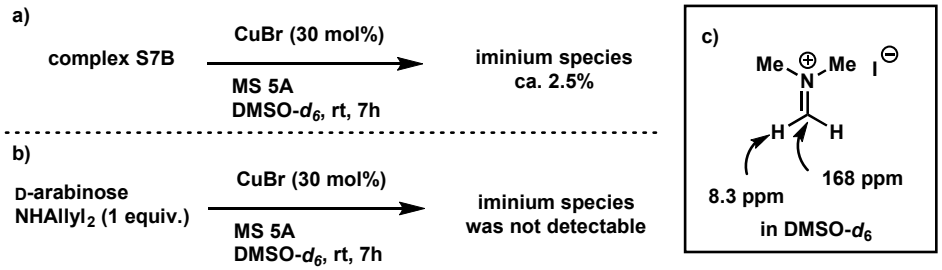


Figure S7-1 a) Pyranose and furanose form of D-arabinose, b) Observed correlations in HMBC analysis of **S7B**, c) Observable HMBC correlations for hemiaminal species

7-2. Reaction of S7B and CuBr



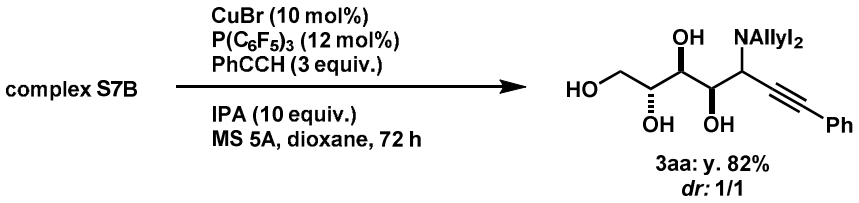
Scheme **S7-1** a) Reaction with complex **S7B** and CuBr catalyst; b) Reaction with arabinose, diallylamine, and CuBr catalyst; c) Reported ^1H and ^{13}C chemical shift value for known iminium species

To a tube containing complex **S7B** (106 mg, 280 μmol as arabinose-derived species), CuBr (12.0 mg, 84.0 μmol) and activated molecular sieves 5A (168 mg), was added DMSO-d_6 (1.0 ml) and the resulting mixture was stirred for 7 h at room temperature. Molecular sieves was removed by the filtration and the resulting DMSO-d_6 solution was analyzed by ^1H and ^{13}C NMR, where a little amount of the iminium species was observed (ca. 2.5% conversion based on ^1H NMR integration). This species showed a sharp singlet peak at 8.08 ppm in ^1H NMR, which correlated with ^{13}C NMR peak at 162.16 ppm in HMQC spectrum. The values of these chemical shifts were in good agreement with a reported iminium species (Scheme S7-1 (c)).[19]

On the other hand, the reaction with arabinose (42.0 mg, 280 μmol) and $NHAllyl_2$ (34.6 μl, 280 μmol) in the absence of $B(OH)_3$ under otherwise identical conditions was performed (Scheme S7-1 (b)). After 7 h, only very weak singlet peaks (< 0.15% ^1H NMR) was observed at 8.08 ppm and no significant peak was observed around 150 – 200 ppm, suggesting that neither iminium species nor aldehyde was formed.

These two experimental results suggested that boron species in **S7B** promotes the formation of the iminium species, which is a key intermediate in the aminoalkynylation reaction.

7-3. Aminoalkynylation reaction using complex S7B as a starting material



To a tube containing complex **S7B** (106 mg, 280 μmol as arabinose-derived species), CuBr (4.0 mg, 28.0 μmol), $P(C_6F_5)_3$ (17.9 mg, 33.6 μmol) and activated MS 5A (336 mg), were added dioxane (1.12 ml), ethynylbenzene (92.2 μl, 840 μmol) and IPA (214 μl, 2.80 mmol). After the degassing procedures (3 x freeze/pump/thaw), the mixture was stirred for 72 h and the reaction was quenched by MeOH. Molecular sieves was removed by filtration and the resulting solution was concentrated *in vacuo* to give crude **3aa**, which was purified by column chromatography to afford pure **3aa** (76.0 mg, 229 mmol, 82% yield). The yield was comparable with the standard reaction, which suggested that **S7B** was possibly involved in the reaction process.

7-4. Summary of section 7

- Arabinose-derived species in both complex **S7A** and **S7B** exist in a pyranose form. These results justify the presumption in the main text that arabinose-derived species mainly exist in a pyranose form.
- Boron species in complex **S7B** had promoted the formation of the iminium intermediate. This result suggests that boric acid promote the aminoalkynylation reaction by accelerating formation of the iminium intermediate.
- Aminoalkynylation reaction with **S7B** as a starting material gave the comparable results as the standard reaction. This result suggests that complex **S7B** is involved in the standard reaction.

8. Tentative Reaction Mechanism

Based on the above results, we propose a hypothetical reaction mechanism shown in Figure S8-1. Boric acid would preferentially form a complex with the 3,4-*cis* diol moiety of arabinose (**1a**), affording complex **B**. Because there are multiple free hydroxy groups in the substrate, several isomeric boron complexes could be formed, including unfavorable complex **A**, where aldehyde formation is inhibited. IPA might accelerate the interconversion of carbohydrate-boron complexes, thus enhancing the desired reaction pathway. Formation of **B** would be beneficial for efficient trapping of the primary hydroxy group, which is generated by ring opening of the hemiacetal structure of **B**. This efficient trapping of the primary hydroxy group would extend the lifetime of the reactive aldehyde **C** and prevent formation of hemiaminal species in the subsequent steps.

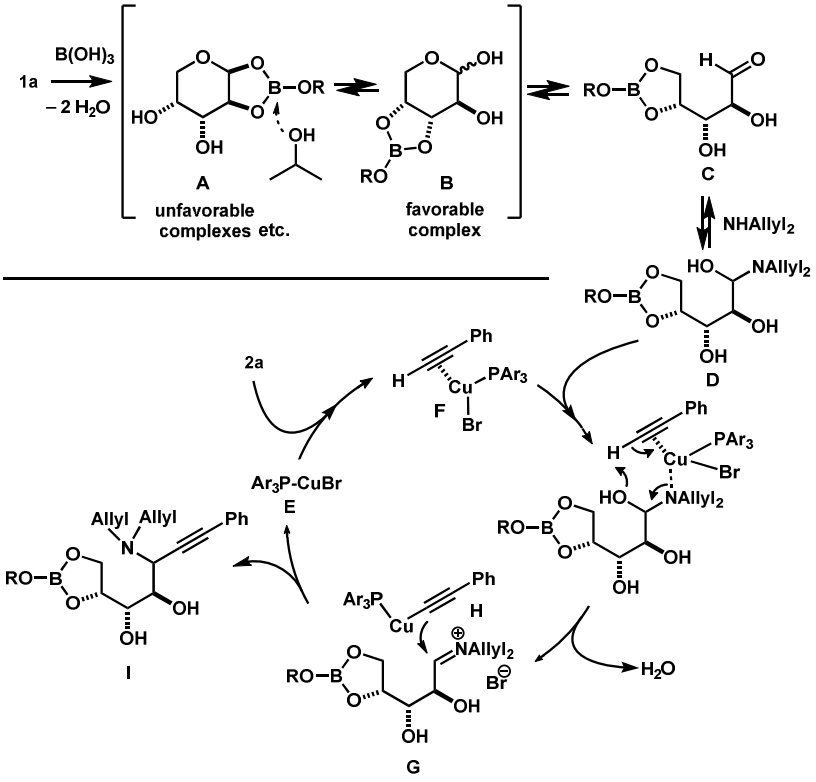


Figure S8-1 Tentative reaction mechanism

After the formation of **C**, the reaction should proceed essentially through the mechanism proposed by Knochel.[20,21] Hemiaminal **D** will form from **C** and diallylamine, which reacts with copper-alkyne complex **F** to afford the nucleophile copper alkynide **H** and the electrophile iminium cation **G**[22]. The nucleophilic addition of **H** to **G** produces propargylamine **I** and regenerates the catalyst **E**.

9. Possible Mechanism for Diastereoselective Induction

It was found that aldose substrates which showed high diastereoselectivity have common structural features: these substrates have a *cis* diol at the 2,3-positions, the positions nearby the iminium carbon (Figure S9-1 (a)). Based on this tendency, we hypothesize that the borate ester formation occurs also at 2,3-postion in prior to the nucleophilic addition and that the complexation at these positions may affect the diastereoselectivity (Figure S9-1 (b)).

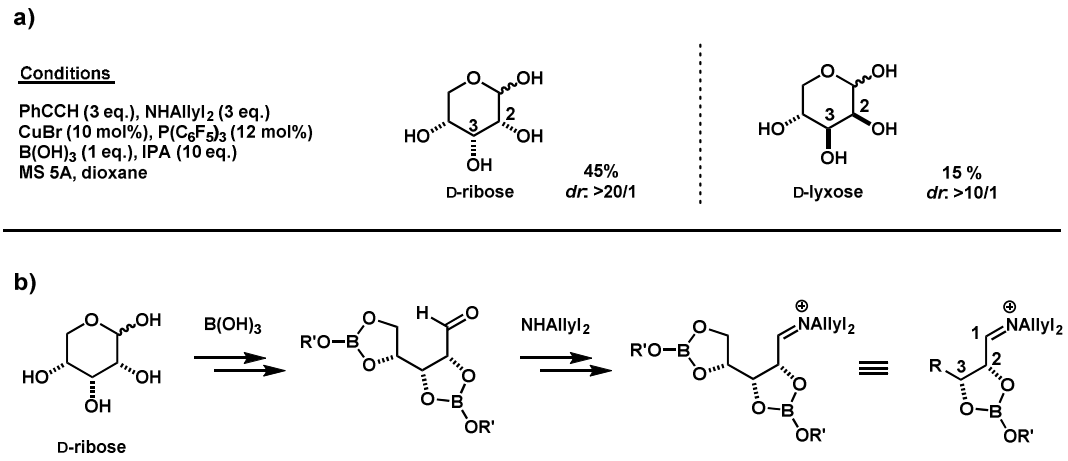


Figure S9-1 a) Observed diastereoselectivity in the reactions with aldopentoses with 2,3-*cis* diol; **b)** Speculated formation of borate ester formation at 2,3-diols in prior to nucleophilic additions

Figure S9-2 describes a possible origin of high stereoselectivity based on this hypothesis. The relative orientation of the iminium C-N double bond is confined so that 1,3-allylic strain between the substituents of C2 and the ally group is minimized. In this fixed conformation of the intermediate, the carbohydrate main chain (depicted as R in the figure) shields one face of the plane defined by the iminium cation, and nucleophilic addition proceeds preferentially from the opposite side, resulting in high diastereoselective induction.[23]

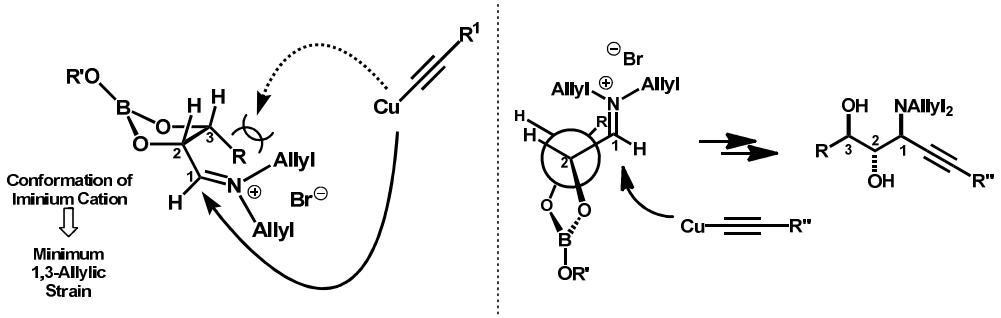


Figure S9-2. Hypothetical mechanism for high diastereoselectivity in the reaction with D-ribose

10. References

(1) White, J. D.; Lincoln, C. M.; Yang, J.; Martin, W. H. C.; Chan, D. B. *J. Org. Chem.* **2008**, *73*, 4139.

(2) Denton, T. T.; Zhang, X.; Cashman, J. R. *J. Med. Chem.* **2004**, *48*, 224.

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(13) This method is based on the presumption that the NOE correlations between 1,3-axial-equatorial and 1,3-diequatorial protons are normally too weak to be detected under the standard measurement conditions.

(14) This result suggests that boric acid does not work simply as a transient protecting group for hydroxy groups in aldoses.

(15) The discussion here presumes that arabinose exists mainly in the pyranose form instead of the furanose form. We confirmed this assuption by HMBC analysis of the arabinose-derived species formed under the conditions similar to those used for the reaction. See section 7 in supporting information.

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(17) Only trace amount of arabinose-derived species existed in the liquid fraction. This result suggested that the complex **S7B** is the major species after the addition of diallylamine

(18) The low yield of complex **S7B** is due to low solubility of arabinose in dioxane in step I. To confirm this point, complex **S7A** was collected by removing the volatiles of the filtrate of the first filtration (step III). The yield of arabinose-derived species in complex **S7A** was 33% (NMR yield), which suggests that most of arabinose was removed by the first filtration as solid. Complete characterization of complex **S7A** was not successful. The protons connected to carbons of arabinose-derived species showed downfield shift by ca. 0.3 - 0.8 ppm compared with pure arabinose in dioxane-d_8. This result suggested that arabinose-derived species form complexes with boron species. HMBC and ^{11}B NMR analysis (dioxane- d_8 as solvent) suggested that arabinose-derived species in this complex also existed in pyranose form and contained boron ester species.

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(21) Although Knochel *et al*. proposed a dimeric structure of the copper catalyst based on their observation of non-linear effects in enantioselective induction, here we show a monomeric copper species for simplicity.

(22) The acceleration effect of the boron species for generation of the iminium species was confirmed by preliminary NMR studies. See section 7-2 in supporting information for details.

(23) Borate ester formation at the 2,3-diol in prior to the nucleophilic addition may occur also with arabinose. In this case, however, the relative stereochemical relationship of the iminium moiety and R is trans. Hence the shielding effect of R substituent does not work effectively, thus inducing no diastereoselectivity in most cases.