Supporting Information
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En Route to Novel Furanoside Mimics Through Stereoselective Zinc-Mediated Propargylation of N-Benzyl-glycofuranosylamines Using Ultrasound Activation

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**GENERAL REMARKS:**

Unless otherwise stated, all reagents were purchased from commercial sources and used as received. THF (99.9% GC) with 2,6-di-tert-buty-4-methylphenol (250 mg/L) as stabilizer was purchased from Sigma–Aldrich Chemical Co., Inc. and purified by passage through a column containing activated alumina under nitrogen pressure (Dry Solvent Station GT S100, GlassTechnology, Geneva, CH). Petroleum ether (PE) had a boiling range of 40–65 °C. NMR spectra were recorded at 298 K with a Bruker Avance 400 MHz spectrometer equipped with a PABBO BBO probe. The structures of 1, (ent)-1, 3-9, 10a-10c and (1R)-11a were assigned
with the aid of $^1$H NMR, $^{13}$C NMR, Distortionless Enhancement by Polarization Transfer (DEPT), Correlation Spectroscopy (COSY), Heteronuclear Multiple Quantum Coherence (HMQC), Heteronuclear Multiple-bond Correlation (HMBC) and Nuclear Overhauser Effect Spectroscopy (NOESY). $^1$H NMR (400 MHz) chemical shift values are listed in parts per million (ppm) downfield from TMS as the internal standard or relative to the corresponding non-deuterated solvent. Data are reported as follows: chemical shift (ppm on the $\delta$ scale), multiplicity ($s =$ singlet, $d =$ doublet, $dd =$ doublet of doublet, $ddd =$ doublet of doublet of doublet, $td =$ triplet of doublet, $t =$ triplet, $p =$ pentuplet and $m =$ multiplet), coupling constant $J$ (Hz), and integration. $^{13}$C NMR (100 MHz) chemical shifts are given in ppm relative to the corresponding non-deuterated solvent or TMS as the internal standard. NMR primary data should be processed by MestReNova. Mass determinations were carried out with an AB Sciex triple quadrupole mass spectrometer. High-resolution mass spectra were recorded with a MaXis ESI qTOF ultrahigh-resolution mass spectrometer (FR2708, Orléans). Infrared spectra were recorded with a Thermo Scientific Nicolet IS10 FTIR spectrometer using diamond ATR golden gate sampling and are reported in wave numbers (cm$^{-1}$). Melting points were measured in open capillary tubes with a Buchi melting point apparatus. Specific optical rotations were measured with a Perkin–Elmer 341 polarimeter in a thermostatted (20 °C) 1 dm long cell with high-pressure sodium lamp and are reported as follows: [α]$_D^{20}$ [solvent, c (g/100 mL)]. Analytical thin-layer chromatography (TLC) was performed with Merck Silica Gel 60 F254 precoated plates. Visualization of the developed chromatogram was performed under ultraviolet light (254 nm) and on staining by immersion in aqueous, acidic ceric ammonium molybdate (CAM; 470 mL H$_2$O, 28 mL H$_2$SO$_4$, 24 g ammonium molybdate, 0.5 g cerium ammonium nitrate) followed by heating on a hot plate. Flash chromatography was performed in air on Silica Gel 60 (230–400 mesh) with petroleum ether (bp 40–65 °C) and ethyl acetate as eluents, unless otherwise stated. Organic solutions were concentrated under reduced pressure with a Buchi rotary evaporator.

**EXPERIMENTAL PROCEDURES AND CHARACTERIZATION DATA:**

$N$-Benzyl-$N$-(3-trimethylsilyl-2-propynyl)-2,3,5-tri-$O$-benzyl-$\alpha$/β-$L$-arabinofuranosylamine (3):

colorless oil. $R_f = 0.55$ (SiO$_2$, PE:EA 8:2). [α]$_D^{20} = -30.6^\circ$ (CHCl$_3$, c = 0.01 g/100 mL). $^1$H NMR (400 MHz, CDCl$_3$/TMS): $\delta$ 7.36–7.15 (m, 20 H, H$_{Ar}$), 5.0 (d, $J = 4.6$ Hz, 1 H, $H_1$), 4.70 (d, $J = 11.8$ Hz, 1 H, 0.5 × OCH$_2$Ph), 4.61–4.49 (m, 5 H, 2.5 × OCH$_2$Ph), 4.23–4.17 (m, 2 H, $H_2 + H_4$), 4.13 (d, $J = 14.2$ Hz, 1 H, 0.5 × NHCH$_2$Ph), 4.02 (dd, $J = 5.8, 4.1$ Hz, 1 H, $H_3$), 3.73 (d, $J = 14.3$ Hz, 1 H, 0.5 × NHCH$_2$Ph), 3.61–3.54 (m, 2 H, OCH$_2$Ph), 0.10–0.20 (m, 9 H, CH$_3$, (TMS)). $^{13}$C NMR (101 MHz, CDCl$_3$/TMS): $\delta$ 139.0 (C, C$_{Ar}$), 138.3 (C, C$_{Ar}$), 138.2 (C, C$_{Ar}$), 138.1 (C, C$_{Ar}$), 128.9–127.2 (CH, CH$_{Ar}$), 103.3 (C, C$_7$ or C$_8$), 96.8 (CH, C$_1$), 89.0 (C, C$_7$ or C$_8$), 85.1 (CH, C$_2$), 83.8 (CH, C$_3$), 80.8 (CH, C$_4$), 73.5 (CH$_2$, OCH$_2$Ph), 72.2 (CH$_2$, OCH$_2$Ph), 71.9 (CH$_2$, OCH$_2$Ph), 70.4 (CH$_2$, C$_5$), 53.3 (CH$_2$, NHCH$_2$Ph), 39.8 (CH$_2$, C$_6$), 0.3 (CH$_3$, TMS). IR (film): $\nu = 3063, 3030, 2922, 2853, 2180, 1729, 1603, 1454, 1363, 1249, 1096, 1073$ cm$^{-1}$. LRMS (ESI): $m/z$ calcd. for C$_{39}$H$_{48}$NO$_4$Si [M + H]$^+$ 620.319062; found: 620.5. HRMS (ESI): $m/z$ calcd. for C$_{39}$H$_{48}$NO$_4$Si [M + H]$^+$ 620.319062; found: 620.319130.
Typical Procedure for the Preparation of N-Benzyl-glycofuranosylamines (1), ent-(1) and (5):

In a 50-mL single-necked round-bottomed flask under argon atmosphere, related 2,3,5-tri-O-benzyl-glycofuranose (6.2 mmol) was dissolved in dry CH₂Cl₂ (6.6 mL) in the presence of 4 Å activated molecular sieves. p-toluenesulfonic acid (6.3 mmol) was added, followed after 10 min of stirring by benzylamine (1.36 mL, 12.5 mmol) and the reaction mixture was stirred for 2 days at room temperature (ca. 20°C). The yellow solution was then filtered through Celite®, the cake washed with CH₂Cl₂ (30 mL). The organic phase was washed twice with saturated aq. NaHCO₃ (60 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude product was purified by silica gel column chromatography eluting with a mixture of ethyl acetate (EA) and petroleum ether (PE) to give the corresponding furanosylamine. The different compounds might be inserted in the next step without purification; The propargylated derivatives being obtained with no loss of the overall yields.

N-Benzyl-2,3,5-tri-O-benzyl-α/β-L-arabinofuranosylamine (1):

Light yellow oil (1.25 g, 69%). α/β (6:4) mixture of anomers which was not assigned. R² 0.38 (SiO₂, PE:EA 8:2). [α]₂⁰ = −15.7°(CHCl₃, c = 1.0 g/100 mL). ¹H NMR (400 MHz, CDCl₃/TMS): δ = 7.36-7.21 (m, 20 H, H Ar maj + H Ar min), 4.87-4.83 (m, 0.6 H, H₂ maj), 4.83-4.79 (m, 0.4 H, H₂ min), 4.64-4.44 (m, 6 H, 3 × OCH₂Ph min + 3 × OCH₂Ph maj), 4.26-4.20 (m, 0.6 H, H₄ maj), 4.10 (d, J = 13.4 Hz, 0.4 H, 0.5 × NHC₂H₂Ph min), 4.05 (d, J = 13.4 Hz, 0.6 H, 0.5 × NHC₂H₂Ph maj), 4.01-3.96 (m, 0.4 H, H₄ min), 3.95 (m, 0.6 H, H₃ maj), 3.93-3.86 (m, 1.8 H, 0.5 × NHC₂H₂Ph min + H₂ maj + H₂ min + H₃ min), 3.83 (d, J = 13.3 Hz, 0.6 H, 0.5 × NHC₂H₂Ph maj), 3.63-3.53 (m, 2 H, H₅ maj + H₅ min), 2.26 (s, 1 H, NHCH₂Ph maj + NHCH₂Ph min). ¹³C NMR (101 MHz, CDCl₃/TMS): δ = 140.5 (C, C Ar NHBn min), 140.2 (C, C Ar NHBn maj), 138.3 (C, C Ar OBN maj), 137.9 (C, C Ar OBN maj), 138.0 (C, C Ar OBN min), 137.9 (C, C Ar OBN min), 128.5-126.9 (CH, CH Ar min + CH Ar maj), 93.7 (CH, C₁ maj), 90.6 (CH, C₁ min), 86.5 (CH, C₂ maj), 83.5 (CH, C₃ maj), 82.6 (CH, C₂ min), 82.6 (CH, C₃ min), 80.6 (CH, C₄ maj), 79.7 (CH, C₄ min), 73.4 (CH₂, OCH₂Ph maj), 72.2 (CH₂, OCH₂Ph min), 72.0 (CH₂, OCH₂Ph maj), 71.8 (CH₂, OCH₂Ph min), 71.7 (CH₂, OCH₂Ph maj), 71.0 (CH₂, C₅ min), 70.8 (CH₂, C₅ maj), 50.1 (CH₂, NHCH₂Ph min), 49.2 (CH₂, NHCH₂Ph maj). IR (film): ν = 3029, 2860, 1495, 1453, 1362, 1265, 1205, 1078, 1026, 732, 694 cm⁻¹. LRMS (ESI): m/z calcd. for C₃₃H₃₆NO₄ [M + H]⁺ 510.263885, found 510.5. HRMS (ESI): m/z calcd. for C₃₃H₃₆NO₄ [M + H]⁺ 510.263885; found: 510.263693.

N-Benzyl-2,3,5-tri-O-benzyl-α/β-d-arabinofuranosylamine ent-(1):

White amorphous solid (0.97 g, 53%). R² 0.50 (SiO₂, PE:EA 7:3). [α]₂⁰ = +13.6°(CHCl₃, c = 1.0 g/100 mL). HRMS (ESI): m/z calcd. for C₃₃H₃₆NO₄ [M + H]⁺ 510.263885; found: 510.263372.
**N-Benzyl-2,3,5-tri-O-benzyl-α/β-D-xylofuranosylamine (5):**

Light yellow oil (1.7 g, 54%), α/β (7:3) mixture of anomers which was not assigned. \( R_f \) 0.48 (SiO₂, PE:EA 8:2). \([\alpha]_D^{20} = -11.7^o\) (CHCl₃, \( c = 1.04\) g/100 mL). \( ^1H\) NMR (250 MHz, CDCl₃/TMS): \( \delta = 7.39-7.12 \) (m, 20 H, H '_', Ar maj + H '_', Ar min), 4.99 (d, \( J = 3.2\) Hz, 0.3 H, H₁ min), 4.73 (d, \( J = 2.5\) Hz, 0.7 H, H₁ maj), 4.62-4.36 (m, 6.3 H, 3 × OCH₂Ph maj + 3 × OCH₂Ph min + H₄ min), 4.36-4.26 (m, 0.7 H, H₄ maj), 4.17-3.80 (m, 3.7 H, H₃ maj + H₂ maj + NCH₂Ph maj + NCH₂Ph min + H₂ min or H₃ min), 4.05 (d, \( J = 2.5\) Hz, 0.7 H, H₃ maj + H₄ min + H₅₅ min + H₄ min or H₃ min). \( ^13C\) NMR (63 MHz, CDCl₃/TMS): \( \delta = 140.5\) (C, C Ar maj), 140.2 (C, C Ar min), 138.3-137.7 (C, C Ar maj + C Ar min), 128.3-126.7 (CH, CH Ar maj + CH Ar min), 94.2 (CH, C₁ maj), 90.1 (CH, C₁ min), 86.9 (CH, C₂ maj), 81.5 (CH, C₃ maj), 81.2 (2 × CH, C₂ min + C₃ min), 78.7 (CH, C₄ maj), 77.0 (CH, C₄ min), 73.3 (CH₂, OCH₂Ph maj + OCH₂Ph min), 72.6 (CH₂, OCH₂Ph min), 72.1 (CH₂, OCH₂Ph min), 72.0 (CH₂, OCH₂Ph maj), 71.4 (CH₂, OCH₂Ph maj), 69.0 (CH₂, C₅ maj), 68.8 (CH₂, C₅ min), 49.9 (CH₂, NCH₂Ph min), 49.6 (CH₂, NCH₂Ph maj). IR (film): \( \nu = 3063, 3058, 3024, 2908, 2827, 1500, 1431, 1117, 1093, 1047, 1005, 726, 695\) cm⁻¹. LRMS (ESI): \( m/z \) calcd. for \( C_{33}H_{36}NO_{4} [M + H]^+ 510.263885\); found: 510.5. HRMS (ESI): \( m/z \) calcd. for \( C_{33}H_{36}NO_{4} [M + H]^+ 510.263885\); found: 510.263965.

**General Procedure for the Propargylation Process:**

**Procedure A:**

In a 10-mL single-necked round-bottomed flask under argon atmosphere was inserted zinc dust (96.2 mg, 1.47 mmol) and iodine (11.2 mg, 0.04 mmol). The flask was placed under vacuum atmosphere and the vessel was heated with an electric heat gun during 5 min. The argon atmosphere was installed de novo and the vessel allowed reaching room temperature. The cycle was repeated once and dry THF (2 mL) was added followed by 3-bromo-1-trimethylsilyl-1-propyne at 0 °C (53 \( \mu \)L, 0.32 mmol) (mixture A). The reaction mixture was allowed to reach room temperature and stirred further for about 2 h. In parallel, a solution of the \( N\)-Benzyl-2,3,5-tri-O-benzyl-α/β-D-xylofuranosylamine derivative (0.10 mmol) in dry THF (2 mL) under argon atmosphere was prepared in a 10-mL single-necked round-bottomed flask (mixture B). A was added to B via cannula, avoiding to cannulate too much zinc powder and the reaction mixture was stirred under ultrasound for 48 h (45 °C, 42 kHz, 0.47W/cm²). The resulting mixture was then filtered through Celite® and rinsed with EA. The organic phase was washed with water, aq. NH₄Cl, saturated aq. NaHCO₃ and dried over MgSO₄. The organic phase was filtered and concentrated under vacuum. The residue was purified by column chromatography (SiO₂, PE:EA 8:2) to give the corresponding propargylated pentitols as a mixture of two diasteromers.

**Procedure B:**

In a 10-mL single-necked round-bottomed flask under argon atmosphere was inserted zinc dust (96.2 mg, 1.47 mmol) and iodine (11.2 mg, 0.04 mmol). The flask was placed under vacuum atmosphere and the vessel was heated with an electric heat gun during 5 min. The argon atmosphere was installed de novo and the vessel allowed reaching room temperature. The cycle was repeated once and dry THF (4 mL) was added followed by 3-bromo-1-trimethylsilyl-1-propyne (53 \( \mu \)L, 0.32 mmol) and \( N\)-Benzyl-2,3,5-tri-O-benzyl-α/β-D-xylofuranosylamine derivative (0.10 mmol) under argon atmosphere. The reaction mixture was
stirred under ultrasound for 48 h (45 °C, 42 kHz, 0.47W/cm²). The resulting mixture was then filtered through Celite® and rinsed with EA. The organic phase was washed with water, aq. NH₄Cl, saturated aq. NaHCO₃ and dried over MgSO₄. The organic phase was filtered and concentrated under vacuum. The residue was purified by column chromatography (SiO₂, PE: EA 8:2) to give the corresponding propargylated pentitols as a mixture of two diastereomers.

1-C-(1R)- and 1-C-(1S)-1-(3-trimethylsilyl-2-propynyl)-2,3,5-tri-O-benzyl-1-benzylamino-1-deoxy-1-arabinitol (1R)-4 and (1S)-4:

Procedure A. Colourless oil (30 mg, 47.5%). 9:1 mixture of diastereomers assumed to be C₁R and C₁S respectively based on Cram Chelate control mechanism. Rf 0.5 (SiO₂, PE:EA 8:2). [α]D²⁰ = −12.7° (CHCl₃, c = 1.1 g/100 mL). 1H NMR (400 MHz, CDCl₃/TMS): δ (major diastereomer) = 7.40-7.15 (m, 20 H, H Ar), 4.76-4.44 (m, 7 H, 3 × OCH₂Ph + OH or NH), 4.02-3.96 (m, 1 H, H 4), 3.93 (dd, J = 7.5, 3.5 Hz, 1 H, H 3), 3.87 (d, J = 12.4 Hz, 1 H, 0.5 × NHCH₂Ph), 3.75 (dd, J = 8.3, 3.4 Hz, 0.9 H, H 2), 3.70-3.58 (m, 3 H, H 5 + H 5′ + 0.5 × NHCH₂Ph), 3.10 (dt, J = 8.6, 4.5 Hz, 1 H, H1), 2.83-2.68 (m, 2 H, CH₂ propargyl), 0.21-0.06 (m, 9 H, TMS). 13C NMR (101 MHz, CDCl₃/TMS): δ = 140.0 (C, C Ar), 138.8 (C, C Ar), 138.5 (C, C Ar), 138.3 (C, C Ar), 128.6-127.3 (CH, CH Ar), 104.0 (C, =C₈), 88.1 (C, C 7≡), 80.4 (CH, C 2), 79.2 (CH, C 3), 74.6 (CH₂, OCH₂Ph), 73.9 (CH₂, OCH₂Ph), 73.5 (CH₂, OCH₂Ph), 71.7 (CH₂, C 5), 70.7 (CH, C 7), 57.2 (CH, C 3), 51.2 (CH₂, NHCH₂Ph), 21.1 (CH₂, C 6), 0.3 (CH₃, TMS). IR (film): ν = 3029, 2862, 2170, 1496, 1453, 1308, 1249, 1091, 1027, 842, 757, 696 cm⁻¹. LRMS (ESI): m/z calcd. for C₃₉H₄₈NO₄Si [M + H]⁺ 622.334712; found 622.5. HRMS (ESI): m/z calcd. for C₃₉H₄₈NO₄Si [M + H]⁺ 622.334712; found: 622.334598.

1-C-(1R)- and 1-C-(1S)-1-(3-trimethylsilyl-2-propynyl)-2,3,5-tri-O-benzyl-1-benzylamino-1-deoxy-D-xylitol (1R)-6 and (1S)-6:

Procedure A. Colourless oil (1.5 g, 62%). (1R)-6: (1S)-6 8:2 mixture of diastereomers. Rf = 0.35 (SiO₂, PE:EA 8:2). [α]D²⁰ = +19.1° (CHCl₃, c = 0.84 g/100 mL). 1H NMR (400 MHz, CDCl₃/TMS): δ (major diastereomer) = 7.36-7.19 (m, 20 H, H Ar maj + H Ar min), 4.71-4.34 (m, 6 H, 3 × OCH₂Ph maj + 3 × OCH₂Ph min), 4.12 (d, J = 6.5 Hz, 0.8 H, H₂ maj), 4.11-4.08 (dd, J = 8.2, 5.8 Hz, 0.8 H, H 4 maj), 4.06-4.00 (m, 0.2 H, H 4 min), 3.88 (dd, J = 12.5 Hz, 0.2 H, 0.5 × NHCH₂Ph maj), 3.85 (d, J = 12.1 Hz, 0.8 H, 0.5 × NHCH₂Ph min), 3.82-3.80 (m, 0.2 H, H 2 min), 3.78 (br d, J = 6.6 Hz, 0.8 H, H 3 maj), 3.70-3.62 (m, 2.2 H, H 5 maj + H 5′ min + H 5′ maj + H 3 min), 3.33 (dd, J = 9.4, 3.6 Hz, 0.8 H, H 1 maj), 3.08 (dd, J = 12.0, 4.0 Hz, 0.2 H, H 1 min), 2.84-2.71 (m, 1 H, H₆ min + H₆ maj), 2.70-2.63 (m, 0.2 H, H₆′ min), 2.48 (dd, J = 16.7, 9.5 Hz, 0.8 H, H₆′ maj), 0.19-0.06 (m, 9 H, TMS maj + TMS min). 13C NMR (101 MHz, CDCl₃/TMS): δ = 139.1 (C, C Ar maj), 138.7 (C, C Ar maj), 138.6 (C, C Ar maj), 138.5 (C, C Ar min), 138.4 (C, C Ar min), 138.2 (C, C Ar maj), 138.1 (C, C Ar min), 137.9 (C, C Ar maj), 128.8-127.5 (CH, CH Ar maj + CH Ar min), 104.2 (C, =C₈ maj), 103.7 (C, =C₈ min), 88.0 (C, C 7≡ min), 87.5 (C, C 7≡ maj), 79.0
1-C-(1R)- and 1-C-(1S)-(3-trimethylsilyl-2-propynyl)-N-benzyl-2,3,5-tri-O-benzyl-1,4-dideoxy-1,4-imino-L-arabinitol (7):

In a single-necked round-bottomed flask surrounded by a reflux condenser, 6 (1.0 g, 1.61 mmol) and pyridine (18 mL) were introduced under argon atmosphere. Activated 4 Å molecular sieves were added and the reaction mixture was stirred for 40 min at room temperature (ca. 20°C). Then, methanesulfonyl chloride (0.31 mL, 4.0 mmol) was added and the mixture was stirred further at 100 °C for 2 h. The crude mixture was filtered through Celite® and the cake washed with EA. The filtrate was concentrated in vacuo, the residue suspended in EA (50 mL) and the organic phase was washed with water (50 mL) and dried over MgSO4. The solid was removed and the filtrate was concentrated in vacuo and co-evaporated three times with toluene. After purification by column chromatography (SiO2, PE: EA 9:1) 7 was obtained as slight yellow oil (0.728 g, 75%). 8:2 mixture of diastereomers (1R)-7: (1S)-7. Rf 0.68 (SiO2, PE: EA 8:2). [α]D20 = −14.5° (CHCl3, c = 0.4 g/100 mL). 1H NMR (400 MHz, CDCl3/TMS): δ = 7.39-7.14 (m, 20 H, H Ar maj + H Ar min), 4.60-4.22 (m, 6 H, 3 × OCH2Ph maj + 3 × OCH2Ph min), 4.12-4.06 (m, 0.4 H, 0.5 × NCH2Ph min + H2 min), 3.97 (d, J = 10.9 Hz, 0.8 H, 0.5 × NCH2Ph maj), 3.95 (br s, 0.8 H, H2 maj), 3.94-3.91 (m, 0.2 H, H3 min), 3.88 (br s, 0.8 H, H3 maj), 3.76 (d, J = 13.9 Hz, 0.8 H, 0.5 × NCH2Ph maj), 3.71 (d, J = 14.6 Hz, 0.2 H, 0.5 × NCH2Ph min), 3.58-3.53 (m, 0.4 H, H5 min + H5’ min), 3.38-3.27 (m, 1.8 H, H1 min + H1 maj + H4 maj), 3.26-3.20 (m, 0.2 H, H4 min), 3.16-3.07 (m, 1.6 H, H4 maj + H5’ maj), 2.56 (dd, J = 16.6, 9.3 Hz, 0.8 H, H6 maj), 2.59-2.44 (m, 0.2 H, H6 min), 2.34 (br s, 0.2 H, H6’ min), 2.40 (dd, J = 16.6, 5.1 Hz, 0.8 H, H6’ maj), 0.19-0.05 (m, 9 H, TMS maj + TMS min). 13C NMR (101 MHz, CDCl3/TMS): δ = 139.6 (C, CAr NBn min), 139.5 (C, CAr NBn maj), 138.7 (C, CAr OBn min), 138.7 (C, CAr OBn maj), 138.5 (C, CAr OBn min), 138.5 (C, CAr OBn maj), 138.5 (C, CAr OBn maj), 129.2-125.4 (CH, CH Ar maj + CH Ar min), 106.0 (C, =C8 maj), 105.2 (C, =C8 min), 86.8 (C, C7 = min), 86.3 (CH, C2 min), 86.0 (CH, C3 min), 85.4 (C, C7 = maj), 83.5 (CH, C2 maj), 82.7 (CH, C3 maj), 73.3 (CH2, OCH2Ph min), 73.0 (CH2, OCH2Ph maj), 72.7 (CH2, OCH2Ph maj), 72.0 (CH2, C5 maj), 71.7 (CH2, OCH2Ph min), 71.6 (CH2, OCH2Ph min), 71.0 (CH2, OCH2Ph maj), 70.6 (CH2, C5 min), 69.7 (CH, C4 maj), 66.5 (CH, C1 maj), 65.2 (CH, C1 min), 63.8 (CH, C1 min), 59.0 (CH2, NCH2Ph maj), 51.4 (CH2, NCH2Ph min), 20.8 (CH2, C6 maj), 19.5 (CH2, C6 min), 0.3 (CH3, TMS maj + TMS min). IR (film): ν = 3029, 2858, 2172, 1495, 1453, 1363, 1248, 1205, 1097, 1071, 1027, 908, 839, 731, 695, 645 cm−1. LRMS (ESI): m/z calcd. for C39H48NO4Si [M + H]+ 622.334712, found 622.334712; m/z calcd. for C39H48NO3Si [M + H]+ 604.324147, found 604.324147.
1-C-(1R)- and 1-C-(1S)-1-(2-propynyl)-N-benzyl-2,3,5-tri-O-benzyl-1,4-dideoxy-1,4-imino-L-arabinitol (1R)-8 and (1S)-8:

To a solution of 7 (0.7 g, 1.16 mmol) in methanol (10.5 mL) was added K$_2$CO$_3$ (186.5 mg, 1.35 mmol) at room temperature. After stirring for 6 h, the solvent was removed under reduced pressure and the mixture was purified by column chromatography (SiO$_2$, PE: EA 8:2). 8 was obtained (0.57 g, 92%) as a yellowish oil, mixture of diastereomers (dr 8:2 (1R)-8: (1S)-8, each having respectively two rotamers (A and B and C and D; not assigned). R$_f$ 0.63 (SiO$_2$, PE:EA 8:2). [α]$_D^{20}$ = +7.4° (CHCl$_3$, c = 1.0 g/100 mL). $^1$H NMR (400 MHz, CDCl$_3$/TMS): δ = 7.38-7.14 (m, 20 H, H$_{Ar}$ maj + H$_{Ar}$ min), 4.55-4.41 (m, 4.3 H, 2 × OCH$_2$Ph maj + 3 × OCH$_2$Ph min), 4.36 (d, J = 12.1 Hz, 0.8 H, 0.5 × OCH$_2$Ph maj), 4.24 (d, J = 12.1 Hz, 0.8 H, 0.5 × OCH$_2$Ph maj), 4.11-4.04 (m, 0.4 H, H$_2$ min + 0.5 × NCH$_2$Ph min), 3.99-3.92 (m, 1.8 H, 0.5 × NCH$_2$Ph maj + 0.5 × NCH$_2$Ph min), 3.56-3.52 (m, 0.4 H, H$_5'$ min + H$_5'$ min), 3.36-3.26 (m, 1.8 H, H$_1$ maj + H$_5$ maj + H$_1$ min), 3.26-3.21 (m, 0.2 H, H$_4$ min), 3.16-3.07 (m, 1.7 H, H$_4$ maj + H$_5$ maj), 2.55 (dd, J = 9.7, 2.6 Hz, 0.3 H, H$_6$ maj rot A), 2.51 (dd, J = 9.6, 2.6 Hz, 0.5 H, H$_6$ maj rot B), 2.52-2.49 (m, 0.02 H, H$_6$ min rot C), 2.47 (dd, J = 4.3, 2.7 Hz, 0.12 H, H$_6$ min rot D), 2.43 (dd, J = 8.9, 2.6 Hz, 0.11 H, H$_6'$ min rot D), 2.39 (dd, J = 8.9, 2.7 Hz, 0.05 H, H$_6'$ min rot C), 2.35 (dd, J = 4.6, 2.7 Hz, 0.5 H, H$_6'$ maj rot B), 2.31 (dd, J = 4.6, 2.7 Hz, 0.3 H, H$_6'$ maj rot A), 1.93 (t, J = 2.6 Hz, 0.1 H, H$_8$ min), 1.89 (t, J = 2.6 Hz, 0.8 H, H$_8$ maj). $^{13}$C NMR (101 MHz, CDCl$_3$/TMS): δ = 139.4 (C, C$_{Ar}$ NBn maj), 139.4 (C, C$_{Ar}$ NBn min), 138.6 (C, C$_{Ar}$ OBn maj), 138.6 (C, C$_{Ar}$ OBn min), 138.5 (C, C$_{Ar}$ OBn maj), 138.4 (C, C$_{Ar}$ OBn min), 138.3 (C, C$_{Ar}$ OBn maj), 138.3 (C, C$_{Ar}$ OBn min), 129.2-126.9 (CH, CH$_{Ar}$ maj + CH$_{Ar}$ min), 86.0 (CH, C$_2$ min), 85.8 (CH, C$_1$ min), 82.9 (CH, =C$_8$ maj rot A or B), 82.9 (CH, C$_5$ maj), 82.3 (CH, =C$_9$ min rot C or D), 82.3 (CH, C$_3$ maj), 73.3, 71.6 and 71.5 (CH$_2$, OCH$_2$Ph min), 73.0 (CH$_2$, OCH$_2$Ph maj), 72.4 (CH$_2$, OCH$_2$Ph maj), 72.0 (CH$_2$, C$_5$ maj), 70.9 (CH$_2$, OCH$_2$Ph maj), 70.5 (CH$_2$, C$_5$ min), 70.4 (CH, C$_8$ min rot C or D), 69.8 (CH, C$_4$ maj), 69.2 (CH, =C$_8$ maj rot A or B), 66.5 (CH, C$_1$ maj), 66.3 (CH, C$_4$ min), 63.8 (CH, C$_1$ min), 59.1 (CH$_2$, NCH$_2$Ph maj), 51.4 (CH$_2$, NCH$_2$Ph min), 19.0 (CH$_2$, C$_6$ maj), 18.1 (CH$_2$, C$_6$ min). IR (film): ν = 3304, 3029, 2859, 1495, 1453, 1363, 1337, 1204, 1098, 1071, 1027, 908, 819, 731, 696, 645 cm$^{-1}$. LRMS (ESI): m/z calcd. for C$_{36}$H$_{38}$NO$_3$ [M + H]$^+$ 532.284621; found: 532.284698. HRMS (ESI): m/z calcd. for C$_{36}$H$_{38}$NO$_3$ [M + H]$^+$ 532.284621; found: 532.284698.

**Standard Procedure for the Cu Click Chemistry:**

In a 25-mL single-necked round-bottomed flask, copper(II) sulphate pentahydrate (24.0 mg, 0.10 mmol) and sodium L-ascorbate (16.7 mg, 0.08 mmol) dissolved in water (4 mL) were added to a solution of the azide (0.22 mmol) and 8 (0.19 mmol) in DMF (4 mL). The mixture was stirred for 2h at room temperature, quenched with water and extracted with CH$_2$Cl$_2$ (50 mL). The combined organic layers were dried over MgSO$_4$ and concentrated under vacuum to afford green oil. The crude residue was purified by column chromatography.

1-C-(1R)-(1-(4-methyl-1,2,3-triazolyl)propanol)-2,3,5-tri-O-benzyl-1,4-dideoxy-1,4-imino-L-arabinitol (1R)-10a:

Amber oil (47 mg, 25%). One diastereomer isolated after purification over chromatography. R$_f$ 0.31 (SiO$_2$, PE: EA 100%). [α]$_D^{20}$ = -4.24° (CHCl$_3$, c = 1.1 g/100 mL). $^1$H NMR (400 MHz, CDCl$_3$/TMS): δ = 7.35-7.15 (m, 21 H, H$_{Ar}$ + H$_8$), 6.83 (s, 1 H, OH), 4.55 (d, J = 12.2 Hz, 1 H,
0.5 × OCH₂Ph), 4.46 (d, J = 12.3 Hz, 1 H, 0.5 × OCH₂Ph), 4.45 (d, J = 12.0 Hz, 1 H, 0.5 × OCH₂Ph), 4.38 (d, J = 12.0 Hz, 1 H, 0.5 × OCH₂Ph), 4.30 (dt, J = 6.7, 2.2 Hz, 2 H, H₁₁), 4.25 (d, J = 12.0 Hz, 1 H, 0.5 × OCH₂Ph), 4.01 (d, J = 12.0 Hz, 1 H, 0.5 × OCH₂Ph), 3.93 (br s, 1 H, H₃), 3.78-3.71 (m, 2 H, 0.5 × NCH₂Ph + H₂), 3.52 (t, J = 5.8 Hz, 2 H, H₂₀), 3.43 (dt, J = 9.2, 4.5 Hz, 1 H, H₁), 3.35 (dd, J = 12.0, 8.0 Hz, 1 H, H₅), 3.17-3.03 (m, 3 H, H₄ + H₅' + H₆), 2.92 (dd, J = 14.4, 4.4 Hz, 1 H, H₆'), 1.97 (p, J = 6.5 Hz, 2H, H₁₀). 13C NMR (101 MHz, CDCl₃/TMS): δ = 145.7 (C, C₇), 139.4 (C, C₉b), 138.7 (C, C₉b), 138.5 (C, C₉b), 138.3 (C, C₉b), 129.4-127.7 (CH, CH₃), 122.1 (CH, C₈), 82.4 (CH, C₉), 82.1 (CH, C₊), 73.0 (CH₂, OCH₂Ph), 71.9 (CH₂, C₅), 71.4 (CH₂, OCH₂Ph), 69.1 (CH, C₁), 66.6 (CH, C₁), 59.0 (CH₂, NCH₂Ph or C₉), 58.8 (CH₂, NCH₂Ph or C₉), 46.7 (CH₂, C₁₁), 32.6 (CH₂, C₁₀), 25.1 (CH₂, C₂). IR (neat): ν = 3342, 2919, 2861, 1453, 1097, 1068 cm⁻¹. LRMS (ESI): m/z calcd. for C₃₉H₄₅N₄O₄ [M + H]⁺ 633.343529; found: 633.4. HRMS (ESI): m/z calcd. for C₃₉H₄₅N₄O₄ [M + H]⁺ 633.343529; found: 633.343532.

1-C-(1R)- and 1-C-(1S)-1-(1-benzyl-4-methyl-1,2,3-triazolyl)-2,3,5-tri-O-benzyl-1,4-dideoxy-1,4-imino-L-arabinitol (1R)-10b and (1S)-10b:

Colourless oil (57 mg, 70%). (1R)-10b: (1S)-10b 8:2. Rₙ 0.6 (SiO₂, PE: EA 6:4). [α]D²⁰ = -7.4° (CHCl₃, c = 1.0 g/100 mL). ¹H NMR (400 MHz, CDCl₃/TMS): δ = 7.38-7.07 (m, 25 H, Hₐr maj + Hₐr min), 7.04 (s, 0.2 H, H₈ min), 6.80 (s, 0.8 H, H₈ maj), 5.39-5.25 (m, 2 H, PhCH₂N triazol maj + PhCH₂N triazol min), 4.52 (d, J = 12.2 Hz, 0.8 H, 0.5 × OCH₂Ph maj), 4.44 (d, J = 12.0 Hz, 0.8 H, 0.5 × OCH₂Ph maj), 4.39-4.33 (m, 1.6 H, OCH₂Ph maj), 4.23 (d, J = 12.1 Hz, 0.8 H, 0.5 × OCH₂Ph maj), 4.06-4.01 (m, 0.2 H, 0.5 × NCH₂Ph min), 3.98 (br s, 0.8 H, H₃ maj), 3.89 (br s, 0.8 H, H₃ maj), 3.82-3.68 (m, 0.4 H, H₂ min + 0.5 × NCH₂Ph min), 3.73 (d, J = 13.9 Hz, 0.8 H, 0.5 × NCH₂Ph maj), 3.67 (d, J = 4.6 Hz, 0.8 H, H₂ maj), 3.59-3.49 (m, 0.4 H, H₅ min + H₅' min), 3.47-3.38 (m, 1 H, H₁ maj + H₁ min), 3.35-3.25 (m, 1 H, H₅ maj + H₅' min), 3.15-3.00 (m, 2.6 H, H₆ maj + H₆' maj + H₆ₙ maj + H₆ₙ min), 2.96-2.87 (m, 0.2 H, H₆ₙ min), 2.90 (dd, J = 14.4, 4.5 Hz, 0.8 H, H₆' maj). ¹³C NMR (101 MHz, CDCl₃/TMS): δ = 146.2 (C, C₇ maj), 145.2 (C, C₇ min), 139.5 (C, C₉bNₙ maj), 139.4 (C, C₉bNₙ maj), 138.6 (C, C₉bNₙ maj), 138.5 (C, C₉bNₙ maj), 138.5 (C, C₉bNₙ maj), 138.4 (C, C₉bNₙ min), 138.2 (C, C₉bOₙ maj), 135.2 (C, C₉bNₙ triazol maj), 135.1 (C, C₉bN triazol maj), 129.3-126.8 (CH, CH₃ maj + CH₄ₙ min), 122.1 (CH, C₈), 121.7 (CH, C₈ maj), 86.1 (CH, C₂ min), 85.6 (CH, C₃ min), 82.5 (CH, C₈ maj), 82.1 (CH, C₈ maj), 73.3 (CH₂, OCH₂Ph min), 73.0 (CH₃, OCH₂Ph min), 73.1 (CH₂, OCH₂Ph maj), 71.9 (CH₂, C₉ maj), 71.5 (CH₂, OCH₂Ph maj), 71.4 (CH₂, OCH₂Ph min), 71.3 (CH₂, OCH₂Ph min), 70.8 (CH₂, OCH₂Ph maj), 69.2 (CH₂, C₅ min), 69.2 (CH, C₄ maj), 66.7 (CH, C₁ maj), 65.0 (CH, C₁ min), 64.7 (CH, C₄ min), 58.8 (CH₂, NCH₂Ph maj), 53.9 (CH₂, PhCH₂N triazol maj + PhCH₂N triazol min), 51.4 (CH₂, NCH₂Ph min), 25.2 (CH₂, C₆ maj), 24.9 (CH₂, C₆ min). IR (film): ν = 3029, 2860, 1495, 1453, 1361, 1265, 1207, 1070, 1027, 909, 820, 732, 696 cm⁻¹. LRMS (ESI): m/z calcd. for C₄₃H₄₅N₄O₃ [M + H]⁺ 665.348618; found: 665.5. HRMS (ESI): m/z calcd. for C₄₃H₄₅N₄O₃ [M + H]⁺ 665.348618; found: 665.348655.

1-C-(1R)- and 1-C-(1S)-1-(1-(4-methoxyphenyl)-4-methyl-1,2,3-triazolyl)-2,3,5-tri-O-benzyl-1,4-dideoxy-1,4-imino-L-arabinitol (1R)-10c and (1S)-10c:

Amber oil (75 mg, 58%). (1R)-10c: (1S)-10c 8:2. Rₙ 0.55 (SiO₂, PE: EA 6:4). [α]D²⁰ = -3.5° (CHCl₃, c = 0.81 g/100 mL). ¹H NMR (400 MHz, CDCl₃/TMS): δ = 7.47-7.40 (m, 2.7 H, Hₕp-
S10

OMePh maj + Hp-OMePh min), 7.38-7.12 (m, 27.4 H, H Bn maj + H Bn min + H 8 maj + H 8 min), 7.01-6.92 (m, 2.6 H, Hp-OMePh maj + Hp-OMePh min), 4.60-4.19 (m, 7.7 H, 3 × OCH 2Ph maj + 3 × OCH2Ph min), 4.11 (d, J = 14.5 Hz, 0.3 H, Hp-OMePh maj + Hp-OMePh min), 4.04 (d, J = 13.8 Hz, 1 H, 0.5 × NCH2Ph maj), 3.99 (t, J = 2 Hz, 0.2 H, H3 min), 3.96 (br s, 1 H, H3 maj), 3.88 (dd, J = 3.3, 1.7 Hz, 0.3 H, H2 maj, 3.86 (s, 3.9 H, OCH3 maj + OCH3 min), 3.84-3.81 (m, 0.3 H, 0.5 × NCH2Ph min), 3.81-3.75 (m, 2 H, 0.5 × NCH2Ph + H2 maj), 3.65-3.53 (m, 0.6 H, H 5 min + H 5' min), 3.49 (dt, J = 9.3, 4.4 Hz, 1.3 H, H1 maj + H1 min), 3.41-3.31 (m, 1.3H, H5 maj + H4 min), 3.20-3.10 (m, 3.3 H, H 4 maj + H 5' maj + H 6 maj + H 6 min), 2.98 (dd, J = 14.5, 1.3 Hz, H 6' maj + H 6' min). 13C NMR (101 MHz, CDCl 3/TMS): δ = 159.6 (C, C10 maj), 159.6 (C, C10 min), 146.2 (C, C7 maj), 145.3 (C, C7 min), 139.6 (C, C NBn min), 139.4 (C, C NBn maj), 138.6 (C, C OBn maj), 138.5 (C, C OBn min), 138.4 (C, C OBn min), 138.4 (C, C OBn min), 138.2 (C, C OBn min), 130.8 (C, C 9 maj), 129.4-127.1 (CH, CHOBn maj + CHOBn min), 122.1 (CH, CHp-OMePh maj), 122.0 (CH, CHp-OMePh min), 120.3 (CH, C 8 min), 120.1 (CH, C 8 maj), 114.7 (2 × CH, CHp-OMePh maj + CHp-OMePh min), 86.0 (CH, C 2 min or C 3 min), 85.8 (CH, C 2 min or C 3 min), 82.4 (CH, C 2 maj or C 3 maj) 82.1 (CH, C 2 maj or C 3 maj), 73.4 (CH2, CHOBn min), 73.1(CH2, OCH2Ph maj), 71.5 (CH2, OCH2Ph maj), 71.5 (CH2, OCH2Ph min), 71.9 (CH2, C 3 maj), 71.4 (CH2, OCH2Ph min), 70.9 (CH2, OCH2Ph maj), 69.4 (CH2, C 3 min), 69.2 (CH, C 4 maj), 66.6 (CH, C 1 maj), 65.0 (CH, C 1 min or C 4 min), 64.9 (CH, C 1 min or C 4 min), 58.8 (CH2, NCH2Ph maj), 55.7 (CH3, OCH3 maj), 51.5 (CH2, NCH2Ph min), 25.1 (CH2, C 6 maj), 24.9 (CH2, C 6 min). IR (neat): ν = 2857, 1520, 1452, 1363, 1253, 1100, 1071 cm–1. LRMS (ESI): m/z calcd. for C 43H45N4O4 [M + H] + 681.343498; found: 681.5. HRMS (ESI): m/z calcd. for C 43H45N4O4 [M + H] + 681.343532.

1-[(1R)-(1-(4-methyl-1,2,3-triazolyl)propanol)-1,4-dideoxy-1,4-imino-L-arabinitol (1R)-11a:

A vigorously stirred solution of (1R)-10a (39 mg, 0.06 mmol), 20% palladium hydroxide on carbon (20 mg) and acetic acid (2 mL) was degassed under vacuum and saturated with hydrogen (H2-filled balloon) five times. The suspension was stirred at rt (ca. 20 °C) for 20 h under slightly positive pressure of hydrogen (balloon) and then filtered over millipore membrane (0.2 μm). Solvent was evaporated and acetic acid co-evaporated with toluene and CH2Cl2. In order to remove residual benzyl groups, the hydrogenation process was repeated for 48 h. Pd(OH)2 was further added (20 mg) after 24 h. After work up (same as previously), crude compound was neutralized by stirring with resin Amberlite IRA-400 (OH– form) in methanol during 30 min. Filtration over sintered-glass funnel, and concentration of the organic phase in vacuo afforded (1R)-11a (13 mg; 81%) as a yellow oil. [α]D20 = −4.24° (CHCl3, c = 1.1 g/100 mL). 1H NMR (400 MHz, MeOD/TMS): δ = 7.79 (s, 1 H, H8), 4.47 (t, J = 7.0 Hz, 2 H, H11), 3.86 (dd, J = 3.7, 1.6 Hz, 1 H, H3), 3.78 (dd, J = 4.0, 1.6 Hz, 1 H, H2), 3.68 (dd, J = 10.8, 4.4 Hz, 1 H, H3), 3.65 (dd, J = 11.2, 4.8 Hz, 1 H, H2), 3.57 (t, J = 6.4 Hz, 2 H, H6), 3.44 (dt, J = 7.3, 4.0 Hz, 1 H, H1), 3.02 (dd, J = 14.7, 7.1 Hz, 1 H, H6), 2.96 (br q, J = 4.8 Hz, 1 H, H4), 2.88 (dd, J = 14.6, 7.5 Hz, 1 H, H6'), 2.09 (p, J = 6.5 Hz, 2 H, H10). 13C NMR (101 MHz, MeOD/TMS): δ = 146.6 (C, C3), 124.2 (CH, C3), 81.2 (CH, C3), 79.1 (CH, C2), 68.4 (CH, C4), 63.5 (CH2, C2), 62.5 (CH, C1), 59.3 (CH2, C6), 48.2 (CH2, C11), 34.0 (CH2, C10), 26.1 (CH2, C6). IR (neat): ν = 3265, 2922, 1652, 1557, 1429, 1216, 1060 cm–1. LRMS (ESI): m/z calcd. for C11H20N4O4 [M + H] + 273.155732; found: 273.0. HRMS (ESI): m/z calcd. for C11H20N4O4 [M + H] + 273.155429; found: 273.15532.
Hydrogenation Reaction to Prove the Stereoselectivity of the Propargylation Process:

2,3,5-tri-O-benzyl-1-C-propyl-1,4-dideoxy-1,4-imino-L-arabinitol (IR)-9 and (IS)-9:

A 10-mL single-necked round-bottomed flask was charged with 8 (50 mg, 0.094 mmol), 2-propanol (0.94 mL), triethylamine (Et3N, 3.3 μL, 0.023 mmol) and 10% Pd–C (14.12 mg) and the reaction mixture was stirred under hydrogen atmosphere for 5 days at 20 °C. The dark suspension was filtered through Celite®, the cake washed with methanol and the filtrate was concentrated in vacuo. (IS)-9 (3.13 mg, 7.4%, Rf = 0.4 (SiO2, PE:EA 3:7)) was separated from (IR)-9 (14.04 mg, 33.5%; Rf = 0.3 (SiO2, PE:EA 3:7)) through column chromatography over silica gel (PE:EA 3:7, L = 14.0 cm, Ø = 2.4 cm) to give the titled compounds as light orange oils.

(IS)-9: [α]D20 = −17.4° (CHCl3, c = 1.04 g/100 mL). 1H NMR (400 MHz, CDCl3/TMS): δ = 7.39-7.20 (m, 15 H, HAr), 4.59-4.46 (m, 6 H, 3 × OCH2Ph), 3.88 (br t, J = 3.4 Hz, 1 H, H3), 3.69 (dd, J = 5.0, 3.2 Hz, 1 H, H2), 3.52 (br d, J = 6.1 Hz, 2 H, H2), 3.39 (td, J = 6.1, 4.1 Hz, 1 H, H4), 3.10 (dt, J = 7.7, 5.4 Hz, 1 H, H1), 2.04 (br s, 1 H, NH), 1.62-1.22 (m, 4 H, H6 + H7), 0.91 (t, J = 7.1 Hz, 3 H, H8). 13C NMR (101 MHz, CDCl3/TMS): δ = 138.4 (C, CAr), 138.4 (C, CAr), 128.5 (CH, CHAr), 128.0 (CH, CHAr), 127.8-127.7 (CH, CHAr), 90.1 (CH, C2), 86.5 (CH, C3), 73.3 (CH2, OCH2Ph), 71.9 (CH2, OCH2Ph), 71.9 (CH2, OCH2Ph), 70.7 (CH2, C5), 61.9 (CH, C1), 61.9 (CH, C1), 36.6 (CH2, C6), 20.1 (CH2, C7), 14.3 (CH3, C8). IR (film): ν = 3030, 2862, 1496, 1454, 1362, 1205, 1092, 1072, 1028, 908, 733 cm−1. LRMS (ESI): m/z calcd. for C29H36NO3 [M + H]+ 446.268970; found: 446.5. HRMS (ESI): m/z calcd. for C29H36NO3 [M + H]+ 446.268973.

(IR)-9: [α]D20 = −34.3° (CHCl3, c = 0.96 g/100 mL). 1H NMR (400 MHz, CDCl3/TMS): δ = 7.39-7.20 (m, 15 H, HAr), 4.62-4.43 (m, 5 H, 2 × OCH2Ph + 0.5 OCH2Ph), 4.37 (d, J = 11.9 Hz, 1 H, 0.5 OCH2Ph), 3.82 (d, J = 3.8 Hz, 1 H, H3), 3.74 (d, J = 3.8 Hz, 1 H, H2), 3.63-3.50 (m, 2 H, H5), 3.28 (td, J = 5.5, 3.8 Hz, 1 H, H4), 3.13 (dt, J = 7.1, 3.8 Hz, 1 H, H1), 1.95 (br s, 1 H, NH), 1.70-1.51 (m, 2 H, H6), 1.46-1.23 (m, 2 H, H7), 0.92 (t, J = 7.3 Hz, 3 H, H8). 13C NMR (101 MHz, CDCl3/TMS): δ = 138.5 (C, CAr), 138.4 (C, CAr), 138.4 (C, CAr), 128.5 (CH, CHAr), 128.5 (CH, CHAr), 127.8-127.7 (CH, CHAr), 85.1 (CH, C3), 84.2 (CH, C2), 73.3 (CH2, OCH2Ph), 71.7 (CH2, OCH2Ph), 71.4 (CH2, C5), 70.9 (CH2, OCH2Ph), 64.7 (CH, C4), 62.1 (CH, C1), 31.0 (CH2, C6), 20.6 (CH2, C7), 14.5 (CH3, C8). IR (film): ν = 3030, 2862, 1496, 1454, 1361, 1205, 1092, 1028, 908, 733 cm−1. LRMS (ESI): m/z calcd. for C29H36NO3 [M + H]+ 446.268970; found: 446.5. HRMS (ESI): m/z calcd. for C29H36NO3 [M + H]+ 446.268973.
$^1$H-NMR (400 MHz) Analysis of α/β-D-arabinofuranosylamine ent-1

C$_{33}$H$_{35}$NO$_4$
MW = 509.64 g/mol
$^{13}$C-NMR (101 MHz) Analysis of $\alpha/\beta$-D-arabinofuranosylamine ent-1
\( ^1H\text{-NMR (400 MHz) Analysis of } \alpha/\beta-L\text{-arabinofuranosylamine}\) 1

\[\text{C}_{33}\text{H}_{35}\text{NO}_4, \text{MW} = 509.64 \text{ g/mol}\]
$^{13}\text{C-NMR}$ (101 MHz) Analysis of $\alpha/\beta$-L-arabinofuranosylamine 1

Chemical structure:

$\text{C}_{33}\text{H}_{35}\text{NO}_{4}$

MW = 509.64 g/mol
$^{13}$C-NMR (101 MHz) Analysis of $N$-Benzyl-$N$-(3-trimethylsilyl-2-propynyl)-L-arabinofuranosylamine 3

\[
\text{C}_{39}\text{H}_{45}\text{NO}_4\text{Si} \\
\text{MW} = 619.86 \text{ g/mol}
\]
$^{13}$C-NMR (101 MHz) Analysis of $N$-Benzyl-$N$-(3-trimethylsilyl-2-propynyl)-l-arabinofuranosylamine 3

$C_{39}H_{45}NO_4Si$  
MW = 619.86 g/mol
$^{1}$H-NMR (400 MHz) Analysis of 1-C-1-(3-trimethylsilyl-2-propynyl)-L-arabinitol 4

C$_{36}$H$_{47}$NO$_4$Si
MW = 621.88 g/mol

(1$R$)-4:(1$S$)-4 9:1
$^{13}$C-NMR (101 MHz) Analysis of 1-C-1-(3-trimethylsilyl-2-propynyl)-L-arabinitol 4

(1R)-4: (1S)-4 9:1

C$_{39}$H$_{47}$NO$_4$Si
MW = 621.88 g/mol
$^1$H-NMR (400 MHz) Analysis of N-Benzyl-2,3,5-tri-O-benzyl-$\alpha/\beta$-D-xylofuranosylamine 5

![N-Benzyl-2,3,5-tri-O-benzyl-$\alpha/\beta$-D-xylofuranosylamine 5](image)

$\text{C}_{33}\text{H}_{56}\text{NO}_4$

MW = 509.64 g/mol
$^{13}$C-NMR (101 MHz) Analysis of $N$-Benzyl-2,3,5-tri-$O$-benzyl-$\alpha/\beta$-$D$-xylofuranosylamine 5

\[ C_{33}H_{35}NO_4 \]

MW = 509.64 g/mol
$^{1}H$-NMR (400 MHz) Analysis of 1-C-1-(3-trimethylsilyl-2-propynyl)-D-xylitol 6

C$_{39}$H$_{47}$NO$_{4}$Si
MW = 621.88 g/mol

(1R)-6:(1S)-6 8:2
$^{13}$C-NMR (101 MHz) Analysis of 1-C-1-(3-trimethylsilyl-2-propynyl)-D-xylitol 6

(1R)-6:(1S)-6 8:2

C$_{39}$H$_{47}$NO$_4$Si
MW = 621.88 g/mol
$^{1}$H-NMR (400 MHz) Analysis of 1-C-1-(3-trimethylsilyl-2-propynyl)-1,4-imino-L-arabinitol 7

C$_{39}$H$_{45}$NO$_3$Si
MW = 603.87 g/mol

(1R)-7:(1S)-7 8:2
$^{13}$C-NMR (101 MHz) Analysis of 1-C-1-(3-trimethylsilyl-2-propynyl)-1,4-imino-L-arabinitol 7

C$_{39}$H$_{45}$NO$_3$Si
MW = 603.87 g/mol

(1R)-7: (1S)-7 8:2
$^1$H-NMR (400 MHz) Analysis of 2-propynyl-1,4-imino-\(L\)-arabinitol 8

\[
\text{R}^1: \text{R}^2 \quad 8:2
\]

\[
\text{C}_{36}\text{H}_{37}\text{NO}_3 \\
\text{MW} = 531.68 \text{ g/mol}
\]

(1\(R\))-8:(1\(S\))-8 8:2
$^{13}$C-NMR (101 MHz) Analysis of 2-propynyl-1,4-imino-L-arabinitol 8

$C_{36}H_{37}NO_3$

MW = 531.68 g/mol

$(1R)$-8:$(1S)$-8 8:2
$^1$H-NMR (400 MHz) Analysis of 1-C-(1S)-propyl-L-arabinitol (1S)-9 (first eluted fraction)
$^{13}$C-NMR (101 MHz) Analysis of $\text{1-C-(1S)-propyl-L-arabinitol (1S)-9} \text{ (first eluted fraction)}$
$^{1}H$-NMR (400 MHz) Analysis of 1-C-(1R)-propyl-L-arabinitol (1R)-9 (second eluted fraction)

C$_{29}$H$_{35}$NO$_{3}$

MW = 445.59 g/mol
$^{13}$C-NMR (400 MHz) Analysis of 1-C-(1R)-propyl-L-arabinitol (1R)-9 (second eluted fraction)

MW = 445.59 g/mol
NOESY Analysis of 1-C-(1R)-propyl-L-arabinitol (1R)-9 (second eluted fraction)

C$_{29}$H$_{35}$NO$_3$  
MW = 445.59 g/mol
\(^1\)H-NMR (400 MHz) Analysis of 1,4-imino-L-arabinitol 10b

C\(_{43}\)H\(_{44}\)N\(_4\)O\(_3\)
MW = 664.83 g/mol

(1R)-10b:(1S)-10b 8:2
$^{13}$C-NMR (101 MHz) Analysis of 1,4-imino-L-arabinitol 10b

\[ \text{C}_{43}\text{H}_{44}\text{N}_4\text{O}_3 \]
MW = 664.83 g/mol

(1R)-10b:(1S)-10b 8:2
$^1$H-NMR (400 MHz) Analysis of imino-L-arabinitol 10c

C$_{43}$H$_{44}$N$_4$O$_4$

MW = 680.83 g/mol

(1R)-10c:(1S)-10c 8:2
$^{13}$C-NMR (101 MHz) Analysis of imino-L-arabinitol $10c$

MW = 680.83 g/mol

C$_{43}$H$_{44}$N$_4$O$_4$

$(1R)$-$10c$:$(1S)$-$10c$ 8:2
$^{1}$H-NMR (400 MHz) Analysis of imino-L-arabinitol (1R)-10a
$^{13}$C-NMR (101 MHz) Analysis of imino-L-arabinitol (1R)-10a
$^1$H-NMR (400 MHz) Analysis of imino-L-arabinitol (1R)-11a

[Chemical structure image]

$\text{C}_{11}\text{H}_{20}\text{N}_4\text{O}_4$

MW $= 272.3$ g/mol
$^{13}$C-NMR (101 MHz) Analysis of imino-L-arabinitol (1R)-**11a**

\[ \text{MW} = 272.3 \text{ g/mol} \]