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Nucleoside Analogues from Branched-Chain Pyranosides

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Reaction of (pyranosid-3-yl)ethanal **2** with ethynylmagnesium bromide or lithium phenylacetylide in THF afforded (2*R*,*S*)-1-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)but-3-yn-2-ols **3a** and **3b**, respectively. Oxidation of **3a** and **3b** yielded the 1-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)but-3-yn-2-ones **4a** and **4b**, which upon treatment with hydrazine and hydrazine derivatives formed the 3-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)pyrazoles **5a**–**5d**. Compounds **4a** and **4b** also underwent reaction with amidinium and guanidinium salts under basic conditions to furnish the 4-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)pyrimidines **8a**–**8f**. Furthermore, treatment of **4a** and **4b** with 2-aminobenzimidazole yielded the 2-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)benzo[4,5]imidazo[1,2-*a*]pyrimidines **11a** and **11b**. Deprotection of **5a** and **8b** in two steps afforded 3(5)-(methyl 3-deoxy-α-D-altropyranosid-3-ylmethyl)-1*H*(2*H*)-pyrazole **7** and 4-(methyl 3-deoxy-α-D-altropyranosid-3-ylmethyl)-2-phenylpyrimidine **10**, respectively. Compound **11a** was treated with AcOH/H_2O to furnish 2-(methyl 2-*O*-benzyl-3-deoxy-α-D-altropyranosid-3-ylmethyl)benzo-[4,5]imidazo[1,2-*a*]pyrimidine **13**.

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Introduction

The development of strategies for the formation of *C*-nucleoside analogues is a topic of current interest in organic synthesis.[1] Iso-*C*-nucleosides constitute a class of nucleoside analogues in which the nucleobase is linked by a carbon–carbon bond to the sugar moiety through a carbon atom other than C1. Interest in the synthesis of iso-*C*-nucleosides as compounds that possess anticancer and antiviral activities is growing.[2,3] Examples of this subclass of nucleosides are relatively rare in the literature, but recently, intensified efforts have been observed.[4–9] Like *C*-nucleosides, iso-*C*-nucleosides often display numerous biological activities that are frequently connected with their increased hydrolytic and enzymatic stability. Nucleoside derivatives that contain a heteroatom or a methylene group as a spacer between the sugar unit and the heterocycle have been synthesized. Among these analogues, carbon-bridge derivatives have been found to act as glycosidase inhibitors.[10,11] Furthermore, connecting the sugar to the heterocyclic systems through carbon may have interesting pharmacological implications.[12–15]

In this paper we report the synthesis of a new series of iso-*C*-nucleosides from 2-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)ethanal **2** that contain spacers.

Results and Discussion

Compound **2** could be obtained in three steps from methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside **1** by reaction with allylmagnesium bromide,[16,17] benzylation of the 2-hydroxy group with benzyl bromide, sodium hydride, and tetrabutylammonium iodide[18,19] in THF, and oxidation of the resultant product with osmium tetraoxide/sodium periodate in 1,4-dioxan/water (10 : 1).[20]

Reaction of the branched-chain monosaccharide **2** with ethynylmagnesium bromide or lithium phenylacetylide in THF afforded, after 4 h at room temperature, butynols **3a** and **3b** as an inseparable mixture of diastereoisomers in 85 and 87% yield, respectively (Scheme 1). Disappearance of the aldehyde signals concurrently with the appearance of the new resonances for the alkyne carbon atoms in the ^{13}C NMR spectra clearly demonstrated the formation of the expected alcohols as *R*,*S* mixtures. A typical long-range coupling of 2.1 Hz between the acetylenic proton and H2 could be observed in the ^{1}H NMR spectrum of **3a**. Moreover, a

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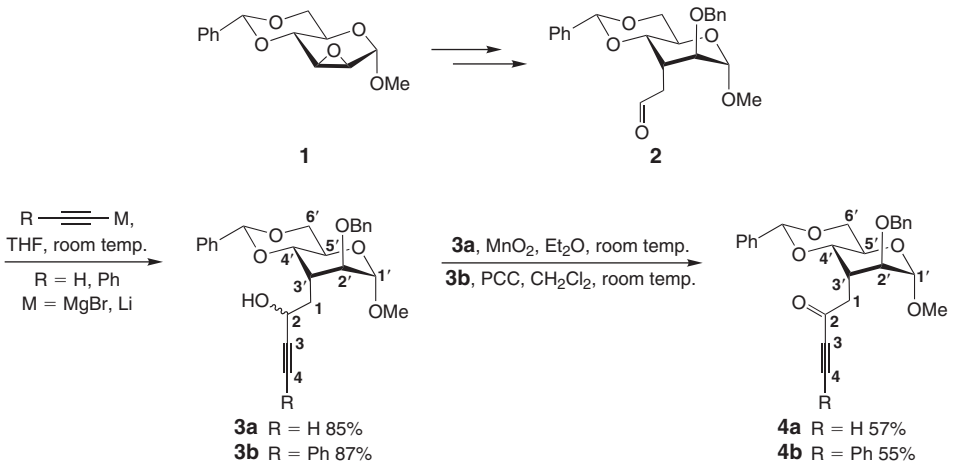


Scheme 1. Synthesis of 1-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)but-3-yn-2-ones **4a** and **4b**.

strong $C_{sp\text{-}H}$ absorption at 3257 cm^{-1} was observed in the IR spectrum of this compound.

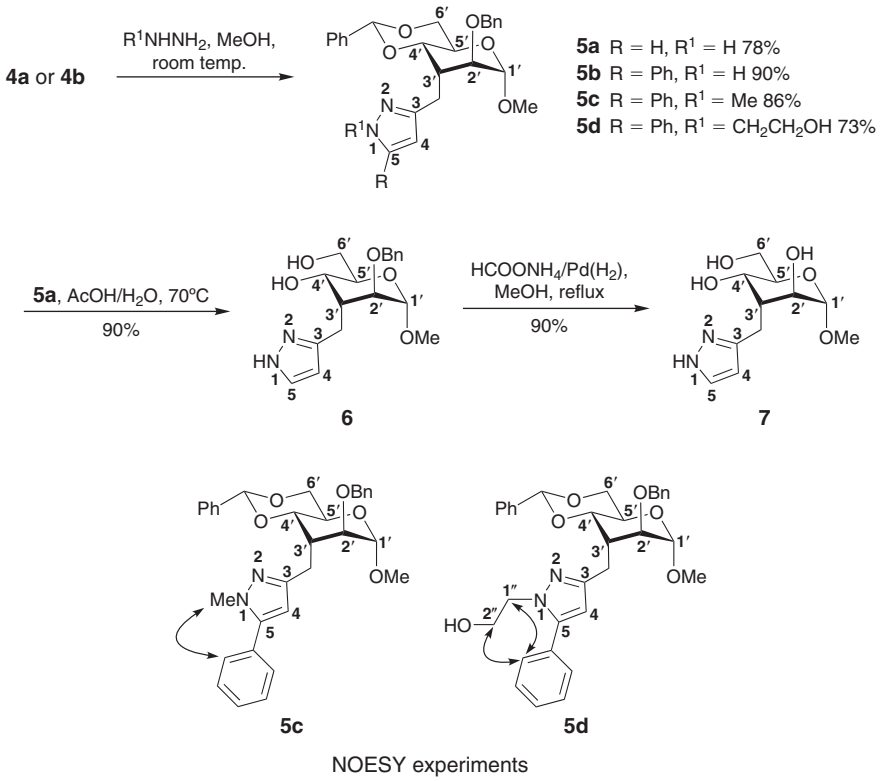
Acetylenic ketones are a versatile class of compounds which can be used as starting materials for the synthesis of numerous heterocycles.[21] In order to obtain the desired (pyranosid-3-yl)butynones, butynols **3a** and **3b** were oxidized with pyridinium chlorochromate (PCC) in dichloromethane to yield compounds **4a** and **4b** in 35 and 55% yield, respectively. The low yield of **4a** could be increased to 57% by using MnO_2 as the oxidizing agent in diethyl ether. All the analytical data were in accordance with the proposed structures. In particular, OH bands were absent in the IR spectra, while typical C═O signals appeared in the ^{13}C NMR spectra.

Treatment of **4a** and **4b** with hydrazine, methylhydrazine, and 2-hydrazinoethanol at room temperature in methanol resulted, after short reaction times, in the formation of the 3-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)pyrazoles **5a**–**5d** in good to excellent yields (70–90%, Scheme 2).

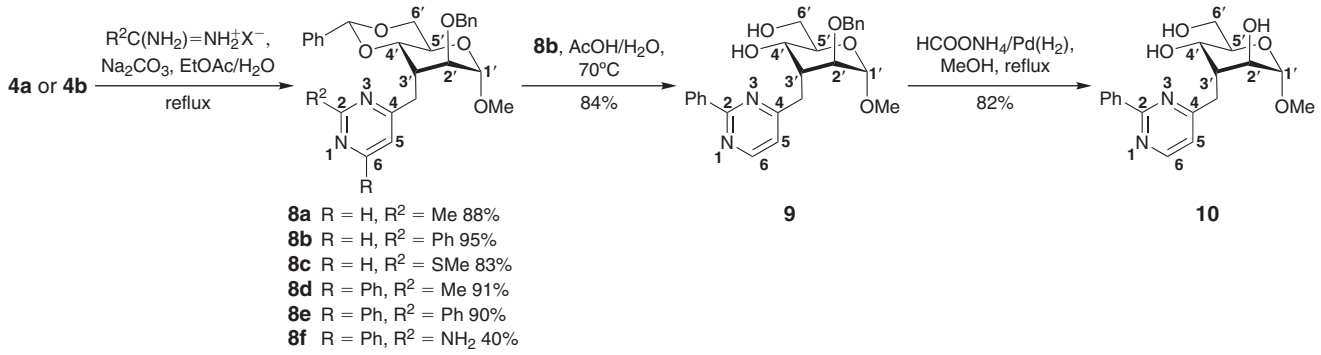
In accordance with literature,[22–24] the preferred position for the first nucleophilic attack at the acetylenic ketone should be the β-carbon atom. Nevertheless, this does not indicate the manner by which ynones will cyclize when allowed to react with unsymmetrical dinucleophiles. Bishop et al.[25] described a highly regioselective cyclization reaction of hydrazine derivatives with aryl-substituted acetylenic ketones. In our hands, with methylhydrazine and 2-hydrazinoethanol, **4a** gave a mixture of two possible regioisomeric pyrazoles that could not be separated. In contrast, reaction of the phenyl substituted ynone **4b** with these hydrazine derivatives followed a highly regioselective reaction pathway that resulted in the formation of pyrazoles **5c** and **5d** in good yields. The structures of pyrazoles **5a**–**5d** were confirmed from spectroscopic data. In particular, signals for a carbonyl group or the acetylenic carbon atoms could not be observed in the IR and ^{13}C NMR spectra. The position of the methyl and 2-hydroxyethyl substituents in the *N*-substituted pyrazoles **5c** and **5d** was determined by NOESY experiments. In the NOESY spectrum of **5c** a correlation was found between the *N*-methyl group and the *ortho* protons of the phenyl ring attached to the pyrazole system. The analogous *ortho* phenyl protons in **5d** gave a similar correlation with the four methylene hydrogen atoms of the 2-hydroxyethyl substituent.

We examined the deprotection of compound **5a** over two steps. Cleavage of the benzylidene group was performed in a mixture of acetic acid and water to afford the 3(5)-(methyl 2-*O*-benzyl-3-deoxy-α-D-altropyranosid-3-ylmethyl)-1*H*(2*H*)-pyrazole **6** in 90% yield. The NMR spectra showed the absence of the benzylidene group, while the mass spectrum displayed a molecular peak that corresponded with the proposed structure. Subsequently, the 2-*O*-benzyl group in compound **6** could be removed by catalytic transfer hydrogenation using 10% palladium on carbon and ammonium formate as the hydrogen donor.[26] The iso-*C*-nucleoside **7** was thus obtained as a white solid in 90% yield. The value determined for the $^3J_{4',5'}$ coupling constant (approx. 8 Hz), which suggests an axial–axial disposition, along with the small $^3J_{1',2'}$ and $^3J_{2',3'}$ values (approx. 2–5 Hz) clearly indicated the presence of the preferred $^1C_4$ conformation in compounds **6** and **7**.

Addlington et al.[27] reported the reaction of acetylenic ketones with amidinium salts using ethyl acetate/water or acetonitrile as solvent and sodium carbonate as base to obtain the corresponding pyrimidines. Following this strategy, ynones **4a** and **4b** were allowed to react with acetamidinium chloride, benzamidinium chloride, *S*-methylisothiouronium sulfate, and guanidinium chloride to afford the corresponding pyrimidine-spacered iso-*C*-nucleosides **8a**–**8f** (Scheme 3). All the reactions, except for the one in which guanidinium chloride was used, proceeded in high yields. As expected, signals for the acetylenic carbon atoms and the carbonyl group were not observed in the ^{13}C NMR spectra. Moreover, mass spectra and elemental analyses were in agreement with the proposed structures.



Scheme 2. Synthesis of 3-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)-pyrazoles **5a**–**5d** and deprotection of **5a**.



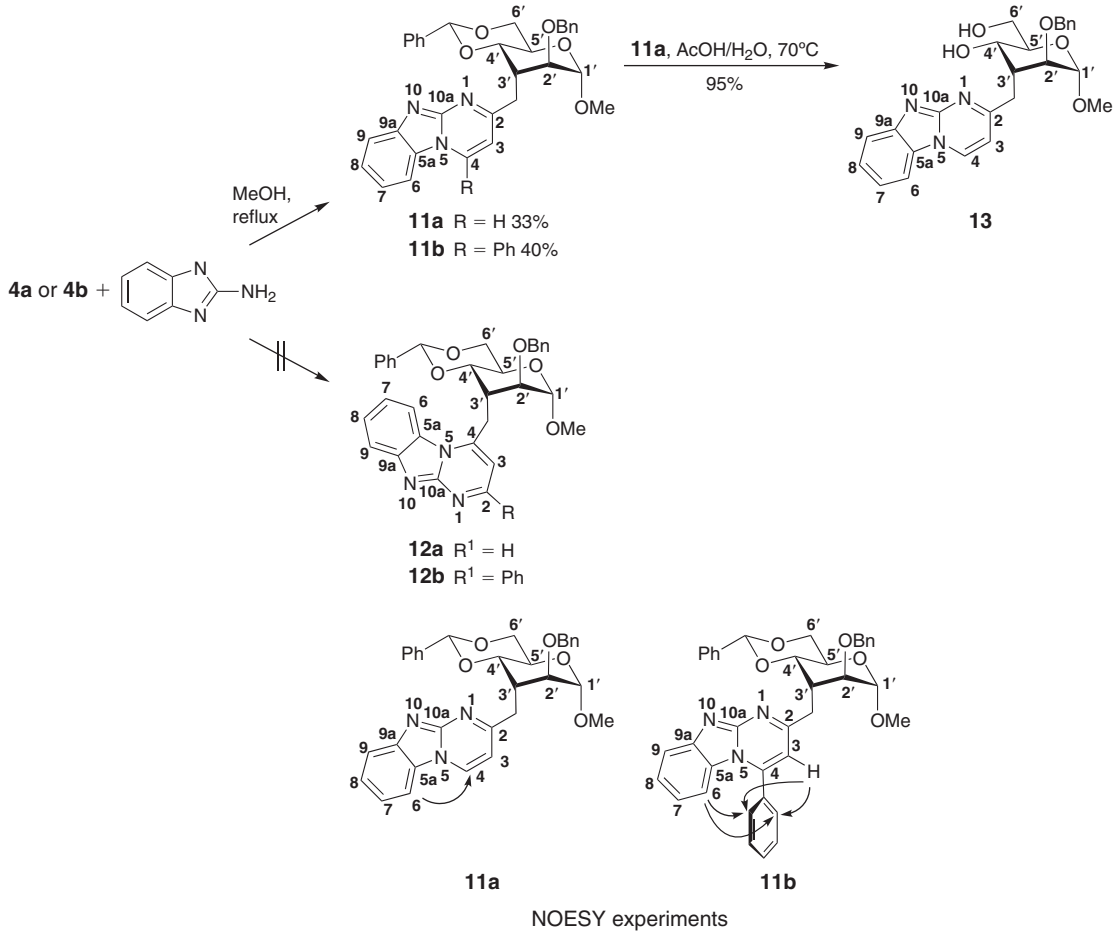
Scheme 3. Synthesis of 4-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)pyrimidines **8a**–**8f** and deprotection of **8b**.

Deprotection of compound **8b** by treatment with aqueous acetic acid afforded 4-(methyl 2-*O*-benzyl-3-deoxy-α-D-altropyranosid-3-ylmethyl)-6-phenylpyrimidine **9** in 84% yield. Compound **9** was subsequently allowed to react with 10% palladium on carbon and ammonium formate to furnish 4-(methyl 3-deoxy-α-D-altropyranosid-3-ylmethyl)-6-phenylpyrimidine **10** in 82% yield. The $^{1}C_{4}$ conformation of this compound was confirmed by NMR spectroscopy.

Compounds **4a** and **4b** were also allowed to react with 2-aminobenzimidazole to afford iso-*C*-nucleosides with a fused heterocyclic unit. From the proposed reaction pathway, isomers **7a** and **7b**, as well as **8a** and **8b**, respectively, were expected to be formed (Scheme 4). However, the ^{13}C NMR spectra of the isolated compounds only showed the presence of compounds **7a** and **7b**, the structures of which were confirmed with the help of NOESY spectroscopy. A correlation was observed for **7a** between H4 and H6, while in the NOESY spectrum of compound **7b**, cross peaks were found between the *ortho* protons of the 4-phenyl ring and H3 and H6. Moreover, the *ortho* hydrogen atoms displayed different chemical shifts (δ 7.40 and 7.24); this indicates that rotation of the phenyl ring around the bond axis is hindered. In the ^{1}H NMR spectrum, the signal for H6 was significantly shifted upfield in comparison to the signal for H9. This is caused by the anisotropy effect of the phenyl ring.

All the remaining spectroscopic data, including mass spectra, were in accordance with the proposed structures.

Reaction of compound **11a** with aqueous acetic acid afforded 2-(methyl 2-*O*-benzyl-3-deoxy-α-D-altropyranosid-3-ylmethyl)benzo[4,5]imidazo[1,2-*a*]pyrimidine **13** in 95%



Scheme 4. Synthesis of 2-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)benzo[4,5]imidazo-[1,2-*a*]pyrimidines **11a** and **11b**, and deprotection of **8b**.

yield. Unfortunately, attempts to remove the benzyl protecting group in compound **13** were unsuccessful.

Conclusions

We described here the synthesis of iso-*C*-nucleosides based on 1-(α-D-altropyranosid-3-yl)but-3-yn-2-ones. These compounds should be suitable to test for antiviral activity in that they are unusual nucleoside analogues of pyrazoles, pyrimidines, and benzo[4,5]imidazo[1,2-*a*]pyrimidine that are attached with a pyranosid-3-yl unit through a methylene group spacer.

Experimental

Instrumentation

Melting points were measured with a Boëtius apparatus and are corrected. Specific rotations were determined with a Polar LμP polarimeter (IBZ Messtechnik). IR spectra were recorded with a Nicolet 205 FT-IR spectrometer. ^{1}H NMR (500.13, 300.13, and 250.13 MHz) and ^{13}C NMR (125.7, 75.5, and 62.9 MHz) spectra were recorded on Bruker AVANCE 500, ARX 300, and AC 250 instruments using $CDCl_3$ as solvent. The spectra were calibrated to TMS (internal ^{1}H, δ 0) and $CDCl_3$ (^{13}C, δ 77.0) signals. The ^{13}C NMR signals were assigned by DEPT and/or two-dimensional ^{13}C–^{1}H correlation spectra. For example, HMBC spectra were recorded for compounds **5b**, **6f**, **7a**, and **7b** in order to assign the quaternary carbon signals. The two-dimensional NOESY spectra for the structure elucidation of **5** and **7** were recorded on an AVANCE 500 spectrometer using a mixing time of 1 s. Mass spectra were recorded on an AMD 402/3 spectrometer (AMD Intectra GmbH). Merck silica gel 60 (230–400 mesh) was used for chromatography. TLC was performed on silica gel 60 GF_{254} (Merck) using UV light and charring with sulfuric acid for detection. Elemental analyses were performed on a Leco CHNS-932 instrument. Solvents were distilled, and if necessary, dried using standard procedures.

*Preparation of (2*R,S*)-1-(Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)-but-3-yn-2-ol **3a***

Ethynylmagnesium bromide (10 mL, 0.5 M solution in THF) was added dropwise to a solution of 2-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)ethanal **2** (0.8 g, 2.0 mmol) in dry THF (10 mL). The mixture was stirred for 4 h at room temperature, poured into water (20 mL), and extracted with dichloromethane (3 × 20 mL). The combined organic phases were then washed with water (2 × 20 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography (toluene/EtOAc, 10 : 1) to afford **3a** as a colourless syrup (0.406 g, 85%; *R*-to-*S* ratio 2 : 3), R_F 0.42 (toluene/EtOAc, 10 : 1), $[\alpha]_D^{22}$ +54.8 (*c* 0.5 in $CHCl_3$) (Found: C 70.7, H 6.8. $C_{25}H_{28}O_6$ requires C 70.7, H 6.7%). ν_{max}/cm^{-1} 3454 (OH), 3257 (CH). δ_H (250 MHz; $CDCl_3$) 7.47–7.26 (10H, m, Ph), 5.61 and 5.59 (1H, 2 s, CHPh), 4.66 and 4.64 (1H, 2 br s, H1′), 4.65 and 4.64 (2H, 2 ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.53–4.41 (1H, m, H2), 4.29 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.21 and 4.19 (1H, 2 dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4'}$ 5.2, H4′), 3.97 and 3.96 (1H, 2 dt, $^3J_{5',6'ax} \approx {}^3J_{4',5'}$ 9.8 and $^3J_{5',6'eq}$ 5.0, H5′), 3.81 and 3.80 (1H, 2 t, $^2J_{6'ax,6''eq}$ 10.0 and $^3J_{5',6'ax}$ 9.8, H6′ax), 3.72 and 3.63 (1H, 2 dd, $^3J_{2',3'}$ 2.0 and $^3J_{1',2'}$ 1.0, H2′), 3.36 and 3.35 (3H, 2 s, OMe), 2.98–2.82 and 2.73–2.60 (1H, 2 m, H3′), 2.43

and 2.42 (1H, 2 d, $^4J_{2,4}$ 2.1, H4), 2.35–2.23 and 2.10–1.96 (2H, 2 m, H1). δ_C (62.9 MHz; $CDCl_3$) 137.7, 137.7, 137.4, and 137.1 (*ipso*-Ph), 129.2, 129.0, 128.5, 128.4, 127.9, and 127.8 (*o*-, *m*-, and *p*-Ph), 102.2 and 101.9 (CHPh), 100.2 and 100.1 (C1′), 84.9 and 84.7 (C3), 78.3 and 77.5 (C2′), 76.0 (C4′), 73.1 and 72.8 (C4), 71.7 (CH_2Ph), 69.4 (C6′), 61.6 and 61.4 (C2), 59.4 and 59.4 (C5′), 55.1 (OMe), 36.0 and 35.6 (C3′), 33.6 and 33.5 (C1). *m/z* (CI) 425 (10%, $[M+H]^{+\bullet}$).

*(2*R,S*)-1-(Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)-4-phenyl-but-3-yn-2-ol* ***3b***

Reaction of **2** (0.8 g, 2.0 mmol) with lithium phenylacetylide (8 mL, 1.0 M solution in THF) was carried out as described above for the preparation of **3a**. The crude product was purified by column chromatography (toluene/EtOAc, 6 : 1) to afford **3b** as a white solid (0.870 g, 87%; *R*-to-*S* ratio 2 : 3), mp 45–48°C, R_F 0.45 (toluene/EtOAc, 6 : 1), $[\alpha]_D^{24}$ +40.2 (*c* 1 in $CHCl_3$) (Found: C 74.4, H 6.6. $C_{31}H_{32}O_6$ requires C 74.4, H 6.4%). ν_{max} (KBr)/cm^{-1} 3453 (OH). δ_H (250 MHz; $CDCl_3$) 7.43–7.12 (15H, m, Ph), 5.61 and 5.60 (1H, 2 s, CHPh), 4.78–4.65 (1H, br s, H2), 4.67 and 4.66 (1H, 2 br s, H1′), 4.64 and 4.63 (2H, 2 ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.29 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0, $^3J_{5',6'eq}$ 5.0, H6′eq), 4.22 and 4.21 (1H, 2 dd, $^3J_{4',5'}$ 10.0, $^3J_{3',4'}$ 5.0, H4′), 3.99 and 3.98 (1H, 2 dt, $^3J_{5',6'ax} \approx {}^3J_{4',5'}$ 10.0, $^3J_{5',6'eq}$ 5.0, H5′), 3.82 and 3.81 (1H, 2 t, $^3J_{5',6'ax} \approx {}^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.80 and 3.68 (1H, 2 dd, $^3J_{2',3'}$ 2.0 and $^3J_{1',2'}$ 1.0, H2′), 3.36 and 3.35 (3H, 2 s, OMe), 2.99–2.88 and 2.83–2.68 (1H, 2 m, H3′), 2.42–2.30 and 2.20–2.06 (2H, 2 m, H1). δ_C (62.9 MHz; $CDCl_3$) 137.8, 137.7, 137.7, and 137.4 (*ipso*-Ph), 131.6, 131.6, 129.1, 129.0, 128.9, 128.4, 128.3, 128.3, 128.2, 128.2, 127.7, 127.7, 127.6, 126.1, and 125.2 (*o*-, *m*-, and *p*-Ph), 122.6 (*ipso*-PhC≡C), 102.1 and 101.9 (CHPh), 100.2 and 100.2 (C1′), 90.1 and 90.0 (C3), 85.1 and 84.7 (C4), 78.3 and 77.5 (C2′), 76.1 (C4′), 71.7 and 71.6 (CH_2Ph), 69.4 (C6′), 62.2 and 62.0 (C2), 59.4 and 59.3 (C5′), 55.0 (OMe), 36.0 and 35.7 (C3′), 33.7 and 33.6 (C1). *m/z* (70 eV) 500 (3%, $[M+H]^{+\bullet}$).

*1-(Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)but-3-yn-2-one* ***4a***

Manganese dioxide (0.86 g, 10.0 mmol) was added to a solution of **3a** (0.640 g, 1.5 mmol) in dry dichloromethane (40 mL). The mixture was stirred for 12 h, filtered, and the residue was washed with EtOAc. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (toluene/EtOAc, 10 : 1) to afford **4a** as white crystals (0.360 g, 57%), mp 119–121°C (ethanol), R_F 0.48 (toluene/EtOAc, 10 : 1), $[\alpha]_D^{23}$ +72.9 (*c* 1 in $CHCl_3$) (Found: C 71.2, H 6.3. $C_{25}H_{26}O_6$ requires C 71.1, H 6.2%). ν_{max} (KBr)/cm^{-1} 3257 (C_{sp}H), 2092 (C≡C), 1687 (CO). δ_H (250 MHz; $CDCl_3$) 7.47–7.28 (10H, m, Ph), 5.59 (1H, s, CHPh), 4.68 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.61 (1H, s, H1′), 4.32–4.23 (1H, m, H6′eq), 4.21–4.12 (1H, m, H4′), 3.86 (1H, dt, $^3J_{5',6'ax} \approx {}^3J_{4',5'}$ 10.0, and $^3J_{5',6'eq}$ 4.0, H5′), 3.79 (1H, t, $^3J_{5',6'ax} \approx {}^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.56 (1H, br s, H2′), 3.34 (3H, s, OMe), 3.17 (1H, s, H4), 3.17–3.11 (3H, m, H1 and H3′). δ_C (62.9 MHz; $CDCl_3$) 186.0 (C2), 137.8 and 137.4 (2 *ipso*-Ph), 129.0, 128.4, 128.2, 127.9, 127.8, and 126.1 (*o*-, *m*-, and *p*-Ph), 101.8 (CHPh), 100.6 (C1′), 81.6 (C3), 78.3 (C4), 76.2 (C4′), 74.9 (C2′), 71.6 (CH_2Ph), 69.4 (C6′), 59.7 (C5′), 55.2 (OMe), 40.8 (C2), 33.5 (C3′). *m/z* (FAB^+) 445 (100%, $[M+Na]^{+\bullet}$).

*1-(Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)-4-phenyl-but-3-yn-2-one* ***4b***

Pyridinium chlorochromate (0.808 g, 3.75 mmol) was added to a solution of **3b** (0.750 g, 1.5 mmol) in dry dichloromethane (40 mL). The mixture was stirred for 12 h, filtered, and the residue was washed with EtOAc. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (toluene/EtOAc, 10 : 1) to afford **4b** as white crystals (0.410 g, 55%), mp 137–140°C (ethanol), R_F 0.54 (toluene/EtOAc, 10 : 1), $[\alpha]_D^{24}$ +133.4 (*c* 1 in $CHCl_3$) (Found: C 74.6, H 6.1. $C_{31}H_{30}O_6$ requires C 74.7, H 6.1%). ν_{max} (KBr)/cm^{-1} 2201 (C≡C), 1669 (CO). δ_H (250 MHz; $CDCl_3$) 7.55–7.28 (15H, m, Ph), 5.62 (1H, s, CHPh), 4.71 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.64 (1H, s, H1′), 4.29 (1H, dd, $^2J_{6'ax,6'eq}$ 9.5 and $^3J_{5',6'eq}$ 4.5, H6′eq), 4.19 (1H, dd, $^3J_{4',5'}$ 9.5 and $^3J_{3',4'}$ 5.0, H4′), 3.91 (1H, dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.5, and $^3J_{5',6'eq}$ 4.5, H5′), 3.82 (1H, app. t, $^3J_{5',6'ax}$ 10.0 and $^2J_{6'ax,6'eq}$ 9.5, H6′ax), 3.64 (1H, br s, H2′), 3.36 (3H, s, OMe), 3.26–3.16 (3H, m, H1 and H3′). δ_C (62.9 MHz; $CDCl_3$) 186.6 (C2), 137.9 and 137.5 (2 *ipso*-Ph), 133.0, 130.6, 128.9, 128.6, 128.4, 128.2, 127.9, 127.8, and 126.1 (*o*-, *m*-, and *p*-Ph), 119.9 (*ipso*-PhC≡C), 101.8 (CHPh), 100.7 (C1′), 90.4 (C4), 88.1 (C3), 76.3 (C4′), 75.1 (C2′), 71.6 (CH_2Ph), 69.4 (C6′), 59.7 (C5′), 55.2 (OMe), 40.7 (C1), 33.8 (C3′). *m/z* (FAB^+) 521 (100%, $[M+Na]^{+\bullet}$).

*3(5)-(Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)-1*H*(2*H*)-pyrazole* ***5a***

A mixture of **4a** (0.210 g, 0.5 mmol) and hydrazine hydrate (0.035 mL, 0.75 mmol) in dry methanol (5 mL) was stirred for 1 h. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (toluene/EtOAc, 1 : 1) to afford **5a** as a white solid (0.170 g, 78%), mp 58–60°C, R_F 0.24 (toluene/EtOAc, 1 : 1), $[\alpha]_D^{21}$ +21.5 (*c* 1 in $CHCl_3$) (Found: C 68.7, H 6.5, N 6.0. $C_{25}H_{28}N_2O_5$ requires C 68.8, H 6.5, N 6.4%). δ_H (250 MHz; $CDCl_3$) 7.52–7.15 (11H, m, H5 and Ph), 6.03 (1H, br s, H4), 5.64 (1H, s, CHPh), 4.65 (1H, s, H1′), 4.40 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.32 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.22 (1H, dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4'}$ 5.2, H4′), 4.06 (1H, dt, $^3J_{5',6'ax} \approx {}^3J_{4',5'}$ 9.8 and $^3J_{5',6'eq}$ 5.0, H5′), 3.83 (1H, app. t, $^3J_{5',6'ax}$ 9.8 and $^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.44 (1H, br s, H2′), 3.41 (3H, s, OMe), 3.17–3.06 (2H, m, 3-CH_2), 2.67–2.55 (1H, m, H3′). δ_C (62.9 MHz; $CDCl_3$) 144.4 (C5), 137.5 and 137.4 (2 *ipso*-Ph), 137.0 (C3), 129.2, 128.4, 128.3, 127.9, 127.8, and 126.2 (*o*-, *m*-, and *p*-Ph), 104.3 (C4), 102.1 (CHPh), 100.5 (C1′), 76.2 (C4′), 75.6 (C2′), 71.7 (CH_2Ph), 69.4 (C6′), 59.3 (C5′), 55.2 (OMe), 39.8 (C3′), 21.8 (3-CH_2).

*3-(Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)-5-phenyl-1*H*-pyrazole* ***5b***

The reaction of **4b** (0.250 g, 0.5 mmol) with hydrazine hydrate (0.035 mL, 0.75 mmol) was carried out as described above for the preparation of **5a**. The crude product was purified by column chromatography (toluene/EtOAc, 1 : 1) to afford **5b** as a white solid (0.230 g, 90%), mp 75–78°C, R_F 0.49 (toluene/EtOAc, 1 : 1), $[\alpha]_D^{24}$ +86.2 (*c* 0.5 in $CHCl_3$) (Found: C 72.8, H 6.4, N 5.2. $C_{31}H_{32}N_2O_5$ requires C 72.6, H 6.3, N 5.5%). δ_H (250 MHz; $CDCl_3$) 7.75–7.72 (2H, m, Ph), 7.52–7.13 (13H, m, Ph), 6.32 (1H, s, H4), 5.64 (1H, s, CHPh), 4.66 (1H, s, H1′), 4.41 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.32 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.23 (1H, dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4'}$ 5.2, H4′), 4.07 (1H, app. dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.8, and $^3J_{5',6'eq}$ 5.0, H5′), 3.85 (1H, t, $^3J_{5',6'ax} \approx {}^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.47 (1H, br s, H2′), 3.44 (3H, s, OMe), 3.10 (2H, d, $^3J_{3\text{-}CH_2,3'}$ 8.6, 3-CH_2), 2.63–2.55 (1H, m, H3′). δ_C (62.9 MHz; $CDCl_3$) 150.9 (C5), 144.4 (C3), 137.5, 137.2, and 133.0 (3 *ipso*-Ph), 129.2, 128.6, 128.4, 128.0, 127.9, 127.8, 127.7, 126.2, 125.5 (*o*-, *m*-, and *p*-Ph), 102.2 (C4), 101.7 (CHPh), 100.4 (C1′), 76.2 (C4′), 75.2 (C2′), 71.8 (CH_2Ph), 69.4 (C6′), 59.3 (C5′), 55.3 (OMe), 39.8 (C3′), 21.8 (3-CH_2). *m/z* (70 eV) 512 (5%, $M^{+\bullet}$).

*1-Methyl-3-(methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)-5-phenyl-1*H*-pyrazole* ***5c***

The reaction of **4b** (0.250 g, 0.5 mmol) with methylhydrazine (0.070 mL, 0.75 mmol) was carried out as described above for the preparation of **5a**. The crude product was purified by column chromatography (toluene/EtOAc, 2 : 1) to afford **5c** as a colourless syrup (0.225 g, 86%), R_F 0.56 (toluene/EtOAc 2 : 1), $[\alpha]_D^{21}$ +40.1 (*c* 0.5 in $CHCl_3$) (Found: C 72.7, H 6.5, N 5.0. $C_{32}H_{34}N_2O_5$ requires C 73.0, H 6.5, N 5.3%). δ_H (250 MHz; $CDCl_3$) 7.52–7.15 (15H, m, Ph), 6.06 (1H, s, H4), 5.65 (1H, s, CHPh), 4.68 (1H, s, H1′), 4.53 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.32 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.22 (1H, dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4'}$ 5.5, H4′), 4.06 (1H, dt, $^3J_{5',6'ax} \approx {}^3J_{4',5'}$ 9.8 and $^3J_{5',6'eq}$ 5.0, H5′), 3.84 (1H, app. t, $^3J_{5',6'ax}$ 9.8 and $^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.82 (3H, s, NMe), 3.69 (1H, br s, H2′), 3.39 (3H, s, OMe), 3.11 (2H, d, $^3J_{3\text{-}CH_2,3'}$ 7.3, 3-CH_2), 2.90–2.76 (1H, m, H3′). δ_C (62.9 MHz; $CDCl_3$)

150.5 (C5), 143.9 (C3), 137.9, 137.8, and 130.9 (3 *ipso*-Ph), 128.9, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.6, and 126.2 (*o*-, *m*-, and *p*-Ph), 105.6 (C4), 101.7 (CHPh), 100.9 (C1′), 76.3 (C4′), 75.4 (C2′), 71.1 (CH_2Ph), 69.6 (C6′), 59.3 (C5′), 55.1 (OMe), 39.4 (C3′), 37.2 (NMe), 22.9 (3-CH_2). *m/z* (70 eV) 526 (5%, $M^{+\bullet}$).

*1-(2-Hydroxyethyl)-3-(methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)-5-phenyl-1*H*-pyrazole* ***5d***

The reaction of **4b** (0.250 g, 0.5 mmol) with 2-hydroxyethylhydrazine (0.050 mL, 0.75 mmol) was carried out as described above for the preparation of **5a**. The crude product was purified by column chromatography (toluene/EtOAc, 1 : 2) to afford **5d** as a white solid (0.203 g, 73%), mp 50–53°C, R_F 0.42 (toluene/EtOAc, 1 : 2), $[\alpha]_D^{24}$ +42.9 (*c* 1 in $CHCl_3$) (Found: C 71.4, H 6.5, N 4.9. $C_{33}H_{36}N_2O_6$ requires C 71.2, H 6.5, N 5.0%). ν_{max} (KBr)/cm^{-1} 3424 (OH). δ_H (500 MHz; $CDCl_3$) 7.51–7.14 (15H, m, Ph), 6.08 (1H, s, H4), 5.64 (1H, s, CHPh), 4.68 (1H, s, H1′), 4.52 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.32 (1H, dd, $^2J_{6'ax,6'eq}$ 10.4 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.23 (1H, dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4}$ 5.4, H4′), 4.14 (2H, t, $^3J_{CH_2OH,CH_2CN}$ 4.6, CH_2OH), 4.05 (1H, app. dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.8, and $^3J_{5',6'eq}$ 5.0, H5′), 3.94–3.83 (2H, m, CH_2N), 3.84 (1H, app. t, $^3J_{5',6'ax}$ 10.0 and $^2J_{6'ax,6'eq}$ 10.4, H6′ax), 3.64 (1H, br s, H2′), 3.39 (3H, s, OMe), 3.21–3.01 (2H, m, 3-CH_2), 2.87–2.80 (1H, m, H3′). δ_C (62.9 MHz; $CDCl_3$) 151.1 (C5), 144.5 (C3), 137.7, 137.6, and 130.4 (3 *ipso*-Ph), 129.0, 128.9, 128.6, 128.5, 128.3, 128.2, 127.8, 127.6, and 126.2 (*o*-, *m*-, and *p*-Ph), 105.7 (C4), 101.9 (CHPh), 100.8 (C1′), 76.3 (C4′), 75.5 (C2′), 71.3 (CH_2Ph), 69.6 (C6′), 62.1 (CH_2OH), 59.3 (C5′), 55.1 (OMe), 50.5 (CH_2N), 39.2 (C3′), 23.1 (3-CH_2). *m/z* (70 eV) 556 (5%, $M^{+\bullet}$).

*3(5)-(Methyl 2-*O*-Benzyl-3-deoxy-α-D-altropyranosid-3-ylmethyl)-1(2*H*)-pyrazole* ***6***

A solution of compound **5a** (0.220 g, 0.5 mmol) in acetic acid (5 mL) and water (0.5 mL) was heated at 70°C for 7 h. Water (10 mL) and $NaHCO_3$ were then added until the solution was neutralized, and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic fractions were washed with water (2 × 50 mL), dried (Na_2SO_4), and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (EtOAc/MeOH, 10 : 1) to afford **6** as a white solid (0.160 g, 90%), mp 53–55°C, R_F 0.49 (EtOAc/MeOH, 10 : 1), $[\alpha]_D^{21}$ +47.6 (*c* 0.5 in MeOH) (Found: C 61.6, H 6.9, N 7.7. $C_{18}H_{24}N_2O_5$ requires C 62.1, H 6.9, N 8.0%). ν_{max} (KBr)/cm^{-1} 3387, 3304 (OH). δ_H [250 MHz; $(CD_3)_2SO$] 12.40 (1H, br s, NH), 7.44 (1H, br s, H5), 7.37–7.20 (5H, m, Ph), 5.99 (1H, br s, H4), 4.94 (1H, br s, 4′-OH), 4.60 (1H, br s, 6′-OH), 4.56 (1H, s, H1′), 4.45 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 3.80–3.68 (1H, m, H4′), 3.67–3.28 (4H, m, H2′, H5′, and H6′), 3.31 (3H, s, OMe), 2.97–2.75 (2H, m, 3-CH_2), 2.32–2.18 (1H, m, H3′). δ_C [62.9 MHz; $(CD_3)_2SO$] 138.6 (*ipso*-Ph), 128.4 and 127.8 (*o*- and *m*-Ph), 127.6 (*p*-Ph), 103.6 (C4), 101.0 (C1′), 76.6 (C2′), 72.5 (C5′), 71.1 (CH_2Ph), 64.2 (C4′), 61.7 (C6′), 54.6 (OMe), 41.5 (C3′), 21.6 (3-CH_2); C3 and C5 are not given as a result of strong signal broadening. *m/z* (70 eV) 349 ($[M + H]^{+\bullet}$).

*3(5)-(Methyl 3-Deoxy-α-D-altropyranosid-3-ylmethyl)-1*H*(2*H*)-pyrazole 7*

A mixture of **6** (0.105 g, 0.3 mmol), ammonium formate (0.1 g), and 10% palladium on carbon (0.200 g, Lancaster) in dry methanol (10 mL) was heated at reflux for 2 h. The catalyst was then filtered off and washed with the solvent, and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography (EtOAc/MeOH, 5 : 1) to afford **7** as a white foam (0.070 g, 90%), R_F 0.39 (EtOAc/MeOH, 5 : 1). $[\alpha]_D^{21}$ +89.5 (*c* 0.4 in MeOH) (Found: C 51.6, H 6.8, N 10.5. $C_{11}H_{18}N_2O_5$ requires C 51.2, H 7.0, N 10.9%). ν_{max} (KBr)/cm^{-1} 3374, 3139, 3113 (OH). δ_H [250 MHz; $(CD_3)_2SO$] 12.40 (1H, br s, NH), 7.42 (1H, br s, H5), 6.02 (1H, d, $^3J_{4,5}$ 1.8, H4), 4.99 (1H, d, $^3J_{2',2'\text{-OH}}$ 4.9, 2′-OH), 4.80 (1H, d, $^3J_{4',4'\text{-OH}}$ 5.5, 4′-OH), 4.56 (1H, t, $^3J_{6',6'\text{-OH}}$ 5.5, 6′-OH), 4.34 (1H, d, $^3J_{1',2'}$ 3.0, H1′), 3.74–3.64 (1H, m, H4′), 3.64–3.40 (3H, m, H5′ and H6′), 3.38 (1H, br s, H2′), 3.29 (3H, s, OMe), 2.95–2.70 (2H, m, 3-CH_2), 2.05–1.92 (1H, m, H3′). δ_C [62.9 MHz; $(CD_3)_2SO$] 103.7 and 103.0 (C4 and C1′), 73.1 (C5′), 68.6 (C2′), 64.2 (C4′), 61.7 (C6′), 54.8 (OMe), 43.7 (C3′), 20.9 (3-CH_2); C3 and C5 are not given as a result of strong signal broadening. *m/z* (70 eV) 259 ($[M + H]^{+\bullet}$).

*2-Methyl-4-(methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)pyrimidine* ***8a***

A mixture of **4a** (0.210 g, 0.5 mmol), acetamidinium chloride (0.061 mg, 0.65 mmol), Na_2CO_3 (0.138 g, 1.38 mmol), water (0.01 mL), and EtOAc (5 mL) was heated at reflux until the starting material disappeared by TLC (24 h). The solution was then filtered and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (toluene/EtOAc, 2 : 1) to afford **8a** as a colourless syrup (0.205 g, 88%), R_F 0.22 (toluene/EtOAc, 2 : 1), $[\alpha]_D^{22}$ +52.5 (*c* 1 in $CHCl_3$) (Found: C 70.2, H 6.7, N 5.9. $C_{27}H_{30}N_2O_5$ requires C 70.1, H 6.5, N 6.1%). δ_H (250 MHz; $CDCl_3$) 8.39 (1H, d, $^3J_{5,6}$ 4.6, H6), 7.44–7.18 (10H, m, Ph), 6.90 (1H, d, $^3J_{5,6}$ 4.6, H5), 5.62 (1H, s, CHPh), 4.65 (1H, s, H1′), 4.54 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.32 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.24 (1H, dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4'}$ 4.3, H4′), 4.03 (1H, app. dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.8, and $^3J_{5',6'eq}$ 5.0, H5′), 3.84 (1H, t, $^3J_{5',6'ax} \approx {}^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.44 (1H, br s, H2′), 3.39 (3H, s, OMe), 3.22–3.07 (3H, m, 4-CH_2 and H3′), 2.69 (3H, s, Me). δ_C (62.9 MHz; $CDCl_3$) 169.5 (C4), 167.7 (C2), 156.2 (C6), 137.6 and 137.5 (2 *ipso*-Ph), 128.9, 128.4, 128.1, 127.79, 127.76, 126.1 (*o*-, *m*-, and *p*-Ph), 118.6 (C5), 101.8 (CHPh), 100.7 (C1′), 75.9 (C4′), 75.3 (C2′), 71.4 (CH_2Ph), 69.5 (C6′), 59.5 (C5′), 55.2 (OMe), 37.7 (C3′), 32.4 (Me), 26.1 (4-CH_2). *m/z* (CI) 463 (100%, $[M + H]^{+\bullet}$).

*4-(Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)-2-phenylpyrimidine* ***8b***

The reaction of **4a** (0.210 g, 0.5 mmol) with benzamidinium chloride (0.102 g, 0.65 mmol) was carried out as described above for the preparation of **8a** (reaction time 3 h). The crude product was purified by column chromatography (toluene/EtOAc, 10 : 1) to afford **8b** as a white solid (0.250 g, 95%), mp 45–48°C, R_F 0.43 (toluene/EtOAc, 10 : 1), $[\alpha]_D^{21}$ +52.3 (*c* 0.5 in $CHCl_3$) (Found: C 73.0, H 6.2, N 5.3. $C_{32}H_{32}N_2O_5$ requires C 73.3, H 6.2, N 5.3%). δ_H (250 MHz; $CDCl_3$) 8.57 (1H, d, $^3J_{5,6}$ 5.2, H6), 8.50–8.47 (2H, m, Ph), 7.49–7.45 (5H, m, Ph), 7.37–7.31 (3H, m, Ph), 7.18–7.08 (5H, m, Ph), 6.98 (1H, d, $^3J_{5,6}$ 5.2, H5), 5.66 (1H, s, CHPh), 4.66 (1H, s, H1′), 4.51 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.34 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.28 (1H, dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4'}$ 5.2, H4′), 4.08 (1H, app. dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.8, and $^3J_{5',6'eq}$ 5.0, H5′), 3.87 (1H, t, $^3J_{5',6'ax} \approx {}^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.46 (1H, br s, H2′), 3.40 (3H, s, OMe), 3.35–3.23 (3H, m, 4-CH_2 and H3′). δ_C (62.9 MHz; $CDCl_3$) 169.6 (C4), 164.2 (C2), 156.6 (C6), 137.9, 137.6, and 137.5 (3 *ipso*-Ph), 130.5, 128.9, 128.5, 128.3, 128.2, 128.17, 127.7, 127.6, and 125.3 (*o*-, *m*-, and *p*-Ph), 119.6 (C5), 101.9 (CHPh), 100.7 (C1′), 75.9 (C4′), 75.3 (C2′), 71.4 (CH_2Ph), 69.5 (C6′), 59.6 (C5′), 55.2 (OMe), 37.5 (C3′), 32.5 (4-CH_2). *m/z* (CI) 525 (100%, $[M + H]^{+\bullet}$).

*4-(Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)-2-methylthiopyrimidine* ***8c***

The reaction of **4a** (0.210 g, 0.5 mmol) with *S*-methylisothiouronium sulfate (0.181 g, 0.65 mmol) was carried out as described above for the preparation of **8a** (reaction time 2 h). The crude product was purified by column chromatography (toluene/EtOAc, 10 : 1) to afford **8c** as a colourless syrup (0.205 g, 83%), R_F 0.47 (toluene/EtOAc, 10 : 1), $[\alpha]_D^{21}$ +61.1 (*c* 0.5 in $CHCl_3$) (Found: C 65.7, H 6.2, N 5.2, S 6.4. $C_{27}H_{30}N_2O_5S$ requires C 65.6, H 6.1, N 5.6, S 6.5%). δ_H (250 MHz; $CDCl_3$) 8.27 (1H, d, $^3J_{5,6}$ 5.2, H6), 7.45–7.14 (10H, m, Ph), 6.74 (1H, d, $^3J_{5,6}$ 5.2, H5), 5.62 (1H, s, CHPh), 4.63 (1H, s, H1′), 4.54 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.31 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.27–4.19 (1H, m, H4′), 4.01 (1H, app. dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.8, and $^3J_{5',6'eq}$ 5.0, H5′), 3.83 (1H, t, $^3J_{5',6'ax} \approx {}^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.41 (1H, br s, H2′), 3.37 (3H, s, OMe), 3.20–3.08 (3H, m, 4-CH_2 and H3′), 2.55 (3H, s, SMe). δ_C (62.9 MHz; $CDCl_3$) 172.1 (C2), 169.8 (C4), 156.5 (C6), 137.6 and 137.5 (2 *ipso*-Ph), 128.9, 128.3, 128.1, 127.8 127.7, and 126.1 (*o*-, *m*-,

and *p*-Ph), 116.8 (C5), 101.7 (CHPh), 100.6 (C1′), 75.8 (C4′), 75.2 (C2′), 71.4 (CH_2Ph), 69.4 (C6′), 59.5 (C5′), 55.1 (OMe), 37.3 (C3′), 32.3 (4-CH_2), 14.0 (SMe). *m/z* (CI) 495 (51%, $[M+H]^{+\bullet}$).

*2-Methyl-4-(methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)-6-phenylpyrimidine* ***8d***

The reaction of **4b** (0.250 g, 0.5 mmol) with acetamidinium chloride (0.061 mg, 0.65 mmol) was carried out as described above for the preparation of **8a** (reaction time 8 h). The crude product was purified by column chromatography (toluene/EtOAc, 10 : 1) to afford **8d** as a white solid (0.245 g, 91%), mp 43–46°C, R_F 0.55 (toluene/EtOAc, 10 : 1), $[\alpha]_D^{23}$ +60.2 (*c* 0.5 in $CHCl_3$) (Found: C 74.0, H 6.4, N 5.0. $C_{33}H_{34}N_2O_5$ requires C 74.0, H 6.4, N 5.2%). δ_H (250 MHz; $CDCl_3$) 7.99–7.96 (2H, m, Ph), 7.48–7.15 (14H, m, Ph and H5), 5.62 (1H, s, CHPh), 4.66 (1H, br s, H1′), 4.55 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.33 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.25 (1H, dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4'}$ 4.3, H4′), 4.07 (1H, app. dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.8, and $^3J_{5',6'eq}$ 5.0, H5′), 3.85 (1H, t, $^3J_{5',6'ax} \approx {}^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.53 (1H, dd, $^3J_{2',3'}$ 2.0 and $^3J_{1',2'}$ 1.0, H2′), 3.41 (3H, s, OMe), 3.29–3.11 (3H, m, 4-CH_2, H3′), 2.76 (3H, s, Me). δ_C (62.9 MHz; $CDCl_3$) 170.0 (C4), 167.9 (C6), 163.7 (C2), 137.6, 137.4, and 137.3 (3 *ipso*-Ph), 130.4, 128.9, 128.8, 128.3 (2×), 128.1, 127.8, 127.2, and 126.1 (*o*-, *m*-, and *p*-Ph), 114.2 (C5), 101.9 (CHPh), 100.8 (C1′), 76.1 (C4′), 75.8 (C2′), 71.5 (CH_2Ph), 69.5 (C6′), 59.6 (C5′), 55.2 (OMe), 37.9 (C3′), 32.9 (4-CH_2), 26.3 (Me). *m/z* (70 eV) 538 (5%, $[M+H]^{+\bullet}$).

*4-(Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)-2,6-diphenylpyrimidine* ***8e***

The reaction of **4b** (0.250 g, 0.5 mmol) with benzamidinium hydrochloride (0.102 g, 0.65 mmol) was carried out as described above for the preparation of **8a**. The crude product was purified by column chromatography (toluene/EtOAc, 10 : 1) to afford **8e** as a white solid (0.270 g, 90%), mp 125–128°C, R_F 0.55 (toluene/EtOAc, 10 : 1), $[\alpha]_D^{24}$ +64.3 (*c* 1 in $CHCl_3$) (Found: C 76.2, H 6.3, N 4.3. $C_{38}H_{36}N_2O_5$ requires C 76.0, H 6.0, N 4.7%). δ_H (250 MHz; $CDCl_3$) 8.65–8.60 (2H, m, Ph), 8.18–8.13 (2H, m, Ph), 7.55–7.43 (9H, m, Ph and H5), 7.33–7.28 (3H, m, Ph), 7.14–7.09 (5H, m, Ph), 5.66 (1H, s, CHPh), 4.67 (1H, br s, H1′), 4.54 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.35 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.30 (1H, dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4'}$ 5.0, H4′), 4.12 (1H, app. dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.8, and $^3J_{5',6'eq}$ 5.0, H5′), 3.88 (1H, t, $^3J_{5',6'ax} \approx {}^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.56 (1H, dd, $^3J_{2',3'}$ 2.0 and $^3J_{1',2'}$ 1.0, H2′), 3.42 (3H, s, OMe), 3.41–3.21 (3H, m, 4-CH_2 and H3′). δ_C (62.9 MHz; $CDCl_3$) 170.2 (C4), 164.1 (C6), 163.5 (C2), 138.2, 137.7, 137.5, and 137.4 (4 *ipso*-Ph), 130.6, 130.4, 128.9, 128.8, 128.38, 128.35, 128.3, 128.2, 127.7, 127.6, 127.2, and 126.1 (*o*-, *m*-, and *p*-Ph), 115.0 (C5), 101.9 (CHPh), 100.8 (C1′), 76.1 (C4′), 75.7 (C2′), 71.4 (CH_2Ph), 69.6 (C6′), 59.7 (C5′), 55.2 (OMe), 37.8 (C3′), 32.9 (4-CH_2). *m/z* (70 eV) 600 (5%, $M^{+\bullet}$).

*2-Amino-4-(methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)-6-phenylpyrimidine* ***8f***

The reaction of **4b** (0.250 g, 0.50 mmol) with guanidinium chloride (0.138 g, 1.3 mmol) was carried out as described above for the preparation of **8a** (reaction time 24 h). The crude product was purified by column chromatography (toluene/EtOAc, 2 : 1) to afford **8f** as a white solid (0.108 g, 40%), mp 78–80°C, R_F 0.34 (toluene/EtOAc, 2 : 1), $[\alpha]_D^{24}$ +56.4 (*c* 1 in $CHCl_3$) (Found: C 71.4, H 6.2, N 7.6. $C_{32}H_{33}N_3O_5$ requires C 71.2, H 6.2, N 7.8%). ν_{max} (KBr)/cm^{-1} 3315, 3192 (NH_2). δ_H (250 MHz; $CDCl_3$) 7.93–7.88 (2H, m, Ph), 7.47–7.18 (13H, m, Ph), 6.90 (1H, s, H5), 5.64 (1H, s, CHPh), 5.13 (2H, br s, NH_2), 4.65 (1H, br s, H1′), 4.53 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.32 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.24 (1H, m, H4′), 4.04 (1H, app. dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.8, and $^3J_{5',6'eq}$ 5.0, H5′), 3.84 (1H, t, $^3J_{5',6'ax} \approx {}^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.56 (1H, dd, $^3J_{2',3'}$ 2.0 and $^3J_{1',2'}$ 1.0, H2′), 3.40 (3H, s, OMe), 3.21–2.98 (3H, m, 4-CH_2 and H3′). δ_C (62.9 MHz; $CDCl_3$) 171.3 (C4), 165.1 (C6), 163.3 (C2), 137.7, 137.6, and 137.6 (3 *ipso*-Ph), 130.2, 128.9, 128.6, 128.4, 128.2, 127.9, 127.8, 127.2, and 126.1 (*o*-, *m*-, and *p*-Ph), 108.3 (C5), 101.9 (CHPh), 100.8 (C1′), 76.0 (C4′), 75.5 (C2′), 71.4 (CH_2Ph), 69.5 (C6′), 59.6 (C5′), 55.2 (OMe), 37.9 (C3′), 32.6 (4-CH_2). *m/z* (70 eV) 539 (2%, $M^{+\bullet}$).

*4-(Methyl 2-*O*-Benzyl-3-deoxy-α-D-altropyranosid-3-ylmethyl)-2-phenylpyrimidine* ***9***

The deprotection of compound **8b** (0.260 g, 0.5 mmol) was carried out as described above for the preparation of **6** (reaction time 12 h). The crude product was purified by column chromatography (EtOAc) to afford **9** as a white foam (0.180 g, 84%), R_F 0.57 (EtOAc), $[\alpha]_D^{21}$ +66.1 (*c* 0.5 in MeOH) (Found: C 68.4, H 6.5, N 5.9. $C_{25}H_{28}N_2O_5$ requires C 68.8, H 6.5, N 6.4%). ν_{max} (KBr)/cm^{-1} 3426, 3363 (OH). δ_H [250 MHz; $(CD_3)_2SO$] 8.68 (1H, d, $^3J_{5,6}$ 5.2, H6), 8.43–8.39 (2H, m, *o*-Ph), 7.21 (1H, d, $^3J_{5,6}$ 5.2, H5), 7.20–7.11 (3H, m, *m*- and *p*-Ph), 5.05 (1H, d, $^3J_{4',4'\text{-OH}}$ 5.2, 4′-OH), 4.64–4.59 (1H, m, 6′-OH), 4.60 (1H, d, $^3J_{1',2'}$ 2.4, H1′), 4.47 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 3.87–3.77 (1H, m, H4′), 3.72–3.44 (3H, m, H5′ and H6′), 3.36–3.33 (1H, br s, H2′), 3.33 (3H, s, OMe), 3.08 (2H, d, $^3J_{4\text{-}CH_2,3'}$ 7.7, 4-CH_2), 2.84–2.72 (1H, m, H3′). δ_C [62.9 MHz; $(CD_3)_2SO$] 170.4 (C4), 163.0 (C2), 157.2 (C6), 138.4 and 137.7 (2 *ipso*-Ph), 130.8, 128.8, 128.3, 127.9, and 127.5 (*o*-, *m*-, and *p*-Ph), 120.0 (C5), 100.7 (C1′), 76.2 (C2′), 72.1 (C5′), 70.9 (CH_2Ph), 64.1 (C4′), 61.7 (C6′), 54.6 (OMe), 40.3 (C3′), 32.6 (4-CH_2). *m/z* (70 eV) 437 ($[M+H]^{+\bullet}$).

4-(Methyl 3-Deoxy-α-D-altropyranosid-3-ylmethyl)-2-phenylpyrimidine ***10***

The deprotection of compound **9** (0.130 g, 0.3 mmol) was carried out as described above for the preparation of **7**. The crude product was purified by column chromatography (EtOAc/MeOH, 10 : 1) to afford **10** as a white solid (0.085 g, 82%), mp 162–164°C, R_F 0.42 (EtOAc/MeOH, 10 : 1), $[\alpha]_D^{21}$ +54.9 (*c* 1 in MeOH) (Found: C 62.4, H 6.5, N 7.6. $C_{18}H_{22}N_2O_5$ requires C 62.4, H 6.4, N 8.1%). ν_{max} (KBr)/cm^{-1} 3424 (OH). δ_H [500 MHz; $(CD_3)_2SO$] 8.74 (1H, d, $^3J_{5,6}$ 5.0, H6), 8.42–8.38 (2H, m, *o*-Ph), 7.54–7.51 (3H, m, *m*- and *p*-Ph), 7.28 (1H, d, $^3J_{5,6}$ 5.0, H5), 5.06 (1H, d, $^3J_{2',2'\text{-OH}}$ 5.2, 2′-OH), 4.90 (1H, d, $^3J_{4',4'\text{-OH}}$ 5.2, 4′-OH), 4.56 (1H, t, $^3J_{6',6'\text{-OH}}$ 6.0, 6′-OH), 4.39 (1H, d, $^3J_{1',2'}$ 3.0, H1′), 3.77 (1H, dt, $^3J_{3',4'} \approx {}^3J_{4',4'\text{-OH}}$ 5.2 and $^3J_{4',5'}$ 8.0, H4′), 3.63 (1H, ddd, $^3J_{5',6'a}$ 3.0, $^3J_{6',6'\text{-OH}}$ 6.0, and $^2J_{6'a,6'b}$ 11.0, H6′a), 3.54 (1H, ddd, $^3J_{5',6'a}$ 3.0, $^2J_{5',6'b}$ 5.5, and $^3J_{4',5'}$ 8.0, H5′), 3.51–3.43 (2H, m, H2′ and H6′b), 3.32 (3H, s, OMe), 3.05 (2H, m, 4-CH_2), 2.46 (1H, m, H3′). δ_C [62.9 MHz; $(CD_3)_2SO$] 170.9 (C4), 163.0 (C2), 157.1 (C6), 137.7 (*ipso*-Ph), 130.8, 128.8, and 127.9 (*o*-, *m*-, and *p*-Ph), 120.0 (C5), 102.9 (C1′), 73.0 (C5′), 68.7 (C2′), 64.1 (C4′), 61.7 (C6′), 54.7 (OMe), 42.7 (C3′), 33.0 (4-CH_2). *m/z* (70 eV) 346 ($M^{+\bullet}$).

*2-(Methyl 2-*O*-Benzyl-4,6-*O*-Benzylidene-3-deoxy-α-D-altropyranosid-3-ylmethyl)benzo[4,5]imidazo-[1,2-a]pyrimidine* ***11a***

A mixture of **4a** (0.210 g, 0.5 mmol) and 2-aminobenzimidazol (0.073 g, 0.55 mmol) in ethanol (5 mL) was heated at reflux for 2 h before being cooled to 20°C, treated with sodium ethanolate (1.5 mmol) in ethanol (5 mL), and stirred for 1 h. After neutralization of the mixture with amberlite IR-120 (Fluka-Chemie), the solvent was removed under reduced pressure and the residue was purified by column chromatography (toluene/EtOAc, 1 : 1) to afford **11a** as a yellow solid (0.201 g, 75%), mp 215–218°C, R_F 0.30 (toluene/EtOAc, 1 : 1), $[\alpha]_D^{21}$ +36.8 (*c* 1 in $CHCl_3$) (Found: C 71.2, H 5.9, N 7.6. $C_{32}H_{31}N_3O_5$ requires C 71.5, H 5.8, N 7.8%). δ_H (250 MHz; $CDCl_3$) 8.39 (1H, d, $^3J_{3,4}$ 7.0, H4), 8.01 (1H, m, $^4J_{7,9}$ 1.0, $^3J_{8,9}$ 8.2, H9), 7.79 (1H, m, $^4J_{6,8}$ 1.2, $^3J_{6,7}$ 7.9, H6), 7.57 (1H, ddd, $^3J_{8,9}$ 8.2, $^3J_{7,8}$ 7.3, and $^4J_{6,8}$ 1.2, H8), 7.43–7.02 (11H, m, Ph, H7), 6.70 (1H, d, $^3J_{3,4}$ 7.0, H3), 5.62 (1H, s, CHPh), 4.70 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.66 (1H, br s, H1′), 4.34 (1H, dd, $^2J_{6'ax,6'eq}$ 10.0 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.28 (1H, dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4'}$ 4.3, H4′), 4.06 (1H, app. dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.8, and $^3J_{5',6'eq}$ 5.0, H5′), 3.86 (1H, t, $^3J_{5',6'ax} \approx {}^2J_{6'ax,6'eq}$ 10.0, H6′ax), 3.66 (1H, dd, $^3J_{2',3'}$ 2.0 and $^3J_{1',2'}$ 1.0, H2′), 3.39 (3H, s, OMe), 3.42–3.27 (3H, m, 2-CH_2 and H3′). δ_C (62.9 MHz; $CDCl_3$) 168.6 (C2), 150.8 (C10a), 144.3 (C9a), 137.7 and 137.6 (2 *ipso*-Ph), 131.7 (C4), 129.0, 128.8, 128.14, 128.05,

127.5, 125.9 (*o*-, *m*-, and *p*-Ph), 126.9 (C5a), 126.1 (C8), 121.5 (C7), 120.4 (C9), 110.2 (C6), 108.6 (C3), 101.5 (CHPh), 100.9 (C1′), 75.8 (C4′), 75.2 (C2′), 71.4 (CH_2Ph), 69.5 (C6′), 59.7 (C5′), 55.2 (OMe), 37.2 (C3′), 33.7 (2-CH_2). *m/z* (70 eV) 537 (67%, $M^{+\bullet}$).

2-(Methyl 2-O*-Benzyl-4,6*-O*-benzylidene-3-deoxy-α-*D*-altropyranosid-3-ylmethyl)-4-phenyl-benzo[4,5]imidazo-[1,2*-a*]pyrimidine **11b***

The reaction of **4b** (0.250 g, 0.5 mmol) with 2-aminobenzimidazol (0.073 g, 0.55 mmol) was carried out as described above for the preparation of **11a** (reaction time 24 h). The crude product was purified by column chromatography (toluene/EtOAc, 1 : 1) to afford **11b** as a yellow solid (0.217 g, 65%), mp 93–95°C, R_F 0.41 (toluene/EtOAc, 1 : 1), $[\alpha]_D^{21}$ +27.9 (*c* 0.5 in $CHCl_3$) (Found: C 74.2, H 5.7, N 7.0. $C_{38}H_{35}N_3O_5$ requires C 74.4, H 5.8, N 6.9%). δ_H (500 MHz; $CDCl_3$) 7.98 (1H, m, $^4J_{7,9}$ 1.0, $^3J_{8,9}$ 8.2, H9), 7.45 (1H, ddd, $^3J_{8,9}$ 8.2, $^3J_{7,8}$ 7.3, and $^4J_{6,8}$ 1.0, H8), 7.66–7.07 (15H, m, Ph), 7.01 (1H, ddd, $^3J_{6,7}$ 8.2, $^3J_{7,8}$ 7.3, and $^4J_{7,9}$ 1.0, H7), 6.60 (1H, m, $^4J_{6,8}$ 1.0, $^3J_{6,7}$ 8.2, H6), 6.56 (1H, s, H3), 5.59 (1H, s, CHPh), 4.77 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 4.67 (1H, s, H1′), 4.33 (1H, dd, $^2J_{6'ax,6'eq}$ 10.4 and $^3J_{5',6'eq}$ 5.0, H6′eq), 4.28 (1H, dd, $^3J_{4',5'}$ 9.8 and $^3J_{3',4'}$ 5.0, H4′), 4.06 (1H, app. dt, $^3J_{5',6'ax}$ 10.0, $^3J_{4',5'}$ 9.8, and $^3J_{5',6'eq}$ 5.0, H5′), 3.85 (1H, app. t, $^3J_{5',6'ax}$ 10.0 and $^2J_{6'ax,6'eq}$ 10.4, H6′ax), 3.75 (1H, br s, H2′), 3.54–3.30 (3H, m, H3′, 2-CH_2), 3.38 (3H, s, OMe). δ_C (62.9 MHz; $CDCl_3$) 168.1 (C2), 151.9 (C4), 148.0 (C10a), 144.8 (C9a), 137.9, 137.7, and 132.2 (3 *ipso*-Ph), 130.8, 129.2, 128.7, 128.3, 128.2, 128.1, 128.0, 125.9, and 125.6 (*o*-, *m*-, and *p*-Ph), 127.5 (C8), 127.4 (C5a), 120.8 (C7), 120.1 (C9), 114.4 (C6), 109.8 (C3), 101.5 (CHPh), 100.9 (C1′), 76.0 (C4′), 75.9 (C2′), 71.5 (CH_2Ph), 69.5 (C6′), 59.7 (C5′), 55.2 (OMe), 37.2 (C3′), 33.7 (2-CH_2). *m/z* (70 eV) 613 (9%, $M^{+\bullet}$).

2-(Methyl 2-O*-Benzyl-3-deoxy-α-*D*-altropyranosid-3-yl-methyl)benzo[4,5]imidazo[1,2*-a*]pyrimidine **13***

The deprotection of compound **11a** (0.270 g, 0.5 mmol) was carried out as described above for the preparation of **6** (reaction time: 17 h). The crude product was purified by column chromatography (EtOAc/MeOH, 10 : 1) to afford **13** as white needles (0.210 g, 95%), mp 210°C (dec.), R_F 0.31 (EtOAc/MeOH, 10 : 1) $[\alpha]_D^{22}$ +36.9 (*c* 0.5 in MeOH) (Found: C 66.7, H, 6.1, N 9.1. $C_{25}H_{27}N_3O_5$ requires C 66.8, H 6.1, N 9.4%). ν_{max} (KBr)/cm^{-1} 3435, 3191 (OH). δ_H [500 MHz; $(CD_3)_2SO$] 9.26 (1H, d, $^3J_{3,4}$ 6.9, H4), 8.23 (1H, d, $^3J_{8,9}$ 8.1, H9), 7.82 (1H, d, $^3J_{6,7}$ 8.1, H6), 7.52 (1H, t, $^3J_{6,7} \approx {}^3J_{7,8}$ 8.1, H7), 7.39 (1H, t, $^3J_{8,9} \approx {}^3J_{7,8}$ 8.1, H8), 7.17–6.99 (5H, m, Ph), 6.97 (1H, d, $^3J_{3,4}$ 6.9, H3), 5.06 (1H, d, $^3J_{4',4'\text{-OH}}$ 5.0, 4′-OH), 4.63 (1H, t, $^3J_{6',6'\text{-OH}}$ 6.0, 6′-OH), 4.60 (1H, d, $^3J_{1',2'}$ 2.5, H1′), 4.50 (2H, ABq, $^2J_{A,B}$ 12.0, CH_2Ph), 3.83 (1H, dt, $^3J_{3',4'} \approx {}^3J_{4',4'\text{-OH}}$ 5.0 and $^3J_{4',5'}$ 8.5, H4′), 3.67 (1H, ddd, $^3J_{5',6'a}$ 2.5, $^3J_{6',6'\text{-OH}}$ 6.0, and $^2J_{6'a,6'b}$ 11.0, H6′a), 3.56 (1H, ddd, $^3J_{5',6'a}$ 2.5, $^3J_{5',6'b}$ 6.5, and $^3J_{4',5'}$ 8.5, H5′), 3.49 (1H, ddd, $^3J_{5',6'b}$ 6.5, $^3J_{6',6'\text{-OH}}$ 6.0, and $^2J_{6'a,6'b}$ 11.0, H6′b), 3.41 (1H, dd, $^3J_{1',2'}$ 2.5 and $^3J_{2',3'}$ 5.5, H2′), 3.34 (3H, s, OMe), 3.20–3.10 (2H, m, 2-CH_2), 2.73 (1H, m, H3′). δ_C [62.9 MHz; $(CD_3)_2SO$] 169.6 (C2), 150.5 (C10a), 143.8 (C9a), 138.4 (*ipso*-Ph), 134.5 (C4), 128.1 and 127.7 (*o*- and *m*-Ph), 127.3 (*p*-Ph), 127.2 (C5a), 125.9 (C8), 121.1 (C7), 119.1 (C9), 112.3 (C6), 108.4 (C3), 100.9 (C1′), 76.1 (C2′), 72.3 (C5′), 70.9 (CH_2Ph), 64.2 (C4′), 61.7 (C6′), 54.6 (OMe), 40.6 (C3′), 33.9 (2-CH_2). *m/z* (70 eV) 449 ($M^{+\bullet}$).

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