Synthesis of Iso-*C*-nucleoside Analogues from 1-(Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)but-3-yn-2-ones

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Dedicated to Prof. Dr. István Farkas on the occasion of his 80th birthday

1-(Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)but-3-yn-2-one (**3a**) reacted with 3-amino-1*H*-1,2,4-triazole and 5-aminopyrazole-4-carboxylic acid derivatives in the presence of base to furnish the triazolo[1,5-*a*]pyrimidine (**5**) and the pyrazolo[1,5-*a*]pyrimidines (**8a – d**), respectively. Treatment of 1-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)-4-phenyl-but-3-yn-2-one (**3b**) with cyanacetamide, 2-cyano-*N*-(4-methoxyphenyl)acetamide und *N*-aryl-3-oxo-butyramides afforded the substituted nicotinonitriles (**11a – d**). Furthermore, reaction of **3b** with 2-benzimidazolyl-acetonitrile yielded the benz[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (**13**). Deprotection of **8d** in two steps afforded the 2-amino-*N*-benzyl-5-(methyl 3-deoxy-α-D-altropyranosid-3-yl-methyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxamide (**10**). Compounds **5** and **11d** were treated with AcOH/H_2O to furnish the 5-(methyl 2-*O*-benzyl-3-deoxy-α-D-altropyranosid-3-yl-methyl)[1,2,4]triazolo[1,5-*a*]pyrimidine (**6**) and the 3-acetyl-1,2-dihydro-1-(4-methoxyphenyl)-6-(methyl 2-*O*-benzyl-3-deoxy-α-D-altropyranosid-3-yl-methyl)-4-phenylpyridin-2-one (**12**), respectively.

Key words: *C*-Nucleoside Analogues, Glycosylalkynone, Pyrazolo[1,5-*a*]pyrimidine, 1,2-Dihydropyridin-2-one, Benz[4,5]imidazo[1,2-*a*]pyridine

Introduction

Iso- or "reversed" nucleosides represent a class of nucleoside analogues in which the nucleobase is linked to the sugar moiety with a carbon atom other than C-1. The syntheses of isonucleosides are interesting because compounds having anticancer and antiviral activities can result [1, 2]. Examples of such nucleosides are relatively rare in the literature but, in the recent years intensified activities could be observed on this field [3, 4]. Like *C*-nucleosides [5 – 7] also iso-*C*-nucleosides show often different biological activities frequently caused by their increased hydrolytic and enzymatic stability [8, 9]. Furthermore, nucleoside derivatives possessing a heteroatom or a methylene group as spacer between the sugar unit and the heterocycle have been synthesized [10, 11]. In this paper we report the synthesis of spacered pyridine-, pyrazolo[1-5*a*]pyrimidine-, [1,2,4]triazolo[1,5-*a*]pyrimidine- and benz[4,5]imidazo[1,2-*a*]pyridine-iso-*C*-nucleoside analogues from 1-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)but-3-yn-2-ones (**3**).

Results and Discussion

Recently, we have described the synthesis of the 1-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)but-3-yn-2-ones (**3a** and **3b**) in five reaction steps from 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside **1** with the (pyranosid-3-yl)ethanal **2** as an intermediate (Scheme 1) [12]. These acetylenic ketones can be used as valuable synthetic intermediates for the preparation of nitrogen heterocycles.

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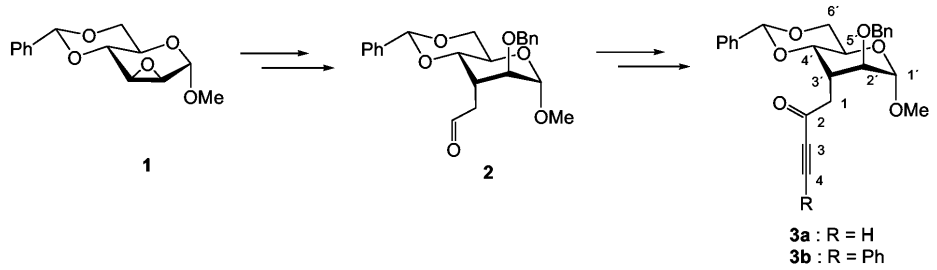
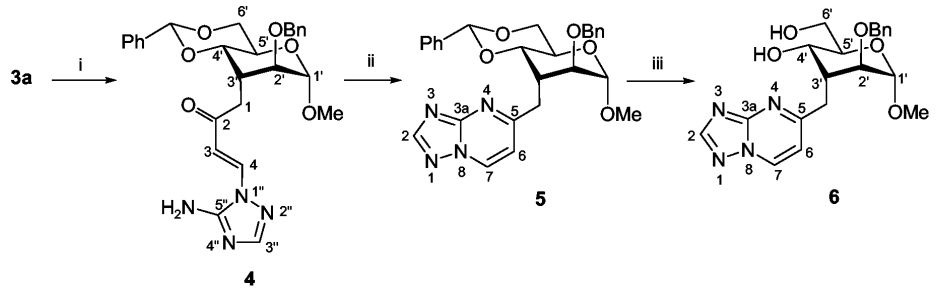


Scheme 1. 1-(Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)but-3-yn-2-ones **3a**, **b**.



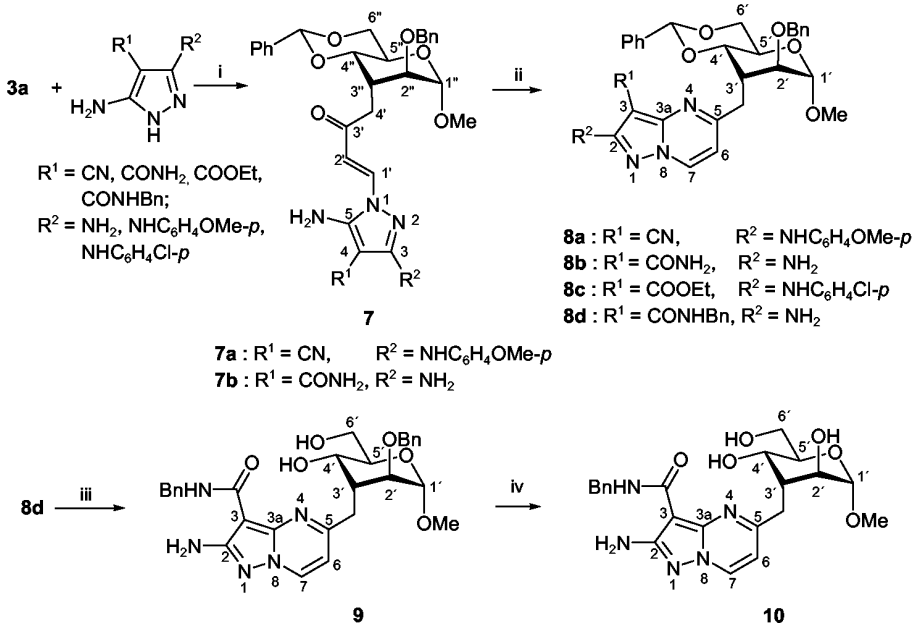
Scheme 2. (i) 3-Amino-1*H*-1,2,4-triazole, EtOH, reflux, 4 h; (ii) NaOEt, r. t. 1 h; (iii) AcOH/H_2O, 70 °C, 5 h.

In order to prepare fused heterocyclic compounds having a spacered monosaccharide unit, ynone **3a** was refluxed with 3-amino-1*H*-1,2,4-triazole in ethanol to furnish (3*E*)-4-(5-amino-1*H*-1,2,4-triazol-1-yl)-1-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)-3-buten-2-one (**4**) as an addition product in 55% yield (Scheme 2). As expected, for the compound **4** no signals of the acetylenic carbon atoms were observed in the ^{13}C NMR spectrum, but resonances were visible belonging to the triazole ring (at $\delta = 151.4$ for C-3" and $\delta = 155.6$ for C-5", respectively). In the ^{1}H NMR spectrum besides the signals of the sugar part, the signals of the NH_2 group and 3-H" at $\delta = 5.40$ and $\delta = 7.49$, respectively, were found. A large coupling constant ($J = 13.0$ Hz) for the coupling between 3-H and 4-H confirmed the (*E*)-configuration of the addition product.

Subsequent treatment of enone **4** with sodium ethanolate at room temperature led to the desired spacered triazolo[1,5-*a*]pyrimidine-iso-*C*-nucleoside **5** in 78% yield. The absence of the carbonyl and the amino signals in the IR and NMR spectra clearly demonstrated the successful course of the cyclization reaction. Moreover, the molecular peak at m/z = 488 and the ^{1}H NMR signals of 6-H, 2-H and 7-H at $\delta = 6.61$, 8.40 and 8.44, respectively, with the coupling between 6-H and 7-H ($J = 7.0$ Hz) confirmed the structure of **5**.

Reaction of compound **5** with aqueous acetic acid afforded the 5-(methyl 2-*O*-benzyl-3-deoxy-α-D-altropyranosid-3-yl-methyl)[1,2,4]triazolo[1,5-*a*]pyrimidine (**6**) in 92% yield. Unfortunately, attempts to split off the benzyl group in compound **6** by catalytic hydrogenation or with iodotrimethylsilane [13, 14], respectively, under several conditions were unsuccessful.

Similarly, polycyclic spacered iso-*C*-nucleosides could be obtained by reaction of ynone **3a** with various 5-aminopyrazole-4-carboxylic acid derivatives in ethanol under reflux followed by treatment with sodium ethanolate at room temperature to afford 2-amino-5-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)pyrazolo-[1,5-*a*]pyrimidine-3-carboxylic acid derivatives **8a – d** in good yields (Scheme 3). In the first step of this reaction as intermediates the 5-amino-3-(amino and 4-methoxyphenylamino, respectively)-1-[(1*E*)-4-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)-3-oxo-1-butenyl]-1*H*-pyrazole-4-carboxylic acid derivatives **7** were formed. Compounds **7a**, **b** were isolated in a pure form and completely characterized. In the ^{1}H NMR spectra of **7a** and **7b** the signals for 1'-H (**7a**: $\delta = 7.85$, **7b**: $\delta = 8.08$) and 2'-H (**7a**: $\delta = 6.54$, **7b**: $\delta = 6.41$) and the coupling constants $^{3}J_{1',2'} = 12.8$ Hz and 13.2 Hz, respectively, proved that the addition of the 5-amino-



Scheme 3. (i) EtOH, reflux; (ii) NaOEt, r. t. 1 h; (iii) AcOH/H_2O, 70 °C, 5 h; (iv) $HCOONH_4$/Pd(H_2), MeOH, reflux.

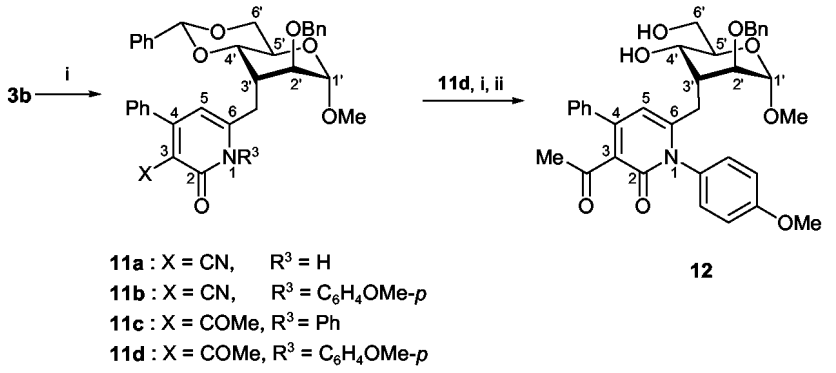
pyrazole-4-carboxylic acid derivatives to the ynone **3a** yielded compounds **7a**, **b** in the (*E*)-configuration. Additionally, no signals of acetylenic carbon atoms were observed in the ^{13}C NMR spectra.

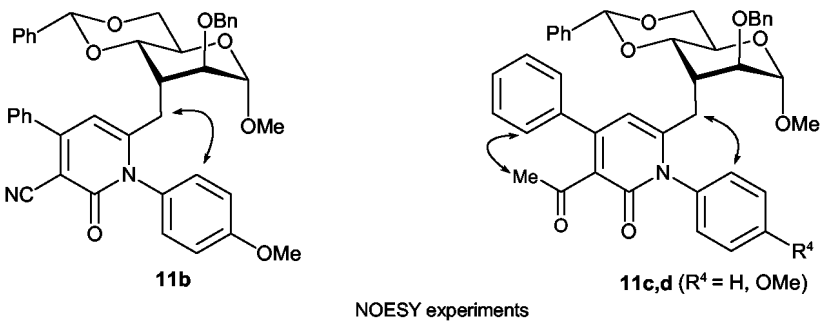
The ^{13}C NMR spectra of compounds **8a – d** showed no signals for a carbonyl group. In addition, the expected molecular peaks and the ^{1}H NMR signals of 6-H and 7-H in the range of $\delta = 6.45 - 6.62$ and $\delta = 8.04 - 8.24$, respectively, with the coupling constants between 6-H and 7-H of $J = 5.0 - 7.0$ Hz confirmed the structures of the compounds **8**.

On compound **8d** deprotection was examined exemplarily. The cleavage of the benzylidene group could be performed in a mixture of acetic acid and water to provide the 2-amino-*N*-benzyl-5-(methyl 2-*O*-benzyl-3-deoxy-α-D-altropyranosid-3-y l-methyl) pyrazolo[1,5-*a*]pyrimidine-3-carboxamide (**9**) in 73% yield. Furthermore, the 2-*O*-benzyl group of compound **9** was removed by catalytic transfer hydrogenation using 10% palladium on carbon and ammonium formate as the hydrogen donor providing the iso-*C*-nucleoside **10** as a white solid in 79% yield. The values of 8.0 – 8.5 Hz for the coupling constants $^{3}J_{4',5'}$ for compounds **9** and **10** indicated an axial-axial disposition of 4'-H and 5'-H. This observation and the small values of $^{3}J_{1',2'}$ and $^{3}J_{2',3'}$ ($\sim 2 - 5$ Hz) in compounds **9** and **10** were strong clues that the $^{4}C_1$ conformation had been retained.

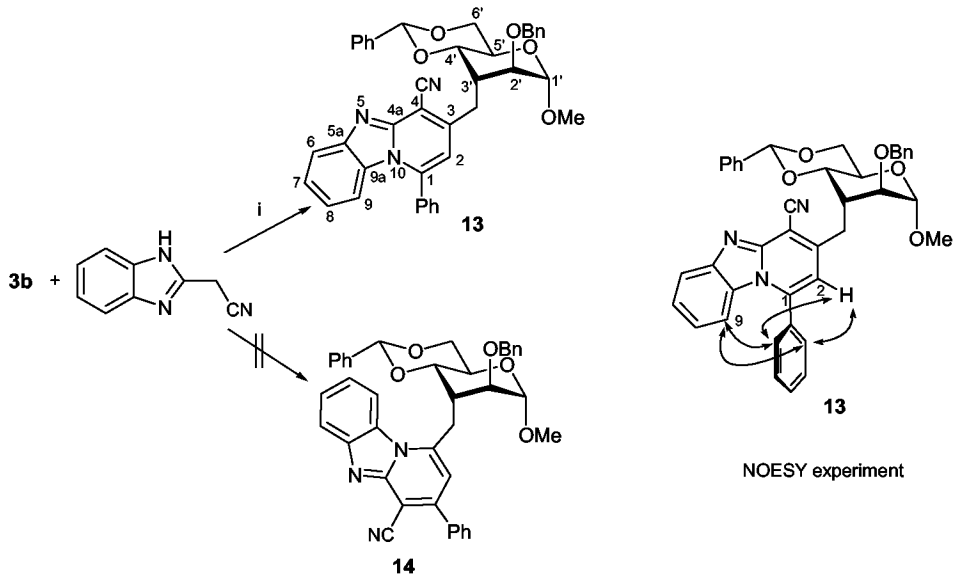
Treatment of acetylenic ketone **3b** with cyanacetamide, 2-cyano-*N*-(4-methoxyphenyl)acetamide, 3-oxo-*N*-phenyl-butyramide und *N*-(4-methoxyphenyl)-3-oxo-butyramide in the presence of potassium carbonate and 18-crown-6 provided the substituted 1,2-dihydropyridin-2-ones **11a – d** in yields of 44 – 77% (Scheme 4). In order to verify the regiochemistry of the reactions, NOESY spectra were measured. For **11b** a correlation was observed between *ortho*-protons of phenyl at N-1 and the methylene spacer. In the NOESY spectra of compounds **11c, d** cross peaks were found not only between the *ortho* protons of aryl at N-1 with the exocyclic methylene group but also between the acetyl group and the *ortho*-protons of the 4-phenyl ring. According to these results, the nucleophilic attack of the carbanionic carbon atom arising from the used carboxamides occurred at C-4 of ynone **3b** and was followed by cyclization through attack of the amide nitrogen atom on the carbonyl group. All the other spectroscopic data including mass spectra were in accordance with the proposed structures.

The deprotection of compound **11d** by treatment with aqueous acetic acid afforded the 3-acetyl-1,2-dihydro-1-(4-methoxyphenyl)-6-(methyl 2-*O*-benzyl-3-deoxy-α-D-altropyranosid-3-yl-methyl)-4-phenylpyridin-2-one (**12**) in 87% yield. Unfortunately, catalytic hydrogenation of compound **12** afforded a





Scheme 4. (i) XCH_2CONHR^3 (X = CN, COMe; R^3 = H, Ph, C_6H_4OMe-*p*), K_2CO_3, 18-crown-6, THF, reflux; (ii) $AcOH/H_2O$, 70 °C, 7 h.



Scheme 5. (i) K_2CO_3, 18-crown-6, THF, reflux.

mixture of products, which could not be separated. The NMR spectra of the mixture showed that the removal of the benzyl group along with the reduction of the acetyl group at pyridone ring took place.

Similarly, the ynone **3b** was allowed to react with 2-benzimidazolyl-acetonitrile in the presence of potassium carbonate and 18-crown-6 in order to synthesize 3-(methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)-1-phenyl-benz[4,5]imidazo[1,2-*a*]pyridine-4-carbonitrile (**13**) which could be isolated as an amorphous dark yellow solid in 57% yield (Scheme 5). In dependency on the preferred direction of attack of the 2-benzimidazolyl-acetonitrile on the ynone isomers **13** and **14** could be formed. In a NOESY experiment of the isolated compound the expected cross peaks were found for the *ortho* protons of the 1-phenyl ring with 2-H and 9-H. These *ortho* hydrogen atoms showed different chemical shifts indicating a hindered rotation of the phenyl ring around the bond axis. A HMBC spectrum of **13** allowed the assignment of all ^{13}C NMR signals.

Experimental Section

General procedures

Solvents were distilled and, if necessary, dried using standard procedures. Melting points were measured with a Boëtius apparatus and are corrected. Specific rotations were determined with a Gyromat HP (Dr. Kernchen Ltd.). IR spectra were recorded with a Nicolet 205 FT-IR spectrometer. ^{1}H NMR (500.13, 300.13 and 250.13 MHz, respectively) and ^{13}C NMR (125.7, 75.5 MHz and 62.9 MHz) spectra were recorded on Bruker instruments AVANCE 500, ARX 300 and AC 250. The calibration of spectra was carried out on TMS (internal ^{1}H) and on solvent signals $CDCl_3$: $\delta(^1\mathrm{H}) = 7.25$, $\delta(^{13}\mathrm{C}) = 77.0$; [D$_6$]-DMSO: $\delta(^1\mathrm{H}) = 2.50$; $\delta(^{13}\mathrm{C}) = 39.7$. The ^{13}C NMR signals were assigned by DEPT and/or two-dimensional ^{13}C,^{1}H correlation spectra. HMBC spectra were recorded for the compounds **8d**, **11c** and **13** in order to assign the quaternary carbon signals. The two-dimensional NOESY spectra for structure elucidation of **11a – d** and **13** were recorded with an AVANCE 500 spectrometer using a mixing time of 1 sec. The mass spectra were measured on an AMD 402/3 spectrometer (AMD Intectra GmbH). For chromatography, Merck silica gel 60 (230 – 400 mesh) was used. TLC was performed on silica gel 60 GF_{254} (Merck) with detection by using UV-light and charring with sulfuric acid. Elemental analysis were performed on a CHNS automatic elemental Flash EA 1112 (ThermoQuest).

*(3E)-4-(5-Amino-1H-1,2,4-triazol-1-yl)-1-(methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)-3-buten-2-one (**4**)*

A mixture of **3a** (0.210 g, 0.5 mmol), 3-amino-1*H*-1,2,4-triazole (0.050 g, 0.6 mmol) and ethanol (5 ml) was heated under reflux for 4 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc). Yield 0.140 g (55%), white solid. – M. p. 82 – 84 °C. – $[\alpha]^{22}_{\mathrm{D}} = +102.2$ (*c* 1.5, $CHCl_3$). – R_f = 0.45 (EtOAc). – IR (KBr): ν = 3376, 3353 (NH_2), 1690 (C=O) cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.66 (dd, 1H, $^3J_{3,4} \sim 13.0$ Hz, $^5J_{3'',4} \sim 1.0$ Hz, H-4), 7.49 (br s, 1H, H-3”), 7.40 – 7.12 (m, 10H, 2 × Ph), 6.64 (d, 1H, H-3), 5.53 (s, 1H, C*H*Ph), 5.40 (br s, NH_2), 4.61 (q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, C*H*$_2$Ph), 4.58 (br s, 1H, H-1’), 4.22 (dd, 1H, $^2J_{6'ax,6'eq} \sim 10.0$ Hz, $^3J_{5',6'eq} \sim 4.0$ Hz, H-6’eq), 4.16 – 4.07 (m, 1H, H-4’), 3.84 (dt, 1H, $^3J_{4',5'} \sim 10.0$ Hz, H-5’), 3.74 (t, 1H, $^3J_{5',6'ax} \sim 10.0$ Hz, H-6’ax), 3.52 (br m, 1H, H-2’), 3.28 (s, 3H, OMe), 3.05 – 2.98 (m, 3H, H-1, H-3’). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.9 (C-2), 155.6 (C-5”), 151.4 (C-3”), 137.9, 137.6 (2 × *i*-Ph), 131.3 (C-4), 129.1, 128.4, 128.2, 127.79, 127.82, 126.2 (*o*-, *m*-, *p*-Ph), 114.4 (C-3), 101.9 (*C*H-Ph), 100.6 (C-1’), 76.9 (C-2’), 75.4 (C-4’), 71.8 (*C*H$_2$-Ph), 69.4 (C-6’), 59.7 (C-5’), 55.2 (OMe), 38.0 (C-1), 34.8 (C-3’). – MS (EI): *m/z* (%) = 506 (5) [M]$^+$. – $C_{27}H_{30}N_4O_6$ (506.22): calcd. C 64.02, H 5.97, N 11.06; found C 63.50, H 5.92, N 10.42.

*5-(Methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)-[1,2,4]triazolo[1,5-a]pyrimidine (**5**)*

Compound **4** (0.253 g, 0.5 mmol) was added to a solution of sodium ethanolate (1.5 mmol) in ethanol (5 ml) and the mixture stirred for 1 h. After neutralization with amberlite IR-120 (Fluka-Chemie GmbH) the solvent was removed under reduced pressure and the residue was purified by column chromatography (toluene/EtOAc 1:1). Yield 190 mg (78%), white solid. – M. p. 65 – 67 °C. – $[\alpha]^{22}_{\mathrm{D}} = +33.5$ (*c* 1.0, $CHCl_3$). – R_f = 0.46 (toluene/EtOAc 1:1). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.44 (d, 1H, $^3J_{6,7} \sim 7.0$ Hz, H-7), 8.40 (s, 1H, H-2), 7.33 – 7.06 (m, 10H, 2 × Ph), 6.81 (d, 1H, H-6), 5.55 (s, 1H, C*H*Ph), 4.59 (br s, 1H, H-1’), 4.58 (q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, C*H*$_2$Ph), 4.27 (dd, 1H, $^2J_{6'ax,6'eq} \sim 10.0$ Hz, $^3J_{5',6'eq} \sim 5.0$ Hz, H-6’eq), 4.20 (dd, 1H, $^3J_{4',5'} \sim 10.0$ Hz, $^3J_{3',4'} \sim 5.0$ Hz, H-4’), 3.97 (dt, 1H, H-5’), 3.78 (t, 1H, $^3J_{5',6'ax} \sim 10.0$ Hz, H-6’ax), 3.48 (br s, 1H, H-2’), 3.32 (s, 3H, OMe), 3.29 (q(AB), 2H, $^2J_{CH_2} \sim 14.3$ Hz, 5-CH$_2$), 3.24 – 3.14 (m, 1H, H-3’). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.4 (C-5), 155.9 (C-2), 155.1 (C-3a), 137.53, 137.50 (2 × *i*-Ph), 134.4 (C-7), 128.9, 128.2, 128.1, 128.0, 127.6, 125.9 (*o*-, *m*-, *p*-Ph), 112.0 (C-6), 101.6 (*C*HPh), 100.8 (C-1’), 75.8 (C-4’), 75.1 (C-2’), 71.4 (*C*H$_2$Ph), 69.4 (C-6’), 59.7

(C-5'), 55.2 (OMe), 37.8 (C-3'), 33.4 (5-CH_2). – MS (EI): *m/z* (%) = 488 (1) $[M]^+$. – $C_{27}H_{28}N_4O_5$ (488.21): calcd. C 66.38, H 5.78, N 11.47; found C 66.38, H 5.75, N 10.89.

*5-(Methyl 2-O-benzyl-3-deoxy-α-D-altropyranosid-3-yl-methyl)[1,2,4]triazolo[1,5-a]pyrimidine (**6**)*

A solution of compound **5** (0.245 g, 0.5 mmol) in acetic acid (5 ml) and water (0.5 ml) was heated at 70 °C for 5 h. Water (10 ml) and $NaHCO_3$ were added until neutralization of the solution. The mixture was extracted with EtOAc (3 × 50 ml), the organic phases were washed with water (2 × 50 ml), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography (EtOAc/MeOH 10:1). Yield 0.185 g (92%), white foam. – M. p. 43 – 45 °C. – $[\alpha]_D^{21} = +75.8$ (*c* 0.4, MeOH). – $R_f = 0.39$ (EtOAc/MeOH 10:1). – IR (KBr): $\nu = 3382$ (OH) cm^{-1}. – ^1H NMR (500 MHz, [D_6]-DMSO): $\delta = 9.15$ (d, 1H, $^3J_{6,7} \sim 7.0$ Hz, H-7), 8.59 (s, 1H, H-2), 7.16 (d, 1H, H-6), 7.17 – 7.09 (m, 5H, Ph), 5.04 (br s, 1H, OH-4'), 4.62 (br s, 1H, OH-6'), 4.59 (d, 1H, $^3J_{1',2'} \sim 2.5$ Hz, H-1'), 4.48 (q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, C*H*$_2$Ph), 3.80 (br m, 1H, H-4'), 3.65 (br d, 1H, $^2J_{6'a,6'b} \sim 11.0$ Hz, H-6'a), 3.54 (ddd, 1H, $^3J_{4',5'} \sim 8.5$ Hz, $^3J_{5',6'a} \sim 2.0$ Hz, $^3J_{5',6'b} \sim 6.5$ Hz, H-5'), 3.52 – 3.46 (m, 1H, H-6'b), 3.35 (dd, 1H, $^3J_{2',3'} \sim 5.5$ Hz, H-2'), 3.34 (s, 3H, OMe), 3.19 – 3.10 (m, 2H, 5-CH_2), 2.68 – 2.61 (m, 1H, H-3'). – ^{13}C NMR (75.5 MHz, [D_6]-DMSO): $\delta = 169.1$ (C-5), 155.7 (C-2), 154.7 (C-3a), 138.3 (*i*-Ph), 136.1 (C-7), 128.1, 127.6 (*o*-, *m*-Ph), 127.4 (*p*-Ph), 112.2 (C-6), 100.8 (C-1'), 75.9 (C-2'), 72.2 (C-5'), 70.8 (*C*H$_2$Ph), 64.2 (C-4'), 61.7 (C-6'), 54.5 (OMe), 40.9 (C-3'), 33.6 (5-CH_2). – MS (CI): *m/z* (%) = 401 (66) $[MH]^+$. – $C_{20}H_{24}N_4O_5$ (400.17): calcd. C 59.99, H 6.04, N 13.99; found C 59.68, H 5.98, N 13.56.

*5-Amino-3-(4-methoxyphenylamino)-1-[(1E)-4-(methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)-3-oxo-but-1-enyl]-1H-pyrazole-4-carbonitrile (**7a**)*

The reaction of **3a** (0.210 g, 0.5 mmol) with 5-amino-3-(4-methoxyphenylamino)-1*H*-pyrazole-4-carbonitrile (115 mg, 0.5 mmol) prepared according to lit. [15, 16] was carried out as described above for the preparation of **4**. The product was purified by column chromatography (toluene/EtOAc 3:1). Yield 0.221 g (68%), yellow solid. – M. p. 129 – 132 °C. – $[\alpha]_D^{23} = +69.0$ (*c* 1.0, $CHCl_3$). – $R_f = 0.21$ (toluene/EtOAc 3:1). – IR (KBr): $\nu = 3421$, 3342 (NH), 2210 (CN), 1671 (C=O) cm^{-1}. – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 7.85$ (d, 1H, $^3J_{1',2'} \sim 12.8$ Hz, H-1'), 7.43 – 7.08 (m, 12H, 2 × Ph, H_o-NHC_6H_4), 6.86 – 6.77 (m, 2H, H_m-NHC_6H_4), 6.54 (d, 1H, H-2'), 6.21 (s, 1H, NH), 5.58 (s, 1H, C*H*Ph), 5.56 (s, 2H, NH_2), 4.60 (s, 1H, H-1"), 4.56 [q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, C*H*$_2$-Ph], 4.23 (dd, 1H, $^2J_{6''ax,6''eq} \sim 10.0$ Hz, $^3J_{5'',6''eq} \sim 4.5$ Hz, H-6"eq), 4.14 (m, 1H, $^3J_{4'',5''} \sim 10.0$ Hz, $^3J_{3'',4''} \sim 4.5$ Hz, H-4"), 3.87 (dt, 1H, H-5"), 3.74 (t, 1H, $^3J_{5'',6''ax} \sim 10.0$ Hz, H-6"ax), 3.71 (*p*-OMe), 3.53 (br m, 1H, H-2"), 3.31 (s, 3H, OMe), 3.06 – 2.90 (m, 3H, H-3", H-4'). – ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 199.9$ (C-3'), 155.1 (C_p-NHC_6H_4), 152.9, 152.0 (C-3, C-5), 137.6, 137.5 (2 × *i*-Ph), 132.9 (C_i-NHC_6H_4), 132.4 (C-1'), 129.1, 128.4, 128.3, 127.9, 126.2 (*o*-, *m*-, *p*-Ph), 119.6 (C_o-NHC_6H_4), 114.3 (C_m-NHC_6H_4), 113.3 (CN), 111.3 (C-2'), 101.8 (*C*H-Ph), 100.4 (C-1"), 76.7 (C-2"), 75.3 (C-4"), 71.8 (*C*H$_2$-Ph), 69.4 (C-6"), 66.8 (C-4), 59.7 (C-5"), 55.5, 55.2 (OMe, *p*-OMe), 38.1 (C-4'), 34.9 (C-3"). – MS (FAB^+): *m/z* (%) = 652 (20) $[MH]^+$. – $C_{36}H_{37}N_5O_7$ (651.27): calcd. C 66.35, H 5.72, N 10.75; found C 66.15, H 5.71, N 10.24.

*3,5-Diamino-1-[(1E)-4-(methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl)-3-oxo-but-1-enyl]-1H-pyrazole-4-carboxamide (**7b**)*

The reaction of **3a** (0.210 g, 0.5 mmol) with 3,5-diamino-1*H*-pyrazole-4-carboxamide (70 mg, 0.5 mmol) [15, 16] was carried out as described above for the preparation of **4**. The product was purified by column chromatography ($CHCl_3$/MeOH 10:1). Yield 0.197 g (70%), yellow solid. – M. p. 147 – 149 °C. – $[\alpha]_D^{24} = +127.0$ (*c* 0.5, $CHCl_3$). – $R_f = 0.29$ ($CHCl_3$/MeOH 10:1). – IR (KBr): $\nu = 3449$, 3437, 3416, 3396, 3388, 3377, 3368 (NH_2), 1670 (C=O) cm^{-1}. – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 8.08$ (d, 1H, $^3J_{1',2'} \sim 13.2$ Hz, H-1'), 7.39 – 7.03 (m, 10H, 2 × Ph), 6.65 (br s, 2H, NH_2), 6.41 (d, 1H, H-2'), 6.38 (br s, 2H, NH_2), 5.50 (s, 1H, C*H*Ph), 4.59 [q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, C*H*$_2$Ph], 4.54 (s, 1H, H-1"), 4.19 (dd, 1H, $^2J_{6''ax,6''eq} \sim 10.0$ Hz, $^3J_{5'',6''eq} \sim 4.0$ Hz, H-6"eq), 4.09 (dd, 1H, $^3J_{4'',5''} \sim 9.5$ Hz, $^3J_{3'',4''} \sim 4.5$ Hz, H-4"), 3.88 – 3.73 (m, 3H, H-5", NH_2), 3.71 (t, 1H, $^3J_{5'',6''ax} \sim 10.0$ Hz, H-6"ax), 3.53 (br s, 1H, H-2"), 3.23 (s, 3H, OMe), 3.13 – 2.92 (m, 3H, H-3", H-4'). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 199.4$ (C-3'), 166.9 (*C*ONH$_2$), 154.5, 152.6 (C-3, C-5), 138.0, 137.5 (2 × *i*-Ph), 132.8 (C-1'), 128.9, 128.4, 128.2, 127.7, 126.2, 125.2 (*o*-, *m*-, *p*-Ph), 110.0 (C-2'), 101.8 (*C*HPh), 100.7 (C-1"), 88.3 (C-4), 77.0 (C-2"), 75.4 (C-4"), 71.6 (*C*H$_2$Ph), 69.4 (C-6"), 59.7 (C-5"), 55.1 (OMe), 38.0 (C-4'), 34.4 (C-3"). – MS (FAB^+): *m/z* (%) = 564 (10) $[MH]^+$. – $C_{29}H_{33}N_5O_7$ (563.24): calcd. C 61.80, H 5.90, N 12.43; found C 61.26, H 5.96, N 11.65.

*2-(4-Methoxyphenyl)-5-(methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)pyrazolo-[1,5-a]pyrimidine-3-carbonitrile (**8a**)*

Method A:

The reaction of **7a** (0.162 g, 0.25 mmol) with a solution of sodium ethanolate (1.5 mmol) in ethanol (5 ml) was carried out as described above for the preparation of **5**.

Method B:

A mixture of **3a** (0.210 g, 0.5 mmol), 5-amino-3-(4-methoxyphenylamino)-1*H*-pyrazole-4-carbonitrile (115 mg, 0.5 mmol) [15, 16] and ethanol (5 ml) was heated under reflux for 4 h. After cooling to 20 °C, the mixture was treated with sodium ethanolate (1.5 mmol) in ethanol (5 ml) for 1 h under stirring. Neutralization with amberlite IR-120 (Fluka-Chemie GmbH) was followed by evaporation of the solvent under reduced pressure and purification of the residue by column chromatography (toluene/EtOAc 6:1).

Yield 0.135 g (85%, method A), 0.250 g (80%, method B), yellow solid. – M. p. 108 – 110 °C. – $[\alpha]_D^{21} = +29.1$ (*c* 1.5, $CHCl_3$). – $R_f = 0.35$ (toluene/EtOAc 6:1). – IR (KBr): $\nu = 3414$ (NH), 2215 (CN) cm^{-1}. – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 8.13$ (d, 1H, $^3J_{6,7} \sim 7.0$ Hz, H-7), 7.46 – 7.38 (m, 2H, H_o-NHC_6H_4), 7.38 – 7.06 (m, 10H, 2 × Ph), 6.87 – 6.80 (m, 2H, H_m-NHC_6H_4), 6.57 (d, 1H, H-6), 6.56 (s, 1H, NH), 5.55 (s, 1H, C*H*Ph), 4.64 (q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, CH_2Ph), 4.60 (s, 1H, H-1'), 4.26 (dd, 1H, $^2J_{6'ax,6'eq} \sim 10.0$ Hz, $^3J_{5',6'eq} \sim 4.7$ Hz, H-6'eq), 4.19 (dd, 1H, $^3J_{4',5'} \sim 10.0$ Hz, $^3J_{3',4'} \sim 4.4$ Hz, H-4'), 3.95 (dt, 1H, H-5'), 3.78 (t, 1H, $^3J_{5',6'ax} \sim 10.0$ Hz, H-6'ax), 3.73 (*p*-OMe), 3.52 (br m, 1H, H-2'), 3.32 (s, 3H, OMe), 3.25 – 3.10 (m, 3H, 5-CH_2, H-3'). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 165.4$ (C-5), 158.1 (C-2), 150.1 (C-3a), 155.7 (C_p-NHC_6H_4), 137.8, 137.6 (2 × *i*-Ph), 134.1 (C-7), 132.5 (C_i-NHC_6H_4), 128.9, 128.2, 128.1, 127.8, 127.6, 126.0 (*o*-, *m*-, *p*-Ph), 120.7 (C_o-NHC_6H_4), 114.5 (C_m-NHC_6H_4), 113.5 (CN), 110.3 (C-6), 101.7 (*C*HPh), 100.9 (C-1'), 75.8 (C-4'), 75.4 (C-2'), 71.6 (CH_2Ph), 69.5 (C-6'), 67.9 (C-3), 59.7 (C-5'), 55.5, 55.2 (*p*-OMe, OMe), 37.4 (C-3'), 32.7 (5-CH_2). – MS (EI): *m/z* (%) = 633 (40) $[M]^+$. – $C_{36}H_{35}N_5O_6$ (633.26): calcd. C 68.23, H 5.57, N 11.05; found C 68.06, H 5.61, N 10.58.

*2-Amino-5-(methyl-2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)pyrazolo[1,5-a]pyrimidine-3-carboxamide (***8b***)*

Method A:

Compound **7b** (0.140 g, 0.25 mmol) was reacted as described above under method A for the preparation of **8a**.

Method B:

Compound **3a** (0.210 g, 0.5 mmol) and 3,5-diamino-1*H*-pyrazole-4-carboxamide (70 mg, 0.5 mmol) [15, 16] were reacted as described above under method B for the preparation of **8a**. Yield 0.120 g (88%, method A), 0.220 g (82%, method B), white solid. – M. p. 105 – 107 °C. – $[\alpha]_D^{22} = +28.7$ (*c* 1.0, $CHCl_3$). – $R_f = 0.40$ (EtOAc). – IR (KBr): $\nu = 3438$, 3425 (NH_2) cm^{-1}. – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 8.07$ (d, 1H, $^3J_{6,7} \sim 6.8$ Hz, H-7), 7.54 (br s, NH_2), 7.42 – 7.24 (m, 5H, Ph), 7.09 – 6.98 (m, 5H, Ph), 6.48 (d, 1H, H-6), 5.63 (br s, NH_2), 5.56 (s, 1H, C*H*Ph), 4.61 (s, 1H, H-1'), 4.40 [q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, CH_2Ph], 4.26 (dd, 1H, $^2J_{6'ax,6'eq} \sim 10.0$ Hz, $^3J_{5',6'eq} \sim 4.8$ Hz, H-6'eq), 4.17 (dd, 1H, $^3J_{4',5'} \sim 10.0$ Hz, $^3J_{3',4'} \sim 5.5$ Hz, H-4'), 3.96 (dt, 1H, H-5'), 3.77 (t, 1H, $^3J_{5',6'ax} \sim 10.0$ Hz, H-6'ax), 3.35 (s, 3H, OMe), 3.33 (br m, 1H, H-2'), 3.18 – 3.08 (m, 2H, 5-CH_2), 2.91 – 2.79 (m, 1H, H-3'). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 166.2$ (*C*ONH_2), 162.8 (C-5), 161.5 (C-2), 147.2 (C-3a), 137.5, 136.9 (2 × *i*-Ph), 133.6 (C-7), 129.1, 128.2, 127.8, 127.7, 126.1 (*o*-, *m*-, *p*-Ph), 108.7 (C-6), 101.9 (*C*H-Ph), 100.2 (C-1'), 87.3 (C-3), 75.8 (C-4'), 74.6 (C-2'), 71.5 (CH_2-Ph), 69.4 (C-6'), 59.5 (C-5'), 55.2 (OMe), 39.2 (C-3'), 32.9 (5-CH_2). – MS (EI): *m/z* (%) = 545 (11) $[M]^+$. – $C_{29}H_{31}N_5O_6$ (545.23): calcd. C 63.84, H 5.73, N 12.84; found C 63.93, H 5.90, N 12.01.

*Ethyl 2-(4-chlorophenylamino)-5-(methyl-2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)-pyrazolo[1,5-a]pyrimidine-3-carboxylate (***8c***)*

The reaction of **3a** (0.210 g, 0.5 mmol) with ethyl 5-amino-3-(4-chlorophenylamino)-1*H*-pyrazole-4-carboxylate (140 mg, 0.5 mmol) [15, 16] was carried out as described above under method B for the preparation of **8a**. The product was purified by column chromatography (toluene/EtOAc 3:1). Yield 0.290 g (85%), white solid. – M. p. 88 – 90 °C. – $[\alpha]_D^{21} = +17.5$ (*c* 0.5, $CHCl_3$). – $R_f = 0.63$ (toluene/EtOAc 3:1). – IR (KBr): $\nu = 3440$ (NH), 1668 (C=O) cm^{-1}. – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 9.01$ (s, 1H NH), 8.24 (d, 1H, $^3J_{6,7} \sim 6.9$ Hz, H-7), 7.62 – 7.54 (m, 2H, H_o-NHC_6H_4), 7.40 – 7.05 (m, 12H, H_m-NHC_6H_4, 2 × Ph), 6.62 (d, 1H, H-6), 5.58 (s, 1H, C*H*Ph), 4.58 (s, 1H, H-1'), 4.54 [q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, CH_2-Ph], 4.39 – 4.18 (m, 3H, OCH_2CH_3, H-6'), 4.21 (dd, 1H, $^3J_{4',5'} \sim 10.0$ Hz, $^3J_{3',4'} \sim 4.4$ Hz, H-4'), 3.98 (dt, 1H, $^3J_{5',6'eq} \sim 4.8$ Hz, H-5'), 3.79 (t, 1H, $^3J_{5',6'ax} \sim^2 J_{6'ax,6'eq} \sim 10.0$ Hz, H-6'ax), 3.49 (br m, 1H, H-2'), 3.32 (s, 3H, OMe), 3.29 – 3.18 (m, 3H, 5-CH_2, H-3'), 1.32 (t, 3H, $^3J \sim 7.0$ Hz, OCH_2CH_3). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 165.4$, 165.1 (*C*OOEt, C-5), 157.9 (C-2), 147.4 (C-3a), 138.9 (C_i-NHC_6H_4), 137.7, 137.6 (2 × *i*-Ph), 134.1 (C-7), 128.9, 128.24, 128.17, 127.8, 127.7, 126.1 (*o*-, *m*-, *p*-Ph, C_m-NHC_6H_4), 126.3 (C_p-NHC_6H_4), 119.2 (C_o-NHC_6H_4), 109.9 (C-6), 101.8 (*C*H-Ph), 100.9 (C-1'), 86.4 (C-3), 75.9 (C-4'), 75.1 (C-2'), 71.2 (CH_2Ph), 69.5 (C-6'), 60.2 (OCH_2CH_3), 59.7 (C-5'), 55.2 (OMe), 37.7 (C-3'), 33.1 (5-CH_2), 14.5 (OCH_2CH_3). MS (EI): *m/z* (%) = 685 (17) $[MH]^+$. – $C_{37}H_{37}ClN_4O_7$ (684.24): calcd. C 64.86, H 5.44, N 8.18; found C 64.75, H 5.56, N 7.63.

*2-Amino-N-benzyl-5-(methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)pyrazolo[1,5-a]-pyrimidine-3-carboxamide (***8d***)*

The reaction of **3a** (0.210 g, 0.5 mmol) with 3,5-diamino-*N*-benzyl-1*H*-pyrazole-4-carboxamide (115 mg, 0.5 mmol)

[15, 16] was carried out as described above under method B for the preparation of **8a**. The product was purified by column chromatography (toluene/EtOAc 1:1). Yield 0.290 g (91%), white solid. – M. p. 72 – 74 °C. – $[\alpha]_D^{22} = +35.8$ (*c* 0.5, $CHCl_3$). – $R_f = 0.37$ (toluene/EtOAc 1:1). – IR (KBr): $\nu = 3442, 3344$ (NH), 1647 (C=O) cm^{-1}. – ^1H NMR (250 MHz, $CDCl_3$): $\delta = 8.14 - 8.04$ (m, 2H, H-7, NH), 7.40 – 6.86 (m, 15H, 3 × Ph), 6.45 (d, 1H, $^3J_{6,7} \sim 5.0$ Hz, H-6), 5.55 (s, 1H, C*H*Ph), 4.66 (dd, 1H, $^3J_{NH,NCH_2} \sim 6.0$ Hz, $^2J_{NCH_2} \sim 15.0$ Hz, NCH_2), 4.54 (dd, 1H, $^3J_{NH,NCH_2} \sim 6.0$ Hz, NCH_2), 4.51 (s, 1H, H-1'), 4.30 – 4.18 (m, 3H, CH_2Ph, H-6'eq), 4.10 (dd, 1H, $^3J_{4',5'} \sim 10.0$ Hz, $^3J_{3',4'} \sim 5.3$ Hz, H-4'), 3.91 (dt, 1H, $^3J_{5',6'eq} \sim 4.7$ Hz, H-5'), 3.76 (t, 1H, $^3J_{5',6'ax} \sim^2 J_{6'ax,6'eq} \sim 10.0$ Hz, H-6'ax), 3.28 (br m, 1H, H-2'), 3.24 (s, 3H, OMe), 3.11 – 3.02 (m, 2H, 5-CH_2), 2.73 – 2.59 (m, 1H, H-3'). – ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 164.5$ (*C*ONH_2), 162.8 (C-5), 161.3 (C-2), 146.7 (C-3a), 139.1, 137.5, 136.8 (3 × *i*-Ph), 133.6 (C-7), 129.1, 128.6, 128.3, 128.1, 127.8, 127.7, 127.2, 127.1, 126.1 (*o*-, *m*-, *p*-Ph), 108.5 (C-6), 101.9 (*C*H-Ph), 100.3 (C-1'), 87.5 (C-3), 75.7 (C-4'), 73.9 (C-2'), 71.3 (*C*H_2-Ph), 69.4 (C-6'), 59.4 (C-5'), 55.1 (OMe), 42.5 (N*C*H_2Ph), 39.3 (C-3'), 32.8 (5-CH_2). – MS (EI): *m/z* (%) = 635 (24) $[M]^+$. – $C_{36}H_{37}N_5O_6$ (635.27): calcd. C 68.02, H 5.87, N 11.02; found C 67.78, H 5.81, N 10.67.

*2-Amino-N-benzyl-5-(methyl 2-O-benzyl-3-deoxy-α-D-altropyranosid-3-yl-methyl)pyrazolo[1,5-a]pyrimidine-3-carboxamide (**9**)*

The deprotection of compound **8d** (0.315 g, 0.5 mmol) was carried out as described above for the preparation of **6** (reaction time 7 h). The product was purified by column chromatography (EtOAc/MeOH 10:1). Yield 0.200 g (73%), white solid. – M. p. 75 – 78 °C. – $[\alpha]_D^{21} = +60.6$ (*c* 0.4, MeOH). – $R_f = 0.41$ (EtOAc/MeOH 10:1). – IR (KBr): $\nu = 3456, 3313, 3200$ (OH, NH_2) cm^{-1}. – ^1H NMR (500 MHz, [D_6]-DMSO): $\delta = 8.68$ (d, 1H, $^3J_{6,7} \sim 7.0$ Hz, H-7), 8.22 (t, 1H, $^3J_{NH,NCH_2} \sim 6.0$ Hz, $NHCH_2$), 7.33 – 7.20 (m, 5H, Ph), 7.13 – 6.98 (m, 5H, Ph), 6.75 (d, 1H, H-6), 6.42 (s, 2H, NH_2), 4.98 (d, 1H, $^3J_{4',OH-4'} \sim 5.2$ Hz, OH-4'), 4.59 (dd, 1H, $^2J_{NCH_2} \sim 15.5$ Hz, NHCH_2), 4.58 (t, 1H, $^3J_{6',OH-6'} \sim 6.0$ Hz, OH-6'), 4.51 (dd, 1H, NHCH_2), 4.50 (d, 1H, $^3J_{1',2'} \sim 2.4$ Hz, H-1'), 4.33 (q (AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, CH_2Ph), 3.83 (dt, 1H, $^3J_{3',4'} \sim 5.2$ Hz, $^3J_{4',5'} \sim 8.5$ Hz, H-4'), 3.63 (ddd, 1H, $^3J_{5',6'a} \sim 2.0$ Hz, $^2J_{6'a,6'b} \sim 11.0$ Hz, H-6'a), 3.50 (ddd, 1H, $^3J_{5',6'b} \sim 6.0$ Hz, H-5'), 3.47 (dt, 1H, H-6'b), 3.29 (dd, 1H, $^3J_{2',3'} \sim 4.8$ Hz, H-2'), 3.24 (s, 3H, OMe), 3.02 (dd, 1H, $^3J_{5-CH_2,3'} \sim 6.0$ Hz, $^2J_{5-CH_2} \sim 14.0$ Hz, 5-CH_2), 2.98 (dd, 1H, $^3J_{CH_{2a},3'} \sim 9.0$ Hz, 5-CH_2b), 2.52 – 2.44 (m, 1H, H-3'). – ^{13}C NMR (75.5 MHz, [D_6]-DMSO): $\delta = 163.9$ (*C*ONH_2), 163.3 (C-5), 161.3 (C-2), 146.4 (C-3a), 139.9, 138.0 (2 × *i*-Ph), 134.8 (C-7), 128.6, 127.9, 127.5, 127.3, 127.0, 126.9 (*o*-, *m*-, *p*-Ph), 108.6 (C-6), 100.5 (C-1'), 86.1 (C-3), 75.2 (C-2'), 71.9 (C-5'), 70.7 (*C*H_2Ph), 64.1 (C-4'), 61.7 (C-6'), 54.4 (OMe), 41.6 (NH*C*H_2Ph), 41.2 (C-3'), 32.8 (5-CH_2). – MS (EI): *m/z* (%) = 547 (8) $[M]^+$. – $C_{29}H_{33}N_5O_6$ (547.24): calcd. C 63.61, H 6.07, N 12.79; found C 62.97, H 6.12, N 12.32.

*2-Amino-N-benzyl-5-(methyl 3-deoxy-α-D-altropyranosid-3-yl-methyl)pyrazolo[1,5-a]pyrimidine-3-carboxamide (**10**)*

A mixture of **9** (0.135 g, 0.25 mmol), ammonium formate (0.1 g), 10% palladium on carbon (0.200 g, Lancaster) in dry MeOH (10 ml) was refluxed for 2 h. The catalyst was filtered off and washed with the solvent. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (EtOAc/MeOH 5:1). Yield 0.090 g (79%), white solid. – M. p. 84 – 86 °C. – $[\alpha]_D^{21} = +52.9$ (*c* 0.5, MeOH). – $R_f = 0.46$ (EtOAc/MeOH 5:1). – IR (KBr): $\nu = 3576, 3462, 3315, 3199$ (OH, NH_2) cm^{-1}. – ^1H NMR (500 MHz, [D_6]-DMSO): $\delta = 8.75$ (d, 1H, $^3J_{6,7} \sim 7.0$ Hz, H-7), 8.29 (t, 1H, $^3J_{NH,NCH_2} \sim 6.0$ Hz, $NHCH_2$), 7.38 – 7.22 (m, 5H, Ph), 6.85 (d, 1H, H-6), 6.40 (s, 2H, NH_2), 5.04 (d, 1H, $^3J_{2',OH-2'} \sim 5.2$ Hz, OH-2'), 4.86 (d, 1H, $^3J_{4',OH-4'} \sim 5.3$ Hz, OH-4'), 4.59 (dd, 1H, $^2J_{CH_2} \sim 15.5$ Hz, NHCH_2), 4.56 (t, 1H, $^3J_{6',OH-6'} \sim 6.0$ Hz, OH-6'), 4.55 (dd, 1H, NHCH_2), 4.35 (d, 1H, $^3J_{1',2'} \sim 3.0$ Hz, H-1'), 3.76 (dt, 1H, $^3J_{3',4'} \sim 5.2$, $^3J_{4',5'} \sim 8.0$ Hz, H-4'), 3.59 (ddd, 1H, $^3J_{5',6'a} \sim 3.0$ Hz, $^2J_{6'a,6'b} \sim 11.0$ Hz, H-6'a), 3.55 – 3.46 (m, 2H, H-5', H-2'), 3.43 (ddd, 1H, $^3J_{5',6'a} \sim 6.0$ Hz, H-6'a), 3.26 (s, 3H, OMe), 3.07 (dd, 1H, $^3J_{CH_2,3'} \sim 8.5$ Hz, $^2J_{CH_2} \sim 14.5$ Hz, 5-CH_2), 3.01 (dd, 1H, $^3J_{CH_2,3'} \sim 6.5$ Hz, 5-CH_2), 2.38 – 2.31 (m, 1H, H-3'). – ^{13}C NMR (75.5 MHz, [D_6]-DMSO): $\delta = 163.9$ (*C*ONH_2), 163.8 (C-5), 161.2 (C-2), 146.4 (C-3a), 139.9 (*i*-Ph), 134.8 (C-7), 128.6, 127.1, 126.9 (*o*-, *m*-, *p*-Ph), 108.7 (C-6), 102.9 (C-1'), 86.0 (C-3), 72.9 (C-5'), 68.5 (C-2'), 64.1 (C-4'), 61.7 (C-6'), 54.6 (OMe), 42.9 (C-3'), 41.7 (NH*C*H_2Ph), 32.9 (5-CH_2). – MS (EI): *m/z* (%) = 457 (12) $[M]^+$. – $C_{22}H_{27}N_5O_6$ (457.19): calcd. C 57.76, H 5.95, N 15.31; found C 57.56, H 5.89, N 15.02.

*1,2-Dihydro-6-(methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)-2-oxo-4-phenylpyridine-3-carbonitrile (**11a**)*

A mixture of **3b** (0.250 g, 0.5 mmol), cyanacetamide (0.063 g, 0.75 mmol), K_2CO_3 (0.120 g, 0.87 mmol), 18-crown-6 (100 mg, 0.38 mmol) in THF (15 ml) was refluxed up to the disappearance of **3b** (8 h, TLC control). The suspension was filtered and the filtrate was concentrated. The residue was purified by column chromatography (toluene/EtOAc 1:1). Yield 0.124 g (44%), white solid. – M. p. 104 – 107 °C. – $[\alpha]_D^{21} = +26.6$ (*c* 1.0, $CHCl_3$). –

$R_f = 0.51$ (toluene/EtOAc 1:1). – IR (KBr): $\nu = 3298$ (NH), 2221 (CN), 1644 (C=O) cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 12.80$ (br s, NH), 7.51 – 7.18 (m, 15H, 3 × Ph), 6.16 (s, 1H, H-5), 5.51 (s, 1H, C*H*Ph), 4.72 (s, 1H, H-1'), 4.70 [q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, CH_2-Ph], 4.35 (dd, 1H, $^2J_{6'ax,6'eq} \sim 10.0$ Hz, $^3J_{5',6'eq} \sim 4.6$ Hz, H-6'eq), 4.20 (dd, 1H, $^3J_{4',5'} \sim 10.0$ Hz, $^3J_{3',4'} \sim 4.6$ Hz, H-4'), 4.13 (dt, 1H, H-5'), 3.79 (t, 1H, $^3J_{5',6'ax} \sim 10.0$ Hz, H-6'ax), 3.69 (br s, 1H, H-2'), 3.47 (s, 3H, OMe), 3.18 (dd, 1H, $^2J_{CH_2} \sim 14.0$ Hz, $^3J_{CH_2,3'} \sim 7.9$ Hz, CH_2), 2.90 – 2.75 (m, 1H, H-3'), 2.75 (dd, 1H, $^2J_{CH_2} \sim 14.0$ Hz, $^3J_{CH_2,3'} \sim 5.2$ Hz, CH_2). – ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 163.7$, 160.8 (C-2, C-4), 154.4 (C-6), 137.7, 137.3, 135.9 (3 × *i*-Ph), 130.4, 128.84, 128.76, 128.4, 128.1, 128.0, 127.93, 127.85, 125.5 (*o*-, *m*-, *p*-Ph), 115.9 (CN), 108.4 (C-5), 101.4 (*C*H-Ph), 99.8 (C-1'), 98.7 (C-3), 77.5 (C-4'), 76.1 (C-2'), 72.4 (CH_2-Ph), 69.3 (C-6'), 59.0 (C-5'), 55.4 (OMe), 39.5 (C-3'), 31.3 (6-CH_2). – MS (EI): *m/z* (%) = 564 (7) $[M]^+$. – $C_{34}H_{32}N_2O_6$ (564.23): calcd. C 72.32, H 5.71, N 4.96; found C 72.08, H 5.68, N 4.66.

*1,2-Dihydro-1-(4-methoxyphenyl)-6-(methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)-2-oxo-4-phenylpyridine-3-carbonitrile (**11b**)*

The reaction of **3b** (0.250 g, 0.5 mmol) with 2-cyano-*N*-(4-methoxy-phenyl)acetamide (0.140 g, 0.75 mmol) was carried out as described above for the preparation of **11a**. The product was purified by column chromatography (toluene/EtOAc 2:1). Yield 0.218 g (65%), white solid. – M. p. 117 – 120 °C. – $[\alpha]_D^{20} = +11.3$ (*c* 0.5, $CHCl_3$). – $R_f = 0.43$ (toluene/EtOAc 2:1). – IR (KBr): $\nu = 2219$ (CN), 1660 (C=O) cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.54 - 7.48$ (m, 4H, 2 × Ph, $C_6H_5CH_2$, C_6H_4), 7.35 – 7.14 (m, 13H, 2 × Ph, $C_6H_5CH_2$, C_6H_4), 7.05 – 7.01 (m, 2H, 2 × Ph, $C_6H_5CH_2$, C_6H_4), 6.29 (s, 1H, H-5), 5.44 (s, 1H, C*H*Ph), 4.64 (s, 1H, H-1'), 4.48 [q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, CH_2Ph], 4.23 (m, 1H, H-6'eq), 3.99 (dd, 1H, $^3J_{4',5'} \sim 9.2$ Hz, $^3J_{3',4'} \sim 5.5$ Hz, H-4'), 3.74 (s, 3H, *p*-OMe), 3.73 – 3.68 (m, 2H, H-5', H-6'ax), 3.39 (br s, 1H, H-2'), 3.31 (s, 3H, OMe), 2.98 – 2.80 (m, 2H, 6-CH_2), 2.35 – 2.28 (m, 1H, H-3'). – ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 162.0$, 160.0 (C-2, C-4), 158.4 (C_p-NC_6H_4), 154.0 (C-6), 137.1, 136.9, 135.8 (3 × *i*-Ph), 130.5, 129.2, 128.7, 128.4, 128.2, 128.1, 128.0, 127.8, 125.7, 125.3 (*o*-, *m*-, *p*-Ph), 128.9 (C_i-NC_6H_4), 115.8 (CN), 115.5, 114.4 (C_o, C_m-NC_6H_4), 108.9 (C-5), 101.2 (*C*H-Ph), 100.1 (C-3), 99.5 (C-1'), 75.2 (C-4'), 74.3 (C-2'), 71.9 (CH_2-Ph), 69.2 (C-6'), 59.0 (C-5'), 55.4, 55.1 (OMe, *p*-OMe), 38.1 (C-3'), 29.6 (6-CH_2). – MS (EI): *m/z* (%) = 670 (14) $[M]^+$. – $C_{41}H_{38}N_2O_7$ (670.27): calcd. C 73.42, H 5.71, N 4.18; found C 73.47, H 5.83, N 3.83.

*3-Acetyl-1,2-dihydro-6-(methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)-1,4-diphenylpyridin-2-one (**11c**)*

The reaction of **3b** (0.250 g, 0.5 mmol) with 3-oxo-*N*-phenyl-butyramide (0.130 g, 0.75 mmol) was carried out as described above for the preparation of **11a**. The product was purified by column chromatography (toluene/EtOAc 1:1). Yield 0.255 g (77%), white solid. – M. p. 99 – 102 °C. – $[\alpha]_D^{22} = +5.8$ (*c* 0.5, $CHCl_3$). – $R_f = 0.23$ (toluene/EtOAc 1:1). – IR (KBr): $\nu = 1699$, 1647 (C=O) cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.50 - 7.10$ (m, 20H, 3 × Ph, $CH_2C_6H_5$), 6.23 (s, 1H, H-5), 5.41 (s, 1H, C*H*Ph), 4.61 (s, 1H, H-1'), 4.48 [q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, CH_2Ph], 4.20 (m, 1H, H-6'eq), 3.96 (dd, 1H, $^3J_{4',5'} \sim 9.5$ Hz, $^3J_{3',4'} \sim 5.2$ Hz, H-4'), 3.69 (t, 1H, $^3J_{5',6'ax} \sim^2 J_{6'ax,6'eq} \sim 10.0$ Hz, H-6'ax), 3.74 – 3.61 (m, 1H, H-5'), 3.44 (br s, 1H, H-2'), 3.27 (s, 3H, OMe), 2.91 – 2.77 (m, 2H, 6-CH_2), 2.40 (s, 3H, COMe), 2.36 – 2.28 (m, 1H, H-3'). – ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 202.1$ (*C*OMe), 161.5 (C-2), 150.5 (C-4), 149.2 (C-6), 137.9, 137.19, 137.16, 137.1 (3 × *i*-Ph, C_i-NC_6H_5), 129.6, 129.5, 128.90, 128.85, 128.80, 128.62, 128.58, 128.5, 128.2, 128.0, 127.9, 127.8, 125.9 (*o*-, *m*-, *p*-Ph), 128.3 (C-3), 109.5 (C-5), 101.2 (*C*HPh), 99.7 (C-1'), 75.3 (C-4'), 74.8 (C-2'), 71.9 (CH_2Ph), 69.2 (C-6'), 58.9 (C-5'), 54.9 (OMe), 37.8 (C-3'), 31.7 (CO*Me*), 28.7 (6-CH_2). – MS (EI): *m/z* (%) = 657 (55) $[M]^+$. – $C_{41}H_{39}NO_7$ (657.27): calcd. C 74.87, H 5.98, N 2.13; found C 74.89, H 6.18, N 1.99.

*3-Acetyl-1,2-dihydro-1-(4-methoxyphenyl)-6-(methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)-4-phenylpyridin-2-one (**11d**)*

The reaction of **3b** (0.250 g, 0.5 mmol) with *N*-(4-methoxyphenyl)-3-oxo-butyramide (0.155 g, 0.75 mmol) was carried out as described above for the preparation of **11a**. The product was purified by column chromatography (toluene/EtOAc 2:1). Yield 0.245 g (71%), white solid. – M. p. 92–94 °C. – $[\alpha]_D^{23} = +29.9$ (*c* 1.0, $CHCl_3$). – $R_f = 0.27$ (toluene/EtOAc 2:1). – IR (KBr): $\nu = 1699$, 1645 (C=O) cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.43 - 6.90$ (m, 19H, 2 × Ph, $C_6H_5CH_2$, C_6H_4), 6.21 (s, 1H, H-5), 5.44 (s, 1H, C*H*Ph), 4.62 (s, 1H, H-1'), 4.48 [q(AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, CH_2-Ph], 4.21 (m, 1H, H-6'eq), 3.98 (m, 1H, H-4'), 3.73 (s, 3H, *p*-OMe), 3.75 – 3.68 (m, 2H, H-5', H-6'ax), 3.47 (br s, 1H, H-2'), 3.29 (s, 3H, OMe), 2.94 – 2.82 (m, 2H, 6-CH_2), 2.32 – 2.29 (m, 1H, H-3'), 2.40 (s, 3H, COMe). – ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 202.1$ (*C*OMe), 161.8 (C-2), 159.7 (C_p-NC_6H_4), 150.3 (C-4), 149.6 (C-6), 138.0, 137.3, 137.1 (3 × *i*-Ph), 129.7, 128.8 (C-3, C_i-NC_6H_4), 129.5, 129.1, 128.8, 128.7, 128.6, 128.3, 128.1, 127.8, 125.8 (*o*-, *m*-, *p*-Ph), 115.5, 114.3 (C_o, C_m-NC_6H_4), 109.5 (C-5), 101.2 (*C*H-Ph), 99.8 (C-1'), 75.3 (C-4'), 74.7 (C-2'), 72.0

(CH_2Ph), 69.3 (C-6'), 59.0 (C-5'), 55.4, 55.0 (OMe, *p*-OMe), 37.8 (C-3'), 31.7 (CO*Me*), 28.8 (6-CH_2). – MS (EI): *m/z* (%) = 687 (50) $[M]^+$. – $C_{42}H_{41}NO_8$ (687.28): calcd. C 73.34, H 6.01, N 2.04; found C 73.02, H 6.28, N 1.87.

*3-Acetyl-1,2-dihydro-1-(4-methoxyphenyl)-6-(methyl 2-O-benzyl-3-deoxy-α-D-altropyranosid-3-yl-methyl)-4-phenylpyridin-2-one (**12**)*

The deprotection of compound **11d** (0.170 g, 0.25 mmol) using acetic acid (5 ml) and water (0.5 ml) was carried out as described above for the preparation of **6** (reaction time 7 h). The product was purified by column chromatography (EtOAc). Yield 0.130 g (87%), white solid. – M. p. 91 – 93 °C. – $[\alpha]_D^{21} = +38.7$ (*c* 0.4, MeOH). – $R_f = 0.26$ (EtOAc). – IR (KBr): $\nu = 3427$ (OH), 1699, 1637 (C=O) cm^{-1}. – ^{1}H NMR (500 MHz, [D$_6$]-DMSO): $\delta = 7.47 - 7.43$ (m, 3H, Ph), 7.35 – 7.32 (m, 2H, H$_o$-NHC$_6$H$_4$), 7.30 – 7.10 (m, 7H, Ph), 7.07 – 7.04 (m, 2H, H$_m$-NHC$_6$H$_4$), 6.28 (s, 1H, H-5), 4.85 (d, 1H, $^3J_{4',OH-4'} \sim 5.5$ Hz, OH-4'), 4.58 (t, 1H, $^3J_{6',OH-6'} \sim 6.0$ Hz, OH-6'), 4.47 (s, 1H, H-1'), 4.42 [q (AB), 2H, $^2J_{CH_2} \sim 12.0$ Hz, C*H*$_2$Ph], 3.80 (s, 3H, *p*-OMe), 3.62 (dt, 1H, $^3J_{3',4'} \sim 5.0$ Hz, $^3J_{4',5'} \sim 7.5$ Hz, H-4'), 3.52 (ddd, 1H, $^3J_{5',6'a} \sim 3.5$ Hz, $^2J_{6'a,6'b} \sim 12.0$ Hz, H-6'a), 3.38 (ddd, 1H, $^3J_{5',6'b} \sim 6.0$ Hz, H-5'), 3.32 – 3.28 (m, 1H, H-6'b), 3.22 (s, 3H, OMe), 3.21 (dd, 1H, $^3J_{2',3'} \sim 6.0$ Hz, H-2'), 2.67 (dd, 1H, $^3J_{CH_2,3'} \sim 8.0$ Hz, $^2J_{CH_2} \sim 15.5$ Hz, 6-CH_2), 2.61 (dd, 1H, $^3J_{CH_2,3'} \sim 7.0$ Hz, 6-CH_2), 2.33 (s, 3H, COMe), 2.08 – 2.02 (m, 1H, H-3'). – ^{13}C NMR (62.9 MHz, [D$_6$]-DMSO): $\delta = 202.2$ (*C*OMe), 161.1 (C-2), 159.3 (C$_p$-NC$_6$H$_4$), 151.1 (C-4), 149.6 (C-6), 138.4, 138.1 (2 × *i*-Ph), 130.2, 127.3 (C-3, C$_i$-NC$_6$H$_4$), 129.7, 128.9, 128.8, 128.4, 127.9, 127.6, 127.5 (C$_o$-NC$_6$H$_4$, *o*-, *m*-, *p*-Ph), 114.6, 114.7 (C$_m$-NC$_6$H$_4$), 107.7 (C-5), 100.6 (C-1'), 76.1 (C-2'), 72.9 (C-5'), 71.1 (*C*H$_2$Ph), 63.8 (C-4'), 61.5 (C-6'), 55.6, 54.5 (OMe, *p*-OMe), 39.2 (C-3'), 31.8 (CO*Me*), 29.4 (6-CH_2). – MS (EI): *m/z* (%) = 599 (45) $[M]^+$. – $C_{35}H_{37}NO_8$ (599.25): HRMS calcd. 599.25189; found 599.25203.

*3-(Methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-D-altropyranosid-3-yl-methyl)-1-phenyl-benz[4,5]imidazo-[1,2-a]pyridine-4-carbonitrile (**13**)*

The reaction of **3b** (0.250 g, 0.5 mmol) with 2-benzimidazolyl-acetonitrile (0.115 g, 0.75 mmol) was carried out as described above for the preparation of **11a**. The product was purified by column chromatography (toluene/EtOAc 8:1). Yield 0.180 g (57%), yellow solid. – M. p. 112 – 114 °C. – $[\alpha]_D^{23} = +10.7$ (*c* 1.0, $CHCl_3$). – $R_f = 0.14$ (toluene/EtOAc 8:1). – IR (KBr): $\nu = 2224$ (CN) cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.03$ (dd, 1H, $^3J_{6,7} \sim 8.0$ Hz, H-6), 7.67 – 7.52 (m, 3H, Ph), 7.47 (dt, 1H, $^3J_{7,8} \sim 8.0$ Hz, $^4J_{7,9} \sim 1.0$ Hz, H-7), 7.36 – 7.04 (m, 11H, Ph), 7.02 (dt, 1H, $^4J_{6,8} \sim 1.0$ Hz, H-8), 6.9. – 6.91 (m, 1H, Ph), 6.57 (s, 1H, H-2), 6.51 (dd, 1H, $^3J_{8,9} \sim 8.0$ Hz, H-9), 5.58 (s, 1H, C*H*Ph), 4.73 (s, 1H, H-1'), 4.57 (s, 2H, C*H*$_2$Ph), 4.35 (dd, 1H, $^2J_{6'ax,6'eq} \sim 10.0$ Hz, $^3J_{5',6'eq} \sim 4.9$ Hz, H-6'eq), 4.25 (dd, 1H, $^3J_{4',5'} \sim 10.0$ Hz, $^3J_{3',4'} \sim 5.2$ Hz, H-4'), 4.12 (dt, 1H, H-5'), 3.84 (t, 1H, $^3J_{5',6'ax} \sim 10.0$ Hz, H-6'ax), 3.55 (br s, 1H, H-2'), 3.48 (dd, 1H, $^2J_{CH_2} \sim 14.0$ Hz, $^3J_{CH_2,3'} \sim 6.5$ Hz, CH_2), 3.45 (s, 3H, OMe), 3.34 (dd, 1H, $^3J_{CH_2,3'} \sim 8.9$ Hz, CH_2), 2.95 – 2.88 (m, 1H, H-3'). – ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 151.9$ (C-3), 147.6 (C-4a), 143.9 (C-5a), 143.4 (C-1), 137.4, 137.2, 132.9 (3 × *i*-Ph), 129.3 (C-9a), 130.7, 129.21, 129.17, 128.8, 128.41, 128.38, 128.2, 128.0, 127.8, 127.7, 126.1, 125.9 (*o*-, *m*-, *p*-Ph, C-7), 121.3 (C-8), 120.3 (C-6), 114.6 (CN), 114.4 (C-9), 114.0 (C-2), 101.7 (*C*H-Ph), 100.1 (C-4), 99.9 (C-1'), 75.95 (C-4'), 75.89 (C-2'), 71.8 (*C*H$_2$Ph), 69.4 (C-6'), 59.3 (C-5'), 55.2 (OMe), 40.2 (C-3'), 30.8 (3-CH_2). – MS (EI): *m/z* (%) = 637 (76) $[M]^+$. – $C_{40}H_{35}N_3O_5$ (637.26): calcd. C 75.33, H 5.53, N 6.59; found C 74.99, H 5.75, N 6.25.

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