Stereoselective synthesis of chiral piperidine derivatives employing arabinopyranosylamine as the carbohydrate auxiliary[1]

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Abstract: Stereoselective synthesis of 2-substituted dehydropiperidinones and their further transformation to variously disubstituted piperidine derivatives was achieved employing D-arabinopyranosylamine as the stereodifferentiating carbohydrate auxiliary. A domino Mannich–Michael reaction of 1-methoxy-3-(trimethylsiloxy)butadiene (Danishefsky's diene) with O-pivaloylated arbinosylaldimines furnished *N*-arabinosyl dehydropiperidinones in high diastereoselectivity. Subsequent conjugate cuprate addition gave 2,6-cis-substituted piperidinones, while enolate alkylation furnished 2,3-trans-substituted dehydropiperidinones. Electrophilic substitution at the enamine structure afforded 5-nitro- and 5-halogen dehydropiperidinones of which the latter were applied in palladium-catalyzed coupling reactions. The absolute configuration of the obtained products was proven by NMR and X-ray structure analysis as well as by syntheses of the alkaloids (+)-coniine and (+)-dihydropinidine.

Key words: piperidine alkaloids, carbohydrate auxiliary, domino Mannich–Michael reaction, conjugate cuprate and hydride addition, electrophilic substitution of enamines.

Résumé : On a réalisé la synthèse stéréosélective de déhydropipéridones substituées en position 2 et leur transformation subséquente en divers dérivés disubstitués de la pipéridine en utilisant de la D-arabinopyranosylamine comme hydrate de carbone auxiliaire permettant de faire une stéréodifférenciation. Une réaction de Mannich–Michael en domino du 1-méthoxy-3-(triméthylsiloxy)butadiène (réactif de Danishefsky) avec de *O*-pivaloyl-arbinosylaldimines conduit à la formation de *N*-arabinosyl déhydropipéridinones avec une grande diastéréosélectivité. Une addition subséquente conjuguée de cuprate fournit les pipéridinones 2,6-cis-substituées alors qu'une alkylation de l'énolate conduit déhydropipéridinones aux 2,3-trans-substituées. Une substitution électrophile de la structure énamine conduit aux 5-nitro- et 5-halogéno-déhydropipéridinones; ces dernières ont par la suite été utilisées dans des réactions de couplage catalysées par le palladiium. La configuration absolue des produits obtenus a été démontrée par RMN et par diffraction des rayons X ainsi que par synthèse des alcaloïdes (+)-coniine et (+)-dihydropinidine.

Mots clés : alcaloïde de la pipéridine, hydrate de carbone auxiliaire, réaction de Mannich–Michael en domino, addition conjuguée de cuprate et d'hydrure, substitution électrophile d'énamines.

[Traduit par la Rédaction]

Introduction

Due to their great diversity in biological and pharmacological activities (1), piperidine alkaloids and synthetic piperidines containing various substitution patterns are considered interesting target structures for drug development. Therefore, these heterocyclic structures are the subject of numerous synthetic, often stereoselective approaches (2).

During the past years, we have developed a strategy for the enantioselective synthesis of piperidine alkaloids using glycosylamines as chiral auxiliaries (3, 4). In this approach, steric, stereoelectronic, and complexing effects of carbohydrates are exploited for diastereofacial differentiation of nucleophilic additions to *N*-glycosyl aldimines. It is a special feature that this methodology offers the possibility of synthesizing both enantiomeric series of chiral piperidines by varying the carbohydrate auxiliary, e.g., employing the (pseudo-)enantiomeric carbohydrates, D-galactosylamine (3) and D-arabinosylamine (4), respectively. Herein, we report full experimental details for the application of D-arabinosylamine **1** in the stereoselective synthesis of 2-substituted *N*-arabinosyl dehydropiperidinones **4** and their subsequent regioselective and stereoselective modification in the preparation of variously substituted piperidines.

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Dedicated to Professor Walter Szarek on the occasion of his 65th birthday.

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Results and discussion

Formation of *N*-arabinosyl dehydropiperidinones

Condensation of 2,3,4-tri-*O*-pivaloyl-α-D-arabinopyranosylamine (**1**) (5) with aliphatic aldehydes in the presence of molecular sieves or with aromatic aldehydes under acidic ca-

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Scheme 1. Stereoselectve synthesis of 2-substituted *N*-arabinosyl dehydropiperidinones.

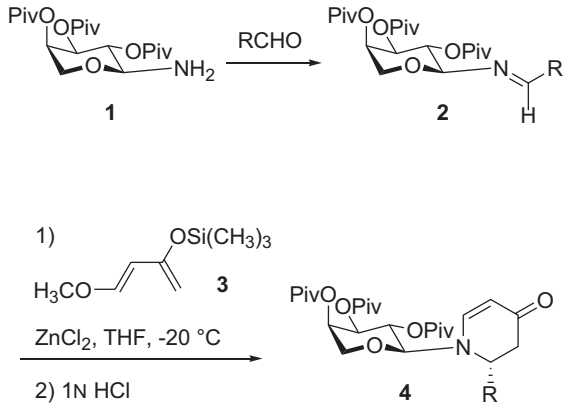


Table 1. Diastereoselective synthesis of 2-substituted *N*-arabinosyl dehydropiperidinones according to Scheme 1.

Product	R	Yield (%)	d.r.
4a	*p*-ClC_6H_4	96[a]	97:3[b]
4b	*p*-$NO_2C_6H_4$	74[a]	86:14,[c] 96:4[b]
4c	C_6H_4	84[a]	92:8[c]
4d	Methyl	49[d]	93:7[b]
4e	Ethyl	67[d]	96:4[c]
4f	Propyl	81[d]	87:13[c]
4g	Isopropyl	72[d]	95:5,[c] 99:1[b]
4h	$(CH_2)_3$OTBDPS	65[d]	90:10,[c] 96:4[b]

[a]Based on imine.
[b]Determined by HPLC after flash chromatography.
[c]Determined by HPLC of the crude product.
[d]Based on amine.

talysis furnished *N*-arabinopyranosylimines **2**. These aldimines reacted with 1-methoxy-3-(trimethylsiloxy)butadiene (Danishefsky's diene, **3**) in a domino Mannich–Michael reaction promoted by zinc chloride to give *N*-(2,3,4-tri-*O*-pivaloyl-α-D-arabinopyranosyl)-5,6-didehydropiperidin-4-ones (**4**) in high yields and high diastereoselectivity (Scheme 1, Table 1).

The stereochemical course of the reaction and hence the configuration of the nitrogen heterocycle in **4** was controlled by the sterically demanding pivaloyl group at C-2 of the carbohydrate auxiliary, which effectively shields the si side of aldimine **2**. Thus, the initial step in the domino Mannich–Michael reaction consists of the nucleophilic addition of Danishefsky's diene **3** at the re side of glycosyl imine **2**.

In contrast, in galactosyl imines **5** reported earlier (3) the re side is efficiently blocked by the C-2 pivaloyl group, leading to *N*-galactosyl dehydropiperidinones **6** bearing the opposite configuration at position 2 of the nitrogen heterocycle (Scheme 2). This is due to the fact that although arabinosylamine belongs to the D series of carbohydrates, it displays almost the mirror image of D-galactosylamine. Thus, by using either D-galactosylamine or its pseudoenantiomer, D-arabinosylamine, enantiomeric dehydropiperidinones are accessible offering the possibility of synthesizing both enantiomers of piperidines by choosing the appropriate auxiliary.

The absolute configuration of the *N*-arabinosyl dehydropiperidinones was proven by X-ray analysis showing **4f** to have (*S*)-configuration (Fig. 1). This compound preferably adopts a conformation in which the planes of the nitrogen heterocycle and the carbohydrate are almost perpendicular to each other allowing optimal overlap of the nonbonding orbital of the nitrogen and the σ* orbital of the C—O bond within the carbohydrate ring (exo-anomeric effect).

Conversion of *N*-arabinosyl dehydropiperidinone **4f** into the well-known alkaloid (*S*)-coniine **10** gave rise to further evidence of the absolute configuration of the nitrogen heterocycle in **4f**, and in addition, demonstrated the applicability of the shown reaction strategy for the stereoselective preparation of chiral 2-substituted piperidine alkaloids. Coniine is a highly toxic alkaloid leading to central respiratory paralysis and was the first alkaloid synthesized chemically (Ladenburg, 1886). In our auxiliary-mediated synthesis, the double bond of *N*-arabinosyl-2-propyl-5,6-

Scheme 2. A pair of (pseudo)-enantiomeric auxiliaries lead to enantiomeric piperidine derivatives.

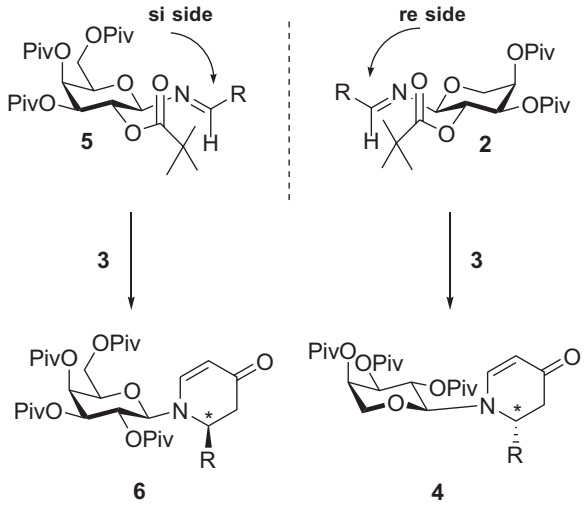
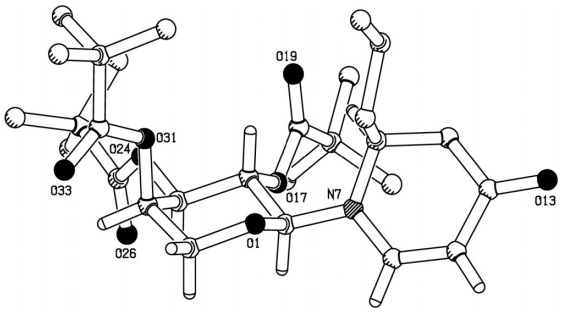
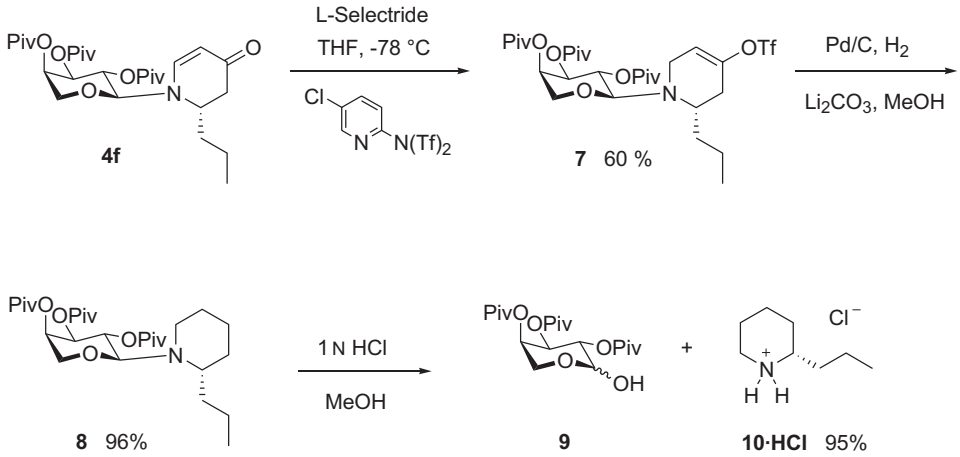


Fig. 1. X-ray structure of *N*-arabinosyl dehydropiperidinone **4f**.



dehydropiperidin-4-one (**4f**) was reduced with lithium tri-*sec*-butylborohydride (L-Selectride®) and the intermediate enolate was subsequently trapped as triflate **7**. Hydrogenation of the enol triflate afforded 2-propylpiperidine **8**. The enantiomerically pure alkaloid was released from the auxiliary by mild acidolysis using dilute HCl in methanol (Scheme 3). The optical rotation value of the formed coniine hydrochloride **10** was in agreement with literature data.

Scheme 3. Synthesis of enantiomerically pure (+)-(6*R*)-coniine hydrochloride.



Derivatization of *N*-arabinosyl dehydropiperidinones

N-Arabinosyl dehydropiperidinones **4** represent versatile precursors for the synthesis of variously substituted nitrogen heterocycles, e.g., the regioselective and stereoselective preparation of 2,6-, 2,5-, and 2,3-disubstituted piperidines.

2,6-cis-Disubstituted piperidines

N-Arabinosyl dehydropiperidinones **4** are α,β-unsaturated carbonyl compounds. Their reactivity as Michael acceptors is reduced because of the vinylogous amide structure. However, cuprate addition was accomplished by activation with hard electrophiles. For example, reaction of Yamamoto cuprates (6) activated by boron trifluoride diethyletherate ($RCu{\cdot}BF_3$) or of Gilman cuprates (8) (R_2CuLi) in combination with chlorotrimethylsilane (7) resulted in the formation of 2,6-cis-disubstituted piperidinones **11** with high diastereoselectivity (Scheme 4, Table 2).

The cis configuration was confirmed by X-ray analysis of **11a** (Fig. 2). The nitrogen heterocycle adopts a twisted conformation with the smaller substituent in axial position, the larger substituent in equatorial position, and a pyramidally configured nitrogen atom. The alignment of the two heterocycles is stabilized by the exo-anomeric effect (compare, Fig. 1).

The observed cis stereoselectivity of the 1,4-addition can be explained by stereoelectronic effects using the X-ray structure of **4f**. Two rotamers A and B, stabilized by the exo-anomeric effect, are expected for *N*-arabinosyl dehydropiperidinones **4** (Scheme 5). Compared with rotamer A, rotamer B benefits from a smaller steric hindrance between the substituent in position 2 of the nitrogen heterocycle and the pivaloyl group at C-2 of the carbohydrate. Thus, the backside of the nitrogen heterocycle is shielded by this pivaloyl group, and the front-side attack of the cuprate results in the favoured cis-substitution pattern.

Enantiomerically pure (+)-dihydropinidine was synthesized to demonstrate the applicability of *N*-arabinosyl dehydropiperidinones **4** in the stereoselective synthesis of cis-2,6-disubstituted piperidine alkaloids. For this purpose, piperidinone derivative **11e** was converted into dithiolane **13** and subsequently treated with Raney nickel to form *N*-arabinosyl piperidine **14**. The enantiomerically pure alkaloid

Scheme 4. Diastereoselective synthesis of 2,6-cis-substituted *N*-arabinosyl piperidinones.

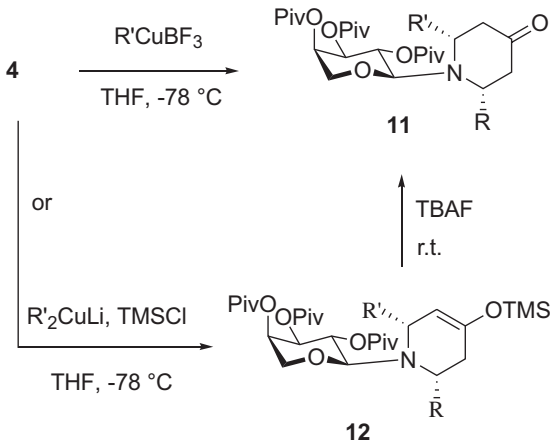
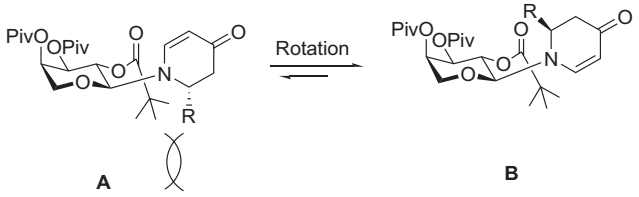


Table 2. Diastereoselective synthesis of 2,6-disubstituted *N*-arabinosyl piperidinones according to Scheme 4.

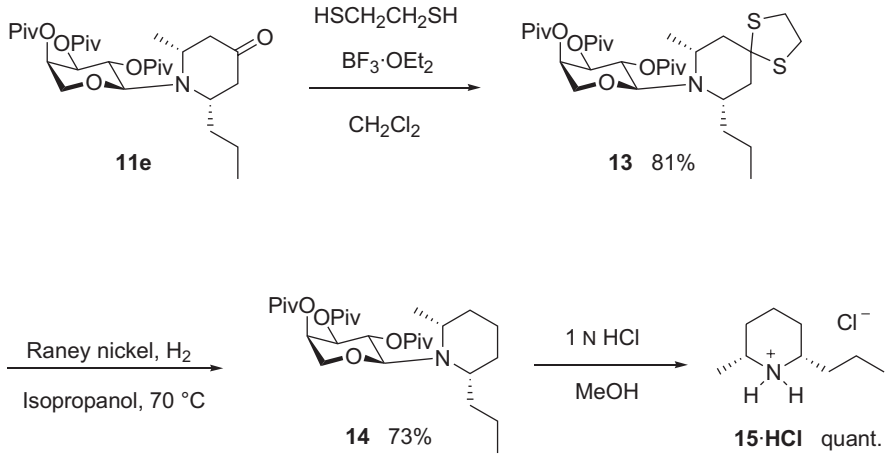
Product	R	R′	Yield (%)	d.r.
11a[a]	*p*Cl-C_6H_5	C_6H_5	72	99:1[b]
11b[a]	*p*Cl-C_6H_5	Allyl	51	98:2[b]
11c[a]	*n*-Propyl	C_6H_5	44	99:1[b]
11d[a]	*n*-Propyl	Allyl	75	94:6[c], 98:2[b]
11e[d]	*n*-Propyl	CH_3	88	91:9[c]

[a]Synthesized using Yamamoto cuprate.
[b]Determined by HPLC after chromatography.
[c]Determined by HPLC of the crude product.
[d]Synthesized using Gilman cuprate.

Scheme 5. Favored conformation of 2-substituted *N*-arabinosyl dehydropiperidinones according to Fig. 1.



Scheme 6. Synthesis of enantiomerically pure (+)-(2*S*,6*R*)-dihydropinidine hydrochloride.



Scheme 7. Electrophilic substitution at the enamine structure of dehydropiperidinones.

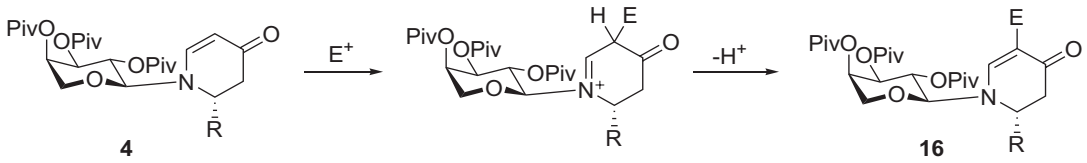
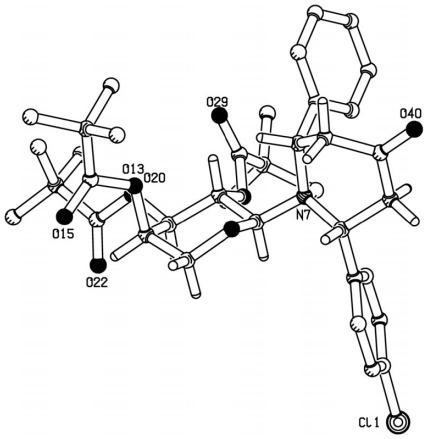


Fig. 2. X-ray structure of *N*-arabinosyl piperidinone **11a**.



hydrochloride **15** was released from the carbohydrate by mild acidolysis with dilute HCl in methanol (Scheme 6). The optical rotation value was in agreement with literature data (9) and confirmed the absolute configuration.

2,5-Disubstituted piperidines

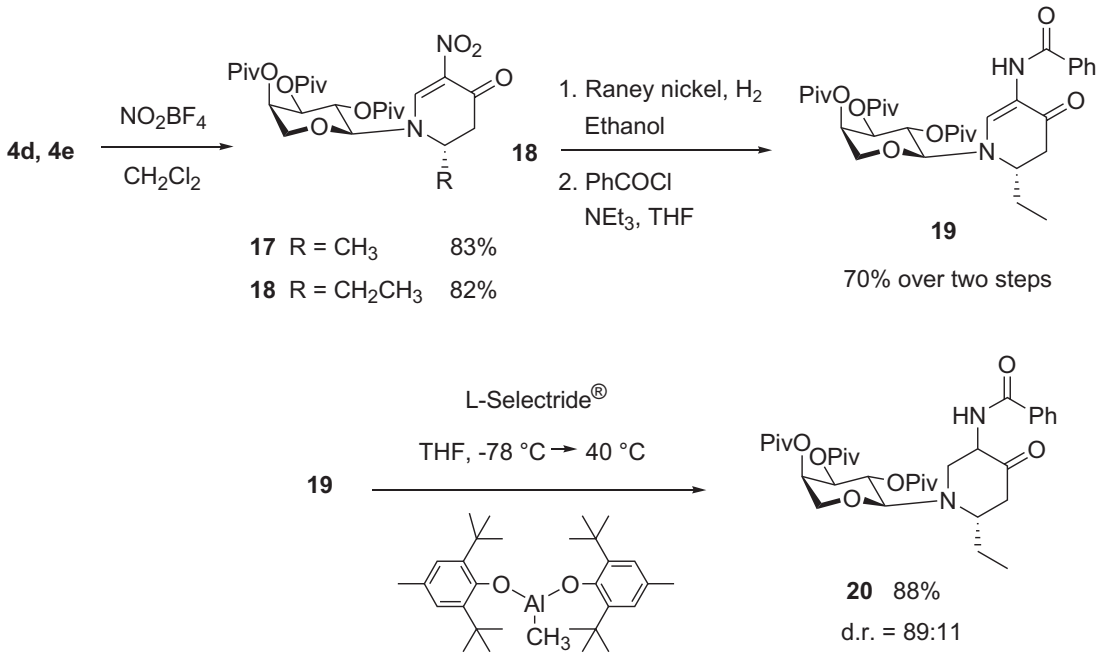
Due to their enamine structure, *N*-arabinosyl dehydropiperidinones **4** are capable of adding electrophiles. Regeneration of the stable conjugated enaminone π system by abstraction of a proton subsequently leads to 2,5-disubstituted dehydropiperidinones **16** (Scheme 7).

In terms of this electrophilic substitution, nitration of **4d** and **4e** was achieved in high yields using nitronium tetrafluoroborate applied as a solution in sulfolane allowing convenient handling of this air sensitive reagent (Scheme 8). Sulfolane can easily be separated from products **17** and **18**, respectively, by washing with water.

Reduction of the nitro group furnished an aminoketone, whose functionality is known to serve as precursor for syntheses of pharmacological important patterns like heterocycles, carbamates, or amides. Successful hydrogenation was achieved with Raney nickel, whereas reduction conditions such as zinc in hydrochloric acid or hydrogen and palladium on charcoal could not be applied. Immediate reaction of the sensitive amine with benzoyl chloride and triethylamine in ethanol gave the *N*-acyl compound **19** (Scheme 8).

N-Arabinosyl dehydropiperidinones that bear no substituent at C-5 of the nitrogen heterocycle, such as **4**, can be completely transformed into the corresponding piperidinones using L-Selectride®. This hydride reagent selectively reduces the double bond of the α,β-unsaturated carbonyl function in terms of a 1,4-addition without affecting the keto function in terms of a 1,2-addition. Using these reaction conditions for the hydrogenation of dehydropiperidinone **19**, a conversion of only 50% of the starting material was observed. Addition of further equivalents of L-Selectride® did not improve the conversion, but reduced already formed piperidin-4-one **20** to the 4-hydroxypiperidine. In contrast, complete chemoselective addition of the hydride was achieved applying an excess L-Selectride® in the presence of the sterically demanding Lewis acid methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD). This reagent has been shown to induce 1,4-addition of organolithiums to α,β-unsaturated ketones (10) and to enable the chemoselective reduction of the double bond of polymer-bound galactosyl dehydropiperidinones (11). The oxygenophilic Lewis acid effectively shields the keto function and, thus, favours the selective hy-

Scheme 8. Nitration of *N*-arabinosyl dehydropiperidinones and subsequent reduction of the obtained products.



dride addition at the β-position even by application of an excess of L-Selectride® for complete conversion of the starting material (Scheme 8).

N-Bromo succinimide and *N*-iodo succinimide were used in electrophilic substitution reactions at the enamine structure of *N*-arabinosyl dehydropiperidinones **4** to furnish halogenated compounds **21** in high yields (Scheme 9, Table 3).

Halogenated dehydropiperidinones **21** constitute vinyl halides capable of reacting in metal-catalyzed coupling reactions. In this way, piperidine derivatives with functionalized aryl substituents at C-5 were accessible. It turned out that iododehydropiperidinones **21** were more suitable in palladium-catalyzed syntheses than the bromo-substituted derivatives. Thus, in Stille reactions (12) applying bromodehydropiperidinone **21g** and phenyltributyl tin, 68% conversion of the starting material was observed after 24 h, while iododehydropiperidinone **21a** reacted faster and was completely consumed under these conditions, although product **22** was isolated in only moderate yield (Scheme 9).

Since boronic acids benefit from a much lower toxicity and an insensitivity to water compared with the tin reagents used in Stille-type reactions, Suzuki–Miyaura coupling conditions (13) were also applied for the synthesis of 5-aryl piperidine derivatives. Reaction of dehydropiperidinone **21c** with *p*-methoxybenzene boronic acid under palladium catalysis resulted in the formation of **23**. The reaction conditions have not yet been optimized (Scheme 9).

Even though the reaction conditions require further optimization, it appears that palladium-catalyzed reactions at C-5 of *N*-arabinosyl dehydropiperidinones **21** suffer from the sterically demanding auxiliary hampering the palladium complex from reaching the reaction site. However, the presented method provides access to 2,5-disubstituted piperidine derivatives containing pharmacologically valuable functionalized aryl substituents.

2,3-trans-Disubstituted N-*arabinosyl dehydropiperidinones*

Functionalization of *N*-arabinosyl dehydropiperidinones **4** at C-3 was achieved by deprotonation with strong bases and subsequent reaction with electrophiles. For this purpose, **4** was treated with lithium bis(trimethylsilyl)amide (LiHMDS), and the intermediate enolate was reacted with alkylhalides to afford 2,3-trans-disubstituted *N*-arabinosyl dehydropiperidinones **24** in high yields (Scheme 10, Table 4).

The coupling constant of product **24a** ($J_{H\text{-}2,H\text{-}3}$ = 11.7 Hz) determined by ^{1}H NMR spectroscopy indicated that these two protons are positioned in an antiperiplanar alignment, while the methyl group, as well as the aryl substituent, are arranged trans to each other and in an equatorial position. The stereoselectivity of the reaction can be explained by assuming that deprotonation of **4** forms a 6π-electron system resulting in an additional flattening of the dehydropiperidinone. The axial position of the substituent at C-2 induces a diastereofacial differentiation of the enolate favouring an attack of the electrophile from the sterically less-hindered side, i.e., trans to the first substituent resulting in the formation of the 2,3-trans-disubstituted compounds **24**.

Conclusions

The described results show that chiral piperidine derivatives of varying substitution patterns, valuable as building blocks for the construction of drugs and natural products, can stereoselectively be synthesized using α-D-arabinopyranosylamine (**1**) as the chiral auxiliary. Imines **2** of **1** undergo domino Mannich–Michael reaction sequences to furnish 2-substituted 5,6-dihydropiperidinones **4** with excellent diastereoselectivity. These compounds are substrates to a versatile modification of the piperidine structure (*i*) by conjugate addition of cuprates to give 2,6-cis-disubstituted piperidinones **11** with high stereoselectivity, (*ii*) to 5-

Scheme 9. Halogenation of *N*-arabinosyl dehydropiperidinones and Stille or Suzuki coupling of the obtained products.

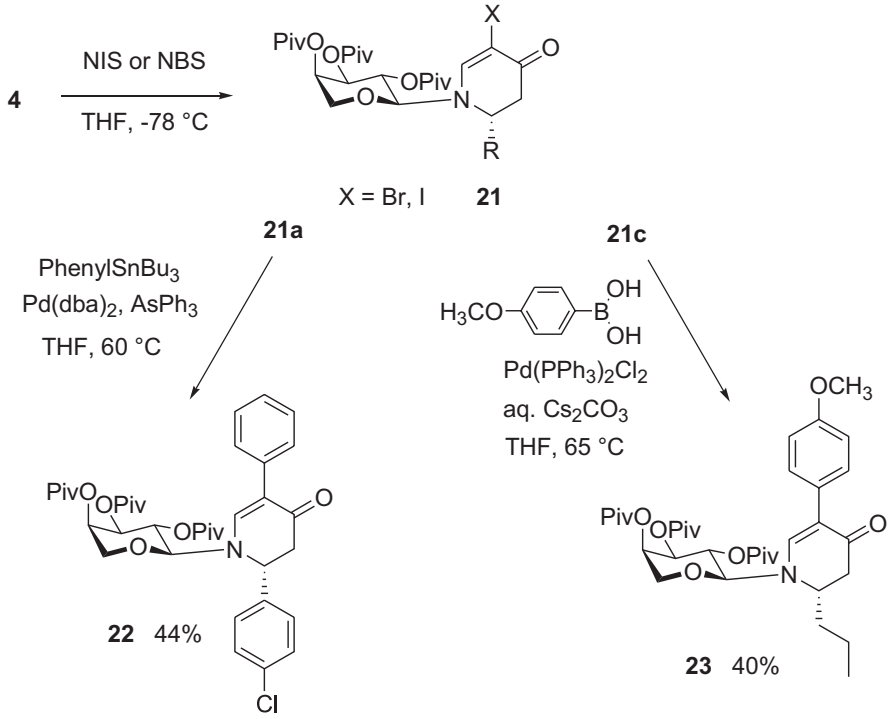
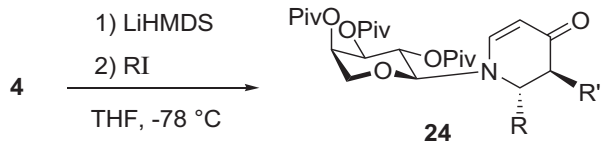


Table 3. Synthesis of halogen dehydropiperidinones according to Scheme 9.

Product	R	X	Yield (%)
21a	*p*-ClC_6H_4-	I	93
21b	Phenyl	I	67
21c	*n*-Propyl	I	69
21d	Isopropyl	I	87
21e	-$C_3H_6OTBDPS$	I	88
21f	*p*-ClC_6H_4-	Br	75
21g	Isopropyl	Br	83
21h	-$C_3H_6OTBDPS$	Br	79

Scheme 10. Stereoselective synthesis of 2,3-trans-substituted piperidine derivatives.



nitrogen-substituted derivatives, and (*iii*) to 5-halogen-substituted derivatives **21** of which the 5-iodo compounds are susceptible to Stille and Suzuku coupling reactions forming 5-aryl dehydropiperidinones. Enolates of the 2-substituted dehydropiperidinones **4** are alkylated to furnish 2,3-trans-disubstituted compounds **24** with excellent stereoselectivity. After reduction of the enaminone structure, the carbohydrate auxiliary can be cleaved off the enantiomerically pure substituted piperidine derivatives by a mild acidolysis.

Table 4. Synthesis of 2,3-disubstituted *N*-arabinosyl dehydropiperidinones according to Scheme 10.

Product	R	R′	Yield (%)	d.r.
24a	*p*-ClC_6H_4	Methyl	73	>95:5[a]
24b	$C_3H_6OTBDPS$	Methyl	87	75:25[a]
24c	$C_3H_6OTBDPS$	Ethyl	70	83:17[a]

[a]Determined by ^1H NMR.

Experimental

General methods

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AC-200, AC-300, or AM-400 spectrometers. Mass spectra were recorded on a Navigator-1 ESI mass spectrometer (ThermoQuest) and a Finnigan MAT 95 spectrometer. Optical rotation values were measured on a PerkinElmer 241 polarimeter. Analytical HPLC were performed with a Phenomenex Luna C18 (2) column (5 μ, 250 mm × 4.6 mm).

Materials

THF was distilled over potassium benzophenone ketyl and CH_2Cl_2 over calcium hydride. 2,3,4-Tri-*O*-pivaloyl-α-D-arabinosylamine (**1**) was synthesized according to the literature procedure (5). Aldehydes used for imine formation were distilled prior to use. A solution of zinc chloride in THF was prepared by melting $ZnCl_2$ under high vacuum and dissolving it in dry THF after recooling. Diene **3** was prepared from 4-methoxybut-3-ene-2-one by the silylation procedure given by Danishefsky and Kitahara (14) followed by repeated careful distillation at moderate temperature (oil bath temperature has to be kept below 70 °C). TLC was performed on

Merck silica gel 60 F_{254} aluminum sheets. Flash chromatography was carried out with ICN Biomedicals silica gel (40–63 μm mesh).

General procedure for the synthesis of *N*-arabinosyl imines 2

Method A (aromatic aldehydes)

The aromatic aldehyde (12 mmol) and acetic acid (12 drops) were added to a solution of amine **1** (10 mmol) in isopropanol (20 mL) and heated to 80 °C for 3 h. The mixture was cooled and kept at 4 °C overnight. The crystallized product was filtered and washed with ice-cold isopropanol. Concentration of the mother liquor provided further amounts of product. The combined samples were, if necessary, recrystallized from *n*-heptane. Characterization was carried out upon the *N*-arabinosyl dehydropiperidinones **4**.

Method B (aliphatic aldehydes)

The aliphatic aldehyde (12 mmol) was added dropwise to a mixture of amine **1** (10 mmol), *n*-pentane (60 mL), and dried molecular sieves (6 g, 4 Å) and stirred for 36 h at room temperature. Filtration through Hyflo® and removal of the solvent in vacuo yielded an amorphous solid, which was used without further purification. Characterization was carried out upon the *N*-arabinosyl dehydropiperidinones **4**.

General procedure for the synthesis of *N*-arabinosyl dehydropiperidinones 4

A solution of $ZnCl_2$ in dry THF (1 mol/L, 11 mL) was added to a solution of imine **2** (10.0 mmol) in dry THF (50 mL) at –78 °C and stirred for 10 min. Danishefsky's diene **3** (2.5 mL, 12.5 mmol) was added. After stirring for 30 min, the solution was allowed to warm to –20 °C. After complete consumption of the starting material (1 to 2 days), the reaction was terminated by addition of 1 N aq. HCl (10 mL). THF was evaporated in vacuo, the residue was dissolved in diethyl ether, and the layers were separated. The organic layer was washed with satd. aq. $NaHCO_3$ (3 × 50 mL), 10% aq. Titriplex III® (2 × 50 mL) and brine, dried over $MgSO_4$, and concentrated.

*(2***R***)-***N***-(2′,3′,4′-Tri-***O***-pivaloyl-α-D-arabinopyranosyl)-2-(***p***-chlorophenyl)-5,6-dehydropiperidin-4-one (4a)*

Imine **2a** (5.10 g, 9.7 mmol) was treated according to the general procedure. Purification was achieved by flash chromatography (petroleum ether – ethyl acetate, 3:1). Yield: 5.49 g (9.0 mmol, 96%); colourless solid; mp 180 °C. R_f 0.18 (petroleum ether – ethyl acetate, 2:1). $[\alpha]^{25}_D$ –28.03° (*c* 1, $CHCl_3$); d.r.: 97:3 (HPLC: 80% CH_3CN, 20% H_2O → 100% CH_3CN, 20 min).^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 7.32–7.19 (m, 5H, aryl, H-6), 5.60 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.8 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.8 Hz, H-2′), 5.25–5.10 (m, 2H, H-4′, H-5), 4.99 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.0 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.2 Hz, H-3′), 4.81 (dd, 1H, $J_{H\text{-}2,H\text{-}3b}$ = 8.3 Hz, $J_{H\text{-}2,H\text{-}3a}$ = 5.9 Hz, H-2), 4.26 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3 Hz, H-1′), 3.83 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.4 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.2 Hz, H-5′a), 3.42 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 12.7 Hz, H-5′b), 2.79 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.1 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 5.9 Hz, H-3a), 2.60 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.1 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 8.3 Hz, H-3b), 1.22, 1.56, 1.10 (3s, 27H, piv-CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 191.1 (C-4), 177.1, 177.1, 177.0 (pivC=O), 149.9 (C-6), 137.2 (ipso-aryl), 134.2 (ipso-aryl), 129.0, 128.4 (aryl), 102.9 (C-5), 89.3 (C-1′), 71.1, 67.9, 65.6 (C-2′, C-3′, C-4′), 66.1 (C-5′), 58.6 (C-2), 43.5 (C-3), 38.9, 38.9, 38.7 ($piv_{quart.}$), 27.2, 27.1, 27.0 (piv-CH_3). ESI-MS for $C_{31}H_{42}ClNO_8$ *m/z*: 592.15 [M(^{35}Cl) + H]$^+$, 594.14 [M(^{37}Cl) + H]$^+$, 614.17 [M(^{35}Cl) + Na]$^+$, 616.17 [M(^{37}Cl) + Na]$^+$, 630.35 [M(^{35}Cl) + K]$^+$, 655.27 [M(^{35}Cl) + Na + CH_3CN]$^+$.

*(2***R***)-***N***-(2′,3′,4′-Tri-***O***-pivaloyl-α-D-arabinopyranosyl)-2-(***p***-nitrophenyl)-5,6-dehydropiperidin-4-one (4b)*

Imine **2b** (2.45 g, 4.6 mmol) was treated according to the general procedure. Purification was carried out by flash chromatography (petroleum ether – ethyl acetate, 5:1 → 3:1). Yield: 2.05 g (3.4 mmol, 74%); yellow solid; mp 179 °C. R_f 0.18 (petroleum ether – ethyl acetate, 2:1). $[\alpha]^{22}_D$ –15.1° (*c* 1, $CHCl_3$); d.r.: 86:14 (HPLC of the crude product), 96:4 (HPLC after flash chromatography), HPLC: 80% CH_3CN, 20% H_2O → 100% CH_3CN, 20 min. ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 8.13 (d, 2H, *J* = 8.8 Hz, aryl), 7.43 (d, 2H, *J* = 8.8 Hz, aryl), 7.22 (d, 1H, *J* = 7.8 Hz, H-6), 5.60 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.5 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.5 Hz, H-2′), 5.20–5.05 (m, 2H, H-4′, H-5), 5.09 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 6.6 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.7 Hz, H-3′), 5.00 (dd, 1H, $J_{H\text{-}2,H\text{-}3a}$ = 6.8 Hz, $J_{H\text{-}2,H\text{-}3b}$ = 3.9 Hz, H-2), 4.47 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3 Hz, H-1′), 3.79 (dd, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, $J_{H\text{-}5'b,H\text{-}4'}$ = 2.0 Hz, H-5′b), 3.53 (d, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 12.7 Hz, H-5′a), 3.01 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.4 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 7.1 Hz, H-3a), 2.53 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.6 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 3.9 Hz, H-3b), 1.89, 1.16, 1.11 (3s, 27H, piv-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 189.9 (C-4), 177.4, 177.1, 176.8 (pivC=O), 150.3 (C-6), 147.5, 147.1, 127.4, 123.8 (aryl), 102.0 (C-5), 91.4 (C-1′), 70.7, 67.7, 66.0, 66.3 (C-2′, C-3′, C-4′, C-5′), 56.6 (C-2), 42.8 (C-3), 39.0, 38.9, 38.8 ($pivC_{quart.}$), 27.2, 27.1, 27.0 (piv-CH_3). ESI-MS for $C_{31}H_{42}N_2O_{10}$ *m/z*: 666.4 [M + Na + MeCN]$^+$, 625.3 [M + Na]$^+$, 603.3 [M + H]$^+$, 501.3 [M – pivOH + H]$^+$.

*(2***R***)-***N***-(2′,3′,4′-Tri-***O***-pivaloyl-α-D-arabinopyranosyl)-2-phenyl-5,6-dehydropiperidin-4-one (4c)*

Imine **2c** (7.40 g, 15.0 mmol) was treated according to the general procedure. Purification was carried out by flash chromatography (petroleum ether – ethyl acetate, 3:1). Yield: 7.06 g (12.7 mmol, 84%); colourless amorpous solid; R_f 0.53 (petroleum ether – ethyl acetate, 4:1). $[\alpha]^{22}_D$ –27.3° (*c* 1, $CHCl_3$); d.r.: 92:8 (HPLC of the crude product: 80% CH_3CN, 20% H_2O → 100% CH_3CN, 20 min. ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 7.40–7.25 (m, 6H, aryl, H-6), 5.60 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.8 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.8 Hz, H-2′), 5.23 (d, 1H, $J_{H\text{-}5,H\text{-}6}$ = 8.3 Hz, H-5), 5.15–5.09 (m, 1H, H-4′), 4.92 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.0 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.2 Hz, H-3′), 4.81 (t, 1H, $J_{H\text{-}2,H\text{-}3a}$ = 7.8 Hz, $J_{H\text{-}2,H\text{-}3b}$ = 7.8 Hz, H-2), 4.17 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3 Hz, H-1′), 3.82 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.7 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 1.9 Hz, H-5′a), 3.34 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 2.71 (d, 2H, *J* = 8.3 Hz, H-3a, H-3b), 1.23, 1.16, 1.09 (3s, 27H, piv-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 191.8 (C-4), 177.2, 177.1, 177.0 (pivC=O), 149.6 (C-6), 138.3 (ipso-aryl), 129.0, 128.7, 127.4 (aryl), 103.5 (H-5), 88.2 (C-1′), 71.4, 68.0, 65.4 (C-2′, C-3′, C-4′), 66.0

(C-5′), 60.6 (C-2), 43.9 (C-3), 39.0, 38.9, 38.8 (pivC$_{quart.}$), 27.2, 27.0 (piv-CH$_3$).

(2S)-N-*(2′,3′,4′-Tri*-O-*pivaloyl*-α-*D*-*arabinopyranosyl)*-2-*methyl*-5,6-*dehydropiperidin*-4-*one (4d)*

Crude imine **2d** (12.5 mmol) was treated according to the general procedure. Purification was achieved by flash chromatography (cyclohexane – ethyl acetate, 3:1 → 2:1). Yield: 3.02 g (6.09 mmol, 49%); colourless amorphous solid. R_f 0.12 (cyclohexane – ethyl acetate, 2:1). $[\alpha]^{22}_D$ +60.48° (*c* 1, $CHCl_3$); d.r.: 93:7 (HPLC after flash chromatography: 80% CH_3CH, 20% H_2O → 95% CH_3CN, 5% H_2O, 30 min). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 6.91 (d, 1H, $J_{H\text{-}6,H\text{-}5}$ = 7.0 Hz, H-6), 5.55 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.26–5.20 (m, 1H, H-4′), 5.13 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.1 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.1 Hz, H-3′), 5.01 (d, 1H, $J_{H\text{-}5,H\text{-}6}$ = 7.7 Hz, H-5), 4.44 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 8.8 Hz, H-1′), 4.02 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.2 Hz, H-5′a), 3.98–3.89 (m, H-1, H-2), 3.67 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 2.68 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.6 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.3 Hz, H-3a), 2.17 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.6 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 1.9 Hz, H-3b), 1.30 (d, 3H, *J* = 6.6 Hz, CH_3), 1.26, 1.11, 1.10 (3s, 27H, piv-CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 192.1 (C-4), 177.2, 177.1, 177.1 (pivC=O), 149.9 (C-6), 99.8 (C-5), 92.0 (C-1′), 71.0, 68.0, 65.9 (C-2′, C-3′, C-4′), 66.1 (C-5′), 49.4 (C-2), 42.6 (C-3), 38.9, 38.9, 38.8 (piv$_{quart}$), 27.1, 27.1, 27.0 (piv-CH_3), 17.7 (CH_3). ESI-MS for $C_{26}H_{41}NO_8$ *m/z*: 496.3 $[M + H]^+$, 518.3 $[M + Na]^+$, 534.3 $[M + K]^+$, 991.6 $[2M + H]^+$, 1013.6 $[2M + Na]^+$, 1029.6 $[2M + K]^+$.

(2S)-N-*(2′,3′,4′-Tri*-O-*pivaloyl*-α-*D*-*arabinopyranosyl)*-2-*ethyl*-5,6-*dehydropiperidin*-4-*one (4e)*

Crude imine **2e** (25 mmol) was treated according to the general procedure. Purification was achieved by flash chromatography (cyclohexane – ethyl acetate, 4:1). Yield: 8.49 g (16.7 mmol, 67%); colourless amorphous solid. R_f 0.19 (cyclohexane – ethyl acetate, 2:1). $[\alpha]^{22}_D$ +79.67° (*c* 1, $CHCl_3$); d.r.: 96:4 (HPLC of the crude product: 80% CH_3CH, 20% H_2O → 95% CH_3CN, 5% H_2O, 30 min). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 6.90 (d, 1H, $J_{H\text{-}6,H\text{-}5}$ = 6.6 Hz, H-6), 5.56 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.4 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.4 Hz, H-2′), 5.26–5.19 (m, 1H, H-4′), 5.12 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.1 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.1 Hz, H-3′), 4.93 (d, 1H, $J_{H\text{-}5,H\text{-}6}$ = 7.0 Hz, H-5), 4.44 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.2 Hz, H-1′), 4.01 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.2 Hz, H-5′a), 3.66 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.6 Hz, H-5′b), 3.67–3.56 (m, 1H, H-2), 2.59 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.7 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.1 Hz, H-3a), 2.37 (d, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.9 Hz, H-3b), 1.98–1.79 (m, 1H, CH_2), 1.78–1.60 (m, 1H, CH_2), 1.25, 1.11, 1.10 (3s, 27H, piv-CH_3), 0.84 (t, 3H, *J* = 7.53 Hz, CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 192.1 (C-4), 177.2, 177.1, 177.0 (pivC=O), 149.9 (C-6), 99.8 (C-5), 92.1 (C-1′), 71.1, 68.0, 66.0 (C-2′, C-3′, C-4′), 66.1 (C-5′), 55.2 (C-2), 39.0, 38.9, 38.7 (piv$_{quart}$), 38.4 (C-3), 27.1, 27.0 (piv-CH_3), 23.6 (CH_2), 10.1 (CH_3). ESI-MS for $C_{27}H_{43}NO_8$ *m/z*: 306.2 $[M - 2pivOH + H]^+$, 510.3 $[M + H]^+$, 532.3 $[M + Na]^+$, 573.3 $[M + Na + MeCN]^+$, 1041.3 $[2M + Na]^+$.

(2S)-N-*(2′,3′,4′-Tri*-O-*pivaloyl*-α-*D*-*arabinopyranosyl)*-2-*n-propyl*-5,6-*dehydropiperidin*-4-*one (4f)*

Crude imine **2f** (25 mmol) was treated according to the general procedure. Purification was achieved by flash chromatography (petroleum ether – ethyl acetate, 3:1). X-ray analysis: space group, $P2_12_12_1$ (orthorhombic); lattice parameters: *a* = 9.8895(13) Å, *b* = 10.1820(11) Å, *c* = 30.614(4) Å, *V* = 3082.7(6) Å^3, *Z* = 4, *F*(000) = 1136; diffractometer: CAD4 Enraf Nonius; irradiation: Cu K_α graphite monochromator.[3] Yield: 10.64 g (20.3 mmol, 81%); colourless solid; mp 192 °C. R_f 0.07 (petroleum ether – ethyl acetate, 3:1). $[\alpha]^{25}_D$ +66.64° (*c* 1, $CHCl_3$); d.r.: 87:13 (HPLC of the crude product: 80% CH_3CN, 20% H_2O → 100% CH_3CN, 20 min). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 6.90 (d, 1H, $J_{H\text{-}6,H\text{-}5}$ = 7.3 Hz, H-6), 5.55 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.5 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.5 Hz, H-2′), 5.30–5.20 (m, 1H, H-4′), 5.13 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.0 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.2 Hz, H-3′), 4.93 (d, 1H, $J_{H\text{-}5,H\text{-}6}$ = 7.3 Hz, H-5), 4.44 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3 Hz, H-1′), 4.02 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.0 Hz, H-5′a), 3.80–3.70 (m, 1H, H-2), 3.67 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 2.60 (dd, 1H, $J_{H\text{-}3a,\ H\text{-}3b}$ = 16.6 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.3 Hz, H-3a), 2.34 (d, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.6 Hz, H-3b), 2.00–1.75 (m, 1H, CH_2), 1.65–1.50 (m, 1H, CH_2), 1.30–1.10 (m, 27H, piv-CH_3), 0.86 (t, 3H, *J* = 7.3 Hz, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 192.2 (C-4), 177.2, 176.8 (pivC=O), 149.9 (H-6), 99.8 (H-5), 92.1 (C-1′), 71.1, 68.0, 66.1 (C-2′, C-3′, C-4′), 66.2 (C-5′), 53.5 (C-2), 39.0 (C-3), 38.9, 38.8, 38.8 (pivC$_{quart.}$), 32.7 (CH_2), 27.2, 27.1, 27.0 (piv-CH_3), 18.9 (CH_2), 13.8 (CH_3). Anal. calcd. for $C_{28}H_{45}NO_8$: C 64.22, H 8.66, N 2.69; found: C 64.20, H 8.60, N 2.63.

(2R)-N-*(2′,3′,4′-Tri*-O-*pivaloyl*-α-*D*-*arabinopyranosyl)*-2-*isopropyl*-5,6-*dehydropiperidin*-4-*one (4g)*

Crude imine **2g** (25 mmol) was treated according to the general procedure. Purification was carried out by flash chromatography. Yield: 9.45 g (18 mmol, 73%); colourless amorphous solid. R_f 0.13 (cyclohexane – ethyl acetate, 3:1). $[\alpha]^{24}_D$ +70.14° (*c* 1, $CHCl_3$); d.r.: 95:5 (HPLC of the crude product), 99:1 (HPLC after flash chromatography), HPLC: 85% CH_3CH, 15% H_2O → 95% CH_3CN, 5% H_2O, 20 min). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.01 (d, 1H, $J_{H\text{-}5,H\text{-}6}$ = 7.8 Hz, H-6), 5.58 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}4'}$ = 9.6 Hz, H-2′), 5.25–5.20 (m, 1H, H-4′), 5.12 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.8 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.1 Hz, H-3′), 4.93 (d, 1H, $J_{H\text{-}5,H\text{-}6}$ = 7.8 Hz, H-5), 4.49 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.0 Hz, H-1′), 3.99 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.3 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.4 Hz, H-5′), 3.67 (dd, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.3 Hz, $J_{H\text{-}5'b,H\text{-}4'}$ = 0.8 Hz, H-5′b), 3.59–3.52 (m, 1H, H-2), 2.59 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.2 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 7.8 Hz, H-3a), 2.40 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.8 Hz, $J_{H\text{-}3b,H\text{-}2}$ =

[3] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5028. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 229785 and 229786 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

2.0 Hz, H-3a), 2.32–2.19 (m, 1H, C*H*(CH_3)$_2$), 1.25, 1.11, 1.10 (3s, 27H, piv-CH_3), 0.89 (d, 3H, J = 7.0 Hz, CH_3), 0.89 (d, 3H, J = 6.6 Hz, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 192.5 (C-4), 177.2, 177.1, 177.0 (pivC=O), 150.3 (C-6), 100.3 (C-5), 91.8 (C-1′), 71.4, 68.0, 65.8 (C-2′, C-3′, C-4′), 66.1 (C-5′), 58.9 (C-2), 38.9, 38.9, 38.8 (piv$_{quart}$), 35.5 (C-3), 32.2 (*C*H(CH_3)$_3$), 27.1, 27.0 (piv-CH_3), 19.5, 17.6 (CH_3). ESI-MS for $C_{28}H_{45}NO_8$ *m/z*: 524.4 [M + H]$^+$, 546.4 [M + Na]$^+$, 587.3 [M + CH_3CN + Na]$^+$, 1069.6 [2M + Na]$^+$.

(2S)-N-*(2′,3′,4′-Tri*-O-*pivaloyl*-α-*D-arabinopyranosyl)*-2-*(3-tert-butyldiphenylsiloxy)propyl*-5,6-*dehydropiperidin*-4-*one (4h)*

Crude imine **2h**, prepared from 4-(*tert*-butyldiphenylsiloxy)butanal (15) according to method B, was treated according to the general procedure. Purification was carried out by flash chromatography (cyclohexane – ethyl acetate, 4:1 → 3:1). Yield: 12.7 g (16.4 mmol, 65%); colourless amorphous solid. R_f 0.33 (petrolether – ethyl acetate, 2:1). $[\alpha]^{25}_D$ +32.84° (*c* 1, $CHCl_3$); d.r.: 90:10 (HPLC of the crude product), 96:4 (HPLC after chromatography), HPLC: 80% CH_3CN, 20% H_2O → 100% CH_3CN, 20 min). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 7.70–7.50 (m, 4H, aryl), 7.46–7.27 (m, 6H, aryl), 6.92 (d, 1H, $J_{H\text{-}6,H\text{-}5}$ = 7.8 Hz, H-6), 5.55 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.5 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.5 Hz, H-2′), 5.29–5.19 (m, 1H, H-4′), 5.12 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.8 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 2.9 Hz, H-3′), 4.98 (d, 1H, $J_{H\text{-}5,H\text{-}6}$ = 7.3 Hz, H-5), 4.44 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 8.8 Hz, H-1′), 4.04–3.90 (m, 1H, H-5′a), 3.81–3.50 (m, 4H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-2, H-5′b, CH_2-O), 2.64 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.8 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.1 Hz, H-3a), 2.34 (d, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.6 Hz, H-3b), 1.99–1.70 (m, 2H, CH_2), 1.69–1.38 (m, 2H, CH_2), 1.22, 1.11, 1.11, 0.99 (4s, 36H, C(CH_3)$_3$). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 191.9 (C-4), 182.0, 177.2, 177.1 (pivC=O), 149.9 (C-6), 135.5, 133.8, 129.6, 127.7 (aryl), 99.8 (C-5), 91.8 (C-1′), 71.1, 68.0, 66.0 (C-2′, C-3′, C-4′), 66.2 (C-5′), 63.5 (CH_2-O), 53.9 (C-2), 39.1 (C-3), 39.0, 38.9, 38.8 (pivC$_{quart.}$), 28.9 (CH_2), 27.4 (CH_2), 27.2, 27.1 (pivCH$_3$), 26.8 (Si-C(*C*H$_3$)$_3$), 19.2 (Si-*C*(CH_3)$_3$). ESI-MS for $C_{44}H_{63}NO_9Si$ *m/z*: 472.1 [M – 3pivOH + H]$^+$, 574.2 [M – 2pivOH + H]$^+$, 700.3 [M – Phenyl], 778.3 [M + H]$^+$, 800.4 [M + Na]$^+$, 816.3 [M + K]$^+$, 841.3 [M + Na + CH_3CN]$^+$.

(2S)-N-*(2′,3′,4′-Tri*-O-*pivaloyl*-α-*D-arabinopyranosyl)*-2-n-*propyl*-4-*(trifluormethansulfonyloxy)*-4,5-*dehydropiperidine (7)*

To a solution of **4f** (1.31 g, 2.50 mmol) and 2-[*N*,*N*-bis(trifluoromethanesulfonyl)amino]-5-chloropyridine (1.18 g, 3.00 mmol) in dry THF (50 mL), L-Selectride® (1 mol/L in THF, 2.75 mL) was added at –78 °C and stirred for 1 h. The solution was allowed to warm slowly and stirred until the starting material was consumed. The reaction was terminated by addition of aq. $NaHCO_3$ (5 mL). THF was removed in vacuo, diethyl ether (100 mL) was added, and the layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo. Flash chromatography (cyclohexane – ethyl acetate, 10:1) of the residue afforded **7** as a colourless amorphous solid (0.98 g, 1.49 mmol, 60%). R_f 0.67 (cyclohexane – ethyl acetate, 3:1). $[\alpha]^{22}_D$ –12.46° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 5.72–5.64 (m, 1H, H-5), 5.40 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.19–5.13 (m, 1H, H-4′), 5.07 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.9 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.3 Hz, H-3′), 4.13 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.2 Hz, H-1′), 3.90 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.1 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.0 Hz, H-5′a), 3.62 (dd, 1H, $J_{H\text{-}6a,H\text{-}6b}$ = 17.6 Hz, $J_{H\text{-}6a,H\text{-}5}$ = 2.6 Hz, H-6a), 3.53 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 3.42 (d, 1H, $J_{H\text{-}6b,H\text{-}6a}$ = 17.3 Hz, H-6b), 3.24–3.11 (m, 1H, H-2), 2.55 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.4 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 2.8 Hz, H-3a), 2.09 (d, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.6 Hz, H-3b), 1.68–1.53 (m, 1H, CH_2), 1.47–1.15 (m, 3H, CH_2), 1.23, 1.12, 1.10 (3s, 27H, pivCH$_3$), 0.89 (t, 3H, J = 7.2 Hz, CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 177.3, 177.3, 177.1 (pivC=O), 146.6 (C-4), 116.1 (C-5), 92.8 (C-1′), 71.6, 68.6, 65.6 (C-2′, C-3′, C-4′), 65.1 (C-5′), 41.8 (C-6), 38.9, 38.7, 38.6 (piv$_{quart.}$), 33.6 (CH_2), 32.6 (CH_2), 27.1, 27.0, 27.0 (pivCH$_3$), 19.8 (CH_2), 14.1 (CH_3). ESI-MS for $C_{29}H_{46}F_3NO_{10}S$ *m/z*: 406.2 [M – pivOH – OTf]$^+$, 508.5 [M – OTf]$^+$, 556.3 [M – pivOH + H]$^+$, 658.3 [M + H]$^+$, 680.3 [M + Na]$^+$, 696.1 [M + K]$^+$, 721.4 [M + Na + CH_3CN]$^+$.

(2S)-N-*(2′,3′,4′-Tri*-O-*pivaloyl*-α-*D-arabinopyranosyl)*-2-n-*propylpiperidine (8)*

Li_2CO_3 (160 mg) and Pd/C (10%, 50 mg) were added to a solution of enol triflate **7** (888 mg, 1.35 mmol) in methanol (100 mL) and stirred for 20 h under a H_2 atmosphere. After filtration through Hyflo®, the solvent was removed in vacuo, and the remaining residue was dissolved in diethyl ether (100 mL). The solution was washed with water (40 mL) and brine (40 mL), dried over $MgSO_4$, and evaporated to dryness to yield pure **8** as a colourless amorphous solid (665 mg, 1.30 mmol, 96%). R_f 0.75 (cyclohexane – ethyl acetate, 4:1). $[\alpha]^{22}_D$ –28.12° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 5.50 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.20–5.11 (m, 1H, H-4′), 5.07 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.7 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.1 Hz, H-3′), 4.33–4.13 (m, 1H, H-1′), 3.90 (d, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 12.8 Hz, H-5′a), 3.51 (d, $J_{H\text{-}5'b,H\text{-}5'a}$ = 12.8 Hz, H-5′b), 3.27–3.06, 2.79–2.54, 2.51–2.27 (3m, 3H, H-2, H-6a, H-6b), 1.72–1.19 (m, 19H, 3CH_2, 2PropylCH_2, pivCH$_3$), 1.23, 1.14, 1.10 (3s, 27H, pivCH$_3$), 0.89 (t, 3H, J = 7.0 Hz, CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 177.4 (pivC=O), 89.3 (C-1′), 72.1, 68.9, 65.1, 65.1 (C-2′, C-3′, C-4′, C-5′), 57.5 (C-2), 45.2 (C-6), 38.9, 38.7, 38.6 (piv$_{quart.}$), 34.8 (CH_2), 31.6 (CH_2), 27.3, 27.1, 27.0 (pivCH$_3$), 26.2 (CH_2), 24.1 (CH_2), 18.8 (CH_2), 14.5 (CH_3). ESI-MS for $C_{28}H_{49}NO_7$ *m/z*: 308.2 [M – 2pivOH + H]$^+$, 410.3 [M – pivOH + H]$^+$, 512.3 [M + H]$^+$, 534.3 [M + Na]$^+$, 550.3 [M + K]$^+$.

(2S)-2-n-*Propylpiperidine hydrochloride (coniine hydrochloride) (10·HCl)*

N-Arabinosyl piperidine **8** (563 mg, 1.1 mmol) in methanol (15 mL) was treated with 1 N HCl (2 mL) and stirred until completion of the reaction (48 h). The solvent was evaporated in vacuo, the residue was dissolved in diethyl ether (35 mL) and extracted with water (5 × 10 mL). Lyophilization of the aqueous layer gave coniine hydrochloride (**10·HCl**) as a colourless amorphous solid (171 mg, 1.0 mmol, 95%). $[\alpha]^{22}_D$ +5.33° (*c* = 1, ethanol); enantiomer (16): $[\alpha]^{22}_D$ –5.8° (*c* 1, methanol). ^{1}H NMR (300 MHz, DMSO, ppm) δ: 9.14 (br s, 1H, NH), 8.99 (br s, 1H, NH),

3.20–3.05 (m, 1H, NCH_2), 3.00–2.84 (m, 1H, H-2), 2.84–2.65 (m, 1H, NCH_2), 1.90–1.15 (m, 10H, CH_2), 0.86 (t, 3H, J = 7.2 Hz, CH_3). ^{13}C NMR (75.4 MHz, DMSO, ppm) δ: 55.5 (C-2), 43.8 (C-6), 35.0 (CH_2), 27.8 (CH_2), 21.9, (CH_2), 21.9 (CH_2), 17.9 (CH_2), 13.8 (CH_3). ESI-MS for $C_8H_{18}ClN$ *m/z*: 128.1 [M – Cl]$^+$, 291.2 [2M(^{35}Cl) – Cl]$^+$, 293.1 [M(^{37}Cl) – Cl]$^+$.

General procedure for the addition of R′Cu·BF_3 complexes to enaminones

The solution of the corresponding Grignard reagent in THF or diethyl ether was added to a suspension of copper salt (1 mmol) in dry THF (5–10 mL) at the temperature given for the corresponding cuprate (given in the following) and stirred until the cuprate was formed (time and change in colour for each compound is given in the following). Subsequently, the cuprate was cooled to –78 °C, $BF_3{\cdot}OEt_2$ (1 mmol) was added and the mixture stirred for 15 min. Dehydropiperidinone **4** in dry THF (20 mL per mmol piperidinone) was added dropwise, and the mixture was stirred for 15 h. In general, a slow increase of temperature was required for complete consumption of the starting material. The reaction was terminated by addition of concd. NH_4OH – satd. NH_4Cl (1:1 *v*/*v*). The mixture was warmed to room temperature (r.t.), diluted with diethyl ether (20 mL), and the layers were seperated. The organic layer was washed with concd. NH_4OH – satd. NH_4Cl (1:1 *v*/*v*), washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography.

*(2*R*,6*S*)*-*N*-*(2′,3′,4′-Tri*-O-*pivaloyl-*α*-*D*-*arabinopyranosyl)-2-(*p*-*chlorophenyl)-6-phenylpiperidin-4-one (11a)*

Piperidinone **11a** was prepared from **4a** (592 mg, 1.0 mmol) according to the general procedure. For the formation of the beige cuprate solution, CuI (952 mg, 5 mmol) and phenylmagnesium bromide (1 mol/L in THF, 5 mL) were treated in THF (30 mL) at –78 °C for 1 h. Purification of **11a** was achieved by flash chromatography (petroleum ether – ethyl acetate, 14:1 → 10:1). Yield: 484 mg (0.7 mmol, 72%); colourless solid; mp 179 °C. X-ray analysis: space group, *P*1 (triklin); lattice parameters: a = 10.1869(6) Å, b = 13.1017(12) Å, c = 15.5126(12) Å, V = 1901.1(3) Å^3, Z = 2, F(000) = 716; diffractometer, CAD4 Enraf Nonius; irradiation, Cu K_α graphite monochromator.[3] R_f 0.55 (petroleum ether – ethyl acetate, 3:1). $[\alpha]^{25}_D$ –35.44° (*c* 1, $CHCl_3$); d.r.: 99:1 (HPLC: 80% CH_3CN, 20% H_2O → 100% CH_3CN, 20 min). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 7.50–7.15 (m, 9H, aryl), 5.36 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.5 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.5 Hz, H-2′), 5.15–5.00 (m, 2H, H-4′, aryl-C*H*-N), 4.90–4.50 (m, 2H, H-3′, aryl-C*H*-N), 4.24 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3 Hz, H-1′), 3.97 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 12.9 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.2 Hz, H-5′a), 3.51–3.25 (m, 2H, H-5′, CH_2C=O), 2.86 (dd, 1H, $J_{gem.}$ = 16.1 Hz, $J_{vic.}$ = 2.4 Hz, CH_2C=O), 2.61 (dd, $J_{gem.}$ = 18.1 Hz, $J_{vic.}$ = 12.7 Hz, CH_2C=O), 2.41 (dd, 1H, $J_{gem.}$ = 18.3 Hz, $J_{vic.}$ = 3.7 Hz, CH_2C=O), 1.26, 1.08, 1.01 (3s, 27H, piv-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 208.0 (C-4), 177.5, 177.2, 175.3 (pivC=O), 144.1, 140.5, 133.8, 129.1, 128.6, 127.1, 126.3 (Aryl), 90.3 (C-1′), 72.9, 68.7, 66.3 (C-2′, C-3′, C-4′), 65.2 (C-5′), 58.3, 53.4 (C-2, C-6), 47.5, 46.4 (C-3, C-5), 39.0, 38.7, 38.6 (pivC$_{quart.}$), 27.2, 27.0 (piv-CH_3). ESI-MS for $C_{37}H_{48}NO_8$: 568.5 [M(^{35}Cl) – pivOH + H]$^+$, 570.6 [M(^{37}Cl) – pivOH + H]$^+$, 670.6 [M(^{35}Cl) + H]$^+$, 672.6 [M(^{37}Cl) + H]$^+$, 692.6 [M(^{35}Cl) + Na]$^+$, 694.6 [M(^{37}Cl) + Na]$^+$, 708.5 [M + K]$^+$.

*(2*R*,6*R*)*-*N*-*(2′,3′,4′-Tri*-O-*pivaloyl-*α*-*D*-*arabinopyranosyl)-2-allyl-6-(*p*-*chlorophenyl)-piperidin-4-one (11b)*

Piperidinone **11b** was prepared from **4a** (592 mg, 1.0 mmol) according to the general procedure. For the formation of the orange cuprate solution, CuCN (358 mg, 4 mmol) and allylmagnesium bromide (1 mol/L in ether, 4 mL) were treated in THF (30 mL) at –40 °C for 0.5 h. Purification of **11b** was performed by flash chromatography (petroleum ether – ethyl acetate, 13:1 → 10:1). Yield: 325 mg (0.5 mmol, 51%); colourless amorphous solid; mp 73 °C. R_f 0.64 (petroleum ether – ethyl acetate, 3:1). $[\alpha]^{25}_D$ +26.64° (*c* 1, $CHCl_3$); d.r.: 98:2 (HPLC: 80% CH_3CN, 20% H_2O → 100% CH_3CN, 20 min. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.40–7.35 (m, 4H, aryl), 5.84–5.71 (m, 1H, C*H*=CH_2), 5.65 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.22–5.12 (m, 3H, H-4′, CH=CH_2), 4.92 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.8 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.1 Hz, H-3′), 4.68 (dd, 1H, $J_{H\text{-}2,H\text{-}3a}$ = 12.1 Hz, $J_{H\text{-}2,H\text{-}3b}$ = 3.9 Hz, H-2), 4.12 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.4 Hz, H-1′), 4.00 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.3 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.4 Hz, H-5′a), 3.80–3.70 (m, 1H, H-6), 3.53 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 12.9 Hz, H-5′b), 2.93 (dd, 1H, $J_{gem.}$ = 16.4 Hz, $J_{vic.}$ = 5.7 Hz, H-5a), 2.71–2.61 (m, 2H, H-5b, H-3a), 2.57 (dd, 1H, $J_{gem.}$ = 18.2 Hz, $J_{vic.}$ = 4.1 Hz, H-3b), 2.47–2.37 (m, 1H, CH_2-CH=CH_2), 2.10–1.99 (m, 1H, CH_2-CH=CH_2), 1.34, 1.26, 1.18 (3s, 27H, piv-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 208.9 (C-4), 177.4, 177.2, 176.8 (pivC=O), 141.0 (ipso-aryl), 134.2 (*C*H=CH_2), 133.7 (ipso-aryl.), 129.0, 128.9 (aryl), 118.4 (CH=*C*H_2), 90.7 (C-1′), 72.7, 68.7, 66.2 (C-2′, C-3′, C-4′), 65.2 (C-5′), 58.4 (C-2), 50.7 (C-6), 47.4 (CH_2), 44.0 (CH_2), 42.0 (CH_2), 38.9, 38.8, 38.8 (pivC$_{quart.}$), 27.3, 27.2, 27.1 (piv-CH_3). ESI-MS for $C_{34}H_{48}ClNO_8$ *m/z*: 430.4 [M(^{35}Cl) – 2pivOH + H]$^+$, 532.5 [M(^{35}Cl) – pivOH + H]$^+$, 534.5 [M(^{37}Cl) – pivOH + H]$^+$, 634.5 [M(^{35}Cl) + H]$^+$, 636.5 [M(^{37}Cl) + H]$^+$, 656.5 [M(^{35}Cl) + Na]$^+$, 658.5 [M(^{37}Cl) + Na]$^+$, 672.6 [M(^{35}Cl) + K]$^+$. Anal. calcd. for $C_{34}H_{48}ClNO_8$ (634.20): C 64.39, H 7.63, N 2.21; found: C 64.42, H 7.83, N 2.13.

*(2S,6S)-*N*-(2′,3′,4′-Tri*-O-*pivaloyl-*α*-*D*-*arabinopyranosyl)-2-phenyl-6-*n*-*propylpiperidin-4-one (11c)*

Piperidinone **11c** was prepared from **4f** (524 mg, 1.0 mmol) according to the general procedure. For the formation of the beige cuprate solution, CuI (952 mg, 5 mmol) and phenylmagnesium bromide (1 mol/L in THF, 5 mL) were treated in THF (30 mL) at –78 °C for 1 h. Purification of **11c** was carried out by flash chromatography (petroleum ether – ethyl acetate, 10:1). Yield: 670 mg (0.4 mmol, 44%); colourless solid. R_f 0.55 (petroleum ether – ethyl acetate, 3:1). $[\alpha]^{26}_D$ –10.37° (*c* 1, $CHCl_3$); d.r.: 99:1 (HPLC: 80% CH_3CN, 20% H_2O → 100% CH_3CN, 20 min). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 7.35–7.10 (m, 5H, aryl), 5.38 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.3 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.3 Hz, H-2′), 5.20–5.12 (m, 1H, H-4′), 5.06 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.5 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.2 Hz, H-3′), 4.90–4.80 (m, 1H, H-6), 4.48 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ =

9.3 Hz, H-1′), 3.98 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 12.9 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.2 Hz, H-5′a), 3.59 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 3.50–3.35 (m, 1H, H-2), 3.13 (dd, 1H, $J_{gem.}$ = 17.1 Hz, $J_{vic.}$ = 5.9 Hz, CH_2C=O), 2.93 (dd, 1H, $J_{gem.}$ = 17.1, $J_{vic.}$ = 3.4 Hz, CH_2C=O), 2.47 (dd, 1H, $J_{gem.}$ = 17.1 Hz, $J_{vic.}$ = 4.4 Hz, CH_2C=O), 2.14 (dd, 1H, $J_{gem.}$ = 17.1 Hz, $J_{vic.}$ = 10.8 Hz, CH_2C=O), 1.70–1.00 (m, 31H, piv-CH_3, CH_2), 0.88 (t, 3H, J = 6.8 Hz, propyl-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 209.8 (C-4), 177.5, 177.2, 176.0 (pivC=O), 143.8, 129.5, 128.2, 126.7 (aryl), 92.2 (C-1′), 72.7, 68.7, 66.7 (C-2′, C-3′, C-4′), 65.3 (C-5′), 55.7 (C-6), 53.9 (C-2), 46.2, 43.8 (C-3, C-5), 39.9 (propyl-CH_2), 38.9, 38.7 (pivC$_{quart.}$), 27.3, 27.2, 27.1 (piv-CH_3), 19.2 (propyl-CH_2), 14.0 (propyl-CH_3). ESI-MS for $C_{34}H_{51}NO_8$ *m/z*: 398.5 [M – piv – 2pivOH + H]$^+$, 500.5 [M – pivOH + H]$^+$, 602.5 [M + H]$^+$, 624.5 [M + Na]$^+$, 640.6 [M + K]$^+$.

*(2**R**,6**S**)-**N**-(2′,3′,4′-Tri-**O**-pivaloyl-α-D-arabinopyranosyl)-2-allyl-6-**n**-propylpiperidin-4-one (11d)*

Piperidinone **11d** was prepared from **4f** (1.05 g, 2.0 mmol) according to the general procedure. For the formation of the orange cuprate solution, CuCN (716 mg, 8 mmol) and allylmagnesium bromide (1 mol/L in ether, 8 mL) were treated in THF (60 mL) at –40 °C for 0.5 h. Purification of **11b** was accomplished by flash chromatography (cyclohexane – ethyl acetate, 10:1). Yield: 0.85 g (1.50 mmol, 75%); colourless crystalline solid; mp 176 °C. R_f 0.52 (cyclohexane – ethyl acetate, 3:1). $[\alpha]^{25}_D$ +7.21° (*c* 1, $CHCl_3$); d.r.: 98:2 (HPLC after flash chromatography), 94:6 (HPLC of the crude product), HPLC: 80% CH_3CN, 20% H_2O → 100% CH_3CN, 20 min). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 5.72–5.60 (m, 1H, C*H*=CH_2), 5.49 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.16 (br s, 1H, H-4′), 5.10–4.98 (m, 3H, H-3′, CH=C*H*$_2$), 4.26 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.4 Hz, H-1′), 3.92 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.1 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 1.7 Hz, H-5′a), 3.56 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 12.9 Hz, H-5′b), 3.60–3.50 (m, 1H, H-6), 3.40–3.30 (m, 1H, H-2), 2.67–2.57 (m, 2H, H-3a, H-5a), 2.39 (d, 1H, $J_{H\text{-}5b,H\text{-}5a}$ = 15.7 Hz, H-5b), 2.25 (m, 2H, $J_{H\text{-}3b,H\text{-}3a}$ = 15.5 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 6.85 Hz, H-3b, C*H*$_2$-CH=CH_2), 2.06–1.95 (m, 1H, C*H*$_2$-CH=CH_2), 1.60–1.50 (m, 1H, C*H*$_2$-CH_2-CH_3), 1.40–1.25 (m, 2H, C*H*$_2$-C*H*$_2$-CH_3), 1.25–1.15 (m, 28H, piv-CH_3, CH_2-C*H*$_2$-CH_3), 0.86 (t, 3H, J = 7.2 Hz, propyl-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 210.5 (C-4), 177.4, 177.2, 176.9 (pivC=O), 135.4 (*C*H=CH_2), 117.6 (CH=*C*H$_2$), 94.6 (C-1′), 72.3, 68.7, 66.3 (C-2′, C-3′, C-4′), 65.1 (C-5′), 58.6 (alkyl-*C*H-N), 44.6 (CH_2), 43.4 (CH_2), 43.0 (CH_2), 40.1 (CH_2), 38.9, 38.8, 38.7 (pivC$_{quart.}$), 27.3, 27.1, 27.1 (piv-CH_3), 19.7 (propyl-CH_2), 14.0 (propyl-CH_3). ESI-MS for $C_{31}H_{51}NO_8$ *m/z*: 362.4 [M – 2pivOH + H]$^+$, 464.5 [M – pivOH + H]$^+$, 566.6 [M + H]$^+$, 588.5 [M + Na]$^+$, 604.5 [M + K]$^+$. Anal. calcd. for $C_{31}H_{51}NO_8$ (565.74): C 65.81, H 9.09, N 2.40; found: C 66.14, H 8.91, N 2.37.

*(2**R**,6**S**)-**N**-(2′,3′,4′-Tri-**O**-pivaloyl-α-D-arabinopyranosyl)-2-methyl-6-**n**-propylpiperidin-4-one (11e)*

A solution of methyllithium in diethyl ether (1.6 mol/L, 9.6 mL, 15.4 mmol) was added dropwise to a cold (–35 °C) suspension of CuI (1.50 g, 8.0 mmol) in dry THF (40 mL). The mixture was warmed to –25 °C in 2 h. During this time, the initially yellow solid was dissolved upon formation of a colourless solution, which was then cooled to –78 °C. Piperidinone **4f** (2.51 g, 4.8 mmol) and TMSCl (3 mL) in dry THF (80 mL) were added and the colour changed to yellow and finally to orange. The reaction mixture was allowed to warm to r.t. within 14 h. The reaction was terminated by addition of concd. NH_4OH – satd. NH_4Cl (1:1 *v/v*) (72 mL), and the mixture was diluted with diethyl ether (250 mL). The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo to yield silylenol ether **12** as an amorphous solid. It was dissolved in THF (48 mL) and a solution of tetrabutylammonia fluoride in THF (1 mol/L, 7.2 mL, 7.2 mmol) was added and the mixture was stirred until **12** was consumed. The solvent was removed in vacuo, the residue was dissolved in diethyl ether (240 mL), washed with water (100 mL) and brine (100 mL), and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by flash chromatography (petroleum ether – ethyl acetate, 5:1) to yield **11e** as a colourless crystalline solid (2.28 g, 4.2 mmol, 88%); mp 162 °C. R_f 0.46 (petroleum ether – ethyl acetate, 3:1). $[\alpha]^{25}_D$ –6.11° (*c* 1, $CHCl_3$); d.r.: 91:9 (HPLC of the crude product), HPLC: 80% CH_3CN, 20% H_2O → 100% CH_3CN, 20 min). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 5.48 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.5 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.5 Hz, H-2′), 5.20–5.10 (m, 1H, H-4′), 5.06 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.8 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.4 Hz, H-3′), 4.23 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3 Hz, H-1′), 3.93 (dd, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, $J_{H\text{-}5'b,H\text{-}4'}$ = 2.0 Hz, H-5′b), 3.85–3.70, 3.45–3.25 (2m, each 1H, H-2, H-6), 3.55 (d, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 12.7 Hz, H-5′a), 2.78 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 15.1 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.8 Hz, H-3a), 2.62 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 15.1 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 5.9 Hz, H-3b), 2.27 (dd, 1H, J_{gem} = 15.6 Hz, $J_{vic.}$ = 6.8 Hz, H-5a), 2.25–2.10 (m, 1H, H-5b), 1.70–1.50 (m, 1H, propyl-CH_2), 1.50–1.00 (m, 33H, piv-CH_3, CH_3, propyl-CH_2), 0.86 (t, 3H, J = 7.1 Hz, propyl-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 210.7 (C-4), 177.4, 177.2, 176.8 (pivC=O), 94.7 (C-1′), 72.2, 68.7, 66.4 (C-2′, C-3′, C-4′), 65.2 (C-5′), 58.7, 48.9 (C-2, C-6), 47.3, 44.3 (C-3, C-5), 40.3 (propyl-CH_2), 38.9, 38.7 (pivC$_{quart.}$), 27.2, 27.1, 27.1 (piv-CH_3), 24.5 (CH_3), 19.8 (propyl-CH_2), 14.0 (propyl-CH_3). Anal. calcd. for $C_{29}H_{49}NO_8$ (539.70): C 64.54, H 9.15, N 2.60; found: C 64.52, H 9.27, N 2.56.

*(2**S**,6**R**)-**N**-(2′,3′,4′-Tri-**O**-pivaloyl-α-D-arabinopyranosyl)-2-**n**-propyl-4-(1,3-dithiolan-2-yl)-6-methylpiperidine (13)*

To a solution of piperidinone **11e** (720 mg, 1.3 mmol) and ethanedithiol (0.22 mL, 2.6 mmol) in dry dichloromethane (9 mL) was added $BF_3{\cdot}OEt_2$ (0.78 mL, 6.7 mmol) at 0 °C. After 1 h the reaction mixture was warmed to r.t. and stirring was continued for 15 h. The mixture was diluted with dichloromethane (45 mL), washed with satd. aq. $NaHCO_3$ (2 × 20 mL) and water, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography to yield **13** as colourless solid (662 mg, 1.1 mmol, 81%); mp 142 °C. R_f 0.29 (petroleum ether – ethyl acetate, 5:1). $[\alpha]^{26}_D$ –24.46° (*c* 1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 5.57 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.8 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.8 Hz, H-2′), 5.25 – 5.15 (m, 1H, H-4′), 4.94 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.8 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 2.9 Hz, H-3′), 4.31 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3 Hz, H-1′), 3.92 (dd, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, $J_{H\text{-}5'b,H\text{-}4'}$ = 2.0 Hz, H-5′b), 3.53 (d, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz,

H-5′a), 3.35–3.20 (m, 4H, SCH_2CH_2S), 3.15–3.00, 2.95–2.80 (2m, each 1H, H-2, H-6), 2.20–1.80 (m, 4H, $2CH_2$), 1.40–1.10 (m, 34 H, piv-CH_3, propyl-CH_2, CH_3), 0.91 (t, 3H, J = 6.8 Hz, propyl-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 177.5, 177.4, 176.8 (piv-CH_3), 88.6 (C-1′), 72.8, 68.8, 68.2 (C-2′, C-3′, C-4′), 65.9 (C-5′), 59.2, 53.6 (C-2, C-6), 50.0 (CH_2), 48.2 (CH_2), 38.9, 38.7, 38.7 (piv-$C_{quart.}$), 38.6 (CH_2), 38.5 (CH_2), 37.0 (CH_2), 27.3, 27.2, 27.1 (piv-CH_3), 21.8 (CH_3), 19.8 (propyl-CH_2), 14.3 (propyl-CH_3). Anal. calcd. for $C_{31}H_{35}NO_7S_2$ (615.89): C 60.45, H 8.67, N 2.27, S 10.41; found: C 60.09, H 8.68, N 2.17, S 10.68.

*(2**R**,6**S**)-**N**-(2′,3′,4′-Tri-**O**-pivaloyl-α-D-arabinopyranosyl)-2-methyl-6-**n**-propylpiperidine (14)*

Raney nickel (5 g) was added to a solution of dithioketal **13** (500 mg, 0.8 mmol) in isopropanol (50 mL) and vigorously stirred for 24 h at 70 °C under H_2 atmosphere. The mixture was filtered through Hyflo®, and the filtrate was concentrated in vacuo to afford pure **14** as a colourless amorphous solid (310 mg, 0.6 mmol, 73%). R_f 0.48 (petroleum ether – ethyl acetate, 5:1). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 5.49 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.5 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.5 Hz, H-2′), 5.20–5.07 (m, 1H, H-4′), 5.01 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.8 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.4 Hz, H-3′), 4.12 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3 Hz, H-1′), 3.89 (dd, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, $J_{H\text{-}5'b,H\text{-}4'}$ = 2.0 Hz, H-5′b), 3.49 (d, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, H-5′a), 3.25–3.10, 3.00–2.85 (2m, each 1H, H-2, H-6), 1.80–1.05 (m, 40 H, piv-CH_3, CH_3, propyl-CH_2, CH_2), 0.86 (t, 3H, J = 7.1 Hz, propyl-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 177.5, 176.7 (pivC=O), 96.8 (C-1′), 72.7, 69.0, 66.0 (C-2′, C-3′, C-4′), 64.8 (C-5′), 38.9, 38.7, 38.7 (piv-$C_{quart.}$), 38.5 (CH_2), 31.7 (CH_2), 28.4 (CH_2), 27.3, 27.1, 27.1 (piv-CH_3), 22.4 (CH_3), 21.5 (CH_2), 15.4 (CH_2), 14.4 (propyl-CH_3).

*(+)-(2**R**,6**S**)-2-methyl-6-**n**-propylpiperidine hydrochloride (dihydropinidine) (15)*

Piperidine **14** (240 mg, 0.46 mmol) was dissolved in methanol (6 mL), treated with 1 N HCl (0.7 mL, 0.70 mmol) and stirred at r.t. for 48 h. The solvent was evaporated in vacuo the residue was dissolved in diethyl ether and extracted with water (3 × 10 mL). Lyophilization of the aqueous layers afforded **15** as colourless solid (quant.); mp 215–220 °C. $[\alpha]^{25}_D$ +11.05° (*c* 1, ethanol) (lit. value (9) $[\alpha]^{25}_D$ +11.6 to +14.2° (ethanol); enantiomer: lit. value (9) $[\alpha]^{25}_D$ –9.1 to –12.7° (ethanol); lit. value (3) $[\alpha]^{22}_D$ –11.1° (*c* 1, ethanol). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 9.07 (br s, 1H, NH), 8.68 (br s, 1H, NH), 3.15–2.80 (m, 2H, H-2, H-6), 1.90–1.00 (m, 13H, $5CH_2$, CH_3), 0.87 (t, 3H, J = 7.1 Hz, propyl-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 56.0, 52.5 (C-2, C-6), 34.82, 29.78, 27.05, 22.01, 18.75, 17.86 ($5CH_2$, CH_3), 13.68 (propyl-CH_3).

*(2**S**)-**N**-(2′,3′,4′-Tri-**O**-pivaloyl-α-D-arabinopyranosyl)-2-methyl-5-nitro-5,6-dehydropiperidin-4-one (17)*

A solution of nitronium tetrafluoroborate in sulfolane (0.5 mol/L, 1.5 mL, 0.75 mmol) was added slowly to **4d** (198 mg, 0.4 mmol) in dichloromethane (4 mL) at –78 °C. The mixture was allowed to reach r.t. and was quenched with satd. aq. $NaHCO_3$. The solvent was removed in vacuo, the residue was dissolved in diethyl ether (20 mL), and extracted with satd. aq. $NaHCO_3$. The aqueous layer was extracted twice with diethyl ether, and the combined organic layers were concentrated in vacuo. For the removal of sulfolane, water was added to the oily residue and stirred until a solid was formed. This was filtered, washed with water, dissolved in diethyl ether, and dried over $MgSO_4$. After removal of the solvent, purification was carried out by flash chromatography (cyclohexane – ethyl acetate, 3:1) to give **17** as a colourless amorphous solid (178 mg, 0.3 mmol, 83%). R_f 0.53 (cyclohexane – ethyl acetate, 1:1). $[\alpha]^{22}_D$ +0.15° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.57 (s, 1H, H-6), 5.51 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.32–5.26 (m, 1H, H-4′), 5.20 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.9 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.3 Hz, H-3′), 4.76 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 8.8 Hz, H-1′), 4.11 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 1.8 Hz, H-5′a), 4.16–4.03 (m, 1H, H-2), 3.81 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 12.9 Hz, H-5′b), 2.82 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.2 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.2 Hz, H-3a), 2.34 (dd, $J_{H\text{-}3b,H\text{-}3a}$ = 16.4, $J_{H\text{-}3b,H\text{-}2}$ = 1.7 Hz, H-3b), 1.35 (d, 3H, J = 7.0 Hz, CH_3), 1.26, 1.11, 1.08 (3s, each 9H, piv-CH_3). ESI-MS for $C_{26}H_{40}N_2O_{10}$ *m/z*: 541.7 $[M + H]^+$, 563.6 $[M + Na]^+$, 579.6 $[M + K]^+$, 604.6 $[M + MeCN + Na]^+$, 1104.2 $[2M + Na]^+$.

*(2**S**)-**N**-(2′,3′,4′-Tri-**O**-pivaloyl-α-D-arabinopyranosyl)-2-ethyl-5-nitro-5,6-dehydropiperidin-4-one (18)*

In a similar manner, dehydropiperidinone **4e** (3.02 g, 5.9 mmol) in dichloromethane (80 mL) was treated with a solution of nitronium tetrafluoroborate in sulfolane (0.5 mol/L, 18 mL, 9 mmol). Purification was carried out by flash chromatography (cyclohexane – ethyl acetate, 3:1) to give **18** as a colourless amorphous solid (2.68 g 4.8 mmol, 82%). R_f 0.57 (cyclohexane – ethyl acetate, 1:1). $[\alpha]^{22}_D$ +28.76° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.58 (s, 1H, H-6), 5.52 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.4 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.4 Hz, H-2′), 5.32–5.26 (m, 1H, H-4′), 5.19 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.1 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.1 Hz, H-3′), 4.78 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 8.8 Hz, H-1′), 4.12 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.2 Hz, H-5′a), 3.87 – 3.71 (m, 1H, H-2), 3.81 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 12.9 Hz, H-5′b), 2.74 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.5 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.3 Hz, H-3a), 2.57 (dd, $J_{H\text{-}3b,H\text{-}3a}$ = 16.5, $J_{H\text{-}3b,H\text{-}2}$ = 1.1 Hz, H-3b), 1.87–1.72 (m, 2H, CH_2), 1.26, 1.11, 1.08 (3s, 27H, piv-CH_3), 0.88 (t, 3H, J = 7.5 Hz, CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 180.1 (C-4), 177.3, 176.9, 176.8 (pivC=O), 153.2 (C-6), 123.5 (C-5), 93.0 (C-1′), 70.2, 67.5, 66.1 (C-2′, C-3′, C-4′), 66.7 (C-5′), 55.9 (C-2), 39.0, 39.0, 38.8 (piv$_{quart}$), 38.5 (C-3), 27.1, 27.0, 27.0 (piv-CH_3), 24.6 (CH_2), 9.9 (CH_3). ESI-MS for $C_{27}H_{42}N_2O_{10}$ (554.63) *m/z*: 555.2 $[M + H]^+$, 577.3 $[M + Na]^+$, 618.4 $[M + Na + MeCN]^+$, 1131.5 $[2M + Na]^+$.

*(2**S**)-**N**-(2′,3′,4′-Tri-**O**-pivaloyl-α-D-arabinopyranosyl)-5-benzamido-2-ethyl-5,6-dehydropiperidin-4-one (19)*

To a suspension of Raney nickel (3 g) in ethanol, saturated with H_2, was added a solution of **18** (4 g, 7.2 mmol) in ethanol (160 mL) and stirred for 22 h under a H_2 atmosphere. The mixture was filtered through Hyflo®, and the filtrate was concentrated in vacuo. The residue was dissolved in diethyl ether, dried over $MgSO_4$, and evaporated to dryness. The remaining solid was dissolved in dry THF. Triethylamine (4.5 mL, 32.4 mmol) and freshly distilled benzoyl chloride (2.5 mL, 21.6 mmol) were added, and the solution was stirred for 10 h at room temperature. After ad-

dition of satd. aq. NH_4Cl (200 mL), the mixture was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo and the crude product was purified by flash chromatography to yield **19** as a colourless amorphous solid (3.2 g, 5.1 mmol, 70%). R_f 0.35 (cyclohexane – ethyl acetate, 2:1). $[\alpha]^{22}_D$ +54.52° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.73 (s, 1H, H-6), 8.40 (br s, 1H, NH), 8.12–8.04 (m, 1H, phenyl), 7.86–7.78 (m, 2H, phenyl), 7.47–7.39 (m, 2H, phenyl), 5.56 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.28–5.22 (m, 1H, H-4′), 5.13 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.1 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.1 Hz, H-3′), 4.60 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 8.8 Hz, H-1′), 4.03 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.4 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.0 Hz, H-5′a), 3.72–3.59 (m, 1H, H-2), 3.69 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 2.79 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 17.3 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.6 Hz, H-3a), 2.55 (dd, $J_{H\text{-}3b,H\text{-}3a}$ = 17.3 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 1.5 Hz, H-3b), 2.04–1.88 (m, 1H, CH_2), 1.87–1.71 (m, 1H, CH_2), 1.26, 1.11, 1.08 (3s, 27H, piv-CH_3), 0.86 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 184.5 (C-4), 177.4, 177.1, 177.0 (pivC=O), 164.4 (NH-C=O), 134.2 (ipso-aryl), 133.5, 131.5, 130.1, 128.6, 128.4, 126.9 (aryl, C-6), 112.4 (C-5), 92.6 (C-1′), 71.0, 68.0, 66.4 (C-2′, C-3′, C-4′), 66.1 (C-5′), 53.9 (C-2), 39.0, 38.9, 38.7 ($piv_{quart.}$), 36.8 (C-3), 27.1, 27.0 (piv-CH_3), 23.7 (CH_2), 10.2 (CH_3). ESI-MS *m/z*: 323.3 [M – 3pivOH + H]$^+$, 425.5 [M – 2pivOH + H]$^+$, 527.5 [M – pivOH + H]$^+$, 651.6 [M + Na]$^+$, 692.8 [M + Na + MeCN]$^+$. HRMS calcd. for $C_{34}H_{48}N_2O_9$: 629.3438; found: 629.3424.

N-*(2′,3′,4′-Tri*-O-*pivaloyl-*α-*D-arabinopyranosyl)-5-benzamido-2-ethylpiperidin-4-one (20)*

(a) Preparation of the aluminum complex MAD

At r.t., trimethylaluminium (2 mol/L in toluene, 0.1 mL) was added to a solution of 2,6-di-*tert*-butyl-4-methylphenol (86 mg, 0.39 mmol) in toluene (3 mL) and stirred until the methane evolution ceased (30 min).

(b) Conjugate hydride addition

The clear solution preapared under (*a*) was cooled to –78 °C and a solution of **19** (25 mg, 0.04 mmol) in THF (2 mL) was added dropwise. After 15 min, L-Selectride® (1 mol/L in THF, 0.08 mL) was added at the same temperature, and the mixture was then allowed to warm to –40 °C within 3 h. The reaction was terminated by addition of acetic acid (0.05 mL), and the solvent was evaporated in vacuo. The residue was dissolved in diethyl ether (50 mL), washed with 1 N HCl (20 mL) and water (20 mL), and dried over $MgSO_4$. Evaporation of the solvent in vacuo afforded the crude product, which was purified by flash chromatography (cyclohexane – ethyl acetate, 5:1) to yield **20** as a colourless amorphous solid (22 mg, 0.035 mmol, 88%). R_f 0.40 (toluene – ethyl acetate, 3:1). $[\alpha]^{22}_D$ +4.90° (*c* 1, $CHCl_3$); d.r.: 89:11 (HPLC: 80% CH_3CH, 20% H_2O → 100% CH_3CN, 30 min); recrystallization from ether afforded the pure major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.80–7.75 (m, 2H, phenyl), 7.50–7.45 (m, 1H, phenyl), 7.44–7.37 (m, 2H, phenyl), 7.01 (d, 1H, $J_{NH,H\text{-}5}$ = 5.8 Hz, NH), 5.52 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.26–5.22 (m, 1H, H-4′), 5.15 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.8 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.5 Hz, H-3′), 4.90–4.80 (m, 1H, H-5), 4.29 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.0 Hz, H-1′), 4.04 (dd, 1H, $J_{H\text{-}6a,H\text{-}6b}$ = 12.7 Hz, $J_{H\text{-}6a,H\text{-}5}$ = 7.6 Hz, H-6a), 3.98 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.1 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.1 Hz, H-5′a), 3.61 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 12.9 Hz, H-5′b), 3.44–3.35 (m, 1H, H-2), 2.87 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 12.9 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.3 Hz, H-3a), 2.79 (dd, 1H, $J_{H\text{-}6b,H\text{-}6a}$ = 13.3 Hz, $J_{H\text{-}6b,H\text{-}5}$ = 10.2, H-6b), 2.47 (dd, $J_{H\text{-}3b,H\text{-}3a}$ = 12.9 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 1.6 Hz, H-3b), 1.63–1.51 (m, 1H, CH_2), 1.43–1.31 (m, 1H, CH_2), 1.30, 1.15, 1.13 (3s, 27H, piv-CH_3), 0.85 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 206.6 (C-4), 177.7, 177.4, 177.1 (pivC=O), 166.6 (NH-C=O), 134.1 (ipso-aryl), 131.5, 128.5, 127.1 (aryl), 95.7 (C-1′), 71.9, 68.3, 66.2, 65.4 (C-2′, C-3′, C-4′, C-5′), 62.7 (C-5), 58.1 (C-2), 49.2 (C-6), 45.1 (C-3), 39.0, 38.8 ($piv_{quart.}$), 27.3, 27.2, 27.1 (piv-CH_3), 25.1 (CH_2), 11.3 (CH_3). ESI-MS for $C_{34}H_{50}N_2O_9$ *m/z*: 325.3 [M – 3pivOH + H]$^+$, 449.5 [M – 2pivOH + Na]$^+$, 551.6 [M – pivOH + Na]$^+$, 631.6 [M + H]$^+$, 653.6 [M + Na]$^+$.

General procedure for the halogenation of dehydropiperidinones 4

To a solution of *N*-arabinosyl dehydropiperidinone **4** (1 mmol) in dry THF (20 mL) were added several equivalents (see for each compound) of solid *N*-bromosuccinimide or *N*-iodosuccinimide at –78 °C and stirred until complete consumption of the starting material. The solution was diluted with diethyl ether (100 mL), washed with 10% aq. $Na_2S_2O_3$ (3 × 20 mL), and the resulting aqueous layers were extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography.

(2R)-N-*(2′,3′,4′-Tri*-O-*pivaloyl-*α-*D-arabinopyranosyl)-2-(*p*-chlorophenyl)-5-iodo-5,6-dehydropiperidin-4-one (21a)*

Iododehydropiperidinone **21a** was synthesized according to the general procedure using **4a** (1.18 g, 2 mmol) and *N*-iodosuccinimide (1.35, 6 mmol). Purification was carried out by flash chromatography (petroleum ether – ethyl acetate, 6:1) to yield **21a** (1.33 g, 1.9 mmol, 93%) as a colourless solid. R_f 0.65 (petroleum ether – ethyl acetate, 2:1); mp 205 °C under decomposition. $[\alpha]^{22}_D$ +3.77° (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.70 (s, 1H, H-6), 7.27 (d, 1H, *J* = 4.3 Hz, aryl), 7.17 (d, 1H, *J* = 8.6 Hz, aryl), 5.56 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.18–5.13 (br s, 1H, H-4′), 5.05 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.0 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.3 Hz, H-3′), 4.91 (t, 1H, $J_{H\text{-}2,H\text{-}3a}$ = 6.3 Hz, $J_{H\text{-}2,H\text{-}3b}$ = 6.3 Hz, H-2), 4.37 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.0 Hz, H-1′), 3.85 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.3 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.0 Hz, H-5′a), 3.49 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 12.9 Hz, H-5′b), 3.05 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.4 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.2 Hz, H-3a), 2.83 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.4 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 6.3 Hz, H-3b), 1.23, 1.16, 1.10 (3s, 27H, $C(CH_3)_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 184.9 (C-4), 177.2, 177.1, 177.0 (pivC=O), 154.7 (C-6), 136.8 (ipso-aryl), 134.2 (ipso-aryl), 129.1, 128.0 (aryl), 89.8 (C-1′), 70.8, 67.7, 66.0 (C-2′, C-3′, C-4′), 66.1 (C-5′), 57.9 (C-2), 42.1 (C-3), 39.0, 38.9, 38.8 ($piv_{quart.}$), 27.2, 27.1, 27.0 (piv-CH_3). ESI-MS for $C_{31}H_{41}ClINO_8$ *m/z*: 718.2 [M(^{35}Cl) + H]$^+$, 720.2 [M(^{37}Cl) + H]$^+$, 740.2 [M(^{35}Cl) + Na]$^+$, 742.2 [M(^{37}Cl) + Na]$^+$.

(2R)-N-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-5-iodo-2-phenyl-5,6-dehydropiperidin-4-one (21b)

Iododehydropiperidinone **21b** was synthesized according to the general procedure using **4c** (1.40 g, 2.51 mmol) and *N*-iodosuccinimide (1.70 g, 7.53 mmol). Purification was achieved by flash chromatography (petroleum ether – ethyl acetate, 8:1) to yield **21b** (1.15 g, 1.68 mmol, 67%) as a pale yellow amorphous solid. R_f 0.58 (cyclohexane – ethyl acetate, 2:1). $[\alpha]^{22}_D$ –11.83° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.76 (s, 1H, H-6), 7.36–7.28 (m, 3H, aryl), 7.27–7.19 (m, 2H, aryl), 5.58 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.16–5.09 (m, 1H, H-4′), 4.99 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.9 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 2.9 Hz, H-3′), 4.91 (dd, 1H, $J_{H\text{-}2,H\text{-}3b}$ = 8.3 Hz, $J_{H\text{-}2,H\text{-}3a}$ = 6.1 Hz, H-2), 4.27 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.2 Hz, H-1′), 3.85 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.2 Hz, H-5′a), 3.41 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 3.01 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.5 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 5.9 Hz, H-3a), 2.88 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.2 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 8.5 Hz, H-3b), 1.25, 1.17, 1.10 (3s, 27H, $C(CH_3)_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 185.5 (C-4), 177.2, 177.1, 177.1 (pivC=O), 154.8 (C-6), 137.8 (ipso-aryl), 129.0, 128.7, 126.9 (aryl), 88.7 (C-1′), 71.0, 67.8, 66.0, 65.8 (C-2′, C-3′, C-4′, C-5′), 59.7 (C-2), 42.4 (C-3), 39.0, 38.8, 38.8 ($piv_{quart.}$), 27.2, 27.2, 27.0 (piv-CH_3). ESI-MS for $C_{31}H_{42}I\,NO_8$ *m/z*: 322.0 [dehydropiperidinone + H + Na]$^+$, 706.0 [M + Na]$^+$, 747.1 [M + Na + MeCN]$^+$.

(2S)-N-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-5-iodo-2-n-propyl-5,6-dehydropiperidin-4-one (21c)

Iododehydropiperidinone **21c** was synthesized according to the general procedure using **4f** (524 mg, 1 mmol) and *N*-iodosuccinimide (900 mg, 4 mmol). Purification was carried out by flash chromatography (petroleum ether – ethyl acetate, 8:1) to yield **21c** (450 mg, 0.7 mmol, 69%) as a colourless amorphous solid. R_f 0.57 (petroleum ether – ethyl acetate, 2:1). $[\alpha]^{26}_D$ +123.19° (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.37 (s, 1H, H-6), 5.50 (t, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.27–5.23 (m, 1H, H-4′), 5.12 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.0 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.3 Hz, H-3′), 4.47 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.0 Hz, H-1′), 4.03 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.3 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.3 Hz, H-5′a), 3.85–3.76 (m, 1H, H-2), 3.69 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.3 Hz, H-5′b), 2.72 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.6 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 5.7 Hz, H-3a), 2.67 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.64 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 2.6 Hz, H-3b), 1.90–1.78 (m, 1H, CH_2), 1.67–1.55 (m, 2H, CH_2), 1.40–1.28 (m, 1H, CH_2), 1.25 (s, 9H, piv-CH_3), 1.11 (s, 18H, piv-CH_3), 0.86 (t, 3H, *J* = 7.2 Hz, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 185.8 (C-4), 177.2, 177.2, 177.0 (pivC=O), 154.4 (C-6), 91.7 (C-1′), 70.8, 67.8, 66.3 (C-2′, C-3′, C-4′), 66.4 (C-5′), 63.1 (C-5), 53.5 (C-2), 38.9, 38.9, 38.8 (piv_{quart}), 37.9, 32.8 (C-3, CH_2), 27.1, 27.1, 27.0 (piv-CH_3), 18.8 (CH_2), 13.7 (CH_3). ESI-MS for $C_{28}H_{44}INO_8$ *m/z*: 446.04 [M – 2pivOH + H]$^+$, 650.21 [M + H]$^+$, 672.19 [M + Na]$^+$, 713.08 [M + Na + CH_3CN]$^+$.

(2R)-N-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-5-iodo-2-isopropyl-5,6-dehydropiperidin-4-one (21d)

Iododehydropiperidinone **21d** was synthesized according to the general procedure using **4g** (4.0 g, 7.6 mmol) and *N*-iodosuccinimide (5.4 g, 24 mmol). Purification was accomplished by flash chromatography to yield **21d** (4.31 g, 6.6 mmol, 87%) as a colourless amorphous solid. R_f 0.49 (cyclohexane – ethyl acetate, 2:1). $[\alpha]^{22}_D$ +122.00° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.45 (s, 1H, H-6), 5.53 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.26–5.21 (m, 1H, H-4′), 5.12 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.9 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.3 Hz, H-3′), 4.51 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.2 Hz, H-1′), 4.03 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.2 Hz, H-5′a), 3.68 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 3.68–3.60 (m, 1H, H-2), 2.77–2.70 (m, 2H, H-3a, H-3b), 2.34–2.17 (m, 1H, C*H*$(CH_3)_2$), 1.26, 1.12, 1.11 (3s, 27H, piv-CH_3), 0.88 (d, 3H, *J* = 7.0 Hz, CH_3), 0.87 (d, 3H, *J* = 6.6 Hz, CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 186.2 (C-4), 177.2, 177.0, 177.0 (pivC=O), 154.8 (C-6), 91.6 (C-1′), 71.1, 67.8, 66.2 (C-2′, C-3′, C-4′), 66.2 (C-5′), 64.2 (C-5), 58.8 (C-2), 39.0, 39.0, 38.8 (piv_{quart}), 34.7 (C-3), 32.3 (*C*H$(CH_3)_3$), 27.2, 27.1, 27.0 (piv-CH_3), 19.6, 17.6 (CH_3). ESI-MS for $C_{28}H_{44}INO_8$ *m/z*: 650.3 [M + H]$^+$, 672.2 [M + Na]$^+$, 688.2 [M + K]$^+$.

(2S)-N-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-2-(3-tert-butyldiphenylsiloxy)propyl-5-iodo-5,6-dehydropiperidin-4-one (21e)

Iododehydropiperidinone **21e** was synthesized according to the general procedure using **4h** (1.56 g, 2 mmol) and *N*-iodosuccinimide (1.35 g, 6 mmol). Purification was performed by flash chromatography (petroleum ether – ethyl acetate, 8:1) to yield **21e** (1.57 g, 1.70 mmol, 87%) as a pale yellow amorphous solid. R_f 0.58 (petroleum ether – ethyl acetate, 2:1). $[\alpha]^{25}_D$ +71.63° (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.63–7.56 (m, 4H, aryl), 7.43–7.32 (m, 7H, aryl, H-6), 5.50 (t, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.26–5.21 (br s, 1H, H-4′), 5.12 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.2 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.1 Hz, H-3′), 4.45 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.0 Hz, H-1′), 3.99 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.3 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.0 Hz, H-5′a), 3.83–3.73 (m, 1H, H-2), 3.69–3.50 (m, 3H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.3 Hz, H-5′b, O-CH_2), 2.75 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.4 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.3 Hz, H-3a), 2.65 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.6 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 1.8 Hz, H-3b), 1.90–1.77 (m, 2H, CH_2), 1.63–1.36 (m, 2H, CH_2), 1.23 (s, 9H, $C(CH_3)_3$), 1.11 (s, 18H, $C(CH_3)_3$), 0.99 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 185.6 (C-4), 177.2, 177.0 (pivC=O), 154.0 (C-6), 135.5, 135.5 (aryl), 133.7, 133.7 (ipso-aryl), 129.6, 127.7 (aryl), 91.5 (C-1′), 70.8, 67.8, 66.3 (C-2′, C-3′, C-4′), 66.3 (C-5′), 63.2 (OCH_2), 53.9 (C-2), 39.0, 38.9, 38.8 ($piv_{quart.}$), 38.2 (C-3), 28.8, 27.6 (CH_2), 27.2, 27.2, 27.0, 26.8 (piv-CH_3, SiC(*C*$H_3)_3$), 19.2 (Si*C*$(CH_3)_3$). ESI-MS for $C_{44}H_{62}INO_9Si$ *m/z*: 826.3 [M – phenyl]$^+$, 904.2 [M + H]$^+$, 926.2 [M + Na]$^+$.

(2R)-N-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-5-bromo-2-(p-chlorophenyl)-5,6-dehydropiperidin-4-one (21f)

Bromodehydropiperidinone **21f** was synthesized according to the general procedure using **4a** (3.5 g, 5.9 mmol) and *N*-bromosuccinimide (2.1 g, 11.8 mmol). Purification was carried out by flash chromatography (cyclohexane – ethyl acetate, 8:1) to yield **21f** (3.0 g, 4.4 mmol, 75%) as a colourless amorphous solid. R_f 0.5 (cyclohexane – ethyl acetate, 2:1). $[\alpha]^{22}_D$ –11.57° (*c* 1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 7.60 (s, 1H, H-6), 7.29 (d, 2H, *J* = 8.8 Hz, aryl), 7.18 (d, 2H, *J* = 8.8 Hz, aryl), 5.56 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ =

9.5 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.5 Hz, H-2′), 5.22–5.13 (m, 1H, H-4′), 5.03 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.0 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.2 Hz, H-3′), 4.87 (t, 1H, $J_{H\text{-}2,H\text{-}3a}$ = 6.6 Hz, $J_{H\text{-}2,H\text{-}3b}$ = 6.6 Hz, H-2), 4.33 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3, H-1′), 3.86 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.0 Hz, H-5′a), 3.47 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 3.00 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.6 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 5.9 Hz, H-3a), 2.78 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.6 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 7.3 Hz, H-3b), 1.23, 1.16, 1.10 (3s, 27H, piv-CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm) δ: 183.7 (C-4), 177.2, 177.1, 177.0 (pivC=O), 150.2 (C-6), 136.5, 134.4 (ipso-aryl), 129.2, 128.2 (aryl), 94.5 (C-5), 89.6 (C-1′), 70.9 (C-3′), 67.8 (C-4′), 66.2 (C-5′), 65.9 (C-2′), 58.3 (C-2), 43.1 (C-3), 39.0, 38.9 ($piv_{quart.}$), 27.2, 27.2, 27.0 (piv-CH_3). ESI-MS for $C_{31}H_{41}BrClNO_8$ *m/z*: 672.5 [M(^{81}Br) + H]$^+$, 692.2 [M(^{79}Br) + Na]$^+$, 694.2 [M(^{81}Br) + Na]$^+$, 708.2 [M(^{79}Br) + K]$^+$, 710.2 [M(^{81}Br) + K]$^+$, 733.2 [M(^{79}Br) + Na + CH_3CN]$^+$, 735.2 [M(^{81}Br) + Na + CH_3CN]$^+$.

*(2***R***)-***N***-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-5-bromo-2-isopropyl-5,6-dehydropiperidin-4-one (21g)*

Bromodehydropiperidinone **21g** was synthesized according to the general procedure using **4g** (2.0 g, 3.8 mmol) and *N*-bromosuccinimide (3.4 g, 19 mmol). Purification was achieved by flash chromatography (cyclohexane – ethyl acetate, 5:1) to yield **21g** (1.7 g, 2.8 mmol, 73%) as a colourless amorphous solid. R_f 0.28 (cyclohexane – ethyl acetate, 3:1). $[\alpha]^{25}_D$ 108.56° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.33 (s, 1H, H-6), 5.53 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.4 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.26–5.20 (m, 1H, H-4′), 5.12 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.9 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.3 Hz, H-3′), 4.50 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.2 Hz, H-1′), 4.02 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.2 Hz, H-5′), 3.69 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 12.9 Hz, H-5′b), 3.63–3.55 (m, 1H, H-2), 2.76 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.9 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 7.4 Hz, H-3a), 2.64 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.9 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 2.6 Hz, H-3b), 2.34–2.13 (m, 1H, C*H*(CH_3)$_2$), 1.25, 1.11, 1.11 (3s, 27H, piv-CH_3), 0.89 (d, 6H, *J* = 7.0 Hz, CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 184.9 (C-4), 177.2, 177.2, 177.0 (pivC=O), 150.2 (C-6), 91.7 (C-5), 91.7 (C-1′), 71.1, 67.8, 66.2 (C-2′, C-3′, C-4′), 66.3 (C-5′), 58.9 (C-2), 39.0, 38.8 (piv_{quart}), 35.6 (C-3), 32.0 (*C*H(CH_3)$_3$), 27.1, 27.0 (piv-CH_3), 19.6, 17.6 (CH_3). ESI-MS for $C_{28}H_{44}BrNO_8$ *m/z*: 602.2 [M(^{79}Br) + H]$^+$, 604.2 [M(^{81}Br) + H]$^+$, 624.2 [M(^{79}Br) + Na]$^+$, 626.2 [M(^{81}Br) + Na]$^+$, 665.3 [M(^{79}Br) + Na + CH_3CN]$^+$, 667.3 [M(^{81}Br) + Na + CH_3CN]$^+$.

*(2***S***)-***N***-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-5-bromo-2-(3′′-tert-butyldiphenylsiloxy)propyl-5,6-dehydropiperidin-4-one (21h)*

Bromodehydropiperidinone **21h** was synthesized according to the general procedure using **4h** (1.17 g, 1.5 mmol) and *N*-bromosuccinimide (0.53 g, 3.0 mmol). Purification was performed by flash chromatography (petroleum ether – ethyl acetate, 4:1) to yield **21h** (1.02 g, 1.2 mmol, 79%) as a colourless amorphous solid. R_f 0.45 (petroleum ether – ethyl acetate, 2:1). $[\alpha]^{24}_D$ +59.95° (*c* 1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 7.65–7.55 (m, 4H, aryl), 7.45–7.30 (m, 6H, aryl), 7.26 (s, 1H, H-6), 5.50 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.3 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.3 Hz, H-2′), 5.30–5.20 (m, 1H, H-4′), 5.12 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.0 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.2 Hz, H-3′), 4.44 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 8.8 Hz, H-1′), 3.99 (d, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,\ H\text{-}4'}$ = 2.0 Hz, H-5′a), 3.85–3.45 (m, 4H, $J_{H\text{-}5'b,\ H\text{-}5'a}$ = 13.2 Hz, H-5′b, CH_2-O, H-2), 2.76 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.6 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 5.9 Hz, H-3a), 2.55 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.6 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 2.0 Hz, H-3b), 1.95–1.70 (m, 2H, CH_2), 1.70–1.40 (m, 2H, CH_2), 1.23 (s, 9H, $C(CH_3)_3$), 1.11 (s, 18H, $C(CH_3)_3$), 0.99 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 184.3 (C-4), 177.2, 177.2, 177.0 (pivC=O), 149.6 (C-6), 135.5, 135.5 (aryl), 133.7, 133.6 (ipso-aryl), 129.6, 127.7 (aryl), 91.6, 91.0 (C-1′, C-5), 70.8, 67.8, 66.2 (C-2′, C-3′, C-4′), 66.3 (C-5′), 63.2 (OCH_2), 53.9 (C-2), 39.0 (C-3), 38.9, 38.9, 38.8 ($piv_{quart.}$), 28.8, 27.5 (CH_2), 27.2, 27.1, 27.0, 26.8 (pivCH_3, SiC(*C*H_3)$_3$), 19.2 (Si*C*(CH_3)$_3$). ESI-MS for $C_{44}H_{62}BrNO_9Si$ *m/z*: 778.2 [(M(^{79}Br) – phenyl]$^+$, 780.2 [M(^{81}Br) – phenyl]$^+$, 856.2 [M(^{79}Br) + H]$^+$, 858.2 [M(^{81}Br) + H]$^+$, 878.1 [M(^{79}Br) + Na]$^+$, 880.1 [M(^{81}Br) + Na]$^+$, 894.1 [M(^{79}Br) + K]$^+$, 896.1 [M(^{81}Br) + K]$^+$, 919.2 [M(^{79}Br) + Na + CH_3CN]$^+$, 921.2 [M(^{81}Br) + Na + CH_3CN]$^+$.

*(2***R***)-***N***-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-2-(p-chlorophenyl)-5-phenyl-5,6-dehydropiperidin-4-one (22)*

A two-necked round bottom flask equipped with a reflux condenser and a septum was charged with iodide **21a** (180 mg, 0.25 mmol), bis(dibenzylideneacetone)palladium (14 mg, 0.025 mmol), and triphenylarsine (31 mg, 0.10 mmol), and then evacuated and flushed with argon. Dry THF (10 mL) was added and the mixture was stirred for 5 min for the formation of the active catalyst (colour change from red to yellow). Phenyl tributyltin 0.16 mL (0.50 mmol) was then added and the solution was heated to 65 °C for 17 h. After cooling, the reaction mixture was treated with 1 mol/L aq. KF (1 mL) and stirred for 30 min. It was then diluted with diethyl ether (50 mL), washed with water, and dried over $MgSO_4$. The solvent was evaporated in vacuo and the product was purified by flash chromatography (cyclohexane – ethyl acetate, 7:1) affording **22** (74 mg, 0.11 mmol, 44%), as a pale yellow amorphous solid. R_f 0.46 (cyclohexane – ethyl acetate, 2:1). $[\alpha]^{22}_D$ –21.30° (*c* 1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ: 7.54–7.10 (m, 10H, H-6, aryl), 5.68 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.5 Hz, $J_{H\text{-}2',\ H\text{-}3'}$ = 9.5 Hz, H-2′), 5.20–5.12 (m, 1H, H-4′), 5.03 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.8 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 2.9 Hz, H-3′), 4.88 (dd, 1H, $J_{H\text{-}2,H\text{-}3a}$ = 7.8 Hz, $J_{H\text{-}2,H\text{-}3b}$ = 5.9 Hz, H-2), 4.37 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3 Hz, H-1′), 3.86 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.4 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 1.7 Hz, H-5′a), 3.47 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 2.96 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.4 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 5.6 Hz, H-3a), 2.75 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.3 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 8.0 Hz, H-3b), 1.20, 1.14, 1.10 (3s, 27H, piv-CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 188.8 (C-4), 177.1, 177.1, 177.0 (pivC=O), 148.7 (C-6), 137.1, 135.0, 134.2 (ipso-aryl), 129.1, 128.4, 128.2, 127.9, 126.5 (aryl), 115.4 (C-5), 89.6 (C-1′), 71.1, 67.9, 65.7 (C-2′, C-3′, C-4′), 66.1 (C-5′), 58.7 (C-2), 44.1 (C-3), 38.9, 38.9, 38.8 ($piv_{quart.}$), 27.2, 27.1, 27.0 (piv-CH_3). ESI-MS for $C_{37}H_{46}ClNO_8$ *m/z*: 668.5 [M(^{35}Cl) + H]$^+$, 690.5 [M(^{35}Cl) + Na]$^+$, 731.4 [M(^{35}Cl) + Na + CH_3CN]$^+$.

*(2***S***)-***N***-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-5-(p-methoxyphenyl)-2-n-propyl-5,6-dehydropiperidin-4-one (23)*

To a solution of **21c** (65 mg, 0.10 mmol), 4-methoxy-

benzene boronic acid (30 mg, 0.60 mmol), and $Pd(PPh_3)_2Cl_2$ (4 mg, 0.02 mmol) in THF (3 mL), aq. Cs_2CO_3 (2 mol/L, 0.25 mL) was added and the mixture was stirred at 65 °C for 20 h. The mixture was filtrated through Hyflo®, and the filtrate was concentrated in vacuo. The residue was diluted in diethyl ether (15 mL), washed with water (3 mL) and brine (1.5 mL), and dried over $MgSO_4$. The product was purified by flash chromatography (cyclohexane – ethyl acetate, 6:1) to yield **23** as a colourless amorphous solid (25 mg, 0.04 mmol, 40%, incomplete conversion). R_f 0.44 (cyclohexane – ethyl acetate, 2:1). $[\alpha]^{22}_D$ +55.18° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.09 (s, 1H, H-6), 7.21 (d, 2H, *J* = 8.8 Hz, aryl), 6.83 (d, 2H, *J* = 8.8 Hz, aryl), 5.61 (t, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.30–5.22 (m, 1H, H-4′), 5.14 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.9 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.3 Hz, H-3′), 4.53 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.2 Hz, H-1′), 4.05 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.2 Hz, H-5′a), 3.82–3.66 (m, 1H, H-2), 3.77 (s, 3H, OCH_3), 3.71 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 12.8 Hz, H-5′b), 2.77 (dd, 1H, $J_{H\text{-}3a,H\text{-}3b}$ = 16.5 Hz, $J_{H\text{-}3a,H\text{-}2}$ = 6.2 Hz, H-3a), 2.54 (dd, 1H, $J_{H\text{-}3b,H\text{-}3a}$ = 16.5 Hz, $J_{H\text{-}3b,H\text{-}2}$ = 1.8 Hz, H-3b), 2.00–1.83 (m, 1H, CH_2), 1.73–1.55 (m, 1H, CH_2), 1.49–1.11 (m, 2H, CH_2), 1.26 (s, 9H, piv-CH_3), 1.12 (s, 9H, piv-CH_3), 1.08 (s, 9H, piv-CH_3), 0.87 (t, 3H, *J* = 7.2 Hz, CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 189.7 (C-4), 177.2, 177.1, 177.1 (pivC=O), 158.1 (*C*-OCH_3), 148.5 (C-6), 129.0 (aryl), 127.8 (ipso-aryl), 113.7 (aryl), 112.0 (C-5), 92.3 (C-1′), 71.1, 67.9, 66.1 (C-2′, C-3′, C-4′), 66.3 (C-5′), 55.3, 53.6 (C-2, OCH_3), 39.4 (C-3), 39.0, 38.9, 38.8 ($piv_{quart.}$), 33.1 (CH_2), 27.1, 27.1, 27.0 (piv-CH_3), 18.9 (CH_2), 13.8 (CH_3). ESI-MS for $C_{35}H_{51}NO_9$ *m*/*z*: 630.4 $[M + H]^+$, 652.3 $[M + Na]^+$, 668.2 $[M + K]^+$.

(2R,3S)-N-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-2-(p-chlorophenyl)-3-methyl-5,6-dehydropiperidin-4-one (24a)

LiHMDS (1 mol/L in THF, 1.2 mL) was added slowly to a cold solution (–78 °C) of **4a** (592 mg, 1.0 mmol) in dry THF (30 mL) and stirred for 1 h. After addition of iodomethane (0.12 mL, 2 mmol), the reaction mixture was stirred for 15 h at the same temperature. The reaction was terminated by addition of satd. aq. NH_4Cl. After warming, the organic layer was washed with satd. aq. NH_4Cl (2 × 50 mL) and the resulting aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatoraphy of the residue (petroleum ether – ethyl acetate, 5:1) furnished **24a** (444 mg, 0.73 mmol, 73%) as a colourless amorphous solid. R_f 0.38 (petroleum ether – ethyl acetate, 2:1); mp 162 °C. $[\alpha]^{25}_D$ –73.44° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.37 (d, 2H, *J* = 8.8 Hz, aryl), 7.31 (d, 2H, *J* = 8.3 Hz, aryl), 7.24–7.20 (m, 1H, H-6), 5.57 (t, 1H, $J_{H\text{-}2',H\text{-}1'}$ = 9.8 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.8 Hz, H-2′), 5.28 (d, 1H, $J_{H\text{-}5,H\text{-}6}$ = 8.3 Hz, H-5), 5.08–5.15 (m, 1H, H-4′), 4.87 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.8 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.4 Hz, H-3′), 4.35 (d, 1H, $J_{H\text{-}2,H\text{-}3}$ = 11.7 Hz, H-2), 4.02 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.3 Hz, H-1′), 3.82 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.7 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 1.9 Hz, H-5′a), 3.28 (d, 1H, $J_{H\text{-}5'b,H\text{-}5'a}$ = 13.2 Hz, H-5′b), 2.57 (dq, 1H, $J_{H\text{-}3,H\text{-}2}$ = 12.0 Hz, $J_{H\text{-}3,methyl}$ = 6.8 Hz, H-3), 1.23, 1.16, 1.08 (3s, 27H, piv-CH_3), 0.89 (d, 3H, *J* = 6.8 Hz, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 194.3 (C-4), 177.2, 177.1, 176.7 (pivC=O), 148.18 (C-6), 136.18, 134.77 (ipso-aryl), 129.46 (aryl), 103.45 (C-5), 87.54 (C-1′), 71.66, 68.02, 67.52 (C-2′, C-3′, C-4′), 65.96 (C-5′), 65.10 (C-2), 46.03 (*C*HCH_3), 38.96, 38.85, 38.77 ($pivC_{quart.}$), 27.15, 27.04 (piv-CH_3), 13.46 (CH_3).

(2S,3S)-N-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-2-(3-tert-butyldiphenylsiloxy)propyl-3-methyl-5,6-dehydropiperidin-4-one (24b)

Disubstituted dehydropiperidinone **24b** was synthesized similarly to **24a** using **4h** (1.01 g, 1.30 mmol), dry THF (40 mL), LiHMDS (1 mol/L in THF, 3.90 mL, 3.90 mmol), and iodomethane (0.32 mL, 5.20 mmol). Purification by flash chromatography (cyclohexane – ethyl acetate, 5:1) yielded **24b** (0.89 g, 1.13 mmol, 87%) as a colourless amorphous solid. R_f 0.41 (cyclohexane – ethyl acetate, 2:1). $[\alpha]^{22}_D$ +0.81° (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.65–7.54 (m, 4H, aryl), 7.46–7.28 (m, 6H, aryl), 6.95 (d, 1H, $J_{H\text{-}6,H\text{-}5}$ = 7.7, H-6), 5.47 (t, $J_{H\text{-}2',H\text{-}1'}$ = 9.6 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.6 Hz, H-2′), 5.24–5.16 (m, 1H, H-4′), 5.07 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 9.7 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.1 Hz, H-3′), 4.93 (dd, 1H, $J_{H\text{-}5,H\text{-}6}$ = 7.4 Hz, H-5), 4.44 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.2 Hz, H-1′), 3.92 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.2 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 1.8 Hz, H-5′a), 3.72–3.40 (m, 3H, H-5′b, O-CH_2), 3.37–3.26 (m, 1H, H-2), 2.36–2.23 (m, 1H, H-3), 1.92–1.70 (m, 1H, CH_2), 1.70–1.40 (m, 2H, CH_2), 1.23 (s, 3H, $C(CH_3)_3$), 1.15–1.06 (m, 21H, $C(CH_3)_3$, CH_3), 1.02 ($C(CH_3)_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 196.4 (C-4), 177.3, 177.1, 176.6 (pivC=O), 146.6 (C-6), 135.5, 135.4 (aryl), 133.7, 133.6 (ipso-aryl), 129.7, 127.7 (aryl), 97.8 (C-5), 90.9 (C-1′), 72.0, 68.0, 65.5 (C-2′, C-3′, C-4′), 66.1 (C-5′), 63.3 (CH_2-O), 61.9 (C-2), 42.5 (C-3), 38.9, 38.8, 38.8 ($pivC_{quart.}$), 28.3 (CH_2), 27.1, 27.1, 27.1, 26.8 ($pivCH_3$, Si-C(*C*H_3)$_3$), 27.0 (CH_2), 19.2 (Si*C*$(CH_3)_3$), 17.7 (CH_3). ESI-MS for $C_{45}H_{65}NO_9Si$ *m*/*z*: 792.5 $[M + H]^+$, 814.5 $[M + Na]^+$, 830.5 $[M + K]^+$.

(2S,3S)-N-(2′,3′,4′-Tri-O-pivaloyl-α-D-arabinopyranosyl)-2-(3-tert-butyldiphenylsiloxy)propyl-3-ethyl-5,6-didehydropiperidin-4-one (24c)

Disubstituted dehydropiperidinone **24c** was synthesized similarly to **24a** using **4h** (1.01 g, 1.30 mmol), dry THF (40 mL), LiHMDS (1 mol/L in THF, 3.25 mL), and iodoethane (0.31 mL, 3.90 mmol). Purification by flash chromatography (cyclohexane – ethyl acetate, 6:1) yielded **24c** (0.74 mg, 0.91 mmol, 70%) as a colourless amorphous solid. R_f 0.50 (cyclohexane – ethyl acetate, 2:1). $[\alpha]^{22}_D$ +4.34° (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.63–7.57 (m, 4H, aryl), 7.43–7.32 (m, 6H, aryl), 6.93 (d, 1H, $J_{H\text{-}6,H\text{-}5}$ = 7.6, H-6), 5.47 (t, $J_{H\text{-}2',H\text{-}1'}$ = 9.4 Hz, $J_{H\text{-}2',H\text{-}3'}$ = 9.4 Hz, H-2′), 5.23–5.20 (m, 1H, H-4′), 5.06 (dd, 1H, $J_{H\text{-}3',H\text{-}2'}$ = 10.0 Hz, $J_{H\text{-}3',H\text{-}4'}$ = 3.3 Hz, H-3′), 4.95 (d, 1H, $J_{H\text{-}5,H\text{-}6}$ = 7.8 Hz, H-5), 4.45 (d, 1H, $J_{H\text{-}1',H\text{-}2'}$ = 9.4 Hz, H-1′), 3.94 (dd, 1H, $J_{H\text{-}5'a,H\text{-}5'b}$ = 13.3 Hz, $J_{H\text{-}5'a,H\text{-}4'}$ = 2.0 Hz, H-5′a), 3.63–3.54 (m, 3H, H-5′b, O-CH_2), 3.47–3.40 (m, 1H, H-2), 1.85–1.76 (m, 1H, H-3), 1.24, 1.12, 1.10, 1.01 (4s, 27H, $(CH_3)_3$), 0.91 (t, 3H, *J* = 7.42 Hz, CH_2CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ: 195.6 (C-4), 177.3, 177.1, 176.6 (pivC=O), 146.3 (C-6), 135.5 (aryl), 133.7, 133.6 (ipso-aryl), 129.7, 127 7 (aryl), 97.7 (C-5), 91.1 (C-1′), 72.0, 68.0, 65.7 (C-2′, C-3′, C-4′), 66.2 (C-5′), 63.2 (CH_2-O), 59.6 (C-3), 49.7 (C-2), 38.9, 38.8, 38.8 ($pivC_{quart.}$), 28.4 (CH_2), 27.1, 27.1, 27.1

(pivCH$_3$), 26.8 (SiC(*C*H$_3$)$_3$), 24.7 (CH$_2$), 19.2 (*C*H$_2$CH$_3$), 11.6 (CH$_2$*C*H$_3$). ESI-MS for $C_{46}H_{67}NO_9Si$ *m/z*: 626.29 [M – phenyl – pivOH]$^+$, 728.24 [M – phenyl]$^+$, 806.34 [M + H]$^+$, 828.26 [M + Na]$^+$, 869.24 [M + Na + CH$_3$CN]$^+$.

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