# Carbocyclic ring closure of hex-5-enopyranosides and pent-4-enofuranosides: a nitrile oxide approach

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Nitrile oxide cycloadditions to protected enopyrano(furano)sides derived from D-glucose and D-ribose afford spiro-isoxazolines in good yield and high diastereoselectivity, which upon Raney Nickel hydrogenation in MeOH–AcOH (6 : 1) undergo N–O bond cleavage followed by spontaneous aldol-like condensation to give good yields of hydroxylated six- and five-membered cyclic enaminones as the main products.

## Introduction

The development of new synthetic methods for the construction of chiral polyoxygenated cyclopentanes and cyclohexanes is of considerable importance in organic synthesis,[1] since these units constitute substructures in many bioactive compounds, such as glycosidase inhibitors,[2] aminoglycoside antibiotics,[3] carbocyclic nucleosides[4] and prostaglandins.[5] Carbohydrates, increasingly used as a chiral pool in natural-products synthesis,[6] are excellent starting materials and the transfer of their chirality to the products is today the most common method for the preparation of chiral polyoxygenated carbocycles. Carbanion cyclisations,[7] 1,3-dipolar cycloadditions,[8] free-radical cyclisations,[9] cyclisations *via* organometallic intermediates[10] and, most recently, ring-closing olefin metathesis[11] are among the methods developed over the last twenty years for carbocyclic ring closure in sugar templates.

Since the discovery, by Ferrier,[12] that easily available hex-5-enopyranosides such as **1** (Fig. 1) are converted into highly functionalised cyclohexane derivatives **2** in the presence of $Hg^{II}$ salts, this remarkable rearrangement (or Ferrier II reaction) has become a popular route to many biologically interesting compounds, such as aminocyclitols, carba-sugars and inositols.[13] The $HgCl_2$ initially used was replaced by the more effective $Hg(OAc)_2$, HgO, $HgSO_4$ and $Hg(O_2CCF_3)_2$, either stoichiometric or catalytic.[14] Furthermore, the problem of toxicity of mercury salts was overcome by using catalytic $PdCl_2$ or $Pd(OAc)_2$.[15] Alternatively, the cyclohexane derivatives **3** and **4** were formed from **2** in carbacyclisation reactions, promoted by $Al^iBu_3$ and $Ti(O^iPr)Cl_3$, respectively, in which the glycosidic bond survives.[16] However, despite its effectiveness for the construction of six-membered carbocycles, the Ferrier II reaction is unsuitable to convert pent-4-enofuranosides into the respective cyclopentanoids.[17]

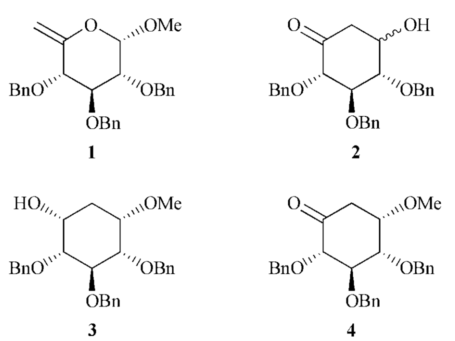



**Fig. 1**

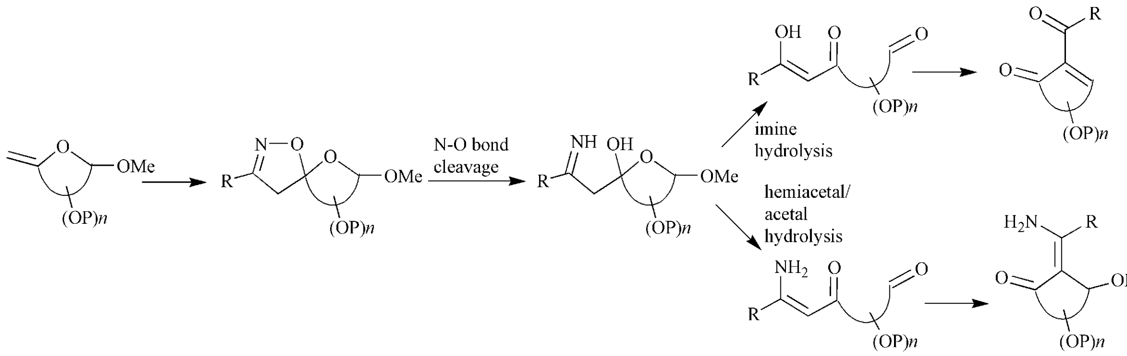
We wished to examined whether the N–O bond cleavage of the isoxazoline ring generated by cycloaddition of nitrile oxides to both hex-5-enopyranosides and pent-4-enofuranosides could lead to the formation of six- and five-membered carbocycles (Scheme 1).[18] It was expected that, depending upon the relative rates of competitive reactions, the N–O bond cleavage by Raney Ni hydrogenation could give either an enamine-aldehyde or a tricarbonyl compound, both suitable for intramolecular aldol-like condensations.

## Results and discussion

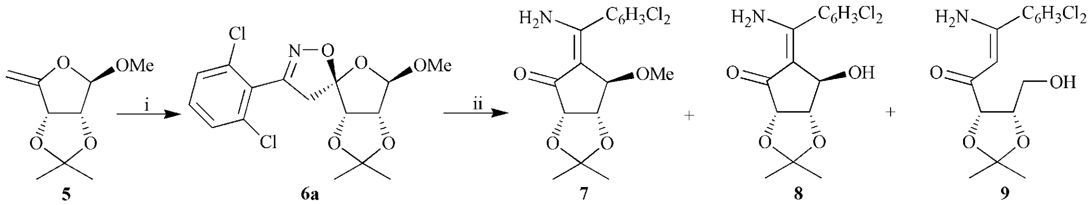
We initially added the stable 2,6-dichlorobenzonitrile oxide to the double bond of pent-4-enofuranoside[19] **5**, by refluxing their solution in methylene dichloride for 4 h. The spiro-isoxazoline **6a** (Scheme 2) was isolated chromatographically as a single diastereoisomer in good yield. The absolute configuration of the newly formed stereocenter in **6a** was determined by NOE experiments: the mutual signal enhancement between one proton of the isoxazoline ring and one methyl of the acetonide group, as well as the enhancement of 1-H (sugar numbering) upon irradiation of both methylene protons of the isoxazoline ring, leave no doubt as to the assigned structure. As expected, the obtained diastereoisomer **6a** was generated by the addition of the nitrile oxide to the less hindered face of the double bond.

The N–O bond cleavage of isoxazolines derived from nitrile oxide cycloadditions to olefins, usually by Raney Ni hydrogenation, gives *β*-hydroxy ketones, being thus an important alternative route to aldol condensation.[20,21] In the special case of cycloadducts to enol ethers, enaminones and further 1,3-diones are produced by the hydrogenation.[21] When Raney Ni or Pd/C in MeOH or tetrahydrofuran (THF) were used as catalysts for the hydrogenation (1 atm) of **6a**, a very complex mixture of products was obtained, but when boric acid (2.2 equiv.) was used as additive in the Raney Ni hydrogenation (1 atm) of **6a** in MeOH–water (9 : 1), the cyclisation products **7** and **8** were isolated, each one in 5% yield, together with the open-structure enaminone **9** (18%). The same results were obtained by varying the concentration of the additive (1.5 to 10 equiv.), with increased yields of the open-chain product **9** at higher concentrations of boric acid, with compound **9** being the only isolated product when 20 equiv. of boric acid were added.

At this point, it was evident that the acidic medium was necessary, but it also assisted the reduction of the aldehyde




**Scheme 1**




**Scheme 2** *Reagents and conditions*: i, 2,6-$Cl_2C_6H_3CNO$, (1.1 equiv.), $CH_2Cl_2$, reflux, 4 h; ii, Raney Ni, $H_2$ (1 atm), MeOH–$CH_3CO_2H$ (6:1), 20 °C, 90 min (for yields see text).

intermediately produced before cyclisation. Furthermore, the low yields of the products should rather be attributed to undesirable hydrolysis caused by the presence of water before cyclisation. Indeed, the yields of **7** (23%) and **8** (18%) were improved and no **9** was formed when MeOH, 2.2 equiv. of boric acid, and $MgSO_4$ were used for the hydrogenolysis of **6a**. Finally, the most satisfactory results were obtained when a mixture of methanol and glacial acetic acid was used as solvent, which in the ratio 6:1 in the presence of $MgSO_4$ gave yields of 64% for **7** and 17% for **8**, while **9** was not detected. The absolute configuration of the C-1 (ribose numbering) stereocenter, bearing the MeO or OH group, in **7** and **8** was assigned on the basis of the lack of any NOE enhancement between 1-H and 2-H as well as from the coupling constant $J_{1,2} = 0$, which indicates a *trans* arrangement between the C-1 and C-2 substituents.[22]

Having established the best conditions for the reductive cyclisation of the spiro-isoxazoline **6a**, a number of spirocycloadducts were prepared by using *in situ* prepared nitrile oxides and also by performing the cycloadditions with the hex-5-enopyranoside **1** (Scheme 3). Both general methods, namely oxidation of aldoximes[23] (R = Me, Et) and dehydration of primary nitroparaffins[24] (R = phenyl, *p*-tolyl), were used for the *in situ* generation of the unstable nitrile oxides. Excellent yields were obtained from the stable nitrile oxides and those generated *in situ* from primary nitroparaffins, while the method of oxidation of aromatic aldoximes afforded moderate yields of cycloadducts. In all reactions, the respective symmetrically 3,4-disubstituted furoxans (1,2,5-oxadiazole *N*-oxides) were formed in low yields (<15%), resulting from the dimerisation of nitrile oxides, which were characterised by comparison of their physical data and NMR spectra with those of authentic samples.[25]

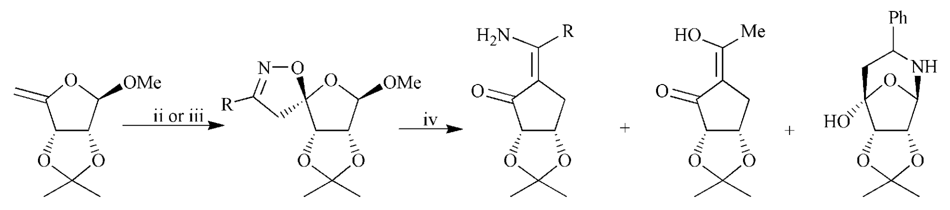
All cycloaddition products of pent-4-enofuranoside **5** were isolated as single diastereoisomers, evidently with the configuration established for **6a**. The cycloadditions to hex-5-enopyranoside **1** were somewhat less selective: products **13a**, **13b** and **13c** were found to be mixtures of diastereoisomers in the ratio 9:1, cycloadduct **13d** was a 17:1 mixture of diastereoisomers (always the major isomer is depicted in Scheme 3), while **13e** was isolated as a single diastereoisomer. NOE experiments confirmed again the assigned structure for the major isomer of **13a**: the signal enhancement of both methylene protons of the isoxazoline ring (18.1 and 6.8%), when irradiating the methyl group, clearly corroborates the stereochemistry assigned.

The less diastereoselective cycloadditions to hex-5-enopyranoside **1** compared with those of pent-4-enofuranoside **5** can be attributed to the strong hindrance of the one face of the double bond of **5**, induced by the acetonide group. In **1**, the benzyloxy groups adopting pseudo-equatorial positions affect the double bond less selectively, because it is more strongly hindered from one face by the methoxy group. The overall effect is that the less hindered face of **5** is more available than that of **1** and this fact is reflected to the reaction time required for the completion of cycloadditions to **1** and **5**. The diastereoselectivity, however, of the cycloadditions is of no importance, since the spiro carbon loses its chirality in the next step. Indeed, when compounds **13a–d** were further used as diastereomeric mixtures, both diastereomers gave the same products.

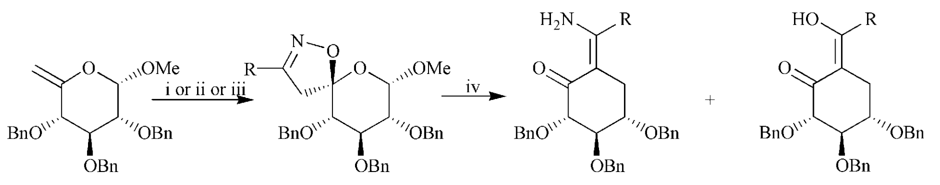
The isoxazoline ring of cycloadducts **6b–e** and **13a–e** was further cleaved by applying the conditions established for **6a** [Raney Ni, $MgSO_4$, $H_2$ (1 atm), MeOH–$CH_3CO_2H$ 6:1, 90 min] to give compounds **10b–e** and **14a–e**, respectively, which were isolated as the main cyclisation products. Compared with compounds **7** and **8** prepared by reductive cyclisation of **6a** under the same conditions, the methoxy or hydroxy group is now missing. Furthermore, when R = alkyl, the respective 1,3-diones were formed as by-products, whereas in one instance the bicyclic product **12d** was isolated. All cyclisation products, which are new compounds, were isolated by column chromatography and characterised by their spectral and analytical data. Despite their dense functionalisation, they were found to be stable enough at room temperature, while they can be stored in the refrigerator for several months without appreciable decomposition.

With the exception of **14a**, the proton shifts (in $CDCl_3$ at 20 °C) of the amino group in all enaminones prepared (**7**–**10**, **14**) appeared at $\delta \approx 5.5$ and $\approx 10.0$ as two broad singlets, which reveal the intramolecular hydrogen bond, demonstrating the geometry of the double bond.[26] These signals were missing in compound **14a** (in $CDCl_3$ at 20 °C), but appeared at $\delta$ 8.0 and 10.05 in DMSO-$d_6$ at 20 °C and coalesced at 50 °C in the same solvent. The diones **11b** and **15b**,**c** exist exclusively as enols, the enolic proton appearing at $\delta \approx 15.5$ for **15b**,**c**.

Scheme 4 could account for the hydrogenation–ring-closure reaction as well as for the formation of by-products. The N–O

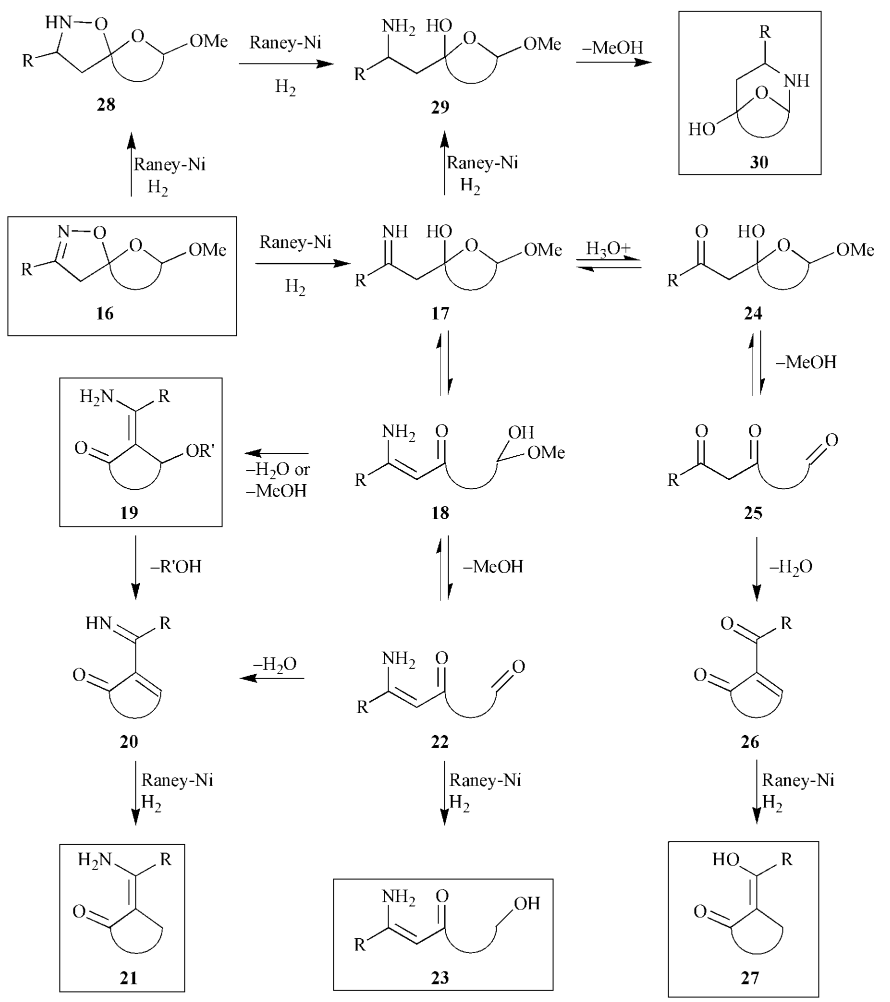



**5** | **6b** R = Me (94%); **c** R = Et (90%); **d** R = Ph (29%); **e** R = $p$-$MeC_6H_4$ (55%) | **10b** R = Me (60%); **c** R = Et (43%); **d** R = Ph (48%); **e** R = $p$-$MeC_6H_4$ (53%) | **11b** (23%) | **12d** (11%)



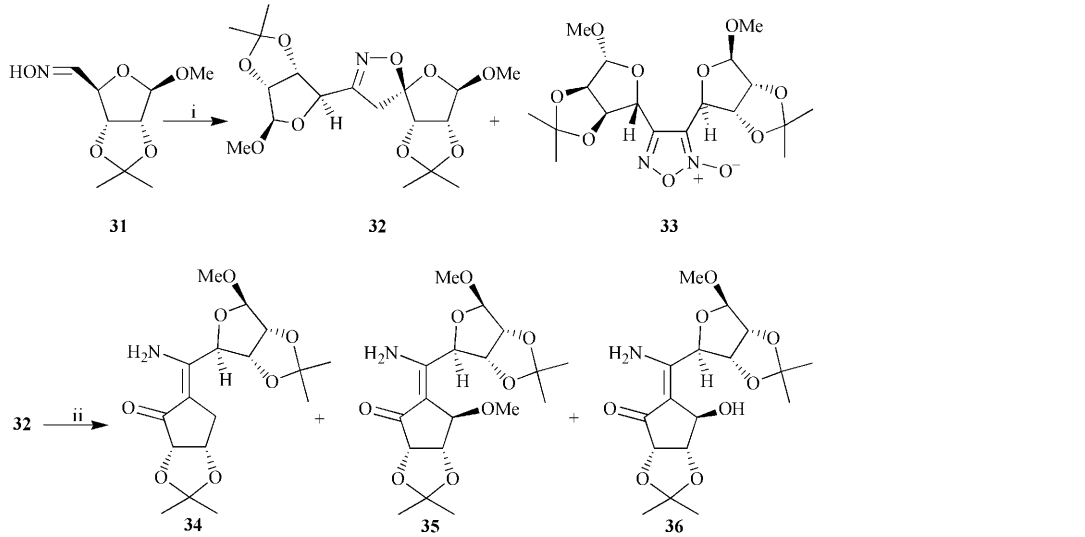

**1** | **13a** R = 2,6-$C_6H_3Cl_2$ (92%); **b** R = Me (91%); **c** R = Et (87%); **d** R = Ph (40%); **e** R = $p$-$MeC_6H_4$ (44%) | **14a** R = 2,6-$C_6H_3Cl_2$ (80%); **b** R = Me (35%); **c** R = Et (29%); **d** R = Ph (52%); **e** R = $p$-$MeC_6H_4$ (51%) | **15b** R = Me (15%); **c** R = Et (15%)

**Scheme 3** *Reagents and conditions*: i, 2,6-$Cl_2C_6H_3CNO$, $CH_2Cl_2$, reflux, 24 h; ii, $RCH_2NO_2$, PhNCO, $Et_3N$, $C_6H_6$, 20 °C, 5 days for **5** or reflux, 7 days for **1**; iii, RCH=NOH, NCS, pyridine, $Et_3N$, $CHCl_3$, reflux, 90 min for **5** or 24 h for **1**; iv, Raney Ni, $H_2$ (1 atm), MeOH–$CH_3CO_2H$ (6:1), 20 °C, 90 min.




**Scheme 4**

bond scission triggered a sequence of reactions with intermediate formation of imine **17** and enaminones **18** or **19**, which easily underwent aldol-like condensation to **20** *via* **19** or **22** with subsequent hydrogenation of the double bond formed to give the final products **21**. It is apparent that the reaction conditions, the nature of substituents and the ring size expected to be formed can affect the reaction pathway. Thus in the case of hydrogenation of adduct **6a** (Scheme 2), the condensation stops



**Scheme 5** *Reagents and conditions*: i, NCS, pyridine, **5**, $Et_3N$, $CHCl_3$, reflux, 90 min, 48%; ii, Raney Ni, $H_2$ (1 atm), MeOH–$CH_3CO_2H$ (6:1), 20 °C, 90 min.

after the first step and it is not followed by elimination, possibly due to steric reasons. In acidic media also, the aldehyde **22** is further reduced to alcohol **23**. When R = alkyl the imine **17**, being less stable, is partially hydrolysed to ketone **24**, before its isomerisation to **18**. Elimination of MeOH from **24** gives the tricarbonyl compound **25**, which after a typical Knoevenagel condensation and hydrogenation of the double bond formed in the intermediate enedione **26** gives the cyclic diketone **27**. Finally, the bicyclic hemiacetal **30** isolated in one case is evidently formed from the amino derivative **29**, which in turn can be generated either by hydrogenation of imine **17** or by hydrogenation of the C=N bond in **16** at first, followed by N–O bond cleavage in intermediate **28**.

The densely functionalised cyclic enaminones **7**, **8**, **10** and **14** are suitable for a number of further synthetic transformations, namely hydrolysis to diones,[27] reduction[28] and condensation to fused heterocycles.[29] When the nitrile oxide is derived from a sugar, the cyclisation product would be a modified *C*-disaccharide. To demonstrate this possibility, the spiro-isoxazoline **32** was prepared in 48% yield from **5** by adding the nitrile oxide generated *in situ* by oxidation of oxime **31**[30] (Scheme 5), together with the nitrile oxide dimer **33**. Further reductive cleavage of the N–O bond of **32** led to the formation of a mixture of enaminones **34**, **35** and **36**, in 24, 11 and 14% yield, respectively. Compound **34** resulted from **32** by analogy to enaminones **10** and **14** (Scheme 3), while **35** and **36** were formed, like enaminones **7** and **8** (Scheme 2), by failure of the intramolecular condensation to go to completion, evidently because of the bulkiness of the substituents.

In short, we have outlined a new approach for converting carbohydrates in carbocycles, which complements the Ferrier method since it can be applied to the synthesis of five-membered rings as well as six-membered ones. The densely functionalised cyclopentane and cyclohexane derivatives are suitable for further transformations and we have demonstrated the possibility of preparing modified *C*-disaccharides by the present method.

## Experimental

Mps were determined on a Kofler hot-stage microscope and are uncorrected. All commercially available reagents were used without further purification. Raney Ni suspension in water was purchased from Fluka. Solvents were dried by standard methods. The progress of the reactions was checked by TLC on Merck silica gel $60F_{254}$ glass plates (0.25 mm). The spots were visualised by heat staining with *p*-anisaldehyde in ethanol–sulfuric acid. Column chromatography was performed with Merck silica gel 60 (0.063–0.200 mm). Optical rotations were determined at room temperature on an A. Krüss P3000 Automatic Digital Polarimeter. $[\alpha]_D$-Values are given in units of $10^{-1}$ deg cm$^2$ g$^{-1}$. The $^1$H and $^{13}$C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Bruker 300 AM spectrometer, with tetramethylsilane (TMS) as internal standard. *J*-Values are given in Hz. Mass spectra were recorded under electron-impact (EI) conditions at 70 eV on a VG TS-250 spectrometer and microanalyses were performed on a Perkin-Elmer 2400-II Element analyser. High-resolution mass spectra (HRMS) were obtained on a VG ZAB-ZSE mass spectrometer under fast-atom bombardment (FAB) conditions with nitrobenzyl alcohol (NBA) as the matrix or on an IONSPEC FTMS spectrometer (matrix-assisted laser-desorption ionisation, MALDI) with 2,5-dihydroxybenzoic acid (DHB) as matrix.

### (5*R*,7*R*,8*R*,9*S*)-3-(2,6-Dichlorophenyl)-8,9-isopropylidenedioxy-7-methoxy-1,6-dioxa-2-azaspiro[4.4]non-2-ene 6a

A solution of **5** (186 mg, 1 mmol) and 2,6-dichlorobenzonitrile oxide (207 mg, 1.1 mmol) in methylene dichloride (5 ml) was refluxed for 4 h. The mixture was then evaporated on a rotavapor and the residue was chromatographed on silica gel with hexane–ethyl acetate 30:1 to give **6a** (247 mg, 66%) as a colorless solid, mp 62–64 °C (from diethyl ether–hexane), $[\alpha]_D$ +77.2 (*c* 0.17, MeOH) (Found: C, 51.29; H, 4.53; N, 3.62. Calc. for $C_{16}H_{17}Cl_2NO_5$: C, 51.35; H, 4.58; N, 3.74%); $\delta_H$ ($CDCl_3$) 1.36 (3H, s, $CMe_2$), 1.45 (3H, s, $CMe_2$), 3.20 (1H, d, *J* 18.7, 4-H$^a$), 3.44 (3H, s, MeO), 3.78 (1H, d, *J* 18.7, 4-H$^b$), 4.78 (1H, d, *J* 5.5, 8-H), 4.87 (1H, d, *J* 5.5, 9-H), 4.95 (1H, s, 7-H) and 7.36 (3H, m, ArH); $\delta_C$ ($CDCl_3$) 24.8 and 26.2 ($CMe_2$), 43.5 (C-4), 54.7 (MeO), 83.2 and 84.2 (C-8, -9), 108.0 (C-7), 112.9 ($CMe_2$), 118.8 (C-5), 127.9, 128.2, 131.0 and 134.9 (ArC), and 154.6 (C-3); *m*/*z* 373/375/377 ($M^+$/$M^+$ + 2/$M^+$ + 4), 359/361/363, 315/317/319, 289/291/293, 255/257/259 and 230/232/234.

### (5*R*,7*S*,8*R*,9*R*,10*S*)-8,9,10-Tris(benzyloxy)-3-(2,6-dichlorophenyl)-7-methoxy-1,6-dioxa-2-azaspiro[4.5]dec-2-ene 13a

A solution of **1** (446 mg, 1 mmol) and 2,6-dichlorobenzonitrile oxide (207 mg, 1.1 mmol) in methylene dichloride (5 ml) was refluxed for 24 h. The mixture was then evaporated on a rotavapor and the residue was chromatographed on silica gel with hexane–ethyl acetate 15:1 to give a mixture of **13a** and its epimer (582 mg, 92%) in the ratio 9:1 (by $^1$H NMR spectroscopy). The major isomer **13a** was crystallised from diethyl ether–hexane as a white solid, mp 75–76.5 °C; $[a]_D$ −95.0 (*c* 0.82, $CHCl_3$) (Found: C, 66.14; H, 5.17; N, 2.12. Calc. for $C_{35}H_{33}Cl_2NO_6$: C, 66.25; H, 5.24; N, 2.21%); $\delta_H$ ($CDCl_3$) 3.30 (1H, d, *J* 18.4, 4-H$^a$), 3.50 (3H, s, MeO), 3.69 (1H, dd, *J* 5.3 and 4.3, 8-H), 3.88 (2H, m, 9-, 10-H) 3.93 (1H, d, *J* 18.4, 4-H$^b$), 4.65 (1H, d, *J* 12.0, PhC*H*$_2$), 4.67 (1H, d, *J* 4.3, 7-H), 4.85 (5H, m, PhC*H*$_2$), 7.35 (18H, m, ArH); $\delta_C$ ($CDCl_3$) 42.8 (C-4), 57.1 (MeO), 73.9, 75.4 and 75.9 (C-8, -9, -10), 78.7, 78.8 and 80.3 (3 × Ph*C*H$_2$), 100.0 (C-7), 111.6 (C-5), 127.65, 127.70, 127.9, 128.0, 128.1, 128.2 (two peaks), 128.3, 128.4, 128.47, 128.50, 131.2, 135.0, 137.8, 137.9, 138.4 (ArC), and 156.1 (C-7).

**General procedure for the nitrile oxide generation from nitroalkanes and their addition to enopyrano(furano)sides 1 and 5**

To a solution of compound **1** or **5** (1 mmol) in benzene (5 ml) were added nitroethane or nitropropane (1.1 mmol), triethylamine (0.1 mmol) and phenyl isocyanate (3.6 mmol) and the mixture was stirred at 20 °C for 5 days (for the reactions of **5**) or refluxed for 7 days (for the reactions of **1**). During this time additional amounts of nitroalkane (3 equiv.) and phenyl isocyanate (9 equiv.) were added in small portions until the disappearance of the enopyrano(furano)side (TLC monitoring). The mixture was subsequently stirred with water (5 ml) for 1 h at 20 °C and extracted with cyclohexane (2 × 10 ml). The organic layer was dried over $Na_2SO_4$, filtered and the solvent was then removed under reduced pressure. Purification of the products was accomplished by column chromatography. The furoxans resulting from the dimerisation of nitrile oxides were eluted first in low yields (<15%), followed by the cycloaddition products.

**(5*R*,7*R*,8*R*,9*S*)-8,9-Isopropylidenedioxy-7-methoxy-3-methyl-1,6-dioxa-2-azaspiro[4.4]non-2-ene 6b.** Compound **6b** was prepared from **5** and nitroethane according to the general procedure above and was isolated by subsequent column chromatography ($CH_2Cl_2$–ethyl acetate 50:1) as a colorless oil (229 mg, 94%), $[a]_D$ +63.4 (*c* 0.88, $CHCl_3$) (Found: C, 54.28; H, 7.01; N, 5.49. Calc. for $C_{11}H_{17}NO_5$: C, 54.31; H, 7.04; N, 5.76%); $\delta_H$ ($CDCl_3$) 1.33 (3H, s, CMe$_2$), 1.44 (3H, s, CMe$_2$), 2.04 (3H, s, 3-Me), 2.87 (1H, d, *J* 18.8, 4-H$^a$), 3.38 (3H, s, MeO), 3.41 (1H, d, *J* 18.8, 4-H$^b$), 4.72 (1H, d, *J* 5.5, 8-H), 4.79 (1H, d, *J* 5.5, 9-H) and 5.01 (1H, s, 7-H); $\delta_C$ ($CDCl_3$) 12.9 (3-Me), 24.8 and 26.2 (C*Me*$_2$), 45.0 (C-4), 54.7 (MeO), 83.2 and 84.3 (C-8, -9), 107.9 (C-7), 112.7 (*C*Me$_2$), 118.1 (C-5) and 156.2 (C-3); *m*/*z* 243 (M$^+$), 228 and 212.

**(5*R*,7*R*,8*R*,9*S*)-3-Ethyl-8,9-isopropylidenedioxy-7-methoxy-1,6-dioxa-2-azaspiro[4.4]non-2-ene 6c.** Compound **6c** was prepared from **5** and nitropropane according to the general procedure above and was isolated by subsequent column chromatography ($CH_2Cl_2$–ethyl acetate 50:1) as a colorless oil (231 mg, 90%), $[a]_D$ +53.6 (c 1.11, $CHCl_3$) (Found: C, 55.83; H, 7.36; N, 5.37. Calc. for $C_{12}H_{19}NO_5$: C, 56.02; H, 7.44; N, 5.44%); $\delta_H$ ($CDCl_3$) 1.19 (3H, t, *J* 7.5, 3-CH$_2$CH$_3$), 1.33 (3H, s, CMe$_2$), 1.45 (3H, s, CMe$_2$), 2.41 (2H, q, *J* 7.5, 3-CH$_2$CH$_3$), 2.87 (1H, d, *J* 18.5, 4-H$^a$), 3.38 (3H, s, MeO), 3.40 (1H, d, *J* 18.5, 4-H$^b$), 4.72 (1H, d, *J* 5.9, 8-H), 4.80 (1H, d, *J* 5.9, 9-H) and 5.01 (1H, s, 7-H); $\delta_C$ ($CDCl_3$) 10.7 (3-CH$_2$*C*H$_3$), 21.2 (3-*C*H$_2$CH$_3$), 24.9 and 26.2 (C*Me*$_2$), 43.5 (C-4), 54.7 (MeO), 83.3 and 84.4 (C-8, -9), 107.9 (C-7), 112.8 (*C*Me$_2$), 118.0 (C-5) and 160.8 (C-3); *m*/*z* 257 (M$^+$), 242, 226 and 200.

**(5*R*,7*S*,8*R*,9*R*,10*S*)-8,9,10-Tris(benzyloxy)-7-methoxy-3-methyl-1,6-dioxa-2-azaspiro[4.5]dec-2-ene 13b.** Compound **13b** (as a mixture with its minor epimer in a 9:1 ratio) was prepared from **1** and nitroethane according to the general procedure above and was isolated by subsequent column chromatography ($CH_2Cl_2$–hexane 3:1) as a colorless oil (458 mg, 91%). The major isomer **13b** was crystallised from diethyl ether–hexane as a white solid, mp 109–110.5 °C; $[a]_D$ −28.2 (*c* 0.57, $CHCl_3$) (Found: C, 71.39; H, 6.53; N, 2.70. Calc. for $C_{30}H_{33}NO_6$: C, 71.55; H, 6.60; N, 2.78%); $\delta_H$ ($CDCl_3$) 2.02 (3H, s, 3-Me), 2.96 (1H, d, *J* 18.2, 4-H$^a$), 3.43 (3H, s, MeO), 3.46 (1H, d, *J* 18.2, 4-H$^b$), 3.64 (1H, dd, *J* 9.6, 4.0, 8-H), 3.76 (1H, dd as t, *J* 9.6, 9-H), 3.84 (1H, d, *J* 9.6, 10-H), 4.60 (1H, d, *J* 4.3, 7-H), 4.63 (1H, d, *J* 12.5, PhC*H*$_2$), 4.71 (1H, d, *J* 10.8, PhC*H*$_2$), 4.78 (1H, d, *J* 12.5, PhC*H*$_2$), 4.80 (2H, m, PhC*H*$_2$), 4.88 (1H, d, *J* 10.8, PhC*H*$_2$), 7.31 (15H, m, ArH); $\delta_C$ ($CDCl_3$) 13.3 (3-Me), 43.8 (C-4), 56.6 (MeO), 73.7, 75.2 and 75.8 (C-8, -9, -10), 78.7, 78.8 and 80.2 (3 × Ph*C*H$_2$), 99.6 (C-7), 110.7 (C-5), 127.6, 127.65, 127.85, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 137.7, 137.9, 138.4 (ArC), and 157.5 (C-3).

**(5*R*,7*S*,8*R*,9*R*,10*S*)-8,9,10-Tris(benzyloxy)-3-ethyl-7-methoxy-1,6-dioxa-2-azaspiro[4.5]dec-2-ene 13c.** Compound **13c** (as a mixture with its minor epimer in a 9:1 ratio) was prepared from **1** and nitropropane according to the general procedure above and was isolated by subsequent column chromatography ($CH_2Cl_2$–hexane 3:1) as a colorless oil (458 mg, 87%). The major isomer **13c** was crystallised from diethyl ether–hexane as a white solid, mp 99–95 °C; $[a]_D$ −32.6 (*c* 1.32, $CHCl_3$) (Found: C, 71.82; H, 6.68; N, 2.76. Calc. for $C_{31}H_{35}NO_6$: C, 71.93; H, 6.82; N, 2.71%); $\delta_H$ ($CDCl_3$) 1.17 (3H, t, *J* 7.4, 3-CH$_2$C*H*$_3$), 2.39 (2H, q, *J* 7.4, 3-C*H*$_2$CH$_3$), 2.99 (1H, d, *J* 18.2, 4-H$^a$), 3.43 (3H, s, MeO), 3.45 (1H, d, *J* 18.2, 4-H$^b$), 3.64 (1H, dd, *J* 9.3, 4.0, 8-H), 3.77 (1H, dd as t, *J* 9.3, 9-H), 3.84 (1H, d, *J* 9.3, 10-H), 4.60 (1H, d, *J* 4.0, 7-H), 4.63 (1H, d, *J* 12.6, PhC*H*$_2$), 4.72 (1H, d, *J* 11.5, PhC*H*$_2$), 4.78 (1H, d, *J* 12.6, PhC*H*$_2$), 4.82 (1H, d, *J* 11.5, PhC*H*$_2$), 4.84 (1H, d, *J* 10.5, PhC*H*$_2$), 4.89 (1H, d, *J* 10.5, PhC*H*$_2$) and 7.32 (15H, m, ArH); $\delta_C$ ($CDCl_3$) 10.9 (3-CH$_2$*C*H$_3$), 21.4 (3-*C*H$_2$CH$_3$), 42.1 (C-4), 56.6 (MeO), 73.8, 75.2 and 75.8 (C-8, -9, -10), 78.8, 78.9 and 80.3 (3 × Ph*C*H$_2$), 99.7 (C-7), 110.6 (C-5), 127.6, 127.7, 127.9, 128.0, 128.05, 128.1, 128.2, 128.3, 128.5, 137.8, 138.0, 138.5 (ArC), and 162.1 (C-3).

**General procedure for the nitrile oxide generation from aldoximes and their addition to enopyrano(furano)sides 1 and 5**

To a solution of benzaldoxime or *p*-methylbenzaldoxime or the oxime **31** [30] (1.2 mmol) in dry $CHCl_3$ (10 ml) were added *N*-chlorosuccinimide (NCS) (155 mg, 1.3 mmol) and dry pyridine (2 drops) and the stirred mixture was refluxed for 20 min. The solution was cooled to room temperature a solution of compound **1** or **5** (1 mmol) and $Et_3N$ (111 mg, 1.1 mmol) in $CHCl_3$ (5 ml) were added, and the mixture was refluxed again for 90 min (for the reactions of **5**) or 24 h (for the reactions of **1**). The solvent was then removed under reduced pressure and purification of the products was accomplished by column chromatography. The furoxans resulting from the dimerisation of nitrile oxides were eluted first in low yields (<15%), followed by the cycloaddition products.

**(5*R*,7*R*,8*R*,9*S*)-8,9-Isopropylidenedioxy-7-methoxy-3-phenyl-1,6-dioxa-2-azaspiro[4.4]non-2-ene 6d.** Compound **6d** was prepared from **5** and benzaldoxime according to the general procedure above and was isolated by subsequent column chromatography (hexane–ethyl acetate 20:1) as a colorless oil (89 mg, 29%), $[a]_D$ +54.5 (*c* 2.98, $CHCl_3$) (Found: C, 62.99; H, 6.21; N, 4.50. Calc. for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59%); $\delta_H$ ($CDCl_3$) 1.35 (3H, s, CMe$_2$), 1.50 (3H, s, CMe$_2$), 3.31 (1H, d, *J* 18.4, 4-H$^a$), 3.41 (3H, s, MeO), 3.78 (1H, d, *J* 18.4, 4-H$^b$), 4.77 (1H, d, *J* 5.6, 8-H), 4.88 (1H, d, *J* 5.6, 9-H), 5.06 (1H, s, 7-H), 7.40 (3H, m, *m*- and *p*-ArH), 7.69 (2H, m, *o*-ArH); $\delta_C$ ($CDCl_3$) 24.8 and 26.3 (C*Me*$_2$), 41.5 (C-4), 54.8 (MeO), 83.3 and 84.4 (C-8, -9), 108.1 (C-7), 112.9 (*C*Me$_2$), 118.7 (C-5), 126.6, 128.6, 129.0, 130.2 (ArC), and 157.1 (C-3); *m*/*z* 305 (M$^+$), 290, 274 and 248.

**(5*R*,7*R*,8*R*,9*S*)-8,9-Isopropylidenedioxy-7-methoxy-3-(4-methylphenyl)-1,6-dioxa-2-azaspiro[4.4]non-2-ene 6e.** Compound **6e** was prepared from **5** and *p*-methylbenzaldoxime according to the general procedure above and was isolated by subsequent column chromatography (hexane–ethyl acetate 15:1) as a colorless oil (176 mg, 55%), $[\alpha]_D$ +59.4 (*c* 0.21, $CHCl_3$) (Found: C, 63.96; H, 6.62; N, 4.44. Calc. for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39%); $\delta_H$ ($CDCl_3$) 1.35 (3H, s, $CMe_2$), 1.49 (3H, s, $CMe_2$), 2.36 (3H, s, Ar$CH_3$), 3.29 (1H, d, *J* 18.4, 4-H$^a$), 3.40 (3H, s, MeO), 3.75 (1H, d, *J* 18.4, 4-H$^b$), 4.76 (1H, d, *J* 5.7, 8-H), 4.87 (1H, d, *J* 5.7, 9-H), 5.05 (1H, s, 7-H), 7.19 (2H, d, *J* 8.1, *m*-ArH), 7.57 (2H, d, *J* 8.1, *o*-ArH); $\delta_C$ ($CDCl_3$) 21.3 (Ar$CH_3$), 24.8 and 26.3 (C*Me*$_2$), 41.6 (C-4), 54.8 (MeO), 83.3 and 84.4 (C-8, -9), 108.1 (C-7), 112.8 (*C*Me$_2$), 118.6 (C-5), 126.2, 126.6, 129.3, 140.4 (ArC), and 157.0 (C-3); *m/z* 319 ($M^+$), 304 and 290.

**(5*R*,7*S*,8*R*,9*R*,10*S*)-8,9,10-Tris(benzyloxy)-7-methoxy-3-phenyl-1,6-dioxa-2-azaspiro[4.5]dec-2-ene 13d.** Compound **13d** (as a mixture with its minor epimer in a 17:1 ratio) was prepared from **1** and benzaldoxime according to the general procedure above and was isolated by subsequent column chromatography (hexane–ethyl acetate 10:1) as a colorless oil (226 mg, 40%). The major isomer **13d** was crystallised from diethyl ether–hexane as a white solid, mp 99–101 °C; $[\alpha]_D$ −30.5 (*c* 2.54, $CHCl_3$) (Found: C, 74.53; H, 6.18; N, 2.47. Calc. for $C_{35}H_{35}NO_6$: C, 74.32; H, 6.24; N, 2.48%); $\delta_H$ ($CDCl_3$) 3.42 (3H, s, MeO), 3.45 (1H, d, *J* 18.3, 4-H$^a$), 3.69 (1H, dd, *J* 9.0, 4.1, 8-H), 3.89 (1H, d, *J* 18.3, 4-H$^b$), 3.90 (2H, m, 9-, 10-H), 4.65 (1H, d, *J* 4.1, 7-H), 4.66 (1H, d, *J* 11.9, PhC*H*$_2$), 4.74 (1H, d, *J* 11.0, PhC*H*$_2$), 4.88 (3H, m, PhC*H*$_2$), 4.92 (1H, d, *J* 11.0, PhC*H*$_2$), 7.49 (18H, m, 3 × *Ph*CH$_2$ and *m*- and *p*-H of 3-Ph), 7.69 (2H, m, *o*-H of 3-Ph); $\delta_C$ ($CDCl_3$) 40.8 (C-4), 57.0 (MeO), 73.8, 75.3 and 75.7 (C-8, -9, -10), 78.5 (two peaks) and 80.2 (3 × Ph*C*H$_2$), 99.8 (C-7), 111.8 (C-5), 126.7, 127.65, 127.66, 127.9, 128.1, 128.15, 128.25, 128.3, 128.5, 128.6, 128.7, 130.5, 137.8, 137.9, 138.5, 141.7 (ArC), and 159.2 (C-3); *m/z* 565 ($M^+$) and 534.

**(5*R*,7*S*,8*R*,9*R*,10*S*)-8,9,10-Tris(benzyloxy)-7-methoxy-3-(4-methylphenyl)-1,6-dioxa-2-azaspiro[4.5]dec-2-ene 13e.** Compound **13e** was prepared as a single diastereoisomer from **1** and *p*-methylbenzaldoxime according to the general procedure above and was isolated by subsequent column chromatography (hexane–ethyl acetate 10:1) as colorless crystals (255 mg, 44%), mp 178–180 °C (from diethyl ether–hexane); $[\alpha]_D$ −47.8 (*c* 0.5, $CHCl_3$) (Found: C, 74.63; H, 6.43; N, 2.35. Calc. for $C_{36}H_{37}NO_6$: C, 74.59; H, 6.43; N, 2.42%); $\delta_H$ ($CDCl_3$) 2.39 (3H, s, Ar$CH_3$), 3.41 (3H, s, MeO), 3.44 (1H, d, *J* 18.0, 4-H$^a$), 3.69 (1H, dd, *J* 9.0, 3.8, 8-H), 3.85 (1H, d, *J* 18.0, 4-H$^b$), 3.88 (2H, m, 9-, 10-H), 4.65 (1H, d, *J* 3.8, 7-H), 4.66 (1H, d, *J* 11.2, PhC*H*$_2$), 4.73 (1H, d, *J* 10.8, PhC*H*$_2$), 4.82 (1H, d, *J* 11.2, PhC*H*$_2$), 4.83 (1H, d, *J* 12.0, PhC*H*$_2$), 4.86 (1H, d, *J* 12.0, PhC*H*$_2$), 4.91 (1H, d, *J* 10.8, PhC*H*$_2$), 7.26 (17H, m, 3 × *Ph*CH$_2$ and 2 × *m*-H of 3-tolyl), 7.57 (2H, d, *J* 7.5, *o*-H of 3-tolyl); $\delta_C$ ($CDCl_3$) 21.4 (Ar*C*H$_3$), 40.3 (C-4), 56.7 (MeO), 73.8, 75.3 and 75.8 (C-8, -9, -10), 78.85, 78.88 and 80.2 (3 × Ph*C*H$_2$), 99.8 (C-7), 111.3 (C-4), 126.3, 126.7, 127.63, 127.66, 127.9, 128.02, 128.08, 128.12, 128.23, 128.32, 128.5, 129.5, 137.8, 137.9, 138.5, 140.8 (ArC), and 158.5 (C-3); *m/z* 579 ($M^+$).

**(5*R*,7*R*,8*R*,9*S*)-8,9-Isopropylidenedioxy-3-[(2′*R*,3′*R*,4′*R*,5′*R*)-3′,4′-isopropylidenedioxy-5′-methoxytetrahydrofuran-2′-yl]-7-methoxy-1,6-dioxa-2-azaspiro[4.4]non-2-ene 32.** Compound **32** was prepared from **5** and oxime **31**[30] according to the general procedure above. Subsequent column chromatography (hexane–ethyl acetate 15:1) gave, first, the dimer **33** (78 mg, 15%) as a colorless oil (Found: C, 50.11; H, 6.19; N, 6.44. Calc. for $C_{18}H_{26}N_2O_{10}$: C, 50.23; H, 6.09; N, 6.51%), followed by compound **32** as colorless crystals (193 mg, 48%), mp 70–72 °C (from diethyl ether–hexane); $[\alpha]_D$ +39.4 (*c* 1.24, $CHCl_3$) (Found: C, 53.92; H, 6.77; N, 3.53. Calc. for $C_{18}H_{27}NO_9$: C, 53.86; H, 6.78; N, 3.49%); $\delta_H$ ($CDCl_3$) 1.32 (6H, s, $CMe_2$), 1.44 (3H, s, $CMe_2$), 1.50 (3H, s, $CMe_2$), 2.96 (1H, d, *J* 18.8, 4-H$^a$), 3.37 (3H, s, MeO), 3.38 (3H, s, MeO), 3.48 (1H, d, *J* 18.8, 4-H$^b$), 4.63 (1H, d, *J* 5.9, 4′-H), 4.71 (1H, d, *J* 5.7, 8-H), 4.77 (1H, d, *J* 5.7, 9-H), 4.95 (1H, s, 2′-H), 5.01 (1H, s, 5′-H), 5.02 (1H, s, 7-H), 5.27 (1H, d, *J* 5.9, 3′-H); $\delta_C$ ($CDCl_3$) 24.9, 25.0, 26.28 and 26.34 (2 × C*Me*$_2$), 41.7 (C-4), 54.8 (MeO), 55.8 (MeO), 81.3, 81.7, 83.2, 84.3 and 85.1 (C-8, -9, -2′, -3′, -4′), 108.1 (C-7), 110.5 (C-5′), 112.6 and 112.9 (2 × *C*Me$_2$), 118.8 (C-5), 158.7 (C-3); *m/z* 401 ($M^+$), 386, 371, 370, 354, 338, 312 and 284.

For furoxan **33**: $\delta_H$ ($CDCl_3$) 1.35 (3H, s, $CMe_2$), 1.38 (3H, s, $CMe_2$), 1.50 (3H, s, $CMe_2$), 1.53 (3H, s, $CMe_2$), 3.13 (3H, s, MeO), 3.19 (3H, s, MeO), 4.73 (1H, d, *J* 5.9, 4′-H), 4.77 (1H, d, *J* 5.7, 4″-H), 5.03 (1H, s, 5′-H), 5.09 (1H, s, 5″-H), 5.35 (1H, s, 2′-H), 5.47 (1H, s, 2″-H), 5.63 (1H, d, *J* 5.7, 3″-H), 5.67 (1H, d, *J* 5.9, 3′-H); $\delta_C$ ($CDCl_3$) 24.8, 24.9 and 26.3 (two peaks) (2 × C*Me*$_2$), 55.2 (MeO), 55.7 (MeO), 76.0, 78.7, 79.1, 80.0, 85.0 and 85.3 (C-2′, C-2″, C3′, C-3″, C-4′, C-4″), 110.3 and 110.6 (C-5′, -5″), 112.4 and 112.9 (2 × *C*Me$_2$), 113.0 (C-5), 156.3 (C-4).

**General procedure for the catalytic hydrogenation of spiro-isoxazolines 6, 13 and 32**

To a solution of **6**, a spiro-compound **13** or **32** (0.5 mmol) in MeOH–AcOH 6:1 (20 ml) were added $MgSO_4$ (200 mg) and a catalytic amount of Raney Ni and the mixture was stirred at room temperature for 90 min under $H_2$. The solids were then filtered off, the solvent was removed under reduced pressure, and purification of the products was accomplished by column chromatography.

**(3*R*,4*S*,5*S*)-2-[(*Z*)-Amino(2,6-dichlorophenyl)methylene]-4,5-isopropylidenedioxy-3-methoxycyclopentanone 7 and (3*R*,4*S*,-5*S*)-2-[(*Z*)-amino(2,6-dichlorophenyl)methylene]-3-hydroxy-4,5-(isopropylidenedioxy)cyclopentanone 8.** Hydrogenation of spiro-isoxazoline **6a** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 4:1) gave compound **7** (115 mg, 64%) as colorless crystals, mp 202 °C (decomp.) (from diethyl ether–hexane), followed by compound **8** (29 mg, 17%) as colorless crystals, mp 88 °C (decomp.) (from diethyl ether–hexane). For (3*R*,4*S*,5*S*)-2-[(*Z*)-amino(2,6-dichlorophenyl)methylene]-4,5-isopropylidenedioxy-3-methoxycyclopentanone **7**: $[\alpha]_D$ +148.3 (*c* 0.29, $CHCl_3$) (Found: C, 53.81; H, 4.68; N, 3.70. $C_{16}H_{17}Cl_2NO_4$ requires C, 53.65; H, 4.78; N, 3.91%); $\delta_H$ ($CDCl_3$) 1.36 (3H, s, $CMe_2$), 1.38 (3H, s, $CMe_2$), 2.95 (3H, s, MeO), 3.90 (1H, s, 3-H), 4.43 (1H, d, *J* 5.9, 5-H), 4.71 (1H, d, *J* 5.9, 4-H), 5.76 (1H, s br, NH), 7.36 (3H, m, ArH), 9.90 (1H, s br, NH); $\delta_C$ ($CDCl_3$) 25.8 and 27.4 (C*Me*$_2$), 55.9 (MeO), 79.2 (C-3), 81.3 and 82.9 (C-4, -5), 103.2 (C-2), 111.9 (*C*Me$_2$), 127.9, 128.0, 131.0, 132.4, 132.7, 134.4 (ArC), 159.3 (=CNH$_2$), 198.5 (C-1); *m/z* 357/359/361 ($M^+$/$M^+ + 2$/$M^+ + 4$), 322/324 and 269/271/273.

For (3*R*,4*S*,5*S*)-2-[(*Z*)-amino(2,6-dichlorophenyl)methylene]-3-hydroxy-4,5-(isopropylidenedioxy)cyclopentanone **8**: $[\alpha]_D$ +93.3 (*c* 0.15, $CHCl_3$) (Found: C, 52.28; H, 4.35; N, 3.94. $C_{15}H_{15}Cl_2NO_4$ requires C, 52.34; H, 4.39; N, 4.07%); $\delta_H$ ($CDCl_3$) 1.34 (3H, s, C*Me*$_2$), 1.36 (3H, s, C*Me*$_2$), 4.32 (1H, s, 3-H), 4.42 (1H, d, *J* 5.3, 5-H), 4.73 (1H, d, *J* 5.3, 4-H), 5.75 (1H, s br, NH), 7.40 (3H, m, ArH), 9.79 (1H, s br, NH); $\delta_C$ ($CDCl_3$) 26.0 and 27.6 (C*Me*$_2$), 73.0 (C-3), 81.0 and 82.0 (C-4, -5), 105.8 (C-2), 112.0 (*C*Me$_2$), 128.3, 128.5, 131.5, 132.5, 133.1, 133.6 (ArC), 158.2 (=*C*NH$_2$), 200.1 (C-1); *m/z* 343/345/347 ($M^+$/$M^+ + 2$/$M^+ + 4$), 308/310 and 232/234.

**(*Z*,4*S*,5*S*)-1-Amino-1-(2,6-dichlorophenyl)-6-hydroxy-4,5-(isopropylidenedioxy)hex-1-en-3-one 9.** Hydrogenation of spiro-isoxazoline **6a** according to the general procedure above using MeOH–water (9 : 1) as solvent in the presence of $H_3BO_3$ (2.2 equiv.) and subsequent column chromatography (hexane–ethyl acetate 4 : 1) gave further to compounds **7** (5%) and **8** (5%), compound **9** as an oil (62 mg, 18%) (Found: C, 52.24; H, 5.06; N, 4.25. Calc. for $C_{15}H_{17}Cl_2NO_4$: C, 52.04; H, 4.95; N, 4.05%); $\delta_H$ ($CDCl_3$) 1.26 (3H, s, $CMe_2$), 1.54 (3H, s, $CMe_2$), 3.09 (1H, s br, OH), 3.65 (1H, dd, *J* 11.5, 7.0, 6-H[a]), 3.73 (1H, dd, *J* 11.5, 6.0, 6-H[b]), 4.54 (1H, m, 5-H), 4.66 (1H, d, *J* 8.1, 4-H), 5.35 (1H, s br, NH), 5.63 (1H, s, 2-H), 7.35 (3H, m, ArH), 10.13 (1H, s br, NH); $\delta_C$ ($CDCl_3$) 25.0 and 27.0 (C*Me*$_2$), 62.0 (C-6), 78.5 and 80.7 (C-4, -5), 94.3 (C-2), 109.8 (*C*Me$_2$), 128.3, 130.8, 133.6, 134.9 (ArC), 159.0 (C-1) and 198.0 (C-3); *m*/*z* 345/347/349 ($M^+$/$M^+ + 2$/$M^+ + 4$).

**(2*S*,3*S*)-5-[(*Z*)-1-Aminoethylidene]-2,3-(isopropylidenedioxy)-cyclopentanone 10b and (2*S*,3*S*)-5-[(*Z*)-1-hydroxyethylidene]-2,3-(isopropylidenedioxy)cyclopentanone 11b.** Hydrogenation of spiro-isoxazoline **6b** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 3 : 1) gave compound **11b** (19 mg, 23%) as an oil (Found: C, 60.74; H, 7.28. $C_{10}H_{14}O_4$ requires C, 60.59; H, 7.12%), followed by compound **10b** (60 mg, 64%) as colorless crystals, mp 165 °C (decomp.) (from diethyl ether–hexane). For (2*S*,3*S*)-5-[(*Z*)-1-aminoethylidene]-2,3-(isopropylidenedioxy)cyclopentanone **10b**: $[a]_D$ −4.4 (*c* 0.5, $CHCl_3$); $\delta_H$ ($CDCl_3$) 1.37 (3H, s, $CMe_2$), 1.41 (3H, s, $CMe_2$), 1.97 (3H, s, =CMe), 2.65 (1H, d, *J* 15.3, 4-H[a]), 2.75 (1H, dd, *J* 15.3, 5.2, 4-H[b]), 4.49 (1H, d, *J* 5.5, 2-H), 4.69 (1H, dd, *J* 5.5, 5.2, 3-H), 5.55 (1H, s br, NH), 9.70 (1H, s br, NH); $\delta_C$ ($CDCl_3$) 20.6 (=C*Me*), 25.6 and 27.4 (C*Me*$_2$), 30.6 (C-4), 74.7 (C-3), 82.2 (C-2), 99.1 (C-5), 110.9 (*C*Me$_2$), 160.5 (=$CNH_2$), 196.7 (C-1) [MALDI-FTMS Found: M + $H^+$, 198.1123. $C_{10}H_{16}NO_3$ (M + $H^+$) require *m*/*z* 198.1130.

For (2*S*,3*S*)-5-[(*Z*)-1-hydroxyethylidene]-2,3-(isopropylidenedioxy)cyclopentanone **11b**: $\delta_H$ ($CDCl_3$) 1.38 (3H, s, $CMe_2$), 1.42 (3H, s, $CMe_2$), 2.11 (3H, s, =CMe), 2.71 (1H, d, *J* 14.5, 4-H[a]), 2.80 (1H, dd, *J* 14.5, 5.5, 4-H[b]), 4.72 (1H, dd, *J* 5.5, 5.0, 3-H), 4.80 (1H, d, *J* 5.0, 2-H); $\delta_C$ ($CDCl_3$) 22.6 (=C*Me*), 25.4 and 27.3 (C*Me*$_2$), 31.0 (C-4), 75.0 (C-3), 81.2 (C-2), 107.4 (C-5), 111.5 (*C*Me$_2$), 186.1 (=COH), 190.5 (C-1).

**(2*S*,3*S*)-5-[(*Z*)-1-Aminopropylidene]-2,3-(isopropylidene-dioxy)cyclopentanone 10c.** Hydrogenation of spiro-isoxazoline **6c** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 3 : 1) gave compound **10c** as colorless crystals (91 mg, 43%), mp 117 °C (decomp.) (from diethyl ether–hexane); $[a]_D \approx 0$ (*c* 0.4, $CHCl_3$) (Found: C, 62.34; H, 8.01; N, 6.52. Calc. for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63%); $\delta_H$ ($CDCl_3$) 1.18 (3H, t, *J* 7.5, $CH_2CH_3$), 1.37 (3H, s, $CMe_2$), 1.40 (3H, s, $CMe_2$), 2.25 (2H, q, *J* 7.5, C*H*$_2$CH$_3$), 2.65 (1H, d, *J* 15.4, 4-H[a]), 2.75 (1H, dd, *J* 15.4, 5.5, 4-H[b]), 4.49 (1H, d, *J* 5.9, 2-H), 4.70 (1H, dd, *J* 5.9, 5.5, 3-H), 5.63 (1H, br s, NH), 9.86 (1H, br s, NH); $\delta_C$ ($CDCl_3$) 10.5 ($CH_2CH_3$), 25.5, 27.1 and 27.4 (C*Me*$_2$, *C*H$_2$CH$_3$), 30.2 (C-4), 74.7 (C-3), 82.2 (C-2), 98.1 (C-5), 110.8 (*C*Me$_2$), 165.3 (=$CNH_2$) and 196.9 (C-1); *m*/*z* 211 ($M^+$), 196, 170 and 153.

**(2*S*,3*S*)-5-[(*Z*)-Amino(phenyl)methylene]-2,3-(isopropylidene-dioxy)cyclopentanone 10d and (1*R*,5*R*,6*S*,7*R*)-6,7-isopropyl-idenedioxy-3-phenyl-8-oxa-2-azabicyclo[3.2.1]octan-5-ol 12d.** Hydrogenation of spiro-isoxazoline **6d** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 3 : 1) gave compound **12d** (16 mg, 11%) as an oil, followed by compound **10d** (62 mg, 48%), mp 165 °C (decomp.) (from diethyl ether–hexane). For (1*R*,5*R*,6*S*,7*R*)-6,7-isopropylidenedioxy-3-phenyl-8-oxa-2-azabicyclo[3.2.1]octan-5-ol **12d**: $\delta_H$ ($CDCl_3$) 1.42 (3H, s, $CMe_2$), 1.56 (3H, s, $CMe_2$), 2.08 (2H, m, 4-$H^2$), 3.22 (2H, br s, NH, OH), 3.87 (1H, dd, *J* 11.8, 4.9, 3-H), 4.44 (1H, d, *J* 5.6, 6-H), 4.82 (1H, d, *J* 5.6, 7-H), 4.91 (1H, s, 1-H), 7.35 (5H, m, ArH); $\delta_C$ ($CDCl_3$) 25.2 and 26.0 (C*Me*$_2$), 39.4 (C-4), 52.9 (C-3), 80.0 and 83.0 (C-6, -7), 88.3 (C-1), 101.5 (C-5), 113.1 (*C*Me$_2$), 126.3, 127.9, 128.8 and 140.9 (ArC) [MALDI-FTMS Found: (M + $H^+$ − $H_2O$), 260.1279. $C_{15}H_{18}NO_3$ (M + $H^+$ − $H_2O$) requires *m*/*z*, 260.1287.

For (2*S*,3*S*)-5-[(*Z*)-amino(phenyl)methyene]-2,3-(isopropylidenedioxy)cyclopentanone **10d**: $[a]_D$ −110.0 (*c* 0.3, $CHCl_3$); $\delta_H$ ($CDCl_3$) 1.38 (3H, s, $CMe_2$), 1.44 (3H, s, $CMe_2$), 2.62 (1H, d, *J* 15.5, 4-H[a]), 2.88 (1H, dd, *J* 15.5, 5.0, 4-H[b]), 4.56 (1H, d, *J* 5.0, 2-H), 4.68 (1H, dd as t, *J* 5.0, 3-H), 5.31 (1H, s br, NH), 7.22 (5H, m, ArH), 9.98 (1H, s br, NH); $\delta_C$ ($CDCl_3$) 25.6 and 27.5 (C*Me*$_2$), 31.4 (C-4), 74.9 (C-3), 82.3 (C-2), 99.2 (C-5), 111.1 (*C*Me$_2$), 127.2, 128.8, 130.2, 136.4 (ArC), 160.2 (=$CNH_2$) and 199.3 (C-1); *m*/*z* 259 ($M^+$) and 201 [MALDI-FTMS Found: M + $Na^+$, 282.1100. $C_{15}H_{17}NNaO_3$ (M + $Na^+$) requires *m*/*z*, 282.1106.

**(2*S*,3*S*)-5-[(*Z*)-Amino(4-methylphenyl)methylene]-2,3-(iso-propylidenedioxy)cyclopentanone 10e.** Hydrogenation of spiro-isoxazoline **6e** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 3 : 1) gave compound **10e** as colorless crystals (72 mg, 53%), mp 195–198 °C (from diethyl ether–hexane); $[a]_D$ −58.9 (*c* 0.17, $CHCl_3$); $\delta_H$ ($CDCl_3$) 1.36 (3H, s, $CMe_2$), 1.42 (3H, s, $CMe_2$), 2.40 (3H, s, Ar*Me*), 2.67 (1H, d, *J* 15.9, 4-H[a]), 2.87 (1H, dd, *J* 15.9, 5.0, 4-H[b]), 4.55 (1H, d, *J* 5.7, 2-H), 4.65 (1H, dd, *J* 5.7, 5.0, 3-H), 5.24 (1H, br s, NH), 7.25 (2H, d, *J* 8.2, *m*-ArH), 7.36 (2H, d, *J* 8.2, *o*-ArH), 9.98 (1H, br s, NH); $\delta_C$ ($CDCl_3$) 21.4 (Ar-*Me*), 25.7 and 27.5 (C*Me*$_2$), 31.5 (C-4), 74.9 (C-3), 82.3 (C-2), 99.1 (C-5), 111.1 (*C*Me$_2$), 127.2, 128.8, 130.2, 140.5 (ArC), 160.4 (=$CNH_2$) and 199.1 (C-1); *m*/*z* 273 ($M^+$), 258 and 215 [MALDI-FTMS Found: M + $H^+$, 274.1433. $C_{16}H_{20}NO_3$ (M + $H^+$) requires *m*/*z*, 274.1443].

**(2*S*,3*R*,4*S*)-6-[(*Z*)-Amino(2,6-dichlorophenyl)methylene]-2,3,4-tris(benzyloxy)cyclohexanone 14a.** Hydrogenation of spiro-isoxazoline **13a** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 7 : 1) gave compound **14a** as colorless crystals (235 mg, 80%), mp 104–105 °C (from diethyl ether–hexane); $[a]_D$ −9.9 (*c* 0.93, $CHCl_3$) (Found: C, 69.68; H, 5.39; N, 2.41. Calc. for $C_{34}H_{31}Cl_2NO_4$: C, 69.39; H, 5.31; N, 2.38%); $\delta_H$ ($CDCl_3$) 2.18 (1H, dd, *J* 14.6, 5.0, 5-H[eq]), 2.22 (1H, dd, *J* 14.6, 8.4, 5-H[ax]), 3.68 (1H, ddd, *J* 8.4, 7.3, 5.0, 4-H), 3.83 (1H, dd as t, *J* 7.3, 3-H), 4.03 (1H, d, *J* 7.3, 2-H), 4.48 (1H, d, *J* 12.0, PhC*H*$_2$), 4.53 (1H, d, *J* 12.0, PhC*H*$_2$), 4.73 (1H, d, *J* 11.0, PhC*H*$_2$), 4.76 (1H, d, *J* 11.0, PhC*H*$_2$), 4.78 (1H, d, *J* 11.5, PhC*H*$_2$), 5.10 (1H, d, *J* 11.5, PhC*H*$_2$), 7.30 (18H, m, ArH); $\delta_C$ ($CDCl_3$) 28.2 (C-5), 71.7, 73.8, 74.2, 78.5 and 84.1 (two peaks) (C-2, -3, -4 and 3 × Ph*C*H$_2$), 99.0 (C-6), 127.4, 127.5, 127.6, 127.9, 128.1, 128.2, 128.3, 128.5, 130.8, 133.4, 134.1, 138.47, 138.52, 138.55 (ArC), 155.3 (=$CNH_2$) and 196.0 (C-1); *m*/*z* 587/589/591 ($M^+$/$M^+ + 2$/$M^+ + 4$) and 495/497/499.

**(2*S*,3*R*,4*S*)-6-[(*Z*)-1-Aminoethylidene]-2,3,4-tris(benzyloxy)-cyclohexanone 14b and (2*S*,3*R*,4*S*)-2,3,4-tris(benzyloxy)-6-[(*Z*)-1-hydroxyethylidene]cyclohexanone 15b.** Hydrogenation of spiro-isoxazoline **13b** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 5 : 1) gave compound **15b** (34 mg, 15%) as a syrup, followed by compound **14b** (80 mg, 35%), also as a syrup.

For (2*S*,3*R*,4*S*)-2,3,4-tris(benzyloxy)-6-[(*Z*)-1-hydroxyethylidene]cyclohexanone **15b**: $[a]_D \approx 0$ (*c* 0.1, $CHCl_3$); $\delta_H$ ($CDCl_3$) 2.13 (3H, s, Me), 2.40 (1H, dd, *J* 14.8, 8.8, 5-H[ax]), 2.69 (1H, dd, *J* 14.8, 5.0, 5-H[eq]), 3.67 (1H, ddd, *J* 8.8, 8.5, 5.0, 4-H), 3.78 (1H, dd as t, *J* 8.5, 7.3, 3-H), 4.17 (1H, d, *J* 7.3, 2-H), 4.66 (1H, d, *J* 12.0, PhC*H*$_2$), 4.72 (1H, d, *J* 12.5, PhC*H*$_2$), 4.76 (1H, d, *J* 12.5, PhC*H*$_2$), 4.79 (1H, d, *J* 11.0, PhC*H*$_2$), 4.83 (1H, d, *J* 12.0, PhC*H*$_2$), 5.04 (1H, d, *J* 11.0, PhC*H*$_2$), 7.35 (15H, m, ArH), 15.5 (1H, br s, OH); $\delta_C$ ($CDCl_3$) 22.6 (Me), 28.7 (C-5), 72.6, 74.7, 75.2, 76.5, 80.2 and 82.5 (C-2, -3, -4 and 3 × Ph*C*H$_2$), 103.9 (C-6), 127.68, 127.71, 127.77, 127.95, 128.1, 128.2, 128.3, 128.35, 128.41, 138.0, 138.3, 138.34 (ArC), 178.6 (=COH) and 198.4 (C-1) [MALDI-FTMS Found: M + Na$^+$, 481.1983. $C_{29}H_{30}NaO_5$ (M + Na$^+$) requires: 481.1991.

For (2*S*,3*R*,4*S*)-6-[(*Z*)-1-aminoethylidene]-2,3,4-tris(benzyloxy)cyclohexanone **14b**: $[a]_D$ +77.2 (*c* 0.1, $CHCl_3$); $\delta_H$ ($CDCl_3$) 2.16 (3H, s, Me), 2.45 (1H, dd, *J* 14.5, 8.2, 5-H$^{ax}$), 2.61 (1H, dd, *J* 14.5, 4.9, 5-H$^{eq}$), 3.73 (1H, ddd, *J* 8.2, 7.0, 4.9, 4-H), 3.79 (1H, dd as t, *J* 7.5, 7.0, 3-H), 3.97 (1H, d, *J* 7.5, 2-H), 4.63 (1H, d, *J* 11.8, PhC*H*$_2$), 4.69 (1H, d, *J* 11.8, PhC*H*$_2$), 4.71 (1H, d, *J* 11.5, PhC*H*$_2$), 4.75 (1H, d, *J* 13.0, PhC*H*$_2$), 4.79 (1H, d, *J* 13.0, PhC*H*$_2$), 5.09 (1H, d, *J* 11.5, PhC*H*$_2$), 5.23 (1H, br s, NH), 7.30 (15H, m, ArH), 10.66 (1H, br s, NH); $\delta_C$ ($CDCl_3$) 21.4 (Me), 28.6 (C-5), 71.9, 74.0, 74.3, 78.5, 83.8 and 83.85 (C-2, -3, -4 and 3 × Ph*C*H$_2$), 97.0 (C-6), 120.0, 124.3, 127.4, 127.5, 127.6, 127.7, 128.0, 128.24, 128.31, 128.36, 129.0, 138.66, 138.71 (ArC), 161.2 (=$CNH_2$) and 192.9 (C-1) [MALDI-FTMS Found: M + H$^+$, 458.2331. $C_{29}H_{32}NO_4$ (M + H$^+$) requires *m*/*z* 458.2331.

**(2*S*,3*R*,4*S*)-6-[(*Z*)-1-Aminopropylidene]-2,3,4-tris(benzyloxy)cyclohexanone 14c and (2*S*,3*R*,4*S*)-2,3,4-tris(benzyloxy)-6-[(*Z*)-1-hydroxypropylidene]cyclohexanone 15c.** Hydrogenation of spiro-isoxazoline **13c** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 5:1) gave compound **15c** (36 mg, 15%) as a syrup, followed by compound **14c** (68 mg, 29%), also as a syrup.

For (2*S*,3*R*,4*S*)-2,3,4-tris(benzyloxy)-6-[(*Z*)-1-hydroxypropylidene]cyclohexanone **15c**: $[a]_D$ ≈0 (*c* 0.1, $CHCl_3$); $\delta_H$ ($CDCl_3$) 1.11 (3H, t, *J* 7.3, $CH_2CH_3$), 2.34–2.48 (3H, m, $CH_2CH_3$ and 5-H$^{ax}$), 2.70 (1H, dd, *J* 14.8, 5.2, 5-H$^{eq}$), 3.67 (1H, ddd, *J* 9.0, 8.9, 5.2, 4-H), 3.78 (1H, dd, *J* 8.9, 7.3, 3-H), 4.19 (1H, d, *J* 7.3, 2-H), 4.67 (1H, d, *J* 11.7, PhC*H*$_2$), 4.74 (1H, d, *J* 12.9, PhC*H*$_2$), 4.77 (1H, d, *J* 11.7, PhC*H*$_2$), 4.78 (1H, d, *J* 11.0, PhC*H*$_2$), 4.81 (1H, d, *J* 12.9, PhC*H*$_2$), 5.05 (1H, d, *J* 11.0, PhC*H*$_2$), 7.35 (15H, m, ArH), 15.5 (1H, br s, OH); $\delta_C$ ($CDCl_3$) 8.1 ($CH_2CH_3$), 28.1 and 29.7 (C-5 and $CH_2CH_3$), 72.6, 74.7, 75.75, 75.8, 80.2 and 82.6 (C-2, -3, -4 and 3 × Ph*C*H$_2$), 103.4 (C-6), 127.7, 127.9, 128.1, 128.2, 128.35, 128.4, 138.1, 138.3, 138.4, 176.5 (=COH) and 198.1 (C-1) [MALDI-FTMS Found: M + Na$^+$, 495.2138. $C_{30}H_{32}NaO_5$ (M + Na$^+$) requires *m*/*z*, 495.2147.

For (2*S*,3*R*,4*S*)-6-[(*Z*)-1-aminopropylidene]-2,3,4-tris(benzyloxy)cyclohexanone **14c**: $[a]_D$ +8.4 (*c* 0.5, $CHCl_3$); $\delta_H$ ($CDCl_3$) 1.13 (3H, t, *J* 7.4, $CH_2CH_3$), 2.23 (2H, q, *J* 7.4, $CH_2CH_3$), 2.47 (1H, dd, *J* 14.5, 8.4, 5-H$^{ax}$), 2.61 (1H, dd, *J* 14.5, 5.0, 5-H$^{eq}$), 3.72 (1H, ddd, *J* 8.4, 7.3, 5.0, 4-H), 3.79 (1H, dd as t, *J* 7.3, 3-H), 3.97 (1H, d, *J* 7.3, 2-H), 4.62 (1H, d, *J* 11.4, PhC*H*$_2$), 4.69 (1H, d, *J* 11.4, PhC*H*$_2$), 4.70 (1H, d, *J* 12.0, PhC*H*$_2$), 4.74 (1H, d, *J* 12.0, PhC*H*$_2$), 4.79 (1H, d, *J* 11.0, PhC*H*$_2$), 5.09 (1H, d, *J* 11.0, PhC*H*$_2$), 5.25 (1H, br s, NH), 7.30 (15H, m, ArH), 10.81 (1H, br s, NH); $\delta_C$ ($CDCl_3$) 11.2 ($CH_2CH_3$), 27.3 and 27.9 (C-5 and $CH_2CH_3$), 71.8, 73.8, 74.2, 78.7, 83.8, 83.9 (C-2, -3, -4 and 3 × Ph*C*H$_2$), 96.2 (C-6), 127.4, 127.5, 127.6, 128.0, 128.2, 128.24, 128.31, 138.6, 138.7 (ArC), 165.9 (=$CNH_2$), 193.1 (C-1) [MALDI-FTMS Found: M + Na$^+$, 494.2311. $C_{30}H_{33}NNaO_4$ (M + Na$^+$) requires *m*/*z*, 494.2307.

**(2*S*,3*R*,4*S*)-6-[(*Z*)-Amino(phenyl)methylene]-2,3,4-tris(benzyloxy)cyclohexanone 14d.** Hydrogenation of spiro-isoxazoline **13d** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 8:1) gave compound **14d** as a syrup (135 mg, 52%), $[a]_D$ +3.0 (*c* 0.3, $CHCl_3$); $\delta_H$ ($CDCl_3$) 2.43 (1H, dd, *J* 15.0, 4.6, 5-H$^{eq}$), 2.50 (1H, dd, *J* 15.0, 7.1, 5-H$^{ax}$), 3.67 (1H, m, 4-H), 3.81 (1H, dd, *J* 7.3, 7.0, 3-H), 4.09 (1H, d, *J* 7.3, 2-H), 4.38 (2H, s, PhC*H*$_2$), 4.67 (1H, d, *J* 11.0, PhC*H*$_2$), 4.74 (1H, d, *J* 11.5, PhC*H*$_2$), 4.76 (1H, d, *J* 11.0, PhC*H*$_2$), 5.08 (1H, br s, NH), 5.09 (1H, d, *J* 11.5, PhC*H*$_2$), 7.30 (20H, m, ArH), 10.34 (1H, br s, NH); $\delta_C$ ($CDCl_3$) 28.1 (C-5), 70.6, 73.3, 73.6, 78.8, 84.1 and 84.2 (C-2, -3, -4 and 3 × Ph*C*H$_2$), 97.4 (C-6), 127.4, 127.5, 127.7, 127.9, 128.2, 128.6, 129.6, 136.9, 138.4, 138.5, 138.6 (ArC), 161.2 (=$CNH_2$) and 195.1 (C-1) [MALDI-FTMS Found: M + Na$^+$, 542.2308. $C_{34}H_{33}NNaO_4$ (M + Na$^+$) requires *m*/*z*, 542.2307].

**(2*S*,3*R*,4*S*)-6-[(*Z*)-Amino(4-methylphenyl)methylene]-2,3,4-tris(benzyloxy)cyclohexanone 14e.** Hydrogenation of spiro-isoxazoline **13e** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 5:1) gave compound **14e** as a syrup (136 mg, 51%), $[a]_D$ −1.3 (*c* 0.3, $CHCl_3$); $\delta_H$ ($CDCl_3$) 2.40 (3H, s, Me), 2.46 (1H, dd, *J* 15.2, 4.0, 5-H$^{eq}$), 2.53 (1H, dd, *J* 15.2, 7.2, 5-H$^{ax}$), 3.67 (1H, m, 4-H), 3.81 (1H, dd, *J* 7.3, 7.2, 3-H), 4.08 (1H, d, *J* 7.3, 2-H), 4.38 (2H, s, PhC*H*$_2$), 4.67 (1H, d, *J* 11.2, PhC*H*$_2$), 4.74 (1H, d, *J* 11.9, PhC*H*$_2$), 4.75 (1H, d, *J* 11.2, PhC*H*$_2$), 5.03 (1H, br s, NH), 5.08 (1H, d, *J* 11.9, PhC*H*$_2$), 7.28 (17H, m, ArH), 7.46 (2H, d, *J* 7.4, *o*-H of $C_6H_4$Me), 10.35 (1H, br s, NH); $\delta_C$ ($CDCl_3$) 21.3 (Me), 28.2 (C-5), 70.7, 73.3, 73.6, 78.9, 84.1 and 84.2 (C-2, -3, -4 and 3 × Ph*C*H$_2$), 97.8 (C-6), 127.4, 127.5, 127.7, 128.0, 128.3, 129.3, 138.5, 138.6, 138.77, 139.8 (ArC), 161.5 (=$CNH_2$), 195.0 (C-1) [MALDI-FTMS Found: M + Na$^+$, 556.2457. $C_{35}H_{35}NNaO_4$ (M + Na$^+$) requires *m*/*z*, 556.2464.

**(2*S*,3*S*)-5-{(*Z*)-Amino[(2′*R*,3′*R*,4′*R*,5′*R*)-3′,4′-isopropylidenedioxy-5′-methoxytetrahydrofuran-2′-yl]methylene}-2,3-(isopropylidenedioxy)cyclopentanone 34, (3*R*,4*S*,5*S*)-2-{(*Z*)-amino[(2′*R*,3′*R*,4′*R*,5′*R*)-3′,4′-isopropylidenedioxy-5′-methoxytetrahydrofuran′2′-yl]methylene}-4,5-isopropylidenedioxy-3-methoxycyclopentanone 35 and (3*R*,4*S*,5*S*)-2-{(*Z*)-amino[(2′*R*,3′*R*,4′*R*,5′*R*)-3′,4′-isopropylidenedioxy-5′-methoxytetrahydrofuran-2′-yl]methylene}-3-hydroxy-4,5-(isopropylidenedioxy)cyclopentanone 36.** Hydrogenation of spiro-isoxazoline **32** according to the general procedure above and subsequent column chromatography (hexane–ethyl acetate 3:1) gave compound **35** (21 mg, 11%) as a syrup, followed by compound **34** (43 mg, 24%), also as a syrup and compound **36** (26 mg, 14%) again as a syrup.

For (2*S*,3*S*)-5-{(*Z*)-amino[(2′*R*,3′*R*,4′*R*,5′*R*)-3′,4′-isopropylidenedioxy-5′-methoxytetrahydrofuran-2′-yl]methylene}-2,3-(isopropylidenedioxy)cyclopentanone **34**: $[a]_D$ +53.1 (*c* 0.35, $CHCl_3$); $\delta_H$ ($CDCl_3$) 1.33 (3H, s, $CMe_2$), 1.37 (3H, s, $CMe_2$), 1.38 (3H, s, $CMe_2$), 1.40 (3H, s, $CMe_2$), 2.56 (1H, d, *J* 15.3, 4-H$^a$), 2.72 (1H, dd, *J* 15.3, 4.7, 4-H$^b$), 3.52 (3H, s, MeO), 4.49 (1H, d, *J* 5.7, 4′-H), 4.59 (1H, d, *J* 5.7, 3′-H), 4.66 (1H, d, *J* 4.5, 2-H), 4.72 (1H, dd as t, *J* 4.5, 3-H), 4.84 (1H, s, 2′-H), 5.15 (1H, s, 5′-H), 6.40 (1H, br s, NH), 9.54 (1H, br s, NH); $\delta_C$ ($CDCl_3$) 25.1, 25.6, 26.6 and 27.4 (2 × C*Me*$_2$), 29.6 (C-4), 56.5 (MeO), 75.0, 81.9, 84.7, 84.9 and 86.0 (C-2, -3, -2′, -3′, -4′), 96.5 (C-5), 111.0, 111.9 and 113.5 (C-5′ and 2 × *C*Me$_2$), 159.9 (=$CNH_2$), 198.4 (C-1); *m*/*z* 355 (M$^+$) and 340 [MALDI-FTMS Found: M + Na$^+$, 378.1526. $C_{17}H_{25}NNaO_7$ (M + Na$^+$) requires *m*/*z* 378.1528].

For (3*R*,4*S*,5*S*)-2-{(*Z*)-amino[(2′*R*,3′*R*,4′*R*,5′*R*)-3′,4′-isopropylidenedioxy-5′-methoxytetrahydrofuran-2′-yl]methylene}-4,5-isopropylidenedioxy-3-methoxycyclopentanone **35**: $[a]_D$ +63.8 (*c* 0.45, $CHCl_3$); $\delta_H$ ($CDCl_3$) 1.31 (3H, s, $CMe_2$), 1.38 (3H, s, $CMe_2$), 1.52 (3H, s, $CMe_2$), 1.53 (3H, s, C*Me*$_2$), 3.44 (3H, s, MeO), 3.53 (3H, s, MeO), 4.34 (1H, s, 3-H), 4.48 (1H, d, *J* 5.9, 5-H), 4.53 (1H, d, *J* 5.9, 4-H), 4.58 (1H, d, *J* 6.0, 4′-H), 4.85 (1H, d, *J* 6.0, 3′-H), 4.91 (1H, s, 2′-H), 5.15 (1H, s, 5′-H), 7.04 (1H, br s, NH), 9.93 (1H, br s, NH); $\delta_C$ ($CDCl_3$) 24.9, 25.5, 26.5 and 27.2 (2 × C*Me*$_2$), 55.9 (MeO), 56.5 (MeO), 78.4, 81.0, 82.3, 84.7, 85.6 and 86.5 (C-5, -4, -3, -2′, -3′, -4′), 100.4 (C-2), 111.1, 112.0 and 112.7 (C-5′ and 2 × *C*Me$_2$), 164.6 (=$CNH_2$), 197.1 (C-1); *m*/*z* 385 (M$^+$), 369, 355 [MALDI-FTMS Found: M + H$^+$, 386.1813. $C_{18}H_{28}NO_8$ (M + H$^+$) requires *m*/*z*, 386.1815].

For (3*R*,4*S*,5*S*)-2-{(*Z*)-amino[(2′*R*,3′*R*,4′*R*,5′*R*)-3′,4′-isopropylidenedioxy-5′-methoxytetrahydrofuran-2′-yl]methylene}-3-hydroxy-4,5-(isopropylidenedioxy)cyclopentanone **36**: $[a]_D$ +74.5 (*c* 0.38, $CHCl_3$); $\delta_H$ ($CDCl_3$) 1.34 (3H, s, $CMe_2$), 1.37 (6H, s, $CMe_2$), 1.57 (3H, s, $CMe_2$), 3.55 (3H, s, OMe), 4.53 (1H, d, $J$ 5.4, 4′-H), 4.62 (1H, d, $J$ 5.8, 5-H), 4.72 (1H, d, $J$ 5.4, 3′-H), 4.76 (1H, dd, $J$ 5.8, 2.7, 4-H), 4.88 (1H, d, $J$ 2.7, 3-H), 4.89 (1H, s, 2′-H), 5.18 (1H, s, 5′-H), 6.69 (1H, br s, NH), 9.83 (1H, br s, NH); $\delta_C$ ($CDCl_3$) 25.2, 25.7, 26.8 and 27.4 ($2 \times CMe_2$), 56.7 (MeO), 71.8 (C-3), 80.8, 82.4, 84.5, 84.7 and 85.3 (C-5, -4, -2′, -3′, -4′), 102.9 (C-2), 110.5, 111.8 and 114.1 (C-5′ and $2 \times CMe_2$), 163.4 (=$CNH_2$) and 204.9 (C-1); $m/z$ 371 ($M^+$), 355, 340 [MALDI-FTMS Found: M + $Na^+$, 394.1482. $C_{17}H_{25}NNaO_8$ (M + $Na^+$) requires $m/z$, 394.1478.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