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Synthesis of oxa-aza spirobicycles by intramolecular hydrogen atom transfer promoted by *N*-radicals in carbohydrate systems

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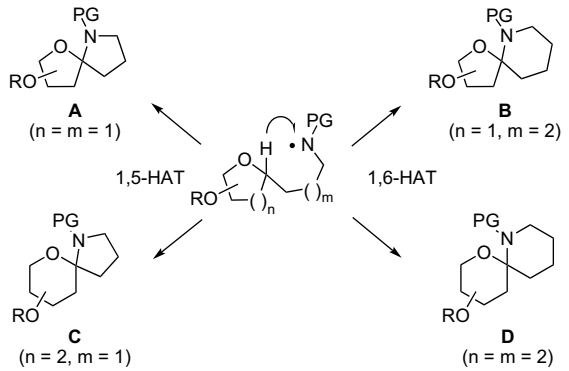
ABSTRACT

The nitrogen-centred radical generated by reaction of an *N*-phosphoramidate or *N*-cyanamide, attached to a tri- or tetramethylene tether extended from the C-1 of a carbohydrate, with (diacetoxyiodo)benzene (DIB) and iodine can undergo a regio- and stereoselective intramolecular hydrogen atom transfer (HAT) reaction to furnish four different oxa-azaspirobicyclic systems: 1-oxa-6-azaspiro[4.4]nonane, 1-oxa-6-azaspiro[4.5]decane, 6-oxa-1-azaspiro[4.5]decane and 1-oxa-7-azaspiro[5.5]undecane. A tandem 1,5- or 1,6-HAT-oxidation-nucleophilic cyclisation mechanism is proposed.

1. Introduction

Hydrogen abstraction, also referred to as hydrogen atom transfer (HAT), is one of the most common and simplest reactions of a neutral radical with an organic substrate. It is particularly useful since the functionalisation of a position considered to be unreactive under classical conditions could be possible.[1] Within their intramolecular version 1,5- and 1,6-HAT reactions promoted by carbon-centred radicals have driven a good deal of research due to their wide range of synthetic applications,[2] especially combining this process with a subsequent radical cyclisation to the effective construction of five and six-membered carbo- and heterocyclic compounds.[3] On the contrary, few studies have been developed for the intramolecular HAT reactions generated by heteroatom-centred radicals and *N*-radicals in particular.[1c,4] In our group we have devoted some attention to this field since in previous papers we have reported on the synthesis of different pyrrolidines and piperidines in carbohydrate and steroidal systems employing *N*-radicals.[5] For that study, intramolecular 1,5- and 1,6-HAT reactions were promoted by aminyl radicals derived from the treatment of a suitably protected amine[6] with a hypervalent iodine reagent in the presence of iodine. These results together with those previously obtained from the *O*-centred radical studies[7] have provided an excellent opportunity to demonstrate the synthetic potential of this methodology for the preparation of different heterocyclic compounds.

In a preliminary communication we have reported the synthesis of some oxa-aza spirobicycles in carbohydrate models performed by employing our 1,5- or 1,6-HAT radical protocol (Scheme 1).[5d]



Scheme 1. Oxa-azaspirobicycles by 1,5- or 1,6-HAT reaction; PG=PO(OR^1)$_2$, CN; R=R^1=alkyl, aryl.

In an extension to this article, the purposes of the present work were: (a) to show that the electrophilic C-1 propylidene or butylidene *N*-radical abstracts a hydrogen atom in a regio- and stereoselective manner at the *pseudoanomeric* position of a *C*-glycoside, (b) to confirm that intramolecular 1,5-HAT, through a six-

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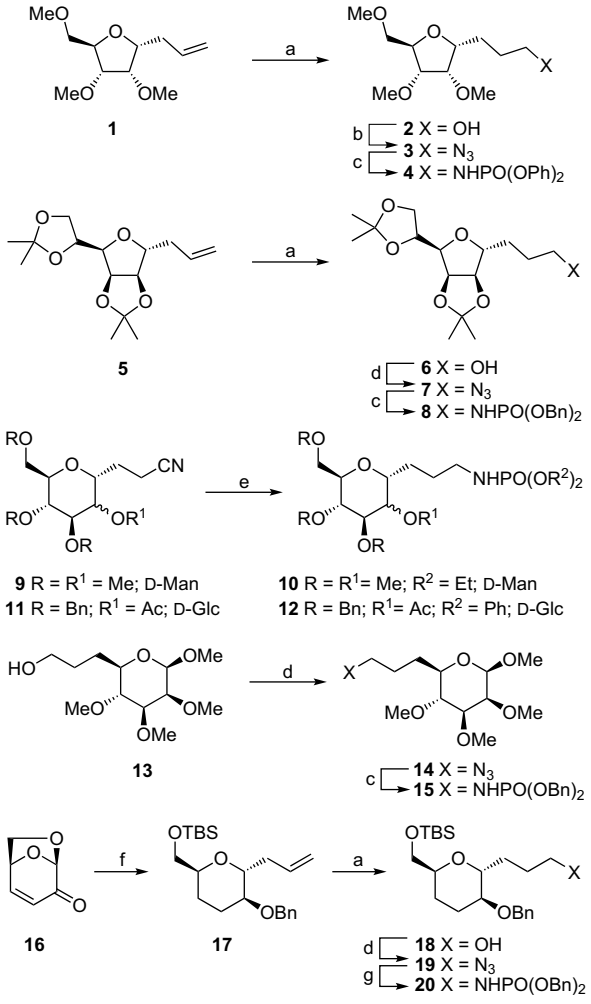
membered transition state (TS) is more favourable and better yielded process than 1,6-HAT, through a more unstable seven-membered TS,[8] (c) to explore the influence of the bulkiness of the amino-protective group employed on the hydrogen abstraction process and (d) to investigate whether electron-withdrawing group (EWG) substituents may perhaps influence the reaction course. It therefore offers the opportunity to study the consecutive HAT-oxidation–nucleophilic cyclisation sequence to synthesise four especially interesting oxa-aza spirocompound systems (spiroaminals)[9] (Scheme 1), which are widespread substructures common to a number of natural products such as: manzamine X,[10] having a 1-oxa-6-azaspiro[4.4]nonane structure **A**, solanum alkaloids[11] and azaspiracid,[12] with a 1-oxa-6-azaspiro[4.5]decane **B**, stemotinine and isostemotinine alkaloids,[13] with a 6-oxa-1-azaspiro[4.5]decane structure **C** and sanglifehrin A,[14] with a 1-oxa-7-azaspiro-[5.5]undecane **D**.

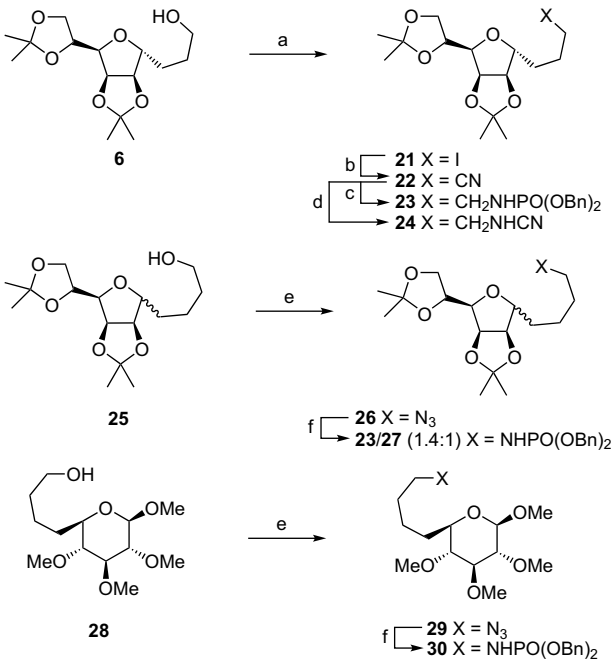
2. Synthesis of substrates and results

Preparation of the majority of the required C-1 three methylene tethered *N*-phosphoramidate *C*-glycoside derivatives was accomplished following a general well-established four-step protocol starting from suitably protected carbohydrates. A Lewis acid-mediated C-glycosidation with allyltrimethylsilane afforded the oct-7-enitols and non-8-enitols, in general with high stereoselectivity,[15] which upon subsequent oxidative hydroboration provided the alcohols **2**, **6**[7e] and **18** in good yield, with the exception of the known alcohol **13**[7e] derived from the corresponding butenyl derivative by reductive ozonolysis (Scheme 2). Transformation of the primary unprotected alcohols into the corresponding azide derivatives by Mitsunobu azidation[16] or conversion into the corresponding mesyl product and subsequent nucleophilic substitution with azide ion gave products **3**, **7**, **14** and **19**. Azides **3**, **7** and **14** were hydrogenated to the consequent amines whereas **19** was submitted to a radical reduction with *n*-tributyltin hydride to avoid the 5-*O*-benzyl deprotection. On the other hand, the known cyanide derivatives **9**[5b] and **11**[5b,17] were reduced to the respective amine products with $LiAlH_4$ treatment. The resulting crude free amines were all treated with the corresponding diethyl, diphenyl, or dibenzylchlorophosphate reagent in the presence of TEA to give the required phosphoramidates **4**, **8**, **10**, **12**, **15** and **20**. It is noteworthy that the choice of phosphonates as protective groups was made regarding their certain application in the amino and amino acid chemistry,[18] to avoid oxidation of the amine group during the formation of the iodoamide intermediate and, at the same time, to control the stability of the *N*-radical during the HAT reaction, but it merits mention that probably the use of other functionalities such as carbamoyl or amide derivatives could be more practical regarding further manipulation at the nitrogen centre because of its facile deprotection. However, in preceding works from this laboratory it was observed that in some cases apparently a lower nucleophilicity of the carbamate group was responsible for the competitive intermolecular attack of the acetate anion coming from the reagent preventing the cyclisation step.[5a]

To further test the scope of the HAT reaction, we also prepared a number of precursors whose phosphoramidyl groups were attached to a four-carbon tether extended from the C-1 of the sugar (Scheme 3). The alcohol **6** was submitted to iodination and cyanation to obtain **22** in 77% yield. Treatment with $LiAlH_4$ gave the



Scheme 2. Synthesis of C-1 propylidenphosphoramidate precursors: (a) (i) $BH_3 \cdot THF$ 1 M, THF, 0 °C to rt; (ii) NaOH 3 M, H_2O_2 (30%), 0 °C to rt, 1 h; (b) $ZnN_6 \cdot 2Py$, Ph_3P, DIAD, rt; (c) (i) H_2, Pd/C 10%, EtOAc; (ii) $(BnO)_2POCl$, TEA, $CHCl_3$, rt; (d) (i) MsCl, Py, 0 °C to rt; (ii) NaN_3, DMF, 80 °C, 2 h; (e) (i) $LiAlH_4$, Et_2O, rt; (ii) $(R^2O)_2POCl$, TEA, $CHCl_3$, rt; (f) (i) $CeCl_3 \cdot 7H_2O$, $NaBH_4$, MeOH, 0 °C to rt; (ii) H_2, Pd/C 10%; (iii) NaH, BnBr, DMF, 0 °C to rt, 71% from **16**; (iv) ATMS, $BF_3 \cdot Et_2O$, CH_3CN, 0 °C to rt, 1.5 h, 93%; (v) TBSCl, imidazole, DMF, rt, 3 h, 83%; (g) (i) Bu_3SnH, AIBN, PhH, reflux; (ii) $(BnO)_2POCl$, TEA, $CHCl_3$, rt, 95%.



Scheme 3. Synthesis of C-1 butylidenphosphoramidate precursors: (a) I_2, Ph_3P, imidazole, PhH, reflux, 0.5 h, 75%; (b) NaCN, DMF, rt, 14 h, 99%; (c) (i) $LiAlH_4$, Et_2O, rt; (ii) TEA, $(BnO)_2POCl$, $CHCl_3$, rt; (d) (i) $LiAlH_4$, Et_2O, rt; (ii) NaOCN, EtOH, H_2O, AcOH, reflux, 1.5 h; (iii) MsCl, Py, 0 °C to rt, 41%; (e) $ZnN_6 \cdot 2Py$, Ph_3P, DIAD, rt; (f) (i) H_2, Pd/C 10%, EtOAc, 23 h; (ii) TEA, $(BnO)_2POCl$, $CHCl_3$, rt.

corresponding amine, which was protected without further purification as *N*-phosphoramidate **23** and *N*-cyanamide **24**, the latter with minor steric hindrance. The phosphoramidates **27** and **30** were prepared accordingly by azidation–reduction–protection starting from the known alcohols **25**[7e] and **28**,[7e] respectively.

The HAT reactions were performed under the oxidative conditions previously developed in our group, by treatment of the corresponding precursors with (diacetoxyiodo)benzene and iodine, and presented in Tables 1 and 2 for the production of different oxa-azaspirocompound structures.[5] Firstly we carried out the synthesis of 1-oxa-6-azaspiro[4.4]nonane and 6-oxa-1-azaspiro[4.5]decane models (substructures **A** and **C**, Scheme 1) to verify the feasibility of this methodology, the results being summarised in Table 1.

The 1,5-HAT reaction of the phenyl and benzyl phosphoramidate furanose derivatives **4** and **8**, derived from D-ribose and D-mannose, respectively, proceeded smoothly to give the expected spirobicyclic products **31** and **32** in good yields (Table 1, entries 1 and 2). Interestingly, the abstraction, in the case of **32**, occurred on the sterically crowded β-side of the furanose ring while the subsequent cyclisation step tentatively took place in a selective manner on the less hindered α-side. In both cases, no NOE correlations were observed between any proton of the furanose ring and 3-H_2 of the pyrrolidine ring and thus the stereochemistry of the quaternary centre was cautiously assigned as indicated.

In order to synthesize a derivative with the spirocentre at C-5, phosphoramidate **15**, derived from D-glucose, was prepared in good yield (entry 3). The HAT reaction gave the two corresponding spirocompounds **33** and **34** in a global yield of 84% and a proportion of 1.5:1, respectively. Assignment of the C-5 stereochemistry was made by contrasting the NOE correlation observed in both isomers: epimer **33** showed an NOE interaction between 1-H and the benzylic protons of the phosphoramidyl group while in **34** the interaction was observed between 1-H and 6-H.

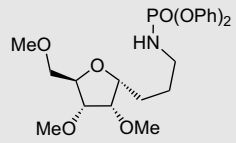
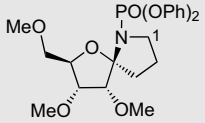
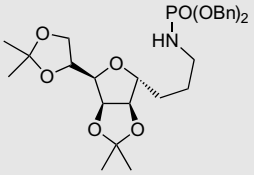
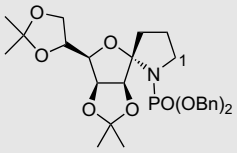
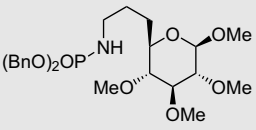
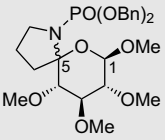
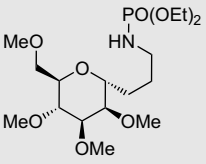
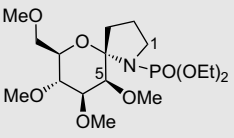
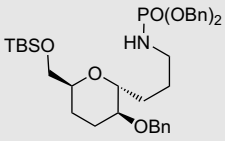
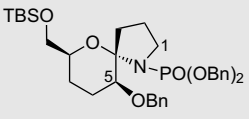
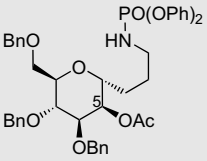
The HAT reaction of the diethyl phosphoramidate **10** and dibenzyl derivative **20** gave the oxa-azaspirobicycles **35** and **36** in moderate yields (entries 4 and 5). The stereochemistry of the spirocentre was established on the basis of an NOE correlation between 5-H and the protons of the ethoxyl of the phosphoramidate group in **35**, and an NOE interaction of 3-H with a benzylic hydrogen of the 5-OBn group in **36**. These results indicate that, analogously to the case of furanose **32** (entry 2), in these two pyranose models the abstraction occurs on the β-side of the molecules while the nucleophilic cyclisation step takes place on the less hindered α-side.

The influence of the protective group at C-5, next to the supposed reacting centre C-4, was subsequently studied in entry 6. The substitution of a methyl ether by an EWG such as an acetyl group inhibited completely the radical abstraction at C-4 and under these conditions the starting material was recovered unchanged.[5b,7a,c,19]

We next tested the 1,6-HAT reaction to assess whether this methodology could prove practical for the synthesis of 1-oxa-6-azaspiro[4.5]decane and 1-oxa-7-azaspiro[5.5]undecane bicycles (substructures **B** and **D**, Scheme 1). The results obtained are summarised in Table 2.

We started our study with phosphoramidate **23** but unfortunately it failed to undergo 1,6-HAT on the sterically crowded β-side of the molecule (Table 2, entry 1). A more unstable seven-membered TS in comparison with precursor **8** (Table 1, entry 2) was postulated as responsible for the failure. In this case only monoiodine **37** and diiodine **38**, which are both produced by 1,5-HAT reactions, were isolated in low yields. Their structures were confirmed spectroscopically and by reductive dehalogenation to the starting amide **23** with the *n*-Bu_3SnH/AIBN system. In contrast, the bicycle **39** could be formed in low yield using the 6*S*-isomeric phosphoramidate **27** where the 1,6-HAT reaction proceeded on the less hindered side of the substrate (entry 2). Although the hydrogen abstraction occurred

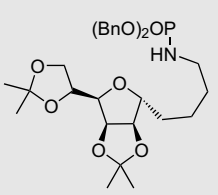
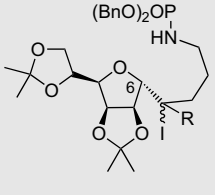
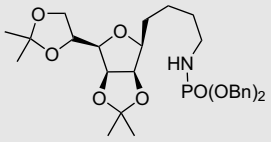
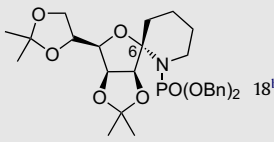
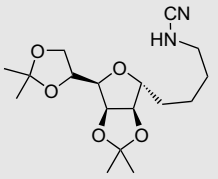
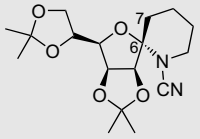
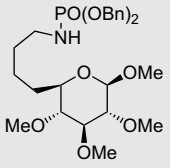
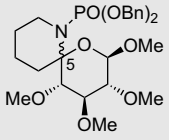
Table 1
Synthesis of 1-oxa-6-azaspiro[4.4]nonane and 6-oxa-1-azaspiro[4.5]decane bicycles by 1,5-HAT[a]

Entry	Substrate	Products	Yield (%)
1	 **4**	 **31**	64
2	 **8**	 **32**	74[b]
3	 **15**	 **33** (5 *R*) **34** (5 *S*)	84 (1.5:1)
4	 **10**	 **35**	52[c]
5	 **20**	 **36**	47
6	 **12**		NR

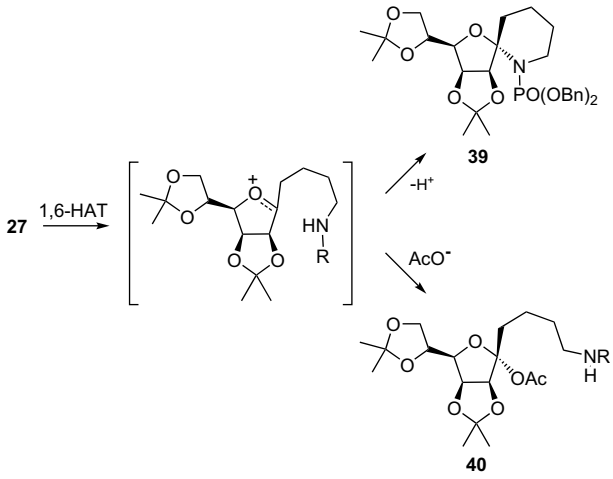
[a] All reactions were performed in dry CH_2Cl_2 (80 mL) containing (diacetoxyiodo)benzene (2.5 mmol), and iodine (1.4 mmol) per mmol of substrate and irradiating with two 80 W tungsten filament lamps at room temperature. Yields of pure products isolated after silica gel chromatography.
[b] Solid $NaHCO_3$ (25 mmol %) was added.
[c] Acetonitrile (80 mL) was used instead of CH_2Cl_2.

with an overall yield of 47%, the formation of the acetyl side product **40** in a substantial amount (29%) decreased the spirocycle **39** yield (Scheme 4). This product **40** might arise from external nucleophilic attack of the acetate anion, coming from the DIB, to the oxycarbenium ion intermediate in competition with the intramolecular cyclisation reaction. The stereochemistry of the quaternary centre in the acetyl derivative could not be determined on the basis of NOE experiments because no clear interactions were observed. The proposed stereochemistry, where the acetate anion adds to the less hindered side of the molecule, was consistent with the deshielding

Table 2
Synthesis of 1-oxa-6-azaspiro[4.5]decane and 1-oxa-7-azaspiro[5.5]undecane bicycles by 1,6-HAT[a]

Entry	Substrate	Products	Yield % (dr)
1	 **23**	 **37** R = H; **38** R = I	14[b]; 30
2	 **27**	 **39**	18[b,c]
3	 **24**	 **41**	48[b]
4	 **30**	 **42** (5*R*); **43** (5*S*)	41[d] (3:1)

[a] All reactions were performed in dry CH_2Cl_2 (80 mL) containing (diacetoxyiodo)benzene (2.5 mmol), and iodine (1.4 mmol) per mmol of substrate and irradiating with two 80 W tungsten filament lamps at room temperature. Yields of pure products isolated after silica gel chromatography.
[b] Solid $NaHCO_3$ (25 mmol %) was added.
[c] Acetate **40** (29%) was also obtained.
[d] Compound **44** (22%) was also obtained.

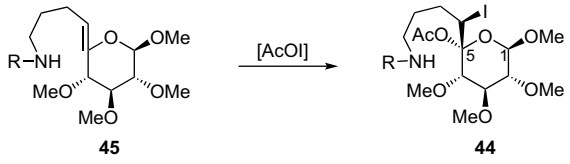


Scheme 4. Side product **40** from Table 2, entry 2; R=PO(OBn)$_2$.

undergone by the furanose ring protons in its ^{1}H NMR spectrum according to similar products found in the literature.[20] The strong hindrance of the β-side of the molecule may also be responsible for the formation of only one isomer of products **39** and **40**.

The model described in entry 3 demonstrates that the steric demand of the amine protector proved to be crucial to the 1,6-HAT and the subsequent cyclisation step. The cyanamide **24** is transformed exclusively into the 1-oxa-6-azaspiro[4.5]decane **41** with absolute regio- and stereoselectivity, albeit in moderate yield. With the voluminous phosphoramidate group only products **37** and **38** derived from more stable 1,6-transition states were formed (entry 1).[21] Also in this model the hydrogen abstraction took place on the more congested β-side of the furanose ring while the cyclisation step occurred on the opposite α-side. The configuration of the spirocentre was tentatively established as indicated because no NOE interactions were observed between 7-H_2 and any of the furanose protons.

Finally, this HAT-cyclisation sequence was further extended to pyranose model **30** derived from D-glucose yielding smoothly the expected bicycles **42** and **43** in moderate yield together with β-iodo ester **44** as a side product. The stereochemistry of the quaternary centre was established on the basis of an NOE correlation between 1-H and 6-H in **43**, an interaction that was not observed in **42**. The formation of **44** can be explained by a trans electrophilic addition of acetyl hypoiodite[22] to the hypothetical *Z*-olefin **45**, resembling Prévost reaction (Scheme 5).[23] Plausibly, this olefin could be generated from the oxycarbenium ion intermediate or by acid-catalysed ring opening of the oxa-azaspirobicycles **42** and **43**. The stereochemistry of **44** was assigned taking into account the strong deshielding of the axial protons at C-1 and C-3 in comparison with those of the starting amine **30**, which suggest an axial acetyl group at C-5.



Scheme 5. Minor product **44** from Table 2, entry 4; R=PO(OBn)$_2$.

It is important to stand out that all the structures were confirmed by ^{1}H and ^{13}C NMR spectra (DEPT, COSY, HSQC and HMBC experiments), revealing in all cases a selective abstraction of the corresponding protons. Likewise, the stereochemistry of the quaternary centre was tentatively assigned in base of intramolecular NOE experiments as it is portrayed in Experimental section in each case.

3. Conclusions

With these examples we have now demonstrated the possibility of using *N*-radicals, generated in situ from the reaction of *N*-phosphoramidates and *N*-cyanamides with the DIB/I_2 system, for the synthesis of four different types of oxa-aza spirobicycles, which are not readily accessible by other methods. The virtues of this reagent are the mildness of the conditions and high protective group tolerance. As observed, the process may be conceptually considered to be an intramolecular N-glycosidation via selective oxidation of the *pseudoanomeric* position of a *C*-glycoside using a 1,5- or 1,6-HAT reaction as the key step. The polarity of the amine protecting group may be very important since the nitrogen acts with an umpolung reactivity during the reaction, first as an electrophilic *N*-radical and then as a nucleophile in the cyclisation step.

4. Experimental

4.1. General

Melting points were determined with a hot-stage apparatus and are uncorrected. Optical rotations were measured at the sodium line at ambient temperature in $CHCl_3$ solutions. IR spectra were recorded in CCl_4 unless otherwise stated. NMR spectra were determined at 400 MHz for ^1H and 100.6 MHz for ^{13}C in $CDCl_3$ unless otherwise indicated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV. Merck silica gel 60 PF (0.063–0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were of analytical grade or were purified by standard procedures prior to use. All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagents for TLC analysis were conducted with 0.5% vanillin in H_2SO_4/EtOH (4:1) and further heating until development of colour.

4.2. Synthesis of precursors for HAT reactions

4.2.1. General procedure for N-phosphoramidate precursors

Starting from azide precursors (1 mmol) in dry EtOAc (29 mL) and with Pd/C 10% (187 mg), the mixture was hydrogenated at rt for 24 h. The suspension was filtered over Celite and concentrated under reduced pressure. Starting from cyanide precursors (1 mmol) in dry THF or Et_2O (6 mL), $LiAlH_4$ (4 mmol) was portionwise added at 0 °C. The mixture was stirred at rt until completion and then a saturated solution of Na_2SO_4 was dropwise added until the grey mixture turned to white. It was filtered and evaporated. The resulting crude amine (1 mmol) in dry $CHCl_3$ (16 mL) was treated at 0 °C with triethylamine (3.5 mmol) and $(RO)_2POCl$ (2 mmol) and stirred at rt. Then it was concentrated and poured directly into the column to chromatography (hexanes/EtOAc).

*4.2.2. 4,7-Anhydro-1,2,3-trideoxy-1-[(diphenoxyphosphoryl)-amino]-5,6,8-tri-O-methyl-D-altro-octitol (**4**)*

Following the general procedure of phosphoramido protection starting from azide **3** (374 mg, 1.44 mmol), diphenylphosphoramidate **4** (342 mg, 0.74 mmol, 51%) was obtained as a colourless oil: $[\alpha]_D$ +16.1 (*c*, 1.30); IR 3271, 2937, 1591, 1487 cm^{-1}; ^1H NMR δ_H 1.48–1.67 (4H, m), 1.93 (1H, m), 3.07–3.13 (2H, m), 3.37 (3H, s), 3.41 (3H, s), 3.42 (1H, dd, *J*=10.9, 3.8 Hz), 3.45 (3H, s), 3.50 (1H, dd, *J*=10.9, 3.3 Hz), 3.69 (1H, dd, *J*=4.5, 4.5 Hz), 3.75 (1H, dd, *J*=6.2, 4.8 Hz), 3.91 (1H, ddd, *J*=8.6, 4.3, 4.3 Hz), 3.99 (1H, ddd, *J*=6.4, 3.8, 3.8 Hz), 7.12–7.33 (10H, m); ^{13}C NMR (50.4 MHz) δ_C 26.5 (CH_2), 28.1 (CH_2, J_P=6.1 Hz), 41.8 (CH_2), 58.5 (CH_3), 59.4 (CH_3), 59.7 (CH_3), 73.1 (CH_2), 79.2 (CH), 79.8 (CH), 80.2 (CH), 81.8 (CH), 120.2 (2×CH), 124.8 (4×CH), 129.6 (4×CH), 150.8 (2×C); MS *m*/*z* (rel intens) 466 (M^++1, <1), 262 (100); HRMS *m*/*z* calcd for $C_{23}H_{33}NO_7P$ 466.1994, found 466.2011. Anal. Calcd for $C_{23}H_{32}NO_7P$: C, 59.35; H, 6.93; N, 3.01. Found: C, 59.38; H, 6.85; N, 2.92.

*4.2.3. 3,6-Anhydro-9-{[bis(benzyloxy)phosphoryl]amino}-7,8,9-trideoxy-1,2:4,5-di-O-isopropylidene-D-glycero-D-manno-nonitol (**8**)*

Following the general procedure of phosphoramido protection starting from azide **7** (85 mg, 0.26 mmol), dibenzylphosphoramidate **8** (85.5 mg, 0.15 mmol, 59%) was obtained as a colourless oil: $[\alpha]_D$ −3.4 (*c*, 1.0); IR 3217, 2937, 1549, 1456 cm^{-1}; ^1H NMR δ_H 1.32 (3H, s), 1.35 (1H, m), 1.36 (3H, s), 1.43 (3H, s), 1.46 (1H, m), 1.48 (3H, s), 1.58–1.65 (2H, m), 2.59 (1H, br s), 2.88 (2H, m), 3.67 (1H, dd, *J*=7.5, 3.7 Hz), 3.96 (1H, ddd, *J*=8.7, 5.0, 0 Hz), 3.98 (1H, dd, *J*=8.6, 4.4 Hz), 4.06 (1H, dd, *J*=8.6, 6.3 Hz), 4.36 (1H, ddd, *J*=6.6, 6.6, 4.7 Hz), 4.38 (1H, dd, *J*=6.2, 0 Hz), 4.68 (1H, dd, *J*=6.0, 3.8 Hz), 5.04 (4H, d, J_P=7.3 Hz), 7.31–7.37 (10H, m); ^{13}C NMR δ_C 24.5 (CH_3), 25.0 (CH_3), 26.0 (CH_3), 26.8 (CH_3), 27.5 (CH_2), 28.0 (CH_2), 40.9 (CH_2), 66.8 (CH_2), 67.9 (2×CH_2), 73.3 (CH), 79.8 (CH), 80.6 (CH), 83.7 (CH), 85.2 (CH), 109.0 (C), 112.5 (C), 127.7 (4×CH), 128.2 (2×CH), 128.4 (4×CH), 136.3 (2×C); MS *m*/*z* (rel intens) 560 (M^+−1, <1), 546 (5), 91 (100); HRMS *m*/*z* calcd for $C_{29}H_{39}NO_8P$ 560.2413, found 560.2404. Anal. Calcd for $C_{29}H_{40}NO_8P$: C, 62.02; H, 7.18; N, 2.49. Found: C, 62.22; H, 6.82; N, 2.74.

*4.2.4. 2,6-Anhydro-7,8,9-trideoxy-9-[(diethoxyphosphoryl)amino]-1,3,4,5-tetra-O-methyl-D-glycero-D-manno-nonitol (**10**)*

Following the general procedure starting from cyanide **9** (1.11 g, 4.07 mmol), **10** (926 mg, 2.24 mmol, 55%) was obtained as a colourless oil: $[\alpha]_D$ +7.5 (*c*, 1.20); IR 3563, 1660, 1455 cm^{-1}; ^1H NMR δ_H 1.29 (6H, t, *J*=7.1 Hz), 1.46–1.58 (2H, m), 1.58–1.67 (2H, m), 2.75 (1H, m), 2.92 (1H, m), 3.31 (1H, dd, *J*=4.8, 3.3 Hz), 3.35 (3H, s), 3.38 (3H, s), 3.39 (1H, dd, *J*=6.2, 3.3 Hz), 3.44 (3H, s), 3.45 (3H, s), 3.48 (1H, dd, *J*=7.4, 2.6 Hz), 3.52–3.58 (2H, m), 3.62 (1H, m), 3.88 (1H, ddd, *J*=9.0, 4.3, 4.3 Hz), 3.97–4.06 (4H, m), 1H from the NH group is missing; ^{13}C NMR (50.4 MHz) δ_C 16.2 (2×CH_3), 26.4 (CH_2), 28.2 (CH_2), 41.0 (CH_2), 57.5 (CH_3), 57.9 (CH_3), 59.1 (CH_3), 59.5 (CH_3), 62.1 (2×CH_2), 71.5 (CH_2), 71.8 (CH), 72.5 (CH), 76.6 (CH), 78.4 (CH), 79.1 (CH); MS *m*/*z* (rel intens) 414 (M^++1, 2), 88 (100); HRMS *m*/*z* calcd for $C_{17}H_{37}NO_8P$ 414.2256, found 414.2281. Anal. Calcd for $C_{17}H_{36}NO_8P$: C, 49.38; H, 8.78; N, 3.39. Found: C, 49.44; H, 8.83; N, 3.13.

*4.2.5. 2,6-Anhydro-1,3,4-tri-O-benzyl-7,8,9-trideoxy-9-[(diphenoxyphosphoryl)amino]-D-glycero-L-gulo-nonitol (**12**)*

Following the general procedure starting from cyanide **11** (370 mg, 0.70 mmol), a deprotected 5-OH product was obtained (319 mg, 0.44 mmol, 63%), which was submitted to acylation with Ac_2O/Py to give **12** (60% overall yield) as a colourless oil: $[\alpha]_D$ +23.1 (*c*, 0.13); IR 3221, 3066, 2934, 2871, 1746, 1454 cm^{-1}; ^1H NMR δ_H 1.42 (1H, m), 1.53 (1H, m), 1.60–1.74 (2H, m), 1.96 (3H, s), 3.10–3.16 (2H, m), 3.32 (1H, m), 3.57–3.67 (4H, m), 3.75 (1H, dd, *J*=8.1, 8.1 Hz), 4.07 (1H, m), 4.47 (1H, d, *J*=11.0 Hz), 4.48 (1H, d, *J*=12.4 Hz), 4.57 (1H, d, *J*=12.4 Hz), 4.69 (1H, d, *J*=11.4 Hz), 4.73 (1H, d, *J*=11.0 Hz), 4.74 (1H, d, *J*=11.4 Hz), 5.01 (1H, dd, *J*=8.6, 5.2 Hz), 7.13–7.33 (25H, m); ^{13}C NMR δ_C 20.9 (CH_3), 22.9 (CH_2), 27.5 (CH_2), 41.4 (CH_2), 68.8 (CH_2), 71.9 (CH), 72.1 (CH), 72.8 (CH), 73.4 (CH_2), 74.5 (CH_2), 74.7 (CH_2), 77.4 (CH), 79.8 (CH), 120.2–129.7 (25×CH), 137.9 (2×C), 138.3 (C), 150.8 (2×C), 170.0 (C); MS *m*/*z* (rel intens) 766 (M^++1, 1), 91 (100); HRMS *m*/*z* calcd for $C_{44}H_{49}NO_9P$, 766.3144, found 766.3145. Anal. Calcd for $C_{44}H_{48}NO_9P$: C, 69.01; H, 6.32; N, 1.83. Found: C, 69.37; H, 6.49; N, 1.76.

*4.2.6. Methyl 8-{[bis(benzyloxy)phosphoryl]amino}-6,7,8-trideoxy-2,3,4-tri-O-methyl-β-D-gluco-octopyranoside (**15**)*

Following the general procedure of phosphoramido protection starting from azide **14** (101.5 mg, 0.33 mmol), dibenzylphosphoramidate **15** (66.7 mg, 0.12 mmol, 38%) was obtained as a colourless oil: $[\alpha]_D$ −5.3 (*c*, 0.94); IR 3217, 2933, 1456, 1234 cm^{-1}; ^1H NMR δ_H 1.40 (1H, dddd, *J*=13.8, 9.0, 9.0, 5.0 Hz), 1.50 (1H, m), 1.66 (1H, m), 1.81 (1H, m), 2.77 (1H, dd, *J*=9.2, 9.2 Hz), 2.87–2.93 (2H, m), 2.92 (1H, dd, *J*=8.5, 8.5 Hz), 3.01 (1H, ddd, *J*=9.3, 9.3, 2.5 Hz), 3.09 (1H, dd, *J*=8.9, 8.9 Hz), 3.43 (3H, s), 3.48 (3H, s), 3.54 (3H, s), 3.59 (3H, s), 4.04 (1H, d, *J*=7.5 Hz), 5.03 (4H, d, J_P=7.0 Hz), 7.30–7.35 (10H, m), 1H from the NH group is missing; ^{13}C NMR δ_C 27.8 (CH_2), 28.4 (CH_2), 41.2 (CH_2), 56.8 (CH_3), 60.4 (CH_3), 60.6 (CH_3), 60.7 (CH_3), 67.9 (2×CH_2), 74.3 (CH), 83.6 (CH), 83.8 (CH), 86.5 (CH), 104.1 (CH), 127.7 (4×CH), 128.2 (2×CH), 128.5 (4×CH), 136.5 (2×C); MS (FAB) *m*/*z* (rel intens) 546 (M^++Na, 3), 524 (1), 91 (100). Anal. Calcd for $C_{26}H_{38}NO_8P$: C, 59.64; H, 7.32; N, 2.68. Found: C, 59.52; H, 7.60; N, 2.54.

4.2.7. 2,6-Anhydro-5-O-benzyl-9-{[bis(benzyloxy)phosphoryl]-amino}-1-O-[tert-butyl(dimethyl)silyl]-3,4,7,8,9-pentadeoxy-D-arabino-nonitol (**20**)

To a solution of the azide **19** (39.4 mg, 0.09 mmol) in dry benzene (3 mL), Bu_3SnH (126 μL, 0.468 mmol) and AIBN (2 mg) were added and the mixture was refluxed for 1.5 h. Then it was evaporated and the obtained crude was submitted to the general protection procedure to give dibenzylphosphoramidate **20** (58.3 mg, 0.09 mmol, 95%) as a colourless oil and as a mixture of two conformers in equilibrium A/B (1:3):[24] $[\alpha]_D$ +14.2 (*c*, 0.39); IR 3220, 2929, 2857, 1455, 1252 cm^{-1}; ^1H NMR δ_H 0.04 (12H, s), 0.87 (18H, s), 1.26–1.82 (16H, m), 2.66 (2H, br s), 2.88–2.90 (4H, m), 3.08–3.14 (2H, m), 3.45–3.49 (2H, m), 3.54–3.70 (6H, m), 4.34 (1H, d, *J*=12.3 Hz, A), 4.46 (1H, d, *J*=12.0 Hz, A), 4.56 (1H, d, *J*=12.0 Hz, B), 4.63 (1H, d, *J*=12.2 Hz, B), 5.00–5.06 (8H, m), 7.24–7.36 (30H, m); ^{13}C NMR δ_C −5.29 (4×CH_3), 18.2 (2×C), 23.4 (2×CH_2), 23.6 (4×CH_2), 25.7 (6×CH_3), 27.6 (2×CH_2), 27.8 (2×CH_2), 41.2 (2×CH_2), 64.3 (CH_2, B), 66.5 (CH_2, A), 67.8 (2×CH_2), 70.3 (CH_2, B), 70.5 (CH_2, A), 71.0 (CH, B), 72.1 (CH, A), 74.3 (CH, B), 75.4 (CH, A), 78.5 (CH, B), 79.2 (CH, A), 128.5–127.5 (30×CH), 136.5 (4×C), 138.5 (2×C); MS *m*/*z* (rel intens) 654 (M^++1, <1), 596 (17); HRMS *m*/*z* calcd for $C_{36}H_{53}NO_6PSi$ 654.3379, found 654.3370. Anal. Calcd for $C_{36}H_{52}NO_6PSi$: C, 66.13; H, 8.02; N, 2.14. Found: C, 66.13; H, 8.04; N, 2.12.

4.2.8. 3,6-Anhydro-10-{[bis(benzyloxy)phosphoryl]amino}-7,8,9,10-tetradeoxy-1,2:4,5-di-O-isopropylidene-D-glycero-D-manno-decitol (**23**)

Following the general procedure starting from cyanide **22** (213 mg, 0.68 mmol), **23** (228.3 mg, 0.40 mmol, 58%) was obtained as a colourless oil: $[\alpha]_D$ −1.75 (*c*, 0.286); IR 3219, 2937, 1455, 1380, 1232 cm^{-1}; ^1H NMR δ_H 1.25–1.29 (2H, m), 1.32 (3H, s), 1.35–1.40 (2H, m), 1.37 (3H, s), 1.40–1.44 (2H, m), 1.42 (3H, s), 1.49 (3H, s), 2.58 (1H, m), 2.84 (2H, ddd, *J*=16.6, 6.9, 6.9 Hz), 3.67 (1H, dd, *J*=7.6, 3.4 Hz), 3.96 (1H, ddd, *J*=9.1, 5.3, 0 Hz), 4.00 (1H, dd, *J*=8.5, 4.7 Hz), 4.07 (1H, dd, *J*=8.5, 6.4 Hz), 4.37 (1H, ddd, *J*=7.0, 7.0, 4.4 Hz), 4.43 (1H, dd, *J*=6.0, 0 Hz), 4.72 (1H, dd, *J*=5.9, 3.8 Hz), 5.04 (4H, d, J_P=8.1 Hz), 7.31–7.37 (10H, m); ^{13}C NMR δ_C 22.6 (CH_2), 24.5 (CH_3), 25.0 (CH_3), 26.0 (CH_3), 26.8 (CH_3), 30.0 (CH_2), 31.1 (CH_2), 41.2 (CH_2), 66.9 (CH_2), 67.8 (2×CH_2), 73.3 (CH), 79.9 (CH), 80.6 (CH), 83.8 (CH), 85.1 (CH), 109.0 (C), 112.5 (C), 127.7 (4×CH), 128.2 (2×CH), 128.4 (4×CH), 136.4 (2×C); MS *m*/*z* (rel intens) 575 (M^+, <1), 560 (7), 91 (100); HRMS *m*/*z* calcd for $C_{30}H_{42}NO_8P$ 575.2648, found 575.3074. Anal. Calcd for $C_{30}H_{42}NO_8P$: C, 62.60; H, 7.35; N, 2.43. Found: C, 62.44; H, 7.33; N, 2.57.

4.2.9. 3,6-Anhydro-10-cyanoamino-7,8,9,10-tetradeoxy-1,2:4,5-di-O-isopropylidene-D-glycero-D-manno-decitol (**24**)

The cyanide **22** (334 mg, 1.07 mmol) was submitted to $LiAlH_4$ reduction as in the general procedure. The resulting crude amine was dissolved in EtOH (48 mL), water (1.4 mL) and acetic acid (0.13 mL), and sodium cyanate was added (104 mg, 1.60 mmol). The mixture was refluxed for 2 h and then it was poured into brine and extracted with ethyl acetate. The organic solution was dried over Na_2SO_4 and evaporated. To a solution of the crude urea in pyridine (4.8 mL), at 0 °C, methanesulphonyl chloride (0.26 mL, 3.39 mmol) was added. After 30 min, the solution was allowed to warm to rt and then it was stirred for 2 h. It was poured into water and extracted with $CHCl_3$. The organic layer was washed with aqueous $NaHCO_3$ and water and evaporated. Column chromatography (hexanes/EtOAc, 7:3) gave the cyanamide **24** (150 mg, 0.44 mmol, 41%) as a colourless oil: $[\alpha]_D$ −7.2 (*c*, 2.50); IR 3251, 2227, 1381 cm^{-1}; ^1H NMR δ_H 1.29 (3H, s), 1.32 (3H, s), 1.32–1.49 (4H, m), 1.40 (3H, s), 1.44 (3H, s), 1.52–1.64 (2H, m), 3.01 (2H, ddd, *J*=13.5, 6.9, 0 Hz), 3.69 (1H, dd, *J*=7.4, 3.7 Hz), 3.97 (2H, dd, *J*=8.5, 4.5 Hz), 4.04 (1H, dd, *J*=8.5, 6.1 Hz), 4.26 (1H, br t, *J*=5.0 Hz), 4.33 (1H, m), 4.45 (1H, dd, *J*=6.1, 0 Hz), 4.71 (1H, dd, *J*=6.1, 3.7 Hz); ^{13}C NMR δ_C 22.4 (CH_2), 24.5 (CH_3), 25.0 (CH_3), 26.0 (CH_3), 26.7 (CH_3), 29.1 (CH_2), 29.9 (CH_2), 45.8 (CH_2), 66.7 (CH_2), 73.3 (CH), 79.9 (CH), 80.6 (CH), 83.8 (CH), 85.1 (CH), 109.0 (C), 112.5 (C), 116.3 (C); MS *m*/*z* (rel intens) 325 (M^+−Me, 39), 101 (100); HRMS *m*/*z* calcd for $C_{16}H_{25}N_2O_5$ 325.1763, found 325.1768. Anal. Calcd for $C_{17}H_{28}N_2O_5$: C, 59.98; H, 8.29; N, 8.23. Found: C, 59.64; H, 8.31; N, 8.59.

4.2.10. 3,6-Anhydro-10-{[bis(benzyloxy)phosphoryl] amino}-7,8,9,10-tetradeoxy-1,2:4,5-di-O-isopropylidene-glycero-D-manno-decitol (**23** and **27**)

Following the general procedure starting from azide **26** (35 mg, 0.10 mmol), **23** and **27** (32.2 mg, 0.06 mmol, 55%) were obtained as a mixture **23**/**27** (1.4:1) and as a colourless oil: IR 3217, 2988, 2935, 2871, 1456, 1380, 1232 cm^{-1}; ^1H NMR δ_H 1.25–1.29 (2H, m), 1.29 (3H, s), 1.32 (3H, s), 1.33–1.43 (6H, m), 1.34 (3H, s), 1.37 (3H, s), 1.40–1.44 (2H, m), 1.42 (6H, s), 1.43 (3H, s), 1.49 (3H, s), 1.61 (2H, m), 1.80 (2H, br s), 2.85 (4H, m), 3.36 (1H, ddd, *J*=6.7, 6.7, 3.8 Hz), 3.40 (1H, dd, *J*=7.4, 3.3 Hz), 3.67 (1H, dd, *J*=7.6, 3.4 Hz), 3.96 (1H, ddd, *J*=9.1, 5.3, 0 Hz), 4.00 (2H, dd, *J*=8.5, 4.7 Hz), 4.04 (1H, dd, *J*=8.0, 6.5 Hz), 4.07 (1H, dd, *J*=8.5, 6.4 Hz), 4.37 (2H, m), 4.43 (1H, dd, *J*=6.0, 0 Hz), 4.52 (1H, dd, *J*=6.2, 3.8 Hz), 4.69 (1H, dd, *J*=6.2, 3.3 Hz), 4.72 (1H, dd, *J*=5.9, 3.8 Hz), 5.04 (8H, d, J_P=8.1 Hz), 7.31–7.37 (20H, m); ^{13}C NMR δ_C 22.6 (CH_2), 22.8 (CH_2), 24.5 (2×CH_3), 25.0 (CH_3), 25.1 (CH_3), 25.6 (CH_3), 26.0 (CH_3), 26.8 (2×CH_3), 27.5 (CH_2), 30.0 (CH_2), 31.1 (CH_2), 31.3 (CH_2), 41.0 (CH_2), 41.2 (CH_2), 66.8 (CH_2), 66.9 (CH_2), 67.8 (4×CH_2), 73.0 (CH), 73.3 (CH), 79.9 (CH), 80.6 (2×CH), 81.1 (CH), 81.4 (CH), 81.8 (CH), 83.8 (CH), 85.1 (CH), 108.9 (C), 109.0 (C), 112.1 (C), 112.5 (C), 127.7 (8×CH), 128.1 (2×CH), 128.2 (2×CH), 128.4 (8×CH), 136.4 (2×C), 137.7 (2×C); MS *m*/*z* (rel intens) 560 (M^+−CH_3, 2), 484 (2), 91 (100); HRMS *m*/*z* calcd for $C_{29}H_{39}NO_8P$ 560.2413, found 560.2419. Anal. Calcd for $C_{30}H_{42}NO_8P$: C, 62.60; H, 7.35; N, 2.43. Found: C, 62.44; H, 7.73; N, 2.57.

4.2.11. Methyl 9-{[bis(benzyloxy)phosphoryl]amino}-6,7,8,9-tetradeoxy-2,3,4-tri-O-methyl-β-D-gluco-nonopyranoside (**30**)

Following the general procedure starting from azide **29** (39.3 mg, 0.14 mmol), **30** (36.6 mg, 0.07 mmol, 52%) was obtained as a crystalline solid: mp 59.6–60.6 °C (*n*-hexane/EtOAc); $[\alpha]_D$ −2.6 (*c*, 1.29); IR 3216, 2934, 1456, 1233 cm^{-1}; ^1H NMR δ_H 1.30 (1H, m), 1.36–1.54 (4H, m), 1.75 (1H, m), 2.78 (1H, dd, *J*=9.2, 9.2 Hz), 2.84–2.91 (2H, m), 2.93 (1H, dd, *J*=8.4, 8.4 Hz), 3.01 (1H, ddd, *J*=9.3, 9.3, 2.4 Hz), 3.10 (1H, dd, *J*=8.9, 8.9 Hz), 3.46 (3H, s), 3.50 (3H, s), 3.54 (3H, s), 3.60 (3H, s), 4.05 (1H, d, *J*=8.0 Hz), 5.03 (4H, d, J_P=7.5 Hz), 7.29–7.36 (10H, m), 1H from the NH group is missing; ^{13}C NMR δ_C 22.6 (CH_2), 31.1 (CH_2), 31.5 (CH_2), 41.3 (CH_2), 56.7 (CH_3), 60.3 (CH_3), 60.6 (CH_3), 60.7 (CH_3), 68.0 (2×CH_2), 74.4 (CH), 83.7 (CH), 83.9 (CH), 86.5 (CH), 104.0 (CH), 127.7 (4×CH), 128.2 (2×CH), 128.5 (4×CH), 136.4 (2×C); MS *m*/*z* (rel intens) 537 (M^+, <1), 88 (100); HRMS *m*/*z* calcd for $C_{27}H_{40}NO_8P$ 537.2491, found 537.2520. Anal. Calcd for $C_{27}H_{40}NO_8P$: C, 60.32; H, 7.50; N, 2.61. Found: C, 60.42; H, 7.49; N, 2.79.

4.3. General procedure for HAT reactions

To a solution of the *N*-phosphoramidate or *N*-cyanamide precursor (1 mmol) in dry CH_2Cl_2 (1.5 mL), DIB (2.5 mmol) and I_2 (1.5 mmol) were added and the mixture was irradiated with two 80 W tungsten lamps at rt. When the starting material was completely consumed, the mixture was poured into a solution of $Na_2S_2O_3$ and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4 and evaporated. Column chromatography of the residue (hexanes/EtOAc) gave the title compound.

4.3.1. (4S)-1,4:4,7-Dianhydro-1,2,3-trideoxy-1-[(diphenoxyphosphoryl)amino]-5,6,8-tri-O-methyl-D-ribo-oct-4-ulose (**31**)

Following the general procedure, diphenylphosphoramide **4** (69.6 mg, 0.15 mmol) gave **31** (44.4 mg, 0.10 mmol, 64%) as a colourless oil: $[\alpha]_D$ −37.9 (*c*, 0.14); IR 2933, 1490, 1279 cm^{-1}; ^1H NMR

δ_H 1.82 (1H, m), 1.90–1.99 (2H, m), 2.20 (1H, m), 3.22 (1H, m), 3.29 (1H, m), 3.29 (3H, s), 3.30 (3H, s), 3.36 (3H, s), 3.38 (1H, dd, J=9.8, 7.4 Hz), 3.62 (1H, m), 3.65 (1H, dd, J=5.7, 1.4 Hz), 3.90 (1H, ddd, J=7.6, 7.6, 1.4 Hz), 4.73 (1H, d, J=5.7 Hz), 7.13–7.32 (10H, m); NOE correlation between 3-H and 5-H was observed; ^{13}C NMR (50.4 MHz) δ_C 23.0 (CH_2), 33.9 (CH_2), 48.4 (CH_2), 57.6 (CH_3), 58.4 (CH_3), 59.1 (CH_3), 73.1 (CH_2), 79.1 (CH), 79.2 (CH), 79.5 (CH), 102.9 (C), 120.3 (CH), 120.6 (CH), 124.7 (2×CH), 124.9 (2×CH), 129.3 (2×CH), 129.6 (2×CH), 150.7 (C), 150.9 (C); MS m/z (rel intens) 463 (M^+, 1), 101 (100); HRMS m/z calcd for $C_{23}H_{30}NO_7P$ 463.1759, found 463.1745. Anal. Calcd for $C_{23}H_{30}NO_7P$: C, 59.61; H, 6.52; N, 3.02. Found: C, 59.69; H, 6.80; N, 3.03.

4.3.2. *(4S)-1,4:4,7-Dianhydro-1-{[bis(benzyloxy)phosphoryl]-amino}-1,2,3-trideoxy-5,6:8,9-di-O-isopropylidene-D-manno-non-4-ulose (**32**)*

Following the general procedure but adding also $NaHCO_3$ (25 mmol %), dibenzylphosphoramide **8** (10.7 mg, 0.02 mmol) gave **32** (5.1 mg, 0.01 mmol, 74%) as a colourless oil: $[\alpha]_D$ +22.0 (*c*, 1.03); IR 2986, 1380, 1265, 1070 cm^{-1}; ^{1}H NMR δ_H 1.34 (3H, s), 1.36 (3H, s), 1.44 (3H, s), 1.46 (3H, s), 1.73 (1H, m), 1.88 (1H, m), 2.00 (1H, m), 2.09 (1H, m), 3.08 (1H, ddd, J=8.8, 8.8, 8.8 Hz), 3.20 (1H, ddd, J=8.8, 8.8, 0 Hz), 3.97 (1H, dd, J=8.5, 4.6 Hz), 4.04 (1H, dd, J=8.5, 6.2 Hz), 4.33 (1H, ddd, J=6.4, 6.4, 5.0 Hz), 4.52 (1H, dd, J=7.1, 3.8 Hz), 4.96 (1H, d, J=11.9 Hz), 4.98 (1H, d, J=11.4 Hz), 5.01 (1H, m), 5.02 (2H, d, J=12.0 Hz), 5.14 (1H, dd, J=5.9, 0 Hz), 7.30–7.38 (10H, m); there was no NOE correlation between any of the hydrogen atoms on the furanose system and 3-H; ^{13}C NMR δ_C 22.6 (CH_2, J_P=9.1 Hz), 24.4 (CH_3), 25.4 (CH_3), 25.9 (CH_3), 26.9 (CH_3), 36.6 (CH_2, J_P=9.1 Hz), 48.4 (CH_2), 66.6 (CH_2), 67.3 (CH_2), 67.7 (CH_2), 73.8 (CH), 79.9 (CH), 81.7 (CH), 86.5 (CH), 104.8 (C), 108.8 (C), 112.0 (C), 127.7 (2×CH), 128.1 (2×CH), 128.2 (2×CH), 128.3 (2×CH), 128.4 (2×CH), 136.2 (2×C); MS m/z (rel intens) 559 (M^+, <1), 544 (4), 91 (100); HRMS m/z calcd for $C_{29}H_{38}NO_8P$ 559.2335, found 559.2344. Anal. Calcd for $C_{29}H_{38}NO_8P$: C, 62.24; H, 6.84; N, 2.50. Found: C, 62.32; H, 6.45; N, 2.68.

4.3.3. *Methyl (5R)-5,8-anhydro-8-{[bis(benzyloxy)-phosphoryl]amino}-6,7,8-trideoxy-2,3,4-tri-O-methyl-β-D-xylo-octo-5-ulopyranoside (**33**) and methyl (5S)-5,8-anhydro-8-{[bis(benzyloxy)phosphoryl]amino}-6,7,8-trideoxy-2,3,4-tri-O-methyl-β-D-xylo-octo-5-ulopyranoside (**34**)*

Following the general procedure, dibenzylphosphoramide **15** (72.8 mg, 0.14 mmol) gave **33** (37 mg, 0.07 mmol, 51%) and **34** (16.4 mg, 0.03 mmol, 33%) as colourless oils. Compound **33**: $[\alpha]_D$ −26.9 (*c*, 0.87); IR 2952, 1273, 1090 cm^{-1}; ^{1}H NMR δ_H 1.75 (1H, m), 1.99–2.04 (2H, m), 2.11 (1H, ddd, J=12.0, 7.3, 0 Hz), 3.01 (1H, dd, J=8.2, 8.2 Hz), 3.26 (1H, m), 3.37 (1H, d, J=9.3 Hz), 3.39 (3H, s), 3.43 (1H, ddd, J=9.6, 8.7, 0 Hz), 3.56 (3H, s), 3.59 (3H, s), 3.66 (3H, s), 4.79 (1H, dd, J=8.7, 8.7 Hz), 4.83 (1H, d, J=8.0 Hz), 5.00 (1H, dd, J=11.7 Hz, J_P=6.7 Hz), 5.03 (1H, dd, J=11.8 Hz, J_P=6.1 Hz), 5.12 (2H, d, J_P=7.0 Hz), 7.29–7.40 (10H, m); an NOE correlation between 1-H and benzylic hydrogen atoms was observed; ^{13}C NMR δ_C 21.5 (CH_2, d, J_P=6.1 Hz), 42.0 (CH_2, d, J_P=9.2 Hz), 50.5 (CH_2), 56.4 (CH_3), 59.6 (CH_3), 60.2 (CH_3), 61.5 (CH_3), 67.3 (CH_2), 67.9 (CH_2), 83.3 (CH), 83.6 (CH), 84.4 (CH), 95.4 (C, d, J_P=6.1 Hz), 99.5 (CH), 127.6 (2×CH), 127.7 (2×CH), 127.9 (CH), 128.1 (CH), 128.3 (2×CH), 128.4 (2×CH), 136.6 (C, d, J_P=6.1 Hz), 137.2 (C, d, J_P=6.1 Hz); MS (FAB) m/z (rel intens) 521 (M^+, 2), 490 (100); HRMS m/z calcd for $C_{25}H_{33}NO_7P$ 490.1994, found 490.1997. Anal. Calcd for $C_{26}H_{36}NO_8P$: C, 59.87; H, 6.96; N, 2.69. Found: C, 59.55; H, 7.21; N, 2.63. Compound **34**: $[\alpha]_D$ −8.4 (*c*, 2.4); IR 2935, 1274, 1094 cm^{-1}; ^{1}H NMR δ_H 1.81–1.90 (3H, m), 2.14 (1H, ddd, J=12.2, 8.7, 7.3 Hz), 3.07 (1H, dd, J=9.4, 9.4 Hz), 3.14 (1H, dd, J=8.5, 8.5 Hz), 3.16 (1H, m), 3.38 (1H, m), 3.41 (3H, s), 3.57 (3H, s), 3.59 (3H, s), 3.63 (3H, s), 4.20 (1H, d, J=8.0 Hz), 4.36 (1H, d, J=9.8 Hz), 5.03 (1H, dd, J=11.9 Hz, J_P=6.9 Hz), 5.07 (1H, dd, J=11.9 Hz, J_P=6.6 Hz), 5.09 (1H, dd, J=12.2 Hz, J_P=6.2 Hz), 5.12 (1H, dd, J=12.2 Hz, J_P=7.2 Hz), 7.27–7.38 (10H, m); an NOE correlation between 1-H and 6-H was observed; ^{13}C NMR δ_C 23.3 (CH_2, d, J_P=9.2 Hz), 30.5 (CH_2, d, J_P=9.2 Hz), 47.9 (CH_2), 56.3 (CH_3), 60.3 (2×CH_3), 60.7 (CH_3), 67.3 (CH_2), 67.4 (CH_2), 80.4 (CH), 83.0 (2×CH), 84.5 (CH), 95.8 (C), 100.7 (CH), 127.5 (2×CH), 127.7 (2×CH), 127.9 (2×CH), 128.1 (CH), 128.3 (2×CH), 136.5 (C, d, J_P=9.2 Hz), 137.1 (C, d, J_P=9.2 Hz); MS m/z (rel intens) 490 (M^+−OCH_3, 1), 88 (100); HRMS m/z calcd for $C_{25}H_{33}NO_7P$ 490.1994, found 490.2022. Anal. Calcd for $C_{26}H_{36}NO_8P$: C, 59.87; H, 6.96; N, 2.69. Found: C, 59.98; H, 6.67; N, 2.77.

4.3.4. *(4S)-1,4:4,8-Dianhydro-1,2,3-trideoxy-1-[(diethoxy-phosphoryl)amino]-5,6,7,9-tetra-O-methyl-D-manno-non-4-ulose (**35**)*

Following the general procedure but using acetonitrile as solvent, phosphoramide **10** (30 mg, 0.07 mmol) gave **35** (15.5 mg, 0.04 mmol, 52%) as a colourless oil: $[\alpha]_D$ +44.5 (*c*, 1.10); IR 2933, 1715, 1455, 1252 cm^{-1}; ^{1}H NMR δ_H 1.29 (6H, t, J=6.9 Hz), 1.72 (1H, m), 1.85 (1H, m), 1.98 (1H, m), 2.19 (1H, ddd, J=13.2, 9.0, 9.0 Hz), 3.14–3.18 (2H, m), 3.23 (1H, dd, J=9.0, 3.5 Hz), 3.33 (3H, s), 3.41 (3H, s), 3.44–3.46 (2H, m), 3.50 (3H, s), 3.51 (3H, s), 3.83 (1H, dd, J=3.5, 3.5 Hz), 3.97–4.10 (5H, m), 4.57 (1H, d, J=3.5 Hz); NOE correlations were observed between 5-H and $PO(OCH_2CH_3)_2$ and between 3-H and the C-5–OMe; ^{13}C NMR (50.4 MHz) δ_C 16.1 (2×CH_3), 22.4 (CH_2, J_P=6.1 Hz), 37.1 (CH_2, J_P=9.1 Hz), 47.5 (CH_2), 58.0 (2×CH_3), 59.0 (CH_3), 59.2 (CH_3), 61.9 (2×CH_2), 71.3 (CH), 73.0 (CH_2), 77.8 (CH), 78.6 (CH), 79.4 (CH), 96.9 (C, J_P=9.1 Hz); MS m/z (rel intens) 411 (M^+, <1), 366 (3), 88 (100); HRMS m/z calcd for $C_{17}H_{34}NO_8P$ 411.2022, found 411.2070. Anal. Calcd for $C_{17}H_{34}NO_8P$: C, 49.63; H, 8.33; N, 3.41. Found: C, 49.33; H, 8.70; N, 3.46.

4.3.5. *(4S)-1,4:4,8-Dianhydro-1-{[bis(benzyloxy)phosphoryl]-amino}-9-O-[tert-butyl(dimethyl)silyl]-1,2,3,6,7-pentadeoxy-D-threo-non-4-ulose (**36**)*

Following the general procedure, phosphoramide **20** (16.2 mg, 0.02 mmol) gave **36** (7.6 mg, 0.01 mmol, 47%) as a colourless oil: $[\alpha]_D$ +13.5 (*c*, 1.0); IR 2929, 2857, 1254, 1101 cm^{-1}; ^{1}H NMR δ_H 0.01 (6H, s), 0.87 (9H, s), 1.65–1.86 (4H, m), 1.86–1.95 (2H, m), 2.21–2.33 (2H, m), 3.23 (1H, m), 3.35 (1H, m), 3.54 (1H, dd, J=10.0, 5.9 Hz), 3.64 (1H, dd, J=10.4, 4.8 Hz), 4.23 (1H, m), 4.65 (1H, d, J=11.1 Hz), 4.67 (1H, dd, J=9.4, 5.2 Hz), 4.73 (1H, d, J=11.8 Hz), 4.98 (1H, dd, J=11.8 Hz, J_P=6.9 Hz), 5.03 (1H, dd, J=11.8 Hz, J_P=6.2 Hz), 5.13 (2H, d, J_P=6.9 Hz), 7.26–7.45 (15H, m); no NOE correlation was observed between 3-H and 5-H; ^{13}C NMR δ_C −5.3 (2×CH_3), 18.2 (C), 23.1 (CH_2), 23.3 (CH_2), 23.6 (CH_2), 25.8 (3×CH_3), 35.0 (CH_2), 48.2 (CH_2), 65.9 (CH_2), 67.2 (2×CH_2), 71.2 (CH), 71.7 (CH_2), 75.1 (CH), 98.0 (C), 127.2–128.3 (15×CH), 136.5 (C), 136.9 (C), 139.0 (C); MS m/z (rel intens) 594 (M^+−^{t}Bu, 6), 91 (100); HRMS m/z calcd for $C_{32}H_{41}NO_6PSi$ 594.2440, found 594.2461. Anal. Calcd for $C_{36}H_{50}NO_6PSi$: C, 66.33; H, 7.73; N, 2.15. Found: C, 66.00; H, 8.12; N, 2.17.

4.3.6. *5,8-Anhydro-1-{[bis(benzyloxy)phosphoryl]amino}-1,2,3,4-tetradeoxy-4-iodo-6,7:9,10-di-O-isopropylidene-D-erythro-L-altro-decitol (**37**) and 3,6-anhydro-10-{[bis(benzyloxy)phosphoryl]-amino}-7,8,9,10-tetradeoxy-7,7-diiodo-1,2:4,5-di-O-isopropylidene-D-glycero-D-manno-decitol (**38**)*

Following the general procedure but adding also $NaHCO_3$ (25 mmol %), dibenzylphosphoramide **23** (204 mg, 0.35 mmol) gave the diastereomeric mixture of monoiodides **37** (34.6 mg, 0.05 mmol, 14%), and diiodide **38** (80.4 mg, 0.10 mmol, 30%) as colourless oils. Compound **37**: IR 3216, 2936, 1745, 1252 cm^{-1}; complex ^{1}H and ^{13}C NMR spectra; MS m/z (rel intens) 686 (M^+−CH_3, 1), 91 (100); HRMS m/z calcd for $C_{29}H_{38}INO_8P$ 686.1379, found 686.1382. Anal. Calcd for $C_{30}H_{41}INO_8P$: C, 51.36; H, 5.89; N, 2.00. Found: C, 51.25; H, 5.88; N, 1.89. Compound **38**: $[\alpha]_D$ −2.6 (*c*,

0.154); IR 3209, 2989, 1381, 1257 cm^{-1}; ^1H NMR δ_H 1.36 (3H, s), 1.41 (3H, s), 1.43 (3H, s), 1.53 (3H, s), 1.81 (2H, dq, *J*=7.3, 7.3, 7.3, 7.3 Hz), 2.07 (1H, m), 2.36 (1H, m), 2.79 (1H, m), 2.96 (2H, dq, *J*=10.2, 6.8, 6.8, 6.8 Hz), 3.82 (1H, d, *J*=2.1 Hz), 3.99 (1H, dd, *J*=8.7, 4.9 Hz), 4.05 (1H, dd, *J*=8.7, 6.1 Hz), 4.35 (1H, ddd, *J*=6.3, 6.3, 5.1 Hz), 4.77 (1H, dd, *J*=7.6, 4.2 Hz), 4.87 (1H, dd, *J*=5.9, 2.5 Hz), 4.94 (1H, dd, *J*=5.9, 3.8 Hz), 5.05 (4H, d, J_P=7.6 Hz), 7.31–7.38 (10H, m); ^{13}C NMR δ_C 23.2 (C), 24.9 (CH_3), 25.2 (CH_3), 26.5 (CH_3), 26.8 (CH_3), 33.8 (CH_2), 40.0 (CH_2), 48.1 (CH_2), 66.6 (CH_2), 68.0 (2×CH_2), 73.7 (CH), 81.0 (CH), 84.1 (CH), 88.7 (CH), 95.0 (CH), 109.2 (C), 113.4 (C), 127.7 (4×CH), 128.3 (2×CH), 128.5 (4×CH), 136.3 (2×C); MS *m*/*z* (rel intens) 812 (M^+−CH_3, 1), 573 (1), 91 (100); HRMS *m*/*z* calcd for $C_{29}H_{37}I_2NO_8P$, 812.0346, found 812.0307. Anal. Calcd for $C_{30}H_{40}I_2NO_8P$: C, 43.55; H, 4.87; N, 1.69. Found: C, 43.59; H, 4.65; N, 1.81.

*4.3.7. (5S)-1,5:5,8-Dianhydro-1-{[bis(benzyloxy)phosphoryl]-amino}-1,2,3,4-tetradeoxy-6,7:9,10-di-O-isopropylidene-D-manno-dec-5-ulose (**39**) and 5-O-acetyl-1-{[bis(benzyloxy)phosphoryl]-amino}-1,2,3,4-tetradeoxy-6,7:9,10-di-O-isopropylidene-α-D-manno-dec-5-ulofuranose (**40**)*

Starting from a mixture of phosphoramidates (**23**/**27**=1.4:1) (98 mg, 0.17 mmol) and following the general procedure adding solid $NaHCO_3$ (25 mmol%) also, the mixture of diastereomers monoiodo **37** (13.6 mg, 0.02 mmol, 25%), diiodo **38** (5.4 mg, 0.01 mmol, 7%), the spirocompound **39** (7.5 mg, 0.01 mmol, 18%) and the acetate **40** (13.2 mg, 0.02 mmol, 29%) were obtained as colourless oils. Compound **39**: $[\alpha]_D$ −5.2 (*c*, 0.65); IR 2926, 2856, 1730, 1456, 1380, 1260 cm^{-1}; ^1H NMR δ_H 1.21–1.75 (4H, m), 1.24 (3H, s), 1.35 (6H, s), 1.44 (3H, s), 1.98–2.07 (2H, m), 3.14 (1H, m), 3.49 (1H, m), 3.86 (1H, dd, *J*=7.9, 3.6 Hz), 3.97 (1H, dd, *J*=8.6, 4.3 Hz), 4.06 (1H, dd, *J*=8.6, 6.2 Hz), 4.33 (1H, ddd, *J*=6.9, 6.9, 5.0 Hz), 4.57 (1H, dd, *J*=5.7, 3.8 Hz), 4.94–5.08 (4H, m), 5.32 (1H, d, *J*=5.7 Hz), 7.32–7.38 (10H, m); no NOE correlation was observed between 4-H and any of the furanose protons; ^{13}C NMR δ_C 20.8 (CH_2), 24.4 (CH_3), 25.3 (CH_3), 25.8 (CH_3), 26.9 (CH_3), 29.7 (CH_2), 30.8 (CH_2), 43.1 (CH_2), 67.0 (CH_2), 68.2 (CH_2), 68.3 (CH_2), 73.2 (CH), 78.9 (CH), 80.5 (CH), 83.9 (CH), 95.9 (C), 109.0 (C), 111.9 (C), 127.9 (4×CH), 128.3 (2×CH), 128.6 (4×CH), 136.0 (2×C); MS *m*/*z* (rel intens) 573 (M^+, <1), 558 (2), 91 (100); HRMS *m*/*z* calcd for $C_{30}H_{40}NO_8P$, 573.2491, found 573.2601. Anal. Calcd for $C_{30}H_{40}NO_8P$: C, 62.81; H, 7.03; N, 2.44. Found: C, 62.66; H, 7.42; N, 2.14. Compound **40**: $[\alpha]_D$ +13.6 (*c*, 0.81); IR 3220, 2937, 1738, 1380, 1252 cm^{-1}; ^1H NMR δ_H 1.31–1.48 (4H, m), 1.32 (3H, s), 1.37 (3H, s), 1.44 (3H, s), 1.46 (3H, s), 2.00 (3H, s), 2.07 (2H, ddd, *J*=9.6, 6.8, 6.8 Hz), 2.70 (1H, m), 2.87–2.91 (2H, m), 3.99 (1H, dd, *J*=8.7, 4.5 Hz), 4.01 (1H, dd, *J*=7.0, 4.0 Hz), 4.07 (1H, dd, *J*=8.9, 6.6 Hz), 4.36 (1H, ddd, *J*=7.3, 6.6, 4.7 Hz), 4.81 (1H, d, *J*=6.1 Hz), 4.88 (1H, dd, *J*=5.6, 3.7 Hz), 5.02 (2H, d, J_P=7.4 Hz), 5.04 (2H, d, J_P=7.4 Hz), 7.31–7.36 (10H, m); no NOE correlations was observed between any of the furanose protons and 4-H nor –OAc hydrogen atoms; ^{13}C NMR δ_C 20.1 (CH_2), 21.8 (CH_3), 24.4 (CH_3), 25.1 (CH_3), 25.8 (CH_3), 26.9 (CH_3), 31.0 (CH_2), 31.2 (CH_2, d, J_P=6.1 Hz), 40.9 (CH_2), 66.8 (CH_2), 67.9 (2×CH_2), 73.0 (CH), 79.5 (CH), 81.3 (CH), 84.7 (CH), 109.2 (C), 113.0 (C), 113.6 (C), 127.7 (4×CH), 128.2 (2×CH), 128.5 (4×CH), 136.4 (2×C), 169.5 (C); MS (FAB) *m*/*z* (rel intens) 656 (M^++Na, 16), 574 (100); HRMS *m*/*z* calcd for $C_{32}H_{44}NNaO_{10}P$ 656.2600, found 656.2568. Anal. Calcd for $C_{32}H_{44}NO_{10}P$: C, 60.65; H, 7.00; N, 2.21. Found: C, 60.47; H, 7.43; N, 2.11.

*4.3.8. (5S)-1,5:5,8-Dianhydro-1-cyanoamino-1,2,3,4-tetradeoxy-6,7:9,10-di-O-isopropylidene-D-manno-dec-5-ulose (**41**)*

Following the general procedure starting from *N*-cyanamide **24** (69.2 mg, 0.20 mmol) but adding solid $NaHCO_3$ (25 mmol %) also, oxa-azaspirocompound **41** (33 mg, 0.10 mmol, 48%) was obtained as a colourless oil: $[\alpha]_D$ −15.2 (*c*, 3.1); IR 2990, 2210, 1372 cm^{-1}; ^1H NMR δ_H 1.34 (3H, s), 1.38 (3H, s), 1.46 (3H, s), 1.48 (3H, s), 1.54–1.63 (2H, m), 1.64–1.78 (4H, m), 3.19 (1H, m), 3.37 (1H, m), 4.01 (1H, dd, *J*=8.8, 4.5 Hz), 4.04 (1H, dd, *J*=7.7, 3.7 Hz), 4.10 (1H, dd, *J*=8.8, 6.4 Hz), 4.37 (1H, m), 4.87 (1H, d, *J*=5.8 Hz), 4.91 (1H, dd, *J*=5.8, 3.4 Hz); no NOE correlation was observed between 4-H and any of the protons of the sugar ring; ^{13}C NMR δ_C 19.7 (CH_2), 23.7 (CH_2), 24.4 (CH_3), 25.3 (CH_3), 25.7 (CH_3), 26.8 (CH_3), 29.5 (CH_2), 47.2 (CH_2), 66.9 (CH_2), 72.9 (CH), 80.1 (CH), 80.2 (CH), 84.0 (CH), 95.7 (C), 109.4 (C), 113.2 (C), 116.0 (C); MS *m*/*z* (rel intens) 323 (M^+−CH_3, 10), 101 (100); HRMS *m*/*z* calcd for $C_{16}H_{23}N_2O_5$ 323.1607, found 323.1601. Anal. Calcd for $C_{17}H_{26}N_2O_5$: C, 60.34; H, 7.74; N, 8.28. Found: C, 60.04; H, 7.76; N, 8.59.

*4.3.9. Methyl (5R)-5,9-anhydro-9-{[bis(benzyloxy)phosphoryl]-amino}-6,7,8,9-tetradeoxy-2,3,4-tri-O-methyl-β-D-xylo-non-5-ulopyranoside (**42**), methyl (5S)-5,9-anhydro-9-{[bis(benzyloxy)-phosphoryl]amino}-6,7,8,9-tetradeoxy-2,3,4-tri-O-methyl-β-D-xylo-non-5-ulopyranoside (**43**) and methyl (5S)-5-O-acetyl-9-{[bis(benzyloxy)phosphoryl]amino}-6,7,8,9-tetradeoxy-2,3,4-tri-O-methyl-6-iodo-β-D-xylo-non-5-ulopyranoside (**44**)*

Following the general procedure starting from **30** (135 mg, 0.25 mmol), a mixture of spirocompound **42** (41.3 mg, 0.08 mmol, 31%) and its epimer **43** (14 mg, 0.03 mmol, 10%) was obtained as colorless oils, jointly with the iodo-acetate **44** (38.2 mg, 0.05 mmol, 22%) as a yellow oil. Compound **42**: $[\alpha]_D$ −3.5 (*c*, 1.9); IR 2935, 1747, 1456, 1261 cm^{-1}; ^1H NMR δ_H 1.41 (1H, m), 1.49–1.63 (2H, m), 1.92 (1H, m), 2.12–2.18 (2H, m), 3.01 (1H, dd, *J*=8.2, 8.2 Hz), 3.14–3.18 (1H, m), 3.15 (1H, d, *J*=8.9 Hz), 3.43 (1H, m), 3.44 (3H, s), 3.54 (3H, s), 3.56 (3H, s), 3.61 (3H, s), 4.41 (1H, d, *J*=8.5 Hz), 4.46 (1H, dd, *J*=8.7, 8.7 Hz), 4.98–5.10 (4H, m), 7.29–7.38 (10H, m); no NOE correlation was observed between 1-H and 6-H; ^{13}C NMR δ_C 20.2 (CH_2), 24.1 (CH_2), 35.5 (CH_2), 43.6 (CH_2), 56.9 (CH_3), 59.9 (CH_3), 60.0 (CH_3), 61.7 (CH_3), 68.0 (CH_2, d, J_P=6.1 Hz), 68.1 (CH_2, d, J_P=6.1 Hz), 81.5 (CH), 84.5 (CH), 87.3 (CH), 88.4 (C), 99.0 (CH), 127.4 (2×CH), 127.8 (CH), 128.0 (2×CH), 128.1 (CH), 128.3 (2×CH), 128.5 (2×CH), 136.6 (C, d, J_P=6.1 Hz), 137.1 (C, d, J_P=6.1 Hz); MS *m*/*z* (rel intens) 504 (M^+−OCH_3, 1), 91 (100); HRMS *m*/*z* calcd for $C_{26}H_{35}NO_7P$, 504.2151, found 504.2055. Anal. Calcd for $C_{27}H_{38}NO_8P$: C, 60.55; H, 7.15; N, 2.62. Found: C, 60.19; H, 7.53; N, 2.55. Compound **43**: $[\alpha]_D$ −3.7 (*c*, 1.6); IR 2927, 1747, 1455, 1260, 1087 cm^{-1}; ^1H NMR δ_H 1.44 (1H, m), 1.52–1.68 (3H, m), 1.76 (1H, m), 1.99 (1H, m), 3.12 (1H, dd, *J*=9.4, 8.0 Hz), 3.17–3.29 (2H, m), 3.26 (1H, dd, *J*=9.4, 6.4 Hz), 3.49 (3H, s), 3.57 (3H, s), 3.58 (3H, s), 3.67 (3H, s), 4.24 (1H, d, *J*=8.0 Hz), 4.71 (1H, d, *J*=9.4 Hz), 4.99–5.14 (4H, m), 7.29–7.39 (10H, m); NOE correlation between 1-H and 6-H was observed; ^{13}C NMR δ_C 16.2 (CH_2), 23.1 (CH_2), 24.5 (CH_2, d, J_P=6.1 Hz), 42.4 (CH_2), 56.4 (CH_3), 60.3 (CH_3), 60.4 (2×CH_3), 67.4 (CH_2), 67.5 (CH_2), 81.3 (CH), 83.7 (CH), 84.6 (CH), 88.8 (C), 99.8 (CH), 127.5 (CH), 127.9 (4×CH), 128.1 (CH), 128.4 (2×CH), 128.5 (2×CH), 136.6 (2×C); MS *m*/*z* (rel intens) 504 (M^+−OCH_3, 1), 88 (100); HRMS *m*/*z* calcd for $C_{26}H_{35}NO_7P$, 504.2151, found 504.2067. Anal. Calcd for $C_{27}H_{38}NO_8P$: C, 60.55; H, 7.15; N, 2.62. Found: C, 60.19; H, 7.52; N, 2.55. Compound **44**: $[\alpha]_D$ +41.8 (*c*, 0.3); IR 3331, 2935, 1748, 1456, 1238 cm^{-1}; ^1H NMR δ_H 1.47 (1H, m), 1.60 (1H, m), 1.68 (1H, m), 1.94 (1H, m), 2.10 (3H, s), 2.83–2.99 (2H, m), 3.14 (3H, s), 3.28 (1H, dd, *J*=7.0, 1.9 Hz), 3.43 (3H, s), 3.44 (3H, s), 3.53 (3H, s), 3.67 (1H, dd, *J*=4.7, 1.9 Hz), 4.73 (1H, d, *J*=4.7 Hz), 4.99 (1H, dd, *J*=10.3, 3.8 Hz), 5.03 (2H, d, J_P=7.5 Hz), 5.04 (2H, d, J_P=7.5 Hz), 5.86 (1H, d, *J*=7.0 Hz), 7.30–7.37 (10H, m), the hydrogen from the NH group is missing; a NOE correlation between 4-H and –OAc hydrogen atoms was observed; ^{13}C NMR δ_C 21.1 (CH_3), 29.7 (CH_2), 30.8 (CH_2), 31.8 (CH), 40.4 (CH_2), 57.2 (CH_3), 58.1 (CH_3), 59.5 (CH_3), 60.1 (CH_3), 67.9 (2×CH_2), 77.2 (CH), 78.6 (CH), 82.8 (CH), 97.7 (CH), 104.3 (C), 127.8 (4×CH), 128.2 (2×CH), 128.4 (4×CH), 136.4 (2×C), 170.7 (C); MS (FAB) *m*/*z* (rel intens) 744 (M^++Na, 10), 722 (3), 91 (100); HRMS *m*/*z* calcd for $C_{29}H_{41}INO_{10}P$ 721.1513, found 721.1481. Anal. Calcd for

$C_{29}H_{41}INO_{10}P$: C, 48.27; H, 5.73; N, 1.94. Found: C, 48.28; H, 5.90; N, 2.09.

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Supplementary data

Detailed experimental procedures and spectral and analytical data for all compounds are provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2009.05.049.

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