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Note

Highly regio- and diastereoselective, acidic clay supported intramolecular nitrile oxide–alkene cycloaddition on D-ribose derived nitriles: an efficient synthetic route to isoxazoline fused five and six membered carbocycles

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ABSTRACT

An efficient synthetic route to isoxazoline fused carbocycles from carbohydrate scaffolds that comprise of free hydroxyl group(s) is described with high regio- and stereoselectivity. Montmorillonite K-10/chloramine T oxidation and in situ intramolecular nitrile oxide–alkene cycloaddition (INOC) of D-ribose derived oximes have been developed for the diversity oriented synthesis of isoxazoline fused five and six membered carbocycles.

Carbohydrates are one of the versatile staring materials for the synthesis of enantiomerically pure highly functionalized carbocycles.[1] Carbohydrate to carbocycle transformation plays an important role for the synthesis of both natural and unnatural biological potent compounds such as gabosines, pericosines, aristeromycin, conduritols, glycosidase inhibitors aminocyclopentitols and modified carbocyclic nucleosides (Fig. 1).[2] In particular, isoxazoline fused carbocycles are imperative synthetic intermediates to a range of biologically active natural products and pharmaceutical agents (e.g., *N*-octyl-4-epi-β-valienamine, tamiflu, cortistatin A and neplanocin A).[3]

In addition, the manipulation of isoxazoline ring has been stimulated interest for a long time due to their high synthetic potential. Isoxazoline fused molecular frameworks interact with appropriate sort of reagent/condition to cleave selectively either C═N bond or N—O bond. The reductive cleavage of the C═N bond produces β-hydroxy ketone which further elaborates to α,β unsaturated ketones, allylic alcohols and 1,3 diols and similarly the selective cleavage of N—O bond in the isoxazoline ring produces 1,3 amino alcohols and β-hydroxy nitriles.[4] The synthetic potential of selectively cleaved products was elegantly demonstrated via their transformations into various bio-active natural products and analogues.[5] While a number of methods have been established for the synthesis of the isoxazoline ring or its derivatives,[6] the 1,3-dipolar cycloaddition of nitrile oxide to unsaturated systems has emerged as one of the most familiar and efficient methods for its fabrication.[7] This is due to at least two reasons, that is, nitrile oxides react with a great diversity of dipolarophiles by virtue of their high reactivities and the reaction products. Among the cycloadditions, intramolecular nitrile oxide–alkene cycloaddition (INOC) on sugar frameworks has attracted much attention of synthetic chemists as a useful and competent method for the fabrication of highly functionalized carbocycles of different ring sizes.[8] In general, the intramolecular reactions are more viable due to stereoelectronic factors, entropically more favourable and close proximity which enable to give good yield. However, the regio- and stereo chemistry of such cycloadditions are governed by the functional groups present in the molecular frameworks[9] and also most of these cycloadditions have been executed with protected hydroxyl groups.[10] The protection/deprotection steps lead to low over all yield, and lengthy steps. Recently, silica gel mediated intramolecular nitrile oxide–alkene cycloaddition on sugar derivatives[11a] with synthetic applications[11b] has been reported, in such cycloadditions the use of acetonide protected sugar derivatives has resulted in a mixture of diastereoisomers[11] towards the fabrication of six membered rings. In addition, the formation of nitrile oxides from oximes is commonly achieved

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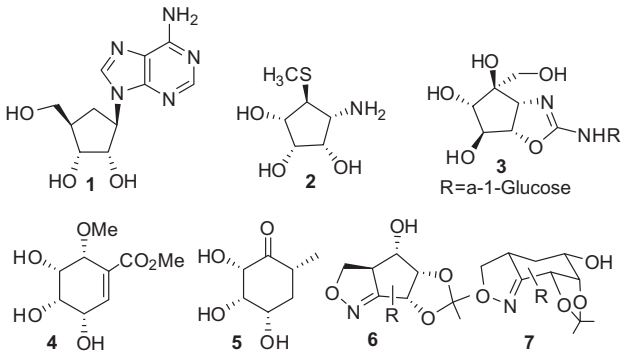


Figure 1. Aristeromycin **1**, mannostatin A **2**, trehazoline **3**, (+) pericosine B **4**, (−) gabosine O **5** and synthetic intermediates (**6** and **7**).

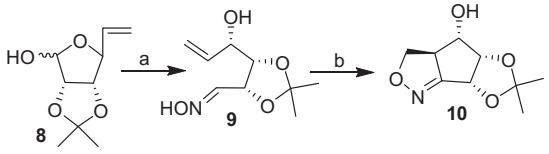
under basic conditions for instance NaOCl, NaOCl with Et_3N, NCS with Et_3N, *t*-BuOI with 2,6 lutidine, etc.[12] Under such conditions, the free hydroxyl groups get deprotonated leading to the deterioration of the desired cycloaddition due to the enhancement of nucleophilicity. Hence search for new and efficient methods is continuing. In view of the above and our interest in the chemistry of carbocyclic nucleosides, we considered developing a versatile and general methodology to isoxazoline fused highly functionalized carbocycles and examined the intra molecular nitrile oxide–alkene cycloaddition on different carbohydrate frameworks having free hydroxyl group(s) under mild acidic support and wish to report our exploratory results here in.

Initially, lactol **8** was converted to its oxime **9** by treating with $NH_2OH{\cdot}HCl$ and $NaHCO_3$ in MeOH and the oxidation of the resulting oxime **9** was achieved by using chloramin-T, which is known for the generation of nitrile oxide from oxime.[13] But under such condition, the desired isoxazoline **10** was isolated in a poor yield (17%). This may be due to the basic nature of chloramin-T which enhances the nucleophilicity of the free hydroxyl group of oxime **9** leading to the impedance of the desired cycloaddition. The ease and efficiency of the preferred cycloaddition increased remarkably when the oxidation of oxime **9** was carried out under mild acidic clay (Montmorillonite K-10) support with chloramin-T. The isoxazoline fused carbocycle **10** was isolated as a sole product with good yield (84%) (Scheme 1).

The spectral features of isoxazoline **10** clearly suggested its gross structure. However, it was difficult to assign the accurate stereochemistry on the basis of spectral data alone. Hence a single crystal X-ray structure of isoxazoline **10** was determined which evidently established the structure of the cycloadduct (Fig. 2).

Several reaction conditions were employed like varying the solvent, temperature and time, however the reaction was best carried out in ethanol at room temperature with chloramin-T and Montmorillonite K-10. It is presumed that under this clay mediated transformation the free hydroxyl group of the substrate coordinates to the clay surface (Fig. 3) which deactivates the nucleophilicity to enhance the favoured cycloaddition.

The generality and the scope of the aforesaid cycloadditions were examined on various ribose derivatives with unmasked



Scheme 1. Reagents and conditions: (a) $NH_2OH{\cdot}HCl$, $NaHCO_3$, MeOH; (b) chloramin-T hydrate, EtOH, Montmorillonite K-10.

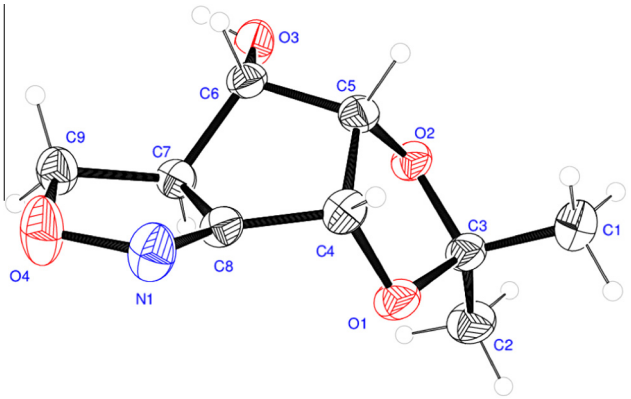


Figure 2. ORTEP diagram of **10** (30% ellipsoid probability).

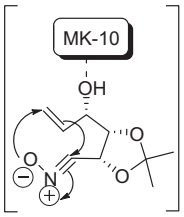
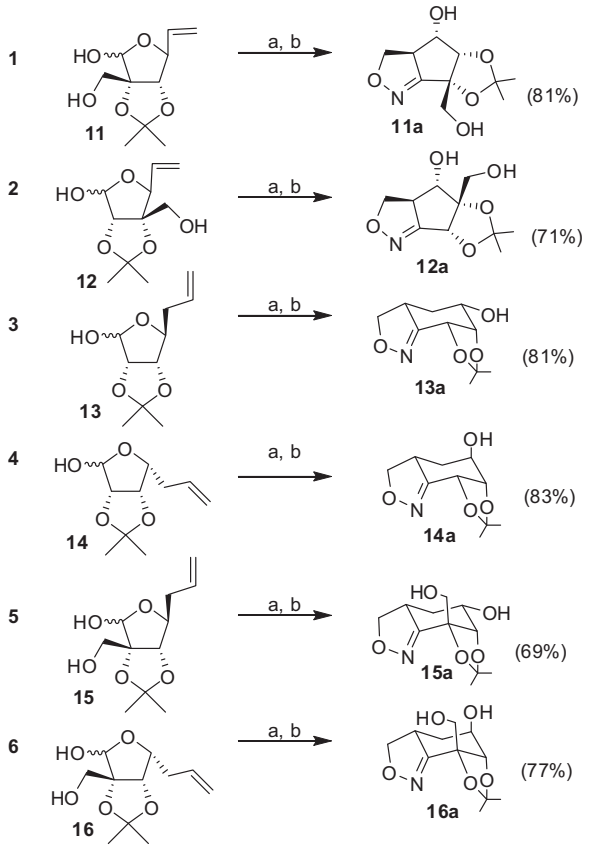


Figure 3. Co-ordination with MK-10.



Scheme 2. INOC on various D ribose derived oximes. Reagents and conditions: (a) $NH_2OH{\cdot}HCl$, $NaHCO_3$, MeOH; (b) chloramin-T hydrate, EtOH, Montmorillonite K-10.

hydroxyl group(s) to obtain highly functionalized isoxazoline fused carbocycles. The different synthesized lactols **11** to **16** were first converted to their corresponding oximes by treating with

$NH_2OH{\cdot}HCl$ and $NaHCO_3$ in MeOH then the resulting oximes were oxidized to nitrile oxides and then in situ [3+2] intra molecular cycloaddition with alkene afforded the isoxazolines **11a**–**16a**, respectively, in good yields as shown in Scheme 2. However compounds **13** and **14** yielded a mixture of diastereoisomers under silica gel condition as reported.[11a] Conversely, acidic medium by MK-10 plays an undefined role by resulting exclusively one diastereomer in each case.

All the synthesized compounds **11a**–**16a** were characterized thoroughly by their spectral analysis and the single crystal X-ray structures of compounds **14a** (Fig. 4) and **15a** (Fig. 5) were further confirmed to portray the exact stereochemistry of the compounds.

The high degree of regio- and diastereoselectivity observed in the above cycloaddition may be explained as follows. There are two modes of INOC reactions, that is, *exo* mode and *endo* mode which leads to either fused or bridged isoxazoline, respectively. In the above INOC reactions the addition of nitrile oxides to alkenes occurs through *exo* mode only because, the *endo* mode leads to the formation of bridged isoxazoline ring containing double bond at bridge head position. Hence such mode of INOC is unfavourable (Fig. 6).

In case of isoxazoline fused five membered carbocycles, the nitrile oxide approaches to the α face of alkene in order to achieve the more stable conformation *cis*/*anti*/*cis*. It is interesting to note that acetonide protected diol creates a five membered ring which governs the cycloaddition at α face through *exo* attack to obtain a *cis*/*anti*/*cis* conformation which resembles the structure of various triquinane natural products[14] such as hirsutic acid and connatusin B. On the other hand, for isoxazoline fused six membered carbocycles, the nitrile oxide comes up to the β face of alkene with an anticipation to attain the less hindered stable conformation.

All the substrates employed above for the cycloaddition were synthesized from the versatile starting material D-ribose **17**. D-Ribose was protected as its 2,3 acetonide **18** by catalytic amount of concd H_2SO_4 in acetone which was treated with vinyl magnesium bromide in THF under Grignard condition to give the stereoselective ring opened triol **19**. Oxidative cleavage of vicinal diol in triol **19** with sodium *m*-periodate afforded lactol **8** in very good yield (Scheme 3).[15] The stereoselective introduction of a hydroxymethyl group into lactols **8** and **18** was successfully accomplished by using K_2CO_3 and formaldehyde solution in methanol to give hydroxymethylated lactols **11** and **20**, respectively.[16] Further the hydroxymethylated lactol **20** was subjected to

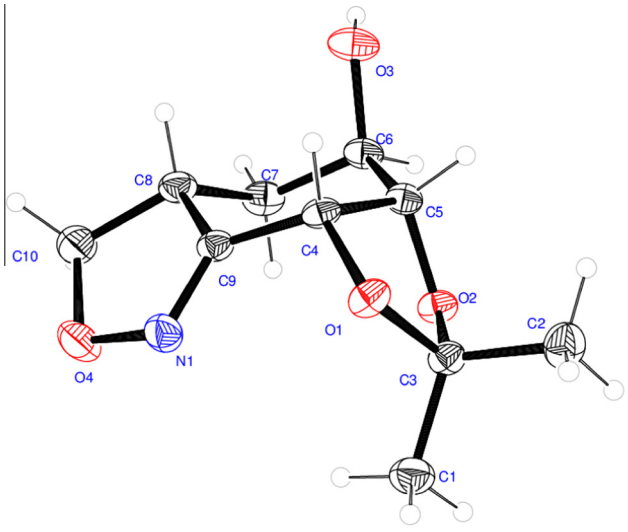


Figure 4. ORTEP diagram of compound **14a** (30% ellipsoid probability).

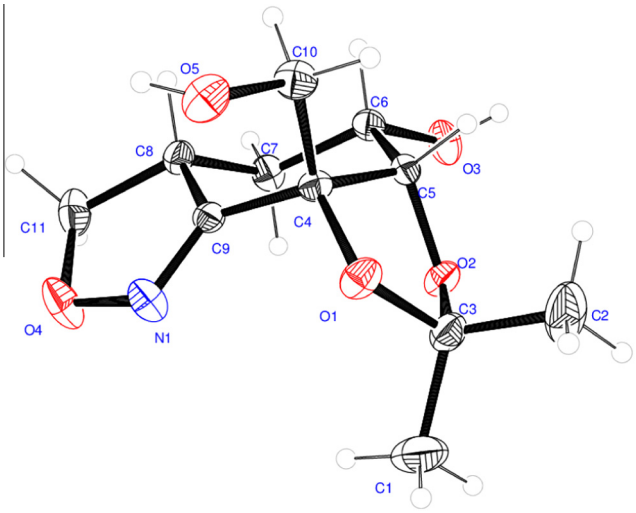


Figure 5. ORTEP diagram of compound **15a** (30% ellipsoid probability).

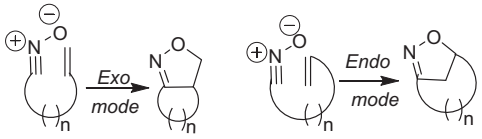
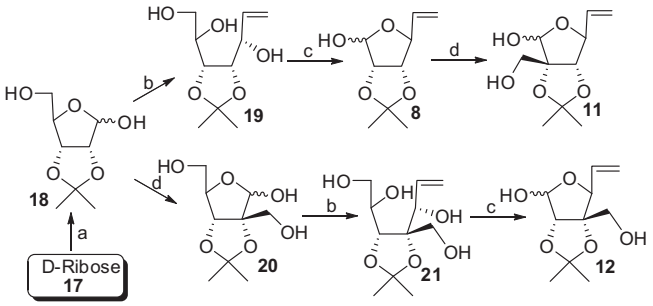


Figure 6. *exo* and *endo* modes of INOC.

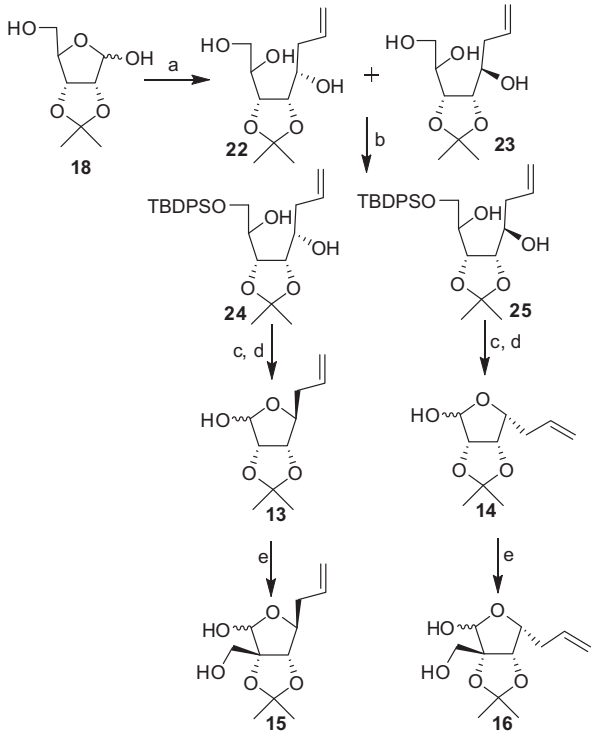


Scheme 3. Synthesis of precursors (for five membered fused carbocycles). Reagents and conditions: (a) acetone, concd H_2SO_4, 92%; (b) vinylmagnesium bromide solution, THF, −78 °C to RT, 88%; (c) $NaIO_4$, H_2O, MC, 85% for **8** and 82% for **12**; (d) K_2CO_3, HCHO soln, MeOH, reflux, 90% for **11** and 86% for **20**.

Grignard reaction with vinyl magnesium bromide in THF followed by oxidative cleavage with $NaIO_4$ to obtain lactol **12**.

Towards lactols **13**–**16**, 2,3 acetonide **18** was treated with allyl magnesium bromide solution in ether under Grignard condition to give an inseparable mixture of diastereomers **22** and **23** which were separated further as their mono-TBDPS protected diols **24** and **25**. The deprotection of silylether by tetrabutyl ammonium fluoride solution followed by oxidative cleavage exhibited lactols **13** and **14**, respectively[17] (Scheme 4). The stereoselective insertion of hydroxymethyl group to the respective lactols afforded the hydroxymethylated lactols **15** and **16** as mentioned earlier.

In conclusion, we have described an efficient, versatile and readily adaptable methodology by using Montmorillonite K-10 supported intramolecular 1,3 dipolar nitrile oxide–alkene cycloaddition of carbohydrate derivatives with unmasked hydroxyl groups for the synthesis of potential isoxazoline fused five and six membered carbocycles. The advantage of the methodology convoys highly regio- and stereoselective synthesis of isoxazoline fused carbocycles and the alleviation of protection/deprotection



Scheme 4. Synthesis of precursors (for six membered fused carbocycles). Reagents and conditions: (a) allyl magnesium bromide solution, ether, −78 °C to RT, 91%; (b) TBDPSCI, Et_3N, MC, DMAP, 23% for **24** and 66% for **25**; (c) TBAF, THF; (d) $NaIO_4$, H_2O, MC 74% for **13** and 71% for **14** (two steps); (e) K_2CO_3, HCHO soln, MeOH, reflux 85% for both **15** and **16**.

steps leading to the synthetic avenues shorter and efficient. The achievement of high degree of regio- and stereo selectivity is, therefore, of paramount importance for further expanding the scope and exploiting the potential of this elegant synthetic methodology.

1. Experimental

1.1. General

Reactions were performed under ambient atmosphere unless otherwise noted. All reagents and solvents were general reagent grade unless otherwise stated. Tetrahydrofuran and diethyl ether were freshly distilled from Na to benzophenone under nitrogen. Dichloromethane was freshly distilled from P_2O_5 under nitrogen. HPLC grade ethanol was used for the cycloaddition reaction. All other reagents and solvents were used as supplied commercially without further purification. Chloramin-T hydrate and Montmorillonite K-10 were purchased from Sigma Aldrich and used as supplied. All reactions were monitored by analytical thin-layer chromatography (TLC) on aluminium-pre coated plates of silica gel (EM 60-F254) purchased from Merck, Germany. Visualization was accomplished with UV light (254 nm) and exposure to *p*-anisaldehyde or $KMnO_4$ stain solutions followed by heating. Column chromatography was generally performed on silica gel (100–200 mesh). Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker 400 at 400 MHz (^1H) or at 100 MHz (^{13}C) in $CDCl_3$ solutions, unless stated otherwise. The NMR data are reported as peak multiplicities: s for singlet, d for doublet, dd for doublet of doublets, t for triplet, q for quartet, br s for broad singlet and m for multiplet. Coupling constants (*J* value) were measured directly from the spectra and are reported in hertz and chemical shifts are reported as parts per million (δ) relative to the solvent peak. IR spectra were obtained on NaCl plates (film) with a Bruker Tensor 27 FT-IR and selected absorbance is reported in cm^{-1}. High-resolution (HR) mass spectrometry data were acquired by a Bruker Daltonics MicroTOF-Q-II Mass Spectrometer using MeOH/CH_3CN as solvent. Single crystal X-ray structures were determined by a Bruker D8 Venture diffractometer equipped with CMOS detector.

1.2. General procedure for oxime formation

To a stirred solution of lactol (1 mmol) in MeOH, hydroxylamine hydrochloride (1.5 mmol) and $NaHCO_3$ (2 mmol) were added. The reaction mixture was stirred at room temperature until the disappearance of the starting material as shown on TLC. Then it was partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered and evaporated. The residue was purified by silica gel column chromatography (hexane/EtOAc) to give oxime which was used for cycloaddition reaction.

1.3. General procedure for the intramolecular nitrile oxide–alkene cycloaddition reaction

To a stirred suspension of oxime (1 mmol) and Montmorillonite K-10 (2× weight of oxime) in EtOH was added drop wise a milky solution of chloramine-T hydrate (1.3 mmol) in EtOH. The reaction mixture was stirred at room temperature until the disappearance of oxime as shown on TLC and the clay was filtered off. Concentration of the filtrate followed by silica gel column chromatography (hexane/EtOAc) of the residue afforded the isoxazoline derivative.

1.4. (3a*S*,4*S*,4a*S*,7a*R*)-6,6-Dimethyl-3a,4,4a,7a-tetrahydro-3*H*-[1,3]dioxolo[4′,5′:4,5]cyclopenta[1,2-*c*]isoxazol-4-ol (10)

Yield: 84%; colourless solid; mp 94–95 °C; $[\alpha]_D^{23}$ +86.4 (*c* 0.25, $CHCl_3$); R_f 0.3 (hexane/EtOAc, 1:1); IR (film) ν_{max}/cm^{-1}: 3382, 2989, 2939, 1644, 1456, 1380; ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.41 (3H, s), 1.56 (3H, s), 2.63 (1H, d, *J* = 8 Hz), 3.75 (1H, br m), 3.90 (1H, dd, *J* = 8, 12 Hz), 4.23 (1H, t, *J* = 8 Hz), 4.66 (1H, dd, *J* = 8, 8 Hz), 4.87 (1H, t, *J* = 4 Hz), 5.05 (1H, d, *J* = 4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 23.99, 25.92, 56.53, 71.96, 73.98, 74.18, 82.95, 112.98, 160.62; HRMS (ESI)(*m*/*z*): calcd for $C_9H_{13}O_4N$ $[M+Na]^+$ 222.0737; found 222.0734.

1.5. (3a*S*,4*S*,4a*S*,7a*S*)-7a-(Hydroxymethyl)-6,6-dimethyl-3a,4,4a,7a-tetrahydro-3*H*[1,3]dioxolo[4′,5′:4,5]cyclopenta[1,2-*c*]isoxazol-4-ol (11a)

Yield: 80%; colourless solid; mp 103–104 °C; $[\alpha]_D^{23}$ +84.0 (*c* 0.25, $CHCl_3$); R_f 0.35 (hexane/EtOAc, 1:1.5); IR (film) ν_{max}/cm^{-1}: 3381, 2990, 2936, 1640, 1456, 1379; ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.48 (3H, s), 1.56 (3H, s), 2.21 (1H, t, *J* = 8 Hz), 2.48 (1H, d, *J* = 12 Hz), 3.81 (1H, dt, *J* = 4, 8 Hz), 3.93 (1H, dd, *J* = 8, 12 Hz), 4.02 (2H, m), 4.19 (1H, dd, *J* = 8, 12 Hz), 4.70 (1H, dd, *J* = 8, 12 Hz), 4.83 (1H, d, *J* = 4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 26.24, 27.16, 57.42, 62.91, 73.92, 74.11, 83.64, 87.53, 113.52, 162.73; HRMS (ESI)(*m*/*z*): calcd for $C_{10}H_{15}O_5N$ $[M+Na]^+$ 252.0842; found 252.0847.

1.6. (3a*S*,4*S*,4a*S*,7a*R*)-4a-(Hydroxymethyl)-6,6-dimethyl-3a,4,4a,7a-tetrahydro-3*H*[1,3]dioxolo[4′,5′:4,5]cyclopenta[1,2-*c*]isoxazol-4-ol (12a)

Yield 71%; colourless viscous liquid; $[\alpha]_D^{23}$ +94.8 (*c* 0.25, $CHCl_3$); R_f 0.2 (hexane/EtOAc, 1:1); IR (film) ν_{max}/cm^{-1}: 3423, 2990, 2939,

1640, 1457, 1379; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.53 (3H, s), 1.59 (3H, s), 1.96 (1H, br s), 2.86 (1H, d, J = 12 Hz), 3.63 (1H, t, J = 8 Hz), 3.71 (1H, dd, J = 4, 12 Hz), 3.77 (1H, d, J = 8 Hz), 3.91 (1H, m), 4.22 (1H, t, J = 8 Hz), 4.70 (1H, t, J = 8 Hz), 5.01 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 26.76, 27.38, 57.85, 63.27, 74.27, 74.54, 93.16, 114.04, 160.3; HRMS (ESI)(m/z): calcd for $C_{10}H_{15}O_5N$ $[M+Na]^+$ 252.0842; found 252.0843.

1.7. (3a*R*,5*S*,5a*S*,8a*R*)-7,7-Dimethyl-3,3a,4,5,5a,8a-hexahydro[1,3]dioxolo[4′,5′:5,6]benzo[1,2-*c*]isoxazol-5-ol (13a)

Yield: 81%; colourless liquid; $[\alpha]_D^{23}$ −61.37 (c 0.28, $CHCl_3$); R_f 0.25 (hexane/EtOAc, 1:2); IR (film) ν_{max}/cm^{-1}: 3423, 2986, 2935, 2249, 1635, 1453, 1379; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.37 (3H, s), 1.49 (3H, s), 1.82 (1H, q, J = 12 Hz), 2.07(1H, t, J = 8 Hz), 2.72 (1H, br s), 3.24 (1H, m), 3.92 (1H, t, J = 8 Hz), 4.01 (1H, d, 8 Hz), 4.40–4.55 (2H, m), 4.85 (1H, d, J = 4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 26.09, 27.31, 32.42, 45.29, 67.61, 70.92, 73.44, 76.68, 111.05, 158.46; HRMS (ESI)(m/z): calcd for $C_{10}H_{15}O_4N$ $[M+Na]^+$ 236.0899; found 236.0898.

1.8. (3a*R*,5*R*,5a*S*,8a*R*)-7,7-Dimethyl-3,3a,4,5,5a,8a-hexahydro-[1,3]dioxolo[4′,5′:5,6]benzo[1,2-*c*]isoxazol-5-ol (14a)

Yield: 83%, colourless solid; mp 145–146 °C; $[\alpha]_D^{23}$ −81.6 (c 0.25, $CHCl_3$); R_f 0.35 (hexane/EtOAc, 1:2); IR (film) ν_{max}/cm^{-1}: 3404, 3056, 2988, 2934, 1631, 1429, 1378, 1328; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.41 (3H, s), 1.53 (3H, s), 1.84–1.92 (1H, m), 2.07–2.14 (1H, m), 2.31 (1H, br s), 3.62–3.73 (1H, m), 3.93 (1H, dd, J = 8, 12 Hz), 4.30 (1H, ddd, J = 4.8, 4.2, 2.4 Hz), 4.40 (1H, s), 4.56 (1H, dd, J = 8, 12 Hz), 5.03 (1H, d, J = 4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 24.19, 25.81, 30.66, 39.73, 65.81, 68.96, 75.39, 76.68, 111.16, 157.01; HRMS (ESI)(m/z): calcd for $C_{10}H_{15}O_4N$ $[M+Na]^+$ 236.0899; found 236.0899.

1.9. (3a*R*,5*S*,5a*S*,8a*S*)-8a-(Hydroxymethyl)-7,7-dimethyl-3,3a,4,5,5a,8a-hexahydro-[1,3]dioxolo[4′,5′:5,6]benzo[1,2-*c*]isoxazol-5-ol (15a)

Yield: 69%; colourless solid; mp 142–143 °C; $[\alpha]_D^{23}$ −54.62 (c 0.47, $CHCl_3$); R_f 0.14 (hexane/EtOAc, 1:2); IR (film) ν_{max}/cm^{-1}: 3410, 2988, 2938, 2882, 1623, 1454, 1379; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.45 (3H, s), 1.53 (3H, s), 1.87 (2H, q, J = 12 Hz), 2.18 (1H, td, J = 4, 8 Hz), 3.27–3.37 (1H, m), 3.75 (1H, d of part of an AB system, J = 12 Hz), 3.85 (1H, d of part of an AB system, J = 12 Hz), 3.96 (1H, t, J = 8 Hz), 4.05 (1H, td, J = 4, 12 Hz), 4.47 (1H, d, J = 4 Hz), 4.58 (1H, dd, J = 8, 12 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 26.74, 27.49, 32.84, 46.362, 63.89, 68.14, 73.86, 78.93, 80.76, 110.77, 159.72; HRMS (ESI)(m/z): calcd for $C_{11}H_{17}O_5N$ $[M+Na]^+$ 266.1004; found 266.1003.

1.10. (3a*R*,5*R*,5a*S*,8a*S*)-8a-(Hydroxymethyl)-7,7-dimethyl-3,3a,4,5,5a,8a-hexahydro[1,3]dioxolo[4′,5′:5,6]benzo[1,2-*c*]isoxazol-5-ol (16a)

Yield: 77%; colourless viscous liquid; $[\alpha]_D^{23}$ +60.8 (c 0.25, $CHCl_3$); R_f 0.21 (hexane/EtOAc, 1:2); IR (film) ν_{max}/cm^{-1}: 3422, 2985, 2933, 1631, 1454, 1383; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.49 (3H, s), 1.54 (3H, s), 1.80 (1H, ddd, J = 4, 8, 16 Hz), 1.95 (1H, br s), 2.32–2.40 (2H, m), 3.76 (1H, dq, J = 4, 12 Hz), 3.87–3.93 (3H, m), 4.08 (1H, dd, J = 4, 8 Hz), 4.54 (1H, s), 4.69 (1H, dd, J = 8, 12 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 26.10, 27.20, 30.79, 40.82, 63.69, 66.77, 76.55, 78.67, 81.72, 111.22, 158.00; HRMS (ESI)(m/z): calcd for $C_{11}H_{17}O_5N$ $[M+Na]^+$ 266.1004, found 266.1004.

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Supplementary data

Supplementary data (characterisation data of compounds, CCDC numbers for compounds **10**, **14a** and **15a** are 978899, 978900 and 978901, respectively, and refinement data in Table 1) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2014.06.007.

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