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Unusual Enantiopure Heterocyclic Skeletons by Lewis Acid Promoted Rearrangements of 1,3-Dioxolanyl-Substituted 1,2-Oxazines

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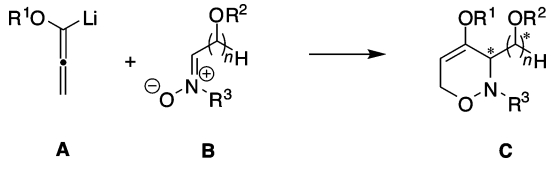
Lewis acid promoted rearrangements of different 4-alkoxy-substituted 1,2-oxazines *syn*-**1** are reported. Depending on the nature of this alkoxy group different reaction pathways are possible either providing bicyclic 1,2-oxazinones **2** or the novel tricyclic products **3**–**5**. A mechanistic rational describing the role of the 4-alkoxy group is presented. The key step for formation of tricyclic skeletons **3**–**5** is a 1,2-alkyl shift. Hydrogenation reactions of these tricyclic compounds gave unsaturated 1,2-oxazines **12** and **13** or tetrahydrofurans **15a**–**c**/**16a**–**c** depending on the time of hydrogenolysis. Tetrahydrofuryl-annulated 1,2-oxazine **12** was used for further transformations into complex substituted tetrahydrofurans. Reduction with sodium cyanoborohydride and subsequent cleavage of the N,O-bond by hydrogenation furnished aminofuran derivative **19**. Alternatively treatment with a strong base such as *n*-butyllithium afforded imidoester **21** via a Beckmann-type fragmentation.

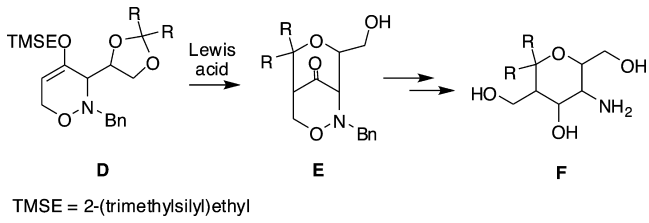
Introduction

Enantiomerically pure 3,6-dihydro-2*H*-1,2-oxazines **C** are easily accessible via stereocontrolled addition of lithiated alkoxyallenes **A** to carbohydrate-derived nitrones **B** and spontaneous cyclization of the primary allene adducts (Scheme 1).[1]



Scheme 1. Synthesis of 3,6-dihydro-2*H*-1,2-oxazines **C** from lithiated alkoxyallenes **A** and nitrones **B**.

The resulting 1,2-oxazines **C** have been employed for the stereoselective synthesis of a variety of highly functionalized compounds such as polyhydroxylated pyrrolidines and azetidines, aminopolyols or new carbohydrate derivatives.[2] In addition, we recently reported on the Lewis acid promoted rearrangement of 4-[2-(trimethylsilyl)ethoxy]-substituted 1,2-oxazines **D** into bicyclic compounds **E** which can be further transformed into enantiopure highly substituted aminopyrans **F** (Scheme 2).[3] These carbohydrate mimetics were already converted into uncommon amino acids and conjugates of carbohydrate mimetics.[4]



Scheme 2. Approach to enantiopure carbohydrate mimetics **F** via **E** by Lewis acid promoted rearrangement of 1,2-oxazines **D**.

In this report we want to disclose our investigations towards the Lewis acid promoted rearrangement of related 1,2-oxazines with other 4-alkoxy substituents leading to unexpected products with tricyclic skeleton and their subsequent transformations into new enantiopure heterocycles.[5]

Results and Discussion

1,3-Dioxolanyl-substituted 1,2-oxazines *syn*-**1** and *anti*-**1** with different 4-alkoxy substituents were prepared in a stereodivergent manner by [3+3]-cyclization of lithiated alkoxyallenes and D-glycerinaldehyde-derived nitrones.[1b] When 4-(*p*-methoxybenzyloxy)-substituted 1,2-oxazine *syn*-**1a** was exposed to tin tetrachloride the expected bicyclic product **2** of type **E** was obtained in 58% yield[6] whereas 4-methoxy, 4-benzyloxy, and 4-*t*BuCH$_2$CH$_2$O groups (*syn*-**1b**–**d**) led to formation of unexpected products **3**–**5** with three annulated heterocycles in reasonable yields (Scheme 3).

The differing reaction pathways leading to compounds **2** and **3**–**5** can be rationalized by the following mechanisms

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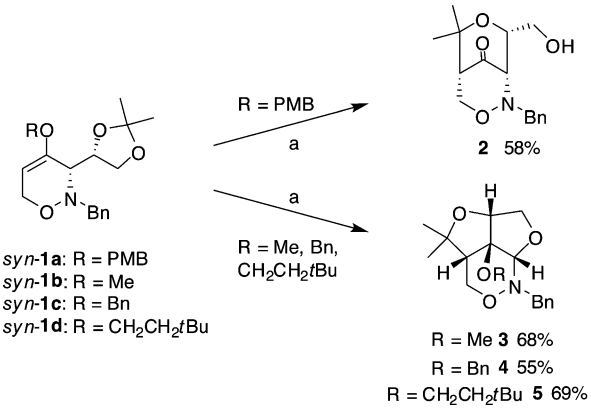
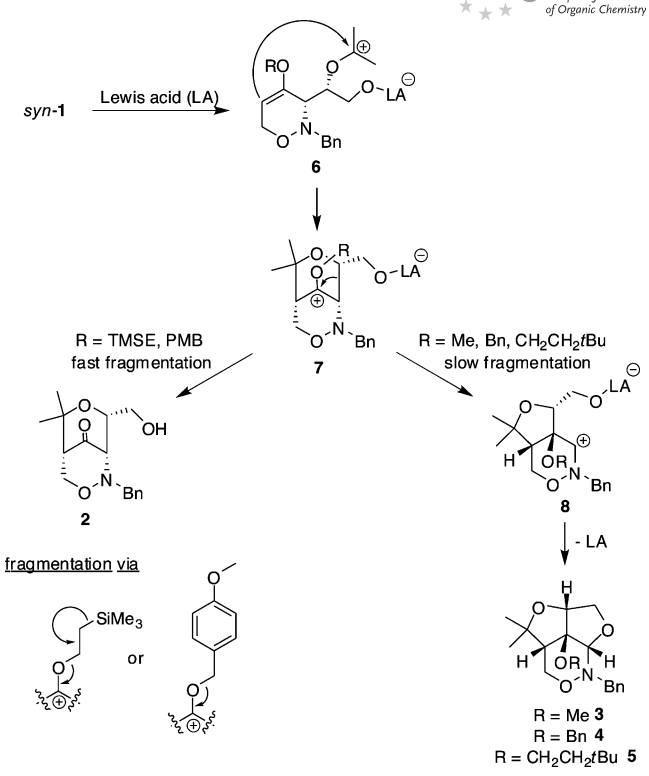
[‡] Responsible for X-ray analyses.



Scheme 3. Lewis acid promoted rearrangements of *syn*-**1** with different 4-alkoxy substituents. Reagents and conditions: a) $SnCl_4$, MeCN, –30 °C to room temp., 6–9 h.

(Scheme 4). Coordination of the Lewis acid to the easier accessible oxygen of the acetonide in *syn*-**1** leads to ring opening and formation of a stabilized carbenium ion **6**. This electrophilic species attacks the enol ether moiety similar to an aldol or Prins-type reaction to form key intermediate **7**. The fate of this intermediate strongly depends on the propensity of group R to undergo a fragmentation. The TMSE and the PMB group can undergo fast fragmentation into ethylene and a TMSX species or into the *p*-methoxybenzyl-cation and thus formation of product **2** is smoothly achieved. Simple alkyl substituents do not smoothly undergo a similar fragmentation and therefore competing pathways are important. The heterocyclic skeleton rearranges via a 1,2-alkyl-shift under retention of configuration delivering the more stable carbenium ion **8** which is stabilized by the nitrogen. A subsequent reaction with the oxygen of the side chain generates the *N*,*O*-acetal and finally compounds **3**–**5**. The different behaviour of benzyl- and PMB-substituted 1,2-oxazines *syn*-**1a** and *syn*-**1c** is quite remarkably which leads either to compound **2** or to product **4**.

The Lewis acid induced reaction of 4-methoxy-substituted 1,2-oxazine *anti*-**1** did not lead to similar products. Instead, the new tricyclic compound **9** was formed in moderate yield. This product can be regarded as an internally protected form of 1,2-oxazinone derivative **10**. Treatment of **9** with 2 N HCl actually furnished **10** which was already obtained by the Lewis acid promoted rearrangement of 4-TMSEO-substituted 1,2-oxazine *anti*-**1**.[3] Alternatively, the N,O-bond of **9** was cleaved with SmI_2 leading to bicyclic compound **11** in good yield.[7] The constitution of tricyclic compound **9** was proven by X-ray crystal structure (Figure 1). Its formation should occur via an intermediate (Scheme 5) where the cationic centre and Lewis acid coordinated oxygen are sufficiently close to create the new five-membered ring acetal. In contrast, the diastereomeric intermediate **7** of the *syn*-series does not allow this cyclization for simple geometric reasons. Therefore, the discussed 1,2-shift is the alternative pathway (Scheme 4).



Scheme 4. Proposed reaction pathways leading to rearrangement products **2** or **3**–**5** via carbenium ions **6** and **7**.

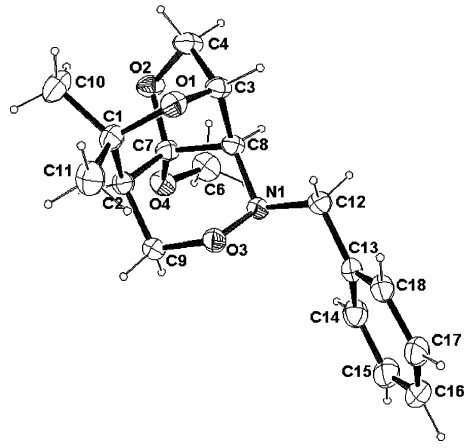
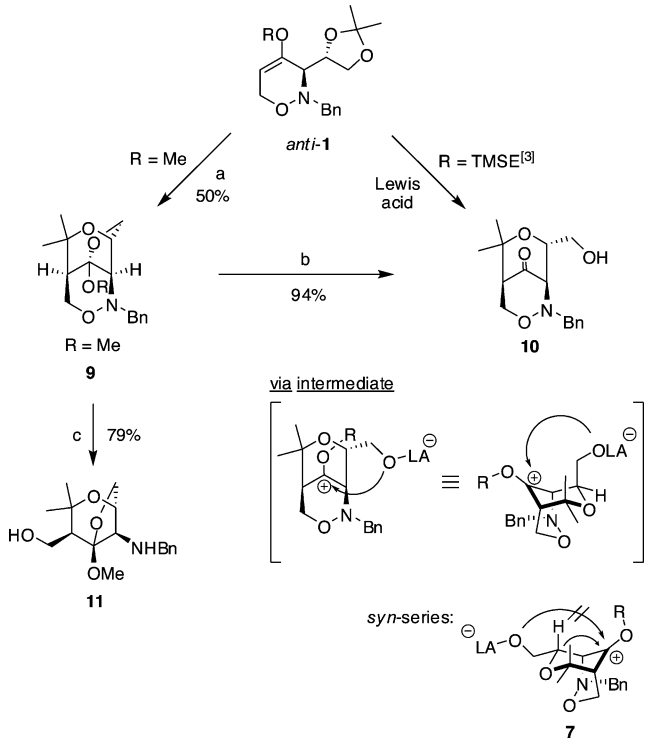
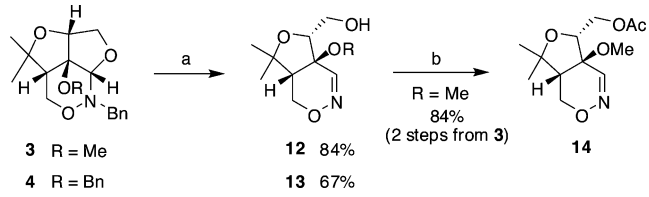


Figure 1. X-ray crystal structure of compound **9**.[8]

Since rearrangement products **3**–**5** are surprisingly stable to strong acidic conditions[9] subsequent transformations were conducted by reductive methods such as hydrogenations. We previously reported that debenzylation and N,O-bond cleavage of 2-*N*-benzyl protected 1,2-oxazines can be induced depending on the time of hydrogenolysis.[10] When tricyclic compounds **3** and **4** were subjected to hydrogenolytic conditions for 1–1.5 h we observed *N*-debenzylation and subsequent ring opening of the *N*,*O*-acetal moiety leading to unsaturated 1,2-oxazines **12** and **13** (Scheme 6). Acetylation of **12** allowed an X-ray crystal structure of the resulting 1,2-oxazine **14** (Figure 2). This was not only an unambiguous proof of the constitution and



Scheme 5. Lewis acid promoted rearrangements of *anti*-**1** leading to tricyclic 1,2-oxazine derivative **9** or 1,2-oxazinone **10**. Reagents and conditions: a) $SnCl_4$, MeCN, –30 °C to room temp., 6 h; b) 2 N HCl/dioxane, room temp., 24 h; c) SmI_2, THF, room temp., 3 h.



Scheme 6. Short period hydrogenolysis of rearrangement products **3** and **4** leading to compounds **12** and **13**. Reagents and conditions: a) H_2, Pd/C, MeOH, room temp., 1–1.5 h; b) Ac_2O, pyridine, room temp., 8 h.

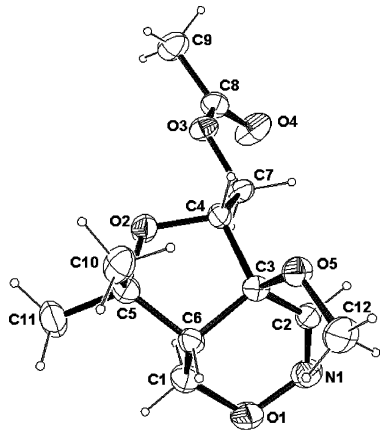
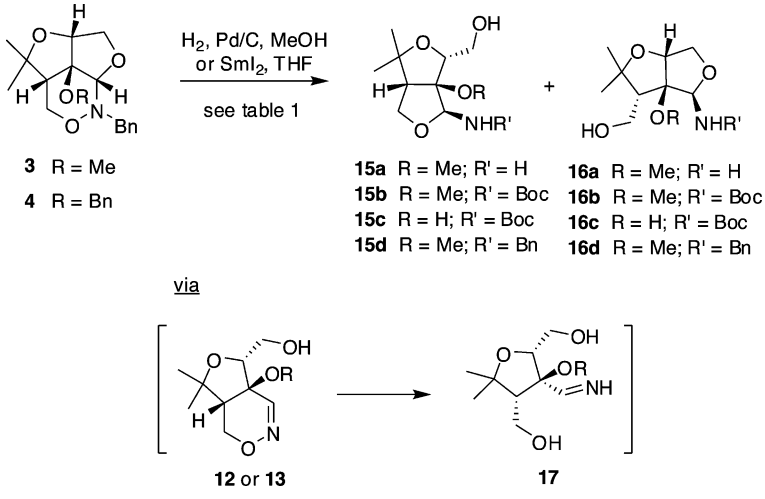


Figure 2. X-ray crystal structure of compound **14**.[8]

configuration of **14** but also of its precursor **3**. This result demonstrates that the 1,2-alkyl shift from intermediate **7** to **8** occurs under retention of configuration (Scheme 4).

Hydrogenolysis of compounds **3** and **4** for a longer period of time (17–18 h) furnished the two isomeric tetrahydrofurans **15** and **16** in moderate to good yields (Scheme 7). Here debenzylation and subsequent ring opening to 1,2-oxazines **12** or **13** is followed by an N,O-bond cleavage. This should provide intermediate **17** with two primary alcohol moieties and one imine unit which can undergo cyclization forming the two regioisomeric *N*,*O*-acetals **15** or **16**.

When substrate **3** was subjected to typical hydrogenation conditions for 17 h the respective tetrahydrofuryl-annulated tetrahydrofurans **15a** and **16a** were obtained in a ratio of 4:1 (Table 1, entry 1).[11] Out of this mixture pure **15a** could be crystallized giving suitable crystals for an X-ray analysis (Figure 3). When these crystals were dissolved in chloroform the mixture of **15a** and **16a** was regenerated in the previously determined ratio. This clearly demonstrates that



Scheme 7. Reductive transformations of rearrangement products **3** and **4** leading to *N*,*O*-acetals **15** and **16**.

the two isomeric forms are in equilibrium. The same hydrogenation reaction with in situ Boc protection furnished analogous products **15b** and **16b** in a ratio of 7:1 (entry 2). Hydrogenolysis of *O*-benzyl-substituted **4** for 18 h led in addition to *O*-debenzylation giving **15c** and **16c** in a ratio of 9:1 after in situ Boc protection (entry 3). The N,O-bond cleavage can alternatively be conducted by reduction with SmI_2 which does not touch the *N*-benzyl group. This results in the formation of products **15d** and **16d** in a ratio of 4:1 (entry 4).

Table 1. Reductive transformations of products **3** and **4** leading to isomeric tetrahydrofurans **15** and **16** after N,O-bond cleavage.

Entry	Substrate	Conditions	Product R	R′	Ratio **15/16**	Yield
1	**3**	H_2, Pd/C, MeOH, 17 h, room temp.	Me **15a/16a**	H	4:1	77%
2	**3**	H_2, Pd/C, Boc_2O, MeOH, 18 h, room temp.	Me **15b/16b**	Boc	7:1	82%
3	**4**	H_2, Pd/C, Boc_2O, MeOH, 18 h, room temp.	H **15c/16c**	Boc	9:1	63%
4	**3**	SmI_2, THF, 6 h, room temp.	Me **15d/16d**	Bn	4:1	43%

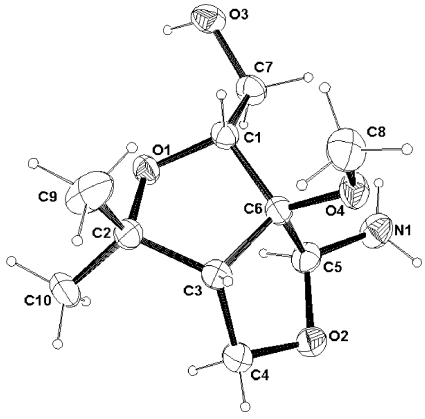
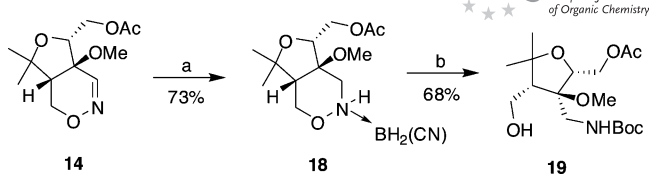


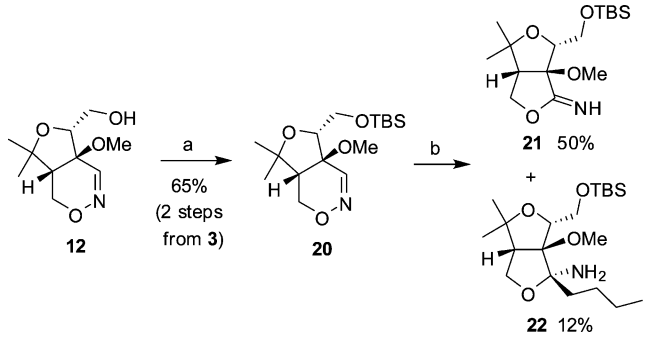
Figure 3. X-ray crystal structure of compound **15a**.[8]

Tetrahydrofuryl-annulated 1,2-oxazines **12**–**14** are ideal precursors for further conversions into new substituted tetrahydrofuran derivatives. This is demonstrated by the synthesis of tetrahydrofuran derivative **19** (Scheme 8). Reduction of **14** with sodium cyanoborohydride afforded saturated 1,2-oxazine **18**, which was still coordinated to $BH_2(CN)$ after chromatographic purification. Subsequent hydrogenolytic cleavage of the N,O-bond gave the hexasubstituted furan derivative **19** in 68% yield. As expected the coordinated boron species was removed in this step. Compounds like **19** could be interesting as novel furanose mimetics.[12]



Scheme 8. Synthesis of tetrahydrofuran derivative **19**. Reagents and conditions: a) $Na(CN)BH_3$, AcOH, room temp., 27 h; b) H_2, Pd/C, Boc_2O, MeOH, room temp., 18 h.

In general, reductive methods such as catalytic hydrogenation, SmI_2 or $Mo(CO)_6$ treatment and zinc in acetic acid[13] are used for the cleavage of N,O-bonds. However, alternative methods have also been explored. Recently we reported the N,O-bond cleavage of 1,2-oxazines by MeOTf and base in an internal redox process.[14] Furthermore, oximes and oxime ethers can be treated by base to give the respective nitriles, a transformation which is known as Beckmann fragmentation.[15] A similar reaction was observed when 1,2-oxazine **20** (obtained by TBS protection of **12**) was treated with a strong base (Scheme 9). Two equivalents of *n*BuLi were added to compound **20** giving imido ester **21** in 50% yield and by-product **22** in 12% yield.

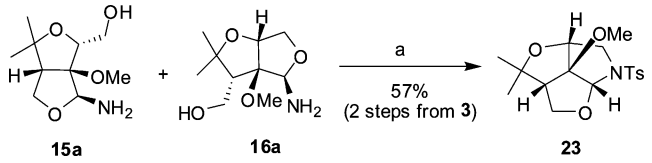


Scheme 9. Base-induced cleavage of the N,O-bond of compound **20** leading to **21** and **22**. Reagents and conditions: a) TBSOTf, NEt_3, CH_2Cl_2, room temp., 8 h; b) *n*BuLi, THF, –40 °C to room temp., 5 h.

We propose that *n*BuLi acts as a base and abstracts a proton at the oxime ether moiety leading to a Beckmann-type fragmentation. This should lead to a nitrile group which is attacked by the remaining alkoxide to give imido ester **21** after subsequent hydrolysis. The reaction pathway to by-product **22** is so far not certain. However, *n*BuLi certainly acts as a nucleophile and either attacks the nitrile or the imido ester moiety at the appropriate stage. The configuration of compound **22** was not proven, but we assume that the nucleophile attacks from the sterically less hindered convex site of the precursor.

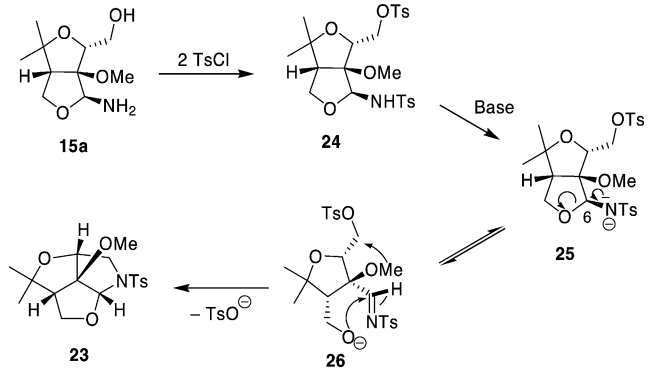
In order to further functionalize the *N,O*-acetals **15a/16a** we planned to introduce leaving groups such as tosylate. Unexpectedly, treatment of **15a/16a** with 2.5 equiv. of tosyl chloride furnished compound **23**, which contains three annulated five-membered rings and is therefore a derivative of 3,6-dioxa-1-azacyclopenta[*cd*]pentalene (Scheme 10).

To rationalize this result we assume that tosylations of the hydroxyl and amino groups of **15a** occur in the first



Scheme 10. Synthesis of tricyclic compound **23**. Reagents and conditions: a) *p*TsCl, DMAP, Et_3N, room temp., 19 h.

steps (Scheme 11). The resulting bistosylated species **24** could be isolated in another experiment. In order to allow cyclization to **23** the configuration at the *N*,*O*-acetal centre has to be changed. We propose that this happens via deprotonation of the tosylated amino group leading to imine **26** which is in equilibrium with **25** and its C-6 epimer. If the tosylated amino group is finally correctly oriented, cyclization to **23** smoothly is feasible.



Scheme 11. Proposed reaction pathway for the conversion of **15a** into tricyclic compound **23**.

Conclusions

In summary, a range of new enantiopure heterocyclic products was synthesized. High molecular complexity is created from simple molecules via a Lewis acid promoted rearrangement of readily available 1,3-dioxolanyl-substituted 1,2-oxazines. The resulting tricyclic products **3**–**5** are good starting points for further transformations. Hydrogenation reactions furnished new 5,6-dihydro-4*H*-1,2-oxazines **12** and **13** or bicyclic tetrahydrofurans **15/16**. These easily accessible intermediates could be converted into interesting compounds such as the tricyclic compound **23** with three annulated five-membered rings or tetrahydrofuran **19**. The rapid and stereocontrolled accessibility of all these new enantiopure heterocycles again demonstrates the great synthetic versatility of 1,2-oxazines derivatives.[16]

Experimental Section

General Methods: Reactions were generally performed under argon in flame-dried flasks. Solvents and reagents were added by syringes. Solvents were dried using standard procedures. Starting materials (*p*-methoxybenzyl)oxyallene,[17] *N*-benzyl-2,3-isopropylidene-D-glyceraldehyde nitrone[18] and *syn*-**1b**–**d**[1b] were prepared according to literature procedures. Reagents were purchased and were used as received without further purification unless otherwise stated. Unless otherwise stated, products were purified by flash chromatography on silica gel (230–400 mesh, Merck or Fluka) or HPLC (Nucleosil 50–5). Unless otherwise stated, yields refer to analytical pure samples. NMR spectra were recorded on Bruker (AC 500) and JEOL (Eclipse 500) instruments. Chemical shifts are reported relative to TMS (^{1}H: δ = 0.00 ppm), $CDCl_3$ (^{13}C: δ = 77.0 ppm), or CD_3OD (^{1}H: δ = 3.31 ppm, ^{13}C: δ = 49.0 ppm). Integrals are in accordance with assignments; coupling constants are given in Hz. All ^{13}C-NMR spectra were proton-decoupled. For detailed peak assignments 2D spectra were measured (COSY, HMBC and HMQC). IR spectra were measured with an FT-IRD spectrometer Nicolet 5 SXC. MS and HRMS analyses were performed with Finnigan MAT 711 (EI, 80 eV, 8 kV), MAT CH7A (ESI-FT ICRMS) and Agilent 6210 (ESI-TOF) instruments. Elemental analyses were carried out with CHN-Analyzer 2400 (Perkin–Elmer). Melting points were measured with a Reichert apparatus Thermovar and are uncorrected. Single-crystal X-ray data were collected on a Bruker-XPS diffractometer (CCD area detector, Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator), empirical absorption correction using symmetry-equivalent reflections (SADABS), structure solution and refinement by SHELXS-97 and SHELXL97 in the WINGX System.[19,20] The hydrogen atoms were located by difference Fourier syntheses.

(3*S*,4′*S*)-2-Benzyl-3-(2′,2′-dimethyl-1′,3′-dioxolan-4′yl)-4-(4-methoxybenzyloxy)-3,6-dihydro-2*H*-1,2-oxazine (*syn*-1a): To a solution of (*p*-methoxybenzyl)oxyallene (300 mg, 1.70 mmol) in THF (3 mL) was added *n*BuLi (1.6 M in hexane, 1.10 mL, 1.70 mmol) at –40 °C. After 5 min the resulting solution was cooled to –78 °C and a solution of (*Z*)-*N*-(1-deoxy-2,3-isopropylidene-D-glycero-1-ylidene)benzylamine *N*-oxide (200 mg, 0.850 mmol) in THF (1 mL) was added dropwise over a period of 5 min. After stirring the reaction mixture for 2 h at –78 °C water (10 mL) was added and the mixture was allowed to come to room temp. Et_2O was added, the phases were separated and the aqueous phase was extracted 3 times with Et_2O. The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. Purification by column chromatography (silica gel, hexane/EtOAc, 6:1) yielded ***syn*-1a** (210 mg, 60%) as colourless crystals; m.p. 55–56 °C. $[\alpha]_D^{22}$ = +36.2 (c = 0.80, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.34, 1.41 (2s, 3 H each, Me), 3.35 (d, J = 7.6 Hz, 1 H, 3-H), 3.81 (s, 3 H, OMe), 3.93 (m_c, 2 H, 5′-H), 4.17 (s, 2 H, NCH_2), 4.18 (dd, J = 3.5, 14.5 Hz, 1 H, 6-H), 4.44 (dt, J = 1.8, 14.5 Hz, 1 H, 6-H), 4.60 (dt, J = 6.5, 7.6 Hz, 1 H, 4′-H), 4.65, 4.72 (AB system, J_{AB} = 10.8 Hz, 2 H, OCH_2), 4.87 (dd, J = 1.8, 3.5 Hz, 1 H, 5-H), 6.90 (m_c, 2 H, Ar), 7.24–7.34 (m, 5 H, Ph), 7.44 (m_c, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 26.2, 26.6 (2q, Me), 55.2 (q, OMe), 58.2 (t, NCH_2), 63.5 (d, C-3), 64.4 (t, C-6), 67.0 (t, C-5′), 69.0 (t, OCH_2), 74.9 (d, C-4′), 93.9 (d, C-5), 108.6 (d, Ar), 127.0, 128.1, 128.4, 128.7, 129.3 (3d, 2s, Ph, Ar), 128.7 (d, Ar), 150.6 (s, C-4), 159.5 (s, Ar) ppm. IR (KBr): $\tilde{\nu}$ = 3100–3000 (=C–H), 3000–2800 (C–H), 1670 (C=C) cm^{-1}. $C_{24}H_{29}NO_5$ (411.5): calcd. C 70.05, H 7.10, N 3.40; found C 69.91, H 7.08, N 3.45.

Typical Procedure for the $SnCl_4$-Induced Rearrangement of 1,2-Oxazines (Method A): To a solution of 1,2-oxazine (1 equiv.) in MeCN (8 mL/mmol of 1,2-oxazine) is added $SnCl_4$ (3 equiv.) at –30 °C and the resulting solution is stirred until reaching 0 °C (3 h). After further stirring (time is given in the individual procedure) the mixture is quenched by water (16 mL/mmol of 1,2-oxazine). Addition of CH_2Cl_2 is followed by separation of the phases and the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo.

(1*S*,5*R*,8*S*)-2-Benzyl-8-(hydroxymethyl)-6,6-dimethyl-3,7-dioxa-2-azabicyclo[3.3.1]nonan-9-one (2):[3] A solution of 1,2-oxazine *syn*-**1a** (100 mg, 0.24 mmol) in MeCN (2 mL) was treated with $SnCl_4$ (91 μL, 0.72 mmol) according to method A and the resulting solution was stirred for further 6 h at room temp. after reaching 0 °C. Purification by column chromatography (silica gel, hexane/EtOAc, 1:1) yielded **2** (40 mg, 58%) as colourless oil.

(2a*R*,4a*R*,7a*S*,7b*S*)-7-Benzyl-7b-methoxy-4,4-dimethylhexahydro-2*H*,4*H*-1,3,6-trioxa-7-azacyclopenta[*cd*]indene (3): A solution of 1,2-oxazine *syn*-**1b** (650 mg, 2.13 mmol) in MeCN (18 mL) was treated with $SnCl_4$ (780 μL, 6.39 mmol) according to method A and the resulting solution was stirred for further 5 h at room temp. after reaching 0 °C. Purification by column chromatography (silica gel, hexane/EtOAc, 2:1) yielded **3** (440 mg, 68%) as colourless oil. $[\alpha]_D^{22}$ = +4.8 (*c* = 0.42, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.35, 1.41 (2s, 3 H each, Me), 2.15 (dd, *J* = 1.1, 5.1 Hz, 1 H, 4a-H), 3.42 (s, 3 H, OMe), 3.85 (dd, *J* = 4.6, 10.4 Hz, 1 H, 2-H), 3.99 (dd, *J* = 1.1, 12.3 Hz, 1 H, 5-H), 4.00 (dd, *J* = 1.0, 10.4 Hz, 1 H, 2-H), 4.01 (d, *J* = 14.2 Hz, 1 H, NCH_2), 4.08 (dd, *J* = 5.1, 12.3 Hz, 1 H, 5-H), 4.22 (d, *J* = 14.2 Hz, 1 H, NCH_2), 4.49 (dd, *J* = 1.0, 4.6 Hz, 1 H, 2a-H), 4.50 (s, 1 H, 7a-H), 7.24–7.40 (m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.6, 30.2 (2q, Me), 47.8 (d, C-4a), 52.9 (q, OMe), 57.6 (t, NCH_2), 67.2 (t, C-5), 71.1 (t, C-2), 84.8 (d, C-2a), 86.0, 90.5 (2s, C-4, C-7b), 93.4 (d, C-7a), 127.3, 128.4, 128.6, 137.2 (3d, s, Ph) ppm. IR (film): ṽ = 3055–3030 (=C–H), 2970–2870 (C–H) cm^{-1}. MS (EI, 80 eV, 150 °C): *m*/*z* (%) = 305 (44) [M^+], 244 (100) [M^+ – OMe – CH_2O], 214 (3) [M^+ – C_7H_7], 91 ($C_7H_7^+$, 57). HRMS: calcd. for $C_{17}H_{23}NO_4$ 305.16272; found 305.16366. $C_{17}H_{23}NO_4$ (305.4): calcd. C 66.86, H 7.59, N 4.59; found C 66.51, H 7.27, N 4.54.

(2a*R*,4a*R*,7a*S*,7b*S*)-7-Benzyl-7b-benzyloxy-4,4-dimethylhexahydro-2*H*,4*H*-1,3,6-trioxa-7-azacyclopenta[*cd*]indene (4): A solution of 1,2-oxazine *syn*-**1c** (890 mg, 2.33 mmol) in MeCN (19 mL) was treated with $SnCl_4$ (880 μL, 6.99 mmol) according to method A and the resulting solution was stirred for further 6 h at room temp. after reaching 0 °C. Purification by column chromatography (silica gel, hexane/EtOAc, 4:1) yielded **4** (486 mg, 55%) as colourless oil. $[\alpha]_D^{22}$ = +2.0 (*c* = 0.76, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.43, 1.47 (2s, 3 H each, Me), 2.31 (dd, *J* = 0.9, 5.2 Hz, 1 H, 4a-H), 3.94 (dd, *J* = 4.5, 10.5 Hz, 1 H, 2-H), 4.07 (dd, *J* = 0.9, 12.4 Hz, 1 H, 5-H), 4.07 (d, *J* = 14.5 Hz, 1 H, NCH_2), 4.08 (dd, *J* = 1.1, 10.5 Hz, 1 H, 2-H), 4.20 (dd, *J* = 5.2, 12.4 Hz, 1 H, 5-H), 4.31 (d, *J* = 14.5 Hz, 1 H, NCH_2), 4.64 (dd, *J* = 1.1, 4.5 Hz, 1 H, 2a-H), 4.67 (s, 1 H, 7a-H), 4.68 (d, *J* = 11.7 Hz, 1 H, OCH_2), 4.80 (d, *J* = 11.7 Hz, 1 H, OCH_2), 7.29–7.48 (m, 10 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.6, 30.3 (2q, Me), 49.1 (d, C-4a), 57.7 (t, NCH_2), 67.4 (t, C-5), 67.6 (t, OCH_2), 71.1 (t, C-2), 85.8 (d, C-2a), 86.2, 90.8 (2s, C-4, C-7b), 93.8 (d, C-7a), 127.3, 127.4, 127.9, 128.4, 128.6, 128.7, 137.3, 138.3 (6d, 2s, Ph) ppm. IR (film): ṽ = 3100–3020 (=C–H), 2980–2850 (C–H) cm^{-1}. MS (EI, 80 eV, 40 °C): *m*/*z* (%) = 381 (39) [M^+], 290 (7) [M^+ – C_7H_7], 287 (39), 244 (100), 121 (81), 91 (89) [$C_7H_7^+$], 78 (54). HRMS: calcd. for $C_{23}H_{27}NO_4$ 381.19401; found 381.19437. $C_{23}H_{27}NO_4$ (381.5): calcd. C 72.42, H 7.13, N 3.67; found C 72.52, H 7.69, N 3.81.

(2a*R*,4a*R*,7a*S*,7b*S*)-7-Benzyl-7b-(3′,3′-dimethylbutoxy)-4,4-dimethylhexahydro-2*H*,4*H*-1,3,6-trioxa-7-azacyclopenta[*cd*]indene (5): A solution of 1,2-oxazine *syn*-**1d** (200 mg, 0.533 mmol) in MeCN (4 mL) was treated with $SnCl_4$ (196 μL, 1.60 mmol) at 0 °C and the resulting solution was stirred for further 6 h at room temp. Then the mixture is quenched by water (8 mL). Addition of CH_2Cl_2 is followed by separation of the phases and the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. Purification by column chromatography (silica gel, hexane/EtOAc, 8:1) yielded **5** (137 mg, 69%) as colourless oil. $[\alpha]_D^{22}$ = +12.6 (*c* = 0.32, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.90 (s, 9 H, *t*Bu), 1.35, 1.40 (2s, 3 H each, Me), 1.48 (m_c, 1 H, CH_2), 1.50 (m_c, 1 H, CH_2), 2.15 (dd, *J* = 1.2, 5.3 Hz, 1 H, 4a-H), 3.54 (m_c, 1 H, CH_2O), 3.68 (m_c, 1 H, CH_2O), 3.90 (m_c, 1 H, 2-H), 3.91 (m_c, 1 H, 2-H), 3.97–4.01 (m, 1 H, 5-H), 4.02 (d, *J* = 13.9 Hz, 1 H, NCH_2), 4.10 (dd, *J* = 5.3, 12.5 Hz, 1 H, 5-H), 4.22 (d, *J* = 13.9 Hz, 1 H, NCH_2), 4.46 (s, 1 H, 7a-H), 4.47 (dd, *J* = 1.2, 4.6 Hz, 1 H, 2a-H), 7.25–7.39 (m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.4, 30.1 (2q, Me), 29.7 (q, *t*Bu), 43.7 (t, CH_2), 48.7 (d, C-4a), 57.5 (t, NCH_2), 62.5 (t, CH_2O), 67.3 (t, C-5), 70.9 (t, C-2), 85.5 (d, C-2a), 85.9 (s, C-4), 90.1 (s, C-7b), 93.3 (d, C-7a), 127.1, 128.2, 128.5, 137.1 (3d, s, Ph) ppm. IR (film): ṽ = 3085–3030 (=C–H), 2955–2865 (C–H) cm^{-1}. MS (EI, 80 eV, 150 °C): *m*/*z* (%) = 375 (33) [M^+], 360 (5) [M^+ – Me], 244 (100), 91 (57) [$C_7H_7^+$]. $C_{22}H_{33}NO_4$ (375.5): calcd. C 70.37, H 8.86, N 3.73; found C 70.11, H 8.81, N 3.50.

(1*S*,4*S*,7*R*,8*R*)-9-Benzyl-7-methoxy-2,2-dimethyl-3,6,10-trioxa-9-azatricyclo[5.4.0.0^{4,8}]undecane (9): A solution of 1,2-oxazine *anti*-**1** (500 mg, 1.64 mmol) in MeCN (11 mL) was treated with $SnCl_4$ (599 μL, 4.91 mmol) according to method A and the resulting solution was stirred for further 3 h at room temp. after reaching 0 °C. Purification by column chromatography (silica gel, hexane/EtOAc, 2:1) yielded **9** (250 mg, 50%) as colourless crystals; m.p. 148–150 °C. $[\alpha]_D^{22}$ = +148.0 (*c* = 0.20, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.38, 1.54 (2s, 3 H each, Me), 1.69 (m_c, 1 H, 1-H), 3.07 (m_c, 1 H, 8-H), 3.35 (s, 3 H, OMe), 3.79 (dd, *J* = 2.3, 9.5 Hz, 1 H, 5-H), 3.89 (d, *J* = 9.5 Hz, 1 H, 5-H), 4.03 (d, *J* = 13.2 Hz, 1 H, NCH_2), 4.05 (ddd, *J* = 1.1, 2.9, 12.0 Hz, 1 H, 11-H), 4.17 (dd, *J* = 1.1, 12.0 Hz, 1 H, 11-H), 4.34 (d, *J* = 13.2 Hz, 1 H, NCH_2), 4.64 (t, *J* = 2.3 Hz, 1 H, 4-H), 7.25–7.40 (m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 33.2, 34.4 (2q, Me), 49.5 (q, OMe), 52.7 (d, C-1), 62.2 (d, C-8), 63.5 (t, NCH_2), 70.7 (t, C-11), 73.8 (t, C-5), 77.0 (d, C-4), 81.4 (s, C-2), 106.6 (s, C-7), 131.3, 132.2, 132.5, 140.5 (3d, s, Ph) ppm. IR (KBr): ṽ = 3055–3030 (=C–H), 2970–2870 (C–H) cm^{-1}. MS (EI, 80 eV, 100 °C): *m*/*z* (%) = 305 (100) [M^+], 274 (20) [M^+ OMe], 91 (62) [$C_7H_7^+$]. $C_{17}H_{23}NO_4$ (305.4): calcd. C 66.86, H 7.59, N 4.59; found C 66.81, H 7.13, N 4.40.

(1*R*,5*S*,8*S*)-2-Benzyl-8-(hydroxymethyl)-6,6-dimethyl-3,7-dioxa-2-azabicyclo[3.3.1]nonan-9-one (10):[3] To a solution of tricyclic compound **9** (146 mg, 0.480 mmol) in 1,4-dioxane (5 mL) was added 2 N HCl (5 mL). The mixture was stirred at room temp. for 16 h and was subsequently neutralized with 2 N NaOH (5 mL). After addition of CH_2Cl_2 the phases were separated und the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. Purification by column chromatography (silica gel, hexane/EtOAc, 1:1) yielded **10** (130 mg, 94%) as colourless crystals.

(1*S*,4*S*,5*R*,8*R*)-(8-Benzylamino-5-methoxy-3,3-dimethyl-2,6-dioxabicyclo[3.2.1]octan-4-yl)methanol (11): 1,2-Diiodoethane (180 mg, 0.638 mmol) and samarium (105 mg, 0.710 mmol) were transferred into a dried flask. THF (8 mL) was added. After the solution turned blue, the mixture was stirred for further 2 h. Tricyclic compound **9** (60 mg, 0.197 mmol) in THF (8 mL) was added and the reaction mixture was stirred for 3 h. After addition of sat. $NaHCO_3$ solution (10 mL) the solution was decanted from the residue and the solvent was removed in vacuo. Product **11** (47 mg, 79%) was obtained in analytically pure form as colourless oil. $[\alpha]_D^{22}$ = –52.9 (*c* = 0.85, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.48, 1.51 (2s, 3 H each, Me), 2.19 (t, *J* = 3.6 Hz, 1 H, 4-H), 3.03 (dd, *J* = 0.8, 2.9 Hz, 1 H, 8-H), 3.30 (s, 3 H, OMe), 3.78 (dd, *J* = 4.3, 11.7 Hz,

1 H, 4-CH_2), 3.86 (d, J = 13.2 Hz, 1 H, NCH_2), 3.86 (dd, J = 2.9, 9.8 Hz, 1 H, 7-H), 3.89 (dd, J = 3.6, 11.7 Hz, 1 H, 4-CH_2), 3.92 (d, J = 13.2 Hz, 1 H, NCH_2), 4.07 (d, J = 9.8 Hz, 1 H, 7-H), 4.20 (t, J = 2.9 Hz, 1 H, 1-H), 7.25–7.34 (m, 10 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 28.6, 35.1 (2q, Me), 48.9 (q, OMe), 52.6 (t, NCH_2), 54.6 (d, C-4), 55.9 (d, C-8), 59.5 (t, 4-CH_2), 68.4 (t, C-7), 76.0 (d, C-1), 76.1 (s, C-3), 108.9 (s, C-5), 127.5, 128.2, 128.7, 138.6 (3d, s, Ph) ppm. IR (film): $\tilde{\nu}$ = 3430 (O–H), 3090–3020 (=C–H), 2970–2870 (C–H) cm^{-1}. MS (EI, 80 eV, 100 °C): m/z (%) = 307 (0.5) [M^+], 292 (0.8) [$M^+ - CH_3$], 91 (100) [$C_7H_7^+$]. HRMS: calcd. for $C_{17}H_{25}NO_4 - CH_3$]: 307.17836; found 307.17771.

Typical Procedure for the Hydrogenation of Tricyclic 1,2-Oxazines (Method B): A suspension of 10% palladium on charcoal (0.25 equiv. Pd) in MeOH (3 mL/mmol of 1,2-oxazine) was saturated with hydrogen for 1 h. After addition of a solution of 1,2-oxazine (1 equiv.) and if required *tert*-butyl dicarbonate (1.5 equiv.) in MeOH (1 mL/mmol of 1,2-oxazine) hydrogen is conducted through the mixture for 30 min. Subsequently the reaction mixture is stirred under an atmosphere of hydrogen for the time given in the individual procedure. The product is filtered through Celite and the solvent is removed in vacuo.

[(4a*R*,5*R*,7a*R*)-4a-Methoxy-7,7-dimethyl-4a,5,7,7a-tetrahydro-1*H*-furo[3,4-*d*][1,2]oxazin-5-yl]methanol (12): Tricyclic compound **3** (100 mg, 0.327 mmol) was hydrogenated for 30 min according to method B. Purification by column chromatography (silica gel, hexane/EtOAc, 1:1) yielded **12** (59 mg, 84%) as colourless oil. $[\alpha]_D^{22}$ = –32.2 (c = 0.85, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.20, 1.36 (2s, 3 H each, Me), 2.40 (dd, J = 5.5, 11.1 Hz, 1 H, 7a-H), 3.22 (s, 3 H, OMe), 3.64 (dd, J = 11.1, 11.9 Hz, 1 H, 1-H), 3.69 (ABX system, J_{AX} = 5.5, J_{AB} = 11.7 Hz, 1 H, 1′-H), 3.75 (ABX system, J_{BX} = 4.8, J_{AB} = 11.7 Hz, 1 H, 1′-H), 4.06 (ddd, J = 0.5, 5.5, 11.9 Hz, 1 H, 1-H), 4.12 (ABX system, J_{BX} = 4.8, J_{AX} = 5.5 Hz, 1 H, 5-H), 7.22 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 22.8, 26.7 (2q, Me), 43.6 (d, C-7a), 52.5 (q, OMe), 61.6 (t, C-1′), 65.6 (t, C-1), 78.8, 81.9 (2s, C-4a, C-7), 85.8 (d, C-5), 150.2 (d, C-4) ppm. IR (film): $\tilde{\nu}$ = 3600–3200 (O–H), 3000–2820 (C–H), 1670–1600 (C=N) cm^{-1}. $C_{10}H_{17}NO_4$ (215.3): calcd. C 55.80, H 7.96, N 6.51; found C 55.39, H 7.70, N 6.42.

[(4a*R*,5*R*,7a*R*)-4a-Benzyloxy-7,7-dimethyl-4a,5,7,7a-tetrahydro-1*H*-furo[3,4-*d*][1,2]oxazin-5-yl]methanol (13): Tricycle **4** (78 mg, 0.20 mmol) was hydrogenated for 30 min according to method B. Purification by column chromatography (silica gel, hexane/EtOAc, 1:1) yielded **13** (40 mg, 67%) as colourless oil. $[\alpha]_D^{22}$ = –37.6 (c = 0.42, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.25, 1.43 (2s, 3 H each, Me), 2.56 (dd, J = 5.6, 11.3 Hz, 1 H, 7a-H), 3.71 (dd, J = 11.3, 11.9 Hz, 1 H, 1-H), 3.76 (ABX system, J_{AX} = 5.0, J_{AB} = 11.9 Hz, 1 H, 1′-H), 3.83 (ABX system, J_{BX} = 4.7, J_{AB} = 11.9 Hz, 1 H, 1′-H), 4.15 (dd, J = 5.6, 11.9 Hz, 1 H, 1-H), 4.27 (ABX system, J_{BX} = 4.7, J_{AX} = 5.0 Hz, 1 H, 5-H), 4.45 (s, 2 H, OCH_2), 7.27–7.39 (m, 5 H, Ph), 7.31 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 22.7, 26.7 (2q, Me), 44.5 (d, C-7a), 61.4 (t, C-1′), 65.6 (t, C-1), 67.2 (t, OCH_2), 78.6, 81.9 (2s, C-4a, C-7), 85.8 (d, C-5), 127.5, 127.7, 128.5, 137.2 (3d, s, Ph), 150.3 (d, C-4) ppm. IR (film): $\tilde{\nu}$ = 3650–3250 cm^{-1} (O–H), 3100–3020 (=C-H), 3000–2830 (C-H), 1605 (C=N). $C_{16}H_{21}NO_4$ (291.3): calcd. C 65.96, H 7.27, N 4.81; found C 65.59, H 7.10, N 4.71.

[(4a*R*,5*R*,7a*R*)-4a-Methoxy-7,7-dimethyl-4a,5,7,7a-tetrahydro-1*H*-furo[3,4-*d*][1,2]oxazin-5-yl]methyl Acetate (14): To a solution of crude product **12** (496 mg, max. 2.32 mmol) in pyridine (10 mL) were added acetic acid anhydride (2.20 mL, 23.0 mmol) and DMAP (40 mg, 0.330 mmol). The resulting solution was stirred for 8 h at room temp. and subsequently water (20 mL) was added. After addition of CH_2Cl_2 the phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic phases were dried and the solvent was removed in vacuo. Purification by column chromatography (silica gel, hexane/EtOAc, 2:1) yielded **14** (472 mg, 84% from **3**) as colourless crystals; m.p. 91 °C. $[\alpha]_D^{22}$ = –85.2 (c = 0.65, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.21, 1.36 (2s, 3 H each, Me), 2.04 (s, 3 H, Ac), 2.40 (dd, J = 5.5, 11.6 Hz, 1 H, 7a-H), 3.22 (s, 3 H, OMe), 3.64 (t, J = 11.6 Hz, 1 H, 1-H), 4.11 (dd, J = 5.5, 11.6 Hz, 1 H, 1-H), 4.16–4.19 (m, 2 H, 1′-H, 5-H), 4.23 (dd, J = 4.6, 5.3 Hz, 1 H, 1′-H), 7.12 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.8 (q, Ac), 22.7, 26.4 (2q, Me), 42.9 (d, C-7a), 52.4 (q, OMe), 62.8 (t, C-1′), 65.7 (t, C-1), 79.1, 82.1 (2s, C-4a, C-7), 83.5 (d, C-5), 149.4 (d, C-4), 170.5 (s, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3040–2830 (C–H), 1745 (C=O), 1660–1590 (C=N) cm^{-1}. $C_{12}H_{19}NO_5$ (257.3): calcd. C 56.02, H 7.44, N 5.44; found C 56.01, H 7.46, N 5.51.

[(1*R*,3a*R*,6*S*,6a*S*)-6-Amino-6a-methoxy-3,3-dimethyltetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-1-yl]methanol (15a) and [(3*R*,3a*S*,4*R*,6a*R*)-4-Amino-3a-methoxy-2,2-dimethylhexahydrofuro[3,4-*b*]furan-3-yl]-methanol (16a): Tricyclic compound **3** (100 mg, 0.327 mmol) was hydrogenated for 17 h according to method B. Purification by column chromatography (silica gel, CH_2Cl_2/MeOH, 20:1) yielded a mixture[10] of **15a** and **16a** (55 mg, 77%) as colourless oil (**15a**/**16a** = 4:1). $[\alpha]_D^{22}$ = +18.6 (c = 1.53, $CHCl_3$). **15a:** ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.22, 1.32 (2s, 3 H each, Me), 2.71 (dd, J = 6.0, 9.1 Hz, 1 H, 3a-H), 3.43 (s, 3 H, OMe), 3.68 (dd, J = 6.0, 9.7 Hz, 1 H, 4-H), 3.70 (dd, J = 7.8, 11.9 Hz, 1 H, 1′-H), 3.80 (dd, J = 5.5, 11.9 Hz, 1 H, 1′-H), 3.97 (dd, J = 9.1, 9.7 Hz, 1 H, 4-H), 4.15 (dd, J = 5.5, 7.8 Hz, 1 H, 1-H), 4.58 (s, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.8, 28.5 (2q, Me), 52.3 (q, OMe), 53.2 (d, C-3a), 61.2 (t, C-1′), 65.0 (t, C-4), 73.5 (d, C-1), 79.5 (s, C-3), 86.7 (d, C-6), 93.7 (s, C-6a) ppm. **16a:** ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.16, 1.31 (2s, 3 H each, Me), 2.59 (dd, J = 5.4, 10.9 Hz, 1 H, 3-H), 3.40 (s, 3 H, OMe), 3.59 (dd, J = 5.4, 12.0 Hz, 1 H, 1′-H), 3.72 (dd, J = 1.6, 10.3 Hz, 1 H, 6-H), 3.87 (dd, J = 10.9, 12.0 Hz, 1 H, 1′-H), 4.08 (dd, J = 5.0, 10.3 Hz, 1 H, 6-H), 4.46 (dd, J = 1.6, 5.0 Hz, 1 H, 6a-H), 4.95 (s, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.7, 30.3 (2q, Me), 48.1 (d, C-3), 51.2 (q, OMe), 59.7 (t, C-1′), 70.0 (t, C-6), 77.6 (d, C-6a), 82.5 (s, C-2), 86.8 (d, C-4), 92.9 (s, C-3a) ppm. IR (film): $\tilde{\nu}$ = 3400 (O–H), 3320 (N–H), 2955–2855 (C–H) cm^{-1}. MS (FAB): m/z (%) = 240 (55) [M^+ + Na], 218 (60) [M^+ + H], 154 (100). $C_{10}H_{19}NO_4$ (217.3): calcd. C 55.28, H 8.81, N 6.45; found C 54.97, H 8.50, N 6.32.

***tert*-Butyl (1*S*,3a*R*,6*R*,6a*S*)-6-(Hydroxymethyl)-6a-methoxy-4,4-dimethylhexahydrofuro[3,4-*c*]furan-1-yl Carbamate (15b) and *tert*-Butyl (3*R*,3a*S*,4*R*,6a*R*)-3-(Hydroxymethyl)-3a-methoxy-2,2-dimethylhexahydrofuro[3,4-*b*]furan-4-yl Carbamate (16b):** Tricyclic compound **3** (100 mg, 0.327 mmol) was hydrogenated for 18 h in presence of *tert*-butyl dicarbonate (214 mg, 0.980 mmol) according to method B. Purification by column chromatography (silica gel, hexane/EtOAc, 1:1) yielded a mixture of **15b** and **16b** (86 mg, 82%) as colourless crystals (**15b**/**16b** = 7:1); m.p. 124–126 °C. $[\alpha]_D^{22}$ = +45.2 (c = 0.86, $CHCl_3$). **15b**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.20, 1.29 (2s, 3 H each, Me), 1.37 (s, 9 H, *t*Bu), 2.56 (dd, J = 4.8, 8.4 Hz, 1 H, 3a-H), 2.70 (br. s, 1 H, OH), 3.31 (s, 3 H, OMe), 3.69 (dd, J = 4.8, 9.7 Hz, 1 H, 3-H), 3.60–3.64 (m, 2 H, 6′-H), 3.87 (dd, J = 8.4, 9.7 Hz, 1 H, 3-H), 4.15 (t, J = 5.8 Hz, 1 H, 6-H), 5.26 (d, J = 8.5 Hz, 1 H, 1-H), 5.59 (d, J = 8.5 Hz, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.6, 27.6 (2q, Me), 28.1, 80.1 (q, s, *t*Bu), 52.7 (q, OMe), 54.1 (d, C-3a), 58.8 (t, C-6′), 65.0 (t, C-3), 77.5 (d, C-6), 79.9 (s, C-4), 82.5 (d, C-1), 92.9 (s, C-6a), 154.6 (s, NCO) ppm. **16b:** ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.24, 1.31 (2s, 3 H each, Me), 1.37 (s, 9 H, *t*Bu), 2.59 (m_c, 1 H, 3-H), 3.32 (s, 3 H,

OMe), 3.62 (m_c, 1 H, 3′-H), 3.66 (dd, J = 1.0, 10.4 Hz, 1 H, 6-H), 3.74 (dd, J = 7.1, 11.0 Hz, 1 H, 3′-H), 3.91 (dd, J = 4.5, 10.4 Hz, 1 H, 6-H), 4.43 (dd, J = 1.0, 4.5 Hz, 1 H, 6a-H), 5.55 (d, J = 9.0 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.2, 31.0 (2q, Me), 28.1 (q, *t*Bu), 50.6 (d, C-3), 51.8 (q, OMe), 58.8 (t, C-3′), 69.8 (t, C-6), 80.1 (d, C-6a), 83.2 (d, C-4), 92.1 (s, C-3a), 159.7 (s, NCO) ppm. Signals of C-2 and the singlet of the *t*Bu group were not detected. IR (KBr): $\tilde{\nu}$ = 3550–3300 (O–H, N–H), 2990–2830 (C–H), 1720 (C=O) cm^{-1}. $C_{15}H_{27}NO_6$ (317.4): calcd. C 56.77, H 8.57, N 4.41; found C 56.85, H 8.53, N 4.36.

***tert*-Butyl (1*S*,3a*R*,6*R*,6a*S*)-6a-Hydroxy-6-(hydroxymethyl)-4,4-dimethylhexahydrofuro[3,4-*c*]furan-1-yl Carbamate (15c) and *tert*-Butyl (3*R*,3a*S*,4*R*,6a*R*)-3a-Hydroxy-3-(hydroxymethyl)-2,2-dimethylhexahydrofuro[3,4-*b*]furan-4-yl Carbamate (16c):** Tricyclic compound **4** (150 mg, 0.393 mmol) was hydrogenated for 18 h in presence of *tert*-butyl dicarbonate (129 mg, 0.591 mmol) according to method B. Purification by column chromatography (silica gel, hexane/EtOAc, 1:4) yielded a mixture of **15c** and **16c** (75 mg, 63%) as colourless oil (**15c/16c** = 9:1). $[a]_D^{22}$ = +35.7 (c = 0.31, $CHCl_3$) **15c:** ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.22, 1.36 (2s, 3 H each, Me), 1.43 (s, 9 H, *t*Bu), 2.45 (dd, J = 5.1, 7.7 Hz, 1 H, 3a-H), 3.18 (br. s, 1 H, OH), 3.64 (dd, J = 5.1, 9.4 Hz, 1 H, 3-H), 3.69 (dd, J = 7.7, 9.4 Hz, 1 H, 3-H), 3.71–3.77 (m, 2 H, 6′-H), 4.04 (dd, J = 5.2, 6.6 Hz, 1 H, 6-H), 5.26 (d, J = 8.0 Hz, 1 H, 1-H), 5.84 (d, J = 8.0 Hz, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.3, 28.1 (2q, Me), 28.3 (q, *t*Bu), 60.4 (d, C-3a), 60.5 (t, C-6′), 65.1 (t, C-3), 80.3 (s, C-4), 81.4 (d, C-6), 83.2 (d, C-1), 88.1 (s, C-6a), 155.2 (s, NCO) ppm. The signal for the singlet of the *t*Bu group was not detected. **16c** (not all signals detected): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.21, 1.35 (2s, 3 H each, Me), 1.43 (s, 9 H, *t*Bu), 2.59 (dd, J = 5.9, 9.9 Hz, 1 H, 3-H), 3.75 (m_c, 1 H, 6-H), 3.91 (m_c, 1 H, 3′-H), 4.00 (m_c, 1 H, 6-H), 4.25 (m_c, 1 H, 3′-H), 4.32 (m_c, 1 H, 6a-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 28.3 (q, *t*Bu), 66.3 (t, C-3′), 70.5 (t, C-6), 85.6 (d, C-6a) ppm. IR (film): $\tilde{\nu}$ = 3650–3150 (O–H), 2990–2830 (C–H), 1700 (C=O) cm^{-1}. MS (EI, 80 eV, 120 °C): m/z (%) = 303 (0.2) [M$^+$], 285 (0.3) [M$^+$ – H_2O], 187 (2) [M$^+$ – NHBoc], 158 (27), 97 (17), 57 (100) $[C_4H_9]^+$. HRMS: calcd. for $C_{14}H_{25}NO_6$ 303.16818; found 303.16744.

[(1*R*,3a*R*,6*S*,6a*S*)-6-Benzylamino-6a-methoxy-3,3-dimethyltetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-1-yl]methanol (15d) and [(3*R*,3a*S*,4*R*,6a*R*)-4-Benzylamino-3a-methoxy-2,2-dimethylhexahydrofuro[3,4-*b*]furan-3-yl]methanol (16d): 1,2-Diiodoethane (679 mg, 2.41 mmol) and samarium (402 mg, 2.71 mmol) were transferred into a dried flask. THF (25 mL) was added. After the solution turned blue, the mixture was stirred for further 2 h. Tricyclic compound **3** (230 mg, 0.750 mmol) in THF (4 mL) was added and the reaction mixture was stirred for 3 h. After addition of sat. $NaHCO_3$ solution (20 mL) the resulting solid was filtered off and CH_2Cl_2 was added. The phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. Purification by column chromatography (silica gel, hexane/EtOAc, 1:1) yielded a mixture of **15d** and **16d** (100 mg, 43%) as colourless oil (**15d/16d** = 4:1). $[a]_D^{22}$ = +37.4 (c = 0.31, $CHCl_3$). **15d**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.24, 1.35 (2s, 3 H each, Me), 2.72 (dd, J = 5.9, 9.3 Hz, 1 H, 3a-H), 3.43 (s, 3 H, OMe), 3.59 (dd, J = 8.4, 11.9 Hz, 1 H, 1′-H), 3.72 (dd, J = 5.9, 9.3 Hz, 1 H, 4-H), 3.80 (dd, J = 5.6, 11.9 Hz, 1 H, 1′-H), 3.90 (d, J = 12.7 Hz, 1 H, NCH_2), 4.05 (t, J = 9.3 Hz, 1 H, 4-H), 4.09 (d, J = 12.7 Hz, 1 H, NCH_2), 4.19 (dd, J = 5.6, 8.4 Hz, 1 H, 1-H), 4.49 (s, 1 H, 6-H), 7.24–7.29, 7.30–7.40 (2m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.8, 28.5 (2q, Me), 50.4 (t, NCH_2), 52.2 (q, OMe), 53.0 (d, C-3a), 61.4 (t, C-1′), 65.2 (t, C-4), 73.1 (d, C-1), 79.5 (s, C-3), 90.5 (d, C-6), 94.2 (s, C-6a), 127.4, 128.5, 128.6, 138.8 (3d, s, Ph) ppm. **16d:** ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.09, 1.32 (2s, 3 H each, Me), 2.61 (dd, J = 5.4, 11.0 Hz, 1 H, 3-H), 3.40 (s, 3 H, OMe), 3.55 (dd, J = 5.4, 12.0 Hz, 1 H, 1′-H), 3.70 (dd, J = 11.0, 12.0 Hz, 1 H, 1′-H), 3.80 (m_c, 1 H, 6-H), 3.90 (d, J = 12.7 Hz, 1 H, NCH_2), 4.09 (d, J = 12.7 Hz, 1 H, NCH_2), 4.14 (dd, J = 4.9, 10.3 Hz, 1 H, 6-H), 4.47 (dd, J = 1.5, 4.9 Hz, 1 H, 6a-H), 4.83 (s, 1 H, 4-H), 7.24–7.29, 7.30–7.40 (2m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 24.7, 30.4 (2q, Me), 48.0 (d, C-3), 50.5 (t, NCH_2), 51.3 (q, OMe), 59.9 (t, C-1′), 70.1 (t, C-6), 77.6 (d, C-6a), 82.4 (s, C-2), 90.4 (d, C-4), 93.3 (s, C-3a), 127.4, 128.5, 128.6, 138.8 (3d, s, Ph) ppm. IR (film): $\tilde{\nu}$ = 3365 (N–H), 3300 (O–H), 3085–3030 (=CH), 2955–2855 (C–H), 1600 (C=C) cm^{-1}. MS (FAB): m/z (%) = 308 (45) [M$^+$ + H], 307 (24) [M$^+$], 264 (17) [M$^+$ + H – 43], 172 (100). HRMS (M$^+$ – CH_3) calcd. for $C_{17}H_{25}NO_4$ 292.15488; found 292.15622.

[(4a*R*,5*R*,7a*R*)-5-(Acetoxymethyl)-4a-methoxy-7,7-dimethylhexahydro-1*H*-furo[3,4-*d*][1,2]oxazin-3-ium-3-yl] (Cyano)dihydroborate (18): To a solution of 1,2-oxazine **14** (180 mg, 0.700 mmol) in AcOH (4 mL) was added $NaBH_3(CN)$ (150 mg, 2.34 mmol) and the resulting solution was stirred at room temp. for 27 h. Subsequently the mixture was poured into sat. $NaHCO_3$ solution (23 mL). After addition of CH_2Cl_2 the phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and the solvent was removed in vacuo. Purification by column chromatography (silica gel, hexane/EtOAc, 1:4) yielded **18** (152 mg, 73%) as colourless crystals; m.p. 150–152 °C. $[a]_D^{22}$ = +48.8 (c = 0.62, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.34, 1.39 (2s, 3 H each, Me), 2.08 (s, 3 H, Ac), 2.20 (dd, J = 1.1, 3.8 Hz, 1 H, 7a-H), 3.19 (ABX system, J_{AX} = 1.9, J_{AB} = 13.8 Hz, 1 H, 4-H), 3.31 (ABX system, J_{BX} = 11.0, J_{AB} = 13.8 Hz, 1 H, 4-H), 3.35 (s, 3 H, OMe), 3.95 (dd, J = 7.2, 12.0 Hz, 1 H, 1′-H), 4.08 (dd, J = 1.1, 13.5 Hz, 1 H, 1-H), 4.11 (dd, J = 3.4, 7.2 Hz, 1 H, 5-H), 4.32 (dd, J = 3.4, 12.0 Hz, 1 H, 1′-H), 4.42 (dd, J = 3.8, 13.5 Hz, 1 H, 1-H), 8.12 (ABX system, J_{AX} = 1.9, J_{BX} = 11.0 Hz, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.8 (q, Ac), 25.5, 30.6 (2q, Me), 43.5 (d, C-7a), 50.7 (q, OMe), 54.0 (t, C-4), 61.7 (t, C-5′), 66.9 (t, C-1), 73.0 (d, C-5), 79.6 (s, C-7), 99.9 (s, C-4a), 170.7 (s, OCO) ppm. The signal of the CN group was not detected. IR (KBr): $\tilde{\nu}$ = 3650–3260 (N–H), 3060–2840 (C–H), 2420 (B–H), 2215 (CN), 1740 (C=O) cm^{-1}. MS (FAB): m/z (%) = 321 (44) [M$^+$ + Na], 299 (100) [M$^+$ + H], 282 [M$^+$ + Na – BH_2CN], 43 (115) $[CH_3CO]^+$. $C_{13}H_{23}BN_2O_5$ (298.1): calcd. C 52.37, H 7.78, N 9.40; found C 52.57, H 7.55, N 9.53.

{(2*R*,3*R*,4*R*)-3-[(*tert*-Butoxycarbonylamino)methyl]-4-(hydroxymethyl)-3-methoxy-5,5-dimethyltetrahydrofuran-2-yl}methyl Acetate (19): 1,2-Oxazine **18** (84 mg, 0.280 mmol) was hydrogenated for 18 h in presence of *tert*-butyl dicarbonate (109 mg, 0.500 mmol) according to method B. Purification by column chromatography (silica gel, hexane/EtOAc, 1:2) yielded **19** (69 mg, 68%) as colourless oil. $[a]_D^{22}$ = +17.6 (c = 0.50, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.23, 1.35 (s, 3 H, Me), 1.40 (s, 9 H, *t*Bu), 2.05 (s, 3 H, Ac), 2.21 (br. s, 1 H, OH), 2.43 (t, J = 7.4 Hz, 1 H, 4-H), 3.25 (dd, J = 3.0, 13.4 Hz, 1 H, 3′-H), 3.33 (s, 3 H, OMe), 3.47 (dd, J = 6.5, 13.4 Hz, 1 H, 3′-H), 3.66 (dd, J = 7.4, 10.5 Hz, 1 H, 4′-H), 3.81 (dd, J = 7.4, 10.5 Hz, 1 H, 4′-H), 3.91 (dd, J = 8.1, 11.7 Hz, 1 H, 1′-H), 4.05 (dd, J = 2.5, 8.1 Hz, 1 H, 2-H), 4.42 (dd, J = 2.5, 11.7 Hz, 1 H, 1′-H), 5.08 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.9 (q, Ac), 24.5, 30.7 (2s, Me), 28.3 (q, *t*Bu), 39.2 (t, C-3′), 50.7 (q, OMe), 53.6 (d, C-4), 59.1 (t, C-4′), 63.4 (t, C-1′), 76.5 (d, C-2), 79.9, 84.2 (2s, 3-C, 5-C), 155.7 (s, NCO), 170.9 (s, OCO) ppm. The signal for the singlet of the *t*Bu group was not detected. IR (film): $\tilde{\nu}$ = 3600–3250 (O–H), 2990–2830 (C–H), 1745–

1685 (C=O) cm^{-1}. MS (FAB): *m/z* (%) = 384 (46) [M^+ + Na], 362 (23) [M^+ + H], 328 (9) [M^+ + Na – C_4H_8], 328 (20) [M^+ + H – C_4H_8], 57 (100) [C_4H_9]$^+$, 43 (81) [Ac^+]. HRMS (EI, 80 eV, 130 °C): *m/z* (%) = (M^+ – CH_3COOH) calcd. for 301.18892; found 301.18755.

(4a*R*,5*R*,7a*R*)-5-[(*tert*-Butyldimethylsiloxy)methyl]-4a-methoxy-7,7-dimethyl-4a,5,7,7a-tetrahydro-1*H*-furo[3,4-*d*][1,2]oxazine (20): To a solution of crude product **12** (456 mg, max. 2.12 mmol) in CH_2Cl_2 (5 mL) were added Et_3N (890 µL, 6.36 mmol) and TBSOTf (730 µL, 3.18 mmol) at 0 °C and the resulting solution was stirred at this temperature for 8 h. Subsequently the mixture was quenched by addition of sat. NH_4Cl solution (10 mL). The phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. Purification by column chromatography (silica gel, hexane/EtOAc, 2:1) yielded **20** (449 mg, 65% from **3**) as colourless oil. $[\alpha]_D^{22}$ = –81.1 (*c* = 0.47, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.03, 0.04 (2s, 3 H each, $SiMe_2$), 0.86 (s, 9 H, *t*Bu), 1.16, 1.35 (2s, 3 H each, Me), 2.37 (dd, *J* = 5.5, 12.1 Hz, 1 H, 7a-H), 3.23 (s, 3 H, OMe), 3.59 (t, *J* = 12.1 Hz, 1 H, 1-H), 3.65 (ABX system, J_{AX} = 7.3, J_{AB} = 11.0 Hz, 1 H, 5′-H), 3.75 (ABX system, J_{BX} = 3.8, J_{AB} = 11.0 Hz, 1 H, 5′-H), 4.08 (ABX system, J_{BX} = 3.8, J_{AX} = 7.3 Hz, 1 H, 5-H), 4.09 (ddd, *J* = 0.5, 5.5, 12.1 Hz, 1 H, 1-H), 7.22 (d, *J* = 0.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = –5.5 (q, $SiMe_2$), 18.2, 25.8 (s, q, *t*Bu), 22.6, 26.4 (2q, Me), 43.3 (d, C-7a), 52.1 (q, OMe), 62.4 (t, C-5′), 65.5 (t, C-1), 79.8, 81.5 (2s, C-4a, C-7), 86.1 (d, C-5), 150.2 (d, C-4) ppm. IR (film): $\tilde{\nu}$ = 2990–2830 (C–H), 1605 (C=N) cm^{-1}. $C_{16}H_{31}NO_4Si$ (329.5): calcd. C 58.32, H 9.48, N 4.25; found C 58.08, H 9.67, N 4.29.

(3a*R*,6*R*,6a*S*)-6-[(*tert*-Butyldimethylsiloxy)methyl]-6a-methoxy-4,4-dimethyltetrahydrofuro[3,4-*c*]furan-1(3*H*)-imine (21) and (3a*R*,1*R*,6*R*,6a*S*)-1-Butyl-6-[(*tert*-butyldimethylsiloxy)methyl]-6a-methoxy-4,4-dimethylhexahydrofuro[3,4-*c*]furan-1-amine (22): To a solution of *n*BuLi (2.5 M in hexane, 240 µL, 0.600 mmol) in THF (2 mL) is dropped over a period of 5 min a solution of 1,2-oxazine **20** (100 mg, 0.300 mmol) in THF (1 mL) at –40 °C. The mixture was allowed to reach room temp. and was stirred for 4 h. Subsequently, the reaction mixture was quenched with water (6 mL). After addition of CH_2Cl_2 the phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. Purification by column chromatography (silica gel, hexane/EtOAc, 6:1 → 1:1) yielded **21** (50 mg, 50%) as colourless crystals and **22** (12 mg, 12%) as colourless oil. **21:** M.p. 52–53 °C. $[\alpha]_D^{22}$ = +12.5 (*c* = 0.82, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.02, 0.03 (2s, 3 H each, $SiMe_2$), 0.86 (s, 9 H, *t*Bu), 1.22, 1.36 (2s, 3 H each, Me), 2.93 (ABX system I, J_{AX} = J_{BX} = 9.3 Hz, 1 H, 3a-H), 3.72 (ABX system II, J_{AX} = 4.0, J_{AB} = 11.2 Hz, 1 H, 6′-H), 3.77 (ABX system II, J_{BX} = 4.0, J_{AB} = 11.2 Hz, 1 H, 6′-H), 4.06 (ABX system II, J_{AX} = J_{BX} = 4.0 Hz, 1 H, 6-H), 4.08 (ABX system I, J_{BX} = J_{AB} = 9.3 Hz, 1 H, 3-H), 4.15 (ABX system I, J_{BX} = J_{AB} = 9.3 Hz, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = –5.7, –5.5 (2q, $SiMe_2$), 18.3, 25.8 (s, q, *t*Bu), 23.4, 25.1 (2q, Me), 50.7 (d, C-3a), 52.6 (q, OMe), 62.0 (t, C-6′), 66.6 (t, C-3), 80.5 (s, C-4), 86.8 (d, C-6), 93.0 (s, C-6a), 170.7 (s, C-1) ppm. IR (KBr): $\tilde{\nu}$ = 3260 (N–H), 3000–2810 (C–H), 1690 (C=N) cm^{-1}. MS (EI, 80 eV, 40 °C): *m/z* (%) = 329 (< 1) [M^+], 314 (4) [M^+ – CH_3], 272 (100) [M^+ – C_4H_9], 298 (< 1) [M^+ – OCH_3], 172 (19), 73 (43). $C_{16}H_{31}NO_4Si$ (329.6): calcd. C 58.32, H 9.48, N 4.25; found C 58.06, H 9.22, N 4.22.

21: $[\alpha]_D^{22}$ = +7.3 (*c* = 0.30, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.07, 0.08 (2s, 3 H each, $SiMe_3$), 0.88 (s, 9 H, *t*Bu), 0.92 (t, *J* = 7.3 Hz, 3 H, Me), 1.26, 1.37 (2s, 3 H each, Me), 1.32–1.45 (m, 4 H, CH_2), 1.60, 1.75 (2 m_c, 1 H each, CH_2), 2.69 (ABX system I, J_{AX} = 6.5, J_{BX} = 9.5 Hz, 1 H, 3a-H), 3.78 (ABX system I, J_{AX} = 6.5, J_{AB} = 9.5 Hz, 1 H, 3-H), 3.83 (ABX system I, J_{BX} = J_{AB} = 9.5 Hz, 1 H, 3-H), 4.01 (ABX system II, J_{AX} = 5.4, J_{AB} = 11.5 Hz, 1 H, 6′-H), 4.06 (ABX system II, J_{BX} = 5.4, J_{AB} = 11.5 Hz, 1 H, 6′-H), 4.15 (ABX system II, J_{AX} = J_{BX} = 5.4 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = –5.3, –5.1 (2q, $SiMe_2$), 14.1 (q, Me), 18.2, 25.9 (q, s, *t*Bu), 23.3, 24.9 (2t, CH_2), 24.8, 27.9 (2q, Me), 36.4 (t, CH_2), 52.7 (q, OMe), 55.5 (d, C-3a), 62.0 (t, C-6′), 63.3 (t, C-3), 78.9, 96.7 (2s, C-6a, C-4), 82.1 (d, C-6) ppm. The signal for C-1 was not detected. IR (film): $\tilde{\nu}$ = 3450–3300 (N–H), 2990–2830 (C–H) cm^{-1}. MS (EI, 80 eV, 50 °C): *m/z* (%) = 387 (1) [M^+], 369 (4) [M^+ – H_2O], 330 (26) [M^+ – C_4H_9], 313 (59), 197 (100) [M^+ – C_4H_9 – OTBS – H_2O], 137 (45), 73 (99). HRMS: calcd. for $C_{20}H_{41}NO_4Si$ 387.28049; found 387.28084.

(2a*R*,4a*R*,6a*R*,6b*S*)-6b-Methoxy-4,4-dimethyl-1-(tolylsulfonyl)hexahydro-1*H*,4*H*-3,6-dioxa-1-azacyclopenta[*cd*]pentalene (23): To a solution of crude product **15a/16a** (211 mg, max. 0.980 mmol) in CH_2Cl_2 (8 mL) was added Et_3N (170 µL, 1.20 mmol), DMAP (29 mg, 0.200 mmol) and *p*TsCl (411 mg, 2.16 mmol) at room temp. and the resulting solution was stirred for 19 h. Subsequently, the mixture was quenched by addition of sat. NH_4Cl solution (15 mL). The phases were separated and the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. Purification by column chromatography (silica gel, hexane/EtOAc, 2:1) yielded **23** (183 mg, 57% from **3**) as colourless crystals; m.p. 103–106 °C. $[\alpha]_D^{22}$ = –66.8 (*c* = 0.27, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.17, 1.28 (2s, 3 H each, Me), 2.42 (s, 3 H, Ar*Me*), 2.65 (dd, *J* = 8.6, 9.3 Hz, 1 H, 4a-H), 3.29 (s, 3 H, OMe), 3.49 (ABX system, J_{AX} = 1.1, J_{AB} = 11.0 Hz, 1 H, 2-H), 3.60 (ABX system, J_{BX} = 5.8, J_{AB} = 11.0 Hz, 1 H, 2-H), 3.77 (t, *J* = 9.3 Hz, 1 H, 5-H), 4.02 (dd, *J* = 8.6, 9.3 Hz, 1 H, 5-H), 4.39 (ABX system, J_{AX} = 1.1, J_{BX} = 5.8 Hz, 1 H, 2a-H), 5.65 (s, 1 H, 6a-H), 7.30 (d, *J* = 8.0 Hz, 2 H, Ar), 7.78 (d, *J* = 8.0 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.5 (q, Ar*Me*), 23.4, 25.9 (2q, Me), 53.5 (t, C-2), 53.7 (q, OMe), 55.5 (d, C-4a), 68.8 (t, C-5), 81.2 (d, C-2a), 83.0 (s, C-4), 94.3 (d, C-6a), 108.4 (s, C-6b), 127.6, 129.6, 137.0, 143.6 (2d, 2s, Ar) ppm. IR (KBr): $\tilde{\nu}$ = 3090–3030 (=C–H), 2990–2830 (C–H), 1345 (O=S=O), 1165 (C–N) cm^{-1}. MS (EI, 80 eV, 130 °C): *m/z* (%) = 353 (7) [M^+], 338 (2) [M^+ – CH_3], 308 (8) [M^+ – CH_3 – OCH_3], 198 (34) [M^+ – $SO_2C_7H_7$], 155 (39) [$C_7H_7SO_2$]$^+$, 91 (100) [C_7H_7]$^+$. HRMS: calcd. for $C_{17}H_{23}NO_5S$ 353.12969; found 353.12877. $C_{17}H_{23}NO_5S$ (353.4): calcd. C 57.77, H 6.56, N 3.96, S 9.07; found C 58.02, H 6.09, N 3.95, S 8.93.

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