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Chemical Papers 67 (1) 66–75 (2013)
DOI: 10.2478/s11696-012-0224-5

ORIGINAL PAPER

Aminohydroxylation of divinylcarbinol and its application to the synthesis of bicyclic hydroxypyrrolidine and aminotetrahydrofuran building blocks

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Received 30 March 2012; Revised 21 May 2012; Accepted 25 May 2012

Dedicated to Professor Štefan Toma on the occasion of his 75th birthday

Aminohydroxylation of prochiral divinylcarbinol and subsequent Pd(II)-catalysed oxy-/amidocarbonylation of aminopentenediols is reported. The method was applied to the preparation of useful building blocks for syntheses of cytotoxic jaspines and glycosidase inhibitor DLX-homologues. The key intermediates, tetrahydrofuranolactones (L-*arabino-II*) and pyrrolidinolactones (L-*arabino-IX* and L-*xylo-IX*), were prepared in a short 2-step sequence from divinylcarbinol.

Keywords: Sharpless aminohydroxylation, Pd(II)-catalysed oxy-/amidocarbonylation, jaspine B, pachastrissamine, DLX-homologues

Introduction

Pachastrissamine (jaspine B, *I*) (Fig. 1), the first naturally occurring anhydrophytosphingosine derivative, is a metabolite isolated from the Okinawa marine sponge *Pachastrissa* sp. (Kuroda et al., 2002). The Debitus research group reported isolation of the same natural product from a different marine sponge *Jaspis* sp. (Ledroit et al., 2003). In anti-cancer assays, this novel sphingosine derivative proved to be the most potent compound against the A549 human lung carcinoma cell line isolated from the *Jaspis* genus. The combination of potent biological properties and relatively straightforward molecular structures has led to the development of a number of its synthetic preparations (Llaveria et al., 2011; Passiniemi & Koskinen, 2011; Yoshimitsu et al., 2011; Srinivas Rao & Venkateswara Rao, 2011; Urano et al., 2010; Salma et al., 2010; Inuki et al., 2009, 2010; Yoshimitsu et al., 2010; Vichare & Chattopadhyay, 2010; Canals et al., 2009; Enders et al., 2008; Abraham et al., 2008, and the articles cited in their review). The biological activities of numerous synthetic analogues and epimers have also been prepared and tested.

Previous investigations in our laboratory have demonstrated that the Pd(II)-catalysed oxy- and amidocarbonylation of unsaturated polyols and amino polyols represent an efficient entry to *cis*-fused 5-membered bicyclic lactones (Gracza et al., 1991; Jäger et al., 1997; Hümmer et al., 1997). This methodology has been used as the key step in a number of natural product syntheses (Gracza & Jäger, 1992, 1994; Dixon et al., 1999; Babjak et al., 2002, 2005; Karlubíková et al., 2011). Here we report on a further application of this versatile methodology to encompass the asymmetric syntheses of the 3,6-anhydro-2,5-dideoxy-5-R-amino-L-*arabino*-1,4-hexonolactones (L-*arabino-IIa*, L-*arabino-IIb*, *N*-R-2,3,6-trideoxy-3,6-imino-L-*arabino*-1,4-hexonolactones (L-*arabino-IXa*, L-*arabino-IXb*), and *N*-R-2,3,6-trideoxy-3,6-imino-L-*xylo*-1,4-hexonolactones (L-*xylo-IXa*, L-*xylo-IXb*).

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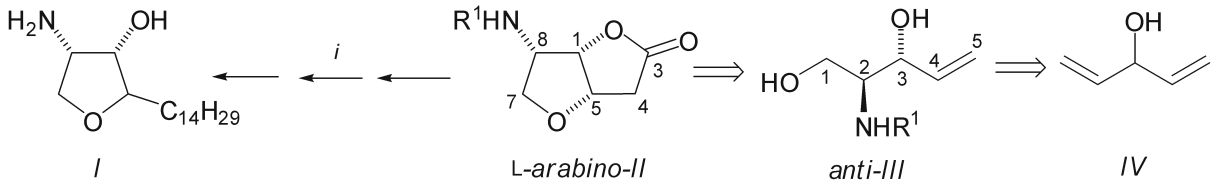

Fig. 1. Retrosynthetic analysis of pachastrissamine (jaspine B) (*I*). Reaction conditions: *i*) multi-step procedure described by Bhaket et al. (2005).

Experimental

Commercial reagents were used without further purification. All solvents were distilled before use. Hexanes refer to the fraction boiling at 60–65 °C. Flash column liquid chromatography (FLC) was performed on silica gel Kieselgel 60 (40–63 μm, 230–400 mesh) using a Buchi Sepacore® preparative MPLC system and analytical thin-layer chromatography (TLC) was performed on aluminium plates pre-coated with either 0.2 mm (DC-Alufolien, Merck) or 0.25 mm silica gel 60 F_{254} (ALUGRAM® SIL G/UV_{254}, Macherey-Nagel). The compounds were visualised by UV fluorescence and by dipping the plates in an aqueous H_2SO_4 solution of cerium sulphate/ammonium molybdate followed by charring with a heat-gun. Melting points were determined on a Büchi B-540 apparatus and are uncorrected. Optical rotations were measured with a JASCO P-2000 polarimeter. FTIR spectra were obtained on a Nicolet 5700 spectrometer (Thermo Electron) equipped with a Smart Orbit (diamond crystal ATR) accessory, using the reflectance technique (4000–400 cm^{-1}). Mass spectra (MS) were measured on an Agilent 1260B LCMS system. An MS detector was assembled with a multimode ion source (ESI + APCI) in positive mode, 50 % scan and 50 % SIM. ^1H (300 MHz or 600 MHz) and ^{13}C NMR (75 MHz or 150 MHz) spectra were recorded on either MercuryPlus or Unity Inova spectrometers (Varian, USA), respectively. Chemical shifts are referenced to the tetramethylsilane (TMS) as internal standard or to the solvent residual peak (^{13}C NMR). Compounds are numbered according to the IUPAC nomenclature.

General procedure for aminohydroxylation with benzyl carbamate

A freshly prepared aqueous solution of NaOH (96 mg, 2.4 mmol) in water (15 mL) was added to a stirred solution of benzyl carbamate (363 mg, 2.4 mmol) in propan-1-ol (*n*-PrOH) (8 mL), followed by the addition of *tert*-butyl hypochlorite (*t*-BuOCl) (261 mg, 2.4 mmol). After 5 min, a solution of ligand (0.1 mmol) in *n*-PrOH (7 mL) was added, followed by the addition of a substrate (2.0 mmol) dissolved in *n*-PrOH (10 mL) and $K_2OsO_2(OH)_4$ (30 mg, 0.08 mmol). This mixture was stirred at ambient temperature for 24 h, then the reaction was quenched by the addition of a saturated sodium metabisulphite solution (20 mL) at 0 °C and stirred for 15 min. The two phases were separated and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with water (20 mL), brine (50 mL), dried with $MgSO_4$, pre-concentrated, and purified by flash chromatography.

General procedure for aminohydroxylation with chloramine T

Chloramine T was dissolved in a mixture of *n*-PrOH (8 mL) and water (15 mL). The ligand was added followed by the same procedure as for aminohydroxylation with benzyl carbamate (Reddy & Sharpless, 1998).

General procedure for desilylation

Aminoalcohol was dissolved in MeOH (10 mL per mmol of substrate) and Dowex® 50W X8 (1 g per mmol of substrate) was added. The reaction mixture was stirred at ambient temperature until completed (overnight). Ionex was removed by filtration, washed with MeOH, and the solution was pre-concentrated. The unprotected product was used in cyclisation without further purification.

General procedure for Pd(II)-catalysed cyclisation

A 25 mL flask equipped with a side inlet with a stopcock was filled with AcONa (anhydrous, 3 eq), $CuCl_2$ (anhydrous, 3 eq), and $PdCl_2$ (0.1 eq). The flask was evacuated, filled with CO via balloon and the solution of a substrate (1.0 eq) in glacial AcOH (10 mL per mmol of substrate) was added. The mixture was vigorously stirred at ambient temperature in the CO atmosphere (balloon) overnight until the mixture changed colour from green to pale brown. The reaction mixture was diluted with EtOAc, filtered through Celite, and pre-concentrated. Purification by flash chromatography on a column of silica gel afforded the appropriate compound.

Results and discussion

In the course of our long-term programme directed

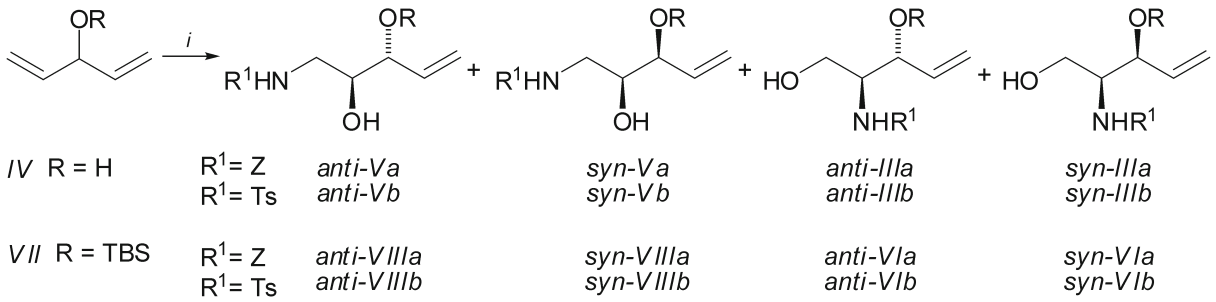

Fig. 2. Aminohydroxylation of *IV* and *VII*. Reaction conditions: *i*) $K_2OsO_4 \cdot 2H_2O$, ligand, R^1NH_2, aq. NaOH, *t*-BuOCl, solvent, ambient temperature.

towards the application of Pd-catalysed cyclisation of unsaturated polyols to natural product synthesis, we decided to apply domino intramolecular Pd-cyclisation/carbonylation as the key step in the synthesis of jaspine B. Our retrosynthetic plan (Fig. 1) called for enantioselective preparation of the (2*S*,3*R*)-2-*N*-R^1-aminopent-4-ene-1,3-diol (*anti-III*) as the key substrate, which is accessible from divinylcarbinol *IV* employing the Sharpless asymmetric aminohydroxylation as the source of chirality. For the second key step, being oxycarbonylating bicyclisation of *anti-III*, we took advantage of recent progress in Pd(II)-catalysed carbonylation of unsaturated polyols, which turned out bicyclic lactones with excellent 1,5-*threo* selectivity (Gracza et al., 1991; Jäger et al., 1997; Gracza & Jäger, 1992, 1994; Dixon et al., 1999; Babjak et al., 2002, 2005).

The study directed towards the synthesis of the lactone L-*arabino-II* started with aminohydroxylation of divinylcarbinol (DVC). DVC, with two potentially reactive enantiotopic vinyl groups, represents a distinguished substrate for asymmetric functionalisation of a double bond. The Sharpless asymmetric epoxidation of this substrate is well established and has been used successfully in a number of total syntheses of natural products (selected papers: e.g. Schreiber et al., 1987; Häfele et al., 1986; Jäger & Hümmer, 1990; Nicolaou et al., 1998; Romero & Wong, 2000; Singh & Guiry, 2009; Wang et al., 2009; Crimmins et al., 2009). Similarly, asymmetric dihydroxylation of protected DVC, pent-1,4-dien-3-yl 4-methoxybenzoate was described with high enantiomeric and diastereomeric excesses (Corey et al., 1995). To the best of our knowledge, the Sharpless asymmetric aminohydroxylation of this unique substrate has not been yet published; however, potential products prepared in this manner constitute interesting chirons for the synthesis of heterocyclic skeletons. Hence, we decided to explore the aminohydroxylation of DVC (*IV*) and *tert*-butyldimethylsilyl ether (*VII*) (Fig. 2). Aminohydroxylation of *IV* was initially carried out using the first generation of the aminohydroxylation reagent reported by Sharpless (Li et al., 1996), i.e. using chloramine T (TsNClNa) as an oxidant nitrogen source. Next, we scrutinised the influence of the *N*-protecting groups of chloramines, ligands and solvent on the yield of aminodiols *III*, *V*, *VI*, *VIII*, as well as the selectivity of the reaction. The results are summarised in Tables 1 and 2.

Both substrates, the unprotected DVC (*IV*) and the *O-tert*-butyldimethylsilyl-protected DVC (*VII*), were found to participate efficiently in the asymmetric aminohydroxylation providing corresponding aminodiols *III*, *V*, *VI*, and *VIII* with *anti*-diastereoselectivity as expected for a matched case (entries 1–13). According to the aminohydroxylation of allylic alcohols (Angelaud et al., 1997) using $(DHQD)_2$Phal-ligand (entries 1, 3, 5, 6, 8, 10, 12), the predominant formation of regioisomers *V* and *VIII* with an amido moiety attached to the terminal carbon was observed. In order to reverse the regioselectivity of the reaction, we performed the reaction employing $(DHQD)_2$AQN as a chiral ligand. Unfortunately, in contrast to the aminohydroxylation of cinnamates (Tao et al., 1998), replacing Phal-core with an anthraquinone (AQN) core of cinchona ligands did not cause a dramatic reversal of the regioselectivity (entries 2, 4, 7, 9, 11, 13). From the results summarised in Table 2, it is clear that neither the change in the ligand structure nor the character of *N*-source and the solvent had a significant influence on the regio- or diastereoselective outcome of the reaction. Aminohydroxylation of *IV* using either benzylcarbamate or sulphonamide afforded an inseparable mixture of products (regio- and diastereomers). Introducing a bulky TBS-protecting group into *VII* did not significantly increase diastereoselectivity of the reaction; however the silylated aminopentenediols *anti-VIII*, *syn-VIII*, and *anti-VI* could be readily separated by flash chromatography.

With the separated aminodiols *anti-VIII*, *syn-VIII*, and *anti-VI* prepared, the following synthesis was conducted in parallel. Firstly, the silyl-protecting group was removed by acidic hydrolysis with Dowex H^+ in methanol and the unprotected aminodiols *anti-V*, *syn-V*, and *anti-III* were subjected to the second crucial step of the syntheses. The domino Pd(II)-cyclisation/oxycarbonylation reaction was carried out under standard reaction conditions (Gracza et al., 1991; Hümmer et al., 1997) affording bicyclic lac-

Table 1. Physical and spectral data of newly prepared compounds

Compound	Physical and spectral data
syn-VIIIa	Yield = 7 % (from *VII*); $[\alpha]_D^{20}$ = –0.5° (c = 1.122, $CHCl_3$) FTIR, $\tilde{\nu}$/cm^{-1}: 3419, 3350, 3066, 3034, 2952, 2927, 2856, 1700, 1518, 1471, 1462, 1251, 1080, 835, 776, 696 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.05, 0.07 (2s, 2 × 3H, $Si(CH_3)_2$), 0.90 (s, 9H, $C(CH_3)_3$), 2.72 (bs, 1H, OH), 3.13 (ddd, 1H, J = 5.1 Hz, J = 7.8 Hz, $J_{1A,1B}$ = 13.2 Hz, H-1A), 3.41 (ddd, 1H, J = 3.3 Hz, J = 6.4 Hz, $J_{1A,1B}$ = 13.3 Hz, H-1B), 3.47–3.57 (m, 1H, H-2), 3.99 (dd, 1H, $J_{2,3}$ = 6.3 Hz, $J_{3,4}$ = 6.9 Hz, H-3), 5.09 (s, 2H, CH_2 in Bn), 5.21 (d, 1H, $J_{4,5A}$ = 11.1 Hz, H-5A), 5.26 (d, 1H, $J_{4,5B}$ = 18.1 Hz, H-5B), 5.83 (ddd, 1H, $J_{3,4}$ = 6.9 Hz, $J_{4,5A}$ = 10.1 Hz, $J_{4,5B}$ = 17.2 Hz, H-4), 7.25–7.40 (m, 5H, Ph) ^{13}C NMR (75 MHz, $CDCl_3$), δ: –5.0, –4.1 (2q, $Si(CH_3)_2$), 18.1 (s, $\underline{C}(CH_3)_3$) 25.8 (q, $C(\underline{C}H_3)_3$), 43.2 (t, C-1), 66.8 (t, CH_2 in Bn), 73.7, 75.4 (2d, C-2, C-3), 117.6 (t, C-5), 126.9, 127.6, 128.5 (all d, Ph), 136.5 (s, Ph), 137.3 (d, C-4), 156.8 (s, NCO) MS, m/z (found/calc.): 366.20/366.21 ($[M + H]^+$, $C_{19}H_{32}NO_4Si$)
anti-VIIIa	Yield = 25 % (from *VII*); $[\alpha]_D^{20}$ = –3.58° (c = 1.575, $CHCl_3$) FTIR, $\tilde{\nu}$/cm^{-1}: 3429, 3344, 2952, 2927, 2856, 1692, 1516, 1471, 1462, 1251, 1077, 1027, 835, 775, 696 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.05, 0.08 (2s, 2 × 3H, $Si(CH_3)_2$), 0.90 (s, 9H, $C(CH_3)_3$), 2.55 (bs, 1H, OH), 3.11 (ddd, 1H, J = 4.1 Hz, J = 7.8 Hz, $J_{1A,1B}$ = 13.3 Hz, H-1A), 3.50 (ddd, 1H, J = 2.9 Hz, J = 7.4 Hz, $J_{1A,1B}$ = 13.3 Hz, H-1B), 3.56–3.67 (m, 1H, H-2), 4.09–4.17 (m, 1H, H-3), 5.10 (s, 2H, CH_2 in Bn), 5.17–5.32 (m, 3H, H-5, NH), 5.81 (ddd, 1H, $J_{3,4}$ = 6.7 Hz, $J_{4,5A}$ = 10.3 Hz, $J_{4,5B}$ = 17.1 Hz, H-4), 7.30–7.38 (m, 5H, Ph) ^{13}C NMR (75 MHz, $CDCl_3$), δ: –5.0, –4.3 (2q, $Si(CH_3)_2$), 18.1 (s, $\underline{C}(CH_3)_3$) 25.7 (q, $C(\underline{C}H_3)_3$), 42.7 (t, C-1), 66.7 (t, CH_2 in Bn), 73.4, 76.0 (2d, C-2, C-3), 117.3 (t, C-5), 128.0, 128.1, 128.4, (all d, Ph), 136.5 (s, Ph), 137.0 (d, C-4), 156.9 (s, NCO) MS, m/z (found/calc.): 366.20/366.21 ($[M + H]^+$, $C_{19}H_{32}NO_4Si$)
anti-VIa	Yield = 14 % (from *VII* in the mixture with *anti-VIIIa*) ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.02, 0.04 (2s, 2 × 3H, $Si(CH_3)_2$), 0.90 (s, 9H, $C(CH_3)_3$), 2.85 (bd, 1H, J = 9.2 Hz, H-2), 3.56–3.66 (m, 2H), 4.02 (bd, 1H, J = 10.5 Hz), 4.51–4.57 (m, 1H), 5.12 (s, 2H, CH_2 in Bn), 5.24 (d, 1H, $J_{4,5A}$ = 10.5 Hz, H-5A), 5.34 (d, 1H, $J_{4,5B}$ = 17.3 Hz, H-5B), 5.57 (bd, 1H, J = 6.4 Hz, NH), 5.86 (ddd, 1H, $J_{3,4}$ = 5.1 Hz, $J_{4,5A}$ = 10.3 Hz, $J_{4,5B}$ = 17.2 Hz, H-4), 7.32–7.37 (m, 5H, Ph) ^{13}C NMR (75 MHz, $CDCl_3$), δ: –5.3, –4.8 (2q, $Si(CH_3)_2$), 18.0 (s, $\underline{C}(CH_3)_3$) 25.7 (q, $C(\underline{C}H_3)_3$), 55.2 (d, C-2), 61.8 (t, C-1), 67.8 (t, CH_2 in Bn), 76.0 (d, C-3), 116.6 (t, C-5), 128.1, 128.5, 128.6, (all d, Ph), 136.4 (s, Ph), 137.4 (d, C-4), 156.1 (s, NCO) MS, m/z (found/calc.): 366.20/366.21 ($[M + H]^+$, $C_{19}H_{32}NO_4Si$)
syn-Va	Yield = 100 %; $[\alpha]_D^{20}$ = –73.86° (c = 1.197, $CHCl_3$), $[\alpha]_D^{20}$ = –18.33° (c = 1.259, CH_3OH) FTIR, $\tilde{\nu}$/cm^{-1}: 3329, 3167, 2915, 2848, 1695, 1525, 1466, 1259, 1028, 994, 718, 697 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.17 (dd, 1H, $J_{1A,2}$ = 6.5 Hz, $J_{1A,1B}$ = 13.6 Hz, H-1A), 3.23 (bs, 1H, OH), 3.35–3.50 (m, 2H, H-1B, OH), 3.51–3.62 (m, 1H, H-2 or H-3), 3.92–4.04 (m, 1H, H-2 or H-3), 5.08 (s, 2H, CH_2 in Bn), 5.22 (d, 1H, $J_{4,5A}$ = 10.4 Hz, H-5A), 5.33 (d, 1H, $J_{4,5B}$ = 17.2 Hz, H-5B), 5.45 (bs, 1H, NH), 5.86 (1H, ddd, $J_{3,4}$ = 6.1 Hz, $J_{4,5A}$ = 10.4 Hz, $J_{4,5B}$ = 16.7 Hz, H-4), 7.25–7.38 (m, 5H, Ph) ^{13}C NMR (75 MHz, $CDCl_3$), δ: 43.4 (t, C-1), 67.0 (t, CH_2 in Bn), 73.2, 73.6 (2d, C-2, C-3), 117.5 (t, C-5), 128.0, 128.1, 128.5 (all d, Ph), 136.2 (s, Ph), 136.8 (d, C-4), 157.2 (s, NCO) MS, m/z (found/calc.): 252.10/252.12 ($[M + H]^+$, $C_{13}H_{18}NO_4$)
anti-Va	Yield = 100 %; $[\alpha]_D^{20}$ = –41.32° (c = 1.086, $CHCl_3$), $[\alpha]_D^{20}$ = –45.07 (c = 1.129, CH_3OH) FTIR, $\tilde{\nu}$/cm^{-1}: 3327, 3033, 2895, 1688, 1532, 1454, 1254, 1213, 1001, 741 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.25–3.42 (m, 4H, H-1, OH), 3.59–3.66 (m, 1H, H-2 or H-3), 4.07 (t, 1H, J = 5.0 Hz, H-2 or H-3), 5.06 (s, 2H, CH_2 in Bn), 5.20 (d, 1H, $J_{4,5A}$ = 10.5 Hz, H-5A), 5.31 (d, 1H, $J_{4,5B}$ = 17.2 Hz, H-5B), 5.60 (bs, 1H, NH), 5.87 (ddd, 1H, $J_{3,4}$ = 6.1 Hz, $J_{4,5A}$ = 10.3 Hz, $J_{4,5B}$ = 16.8 Hz, H-4), 7.25–7.35 (m, 5H, Ph) ^{13}C NMR (75 MHz, $CDCl_3$), δ: 42.6 (t, C-1), 66.7 (t, CH_2 in Bn), 73.2, 73.9 (2d, C-2, C-3), 117.3 (t, C-5), 128.0, 128.1, 128.4 (all d, Ph), 136.1 (s, Ph), 136.3 (d, C-4), 157.6 (s, NCO) MS, m/z (found/calc.): 252.10/252.12 ($[M + H]^+$, $C_{13}H_{18}NO_4$)
anti-IIIa[a]	Yield = 100 % ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.38 (t, 1H, J = 5.1 Hz, H-2), 3.67–3.75 (m, 2H), 3.94 (dd, 1H, J = 4.0 Hz, J = 12.0 Hz), 4.35–4.42 (m, 1H), 5.11 (s, 2H, CH_2 in Bn), 5.22–5.43 (m, 2H, H-5), 5.65 (bd, 1H, J = 6.8 Hz, NH), 5.83–5.99 (m, 1H, H-4), 7.32–7.38 (m, 5H, Ph) ^{13}C NMR (75 MHz, $CDCl_3$), δ: 55.2 (d, C-2), 62.1 (t, C-1), 67.0 (t, CH_2 in Bn), 74.7 (d, C-3), 116.7 (t, C-5), 128.1, 128.2, 128.5 (all d, Ph), 136.2 (s, Ph), 137.2 (d, C-4), 156.5 (s, NCO) MS, m/z (found/calc.): 252.10/252.12 ($[M + H]^+$, $C_{13}H_{18}NO_4$)

Table 1. (continued)

Compound	Physical and spectral data
L-*xylo-IXa*[b]	Yield = 64 % (from *syn-VIIIa*); $[\alpha]_D^{20}$ = –47.7° (c = 0.31, MeOH) Yield = 14 % (2 steps from *IV*); $[\alpha]_D^{20}$ = –6.9° (c = 1.017, MeOH) FTIR, $\tilde{\nu}$/cm^{-1}: 3381, 2945, 1784, 1674, 1417, 1350, 1216, 1198, 1166, 1116, 1041, 696 ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.67–2.92 (m, 2H, H-4), 3.53–3.62 (m, 1H, H-7A), 3.74, 3.81 (2d, 1H, $J_{7A,7B}$ = 12.5 Hz, H-7B), 4.47 (bs, 1H, H-8), 4.65, 4.68 (2t, 1H, $J_{1,5}$ = 5.1 Hz, $J_{4,5}$ = 5.7 Hz, H-5), 4.78, 4.80 (2d, 1H, $J_{1,5}$ = 4.3 Hz, H-1), 5.08–5.21 (m, 2H, CH_2 in Bn), 7.31–7.39 (m, 5H, Ph) ^{13}C NMR (125 MHz, $CDCl_3$), δ: 34.9, 35.7 (2t, C-4), 52.6, 52.8 (2t, C-7), 56.5, 56.9 (2d, C-5), 67.5, 67.7 (2t, CH_2 in Bn), 71.2, 71.9 (2d, C-8), 85.7, 86.5 (2d, C-1), 128.0, 128.2, 128.3, 128.4, 128.6, 128.7 (all d, Ph), 135.9, 136.0 (2s, Ph), 154.4, 154.7 (2s, NCO_2), 174.6, 175.0 (2s, C-3) MS, m/z (found/calc.): 144.10/144.06 ($[M - Z + H]^+$, $C_6H_{10}NO_3$)[c]
L-*arabino-IXa*[b]	Yield = 64 % (from *anti-VIIIa*); $[\alpha]_D^{20}$ = +15.4° (c = 0.967, MeOH), $[\alpha]_D^{20}$ = +18.1° (c = 1.00, $CHCl_3$) Yield = 23 % (2 steps from *IV*) $[\alpha]_D^{20}$ = +2.9° (c = 1.132, MeOH) FTIR, $\tilde{\nu}$/cm^{-1}: 3400, 2952, 1777, 1678, 1498, 1415, 1356, 1151, 1093, 697 ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.70–2.92 (m, 2H, H-4), 3.34 (dd, 1H, $J_{7A,8}$ = 7.5 Hz, $J_{7A,7B}$ = 11.3 Hz, H-7A), 3.41 (dd, 1H, $J_{7A,8}$ = 6.6 Hz, $J_{7A,7B}$ = 11.6 Hz, H-7A), 3.85–3.90 (m, 1H, H-7B), 4.35–4.39 (m, 1H, H-8), 4.49 (dt, 1H, J = 3.1 Hz, J = 7.1 Hz, J = 7.1 Hz, H-5), 4.54 (dt, 1H, J = 2.6 Hz, J = 6.7 Hz, J = 6.7 Hz, H-5), 4.93 (t, 1H, J = 5.0 Hz, H-1), 5.07–5.18 (m, 2H, CH_2 in Bn), 7.30–7.38 (m, 5H, Ph) ^{13}C NMR (125 MHz, $CDCl_3$), δ: 35.8, 36.5 (2t, C-4), 49.9, 50.4 (2t, C-7), 55.7, 56.3 (2d, C-5), 67.5, 67.6 (2t, CH_2 in Bn), 69.7, 70.5 (2d, C-8), 81.6, 82.2 (2d, C-1), 128.0, 128.1, 128.3, 128.4, 128.5, 128.6 (all d, Ph), 135.9 (s, Ph), 154.0, 154.4 (2s, NCO_2), 175.2, 175.4 (2s, C-3) MS, m/z (found/calc.): 144.10/144.06 ($[M - Z + H]^+$, $C_6H_{10}NO_3$)[c]
L-*xylo-IIa*	Yield = 5 % (2 steps from *IV*); $[\alpha]_D^{20}$ = –2.6° (c = 1.29, MeOH) FTIR, $\tilde{\nu}$/cm^{-1}: 3313, 3033, 2947, 1782, 1696, 1526, 1454, 1333, 1309, 1231, 1187, 1146, 1069, 1034, 697 ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.63 (d, 1H, $J_{4A,4B}$ = 18.8 Hz, H-4A), 2.74 (dd, 1H, $J_{4B,5}$ = 6.4 Hz, $J_{4A,4B}$ = 18.8 Hz, H-4B), 3.81 (d, 1H, $J_{7A,7B}$ = 9.6 Hz, H-7A), 4.03 (dd, 1H, $J_{7B,8}$ = 4.6 Hz, $J_{7A,7B}$ = 9.7 Hz, H-7B), 4.33–4.36 (m, 1H, H-8), 4.79–4.84 (m, 1H, H-5), 4.95–4.99 (m, 1H, H-1), 5.12 (s, 2H, CH_2 in Bn), 5.16 (bs, 1H, NH), 7.30–7.38 (m, 5H, Ph) ^{13}C NMR (125 MHz, $CDCl_3$), δ: 35.6 (t, C-4), 56.6 (d, C-8), 67.2 (t, CH_2 in Bn), 70.7 (t, C-7), 76.9 (d, C-5), 86.7 (d, C-1), 128.2, 128.4, 128.6 (all d, Ph), 135.8 (s, Ph), 155.5 (s, NCO_2), 174.9 (s, C-3) MS, m/z (found/calc.): 144.10/144.06 ($[M - Z + H]^+$, $C_6H_{10}NO_3$)[c]
L-*arabino-IIa*	Yield = 56 % (from *anti-VIa*); $[\alpha]_D^{20}$ = +18.1° (c = 1.125, MeOH), $[\alpha]_D^{20}$ = +13.9° (c = 1.125, $CHCl_3$) Yield = 8 % (2 steps from *IV*); $[\alpha]_D^{20}$ = +4.3° (c = 0.98, MeOH) FTIR, $\tilde{\nu}$/cm^{-1}: 3307, 2952, 1779, 1694, 1531, 1417, 1246, 1187, 1147, 1082, 1070, 976, 900, 839, 738, 696 ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.69 (d, 1H, $J_{4A,4B}$ = 18.9 Hz, H-4A), 2.82 (dd, 1H, $J_{4B,5}$ = 6.4 Hz, $J_{4A,4B}$ = 18.9 Hz, H-4B), 3.50 ("t", 1H, $J_{7A,7B}$ = $J_{7A,8}$ = 9.3 Hz, H-7A), 4.16 ("t", 1H, $J_{7A,7B}$ = $J_{7B,8}$ = 8.2 Hz, H-7B) 4.48–4.55 (m, 1H, H-8), 4.83 (dd, 1H, $J_{1,5}$ = 4.3 Hz, $J_{4,5}$ = 6.4 Hz, H-5), 4.97 ("t", 1H, $J_{1,5}$ = $J_{1,8}$ = 4.3 Hz, H-1) 5.12 (s, 2H, Bn), 5.23 (d, 1H, $J_{NH,8}$ = 8.0 Hz, NH), 7.31–7.39 (m, 5H, Ph) ^{13}C NMR (125 MHz, $CDCl_3$), δ: 36.6 (t, C-4), 53.7 (d, C-8), 67.3 (t, Bn), 68.9 (t, C-7), 77.3 (d, C-5), 82.1 (d, C-1), 128.1, 128.3, 128.6 (all d, Ph), 135.9 (s, Ph), 155.8 (s, NCO_2), 174.7 (s, C-3) MS, m/z (found/calc.): 144.10/144.06 ($[M - Z + H]^+$, $C_6H_{10}NO_3$)[c]
syn-VIIIb	Yield = 4 % (from *VII*); $[\alpha]_D^{20}$ = –1.64° (c = 1.094, $CHCl_3$) FTIR, $\tilde{\nu}$/cm^{-1}: 3506, 3275, 2927, 2856, 1599, 1462, 1404, 1327, 1252, 1158, 1090, 835, 777, 664, 551 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.03, 0.05 (2s, 2 × 3H, $Si(CH_3)_2$), 0.86 (s, 9H, $C(CH_3)_3$), 2.43 (s, 3H, CH_3 in Ts), 2.56 (d, 1H, $J_{2,OH}$ = 4.0 Hz, OH), 2.88 (ddd, 1H, $J_{1A,NH}$ = 5.4 Hz, $J_{1A,2}$ = 6.8 Hz, $J_{1A,1B}$ = 12.3 Hz, H-1A), 3.08 (ddd, 1H, $J_{1B,2}$ = 5.4 Hz, $J_{1B,NH}$ = 6.8 Hz, $J_{1A,1B}$ = 12.3 Hz, H-1B), 3.45–3.53 (m, 1H, H-2), 4.02 (dd, 1H, $J_{1A,NH}$ = 5.4 Hz, $J_{1B,NH}$ = 6.8 Hz, NH), 4.84 (dd, 1H, $J_{2,3}$ = 6.0 Hz, $J_{3,4}$ = 7.0 Hz, H-3), 5.17–5.29 (m, 2H, H-5), 5.73 (ddd, 1H, $J_{3,4}$ = 7.0 Hz, $J_{4,5A}$ = 10.3 Hz, $J_{4,5B}$ = 17.3 Hz, H-4), 7.31 (d, 2H, J = 8.1 Hz, Ts), 7.73 (d, 2H, J = 8.3 Hz, Ts) ^{13}C NMR (75 MHz, $CDCl_3$), δ: –5.0, –4.1 (2q, $Si(CH_3)_2$), 18.1 (s, $\underline{C}(CH_3)_3$), 21.5 (q, CH_3 in Ts), 25.7 (q, $C(\underline{C}H_3)_3$), 44.7 (t, C-1), 72.6, 75.2 (2d, C-2, C-3), 118.2 (t, C-5), 127.1, 129.7, 136.9 (all d, Ph, C-4), 136.5, 143.5 (2s, Ph) MS, m/z (found/calc.): 386.20/386.17 ($[M + H]^+$, $C_{18}H_{32}NO_4SSi$)

Table 1. (continued)

Compound	Physical and spectral data
anti-VIIIb	Yield = 18 % (from *VII*); $[\alpha]_D^{20}$ = –12.33° (c = 1.088, $CHCl_3$) FTIR, $\tilde{\nu}$/cm^{-1}: 3494, 3275, 2954, 2927, 2856, 1599, 1495, 1471, 1402, 1324, 1252, 1157, 1090, 835, 777, 662, 551 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.02, 0.05 (2s, 2 × 3H, $Si(CH_3)_2$), 0.87 (s, 9H, $C(CH_3)_3$), 2.33 (d, 1H, $J_{2,OH}$ = 4.0 Hz, OH), 2.43 (s, 3H, CH_3 in Ts), 2.89 (ddd, 1H, $J_{1A,NH}$ = 3.5 Hz, $J_{1A,2}$ = 7.5 Hz, $J_{1A,1B}$ = 12.7 Hz, H-1A), 3.18 (ddd, 1H, $J_{1B,NH}$ = 3.5 Hz, $J_{1B,2}$ = 8.6 Hz, $J_{1A,1B}$ = 12.4 Hz, H-1B), 3.55 (ddd, 1H, $J_{2,OH}$ = 4.0 Hz, $J_{1A,2}$ = 7.5 Hz, $J_{1A,2}$ = 8.6 Hz, H-2), 4.10 (dd, 1H, $J_{1A,NH}$ = 3.5 Hz, $J_{1B,NH}$ = 4.9 Hz, NH), 5.01–5.10 (m, 1H, H-3), 5.15–5.26 (m, 2H, H-5), 5.69 (ddd, 1H, $J_{3,4}$ = 6.5 Hz, $J_{4,5A}$ = 10.4 Hz, $J_{4,5B}$ = 17.1 Hz, H-4), 7.31 (d, 2H, J = 8.1 Hz, Ts), 7.73 (d, 2H, J = 8.2 Hz, Ts) ^{13}C NMR (75 MHz, $CDCl_3$), δ: –5.0, –4.4 (2q, $Si(CH_3)_2$), 18.0 (s, $\underline{C}(CH_3)_3$), 21.5 (q, CH_3 in Ts), 25.7 (q, $C(\underline{C}H_3)_3$), 44.6 (t, C-1), 72.2, 76.0 (2d, C-2, C-3), 117.7 (t, C-5), 127.1, 129.7, 136.7 (all d, Ph, C-4), 136.6, 143.4 (2s, Ph) MS, m/z (found/calc.): 386.20/386.17 ($[M + H]^+$, $C_{18}H_{32}NO_4SSi$)
anti-VIb	Yield = 8 % (from *VII*); $[\alpha]_D^{20}$ = +12.46° (c = 1.046, $CHCl_3$) FTIR, $\tilde{\nu}$/cm^{-1}: 3510, 3284, 2953, 2928, 2885, 2856, 1598, 1471, 1404, 1327, 1252, 1158, 1089, 835, 813, 778, 665, 551 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.02, 0.09 (2s, 2 × 3H, $Si(CH_3)_2$), 0.88 (s, 9H, $C(CH_3)_3$), 2.41 (s, 3H, CH_3 in Ts), 2.65 (dd, 1H, J = 2.5 Hz, J = 9.9 Hz, H-2), 3.12 (ddd, 1H, J = 3.4 Hz, J = 3.5 Hz, J = 11.1 Hz, H-1A), 3.25 (ddd, 1H, J = 3.9 Hz, J = 10.1 Hz, J = 13.9 Hz, H-1B), 3.84 (dt, 1H, J = 2.8 Hz, J = 2.8 Hz, J = 11.7 Hz), 4.39–4.45 (m, 1H, H-3), 5.16–5.32 (m, 2H, H-5), 5.73 (ddd, 1H, $J_{3,4}$ = 5.7 Hz, $J_{4,5A}$ = 10.5 Hz, $J_{4,5B}$ = 17.1 Hz, H-4), 7.30 (d, 2H, J = 8.1 Hz, Ts), 7.76 (d, 2H, J = 8.3 Hz, Ts) ^{13}C NMR (75 MHz, $CDCl_3$), δ: –5.0, –4.7 (2q, $Si(CH_3)_2$), 18.0 (s, $\underline{C}(CH_3)_3$), 21.5 (q, CH_3 in Ts), 25.7 (q, $C(\underline{C}H_3)_3$), 57.7 (d, C-2), 61.3 (t, C-1), 77.1 (d, C-3), 117.2 (t, C-5), 127.1, 129.7, 137.0, 137.4, 143.6 (Ph, C-4) MS, m/z (found/calc.): 386.20/386.17 ($[M + H]^+$, $C_{18}H_{32}NO_4SSi$)
syn-Vb	Yield = 100 %; $[\alpha]_D^{20}$ = –6.429° (c = 1.454, $CHCl_3$) FTIR, $\tilde{\nu}$/cm^{-1}: 3255, 2924, 2854, 1712, 1597, 1495, 1427, 1400), 1319, 1153, 1086, 1032, 1005, 813, 661, 549 ^{1}H NMR (300 MHz, CD_3OD), δ: 2.43 (s, 3H, CH_3 in Ts), 2.80 (dd, 1H, $J_{1A,2}$ = 7.6 Hz, $J_{1A,1B}$ = 13.0 Hz, H-1A), 3.02 (dd, 1H, $J_{1B,2}$ = 4.6 Hz, $J_{1A,1B}$ = 13.0 Hz, H-1B), 3.52 (td, 1H, $J_{1B,2}$ = 4.6 Hz, $J_{2,3}$ = 4.6 Hz, $J_{1A,2}$ = 7.6 Hz, H-2), 4.00 (tdd, 1H, $J_{3,5A}$ = $J_{3,5B}$ = 1.5 Hz, $J_{2,3}$ = 4.6 Hz, $J_{3,4}$ = 6.0 Hz, H-3), 5.14 (td, 1H, $J_{3,5A}$ = $J_{5A,5B}$ = 1.5 Hz, $J_{4,5A}$ = 10.5 Hz, H-5A), 5.26 (td, 1H, $J_{3,5B}$ = $J_{5A,5B}$ = 1.5 Hz, $J_{4,5B}$ = 17.3 Hz, H-5B), 5.86 (ddd, 1H, $J_{3,4}$ = 6.0 Hz, $J_{4,5A}$ = 10.5 Hz, $J_{4,5B}$ = 16.8 Hz, H-4), 7.38 (d, 2H, J = 8.1 Hz, Ts), 7.73 (d, 2H, J = 8.3 Hz, Ts) ^{13}C NMR (75 MHz, CD_3OD), δ: 21.5 (q, CH_3 in Ts), 46.5 (t, C-1), 74.1, 74.6 (2d, C-2, C-3), 116.7 (t, C-5), 128.1, 130.8 (all d, Ph), 138.7 (s, Ph), 138.9 (d, C-4), 144.7 (s, Ph) MS, m/z (found/calc.): 272.00/272.09 ($[M + H]^+$, $C_{12}H_{18}NO_4S$)
anti-Vb	Yield = 100 %; $[\alpha]_D^{20}$ = –7.98° (c = 0.978, $CHCl_3$) FTIR, $\tilde{\nu}$/cm^{-1}: 3444, 3276, 2992, 2873, 1597, 1495, 1427, 1402, 1319, 1152, 1089, 813, 660, 549 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.42 (s, 3H, CH_3 in Ts), 3.02 (dd, 1H, $J_{1A,2}$ = 7.0 Hz, $J_{1A,1B}$ = 13.4 Hz, H-1A), 3.13 (dd, 1H, $J_{1B,2}$ = 3.4 Hz, $J_{1A,1B}$ = 13.4 Hz, H-1B), 3.67–3.75 (m, 1H, H-2), 4.21 (dd, 1H, $J_{2,3}$ = 5.0 Hz, $J_{3,4}$ = 6.0 Hz, H-3), 5.23 (d, 1H, $J_{4,5A}$ = 10.5 Hz, H-5A), 5.32 (d, 1H, $J_{4,5B}$ = 17.3 Hz, H-5B), 5.82 (ddd, 1H, $J_{3,4}$ = 6.1 Hz, $J_{4,5A}$ = 10.5 Hz, $J_{4,5B}$ = 16.9 Hz, H-4), 7.30 (d, 2H, J = 8.2 Hz, Ts), 7.73 (d, 2H, J = 8.2 Hz, Ts) ^{13}C NMR (75 MHz, $CDCl_3$), δ: 21.5 (q, CH_3 in Ts), 44.3 (t, C-1), 72.3, 74.1 (2d, C-2, C-3), 117.8 (t, C-5), 127.0, 129.8 (all d, Ph), 135.9 (d, C-4), 136.4, 143.6 (all s, Ph) MS, m/z (found/calc.): 272.00/272.09 ($[M + H]^+$, $C_{12}H_{18}NO_4S$)
anti-IIIb	Yield = 100 %; $[\alpha]_D^{20}$ = –2.735° (c = 1.077, $CHCl_3$) FTIR, $\tilde{\nu}$/cm^{-1}: 3423, 3271, 2924, 1714, 1599, 1427, 1402, 1320, 1306, 1152, 1089, 1034, 929, 813, 662, 547 ^{1}H NMR (300 MHz, CD_3OD), δ: 2.42 (s, 3H, CH_3 in Ts), 3.21 (ddd, 1H, $J_{1A,2}$ = 5.1 Hz, $J_{1B,2}$ = 5.1 Hz, $J_{2,3}$ = 5.9 Hz, H-2), 3.43 (dd, 1H, $J_{1A,2}$ = 5.1 Hz, $J_{1A,1B}$ = 11.3 Hz, H-1A), 3.57 (dd, 1H, $J_{1B,2}$ = 5.0 Hz, $J_{1A,1B}$ = 11.3 Hz, H-1B), 4.08 (tt, 1H, $J_{3,5A}$ = 1.5 Hz, $J_{3,5B}$ = 1.5 Hz, $J_{2,3}$ = 5.9 Hz, $J_{3,4}$ = 5.9 Hz, H-3), 5.05 (dt, 1H, $J_{3,5A}$ = 1.5 Hz, $J_{5A,5B}$ = 1.5 Hz, $J_{4,5A}$ = 10.5 Hz, H-5A), 5.21 (d, 1H, $J_{3,5B}$ = 1.5 Hz, $J_{5A,5B}$ = 1.5 Hz, $J_{4,5B}$ = 17.2 Hz, H-5B), 5.75 (ddd, 1H, $J_{3,4}$ = 6.1 Hz, $J_{4,5A}$ = 10.5 Hz, $J_{4,5B}$ = 16.9 Hz, H-4), 7.39 (d, 2H, J = 8.2 Hz, Ts), 7.76 (d, 2H, J = 8.2 Hz, Ts) ^{13}C NMR (75 MHz, CD_3OD), δ: 21.5 (q, CH_3 in Ts), 60.6 (d, C-2), 62.0 (t, C-1), 73.7 (d, C-3), 116.7 (t, C-5), 128.2, 130.6 (all d, Ph), 139.1 (d, C-4), 140.1, 144.5 (all s, Ph) MS, m/z (found/calc.): 272.00/272.09 ($[M + H]^+$, $C_{12}H_{18}NO_4S$)

Table 1. (continued)

Compound	Physical and spectral data
L-*xylo-IXb*	Yield = 80 % (from *syn-VIIIb*); $[\alpha]_D^{20}$ = +2.3° (*c* = 0.87, CH_3OH) FTIR, $\tilde{\nu}$ /cm^{-1}: 3483, 2920, 1782, 1598, 1456, 1401, 1337, 1155, 1089, 1042, 813, 656, 588, 545 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.45 (s, 3H, CH_3 in Ts), 2.82 (dd, 1H, $J_{4A,5}$ = 6.5 Hz, $J_{4A,4B}$ = 18.6 Hz, H-4A), 2.97 (d, 1H, $J_{4A,4B}$ = 18.6 Hz, H-1B), 3.50 (d, 1H, $J_{7A,7B}$ = 12.5 Hz, H-7A), 3.66 (dd, 1H, $J_{7B,8}$ = 3.8 Hz, $J_{7A,7B}$ = 12.5 Hz, H-7B), 4.41–4.46 (m, 1H, H-8), 4.50 (dd, 1H, $J_{1,5}$ = 5.7 Hz, $J_{4A,5}$ = 6.5 Hz, H-5), 4.71 (d, 1H, $J_{1,8}$ = 5.2 Hz, $J_{1,5}$ = 5.7 Hz, H-1), 7.35 (d, 2H, *J* = 8.1 Hz, Ts), 7.74 (d, 2H, *J* = 8.3 Hz, Ts) ^{13}C NMR (75 MHz, $CDCl_3$), δ: 21.6 (q, CH_3 in Ts), 36.2 (t, C-4), 54.5 (t, C-7), 58.6 (d, C-5), 72.4 (d, C-8), 86.6 (d, C-1), 127.6, 129.9 (all d, Ph), 134.4, 144.4 (all s, Ph), 174.3 (s, C-3) MS, *m*/*z* (found/calc.): 298.10/298.07 ($[M + H]^+$, $C_{13}H_{16}NO_5S$)
L-*arabino-IXb*	Yield = 83 % (from *anti-VIIIb*); $[\alpha]_D^{20}$ = +18.7° (*c* = 1.08, CH_3OH); m.p. = 138–140 °C FTIR, $\tilde{\nu}$/cm^{-1}: 3421, 2889, 1756, 1599, 1496, 1471, 1404, 1341, 1160, 1090, 938, 660, 575, 539 ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.46 (s, 3H, CH_3 in Ts), 2.87–2.89 (m, 2H, H-4), 3.46 (dd, 1H, $J_{7A,8}$ = 6.1 Hz, $J_{7A,7B}$ = 11.1 Hz, H-7A), 3.50 (dd, 1H, $J_{7B,8}$ = 5.8 Hz, $J_{7A,7B}$ = 11.1 Hz, H-7B), 4.09–4.14 (m, 1H, H-8), 4.29 (d, 1H, $J_{OH,8}$ = 6.5 Hz, OH), 4.38 (m, 1H, H-5), 4.81 (dd, 1H, *J* = 4.4 Hz, *J* = 6.7 Hz H-1), 7.38 (d, 2H, *J* = 8.1 Hz, Ts), 7.73 (d, 2H, *J* = 8.3 Hz, Ts) ^{13}C NMR (125 MHz, $CDCl_3$), δ: 21.5 (q, CH_3 in Ts), 37.0 (t, C-4), 52.3 (t, C-7), 57.7 (d, C-5), 70.0 (d, C-8), 81.9 (d, C-1), 127.4, 130.2 (all d, Ph), 134.4, 144.4 (all s, Ph), 175.1 (s, C-3) MS, *m*/*z* (found/calc.): 298.10/298.07 ($[M + H]^+$, $C_{13}H_{16}NO_5S$)
L-*arabino-IIb*	Yield = 76 % (from *anti-VIb*); $[\alpha]_D^{20}$ = +85.1° (*c* = 1.15, $CHCl_3$), $[\alpha]_D^{20}$ = +66.9° (*c* = 1.19, CH_3OH) FTIR, $\tilde{\nu}$/cm^{-1}: 3500, 3249, 2925, 2856, 1779, 1599, 1452, 1330, 1155, 1084, 1057, 814, 662, 544 ^{1}H NMR (600 MHz, CD_3OD), δ: 2.43 (s, 3H, CH_3 in Ts), 2.48 (d, 1H, $J_{4A,4B}$ = 18.8 Hz, H-4A), 2.84 (dd, 1H, $J_{4B,5}$ = 5.9 Hz, $J_{4A,4B}$ = 18.7 Hz, H-4B), 3.39 (dd, 1H, $J_{7A,7B}$ = 8.9 Hz, $J_{7A,8}$ = 9.7 Hz, H-7A), 3.77 (dd, 1H, $J_{7B,8}$ = 7.7 Hz, $J_{7A,7B}$ = 8.6 Hz, H-7B), 4.05 (ddd, 1H, $J_{1,8}$ = 4.4 Hz, $J_{7B,8}$= 7.7 Hz, $J_{7A,8}$ = 9.7 Hz, H-8), 4.67–4.73 (m, 2H, H-5, H-1), 7.39 (d, 2H, *J* = 8.1 Hz, Ts), 7.80 (d, 2H, *J* = 8.3 Hz, Ts) ^{13}C NMR (125 MHz, CD_3OD), δ: 21.5 (q, CH_3 in Ts), 37.5 (t, C-4), 56.9 (d, C-8), 69.3 (t, C-7), 79.0 (d, C-5), 83.6 (d, C-1), 128.2, 130.9 (all d, Ph), 139.6, 145.0 (all s, Ph), 177.6 (s, C-3) MS, *m*/*z* (found/calc.): 298.10/298.07 ($[M + H]^+$, $C_{13}H_{16}NO_5S$)

a) All data were determined from the mixture with *anti-Va*; *b*) mixture of conformers; *c*) for Z, see Table 2.

Table 2. Influence of ligand structure, solvent, and chloramine substituents on asymmetric hydroxyamination of *I*

Entry	R	R^1	Ligand	Solvent	*anti-V*/*syn-V*/*anti-III*/*syn-III*[a] *VIII*/*syn-VIII*/*anti-VI*/*syn-VI*[a]	Yield[b]/%
1	H	Z	$(DHQD)_2Phal$	*n*-PrOH	6/3/1/ < 0.5	82
2	H	Z	$(DHQD)_2AQN$	*n*-PrOH	13/6/1/ < 0.5	60
3	H	Z	$(DHQD)_2Phal$	CH_3CN	7/3/1/ < 0.5	56
4	H	Z	$(DHQD)_2AQN$	CH_3CN	5/2/1/ < 0.5	54
5	H	Ts	$(DHQD)_2Phal$	*n*-PrOH	6/3/1/ < 0.5	57
6	TBS	Z	$(DHQD)_2Phal$	*n*-PrOH	3/2/1/ < 0.5	42
7	TBS	Z	$(DHQD)_2AQN$	*n*-PrOH	3/1/1/ < 0.5	65
8	TBS	Z	$(DHQD)_2Phal$	CH_3CN	5/3/1/ < 0.5	42
9	TBS	Z	$(DHQD)_2AQN$	CH_3CN	4/3/1/ < 0.5	45
10	TBS	Ts	$(DHQD)_2Phal$	*n*-PrOH	3/1/1/ < 0.5	53
11	TBS	Ts	$(DHQD)_2AQN$	*n*-PrOH	2/1/1/ < 0.5	42
12	TBS	Ts	$(DHQD)_2Phal$	CH_3CN	5/3/1/ < 0.5	48
13	TBS	Ts	$(DHQD)_2AQN$	CH_3CN	4/3/1/ < 0.5	55

a) Ratio of stereomers was estimated on the basis of ^{13}C NMR spectral data of crude reaction mixtures; *b*) overall yield.

tones L-*arabino-IIa*, *-IIb*, L-*arabino-IXa*, *-IXb*, and L-*xylo-IXa*, *-IXb*, respectively, with high regio- and *threo*-selectivity in moderate to good yields (Fig. 3). In addition, when the mixture of all isomers *III* and *V* underwent oxycarbonylation, all four products *II* and *IX* were successfully separated, albeit with decreased optical purity. The configuration of pyrrolidinolactones L-*arabino-IXa*, *-IXb* and L-*xylo-IXa*, *-IXb* was established by comparing the ^{1}H NMR data and specific rotation with the literature data of *N*-benzyloxycarbonyl-2,3,6-trideoxy-3,6-imino-D-*arabino*-1,4-hexonolactone (Jäger & Hümmer, 1990; Hümmer et al., 1997; $[\alpha]_D^{22}$ –71.6° (*c* = 0.666, $CHCl_3$)). These pyrrolidinolactones serve as precursors for syntheses of hydroxypyrrolidines (1,4-iminoglycitols) known to show high activity against glycosidases (Fleet et al., 1985; Bashyal et al., 1987; Winkler & Holan, 1989). 3,6-Anhydro-2,5-dideoxy-5-

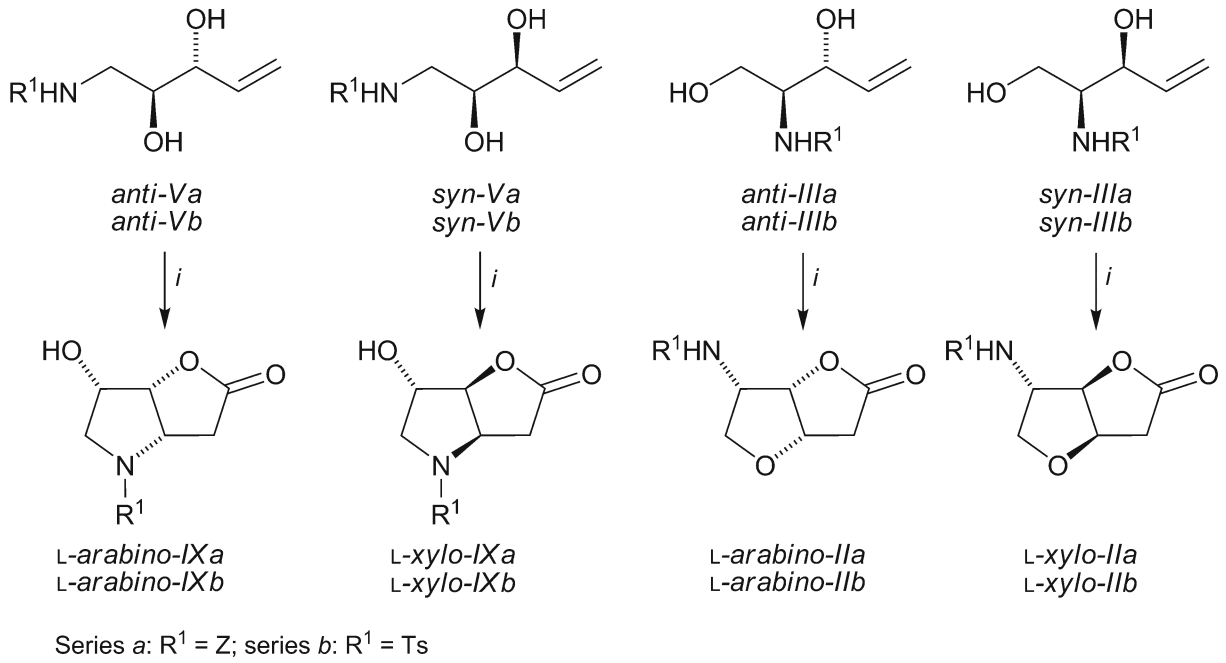

Fig. 3. Domino Pd(II)-cyclisation/oxycarbonylation reaction of *V* and *III*. Reaction conditions: *i*) $PdCl_2$ (0.1 eq), $CuCl_2$ (3 eq), AcONa (3 eq), AcOH, CO (balloon).

benzyloxyamino-L-*arabino*-1,4-hexonolactone (L-*arabino-IIa*) is an intermediate in the synthesis of 2-*epi*-jaspine B from L-serine (Bhaket et al., 2005).

Conclusions

In conclusion, the present study shows that the Sharpless aminohydroxylation may be applied to both protected and unprotected divinylcarbinol so as to furnish all isomers of aminopent-4-enediol intermediates for organic synthesis. The transformation proceeds with *anti*-diastereoselectivity (up to 4 : 1) and good regioselectivity (up to 19 : 1) in favour of 1-amino regioisomers *V* and *VIII*. The Pd(II)-catalysed oxy- and amidocarbonylation of aminopent-4-enediols *III* and *V* provided regio- and diastereoselectively lactones *IX* and *X*, respectively. The synthetic approach was applied in a short formal synthesis of 2-*epi*-jaspine B. In addition, the bicyclic pyrrolidinolactones L-*arabino-IXa*, *-IXb* and L-*xylo-IXa*, *-IXb* constitute new types of unnatural proline analogues, i.e. dihydroxy-homoproline derivatives.

Acknowledgements. This work was financially supported by the Slovak grant agencies (VEGA, Slovak Academy of Sciences and Ministry of Education, Bratislava, project no. 1/0236/09; APVV, Bratislava, project no. APVT-0203-10, and ASFEU, Bratislava, ITMS projects nos. 26240120001, 26240120025).

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