Synthesis and α-Mannosidase Inhibitory Evaluation of (2*R*,3*R*,4*S*)- and (2*S*,3*R*,4*S*)-2-(Aminomethyl)pyrrolidine-3,4-diol Derivatives

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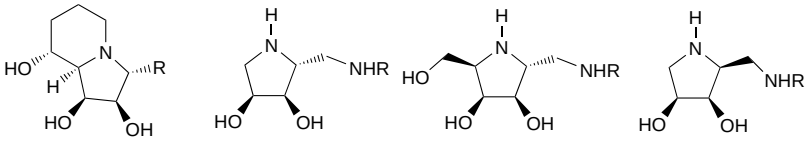
The synthesis of 46 derivatives of (2*R*,3*R*,4*S*)-2-(aminomethyl)pyrrolidine-3,4-diol is reported (*Scheme 1* and *Fig. 3*), and their inhibitory activities toward α-mannosidases from jack bean (B) and almonds (A) are evaluated (*Table*). The most-potent inhibitors are (2*R*,3*R*,4*S*)-2-{[([1,1′-biphenyl]-4-ylmethyl)amino]methyl}-pyrrolidine-3,4-diol (**3fs**; IC_{50}(B) = 5 μM, K_i = 2.5 μM) and (2*R*,3*R*,4*S*)-2-{[(1*R*)-2,3-dihydro-1*H*-inden-1-ylamino]methyl}pyrrolidine-3,4-diol (**3fu**; IC_{50}(B) = 17 μM, K_i = 2.3 μM). (2*S*,3*R*,4*S*)-2-(Aminomethyl)pyrrolidine-3,4-diol (**6**, R=H) and the three 2-(*N*-alkylamino)methyl derivatives **6fh**, **6fs**, and **6f** are prepared (*Scheme 2*) and found to inhibit also α-mannosidases from jack bean and almonds (*Table*). The best inhibitor of these series is (2*S*,3*R*,4*S*)-2-{[(2-thienylmethyl)amino]methyl}pyrrolidine-3,4-diol (**6o**; IC_{50}(B) = 105 μM, K_i = 40 μM). As expected (see *Fig. 4*), diamines **3** with the configuration of α-D-mannosides are better inhibitors of α-mannosidases than their stereoisomers **6** with the configuration of β-D-mannosides. The results show that an aromatic ring (benzyl, [1,1′-biphenyl]-4-yl, 2-thienyl) is essential for good inhibitory activity. If the C-chain that separates the aromatic system from the 2-(aminomethyl) substituent is longer than a methano group, the inhibitory activity decreases significantly (see *Fig. 7*). This study shows also that α-mannosidases from jack bean and from almonds do not recognize substrate mimics that are bulky around the *O*-glycosidic bond of the corresponding α-D-mannopyranosides. These observations should be very useful in the design of better α-mannosidase inhibitors.

Introduction. – The specific inhibition of *N*-linked glycoprotein-processing α-mannosidases may provide a useful anticancer strategy [1]. Clinical trials have shown that swainsonine (**1**), a natural α-mannosidase inhibitor that contains a 4-amino-4-deoxy-mannofuranoyl moiety [2][3], reduces solid tumors and hematological malignancies [4]. Analogues **2** have also shown interesting properties (*Fig. 1*) [5].



1 R = H
2 R = $ArCH_2CH_2$
3 R = $ArCH_2$
4 R = H
5 R = $ArCH_2$
6

Fig. 1. *Swainsonine and synthetic analogues*

Mannosidase inhibitors mediate increased secretion of mutant α1-antitrypsin Z. They are, thus, leads in the development of drugs for the chemoprophylaxis of liver injury and emphysema in patients with α1-antitrypsin Z deficiency [6]. Simpler

synthetic analogues of swainsonine are also potent α-mannosidase inhibitors [3][7]. Mannostatin A and B isolated from the soil microorganism *Streptoverticillum verticillus* [8] and a synthetic analogue [9] are probably the most-potent inhibitors of α-mannosidases reported so far [7][10]. Often, α-mannosidase inhibitors that are monosaccharide mimics [11][12] inhibit also other types of glycosidases [13], in particular α-L-fucosidases [11][14]. To become a drug, a good inhibitor must satisfy a number of conditions [15], apart from its low toxicity and enzyme specificity. One of these is membrane permeability, which often requires the presence of lyophilic groups. In a preliminary note, we have demonstrated that (2*R*,3*R*,4*S*)-3,4-dihydroxypyrrolidin-2-yl derivatives such as **3** are selective α-mannosidase inhibitors. In the case of **3f** (R = $PhCH_2$), derived from the weak and nonselective inhibitor **4** and benzaldehyde, competitive inhibition ($K_i = 7.4$ μM) of α-mannosidase from jack bean has been found [16]. This enzyme was chosen because it is a useful model for mammalian α-mannosidases such as *Golgi* α-mannosidase II [17]. Similar results have been reported by *Saotome* and co-workers [18] with derivative **5**. In the meantime, we have shown that imines resulting from the reaction of vicinal diamino compounds **4** with aromatic aldehydes can model the inhibitory activities of the corresponding products of reduction, the diamino derivatives **3**. This constitutes an efficient tool for the fast discovery of glycosidase inhibitors (and possibly inhibitors of other enzymes) that has led us to prepare further analogues of diamino compounds **3** [19]. We report here their synthesis and their inhibitory activities toward α-mannosidase from jack bean (B) and α-mannosidase from almonds (A). The study allows us to approach a structure-activity relationship that should be useful in the design of better α-mannosidase inhibitors, and hopefully of potent anticancer drugs. The most-potent α-mannosidase inhibitors reported in this paper are shown in *Fig. 2*. They are all competitive inhibitors that inhibit α-mannosidase from jack bean better than α-mannosidase from almonds.

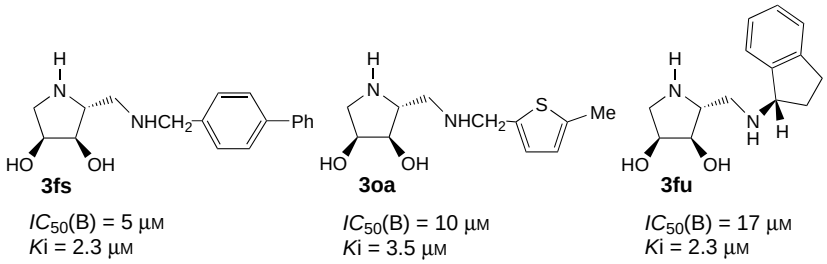


Fig. 2. *The most-potent new competitive α-mannosidase inhibitors.* B = jack bean.

We have also prepared a few 2-epimers **6** of the diamino compounds **3** (see *Fig. 3*). As expected from our working hypothesis (see model of *Fig. 4*) for the inhibition of α-mannosidases, diamino derivatives **6** are less active, in general, than their 2-epimers **3**.

Results and Discussion. – *Synthesis.* Following *Fleet*'s method [20], we converted D-gulonolactone to **7** that was then transformed into aldehyde **8** (33% overall yield based

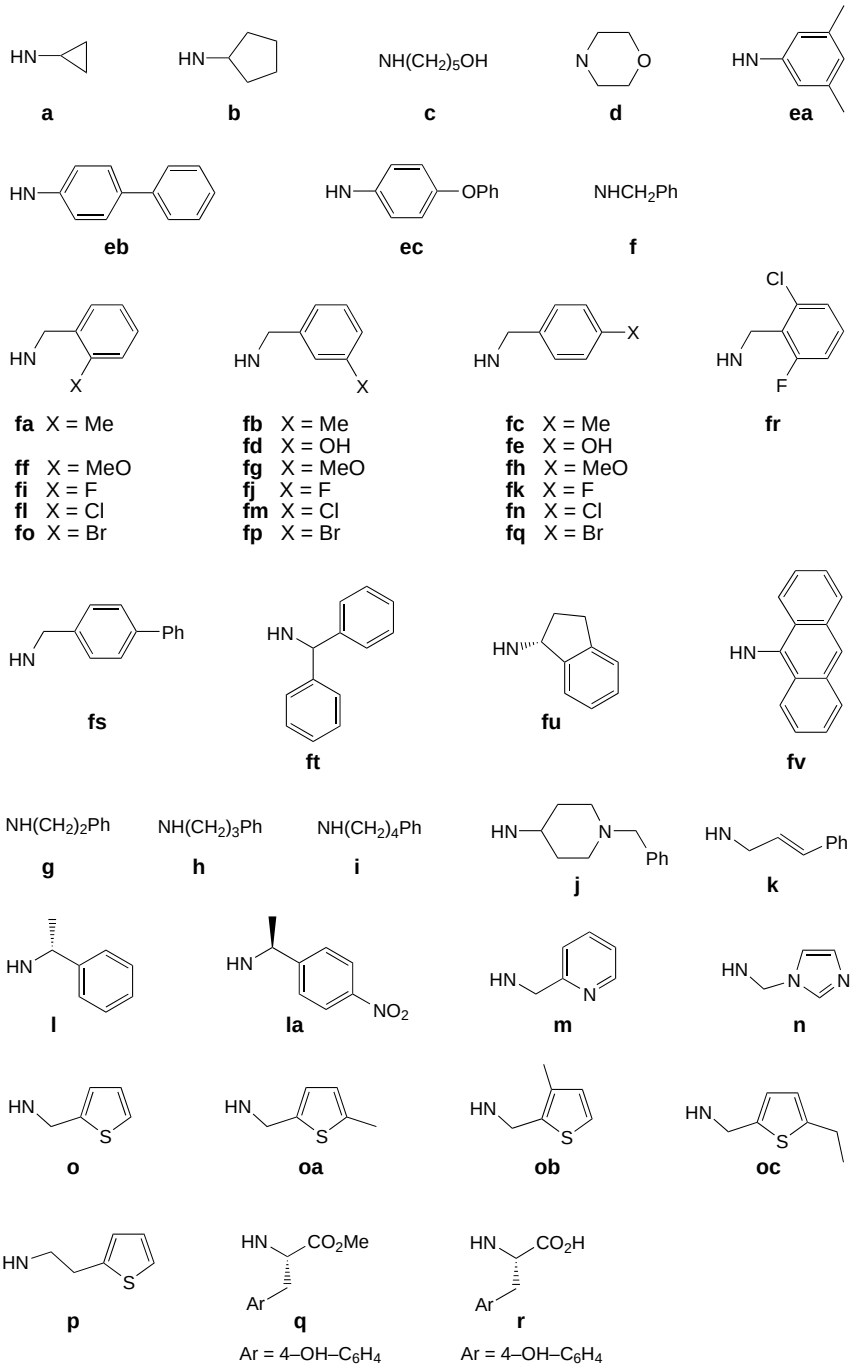


Fig. 3. *NR Groups in* **3**, **6**, **9**, *and* **18** *with corresponding key letters.* Compounds **3fa**–**fe**, **3fs**, **3k**, and **3oa**–**oc** were prepared by *Method B*; **3p** was prepared by *Method C*; **6** (R = H), **6f**, **6fh**, **6fs**, **6fu**, and **6o** were derived from D-ribose; all other compounds were obtained according to *Method A* (see *Scheme 1*, below).

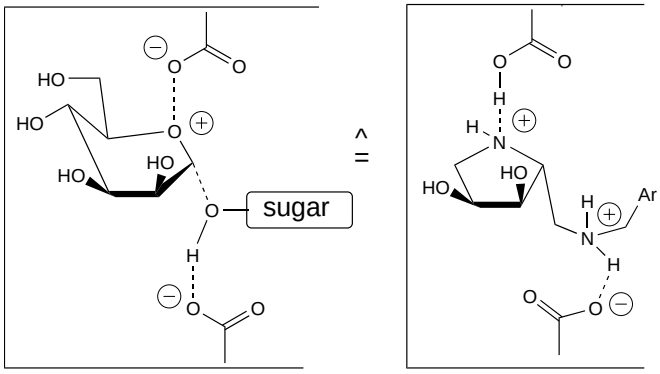


Fig. 4. *Dicationic mimics of a transition or intermediate structure of an α-mannosidase-catalyzed hydrolysis of an α-*D*-mannopyranoside*

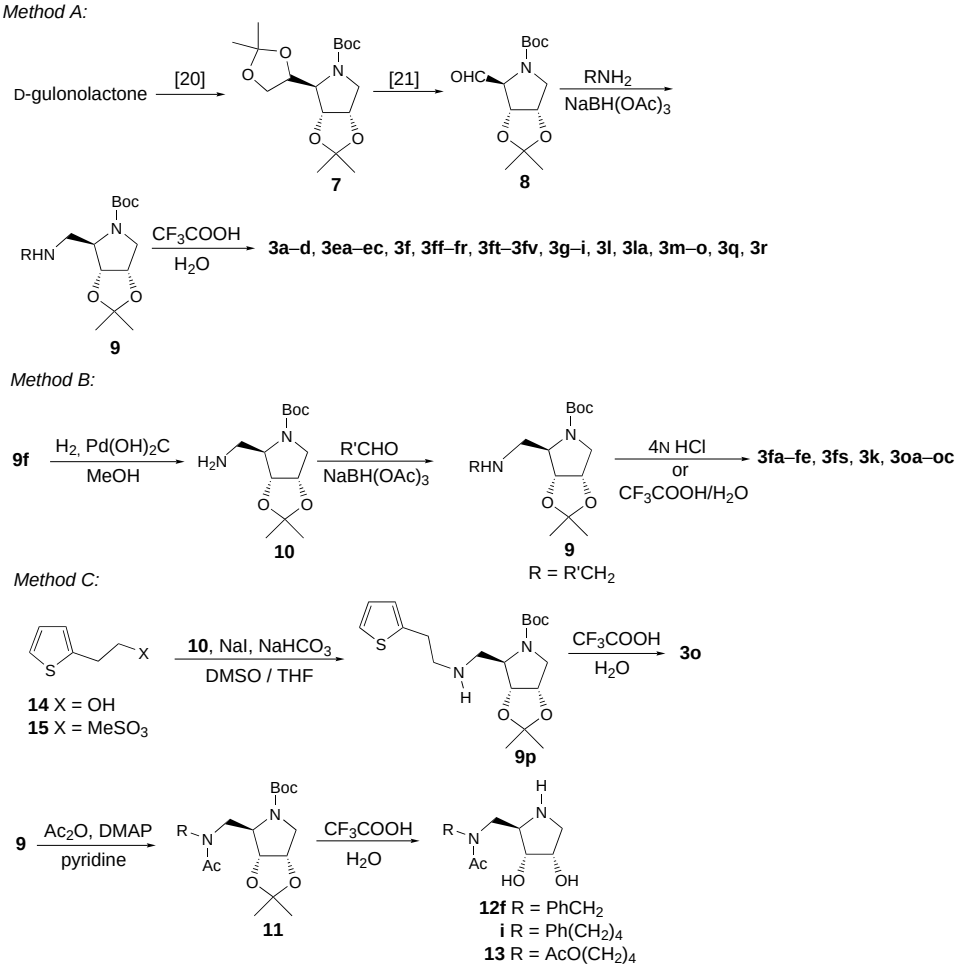
on D-gulonolactone, seven steps) [21] (*Scheme 1*, *Method A*). Aldehyde **8** reacted with 1 equiv. of primary amine RNH_2, in anhydrous 1,2-dichloroethane at 20°, giving the corresponding imines that were reduced *in situ* with $NaBH(OAc)_3$ into the corresponding amines **9** (65–90% yield). Deprotection in acidic medium (CF_3COOH/H_2O 4:1 or 4N HCl) provided the corresponding diamines **3** in quantitative yields[1]).

Hydrogenolysis (H_2, $Pd(OH)_2$/charcoal, MeOH) of the benzylamino derivative **3f**, followed by acid-mediated deprotection afforded diamino derivative **4** (for an alternative synthesis of **4**, see [22]). Primary-amino compound **10** [16] was used to generate a number of derivatives **3** by reductive amination with aldehydes in 1,2-dichloroethane (*Scheme 1*, *Method B*). Acetamido derivatives **12f** [16], **12i**, and **13** were prepared by acetylation of **9** under classical conditions (Ac_2O, pyridine, *N*,*N*-dimethylpyridin-4-amine (DMAP)) followed by hydrolysis of the resulting crude acetamides **11** (see [16]). The synthesis of the 2-(2-thienyl)ethyl derivative **3p** could not be carried out *via* reductive amination of 2-(2-thienyl)ethanal with **10** as we could not find a suitable method for the oxidation of 2-(2-thienyl)ethanol (**14**). We, thus, transformed **14** to the corresponding mesylate **15** by esterification with methanesulfonyl chloride and Et_3N. Coupling of **15** with **10** ($NaHCO_3$, NaI, THF/DMSO, 20°) afforded diamino compound **9p** in a mediocre yield (25%), which was hydrolyzed in acidic medium to provide derivative **3p** (100%) (*Scheme 1*, *Method C*).

Diamino compound **6** (R = H) was derived from D-ribose following the method described by *Kim* and co-workers (*Scheme 2*) [23]. The intermediate primary alcohol derivative **16** was oxidized under *Swern* conditions (88% yield) and reductive amination with benzylamine, 4-methoxybenzylamine, (1*R*)-2,3-dihydro-1*H*-inden-1-amine and 2-thiophene-2-methanamine afforded the corresponding protected diamino compounds **18**, which were hydrolyzed under acidic conditions (CF_3COOH/H_2O 4:1)

[1]) For the key letters **a**–**d**, **ea**–**ec**, **f**, **fa**–**fv**, **g**–**l**, **la**, **m**–**o**, **oa**–**oc**, and **p**–**r**, see *Fig. 3*.

Scheme 1. *Synthesis of Derivatives* **3** *and* N-*Acetamido Derivatives* **12** *and* **13**[1])

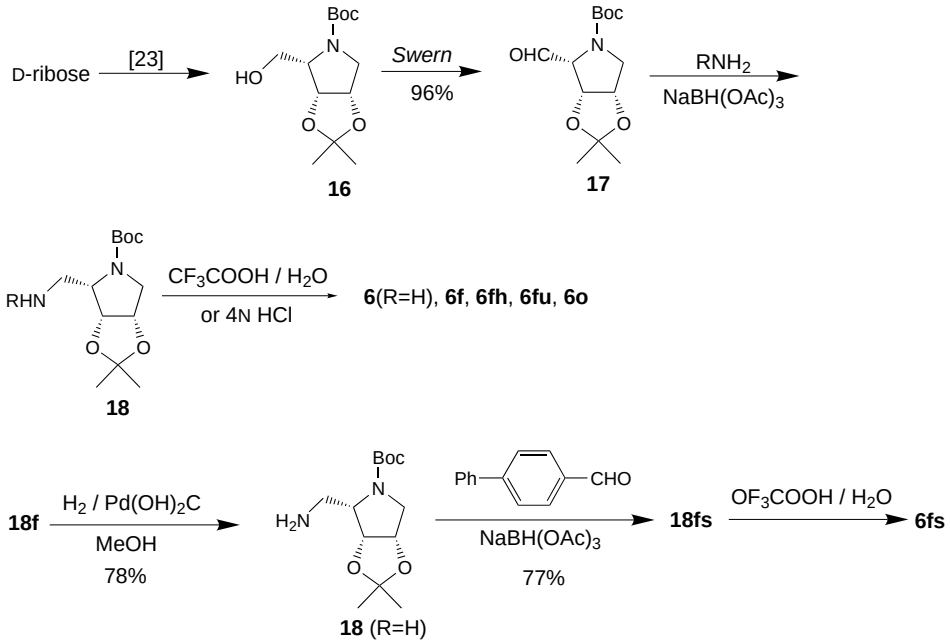


to give derivatives **6f** [24], **6fh**, **6fu** [24], and **6o**, respectively. Derivative **6fs** was obtained by debenzylation of **18f** and subsequent reductive amination with [1,1′-biphenyl]-4-carboxaldehyde in the presence of $NaBH(OAc)_3$ to produce **18fs** in 58% yield. Quantitative acidic treatment gave the desired diamine **6fs**.

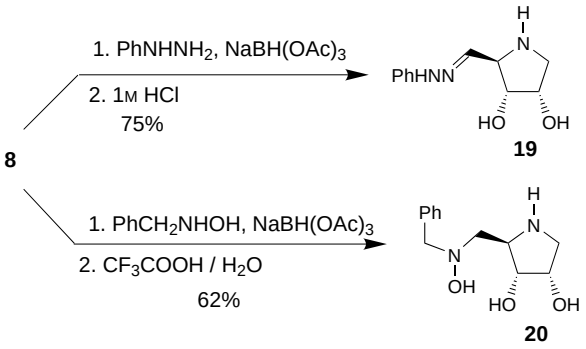
To complete our study, we also prepared hydrazone **19** and *N*-hydroxy derivative **20** as outlined in *Scheme 3*.

Inhibitory Activities. – The 4-nitrophenyl α-D-mannopyranoside was used as substrate, and the commercially available α-mannosidase (EC 3.2.1.24) from jack bean and from almonds were used as catalysts of buffered (pH 5.0) hydrolysis [25]. Our results are summarized in the *Table*.

Scheme 2. *Synthesis of Derivatives* **6**[1])



Scheme 3



As expected, diamino compounds **3** that have the configuration of α-D-mannosides for centers C(1), C(2), and C(3) (carbohydrate numbering) are better inhibitors than their stereoisomers **6**, the configuration of which corresponds to β-D-mannosides. Surprisingly, the unsubstituted primary-amino derivative **6** (R = H) is more active than its isomer **4** toward the two enzymes used in this study (**6** (R = H): IC_{50}(B) = 30 μM, IC_{50}(A) = 165 μM; **4**: IC_{50}(B) = 150 μM, IC_{50}(A) = 1000 μM). The largest selectivity between diamino derivatives **3** and **6** is observed with the most-potent derivatives such as **3fs** (IC_{50}(B) = 5 μM) *vs.* **6fs** (IC_{50}(B) = 800 μM) and **3fu** (IC_{50}(B) = 17 μM) *vs.* **6fu**

Table. *Inhibitory Activities toward α-Mannosidase from Jack Bean* (**B**) *and from Almonds* (**A**) *of (2*R,*3*R,*4*S*)-3,4-Dihydroxypyrrolidin-2-yl Derivatives* **3** *and of (2*S,*3*R,*4*S*)-3,4-dihydroxypyrrolidin-2-yl Derivatives* **6**. Percentage of inhibition at 1mM concentration, IC_{50} and K_i values in μM, when measured at optimal pH and 25°. All inhibitors are competitive (*Lineweaver-Burk* plots), except when indicated; m.t. = mixed type of inhibition. n.i. = no inhibition at 1mM concentration.

	4	**3a**	**3b**	**3c**	**3d**	**3ea**	**3eb**	**3ec**	**3f**	**3fa**	**3fb**
B	81%	58%	60%	44%	n.i.	62%	83%	87%	92%	95%	95%
IC_{50}	150	650	560			560	250	130	60	45	60
K_i	53					190	56	66	7.4	11	10 (m.t.)
A	51%	46%	53%	21%	n.i.	n.i.	31%	45%	69%	78%	79%
IC_{50}	1000		1000						230	170	200
K_i										71	52
	3fc	**3fd**	**3fe**	**3ff**	**3fg**	**3fh**	**3fi**	**3fj**	**3fk**	**3fl**	**3fm**
B	98%	97%	97%	86%	96%	98%	91%	88%	95%	93%	94%
IC_{50}	20	34	23	105	35	10	75	140	36	29	38
K_i	3.0 (m.t.)	8.4	5.0	20 (m.t.)	9.2	7.0	20	36	9.5	13	12
A	85%	82%	86%	74%	83%	80%	69%	58%	78%	74%	73%
IC_{50}	62	140	80	300	87	70	450		270	170	280
K_i	35	60	20		47	54				53	
	3fn	**3fo**	**3fp**	**3fq**	**3fr**	**3fs**	**3ft**	**3fu**	**3fv**	**3g**	**3h**
B	95%	94%	95%	96%	78%	99%	85%	98%	80%	68%	87%
IC_{50}	35	36	35	30	255	5	375	17	220	300	200
K_i	10	11	10	8.5		2.5		2.3			
A	73%	77%	80%	78%	53%	82%	74%	89%	47%	45%	67%
IC_{50}	270	220	140	140	1000	75	350	105			520
K_i			39	47		20		21			
	3i	**3j**	**3k**	**3l**	**3la**	**3m**	**3n** [16]	**3o**	**3oa**	**3ob**	**3oc**
B	68%	n.i.	97%	66%	90%	88%	n.i.	89%	98%	92%	96%
IC_{50}	380		16	440	70	174		85	10	44	26
K_i	120		9.5	170	26	34		26	3.5	18	6.4
A	47%	n.i.	78%	48%	77%	53%	n.i.	68%	86%	75%	81%
IC_{50}			150		110			350	100	130	135
K_i			53		31			98	19	61	33
	3p	**3q**	**3r**	**6** (R = H)	**6f** [24]	**6fh**	**6fs**	**6o**	**6fu** [24]		
B	72%	n.i.	n.i.	92%	72%	88%	57%	84%	73%		
IC_{50}	260			30	361	110	800	105	397		
K_i				92	105	56		40	12		
A	50%	n.i.	n.i.	67%	44%	60%	85%	58%	38%		
IC_{50}				165	n.i.	230	155	290			
K_i				97	n.i.	135	95	83			

(IC_{50}(B) = 397 μM). In all cases, α-mannosidase from jack bean (B) responds better than α-mannosidase from almonds (A) toward our diamino compounds. The selectivity factor (IC_{50}(B)/IC_{50}(A)) never surpass 8, except for the most-potent inhibitors such as **3fs**, for which it reaches a value of 15.

It has been found, from a statistical analysis with eleven proteins, that molecular motifs containing a 1,1′-biphenyl moiety are high-affinity ligands for proteins [26]. It is, thus, not surprising that the ([1,1′-biphenyl]-4-ylmethyl)amino derivative **3fs** shows the lowest IC_{50} value of all our diamino compounds. Considering inhibition constants, the

(dihydroindenyl)amino derivative **3fu** is also a good inhibitor of α-mannosidase from jack bean, as well as the [(5-methyl-2-thienyl)methyl]amino derivative **3oa** (IC_{50}(B) = 17 and 10 μM, K_i = 2.3 and 3.5 μM, resp.). In agreement with our working hypothesis (see model of *Fig. 4*), all our inhibitors are competitive (*Fig. 5*). Exceptions are **3fb**, **3ff**, and **3fc** with α-mannosidase from jack bean, as well as **6f** [24] for the inhibition of α-mannosidase from almonds that all showed mixed-type inhibition (*Fig. 6*).

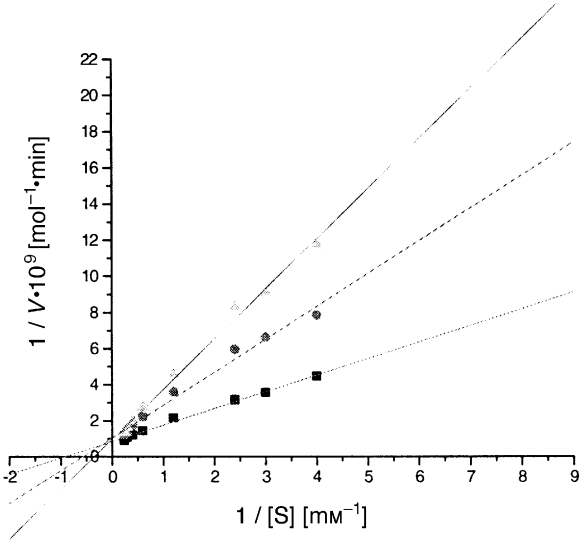


Fig. 5. Lineweaver–Burk *plots for the inhibition of α-mannosidase from jack bean* (pH 5, 25°) *by (2*R,*3*R,*4*S*)-2-{[([1,1'-biphenyl]-4-ylmethyl)amino]methyl}pyrrolidine-3,4-diol* (**3fs**)

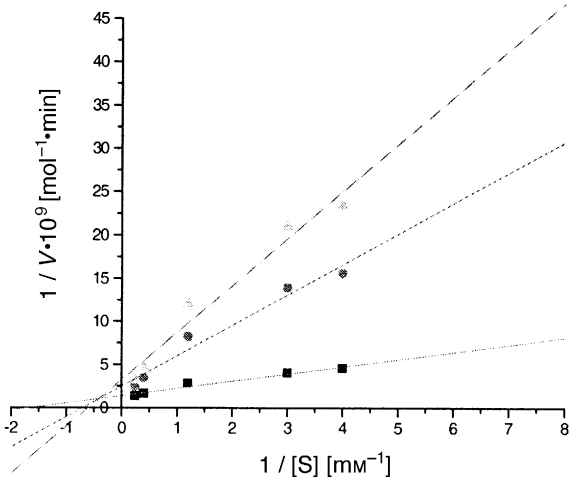
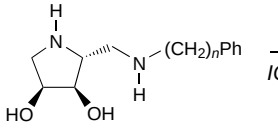


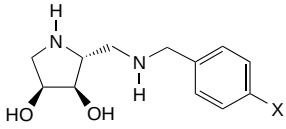
Fig. 6. Lineweaver–Burk *plots for the inhibition of α-mannosidase from jack bean* (pH 5, 25°) *by (2*R,*3*R,*4*S*)-2-{[(3-methylbenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fb**)

The 3,5-dimethylphenylamino derivative **3ea** is a weak inhibitor, whereas the benzylamino derivative **3f** and its substituted analogues are potent inhibitors. The

inhibitory activity decreases significantly on increasing the length of the alkane chain separating the phenyl group from the aminomethyl moiety, as summarized in *Fig. 7*. Interestingly, rigidification of the C_3-alkane chain of **3h** by a (*E*)-double bound improves the inhibitory activity (see **3k**: $IC_{50}(B) = 16$ μM, $K_i = 9.5$ μM). Exchange of the phenyl group of **3f** by a pyridin-2-yl group (see **3m**: $IC_{50}(B) = 174$ μM) results in a decrease in activity. With the imidazol-1-yl derivative **3n** [16], no inhibition was detected at 1 mM concentration. In contrast, the (2-(thienyl)methyl)amino analogues **3o**, and especially **3oa**, are as potent α-mannosidase inhibitors as **3f** and **3fc**, respectively. The results obtained with **3a**–**d** demonstrate that the presence of an aromatic ring is essential for good inhibitory activity. The poor inhibition observed with **3ea**, **3eb**, **3ec**, **3fr**, **3ft**, **3fv**, **3j**, **3q**, and **3r** suggest that the α-mannosidases (A, B) assayed in this work cannot accommodate voluminous groups in the vicinity of the aminomethyl moiety of the inhibitor. It appears, therefore, that the active sites of these enzymes are like a mouth that closes onto the 'glycosidic' bond of the substrates once they have penetrated them. This hypothesis is consistent with the observation of better inhibitory activities for the *para*-substituted benzylamino derivatives (see **3fc**, **3fe**, **3fh**, **3fk**, **3fn**, and **3fq**) than for the corresponding *meta*-substituted (see **3fb**, **3fd**, **3fg**, **3fj**, **3fm**, and **3fp**) and *ortho*-substituted analogues (see **3fa**, **3ff**, **3fi**, **3fl**, and **3fo**). The nature of the *para*-substituent does not significantly affect the inhibitory activity (*Fig. 7*).



	3f (*n* = 1)	**3g** (*n* = 2)	**3h** (*n* = 3)	**3i** (*n* = 4)
IC_{50}(B) [μM]	60	300	200	380



	3fh	**3fc**	**3fe**	**3fq**	**3fn**	**3fk**	**3f**
X	MeO	Me	OH	Br	Cl	F	H
IC_{50}(B) [μM]	10	20	23	30	35	36	60

Fig. 7. *Selected inhibitory data*

In the case of the (2-thienylmethyl)amino derivatives **3o**, 5-methyl (see **3oa**: $IC_{50}(B) = 10$ μM) and 5-ethyl (see **3oc**: $IC_{50}(B) = 26$ μM), substitutions of the thiophene ring lead to improved activities in comparison with the 3-methyl substitution (see **3ob**: $IC_{50}(B) = 44$ μM), a trend that parallels that found for the corresponding benzylamines **3f**.

In agreement with our model (see *Fig. 4*), the 2-(acetamidomethyl)pyrrolidine-3,4-diols **12f**, **12i**, and **13** do not inhibit α-mannosidases A and B. Probably, the same steric factor invoked above can be retained in these cases, together with the fact that the acetamido groups, being less basic than the corresponding amino moieties, cannot make a strong electrostatic interaction with the carboxylic acid of the active site. This hypothesis is consistent with the observation that the *N*-hydroxy derivatives, *e.g.* **20**, do not inhibit α-mannosidases. Phenylhydrazone **19** was prepared to imitate benzylamine **3f**. Perhaps the rigidity of the imino double bond and the weaker basicity of the

hydrazone function compared with that of a secondary amine are the cause of its lack of inhibitory activity toward α-mannosidase from jack bean and from almonds.

Conclusions. – (2*R*,3*R*,4*S*)-2-[(Benzylamino)methyl]pyrrolidine-3,4-diols substituted at the *para*-position of the benzyl group are active α-mannosidase inhibitors with K_i values in the low μM range. They are more active than their (2*S*,3*R*,4*S*)-epimers. Substitution at the benzylic CH_2 group or at the *ortho*- and *meta*-position of the aromatic ring decreases the inhibitory activity. *N*-Acetylation and *N*-hydroxylation of the benzylamino group result in a complete loss of the inhibitory activity. (2*R*,3*R*,4*S*)-2-{[(5-alkyl-2-thienyl)-amino]methyl}pyrrolidine-3,4-diols are also potent inhibitors of α-mannosidase from jack bean.

This work was supported by the *Swiss National Science Foundation* (Grant No 2100-063567.00/1) and the *Office Fédéral de l'Enseignement et de la Recherche* (COST D13/0001/99). We are grateful to the *Serono Pharmaceutical Research Institute* (Plan-les-Ouates, Switzerland) for the generous gift of primary amines and to Mr. *Martial Rey* and Mr. *Francisco Sepúlveda* for their technical assistance.

Experimental Part

General. All commercially available reagents (*Fluka*, *Aldrich*) were used without further purification. Solvents were dried by standard methods. The light petroleum ether used refers to the fraction boiling at 40–60°. Solns. after reactions and extractions were evaporated in a rotatory evaporator under reduced pressure. Liquid/solid flash chromatography (FC): silica gel *60* (*Merck* No. 9385, 240-400 mesh). TLC (reaction monitoring): *Merck* silica gel $60F_{254}$ plates; detection by UV light, *Pancaldi* reagent ($(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O) or $KMnO_4$. IR Spectra: *Perkin-Elmer 1420* spectrometer; in cm^{-1}. Optical rotations: at r.t.; *Jasco DIP-370* polarimeter; $[\alpha]_D$ in 10^{-1} deg cm^2 g^{-1}. ^{1}H-NMR Spectra: *Bruker ARX-400* spectrometer (400 MHz); δ(H) in ppm rel. to the solvent's residual ^{1}H signal ($CHCl_3$, δ(H) 7.27; CH_3OD, δ(H) 3.31) as internal reference; all ^{1}H assignments were confirmed by 2D-COSY-45 and 2D-NOESY experiments. ^{13}C-NMR Spectra: same instrument as for ^{1}H (100.6 MHz); δ(C) in ppm rel. to the solvent's C-signal ($CDCl_3$, δ(C) 77.0; CD_3OD, δ(C) 49.8) as internal reference; all ^{13}C assigments were confirmed by 2D-HMQC; coupling constants *J* in Hz. MS: *Nermag R 10-10C*, chemical-ionization (NH_3) mode; *m*/*z* (% rel. to the base peak (=100%)). Elemental analyses: *Ilse Beetz*, D-96301 Kronach, Germany.

Diamino Compounds **3** *by* Method A: *Reductive Amination of* N-*[(*tert-*Butoxy)carbonyl]-2,5-imino-2,5-dideoxy*-L-*ribose* (**8**). $NaBH(OAc)_3$ (1.4 equiv.) was added portionwise to stirred 0.5M aldehyde **8** and 0.5M primary amine RNH_2 in abs. $ClCH_2CH_2Cl$ at 20°. After complete disappearance of **8** (TLC control), the soln. was poured into sat. $NaHCO_3$ soln. (5 ml per mmol of **8**). The aq. phase was extracted with AcOEt (10 ml per mmol of **8**, 3 times), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue submitted to FC (silica gel, *Merck 7734* or *9385*) [27]: pure **9**.

Diamino Compounds **9** *by* Method B: *Reductive Amination of* tert-*Butyl (3a*R,*4*R,*6a*S*)-4-(Aminomethyl)tetrahydro-2,2-dimethyl-5*H-*[1,3]dioxolo[4,5*-c*]pyrrole-5-carboxylate* (**10**). $NaBH(OAc)_3$ (1.4 equiv.) was added portionwise to stirred 0.5M amino derivative **10** and 0.5M aldehyde RCHO in abs. $ClCH_2CH_2Cl$ at 20°. After complete disappearance of **10** (TLC control), the soln. was poured into sat. aq. $NaHCO_3$ soln. (5 ml per mmol of **10**). The aq. phase was extracted with AcOEt (10 ml per mmol of **10**, 3 times), the combined org. extract dried ($MgSO_4$) and evaporated and the residue submitted to FC (silica gel, *Merck 7734* or *9385*) [27]: pure **9**.

Deprotection of **9** *to* **3**. *Method Aa:* A 5–10% soln. of **9** in CF_3COOH/H_2O 4:1 was stirred at 20° for 1 h. After evaporation, the residue was purified by FC (silica gel).

Method Ab: A 5–10% soln. of **9** in 4M aq. HCl was stirred at 20° for 1 h. After evaporation, the residue was purified by FC (silica gel or alumina).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-[(Cyclopropylamino)methyl]tetrahydro-2,2-dimethyl-5*H-*[1,3]dioxolo[4,5*-c*]-pyrrole-5-carboxylate* (**9a**). By *Method A*, with **8** (108 mg, 0.40 mmol), cyclopropylamine (23 mg, 0.40 mmol), $NaBH(OAc)_3$ (118 mg, 0.56 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (CH_2Cl_2/MeOH 97:3) gave 54 mg (43%) of

9a, 1.3:1 mixture of rotamers α and β. $[\alpha]_{589}^{25}=-37$, $[\alpha]_{577}^{25}=-39$, $[\alpha]_{546}^{25}=-42$, $[\alpha]_{435}^{25}=-72$, $[\alpha]_{405}^{25}=-87$ ($c=0.78$, CH_2Cl_2). UV (MeCN): 274 (1155), 200 (4520). IR (film): 2980, 2935, 1690, 1475, 1410, 1210, 1175, 1125, 1055, 980, 860, 830, 770. ^{1}H-NMR (400 MHz, MeOD): 4.73 (*m*, H–C(6a)); 4.57 (*m*, H–C(3a)); 4.12 (*m*, H–C(4)); 3.76 (*d*, $^2J=12.8$, 1 H–C(6)); 3.37 (*m*, 1 H–C(6)); 2.72 (*m*, 2 H–C(1′)); 2.20 (*m*, H–C(1″)); 1.47 (*s*, (*t*-Bu)$_\alpha$); 1.46 (*s*, (*t*-Bu)$_\beta$); 1.39 (*s*, 1 Me); 1.28 (*s*, 1 Me); 0.46 (*m*, 2 H–C(2″)); 0.34 (*m*, 2 H–C(3″)). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\beta$); 157.3 (*s*, $NCOO_\alpha$); 113.4 (*s*); 85.3 (*d*, ^1J(C,H) = 157, C(3a)$_\alpha$); 84.8 (*d*, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_β); 81.6 (*d*, ^1J(C,H) = 151, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.5 (*d*, ^1J(C,H) = 147, C(4)$_\alpha$); 65.2 (*d*, ^1J(C,H) = 146, C(4)$_\beta$); 53.7 (*t*, ^1J(C,H) = 147, C(6)$_\alpha$); 53.1 (*t*, ^1J(C,H) = 144, C(6)$_\alpha$); 50.9 (*t*, ^1J(C,H) = 146, C(1′)$_\alpha$); 50.7 (*t*, ^1J(C,H) = 145, C(1′)$_\beta$); 32.0 (*d*, ^1J(C,H) = 172, C(1″)$_\alpha$); 31.9 (*d*, ^1J(C,H) = 171, C(1″)$_\alpha$); 29.6 (*q*, ^1J(C,H) = 128, Me_3C); 28.1 (*q*, ^1J(C,H) = 129, Me); 25.8 (*q*, ^1J(C,H) = 126, Me); 7.8 (*t*, ^1J(C,H) = 162, C(2″)$_\alpha$); 7.5 (*t*, ^1J(C,H) = 161, C(2″)$_\beta$); 7.2 (*t*, ^1J(C,H) = 161, C(3″)$_\beta$); 7.0 (*t*, ^1J(C,H) = 162, C(3″)$_\alpha$). CI-MS (NH_3): 313 (67, $[M+H]^+$), 297 (1), 257 (92), 239 (7), 182 (11), 142 (9), 112 (17), 84 (10). Anal. calc. for $C_{16}H_{28}N_2O_4$ (312.43): C 61.51, H 9.03; found: C 61.49, H 9.03.

*(2*R*,3*R*,4*S*)-2-[(Cyclopropylamino)methyl]pyrrolidine-3,4-diol* (**3a**). By *Method Aa*, with **9a** (30 mg). FC (MeCN/NH_4OH 4:1) gave 23 mg (100% of **3a**). $[\alpha]_{589}^{25}=+79$, $[\alpha]_{577}^{25}=+82$, $[\alpha]_{546}^{25}=+92$, $[\alpha]_{435}^{25}=+139$ ($c=0.10$, MeOH). UV (MeCN): 204 (785). IR (KBr): 3420, 3110, 2950, 1680, 1445, 1370, 1205, 1135, 1055, 1020, 840, 800, 725. ^{1}H-NMR (400 MHz, D_2O): 4.30 (*m*, H–C(4)); 3.99 (*dd*, ^3J(3,4) = 4.6, ^3J(3,2) = 8.0, H–C(3)); 3.47 (*ddd*, ^3J(2,1′) = 4.2, ^3J(2,3) = 8.0, ^3J(2,1′) = 8.0, H–C(2)); 3.37 (*dd*, ^3J(5,4) = 4.9, $^2J=12.6$, 1 H–C(5)); 3.17 (*m*, 1 H–C(5), 1 H–C(1′)); 2.99 (*dd*, ^3J(1′,2) = 8.0, $^2J=13.6$, 1 H–C(1′)); 2.36 (*m*, H–C(1″)); 0.65 (*m*, 2 H–C(2″); 0.51 (*m*, 2 H–C(3″)). ^{13}C-NMR (100.6 MHz, D_2O): 76.9 (*d*, ^1J(C,H) = 145, C(3)); 72.6 (*d*, ^1J(C,H) = 148, C(4)); 61.8 (*d*, ^1J(C,H) = 143, C(2)); 52.3 (*t*, ^1J(C,H) = 144, C(5), C(1′)); 32.2 (*d*, ^1J(C,H) = 176, C(1″)); 7.0 (*t*, ^1J(C,H) = 162, C(2″)); 6.8 (*t*, ^1J(C,H) = 164, C(3″)). CI-MS (NH_3): 173 (40, $[M+H]^+$), 155 (3), 143 (22), 133 (6), 112 (31), 102 (51), 85 (35).

tert-*Butyl (3a*R,4R,*6a*S*)-4[(Cyclopentylamino)methyl]tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9b**). By *Method A*, with **8** (141 mg, 0.52 mmol), cyclopentylamine (44 mg, 0.52 mmol), $NaBH(OAc)_3$ (154 mg, 0.73 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (CH_2Cl_2/MeOH 95:5) gave 80 mg (47% of **9b**), 1.1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25}=-49$, $[\alpha]_{577}^{25}=-48$, $[\alpha]_{546}^{25}=-47$, $[\alpha]_{435}^{25}=-78$, $[\alpha]_{405}^{25}=-98$ ($c=0.63$, CH_2Cl_2). UV (MeCN): 273 (1905), 199 (3000). IR (film): 2955, 2870, 1695, 1455, 1405, 1210, 1170, 1125, 1055, 975, 860, 770. ^{1}H-NMR (400 MHz, MeOD): 4.76 (*m*, H–C(6a)); 4.62 (*m*, H–C(3a)); 4.13 (*m*, H–C(4)); 3.79 (*m*, 1 H–C(6)); 3.42 (*m*, 1 H–C(6)); 3.12 (*m*, H–C(1″)); 2.64 (*d*, ^3J(1′,4) = 7.0, 2 H–C(1′)); 1.90 (*m*, 2 H–C(2″)); 1.73 (*m*, 2 H–C(5″)); 1.58 (*m*, 2 H–C(4″)); 1.51 (*s*, (*t*-Bu)$_\beta$); 1.50 (*s*, (*t*-Bu)$_\alpha$); 1.42 (*s*, 1 Me); 1.36 (*m*, 2 H–C(3″)); 1.32 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.6 (*s*, $NCOO_\beta$); 157.3 (*s*, $NCOO_\alpha$); 113.4 (*s*); 85.4 (*d*, ^1J(C,H) = 156, C(3a$_\alpha$)); 84.9 (*d*, ^1J(C,H) = 156, C(3a$_\beta$)); 82.4 (*s*, Me_3CO_2); 82.1 (*s*, Me_3CO_β); 81.6 (*d*, ^1J(C,H) = 158, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.8 (*d*, ^1J(C,H) = 147, C(4)$_\alpha$); 65.4 (*d*, ^1J(C,H) = 147, C(4)$_\beta$); 61.6 (*d*, ^1J(C,H) = 139, C(1″)$_\beta$); 61.3 (*d*, ^1J(C,H) = 132, C(1″)$_\alpha$); 53.7 (*t*, ^1J(C,H) = 144, C(6)$_\beta$); 53.1 (*t*, ^1J(C,H) = 142, C(6)$_\alpha$); 50–49 (C(1′)); 34.5 (*t*, ^1J(C,H) = 127, C(2″), C(3″)); 29.6 (*q*, ^1J(C,H) = 128, Me_3C_α); 29.5 (*q*, ^1J(C,H) = 126, Me_3C_β); 28.1 (*q*, ^1J(C,H) = 126, Me); 25.8 (C(4″), C(5″), Me). CI-MS (NH_3): 341 (87, $[M+H]^+$), 340 (8, M^+), 325 (7), 285 (32), 243 (8), 187 (12), 142 (9), 98 (100), 84 (24). Anal. calc. for $C_{18}H_{32}N_2O_4$ (340.49): C 63.50, H 9.47; found: C 63.52, H 9.54.

*(2*R*,3*R*,4*S*)-2-[(Cyclopentylamino)methyl]pyrrolidine-3,4-diol* (**3b**). By *Method Aa*, with **9b** (44 mg). FC (MeCN/NH_4OH 4:1) gave 25 mg (100% of **3b**). $[\alpha]_{589}^{25}=+74$, $[\alpha]_{577}^{25}=+74$, $[\alpha]_{546}^{25}=+96$, $[\alpha]_{435}^{25}=+147$ ($c=0.21$, MeOH). IR (KBr): 3420, 2955, 1560, 1420, 1110, 810. ^{1}H-NMR (400 MHz, D_2O): 4.21 (*m*, H–C(4)); 3.87 (*dd*, ^3J(3,4) = 5.1, ^3J(3,2) = 7.8, H–C(3)); 3.48 (*q*, $^3J=7.1$, H–C(1″)); 3.25 (*m*, H–C(2), 1 H–C(5)); 3.17 (*dd*, ^3J(1′,2) = 4.2, $^2J=11.7$, 1 H–C(1′)); 2.92 (*m*, 1 H–C(5), 1 H–C(1′)); 2.07 (*m*, 2 H–C(5″)); 1.75 (*m*, 2 H–C(4″)); 1.62 (*m*, 2 H–C(3″)); 1.57 (*m*, 2 H–C(2″)). ^{13}C-NMR (100.6 MHz, D_2O): 77.8 (*d*, C(3)); 73.4 (*d*, C(4)); 62.1 (*d*, C(1″)); 60.9 (*d*, C(2)); 52.7, 52.2 (2*t*, C(5), C(1′)); 32.6 (*t*, C(2″), C(5″)); 26.1 (*t*, C(3″), C(4″)). CI-MS (NH_3): 201 (100, $[M+H]^+$), 116 (2), 98 (40), 85 (21).

tert-*Butyl (3a*R,*4*R,*6a*S*)-Tetrahydro-4-{[(5-hydroxypentyl)amino]methyl}-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9c**). By *Method A*, with **8** (153 mg, 0.56 mmol), 5-aminopentan-1-ol (58 mg, 0.56 mmol), $NaBH(OAc)_3$ (166 mg, 0.78 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (CH_2Cl_2/MeOH 4:1) gave 80 mg (40% of **9c**), 1.2:1 mixture of rotamers α and β. $[\alpha]_{589}^{25}=-30$, $[\alpha]_{577}^{25}=-35$, $[\alpha]_{546}^{25}=-37$, $[\alpha]_{435}^{25}=-62$, $[\alpha_{405}^{25}=-74$ ($c=0.49$, CH_2Cl_2). UV (MeCN): 201 (4530). IR (film): 3420, 2980, 2935, 2865, 1680, 1480, 1455, 1410, 1370, 1210, 1160, 1130, 1055, 975, 855, 770. ^{1}H-NMR (400 MHz, MeOD): 4.77 (*m*, H–C(6a)); 4.63 (*d*, ^3J(3a,6a) = 6.0, H–C(3a)$_\beta$); 4.60 (*d*, ^3J(3a,6a) = 5.7, H–C(3a)$_\alpha$); 4.19 (*t*, ^3J(4,1′) = 7.1, H–C(4)$_\beta$); 4.13 (*t*, ^3J(4,1′) = 7.0, H–C(4)$_\alpha$); 3.86 (*d*, ^3J(6,6a) = 5.3, 1 H–C(6)$_\beta$); 3.83 (*d*, ^3J(6,6a) = 5.2, 1 H–C(6)$_\alpha$); 3.59 (*t*, ^3J(5″,4″) = 6.5, 2 H–C(5″)); 3.42

(d, ^3J(6,6a) = 4.6, 1 H–C(6)$_\alpha$); 3.39 (d, ^3J(6,6a) = 4.3, 1 H–C(6)$_\beta$); 2.68 (m, 2 H–C(1′), 2 H–C(1″)); 1.57 (m, 2 H–C(2″), 2 H–C(4″)); 1.51 (s, (t-Bu)$_\beta$); 1.50 (s, (t-Bu)$_\alpha$); 1.41 (m, 2 H–C(3″), 1 Me); 1.33 (s, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 163.2 (s, NCOO$_\beta$); 163.0 (s, NCOO$_\alpha$); 113.5 (s); 85.4 (d, ^1J(C,H) = 157, C(3a)$_\beta$); 84.8 (d, ^1J(C,H) = 158, C(3a)$_\alpha$); 82.5 (s, Me$_3$CO$_\beta$); 82.4 (s, Me$_3$CO$_\alpha$); 81.6 (d, ^1J(C,H) = 161, C(6a)$_\alpha$); 80.9 (d, ^1J(C,H) = 157, C(6a)$_\beta$); 65.5 (d, ^1J(C,H) = 145, C(4)$_\alpha$)); 64.9 (d, ^1J(C,H) = 149, C(4)$_\beta$); 63.6 (t, ^1J(C,H) = 141, C(5″)); 53.6 (t, ^1J(C,H) = 131, C(6)$_\alpha$); 53.0 (t, ^1J(C,H) = 133, C(6)$_\beta$); 51.3 (t, ^1J(C,H) = 132, C(1′)); 50.9 (t, ^1J(C,H) = 130, C(1″)); 34.3 (t, ^1J(C,H) = 125, C(2″)); 31.1 (t, ^1J(C,H) = 126, C(4″)); 30.7 (t, ^1J(C,H) = 126, C(3″)); 29.5 (q, ^1J(C,H) = 126, *Me*$_3$C); 28.0 (q, ^1J(C,H) = 126, Me); 25.8 (q, ^1J(C,H) = 125, Me). CI-MS (NH_3): 359 (100, $[M+H]^+$), 358 (71, M^+), 303 (11), 285 (3), 243 (3), 143 (3), 116 (68), 85 (5). Anal. calc. for $C_{18}H_{34}N_2O_5$ (358.47): C 60.31, H 9.56, N 7.81, O 22.32; found: C 60.16, H 9.60, N 7.73, O 22.51.

*(2*R*,3*R*,4*S*)-2-{[(5-Hydroxypentyl)amino]methyl}pyrrolidine-3,4-diol* (**3c**). By *Method Aa*, with **9c** (15 mg). FC (MeCN/NH_4OH 4:1) gave 11 mg (100% of **3c**). $[\alpha]^{25}_{577} = +8$, $[\alpha]^{25}_{546} = +13$, $[\alpha]^{25}_{435} = +22$, $[\alpha]^{25}_{405} = +28$ ($c = 0.2$, MeOH). IR (film): 3415, 2985, 1620, 1400, 1265, 1115, 800, 670, 605, 470. ^{1}H-NMR (400 MHz, D_2O): 4.45 (m, H–C(4)); 4.28 (m, H–C(3)); 3.87 (m, H–C(2)); 3.66 (m, 1 H–C(5), 2 H–C(1′), 2 H–C(5″)); 3.49 (m, 1 H–C(5)); 3.24 (m, 2 H–C(1″)); 1.82 (m, 2 H–C(2″)); 1.65 (m, 2 H–C(4″)); 1.51 (m, 2 H–C(3″)). ^{13}C-NMR (100.6 MHz, D_2O): 76.4 (C(3)); 71.2 (C(4)); 63.7 (C(5″)); 58.7 (C(2)); 53.1 (C(5)); 51.0 (C(1″)); 49.4 (C(1′)); 33.1 (C(4″)); 27.7 (C(2″)); 24.6 (C(3″)).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-2,2-dimethyl-4-(morpholin-4-ylmethyl)-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9d**). By *Method A*, with **8** (125 mg, 0.46 mmol), morpholine (40 µl, 0.46 mmol), $NaBH(OAc)_3$ (137 mg, 0.64 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt/light petroleum ether 4:1) gave 116 mg (73% of **9d**), 1.5:1 mixture of rotamers α and β. $[\alpha]^{25}_{589} = -10$, $[\alpha]^{25}_{577} = -9$, $[\alpha]^{25}_{546} = -13$, $[\alpha]^{25}_{435} = -17$, $[\alpha]^{25}_{405} = -20$ ($c = 0.30$, CH_2Cl_2). UV (MeCN): 203 (1740). IR (film): 2980, 2935, 2855, 2810, 1695, 1480, 1455, 1410, 1370, 1270, 1210, 1170, 1120, 1055, 1010, 865, 770, 735, 665, 635. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.76–4.72 (m, H–C(6a)); 4.70 (d, ^3J(3a,6a) = 6.8, H–C(3a)$_\alpha$); 4.68 (d, ^3J(3a,6a) = 6.8, H–C(3a)$_\beta$); 4.23–4.20 (m, H–C(4)$_\beta$); 4.06–4.03 (m, H–C(4)$_\alpha$); 3.87 (d, ^2J = 12.8, 1 H–C(6)$_\alpha$)); 3.80 (d, ^2J = 13.1, 1 H–C(6)$_\beta$)); 3.70 (m, 2 H–C(2″), 2 H–C(6″)); 3.35–3.31 (m, 2 H–C(6)); 2.58–2.42 (2m, 2 H–C(3″), 2 H–C(5″)); 2.34 (dd, ^3J(1′,4) = 4.7, ^{2} = 12.8, 1 H–C(1′)); 2.25 (dd, ^3J(1′,4) = 9.5, ^2J = 12.8, 1 H–C(1′)); 1.47 (s, t-Bu); 1.33 (2s, 2 Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 154.3 (NCOO); 111.6 (Me$_2$*C*); 83.7 (C(3a)$_\alpha$); 82.8 (C(3a)$_\beta$); 79.8 (Me$_3$*C*O); 79.5 (C(6a)$_\beta$); 78.6 (C(6a)$_\alpha$); 67.0 (C(2″), C(6″)); 61.4 (C(4)$_\alpha$); 61.0 (C(4)$_\beta$); 58.6 (C(6)$_\alpha$); 57.7 (C(6)$_\beta$); 54.2 (C(3″), C(5″)); 51.9 (C(1′)$_\beta$); 51.4 (C(1′)$_\alpha$); 28.4 (*Me*$_3$C); 26.9 (Me); 25.1 (Me). CI-MS (NH_3): 343 (110, $[M+H]^+$), 287 (7), 100 (51). Anal. calc. for $C_{17}H_{30}N_2O_5$ (342.43): C 59.58, H 8.83, N 8.18; found: C 59.50, H 8.81, N 8.13.

*(2*R*,3*R*,4*S*)-2-(Morpholin-4-ylmethyl)pyrrolidine-3,4-diol* (**3d**). By *Method Aa*, with **9d** (40 mg). FC (MeCN/NH_4OH 4:1) gave 25 mg (100% of **3d**). $[\alpha]^{25}_{577} = +23$ ($c = 0.2$, MeOH). UV (MeCN): 199 (2100). IR (film): 3400–3000, 1430, 1200, 1135, 910, 805, 775. ^{1}H-NMR (400 MHz, D_2O): 4.08–4.05 (m, H–C(4)); 3.66 (t, ^3J(2″,3″) = ^3J(6″,5″) = 4.4, 2 H–C(2″), 2 H–C(6″)); 3.65 (m, H–C(3)); 3.15–3.11 (m, H–C(2), 1 H–C(5)); 2.76 (dd, ^3J(4,5) = 2.8, ^2J = 12.5, 1 H–C(5)); 2.62 (dd, ^3J(1′,2) = 3.2, ^2J = 13.3, 1 H–C(1′)); 2.55–2.39 (m, 2 H–C(3″), 2 H–C(5″), 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, D_2O): 77.8 (C(3)); 72.8 (C(4)); 68.6 (C(2″), C(6″)); 63.5 (C(2)); 60.1 (C(5)); 55.3 (C(3″), C(5″)); 52.5 (C(1′)). CI-MS (NH_3): 203 (40, $[M+H]^+$), 100 (100).

tert-*Butyl (3a*R*,4*R*,6a*S*)-4-{[3,5-Dimethylphenyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9ea**). By *Method A*, with **8** (136 mg, 0.50 mmol), 3,5-dimethylaniline (61 mg, 0.50 mmol), $NaBH(OAc)_3$ (148 mg, 0.70 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt/light petroleum ether 1:9) gave 90 mg (48% of **9ea**), 1.7:1 mixture of rotamers α and β. $[\alpha]^{25}_{589} = -21$, $[\alpha]^{25}_{577} = -21$, $[\alpha]^{25}_{546} = -23$, $[\alpha]^{25}_{435} = -38$, $[\alpha]^{25}_{405} = -45$ ($c = 0.49$, CH_2Cl_2). UV (MeCN): 251 (8830), 215 (14205). IR (film): 3390, 2980, 1695, 1680, 1605, 1520, 1470, 1455, 1415, 1340, 1160, 1125, 1055, 860, 820, 770, 695, 665. ^{1}H-NMR (400 MHz, MeOD): 6.30 (m, 3 arom. H); 4.76 (m, H–C(6a)); 4.68 (m, H–C(3a)); 4.22 (m, H–C(4)); 3.78 (d, ^2J = 12.9, 1 H–C(6)$_\alpha$); 3.69 (d, ^2J = 12.9, 1 H–C(6)$_\beta$); 3.39 (dd, ^3J(6,6a) = 5.0, ^2J = 12.9, 1 H–C(6)$_\beta$); 3.33 (dd, ^3J(6,6a) = 5.0, ^2J = 12.9, 1 H–C(6)$_\alpha$); 3.17 (m, 2 H–C(1′)); 2.21 (s, arom. Me); 1.50 (s, (t-Bu)$_\beta$); 1.46 (s, (t-Bu)$_\alpha$); 1.41 (s, 1 Me); 1.32 (s, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.4 (s, NCOO$_\alpha$); 157.3 (s, NCOO$_\beta$); 150.5 (s, arom. C); 140.6 (s, 2 arom. C); 120.9 (d, ^1J(C,H) = 155, arom. C); 113.4 (s); 112.3 (d, ^1J(C,H) = 154, 2 arom. C); 85.1 (d, ^1J(C,H) = 157, C(3a)$_\alpha$); 84.8 (d, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (s, Me$_3$*C*O$_\alpha$); 82.1 (s, Me$_3$*C*O$_\beta$); 81.7 (d, ^1J(C,H) = 158, C(6a)$_\beta$); 81.0 (d, ^1J(C,H) = 149, C(6a)$_\alpha$); 65.5 (d, ^1J(C,H) = 146, C(4)$_\beta$); 65.3 (d, ^1J(C,H) = 149, C(4)$_\alpha$); 54.2 (t, ^1J(C,H) = 143, C(6)$_\beta$); 53.2 (t, ^1J(C,H) = 144, C(6)$_\alpha$); 45.6 (t, ^1J(C,H) = 136, C(1′)$_\beta$); 45.1 (t, ^1J(C,H) = 136, C(1′)$_\alpha$); 29.6 (q, ^1J(C,H) = 123, *Me*$_3$C); 28.1 (q, ^1J(C,H) = 127, Me); 25.9 (q, ^1J(C,H) = 128, Me); 22.6 (q, ^1J(C,H) = 126, arom. Me). CI-MS (NH_3): 377 (100, $[M+H]^+$), 376 (46, M^+), 321 (20), 303 (3), 176 (1), 134 (50), 85 (4).

*(2*R*,3*R*,4*S*)-2-{[(3,5-Dimethylphenyl)amino]methyl}pyrrolidine-3,4-diol* (**3ea**). By *Method Aa*, with **9ea** (22 mg). FC (MeCN/NH_4OH 4:1) gave 20 mg (100% of **3ea**). $[\alpha]_{589}^{25} = +24$, $[\alpha]_{577}^{25} = +26$, $[\alpha]_{546}^{25} = +25$, $[\alpha]_{435}^{25} = +35$ ($c = 0.25$, MeOH). IR (film): 3405, 3235, 3065, 1670, 1605, 1435, 1430, 1205, 1185, 1135, 845, 800, 725, 665. ^{1}H-NMR (400 MHz, D_2O): 6.62 (*s*, 1 arom. H); 6.55 (*s*, 2 arom. H); 4.46 (*m*, H−C(4)); 4.25 (*dd*, $^3J(3,4) = 4.1$, $^3J(3,2) = 8.5$, H−C(3)); 3.83 (*ddd*, $^3J(2,1') = 4.2$, $^3J(2,3) = 8.5$, $^3J(2,1') = 8.5$, H−C(2)); 3.61 (*m*, 1 H−C(5), 2 H−C(1′)); 3.42 (*d*, $^2J = 13.0$, 1 H−C(5)); 2.29 (*s*, 2 arom. Me). ^{13}C-NMR (100.6 MHz, D_2O): 150.0 (*s*, arom. C); 142.7 (*s*, 2 arom. C); 122.9 (*d*, $^1J(C,H) = 158$, arom. C); 114.0 (*d*, $^1J(C,H) = 151$, 2 arom. C); 75.5 (*d*, $^1J(C,H) = 146$, C(3)); 71.8 (*d*, $^1J(C,H) = 155$, C(4)); 62.2 (*d*, $^1J(C,H) = 146$, C(2)); 51.9 (*t*, $^1J(C,H) = 148$, C(5)); 45.3 (*t*, $^1J(C,H) = 136$, C(1′)); 22.9 (*q*, $^1J(C,H) = 127$, arom. Me). CI-MS (NH_3): 237 (100, $[M+H]^+$), 219 (1), 146 (1), 135 (85), 121 (14), 102 (39), 85 (21).

*(2*R*,3*R*,4*S*)-2-[([1,1′-Biphenyl]-4-ylamino)methyl]pyrrolidine-3,4-diol* (**3eb**). By *Method A*, with **8** (72 mg, 0.27 mmol), [1,1′-biphenyl]-4-amine (45 mg, 0.27 mmol), $NaBH(OAc)_3$ (79 mg, 0.38 mmol), and $ClCH_2CH_2Cl$ (2.5 ml). Then, by *Method Aa*, with crude **9eb** (27 mg). FC (MeCN/NH_4OH 2:1) gave 18 mg (100% of **3eb**). $[\alpha]_{589}^{25} = +160$, $[\alpha]_{577}^{25} = +346$ ($c = 0.70$, MeOH). UV (MeCN): 292 (7300), 213 (6200). ^{1}H-NMR (400 MHz, MeOD): 7.57 (*d*, $^3J = 7.5$, 2 arom. H); 7.49 (*d*, $^3J = 7.5$, 2 arom. H); 7.40 (*dd*, $^3J = 7.5$, $^3J = 7.6$, 2 arom. H); 7.26 (*t*, $^3J = 7.6$, 1 arom. H); 6.85 (*d*, $^3J = 7.5$, 2 arom. H); 4.32 (*ddd*, $^3J(4,5) = 4.2$, $^3J(4,3) = 4.2$, $^3J(4,5) = 1.7$, H−C(4)); 4.12 (*dd*, $^3J(3,4) = 4.2$, $^3J(3,2) = 8.6$, H−C(3)); 3.82 (*ddd*, $^3J(2,1') = 1.8$, $^3J(2,3) = 9.2$, $^3J(2,1') = 8.6$, H−C(2)); 3.69 (*dd*, $^3J(5,4) = 4.2$, $^2J = 14.5$, 1 H−C(5)); 3.52 (*m*, 1 H−C(5), 1 H−C(1′)); 3.31 (*dd*, $^3J(1',2) = 1.8$, $^2J = 12.5$, H−C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 151.2, 144.9, 134.7 (arom. C); 117.1, 129.6, 129.7, 131.3, 132.2 (arom. C); 77.4 (C(3)); 73.5 (C(4)); 64.1 (C(2)); 53.4 (C(5)); 46.9 (C(1′)). CI-MS (NH_3): 285 (100, $[M+H]^+$), 170 (7), 116 (11).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-2,2-dimethyl-4-{[(4-phenoxyphenyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9ec**). By *Method A*, with **8** (121 mg, 0.45 mmol), 4-phenoxybenzenamine (83 mg, 0.45 mmol), $NaBH(OAc)_3$ (134 mg, 0.63 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (Et_2O/light petroleum ether 2:3) gave 141 mg (72% of **9ec**), 1.6:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -8$, $[\alpha]_{577}^{25} = -9$, $[\alpha]_{546}^{25} = -12$, $[\alpha]_{435}^{25} = -20$, $[\alpha]_{405}^{25} = -26$ ($c = 0.46$, CH_2Cl_2). UV (MeCN): 254 (18900), 212 (15485). IR (film): 3020, 2980, 2935, 1685, 1590, 1510, 1490, 1410, 1370, 1215, 1160, 1130, 1055, 870, 760, 670. ^{1}H-NMR (400 MHz, MeOD): 7.26 (*m*, 2 arom. H); 6.98 (*t*, $^3J = 7.3$, 1 arom. H); 6.87 (*m*, 4 arom. H); 6.71 (*m*, 2 arom. H); 4.77 (*t*, ^3J(6a,3a) = 5.3, ^3J(6a,6) = 5.3, H−C(6a)); 4.68 (*m*, H−C(3a)); 4.23 (*m*, H−C(4)); 3.82 (*d*, $^2J = 12.9$, 1 H−C(6)$_\alpha$); 3.71 (*d*, $^2J = 12.8$, 1 H−C(6)$_\beta$); 3.38 (*m*, 2 H−C(6)); 3.16 (*m*, 2 H−C(1′)); 1.49 (*s*, (*t*-Bu)$_\beta$); 1.47 (*s*, (*t*-Bu)$_\alpha$); 1.41 (*s*, 1 Me); 1.31 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 161.4 (*s*, arom. C); 157.3 (*s*, $NCOO_\beta$); 157.1 (*s*, $NCOO_\alpha$); 149.4 (*s*, arom. C); 147.1 (*s*, arom. C); 131.4 (*d*, $^1J(C,H) = 159$, 2 arom. C); 123.7 (*d*, $^1J(C,H) = 161$, arom. C); 123.0 (*d*, $^1J(C,H) = 165$, 2 arom. C); 118.8 (*d*, $^1J(C,H) = 154$, 2 arom. C); 115.3 (*d*, $^1J(C,H) = 159$, arom. C); 115.2 (*d*, $^1J(C,H) = 158$, arom. C); 113.4 (*s*); 85.2 (*d*, $^1J(C,H) = 157$, C(3a)$_\alpha$); 84.8 (*d*, $^1J(C,H) = 157$, C(3a)$_\beta$); 82.4 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_β); 81.5 (*d*, $^1J(C,H) = 159$, C(6a)$_\beta$); 80.8 (*d*, $^1J(C,H) = 158$, C(6a)$_\alpha$); 65.3 (*d*, $^1J(C,H) = 146$, C(4)$_\beta$); 64.9 (*d*, $^1J(C,H) = 148$, C(4)$_\alpha$); 54.1 (*t*, $^1J(C,H) = 143$, C(6)$_\beta$); 53.1 (*t*, $^1J(C,H) = 144$, C(6)$_\alpha$); 45.8 (*t*, $^1J(C,H) = 136$, C(1′)$_\beta$); 45.5 (*t*, $^1J(C,H) = 136$, C(1′)$_\alpha$); 29.6 (*q*, $^1J(C,H) = 127$, Me_3C); 28.0 (*q*, $^1J(C,H) = 126$, Me); 25.9 (*q*, $^1J(C,H) = 127$, Me). CI-MS (NH_3): 441 (100, $[M+H]^+$), 440 (33, M^+), 385 (30), 334 (4), 242 (4), 198 (19), 142 (3), 85 (8). Anal. calc. for $C_{25}H_{32}N_2O_5$ (440.56): C 68.16, H 7.32; found: C 68.18, H 7.41.

*(2*R*,3*R*,4*S*)-2-{[(4-Phenoxyphenyl)amino]methyl}pyrrolidine-3,4-diol* (**3ec**). By *Method Aa*, with **9ec** (40 mg). FC (MeCN/NH_4OH 4:1) gave 40 mg (100% of **3ec**). $[\alpha]_{589}^{25} = +30$, $[\alpha]_{577}^{25} = +30$, $[\alpha]_{546}^{25} = +40$, $[\alpha]_{435}^{25} = +52$, $[\alpha]_{405}^{25} = +55$ ($c = 0.19$, MeOH). UV (MeCN): 306 (2850), 250 (17225), 208 (20385). IR (film): 3060, 2990, 1665, 1510, 1440, 1180, 1140, 890, 840, 800, 745, 725, 690, 665. ^{1}H-NMR (400 MHz, MeOD): 7.30 (*m*, 2 arom. H); 7.02 (*t*, $^3J = 7.4$, 1 arom. H); 6.89 (*m*, 4 arom. H); 6.77 (*m*, 2 arom. H); 4.32 (*m*, H−C(4)); 4.11 (*dd*, $^3J(3,2) = 8.8$, $^3J(3,4) = 4.1$, H−C(3)); 3.77 (*ddd*, $^3J(2,1') = 3.7$, $^3J(2,3) = 8.8$, $^3J(2,1') = 8.8$, H−C(2)); 3.62 (*dd*, $^3J(1',2) = 3.7$, $^2J = 14.3$, 1 H−C(1′)); 3.52 (*m*, 1 H−C(1′), 1 H−C(5)); 3.30 (*dd*, $^3J(5,4) = 1.9$, $^2J = 12.6$, 1 H−C(5)). ^{13}C-NMR (100.6 MHz, MeOD): 161.3 (*s*, arom. C); 150.5 (*s*, arom. C); 146.6 (*s*, arom. C); 131.4 (*d*, $^1J(C,H) = 159$, 2 arom. C); 124.0 (*d*, $^1J(C,H) = 168$, arom. C); 122.9 (*d*, $^1J(C,H) = 161$, 2 arom. C); 118.9 (*d*, $^1J(C,H) = 161$, 2 arom. C); 116.2 (*d*, $^1J(C,H) = 159$, 2 arom. C); 75.7 (*d*, $^1J(C,H) = 145$, C(3)); 71.9 (*d*, $^1J(C,H) = 152$, C(4)); 62.3 (*d*, $^1J(C,H) = 146$, C(2)); 51.7 (*t*, $^1J(C,H) = 149$, C(5)); 45.7 (*t*, $^1J(C,H) = 138$, C(1′)). CI-MS (NH_3): 301 (100, $[M+H]^+$), 283 (3), 263 (8), 237 (2), 209 (85), 186 (62), 163 (2), 129 (6), 102 (52).

tert-*Butyl (3a*R*,4*R*,6a*S*)-4-[(Benzylamino)methyl]tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9f**). By *Method A*, with **8** (3.05 g, 11.3 mmol), benzylamine (1.2 ml, 11.3 mmol), $NaBH(OAc)_3$ (3.34 g, 15.8 mmol), and $ClCH_2CH_2Cl$ (100 ml). FC (AcOEt/light petroleum ether 8:2) gave 3.0 g (74% of **9f**),

1.2:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -36$, $[\alpha]_{577}^{25} = -37$, $[\alpha]_{546}^{25} = -40$, $[\alpha]_{435}^{25} = -68$, $[\alpha]_{405}^{25} = -82$ ($c = 0.57$, CH_2Cl_2). UV (MeCN): 211 (8065). IR (film): 3340, 2980, 2935, 1695, 1455, 1405, 1210, 1160, 1125, 1055, 980, 860, 740, 700. ^{1}H-NMR (400 MHz, MeOD): 7.35 (*m*, 5 arom. H); 4.76 (*m*, H–C(6a)); 4.64 (*d*, ^3J(3a,6a) = 5.9, H–C(3a)$_\alpha$);4.58(*d*, ^3J(3a,6a) = 5.9, H–C(3a)$_\beta$);4.15(*t*, ^3J(4,1′) = 6.5,H–C(4)$_\beta$);4.08(*t*, ^3J(4,1′) = 6.5,H–C(4)$_\alpha$); 3.85–3.75 (*m*, 1 H–C(6), 2 H–C(1″)); 3.36 (*m*, 1 H–C(6)); 2.64 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.42 (*s*, *t*-Bu); 1.32 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, NCOO$_\beta$); 157.2 (*s*, NCOO$_\alpha$); 141.8 (*s*, arom. C); 130.3 (*d*, ^1J(C,H) = 159, 3 arom. C); 129.0 (*d*, ^1J(C,H) = 157, 2 arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 156, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 157, C(3a)$_\beta$); 82.2 (*s*, Me$_3$CO$_\alpha$); 82.1 (*s*, Me$_3$CO$_\beta$); 81.6 (*d*, ^1J(C,H) = 152, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 146, C(4)$_\alpha$); 65.2 (*d*, ^1J(C,H) = 143, C(4)$_\beta$); 55.1 (*t*, ^1J(C,H) = 135, C(1″)); 53.8 (*t*, ^1J(C,H) = 145, C(6)$_\beta$); 53.3 (*t*, ^1J(C,H) = 143, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 127, *Me*$_3$C); 28.1 (*q*, ^1J(C,H) = 122, Me); 25.8 (*q*, ^1J(C,H) = 129, Me). CI-MS (NH_3): 363 (100, $[M+H]^+$), 336 (13), 307 (37), 247 (9), 178 (11), 153 (19), 120 (50). Anal. calc. for $C_{20}H_{30}N_2O_4$ (362.49): C 66.27, H 8.34; found: C 66.35, H 8.26.

*(2*R*,3*R*,4*S*)-2-[(Benzylamino)methyl]pyrrolidine-3,4-diol* (**3f**). By *Method Aa*, with **9f** (23 mg). FC (MeCN/NH_4OH 4:1) gave 25 mg (100% of **3f**). IR(film): 3450, 1675, 1435, 1205, 1130, 845, 800, 760, 725, 700. ^{1}H-NMR (400 MHz, D_2O): 7.54 (*m*, 5 arom. H); 4.37 (*ddd*, ^3J(4,5) = 1.6, ^3J(4,5) = 4.2, ^3J(4,3) = 4.2, H–C(4)); 4.29 (*m*, H–C(1″)); 4.16 (*dd*, ^3J(3,4) = 4.2, ^3J(3,2) = 8.6, H–C(3)); 3.73 (*ddd*, ^3J(2,1′) = 4.2, ^3J(2,3) = 8.6, ^3J(2,1′) = 8.6, H–C(2)); 3.52 (*dd*, ^3J(5,4) = 4.2, ^2J = 13.1, 1 H–C(5)); 3.46 (*m*, 2 H–C(1′)); 3.37 (*dd*, ^3J(5,4) = 1.6, ^2J = 13.1, 1 H–C(5)). ^{13}C-NMR (100.6 MHz, D_2O): 134.2 (*s*, arom. C); 132.2 (*d*, ^1J(C,H) = 157, 2 arom. C); 131.9 (*d*, ^1J(C,H) = 159, arom. C); 131.7 (*d*, ^1J(C,H) = 162, 2 arom. C); 76.6 (*d*, ^1J(C,H) = 146, C(3)); 71.7 (*d*, ^1J(C,H) = 156, C(4)); 59.6 (*d*, ^1J(C,H) = 145, C(2)); 54.4 (*t*, ^1J(C,H) = 145, C(1″)); 52.8 (*t*, ^1J(C,H) = 146, C(5)); 49.6 (*t*, ^1J(C,H) = 144, C(1′)). CI-MS (NH_3): 223 (100, $[M+H]^+$), 222 (43, M^+), 211 (4), 120 (22), 91 (25), 77 (29).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-2,2-dimethyl-4-{[(2-methylbenzyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9fa**). By *Method B*, with **10** (148 mg, 0.54 mmol), *o*-tolualdehyde (65 mg, 0.54 mmol), $NaBH(OAc)_3$ (161 mg, 0.76 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt) gave 139 mg (68% of **9fa**), 1.15:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -51$, $[\alpha]_{577}^{25} = -56$, $[\alpha]_{546}^{25} = -64$, $[\alpha]_{435}^{25} = -115$, $[\alpha]_{405}^{25} = -141$ ($c = 0.40$, CH_2Cl_2). UV (MeCN): 250 (3400), 211 (15000). IR (film): 3335, 2980, 2935, 1700, 1455, 1405, 1210, 1170, 1125, 1055, 975, 860, 745. ^{1}H-NMR (400 MHz, MeOD): 7.30 (*m*, 1 arom. H); 7.17 (*m*, 3 arom. H); 4.74 (*m*, H–C(6a)); 4.65 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.61 (*d*, ^3J(3a,6a) = 5.7, H–C(3a)$_\beta$); 4.20–4.15 (*m*, H–C(4)); 3.81 (*m*, 1 H–C(6), 2 H–C(1″)); 3.38 (*m*, 1 H–C(6)); 2.72 (*m*, 2 H–C(1′)); 2.37 (*s*, arom. Me); 1.50 (*s*, 1 Me); 1.44 (*s*, (*t*-Bu)$_\beta$); 1.43 (*s*, (*t*-Bu)$_\alpha$); 1.32 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (NCOO$_\beta$); 157.1 (NCOO$_\alpha$); 139.7 (arom. C); 138.3 (arom. C); 132.1 (arom. C); 130.3 (arom. C); 129.0 (arom. C); 127.7 (arom. C); 113.3 (Me$_2$*C*); 85.6 (C(3a)$_\alpha$); 85.0 (C(3a)$_\beta$); 82.2 (Me$_3$*C*O$_\alpha$); 82.1 (Me$_3$*C*O$_\beta$); 81.6 (C(6a)$_\beta$); 80.8 (C(6a)$_\alpha$); 65.9 (C(4)$_\alpha$); 65.3 (C(4)$_\beta$); 53.9 (C(6)$_\beta$); 53.3 (C(6$_\alpha$)); 52.8 (C(1″)); 50–49 (C(1′)); 29.6 (*Me*$_3$C); 27.9 (Me); 25.6 (Me); 20.0 (arom. Me). CI-MS (NH_3): 378 (98, $[M+H]^+$), 377 (100, M^+), 321 (47), 277 (8), 238 (9), 187 (6), 134 (27), 105 (54), 85 (5). Anal. calc. for $C_{21}H_{32}N_2O_4$ (376.51): C 66.99, H 8.57; found: C 66.86, H 8.50.

*(2*R*,3*R*,4*S*)-2-{[(2-Methylbenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fa**). By *Method Aa*, with **9fa** (30 mg). FC (MeCN/NH_4OH 4:1) gave 20 mg (100% of **3fa**). $[\alpha]_{589}^{25} = +12$, $[\alpha]_{577}^{25} = +16$, $[\alpha]_{546}^{25} = +16$, $[\alpha]_{435}^{25} = +31$, $[\alpha]_{405}^{25} = +33$ ($c = 0.39$, MeOH). UV (MeCN): 265 (350), 210 (3250). IR (film): 3060, 1660, 1420, 1200, 1135, 840, 800, 750, 720. ^{1}H-NMR (400 MHz, MeOD): 7.43 (*d*, ^3J = 6.7, 1 arom. H); 7.27 (*m*, 3 arom. H); 4.27 (*ddd*, ^3J(4,5) = 1.5, ^3J(4,5) = 4.0, ^3J(4,3) = 4.0, H–C(4)); 4.12 (*AB*, 2 H–C(1″)); 4.06 (*dd*, ^3J(3,4) = 4.0, ^3J(3,2) = 8.6, H–C(3)); 3.72 (*ddd*, ^3J(2,1′) = 4.1, ^3J(2,3) = 8.6, ^3J(2,1′) = 8.6, H–C(2)); 3.49 (*dd*, ^3J(5,4) = 4.0, ^2J = 12.6, 1 H–C(5)); 3.40–3.29 (*m*, 1 H–C(5), 2 H–C(1′)); 2.42 (*s*, arom. Me). ^{13}C-NMR (100.6 MHz, MeOD): 139.1 (*s*, arom. C); 135.5 (*s*, arom. C); 132.6 (*d*, ^1J(C,H) = 158, arom. C); 131.4 (*d*, ^1J(C,H) = 159, arom. C); 130.5 (*d*, ^1J(C,H) = 161, arom. C); 128.2 (*d*, ^1J(C,H) = 161, arom. C); 76.3 (*d*, ^1J(C,H) = 145, C(3)); 71.7 (*d*, ^1J(C,H) = 149, C(4)); 61.0 (*d*, ^1J(C,H) = 148, C(2)); 52.2, 52.0 (2*t*, ^1J(C,H) = 149, ^1J(C,H) = 145, C(5), C(1″)); 50–49 (C(1′)); 22.2 (*q*, ^1J(C,H) = 127, arom. Me). CI-MS (NH_3): 237 (100, $[M+H]^+$), 134 (9), 122 (2), 105 (24), 85 (12).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-2,2-dimethyl-4-{[(3-methylbenzyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9fb**). By *Method B*, with **10** (100 mg, 0.37 mmol), *m*-tolualdehyde (44 mg, 0.37 mmol), $NaBH(OAc)_3$ (109 mg, 0.51 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt) gave 40 mg (30% of **9fb**), 1.2:1 mixture of rotamers. $[\alpha]_{589}^{25} = -30$, $[\alpha]_{577}^{25} = -30$, $[\alpha]_{546}^{25} = -40$, $[\alpha]_{435}^{25} = -76$, $[\alpha]_{405}^{25} = -96$ ($c = 0.43$, CH_2Cl_2). UV (MeCN): 213 (11770). IR (film): 3335, 2980, 2935, 1695, 1610, 1455, 1405, 1370, 1210, 1170, 1125, 1055, 975, 860, 770, 700. ^{1}H-NMR (400 MHz, MeOD): 7.24–7.08 (*m*, 4 arom. H); 4.76 (*m*, H–C(6a)); 4.63

(d, ^3J(3a,6a) = 5.7, H–C(3a)$_\alpha$); 4.57 (d, ^3J(3a,6a) = 5.9, H–C(3a)$_\beta$); 4.20 (m, H–C(4)$_\beta$); 4.09 (m, H–C(4)$_\alpha$); 3.83–3.71 (m, 1 H–C(6), 2 H–C(1″)); 3.37 (m, 1 H–C(6)); 2.65 (m, 2 H–C(1′)); 2.35 (s, arom. Me); 1.49 (s, 1 Me); 1.42 (s, t-Bu); 1.31 (s, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.6 (s, NCOO$_\beta$); 157.3 (s, NCOO$_\alpha$); 141.6 (s, arom. C); 140.0 (s, arom. C); 131.0 (d, ^1J(C,H) = 155, arom. C); 130.3 (d, ^1J(C,H) = 159, arom. C); 129.8 (d, ^1J(C,H) = 157, arom. C); 127.3 (d, ^1J(C,H) = 156, arom. C); 113.5 (s); 85.5 (d, ^1J(C,H) = 156, C(3a)$_\alpha$); 84.9 (d, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (s, Me$_3$CO$_\alpha$); 82.2 (s, Me$_3$CO$_\beta$); 81.6 (d, ^1J(C,H) = 151, C(6a)$_\beta$); 80.9 (d, ^1J(C,H) = 157, C(6a)$_\alpha$); 65.8 (d, ^1J(C,H) = 149, C(4)$_\alpha$); 65.1 (d, ^1J(C,H) = 142, C(4)$_\beta$); 55.0 (t, ^1J(C,H) = 134, C(1″)); 53.7 (t, ^1J(C,H) = 143, C(6)$_\beta$); 53.2 (t, ^1J(C,H) = 142, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (q, ^1J(C,H) = 127, *Me*$_3$C); 28.0 (q, ^1J(C,H) = 129, Me); 25.8 (q, ^1J(C,H) = 126, Me); 22.3 (q, ^1J(C,H) = 126, arom. Me). CI-MS (NH_3): 377 (100, $[M+H]^+$), 321 (46), 277 (3), 243 (4), 187 (9), 134 (37), 105 (67), 77 (11). Anal. calc. for $C_{21}H_{32}N_2O_4$ (376.51): C 66.99, H 8.57; found: C 67.01, H 8.60.

*(2*R*,3*R*,4*S*)-2-{[(3-Methylbenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fb**). By *Method Aa*, with **9fb** (40 mg). FC (MeCN/NH_4OH 4:1) gave 25 mg (100% of **3fb**). $[\alpha]_{589}^{25} = +12$, $[\alpha]_{577}^{25} = +14$, $[\alpha]_{546}^{25} = +15$, $[\alpha]_{435}^{25} = +20$, $[\alpha]_{405}^{25} = +21$ ($c = 0.34$, MeOH). UV (MeCN): 262 (920), 217 (3000), 205 (860). IR (film): 3070, 1650, 1470, 1440, 1175, 840, 800, 725, 700. ^{1}H-NMR (400 MHz, MeOD): 7.35–7.22 (m, 4 arom. H); 4.27 (ddd, ^3J(4,5) = 1.4, ^3J(4,5) = 4.0, ^3J(4,3) = 4.0, H–C(4)); 4.16 (s, 2 H–C(1″)); 4.08 (dd, ^3J(3,4) = 4.0, ^3J(3,2) = 8.9, H–C(3)); 3.77 (ddd, ^3J(2,1′) = 5.0, ^3J(2,3) = 8.9, ^3J(2,1′) = 8.9, H–C(2)); 3.52 (dd, ^3J(5,4) = 4.0, ^2J = 12.6, 1 H–C(5)); 3.43–3.31 (m, 1 H–C(5), 2 H–C(1′)); 2.39 (s, arom. Me). ^{13}C-NMR (100.6 MHz, MeOD): 140.8 (s, arom. C); 135.2 (s, arom. C); 132.2 (d, ^1J(C,H) = 157, arom. C); 131.6 (d, ^1J(C,H) = 159, arom. C); 130.8 (d, ^1J(C,H) = 161, arom. C); 128.6 (d, ^1J(C,H) = 160, arom. C); 76.4 (d, ^1J(C,H) = 144, C(3)); 71.4 (d, ^1J(C,H) = 155, C(4)); 59.9 (d, ^1J(C,H) = 147, C(2)); 54.1 (t, ^1J(C,H) = 142, C(1″)); 52.4 (t, ^1J(C,H) = 149, C(5)); 50–49 (C(1′)); 22.2 (q, ^1J(C,H) = 127, arom. Me). CI-MS (NH_3): 237 (100, $[M+H]^+$), 205 (1), 154 (2), 134 (19), 120 (4), 105 (31), 85 (14).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-2,2-dimethyl-4-{[(4-methylbenzyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9fc**). By *Method B*, with **10** (105 mg, 0.39 mmol), *p*-tolualdehyde (46 mg, 0.39 mmol), $NaBH(OAc)_3$ (114 mg, 0.54 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt) gave 42 mg (29% of **9fc**), 1.3:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -41$, $[\alpha]_{577}^{25} = -44$, $[\alpha]_{546}^{25} = -47$, $[\alpha]_{435}^{25} = -81$, $[\alpha]_{405}^{25} = -95$ (c = 0.42, CH_2Cl_2). UV (MeCN): 273 (1300), 265 (1475), 212 (13870). IR (film): 2980, 2935, 1695, 1690, 1515, 1480, 1455, 1405, 1380, 1365, 1210, 1170, 1125, 1055, 975, 860, 805, 770. ^{1}H-NMR (400 MHz, MeOD): 7.22 (m, 4 arom. H); 4.74 (m, H–C(6a)); 4.63 (d, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.57 (d, ^3J(3a,6a) = 5.7, H–C(3a)$_\beta$); 4.18 (t, ^3J(4,1′) = 6.6, H–C(4)$_\beta$); 4.07 (t, ^3J(4,1′) = 6.4, H–C(4)$_\alpha$); 3.77 (m, 1 H–C(6), 2 H–C(1″)); 3.37 (m, 1 H–C(6)); 2.62 (m, H–C(1′)); 2.34 (s, arom. Me); 1.50 (s, 1 Me); 1.42 (s, t-Bu); 1.31 (s, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.6 (s, NCOO$_\beta$); 157.3 (s, NCOO$_\alpha$); 138.7 (s, 2 arom. C); 130.9 (d, ^1J(C,H) = 158, 2 arom. C); 130.2 (d, ^1J(C,H) = 157, 2 arom. C); 113.4 (s); 85.5 (d, ^1J(C,H) = 157, C(3a)$_\alpha$); 85.0 (d, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (s, Me$_3$CO$_\alpha$); 82.1 (s, Me$_3$CO$_\beta$); 81.6 (d, ^1J(C,H) = 154, C(6a)$_\beta$); 80.9 (d, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.9 (d, ^1J(C,H) = 147, C(4)$_\alpha$); 65.3 (d, ^1J(C,H) = 145, C(4)$_\beta$); 54.8 (t, ^1J(C,H) = 134, C(1″)); 53.8 (t, ^1J(C,H) = 144, C(6)$_\beta$); 53.3 (t, ^1J(C,H) = 143, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (q, ^1J(C,H) = 127, *Me*$_3$C); 28.1 (q, ^1J(C,H) = 128, Me); 25.8 (q, ^1J(C,H) = 127, Me); 22.0 (q, ^1J(C,H) = 126, arom. Me). CI-MS (NH_3): 377 (100, $[M+H]^+$), 343 (2), 321 (28), 275 (3), 187 (4), 105 (65), 77 (6). Anal. calc. for $C_{21}H_{32}N_2O_4$ (376.52): C 66.99, H 8.57; found: C 67.17, H 8.55.

*(2*R*,3*R*,4*S*)-2-{[(4-Methylbenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fc**). By *Method Aa*, with **9fc** (42 mg). FC (MeCN/NH_4OH 4:1) gave 26 mg (100% of **3fc**). $[\alpha]_{589}^{25} = +6$, $[\alpha]_{577}^{25} = +10$, $[\alpha]_{546}^{25} = +13$ (c = 0.43, MeOH). UV (MeCN): 260 (870), 219 (4300), 204 (750). IR (film): 3415, 3060, 2905, 1675, 1470, 1435, 1180, 1135, 840, 800, 725. ^{1}H-NMR (400 MHz, MeOD): 7.39 (d, ^3J = 8.0, 2 arom. H); 7.27 (d, ^3J = 8.0, 2 arom. H); 4.26 (ddd, ^3J(4,5) = 1.5, ^3J(4,5) = 4.0, ^3J(4,3) = 4.0, H–C(4)); 4.15 (s, 2 H–C(1″)); 4.06 (dd, ^3J(3,4) = 4.0, ^3J(3,2) = 8.9, H–C(3)); 3.73 (ddd, ^3J(2,1′) = 4.8, ^3J(2,3) = 8.9, ^3J(2,1′) = 8.9, H–C(2)); 3.50 (dd, ^3J(5,4) = 4.0, ^2J = 12.6, 1 H–C(5)); 3.45–3.34 (m, 1 H–C(5), 2 H–C(1′)); 2.39 (s, arom. Me). ^{13}C-NMR (100.6 MHz, MeOD): 141.1 (s, arom. C); 132.2 (s, arom. C); 131.5 (d, ^1J(C,H) = 159, 4 arom. C); 76.4 (d, ^1J(C,H) = 144, C(3)); 71.5 (d, ^1J(C,H) = 151, C(4)); 60.1 (d, ^1J(C,H) = 146, C(2)); 53.9 (t, ^1J(C,H) = 147, C(1″)); 52.4 (t, ^1J(C,H) = 145, C(5)); 50–49 (C(1′)); 22.1 (q, ^1J(C,H) = 135, arom. Me). CI-MS (NH_3): 237 (100, $[M+H]^+$), 211 (2), 134 (19), 122 (8), 105 (28), 85 (10).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-{[(3-hydroxybenzyl)amino]methyl}-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9fd**). By *Method B*, with **10** (94 mg, 0.35 mmol), 3-hydroxybenzaldehyde (42 mg, 0.35 mmol), $NaBH(OAc)_3$ (102 mg, 0.48 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 76 mg (58% of **9fd**), 1.3:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -27$, $[\alpha]_{577}^{25} = -29$, $[\alpha]_{546}^{25} = -37$, $[\alpha]_{435}^{25} = -67$, $[\alpha]_{405}^{25} = -79$ (c = 0.44, CH_2Cl_2). UV (MeCN): 281 (2310), 274 (2510), 206 (9360). IR (film): 3335, 2980, 2935, 1690,

1590, 1455, 1415, 1370, 1275, 1245, 1210, 1160, 1130, 1055, 860, 785, 740, 700. ^{1}H-NMR (400 MHz, MeOD): 7.17 (*m*, 1 arom. H); 6.81 (*m*, 2 arom. H); 6.71 (*d*, ^3J = 7.3, 1 arom. H); 4.77 (*m*, H–C(6a)); 4.64 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.59 (*d*, ^3J(3a,6a) = 5.6, H–C(3a)$_\beta$); 4.18 (*dd*, ^3J(4,1′) = 6.5, ^3J(4,1′) = 6.6, H–C(4)$_\beta$); 4.08 (*dd*, ^3J(4,1′) = 6.6, ^3J(4,1′) = 6.7, H–C(4)$_\alpha$); 3.75 (*m*, 1 H–C(6), 2 H–C(1″)); 3.38 (*m*, 1 H–C(6)); 2.65 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.44 (*s*, (*t*-Bu)$_\alpha$); 1.43 (*s*, (*t*-Bu)$_\beta$); 1.32 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 159.5 (*s*, arom. C); 157.6 (*s*, NCOO$_\beta$); 157.3 (*s*, NCOO$_\alpha$); 143.3 (*s*, arom. C); 131.3 (*d*, ^1J(C,H) = 158, arom. C); 121.3 (*d*, ^1J(C,H) = 159, arom. C); 117.0 (*d*, ^1J(C,H) = 158, arom. C); 116.0 (*d*, ^1J(C,H) = 159, arom. C); 113.4 (*s*); 85.6 (*d*, ^1J(C,H) = 157, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 157, C(3a)$_\beta$); 82.4 (*s*, Me$_3$*C*O$_\alpha$); 82.2 (*s*, Me$_3$*C*O$_\beta$); 81.6 (*d*, ^1J(C,H) = 157, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 146, C(4)$_\alpha$); 65.3 (*d*, ^1J(C,H) = 146, C(4)$_\beta$); 55.0 (*t*, ^1J(C,H) = 135, C(1″)); 53.8 (*t*, ^1J(C,H) = 143, C(6)$_\beta$); 53.3 (*t*, ^1J(C,H) = 144, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 127, *Me*$_3$C); 28.1 (*q*, ^1J(C,H) = 127, Me); 25.8 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 379 (100, $[M+H]^+$), 343 (6), 323 (22), 273 (5), 217 (3), 153 (47), 136 (79), 84 (9).

*(2*R*,3*R*,4*S*)-2-{[(3-Hydroxybenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fd**). By *Method Aa*, with **9fd** (40 mg). FC (MeCN/NH_4OH 4 : 1) gave 25 mg (100% of **3fd**). $[\alpha]_{589}^{25} = +16$ (c = 0.22, CH_2Cl_2). UV (MeCN): 222 (4995). IR (KBr): 3420, 2930, 1675, 1590, 1460, 1280, 1200, 1135, 790, 695. ^{1}H-NMR (400 MHz, MeOD): 7.17 (*t*, ^3J = 7.8, arom. H); 6.86–6.71 (*m*, 3 arom. H); 4.16 (*ddd*, ^3J(4,5) = 2.5, ^3J(4,5) = 4.5, ^3J(4,3) = 4.5, H–C(4)); 3.85 (*dd*, ^3J(3,4) = 4.5, ^3J(3,2) = 7.9, H–C(3)); 3.81 (*s*, 2 H–C(1″)); 3.38 (*m*, H–C(2)); 3.30 (*dd*, ^3J(5,4) = 4.5, ^2J = 12.4, 1 H–C(5)); 3.08 (*dd*, ^3J(5,4) = 2.5, ^2J = 12.4, 1 H–C(5)); 2.98 (*dd*, ^3J(1′,2) = 4.4, ^2J = 12.8, 1 H–C(1′)); 2.80 (*dd*, ^3J(1′,2) = 8.6, ^2J = 12.8, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 159.6 (*s*, arom. C); 142.0 (*s*, arom. C); 131.9 (*d*, ^1J(C,H) = 160, arom. C); 121.5 (*d*, ^1J(C,H) = 160, arom. C); 117.2 (*d*, ^1J(C,H) = 157, arom. C); 116.2 (*d*, ^1J(C,H) = 159, arom. C); 76.8 (*d*, ^1J(C,H) = 146, C(3)); 72.7 (*d*, ^1J(C,H) = 152, C(4)); 62.6 (*d*, ^1J(C,H) = 143, C(2)); 55.0 (*t*, ^1J(C,H) = 136, C(1″)); 52.3 (*t*, ^1J(C,H) = 142, C(5)); 51.2 (*t*, ^1J(C,H) = 136, C(1′)). CI-MS (NH_3): 239 (100, $[M+H]^+$), 229 (2), 124 (17), 107 (33), 85 (21).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-4-{[(4-hydroxybenzyl)amino]methyl}-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9fe**). By *Method B*, with **10** (98 mg, 0.36 mmol), 4-hydroxybenzaldehyde (44 mg, 0.36 mmol), $NaBH(OAc)_3$ (107 mg, 0.50 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 57 mg (42% of **9fe**), 1.3 : 1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -30$, $[\alpha]_{577}^{25} = -33$, $[\alpha]_{546}^{25} = -40$, $[\alpha]_{435}^{25} = -72$, $[\alpha]_{405}^{25} = -96$ (c = 0.37, CH_2Cl_2). UV (MeCN): 277 (3320), 224 (11945), 204 (12075). IR (film): 3340, 2980, 2935, 1675, 1610, 1515, 1455, 1415, 1370, 1260, 1215, 1165, 1125, 1055, 975, 855, 830, 760. ^{1}H-NMR (400 MHz, MeOD): 7.16 (*d*, ^3J = 8.5, 2 arom. H); 6.77 (*m*, 2 arom. H); 4.75 (*m*, H–C(6a)); 4.61 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.56 (*d*, ^3J(3a,6a) = 5.7, H–C(3a)$_\beta$); 4.18 (*t*, ^3J(4,1′) = 6.7, H–C(4)$_\beta$); 4.06 (*t*, ^3J(4,1′) = 6.6, H–C(4)$_\alpha$); 3.79–3.64 (*m*, 1 H–C(6), 2 H–C(1″)); 3.36 (*m*, 1 H–C(6)); 2.62 (*m*, 2 H–C(1′)); 1.49 (*s*, 1 Me); 1.42 (*s*, (*t*-Bu)$_\alpha$); 1.41 (*s*, (*t*-Bu)$_\beta$); 1.31 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 158.6 (*s*, arom. C); 157.6 (*s*, NCOO$_\beta$); 157.3 (*s*, NCOO$_\alpha$); 132.4 (*s*, arom. C); 131.6 (*d*, ^1J(C,H) = 157, 2 arom. C); 117.0 (*d*, ^1J(C,H) = 158, 2 arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 157, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 156, C(3a)$_\beta$); 82.4 (*s*, Me$_3$*C*O$_\alpha$); 82.2 (*s*, Me$_3$*C*O$_\beta$); 81.6 (*d*, ^1J(C,H) = 155, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.8 (*d*, ^1J(C,H) = 148, C(4)$_\alpha$); 65.1 (*d*, ^1J(C,H) = 146, C(4)$_\beta$); 54.5 (*t*, ^1J(C,H) = 136, C(1″)); 53.7 (*t*, ^1J(C,H) = 145, C(6)$_\beta$); 53.2 (*t*, ^1J(C,H) = 144, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 129, *Me*$_3$C); 28.0 (*q*, ^1J(C,H) = 125, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 380 (75, $[M+H]^+$), 379 (100, M^+), 323 (17), 273 (27), 217 (21), 171 (1), 136 (14), 107 (7), 71 (9). Anal. calc. for $C_{20}H_{30}N_2O_5$ (378.50): C 63.47, H 7.99; found: C 63.28, H 7.95.

*(2*R*,3*R*,4*S*)-2-{[(4-Hydroxybenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fe**). By *Method Aa*, with **9fe** (37 mg). FC (MeCN/NH_4OH 4 : 1) gave 23 mg (100% of **3fe**). $[\alpha]_{589}^{25} = +35$, $[\alpha]_{577}^{25} = +39$, $[\alpha]_{546}^{25} = +40$ (c = 0.37, MeOH). UV (MeCN): 276 (1250), 224 (4895), 207 (790). IR (KBr): 3400, 2940, 1735, 1705, 1605, 1515, 1455, 1255, 1170, 1105, 1030, 835, 770. ^{1}H-NMR (400 MHz, MeOD): 7.21 (*d*, ^3J = 8.6, 2 arom. H); 6.79 (*d*, ^3J = 8.6, 2 arom. H); 4.09 (*m*, H–C(4)); 3.77 (*s*, 2 H–C(1″)); 3.74 (*dd*, ^3J(3,4) = 4.9, ^3J(3,2) = 7.6, H–C(3)); 3.23 (*ddd*, ^3J(2,1′) = 4.8, ^3J(2,3) = 7.6, ^3J(2,1′) = 8.1, H–C(2)); 3.20 (*dd*, ^3J(5,4) = 4.8, ^2J = 12.2, 1 H–C(5)); 2.94 (*dd*, ^3J(5,4) = 3.0, ^2J = 12.2, 1 H–C(5)); 2.90 (*dd*, ^3J(1′,2) = 4.8, ^2J = 12.3, 1 H–C(1′)); 2.72 (*dd*, ^3J(1′,2) = 8.1, ^2J = 12.3, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 158.9 (*s*, arom. C); 131.8 (*d*, ^1J(C,H) = 156, 2 arom. C); 131.3 (*s*, arom. C); 117.1 (*d*, ^1J(C,H) = 158, 2 arom. C); 77.7 (*d*, ^1J(C,H) = 144, C(3)); 73.2 (*d*, ^1J(C,H) = 151, C(4)); 62.7 (*d*, ^1J(C,H) = 143, C(2)); 54.7 (*t*, ^1J(C,H) = 136, C(1″)); 52.9 (*t*, ^1J(C,H) = 141, C(5)); 52.6 (*t*, ^1J(C,H) = 135, C(1′)). CI-MS (NH_3): 239 (61, $[M+H]^+$), 229 (2), 208 (12), 159 (5), 133 (100), 102 (80), 85 (26).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-4-{[(2-methoxybenzyl)amino]methyl}-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9ff**). By *Method A*, with **8** (94 mg, 0.35 mmol), 2-methoxybenzylamine (47 mg, 0.35 mmol), $NaBH(OAc)_3$ (104 mg, 0.49 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 78 mg (58% of **9ff**), 1.3 : 1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -24$, $[\alpha]_{577}^{25} = -27$, $[\alpha]_{546}^{25} = -32$, $[\alpha]_{435}^{25} = -56$, $[\alpha]_{405}^{25} =$

-70 ($c = 0.53$, CH_2Cl_2). UV (MeCN): 272 (2730), 218 (9720), 206 (9500). IR (film): 2980, 2935, 2840, 1690, 1600, 1590, 1495, 1465, 1405, 1370, 1240, 1215, 1175, 1125, 1055, 1030, 975, 860, 755, 665. ^{1}H-NMR (400 MHz, MeOD): 7.28 (*m*, 2 arom. H); 6.96 (*m*, 2 arom. H); 4.73 (*m*, H–C(6a)); 4.56 (*m*, H–C(3a)); 4.15 (*dd*, $^3J(4,1') = 6.8$, $^3J(4,1') = 6.2$, H–C(4)$_\beta$); 4.09 (*dd*, $^3J(4,1') = 6.8$, $^3J(4,1') = 6.2$, H–C(4)$_\alpha$); 3.87 (*s*, MeO); 3.80 (*m*, 1 H–C(6), 1 H–C(6)$_\beta$, 2 H–C(1″)); 3.34 (*m*, 1 H–C(6)$_\beta$); 3.23 (*dd*, $^3J(6,6a) = 4.8$, $^2J = 12.9$, 1 H–C(6)$_\alpha$); 2.63 (*m*, 2 H–C(1′)); 1.50 (*s*, Me); 1.43 (*s*, (*t*-Bu)$_\beta$); 1.41 (*s*, (*t*-Bu)$_\alpha$); 1.31 (*s*, Me). ^{13}C-NMR (100.6 MHz, MeOD): 160.1 (arom. C); 157.6 (NCOO$_\beta$); 157.3 (NCOO$_\alpha$); 132.0 (arom. C); 130.7 (arom. C); 130.3 (arom. C); 122.3 (arom. C); 113.5 (Me$_2$*C*); 112.4 (arom. C); 85.6 (C(3a)$_\alpha$); 85.0 (C(3a)$_\beta$); 82.4 (Me$_3$*C*O$_\alpha$); 82.2 (Me$_3$*C*O$_\beta$); 81.6 (C(6a)$_\beta$); 80.9 (C(6a)$_\alpha$); 65.8 (C(4)$_\alpha$); 65.3 (C(4)$_\beta$); 56.5 (MeO); 53.7 (C(6)$_\beta$); 53.0 (C(6)$_\alpha$); 50–49 (C(1′), C(1″)); 29.5 (*Me*$_3$C); 28.0 (Me); 25.8 (Me). CI-MS (NH_3): (100, $[M+H]^+$), 392 (61), 337 (27), 273 (9), 217 (6), 171 (2), 150 (22), 121 (27), 91 (15). Anal. calc. for $C_{21}H_{32}N_2O_5$ (392.53): C 64.26, H 8.22, N 7.14; found: C 63.88, H 8.06, N 7.19.

*(2*R*,3*R*,4*S*)-2-{[(2-Methoxybenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3ff**). By *Method Aa*, with **9ff** (30 mg). FC (MeCN/NH_4OH 4:1) gave 32 mg (100% of **3ff**). $[\alpha]^{25}_{589} = +14$, $[\alpha]^{25}_{577} = +15$, $[\alpha]^{25}_{546} = +16$, $[\alpha]^{25}_{435} = +29$, $[\alpha]^{25}_{405} = +36$ ($c = 0.31$, MeOH). UV (MeCN): 274 (1540), 220 (4065), 202 (4725). IR (film): 3040, 1670, 1500, 1440, 1325, 1290, 1255, 1200, 1135, 1025, 840, 800, 760, 725. ^{1}H-NMR (400 MHz, MeOD): 7.41 (*m*, 2 arom. H); 7.08 (*d*, $^3J = 8.2$, 1 arom. H); 7.01 (*ddd*, $^3J = 7.5$, $^3J = 8.2$, $^4J = 0.6$, 1 arom. H); 4.23 (*ddd*, $^3J(4,5) = 1.8$, $^3J(4,5) = 4.1$, $^3J(4,3) = 4.2$, H–C(4)); 4.14 (*s*, 2 H–C(1″)); 3.98 (*dd*, $^3J(3,4) = 4.2$, $^3J(3,2) = 8.5$, H–C(3)); 3.94 (*s*, MeO); 3.62 (*ddd*, $^3J(2,1') = 4.6$, $^3J(2,3) = 8.5$, $^3J(2,1') = 8.5$, H–C(2)); 3.40 (*dd*, $^3J(5,4) = 4.1$, $^2J = 12.5$, 1 H–C(5)); 3.22 (*m*, 1 H–C(1′), 1 H–C(5)); 3.13 (*dd*, $^3J(1',2) = 4.6$, $^2J = 13.3$, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 158.4 (*s*, arom. C); 132.9 (*d*, ^1J(C,H) = 157, arom. C); 132.5 (*d*, ^1J(C,H) = 160, arom. C); 124.7 (*s*, arom. C); 122.7 (*d*, ^1J(C,H) = 162, arom. C); 112.7 (*d*, ^1J(C,H) = 160, arom. C); 76.7 (*d*, ^1J(C,H) = 144, C(3)); 72.1 (*d*, ^1J(C,H) = 149, C(4)); 60.6 (*d*, ^1J(C,H) = 145, C(2)); 56.9 (*q*, ^1J(C,H) = 145, MeO); 52.4 (*t*, ^1J(C,H) = 144, C(1″)); 50–49 (C(5), C(1′)). CI-MS (NH_3): 253 (81, $[M+H]^+$), 235 (6), 192 (5), 163 (3), 150 (53), 136 (33), 121 (100), 108 (52), 91 (35).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-4-{[(3-methoxybenzyl)amino]methyl}-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9fg**). By *Method A*, with **8** (97 mg, 0.36 mmol), 3-methoxybenzylamine (49 mg, 0.36 mmol), $NaBH(OAc)_3$ (106 mg, 0.50 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 77 mg (55% of **9fg**), 1.2:1 mixture of rotamers α and β. $[\alpha]^{25}_{589} = -20$, $[\alpha]^{25}_{577} = -22$, $[\alpha]^{25}_{546} = -29$, $[\alpha]^{25}_{435} = -51$, $[\alpha]^{25}_{405} = -64$ ($c = 0.49$, CH_2Cl_2). UV (MeCN): 273 (2435), 203 (15120). IR (film): 2980, 2940, 1695, 1600, 1585, 1490, 1455, 1405, 1370, 1265, 1210, 1160, 1125, 1055, 860, 780, 740, 695. ^{1}H-NMR (400 MHz, MeOD): 7.26 (*m*, 1 arom. H); 6.96 (*s*, 1 arom. H); 6.93 (*d*, $^3J = 7.5$, 1 arom. H); 6.84 (*d*, $^3J = 7.5$, 1 arom. H); 4.76 (*m*, H–C(6a)); 4.65 (*d*, $^3J(3a,6a) = 5.8$, H–C(3a)$_\alpha$); 4.59 (*d*, $^3J(3a,6a) = 5.6$, H–C(3a)$_\beta$); 4.19 (*m*, H–C(4)$_\beta$); 4.08 (*m*, H–C(4)$_\alpha$); 3.82 (s, MeO); 3.79 (*m*, 2 H–C(1″), 1 H–C(6)); 3.38 (*m*, 1 H–C(6)); 2.65 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.43 (*s*, *t*-Bu); 1.32 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 162.2 (*s*, arom. C); 157.5 (*s*, NCOO$_\beta$); 157.2 (*s*, NCOO$_\alpha$); 143.4 (*s*, arom. C); 131.3 (*d*, ^1J(C,H) = 159, arom. C); 122.4 (*d*, ^1J(C,H) = 158, arom. C); 115.7 (*d*, ^1J(C,H) = 158, arom. C); 114.7 (*d*, ^1J(C,H) = 161, arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 156, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (*s*, Me$_3$*C*O$_\alpha$); 82.1 (*s*, Me$_3$*C*O$_\beta$); 81.6 (*d*, ^1J(C,H) = 143, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 148, C(4)$_\alpha$); 65.3 (*d*, ^1J(C,H) = 145, C(4)$_\beta$); 56.5 (*q*, ^1J(C,H) = 144, MeO); 55.1 (*t*, ^1J(C,H) = 135, C(1″)); 53.8 (*t*, ^1J(C,H) = 143, C(6)$_\beta$); 53.3 (*t*, ^1J(C,H) = 144, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 126, *Me*$_3$C); 28.1 (*q*, ^1J(C,H) = 127, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 393 (94, $[M+H]^+$), 363 (8), 337 (24), 287 (5), 258 (100), 231 (9), 166 (70), 121 (42), 91 (12). Anal. calc. for $C_{21}H_{32}N_2O_5$ (392.53): C 64.26, H 8.22; found: C 64.36, H 8.29.

*(2*R*,3*R*,4*S*)-2-{[(3-Methoxybenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fg**). By *Method Aa*, **9fg** (33 mg). FC (MeCN/NH_4OH 4:1) gave 21 mg (100% of **3fg**). $[\alpha]^{25}_{589} = +16$, $[\alpha]^{25}_{577} = +26$, $[\alpha]^{25}_{546} = +26$, $[\alpha]^{25}_{435} = +37$, $[\alpha]^{25}_{405} = +42$ ($c = 0.12$, MeOH). UV (MeCN): 275 (1625), 220 (4555), 204 (6325). IR (film): 3055, 1670, 1435, 1265, 1205, 1140, 1040, 895, 840, 800, 725, 700. ^{1}H-NMR (400 MHz, MeOD): 7.32 (*m*, 1 arom. H); 7.05 (*m*, 2 arom. H); 6.93 (*m*, 2 arom. H); 4.25 (*m*, H–C(4)); 4.05 (*s*, 2 H–C(1″)); 4.02 (*dd*, $^3J(3,2) = 8.8$, $^3J(3,4) = 4.1$, H–C(3)); 3.84 (*s*, MeO); 3.65 (*ddd*, $^3J(2,1') = 4.6$, $^3J(2,3) = 8.8$, $^3J(2,1') = 8.8$, H–C(2)); 3.46 (*dd*, $^3J(5,4) = 4.1$, $^2J = 12.6$, 1 H–C(5)); 3.27 (*m*, 1 H–C(5), 1 H–C(1′)); 3.15 (*dd*, $^3J(1',2) = 8.8$, $^2J = 13.4$, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 164.2 (*s*, arom. C); 139.2 (*s*, arom. C); 131.8 (*d*, ^1J(C,H) = 160, arom. C); 123.1 (*d*, ^1J(C,H) = 160, arom. C); 116.3 (*d*, ^1J(C,H) = 158, arom. C); 115.9 (*d*, ^1J(C,H) = 166, arom. C); 76.2 (*d*, ^1J(C,H) = 145, C(3)); 71.8 (*d*, ^1J(C,H) = 154, C(4)); 61.1 (*d*, ^1J(C,H) = 147, C(2)); 56.6 (*t*, ^1J(C,H) = 144, MeO); 54.4 (*t*, ^1J(C,H) = 144, C(1″)); 52.1 (*t*, ^1J(C,H) = 148, C(5)); 50–49 (C(1′)). CI-MS (NH_3): 253 (100, $[M+H]^+$), 240 (28), 222 (18), 197 (2), 184 (10), 150 (9), 121 (12), 102 (6).

tert-*Butyl (3a*R,*4*R,*6a*S*)-Tetrahydro-4-{[(4-methoxybenzyl)amino]methyl}-2,2-dimethyl-5*H-*[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9fh**). By *Method A*, with **8** (134 mg, 0.49 mmol), 4-methoxybenzylamine (65 µl, 0.49 mmol), $NaBH(OAc)_3$ (145 mg, 0.69 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 157 mg (81% of **9fh**), 1.2:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -32$, $[\alpha]_{577}^{25} = -36$, $[\alpha]_{546}^{25} = -39$, $[\alpha]_{435}^{25} = -68$, $[\alpha]_{405}^{25} = -83$ ($c = 0.58$, CH_2Cl_2). UV (MeCN): 276 (2905), 225 (11910), 203 (11315). IR (film): 2980, 2935, 2835, 1695, 1690, 1610, 1515, 1455, 1405, 1245, 1175, 1125, 1055, 1040. ^{1}H-NMR (400 MHz, MeOD): 7.26 (*m*, 2 arom. H); 6.89 (*m*, 2 arom. H); 4.73 (*m*, H–C(6a)); 4.62 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.56 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\beta$); 4.18 (*dd*, ^3J(4,1′) = 6.5, ^3J(4,1′) = 6.8, H–C(4)$_\beta$); 4.06 (*dd*, ^3J(4,1′) = 6.7, ^3J(4,1′) = 6.6, H–C(4)$_\alpha$); 3.79 (*s*, MeO); 3.73 (*m*, 1 H–C(6), 2 H–C(1″)); 3.38 (*m*, 1 H–C(6)); 2.62 (*m*, 2 H–C(1′)); 1.49 (*s*, Me); 1.42 (*s*, (*t*-Bu)$_\alpha$); 1.41 (*s*, (*t*-Bu)$_\beta$); 1.31 (*s*, 2 Me). ^{13}C-NMR (100.6 MHz, MeOD): 161.2 (*s*, arom. C); 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 133.7 (*s*, arom. C); 131.5 (*d*, ^1J(C,H) = 158, 2 arom. C); 115.7 (*d*, ^1J(C,H) = 159, 2 arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 158, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.2 (*s*, Me_3CO_β); 81.6 (*d*, ^1J(C,H) = 148, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 159, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 145, C(4)$_\alpha$); 65.2 (*d*, ^1J(C,H) = 144, C(4)$_\beta$); 56.5 (*q*, ^1J(C,H) = 144, MeO); 54.5 (*t*, ^1J(C,H) = 135, C(1″)); 53.8 (*t*, ^1J(C,H) = 143, C(6)$_\beta$); 53.3 (*t*, ^1J(C,H) = 142, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 127, *Me*$_3$C); 28.1 (*q*, ^1J(C,H) = 127, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 393 (100, $[M+H]^+$), 337 (15), 273 (13), 187 (1), 150 (5), 121 (24), 84 (33). Anal. calc. for $C_{21}H_{32}N_2O_5$ (392.53): C 64.26, H 8.22; found: C 64.31, H 8.09.

*(2*R,*3*R,*4*S*)-2-{[(4-Methoxybenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fh**). By *Method Aa*, with **9fh** (33 mg). FC (MeCN/NH_4OH 4:1) gave 30 mg (100% of **3fh**). $[\alpha]_{589}^{25} = +9$, $[\alpha]_{577}^{25} = +12$, $[\alpha]_{546}^{25} = +13$, $[\alpha]_{435}^{25} = +25$, $[\alpha]_{405}^{25} = +29$ ($c = 0.30$, MeOH). UV (MeCN): 274 (1785), 228 (10225), 202 (9235). IR (film): 3055, 1660, 1515, 1470, 1445, 1345, 1305, 1255, 1180, 1130, 1030, 840, 815, 800, 740, 725, 705. ^{1}H-NMR (400 MHz, MeOD): 7.39 (*d*, ^3J = 8.7, 2 arom. H); 6.96 (*d*, ^3J = 8.7, 2 arom. H); 4.23 (*m*, H–C(4)); 4.05 (*s*, 2 H–C(1″)); 4.01 (*dd*, ^3J(3,4) = 4.0, ^3J(3,2) = 8.6, H–C(3)); 3.82 (*s*, MeO); 3.64 (*ddd*, ^3J(2,1′) = 4.3, ^3J(2,3) = 8.6, ^3J(2,1′) = 8.6, H–C(2)); 3.43 (*dd*, ^3J(5,4) = 4.0, ^2J = 12.6, 1 H–C(5)); 3.26 (*m*, 1 H–C(5), 1 H–C(1′)); 3.17 (*dd*, ^3J(1′,2) = 8.6, ^2J = 13.4, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 162.3 (*s*, arom. C); 132.7 (*d*, ^1J(C,H) = 163, 2 arom. C); 128.4 (*s*, arom. C); 116.1 (*d*, ^1J(C,H) = 164, 2 arom. C); 76.4 (*d*, ^1J(C,H) = 145, C(3)); 71.8 (*d*, ^1J(C,H) = 154, C(4)); 60.7 (*d*, ^1J(C,H) = 146, C(2)); 56.6 (*t*, ^1J(C,H) = 144, MeO); 53.8 (*t*, ^1J(C,H) = 141, C(1″)); 52.3 (*t*, ^1J(C,H) = 147, C(5)); 50–49 (C(1′)). CI-MS (NH_3): 253 (100, $[M+H]^+$), 215 (3), 180 (2), 150 (7), 121 (84), 102 (16), 77 (26).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-{[(2-Fluorobenzyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H-*[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9fi**). By *Method A*, with **8** (67 mg, 0.25 mmol), 2-fluorobenzylamine (31 mg, 0.25 mmol), $NaBH(OAc)_3$ (73 mg, 0.35 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt/light petroleum ether 8:2) gave 52 mg (55% of **9fi**), 1.3:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -26$, $[\alpha]_{577}^{25} = -27$, $[\alpha]_{546}^{25} = -33$, $[\alpha]_{435}^{25} = -61$, $[\alpha]_{405}^{25} = -73$ ($c = 0.36$, CH_2Cl_2). UV (MeCN): 268 (1800), 262 (1910), 206 (11900). IR (film): 3340, 2980, 2935, 1695, 1585, 1490, 1455, 1405, 1160, 1125, 1055, 975, 860, 760. ^{1}H-NMR (400 MHz, MeOD): 7.44 (*m*, ^3J = 7.5, 1 arom. H); 7.32 (*m*, 1 arom. H); 7.19 (*m*, 1 arom. H); 7.10 (*m*, 1 arom. H); 4.77 (*m*, H–C(6a)); 4.65 (*d*, ^3J(3a,6a) = 5.7, H–C(3a)$_\alpha$); 4.61 (*d*, ^3J(3a,6a) = 5.6, H–C(3a)$_\beta$); 4.18 (*t*, ^3J(4,1′) = 6.4, H–C(4)$_\beta$); 4.09 (*t*, ^3J(4,1′) = 6.3, H–C(4)$_\alpha$); 3.87 (*m*, 1 H–C(6), 2 H–C(1″)); 3.39 (*m*, 1 H–C(6)); 2.67 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.44 (*s*, (*t*-Bu)$_\beta$); 1.43 (*s*, (*t*-Bu)$_\alpha$); 1.33 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 165.4 (*d*, ^2J(C,F) = 245, arom. C); 157.6 (*s*, $NCOO_\beta$); 157.3 (*s*, $NCOO_\alpha$); 132.5 (*s*, arom. C); 131.0 (*d*, ^1J(C,H) = 161, arom. C); 126.2 (*d*, ^1J(C,H) = 161, arom. C); 117.1 (*d*, ^1J(C,H) = 160, ^2J(C,C,F) = 22, arom. C); 116.9 (*d*, ^1J(C,H) = 160, arom. C); 113.4 (*s*); 85.6 (*d*, ^1J(C,H) = 154, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 155, C(3a)$_\beta$); 82.4 (*s*, Me_3CO_α); 82.2 (*s*, Me_3CO_α); 81.6 (*d*, ^1J(C,H) = 156, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 159, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 144, C(4)$_\alpha$); 65.3 (*d*, ^1J(C,H) = 145, C(4)$_\beta$); 53.8 (*t*, ^1J(C,H) = 142, C(6)$_\beta$); 53.2 (*t*, ^1J(C,H) = 143, C(6)$_\alpha$); 50–49 (C(1′)); 48.3 (*t*, ^1J(C,H) = 136, C(1″)); 29.5 (*q*, ^1J(C,H) = 127, *Me*$_3$C); 28.1 (*q*, ^1J(C,H) = 126, Me); 25.8 (*q*, ^1J(C,H) = 125, Me). CI-MS (NH_3): 381 (100, $[M+H]^+$), 325 (53), 272 (6), 232 (31), 186 (15), 142 (21), 109 (41), 84 (7). Anal. calc. for $C_{20}H_{29}FN_2O_4$ (380.48): C 63.14, H 7.68; found: C 63.07, H 7.64.

*(2*R,*3*R,*4*S*)-2-{[(2-Fluorobenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fi**). By *Method Aa*, with **9fi** (31 mg). FC (MeCN/NH_4OH 4:1) gave 19 mg (100% of **3fi**). $[\alpha]_{589}^{25} = +17$, $[\alpha]_{577}^{25} = +19$, $[\alpha]_{546}^{25} = +22$, $[\alpha]_{435}^{25} = +38$, $[\alpha]_{405}^{25} = +45$ ($c = 0.26$, MeOH). UV (MeCN): 273 (6705), 260 (5500), 213 (1775). IR (film): 3385, 1675, 1440, 1200, 1140, 840, 800, 760, 720. ^{1}H-NMR (400 MHz, MeOD): 7.55 (*t*, ^3J = 7.6, 1 arom. H); 7.48 (*m*, 1 arom. H); 7.26 (*m*, 2 arom. H); 4.27 (*m*, H–C(4), 2 H–C(1″)); 4.07 (*dd*, ^3J(3,4) = 3.9, ^3J(3,2) = 9.0, H–C(3)); 3.75 (*m*, H–C(2)); 3.51 (*dd*, ^3J(5,4) = 3.9, ^2J = 12.6, 1 H–C(5)); 3.45–3.32 (*m*, 2 H–C(1′), 1 H–C(5)). ^{13}C-NMR (100.6 MHz, MeOD): 165.0 (*d*, ^1J(C,F) = 245, arom. C); 133.7 (2*d*, ^1J(C,H) = 167, 2 arom. C); 133.3 (*s*, arom. C); 127.1 (*d*, ^1J(C,H) = 160, arom. C); 117.6 (*dd*, ^1J(C,H) = 161, ^2J(C,F) = 22, arom. C); 76.4 (*d*, ^1J(C,H) = 144, C(3)); 71.4 (*d*, ^1J(C,H) = 154, C(4)); 60.0 (*d*, ^1J(C,H) = 143, C(2)); 52.4 (*t*, ^1J(C,H) =

148, C(5)); 50–49 (C(1′)); 47.4 (*t*, ^1J(C,H) = 145, C(1″)). CI-MS (NH_3): 241 (15, $[M+H]^+$), 209 (1), 138 (54), 124 (16), 109 (100), 102 (41), 85 (47).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-{[(3-Fluorobenzyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9fj**). By *Method A*, with **8** (111 mg, 0.41 mmol), 3-fluorobenzylamine (51 mg, 0.41 mmol), $NaBH(OAc)_3$ (122 mg, 0.57 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 104 mg (67% of **9fj**), 1.1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -24$, $[\alpha]_{577}^{25} = -25$, $[\alpha]_{546}^{25} = -31$, $[\alpha]_{435}^{25} = -59$, $[\alpha]_{405}^{25} = -73$ ($c = 0.43$, CH_2Cl_2). UV (MeCN): 269 (3440), 262 (3580), 205 (18190). IR (film): 3335, 2980, 2935, 1695, 1590, 1490, 1455, 1405, 1250, 1210, 1170, 1125, 1055, 975, 865, 785, 685. ^{1}H-NMR (400 MHz, MeOD): 7.36 (*m*, 1 arom. H); 7.17 (*m*, 2 arom. H); 7.00 (*m*, 1 arom. H); 4.77 (*m*, H–C(6a)); 4.67 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.61 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\beta$); 4.18 (*dd*, ^3J(4,1′) = 6.4, ^3J(4,1′) = 6.8, H–C(4)$_\beta$); 4.08 (*dd*, ^3J(4,1′) = 6.4, ^3J(4,1′) = 6.5, H–C(4)$_\alpha$); 3.80 (*m*, 1 H–C(6), 2 H–C(1″)); 3.39 (*m*, 1 H–C(6)); 2.65 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.44 (*s*, (*t*-Bu)$_\alpha$); 1.43 (*s*, (*t*-Bu)$_\beta$); 1.33 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 165.3 (*d*, ^1J(C,F) = 246, arom. C); 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 145.0 (*s*, arom. C); 132.0 (*d*, ^1J(C,H) = 163, arom. C); 125.9 (*d*, ^1J(C,H) = 161, arom. C); 116.6 (*dd*, ^1J(C,H) = 160, ^2J(C,F) = 22, arom. C); 115.5 (*dd*, ^1J(C,H) = 163, ^2J(C,F) = 21, arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 157, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 159, C(3a)$_\beta$); 82.2 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_α); 81.6 (*d*, ^1J(C,H) = 155, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 159, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 146, C(4)$_\alpha$); 65.2 (*d*, ^1J(C,H) = 146, C(4)$_\beta$); 54.5 (*t*, ^1J(C,H) = 135, C(1″)); 53.9 (*t*, ^1J(C,H) = 143, C(6)$_\beta$); 53.4 (*t*, ^1J(C,H) = 142, C(6)$_\alpha$); 50–49 (C(1′)); 29.6 (*q*, ^1J(C,H) = 128, Me_3C); 28.1 (*q*, ^1J(C,H) = 127, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 381 (100, $[M+H]^+$), 325 (51), 281 (14), 243 (4), 187 (8), 138 (26), 109 (41), 85 (8). Anal. calc. for $C_{20}H_{29}FN_2O_4$ (380.48): C 63.14, H 7.68; found: C 63.09, H 7.64.

*(2*R,*3*R,*4*S*)-2-{[(3-Fluorobenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fj**). By *Method Aa*, with **9fj** (40 mg). FC (MeCN/NH_4OH 4:1) gave 25 mg (100% of **3fj**). $[\alpha]_{589}^{25} = +3$, $[\alpha]_{577}^{25} = +5$, $[\alpha]_{546}^{25} = +7$, $[\alpha]_{435}^{25} = +25$, $[\alpha]_{405}^{25} = +36$ ($c = 0.15$, MeOH). UV (MeCN): 268 (1330), 216 (3500). IR (film): 3410, 1675, 1445, 1200, 1140, 840, 800, 725. ^{1}H-NMR (400 MHz, MeOD): 7.42 (*m*, 1 arom. H); 7.25 (*m*, 2 arom. H); 7.11 (*dt*, $^3J = 8.1$, $^4J = 1.8$, 1 arom. H); 4.26 (*ddd*, ^3J(4,5) = 1.6, ^3J(4,5) = 4.0, ^3J(4,3) = 4.0, H–C(4)); 4.09 (*AB*, H–C(1″)); 4.06 (*dd*, ^3J(3,4) = 4.0, ^3J(3,2) = 8.8, H–C(3)); 3.71 (*ddd*, ^3J(2,3) = 8.8, ^3J(2,1′) = 8.8, ^3J(H(2,1′) = 4.2, H–C(2)); 3.49 (*dd*, ^3J(5,4) = 4.0, $^2J = 12.6$, 1 H–C(5)); 3.33 (*m*, 1 H–C(1′)); 3.28 (*m*, 1 H–C(5)); 3.22 (*dd*, ^3J(1′,2) = 8.8, $^2J = 13.4$, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 166.5 (*d*, ^1J(C,F) = 249, arom. C); 140.2 (*s*, arom. C); 132.5 (*d*, ^1J(C,H) = 163, arom. C); 126.9 (*d*, ^1J(C,H) = 163, arom. C); 117.6 (*dd*, ^1J(C,H) = 148, ^2J(C,F) = 22, arom. C); 117.3 (*dd*, ^1J(C,H) = 150, ^2J(C,F) = 22, arom. C); 76.1 (*d*, ^1J(C,H) = 144, C(3)); 71.6 (*d*, ^1J(C,H) = 150, C(4)); 60.9 (*d*, ^1J(C,H) = 146, C(2)); 53.9 (*t*, ^1J(C,H) = 141, C(1″)); 52.1 (*t*, ^1J(C,H) = 149, C(5)); 50–49 (C(1′)). CI-MS (NH_3): 241 (100, $[M+H]^+$), 223 (1), 138 (11), 126 (6), 102 (26), 85 (32).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-{[(4-Fluorobenzyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo-[4,5-c]pyrrole-5-carboxylate* (**9fk**). By *Method A*, with **8** (91 mg, 0.34 mmol), 4-fluorobenzylamine (42 mg, 0.34 mmol), $NaBH(OAc)_3$ (100 mg, 0.47 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 102 mg (80% of **9fk**), 1.1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -39$, $[\alpha]_{577}^{25} = -40$, $[\alpha]_{546}^{25} = -47$, $[\alpha]_{435}^{25} = -80$, $[\alpha]_{405}^{25} = -97$ ($c = 0.51$, CH_2Cl_2). UV (MeCN): 272 (1845), 265 (2070), 207 (12370). IR (film): 3335, 2980, 2935, 1700, 1685, 1680, 1600, 1510, 1480, 1455, 1400, 1370, 1225, 1180, 1165, 1125, 1055, 980, 855, 825, 770. ^{1}H-NMR (400 MHz, MeOD): 7.38 (*d*, $^3J = 8.2$, 2 arom. H); 7.07 (*m*, 2 arom. H); 4.76 (*m*, H–C(6a)); 4.64 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.59 (*d*, ^3J(3a,6a) = 5.6, H–C(3a)$_\beta$); 4.18 (*dd*, ^3J(4,1′) = 6.5, ^3J(4,1′) = 6.7, H–C(4)$_\beta$); 4.07 (*dd*, ^3J(4,1′) = 6.5, ^3J(4,1′) = 6.4, H–C(4)$_\alpha$); 3.76 (*m*, 1 H–C(6), 2 H–C(1″)); 3.38 (*m*, 1 H–C(6)); 2.64 (*m*, 2 H–C(1′)); 1.49 (*s*, 1 Me); 1.42 (*s*, (*t*-Bu)$_\alpha$); 1.41 (*s*, (*t*-Bu)$_\beta$); 1.31 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 164.3 (*d*, ^2J(C,F) = 245, arom. C); 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 137.9 (*s*, arom. C); 132.1 (*d*, ^1J(C,H) = 160, 2 arom. C); 117.0 (*dd*, ^1J(C,H) = 163, ^2J(C,F) = 22, arom. C); 116.8 (*dd*, ^1J(C,H) = 163, ^2J(C,F) = 22, arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 158, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 158, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_β); 81.6 (*d*, ^1J(C,H) = 155, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 146, C(4)$_\alpha$); 65.2 (*d*, ^1J(C,H) = 145, C(4)$_\beta$); 55.0 (*t*, ^1J(C,H) = 135, C(1″)); 54.3 (*t*, ^1J(C,H) = 145, C(6)$_\beta$); 53.8 (*t*, ^1J(C,H) = 144, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 127, Me_3C); 28.1 (*q*, ^1J(C,H) = 124, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 382 (100, $[M+H]^+$), 381 (75, M^+), 325 (29), 279 (1), 217 (6), 138 (11), 109 (27), 85 (4). Anal. calc. for $C_{20}H_{29}FN_2O_4$ (380.48): C 63.14, H 7.68, N 7.36; found: C 63.11, H 7.72, N 7.27.

*(2*R,*3*R,*4*S*)-2-{[(4-Fluorobenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fk**). By *Method Aa*, with **9fk** (30 mg). FC (MeCN/NH_4OH 4:1) gave 19 mg (100% of **3fk**). $[\alpha]_{589}^{25} = +9$, $[\alpha]_{577}^{25} = +15$, $[\alpha]_{546}^{25} = +19$ ($c = 0.21$, MeOH). UV (MeCN): 271 (3060), 214 (2615). IR (film): 3200, 3050, 2890, 1660, 1440, 1265, 1195, 1135, 840, 800, 735. ^{1}H-NMR (400 MHz, MeOD): 7.60 (*m*, 2 arom. H); 7.22 (*dd*, $^3J = 8.8$, 2 arom. H); 4.29 (*m*, H–C(4), 2 H–C(1″)); 4.12 (*dd*, ^3J(3,4) = 3.9, ^3J(3,2) = 9.2, H–C(3)); 3.85 (*m*, H–C(2)); 3.57 (*dd*, ^3J(5,4) = 3.9, $^2J = 12.7$, 1 H–C(5)); 3.52 (*m*, 2 H, H–C(1′)); 3.39 (*m*, 1 H–C(5)). ^{13}C-NMR (100.6 MHz,

MeOD): 165.6 (*d*, ^1J(C,F) = 247, arom. C); 134.2 (*d*, ^1J(C,H) = 161, 2 arom. C); 130.1 (*s*, arom. C); 117.8 (*dd*, ^1J(C,H) = 167, ^2J(C,F) = 27, 2 arom. C); 76.5 (*d*, ^1J(C,H) = 145, C(3)); 71.2 (*d*, ^1J(C,H) = 150, C(4)); 59.3 (*d*, ^1J(C,H) = 140, C(2)); 53.2 (*t*, ^1J(C,H) = 144, C(1″)); 52.6 (*t*, ^1J(C,H) = 146, C(5)); 50–49 (C(1′)). CI-MS (NH_3): 241 (11, $[M+H]^+$), 215 (3), 200 (19), 171 (25), 153 (6), 142 (43), 124 (41), 109 (100), 95 (25), 85 (33).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-{[(2-Chlorobenzyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9fl**). By *Method A*, with **8** (90 mg, 0.33 mmol), 2-chlorobenzylamine (47 mg, 0.33 mmol), $NaBH(OAc)_3$ (99 mg, 0.46 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt/light petroleum ether 1:1) gave 95 mg (72% of **9fl**), 1.4:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -23$, $[\alpha]_{577}^{25} = -25$, $[\alpha]_{546}^{25} = -29$, $[\alpha]_{435}^{25} = -55$, $[\alpha]_{405}^{25} = -70$ ($c = 0.52$, CH_2Cl_2). UV (MeCN): 210 (14140). IR (film): 3335, 2980, 1680, 1595, 1575, 1415, 1160, 1055, 975, 860, 755, 675. ^{1}H-NMR (400 MHz, MeOD): 7.49 (*m*, 1 arom. H); 7.41 (*m*, 1 arom. H); 7.33 (*m*, 2 arom. H); 4.78 (*m*, H–C(6a)); 4.67 (*d*, ^3J(3a,6a) = 5.9, H–C(3a)$_\alpha$); 4.64 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\beta$); 4.18 (*t*, ^3J(4,1′) = 6.2, H–C(4)$_\alpha$); 4.09 (*t*, ^3J(4,1′) = 6.4, H–C(4)$_\beta$); 3.92 (*m*, 2 H–C(1″)); 3.80 (*d*, ^2J = 12.8, 1 H–C(6)); 3.39 (*m*, 1 H–C(6)); 2.68 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.44 (*s*, (*t*-Bu)$_\alpha$); 1.43 (*s*, (*t*-Bu)$_\beta$); 1.33 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 139.2 (*s*, arom. C); 135.6 (*s*, arom. C); 132.2 (*d*, ^1J(C,H) = 159, arom. C); 131.4 (*d*, ^1J(C,H) = 166, arom. C); 130.6 (*d*, ^1J(C,H) = 156, arom. C); 129.0 (*d*, ^1J(C,H) = 162, arom. C); 113.4 (*s*); 85.6 (*d*, ^1J(C,H) = 157, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 158, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_β); 81.6 (*d*, ^1J(C,H) = 156, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 159, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 146, C(4)$_\alpha$); 65.4 (*d*, ^1J(C,H) = 143, C(4)$_\beta$); 53.9 (*t*, ^1J(C,H) = 143, C(6)$_\beta$); 53.3 (*t*, ^1J(C,H) = 144, C(6)$_\alpha$); 52.5 (*t*, ^1J(C,H) = 138, C(1″)); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 128, Me_3C); 28.1 (*q*, ^1J(C,H) = 127, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 397 (100, M^+), 341 (39), 295 (3), 264 (14), 242 (8), 217 (21), 154 (19), 125 (24), 89 (6). Anal. calc. For $C_{20}H_{29}ClN_2O_4$ (396.53): C 60.52, H 7.36; found: C 60.42, H 7.22.

*(2*R,*3*R,*4*S*)-2-{[(2-Chlorobenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fl**). By *Method Aa*, with **9fl** (28 mg). FC ($MeCN/NH_4OH$ 4:1) gave 18 mg (100% of **3fl**). $[\alpha]_{589}^{25} = +7$, $[\alpha]_{577}^{25} = +10$, $[\alpha]_{546}^{25} = +12$ (c = 0.60, MeOH). UV (MeCN): 261 (590), 217 (2985). IR (film): 3200, 3065, 2900, 1665, 1470, 1445, 1185, 840, 800, 760, 725, 680. ^{1}H-NMR (400 MHz, MeOD): 7.59 (*m*, 1 arom. H); 7.49 (*m*, 1 arom. H); 7.38 (*m*, 2 arom. H); 4.26 (*m*, H–C(4), 2 H–C(1″)); 4.07 (*dd*, ^3J(3,4) = 3.9, ^3J(3,2) = 8.7, H–C(3)); 3.73 (*ddd*, ^3J(2,3) = 8.7, ^3J(2,1′) = 8.7, ^3J(2,1′) = 4.2, H–C(2)); 3.50 (*dd*, ^3J(5,4) = 3.9, ^2J = 12.6, 1 H–C(5)); 3.34–3.15 (*m*, 2 H–C(1′), 1 H–C(5)). ^{13}C-NMR (100.6 MHz, MeOD): 136.2 (*s*, arom. C); 135.0 (*s*, arom. C); 133.1 (*d*, ^1J(C,H) = 161, arom. C); 132.0 (*d*, ^1J(C,H) = 165, arom. C); 131.7 (*d*, ^1J(C,H) = 165, arom. C); 129.4 (*d*, ^1J(C,H) = 163, arom. C); 76.1 (*d*, ^1J(C,H) = 144, C(3)); 71.6 (*d*, ^1J(C,H) = 150, C(4)); 61.0 (*d*, ^1J(C,H) = 146, C(2)); 52.1 (*t*, ^1J(C,H) = 149, C(5)); 51.7 (*t*, ^1J(C,H) = 144, C(1″)); 50–49 (C(1′)). CI-MS (NH_3): 257 (100, M^+), 241 (3), 154 (15), 142 (4), 125 (19), 102 (18), 85 (26).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-{[(3-Chlorobenzyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9fm**). By *Method A*, with **8** (109 mg, 0.40 mmol), 3-chlorobenzylamine (57 mg, 0.40 mmol), $NaBH(OAc)_3$ (119 mg, 0.56 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 86 mg (54% of **9fm**), 1.1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -27$, $[\alpha]_{577}^{25} = -31$, $[\alpha]_{546}^{25} = -32$, $[\alpha]_{435}^{25} = -53$, $[\alpha]_{405}^{25} = -65$ (c = 0.44, CH_2Cl_2). UV (MeCN): 211 (11315). IR (film): 3340, 2980, 2935, 1705, 1685, 1600, 1575, 1475, 1460, 1400, 1370, 1210, 1160, 1125, 1055, 975, 860, 780, 685. ^{1}H-NMR (400 MHz, MeOD): 7.42 (*s*, 1 arom. H); 7.31 (*m*, 3 arom. H); 4.77 (*m*, H–C(6a)); 4.67 (*d*, ^3J(3a,6a) = 5.9, H–C(3a)$_\alpha$); 4.61 (*d*, ^3J(3a,6a) = 5.9, H–C(3a)$_\beta$); 4.18 (*dd*, ^3J(4,1′) = 6.5, ^3J(4,1′) = 6.9, H–C(4)$_\beta$); 4.07 (*dd*, ^3J(4,1′) = 6.6, ^3J(4,1′) = 6.3, H–C(4)$_\alpha$); 3.79 (*m*, 1 H–C(6), 2 H–C(1″)); 3.40 (*m*, 1 H–C(6)); 2.66 (*m*, 2 H–C(1′)); 1.47 (*s*, 1 Me); 1.44 (*s*, (*t*-Bu)$_\alpha$); 1.43 (*s*, (*t*-Bu)$_\beta$); 1.33 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 144.5 (*s*, arom. C); 136.2 (*s*, arom. C); 131.8 (*d*, ^1J(C,H) = 163, arom. C); 130.2 (*d*, ^1J(C,H) = 160, arom. C); 129.0 (*d*, ^1J(C,H) = 166, arom. C); 128.6 (*d*, ^1J(C,H) = 162, arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 159, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 162, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_β); 82.2 (*s*, Me_3CO_α); 81.6 (*d*, ^1J(C,H) = 154, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 159, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 147, C(4)$_\alpha$); 65.2 (*d*, ^1J(C,H) = 147, C(4)$_\beta$); 54.5 (*t*, ^1J(C,H) = 134, C(1″)); 53.9 (*t*, ^1J(C,H) = 143, C(6)$_\beta$); 53.4 (*t*, ^1J(C,H) = 141, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 127, Me_3C); 28.1 (*q*, ^1J(C,H) = 125, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 397 (100, $[M+H]^+$), 363 (3), 341 (56), 297 (5), 261 (14), 216 (6), 142 (8), 125 (16), 85 (5). Anal. calc. for $C_{20}H_{29}ClN_2O_4$ (396.53): C 60.52, H 7.36, N 7.06; found: C 60.56, H 7.29, N 6.95.

*(2*R,*3*R,*4*S*)-2-{[(3-Chlorobenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fm**). By *Method Aa*, with **9fm** (32 mg). FC ($MeCN/NH_4OH$ 4:1) gave 21 mg (100% of **3fm**). $[\alpha]_{589}^{25} = +16$, $[\alpha]_{577}^{25} = +16$, $[\alpha]_{546}^{25} = +21$ (c = 0.56, MeOH). UV (MeCN): 217 (3545). IR (film): 3075, 1670, 1650, 1470, 1440, 1200, 1130, 840, 800, 725. ^{1}H-NMR (400 MHz, MeOD): 7.56 (*s*, 1 arom. H); 7.42 (*m*, 3 arom. H); 4.26 (*m*, H–C(4)); 4.15 (*AB*, ^2J = 16.1, 2 H–C(1″)); 4.07 (*dd*, ^3J(3,4) = 3.9, ^3J(3,2) = 8.9, H–C(3)); 3.74 (*ddd*, ^3J(2,1′) = 4.4, ^3J(2,3) = 8.9, ^3J(2,1′) = 8.9, H–C(2)); 3.51 (*dd*, ^3J(5,4) = 3.9, ^2J = 12.6, 1 H–C(5)); 3.38–3.32 (*m*, 1 H–C(5), 2 H–C(1′)). ^{13}C-NMR

(100.6 MHz, MeOD): 138.9 (*s*, arom. C); 136.6 (*s*, arom. C); 132.4 (*d*, ^1J(C,H) = 164, arom. C); 131.4 (*d*, ^1J(C,H) = 166, arom. C); 130.8 (*d*, ^1J(C,H) = 163, arom. C); 129.7 (*d*, ^1J(C,H) = 165, arom. C); 76.2 (*d*, ^1J(C,H) = 144, C(3)); 71.4 (*d*, ^1J(C,H) = 155, C(4)); 60.4 (*d*, ^1J(C,H) = 146, C(2)); 53.6 (*t*, ^1J(C,H) = 141, C(1″)); 52.3 (*t*, ^1J(C,H) = 144, C(5)); 50–49 (C(1′)). CI-MS (NH_3): 257 (62, M^+), 243 (19), 223 (9), 203 (3), 173 (7), 159 (41), 133 (100), 116 (87), 98 (16).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-[[(4-Chlorobenzyl)amino]methyl]tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9fn**). By *Method A*, with **8** (94 mg, 0.35 mmol), 4-Chlorobenzylamine (49 mg, 0.35 mmol), $NaBH(OAc)_3$ (103 mg, 0.49 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 99 mg (72% of **9fn**), 1.1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -37$, $[\alpha]_{577}^{25} = -39$, $[\alpha]_{546}^{25} = -42$, $[\alpha]_{435}^{25} = -71$, $[\alpha]_{405}^{25} = -84$ (c = 0.45, CH_2Cl_2). UV (MeCN): 219 (12370). IR (film): 3335, 2980, 2935, 1705, 1680, 1600, 1490, 1455, 1400, 1365, 1210, 1170, 1125, 1090, 1055, 1015, 975, 860, 805, 770. ^{1}H-NMR (400 MHz, MeOD): 7.35 (*m*, 4 arom. H); 4.77 (*m*, H–C(6a)); 4.66 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.60 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\beta$); 4.18 (*dd*, ^3J(4,1′) = 6.6, ^3J(4,1′) = 6.1, H–C(4)$_\beta$); 4.07 (*dd*, ^3J(4,1′) = 6.4, ^3J(4,1′) = 6.3, H–C(4)$_\alpha$); 3.77 (*m*, 1 H–C(6), 2 H–C(1″)); 3.38 (*m*, 1 H–C(6)); 2.65 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.43 (*s*, *t*-Bu); 1.33 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 140.8 (*s*, arom. C); 134.6 (*s*, arom. C); 131.9 (*d*, ^1J(C,H) = 163, 2 arom. C); 129.5 (*d*, ^1J(C,H) = 165, 2 arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 158, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 158, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_β); 81.6 (*d*, ^1J(C,H) = 155, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 147, C(4)$_\alpha$); 65.2 (*d*, ^1J(C,H) = 146, C(4)$_\beta$); 54.3 (*t*, ^1J(C,H) = 134, C(1″)); 53.9 (*t*, ^1J(C,H) = 144, C(6)$_\beta$); 53.4 (*t*, ^1J(C,H) = 143, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 127, Me_3C); 28.1 (*q*, ^1J(C,H) = 124, Me) ; 25.8 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 398 (100, $[M+H]^+$), 397 (82, M^+), 363 (1), 341 (44), 297 (4), 266 (21), 243 (4), 187 (5), 142 (15), 125 (27), 89 (6). Anal. calc. for $C_{20}H_{29}ClN_2O_4$ (396.53): C 60.52, H 7.36, N 7.06; found: C 60.42, H 7.22, N 6.96.

*(2*R,*3*R,*4*S*)-2-[[(4-chlorobenzyl)amino]methyl]pyrrolidine-3,4-diol* (**3fn**). By *Method Aa*, with **9fn** (42 mg). FC (MeCN/NH_4OH 4:1) gave 27 mg (100% of **3fn**). $[\alpha]_{589}^{25} = +13$, $[\alpha]_{577}^{25} = +15$, $[\alpha]_{546}^{25} = +18$, $[\alpha]_{435}^{25} = +31$, $[\alpha]_{405}^{25} = +36$ (c = 0.78, MeOH). UV (MeCN): 221 (4720). IR (film): 3070, 1670, 1495, 1435, 1200, 1135, 1015, 840, 800, 725, 600. ^{1}H-NMR (400 MHz, MeOD): 7.49 (*d*, ^3J = 8.5, 2 arom. H); 7.42 (*d*, ^3J = 8.5, 2 arom. H); 4.26 (*m*, H–C(4)); 4.13 (*AB*, ^2J = 16.5, 2 H–C(1″)); 4.07 (*dd*, ^3J(3,4) = 3.9, ^3J(3,2) = 8.9, H–C(3)); 3.73 (*ddd*, ^3J(2,1′) = 4.4, ^3J(2,3) = 8.9, ^3J(2,1′) = 8.9, H–C(2)); 3.51 (*dd*, ^3J(5,4) = 3.9, ^2J = 12.6, 1 H–C(5)); 3.38–3.27 (*m*, 1 H–C(5), 2 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 136.6 (*s*, arom. C); 135.1 (*s*, arom. C); 133.0 (*d*, ^1J(C,H) = 162, 2 arom. C); 130.9 (*d*, ^1J(C,H) = 167, 2 arom. C); 76.2 (*d*, ^1J(C,H) = 143, C(3)); 71.4 (*d*, ^1J(C,H) = 151, C(4)); 60.4 (*d*, ^1J(C,H) = 146, C(2)); 53.5 (*t*, ^1J(C,H) = 141, C(1″)); 52.3 (*t*, ^1J(C,H) = 141, C(5)); 50–49 (C(1′)). CI-MS (NH_3): 257 (100, M^+), 211 (6), 180 (17), 154 (20), 142 (33), 133 (24), 116 (14), 102 (30), 85 (22).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-[[(2-Bromobenzyl)amino]methyl]tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9fo**). By *Method A*, with **8** (94 mg, 0.35 mmol), 2-bromobenzylamine (77 mg, 0.35 mmol), $NaBH(OAc)_3$ (103 mg, 0.49 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 92 mg (60% of **9fo**), 1.1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -32$, $[\alpha]_{577}^{25} = -33$, $[\alpha]_{546}^{25} = -37$, $[\alpha]_{435}^{25} = -55$, $[\alpha]_{405}^{25} = -76$ (c = 0.43, CH_2Cl_2) UV (MeCN): 218 (8385), 201 (1440), 196 (1490). IR (film): 3335, 2980, 2935, 1690, 1455, 1405, 1370, 1210, 1160, 1125, 1055, 975, 860, 755, 660. ^{1}H-NMR (400 MHz, MeOD): 7.61 (*d*, ^3J = 8.1, 1 arom. H); 7.47 (*d*, ^3J = 7.5, 1 arom. H); 7.39 (*m*, 1 arom. H); 7.22 (*t*, ^3J = 7.5, 1 arom. H); 4.77 (*m*, H–C(6a)); 4.67 (*d*, ^3J(3a,6a) = 6.0, H–C(3a)$_\alpha$); 4.63 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\beta$); 4.18 (*t*, ^3J(4,1′) = 6.2, H–C(4)$_\beta$); 4.09 (*t*, ^3J(4,1′) = 6.3, H–C(4)$_\alpha$); 3.91 (*s*, 2 H–C(1″)); 3.79 (*d*, ^2J = 12.9, 1 H–C(6), 1 H–C(6)$_\beta$); 3.41 (*d*, ^3J(6,6a) = 5.0, 1 H–C(6)$_\beta$); 3.38 (*d*, ^3J(6,6a) = 5.1, 1 H–C(6)$_\alpha$); 2.67 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.44 (*s*, (*t*-Bu)$_\beta$); 1.43 (*s*, (*t*-Bu)$_\alpha$); 1.33 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 140.7 (*s*, arom. C); 134.8 (*d*, ^1J(C,H) = 159, arom. C); 132.4 (*d*, ^1J(C,H) = 151, arom. C); 131.0 (*d*, ^1J(C,H) = 163, arom. C); 129.6 (*d*, ^1J(C,H) = 170, arom. C); 125.8 (*s*, arom. C); 113.4 (*s*); 85.6 (*d*, ^1J(C,H) = 157, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.2 (*s*, Me_3CO_α); 81.6 (*d*, ^1J(C,H) = 155, C(6a)$_\beta$); 80.6 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 146, C(4)$_\alpha$); 65.4 (*d*, ^1J(C,H) = 144, C(4)$_\beta$); 55.0 (*t*, ^1J(C,H) = 134, C(1″)); 53.9 (*t*, ^1J(C,H) = 144, C(6)$_\beta$); 53.3 (*t*, ^1J(C,H) = 142, C(6)$_\alpha$); 50–49 (C(1′)); 29.6 (*q*, ^1J(C,H) = 128, Me_3C); 28.1 (*q*, ^1J(C,H) = 128, 1 Me); 25.8 (*q*, ^1J(C,H) = 126, 1 Me). CI-MS (NH_3): 444 (67), 443 (100), 442 (78), 441 (71), 387 (19), 385 (22), 354 (10), 352 (7), 243 (8), 200 (22), 198 (23), 142 (13), 118 (5), 85 (7). Anal. calc. for $C_{20}H_{29}BrN_2O_4$ (441.39): C 54.43, H 6.62, N 6.35; found: C 54.61, H 65.61, N 6.40.

*(2*R,*3*R,*4*S*)-2-[[(2-Bromobenzyl)amino]methyl]pyrrolidine-3,4-diol* (**3fo**). By *Method Aa*, with **9fo** (79 mg). FC (MeCN/NH_4OH 4:1) gave 54 mg (100% of **3fo**). $[\alpha]_{589}^{25} = +3$, $[\alpha]_{577}^{25} = +7$, $[\alpha]_{546}^{25} = +9$ (c = 0.43, MeOH). UV (MeCN): 279 (10480), 259 (8630), 217 (2810). IR (film): 3200, 3065, 1670, 1440, 1200, 1135, 1030, 840, 800, 755, 720. ^{1}H-NMR (400 MHz, MeOD): 7.55 (*dd*, ^3J = 8.0, ^4J = 1.0, 1 arom. H); 7.55 (*dd*, ^3J = 7.6, ^4J = 1.5,

1 arom. H); 7.40 (*td*, ^3J = 7.6, ^4J = 1.0, 1 arom. H); 7.26 (*td*, ^3J = 8.0, ^4J = 1.5, 1 arom. H); 4.27 (*m*, H–C(4)); 4.10 (*s*, 2 H–C(1″)); 4.03 (*dd*, ^3J(3,4) = 4.0, ^3J(3,2) = 8.4, H–C(3)); 3.66 (*ddd*, ^3J(2,1′) = 3.9, ^3J(2,3) = 8.4, ^3J(2,1′) = 8.4, H–C(2)); 3.45 (*dd*, ^3J(5,4) = 4.0, ^2J = 12.6, 1 H–C(5)); 3.39–3.00 (*m*, 1 H–C(5), 2 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 134.9 (*d*, ^1J(C,H) = 167, arom. C); 132.7 (*d*, ^1J(C,H) = 161, arom. C); 132.4 (*s*, arom. C); 131.6 (*d*, ^1J(C,H) = 165, arom. C); 129.9 (*d*, ^1J(C,H) = 164, arom. C); 126.0 (*s*, arom. C); 75.9 (*d*, ^1J(C,H) = 145, C(3)); 71.8 (*d*, ^1J(C,H) = 149, C(4)); 61.9 (*d*, ^1J(C,H) = 144, C(2)); 54.5 (*t*, ^1J(C,H) = 141, C(1″)); 51.8 (*t*, ^1J(C,H) = 143, C(5)); 50–49 (C(1′)). CI-MS (NH_3): 303 (37), 301 (38), 229 (15), 202 (34), 200 (51), 188 (82), 186 (100), 171 (31), 169 (30), 158 (25), 156 (28), 106 (74), 84 (55).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-{[(3-Bromobenzyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9fp**). By *Method A*, with **8** (153 mg, 0.56 mmol), 3-bromobenzylamine (126 mg, 0.56 mmol), $NaBH(OAc)_3$ (168 mg, 0.79 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt) gave 129 mg (52% of **9fp**), 1.2:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -29$, $[\alpha]_{577}^{25} = -33$, $[\alpha]_{546}^{25} = -34$, $[\alpha]_{435}^{25} = -53$, $[\alpha]_{405}^{25} = -67$ (c = 0.78, CH_2Cl_2). UV (MeCN): 260 (1280), 219 (7725). IR (film): 3340, 2980, 2935, 1680, 1570, 1475, 1455, 1405, 1365, 1210, 1170, 1125, 1055, 860, 775, 685, 670. ^{1}H-NMR (400 MHz, MeOD): 7.57 (*s*, 1 arom. H); 7.42 (*m*, 1 arom. H); 7.31 (*m*, 1 arom. H); 7.25 (*m*, 1 arom. H); 4.75 (*m*, H–C(6a)); 4.65 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.59 (*d*, ^3J(3a,6a) = 5.7, H–C(3a)$_\beta$); 4.17 (*t*, ^3J(4,1′) = 6.5, H–C(4)$_\beta$); 4.05 (*t*, ^3J(4,1′) = 6.3, H–C(4)$_\alpha$); 3.84–3.73 (*m*, 1 H–C(6), 2 H–C(1″)); 3.38 (*m*, 1 H–C(6)); 2.62 (*m*, 2 H–C(1′)); 1.49 (*s*, 1 Me); 1.43 (*s*, (*t*-Bu)$_\alpha$); 1.42 (*s*, (*t*-Bu)$_\beta$); 1.32 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 144.8 (*s*, arom. C); 133.2 (*d*, ^1J(C,H) = 165, arom. C); 132.0 (*d*, ^1J(C,H) = 168, 2 arom. C); 129.0 (*d*, ^1J(C,H) = 164, arom. C); 124.3 (*s*, arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 158, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 158, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_β); 81.6 (*d*, ^1J(C,H) = 152, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 147, C(4)$_\alpha$); 65.2 (*d*, ^1J(C,H) = 147, C(4)$_\beta$); 54.4 (*t*, ^1J(C,H) = 136, C(1″)); 53.9 (*t*, ^1J(C,H) = 144, C(6)$_\beta$); 53.4 (*t*, ^1J(C,H) = 145, C(6)$_\alpha$); 50–49 (C(1′)); 29.6 (*q*, ^1J(C,H) = 126, Me_3C); 28.1 (*q*, ^1J(C,H) = 127, Me); 25.8 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 444 (83), 443 (100), 442 (62), 441 (74), 387 (28), 385 (32), 343 (19), 341 (20), 243 (7), 200 (18), 198 (19), 142 (16), 119 (3), 85 (9). Anal. calc. for $C_{20}H_{29}BrN_2O_4$ (441.39): C 54.43, H 6.62, N 6.35; found: C 54.52, H 6.71, N 6.32.

*(2*R,*3*R,*4*S*)-2-{[(3-Bromobenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fp**). By *Method Aa*, with **9fp** (100 mg). FC ($MeCN/NH_4OH$ 4:1) gave 68 mg (100% of **3fp**). $[\alpha]_{589}^{25} = +18$, $[\alpha]_{577}^{25} = +19$, $[\alpha]_{546}^{25} = +23$, $[\alpha]_{435}^{25} = +38$, $[\alpha]_{405}^{25} = +43$ (c = 0.43, MeOH). UV (MeCN): 275 (13430), 259 (10790), 216 (3330). IR (film): 3065, 1670, 1435, 1265, 1200, 1140, 840, 800, 735. ^{1}H-NMR (400 MHz, MeOD): 7.69 (*d*, ^4J = 1.4, 1 arom. H); 7.53 (*dd*, ^3J = 7.9, ^4J = 1.0, 1 arom. H); 7.45 (*dd*, ^3J = 7.7, ^4J = 1.0, 1 arom. H); 7.34 (*dd*, ^3J = 7.7, ^3J = 7.9, 1 arom. H); 4.28 (*m*, H–C(4)); 4.06 (*m*, H–C(3), 2 H–C(1″)); 3.72 (*ddd*, ^3J(2,1′) = 4.0, ^3J(2,3) = 8.8, ^3J(2,1′) = 8.8, H–C(2)); 3.51 (*dd*, ^3J(5,4) = 4.1, ^2J = 12.6, 1 H–C(5)); 3.35 (*m*, 1 H–C(5)); 3.30–3.20 (*m*, 2 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 140.6 (arom. C); 134.0 (arom. C); 133.2 (arom. C); 132.4 (arom. C); 129.8 (arom. C); 124.5 (arom. C); 76.0 (C(3)); 71.6 (C(4)); 61.2 (C(2)); 53.9 (C(1″)); 52.1 (C(5)); 50–49 (C(1′)). CI-MS (NH_3): 303 (97), 301 (100), 279 (1), 223 (11), 171 (4), 133 (9), 102 (18).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-{[(4-Bromobenzyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9fq**). By *Method A*, with **8** (102 mg, 0.37 mmol), 4-bromobenzylamine (83 mg, 0.37 mmol), $NaBH(OAc)_3$ (112 mg, 0.53 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt) gave 47 mg (28% of **9fq**), 1.1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -35$, $[\alpha]_{577}^{25} = -41$, $[\alpha]_{546}^{25} = -45$, $[\alpha]_{435}^{25} = -55$, $[\alpha]_{405}^{25} = -73$ (c = 0.31, CH_2Cl_2). UV (MeCN): 222 (16595). IR (film): 2980, 1685, 1460, 1405, 1160, 1055, 1010. ^{1}H-NMR (400 MHz, MeOD): 7.50 (*m*, 2 arom. H); 7.30 (*d*, ^3J = 8.5, 2 arom. H); 4.77 (*m*, H–C(6a)); 4.66 (*d*, ^3J(3a,6a) = 6.1, H–C(3a)$_\alpha$); 4.61 (*d*, ^3J(3a,6a) = 5.5, H–C(3a)$_\beta$); 4.15 (*t*, ^3J(4,1′) = 7.1, H–C(4)$_\beta$); 4.08 (*t*, ^3J(4,1′) = 6.5, H–C(4)$_\alpha$); 3.80–3.73 (*m*, 1 H–C(6), 2 H–C(1″)); 3.39 (*m*, 1 H–C(6)); 2.65 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.44 (*s*, (*t*-Bu)$_\alpha$); 1.43 (*s*, (*t*-Bu)$_\beta$); 1.33 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 141.3 (*s*, arom. C); 133.4 (*d*, ^1J(C,H) = 168, 2 arom. C); 132.2 (*d*, ^1J(C,H) = 158, 2 arom. C); 122.6 (*s*, arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 152, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 160, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_β); 81.6 (*d*, ^1J(C,H) = 153, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 160, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 146, C(4)$_\alpha$); 65.3 (*d*, ^1J(C,H) = 148, C(4)$_\beta$); 54.4 (*t*, ^1J(C,H) = 137, C(1″)); 53.9 (*t*, ^1J(C,H) = 144, C(6)$_\beta$); 53.4 (*t*, ^1J(C,H) = 142, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 126, Me_3C); 28.1 (*q*, ^1J(C,H) = 127, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 443 (100), 441 (83), 415 (3), 413 (3), 387 (19), 385 (23), 363 (6), 274 (16), 243 (4), 218 (19), 142 (10), 85 (5). Anal. calc. for $C_{20}H_{29}BrN_2O_4$ (441.39): C 54.43, H 6.62, N 6.35; found: C 54.70, H 6.61, N 6.43.

*(2*R,*3*R,*4*S*)-2-{[(4-Bromobenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fq**). By *Method Aa*, with **9fq** (30 mg). FC ($MeCN/NH_4OH$ 4:1) gave 20 mg (100% of **3fq**). $[\alpha]_{589}^{25} = +9$, $[\alpha]_{577}^{25} = +13$, $[\alpha]_{546}^{25} = +22$ (c = 0.26, MeOH). UV (MeCN): 275 (6000), 222 (6900). ^{1}H-NMR (400 MHz, MeOD): 7.60 (*d*, ^3J = 8.6, 2 arom. H); 7.43 (*d*, ^3J = 8.6, 2 arom. H); 4.28 (*ddd*, ^3J(4,5) = 1.4, ^3J(4,5) = 4.0, ^3J(4,3) = 4.0, H–C(4)); 4.12 (*AB*, ^2J = 11.2,

2 H–C(1″)); 4.08 (*dd*, ^3J(3,4) = 4.0, ^3J(3,2) = 8.9, H–C(3)); 3.74 (*ddd*, ^3J(2,1′) = 4.4, ^3J(2,3) = 8.9, ^3J(2,1′) = 8.9, H–C(2)); 3.52 (*dd*, ^3J(5,4) = 4.0, ^2J = 12.6, 1 H–C(5)); 3.39–3.29 (*m*, 1 H–C(5), 2 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 135.9 (*s*, arom. C); 133.9 (*d*, ^1J(C,H) = 168, 2 arom. C); 133.3 (*d*, ^1J(C,H) = 163, 2 arom. C); 124.6 (*s*, arom. C); 76.3 (*d*, ^1J(C,H) = 143, C(3)); 71.5 (*d*, ^1J(C,H) = 151, C(4)); 60.5 (*d*, ^1J(C,H) = 148, C(2)); 53.6 (*t*, ^1J(C,H) = 141, C(1″)); 52.2 (*t*, ^1J(C,H) = 136, C(5)); 50–49 (C(1′)). CI-MS (NH_3): 303 (96), 301 (100), 279 (3), 223 (14), 188 (10), 186 (11), 133 (23), 102 (20).

tert-*Butyl (3a*R,*4*S,*6a*S*)-4-{[(2-Chloro-6-fluorobenzyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9fr**). By *Method A*, with **8** (82 mg, 0.30 mmol), 2-chloro-6-fluorobenzylamine (48 mg, 0.30 mmol), $NaBH(OAc)_3$ (89 mg, 0.42 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt/light petroleum ether 8:2) gave 87 mg (69% of **9fr**), 1.2:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -41$, $[\alpha]_{577}^{25} = -42$, $[\alpha]_{546}^{25} = -48$, $[\alpha]_{435}^{25} = -73$, $[\alpha]_{405}^{25} = -92$ (*c* = 0.46, CH_2Cl_2). UV (MeCN): 273 (1745), 266 (1935), 220 (9940). IR (film): 3340, 3085, 2980, 2935, 1700, 1605, 1580, 1455, 1405, 1245, 1210, 1170, 1125, 1055, 860, 780, 725. ^{1}H-NMR (400 MHz, MeOD): 7.32 (*m*, 2 arom. H); 7.13 (*m*, arom. H); 4.73 (*m*, H–C(6a)); 4.61 (*d*, ^3J(3a,6a) = 5.7, H–C(3a)$_\alpha$); 4.58 (*d*, ^3J(3a,6a) = 5.6, H–C(3a)$_\beta$); 4.13 (*t*, ^3J(4,1′) = 6.0, H–C(4)$_\beta$); 4.05 (*t*, ^3J(4,1′) = 6.1, H–C(4)$_\alpha$); 4.00 (br. *s*, 2 H–C(1″)); 3.76 (*d*, ^2J = 12.9, 1 H–C(6)); 3.36 (*m*, 1 H–C(6)); 2.64 (*m*, 2 H–C(1′)); 1.47 (*s*, 1 Me); 1.43 (*s*, (*t*-Bu)$_\alpha$); 1.41 (*s*, (*t*-Bu)$_\beta$); 1.30 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 163.9 (*d*, ^1J(C,F) = 242, arom. C); 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 137.4 (*s*, arom. C); 131.7 (*d*, ^1J(C,H) = 166, arom. C); 127.5 (*d*, ^1J(C,H) = 170, arom. C); 127.2 (*d*, ^2J(C,F) = 29, arom. C); 116.1 (*dd*, ^1J(C,H) = 161, ^2J(C,F) = 20, arom. C); 113.4 (*s*); 85.7 (*d*, ^1J(C,H) = 158, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 158, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_β); 81.6 (*d*, ^1J(C,H) = 155, C(6a)$_\beta$); 80.8 (*d*, ^1J(C,H) = 159, C(6a)$_\alpha$); 66.0 (*d*, ^1J(C,H) = 147, C(4)$_\alpha$); 65.5 (*d*, ^1J(C,H) = 147, C(4)$_\beta$); 53.9 (*t*, ^1J(C,H) = 145, C(6)$_\beta$); 53.3 (*t*, ^1J(C,H) = 144, C(6)$_\alpha$); 50–49 (C(1′)); 45.5 (*t*, ^1J(C,H) = 139, C(1″)); 29.5 (*q*, ^1J(C,H) = 128, *Me*$_3$C); 28.1 (*q*, ^1J(C,H) = 128, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 416 (100, $[M+H]^+$), 415 (80, M^+), 383 (5), 359 (37), 313 (4), 271 (3), 243 (13), 215 (6), 172 (35), 143 (25), 107 (3), 85 (12). Anal. calc. for $C_{20}H_{28}ClFN_2O_4$ (414.92): C 57.90, H 6.80, N 6.75; found: C 57.99, H 6.72, N 6.61.

*(2*R,*3*R,*4*S*)-2-{[(2-Chloro-6-fluorobenzyl)amino]methyl}pyrrolidine-3,4-diol* (**3fr**). By *Method Aa*, with **9fr** (30 mg). FC (MeCN/NH_4OH 4:1) gave 20 mg (100% of **3fr**). $[\alpha]_{589}^{25} = +10$, $[\alpha]_{577}^{25} = +13$, $[\alpha]_{546}^{25} = +17$ (*c* = 0.59, MeOH). UV (MeCN): 273 (14075), 216 (4460). IR (film): 3065, 1670, 1650, 1470, 1205, 1145, 840, 800, 725. ^{1}H-NMR (400 MHz, MeOD): 7.44–7.34 (*m*, 2 arom. H); 7.18 (*t*, ^3J = 8.4, 2 arom. H); 4.26 (*m*, H–C(4)); 4.21 (*s*, 2 H–C(1″)); 4.03 (*dd*, ^3J((3,4) = 3.9, ^3J(3,2) = 8.6, H–C(3)); 3.66 (*ddd*, ^3J(2,1′) = 3.9, ^3J(2,3) = 8.6, ^3J(2,1′) = 8.6, H–C(2)); 3.46 (*dd*, ^3J(5,4) = 3.9, ^2J = 12.5, H–C(5)); 3.29 (*dd*, ^3J(5,4) = 1.6, ^2J = 12.5, H–C(5)); 3.21 (*dd*, ^3J(1′,2) = 3.9, ^2J = 13.3, 1 H–C(1′)); 3.12 (*m*, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 164.1 (*d*, ^1J(C,F) = 248, arom. C); 137.7 (*s*, arom. C); 132.7 (*d*, ^1J(C,H) = 165, arom. C); 127.7 (*d*, ^1J(C,H) = 169, arom. C); 120.4 (*s*, arom. C); 116.4 (*dd*, ^1J(C,H) = 165, ^2J(C,F) = 23, arom. C); 76.0 (*d*, ^1J(C,H) = 144, C(3)); 71.7 (*d*, ^1J(C,H) = 153, C(4)); 61.7 (*d*, ^1J(C,H) = 146, C(2)); 51.9 (*t*, ^1J(C,H) = 145, C(5)); 50–49 (C(1′)); 45.1 (*t*, ^1J(C,H) = 144, C(1″)). CI-MS (NH_3): 275 (100, M^+), 257 (12, $[M-H_2O]^+$), 239 (6), 205 (5), 177 (25), 160 (42), 143 (27), 126 (35), 102 (17).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-{[([1,1′-Biphenyl]-4-ylmethyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9fs**). By *Method B*, with **10** (104 mg, 0.38 mmol), [1,1′-biphenyl]-4-carboxaldehyde (70 mg, 0.38 mmol), $NaBH(OAc)_3$ (113 mg, 0.53 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 124 mg (74% of **9fs**), 1.3:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -30$, $[\alpha]_{577}^{25} = -32$, $[\alpha]_{546}^{25} = -36$, $[\alpha]_{435}^{25} = -67$, $[\alpha]_{405}^{25} = -84$ (*c* = 0.45, CH_2Cl_2). UV (MeCN): 251 (22873), 215 (17570). IR (film): 3020, 2935, 1690, 1455, 1410, 1370, 1215, 1160, 1130, 1055, 775, 755, 670. ^{1}H-NMR (400 MHz, MeOD): 7.61 (*m*, 4 arom. H); 7.42 (*m*, 4 arom. H); 7.34 (*m*, 1 arom. H); 4.74 (*m*, H–C(6a)); 4.65 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.59 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\beta$); 4.20 (*t*, ^3J(4,1′) = 6.7, H–C(4)$_\beta$); 4.09 (*t*, ^3J(4,1′) = 6.3, H–C(4)$_\alpha$); 3.80 (*m*, 1 H–C(6), 2 H–C(1″)); 3.38 (*m*, 1 H–C(6)); 2.66 (*m*, 2 H–C(1′)); 1.49 (*s*, 1 Me); 1.42 (*s*, (*t*-Bu)$_\alpha$); 1.41 (*s*, (*t*-Bu)$_\beta$); 1.26 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.3 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 143.1 (*s*, arom. C); 142.6 (*s*, arom. C); 141.0 (*s*, arom. C); 130.8 (*d*, ^1J(C,H) = 162, arom. C); 129.2 (*d*, ^1J(C,H) = 160, arom. C); 128.7 (*d*, ^1J(C,H) = 159, arom. C); 113.4 (*s*); 85.6 (*d*, ^1J(C,H) = 157, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 155, C(3a)$_\beta$); 82.0 (*s*, Me_3CO_β); 81.9 (*s*, Me_3CO_α); 81.7 (*d*, (C,H) = 50, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 159, C(6a)$_\alpha$); 66.0 (*d*, ^1J(C,H) = 146, C(4)$_\alpha$); 65.3 (*d*, ^1J(C,H) = 149, C(4)$_\beta$); 54.8 (*t*, ^1J(C,H) = 131, C(1″)); 53.9 (*d*, ^1J(C,H) = 143, C(6)$_\beta$); 53.4 (*d*, ^1J(C,H) = 144, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 127, *Me*$_3$C); 28.1 (*q*, ^1J(C,H) = 126, Me); 25.8 (*q*, ^1J(C,H) = 125, Me). CI-MS (NH_3): 439 (100, $[M+H]^+$), 383 (6), 339 (2), 273 (10), 215 (13), 196 (31), 167 (93), 142 (36), 85 (14). Anal. calc. for $C_{26}H_{34}N_2O_4$ (438.60): C 71.21, H 7.81; found: C 71.19, H 7.73.

*(2*R,*3*R,*4*S*)-2-{[([1,1′-Biphenyl]-4-ylmethyl)amino]methyl}pyrrolidine-3,4-diol* (**3fs**). By *Method Aa*, from **9fs** (44 mg). FC (MeCN/NH_4OH 4:1) gave 30 mg (100% of **3fs**). $[\alpha]_{589}^{25} = +21$, $[\alpha]_{577}^{25} = +23$, $[\alpha]_{546}^{25} = +24$,

$[\alpha]_{435}^{25} = +38$, $[\alpha]_{405}^{25} = +40$ ($c = 0.37$, MeOH). UV (MeCN): 260 (9050), 253 (9660), 211 (10000). IR (film): 3420, 1685, 1410, 1205, 1140, 840, 800, 765, 725, 700. ^{1}H-NMR (400 MHz, MeOD): 7.67 (*m*, 4 arom. H); 7.54 (*m*, 2 arom. H); 7.46 (*m*, 2 arom. H); 7.36 (*m*, arom. H); 4.25 (*ddd*, $^3J(4,5) = 1.7$, $^3J(4,3) = 4.0$, $^3J(4,5) = 4.0$, H–C(4)); 4.09 (*AB*, 2 H–C(1″)); 4.03 (*dd*, $^3J(3,4) = 4.0$, $^3J(3,2) = 8.5$, H–C(3)); 3.67 (*ddd*, $^3J(2,1') = 4.1$, $^3J(2,3) = 8.7$, $^3J(2,1') = 8.7$, H–C(2)); 3.46 (*dd*, $^3J(5,4) = 4.0$, $^2J = 12.6$, 1 H–C(5)); 3.29–3.25 (*m*, 1 H–C(1′), 1 H–C(5)); 3.15 (*dd*, $^3J(1',2) = 8.9$, $^2J = 13.3$, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 143.3 (arom. C); 142.7 (arom. C); 137.0 (arom. C); 131.5, 130.8, 129.4, 129.2, 128.8 (9 arom. C); 76.2 (C(3)); 71.8 (C(4)); 61.3 (C(2)); 54.2 (C(1″)); 52.1 (C(5)); 50–49 (C(1′)). CI-MS (NH_3): 299 (100, M^+), 280 (8), 265 (3), 229 (3), 211 (21), 184 (9), 167 (67), 152 (6), 115 (4), 85 (17).

tert-*Butyl (3a*R,*4*R,*6a*S)*-4-[(Benzhydrylamino)methyl]tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]-pyrrole-5-carboxylate* (**9ft**). By *Method A*, with **8** (138 mg, 0.51 mmol), α-phenylbenzenemethanamine (93 mg, 0.51 mmol), $NaBH(OAc)_3$ (151 mg, 0.71 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt/light petroleum ether 2:8) gave 174 mg (78% of **9ft**), 1.5:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -21$, $[\alpha]_{577}^{25} = -26$, $[\alpha]_{546}^{25} = -27$, $[\alpha]_{435}^{25} = -49$, $[\alpha]_{405}^{25} = -59$ ($c = 0.54$, CH_2Cl_2). UV (MeCN): 208 (16775). IR (film): 3060, 2980, 2935, 1690, 1490, 1455, 1410, 1265, 1210, 1170, 1125, 1055, 870, 740, 705. ^{1}H-NMR (400 MHz, MeOD): 7.41 (*m*, 4 arom. H); 7.32 (*m*, 4 arom. H); 7.21 (*m*, 2 arom. H); 4.86 (*m*, H–C(1″)); 4.72 (*m*, H–C(6a)); 4.65 (*d*, ^3J(3a,6a) = 5.9, H–C(3a)$_\alpha$); 4.57 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\beta$); 4.19 (*t*, $^3J(4,1') = 6.4$, H–C(4)$_\beta$); 4.13 (*t*, $^3J(4,1') = 6.5$, H–C(4)$_\alpha$); 3.78 (*m*, 1 H–C(6)); 3.41 (*d*, ^3J(6,6a) = 4.9, H–C(6)$_\beta$); 3.38 (*d*, ^3J(6,6a) = 5.0, H–C(6)$_\alpha$); 2.65 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.43 (*s*, (*t*-Bu)$_\beta$); 1.38 (*s*, (*t*-Bu)$_\alpha$); 1.32 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 146.1 (*s*, 2 arom. C); 130.3 (*d*, ^1J(C,H) = 154, 4 arom. C); 129.3, 129.1 (*d*, ^1J(C,H) = 158, 4 arom. C); 128.9 (*d*, ^1J(C,H) = 145, 2 arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 156, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 158, C(3a)$_\beta$); 82.2 (*s*, Me_3CO_β); 82.1 (*s*, Me_3CO_α); 81.6 (*d*, ^1J(C,H) = 155, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 69.2 (*d*, ^1J(C,H) = 136, C(1″)$_\alpha$); 69.0 (*d*, ^1J(C,H) = 136, C(1″)$_\beta$); 66.2 (*d*, ^1J(C,H) = 147, C(4)$_\alpha$); 65.5 (*d*, ^1J(C,H) = 146, C(4)$_\beta$); 54.1 (*t*, ^1J(C,H) = 144, C(6)$_\beta$); 53.5 (*t*, ^1J(C,H) = 143, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 127, Me_3C); 28.1 (*q*, ^1J(C,H) = 127, Me); 25.9 (*q*, ^1J(C,H) = 129, Me). CI-MS (NH_3): 440 (100, $[M + H]^+$), 439 (76, M^+), 383 (24), 337 (2), 271 (1), 215 (13), 167 (53), 142 (7), 91 (5). Anal. calc. for $C_{26}H_{34}N_2O_4$ (438.59): C 71.21, H 7.81; found: C 71.27, H 7.73.

*(2*R,*3*R,*4*S*)-2-[(Benzhydrylamino)methyl]pyrrolidine-3,4-diol* (**3ft**). By *Method Aa*, with **9ft** (32 mg). FC ($MeCN/NH_4OH$ 4:1) gave 21 mg (100% of **3ft**). $[\alpha]_{589}^{25} = +30$, $[\alpha]_{577}^{25} = +32$, $[\alpha]_{546}^{25} = +35$, $[\alpha]_{435}^{25} = +42$ ($c = 0.35$, MeOH). UV (MeCN): 223 (88300), 203 (1385). IR (film): 3305, 3030, 1675, 1455, 1205, 1135, 840, 800, 720, 705. ^{1}H-NMR (400 MHz, MeOD): 7.44 (*m*, 4 arom. H); 7.34 (*m*, 4 arom. H); 7.24 (*m*, 2 arom. H); 4.91 (*s*, H–C(1″)); 4.20 (*ddd*, $^3J(4,5) = 2.4$, $^3J(4,5) = 4.4$, $^3J(4,3) = 4.4$, H–C(4)); 3.92 (*dd*, $^3J(3,4) = 4.4$, $^3J(3,2) = 8.5$, H–C(3)); 3.50 (*ddd*, $^3J(2,1') = 4.3$, $^3J(2,3) = 8.5$, $^3J(2,1') = 8.5$, H–C(2)); 3.38 (*dd*, $^3J(5,4) = 4.4$, $^2J = 12.4$, 1 H–C(5)); 3.17 (*dd*, $^3J(5,4) = 2.4$, $^2J = 12.4$, 1 H–C(5)); 2.95 (*dd*, $^3J(1',2) = 4.3$, $^2J = 13.0$, 1 H–C(1′)); 2.77 (*dd*, $^3J(1',2) = 8.5$, $^2J = 13.0$, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 145.8 (*s*, arom. C); 145.7 (*s*, arom. C); 130.4 (*d*, ^1J(C,H) = 149, 4 arom. C); 129.3 (*d*, ^1J(C,H) = 156, 4 arom. C); 129.0 (*d*, ^1J(C,H) = 164, 2 arom. C); 76.1 (*d*, ^1J(C,H) = 145, C(3)); 72.2 (*d*, ^1J(C,H) = 153, C(4)); 69.1 (*d*, ^1J(C,H) = 136, C(1″)); 63.3 (*d*, ^1J(C,H) = 145, C(2)); 52.0 (*t*, ^1J(C,H) = 147, C(5)); 50–49 (C(1′)). CI-MS (NH_3): 299 (100, $[M+H]^+$), 226 (2), 196 (15), 182 (24), 167 (51), 133 (3), 120 (8), 102 (15), 85 (8).

tert-*Butyl (3a*R,*4*R,*6a*S)*-4-[(1*R*)2,3-Dihydro-1*H*-inden-1-ylamino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9fu**). By *Method A*, with **8** (179 mg, 0.66 mmol), (1*R*)-2,3-dihydro-1*H*-inden-1-amine (88 mg, 0.66 mmol), $NaBH(OAc)_3$ (196 mg, 0.92 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt) gave 179 mg (70% of **9fu**), 1.1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -63$, $[\alpha]_{577}^{25} = -66$, $[\alpha]_{546}^{25} = -67$, $[\alpha]_{435}^{25} = -104$, $[\alpha]_{405}^{25} = -180$ ($c = 0.53$, CH_2Cl_2). UV (MeCN): 272 (3015), 266 (3110), 217 (10235), 203 (1695). IR (film): 3330, 2980, 2935, 1695, 1475, 1455, 1405, 1365, 1210, 1160, 1125, 1055, 975, 860, 750. ^{1}H-NMR (400 MHz, MeOD): 7.38 (*m*, 1 arom. H); 7.25 (*m*, 3 arom. H); 4.77 (*m*, H–C(6a)); 4.71 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.67 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\beta$); 4.31 (*t*, $^3J(1'',2'') = 6.6$, H–C(1″)); 4.18 (*t*, $^3J(4,1') = 6.6$, H–C(4)$_\beta$); 4.11 (*t*, $^3J(4,1') = 6.5$, H–C(4)$_\alpha$); 3.82 (*d*, ^3J(6,6a) = 6.7, 1 H–C(6)$_\beta$); 3.78 (*d*, ^3J(6,6a) = 6.9, 1 H–C(6)$_\alpha$); 3.44 (*m*, 1 H–C(6)$_\alpha$, 1 H–C(6)$_\beta$); 3.06 (*m*, 1 H–C(3″)); 2.87–2.75 (*m*, 1 H–C(3″), 2 H–C(1′)); 2.39 (*m*, 1 H–C(2″)); 1.90 (*m*, 1 H–C(2″)); 1.51 (*s*, 1 Me); 1.48 (*s*, (*t*-Bu)$_\beta$); 1.44 (*s*, (*t*-Bu)$_\alpha$); 1.34 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\alpha$); 157.2 (*s*, $NCOO_\beta$); 146.3 (*s*, arom. C); 145.8 (*s*, arom. C); 129.5 (*d*, ^1J(C,H) = 159, arom. C); 128.2 (*d*, ^1J(C,H) = 154, arom. C); 126.6 (*d*, ^1J(C,H) = 157, arom. C); 126.0 (*d*, ^1J(C,H) = 152, arom. C); 113.4 (*s*); 85.5 (*d*, ^1J(C,H) = 158, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.2 (*s*, Me_3CO_α); 81.5 (*d*, ^1J(C,H) = 157, C(6a)$_\beta$); 80.8 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 66.1 (*d*, ^1J(C,H) = 144, C(4)$_\alpha$); 65.6 (*d*, ^1J(C,H) = 144, C(4$_\beta$)); 65.0 (*d*, ^1J(C,H) = 139, C(1″)$_\alpha$); 64.8 (*d*, ^1J(C,H) = 142, C(1″)$_\beta$); 53.9 (*t*, ^1J(C,H) = 144, C(6)$_\beta$); 53.4 (*t*, ^1J(C,H) = 144, C(6)$_\alpha$); 48.5 (*t*, ^1J(C,H) = 136, C(1′)$_\beta$); 48.2

(t, ^1J(C,H) = 134, C(1′)$_\alpha$); 34.5 (t, ^1J(C,H) = 130, C(2″)$_\alpha$); 34.4 (t, ^1J(C,H) = 129, C(2″)$_\beta$); 32.0 (t, ^1J(C,H) = 131, C(3″)); 29.5 (q, ^1J(C,H) = 127, *Me*$_3$C); 28.1 (q, ^1J(C,H) = 127, Me); 25.8 (q, ^1J(C,H) = 127, Me). CI-MS (NH_3): 390 (100, $[M+H]^+$), 389 (81, M^+), 363 (3), 333 (28), 289 (15), 242 (4), 215 (10), 179 (6), 117 (33), 91 (6). Anal. calc. for $C_{22}H_{32}N_2O_4$ (388.53): C 68.01, H 8.30, N 7.21; found: C 67.93, H 8.25.

*(2*R*,3*R*,4*S*)-2-{[(1*R*)-2,3-Dihydro-1*H*-inden-1-ylamino]methyl}pyrrolidine-3,4-diol* (**3fu**). By *Method Aa*, with **9fu** (40 mg). FC (MeCN/NH_4OH 4:1) gave 25 mg (100% of **3fu**). $[\alpha]^{25}_{589} = +10$, $[\alpha]^{25}_{577} = +16$, $[\alpha]^{25}_{546} = +18$, $[\alpha]^{25}_{435} = +23$ ($c = 0.36$, MeOH). UV (MeCN): 272 (1010), 218 (3590), 204 (670). IR (film): 3090, 2860, 1695, 1670, 1650, 1435, 1190, 1150, 1025, 975, 840, 800, 760, 725. ^{1}H-NMR (400 MHz, MeOD): 7.55 (d, $^3J = 7.3$, arom. H); 7.30 (m, 3 arom. H); 4.66 (dd, ^3J(1″,2″) = 5.0, ^3J(1″,2″) = 7.3, H−C(1″)); 4.26 (ddd, ^3J(4,5) = 1.3, ^3J(4,5) = 4.0, ^3J(4,3) = 4.0, H−C(4)); 4.07 (dd, ^3J(3,4) = 4.0, ^3J(3,2) = 8.7, H−C(3)); 3.70 (ddd, ^3J(2,1′) = 4.1, ^3J(2,3) = 8.7, ^3J(2,1′) = 8.7, H−C(2)); 3.48 (dd, ^3J(5,4) = 4.0, $^2J = 12.6$, 1 H−C(5)); 3.37 (m, 1 H−C(5), 2 H−C(1′)); 3.18 (m, 1 H−C(3″)); 2.95 (m, 1 H−C(3″)); 2.52 (m, 1 H−C(2″)); 2.14 (m, 1 H−C(2″)). ^{13}C-NMR (100.6 MHz, MeOD): 146.6 (s, arom. C); 141.9 (s, arom. C); 131.0 (d, ^1J(C,H) = 160, arom. C); 128.7 (d, ^1J(C,H) = 166, arom. C); 127.1 (d, ^1J(C,H) = 161, 2 arom. C); 76.3 (d, ^1J(C,H) = 144, C(3)); 71.6 (d, ^1J(C,H) = 155, C(4)); 65.6 (d, ^1J(C,H) = 146, C(1″)); 61.1 (d, ^1J(C,H) = 146, C(2)); 52.2 (t, ^1J(C,H) = 146, C(5)); 47.3 (t, ^1J(C,H) = 141, C(1′)); 32.5 (t, ^1J(C,H) = 132, C(2″)); 31.9 (t, ^1J(C,H) = 132, C(3″)). CI-MS (NH_3): 249 (100, $[M+H]^+$), 229 (20), 211 (26), 195 (2), 146 (14), 133 (38), 117 (51), 102 (28), 85 (20).

*(2*R*,3*R*,4*S*)-2-{[(9-Anthrylmethyl)amino]methyl}pyrrolidine-3,4-diol* (**3fv**). By *Method B*, with **10** (113 mg, 0.41 mmol), anthracene-9-carboxaldehyde (86 mg, 0.41 mmol), $NaBH(OAc)_3$ (123 mg, 0.58 mmol), and $ClCH_2CH_2Cl$ (4 ml). Then by *Method Aa*, with crude **9fv** (45 mg). FC (MeCN/NH_4OH 4:1) gave 30 mg (100% of **3fv**). $[\alpha]^{25}_{589} = +5$, $[\alpha]^{25}_{577} = +8$, $[\alpha]^{25}_{546} = +12$ ($c = 0.10$, CH_2Cl_2). UV (MeCN): 272 (10130), 255 (9015), 215 (3140). ^{1}H-NMR (400 MHz, MeOD): 8.62 (s, 1 arom. H); 8.49 (d, $^3J = 8.9$, 2 arom. H); 8.13 (d, $^3J = 8.5$, 2 arom. H); 7.65 (m, 2 arom. H); 7.57 (m, 2 arom. H); 5.10 (*AB*, H−C(1″)); 4.26 (ddd, ^3J(4,5) = 1.8, ^3J(4,5) = 4.0, ^3J(4,3) = 4.0, H−C(4)); 4.07 (dd, ^3J(3,4) = 4.0, ^3J(3,2) = 8.4, H−C(3)); 3.73 (ddd, ^3J(2,1′) = 4.3, ^3J(2,3) = 8.4, ^3J(2,1′) = 8.4, H−C(2)); 3.48 (m, 1 H−C(5), 2 H−C(1′)); 3.29 (dd, ^3J(5,4) = 1.8, $^2J = 12.5$, 1 H−C(5)). ^{13}C-NMR (100.6 MHz, MeOD): 136.3 (arom. C); 133.9 (arom. C); 132.9 (arom. C); 131.3 (2 arom. C); 130.8 (arom. C); 128.8 (2 arom. C); 127.2 (2 arom. C); 127.0 (arom. C); 125.7 (2 arom. C); 76.3 (C(3)); 71.7 (C(4)); 61.4 (C(2)); 52.1 (C(1′)); 50–49 (C(5)); 46.5 (C(1″)). CI-MS (NH_3): 322 (11, M^+), 251 (4), 208 (100), 192 (50), 180 (42), 152 (45), 115 (46), 102 (70), 91 (44).

tert-*Butyl(3a*R*,4*R*,6a*S*)-Tetrahydro-2,2-dimethyl-4{[(2-phenylethyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-*c*]-pyrrole-5-carboxylate* (**9g**). By *Method A*, with **8** (85 mg, 0.31 mmol), 2-phenylethylamine (38 mg, 0.31 mmol), $NaBH(OAc)_3$ (93 mg, 0.44 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 80 mg (68% of **9g**), 1.05:1 mixture of rotamers α and β. $[\alpha]^{25}_{589} = -32$, $[\alpha]^{25}_{577} = -35$, $[\alpha]^{25}_{546} = -43$, $[\alpha]^{25}_{435} = -75$, $[\alpha]^{25}_{405} = -93$ ($c = 0.40$, CH_2Cl_2). UV (MeCN): 210 (9065). IR (film): 3585, 2980, 2935, 1690, 1455, 1410, 1370, 1215, 1170, 1125, 1055, 860, 755, 700, 665. ^{1}H-NMR (400 MHz, MeOD): 7.25 (m, 5 arom. H); 4.71 (m, H−C(6a)); 4.57 (m, H−C(3a)); 4.13 (dd, ^3J(4,1′) = 6.6, ^3J(4,1′) = 6.4, H−C(4)$_\beta$); 4.08 (dd, ^3J(4,1′) = 6.6, ^3J(4,1′) = 6.5, H−C(4)$_\alpha$); 3.80 (d, ^2J = 12.9, 1 H−C(6)$_\alpha$); 3.76 (d, $^2J = 13.1$, 1 H−C(6)$_\beta$); 3.28 (m, 1 H−C(6), 1 H−C(6)$_\beta$); 2.88–2.80 (m, 2 H−C(1″), 2 H−C(2″)); 2.67 (m, 2 H−C(1′)); 1.47 (s, (*t*-Bu)$_\beta$); 1.45 (s, (*t*-Bu)$_\alpha$); 1.41 (s, 1 Me); 1.30 (s, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.4 (s, $NCOO_\beta$); 157.3 (s, $NCOO_\alpha$); 141.9 (s, arom. C); 130.6 (d, ^1J(C,H) = 157, arom. C); 130.5 (d, ^1J(C,H) = 160, arom. C); 130.4 (d, ^1J(C,H) = 160, arom. C); 128.2 (d, ^1J(C,H) = 161, arom. C); 128.1 (d, ^1J(C,H) = 161, arom. C); 113.4 (s); 85.5 (d, ^1J(C,H) = 158, C(3a)$_\alpha$); 84.9 (d, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (s, Me_3CO_α); 82.1 (s, Me_3CO_β); 81.6 (d, ^1J(C,H) = 153, C(6a)$_\beta$); 80.9 (d, ^1J(C,H) = 159, C(6a)$_\alpha$); 65.8 (d, ^1J(C,H) = 146, C(4)$_\alpha$); 65.3 (d, ^1J(C,H) = 146, C(4)$_\beta$); 53.8 (t, ^1J(C,H) = 143, C(6)$_\beta$); 53.1 (t, ^1J(C,H) = 142, C(6)$_\alpha$); 52.9, 52.8 (2t, ^1J(C,H) = 126, ^1J(C,H) = 127, C(1′), C(1″)); 37.7 (t, ^1J(C,H) = 129, C(2″)); 29.6 (q, ^1J(C,H) = 127, *Me*$_3$C); 28.0 (q, ^1J(C,H) = 126, Me); 25.8 (q, ^1J(C,H) = 127, Me). CI-MS (NH_3): 377 (100, $[M+H]^+$), 321 (41), 303 (5), 285 (16), 229 (22), 211 (1), 185 (23), 134 (32), 105 (30), 91 (14). Anal. calc. for $C_{21}H_{32}N_2O_4$ (376.53): C 66.99, H 8.57; found: C 67.01, H 8.46.

*(2*R*,3*R*,4*S*)-2-{[(2-Phenylethyl)amino]methyl}pyrrolidine-3,4-diol* (**3g**). By *Method Aa*, with **9g** (25 mg). FC (MeCN/NH_4OH 4:1) gave 16 mg (100% of **3g**). $[\alpha]^{25}_{589} = +12$, $[\alpha]^{25}_{577} = +13$, $[\alpha]^{25}_{546} = +13$, $[\alpha]^{25}_{435} = +30$, $[\alpha]^{25}_{405} = +35$ ($c = 0.32$, MeOH). UV (MeCN): 260 (475), 208 (4140). IR (film): 3030, 1675, 1435, 1205, 1135, 840, 800, 750, 725, 700. ^{1}H-NMR (400 MHz, MeOD): 7.38–7.27 (m, 5 arom. H); 4.25 (m, H−C(4)); 4.03 (dd, ^3J(3,4) = 4.1, ^3J(3,2) = 8.7, H−C(3)); 3.68 (ddd, ^3J(2,1′) = 4.3, ^3J(2,3) = 8.7, ^3J(2,1′) = 8.7, H−C(2)); 3.46 (dd, ^3J(5,4) = 3.8, $^2J = 12.6$, 1 H−C(5)); 3.40–3.20 (m, 2 H−C(1′), 2 H−C(1″), H−C(5)); 3.00 (t, ^3J(2″,1″) = 7.9, 2 H−C(2″)). ^{13}C-NMR (100.6 MHz, MeOD): 139.6 (s, arom. C); 130.6 (d, ^1J(C,H) = 161, 3 arom. C); 128.8 (d, ^1J(C,H) = 161, 2 arom. C); 76.4 (d, ^1J(C,H) = 145, C(3)); 71.7 (d, ^1J(C,H) = 154, C(4)); 60.2 (d, ^1J(C,H) =

148, C(2)); 52.0 (*t*, ^1J(C,H) = 148, C(1″)); 50–49 (C(1′), C(5)); 35.3 (*t*, ^1J(C,H) = 129, C(2″)). CI-MS (NH_3): 237 (100, $[M + H]^+$), 145 (5), 134 (20), 116 (3), 102 (21), 85 (18).

tert-*Butyl (3a*R,*4*R,*6a*S*)-Tetrahydro-2,2-dimethyl-4{[(3-phenylpropyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9h**). By *Method A*, with **8** (89 mg, 0.33 mmol), 3-phenylpropylamine (44 mg, 0.33 mmol), $NaBH(OAc)_3$ (97 mg, 0.46 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 53 mg (40% of **9h**), 1.1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -25$, $[\alpha]_{577}^{25} = -26$, $[\alpha]_{546}^{25} = -33$, $[\alpha]_{435}^{25} = -163$, $[\alpha]_{405}^{25} = -204$ ($c = 0.46$, CH_2Cl_2). UV (MeCN): 261 (1985), 210 (17890). IR (film): 3335, 2980, 2935, 1695, 1495, 1480, 1455, 1405, 1365, 1210, 1170, 1125, 1055, 975, 860, 745, 700. ^{1}H-NMR (400 MHz, MeOD): 7.28 (*m*, 5 arom. H); 4.76 (*m*, H–C(6a)); 4.60 (*m*, H–C(3a)); 4.17 (*t*, ^3J(4,1′) = 6.4, H–C(4)$_\beta$); 4.11 (*t*, ^3J(4,1′) = 6.9, H–C(4)$_\alpha$); 3.82 (*m*, 1 H–C(6)); 3.40 (*m*, 1 H–C(6)); 2.66 (*m*, 2 H–C(1′), 2 H–C(1″), 2 H–C(2″)); 1.85 (*m*, 2 H–C(3″)); 1.50 (*s*, *t*-Bu); 1.43 (*s*, 1 Me); 1.33 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.6 (*s*, $NCOO_\beta$); 157.3 (*s*, $NCOO_\alpha$); 144.1 (*s*, arom. C); 130.2 (*d*, ^1J(C,H) = 160, 4 arom. C); 127.7 (*d*, ^1J(C,H) = 161, arom. C); 113.5 (*s*); 85.4 (*d*, ^1J(C,H) = 156, C(3a)$_\alpha$); 84.8 (*d*, ^1J(C,H) = 156, C(3a)$_\beta$); 82.4 (*s*, Me_3CO_α); 82.2 (*s*, Me_3CO_β); 81.6 (*d*, ^1J(C,H) = 156, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.6 (*d*, ^1J(C,H) = 147, C(4)$_\alpha$); 65.2 (*d*, ^1J(C,H) = 145, C(4)$_\beta$); 53.7 (*t*, ^1J(C,H) = 144, C(6)$_\beta$); 53.1 (*t*, ^1J(C,H) = 145, C(6)$_\alpha$); 50–49 (C(1′), C(1″)); 35.4 (*t*, ^1J(C,H) = 127, C(2″)); 33.2 (*t*, ^1J(C,H) = 126, C(3″)); 29.6 (*q*, ^1J(C,H) = 127, Me_3C); 28.1 (*q*, ^1J(C,H) = 125, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 392 (100, $[M + H]^+$), 391 (89, M^+), 335 (27), 285 (2), 243 (5), 178 (13), 148 (35), 117 (4), 91 (25). Anal. calc. for $C_{22}H_{34}N_2O_4$ (390.55): C 67.70, H 8.78; found: C 67.66, H 8.66.

*(2*R,*3*R,*4*S*)-2-{[(3-Phenylpropyl)amino]methyl}pyrrolidine-3,4-diol* (**3h**). By *Method Aa*, with **9h** (20 mg). FC (MeCN/NH_4OH 4:1) gave 13 mg (100% of **3h**). $[\alpha]_{589}^{25} = +1$, $[\alpha]_{577}^{25} = +2$, $[\alpha]_{546}^{25} = +5$ ($c = 0.32$, MeOH). UV (MeCN): 322 (755), 216 (2490), 203 (640). IR (film): 3055, 1670, 1440, 1265, 1205, 1145, 1040, 845, 800, 740, 705. ^{1}H-NMR (400 MHz, MeOD): 7.35–7.20 (*m*, 5 arom. H); 4.24 (*ddd*, ^3J(4,5) = 1.5, ^3J(4,5) = 4.0, ^3J(4,3) = 4.0, H–C(4)); 4.04 (*dd*, ^3J(3,4) = 4.0, ^3J(3,2) = 8.8, H–C(3)); 3.68 (*ddd*, ^3J(2,1′) = 5.1, ^3J(2,3) = 8.8, ^3J(2,1′) = 8.8, H–C(2)); 3.48 (*dd*, ^3J(5,4) = 4.0, ^2J = 12.6, 1 H–C(5)); 3.38 (*m*, 2 H–C(1′)); 3.29 (*dd*, ^3J(5,4) = 1.5, ^2J = 12.6, 1 H–C(5)); 3.08 (*m*, 2 H–C(1″)); 2.75 (*t*, ^3J(3″, 2″) = 7.5, 2 H–C(3″)); 2.07 (*m*, 2 H–C(2″)). ^{13}C-NMR (100.6 MHz, MeOD): 142.6 (*s*, arom. C); 130.5 (*d*, ^1J(C,H) = 160, 2 arom. C); 130.2 (*d*, ^1J(C,H) = 160, 2 arom. C); 128.2 (*d*, ^1J(C,H) = 161, arom. C); 76.7 (*d*, ^1J(C,H) = 144, C(3)); 71.6 (*d*, ^1J(C,H) = 152, C(4)); 59.6 (*d*, ^1J(C,H) = 146, C(2)); 52.6 (*t*, ^1J(C,H) = 144, C(5)); 50–49 (C(1′), C(1″)); 34.5 (*t*, ^1J(C,H) = 129, C(3″)); 30.3 (*t*, ^1J(C,H) = 130, C(2″)). CI-MS (NH_3): 251 (100, $[M + H]^+$), 148 (9), 136 (2), 115 (2), 102 (18), 85 (21).

tert-*Butyl (3a*R,*4*R,*6a*S*)-Tetrahydro-2,2-dimethyl-4-{[(4-phenylbutyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9i**). By *Method A*, with **8** (130 mg, 0.48 mmol), 4-phenylbutylamine (76 µl, 0.48 mmol), $NaBH(OAc)_3$ (142 mg, 0.67 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 100 mg (52% of **9i**), 1.2:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -39$, $[\alpha]_{577}^{25} = -42$, $[\alpha]_{546}^{25} = -47$, $[\alpha]_{435}^{25} = -79$, $[\alpha_{405}^{25} = -94$ ($c = 0.35$, CH_2Cl_2). IR (film): 3325, 3000, 2980, 2935, 2860, 1695, 1605, 1495, 1455, 1405, 1365, 1210, 1170, 1125, 1055, 975, 860, 750, 700, 665. ^{1}H-NMR (400 MHz, MeOD): 7.30–7.16 (*m*, 5 arom. H); 4.71 (*m*, H–C(6a)); 4.58 (*m*, H–C(3a)); 4.14 (*m*, H–C(4)$_\beta$); 4.04 (*m*, H–C(4)$_\alpha$); 3.89 (*d*, ^2J = 12.9, 1 H–C(6)$_\alpha$); 3.78 (*d*, ^2J = 12.9, 1 H–C(6)$_\beta$); 3.35 (*dd*, ^3J(6,6a) = 5.1, ^2J = 12.9, 1 H–C(6)); 2.68–2.60 (*m*, 2 H–C(1′), 2 H–C(1″), 2 H–C(4″)); 1.68–1.61 (*m*, 2 H–C(2″)); 1.56–1.49 (*m*, 2 H–C(3″)); 1.46 (*s*, *t*-Bu); 1.45 (*s*, 1 Me); 1.31 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 154.6 (NCOO); 125.7 (arom. C); 111.5 (Me_2C); 83.9 (C(3a)$_\alpha$); 83.2 (C(3a)$_\beta$); 79.8 (Me_3CO); 79.5 (C(6a)$_\beta$); 78.8 (C(6a)$_\alpha$); 63.7 (C(4)$_\alpha$); 63.4 (C(4)$_\beta$); 52.4 (C(6)$_\beta$); 51.9 (C(6)$_\alpha$); 50.2 (C(1′)$_\alpha$); 49.8 (C(1′)$_\beta$); 49.8 (C(1″)); 35.8 (C(4″)); 29.8 (C(2″)); 29.1 (C(3″)); 28.4 (Me_3C); 27.0 (Me); 25.0 (Me). CI-MS (NH_3): 405 (100, $[M + H]^+$), 349 (21), 162 (71), 91 (67). Anal. calc. for $C_{23}H_{36}N_2O_4$ (404.55): C 68.29, H 8.97, N 6.92; found: C 68.16, H 8.95, N 6.92.

*(2*R,*3*R,*4*S*)-2-{[(4-Phenylbutyl)amino]methyl}pyrrolidine-3,4-diol* (**3i**). By *Method Aa*, with **9i** (20 mg). FC (MeCN/NH_4OH 4:1) gave 13 mg (100% of **3i**). $[\alpha]_{589}^{25} = +10$, $[\alpha]_{577}^{25} = +10$, $[\alpha]_{546}^{25} = +20$, $[\alpha]_{435}^{25} = +60$, $[\alpha]_{405}^{25} = +68$ ($c = 0.50$, H_2O). UV (MeCN): 209 (6100). IR (film): 3500–2800, 1670, 1440, 1205, 1135, 840, 800, 725, 700. ^{1}H-NMR (400 MHz, MeOD): 7.28–7.14 (*m*, 5 arom. H); 4.20 (*ddd*, ^3J(4,5) = 1.3, ^3J(4,5) = 4.1, ^3J(4,3) = 4.1, H–C(4)); 3.99 (*dd*, ^3J(3,4) = 4.1, ^3J(3,2) = 9.1, H–C(3)); 3.54 (*ddd*, ^3J(2,1′) = 5.0, ^3J(2,3) = 9.1, ^3J(2,1′) = 9.1, H–C(2)); 3.38–3.25 (*m*, 1 H–C(5), 2 H–C(1′)); 3.17 (*dd*, ^3J(5,4) = 1.3, ^2J = 13.2, 1 H–C(5)); 3.04–2.97 (*m*, 2 H–C(1″)); 2.57 (*m*, 2 H–C(4″)); 1.60 (*m*, 2 H–C(2″), 2 H–C(3″)). ^{13}C-NMR (100.6 MHz, MeOD): 144.7, 131.2, 131.1, 128.6 (arom. C); 76.8 (C(3)); 71.7 (C(4)); 59.0 (C(2)); 53.1 (C(5)); 50.9 (C(1″)); 50.1 (C(1′)); 36.8 (C(4″)); 27.5, 30.0 (C(2″), C(3″)). CI-MS (NH_3): 265 (100, $[M + H]^+$), 162 (78), 91 (99).

tert-*Butyl (3a*R,*4*R,*6a*S*)-4-{[(1-Benzylpiperidin-4-yl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9j**). By *Method A*, with **8** (100 mg, 0.37 mmol), 1-benzylpiperidin-4-amine (76 µl, 0.37 mmol), $NaBH(OAc)_3$ (110 mg, 0.52 mmol), and $ClCH_2CH_2Cl$ (2.5 ml). FC (CH_2Cl_2/MeOH 4:1):

125 mg (76% of **9j**), 1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -26$, $[\alpha]_{577}^{25} = -32$, $[\alpha]_{546}^{25} = -35$, $[\alpha]_{435}^{25} = -59$, $[\alpha]_{405}^{25} = -69$ ($c = 0.29$, CH_2Cl_2). UV (MeCN): 217 (26400), 190 (2520). IR (film): 2980, 2935, 2800, 1695, 1455, 1405, 1215, 1200, 1120, 1055, 980, 860, 740, 700. ^{1}H-NMR (400 MHz, MeOD): 7.36–7.27 (*m*, 5 arom. H); 4.74 (*m*, H–C(6a)); 4.64 (*d*, ^3J(3a,6a) = 5.9, H–C(3a)$_\beta$); 4.61 (*d*, ^3J(3a,6a) = 5.9, H–C(3a)$_\alpha$); 4.12 (*m*, H–C(4)$_\beta$); 4.07 (*m*, H–C(4)$_\alpha$); 3.82 (*d*, ^2J = 12.6, 1 H–C(6)$_\beta$); 3.79 (*d*, ^2J = 12.7, 1 H–C(6)$_\alpha$); 3.57 (*s*, ArCH_2); 3.41 (*dd*, ^3J(6,6a) = 4.7, ^2J = 12.7, 1 H–C(6)$_\beta$); 3.35 (*dd*, ^3J(6,6a) = 4.8, ^2J = 12.6, 1 H–C(6)$_\alpha$); 2.92 (m, H$_{ax}$–C(2″), H$_{ax}$–C(6″)); 2.70 (*m*, 2 H–C(1′)); 2.56 (*m*, H–C(4″)); 2.13 (*m*, H$_{eq}$–C(2″), H$_{eq}$–C(6″)); 1.92 (*m*, H$_{ax}$–C(3″), H$_{ax}$–C(5″)); 1.49 (*s*, *t*-Bu); 1.46 (*m*, H$_{eq}$–C(3″), H$_{eq}$–C(5″)); 1.42 (*s*, 1 Me); 1.32 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.6, 157.3 (NCOO); 139.1, 139.0 (arom. C); 131.7, 130.2, 129.4 (5 arom. C); 113.4 (Me$_2$*C*); 85.4, 84.8 (C(3a)); 82.4. 82.2 (Me$_3$*C*O); 81.6, 80.9 (C(6a)); 65.9, 65.4 (C(4)); 64.7 (C(6)); 56.4, 56.2 (C(4″)); 54.0 (C(1′)); 53.8, 53.2 (C(2″), C(6″)); 47.8 (Ar*C*H$_2$); 33.5, 33.4, 33.3, 33.2 (C(3″), C(5″)); 29.6 (*Me*$_3$C); 28.1 (Me); 25.8 (Me). CI-MS (NH_3): 446 (29, $[M+H]^+$), 372 (5), 273 (6), 203 (100), 91 (87). Anal. calc. for $C_{25}H_{39}N_3O_4$ (445.60): C 67.39, H 8.82, N 9.43; found: C 67.37, H 8.83, N 9.51.

*(2*R*,3*R*,4*S*)-2-{[(1-Benzylpiperidin-4-yl)amino]methyl}pyrrolidine-3,4-diol* (**3j**). By *Method Aa*, with **9j** (40 mg). FC (MeCN/NH_4OH 5:1) gave 30 mg (100% of **3j**). $[\alpha]_{589}^{25} = +307$, $[\alpha]_{577}^{25} = +374$, $[\alpha]_{546}^{25} = +477$, $[\alpha]_{435}^{25} = +609$ ($c = 1.0$, MeOH). UV (MeCN): 213 (1800). IR (film): 3500–2900, 1675, 1635, 1575, 1435, 1370, 1205, 840, 800, 725, 705. ^{1}H-NMR (400 MHz, D_2O/MeOD 75:25): 7.57–7.51 (*m*, 5 arom. H); 4.38 (*m*, H–C(4)); 4.36 (*s*, ArCH_2); 4.23 (*dd*, ^3J(3,4) = 3.8, ^3J(3,2) = 9.5, H–C(3)); 3.85 (*m*, H–C(2)); 3.69–3.62 (*m*, H–C(4″), 1 H–C(1′), 1 H–C(5)); 3.56 (*dd*, ^3J(5,4) = 2.5, ^2J = 12.3, 1 H–C(5)); 3.46 (*d*, ^2J = 13.1, 1 H–C(1′)); 3.15, 2.47, 1.99, 1.47 (4*m*, 2 H–C(2″), 2 H–C(3″), 2 H–C(5″), 2 H–C(6″)). ^{13}C-NMR (100.6 MHz, D_2O/MeOD 75:25): 138.7 (arom. C); 133.0, 132.2, 131.2 (5 arom. C); 75.7 (C(3)); 70.3 (C(4)); 62.4 (C(2)); 58.1 (C(5)); 55.0 (C(4″)); 52.5 (C(1′)); 52.0 (C(2″), C(6″)); 46.0 (Ar*C*H$_2$); 27.1 (C(3″), C(5″)). CI-MS (NH_3): 306 (56, $[M+H]^+$), 279 (4), 203 (17), 172 (17), 91 (100).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-2,2-dimethyl-4-{[[(2*E*)-3-phenylprop-2-enyl]amino}methyl}-5*H*-[1,3]dioxolo [4,5-c]pyrrole-5-carboxylate* (**9k**). By *Method B*, with **10** (105 mg, 0.39 mmol), cinnamaldehyde (51 mg, 0.39 mmol), $NaBH(OAc)_3$ (114 mg, 0.54 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt) gave 35 mg (24% of **9k**), 1.15:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -26$, $[\alpha]_{577}^{25} = -28$, $[\alpha]_{546}^{25} = -33$, $[\alpha]_{435}^{25} = -60$, $[\alpha]_{405}^{25} = -75$ ($c = 0.36$, CH_2Cl_2). UV (MeCN): 250 (22560), 210 (24845). IR (film): 3340, 2980, 2935, 1695, 1600, 1455, 1415, 1170, 1055, 970, 860, 745, 695. ^{1}H-NMR (400 MHz, MeOD): 7.43 (*m*, 2 arom. H); 7.33 (*m*, 2 arom. H); 7.25 (*m*, 1 arom. H); 6.60 (*d*, ^3J(3″,2″) = 15.9, H–C(3″)); 6.33 (*m*, H–C(2″)); 4.77 (*m*, H–C(6a)); 4.67 (*d*, ^3J(3a,6a) = 5.7, H–C(3a)$_\alpha$); 4.64 (*d*, ^3J(3a,6a) = 5.7, H–C(3a)$_\beta$); 4.20 (*t*, ^3J(4,1′) = 6.7, H–C(4)$_\beta$); 4.15 (*t*, ^3J(4,1′) = 6.7, H–C(4)$_\alpha$); 3.84 (*d*, ^3J(6,6a) = 5.2, 1 H–C(6)$_\beta$); 3.81 (*d*, ^3J(6,6a) = 5.5, 1 H–C(6)$_\alpha$); 3.41 (*m*, 1 H–C(6)$_\alpha$), 1 H–(6)$_\beta$, 2 H–C(1″)); 2.75 (*m*, 2 H–C(1′)); 1.50 (*s*, (*t*-Bu)$_\beta$); 1.48 (*s*, (*t*-Bu)$_\alpha$); 1.43 (*s*, 1 Me); 1.33 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.6 (*s*, NCOO$_\beta$); 157.3 (*s*, NCOO$_\alpha$); 139.3 (*s*, arom. C); 134.2 (*d*, ^1J(C,H) = 151, C(3″)); 130.4 (*d*, ^1J(C,H) = 159, 2 arom. C); 129.4 (*d*, ^1J(C,H) = 155, arom. C); 129.2 (*d*, ^1J(C,H) = 152, C(2″)); 128.2 (*d*, ^1J(C,H) = 158, 2 arom. C); 113.5 (*s*); 85.4 (*d*, ^1J(C,H) = 156, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 156, C(3a)$_\beta$); 82.4 (*s*, Me$_3$*C*O$_\alpha$); 82.2 (*s*, Me$_3$*C*O$_\beta$); 81.7 (*d*, ^1J(C,H) = 155, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.8 (*d*, ^1J(C,H) = 148, C(4)$_\alpha$); 65.2 (*d*, ^1J(C,H) = 144, C(4)$_\beta$); 53.7 (*t*, ^1J(C,H) = 141, C(6)$_\beta$); 53.1 (C(6)$_\alpha$), C(1″)); 50–49 (C(1′)); 29.6 (*q*, ^1J(C,H) = 127, *Me*$_3$C); 28.1 (*q*, ^1J(C,H) = 126, Me); 25.8 (*q*, ^1J(C,H) = 126, Me). CI-MS (NH_3): 390 (67, $[M+H]^+$), 389 (100, M^+), 333 (60), 287 (5), 243 (2), 187 (5), 117 (84), 91 (14). Anal. calc. for $C_{22}H_{32}N_2O_4$ (388.53): C 68.01, H 8.30; found: C 67.95, H 8.15.

*(2*R*,3*R*,4*S*)-2-{[[(2*E*)-3-Phenylprop-2-enyl]amino}methyl}pyrrolidine-3,4-diol* (**3k**). By *Method Aa*, with **9k** (35 mg). FC (MeCN/NH_4OH 4:1) gave 23 mg (100% of **3k**). $[\alpha]_{589}^{25} = +11$, $[\alpha]_{577}^{25} = +11$, $[\alpha]_{546}^{25} = +15$ ($c = 0.33$, MeOH). UV (MeCN): 272 (20100), 259 (19000), 217 (6870). IR (film): 3205, 3060, 1670, 1445, 1200, 1135, 970, 840, 800, 725, 695. ^{1}H-NMR (400 MHz, MeOD): 7.49 (*m*, 2 arom. H); 7.36–7.28 (*m*, 3 arom. H); 6.86 (*d*, ^3J(3″,2″) = 15.9, H–C(3″)); 6.33 (*dt*, ^3J(2″,1″) = 7.1, ^3J(2″,3″) = 15.9, H–C(2″)); 4.25 (*ddd*, ^3J(4,5) = 1.3, ^3J(4,5) = 3.9, ^3J(4,3) = 3.9, H–C(4)); 4.08 (*dd*, ^3J(3,4) = 3.9, ^3J(3,2) = 9.0, H–C(3)); 3.85 (*m*, 2 H–C(1″)); 3.75 (*m*, H–C(2)); 3.51 (*dd*, ^3J(5,4) = 3.9, ^2J = 12.6, 1 H–C(5)); 3.45 (*m*, 2 H–C(1′)); 3.31 (*m*, 1 H–C(5)). ^{13}C-NMR (100.6 MHz, MeOD): 140.0 (C(3″)); 130.0 (arom. C); 130.6, 130.5, 128.7 (5 arom. C); 121.5 (C(2″)); 76.5 (C(3)); 71.4 (C(4)); 59.7 (C(2)); 52.6, 52.2 (C(1″), C(5)); 48.6 (C(1′)). CI-MS (NH_3): 249 (4, $[M+H]^+$), 169 (3), 146 (11), 132 (30), 117 (100), 102 (38), 91 (31), 85 (25), 77 (23).

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-2,2-dimethyl-4-{[[(1*R*)-1-phenylethyl]amino}methy}-5*H*-[1,3]dioxolo[4,5-c] pyrrole-5-carboxylate* (**9l**). By *Method A*, with **8** (100 mg, 0.37 mmol), (*αR*)-α-methylbenzenemethanamine (47 µl, 0.37 mmol), $NaBH(OAc)_3$ (110 mg, 0.52 mmol), and $ClCH_2CH_2Cl$ (2.5 ml). FC (AcOEt/light petroleum ether 4:1) gave 96 mg (69% of **9l**), 1.3:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -23$, $[\alpha]_{577}^{25} = -32$, $[\alpha]_{546}^{25} = -40$, $[\alpha]_{435}^{25} = -68$, $[\alpha]_{405}^{25} = -83$ ($c = 0.30$, CH_2Cl_2). IR (film): 3330, 3060, 2980, 2935, 1695, 1680, 1480,

1455, 1405, 1370, 1210, 1170, 1125, 1055, 970, 865, 765, 700, 665. ^{1}H-NMR (400 MHz, MeOD): 7.36–7.27 (*m*, 5 arom. H); 4.75 (*dd*, ^3J(H–C(6a),6) = 5.8, ^3J(6a,3a) = 5.8, H–C(6a)$_\alpha$); 4.71 (*dd*, ^3J(6a),6) = 5.9, ^3J(6a,3a) = 5.9, H–C(6a)$_\beta$); 4.59 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.49 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\beta$); 4.14 (*t*, ^3J(4,1′) = 5.7, H–C(4)$_\beta$); 4.02 (*t*, ^3J(4,1′) = 7.0, H–C(4)$_\alpha$); 3.89 (*q*, ^3J = 6.5, H–C(1″)); 3.77 (*d*, ^2J = 13.1, 1 H–C(6)); 3.29 (*dd*, ^3J(6,6a) = 5.8, ^2J = 13.1, 1 H–C(6)); 2.60 (*dd*, ^3J(1′,4) = 5.7, ^2J = 12.2, 1 H–C(1′)$_\beta$); 2.53 (*dd*, ^3J(1′,4) = 7.0, ^2J = 12.4, 1 H–C(1′)$_\alpha$); 2.44(*d*, ^2J = 12.2, 1 H–C(1′)$_\beta$); 2.42 (*d*, ^2J = 12.4, 1 H–C(1′)$_\alpha$); 1.52 (*s*, (*t*-Bu)$_\beta$); 1.43 (*s*, (*t*-Bu)$_\alpha$); 1.38 (*d*, ^3J = 6.5, 1 Me$_\alpha$); 1.37 (*d*, ^3J = 6.5, 1 Me$_\beta$); 1.30 (*s*, 1 Me); 1.32 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 146.4, 129.6, 128.2, 127.8 (arom. C); 112.5 (Me$_2$*C*); 84.6 (C(3a)$_\alpha$); 84.2 (C(3a)$_\beta$); 81.5 (Me$_3$*C*O); 80.8 (C(6a)$_\beta$); 80.1 (C(6a)$_\alpha$); 65.2 (C(4)$_\alpha$); 64.6 (C(4)$_\beta$); 59.4 (C(6)$_\alpha$); 59.1 (C(6)$_\beta$); 53.0 (C(1′)$_\beta$); 52.3 (C(1′)$_\alpha$); 50–49 (C(1″)); 28.7 (*Me*$_3$C); 27.2 (Me); 24.9 (Me); 24.3 (*Me*–C(1″)$_\alpha$); 24.2 (*Me*–C(1″)$_\beta$). CI-MS (NH_3): 377 (100, $[M+H]^+$), 321 (7), 215 (4), 105 (9). Anal. calc. for $C_{21}H_{32}N_2O_4$ (376.49): C 66.99, H 8.57, N 7.44; found: C 70.01, H 8.54, N 7.41.

*(2*R*,3*R*,4*S*)-2-{[[(1*R*)-1-Phenylethyl]amino}methyl}pyrrolidine-3,4-diol* (**3l**). By *Method Aa*, with **9l** (30 mg). FC (MeCN/NH_4OH 4:1) gave 21 mg (100% of **3l**). $[\alpha]_{589}^{25} = +8$ (*c* = 0.80, MeCN). UV (MeCN): 196 (6000). IR (film): 3500–3000, 1675, 1430, 1200, 1135, 835, 800, 720, 700. ^{1}H-NMR (400 MHz, MeOD): 7.43–7.36 (*m*, 5 arom. H); 4.21 (*q*, ^3J = 6.8, H–C(1″)); 4.16 (*ddd*, ^3J(4,5) = 4.1, ^3J(4,3) = 4.3, ^3J(4,5) = 1.4, H–C(4)); 3.87 (*dd*, ^3J(3,4) = 4.3, ^3J(3,2) = 8.7, H–C(3)); 3.48 (*ddd*, ^3J(2,3) = 8.7, ^3J(2,1′) = 8.9, ^3J(2,1′) = 4.2, H–C(2)); 3.26 (*dd*, ^3J(5,4) = 4.2, ^2J = 13.0, 1 H–C(5)); 3.23 (*m*, 1 H–C(1′), 2 H–C(5)); 2.87 (*dd*, ^3J(1′,2) = 8.9, ^2J = 13.4, 1 H–C(1′)); 1.52 (*d*, ^2J = 6.8, Me–C(1″)). ^{13}C-NMR (100.6 MHz, MeOD): 140.5, 131.8, 131.7, 130.0 (arom. C); 76.6 (C(3)); 72.0 (C(4)); 61.1 (C(1″)); 60.3 (C(2)); 52.6 (C(5)); 48.7 (C(1′)); 21.9 (*Me*–C(1′)). CI-MS (NH_3): 237 (100, $[M+H]^+$), 134 (42), 120 (30), 105 (73), 85 (20).

*(2*R*,3*R*,4*S*)-2-{[[(1*S*)-1-(4-Nitrophenyl)ethyl]amino}methyl}pyrrolidine-3,4-diol* (**3la**). By *Method A*, with **8** (100 mg, 0.37 mmol), (α*S*)-α-methyl-4-nitrobenzenemethanamine (75 mg, 0.37 mmol), $NaBH(OAc)_3$ (110 mg, 0.52 mmol), and $ClCH_2CH_2Cl$ (3 ml). Then by *Method Aa*, with crude **9la** (100 mg). FC (MeCN/NH_4OH 4:1) gave 66 mg (100% of **3la**). $[\alpha]_{589}^{25} = +6$ (*c* = 0.38, MeOH). UV (MeCN): 272 (3100), 216 (2550). ^{1}H-NMR (400 MHz, MeOD): 8.30 (*d*, ^3J = 8.7, 2 arom. H); 7.76 (*d*, ^3J = 8.7, 2 arom. H); 4.32 (*q*, ^3J = 6.7, H–C(1″)); 4.27 (*m*, H–C(4)); 4.04 (*dd*, ^3J(3,4) = 4.0, ^3J(3,2) = 8.8, H–C(3)); 3.67 (*ddd*, ^3J(2,3) = 8.8, ^3J(2,1′) = 9.1, ^3J(2,1′) = 3.8, H–C(2)); 3.54 (*dd*, ^3J(5,4) = 4.0, ^2J = 12.6, 1 H–C(5)); 3.33 (*dd*, ^3J(5,4) = 1.5, ^2J = 12.6, 1 H–C(5)); 3.20 (*dd*, ^3J(1′,2) = 9.1, ^2J = 13.5, 1 H–C(1′)); 3.07 (*dd*, ^3J(1′,2) = 3.8, ^2J = 13.5, 1 H–C(1′)); 1.60 (*d*, ^3J = 6.7, Me–C(1″)). ^{13}C-NMR (100.6 MHz, MeOD): 151.7 (arom. C); 132.1 (2 arom. C); 127.6 (2 arom. C); 122.2 (arom. C); 77.5 (C(3)); 73.1 (C(4)); 63.1 (C(2)); 62.2 (C(1″)); 53.7 (C(5)); 49.6 (C(1′)); 24.2 (*Me*–C(1′)). CI-MS (NH_3): 282 (100, $[M+H]^+$), 180 (2), 151 (3), 102 (16), 85 (7). Anal. calc. for $C_{13}H_{19}N_3O_4$ (281.31): C 55.51, H 6.81, N 14.94; found: C 55.48, H 6.79, N 14.90.

tert-*Butyl (3a*R*,4*R*,6a*S*)-Tetrahydro-2,2-dimethyl-4-{[(pyridin-2-ylmethyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-c] pyrrole-5-carboxylate* (**9m**). By *Method A*, with **8** (96 mg, 0.35 mmol), pyridine-2-methanamine (38 mg, 0.35 mmol), $NaBH(OAc)_3$ (105 mg, 0.50 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 82 mg (64% of **9m**), 1.4:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -34$, $[\alpha]_{577}^{25} = -35$, $[\alpha]_{546}^{25} = -38$, $[\alpha]_{435}^{25} = -68$, $[\alpha]_{405}^{25} = -83$ (*c* = 0.37, CH_2Cl_2). UV (MeCN): 261 (4560), 205 (8220). IR (film): 3330, 2980, 2935, 1690, 1590, 1570, 1475, 1460, 1405, 1370, 1210, 1175, 1125, 1055, 995, 975, 860, 760. ^{1}H-NMR (400 MHz, MeOD): 8.53 (*m*, 1 arom. H); 7.85 (*t*, ^3J = 7.7, 1 arom. H); 7.51 (*d*, ^3J = 7.7, 1 arom. H); 7.34 (*m*, 1 arom. H); 4.79 (*m*, H–C(6a)); 4.69 (*d*, ^3J(3a,6a) = 6.0, H–C(3a)$_\alpha$); 4.66 (*d*, ^3J(3a,6a) = 5.9, H–C(3a)$_\beta$); 4.17 (*dd*, ^3J(4,1′) = 6.0, ^3J(4,1′) = 6.3, H–C(4)$_\beta$); 4.11 (*dd*, ^3J(4,1′) = 6.1, ^3J(4,1′) = 6.4, H–C(4)$_\alpha$); 3.94 (*m*, 2 H–C(1″)); 3.80 (*m*, 1 H–C(6)); 3.41 (*m*, 1 H–C(6)); 2.71 (*m*, 2 H–C(1′)); 1.50 (*s*, 1 Me); 1.45 (*s*, (*t*-Bu)$_\alpha$); 1.44 (*s*, (*t*-Bu)$_\beta$); 1.34 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 161.5 (*s*, arom. C); 157.4 (*s*, NCOO$_\beta$); 157.2 (*s*, NCOO$_\alpha$); 150.7 (*d*, ^1J(C,H) = 180, arom. C); 139.5 (*d*, ^1J(C,H) = 164, arom. C); 124.8 (*d*, ^1J(C,H) = 164, arom. C); 124.5 (*d*, ^1J(C,H) = 166, arom. C); 113.4 (*s*); 85.6 (*d*, ^1J(C,H) = 157, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 156, C(3a)$_\beta$); 82.3 (*s*, Me$_3$*C*O$_\alpha$); 82.1 (*s*, Me$_3$*C*O$_\beta$); 81.6 (*d*, ^1J(C,H) = 150, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 159, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 148, C(4)$_\alpha$); 65.5 (*d*, ^1J(C,H) = 145, C(4)$_\beta$); 56.1 (*t*, ^1J(C,H) = 136, C(1″)); 54.0 (*t*, ^1J(C,H) = 142, C(6)$_\beta$); 53.3 (*t*, ^1J(C,H) = 143, C(6)$_\alpha$); 50–49 (C(1′)); 29.5 (*q*, ^1J(C,H) = 127, *Me*$_3$C); 28.1 (*q*, ^1J(C,H) = 129, Me); 25.8 (*q*, ^1J(C,H) = 128, Me). CI-MS (NH_3): 364 (100, $[M+H]^+$), 348 (3), 308 (10), 264 (28), 215 (16), 171 (3), 121 (99), 93 (43). Anal. calc. for $C_{19}H_{29}N_3O_4$ (363.48): C 62.79, H 8.04, N 11.56; found: C 62.83, H 7.97, N 11.37.

*(2*R*,3*R*,4*S*)-2-{[(Pyridin-2-ylmethyl)amino]methyl}pyrrolidine-3,4-diol* (**3m**). By *Method Aa*, with **9m** (20 mg). FC (MeCN/NH_4OH 4:1) gave 12 mg (100% of **3m**). $[\alpha]_{589}^{25} = +9$, $[\alpha]_{577}^{25} = +9$, $[\alpha]_{546}^{25} = +18$ (*c* = 0.22, MeOH). UV (MeCN): 256 (4460), 211 (5895). IR (film): 3300, 2930, 1675, 1595, 1435, 1200, 1130, 835, 800, 760, 720. ^{1}H-NMR (400 MHz, MeOD): 8.54 (*m*, 1 arom. H); 7.84 (*m*, 1 arom. H); 7.47 (*d*, ^3J = 7.8, 1 arom. H); 7.34 (*m*, 1 arom. H); 4.20 (*m*, H–C(4)); 3.99 (*m*, 2 H–C(1″)); 3.92 (*dd*, ^3J(3,4) = 4.3, ^3J(3,2) = 7.7, H–C(3)); 3.42

(m, H–C(2)); 3.38 (m, 1 H–C(5)); 3.16 (dd, ^3J(5,4) = 2.5, ^2J = 12.3, 1 H–C(5)); 3.00 (dd, ^3J(1′,2)) = 4.3, ^2J = 13.0, 1 H–C(1′)); 2.87 (dd, ^3J(1′,2) = 7.9, ^2J = 13.0, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, MeOD): 161.2 (s, arom. C); 150.6 (d, ^1J(C,H) = 179, arom. C); 139.7 (d, ^1J(C,H) = 164, arom. C); 125.0 (d, ^1J(C,H) = 161, arom. C); 124.7 (d, ^1J(C,H) = 166, arom. C); 76.2 (d, ^1J(C,H) = 143, C(3)); 72.7 (d, ^1J(C,H) = 152, C(4)); 63.4 (d, ^1J(C,H) = 145, C(2)); 55.6 (t, ^1J(C,H) = 136, C(1″)); 52.1 (t, ^1J(C,H) = 145, C(5)); 50–49 (C(1′)). CI-MS (NH_3): 224 (7, $[M+H]^+$), 220 (8), 191 (3), 163 (2), 143 (8), 121 (54), 109 (19), 93 (100), 79 (20).

tert-*Butyl (3a*R,*4*R,*6a*S)*-Tetrahydro-2,2-dimethyl-4-{[(2-thienylmethyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9o**). By *Method A*, with **8** (103 mg, 0.38 mmol), thiophene-2-methanamine (43 mg, 0.38 mmol), $NaBH(OAc)_3$ (113 mg, 0.53 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt/light petroleum ether 2:1) gave 109 mg (78% of **9o**), 1.4:1 mixture of rotamers α and β. $[\alpha]^{25}_{589} = -41$, $[\alpha]^{25}_{577} = -44$, $[\alpha]^{25}_{546} = -49$, $[\alpha]^{25}_{435} = -86$, $[\alpha]^{25}_{405} = -104$ ($c = 0.57$, CH_2Cl_2). UV (MeCN): 238 (8655), 205 (7090). IR (film): 2980, 1695, 1605, 1515, 1455, 1410, 1370, 1260, 1170, 1125, 1055, 850, 735, 700. ^{1}H-NMR (400 MHz, MeOD): 8.00 (m, H–C(5‴)); 7.30 (m, H–C(3‴)); 7.01 (m, H–C(4‴)); 4.76 (m, H–C(6a)); 4.64 (d, ^3J(3a,6a) = 5.9, H–C(3a)$_\alpha$); 4.60 (d, ^3J(3a,6a) = 5.9, H–C(3a)$_\beta$); 4.14 (dd, ^3J(4,1′) = 6.2, ^3J(4,1′) = 6.4, H–C(4)$_\beta$); 4.06 (dd, ^3J(4,1′) = 6.2, ^3J(4,1′) = 6.3, H–C(4)$_\alpha$); 3.99 (m, 2 H–C(1″)); 3.78 (d, ^3J(6,6a) = 4.7, 2 H–C(6)$_\beta$); 3.75 (d, ^3J(6,6a) = 4.7, 2 H–C(6)$_\alpha$); 2.68 (m, 2 H–C(1′)); 1.49 (s, (t-Bu)$_\beta$); 1.44 (s, (t-Bu)$_\alpha$); 1.42 (s, 1 Me); 1.31 (s, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.4 (s, $NCOO_\beta$); 157.2 (s, $NCOO_\alpha$); 133.4 (d, ^1J(C,H) = 167, C(5‴)); 128.5 (d, ^1J(C,H) = 167, C(4‴)); 126.4 (d, ^1J(C,H) = 166, C(3‴)); 113.3 (s); 85.6 (d, ^1J(C,H) = 157, C(3a)$_\alpha$); 85.0 (d, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (s, Me_3CO_α); 82.1 (s, Me_3CO_β); 81.6 (d, ^1J(C,H) = 151, C(6a)$_\beta$); 80.9 (d, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.9 (d, ^1J(C,H) = 147, C(4)$_\alpha$); 65.3 (d, ^1J(C,H) = 146, C(4)$_\beta$); 54.1 (t, ^1J(C,H) = 144, C(6)$_\beta$); 53.5 (t, ^1J(C,H) = 143, C(6)$_\alpha$); 50–49 (C(1′), C(1″)); 29.6 (q, ^1J(C,H) = 127, Me_3C); 28.1 (q, ^1J(C,H) = 129, Me); 25.9 (q, ^1J(C,H) = 127, Me). CI-MS (NH_3): 369 (6, $[M+H]^+$), 368 (4, M^+), 313 (12), 267 (4), 187 (5), 142 (19), 97 (100). Anal. calc. for $C_{18}H_{28}N_2O_4S$ (368.51): C 58.67, H 7.66; found: C 58.77, H 7.68.

*(2*R,*3*R,*4*S)*-2-{[(2-Thienylmethyl)amino]methyl}pyrrolidine-3,4-diol* (**3o**). By *Method Aa*, with **9o** (48 mg). FC ($MeCN/NH_4OH$ 4:1) gave 29 mg (100% of **3o**). IR (film): 3100, 1680, 1435, 1200, 1140, 840, 800, 725. ^{1}H-NMR (400 MHz, D_2O): 7.56 (d, ^3J = 5.1, H–C(5‴)); 7.26 (d, ^3J = 3.4, H–C(3‴)); 7.17 (m, H–C(4‴)); 4.40 (m, H–C(4)); 4.39 (s, 2 H–C(1″)); 4.15 (dd, ^3J(3,4) = 4.2, ^3J(3,2) = 8.6, H–C(3)); 3.70 (ddd, ^3J(2,1′) = 4.6, ^3J(2,3) = 8.6, ^3J(2,1′) = 8.6, H–C(2)); 3.55 (dd, ^3J(5,4) = 4.2, ^2J = 13.0, 1 H–C(5)); 3.36 (m, 1 H–C(5), 1 H–C(1′)); 3.24 (dd, ^3J(1′,2) = 8.6, ^2J = 13.5, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, D_2O): 131.5 (d, ^1J(C,H) = 170, C(3‴)); 130.0 (d, ^1J(C,H) = 169, C(5‴)); 129.8 (d, ^1J(C,H) = 170, C(4‴)); 76.3 (d, ^1J(C,H) = 145, C(3)); 71.8 (d, ^1J(C,H) = 154, C(4)); 60.6 (d, ^1J(C,H) = 145, C(2)); 52.4 (t, ^1J(C,H) = 145, C(5)); 49.3 (t, ^1J(C,H) = 140, C(1′)); 48.5 (t, ^1J(C,H) = 143, C(1″)). CI-MS (NH_3): 229 (100, $[M+H]^+$), 211 (42, $[M+H-H_2O]^+$), 191 (3), 158 (6), 114 (10), 97 (37), 85 (9).

tert-*Butyl (3a*R,*4*S,*6a*S)*-Tetrahydro-2,2-dimethyl-4-{{[(5-methyl-2-thienyl)methyl]amino}methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9oa**). By *Method B*, with **10** (130 mg, 0.48 mmol), 5-methylthiophene-2-carboxaldehyde (60 mg, 0.48 mmol), $NaBH(OAc)_3$ (142 mg, 0.67 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt/light petroleum ether 2:1) gave 115 mg (63% of **9oa**), 1.3:1 mixture of rotamers α and β. $[\alpha]^{25}_{589} = -51$, $[\alpha]^{25}_{577} = -52$, $[\alpha]^{25}_{546} = -55$, $[\alpha]^{25}_{435} = -88$, $[\alpha]^{25}_{405} = -123$ ($c = 0.27$, CH_2Cl_2). UV (MeCN): 291 (1065), 239 (8425). IR (film): 3330, 2980, 2935, 1695, 1455, 1405, 1370, 1210, 1165, 1125, 1055, 855, 800. ^{1}H-NMR (400 MHz, MeOD): 6.75 (d, ^3J = 3.3, 1 arom. H); 6.62 (br. s, 1 arom. H); 4.76 (m, H–C(6a)); 4.65 (d, ^3J(3a,6a) = 5.8, H–C(3a)$_\alpha$); 4.61 (d, ^3J(3a,6a) = 5.9, H–C(3a)$_\beta$); 4.15 (t, ^3J(4,1′) = 6.1, H–C(4)$_\beta$); 4.06 (t, ^3J(4,1′) = 6.1, H–C(4)$_\alpha$); 3.90 (m, 2 H–C(1″)); 3.78 (d, ^2J = 12.9, 1 H–C(6)); 3.42 (m, 1 H–C(6)); 2.67 (AB, 2 H–C(1′)); 2.46 (s, arom. Me); 1.50 (s, 1 Me); 1.46 (s, (t-Bu)$_\alpha$); 1.43 (s, (t-Bu)$_\beta$); 1.33 (s, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (s, $NCOO_\alpha$); 157.2 (s, $NCOO_\beta$); 143.0 (s, arom. C); 141.0 (s, arom. C); 127.4 (d, ^1J(C,H) = 164, arom. C); 126.6 (d, ^1J(C,H) = 164, arom. C); 113.4 (s); 85.6 (d, ^1J(C,H) = 157, C(3a)$_\alpha$); 85.0 (d, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (s, Me_3CO_α); 82.1 (s, Me_3CO_β); 81.7 (d, ^1J(C,H) = 157, C(6a)$_\beta$); 80.9 (d, ^1J(C,H) = 158, C(6a)$_\alpha$); 66.0 (d, ^1J(C,H) = 146, C(4)$_\alpha$); 65.4 (d, ^1J(C,H) = 144, C(4)$_\beta$); 54.1 (t, ^1J(C,H) = 145, C(6)$_\beta$); 53.5 (t, ^1J(C,H) = 144, C(6)$_\alpha$); 50–49 (C(1′), C(1″)); 29.5 (q, ^1J(C,H) = 127, Me_3C); 28.1 (q, ^1J(C,H) = 126, Me); 25.8 (q, ^1J(C,H) = 127, Me); 16.1 (q, ^1J(C,H) = 128, arom. Me). CI-MS (NH_3): 384 (100, $[M+H]^+$), 383 (80, M^+), 327 (39), 281 (7), 243 (2), 215 (10), 187 (2), 111 (56), 85 (7). Anal. calc. for $C_{19}H_{30}N_2O_4S$ (382.54): C 59.66, H 7.91, N 7.32; found: C 59.61, H 7.94, N 7.22.

*(2*R,*3*R,*4*S)*-2-{{[(5-Methyl-2-thienyl)methyl]amino}methyl}pyrrolidine-3,4-diol* (**3oa**). By *Method Aa*, with **9oa** (31 mg). FC ($MeCN/NH_4OH$ 4:1) gave 20 mg (100% of **3oa**). $[\alpha]^{25}_{589} = +6$, $[\alpha]^{25}_{577} = +14$, $[\alpha]^{25}_{546} = +17$, $[\alpha]^{25}_{435} = +31$ ($c = 0.14$, MeOH). UV (MeCN): 238 (3255). IR (film): 3200, 3065, 1670, 1445, 1200, 1140, 840, 800, 725. ^{1}H-NMR (400 MHz, MeOD): 7.00 (d, ^3J = 3.3, 1 arom. H); 6.74 (d, ^3J = 3.3, 1 arom. H); 4.28 (m, H–C(4), 2 H–C(1″)); 4.07 (dd, ^3J(3,4) = 4.0, ^3J(3,2) = 8.8, H–C(3)); 3.71 (ddd, ^3J(2,1′) = 4.5, ^3J(2,3) = 8.8,

$^3J(2,1') = 8.8$, H–C(2)); 3.52 (*dd*, $^3J(5,4) = 4.0$, $^2J = 12.6$, 1 H–C(5)); 3.34–3.26 (*m*, 1 H–C(5), 2 H–C(1′)); 2.50 (*s*, arom. Me). ^{13}C-NMR (100.6 MHz, MeOD): 143.9 (*s*, arom. C); 135.7 (*s*, arom. C); 131.0 (*d*, ^1J(C,H) = 165, arom. C); 127.4 (*d*, ^1J(C,H) = 166, arom. C); 76.2 (*d*, ^1J(C,H) = 144, C(3)); 71.5 (*d*, ^1J(C,H) = 152, C(4)); 60.4 (*d*, ^1J(C,H) = 147, C(2)); 52.2 (*t*, ^1J(C,H) = 149, C(5)); 48.6, 48.4 (2*t*, ^1J(C,H) = 141, C(1′), C(1″)); 16.1 (*q*, ^1J(C,H) = 129, arom. Me). CI-MS (NH_3): 243 (96, $[M+H]^+$), 242 (12, M^+), 229 (61), 211 (67), 195 (19), 179 (49), 161 (16), 145 (37), 133 (88), 111 (100), 86 (18).

tert-*Butyl (3a*R,*4*R,*6a*S)*-Tetrahydro-2,2-dimethyl-4-{[[(3-methyl-2-thienyl)methyl]amino}methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9ob**). By *Method B*, with **10** (139 mg, 0.51 mmol), 3-methylthiophene-2-carboxaldehyde (64 mg, 0.51 mmol), $NaBH(OAc)_3$ (151 mg, 0.71 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt/light petroleum ether 1:1) gave 84 mg (43% of **9ob**), 1.4:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -41$, $[\alpha]_{577}^{25} = -48$, $[\alpha]_{546}^{25} = -57$, $[\alpha]_{435}^{25} = -111$, $[\alpha]_{405}^{25} = -146$ (*c* = 0.37, CH_2Cl_2). UV (MeCN): 238 (7250). IR (film): 3330, 2980, 2930, 1690, 1455, 1405, 1210, 1170, 1125, 1055, 765, 770, 710. ^{1}H-NMR (400 MHz, MeOD): 7.18 (*m*, 1 arom. H); 6.80 (*m*, 1 arom. H); 4.75 (*m*, H–C(6a)); 4.64 (*m*, H–C(3a)); 4.06 (*m*, H–C(4)); 3.91 (*s*, 2 H–C(1″)); 3.76 (*d*, $^2J = 12.8$, 1 H–C(6)); 3.40 (*m*, 1 H–C(6)); 2.68 (*m*, 2 H–C(1′)); 2.22 (*s*, arom. Me); 1.49 (*s*, 1 Me); 1.45 (*s*, (*t*-Bu)$_\alpha$); 1.42 (*s*, (*t*-Bu)$_\beta$); 1.31 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 138.3 (*s*, arom. C); 136.1 (*s*, arom. C); 131.8 (*d*, ^1J(C,H) = 162, arom. C); 124.7 (*d*, ^1J(C,H) = 186, arom. C); 113.4 (*s*); 85.6 (*d*, ^1J(C,H) = 157, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_β); 81.7 (*d*, ^1J(C,H) = 157, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 66.0 (*d*, ^1J(C,H) = 146, C(4)$_\alpha$); 65.4 (*d*, ^1J(C,H) = 146, C(4)$_\beta$); 54.1 (*t*, ^1J(C,H) = 142, C(6)$_\beta$); 53.5 (*t*, ^1J(C,H) = 144, C(6)$_\alpha$); 50–49 (C(1′)); 47.4 (*t*, ^1J(C,H) = 136, C(1″)); 29.5 (*q*, ^1J(C,H) = 127, Me_3C); 28.1 (*q*, ^1J(C,H) = 127, Me); 25.8 (*q*, ^1J(C,H) = 127, Me); 14.6 (*q*, ^1J(C,H) = 127, arom. Me). CI-MS (NH_3): 384 (100, $[M+H]^+$), 383 (93, M^+), 327 (28), 281 (4), 215 (8), 171 (2), 111 (54), 85 (8). Anal. calc. for $C_{19}H_{30}N_2O_4S$ (382.54): C 59.66, H 7.91, N 7.32; found: C 59.75, H 7.98, N 7.31.

*(2*R,*3*R,*4*S*)-2-{[[(3-Methyl-2-thienyl)methyl]amino}methyl}pyrrolidine-3,4-diol* (**3ob**). By *Method Aa*, with **9ob** (30 mg). FC ($MeCN/NH_4OH$ 4:1) gave 20 mg (100% of **3ob**). $[\alpha]_{589}^{25} = +18$, $[\alpha]_{577}^{25} = +19$, $[\alpha]_{546}^{25} = +21$, $[\alpha]_{435}^{25} = +31$ (*c* = 0.37, MeOH). UV (MeCN): 274 (2245), 237 (5135), 198 (845). IR (film): 3055, 1670, 1440, 1310, 1200, 1025, 840, 800, 725. ^{1}H-NMR (400 MHz, MeOD): 7.38 (*d*, $^3J = 5.1$, 1 arom. H); 6.92 (*d*, $^3J = 5.1$, 1 arom. H); 4.32 (*s*, H–C(1″)); 4.26 (*ddd*, $^3J(4,5) = 1.4$, $^3J(4,5) = 3.9$, $^3J(4,3) = 3.9$, H–C(4)); 4.08 (*dd*, $^3J(3,4) = 3.9$, $^3J(3,2) = 8.9$, H–C(3)); 3.74 (*ddd*, $^3J(2,1') = 4.7$, $^3J(2,3) = 8.9$, $^3J(2,1') = 8.9$, H–C(2)); 3.52 (*dd*, $^3J(5,4) = 3.9$, $^2J = 12.6$, 1 H–C(5)); 3.39–3.32 (*m*, 1 H–C(5), 2 H–C(1′)); 2.31 (*s*, arom. Me). ^{13}C-NMR (100.6 MHz, MeOD): 140.1 (*s*, arom. C); 132.2 (*d*, ^1J(C,H) = 166, arom. C); 131.1 (*s*, arom. C); 127.4 (*d*, ^1J(C,H) = 179, arom. C); 76.3 (*d*, ^1J(C,H) = 144, C(3)); 71.4 (*d*, ^1J(C,H) = 154, C(4)); 60.3 (*d*, ^1J(C,H) = 147, C(2)); 52.3 (*t*, ^1J(C,H) = 145, C(5)); 48.4 (*t*, ^1J(C,H) = 141, C(1′)); 46.4 (*t*, ^1J(C,H) = 142, C(1″)); 14.7 (*q*, ^1J(C,H) = 128, arom. Me). CI-MS (NH_3): 243 (33, $[M+H]^+$), 144 (3), 134 (17), 116 (32), 93 (69), 76 (100).

tert-*Butyl (3a*R,*4*R,*6a*S)*-Tetrahydro-2,2-dimethyl-4-{[[(5-ethyl-2-thienyl)methyl]amino}methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**9oc**). By *Method B*, with **10** (106 mg, 0.39 mmol), 5-ethylthiophene-2-carboxaldehyde (55 mg, 0.39 mmol), $NaBH(OAc)_3$ (115 mg, 0.54 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt/light petroleum ether 1:1) gave 111 mg (72% of **9oc**), 1.3:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -49$, $[\alpha]_{577}^{25} = -58$, $[\alpha]_{546}^{25} = -67$, $[\alpha]_{435}^{25} = -131$, $[\alpha]_{405}^{25} = -174$ (*c* = 0.37, CH_2Cl_2). UV (MeCN): 290 (1705), 240 (11745), 210 (2765). IR (film): 3360, 3045, 2850, 1675, 1435, 1340, 1200, 1135, 840, 800, 720. ^{1}H-NMR (400 MHz, MeOD): 6.76 (*d*, $^3J = 3.3$, 1 arom. H); 6.65 (br. *s*, 1 arom. H); 4.76 (*m*, H–C(6a)); 4.64 (*d*, ^3J(3a,6a) = 5.5, H–C(3a)$_\alpha$); 4.59 (*d*, ^3J(3a,6a) = 5.8, H–C(3a)$_\beta$); 4.14 (*t*, $^3J(4,1') = 6.3$, H–C(4)$_\beta$); 4.05 (*dd*, $^3J(4,1') = 6.1$, $^3J(4,1') = 6.5$, H–C(4)$_\alpha$); 3.90 (*AB*, 2 H–C(1″)); 3.77 (*d*, $^2J = 12.8$, 1 H–C(6)); 3.39 (*m*, 1 H–C(6)); 2.82 (*q*, $^3J = 7.5$, MeCH_2); 2.68 (*AB*, 2 H–C(1′)); 1.49 (*s*, 1 Me); 1.45 (*s*, (*t*-Bu)$_\alpha$); 1.42 (*s*, (*t*-Bu)$_\beta$); 1.32 (*s*, 1 Me); 1.30 (*t*, $^3J = 7.5$, *Me*CH_2). ^{13}C-NMR (100.6 MHz, MeOD): 157.5 (*s*, $NCOO_\beta$); 157.2 (*s*, $NCOO_\alpha$); 148.8 (*s*, arom. C); 142.6 (*s*, arom. C); 127.3 (*d*, ^1J(C,H) = 166, arom. C); 124.8 (*d*, ^1J(C,H) = 165, arom. C); 113.4 (*s*); 85.6 (*d*, ^1J(C,H) = 158, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (*s*, Me_3CO_α); 82.1 (*s*, Me_3CO_β); 81.7 (*d*, ^1J(C,H) = 157, C(6a)$_\beta$); 80.9 (*d*, ^1J(C,H) = 157, C(6a)$_\alpha$); 66.0 (*d*, ^1J(C,H) = 147, C(4)$_\alpha$); 65.3 (*d*, ^1J(C,H) = 147, C(4)$_\beta$); 54.0 (*t*, ^1J(C,H) = 146, C(6)$_\beta$); 53.5 (*t*, ^1J(C,H) = 142, C(6)$_\alpha$); 50–49 (C(1′), C(1″)); 29.5 (*q*, ^1J(C,H) = 127, Me_3C); 28.1 (*q*, ^1J(C,H) = 127, Me); 25.8 (*q*, ^1J(C,H) = 127, Me); 25.3 (*t*, ^1J(C,H) = 125, Me*C*H_2); 14.6 (*q*, ^1J(C,H) = 123, *Me*CH_2). CI-MS (NH_3): 397 (100, $[M+H]^+$), 341 (16), 295 (2), 215 (2), 125 (25), 84 (6). Anal. calc. for $C_{20}H_{32}N_2O_4S$ (396.57): C 60.58, H 8.13, N 6.75; found: C 60.64, H 8.10, N 6.61.

*(2*R,*3*R,*4*S*)-2-{[[(3-Ethyl-2-thienyl)methyl]amino}methyl}pyrrolidine-3,4-diol* (**3oc**). By *Method Aa*, with **9oc** (30 mg). FC ($MeCN/NH_4OH$ 4:1) gave 19 mg (100% of **3oc**). $[\alpha]_{589}^{25} = +11$, $[\alpha]_{577}^{25} = +12$, $[\alpha]_{546}^{25} = +15$ (*c* = 0.50, MeOH). UV (MeCN): 239 (1790), 204 (270). IR (film): 3080, 1670, 1435, 1200, 840, 800, 725. ^{1}H-NMR (400 MHz, MeOD): 7.02 (*d*, $^3J = 3.4$, 1 arom. H); 6.77 (*d*, $^3J = 3.4$, 1 arom. H); 4.30 (*s*, 2 H–C(1″)); 4.26

(*m*, H–C(4)); 4.06 (*dd*, ^3J(3,4) = 3.9, ^3J(3,2) = 8.9, H–C(3)); 3.72 (*ddd*, ^3J(2,1′) = 4.6, ^3J(2,3) = 8.6, ^3J(2,1′) = 8.6, H–C(2)); 3.51 (*dd*, ^3J(5,4) = 3.9, ^2J = 12.6, 1 H–C(5)); 3.39–3.33 (*m*, 1 H–C(5), 2 H–C(1′)); 2.85 (*q*, ^3J = 7.5, MeCH_2); 1.31 (*t*, ^3J = 7.5, *Me*CH$_2$). ^{13}C-NMR (100.6 MHz, MeOD): 152.2 (*s*, arom. C); 135.5 (*s*, arom. C); 131.1 (*d*, ^1J(C,H) = 165, arom. C); 125.7 (*d*, ^1J(C,H) = 170, arom. C); 76.3 (*d*, ^1J(C,H) = 145, C(3)); 71.4 (*d*, ^1J(C,H) = 160, C(4)); 60.2 (*d*, ^1J(C,H) = 146, C(2)); 52.3 (*t*, ^1J(C,H) = 149, C(5)); 50–49 (*t*, C(1′), C(1″)); 25.2 (*t*, ^1J(C,H) = 126, MeCH$_2$); 17.3 (*q*, ^1J(C,H) = 128, *Me*CH$_2$). CI-MS (NH_3): 257 (100, $[M+H]^+$), 229 (26), 211 (21), 174 (6), 154 (13), 125 (68), 102 (16).

tert-*Butyl (3a*R,*4*R,*6a*S*)-Tetrahydro-2,2-dimethyl-4-{{[2-(2-thienyl)ethyl]amino}methyl}-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9p**). To a soln. of **10** (30 mg, 0.11 mmol, 1 equiv.) in 0.5 ml of THF/DMSO 4:1 was added $NaHCO_3$ (18 mg, 0.22 mmol, 2 equiv.), followed by a soln. of 2-(2-thienyl)ethyl methanesulfonate (**15**; 23 mg, 0.11 mmol, 1 equiv.) in 0.5 ml of THF/DMSO 4:1, and finally NaI (5 mg, 0.032 mmol, 0.3 equiv.). After 12 h, a sat. aq. $NaHCO_3$ soln. (3 ml) was added. The aq. layer was extracted with AcOEt (3 × 10 ml), the combined org. extract dried ($MgSO_4$) and evaporated, and the crude product purified by FC (AcOEt/light petroleum ether 8:2): 12 mg (25%), of **9p**), 1.1:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -34$, $[\alpha]_{577}^{25} = -37$, $[\alpha]_{546}^{25} = -39$, $[\alpha]_{435}^{25} = -183$, $[\alpha]_{405}^{25} = -211$ (c = 0.57, CH_2Cl_2). UV (MeCN): 235 (7235), 197 (5950). IR (film): 3020, 2985, 2940, 1685, 1460, 1385, 1370, 1215, 1160, 1130, 1055, 765, 670. ^{1}H-NMR (400 MHz, MeOD): 7.24 (*m*, 1 arom. H); 6.96 (*m*, 1 arom. H); 6.90 (*m*, 1 arom. H); 4.75 (*m*, H–C(6a)); 4.61 (*m*, H–C(3a)); 4.15 (*t*, ^3J(4,1′) = 6.9, H–C(4)$_\beta$); 4.10 (*t*, ^3J(4,1′) = 6.7, H–C(4)$_\alpha$); 3.82 (*d*, ^2J = 12.9, 1 H–C(6)$_\alpha$); 3.78 (*d*, ^2J = 13.3, 1 H–C(6)$_\beta$); 3.39 (*m*, 1 H–C(6), 1 H–C(6)$_\beta$); 3.04 (*m*, 2 H–C(1″)); 2.92 (*m*, 2 H–C(2″)); 2.73 (*m*, 2 H–C(1′)); 1.49 (*s*, (*t*-Bu)$_\beta$); 1.48 (*s*, (*t*-Bu)$_\alpha$); 1.43 (*s*, 1 Me); 1.33 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 156.9 (*s*, NCOO$_\beta$); 156.7 (*s*, NCOO$_\alpha$); 144.2 (*s*, arom. C); 128.7 (*d*, ^1J(C,H) = 169, arom. C); 127.0 (*d*, ^1J(C,H) = 168, arom. C); 125.4 (*d*, ^1J(C,H) = 166, arom. C); 113.0 (*s*); 85.6 (*d*, ^1J(C,H) = 160, C(3a)$_\alpha$); 84.9 (*d*, ^1J(C,H) = 159, C(3a)$_\beta$); 82.2 (*s*, Me$_3$CO$_\alpha$); 82.0 (*s*, Me$_3$CO$_\beta$); 81.6 (*d*, ^1J(C,H) = 157, C(6a)$_\beta$); 81.0 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 65.9 (*d*, ^1J(C,H) = 144, C(4)$_\alpha$); 65.4 (*d*, ^1J(C,H) = 141, C(4)$_\beta$); 53.9, 53.2, 53.0, 52.9 (4*t*, C(6)$_\alpha$, C(6)$_\beta$, C(1′), C(1″)); 31.7 (*t*, ^1J(C,H) = 125, C(2″)); 29.6 (*q*, ^1J(C,H) = 127, *Me*$_3$C); 28.0 (*q*, ^1J(C,H) = 128, Me); 25.8 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 383 (100, $[M+H]^+$), 327 (11), 285 (11), 229 (7), 185 (5), 111 (5). Anal. calc. for $C_{19}H_{30}N_2O_4S$ (382.54): C 59.66, H 7.91; found: C 59.40, H 7.88.

*(2*R,*3*R,*4*S*)-2-{{[2-(2-Thienyl)ethyl]amino}methyl}pyrrolidine-3,4-diol* (**3p**). By *Method Aa*, with **9p** (30 mg). FC (MeCN/NH_4OH 4:1) gave 19 mg (100% of **3p**). $[\alpha]_{589}^{25} = +11$, $[\alpha]_{577}^{25} = +12$, $[\alpha]_{546}^{25} = +13$, $[\alpha]_{435}^{25} = +27$ (c = 0.35, MeOH). UV (MeCN): 234 (6265), 206 (855). IR (film): 3360, 3045, 2850, 1675, 1435, 1200, 1135, 840, 800, 720. ^{1}H-NMR (400 MHz, MeOD): 7.28 (*dd*, ^3J = 5.1, ^4J = 1.2, 1 arom. H); 6.98 (*m*, 2 arom. H); 4.24 (*ddd*, ^3J(4,5) = 2.2, ^3J(4,5) = 4.0, ^3J(4,3) = 4.0, H–C(4)); 4.02 (*dd*, ^3J(3,4) = 4.0, ^3J(3,2) = 8.6, H–C(3)); 3.64 (*ddd*, ^3J(2,1′) = 4.3, ^3J(2,1′) = 8.6, ^3J(2,3) = 8.6, H–C(2)); 3.44 (*dd*, ^3J(5,4) = 4.0, ^2J = 12.6, 1 H–C(5)); 3.38 (*m*, 1 H–C(1′)); 3.26 (*m*, 1 H–C(5)); 3.18 (*m*, 1 H–C(1′), 2 H–C(1″), 2 H–C(2″)). ^{13}C-NMR (100.6 MHz, MeOD): 142.0 (*s*, arom. C); 129.0 (*d*, ^1J(C,H) = 168, arom. C); 127.7 (*d*, ^1J(C,H) = 158, arom. C); 126.1 (*d*, ^1J(C,H) = 179, arom. C); 76.3 (*d*, ^1J(C,H) = 145, C(3)); 71.8 (*d*, ^1J(C,H) = 154, C(4)); 60.9 (*d*, ^1J(C,H) = 146, C(2)); 52.3 (*t*, ^1J(C,H) = 149, C(5)); 50–49 (C(1′), C(1″)); 30.1 (*t*, ^1J(C,H) = 132, C(2″)). CI-MS (NH_3): 243 (100, $[M+H]^+$), 209 (6), 140 (9), 128 (14), 84 (6).

tert-*Butyl(3a*R,*4*R,*6a*S*)-Tetrahydro-4-{{[1-(4-hydroxybenzyl)-2-methoxy-2-oxoethyl]amino}methyl}-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate* (**9q**). By *Method A*, with **8** (84 mg, 0.31 mmol), L-tyrosine methyl ester (61 mg, 0.31 mmol), $NaBH(OAc)_3$ (92 mg, 0.43 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (Et_2O/light petroleum ether 5:1) gave 90 mg (65% of **9q**), 1.9:1 mixture of rotamers α and β. $[\alpha]_{589}^{25} = -50$, $[\alpha]_{577}^{25} = -51$, $[\alpha]_{546}^{25} = -50$, $[\alpha]_{435}^{25} = -78$, $[\alpha]_{405}^{25} = -89$ (c = 0.54, CH_2Cl_2). UV (MeCN): 278 (3090), 225 (11280), 202 (12810). IR (KBr): 3400, 2985, 1740, 1670, 1615, 1595, 1520, 1420, 1370, 1210, 1170, 1130, 1055, 975, 855, 770. ^{1}H-NMR (400 MHz, MeOD): 7.03 (*d*, ^3J = 8.3, 2 arom. H); 6.74 (*d*, ^3J = 8.3, 2 arom. H); 4.57 (*m*, H–C(6a)); 4.49 (*m*, H–C(3a)); 3.98 (*m*, H–C(4)$_\beta$); 3.92 (*m*, H–C(4)$_\alpha$); 3.70 (*m*, 1 H–C(6), CO_2Me); 3.52 (*t*, ^3J(1″,2″) = 6.0, 2 H–C(1″)); 3.39 (*m*, 1 H–C(6)); 2.91 (*dd*, ^3J(2″,1″) = 6.0, ^2J = 15.0, H–C(2″)$_\beta$); 2.83 (*m*, H–C(2″)$_\alpha$), 1 H–C(1′)); 2.48 (*m*, 1 H–C(1′)); 1.49 (*s*, (*t*-Bu)$_\beta$); 1.48 (*s*, (*t*-Bu)$_\alpha$); 1.41 (*s*, 1 Me); 1.29 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 158.1 (*s*, NCOO); 132.1 (*d*, ^1J(C,H) = 156, arom. C); 130.3 (*s*, arom. C); 117.0 (*d*, ^1J(C,H) = 158, arom. C); 113.3 (*s*); 85.8 (*d*, ^1J(C,H) = 157, C(3a)$_\alpha$); 85.0 (*d*, ^1J(C,H) = 157, C(3a)$_\beta$); 82.3 (*s*, Me$_3$CO$_\alpha$); 82.2 (*s*, Me$_3$CO$_\beta$); 81.5 (*d*, ^1J(C,H) = 158, C(6a)$_\beta$); 80.7 (*d*, ^1J(C,H) = 158, C(6a)$_\alpha$); 66.2 (*d*, ^1J(C,H) = 146, C(4)$_\alpha$); 65.8 (*d*, ^1J(C,H) = 145, C(4)$_\beta$); 65.4 (*d*, ^1J(C,H) = 142, C(1″)$_\beta$); 65.2 (*d*, ^1J(C,H) = 140, C(1″)$_\alpha$); 54.6 (*t*, ^1J(C,H) = 143, C(6)$_\beta$); 54.1 (*t*, ^1J(C,H) = 144, C(6)$_\alpha$); 53.0 (*q*, ^1J(C,H) = 125, CO_2Me); 50–49 (C(1′)); 40.2 (*t*, ^1J(C,H) = 126, C(2″)); 29.5 (*q*, ^1J(C,H) = 127, *Me*$_3$C); 28.0 (*q*, ^1J(C,H) = 128, Me); 25.8 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 451 (90, $[M+H]^+$), 450 (60, M^+), 395 (29), 345 (41), 287 (37), 243 (45),

217 (35), 183 (100), 142 (49), 84 (38). Anal. calc. for $C_{23}H_{34}N_2O_7$ (450.55): C 61.32, H 7.61; found: C 61.56, H 7.54.

*2-{[[(2*R*,3*R*,4*S*)-3,4-Dihydroxypyrrolidin-2-yl]methyl]amino}-3-(4-hydroxyphenyl)propanoic Acid* (**3r**). By *Method Aa*, with **9q** (47 mg). FC (MeCN/NH_4OH 4:1) gave 30 mg (100% of **3r**). IR (KBr): 3425, 2950, 1680, 1515, 1440, 1205, 1135, 840, 800, 725, 670, 520, 420. ^{1}H-NMR (400 MHz, D_2O; for numbering, see **3p**): 7.21 (*d*, ^3J = 7.0, 2 arom. H); 6.93 (*d*, ^3J = 7.0, 2 arom. H); 4.38 (*m*, H–C(4)); 3.98 (*dd*, $^3J(1'',2'')$ = 6.0, $^3J(1'',2'')$ = 6.7, H–C(1″)); 3.87 (*dd*, $^3J(5,4)$ = 4.9, ^2J = 14.0, 1 H–C(5)); 3.78 (*m*, H–C(3), H–C(2)); 3.55 (*d*, ^2J = 14.0, 1 H–C(5)); 3.32 (*d*, ^2J = 13.0, 1 H–C(1′)); 3.13 (*m*, 2 H–C(2″)); 2.59 (*m*, 1 H–C(1′)). ^{13}C-NMR (100.6 MHz, D_2O; for numbering, see **3p**): 157.1 (*s*, arom. C); 133.1 (*d*, ^1J(C,H) = 158, 2 arom. C); 131.1 (*s*, arom. C); 117.9 (*d*, ^1J(C,H) = 157, 2 arom. C); 76.8 (*d*, ^1J(C,H) = 147, C(3)); 70.5 (*d*, ^1J(C,H) = 161, C(4)); 59.8 (*d*, ^1J(C,H) = 146, C(2)); 59.2 (*d*, ^1J(C,H) = 142, C(1″)); 54.1 (*t*, ^1J(C,H) = 145, C(5)); 43.7 (*t*, ^1J(C,H) = 143, C(1′)); 38.4 (*t*, ^1J(C,H) = 130, C(2″)). CI-MS (NH_3): 279 (100, $[M+H-H_2O]^+$), 260 (45), 242 (10), 196 (45), 171 (61), 143 (7), 95 (21).

tert-*Butyl (3a*R*,4*S*,6a*S*)-4-(Aminomethyl)-tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**18**; R = H). A soln. of **18f** (413 mg, 1.14 mmol) in anh. MeOH (25 ml) was stirred at r.t. under 1 atm of H_2 in the presence of a cat. amount of 10% $Pd(OH)_2$/C for 2 h. The precipitate was filtered off through a pad of *Celite*, and the solvent was evaporated. The crude product was purified by FC (silica gel, CH_2Cl_2/MeOH 4:1): 243 mg (78%) of **18** (R = H). $[\alpha]_{589}^{25}$ = +48, $[\alpha]_{577}^{25}$ = +50, $[\alpha]_{546}^{25}$ = +55, $[\alpha]_{435}^{25}$ = +87, $[\alpha]_{405}^{25}$ = +102 (*c* = 0.48, CH_2Cl_2). UV (MeCN): 267 (800), 202 (4570). IR (KBr): 3370, 2980, 2940, 1695, 1455, 1395, 1245, 1210, 1170, 1120, 1085, 860. ^{1}H-NMR (400 MHz, MeOD): 4.91 (*dd*, ^3J(3a,6a) = 6.5, ^3J(3a,4) = 6.5, H–C(3a)); 4.81 (*m*, H–C(6a)); 3.86 (*m*, H–C(4)); 3.75 (*dd*, ^3J(6,6a) = 6.8, ^2J = 12.4, 1 H–C(6)); 3.39 (*dd*, ^3J(6,6a) = 3.1, ^2J = 12.4, 1 H–C(6)); 3.07 (*dd*, $^3J(1',4)$ = 4.5, ^2J = 12.9, 1 H–C(1′)); 2.96 (*dd*, $^3J(1',4)$ = 8.5, ^2J = 12.9, 1 H–C(1′)); 1.55 (*s*, 1 Me); 1.51 (*s*, *t*-Bu); 1.39 (*s*, Me). ^{13}C-NMR (100.6 MHz, MeOD): 157.2 (*s*, NCOO); 114.5 (*s*); 82.5 (*d*, ^1J(C,H) = 159, C(3a)); 82.3 (*s*, Me_3CO); 79.9 (*d*, ^1J(C,H) = 158, C(6a)); 63.4 (*d*, ^1J(C,H) = 143, C(4)); 53.2 (*t*, ^1J(C,H) = 145, C(6)); 43.2 (*t*, ^1J(C,H) = 138, C(1′)); 29.5 (*q*, ^1J(C,H) = 127, Me_3C); 27.5 (*q*, ^1J(C,H) = 127, Me); 25.9 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 273 (100, $[M+H]^+$), 272 (8), 243 (5), 217 (81), 201 (4), 187 (15), 173 (46), 142 (19), 112 (4), 84 (9). Anal. calc. for $C_{13}H_{24}N_2O_4$ (272.36): C 57.33, H 8.88; found: C 57.15, H 8.85.

*(2*S*,3*R*,4*S*)-2-(Aminomethyl)pyrrolidine-3,4-diol* (**6**; R = H). By *Method Ab*, with **18** (R = H; 47 mg). FC (MeCN/NH_4OH 1:1) gave 11 mg (100% of **6**) (R = H). $[\alpha]_{589}^{25}$ = +13, $[\alpha]_{577}^{25}$ = +16, $[\alpha]_{546}^{25}$ = +20, $[\alpha]_{435}^{25}$ = +33, $[\alpha]_{405}^{25}$ = +37 (*c* = 0.40, H_2O). UV (MeCN): 276 (1995), 198 (810). IR (KBr): 3410, 2980, 1680, 1635, 1405, 1205, 1135, 990, 800, 725, 670, 565. ^{1}H-NMR (400 MHz, D_2O): 4.61–4.55 (*m*, H–C(3), H–C(4)); 4.09 (*m*, H–C(2)); 3.70 (*dd*, $^3J(1',2)$ = 6.9, ^2J = 13.8, 1 H–C(1′)); 3.63 (*dd*, $^3J(5,4)$ = 6.2, ^2J = 12.3, 1 H–C(5)); 3.53 (*dd*, $^3J(1',2)$ = 6.0, ^2J = 13.8, 1 H–C(1′)); 3.39 (*dd*, $^3J(5,4)$ = 5.6, ^2J = 12.3, 1 H–C(5)). ^{13}C-NMR (100.6 MHz, D_2O): 72.6, 72.3 (2*d*, ^1J(C,H) = 154, ^1J(C,H) = 152, C(3), C(4)); 59.7 (*d*, ^1J(C,H) = 146, C(2)); 50.7 (*t*, ^1J(C,H) = 149, C(5)); 39.1 (*t*, ^1J(C,H) = 146, C(1′)). CI-MS (NH_3): 133 (16, $[M+H]^+$), 116 (16), 102 (100), 98 (6), 89 (5), 85 (49), 73 (7).

tert-*Butyl (3a*R*,4*S*,6a*S*)-Tetrahydro-2,2-dimethyl-4-{[(4-methoxybenzyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**18fh**). By *Method A*, with **17** (100 mg, 0.37 mmol), 4-methoxybenzylamine (48 µl, 0.37 mmol), $NaBH(OAc)_3$ (109 mg, 0.52 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt) gave 81 mg (56% of **18fh**). $[\alpha]_{589}^{25}$ = +43, $[\alpha]_{577}^{25}$ = +45, $[\alpha]_{546}^{25}$ = +52, $[\alpha]_{435}^{25}$ = +81, $[\alpha]_{405}^{25}$ = +100 (*c* = 0.50, CH_2Cl_2). UV (MeCN): 276 (4005), 225 (16400), 203 (16270). IR (film): 3340, 2980, 2935, 2835, 1695, 1615, 1585, 1515, 1455, 1395, 1300, 1245, 1210, 1170, 1115, 1085, 1035, 995, 885, 860, 820, 770. ^{1}H-NMR (400 MHz, MeOD): 7.25 (*d*, ^3J = 8.6, 2 arom. H); 6.86 (*d*, ^3J = 8.6, 2 arom. H); 4.79 (*t*, $^3J(3a,6a)$ = 6.7, $^3J(3a,4)$ = 6.7, H–C(3a)); 4.71 (*m*, H–C(6a)); 4.05 (*dt*, $^3J(4,1')$ = 6.7, $^3J(4,3a)$ = 6.7, H–C(4)); 3.80 (*s*, MeO); 3.77 (*s*, 2 H–C(1″)); 3.73 (*m*, 1 H–C(6)); 3.34 (*dd*, $^3J(6,6a)$ = 3.8, ^2J = 12.4, 1 H–C(6)); 2.90 (*m*, 2 H–C(1′)); 1.47 (*s*, 1 Me); 1.42 (*s*, *t*-Bu); 1.34 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 158.6 (*s*, NCOO); 154.4 (*s*, arom. C); 132.6 (*s*, arom. C); 129.2 (*d*, ^1J(C,H) = 157, 2 arom. C); 113.7 (*d*, ^1J(C,H) = 159, 2 arom. C); 112.7 (*s*); 80.2 (*d*, ^1J(C,H) = 156, C(3a)); 80.0 (*s*, Me_3CO); 77.9 (*d*, ^1J(C,H) = 147, C(6a)); 59.3 (*d*, ^1J(C,H) = 144, C(4)); 55.2 (*q*, ^1J(C,H) = 144, MeO); 53.3 (*t*, ^1J(C,H) = 134, C(1″)); 50.7 (*t*, ^1J(C,H) = 145, C(6)); 48.7 (*t*, ^1J(C,H) = 137, C(1′)); 28.3 (*q*, ^1J(C,H) = 127, Me_3C); 26.3 (*q*, ^1J(C,H) = 127, Me); 25.0 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 393 (100, $[M+H]^+$), 392 (15, M^+), 337 (5), 273 (5), 258 (5), 154 (8), 137 (10), 121 (20), 84 (53). Anal. calc. for $C_{21}H_{32}N_2O_5$ (392.53): C 64.26, H 8.22, N 7.14; found: C 64.11, H 8.31, N 7.14.

*(2*S*,3*R*,4*S*)-2-{[(4-Methoxybenzyl)amino]methyl}pyrrolidine-3,4-diol* (**6fh**). By *Method Aa*, with **18fh** (22 mg). FC (MeCN/NH_4OH 4:1) gave 14 mg (100% of **6fh**). UV (MeCN): 328 (200), 227 (5000), 201 (5700). IR (film): 3420, 1675, 1440, 1255, 1205, 1135, 1040, 840, 800, 725. ^{1}H-NMR (400 MHz, MeOD): 7.46 (*d*, ^3J = 8.7, 2 arom. H); 7.01 (*d*, ^3J = 8.7, 2 arom. H); 4.39 (*m*, H–C(3), H–C(4)); 4.26 (*s*, 2 H–C(1″)); 4.00

(*m*, H–C(2)); 3.84 (*s*, MeO); 3.65 (*dd*, $^3J(1',2) = 5.8$, $^2J = 13.5$, 1 H–C(1')); 3.41 (*m*, 1 H–C(1'), 1 H–C(5)); 3.26 (*dd*, $^3J(5,4) = 4.9$, $^2J = 11.9$, 1 H–C(5)). ^{13}C-NMR (100.6 MHz, MeOD): 164.2 (arom. C); 133.5 (2 arom. C); 124.7 (arom. C); 116.5 (2 arom. C); 73.0 (C(3)); 72.4 (C(4)); 58.9 (C(2)); 56.7 (MeO); 53.4 (C(1'')); 50–49 (C(5)); 46.2 (C(1')). CI-MS (NH_3): 253 (67, $[M+H]^+$), 232 (4), 211 (2), 170 (5), 150 (13), 121 (100), 108 (24), 95 (14).

tert-*Butyl (3a*R,*4*S,*6a*S*)-4-{[([1,1'-Biphenyl]-4-ylmethyl)amino]methyl}tetrahydro-2,2-dimethyl-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**18fs**). By *Method B*, with **18** (R = H; 81 mg, 0.30 mmol), [1,1'biphenyl]-4-carboxaldehyde (81 mg, 0.30 mmol), $NaBH(OAc)_3$ (88 mg, 0.42 mmol), and $ClCH_2CH_2Cl$ (3 ml). FC (AcOEt) gave 100 mg (77% of **18fs**). $[\alpha]_{589}^{25} = +34$, $[\alpha]_{577}^{25} = +35$, $[\alpha]_{546}^{25} = +40$, $[\alpha]_{435}^{25} = +65$, $[\alpha]_{405}^{25} = +76$ (c = 0.46, CH_2Cl_2). UV (MeCN): 308 (4000), 260 (20600), 215 (18600). IR (film): 3335, 2980, 2935, 1695, 1490, 1455, 1395, 1245, 1210, 1165, 1085, 860, 760, 700. ^{1}H-NMR (400 MHz, MeOD): 7.59 (*m*, 4 arom. H); 7.44 (*m*, 4 arom. H); 7.33 (*m*, arom. H); 4.82 (*dd*, $^3J(3a,6a) = 6.6$, $^3J(3a,4) = 6.6$, H–C(3a)); 4.73 (*m*, H–C(6a)); 4.10 (*m*, H–C(4)); 3.88 (*s*, 2 H–C(1'')); 3.79 (*m*, 1 H–C(6)); 3.35 (*dd*, $^3J(6,6a) = 3.6$, $^2J = 12.4$, 1 H–C(6)); 2.95 (*m*, 2 H–C(1')); 1.48 (*s*, 1 Me); 1.42 (*s*, *t*-Bu); 1.35 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 154.4 (*s*, NCOO); 141.1 (*s*, arom. C); 139.9 (*s*, arom. C); 139.6 (*s*, arom. C); 128.7 (*d*, ^1J(C,H) = 168, 2 arom. C); 128.5 (*d*, ^1J(C,H) = 167, 2 arom. C); 127.1 (3*d*, ^1J(C,H) = 153, ^1J(C,H) = 163, ^1J(C,H) = 162, 5 arom. C); 112.7 (*s*); 80.2 (*d*, ^1J(C,H) = 157, C(3a)); 80.0 (*s*, Me_3CO); 77.9 (*d*, ^1J(C,H) = 156, C(6a)); 59.3 (*d*, ^1J(C,H) = 144, C(4)); 53.6 (*t*, ^1J(C,H) = 134, C(1'')); 50.7 (*t*, ^1J(C,H) = 142, C(6)); 48.9 (*t*, ^1J(C,H) = 136, C(1')); 28.4 (*q*, ^1J(C,H) = 127, Me_3C); 26.4 (*q*, ^1J(C,H) = 127, Me); 25.0 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 439 (100, $[M+H]^+$), 383 (12), 363 (20), 337 (2), 315 (10), 243 (5), 215 (10), 196 (16), 182 (22), 167 (42), 142 (9), 120 (3), 85 (8). Anal. calc. for $C_{26}H_{34}N_2O_4$ (438.60): C 71.21, H 7.81, N 6.39; found: C 70.99, H 7.71, N 6.24.

*(2*S,*3*R,*4*S*)-2-{[([1,1'-Biphenyl]-4-ylmethyl)amino]methyl}pyrrolidine-3,4-diol* (**6fs**). By *Method Aa*, with **18fs** (22 mg). FC (MeCN/NH_4OH 4:1) gave 14 mg (100% of **6fs**). $[\alpha]_{589}^{25} = +7$ (c = 0.46, MeOH). UV (MeCN): 260 (7560), 206 (16800). IR (film): 3400–2950, 1670, 1470, 1435, 1200, 1140, 1025, 840, 800, 765, 725, 700. ^{1}H-NMR (400 MHz, MeOD): 7.68 (*d*, $^3J = 8.2$, 2 arom. H); 7.64 (*d*, $^3J = 8.2$, 2 arom. H); 7.57 (*d*, $^3J = 8.2$, 2 arom. H); 7.47 (*dd*, $^3J = 7.3$, $^3J = 8.2$, 2 arom. H); 7.37 (*m*, 1 arom. H); 4.38 (*m*, H–C(4)); 4.34 (*m*, H–C(3)); 4.20 (*AB*, 2 H–C(1'')); 3.87 (*m*, 1 H–C(2)); 3.40 (*m*, 1 H–C(1'), 1 H–C(5)); 3.31 (*dd*, $^3J(1',2) = 6.8$, $^2J = 13.4$, 1 H–C(1')); 3.19 (*dd*, $^3J(5,4) = 5.8$, $^2J = 11.6$, 1 H–C(5)). ^{13}C-NMR (100.6 MHz, MeOD): 143.9 (arom. C); 142.5 (arom. C); 134.8 (arom. C); 131.9 (2 arom. C); 130.8 (2 arom. C); 129.6 (arom. C); 129.4 (2 arom. C); 128.8 (2 arom. C); 73.1 (C(3)); 72.7 (C(4)); 60.1 (C(2)); 53.9 (C(1'')); 50–49 (C(5)); 47.2 (C(1')). CI-MS (NH_3): 299 (100, $[M+H]^+$), 280 (1), 245 (4), 215 (13), 196 (26), 182 (8), 167 (60), 152 (6), 115 (10), 102 (19), 85 (42).

tert-*Butyl (3a*R,*4*S,*6a*S*)-Tetrahydro-2,2-dimethyl-4-{[(2-thienylmethyl)amino]methyl}-5*H*-[1,3]dioxolo[4,5-*c*]pyrrole-5-carboxylate* (**18o**). By *Method A*, with **17** (98 mg, 0.36 mmol), thiophene-2-methanamine (36 µl, 0.36 mmol), $NaBH(OAc)_3$ (107 mg, 0.51 mmol), and $ClCH_2CH_2Cl$ (4 ml). FC (AcOEt/light petroleum ether 2:1) gave 75 mg (56% of **18o**). $[\alpha]_{589}^{25} = +34$, $[\alpha]_{577}^{25} = +39$, $[\alpha]_{546}^{25} = +44$, $[\alpha]_{435}^{25} = +65$, $[\alpha]_{405}^{25} = +77$ (c = 0.44, CH_2Cl_2). UV (MeCN): 235 (12705), 200 (8675). IR (film): 3340, 2980, 2935, 2835, 1695, 1460, 1395, 1250, 1210, 1165, 1115, 1085, 990, 855, 770, 700. ^{1}H-NMR (400 MHz, MeOD): 7.20 (*m*, H–C(5''')); 6.94 (*m*, H–C(3'''), H–C(4''')); 4.80 (*dd*, $^3J(3a,6a) = 6.7$, $^3J(3a,4) = 6.7$, H–C(3a)); 4.72 (*m*, H–C(6a)); 4.06 (*m*, H–C(4)); 4.03 (*s*, 2 H–C(1'')); 3.78 (*m*, 1 H–C(6)); 3.34 (*dd*, $^3J(6,6a) = 3.8$, $^2J = 12.5$, 1 H–C(6)); 2.95 (*m*, 2 H–C(1')); 1.47 (*s*, 1 Me); 1.42 (*s*, *t*-Bu); 1.34 (*s*, 1 Me). ^{13}C-NMR (100.6 MHz, MeOD): 154.3 (*s*, NCOO); 144.3 (*s*, C(2'')); 126.5 (*d*, ^1J(C,H) = 167, C(5''')); 124.7, 124.2 (2*d*, ^1J(C,H) = 166, ^1J(C,H) = 167, C(3'''), C(4''')); 112.7 (*s*); 80.1 (*s*, Me_3CO); 80.0 (*d*, ^1J(C,H) = 157, C(3a)); 77.8 (*d*, ^1J(C,H) = 145, C(6a)); 59.2 (*d*, ^1J(C,H) = 144, C(4)); 50.6 (*t*, ^1J(C,H) = 147, C(6)); 48.6, 48.4 (2*t*, ^1J(C,H) = 136, C(1'), C(1'')); 28.3 (*q*, ^1J(C,H) = 127, Me_3C); 26.3 (*q*, ^1J(C,H) = 127, Me); 25.0 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 369 (100, $[M+H]^+$), 368 (30, M^+), 313 (28), 269 (8), 243 (1), 208 (3), 142 (7), 126 (8), 112 (8), 97 (28). Anal. calc. for $C_{18}H_{28}N_2O_4S$ (368.51): C 58.67, H 7.66; found: C 58.66, H 7.70.

*(2*S,*3*R,*4*S*)-2-{[(2-Thienylmethyl)amino]methyl}pyrrolidine-3,4-diol* (**6o**). By *Method Aa*, with **18o** (22 mg). FC (MeCN/NH_4OH 4:1) gave 14 mg (100% of **6o**). $[\alpha]_{589}^{25} = +2$ (c = 0.41, MeOH). UV (MeCN): 277 (910), 233 (5980), 200 (3300). IR (film): 3020, 1675, 1435, 1215, 1135, 760, 670, 465. ^{1}H-NMR (400 MHz, MeOD): 7.48 (*m*, H–C(5''')); 7.22 (*m*, H–C(3''')); 7.07 (*m*, H–C(4''')); 4.40 (*m*, H–C(4)); 4.36 (*AB*, 2 H–C(1'')); 4.31 (*m*, H–C(3)); 3.85 (*m*, H–C(2)); 3.42 (2*d*, 1 H–C(5), 1 H–C(1')); 3.28 (*dd*, $^3J(1',2) = 7.1$, $^2J = 13.3$, 1 H–C(1')); 3.21 (*dd*, $^3J(5,4) = 6.2$, $^2J = 11.7$, 1 H–C(5)). ^{13}C-NMR (100.6 MHz, MeOD): 138.2 (*s*, C(2'')); 130.9 (*d*, ^1J(C,H) = 162, C(3''')); 129.2 (*d*, ^1J(C,H) = 164, C(5''')); 128.9 (*d*, ^1J(C,H) = 163, C(4''')); 72.9 (*d*, ^1J(C,H) = 152, C(3)); 72.6 (*d*, ^1J(C,H) = 149, C(4)); 60.5 (*d*, ^1J(C,H) = 145, C(2)); 50–49 (C(5)); 48.4 (*t*, ^1J(C,H) = 143, C(1'')); 46.6 (*t*, ^1J(C,H) = 145, C(1')). CI-MS (NH_3): 229 (6, $[M+H]^+$), 140 (2), 126 (18), 106 (17), 97 (100), 85 (35), 70 (3).

*N-{[(2*R*,3*R*,4*S*)-3,4-Dihydroxypyrrolidin-2-yl]methyl}-*N*-(4-phenylbutyl)acetamide* (**12i**). According to [16]. ^{1}H-NMR (400 MHz, D_2O; for numbering, see **3i**): 7.31–7.17 (*m*, 5 arom. H); 4.25 (*m*, H–C(4)); 3.99 (*dd*, $^3J(3,4) = 4.1$, $^3J(3,2) = 9.4$, H–C(3)); 3.79 (*dd*, $^3J(1',2) = 8.6$, $^2J = 15.1$, 1 H–C(1')); 3.53–3.47 (*m*, H–C(2), 1 H–C(5)); 3.42 (*dd*, $^3J(1',2) = 2.3$, $^2J = 15.1$, 1 H–C(1')); 3.32 (*m*, 2 H–C(1'')); 3.17 (*d*, $^2J = 13.3$, 1 H–C(5)); 2.61 (*m*, 2 H–C(4'')); 2.03 (*s*, AcN); 1.57 (*m*, 2 H–C(2''), 2 H–C(3'')). ^{13}C-NMR (100.6 MHz, D_2O; for numbering, see **3i**): 178.4 (C=O), 75.1 (C(3)), 71.3 (C(4)), 62.8 (C(2)), 52.7, 52.3 (C(5), C(1'')), 48.7 (C(1')), 37.0 (C(4'')); 30.1, 29.4 (C(2''), C(3'')); 22.8 (*Me*CON). CI-MS (NH_3): 307 (12, $[M+H]^+$), 288 (21), 271 (3), 204 (7), 162 (10), 115 (53), 102 (100), 91 (36).

*N-[4-(Acetyloxy)butyl]-N-{[(2*R*,3*R*,4*S*)-3,4-dihydroxypyrrolidin-2-yl]methyl}acetamide* (**13**). According to [16]. ^{1}H-NMR (400 MHz, D_2O; for numbering, see **3i**): 4.25 (*ddd*, $^3J(4,5) = 1.2$, $^3J(4,5) = 4.0$, $^3J(4,3) = 4.1$, H–C(4)); 4.04–4.00 (*m*, H–C(3), 2 H–C(4'')); 3.85 (*dd*, $^3J(1',2) = 8.8$, $^2J = 15.2$, 1 H–C(1')); 3.54 (*ddd*, $^3J(2,1') = 2.5$, $^3J(2,1') = 8.8$, $^3J(2,3) = 9.2$, H–C(2)); 3.49–3.43 (*m*, 1 H–C(5), 1 H–C(1')); 3.35 (*m*, 2 H–C(1'')), 3.19 (*dd*, $^3J(5,4) = 1.2$, $^2J = 12.0$, 1 H–C(5)); 2.06, 1.98 (2*s*, AcN, AcO); 1.60–1.58 (*m*, 2 H–C(2''), 2 H–C(3'')). ^{13}C-NMR (100.6 MHz, D_2O; for numbering, see **3i**): 178.5, 177.2 (2 C=O); 75.0 (C(3)); 71.3 (C(4)); 67.4 (C(4'')); 62.9 (C(2)); 52.5 (C(1'')); 52.3 (C(5)); 48.6 (C(1')); 27.4, 26.7 (C(2''), C(3'')); 22.9, 22.8 (*Me*CON, *Me*COO). CI-MS (NH_3): 289 (20, $[M+H]^+$), 270 (6), 115 (18), 137 (2), 102 (72), 84 (100).

*(2*R*,3*R*,4*S*)-3,4-Dihydroxypyrrolidine-2-carboxaldehyde Phenylhydrazone* (**19**). To a soln. of **8** (91 mg, 0.340 mmol) in $Cl(CH_2)_2Cl$ (2.5 ml) was added phenylhydrazine (33 µl, 0.340 mmol), and the mixture was stirred at 20° for 4 h. The solvent was evaporated and the residue taken up in 1M aq. HCl (2 ml). After strirring for 30 min at 20°, the solvent was evaporated and the residue purified by FC (silica gel, MeCN/NH_4OH 4:1): **19** (56 mg, 75%). Pale yellow oil. $[\alpha]_{589}^{25-} + 19$ ($c = 0.24$, MeOH). ^{1}H-NMR (400 MHz, MeOD): 7.27–7.13 (*m*, 2 arom. H, H–C(1')); 7.04 (*m*, 2 arom. H); 6.81 (*m*, 1 arom. H); 4.36 (*m*, H–C(4)); 4.24 (*m*, H–C(2), H–C(3)); 3.57 (*dd*, $^3J(4,5) = 4.9$, $^2J = 12.5$, 1 H–C(5)); 3.30 (*dd*, $^3J(4,5) = 2.8$, $^2J = 12.5$, 1 H–C(5)). ^{13}C-NMR (100.6 MHz, MeOD): 163.7 (C(1')); 131.1 (arom. C); 130.9 (2 arom. C); 121.8 (arom. C); 114.2 (2 arom. C); 76.6 (C(3)); 71.7 (C(4)); 63.8 (C(2)); 51.5 (C(5)). CI-MS (NH_3): 222 (5, $[M+H]^+$), 186 (4), 171 (16), 137 (2), 109 (16), 93 (100), 77 (9).

*(2*R*,3*R*,4*S*)-2-{[Benzyl(hydroxy)amino]methyl}pyrrolidine-3,4-diol* (**20**). To a soln. of **8** (80 mg, 0.295 mmol) in $Cl(CH_2)_2Cl$ (2 ml) were added *N*-benzylhydroxylamine hydrochloride (47 mg, 0.295 mmol) and $NaBH(OAc)_3$ (88 mg, 0.413 mmol). The mixture was stirred at 20° for 12 h and then poured into sat. aq. $NaHCO_3$ soln. (15 ml). The aq. layer was extracted with AcOEt (3 × 15 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated. The residue was taken up in 80% aq. CF_3COOH soln. (4 ml) and stirred for 30 min at 20°. The solvent was evaporated and the residue submitted to FC (silica gel, MeCN/NH_4OH 4:1): **20** (44 mg, 62%). Colorless oil. $[\alpha]_{589}^{25-} + 5$ ($c = 0.28$. MeOH). UV (MeCN): 298 (620), 212 (1540). IR (film): 3400–2945, 1680, 1435, 1375, 1205, 1135, 1040, 920, 835, 800, 760, 725. ^{1}H-NMR (400 MHz, MeOD): 7.59–7.28 (*m*, 5 arom. H); 4.28 (*ddd*, $^3J(4,5) = 1.8$, $^3J(4,5) = 4.0$, $^3J(4,3) = 4.0$, H–C(4)); 4.11 (*dd*, $^3J(3,4) = 4.0$, $^3J(3,2) = 8.9$, H–C(3)); 3.97 (*AB*, 2 H–C(1'')); 3.79 (*ddd*, $^3J(1',2) = 2.5$, $^3J(2,1') = 8.9$, $^3J(2,3) = 8.9$, H–C(2)); 3.48 (*dd*, $^3J(5,4) = 4.0$, $^2J = 12.7$, 1 H–C(5)); 3.30 (*dd*, $^3J(5,4) = 1.8$, $^2J = 12.7$, 1 H–C(5)); 3.21 (*dd*, $^3J(1',2) = 2.5$, $^2J = 14.0$, 1 H–C(1')); 3.48 (*dd*, $^3J(1',2) = 8.9$, $^2J = 14.0$, 1 H–C(1')). ^{13}C-NMR (100.6 MHz, MeOD): 138.8 (*s*, arom. C); 131.6 (*d*, $^1J(C,H) = 152$, 2 arom. C); 130.1 (*d*, $^1J(C,H) = 160$, 2 arom. C); 129.4 (*d*, $^1J(C,H) = 151$, arom. C); 75.4 (*d*, $^1J(C,H) = 145$, C(3)); 71.5 (*d*, $^1J(C,H) = 154$, C(4)); 67.0 (*t*, $^1J(C,H) = 135$, C(1'')); 61.7 (*d*, $^1J(C,H) = 147$, C(2)); 59.9 (*t*, $^1J(C,H) = 135$, C(1')); 51.7 (*t*, $^1J(C,H) = 146$, C(5)). CI-MS (NH_3): 239 (59, $[M+H]^+$), 223 (52), 196 (11), 174 (2), 133 (6), 120 (30), 106 (33), 91 (100).

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Received October 11, 2002