(1*S*,2*S*,3*R*,6*R*)-6-Aminocyclohex-4-ene-1,2,3-triol (= (−)-Conduramine B-1) Is a Selective Inhibitor of α-Mannosidases. Its Inhibitory Activity Is Enhanced by *N*-Benzylation

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(−)- and (+)-Conduramine B-1 ((−)- and (+)-**5**, resp.) have been derived from (+)- and (−)-7-oxabicyclo[2.2.1]hept-5-en-2-one ('naked sugars' of the first generation). Although (−)-**5** imitates the structure of β-glucosides, it does not inhibit β-glucosidases but inhibits α-mannosidases selectively. *N*-Benzylation of (−)-**5** improves the potency of conduramine B-1 as α-mannosidase inhibitor and also generates compounds inhibiting β-glucosidases. For instance, (−)-*N*-benzyl-conduramine B-1 ((−)-**19a**) is a competitive inhibitor of β-glucosidase from almonds (IC_{50} = 32 μM, K_i = 10 μM) and a weak inhibitor of α-mannosidases from jack bean (IC_{50} = 171 μM) and from almonds (IC_{50} = 225 μM) whereas (−)-*N*-(4-phenylbenzyl)conduramine B-1 ((−)-**19g**) is a good inhibitor of α-mannosidase from jack beans (IC_{50} = 29 μM, K_i = 4.8 μM) and a weaker inhibitor of β-glucosidase from almonds (IC_{50} = 32 μM, K_i = 7.8 μM) (*Table 1*).

Introduction. – Aberrant glycosylation of glycoproteins and glycolipids was reported to be one of the molecular changes that accompany malignant transformations [1]. As both catabolic and processing glycosidases are involved in the transformation of normal cells to cancer cells and in tumor-cell invasion and migration [2], it has been proposed that the specific inhibition of α-mannosidases involved in the addition of *N*-linked carbohydrates to glycoproteins may provide new anticancer strategy [3]. Swainsonine (**1**), a natural inhibitor of *Golgi* α-mannosidase II, which contains a 4-amino-4-deoxy-mannofuranose moiety [4], decreases the growth of solid tumors and hematological malignancies [5]. Subcutaneous administration of swainsonine completely inhibited the growth and the formation of lung metastases of sarcoma [6]. Nevertheless, the toxicity observed for this alkaloid as well as the undesired co-inhibition of lysosomal fucosidases resulted in the search for new, more selective α-mannosidases inhibitors [7]. Some analogues of swainsonine as well as simpler derivatives have shown interesting inhibitory properties [8–10]. Our group previously reported that 3,4-dihydroxypyrrolidin-2-yl derivatives such as **2**–**4** (*Fig. 1*) are selective and competitive inhibitors of α-mannosidase from jack beans [11–13]. This enzyme is a useful model for mammalian α-mannosidases such as *Golgi* α-mannosidase II [14]. We have found that esters of **4** inhibit the growth of human glioblastoma and melanoma cells [13].

Recently we reported that (−)-conduramine B-1 ((−)-**5**); *Fig. 2*) does not inhibit β-glucosidases and β-xylosidases although this compound mimicks β-glycopyranosides and β-xylopyranosides [15]. We found, however, that *N*-benzyl derivatives of (−)-**5** are good competitive inhibitors of these enzymes. The most potent β-glucosidase inhib-

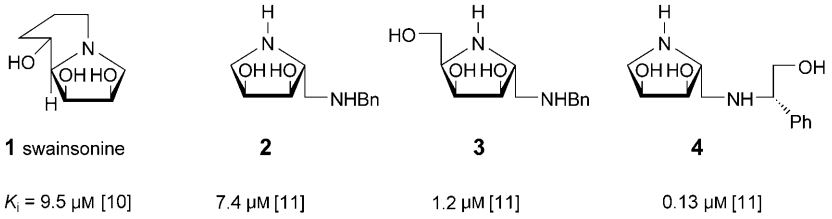


Fig. 1. *Examples of α-mannosidase inhibitors from jack bean*

itor, (−)-*N*-(4-phenylbenzyl)conduramine B-1 (=(−)-*N*-[(1,1′-biphenyl]-4-ylmethyl]-conduramine B-1; **6**≡**19g**) was also the most selective inhibitor in assays involving *α*-glucosidases from rice and yeast, amyloglucosidase form *Aspergillus niger* and *Rhizopus* mold, *β*-glucosidases from almonds and *Caldocellum saccharolyticum* and *β*-xylosidase form *Aspergillus niger* [15]. Thus **6** and other *N*-benzyl derivatives of (−)-conduramine B-1 should be tested for their ability to act as chemical chaperones and for their therapeutic potential for the *Gaucher*'s disease [16]. With a structure having one hydroxymethyl group less than *β*-valienamine derivative **7** [17], which was shown to act as a chemical chaperone [18] accelerating transport and maturation of F2-3I mutant *β*-glucosidase [17], **6** and analogues are expected to be more hydrophobic than **7** and thus to have a better chance to become oral active drugs in the treatment of *Gaucher*'s disease.

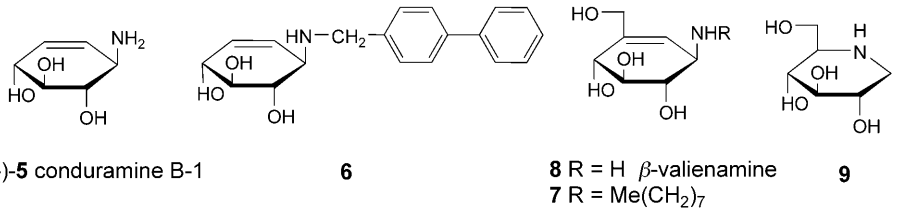


Fig. 2. *(−)-Conduramine B-1 and analogs*

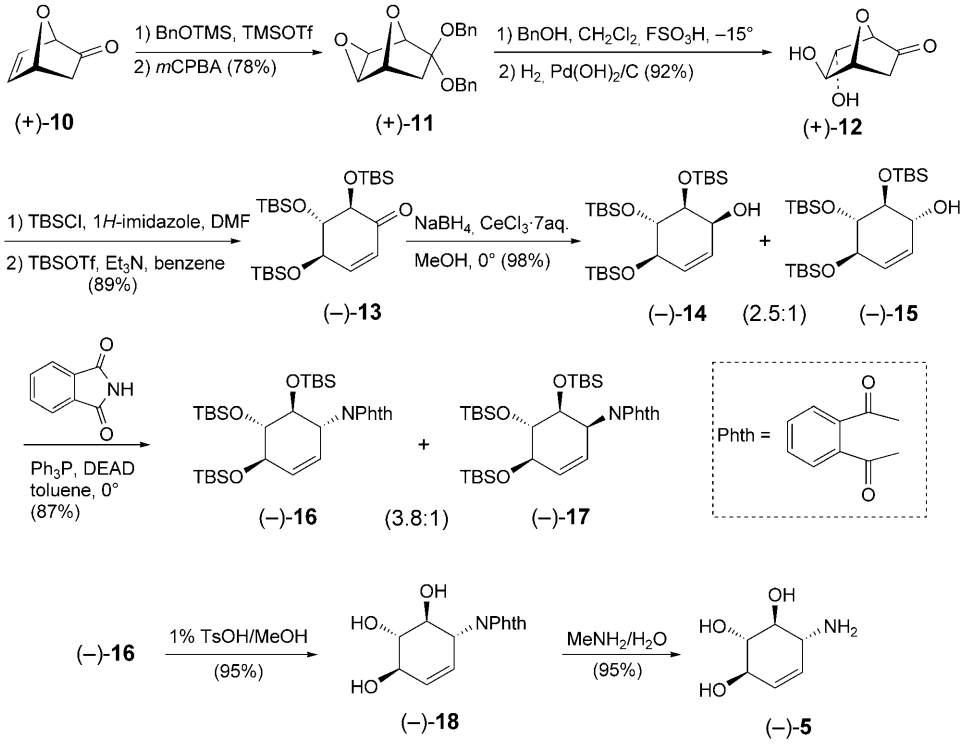
Recently, *Ogawa* and co-workers [19] reported that *β*-valienamine (**8**), as (−)-conduramine B ((−)-**5**), does not inhibit *β*-glucosidase from almonds but is a weak inhibitor (IC_{50} = 190 μM) of *α*-mannosidase from jack beans. Interestingly, 1-deoxymannonojirimycin (**9**; *Fig. 2*) is not a much better inhibitor (IC_{50} = 150 μM) of this enzyme than **8**. Inspired by these unexpected results, we now assayed (−)-conduramine B-1 toward glycosidases and found that it inhibits *α*-mannosidases from jack beans and from almonds, whereas it does not inhibit any of the other glycosidases (*α*-L-fucosidase, *α*-galactosidases, *β*-galactosidases, *α*-glucosidases, amyloglucosidases, *β*-glucosidases, *β*-mannosidase, *β*-xylosidase, *α*-*N*-acetylgalactosaminidases, *β*-*N*-acetyl glucosaminidases). With the hope to enhance the inhibitory activity of (−)-conduramine B-1, we prepared several *N*-substituted derivatives (some of them have been presented in our preliminary communication [15]) and assayed them toward 21 commercially available glycosidases.

As for the inhibition of *β*-glucosidases from almonds and from *Saccharomyces cerevisiae*, (−)-*N*-(4-phenylbenzyl)conduramine B-1 presented the highest inhibitory

activity toward α-mannosidases from jack bean ($K_i = 4.8$ μM, $IC_{50} = 29$ μM) and from almonds ($K_i = 16$ μM, $IC_{50} = 32$ μM). Expectedly, (+)-conduramine B-1 and its *N*-substituted derivatives did not inhibit these enzymes at 1 mM concentration.

Results. – (−)-Conduramine B-1 ((−)-**5**) was derived from (+)-7-oxabicyclo[2.2.1]-hept-5-en-2-one [20] ((+)-**10**), a naked sugar of the first generation [21], applying chemistry reported for the synthesis of (−)-conduritol F [22] (*Scheme 1*). Reduction of cyclohexenone (−)-**13** (obtained *via* (+)-**11** and (+)-**12**) [22] with $NaBH_4/CeCl_3 \cdot 7\,H_2O$ in MeOH (0°, 3 h) gave a 2.5 : 1 mixture of conduritol F and conduritol B derivatives (−)-**14** and (−)-**15**, respectively, in 98% yield. Treatment of this mixture with phthalimide, diethyl azodicarboxylate (= diethyl diazenedicarboxylate; DEAD) and Ph_3P (all to the amount of 1.25 equiv.) [23] in dry toluene (0°, 12 h) provided a 3.8 : 1 mixture of *N*-substituted phthalimides (−)-**16** and (−)-**17** (87%) that were separated by flash chromatography (silica gel). Under acidic conditions (1% TsOH in MeOH, 65°, 3 h), (−)-**16** was converted into triol (−)-**18** in 95% yield. Transaminolysis of (−)-**18** with $MeNH_2$ (41% in H_2O, 20°, 20 min) and purification by ion exchange (*Dowex-50W* (H^+ form), 2N NH_4OH/H_2O) provided pure (−)-conduramine B-1 ((−)-**5**) in 95% yield (*Scheme 1*).

Scheme 1. *Synthesis of (−)-Conduramine B-1 ((−)-***5**



TMS = Me_3Si, *m*CPBA = 3-chloroperbenzoic acid, TBS = $^tBuMe_2Si$, DEAD = EtOOCN=NCOOEt, Phth = phthaloyl

The *N*-substituted derivatives (−)-**19a**–**i** were prepared by standard reductive amination of the corresponding aldehyde [11] (*Scheme 2*). Starting with 'naked sugar' (−)-7-oxabicyclo[2.2.1]hept-5-en-2-one ((−)-**10** [20]), (+)-conduramine B-1 ((+)-**5**) and its derivatives (+)-*ent*-**19a**–**i** were prepared with the same ease. As the latter compounds had none or only very weak inhibitory activities on the glycosidases assayed (see below), we continued our exploration of the effect of *N*-substitution of conduramine B-1 on its glycosidase inhibitory activities by preparing racemic (±)-**5** and its *N*-substituted derivatives (±)-**19j**–**z** and *N,N*-disubstituted derivatives (±)-**20aa**–**dd** (*Scheme 2*).

To learn about the importance of the conformation of the aminotriol unit of (−)- and (+)-conduramine B-1 on their glycosidase inhibitory activities, we prepared (±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-aminocyclohexane-1,2,3-triol (=(±)-dihydroconduramine B-1; (±)-**21**[1])) by catalytical hydrogenation of (±)-**5** (*Scheme 3*).

Aldehydes **23n**–**p** and **23t**,**u** used in the syntheses of (±)-**19n**–**p** and (±)-**19t**,**u** were prepared by nucleophilic displacement of 4-fluorobenzaldehyde with the corresponding 4-substituted or fused phenols **22** following known procedures [25] (*Scheme 4*). Aldehyde **23q** was obtained in a similar way *via* enol ether **24**.

Reduction of (±)-**19q** by $NaBH_4$ (MeOH, 25°) gave a 1:1 mixture of diastereoisomers (±)-**19r** (see above, *Scheme 2*) in 89% yield. The synthesis of (±)-**19s** started with the reductive amination of aldehyde **24** with (±)-**5** and $NaBH(OAc)_3$ (25°, MeOH). Staying overnight in dry MeOH, the intermediate aryl enol ether was completely methanolyzed into dimethyl acetal (±)-**19s** (60% yield).

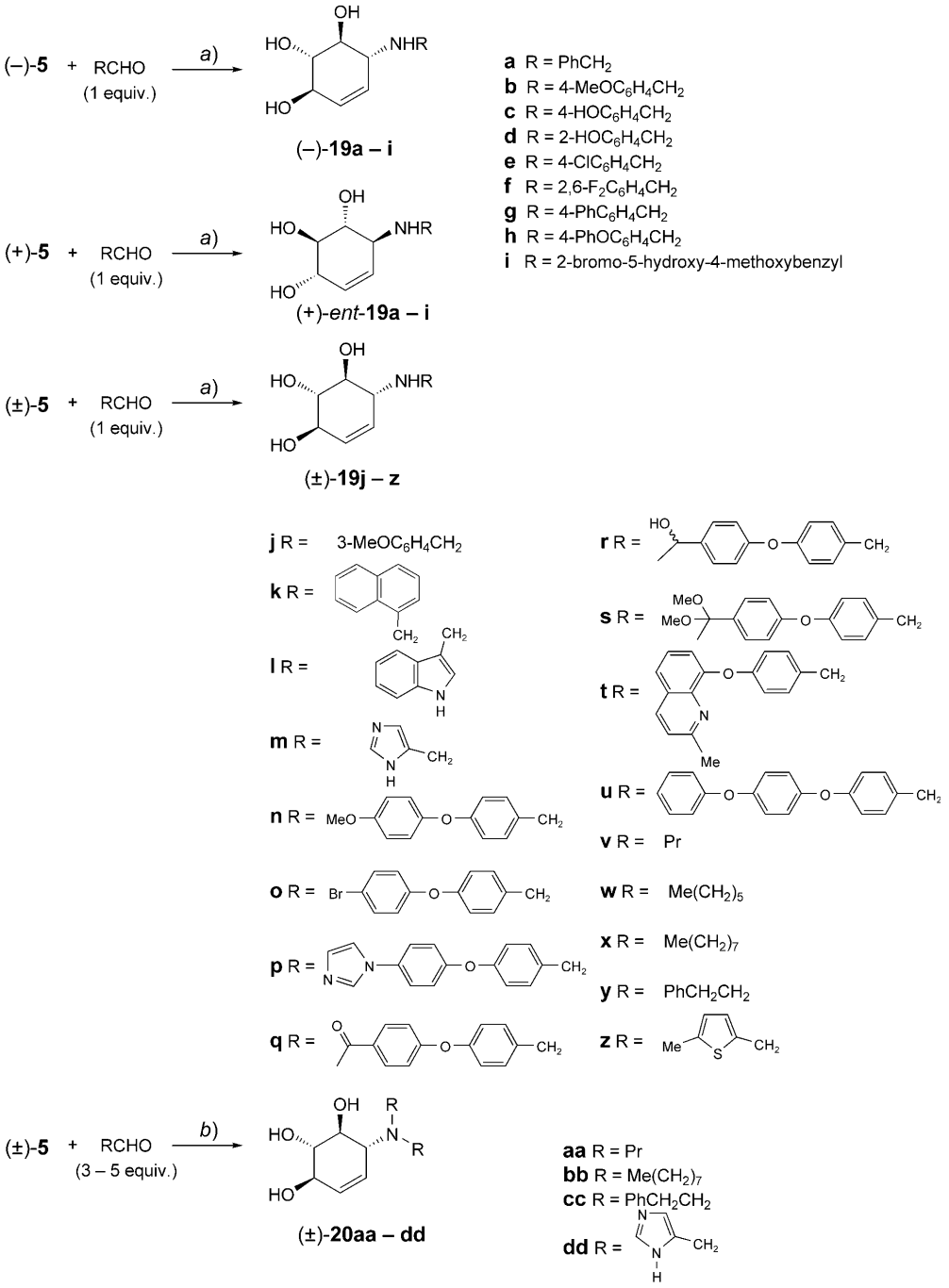
To evaluate the role of the aromatic appendage of conduramine B-1 derivatives (±)-**19p**,**t**,**u**, we prepared the simpler secondary amines **26**–**30** from aldehydes **23p**,**t**,**u** and primary amines **25** (*Scheme 4*) and submitted them to the enzymatic assays in parallel with the testing of (−)- and (+)-conduramine B-1 and their *N*-substituted derivatives (see below).

All compounds shown in the *Table* were tested for their inhibitory activity toward 21 commercially available glycosidases [26]. At 1 mM concentration they did not inhibit α-fucosidase from bovine epididymis, α-galactosidase from *Escherichia coli*, β-galactosidase from *E. coli*, from *Aspergillus niger*, and from *Aspergillus orizae*, α-glucosidase form yeast and from rice, β-mannosidase from *Helix pomatia*, α-*N*-acetylgalactosaminidase from chicken liver and β-*N*-acetylglucosaminidase from jack bean and from bovine epididymis A and B. Compounds **26** and **27** showed *ca.* 50% inhibition of α-L-fucosidase from bovine epididymis and **29** 62% inhibition of α-glucosidase from yeast at 1 mM concentration. The phthalimide (±)-**18** was also assayed and shown to be a weak inhibitor of β-mannosidase from *Helix pomatia* (37% inhibition at 1 mM concentration). The results for nine other enzymes are summarized in the *Table*.

Discussion. – The most striking finding is that (−)-conduramine B-1 ((−)-**5**), that imitates β-glucopyranosides, is not recognized by β-glucosidases from almonds and from *Saccharomyces cerevisiae* but inhibits α-mannosidases from jack beans and from almonds. Interestingly, (+)-conduramine B-1 ((+)-**5**) and dihydroconduramine

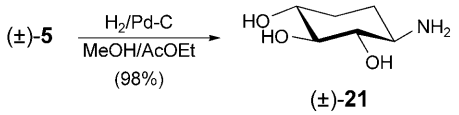
[1]) Dihydroconduramine B-1 has not been described yet. For other stereoisomers, see [24].

Scheme 2. *Synthesis of N-Substituted Conduramine B-1 Derivatives*



a) $NaBH(OAc)_3$, MeOH, 20°, 2 – 5 h. *b*) $NaBH(OAc)_3$, MeOH, 20°, overnight.

Scheme 3. *Synthesis of (±)-Dihydrocondramine B-1 ((±)-***21***)*



B-1 ((±)-**21**) do not inhibit any of the enzymes assayed, except for a weak (57% at 1 mM) inhibition of β-xylosidase from *Aspergillus niger* by (±)-**21**. We attribute the ability of (−)-**5** to recognize α-mannosidases to its most stable pseudo-chair conformation shown in *Fig. 3*. Interestingly, this conformation can be superposed with an envelope conformation of (2*R*,3*R*,4*S*)-2-(aminomethyl)pyrrolidine-3,4-diol (**31**), an α-mannosidase inhibitor. Thus the 3,4-dihydroxy and 1-amino moieties of (−)-**5** (trivial atom numbering) coincide with the 3,4-diol and the primary amine units of **31** (*Fig. 3*).

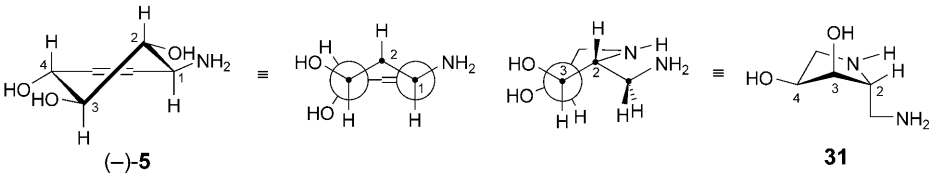


Fig. 3. *Representation of the functional groups of (−)-**5** and **31** that can occupy the same sites in the active site of α-mannosidases* (trivial atom numbering of (−)-**5**)

Although (−)-**5** does not inhibit β-glucosidases, we found that *N*-benzyl derivatives are good and competitive inhibitors of these enzymes (see, *e.g.*, (−)-**19a** (*N*-benzyl) and (−)-**19g** (*N*-(4-phenylbenzyl)) that showed $K_i = 10$ and 7.8 μM, respectively, toward β-glucosidase from almonds). Now we find that the inhibitory activity of conduramine B-1 ((−)-**5**) toward α-mannosidase is also enhanced by *N*-benzylation, and it is also (−)-**19g** that is the most potent α-mannosidase inhibitor ($K_i = 4.8$ μM, α-mannosidase from jack beans). Comparing the IC_{50} values of the *Table*, one finds that (−)-**19g** is the most selective inhibitor of α-mannosidases, whereas (−)-**19a** is a better inhibitor of β-glucosidase from almonds than of α-mannosidases.

Although many structural variations have been carried out in this work, we have not found yet the *N*-substituted conduramine B-1 derivative that is either a highly selective inhibitor of β-glucosidases or a highly selective inhibitor of α-mannosidases. Not unexpectedly, (+)-conduramine B-1 ((+)-**5**) and its *N*-substituted derivatives (+)-*ent*-**19** are not recognized at all neither by β-glucosidases, nor by α-mannosidases. However, one notes that (+)-*ent*-**19a**,**c**–**f** are weak to moderate inhibitors of amyloglucosidases from *Aspergillus niger* and from *Rhizopus* mold, whereas (+)-**5** is not. This demonstrates again the importance of the *N*-benzyl appendages of these inhibitors in their ability to recognize the glycosidases.

Except for **28**, that inhibits α-mannosidase from jack bean moderately (85% inhibition at 1 mM concentration), amines **26**, **27**, **29**, and **30** do not recognize this enzyme. All compounds **26**–**30** ignore α-mannosidase from almonds. Thus, the (−)-conduramine B-1 moiety is required for efficient recognition of α-mannosidases. Interestingly, **26**–**28** are weak inhibitors of β-glucosidase from almonds (34, 32, and 69%, resp., at 1 mM con-

Table. *Inhibitory Activities of Conduramine B-1 and Its Derivatives and of Amines* **26**–**30**. Percentage of inhibiton at 1 mM concentration, IC_{50} (italic) and K_i (italic) at optimal pH. When established (K_i measurements, *Lineweaver-Burk* plots), inhibitions are competitive, except when indicated. M = Mixed-type inhibition; n.i. = no inhibition at 1 mM, n.m. = not measured.

	α-Gal	β-Gal	Amyloglu.		β-Glucosidase		α-Mannosidases		β-Xylosidase
	[a])	[b])	[c])	[d])	[e])	[f])	[g])	[h])	[i])
(−)-**5**	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	72%	67%	n.i.
(−)-**19a**	n.i.	46%	n.i.	n.i.	96% *32*[j]) *10*[k])	43%	78% *171*[j])	79% *225*[j])	74%
(−)-**19b**	n.i.	76%	n.i.	n.i.	95% *52*[j]) *25*[k])	68%	91% *91*	86% *86*[j])	74%
(−)-**19c**	n.i.	23%	31%	57%	93% *72*[j])	56%	90% *100*[j])	86% *183*[j])	67%
(−)-**19d**	n.i.	46%	n.i.	20%	62% *553*[j])	27%	40%	60%	n.i.
(−)-**19e**	n.i.	76%	n.i.	n.i.	96% *35*[j])	84% *185*[j])	92% *91*[j])	90% *77*[j])	n.i.
(−)-**19f**	n.i.	41%	n.i.	n.i.	85%	39%	90%	80%	n.i.
(−)-**19g**	n.i.	97%	n.i.	n.i.	97% *32*[j]) *7.8*[k])	94% *35*[j])	97% *29*[j]) *4.8*[k])	94% *32*[j]) *16*[k]) (M)	n.i.
(−)-**19h**	n.i.	96%	n.i.	n.i.	97% *43*[j]) *13*[k])	71% *52*[j])	96% *40*[j]) *14*[k])	90% *63*[j])	n.i.
(−)-**19i**	n.i.	34%	n.i.	n.i.	n.i.	43%	79% *154*[j])	51%	n.i.
(+)-**5**	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.
(+)-*ent*-**19a**	n.i.	n.i.	67%	72%	51%	n.i.	n.i.	n.i.	n.i.
(+)-*ent*-**19b**	n.i.	33%	n.i.	n.i.	31%	n.i.	n.i.	n.i.	n.i.
(+)-*ent*-**19c**	n.i.	n.i.	94%	85%	29%	n.i.	n.i.	n.i.	n.i.
(+)-*ent*-**19d**	n.i.	n.i.	42%	41%	n.i.	n.i.	n.i.	n.i.	n.i.
(+)-*ent*-**19e**	n.i.	27%	45%	72%	82%	n.i.	n.i.	n.i.	n.i.
(+)-*ent*-**19f**	n.i.	47%	50%	72%	n.i.	n.i.	n.i.	n.i.	n.i.
(+)-*ent*-**19g**	n.i.	63%	n.i.	n.i.	56%	n.i.	n.i.	n.i.	n.i.
(+)-*ent*-**19h**	n.i.	60%	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.
(+)-*ent*-**19i**	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.
(±)-**21**	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	57%
(±)-**19j**	n.i.	56%	n.i.	n.i.	75%	29%	81%	76%	n.i.
(±)-**19k**	n.i.	74%	n.i.	39%	59%	77%	84%	76%	n.i.
(±)-**19l**	n.i.	n.i.	n.i.	29%	n.i.	n.i.	63%	73%	n.i.
(±)-**19m**	n.i.	n.i.	n.i.	68%	37%	n.i.	83%	88%	n.i.
(±)-**19n**	n.i.	89%	n.i.	n.i.	82% *82*[j])	n.m.	74% *287*[j])	n.m.	n.i.
(±)-**19o**	n.i.	91%	n.i.	n.i.	77% *60*[j])	n.m.	83% *210*[j])	n.m.	n.i.
(±)-**19p**	n.i.	91%	n.i.	65%	69%	n.m.	85%	n.m.	n.i.
(±)-**19q**	n.i.	89%	n.i.	n.i.	81% *82*[j])	n.m.	82% *206*[j])	n.m.	n.i.

Table (cont.)

	α-Gal	β-Gal	Amyloglu.		β-Glucosidase		α-Mannosidases		β-Xylosidase
	[a])	[b])	[c])	[d])	[e])	[f])	[g])	[h])	[i])
(±)-**19r**	n.i.	85%	n.i.	n.i.	n.i.	n.m.	76% *275*[j])	n.m	n.i.
(±)-**19s**	n.i.	92%	n.i.	n.i.	80% *64*[j])	n.m.	84% *202*[j])	n.m.	n.i.
(±)-**19t**	n.i.	90%	n.i.	n.i.	69%	n.m.	85%	n.m.	n.i.
(±)-**19u**	n.i.	82%	n.i.	n.i.	77% *98*[j])	n.m.	75% *185*[j])	n.m.	n.i.
(±)-**19v**	n.i.	36%	n.i.	30%	80% *66*[j])	n.m.	61%	74%	n.i.
(±)-**19w**	n.i.	67%	n.i.	n.i.	92% *32*[j])	n.m.	79%	77%	n.i.
(±)-**19x**	n.i.	74%	n.i.	n.i.	85% *69*[j])	n.m.	88%	77%	n.i.
(±)-**19y**	n.i.	75%	n.i.	30%	80% *66*[j])	n.m.	61%	74%	n.i.
(±)-**19z**	n.i.	37%	n.i.	23%	75%	31%	82%	83%	n.i.
(±)-**20aa**	25%	n.i.	n.i.	n.i.	36%	n.i.	n.i.	n.i.	n.i.
(±)-**20bb**	n.i.	67%	n.i.	n.i.	83%	n.i.	n.i.	n.i.	n.i.
(±)-**20cc**	n.i.	39%	n.i.	n.i.	36%	n.i.	n.i.	n.i.	n.i.
(±)-**20dd**	n.i.	43%	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.
26	n.i.	79%	34%	74%	34%	n.m.	n.i.	n.m.	n.i.
27	n.i.	71%	45%	58%	32%	n.m.	n.i.	n.m.	n.i.
28	n.i.	90%	n.i.	n.i.	69%	n.m.	85%	n.m.	n.i.
29	n.i.	66%	n.i.	n.i.	n.i.	n.m.	n.i.	n.i.	n.i.
30	n.i.	61%	n.i.	n.i.	n.i.	n.m.	n.i.	n.i.	n.i.

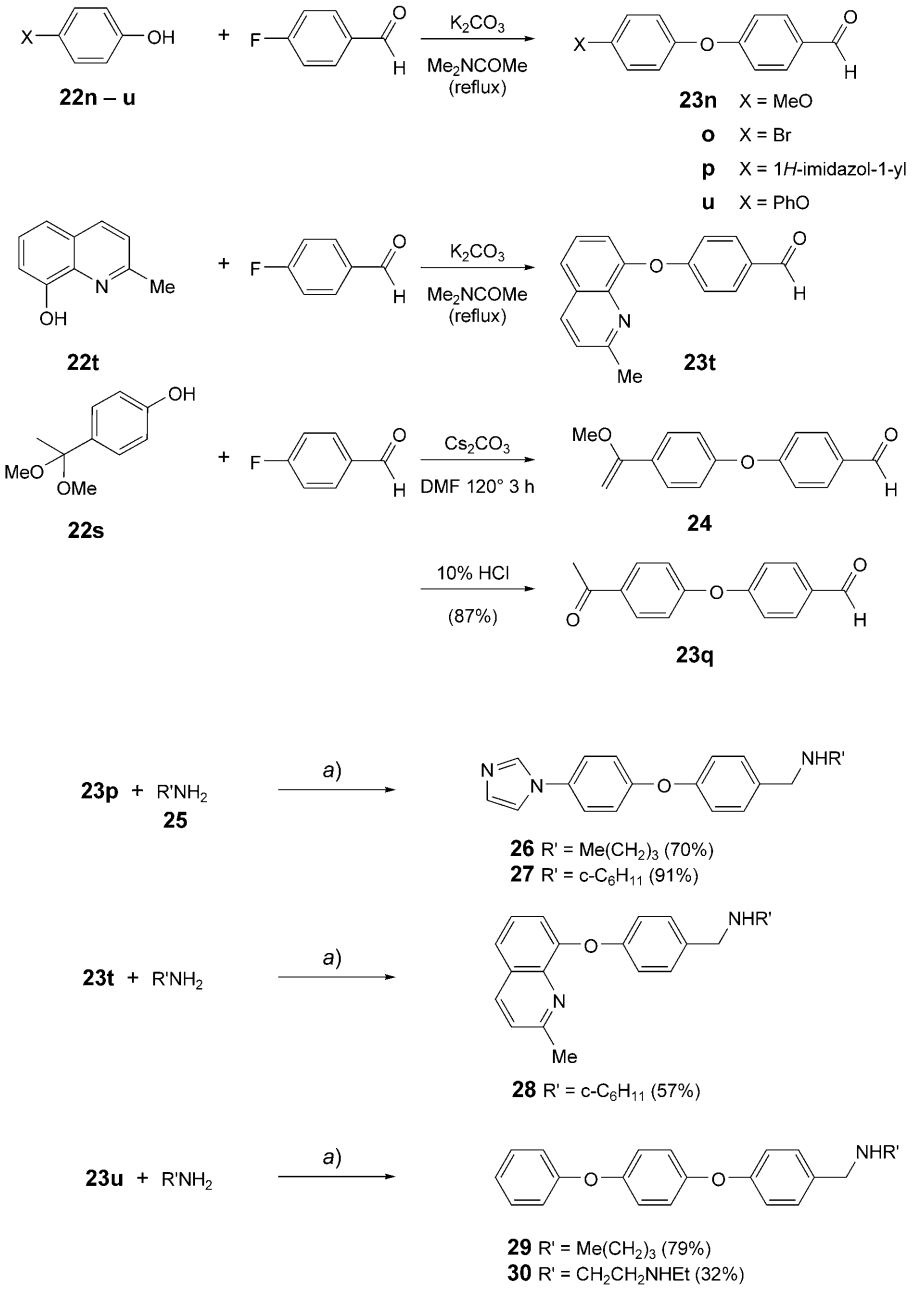
[a]) α-Galactosidase from coffee beans. [b]) β-Galactosidase from bovine liver. [c]) Amyloglucosidase from *Aspergillus niger*. [d]) Amyloglucosidase from *Rhizopus* mold. [e]) β-Glucosidase from almonds. [f]) β-Glucosidase from *Saccharomyces cerevisiae*. [g]) α-Mannosidase from jack beans. [h]) α-Mannosidase from almonds. [i]) β-Xylosidase from *Aspergillus niger*. [j]) IC_{50} in μM. [k]) K_i in μM.

centration). This suggests that the aromatic moieties of these systems contribute to the recognition of the β-glucosidases.

Probably for steric reasons, the *N*,*N*-disubstituted analogues of conduramines B-1 do not inhibit α-mannosidases. A different situation is seen with β-glucosidase from almonds which is inhibited by (±)-**20aa**, (±)-**20bb**, and (±)-**20cc**, however, with low potencies. Most of our amines are weak inhibitors of β-galactosidase from bovine liver. The data shown in the *Table* demonstrate that this is not typical of the (−)- or (+)-conduramine B-1 moiety.

Conclusion. – Although (−)-conduramine B-1 ((−)-**5**) that imitates β-glucopyranosides is not recognized by β-glucosidases, it is a moderate inhibitor of α-mannosidases. (−)-*N*-Benzylconduramine B-1 ((−)-**19a**) is a better inhibitor of β-glucosidases than of α-mannosidases. In contrast, (−)-*N*-(4-phenylbenzyl)conduramine B-1 ((−)-**19g**) is a slightly better inhibitor of α-mannosidases than of β-glucosidases. The ability of (−)-conduramine B-1 and its *N*-substituted derivatives to inhibit α-mannosidases is attrib-

Scheme 4. *Preparation of Aldehydes and Amine Derivatives*



a) $NaBH(OAc)_3$ (1.4 equiv.), MeOH, r.t.

uted to the fact that their 3,4-diol and 1-amino moieties (trivial atom numbering, see *Fig. 3*) might occupy the same sites of the active site of α-mannosidases as the 3,4-diol and 2-(aminomethyl) units of (2*R*,3*R*,4*S*)-2-(aminomethyl)pyrrolidine-3,4-diol and derivatives of this diamine that are potent α-mannosidase inhibitors.

This work was supported by the *Secretariat d'Etat à l'Education et à la Recherche* (*SER*) and the *FP6 European TRIoH* project (No. 03.0738 *OFES*). We thank Mr. *Martial Rey* and S. *Reddy Dubbaka* for their technical help.

Experimental Part

1. *General.* All commercially available reagents (*Fluka*, *Aldrich*, *Acros Organics*) were used without further purification. Solvents were dried by standard methods. Light petroleum ether used refers to the fraction boiling between 40–60°. Solvents after reactions and extractions were evaporated in a rotatory evaporator *in vacuo*. 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), $KMnO_4$, or 1% ninhydrin in MeOH. Liquid/solid flash chromatography (FC): silica gel *60* (*Merck* No. 9385, 240–400 mesh) or neutral alumina CC = Column chromatography. M.p.: *Büchi-SMP-20* apparatus; uncorrected. Optical rotations: at 25°; *Jasco DIP-370* polarimeter or *Jasco P-1020* polarimeter; $[\alpha]_D$ in 10^{-1} deg cm^2 g^{-1}. IR Spectra: *Perkin-Elmer 1420* spectrometer; in cm^{-1}. NMR Spectra: *Bruker ARX-400* spectrometer (^{1}H at 400 MHz; ^{13}C at 100.6 MHz); δ in ppm rel. to the solvent's residual ^{1}H or to the ^{13}C signal ($CDCl_3$: δ(H) 7.27, δ(C) 77.0; CD_3OD: δ(H) 3.31, δ(C) 49.8) as internal reference; all ^{1}H assignments were confirmed by 2D-COSY-45 and 2D-NOESY experiments and all ^{13}C assignments 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.

2. *Glycosidase Inhibition Assays.* See [26].

3. *(±)-(1*RS,*2*SR,*3*SR,*4*RS*)- and (±)-(1*RS,*2*SR,*3*SR,*4*SR*)-1,2,3-Tris[[(*tert*-*butyl*)*dimethylsilyl*]*oxy*}-4-*phthalimidocyclohex-5-ene*[2]) *(=(±)-2-{(1*RS,*4*RS,*5*SR,*6*SR*)-4,5,6-Tris[[(*tert*-*butyl*)*dimethylsilyl*]*oxy*}*cyclohex-2-en-1-yl*}- *and (±)-2-{(1*RS,*4*SR,*5*RS,*6*RS*)-4,5,6-Tris[[(*tert*-*butyl*)*dimethylsilyl*]*oxy*}*cyclohex-2-en-1-yl*}-*1*H-*isoindole-1,3(2*H)-*dione*, resp.; (±)-**16** and (±)-**17**, resp.). A soln. of DEAD (2.26 ml, 14.57 mmol, 1.25 equiv.) in dry toluene (15 ml) was added dropwise to (±)-**14**/(±)-**15** *ca.* 2.5:1 [22] (5.70 g, 11.66 mmol), phthalimide (2.14 g, 14.57 mmol, 1.25 equiv.), and PPh_3 (3.82 g, 14.57 mmol, 1.25 equiv.) in dry toluene (85 ml) at 0°, and the mixture was stirred at 0° for 12 h (TLC monitoring). After 12 h, the suspension was filtered off, and H_2O was added. The mixture was extracted with Et_2O (3×), the combined org. extract was washed with brine, dried ($MgSO_4$), and evaporated, and the residue was subjected to FC (silica gel, AcOEt/light petroleum ether 4:96). The obtained white solid (6.2 g, 87%) resubjected to CC (AcOEt/hexane 1:99 → 5:95): (±)-**16** (3.7 g) and (±)-**17** (0.64 g).

*Data of (±)-***16**. White needles. M.p. 83–85°. UV (MeCN): 233 (7533), 225 (6855), 221 (6456), 195 (816). IR (KBr): 2933, 2857, 1776, 1719, 1473, 1387, 1258, 1160, 1128, 1059, 1003, 891, 781, 716. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.85–7.80 (*m*, 2 arom. H); 7.74–7.69 (*m*, 2 arom. H); 5.93 (*ddd*, ^3J(6,5) = 10.0, ^3J(6,4) = ^3J(6,1) = 3.0, H–C(6)); 5.59 (*ddd*, ^3J(5,6) = 10.0, ^3J(5,4) = ^3J(5,1) = 3.0, H–C(5)); 4.90–4.86 (*m*, H–C(4)); 4.35–4.31 (*m*, H–C(1)); 4.23 (*dd*, ^3J(3,2) = ^3J(3,4) = 6.0, H–C(3)); 3.83 (*dd*, ^3J(2,3) = ^3J(2,1) = 6.0, H–C(2)); 0.93, 0.86, 0.78 (3*s*, 3 ^{t}BuSi); 0.13, 0.12, 0.07, 0.05 (4*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 168.0 (*s*, 2 arom. C); 133.9 (*d*, ^1J(C,H) = 164, 2 arom. C); 132.1 (*s*, 2 arom. C); 132.0 (*d*, ^1J(C,H) = 162, C(6)); 125.2 (*d*, ^1J(C,H) = 162, C(5)); 123.1 (*d*, ^1J(C,H) = 170, 2 arom. C); 78.1 (*d*, ^1J(C,H) = 146, C(2)); 73.3 (*d*, ^1J(C,H) = 145, C(3)); 72.2 (*d*, ^1J(C,H) = 144, C(1)); 53.8 (*d*, ^1J(C,H) = 142, C(4)); 26.4, 26.2, 26.0 (3*q*, ^1J(C,H) = 125, 3 *Me*$_3$C); 18.3, 18.1, 17.8 (3*s*, 3 Me$_3$*C*); −3.1, −3.2, −3.5, −3.7, −4.1, −4.7 (6*q*, ^1J(C,H) = 119, 6 MeSi). CI-MS (NH_3): 560 (23), 428 (9), 354 (12), 329 (48), 314 (8), 288 (17), 231 (6), 167 (4), 147 (29), 115 (14), 99 (5), 75 (52), 73 (100). HR-MALDI-TOF-MS: 640.3283 ($C_{32}H_{55}NNaO_5Si_3^+$, $[M+Na]^+$; calc. 640.3286). Anal. calc. for $C_{32}H_{55}NO_5Si_3$ (617.339): C 62.19, H 8.97, N 2.27; found: C 61.89, H 8.70, N 2.11.

*(−)-(1*R,*2*S,*3*S,*4*R*)-1,2,3-Tris[[(*tert*-*butyl*)*dimethylsilyl*]*oxy*}-4-*phthalimidocyclohex-5-ene*[2]) *(=(−)-2-{(1*R,*4*R,*5*S,*6*S*)-4,5,6-Tris[[(*tert*-*butyl*)*dimethylsilyl*]*oxy*}*cyclohex-2-en-1-yl*}-*1*H-*isoindole-1,3(2*H)-*dione*; (−)-**16**). As described for (±)-**16**/(±)-**17**, with (−)-**14**/(−)-**15** 2.5:1 derived from (+)-**10** [22]: 69% of the major isomer

[2]) Systematic names are given in parentheses

(−)-**16**; $[\alpha]_{589}^{25} = -126$, $[\alpha]_{577}^{25} = -132$, $[\alpha]_{435}^{25} = -274$, $[\alpha]_{405}^{25} = -340$ ($c = 0.54$, $CHCl_3$). HR-MALDI-TOF-MS: 640.3281 ($C_{32}H_{55}NNaO_5Si_3^+$, $[M+Na]^+$; calc. 640.3286).

Enatiomer (+)-**16**. As described for (±)-**16**/(±)-**17**, starting from (−)-**10**: 66% of the major isomers (+)-**16**. $[\alpha]_{589}^{25} = +118$, $[\alpha]_{577}^{25} = +122$, $[\alpha]_{435}^{25} = +260$, $[\alpha]_{405}^{25} = +327$ ($c = 0.545$, $CHCl_3$). HR-MALDI-TOF-MS: 640.3209 ($C_{32}H_{55}NNaO_5Si_3^+$, $[M+Na]^+$; calc. 640.3286).

Data of (±)-**17**. Colorless oil. UV (MeCN): 293 (2150), 260 (995), 235 (7188). IR (KBr): 2930, 2858, 1778, 1719, 1742, 1391, 1325, 1257, 1189, 1079, 1006, 867, 835, 774, 719. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.85–7.82 (*m*, 2 arom. H); 7.74–7.69 (*m*, 2 arom. H); 6.01 (br. *d*, $^3J(6,5) = 10.0$, H–C(6)); 5.81 (br. *d*, $^3J(5,6) = 10.0$, H–C(5)); 5.09 (br. *m*, H–C(4)); 4.04–3.94 (2 br. *m*, H–C(3), H–C(2), H–C(1)); 0.97 , 0.94, 0.76 (3*s*, 3 ^{t}BuSi); 0.22, 0.16, 0.14, 0.13, −0.02, −0.4 (6*s*, 6 MeSi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 168.3 (*s*, 2 arom. C); 133.8 (*d*, $^1J(C,H) = 164$, 2 arom. C); 132.1 (*s*, 2 arom. C); 127.0 (*d*, $^1J(C,H) = 160$, C(6)); 123.0 (*d*, $^1J(C,H) = 160$, C(5)); 122.9 (*d*, $^1J(C,H) = 165$, 2 arom. C); 74.5 (*d*, $^1J(C,H) = 148$, C(2)); 70.5, 69.1 (2*d*, $^1J(C,H) \approx 144$, C(1), C(3)); 49.8 (*d*, $^1J(C,H) = 139$, C(4)); 26.2, 25.8, 25.7 (3*q*, $^1J(C,H) = 125$, 3 Me_3C); 18.5, 17.9, 17.8 (3*s*, 3 Me_3C); −4.3, −4.35, −4.4, −4.5, −4.6, −5.4 (6*q*, $^1J(C,H) = 119$, 6 MeSi). HR-MALDI-TOF-MS: 640.3143 ($C_{32}H_{55}NNaO_5Si_3^+$, $[M+Na]^+$; calc. 640.3286). Anal. calc. for $C_{32}H_{55}NO_5Si_3$ (617.339): C 62.19, H 8.97, N 2.27; found: C 62.03, H 9.05, N 2.10.

*(−)-(1*R*,2*S*,3*S*,4*S*)-1,2,3-Tris[[(*tert*-butyl)dimethylsilyl]oxy]-4-phthalimidocyclohex-5-ene*[2]) (=*(−)-2-[(1*S*,4*R*,5*S*,6*S*)-4,5,6-Tris[[(*tert*-butyl)dimethylsilyl]oxy}cyclohex-2-en-1-yl]-1*H*-isoindole-1,3(2*H*)-dione*; (−)-**17**). As described above for (±)-**16**/(±)-**17** starting from (+)-**10**: $[\alpha]_{589}^{25} = -50$, $[\alpha]_{577}^{25} = -51$, $[\alpha]_{435}^{25} = -99$, $[\alpha]_{405}^{25} = -128$ ($c = 0.44$, $CHCl_3$). HR-MALDI-TOF-MS: 640.3283 ($C_{32}H_{55}NNaO_5Si_3^+$, $[M+Na]^+$; calc. 640.3286).

Enantiomer (+)-**17**. As described above for (±)-**16**/(±)-**17** starting with (−)-**10**: 21% of the minor isomer (+)-**17**. $[\alpha]_{589}^{25} = +49$, $[\alpha]_{577}^{25} = +50$, $[\alpha]_{435}^{25} = +99$, $[\alpha]_{405}^{25} = +114$ ($c = 0.29$, $CHCl_3$). HR-MALDI-TOF-MS: 640.3263 ($C_{32}H_{55}NNaO_5Si_3^+$, $[M+Na]^+$; calc. 640.3286).

4. *(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-Phthalimidocyclohex-5-ene-1,2,3-triol*[2]) (=*(±)-2-[(1*RS*,4*RS*,5*SR*,6*SR*)-4,5,6-Trihydroxycyclohex-2-en-1-yl]-1*H*-isoindole-1,3(2*H*)-dione*; (±)-**18**). Compound (±)-**16** (2.5 g, 4.04 mmol) was dissolved in 1% TsOH in MeOH (30 ml) and stirred under reflux for 30 min (TLC monitoring). The solvent was evaporated and the residue subjected to FC (AcOEt/hexane 4 : 1, then pure AcOEt, then MeOH/AcOEt 5 : 95): 1.05 g (95%) of (±)-**18**. White crystals. M.p. 227–229° (from MeOH/Et_2O). UV (MeOH): 293 (1736), 237 (3937), 196 (537). IR (KBr): 3551, 3462, 3401, 1768, 1703, 1467, 1399, 1264, 1132, 1110, 1066, 1029, 995, 945, 871, 791. ^{1}H-NMR (400 MHz, CD_3OD): 7.90–7.82 (*m*, 4 arom. H); 5.75 (*ddd*, $^3J(5,6) = 10.2$, $^3J(5,4) = {}^3J(5,1) = 2.6$, H–C(5)); 5.55 (*ddd*, $^3J(6,5) = 10.2$, $^3J(6,4) = {}^3J(6,1) = 2.6$, H–C(6)); 4.85–4.82 (*m*, H–C(4)); 4.29–4.25 (*m*, H–C(1)); 4.23 (*dd*, $^3J(3,2) = 10.1$, $^3J(3,4) = 9.4$, H–C(3)); 3.58 (*dd*, $^3J(2,3) = 10.1$, $^3J(2,1) = 8.0$, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 169.6 (*s*, 2 *C*O); 135.4 (*d*, $^1J(C,H) = 164$, 2 arom. C); 133.3 (*s*, 2 arom. C); 132.3 (*d*, $^1J(C,H) = 162$, C(5)); 126.8 (*d*, $^1J(C,H) = 162$, C(6)); 124.1 (2*d*, $^1J(C,H) = 165$, 2 arom. C); 78.5 (*d*, $^1J(C,H) = 140$, C(2)); 73.7 (*d*, $^1J(C,H) = 144$, C(1)); 71.9 (*d*, $^1J(C,H) = 147$, C(3)); 55.6 (*d*, $^1J(C,H) = 140$, C(4)). CI-MS (NH_3): 228 (15), 215 (17), 186 (23), 160 (8), 148 (18), 130 (34), 110 (100), 104 (52), 99 (27), 82 (52), 76 (74), 71 (5). HR-MALDI-TOF-MS: 298.1320 ($C_{14}H_{13}NNaO_5^+$, $[M+Na]^+$; calc. 298.0691).

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-Phthalimidocyclohex-5-ene-1,2,3-triol*[2]) (=*(−)-2-[(1*R*,4*R*,5*S*,6*S*)-4,5,6-Trihydroxycyclohex-2-en-1-yl]-1*H*-isoindole-1,3(2*H*)-dione*; (−)-**18**). As described for (±)-**18**, with (−)-**16**: (−)-**18** (95%). $[\alpha]_{589}^{25} = -229$, $[\alpha]_{577}^{25} = -227$, $[\alpha]_{435}^{25} = -476$, $[\alpha]_{405}^{25} = -612$ ($c = 0.105$, MeOH). HR-MALDI-TOF-MS: 298.0693 ($C_{14}H_{13}NNaO_5^+$, $[M+Na]^+$; calc. 298.0691).

Enantiomer (+)-**18**. As described for (±)-**18**, with (+)-**16**: (+)-**18** (92%). $[\alpha]_{589}^{25} = +226$, $[\alpha]_{577}^{25} = +227$, $[\alpha]_{435}^{25} = +474$, $[\alpha]_{405}^{25} = +605$ ($c = 0.105$, MeOH). HR-MALDI-TOF-MS: 298.0610 ($C_{14}H_{13}NNaO_5^+$, $[M+Na]^+$; calc. 298.0691).

5. *(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-Aminocyclohex-5-ene-1,2,3-triol*[2]) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-Aminocyclohex-4-ene-1,2,3-triol* = rac-*Conduramine B-1*; (±)-**5**). A 40% aq. $MeNH_2$ soln. (15 ml) was added to (±)-**18** (1.1 g, 3.99 mmol). Stirring at 20° was continued for *ca.* 45 min (TLC monitoring). After evaporation, the residue was purified by ion exchange (*Dowex-50 W* (H^+ form), 2N NH_4OH): pure (±)-**5** (0.55 g; 95%). Pure (±)-**5** was also obtained by FC (silica gel, 25% aq. NH_3 soln./MeCN 1 : 4). Very hygroscopic crystals. UV(MeOH): 207 (965). IR (film): 3342, 2862, 1648, 1618, 1577, 1402, 1373, 1343, 1296, 1267, 1124, 1083, 1019, 962, 786, 624. ^{1}H-NMR (400 MHz, CD_3OD): 5.62 (*ddd*, $^3J(5,6) = 10.2$, $^3J(5,4) = {}^3J(5,1) = 2.4$, H–C(5)); 5.54 (*ddd*, $^3J(6,5) = 10.2$, $^3J(6,4) = {}^3J(6,1) = 2.4$, H–C(6)); 4.10–4.08 (*m*, H–C(1)); 3.42 (*dd*, $^3J(2,3) = 9.8$, $^3J(2,4) = 7.8$, H–C(2)); 3.47–3.26 (*m*, H-C(4), H–C(3)). ^{13}C-NMR (100.6 MHz, CD_3OD): 131.3 (*d*, $^1J(C,H) = 162$, C(5)); 129.7 (*d*, $^1J(C,H) = 162$, C(6)); 77.8, 77.7 (2*d*, $^1J(C,H) \approx 143$, C(3), C(2)); 73.8 (*d*, $^1J(C,H) = 144$, C(1)); 55.7 (*d*, $^1J(C,H) = 139$, C(4)). CI-MS (NH_3): 117 (2), 104 (5), 98 (4), 86 (4), 85 (100), 76 (2). HR-MALDI-TOF-MS: 146.0815 ($C_6H_{12}NO_3^+$, $[M+H]^+$; calc. 146.0817). Anal. calc. for $C_6H_{11}NO_3$ (145.074): C 49.65, H 7.64; found: C 50.01, H 7.51.

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-Aminocyclohex-5-ene-1,2,3-triol*[2]) (=*(−)-(1*S*,2*S*,3*R*,6*R*)-6-Aminocyclohex-4-ene-1,2,3-triol*=*(−)-Conduramine B-1*; (−)-**5**). As described for (±)-**5**, with (−)-**18**: (−)-**5** (90%). $[\alpha]_{589}^{25}=-173$, $[\alpha]_{577}^{25}=-174$, $[\alpha]_{435}^{25}=-341$, $[\alpha]_{405}^{25}=-421$ ($c=0.29$, MeOH). HR-MALDI-TOF-MS: 146.0837 ($C_6H_{12}NO_3^+$, $[M+H]^+$; calc. 146.0817).

*Enantiomer (+)-***5**. As described for (±)-**5**, with (+)-**18**: (+)-**5** (90%). $[\alpha]_{589}^{25}=+173$, $[\alpha]_{577}^{25}=+175$, $[\alpha]_{435}^{25}=+350$, $[\alpha]_{405}^{25}=+428$ ($c=0.29$, MeOH). HR-MALDI-TOF-MS: 146.0837 ($C_6H_{12}NO_3^+$, $[M+H]^+$; calc. 146.0817).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-(Acetylamino)cyclohex-5-ene-1,2,3-triyl Triacetate*[2]) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-(Acetylamino)cyclohex-4-ene-1,2,3-triyl Triacetate)*. To (±)-**5** (0.15 g, 0.103 mmol) were added pyridine (1 ml), Ac_2O (1 ml), and *N*,*N*-dimethylpyridin-4-amine (DMAP; 0.01 g), and after stirring at 20° for 20 h, AcOEt was added. The soln. was washed successively with dil. aq. HCl soln., sat. aq. Na_2CO_3 soln., and brine, dried ($MgSO_4$), and evaporated and the residue subjected to pure FC (hexanes/AcOEt 1:1 and hexane/AcOEt 5:95): pure *(±)-tetra*-N,O,O,O-*acetylconduramine B-1* (0.023 g, 72%). Colorless crystals. M.p. 141–143° (light petroleum ether/AcOEt). UV ($CHCl_3$): 241 (608). IR (KBr): 3264, 2958, 1750, 1653, 1569, 1374, 1252, 1225, 1052, 961. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.75 (br. *d*, *J* = 8.4, N*H*Ac); 5.72–5.60 (2*ddd*, ^3J(6,5) = 10.2, ^3J(6,4) = ^3J(6,1) = ^3J(5,4) = ^3J(5,1) = 2.0, H–C(6), H–C(5)); 5.58–5.53 (*m*, H–C(1)); 5.39 (*dd*, ^3J(2,3) = 10.7, ^3J(2,1) = 8.0, H–C(2)); 5.09 (*dd*, ^3J(3,2) = 10.7, ^3J(3,4) = 9.3, H–C(3)); 4.93–4.85 (*m*, H–C(4)); 2.07, 2.06, 2.05, 1.97 (4*s*, 4 MeCO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 171.6, 170.8, 170.4, 170.1 (4*s*, 4 Me*C*O); 131.0, 126.4 (2*d*, ^1J(C,H) = 167, C(6), C(5)); 72.3 (*d*, ^1J(C,H) = 140, C(3)); 72.1 (*d*, ^1J(C,H) = 146, C(1)); 71.8 (*d*, ^1J(C,H) = 140, C(2)); 51.3 (*d*, ^1J(C,H) = 136, C(4)); 23.6, 21.3, 21.1, 21.0 (4*q*, ^1J(C,H) = 130, 4 *Me*CO). CI-MS (NH_3): 255 (9), 183 (4), 152 (57), 140 (20), 133 (13), 127 (28), 110 (100), 99 (13), 85 (26), 81 (33), 77 (2), 70 (9). HR-MALDI-TOF-MS: 352.0781 ($C_{14}H_{19}KNO_7^+$, $[M+K]^+$; calc. 352.0799).

6. N-*Benzyl- and* N-*Alkyl-Substituted Derivatives* **19** *of Conduramine B-1. General Procedure* (*G.P.*): $NaBH(OAc)_3$ (1.4 equiv.) was added portionwise to a stirred soln. of (±)-**5** (0.4 mmol) and an appropriate aldehyde (0.4 mmol) in abs. MeOH (2 ml) at 20°. After complete disappearance of (±)-**5** (TLC control; longer reaction time for the formation of aliphatic imines than for aromatic imines, *i.e.*, 12 h *vs.* 2–5 h), the solvent was evaporated and the residue subjected to FC (light petroleum ether/AcOEt 1:1 → AcOEt → MeCN → 25% aq. NH_3 soln./MeCN 1:9 → 1:4).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-(Benzylamino)cyclohex-5-ene-1,2,3-triol*[2]) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-(Benzylamino)cyclohex-4-ene-1,2,3-triol*; (±)-**19a**). According to the *G.P.*, from (±)-**5** and benzaldehyde (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19a** (81%). Solid foam. UV (MeOH): 260 (358), 258 (352), 215 (3290). IR (KBr): 3406, 1612, 1543, 1420, 1211, 1126, 1036, 1012, 668. ^{1}H-NMR (400 MHz, CD_3OD): 7.45–7.30 (*m*, 5 arom. H); 7.76–7.72 (*m*, H–C(6), H–C(5)); 4.12 (*dd*, ^3J(1,2) = 7.9, ^3J(1,6) = 3.2, H–C(1)); 4.05 (*d*, ^3J = 12.9, 1 H, ArCH_2N); 3.93 (*d*, ^3J = 12.9, 1 H, ArCH_2N); 3.59 (*dd*, ^3J(3,2) = 10.0, ^3J(3,4) = 8.7, H–C(3)); 3.46 (*dd*, ^3J(4,3) = 8.7, ^3J(4,5) = 3.2, H–C(4)); 3.43 (*dd*, ^3J(2,3) = 10.0, ^3J(2,1) = 7.9, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 138.8 (*s*, arom. C); 132.9, 126.1 (2*d*, ^1J(C,H) = 162, C(6), C(5)); 130.0 (*d*, ^1J(C,H) = 158, 2 arom. C); 129.7 (*d*, ^1J(C,H) = 160, 2 arom. C); 128.8 (*d*, ^1J(C,H) = 160, arom. C); 77.9 (*d*, ^1J(C,H) = 145, C(2)); 73.9 (*d*, ^1J(C,H) = 138, C(3)); 73.4 (*d*, ^1J(C,H) = 147, C(1)); 61.4 (*d*, ^1J(C,H) = 136, C(4)); 50.8 (*t*, ^1J(C,H) = 137, Ar*C*H$_2$N). CI-MS (NH_3): 237 (2, $[M+2H]^+$), 176 (33), 175 (100), 161 (16), 149 (4), 132 (9), 117 (8), 106 (34), 104 (17), 91 (94), 84 (73), 80 (3), 77 (7). HR-MALDI-TOF-MS: 258.1102 ($C_{13}H_{17}NNaO_3^+$, $[M+Na]^+$; calc. 258.1106). Anal. calc. for $C_{13}H_{17}NO_3$ (235.121): C 66.36, H 7.28, N 5.95; found: C 65.87, H 7.01, N 6.04.

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-(Benzylamino)cyclohex-5-ene-1,2,3-triol* (=*(−)-(1*S*,2*S*,3*R*,6*R*)-6-(Benzylamino)cyclohex-4-ene-1,2,3-triol*; (−)-**19a**). According to the *G.P.*, with (−)-**5** and benzaldehyde: (−)-**19a** (79%). $[\alpha]_{589}^{25}=-135$, $[\alpha]_{577}^{25}=-148$, $[\alpha]_{435}^{25}=-244$, $[\alpha]_{405}^{25}=-267$ ($c=0.11$, MeOH). HR-MALDI-TOF-MS: 258.1102 ($C_{13}H_{17}NNaO_3^+$, $[M+Na]^+$; calc. 258.1106).

*Enantiomer (+)-ent-***19a**. According to the *G.P.*, with (+)-**5** and benzaldehyde: (+)-**19** (82%). $[\alpha]_{589}^{25}=+87$, $[\alpha]_{577}^{25}=+91$, $[\alpha]_{435}^{25}=+184$, $[\alpha]_{405}^{25}=+224$ ($c=0.075$, MeOH). HR-MALDI-TOF-MS: 258.1102 ($C_{13}H_{17}NNaO_3^+$, $[M+Na]^+$; calc. 258.1106).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(4-Methoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*[2]) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(4-Methoxybenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19b**). According to the *G.P.*, with (±)-**5** and 4-methoxybenzaldehyde (TLC monitoring, MeOH/AcOEt 2:3): (±)-**19b** (96%). Solid foam. UV (MeOH): 274 (1208), 230 (4234), 198 (366). IR (KBr): 3382, 1613, 1560, 1516, 1411, 1253, 1181, 1122, 1032, 818, 653. ^{1}H-NMR (400 MHz, CD_3OD): 7.36 (*d*, ^3J = 8.6, 2 arom. H); 6.96 (*d*, ^3J = 8.6, 2 arom. H); 5.81 (*ddd*, ^3J(5,6) = 10.3, ^3J(5,4) = ^3J(5,1) = 2.0, H–C(5)); 5.74 (*ddd*, ^3J(6,5) = 10.3, ^3J(6,4) = ^3J(6,1) = 2.0, H–C(6)); 4.13–4.09 (*m*, H–C(1)); 4.08 (*d*, ^3J = 12.9, 1 H, ArCH_2N); 3.98 (*d*, ^3J = 12.9, 1 H, ArCH_2N); 3.62 (*dd*, ^3J(3,2) = 9.8, ^3J(3,4) = 9.0, H–C(3)); 3.57–3.52 (*m*, H–C(4)); 3.43 (*dd*, ^3J(2,3) = 9.8, ^3J(2,1) = 7.9, H–C(2)). ^{13}C-NMR (100.6

MHz, CD_3OD): 161.6 (*s*, arom. C); 135.4 (*d*, ^1J(C,H) = 163, C(5)); 132.1 (*d*, ^1J(C,H) = 158, 2 arom. C); 126.8 (*s*, arom. C); 123.0 (*d*, ^1J(C,H) = 163, C(6)); 115.4 (*d*, ^1J(C,H) = 161, 2 arom. C); 77.6 (*d*, ^1J(C,H) = 143, C(2)); 73.0 (*d*, ^1J(C,H) = 141, C(1)); 72.6 (*d*, ^1J(C,H) = 141, C(3)); 61.3 (*d*, ^1J(C,H) = 142, C(4)); 55.8 (*q*, ^1J(C,H) = 144, *Me*O); 49.6 (*t*, ^1J(C,H) = 139, Ar*C*H_2N). CI-MS (NH_3): 267 (2, $[M+2H]^+$), 205 (1), 136 (4), 122 (21), 121 (100), 84 (2), 77 (2). HR-MALDI-TOF-MS: 288.1219 ($C_{14}H_{19}NNaO_4^+$, $[M+Na]^+$; calc. 288.1212).

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-[(4-Methoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*^{2}) (= *(−)-(1*S*,2*S*,3*R*,6*R*)-6-[(4-Methoxybenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (−)-**19b**). According to the *G.P.*, with (−)-**5** and 4-methoxybenzaldehyde: (−)-**19b** (83%). $[\alpha]_{589}^{25} = -85$, $[\alpha]_{577}^{25} = -87$, $[\alpha]_{435}^{25} = -138$, $[\alpha]_{405}^{25} = -212$ (*c* = 0.17, MeOH). HR-MALDI-TOF-MS: 288.1271 ($C_{14}H_{19}NNaO_4^+$, $[M+Na]^+$; calc. 288.1212).

Enantiomer (+)-ent-**19b**. According to the *G.P.*, from (+)-**5** and 4-methoxybenzaldehyde: (+)-**19b** (90%). $[\alpha]_{589}^{25} = +97$, $[\alpha]_{577}^{25} = +103$, $[\alpha]_{435}^{25} = +201$, $[\alpha]_{405}^{25} = +245$ (*c* = 0.35, MeOH). HR-MALDI-TOF-MS: 288.1232 ($C_{14}H_{19}NNaO_4^+$, $[M+Na]^+$; calc. 288.1212).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(4-Hydroxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*^{2}) (= *((±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(4-Hydroxybenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19c**). According to the *G.P.*, with (±)-**5** and 4-hydroxybenzaldehyde (TLC monitoring, MeOH/AcOEt 2:3): (±)-**19c** (94%). Solid foam. UV (MeOH): 276 (1230), 229 (4178), 197 (402). IR (KBr): 3382, 1616, 1560, 1519, 1410, 1256, 1125, 1017, 834, 654. ^{1}H-NMR (400 MHz, CD_3OD): 7.27 (*d*, ^3J = 8.4, 2 arom. H); 6.82 (*d*, ^3J = 8.4, 2 arom. H); 5.81 (*ddd*, ^3J(5,6) = 10.0, ^3J(5,4) = ^3J(5,1) = 3.0, H−C(5)); 5.74 (*ddd*, ^3J(6,5) = 10.0, ^3J(6,4) = ^3J(6,1) = 3.0, H−C(6)); 4.12–4.08 (*m*, H−C(1)); 4.08 (*d*, ^3J = 12.8, 1 H, ArCH_2N); 4.00 (*d*, ^3J = 12.8, 1 H, ArCH_2N); 3.68–3.57 (*m*, H−C(4), H−C(3)); 3.43 (*dd*, ^3J(2,3) = 9.8, ^3J(2,1) = 7.9, H−C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 159.4 (*s*, arom. C); 135.5 (*d*, ^1J(C,H) = 163, C(5)); 132.2 (*d*, ^1J(C,H) = 157, 2 arom. C); 125.2 (*s*, arom. C); 122.9 (*d*, ^1J(C,H) = 163, C(6)); 116.8 (*d*, ^1J(C,H) = 159, 2 arom. C); 77.6 (*d*, ^1J(C,H) = 142, C(2)); 73.0 (*d*, ^1J(C,H) = 142, C(1)); 72.7 (*d*, ^1J(C,H) = 142, C(3)); 61.2 (*d*, ^1J(C,H) = 142, C(4)); 49.8 (*t*, ^1J(C,H) = 139, Ar*C*H_2N). CI-MS (NH_3): 252 (38, $[M+H]^+$), 244 (6), 231 (43), 230 (93), 225 (15), 144 (4), 122 (6), 109 (23), 108 (81), 94 (54), 90 (4), 85 (100), 78 (7). HR-MALDI-TOF-MS: 274.1043 ($C_{13}H_{17}NNaO_5^+$, $[M+Na]^+$; calc. 274.1055). Anal. calc. for $C_{13}H_{17}NO_5$ (251.116): C 62.14, H 6.82, N 5.57; found: C 62.40, H 6.70, N 5.43.

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-[(4-Hydroxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*^{2}) (= *(−)-(1*S*,2*S*,3*R*,6*R*)-6-[(4-Hydroxybenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (−)-**19c**). According to the *G.P.*, with (−)-**5** and 4-hydroxybenzaldehyde: (−)-**19c** (90%). $[\alpha]_{589}^{25} = -88$, $[\alpha]_{577}^{25} = -89$, $[\alpha]_{435}^{25} = -200$, $[\alpha]_{405}^{25} = -256$ (*c* = 0.282, MeOH). HR-MALDI-TOF-MS: 274.1059 ($C_{13}H_{17}NNaO_5^+$, $[M+Na]^+$; calc. 274.1055).

Enantiomer (+)-ent-**19c**. According to the *G.P.*, with (+)-**5** and 4-hydroxybenzaldehyde: (+)-*ent*-**19c** (85%). $[\alpha]_{589}^{25} = +101$, $[\alpha]_{577}^{25} = +113$, $[\alpha]_{435}^{25} = +225$, $[\alpha]_{405}^{25} = +278$ (*c* = 0.30, MeOH). HR-MALDI-TOF-MS: 274.1034 ($C_{13}H_{17}NNaO_5^+$, $[M+Na]^+$; calc. 274.1055).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(2-Hydroxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*^{2}) (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(2-Hydroxybenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19d**). According to the *G.P.*, with (±)-**5** and 2-hydroxybenzaldehyde (TLC monitoring, MeOH/AcOEt 2:3): (±)-**19d** (93%). Solid foam. UV (MeOH): 275 (2198), 222 (3434), 198 (409). IR (KBr): 3395, 1560, 1460, 1410, 1255, 1123, 1037, 1015, 760, 655. ^{1}H-NMR (400 MHz, CD_3OD): 7.28–7.22 (*m*, 2 arom. H); 6.89–6.84 (*m*, 2 arom. H); 5.84 (*ddd*, ^3J(5,6) = 10.0, ^3J(5,4) = ^3J(5,1) = 3.0, H−C(5)); 5.79 (*ddd*, ^3J(6,5) = 10.0, ^3J(6,4) = ^3J(6,1) = 3.0, H−C(6)); 4.20 (*d*, ^3J = 13.0, 1 H, ArCH_2N); 4.15 (*d*, ^3J = 13.1, 1 H, ArCH_2N); 4.15–4.10 (*m*, H−C(1)); 3.67 (*dd*, ^3J(3,2) = ^3J(3,4) = 9.1, H−C(3)); 3.65–3.61 (*m*, H−C(4)); 3.46 (*dd*, ^3J(2,3) = 9.5, ^3J(2,1) = 8.1, H−C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 157.8 (*s*, arom. C); 134.9 (*d*, ^1J(C,H) = 163, C(5)); 131.8 (*d*, ^1J(C,H) = 157, arom. C); 131.3 (*d*, ^1J(C,H) = 159, arom. C); 123.5 (*d*, ^1J(C,H) = 163, C(6)); 121.5 (*s*, arom. C); 120.8 (*d*, ^1J(C,H) = 161, arom. C); 116.4 (*d*, ^1J(C,H) = 158, arom. C); 77.7 (*d*, ^1J(C,H) = 141, C(2)); 73.2, 72.7 (2*d*, ^1J(C,H) ≈ 141, C(3), C(1)); 61.5 (*d*, ^1J(C,H) = 144, C(4)); 46.8 (*t*, ^1J(C,H) = 141, Ar*C*H_2N). CI-MS (NH_3): 251 (7, M^+), 146 (7), 124 (82), 109 (2), 106 (100), 85 (7), 78 (63), 77 (38). HR-MALDI-TOF-MS: 252.1204 ($C_{13}H_{18}NO_4^+$, $[M+H]^+$; calc. 252.1236). Anal. calc. for $C_{13}H_{17}NO_5$ (251.116): C 62.14, H 6.82, N 5.57; found: C 62.33, H 6.68, N 5.40.

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-[(2-Hydroxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*^{2}) (= *(−)-(1*S*,2*S*,3*R*,6*R*)-6-[(2-Hydroxybenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (−)-**19d**). According to the *G.P.*, with (−)-**5** and 2-hydroxybenzaldehyde: (−)-**19d** (93%). $[\alpha]_{589}^{25} = -101$, $[\alpha]_{577}^{25} = -104$, $[\alpha]_{435}^{25} = -162$, $[\alpha]_{405}^{25} = -191$ (*c* = 0.167, MeOH). HR-MALDI-TOF-MS: 274.1045 ($C_{13}H_{17}NNaO_4^+$, $[M+Na]^+$; calc. 274.1055).

Enantiomer (+)-ent-**19d**. According to the *G.P.*, with (+)-**5** and 2-hydroxybenzaldehyde: (+)-*ent*-**19d** (87%). $[\alpha]_{589}^{25} = +97$, $[\alpha]_{577}^{25} = +100$, $[\alpha]_{435}^{25} = +155$, $[\alpha]_{405}^{25} = +183$ (*c* = 0.15, MeOH). HR-MALDI-TOF-MS: 274.1069 ($C_{13}H_{17}NNaO_4^+$, $[M+Na]^+$; calc. 274.1055).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(4-Chlorobenzyl)amino]cyclohex-5-ene-1,2,3-triol*^{2}) (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(4-Chlorobenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19e**). According to the *G.P.*, with (±)-**5** and 4-

chlorobenzaldehyde (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19e** (99%). Solid foam. UV (MeOH): 275 (1089), 267 (1241), 228 (4266), 197 (554). IR (KBr): 3376, 1612, 1560, 1411, 1093, 1015, 959, 805. ^{1}H-NMR (400 MHz, CD_3OD): 7.42 (*d*, ^3J = 8.6, 2 arom. H); 7.39 (*d*, ^3J = 8.6, 2 arom. H); 5.74 (br. *s*, H–C(6), H–C(5)); 4.10 (*dd*, $^3J(1,2)$ = 7.8, $^3J(1,6)$ = 3.0, H–C(1)); 4.05 (*d*, ^3J = 13.2, 1 H, ArCH_2N); 3.94 (*d*, ^3J = 13.2, 1 H, ArCH_2N); 3.59 (*dd*, $^3J(3,2)$ = 9.9, $^3J(3,4)$ = 8.8, H–C(3)); 3.45 (*dd*, $^3J(4,3)$ = 8.8, $^3J(4,5)$ = 3.0, H–C(4)); 3.43 (*dd*, $^3J(2,3)$ = 9.9, $^3J(2,1)$ = 7.8, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 135.6 (*s*, arom. C); 135.3 (*s*, arom. C); 134.3 (*d*, ^1J(C,H) = 162, C(5)); 132.0 (*d*, ^1J(C,H) = 161, 2 arom. C); 129.9 (*d*, ^1J(C,H) = 166, 2 arom. C); 124.4 (*d*, ^1J(C,H) = 162, C(6)); 77.7 (*d*, ^1J(C,H) = 139, C(2)); 73.2, 73.1 (2*d*, ^1J(C,H) ≈141, C(3), C(1)); 61.5 (*d*, ^1J(C,H) = 140, C(4)); 49.6 (*t*, ^1J(C,H) = 138, ArCH_2N). CI-MS (NH_3): 271 (23, $[M+2H]^+$), 158 (21), 153 (10), 143 (10), 140 (12), 127 (56), 125 (100), 106 (12), 91 (6), 85 (15), 84 (29). HR-MALDI-TOF-MS: 292.0712 ($C_{13}H_{16}ClNNaO_3^+$, $[M+Na]^+$; calc. 292.0716).

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-[(4-Chlorobenzyl)amino]cyclohex-5-ene-1,2,3-triol*[2] (= *(−)-(1*S*,2*S*,3*R*,6*R*)-6-[(4-Chlorobenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (−)-**19e**). According to the *G.P.*, with (−)-**5** and 4-chlorobenzaldehyde: (−)-**19e** (95%). $[\alpha]_{589}^{25} = -143$, $[\alpha]_{577}^{25} = -150$, $[\alpha]_{435}^{25} = -265$, $[\alpha]_{405}^{25} = -309$ (*c* = 0.162, MeOH). HR-MALDI-TOF-MS: 292.0714 ($C_{13}H_{16}ClNNaO_3^+$, $[M+Na]^+$; calc. 292.0716).

Enantiomer (+)-ent-**19e**. According to the *G.P.*, with (+)-**5** and 4-chlorobenzaldehyde: (+)-*ent*-**19e** (94%). $[\alpha]_{589}^{25} = +144$, $[\alpha]_{577}^{25} = +148$, $[\alpha]_{435}^{25} = +267$, $[\alpha]_{405}^{25} = +301$ (*c* = 0.16, MeOH). HR-MALDI-TOF-MS: 292.0721 ($C_{13}H_{16}ClNNaO_3^+$, $[M+Na]^+$; calc. 292.0716).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(2,6-Difluorobenzyl)amino]cyclohex-5-ene-1,2,3-triol*[2]) (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(2,6-Difluorobenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19f**). According to the *G.P.*, with (±)-**5** and 2,6-difluorobenzaldehyde (TLC monitoring), MeOH/AcOEt 3:7): (±)-**19f** (77%). Solid foam. UV (MeOH): 261 (665), 214 (2940), 198 (292). IR (KBr): 3365, 1627, 1593, 1560, 1470, 1419, 1266, 1229, 1127, 1048, 1018, 782. ^{1}H-NMR (400 MHz, CD_3OD): 7.42–7.33 (*m*, arom. H); 7.05–6.98 (*m*, 2 arom. H); 5.75 (*ddd*, $^3J(5,6)$ = 10.0, $^3J(5,4) = {}^3J(5,1)$ = 3.0, H–C(5)); 5.69 (*ddd*, $^3J(6,5)$ = 10.0, $^3J(6,4) = {}^3J(6,1)$ = 3.0, H–C(6)); 4.13–4.07 (*m*, H–C(1)); 4.05 (*d*, ^3J = 13.3, 1 H, ArCH_2N); 3.97 (*d*, ^3J = 13.1, 1 H, ArCH_2N); 3.49 (*dd*, ^3J(3,2) = 10.0, $^3J(3,4)$ = 8.5, H–C(3)); 3.41 (*dd*, $^3J(2,3)$ = 10.0, $^3J(2,1)$ = 7.6, H–C(2)); 3.32–3.27 (*m*, H–C(4)). ^{13}C-NMR (100.6 MHz, CD_3OD): 163.1 (*d*, ^1J(C,F) = 247, 2 arom. C); 132.5 (*d*, ^1J(C,H) = 162, C(5)); 131.4 (*d*, ^1J(C,H) = 165, arom. C); 126.4 (*d*, ^1J(C,H) = 162, C(6)); 112.5 (*s*, arom. C); 112.4 (*dd*, ^1J(C,F) = 166, ^2J(C,F) = 25, 2 arom. C); 77.9 (*d*, ^1J(C,H) = 144, C(2)); 73.9 (*d*, ^1J(C,H) = 137, C(1)); 73.6 (*d*, ^1J(C,H) = 143, C(3)); 61.3 (*d*, ^1J(C,H) = 140, C(4)); 37.7 (*t*, ^1J(C,H) = 140, ArCH_2N). CI-MS (NH_3): 272 (3, $[M+H]^+$), 242 (2), 211 (28), 144 (2), 142 (6), 127 (82), 107 (5), 84 (100), 82 (3). HR-MALDI-TOF-MS: 272.1012 ($C_{13}H_{16}F_2NO_3^+$, $[M+H]^+$; calc. 272.1098).

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-[(2,6-Difluorobenzyl)amino]cyclohex-5-ene-1,2,3-triol*[2]) (= *(−)-(1*S*,2*S*,3*R*,6*R*)-6-[(2,6-Difluorobenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (−)-**19f**). According to the *G.P.*, with (−)-**5** and 2,6-difluorobenzaldehyde: (−)-**19f** (87%). $[\alpha]_{589}^{25} = -76$, $[\alpha]_{577}^{25} = -96$, $[\alpha]_{435}^{25} = -228$, $[\alpha]_{405}^{25} = -270$ (*c* = 0.105, MeOH). HR-MALDI-TOF-MS: 294.0981 ($C_{13}H_{15}F_2NNaO_3^+$, $[M+Na]^+$; calc. 294.0918).

Enantiomer (+)-ent-**19f**. According to the *G.P.*, with (+)-**5** and 2,6-difluorobenzaldehyde: (+)-*ent*-**19f** (85%). $[\alpha]_{589}^{25} = +74$, $[\alpha]_{577}^{25} = +95$, $[\alpha]_{435}^{25} = +223$, $[\alpha]_{405}^{25} = +266$ (*c* = 0.105, MeOH). HR-MALDI-TOF-MS: 294.0909 ($C_{13}H_{15}F_2NNaO_3^+$, $[M+Na]^+$; calc. 294.0918).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[([1,1′-Biphenyl]-4-ylmethyl)amino]cyclohex-5-ene-1,2,3-triol*[2]) (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[([1,1′-Biphenyl]-4-ylmethyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19g**). According to the *G.P.*, with (±)-**5** and 4-phenylbenzaldehyde (= [1,1′-biphenyl]-4-carboxaldehyde) (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19g** (98%). Colorless foam. UV (MeOH): 268 (6370), 249 (7161), 217 (5451), 199 (938). IR (KBr): 3363, 2854, 1560, 1409, 1338, 1123, 1040, 1008, 957, 763, 696. ^{1}H-NMR (400 MHz, CD_3OD): 7.68–7.61 (*m*, 4 arom. H); 7.54–7.32 (*m*, 5 arom. H); 5.85 (*ddd*, $^3J(5,6)$ = 10.4, $^3J(5,4) = {}^3J(5,1)$ = 2.0, H–C(5)); 5.80 (*ddd*, $^3J(6,5)$ = 10.3, $^3J(6,4) = {}^3J(6,1)$ = 2.0, H–C(6)); 4.15 (*d*, ^3J = 13.0, 1 H, ArCH_2N); 4.12 (*dd*, $^3J(1,2)$ = 7.9, $^3J(1,6)$ = 3.1, H–C(1)); 4.03 (*d*, ^3J = 13.0, 1 H, ArCH_2N); 3.63 (*dd*, $^3J(3,2)$ = 9.7, $^3J(3,4)$ = 8.8, H–C(3)); 3.53 (*dd*, $^3J(4,3)$ = 8.8, $^3J(4,5)$ = 3.1, H–C(4)); 3.45 (*dd*, $^3J(2,3)$ = 9.8, $^3J(2,1)$ = 7.9, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 142.6 (*s*, arom. C); 141.6 (*s*, arom. C); 135.1 (*s*, arom. C); 134.7 (*d*, ^1J(C,H) = 163, C(5)); 131.0 (*d*, ^1J(C,H) = 159, 2 arom. C); 129.9 (*d*, ^1J(C,H) = 161, 2 arom. C); 128.6 (*d*, ^1J(C,H) = 160, arom. C); 128.4 (*d*, ^1J(C,H) = 160, 2 arom. C); 127.9 (*d*, ^1J(C,H) = 159, 2 arom. C); 123.9 (*d*, ^1J(C,H) = 158, C(6)); 77.7 (*d*, ^1J(C,H) = 139, C(2)); 73.1, 73.0 (2*d*, ^1J(C,H) ≈ 144, C(3), C(1)); 61.4 (*d*, ^1J(C,H) = 141, C(4)); 49.9 (*t*, ^1J(C,H) = 142, ArCH_2N). CI-MS (NH_3): 313 (7, $[M+2H]^+$), 252 (19), 168 (51), 167 (100), 165 (22), 152 (14), 128 (8), 117 (8), 106 (11), 89 (5), 84 (17), 76 (24). HR-MALDI-TOF-MS: 334.1414 ($C_{19}H_{21}NNaO_3^+$, $[M+Na]^+$; calc. 334.1419).

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-[((1,1′-Biphenyl]-4-ylmethyl)amino]cyclohex-5-ene-1,2,3-triol*[2] (=*(−)-(1*S*,2*S*,3*R*,6*R*)-6-[((1,1′-Biphenyl]-4-ylmethyl)amino]cyclohex-4-ene-1,2,3-triol*; (−)-**19g**). According to the *G.P.*, with (−)-**5** and 4-phenylbenzaldehyde: (−)-**19g** (96%). $[\alpha]_{589}^{25} = -98$, $[\alpha]_{577}^{25} = -100$, $[\alpha]_{435}^{25} = -201$, $[\alpha]_{405}^{25} = -238$ ($c = 0.13$, MeOH). HR-MALDI-TOF-MS: 334.1413 ($C_{19}H_{21}NNaO_3^+$, $[M+Na]^+$; calc. 334.1419).

Enantiomer (+)-ent-**19a**. According to the *G.P.*, with (+)-**5** and 4-phenylbenzaldehyde: (+)-*ent*-**19g** (92%). $[\alpha]_{589}^{25} = +107$, $[\alpha]_{577}^{25} = +125$, $[\alpha]_{435}^{25} = +220$, $[\alpha]_{405}^{25} = +243$ ($c = 0.15$, MeOH). HR-MALDI-TOF-MS: 334.1409 ($C_{19}H_{21}NNaO_3^+$, $[M+Na]^+$; calc. 334.1419).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(4-Phenoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*[2] (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(4-Phenoxybenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19h**). According to the *G.P.*, with (±)-**5** and 4-phenoxybenzaldehyde (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19h** (93%). Colorless foam. UV (MeOH): 271 (1445), 238 (4030), 198 (479). IR (KBr): 3386, 1590, 1560, 1489, 1409, 1243, 1114, 1018, 872, 692. ^{1}H-NMR (400 MHz, CD_3OD): 7.46 (*d*, $^3J = 8.5$, 2 arom. H); 7.41–7.36 (*m*, 2 arom. H); 7.18 (*t*, $^3J = 7.4$, 1 arom. H); 7.02 (*m*, 4 arom. H); 5.86 (*ddd*, $^3J(5,6) = 10.0$, $^3J(5,4) = {}^3J(5,1) = 3.0$, H–C(5)); 5.78 (*ddd*, $^3J(6,5) = 10.0$, $^3J(6,4) = {}^3J(6,1) = 3.0$, H–C(6)); 4.20 (*d*, $^3J = 13.1$, 1 H, ArCH_2N); 4.15–4.10 (*m*, H–C(1)); 4.13 (*d*, $^3J = 13.1$, 1 H, ArCH_2N); 3.74–3.61 (*m*, H–C(4), H–C(3)); 3.46 (*dd*, $^3J(2,3) = 9.2$, $^3J(2,1) = 7.7$, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 159.4 (*s*, arom. C); 158.1 (*s*, arom. C); 135.2 (*d*, ^1J(C,H) = 163, C(5)); 132.3 (*d*, ^1J(C,H) = 159, 2 arom. C); 131.0 (*d*, ^1J(C,H) = 159, 2 arom. C); 130.1 (*s*, arom. C); 124.9 (*d*, ^1J(C,H) = 159, arom. C); 123.4 (*d*, ^1J(C,H) = 163, C(6)); 120.3 (*d*, ^1J(C,H) = 161, 2 arom. C); 119.8 (*d*, ^1J(C,H) = 162, 2 arom. C); 77.7 (*d*, ^1J(C,H) = 143, C(2)); 73.0, 72.8 (2*d*, ^1J(C,H) ≈ 142, C(3), C(1)); 61.4 (*d*, ^1J(C,H) = 144, C(4)); 49.6 (*t*, ^1J(C,H) = 138, ArCH_2N). HR-MALDI-TOF-MS: 350.1374 ($C_{19}H_{21}NNaO_4^+$, $[M+Na]^+$; calc. 350.1368). Anal. calc. for $C_{19}H_{21}NO_4$ (327.147): C 69.71, H 6.47, N 4.28; found: C 70.01, H 6.33, N 4.11.

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-[(4-Phenoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*[2] (=*(−)-(1*S*,2*S*,3*R*,6*R*)-6-[(4-Phenoxybenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (−)-**19h**). According to the *G.P.*, with (−)-**5** and 4-phenoxybenzaldehyde: (−)-**19h** (91%). $[\alpha]_{589}^{25} = -94$, $[\alpha]_{577}^{25} = -96$, $[\alpha]_{435}^{25} = -196$, $[\alpha]_{405}^{25} = -231$ ($c = 0.142$, MeOH). HR-MALDI-TOF-MS: 350.1358 ($C_{19}H_{21}NNaO_4^+$, $[M+Na]^+$; calc. 350.1368).

Enantiomer (+)-ent-**19h**. According to the *G.P.*, with (+)-**5** and 4-phenoxybenzaldehyde: (+)-*ent*-**19h** (90%). $[\alpha]_{589}^{25} = +102$, $[\alpha]_{577}^{25} = +109$, $[\alpha]_{435}^{25} = +215$, $[\alpha]_{405}^{25} = +266$ ($c = 0.27$, MeOH). HR-MALDI-TOF-MS: 350.1356 ($C_{19}H_{21}NNaO_4^+$, $[M+Na]^+$; calc. 350.1368).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(2-Bromo-5-hydroxy-4-methoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*[2] (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(2-Bromo-5-hydroxy-4-methoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*; (±)-**19i**). According to the *G.P.*, with (±)-**5** and 2-bromo-5-hydroxy-4-methoxybenzaldehyde (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19i** (76%). Colorless solid. UV (MeOH): 287 (2721), 260 (899), 233 (4971), 196 (707). IR (KBr): 3358, 1610, 1560, 1508, 1419, 1269, 1211, 1169, 1027, 800, 660. ^{1}H-NMR (400 MHz, CD_3OD): 7.16 (*s*, arom. H); 7.00 (*s*, arom. H); 5.79 (br. *s*, H–C(6), H–C(5)); 4.13 (*dd*, $^3J(1,2) = 7.9$, $^3J(1,6) = 3.2$, H–C(1)); 4.06 (*d*, $^3J = 13.2$, 1 H, ArCH_2N); 3.99 (*d*, $^3J = 13.2$, 1 H, ArCH_2N); 3.61 (*dd*, $^3J(3,2) = 9.8$, $^3J(3,4) = 8.8$, H–C(3)); 3.52 (*dd*, $^3J(4,3) = 8.8$, $^3J(4,6) = 3.2$, H–C(4)); 3.43 (*dd*, $^3J(2,3) = 9.8$, $^3J(2,1) = 7.9$, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 149.9 (*s*, arom. C); 147.6 (*s*, arom. C); 133.7 (*d*, ^1J(C,H) = 162, C(5)); 129.0 (*s*, arom. C); 125.1 (*d*, ^1J(C,H) = 162, C(6)); 118.9 (*d*, ^1J(C,H) = 159, arom. C); 116.9 (*d*, ^1J(C,H) = 164, arom. C); 113.8 (*s*, arom. C); 77.8 (*d*, ^1J(C,H) = 145, C(2)); 73.4, 73.3 (2*d*, ^1J(C,H) ≈ 142, C(3), C(1)); 61.4 (*d*, ^1J(C,H) = 138, C(4)); 56.7 (*q*, ^1J(C,H) = 145, MeO); 50.0 (*t*, ^1J(C,H) = 139, ArCH_2N). CI-MS (NH_3): 360 (5, $[M+H]^+$), 302 (64), 299 (37), 262 (10), 229 (14), 217 (32), 215 (24), 152 (11), 140 (22), 137 (30), 125 (22), 123 (59), 110 (100), 96 (19), 94 (17), 80 (16), 70 (7). HR-MALDI-TOF-MS: 382.0205 ($C_{14}H_{18}BrNNaO_5^+$, $[M+Na]^+$; calc. 382.0266).

*(−)-(1*R*,2*S*,3*S*,4*R*)-4-[(2-Bromo-5-hydroxy-4-methoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*[2] (=*(−)-(1*S*,2*S*,3*R*,6*R*)-6-[(2-Bromo-5-hydroxy-4-methoxybenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (−)-**19i**). According to the *G.P.*, with (−)-**5** and 2-bromo-5-hydroxy-4-methoxybenzaldehyde: (−)-**19i** (80%). $[\alpha]_{589}^{25} = -70$, $[\alpha]_{577}^{25} = -73$, $[\alpha]_{435}^{25} = -148$, $[\alpha]_{405}^{25} = -189$ ($c = 0.332$, MeOH). HR-MALDI-TOF-MS: 382.0259 ($C_{14}H_{18}BrNNaO_5^+$, $[M+Na]^+$; calc. 382.0266).

Enantiomer (+)-ent-**19i**. According to the *G.P.*, with (+)-**5** and 2-bromo-5-hydroxy-4-methoxybenzaldehyde: (+)-*ent*-**19i** (88%). $[\alpha]_{589}^{25} = +74$, $[\alpha]_{577}^{25} = +77$, $[\alpha]_{435}^{25} = +156$, $[\alpha]_{405}^{25} = +192$ ($c = 0.30$, MeOH). HR-MALDI-TOF-MS: 382.0266 ($C_{14}H_{18}BrNNaO_5^+$, $[M+Na]^+$; calc. 382.0266).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(3-Methoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol*[2] (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(3-Methoxybenzyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19j**). According to the *G.P.*, with (±)-**5** and 3-methoxybenzaldehyde (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19j** (77%). Colorless solid. UV (MeOH): 280 (845), 274 (907), 220 (2586), 196 (266). IR (KBr): 3373, 1604, 1560, 1516, 1458, 1413, 1268, 1124, 1038, 960, 783, 694. ^{1}H-NMR (400 MHz, CD_3OD): 7.34–7.30 (*m*, 1 arom. H); 7.04–7.00 (*m*, 2 arom.

H); 6.95–6.90 (*m*, 1 arom. H); 5.81 (*ddd*, $^3J(5,6)=10.0$, $^3J(5,4)=^3J(5,1)=3.0$, H–C(5)); 5.74 (*ddd*, $^3J(6,5)=10.0$, $^3J(6,4)=^3J(6,1)=3.0$, H–C(6)); 4.15–4.10 (*m*, H–C(1)); 4.12 (*d*, $^3J=13.0$, 1 H, ArCH_2N); 4.03 (*d*, $^3J=13.0$, 1 H, ArCH_2N); 3.63 (*dd*, $^3J(3,2)=9.7$, $^3J(3,4)=8.9$, H–C(3)); 3.59–3.54 (*m*, H–C(4)); 3.43 (*dd*, $^3J(2,3)=9.7$, $^3J(2,1)=8.0$, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 161.6 (*s*, arom. C); 136.9 (*s*, arom. C); 135.2 (*d*, ^1J(C,H)=163, C(5)); 131.1 (*d*, ^1J(C,H)=160, arom. C); 123.3 (*d*, ^1J(C,H)=163, C(6)); 122.6 (*d*, ^1J(C,H)=160, arom. C); 115.9 (*d*, ^1J(C,H)=158, arom. C); 115.3 (*d*, ^1J(C,H)=160, arom. C); 77.6 (*d*, ^1J(C,H)=140, C(2)); 73.0, 72.8 (2*d*, ^1J(C,H)≈142, C(3), C(1)); 61.5 (*d*, ^1J(C,H)=142, C(4)); 55.8 (*q*, ^1J(C,H)=144, MeO); 50.2 (*t*, ^1J(C,H)=141, 1 C, Ar*C*H$_2$N). CI-MS (NH_3): 265 (3, M^+), 232 (5), 205 (47), 176 (5), 163 (5), 144 (21), 138 (7), 136 (35), 122 (21), 121 (100), 107 (41), 91 (17), 84 (65), 77 (3). HR-MALDI-TOF-MS: 288.1203 ($C_{14}H_{19}NNaO_4^+$, $[M+Na]^+$; calc. 288.1212). Anal. calc. for $C_{14}H_{19}NO_4$ (265.131): C 63.38, H 7.22, N 5.58; found: C 63.02, H 7.00, N 5.69.

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(1-Naphthylmethyl)amino]cyclohex-5-ene-1,2,3-triol*^{2}) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(Naphthalen-1-ylmethyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19k**). According to the *G.P.*, with (±)-**5** and 1-naphthaldehyde (=naphthalene-1-carboxaldehyde) (TLC monitoring, MeOH/AcOEt 1:4): (±)-**19k** (79%). Colorless solid. UV (MeOH): 291 (3582), 280 (4998), 227 (5467), 218 (4853), 208 (3977). IR (KBr): 3414, 1610, 1559, 1460, 1419, 1121, 1036, 780, 668. ^{1}H-NMR (400 MHz, CD_3OD): 8.18 (*d*, $^3J=8.5$, 1 arom. H); 7.96–7.89 (*m*, 2 arom. H); 7.67–7.49 (*m*, 4 arom. H); 5.85 (br. *s*, H–C(6), H–C(5)); 4.62 (*d*, $^3J=13.2$, 1 H, ArCH_2N); 4.56 (*d*, $^3J=13.2$, 1 H, ArCH_2N); 4.16 (*dd*, $^3J(1,2)=8.1$, $^3J(1,6)=3.2$, H–C(1)); 3.77 (*dd*, $^3J(3,2)=9.3$, $J(3,4)=8.8$, H–C(3)); 3.73 (*dd*, $^3J(4,3)=8.8$, $^3J(4,6)=3.2$, H–C(4)); 3.51 (*dd*, $^3J(2,3)=9.3$, $^3J(2,1)=8.1$, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 135.5 (*s*, arom. C); 134.4 (*d*, ^1J(C,H)=162, C(5)); 132.9 (*s*, arom. C); 132.4 (*s*, arom. C); 130.3 (*d*, ^1J(C,H)=160, arom. C); 130.0 (*d*, ^1J(C,H)=160, arom. C); 129.2 (*d*, ^1J(C,H)=158, arom. C); 127.9 (*d*, ^1J(C,H)=160, arom. C); 127.2 (*d*, ^1J(C,H)=160, arom. C); 126.5 (*d*, ^1J(C,H)=161, arom. C); 124.7 (*d*, ^1J(C,H)=162, C(6)); 124.2 (*d*, ^1J(C,H)=158, arom. C); 77.8 (*d*, ^1J(C,H)=142, C(2)); 73.3, 73.1 (2*d*, ^1J(C,H)≈142, C(3), C(1)); 62.2 (*d*, ^1J(C,H)=140, C(4)); 47.7 (*t*, ^1J(C,H)=139, Ar*C*H$_2$O). CI-MS (NH_3): 285 (5, M^+), 226 (75), 225 (62), 157 (5), 142 (73), 141 (100), 128 (5), 115 (18), 84 (95), 77 (2). HR-MALDI-TOF-MS: 286.1522 ($C_{17}H_{20}NO_3^+$, $[M+H]^+$; calc. 286.1443).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(1*H*-Indol-3-ylmethyl)amino]cyclohex-5-ene-1,2,3-triol*^{2}) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(1*H*-Indol-3-ylmethyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19l**). According to the *G.P.*, with (±)-**5** and 1*H*-indole-3-carboxaldehyde (TLC monitoring, 25% aq. NH_3 soln./MeCN 1:9): (±)-**19l** (30%). Colorless solid. UV (MeOH): 287 (3842), 276 (4439), 270 (2261), 225 (4837). IR (KBr): 3382, 1616, 1457, 1419, 1243, 1111, 1034, 748. ^{1}H-NMR (400 MHz, CD_3OD): 7.73 (*d*, $^3J=7.8$, 1 arom. H); 7.52 (*s*, 1 arom. H); 7.44 (*d*, $^3J=8.0$, 1 arom. H); 7.23–7.11 (*m*, 2 arom. H); 5.93 (*ddd*, $^3J(5,6)=10.4$, $^3J(5,4)=^3J(5,1)=2.0$, H–C(5)); 5.83 (*ddd*, $^3J(6,5)=10.4$, $^3J(6,4)=^3J(6,1)=2.0$, H–C(6)); 4.54 (br. *s*, ArCH_2N); 4.15–4.12 (*m*, H–C(1)); 3.86–3.80 (*m*, H–C(4)); 3.80 (*dd*, $^3J(3,4)=^3J(3,2)=8.5$, H–C(3)); 3.45 (*dd*, $^3J(2,3)=^3J(2,1)=8.5$, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 138.0 (*s*, arom. C); 136.5 (*d*, ^1J(C,H)=163, C(5)); 127.9 (*s*, arom. C); 127.8 (*d*, ^1J(C,H)=182, arom. C); 123.3 (*d*, ^1J(C,H)=158, arom. C); 121.7 (*d*, ^1J(C,H)=163, C(6)); 120.9 (*d*, ^1J(C,H)=159, arom. C); 119.0 (*d*, ^1J(C,H)=158, arom. C); 112.8 (*d*, ^1J(C,H)=159, arom. C); 106.4 (*s*, arom. C); 77.6 (*d*, ^1J(C,H)=146, C(2)); 72.9 (*d*, ^1J(C,H)=143, C(1)); 72.3 (*d*, ^1J(C,H)=142, C(3)); 61.0 (*d*, ^1J(C,H)=138, C(4)); 41.3 (*t*, ^1J(C,H)=144, Ar*C*H$_2$N). HR-MALDI-TOF-MS: 297.1856 ($C_{15}H_{18}N_2NaO_3^+$, $[M+Na]^+$; calc. 297.1215). Anal. calc. for $C_{15}H_{18}N_2O_3$ (274.1317): C 65.68, H 6.61, N 10.21; found C 66.01, H 6.81, N 10.32.

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(1*H*-Imidazol-5-ylmethyl)amino]cyclohex-5-ene-1,2,3-triol*^{2}) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(1*H*-imidazol-5-ylmethyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19m**). According to the *G.P.*, with (±)-**5** and 1*H*-imidazole-4-carboxaldehyde. FC (25% aq. NH_3 soln./MeCN 1:4): (±)-**19m** (10%). Yellowish oil. ^{1}H-NMR (400 MHz, CD_3OD): 7.75 (*s*, 1 arom. H); 7.01 (*s*, 1 arom. H); 5.81 (*ddd*, $^3J(5,6)=10.4$, $^3J(5,4)=^3J(5,1)=2.2$, H–C(5)); 5.74 (*ddd*, $^3J(6,5)=10.4$, $^3J(6,4)=^3J(6,1)=2.2$, H–C(6)); 4.15 (*d*, $^3J=13.9$, 1 H, ArCH_2N); 4.10 (*m*, H–C(1)); 4.07 (*d*, $^3J=13.9$, 1 H, ArCH_2N); 3.68–3.42 (*m*, H–C(4), H–C(3)), H–C(2)). HR-MALDI-TOF-MS: 248.1070 ($C_{10}H_{15}N_3NaO_3^+$, $[M+H]^+$; calc. 248.1011).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[[4-(4-Methoxyphenoxy)benzyl]amino]cyclohex-5-ene-1,2,3-triol*^{2}) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[[4-(4-Methoxyphenoxy)benzyl]amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19n**). According to the *G.P.*, with (±)-**5** and **23n** (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19n** (84%). Colorless solid. UV (MeOH): 280 (2708), 274 (2765), 260 (2479), 238 (8066). IR (KBr): 3380, 1614, 1542, 1501, 1441, 1232, 1034, 834. ^{1}H-NMR (400 MHz, CD_3OD): 7.45 (*d*, $^3J=8.6$, 2 arom. H); 7.00–6.94 (*m*, 6 arom. H); 5.89 (*ddd*, $^3J(5,6)=10.3$, $^3J(5,4)=^3J(5,1)=2.0$, H–C(5)); 5.77 (*ddd*, $^3J(6,5)=10.3$, $^3J(6,5)=^3J(6,1)=2.3$, H–C(6)); 4.23 (*d*, $^3J=13.1$, 1 H, ArCH_2N); 4.18 (*d*, $^3J=13.1$, 1 H, ArCH_2N); 4.16–4.12 (*m*, H–C(1)); 3.80 (br. *s*, *Me*); 3.76–3.71 (*m*, H–C(4), H–C(3)); 3.46 (*dd*, $^3J(2,3)=9.6$, $^3J(2,1)=7.9$, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 160.8 (*s*, arom. C); 157.9 (*s*, arom. C); 150.8 (*s*, arom. C); 135.8 (*d*, ^1J(C,H)=164, C(5)); 132.4 (*d*, ^1J(C,

H) = 159, 2 arom. C); 128.2 (*s*, arom. C); 122.5 (*d*, ^1J(C,H) = 164, C(6)); 122.1 (*d*, ^1J(C,H) = 162, 2 arom. C); 118.6 (*d*, ^1J(C,H) = 162, 2 arom. C); 116.0 (*d*, ^1J(C,H) = 161, 2 arom. C); 77.6 (*d*, ^1J(C,H) = 144, C(2)); 72.8 (*d*, ^1J(C, H) = 143, C(1)); 72.5 (*d*, ^1J(C,H) = 142, C(3)); 61.4 (*d*, ^1J(C,H) = 143, C(4)); 56.0 (*t*, ^1J(C,H) = 144, MeO); 49.5 (*t*, ^1J(C,H) = 142, Ar*C*H$_2$N). CI-MS (NH_3): 357 (10, $[M]^+$), 297 (23), 213 (100), 141 (5), 115 (3), 107 (6), 90 (18), 84 (27), 77 (27). HR-MALDI-TOF-MS: 380.1477 ($C_{20}H_{23}NNaO_5^+$, $[M+Na]^+$; calc. 380.1474).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-{[4-(4-Bromophenoxy)benzyl]amino}cyclohex-5-ene-1,2,3-triol*[2]) (= *(±)-(1*RS*, 2*RS*,3*SR*,6*SR*)-6-{[4-(4-Bromophenoxy)benzyl]amino}cyclohex-4-ene-1,2,3-triol*; (±)-**19o**). According to the *G.P.*, with (±)-**5** and **23o** (TLC monitoring, MeOH/AcOEt 1:4): (±)-**19o** (56%). Colorless solid. UV (MeOH): 269 (2278), 260 (2555), 238 (8955). IR (KBr): 3382, 1612, 1579, 1483, 1421, 1242, 1010. ^{1}H-NMR (400 MHz, CD_3OD): 7.54–7.51 (*m*, 4 arom. H); 7.06 (*d*, ^3J = 8.6, 2 arom. H); 6.96 (*d*, ^3J = 8.9, 2 arom. H); 5.90 (*ddd*, ^3J(5,6) = 10.3, ^3J(5,4) = ^3J(5,1) = 2.3, H–C(5)); 5.80 (*ddd*, ^3J(6,5) = 10.3, ^3J(6,4) = ^3J(6,1) = 2.3, H–C(6)); 4.27 (*d*, ^3J = 13.1, 1 H, ArC*H*$_2$N); 4.22 (*d*, ^3J = 13.1, 1 H, ArC*H*$_2$N); 4.16–4.12 (*m*, H–C(1)); 3.78–3.71 (2*m*, H–C(4), H–C(3)); 3.47 (*dd*, ^3J(2,3) = 9.6, ^3J(2,1) = 7.9, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 158.9 (*s*, arom. C); 157.6 (*s*, arom. C); 135.8 (*d*, ^1J(C,H) = 164, C(5)); 134.0 (*d*, ^1J(C,H) = 167, 2 arom. C); 132.7 (*d*, ^1J(C,H) = 160, 2 arom. C); 130.0 (*s*, arom. C); 122.8 (*d*, ^1J(C,H) = 164, C(6)); 122.0 (*d*, ^1J(C,H) = 164, 2 arom. C); 120.2 (*d*, ^1J(C,H) = 164, 2 arom. C); 117.2 (s, arom. C); 77.6 (*d*, ^1J(C,H) = 145, C(2)); 72.9 (*d*, ^1J(C, H) = 142, C(1)); 72.6 (*d*, ^1J(C,H) = 139, C(3)); 61.5 (*d*, ^1J(C,H) = 145, C(4)); 49.5 (*t*, ^1J(C,H) = 137, Ar*C*H$_2$N). CI-MS (NH_3): 347 (5), 263 (37), 261 (38), 149 (17), 107 (10), 101 (14), 86 (100), 84 (54), 76 (21), 70 (21). HR-MALDI-TOF-MS: 428.0487 ($C_{19}H_{20}BrNNaO_4^+$, $[M+Na]^+$; calc. 428.0473).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-{[4-[4-(1*H*-Imidazol-1-yl)phenoxy]benzyl]amino}cyclohex-5-ene-1,2,3-triol*[2]) (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-{[4-[4-(1*H*-Imidazol-1-yl)phenoxy]benzyl]amino}cyclohex-4-ene-1,2,3-triol*; (±)-**19p**). According to the *G.P.*, with (±)-**5** and **23p** (TLC monitoring, 25% aq. NH_3 soln./MeCN 1:9): (±)-**19p** (57%). Colorless solid. UV (MeOH): 253 (10000), 199 (1270). IR (KBr): 3386, 1519, 1506, 1242, 1115, 1060, 836. ^{1}H-NMR (400 MHz, CD_3OD): 8.11 (*s*, 1 arom. H); 7.58 (*d*, ^3J = 8.8, 2 arom. H); 7.56 (*s*, 1 arom. H); 7.46 (*d*, ^3J = 8.5, 2 arom. H); 7.17 (*s*, 1 arom. H); 7.16 (*d*, ^3J = 8.6, 2 arom. H); 7.09 (*d*, ^3J = 8.4, 2 arom. H); 5.86, 5.79 (2*ddd*, ^3J(6,5) = ^3J(5,6) = 10.4, ^3J(6,4) = ^3J(5,4) = ^3J(6,1) = ^3J(5,1) = 2.3, H–C(6), H–C(5)); 4.22 (*d*, ^3J = 13.1, 1 H, ArC*H*$_2$N)); 4.14 (*d*, ^3J = 13.1, 1 H, ArC*H*$_2$N); 4.16–4.13 (*m*, H–C(1)); 3.73–3.60 (*m*, H–C(4), H–C(3)); 3.47 (*t*, ^3J(2,3) = ^3J(2,1) = 8.3, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 158.6 (*s*, arom. C); 157.7 (*s*, arom. C); 137.0 (*d*, ^1J(C,H) = 210, arom. C); 135.1 (*d*, ^1J(C,H) = 163, C(5)); 134.2 (*s*, arom. C); 132.5 (*d*, ^1J(C,H) = 160, 2 arom. C); 131.2 (*s*, arom. C); 130.1 (*d*, ^1J(C,H) = 191, arom. C); 124.2 (*d*, ^1J(C,H) = 163, 2 arom. C); 123.6 (*d*, ^1J(C,H) = 163, C(6)); 121.1 (*d*, ^1J(C,H) = 163, 2 arom. C); 120.2 (*d*, ^1J(C,H) = 162, 2 arom. C); 120.0 (*d*, ^1J(C,H) = 192, arom. C); 77.7 (*d*, ^1J(C,H) = 141, C(2)); 73.1, 73.0 (2*d*, ^1J(C,H) = 142, C(3), C(1)); 61.5 (*d*, ^1J(C,H) = 142, C(4)); 49.7 (*t*, ^1J(C,H) = 139, Ar*C*H$_2$N). HR-MALDI-TOF-MS: 416.1580 ($C_{22}H_{23}N_3NaO_4^+$, $[M+Na]^+$; calc. 416.1586). Anal. calc. for $C_{22}H_{23}N_3O_4$ (393.1689): C 67.16, H 5.89, N 10.68; found: C 67.10, H 6.00, N 10.82.

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-{[4-(4-Acetylphenoxy)benzyl]amino}cyclohex-5-ene-1,2,3-triol*[2]) (= *(±)-1-{4-[4-({[(1*RS*,2*RS*,3*SR*,6*SR*)-4,5,6-Trihydroxycyclohex-2-en-1-yl]amino}methyl)phenoxy]phenyl}ethanone*; (±)-**19q**). According to the *G.P.*, with (±)-**5** and **23q** (TLC monitoring, MeOH/AcOEt 1:4): (±)-**19q** (64%). Colorless solid. UV (MeOH): 273 (8340), 259 (7980), 225 (6960). IR (KBr): 3387, 1677, 1594, 1500, 1418, 1260, 1098, 1022. ^{1}H-NMR (400 MHz, CD_3OD): 8.03 (*d*, ^3J = 8.7, 2 arom. H); 7.56 (*d*, ^3J = 8.3, 2 arom. H); 7.14 (*d*, ^3J = 8.4, 2 arom. H); 7.06 (*d*, ^3J = 8.7, 2 arom. H); 5.87 (*ddd*, ^3J(5,6) = 10.3, ^3J(5,4) = ^3J(5,1) = 2.1, H–C(5)); 5.79 (*ddd*, ^3J(6, 5) = 10.3, ^3J(6,4) = ^3J(6,1) = 2.1, H–C(6)); 4.24 (*d*, ^3J = 13.0, 1 H, ArC*H*$_2$N); 4.17 (*d*, ^3J = 13.0, 1 H, ArC*H*$_2$N); 4.16–4.12 (*m*, H–C(1)); 3.75–3.65 (*m*, H–C(4), H–C(3)); 3.47 (*dd*, ^3J(2,3) = 8.9, ^3J(2,1) = 8.1, H–C(2)); 2.57 (br. *s*, Me). ^{13}C-NMR (100.6 MHz, CD_3OD): 199.2 (*s*, *C*OMe); 163.1 (*s*, arom. C); 157.4 (*s*, arom. C); 135.2 (*d*, ^1J(C,H) = 163, C(5)); 133.4 (*s*, arom. C); 132.6 (*d*, ^1J(C,H) = 160, 2 arom. C); 132.1 (*s*, arom. C); 132.0 (*d*, ^1J(C,H) = 160, 2 arom. C); 123.5 (*d*, ^1J(C,H) = 163, C(6)); 121.4 (*d*, ^1J(C,H) = 162, arom. C); 118.6 (*d*, ^1J(C, H) = 162, 2 arom. C); 77.7 (*d*, ^1J(C,H) = 140, C(2)); 73.0, 72.9 (2*d*, ^1J(C,H) ≈ 142, C(3), C(1)); 61.5 (*d*, ^1J(C, H) = 141, C(4)); 49.7 (*t*, ^1J(C,H) = 138, Ar*C*H$_2$N); 26.6 (*q*, ^1J(C,H) = 128, CO*Me*). CI-MS (NH_3): 309 (15), 225 (100), 167 (11), 149 (35), 121 (22), 110 (18), 98 (16), 84 (42), 76 (41), 70 (12). HR-MALDI-TOF-MS: 370.1590 ($C_{21}H_{24}NO_5^+$, $[M+H]^+$; calc. 370.1654).

*1:1 Mixture of (±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-{[4-[4-[(1*RS*)- and (±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-{[4-[4-[(1*SR*)-1-Hydroxyethyl]phenoxy}benzyl]amino}cyclohex-5-ene-1,2,3-triol*[2]) (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-{[4-[4-[(1*RS*) and (±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-{[4-[4-[(1*SR*)-1-Hydroxyethyl]phenoxy}benzyl]amino}cyclohex-4-ene-1,2,3-triol*; (±)-**19r**). A mixture of (±)-**19q** (0.03 g, 0.081 mmol) in anh. MeOH (1.5 ml) and $NaBH_4$ (0.0046 g, 0.121 mmol, 1.5 equiv.) was stirred at 20° overnight. After evaporation, the residue was purified by FC (silica gel) (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19r** (89%). Colorless solid. IR (KBr): 3385, 1602, 1502, 1241,

1084, 1013, 834. ^{1}H-NMR (400 MHz, CD_3OD): 7.37 (*d*, ^3J = 7.9, 4 arom. H); 6.95 (*d*, ^3J = 7.2, 4 arom. H); 5.75, 5.66 (2*ddd*, $^3J(6,5) = {}^3J(5,6) = 10.3$, $^3J(6,4) = {}^3J(5,4) = {}^3J(6,1) = {}^3J(5,1) = 2.3$, H–C(6), H–C(5)); 4.83 (*q*, ^3J = 6.4, MeC*H*(OH); 4.13–4.08 (*m*, H–C(1)); 3.92 (*d*, ^3J = 12.8, 1 H, ArCH_2N); 3.75 (*d*, ^3J = 12.8, 1 H, ArCH_2N); 3.52 (*dd*, $^3J(3,2) = 9.8$, $^3J(3,4) = 8.7$, H–C(3)); 3.46 (*dd*, $^3J(2,3) = 9.8$, $^3J(2,1) = 7.7$, H–C(2)); 3.36 (br. *m*, H–C(4)); 1.45 (*d*, ^3J = 6.4, *Me*). ^{13}C-NMR (100.6 MHz, CD_3OD): 158.1 (*s*, arom. C); 157.7 (*s*, arom. C); 135.5 (*s*, arom. C); 131.4 (*d*, ^1J(C,H) = 161, C(5)); 131.2 (*d*, ^1J(C,H) = 161, 2 arom. C); 129.9 (*s*, arom. C); 128.0 (*d*, ^1J(C,H) = 162, 2 arom. C); 127.8 (*d*, ^1J(C,H) = 161, C(5)); 119.7 (*d*, ^1J(C,H) = 161, 4 arom. C); 78.0 (*d*, ^1J(C,H) = 144, C(2)); 74.5 (*d*, ^1J(C,H) = 141, C(3)); 73.6 (*d*, ^1J(C,H) = 142, C(1)); 70.3 (*d*, ^1J(C,H) = 143, MeCH(OH); 61.3 (*d*, ^1J(C,H) = 144, C(4)); 50.6 (*t*, ^1J(C,H) = 139, ArCH_2N); 25.6 (*q*, ^1J(C,H) = 126, *Me*). CI-MS (NH_3): 372 (13, $[M+H]^+$), 305 (21), 231 (4), 188 (15), 168 (7), 149 (57), 144 (48), 122 (20), 104 (100), 91 (61), 79 (39), 71 (29). HR-MALDI-TOF-MS: 394.5398 ($C_{21}H_{25}NNaO_5^+$, $[M+Na]^+$; calc. 394.1630).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-{[4-[4-(1,1-Dimethoxyethyl)phenoxy]benzyl]amino}cyclohex-5-ene-1,2,3-triol*[2]) (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-{[4-[4-(1,1-Dimethoxyethyl)phenoxy]benzyl]amino}cyclohex-4-ene-1,2,3-triol*; (±)-**19s**). According to the *G.P.*, with (±)-**5** and **24** in MeOH (TLC monitoring, MeOH/AcOEt 1:4): (±)-**19s** (60%). Solid. UV (MeOH): 265 (2965), 236 (6448), 202 (1487). IR (KBr): 3374, 1601, 1502, 1420, 1245, 1094, 878. ^{1}H-NMR (400 MHz, CD_3OD): 7.54 (*d*, ^3J = 8.5, 2 arom. H); 7.49 (*t*, ^3J = 8.6, 2 arom. H); 7.05 (*d*, ^3J = 8.5, 2 arom. H); 6.99 (*t*, ^3J = 8.7, 2 arom. H); 5.93 (*ddd*, $^3J(5,6) = 10.3$, $^3J(5,4) = {}^3J(5,1) = 2.3$, H–C(5)); 5.82 (*ddd*, $^3J(6,5) = 10.3$, $^3J(6,4) = {}^3J(6,1) = 2.3$, H–C(6)); 4.30 (br. *s*, ArCH_2N); 4.17–4.14 (*m*, H–C(1)); 3.86–3.78 (*m*, H–C(4), H-C(3)); 3.47 (*dd*, $^3J(2,3) = 8.9$, $^3J(2,1) = 7.8$, H–C(2)); 3.18 (br. *s*, 2 MeO); 1.52 (*s*, Me). ^{13}C-NMR (100.6 MHz, CD_3OD): 159.6 (*s*, arom. C); 157.4 (*s*, arom. C); 136.5 (*d*, ^1J(C,H) = 163, C(5)); 133.0 (*s*, arom. C); 132.9 (2*d*, ^1J(C,H) = 160, 2 arom. C); 132.0 (*s*, arom. C); 129.1 (*d*, ^1J(C,H) = 161, 2 arom. C); 121.8 (*d*, ^1J(C,H) = 163, C(6)); 119.9 (*d*, ^1J(C,H) = 162, 2 arom. C); 119.7 (*d*, ^1J(C,H) = 162, 2 arom. C); 102.7 (*s*, Me*C*(OMe)$_2$); 77.5 (*d*, ^1J(C,H) = 142, C(2)); 72.8, 72.3 (2*d*, ^1J(C,H) ≈ 143, C(3), C(1)); 61.6 (*d*, ^1J(C,H) = 137, C(4)); 49.4 (*t*, ^1J(C,H) = 141, ArCH_2N); 49.2 (*q*, ^1J(C,H) = 142, 2 *Me*O); 26.4 (*q*, ^1J(C,H) = 127, *Me*). CI-MS (NH_3): 333 (3), 309 (18), 240 (13), 225 (100), 197 (20), 181 (13), 155 (28), 149 (50), 128 (17), 121 (38), 107 (48), 94 (47), 84 (32), 77 (45). HR-MALDI-TOF-MS: 438.1820 ($C_{23}H_{29}NNaO_6^+$, $[M+Na]^+$; calc. 438.1893).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-{[4-[(2-Methylquinolin-8-yl)oxy]benzyl]amino}cyclohex-5-ene-1,2,3-triol*[2]) (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-{[4-[(2-Methylquinolin-8-yl)oxy]benzyl]amino}cyclohex-4-ene-1,2,3-triol*; (±)-**19t**). According to the *G.P.*, with (±)-**5** and **23t** (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19t** (81%). Colorless solid. UV (MeOH): 292 (4089), 279 (4333), 244 (11828). IR (KBr): 3395, 1609, 1560, 1508, 1430, 1236, 1079. ^{1}H-NMR (400 MHz, CD_3OD): 8.26 (*d*, ^3J = 8.5, 1 arom. H); 7.67 (*d*, ^3J = 8.0, 1 arom. H); 7.50–7.43 (*m*, 4 arom. H); 7.16 (*d*, ^3J = 7.5, 1 arom. H); 7.08 (*d*, ^3J = 8.5, 2 arom. H); 5.87, 5.76 (2*ddd*, $^3J(6,5) = {}^3J(5,6) = 10.3$, $^3J(6,4) = {}^3J(5,4) = {}^3J(6,1) = {}^3J(5,1) = 2.4$, H–C(6), H–C(5)); 4.24 (*d*, ^3J = 13.1, 1 H, ArCH_2N); 4.18 (*d*, ^3J = 13.1, 1 H, ArCH_2N); 4.13–4.11 (*m*, H–C(1)); 3.75–3.70 (*m*, H–C(4), H–C(3)); 3.46 (*dd*, $^3J(2,3) = 8.9$, $^3J(2,1) = 7.8$, H–C(2)); 2.68 (br. *s*, Me). ^{13}C-NMR (100.6 MHz, CD_3OD): 160.8 (*s*, arom. C); 159.7 (*s*, arom. C); 153.3 (*s*, arom. C); 141.4 (*s*, arom. C); 138.3 (*d*, ^1J(C,H) = 162, arom. C); 135.7 (*d*, ^1J(C,H) = 163, C(5)); 132.5 (*d*, ^1J(C,H) = 160, 2 arom. C); 129.9 (*s*, arom. C); 129.7 (*s*, arom. C); 127.1 (*d*, ^1J(C,H) = 163, arom. C); 124.5 (*d*, ^1J(C,H) = 161, arom. C); 124.4 (*d*, ^1J(C,H) = 161, arom. C); 122.9 (*d*, ^1J(C,H) = 163, C(6)); 120.3 (*d*, ^1J(C,H) = 162, 2 arom. C); 118.6 (*d*, ^1J(C,H) =160, arom. C); 77.6 (*d*, ^1J(C,H) = 141, C(2)); 73.0 (*d*, ^1J(C,H) = 143, C(1)); 72.7 (*d*, ^1J(C,H) = 141, C(3)); 61.6 (*d*, ^1J(C,H) = 143, C(4)); 49.6 (*t*, ^1J(C,H) = 138, ArCH_2N); 24.7 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 393 (3, $[M+H]^+$), 333 (19), 249 (95), 248 (100), 218 (8), 204 (6), 143 (18), 124 (6), 115 (26), 103 (5), 89 (19), 77 (12). HR-MALDI-TOF-MS: 415.1601 ($C_{23}H_{24}N_2NaO_4^+$, $[M+Na]^+$; calc. 415.1634).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-{[4-(4-Phenoxyphenoxy)benzyl]amino}cyclohex-5-ene-1,2,3-triol*[2]) (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-{[4-(4-Phenoxyphenoxy)benzyl]amino}cyclohex-4-ene-1,2,3-triol*; (±)-**19u**). According to the *G.P.*, with (±)-**5** and **23u** (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19u** (70%). Colorless solid. UV (MeOH): 271 (3040), 260 (3460), 241 (10357). IR (KBr): 3378, 1609, 1511, 1488, 1225, 1023, 867. ^{1}H-NMR (400 MHz, CD_3OD): 7.48 (*d*, ^3J = 8.5, 2 arom. H); 7.36 (*t*, ^3J = 7.6, 2 arom. H); 7.11 (*t*, ^3J = 7.4, 1 arom. H); 7.05–6.98 (*m*, 8 arom. H); 5.87 (*ddd*, $^3J(5,6) = 10.3$, $^3J(5,4) = {}^3J(5,1) = 2.3$, H–C(5)); 5.77 (*ddd*, $^3J(6,5) = 10.3$, $^3J(6,4) = {}^3J(6,1) = 2.3$, H–C(6)); 4.22 (*d*, ^3J = 13.1, 1 H, ArCH_2N); 4.16 (*d*, ^3J = 13.1, 1 H, ArCH_2N); 4.15–4.10 (*m*, H–C(1)); 3.75–3.67 (*m*, H–C(4), H–C(3)); 3.46 (*dd*, $^3J(2,3) = 8.9$, $^3J(2,1) = 8.2$, H-C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 160.0 (*s*, arom. C); 159.1 (*s*, arom. C); 154.8 (*s*, arom. C); 153.5 (*s*, arom. C); 135.5 (*d*, ^1J(C,H) = 161, C(5)); 132.5 (*d*, ^1J(C,H) = 159, 2 arom. C); 130.9 (*d*, ^1J(C,H) = 157, 2 arom. C); 129.5 (*s*, arom. C); 124.3 (*d*, ^1J(C,H) = 159, arom. C); 123.0 (*d*, ^1J(C,H) = 161, C(6)); 122.0 (*d*, ^1J(C,H) = 164, 2 arom. C); 121.5 (*d*, ^1J(C,H) = 162, 2 arom. C); 119.4 (*d*, ^1J(C,H) = 162, 2 arom. C); 119.3 (*d*, ^1J(C,H) = 160, 2 arom. C); 77.6 (*d*, ^1J(C,H) = 142, C(2)); 73.0 (*d*, ^1J(C,H) = 142, C(1)); 72.8 (*d*, ^1J(C,H) = 142, C(3)); 61.5 (*d*, ^1J(C,H) = 137, C(4)); 49.6 (*t*, ^1J(C,H) = 141, ArCH_2N). CI-MS (NH_3): 420 (8, $[M+H]^+$), 359 (28), 290 (5), 275

(100), 181 (13), 154 (10), 141 (10), 115 (17), 107 (11), 84 (30), 77 (62). HR-MALDI-TOF-MS: 442.1644 ($C_{25}H_{25}NNaO_5^+$, $[M+Na]^+$; calc. 442.1630).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-(Propylamino)cyclohex-5-ene-1,2,3-triol*[2]) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-(Propylamino)cyclohex-4-ene-1,2,3-triol*; (±)-**19v**). According to the *G.P.*, with (±)-**5** and propanal (TLC monitoring, MeOH/AcOEt 1:3): (±)-**19v** (77%). Pale yellowish oil. UV (MeOH): 213 (867). IR (KBr): 3320, 2924, 1464, 1377, 1132, 1043, 996. ^{1}H-NMR (400 MHz, CD_3OD): 5.71–5.63 (br. *m*, H–C(6), H–C(5)); 4.11–4.07 (*m*, H–C(1)); 3.48 (*dd*, $^3J(3,4)=8.2$, $^3J(3,2)=10.3$, H–C(3)); 3.43 (*dd*, $^3J(2,3)=10.3$, $^3J(2,1)=7.3$, H–C(2)); 3.34–3.15 (*m*, H–C(4), $CH_2(1')$); 2.09 (*sext.*, $^3J(2',3')=^3J(2',1')=7.4$, $CH_2(2')$); 0.99 (*t*, $^3J(3',2')=7.4$, Me). ^{13}C-NMR (100.6 MHz, CD_3OD): 131.3, 126.9 (2*d*, ^1J(C,H) = 162, C(6), C(5)); 77.9 (*d*, ^1J(C,H) = 144, C(2)); 74.1, 73.7 (2*d*, ^1J(C,H) ≈ 138, C(3), C(1)); 60.7 (*d*, ^1J(C,H) = 131, C(4)); 54.7 (*t*, ^1J(C,H) = 138, C(1′)); 22.0 (*t*, ^1J(C,H) = 126, C(2′)); 14.3 (*q*, ^1J(C,H) = 126, *Me*). CI-MS (NH_3): 167 (26), 146 (2), 122 (2), 110 (3), 98 (6), 84 (100), 81 (6), 70 (8). HR-MALDI-TOF-MS: 226.0818 ($C_9H_{17}KNO_5^+$, $[M+K]^+$; calc. 226.0846).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-(Hexylamino)cyclohex-5-ene-1,2,3-triol*[2]) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-(Hexylamino)cyclohex-4-ene-1,2,3-triol*; (±)-**19w**). According to the the *G.P.*, with (±)-**5** and hexanal (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19w** (62%). Colorless oil. UV (MeOH): 207 (1507). IR (KBr): 3375, 2925, 1634, 1456, 1383, 1037, 960. ^{1}H-NMR (400 MHz, CD_3OD): 5.71–5.63 (br. *m*, H–C(6), H–C(5)); 4.07 (*m*, H–C(1)); 3.49 (*dd*, $^3J(3,2)=10.0$, $^3J(3,4)=8.5$, H–C(3)); 3.43 (*dd*, $^3J(2,3)=10.0$, $^3J(2,1)=7.6$, H–C(2)); 3.35–3.33 (*m*, H–C(4)); 2.85–2.77, 2.68–2.61 (2*m*, $CH_2(1')$); 1.60–1.51 (*m*, $CH_2(2')$; 1.42–1.30 (*m*, $CH_2(3')$, $CH_2(4')$, $CH_2(5')$); 0.92 (*t*, $^3J(6',5')=7.0$, Me). ^{13}C-NMR (100.6 MHz, CD_3OD): 132.5, 126.7 (2*d*, ^1J(C,H) ≈ 161, C(6), C(5)); 77.9 (*d*, ^1J(C,H) = 140, C(2)); 73.8, 73.5 (2*d*, ^1J(C,H) ≈ 144, C(3), C(1)); 62.0 (*d*, ^1J(C,H) = 143, C(4)); 47.0 (*t*, ^1J(C,H) = 131, C(1′)); 32.8 (*t*, ^1J(C,H) = 131, C(2′)); 30.2, 27.9, 23.6 (3*t*, ^1J(C,H) = 124, C(3′), C(4′), C(5′)); 14.4 (*q*, ^1J(C,H) = 124, Me). CI-MS (NH_3): 230 (3), 170 (10), 169 (100), 158 (5), 140 (31), 126 (3), 112 (12), 98 (48), 94 (7), 84 (33), 80 (12), 70 (9). HR-MALDI-TOF-MS: 230.1709 ($C_{12}H_{24}NO_3^+$, $[M+H]^+$; calc. 230.1756). Anal. calc. for $C_{12}H_{23}NO_3$ (229.167): C 62.85, H 10.11, N 6.11; found: C 63.11, H 10.40, N 6.27.

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-(Octylamino)cyclohex-5-ene-1,2,3-triol*[2]) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-(Octylamino)cyclohex-4-ene-1,2,3-triol*; (±)-**19x**). According to the *G.P.*, with (±)-**5** and octanal (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19x** (53%). Oil. UV (MeOH): 207 (1052). IR (KBr): 3374, 2926, 2855, 1560, 1419, 1123, 1034, 781. ^{1}H-NMR (400 MHz, CD_3OD): 5.87 (*ddd*, $^3J(5,6)=10.4$, $^3J(5,4)=^3J(5,1)=2.0$, H–C(5)); 5.70 (*ddd*, $^3J(6,5)=10.4$, $^3J(6,4)=^3J(6,1)=2.0$, H–C(6)); 4.14–4.11 (*m*, H–C(1)); 3.74–3.69 (*m*, H–C(4)); 3.66 (*dd*, $^3J(3,2)=^3J(3,4)=9.5$, H–C(3)); 3.45 (*dd*, $^3J(2,3)=9.5$, $^3J(2,1)=8.1$, H–C(2)); 3.10–2.95 (*m*, $CH_2(1')$); 1.73–1.63 (*m*, $CH_2(2')$); 1.46–1.27 (*m*, $CH_2(3')$, $CH_2(4')$, $CH_2(5')$, $CH_2(6')$, $CH_2(7')$); 0.92 (*t*, $^3J(8',7')=7.0$, *Me*). ^{13}C-NMR (100.6 MHz, CD_3OD): 135.9 (*d*, ^1J(C,H) = 161, C(5)); 122.4 (*d*, ^1J(C,H) = 165, C(6)); 77.5 (*d*, ^1J(C,H) = 140, C(2)); 72.9 (*d*, ^1J(C,H) = 139, C(1)); 72.2 (*d*, ^1J(C,H) = 145, C(3)); 61.9 (*d*, ^1J(C,H) = 144, C(4)); 46.3 (*t*, ^1J(C,H) = 142, C(1′)); 32.9 (*t*, ^1J(C,H) = 125, C(2′)); 30.2, 30.3, 28.1, 27.8, 23.7 (5*t*, 5 C(3′), C(4′), C(5′), C(6′), C(7′)); 14.4 (*q*, ^1J(C,H) = 124, *Me*). CI-MS (NH_3): 258 (6, $[M+H]^+$), 198 (43), 197 (100), 168 (53), 158 (5), 154 (2), 140 (12), 130 (5), 122 (7), 111 (8), 98 (69), 84 (39), 80 (17), 70 (13). HR-MALDI-TOF-MS: 280.1880 ($C_{14}H_{27}NNaO_3^+$, $[M+Na]^+$; calc. 280.1889).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(2-Phenylethyl)amino]cyclohex-5-ene-1,2,3-triol*[2]) (=*(±)-(1*SR*,2*SR*,3*RS*,6*RS*)-6-[(2-Phenylethyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**19y**). According to the *G.P.*, with (±)-**5** and 2-phenylethanal (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19y** (42%). Colorless solid. UV (MeOH): 212 (3652). IR (KBr): 3384, 1569, 1413, 1125, 1030, 753, 701. ^{1}H-NMR (400 MHz, CD_3OD): 7.37–7.23 (*m*, 5 arom. H); 5.87 (*ddd*, $^3J(5,6)=10.4$, $^3J(5,4)=^3J(5,1)=2.0$, H–C(5)); 5.72 (*ddd*, $^3J(6,5)=10.4$, $^3J(6,4)=^3J(6,1)=2.0$, H–C(6)); 4.12 (*dd*, $^3J(1,2)=8.0$, $^3J(1,6)=2.0$, H–C(1)); 3.77–3.72 (*m*, H–C(4)); 3.66 (*dd*, $^3J(3,4)=8.5$, $^3J(3,2)=9.6$, H–C(3)); 3.46 (*dd*, $^3J(2,3)=9.6$, $^3J(2,1)=8.0$, H–C(2)); 3.35–3.20 (*m*, $CH_2(1')$); 3.00 (*t*, $^3J(2',1')=7.0$, $CH_2(2')$). ^{13}C-NMR (100.6 MHz, CD_3OD): 138.6 (*s*, arom. C); 135.7 (*d*, ^1J(C,H) = 164, C(5)); 129.8 (*d*, ^1J(C,H) = 160, 2 arom. C); 129.7 (*d*, ^1J(C,H) = 161, 2 arom. C); 128.0 (*d*, ^1J(C,H) = 154, arom. C); 122.7 (*d*, ^1J(C,H) = 164, C(6)); 77.6 (*d*, ^1J(C,H) = 140, C(2)); 72.9 (*d*, ^1J(C,H) = 140, C(1)); 72.4 (*d*, ^1J(C,H) = 139, C(3)); 61.9 (*d*, ^1J(C,H) = 140, C(4)); 47.7 (*t*, ^1J(C,H) = 142, C(1′)); 34.3 (*t*, ^1J(C,H) = 128, C(2′)). CI-MS (NH_3): 250 (1, $[M+H]^+$), 213 (1), 189 (19), 169 (3), 158 (100), 122 (18), 105 (48), 98 (87), 85 (70), 77 (28), 70 (11). HR-MALDI-TOF-MS: 250.1409 ($C_{14}H_{20}NO_3^+$, $[M+H]^+$; calc. 250.1443).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-{[(5-Methyl-2-thienyl)methyl]amino}cyclohex-5-ene-1,2,3-triol*[2]) (=*(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-{[(5-Methyl-2-thienyl)methyl]amino}cyclohex-4-ene-1,2,3-triol*; (±)-**19z**). According to the *G.P.* with (±)-**5** and 5-methyltiophene-2-carboxaldehyde (TLC monitoring, MeOH/AcOEt 3:7): (±)-**19z** (30%). Colorless solid. UV (MeOH): 248 (1656), 196 (249). IR (KBr): 3378, 1611, 1560, 1542, 1420, 1125, 1036, 1011, 960, 802, 781, 686. ^{1}H-NMR (400 MHz, CD_3OD): 6.99 (*d*, $^3J=3.4$, arom. H); 6.72 (*d*, $^3J=3.5$,

arom. H); 5.82 (*ddd*, $^3J(5,6)=10.0$, $^3J(5,4)=^3J(5,1)=3.0$, H–C(5)); 5.73 (*ddd*, $^3J(6,5)=10.0$, $^3J(6,4)=^3J(6,1)=3.0$, H–C(6)); 4.35 (*d*, $^3J=14.2$, 1 H, ArCH_2N); 4.31 (*d*, $^3J=14.2$, 1 H, ArCH_2N); 4.14–4.09 (*m*, H–C(1)); 3.70–3.60 (*m*, H–C(4), H–C(3)); 3.44 (*dd*, $^3J(2,3)=9.6$, $^3J(2,1)=8.0$, H–C(2)); 2.49 (*s*, Me). ^{13}C-NMR (100.6 MHz, CD_3OD): 142.9 (*s*, arom. C); 135.0 (*s*, arom. C); 134.9 (*d*, ^1J(C,H) = 163, C(5)); 130.1 (*d*, ^1J(C,H) = 165, arom. C); 126.5 (*d*, ^1J(C,H) = 165, arom. C); 123.6 (*d*, ^1J(C,H) = 163, C(6)); 77.6 (*d*, ^1J(C,H) = 141, C(2)); 73.1, 73.0 (2*d*, ^1J(C,H) ≈ 142, C(3), C(1)); 60.9 (*d*, ^1J(C,H) = 143, C(4)); 44.8 (*t*, ^1J(C,H) = 142, Ar*C*H$_2$N); 15.2 (*q*, ^1J(C,H) = 129, *Me*). CI-MS (NH_3): 256 (12, $[M+H]^+$), 195 (13), 140 (18), 127 (11), 117 (5), 111 (100), 85 (5), 84 (20). HR-MALDI-TOF-MS: 256.1012 ($C_{12}H_{18}NO_3S^+$, $[M+H]^+$; calc. 256.1007).

7. N,N-*Disubstituted Derivatives* **20** *of (±)-conduramine B-1*. $NaBH(OAc)_3$ (5 equiv.) was added portionwise within *ca.* 6 h to a stirred mixture of (±)-**5** (0.4 mmol) and aldehyde (propanal, octanal, 2-phenylethanal, 3 equiv.) in abs. MeOH (3 ml) at 20°. After stirring at 20° for *ca.* 6 h, the solvent was evaporated and the residue purified by FC (silica gel, light petroleum ether/AcOEt 1:1 → AcOEt → MeCN → 25% aq. NH_3 soln./MeCN 0.5:9.5).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-(Dipropylamino)cyclohex-5-ene-1,2,3-triol*[2] (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(Dipropyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**20aa**). As described above, with (±)-**5** and propanal in excess (TLC monitoring, MeOH/AcOEt 1:4): (±)-**20aa** (60%). Colorless oil. UV (MeOH): 216 (1748). IR (KBr): 3372, 1570, 1453, 1411, 1208, 1100, 1025, 966, 736, 699. ^{1}H-NMR (400 MHz, CD_3OD): 5.86 (*ddd*, $^3J(5,6)=10.4$, $^3J(5,4)=^3J(5,1)=2.2$, H–C(5)); 5.73 (*ddd*, $^3J(6,5)=10.4$, $^3J(6,4)=^3J(6,1)=2.2$, H–C(6)); 4.15–4.10 (*m*, H–C(1)); 3.85–3.79 (*m*, H–C(4)); (*dd*, $^3J(3,4)=9.8$, $^3J(3,2)=9.8$, H–C(3)); 3.48 (*dd*, $^3J(2,3)=9.8$, $^3J(2,1)=8.1$, H–C(2)); 2.99–2.80 (*m*, 2 CH_2(1′)); 1.68 (*sext.*, $^3J(2',3')=^3J(2',1')=7.4$, 2 CH_2(2′)); 0.98 (*t*, $^3J(3',2')=7.4$, 2 Me). ^{13}C-NMR (100.6 MHz, CD_3OD): 135.7 (*d*, ^1J(C,H) = 162, C(5)); 123.2 (*d*, ^1J(C,H) = 162, C(6)); 77.9 (*d*, ^1J(C,H) = 140, C(2)); 72.9 (*d*, ^1J(C,H) = 146, C(1)); 71.3 (*d*, ^1J(C,H) = 140, C(3)); 66.2 (*d*, ^1J(C,H) = 136, C(4)); 55.0 (*t*, ^1J(C,H) = 137, 2 C(1′)); 21.2 (*t*, ^1J(C,H) = 127, 2 C(2′)); 14.7 (*q*, ^1J(C,H) = 126, 2 *Me*). CI-MS (NH_3): 230 (12, $[M+H]^+$), 200 (9), 170 (36), 169 (100), 140 (46), 126 (11), 110 (13), 100 (6), 98 (29), 83 (15), 72 (47), 70 (11). HR-MALDI-TOF-MS: 230.2180 ($C_{12}H_{24}NO_3^+$, $[M+H]^+$; calc. 230.1756). Anal. calc. for $C_{12}H_{23}NO_3$ (229.168): C 62.85, H 10.11, N. 6.11; found: C 62.50, H 10.47, N 6.00.

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-(Dioctylamino)cyclohex-5-ene-1,2,3-triol*[2] (= *(±)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(Dioctyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**20bb**). As described above, with (±)-**5** and an excess of octanal (TLC monitoring, MeOH/AcOEt 0.5:95): (±)-**20bb** (68%). Colorless oil. UV (MeOH): 260 (872), 206 (3508). IR (KBr): 3381, 2927, 1467, 1378, 1104, 965, 779. ^{1}H-NMR (400 MHz, CD_3OD): 5.66 (br. *s*, H–C(6), H–C(5)); 4.06 (*dd*, $^3J(1,2)=7.9$, $^3J(1,6)=3.2$, H–C(1)); 3.54 (*dd*, $^3J(3,2)=9.9$, $^3J(3,4)=8.7$, H–C(3)); 3.43 (*dd*, $^3J(2,3)=9.9$, $^3J(2,1)=7.9$, H–C(2)); 3.38 (*dd*, $^3J(4,3)=8.7$, $^3J(4,5)=3.2$, H–C(4)); 2.65–2.48 (*m*, 4 H–C(1′)); 1.51–1.29 (2 br. *m*, 24 H, CH_2(2′) CH_4(3′), CH_2(4′), CH_2(5′), CH_2(6′), CH_2(7′)); 0.92 (*t*, $^3J(8',7')=7.0$, 2 *Me*). ^{13}C-NMR (100.6 MHz, CD_3OD): 132.5, 127.8 (2*d*, ^1J(C,H) = 160, C(6), C(5)); 78.4 (*d*, ^1J(C,H) = 139, C(2)); 73.4 (*d*, ^1J(C,H) = 140, C(1)); 72.6 (*d*, ^1J(C,H) = 143, C(3)); 65.5 (*d*, ^1J(C,H) = 136, C(4)); 52.8 (*t*, ^1J(C,H) = 131, 2 C(1′)); 33.0, 30.7, 30.5, 29.9, 28.5, 23.7 (6*t*, 12 C, C(2′), C(3′), C(4′), C(5′), C(6′), C(7′)); 14.4 (*q*, ^1J(C,H) = 125, 2 Me). CI-MS (NH_3): 369 (12, M^+), 353 (5), 311 (22), 310 (100), 271 (6), 143 (2), 112 (2). HR-MALDI-TOF-MS: 370.3859 ($C_{22}H_{44}NO_3^+$, $[M+H]^+$; calc. 370.3321).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[Bis(2-phenylethyl)amino]cyclohex-5-ene-1,2,3-triol*[2] ((±)-*(1*RS*,2*RS*,3*SR*, *6*SR*)-6-[Bis(2-phenylethyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**20cc**). As described above, with (±)-**5** and an excess of 2-phenylethanal (TLC monitoring, MeOH/AcOEt 5:95): (±)-**20cc** (49%). UV (MeOH): 285 (1017), 260 (1216), 217 (3637). IR (KBr): 3419, 2927, 1559, 1496, 1452, 1261, 1098, 1029, 965. ^{1}H-NMR (400 MHz, CD_3OD): 7.30–7.13 (*m*, 10 arom. H); 5.65, 5.61 (2*ddd*, $^3J(6,5)=^3J(5,6)=10.6$, $^3J(6,4)=^3J(5,4)=^3J(6,1)=^3J(5,1)=2.2$, H–C(6), H–C(5)); 4.04–4.01 (*m*, H–C(1)); 3.50–3.35 (*m*, H–C(4), H–C(3), H–C(2)); 2.96–2.71 (*m*, 2 CH_2(1′), 2 CH_2(2′)). ^{13}C-NMR (100.6 MHz, CD_3OD): 141.9 (*s*, 2 arom. C); 132.4, 128.0 (2*d*, ^1J(C,H) = 161, C(6), C(5)); 129.9 (*d*, ^1J(C,H) = 157, 4 arom. C); 129.4 (*d*, ^1J(C,H) = 159, 4 arom. C); 127.0 (*d*, ^1J(C,H) = 160, 2 arom. C); 78.2 (*d*, ^1J(C,H) = 143, C(2)); 73.5, 72.8 (2*d*, ^1J(C,H) ≈ 137, C(3), C(1)); 65.4 (*d*, ^1J(C,H) = 132, C(4)); 54.7 (*t*, ^1J(C,H) = 133, 2 C(1′)); 36.6 (*t*, ^1J(C,H) = 128, 2 C(2′)). CI-MS (NH_3): 293 (1), 262 (34), 202 (2), 149 (2), 134 (36), 110 (5), 105 (100), 91 (22), 83 (13), 79 (9), 77 (16), 71 (2). HR-MALDI-TOF-MS: 354.2095 ($C_{22}H_{28}NO_3^+$, $[M+H]^+$; calc. 354.2069).

*(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[Bis(1*H*-imidazol-5-ylmethyl)amino]cyclohex-5-ene-1,2,3-triol*[2] (= *(±)-(1*RS*, 2*RS*,3*SR*,6*SR*)-6-[Bis(1*H*-imidazol-5-ylmethyl)amino]cyclohex-4-ene-1,2,3-triol*; (±)-**20dd**). As described above, with (±)-**5** and an excess of 1H-imidazole-4-carboxaldehyde (TLC monitoring, 25% aq. NH_3 soln./MeCN 1:4): (±)-**20dd** (33%). Colorless solid. UV (MeOH): 217 (6477), 213 (5990). IR (KBr): 3385, 1654, 1560, 1438, 1278, 1092, 1051, 1016, 950, 781, 624. ^{1}H-NMR (400 MHz, CD_3OD): 7.79 (*s*, 2 arom. H); 7.01 (*s*, 2 arom. H); 5.82 (br. *s*, H–C(6), H–C(5)); 4.06 (*dd*, $^3J(1,2)=8.0$, $^3J(1,6)=3.0$, H–C(1)); 3.80 (*d*, $^3J=14.3$, 1 H,

ArCH_2N); 3.71–3.61 (*m*, H–C(4), H–C(3)); 3.68 (*d*, ^3J = 14.3, 1 H, ArCH_2N); 3.38 (*dd*, ^3J(2,3) = 10.0, ^3J(2,1) = 8.0, H–C(2)). ^{13}C-NMR (100.6 MHz, CD_3OD): 137.2 (*d*, ^1J(C,H) = 209, 2 arom. C); 136.5 (*s*, 2 arom. C); 133.8, 127.8 (2*d*, ^1J(C,H) = 160, C(6), C(5)); 121.2 (*d*, ^1J(C,H) = 190, 2 arom. C); 79.1 (*d*, ^1J(C,H) = 142, C(2)); 74.4, 73.3 (2*d*, ^1J(C,H) ≈ 106, C(3), C(1)); 65.8 (*d*, ^1J(C,H) = 135, C(4)); 48.2 (*t*, ^1J(C,H) = 136, 2 Ar*C*H_2N). HR-MALDI-TOF-MS: 306.1825 ($C_{14}H_{20}N_5O_3^+$, $[M+H]^+$; calc. 306.1566).

8. *(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-Aminocyclohexane-1,2,3-triol (= (±)-Dihydroconduramine B-1*; (±)-**21**). A soln. of (±)-**5** (0.046 g, 0.32 mmol) in MeOH/AcOEt (10 ml) was stirred under H_2 for 5 h in the presence of 10% Pd/C (0.02 g). The soln. was passed trough *Celite* and evaporated: (±)-**21** (0.045 g, 98%) . White solid. M.p. 171–173° (dec.). IR (KBr): 3352, 2952, 1618, 1514, 1330, 1075, 1041, 552. ^{1}H-NMR (400 MHz, CD_3OD): 3.47–3.41 (*m*, H–C(1)); 3.59 (*dd*, ^3J(3,2) = 10.0, ^3J(3,4) = 9.0, H–C(3)); 3.19 (*dd*, ^3J(2,3) = 9.0, ^3J(2,1) = 9.0, H–C(2)); 3.06–2.97 (*m*, H–C(4)); 2.07–1.96 (*m*, H_a–C(5), H_a–C(6)); 1.57–1.38 (*m*, H_b–C(5), H_b–C(6)). ^{13}C-NMR (100.6 MHz, CD_3OD): 79.4 (*d*, ^1J(C,H) = 141, C(2)); 75.0 (*d*, ^1J(C,H) = 143, C(3)); 73.1 (*d*, ^1J(C,H) = 135, C(1)); 55.0 (*d*, ^1J(C,H) = 150, C(4)); 30.4, 25.9 (2*t*, ^1J(C,H) ≈ 131, C(6), C(5)). CI-MS (NH_3): 147 (9, M^+), 135 (16), 132 (29), 130 (12), 112 (61), 109 (100), 100 (20), 98 (98), 94 (43), 91 (10), 88 (43), 86 (73), 82 (30), 79 (22), 73 (36), 70 (26). HR-MALDI-TOF-MS: 148.0971 ($C_6H_{14}NO_3^+$, $[M+H]^+$; calc. 148.0974).

9. *Aldehydes* **23** *and Precursors* **22s** *and* ***24***. *4-(4-Methoxyphenoxy)benzaldehyde* (**23n**) According to [25]: **23n** (68%). Colorless crystals. M.p. 60° (from hexane) ([25]: 59.5–60.5° (from hexane)). ^{1}H-NMR (400 MHz, $CDCl_3$): 9.92 (*s*, C*H*O); 7.84 (*d*, ^3J = 8.7, 2 arom. H); 7.07–6.93 (*m*, 6 arom. H); 3.85 (*s*, *Me*O). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 189.7 (*d*, ^1J(C,H) = 173, *C*HO); 164.0 (*s*, arom. C); 156.8 (*s*, arom. C); 148.0 (*s*, arom. C); 131.9 (*d*, ^1J(C,H) = 161, 2 arom. C); 130.8 (*s*, arom. C); 121.7 (*d*, ^1J(C,H) = 162, arom. C); 116.6 (*d*, ^1J(C,H) = 162, arom. C); 115.0 (*d*, ^1J(C,H) = 163, 2 arom. C); 55.5 (*q*, ^1J(C,H) = 144, *Me*O).

4-(4-Bromophenoxy)benzaldehyde (**23o**). According to [25]: **23o** (44%). Colorless crystals. M.p. 68° (from hexane) ([25]: 67–68° (from hexane)). ^{1}H-NMR (400 MHz, $CDCl_3$): 9.95 (*s*, C*H*O); 7.88 (*d*, ^3J = 8.6, 2 arom. H); 7.54 (*d*, ^3J = 8.7, 2 arom. H); 7.08 (*d*, ^3J = 8.6, 2 arom. H); 6.99 (*d*, ^3J = 8.7, 2 arom. H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 189.6 (*d*, ^1J(C,H) = 174, CHO); 162.5 (*s*, arom. C); 154.3 (*s*, arom. C); 133.1 (*d*, ^1J(C,H) = 167, 2 arom. C); 131.9 (*d*, ^1J(C,H) = 162, 2 arom. C); 131.5 (*s*, arom. C); 122.0 (*d*, ^1J(C,H) = 163, arom. C); 117.7 (*d*, ^1J(C,H) = 163, arom. C).

*4-[4-(1*H*-Imidazol-1-yl)phenoxy]benzaldehyde* (**23p**). According to [25]: **23p** (50%). Purification by FC (10 → 15% MeOH/AcOEt). White solid. UV (MeOH): 295 (3342), 271 (3164), 252 (3301). IR (KBr): 1689, 1593, 1579, 1519, 1498, 1236, 1156, 1057, 835. ^{1}H-NMR (400 MHz, CD_3OD): 9.92 (*s*, C*H*O); 8.15 (*s*, 1 arom. H); 7.94 (*d*, ^3J = 8.7, 2 arom. H); 7.65 (*d*, ^3J = 8.8, 2 arom. H); 7.59 (*s*, 1 arom. H); 7.27 (*d*, ^3J = 8.8, 2 arom. H); 7.17–7.14 (*m*, 3 arom. H). ^{13}C-NMR (100.6 MHz, CD_3OD): 192.6 (*d*, ^1J(C,H) = 175, CHO); 164.1 (*s*, arom. C); 156.0 (*s*, arom. C); 137.0 (*d*, ^1J(C,H) = 211, arom. C); 135.2 (*s*, arom. C); 133.3 (*s*, arom. C); 131.1 (*d*, ^1J(C,H) = 162, 2 arom. C); 130.3 (*d*, ^1J(C,H) = 191, arom. C); 124.3 (*d*, ^1J(C,H) = 163, 2 arom. C); 122.6 (*d*, ^1J(C,H) = 164, 2 arom. C); 119.9 (*d*, ^1J(C,H) = 193, arom. C); 119.0 (*d*, ^1J(C,H) = 164, 2 arom. C). CI-MS (NH_3): 265 (27, $[M+H]^+$), 264 (100, M^+), 263 (20, $[M-H]^+$), 237 (18), 224 (12), 116 (12), 104 (12), 89 (71), 77 (29). HR-MALDI-TOF-MS: 265.0186 ($C_{16}H_{13}N_2O_2^+$, $[M+H]^+$; calc. 265.0977).

4-(4-Phenoxyphenoxy)benzaldehyde (**23u**). According to [25]: **23a** (60%). Colorless crystals. M.p. 45–47° (hexane) ([25]: 46–48° (hexane)). ^{1}H-NMR (400 MHz, $CDCl_3$): 9.94 (*s*, CHO); 7.87 (*d*, ^3J = 8.4, 2 arom. H); 7.38 (*t*, ^3J = 8.0, 2 arom. H); 7.16–7.05 (*m*, 9 arom. H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 190.7 (*d*, ^1J(C,H) = 173, CHO); 163.5 (*s*, arom. C); 157.1 (*s*, arom. C); 154.1 (*s*, arom. C); 150.2 (*s*, arom. C); 131.9 (*d*, ^1J(C,H) = 162, 2 arom. C); 131.1 (*s*, arom. C); 129.8 (*d*, ^1J(C,H) = 159, 2 arom. C); 123.4 (*d*, ^1J(C,H) = 159, arom. C); 121.8 (*d*, ^1J(C,H) = 153, arom. C); 120.2 (*d*, ^1J(C,H) = 153, arom. C); 118.7 (*d*, ^1J(C,H) = 158, arom. C); 117.0 (*d*, ^1J(C,H) = 163, 2 arom. C).

4-[(2-Methylquinolin-8-yl)oxy]benzaldehyde (**23t**). According to [25] followed by FC (20 → 30% AcOEt/hexane): **23t** (51%). White crystals. M.p. 93–95° (from AcOEt/hexane). UV ($CHCl_3$): 307 (3802), 287 (3743), 272 (3472), 267 (3484), 261 (3404), 256 (3559). IR (KBr): 1688, 1601, 1499, 1427, 1320, 1232, 1158, 820. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.93 (*s*, CHO); 8.11 (*d*, ^3J = 8.4, 1 arom. H); 7.85 (*d*, ^3J = 8.6, 2 arom. H); 7.67 (*d*, ^3J = 8.1, arom. H); 7.47 (*t*, ^3J = 7.2, 1 arom. H); 7.36–7.25 (*m*, 2 arom. H); 7.12 (*d*, ^3J = 8.5, 2 arom. H); 2.69 (br. *s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 190.9 (*d*, ^1J(C,H) = 173, CHO); 164.0 (*s*, arom. C); 159.6 (*s*, arom. C); 150.9 (*s*, arom. C); 140.8 (*s*, arom. C); 136.2 (*d*, ^1J(C,H) = 162, arom. C); 131.8 (*d*, ^1J(C,H) = 161, 2 arom. C); 131.2 (*s*, arom. C); 128.3 (*s*, arom. C); 125.6 (*d*, ^1J(C,H) = 164, arom. C); 124.5 (*d*, ^1J(C,H) = 160, arom. C); 123.0 (*d*, ^1J(C,H) = 162, arom. C); 119.4 (*d*, ^1J(C,H) = 162, arom. C); 118.1 (*d*, ^1J(C,H) = 164, 2 arom. C); 25.7 (*q*, ^1J(C,H) = 127, *Me*). CI-MS (NH_3): 264 (44, $[M+H]^+$), 263 (87, M^+), 262 (100, $[M-H]^+$), 234 (13), 204 (5), 103 (6), 88 (15), 84 (84), 77 (11). HR-MALDI-TOF-MS: 264.3860 ($C_{17}H_{14}NO_2^+$, $[M+H]^+$; calc. 264.1025). Anal. calc. for $C_{16}H_{14}O_3$ (254.094): C 77.55, H 4.98; found: C 77.43, H 5.05.

4-(4-Acetylphenoxy)benzaldehyde (**23q**). A soln. of **24** (0.4 g, 1.57 mmol) in 1M HCl (5 ml) was stirred at 50° for 30 min. Subsequently, the solvent was evaporated and the residue subjected to FC (10 → 15% AcOEt/hexane): 0.33 g (87%) of **23q**. Colorless crystals. M.p. 57–59° (slow evaporation of hexane). UV ($CHCl_3$): 294 (2491), 287 (2457), 263 (2220), 256 (2392). IR (KBr): 1694, 1681, 1591, 1504, 1416, 1359, 1303, 1245, 1163, 1107, 836. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.97 (*s*, CHO); 8.00 (*d*, ^3J = 8.7, 2 arom. H); 7.91 (*d*, ^3J = 8.6, 2 arom. H); 7.16–7.10 (*m*, 4 arom. H); 2.63 (*s*, COMe). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 196.1 (*s*, *C*OMe); 190.5 (*s*, ^1J(C,H) = 173, *C*HO); 161.4 (*s*, arom. C); 159.6 (*s*, arom. C); 133.3 (*s*, arom. C); 132.2 (*s*, arom. C); 132.0 (*d*, ^1J(C,H) = 162, 2 arom. C); 130.7 (*d*, ^1J(C,H) = 162, 2 arom. C); 119.1 (*d*, ^1J(C,H) = 163, 2 arom. C); 118.9 (*d*, ^1J(C,H) = 164, 2 arom. C); 26.5 (*q*, ^1J(C,H) = 128, CO*Me*). CI-MS (NH_3): 241 (17, $[M+H]^+$), 240 (36, $M]^+$), 226 (21), 225 (100), 141 (17), 139 (11), 115 (27), 92 (16), 77 (21), 75 (10). HR-MALDI-TOF-MS: 241.0869 ($C_{15}H_{13}O_3^+$, $[M+H]^+$; calc. 241.0865). Anal. calc. for $C_{15}H_{12}O_3$ (240.078): C 74.99, H 5.03; found: C 74.97, H 5.10.

4-Hydroxyacetophenone Dimethyl Acetal [= 4-(1,1-Dimethoxyethyl)phenol; **22s**). A mixture of 4-hydroxyacetophenone (8.0 g, 0.059 mol), trimethyl orthoformate (7.12 ml, 0.065 mol), anh. MeOH (20 ml), and conc. H_2SO_4 soln. (2 drops) was allowed to stand at 20° for 24 h. After the addition of an excess of anh. Na_2CO_3, the precipitate was filtered off, the solvent evaporated [27], and the residue subjected to FC (15% AcOEt/hexane): **22s** (9.0 g, 84%). Viscous yellow-red liquid that crystallized at +4° into a greenish solid. UV (MeOH): 273 (2793), 259 (2588), 231 (2601). IR (KBr): 3283, 1615, 1515, 1443, 1375, 1224, 1094, 1026, 838. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.35 (*m*, 2 arom. H); 6.83–6.77 (*m*, 2 arom. H); 3.19 (*s*, 2 MeO); 1.54 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 155.3 (*s*, arom. C); 134.8 (*s*, arom. C); 127.7 (*d*, ^1J(C,H) = 159, 2 arom. C); 114.9 (*d*, ^1J(C,H) = 158, 2 arom. C); 101.7 (*s*, Me*C*(OMe)$_2$); 45.3 (*q*, ^1J(C,H) = 142, 2 MeO); 26.0 (*q*, ^1J(C,H) = 127, Me). CI-MS (NH_3): 167 (2), 151 (15), 149 (100), 133 (13), 121 (24), 120 (39), 107 (22), 94 (6), 91 (26), 77 (9).

4-[4-(1-Methoxyethenyl)phenoxy]benzaldehyde (**24**). The mixture of **22s** (1.5 g, 8.22 mmol) and Cs_2CO_3 (1.47 g, 4.25 mmol) was stirred and heated at 120° for 1h. After this time, 4-fluorobenzaldehyde (0.88 ml, 8.22 mmol) was added dropwise. After 2 h, the mixture was allowed to cool to r.t. and diluted with H_2O and $CHCl_3$. The org. layer was separated, dried (Na_2SO_4), and evaporated, and the resulting crude mixture purified by FC (6% AcOEt/hexanes): **24** (0.38 g, 18%). M.p. 65–67° (from AcOEt/light petroleum ether). UV ($CHCl_3$): 297 (5001), 292 (4973), 290 (4945), 261 (4335), 257 (4808). IR (KBr): 1686, 1593, 1498, 1308, 1243, 1044, 878, 810. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.94 (*s*, CHO); 7.86 (*d*, ^3J = 8.7, 2 arom. H); 7.68 (*d*, ^3J = 8.7, 2 arom. H); 7.07 (*t*, ^3J = 8.1, 4 arom. H); 4.66 (*d*, ^3J = 2.9, 1 H, CH_2=C); 4.26 (*d*, ^3J = 2.9, 1 H, CH_2=C); 3.78 (*s*, MeO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 190.8 (*s*, ^1J(C,H) = 173, CHO); 163.0 (*s*, CH_2=*C*); 160.0 (*s*, arom. C); 155.2 (*s*, arom. C); 133.5 (*s*, arom. C); 132.0 (*d*, ^1J(C,H) = 162, 2 arom. C); 131.3 (*s*, arom. C); 127.2 (*d*, ^1J(C,H) = 162, 2 arom. C); 120.0 (*d*, ^1J(C,H) = 162, 2 arom. C); 117.7 (*d*, ^1J(C,H) = 160, 2 arom. C); 81.8 (*t*, ^1J(C,H) = 160, *C*H_2=C); 55.4 (*q*, ^1J(C,H) = 144, MeO). CI-MS (NH_3): 255 (14, $[M+H]^+$), 254 (64, M^+), 253 (100, $[M-H]^+$), 225 (20), 223 (32), 149 (27), 133 (24), 126 (8), 115 (11), 102 (10), 91 (11), 83 (5), 77 (23). HR-MALDI-TOF-MS: 255.1074 ($C_{16}H_{15}O_3^+$, $[M+H]^+$; calc. 255.1021). Anal. calc. for $C_{16}H_{14}O_3$: (254.094): C 75.57, H 5.55; found: C 75.47, H 5.61.

10. *Secondary Amines* **26**–**30**. N-*{4-[4-(1*H*-Imidazol-1-yl)phenoxy]benzyl}butan-1-amine* (**26**). NaBH(OAc)$_3$ (0.112 g, 0.53 mmol, 1.4 equiv.) was added portionwise within *ca.* 2 h to a stirred soln. of **23p** (0.1 g, 0.378 mmol) and butan-1-amine (0.038 ml, 0.378 mmol) in anh. MeOH (4 ml) at 20°. After complete disappearance of **23p** (TLC monitoring), the solvent was evaporated and the residue subjected to FC (MeOH/AcOEt/25% aq. NH_3 soln. 15 : 83 : 2): **26** (0.085 g, 70%). Yellowish oil. UV (MeOH): 266 (5730), 255 (6516). IR (KBr): 3397, 1601, 1517, 1303, 1240, 1171, 1058, 963, 834. ^{1}H-NMR (400 MHz, CD_3OD): 8.09 (*s*, arom. H); 7.56–7.54 (*m*, 3 arom. H); 7.44 (*d*, ^3J = 8.5, 2 arom. H); 7.16 (*s*, arom. H); 7.13 (*d*, ^3J = 8.9, 2 arom. H); 7.06 (*d*, ^3J = 8.5, 2 arom. H); 3.90 (br. *s*, ArCH_2N); 2.75 (*t*, ^3J(1,2) = 7.6, CH_2(1)); 1.60 (*quint.*, ^3J(2,3) = ^3J(2,1) = 7.7, CH_2(2)); 1.40 (*sext.*, ^3J(3,4) = ^3J(3,2) = 7.6, CH_2(3)); 0.97 (*t*, ^3J(4,3) = 7.3, Me). ^{13}C-NMR (100.6 MHz, CD_3 OD): 158.0 (*s*, arom. C); 157.9 (*s*, arom. C); 137.0 (*d*, ^1J(C,H) = 210, arom. C); 134.0 (*s*, arom. C); 133.6 (*s*, arom. C); 131.9 (*d*, ^1J(C,H) = 162, 2 arom. C); 130.1 (*d*, ^1J(C,H) = 191, arom. C); 124.1 (*d*, ^1J(C,H) = 163, 2 arom. C); 120.9 (*d*, ^1J(C,H) = 163, 2 arom. C); 120.2 (*d*, ^1J(C,H) = 161, 2 arom. C); 120.0 (*d*, ^1J(C,H) = 192, arom. C); 53.0 (*t*, ^1J(C,H) = 138, Ar*C*H_2NH); 49.2 (*t*, ^1J(C,H) = 138, C(1)); 31.5 (*t*, ^1J(C,H) = 127, C(2′)); 21.3 (*t*, ^1J(C,H) = 125, C(3′)); 14.2 (*q*, ^1J(C,H) = 125, C(4)). CI-MS (NH_3): 321 (4, M^+), 320 (2, $[M-H]^+$), 250 (26), 249 (100), 125 (6), 107 (3), 89 (13), 77 (5). HR-MALDI-TOF-MS: 322.0816 ($C_{20}H_{24}N_3O^+$, $[M+H]^+$; calc. 322.1919).

N-*{4-[4-(1*H*-Imidazol-1-yl)phenoxy]benzyl}cyclohexanamine* (**27**). As described for **26**, with **23p** and cyclohexanamine. FC (MeOH/AcOEt/25% aq. NH_3 soln. 20 : 78 : 2): **27** (91%). Colorless oil that solidified at +4°. IR (KBr): 3420, 2929, 1515, 1504, 1231, 1060, 873. UV (MeOH): 265 (4457), 263 (4446), 254 (4996). ^{1}H-NMR (400 MHz, CD_3OD): 8.09 (*s*, arom. H); 7.57–7.54 (*m*, 3 arom. H); 7.41 (*d*, ^3J = 8.4, 2 arom. H); 7.16–7.12 (*m*, 3 arom.

H); 7.05 (*d*, ^3J = 8.5, 2 arom. H); 3.85 (br. *s*, ArCH_2N); 2.63–2.55 (*m*, 1 H, chx); 2.03–1.78 (*m*, 4 H, chx); 1.68 (br. *m*, NH); 1.39–1.15 (*m*, 6 H, chx). ^{13}C-NMR (100.6 MHz, CD_3OD): 158.2 (*s*, arom. C); 157.5 (*s*, arom. C); 137.0 (*d*, ^1J(C,H) = 210, arom. C); 135.5 (*s*, arom. C); 133.9 (*s*, arom. C); 131.5 (*d*, ^1J(C,H) = 159, 2 arom. C); 130.1 (*d*, ^1J(C,H) = 191, arom. C); 124.2 (*d*, ^1J(C,H) = 163, 2 arom. C); 120.7 (*d*, ^1J(C,H) = 163, 2 arom. C); 120.2 (*d*, ^1J(C,H) = 161, 2 arom. C); 120.0 (*d*, ^1J(C,H) = 192, arom. C); 57.3 (*d*, ^1J(C,H) = 138, 1 C, chx); 50.3 (*t*, ^1J(C,H) = 136, Ar*C*H_2NH); 33.2 (*t*, ^1J(C,H) = 126, 2 C, chx); 27.0 (*t*, ^1J(C,H) = 128, 1 C, chx); 26.1 (*t*, ^1J(C,H) = 127, 2 C, chx). CI-MS (NH_3): 348 (7, $[M+H]^+$), 347 (18, M^+), 346 (2, $[M-H]^+$), 249 (100), 125 (7), 116 (4), 107 (4), 91 (3), 89 (15), 77 (6). HR-MALDI-TOF-MS: 348.2009 ($C_{22}H_{26}N_3O^+$, $[M+H]^+$; calc. 348.2076).

N-*{4-[(2-Methylquinolin-8-yl)oxy]benzyl}cyclohexanamine* (**28**). As described for **26**, with **23t** and cyclohexanamine. FC (MeOH/AcOEt 3:7): **28** (57%). Colorless solid. UV ($CHCl_3$): 318 (2856), 273 (4455), 269 (4118), 250 (4814). IR (KBr): 3404, 2936, 1603, 1509, 1466, 1430, 1325, 1252, 1174, 1076, 835. ^{1}H-NMR (400 MHz, CD_3OD): 8.30 (*d*, ^3J = 8.5, 1 arom. H); 7.73 (*d*, ^3J = 8.2, 1 arom. H); 7.55–7.48 (*m*, 4 arom. H); 7.23 (*d*, ^3J = 7.7, 1 arom. H); 7.12 (*d*, ^3J = 8.6, 2 arom. H); 4.23 (br. *s*, ArCH_2N); 3.18–3.14 (*m*, 1 H, chx); 2.70 (br. *s*, *Me*); 2.23–1.91 (2*m*, 4 H, chx); 1.75 (br. *m*, NH); 1.48–1.25 (*m*, 6 H, chx). ^{13}C-NMR (100.6 MHz, CD_3OD): 160.9 (*s*, arom. C); 160.4 (*s*, arom. C); 152.9 (*s*, arom. C); 141.5 (*s*, arom. C); 138.3 (*d*, ^1J(C,H) = 163, arom. C); 132.8 (*d*, ^1J(C,H) = 160, 2 arom. C); 129.8 (*s*, arom. C); 129.0 (*s*, arom. C); 127.0 (*d*, ^1J(C,H) = 161, arom. C); 124.8 (*d*, ^1J(C,H) = 162, arom. C); 124.4 (*d*, ^1J(C,H) = 164, arom. C); 120.2 (*d*, ^1J(C,H) = 163, 2 arom. C); 119.1 (*d*, ^1J(C,H) = 163, arom. C); 58.4 (*d*, ^1J(C,H) = 140, 1 C, chx); 48.8 (*t*, ^1J(C,H) = 144, Ar*C*H_2NH); 30.4 (*t*, ^1J(C,H) = 128, 2 C, chx); 26.1 (*t*, ^1J(C,H) = 127, 1 C, chx); 25.6 (*t*, ^1J(C,H) = 129, 2 C, chx); 24.7 (*q*, ^1J(C,H) = 128, Me). CI-MS (NH_3): 347 (2, $[M+H]^+$), 346 (6, $[M]^+$), 345 (1, $[M-H]^+$), 262 (4), 248 (100), 130 (2), 115 (11), 89 (7), 77 (5). HR-MALDI-TOF-MS: 369.1909 ($C_{23}H_{26}N_2NaO^+$, $[M+Na]^+$; calc. 369.1943).

N-*[4-(4-Phenoxyphenoxy)benzyl]butan-1-amine* (**29**). As described for **26**, with **23u** and butan-1-amine: **29** (79%). Colorless solid. M.p. 189–192° (from $CHCl_3$/light petroleum ether). UV (MeOH): 246 (8773), 199 (1183). IR (KBr): 3447, 2957, 2799, 1587, 1499, 1244, 1069, 832. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55 (*d*, ^3J = 8.3, 2 arom. H); 7.36 (*t*, ^3J = 7.6, 2 arom. H); 7.11 (*t*, ^3J = 7.3, 1 arom. H); 7.05–6.93 (*m*, 8 arom. H); 3.99 (br. *s*, ArCH_2N); 2.79 (*t*, ^3J(1,2) = 7.6, CH_2(1)); 1.86 (*quint*, ^3J(2,3) = ^3J(2,1) = 7.5, CH_2(2)); 1.38 (*sext.*, ^3J(3,4) = ^3J(3,2) = 7.5, CH_2(3)); 0.91 (*t*, ^3J(4,3) = 7.3, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 159.2 (*s*, arom. C); 157.5 (*s*, arom. C); 153.4 (*s*, arom. C); 151.3 (*s*, arom. C); 132.1 (*d*, ^1J(C,H) = 160, 2 arom. C); 129.8 (*d*, ^1J(C,H) = 159, 2 arom. C); 124.1 (*s*, arom. C); 123.2 (*d*, ^1J(C,H) = 159, arom. C); 121.3 (*d*, ^1J(C,H) = 162, 2 arom. C); 120.5 (*d*, ^1J(C,H) = 163, 2 arom. C); 118.4 (*d*, ^1J(C,H) = 161, 2 arom. C); 117.9 (*d*, ^1J(C,H) = 162, 2 arom. C); 49.9 (*t*, ^1J(C,H) = 141, Ar*C*H_2N); 45.7 (*t*, ^1J(C,H) = 141, C(1)); 27.9 (*t*, ^1J(C,H) = 125, C(2)); 20.1 (*t*, ^1J(C,H) = 125, C(3)); 13.5 (*q*, ^1J(C,H) = 124, *Me*). CI-MS (NH_3): 248 (4, $[M+H]^+$), 247 (10, M^+), 246 (4, $[M-H]^+$), 275 (100), 181 (6), 138 (7), 115 (10), 90 (19), 77 (30). HR-MALDI-TOF-MS: 348.1908 ($C_{23}H_{26}NO_2^+$, $[M+H]^+$; calc. 348.1964).

N-*Ethyl*-N′-*[4-(4-phenoxyphenoxy)benzyl]ethane-1,2-diamine* (**30**). As described for **26**, with **23u** and *N*-ethylethane-1,2-diamine. FC (25% aq. NH_3 soln./MeCN 1:9): **30** (32%). Yellowish oil. UV (MeOH): 270 (3253), 248 (6283), 199 (876). IR (KBr): 3420, 2929, 1515, 1509, 1231, 1060, 813. ^{1}H-NMR (400 MHz, CD_3OD): 7.40–7.33 (*m*, 4 arom. H); 7.11 (*t*, ^3J = 7.4, arom. H); 7.02–6.94 (*m*, 8 arom. H); 3.91 (br. *s*, ArCH_2NH); 2.99 (*t*, ^3J(1,2) = 6.1, CH_2(1)); 2.93 (*q*, ^3J = 7.3, MeCH_2N; 2.85 (*t*, ^3J(2,1) = 6.1, CH_2(2)); 1.26 (*t*, ^3J = 7.3, *Me*CH_2N). ^{13}C-NMR (100.6 MHz, CD_3OD): 159.2 (*s*, arom. C); 158.6 (*s*, arom. C); 154.3 (*s*, arom. C); 154.2 (*s*, arom. C); 135.1 (*s*, arom. C); 131.1 (*d*, ^1J(C,H) = 158, 2 arom. C); 130.9 (*d*, ^1J(C,H) = 159, 2 arom. C); 124.2 (*d*, ^1J(C,H) = 160, arom. C); 121.5 (*d*, ^1J(C,H) = 162, 4 arom. C); 119.3 (*d*, ^1J(C,H) = 161, 4 arom. C); 53.4 (*t*, ^1J(C,H) = 135, Ar*C*H_2N); 47.9 (*t*, ^1J(C,H) = 140, C(1′)); 46.2 (*t*, ^1J(C,H) = 136, C(2′)); 44.0 (*t*, ^1J(C,H) = 137, Me*C*H_2N); 12.4 (*q*, ^1J(C,H) = 127, *Me*CH_2N). CI-MS (NH_3): 362 (1, $[M]^+$), 305 (16), 303 (13), 276 (27), 275 (100), 115 (10), 90 (10), 77 (17). HR-MALDI-TOF-MS: 362.4928 ($C_{23}H_{26}N_2O_2^+$, $[M+H]^+$; calc. 362.1994).

REFERENCES

[1] S. Hakomori, *Cancer Res.* **1985**, *45*, 2405.

[2] J. W. Dennis, M. Granovsky, C. E. Warren, *Biochim. Biophys. Acta* **1999**, *1473*, 21.

[3] K. Olden, P. Breton, K. Grzegorzewski, Y. Yasuda, B. L. Gause, O. A. Oredipe, S. A. Newton, S. L. White, *Pharmacol. Ther.* **1991**, *50,* 285; J. M. van den Elsen, D. A. Kuntz, D. R. Rose, *EMBO J* **2001**, *20,* 3008; N. Asano, *Glycobiology* **2003**, *13,* 93R.

[4] S. M. Colegate, P. R. Dorling, C. R. Huxtable, *Austr. J. Chem.* **1979**, *32,* 2257.

[5] P. E. Goss, C. L. Reid, D. Bailey, J. W. Dennis, *Clin. Cancer Res.* **1997**, *3,* 1077.

[6] T. Kino, N. Inamura, K. Nakahara, S. Kiyoto, T. Goto, H. Terano, M. Kohsaka, H. Aoki, H. Imanaka, *J. Antibiot.* **1985**, *38,* 936.
[7] J. G. Donnelly, *Therap. Drug Monitoring* **2004**, *26*, 231.
[8] W. H. Pearson, L. Guo, *Tetrahedron Lett.* **2001**, *42*, 8267; J. W. Dennis, S. L. White, A. M. Freer, D. Dime, *Biochem. Pharmacol.* **1993**, *46*, 1459.
[9] W. H. Pearson, E. J. Hembre, *Tetrahedron Lett.* **2001**, *42*, 8273.
[10] G. W. J. Fleet, P. W. Smith, S. V. Evans, L. E. Fellows, *J. Chem. Soc., Chem. Commun.* **1984**, 1240; see also C. W. Ekhart, M. H. Fechter, P. Hadwiger, E. Mlaker, A. E. Stütz, A. Tauss, T. M. Wrodnigg, in 'Iminosugars as Glycosidase Inhibitors: Nojirimycin and Beyond', Ed. A. E. Stütz, Wiley-VCH, Weinheim, 1999, p. 253; T. Granier, F. Gaiser, L. Hintermann, A. Vasella, *Helv. Chim. Acta* **1997**, *80*, 1443; N. Panday, T. Granier, A. Vasella, *Helv. Chim. Acta* **1989**, *81*, 475; N. Panday, A. Vasella, *Synthesis* **1999**, 1459; N. Panday, Y. Canac, A. Vasella, *Helv. Chim. Acta* **2000**, *83*, 58; A. Vasella, G. J. Davies, M. Boehm, *Curr. Opin. Chem. Biol.* **2002**, *6*, 619; M. Terinek, A. Vasella, *Helv. Chim. Acta* **2003**, *86*, 3482; M. Hrmova, R. De Gori, B. J. Smith, A. Vasella, J. N. Varghese, G. B. Fincher, *J. Biol. Chem.* **2004**, *279*, 4970; M. Terinek, A. Vasella, *Helv. Chim. Acta* **2004**, *87*, 3035; M. Terinek, A. Vasella, *Helv. Chim. Acta* **2005**, *88*, 10.
[11] F. Popowycz, S. Gerber-Lemaire, R. Demange, E. Rodriguez-García, A. T Carmona Asenjo, I. Robina, P. Vogel, *Bioorg. Med. Chem*. Lett. **2001**, *11*, 2489; F. Popowycz, S. Gerber-Lemaire, E. Rodriguez-García, C. Schütz, P. Vogel, *Helv. Chim. Acta* **2003**, *86*, 1914.
[12] F. Popowycz, S. Gerber-Lemaire, C. Schütz, P. Vogel, *Helv. Chim. Acta* **2004**, *87*, 800; see also C. Saotome, C.-H. Wong, O. Kanie, *Chem. Biol*. **2001**, *8*, 1061.
[13] H. Fiaux, F. Popowycz, S. Favre, C. Schütz, P. Vogel, S. Gerber-Lemaire, L. Juillerat-Jeanneret, *J. Med. Chem.* **2005**, *48*, 4237.
[14] S. Howard, S. He, S. G. Withers, *J. Biol. Chem.* **1998**, *273*, 2067.
[15] R. Łysek, C. Schütz, P. Vogel, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3071.
[16] A. Beutler, G. A. Grabowski, in 'The Metabolic and Molecular Bases of Inherited Disease', 8th edn., Eds. C. R. Scrvier, A. L. Beaudet, D. Valle, W. S. Sly, B. Childs, K. W. Kinzler, and B. Vogelstein, McGraw-Hill, New York, 2001, p. 3635.
[17] H. Lin, Y. Sugimoto, Y. Ohsaki, H. Ninomiya, A. Oka, M. Taniguchi, H. Ida, Y. Eto, S. Ogawa, Y. Matsuzaki, M. Sawa, T. Inoue, K. Higaki, E. Nanba, K. Ohno, Y. Suzuki, *Biochim. Biophys. Acta* **2004**, *1689*, 219.
[18] J.-Q. Fan, *Trends Pharmacol. Sci*. **2003**, *24*, 355; T. Kolter, M. Wendeler, *ChemBioChem* **2003**, *4*, 260 and ref. cit therein; J. Matsuda, O. Suzuki, A. Oshima, Y. Yamamoto, A. Noguchi, K. Takimoto, M. Itoh, Y. Matsuzaki, Y. Yasuda, S. Ogawa, Y. Sakata, E. Nanba, K. Higaki, Y. Ogawa, L. Tominaga, K. Ohno, H. Iwasaki, H. Watanabe, R. O. Brady, Y. Suzuki, *PANS* **2003**, *100*, 15912.
[19] S. Ogawa, Y. Sakata, N. Ito, M. Watanabe, K. Kabayama, M. Itoh, T. Korenaga, *Bioorg. Med. Chem.* **2004**, *12*, 995.
[20] A. Forster, T. Kovac, H. Mosimann, P. Renaud, P. Vogel, *Tetrahedron: Asymmetry* **1999**, *10*, 567.
[21] P. Vogel, D. Fattori, F. Gasparini, C. Le Drian, *Synlett* **1990**, 173; P. Vogel. J. Cossy, J. Plumet, O. Arjona, *Tetrahedron* **1999**, *55*, 13521; P. Vogel, *Curr. Org. Chem*. **2000**, *4*, 455; P. Vogel, in 'Glycoscience, Chemistry and Biology', Eds. B. Fraser-Reid, K. Tatsuta, and J. Thiem, Springer-Verlag, Berlin, 2001, Vol. II, Chapt. 4.4, p. 1023.
[22] C. Le Drian, J.-P. Vionnet, P. Vogel, *Helv. Chim. Acta* **1990**, *73*, 161.
[23] O. Mitsunobu, *Synthesis* **1981**, 1; see also P. Renaut, J. Millet, C. Sepulchre, J. Theveniaux, V. Barberousse, V. Jeanneret, P. Vogel. *Helv. Chim. Acta* **1998**, *81*, 2043.
[24] G. Kresze, G. Schulz, J. Firl, *Angew. Chem*. **1963**, *75*, 375; T. Hudlicky, H. F. Olivo, *Tetrahedron Lett*. **1991**, *32*, 6077; T. Hudlicky, H. Luna, H. F. Olivo, C. Andersen, T. Nugent, J. D. Price, *J. Chem. Soc., Perkin Trans 1* **1991**, 2907; M. G. Banwell, N. Haddad, T. Hudlicky, T. C. Nugent, M. F. Mackay, S. L. Richards, *J. Chem. Soc., Perkin Trans 1* **1997**, 1779; S. H. Lee, C. S. Cheong, *Bull. Korean Chem. Soc.* **2000**, *21*, 1061.
[25] G. W. Yeager, D. N. Schissel, *Synthesis* **1991**, 63; R. C. Desai, W. Han, E. J. Metzger, J. P. Bergman, D. F. Gratale, K. L. MacNaul, J. P. Berger, T. W. Doebber, K. Leung, D. E. Moller, J. V. Heck, S. P. Sahoo, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 2795.
[26] I. Pastuszak, R. J. Molyneux, L. F. James, A. D. Elbein, *Biochemistry* **1990**, *29*, 1886; A, Brandi, S. Cicchi, F. M. Cordero, R. Frignoli, A. Goti, S. Picasso, P. Vogel, *J. Org. Chem*. **1995**, *60*, 6806.
[27] R. A. McClelland, K. M. Engell, T. S. Larsen, P. E. Sørensen, *J. Chem. Soc., Perkin Trans 2* **1994**, 2199.

Recieved June 30, 2005