

**(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**

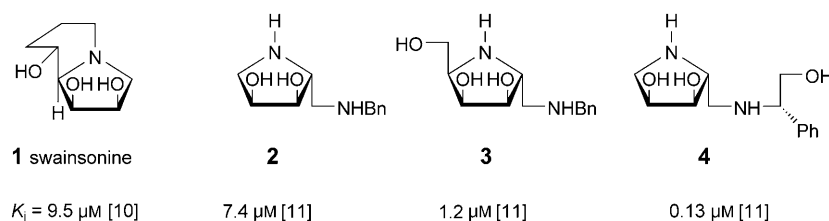
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(–)- and (+)-Conduramine B-1 ((–)- and (+)-**5**, resp.) have been derived from (+)- and (–)-7-oxabicyclo[2.2.1]hept-5-en-2-one ('naked sugars' of the first generation). Although (–)-**5** imitates the structure of β -glucosides, it does not inhibit 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 μ M, K_i = 10 μ M) and a weak inhibitor of α -mannosidases from jack bean (IC_{50} = 171 μ M) and from almonds (IC_{50} = 225 μ M) whereas (–)-*N*-(4-phenylbenzyl)conduramine B-1 ((–)-**19g**) is a good inhibitor of α -mannosidase from jack beans (IC_{50} = 29 μ M, K_i = 4.8 μ M) and a weaker inhibitor of β -glucosidase from almonds (IC_{50} = 32 μ M, K_i = 7.8 μ M) (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** $\equiv$ **19g**) was also the most selective inhibitor in assays involving α -glucosidases from rice and yeast, amyloglucosidase from *Aspergillus niger* and *Rhizopus* mold, β -glucosidases from almonds and *Caldocellum saccharolyticum* and β -xylosidase from *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.

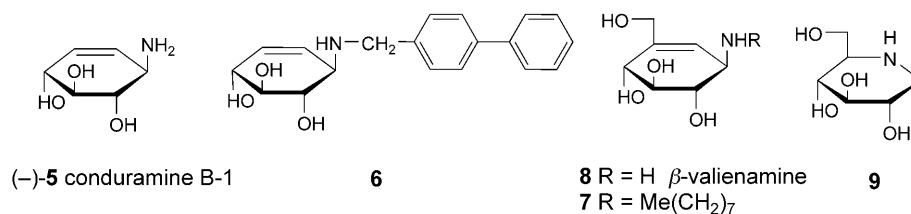


Fig. 2. (–)-Conduramine B-1 and analogs

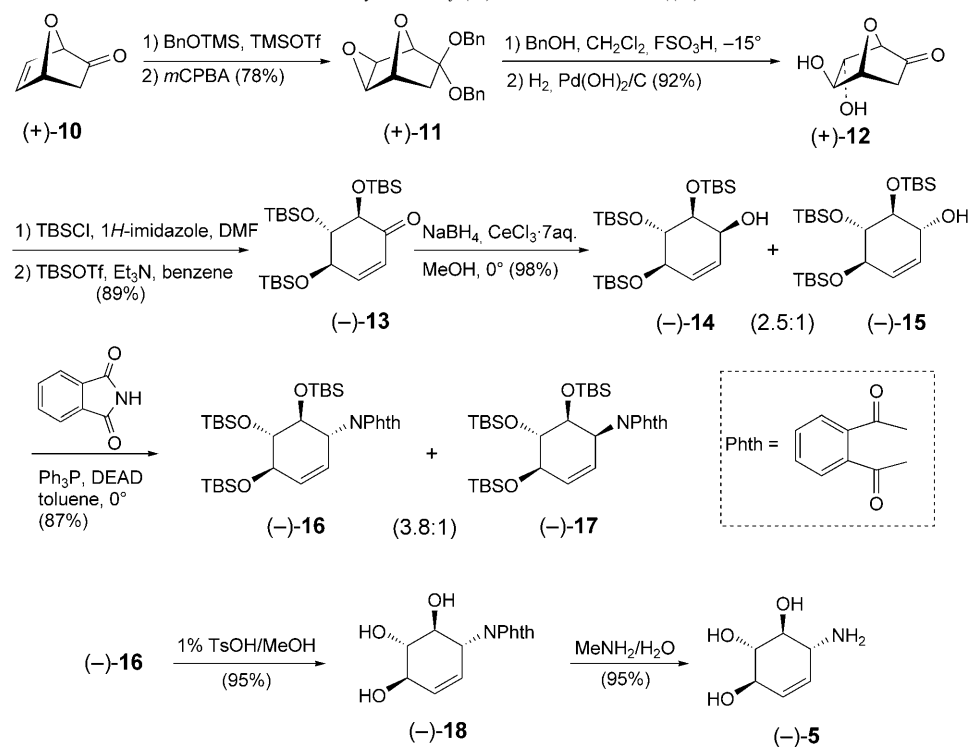
Recently, Ogawa and co-workers [19] reported that β -valienamine (**8**), as (–)-conduramine B ((–)-**5**), does not inhibit β -glucosidase from almonds but is a weak inhibitor ($IC_{50} = 190 \mu\text{M}$) of α -mannosidase from jack beans. Interestingly, 1-deoxymannonojirimycin (**9**; Fig. 2) is not a much better inhibitor ($IC_{50} = 150 \mu\text{M}$) 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 ($K_i = 4.8 \mu\text{M}$, $IC_{50} = 29 \mu\text{M}$) and from almonds ($K_i = 16 \mu\text{M}$, $IC_{50} = 32 \mu\text{M}$). 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 $\text{NaBH}_4/\text{CeCl}_3 \cdot 7 \text{H}_2\text{O}$ 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 $\text{NH}_4\text{OH}/\text{H}_2\text{O}$) 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 = $t\text{BuMe}_2\text{Si}$, DEAD = $\text{EtOOCN}=\text{NCOOEt}$, 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**.

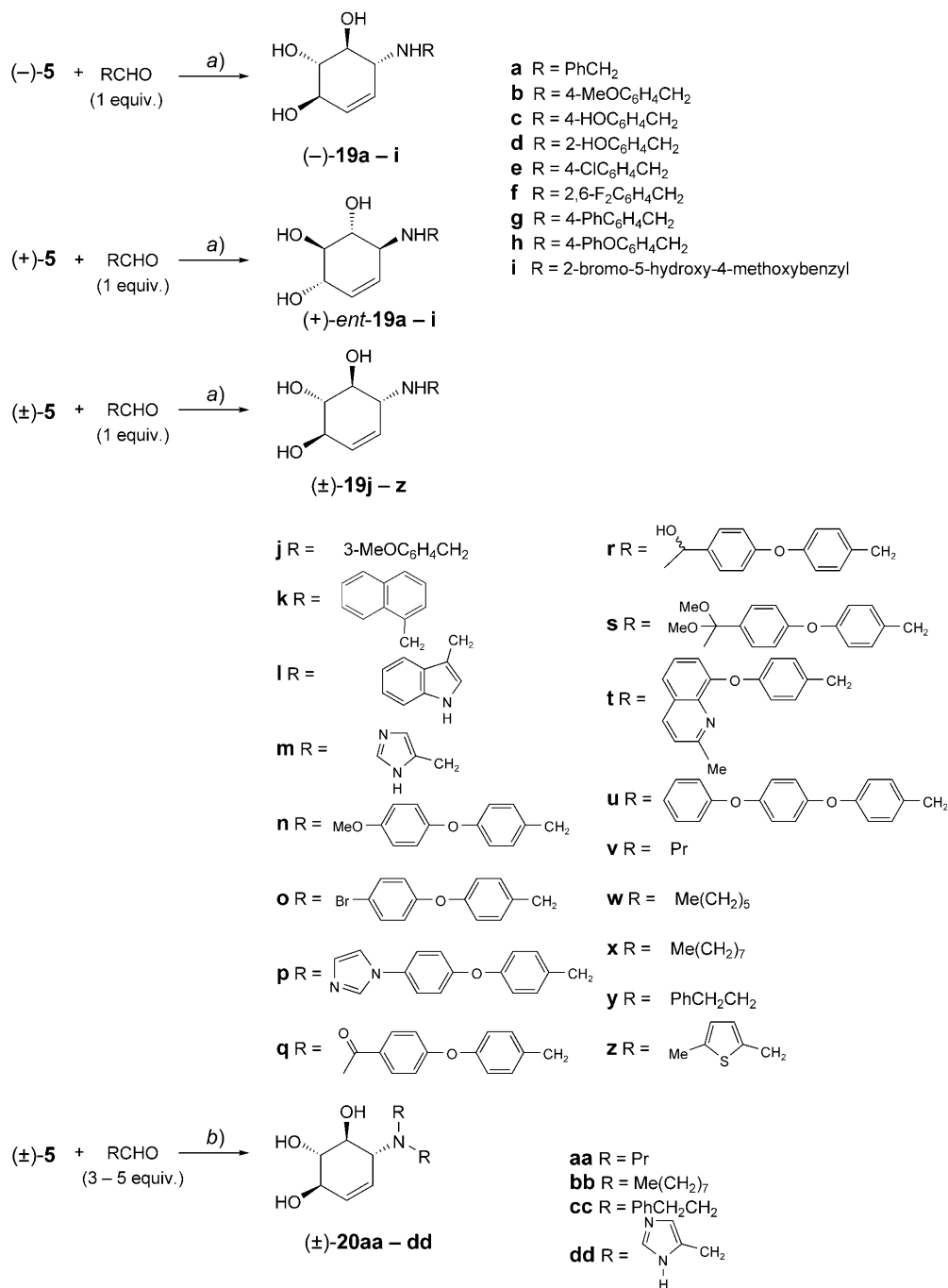
Reduction of (±)-**19q** by NaBH₄ (MeOH, 25°) gave a 1:1 mixture of diastereoisomers (±)-**19r** (see above, *Scheme 2*) in 89% yield. The synthesis of (±)-**19s** started with the reductive amination of aldehyde **24** with (±)-**5** and NaBH(OAc)₃ (25°, MeOH). Staying overnight in dry MeOH, the intermediate aryl enol ether was completely methanolized 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).

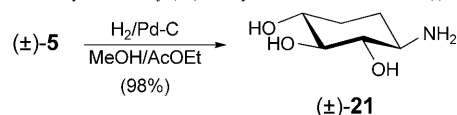
All compounds shown in the *Table* were tested for their inhibitory activity toward 21 commercially available glycosidases [26]. At 1 mM concentration they did not inhibit α-fucosidase from bovine epididymis, α-galactosidase from *Escherichia coli*, β-galactosidase from *E. coli*, from *Aspergillus niger*, and from *Aspergillus oryzae*, α-glucosidase from 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 ($\pm$)-Dihydroconduramine B-1 (($\pm$)-**21**)

B-1 (($\pm$)-**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 ($\pm$)-**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).

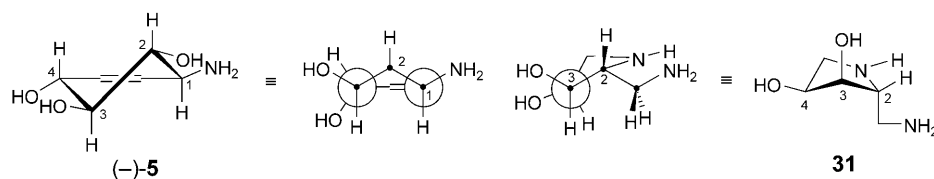


Fig. 3. Representation of the functional groups of (–)-**5** and **31** that can occupy the same sites in the active site of α -mannosidases (trivial atom numbering of (–)-**5**)

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 $7.8 \mu\text{M}$, 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 ($K_i = 4.8 \mu\text{M}$, 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 inhibitor 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.
(+)- <i>ent</i> - 19a	n.i.	n.i.	67%	72%	51%	n.i.	n.i.	n.i.	n.i.
(+)- <i>ent</i> - 19b	n.i.	33%	n.i.	n.i.	31%	n.i.	n.i.	n.i.	n.i.
(+)- <i>ent</i> - 19c	n.i.	n.i.	94%	85%	29%	n.i.	n.i.	n.i.	n.i.
(+)- <i>ent</i> - 19d	n.i.	n.i.	42%	41%	n.i.	n.i.	n.i.	n.i.	n.i.
(+)- <i>ent</i> - 19e	n.i.	27%	45%	72%	82%	n.i.	n.i.	n.i.	n.i.
(+)- <i>ent</i> - 19f	n.i.	47%	50%	72%	n.i.	n.i.	n.i.	n.i.	n.i.
(+)- <i>ent</i> - 19g	n.i.	63%	n.i.	n.i.	56%	n.i.	n.i.	n.i.	n.i.
(+)- <i>ent</i> - 19h	n.i.	60%	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.
(+)- <i>ent</i> - 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)
($\pm$)- 19r	n.i.	85%	n.i.	n.i.	n.i.	n.m.	76% 275 ^j)	n.m.	n.i.
($\pm$)- 19s	n.i.	92%	n.i.	n.i.	80% 64 ^j)	n.m.	84% 202 ^j)	n.m.	n.i.
($\pm$)- 19t	n.i.	90%	n.i.	n.i.	69%	n.m.	85%	n.m.	n.i.
($\pm$)- 19u	n.i.	82%	n.i.	n.i.	77% 98 ^j)	n.m.	75% 185 ^j)	n.m.	n.i.
($\pm$)- 19v	n.i.	36%	n.i.	30%	80% 66 ^j)	n.m.	61%	74%	n.i.
($\pm$)- 19w	n.i.	67%	n.i.	n.i.	92% 32 ^j)	n.m.	79%	77%	n.i.
($\pm$)- 19x	n.i.	74%	n.i.	n.i.	85% 69 ^j)	n.m.	88%	77%	n.i.
($\pm$)- 19y	n.i.	75%	n.i.	30%	80% 66 ^j)	n.m.	61%	74%	n.i.
($\pm$)- 19z	n.i.	37%	n.i.	23%	75%	31%	82%	83%	n.i.
($\pm$)- 20aa	25%	n.i.	n.i.	n.i.	36%	n.i.	n.i.	n.i.	n.i.
($\pm$)- 20bb	n.i.	67%	n.i.	n.i.	83%	n.i.	n.i.	n.i.	n.i.
($\pm$)- 20cc	n.i.	39%	n.i.	n.i.	36%	n.i.	n.i.	n.i.	n.i.
($\pm$)- 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.

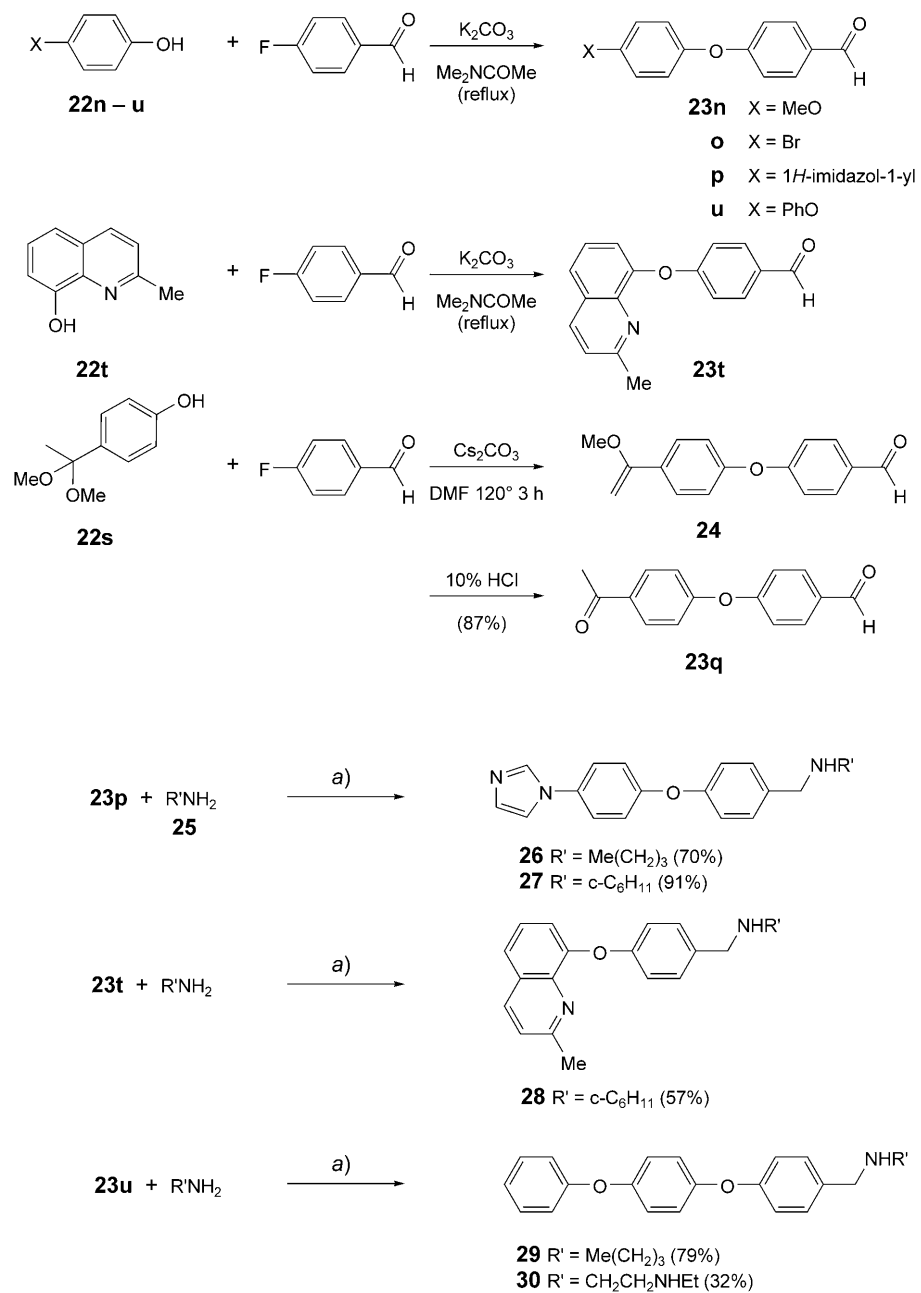
a) α -Galactosidase from coffee beans. b) β -Galactosidase from bovine liver. c) Amyloglucosidase from *Aspergillus niger*. d) Amyloglucosidase from *Rhizopus* mold. e) β -Glucosidase from almonds. f) β -Glucosidase from *Saccharomyces cerevisiae*. g) α -Mannosidase from jack beans. h) α -Mannosidase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

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 ($\pm$)-**20aa**, ($\pm$)-**20bb**, and ($\pm$)-**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.

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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 60F₂₅₄ plates; detection by UV light, *Pancaldi* reagent ((NH₄)₆MoO₄·Ce(SO₄)₂·H₂SO₄·H₂O), KMnO₄ 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; [α]_D in 10⁻¹ deg cm² g⁻¹. IR Spectra: *Perkin-Elmer 1420* spectrometer; in cm⁻¹. NMR Spectra: *Bruker ARX-400* spectrometer (¹H at 400 MHz; ¹³C at 100.6 MHz); δ in ppm rel. to the solvent's residual ¹H or to the ¹³C signal (CDCl₃: δ (H) 7.27, δ (C) 77.0; CD₃OD: δ (H) 3.31, δ (C) 49.8) as internal reference; all ¹H assignments were confirmed by 2D-COSY-45 and 2D-NOESY experiments and all ¹³C assignments by 2D-HMQC; coupling constants *J* in Hz. MS: *Nermag R-10-10C*, chemical-ionization (NH₃) 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*R*,2*S*,3*R*,4*R*)- and (±)-(1*R*,2*S*,3*R*,4*R*)-1,2,3-*Tris*[[*tert*-butyl]dimethylsilyl]oxy]-4-phthalimidocyclohex-5-ene²) (= (±)-2-[(1*R*,4*R*,5*R*,6*S*)-4,5,6-*Tris*[[*tert*-butyl]dimethylsilyl]oxy]cyclohex-2-en-1-yl]- and (±)-2-[(1*R*,4*R*,5*R*,6*R*)-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 PPh₃ (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 H₂O was added. The mixture was extracted with Et₂O (3×), the combined org. extract was washed with brine, dried (MgSO₄), 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. ¹H-NMR (400 MHz, CDCl₃): 7.85–7.80 (*m*, 2 arom. H); 7.74–7.69 (*m*, 2 arom. H); 5.93 (*ddd*, ³*J*(6,5)=10.0, ³*J*(6,4)=³*J*(6,1)=3.0, H–C(6)); 5.59 (*ddd*, ³*J*(5,6)=10.0, ³*J*(5,4)=³*J*(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*, ³*J*(3,2)=³*J*(3,4)=6.0, H–C(3)); 3.83 (*dd*, ³*J*(2,3)=³*J*(2,1)=6.0, H–C(2)); 0.93, 0.86, 0.78 (3*s*, 3 ^tBuSi); 0.13, 0.12, 0.07, 0.05 (4*s*, 6 MeSi). ¹³C-NMR (100.6 MHz, CDCl₃): 168.0 (*s*, 2 arom. C); 133.9 (*d*, ¹*J*(C,H)=164, 2 arom. C); 132.1 (*s*, 2 arom. C); 132.0 (*d*, ¹*J*(C,H)=162, C(6)); 125.2 (*d*, ¹*J*(C,H)=162, C(5)); 123.1 (*d*, ¹*J*(C,H)=170, 2 arom. C); 78.1 (*d*, ¹*J*(C,H)=146, C(2)); 73.3 (*d*, ¹*J*(C,H)=145, C(3)); 72.2 (*d*, ¹*J*(C,H)=144, C(1)); 53.8 (*d*, ¹*J*(C,H)=142, C(4)); 26.4, 26.2, 26.0 (3*q*, ¹*J*(C,H)=125, 3 Me₃C); 18.3, 18.1, 17.8 (3*s*, 3 Me₃C); –3.1, –3.2, –3.5, –3.7, –4.1, –4.7 (6*q*, ¹*J*(C,H)=119, 6 MeSi). CI-MS (NH₃): 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 (C₃₂H₅₅NNaO₅Si₃⁺, [*M*+Na]⁺; calc. 640.3286). Anal. calc. for C₃₂H₅₅NO₅Si₃ (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-ene²) (= (–)-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 ($\text{C}_{32}\text{H}_{55}\text{NNaO}_5\text{Si}_3^+$, $[M + \text{Na}]^+$; calc. 640.3286).

Enantiomer (+)-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 ($\text{C}_{32}\text{H}_{55}\text{NNaO}_5\text{Si}_3^+$, $[M + \text{Na}]^+$; 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. $^1\text{H-NMR}$ (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 (3s, 3 $^t\text{BuSi}$); 0.22, 0.16, 0.14, 0.13, –0.02, –0.4 (6s, 6 MeSi). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3): 168.3 (s , 2 arom. C); 133.8 (d , $^1J(\text{C,H}) = 164$, 2 arom. C); 132.1 (s , 2 arom. C); 127.0 (d , $^1J(\text{C,H}) = 160$, C(6)); 123.0 (d , $^1J(\text{C,H}) = 160$, C(5)); 122.9 (d , $^1J(\text{C,H}) = 165$, 2 arom. C); 74.5 (d , $^1J(\text{C,H}) = 148$, C(2)); 70.5, 69.1 (2d, $^1J(\text{C,H}) \approx 144$, C(1), C(3)); 49.8 (d , $^1J(\text{C,H}) = 139$, C(4)); 26.2, 25.8, 25.7 (3q, $^1J(\text{C,H}) = 125$, 3 Me_3C); 18.5, 17.9, 17.8 (3s, 3 Me_3C); –4.3, –4.35, –4.4, –4.5, –4.6, –5.4 (6q, $^1J(\text{C,H}) = 119$, 6 MeSi). HR-MALDI-TOF-MS: 640.3143 ($\text{C}_{32}\text{H}_{55}\text{NNaO}_5\text{Si}_3^+$, $[M + \text{Na}]^+$; calc. 640.3286). Anal. calc. for $\text{C}_{32}\text{H}_{55}\text{NO}_5\text{Si}_3$ (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-ene² (= (–)-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 ($\text{C}_{32}\text{H}_{55}\text{NNaO}_5\text{Si}_3^+$, $[M + \text{Na}]^+$; 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 ($\text{C}_{32}\text{H}_{55}\text{NNaO}_5\text{Si}_3^+$, $[M + \text{Na}]^+$; calc. 640.3286).

4. (±)-(1*R*,2*S*,3*R*,4*R*)-4-Phthalimidocyclohex-5-ene-1,2,3-triol² (= (±)-2-[(1*R*,4*R*,5*S*,6*R*)-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/Et₂O). 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. $^1\text{H-NMR}$ (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)). $^{13}\text{C-NMR}$ (100.6 MHz, CD_3OD): 169.6 (s , 2 CO); 135.4 (d , $^1J(\text{C,H}) = 164$, 2 arom. C); 133.3 (s , 2 arom. C); 132.3 (d , $^1J(\text{C,H}) = 162$, C(5)); 126.8 (d , $^1J(\text{C,H}) = 162$, C(6)); 124.1 (2d, $^1J(\text{C,H}) = 165$, 2 arom. C); 78.5 (d , $^1J(\text{C,H}) = 140$, C(2)); 73.7 (d , $^1J(\text{C,H}) = 144$, C(1)); 71.9 (d , $^1J(\text{C,H}) = 147$, C(3)); 55.6 (d , $^1J(\text{C,H}) = 140$, 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 ($\text{C}_{14}\text{H}_{13}\text{NNaO}_5^+$, $[M + \text{Na}]^+$; calc. 298.0691).

(–)-(1*R*,2*S*,3*S*,4*R*)-4-Phthalimidocyclohex-5-ene-1,2,3-triol² (= (–)-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 ($\text{C}_{14}\text{H}_{13}\text{NNaO}_5^+$, $[M + \text{Na}]^+$; 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 ($\text{C}_{14}\text{H}_{13}\text{NNaO}_5^+$, $[M + \text{Na}]^+$; calc. 298.0691).

5. (±)-(1*R*,2*S*,3*R*,4*R*)-4-Aminocyclohex-5-ene-1,2,3-triol² (= (±)-2-[(1*R*,2*R*,3*S*,6*R*)-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), 2*N* 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. $^1\text{H-NMR}$ (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)). $^{13}\text{C-NMR}$ (100.6 MHz, CD_3OD): 131.3 (d , $^1J(\text{C,H}) = 162$, C(5)); 129.7 (d , $^1J(\text{C,H}) = 162$, C(6)); 77.8, 77.7 (2d, $^1J(\text{C,H}) \approx 143$, C(3), C(2)); 73.8 (d , $^1J(\text{C,H}) = 144$, C(1)); 55.7 (d , $^1J(\text{C,H}) = 139$, C(4)). CI-MS (NH_3): 117 (2), 104 (5), 98 (4), 86 (4), 85 (100), 76 (2). HR-MALDI-TOF-MS: 146.0815 ($\text{C}_6\text{H}_{12}\text{NO}_3^+$, $[M + \text{H}]^+$; calc. 146.0817). Anal. calc. for $\text{C}_6\text{H}_{11}\text{NO}_3$ (145.074): C 49.65, H 7.64; found: C 50.01, H 7.51.

(-)-(1R,2S,3S,4R)-4-Aminocyclohex-5-ene-1,2,3-triol² (= (-)-(1S,2S,3R,6R)-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).

(±)-(1R,2SR,3SR,4RS)-4-(Acetylaminocyclohex-5-ene-1,2,3-triyl Triacetate²) (= (±)-(1RS,2RS,3SR,6SR)-6-(Acetylaminocyclohex-4-ene-1,2,3-triyl Triacetate). To (±)-**5** (0.15 g, 0.103 mmol) were added pyridine (1 ml), Ac₂O (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. Na₂CO₃ soln., and brine, dried (MgSO₄), and evaporated and the residue subjected to pure FC (hexanes/AcOEt 1:1 and hexane/AcOEt 5:95): pure (±)-tetra-N,O,O-acetylconduramine B-1 (0.023 g, 72%). Colorless crystals. M.p. 141–143° (light petroleum ether/AcOEt). UV (CHCl₃): 241 (608). IR (KBr): 3264, 2958, 1750, 1653, 1569, 1374, 1252, 1225, 1052, 961. ¹H-NMR (400 MHz, CDCl₃): 5.75 (br. d, $J = 8.4$, NHAc); 5.72–5.60 (2ddd, ³ $J(6,5) = 10.2$, ³ $J(6,4) = ^3J(6,1) = ^3J(5,4) = ^3J(5,1) = 2.0$, H–C(6), H–C(5)); 5.58–5.53 (*m*, H–C(1)); 5.39 (*dd*, ³ $J(2,3) = 10.7$, ³ $J(2,1) = 8.0$, H–C(2)); 5.09 (*dd*, ³ $J(3,2) = 10.7$, ³ $J(3,4) = 9.3$, H–C(3)); 4.93–4.85 (*m*, H–C(4)); 2.07, 2.06, 2.05, 1.97 (4s, 4 MeCO). ¹³C-NMR (100.6 MHz, CDCl₃): 171.6, 170.8, 170.4, 170.1 (4s, 4 MeCO); 131.0, 126.4 (2d, ¹ $J(C,H) = 167$, C(6), C(5)); 72.3 (*d*, ¹ $J(C,H) = 140$, C(3)); 72.1 (*d*, ¹ $J(C,H) = 146$, C(1)); 71.8 (*d*, ¹ $J(C,H) = 140$, C(2)); 51.3 (*d*, ¹ $J(C,H) = 136$, C(4)); 23.6, 21.3, 21.1, 21.0 (4q, ¹ $J(C,H) = 130$, 4 MeCO). CI-MS (NH₃): 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. NH₃ soln./MeCN 1:9 → 1:4).

(±)-(1RS,2SR,3SR,4RS)-4-(Benzylaminocyclohex-5-ene-1,2,3-triol²) (= (±)-(1RS,2RS,3SR,6SR)-6-(Benzylaminocyclohex-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. ¹H-NMR (400 MHz, CD₃OD): 7.45–7.30 (*m*, 5 arom. H); 7.76–7.72 (*m*, H–C(6), H–C(5)); 4.12 (*dd*, ³ $J(1,2) = 7.9$, ³ $J(1,6) = 3.2$, H–C(1)); 4.05 (*d*, ³ $J = 12.9$, 1 H, ArCH₂N); 3.93 (*d*, ³ $J = 12.9$, 1 H, ArCH₂N); 3.59 (*dd*, ³ $J(3,2) = 10.0$, ³ $J(3,4) = 8.7$, H–C(3)); 3.46 (*dd*, ³ $J(4,3) = 8.7$, ³ $J(4,5) = 3.2$, H–C(4)); 3.43 (*dd*, ³ $J(2,3) = 10.0$, ³ $J(2,1) = 7.9$, H–C(2)). ¹³C-NMR (100.6 MHz, CD₃OD): 138.8 (*s*, arom. C); 132.9, 126.1 (2d, ¹ $J(C,H) = 162$, C(6), C(5)); 130.0 (*d*, ¹ $J(C,H) = 158$, 2 arom. C); 129.7 (*d*, ¹ $J(C,H) = 160$, 2 arom. C); 128.8 (*d*, ¹ $J(C,H) = 160$, arom. C); 77.9 (*d*, ¹ $J(C,H) = 145$, C(2)); 73.9 (*d*, ¹ $J(C,H) = 138$, C(3)); 73.4 (*d*, ¹ $J(C,H) = 147$, C(1)); 61.4 (*d*, ¹ $J(C,H) = 136$, C(4)); 50.8 (*t*, ¹ $J(C,H) = 137$, ArCH₂N). CI-MS (NH₃): 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 C₁₃H₁₇NO₃ (235.121): C 66.36, H 7.28, N 5.95; found: C 65.87, H 7.01, N 6.04.

(-)-(1R,2S,3S,4R)-4-(Benzylaminocyclohex-5-ene-1,2,3-triol (= (-)-(1S,2S,3R,6R)-6-(Benzylaminocyclohex-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).

(±)-(1RS,2SR,3SR,4RS)-4-[(4-Methoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(1RS,2RS,3SR,6SR)-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. ¹H-NMR (400 MHz, CD₃OD): 7.36 (*d*, ³ $J = 8.6$, 2 arom. H); 6.96 (*d*, ³ $J = 8.6$, 2 arom. H); 5.81 (*ddd*, ³ $J(5,6) = 10.3$, ³ $J(5,4) = ^3J(5,1) = 2.0$, H–C(5)); 5.74 (*ddd*, ³ $J(6,5) = 10.3$, ³ $J(6,4) = ^3J(6,1) = 2.0$, H–C(6)); 4.13–4.09 (*m*, H–C(1)); 4.08 (*d*, ³ $J = 12.9$, 1 H, ArCH₂N); 3.98 (*d*, ³ $J = 12.9$, 1 H, ArCH₂N); 3.62 (*dd*, ³ $J(3,2) = 9.8$, ³ $J(3,4) = 9.0$, H–C(3)); 3.57–3.52 (*m*, H–C(4)); 3.43 (*dd*, ³ $J(2,3) = 9.8$, ³ $J(2,1) = 7.9$, H–C(2)). ¹³C-NMR (100.6

MHz, CD₃OD): 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, MeO); 49.6 (t, ¹J(C,H)=139, ArCH₂N). CI-MS (NH₃): 267 (2, [M+2H]⁺), 205 (1), 136 (4), 122 (21), 121 (100), 84 (2), 77 (2). HR-MALDI-TOF-MS: 288.1219 (C₁₄H₁₉NNaO₄⁺, [M+Na]⁺; calc. 288.1212).

(-)-(1R,2S,3S,4R)-4-[(4-Methoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol² ((-)-(1S,2S,3R,6R)-6-[(4-Methoxybenzyl)amino]cyclohex-4-ene-1,2,3-triol; (-)-**19b**). According to the *G.P.*, with (-)-**5** and 4-methoxybenzaldehyde: (-)-**19b** (83%). [α]₅₈₉²⁵ = -85, [α]₅₇₇²⁵ = -87, [α]₄₃₅²⁵ = -138, [α]₄₀₅²⁵ = -212 (*c* = 0.17, MeOH). HR-MALDI-TOF-MS: 288.1271 (C₁₄H₁₉NNaO₄⁺, [M+Na]⁺; calc. 288.1212).

Enantiomer (+)-ent-**19b**. According to the *G.P.*, from (+)-**5** and 4-methoxybenzaldehyde: (+)-**19b** (90%). [α]₅₈₉²⁵ = +97, [α]₅₇₇²⁵ = +103, [α]₄₃₅²⁵ = +201, [α]₄₀₅²⁵ = +245 (*c* = 0.35, MeOH). HR-MALDI-TOF-MS: 288.1232 (C₁₄H₁₉NNaO₄⁺, [M+Na]⁺; calc. 288.1212).

(±)-(1R,2SR,3SR,4RS)-4-[(4-Hydroxybenzyl)amino]cyclohex-5-ene-1,2,3-triol² ((±)-(1RS,2RS,3SR,6SR)-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. ¹H-NMR (400 MHz, CD₃OD): 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, ArCH₂N); 4.00 (d, ³J = 12.8, 1 H, ArCH₂N); 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)). ¹³C-NMR (100.6 MHz, CD₃OD): 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, ArCH₂N). CI-MS (NH₃): 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 (C₁₃H₁₇NNaO₃⁺, [M+Na]⁺; calc. 274.1055). Anal. calc. for C₁₃H₁₇NO₃ (251.116): C 62.14, H 6.82, N 5.57; found: C 62.40, H 6.70, N 5.43.

(-)-(1R,2S,3S,4R)-4-[(4-Hydroxybenzyl)amino]cyclohex-5-ene-1,2,3-triol² ((-)-(1S,2S,3R,6R)-6-[(4-Hydroxybenzyl)amino]cyclohex-4-ene-1,2,3-triol; (-)-**19c**). According to the *G.P.*, with (-)-**5** and 4-hydroxybenzaldehyde: (-)-**19c** (90%). [α]₅₈₉²⁵ = -88, [α]₅₇₇²⁵ = -89, [α]₄₃₅²⁵ = -200, [α]₄₀₅²⁵ = -256 (*c* = 0.282, MeOH). HR-MALDI-TOF-MS: 274.1059 (C₁₃H₁₇NNaO₃⁺, [M+Na]⁺; calc. 274.1055).

Enantiomer (+)-ent-**19c**. According to the *G.P.*, with (+)-**5** and 4-hydroxybenzaldehyde: (+)-ent-**19c** (85%). [α]₅₈₉²⁵ = +101, [α]₅₇₇²⁵ = +113, [α]₄₃₅²⁵ = +225, [α]₄₀₅²⁵ = +278 (*c* = 0.30, MeOH). HR-MALDI-TOF-MS: 274.1034 (C₁₃H₁₇NNaO₃⁺, [M+Na]⁺; calc. 274.1055).

(±)-(1RS,2SR,3SR,4RS)-4-[(2-Hydroxybenzyl)amino]cyclohex-5-ene-1,2,3-triol² ((±)-(1RS,2RS,3SR,6SR)-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. ¹H-NMR (400 MHz, CD₃OD): 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, ArCH₂N); 4.15 (d, ³J = 13.1, 1 H, ArCH₂N); 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)). ¹³C-NMR (100.6 MHz, CD₃OD): 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 (2d, ¹J(C,H) ≈ 141, C(3), C(1)); 61.5 (d, ¹J(C,H)=144, C(4)); 46.8 (t, ¹J(C,H)=141, ArCH₂N). CI-MS (NH₃): 251 (7, M⁺), 146 (7), 124 (82), 109 (2), 106 (100), 85 (7), 78 (63), 77 (38). HR-MALDI-TOF-MS: 252.1204 (C₁₃H₁₈NO₄⁺, [M+H]⁺; calc. 252.1236). Anal. calc. for C₁₃H₁₇NO₃ (251.116): C 62.14, H 6.82, N 5.57; found: C 62.33, H 6.68, N 5.40.

(-)-(1R,2S,3S,4R)-4-[(2-Hydroxybenzyl)amino]cyclohex-5-ene-1,2,3-triol² ((-)-(1S,2S,3R,6R)-6-[(2-Hydroxybenzyl)amino]cyclohex-4-ene-1,2,3-triol; (-)-**19d**). According to the *G.P.*, with (-)-**5** and 2-hydroxybenzaldehyde: (-)-**19d** (93%). [α]₅₈₉²⁵ = -101, [α]₅₇₇²⁵ = -104, [α]₄₃₅²⁵ = -162, [α]₄₀₅²⁵ = -191 (*c* = 0.167, MeOH). HR-MALDI-TOF-MS: 274.1045 (C₁₃H₁₇NNaO₃⁺, [M+Na]⁺; calc. 274.1055).

Enantiomer (+)-ent-**19d**. According to the *G.P.*, with (+)-**5** and 2-hydroxybenzaldehyde: (+)-ent-**19d** (87%). [α]₅₈₉²⁵ = +97, [α]₅₇₇²⁵ = +100, [α]₄₃₅²⁵ = +155, [α]₄₀₅²⁵ = +183 (*c* = 0.15, MeOH). HR-MALDI-TOF-MS: 274.1069 (C₁₃H₁₇NNaO₃⁺, [M+Na]⁺; calc. 274.1055).

(±)-(1RS,2SR,3SR,4RS)-4-[(4-Chlorobenzyl)amino]cyclohex-5-ene-1,2,3-triol² ((±)-(1RS,2RS,3SR,6SR)-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): ($\pm$)-**19e** (99%). Solid foam. UV (MeOH): 275 (1089), 267 (1241), 228 (4266), 197 (554). IR (KBr): 3376, 1612, 1560, 1411, 1093, 1015, 959, 805. $^1\text{H-NMR}$ (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 , $\text{H-C}(6)$, $\text{H-C}(5)$); 4.10 (dd , $^3J(1,2)=7.8$, $^3J(1,6)=3.0$, $\text{H-C}(1)$); 4.05 (d , $^3J=13.2$, 1 H, ArCH_2N); 3.94 (d , $^3J=13.2$, 1 H, ArCH_2N); 3.59 (dd , $^3J(3,2)=9.9$, $^3J(3,4)=8.8$, $\text{H-C}(3)$); 3.45 (dd , $^3J(4,3)=8.8$, $^3J(4,5)=3.0$, $\text{H-C}(4)$); 3.43 (dd , $^3J(2,3)=9.9$, $^3J(2,1)=7.8$, $\text{H-C}(2)$). $^{13}\text{C-NMR}$ (100.6 MHz, CD_3OD): 135.6 (s , arom. C); 135.3 (s , arom. C); 134.3 (d , $^1J(\text{C,H})=162$, C(5)); 132.0 (d , $^1J(\text{C,H})=161$, 2 arom. C); 129.9 (d , $^1J(\text{C,H})=166$, 2 arom. C); 124.4 (d , $^1J(\text{C,H})=162$, C(6)); 77.7 (d , $^1J(\text{C,H})=139$, C(2)); 73.2, 73.1 (2 d , $^1J(\text{C,H})\approx 141$, C(3), C(1)); 61.5 (d , $^1J(\text{C,H})=140$, C(4)); 49.6 (t , $^1J(\text{C,H})=138$, ArCH_2N). CI-MS (NH_3): 271 (23, $[M+2\text{H}]^+$), 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 ($\text{C}_{13}\text{H}_{16}\text{ClNNaO}_3^+$, $[M+\text{Na}]^+$; calc. 292.0716).

(-)-(1R,2S,3S,4R)-4-[(4-Chlorobenzyl)amino]cyclohex-5-ene-1,2,3-triol²) (= (-)-(1S,2S,3R,6R)-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 ($\text{C}_{13}\text{H}_{16}\text{ClNNaO}_3^+$, $[M+\text{Na}]^+$; 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 ($\text{C}_{13}\text{H}_{16}\text{ClNNaO}_3^+$, $[M+\text{Na}]^+$; calc. 292.0716).

($\pm$)-(1R,2SR,3SR,4RS)-4-[(2,6-Difluorobenzyl)amino]cyclohex-5-ene-1,2,3-triol²) (= ($\pm$)-(1RS,2RS,3SR,6SR)-6-[(2,6-Difluorobenzyl)amino]cyclohex-4-ene-1,2,3-triol; ($\pm$)-**19f**). According to the *G.P.*, with ($\pm$)-**5** and 2,6-difluorobenzaldehyde (TLC monitoring, MeOH/AcOEt 3 : 7): ($\pm$)-**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. $^1\text{H-NMR}$ (400 MHz, CD_3OD): 7.42–7.33 (m , arom. H); 7.05–6.98 (m , 2 arom. H); 5.75 (ddd , $^3J(5,6)=10.0$, $^3J(5,4)=^3J(5,1)=3.0$, $\text{H-C}(5)$); 5.69 (ddd , $^3J(6,5)=10.0$, $^3J(6,4)=^3J(6,1)=3.0$, $\text{H-C}(6)$); 4.13–4.07 (m , $\text{H-C}(1)$); 4.05 (d , $^3J=13.3$, 1 H, ArCH_2N); 3.97 (d , $^3J=13.1$, 1 H, ArCH_2N); 3.49 (dd , $^3J(3,2)=10.0$, $^3J(3,4)=8.5$, $\text{H-C}(3)$); 3.41 (dd , $^3J(2,3)=10.0$, $^3J(2,1)=7.6$, $\text{H-C}(2)$); 3.32–3.27 (m , $\text{H-C}(4)$). $^{13}\text{C-NMR}$ (100.6 MHz, CD_3OD): 163.1 (d , $^1J(\text{C,F})=247$, 2 arom. C); 132.5 (d , $^1J(\text{C,H})=162$, C(5)); 131.4 (d , $^1J(\text{C,H})=165$, arom. C); 126.4 (d , $^1J(\text{C,H})=162$, C(6)); 112.5 (s , arom. C); 112.4 (dd , $^1J(\text{C,F})=166$, $^2J(\text{C,F})=25$, 2 arom. C); 77.9 (d , $^1J(\text{C,H})=144$, C(2)); 73.9 (d , $^1J(\text{C,H})=137$, C(1)); 73.6 (d , $^1J(\text{C,H})=143$, C(3)); 61.3 (d , $^1J(\text{C,H})=140$, C(4)); 37.7 (t , $^1J(\text{C,H})=140$, ArCH_2N). CI-MS (NH_3): 272 (3, $[M+\text{H}]^+$), 242 (2), 211 (28), 144 (2), 142 (6), 127 (82), 107 (5), 84 (100), 82 (3). HR-MALDI-TOF-MS: 272.1012 ($\text{C}_{13}\text{H}_{16}\text{F}_2\text{NO}_3^+$, $[M+\text{H}]^+$; calc. 272.1098).

(-)-(1R,2S,3S,4R)-4-[(2,6-Difluorobenzyl)amino]cyclohex-5-ene-1,2,3-triol²) (= (-)-(1S,2S,3R,6R)-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 ($\text{C}_{13}\text{H}_{15}\text{F}_2\text{NNaO}_3^+$, $[M+\text{Na}]^+$; 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 ($\text{C}_{13}\text{H}_{15}\text{F}_2\text{NNaO}_3^+$, $[M+\text{Na}]^+$; calc. 294.0918).

($\pm$)-(1RS,2SR,3SR,4RS)-4-[(1,1'-Biphenyl)-4-ylmethyl]amino]cyclohex-5-ene-1,2,3-triol²) (= ($\pm$)-(1RS,2RS,3SR,6SR)-6-[(1,1'-Biphenyl)-4-ylmethyl]amino]cyclohex-4-ene-1,2,3-triol; ($\pm$)-**19g**). According to the *G.P.*, with ($\pm$)-**5** and 4-phenylbenzaldehyde (= [1,1'-biphenyl]-4-carboxaldehyde) (TLC monitoring, MeOH/AcOEt 3 : 7): ($\pm$)-**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. $^1\text{H-NMR}$ (400 MHz, CD_3OD): 7.68–7.61 (m , 4 arom. H); 7.54–7.32 (m , 5 arom. H); 5.85 (ddd , $^3J(5,6)=10.4$, $^3J(5,4)=^3J(5,1)=2.0$, $\text{H-C}(5)$); 5.80 (ddd , $^3J(6,5)=10.3$, $^3J(6,4)=^3J(6,1)=2.0$, $\text{H-C}(6)$); 4.15 (d , $^3J=13.0$, 1 H, ArCH_2N); 4.12 (dd , $^3J(1,2)=7.9$, $^3J(1,6)=3.1$, $\text{H-C}(1)$); 4.03 (d , $^3J=13.0$, 1 H, ArCH_2N); 3.63 (dd , $^3J(3,2)=9.7$, $^3J(3,4)=8.8$, $\text{H-C}(3)$); 3.53 (dd , $^3J(4,3)=8.8$, $^3J(4,5)=3.1$, $\text{H-C}(4)$); 3.45 (dd , $^3J(2,3)=9.8$, $^3J(2,1)=7.9$, $\text{H-C}(2)$). $^{13}\text{C-NMR}$ (100.6 MHz, CD_3OD): 142.6 (s , arom. C); 141.6 (s , arom. C); 135.1 (s , arom. C); 134.7 (d , $^1J(\text{C,H})=163$, C(5)); 131.0 (d , $^1J(\text{C,H})=159$, 2 arom. C); 129.9 (d , $^1J(\text{C,H})=161$, 2 arom. C); 128.6 (d , $^1J(\text{C,H})=160$, arom. C); 128.4 (d , $^1J(\text{C,H})=160$, 2 arom. C); 127.9 (d , $^1J(\text{C,H})=159$, 2 arom. C); 123.9 (d , $^1J(\text{C,H})=158$, C(6)); 77.7 (d , $^1J(\text{C,H})=139$, C(2)); 73.1, 73.0 (2 d , $^1J(\text{C,H})\approx 144$, C(3), C(1)); 61.4 (d , $^1J(\text{C,H})=141$, C(4)); 49.9 (t , $^1J(\text{C,H})=142$, ArCH_2N). CI-MS (NH_3): 313 (7, $[M+2\text{H}]^+$), 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 ($\text{C}_{19}\text{H}_{21}\text{NNaO}_3^+$, $[M+\text{Na}]^+$; calc. 334.1419).

(–)-(1*R*,2*S*,3*S*,4*R*)-4-[(1,1'-Biphenyl)-4-ylmethyl]amino]cyclohex-5-ene-1,2,3-triol²) (= (–)-(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*R*,2*S*,3*R*,4*R*)-4-[(4-Phenoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(1*R*,2*S*,3*R*,6*S*)-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. ¹H-NMR (400 MHz, CD₃OD): 7.46 (*d*, ³*J* = 8.5, 2 arom. H); 7.41–7.36 (*m*, 2 arom. H); 7.18 (*t*, ³*J* = 7.4, 1 arom. H); 7.02 (*m*, 4 arom. H); 5.86 (*ddd*, ³*J*(5,6) = 10.0, ³*J*(5,4) = ³*J*(5,1) = 3.0, H–C(5)); 5.78 (*ddd*, ³*J*(6,5) = 10.0, ³*J*(6,4) = ³*J*(6,1) = 3.0, H–C(6)); 4.20 (*d*, ³*J* = 13.1, 1 H, ArCH₂N); 4.15–4.10 (*m*, H–C(1)); 4.13 (*d*, ³*J* = 13.1, 1 H, ArCH₂N); 3.74–3.61 (*m*, H–C(4), H–C(3)); 3.46 (*dd*, ³*J*(2,3) = 9.2, ³*J*(2,1) = 7.7, H–C(2)). ¹³C-NMR (100.6 MHz, CD₃OD): 159.4 (*s*, arom. C); 158.1 (*s*, arom. C); 135.2 (*d*, ¹*J*(C,H) = 163, C(5)); 132.3 (*d*, ¹*J*(C,H) = 159, 2 arom. C); 131.0 (*d*, ¹*J*(C,H) = 159, 2 arom. C); 130.1 (*s*, arom. C); 124.9 (*d*, ¹*J*(C,H) = 159, arom. C); 123.4 (*d*, ¹*J*(C,H) = 163, C(6)); 120.3 (*d*, ¹*J*(C,H) = 161, 2 arom. C); 119.8 (*d*, ¹*J*(C,H) = 162, 2 arom. C); 77.7 (*d*, ¹*J*(C,H) = 143, C(2)); 73.0, 72.8 (2*d*, ¹*J*(C,H) ≈ 142, C(3), C(1)); 61.4 (*d*, ¹*J*(C,H) = 144, C(4)); 49.6 (*t*, ¹*J*(C,H) = 138, ArCH₂N). 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-triol²) (= (–)-(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*R*,2*S*,3*R*,4*R*)-4-[(2-Bromo-5-hydroxy-4-methoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(1*R*,2*S*,3*R*,6*S*)-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. ¹H-NMR (400 MHz, CD₃OD): 7.16 (*s*, arom. H); 7.00 (*s*, arom. H); 5.79 (*br. s*, H–C(6), H–C(5)); 4.13 (*dd*, ³*J*(1,2) = 7.9, ³*J*(1,6) = 3.2, H–C(1)); 4.06 (*d*, ³*J* = 13.2, 1 H, ArCH₂N); 3.99 (*d*, ³*J* = 13.2, 1 H, ArCH₂N); 3.61 (*dd*, ³*J*(3,2) = 9.8, ³*J*(3,4) = 8.8, H–C(3)); 3.52 (*dd*, ³*J*(4,3) = 8.8, ³*J*(4,6) = 3.2, H–C(4)); 3.43 (*dd*, ³*J*(2,3) = 9.8, ³*J*(2,1) = 7.9, H–C(2)). ¹³C-NMR (100.6 MHz, CD₃OD): 149.9 (*s*, arom. C); 147.6 (*s*, arom. C); 133.7 (*d*, ¹*J*(C,H) = 162, C(5)); 129.0 (*s*, arom. C); 125.1 (*d*, ¹*J*(C,H) = 162, C(6)); 118.9 (*d*, ¹*J*(C,H) = 159, arom. C); 116.9 (*d*, ¹*J*(C,H) = 164, arom. C); 113.8 (*s*, arom. C); 77.8 (*d*, ¹*J*(C,H) = 145, C(2)); 73.4, 73.3 (2*d*, ¹*J*(C,H) ≈ 142, C(3), C(1)); 61.4 (*d*, ¹*J*(C,H) = 138, C(4)); 56.7 (*q*, ¹*J*(C,H) = 145, MeO); 50.0 (*t*, ¹*J*(C,H) = 139, ArCH₂N). CI-MS (NH₃): 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-triol²) (= (–)-(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*R*,2*S*,3*R*,4*R*)-4-[(3-Methoxybenzyl)amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(1*R*,2*S*,3*R*,6*S*)-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. ¹H-NMR (400 MHz, CD₃OD): 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, ArCH₂N); 4.03 (*d*, $^3J=13.0$, 1 H, ArCH₂N); 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)). ¹³C-NMR (100.6 MHz, CD₃OD): 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 (*2d*, $^1J(C,H)\approx 142$, 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, ArCH₂N). CI-MS (NH₃): 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 (C₁₄H₁₉NNaO₄⁺, [*M*+Na]⁺; calc. 288.1212). Anal. calc. for C₁₄H₁₉NO₄ (265.131): C 63.38, H 7.22, N 5.58; found: C 63.02, H 7.00, N 5.69.

(±)-(1*R*S,2*S*R,3*S*R,4*R*S)-4-[(1-Naphthylmethyl)amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(1*R*S,2*R*S,3*S*R,6*S*R)-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. ¹H-NMR (400 MHz, CD₃OD): 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, ArCH₂N); 4.56 (*d*, $^3J=13.2$, 1 H, ArCH₂N); 4.16 (*dd*, $^3J(1,2)=8.1$, $^3J(1,6)=3.2$, H–C(1)); 3.77 (*dd*, $^3J(3,2)=9.3$, $^3J(3,4)=8.8$, 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)). ¹³C-NMR (100.6 MHz, CD₃OD): 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 (*2d*, $^1J(C,H)\approx 142$, C(3), C(1)); 62.2 (*d*, $^1J(C,H)=140$, C(4)); 47.7 (*t*, $^1J(C,H)=139$, ArCH₂O). CI-MS (NH₃): 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 (C₁₇H₂₀NO₃⁺, [*M*+H]⁺; calc. 286.1443).

(±)-(1*R*S,2*S*R,3*S*R,4*R*S)-4-[(1*H*-Indol-3-ylmethyl)amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(1*R*S,2*R*S,3*S*R,6*S*R)-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. NH₃ 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. ¹H-NMR (400 MHz, CD₃OD): 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*, ArCH₂N); 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)). ¹³C-NMR (100.6 MHz, CD₃OD): 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*, $^1J(C,H)=144$, ArCH₂N). HR-MALDI-TOF-MS: 297.1856 (C₁₅H₁₈N₂NaO₃⁺, [*M*+Na]⁺; calc. 297.1215). Anal. calc. for C₁₅H₁₈N₂O₃ (274.1317): C 65.68, H 6.61, N 10.21; found C 66.01, H 6.81, N 10.32.

(±)-(1*R*S,2*S*R,3*S*R,4*R*S)-4-[(1*H*-Imidazol-5-ylmethyl)amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(1*R*S,2*R*S,3*S*R,6*S*R)-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. NH₃ soln./MeCN 1:4): (±)-**19m** (10%). Yellowish oil. ¹H-NMR (400 MHz, CD₃OD): 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, ArCH₂N); 4.10 (*m*, H–C(1)); 4.07 (*d*, $^3J=13.9$, 1 H, ArCH₂N); 3.68–3.42 (*m*, H–C(4), H–C(3)), H–C(2)). HR-MALDI-TOF-MS: 248.1070 (C₁₀H₁₅N₃NaO₃⁺, [*M*+H]⁺; calc. 248.1011).

(±)-(1*R*S,2*S*R,3*S*R,4*R*S)-4-[[4-(4-Methoxyphenoxy)benzyl]amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(1*R*S,2*R*S,3*S*R,6*S*R)-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. ¹H-NMR (400 MHz, CD₃OD): 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*, $^3J(6,5)=10.3$, $^3J(6,4)=^3J(6,1)=2.3$, H–C(6)); 4.23 (*d*, $^3J=13.1$, 1 H, ArCH₂N); 4.18 (*d*, $^3J=13.1$, 1 H, ArCH₂N); 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)). ¹³C-NMR (100.6 MHz, CD₃OD): 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, $^1J(\text{C,H}) = 164$, C(6)); 122.1 (d, $^1J(\text{C,H}) = 162$, 2 arom. C); 118.6 (d, $^1J(\text{C,H}) = 162$, 2 arom. C); 116.0 (d, $^1J(\text{C,H}) = 161$, 2 arom. C); 77.6 (d, $^1J(\text{C,H}) = 144$, C(2)); 72.8 (d, $^1J(\text{C,H}) = 143$, C(1)); 72.5 (d, $^1J(\text{C,H}) = 142$, C(3)); 61.4 (d, $^1J(\text{C,H}) = 143$, C(4)); 56.0 (t, $^1J(\text{C,H}) = 144$, MeO); 49.5 (t, $^1J(\text{C,H}) = 142$, ArCH₂N). CI-MS (NH₃): 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 (C₂₀H₂₃NNaO₃⁺, [M + Na]⁺; calc. 380.1474).

(±)-(IRS,2SR,3SR,4RS)-4-[[4-(4-Bromophenoxy)benzyl]amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(IRS,2RS,3SR,6SR)-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. ¹H-NMR (400 MHz, CD₃OD): 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, ArCH₂N); 4.22 (d, $^3J = 13.1$, 1 H, ArCH₂N); 4.16–4.12 (m, H–C(1)); 3.78–3.71 (2m, H–C(4), H–C(3)); 3.47 (dd, $^3J(2,3) = 9.6$, $^3J(2,1) = 7.9$, H–C(2)). ¹³C-NMR (100.6 MHz, CD₃OD): 158.9 (s, arom. C); 157.6 (s, arom. C); 135.8 (d, $^1J(\text{C,H}) = 164$, C(5)); 134.0 (d, $^1J(\text{C,H}) = 167$, 2 arom. C); 132.7 (d, $^1J(\text{C,H}) = 160$, 2 arom. C); 130.0 (s, arom. C); 122.8 (d, $^1J(\text{C,H}) = 164$, C(6)); 122.0 (d, $^1J(\text{C,H}) = 164$, 2 arom. C); 120.2 (d, $^1J(\text{C,H}) = 164$, 2 arom. C); 117.2 (s, arom. C); 77.6 (d, $^1J(\text{C,H}) = 145$, C(2)); 72.9 (d, $^1J(\text{C,H}) = 142$, C(1)); 72.6 (d, $^1J(\text{C,H}) = 139$, C(3)); 61.5 (d, $^1J(\text{C,H}) = 145$, C(4)); 49.5 (t, $^1J(\text{C,H}) = 137$, ArCH₂N). CI-MS (NH₃): 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 (C₁₉H₂₀BrNNaO₄⁺, [M + Na]⁺; calc. 428.0473).

(±)-(IRS,2SR,3SR,4RS)-4-[[4-(1*H*-Imidazol-1-yl)phenoxy]benzyl]amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(IRS,2RS,3SR,6SR)-6-[[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. NH₃ soln./MeCN 1:9): (±)-**19p** (57%). Colorless solid. UV (MeOH): 253 (10000), 199 (1270). IR (KBr): 3386, 1519, 1506, 1242, 1115, 1060, 836. ¹H-NMR (400 MHz, CD₃OD): 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 (2ddd, $^3J(6,5) = ^3J(5,6) = 10.4$, $^3J(6,4) = ^3J(5,4) = ^3J(6,1) = ^3J(5,1) = 2.3$, H–C(6), H–C(5)); 4.22 (d, $^3J = 13.1$, 1 H, ArCH₂N); 4.14 (d, $^3J = 13.1$, 1 H, ArCH₂N); 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)). ¹³C-NMR (100.6 MHz, CD₃OD): 158.6 (s, arom. C); 157.7 (s, arom. C); 137.0 (d, $^1J(\text{C,H}) = 210$, arom. C); 135.1 (d, $^1J(\text{C,H}) = 163$, C(5)); 134.2 (s, arom. C); 132.5 (d, $^1J(\text{C,H}) = 160$, 2 arom. C); 131.2 (s, arom. C); 130.1 (d, $^1J(\text{C,H}) = 191$, arom. C); 124.2 (d, $^1J(\text{C,H}) = 163$, 2 arom. C); 123.6 (d, $^1J(\text{C,H}) = 163$, C(6)); 121.1 (d, $^1J(\text{C,H}) = 163$, 2 arom. C); 120.2 (d, $^1J(\text{C,H}) = 162$, 2 arom. C); 120.0 (d, $^1J(\text{C,H}) = 192$, arom. C); 77.7 (d, $^1J(\text{C,H}) = 141$, C(2)); 73.1, 73.0 (2d, $^1J(\text{C,H}) = 142$, C(3), C(1)); 61.5 (d, $^1J(\text{C,H}) = 142$, C(4)); 49.7 (t, $^1J(\text{C,H}) = 139$, ArCH₂N). HR-MALDI-TOF-MS: 416.1580 (C₂₂H₂₃N₃NaO₄⁺, [M + Na]⁺; calc. 416.1586). Anal. calc. for C₂₂H₂₃N₃O₄ (393.1689): C 67.16, H 5.89, N 10.68; found: C 67.10, H 6.00, N 10.82.

(±)-(IRS,2SR,3SR,4RS)-4-[[4-(4-Acetylphenoxy)benzyl]amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-1-[[4-[[4-((IRS,2RS,3SR,6SR)-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. ¹H-NMR (400 MHz, CD₃OD): 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, ArCH₂N); 4.17 (d, $^3J = 13.0$, 1 H, ArCH₂N); 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). ¹³C-NMR (100.6 MHz, CD₃OD): 199.2 (s, COMe); 163.1 (s, arom. C); 157.4 (s, arom. C); 135.2 (d, $^1J(\text{C,H}) = 163$, C(5)); 133.4 (s, arom. C); 132.6 (d, $^1J(\text{C,H}) = 160$, 2 arom. C); 132.1 (s, arom. C); 132.0 (d, $^1J(\text{C,H}) = 160$, 2 arom. C); 123.5 (d, $^1J(\text{C,H}) = 163$, C(6)); 121.4 (d, $^1J(\text{C,H}) = 162$, arom. C); 118.6 (d, $^1J(\text{C,H}) = 162$, 2 arom. C); 77.7 (d, $^1J(\text{C,H}) = 140$, C(2)); 73.0, 72.9 (2d, $^1J(\text{C,H}) \approx 142$, C(3), C(1)); 61.5 (d, $^1J(\text{C,H}) = 141$, C(4)); 49.7 (t, $^1J(\text{C,H}) = 138$, ArCH₂N); 26.6 (q, $^1J(\text{C,H}) = 128$, COMe). CI-MS (NH₃): 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 (C₂₁H₂₄NO₄⁺, [M + H]⁺; calc. 370.1654).

1:1 Mixture of (±)-(IRS,2SR,3SR,4RS)-4-[[4-[(IRS)- and (±)-(IRS,2SR,3SR,4RS)-4-[[4-[(IRS)-1-Hydroxyethyl]phenoxy]benzyl]amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(IRS,2RS,3SR,6SR)-6-[[4-[(IRS)- and (±)-(IRS,2RS,3SR,6SR)-6-[[4-[(IRS)-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 NaBH₄ (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. $^1\text{H-NMR}$ (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 ($2ddd$, $^3J(6,5)=^3J(5,6)=10.3$, $^3J(6,4)=^3J(5,4)=^3J(6,1)=^3J(5,1)=2.3$, H–C(6), H–C(5)); 4.83 (q , $^3J=6.4$, $\text{MeCH}(\text{OH})$); 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). $^{13}\text{C-NMR}$ (100.6 MHz, CD_3OD): 158.1 (s , arom. C); 157.7 (s , arom. C); 135.5 (s , arom. C); 131.4 (d , $^1J(\text{C,H})=161$, C(5)); 131.2 (d , $^1J(\text{C,H})=161$, 2 arom. C); 129.9 (s , arom. C); 128.0 (d , $^1J(\text{C,H})=162$, 2 arom. C); 127.8 (d , $^1J(\text{C,H})=161$, C(5)); 119.7 (d , $^1J(\text{C,H})=161$, 4 arom. C); 78.0 (d , $^1J(\text{C,H})=144$, C(2)); 74.5 (d , $^1J(\text{C,H})=141$, C(3)); 73.6 (d , $^1J(\text{C,H})=142$, C(1)); 70.3 (d , $^1J(\text{C,H})=143$, $\text{MeCH}(\text{OH})$); 61.3 (d , $^1J(\text{C,H})=144$, C(4)); 50.6 (t , $^1J(\text{C,H})=139$, ArCH_2N); 25.6 (q , $^1J(\text{C,H})=126$, 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 ($\text{C}_{21}\text{H}_{25}\text{NNaO}_4^+$, $[M+Na]^+$; calc. 394.1630).

($\pm$)-**(1RS,2SR,3SR,4RS)-4-[[4-[(1,1-Dimethoxyethyl)phenoxy]benzyl]amino]cyclohex-5-ene-1,2,3-triol²** (= ($\pm$)-**(1RS,2RS,3SR,6SR)-6-[[4-[(1,1-Dimethoxyethyl)phenoxy]benzyl]amino]cyclohex-4-ene-1,2,3-triol**; ($\pm$)-**19s**). According to the *G.P.*, with ($\pm$)-**5** and **24** in MeOH (TLC monitoring, MeOH/AcOEt 1:4): ($\pm$)-**19s** (60%). Solid. UV (MeOH): 265 (2965), 236 (6448), 202 (1487). IR (KBr): 3374, 1601, 1502, 1420, 1245, 1094, 878. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (100.6 MHz, CD_3OD): 159.6 (s , arom. C); 157.4 (s , arom. C); 136.5 (d , $^1J(\text{C,H})=163$, C(5)); 133.0 (s , arom. C); 132.9 ($2d$, $^1J(\text{C,H})=160$, 2 arom. C); 132.0 (s , arom. C); 129.1 (d , $^1J(\text{C,H})=161$, 2 arom. C); 121.8 (d , $^1J(\text{C,H})=163$, C(6)); 119.9 (d , $^1J(\text{C,H})=162$, 2 arom. C); 119.7 (d , $^1J(\text{C,H})=162$, 2 arom. C); 102.7 (s , $\text{MeC}(\text{OMe})_2$); 77.5 (d , $^1J(\text{C,H})=142$, C(2)); 72.8, 72.3 ($2d$, $^1J(\text{C,H}) \approx 143$, C(3), C(1)); 61.6 (d , $^1J(\text{C,H})=137$, C(4)); 49.4 (t , $^1J(\text{C,H})=141$, ArCH_2N); 49.2 (q , $^1J(\text{C,H})=142$, 2 MeO); 26.4 (q , $^1J(\text{C,H})=127$, 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 ($\text{C}_{25}\text{H}_{29}\text{NNaO}_6^+$, $[M+Na]^+$; calc. 438.1893).

($\pm$)-**(1RS,2SR,3SR,4RS)-4-[[4-[(2-Methylquinolin-8-yl)oxy]benzyl]amino]cyclohex-5-ene-1,2,3-triol²** (= ($\pm$)-**(1RS,2RS,3SR,6SR)-6-[[4-[(2-Methylquinolin-8-yl)oxy]benzyl]amino]cyclohex-4-ene-1,2,3-triol**; ($\pm$)-**19t**). According to the *G.P.*, with ($\pm$)-**5** and **23t** (TLC monitoring, MeOH/AcOEt 3:7): ($\pm$)-**19t** (81%). Colorless solid. UV (MeOH): 292 (4089), 279 (4333), 244 (11828). IR (KBr): 3395, 1609, 1560, 1508, 1430, 1236, 1079. $^1\text{H-NMR}$ (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 ($2ddd$, $^3J(6,5)=^3J(5,6)=10.3$, $^3J(6,4)=^3J(5,4)=^3J(6,1)=2.4$, 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). $^{13}\text{C-NMR}$ (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 , $^1J(\text{C,H})=162$, arom. C); 135.7 (d , $^1J(\text{C,H})=163$, C(5)); 132.5 (d , $^1J(\text{C,H})=160$, 2 arom. C); 129.9 (s , arom. C); 129.7 (s , arom. C); 127.1 (d , $^1J(\text{C,H})=163$, arom. C); 124.5 (d , $^1J(\text{C,H})=161$, arom. C); 124.4 (d , $^1J(\text{C,H})=161$, arom. C); 122.9 (d , $^1J(\text{C,H})=163$, C(6)); 120.3 (d , $^1J(\text{C,H})=162$, 2 arom. C); 118.6 (d , $^1J(\text{C,H})=160$, arom. C); 77.6 (d , $^1J(\text{C,H})=141$, C(2)); 73.0 (d , $^1J(\text{C,H})=143$, C(1)); 72.7 (d , $^1J(\text{C,H})=141$, C(3)); 61.6 (d , $^1J(\text{C,H})=143$, C(4)); 49.6 (t , $^1J(\text{C,H})=138$, ArCH_2N); 24.7 (q , $^1J(\text{C,H})=127$, 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 ($\text{C}_{23}\text{H}_{24}\text{N}_2\text{NaO}_4^+$, $[M+Na]^+$; calc. 415.1634).

($\pm$)-**(1RS,2SR,3SR,4RS)-4-[[4-(4-Phenoxyphenoxy)benzyl]amino]cyclohex-5-ene-1,2,3-triol²** (= ($\pm$)-**(1RS,2RS,3SR,6SR)-6-[[4-(4-Phenoxyphenoxy)benzyl]amino]cyclohex-4-ene-1,2,3-triol**; ($\pm$)-**19u**). According to the *G.P.*, with ($\pm$)-**5** and **23u** (TLC monitoring, MeOH/AcOEt 3:7): ($\pm$)-**19u** (70%). Colorless solid. UV (MeOH): 271 (3040), 260 (3460), 241 (10357). IR (KBr): 3378, 1609, 1511, 1488, 1225, 1023, 867. $^1\text{H-NMR}$ (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)). $^{13}\text{C-NMR}$ (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 , $^1J(\text{C,H})=161$, C(5)); 132.5 (d , $^1J(\text{C,H})=159$, 2 arom. C); 130.9 (d , $^1J(\text{C,H})=157$, 2 arom. C); 129.5 (s , arom. C); 124.3 (d , $^1J(\text{C,H})=159$, arom. C); 123.0 (d , $^1J(\text{C,H})=161$, C(6)); 122.0 (d , $^1J(\text{C,H})=164$, 2 arom. C); 121.5 (d , $^1J(\text{C,H})=162$, 2 arom. C); 119.4 (d , $^1J(\text{C,H})=162$, 2 arom. C); 119.3 (d , $^1J(\text{C,H})=160$, 2 arom. C); 77.6 (d , $^1J(\text{C,H})=142$, C(2)); 73.0 (d , $^1J(\text{C,H})=142$, C(1)); 72.8 (d , $^1J(\text{C,H})=142$, C(3)); 61.5 (d , $^1J(\text{C,H})=137$, C(4)); 49.6 (t , $^1J(\text{C,H})=141$, 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 ($\text{C}_{25}\text{H}_{25}\text{NNaO}_3^+$, $[M + \text{Na}]^+$; calc. 442.1630).

($\pm$)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-(Propylamino)cyclohex-5-ene-1,2,3-triol²) (= ($\pm$)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-(Propylamino)cyclohex-4-ene-1,2,3-triol; ($\pm$)-**19v**). According to the *G.P.*, with ($\pm$)-**5** and propanal (TLC monitoring, MeOH/AcOEt 1:3): ($\pm$)-**19v** (77%). Pale yellowish oil. UV (MeOH): 213 (867). IR (KBr): 3320, 2924, 1464, 1377, 1132, 1043, 996. ¹H-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*, ³*J*(3,4)=8.2, ³*J*(3,2)=10.3, H–C(3)); 3.43 (*dd*, ³*J*(2,3)=10.3, ³*J*(2,1)=7.3, H–C(2)); 3.34–3.15 (*m*, H–C(4), $\text{CH}_2(1')$); 2.09 (*sext.*, ³*J*(2',3')=³*J*(2',1')=7.4, $\text{CH}_2(2')$); 0.99 (*t*, ³*J*(3',2')=7.4, Me). ¹³C-NMR (100.6 MHz, CD_3OD): 131.3, 126.9 (*2d*, ¹*J*(C,H)=162, C(6), C(5)); 77.9 (*d*, ¹*J*(C,H)=144, C(2)); 74.1, 73.7 (*2d*, ¹*J*(C,H)≈138, C(3), C(1)); 60.7 (*d*, ¹*J*(C,H)=131, C(4)); 54.7 (*t*, ¹*J*(C,H)=138, C(1')); 22.0 (*t*, ¹*J*(C,H)=126, C(2')); 14.3 (*q*, ¹*J*(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 ($\text{C}_9\text{H}_{17}\text{KNO}_3^+$, $[M + \text{K}]^+$; calc. 226.0846).

($\pm$)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-(Hexylamino)cyclohex-5-ene-1,2,3-triol²) (= ($\pm$)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-(Hexylamino)cyclohex-4-ene-1,2,3-triol; ($\pm$)-**19w**). According to the *G.P.*, with ($\pm$)-**5** and hexanal (TLC monitoring, MeOH/AcOEt 3:7): ($\pm$)-**19w** (62%). Colorless oil. UV (MeOH): 207 (1507). IR (KBr): 3375, 2925, 1634, 1456, 1383, 1037, 960. ¹H-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*, ³*J*(3,2)=10.0, ³*J*(3,4)=8.5, H–C(3)); 3.43 (*dd*, ³*J*(2,3)=10.0, ³*J*(2,1)=7.6, H–C(2)); 3.35–3.33 (*m*, H–C(4)); 2.85–2.77, 2.68–2.61 (*2m*, $\text{CH}_2(1')$); 1.60–1.51 (*m*, $\text{CH}_2(2')$); 1.42–1.30 (*m*, $\text{CH}_2(3')$, $\text{CH}_2(4')$, $\text{CH}_2(5')$); 0.92 (*t*, ³*J*(6',5')=7.0, Me). ¹³C-NMR (100.6 MHz, CD_3OD): 132.5, 126.7 (*2d*, ¹*J*(C,H)≈161, C(6), C(5)); 77.9 (*d*, ¹*J*(C,H)=140, C(2)); 73.8, 73.5 (*2d*, ¹*J*(C,H)≈144, C(3), C(1)); 62.0 (*d*, ¹*J*(C,H)=143, C(4)); 47.0 (*t*, ¹*J*(C,H)=131, C(1')); 32.8 (*t*, ¹*J*(C,H)=131, C(2')); 30.2, 27.9, 23.6 (*3t*, ¹*J*(C,H)=124, C(3'), C(4'), C(5')); 14.4 (*q*, ¹*J*(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 ($\text{C}_{12}\text{H}_{24}\text{NO}_3^+$, $[M + \text{H}]^+$; calc. 230.1756). Anal. calc. for $\text{C}_{12}\text{H}_{23}\text{NO}_3$ (229.167): C 62.85, H 10.11, N 6.11; found: C 63.11, H 10.40, N 6.27.

($\pm$)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-(Octylamino)cyclohex-5-ene-1,2,3-triol²) (= ($\pm$)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-(Octylamino)cyclohex-4-ene-1,2,3-triol; ($\pm$)-**19x**). According to the *G.P.*, with ($\pm$)-**5** and octanal (TLC monitoring, MeOH/AcOEt 3:7): ($\pm$)-**19x** (53%). Oil. UV (MeOH): 207 (1052). IR (KBr): 3374, 2926, 2855, 1560, 1419, 1123, 1034, 781. ¹H-NMR (400 MHz, CD_3OD): 5.87 (*ddd*, ³*J*(5,6)=10.4, ³*J*(5,4)=³*J*(5,1)=2.0, H–C(5)); 5.70 (*ddd*, ³*J*(6,5)=10.4, ³*J*(6,4)=³*J*(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*, ³*J*(3,2)=³*J*(3,4)=9.5, H–C(3)); 3.45 (*dd*, ³*J*(2,3)=9.5, ³*J*(2,1)=8.1, H–C(2)); 3.10–2.95 (*m*, $\text{CH}_2(1')$); 1.73–1.63 (*m*, $\text{CH}_2(2')$); 1.46–1.27 (*m*, $\text{CH}_2(3')$, $\text{CH}_2(4')$, $\text{CH}_2(5')$, $\text{CH}_2(6')$, $\text{CH}_2(7')$); 0.92 (*t*, ³*J*(8',7')=7.0, Me). ¹³C-NMR (100.6 MHz, CD_3OD): 135.9 (*d*, ¹*J*(C,H)=161, C(5)); 122.4 (*d*, ¹*J*(C,H)=165, C(6)); 77.5 (*d*, ¹*J*(C,H)=140, C(2)); 72.9 (*d*, ¹*J*(C,H)=139, C(1)); 72.2 (*d*, ¹*J*(C,H)=145, C(3)); 61.9 (*d*, ¹*J*(C,H)=144, C(4)); 46.3 (*t*, ¹*J*(C,H)=142, C(1')); 32.9 (*t*, ¹*J*(C,H)=125, C(2')); 30.2, 30.3, 28.1, 27.8, 23.7 (*5t*, 5 C(3'), C(4'), C(5'), C(6'), C(7')); 14.4 (*q*, ¹*J*(C,H)=124, Me). CI-MS (NH_3): 258 (6, $[M + \text{H}]^+$), 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 ($\text{C}_{14}\text{H}_{27}\text{NNaO}_3^+$, $[M + \text{Na}]^+$; calc. 280.1889).

($\pm$)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(2-Phenylethyl)amino]cyclohex-5-ene-1,2,3-triol²) (= ($\pm$)-(1*SR*,2*SR*,3*RS*,6*RS*)-6-[(2-Phenylethyl)amino]cyclohex-4-ene-1,2,3-triol; ($\pm$)-**19y**). According to the *G.P.*, with ($\pm$)-**5** and 2-phenylethanal (TLC monitoring, MeOH/AcOEt 3:7): ($\pm$)-**19y** (42%). Colorless solid. UV (MeOH): 212 (3652). IR (KBr): 3384, 1569, 1413, 1125, 1030, 753, 701. ¹H-NMR (400 MHz, CD_3OD): 7.37–7.23 (*m*, 5 arom. H); 5.87 (*ddd*, ³*J*(5,6)=10.4, ³*J*(5,4)=³*J*(5,1)=2.0, H–C(5)); 5.72 (*ddd*, ³*J*(6,5)=10.4, ³*J*(6,4)=³*J*(6,1)=2.0, H–C(6)); 4.12 (*dd*, ³*J*(1,2)=8.0, ³*J*(1,6)=2.0, H–C(1)); 3.77–3.72 (*m*, H–C(4)); 3.66 (*dd*, ³*J*(3,4)=8.5, ³*J*(3,2)=9.6, H–C(3)); 3.46 (*dd*, ³*J*(2,3)=9.6, ³*J*(2,1)=8.0, H–C(2)); 3.35–3.20 (*m*, $\text{CH}_2(1')$); 3.00 (*t*, ³*J*(2',1')=7.0, $\text{CH}_2(2')$). ¹³C-NMR (100.6 MHz, CD_3OD): 138.6 (*s*, arom. C); 135.7 (*d*, ¹*J*(C,H)=164, C(5)); 129.8 (*d*, ¹*J*(C,H)=160, 2 arom. C); 129.7 (*d*, ¹*J*(C,H)=161, 2 arom. C); 128.0 (*d*, ¹*J*(C,H)=154, arom. C); 122.7 (*d*, ¹*J*(C,H)=164, C(6)); 77.6 (*d*, ¹*J*(C,H)=140, C(2)); 72.9 (*d*, ¹*J*(C,H)=140, C(1)); 72.4 (*d*, ¹*J*(C,H)=139, C(3)); 61.9 (*d*, ¹*J*(C,H)=140, C(4)); 47.7 (*t*, ¹*J*(C,H)=142, C(1')); 34.3 (*t*, ¹*J*(C,H)=128, C(2')). CI-MS (NH_3): 250 (1, $[M + \text{H}]^+$), 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 ($\text{C}_{14}\text{H}_{20}\text{NO}_3^+$, $[M + \text{H}]^+$; calc. 250.1443).

($\pm$)-(1*RS*,2*SR*,3*SR*,4*RS*)-4-[(5-Methyl-2-thienyl)methyl]amino]cyclohex-5-ene-1,2,3-triol²) (= ($\pm$)-(1*RS*,2*RS*,3*SR*,6*SR*)-6-[(5-Methyl-2-thienyl)methyl]amino]cyclohex-4-ene-1,2,3-triol; ($\pm$)-**19z**). According to the *G.P.* with ($\pm$)-**5** and 5-methylthiophene-2-carboxaldehyde (TLC monitoring, MeOH/AcOEt 3:7): ($\pm$)-**19z** (30%). Colorless solid. UV (MeOH): 248 (1656), 196 (249). IR (KBr): 3378, 1611, 1560, 1542, 1420, 1125, 1036, 1011, 960, 802, 781, 686. ¹H-NMR (400 MHz, CD_3OD): 6.99 (*d*, ³*J*=3.4, arom. H); 6.72 (*d*, ³*J*=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, ArCH₂N); 4.31 (d, $^3J=14.2$, 1 H, ArCH₂N); 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). ¹³C-NMR (100.6 MHz, CD₃OD): 142.9 (s, arom. C); 135.0 (s, arom. C); 134.9 (d, $^1J(\text{C,H})=163$, C(5)); 130.1 (d, $^1J(\text{C,H})=165$, arom. C); 126.5 (d, $^1J(\text{C,H})=165$, arom. C); 123.6 (d, $^1J(\text{C,H})=163$, C(6)); 77.6 (d, $^1J(\text{C,H})=141$, C(2)); 73.1, 73.0 (2d, $^1J(\text{C,H})\approx 142$, C(3), C(1)); 60.9 (d, $^1J(\text{C,H})=143$, C(4)); 44.8 (t, $^1J(\text{C,H})=142$, ArCH₂N); 15.2 (q, $^1J(\text{C,H})=129$, Me). CI-MS (NH₃): 256 (12, [M+H]⁺), 195 (13), 140 (18), 127 (11), 117 (5), 111 (100), 85 (5), 84 (20). HR-MALDI-TOF-MS: 256.1012 (C₁₂H₁₈NO₃S⁺, [M+H]⁺; calc. 256.1007).

7. N,N-Disubstituted Derivatives **20** of (±)-conduramine B-I. NaBH(OAc)₃ (5 equiv.) was added portion-wise 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. NH₃ soln./MeCN 0.5:9.5).

(±)-(1RS,2SR,3SR,4RS)-4-(Dipropylamino)cyclohex-5-ene-1,2,3-triol²) (= (±)-(1RS,2RS,3SR,6SR)-6-[(Dipropylamino)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. ¹H-NMR (400 MHz, CD₃OD): 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 CH₂(1')); 1.68 (sext., $^3J(2',3')=^3J(2',1')=7.4$, 2 CH₂(2')); 0.98 (t, $^3J(3',2')=7.4$, 2 Me). ¹³C-NMR (100.6 MHz, CD₃OD): 135.7 (d, $^1J(\text{C,H})=162$, C(5)); 123.2 (d, $^1J(\text{C,H})=162$, C(6)); 77.9 (d, $^1J(\text{C,H})=140$, C(2)); 72.9 (d, $^1J(\text{C,H})=146$, C(1)); 71.3 (d, $^1J(\text{C,H})=140$, C(3)); 66.2 (d, $^1J(\text{C,H})=136$, C(4)); 55.0 (t, $^1J(\text{C,H})=137$, 2 C(1')); 21.2 (t, $^1J(\text{C,H})=127$, 2 C(2')); 14.7 (q, $^1J(\text{C,H})=126$, 2 Me). CI-MS (NH₃): 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 (C₁₂H₂₃NO₃⁺, [M+H]⁺; calc. 230.1756). Anal. calc. for C₁₂H₂₃NO₃ (229.168): C 62.85, H 10.11, N 6.11; found: C 62.50, H 10.47, N 6.00.

(±)-(1RS,2SR,3SR,4RS)-4-(Diocetylaminocyclohex-5-ene-1,2,3-triol²) (= (±)-(1RS,2RS,3SR,6SR)-6-[(Diocetylaminocyclohex-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. ¹H-NMR (400 MHz, CD₃OD): 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, CH₂(2') CH₄(3'), CH₂(4'), CH₂(5'), CH₂(6'), CH₂(7')); 0.92 (t, $^3J(8',7')=7.0$, 2 Me). ¹³C-NMR (100.6 MHz, CD₃OD): 132.5, 127.8 (2d, $^1J(\text{C,H})=160$, C(6), C(5)); 78.4 (d, $^1J(\text{C,H})=139$, C(2)); 73.4 (d, $^1J(\text{C,H})=140$, C(1)); 72.6 (d, $^1J(\text{C,H})=143$, C(3)); 65.5 (d, $^1J(\text{C,H})=136$, C(4)); 52.8 (t, $^1J(\text{C,H})=131$, 2 C(1')); 33.0, 30.7, 30.5, 29.9, 28.5, 23.7 (6t, 12 C, C(2'), C(3'), C(4'), C(5'), C(6'), C(7')); 14.4 (q, $^1J(\text{C,H})=125$, 2 Me). CI-MS (NH₃): 369 (12, M⁺), 353 (5), 311 (22), 310 (100), 271 (6), 143 (2), 112 (2). HR-MALDI-TOF-MS: 370.3859 (C₂₂H₄₄NO₃⁺, [M+H]⁺; calc. 370.3321).

(±)-(1RS,2SR,3SR,4RS)-4-[Bis(2-phenylethyl)amino]cyclohex-5-ene-1,2,3-triol²) ((±)-(1RS,2RS,3SR,6SR)-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. ¹H-NMR (400 MHz, CD₃OD): 7.30–7.13 (m, 10 arom. H); 5.65, 5.61 (2ddd, $^3J(6,5)=^3J(5,6)=10.6$, $^3J(6,4)=^3J(5,4)=^3J(6,1)=^3J(5,1)=2.2$, 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 CH₂(1'), 2 CH₂(2')). ¹³C-NMR (100.6 MHz, CD₃OD): 141.9 (s, 2 arom. C); 132.4, 128.0 (2d, $^1J(\text{C,H})=161$, C(6), C(5)); 129.9 (d, $^1J(\text{C,H})=157$, 4 arom. C); 129.4 (d, $^1J(\text{C,H})=159$, 4 arom. C); 127.0 (d, $^1J(\text{C,H})=160$, 2 arom. C); 78.2 (d, $^1J(\text{C,H})=143$, C(2)); 73.5, 72.8 (2d, $^1J(\text{C,H})\approx 137$, C(3), C(1)); 65.4 (d, $^1J(\text{C,H})=132$, C(4)); 54.7 (t, $^1J(\text{C,H})=133$, 2 C(1')); 36.6 (t, $^1J(\text{C,H})=128$, 2 C(2')). CI-MS (NH₃): 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 (C₂₂H₂₈NO₃⁺, [M+H]⁺; calc. 354.2069).

(±)-(1RS,2SR,3SR,4RS)-4-[Bis(1H-imidazol-5-ylmethyl)amino]cyclohex-5-ene-1,2,3-triol²) (= (±)-(1RS,2RS,3SR,6SR)-6-[Bis(1H-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. NH₃ 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. ¹H-NMR (400 MHz, CD₃OD): 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,

ArCH₂N); 3.71–3.61 (*m*, H–C(4), H–C(3)); 3.68 (*d*, ³*J* = 14.3, 1 H, ArCH₂N); 3.38 (*dd*, ³*J*(2,3) = 10.0, ³*J*(2,1) = 8.0, H–C(2)). ¹³C-NMR (100.6 MHz, CD₃OD): 137.2 (*d*, ¹*J*(C,H) = 209, 2 arom. C); 136.5 (*s*, 2 arom. C); 133.8, 127.8 (2*d*, ¹*J*(C,H) = 160, C(6), C(5)); 121.2 (*d*, ¹*J*(C,H) = 190, 2 arom. C); 79.1 (*d*, ¹*J*(C,H) = 142, C(2)); 74.4, 73.3 (2*d*, ¹*J*(C,H) ≈ 106, C(3), C(1)); 65.8 (*d*, ¹*J*(C,H) = 135, C(4)); 48.2 (*t*, ¹*J*(C,H) = 136, 2 ArCH₂N). HR-MALDI-TOF-MS: 306.1825 (C₁₄H₂₀N₅O₃⁺, [*M* + H]⁺; calc. 306.1566).

8. (±)-(1*R*S,2*S*R,3*S*R,4*R*S)-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 H₂ for 5 h in the presence of 10% Pd/C (0.02 g). The soln. was passed through *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. ¹H-NMR (400 MHz, CD₃OD): 3.47–3.41 (*m*, H–C(1)); 3.59 (*dd*, ³*J*(3,2) = 10.0, ³*J*(3,4) = 9.0, H–C(3)); 3.19 (*dd*, ³*J*(2,3) = 9.0, ³*J*(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)). ¹³C-NMR (100.6 MHz, CD₃OD): 79.4 (*d*, ¹*J*(C,H) = 141, C(2)); 75.0 (*d*, ¹*J*(C,H) = 143, C(3)); 73.1 (*d*, ¹*J*(C,H) = 135, C(1)); 55.0 (*d*, ¹*J*(C,H) = 150, C(4)); 30.4, 25.9 (2*t*, ¹*J*(C,H) ≈ 131, C(6), C(5)). CI-MS (NH₃): 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 (C₆H₁₄NO₃⁺, [*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)). ¹H-NMR (400 MHz, CDCl₃): 9.92 (*s*, CHO); 7.84 (*d*, ³*J* = 8.7, 2 arom. H); 7.07–6.93 (*m*, 6 arom. H); 3.85 (*s*, MeO). ¹³C-NMR (100.6 MHz, CDCl₃): 189.7 (*d*, ¹*J*(C,H) = 173, CHO); 164.0 (*s*, arom. C); 156.8 (*s*, arom. C); 148.0 (*s*, arom. C); 131.9 (*d*, ¹*J*(C,H) = 161, 2 arom. C); 130.8 (*s*, arom. C); 121.7 (*d*, ¹*J*(C,H) = 162, arom. C); 116.6 (*d*, ¹*J*(C,H) = 162, arom. C); 115.0 (*d*, ¹*J*(C,H) = 163, 2 arom. C); 55.5 (*q*, ¹*J*(C,H) = 144, MeO).

4-(4-Bromophenoxy)benzaldehyde (**23o**). According to [25]: **23o** (44%). Colorless crystals. M.p. 68° (from hexane) ([25]: 67–68° (from hexane)). ¹H-NMR (400 MHz, CDCl₃): 9.95 (*s*, CHO); 7.88 (*d*, ³*J* = 8.6, 2 arom. H); 7.54 (*d*, ³*J* = 8.7, 2 arom. H); 7.08 (*d*, ³*J* = 8.6, 2 arom. H); 6.99 (*d*, ³*J* = 8.7, 2 arom. H). ¹³C-NMR (100.6 MHz, CDCl₃): 189.6 (*d*, ¹*J*(C,H) = 174, CHO); 162.5 (*s*, arom. C); 154.3 (*s*, arom. C); 133.1 (*d*, ¹*J*(C,H) = 167, 2 arom. C); 131.9 (*d*, ¹*J*(C,H) = 162, 2 arom. C); 131.5 (*s*, arom. C); 122.0 (*d*, ¹*J*(C,H) = 163, arom. C); 117.7 (*d*, ¹*J*(C,H) = 163, arom. C).

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. ¹H-NMR (400 MHz, CD₃OD): 9.92 (*s*, CHO); 8.15 (*s*, 1 arom. H); 7.94 (*d*, ³*J* = 8.7, 2 arom. H); 7.65 (*d*, ³*J* = 8.8, 2 arom. H); 7.59 (*s*, 1 arom. H); 7.27 (*d*, ³*J* = 8.8, 2 arom. H); 7.17–7.14 (*m*, 3 arom. H). ¹³C-NMR (100.6 MHz, CD₃OD): 192.6 (*d*, ¹*J*(C,H) = 175, CHO); 164.1 (*s*, arom. C); 156.0 (*s*, arom. C); 137.0 (*d*, ¹*J*(C,H) = 211, arom. C); 135.2 (*s*, arom. C); 133.3 (*s*, arom. C); 131.1 (*d*, ¹*J*(C,H) = 162, 2 arom. C); 130.3 (*d*, ¹*J*(C,H) = 191, arom. C); 124.3 (*d*, ¹*J*(C,H) = 163, 2 arom. C); 122.6 (*d*, ¹*J*(C,H) = 164, 2 arom. C); 119.9 (*d*, ¹*J*(C,H) = 193, arom. C); 119.0 (*d*, ¹*J*(C,H) = 164, 2 arom. C). CI-MS (NH₃): 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 (C₁₆H₁₃N₃O₂⁺, [*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)). ¹H-NMR (400 MHz, CDCl₃): 9.94 (*s*, CHO); 7.87 (*d*, ³*J* = 8.4, 2 arom. H); 7.38 (*t*, ³*J* = 8.0, 2 arom. H); 7.16–7.05 (*m*, 9 arom. H). ¹³C-NMR (100.6 MHz, CDCl₃): 190.7 (*d*, ¹*J*(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*, ¹*J*(C,H) = 162, 2 arom. C); 131.1 (*s*, arom. C); 129.8 (*d*, ¹*J*(C,H) = 159, 2 arom. C); 123.4 (*d*, ¹*J*(C,H) = 159, arom. C); 121.8 (*d*, ¹*J*(C,H) = 153, arom. C); 120.2 (*d*, ¹*J*(C,H) = 153, arom. C); 118.7 (*d*, ¹*J*(C,H) = 158, arom. C); 117.0 (*d*, ¹*J*(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 (CHCl₃): 307 (3802), 287 (3743), 272 (3472), 267 (3484), 261 (3404), 256 (3559). IR (KBr): 1688, 1601, 1499, 1427, 1320, 1232, 1158, 820. ¹H-NMR (400 MHz, CDCl₃): 9.93 (*s*, CHO); 8.11 (*d*, ³*J* = 8.4, 1 arom. H); 7.85 (*d*, ³*J* = 8.6, 2 arom. H); 7.67 (*d*, ³*J* = 8.1, arom. H); 7.47 (*t*, ³*J* = 7.2, 1 arom. H); 7.36–7.25 (*m*, 2 arom. H); 7.12 (*d*, ³*J* = 8.5, 2 arom. H); 2.69 (*br. s*, Me). ¹³C-NMR (100.6 MHz, CDCl₃): 190.9 (*d*, ¹*J*(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*, ¹*J*(C,H) = 162, arom. C); 131.8 (*d*, ¹*J*(C,H) = 161, 2 arom. C); 131.2 (*s*, arom. C); 128.3 (*s*, arom. C); 125.6 (*d*, ¹*J*(C,H) = 164, arom. C); 124.5 (*d*, ¹*J*(C,H) = 160, arom. C); 123.0 (*d*, ¹*J*(C,H) = 162, arom. C); 119.4 (*d*, ¹*J*(C,H) = 162, arom. C); 118.1 (*d*, ¹*J*(C,H) = 164, 2 arom. C); 25.7 (*q*, ¹*J*(C,H) = 127, Me). CI-MS (NH₃): 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 (C₁₇H₁₄NO₂⁺, [*M* + H]⁺; calc. 264.1025). Anal. calc. for C₁₆H₁₄O₃ (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 (CHCl₃): 294 (2491), 287 (2457), 263 (2220), 256 (2392). IR (KBr): 1694, 1681, 1591, 1504, 1416, 1359, 1303, 1245, 1163, 1107, 836. ¹H-NMR (400 MHz, CDCl₃): 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). ¹³C-NMR (100.6 MHz, CDCl₃): 196.1 (s, COMe); 190.5 (s, ¹J(C,H)=173, CHO); 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, COMe). CI-MS (NH₃): 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 (C₁₅H₁₃O₃⁺, [M+H]⁺; calc. 241.0865). Anal. calc. for C₁₅H₁₂O₃ (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. H₂SO₄ soln. (2 drops) was allowed to stand at 20° for 24 h. After the addition of an excess of anh. Na₂CO₃, 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. ¹H-NMR (400 MHz, CDCl₃): 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). ¹³C-NMR (100.6 MHz, CDCl₃): 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, MeC(OMe)₂); 45.3 (q, ¹J(C,H)=142, 2 MeO); 26.0 (q, ¹J(C,H)=127, Me). CI-MS (NH₃): 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 Cs₂CO₃ (1.47 g, 4.25 mmol) was stirred and heated at 120° for 1 h. 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 H₂O and CHCl₃. The org. layer was separated, dried (Na₂SO₄), 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 (CHCl₃): 297 (5001), 292 (4973), 290 (4945), 261 (4335), 257 (4808). IR (KBr): 1686, 1593, 1498, 1308, 1243, 1044, 878, 810. ¹H-NMR (400 MHz, CDCl₃): 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, CH₂=C); 4.26 (d, ³J=2.9, 1 H, CH₂=C); 3.78 (s, MeO). ¹³C-NMR (100.6 MHz, CDCl₃): 190.8 (s, ¹J(C,H)=173, CHO); 163.0 (s, CH₂=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, CH₂=C); 55.4 (q, ¹J(C,H)=144, MeO). CI-MS (NH₃): 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 (C₁₆H₁₃O₃⁺, [M+H]⁺; calc. 255.1021). Anal. calc. for C₁₆H₁₄O₃: (254.094): C 75.57, H 5.55; found: C 75.47, H 5.61.

10. Secondary Amines **26–30**. N-[4-[4-(1H-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. NH₃ 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. ¹H-NMR (400 MHz, CD₃OD): 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, ArCH₂N); 2.75 (t, ³J(1,2)=7.6, CH₂(1)); 1.60 (quint., ³J(2,3)=³J(2,1)=7.7, CH₂(2)); 1.40 (sext., ³J(3,4)=³J(3,2)=7.6, CH₂(3)); 0.97 (t, ³J(4,3)=7.3, Me). ¹³C-NMR (100.6 MHz, CD₃OD): 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, ArCH₂NH); 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 (NH₃): 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 (C₂₀H₂₄N₃O⁺, [M+H]⁺; calc. 322.1919).

N-[4-[4-(1H-Imidazol-1-yl)phenoxy]benzyl]cyclohexanamine (**27**). As described for **26**, with **23p** and cyclohexanamine. FC (MeOH/AcOEt/25% aq. NH₃ 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). ¹H-NMR (400 MHz, CD₃OD): 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*, $^1J(\text{C,H})=210$, arom. C); 135.5 (*s*, arom. C); 133.9 (*s*, arom. C); 131.5 (*d*, $^1J(\text{C,H})=159$, 2 arom. C); 130.1 (*d*, $^1J(\text{C,H})=191$, arom. C); 124.2 (*d*, $^1J(\text{C,H})=163$, 2 arom. C); 120.7 (*d*, $^1J(\text{C,H})=163$, 2 arom. C); 120.2 (*d*, $^1J(\text{C,H})=161$, 2 arom. C); 120.0 (*d*, $^1J(\text{C,H})=192$, arom. C); 57.3 (*d*, $^1J(\text{C,H})=138$, 1 C, *chx*); 50.3 (*t*, $^1J(\text{C,H})=136$, ArCH_2NH); 33.2 (*t*, $^1J(\text{C,H})=126$, 2 C, *chx*); 27.0 (*t*, $^1J(\text{C,H})=128$, 1 C, *chx*); 26.1 (*t*, $^1J(\text{C,H})=127$, 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 ($\text{C}_{22}\text{H}_{26}\text{N}_3\text{O}^+$, $[M+H]^+$; 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. ^1H -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*, $^1J(\text{C,H})=163$, arom. C); 132.8 (*d*, $^1J(\text{C,H})=160$, 2 arom. C); 129.8 (*s*, arom. C); 129.0 (*s*, arom. C); 127.0 (*d*, $^1J(\text{C,H})=161$, arom. C); 124.8 (*d*, $^1J(\text{C,H})=162$, arom. C); 124.4 (*d*, $^1J(\text{C,H})=164$, arom. C); 120.2 (*d*, $^1J(\text{C,H})=163$, 2 arom. C); 119.1 (*d*, $^1J(\text{C,H})=163$, arom. C); 58.4 (*d*, $^1J(\text{C,H})=140$, 1 C, *chx*); 48.8 (*t*, $^1J(\text{C,H})=144$, ArCH_2NH); 30.4 (*t*, $^1J(\text{C,H})=128$, 2 C, *chx*); 26.1 (*t*, $^1J(\text{C,H})=127$, 1 C, *chx*); 25.6 (*t*, $^1J(\text{C,H})=129$, 2 C, *chx*); 24.7 (*q*, $^1J(\text{C,H})=128$, 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 ($\text{C}_{23}\text{H}_{26}\text{N}_2\text{NaO}^+$, $[M+\text{Na}]^+$; 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. ^1H -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*, $^3J(1,2)=7.6$, $\text{CH}_2(1)$); 1.86 (*quint*, $^3J(2,3)=^3J(2,1)=7.5$, $\text{CH}_2(2)$); 1.38 (*sext.*, $^3J(3,4)=^3J(3,2)=7.5$, $\text{CH}_2(3)$); 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*, $^1J(\text{C,H})=160$, 2 arom. C); 129.8 (*d*, $^1J(\text{C,H})=159$, 2 arom. C); 124.1 (*s*, arom. C); 123.2 (*d*, $^1J(\text{C,H})=159$, arom. C); 121.3 (*d*, $^1J(\text{C,H})=162$, 2 arom. C); 120.5 (*d*, $^1J(\text{C,H})=163$, 2 arom. C); 118.4 (*d*, $^1J(\text{C,H})=161$, 2 arom. C); 117.9 (*d*, $^1J(\text{C,H})=162$, 2 arom. C); 49.9 (*t*, $^1J(\text{C,H})=141$, ArCH_2N); 45.7 (*t*, $^1J(\text{C,H})=141$, C(1)); 27.9 (*t*, $^1J(\text{C,H})=125$, C(2)); 20.1 (*t*, $^1J(\text{C,H})=125$, C(3)); 13.5 (*q*, $^1J(\text{C,H})=124$, 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 ($\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_2^+$, $[M+H]^+$; 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. ^1H -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*, $^3J(1,2)=6.1$, $\text{CH}_2(1)$); 2.93 (*q*, $^3J=7.3$, MeCH_2N); 2.85 (*t*, $^3J(2,1)=6.1$, $\text{CH}_2(2)$); 1.26 (*t*, $^3J=7.3$, MeCH_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*, $^1J(\text{C,H})=158$, 2 arom. C); 130.9 (*d*, $^1J(\text{C,H})=159$, 2 arom. C); 124.2 (*d*, $^1J(\text{C,H})=160$, arom. C); 121.5 (*d*, $^1J(\text{C,H})=162$, 4 arom. C); 119.3 (*d*, $^1J(\text{C,H})=161$, 4 arom. C); 53.4 (*t*, $^1J(\text{C,H})=135$, ArCH_2N); 47.9 (*t*, $^1J(\text{C,H})=140$, C(1')); 46.2 (*t*, $^1J(\text{C,H})=136$, C(2')); 44.0 (*t*, $^1J(\text{C,H})=137$, MeCH_2N); 12.4 (*q*, $^1J(\text{C,H})=127$, MeCH_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 ($\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_2^+$, $[M+H]^+$; calc. 362.1994).

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