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A new family of planar-chiral symmetric and unsymmetric salens based on the [2.2]paracyclophane skeleton

Tat'yana I. Danilova,[a] Valeria I. Rozenberg,[a,*] Evgenii V. Vorontsov,[a] Zoya A. Starikova[a] and Henning Hopf[b,*]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science, Vavilova 28, 119991 Moscow, Russia*
[b]*Institute of Organic Chemistry, Technical University of Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany*

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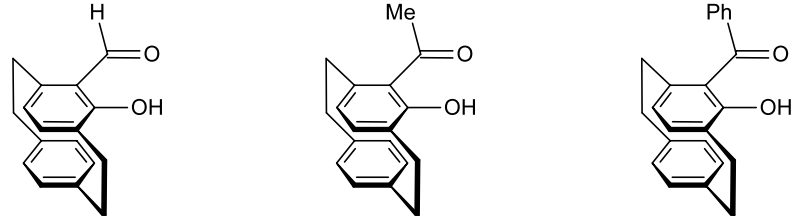
Abstract—Planar-chiral *ortho*-hydroxy[2.2]paracyclophanyl ketones as well as *ortho*-hydroxy[2.2]paracyclophanyl aldehyde were employed as building blocks for the design of a new family of chiral salen type ligands in which the chiral environment can be organized by the planar chiral fragments of [2.2]paracyclophane and modified by introduction of the chiral diamine part. A new family of four different types of chiral salens was successfully synthesized using both direct and stepwise approaches.

1. Introduction

Chiral salens are one of the most popular and widely applicable ligands in asymmetric synthesis and their metal complexes are now used as catalysts for various stereoselective processes.[1,2] Until recently the majority of chiral salens has been synthesized from achiral salicylaldehyde derivatives, the asymmetry being introduced by its ethylenediamine components.[3,4] Occasionally the stereogenic centers have been incorporated through the aromatic moieties of the salen.[5,6] The second generation of salen type ligands containing a binaphthyl group with axial chirality as the carbonyl part has also successfully been employed as chiral ligands.[7,8] However, only little attention has been paid to salens with planar-chiral salicyladehyde moieties. Thus, the salen obtained from planar-chiral 2-hydroxyferrocenylcarbaldehyde and ethylenediamine (EDA) is apparently unstable towards air oxidation and has, as far as we know, not been used as a chiral ligand.[9] Furthermore, there has only been one report on the synthesis and application in asymmetric synthesis of salens based on a planar-chiral analogue of salicylaldehyde—4-formyl-5-hydroxy[2.2]paracyclophane[10,11] (FHPC) **1**, new ligands which possess significant potential as Lewis acids for Ti(IV)-catalyzed asymmetric trimethylsilylcyanation of benzaldehyde.[12]

Recently we described two effective methods for the preparation of enantiomerically pure *ortho*-acylhydroxy[2.2]paracyclophanes (Fig. 1), 4-acetyl-5-hydroxy-(AHPC), **2** and 4-benzoyl-5-hydroxy[2.2]-



(*S*)- or (*R*)-FHPC **1** (*S*)- or (*R*)-AHPC **2** (*S*)- or (*R*)-BHPC **3**

Figure 1.

* Corresponding authors. Tel.: 007-095-135-9268, fax: 007-095-135-5085 (V.I.R.); Tel.: +49(0)531-391-5255; fax: +49(0)531-391-5388 (H.H.); e-mail: lera@ineos.ac.ru; h.hopf@tu-bs.de

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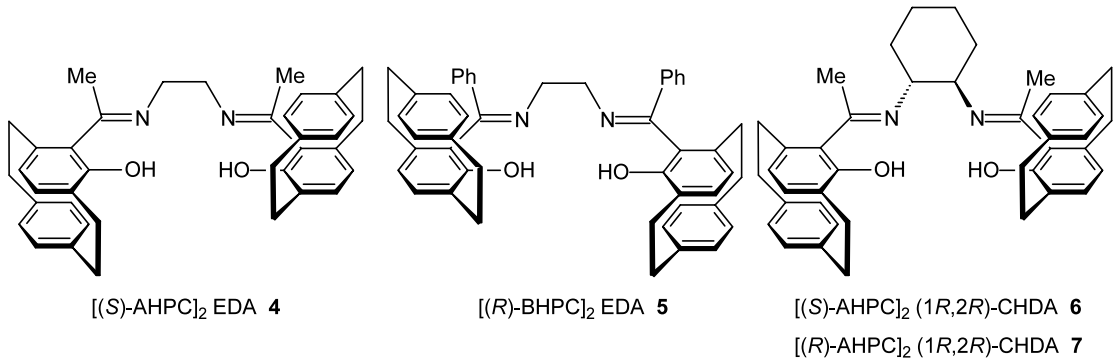


Figure 2.

paracyclophane (BHPC), **3**[13] and a new simplified approach to 4-formyl-5-hydroxy[2.2]paracyclophane (FHPC) **1**.[14] This prompted us to react these carbonyl compounds with both achiral and chiral diamines for the directed synthesis of various salens.

Thus, herein we present a unique collection of 11 enantiomerically pure symmetric and unsymmetric salens from [2.2]paracyclophanes with two or four chirogenic elements, obtained by combination of **2**, **3** and aldehyde **1** with EDA and (1*R*,2*R*)-cyclohexanediamine ((1*R*,2*R*)-CHDA), using both straight and stepwise approaches.

2. Results and discussion

The prepared salens may be classified by the structural and configurational features of their carbonyl components into four different types.

2.1. Type I: Structurally and configurationally symmetric salens

Salens of this type are C_2-symmetric, and can therefore be synthesized from identical carbonyl fragments. Such salens derived from planar-chiral aldehyde **1** and several chiral and achiral diamines have already been prepared by us recently.[12] Herein four new salens **4**–**7** (Fig. 2) of Type I were obtained starting from enantiomerically pure ketones **2** or **3** with EDA and (1*R*,2*R*)-CHDA using a straight approach, in which two identical carbonyl moieties are attached to the two sides of the diamine. It should be noted that in contrast to countless examples of salens based on salicylaldehyde, there have only been very few reports of salens for which *ortho*-hydroxyaryl ketones have been employed as aromatic moieties.[15–17] Ketones, and especially sterically hindered ones, are less reactive than aldehydes towards amines, and often the search for conditions for the synthesis of Schiff bases from ketones is a real problem.[18,19]

Under Lewis acid (Et_2SnCl_2) catalysis[20] the reaction of **2** with EDA and (*R*,*R*)-CHDA proceeded efficiently, and the corresponding salens **4**, **6** and **7** were obtained in good to excellent yields (Fig. 2, 70–98%). The more shielded **3** does not react with diamines in the presence of Et_2SnCl_2, and only when a catalytic quantity of $TiCl_4$ was applied was the expected **5** with EDA obtained, although the yield was lower (30%). In all cases the 1:1 mixture of enantiomerically pure ketone and diamine was refluxed in toluene in the presence of the catalyst while removing the water with a Dean–Stark trap over 24–30 h. The crude product was passed through a short column filled with SiO_2 for removal of traces of the corresponding mono-imine, and the desired salen was obtained in high yield.

The structure of **6** was determined by X-ray structural analysis, and the result is shown in Figure 3.

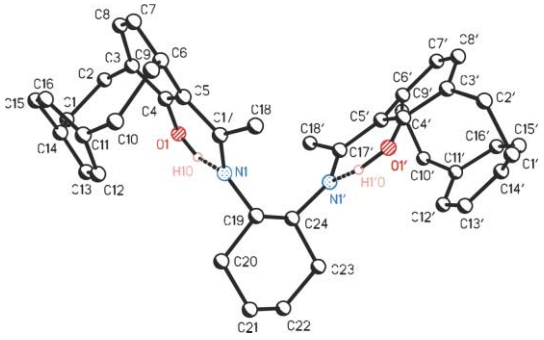
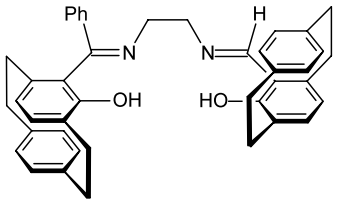
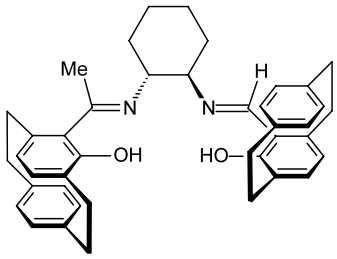


Figure 3.

A specific feature of the next three types of salens is the absence of symmetry. Obviously, for the preparation of salens of type II, III and IV the straightforward synthetic approach is no longer applicable and a stepwise condensation methodology has to be applied instead. This methodology was elaborated for the synthesis of unsymmetric salens and includes the formation of an intermediate chiral half unit from a first carbonyl moiety with the diamine followed by the construction of the desired salen by reacting the remaining free amino-group with a second carbonyl component structurally different from the first.[21] To the best of our knowledge there have been very few reports on the synthesis of unsymmetric salens including two different salicylaldehyde fragments[22–24] and only two reports of such salens combining a salicylaldehyde and a 1-(2-hydroxy-



[(*S*)-BHPC][(*S*)-FHPC] EDA **12**



[(*S*)-AHPC][(S)-FHPC] (1*R*,2*R*)-CHDA **13**
[(*R*)-AHPC][(R)-FHPC] (1*R*,2*R*)-CHDA **14**

Figure 4.

phenyl)ketone fragment.[25,26] More precisely all unsymmetric salens mentioned above should be called structurally unsymmetric. The specific character of the planar-chiral carbonyl [2.2]paracyclophane derivatives allow us to extend the classification of 'symmetric or unsymmetric' salens from only structural to both structural and configurational identity or non-identity of their carbonyl fragments. So in this study the concept of structurally and configurationally symmetric and unsymmetric salens will be introduced.

2.2. Type II: Structurally unsymmetric, configurationally symmetric salens

Such salens are obtained by combining a ketone fragment and an aldehyde fragment having the same configuration.

For the preparation of salens **12**, **13** and **14** of this type (Fig. 4) the stepwise technique was employed and the three corresponding chiral hemisalens (or chiral half units) **8**–**10** were synthesized first (Fig. 5).

The chiral half unit [(*S*)-BHPC]EDA **8** was obtained from (*S*)-BHPC **3** with an excess of EDA and $TiCl_4$ in 80% yield as a deep red oil, which then became semisolid. The hemisalens [(*S*)-AHPC](1*R*,2*R*)-CHDA **9** and [(*R*)-AHPC](1*R*,2*R*)-CHDA **10** were synthesized from the corresponding enantiomers of **2** with an excess of (1*R*,2*R*)-CHDA without catalyst in about 80% yield as deep yellow powders. All reactions were carried out in boiling toluene removing the water with a Dean–Stark trap over 10–30 h. Traces of the corresponding salens were removed by preparative column chromatography on SiO_2 (toluene/EtOH from 40/1 to 10/1). The stability of hemisalens **8**–**10** allowed their isolation and characterization, in contrast to the reported examples of their aromatic analogues.[25,26]

Salens **12**–**14** were synthesized by condensation of equivalent quantities of hemisalens **8**–**10** with aldehyde **1** of the same configuration as the first ketone component. The reactions proceeded in boiling toluene with Et_2SnCl_2 as a catalyst to produce the desired salens in good to excellent yield as the only products. The X-ray structure of **12** is shown in Figure 6

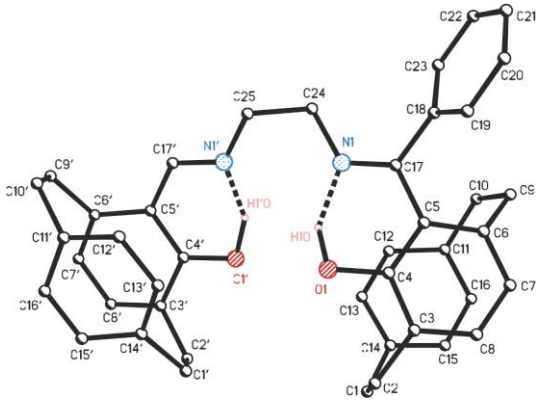
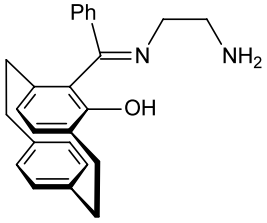
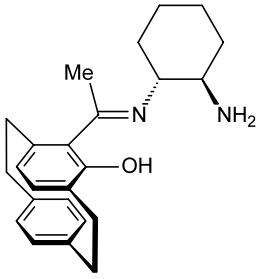


Figure 6.

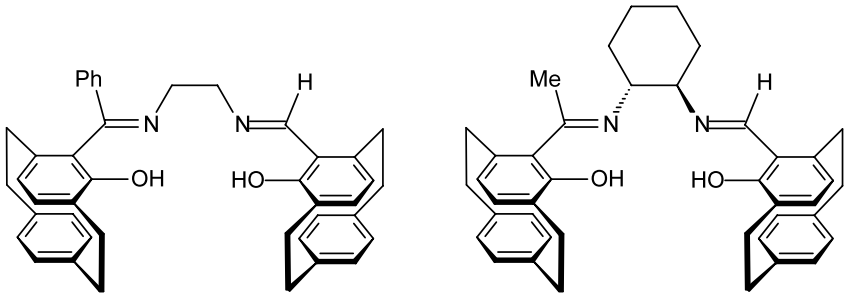


[(*S*)-BHPC] EDA **8**



[(*S*)-AHPC] (1*R*,2*R*)-CHDA **9**
[(*R*)-AHPC] (1*R*,2*R*)-CHDA **10**

Figure 5.



[(*S*)-BHPC][(*R*)-FHPC] EDA **15**

[(*S*)-AHPC][(*R*)-FHPC] (1*R*,2*R*)-CHDA **16**

[(*R*)-AHPC][(*S*)-FHPC] (1*R*,2*R*)-CHDA **17**

Figure 7.

[(*S*)-BHPC] EDA **8** —(*R*) - **1**→ [(*S*)-BHPC][(*R*)-FHPC] EDA **15**

[(*S*)-AHPC] (1*R*,2*R*)-CHDA **9** —(*R*) - **1**→ [(*S*)-AHPC][(*R*)-FHPC] (1*R*,2*R*)-CHDA **16**

[(*R*)-AHPC] (1*R*,2*R*)-CHDA **10** —(*S*) - **1**→ [(*R*)-AHPC][(*S*)-FHPC] (1*R*,2*R*)-CHDA **17**

Scheme 1. The preparation of salens **15**–**17**.

2.3. Type III: Structurally and configurationally unsymmetric salens

This type includes salens obtained from a ketone fragment and an aldehyde fragment having opposite configurations (Fig. 7).

Salens **15**–**17** were synthesized in accordance with the stepwise approach from hemisalens **8**–**10** and aldehyde **1**, but the absolute configuration of **1** was opposite to the configuration of the first ketone component in each case (Scheme 1).

For salen **17** an X-ray investigation was also carried out (Fig. 8).

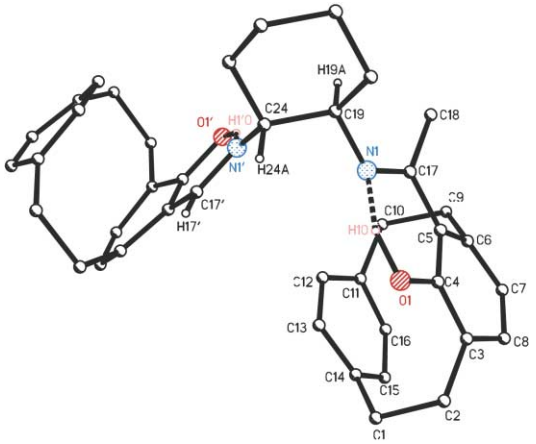


Figure 8.

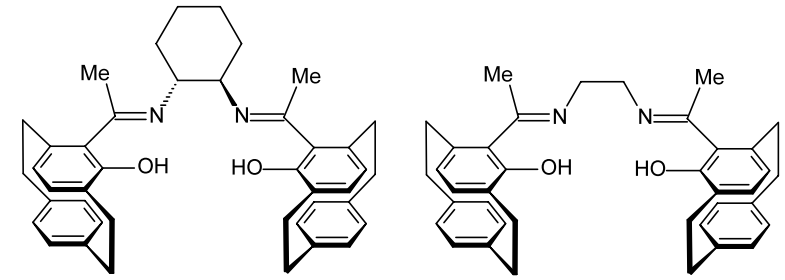
2.4. Type IV: Structurally symmetric, configurationally unsymmetric salens

Such salens were constructed from two structurally identical carbonyl components having opposite absolute configurations. The specific feature of this type of salens is that they are chiral only when its diamine part is chiral. In this study type IV is represented by the salen **11** (Fig. 9) obtained from AHPC **2** and (1*R*,2*R*)-CHDA.

Salen **11** was prepared by condensation of hemisalen **10** with (*S*)-**2** under Et_2SnCl_2 catalysis. The reaction proceeds slowly and because of its reversibility produces the desired [(*R*)-AHPC][(*S*)-AHPC](1*R*,2*R*)-CHDA-**11** (43%) together with salens [(*S*)-AHPC]$_2$(1*R*,2*R*)-CHDA **6** (7%) and [(*R*)-AHPC]$_2$(1*R*,2*R*)-CHDA **7** (7%) as side products. These accompanying minor products were easily removed by preparative column chromatography. The fact that we succeeded to separate salens **6**, **7** (Type I) and **11** (Type IV) means, that in principle, it is possible to obtain all of them in diastereomerically pure form starting from *rac*-AHPC **2** and (1*R*,2*R*)-CHDA using the general direct approach.

The second representative of type IV is [(*S*)-AHPC][(*R*)-AHPC]EDA **18** (Fig. 9). Being constructed from (*R*)-**2**, (*S*)-**2** and achiral EDA, **18**, as mentioned above is a *meso*-form and has no optical activity. A single crystal of **18** was obtained and the result of the X-ray study is shown in Figure 10.

In this study we first used the planar-chiral *ortho*-hydroxy[2.2]paracyclophanyl ketones **2** and **3** and the aldehyde **1** as building blocks for the construction of four types of structurally and configurationally symmetric and unsymmetric salens. Very recently we pre-



[(*S*)-AHPC][(*R*)-AHPC] (1*R*,2*R*)-CHDA **11** [(*S*)-AHPC][(*R*)-AHPC] EDA **18**

Figure 9.

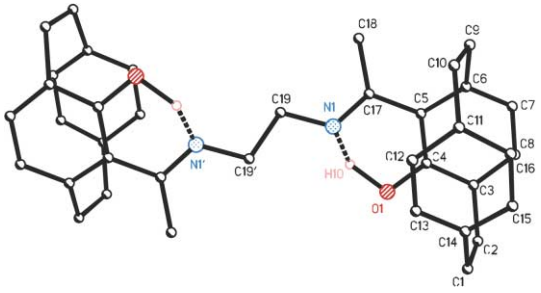


Figure 10.

pared stable Cu(II) [as well as Mn(III)] complexes[27] with diastereomeric salens **4** and **18**, and an X-ray investigation of them was carried out. These complexes shown in Figure 11, have a different three-dimensional environment around the central metal. Replacement of the achiral diamine component by a chiral one should provide different chiral environments for such types of complexes.

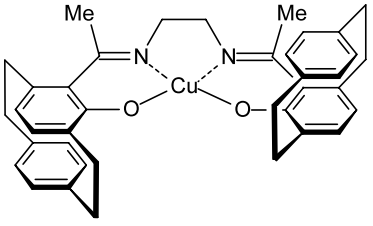
The application of all presented salens and hemisalens as chiral ligands in asymmetric catalysis is under investigation now and will be reported at a later date.

3. Experimental

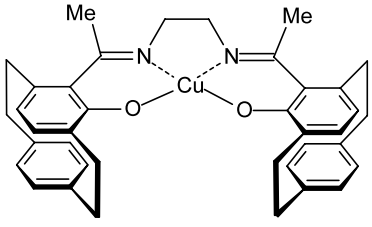
Toluene and heptane were distilled and used without further purification. Ethylenediamine was distilled over Na before use. (1*R*,2*R*)-(+)-1,2-diaminocyclohexane was purchased from Aldrich and used without purification. TLC analyses were performed on silica gel pre-coated plates «SORBFIL» PTLC-A-UV. Column chromatography was performed on Kieselgel 60 (Merck). NMR: Bruker AMX-400 (400.13 MHz for ^{1}H), $CDCl_3$ as solvent, δ_H ($CHCl_3$ impurity) = 7.27. MS: KRATOS MS890A (70 eV). Optical rotations: EPO-1 in thermostated cell at 22°C. Enantiomerically pure 4-formyl-5-hydroxy- **1**,[11] 4-acetyl-5-hydroxy- **2**[13] and 4-benzoyl-5-hydroxy[2.2]paracyclophane **3**[13,14] was obtained according to a literature procedures.

3.1. Preparation of salens 4–7

3.1.1. [(*S*)-AHPC]$_2$EDA 4. The solution of 0.140 g (0.524 mmol) (*S*)-**2**, 0.035 ml (0.032 g, 0.524 mmol) of EDA in 8 ml of toluene was refluxed in an apparatus equipped with Dean–Stark trap filled with anhydrous $MgSO_4$ for 24 h. After solvent removal orange crude product (0.149 g) was purified by column chromatography on SiO_2 (eluent toluene/ethylacetate 10/1) to provide 0.138 g (95%) of **4**. Analytically pure **4** was obtained by crystallization from toluene/heptane 1/2.5. Mp 233.5–235-5°C; $[\alpha]_D^{22} = -695.5$ (*c* 0.224, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 6H, -CH_3), 2.49–2.60 (m, 2H, -C*H*H-CH_2-), 2.70–2.85 (m, 2H, -C*H*H-CH_2-), 2.91–3.22 (m, 8H, -CH_2-CH*H*-,), 3.33–3.45 (m, 4H, -C*H*H-CH_2-), 3.95 (br. s, 4H, -NCH_2), 6.23 (d, 2H, ^3J = 7.8 Hz, H-7 or H-8), 6.43 (d, 2H, ^3J = 7.8 Hz, H-7 or H-8), 6.46 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-12 or H-13), 6.50 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-15 or H-16), 6.63 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-15 or H-16), 7.17 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-12 or H-13), 15.3 (br. s, 2H, -O*H*). Anal. calcd for $C_{38}H_{40}N_2O_2$ (556.10): C, 82.07; H, 7.19; N, 5.04. Found: C, 82.01; H, 7.23; N, 5.00; MS (70 eV): *m*/*z* (%) = 556 (23, M^+), 249 (21), 174 (50), 162 (30), 145 (50), 131 (25), 104 (100).



Cu(II)L*; L* = *chiral* - [(*S**)-AHPC]$_2$ EDA



Cu(II)L; L = *meso* - [(*S*)-AHPC][(*R*)-AHPC] EDA

Figure 11.

3.1.2. [(*R*)-BHPC]$_2$EDA 5. To the boiling solution of 0.120 g (0.366 mmol) (*R*)-**3** and 0.074 ml (0.066 g, 1.100 mmol) of EDA in 6 ml of toluene, 0.020 ml (0.035 g, 0.183 mmol) of $TiCl_4$ was carefully added. The resulting brown slurry was refluxed while the reaction water was removed with a Dean–Stark trap filled with anhydrous $MgSO_4$ for 20 h. The reaction mixture was cooled to room temperature, diluted with 15 ml of toluene and 20 ml of 1N HCl. Organic fractions were washed with H_2O (2×10 ml) and dried with Na_2SO_4. After solvent removal, the crude orange semisolid was purified by column chromatography on SiO_2 (eluent: CH_2Cl_2) to provide 0.038 g (30%) of **5** as well as 0.063 g (52%) of starting **3**. Analytically pure **5** was obtained by crystallization from toluene. Mp 261.5–262.5°C; $[\alpha]_D^{22}$ = +855.35 (*c* 0.218, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.76–1.85 (m, 2H, -C*H*H-CH_2-), 2.20–2.36 (m, 2H, -C*H*H-CH_2-), 2.36–2.50 (m, 2H, -C*H*H-CH_2-), 2.51–2.70 (m, 2H, -CH_2-CH_2-), 2.80–2.95 (m, 2H, -C*H*H-CH_2-), 2.96–3.10 (m, 2H, -C*H*H-CH_2-), 3.23–3.32 (m, 2H, -C*H*H-CH_2-), 3.45–3.60 (m, 2H, -C*H*H-CH_2-, 2H, -NCH_2-), 3.90–4.10 (m, 2H, -NCH_2 -), 6.08 (d, 2H, ^3J = 7.8 Hz, H-7 or H-8), 6.48 (m, 4H, PC arom. H), 6.58 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, PC arom. H), 6.73 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, PC arom. H), 7.20–7.38 (m, 4H, arom. H), 7.38–7.50 (m, 2H, PC arom. H, 6H, arom. H), 16.3 (br. s, 2H, -O*H*). Anal. calcd for $C_{48}H_{44}N_2O_2$·0.1(CH_2Cl_2) (688.98): C, 83.85; H, 6.38; N, 4.06. Found: C, 83.77; H, 6.42; N, 3.96; MS (70 eV) *m*/*z* (%) = 680 (26, M^+), 328 (8), 236 (37), 178 (40), 165 (25), 104 (100).

3.1.3. [(*S*)-AHPC]$_2$(1*R*,2*R*)-CHDA 6. The suspension of 0.220 g (0.827 mmol) of (*S*)-**2**, 0.094 g (0.827 mmol) of (1*R*,2*R*)-CHDA and catalytic quantity of Et_2SnCl_2 in 8 ml of toluene was refluxed as above for 30 h. After solvent removal, the crude orange solid was purified by column chromatography on SiO_2 (eluent-toluene/ethylacetate 10/1) to provide 0.175 g (70%) of **6**. Analytically pure **6** was obtained by crystallization from toluene/heptane 5/2. Mp 262–263°C; $[\alpha]_D^{22}$ = −1063.7 (*c* 0.204, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.62–1.73 (m, 2H, -CH_2-CHDA), 1.79–1.95 (m, 2H, -CH_2- CHDA), 1.97–2.07 (m, 2H, -CH_2- CHDA), 2.08–2.17 (m, 2H, -CH_2-CHDA), 2.30 (s, 6H, -CH_3), 2.38–2.60 (m, 4H, -C*H*H-CH_2-), 2.72–2.86 (m, 2H, -C*H*H-CH_2-), 2.90–3.00 (m, 2H, -C*H*H-CH_2-), 3.04–3.15 (m, 4H, -C*H*H-CH_2-), 3.21–3.45 (m, 4H, -C*H*H-CH_2-), 3.90–4.05 (m, 2H, -C*H*N=), 6.10 (d, 2H, ^3J = 7.8 Hz, H-7 or H-8), 6.28 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-12 or H-13), 6.33 (d, 2H, ^3J = 7.8 Hz, H-7 or H-8), 6.43 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-15 or H-16), 6.57 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-15 or H-16), 6.94 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-12 or H-13), 15.9 (br. s, 2H, -O*H*,). Anal. calcd for $C_{42}H_{46}N_2O_2$ (610.79): C, 82.59; H, 7.59; N, 4.58. Found C, 82.75; H, 7.48; N, 4.47; MS (70 eV): *m*/*z* (%) = 611 (40, M^+), 160 (66), 145 (43), 115 (32), 104 (100).

3.1.4. [(*R*)-AHPC]$_2$(1*R*,2*R*)-CHDA 7. The synthesis was carried out as described for the **6**, starting from 0.266 g (1.000 mmol) of (*R*)-**2**, 0.114 g (1.000 mmol) of (1*R*,2*R*)-CHDA and catalytic quantity of Et_2SnCl_2 to yield 0.245 g (80%) of **7.** Analytically pure **7** was obtained by crystallization from toluene/heptane 5/2. Mp 271–272°C; $[\alpha]_D^{22}$ = +613.3 (*c* 0.196, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.46–1.75 (m, 4H, -CH_2- CHDA), 1.79–1.92 (m, 2H, -CH_2- CHDA), 1.94–2.08 (m, 2H, -CH_2- CHDA), 2.52 (s, 6H, -CH_3), 2.46–2.60 (m, 2H, -C*H*H-CH_2-), 2.76–2.91 (m, 4H, -C*H*H-CH_2-), 2.94–3.11 (m, 4H, -CH_2-CH_2-), 3.12–3.28 (m, 4H, -C*H*H-CH_2-), 3.40–3.50 (m, 2H, -CH*H*-CH_2-), 3.90–4.05 (m, 2H, -C*H*N=), 6.10 (d, 2H, ^3J = 7.8 Hz, H-7 or H-8), 6.37 (d, 2H, ^3J = 7.8 Hz, H-7 or H-8), 6.43 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-12 or H-13), 6.55 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-15 or H-16), 6.63 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-15 or H-16), 7.00 (dd, 2H, ^3J = 7.8, ^4J = 1.8 Hz, H-12 or H-13), 15.70 (br. s, 2H, -O*H*). Anal. calcd for $C_{42}H_{46}N_2O_2$ (610.79): C, 82.59; H, 7.59; N, 4.58. Found: C, 82.70; H, 7.72; N, 4.66; MS (70 eV): *m*/*z* (%) = 611 (25, M^+), 160 (67), 145 (46), 115 (35), 104 (100).

3.2. Preparation of chiral half units 8–10

3.2.1. [(*S*)-BHPC]EDA 8. To the boiling solution of 0.100 g (0.305 mmol) (*S*)-**3** and 0.102 ml (0.920 g, 1.520 mmol) of EDA in 8 ml of toluene, 0.166 ml (0.289 g, 1.520 mmol) of $TiCl_4$ was carefully added, and the dark red slurry was refluxed as above for 10 h. The reaction mixture was cooled to room temperature and diluted with satd Na_2CO_3 solution until pH >7. The organic layer was separated, the aqueous fraction was neutralized with 1N HCl until pH 5 and additionally extracted with CH_2Cl_2 (2×15). The organic fractions were washed with H_2O (20 ml) and dried with Na_2SO_4. After cooling and solvent removal the crude product was purified by column chromatography on SiO_2 (toluene/EtOH 20/1 to 5/1 as eluents) to yield 0.960 g (85%) of **8** as deep red oil, which was used without further purification. ^{1}H NMR ($CDCl_3$): δ 1.50–2.00 (m, 1H, -CH_2-, 2H, -NH_2), 2.14–2.45 (m, 3H, -C*H*H-CH_2-), 2.46–2.65 (m, 1H, -C*H*H-CH_2-), 2.73–2.90 (m, 1H, -CH_2N=), 2.90–3.13 (m, 2H, -CH_2NH_2), 3.13–3.27 (m, 1H, -C*H*H-CH_2-), 3.28–3.42 (m, 1H, -C*H*H-CH_2-), 3.42–3.57 (m, 1H, -CH_2N=), 3.57–3.79 (m, 1H, -CH_2-), 6.04 (d, 1H, ^3J = 7.8 Hz, H-7 or H-8), 6.40–6.50 (m, 3H, PC arom. H), 6.56 (dd, 1H, ^3J = 7.8, ^4J = 1.8 Hz, PC arom. H), 7.05 (dd, 1H, ^3J = 7.8, ^4J = 1.8 Hz, PC arom. H), 7.21–7.39 (m, 2H, arom. H), 7.40–7.55 (m, 3H, arom. H), 16.4 (br. s, 1H, -O*H*).-MS (70 eV): *m*/*z* (%) = 370 (26, M^+), 328 (8), 266 (42), 236 (92), 178 (45), 104 (100).

3.2.2. [(*S*)-AHPC](1*R*,2*R*)-CHDA 9. The solution of 0.200 g (0.750 mmol) (*S*)-**2**, 0.260 g (2.260 mmol) of (1*R*,2*R*)-CHDA in 8 ml of toluene was refluxed as above for 18 h. After solvent removal the crude product was purified by column chromatography on SiO_2 (toluene and toluene/EtOH 4/1 as eluents) to remove the traces of corresponding salen. The hemisalen **9** 0.230 g (85%) was obtained as orange semisolid compound. $[\alpha]_D^{22}$ = −709.9 (*c* 0.202, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.48–1.77 (m, 4H, -CH_2- CHDA, 2H, -NH_2), 1.78–2.01 (m, 4H, -CH_2- CHDA), 2.35 (s, 3H, -CH_3), 2.46–2.62 (m, 2H, -C*H*H-CH_2-), 2.80–2.93 (m, 1H, -C*H*H-CH_2-), 2.94–3.20 (m, 3H, -CH*H*-CH_2-, 1H, -C*H*N=), 3.32–3.47 (m, 3H, -C*H*H-CH_2-, 1H, -C*H*N=), 6.21 (d, 1H,

$^3J=7.8$ Hz, H-7 or H-8), 6.31 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-12 or H-13), 6.42 (d, 1H, $^3J=7.8$ Hz, H-7 or H-8), 6.45 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-15 or H-16), 6.60 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-15 or H-16), 6.97 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-12 or H-13), 15.86 (br. s., 1H, -O*H*). Anal. calcd for $C_{24}H_{30}N_2O$ (362.50): C, 79.52; H, 8.34; N, 7.73. Found: C, 79.70; H, 8.53; N, 7.49; MS (70 eV): m/z (%) = 362 (36, M^+), 258 (40), 174 (30), 162 (100), 104 (34).

3.2.3. [(*R*)-AHPC](1*R*,2*R*)-CHDA 10. The synthesis was carried out as described for **9**, starting from 0.190 g (0.715 mmol) of (*R*)-**2**, 0.245 g (2.150 mmol) of (1*R*,2*R*)-CHDA to yield 0.207 g (80%) of **10**. $[\alpha]_D^{22}=+464.2$ (*c* 0.316, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.29–1.55 (m, 4H, -C*H*$_2$- CHDA), 1.58–1.85 (m, 4H, -C*H*$_2$- CHDA, 2H, -N*H*$_2$), 1.93–2.10 (m, 1H, -C*H*$_2$- CHDA), 2.35 (s, 3H, -C*H*$_3$), 2.45–2.60 (m, 1H, -C*H*H-CH$_2$-), 2.62–2.80 (m, 1H, -C*H*H-CH$_2$-), 2.87–2.99 (m, 1H, -CH*H*-CH$_2$-), 3.00–3.23 (m, 2H, -C*H*H-CH$_2$-, 1H, -C*H*N=), 3.23–3.48 (m, 3H, -CH*H*-CH$_2$-, 1H, -C*H*N=), 6.18 (d, 1H, $^3J=7.8$ Hz, H-7 or H-8), 6.32 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-12 or H-13), 6.40 (d, 1H, $^3J=7.8$ Hz, H-7 or H-8), 6.49 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-15 or H-16), 6.63 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-15 or H-16), 6.95 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-12 or H-13), 16.00 (br. s., 1H, -O*H*). Anal. calcd for $C_{24}H_{30}N_2O$ (362.50): C, 79.52; H, 8.34; N, 7.73. Found: C, 79.73; H, 8.32; N, 7.93; MS (70 eV): m/z (%) = 362 (40, M^+), 258 (45), 266 (19), 104 (34).

3.3. Preparation of salens 11–17

3.3.1. [(*R*)-AHPC][(*S*)-AHPC](1*R*,2*R*)-CHDA 11. The solution of 0.100 g (0.280 mmol) of **10** with 0.071 g (0.280 mmol) of (*S*)-**2** and a catalytic amount of Et_2SnCl_2 in 8 ml of toluene was refluxed in an apparatus equipped with a Dean–Stark trap filled with anhydrous $MgSO_4$ for 18 h. The crude product was separated by column chromatography (SiO_2, toluene/ethylacetate 10/1). From the combined fractions with R_f 0.7 0.012 g (7%) of **6** was obtained; from the combined fractions with R_f 0.4 0.074 g (43%) of **11** was obtained and from the combined fractions with R_f 0.2 0.011 g (7%) of **7** was obtained. Analytically pure (0.052 g, 30%) was obtained by crystallization from heptane. Mp (decomposition) 255–256°C; $[\alpha]_D^{22}=-463.5$ (*c* 0.230, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.43–1.82 (m, 3H, -C*H*$_2$- CHDA), 1.77–1.92 (m, 3H, -C*H*$_2$- CHDA), 1.93–2.11 (m, 2H, -C*H*$_2$- CHDA), 2.38 (s, -C*H*$_3$, 3H), 2.39–2.48 (m, 1H, -C*H*H-CH$_2$-), 2.50 (s, 3H, -C*H*$_3$), 2.51–2.66 (m, 4H, -C*H*H-CH$_2$-), 2.78–2.92 (m, 3H, -C*H*$_2$-CH$_2$-), 2.93–3.10 (m, 3H, -C*H*H-CH$_2$-), 3.11–3.25 (m, 2H, -C*H*H-CH$_2$-), 3.26–3.39 (m, 2H, -C*H*H-CH$_2$-), 3.40–3.50 (m, 1H, -C*H*H-CH$_2$-), 3.89–3.95 (m, 1H, -C*H*N=), 3.96–4.10 (m, 1H, -C*H*N=), 5.53 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.03 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.08 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.25 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.35 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.36–6.48 (m, 4H, PC arom. H), 6.52 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.57 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 7.02 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz), 15.50 (br. s, 2H, -O*H*). Anal. calcd for $C_{42}H_{46}N_2O_2$ (610.79): C, 82.59; H, 7.59; N, 4.58. Found C, 82.65; H, 7.43; N, 4.39; MS (70 eV): m/z (%) = 611 (30, M^+), 160 (70), 145 (45), 115 (37), 104 (100).

3.3.2. [(*S*)-BHPC][(*S*)-FHPC]EDA 12. The solution of 0.100 g (0.270 mmol) of **8**, 0.068 g (0.270 mmol) of (*S*)-**1** and a catalytic amount of Et_2SnCl_2 in 8 ml of toluene was refluxed as above for 10–12 h. After solvent removal, the crude orange solid was purified by column chromatography on SiO_2 (eluent CH_2Cl_2) to provide 0.114 g (70%) of **12**. Analytically pure **12** was obtained by crystallization from toluene/heptane 2/1. Mp 216.5–217.5°C; $[\alpha]_D^{22}=-1042.6$ (*c* 0.216, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.71–1.85 (m, 1H, -C*H*H-CH$_2$-), 2.19–2.30 (m, 1H, -C*H*H-CH$_2$-), 2.31–2.47 (m, 1H, -C*H*H-CH$_2$-), 2.52–2.70 (m, 2H, -C*H*H-CH$_2$-), 2.80–2.92 (m, 3H, -C*H*H-CH$_2$-), 3.00–3.10 (m, 2H, -C*H*H-CH$_2$-), 3.15–3.32 (m, 3H, -C*H*H-CH$_2$-), 3.40–3.60 (m, 1H, -C*H*H-CH$_2$-, 2H, -C*H*$_2$N=), 3.62–3.75 (m, 1H, -C*H*H-CH$_2$-), 3.75–3.92 (m, 1H, -C*H*H-CH$_2$-), 3.92–4.12 (m, 2H, -C*H*$_2$N=), 6.05 (d, 1H, $^3J=7.8$ Hz, PC arom H), 6.17 (d, 1H, $^3J=7.8$ Hz, PC arom H), 6.35 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.39–6.48 (m, 4H, PC arom. H), 6.50–6.60 (m, 2H, PC arom. H), 6.62 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.92 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 7.12 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 7.20–7.38 (m, 2H, arom. H), 7.40–7.53 (m, 3H, arom. H), 8.30 (s, -C*H*=N, 1H) 13.90 (br. s, 1H, -O*H*). 16.30 (br. s, 1H, -O*H*). Anal. calcd for $C_{42}H_{40}N_2O_2$ (604.74): C, 83.41; H, 6.67; N, 4.63. Found: C, 83.36; H, 6.70; N, 4.61; MS (70 eV): m/z (%) = 605 (35, M^+), 250 (28), 236 (34), 224 (12), 160 (20), 146 (24), 104 (100).

3.3.3. [(*S*)-AHPC][(*S*)-FHPC](1*R*,2*R*)-CHDA 13. The synthesis was carried out as described for **12**, starting from 0.100 g (0.280 mmol) of **9**, 0.071 g (0.280 mmol) of (*S*)-**1** and a catalytic quantity of Et_2SnCl_2 to yield 0.140 g (83%) of **13.** Analytically pure **13** was obtained by crystallization from toluene/heptane 1/1. Mp (decomposition) 254°C; $[\alpha]_D^{22}=-1165.6$ (*c* 0.186, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.49–1.71 (m, 3H, -C*H*$_2$- CHDA), 1.79–2.13 (m, 4H, -C*H*$_2$- CHDA), 2.13 (s, 3H, -C*H*$_3$), 2.13–2.24 (1H, -C*H*$_2$- CHDA), 2.41–2.59 (m, 3H, -C*H*H-CH$_2$-), 2.63–2.85 (m, 3H, -C*H*H-CH$_2$-), 2.91–3.22 (m, 6H, -C*H*H-CH$_2$-), 3.23–3.48 (m, 4H, -C*H*H-CH$_2$-, 1H, -C*H*N=), 3.77–3.89 (m, 1H, -C*H*N=), 6.10 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.15 (d, 1H, $^3J=7.8$ Hz, PC arom. H′), 6.20 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.26–6.34 (m, 2H, PC arom. H), 6.36 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.39 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.46 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.54 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.56 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.82 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom H), 6.96 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 8.17 (s, 1H, -C*H*=N), 14.07 (br. s., 1H, -O*H*). 15.55 (br. s., 1H, -O*H*). Anal. calcd for $C_{41}H_{44}N_2O_2$ (596.78): C, 82.51; H, 7.43; N, 4.70. Found: C, 82.09; H, 7.47; N, 4.55; MS (70 eV): m/z (%) = 597 (18, M^+), 160 (64), 146 (29), 104 (100).

3.3.4. [(*R*)-AHPC][(*R*)-FHPC](1*R*,2*R*)-CHDA 14. The synthesis was carried out as described for **12**, starting from 0.100 g (1.540 mmol) of **10**, 0.071 g (0.280 mmol) of (*R*)-**1** and a catalytic quantity of Et_2SnCl_2 to yield 0.145 g (86%) of **14.** Analytically pure **14** was obtained

by crystallization from toluene/heptane 1/1. Mp (with slight decomposition) 255.5–256.5°C; $[\alpha]_D^{22}=+612.4$ (*c* 0.226, $CHCl_3$); ^1H NMR (($CDCl_3$): δ 1.42–1.8 (m, 4H, -C*H*$_2$- CHDA), 1.82–2.13 (m, 3H, -C*H*$_2$- CHDA), 2.25–2.35 (s, 3H, -C*H*$_3$, 1H, -C*H*$_2$- CHDA), 2.45–2.65 (m, 2H, -C*H*H-CH$_2$-), 2.70–2.85 (m, 1H, -C*H*H-CH$_2$-), 2.84–3.35 (m, 10H, -CH$_2$-), 3.37–3.60 (m, 3H, -C*H*H-CH$_2$-), 3.70–3.85 (m, 2H, -C*H*N=), 6.13 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.19 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.26 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.38 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.43 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.45–6.65 (m, 5H, PC arom. H), 6.87 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 7.01 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 8.40 (s, 1H, -C*H*=N), 14.50 (br. s., 1H, -O*H*). 15.65 (br. s., 1H, -O*H*). Anal. calcd for $C_{41}H_{44}N_2O_2$ (596.78): C, 82.51; H, 7.43; N, 4.70. Found: C, 82.67; H, 7.32; N, 4.82; MS (70 eV): *m*/*z* (%) = 597 (14, M^+), 596 (29), 160 (60), 104 (100).

3.3.5. [(*S*)-BHPC][(*R*)-FHPC]EDA 15. The synthesis was carried out as described for **12**, starting from 0.100 g (0.270 mmol) of **8**, 0.068 g (0.280 mmol) of (*R*)-**1** and a catalytic quantity of Et_2SnCl_2 to yield 0.127 g (73%) of **15.** Analytically pure **15** was obtained by crystallization from heptane. Mp 128–130°C; $[\alpha]_D^{22}=-175.1$ (*c* 0.18, $CHCl_3$); ^1H NMR (($CDCl_3$): δ 1.70–1.85 (m, 1H, -C*H*H-CH$_2$-), 2.10–2.30 (m, 2H, -C*H*$_2$-), 2.52–2.67 (m, 2H, -C*H*$_2$-CH$_2$-), 2.73–2.95 (m, 3H, -C*H*$_2$-), 2.96–3.17 (m, 4H, -C*H*$_2$-), 3.18–3.25 (m, 1H, -CH*H*-CH$_2$-), 3.35–3.60 (m, 3H, -C*H*$_2$-), 3.63–3.75 (m, 1H, -CH*H*-CH$_2$-), 3.95–4.10 (m, 2H, -C*H*N=, 1H, -C*H*H-CH$_2$-), 6.00–6.10 (m, 2H, PC arom. H), 6.15 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.30–6.48 (m, 5H, PC arom. H), 6.50 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.52 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.73 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 7.00 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 7.31–7.42 (m, 2H, arom. H), 7.44–7.60 (m, 3H, arom. H), 8.40 (s, -C*H*=N, 1H), 14.01 (br. s, 1H, -O*H*). 16.40 (br. s, 1H, -O*H*). Anal. calcd for $C_{42}H_{40}N_2O_2$ (604.74): C, 83.41; H, 6.67; N, 4.63. Found: C, 83.56; H, 6.82; N, 4.50; MS (70 eV): *m*/*z* (%) = 605 (14, M^+), 604 (30), 250 (30), 236 (34), 224 (14), 160 (18), 147 (16), 104 (100).

3.3.6. [(*S*)-AHPC][(*R*)-FHPC](1*R*,2*R*)-CHDA 16. The synthesis was carried out as described for **12**, starting from 0.100 g (0.280 mmol) of **9**, 0.710 g (0.280 mmol) of (*R*)-**1** and a catalytic quantity of Et_2SnCl_2 to yield 0.148 g (88%) of **16.** Analytically pure **16** was obtained by crystallization from toluene/heptane 5/1. Mp 251–252°C; $[\alpha]_D^{22}=-420.0$ (*c* 0.220, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.42–1.60 (m, 2H, -C*H*$_2$- CHDA), 1.62–1.78 (m, 1H, -C*H*$_2$- CHDA), 1.79–2.13 (m, 5H, -C*H*$_2$- CHDA), 2.45 (s, 3H, -C*H*$_3$), 2.40–2.70 (br. 4H, -CH*H*-CH$_2$-), 2.72–3.20 (m, 8H, -C*H*H-CH$_2$-), 3.22–3.36 (m, 2H, -C*H*H-CH$_2$-), 3.37–3.55 (m, 1H, -C*H*N=, 2H, -C*H*H-CH$_2$-), 3.90–4.00 (m, 1H, -C*H*N=), 5.50 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.00 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.10 (d, 1H $^3J=7.8$ Hz, PC arom. H), 6.26-6.45 (m, 7H, PC arom. H), 6.56 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.82 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom H), 8.17 (s, 1H, -C*H*=N), 14.20 (br. s, 1H, -O*H*). 16.00 (br. s, 1H, -O*H*). Anal. calcd for $C_{41}H_{44}N_2O_2$ (596.78): C, 82.51; H, 7.43; N, 4.70. Found: C, 82.69; H, 7.43; N, 4.59; MS (70 eV): *m*/*z* (%) = 597 (20, M^+), 596 (34), 160 (60), 146 (30), 104 (100).

3.3.7. [(*R*)-AHPC][(*S*)-FHPC](1*R*,2*R*)-CHDA 17. The synthesis was carried out as described for **12**, starting from 0.100 g (0.280 mmol) of **10**, 0.071 g (0.280 mmol) of (*S*)-**1** and a catalytic quantity of Et_2SnCl_2 to yield 0.150 g (90%) of **17.** Analytically pure **17** was obtained by crystallization from toluene/heptane 2/1. Mp 209.5–211°C; $[\alpha]_D^{22}=-371.4$ (*c* 0.178, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.43–1.82 (m, 4H, -C*H*$_2$- CHDA), 1.87–2.09 (m, 4H, -C*H*$_2$- CHDA, 1H, -C*H*H-CH$_2$-), 2.19 (s, 3H, -C*H*$_3$), 2.41–2.53 (m, 2H, -C*H*H-C*H*$_2$–), 2.50–2.66 (m, 1H, -CH*H*-CH$_2$-), 2.66–2.89 (m, 4H, -CH*H*-CH$_2$-), 2.89–3.00 (m, 1H, -C*H*H-CH$_2$-), 3.00–3.27 (m, 4H, -C*H*H-CH$_2$-), 3.28–3.35 (m, 1H, -C*H*H-CH$_2$-), 3.36–3.55 (m, 2H, -C*H*$_2$-CH$_2$-, 1H, -C*H*N=), 3.77–3.89 (m, 1H, -C*H*N=), 5.78 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.00 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.13 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.27 (d, 1H, $^3J=7.8$ Hz, PC arom. H), 6.30 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.39–6.48 (m, 3H, PC arom. H), 6.46 (d, 1H, $^3J=7.8$ Hz, PC arom H), 6.56 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 6.74 (dd, 1H, $^3J=7.8$, $^4J=$ 1.8 Hz, PC arom. H), 6.91 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, PC arom. H), 8.40 (s, 1H -C*H*=N), 14.30 (br. s, 1H, -O*H*). 15.60 (br. s, 1H, -O*H*). Anal. calcd for $C_{41}H_{44}N_2O_2{\cdot}1.5(C_7H_8)$ (734.90): C, 84.18; H, 7.62; N, 3.83. Found: C, 84.41; H, 7.74; N, 4.07; MS (70 eV): *m*/*z* (%) = 597 (25, M^+), 596 (52), 160 (65), 145 (34), 104 (100).

3.4. Preparation of salen 18

3.4.1. *meso*-[(*S*)-AHPC][(*R*)-AHPC]EDA 18. The synthesis was carried out as described for **4**, starting from 0.300 g (1.130 mmol) of *rac*-**2**, 0.075 ml (0.068 g, 1.130 mmol) of EDA and a catalytic quantity of Et_2SnCl_2 to yield 0.320 g (98%) of the diastereomeric mixture of *chiral*-/*meso*-[AHPC]$_2$EDA with 1/1 ratio (determined by ^1H NMR). The diastereomeric mixture was separated by column chromatography (SiO_2, heptane/ethylacetate/Et_3N 70/10/0.5). From the combined fractions with R_f 0.45 0.094 g (30%) of *chiral*-[(*S**)-AHPC]$_2$EDA **4** was obtained with de 65% (according to ^1H NMR analysis); from the combined fractions with R_f 0.35 0.063 g (20%) of **18** with de 65% (^1H NMR analysis) was obtained. The mixed fraction (0.163 g) was also obtained. Diastereomerically pure **18** (0.022 g, 7%) was obtained by crystallization of the fraction with de 65% from toluene. Mp (decomposition) 243°C; ^1H NMR ($CDCl_3$): δ 2.42 (s, 3H, -C*H*$_3$), 2.43–2.53 (m, 1H, -C*H*H-CH$_2$-), 2.70–2.80 (m, 1H, -C*H*H-CH$_2$-), 2.90–3.15 (m, 4H, -C*H*H-CH$_2$-), 3.33–3.43 (m, 2H, -C*H*H-CH$_2$-), 3.93–4.05 (m, 2H, -C*H*$_2$N=), 6.20 (d, 1H, $^3J=7.8$ Hz, H-7 or H-8), 6.36 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-12 or H-13), 6.39 (d, 1H, $^3J=7.8$ Hz, H-7 or H-8), 6.47 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-15 or H-16), 6.61 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-15 or H-16), 6.96 (dd, 1H, $^3J=7.8$, $^4J=1.8$ Hz, H-12 or H-13), 15.3 (br.

s, 1H, -O*H*). Anal. calcd for $C_{38}H_{40}N_2O_2$ (556.10): C, 82.08; H, 7.19; N, 5.04. Found: C, 81.96; H, 7.40; N, 5.06; MS (70 eV): m/z (%) = 556 (28, M^+), 249 (23), 162 (40), 145 (50), 104 (100).

3.5. X-Ray crystallographic study of salens 6, 12, 17 and 18

X-Ray structure of 6: crystal data: $C_{42}H_{46}N_2O_2 \cdot 0.5(C_6H_6)$, MW = 610.20 g mol^{-1}, orange plates, monoclinic, space group $C2$, $Z = 4$, $a = 28.943(3)$, $b = 8.2893(9)$, $c = 18.860(2)$ Å, $\beta = 128.417(2)°$, $R_1 = 0.0446$.

X-Ray structure of 12: crystal data: $C_{42}H_{40}N_2O_2$, MW = 604.76 g mol^{-1}, orange needles, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 8.415(1)$, $b = 13.635(2)$, $c = 27.214(3)$ Å, $R_1 = 0.0701$.

X-Ray structure of 17: crystal data: $C_{41}H_{44}N_2O_2 \cdot (C_7H_8)$, MW = 596.20 g mol^{-1}, orange plates, monoclinic, space group $P2_1$, $Z = 4$, $a = 16.891(2)$, $b = 9.210(1)$, $c = 24.003(7)$ Å, $\beta = 98.82(1)°$, $R_1 = 0.0578$

X-Ray structure of 18: crystal data: $C_{38}H_{40}N_2O_2 \cdot (C_6H_6)$ MW = 556.20 g mol^{-1}, yellow plates, monoclinic, space group $P2_1$, $Z = 4$, $a = 7.883(2)$, $b = 22.751(5)$, $c = 9.548(2)$ Å, $\beta = 95.24(3)$, $R_1 = 0.0809$.

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector for **6**, **12** and **17** at 110 K and CAD4 Enraf–Nonius for **18** at 293 K, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by the full-matrix least-squares against F^2 in anisotropic (for no-hydrogen atoms) and isotropic (for H atoms) approximation. All calculations were performed on an IBM PC/AT using the SHELXTL software [G. M. Sheldrick, SHELXTL-97, Version 5.10, Bruker AXS Inc., Madison, WI, 53719, USA]. Crystallographic data for structures **6**, **12**, **17** and **18** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications (Ref. Numbers CCDC 203090–203093, respectively). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

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