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INTRAMOLECULAR VS. INTERMOLECULAR INDUCTION IN THE DIASTEREOSELECTIVE CATALYTIC REDUCTION OF ENANTIOMERICALLY PURE KETONES WITH BORANE IN THE PRESENCE OF CYCLIC β-AMINO ALCOHOLS

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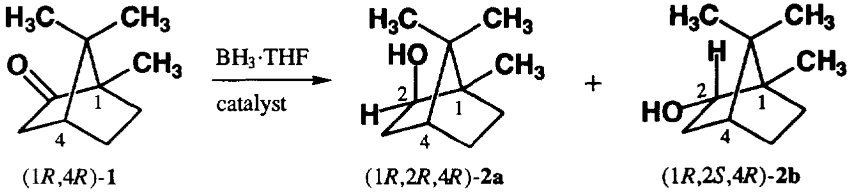
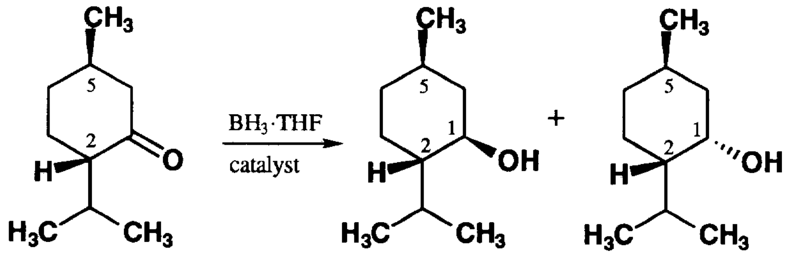
Abstract: Asymmetric reduction of various enantiomerically pure ketones was carried out by using oxazaborolidine catalysts with a variety of achiral and chiral ligands. The efficiency of chiral 1,2-amino alcohols as well as the effect of the stereogenic centers in the substrate on the catalytic asymmetric reduction were studied. It was found that the corresponding secondary alcohols were obtained with extremely high stereoselectivities with the proper choice of chiral ligands although a considerably large double asymmetric induction was observed in some cases.

Introduction

The stereoselective synthesis of optically active secondary alcohols is a well studied theme in organic chemistry. In particular the 1,3,2-oxazaborolidines[1], borane modified with chiral β-amino alcohols, show a high ability to promote the asymmetric reduction of prochiral ketones and the desired end products were obtained in *ee*'s up to 100 %.



In earlier reports we described the synthesis of chiral ligands derived from α-amino acids[2] and their succesful application in asymmetric transformation reactions such as the enantioselective addition of diethylzinc to aldehydes and the enantioselective reduction of prochiral ketones with $BH_3 \cdot THF$.

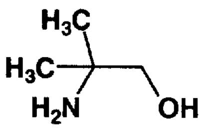


(2*S*,5*R*)-3 (1*R*,2*S*,5*R*)-**4a** (1*S*,2*S*,5*R*)-**4b**

Now, we would like to describe the stereoselective reduction of enantiomeric pure ketones like camphor (1*R*,4*R*)-**1** and menthone (2*S*,5*R*)-**3**. One of the most interesting points involved in this reaction is whether the stereogenic centers of the substrate molecule have a strong influence upon the way of asymmetric induction by chiral catalyst or not. This was studied by other groups[3] e.g. for asymmetric hydrogenation of dehydrodipeptides[4] and the addition of dialkylzincs to aldehydes[5].

Results and discussion

Treatment of the chiral ketones (1*R*,4*R*)-**1** and (2*S*,5*R*)-**3** with borane in the presence of achiral or chiral aminoalcohols in THF at 30°C gave the secondary alcohols **2a,b** or **4a,b** in high chemical yields (see table 1). 2-Amino-2-methyl-1-propanol **5** has been used as an example of achiral aminoalcohols. On the other hand the following chiral aminoalcohols have been used as ligands in the reduction of chiral ketones (1*R*,4*R*)-**1** and (2*S*,5*R*)-**3** with borane: (*S*)-1-(1'amino1'-phenylmethyl)cyclopentanol (*S*)-**6a**, (*R*)-1-(1'-amino-1'-phenylmethyl)cyclopentanol[6] (*R*)-**6b**, (*S*)-1-(1'amino1'-phenylmethyl)cyclohexanol (*S*)-**7**, (*S*)-1-pyrrolidine-2-yl-cyclopentanol (*S*)-**8**, (*S*)-1-pyrrolidine-2-yl-cyclohexanol (*S*)-**9**, (*S*)-2-(diphenyl-hydroxymethyl)-pyrrolidine[7] (*S*)-**10a** and (*R*)-2-(diphenylhydroxymethyl)pyrrolidine[8] (*R*)-**10b**.



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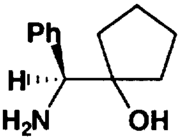
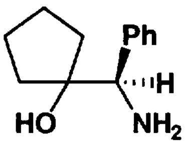
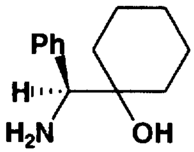


(*S*)-**6a**

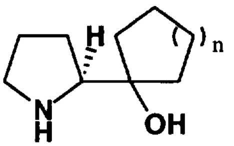


(*R*)-**6b**

Conversion of the β-amino alcohols **5**, (*S*)-**6a**, (*R*)-**6b**, (*S*)-**7**, (*S*)-**8**, (*S*)-**9**, (*S*)-**10a** and(*R*)-**10b** to oxazaborolidines was accomplished by treating with BH_3·THF. The oxazaborolidines have been prepared *in situ* and have not been isolated.



(*S*)-**7**



n=1: (*S*)-**8**
n=2: (*S*)-**9**

The results obtained with oxazaborolidines as catalysts for the reduction of chiral ketones by borane in THF are summarized in table 1.

Table 1. Diastereoselective reduction of camphor (1*R*,4*R*)-**1** and menthone (2*S*,5*R*)-**3**

entry	ketone	reducing agent	ref.	yield [%]	alcohol
1	(1*R*,4*R*)-**1**	$LiAlH_4$	9	91	**2a**:**2b** = 90 : 10
2	(1*R*,4*R*)-**1**	$(\eta_5\text{-}C_5H_5)_2Zr(H)Cl$	10	44	**2a**:**2b** = 75 : 25
3	(1*R*,4*R*)-**1**	$TiCl_4$-Mg	11	90	**2a**:**2b** = 64 : 36
4	(1*R*,4*R*)-**1**	10 mol%**5**/BH_3	–	94	**2a**:**2b** = 59 : 41[a)]
5	(1*R*,4*R*)-**1**	10 mol%(*S*)-**6a**/BH_3	–	100	**2a**:**2b** = >95 : 5[a)]
6	(1*R*,4*R*)-**1**	10 mol%(*R*)-**6b**/BH_3	–	91	**2a**:**2b** = 6 : 94[a)]
7	(1*R*,4*R*)-**1**	10 mol%(*S*)-**7**/BH_3	–	91	**2a**:**2b** = 90 : 10[a)]
8	(1*R*,4*R*)-**1**	10 mol%(*S*)-**8**/BH_3	–	93	**2a**:**2b** = 92 : 8[a)]
9	(1*R*,4*R*)-**1**	10 mol%(*S*)-**9**/BH_3	–	90	**2a**:**2b** = 84 : 16[a)]
10	(1*R*,4*R*)-**1**	10 mol%(*S*)-**10a**/BH_3	–	95	**2a**:**2b** = >95 : 5[a)]
11	(1*R*,4*R*)-**1**	10 mol%(*R*)-**10b**/BH_3	–	85	**2a**:**2b** = 10 : 90[a)]
12	(2*S*,5*R*)-**3**	$Na_2S_2O_4$	12	90	**4a**:**4b** = 66 : 34
13	(2*S*,5*R*)-**3**	$Na_2S_2O_4$/*β*-cyclodextrine	12	76	**4a**:**4b** = 78 : 22
14	(2*S*,5*R*)-**3**	10 mol%**5**/BH_3	–	94	**4a**:**4b** = 62 : 38[a)]
15	(2*S*,5*R*)-**3**	10 mol%(*S*)-**6a**/BH_3	–	91	**4a**:**4b** = 86 : 14[a)]
16	(2*S*,5*R*)-**3**	10 mol%(*R*)-**6b**/BH_3	–	97	**4a**:**4b** = 25 : 75[a)]
17	(2*S*,5*R*)-**3**	10 mol%(*S*)-**10a**/BH_3	–	92	**4a**:**4b** = 94 : 6[a)]
18	(2*S*,5*R*)-**3**	10 mol%(*R*)-**10b**/BH_3	–	82	**4a**:**4b** = 27 : 73[a)]

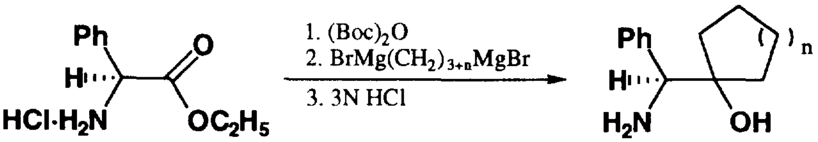
[a] The ratio of the alkohols **2a**/**2b** and **4a**/**4b** was determined by ^{1}H-NMR analysis of the recovered residue.

A variety of achiral hydride reagents were previously observed to form predominantely one diastereomer in the reduction of camphor and menthone. As can be seen from table 1, the achiral aminoalkohol 2-amino-2-methyl-1-propanol **5** catalyses the reaction with a diastereoselective ratio of **2a**:**2b**=59:41 and **4a**:**4b**=62:38. These results show that the chirality of the substrates is preferable to construct the alcohols **2a** or **4a**. This selectivity can also be observed with other achiral reducing agents, for example $LiAlH_4$.

The use of borane and catalytic amounts of chiral aminoalcohols with the right absolute configuration leads to an increased diastereoselectivity (chiral double recognition). On the other hand oxazaborolidine catalyzed reductions managed to override the preference observed in the uncatalyzed reductions. The chiral catalyst (*S*)-**6a**, (*R*)-**6b**, (*S*)-**7**, (*S*)-**8**, (*S*)-**9**, (*S*)-**10a** and(*R*)-**10b** can clearly control the stereochemistry of the reaction to a large degree. Thus, the stereoselectivity of the new stereogenic center is mainly affected by the stereochemistry of the chiral catalyst (e.g. entry 5 compared with entry 6) and not by the stereogenic centers in ketones (1*R*,4*R*)-**1** or (2*S*,5*R*)-**3**. The catalytic reduction can generate either the *S* or *R* configuration at the new stereogenic center, although the chiral centers of the substrate have a strong influence upon the diastereoselectivity in reductions with achiral agents. The aminoalcohols **6-10** are available in both configurations in contrast to *β*-cyclodextrine (entry 13). We obtained similar results in the asymmetric reduction of other chiral ketones, for example steroids[13].

Synthesis of catalysts

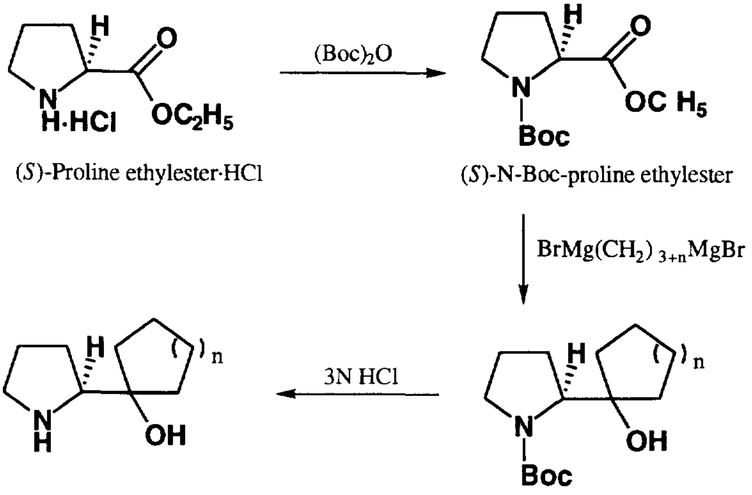
The synthesis of the amino alcohols (*R*)-**6b**, (*S*)-**10a** and (*R*)-**10b** is described in the literature[6-8]. The new cyclic amino alcohols (*S*)-1-(1'amino1'-phenylmethyl)cyclopentanol (*S*)-**6a**, (*S*)-1-(1'amino1'-phenylmethyl)cyclohexanol (*S*)-**7**, (*S*)-1-pyrrolidine-2-yl-cyclo-pentanol (*S*)-**8** and (*S*)-1-pyrrolidine-2-yl-cyclohexanol (*S*)-**9** were obtained *via* an improved procedure from the corresponding amino acids.



(*S*)-Phenylglycine ethylester·HCl

n=1: (*S*)-**6a**
n=2: (*S*)-**7**

Previously, we have synthesized alicyclic β-amino alcohols by a reaction of amino acid ethyl ester hydrochlorides with 1,4-bis(brommagnesio)butane. This method is not applicable to secondary amino acids such as proline and is limited to the formation of five-membered ring systems. These products are usually not isolable because of extensive contamination by impurities due to several side reactions.



(*S*)-Proline ethylester·HCl

(*S*)-N-Boc-proline ethylester

n=1: (*S*)-**8**
n=2: ( )-**9**

n=1: (*S*)-N-(Boc)-**8**
n=2: (*S*)-N-(Boc)-**9**

We found that the conversion of the corresponding N-Boc-protected amino acid esters[14] was much more effective for the synthesis of (primary *and* secondary) amino alcohols with a cyclopentanol- or cyclohexanol building block. In addition to higher yields (up to 82.5 %) the utilization of the Boc-protecting group eases the work-up either by crystallization or (flash-) chromatography.

Experimental Section

All reactions were carried out in oven dried glassware, under argon atmosphere and using anhydrous solvents. Melting points were taken on a melting point apparatus according to Dr. Linström and are uncorrected. Optical rotations were measured on a Perkin-Elmer automatic polarimeter. IR spectra were recorded on a Philips PU 9706 spectrophotometer. The ^{1}H-NMR and ^{13}C-NMR spectra were registrated on a Bruker AM 300 spectrometer using TMS as internal standard. Mass spectra were recorded on a Finnigan-MAT 212 (data system 300; CI, *i*-butane). Elemental analyses (C, H, N) were performed on a Carlo Erba Stumentalione (MOD 1104) analyzer. Commercially available chemicals were used. The amino alcohols (*R*)-**6b**, (*S*)-**10a** and (*R*)-**10b** were prepared according to the literature[6-8].

Asymmetric reduction of chiral ketones (typical procedure): In a typical procedure a mixture of the respective ketone (5 mmol) in 5 mL dry THF was slowly added within 1 hour to a solution of the catalyst **5**, (*S*)-**6a**, (*R*)-**6b**, (*S*)-**7**, (*S*)-**8**, (*S*)-**9**, (*S*)-**10a** and(*R*)-**10b** (10 mol%) and borane-THF complex (5.5 mmol) in 5 mL dry THF at 30°C. After stirring for 3 hours at 30°C the reaction mixture was hydrolyzed with 12.5 mL 2 N HCl and extracted three times with 10 mL *tert*-butylmethyl ether. The combined organic layers were sucessivley washed with 12.5 mL 2N NaOH and 10 mL NaCl solution, dried ($MgSO_4$) and concentrated under reduced pressure. The obtained crude product was analysed by ^{1}H-NMR in order to avoid enrichement of one diastereomer by crystallization; for *H*-COH, δ 3.60 ppm for **2a** and 4.00 ppm for **2b**; 3.38 ppm for **4a** and 4.10 ppm for **4b**.

N-Boc-Aminoalcohols: (*S*)-N-Boc-6a, (*S*)-N-Boc-7, (*S*)-N-Boc-8, (*S*)-N-Boc-9;
General procedure

A Grignard reagent (160 mmol) was prepared under argon atmosphere from magnesium (134 mmol) and 1,4-dibrombutane respectively 1,5-dibrompentane (65 mmol) in dry THF (200 mL). The ethyl ester of N-Boc-protected amino acids (20 mmol) was added to the bis(brommagnesio)alkane solution over 30 min at 0 to 5°C with ice-salt bath cooling. After the addition, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. After 16 hours the reaction mixture was hydolyzed with saturateted NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic extracts were evaporated under reduced pressure to remove the solvents. The residue was dissolved in 150 mL diethyl ether, washed with brine, dried over anhydrous magnesium sulfate and concentrated again under reduced pressure. The obtained crude products were purified by recristallization or flash chromatography. The individual work-up is described below.

(*S*)-N-(t-Butyloxycarbonyl)-1-(1'-amino-1'-phenylmethyl)cyclopentanol (*S*)-N-Boc-6a: work-up: purification by chromatography (silica gel 60, eluent: *n*-hexane / EtOAc 7 : 3, R_f-value: 0.55); yield: 4.19 g, (71.9%), m.p. 110-112 °C; $[\alpha]_{20}^{D}$ = + 16.5 (*c* = 1, $CHCl_3$); IR (KBr): ν = 3550-3350 cm^{-1} (NH, OH), 1665

(C=O); ^{1}H-NMR ($CDCl_3$): δ = 1.08-1.88 (m, 18H, cyclo-CH_2, *tert*-butyl-CH_3, OH), 4.58 (d, *J* = 8.7 Hz, 1H, 1'-H), 5.73 (d, *J* = 8.5 Hz, 1H, NH), 7.25-7.36 (m, 5H, Ar-H); ^{13}C-NMR ($CDCl_3$): δ= 23.56, 29.24, 37.84, 39.02 (4C, cyclopentyl-CH_2), 28.34 (3C, *tert*-butyl-CH_3), 61.94 (1C, C-1'), 79.32 (1C, C–O–C), 84.54 (1C, cyclopentyl-C1), 127.36-128.24 (5C, Ar-C), 140.26 (1C, q.-Ar-C), 155.52 (1C, C=O); MS (CI, *i*-butane): 292 (MH^+, 100%); Anal. calc. for $C_{17}H_{25}NO_3$ (291.39): C, 70.07; H, 8.65; N, 4.81. Found: C, 70.15, H. 8.68; N, 4.79.

(*S*)-N-(t-Butyloxycarbonyl)-1-(1'-amino-1'-phenylmethyl)cyclohexanol (*S*)-N-Boc-7: work-up: crystallization of the crude product from CH_2Cl_2/PE; yield: 2.56 g, (41.9%); m.p. 124-126 °C; $[\alpha]_{20}^{D}$ = + 8.8 (*c* = 1, $CHCl_3$); IR (KBr): ν = 3520-3340 cm^{-1} (NH, OH), 1660 (C=O); ^{1}H-NMR ($CDCl_3$): δ = 1.08-1.60 (m, 19H, cyclo-CH_2, *tert*-butyl-CH_3), 1.85 (s, 1H, OH), 4.56 (d, *J* = 9.1 Hz, 1H, 1'-H), 5.62 (d, *J* = 8.3 Hz, 1H, NH), 7.25-7.35 (m, 5H, Ar-H); ^{13}C-NMR ($CDCl_3$): δ = 21.60, 21.90, 25.37, 34.94, 35.72 (5C, cyclohexyl-CH_2), 28.37 (3C, *tert*-butyl-CH_3), 61.91 (1C, C-1'), 73.38 (1C, cyclohexyl-C-1), 79.31 (1C, C–O–C), 127.10-128.11 (5C, Ar-C), 139.59 (1C, q.-Ar-C), 155.76 (1C, C=O); MS (CI, *i*-butane): 306 (MH^+, 100%); Anal. calc. for $C_{18}H_{27}NO_3$ (305.42): C, 70.79; H, 8.91; N, 4.59. Found: C, 70.84, H. 8.92; N, 4.48.

(*S*)-N-(t-Butyloxycarbonyl)-1-pyrrolidine-2-yl-cyclopentanol (*S*)-N-Boc-8: work-up: crystallization of the crude product from CH_2Cl_2/*n*-hexane or purification by flash chromatography (silica gel 60, eluent: *n*-hexane / EtOAc 8 : 2, R_f-value: 38); yield: 4.21 g, (82.5%); m.p. 108 °C; $[\alpha]_{20}^{D}$ = – 93.3 (*c* = 0.4, CH_2Cl_2); IR (KBr): ν = 3700-3400 cm^{-1} (OH), 1690-1650 (C=O); ^{1}H-NMR ($CDCl_3$): δ = 1.46 (s, 9H, *tert*-butyl-CH_3), 1.49–1.74 (m, 8H, cyclo-CH_2), 1.74-1.93, 1.93-2.14 (2m, 4H, 2xH3', 2xH4'), 3.13-3.26 (m, 1H, 1xH5'), 3.58-3.72 (m, 1H, 1xH5'), 3.97-4.09 (m, 1H, H2'), 5.01 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$): δ = 23.48, 24.35, 28.73, 30.94, 35.42, 38.52 (6C, cyclopentyl-CH_2, C3', C4'), 28.42 (3C, *tert*-butyl-CH_3), 48.28 (1C, C5'), 65.10 (1C, C2'), 80.03 (1C, C–O), 85.49 (1C, C–OH), 159.48 (1C, C=O); MS (CI, *i*-butane): 256 (MH^+, 100%); Anal. calc. for $C_{14}H_{25}NO_3$ (255.18): C, 65.83; H, 9.87; N, 5.49. Found: C, 65.90; H, 9.89; N, 5.52.

(*S*)-N-(t-Butyloxycarbonyl)-1-pyrrolidine-2-yl-cyclohexanol (*S*)-N-Boc-9: work-up: crystallization of the crude product from CH_2Cl_2/*n*-hexane or purification by flash chromatography (silica gel 60, eluent: *n*-hexane / EtOAc 7 : 3, R_f-value: 0.65); yield: 2.25 g, (41.8%); m.p. 83 °C; $[\alpha]_{20}^{D}$ = – 78.9 (*c* = 1, CH_2Cl_2); IR (KBr): ν = 3680-3400 cm^{-1} (OH), 1685-1650 (C=O); ^{1}H-NMR ($CDCl_3$): δ = 0.97-2.06 (m, 14H, cyclo-CH_2, 2xH3', 2xH4'); 1.44 (s, 9H, *tert*-butyl-CH_3); 3.05-3.19 (m, 1H, 1xH5'), 3.54-3.72 (m, 1H, 1xH5'), 3.78-3.91 (m, 1H, 1xH2'), 5.06 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$): δ = 21.31, 21.37, 24.48, 26.07, 27.91, 30.45, 35.58 (7C, cyclohexyl-CH_2, C3', C4'), 28.39 (3C, *tert*-butyl-CH_3), 48.12 (1C, C5'), 67.17 (1C, C2'), 74.17 (1C, C-OH), 80.19 (1C, C–O–C), 157.81 (1C, C=O); MS (CI, *i*-butane): 270 (MH^+, 100%); Anal. calc. for $C_{15}H_{27}NO_3$ (269.38): C, 66.88; H, 10.10; N, 5.20. Found: C, 66.85, H, 10.14; N, 5.21.

Aminoalcohols (*S*)-6a, (*S*)-7, (*S*)-8, (*S*)-9; General procedure

The protected amino alcohol (5 mmol) was treated at room temperature with 50 mL 3 N HCl in 50 mL acetic acid. After 3 h the mixture was concentrated under reduced pressure and the residue washed twice with diethyl ether. The aqueous layer was basified with 20 % aq NaOH followed by an extraction with CH_2Cl_2 (4 x 40 mL). The combined organic layers were dried over $MgSO_4$. Evaporation under vacuo afforded the pure amino alcohol.

(*S*)-1-(1'-Amino-1'-phenylmethyl)cyclopentanol (*S*)-6a: yield: 0.94 g, (98.3%), m.p. 82-84 °C; $[\alpha]_{20}^{D}$ = + 22.2 (*c* = 1, $CHCl_3$); IR (KBr): ν = 3340-3000 cm^{-1} (NH, OH); ^1H-NMR ($CDCl_3$): δ = 1.19-1.78 (m, 8H, cyclo-CH_2), 2.04 (s, 3H, NH_2, OH), 3.88 (s, 1H, 1'-H), 7.26-7.38 (m, 5H, Ar-H); ^{13}C-NMR ($CDCl_3$): δ = 23.62, 23.70 (2C, cyclopentyl-C-3 and C-4), 36.1, 38.1 (2C, cyclopentyl-C-2 and C-5) 63.26 (1C, C-1'), 83.97 (1C, cyclopentyl-C-1), 127.21-128.48 (5C, Ar-C), 142.91 (1C, q.-Ar-C); MS (CI, *i*-butane): 192 (MH^+, 100%); Anal. calc. for $C_{12}H_{17}NO$ (191.27): C, 75.35; H, 8.96; N, 7.32. Found: C, 75.20, H. 8.98; N, 7.28.

(*S*)-1-(1'-Amino-1'-phenylmethyl)cyclohexanol (*S*)-7: yield: 0.98 g, (95.5%), m.p. 62-64 °C; $[\alpha]_{20}^{D}$ = – 3.5 (*c* = 1, $CHCl_3$); IR (KBr): ν =3340-3180 cm^{-1} (NH, OH); ^1H-NMR ($CDCl_3$): δ = 1.09-1.78 (m, 10H, cyclo-CH_2), 2.45 (s, 3H, NH_2, OH), 3.77 (s, 1H, 1'-H), 7.27-7.33 (m, 5H, Ar-H); ^{13}C-NMR ($CDCl_3$): δ = 21.67, 21.91, 25.73, 33.37, 35.58 (5C, cyclohexyl-C) 64.00 (1C, C-1'), 72.41 (1C, cyclopentyl-C-1), 127.26-128.07 (5C, Ar-C), 141.95 (1C, q.-Ar-C); MS (CI, *i*-butane): 206 (MH^+, 100%); Anal. calc. for $C_{13}H_{19}NO$ (205.30): C, 76.06; H, 9.33; N, 6.82. Found: C, 76.10, H. 9.31; N, 6.85.

(*S*)-1-Pyrrolidine-2-yl-cyclopentanol (*S*)-8: yield: 0.77 g, (99.3%); m.p. 34 °C; $[\alpha]_{20}^{D}$ = – 36.9 (*c* = 0.3, CH_2Cl_2); IR (KBr): ν = 3680-3410 cm^{-1} (NH, OH); ^1H-NMR ($CDCl_3$): δ = 1.31–1.89 (m, 12H, cyclo-CH_2, 2xH3', 2xH4'), 2.77-3.18 (m, 4H, NH, 2xH5', H2'); ^{13}C-NMR ($CDCl_3$): δ = 23.97, 25.83, 26.27, 36.16, 39.72, 46.81 (6C, cyclopentyl-CH_2, C3', C4'), 66.19 (1C, C5'), 76.63 (1C, C2'), 81.75 (1C, C-OH); MS (CI, *i*-butane): 156 (MH^+, 100%); Anal. calc. for $C_9H_{17}NO$ (155.13): C, 69.62; H, 11.04; N, 9.03. Found: C, 69.68; H, 11.09; N, 9.05.

(*S*)-1-pyrrolidine-2-yl-cyclohexanol (*S*)-9: yield: 0.80 g, (94.6%); m.p. 54 °C; $[\alpha]_{20}^{D}$ = – 46.7 (*c* = 0.5, CH_2Cl_2); IR (KBr): ν = 3690-3430 cm^{-1} (NH, OH); ^1H-NMR ($CDCl_3$): δ = 1.09–1.34, 1.36–1.83 (2m, 15H, cyclo-CH_2, 2xH3', 2xH4', NH), 2.66 (s, 1H, OH), 2.81-3.10 (m, 3H, 2xH5', H2'); ^{13}C-NMR ($CDCl_3$): δ = 21.92, 21.94, 24.97, 25.87, 26.01, 33.87, 37.13 (7C, cyclohexyl-CH_2, C3', C4'), 46.63 (1C, C5'), 65.88 (1C, C2'), 70.52 (1C, C-OH); MS (CI, *i*-butane): 170 (MH^+, 100%); Anal. calc. for $C_{10}H_{19}NO$ (169.15): C, 70.94; H, 11.32; N, 8.28. Found: C, 70.99, H, 11.35; N, 8.30.

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