163. Chiral Diselenides from Benzylamines: Catalysts in the Diethylzinc Addition to Aldehydes

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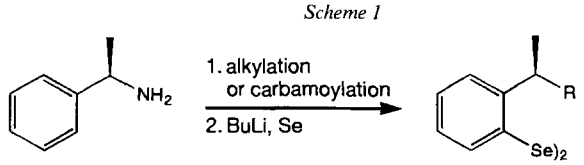
A series of new chiral diselenides with a N-atom in the side chain was prepared by a short synthetic sequence (*Scheme 1*). Only 1 mol-% of these diselenides catalyzed very effectively the diethylzinc addition to various aromatic and α,β-unsaturated aldehydes yielding the secondary alcohols in up to 98% ee (*Scheme 2* and *Tables 1* and *2*). An asymmetric amplification was observed with these catalysts. Detailed NMR studies were performed to characterize the catalytically active species.

Introduction. – The enantioselective addition of dialkylzinc reagents to aldehydes can be catalyzed by chiral compounds. A huge variety of catalysts is available to perform the addition reaction affording optically active secondary alcohols [1] [2]. Diols, diamines, and amino alcohols were found to be highly efficient catalysts for this reaction. Recently, it was shown that also S- [3] and Se-containing [4] amines are able to catalyze Et_2Zn addition reactions. Mechanistic studies have shown that the Zn species acts as a *Lewis* acid for carbonyl activation and as an organometallic reagent for the nucleophilic addition [2b]. Since functionalized organozinc reagents can be prepared easily, the access to various optically active secondary alcohols is possible [5].

2. Results and Discussion. – Chiral diselenides **1** could be prepared in a few steps from both enantiomers of the commercially available 1-phenylethylamine. In the first step, the amine was alkylated with MeI (leading to **1a**), EtI (leading to **1c**), or 1,4-dibromobutane (leading to **1d**). The mono-methylated amine (leading to **1b**) was synthesized *via* a sequence of (*tert*-butoxy)carbonyl (Boc) protection, methylation, and deprotection. The urea derivative (leading to **1e**) was obtained by treatment of the amine with dimethylcarbamoyl chloride. *ortho*-Deprotonation was then achieved by treatment with *t*-BuLi [6]. Addition of selenium generated the selenolates and, after oxidative workup, the corresponding diselenides **1** (see *Scheme 1*).

Scheme 1



1a R=Me_2N (66%)
b R=MeNH (29%)
c R=Et_2N (53%)
d R=pyrrolidin-1-yl (83%)
e R=$Me_2NC(O)NH$ (39%)

We recently reported that these diselenides can catalyze very efficiently the Et_2Zn addition to aldehydes [4b]. Only 1 mol-% of the diselenide was necessary to obtain complete conversion of the aldehydes to the secondary alcohols, as shown in *Scheme 2* and *Table 1* for the addition to benzaldehyde in the presence of the alkyl-substituted diselenides **1a–d**. Among these compounds, the pyrrolidinyl-substituted diselenide **1d** was the best catalyst affording the secondary alcohol **2** in high yield and optical purity. The urea derivative **1e**, however, showed only low catalytic activity.

Scheme 2

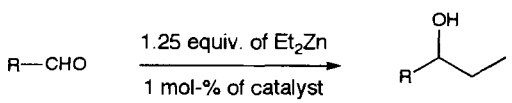


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Table 1. *Addition of Diethylzinc to Benzaldehyde in the Presence of Various Catalysts*[a])

Catalyst	**2** (R = Ph)		
	Yield [%]	ee [%][b])	Configuration
(*S,S*)-**1a**	87	92	(*R*)
(*R,R*)-**1b**[c])	48	82	(*S*)
(*R,R*)-**1c**	57	91	(*S*)
(*R,R*)-**1d**	91	97	(*S*)
(*R,R*)-**1d**[c])	97	98	(*S*)
(*R,R*)-**1e**	50	4	(*S*)
(*S*)-**4**	17	55	(*R*)

[a]) The reactions were performed at room temperature with 1 mol-% of the catalyst. [b]) The ee values of **2** were determined by GC. [c]) The reaction was carried out at 0°.

Et_2Zn was added to various substituted benzaldehydes in the presence of the best catalyst **1d** (see *Scheme 2* and *Table 2*). Independently from the electronic nature of the aromatic ring, excellent yields and enantiomeric ratios were obtained (*Entries 1–10*).

Table 2. *Addition of Diethylzinc to Aldehydes in the Presence of 1 mol-% of* (R,R)-**1d** *as Catalyst*[a])

Entry	Aldehyde	Secondary alcohol **2**	
		Yield [%]	ee [%]
1	benzaldehyde	97	98
2	1-naphthaldehyde	80	90
3	2-bromobenzaldehyde	78	91
4	2-bromo-3-methylbenzaldehyde	79	92
5	3-(trifluoromethyl)benzaldehyde	98	97
6	4-(trifluoromethyl)benzaldehyde	98	98
7[b])	4-methoxybenzaldehyde	77	93
8	4-(*tert*-butyl)benzaldehyde	67	98
9	3,5-bis(trifluoromethyl)benzaldehyde	90	98
10	2,3,4,5-tetrafluorobenzaldehyde	95	97
11	2-bromocyclopent-1-ene-1-carbaldehyde	97	98
12	2-bromocyclohex-1-ene-1-carbaldehyde	81	97

[a]) The reactions were carried out at 0°. [b]) 5 mol-% of (*S,S*)-**1a** was used.

ortho-Substitution caused little decrease in the efficiency (*Entries 2–4*). Even with α,β-unsaturated aldehydes, almost enantiomerically pure allylic alcohols were obtained (*Entries 11* and *12*).

The phenomenon of 'asymmetric amplification', which is described by a nonlinear relationship of the optical purities of the catalyst and the product, was observed for the addition of Et_2Zn to benzaldehyde catalyzed by various amino alcohols and other compounds [2b–d]. We examined the Et_2Zn addition to benzaldehyde catalyzed by optically enriched **1a**. The catalyst was prepared by mixing optically pure (*R*,*R*)- and (*S*,*S*)-**1a** and its ee determined by optical rotation. The reactions were run under identical conditions with 1 mol-% of the catalyst and stopped after 3 h. The results obtained with the optically enriched catalyst **1a** are summarized in *Table 3* and the *Figure*. With a catalyst of 86% ee, the product **2** still had 91% ee, and even with **1a** of only 8% ee, an enantiomeric excess of 23% was found. A concentration-dependence study of the asymmetric amplification showed an increase of the enantiomeric excess (19, 28, and 29% ee) in **2** with increasing concentration (0.001, 0.01 and 0.1M, resp.) of a catalyst having 9% ee.

Table 3. *Asymmetric Amplification*

Catalyst (*S*,*S*)-**1a** ee [%]	Product **2** ee [%]
> 99	92
86	91
51	76
26	56
8	23

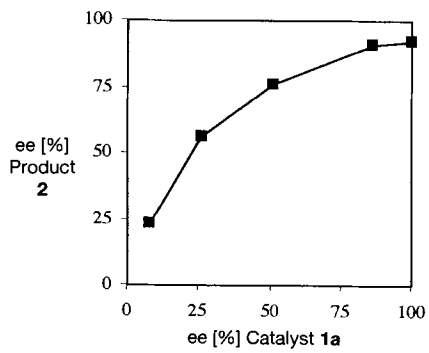


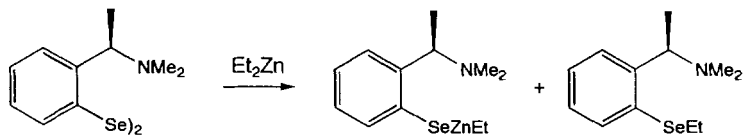
Figure. *Asymmetric amplification*

The use of amino alcohols as catalysts in Et_2Zn addition reactions has been investigated extensively. It is known that they behave as bidentate ligands to coordinate Zn *via* the N- and O-atom in forming oxazazincolidine species. The DAIB (*N*,*N*-dimethylaminoisoborneol) catalyst investigated by *Noyori* and coworkers [2a–c] forms catalytically inactive *meso* dimeric species and chiral dimeric species which are in equilibrium with the catalytically active monomers. This behavior results in a concentration dependence of the asymmetric amplification.

To get a closer insight into the diselenide-catalyzed addition reaction and to identify the catalytically active species, further experiments were performed. Although **1d** is the most powerful catalyst in this series, we decided to carry out these investigations with diselenide **1a** because of the simpler NMR spectra. First, we isolated and analyzed the catalytic addition reaction and found a mixture of diselenide **1a** (31%) and ethyl selenide **4** (45%; *Scheme 3*). Selenide **4** was formed by an Et transfer from Et_2Zn to diselenide **1a** generating the zinc selenolate **3**. The selenolate **3** was reoxidized during workup reforming the diselenide **1a**. The independently synthesized ethyl selenide **4** showed poor catalytic activity: the secondary alcohol **2** was obtained in only 17% yield with 55% ee

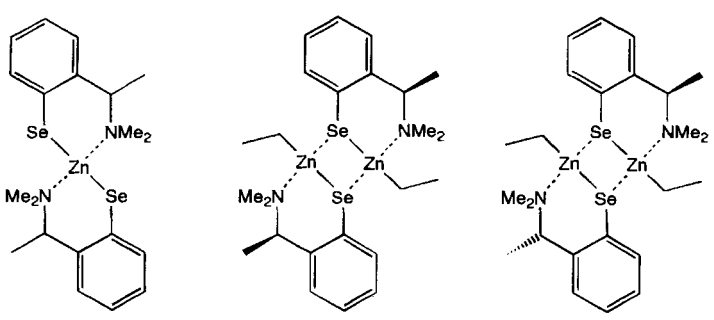
(*Table 1*). This means that **4** is not the dominant catalytically active species. We assume the γ-aminoselenolate **3** to be the active catalyst in the Et_2Zn addition to benzaldehyde in the presence of **1a**. To prove this assumption and to understand the reaction and coordination chemistry of diselenides **1**, a series of NMR titrations of selenides with Et_2Zn were performed. First, we investigated the behavior of ethyl selenide **4** (*ca.* 0.1M in $CDCl_3$) in the presence of 0, 1, 3, and 5 equiv. of Et_2Zn by ^1H- and ^{13}C-NMR. We observed: *1*) a continuous downfield shift of most of the signals of **4** with increasing amounts of Et_2Zn, *2*) broad signals for the benzylic CH and the CH_2Se groups in the ^1H- and ^{13}C-NMR, *3*) a splitting of the diastereoisotopic protons of the CH_2Se group into two *q*'s after the addition of 5 equiv. of Et_2Zn, and *4*) only one set of NMR signals and no concentration dependence for Et_2Zn. We, therefore, conclude that in compound **4**, both the N- and Se-atom are weakly coordinated to Zn.

Scheme 3



1a **3** **4**

Next, we titrated the enantiomerically pure catalyst (*S,S*)-**1a** and a racemic (1:1) and enantiomerically enriched mixture (2:1) of (*S,S*)-**1a** and (*R,R*)-**1a** in $CDCl_3$ with Et_2Zn. Addition of less than 0.5 equiv. of Et_2Zn resulted in the formation of **4** and a zinc selenolate. Remarkable for the latter, present in all three mixtures, is the downfield shift with respect to **1a** of the benzylic proton (δ 4.5 ppm, $\Delta\delta = +0.7$ ppm) with a line width of 35 Hz and the downfield shift of one of the *N*-methyl groups (δ 2.66 ppm, $\Delta\delta = +0.4$ ppm) with a line width of 14 Hz. All other resonances were very similar to those of **1a**. Since there was no EtZn group detectable, we assigned the species formed to structure **5** where two selenolate moieties are coordinated *via* the Se- and N-atom to one Zn atom. Although a chiral or a *meso* complex **5** is possible with a (*S,S*)/(*R,R*) mixture of catalysts **1a**, no differences were observed in the spectra. The formation of **5** was slow and took 0.5 to 1 h to go to completion at room temperature. This two-step process started with a fast Et transfer from Et_2Zn to diselenide **1a** forming **4** and **6**. The subsequent slow reaction of **6** with **1a** to **5** can be monitored by NMR. A structure similar to **5** was identified by *van Koten* and coworkers for the corresponding S-system by X-ray analysis [3a].



5 **6** **7**

Further addition of Et_2Zn (up to 12 equiv.) to (*S,S*)-**1a** or (*S,S*)/(*R,R*)-**1a** (1:1 and 2:1) resulted in the formation of new species which showed slightly different resonances in the enantiomerically pure catalyst and in the racemic mixture. After addition of 0.5 to 1 equiv. of Et_2Zn, coordinated EtZn groups and no free Et_2Zn were observed. The benzylic proton of **5** moved *ca.* 1 ppm upfield (δ 4.5 → 3.6 ppm, enantiomerically pure catalyst; δ 4.5 → 3.4 ppm, racemic catalyst). The *d* of the benzylic Me group of **5** moved 0.3 ppm downfield for the enantiomerically pure catalyst (δ 1.34 → 1.64 ppm) and *ca.* 0.4 ppm downfield for the racemic one (δ 1.34 → 1.72 ppm). Titration of the enantiomerically enriched mixture (*S,S*)/(*R,R*)-**1a** 2:1 showed the coexistence of these two species at all concentrations investigated (up to 5 equiv. of Et_2Zn). The formation of two different complexes is a proof of aggregation of these catalysts leading probably to a *meso* and a chiral dimeric species. In analogy to the work of *Noyori* and coworkers, we assigned the dimeric structures **6** and **7** to the chiral and *meso* complexes, respectively. The spectra of the titrations of (*S,S*)-**1a** were independent from the initial diselenide concentration between 0.015 and 0.1M. A participation of the ethyl selenide **4** in these aggregates could be excluded by the data.

The dynamic behavior of the complexes **6** and **7** at equal concentrations was different. The enantiomerically pure catalyst showed faster exchange than the racemic one: *1*) The broadening and coalescence of coordinated EtZn with free Et_2Zn occurred with less Et_2Zn in the enantiomerically pure catalyst than in the racemic one. *2*) The *N*-methyl groups of the racemic mixture showed two signals with different line widths (11 and 15 Hz, independent from the Et_2Zn concentration). This can be explained by an exchange of **6** with another species, but not with a N-inversion. In the enantiomerically pure catalyst, the two signals were again different in line width but near coalescence (δ 2.3–2.7 ppm). Only with high Et_2Zn concentrations, two separate signals could be observed (δ 2.36 and 2.51; line width 20 and 30 Hz, resp.). *3*) The benzylic proton of the enantiomerically pure catalyst showed a broad signal between δ 3.3 and 3.9 ppm for **6** which sharpened with increasing Et_2Zn concentrations (δ 3.6 ppm, line width 50 Hz). Compound **7** (racemic mixture) showed a constant line width of 40 Hz (δ 3.5 ppm) at all Et_2Zn concentrations. After addition of up to 1 equiv. of Et_2Zn, distinct signals for **5** and **6** (resp. **7**) could be seen. This behavior and the line-shape of the benzylic proton of **6** indicates that, besides the probable exchange between **5** and **6** (resp. **7**), another exchange process is going on.

Although the complexes **5**–**7** showed that they are in dynamic exchange with other species, there is no exchange between the chiral complexes **6** and the *meso* complexes **7** on the NMR time scale. This could be shown by the titration of the enantiomerically enriched mixture, in which the *d*'s of the benzylic Me groups of **6** and **7** moved closer together and, after addition of 5 equiv. of Et_2Zn, partially overlapped. If an exchange between **6** and **7** had occurred, one common *d* would have been observed. The faster exchange reaction of **6** compared to **7** is a possible explanation for the asymmetric amplification observed.

3. Conclusions. – A variety of chiral diselenides **1** were prepared in a short synthesis from 1-phenylethylamine as starting material. These diselenides can be used as very efficient pro-catalysts for the Et_2Zn addition to aldehydes. Catalytically active zinc selenolates are formed after treatment of the diselenides with Et_2Zn and catalyze the highly stereoselective ethylation of different aldehydes. With catalyst **1a**, we found an asymmetric amplification. By NMR studies it was shown that this catalyst is aggregated.

The aggregates like **6** and **7** are in dynamic exchange with other species. In analogy to the work of *Noyori* [2a–c], these species may be monomers of type **3**. With respect to the Et_2Zn addition to aldehydes, we found that the spectroscopic and chemical properties are in accordance with the well investigated properties of amino alcohols.

Futher studies dealing with the preparation of new chiral diselenides and their application in catalytic as well as stoichiometric reactions are in progress.

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Experimental Part

General. All reactions were performed under Ar with anh. solvents. $[\alpha]_D$: *Perkin-Elmer-141* polarimeter. IR Spectra: *Perkin-Elmer-781* spectrophotometer. ^{1}H-, ^{13}C-, and ^{19}F-NMR Spectra: *Varian-Gemini-300* spectrometer; in $CDCl_3$; chemical shifts δ in ppm rel. to $SiMe_4$ as internal standard (^{19}F: (trifluoromethyl)benzene (= 0 ppm) as external standard), coupling constants J in Hz; ^{13}C multiplicities by the APT puls sequence. ^{77}Se-NMR Spectra: *Varian-Gemini-400* spectrometer; in $CDCl_3$, with diphenyl diselenide (= 475 ppm) as external standard. MS: *Finnigan-MAT-312* apparatus.

(R,R)-Bis{2-[1-(dimethylamino)ethyl]phenyl} Diselenide (**1a**). To a soln. of (*R*)-*N*,*N*-dimethyl-1-phenylethylamine (1.49 g, 10 mmol) in dry pentane (15 ml) was added 1.7M *t*-BuLi in pentane (6.5 ml, 11 mmol). After stirring for 3 h, the lithium salt precipitated and was dissolved by adding dry THF (5 ml). Elemental Se (1.18 g, 15 mmol) was added and stirring continued for 3 h. Aq. sat. NH_4Cl soln. was added and the soln. extracted with $CHCl_3$ (5 × 50 ml). The combined org. phase was dried and evaporated and the residue purified by flash chromatography (FC; silica gel, *t*-BuOMe/pentane 1:1): **1a** (1.51 g, 66%). Yellow solid. M.p. 60–64°. $[\alpha]_D^{25}$ = +93.5 (*c* = 1.00, $CHCl_3$). IR (KBr): 3060, 2972, 2938, 2856, 2817, 2777, 1584, 1561, 1455, 1438, 1320, 1263, 1184, 1077, 1043, 1026, 945, 775, 741. ^{1}H-NMR: 1.35 (*d*, *J* = 6.5, 6 H); 2.26 (*s*, 12 H); 3.77 (*q*, *J* = 6.5, 2 H); 7.05–7.25 (*m*, 6 H); 7.84 (*dd*, *J* = 7.5, 1.5, 2 H). ^{13}C-NMR: 14.1 (*q*, 2 C); 41.0 (*q*, 4 C); 63.6 (*d*, 2 C); 125.9 (*d*, 2 C); 126.2 (*d*, 2 C); 127.6 (*d*, 2 C); 131.4 (*d*, 2 C); 133.3 (*s*, 2 C); 144.1 (*s*, 2 C). ^{77}Se-NMR: 454.1. CI-MS: 457 (21, $[M + H]^+$), 228 (44), 46 (100). Anal. calc. for $C_{20}H_{28}N_2Se_2$ (456.06): C 52.87, H 6.21, N 6.17; found: C 53.00, H 6.00, N 6.05.

(R)-N-[(tert-Butoxy)carbonyl]-1-phenylethylamine [7]. (*R*)-1-Phenylethylamine (1.82 g, 15 mmol) and 3 ml of Et_3N were dissolved in 30 ml of dry CH_2Cl_2. The mixture was cooled in an ice bath, and di(*tert*-butyl) dicarbonate (4.95 g, 22.5 mmol) was added. The reaction was stirred overnight, during which r.t. was reached. H_2O (50 ml) was added and the mixture extracted with CH_2Cl_2 (3 × 50 ml). The combined org. phase was washed with H_2O (50 ml), dried (Na_2CO_3), and evaporated and the residue purified by FC (silica gel, pentane/*t*-BuOMe 4:1) affording (*R*)-*N*-[(*tert*-butoxy)carbonyl]-1-phenylethylamine (3.28 g, 98%).

(R)-N-[(tert-Butoxy)carbonyl]-N-methyl-1-phenylethylamine. NaH (2.8 g, 70 mmol; 60% in mineral oil, washed 3× with pentane) was dispersed in THF (20 ml). (*R*)-*N*-[(*tert*-Butoxy)carbonyl]-1-phenylethylamine (3.28 g, 14.8 mmol) in THF (10 ml) and MeI (5 ml, 80 mmol) were added and stirred for 24 h. H_2O (100 ml) and pentane (100 ml) were added. The aq. phase was extracted with pentane (3 × 30 ml) and the combined org. phase washed with H_2O (2 × 30 ml), dried ($MgSO_4$), and evaporated: (*R*)-*N*-[(*tert*-butoxy)carbonyl]-*N*-methyl-1-phenylethylamine (3.50 g, 100%). ^{1}H-NMR: 1.487 (*s*, 9 H); 1.492 (*d*, *J* = 7.0, 3 H); 2.58 (br. *s*, 3 H); 5.48 (br. *s*, 1 H); 7.21–7.35 (*m*, 5 H). ^{13}C-NMR: 16.3 (br. *q*); 28.2 (*q*); 28.4 (*q*, 3 C); 52.6 (br. *d*); 79.4 (*s*); 126.8 (br. *d*, 2 C); 126.9 (*d*); 128.2 (*d*, 2 C); 141.4 (*s*); 155.8 (br. *s*).

(R)-N-Methyl-1-phenylethylamine. (*R*)-*N*-[(*tert*-Butoxy)carbonyl]-*N*-methyl-1-phenylethylamine (3.50 g, 14.8 mmol) was dissolved in AcOEt (20 ml) and refluxed with 3M HCl (30 ml) for 1 h. The homogeneous mixture was cooled and 50% aq. KOH soln. added until the soln. was basic. The aq. phase was extracted with CH_2Cl_2 (4 × 30 ml) and the combined org. phase dried (Na_2CO_3) and evaporated: colorless liquid of (*R*)-*N*-methyl-1-phenylethylamine (1.41 g, 70%). ^{1}H-NMR: 1.35 (*d*, *J* = 6.6, 3 H); 1.48 (br. *s*, NH); 2.31 (*s*, 3 H); 3.63 (*q*, *J* = 6.6, 1 H); 7.20–7.36 (*m*, 5 H). ^{13}C-NMR: 23.9 (*q*); 34.5 (*q*); 60.2 (*d*); 126.6 (*d*, 2 C); 126.9 (*d*); 128.4 (*d*, 2 C); 145.4 (*s*).

(R,R)-Bis{2-[1-(methylamino)ethyl]phenyl} Diselenide (**1b**). To a soln. of (*R*)-*N*-methyl-1-phenylethylamine (676 mg, 5 mmol) in dry pentane (20 ml) was added *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.35 ml, 2.5 mmol) and 2M BuLi in pentane (5 ml, 10 mmol). After stirring for 4 h at r.t., the soln. was cooled to −78°, and

dry THF (20 ml) was added. Se (395 mg, 5 mmol) was added and the soln. stirred 15 min at −78° and then allowed to warm up until all Se was dissolved. The soln. was hydrolyzed with a sat. NH_4Cl soln. and diluted with ice water (20 ml) and *t*-BuOMe (100 ml). The mixture was filtered through *Celite* to remove precipitated Se. The aq. phase was washed with *t*-BuOMe (3 × 30 ml). The ether phases were discarded. Extraction of the H_2O phase with CH_2Cl_2 (3 × 50 ml), drying of the combined CH_2Cl_2 phase (Na_2CO_3), evaporation, and heating of the residue in vacuum (3 h, 50°/0.1 mbar) yielded **1b** (304 mg, 29%). Yellow oil. $[\alpha]_D^{25} = -80.3$ ($c = 0.76$, $CHCl_3$). IR ($CHCl_3$): 3291, 3058, 2967, 2952, 2856, 2792, 1583, 1564, 1464, 1436, 1137, 1121, 1024, 802, 756, 725. ^{1}H-NMR: 1.40 (*d*, $J = 6.6$, 6 H); 1.52 (br. *s*, 2 NH); 2.34 (*s*, 6 H); 4.02 (*q*, $J = 6.6$, 2 H); 7.04 (*td*, $J = 7.5$, 1.6, 2 H); 7.13 (*td*, $J = 7.4$, 1.3, 2 H); 7.25 (*dd*, $J = 7.5$, 1.7, 2 H); 7.81 (*dd*, $J = 7.8$, 1.3, 2 H). ^{13}C-NMR: 21.3 (*q*, 2 C); 33.9 (*q*, 2 C); 59.6 (*d*, 2 C); 126.1 (*d*, 2 C); 126.3 (*d*, 2 C); 127.4 (*d*, 2 C); 130.9 (*s*, 2 C); 131.4 (*d*, 2 C); 140.0 (*s*, 2 C). ^{77}Se-NMR: 432.6. EI-MS: 428 (1, M^+), 214 (100), 198 (36), 183 (58), 134 (33), 118 (11), 104 (19), 91 (16), 77 (14). Anal. calc. for $C_{18}H_{24}N_2Se_2$ (426.32): C 50.73, H 5.68, N 6.57; found: C 50.97, H 5.59, N 6.80.

(R)-N,N-Diethyl-1-phenylethylamine. (*R*)-1-Phenylethylamine (2.42 g, 20 mmol), EtI (9.4 g, 60 mmol), and powdered KOH (5.0 g, 89 mmol) were dissolved in DMSO (40 ml) at 0° and stirred at r.t. for 20 h. Crashed ice, H_2O (200 ml), and pentane (100 ml) were added. The org. phase was extracted with H_2O (4 × 50 ml). The aq. phases were extracted with pentane (50 ml). The combined org. phases were dried (Na_2CO_3) and evaporated. Bulb-to-bulb distillation (75°/0.2 mbar) yielded 3.12 g (88%) of (*R*)-*N,N*-diethyl-1-phenylethylamine. Colorless liquid. ^{1}H-NMR: 1.00 (*t*, $J = 7.1$, 6 H); 1.35 (*d*, $J = 6.8$, 3 H); 2.47–2.63 (*m*, 4 H); 3.81 (*q*, $J = 6.6$, 1 H); 7.23–7.39 (*m*, 5 H). ^{13}C-NMR: 12.2 (*q*, 2 C); 18.4 (*q*); 42.9 (*t*, 2 C); 59.2 (*d*); 126.5 (*d*); 127.6 (*d*, 2 C); 128.0 (*d*, 2 C); 145.3 (*s*).

(R,R)-Bis{2-[1-(diethylamino)ethyl]phenyl} Diselenide (**1c**). To a soln. of (*R*)-*N,N*-diethyl-1-phenylethylamine (886 mg, 5 mmol) in dry pentane (30 ml) was added 1.6M *t*-BuLi in pentane (4.0 ml, 6.4 mmol) at 0°. After stirring for 60 h at r.t., the slurry was cooled to 0°, dry THF (20 ml) was added, and stirring continued for 10 min. The soln. was cooled to −78°, and Se (395 mg, 5 mmol) was added. The mixture was warmed up to 0°, until all Se was dissolved. HCl (15 ml of a 1M soln.), *t*-BuOMe (50 ml), and ice water (100 ml) were added. A red precipitate of Se was formed and the whole mixture was filtered through *Celite*. The org. phase was separated and discarded. A 1M NaOH soln. was added to the aq. phase until the soln. was basic. The aq. phase was extracted with *t*-BuOMe (3 × 50 ml), the extract dried ($MgSO_4$) and evaporated, and the residue purified by FC (silica gel, pentane/*t*-BuOMe 2:1) affording **1c** (678 mg, 53%) and (*R*)-*N,N*-diethyl-1-phenylethylamine (295 mg, 33%). **1c**: Yellow oil. $[\alpha]_D^{25} = +2.2$ ($c = 1.10$, $CHCl_3$). IR ($CHCl_3$): 3019, 2975, 2823, 1583, 1515, 1462, 1430, 1372, 1220, 778–733. ^{1}H-NMR: 1.06 (*t*, $J = 7.1$, 12 H); 1.39 (*d*, $J = 6.7$, 6 H); 2.52–2.71 (*m*, 8 H); 4.08 (*q*, $J = 6.6$, 2 H); 7.04–7.20 (*m*, 6 H); 7.82 (*dd*, $J = 7.5$, 1.6, 2 H). ^{13}C-NMR: 12.1 (*q*, 4 C); 14.8 (*q*, 2 C); 42.6 (*t*, 4 C); 60.5 (*d*, 2 C); 125.7 (*d*, 2 C); 126.5 (*d*, 2 C); 127.4 (*d*, 2 C); 131.5 (*d*, 2 C); 133.1 (*s*, 2 C); 145.0 (*s*, 2 C). ^{77}Se-NMR: 439.1. EI-MS: 512 (1, M^+), 256 (100), 183 (30), 176 (12), 104 (24), 72 (44). Anal. calc. for $C_{24}H_{36}N_2Se_2$ (510.49): C 56.47, H 7.11, N 5.49; found: C 56.40, H 6.89, N 5.38.

(R,R)-Bis{2-[1-(pyrrolidin-1-yl)ethyl]phenyl} Diselenide (**1d**). To a soln. of (*R*)-1-(1-phenylethyl)-pyrrolidine [8] (1.75 g, 10 mmol) in dry pentane (10 ml) was added 1.6M *t*-BuLi in pentane (6.25 ml, 10 mmol). After stirring for 40 h, the soln. was cooled to −78°, and dry THF (10 ml) was added. The mixture was allowed to warm up to r.t. to destroy excess *t*-BuLi and was again cooled to −78°. After addition of Se (0.79 g, 10 mmol), the soln. was warmed up to r.t. and, when all Se was dissolved, quenched by adding sat. aq. NH_4Cl soln. The mixture was extracted with *t*-BuOMe (5 × 50 ml), the combined org. phase dried and evaporated, and the residue purified by FC (silica gel, acetone/pentane 1:3): **1d** (2.11 g, 83%). Yellow oil. $[\alpha]_D^{25} = -42.1$ ($c = 0.82$, $CHCl_3$). IR ($CHCl_3$): 2973, 2805, 1584, 1462, 1434, 1371, 1219, 1143. ^{1}H-NMR: 1.44 (*d*, $J = 6.6$, 6 H); 1.80 (*m*, 8 H); 2.58 (*m*, 8 H); 3.74 (*q*, $J = 6.6$, 2 H); 7.06 (*td*, $J = 7.5$, 1.7, 2 H); 7.13 (*td*, $J = 7.2$, 1.4, 2 H); 7.23 (*dd*, $J = 7.5$, 1.6, 2 H); 7.79 (*dd*, $J = 7.8$, 1.4, 2 H). ^{13}C-NMR: 19.0 (*q*, 2 C); 23.7 (*t*, 4 C); 51.1 (*t*, 4 C); 63.7 (*d*, 2 C); 126.0 (*d*, 2 C); 126.5 (*d*, 2 C); 127.4 (*d*, 2 C); 131.3 (*d*, 2 C); 131.3 (*s*, 2 C); 144.9 (*s*, 2 C). ^{77}Se-NMR: 439.9. EI-MS: 508 (0.5, M^+), 254 (100), 183 (27), 174 (28), 104 (23), 91 (11), 70 (62). Anal. calc. for $C_{24}H_{32}N_2Se_2$ (506.45): C 56.92, H 6.37, N 5.53; found: C 56.85, H 6.12, N 5.58.

(R)-1,1-Dimethyl-3-(1-phenylethyl)urea. To (*R*)-1-phenylethylamine (3.63 g, 30 mmol) and Na_2CO_3 (6 g, 56 mmol) in 70 ml of dry CH_2Cl_2 was added dimethylcarbamoyl chloride (3.2 ml, 35 mmol). The mixture was stirred for 60 h at r.t. H_2O (50 ml) was added, the mixture slowly acidified with 1M HCl and extracted with CH_2Cl_2 (3 × 50 ml), the extract washed with H_2O (50 ml), dried ($MgSO_4$), and evaporated, and the residue dried under high vacuum for 3 h: 5.70 g (99%) of (*R*)-1,1-dimethyl-3-(1-phenylethyl)urea. White solid. M.p. 108–110°. ^{1}H-NMR: 1.49 (*d*, $J = 6.9$, 3 H); 2.90 (*s*, 6 H); 4.56 (br. *d*, 1 H); 5.02 (*quint.*, $J = 7.0$, 1 H); 7.22–7.36 (*m*, 5 H). ^{13}C-NMR: 22.6 (*q*); 36.1 (*q*, 2 C); 50.0 (*d*); 126.1 (*d*, 2 C); 127.0 (*d*); 128.5 (*d*, 2 C); 144.6 (*s*); 157.6 (*s*, 2 C). EI-MS: 192 (47, M^+), 177 (11), 120 (42), 105 (50), 72 (100). Anal. calc. for $C_{11}H_{16}N_2O$ (192.26): C 68.72, H 8.39, N 14.57; found: C 68.74, H 8.38, N 14.57.

(R,R)-Bis{2-{1-{[(dimethylamino)carbonyl]amino}ethyl}phenyl} Diselenide (**1e**). To a soln. of (*R*)-1,1-dimethyl-3-(1-phenylethyl)urea (2.88 g, 15 mmol) in dry THF (30 ml) was added 1.6M *t*-BuLi in pentane (18.8 ml, 30 mmol). After stirring for 4 h at −50°, Se (1.17 g, 14.8 mmol) was added and stirring continued for 45 min at −50°. Then the mixture was allowed to warm up to r.t. and, after all Se was dissolved, poured on sat. aq. NH_4Cl soln. (100 ml) and washed with *t*-BuOMe (2 × 50 ml). The org. phases were discarded. Then 1M HCl was added until the soln. was acidic, the mixture extracted with *t*-BuOMe (2 × 50 ml) and CH_2Cl_2 (2 × 50 ml), the extract dried ($MgSO_4$) and evaporated, and the residual oil (2.3 g) purified by refluxing in *t*-BuOMe: 1.58 g (39%) of **1e**. Yellow powder. M.p. 211–215°. $[\alpha]_D^{25} = +3.8$ (*c* = 0.64, $CHCl_3$). IR (KBr): 3307, 3054, 2972, 2928, 1628, 1518, 1458, 1377, 1225, 1209, 1025, 759. ^{1}H-NMR: 1.47 (*d*, *J* = 6.8, 6 H); 2.89 (*s*, 6 H); 4.66 (br. *d*, *J* = 6.6, 1 H); 5.24 (*quint.*, *J* = 6.8, 2 H); 7.14 (*td*, *J* = 7.4, 1.8, 2 H); 7.22 (*td*, *J* = 7.4, 1.4, 2 H); 7.28 (*dd*, *J* = 7.7, 1.7, 2 H); 7.77 (*dd*, *J* = 7.7, 1.3, 2 H). ^{13}C-NMR: 21.5 (*q*, 2 C); 36.0 (*q*, 4 C); 50.4 (*d*, 2 C); 126.0 (*d*, 2 C); 127.8 (*d*, 2 C); 128.2 (*d*, 2 C); 130.7 (*s*, 2 C); 133.7 (*d*, 2 C); 144.2 (*s*, 2 C); 157.2 (*s*, 2 C). ^{77}Se-NMR: 439.1. EI-MS: 542 (1.5, M^+), 272 (14), 191 (29), 184 (25), 104 (12), 89 (49), 72 (100). Anal. calc. for $C_{22}H_{32}N_4O_2Se_2$ (540.43): C 48.89, H 5.60, N 10.37; found: C 48.73, H 5.50, N 10.24.

(S)-{2-[1-(Dimethylamino)ethyl]phenyl} Ethyl Selenide (**4**). To a soln. of (*S,S*)-**1a** (47.7 mg, 0.1 mmol) in dry Et_2O (5 ml) was added 1M Br_2 in CCl_4 (0.12 ml, 0.12 mmol) at −78°. After 5 min, 1M EtMgBr in THF (0.3 ml, 0.3 mmol) was added and stirring continued until the color had disappeared (1 h). H_2O was added and the mixture extracted 3× with *t*-BuOMe. The combined org. phase was washed with H_2O, dried ($MgSO_4$), and evaporated and the residue purified by FC (silica gel, acetone): **4** (34 mg, 66%). Yellow oil. IR ($CHCl_3$): 3063, 2979, 2866, 2823, 2779, 1601, 1586, 1497, 1457, 1371, 1267, 1178, 1135, 1049. ^{1}H-NMR: 1.31 (*d*, *J* = 6.7, 3 H); 1.43 (*t*, *J* = 7.5, 3 H); 2.21 (*s*, 6 H); 2.87 (*q*, *J* = 7.5, ^2J(Se,H) = 11.4, 2 H); 3.75 (*q*, *J* = 6.6, 1 H); 7.13 (*td*, *J* = 7.4, 1.8, 1 H); 7.20 (*td*, *J* = 7.4, 1.5, 1 H); 7.40 (*dd*, *J* = 7.7, 1.8, 1 H); 7.43 (*dd*, *J* = 7.5, 1.3, 1 H). ^{13}C-NMR: 14.9 (*q*); 17.4 (*q*); 20.6 (*t*); 42.4 (*q*, 2 C); 63.5 (*d*); 126.2 (*d*); 126.9 (*d*); 127.1 (*d*); 130.9 (*d*); 131.9 (*s*); 145.6 (*s*). ^{77}Se-NMR: 287.7. EI-MS: 257 (16, M^+), 242 (32), 228 (59), 183 (30), 148 (25), 104 (37), 91 (31), 72 (100).

General Method for the Addition of Diethylzinc to Aldehydes, Catalyzed by Diselenides. To a cold (0°) soln. of diselenide **1** (0.02 mmol) in toluene (10 ml), Et_2Zn (2.5 mmol) and, after 10 min, the aldehyde (2 mmol) were added. After stirring for 15–20 h at 0°, 1N HCl (5 ml) and H_2O (40 ml) were added. The soln. was extracted 3× with *t*-BuOMe (40 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (silica gel, pentane/*t*-BuOMe 4:1). The solvent was completely removed by heating to 45°/50 mbar for 1 h (no loss of the volatile product). The enantiomeric excess of the secondary alcohol was determined by GC (*Chrompack*, β-CD-permethylated, 25 m). The conditions (see below) were checked with the corresponding racemates.

(−)-(S)-1-Phenylpropan-1-ol [3c]. Colorless oil. Yield 97%. GC (80→140° with 1°/min): 98% ee. $[\alpha]_D^{25} = -46.3$ (*c* = 1.12, $CHCl_3$).

(−)-(S)-1-(Naphthalen-1-yl)propan-1-ol [9]. Colorless oil. Yield 80%. GC (80→160° with 1°/min): 90% ee. $[\alpha]_D^{25} = -51.0$ (*c* = 0.94, $CHCl_3$).

(−)-1-(2-Bromophenyl)propan-1-ol [10]. Colorless oil. Yield 78%. GC (80→160° with 5°/min): 91% ee. $[\alpha]_D^{25} = -44.0$ (*c* = 1.16, $CHCl_3$).

(−)-1-(2-Bromo-3-methylphenyl)propan-1-ol. (2-Bromo-3-methylbenzaldehyde was prepared as described in [11]). White crystals. M.p. 57–59°. Yield 79%. GC (140° isotherm): 92% ee. $[\alpha]_D^{25} = -46.4$ (*c* = 1.15, $CHCl_3$). IR ($CHCl_3$): 3604, 3444, 2968, 2934, 1463, 1267, 1178, 1135, 1049, 1017. ^{1}H-NMR: 1.01 (*d*, *J* = 7.4, 3 H); 1.61–1.86 (*m*, 2 H); 2.01 (*d*, *J* = 3.3, 1 H); 2.42 (*s*, 3 H); 5.08 (*quint.*, *J* = 3.9, 1 H); 7.15 (*d*, *J* = 7.4, 1 H); 7.22 (*t*, *J* = 7.4, 1 H); 7.36 (*d*, *J* = 7.4, 1 H). ^{13}C-NMR: 10.1 (*q*); 23.7 (*q*); 30.4 (*t*); 74.4 (*d*); 124.6 (*d*); 124.7 (*s*); 127.0 (*d*); 129.5 (*d*); 138.1 (s); 144.0 (*s*). EI-MS: 230/228 (14, M^+), 201 (97), 199 (100), 173 (16), 171 (18), 92 (46), 91 (39), 65 (10).

(+)-1-[3-(Trifluoromethyl)phenyl]propan-1-ol. Colorless oil. Yield 98%. GC (90→120° with 1°/min): 97% ee. $[\alpha]_D^{25} = +28.9$ (*c* = 1.07, $CHCl_3$). IR ($CHCl_3$): 3604, 3418, 2968, 2936, 2878, 1601, 1452, 1329, 1178, 1132, 1073, 1049. ^{1}H-NMR: 0.91 (*t*, *J* = 7.4, 3 H); 1.77 (*m*, 2 H); 2.44 (br. *s*, 1 H); 4.63 (*t*, *J* = 6.5, 1 H); 7.43–7.54 (*m*, 3 H); 7.59 (*s*, 1 H). ^{13}C-NMR: 9.8 (*q*); 32.0 (*t*); 75.3 (*d*); 122.7 (*d*, ^3J(C,F) = −3.7); 124.2 (*s*, ^1J(C,F) = −274); 124.2 (*d*, ^3J(C,F) = −3.8); 128.8 (*d*); 129.3 (*d*); 130.7 (*s*, ^2J(C,F) = −32); 145.5 (*s*). ^{19}F-NMR: −0.2. EI-MS: 204 (3, M^+), 185 (5), 175 (100), 145 (8), 127 (62), 77 (6).

(−)-(S)-1-[4-(Trifluoromethyl)phenyl]propan-1-ol [12]. Colorless oil. Yield 98%. GC (80→140° with 3°/min): 98% ee. $[\alpha]_D^{25} = -31.0$ (*c* = 1.20, $CHCl_3$). IR (NaCl): 3358, 2971, 2938, 2880, 1620, 1418, 1332, 1165, 1124, 1068, 1017, 846. ^{1}H-NMR: 0.91 (*t*, *J* = 7.4, 3 H); 1.77 (*m*, 2 H); 2.22 (*s*, 1 H); 4.65 (*t*, *J* = 6.5, 1 H); 7.43 (*d*, *J* = 8.1, 2 H); 7.59 (*d*, *J* = 8.1, 2 H). ^{13}C-NMR: 9.8 (*q*); 32.0 (*t*); 75.2 (*d*); 124.2 (*s*, ^1J(C,F) = −274); 125.3 (*d*, ^3J(C,F) = −3.7, 2 C); 126.2 (*d*, 2 C); 129.7 (*s*, ^2J(C,F) = −32); 148.5 (*s*). EI-MS: 204 (4, M^+), 185 (4), 175 (100), 147 (12), 127 (68), 77 (8).

(+)-(R)-1-(4-Methoxyphenyl)propan-1-ol [2a]. Colorless oil. Yield 77%. GC (80→160° with 1°/min): 93% ee. $[\alpha]_D^{25} = +35.5$ ($c = 0.77$, $CHCl_3$).

(−)-1-[4-(2,2-Dimethylethyl)phenyl]propan-1-ol [13]. Colorless oil. Yield 67%. GC (100→135° with 0.4°/min): 98% ee. $[\alpha]_D^{25} = -35.5$ ($c = 1.00$, $CHCl_3$).

(−)-1-[3,5-Bis(trifluoromethyl)phenyl]propan-1-ol. White crystals. Yield 90%. GC (100→115° with 1°/min): 98% ee. $[\alpha]_D^{25} = -23.5$ ($c = 1.10$, $CHCl_3$). IR (KBr): 3330, 2978, 2885, 1466, 1384, 1353, 1278, 1168, 1120, 1050. ^{1}H-NMR: 0.97 (*t*, $J = 7.4$, 3 H); 1.81 (*quint.*, $J = 7.0$, 2 H); 2.05 (br. *s*, 1 H); 4.78 (*t*, $J = 6.3$, 1 H); 7.79 (*s*, 1 H); 7.82 (*s*, 2 H). ^{13}C-NMR: 9.7 (*q*); 32.2 (*t*); 74.6 (*d*); 121.4 (*d*); 123.4 (*s*, ^1J(C,F) = −274, 2 C); 126.1 (*d*, 2 C); 131.6 (*q*, ^1J(C,F) = −33); 147.1 (*s*). EI-MS: 272 (0.2, M^+), 253 (12), 243 (100), 195 (48), 145 (8), 127 (4).

(−)-1-(2,3,4,5-Tetrafluorophenyl)propan-1-ol. (2,3,4,5-Tetrafluorobenzaldehyde was prepared as described in [14]). Colorless oil. Yield 95%. GC (90→120° with 1°/min): 97% ee. $[\alpha]_D^{25} = -19.9$ ($c = 1.18$, $CHCl_3$). IR ($CHCl_3$): 3605, 3411, 2970, 2937, 2879, 1631, 1523, 1486, 1364, 1266, 1178, 1134, 1049. ^{1}H-NMR: 0.96 (*t*, $J = 7.4$, 3 H); 1.77 (*quint.*, $J = 7.0$, 2 H); 1.99 (br. *s*, 1 H); 4.96 (*t*, $J = 6.2$, 1 H); 7.08–7.19 (*m*, 1 H). ^{13}C-NMR: 9.4 (*q*); 30.9 (*t*); 68.5 (*s*); 108.3 (*d*, ^2J(C,F) = −20); 128.1 (*s*, ^2J(C,F) = −22); 139.4 (*s*, ^1J(C,F) = −254, ^2J(C,F) = −13.2, −12.2, ^3J(C,F) = −3.6); 140.3 (*s*, ^1J(C,F) = −255, ^2J(C,F) = −13.5, −12.5, ^3J(C,F) = −3.3); 144.3 (*s*, ^1J(C,F) = −247, ^2J(C,F) = −10.3, ^3J(C,F) = −3.3); 147.2 (*s*, ^1J(C,F) = −249, ^2J(C,F) = −10.3, ^3J(C,F) = −3.0, −3.0). ^{19}F-NMR: −76.6; −83.0; −93.8; −95.3. EI-MS: 208 (22, M^+), 179 (100), 151 (39), 101 (9).

(+)-1-(2-Bromocyclopent-1-enyl)propan-1-ol. (2-Bromocyclopent-1-ene-1-carboxaldehyde was prepared as described in [15]). Colorless oil. Yield 97%. GC (90→120° with 1°/min): 98% ee. $[\alpha]_D^{25} = +4.8$ ($c = 0.83$, $CHCl_3$). IR ($CHCl_3$): 3604, 3439, 2966, 2936, 2855, 1650, 1463, 1266, 1178, 1134, 1049. ^{1}H-NMR: 0.91 (*t*, $J = 7.4$, 3 H); 1.48–1.73 (*m*, 3 H); 1.95 (*quint.*, $J = 7.4$, 2 H); 2.30 (*m*, 1 H); 2.45 (*m*, 1 H); 2.65 (*m*, 2 H); 4.49 (*t*, $J = 7.1$, 1 H). ^{13}C-NMR: 9.9 (*q*); 21.7 (*t*); 28.0 (*t*); 29.4 (*t*); 40.2 (*t*); 71.0 (*d*); 117.5 (*s*); 142.2 (*s*). EI-MS: 204/206 (1, M^+), 177 (63), 175 (67), 125 (43), 96 (37), 67 (100), 57 (37).

(+)-1-(2-Bromocyclohex-1-enyl)propan-1-ol. (2-Bromocyclohex-1-ene-1-carboxaldehyde was prepared as described in [15]). Colorless oil. Yield 81%. GC (95→135° with 1°/min): 97% ee. $[\alpha]_D^{25} = +14.5$ ($c = 1.20$, $CHCl_3$). IR ($CHCl_3$): 3344, 2935, 2859, 1681, 1651, 1448, 1436, 1333, 1267, 1243, 1192, 1139, 1090, 1032, 1008, 968. ^{1}H-NMR: 0.93 (*t*, $J = 7.4$, 3 H); 1.50–1.71 (*m*, 7 H); 2.05 (*m*, 1 H); 2.25 (*m*, 1 H); 2.50 (*m*, 2 H); 4.68 (*t*, $J = 7.0$, 1 H). ^{13}C-NMR: 10.0 (*q*); 22.1 (*t*); 24.8 (*t*); 25.0 (*t*); 27.2 (*t*); 36.9 (*t*); 75.5 (*d*); 120.3 (*s*); 137.3 (*s*). EI-MS: 218/220 (5, M^+), 189 (94), 139 (27), 110 (22), 91 (14), 81 (100), 57 (37).

NMR Titration of **4** *with* Et_2Zn. Ethyl selenide **4** (20 mg, 0.078 mmol) was placed in an NMR tube and the tube sealed with a septum and purged with Ar. $CDCl_3$ (0.8 ml; filtered through Al_2O_3, dried over 3 Å molecular sieves, and degassed with Ar) was added. The ^{1}H- and ^{13}C-NMR were measured with 0, 1, 3, and 5 equiv. (0, 80, 240, and 400 µl, resp.) of 1M Et_2Zn in $CDCl_3$. The δ are given for 0 equiv., and the changes in chemical shift $\Delta\delta$ (+means downfield shift) after addition of 5 equiv. of Et_2Zn are indicated. The signals of Et_2Zn did not shift during the titration.

Et_2Zn: ^{1}H-NMR: 0.28 (*q*, $J = 8.2$, 4 H); 1.14 (*t*, $J = 8.2$, 6 H). ^{13}C-NMR: 6.2 (*t*); 10.2 (*q*).

4: ^{1}H-NMR: 1.31 (br., $\Delta\delta = +0.15$); 1.43 ($\Delta\delta = +0.06$); 2.21 ($\Delta\delta = +0.11$); 2.87 ($\Delta\delta = +0.17$); 3.75 ($\Delta\delta = +0.09$); 7.13 ($\Delta\delta = +0.10$); 7.20 ($\Delta\delta = +0.03$); 7.40 ($\Delta\delta = -0.08$); 7.43 ($\Delta\delta = +0.02$). ^{13}C-NMR: 14.9 ($\Delta\delta = -0.5$); 17.4 ($\Delta\delta = -0.8$); 20.6 (invisible br.); 42.4 ($\Delta\delta = +1.5$); 63.5 (br., $\Delta\delta = +2.0$); 126.2 ($\Delta\delta = +0.7$); 126.9 ($\Delta\delta = +1.3$); 127.1 ($\Delta\delta = +1.8$); 130.9 ($\Delta\delta = +0.5$); 131.9 (invisible br.); 145.6 (invisible br.).

NMR Titration of **1a** *with* Et_2Zn. In a parallel titration, chiral and racemic **1a** (7 mg, 0.015 mmol each) were placed in an NMR tube. The samples were prepared as described for **4** and the ^{1}H-NMR in $CDCl_3$ measured after addition of 0, 0.8, 1, 2, 4, and 8 equiv. (0, 12, 15, 30, 60, and 120 µl, resp.) of 1M Et_2Zn. Similar experiments were performed with (*S,S*)-**1a** (21 mg, 0.045 mmol) and 0, 0.4, 0.8, 1, 2, 4, and 12 equiv. of Et_2Zn, with (*S,S*)-**1a** (35 mg, 0.077 mmol) and 0, 0.5, 1, 1.5, and 2.5 equiv. of Et_2Zn, and with (*S,S*)-**1a** (15.8 mg, 0.035 mmol)/(*R,R*)-**1a** (7.9 mg, 0.017 mmol) and 0, 0.5, 1, 2, 3, 4, and 5 equiv. of Et_2Zn. No sharp signals could be observed in the ^{13}C-NMR. The arrow (→) indicates the change of δ during Et_2Zn addition.

5: ^{1}H-NMR: 1.34 (br. *s*, 3 H); 2.27 (br. *s*, 3 H); 2.66 (br. *s*, $\omega_{1/2} = 14$, 3 H); 4.5 (br. *s*, $\omega_{1/2} = 35$, 1 H); 7.0–7.2 (*m*, 3 H); 7.81–7.84 (*m*, 1 H).

6: ^{1}H-NMR: 0.07 (br. *q*, $J = 8$, 2 H); 0.96 (*t*, $J = 8$, 3 H); 1.64→1.69 (br. *d*, $J = 6.9$, 3 H); 2.38→2.36 (br., $w_{1/2} = 20$, 3 H); 2.51→2.53 (br., $w_{1/2} = 30$, 3 H); 3.3–3.9→3.6 (br., $w_{1/2}$ *ca.* 100→50, 1 H); 6.99–7.01 (br. *m*, 1 H); 7.09–7.12 (*m*, 2 H); 7.68–7.71 (*m*, 1 H).

7: ^{1}H-NMR: 0.03 (br. *q*, $J = 8$, 2 H); 0.92 (*t*, $J = 8$, 3 H); 1.72 (br. *d*, $J = 6.9$, 3 H); 2.27→2.32 (br., $w_{1/2} = 11$, 3 H); 2.65→2.59 (br., $w_{1/2} = 15$, 3 H); 3.40→3.50 (br., $w_{1/2} = 40$, 1 H); 6.95–6.98 (br. *m*, 1 H); 7.08–7.12 (*m*, 2 H); 7.67–7.70 (*m*, 1 H).

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