

electrospray ions. A voltage of -2500 V was applied to the electrospray needle, which was held $1\text{--}3\text{ cm}$ away from the inlet to the vacuum.

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Engineering Catalysts for Enantioselective Addition of Diethylzinc to Aldehydes with Racemic Amino Alcohols: Nonlinear Effects in Asymmetric Deactivation of Racemic Catalysts**

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“Asymmetric amplification” or the “positive nonlinear effect” ((+)-NLE) is a very attractive phenomenon in catalytic asymmetric processes, since it gives enantioselectivities which are improved with respect to the expectations based on the *ee* value of the auxiliary.^[1–7] Therefore, because of asymmetric amplification, high-enantiopurity chiral ligands need not necessarily be applied to achieve high enantiopurities of product. Nevertheless one has to make a partial resolution of the chiral ligands from their racemic forms. Interestingly, asymmetric catalysis with racemic catalysts has been successfully achieved by “chiral poisoning”^[8] or “asymmetric activation”^[9] strategy.

After the first report on the nonlinear effect in asymmetric catalysis by Kagan and co-workers,^[2] the early experiments with strong asymmetric amplification were demonstrated by Oguni et al. in 1988 and by Noyori et al. in 1989 for enantioselective addition of diethylzinc to aldehydes.^[3] In this type of alkylation, the asymmetric amplification is well recognized to be a consequence of an in situ increase in the *ee* value of the active catalyst, since racemic ligand is trapped in the more stable, unreactive *meso* species.^[7] The recent treatment by Noyori and co-workers^[7b] of the systems involving the dynamic monomer–dimer equilibria where the monomers are active species is complementary to the ML_n models of Girard and Kagan.^[1b] In principle, if racemic ligands are used alone, the reaction will definitely give racemic product. The addition of an alternative nonracemic additive (which should be cheap and easily obtainable) to the racemic catalyst system may enantioselectively generate a new species of dinuclear zinc complex with one enantiomer of racemic ligand through “non-self-recognition”^[7a] to release the opposite enantiomer of catalyst for asymmetric catalysis. To exemplify this strategy, we choose Oguni et al.’s racemic amino alcohols to carry out asymmetric catalysis by adding nonracemic additives. In this contribution, we report our results on the first example of highly enantioselective addition of diethylzinc to aldehydes with the catalysis of racemic amino alcohols in the presence of chiral additives.

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We began this work by investigating the effect of various random chiral additives, such as amino acids, tartaric acid, diols, diamine, diimine, and simple amino alcohols, on the enantioselectivity of ethylation of benzaldehyde (**1a**) with diethylzinc catalyzed by racemic DB1. In some cases, we could really see the influences of the chiral additives on the asymmetric induction of the reaction. For example, (*R*)-1,1'-bi-2-naphthol (BINOL) alone catalyzed the reaction to give the *R* product (8.2% *ee*), but the addition of (*R*)-BINOL to the reaction system catalyzed by racemic DB1 resulted in the formation of *S* product (8.5% *ee*). Similarly, the reaction promoted by (*S*)-2-*N,N*-dimethylamino-2'-hydroxy-1,1'-binaphthyl (DM-NOBIN) yielded *S* product (89% *ee*) and the addition of (*S*)-DM-NOBIN to the racemic DB1 system gave *R* product (38% *ee*). These data could be interpreted by a phenomenon where a catalytically inert heterochiral dimeric zinc complex may be formed between the chiral additive and one of the enantiomers of racemic amino alcohol through non-self-recognition; as a result the zinc complex of racemic amino alcohol is enantioselectively enriched and catalyzes the reaction to give the nonracemic product. From the primary random screening, we found amino alcohols to be one type of effective chiral additive candidates for this purpose (Scheme 1).

High-throughput screening (HTS) is essential for tuning a variety of modifications in lead optimization^[10] and has been found to be an effective technique for finding the most efficient catalysts for asymmetric reactions as well.^[11] With the lead result mentioned above, a library of optically active amino alcohols (AA1–AA13; Scheme 1) was then created by parallel synthesis from amino acids, and a family of racemic amino alcohols (DB1–DB5), which have been reported to show significant asymmetric amplification,^[3a] was also formed. The combined use of 10 mol % of the racemic amino alcohols (DB1–DB5) and half an equivalent amount (5 mol %) of optically active additives (AA1–AA13) in the presence of diethylzinc formed a chiral catalyst library of 65 members, which were then evaluated with HPLC-CD techni-

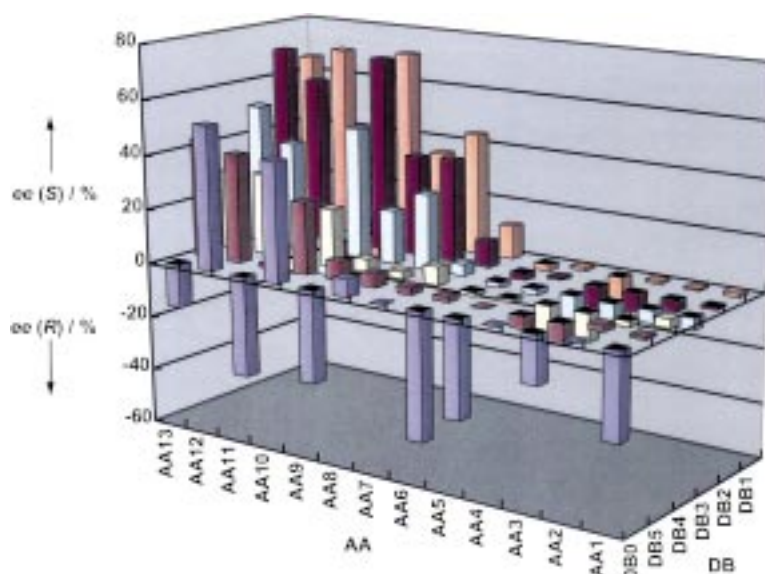
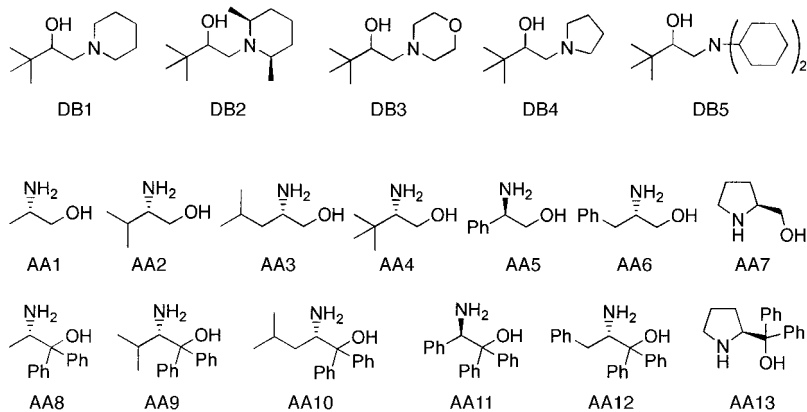


Figure 1. High-throughput evaluation of the catalyst library generated from racemic amino alcohols (DB1–DB5) and chiral additives (AA1–AA13) for enantioselective addition of diethylzinc to benzaldehyde.

ques.^[9f] Figure 1 shows the details of the screening results. It is obvious that the chiral additives with large steric hindrance at the hydroxy-functionalized carbon, AA8–AA13, were more influential on the enantioselectivity of the reaction than the simple amino alcohols, AA1–AA7. Particularly AA10, AA12, and AA13 showed significant synergetic effects on the enantioselectivity of the reaction. For example, with only AA13 (5 mol %) as the chiral inducer, (*R*)-1-phenylpropanol was obtained with 15.6% *ee*. However, the addition of racemic DB1 or DB2 (10 mol %) to the AA13-catalyzed reaction system resulted in the formation of the *S* product in 65.8% and 70.4% *ee*, respectively.

The reactions catalyzed by the better combinations, AA12/DB1, AA12/DB2, AA13/DB1, and AA13/DB2, were further optimized in parallel by varying the molar ratio of racemic DB to chiral AA and decreasing the reaction temperature to -20°C and -40°C . We were pleased to find that (*S*)-1-phenylpropanol could be obtained with up to 92.7% *ee* and in >95% yield under the catalysis of AA13/DB2 (ratio: 1/2; 5 mol % of AA13) at -40°C . Catalyst combinations AA12/DB1, AA12/DB2, AA13/DB1, and AA13/DB2 also proved to be effective for the ethylation of a variety of aldehydes under the optimized conditions (Table 1). To the best of our knowledge, this work represents the first example of highly enantioselective addition of diethylzinc to benzaldehyde with the catalysis of racemic amino alcohols in the presence of chiral additives.

In an effort to elucidate the mechanism for the asymmetric induction, the quantitative effect of chiral additive on the reaction rate was investigated by rapid quenching of the reaction and HPLC analysis with 1-phenylethanol as internal standard (Table 2). It was found that both (*R*)- and (*S*)-DB1 homochiral



Scheme 1. Racemic (DB) and nonracemic (AA) ligands employed for creating the chiral catalyst library.

Table 1. Enantioselectivities for the ethylation of aldehydes with catalysis by racemic DB in the presence of optically active AA.^[a] Parallel screening of matched substrate/catalyst pairs.

$$\text{RCHO} \quad \text{1} + \text{Et}_2\text{Zn} \xrightarrow[\text{CH}_2\text{Cl}_2/\text{hexane}]{\text{DB / AA}} \text{R-CH(OH)-CH}_3 \quad \text{2}$$

Entry	R	<i>ee</i> values [%]			
		AA12/DB1	AA12/DB2	AA13/DB1	AA13/DB2
1	phenyl (a)	86.0	86.1	92.7	90.6
2	<i>p</i> -chlorophenyl (b)	69.9	82.3	84.6	92.1
3	<i>m</i> -tolyl (c)	85.7	81.0	90.1	87.3
4	<i>p</i> -anisyl (d)	87.5	90.3	90.0	91.4
5	<i>trans</i> -styryl (e)	67.7	82.3	69.4	69.4
6	<i>o</i> -anisyl (f)	69.8	76.7	74.5	86.3
7	ferrocenyl (g)	81.9	90.6	91.7	72.9
8	<i>p</i> -dimethylamino-phenyl (h)	23.6	55.6	36.2	81.0 ^[b]
9	α -naphthyl (i)	69.9	72.2	69.3	86.3
10	<i>p</i> -tolyl (j)	74.7	80.0	82.4	80.0
11	<i>m</i> -anisyl (k)	79.2	80.7	76.9	76.4
12	<i>p</i> -bromophenyl (l)	76.6	73.6	82.7	79.5
13 ^[c]	<i>trans</i> -propenyl (m)	78.3	84.4	80.7	84.4

[a] All of the reactions were carried out at -40°C in CH_2Cl_2 /hexane mixed solvent for 48 h with catalysis by racemic DB1 (10 mol %) and optically active AA (5 mol %) unless otherwise stated. The conversions of the aldehydes were $>90\%$. All the *ee* values were determined by HPLC or GC on chiral columns. [b] The reaction was carried out at 0°C . [c] The reaction was carried out at -20°C .

Table 2. The quantitative effect of chiral additive AA13 on the rate of reaction, with **1a** as the substrate and DB1 as the catalyst.^[a]

Entry	Config. of DB1	DB1 [mol %]	AA13 [mol %]	Yield [%] ^[b]	<i>ee</i> value [%] ^[c]	Config. of 2a ^[d]
1	<i>S</i>	5	0	16.0	95.0	<i>S</i>
2	<i>S</i>	5	5	6.0	91.1	<i>S</i>
3	<i>R</i>	5	5	1.6	66.2	<i>R</i>
4	$\pm$	5	0	1.6	0	–
5	–	0	5	0.7	15.9	<i>R</i>
6	$\pm$	10	5	5.7	65.8	<i>S</i>

[a] The reaction was carried at 0°C and quenched with an aqueous solution of NH_4Cl after 5 min. [b] The yield was determined by HPLC with 1-phenylethanol as the internal standard. [c] Determined by HPLC on a Chiralcel OD column. [d] Determined from optical rotation measurements and HPLC retention times on a Chiralcel OD column in comparison with authentic samples.

catalysts were deactivated by AA13 (entry 1 compared with entries 2 and 3, respectively), which indicated some interactions between them. However the levels of deactivation for the *R* and *S* catalysts by AA13 were quite different. The reaction catalyzed by (*S*)-DB1/AA13 is 3.8 times as fast as that catalyzed by (*R*)-DB1/AA13 (entries 2 and 3, respectively). ($\pm$)-DB1 and AA13 on their own were found to be catalytically much less reactive (entries 4 and 5). However, use of ($\pm$)-DB1 combined with half an equivalent of AA13 yielded the product 3.6 and 8.1 times as fast as the reactions with the separate component ligands, respectively (entry 6 versus entries 4 and 5). Obviously, such synergetic effects are due to the interaction differences between the AA13–zinc complex and the complexes of (*S*)-DB1 and (*R*)-DB1 with zinc.

The nonlinear effect in the present catalytic system was also disclosed by an investigation of the influence of molar ratios between AA13 and (*R*)-DB1 or (*S*)-DB1 on the enantioselectivity of the reaction.^[12] The different behavior of the nonlinear effects in the AA13/(*R*)-DB1 and AA13/(*S*)-DB1 systems again supported the presence of non-self-recognition between AA13 and DB and also indicated the differences in their non-self interactions.

In conclusion, we have shown the first examples of a highly enantioselective addition of diethylzinc to aldehydes with the catalysis of racemic amino alcohols in the presence of chiral additives, through an asymmetric deactivation strategy with a combinatorial approach. The mechanism of asymmetric induction and the nonlinear effect in chiral deactivation were also studied. This work demonstrated that clever combined use of asymmetric deactivation strategies and combinatorial chemistry approaches will provide a powerful tool for designing and finding new, practical, and efficient asymmetric catalytic systems.

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- [12] Experimental data, including synthetic details and ¹HNMR spectroscopic data for racemic and nonracemic ligands and full data for the evaluation of the catalyst library, as well as the graphical representation for investigation of the nonlinear effect in the present catalytic system, have been included in the Supporting Information.

SrN and SrN₂: Diazenides by Synthesis under High N₂-Pressure**

Gudrun Auffermann, Yurii Prots, and Rüdiger Kniep*

In the binary system Sr–N, only the existence of Sr₂N is certain.^[1] This compound crystallizes in the CdCl₂ structure (layers of octahedra, Figure 1 left). Reports on a binary phase with the stoichiometry “SrN”^[2] were corrected afterwards as these solids also contained hydrogen or carbon.^[1, 3]

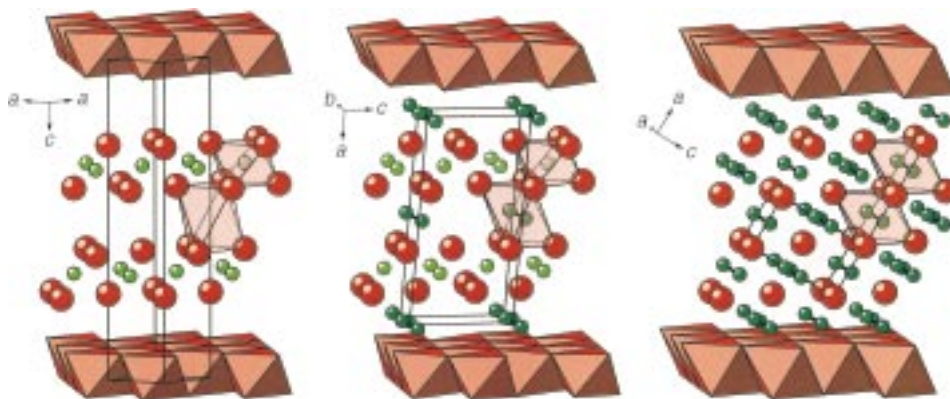


Figure 1. Crystal structures of Sr₂N (left), SrN ≡ (Sr²⁺)₄[N^{3−}]₂[N₂^{2−}] (center), and SrN₂ ≡ Sr²⁺[N₂^{2−}] (right). The top and bottom boundaries of the figures are represented by layers of Sr₆ octahedra (polyhedral representation), occupied by [N^{3−}] (Sr₂N, SrN) or [N₂^{2−}] (SrN₂), respectively. Ball-and-stick representations between the polyhedral layers: Sr²⁺, red; [N^{3−}], light green; [N₂^{2−}], dark green. The transparent octahedra contribute to a better visualization.

Recently, we carried out high-pressure experiments for the preparation of strontium–nitrogen compounds using our modified high-pressure equipment, which was originally constructed by Bronger and Auffermann^[4] for the syntheses of extremely air- and moisture-sensitive metal hydrides and hydridometalates.

Using Sr₂N (blue-black powder with metallic luster) as the starting material (reaction temperature 920 K, reaction time 72 h), we obtained single-phase SrN (black-gray powder) under an N₂ pressure of 400 bar and single-phase SrN₂ (brown powder) under an N₂ pressure of 5500 bar.^[5] No impurities of the phases were detected by X-ray and neutron diffraction investigations at ambient pressure^[6] nor by chemical analysis.^[12] The contents of carbon, hydrogen, and oxygen were below the detection limits.

The crystal structures of SrN and SrN₂ were solved by a combination of X-ray and neutron diffraction experiments on air- and moisture-sensitive microcrystalline powders.^[6] The neutron diffraction diagrams (observed, calculated, and difference profile) are given in Figure 2. The crystal structures

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