

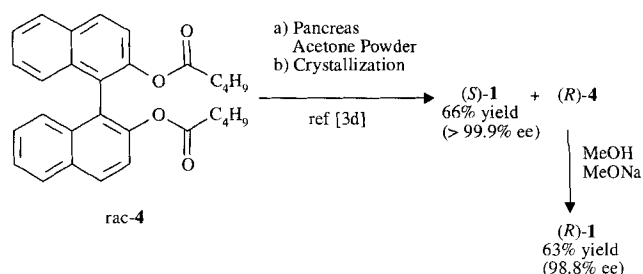
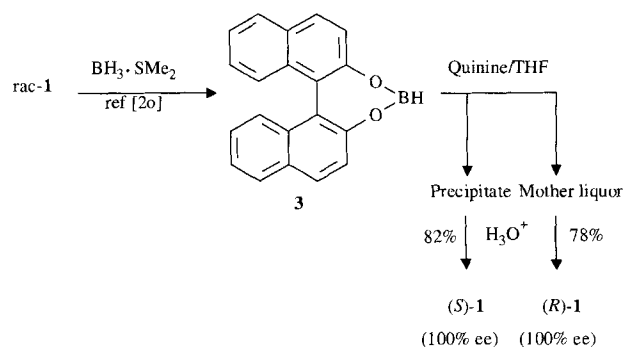
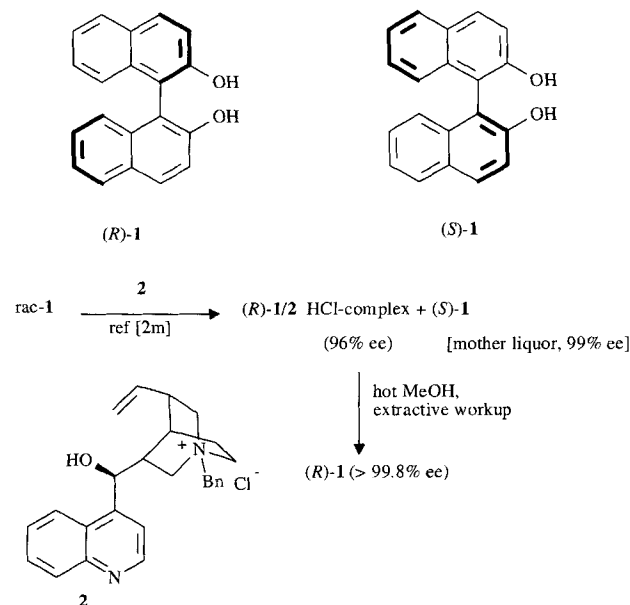
**2,2'-Dihydroxy-1,1'-binaphthalene (BINOL): A Chiral C<sub>2</sub>-Symmetric Ligand for Stereoselective Carbon–Carbon Bond Forming Reactions**

Reinhold Zimmer and Jutta Suhrbier

Dresden, Institut für Organische Chemie der Technischen Universität

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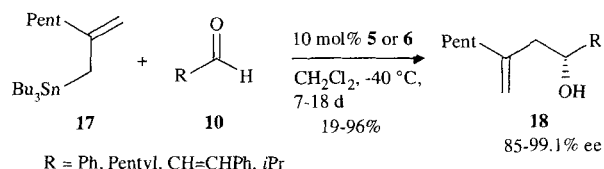
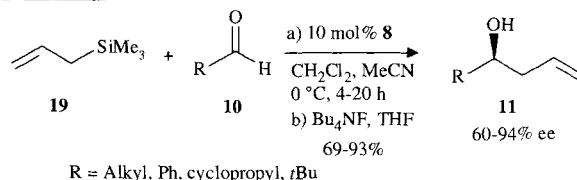
Asymmetric catalysis is one of the important strategies in organic synthesis to generate one or more new stereogenic centers. In particular, the preparation and application of optically pure ligands, especially C<sub>2</sub>-symmetric compounds, have received considerable interest. Thus, both enantiomers of 2,2'-Dihydroxy-1,1'-binaphthalene (**1**; abbreviated as BINOL) serve as ligands of choice for a variety of stereoselective carbon–carbon bond forming reactions, *e.g.*, (hetero) Diels–Alder reactions, aldol additions, allylations and alkylations of carbonyl compounds, carbonyl–ene reactions etc. [1]. There are numerous methods for the preparation of (*R*)- and (*S*)-**1** starting from the racemic material. Most of the approaches transform **1** into diastereomeric derivatives (*e.g.*, cyclic phosphate or boron ester) and subsequent fractional crystallization



followed by hydrolysis lead to the enantiomeric pure (*R*)- and/or (*S*)-**1** [2]. The compound **1** can also be resolved by enzymatic methods [3] or by enrichment of the optical purity of scalemic **1** [4]. In addition, there are also a few methods to synthesize (*R*)- and (*S*)-**1** *via* asymmetric oxidative coupling of  $\beta$ -naphthols in the presence of chiral amines [2b, f, g, l].

Since many chiral alcohols are valuable intermediates for the preparation of optically pure pharmaceutical and agricultural products, the development of highly effective procedures for the alkylation (allylation) of aldehydes is of substantial interest in synthetic organic chemistry. Consequently, many methods dealing with stereoselective reactions using titanium–BINOL catalysts (*e.g.*, **5–8**) have been published. In the

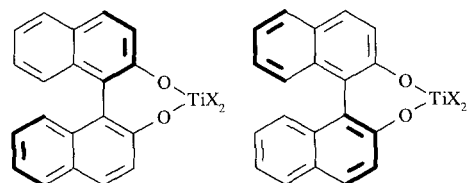
beginning of the nineties, pioneer studies of Keck [5], Mikami [6], Tagliavini and Umani-Ronchi [7] for the powerful catalytic asymmetric additions of allylstannanes (allylation reactions), enolates (aldol-type reactions) and olefins (ene-reactions) to a variety of aldehydes using catalysts **5** and **7** were reported. In the last years, there are a few interesting articles describing BINOL-systems as catalysts for asymmetric allylation reactions. Brückner and Weigand reported on the preparation of optically pure homoallyl alcohols (*e.g.*, **18**) starting from  $\beta$ -substituted allylstannanes (*e.g.*, **17**) and various aldehydes, which gave maximum enantioselectivities using titanium-derived catalysts **5** and **6** [8]. In contrast to the previously described allylation reactions, Brückner's protocol works very well in the absence of molecular sieves. An extension of the asymmetric allylation reaction employing the non-toxic and less reactive allyltrimethylsilane (**19**) [9] has been studied by Carreira and Gauthier [10] and a moderate to good level of enantioselectivity has been achieved by using the new difluoro BINOL catalyst **8**. Faller *et al.* have found a remarkable positive nonlinear effect in the reaction of benzaldehyde and allyltributylstannane (**9**), wherein the *ee*-value of the resulting product significantly exceeds the enantiomeric purity of the titanium-derived BINOL catalyst **5** employed [11]. Similar positive nonlinear effects in correlating product enantiomeric purity with the enantiomeric excess of **1** were discussed by Keck (allylation reaction) [5b] and Mikami (ene-reaction) [6a]. Yu and coworkers have demonstrated a dramatic acceleration of the catalytic allylation of achiral aldehydes by

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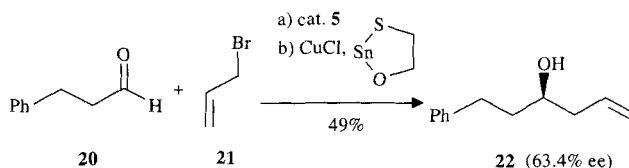
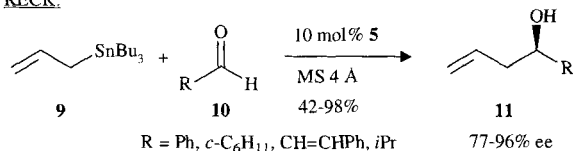
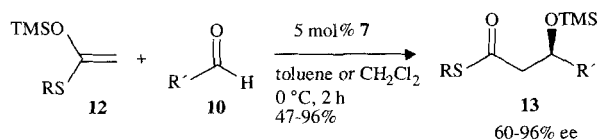
the utilization of the synergetic reagent Et<sub>2</sub>M-S*t*Pr (M = B, Al) [12]. More recently, Corey has discussed the occurrence of formyl C-H...O hydrogen bonding of aldehydes with chiral Lewis-acid catalysts as a key to the understanding of absolute stereochemistry [13].

First examples of catalytic asymmetric allylation of aryl-substituted aldehydes in a Sn(II) mediated Barbier reaction were reported by Majumdar [14] and the best result in enantiomeric excess is given for the reaction of **20** and **21** in the presence of (*R*)-BINOL-Ti(O*i*Pr)<sub>2</sub> (**5**). In addition to the titanium species **5**–**8**, BINOL (**1**) stands out as a most effective C<sub>2</sub>-symmetric diol ligand useful also for a variety of other metal-ion mediated asymmetric reactions with similar good selectivities as described above (*e.g.* zirconium [15] and boron [16]).

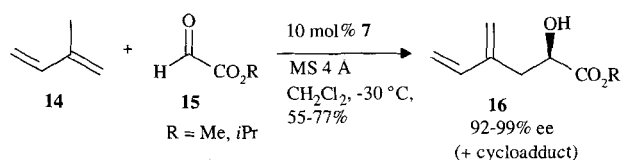
It should be noted, that the first optically active poly-BINOL was prepared successfully. It forms a catalyst with Et<sub>2</sub>AlCl [17] but no enantioselectivity was obtained in the Mukaiyama reaction.



5: X = OiPr; 6: X = OEt; 7: X = Cl; 8: X = F

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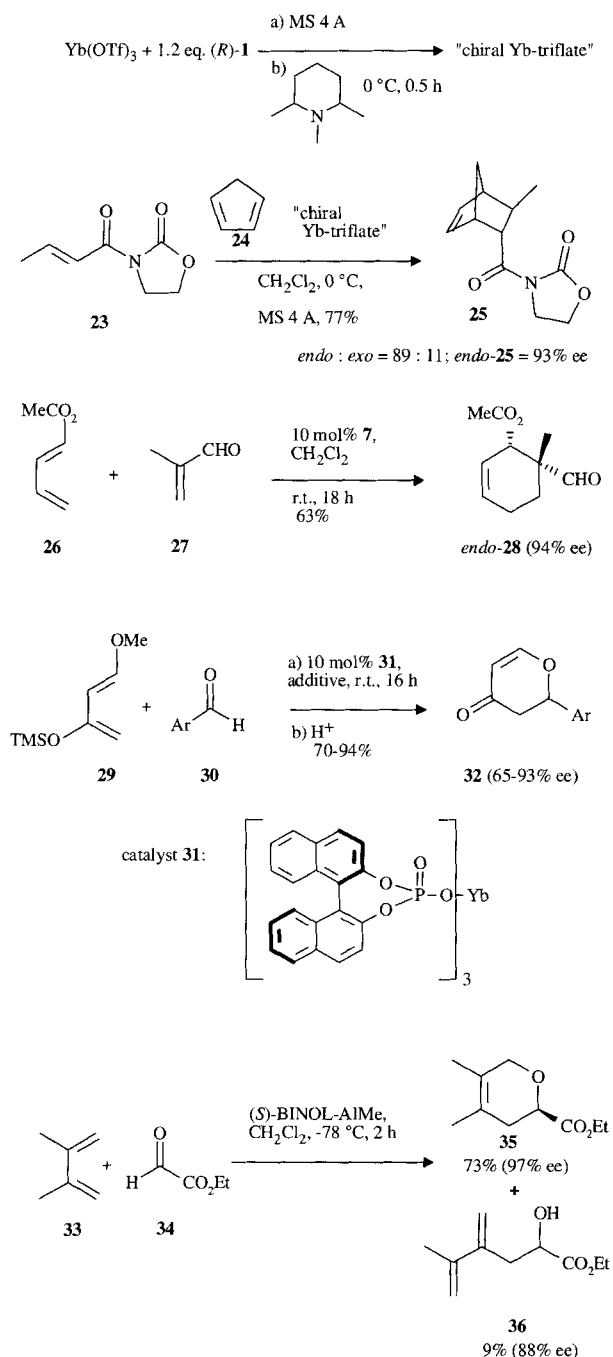
R = Et, *t*Bu; R' = CH<sub>2</sub>O*Bn*, CH<sub>2</sub>Cl, Octyl, *i*Pr, CH=CHMe



The Diels–Alder reaction is a widely used cycloaddition reaction, and the development of efficient stereoselective catalysts for this reaction is expected. However, chiral scandium and ytterbium-BINOL catalysts, prepared from corresponding metal triflates, and a tertiary amine as additive are quite effective in the enantioselective [4+2]-cycloaddition (*e.g.*, **23**+**24** → **25**) [18, 19]. The Yb(OTf)<sub>3</sub>/1-complex is also suitable for enantioselective inverse electron-demand Diels–Alder reactions of 3-carbomethoxy-2-pyrone with various vinyl ethers and vinyl sulphides leading to bicyclic lactones with good *ee* (up to 95%) [20]. BINOL-derived titanium catalysts

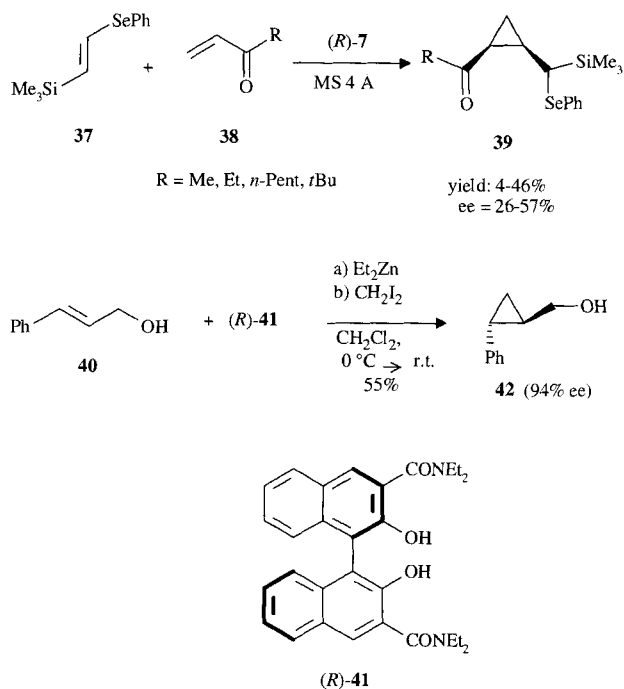
are also applicable in cycloadditions forming carbocyclic compounds. As an example the preparation of the cyclohexene derivative **28** from methacrolein (**27**) and diene **26** using 10 mol% of catalyst **7** in toluene (94% *ee*, 99% *endo* product) is noteworthy [21]. On the other hand, when the same reaction was performed in dichloromethane instead of toluene a dramatic decrease of the stereoselectivity in this cycloaddition reaction was observed.

Interestingly, several reports described the critical importance of additives in the stereocontrolled cycloaddition reaction. For example, the influence of adding chiral activators on



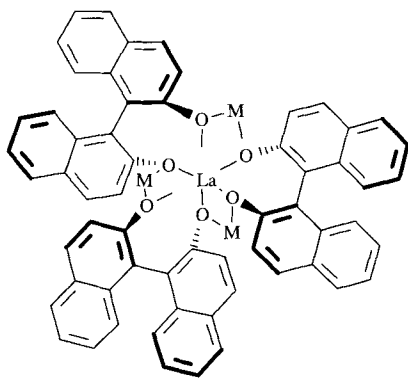
catalyst **5** [22] or the use of molecular sieves with differing moisture content [23] have been examined. Inanaga has briefly reported the asymmetric hetero-Diels–Alder reaction of aromatic aldehydes **30** and Danishefsky's diene **29** in the presence of the chiral Yb-phosphate catalyst **31** [24]. In this cycloaddition 2,6-lutidine was found to be an effective additive thus achieving the product **32** in high enantioselectivities (up to 93%). Recently, Jørgensen has described a new highly chemo- and enantioselective hetero-Diels–Alder reaction of conjugated dienes containing allylic C–H bonds with electron deficient aldehydes in the presence of (*S*)-BINOL–AlMe [25]. Reaction of 1,3-diene **33** and ethyl glyoxylate (**34**) gave the cycloadduct **35** as major product with an excellent *ee*-value (97%) besides the ene product **36** as minor component with a lower enantioselectivity (88% *ee*).

Asymmetric [2+1] cycloadditions can be performed using the chiral Lewis acid **7** [26] and zinc-BINOL derivatives [27]. The resulting cyclopropanes are in moderate to good optical yields.

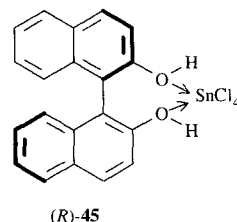
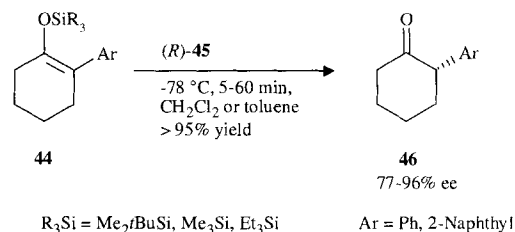


An elegant exploitation of BINOL derivatives is given by Shibasaki and Sasai through their commercially available (*R*)- and (*S*)-configured tri-lithium-tris[1,1'-bi-(2-naphtholato)]lanthanate (**43**) which received the FLUKA price for the reagent of the year 1996. A review article dealing with a wide range of the multifunctional dimetal complex **43** and related Lewis acids thereof as highly effective catalysts for nitroaldol reactions, tandem-Michael-aldoladditions, hydrophosphonylation reactions *etc.* has appeared recently [28].

Worth mentioning is also the development in asymmetric protonation using tin-BINOL-complex (*R*)-**45**, which is *in situ* generated from SnCl<sub>4</sub> and (*R*)-**1** [29]. Thus, the reaction of **45** with silyl enol ethers **44** leads to ketones **46** with enantiomeric excesses of 77–96%.



43 M: Li, Na or K



The ever increasing number of publications describing novel and wide ranging applications of BINOL (**1**) demonstrates its usefulness as chiral C<sub>2</sub>-symmetric ligand for stereoselective C–C-Bond forming reactions.

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Address for correspondence:

Dr. R. Zimmer

Technische Universität Dresden

Institut für Organische Chemie

Mommsenstrasse 13

D-01062 Dresden

E-mail: Reinhold.Zimmer@chemie.tu-dresden.de