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Review

Synthesis and application of new chiral catalysts for asymmetric alkynylation reactions

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Contents

Abstract

Various combinations of chiral ligands and transition metal sources have been used as catalysts in the enantioselective alkynylation of aldehydes and ketones. The results of previous studies and current investigations are reviewed. The factors governing the yields and enantioselectivities are discussed.

Keywords: Asymmetric catalysis; Enantioselectivity; Alkynylation; Nucleophilic addition

1. Introduction

Optically active propargylic alcohols are versatile building blocks for the synthesis of a wide range of natural products and pharmaceuticals [1]. Although the most common approach to these compounds is the direct reduction of alkynyl ketones, the alkynylation of aldehydes by organometallic reagents has a strategic advantage because it forms a new C–C bond with concomitant creation of a stereogenic center in a single transformation, while in the former approach the C–C bond and the new chiral center are formed separately. Among many organometallic nucleophiles, organozinc reagents can tolerate the presence of many functional groups that are reactive towards organolithium and Grignard reagents. This property renders the organozinc species attractive useful alternatives to the highly active reagents.

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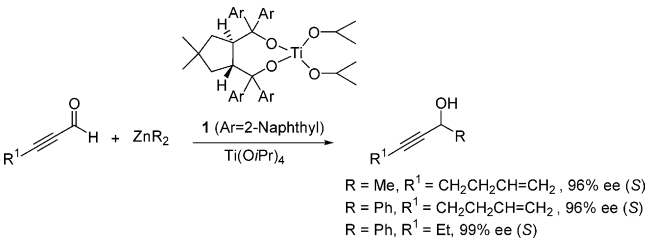
The scope of this review is focused on the asymmetric alkynylzinc addition catalyzed by chiral transition metal complexes.

2. Enantioselective alkynylation of aldehydes

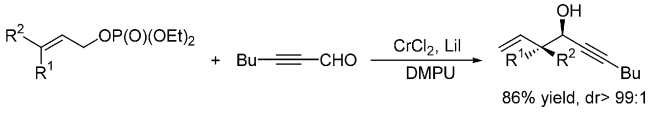
2.1. Enantioselective alkylation of alkynyl aldehydes

Seebach et al. obtained secondary propargylic alcohols of very high enantiopurity (up to 99% ee) via the addition of dialkylzinc to alkynyl aldehydes in the presence of chiral Ti-TADDOLate **1** (Eq. (1)) [2,3].



(1)

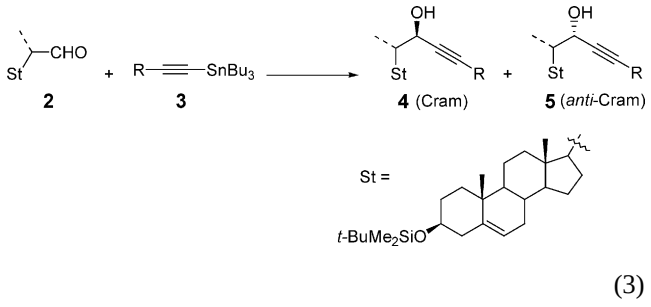
Knochel and co-workers reported the reaction of γ-disubstituted allylic phosphates with alkynyl aldehydes and $CrC1_2$ in the presence of catalytic amount of LiI in DMPU. Again, the reaction proceeded with high stereoselectivity (Eq. (2)) [4].



(2)

2.2. Enantioselective alkynylation of aldehydes with other alkynyl organometallic reagents

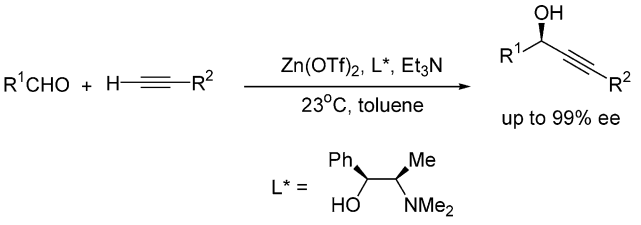
Yamamoto et al. found that the reaction of a steroidal aldehyde **2** with stannylacetylene **3** produced the Cram isomer **4** with high diastereoselectivity (at least 85:15) (Eq. (3)). High selectivity also occurred in the reaction of **2** with allylstannane and allylsilane [5].



(3)

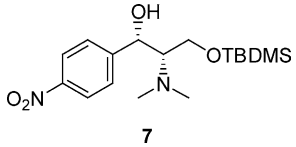
Krause and Seebach prepared R≡Ti(O*i*Pr)$_3$ and used it in the alkynylation of aldehydes with only low to moderate diastereoselectivity [6]. Baldoli et al. added lithium acetylides and ethynyl magnesium bromide to chiral *ortho*-substituted benzaldehyde tricarbonylchromium complexes and obtained alkynyl alcohols in good yields with excellent diastereoselectivity (≥98% de) [7].

Carreira and co-workers reported an efficient system using stoichiometric amount of *N*-methylephedrine **6** and $Zn(OTf)_2$ to promote the reaction of terminal alkynes with a variety of aromatic or aliphatic aldehydes to give very high enantioselectivities (92–99% ees) (Eq. (4)) [8]. Later on, these investigators also successfully carried out the reaction using catalytic amounts of $Zn(OTf)_2$ and **6**. The catalyst system was excellent for aliphatic aldehydes but was less effective for aromatic substrates [9,10].

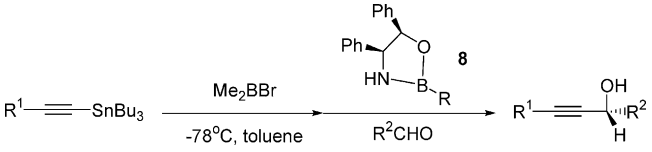


(4)

More recently, Jiang et al. prepared a new chiral amino alcohol ligand **7** (1*S*,2*S*)-2-*N*,*N*-dimethylamino-1-(*p*-nitrophenyl)-3-(*t*-butyl-dimethylsilyloxy)-propane-1-ol and used it stoichiometrically in asymmetric alkynylation reaction to give high yields and up to 99% ee [11]. Besides $Zn(OTf)_2$, $ZnCl_2$ [12] and $Zn(ODf)_2$ [13] were also proved to be effective for this transformation, comparable chemical yields and selectivities were obtained in most cases.



Corey and Cimprich described the use of chiral oxazaborolidine **8** as catalyst for the enantioselective addition of alkynylboranes to aldehydes with up to 97% ee at low temperature (Eq. (5)) [14].



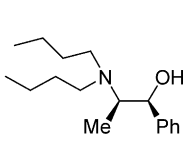
(5)

2.3. Enantioselective alkynylation of aldehydes with alkynylzinc reagents

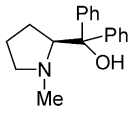
Unlike the catalytic enantioselective addition of dialkyl- and alkenylzinc compounds to aldehydes which are promoted

by hundreds of catalysts, the current methods for asymmetric alkynylation are still less developed due to either the requirement of large (stoichiometric) amounts of catalysts, limited source of reagents, or the formation of considerable amounts of alkylated byproducts [15,16]. Highly enantioselective catalytic alkynylmetal addition to aldehydes has been developed only recently.

Soai and Niwa [15], Tombo et al. [17], Ishizaki and Hoshino [18] and Li et al. [19] have reported the asymmetric alkynylzinc addition to aldehydes, respectively. Using chiral ligands **9**–**16**, only low to moderate enantioselectivities were obtained.



9 (1*S*,2*R*)-DBNE



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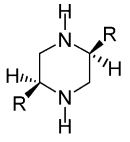
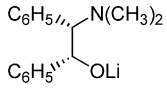
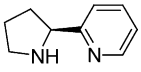


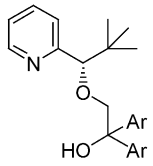
11a R = $PhCH_2$
b R = *i*Pr



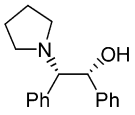
12



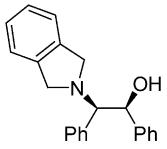
13



14a Ar = α-Naphthyl
b Ar = β-Naphthyl
c Ar = Ph

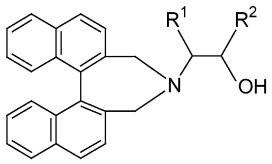


(1*R*,2*S*)-**15**



(1*S*,2*R*)-**16**

It was anticipated that introducing rigid binaphthyl group into an amino alcohol might have some structural advantages over traditional amino alcohol in asymmetric catalysis. Thus, ligands **17**–**20** with binaphthyl backbones were synthesized and one of them, (1*R*,2*S*,3*R*)-**17**, was found to be highly effective in the asymmetric alkynylation of aldehydes [20]. In the presence of dimethylzinc, various aromatic aldehydes were converted to the corresponding chiral propargylic alcohols in 61–93% ees. This catalyst was found to work well in the alkynylation of aromatic aldehydes using both aromatic and aliphatic acetylenes as nucleophile, while aliphatic aldehydes were found to give low enantioselectivities (36% ee for the alkynylation of cyclohexanecarboxaldehyde). Compared with chiral ligands **15** and **16**, (1*R*,2*S*,3*R*)-**17** showed significantly superior efficacy under identical reaction conditions.



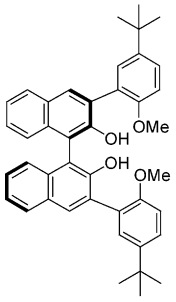
(1*R*,2*S*,3*R*)-**17**, R^1 = Ph, R^2 = Ph
(1*R*,2*R*,3*S*)-**18**, R^1 = Ph, R^2 = Ph
(1*S*,2*S*,3*R*)-**19**, R^1 = Ph, R^2 = Ph
(1*R*,2*R*,3*S*)-**20**, R^1 = CH_3, R^2 = Ph

The combination of chiral BINOL with various metal salts have been widely used in asymmetric reactions. Previous studies revealed that chiral catalysts derived from 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthyl ligands (H_8-BINOL) exhibited higher efficiency and enantioselectivity for many asymmetric transformations than those using BINOL ligand [21], probably due to the steric and electronic modulations in the binaphthyl backbone.

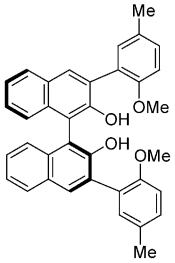
The use of chiral Ti(O*i*Pr)$_4$-BINOL and Ti(O*i*Pr)$_4$-H_8BINOL catalysts in asymmetric alkynylation was studied [22]. Various aldehydes were converted to the corresponding propargylic alcohols with very good enantioselectivities (96% ee for the alkynylation of 3-nitrobenzaldehyde) and yields. The system was also applicable to aliphatic aldehydes and moderate to good ees were obtained in most cases. The reactions catalyzed by (*R*)-H_8-BINOL gave significantly higher ees than those obtained from (*R*)-BINOL.

Moore and Pu also reported a similar system in this reaction with up to 98% ee for aromatic aldehydes [23]. To avoid the side product of ethyl addition, they developed a method involving the refluxing of phenylacetylene with diethylzinc before the reaction. Later, they demonstrated that the Ti(O*i*Pr)$_4$-BINOL catalyst was also efficient for the asymmetric alkynylation of aliphatic aldehydes as well as α,β-unsaturated aldehydes [24].

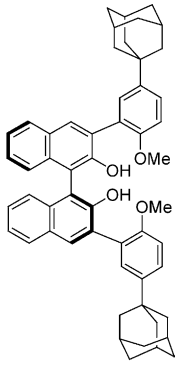
Further structural modifications on the BINOL ligand revealed that though chiral catalysts (*R*)-**21** and (*S*)-**22** gave reasonable enantioselectivities (up to 92% ee) in the asymmetric alkynylation, they were not as efficient as simple chiral BINOL [25]. 1,1′-Binaphthyl compound (*S*)-**23** containing more bulky 3,3′-aryl substituents catalyzed the reaction of terminal alkyne with various aromatic aldehydes (80–94% ees) even without the use of titanium complex [26].



(*R*)-**21**

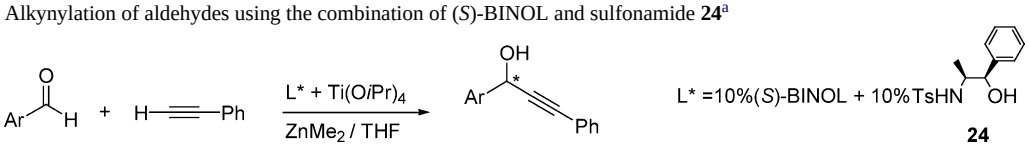


(*S*)-**22**



(*S*)-**23**

Table 1
Alkynylation of aldehydes using the combination of (*S*)-BINOL and sulfonamide **24**[a]



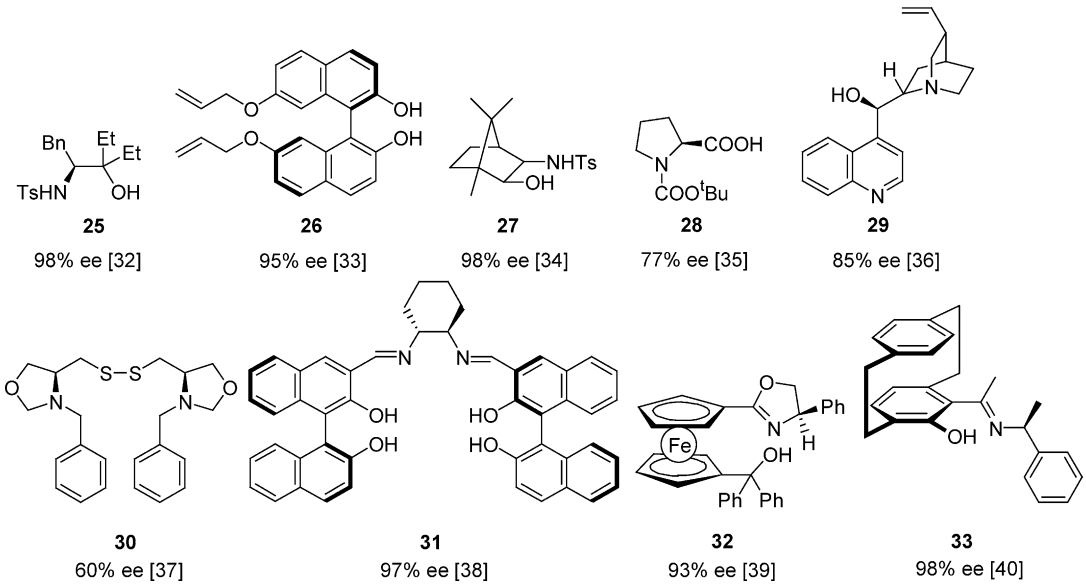
Entry	Aldehyde	Yield (%)	ee (%)
1	Benzaldehyde	83	96(*R*)
2	2-Nitrobenzaldehyde	83	88(*R*)
3	3-Nitrobenzaldehyde	82	99.7(*R*)
4	4-Nitrobenzaldehyde	82	99(*R*)
5	4-Bromobenzaldehyde	85	99(*R*)
6	3-Chlorobenzaldehyde	84	97(*R*)
7	4-Chlorobenzaldehyde	86	95(*R*)
8	2-Naphthaldehyde	81	95(*R*)
9	4-Anisaldehyde	78	95(*R*)
10	4-Tolualdehyde	79	92(*R*)

[a] The ratio of ligands (BINOL + sulfonamide **24**) to Ti(O*i*Pr)$_4$ was 1.0:1.5; 0 °C; 24–48 h.

The self-assembly of several components into a highly enantioselective catalyst for asymmetric reaction is a new frontier in organic synthesis. Mikami et al. reported the self-assembly of several chiral ligand components into a highly enantioselective titanium catalyst for carbonyl–ene reactions [27]. Following this work, we reported a chiral self-assembled titanium catalyst for asymmetric alkynylation, and the use of (*S*)-BINOL and chiral sulfonamide **24** proved to be the best combination in the reaction. Both the catalytic activity and enantioselectivity (99.7% ee) were substantially better than all previously reported results (Table 1) [28].

Asymmetric catalytic reactions are often sensitive to small changes in reaction conditions. Sometimes the addition of small (usually also catalytic) amounts of achiral compounds can enhance the yields and enantioselectivities [29]. We found that the activation of chiral Ti(O*i*Pr)$_4$-BINOL complexes by achiral activators, e.g. phenol, provided higher levels of enantioselectivity than that attained by using enantiopure catalyst alone in the alkynylation of both aromatic and aliphatic aldehydes [30]. Pu and co-workers also found that the addition of hexamethylphosphoramide (HMPA) in the catalyst system helped to generate alkynylzinc reagent under milder condition (room temperature) and afforded high enantioselectivity [31].

Recent attempts to improve the activity and enantioselectivity of the asymmetric alkynylation led to the development of other types of chiral ligands **25**–**33** including sulfonamide, N-terminal protected amino acid, cinchonidine, salen and ferrocenyl oxazoline [32–40].



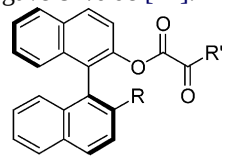
3. Enantioselective alkynylation of ketoesters

Chiral tertiary α-hydroxyesters are important building blocks and synthetic intermediates for the preparation of biologically active substances. The synthesis of this class of compound may be accomplished through the diastereoselective addition of organometallic reagents to

chiral α-ketoesters. Obviously the development of catalytic enantioselective addition of alkynyl species to prochiral α-ketoesters is of even higher interest.

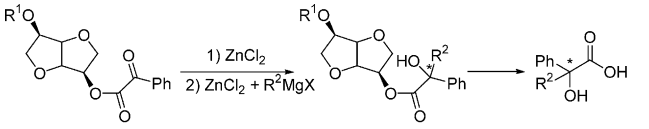
3.1. Chiral auxiliary directed stereoselective alkylation of α-ketoesters

Sugimura and Watanabe reported the diastereoselective 1,2-additions of bromomagnesium triorganozincates to prochiral ketoesters to afford the corresponding α-hydroxyesters in good yields [41]. Similarly, the addition of MeZnI to the α-ketoesters of axially chiral 1,1′-binaphthalen-2-ol derivatives **34** gave 84% de [42].



34

Using dehydromannitol as chiral auxiliary, the diastereoselective addition of organozinc reagents to phenylglyoxylates **35** afforded, after saponification, the desired α-hydroxy acids **36** with 60–99% ees (Eq. (6)) [43].

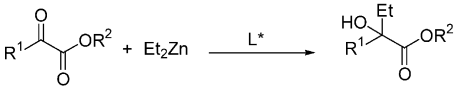


35

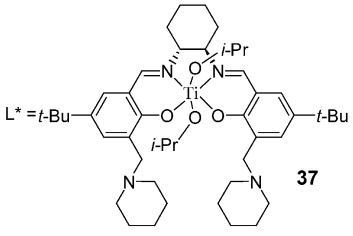
36 R^1 = Bn, R^2 = *i*Pr
53% yield, >99% de (S)

(6)

A transition-state analysis on the alkylzinc addition to aldehydes indicated that the presence of an additional Lewis base coordinated to Me_2Zn significantly increased the nucleophilicity of Me_2Zn and led to a more efficient reaction [44]. Indeed, DiMauro and Kozlowski found that bifunctional amino salen complex **37** catalyzed the addition of diethylzinc to α-ketoesters to give the corresponding α-hydroxyester in 96% isolated yield with 78% ee (Eq. (7)) [45,46]. This result was attributed to the crucial role played by the piperidine groups, which acted as an activating Lewis base.



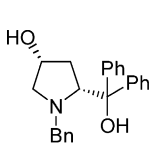
R^1 = Ph, R^2 = Et, 99% conv, 56% ee (*R*)
R^1 = Ph, R^2 = Me, 99% conv, 78% ee (*R*)
R^1 = *p*-MeO-C_6H_4, R^2 = Et, 99% conv, 52% ee (*R*)



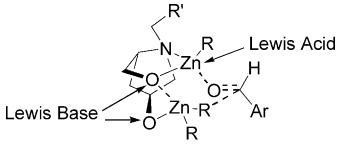
37

(7)

Shibasaki and co-workers prepared a series of multifunctional compounds **38a** [47]. The 4-hydroxyl group on the pyrrolidine ring *cis*- to the 2-carbinol functional group was designed to react with dimethylzinc to form a zinc alkoxide, which provided an additional Lewis base site (**38b**). In the presence of chiral ligand **38a**, the addition of dimethylzinc to α-ketoester proceeded smoothly, yielding the corresponding α-hydroxyl alcohol in up to 96% ee.



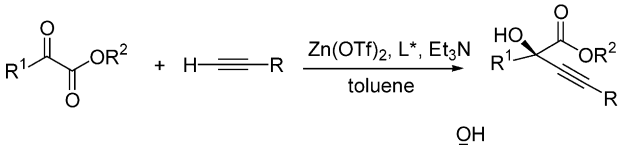
38a



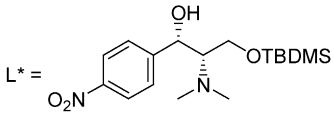
38b

3.2. Enantioselective alkynylation of ketoesters

Recently, Jiang et al. reported the asymmetric addition of terminal alkynes to α-ketoesters using inexpensive amino alcohol **7** in combination with $Zn(OTf)_2$ as the catalyst, and the corresponding tertiary propargylic alcohols were obtained in high yields and up to 94% ee (Eq. (8)) [48].



L* =



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(8)

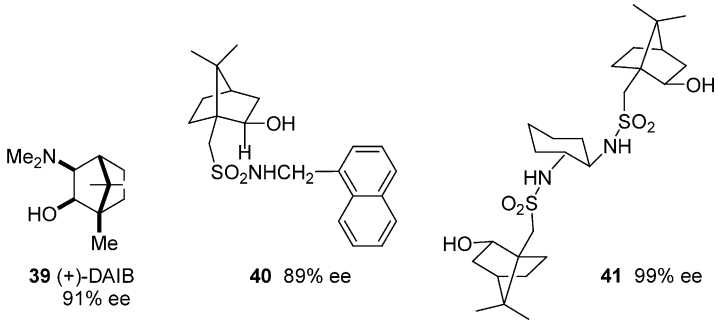
4. Enantioselective alkynylation of ketones

Unlike the additions of dialkylzinc reagents to aldehydes, which are promoted by hundreds of catalysts, only a few catalysts are useful for the addition of alkyl groups to ketones, and most of them required high catalyst loadings and long reaction time.

4.1. Enantioselective alkylation of ketones

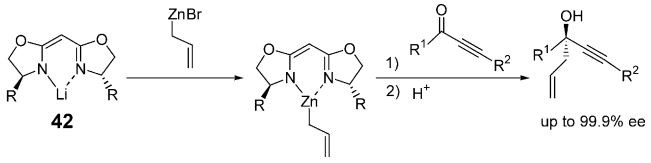
The enantioselective addition of diphenylzinc to aromatic ketones was first reported by Dosa and Fu [49]. They found that DAIB **39** was an effective catalyst for the asymmetric addition of Ph_2Zn to a variety of aryl–alkyl and dialkyl ketones, and the quaternary stereocenters were created with good to excellent stereocontrol.

Using camphorsulfonamide alcohol **40**, Ramón and Yus achieved the first catalytic dialkylzinc addition to ketones with up to 89% ee [50,51]. A breakthrough came when Walsh and co-workers reported the use of chiral bis(sulfonamide) diol ligand **41** [52]. Excellent results (as high as 99% ee even in 2 mol% catalyst loadings) were obtained for the addition of dialkylzinc to ketones. Later, this catalyst was proved by several groups to be highly efficient for a broad range of substrates, including aliphatic ketones, aromatic ketones and conjugated enones [53–57]. The organozinc reagents included alkylzinc, arylzinc [58,59] and allylzinc [60] species.



39 (+)-DAIB 91% ee **40** 89% ee **41** 99% ee

The enantioselective addition of allylzinc reagents to alkynyl ketones catalyzed by a bisoxazoline catalyst **42** was reported by Nakamura et al. (Eq. (9)) [61]. High ee values were obtained in most cases.



42

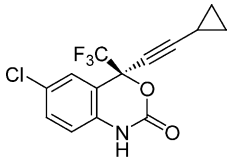
(9)

4.2. Enantioselective alkynylation of ketones with other organometallic reagents

The stereoselective formation of C–C bonds is of great importance for the synthesis of enantiomerically pure natural products and pharmaceuticals. A broad repertoire of chiral auxiliaries, reagents, and catalysts can be utilized for the reliable generation of tertiary stereocenters. The synthesis of organic compounds containing quaternary stereocenters is still a challenging task.

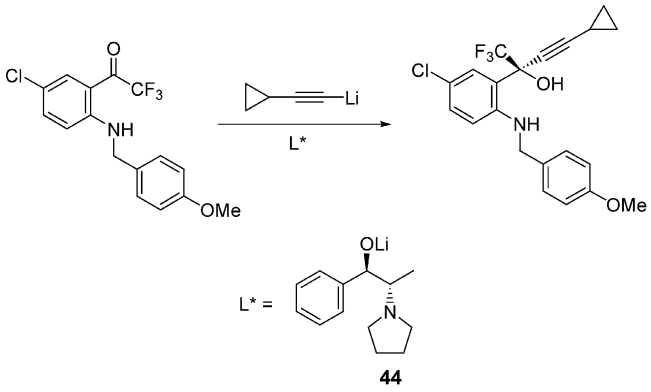
Our research interest was focused on the synthesis of chiral tertiary propargylic alcohols, a class of compounds useful as pharmaceutical intermediates. There are several methods for the synthesis of these compounds: (1) reaction of alkynyl halides with indium [62] or $CrCl_2$, followed by the reaction with ketones; (2) catalytic C–H activation of alkynes with strong bases, such as cesium hydroxide [63] or potassium *t*-butoxide [64], followed by the reaction with ketones; (3) direct alkynylation of ketones by alkynyllithium or alkynylmagnesium; (4) alkynylation of ketones by propargylic bromide using phase-transfer catalyst system such as KOH(s)/18-crown-6/benzene [65,66]; (5) electrochemical propargylation of ketones with propargylic bromides [67].

The synthesis of these compounds by the catalytic asymmetric addition of carbon nucleophiles to ketones has achieved only limited success. A good example is the enantioselective synthesis of efavirenz **43**, a potent nonnucleosidal HIV reverse transcriptase inhibitor that has been approved by the USFDA for the treatment of AIDS [68].



43 Efavirenz

Thompson et al. realized the addition of lithium-cyclopropyl acetylide to *p*-methoxybenzyl-protected ketoaniline in 98–99% ee (Eq. (10)) [69–72]. However, the success of the reaction relies on the application of large amounts of catalyst and the protection of the aniline moiety.

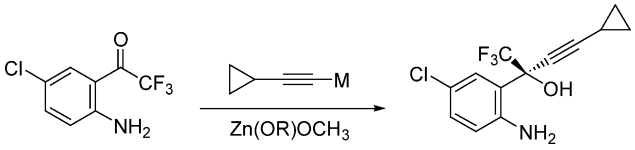


44

(10)

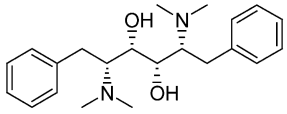
Tan et al. reported the direct alkynylation of ketoaniline (up to 99.2% ee) using alkynyllithium or alkynylmagne-

sium reagents with stoichiometric amounts of chiral zinc aminoalkoxides (Eq. (11)) [73]. The reaction has been carried out successfully on a multi-kilogram scale and is probably the most efficient synthesis of efavirenz to date.



(11)

Jiang and Feng also studied the asymmetric alkynylation of PMB-protected ketoaniline. Excellent ee (99%) was obtained using lithium cyclopropylacetylide as nucleophile and C_2-symmetric diamino diols **45** as chiral ligand [74].

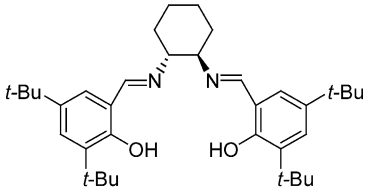


45

4.3. Enantioselective alkynylation of ketones with alkynylzinc reagents

High enantioselectivities have been achieved for the alkynylation of activated ketones with active organometallic reagents, as described in Section 4.2. Tan et al.'s asymmetric alkynylation reaction is in fact a stoichiometric alkynylzinc (prepared in situ from alkynylithium or Grignard reagents) addition to activated ketones [73]. The alkynylation of unactivated simple ketones is still an important challenge. Unlike the alkynylzinc addition to aldehydes, the asymmetric alkynylzinc addition to ketones has been substantially less developed, mostly due to the low reactivity of the reaction.

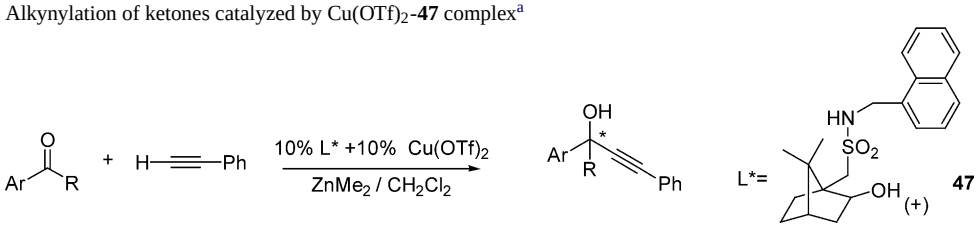
Recently, Cozzi found that the enantiomerically pure salen **46** (20 mol%) catalyzed the reaction of phenylacetylene with acetophenone in the presence of Me_2Zn to give the corresponding propargylic tertiary alcohol in 72% yield and 61% ee [75]. When these conditions were applied in the additions of various alkynes to different ketones, ees up to 81% were achieved.



46 (*R*,*R*)-salen
60% ee

At about the same time, we also reported the asymmetric addition of alkynylzinc to aromatic ketones with catalytic amount of chiral $Cu(OTf)_2$-camphorsulfonamide **47** complex (Table 2) [76]. This catalyst system was highly efficient for a variety of aromatic ketones, and substituents at the *ortho*-position of the substrate had a favorable effect on the enantioselectivity. The best enantioselectivity (97%) was observed in the alkynylation of 2′-chloroacetophenone. It was possible that the proper steric hindrance of the *ortho*-substituents restricted the orientation of the substrates and thus resulted in higher enantioselectivities for the alkynylation of such ke-

Table 2
Alkynylation of ketones catalyzed by $Cu(OTf)_2$-**47** complex[a]



47

Entry	Ketone	Yield (%)	Ee (%)
1	Acetophenone	92	88(+)
2	2′-Bromoacetophenone	65	96(−)
3	2′-Chloroacetophenone	94	97(−)
4	2′-Fluoroacetophenone	91	96(−)
5	2′-Methylacetophenone	49	96(−)
6	3′-Bromoacetophenone	80	82(+)
7	4′-Bromoacetophenone	75	91(+)
8	3′-Methylacetophenone	83	86(+)
9	4′-Methylacetophenone	77	92(+)
10	4′-(Trifluoromethyl)acetophenone	82	93(+)[b]
11	2′-Naphthacetophenone	75	85(+)
12	Propiophenone	57	71(+)
13	4′-(Ferrocenyl)acetophenone	62	90(+)[b]
14	3-Methyl-2-butanone	90	88(−)[b]
15	*trans*-4-Phenyl-3-buten-2-one	95	85

[a] Ketone:ligand:$Cu(OTf)_2$:Me_2Zn = 0.4:0.04:0.04:1.2 (molar ratio), CH_2Cl_2 as solvent, 0 °C for 48 h.
[b] Unpublished work.

tones. To the best of our knowledge, this is the highest result for the asymmetric addition of alkynylzinc reagents to ketones.

5. Conclusions

In summary, the study on the synthesis of optically active propargylic alcohols is of great importance, and significant advancement has been achieved in recent years. It is expected that more and more chiral catalysts will be developed to expand the scope of these reactions and to facilitate the practical applications of these methods for the synthesis of high-valued pharmaceutical products.

Acknowledgements

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