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Highly Enantioselective Addition of Trimethylsilylacetylene to Aldehydes Catalyzed by a Zinc–Amino-Alcohol Complex

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The enantioselective alkynylation of aldehydes is one of the most useful carbon–carbon bond-forming reactions for the preparation of chiral propargylic alcohols,[1] which are versatile building blocks for fine chemicals, pharmaceuticals, and natural products.[2,3] Accordingly, much progress has been made in the asymmetric addition of terminal alkynes to aldehydes, which has been established as a reliable platform for the efficient synthesis of a wide array of chiral propargylic alcohols.[1,4] Various alkyne derivatives such as arylacetylene, alkylacetylene, ethynylcyclohexene, acetalacetylene, methyl propiolate, 1,3-diyne, and trimethylsilylacetylene have been used as the alkyne nucleophiles.[1] Among these nucleophiles, trimethylsilylacetylene is highly attractive due to the potential application of the corresponding trimethylsilyl alkynol product. The product can be easily desilylated to give the corresponding terminal alkynol, which can further be used as the precursor to carry out the alkylation or the Sonogashira coupling for the synthesis of some natural products and useful chemicals.[5] A variety of effective catalytic systems including amino-alcohol–Zn,[6] imino-alcohol–Zn,[7] hydroxyl-carboxyamide–Zn,[8] proline-derived dinuclear Zn,[4i] bisoxazolidine–Zn,[4j] 1,1′-bi-2-naphthol (BINOL)–Ti,[9] bisphosphine–Cu^{I},[10] sulfonamide-alcohol–Ti,[11] and bis(oxazolinyl)phenyl–Ru[4q] have been developed for the addition of trimethylsilylacetylene to aldehydes. In particular, by using catalytic systems such as Trost's proline-derived dinuclear Zn,[4i] Wolf's bisoxazolidine–Zn,[4j] Pu's BINOL–Ti,[9b] Wang's sulfonamide alcohol–Ti,[11] and Nishiyama's bis(oxazolinyl)-phenyl–Ru,[4q] excellent enantioselectivity (>90% enantiomeric excess (*ee*)) can be achieved in the addition of trimethylsilylacetylene to aldehydes. Among the catalytic systems reported so far for the alkynylation of aldehydes, the amino-alcohol–Zn system is particularly noteworthy in terms of its operational simplicity and mild reaction conditions. The amino-alcohol–Zn catalytic system has attracted much attention since the pioneering contribution from Carreira and co-workers, who demonstrated that by using a combination of $Zn(OTf)_2$ and *N*-methylephedrine, the addition of terminal acetylenes to aldehydes afforded the desired products in high yields and enantioselectivities.[4b,12] However, to the best of our knowledge, no impressive amino-alcohol–Zn system (except for Trost's dinuclear Zn catalyst) for the alkynylation of aldehydes with trimethylsilylacetylene has been reported so far, therefore a new, generally applicable procedure using amino-alcohol–Zn would still be highly desirable.[13] In this context, we conceived the possibility of introducing a new type of 1, 4-amino alcohol, based on the chiral cyclopropane backbone (**1**–**3**), which might serve as an excellent chiral ligand in the alkynylation of aldehydes with trimethylsilylacetylene. Herein, we report the highly enantioselective addition of trimethylsilylacetylene to a wide range of aldehydes catalyzed by the zinc complexes of chiral 1,4-amino alcohols.

Recently we reported a series of chiral amino alcohols based on the cyclopropane backbone, which exhibited an advantageous combination of structural rigidity, low molecular weight on a well-defined and highly variable platform, and unusual bond angles. By using these amino alcohols in combination with dialkylzinc, the addition of dialkylzinc or some alkyne derivatives to aldehydes could be carried out with high enantioselectivity.[4o,13] As a continuing effort to develop highly enantioselective alkynylation catalysts, we speculated that modification of the ligand structure, by introducing another chiral center on the side chain of the chiral cyclopropane backbone, might provide extra steric discriminations that may enhance the enantioselectivity. With this in mind, new chiral ligands **1**, **2**, and **3** were designed and synthesized by introduction of the (*R*)- and (*S*)-prolinols into the side chain of a chiral cyclopropane backbone by using a four-step reaction (Scheme 1). To increase the steric effect, the hydroxyl group in prolinol was protected with *tert*-butyldimethylsilyl (TBDMS) or *tert*-butyldiphenylsilyl (TBDPS).

With the amino alcohols **1**, **2**, and **3** in hand, our initial attempts at amino-alcohol–Zn-catalyzed asymmetric addition of trimethylsilylacetylene to aldehydes commenced with the reactions of benzaldehyde and trimethylsilylacetylene. Table 1 presents the results of the model reaction between benzaldehyde and trimethylsilylacetylene, in which we established appropriate reaction conditions by screening

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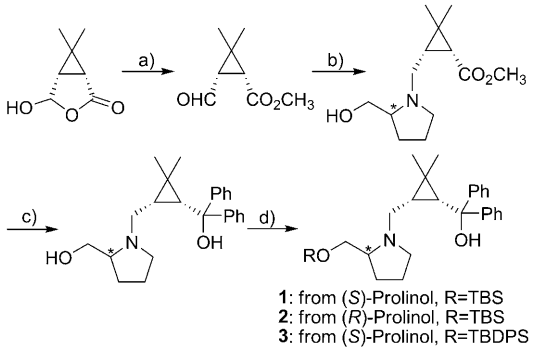
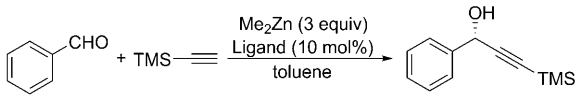


Scheme 1. Synthesis of amino alcohol ligands. TBS = *tert*-butylsilyl. Reaction conditions: a) TsOH (0.2 equiv), CH_3OH, reflux, 5 h, CH_3CO_2Na (0.4 equiv), and $(COOH)_2$ (0.5% aq.). b) $NaBH_3CN$(0.5 equiv), Prolinol (2 equiv), H_2SO_4 (0.5 equiv), and CH_3OH. c) PhMgCl (4 equiv), and THF at room temperature, 24 h. d) *tert*-butyldimethylsilyl (TBDMS) or *tert*-butyldiphenylsilyl (TBDPS) (2 equiv), imidazole (3 equiv), and CH_2Cl_2.

Table 1. Enantioselective addition of trimethylsilylacetylene to benzaldehyde catalyzed by ligands **1**–**3**.[a]



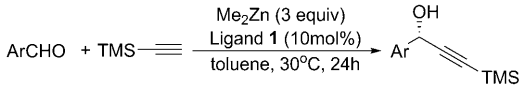
Entry	Ligand	*T* [°C]	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**1**	30	24	78	94
2	**2**	30	24	58	36
3	**3**	30	24	80	92
4	**1**	0	48	48	94
5	**1**	−20	48	trace	n.d.
6[d]	**1**	30	24	83	93

[a] Three equivalents of trimethylsilylacetylene were used. [b] Yield of isolated product. [c] Determined by HPLC. [d] 20 mol% of ligand was used.

amino alcohols under different conditions. Initially, benzaldehyde was treated with trimethylsilylacetylene in toluene at 30°C in the presence of **1** (10 mol%), and the reaction proceeded smoothly to give the corresponding propargylic alcohols in 78% yield and with an excellent 94% *ee* (Table 1, entry 1). In sharp contrast, whereas ligand **2** was employed under otherwise identical conditions, the alkynylation reaction only afforded the product in 58% yield and with a poor 36% *ee* (Table 1, entry 2). On the contrary, ligand **3**, with the same configuration as ligand **1**, could deliver the product in 80% yield, albeit with a slightly lower 92% *ee* (Table 1, entry 3). This shows that the chiral center in pyrrolidine plays the decisive role, which explains the dramatic differences in the catalytic results. In the presence of **1** (10 mol%), lowering the reaction temperature to 0°C resulted in a dramatic decrease in reactivity (Table 1, entry 1 vs. entry 4). When the reaction temperature continued to be lowered to −20°C, the catalyst was nearly inert (Table 1, entry 1 vs. entry 5). When the amount of ligand **1** was increased from 10 to 20 mol%, the alkynol product was obtained in slightly improved yield, albeit with a slightly lower *ee* value (Table 1, entry 1 vs. entry 6).

By using **1** (10 mol%) as the ligand, a range of aromatic aldehydes were examined in toluene at 30°C (Table 2). A variety of aromatic aldehydes underwent the addition reaction, providing the anticipated chiral alkynol products in good yields and with consistently excellent *ee* values (≥90%) (Table 2, entries 1–14). A wide range of aryl groups, with electron-donating or withdrawing substituents on the benzene ring, could be tolerated in the process; in particular, when 4-methoxybenzaldehyde was used as substrate, the best *ee* value of 97% was obtained (Table 2, entry 11). In addition, aromatic aldehydes with 1-naphthyl (Table 2, entry 12), 2-naphthyl (entry 13), or heteroaryl groups such as 1-furyl (entry 14) also smoothly underwent the addition reaction, to readily afford the corresponding alkynol products with excellent enantioselectivities (90–95% *ee*) and in good yields (Table 2, entries 12–14). All these results demonstrate the high efficiency of the new amino alcohol ligand **1**.

Table 2. Enantioselective addition of trimethylsilylacetylene to aromatic aldehydes.[a]

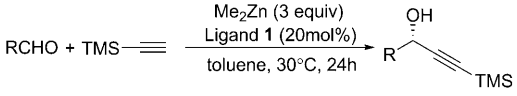


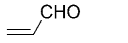
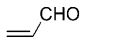
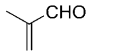
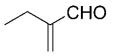
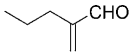
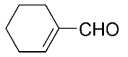
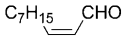
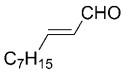
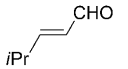
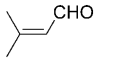
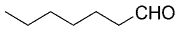
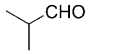
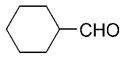
Entry	R	Yield [%][b]	*ee* [%][c]
1	Ph	78	94
2[d]	*o*FC_6H_4	62	94
3[d]	*m*FC_6H_4	61	93
4	*p*FC_6H_4	66	96
5	*p*ClC_6H_4	62	96
6[d]	*o*$CH_3C_6H_4$	77	95
7[d]	*m*$CH_3C_6H_4$	78	94
8	*p*$CH_3C_6H_4$	76	95
9	*o*$CH_3OC_6H_4$	70	94
10	*m*$CH_3OC_6H_4$	72	96
11	*p*$CH_3OC_6H_4$	84	97
12	1-naphthyl	84	95
13	2-naphthyl	73	94
14	1-furaldehyde	60	90

[a] Three equivalents of trimethylsilylacetylene were used. [b] Yield of isolated product. [c] Determined by HPLC. [d] Absolute configuration has not been assigned.

After successfully evaluating the alkynylation of aromatic aldehydes with trimethylsilylacetylene, we were delighted to find out that even α,β-unsaturated and aliphatic aldehydes could also undergo the alkynylation reaction in the presence of amino alcohol **1**, albeit with a slightly lower *ee* value (Table 3, entries 1–13). Initially, by using a standard 10 mol% of **1**, the alkynylation reaction proceeded to afford the product with 63% *ee* and a poor yield of 40% (Table 3, entry 1). After the catalyst loading was increased to 20 mol%, the product was obtained with an improved 83% *ee* and in 68% yield (Table 3, entry 2). Therefore, the reaction of a range of distinctly substituted α,β-unsaturated

Table 3. Enantioselective addition of trimethylsilylacetylene to α,β-unsaturated and aliphatic aldehydes.[a]

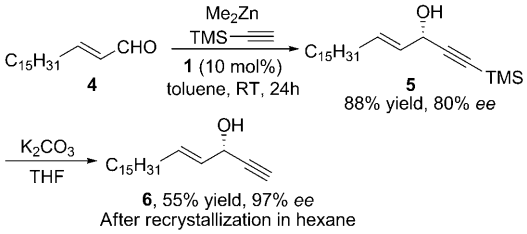


Entry	Aldehyde	Yield [%][b]	*ee* [%][c]
1[d]		40	63
2		68	83
3		82	92
4[e]		71	94
5[e]		70	94
6		88	94
7		82	85
8		80	85
9		62	83
10[e]		74	84
11		62	76
12		78	82
13		80	87

[a] Three equivalents of trimethylsilylacetylene were used. [b] Yield of isolated product. [c] Determined by HPLC. [d] 10 mol% of ligand was used. [e] Absolute configuration has not been assigned.

and aliphatic aldehydes with trimethylsilylacetylene was investigated in the presence of 20 mol% of amino alcohol **1** (Table 3). The substituent at the α-carbon of the α,β-unsaturated aldehyde appeared to have a great influence on the enantioselectivity of the reaction. α-Alkyl substituted α,β-unsaturated aldehydes underwent the addition reaction in 92–94% *ee* with good yields (Table 3, entries 3–6). In contrast, the reactions with acrylaldehyde (Table 3, entry 2), β-alkyl (entries 7–9), and β,β′-dialkyl (entry 10) substituted aldehydes were somewhat sluggish to react, leading to the corresponding products with 80–85% *ee*. The nature and number of the substituent at the β-carbon of the α,β-unsaturated aldehyde does not have an impact on the reaction course (Table 3, entries 7–10). In addition, the *E* and *Z* structure of the alkenes has no effect on enantioselectivity (Table 3, entries 7 and 8). The addition reactions of aliphatic aldehydes with a substituent at the α-carbon provided the alkynol products with comparable *ee* values to α,β-unsaturated aldehydes (Table 3, entries 12 and 13), however the straight chain of the aliphatic aldehyde only afforded the product with 76% *ee* (Table 3, entry 11). These results represent major progress in the amino-alcohol–Zn catalyzed addition reactions of trimethylsilylacetylene to aliphatic and α,β-unsaturated aldehydes. The new addition reactions would provide a generally applicable procedure for the synthesis of the alkyl substituted 3-silylpropargylic alcohols for further desilylated derivatives, which are the key units or building blocks in natural product synthesis.

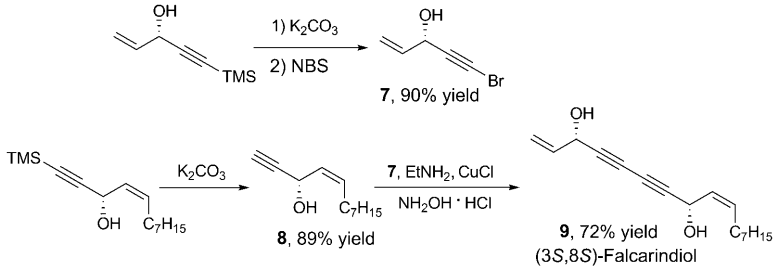
Chiral alkynols are valuable synthetic building blocks. For example, the alkynol product **5** (prepared from the addition reaction of trimethylsilylacetylene to (*E*)-octadec-2-enal (**4**)), was easily desilylated to furnish a type of marine alkynol **6**, which has been separated from the sponge Cribrochalina vasculum and shows in vitro immunosuppressive and antitumor activities (Scheme 2).[14] The *ee* value of **6** could



Scheme 2. Synthesis of marine alkynol product **6**.

be increased to 97% by simple recrystallization. Compared with the reported multistep synthetic strategy,[15] the synthesis of **6** with alkynylation as a key step is quite brief. The synthetic utility of our reaction was further exemplified by the concise synthesis of falcarindiol,[16] which is a representative alkynol natural product and exhibited antimicrobial, antibacterial, antifungal, and antiproliferative activities.[3b,17] Previously, cumbersome procedures were required to obtain (3*S*, 8*S*)-falcarindiol, with asymmetric ynone reduction as the key step.[18] With our current approach, (3*S*,8*S*)-falcarindiol can be easily accessed in very short route (Scheme 3).

In conclusion, we have developed an amino-alcohol–Zn catalyzed highly enantioselective addition of trimethylsilyl-



Scheme 3. Synthesis of (3*S*,8*S*)-falcarindiol. NBS = *N*-bromosuccinimide.

acetylene to aromatic, α,β-unsaturated and aliphatic aldehydes. The alkynylation is broad in scope with respect to aldehyde substrates. Notably, the catalytic procedure eliminates the need for commonly used additives, such as small amounts of amine. The synthetic utility of this method was demonstrated in the concise syntheses of two biologically active alkynol natural products. The salient features of this protocol, such as its operational simplicity, mild reaction conditions, and the cheap and easy preparation of amino alcohol ligands, suggest that it has good potential for extensive application of these reactions in the synthesis of chiral alkynols.

Experimental Section

In a flame-dried Schlenk tube under nitrogen atmosphere, trimethylsilylacetylene (0.42 mL, 3.0 mmol, 3 equiv) and Me_2Zn solution (2.5 mL, 1.2 M in toluene, 3 mmol, 3 equiv) were dissolved in dry toluene (3.5 mL), and the solution was stirred for 90 min at 30 °C, then transferred by the syringe to another flame-dried Schlenk tube containing the amino alcohol ligand (0.1 mmol, 0.1 equiv, or 0.2 mmol, 0.2 equiv). After the resulting solution was stirred for 30 min at 30 °C, the aldehyde (1 mmol) was added and the reaction mixture was stirred at the same temperature for 24 h. The reaction was quenched with saturated NH_4Cl aqueous solution (5 mL) at 0 °C and extracted with diethyl ether (3×10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (SiO_2, particle size 32–63 mm; eluent: hexane/ether (9:1)) to afford the corresponding pure propargylic alcohols. The enantiomeric excess was determined by HPLC (Chiralcel OD or AD, 10% of *i*PrOH in hexane if not stated otherwise). For additional details, see the Supporting Information.

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Keywords: addition reaction · alkynylation · amino alcohols · asymmetric catalysis · zinc

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