CHINESE JOURNAL OF CATALYSIS
Volume 31, Issue 9, 2010
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Chin J Catal, 2010, 31: 1098–1102.

RESEARCH PAPER

Methylsulfonyl-Based Sulfamide-Amine Alcohol as a Ligand for Enantioselective Alkynylation of Aldehydes

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Abstract: Chiral methylsulfonyl-based sulfamide-amine alcohol (SAA) ligands were synthesized from commercially available starting materials in two simple steps. Methylsulfonyl-based SAA ligands catalyzed the asymmetric alkynylation of various aldehydes using alkynylzinc to provide chiral propargyl alcohols with moderate to good enantioselectivity up to 83% ee.

Key words: sulfamide-amine alcohol; enantioselective addition; alkynylation; aldehyde

The catalytic enantioselective addition of terminal alkynes to aldehydes is a very useful method for the synthesis of chiral propargyl alcohols, which are important versatile building blocks of many biologically active compounds and natural products [1–4]. In recent years, chiral ligands, such as *N*-methyl ephedrine [5,6], sulfonamide alcohol [7,8], BINOL and its derivatives [9–12], have successfully been used in this reaction. However, Ti(O-^{i}Pr)$_4$ or other metal species are usually necessary in most of these catalytic systems [13–17]. On the other hand [18–32], efficient ligands that can be prepared from cheap and easily available starting materials in a few synthetic steps and that are designed for facile structural variations are still particularly useful. The design of chiral ligands is the key to new enantioselective catalysts from a practical viewpoint [33,34]. We have reported a series of chiral *p*-tolyl sulfonyl (Ts)-based sulfamide-amine alcohol (SAA) ligands for asymmetric diethylzinc addition to aldehydes without the use of a titanium complex [35]. We also found that Ts-based and trifluoromethanesulfonyl (Tf)-based SAA were also effective for the asymmetric alkynylation of carbonyl compounds [36–38]. In order to understand the electronic and steric effects of chiral SAA on asymmetric alkynylation of aldehydes and as part of extending the application of our SAA ligands, we report methylsulfonyl (Ms)-based SAA catalyzed enantioselective alkynylation of aldehydes under very mild conditions without using moisture sensitive Ti(O-^{i}Pr)$_4$ and Zn(OTf)$_2$.

1 Experimental

1.1 Typical procedure for the preparation of Ms-based SAA (4a)

Methanesulfonyl chloride (1.7 ml, 22 mmol) was added dropwise over 1.5 h to (*S*)-alaninol (1.37 g, 10 mmol) and triethylamine (2.8 ml, 20 mmol) in dry CH_2C1_2 (60 ml) under argon at –20 °C. Stirring was continued at this temperature for an additional 30 min, after which the flask was kept at –30 °C overnight. The cold solution was then washed with 0.1 mol/L HC1 (10 ml × 2) and saturated aqueous $NaHCO_3$ (15 ml). The organic phase was dried ($MgSO_4$) and the solvent evaporated to leave the corresponding aziridine (**6**) as a white solid. Without purification, the aziridine and (–)-ephedrine were dissolved in dry acetonitrile (60 ml) and the mixture was stirred under reflux for 2 d. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give the pure ligand. When the R group was changed to benzyl or methyl group, the triethylamine was changed to 4-dimethylaminopyridine (DMAP) and K_2CO_3, respectively, and the solvent was changed to acetonitrile. The spectral data of Ms-based ligands are listed below.

N-[(*R*)-2-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-1-phenylethyl]methanesulfonamide (4a): white solid, 41% yield. mp: 127–128 °C; ^{1}H NMR: δ1.09 (d, J = 6.4 Hz, 3H), 2.07 (s, 3H), 2.409 (s, 3H), 2.48 (dd, J = 12 Hz,

Received date: 2 February 2010.
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Foundation item: Supported by the National Basic Research Program of China (973 Program, 2010CB833300).

DOI: 10.1016/S1872-2067(10)60106-4

1H), 2.67 (dd, J = 4.4 Hz, 1H), 2.84 (dt, J = 6.4 Hz, 1H), 4.38 (dd, J = 4.4 Hz, 1H), 4.67 (d, J = 6.4 Hz, 1H), 7.26–7.42 (m, 10H); ^{13}C NMR: δ 10.52, 35.42, 42.01, 55.46, 62.00, 65.86, 75.69, 126.31, 127.55, 127.91, 128.32, 128.86, 128.92, 139.98, 143.49.

N-[(*R*)-2-[[(1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-1-phenylethyl]methanesulfonamide (4b): white solid, 31% yield. mp: 162–163 °C; ^{1}H NMR: δ 0.65 (d, J = 6.8 Hz, 3H), 2.36 (m, 4H), 2.54 (d, J = 6.4 Hz, 1H), 2.61 (s, 3H), 2.73 (dd, J = 9.6 and 12.8 Hz, 1H), 4.24 (d, J = 9.6 Hz, 1H), 4.58 (dd, J = 6.4 and 9.2 Hz, 1H), 7.22–7.41 (m, 10H); ^{13}C NMR: δ 8.40, 37.29, 42.10, 56.10, 58.71, 66.07, 74.96, 127.14, 127.52, 127.15, 128.49, 129.23, 140.24, 141.93.

N-[(*S*)-2-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-1-phenylethyl]methanesulfonamide (4c): white solid, 25% yield. mp: 110–112 °C; ^{1}H NMR: δ 0.97 (d, J = 6.8 Hz, 3H), 2.24 (s, 2H), 2.37 (s, 3H), 2.49 (dd, J = 4.8 and 12.8 Hz, 1H), 2.63 (dd, J = 12.8 and 10 Hz, 1H), 2.88 (m, J = 6.8 and 5.6, 1H), 4.45 (dd, J = 10 and 4.8 Hz, 1H), 4.64 (d, J = 5.6 Hz, 1H), 7.25–7.45 (m, 10H); ^{13}C NMR: δ 8.95, 39.36, 41.94, 55.74, 58.92, 64.22, 76.84, 126.77, 127.50, 127.82, 128.26, 128.71, 128.94, 140.26, 143.07.

N-[(*S*)-2-[[(1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-1-phenylethyl]methanesulfonamide (4d): white solid, 20% yield. mp: 149–151 °C; ^{1}H NMR: δ 0.67 (d, J = 6.8 Hz, 3H), 2.42 (dd, J = 12.8 and 6.0 Hz, 1H), 2.37 (s, 3H), 2.56–2.59 (m, 1H), 2.61 (s, 3H), 2.75 (dd, J = 9.2 and 12.8 Hz, 1H), 4.25 (d, J = 9.6 Hz, 1H), 4.59 (dd, J = 6.0 and 9.2 Hz, 1H), 7.30–7.41 (m, 10H); ^{13}C NMR: δ 8.41, 37.37, 42.11, 56.07, 58.66, 65.97, 75.00, 127.14, 127.51, 128.15, 128.50, 129.01, 129.23, 140.19, 141.91.

N-[(*R*)-1-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]propan-2-yl]methanesulfonamide (5): white solid, 41% yield. mp: 124–125 °C; ^{1}H NMR: δ 0.70 (d, J = 4.8 and 6.4 Hz, 3H), 1.22 (dd, J = 12.8 and 6.4 Hz, 3H), 2.20–2.24 (m, 1H), 2.33 (d, J = 5.2 Hz, 3H), 2.49 (dd, J = 8.8 and 12.8 Hz, 1H), 2.59–2.65 (m, 1H), 3.03 (d, J = 4 Hz, 3H), 3.60 (d, J = 6 Hz, 1H), 4.26 (dd, J = 4.4 and 9.6 Hz, 1H), 7.24–7.35 (m, 5H); ^{13}C NMR: δ 7.96, 20.41, 37.91, 41.92, 48.02, 58.39, 65.93, 75.03, 127.51, 128.12, 128.51, 141.84.

N-[(*R*)-1-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-3-phenylpropan-2-yl]methanesulfonamide (6): white solid, 48% yield. mp: 104–105 °C; ^{1}H NMR: δ 0.74 (d, J = 6.8 Hz, 3H), 2.30 (s, 3H), 2.36 (s, 3H), 2.56–2.68 (m, 3H), 2.71 (dd, J = 2.4 and 6.8 Hz, 1H), 3.06 (dd, J = 4.4 and 14 Hz, 1H), 3.71 (m, 1H), 4.31 (d, J = 9.6 Hz, 1H), 7.22–7.41 (m, 10H); ^{13}C NMR: δ 8.18, 36.66, 40.16, 41.11, 55.54, 59.91, 66.66, 75.22, 127.07, 127.64, 128.09, 128.53, 128.91, 129.85, 138.34, 141.74.

1.2 Typical procedure for asymmetric addition of phenylacetylene to aldehydes

Under argon, the chiral ligand (10 mol%, 0.025 mmol) was mixed with dry *n*-hexane (1.0 ml) at room temperature and stirred for 10 min. Then Et_2Zn (10 wt% in *n*-hexane, 0.9 ml) and phenylacetylene (54 μl, 0.5 mmol) were added by a syringe. After the mixture was stirred at room temperature for another 1 h, aldehyde (0.25 mmol) was added. The resulting mixture was stirred for 24 h at room temperature. Then the reaction was quenched with aqueous HCl (5%) and the mixture was extracted with ether (6 ml). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by flash column chromatography to give the product.

1,3-Diphenylprop-2-yn-1-ol (7a). Retention time, t_{major} = 11.6 min and t_{minor} = 21.1 min.

1-(2-Methylphenyl)-3-phenylprop-2-yn-1-ol (7b). Retention time, t_{major} = 9.3 min and t_{minor} = 21.1 min. ^{1}H NMR: δ 2.45 (s, 3H), 2.58 (s, 1H), 5.78 (s, 1H), 7.17–7.29 (m, 6H), 7.42–7.45 (m, 2H), 7.69–7.70 (m, 1H); ^{13}C NMR: δ 19.1, 63.0, 86.6, 88.8, 122.7, 126.4, 126.7, 128.4, 128.6, 128.7, 130.9, 131.9, 136.2, 138.5.

1-(3-methylphenyl)-3-phenylprop-2-yn-1-ol (7c) [14]. Retention time, t_{major} = 10.6 min and t_{minor} = 25.7 min.

1-(3-Methoxyphenyl)-3-phenylprop-2-yn-1-ol (7d). Retention time, t_{major} = 16.8 min and t_{minor} = 29.6 min. ^{1}H NMR: δ 2.52 (s, 1H), 3.80 (s, 3H), 5.64 (m, 1H), 6.86–6.88 (m, 1H), 7.16–7.19 (m, 2H), 7.29–7.31 (m, 4H), 7.44–7.47 (m, 2H); ^{13}C NMR: δ 55.5, 65.1, 86.7, 88.9, 112.3, 114.3, 119.2, 122.6, 128.5, 128.8, 129.9, 131.9, 142.4, 160.0.

1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-ol (7e). Retention time, t_{major} = 15.1 min and t_{minor} = 30.4 min. ^{1}H NMR: δ 3.39 (s, 1H), 3.84 (s, 3H), 5.96 (s, 1H), 6.88–7.01 (m, 2H), 7.28–7.32 (m, 4H), 7.46–7.49 (m, 2H), 7.65–7.68 (m, 1H); ^{13}C NMR: δ 55.3, 60.7, 85.6, 88.8, 110.8, 120.6, 127.7, 128.1, 128.2, 129.5, 131.5, 156.5.

1-(3-Fluorophenyl)-3-phenylprop-2-yn-1-ol (7f). Retention time, t_{major} = 9.2 min and t_{minor} = 27.3 min. ^{1}H NMR: δ 2.621 (s, 1H), 5.67 (s, 1H), 7.00–7.02 (m, 1H), 7.29–7.36 (m, 6H), 7.45–7.47 (m, 2H); ^{13}C NMR: δ 64.6, 87.1, 88.3, 113.8, 114.0, 116.4, 115.6, 128.6, 129.0, 130.3, 132.0, 143.0, 164.0.

1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-ol (7g) [14]. Retention time, t_{major} = 9.0 min and t_{minor} = 26.2 min.

1-(4-chlorophenyl)-3-phenylprop-2-yn-1-ol (7h). Retention time, t_{major} = 9.4 min and t_{minor} = 29.0 min. ^{1}H NMR: δ 2.78 (s, 1H), 5.63 (s, 1H), 7.27–7.35 (m, 5H), 7.43–7.45 (m, 2H), 7.50–7.52 (m, 2H); ^{13}C NMR: δ 64.5,87.1, 88.4, 122.3, 128.3, 128.5, 128.9, 131.1, 131.9, 134.3, 139.2.

1-(3,5-Dichlorophenyl)-3-phenylprop-2-yn-1-ol (7i). Retention time, t_{major} = 6.6 min and t_{minor} = 29.6 min. ^{1}H NMR: δ 3.02 (s, 1H), 5.59 (s, 1H), 7.27–7.35 (m, 4H), 7.42–7.45 (m, 4H); ^{13}C NMR: δ 63.9, 87.5, 87.6, 121.9, 125.3, 128.0, 128.6, 129.1, 132.0, 135.3, 143.9.

1-(3-Trifluoromethylphenyl)-3-phenylprop-2-yn-1-ol (7j). Retention time, t_{major} = 7.6 min and t_{minor} = 36.7 min. ^{1}H

NMR: δ 2.70 (s, 1H), 5.73 (s, 1H), 7.23–7.35 (m, 3H), 7.45–7.51 (m, 3H), 7.58–7.60 (m, 1H), 7.77–7.79 (m, 1H), 7.87 (s, 1H); ^{13}C NMR: δ 64.6, 87.5, 88.1, 122.2, 123.7,125.4, 128.6, 129.1, 129.3, 130.3,131.0, 131.3, 132.0, 141.2.

1-(4-Trifluoromethylphenyl)-3-phenylprop-2-yn-1-ol (7k). Retention time, t_{major} = 8.4 min and t_{minor} = 42.0 min. ^{1}H NMR: δ 2.56 (s, 1H), 5.74 (s, 1H), 7.25–7.37 (m, 3H), 7.45–7.47 (m, 2H), 7.64–7.74 (m, 4H); ^{13}C NMR: δ 64.6, 87.5, 88.1, 122.2, 125.8, 127.2, 128.6, 129.1, 132.0, 144.6.

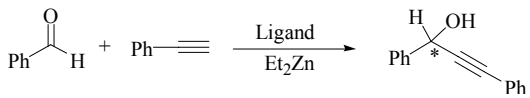
1-(1-Naphthyl)-3-phenylprop-2-yn-1-ol (7l) [14]. Retention time, t_{major} = 17.1 min and t_{minor} = 36.6 min.

2 Results and discussion

As shown in Scheme 1, in the traditional method [39], the chiral amino alcohols (**1**) first reacted with two equivalent methanesulfonyl chloride to afford substituted derivatives (**2**). Treatment with NaH resulted in *N*-methanesulfonyl aziridine (**3**). In this work, **1** was reacted with methanesulfonyl chloride to give **3** directly, and then without purification, reacted with natural chiral (–)-ephedrine or (+)-pseudoephedrine to give the corresponding Ms-based SAA ligands (**4**) in two simple steps. The Ms-based SAA ligands are cheap and very stable in air.

The enantioselective addition of alkynylzinc to benzaldehyde was first examined in the presence of 0.1 equivalent chiral Ms-based SAA ligand in toluene. As shown in Table 1, the matching of the stereogenic centers and substituent on the ligands had a large effect on the reaction. **4a** was more effective than **4b**, **4c**, and **4d**, which have the same substituent as **4a** (Table 1, entries 1–4). Changing the substituent from phenyl to methyl or benzyl group led to less enantioselectivity (Table 1, entries 5 and 6). Clearly, **4a** was an effective chiral ligand for this asymmetric reaction.

Table 1 Asymmetric alkynylation of benzaldehyde catalyzed by Ms-based SAA



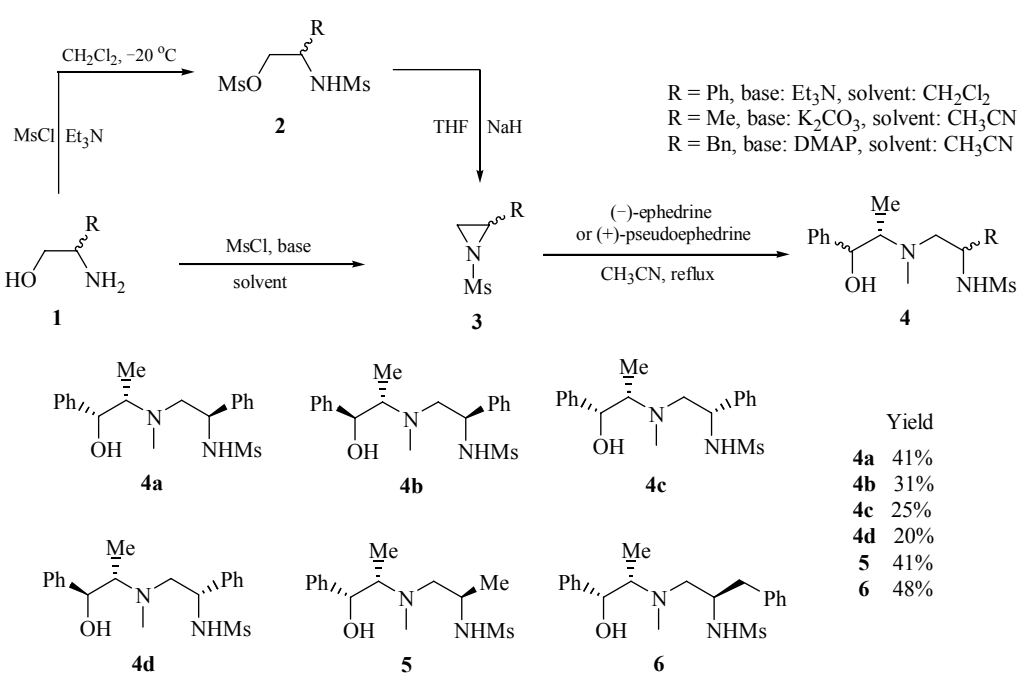
Entry	Ligand	Yield[a] (%)	ee[b] (%)
1	**4a**	99	65
2	**4b**	96	33
3	**4c**	80	9
4	**4d**	99	45
5	**5**	78	3
6	**6**	79	31

Reaction conditions: phenylacetylene:Et_2Zn:aldehyde:ligand = 2.0:2.2:1:0.1, toluene 1 ml, rt, 24 h.

[a]Isolated yield.

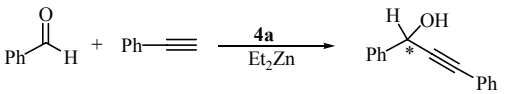
[b]Determined by HPLC on a Chiracel OD-H column.

To improve the enantioselectivity, the reaction conditions were optimized using benzaldehyde as the substrate (Table 2). The reactions were strongly influenced by the amount of ligand, reaction temperature, and solvent. At room temperature, increasing the amount of ligand **4a** to 20 mol% did not improve the selectivity, while decreasing the amount of **4a** to 5 mol% gave a chiral product with only 43% ee (Table 2, entries 1–3). Lower reaction temperatures did not improve the enantioselectivities (Table 2, entries 4 and 5). When the reaction was carried out in THF, low ee values were obtained (Table 2, entry 6). However, there was no enhancement in



Scheme 1. Synthesis of Ms-based SAA.

Table 2 Optimization of reaction conditions



Entry	Content of **4a** (mol%)	t/°C	Solvent	Yield (%)	ee (%)
1	5	rt	toluene	66	43
2	10	rt	toluene	99	65
3	20	rt	toluene	98	65
4	10	0	toluene	98	54
5	10	–20	toluene	98	31
6	10	rt	THF	50	40
7	10	rt	*n*-hexane	78	70
8	10	rt	DCM	53	62
9	10	rt	Et_2O	99	62

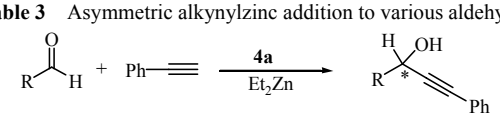
Reaction conditions are the same as in Table 1 except for the solvent and reaction temperature.

enantioselectivity when dichloromethane (DCM) and Et_2O was used as the solvent (Table 2, entries 8 and 9). The best ee of 70% was obtained in *n*-hexane (Table 2, entry 7).

Having optimized the asymmetric alkynylation of benzaldehyde with phenylacetylene using **4a**, we decided to screen various aldehydes. As can be seen from the summarized results in Table 3, **4a** was efficient for all of the aromatic aldehydes studied. Propargylic alcohols were obtained with up to 83% ee and up to 91% yield.

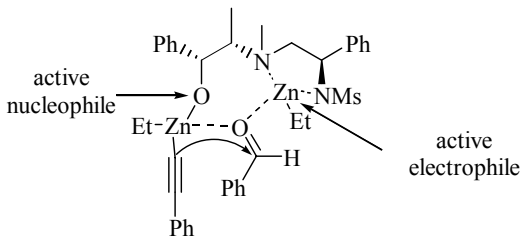
In order to explain the catalytic reaction mechanism with the Ms-based SAA ligands, proposed transition states are shown in Scheme 2. When **4a** was used, the β-amino zinc atom acts as the Lewis acid center to active the aldehyde, while the oxygen atom of alkoxyl acts as the Lewis base center to independently activate the alkynylzinc nucleophile [33,34]. This explains how the SAA ligands catalyzed the enantioselective alkynylzinc addition to aldehydes without

Table 3 Asymmetric alkynylzinc addition to various aldehydes



Entry	R	Yield (%)	ee (%)
1	Ph	78	70
2	*o*-Me-Ph	84	83
3	*m*-Me-Ph	85	75
4	*m*-MeO-Ph	76	60
5	*p*-MeO-Ph	65	60
6	*m*-F-Ph	70	66
7	*p*-F-Ph	77	64
8	*p*-Cl-Ph	79	64
9	3,5-2Cl-Ph	75	68
10	*m*-CF_3-Ph	76	55
11	*p*-CF_3-Ph	66	60
12	1-naphthyl	91	81

Reaction conditions are the same as in Table 1 except the solvent is *n*-hexane.



Scheme 2. Proposed transition states of the reaction.

moisture sensitive $Ti(O\text{-}^iPr)_4$ and $Zn(OTf)_2$, which were needed in the literature [5–12,18–21].

3 Conclusions

New convenient chiral Ms-based SAA ligands were prepared from commercially available starting materials in two simple steps. Ms-based SAA **4a** catalyzed the asymmetric alkynylation of aromatic aldehydes with up to 83% ee. The cheap Ms-based SAA **4a** is a practical laboratory ligand for the enantioselective alkynylation of aromatic aldehydes under very mild conditions that do not need moisture sensitive $Ti(O\text{-}^iPr)_4$ and $Zn(OTf)_2$.

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