Tetrahedron: *Asymmetry* 20 (2009) 2733–2736

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Highly enantioselective addition of methyl propiolate to aldehydes catalyzed by a titanium(IV) complex of a β-hydroxy amide

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ARTICLE INFO

Article history:
Received 12 October 2009
Accepted 24 November 2009
Available online 6 January 2010

ABSTRACT

Three chiral β-hydroxy amide ligands were prepared by the reaction of benzyl chloride with amino alcohols derived from L-tyrosine. The titanium(IV) complex of chiral ligand **4a** was found to be an effective catalyst for the asymmetric addition of methyl propiolate to aliphatic and aromatic aldehydes. The γ-hydroxy-α,β-acetylenic esters were obtained in excellent enantiomeric excesses (up to 94% ee) under optimized conditions.

1. Introduction

The catalytic enantioselective addition of terminal alkynes to aldehydes is one of the most useful procedures for the formation of carbon–carbon bonds because this process can produce synthetically very useful chiral propargyl alcohols.[1] Although many studies have been reported in this area, most of them focus on the asymmetric addition of monoaryl or monoalkyl alkynes to aldehydes.[2–6] The product resulting from the addition of propiolate to an aldehyde is a γ-hydroxy-α,β-acetylenic ester, an extremely versatile synthetic intermediate. Functional group transformations can elaborate the adduct into a variety of useful building blocks. The direct asymmetric addition of an alkyl propiolate to aldehydes has proven to be a challenge. This may be due to the greater sensitivity and different reactivity of alkynoates in contrast with simple alkyl and aryl alkynes. The asymmetric reaction of alkynoates to aldehydes was first reported by Pu et al.[7a] Pu discovered that in the presence of diethylzinc, hexamethylphosphoramide (HMPA), and titanium tetraisopropoxide, (*S*)-1,1′-bi-2-naphthol (BINOL) can efficiently catalyze the enantioselective reaction of methyl propiolate with aromatic aldehydes with high enantioselectivity at room temperature.[7] However, HMPA is a strong carcinogen. Since then, the studies of other catalytic systems were quickly reported. Trost demonstrated a practical and general alkynylation of α,β-unsaturated aldehydes using a proline-derived dinuclear zinc catalytic system in high ee values and yields.[8] Wang reported with the use of a β-sulfonamide alcohol as a ligand, the asymmetric addition of methyl propiolate to aromatic aldehydes, which proceeded smoothly in combination with diethylzinc, 1,2-dimethoxyethane and titanium tetraisopropoxide.[9] Without titanium tetraisopropoxide, the cyclopropane-based amino alcohol–zinc complex proved to be an excellent enantioselective catalyst system for the asymmetric addition of methyl propiolate to aromatic aldehydes under mild conditions.[10] Recently, good enantioselectivities have been observed for the alkyl propiolate addition to aliphatic aldehydes when a novel H_8-BINOL-based chiral ligand was used as an effective catalyst in the presence of diethylzinc and titanium tetraisopropoxide, alleviating the need for any Lewis base additive.[11] Among the catalytic methods developed, fewer excellent chiral ligands have been disclosed in the efficient catalytic asymmetric addition of methyl propiolate to both aliphatic and aromatic aldehydes.

Due to the potential coordination and H-bond donor ability of β-hydroxy amides, some of them have been applied to asymmetric catalysis. In our group, we have already developed chiral β-hydroxy amide ligands, and successfully introduced them into the asymmetric addition of phenylacetylene to aliphatic, vinyl, and aromatic aldehydes to obtain high enantioselectivities.[12] As part of the development of β-hydroxy amide chiral ligands, we synthesized chiral β-hydroxy amides **4a**–**c** from (*S*)-tyrosine. Herein, we report the addition of asymmetric methyl propiolate to aliphatic and aromatic aldehydes catalyzed by the titanium(IV) complex of ligand **4a**.

2. Results and discussion

Chiral ligands **4a**–**c** were conveniently synthesized using inexpensive (*S*)-tyrosine as the starting material (Scheme 1). We initiated the reaction of methyl propiolate with isovaleraldehyde in the presence of 0.25 equiv chiral ligand **4a**, diethylzinc, and titanium tetraisopropoxide in toluene, the expected propargylic alcohol was obtained in 75% ee (Table 1, entry 1). Some reports have shown that the Lewis bases can enhance the reaction of alkynoates with aldehydes[4c,9,13] and that the Lewis base played an important role in this reaction. In comparison with the Lewis bases HMPA and 1,2-dimethoxyethane (DME), tertiary amine *N*-methylimidozole

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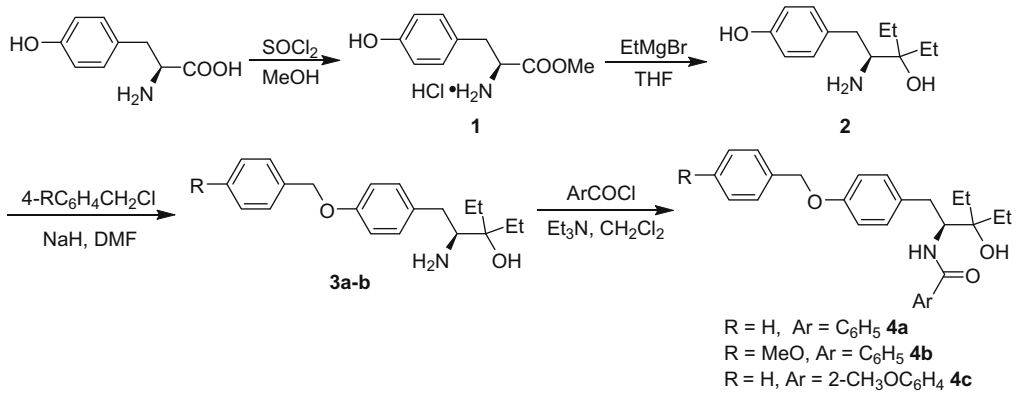
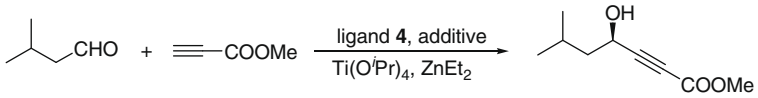
0957-4166/$ - see front matter
doi:10.1016/j.tetasy.2009.11.022



Scheme 1. Synthesis of chiral ligands **4a–c**.

Table 1
Optimization of reaction conditions[a]



Entry	Ligand	*L* (mol %)	Solvent	Additive (equiv)	*L*/Ti(O^{i}Pr)$_4$	Yield[b] (%)	ee[c] (%)
1	**4a**	25	Toluene	—	1/1	88	75
2	**4a**	25	Toluene	HMPA (1)	1/1	90	77
3	**4a**	25	Toluene	NMI (0.05)	1/1	65	68
4	**4a**	25	Toluene	TEA (0.05)	1/1	69	71
5	**4a**	25	Toluene	TMEDA (0.05)	1/1	71	74
6	**4a**	25	Toluene	DME (1)	1/1	88	85
7	**4b**	25	Toluene	DME (1)	1/1	82	81
8	**4c**	25	Toluene	DME (1)	1/1	84	75
9	**4a**	25	Toluene	DME (0.75)	1/1	76	79
10	**4a**	25	Toluene	DME (1.5)	1/1	73	84
11	**4a**	25	CH_2Cl_2	DME (1)	1/1	84	76
12	**4a**	25	THF	DME (1)	1/1	Trace	—
13	**4a**	25	Toluene	DME (1)	1/2	82	81
14	**4a**	25	Toluene	DME (1)	1/3	80	80
15[d]	**4a**	25	Toluene	DME (1)	1/1	73	79
16	**4a**	30	Toluene	DME (1)	1/1	88	88

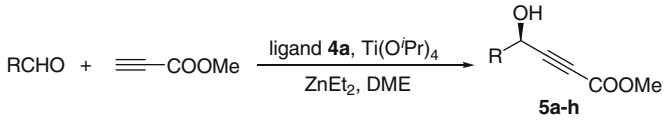
[a] Methyl propiolate/$ZnEt_2$/isovaleraldehyde = 3:3:1 (molar ratio); reaction time: 12 h; reaction temperature: rt.
[b] Isolated yield.
[c] Determined by HPLC analysis of its acetate ester.
[d] Reaction temperature: 0 °C.

(NMI), triethylamine (TEA) and *N*,*N*,*N*,*N*-tetramethylethane-1,2-diamine (TMEDA) are stronger bases. To improve the enantioselectivity, HMPA (1 equiv),[4c] NMI (0.05 equiv),[13] TEA (0.05 equiv), TMEDA (0.05 equiv), and DME (1 equiv)[9] were used as additives; DME was found to be the best choice (Table 1, entries 2–6). Methyl 4-hydroxy-6-methylhept-2-ynoate was afforded in 88% yield and 85% ee (Table 1, entry 6). Using ligands **4b** and **4c**, which have a methoxy group, resulted in a lower enantioselectivity than ligand **4a** (Table 1, entries 7 and 8). Hence, ligand **4a** was chosen to be the optimal chiral ligand to facilitate this alkynoate addition reaction.

Further optimization studies were carried out using ligand **4a** in combination with diethylzinc, DME, and titanium tetraisopropoxide. The enantioselectivities of the reaction were strongly affected by the reaction conditions. Changing the amount of DME from 1 equiv to 0.75 equiv afforded a lower enantioselectivity (Table 1, entry 9). Subsequently, when 1.5 equiv of DME were used, the reaction retained a good ee of 84% (Table 1, entry 10). Other solvents such as CH_2Cl_2 and THF were also examined (Table 1, entries 11 and 12). We were unable to detect the excepted product when THF was used as a solvent. Hence toluene was found to be a suitable solvent. Increasing the amount of Ti(O^{i}Pr)$_4$ resulted in a decrease in enantioselectivity (Table 1, entries 13 and 14). To further improve the enantioselectivity, the temperature effect was also observed. The result showed that only 79% ee was obtained under 0 °C (Table 1, entry 15). Subsequently, by increasing the catalyst loading to 30 mol %, the ee value of methyl 4-hydroxy-6-methylhept-2-ynoate was improved to 88%, while the yield remained high at 88% (Table 1, entry 16). Thus, entry 16 in Table 1 was identified as the optimized reaction procedure.

The generality of this catalytic system for methyl propiolate asymmetric addition to aliphatic, *trans*-cinnamaldehyde, and aromatic aldehydes was examined using the titanium(IV) complex of ligand **4a** under the optimized reaction conditions. As shown in Table 2, for aliphatic aldehydes, and enantiomerically active γ-hydroxy-α,β-acetylenic esters could be obtained in 78–91% ee in the presence of chiral ligand **4a**. The less sterically hindered aliphatic aldehydes resulted in good enantioselectivities ranging from 86% to 88% ee (Table 2, entries 1–5). It is noteworthy that for 2-phenylacetaldehyde, an excellent enantioselectivity of 91% ee was obtained (Table 2, entry 6). The aldehydes with bulky groups gave lower enantioselectivities (Table 2, entries 7 and 8). We also examined α,β-unsaturated aldehydes as electrophiles to produce chiral propargylic allylic alcohols, recently shown to be an efficient substrate in a metal-catalyzed cyclization reactions. The ee value was 85% for *trans*-cinnamaldehyde. As the results summarized in

Table 2
Asymmetric addition of methyl propiolate to aliphatic aldehydes promoted by ligand **4a**[a]



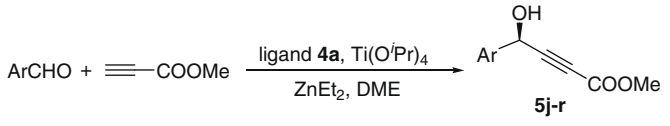
5a-h

Entry	Aldehyde	Product	Yield[b] (%)	ee[c] (%) (Config.)[d]	$[\alpha]_D^{20}$
1	CH_3CH_2CHO	**5a**	89	87	+8
2	$CH_3CH_2CH_2CHO$	**5b**	87	87	+3
3	$(CH_3)_2CHCHO$	**5c**	90	86	+7
4	$(CH_3)_2CHCH_2CHO$	**5d**	88	88	+3
5	$CH_3(CH_2)_5CHO$	**5e**	76	86	+3
6	$PhCH_2CHO$	**5f**	70	91	+4
7	$(CH_3)_3CCHO$	**5g**	86	78	+4
8	*c*-$C_6H_{11}CHO$	**5h**	82	81 (*R*)	+2
9	(*E*)-PhCH=CHCHO	**5i**	68	85	+3

[a] Methyl propiolate/$ZnEt_2$/aldehyde/$Ti(O^iPr)_4$/**4a** = 3:3:1:0.3:0.3 (molar ratio); reaction time: 12 h; reaction temperature: rt.
[b] Isolated yield.
[c] Ee values of **5a**–**g** were determined by HPLC analysis of acetate esters using Chiralcel column.
[d] Absolute configuration of the products was based on measurement of the HPLC and comparison with the literature values (Ref. 6).

Table 3, excellent enantioselectivities (90–93% ee) were achieved for the reaction of methyl propiolate with aromatic aldehydes containing electron-donating or electron-withdrawing substituents at the *para*-position. The best enantioselectivity of 94% ee was obtained for the 2-naphthaldehyde. On the other hand, the large sterically hindered *ortho*-chlorobenzaldehyde resulted in lower enantioselectivity (Table 3, entry 3). The results showed that this catalytic system has a broad generality for aliphatic and aromatic aldehydes.

Table 3
Asymmetric addition of methyl propiolate to aromatic aldehydes promoted by ligand **4a**[a]



5j-r

Entry	Aldehyde	Product	Yield[b] (%)	ee[c] (%) (Config.)[d]	$[\alpha]_D^{20}$
1	C_6H_5CHO	**5j**	88	93 (*R*)	+4
2	4-FC_6H_4CHO	**5k**	82	90	+8
3	2-ClC_6H_4CHO	**5l**	85	87	−27
4	4-ClC_6H_4CHO	**5m**	77	90	+4
5	4-BrC_6H_4CHO	**5n**	83	91	+7
6	1-$C_{10}H_7CHO$	**5o**	79	90	−22
7	2-$C_{10}H_7CHO$	**5p**	81	94	−4
8	4-$CH_3C_6H_4CHO$	**5q**	72	92	+4
9	4-$CH_3OC_6H_4CHO$	**5r**	78	92	+6

[a] Methyl propiolate/$ZnEt_2$/aldehyde/$Ti(O^iPr)_4$/**4a** = 3:3:1:0.3:0.3 (molar ratio); reaction time: 12 h; reaction temperature: rt.
[b] Isolated yield.
[c] Determined by HPLC analysis using a Chiralcel column.
[d] Absolute configuration of the products was based on measurement of the HPLC and comparison with the literature value (Ref. 4a).

3. Conclusions

In conclusion, the chiral β-hydroxy amide ligands were synthesized and used in the reaction of catalytic asymmetric addition of methyl propiolate to aliphatic and aromatic aldehydes under mild conditions. The titanium(IV) complex of chiral ligand **4a** was proven to be an effective catalyst for this reaction and the γ-hydroxy-α,β-acetylenic esters were obtained in high enantiomeric excesses (up to 94% ee). Currently, we are further expanding the applicability of this β-hydroxy amide to other kinds of asymmetric catalytic reaction.

4. Experimental

4.1. General

All reactions were carried out under a nitrogen atmosphere. All solvents used were dried and the aldehydes were purified by standard methods. $Ti(O^iPr)_4$ was freshly distilled prior to use. Melting points were taken on an XT-4 melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on Varian Bruker-400 MHz spectrometers with TMS as an internal standard. IR spectra were obtained on NEXUS 670 FT-IR spectrometer in KBr disc. HRMS data were measured with ESI techniques (Bruker Apex II). Optical rotations were measured on a Perkin–Elmer 341 polarimeter. Enantiomeric excess values were determined by HPLC with Chiralcel column on Waters 600 Delta.

Amino alcohols **3a**–**b**,[12c] chiral ligands **4a**–**b**,[12c] and diethylzinc[14] (0.9 M solution in toluene) were prepared according to the literature methods.

4.2. Synthesis of chiral ligand β-hydroxy amide 4c

A solution of 2-methoxybenzoyl chloride (5.5 mmol) in CH_2Cl_2 (20 mL) was added to a cold (0 °C) solution of amino alcohol **3** (5.00 mmol) and NEt_3 (0.77 mL, 5.5 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was washed with 1 M HCl (3 × 10 mL), saturated aqueous $NaHCO_3$ (3 × 10 mL), and brine (3 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The yellow residue was purified by column chromatography to afford β-hydroxy amide **4c**.

4.2.1. *N*-((*S*)-1-(4-(Benzyloxy)phenyl)-3-ethyl-3-hydroxypentan-2-yl)-2-methoxybenzamide 4c

White needle solid, yield 42%; mp 116–117 °C; $[\alpha]_D^{20} = -115$ (*c* 1.00, acetone). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.93–1.00 (m, 6H), 1.57–1.68 (m, 3H), 1.73–1.79 (m, 1H), 2.82 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.06 (dd, *J* = 14.4, 3.2 Hz, 1H), 3.17 (br, 1H), 3.81 (s, 3H), 4.23–4.29 (m, 1H), 5.00 (s, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.31–7.45 (m, 6H), 7.94 (d, *J* = 8.4 Hz, 1H), 8.08 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 7.72, 8.00, 27.94, 28.47, 34.36, 55.90, 57.69, 69.99, 76.87, 111.40, 114.80, 121.29, 121.59, 127.43, 127.86, 128.52, 130.04, 131.56, 132.29, 132.68, 137.15, 157.26, 157.41, 166.13. IR (KBr) ν_{max}: 3359, 2974, 2937, 1632, 1548, 1512, 1299, 1241, 1178 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{33}NO_4$ (M+H): 448.2482; Found: 448.2472.

4.3. General procedure for the asymmetric addition of methyl propiolate to aldehydes

Under a nitrogen atmosphere, to a solution of **4a** (0.09 mmol), DME (0.3 mmol, 32.5 μL), and diethylzinc (1 mL, 0.9 mol/L in toluene, 0.9 mmol) in 5 mL anhydrous toluene, methyl propiolate (0.9 mmol, 80.1 μL) was added in one portion. After the solution was stirred at room temperature for 6 h, $Ti(O^iPr)_4$ (0.09 mmol, 26.6 μL) was added and stirred for half an hour. Then, the aldehyde (0.3 mmol) was added in one portion and the reaction was allowed to proceed at room temperature for 12 h. The mixture was treated with saturated ammonia chloride and extracted with diethyl ether. The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product was purified by

flash column chromatography (silica gel, 12.5–15% EtOAc in petroleum ether) to give the γ-hydroxy-α,β-acetylenic esters **5a–r**.

4.4. General procedure for the acetylation of γ-hydroxy-α,β-acetylenic ester 5a–g

To a solution of γ-hydroxy-α,β-acetylenic esters **5a**–**g** in 2 mL dichloromethane, triethylamine (1.1 equiv), and acetyl chloride (1.1 equiv) were added and stirred for half an hour at room temperature. The mixture was quenched with water and extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The crude products were purified by flash column chromatography (silica gel, 6% EtOAc in petroleum ether) to give the products **6a**–**g** for HPLC analysis.

4.4.1. Methyl 4-acetoxyhex-2-ynoate 6a

Yield 89%, 87% ee determined by HPLC analysis of its acetate ester (OD-H column, hexane/*i*-PrOH = 99/1, l mL/min); retention time: t_{major} = 8.849 min, t_{minor} = 8.078 min.

4.4.2. Methyl 4-acetoxyhept-2-ynoate 6b

Yield 87%, 87% ee determined by HPLC analysis of its acetate ester (AS-H column, hexane/*i*-PrOH = 99/1, l mL/min); retention time: t_{major} = 7.928 min, t_{minor} = 12.270 min.

4.4.3. Methyl 4-acetoxy-5-methylhex-2-ynoate 6c

Yield 90%, 86% ee determined by HPLC analysis of its acetate ester (OD-H column, hexane/*i*-PrOH = 99/1, l mL/min); retention time: t_{major} = 7.356 min, t_{minor} = 5.933 min.

4.4.4. Methyl 4-acetoxy-6-methylhept-2-ynoate 6d

Yield 88%, 88% ee determined by HPLC analysis of its acetate ester (OD-H column, hexane/*i*-PrOH = 99/1, l mL/min); retention time: t_{major} = 9.715 min, t_{minor} = 6.004 min.

4.4.5. Methyl 4-acetoxydec-2-ynoate 6e

Yield 76%, 86% ee determined by HPLC analysis of its acetate ester (AS-H column, hexane/*i*-PrOH = 99/1, l mL/min); retention time: t_{major} = 8.624 min, t_{minor} = 5.725 min.

4.4.6. Methyl 4-acetoxy-5-phenylpent-2-ynoate 6f

Yield 70%, 91% ee determined by HPLC analysis of its acetate ester (OD-H column, hexane/*i*-PrOH = 99/1, l mL/min); retention time: t_{major} = 12.217 min, t_{minor}= 16.422 min.

4.4.7. Methyl 4-acetoxy-5,5-dimethylhex-2-ynoate 6g

Yield 86%, 78% ee determined by HPLC analysis of its acetate ester (AS-H column, hexane/*i*-PrOH = 99/1, l mL/min); retention time: t_{major}= 5.822 min, t_{minor}= 5.002 min.

Acknowledgment

This work was supported by National Natural Science Foundation of China (NSFC 20702022, 20621091 and J0730425).

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