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Synthesis of a C_1 symmetric BINOL–terpyridine ligand and highly enantioselective methyl propiolate addition to aromatic aldehydes

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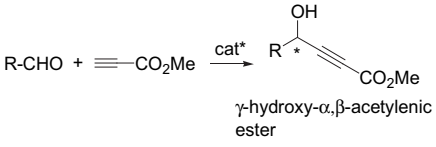
ABSTRACT

A novel C_1 symmetric BINOL–terpyridine ligand (*R*)-**5** is synthesized. This ligand in combination with $ZnEt_2$ and $Ti(O^iPr)_4$ is found to catalyze the highly enantioselective reaction (up to 98% ee) of methyl propiolate with a variety of aromatic aldehydes at 0 °C to give the synthetically useful γ-hydroxy-α,β-acetylenic esters. In comparison with the previously reported BINOL system, the use of (*R*)-**5** requires a reduced amount of the chiral ligand without the addition of a Lewis base. It shows higher enantioselectivity for a number of substrates.

1. Introduction

The asymmetric addition of methyl propiolate to aldehydes is a very convenient way to generate chiral γ-hydroxy-α,β-acetylenic esters that are very useful highly functional synthons in organic synthesis (Scheme 1).[1] However, there are very few catalysts that have been developed for this reaction. In 2006, we reported the catalyst system of 1,1′-bi-2-naphthol (BINOL) in combination with $ZnEt_2$, $Ti(O^iPr)_4$, and HMPA for the highly enantioselective addition of methyl propiolate to aromatic aldehydes.[2a,b] Later, You found that using *N*-methylimidazole in place of HMPA can reduce the loading of both BINOL and the additive for the reaction of methyl propiolate with benzaldehyde but requires a longer reaction time.[2c] Trost found a chiral amino alcohol ligand in combination with $ZnEt_2$ can catalyze the asymmetric reaction of methyl propiolate with a few α,β-unsaturated aldehydes.[3] Additional reports also appeared on the catalytic asymmetric reaction of methyl propiolate with aldehydes.[4] Although many other catalysts have been developed recently for the asymmetric alkynylzinc addition to aldehydes, they are not known to be able to catalyze the reaction of methyl propiolate with aldehydes.[5] This is probably because the alkynylzinc reagent generated from methyl propiolate is less nucleophilic than those from other alkynes and it presents more stringent requirements for the catalysts in order to activate as well as control the stereochemistry for the subsequent addition to aldehydes.



Scheme 1. Asymmetric addition of methyl propiolate to aldehydes to generate chiral γ-hydroxy-α,β-acetylenic esters.

In the BINOL-catalyzed methyl propiolate addition, the additives, such as HMPA or *N*-methylimidazole, are needed in order for the reaction to occur.[2] It is proposed that these additives act as Lewis bases to coordinate to $ZnEt_2$ to activate the deprotonation of methyl propiolate to form the corresponding alkynylzinc. In order to increase the efficiency for this catalytic reaction, we have explored a strategy to incorporate a Lewis base into the BINOL ligand.[6] The reaction of BINOL with alkyl or alkoxy metal complexes can generate chiral Lewis acid complexes that have been employed as catalysts in many organic reactions.[7] Multipyridine-based ligands have also been used extensively as Lewis basic ligands to coordinate to a variety of metal centers.[8] Previously the 6-position of BINOL has been linked with a terpyridine to build dendritic materials,[9] but no catalyst is developed from the BINOL–terpyridine conjugate. Nitrogen-based heterocycles have also been linked to BINOL to modify the catalytic properties of the chiral catalysts.[6] We have constructed a BINOL–terpyridine ligand in order to generate new chiral Lewis acid–Lewis base catalysts.[10] Herein, we report our synthesis of the C_1 symmetric BINOL–terpyridine ligand and its application in the highly enantioselective reaction of methyl propiolate with aldehydes.

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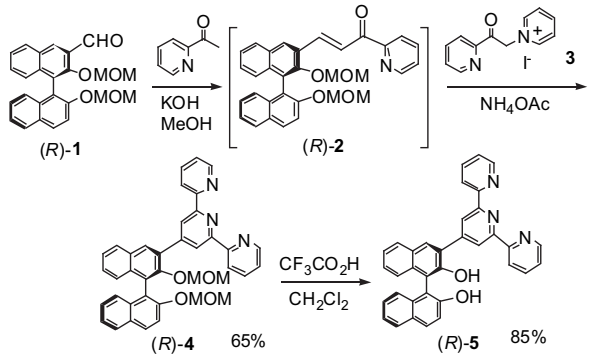
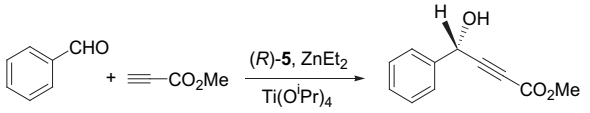
2. Results and discussion

Scheme 2 shows the synthesis of a novel BINOL–terpyridine ligand (*R*)-**5**. Compound (*R*)-**1** was obtained in two steps from BINOL following a literature procedure.[11] Reaction of (*R*)-**1** with 2-acetylpyridine in the presence of KOH in methanol gave (*R*)-**2**. Without isolation, (*R*)-**2** was treated with compound **3**[12a] in the presence of ammonium acetate to give the terpyridine compound (*R*)-**4** in 65% yield.[12b] Removal of the MOM protecting groups of (*R*)-**4** under acidic conditions gave the BINOL–terpyridine ligand (*R*)-**5** in 85% yield. This compound contains a BINOL unit, capable of binding a Lewis acidic metal, and a terpyridine unit that can serve as a Lewis basic site to assist the Lewis acid catalysis at the BINOL site.



Scheme 2. Synthesis of the BINOL–terpyridine ligand (*R*)-**5**.

We have tested the use of (*R*)-**5** to catalyze the reaction of methyl propiolate with benzaldehyde (Scheme 3). The initial screening experiments are listed in Table 1. It showed that in methylene chloride, the γ-hydroxy-α,β-acetylenic ester product could be obtained at room temperature with excellent enantioselectivity though the yield was low (entry 5). The configuration of the product was determined to be S by comparing its optical rotation with that reported.[2a] In other solvents, almost no product was observed. In methylene chloride, the effect of the amount of $Ti(O^iPr)_4$ on the reaction was studied. It was found that reducing the amount of $Ti(O^iPr)_4$ from 100 mol % to 50 mol % increased the yield to 40% while maintaining the excellent enantioselectivity (entry 7). Further reducing the amount of $Ti(O^iPr)_4$ decreased the enantioselectivity. In the absence of $Ti(O^iPr)_4$, the product could still be obtained but with lower yield and diminished enantioselectivity (entry 12). Interestingly, the product configuration was R, opposite to that obtained in the presence of $Ti(O^iPr)_4$. This indicates that $Ti(O^iPr)_4$ is important in the catalytic step that controls the enantioselectivity. Increasing the amount of the chiral ligand in entry 13 did not significantly change the enantioselectivity and yield in comparison with that observed in entry 7. Decreasing the amount of (*R*)-**5** slightly reduced the ee from entry 7 (entry 14). When the reaction time after the addition of benzaldehyde was prolonged from 4 h to 24 and 48 h, the yield of the reaction was increased to 53% (entry 15) and 82% (entry 16), respectively, but with a slight decrease of ee. When the temperature with the addition of benzaldehyde was reduced to 0 °C, after 48 h, the product was obtained with 95% ee and 80% yield (entry 17). Thus, the conditions of entry 17 are chosen as the optimized.



Scheme 3. Reaction of methyl propiolate with benzaldehyde in the presence of (*R*)-**5**, $ZnEt_2$, and $Ti(O^iPr)_4$.

Table 1
Results for the reaction of methyl propiolate with benzaldehyde in the presence of (*R*)-**5**, $ZnEt_2$, and $Ti(O^iPr)_4$

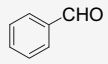
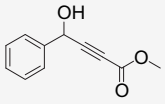
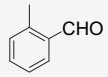
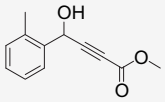
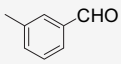
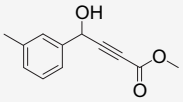
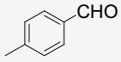
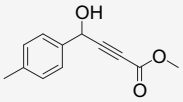
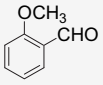
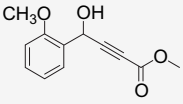
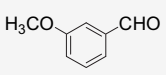
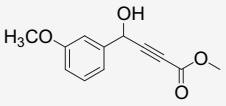
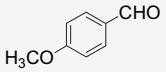
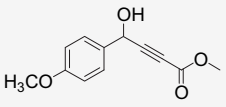
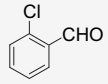
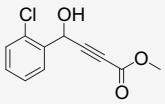
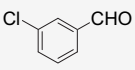
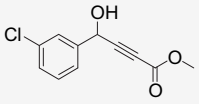
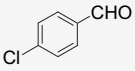
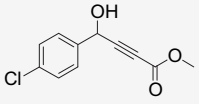
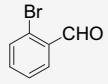
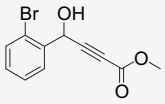
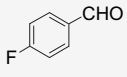
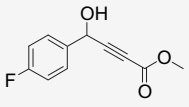
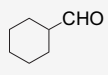
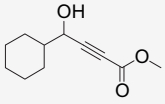
Entry[a]	(*R*)-**5** (mol %)	Solvent	$Ti(O^iPr)_4$ (mol %)	Isolated yield (%)	ee (%)
1	20	THF	100	trace	
2	20	THF	0	~0	
3	20	Et_2O	100	~0	
4	20	Toluene	100	~0	
5	20	CH_2Cl_2	100	14	95
6	20	CH_2Cl_2	60	16	95
7	20	CH_2Cl_2	50	40	95
8	20	CH_2Cl_2	40	38	95
9	20	CH_2Cl_2	30	32	90
10	20	CH_2Cl_2	20	38	84
11	20	CH_2Cl_2	10	29	6
12	20	CH_2Cl_2	0	21	−10
13	30	CH_2Cl_2	50	38	95
14	10	CH_2Cl_2	50	40	92
15[b]	20	CH_2Cl_2	50	53	92
16[c]	20	CH_2Cl_2	50	82	91
17[d]	**20**	**CH_2Cl_2**	**50**	**80**	**95**

[a] Following conditions were used unless otherwise indicated: $ZnEt_2$/methyl propiolate/benzaldehyde/(*R*)-**5**=4:4:1:0.2. A mixture of (*R*)-**5**, methyl propiolate, $ZnEt_2$, and $Ti(O^iPr)_4$ was stirred at rt for 24 h. Benzaldehyde was then added and the reaction mixture was stirred at rt for 4 h.
[b] After addition of benzaldehyde, the reaction was conducted at rt for 24 h.
[c] After addition of benzaldehyde, the reaction was conducted at rt for 48 h.
[d] After addition of benzaldehyde, the reaction was conducted at 0 °C for 48 h.

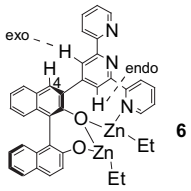
The high enantioselectivity of (*R*)-**5** for the reaction of methyl propiolate with benzaldehyde has prompted us to explore the use of this chiral ligand to catalyze the reaction of methyl propiolate with various aromatic aldehydes. Table 2 summarizes the results obtained by applying the conditions of entry 17 in Table 1. As shown in Table 2, (*R*)-**5** in combination with $ZnEt_2$ and $Ti(O^iPr)_4$ exhibits excellent enantioselectivity for the reaction of methyl propiolate with benzaldehydes containing electron-donating and electron-withdrawing substituents at the *o*-, *m*-, or *p*-positions. In many cases, the observed ee's are higher than those using BINOL, $ZnEt_2$, $Ti(O^iPr)_4$, and HMPA.[2a] In addition, less amount of the chiral ligand (*R*)-**5** (20 mol %) than BINOL (40 mol %) is needed and no external base additive is used. The configuration of the product from (*R*)-**5** is found to be *S*, which is the same as that obtained by using (*R*)-BINOL. This indicates that in both cases, the chirality control provided by the BINOL unit is similar. The enantioselectivity of (*R*)-**5** is found to be not good for the reaction of an aliphatic aldehyde (entry 13). For a recent report on the highly enantioselective reaction of methyl propiolate with aliphatic aldehydes in the presence of a chiral catalyst, see Ref. 4c.

We have conducted a NMR spectroscopic study for the interaction of (*R*)-**5** with $ZnEt_2$. In $CDCl_3$, when (*R*)-**5** was treated with 2 equiv of $ZnEt_2$, the ^1H NMR spectrum indicated the formation of a major product together with other minor products. Three singlets at δ 8.46, 7.49, and 6.61 in a 1:1:1 ratio were observed for the aromatic signals of the major product. Compound **6** is proposed as one of the possible structures for the major zinc complex generated from the reaction of (*R*)-**5** with two equivalents of $ZnEt_2$. In **6**, because of the O–N chelate coordination to the Zn center, the central pyridine ring should contain an *endo* H and an *exo* H and the *endo* H signal should be shifted upfield because of the shielding by the Zn center. Therefore, the original singlet for the protons on the central pyridine ring of (*R*)-**5** at δ 8.77 (2H) in the ^1H NMR spectrum is probably changed to the two singlets at δ 8.46 (*exo* H) and 6.61 (*endo* H) in that of **6**. The singlet at δ 7.49 is assigned to the proton at the position 4 of the BINOL unit of **6**. When more than 2 equiv of $ZnEt_2$ was added, most of the zinc complexes precipitated out and the ^1H NMR spectrum showed

Table 2
Results for the reaction of methyl propiolate with aromatic aldehydes in the presence of (*R*)-**5**, $ZnEt_2$, and $Ti(O^iPr)_4$

Entry	Aldehyde	Product	Isolated yield (%)	ee (%)
1			80	95
2			86	90
3			92	92
4			90	95
5			83	98
6			86	93
7			80	95
8			96	92
9			94	88
10			89	98
11			82	93
12			88	87
13			70	47

diminished aromatic signals. This situation did not change significantly with the addition of $Ti(O^iPr)_4$ and benzaldehyde. The formation of a complex like **6** indicates a possible cooperation between the BINOL and the terpyridine units.



6

We have also tested the use of 4-chloro-2,2′,6′2″-terpyridine in place of HMPA or NMI as a Lewis base additive for the BINOL–$Ti(O^iPr)_4$–$ZnEt_2$ catalyzed reaction of methyl propiolate with benzaldehyde,[2] but only low enantioselectivity (≤37% ee) was observed. This demonstrates that the intramolecular cooperation of the terpyridine and BINOL units in (*R*)-**5**, probably involving complexes like **6**, is very important for its high enantioselectivity.

The effect of the ee of (*R*)-**5** on the ee of the product for the reaction of methyl propiolate with benzaldehyde has been studied. The data summarized in Table 3 shows a linear relationship. This demonstrates that the catalytically active species when (*R*)-**5** is used for the reaction of methyl propiolate with benzaldehyde is probably monomeric.

Table 3
The relationship between the ee of (*R*)-**5** and that of the addition product

Entry[a]	ee of (*R*)-**5** (%)	ee(%)
1	0	3
2	20	23
3	40	42
4	60	60
5	80	82
6	99	90

[a] Et_2Zn/methyl propiolate/benzaldehyde/(*R*)-**5**/$Ti(O^iPr)_4$=4:4:1:0.2:0.5, all the reactions were conducted at room temperature.

In summary, a novel C_1 symmetric BINOL–terpyridine ligand (*R*)-**5** has been synthesized. This ligand in combination with $ZnEt_2$ and $Ti(O^iPr)_4$ is found to catalyze the highly enantioselective reaction of methyl propiolate with aromatic aldehydes to give the synthetically useful γ-hydroxy-α,β-acetylenic esters. In comparison with the previously reported BINOL system, the use of (*R*)-**5** requires a reduced amount of the chiral ligand and no addition of a Lewis base. It also shows higher enantioselectivity for a number of substrates. This study demonstrates that the combination of BINOL and terpyrideine ligands has great potential in developing novel bifunctional chiral catalysts.

3. Experimental

3.1. General data

The ^1H and ^{13}C NMR spectra were measured on a Bruker AM400 NMR spectrometer (400 MHz) with $CDCl_3$ as solvent and recorded in parts per million relative to internal tetramethylsilane standard. HRMS data were determined on a Bruker Daltonics Bio TOF. Optical rotations were measured on a Perkin–Elmer 341 automatic polarimeter. Enantiomeric excesses (ee) were determined by HPLC using corresponding commercial chiral column as stated in the experimental procedures with UV detection at 223 nm. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from CaH_2 under nitrogen before use.

*3.1.1. Preparation and characterization of (R)-3-(4′-2,2′:6′2″-terpyridine)-2,2′-bis(methoxymethyl)-1,1′-bi-2-naphthol, (R)-**4**.* A mixture of 2-acetylpyridine (0.91 g, 7.5 mmol), (*R*)-**1** (2.01 g, 5 mmol), and

KOH (0.17 g, 3.0 mmol) in methanol (40 mL) was stirred in an ice bath for 12 h. Then, 1-(pyridylcaobonylmethyl)pyridium iodide (**3**) (2.45 g, 7.5 mmol) and ammonium acetate (3.85 g, 50 mmol) were added and the resulting mixture was heated at refluxed for 48 h. After evaporation, the residue was purified by column chromatography on silica gel eluted with petroleum ether/ethyl acetate (6:1) to afford the product (*R*)-**4** in 65% yield (1.93 g) as a light yellow solid. ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.85 (s, 2H), 8.72 (d, 2H, J=4.0 Hz), 8.68 (d, 2H, J=4.0 Hz), 8.19 (s, 1H), 7.97 (d, 1H, J=3.6 Hz), 7.86–7.80 (ddd, 5H, J=6.4, 6.0, 2.8 Hz), 7.59 (d, 2H, J=8.8 Hz), 7.21–7.45 (m, 8H), 5.21 (t, 2H), 4.45 (t, 2H), 3.30 (s, 3H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.3, 155.5, 152.8, 151.1, 149.2, 136.8, 134.1, 134.0, 133.5, 130.9, 130.6, 129.7, 129.6, 128.3, 127.8, 126.7, 126.5, 125.9, 125.8, 124.1, 123.7, 122.0, 121.3, 120.7, 116.3, 99.0, 94.7, 77.3, 76.3, 56.1. HRMS (ES^+) calcd for $C_{39}H_{31}N_3O_4$ (M+H): 606.2393, found: 606.1713.

*3.1.2. Preparation and characterization of (R)-3-(4′-2,2′:6′2″-terpyridine)-1,1′-bi-2-naphthol, (R)-**5**.* To a solution of (*R*)-**4** (1.93 g, 3 mmol) in CH_2Cl_2, CF_3COOH (3.2 mL, 30 mmol) was added, and the solution was stirred for 12 h. A saturated $NaHCO_3$ solution (30 mL) was added to quench the reaction. CH_2Cl_2 (50 mL) was used for extraction and the combined organic layer was dried over Na_2SO_4. After removal of the organic solvent under reduced pressure, the residue was purified by column chromatography on silica gel eluted with petroleum ether/ethyl acetate (3:1) to afford the product (*R*)-**5** in 85% yield (1.40 g) as a light yellow solid. $[\alpha]_D^{20}$ +111.4 (*c* 0.72, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.76 (s, 2H), 8.62 (d, 2H, J=8.0 Hz), 8.52 (d, 2H, J=4.8 Hz), 8.26 (s, 1H), 7.93 (d, 1H, J=8.0 Hz), 7.84 (ddd, 4H, J=7.6, 8.4, 7.6 Hz), 7.21–7.45 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.9, 154.6, 153.1, 151.4, 149.6, 148.5, 137.0, 136.8, 134.0, 133.8, 131.6, 130.5, 129.0, 128.9, 128.8, 128.0, 127.5, 125.1, 124.3, 123.9, 123.4, 122.0, 121.3, 117.9, 113.0, 112.3. HRMS (ES^+) calcd for $C_{35}H_{23}N_3O_2$ (M+H): 518.1869, found: 518.1869.

3.2. General procedure for the catalytic asymmetric process

Under nitrogen, to a flask containing (*R*)-**5** (25.9 mg, 0.05 mmol, 20 mol %) in dry CH_2Cl_2 was sequentially added methyl propiolate (85 μL, 1.0 mmol), $ZnEt_2$ (0.67 mL, 1.5 M in toluene, 1.0 mmol), and $Ti(O^iPr)_4$ (125 μL, 1.0 M in toluene, 0.125 mmol). The reaction mixture was stirred at room temperature for 24 h. An aldehyde (0.25 mmol) was then added at 0 °C and the reaction was allowed to proceed at 0 °C for 48 h. Saturated aqueous ammonium chloride was added to quench the reaction, and CH_2Cl_2 was used for extraction. After the organic solution was dried over Na_2SO_4 and filtered, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluted with petroleum ether/ethyl acetate (9:1) to afford the product. The ee's were determined by HPLC analysis (OD-H column. Eluent: *n*-Hexane/*i*-PrOH).

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Supplementary data

The characterization data of the catalytic asymmetric reaction products and the NMR and IR spectra are provided. Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2010.01.058.

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