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Catalytic asymmetric carbon–carbon bond forming reactions catalyzed by tetrahydroisoquinoline (TIQ) *N,N′*-dioxide ligands

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ABSTRACT

The use of TIQ-*N,N′*-dioxide ligands in asymmetric C–C bond forming reactions is described. In the Michael addition of cyclohexane-1,3-dione and malonates to β,γ-unsaturated α-ketoesters, excellent yields (up to 93%) and moderate to good enantioselectivities (70–89% *ee*) were obtained. The catalytic hetero-ene reaction of 2-methoxypropene with phenylglyoxal gave the ene product in excellent yield (95%) with moderate enantioselectivity (77% *ee*). The catalyst system performed well at temperatures ranging from 0 to 30 °C and relatively low catalyst loading (0.2–5 mol %) with dichloromethane being the preferred solvent for all reactions.

1. Introduction

Asymmetric catalysis has been a major subject of interest due to the search for enantiomerically pure biologically active compounds.[1] The catalytic asymmetric Michael addition reaction is very important in organic synthesis because it is a powerful method for the construction of stereocenters.[2,3] It is also the most widely used reaction for C–C bond formations whereby nucleophiles (donors) are added to alkenes or alkynes attached to an electron withdrawing group (acceptors) to generate new stereogenic centers.[4] In addition, the broad range of donor atoms includes S, O, and N, which has increased the scope of Michael addition reactions. The most common acceptors reported are based on α,β-unsaturated carbonyl compounds as compared to β,γ-unsaturated α-ketoesters.[5–19] The use of this latter group in the synthesis of biological active compounds is steadily gaining interest.[20]

The catalytic asymmetric hetero-ene reaction is also one of the simplest ways for C–C bond formation and for the derivatization of allylic C–H bonds.[21] There are only a few cases where enol ethers have been reported for this type of reaction due to their instability in the presence of a Lewis acid and the competitive Mukaiyama aldol reaction (Scheme 1).[22–26] Jacobsen et al. reported the only successful enantioselective reaction of aryl aldehydes with an alkyl enol ether via Lewis acid activation, which afforded the ene product with up to 97% yield and 96% *ee*.[26] The first catalytic enantioselective hetero-ene reaction of alkyl enol ethers with 1,2-dicarbonyl compounds in excellent yields (up to 98%) with >99% *ee* was reported by Feng et al. using *N*-oxide ligands.[27]

N-Oxides have emerged as promising ligands for chiral catalysis because they offer excellent electron donating properties, which are required for complexation with metal ions.[28] There have been several reports on the use of *N,N′*-dioxides as tetradentate ligands coordinated to metal ions for a range of reactions affording excellent yields and selectivity. These reactions include asymmetric cycloadditions[29–33] and enantioselective nucleophilic additions to C=O and C=N bonds.[34–38,30] Stereoselective conjugate additions between α,β-unsaturated compounds and nucleophiles[39–41] have also been achieved.

Over the past few years, we have developed the tetrahydroisoquinoline (TIQ) scaffold either as ligands or catalysts for various applications. These reactions include catalytic asymmetric transfer hydrogenations (ATH),[42,43] Henry type C–C bond formations,[44,45] high pressure hydrogenations of unsymmetrical olefins,[46] conjugate addition reactions,[47] and as organocatalysts for Diels–Alder reactions.[48] We recently demonstrated the use of TIQ based *N*-oxides as organocatalysts for the asymmetric allylation of aldehydes[49] and for enantioselective conjugate addition of thioglycolate to a range of chalcones using metal complexes.[50] Herein, we report the use of C_2-symmetric TIQ *N,N′*-dioxide ligands complexed with metal ions for enantioselective Michael addition of cyclic diketones and malonates to β,γ-unsaturated α-ketoesters. We also report the catalytic hetero ene reaction of glyoxal with enol ether.

2. Results and discussion

Since Dong et al. reported the use of *N,N′*-dioxide(II) complexes as effective chiral Lewis acid catalysts for enantioselective Michael addition reactions,[51] we first chose the chiral *N′N*-dioxide ligand **L1** (Fig. 1). Ligand **L1** was previously synthesized for the asymmetric

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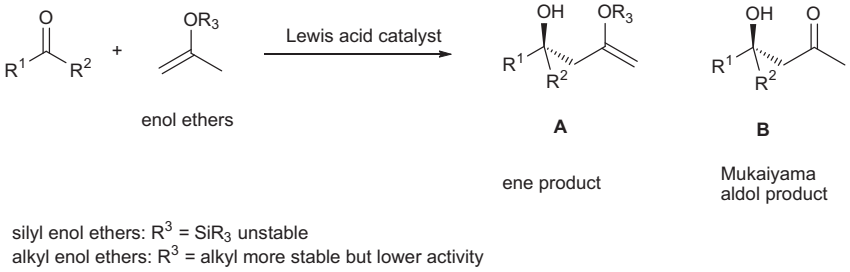


Scheme 1. Competing formation of ene product A and the Mukaiyama aldol product B in the Lewis acid catalyzed addition of enol ethers to electrophiles.

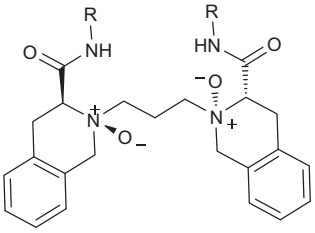


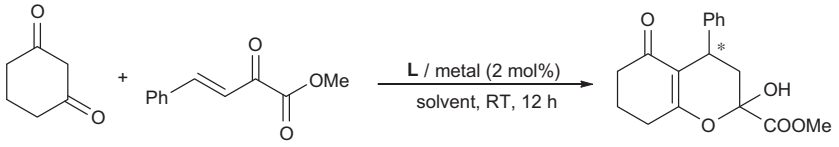
Figure 1. Chiral *N*-oxide ligands used herein.

conjugate addition of thioglycolate to a range of chalcones.[52] This ligand was complexed with $Cu(OTf)_2$, and evaluated in the reaction of cyclic diketone **2a** with β,γ-unsaturated α-ketoester **1a** in CH_2Cl_2 at room temperature to afford the addition product **3a** in 72% yield and with 30% *ee* (Table 1, entry 1). The ^1H NMR and ^{13}C NMR spectra showed that the product was obtained as an equilibrating mixture of anomers and that the cyclic compound was the major product.[53] Only one pair of enantiomers was detected by HPLC because the equilibrium was very rapid, although it was slow enough for both compounds to show up in NMR.[53,51] In our previous report we showed that ligands with bulky groups at the *ortho* positions of aniline, such as isopropyl in **L2**, could give the Michael adduct with higher enantioselectivities[52] (Table 1, entry 1 vs 2). With **L2** being the best ligand, we next carried out the reaction of **1a** with **2a** in different solvents. The results indicated that the choice of solvent had a significant effect on the rate and enantioselectivity of the reaction (Table 1, entries 2–6). Solvents such as chloroform, tetrahydrofuran, acetonitrile, and 1,2-dichloroethane provided lower enantioselectivities of **3a** compared to dichloromethane. Several other Lewis acids were also investigated however there was no further improvement in the results (Table 1, entries 7–10). It should also be noted that neither the metal nor the ligand alone promoted the reaction (Table 1, entries 11 and 12), therefore the preparation of a metal complex beforehand was unnecessary.

Under the optimized conditions (Table 1, entry 2), the scope of substrates for the asymmetric conjugate addition of cyclic diketones to various β,γ-unsaturated α-ketoesters was extended and the results are shown in Table 2. Ketoesters with both electron-donating and electron-withdrawing groups at the *para* position were well tolerated in terms of enantioselectivity and yields, with up to 91% yield and 89% *ee* being obtained (Table 2, entries 1–7). A fused ring β,γ-unsaturated α-ketoester **1h** was also a suitable substrate for the reaction, giving the corresponding product in moderate yield and *ee* (Table 2, entry 8).

With the results from our previous work on asymmetric conjugate addition reactions[52] and from these optimized reaction conditions (Table 1), we concluded that the TIQ-*N*′*N*-dioxide ligands are

Table 1
Asymmetric conjugate addition of cyclohexane-1,3-dione **1a** to ketoester **2a** catalyzed by ligands **L1** and **L2**

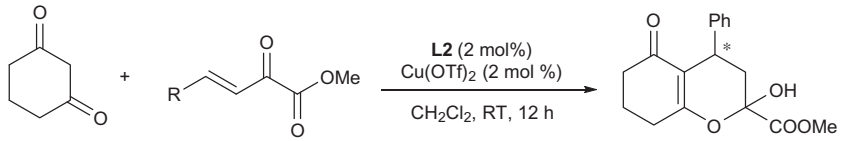


1a **2a** **3a**

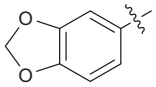
Entry	Ligand	Metal	Solvent	Yield[a] (%)	*ee*[b] (%)
1	**L1**	$Cu(OTf)_2$	CH_2Cl_2	72	30
2	**L2**	$Cu(OTf)_2$	CH_2Cl_2	90	82
3	**L2**	$Cu(OTf)_2$	$CHCl_3$	89	20
4	**L2**	$Cu(OTf)_2$	$ClCH_2CH_2Cl$	81	43
5	**L2**	$Cu(OTf)_2$	CH_3CN	76	10
6	**L2**	$Cu(OTf)_2$	THF	65	10
7	**L2**	$La(OTf)_3$	CH_2Cl_2	92	*rac*
8	**L2**	$Sc(OTf)_3$	CH_2Cl_2	40	36
9	**L2**	$Yb(OTf)_3$	CH_2Cl_2	88	41
10	**L2**	$In(OTf)_3$	CH_2Cl_2	72	*rac*
11[c]	**L2**	—	CH_2Cl_2	No reaction	—
12[d]	—	$Cu(OTf)_2$	CH_2Cl_2	No reaction	—

Unless otherwise noted, the reactions were performed with **1a** (0.12 mmol), **2a** (0.10 mmol), *N*,*N*′-dioxide (0.01 mmol), and metal (0.01 mmol) in solvent (1.0 mL) at room temperature for 12 h.
[a] Yield of the isolated product.
[b] Determined by HPLC analysis (Chiralpak IA).
[c] With the ligand only.
[d] With the metal only.

Table 2
Substrate scope for the asymmetric conjugate addition of hexane-1,3-dione to β,γ-unsaturated α-ketoesters



1a 2 3

Entry	R	Yield[a] (%)	*ee*[b] (%)	Product
1	Ph	90	82	**3a**
2	4-MeC_6H_4	88	74	**3b**
3	4-$MeOC_6H_4$	91	89	**3c**
4	4-FC_6H_4	87	79	**3d**
5	4-ClC_6H_4	79	78	**3e**
6	4-$NO_2C_6H_4$	68	70	**3f**
7		70	77	**3g**
8	2-Naphthyl	74	71	**3h**

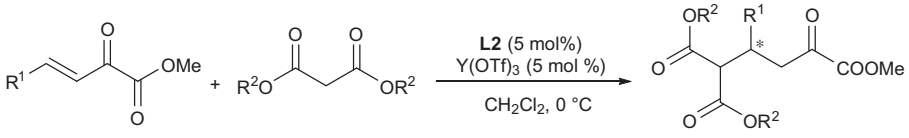
Unless otherwise noted, the reactions were performed with **1a** (0.12 mmol), **2** (0.10 mmol), *N,N′*-dioxide **L2** (2 mol %), and $Cu(OTf)_2$ (2 mol %) in CH_2Cl_2 (1.0 mL) at room temperature for 12 h.
[a] Yield of the isolated product.
[b] Determined by HPLC analysis (Chiralpak IA).

similar to the *N*-oxide ligands reported by Feng et al.[1] We decided to investigate different substrates for the asymmetric Michael addition of malonates to β,γ-unsaturated α-ketoester using **L2**-$Y(OTf)_3$.

In general, the scope of this transformation was found to be relatively wide as different substituents on the β,γ-unsaturated α-ketoesters led to the corresponding addition product in good yields and enantioselectivities (Table 3, entries 1–6). The electronic nature of the substituents on the ketoesters had an influence on the reaction yield, but did not have an effect on the selectivity of the products. For example, the ketoesters with an electron-donating group showed higher reactivity (Table 3, entry 2), than electron-withdrawing substituents, while the selectivity remained similar (Table 3, entries 4 and 5). It should be noted that the condensed ring performed well, giving the corresponding product in relatively good yield and enantioselectivity (Table 3, entry 6). When the ester group on the malonate was changed from methyl to ethyl, the *ee* did not change (Table 3, entries 1–9) and even when it was altered to a larger group such as *i*-Pr (Table 2, entries 10–13), the *ee* was unaffected.

We next decided to examine the benchmark reaction for the addition of alkyl enol ether **7** to phenylglyoxal **6** as another C–C bond formating reaction. Zheng et al. showed that the Mukaiyama aldol product, which arises due to the high reactivity of glyoxals and the hydrolysis of **9** under acidic conditions can be avoided by low catalytic loading and by using the less reactive $Cu(OTf)_2$

Table 3
Substrate scope for the asymmetric Michael addition of malonates to β,γ-unsaturated α-ketoesters

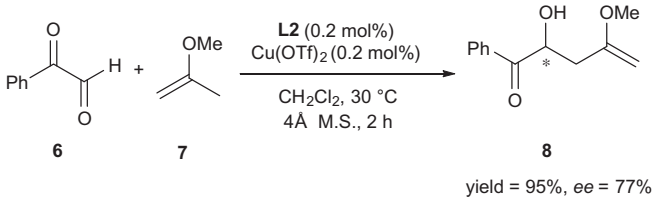


2 4 5

Entry	R^2, R^1	Time (h)	Yield[a] (%)	*ee*[b] (%)
1	Me, Phe	5	89	85
2	Me, 4-MeC_6H_4	12	76	81
3	Me, 4-$MeOC_6H_4$	8	93	87
4	Me, 4-FC_6H_4	8	63	71
5	Me, 4-ClC_6H_4	8	61	83
6	Me, 2-napthyl	12	84	73
7	Et, Phe	10	85	81
8	Et, 4-$MeOC_6H_4$	10	76	84
9	Et, 4-ClC_6H_4	10	72	80
10	*i*-Pr, Phe	8	68	82
11	*i*-Pr, 4-$MeOC_6H_4$	9	70	84
12	*i*-Pr, 4-FC_6H_4	10	69	79
13	*i*-Pr, 4-ClC_6H_4	10	67	82

Unless otherwise noted, the reactions were performed with **2** (0.10 mmol), *N,N′*-dioxide **L2** (5 mol %), and $Y(OTf)_3$ (5 mol %) in a CH_2Cl_2, then malonates **4** were added at 0 °C. The reaction mixture was stirred at 0 °C for the indicated time.
[a] Isolated yield.
[b] Determined by HPLC analysis (Chiralpak IA).

complex compared to $Mg(OTf)_2$.[27] The reaction shown in Scheme 2, proceeded smoothly in excellent yield and with moderate *ee* using **L2**-$Cu(OTf)_2$ complex at 0.2 mol % catalyst loading to hinder the Mukaiyama aldol reaction.



Scheme 2. Catalytic asymmetric hetero ene reaction of glyoxal with 2-methoxypropene.

3. Conclusion

We have demonstrated the use of C2-symmetric TIQ-*N*′*N*-dioxides as efficient ligands for C–C bond forming reactions. High yields (up to 95%), moderate enantioselectivities (up to 89% *ee*), a broad range of substrates, and mild reaction conditions demonstrate the potential of this catalytic system for other asymmetric transformations. The choice of solvent also played an important role in the selectivity of these reactions with dichloromethane being the most efficient for all three of the C–C bond forming reactions reported herein. The Michael addition reaction of ketoesters with cyclohexane1,3-dione (Tables 1 and 2) and malonate (Table 3) required 2 and 5 mol % catalytic loading, respectively, to achieve the best results. The benchmark hetero-ene reaction proceeded smoothly with relatively low catalyst loading (0.2 mol %) allowing us to avoid the Mukaiyama product. A comparative study of our TIQ-*N*′*N*-dioxide with Fengfs bis *N*-oxide ligands demonstrated complementarity in their behavior, however our system did not achieve equivalent yields and selectivities. Further studies of the application of this catalyst to other reactions are currently ongoing in our laboratory.

4. Experimental

4.1. Ligands L1 and L2

The TIQ-*N*′*N*-dioxide ligands **L1** and **L2** were synthesized using the same procedure reported in the literature.[52]

4.2. General procedure for the enantioselective conjugate addition of cyclic diketones to β,γ-unsaturated α-ketoesters

Dichloromethane (1.0 mL) was added to a mixture of ligand **L2** (2.98 mg, 0.004 mmol), $Cu(OTf)_2$ (1.45 mg, 0.004 mmol), and β,γ-unsaturated α-ketoesters (38.0 mg, 0.2 mmol) and diketone (22.4 mg, 0.2 mmol), then stirred at room temperature for 12 h. After the reaction was complete (monitored by TLC), the mixture was purified by column chromatography on silica gel (ethyl acetate/hexane = 1:2) to afford the desired product as a white solid in 90% yield. The enantioselectivity was determined by chiral HPLC (Chiralpak IA, hexane/*i*-PrOH = 80/10, flow rate 1.0 mL/min, λ = 254 nm).

4.3. General procedure for the asymmetric Michael addition of malonates to β,γ-unsaturated α-ketoesters

A solution of ligand **L2** (3.8 mg, 0.005 mmol), $Y(OTf)_3$ (2.68 mg, 0.005 mmol), and β,γ-unsaturated α-ketoesters (19.1 mg, 0.10 mmol) in anhydrous dichloromethane (0.2 mL) was stirred at room temperature for 30 min. The reaction mixture was cooled to 0 °C and dimethyl malonate (0.12 mmol, 14 μL) was added, after which the reaction mixture was stirred at 0 °C for 8 h while being monitored by TLC. The solvents were evaporated under reduced pressure and the residue was purified through column chromatography (hexane/ethyl acetate = 4:1) to afford the pure conjugated product as a yellow oil in 95% yield. The enantioselectivity was determined by chiral HPLC (Chiralpak IA, hexane/*i*-PrOH = 80/10, flow rate 1.0 mL/min, λ = 254 nm).

4.4. Typical procedure for the catalytic asymmetric hetero-ene reaction of glyoxal with 2-methoxypropene

A mixture of 100 μL (0.002 mmol) of catalyst solution (0.002 M $Cu(OTf)_2$-**L2** in CH_2Cl_2), phenylglyoxal (0.1 mmol), and 3 Å MS (50 mg) was stirred at 30 °C for 30 min. Then, 2-methoxypropene (1.25 equiv) was added at room temperature under nitrogen. The reaction mixture was then allowed to reflux for 2 h while being monitored by TLC and was directly purified by column chromatography on silica gel (ethyl acetate/hexane = 1:10). The pure ene product was obtained in 90% yield as a colorless liquid. The enantioselectivity was determined by chiral HPLC using a DAICEL CHIRALCEL AS-H column, 2-propanol/*n*-hexane = 10/80, flow rate = 0.8 mL/min, λ = 254 nm.

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