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# Catalytic Asymmetric 1, 3-Dipolar Cycloaddition Reaction of Nitrones with α′-Phosphoric Enones by a Chiral Ligand-Copper(II) Triflate Complex

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**Abstract:** Using the $C_2$-symmetric bis-oxazoline copper(II) catalyst **6f** as a chiral Lewis acid, α′-phosphoric enones **2** undergo 1,3-dipolar cycloaddition with nitrones **3** to provide isoxazolidines **4** with very high enantioselectivity and *endo/exo* selectivity.

**Keywords:** asymmetric catalysis; copper salts; cycloaddition; Lewis acids; synthetic methods

1,3-Dipolar cycloaddition reactions of nitrones with alkenes have proved to be synthetically very useful, providing important isoxazolidine adducts used for preparing 3-amino alcohols and alkaloids.[1] During the past two decades various enantioselective total syntheses have been achieved using chiral isoxazolidines derived from asymmetric 1,3-dipolar cycloaddition reactions.[2] However, the asymmetric 1,3-dipolar cycloaddition reaction was mainly achieved by incorporating chiral centers in the nitrone and/or the alkene.

The chiral Lewis acid-catalyzed asymmetric 1,3-dipolar cycloaddition reactions have mainly utilized the metal-assisted activation of electron-deficient alkenes through formation of 1,4- or 1,5-metal-chelated species.[3] Contrary to the Lewis acid-catalyzed asymmetric Diels–Alder reactions,[4] the application of Lewis acids in asymmetric 1,3-dipolar cycloaddition reactions is relatively unexplored. Previously reported alkene templates include *N*-enoyl derivatives of oxazolidinones **1**,[5] pyrrolidinone,[6] and pyrazolidinone,[7] as well as the recently reported α′-hydroxy enones.[8] We have been interested in using α′-phosphoric enones **2** in asymmetric reactions based on two factors. First, α′-phosphoric enone templates can form 1,5-metal-chelated species (Figure 1).[9] Second, they can be readily converted into enones by the Horner–Wadsworth–Emmons (HWE) reaction[10] and also can be removed to provide ketones.[11]

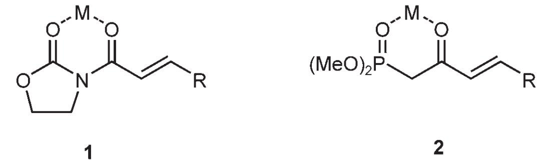


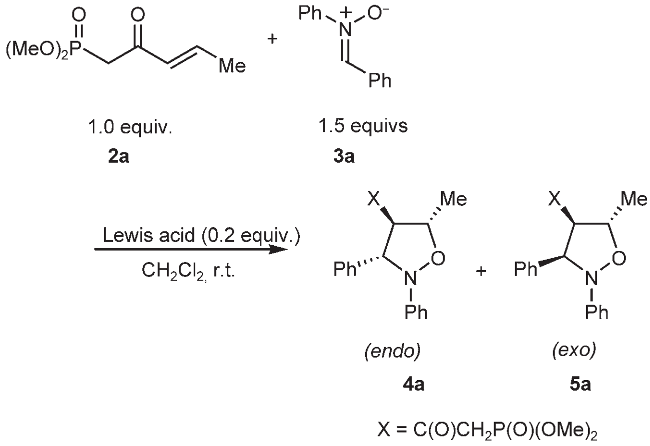
**Figure 1.** 1,5-Chelation of oxazolidinone **1** and α′-phosphoric enone **2**.

Recently, we have reported catalytic enantioselective Friedel–Crafts alkylations of indoles using α′-phosphoric enones in which the enantioselectivities of up to 98% *ee* were obtained.[12] In our continued effort to examine the synthetic efficiency of α′-phosphoric enone templates in enantioselective organic reactions, we have studied the Lewis acid-catalyzed asymmetric 1,3-dipolar cycloaddition reaction of nitrones.

We initially screened several Lewis acids for 1,3-dipolar cycloaddition of phosphoric enone **2a** with nitrone **3a**. The similar reaction was reported previously, where an 83:17 *endo/exo* selectivity using dichlorodiisopropoxytitanium was obtained.[13] Among the Lewis acids tested, cupric triflate gave the best result in terms of the highest *endo/exo* selectivity and the reaction rate. Magnesium triflate was also somewhat effective but slowed down the reaction as shown in Table 1.

Our next attention was given to the nitrone additions to substrate **2a** using a catalytic amount (20 mol%) of chiral Lewis acids derived from cupric triflate and bis-oxazoline (Box) derivatives (Figure 2) in dichloromethane.[14] As shown in Table 2, several features are noteworthy. First, among the chiral ligands tested in this study, (4*R*,5*S*)-diPh-Box **6f** was most attractive, giving the highest enantioselectivity along with very high *endo/exo* selectivity (entries 3 and 4). Second, the chemical yields of the present reaction were not high, ranging from 40% to 63% (entries 1–4). The addition of 4 Å molecular sieves improved the chemical yield significantly but lowered the enantiose-

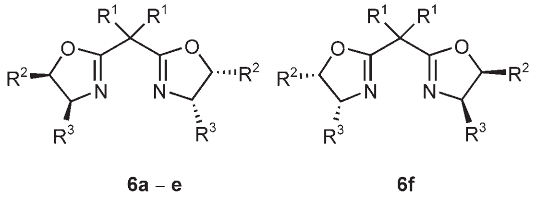
**Table 1.** Screening of Lewis acids.



| Lewis Acid | Time [h] | Yield [%][a] | *endo/exo*[b] |
|---|---|---|---|
| $Cu(OTf)_2$ | 3 | 57 | 97:3 |
| $Zn(OTf)_2$ | 3 | 69 | 86:14 |
| $Sc(OTf)_3$ | 3 | 37 | 75:25 |
| $Mg(OTf)_2$ | 20 | 76 | 91:9 |

[a] Isolated yield.

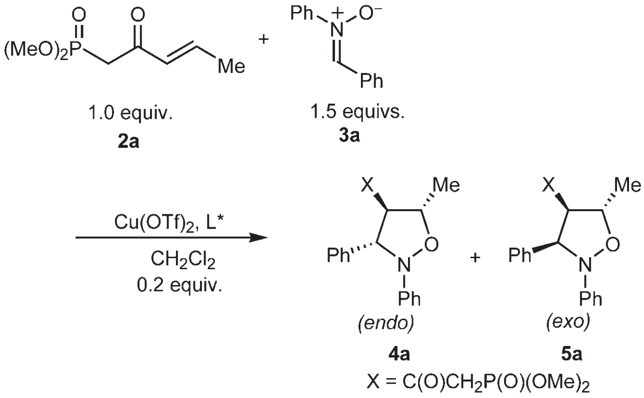
[b] Determined by $^1H$ NMR.



$R^1$ = Me, $R^2$ = H, $R^3$ = Ph (*S*)-Ph-Box **6a**
$R^1$ = Me, $R^2$, $R^3$ = In (*S*)-In-Box **6b**
$R^1$ = $CH_2CH_2$, $R^2$, $R^3$ = In (*S*)-In-Cp-Box **6c**
$R^1$ = Me, $R^2$ = H, $R^3$ = *i*-Pr (*S*)-*i*-Pr-Box **6d**
$R^1$ = Me, $R^2$ = H, $R^3$ = *t*-Bu (*S*)-*t*-Bu-Box **6e**
$R^1$ = Me, $R^2$ = Ph, $R^3$ = Ph (4*R*,5*S*)-diPh-Box **6f**

**Figure 2.** Chiral bis-oxazoline (Box) ligands.

**Table 2.** Screening of chiral ligands in the Cu(II)-catalyzed 1,3-dipolar cycloaddition.



| Entry | L* | *T* [°C] | *t* [h] | Yield [%][a] | *endo/exo*[b] | *ee* [%][c] |
|---|---|---|---|---|---|---|
| 1 | **6a** | 0 | 12 | 41 | 97:3 | 79 |
| 2 | **6b** | 0 | 12 | 63 | 94:6 | 61 |
| 3 | **6f** | 0 | 12 | 57 | 96:4 | 90 |
| 4 | **6f** | r.t. | 4 | 40 | 96:4 | 84 |
| 5 | **6a** | r.t. | 4 | 46 | 96:4 | 65[d] |
| 6 | **6f** | r.t. | 4 | 80 | 98:2 | 82[d] |
| 7 | **6a** | −40 | 60 | 61 | 98:2 | 65[d] |
| 8 | **6f** | −40 | 60 | 74 | 98:2 | 89[d] |
| 9 | **6c** | −40 | 60 | 77 | 88:12 | 83[d] |
| 10 | **6d** | 0 | 24 | 48 | 91:9 | 0 |
| 11 | **6e** | 0 | 24 | 0 | | |

[a] Isolated yield.

[b] The *endo/exo* ratio was determined by $^1H$ NMR spectroscopy.

[c] The *ee* was determined by chiral HPLC.

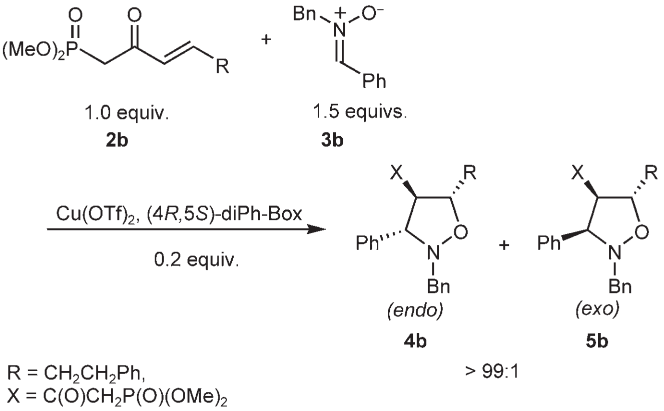
[d] In the presence of 4 Å molecular sieves.

lectivity to some extent (entries 5–9). The effect of molecular sieves in the asymmetric reactions has been noted previously.[15] Finally, the chiral ligands bearing alkyl substituents were totally unsuccessful (entries 10 and 11). The reaction using **6d** gave a mixture of racemic products, whereas the reaction using **6e** did not occur.

To optimize the reaction conditions, we briefly examined the solvent effect using (*4R,5S*)-diPh-Box **6f** and the result was very promising as shown in Table 3. When the same reaction was repeated in toluene at 0 °C, the reaction was faster and the yield improved significantly (entry 2). Even more gratifyingly, a high enantioselectivity (99% *ee*) was achieved along with a better *endo/exo* selectivity (99:1). Tetrahydrofuran was also very effective and comparable to toluene (entry 3). Since nitrone **3b** was slightly soluble in toluene, two mixed solvent systems were examined and similar results were obtained without any problems (entries 4 and 5). To test the catalytic ability of cupric triflate, we reduced the amount of the catalyst to 10 mol%. The reaction of **2b** with **3b** in the presence of 10 mol% cupric triflate and **6f** in tetrahydrofuran at 0 °C gave the same enantioselectivity, *endo/exo* selectivity, and chemical yield but was slowed down slightly (26 h *vs.* 20 h for 20 mol% catalyst). Thus, the remaining reactions were normally carried out using 10 mol% cupric triflate and 12 mol% **6f** in tetrahydrofuran at 0 °C.

The experimental results obtained in this study are summarized in Table 4. Several noteworthy features are apparent. First, the present 1,3-dipolar cycloaddition reactions proceeded smoothly, yielding the isoxazolidine adducts in high yields with almost complete *endo* selectivities (>99:1) for the nitrones **3a** and **3b**. Second, *N*-benzyl nitrone **3b** exhibited higher enantioselectivities than *N*-phenyl nitrone **3a**. For instance, the reaction of α′-phosphoric enone **2a** ($R^1$ = Me)

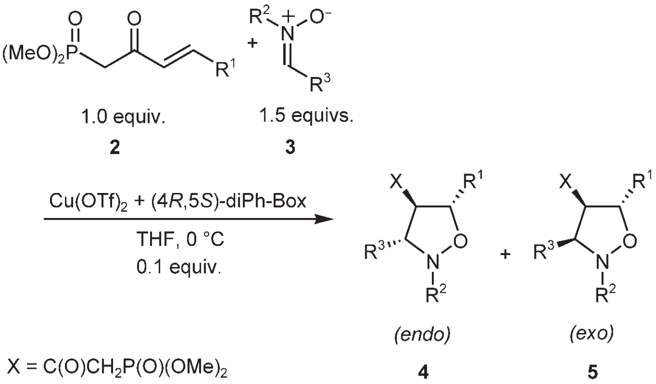
**Table 3.** Effect of solvent in the 1,3-dipolar cycloadditions.



| Entry | Solvent | $T$ [°C] | $t$ [h] | Yield [%][a] | *ee* [%][b] |
|---|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | r.t. | 48 | 43 | 85 |
| 2 | toluene | 0 | 20 | 97 | 99 |
| 3 | THF | 0 | 20 | 82 | 99 |
| 4 | toluene + $CH_2Cl_2$ | 0 | 20 | 92 | 99[c] |
| 5 | toluene + THF | 0 | 20 | 95 | 99[c] |

[a] Isolated yield.
[b] The *ee* was determined by chiral HPLC.
[c] A 1:1 ratio of the two solvents.

**Table 4.** Cu(II)-catalyzed 1,3-dipolar cycloaddition of nitrones **3** with α′-phosphoric enones **2**.



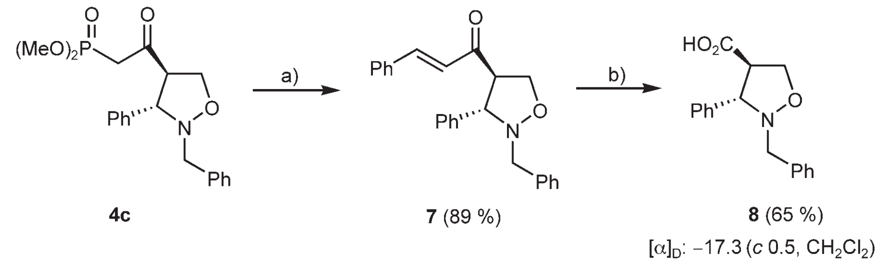
| Entry | $R^1$ | $R^2$ | $R^3$ | $t$ [h] | Yield [%][a] | *endo*/*exo*[b] | *ee* [%][c] |
|---|---|---|---|---|---|---|---|
| 1 | $(CH_2)_2Ph$ | Bn | Ph | 26 | 82 | > 99:1 | 99 |
| 2 | $(CH_2)_2Ph$ | Ph | Ph | 8 | 92 | > 99:1 | 86 |
| 3 | Me | Bn | Ph | 8 | 90 | > 99:1 | 91 |
| 4 | Me | Ph | Ph | 6 | 92 | > 99:1 | 85 |
| 5 | Et | Bn | Ph | 10 | 89 | > 99:1 | 93 |
| 6 | *i*-Pr | Ph | Ph | 48 | 81 | > 99:1 | 84 |
| 7 | *i*-Pr | Bn | Ph | 48 | 87 | > 99:1 | 93 |
| 8 | *t*-Bu | Ph | Ph | 48 | 92 | > 99:1 | 99 |
| 9 | *t*-Bu | Bn | Ph | 7 d | 79[d] | > 99:1 | 99 |
| 10 | H | Bn | Ph | 4 | 75 | > 99:1 | 90 |
| 11 | Ph | Bn | Ph | 12 | 0 | | |
| 12 | Me | Bn | Et | 6 | 76 | 6:5 | 73 (75)[e] |
| 13 | Me | Bn | $(CH_2)_2Ph$ | 4 | 94 | 6:5 | 83 (80)[e] |
| 14 | Me | Bn | *i*-Pr | 24 | 91 | 10:1 | 87 (47)[e] |
| 15 | Me | Bn | *c*-Hex | 4 | 65 | > 99:1 | 84 |

[a] Isolated yield.
[b] The *endo/exo* ratio was determined by $^1$H NMR spectrum.
[c] The *ee* was determined by chiral HPLC.
[d] The starting material (15%) was recovered.
[e] Numbers in parentheses indicate *ee* of minor diastereomers.

with **3b** under the same conditions gave 91% *ee* (entry 3), whereas the reaction with **3a** gave 85% *ee* (entry 4). Similar phenomena have been observed consistently throughout the experiments. Third, as the substituent $R^1$ was changed from primary alkyl to tertiary alkyl, the reaction was slowed down but the enantioselectivity was increased to some extent, even though the enantioselectivity was not proportional to the steric bulkiness of the substituent. Finally, the reaction of α′-phosphoric cinnamyl enone ($R^1$ = Ph) did not proceed and the starting material was recovered unchanged (entry 11).

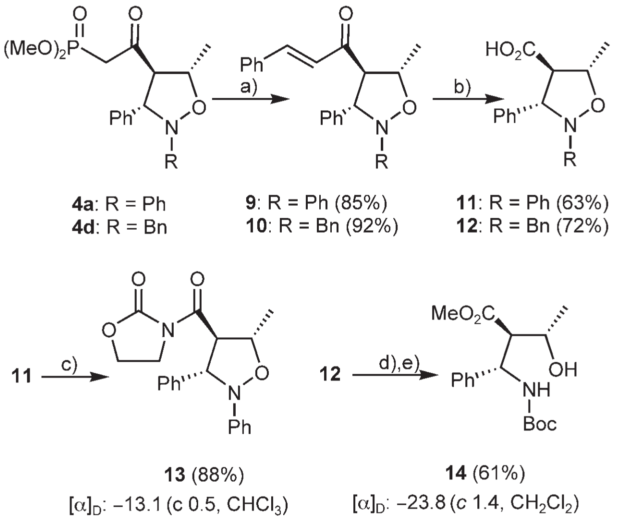
According to our brief studies with the nitrones derived from aliphatic aldehydes, they exhibited inferior results, depending on the structure of the nitrones to some extent (entries 12–15). The nitrones derived from primary aliphatic aldehydes did not show appreciable *endo/exo* selectivities, while giving good enantioselectities (entries 12 and 13). However, the nitrones derived from secondary aliphatic aldehydes showed higher *endo/exo* selectivities than the former (entries 14 and 15). Similar low *endo/exo* selectivities with the aliphatic alkyl nitrones were observed previously.[16]

To determine the absolute configuration of isoxazoline adduct **4**, **4c** was converted into the previously known compound **8** as shown Scheme 1. Treatment of **4c** with benzaldehyde and potassium carbonate in ethanol at room temperature for 2 h afforded enone **7** in 89% yield.[17] Enone **7** was converted to carboxylic acid **8** using osmium tetroxide with sodium periodate. On comparison of the optical rotation value and spectral data of **8** with those of the previously known compound,[8] the absolute configuration could be assigned as (3*S*,4*R*) in isoxazolidine ring. For further comparison, two additional isoxazoline adducts **4a** and **4d** were also converted into the previously known compounds **13**[5c] and **14**,[16] respectively (Scheme 2). Initially, **11** and **12** were obtained from **4a** and **4d** by the same routine operations. The previously known compound **14** was obtained from **12** by esterification, hydrogenolysis, and the subsequent protection of the amino group by the Boc group. The optical rotation value and the spectral data clearly indicate that **14**



a) PhCHO, $K_2CO_3$, EtOH; b) $OsO_4$, $NaIO_4$, dioxane/$H_2O$ (3/1)

**Scheme 1.** Conversion of isoxazolidine adduct **4c** into **8**.



a) PhCHO, $K_2CO_3$, EtOH; b) $OsO_4$, $NaIO_4$, dioxane/$H_2O$ (3/1);
c) *n*-BuLi, trimethylacetyl chloride; *n*-BuLi, 2-oxazolidone, THF;
d) $SOCl_2$, MeOH, reflux; e) $Pd(OH)_2$ on C, $Boc_2O$, $H_2$, MeOH

**Scheme 2.** Conversion of **4a** and **4d** into **13** and **14**.

should be (2*R*,3*S*)-methyl 2-[(*S*)-(*tert*-butoxycarbonylamino)(phenyl)methyl]-3-hydroxybutanoate.[16] Furthermore, **11** was also converted into oxazolidinone **13** by routine operations[18] and the same conclusion was also obtained by comparison of the optical rotation value of **13** and that of the known compound.[5c]

The copper(II)-bis(oxazoline)-catalyzed enantioselective reactions have been relatively well studied and it is understood that the Cu(II)-bis(oxazoline) enone complexes might exist as square planar intermediates.[19] Based on the observed enantioselectivity in this study, the *s-trans* enone template in the distorted square planar geometry would be possible (Figure 3). Although a clear answer for the control of the conformation of enone templates awaits further studies, it could result from a π–π stabilization of the transition state.[20]

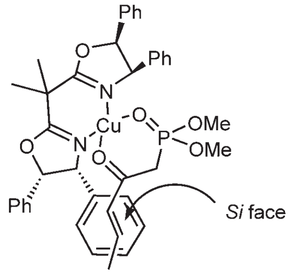


**Figure 3.** Stereochemical model for the catalyst-substrate complex.

In conclusion, we have found that the α′-phosphoric enone bidentate template is highly efficient for the catalytic asymmetric 1,3-dipolar cycloaddition of nitrones. Using the chiral Lewis acid, $Cu(OTf)_2$/(4*R*,5*S*)-diPh-Box as catalyst, the isoxazolidine adducts were obtained in high yields with high *exo*/*endo* selectivities and high enanitioselectivities.

## Experimental Section

### Typical Procedure

Copper(II) trifluoromethanesulfonate (7 mg, 0.02 mmol) and (4*R*,5*S*)-diPh-Box **6f** (11 mg, 0.022 mmol) dissolved in THF (2 mL) were stirred for 4 h at room temperature. Then, (*E*)-dimethyl 2-oxopent-3-enylphosphonate (**2a**, 38 mg, 0.2 mmol) dissolved in THF (1 mL) was added to the reaction mixture. After being stirred for additional 30 min at 0 °C, a solution of *N*-benzylidenebenzeneamine oxide (**3a**, 59 mg, 0.3 mmol) in THF (1 mL) was added to the reaction mixture. The reaction mixture was stirred for 6 h at 0 °C, then concentrated under reduced pressure. The residue was purified by a silica gel column chromatography using ethyl acetate and *n*-hexane (2:1) as eluant to give dimethyl 2-[(3*R*,4*S*,5*R*)-5-methyl-2,3-diphenylisoxazolidin-4-yl]-2-oxoethylphosphonate (**4a**); yield: 72 mg (92 %); $[\alpha]_D$: −54.12° (*c* 4.13, $CH_2Cl_2$); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 1.49$ (d, 3H, $J = 5.99$ Hz), 2.94 (m, 2H), 3.57, (m, 1H), 3.60 (dd, 6H, $J_1 = 11.28$, $J_2 = 24.72$ Hz), 4.43 (m, 1H), 4.94 (d, 1H, $J = 7.27$ Hz), 6.91 (m, 3H), 7.19 (m, 2H), 7.28 (m, 1H), 7.36 (m, 2H), 7.48 (d, 2H, $J = 9.41$ Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta =$ 17.5, 40.9 (42.2), 52.7 (52.8, 52.9, 53.0), 73.4, 73.7, 77.2, 114.2, 121.7, 126.5, 127.9, 128.8, 129.0, 141.3, 151.3, 198.4 (198.4); IR (NaCl): ν = 1712, 1597, 1488, 1453, 1259, 1181, 1031, 880, 804, 757, 699 cm$^{-1}$; HR-MS (ESI): $m/z$ = 390.1465, calcd. for $C_{20}H_{25}NO_5P$ $[M+H]^+$: 390.1469. The product ratio was determined by HPLC analysis (Chiral AS-H, *i*-PrOH/hexane = 30/70, 0.5 mL min$^{-1}$, 220 nm); $t_r$ = 25.69 min (major), $t_r$ = 30.52 min (minor).

## Acknowledgements

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