

Chiral Brønsted Acid Catalyzed Enantioselective Addition of α -Isocyanoacetamides to Aldehydes

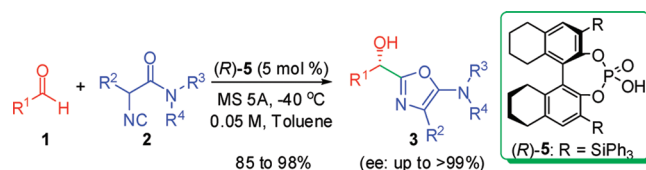
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ABSTRACT



A clean and highly efficient enantioselective addition of α -isocyanoacetamides to aliphatic aldehydes catalyzed by chiral phosphoric acid in the presence of MS 5 Å in toluene at $-40\text{ }^{\circ}\text{C}$ was developed. Excellent yields (85–98%) and good to excellent enantioselectivities (up to >99% ee) were achieved.

The classic Passerini (P-3CR)¹ and Ugi² (U-4CR) reactions based on the isocyanide multicomponent reactions (IMCRs) have been well developed and widely used to generate molecular complexity and molecular diversity for natural product synthesis and drug discovery.³ All of the above-mentioned multicomponent reactions involve the α -addition of isocyanide to both electrophiles and nucleophiles to form polyfunctionalized molecules. Although some chiral substrate⁴ or chiral auxiliary⁵ controlled diastereoselective α -additions of isocyanides to aldehydes have been reported in the past decades,⁶ the development of the enantioselective

α -addition of isocyanide to aldehydes still remains a significant challenge. Despite some efforts toward the asymmetric version of the reactions, only limited examples succeeded in achieving high enantioselectivities.⁷ Zhu, Wang, and co-workers reported two examples of enantioselective α -additions of α -isocyanoacetamides to aldehydes catalyzed by chiral salen-Al⁸ and phosphoric acid-Al complexes.⁹ The desired 2-(1-hydroxyalkyl)-5-aminooxazoles were obtained in good to excellent yields, but only moderate to good enantioselectivities (50–87% ee) were given. Shibasaki, Matsunaga, and co-workers revealed that by using their heterobimetallic Ga(OiPr)₃/Yb(OTf)₃/Schiff base complex as

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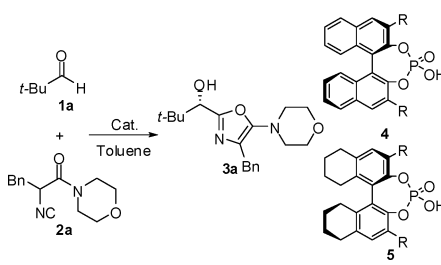
catalyst, the α -additions of α -isocyanoacetamides to aldehydes afforded excellent enantioselectivities (88–98% ee).¹⁰ Very recently, a chiral phosphoric acid catalyzed α -addition of α -isocyanoacetamides to imines providing 2-(1-aminoalkyl)-5-aminoxazoles in moderate to good enantioselectivities¹¹ was reported by Zhu, Wang, and co-workers. However, the authors failed to obtain high ee in the α -additions of α -isocyanoacetamides to aldehydes in the presence of these catalysts. Herein, we report the chiral phosphoric acid catalyzed α -addition of α -isocyanoacetamides to aldehydes, leading to products in excellent yields (85–98%) with up to >99% ee.

Chiral phosphoric acids have been extensively studied and are well-established as versatile chiral Brønsted acid¹² catalysts, especially in the catalytic asymmetric nucleophilic addition to imines, 1,4-addition and transfer hydrogenation reactions.^{13,14} However, the chiral phosphoric acid catalyzed nucleophilic addition to aldehydes was rarely reported. We hypothesized that chiral phosphoric acids should catalyze the α -addition reaction and control the enantioselectivity through the hydrogen bonding between the catalyst and aldehydes.

To validate this, we began our investigation with a reaction by using pivalaldehyde (**1a**) and 2-isocyano-1-morpholino-3-phenyl propan-1-one (**2a**) as reactants and racemic 1,1'-binaphthyl-2,2'-diyl hydrogenphosphate (*rac*-**4**) as catalyst in toluene at room temperature. To our delight, the addition reaction proceeded smoothly in the presence of *rac*-**4** to

afford racemic oxazole in 90% yield. This encouraged us to further investigate various chiral phosphoric acids in the reaction, and the results are summarized in Table 1. All the

Table 1. α -Addition of α -Isocyanoacetamides to Pivalaldehyde Catalyzed by Different Chiral Phosphoric Acids at Room Temperature^a



(*R*)-**4a**: R = Ph
(*R*)-**4b**: R = SiPh₃
(*R*)-**4c**: R = 4-ClC₆H₄
(*R*)-**4d**: R = 4-NO₂C₆H₄
(*R*)-**4e**: R = 4-*i*-BuC₆H₄
(*R*)-**4f**: R = 1-Naphthyl
(*R*)-**4g**: R = 2-Naphthyl
(*R*)-**4h**: R = 9-Phenylanthryl
(*R*)-**4i**: R = 9-Anthryl
(*R*)-**4j**: R = TRIPPh
(*R*)-**4k**: R = Mes
(*R*)-**5**: R = SiPh₃

entry	catalyst (5 mol %)	time (h)	yield ^b (%)	ee ^c (%)
1	(<i>R</i>)- 4a	2	90	15
2	(<i>R</i>)- 4b	2	94	45
3	(<i>R</i>)- 4c	2	91	18
4	(<i>R</i>)- 4d	12	48	29
5	(<i>R</i>)- 4e	5	95	48
6	(<i>R</i>)- 4f	5	90	39
7	(<i>R</i>)- 4g	2	98	37
8	(<i>R</i>)- 4h	2	89	45
9	(<i>R</i>)- 4i	2	85	48
10	(<i>R</i>)- 4j	2	93	53
11	(<i>R</i>)- 4k	2	90	9
12	(<i>R</i>)- 5	1.5	97	56

^a The reactions were performed with pivalaldehyde (0.2 mmol, 2.0 equiv) and 2-isocyano-1-morpholino-3-phenylpropan-1-one (0.1 mmol, 1.0 equiv) in the presence of 5 mol % (*R*)-**5** (0.005 mmol) in 1 mL of toluene at rt (23 °C). ^b Isolated yield. ^c Determined by chiral HPLC analysis.

chiral catalysts could afford the products in excellent yields except (*R*)-**4d** (Table 1, entry 4), which gave only 48% yield, and this may be mainly due to the formation of an unknown side product. Unfortunately, the enantioselectivities varied significantly from 9% to 56% ee. Catalysts (*R*)-**4j** and (*R*)-**5** were found to be the best considering the enantioselectivities (53% and 56% ee in Table 1, entries 10 and 12), most probably because of bearing more sterically hindered groups on the 3,3'-positions of these catalysts.

Further investigation of the solvent effect of this reaction was carried out by using (*R*)-**5** as catalyst at room temperature. Common solvents such as DCM, CHCl₃, toluene, benzene, and TBME (Table 2, entries 1, 2, and 4–6) are all good reaction mediators for this reaction, and all gave excellent yields (>90%). Notably, even hexane, which afforded the product in 89% yield and 56% ee (Table 2, entry 3), but in a relatively longer time (6 h) mainly due to the low solubility of the reactant. Among these solvents, toluene was found to be the best (Table 2, entry 5). Next, we examined the effect of reaction temperature in toluene using (*R*)-**5**. The most appropriate temperature we found was –40 °C as the product was obtained in 98% yield and 77% ee in 24 h. With the decreasing of the temperature from –40 °C to –60 °C, the reaction became much slower and the

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Table 2. α -Addition of α -Isocyanoacetamides to Aldehyde Catalyzed by (*R*)-**5** at $-40\text{ }^{\circ}\text{C}$ in Different Solvents and Additives^a

entry	R ¹	solvent	<i>t</i> (°C)	time (h)	yield ^b (%)	ee ^c (%)
1	<i>t</i> -Bu	DCM	rt	2	95	31
2	<i>t</i> -Bu	CHCl ₃	rt	2	94	37
3	<i>t</i> -Bu	hexane	rt	6	89	56
4	<i>t</i> -Bu	toluene	rt	2	97	57
5	<i>t</i> -Bu	benzene	rt	2	95	57
6	<i>t</i> -Bu	TBME	rt	4	90	56
7	<i>t</i> -Bu	toluene	-20	10	95	68
8	<i>t</i> -Bu	toluene	-40	24	95	73
9	<i>t</i> -Bu	toluene	-60	48	85	72
10 ^d	<i>t</i> -Bu	toluene	-40	24	98	76
11 ^e	<i>t</i> -Bu	toluene	-40	24	96	77
12 ^e	<i>i</i> -Pr	toluene	-40	24	95	92

^a The reactions were performed with pivalaldehyde (0.2 mmol, 2.0 equiv) and 2-isocyano-1-morpholino-3-phenylpropan-1-one (0.1 mmol, 1.0 equiv) in the presence of 5 mol % (*R*)-**5** (0.005 mmol) in 1 mL of toluene at room temperature. ^b Isolated yield. ^c Determined by chiral HPLC analysis. ^d 100 mg of MS 4 Å was added. ^e 100 mg of MS 5 Å was added.

enantioselectivity was not improved at all; only 85% yield was obtained (Table 2, entry 9). Furthermore, the molecular sieves (MS) were revealed to be useful in improving the asymmetric induction, the best ee (77%) was then achieved when MS 5 Å was added into the reaction (Table 2, entry 11). Overall, the optimum reaction condition was established with 5 mol % of (*R*)-**5** in the presence of MS 5 Å in toluene at $-40\text{ }^{\circ}\text{C}$. To our surprise, the ee value could be dramatically increased to 92% when isobutyraldehyde, instead of pivalaldehyde, was utilized under the identical conditions (Table 2, entry 12).

The scope of the α -addition reaction was evaluated. Oxazoles synthesized are listed in Figure 1. The reaction is applicable to a wide range of aliphatic aldehydes including acetaldehyde, isobutyraldehyde, pivalaldehyde, and octanal. The excellent yields and good to excellent enantioselectivities were attainable within 24 h. Notably, the ee value was increased with the longer chain aldehydes; for example, lower ee were obtained when acetaldehyde (**3e**, ee = 69%) and propionaldehyde (**3f**, ee = 73%) were used, and with the increased steric hindrance of the aldehydes, the ee values were improved from 77% to 89% (from **3g** to **3l**). Unfortunately, when aromatic benzaldehyde was employed in the α -addition reaction, the reaction could not happen. In addition, different DL-phenylalanine derived α -isocyanoacetamides varied from morpholine **3a** to pyridine **3b** and dibenzyl **3c** were also investigated in the reaction, and excellent yields and enantioselectivities were achieved. Surprisingly, 99% ee was obtained with the substrate 2-isocyano-3-phenyl-1-(piperidin-1-yl)propan-1-one (**3b**). Less satisfactory result was found in the reaction of α -isocyanoacetamide **3d** (derived from DL-2-phenylglycine) with

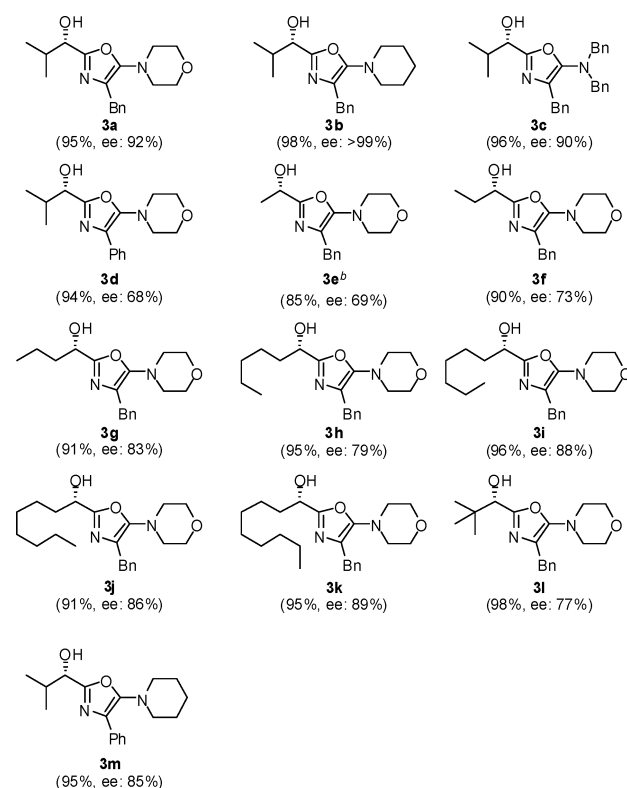


Figure 1. Substrate scope of the α -addition of α -isocyanoacetamides to aldehyde catalyzed by (*R*)-**5**. The reactions were performed with aldehyde (0.2 mmol, 2.0 equiv) and α -isocyanoacetamide (0.1 mmol, 1.0 equiv) in the presence of 5 mol % (*R*)-**5** (0.005 mmol) and 0.1 g of MS 5 Å in 1 mL of toluene at $-40\text{ }^{\circ}\text{C}$. For **3e**, 5.0 equiv of acetaldehyde was used.

isobutyraldehyde; the ee value was just moderate (ee = 68%). The similar substrate that was also derived from DL-2-phenylglycine gave the desired product **3m** in excellent yield (95%) and good enantioselectivity (ee = 85%). The absolute configuration of these compounds was determined to be (*S*) by comparing the optical rotation value and chiral HPLC

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spectra with those of the known compounds.^{9c} The X-ray crystal structure of oxazole **3d** is shown in Figure 2.

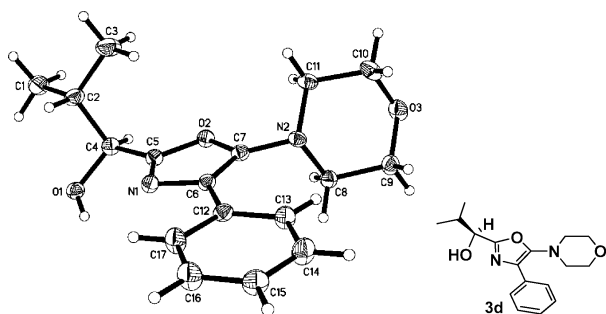
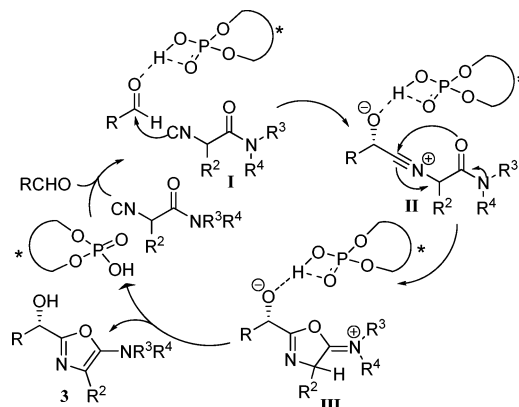


Figure 2. X-ray crystal structure of **3d**.

Based on the previous study on phosphoric acid catalysts,¹⁶ we hereby propose the mechanism of the reaction (Scheme 1). First, the aldehyde is activated by the chiral phosphoric acid catalyst through the hydrogen bonding, which is then attacked by the isocyano group to form the intermediate **II**. The following cyclization leads to the formation of oxazole ring intermediate **III**. The subsequent cleavage of **III** releases product **3** and the catalyst. The recovery of the catalyst completes the catalytic cycle.¹¹

In conclusion, a clean and highly efficient enantioselective α -addition of α -isocyanoacetamides to aliphatic aldehydes catalyzed by the chiral phosphoric acid in the presence of MS 5 Å in toluene has been developed. For all cases, excellent yields and good to excellent enantioselectivities

Scheme 1. Proposed Mechanism of the α -Addition of α -Isocyanoacetamides to Aldehyde



were achieved. Further investigation to understand the reaction mechanism, exploration of other types of reactions, and application to synthesize other important chiral compounds are underway.

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Supporting Information Available: Experimental procedures and analytical data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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