

# The synthesis of N–Zn, N–Cu complexes involving 2-amino pyridine and ethylenediamine ligands and application to the Henry reaction

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**Abstract.** The synthesis and characterization of a series of N–Zn, N–Cu complexes with 2-amino pyridine and ethylenediamine ligands (1a–b and 2a–b) have been described. They were synthesized with a simple, one-pot method, and the crystal structures of 1a, 1b, 2a and 2b were determined by X-ray crystallography. The complexes were also characterized by NMR, IR, and elemental analysis. They were used as the catalysts in an application to the Henry reaction, and high yields were obtained under the optimum conditions.

**Keywords.** N–Zn, N–Cu complexes; 2-amino pyridine; ethylenediamine; X-ray crystallography; Henry reaction.

## 1. Introduction

N–Zn and N–Cu complexes occupy an important position in organometallic chemistry. They have been reported in many literature.<sup>1–7</sup> For example, as catalysts, they have shown high activities in organic reactions and polymerizations.<sup>8–14</sup> Inspired by this work, we first synthesized novel N–Zn, N–Cu complexes with a simple, one-pot method, and the crystal structures of 1a, 1b, 2a and 2b were obtained and were also characterized by NMR, IR and elemental analysis.

The Henry reaction, or the nitroaldol reaction, is an important organic reaction for constructing C–C bonds. For example, it allows access to intermediate functionalized structure motifs, such as 1,2-amino alcohol and  $\alpha$ -hydroxy carboxylic acids. Many literature reports have detailed these synthetic methods. A major question that needs to be addressed is how to obtain the products in an efficient way. In this paper, we carefully investigated the Henry reaction and achieved satisfactory results.<sup>15–17</sup>

## 2. Experimental

### 2.1 Preparation of bis(2-aminopyridine)zinc complexes (catalyst 1a)

1.88 g (0.02 mmol) of 2-aminopyridine, and 2.19 g (0.01 mmol) of  $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  were added under anhydrous and oxygen-free condition to a dry 100 mL Schlenk flask. They were dissolved in 30 mL of dry alcohol, and the reaction mixture was refluxed for 14 h. The mixture was filtered to furnish white crystals (0.45 g, yield 12%). <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ , 27°C),  $\delta$  (ppm) = 7.96 (*d*,  $J$  = 6.5 Hz, 1H), 7.44 ~ 7.49 (*m*, 2H), 6.62 (*t*, 2H), 6.52 (*d*,  $J$  = 1 Hz, 2H), 5.61 (*brs*, 4H), 2.07 (*s*, 6H). IR (KBr): 3353, 3199, 1741, 1734, 1667, 1650, 1622, 1582, 1571, 1553, 1496, 1454, 1391, 1333, 1271, 1162, 1048, 1010, 931, 842, 790, 769, 744, 682, 650, 573, 556, 521, 479, 455, 422. Elemental analysis: Anal Calcd. For  $\text{Zn}[\text{C}_7\text{H}_9\text{N}_2\text{O}_2]_2$ : C, 45.52%; H, 4.86%; N, 15.14%; Found: C, 45.96%; H, 4.84%; N, 15.66%.

### 2.2 Preparation of bis(2-aminopyridine)copper complexes (catalyst 1b)

0.94 g (0.010 mmol) of 2-aminopyridine, and 1.09 g (0.005 mmol) of  $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  were added under

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anhydrous and oxygen-free conditions to a dry 100 mL Schlenk flask. They were dissolved in 15 mL of dry acetonitrile, and the reaction mixture was refluxed for 14 h. The solvent was filtered to give the dark green crystals (0.97 g, yield 40%). IR (KBr) 3353, 3199, 1741, 1734, 1667, 1650, 1622, 1582, 1571, 1553, 1496, 1454, 1391, 1333, 1271, 1162, 1048, 1010, 931, 842, 790, 769, 744, 682, 650, 620, 573, 556, 521, 479, 455, 422. Elemental analysis: Anal Calcd. For  $\text{Cu}[\text{C}_7\text{H}_6\text{N}_2\text{O}_2]_2$ : C, 45.40%; H, 4.86%; N, 15.14%; Found: C, 45.36%; H, 4.80%; N, 14.74%.

### 2.3 Preparation of mono ethylenediamine zinc complexes (catalyst 2a)

0.66 mL (0.01 mmol) of 1,2-ethylenediamine, and 2.19 g (0.01 mmol) of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  were added under anhydrous and oxygen-free conditions to a dry 100 mL Schlenk flask. They were dissolved in 15 mL of dry alcohol, and the reaction mixture was refluxed for 14 h. The solvent was filtrated to give the white crystals (0.38 g, yield 15%).  $^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ , 27°C)  $\delta$  (ppm) = 2.85 (s, 4H), 2.43 (s, 6H), 1.96 (s, 4H). IR (KBr): 3494, 3103, 2319, 1651, 1647, 1565, 1470, 1428, 1418, 1405, 1377, 1338, 1179, 1025, 978, 932, 727, 684, 616, 600, 509. Elemental analysis: Anal Calcd. For  $\text{Zn}[\text{C}_6\text{H}_{14}\text{N}_2\text{O}_4]$ : C, 29.63%; H, 5.76%; N, 11.52%; Found: C, 29.24%; H, 6.06%; N, 11.89%.

### 2.4 Preparation of ethylenediamine copper complexes (catalyst 2b)

0.66 mL (0.01 mmol) of ethylenediamine, and 2.19 g (0.01 mmol)  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  were added under anhydrous and oxygen-free conditions to a dry 100 mL Schlenk flask. They were dissolved in 15 mL of dry ethylnitrile, and the reaction mixture was refluxed for 14 h. The solvent was filtered to give the black crystals (0.38 g, yield 14.6%). IR (KBr) 3970, 3950, 3920, 3900, 3840, 3820, 3790, 3770, 3740, 3490, 3150, 1620, 1590, 1550, 1420, 1340, 1280, 1190, 1110, 1050, 926, 881, 715, 683, 650, 625, 540, 482, 455, 422. Elemental analysis: Anal Calcd. For  $\text{Cu}[\text{C}_6\text{H}_{20}\text{N}_2\text{O}_7]$ : C, 24.32%; H, 6.76%; N, 9.46%; Found: C, 24.62%; H, 6.73%; N, 9.54%.

### 2.5 2-Nitro-1-phenylethanol

Catalyst 2b (0.0875 g, 0.296 mmol), benzaldehyde (0.10 mL, 0.986 mmol), 0.01 mL of  $\text{Et}_3\text{N}$  and nitro-

methane (0.20 mL, 3.702 mmol) were successively combined at room temperature. After 19 h, the reaction was quenched. Further purification was performed on silica gel. The title compound was obtained as a colourless oil. The percentage conversion of benzaldehyde to 2-nitro-1-phenylethanol was established according to the content ratio of the remainder of benzaldehyde to the formation of 2-nitro-1-phenylethanol given by  $^1\text{H}$ NMR.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 7.28 ~ 7.32 (m, 5H, Ar-H), 5.32 ~ 5.35 (d,  $J$  = 9.18 Hz, 1H, -CH), 4.38 ~ 4.56 (m, 2H, -CH<sub>2</sub>), 3.89 (br, 1H, -OH).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) 138.30 128.92 (x2), 128.82, 125.98 (x2), 81.16, 70.91. HRMS (EI):  $m/z$  (%): Anal calcd for  $\text{C}_8\text{H}_9\text{NO}_3$ : 167.0582; found: 167.0588.

## 3. Results and discussion

### 3.1 Synthesis of complexes

Following treatment of the ligands 2-amino pyridine and 1,2-ethylenediamine with  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  or  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in ethanol, THF or acetonitrile, the corresponding complexes were obtained after refluxing for 14 h. The crystal structures of 1a, 2a, 1b and 2b were also obtained (figure 1).

### 3.2 Crystal structure

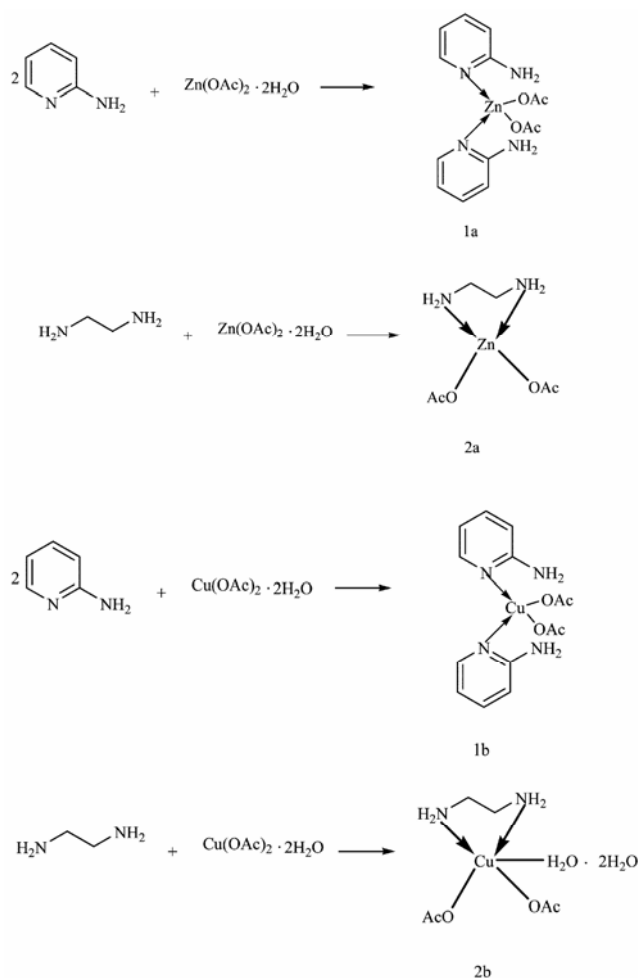
**3.2a Structure determination:** The structures of 1a, 2a, 1b, 2b were studied by X-ray diffraction (figures 2–5). Tables 1–4 lists the selected bond lengths and angles for the four compounds.

The complexes 1a and 2a were composed of 2-amino pyridine ligands, a  $\text{Zn}(\text{Ac})_2$  core, and the  $\text{Cu}(\text{Ac})_2$  core, respectively. The bond length of O(4)~Zn (1.961 Å) was longer than that of O(2)~Zn (1.987 Å). The bond angle of O(2)–Zn–N(1) at 104.3° was not equal to the bond angle O(4)–Zn–N(3) at 99.98°. It deserves to mention that there exists hydrogen bonds in complexes 1a and 2a. Four 2-amino pyridine molecules, two  $\text{Zn}(\text{Ac})_2$  cores or two  $\text{Cu}(\text{Ac})_2$  cores are connected together to construct a hydrogen bonded dinuclear structure (tables 1–4).

The complex 1b was composed of 1,2-ethylenediamine, and a  $\text{Zn}(\text{Ac})_2$  core (figure 2). The bonds of C(1)~C(5) and the N(1) atom and C(6)~C(10) and the N(3) atom are co-planar, and the bond lengths are in the range of 1.349 ~ 1.490 Å. The C–C–C angles are nearly 120°, and the com-

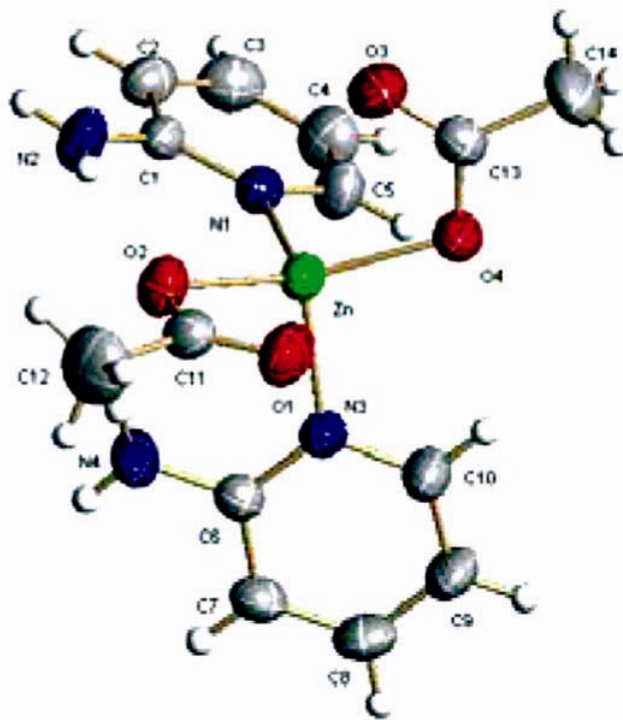
plexed bond lengths of N(1)~Zn and N(3)~Zn are 2.064(19) and 2.068(19) Å, respectively. The C(11)~O(2), C(13)~O(4) bond distances are all nearly equal to 1.22 Å, indicating some double-bond character. The bond length of O(4)~Zn 1.961 Å is longer than that of O(2)~Zn 1.987 Å. The bond angle of O(2)~Zn~N(1) 104.3° is not equal to O(4)~Zn~N(3) at 99.98°. There also exists hydrogen bonds in this complex. Two 1,2-ethylenediamine molecules and two Zn(Ac)<sub>2</sub> cores are connected together to construct a hydrogen bonded dinuclear structure. The hydrogen-bond distances of N(4)~H(4B)----O(3), N(4)~H(2B)----O(1), N(4)~H(2A)----O(3) and N(4)~H(4A)----O(1) are 3.043 Å, 2.922 Å, 3.038 Å, 2.918 Å and 3.043 Å, respectively (tables 5 and 6).

The structure of complex 2b is very interesting. It is composed of 1,2-ethylene diamine, a Cu(Ac)<sub>2</sub> core and three H<sub>2</sub>O molecules. The copper atoms are

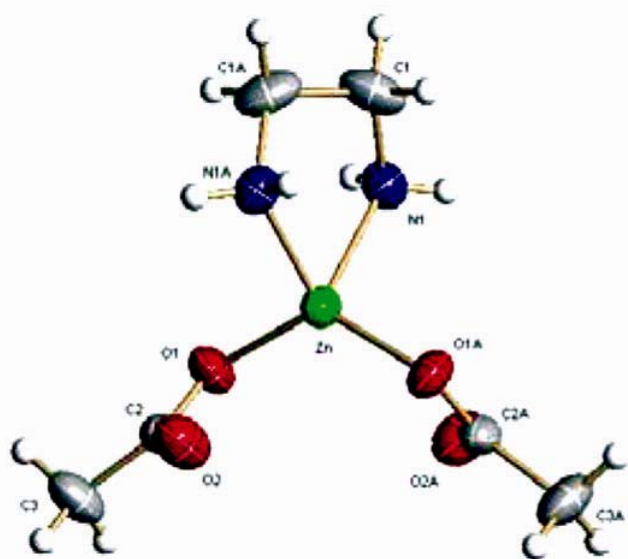


**Figure 1.** The synthetic routes of complexes.

connected to each other through the oxygen atoms in the water molecules, which are complexed with the Cu atom (figure 6). The bond length of Cu(1)~N(2) at 2.012 Å and Cu(1)~N(1) at 2.019 Å are not equal. The bond angle of Cu(2)~O(1)~O(3) is 86.99°, and is nearly equal to the bond angle of Cu(2)~O(1)~O(3) at 86.70° (tables 5 and 6).



**Figure 2.** The crystal structure of complex 1a.



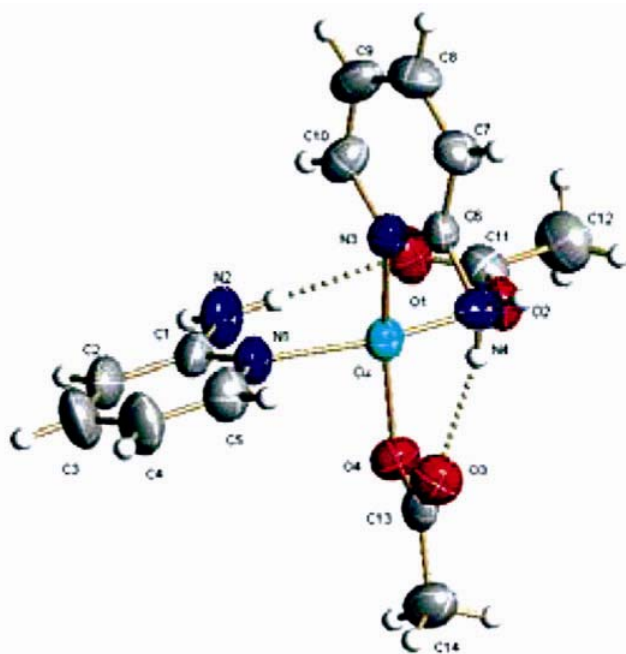
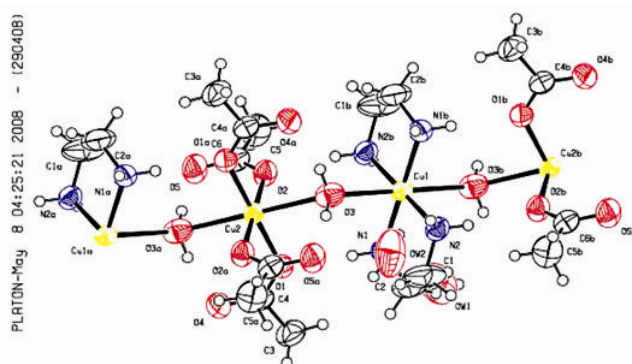
**Figure 3.** The crystal structure of complex 1b.

**Table 1.** Selected bond lengths (Å) and bond angles (°) for *N*-Zn complex (catalyst 1a).

Bond	Distance (Å)	Bond	Angles (°)
Zn–O(4)	1.9614(17)	O(4)–Zn–O(2)	138.36(8)
Zn–O(2)	1.9865(17)	O(4)–Zn–N(1)	103.53(8)
Zn–N(1)	2.0643(19)	O(4)–Zn–N(3)	99.98(7)
Zn–N(3)	2.0697(19)	N(1)–Zn–N(3)	100.49(8)
O(1)–C(11)	1.220(3)	C(11)–O(2)–Zn	105.25(16)
O(2)–C(11)	1.277(3)	C(5)–N(1)–C(1)	118.0(2)
O(3)–C(13)	1.225(3)	C(5)–N(1)–Zn	113.53(17)
O(4)–C(13)	1.276(3)	C(1)–N(1)–Zn	128.49(16)
N(1)–C(5)	1.349(3)	C(6)–N(3)–C(10)	117.9(2)
N(1)–C(1)	1.353(3)	C(6)–N(3)–Zn	124.10(16)
N(2)–C(1)	1.335(3)	C(10)–N(3)–Zn	117.90(17)
N(3)–C(6)	1.340(3)	N(2)–C(1)–N(1)	118.7(2)
N(3)–C(10)	1.353(3)	N(2)–C(1)–C(2)	121.0(2)
N(4)–C(6)	1.348(3)	N(1)–C(1)–C(2)	120.3(2)

**Table 2.** Selected bond lengths (Å) and angles (°) for *N*-Zn complex (catalyst 2a).

Bond	Distance	Bond	Angles (°)
Zn–O(1)#1	1.9878(13)	O(1)#1–Zn–O(1)	130.85(8)
Zn–O(1)	1.9878(13)	O(1)#1–Zn–N(1)	110.62(6)
Zn–N(1)	2.0726(17)	O(1)–Zn–N(1)	105.10(6)
Zn–N(1)#1	2.0726(17)	O(1)#1–Zn–N(1)#1	105.10(6)
O(1)–C(2)	1.281(2)	O(1)–Zn–N(1)#1	110.62(6)
O(2)–C(2)	1.231(2)	N(1)–Zn–N(1)#1	85.12(10)
N(1)–C(1)	1.480(3)	C(2)–O(1)–Zn	104.78(12)
C(1)–C(1)#1	1.484(6)	C(1)–N(1)–Zn	105.25(13)
C(2)–C(3)	1.498(3)	N(1)–C(1)–C(1)#1	108.99(17)

**Figure 4.** The crystal structure of complex 2a.**Figure 5.** The crystal structure of complex 2b.

### 3.3 Application to Henry reaction

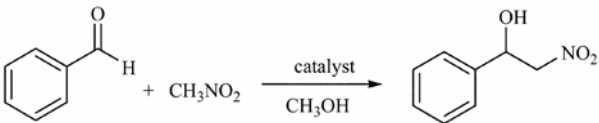
Complexes 1a, 2a, 1b and 2b were used as the catalysts in the Henry reaction. At room temperature after 72 h, moderate yields were obtained. After adding  $\text{Et}_3\text{N}$  (30 mol%) to the reaction, the yields were greatly improved and the reactions were faster

**Table 3.** Selected bond lengths (Å) and angles (°) for N–Zn complex (catalyst 1b).

Bond	Distance	Bond	Angles (°)
Cu–O(4)	1.969(3)	O(4)–Cu–O(2)	90.87(12)
Cu–O(2)	1.974(3)	O(4)–Cu–N(3)	165.11(13)
Cu–N(3)	1.991(4)	O(2)–Cu–N(1)	164.05(13)
Cu–N(1)	2.006(3)	N(3)–Cu–N(1)	93.71(14)
O(1)–C(11)	1.236(6)	C(11)–O(2)–Cu	105.1(3)
O(2)–C(11)	1.258(5)	C(1)–N(1)–C(5)	119.5(4)
O(3)–C(13)	1.238(5)	C(1)–N(1)–Cu	122.6(3)
O(4)–C(13)	1.258(5)	C(5)–N(1)–Cu	117.2(3)
N(1)–C(1)	1.337(6)	C(6)–N(3)–C(10)	118.4(4)
N(1)–C(5)	1.362(6)	C(6)–N(3)–Cu	122.7(3)
N(2)–C(1)	1.336(7)	C(10)–N(3)–Cu	117.8(3)
N(3)–C(6)	1.333(5)	N(2)–C(1)–N(1)	117.6(4)
N(3)–C(10)	1.359(6)	N(2)–C(1)–C(2)	121.8(5)
N(4)–C(6)	1.347(6)	N(1)–C(1)–C(2)	120.6(5)

**Table 4.** Selected bond lengths (Å) and angles (°) for N–Cu complex (catalyst 2b).

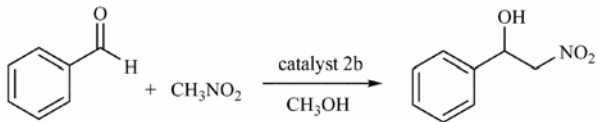
Bond	Distance	Bond	Distance
Cu(1)–N(2)_\$2	2.0128 (0.0036)	N(2)–Cu(1)–N(2)_\$2	180.00 (0.00)
Cu(1)–N(2)	2.0128 (0.0036)	N(1)–Cu(1)–N(2)	84.87 (0.16)
Cu(1)–N(1)	2.0191 (0.0037)	N(1)_\$2–Cu(1)–N(2)	95.13 (0.16)
Cu(1)–N(1)_\$2	2.0191 (0.0037)	N(1)_\$2–Cu(1)–N(1)	180.00 (0.00)
Cu(2)–O(2)_\$4	2.0248 (0.0032)	O(2)–Cu(2)–O(2)_\$4	180.00 (0.00)
Cu(2)–O(2)	2.0248 (0.0032)	O(1)–Cu(2)–O(2)_\$4	91.27 (0.13)
Cu(2)–O(1)_\$4	2.0384 (0.0032)	O(3)_\$4–Cu(2)–O(2)_\$4	86.70 (0.13)
Cu(2)–O(1)	2.0384 (0.0032)	O(1)_\$4–Cu(2)–O(2)	91.27 (0.13)
Cu(2)–O(3)_\$4	2.3581 (0.0042)	O(3)_\$4–Cu(2)–O(2)	93.30 (0.13)
Cu(2)–O(3)	2.3581 (0.0042)	O(3)_\$4–Cu(2)–O(1)_\$4	86.99 (0.12)

**Table 5.** Effect of catalysts<sup>a</sup>


Entry	Catalyst	Time (h)	Conv (%) <sup>b</sup>
1	1a	72	43
2	1a + Et <sub>3</sub> N	19	88
3	1b	72	34
4	1b + Et <sub>3</sub> N	19	90
5	2a	72	40
6	2a + Et <sub>3</sub> N	19	73
7	2b	72	52
8	2b + Et <sub>3</sub> N	19	94

<sup>a</sup>Reactions were carried out on 0.1 mL (1 mmol) of PhCHO with 0.5 mL CH<sub>3</sub>NO<sub>2</sub> in 2 mL CH<sub>3</sub>OH for 19 h at room temperature (20–30°C)

<sup>b</sup>The conv.% was determined by <sup>1</sup>HNMR analysis

**Table 6.** Effect of solvents.


Entry	Catalyst	Solvent	Time (h)	Conv (%) <sup>b</sup>
1	2b + Et <sub>3</sub> N	CH <sub>3</sub> OH	19	94
2	2b + Et <sub>3</sub> N	THF	19	92
3	2b + Et <sub>3</sub> N	Ether	19	92
4	2b + Et <sub>3</sub> N	CH <sub>2</sub> Cl <sub>2</sub>	19	76
5	2b + Et <sub>3</sub> N	CHCl <sub>3</sub>	19	90
6	2b + Et <sub>3</sub> N	Hexane	19	86

<sup>a</sup>Reactions were carried out on 0.1 mL (1 mmol) of PhCHO with 0.5 mL CH<sub>3</sub>NO<sub>2</sub> in 2 mL CH<sub>3</sub>OH for 19 h at room temperature (20–30°C)

<sup>b</sup>The conv.% was determined by <sup>1</sup>HNMR analysis

(table 5). We also examined the effect of the solvents (e.g. methanol, THF, toluene, dichloro-

methane, ether, trichloromethane) on the yield of the reaction (table 6), and methanol was found to be the best choice for this reaction, giving 94% yield.

#### 4. Conclusions

In summary, we have synthesized a series of the complexes and obtained their crystal structures. The novelty of this methodology can be summarized as follows: (i) we have synthesized a series of catalysts in a simple, novel, and easy to operate method, (ii) we reported a novel catalytic Henry reaction at room temperature, and obtained satisfactory results. Further work will be devoted to researching the products of the other aldehydes and applying the catalysts to other organic reactions such as the Baylis–Hillman reaction, Aldol reaction, etc.

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