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Versatile Supramolecular Copper(II) Complexes for Henry and Aza-Henry Reactions

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Abstract: Chiral supramolecular metal-organic frameworks assembled from copper complexes catalyse Henry and aza-Henry reactions of aromatic and aliphatic aldehydes and *N*-protected aromatic imines in high yield and good to excellent enantioselectivity. Reactions can be performed in the absence of base in ethanol or water.

Keywords: aza-Henry reaction; catalysis; copper(II); enantioselectivity; Henry reaction

The Henry (nitroaldol) reaction[1] is one of the most useful carbon-carbon bond forming reactions in synthetic chemistry. The resulting β-hydroxy nitro products are versatile building blocks to prepare biologically significant compounds such as β-amino alcohols and α-hydroxy carboxylic acids.[2] In recent years various organocatalytic[3] and metal-organic[4] systems have been developed to accomplish the enantioselective Henry reaction. Among them, the Cu-catalyzed Henry reaction has received much attention due to the mild reaction conditions which do not require additives such as organic bases.[4f–j] Except for a few cases[4j–l] most Cu complexes contain a symmetrical, four-dentate ligand sphere.

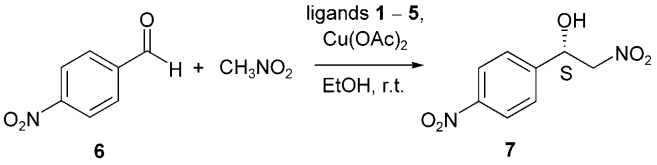
We wish to report here on the synthesis, structure and catalytic efficiency of self assembled supramolecular Cu(II) complexes based on ligands with C_2 and C_1 symmetry.

We first screened the Cu(II) complexes of several C_2 symmetric ligands **1**–**5** for catalysis of the Henry reaction of aldehyde **6** and CH_3NO_2 (Table 1), in all cases product **7** was *S* configured. Ligands **1**–**5** were easily available from diaminocyclohexane **8** and aldehydes **9**–**13** and subsequent reduction of the Schiff bases **14**–**18** (Scheme 1). The Cu(II) complexes of **1**–**5** were formed *in situ*. We discovered that **19**, the Cu(II) complex of **5** (Scheme 2), was the most efficient catalyst within this group. X-ray analysis of suitable crystals of **19** revealed an interesting supramolecular structure in which the Cu(II) coordinates to the nitrogens of the chiral diamine unit and to the pyridine nitrogens of the adjacent complex (Figure 1).

The X-ray structure further revealed a coordination mode (**19-A**) that forms triangular cavities (**19-B**) (Figure 1) and a lamellar framework (**19-C**) (Figure 2).

In order to understand whether the polymeric nature of the catalyst **19** is maintained in solution we measured UV, CD spectra (Figure 3) and DLS (dy-

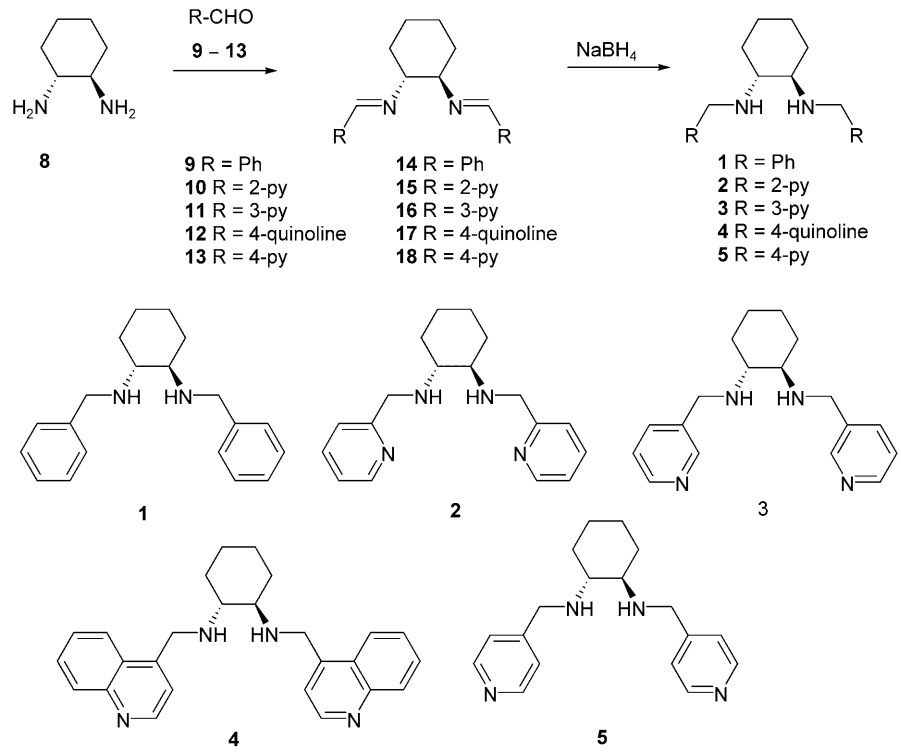
Table 1. Enantioselective Henry reactions of CH_3NO_2 with *para*-nitrobenzaldehyde **6** in the presence of Cu(II) complexes of ligands **1**–**5**.[a]



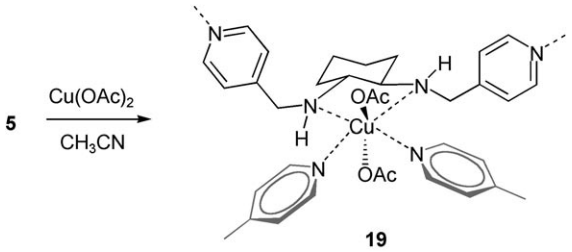
6 7

Ligand	Time [h]	Yield [%][b]	*ee* [%][c]
1	4	90	53
2	1.5	95	2
3	1.5	62	70
4	1.5	92	65
5	1.5	95	87

[a] All reactions were performed on a 0.20 mmol scale with 5 mol% of Cu(II) complex at a 0.5 M concentration and 5 equiv. of nitromethane in EtOH at room temperature.
[b] Yields of isolated hydroxy nitro compounds.[c] Enantiomeric excess (*ee*) was determined by HPLC using a Chiralcel OD-H column. The absolute configuration of products was determined as *S* by comparison of their optical rotations with literature values.[4]



Scheme 1. Synthesis of ligands **1**–**5**.



Scheme 2. Structure of complex **19**.

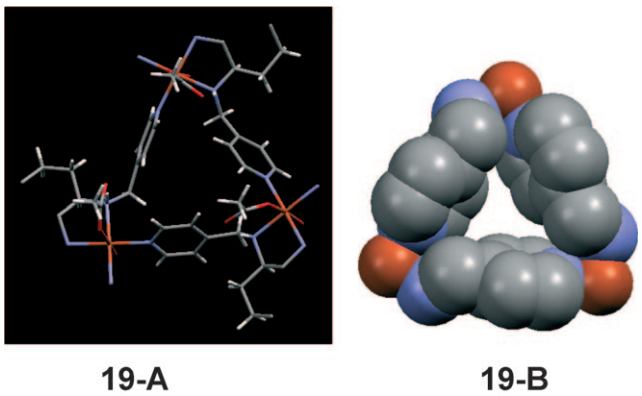


Figure 1. X-ray structure of complex **19**.

namic light scattering, Figure 4) in the time frame of the Henry reaction and in the solvent EtOH/H_2O (9:1) where catalytic reactions could be performed.

The DSL measurement demonstrates that the particle size of oligomeric **19** in solution slowly grows to approach a value of about 37 nm. Together with nearly constant CD and UV spectra these experiments suggest that **19** maintains the framework of the solid state to a certain extent in solution. Further support for an intact coordination sphere of Cu(II) in solution comes from the fact that the *ee* values of the product of the standard reaction **6**→**7** do not change significantly within 25 h (Figure 5).

Finally, the substrate scope of **19** was investigated (Table 2). The results show that aromatic and aliphatic aldehydes react in very good yields with nitromethane producing β-nitro alcohols in modest to good enantioselectivities. As it was not possible to improve the *ee* values either by changing concentrations, temperature or solvent we decided to investigate C_1 symmetrical ligands for Cu(II), a less explored class of copper complexes.

For this purpose three ligands **20**–**22** were synthesized. Scheme 3 shows the preparation of **22**. The diamine **8** was first condensed with 4-formylpyridine **13** to obtain the monoamine **23**; further reaction with the aldehyde **24** gave the salen **25** in 52% yield over two steps. $NaBH_4$ reduction of **25** furnished quantitatively the ligand **22**.

In order to evaluate optimal reaction conditions *para*-nitrobenzaldehyde **6** was transformed into the β-hydroxy nitro product **7** (Scheme 4) using ligands **20**–**22**, and various Cu(II) salts and solvents (see Support-

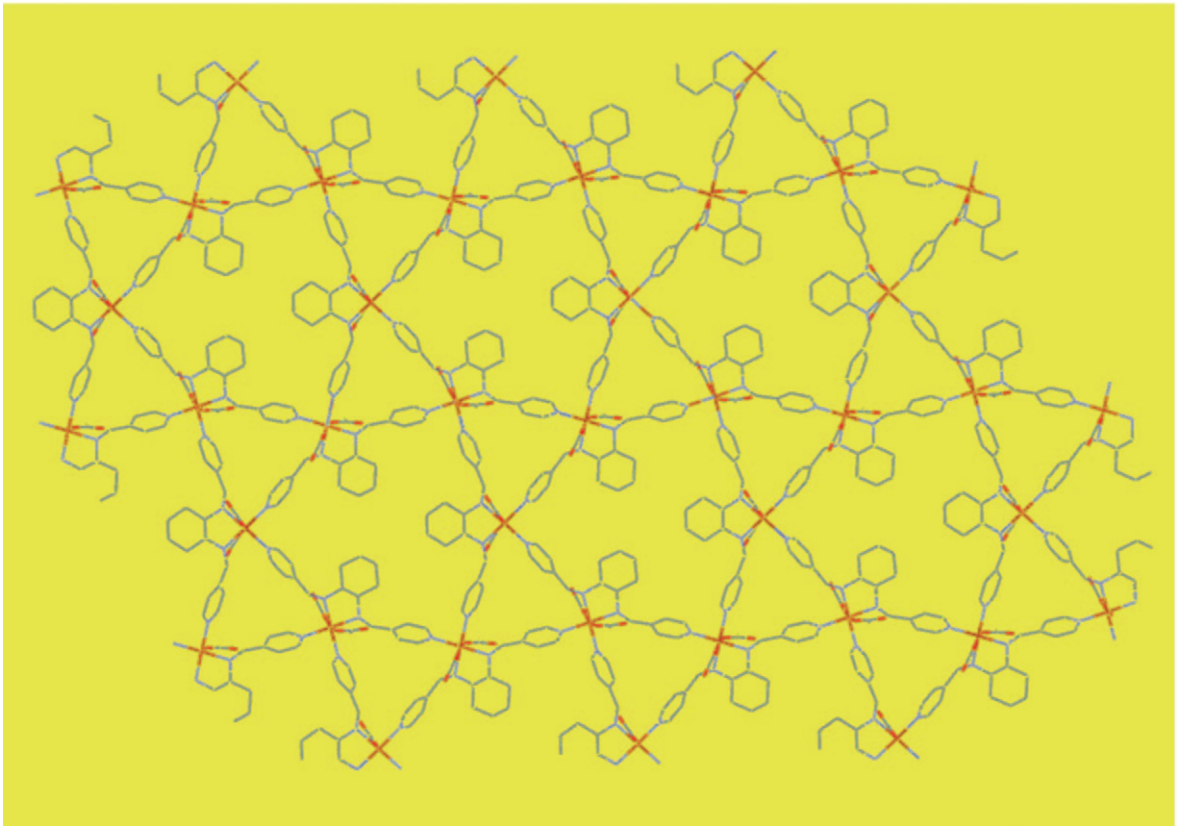


Figure 2. 2-D polymeric framework (**19-C**) of complex **19**.

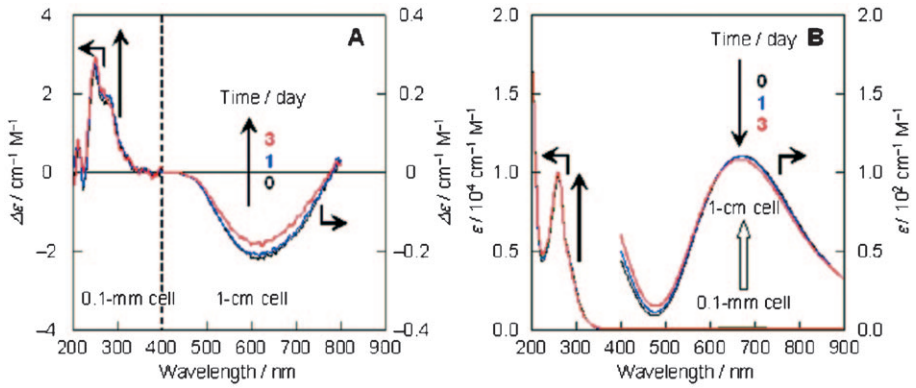


Figure 3. Time-dependent CD (**A**) and UV spectra (**B**) of **19** in EtOH/H_2O 9:1.

ing Information). Accordingly both yields (95%) and *ee* values (96%) approach very good figures for ligand **22** in EtOH and in the presence of the soft counterion acetate. Consequently these conditions were then employed to investigate the scope of the catalytic procedure.

From the results in Table 3 it is clear that aldehydes with electron-withdrawing substituents react faster and in general furnish β-nitro alcohols with *ee* values and yields well above 90%. In contrast, electron-donating groups slow down the reaction and in some cases (entries 9, 11 and 13) moderate yields but still acceptable *ee* values were obtained. Interestingly the aliphatic aldehydes behave well and give excellent yields and *ee* values; except for a few cases[5a–c] this is rather an exception than the rule for Cu complex-catalyzed Henry reactions.[5d–i]

In order to gain information on the structure of the copper complex of **22**, $Cu(OAc)_2$ was added to ligand **22** in CH_3CN (Scheme 5) producing bright green crystals suitable for X-ray crystallography (for details, see Supporting Information). The X-ray structure of complex **26** shows indeed that ligand **22** is tridentate and that one residual acetate unit coordinates to Cu(II)

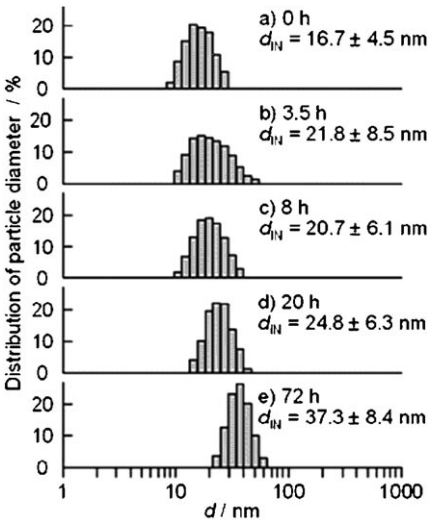


Figure 4. Time-dependent DSL of **19** in EtOH/H_2O 9:1.

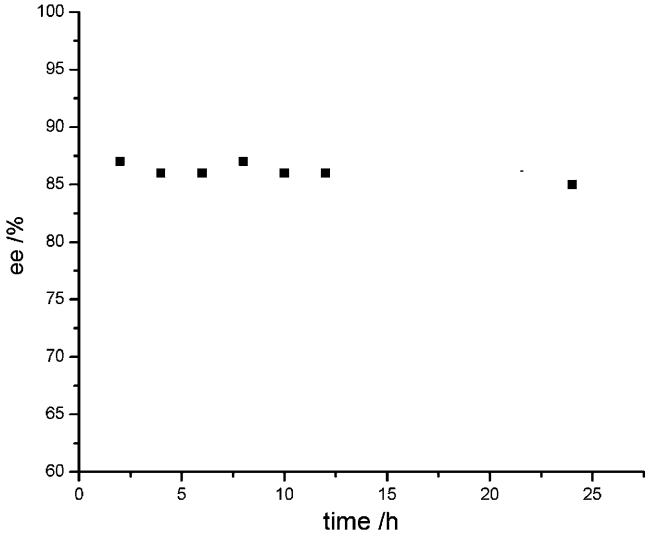


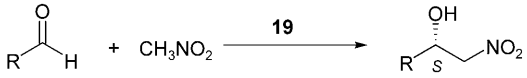
Figure 5. Enantiomeric excess (*ee*) of **7** as a function of time during the reaction of *para*-nitrobenzaldehyde **6** and nitromethane in EtOH catalyzed by **19** (5 mol%).

(Figure 6a) which is believed to be exchanged for the components of the Henry reaction, *vide infra*.

Figure 6b shows an extended view of the structure in which the individual Cu complexes are connected *via* H-bridges between the non-coordinating pyridine N and the H–N group adjacent to the phenolate. This interaction leads to a unique single-stranded *M* left-handed helix with a pitch of 8.65 Å.

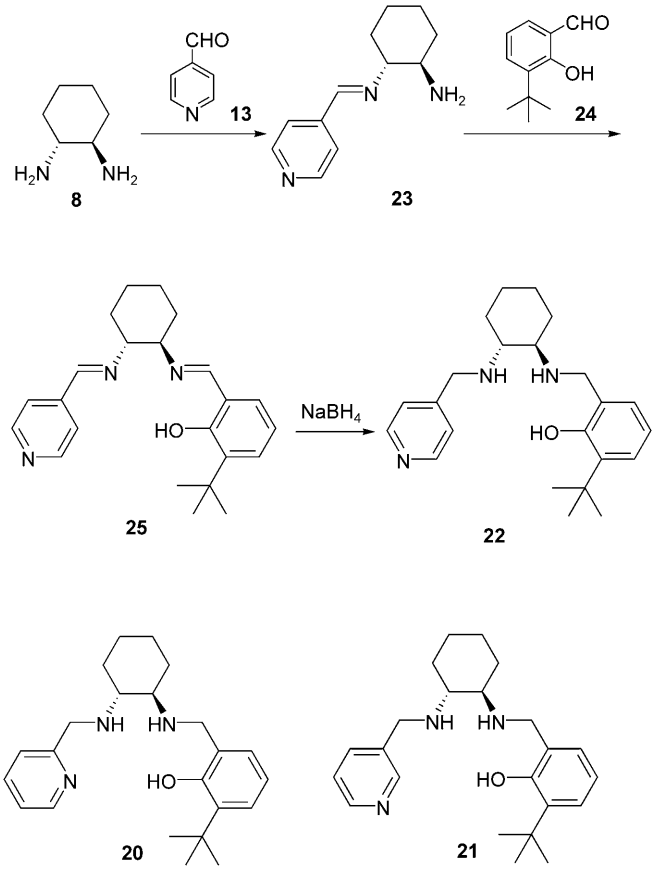
In EtOH the free ligand **22** display a π-π^* transition at 245 nm, the complex **26** shows a positive Cotton effect at 245 nm and a negative mlct band at 425 nm (Figure 7) in agreement with the *M* handedness[6]of the helix also observed in the X-ray structure of **26**.

Table 2. Enantioselective Henry reactions of CH_3NO_2 with various aldehydes in the presence of complex **19**.

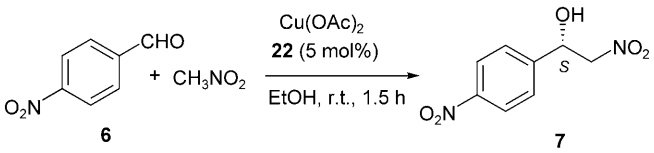


Entry[a]	Aldehyde (R)	Time [h]	Yield [%][b]	*ee* [%][c]
1	4-$NO_2C_6H_4$	12	94	86
2	2-$NO_2C_6H_4$	12	95	90
3	3-$NO_2C_6H_4$	12	93	82
4	3-pyridyl	12	92	87
5	4-pyridyl	12	90	80
6	Ph	72	62	84
7	4-ClC_6H_4	60	94	85
8	4-FC_6H_4	72	88	82
9	2-MeC_6H_4	72	73	73
10	4-MeC_6H_4	72	66	80
11	1-naphthyl	60	85	85
12	4-$MeOC_6H_4$	72	65	75
13	*n*-butyl	48	87	83
14	*tert*-butyl	48	82	85
15	*c*-hexyl	48	91	86

[a] All reactions were performed on a 0.20 mmol scale with 5 mol% of **19** at a 0.5 M concentration and 5 equiv. of nitromethane in EtOH at room temperature.
[b] See Table 1.
[c] See Table 1.

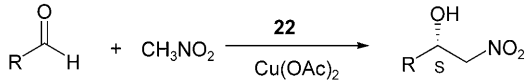


Scheme 3. Synthesis of C_1 symmetrical ligand **22**, and structures of ligands **20** and **21**.



Scheme 4. Henry reaction to screen for optimal reaction conditions.

Table 3. Enantioselective Henry reactions of CH_3NO_2 with various aldehydes in the presence of **22**, $Cu(OAc)_2$.



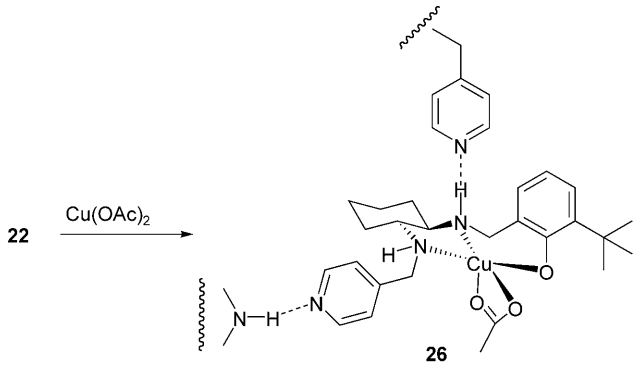
Entry[a]	Aldehyde (R)	Time [h]	Yield [%][d]	*ee* [%][e]
1[b]	4-$NO_2C_6H_4$	1.5	95	96
2[b]	2-$NO_2C_6H_4$	1.5	94	98
3[b]	3-$NO_2C_6H_4$	1.5	95	96
4[b]	3-pyridyl	1.5	94	96
5[b]	4-pyridyl	1.5	96	95
6[b]	Ph	48	75	90
7[b]	4-ClC_6H_4	24	65	90
8[b]	4-FC_6H_4	24	72	87
9[c]	2-thiophenyl	60	58	93
10[c]	2-MeC_6H_4	60	63	88
11[c]	4-MeC_6H_4	60	54	93
12[c]	1-naphthyl	60	75	93
13[c]	4-$MeOC_6H_4$	60	51	85
14[c]	*n*-butyl	60	88	98
15[c]	*tert*-butyl	60	91	99
16[c]	*c*-hexyl	60	92	98

[a] All reactions were performed on a 0.20 mmol scale with 5 mol% of **22**, $Cu(OAc)_2$ at a 0.5 M concentration and 5 equiv. of nitromethane in EtOH.
[b] Reactions were run at room temperature.
[c] Reactions were run at 0 °C.
[d] See Table 1.
[e] See Table 1.

Furthermore, monitoring the standard reaction **6**→**7** revealed a constant enantiomeric excess (*ee*) for **7** within the time frame of the reaction (Figure 8). Accordingly the supramolecular, helical structure of the crystalline complex **26** is maintained in EtOH, the preferred solvent of the Henry reaction.

A reaction sequence is proposed in which the acetate unit of **26** is replaced by the two reactants such that the nitronate attacks preferentially the *re* face of the aldehyde. After release of the product addition of aldehyde and CH_3NO_2 regenerates the intermediate **27** closing the cycle (Scheme 6).

The addition of nitroalkanes to imines, known as the aza-Henry (or nitro-Mannich) reaction also provides a versatile tool for C–C bond formation. The resulting products, β-nitro amines, are readily converted into 1,2-diamines[7] or α-amino acids.[8] While various



Scheme 5. Formation of catalyst **26**.

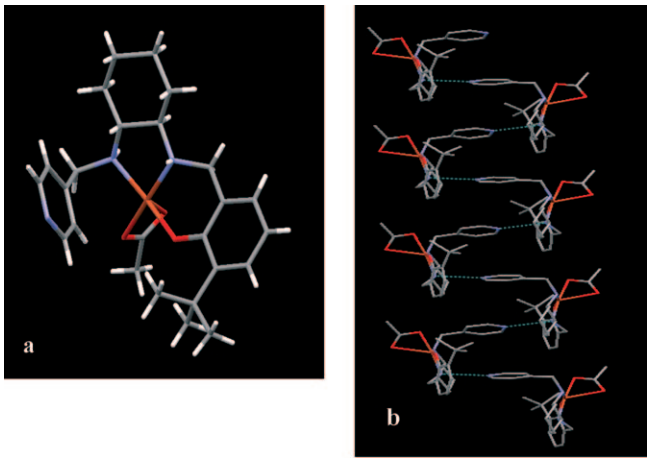


Figure 6. X-ray structure of the Cu(II) complex **26**; **a**) single unit, **b**) the helical structure of hydrogen bonded complex **26**.

chiral metal complexes and organocatalysts have been reported for the enantioselective catalysis of this reaction,[9–11] the results shown in Table 4 demonstrate that our catalyst **26** is also applicable to the aza-Henry reaction using *N*-protected imines and nitromethane.

Results of the aza-Henry reaction with catalyst **26** are comparable to those of the reaction with aromatic aldehydes and show the same trend in reactivity concerning the presence of electron withdrawing groups at the aldehyde substrate, see Table 4. In general, *ee* values above 90% were observed which is well within the best results for this reaction reported so far.[10] Besides its unusual structure catalyst **26** has another interesting feature, the complex is water soluble. Accordingly we investigated Henry and aza-Henry reactions with a few substrates in water (for details, see Supporting Information). In general yields were similar to those observed in EtOH, whereas the *ee* values dropped by 5–12%. Nevertheless, a metal complex catalyzing Henry and aza-Henry reactions in water with both high yields and *ee* values is unprecedented.[12]

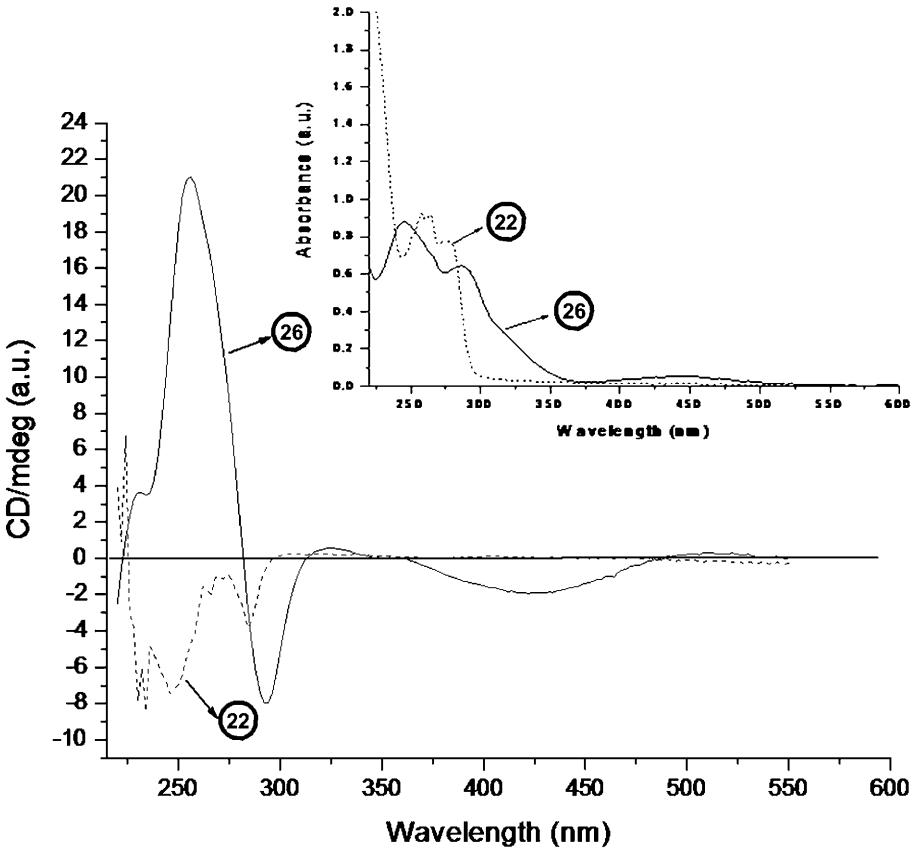


Figure 7. CD and UV/Vis spectra (inset) of **26** and **22** in EtOH.

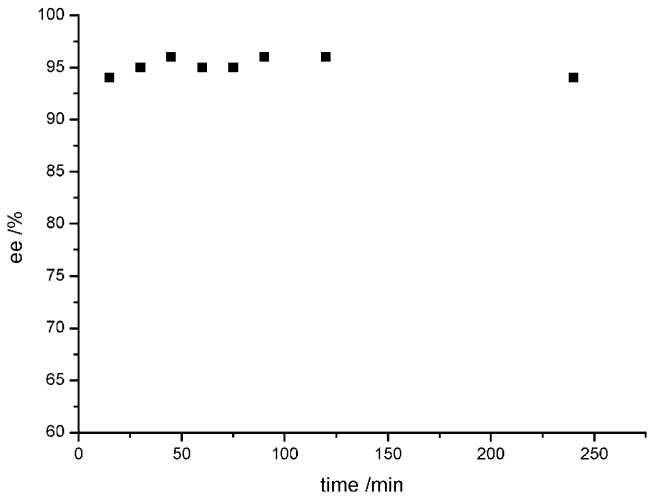


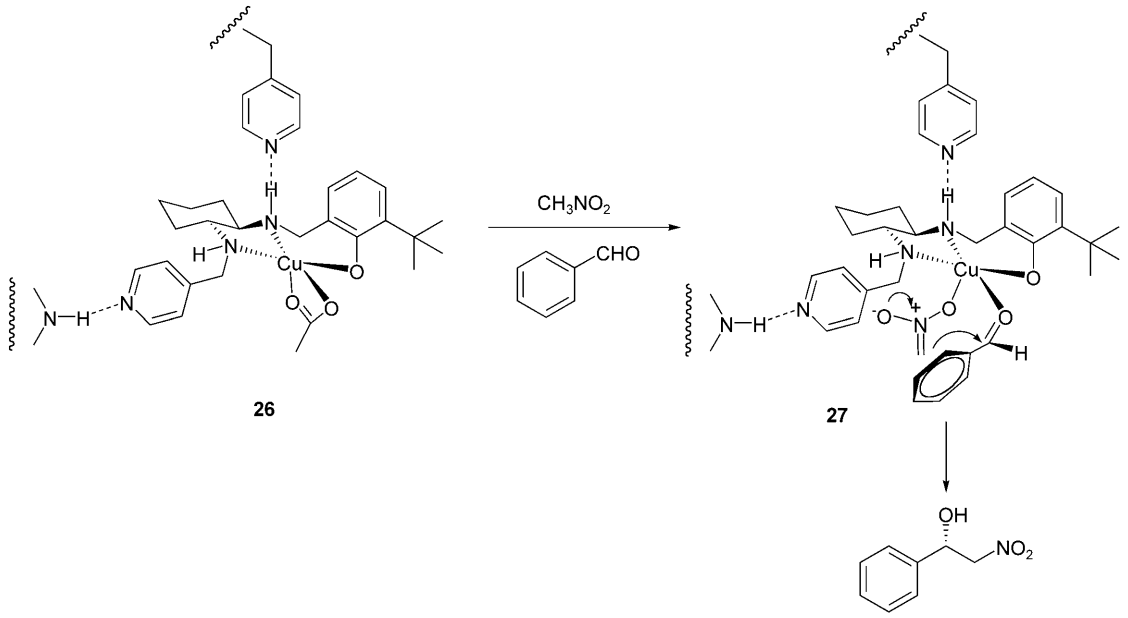
Figure 8. Plot of *ee* (%) change with time (min.) during the reaction of *para*-nitrobenzaldehyde and nitromethane in EtOH catalyzed by **26** (5 mol%).

In summary, Cu(II) complex **26** can be easily prepared and catalyzes Henry and aza-Henry reactions under base-free conditions in protic solvents with high yields and *ee* values up to 99%. These results compare well with Cu(II) complexes of chiral imidazoline-aminophenol ligands[4j], chiral aminopyridine ligands[4m] (Henry reaction) and chiral *N*,*N*′-dioxide Cu(I) complexes[11m] (aza-Henry reaction), and are superior to other recently published Cu(II) complexes with ligands such as chrial Schiff-bases,[4k] bis(2-pyridylmethylidene)-(*R*,*R*)-1,2-diaminocyclohexane[4n] or borabox.[5i] Furthermore, these results document a rare example of one simple complex catalyzing both Henry and aza-Henry reactions with very high enantioselectivity.

Experimental Section

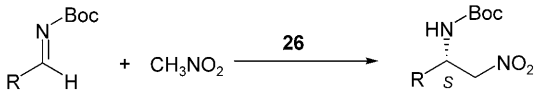
Typical Experimental Procedure for Henry and Aza-Henry reactions

Compound **22** (3.7 mg, 0.01 mmol) and $Cu(OAc)_2$ (1.8 mg, 0.01 mmol) were added to a screw-capped vial containing a stir bar. Anhydrous EtOH (0.4 mL) was then added, and a clear green solution formed under stirring, which was continued for 30 min at room temperature, or then cooled to 0 °C as indicated. To the resulting solution nitromethane (0.13 mL, 1.0 mmol, 5 equiv.) and various aldehydes or *N*-Boc imines (0.2 mmol, 1 equiv.) were added. After stirring



Scheme 6. Proposed mechanism of Henry reactions catalyzed by **26**.

Table 4. Enantioselective aza-Henry reactions of CH_3NO_2 with various aromatic imines in the presence of **26**.



Entry[a]	Imines (R)	Time [h]	Yield [%][d]	*ee* [%][e]
1[b]	4-$NO_2C_6H_4$	2	92	95
2[b]	2-$NO_2C_6H_4$	2	99	96
3[b]	3-$NO_2C_6H_4$	2	93	96
4[b]	3-pyridyl	2	99	93
5[b]	4-$MeO_2CC_6H_4$	6	80	95
6[b]	4-CNC_6H_4	4	92	93
7[c]	Ph	60	80	97
8[c]	1-naphthyl	48	81	93
9[c]	2-MeC_6H_4	72	65	96
10[c]	4-MeC_6H_4	72	62	84
11[c]	4-$CF_3C_6H_4$	72	75	93
12[c]	4-$MeOC_6H_4$	72	71	80
13[c]	3-$MeOC_6H_4$	72	65	90
14[c]	4-ClC_6H_4	72	68	85

[a] All reactions were performed on a 0.20 mmol scale with 5 mol% of **26** at a 0.5 M concentration and 5 equiv. of nitromethane in EtOH.
[b] Reactions were run at room tempertaure.
[c] Reactions were run at 0 °C.
[d] Yields of isolated *N*-Boc-β-amino nitro compounds.
[e] Enantiomeric excess (*ee*) was determined by HPLC using Chiralcel OD-H or AD-H columns. The absolute configuration of products was determined as *S* by comparison of their optical rotations with literature values.[11]

for the time indicated the volatile components were removed under reduced pressure and the crude product was purified by column chromatography.

Acknowledgements

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