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Synthesis of "Click BOX" ligands and preliminary results on their application in the asymmetric copper catalysed Henry reaction of *o*-methoxybenzaldehyde

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ABSTRACT

Two new chiral "click BOX" ligands have been synthetised with high yields starting from commercially available dimethyl propargylmalonate and optically pure alkanolamines, followed by copper catalysed cycloaddition (CuAAC) and oxazoline ring formation. Catalytic activity of the new ligands has been tested in the copper mediated Henry addition. The model reaction between nitromethane and *o*-anisaldehyde affords the related 1-(2-methoxyphenyl)-2-nitroethanol in high yields (up to 92%) and moderate enantioselectivities (up to 67% e.e.) under straightforward experimental conditions.

Introduction

The addition of a nitroalkane compound to the carbonyl group of an aldehyde or ketone is a useful tool to build up a new C–C bond. This process is known as Henry or nitroaldol reaction (see Scheme 1) [1]. The value of nitroaldol products arises from their potential transformation into other synthons useful in pharmaceutical and natural products synthesis [2]. The β-nitroalcohols obtained with this efficient reaction can undergo to dehydration to get nitroalkenes or oxidation to get ketones that are important building blocks in organic synthesis. In this case the stereogenic carbon obtained as a consequence of the addition of the nitroalkane (C_α and/or C_β) is lost and the enantioselectivity of the process becomes irrelevant. In all the other reactions involving the nitroalcohol adduct (reduction of the nitro group or its replacement by nucleophiles) in which the newly formed stereocentres are retained in the target molecule, the control of the stereochemical step is of crucial importance [1b-d]. The Henry reaction can be promoted by a base such as an amine and/or be metal catalysed.

In this regard, Shibasaki and co-workers published the most impressive development by applying a bifunctional multimetallic catalyst based on lanthanum and lithium with the conjugate base of binaphthol serving as chiral auxiliary [3]. Since then, other examples based on the hypothesis that the metal acts as weak Lewis acid site and the ligand as moderate Brønsted base, have been described [1c,4]. Assuming this, a properly designed organometallic complex can activate the nitro compound and the carbonyl group at the same time during the catalytic cycle [5]. Copper, chromium and nickel complexes among others have been applied to the catalytic version of the asymmetric nitroaldol reaction [6]. Particularly, copper (I or II) complexes are preferable due to their availability, low toxicity and to their good tolerance to moisture and air. Moreover, several chiral ligands have been developed and a remarkable improvement in the field has been achieved. The first example of copper catalysed Henry reaction has been reported by Jørgensen and co-workers demonstrating the potential of bisoxazoline (BOX) ligands in this process [6a,7]. Ever since, many other nitrogen-based ligands have been developed and exploited in the copper catalysed Henry reaction. Among the others, 1,2-bis (sulfonamide)-diamine [8], 1,2-diamine [9], 1,3-diamine [10], sulfonyldiamine [11], iminopyridine [12], pyrrolidine [13], oxazoline, together with the above mentioned bisoxazoline [6a,7,14] ligands have been reported (Fig. 1).

Some of the authors have been recently involved in the synthesis of new nitrogen-based chiral ligands and their application to various metal catalysed enantioselective reactions [12c,15]. In line with this, we designed new chiral ligands obtained by derivatisation of a well-known privileged structure, namely a bisoxazoline [16]. As reviewed by Tang, the addition of an extra coordinating group in the backbone of a bisoxazoline ligand has shown to increase the stereogenic control in the outcome of various reactions. In this approach for ligand design, the "side arm" may play multiple roles, *e.g.* as ligating group, as steric group, as directing group [17]. Similarly, we design a new BOX ligand bearing a 1,2,3-triazole aromatic ring as "side arm", see Fig. 2.

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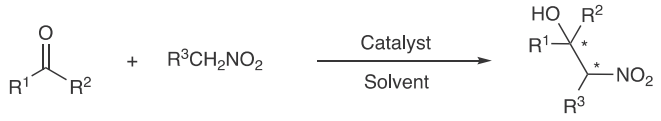


Scheme 1. Henry reaction of ketones with nitroalkanes.

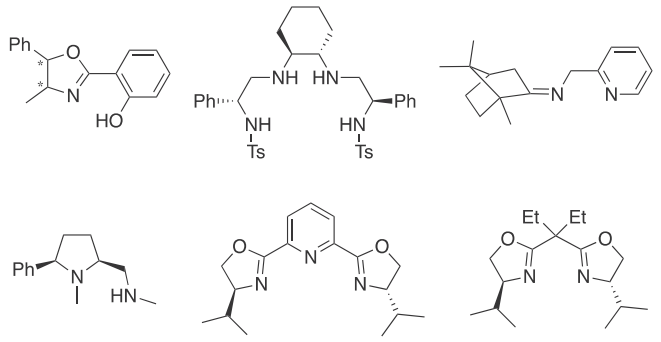


Fig. 1. Selected examples of nitrogen-based ligands used in copper catalysed asymmetric Henry reaction.

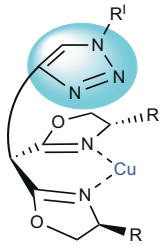


Fig. 2. Design of the "click BOX" ligands.

We assumed that this modification could have altered the steric and/or the electronic microenvironment around copper, leading to an increase in the enantioselectivity of the Henry reaction.

Since the breakthrough in triazole chemistry came in the early 2000s [18], 1,4-disubstituted 1,2,3-triazole related compounds have found applications as ligands for a number of transition-metal catalysed organic reactions [19]. Triazoles found also application as stabilising ligands in the Copper(I)-catalyzed Azide-Alkyne Cycloaddition (CuAAC) [20] or as organocatalysts [21]. To the best of our knowledge there are few examples reported in the literature dealing with BOX type ligands modified with a triazole moiety [22]. In all these examples, the introduction of the triazole proved to be beneficial for the outcome of the tested reactions. In particular, for aza-BOX derivate **1** (see Fig. 3) although it looks an ideal set up to be a tridentate ligand, Reiser and co-workers proved that it does not coordinate intramolecularly but rather it forms a polymeric structure bridged by copper atoms [22b]. The better outcome obtained in the conjugate addition catalysed by $Cu(OTf)_2$/**1** as compared to the parent $Cu(OTf)_2$/**2**, has been addressed to a weaker coordinating ability of triazole which in turn, by dissociation will lead to an active species that gives rise to high selectivity. Similar behaviour has been described also for chiral C_3-symmetric trisoxazoline (TRISOX) based copper complexes, where the hemilability of one of the oxazoline ring tuned the electronic and steric properties of the catalyst, influencing enantioselectivity and reactivity [23]. All the mentioned considerations prompted us to design the synthesis of our "click BOX" ligands.

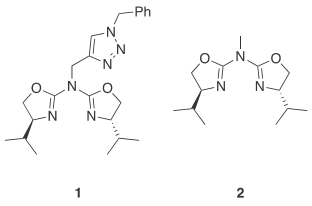


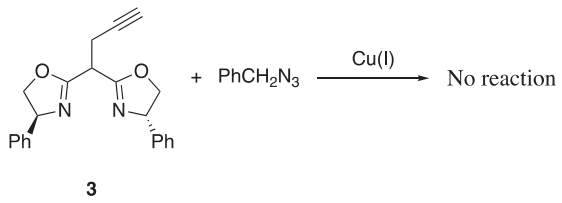
Fig. 3. "Click Aza-BOX" and Aza-BOX ligands applied in Michael addition by Reiser's group.

Result and discussion

Synthesis of the ligands

The straight synthetic procedure to obtain our "click BOX" ligands would be the direct modification of the known propargyl-functionalised BOX derivate **3** synthetised in Gade's lab [24]. Unfortunately, CuAAC did not work in our experimental conditions (see Scheme 2). By rethinking the synthetic procedure, we envisaged to get the formation of the oxazoline rings in the last step of the synthesis. Therefore, starting from commercially available dimethyl propargylmalonate we obtained the diamide intermediates **6a-b** by reaction with (*S*)-phenylglycinol (R = Ph, **5a**) or (*S*)-valinol (R = ^{i}Pr, **5b**) in refluxing anhydrous toluene (see Scheme 3). Compounds **6a** and **6b** were isolated with almost quantitative yields in line with what is reported in the literature [24].

To afford the triazole moiety in the ligand structure, benzyl bromide is reacted with sodium azide in a mixture of ^{t}BuOH and water (1:1) to get benzylazide. This reaction can be monitored by GC analysis until quantitative conversion of the starting bromide. Before proceeding with the CuAAC between benzylazide and the alkyne moiety in the amides (**6a** or **6b**), it is necessary to remove any trace of the halide to avoid inhibition of the cycloaddition reaction [25]. This can be obtained by filtrating off the silver bromide obtained by addition of stoichiometric $AgNO_3$ at the end of this step. As shown in Scheme 4, CuAAC reaction is carried out in a mixture 1:1 of ^{t}BuOH and water in the presence of copper(II) acetate and sodium ascorbate for 12 h at 60 °C. The two click diamides **7a** and **7b** were obtained with 88 and 87% isolated yield respectively. To attain the formation of the oxazoline rings it is necessary to activate the hydroxyl groups by reaction with thionyl chloride. The chlorides **8a** and **8b** thus obtained could be isolated (86 and 70% yield respectively for R = Ph and R = ^{i}Pr). Alternatively, after elimination of the unreacted $SOCl_2$ under vacuum, the chlorides can directly undergo to cyclisation in a methanolic solution of sodium hydroxide (Scheme 4). Finally,



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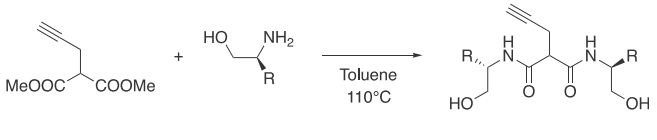
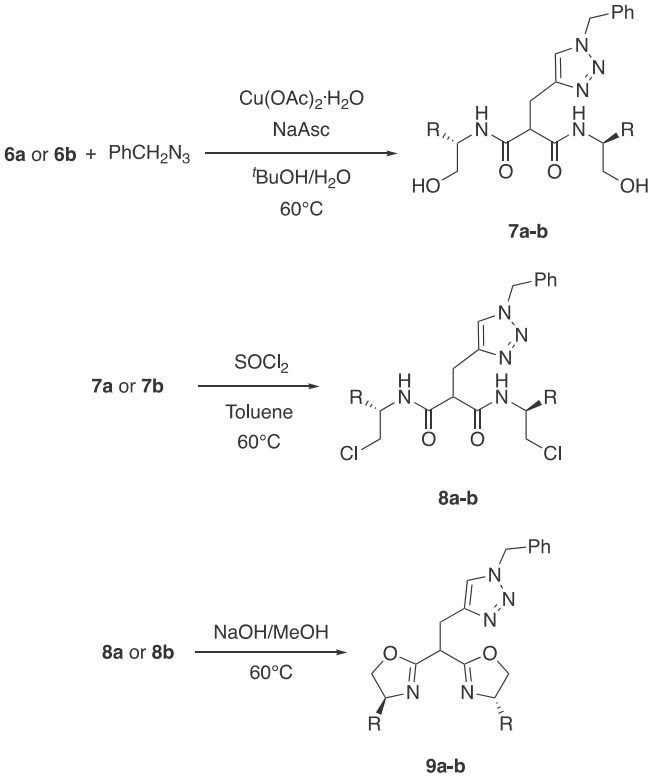
Scheme 2. Direct modification of the propargyl-functionalised BOX ligand.

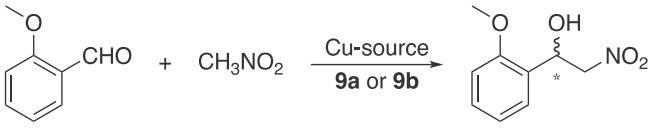


4 **5a-b** **6a-b**

Scheme 3. Synthesis of propargylmalonamides **6a** (R = Ph) and **6b** (R = ^{i}Pr).



Scheme 4. Synthesis of "click BOX" ligands **9a** (R = Ph) and **9b** (R = ^{i}Pr).



Scheme 5. Addition of nitromethane to *o*-anisaldehyde.

"click BOX" ligands **9a** and **9b** were obtained with 72 and 70% yield respectively, after precipitation from a CH_2Cl_2/pentane mixture.

Henry reaction

The activity of the new "click BOX" ligands was proved in the Henry addition of nitromethane to *o*-anisaldehyde as model substrate (see Scheme 5). All reactions were carried out using active catalytic species formed *in situ* before the addition of the substrate. We initially carried out the Henry reaction by using 10 mol% of copper(II) triflate as metal source, accordingly with the conditions described by Jørgensen for the addition to ethyl pyruvate [6a]. As shown in Table 1, all reactions were carried out for 48 h at room temperature (unless stated differently), either in ethanol or nitromethane. We observed that, copper triflate itself does not catalyse the addition of nitromethane to *o*-anisaldehyde, not even with 10 mol% of NEt_3 (Table 1, entries 1–2). Moreover, only traces of the nitroaldol product are obtained when the catalytic system is formed *in situ* by dissolving the $Cu(OTf)_2$ with 1.1 equivalents of ligand **9a** and nitromethane is used as solvent (Table 1, entry 3). Interestingly, in ethanol we observed quantitative conversion but 2-methoxybenzaldehyde diethyl acetal is formed instead (Table 1, entry 4), alike what previously reported for similar systems [26].

By changing the copper source in favour of the more basic acetate (without the addition of ligand) the reaction proceeded only in presence of 10 mol% of organic base (Table 1, entries 5–6). Unlike this, the complex formed by copper(II) acetate and ligand **9a** yielded, in ethanol, 79% of the desired nitroalcohol with 51% enantiomeric excess (Table 1, entry 7). At comparable reaction conditions, the parent BOX ligand lacking of the triazole "arm" led to 62% yield of 1-(2-methoxyphenyl)-2-nitroethanol and to a poorer e.e. (19%) [22d]. In our study we also tested the activity of copper(I) complexes. More in detail, the reaction carried out in ethanol with the copper(I) thiophene-2-carboxylate/**9a** complex led to 1-(2-methoxyphenyl)-2-n itroethanol with 73% yield and with 54% e.e. (Table 1, entry 8). Switching to copper iodide as the metal source we observed a decreasing in both the yield and the stereoselectivity respectively to 30% and 18% (Table 1, entry 9). We further studied the reactivity of $Cu(OAc)_2$-$\cdot H_2O$/"click BOX" ligand complexes in our test reaction. For ligand **9a**, if nitromethane is used as solvent, we observed higher yield (up to 92%) with broadly unchanged stereoselectivity as compared with the reaction in ethanol (Table 1, entries 7 and 10). Furthermore, the addition of 10 mol% of triethylamine to $Cu(OAc)_2\cdot H_2O$/**9a** complex led to quantitative yield but it was detrimental for the stereoselectivity (Table 1, entry 11) indicating that the competitive based catalysed

Table 1
Enantioselective Henry Reaction of *o*-methoxybenzaldehyde with nitromethane in the presence of ligands **9a** and **9b**[a].

Entry	Catalyst	Ligand	solvent	Yield %[b]	e.e. % (conf.)[c]
1	$Cu(OTf)_2$	–	CH_3NO_2	0	nd
2	$Cu(OTf)_2/NEt_3$	–	CH_3NO_2	0	Nd
3	$Cu(OTf)_2$	**9a**	CH_3NO_2	< 5	Nd
4	$Cu(OTf)_2$	**9a**	EtOH	0[d]	Nd
5	$Cu(OAc)_2\cdot H_2O$	–	CH_3NO_2	0	Nd
6	$Cu(OAc)_2\cdot H_2O/NEt_3$	–	CH_3NO_2	86[e]	Nd
7	$Cu(OAc)_2\cdot H_2O$	**9a**	EtOH	79	51(*S*)
8	CuTC	**9a**	EtOH	73	54(*S*)
9	CuI	**9a**	EtOH	30	18(*S*)
10	$Cu(OAc)_2\cdot H_2O$	**9a**	CH_3NO_2	92	50(*S*)
11	$Cu(OAc)_2\cdot H_2O/NEt_3$	**9a**	CH_3NO_2	99	< 5
12	$Cu(OAc)_2\cdot H_2O$	**9a**	CH_3NO_2	0[f]	Nd
13	$Cu(OAc)_2\cdot H_2O$	**9b**	CH_3NO_2	90	60(*S*)
14	$Cu(OAc)_2\cdot H_2O$	**9b**	CH_3NO_2	25[g]	67(*S*)

[a] General reaction conditions: ligand/Cu source/Substrate = 1.1:1:10; reaction performed at room temperature unless otherwise stated; reaction time: 48 h.
[b] Isolated yield after flash chromatography.
[c] Determined by HPLC analysis by comparing a known sample of 1-(2-methoxyphenyl)-2-nitroethan-1-ol.
[d] The isolated product was the *o*-anisaldehyde diethyl acetal 99%.
[e] Traces of side product (*E*)-1-methoxy-2-(2-nitrovinyl)benzene was also obtained.
[f] Reaction performed at −20 °C.
[g] Reaction performed at 0 °C.

Henry reaction is faster than the metal mediated. Lowering the reaction temperature to −20 °C led to an unactive catalyst system (Table 1, entry 12). This outcome and the known better performance commonly observed for the oxazoline ring with isopropyl substituent in terms of stereoselectivity [16b], prompted us to continue our studies with ligand **9b**. The catalyst $Cu(OAc)_2{\cdot}H_2O$/**9b** showed similar activity as compared with the system containing **9a**, however ligand **9b** promoted an increment in the stereoselectivity (Table 1, entry 13). As shown in Table 1 (entry 14), with the same catalyst, the enantiomeric excess is further improved (up to 67%) carrying out the reaction at 0 °C. Finally all the reactions carried out with the *in situ* formed copper complexes were selective toward the nitroalcohol with only traces of (*E*)-1-methoxy-2-(2-nitrovinyl)benzene (< 1% by GC analysis).

Conclusion

In conclusion, we have developed a new catalytic system for the copper-catalysed enantioselective nitroaldol reaction. This system uses copper(II) acetate in combination with a "click BOX" ligand. The ligands are synthetised starting from commercially available dimethyl propargylmalonate and optically pure alkanolamines followed by CuAAC and oxazoline rings formation. Both ligands **9a** and **9b** are obtained with high yields. Coupling between nitromethane and *o*-anisaldehyde was used as test reaction to assess catalytic activity and stereoselectivity. The new copper(II)/"click BOX" complexes afforded the related 1-(2-methoxyphenyl)-2-nitroethanol in high yields (up to 92%) and moderate enantioselectivities (up to 67% e.e.). Although we do not have any experimental insight about the coordinating mode of our "click BOX" ligand, we did demonstrate that in our case the addition of a triazole "side arm" resulted in a performance improvement of the catalytic complex as compared with the outcomes described for the parent bisoxazoline. Further studies are in progress to exploit these ligands in other catalytic enantioselective reactions.

CRediT authorship contribution statement

Daniela Giunta: Investigation, Resources, Methodology, Writing-review & editing. **Antonio Arras:** Investigation, Resources, Writing-review & editing. **Paola Peluso:** Resources. **Maurizio Solinas:** Conceptualization, Methodology, Investigation, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rechem.2021.100122.

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