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A Bis(Triazolecarboxamido) Ligand for Enantio- and Regioselective Molybdenum-Catalyzed Asymmetric Allylic Alkylation Reactions

Erhan Ozkal[a] and Miquel A. Pericàs[a,b,*]

[a] Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, E-43007 Tarragona, Spain
Fax: (+34)-97-792-0222; phone: (+34)-97-792-0200; e-mail: mapericas@iciq.es
[b] Departament de Química Orgànica, Universitat de Barcelona, E-08028 Barcelona, Spain

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Abstract: A modular, enantiomerically pure bis(1*H*-1,2,3-triazole-4-carboxamide) has been assembled from *N*,*N*′-[(1*R*,2*R*)-cyclohexane-1,2-diyl]-dipropiolamide through a copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction and evaluated as a ligand in the molybdenum-catalyzed asymmetric allylic alkylation (MoAAA) reaction, very high regio- and enantioselectivities being recorded.

Keywords: allylic substitution; asymmetric catalysis; click chemistry; copper; molybdenum; triazoles

In the beginning of the 21st century, the introduction of the click chemistry concept[1] revolutionized in many aspects the way of thinking of the synthetic community. This change of paradigm, with the generation of 1,2,3-triazole-1,4-diyl connectors by CuAAC reactions[2] as the flagship, has been exploited by countless authors in many different fields. Indeed, applications as disparate as modification of biological systems and use in materials chemistry have been described, taking advantage of the broad applicability of the alkyne-azide cycloaddition and of the possibility of post-modification of functional groups with orthogonal approaches.[3]

The use of triazole-containing ligands prepared by CuAAC is a relatively new approach to catalysis, but a number of applications have been reported.[4] Transition metal-catalyzed reactions mediated by such *click ligands* have several advantages, such as the fine tuning enabled by the easy generation of structural diversity on the triazole moieties. These heterocycles, in turn, behave as efficient metal-complexing units, especially when cooperativity is involved.[4a–f,5] We have summarized in Figure 1 the structures of some known triazole-based ligands and the types of reactions they catalyze.

Tris(triazole) ligands **I**[4a] and **II**[4e] have found application in the copper-catalyzed alkyne-azide cycloaddition reaction for the regioselective preparation of 1,4-disubstituted 1,2,3-triazoles.

In addition, ligand **II** has been conveniently immobilized onto a polystyrene-based resin, and the supported catalyst retains the high catalytic activity of the monomer while allowing for repeated recycling.[6] Despite the numerous applications in the CuAAC reaction,[7] the catalytic use of triazole-containing ligands has a much broader scope due to the versatile chelating ability of the N-2 or N-3 atoms in the tria-

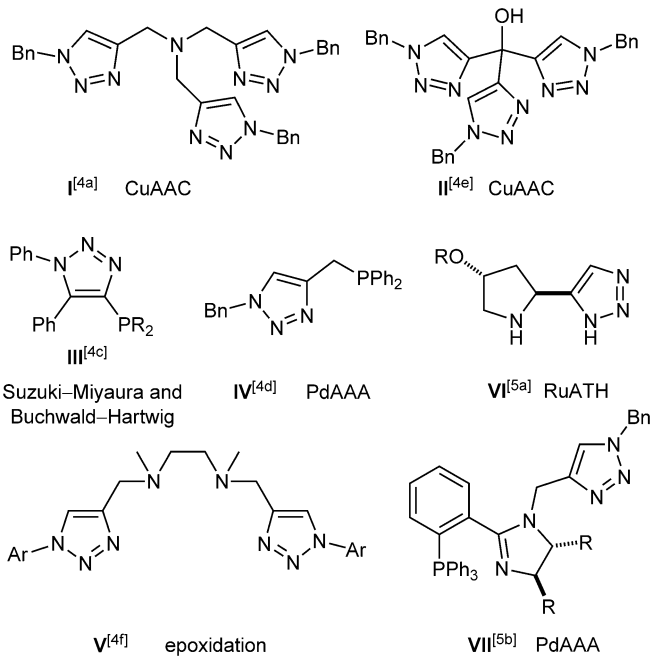


Figure 1. Triazole-based CuAAC ligands used in metal-catalyzed reactions.

zole structure.[8] This feature has been exploited to generate catalytically active monophosphines of the *P,N*-type, like ClickPhos **III**[4c] and ClickPhine **IV**,[4d] ferrocenyldiphosphines (ClickFerrophos[10b,d]), and multidentate ligands like **V**[4f] suitable for the coordination of divalent cations. Even C-5 can be a chelating centre through carbene formation,[9a] and applications of these carbene complexes in metal-catalyzed reactions have lately been described.[9b–f]

Recently, enantiopure 2-triazolylpyrrolidines derived from 4-hydroxyproline have been used as ligands for Ru in the transfer hydrogenation of ketones (structure **VI** in Figure 1). Chelation in the catalytically active species necessarily involves the triazole moiety, and the reduction process takes place with high TOF and enantioselectivity.[5a] Even in cases where the triazole moiety was supposed to act as an innocent bystander (structure **VII** in Figure 1), NMR studies and theoretical calculations indicate that chelation involving the triazole moiety is preferred over standard *P,N*-coordination and leads to very high enantioselectivity in Pd-catalyzed asymmetric allylic amination.[5b] Additional examples of catalytic enantioselective reactions with triazole-containing ligands[10] are scarce and in most cases the enantioselectivities achieved are only moderate.

The asymmetric allylic alkylation reaction[11] (AAA), is one of the most powerful enantioselective carbon-carbon and carbon-heteroatom bond forming methodologies and it has been extensively studied with different metals. Interestingly, molybdenum provides an alternative to palladium as it furnishes products with complementary regioselectivity (high branched to linear preference).[12] The Mo-catalyzed asymmetric allylic alkylation (MoAAA) has been investigated by Trost and others, and C_2-symmetric ligands providing high levels of asymmetric induction in the reaction have been identified.[12d,13] Although the scope of nucleophiles preferentially affording the branched substitution product is wider with iridium catalysis,[14] MoAAA is more attractive due to the much lower cost of the metal precursor and its experimental ease of handling under microwave conditions.[15] The introduction by Trost[16a] and Pfaltz[16b] of new ligands (structures **A** and **B** in Figure 2) able to induce high regio- and enantioselectivity in the reaction generated great interest in this transformation. Since then, a plethora of mechanistic studies and synthetic applications of this robust methodology has been reported.[17]

Given the crucial role played by σ donor nitrogen ligands in MoAAA, we thought that triazoles might also play this role and provide highly active and selective catalytic species. In fact, Lammertsma et al. showed that triazoles in an appropriate geometrical arrangement efficiently bind Mo(0).[18] Consequently, we envisaged that enantiomerically pure bis(1*H*-1,2,3-triazole-4-carboxamides) **C** (Figure 2), readily available from commercially available materials through CuAAC reactions, would provide rapid access to a new ligand family for MoAAA. Herein, we present the preparation of the first member of this family, as well as the study of its catalytic activity, enantio- and regioselectivity in the MoAAA of cinnamyl derivatives with dimethyl malonate under conventional and microwave heating.

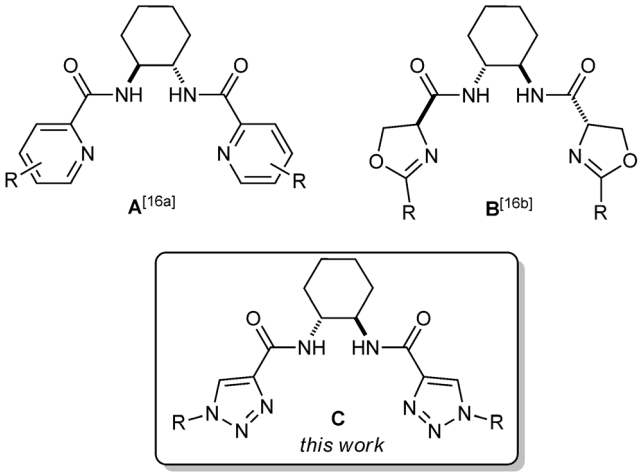


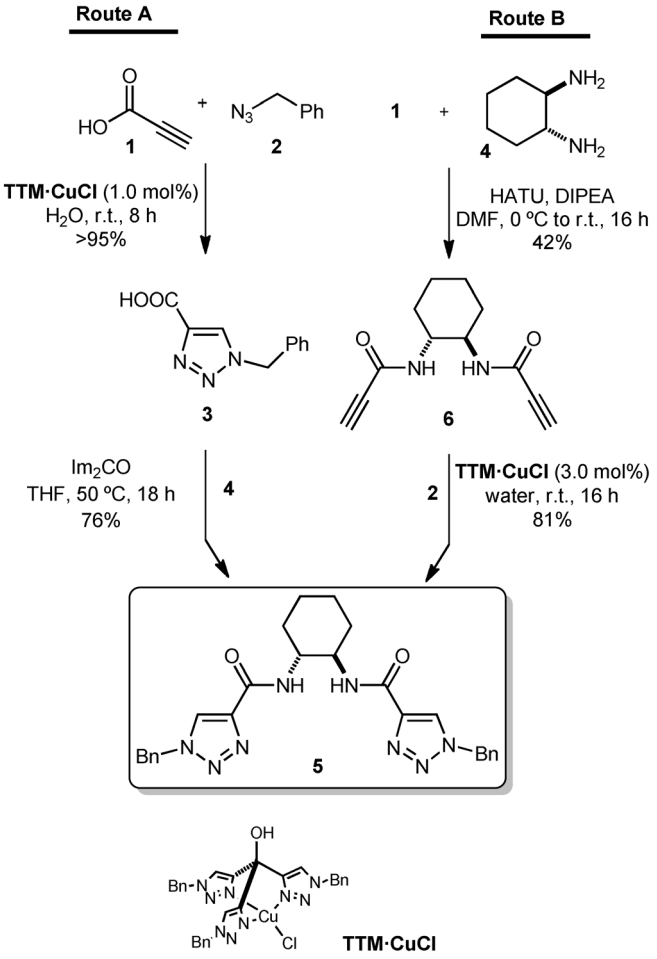
Figure 2. General structure of ligands for MoAAA reactions.

Two different strategies were envisaged for the preparation of the target ligand: (a) double amidation of (1*R*,2*R*)-cyclohexane-1,2-diamine (CHDA) followed by CuAAC reaction with benzyl azide, and (b) double amide formation from 1-benzyl-1*H*-1,2,3-triazole-4-carboxylic and CHDA (Scheme 1).

In the first strategy (Route a), the CuAAC reaction of propiolic acid (**1**) and benzyl azide (**2**) was performed using the **TTM·CuCl** catalyst[4e] at room temperature on water.[19] After a simple filtration, triazole **3** could be directly used in the next step, the amide coupling with CHDA (**4**) promoted by carbonyldiimidazole. This approach afforded the tetradentate ligand **5** in high overall yield (72%) and purity.

Afterwards, we aimed to develop a more modular strategy that hinged on the synthesis of a common intermediate, from which a family of ligands could be prepared by click reaction with a set of azides (Route b). Thus, **6** was generated from **1** and **4** using HATU (1-[bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo-[4,5-*b*]pyridinium 3-oxide hexafluorophosphate) as a condensing agent and, without further purification, the crude material was subjected to CuAAC reaction with **2** mediated by **TTM·CuCl**, to afford **5** in 34% overall yield.

With **5** in hand, reaction conditions for the MoAAA reaction were optimized using cinnamyl methyl carbonate (**7a**) as the substrate,[20] dimethyl malonate (**8**) as the pronucleophile, and sodium hy-

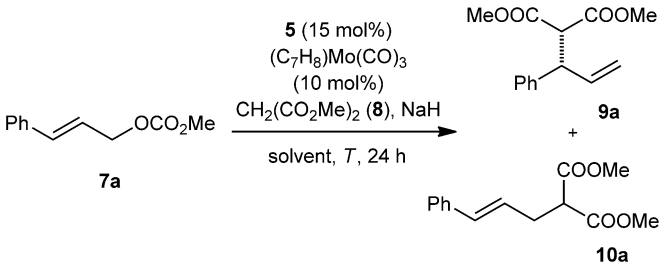


Scheme 1. Synthesis of ligand **5**.

dride as a base. According to our expectations, dimethyl 2-(1-phenylallyl)malonate (**9a**) was obtained in all cases as the major reaction product. In preliminary experiments, different sources of Mo(0) were tested. While somehow erratic results were recorded with $Mo(CO)_3(NCCH_2CH_3)_3$ [tricarbonyltris(propionitrile)molybdenum], the most reproducible results were obtained with the rather labile $C_7H_8Mo(CO)_3$, tricarbonyl(cycloheptatriene)molybdenum, which was adopted for the rest of the study. The much cheaper $Mo(CO)_6$ (molybdenum hexacarbonyl) required substantially longer incubation time for the generation of the catalytically active species and was disregarded at this stage. However, it is known that $Mo(CO)_6$ is the most convenient catalyst precursor for reactions run with microwave activation.[15]

The influence of solvent and temperature on the MoAAA reaction was next studied (Table 1). Working in THF (entry 1) excellent regio- and enantiocontrol were achieved even when a reaction temperature of 60 °C was required. In any case, conversion in this solvent was low (*ca.* 20%), and we reasoned that this could be due to the low solubility of **5** in this medium.

Table 1. Solvent optimization in the MoAAA reaction mediated by **5**.[a]



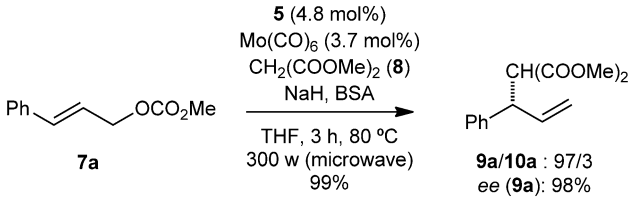
Entry	Solvent	*T* [°C]	Yield [%][b]	**9a**:**10a**[c]	*ee* [%][d]
1	THF	60	20	95:5	95
2	DCE	75	14	94:6	–[e]
3	DCE-THF (1:2)	75	73	93:7	98
4	DCE-THF (1:1)	75	80	97:3	98

[a] As described in the experimental section.
[b] Isolated yield.
[c] By ^{1}H NMR of the reaction crude.
[d] By chiral HPLC.
[e] Not determined.

1,2-Dichloroethane (DCE) was found to be useful in order to solubilize the ligand. Nevertheless, under these conditions the sodium salt of dimethyl malonate (generated *in situ*) had very limited solubility, which again resulted in a low yield (entry 2). Use of a mixture of both solvents seemed to work, but the best conditions found implied the separation of these two events in two different flasks: one for the metal-ligand complexation in DCE and another for the malonate deprotonation in THF (entries 3 and 4). The use of the same volumes of both solvents (entry 4) turned out to be optimal. Under these conditions, the reaction between **7a** and **8** mediated by **5** required a reaction time of 24 h, similar to Pfaltz's results but longer than the 4 h time required with the Trost ligand for a comparable yield and selectivity.[16]

We were also curious on the possibility of using **5** in microwave-assisted MoAAA, since this would presumably allow the use of cheap and bench-top stable molybdenum hexacarbonyl for the generation of the catalytic species.[15] After some optimization, we found that under these conditions the reaction can be conveniently performed at 80 °C in THF with the same regio- and enantioselectivity as under thermal conditions, but in a considerably shorter reaction time and at a much lower catalyst loading (Scheme 2). Interestingly, the reaction temperature in this experiment favourably compares with that reported for analogous pyridyl-based ligands (160 °C), although in that case reaction times are considerably shorter.[15]

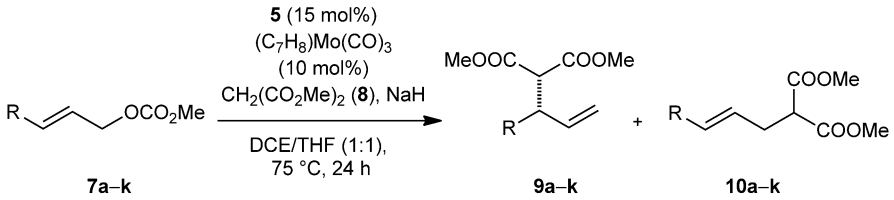
After having identified optimized sets of reaction conditions under standard and microwave activation, the stage was set to determine the scope of the



Scheme 2. Microwave-assisted MoAAA reaction of **7a** with **8** mediated by **5**.

MoAAA reaction mediated by bis(triazolecarboxamide) **5**. This part of the study was performed under standard thermal conditions, and the results are summarized in Table 2. A range of aromatic allylic carbonates with different substitution patterns was evaluated and, in general, excellent results in terms of yield, enantio- and regioselectivity were achieved with substrates involving an aromatic or heteroaromatic residue (R). Thus, either electron-donating (entries 2 and 3), electron-withdrawing (entries 4–6) and sterically demanding R groups (entries 3, 7, and 10) were found

Table 2. Scope of the MoAAA reaction mediated by **5**.[a]



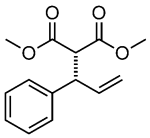
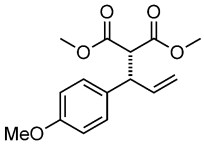
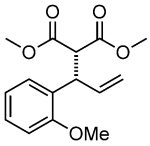
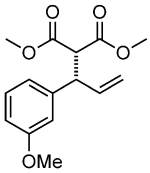
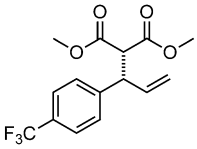
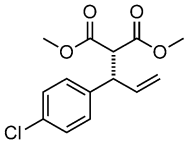
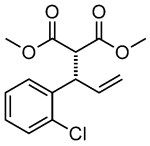
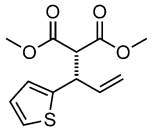
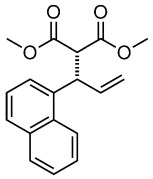
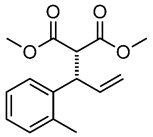
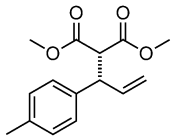
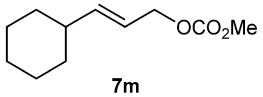
Entry	Product		Yield [%][b]	**9**:**10**[c]	ee [%][d]
1		**9a**	80	97:3	98
2		**9b**	98	98:2	97
3		**9c**	94	97:3	99
4		**9d**	52	93:7	99
5		**9e**	76	90:10	99
6		**9f**	89	94:6	99
7[e]		**9g**	94 (92)	95:5 (91:9)	95 (97)

Table 2. (Continued)

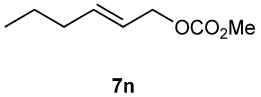
Entry	Product		Yield [%][b]	**9**:**10**[c]	ee [%][d]
8		**9h**	99	93:7	98
9		**9i**	88	96:4	97
10		**9j**	95	97:3	98
11		**9k**	84	95:5	95

[a] Reaction conditions as described in the experimental section.
[b] Isolated yield.
[c] By ^{1}H NMR of the reaction crude.
[d] By chiral HPLC.
[e] Results at 1.0 mmol scale are given in parentheses.

to work very well, as it also happened for the 1-naphthyl (entry 9) and 2-thienyl (entry 8) substituents. In general, despite the fact that the reaction was carried out at 75 °C for 24 h, no deterioration of *ee* was observed with this kind of substrate. Not unexpectedly,[13] when alkyl-substituted substrates like **7m** or **7n** were used in the reaction, no conversion was observed.



7m



7n

In conclusion, a C_2-symmetrical, tetradentate ligand (**5**) containing two 1,2,3-triazole units as metal-coordinating elements has been developed through an operationally simple, CuAAC-based procedure. The catalytic species formed by interaction of **5** with either tricarbonyl(cycloheptatriene)molybdenum (for standard thermal conditions) or with molybdenum hexacarbonyl (for microwave promoted reactions) represents one of the first practical catalytic systems where triazole units are the key for catalytic activity and enantioselectivity, participating in the chelation of the metal. The excellent selectivities observed with **5** make this ligand a possible candidate for further development in different metal-mediated reactions. Moreover, the modular synthesis of the ligand (Scheme 1, Route b) enables an easy approach to the generation of a ligand library with controlled diversity, which would help to further extend its applicability.

Experimental Section

General Experimental Procedure for MoAAA with 5

To a 15-mL round-bottom vial (Ø = 1 cm), tricarbonyl(cycloheptatriene)molybdenum (5.9 mg, 0.022 mmol, 10 mol%) and ligand **5** (16 mg, 0.033 mmol, 15 mol%) were added in the glovebox. To another vial, sodium hydride (10.4 mg, 0.434 mmol, 2.0 equiv.) was added in the glovebox. The vials were evacuated and re-filled with argon 3 times. To the catalyst vial 1,2-dichloroethane (1 mL) was added, and the mixture was stirred at 75 °C for 15 min. Tetrahydrofuran (1 mL) and dimethyl malonate (0.063 g, 0.48 mmol, 2.2 equiv.) were simultaneously added to the vial containing NaH, and the mixture was stirred at room temperature for 15 min, until a clear solution formed. The catalyst was transferred to the vial containing the nucleophile *via* cannula, and the appropriate allylic carbonate (electrophile) (0.217 mmol, 1 equiv.) was added *via* syringe. The reaction mixture was stirred at 75 °C for 24 h, then poured into water (5 mL) and extracted with diethyl ether (3 × 10 mL). The organic layers were dried over magnesium sulfate, filtered and concentrated under re-

duced pressure, and the **9**/**10** ratio was determined by ^{1}H NMR of the crude. Purification was performed by flash column chromatography (silicagel, Ø = 1 cm, h = 15 cm), eluting with hexanes-ethyl acetate (98:2).

Experimental Procedure for Microwave-Assisted MoAAA with 5

Two different stock solutions were prepared: *Solution-1* was prepared by adding dimethyl malonate (**8**) (880 μL, 7.70 mmol) to a suspension of sodium hydride (16.2 mg, 0.680 mmol) in tetrahydrofuran (10 mL), and *Solution-2*, was prepared by dissolving **7a** (1.36 g, 7.10 mmol) in tetrahydrofuran (10 mL). Molybdenum hexacarbonyl (6.9 mg, 0.026 mmol) and **5** (17 mg, 0.034 mmol) were placed in a microwave vial that was evacuated and re-filled with argon for 3 times. *Solution-1* (1.5 mL, 1.16 mmol of the nucleophile), *Solution-2* (1 mL, 0.71 mmol of the electrophile) and *N,O*-bis(trimethylsilyl)acetamide (BSA) (220 μL) were added and the sample was heated in the microwave cavity in a CEM Discover microwave reactor with the following set of options: maximum power = 300 W; ramp time: up to 30 min (until set temperature achieved); hold time: 3 h; temperature = 80 °C and power max mode kept on; maximum pressure = 300 psi with stirring on. After 3 h, the reaction mixture was diluted with diethyl ether (10 mL) and the orange solution was filtered and analyzed by ^{1}H NMR for the **9a/10a** ratio. Purification was performed by flash column chromatography (silica gel, Ø = 1 cm, h = 15 cm), eluting with hexanes-ethyl acetate (98:2).

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