



A metalloptoid as an efficient bioinspired cooperative catalyst for the aerobic oxidative synthesis of imines



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ABSTRACT

Enzymatic catalysis is largely based on intramolecular cooperativity between a metal center and functional organic molecules located on one scaffold. Inspired by this concept we have designed the metalloptoid trimer **BT**, which is a unique intramolecular cooperative oxidation catalyst incorporating two catalytic centers, phenanthroline-copper and TEMPO, as well as one non-catalytic benzyl group. Herein we explore the capability of **BT** to act as an efficient catalyst for the oxidative synthesis of imines, which are versatile intermediates in the fine chemicals and pharmaceutical industries. We demonstrate that **BT**, combined with CuI, can catalyze the production of benzyl, aryl, heteroaryl, allylic and aliphatic imines from various alcohols and amines with a turn-over-number up to 45 times higher than this achieved when phenanthroline, copper and TEMPO are mixed in solution. Moreover, in low catalyst(s) loading, **BT** enables transformations that are not possible when a mixture of the individual catalysts is employed.

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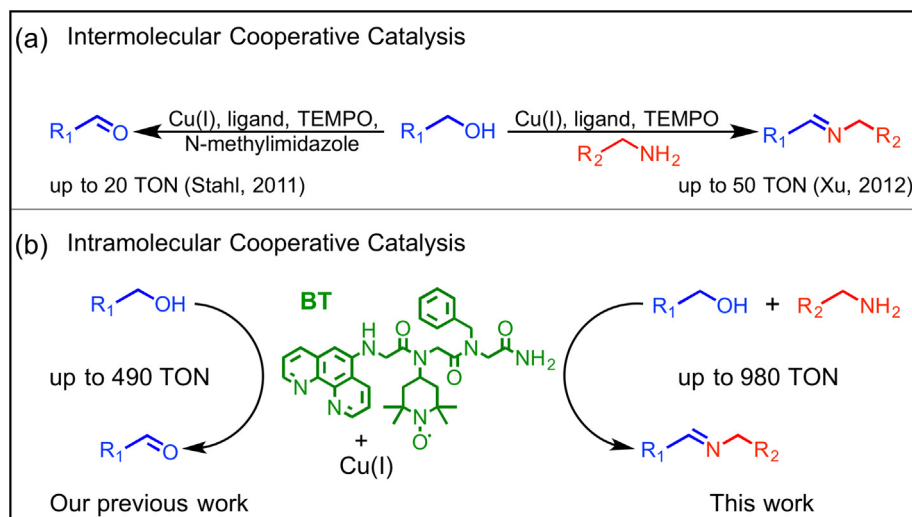
1. Introduction

The search for new catalysts is one of the highest priorities for chemists, both in academia and industry, seeking to run processes at ambient temperatures and pressures, with reasonable reaction rates and a high turnover numbers, and with high selectivity. The gains from improving catalysts are enormous both financially and environmentally, leading to increased reaction efficiency, selectivity and products availability, as well as to the reduction of harmful waste. In nature, enzymes promote chemical and biological reactions with exquisite efficiency and selectivity under very mild conditions. Enzymatic catalysis is largely based on the cooperativity between a metal center and functional organic molecules located at the surrounding folds of the protein (intramolecular cooperative catalysis). This cooperativity leads to the creation of catalytic pockets, which enable enzymes' high specificity and efficiency [1]. The concept of cooperativity has inspired the design of cooperative catalytic systems [2], specifically the combination between a transition metal catalyst and an organocatalyst, which are used as a mixture in solution (intermolecular cooperative catalysis) [3,4]. One example is the combination between Cu(I) complexes and nitroxyl catalysts, which has led to the development of various homogeneous catalytic systems for the aerobic oxidation of alcohols to aldehydes and ketones (Scheme 1a, left) [5–8],

lactonization of diols [9] and oxidative coupling of alcohols and amines to imines [10] or to nitriles and amides [11,12]. Among these transformations, the production of imines is especially important because the highly reactive C=N bond can undergo a variety of subsequent organic reactions such as reduction, addition, cyclization, and aziridination [13], enabling the synthesis of fine chemicals as well as of pharmaceutically and biologically active compounds [14]. Several protocols for the synthesis of imines have been developed [15], with the most attractive one being the oxidative cross-coupling of alcohols with amines (Scheme 1a, right) [16], which has a potential to utilize widely available and inexpensive starting substrates, while producing only hydrogen and water as byproducts [17]. Various homogeneous catalytic systems have been reported for this reaction sequence, some exploit earth abundant metal ions such as Cu [10,18] and Fe [19], mild conditions and air or molecular oxygen as the oxidant. These systems, however, employ 2–5 mol% catalysts, therefore the highest turn-over-number (TON) possible, at the maximum of 100% conversion is 50. Although these systems are practical and applies to a large scope of substrates, the low TON is a significant drawback. Moreover, such systems often require addition of base, ligands, and the use of excess alcohols or amines, which can lead to separation problems. Consequently, recyclable heterogeneous catalytic systems were also developed, and high TON could be achieved after multiple recoveries of the catalyst [20]. But these systems also have some drawbacks including requirements for high reaction temperatures, stoichiometric oxidants and less available noble

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Scheme 1. Intermolecular (a) vs. intramolecular (b) catalytic system utilized for the oxidation of primary alcohols and for the oxidative synthesis of imines.

metal ions. In order to overcome the limitations of both homogeneous and heterogeneous procedures there is a need to design a catalyst that will operate in mild conditions, preferably at room temperature and under air or oxygen atmosphere, and will perform with both high conversions and high TON towards the production of imines from a broad scope of alcohol and amines.

One approach for increasing catalytic efficiencies (and selectivities) while maintaining mild reaction conditions is to design intramolecular cooperative catalytic systems in which the catalytic groups are tethered in close proximity to each other [21,22]. This configuration will create a confined catalytic pocket similar to the catalytic sites in enzymes [23]. Adopting such approach, we have recently developed a peptidomimetic catalyst, namely a metal-binding peptoid [24] trimer bearing 1,10-phenanthroline (Phen), TEMPO and a non-catalytic benzyl group (**BT**, Scheme 1b) [25]. We have discovered that the presence of at least one bulky non-catalytic group induces steric constraints on the two catalytic groups, leading to a highly active intramolecular cooperative catalyst [25]. This catalyst, in the combination with Cu(I) and N-methyl imidazole (NMI), enabled the oxidation of various benzylic, allylic and less activated aliphatic primary alcohols at room temperature with TON of up to 16 times higher than a mixture of the Phen, TEMPO, CuI and NMI (the intermolecular cooperative catalytic system, Scheme 1) [25]. Herein we were interested to exploit **BT** as an intramolecular cooperative catalyst for the oxidative synthesis of imines and investigate whether it can enable high TON in mild conditions.

2. Results and discussion

The peptoid catalyst **BT** was synthesized on solid support using the submonomer method [26], as was previously published. The peptoid was characterized by Reverse Phase High Performance Liquid Chromatography (RP-HPLC) and mass spectrometry (MS), cleaved from the resin, purified by HPLC (>99%) and lyophilized to dryness. The ability of **BT**, in combination with a Cu salt, to catalyze the oxidative coupling of alcohols and amines was initially tested using benzyl alcohol **1** and benzyl amine **2** (Table 1), which were chosen as the model substrates to perform and optimize the reaction protocol described in Scheme 1b (right). We have started our investigations by stirring these two substrates in acetonitrile for 12 hours at room temperature under air, with 1 mol% of **BT** and 1 mol% of CuI, and gradually decreased the loading of **BT** and

Table 1
Optimization studies.^a

Entry	CuI (mol%)	BT (mol%)	Time (h)	Conversion (%) ^b	TON
1	1	1	12	>99	100
2	0.5	0.5	12	>99	200
3	0.25	0.25	12	>99	400
4	0.2	0.2	12	90	450
5	0.1	0.1	12	51	510
6	0.05	0.05	24	32	640
7	0.01	0.01	24	2	–
8 ^c	0.2	0.2	12	>99	500
9 ^c	0.1	0.1	12	54	540
10 ^{c,d}	0.1	0.1	12	77	770
11 ^c	0.1	0.1	24	98	980
12	–	0.2	24	NR	–
13	0.2	–	24	Trace	–

^a Reactions were performed in acetonitrile (0.5 mL) at room temperature and under air, with 1.0 equiv. of benzyl alcohol, with 1.1 equiv. amine.

^b Conversions were determined by gas chromatography.

^c Under oxygen atmosphere.

^d 30 °C.

CuI to 0.01 mol% (Table 1, entries 1–7). In the first three reactions, >99% of (E)-N-benzylidene-1-phenylmethanamine **3** was obtained as detected by GC, thus we have succeeded to increase the overall TON of the reaction from 50, as was previously reported, to 400 by using **BT** and Cu as an intramolecular cooperative catalytic system (Table 1, entries 1–3). No other products such as benzyl aldehyde or (E)-N-benzylidene-1-phenylmethanamide were detected, thus the overall selectivity of the reaction was 100%. Further decrease in the catalyst loading to 0.2 and 0.1 mol%, resulted in a decrease in the overall conversion from about 100% to 90% or 51%, respectively and 10% or 49% of unreacted alcohol were observed by the GC in each case correspondingly (Table 1, entries 4–5). Using lower catalyst loadings required a longer reaction time and the product formation in these cases was not sufficient (Table 1, entries 6–7).

In order to maintain a low catalyst loading we decided to attach a small oxygen balloon in atmospheric pressure to the reaction vessel and conduct the reaction with 0.2 mol% of **BT** and CuI under oxygen atmosphere. In these conditions, 99% of imine was obtained, leading to an increase in the TON from 400 to about

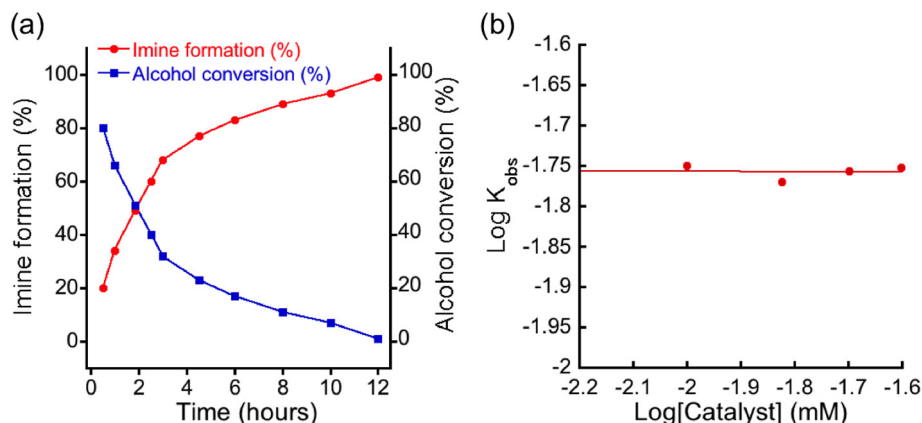
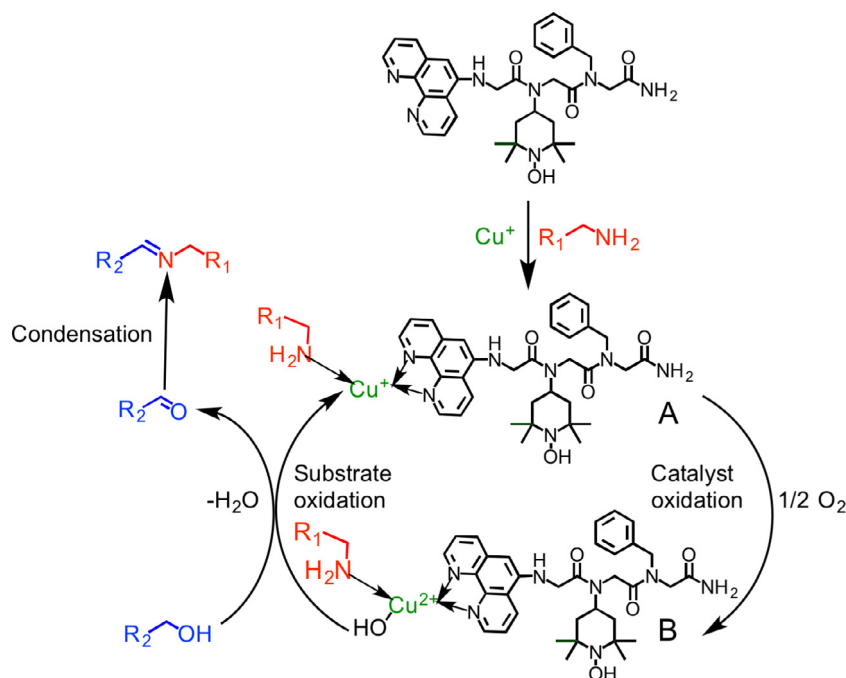


Fig. 1. Kinetic description of **BT** catalyzed oxidative synthesis of imine **3** from alcohol **1** and amine **2**. (a) Reaction profile for the formation of **3** and the conversion of **2** with 0.2 mol% of **BT** and CuI, at rt. under oxygen atmosphere. (b) Rates and order of the reaction with respect to the catalyst, in the first two hours of the reaction with 0.2, 0.3, 0.4 and 0.5 mol% of **BT** and CuI, at rt. under oxygen atmosphere.



Scheme 2. Proposed mechanism for the catalytic oxidative synthesis of imines by **BT**.

500. (Table 1, entry 8). Encouraged by these results we wished to try and increase the TON even more by using only 0.1 mol% catalyst. First, we conducted a reaction with 0.1 mol% catalyst under oxygen atmosphere, but obtained only a slight increase in conversion, 54% (Table 1, entry 9) rather than 51% that was obtained under air. Aiming to improve the conversion further, we conducted two more reactions under oxygen atmosphere, one at 30 °C instead of at room temperature and one for 24 h, instead of 12 h. The first reaction led to 77% imine formation (770 TON) while the second reaction resulted in almost full conversion with 980 TON (Table 1, entries 10–11).

Notably, both **BT** and CuI are crucial for this reaction, and in lack of either one there is no aldehyde or imine formation (Table 1, entries 12–13). In fact, the catalyst is actually a (**BT**)Cu complex [5a,b,25] generated in situ from **BT** and CuI under the reaction conditions, as evident from both MS and UV–Vis spectra (Figs. S7 and S8). Additionally, in the presence of **BT**, CuI showed to promote imine formation with the highest conversion compared

to other copper salts tested in 0.5 mol% loading at room temperature for 12 hours, including Cu(OTf)₂ (98%), CuCl (72%) and Cu(OAc)₂ (6%). It is also notable from Table 1, that the catalytic performance of (**BT**)Cu does not change in the loading range of 1 mol% to 0.25 mol% and only at 0.2 mol%, the activity starts to decrease with decrease in the catalysts concentration. Moreover, control experiments in which 0.2 or 0.1 mol% of Phen, CuI and TEMPO (the intermolecular catalytic system) were mixed together in the presence of compounds **1** and **2**, afforded only 21% and 16% conversion to imine **3** (105 and 160 TON), respectively. Overall, these observations support the intramolecular cooperative action mode of the catalyst (**BT**)Cu, demonstrating its ability to result in an increase of the TON in this model reaction from 160 to about 1000 at almost full conversion.

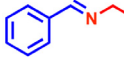
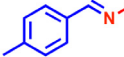
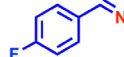
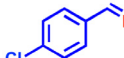
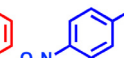
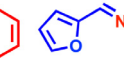
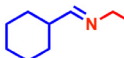
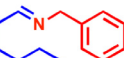
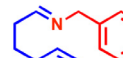
Before evaluating the substrate scope of the reaction, we have performed a kinetic study aiming to reveal the reaction pathway and to understand the effect of catalyst loading in the formation

of imine **3** from alcohol **1** and amine **2**. First, time-dependent experiments were performed under optimized conditions (Table 1, entry 8) and the product formation as well as the alcohol conversion, both analyzed by GC, were detected by continuous sampling at different time intervals. The formation of **3** as the major product was observed during the entire reaction along with a constant low amount of aldehyde (<1%) indicating that this is the intermediate in the reaction (Fig. 1a) [5a]. Second, to find out the rate of the reaction (k_{obs}) and the order of the reaction with respect to the catalysts **BT** and Cu, we conducted time dependent experiments in three more different loadings of both **BT** and CuI, namely 0.5, 0.4 and 0.3 mol%, which correspond to concentrations of 0.025, 0.02 and 0.015 mM, respectively. From the obtained data we generated three more graphs similar to the one presented in Fig. 1a, red line. Based on these results, we constructed four new graphs by plotting the concentration of imine **3** vs. the time at the first three time intervals. The slope of each linear curve represents the k_{obs} value of each reaction (Figs. S3–S6). The log of each k_{obs} value was then calculated and plotted against the log of the concentration of **BT** (Fig. 1b). The obtained straight line with a slope of $a=0$ indicates that the reaction is zero order with respect to the catalyst in the tested concentrations and in the first two hours of the reaction, providing a clear proof for the intramolecular reaction mode of our catalytic system. In contrast, the rate of the oxidation of primary alcohols to the corresponding aldehydes catalyzed by a mixture of the individual catalysts Cu and TEMPO, was found to be one with respect to these catalysts, as expected for the intermolecular system (see Scheme 1a) [5b]. Subsequently, the mechanism of this oxidation reaction was described in details by Stahl *et al.* and was supported by their experimental results [5b]. Following this proposed mechanism and the conclusion from our kinetic study, we have monitored the oxidative synthesis of imine **3** from amine **2** and alcohol **1** by MS, identified some intermediates that are comparable to the ones envisioned by Stahl *et al.* [5b] and proposed a full mechanism for this **BT**(Cu)-catalyzed oxidative synthesis of imines (Figs. S9–S12 and Scheme 1S). A summary of our proposed mechanism is shown in Scheme 2. This mechanism includes the activation of **BT** by both CuI and the reacting amine to form the initial intermediate A. Thereafter, a multi step aerobic oxidation of A lead to intermediate B, in which Cu(I) is already oxidized to Cu(II), and this further oxidizes the alcohol to aldehyde, via dehydration. In the presence of the primary amine, this aldehyde is converted to the corresponding imine by condensation. As stated above, this proposed mechanism is supported by previous literature and MS analysis.

The conditions in which >99% conversion was obtained, namely, a 12 h reaction with 0.2 mol% of **BT**/CuI at room temperature and under oxygen atmosphere, were applied to a variety alcohols and amines to extend the scope of this reaction. First, we have reacted different alcohols with benzyl amine **2** (Table 2) in order to evaluate the activity of the alcohols in this reaction. As shown in Table 2, various imines (**3–8**) could be obtained by the reaction of benzyl amine with electron-deficient and electron-rich substituent benzylic alcohols at the para position including ones having reactive functional group such as fluoro, chloro and nitro, in excellent conversions and high TON. Consequently, we have reduced the amount of **BT** and CuI to 0.1 mol% and were able to maintain the high conversion while significantly increasing the TON in the case of imines **3–6** and **8** up to 980. The use of **BT** and CuI was also efficient for the synthesis of imines from aliphatic alcohols (imines **9–12**). Although both conversions and TON were lower when less activated alcohols were used, these can still be considered excellent as the intermolecular catalytic system failed to catalyze the formation of these imines, producing only 3–8% conversion to imines **9–12**, in the same catalysts loading, with TON lower than 40.

Table 2

BT and Cu-catalyzed aerobic oxidative synthesis of imine from various alcohols and amine **2**.^a

$\text{R-OH} + \text{H}_2\text{N-Ph} \xrightarrow[\text{reaction conditions}]{\text{BT, CuI}} \text{R-N-Ph}$			
 3 , >99%, 495 TON 98%, 980 TON ^b Isolated yield: 90%	 4 , >99%, 495 TON 90%, 900 TON ^b	 5 , >99%, 495 TON 92%, 920 TON ^b Isolated yield: 93%	
 6 , >99%, 495 TON 95%, 950 TON ^b	 7 , >99%, 495 TON	 8 , >99%, 495 TON 88%, 880 TON ^b Isolated yield: 86%	
 9 , 59%, 295 TON ^c 7%, 35 TON ^{c,d}	 10 , 81%, 405 TON ^c 8%, 40 TON ^{c,d}	 11 , 79%, 390 TON ^c	 12 , 75%, 375 TON ^c 5%, 25 TON ^{c,d}

^a Reactions were performed in acetonitrile (0.5 mL) at room temperature with 2.5 mmol alcohol, 2.75 mmol amine, 0.2 mol% **BT** and 0.2 mol% CuI under oxygen atmosphere for 12 h.

^b 0.1 mol% **BT** and CuI, 24 h.

^c 24 h.

^d The intermolecular catalytic system, namely a mixture of Phen (0.2 mol%) and TEMPO (0.2 mol%) was used instead of **BT**. Conversions were determined by gas chromatography.

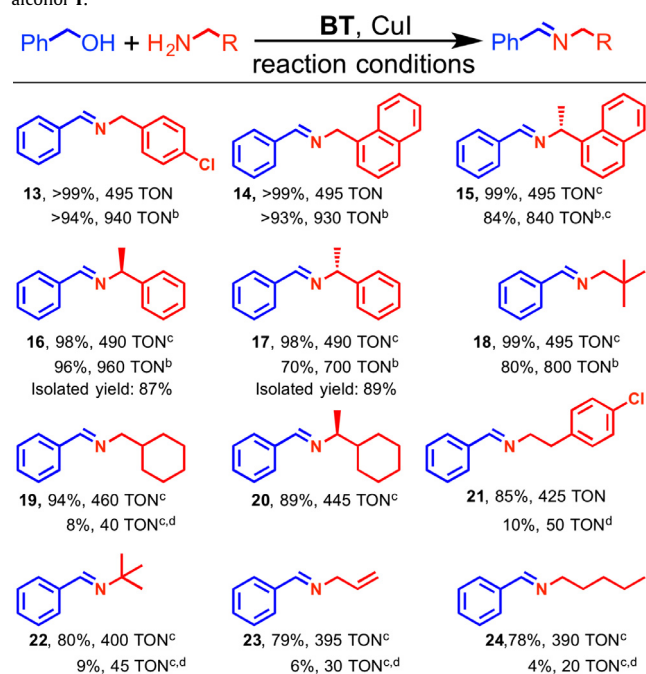
These results demonstrate the strength of our intramolecular catalytic system, which enables reactivity of alcohols that are unreactive when the intermolecular cooperative catalytic system is employed. Moreover, three selected imines, which were obtained in >99% conversion, namely **3**, **5** and **8**, were isolated from the reaction mixture by chromatography, purified and characterized by ¹H and ¹³C NMR spectroscopy (Figs. S13–S15). Isolated yields of all three imines were about 90%, consistent with the high conversions of the corresponding substrates, thus establishing the practicality of our system.

Second, we have reacted different amines with benzyl alcohol **1** (Table 3) in order to evaluate the activity of the amines in this reaction. As shown in Table 3, various imines (**13–17**) could be obtained by the reaction of benzyl alcohol **1** with aromatic amines, including the sterically more hindered α -substituted amines (chiral substituents), which produce the corresponding chiral imines in excellent to quantitative conversions with high TON. Consequently, we have reduced the amount of **BT** and CuI to 0.1 mol% and were able to maintain the high conversion while significantly increasing the TON in all cases, up to 930 and 960, respectively, for imines **14** and **16**.

The use of **BT** and CuI was also efficient for the synthesis of imines from aliphatic amines (imines **18–24**), especially in the case of imine **18**, where full conversion was achieved and high TON was obtained even when the catalysts loading was reduced to 0.1 mol%. The same trend of reduced conversions and TON when less activated alkyl alcohols were used, is also seen here with less activated amines, but again, these can still be considered excellent as the intermolecular catalytic system failed to catalyze the formation of the corresponding imines, producing only 4–10% conversion of amines **19**, **21–24**, in the same catalysts loading, with TON lower than 50. From this set, two selected imines, which were obtained in >99% conversion, namely **16** and **17**, were isolated from the reaction mixture by chromatography, purified and characterized by

Table 3

BT and Cu-catalyzed aerobic oxidative synthesis of imine from various amines and alcohol **1**.^a



^a Reactions were performed in acetonitrile (0.5 mL) at room temperature with 2.5 mmol alcohol, 2.75 mmol amine, 0.2 mol% **BT** and 0.2 mol% CuI under oxygen atmosphere for 12 h.

^b 0.1 mol% **BT** and CuI, 24 h.

^c 24 h.

^d The intermolecular catalytic system, namely a mixture of Phen (0.2 mol%) and TEMPO (0.2 mol%) was used instead of **BT**. Conversions were determined by gas chromatography.

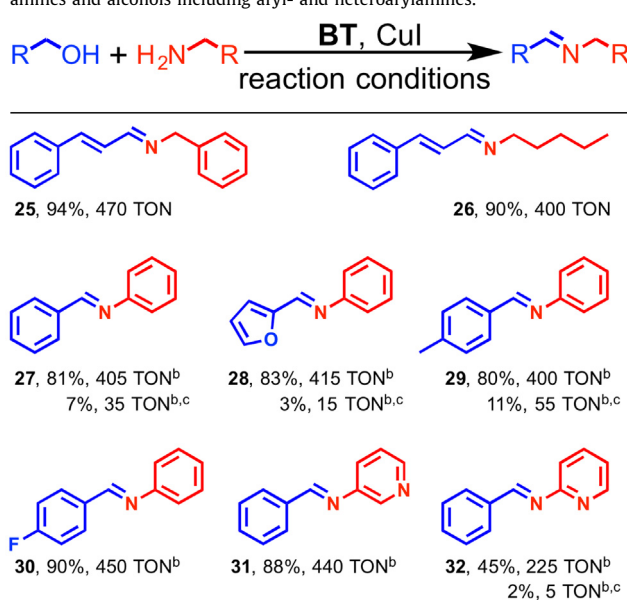
¹H and ¹³C NMR spectroscopy (Figs. S16 and S17). Isolated yields in both cases were about 90%, consistent with the high conversions of the corresponding substrates.

Finally, we wished to demonstrate the more challenging synthesis of α - β -unsaturated imines (azadienes), aryl- and heteroaryl-imines (Table 4). Azadienes play a crucial role in synthetic chemistry, specifically in the construction of hetero Diels alder reaction products [27]. As shown in Table 4, cinnamyl alcohol reacted efficiently with various amines in room temperature, when the reaction was catalyzed by 0.2 mol% **BT**/CuI for 24 h, producing azadienes **27–30** in high yields and TON. Moreover, the intramolecular cooperative catalytic system was also applicable for the synthesis of imines **31–36** from electron-deficient and much less reactive aryl- and heteroaryl amines, with good conversions and high TON of up to 450. As these amines are less basic and less nucleophilic than the aliphatic ones, they were seldom successfully used as substrates in previous reports because these reactions usually require large amounts of bases and heating at high temperatures [19,28], while in our cases, a slight heating to 35–40 °C and 2 equiv. of NMI (0.4 mol%) are employed. Moreover, control experiments showed that using the intermolecular catalytic system in the same reaction conditions resulted in conversions lower than 11%, with the highest TON being only 55. In the synthesis of imine **36**, we have obtained a TON 45 times higher when using our intramolecular cooperative catalytic system (225 TON) than when using a mixture of the individual catalysts (only 5 TON).

In summary, we have developed a general and highly efficient method, based on an intramolecular cooperative catalytic system that employs Phen and TEMPO, for the oxidative coupling of alcohols and amines to form imines under mild conditions and aerobic atmosphere. This has enabled the synthesis of various imines from

Table 4

BT and Cu-catalyzed aerobic oxidative synthesis of azadienes and imine from various amines and alcohols including aryl- and heteroaryl amines.^a



^a Reactions were performed in acetonitrile (0.5 mL) at room temperature with 2.5 mmol alcohol, 2.75 mmol amine, 0.2 mol% **BT** and 0.2 mol% CuI under oxygen atmosphere for 24 h.

^b 35–40 °C, 0.4 mol% NMI was added.

^c The intermolecular catalytic system, namely a mixture of Phen (0.2 mol%) and TEMPO (0.2 mol%) was used instead of **BT**. Conversions were determined by gas chromatography.

both activated (benzyl) as well as less activated (aryl, heteroaryl, allylic and aliphatic) primary alcohols and amines, with TON up to 45 times higher than the ones obtained using the intermolecular cooperative catalytic system, in which Phen and TEMPO are mixed together in solution. Detailed kinetic studies showed that the high activity does not depend on the catalyst concentration in the catalyst loading range of 1–0.2 mol%, establishing the intramolecular cooperative reaction mode of our catalytic system. Due to the high activity of our catalytic system, we could demonstrate its high potential in the preparation of products that are difficult to produce using the intermolecular cooperative catalytic system such as α - β -unsaturated and heteroaryl imines [10a]. The approach described herein holds promise for wide spread implementation in organic synthesis and enhancement of the practical utility of methods that use solution mixtures of individual catalysts. Moreover, This concept of intramolecular cooperative catalysis by synthetic biomimetic sequences should be generally applicable to different achiral and chiral peptidomimetic oligomers, with numerous catalysts, for a variety of efficient chemical processes including enantioselective transformations.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcat.2017.09.018>.

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