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Copper(I)-Catalyzed Highly Enantioselective [3+3]-Cycloaddition of β-Aryl/alkyl Vinyl Diazoacetates with Nitrones

--Manuscript Draft--

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Keywords:	Copper(I); enantioselective; [3+3]-cycloaddition; β-aryl/alkyl vinyl diazoacetates; nitrones
Abstract:	β-Aryl/alkyl vinyl diazoacetates were investigated in metallo-vinylcarbene reactions with nitrones, revealing a Rh 2 (OAc) 4 -catalyzed cyclopropene dimerization reaction and a copper(I) catalyzed [3+3]-cycloaddition of nitrones. The chiral cyclopropyl-In-SaBox ligand with copper(I) catalysis could realize the asymmetric version of the cycloaddition reaction, delivering various 3,6-dihydro-1,2-oxazine derivatives in good yield and with excellent enantioselectivity under mild conditions.
Response to Reviewers:	Dear Dr. Richard, We would like to sincerely thank you for arranging the prompt and thorough review of our manuscript. We were happy to find that referees were impressed with our report. Here are our comments and responses. Reviewer 1: Question 1: This reviewer would suggest the inclusion of more examples of β-alkyl vinyl diazo compounds for revision. Surrently there is only one example of 1g that provided 40% yield and 80% ee, much lower than aryl-substituted substrates. It is unclear if the lower yield and ee resulted from the alkyl substituents. Additional examples will help to bring some insight to the questions. Response: We have synthesized two β-alkyl vinyl diazo compounds (1i: β-Bn and 1j: β-CH2CH2OTBS) and tested their reactivities in [3+3]-cycloaddition reaction, the corresponding products 6i and 6j were isolated in 36% yield, 57% ee and 20% yield, 83% ee, separately. These results have indicated, as expected, that the β-alkyl vinyl diazo compounds give a much lower yield and ee compare with β-aryl vinyl diazo compounds. Question 2: There are some typos or minor mistakes found in the manuscript. Response: These typos or minor mistakes have been corrected. Reviewer 2: Question 1: I am not a fan of the default chemdraw arrows and encourage authors to draw their own mechanistic arrows with the tool that looks like a fountain pen. In looking at Scheme 2, I think novice readers would struggle to understand the mechanistic arrows. Specifically in box A electrons appear to be attacking a Ph group, and in box B the TBS oxygen is not donating electrons to the carbon to which it is attached, but rather an adjacent carbon. These sloppy drawings should be more carefully crafted. Given the discussion in Scheme 2 showing formation of 5 or 6 membered rings, it is instinctive to expect a statement or see in the graphic that the 5 membered ring product is not observed in Table 2. I think "Ene" reaction should not be capitalized. Efficient formation of 6g is somewhat surprising, and additional commentary would be appreciated. Methyl seems a rather poor donor to push the reaction one way so effectively.

	Fix "3chiral" in the Conclusions. SI page 2, I find the use of bolded bonds to indicate where bond formation occurred not necessary, as most readers of the SI will have read the manuscript first. The bold lines can be confusing. Consider using color if showing bond formation is desired. Response: The Chemdraw arrows in Scheme 2 has been carefully revised, and the statements and revisions have been added in the right place. Question 2: Only 6c is representative of a moderately electron withdrawing group on the diazo component. Are more electron withdrawing groups compatible? Response: We synthesized a more electron withdrawing group (CF3) substituted vinyl diazo compound 1d and tested the reaction of nitrone 5a, the desired product 6d could be obtained in 31% yield and 85% ee. These results are consistent with our proposal. Reviewer 3: Question: - Adding an hypothesis/explanation for the fact that formation of 2a is slow for Cu but fast for Rh would be good (reduced electrophilicity for Cu-carbenes compared to Rh-carbenes?) Response: The explanation has been added in the appropriate place. “These reactions suggested that the donor-acceptor cyclopropenes are formed at a much slower rate with Cu(I) than with either Rh(II) or Ag(I) catalysts, presumably because Cu(I) tetrakis(acetonitrile) is less capable of association with the polarized C=C than are either rhodium(II)acetate or AgNTf2.” Other errors, including the footnotes, reference [15] (CCDC numbers), graphical abstract have also been corrected.
Additional Information:	
Question	**Response**
Submitted solely to this journal?	Yes
Has there been a previous version?	No
Dedication	Dedicated to Prof. E. Peter Kündig on the occasion of his 75th birthday.
The corresponding author(s) and co-author(s) have the option of making their article open access through our OnlineOpen service (fee applicable). Please indicate here if you are likely to publish your article in an open-access format.	No / Don't know

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Copper(I)-Catalyzed Highly Enantioselective [3+3]-Cycloaddition of β-Aryl/alkyl Vinyl Diazoacetates with Nitrones

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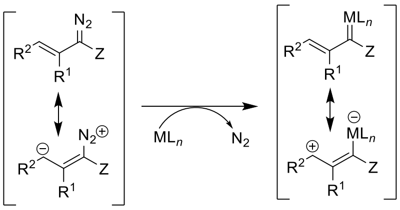
Dedicated to Prof. *E. Peter Kündig* on the occasion of his 75th birthday.

β-Aryl/alkyl vinyl diazoacetates were investigated in metallo-vinylcarbene reactions with nitrones, revealing a $Rh_2(OAc)_4$-catalyzed cyclopropene dimerization reaction and a copper(I) catalyzed [3+3]-cycloaddition of nitrones. The chiral cyclopropyl-In-SaBox ligand with copper(I) catalysis could realize the asymmetric versionof the cycloaddition reaction, delivering various 3,6-dihydro-1,2-oxazine derivatives in good yield and with excellent enantioselectivity under mild conditions.

Keywords: Copper(I)• enantioselective • [3+3]-cycloaddition • β-aryl/alkyl vinyl diazoacetates • nitrones

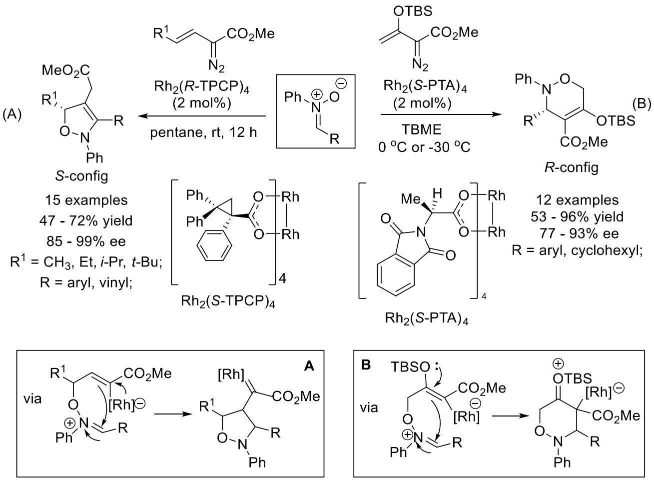
Introduction

Because of their dipolar character, vinyl diazo compounds are uniquely suited to undergo a greater diversity of transformations than their alkyl, aryl, or acyl counterparts.[1-5] Polarization from the diazo functional group renders the vinylogous carbon of vinyl diazo compounds nucleophilic and for metallo-vinylcarbenes electrophilic (Scheme 1). This is especially evident in vinylogous addition and cycloaddition reactions of styryldiazoacetates and enoldiazoacetates catalyzed by dirhodium(II), copper(I), and gold(I) catalysts.[6-9]



Scheme 1. Umpolung from vinyl diazo compounds to metallo-vinylcarbenes.

There are differences in the outcome of reactions with styryldiazoacetates and their alkyl counterparts compared to those with enoldiazoacetates, and an explanation has been given in dirhodium(II) catalyzed reactions with nitrones that this difference is due to the configurational differences of the intermediate vinylogous ylides.[10] In comparison, however, silyl-group protected enol diazo compounds have shown a remarkable facility to undergo [3+*n*, *n* = 1-5]-cycloaddition reactions.[11] An example of the differences of vinyl diazoacetates with γ-aryl or alkyl groups[10] compared with those having a β-siloxy group[12] in cycloaddition reactions with nitrones is provided in Scheme 2. This divergence was reported to be due to conformational influences by the carbene on the dirhodium(II) framework.[10] Our explanation of the difference in product formation is that the stabilization afforded the intermediate by electron donation from the silyl ether (**B**) is not available to vinyl diazoacetates with γ-aryl or alkyl groups (**A**). We anticipated that other electron donating groups at the β position would also allow cycloadditions like those of enoldiazoacetates, and we have selected β-aryl and alkyl substituents for this study. Obviously, strong electron-donating groups in place of the siloxy group (e.g., OR, OAc, halide) in these vinyl diazo compounds should facilitate cycloaddition reactions with the same or similar yields and selectivities, but these compounds are not yet accessible.

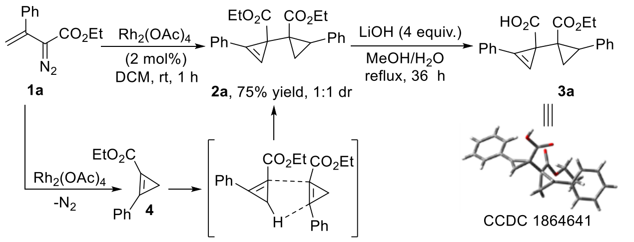


Scheme 2. (**A**) The γ-alkyl or aryl group of vinyl diazo compounds favors cycloaddition to the carbon-carbon double bond. (**B**) The β-siloxy group of vinyl diazo compounds provides a pathway for [3+3]-cycloaddition.

Results and Discussion

We began our investigation by choosing ethyl 2-diazo-3-phenylbutanoate (**1a**) as the model substrate. We anticipated that, like enoldiazoacetates, **1a** would form its corresponding donor-acceptor cyclopropene via its metallo-vinylcarbene intermediate,[13] but that this cyclopropene would be a resting state for the metallo-vinylcarbene.[14] Instead, using commercially available

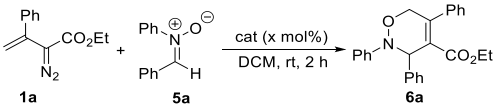
$Rh_2(OAc)_4$ as the catalyst, dimerization of the anticipated donor-acceptor cyclopropene proceeded with high efficiency in DCM at room temperature. The corresponding product **2a** was isolated in 75% yield with 1:1 dr, and the structure of derivative **3a** was confirmed by X-ray diffraction (Scheme 3).[1] This result confirmed the formation of donor-acceptor cyclopropene **4** as the reaction intermediate and its dimerization by a presumed intermolecular ene reaction to give the final product **2a**.[15-16]



Scheme 3. $Rh_2(OAc)_4$-catalysed dimerization of β-phenylvinyldiazoacetate **1a**.

Would the intermolecular ene reaction prevent access by β-arylvinyldiazoacetates to [3+*n*]-cycloaddition reactions? To address this question, we turned our attention to the metal catalyzed [3+3]-cycloaddition reaction of **1a** with nitrone **5a**. Various metal catalysts were employed, and the results are summarized in Table 1. Use of $Rh_2(OAc)_4$ and $AgNTf_2$ catalysts, which were efficient catalysts in previous cycloaddition of enoldiazo compounds,[5, 7, 10] gave only trace amounts of the cycloaddition product **6a**. Spectral analyses showed that dimerization was the dominant process (Table 1, entries 1 and 2). In addition, gold(I) catalysts, including IPrAuCl, JohnPhoAuCl, and even JohnPhoAu(CH_3CN)SbF_6, were less reactive, and mostly starting material remained after a reaction time of 2 h (Table1, entries 3-5). Fortunately, when the reaction was performed in the presence of copper(I) catalyst $Cu(CH_3CN)_4BF_4$, the desired [3+3]-cycloaddition reaction occurred instead of the dimerization reaction, affording **6a** in 67% yield (Table 1, entry 6). These reactions suggested that the donor-acceptor cyclopropenes are formed at a much slower rate with Cu(I) than with either Rh(II) or Ag(I) catalysts, presumably because Cu(I) tetrakis(acetonitrile) is less capable of association with the polarized C=C than are either rhodium(II)acetate or AgNTf2.

Table 1. metal-catalyzed [3+3]-cycloaddition of β-phenyl vinyl diazoacetate **1a** and nitrone **5a.**

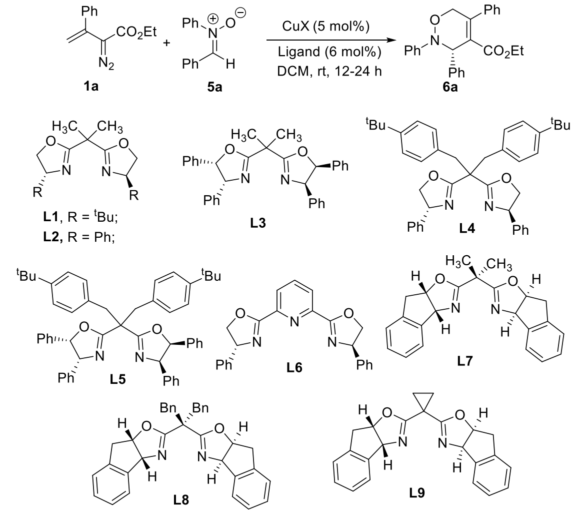


Entry[a]	Cat	X mol%	Yield of 6a (%)[b]
1	$Rh_2(OAc)_4$	2 mol%	5% (84% yield of **2a**)
2	$AgNTf_2$	5 mol%	trace (90% yield of **2a**)
3	IPrAuCl	5 mol%	No reaction
4	JohnPhoAuCl	5 mol%	No reaction
5	JohnPhoAu(CH_3CN)SbF_6	5 mol%	trace
6	$Cu(CH_3CN)_4BF_4$	5 mol%	67% (trace amount of **2a**)

[a] Reactions were performed with **1a** (0.2 mmol) and **5a** (0.2 mmol) in DCM (2 mL) for 2 h. [b] Yields of isolated product.

Recent progress with enantioselective cycloaddition reactions of enoldiazo compounds[17-19] prompted us to examine enantiocontrol in the [3+3] cycloaddition of β-aryl/alkyl vinyldiazoacetates with nitrones catalyzed by copper(I) complexes with chiral ligands. Various Box ligands coordinated with $Cu(CH_3CN)_4BF_4$ were evaluated, and the results are summarized in Table 2. Bidentate ligands (bis-oxazoline) (**L1**-**L3**), double-side arm bisoxazoline (Sabox) ligands (**L4** and **L5**), and a tridentate ligand (Pybox) (**L6**) revealed that **6a** was generated in only low to moderate yields and enantiomeric excesses (Table 2, entries 1-5). Fortunately, the In-SaBox ligands showed a higher reactivity and enantioselectivity (Table 2, entries 6-9), and the cyclopropyl-In-SaBox **L9** stood out as the best choice (entry 9) with **6a** formed in 40% yield with 86% ee. Further optimization by changing the ratio of reactants revealed that use of 1.5 equivalent vinyl diazoacetate **1a** improved the yield of **6a** to 70% (Table 2, entries 10 and 11). The counter ion of tetrakis(acetonitrile) copper(I) complexes has little influence on the results (Table 2. entries 11 and 12) but use of copper(I) triflate resulted in a significant decrease in product yield. Decreasing the reaction temperature to 0 °C and prolonging the reaction to 24 h gave the best results (Table 2, entry 14).

Table 2. Optimization of copper(I) catalyzed asymmetric [3+3]-cycloaddition of β-phenyl vinyl diazoacetate **1a** and nitrone **5a.**



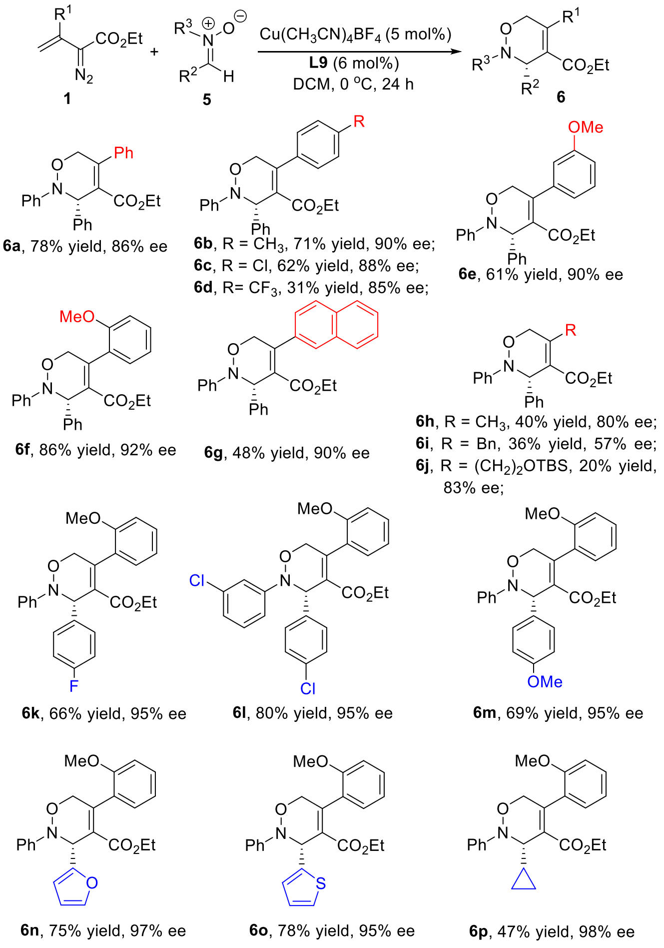
Entry[a]	CuX/Ligand	Yield of 6a (%)[b]	ee of 6a (%)[c]
1	$Cu(CH_3CN)_4 \cdot BF_4$/**L1**	72	race
2	$Cu(CH_3CN)_4 \cdot BF_4$/**L2**	55	14
3	$Cu(CH_3CN)_4 \cdot BF_4$/**L3**	12	40
4	$Cu(CH_3CN)_4 \cdot BF_4$/**L4**	10	86
5	$Cu(CH_3CN)_4 \cdot BF_4$/**L5**	30	9
6	$Cu(CH_3CN)_4 \cdot BF_4$/**L6**	72	race
7	$Cu(CH_3CN)_4 \cdot BF_4$/**L7**	31	70
8	$Cu(CH_3CN)_4 \cdot BF_4$/**L8**	13	73
9	$Cu(CH_3CN)_4 \cdot BF_4$/**L9**	40	86

10[d]	$Cu(CH_3CN)_4 \cdot BF_4$/**L9**	55	86
11[e]	$Cu(CH_3CN)_4 \cdot BF_4$/**L9**	70	86
12 [e],[f]	$Cu(CH_3CN)_4 \cdot PF_6$/**L9**	75	86
13[e],[f]	$(CuOTf)_2$·toluene/**L9**	45	86
14[e],[f]	$Cu(CH_3CN)_4 \cdot BF_4$/**L9**	78	86
15[e],[g]	$Cu(CH_3CN)_4 \cdot BF_4$/**L9**	<10	-

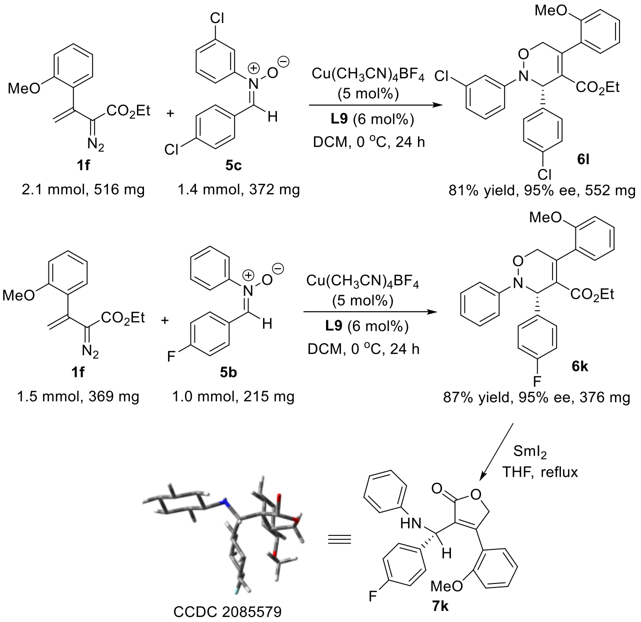
[a] Reactions were performed with **1a** (0.2 mmol), **5a** (0.2 mmol), CuX (5 mol%) and **ligand** (6 mol%) in DCM (2 mL) for 12 h. [b] Yield of isolated product. [c] ee value was determined by HPLC. [d] 1.5 equiv. **5a** was used. [e] 1.5 equiv. **1a** was used. [f] Reaction was carried out at 0 °C for 24 h. [g] Reaction was carried out at -20 °C for 24 h.

With the optimized reaction conditions in hand, we examined the scope of copper(I) catalyzed asymmetric [3+3]-cycloaddition of β-aryl/alkyl vinyl diazoacetates **1** and nitrones **5** (Scheme 4). Vinyl diazoacetates with modest electron-withdrawing or electron-donating substituents on the para-position of phenyl ring produced the corresponding products **6b** and **6c** in good yields and enantioselectivities (71% yield, 90% ee and 62% yield, 88% ee, respectively). However, strong electron-withdrawing group (CF_3) on the para-position of phenyl ring could only give the desired product **6d** in 31% yield with 85% ee. In addition, substituents on the ortho- and meta-position of the phenyl ring were also tolerated, and the ortho-methoxyphenyl substituted vinyl diazoacetate afford the desired product **6f** in 86% yield with 92% ee. However, due to the strong electron-donation effect on the para position, the precursor for the synthesis of β-para-methoxyphenyl substituted vinyl diazoacetaste was not accessible. The β-naphthyl substituted vinyl diazo compound **1g** underwent the reaction, giving product **6g** in 48% yield and 90% ee. As we expected, the β-alkyl substituted vinyl diazo compounds (**1h-1j**) reacted with nitrone **5a** to provide the cycloaddition products (**6h-6j**) in lower yields and selectivities (20%-40% yields and 57%-83% ees).

Since the ortho-methoxyphenyl substituted vinyl diazoacetate **1f** provided the highest yield and stereocontrol, additional reactions with nitrones were performed with this reactant. The results (Scheme 5) show that electron-deficient (**5b** and **5c**) or -rich (**5d**) substituents on the aryl group of the nitrone reacted with **1f** smoothly to give the corresponding products in good yields (66–80%) and with excellent enantioselectivities (95% ee, **6k–6m**). Heterocycle-substituted nitrones like 2-furyl nitrone (**5e**) and 2-thiophenyl (**5f**) also delivered the desired products with isolated yields above 78% and up to 97% ee. When the *N*-phenylnitrone with a *C*-cyclopropyl group was used (**5g**), the cycloaddition product (**6p**) was obtained in moderate yield (47%) with excellent enantioselectivity (98% ee). In addition, large-scale reactions were performed between **1f** and **5c** or **5b**, and the 3,6-dihydro-1,2-oxazine products **6l** and **6k** were isolated in 81% yield and 87% yield, respectively, with 95% ee (Scheme 5). Furthermore, the absolute configuration of 3,6-dihydro-1,2-oxazine **6k** was determined to be (*S*) by X-ray diffraction of the derivative **7k**.[1]



Scheme 4. Scope of copper(I) catalyzed asymmetric [3+3] cycloaddition of β-aryl/alkyl vinyl diazoacetates **1** and nitrones **5**.



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[1] CCDC 1864641 (**3a**) and 2085579 (**7k**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Scheme 5. Large scale reaction.

Based on the experimental data, a probable reaction mechanism for copper(I)-catalyzed [3+3]-cycloaddition of β-aryl vinyl diazoacetates with nitrones is proposed in Figure 1. The copper(I) complex reacts with vinyl diazoacetate **1** to give metallo-vinylcarbene intermediate **int-I**. Subsequently, **int-II** is captured by nitrone **5** to afford the **int-II**. Intramolecular cyclization of **int-II**, and elimination of copper(I) complex delivers the final 3,6-dihydro-1,2-oxazine product **6**. Significantly, compared to the [3+3]-cycloaddition process using rhodium(II) or silver(I) catalysts, the copper(I) catalyzed formation of donor-acceptor cyclopropenes and their subsequent dimerization is much slower; only trace amounts of dimerization products were detected in the copper(I) catalysed reactions.

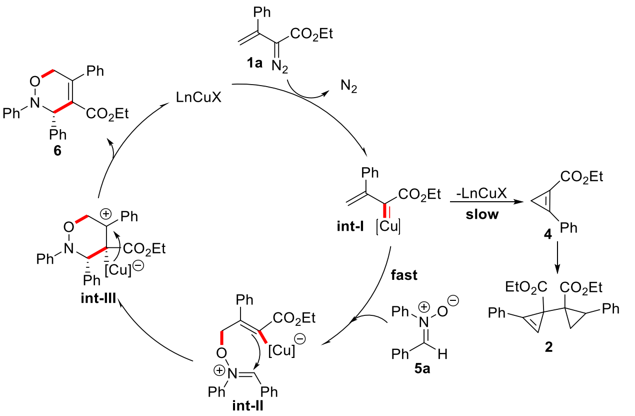

Figure 1. Proposed Reaction Mechanism.

Conclusions

In summary, we have realized $Rh_2(OAc)_4$ catalyzed dimerization reaction of β-phenyl vinyl diazoacetate, and copper(I) catalyzed [3+3]-cycloaddition of β-aryl/alkyl vinyl diazoacetate with nitrones. In addition, the chiral cyclopropyl-In-SaBox ligand with a cationic copper(I) catalyst provides the asymmetric [3+3] version, delivering various 3,6-dihydro-1,2-oxazine derivatives in good yield and excellent enantioselectivity.

Acknowledgements

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Author Contribution Statement

M. P. Doyle conceived this work. H. F. Zheng designed and performed the experiments. I. Faghihi synthesized some vinyl diazoacetates and nitrone substrates. H. F. Zheng and M. P. Doyle discussed the results and wrote the manuscript.

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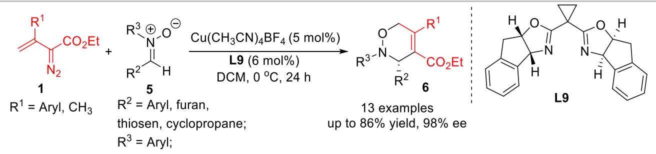

Twitter

Beta-substituted vinyl diazoacetates undergo a rhodium(II)-catalyzed cyclopropene dimerization but a copper(I) catalyzed [3+3]-cycloaddition with nitrones.

Supporting Information

Figure1

Scheme 1

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Native Chemdraw files
scheme 1.cdx

Scheme 2

Scheme 3

Scheme 4

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Scheme 5

Table 1

Table 2

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