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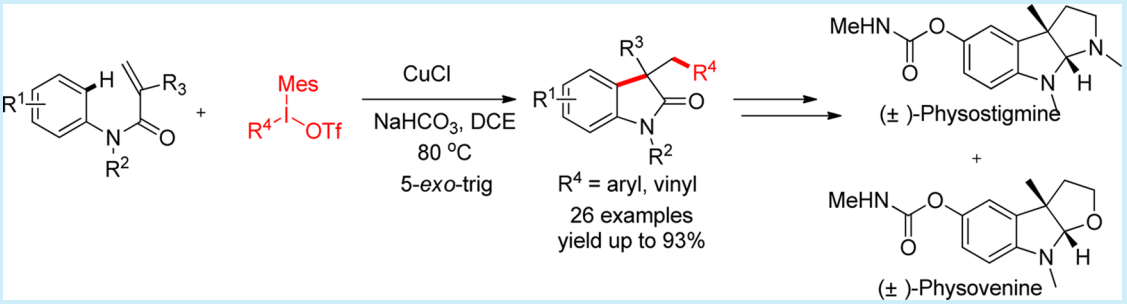
Copper(I)-Catalyzed Aryl or Vinyl Addition to Electron-Deficient Alkenes Cascaded by Cationic Cyclization

Bing Zhou,* Wei Hou, Yaxi Yang, Huijin Feng, and Yuanchao Li*

Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 555 Zu Chong Zhi Road, Shanghai 201203, PR China

Supporting Information



ABSTRACT: An exoselective copper-catalyzed arylation− and vinylation−carbocyclization of electron-deficient alkenes was developed to provide rapid and efficient access to a variety of functionalized 3,3-disubstituted oxindoles. With this method, a highly efficient and concise formal synthesis of (±)-physostigmine and (±)-physovenine has been completed.

Selective conjugated addition of aryl and alkenyl groups to electron-deficient alkenes was conventionally achievable through nucleophilic addition of aryl or alkenyl anions such as aryl cuprates and other organometallic reagents.[1] These reactions are the foundations and very important for organic synthesis. However, these approaches require the use of stoichiometric organometallic reagents and often suffer from harsh conditions and low functional group tolerance. Catalytic addition to alkenes using aryl radicals has certain advantages, but using alkenyl radicals is very rare.[2] Therefore, the further development of catalytic methods for introduction of aryl and vinyl groups to alkenes is highly desirable and of prime synthetic value.

A combination of Cu catalyst and diaryliodonium salts[3] has recently emerged as a very useful and efficient strategy for arylation via a high oxidation state Cu(III)−aryl intermediate which behaves as an activated aromatic electrophile.[4] Despite great advances, arylation of alkenes remain relatively unexplored.[5−7] In 2012, Gaunt and co-workers reported the first example of Cu(I)-catalyzed arylation of simple alkenes with diaryliodonium salts.[5] When cyclic electron-rich enamides were employed as substrates, the aryl groups of diaryliodonium salts were transferred to C-3 position of enamides.[6] Very recently, a CuCl-catalyzed arylation of allylic amide followed by trapping carbocation with oxygen atom of amide carbonyl group was reported to furnish 5,6-dihydro-4*H*-1,3-oxazines.[7]

Despite the significance of the aforementioned works, the scope of the reported alkene substrates is limited to electron-rich or simple alkenes, and there is no report on arylation and vinylation of electron-deficient alkenes, thus proving to be a formidable challenge. In continuation of our interest in transition-metal-catalyzed C−H functionalization,[8] we herein report the first example of copper-catalyzed arylation− and vinylation−carbocyclization of electron-deficient alkenes with diaryliodonium and vinyl(aryl)iodonium salts. The reaction yields a class of highly functionalized 3,3′-dicarbonsubstituted oxindoles,[9,10] which feature motifs found in a number of bioactive natural products and pharmaceutical molecules.[11]

Our synthetic attempts began with reaction of **1a** and diphenyliodonium salt (**2a**) under different catalysts (Table S1, Supporting Information). Only a trace amount of anticipated product **3a** (for the structure, see Scheme 1) was detected using CuCl, CuTc, or CuOTf as catalyst. To our delight, when phenylmesityliodonium salt (**2b**) was used as the aryl donor and CuCl as the catalyst, **3a** was isolated in 30% yield. Subsequently, various Cu- and Fe-based catalysts were screened. CuCl gave a relatively higher yield than $FeCl_2$ and other Cu(I) salts such as CuOAc, CuOTf, and CuTc. We also examined the effect of bases because previous studies showed that an addition of 2,6-di-*tert*-butylpyridine was crucial for Cu-catalyzed aryl transfer.[3−6] Surprisingly, the desired product **3a** was not detected when 2,6-di-*tert*-butylpyridine (DTBP) or pyridine was added. Interestingly, a dramatic increase of reaction yield (57%) was observed when $NaHCO_3$ was employed . In order to further improve the yield, a series of solvents were screened, and DCE was found to be optimal (77% yield). No product **3a** was observed in the absence of CuCl or in the presence of Cu(II) salts such as $Cu(OAc)_2$ and $CuCl_2$, indicating the importance of Cu(I) species for successful aryl transfer.

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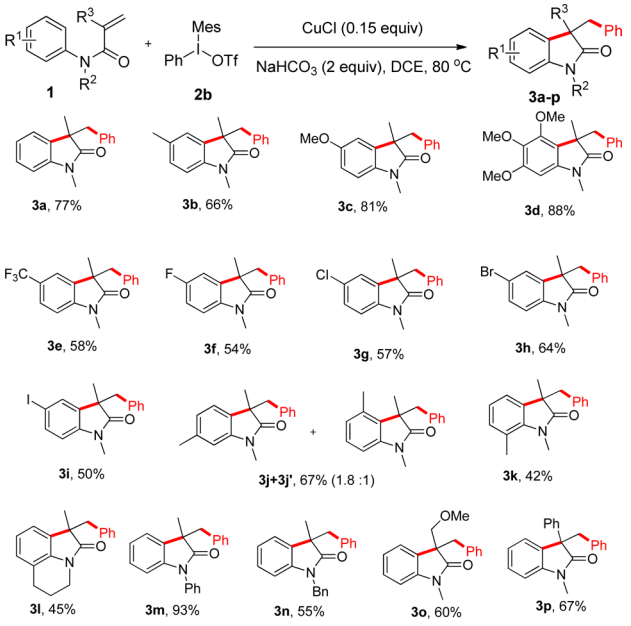
Scheme 1. Substrate Scope[a]

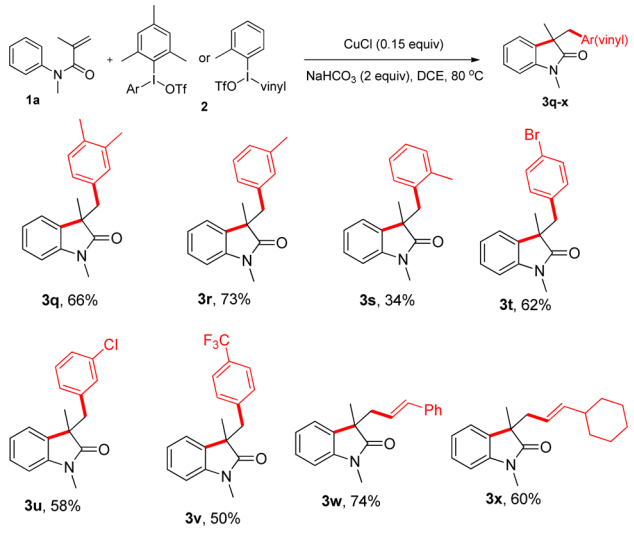


[a]Isolated yields. See the Supporting Information for details.

With the optimized reaction conditions in hand, the substrate scope of phenylacrylamide was subsequently explored, and the results are summarized in Scheme 1. Generally, phenylacrylamides tethering electron-donating groups on the phenyl ring were successfully converted to the desired products (**3b**–**d**) in good yield (66–88%). The phenylacrylamides tethering an electron-withdrawing CF_3 group on the phenyl ring provided **3e** in relatively low yield (58%). Notably, the halo substitutions (F, Cl, Br, and I) on *N*-phenylacrylamides were well tolerated, providing the corresponding oxindoles in 50–64% yield (**3f**–**i**). The substrate bearing a *meta* methyl group on phenylacrylamide gave a mixture of two regioisomers in 67% yield with poor selectivity (**3j**:**3j′** = 1.8:1). The phenylacrylamide with methyl groups at the *ortho* position produced a relatively low yield of **3k** (42%). To our delight, a novel tricyclic oxindole derivative **3l** was successfully obtained in 45% yield from the corresponding tetrahydroquinoline substrate. When the *N*-methyl substituent of phenylacrylamide was replaced by a phenyl group, the reaction yield of **3m** was increased to 93%. The *N*-benzyl derivative was also compatible with the reaction conditions, affording the corresponding product **3n** in 55% yield. To our delight, when the R^3 group was CH_2OMe or phenyl, the corresponding acrylamides were also compatible with the optimal conditions, affording **3o** and **3p** in moderate yield.

The substrate scope of diaryliodonium salts was also examined (Scheme 2). Diaryliodonium salts tethering a methyl group at the *para* and *meta* position of the phenyl ring were tolerable, affording **3q** and **3r** in 66% and 73% yield, respectively. However, diaryliodonium salt bearing a methyl group at *ortho* position of the phenyl ring produced **3s** in low yield (34%), suggesting the steric hindrance of the aryl group attenuates the reactivity of its transfer. Halogen (**3t** and **3u**) and electron-withdrawing (**3v**) substituents were well tolerated, emphasizing the generality of this method. Furthemore, we tested whether alkenyl transfer to phenylacrylamide **1a** was possible using vinylmesityliodonium triflates as reagents.[12] To our great delight, styrenyl- and cyclohexyl-substituted vinyl

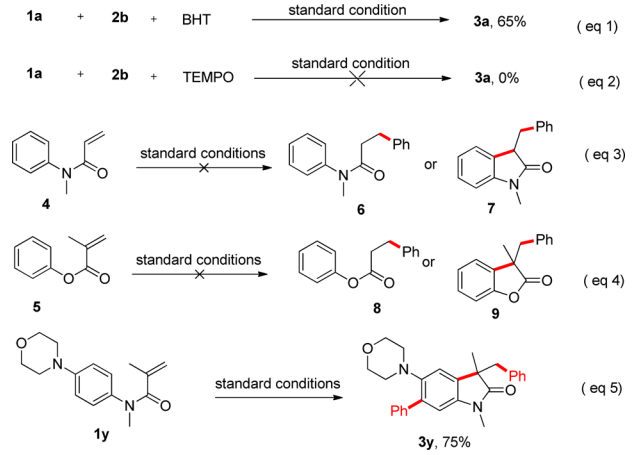
Scheme 2. Substrate Scope of Aryliodonium Salts[a]



[a]Isolated yields. See the Supporting Information for details.

were readily transferred, affording the corresponding vinyl-substituted oxindoles in good yields (74% of **3w** and 60% of **3x**). To the best of our knowledge, this is the first example of Cu-catalyzed 1,2-vinylarylation of an electron-deficient alkene.[13]

To gain additional mechanistic insights, we carried out several control experiments. First, we performed reactions of **1a** and **2b** in the presence of radical scavengers (2 equiv) under optimal reaction conditions (eq 1 and 2). In the presence of



radical scavenger 2,6-di-*tert*-butyl-4-methylphenol (BHT), the product **3a** was isolated in 65% yield. On the contrary, we did not isolate any **3a** in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (2 equiv). We surmised that the detrimental effect of TEMPO could result from its interaction with Cu(I), leading to Cu(II)[14] which has proven ineffective for this reaction. In addition, reaction of phenylacrylamides **4** and **5** with **2b** under the standard reaction conditions provided no products of **6**–**9** but recovery of **4** and **5** (eqs 3 and 4). If an electrophilic Cu(III)–phenyl species was involved, the monosubstituted olefin of **4** and the phenol ester of **5** make both substrates less nucleophilic than **1a**, which could account for the observed lower reactivity. In addition, when phenylacrylamide **1y** was used as the substrate, we isolated **3y** in 75% yield with a second arylation on the phenyl ring of **1y** (eq 5).

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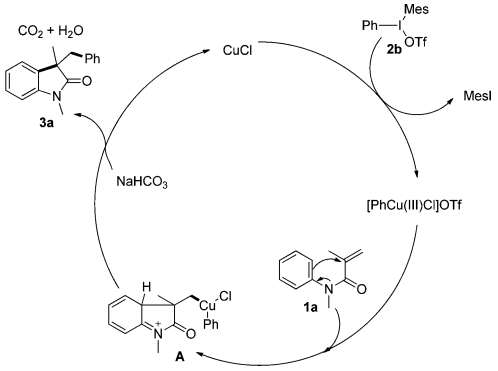
The Cu(III)−phenyl species undergoes a electrophilic addition to the very electron-rich phenyl ring of **1y** followed by reductive elimination and tautomerization, which could account for the formation of **3y** rather than a radical pathway.

In view of our data presented above, we tentatively proposed a cationic reaction mechanism as shown in Scheme 3. Initially,

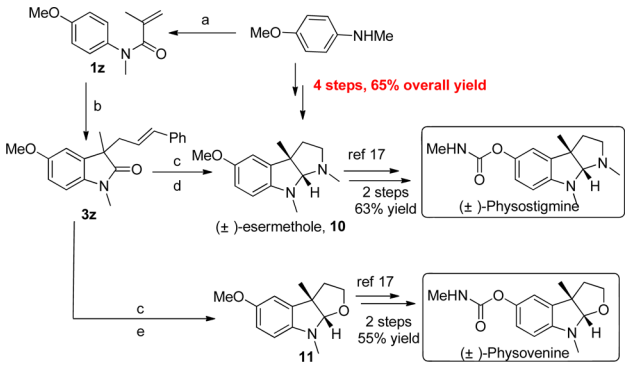
Scheme 3. Proposed Reaction Mechanism



an oxidative insertion of Cu(I) into the diaryliodonium salt gives an electrophilic Cu(III)−aryl intermediate which undergoes an electrophilic addition to afford intermediate **A**. Finally, rearomatization and reductive elimination provide the desired oxindole **3a** and regenerate Cu(I) catalyst.

In order to demonstrate the strength of our methodology, it was applied to accomplish concise formal total syntheses of (±)-physostigmine and (±)-physovenine (Scheme 4).

Scheme 4. Formal Total Synthesis of (±)-Physovenine and (±)-Physostigmine[a]



[a]Reaction conditions: (a) methacryloyl chloride, Et_3N, DCM, rt, overnight, 95%; (b) vinyl(aryl)iodonium triflates, CuCl, $NaHCO_3$, DCE, 80 °C, 3 h under Ar atmosphere, 80% yield; (c) O_3, DCM/MeOH = 1:1, −78 °C, 3 min; then Me_2S, rt, 94%; (d) $MeNH_2$·HCl, Et_3N, $MgSO_4$, THF; then $LiAlH_4$, THF, reflux, 90%; (e) $LiAlH_4$, THF, rt, 92%.

(−)-Physostigmine is a natural alkaloid that shows potent inhibitory activities against acetylcholinesterase and butyrylcholinesterase.[15] (−)-Physostigmine has been a marketed drug for treatment of glaucoma and severe anticholinergic toxicity, and (−)-physovenine has biological activities in vitro and in animal models similar to those of (−)-physostigmine.[15,16] Treatment of 4-methoxy-*N*-methylaniline with methacryloyl chloride afforded conjugated enamide **1z**, which was subsequently subjected to the key Cu(I)-catalyzed vinylation−cyclization, providing the desired **3z** in 76% yield over two steps. Ozonolysis of **3z** followed by reductive amination in the presence of methylamine and $LiAlH_4$ furnished (±)-esermethole **10** in 86% yield over two steps. Additional two-step modification[17] of **10** yielded (±)-physostigmine in 63% yield. On the other hand, ozonolysis of **3z** followed by direct reduction with $LiAlH_4$ at room temperature gave tricyclic amine **11** in 88% yield over two steps. (±)-Physovenine has been synthesized from **11** in two steps.[17] Thus, Cu(I)-catalyzed vinylation−carbocyclization enables the formal total synthesis of (±)-physostigmine and (±)-physovenine in a very efficiant manner.[17]

In conclusion, we have developed a novel copper(I) chloride catalyzed 1,2-diarylation or vinylarylation of electron-deficient alkenes. This transformation tolerates a wide range of diaryl- and vinyl(aryl)iodonium triflates and versatile substitutions on phenylacrylamides, providing efficient access to a variety of functionalized 3,3-disubstituted oxindoles. Using the vinyl addition−cyclization method, highly efficient and concise formal syntheses of (±)-physostigmine and (±)-physovenine have been accomplished in six steps in 41% and 36% overall yield, respectively. Further applications of the method in the syntheses of complex bioactive natural products and analogues are currently in progress and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization of products, and copies of ^1H and ^{13}C NMR spectra. The material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhoubing2012@hotmail.com.
*E-mail: ycli@mail.shcnc.ac.cn.

Notes

The authors declare no competing financial interest.

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