

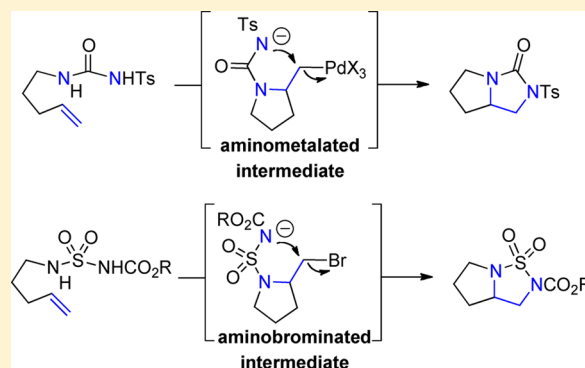
Development of Intramolecular Vicinal Diamination of Alkenes: From Palladium to Bromine Catalysis

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ABSTRACT: Palladium catalysis has been instrumental in the development of the intramolecular diamination of alkenes. Reagent combinations of a palladium catalyst and iodosobenzene diacetate or copper(II) salts, respectively, represent the broad applicability and mechanistic variation. Recent work has established alternative copper and bromine catalysts. The occupation with this reaction has also contributed to the development of high oxidation state metal catalysis in alkene difunctionalization and significantly broadened the spectrum of Pd-catalyzed C–N bond-forming reactions in general.



Vicinal diamines constitute an important functional motif in organic chemistry.¹ They are present in a variety of molecules of biological and pharmaceutical interest, serve as useful building blocks in synthesis, and represent excellent ligands for functional transition metal complexes or for advanced polymeric ligands in supramolecular recognition events. The synthetic approach to this class of compounds usually requires multistep transformations. An attractive route should consist of a direct diamination of alkenes, following the successful development of the now well-established dihydroxylation and aminohydroxylation reactions.^{2,3} Prior to 2005, a series of metal-mediated processes demonstrated the general feasibility of such an approach. These reactions were summarized previously.^{4,5}

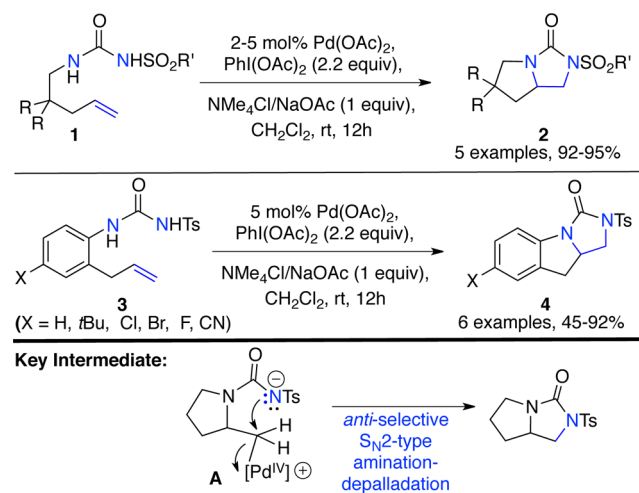
METHOD DEVELOPMENT

The advent of metal-catalyzed oxidation reaction for intramolecular diamination of alkenes has greatly improved the access to this class of compounds.^{6,7} In particular, the development of suitable palladium catalysis has been instrumental in realizing the first examples of intramolecular diamination reactions of unfunctionalized alkenes.

In 2005, we reported the first successful example of this type of transformation.⁸ *N*-Sulfonylated ureas were used as nitrogen source in the oxidation of tethered ω -alkenes **1** and **3**. A combination of a catalytic amount of palladium acetate and iodosobenzene diacetate as oxidant together with an acetate base were identified as suitable conditions for this diamination. The overall transformation proceeds under remarkably mild conditions and is characterized by its robustness as several commercially available palladium salts and hypervalent iodine reagents promote it. A range of substrates undergoes this transformation that is particularly efficient for formation of five-

membered annelated ring products **2** and **4** (Scheme 1). Six- and seven-membered ring annelation proceeds as well, although the former ones require significantly enhanced reaction times.

Scheme 1. Palladium-Catalyzed Diamination of Alkenes Using Ureas as Nitrogen Sources



This reaction was identified as an example of the growing class of palladium(II/IV) catalysis.^{9,10} An account of the mechanistic details has been provided.¹¹ On the basis of NMR titration studies, deuterium labeling, and Hammett correlation studies, a conclusive picture of the catalytic cycle was obtained. The underlying reaction concept is best described as a two-step

Received: November 29, 2012

Published: February 25, 2013

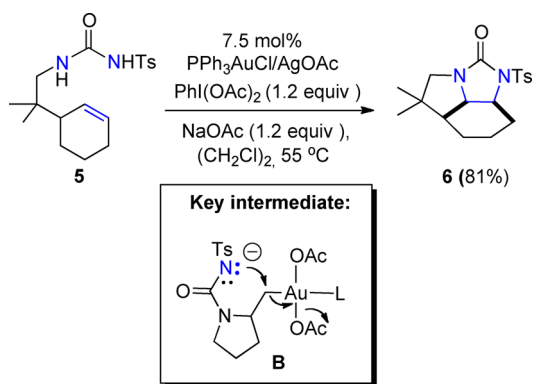
process consisting of a rate-limiting intramolecular *syn*-aminopalladation^{12,13} followed by a second C–N bond formation that proceeds through a palladium(IV) catalyst state A.

Based on labeling studies, the final C–N bond formation must proceed with inversion of configuration. An S_N2-transition state developed from intermediate A by internal attack was proposed to be involved in this step. It is reminiscent of the one from the platinum(IV) catalyzed methane oxidation in the Shilov reaction.¹⁴ The required nucleophilicity of the participating nitrogen anion confirms the design of the *N*-tosylated urea. Other substituents may result in competing aminoxygenation within isourea formation or in acetate incorporation from the hypervalent iodine oxidant.¹⁵

A study on the effect of the pK_a of nitrogen groups in methyl palladium(II) model complexes confirmed the requirement for stabilized nitrogen anions in reductive C–N bond formation from monomeric palladium(IV) complexes.¹⁶

The overall process of *syn*-aminopalladation/*anti*-C–N bond formation may in some cases limit the scope of the reaction. For example, cyclic alkenes such as **5** are beyond the scope of the palladium catalysis. This prompted the address of alternative reactivity, and a gold(I/III) redox process was subsequently developed.¹⁷ Since it is known from extensive work on related hydroamination reactions that gold(I) promotes *anti*-aminoauration,^{18,19} the overall sequence allows to use cyclic alkenes such as in **5** (Scheme 2). The reaction requires the presence of acetate base and uses hypervalent iodine PhI(OAc)₂ as terminal oxidant.

Scheme 2. Gold(I/III)-Catalyzed Diamination of Internal Alkene **5**

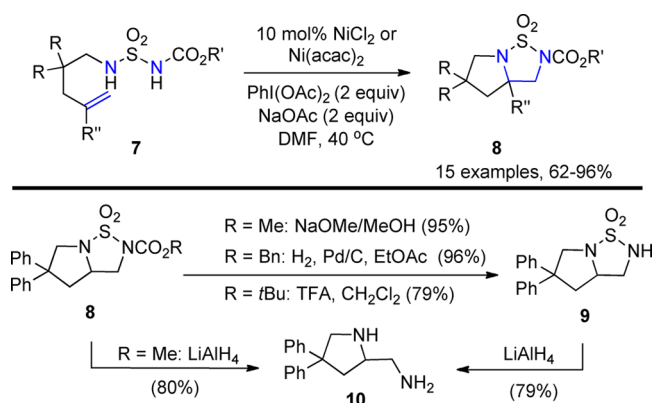


Triphenylphosphine gold(I) acetate as catalyst source gave the best results. The overall stereochemical outcome from *anti*-aminoauration/*anti*-C–N bond was confirmed for terminal alkenes through a deuterium-labeling study. The involvement of a gold(III) catalyst state in the final step was concluded from a control experiment using model complex PPh₃-AuMe, oxidation of which was monitored by ¹H and ³¹P NMR. As in the case of the palladium(IV) intermediate, reductive elimination from gold(III) occurs through an S_N2-type transition state from intermediate B. It appears that the application of metal high oxidation state catalysis represents a general concept for alkyl-nitrogen bond formation. This accomplishment is a direct consequence of the development of intramolecular diamination of alkenes and may also apply to the case of intermolecular coupling reactions.^{16,20,21}

The palladium catalyst can also be replaced by nickel salts such as nickel(II) chloride or acetate.²² In addition to the

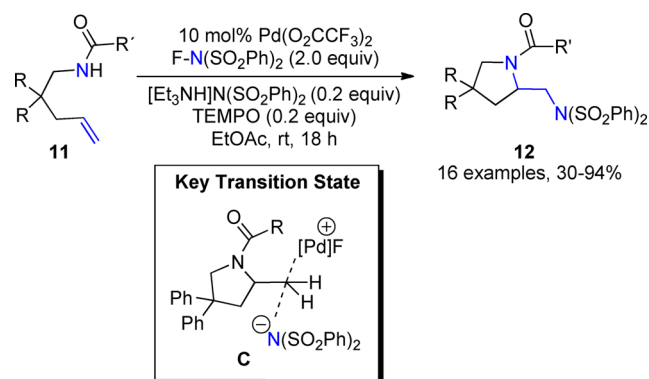
established diamination of urea substrates, nickel catalysis allows the use of sulfamides **7** as nitrogen source in diamination, for which palladium only promotes amino-acetoxylation reactions. This sulfamide protocol is a particularly attractive diamination variant as it gives rise to cyclic sulfamides **8** with a variety of different carbamate groups. As a consequence, sequential deprotection of the two nitrogen atoms via sulfamide **9** as well as complete deprotection to **10** within a single-step process are possible (Scheme 3).

Scheme 3. Nickel(II)-Catalyzed Intramolecular Diamination of Alkenes Using Sulfamide Groups as Nitrogen Sources and Deprotection Pathways to Free Aminomethylene Pyrrolidine



An important contribution was made by Michael, who discovered that NFSI could be employed as oxidant/nitrogen source resulting in a palladium-catalyzed intra-/intermolecular diamination approach (Scheme 4).^{20,23} This diamination

Scheme 4. Palladium(II/IV)-Catalyzed Intra-/Intermolecular Diamination

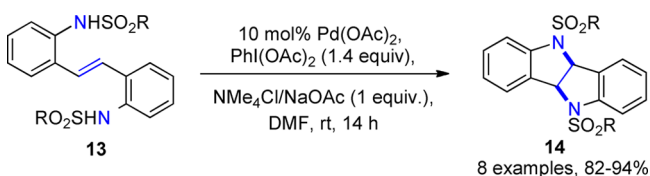


reaction proceeds under robust conditions and is a very useful synthetic addition, especially where subsequent derivatization of the aminomethyl pyrrolidine products **12** is concerned. The reaction was demonstrated to work for a range of different nitrogen substituents, but remains limited to terminal alkenes. Mechanistic studies by Michael suggest that the reaction proceeds through an initial *anti*-aminopalladation, which differs from the *syn*-processes in related intramolecular reactions.^{11–13} It is followed by palladium oxidation with the electrophilic fluorine of NFSI. The resulting transition state C undergoes reductive C–N bond formation upon nucleophilic attack at the α-carbon to Pd(IV) in a step that is reminiscent of the S_N2

reaction pathway in related intramolecular diamination reactions.¹¹ The chemistry of these C–N bond forming reactions was recently investigated by Alvarez and Muñiz through a combination of experiment and theory.²¹

Internal alkenes can also be employed. An initial result described the use of stilbene derivatives **13**, which under palladium(II/IV) catalysis undergo clean diamination upon transfer of the two sulfonamides (Scheme 5).²⁴ This oxidation

Scheme 5. Synthesis of Bisindolines through Pd(II/IV) Catalysis

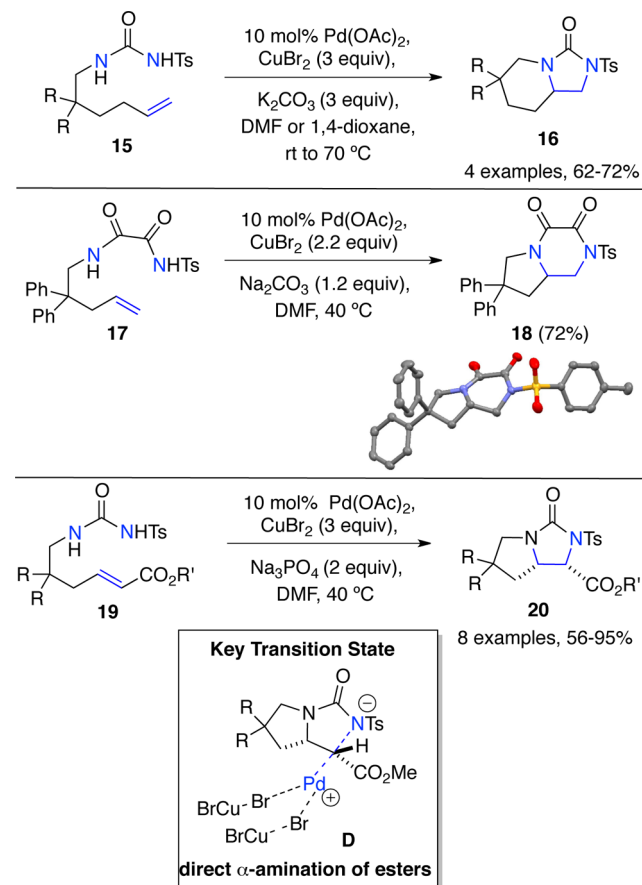


to the corresponding bisindolines **14** proceeds in a selective manner as exclusively the C₂-symmetric products are formed and no potential overoxidation to the corresponding bisindols is observed. The two carbon–nitrogen bond-forming reactions proceed with identical nitrogen sources, albeit at different palladium catalyst oxidation states. While the aminopalladation requires a Pd(II) state, the second C–N bond installment is believed to proceed through a Pd(IV) intermediate demonstrating the enormous flexibility of the palladium catalyst. An alternative metal-free transformation was recently reported by Chang.²⁵

In addition to high oxidation state palladium catalysis, the use of copper(II) salts as oxidants has enabled the realization of additional reactions. Barluenga and Muñiz reported that the described ω -alkenyl urea precursors **1** were found to undergo clean diamination using a combination of a palladium(II) catalyst and copper(II) bromide.²⁶ This protocol is also useful for the diamination under six-membered ring annelation from **15** to **16** (Scheme 6), a process that is rather slow within the related Pd(II)/PhI(OAc)₂ system. With the availability of copper reoxidants, it can be foreseen that additional examples will arise using this methodology. For example, the Muñiz group investigated the use of an oxalimide **17** as a nitrogen source.²⁷ The resulting pyrazine-2,3-dione **18** is an interesting structural variant of the more common pyrazine-2,5-dione motif and should serve as precursor in the synthesis of annelated pyrazines.

In an additional development of palladium(II)/copper(II) catalysis, acrylate derivatives could be employed for diamination reactions that lead to 1,2,3-trifunctionalized products (Scheme 6).²⁸ Depending on the individual nitrogen group, an entry into different diastereomeric series was obtained. Urea groups **19** underwent formation of *syn*-configured products **20**. The overall diastereoselectivity depends on the ester group size, with small *n*-alkyl substituents being preferred over larger ones such as *t*-butyl and benzyl. This reaction outcome was rationalized on the basis of the established sequence of base-mediated *syn*-aminopalladation followed by direct second amination through a transient oxidation transition state **D** involving a nucleophilic substitution. This reaction is of particular importance as it demonstrates that transition metal catalysis can install C–N bonds in α -position to carboxylic groups, which constitutes an uncommon approach to amino

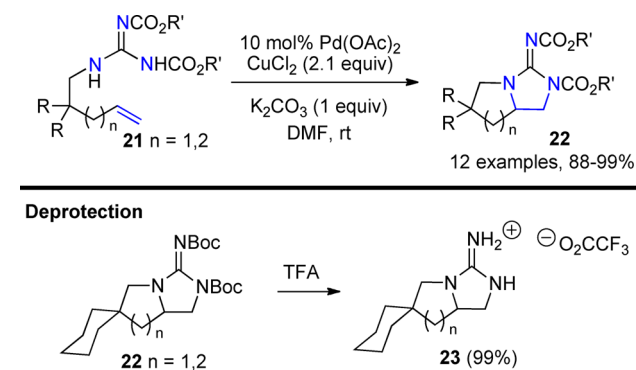
Scheme 6. Diamination within the Pd(II)/Cu(II) System: Piperidine Annelation, Pyrazine-2,3-dione Synthesis, And Diamination of Acrylates



acid synthesis. The potential of such a transition metal catalyzed α -amination of esters remains widely unexplored.

Copper(II) chloride as mild reoxidant provides conditions for the intramolecular diamination using guanidines **21** as nitrogen source (Scheme 7).²⁹ It provides suitable rates for the

Scheme 7. Synthesis of Cyclic Guanidines through Intramolecular Diamination of Alkenes



corresponding piperidine annelation reactions as well. Such an approach should be of synthetic use as the protected guanidine products **22** provide access to an easy handling of these otherwise highly polar groups. The diamination protocol was developed for the two standard carbamate groups Boc and Cbz,

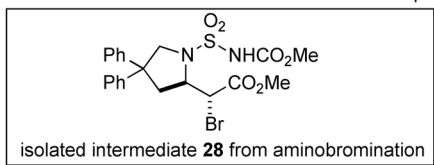
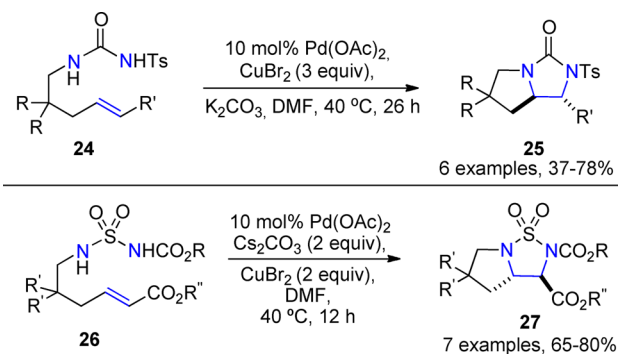
which allow for a convenient deprotection to the free guanidines **23** following the oxidation process.

The present transformation constitutes an interesting concept for the synthesis of cyclic guanidines as traditional approaches may require up to three individual C–N bond forming events. For the oxidative cycloguanidination within the intramolecular diamination of alkenes, these are reduced to two steps and proceed with complete diastereoselectivity.

The general catalytic cycle for palladium(II)/copper(II) diamination starts with a base-induced *syn*-aminopalladation. Obviously, due to a lower oxidation potential copper(II) salts are unable to provide palladium(IV) intermediates. Instead, the mechanistic rationale for the C–N bond installation using copper oxidants is based on the *transient oxidation* concept.^{30–32} Upon electron transfer from palladium to copper, the σ -alkyl carbon is rendered more electrophilic inducing an S_N2 -reaction with the nitrogen nucleophile in proximity. This transient oxidation state such as **D** (Scheme 6) leads to the direct regeneration of the palladium(II) catalyst upon product formation. The reduced copper compound should in principle be prone to aerobic reoxidation, however, the basic conditions of the overall reaction have rendered this aim problematic.³³

The Pd(II)/Cu(II) system performs well in the diamination of internal alkenes **24** as well.²⁶ This reaction leads to diamination products as major products (Scheme 8), together

Scheme 8. Palladium-Catalyzed Intramolecular Diamination of Acrylates through Aminobrominated Intermediates



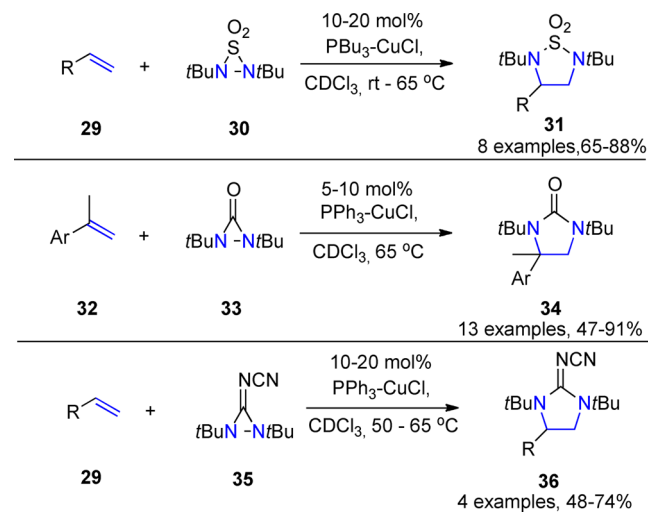
with the corresponding isourea derivatives as minor byproducts (5–31%). On the basis of the observed relative stereochemistry of the products **25**, the involvement of aminohalogenated intermediates was postulated and confirmed by control experiments. The reaction works best for aryl-substituted alkenes and reasonably well for alkyl substituted ones. β -Hydride elimination processes compete with the diamination in the latter reactions.

Contrary to ureas **20**, the corresponding sulfamides **26** generate *anti*-configured 2,3-diamino esters **27**.³⁴ Again, this reaction is of broad scope and due to the carbamoyl group of the sulfamate offers room for diversification. The reactions proceed with somewhat lower diastereomeric ratio but also suffer less from steric size of the ester substituents. A reaction of **26** at room temperature led to the isolation of the *syn*-

aminobromination product **28**, which could be cleanly converted to the *anti*-configured diamine **27** upon treatment with base. This result demonstrates that the reaction is actually a palladium-catalyzed aminobromination followed by nucleophilic substitution through the second nitrogen atom of the sulfamide. As a result, the corresponding diastereomeric 2,3-diamino esters **20** and **27** are available from the same catalyst system depending on the choice of the nitrogen group. This opens an interesting approach to this class of compounds.³⁵

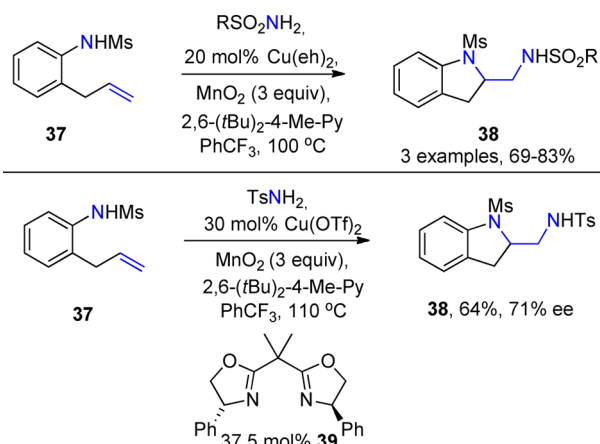
Overall, the palladium(II)/copper(II) system demonstrated a remarkable applicability to a variety of different substrates. In addition to our work on palladium catalysis, other groups developed important diamination protocols based on copper catalysis. Shi developed several protocols for the copper-catalyzed diamination of simple alkenes.^{36–38} These protocols make use of known diaziridine derivatives **30**, **33** and **35** as nitrogen sources, and they proceed as an inter/intramolecular diamination reaction (Scheme 9). For example, with *di-tert*-

Scheme 9. Copper-Catalyzed Diamination Using Diaziridines as Nitrogen Sources



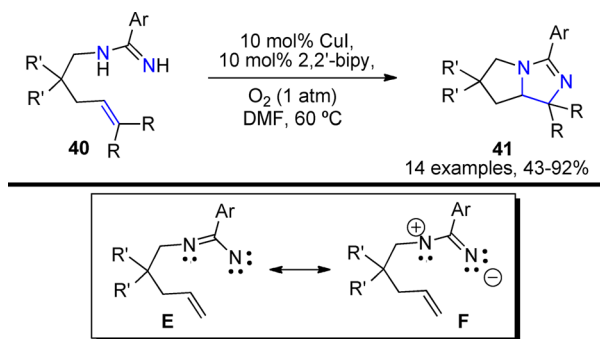
butylthiadiaziridine **30**, a series of terminal alkenes **29**, preferentially styrenes and derivatives, were conveniently transformed into the corresponding cyclic diamines **31**. A related robust reaction using a diaziridinone **33** forms cyclic ureas **34** from the oxidation of 1,1-disubstituted alkenes **32** in good to excellent yields. A guanidination reaction on alkenes **29** was finally realized using a related diaziridine reagent **35**, where the products **36** can be converted into the free guanidines by sequential treatment with HCl/*t*-BuOH and concentrated HCl. These copper-catalyzed diamination reactions are believed to proceed through oxidative insertion of the copper(I) catalyst into the N–N bond followed by addition of a nitrogen radical to the double bond. The resulting carbon based radical combines with the second nitrogen atom, releasing the original copper(I) catalyst during the closure to the cyclic diamination product. The development of catalytic 1,2-diamination reactions of 1,3-dienes³⁹ could also be extended significantly by use of these diaziridine reagents **30** and **33**.^{40–54}

Following extensive work on copper(II)-mediated diamination of alkenes,^{55–57} Chemler devised an intra-/intermolecular diamination of *N*-mesyl-2-allylanilines **37** (Scheme 10).⁵⁸ This reaction employs a specially developed copper catalyst with 2-ethylhexanoate as counteranion and uses unactivated sulfona-

Scheme 10. Copper-Catalyzed Diamination under Intra-/Intermolecular Reaction Control (eh = 2-Ethylhexanoate)

mides as the nitrogen source in the second C–N bond-forming step. Chemler could also show that upon application of a catalyst derived from copper triflate and the chiral bisoxazoline ligand (*R,R*)-Ph-BOX **39** the reaction of **37** can be performed in an enantioselective manner giving rise to diamine **38** with 71% ee. This accomplishment represents the proof of principle for the asymmetric diamination of alkenes under metal catalysis. Although the resolution of simple diamine building blocks may always constitute a useful and economic route, late stage synthetic application calls for diastereoselective and, in particular, enantioselective protocols. The example by Chemler demonstrates that such transformations may indeed be accomplished. It is also worth mentioning that Shi achieved asymmetric diamination reactions of 1,3-dienes and dehydrogenative diamination reactions of alkenes.^{42,46–49}

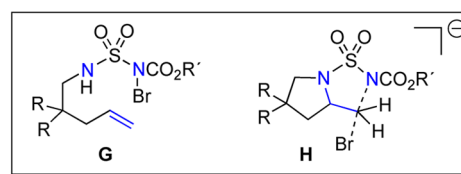
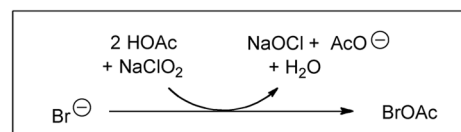
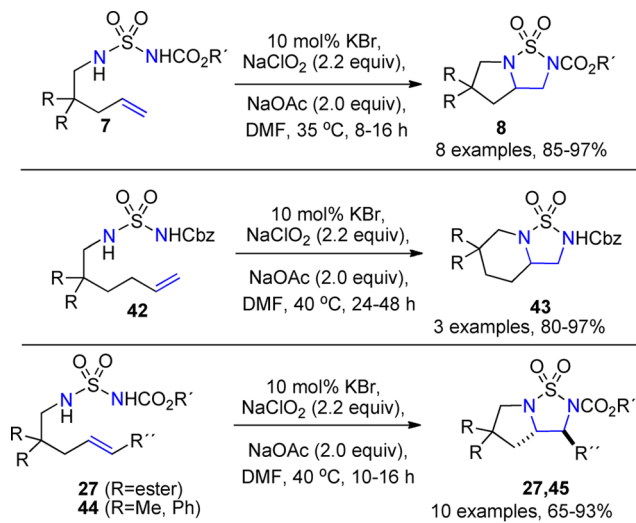
Chiba reported an elegant aerobic copper-catalyzed diamination using amidines **40** as nitrogen sources, which can be generated readily from condensation of primary amines and nitriles (Scheme 11).⁵⁹ The reaction under pyrrolidine

Scheme 11. Copper-Catalyzed Aerobic Intramolecular Diamination with Amidines As Nitrogen sources

annelation proceeds well including for internal alkenes, while concomitant 6-membered ring formation was found to be beyond the scope of this reaction. The authors suggested a mechanistic scenario that starts with oxidative interaction of (bipy)CuI and dioxygen to a higher oxidation state copper(II) superoxo or peroxy species. Sequential single-electron oxidation of **40** would finally provide the nitrene **E** as the key intermediate. Its 1,3-dipolar resonance form **F** engages in an intramolecular [3 + 2]-cycloaddition with the alkene. The

concerted mechanism of this cyclization ensures formation of the cyclic amidine products **41** with complete diastereoselectivity for internal alkenes. The catalyst thus does not participate in the actual diamination, but rather in the formation of the reactive dipolar species. The active Cu(II) is continuously regenerated by aerobic oxidation of its reduced Cu(I) precursor.

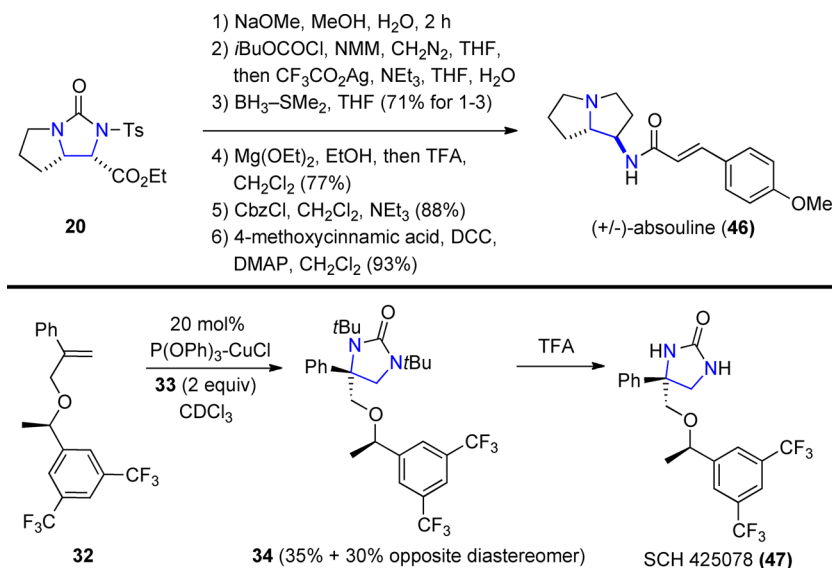
Finally, a recent report on main group oxidation catalysis provided a protocol for metal-free diamination reactions (Scheme 12).⁶⁰ This work is related to the earlier observation

Scheme 12. Examples of Metal-Free Diamination of Terminal Alkenes Using Bromine Catalysis

that intermediates arising from aminohalogenation of the alkene are effectively transformed into the corresponding diamine product upon a subsequent nucleophilic amination reaction (Scheme 8). In the present case, a combination of any given bromide source and PhI(OAc)₂ was found to promote intramolecular diamination reactions. Although originally observed in the diamination of an ω -alkenyl urea **1**, it was investigated in detail for reactions with the corresponding sulfamides **7** due to their higher structural variability and easier posterior deprotection of products **8**. In particular, the combination of KBr as catalyst source and sodium chlorite as terminal oxidant was considered a particularly attractive catalytic system. It works well for a series of alkenes including diastereoselective reactions.

The reaction is equally applicable to usually problematic piperidine annelation. For the bromine catalysis, alkenes **42** are cleanly converted into the corresponding products **43** with very good to excellent yields. The application of this catalysis to the intramolecular diamination of internal alkenes **26** proceeds also

Scheme 13. Application of Intramolecular Diamination Reactions in Synthesis of Absouline 46 and SCH 425078 47



with excellent results for alkenes bearing phenyl and methyl substituents. The corresponding products **27** are obtained with high diastereoselectivities. For acrylates **44**, excellent conversion is observed, however, the diastereoselectivities for products **45** are lower than in the comparable reactions using the palladium(II)/copper(II) catalyst system (Scheme 8). Acetyl hypobromite was assumed to be the actual oxidant in all these reactions forming from oxidation of the bromide anion. *N*-Bromination of the more acidic N–H bond of the sulfamide generates intermediate **G**, from which *anti*-aminobromination takes place. The resulting intermediate forms the cyclic diamination product through an S_N2-transition state **H** releasing the bromine catalyst as bromide. This pathway is in agreement with deuterium labeling for terminal alkenes and with the relative stereochemistry of the obtained *trans*-isomers **27** and **45**.

These metal-free reaction conditions should stimulate further development in the area. In particular, it should be instructive for the design of suitable catalysts for the intermolecular diamination of alkenes, where metal-free reactions have been developed based on stoichiometric amounts of hypervalent iodine(III) reagents.^{61–64}

■ SYNTHETIC APPLICATIONS

The availability of suitable protocols for a vicinal diamination of alkenes should greatly facilitate the introduction of vicinal diamino groups from simple alkenes at a given stage of a synthesis. In a demonstration of the feasibility of this concept, Muñiz reported the use of 2,3-diamino carboxylic ester **20** as a starting point for a subsequent short synthesis of the alkaloid absouline **46** (Scheme 13).²⁸

Finally, the copper-catalyzed diamination of *gem*-disubstituted alkenes gave rise to an intermediate for the synthesis of the NK1 antagonist SCH 425078.³⁷ With di-*tert*-butyldiaziridinone **33** as the nitrogen source, the chiral allylic ether **32** was oxidized to the desired product **34** in 35% yield together with the opposite diastereomer (30%). Cleavage of the *tert*-butyl groups gave the free target compound **47**, demonstrating the power of this diamination reaction for late stage introduction of two nitrogen atoms.

■ CONCLUSION

Since our initial discovery in 2005, the development of intramolecular diamination reactions of alkenes has significantly enabled the synthetic access to the class of vicinal diamines. A series of different catalytic reactions including palladium catalysis, related high oxidation state catalysis, and several protocols based on copper catalysis have now become available. The future of the field looks bright, especially in view of the recent first accomplishments of palladium-catalyzed diamination reactions under entire intermolecular reaction control.^{65–67}

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Notes

The authors declare no competing financial interest.

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Claudio Martínez completed his Ph.D. with Prof. Angel de Lera at the University of Vigo and has been a postdoctoral researcher in the laboratory of Prof. Muñiz since 2011.



Prof. Kilian Muñiz is an ICREA Research Professor at the Institute of Chemical Research of Catalonia (ICIQ), where he focuses on the development of new oxidative amination reactions.

■ ACKNOWLEDGMENTS

We thank the Spanish Ministry for Economy for support (CTQ2011-25027). K.M. thanks the former members of his group for their intellectual and experimental contributions, particularly C. H. Hövelmann, J. Streuff, A. Iglesias, A. Núñez, E. Campos-Gómez, Y. Fang, P. Chávez, and J. Kirsch.

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