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Ruthenium-catalyzed direct oxidative alkenylation of arenes through twofold C–H bond functionalization

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Significant progress has been accomplished in direct olefinations through twofold C–H bond functionalization of arenes and heteroarenes employing readily accessible, selective and relatively inexpensive ruthenium catalysts. Particularly, ruthenium(II) complexes have allowed challenging direct double C–H/C–H bond alkenylations of arenes with ample scope. These catalysts set the stage for step-economical C–H/C–H bond functionalization with electron-rich as well as electron-deficient arenes and heteroarenes, and, thereby, provide versatile access to diversely decorated styrenes.

Introduction

Styrene derivatives are useful intermediates in synthetic organic chemistry and represent key structural motifs in naturally occurring products[1] as well as in various compounds with activities of relevance to, among others, crop protection, medicinal chemistry[2] or materials sciences.[3] Among other methods, conventional transition metal-catalyzed[4] cross-coupling reactions have matured to being reliable tools for the formation of C_{sp^2}–C_{sp^2} bonds. Based on pioneering studies by the groups of Mizoroki[5a] and Heck,[5b] regioselective syntheses of styrenes,[6] including naturally occurring products,[7] have predominantly exploited palladium catalysts for reactions between pre-functionalized aryl (pseudo)halides and alkenes (Scheme 1a).[8]

Despite its remarkable importance and the thus achieved considerable advances in organic synthesis, the Mizoroki–Heck reaction is accompanied by the formation of a stoichiometric amount of potentially hazardous halide salt which can cause significant environmental pollution. For this reason, recent interest has shifted towards the development of more environmentally friendly halide-free alkenylations. Alternative procedures of olefinic arylations employing stoichiometric amounts of palladium chloride and organomercury, -tin, or -lead arenes *in lieu* of aryl halides were reported even before the palladium-catalyzed Mizoroki–Heck reaction.[9] Further development

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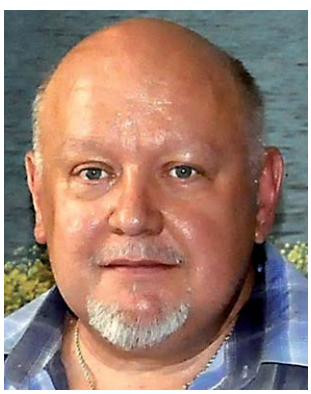

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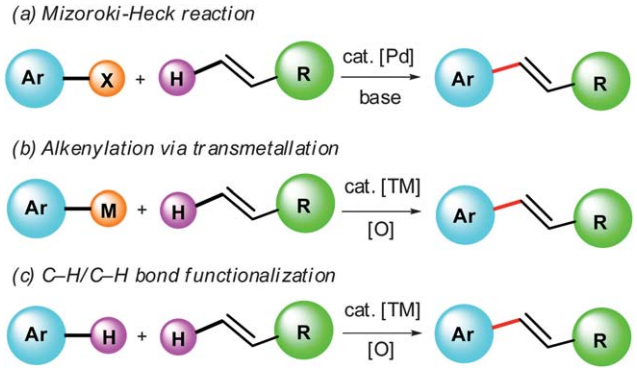


Scheme 1 Strategies for streamlining of styrene synthesis.

resulted in the elaboration of the palladium-catalyzed[10] version of the oxidative halogen-free Heck reaction *via* transmetallation (Scheme 1b; M = B, Hg, Si).[11] The required organometallic nucleophilic reagents, particularly when bearing functional groups, are, however, often not commercially available or are relatively expensive. Their preparation from the corresponding (hetero)arenes usually involves numerous synthetic operations, during which additional undesired by-products are formed, as they are during the oxidative alkenylations through transmetallation themselves. On the other hand, direct alkenylation reactions through cleavage of two C–H bonds[12] represent an environmentally benign and economically more attractive strategy (Scheme 1c). Importantly, this approach is not only advantageous with respect to the overall minimization of by-product formation (atom-economy),[13] but also allows for a streamlining of organic syntheses by significantly reducing the number of required reaction steps (step-economy).

In 1967, Fujiwara and Moritani reported the first example of catalyzed direct oxidative coupling of simple arenes with styrene through a twofold C–H bond activation approach, wherein the C–H bond of the alkene was replaced with the aromatic moiety in the presence of a palladium catalyst.[14] Subsequently, a plethora of synthetically useful protocols for palladium-catalyzed direct oxidative couplings between arenes and alkenes (Scheme 1c) have been devised, with notable recent advances achieved by *inter alia* Miura and Satoh, as well as Yu.[11,15] Importantly, efficient and selective, yet relatively expensive rhodium catalysts have also been developed in recent years.[16,17]

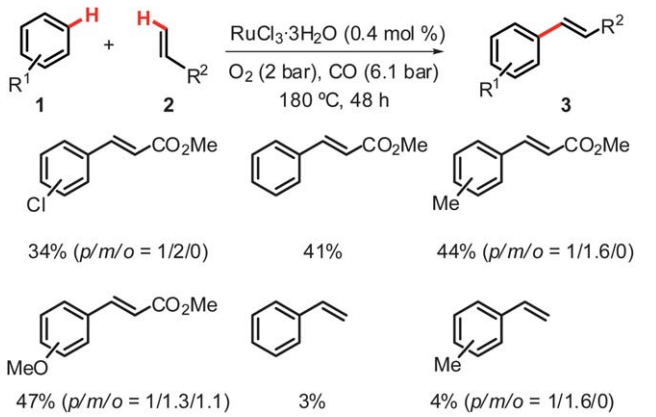
In contrast, significantly less expensive[18] ruthenium[19] complexes have only recently been exploited as catalysts for oxidative C–H bond alkenylations on arenes.[20] Herein, we summarize the recent rapid development of ruthenium-catalyzed direct oxidative alkenylations of arenes by twofold C–H bond cleavage until autumn 2012.

Direct alkenylations

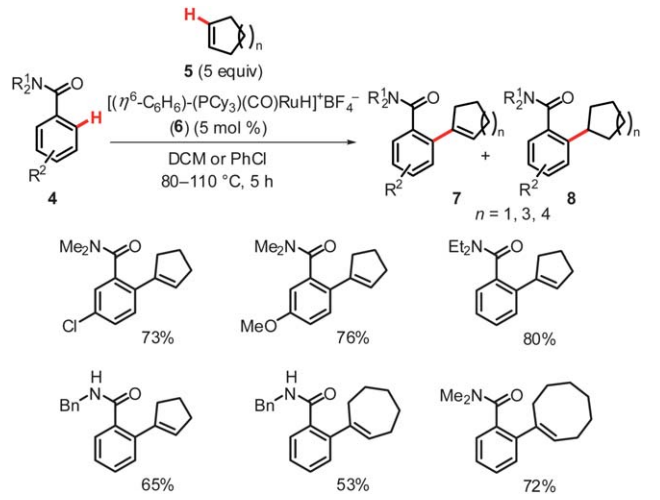
A pioneering example of ruthenium-catalyzed oxidative couplings of arenes with olefins to produce aryl alkenes, notably applying oxygen as the terminal oxidant, was reported by Milstein and co-workers (Scheme 2).[21] According to this protocol, styrene derivatives **3** were obtained in moderate yields from substituted simple arenes and Michael acceptors, while the yields with non-activated alkenes were unfortunately rather low. The complexes $RuCl_3 \cdot 3H_2O$, $[Ru(CO)_3Cl_2]_2$, $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, $Ru(NO)Cl_3 \cdot 5H_2O$ and $Ru(F_3CCOCHCOCF_3)_3$ demonstrated essentially the same catalytic activity, whereas $Ru_3(CO)_{12}$ was much less effective. Comparable results were obtained when utilizing an excess of the alkene as the scavenger of the formed hydrogen instead of using an atmosphere of oxygen. On the other hand, addition of copper(II) salts as potential co-catalysts did not display any beneficial effect on the catalytic reaction (*vide infra*). With substrates C_6H_6 and C_6D_6, a kinetic isotope effect (KIE) of $k_H/k_D = 2$ was measured in the reaction with methylacrylate. Unfortunately, major limitations of this protocol were represented by the low reactivity of simple alkenes as well as the unsatisfactory low site-selectivities with substituted arenes. For instance, toluene delivered a difficult to separate mixture of *para*- and *meta*-substituted regioisomers in a ratio of 1 to 1.6.

Oxidative alkenylations of arenes with electron-withdrawing substituents

The low selectivities observed in reactions of simple arenes were successfully addressed with the aid of Lewis-basic functional groups for chelation-assisted C–H bond functionalization.[12f] Thus, oxidative alkenylations of arenes with electron-withdrawing coordinating substituents proved viable with ruthenium(II) catalysts. Particularly, twofold C–H bond functionalizations with benzamides and their derivatives were accomplished. The cationic ruthenium hydride complex $[(\eta^6\text{-}C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ (**6**) was found to enable highly site-selective oxidative C–H bond alkenylations of substituted benzamides with unactivated alkenes **5** to give *ortho*-alkenylamides **7** in good yields (52–84%) (Scheme 3), as described by Yi and co-workers.[22] In contrast to the previous report,[21] a negligible isotope effect of $k_H/k_D = 1.1$ was found for the competition reaction between $C_6H_5C(O)NEt_2$ and $C_6D_5C(O)NEt_2$ with cyclopentene, thus highlighting a reversible arene C–H bond activation step.[22] Further detailed kinetic as well as spectroscopic studies supported a mechanism involving a rapid vinyl C–H activation followed by a rate-limiting C–C bond forming



Scheme 2 Ruthenium-catalyzed direct alkenylations with simple arenes.



Scheme 3 Direct oxidative alkenylations of benzamides **4** with unactivated alkenes **5** employing ruthenium hydride complex $[(\eta^6\text{-}C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ (**6**).

reductive elimination. Since an external oxidant was not employed in these alkenylations, an excess of the alkene **5** as well as of the newly formed alkenylated benzamide **7** served here as the hydrogen scavenger. Therefore, the products **7** were unfortunately contaminated with hydrogenated benzamides **8** (0–13% for cyclic and 17–70% for ring-opened alkenes).

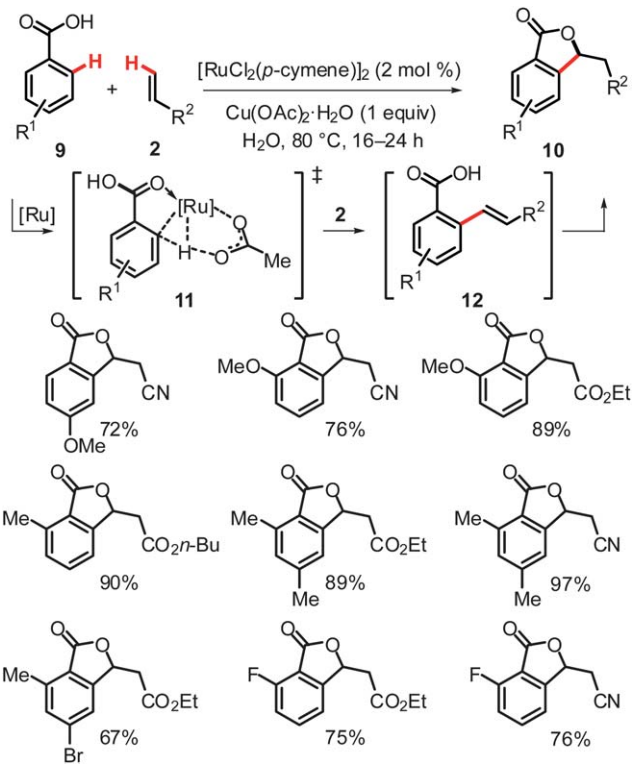
The ruthenium(II)-catalyzed oxidative C–H bond alkenylation of benzoic acids **9** with acrylates and acrylonitriles **2** smoothly proceeded in water as an environmentally benign, nontoxic reaction medium,[23] under exceedingly mild reaction conditions with $Cu(OAc)_2 \cdot H_2O$ as the oxidant (Scheme 4).[24]

Notably, a high catalytic activity was accomplished in the absence of any further additives. Yet, the expected alkenylated benzoic acids were not isolated, but the alkenylation products **12** immediately underwent a subsequent intramolecular oxa-Michael reaction, affording isobenzofuran-1(3*H*)-ones **10** in high yields. Experimental mechanistic studies with isotopically labeled substrates were suggestive of a kinetically relevant C–H bond ruthenation through acetate assistance[12d] in the transition state **11**.

A comparable phenomenon was observed in the ruthenium(II)-catalyzed oxidative alkenylation of benzanilide (**4a**) with *n*-butyl acrylate (**2a**). Indeed, the initially formed styrene derivative underwent an intramolecular aza-Michael addition to give bicyclic benzamide **13** (Scheme 5).[25]

Satoh, Miura and co-workers, on the other hand, reported on the use of $[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst, along with $AgSbF_6$ as the additive, for oxidative alkenylations of benzamides **4**.[26] The protocol was widely applicable and compared favorably with palladium- or rhodium-catalyzed processes, due to the catalyst's relatively lower cost. Employment of $AgSbF_6$ as the co-catalyst, along with $[Ru(p\text{-cymene})Cl_2]_2$ and $Cu(OAc)_2 \cdot H_2O$, enabled *N*,*N*-disubstituted benzamides **4** to smoothly undergo the site-selective alkenylation (Scheme 6).[26] Notably, the reaction did not proceed in the absence of the silver salt.

Subsequently, these reaction conditions were also successfully employed for the high-yielding alkenylation of cyclic *N*-protected isoquinolone **15** with styrene (Scheme 7).[27]



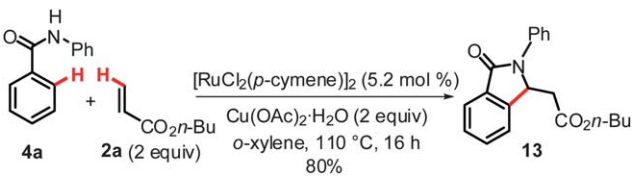
Scheme 4 Ruthenium-catalyzed oxidative alkenylation of benzoic acids **9** in water.

In independent studies, our research group simultaneously found that the use of less expensive KPF_6 instead of $AgSbF_6$ as the co-catalytic additive enabled the twofold C–H bond functionalizations of *N*-monoalkylated aromatic amides with ample scope and comparable efficacy (Scheme 8).[28] It is noteworthy that the reaction of the secondary amides **4** occurred most effectively in water as the reaction medium.[23,28,29]

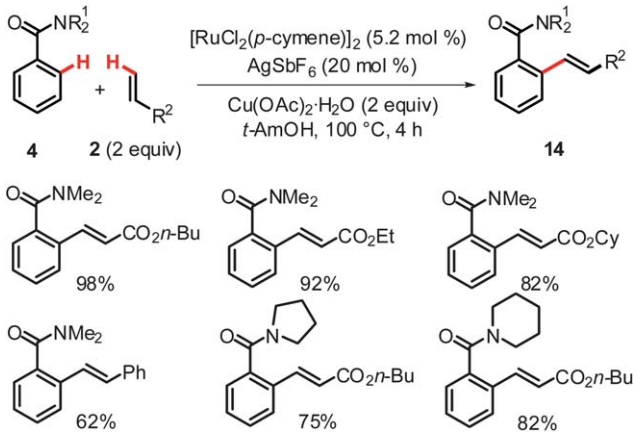
This catalytic efficacy was ensured by a cationic ruthenium(II) complex, which was generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$ and the additive KPF_6. In contrast to previous reports,[22] mechanistic studies with isotopically labeled substrates indicated the cycloruthenation to be kinetically relevant, with an intramolecular KIE of $k_H/k_D \approx 5.4$ (Scheme 9).[28]

Notably, the alkenylation of *N*-(pentafluorophenyl)benzamide under these reaction conditions was accompanied by an intramolecular aza-Michael addition of the intermediate cross-dehydrogenative alkenylation product.[28]

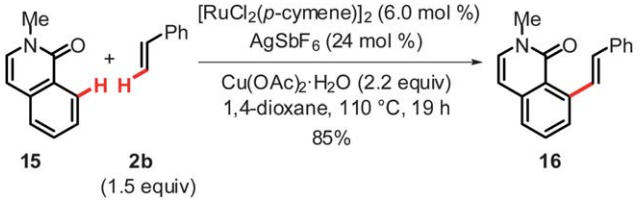
Alternatively, ruthenium-catalyzed C–H bond olefination of benzamides can be realized with pre-functionalized starting



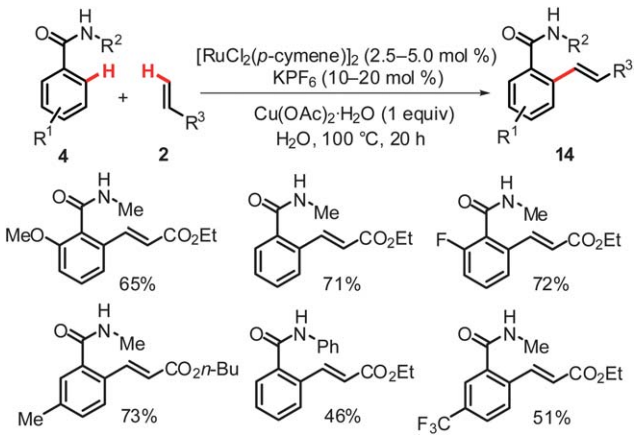
Scheme 5 Ruthenium(II)-catalyzed oxidative alkenylation–aza-Michael reaction sequence with benzanilide (**4a**).



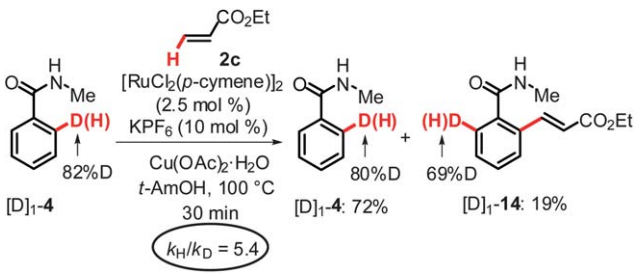
Scheme 6 Ruthenium-catalyzed oxidative alkenylation of benzamides **4** with $AgSbF_6$ as the additive.



Scheme 7 Ruthenium-catalyzed oxidative alkenylation of isoquinolone **15**.



Scheme 8 Oxidative alkenylations of secondary benzamides **4** in water with KPF_6 as the co-catalyst.



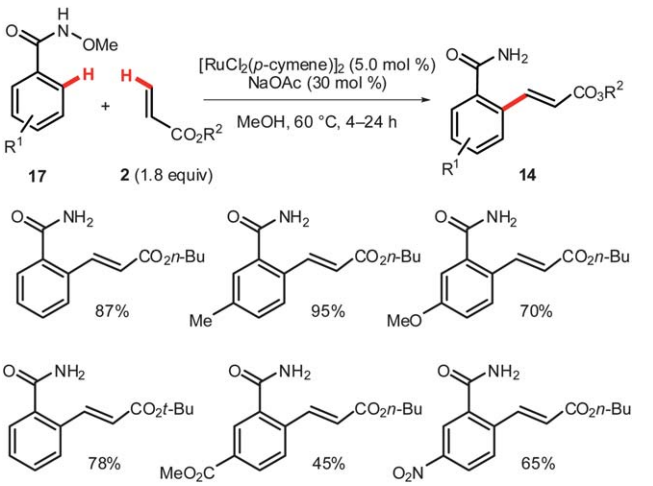
Scheme 9 Direct alkenylation with labeled substrate $[D]_1$-**4**.

materials bearing an internal oxidizing directing group, such as in *N*-methoxybenzamides **17** (*cf.* ref. 20*h*,*j*). The ruthenium-catalyzed reactions of substrates **17** with acrylates **2** in MeOH resulted in C–H bond alkenylations of the methoxybenzamides **17**, affording olefinated *N*–H-free benzamides **14** (Scheme 10).[30] This transformation occurred under rather mild reaction conditions and turned out to be an exclusively *ortho*- as well as mono-selective process. Intriguingly, the reactions with styrenes or norbornadiene in CF_3CH_2OH as the solvent resulted in twofold C–H/N–H functionalizations providing 3,4-dihydroisoquinolinone derivatives as the products.[20h] Mechanistic studies revealed an irreversible C–H bond metallation step *via* acetate[12d] assistance.[30,31]

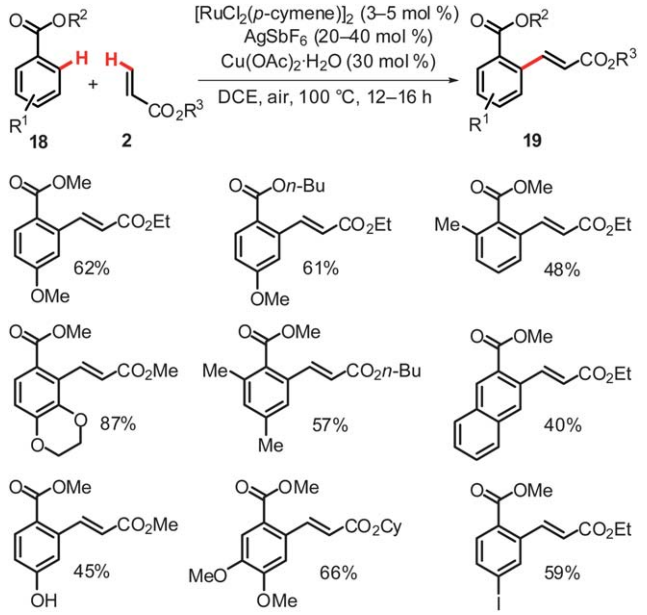
In contrast to the above-discussed chelation-assisted alkenylations of benzamides, analogous ruthenium-catalyzed oxidative functionalizations of readily available, yet only weakly coordinating esters **18** have until recently proven elusive. Yet, the research groups of Ackermann[32] and Jeganmohan[33] independently disclosed reaction conditions for the versatile oxidative direct functionalization of diversely decorated esters **18** (Scheme 11).

Thus, a catalytic system comprising $[Ru(p\text{-cymene})Cl_2]_2$, $AgSbF_6$ and co-catalytic amounts of $Cu(OAc)_2\cdot H_2O$ utilizing air as the ideal terminal oxidant allowed for efficient aerobic C–H bond alkenylations between aryl- and alkenyl-substituted esters in a highly chemo-, diastereo- and site-selective fashion.

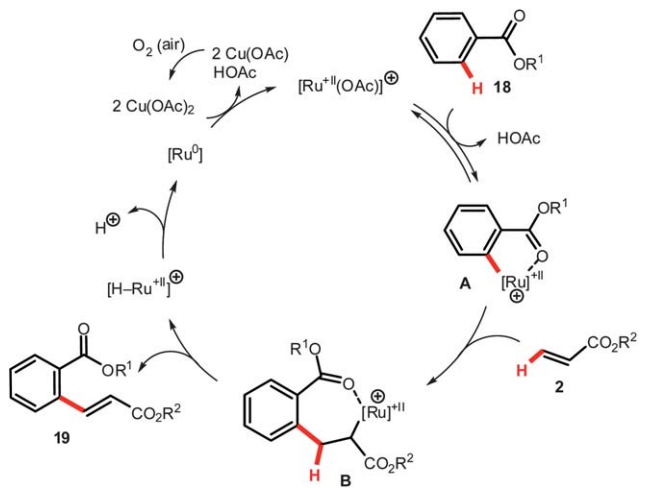
Mechanistic studies by our research group with isotopically labeled substrates or in the presence of the cosolvent D_2O highlighted a H/D scrambling, thus indicating the C–H bond ruthenation step to be reversible in nature.[32] Intermolecular competition experiments between differently substituted benzoates **18** revealed electron-rich esters to be preferentially alkenylated. Based on these mechanistic studies, we proposed the catalytic cycle to involve an initial reversible acetate-assisted[12d,31] cycloruthenation of benzamide **18** with a cationic ruthenium(II) complex to form complex **A**[34] (Scheme 12).[32] Subsequent coordinative insertion of alkene **2** and β-hydride



Scheme 10 Ruthenium-catalyzed oxidative C–H bond alkenylation of *N*-methoxybenzamides **17** with an internal oxidizing directing group.



Scheme 11 Ruthenium-catalyzed oxidative alkenylations of weakly coordinating benzoates **18**.

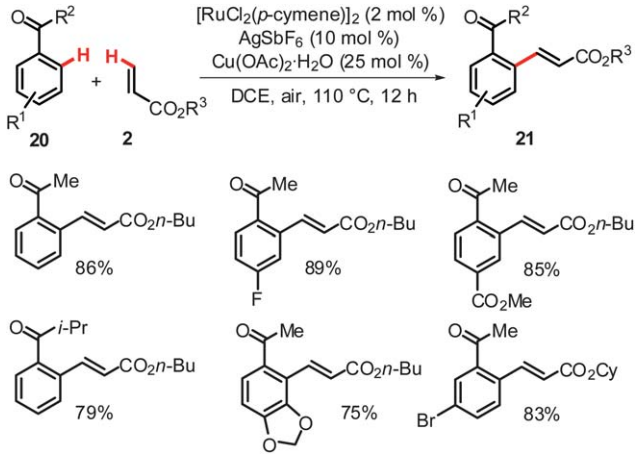


Scheme 12 Mechanistic rationale for the oxidative alkenylation of weakly coordinating esters **18**.

elimination in complex **B** furnishes desired product **19**, while reductive elimination and reoxidation by $Cu(OAc)_2$ regenerate the catalytically active cationic species.

The catalytic system consisting of $[Ru(p\text{-cymene})Cl_2]_2$, $AgSbF_6$ and $Cu(OAc)_2 \cdot H_2O$ was also found to be effective for alkenylations of phenones, as was reported by Jeganmohan and Padala.[35] Indeed, a ruthenium-catalyzed C–H bond functionalization of aromatic ketones **20** provided alkenylated products **21** in 75–89% and 55–62% yield, when using substituted acrylates and styrenes **2**, respectively (Scheme 13).

Interestingly, the alkenylation of methyl *p*-acetylbenzoate (entry 3, R^1 = *p*-CO_2Me, R^2 = Me) demonstrated the relative directing group ability of the acetyl substituent as compared to the methoxycarbonyl directing group. Remarkably, with



Scheme 13 Ruthenium-catalyzed oxidative alkenylation of phenones **20**.

$RuH_2(CO)(PPh_3)_3$ or $[(\eta^6\text{-}C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ (**6**)[22] as the catalysts, the hydroarylation of acrylates **2** with phenones **20** was observed.[35]

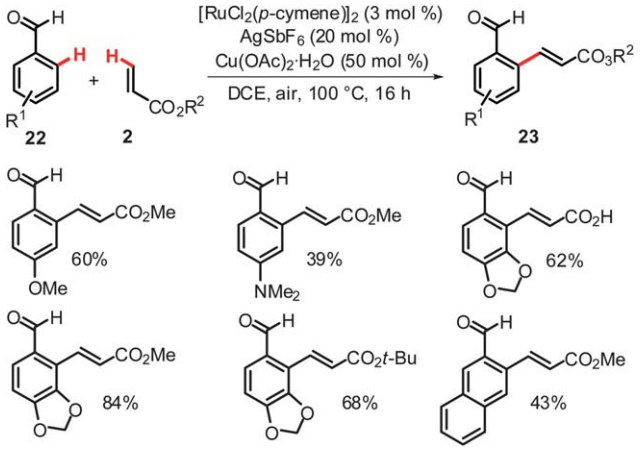
Substituted benzaldehydes **22** were alkenylated with acrylates **2** employing this catalytic system as well, albeit with lower yields of the olefinated products **23** (Scheme 14).[36]

Oxidative alkenylations of electron-rich arenes

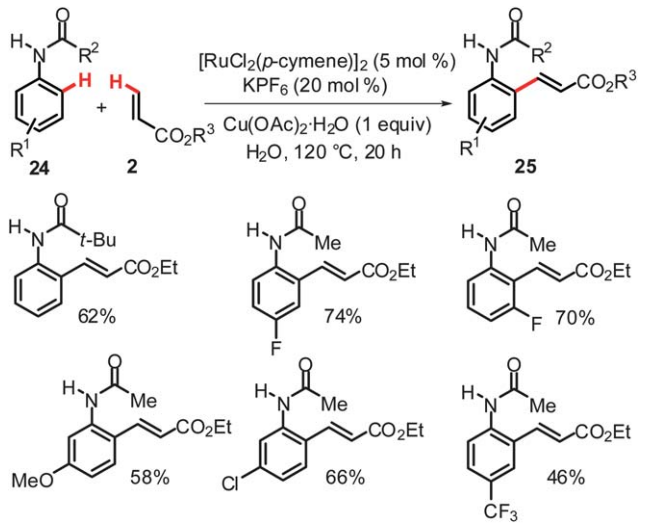
Until very recently, ruthenium-catalyzed oxidative alkenylations through twofold C–H bond functionalizations have proven to be limited to (hetero)arenes bearing electron-withdrawing groups. Challenging oxidative olefinations with electron-rich arenes, on the other hand, were elaborated very recently with $[Ru(p\text{-cymene})Cl_2]_2$, KPF_6 and $Cu(OAc)_2 \cdot H_2O$ as the catalytic system (Scheme 15).[28]

Remarkably, the oxidative alkenylation of anilides **24** proved to be most effective with water as the reaction medium and provided an expedient access to differently decorated arenes **25**.

Moreover, the catalytic system generated from $[Ru(p\text{-cymene})Cl_2]_2$, $AgSbF_6$ and $Cu(OAc)_2 \cdot H_2O$ enabled highly efficient oxidative alkenylations of electron-rich aryl carbamates **26** with



Scheme 14 Ruthenium-catalyzed oxidative alkenylation of benzaldehydes **22**.



Scheme 15 Oxidative alkenylation of anilides **24**.

weakly coordinating and removable directing groups. These catalytic conditions allowed for highly productive cross-dehydrogenative C–H bond functionalizations of **26** in a chemo-, diastereo- and site-selective fashion affording diversely decorated phenol derivatives **27** (Scheme 16).[37]

Oxidative alkenylations of arenes with heterocyclic directing groups

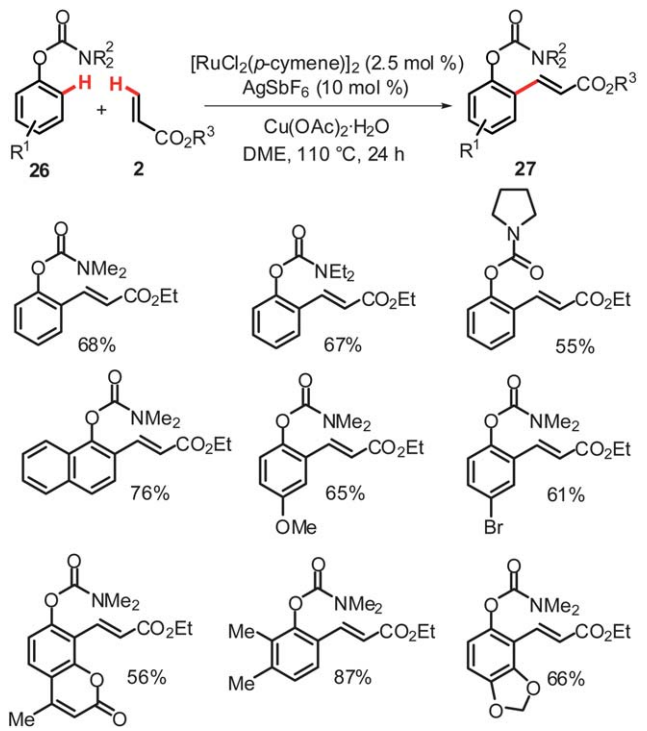
Dixneuf and co-workers reported on the synthesis of alkenylated *N*-arylpyrazoles **29** *via* ruthenium-catalyzed oxidative C–H bond olefination in *N*-phenylpyrazole (**28**) with acrylates and acrylamides **2** employing $[Ru(OAc)_2(p\text{-cymene})]$ as the catalyst in HOAc as the solvent under air (Scheme 17).[38]

Unfortunately, in many cases the product **29** was contaminated with by-product **30** generated through dehydrogenative homocoupling. Thus, under the optimized conditions, only 1–2% of impurity was observed for alkenylation with acrylates and acrylamides. However, biaryl **30** was the main reaction product in the attempted alkenylation with styrenes.

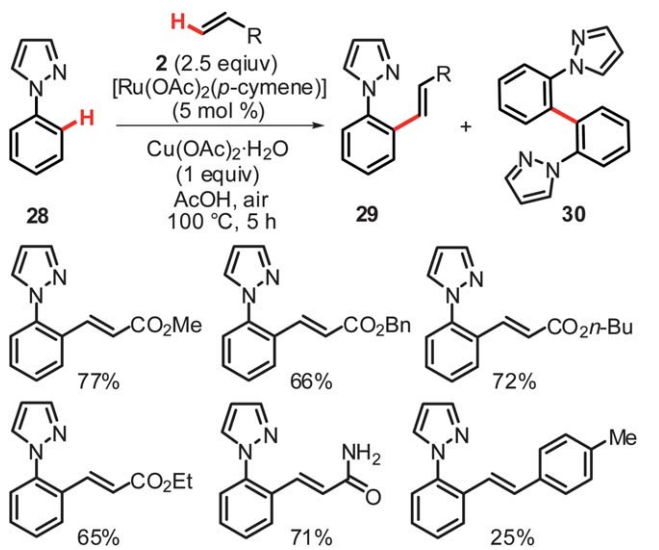
Employing $[Ru(p\text{-cymene})Cl_2]_2$ instead of $[Ru(OAc)_2(p\text{-cymene})]$, along with a higher loading of $Cu(OAc)_2\cdot H_2O$ in DMF as the solvent suppressed the competitive homocoupling reaction, as was disclosed by Satoh, Miura and co-workers (Scheme 18).[25] Yet, here the formation of mixtures of mono- (**29**) and bis-alkenylated product **31** was predominantly observed.

Significantly lower yields were obtained in alkenylations of 2-phenylazoles **32** with $[Ru(p\text{-cymene})Cl_2]_2$ in *t*-AmOH as the solvent.[25] Here, the reaction efficacy was considerably improved through the addition of $AgSbF_6$ as the co-catalyst. Indeed, in the presence of $[Ru(p\text{-cymene})Cl_2]_2$, $AgSbF_6$ and $Cu(OAc)_2\cdot H_2O$, regioselective C–H bond cleavage efficiently proceeded, affording the corresponding alkenylated azoles **33** in 57–82% yields (Scheme 19).[26]

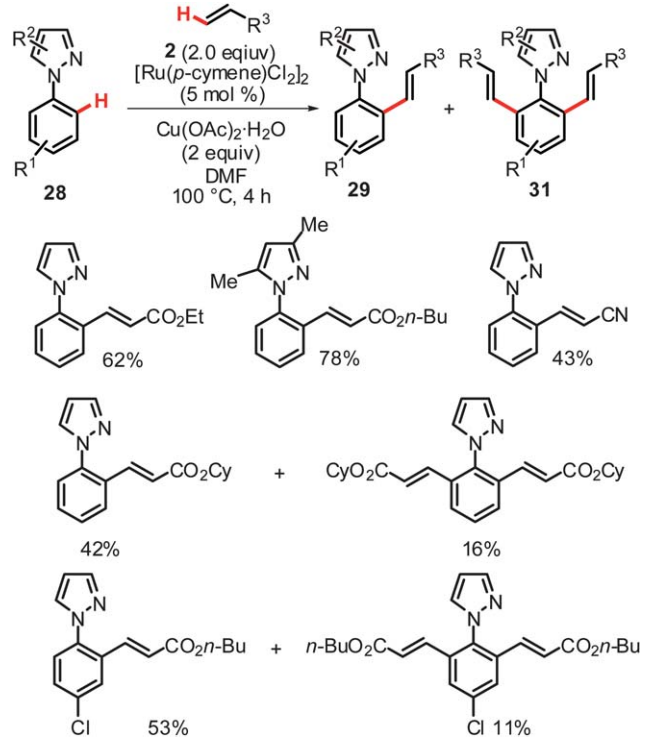
Monoalkenylations of aromatic C–H bonds directed by an oxazoline group in substrates **34** were found to take place somewhat more productively when using $[Ru(p\text{-cymene})Cl_2]_2$ along with *rac*-BNPAH (*i.e.* with BNPAH instead of $AgSbF_6$ as the co-catalyst: conversion 88 *vs.* 62% for alkenylation of 2-phenyloxazoline with methylacrylate), in EtOH at 80 °C (Scheme 20; BNPAH = 1,1′-binaphthyl-2,2′-diyl hydrogenphosphate).[39] The reaction afforded bifunctional alkenes **35** in moderate to good yields (32–85% for acrylates, 55–57% for acrylamides, 40–65% for styrenes). However, less expensive KPF_6 gave very similar results as the additive (yields 48 and 57% for alkenylation of 2-phenyloxazoline with methylacrylate and styrene, respectively).[39] Furthermore, it is noteworthy that a phosphoric acid



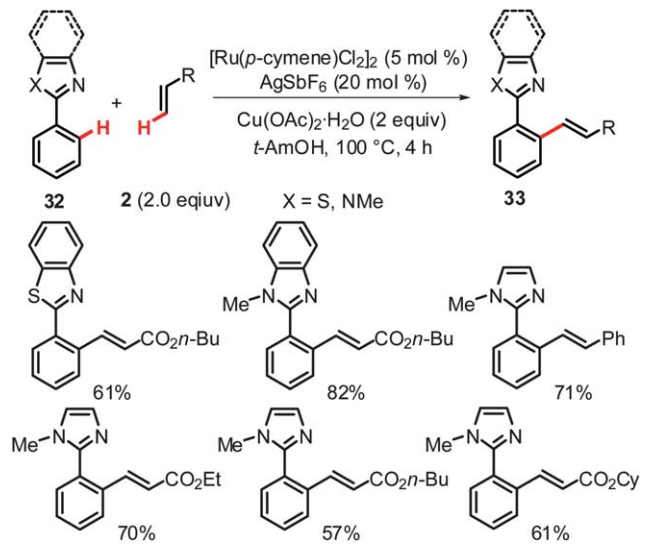
Scheme 16 Oxidative alkenylation of aryl carbamates **26**.



Scheme 17 Ruthenium-catalyzed oxidative alkenylation of *N*-phenylpyrazole (**28**).

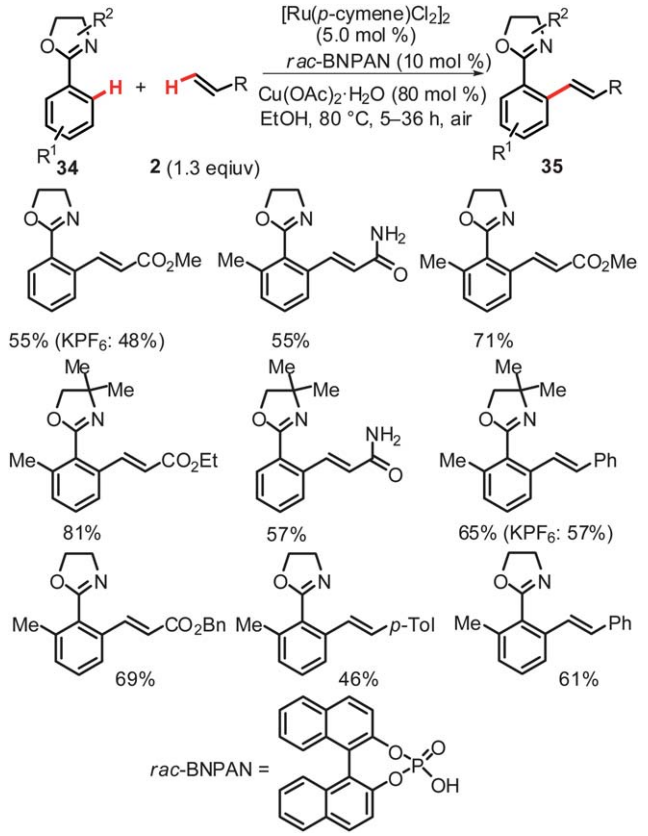


Scheme 18 Improved ruthenium-catalyzed oxidative alkenylation of *N*-phenylpyrazoles (**28**).

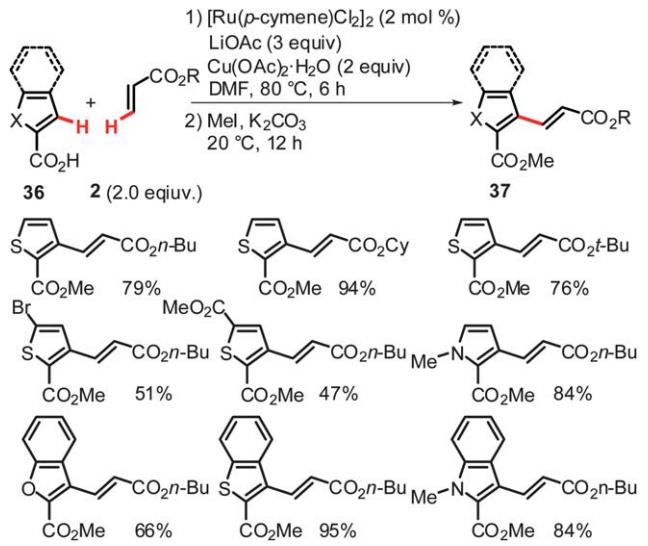


Scheme 19 Ruthenium-catalyzed oxidative alkenylation of 2-phenylazoles **32**.

diester was already utilized in 2008 as the co-catalyst in ruthenium-catalyzed C–H bond functionalizations.[31g]



Scheme 20 Ruthenium-catalyzed oxidative alkenylation of 2-phenyloxazolines **34**. Yields in parentheses: with KPF_6 (10 mol %) instead of *rac*-BNPAH.

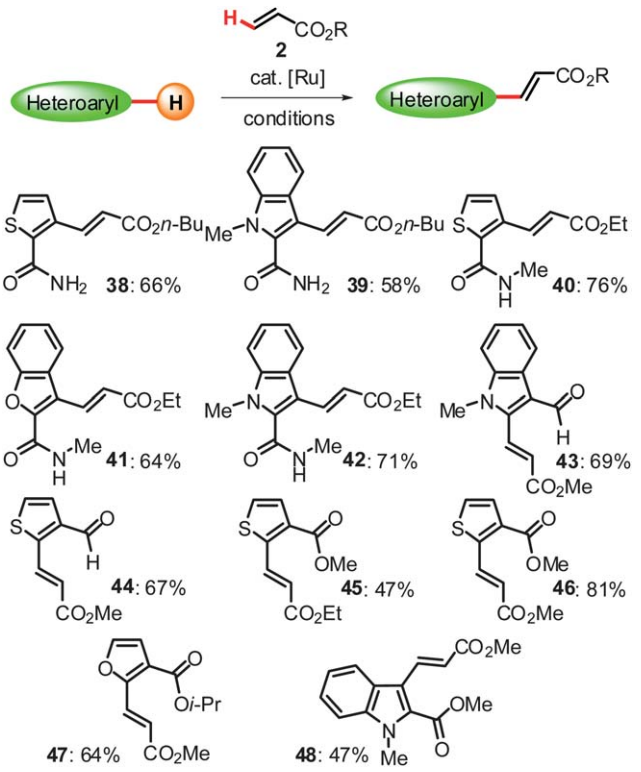


Scheme 21 Ruthenium-catalyzed oxidative alkenylation of heterocyclic carboxylic acids **36**.

Direct alkenylations of heteroarenes

Ruthenium catalysts for oxidative C–H/C–H alkenylation reactions of heterocyclic compounds have hitherto been less explored as compared to palladium or rhodium complexes. Essentially, ruthenium-catalyzed alkenylations of heteroarenes with various directing groups were achieved with the catalytic systems described above, albeit with different catalytic efficacies. Among the site-selectivity-ensuring Lewis-basic directing groups, the carboxyl group turned out to be particularly useful in organic synthesis, as it can be readily removed or transformed. However,

Table 1 Ruthenium-catalyzed oxidative alkenylations of substituted heteroarenes[a]



Entry	Product	Directing group	Conditions	Ref.
1	**38**	–C(O)NHOMe	A	30
2	**39**	–C(O)NHOMe	A	30
3	**40**	–C(O)NHMe	B	28
4	**41**	–C(O)NHMe	B	28
5	**42**	–C(O)NHMe	B	28
6	**43**	–CHO	C	36
7	**44**	–CHO	C	36
8	**45**	$-CO_2Me$	C	32
9	**46**	$-CO_2Me$	C	33
10	**47**	$-CO_2i$-Pr	C	33
11	**48**	$-CO_2Me$	C	33

[a] *Reaction conditions*: A: $[Ru(p\text{-cymene})Cl_2]_2$ (5.0 mol%), NaOAc (30 mol %), MeOH, 80 °C; B: $[Ru(p\text{-cymene})Cl_2]_2$ (5.0 mol%), KPF_6 (20 mol%), $Cu(OAc)_2 \cdot H_2O$ (1 equiv.), H_2O, 120 °C; C: $[Ru(p\text{-cymene})Cl_2]_2$ (3–5 mol %), $AgSbF_6$ (20 mol%), $Cu(OAc)_2 \cdot H_2O$ (30–50 mol%), air, DCE, 100 °C.

these acids were found to readily undergo decarboxylations[40] under the palladium-catalyzed, and to a lesser extent under the rhodium-catalyzed, oxidative reaction conditions. Since decarboxylations are sluggish under ruthenium catalysis, the carboxyl function was expected to remain within the alkenylated products. Indeed, Satoh, Miura and co-workers elegantly explored $[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst, along with LiOAc as the stoichiometric additive in DMF as the solvent, for successful olefinations of thiophene-, benzothiophene-, benzofuran-, pyrrole-, and indolecarboxylic acids **36** to obtain the desired 3-alkenylated products **37**. Notably, these transformations proceeded without loss of the valuable carboxyl function in good to excellent yields after subsequent methylation (Scheme 21).[41]

The experimental results of the subsequent efforts of other research groups are summarized in Table 1 and highlight that various *N*-methoxy benzamides, secondary amides, aldehydes or esters could be employed for chemo- and site-selective ruthenium-catalyzed twofold C–H bond functionalizations of these valuable scaffolds.

Conclusions

Recent years have witnessed a tremendous development in catalytic C–H bond functionalizations. Despite this notable advance, inexpensive, yet highly selective ruthenium catalysts were until very recently under-recognized for oxidative alkenylations through challenging double C–H bond functionalization. Particularly, the mechanistic insight into carboxylate assistance[12d,31] for effective C–H bond ruthenations has, however, set the stage for the recent rapid development of versatile oxidative alkenylations of arenes and heteroarenes. Thus, challenging oxidative C–H/C–H bond olefination reactions have proven viable with ruthenium(II) complexes with considerable progress being accomplished in the past two years. Whereas early reports utilized stoichiometric amounts of antibacterial $Cu(OAc)_2 \cdot H_2O$ as the sacrificial oxidant, more recently developed methods were found to be broadly applicable towards aerobic oxidations with ambient air as the ideal terminal oxidant. Notable features of the ruthenium(II) catalysts include the remarkably broad substrate scope and the extraordinarily high chemo- and site-selectivity, as reflected by the outstanding functional group tolerance and excellent catalytic activity with water as the reaction medium. Notably, the significantly lower price of easily available and more stable ruthenium complexes renders them more attractive as compared with both palladium or rhodium catalysts. While cross-dehydrogenative alkenylations of electron-deficient arenes and heteroarenes mostly occurred through carboxylate-assisted C–H bond metallation, cationic ruthenium(II) complexes allowed for effective transformations of electron-rich substrates *via* a reversible C–H bond activation. Considering the practical importance of atom- and step-economical C–H bond alkenylations for natural product synthesis, drug discovery and crop protection, along with the unique features of the robust ruthenium catalysts, significant further progress is expected in this rapidly evolving research area.

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