ACS Catalysis

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Recent Advances on Ester Synthesis via Transition-Metal Catalyzed C−H Functionalization

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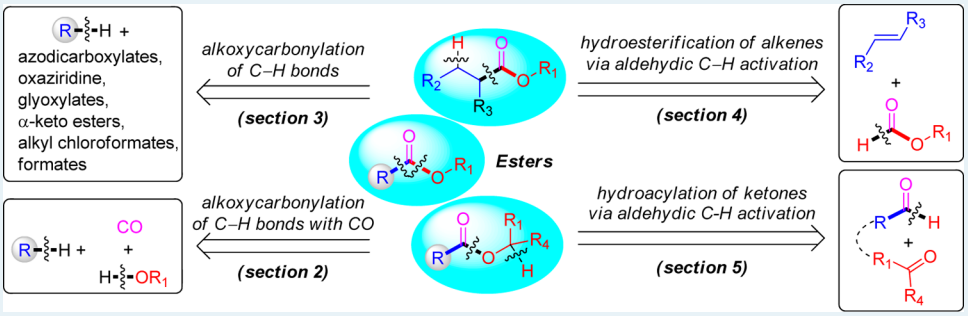


ABSTRACT: Esters are valuable commodity chemicals widely found in agrochemicals, pharmaceuticals, and advanced materials. They are also important synthetic building blocks for chemical transformation. Recent advances of ester synthesis via transition-metal-catalyzed C−H activation have provided highly efficient and atom-economical alternatives to the traditional methods. Herein, we summarize recent advances on ester synthesis via transition-metal-catalyzed C−H activation. On the basis of the modes of reactivity and the types of C−H bonds, transition-metal-catalyzed alkoxycarbonylation of C−H bonds with various esterification reagents will be discussed in sections 2 and 3. Finally, hydroesterification/hydroacylation of C−C or C−O double bonds via formate C−H activation will be discussed in sections 4 and 5.

KEYWORDS: *transition metal, alkoxycarbonylation, C−H activation, hydroesterification, hydroacylation*

1. INTRODUCTION

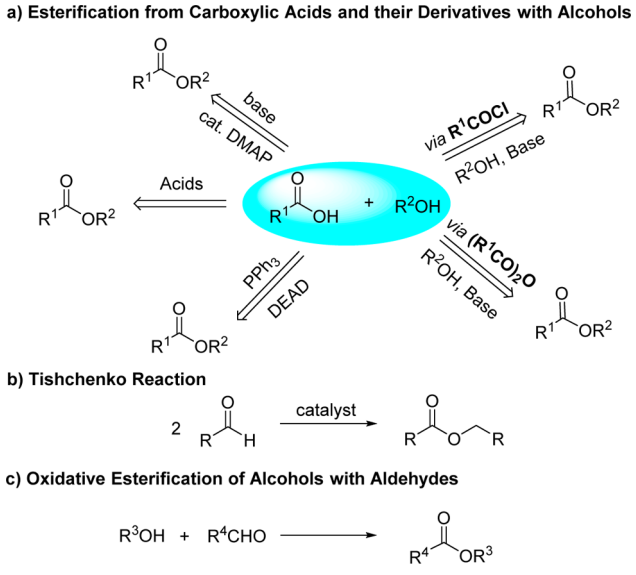
Ester compounds, irrespective of whether they are acyclic or cyclic, are among the most important functional groups and are found widely in fine chemicals, natural products, and polymers.[1] In addition, ester groups play an irreplaceable role for protection of carboxylic acids and hydroxy groups. Traditionally, esters are mainly generated from the reaction between the corresponding carboxylic acids or their derivatives with alcohols under acidic or basic conditions (Scheme 1a). Generally, multisteps are needed to generate the pre-existing carboxyl and hydroxyl functional groups in this transformation. To meet the demand of atom- and redox-economy and sustainable chemistry, continuous efforts have been made to develop efficient and environmentally benign approaches for the synthesis of esters. The Tishchenko reaction of aldehydes to the corresponding esters represents one of these economical strategies, albeit suffering with limited substrate scope and the generation of undesired side products, such as acids and alcohols (Scheme 1b).[2] Furthermore, direct oxidative esterification of aldehydes with alcohols has been extensively investigated as a complementary strategy to traditional methods (Scheme 1c).[3] This kind of reaction has been well summarized in several reviews with admirable efforts and will not be discussed in this review.[3]

Over the last few decades, transition-metal-catalyzed direct functionalization of C−H bonds has emerged as a powerful strategy for the construction of C−C or C−heteroatom bonds because of its environmentally benign and cost-effective features.[4] In this review, we will discuss recent advances on the synthesis of esters via transition-metal-catalyzed C−H activation. On the basis of the modes of reactivity and the types of C−H bonds, this review is divided into four sections (Scheme 2): (1) direct alkoxycarbonylation of C−H bonds with carbon monoxide and alcohols (section 2); (2) direct alkoxycarbonylation of C−H bonds with other esterification reagents as carboxylate sources (section 3); (3) hydroesterification of alkenes with formates via formate C−H bond activation (section 4); (4) hydroacylation of carbonyl compounds via aldehydic C−H bond activation (section 5). Generally, the first two sections involve transition-metal-catalyzed directed or nondirected activation of aryl C(sp^2)−H, alkenyl C(sp^2)−H, alkynyl C(sp)−H, and alkyl C(sp^3)−H to form the metalated intermediate **Int-A**, followed by alkoxycarbonylation, whereas the last two sections formally involve the breaking of aldehydic C−H bond and the addition

Received: January 12, 2015
Revised: February 7, 2015
Published: February 10, 2015

DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

Scheme 1. Strategies for Esters Synthesis



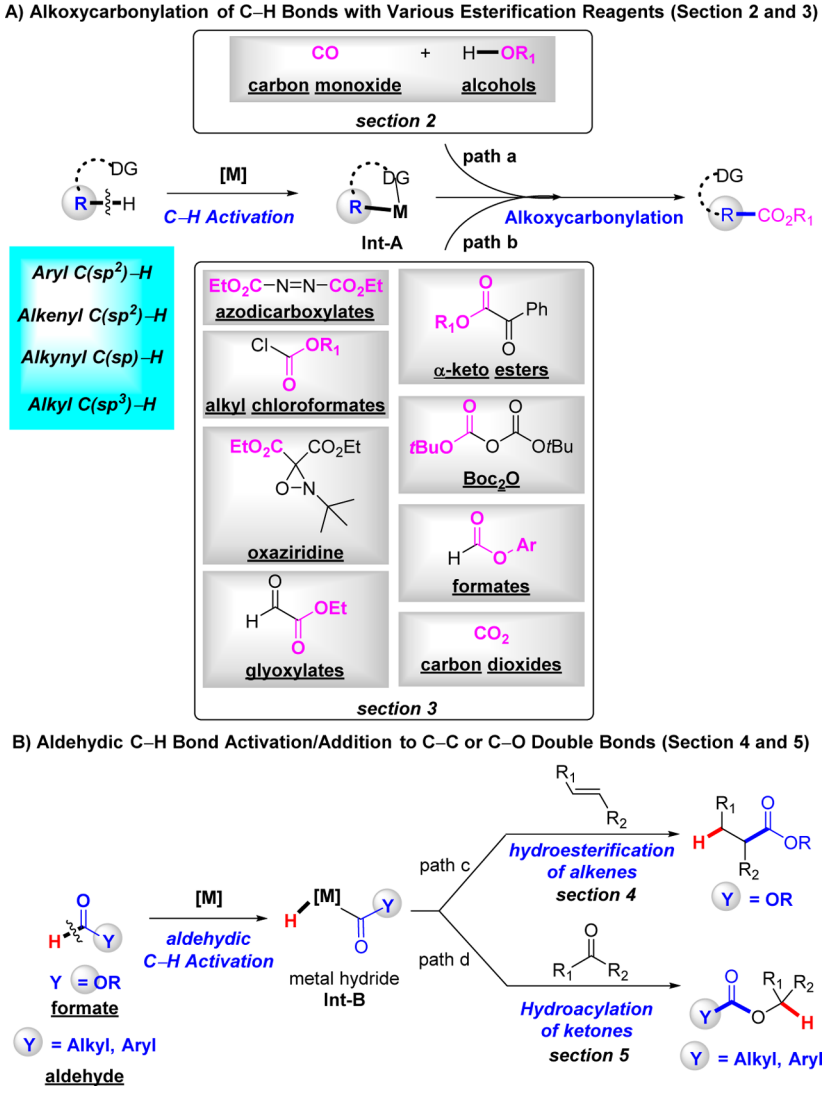
of the resulting metal hydride **Int-B** across C−C or C−O double bonds.

2. ALKOXYCARBONYLATION OF C−H BONDS WITH CO

Carbon monoxide is a cost-efficient C_1 building block to access carboxylic acids and their derivatives. Hydroformylation with carbon monoxide and hydrogen was discovered accidentally in 1938 by Otto Roelen.[5] It allows the introduction of hydrogen and a formyl group in an atom-economical manner (Scheme 3a). After that, the pioneering work of hydrocarboxylation with carbon monoxide and water was revealed by Walter Reppe,[6] which makes the straightforward and atom efficient preparation of saturated carboxylic acids possible (Scheme 3b). Since then, significant progress has been made on carbonylation chemistry by using carbon monoxide.

The carbonylation of aryl halides (ArX) or arylmetallic compounds (ArM) with CO and appropriate nucleophiles, such as alcohols, amines, and carbon nucleophiles is one of the most important carbonylation reactions.[7] The pioneering work of this area was reported by Heck and co-workers in the 1970s.[8] Although this carbonylation reactions have become a valuable

Scheme 2. Ester Synthesis via Transition-Metal-Catalyzed C−H Activation



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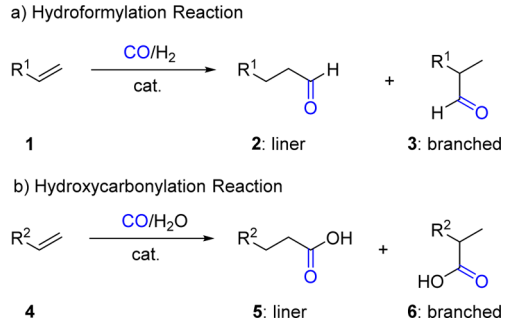
Scheme 3. Hydroformylation and Hydroxycarbonylation of Alkenes



tool in organic synthesis, the need for prefunctionalized starting materials has prompted chemists to investigate more atom- and step-economic alternatives. In this context, transition-metal-catalyzed direct oxidative carbonylation of C−H bonds with CO in the presence of various nucleophiles has been recognized as a novel strategy to the access of value-added bulk and fine chemicals, such as valuable carboxylic acids, methyl propionate, linear fatty acids, and amides.[9]

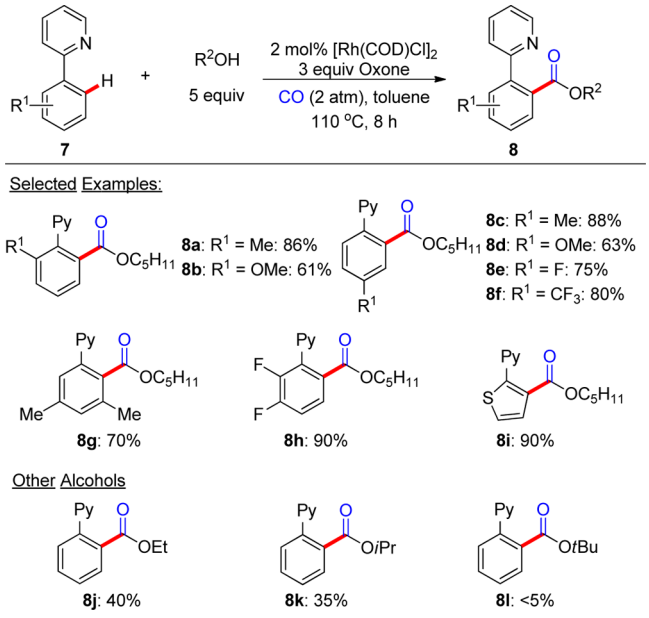
Since the seminal work of Fujiwara in 1980,[10,11] a number of carbonylation reactions via aromatic C−H functionalization with various nucleophiles, such as amines,[12] carboxyl,[13] alkenes,[14] and arenes[15] have been reported recently. These carbonylation reactions are not the topic of this review. Here we will focus on the synthesis of esters via transition-metal catalyzed alkoxy/phenoxycarbonylation reactions of unactivated C−H bonds with a variety of alcohols and phenols as nucleophiles.

2.1. Alkoxycarbonylation of Aryl C(sp^2)−H Bonds with CO. The first significant result in alkoxycarbonylation consisted of the rhodium-catalyzed C(sp^2)−H bond activation directed by pyridyl.[16] Considering the difficulty of Pd-catalyzed *ortho*-selective C−H bond carbonylation because the depalladation process is often complicated by the reduction of Pd(II) to Pd(0) under CO atmosphere,[17] $[Rh(COD)Cl]_2$ was recognized as an efficient catalyst by Zhang and co-workers to overcome this challenge. In this study, inexpensive, safe, and environmentally benign Oxone was found to be a particularly effective terminal oxidant in this rhodium-catalyzed alkoxycarbonylation reaction. Subsequent selective monocarbonylation of functionalized 2-phenylpyridines were successfully achieved with *n*-pentanol in acceptable to excellent yields (Scheme 4). However, ethanol and 2-propanol afforded lower yields of the carbonylation products (**8k**). Finally, when *t*-BuOH was employed, only a trace amount of the desired product (**8l**) was observed.

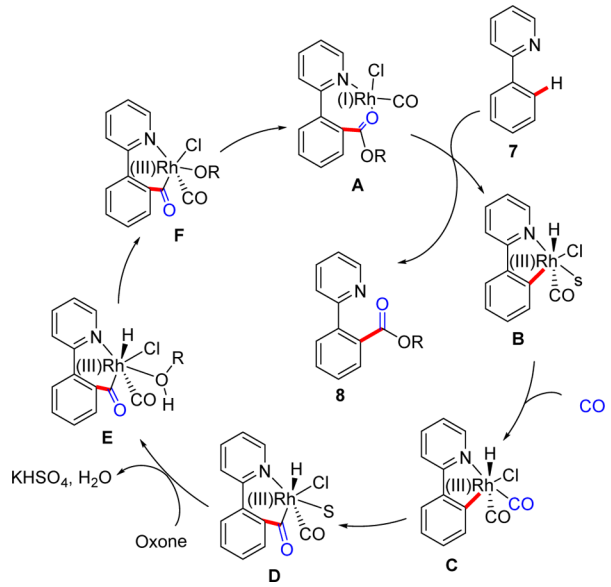
A plausible mechanism of this oxidative carbonylation reaction was proposed (Scheme 5). Initial coordination of the Rh(I) to the chelating heteroatom of **7**, followed by oxidative addition of an aromatic C−H bond, provides a Rh(III) complex **B**. Insertion of CO, followed by coordination of alcohol, forms intermediate **E**. Reductive elimination from **F** gives the carbonylation product **8** and the active catalyst species Rh(I) (Scheme 5). The alcoholysis of acylrhodium species **E** is less likely because the alkoxycarbonylation reaction does not occur at all in the absence of Oxone even when stoichiometric amount of $[Rh(COD)Cl]_2$ was used.

In 2009, palladium-catalyzed C−H alkoxycarbonylation was reported by the Booker-Milburn group.[12b] Initially, *m*-toluidine

Scheme 4. Rhodium-Catalyzed C−H Alkoxycarbonylation of 2-Arylpyridines



Scheme 5. Proposed Mechanism of Rh(I)-Catalyzed Alkoxycarbonylation Reaction



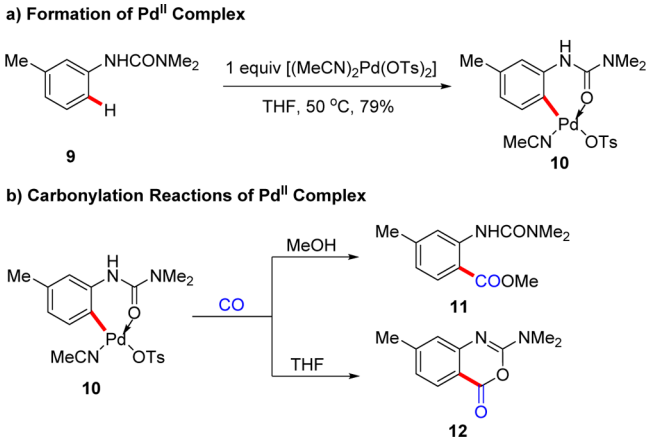
urea was employed with one equivalent of $[Pd(OTs)_2(MeCN)_2]$[18] in anhydrous THF, and this led to rapid precipitation of the *ortho*-palladate **10** (Scheme 6a), which was converted to the methoxycarbonylation product with MeOH under 1 atm pressure of CO or cyclic imidate in the absence of MeOH (Scheme 6b).

This methoxycarbonylation reaction proceeded readily at room temperature when THF was used as cosolvent (MeOH/THF = 1:1). The introduction of electron-withdrawing groups at the *para* position resulted in decreased activity (Scheme 7, **14g**), indicating that an electrophilic palladation process is plausible.

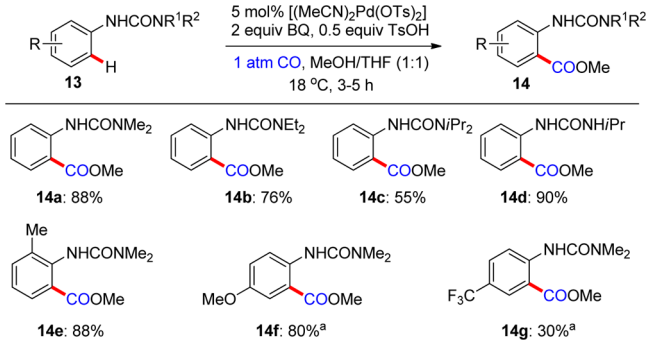
In 2010, Shi and co-workers reported a palladium-catalyzed alkoxycarbonylation of C−H bonds using *N*,*N*-dimethylamine as directing group.[19] LiCl was found to be crucial for this

DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

Scheme 6. Stoichiometric Reaction of *m*-Toluidine Urea with $[Pd(OTs)_2(MeCN)_2]$ and Methoxycarbonylation of Pd(II) Complex 10



Scheme 7. Palladium-Catalyzed Methoxycarbonylation of Aryl Urea Derivatives

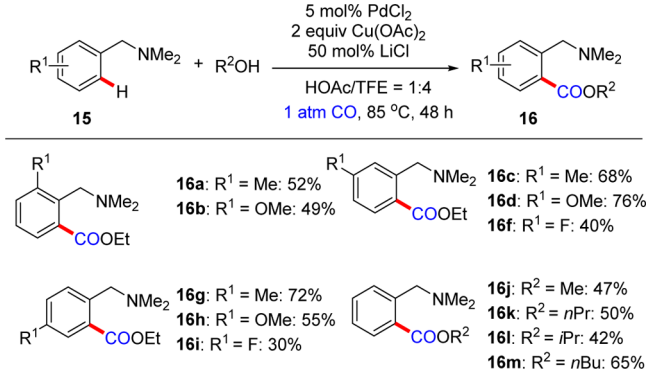


[a]Reactions were carried out at 50 °C

alkoxylcarbonylation reaction. A variety of substituted *N*,*N*-dimethylbenzylamines were tolerated under the optimized conditions and gave the desired esters in moderate to good isolated yields (Scheme 8). Primary alcohols reacted better than secondary ones (**16k**, **16l**).

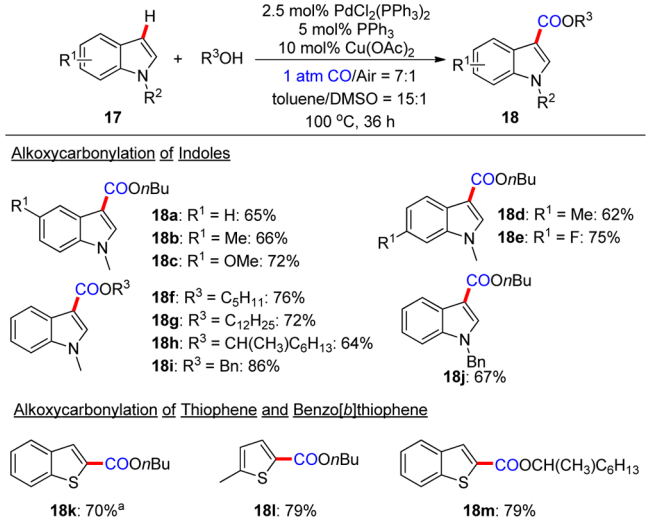
Indoles are abundant and an important class of heterocycles found in natural products, pharmaceuticals, and advanced materials.[20] As a consequence, significant research effort has been directed toward the site- and stereoselective functionalization of the indole ring system.[21] Lei and co-workers

Scheme 8. Palladium-Catalyzed Alkoxycarbonylation of *N*,*N*-Dimethylbenzylamines



investigated the Pd(II)-catalyzed C−H alkoxycarbonylation of indole derivatives recently.[22] Delightfully, butyl 1-methyl-1*H*-indole- 3-carboxylate was obtained in 65% yield with a catalytic amount of $PdCl_2(PPh_3)_2$, PPh_3, and $Cu(OAc)_2$ in a mixed solvent of toluene and DMSO under an atmosphere of CO and air (1 atm, CO/air = 7:1). Alkoxycarbonylation of C5, C6, or C7 substituted indoles was tested in the optimized conditions, and both electron-donating and electron-withdrawing substituents on indole ring were tolerated well in this oxidative carbonylation condition (Scheme 9). It is noteworthy that the

Scheme 9. Palladium-Catalyzed C−H Alkoxycarbonylation of Heteroarenes



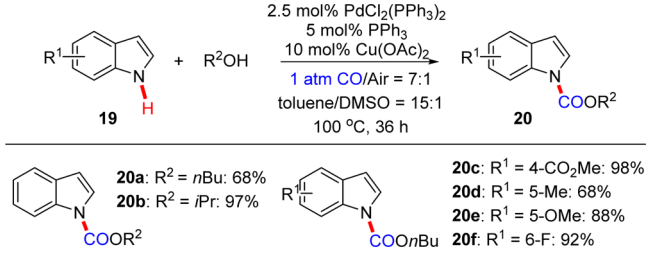
[a]Five mol % $PdCl_2(PPh_3)_2$, 10 mol % PPh_3, 2 equiv $Cu(OAc)_2$, 1 atm CO, 50 h

carbonylation exclusively occurred at the 3-position of indoles to afford the desired esters in good yields, whereas thiophene and benzo[*b*]thiophene were readily carbonylated in the 2-position (**18l**, **18k**). In addition, a variety of primary and secondary aliphatic alcohols were compatible with this reaction (**18f−i**).

This effective protocol could also be applied to N−H indoles to afford the corresponding carbamates in good to excellent yields (Scheme 10). Various indoles with both electron-donating and -withdrawing groups worked well under the optimized conditions and gave the desired *N*-carbonylation products in good yields.

In the same year, Li and co-workers developed an approach for the synthesis of indole-3-carboxylates through C−H activation catalyzed by Rh(III).[23] After optimizing various

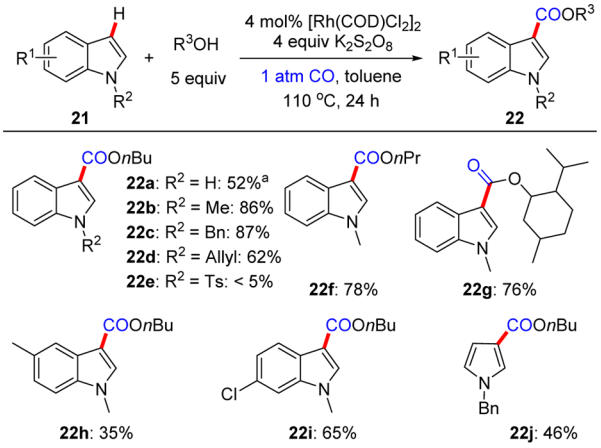
Scheme 10. Palladium-Catalyzed N−H Alkoxycarbonylation of Indoles



DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

reaction parameters, $[Rh(COD)Cl]_2$ was employed as the catalyst with 2 mol % $K_2S_2O_8$ as the stoichiometric oxidant. The carbonylation occurred selectively at the 3-position of indoles with both primary and secondary alcohols (Scheme 11). A number of protecting groups, such as methyl (**22b**), benzyl (**22c**), and allyl (**22d**), were tolerated under the optimized conditions. However, only a trace amount of the desired ester was obtained when *N*-tosylindole was used as substrate (**22e**), indicating that the reaction might proceed through an electrophilic metalation process. Interestingly, NH-free indole was regioselectively carboxylated at the C-3 position (**22a**) under this oxidative carbonylation conditions.

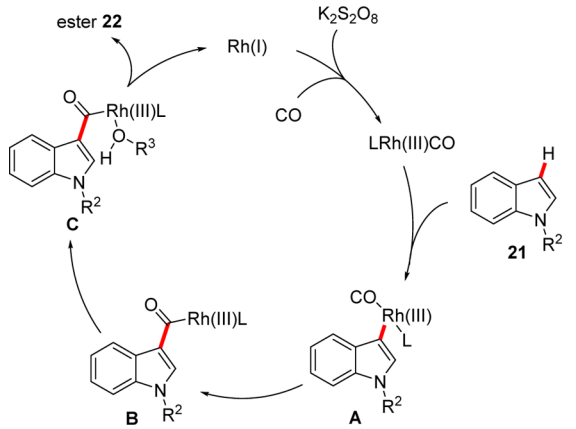
Scheme 11. Rhodium-Catalyzed C−H Alkoxycarbonylation of Indoles



[a]90 °C, 48 h.

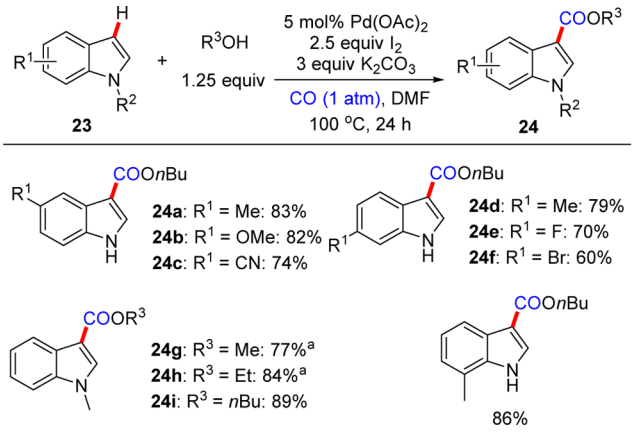
The carbonylation product was not observed when a stoichiometric amount of $[Rh(COD)Cl]_2$ was added in the absence of oxidants. Therefore, they proposed that the carbonylation reaction proceeded through a Rh(I)/Rh(III) catalytic cycle including the following steps (Scheme 12): (a) the oxidation of $[Rh(COD)Cl]_2$ to generate a Rh(III) carbonyl species; (b) electrophilic metalation with indole at the C-3 position to give **A**; (c) insertion of CO to C−Rh bond to produce intermediate **B**; (d) the coordination of alcohol with intermediate **B** to form intermediate **C**; (e) reductive elimination to afford the desired ester **22** and regenerate precatalyst Rh(I).

Scheme 12. Proposed Mechanism



On the basis of the work by the Daugulis group,[24] Li and co-workers rationalized that the Pd(0)/I_2 would be an ideal catalytic system to enable the regioselective alkoxycarbonylation of indoles via a one-pot, two-step sequence: oxidative iodination of indoles and subsequent carbonylation. After extensive optimization, a catalytic amount of $Pd(OAc)_2$, 2.5 equiv of I_2, and 3 equiv of K_2CO_3 in DMF with a balloon pressure of CO were found to be superior conditions for this cascade carbonylation reactions (Scheme 13).[25]

Scheme 13. Palladium-Catalyzed C−H Alkoxycarbonylation of Indoles via Sequential Iodination/Carbonylation

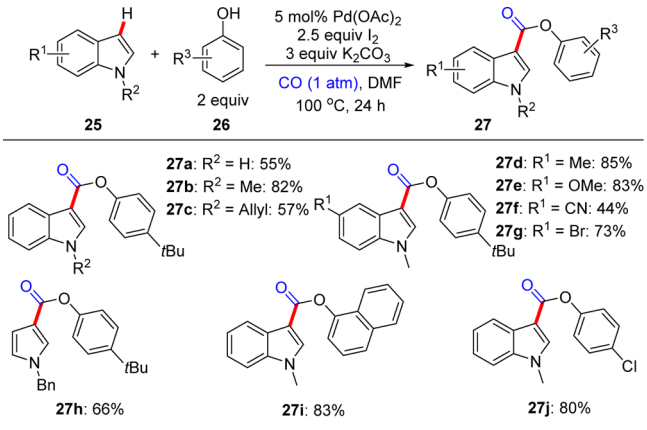


[a]80 °C, 48 h.

Generally, NH-free indoles containing electron-donating groups showed better reactivity compared with those containing electron-withdrawing groups as described in Scheme 13. Using the same carbonylation conditions, Br-substituted indole was carbonylated to give **24f** in 60% yield, thus providing the possibility for further functionalizations.

After the investigation of aliphatic alcohols as nucleophiles, they found that phenols were also compatible with this $Pd(OAc)_2/I_2$ catalytic system (Scheme 14). This process is of particular interest because it provides a simple and efficient approach for the synthesis of phenyl indole-3-carboxylate structures in one-step.

Scheme 14. Palladium-Catalyzed C−H Phenoxycarbonylation of Indoles



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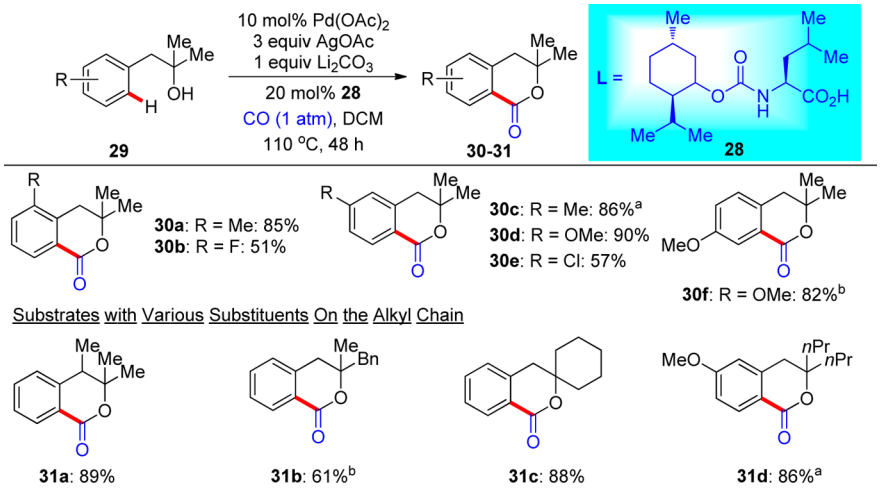
Scheme 15. Palladium-Catalyzed Hydroxyl-Directed C−H Alkoxycarbonylation

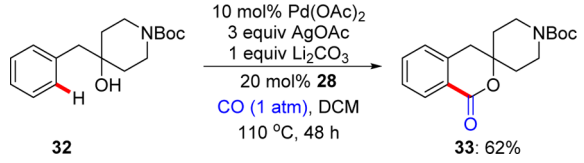


[a]80 °C. [b]90 °C.

Pd(II)-catalyzed hydroxyl directed *ortho*-C(sp^2)−H carbonylation of phenethyl alcohols to form lactones was reported by Yu et al. recently.[26] The following optimized conditions, 10 mol % $Pd(OAc)_2$, 20 mol % **L**, 1 equiv Li_2CO_3, and 3 equiv AgOAc in DCM, were identified after screening of various reaction parameters, and N-monoprotected α-amino acid (**28**) was found to promote this transformation as a highly effective ligand. The scope of the reaction was evaluated with regard to the electronic properties and steric effects (Scheme 15). Furthermore, *meta*-substituted substrates reacted regioselectively at the less sterically hindered position (**30c**−**30e**). Finally, sterically bulky substituents on the alkyl chain adjacent to the hydroxyl did not retard this transformation (**31b**, **31c**).

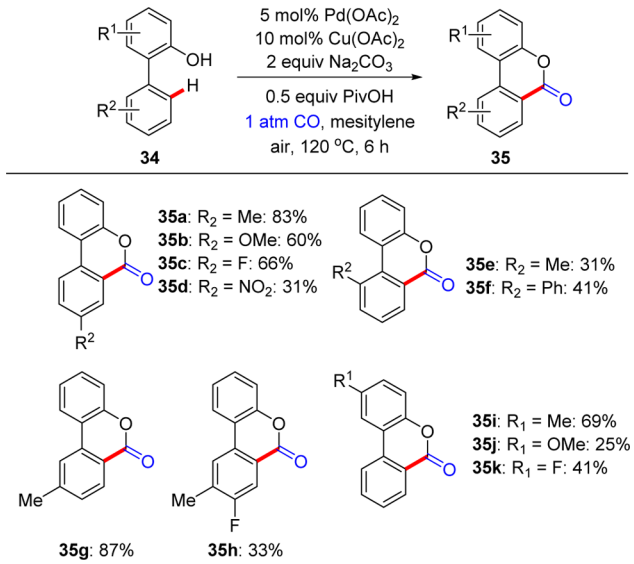
The carbonylation reaction could also be applied to the synthesis of bioactive compounds, as demonstrated in Scheme 16. *N*-Boc-protected cyclic lactone **33**, a histamine release inhibitor, was prepared in 62% yield under the standard reaction conditions.

Scheme 16. Synthesis of Histamine Release Inhibitor via Palladium-Catalyzed Hydroxyl-Directed C−H Alkoxycarbonylation



Biaryl lactones and their derivatives are found in pharmaceuticals, natural products, and advanced materials.[27] Consequently, intramolecular carbonylation of phenols through C(sp^2)−H bond activation have received tremendous interest.[28] In 2013, Shi and co-workers reported the synthesis of dibenzopyranones via the palladium-catalyzed direct carbonylation of 2-arylphenols with CO (Scheme 17).[28a] Notably, the electronic properties of $\mathbf{R^1}$ have greater impact on the reaction compared with $\mathbf{R^2}$. For example, the electron-withdrawing group (**35k**) gave higher yield than the electron-donating group (**35j**). However, the electron-deficient group (**35c**) gave similar yield with the electron-rich group (**35b**).

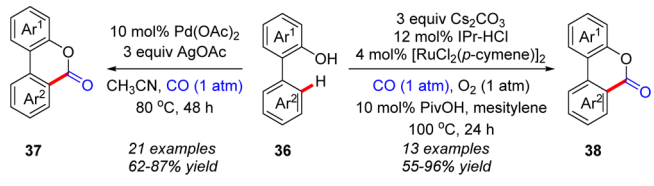
Scheme 17. Palladium-Catalyzed C−H Carbonylation of 2-Arylphenols



In the same year, a similar Pd(II)-catalyzed intramolecular carbonylation of arylphenols was reported by Chuang and co-workers. Notably, the reaction proceeded smoothly in the presence of 3 equiv of AgOAc without any other additives (Scheme 18).[28b]

In an effort to construct heterocyclic compounds, Inamoto and co-workers also demonstrated the synthesis of dibenzopyranones via Ru-catalyzed C−H carbonyltion of 2-arylphenols.[28c] The intramolecular carbonylation of various 2-arylphenols was

Scheme 18. Palladium or Ruthenium-Catalyzed C−H Carbonylation of 2-Arylphenols

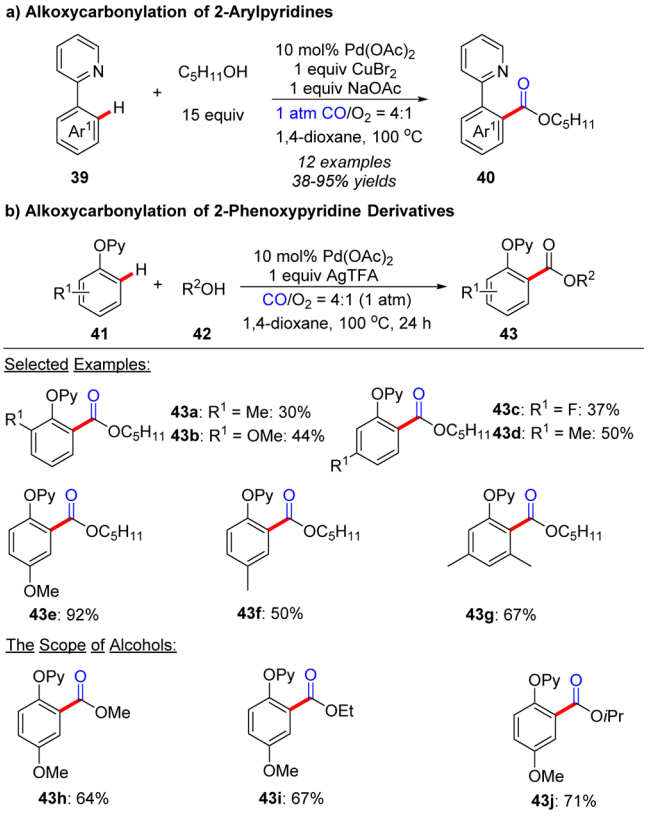


DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

successfully achieved by using 10 mol % PivOH, 4 mol % $[RuCl_2(p\text{-cymene})]_2$, 12 mol % IPr·HCl and 3 equiv of Cs_2CO_3 in mesitylene under a balloon pressure of a mixture of CO and O_2 (Scheme 18).

In our continuous studies of the C−H carbonylation reactions (Scheme 19a),[29] we developed an efficient protocol

Scheme 19. Palladium-Catalyzed Pyridyl Directed C−H Alkoxycarbonylation Reaction

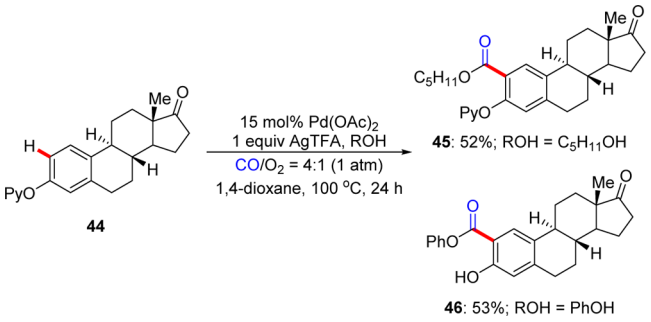


for the synthesis of aryl carboxylic esters via Pd(II)-catalyzed alkoxycarbonylation of 2-phenoxypyridines under atmospheric pressure of CO and O_2 (Scheme 19b).[30] AgTFA was found to be the ideal oxidant and the carbonylation product was obtained in 75% isolated yield. Both electron-withdrawing and electron-donating substituents are compatible with the optimized reaction conditions. Furthermore, various aliphatic alcohols reacted smoothly to give the corresponding esters in good yields.

This protocol was applied to the late-stage modification of estrone (Scheme 20). The pyridyl auxiliary was introduced via a copper-catalyzed C−O bond formation reaction.[31] Subsequently, the alkoxycarbonylation reaction was achieved regioselectively at the less sterically hindered C−H bond under our standard conditions.

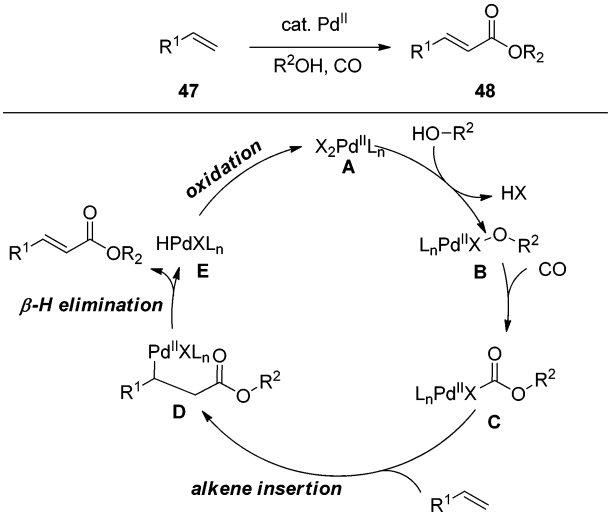
Despite these significant advances in direct alkoxycarbonylation of aromatic $C(sp^2)$−H bonds, transition-metal-catalyzed alkenyl $C(sp^2)$−H bonds activation and alkoxycarbonyltion for the synthesis of α,β-unsaturated carboxylic esters has not yet been realized. However, the synthesis of α,β-unsaturated carboxylic esters[32] and α,β-unsaturated lactones[33] via oxidative carboxylation/palladation of alkenes followed by β-H elimination without the C−H activation has been well studied

Scheme 20. Alkoxy/Phenoxycarbonylation of Estrone



(Scheme 21). These reactions will not be discussed considering the topic of this review.

Scheme 21. Mechanism of Synthesis of α,β-Unsaturated Carboxylic Esters by β-H Elimination



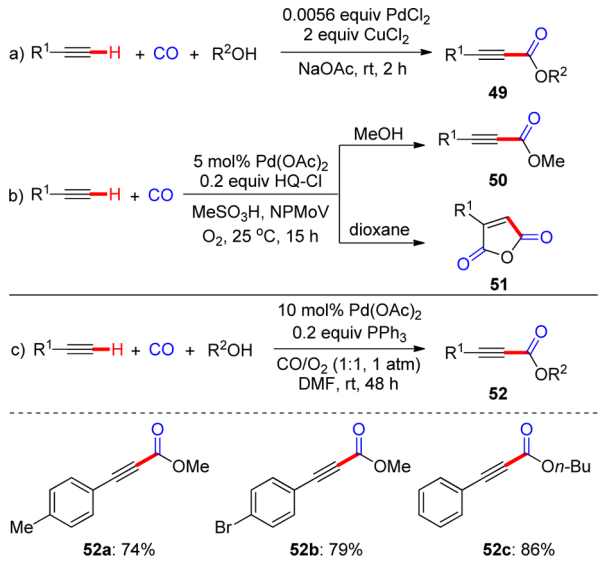
2.2. Alkoxycarbonylation of Alkynyl C(sp)−H Bonds with CO. The first synthesis of α,β-alkynyl esters by palladium-catalyzed carbonylation of terminal alkynes was reported by Tsuji et al. in 1980 (Scheme 22a).[34] Two decades later, the Ishii group developed a multicatalytic system consisting of $Pd(OAc)_2$, hydroquinone and molybdovanadophosphate (NPMoV) under CO and O_2 (CO/O_2 = 10:0.5 atm) to afford α,β-alkynyl esters (Scheme 22b).[35] In 2004, Yamamoto and co-workers reported a protocol for the alkoxycarbonylation of terminal alkynes using a $Pd(OAc)_2/Ph_3P$ catalytic system under an atmospheric pressure of CO/O_2 in DMF as solvent at room temperature (Scheme 22c).[36] Terminal alkynes such as phenylacetylene were converted into ynoates such as bromo phenylpropiolate (**52b**) in 79% yield.

In 2013, Bhanage and co-workers reported the synthesis of α,β-alkynyl esters via oxidative alkoxycarbonylation of terminal alkynes catalyzed by Pd/C.[37] The α,β-alkynyl esters were produced in good yields under the standard conditions (Scheme 23).

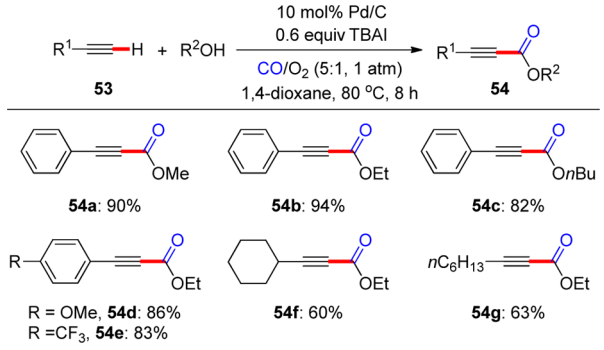
2.3. Alkoxycarbonylation of Allylic/Benzylic $C(sp^3)$−H Bonds with CO. Palladium-catalyzed direct alkoxycarbonylation of of allylic C−H bonds with carbon monoxide was realized by Jiang and co-workers in 2011 (Scheme 24a).[38] Shortly after, Huang and co-workers reported the carbonylation of toluene derivatives with CO and alcohols in the presence of

DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

Scheme 22. Palladium-Catalyzed Alkoxycarbonylation of Alkynes



Scheme 23. Pd/C-Catalyzed Alkoxycarbonylation of Terminal Alkynes



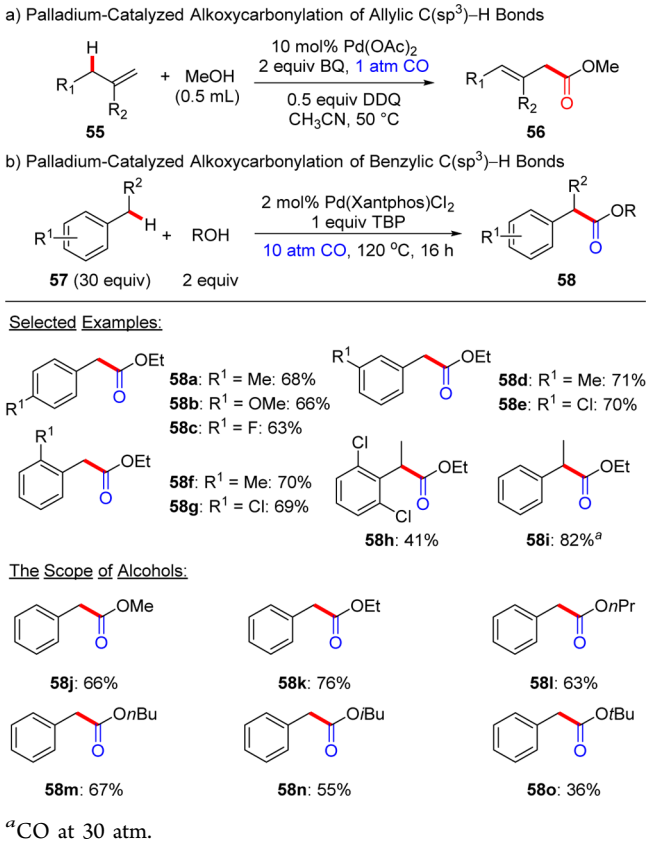
palladium as the catalyst and di-*tert*-butyl peroxide (TBP) as the oxidant.[39] DTBP was acted as a radical initiator to activate the benzylic C(sp^3)−H bonds (Scheme 24b).

A plausible reaction mechanism was illustrated after a series of control experiments, and kinetic isotope effect experiments were conducted (Scheme 25a). The observed isotopic effects (k_H/k_D = 4.9) described in Scheme 25a indicated that the benzylic C−H bond cleavage step might be the rate-limiting step of this alkoxycarbonylation reaction. A plausible mechanism was proposed by the authors. First, benzylic hydrogen was abstracted by an alkoxyl radical, which was generated by the homolytic cleavage of the TBP. Subsequently, benzyl palladium species (**A**) was produced by the reaction of benzyl radical with palladium and the oxidant. Finally, the benzyl palladium species (**B**) underwent CO insertion and reductive elimination to afford the desired alkoxycarbonylation product (Scheme 25b).

3. ALKOXYLCARBONYLATION OF C−H BONDS WITH OTHER ESTERIFICATION REAGENTS

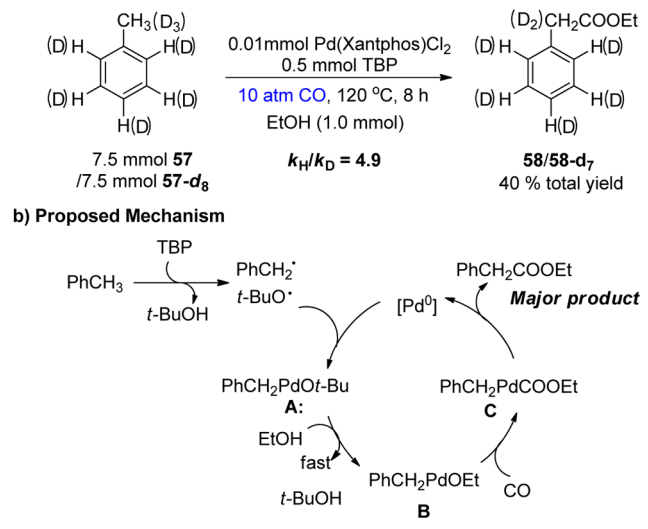
Although CO is a versatile and inexpensive C_1 building block, there are some major disadvantages, such as its toxicity, gaseous form and flammability, which make it less convenient to handle and transport. In consideration of these limitations, carbonylation reactions that can be conducted without the direct using

Scheme 24. Palladium-Catalyzed Alkoxycarbonylation of Allylic/Benzylic C(sp^3)−H Bonds



[a]CO at 30 atm.

Scheme 25. Kinetic Isotope Effect Studies and Plausible Reaction Mechanism



of carbon monoxide have therefore attracted considerable attention.[40] In this section, the synthesis of esters via transition-metal-catalyzed alkoxycarbonylation of aryl C(sp^2)−H bonds with other esterification reagents, such as azodicarboxylates,[41] alkyl chloroformates,[42] oxaziridine,[43] glyoxylates,[44] α-keto esters,[45] di-*tert*-butyl dicarbonate (Boc_2O),[46] formates,[47] and carbon dioxide (CO_2),[51] will be discussed.

DOI: 10.1021/acscatal.5b00050
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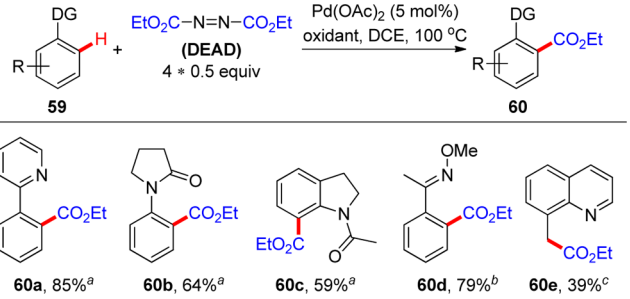
Azodicarboxylates have been widely employed in organic synthesis because they are readily available and easy to use. However, they have rarely been used as the esterification reagents. In 2008, Yu and co-workers described the first example of Pd-catalyzed ethoxycarbonylation of aryl C−H bonds with diethyl azodicarboxylate (DEAD).[41a] A variety of substrates bearing different directing groups, such as 2-phenylpyridine (**59a**), pyrrolidinone (**59b**), acetylindoline (**59c**) and *O*-methyl oxime (**59d**), were compatible with this protocol (Scheme 26). Notably, the reaction of 8-methylquinoline (**59e**) with DEAD proceeded well under the optimized conditions to give the C(sp^3)−H carbonylation product **60e** in moderate yield.

Scheme 26. Pd-Catalyzed Ethoxycarbonylation of Aryl C−H Bonds and Benzyl C(sp^3)−H Bond with DEAD



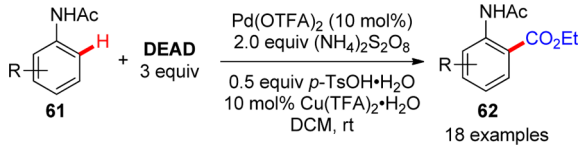
[a]Oxone as oxidant. [b]$K_2S_2O_8$ as oxidant. [c]10 mol % $Cu(OAc)_2$ and 3 equiv of Oxane.

On the basis of several control experiments, they proposed that the resultant palladacycle **I** was oxidized to high-valent palladium intermediate **II** by the ethoxyacyl radicals, which was generated from thermal decomposition of DEAD. Subsequent reductive elimination gave the desired product (Scheme 27).

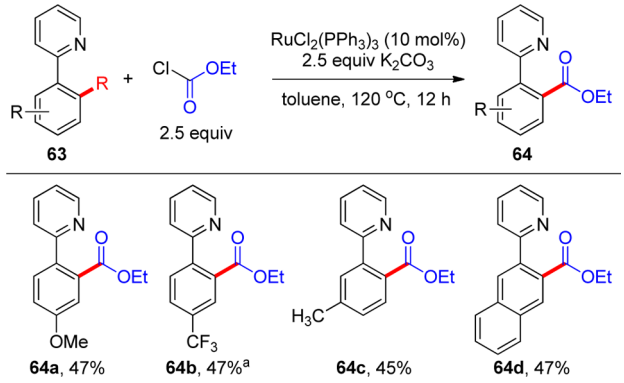
Recently, the You group reported a Pd-catalyzed ethoxycarbonylation of anilides at room temperature.[41b] Notably, the addition of *p*-TsOH is crucial for the success of this transformation, and a broad range of anilides bearing different functional groups reacted smoothly under the standard conditions (Scheme 28).

Friedel−Crafts acylation of electron-rich aromatic compounds with acyl chlorides has been recognized as one of the most efficient methods for the introduction of carbonyl groups.[48] On the basis of this result, Kakiuchi and co-workers demonstrated the first ruthenium-catalyzed alkoxycarbonylation of 2-arylpyridines using alkyl chloroformates as esterification reagents.[42] Alkoxycarbonylation of both *p*-methoxyphenylpyridines and *p*-trifluoromethylphenylpyridines gave monoesters **64a** and **64b** in similar yields. The advantage of this protocol is that no oxidants are needed (Scheme 29).

Scheme 28. Pd-Catalyzed Ethoxycarbonylation of Anilides with DEAD



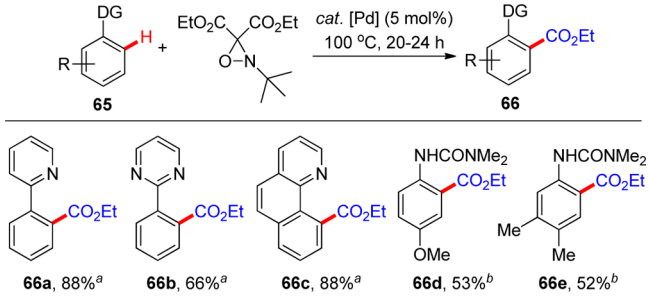
Scheme 29. Ruthenium-Catalyzed Alkoxycarbonylation of 2-Arylpyridines with Alkyl Chloroformates



[a]Diester product was isolated with 8% yield.

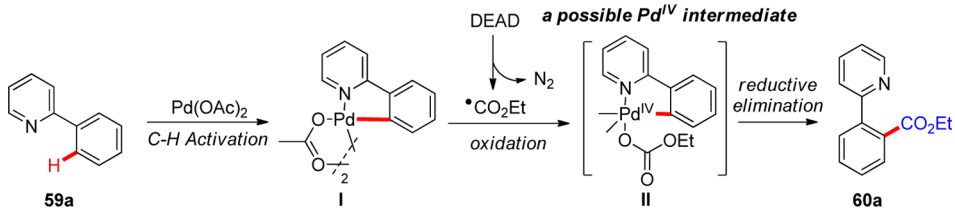
During their ongoing investigations of the reactivity and synthetic application of diaziridine and its derivatives, Shi and co-workers reported a Pd-catalyzed alkoxycarbonylation of aryl C−H bonds with oxaziridines.[43] Both 2-arylpyridines and aryl arenes reacted smoothly in this novel protocol and gave the desired esters in moderate to good yields (Scheme 30). A Pd(II)/Pd(IV) catalytic cycle was proposed, which involved the insertion of Pd(II) into the N−O bond of oxaziridine to generate the Pd(IV) intermediate.

Scheme 30. Pd-Catalyzed Alkoxycarbonylation of Aryl C−H Bonds with Oxaziridine



[a]10 mol % $PdCl_2$, $CHCl_3$, 24 h. [b]15 mol % $Pd(MeCN)_4(BF_4)_2$, toluene, 20 h.

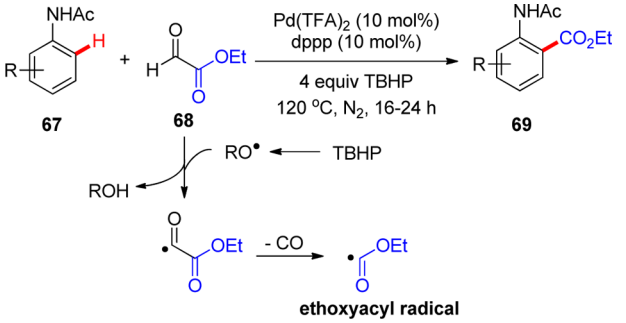
Scheme 27. Plausible Mechanism



DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

Li,[49a] Cheng,[49b] and Kwong[49c] have reported that aldehydes can undergo Pd-catalzyed dehydrogenative coupling with aryl C−H bonds to generate aryl ketones by the use of TBHP as oxidant. Inspired by these works, the Tan group reported the synthesis of anthranilic esters via Pd-catalyzed dehydrogenative/decarbonylative coupling of anilides with glyoxylates in a similar mode of reaction.[44] The reaction proceeded well in toluene using $Pd(TFA)_2$-dppp as catalyst. A broad range of anilides bearing synthetically useful functional groups are tolerated under the standard conditions (Scheme 31). An ethoxyacyl radical was generated from the TBHP induced hydrogen abstraction and decarbonylation of glyoxylate **68**.

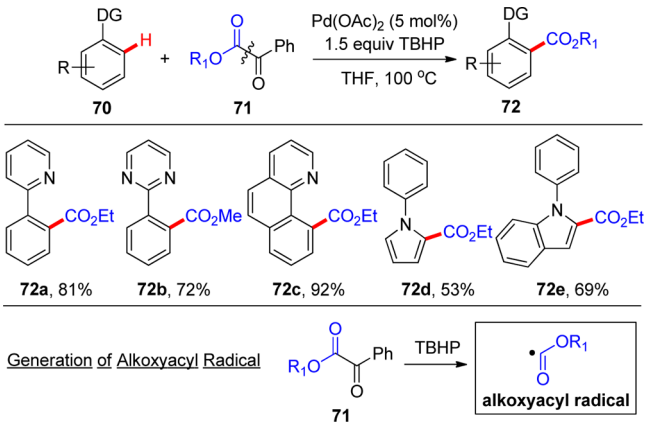
Scheme 31. Pd-Catalyzed Dehydrogenative/Decarbonylative Coupling of Anilides with Glyoxylate



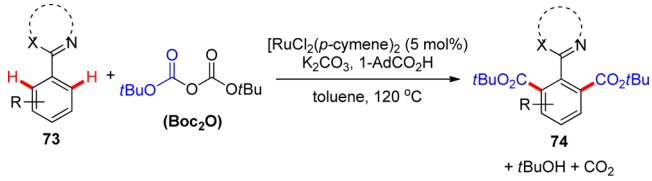
Inspired by Tan's work,[44] the Wang group realized that the reaction of α-keto esters with TBHP could also generate alkoxyacyl radicals, which could then be used for the Pd-catalyzed alkoxycarbonylation of aryl C−H bonds in a similar reaction mechanism. On the basis of this rational design, the optimized reaction conditions were established by the use of 5 mol % palladium acetate and 1.5 equiv of TBHP in THF.[45] A variety of substrates, such as 2-arylpyridines, 2-arylquinolines, benzo[*h*]quinolines, 2-phenylpyrimidines, *N*-pyrimidine pyrroles and *N*-pyrimidine indoles, reacted smoothly with α-keto esters to give the corresponding esters in good yields (Scheme 32).

Recently, Xu and co-workers reported a Ru-catalyzed dialkoxycarbonylation of arenes with Boc_2O (Scheme 33).[46] Notably, this is the first example of the use of commercially available Boc_2O as the esterifiction reagent in C−H bond activation reaction.

Scheme 32. Pd-Catalyzed Alkoxycarbonylation of Aryl C−H Bonds with α-Keto Esters

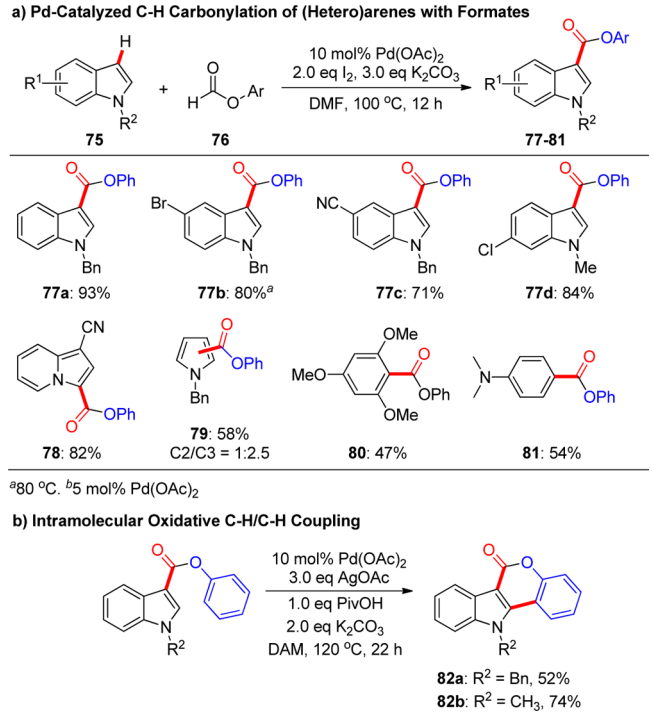


Scheme 33. Pd-Catalyzed Dialkoxycarbonylation of Aryl C−H Bonds with Boc_2O



Formates are inexpensive, less toxic C1 building blocks and can be handled more easily than carbon monoxide.[50] In 2014, You and co-workers reported an efficient approach to (hetero)aryl carboxylic esters by using aryl formate esters as carbonyl source.[47a] The corresponding esters were isolated in moderate to good yields under their optimized conditions (Scheme 34). A broad range of functional groups and electron-rich (hetero)arenes are compatible with this protocol. Finally, an intramolecular dehydrogenative coupling of the resulting esters has been developed to give various indolo[3,2-*c*]coumarins (Scheme 34b).

Scheme 34. Pd-Catalyzed C−H Carbonylation of (Hetero)arenes with Formates and Intramolecular Dehydrogenative Coupling

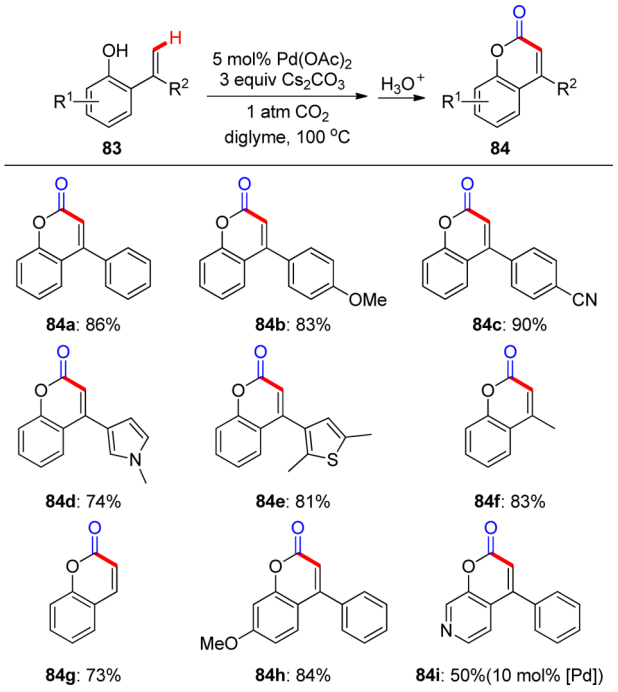


[a]80 °C. [b]5 mol % $Pd(OAc)_2$.

A rare example of carboxylation of alkenyl C−H bonds with CO_2 was reported by Iwasawa and co-workers in 2013.[51] A series of coumarins with various different substituents on the phenyl ring were obtained in good to excellent yields (Scheme 35). It has been found that the pyrrole and thiophene group also afforded the desired carboxylation in good yields (**84d** and **84e**).

DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

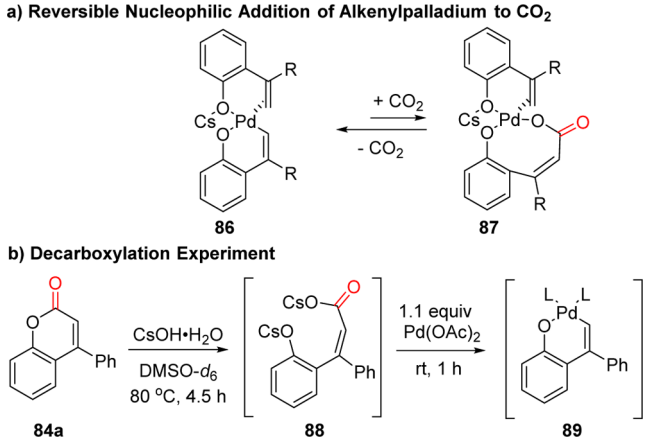
Scheme 35. Palladium-Catalyzed Carboxylation of Alkenyl C−H Bonds with CO_2



To elucidate the mechanism of the transformation, α-phenyl-2-hydroxystyrene was treated with 1 equiv of $Pd(OAc)_2$ in DMSO-d_6 at room temperature to produce the cyclometalated complex **85**, which was generated via alkenyl C−H bond cleavage. In contrast, alkenyl palladium intermediate **86** was obtained when the reaction was conducted in the presence of 0.5 equiv of $Pd(OAc)_2$ and 3 equiv of Cs_2CO_3 (Scheme 36). Notably, the stoichiometric reaction of complexes **85** and **86** with CO_2 did not proceed; however, when $Pd(OAc)_2$ was replaced with complex **85** or **86** under the standard conditions, the desired coumarin was observed.

They rationalized that these results were due to the reversible nucleophilic addition of the alkenylpalladium intermediate to CO_2 with the carboxylation process unfavorable (Scheme 37a). This was confirmed by the decarboxylation of cesium carboxylate **88** in the presence of 1 equiv of $Pd(OAc)_2$ (Scheme 37b).

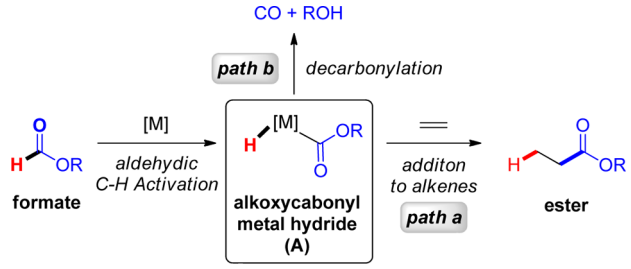
Scheme 37. Decarboxylation of Palladium Carboxylate Complexes



4. HYDROESTERIFICATION OF ALKENES WITH FORMATES VIA FORAMTE C−H ACTIVATION

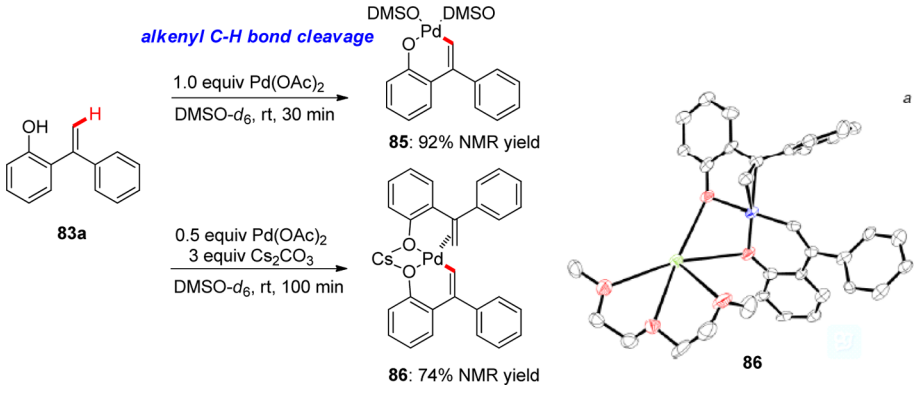
Transition-metal-catalyzed hydroesterification of alkenes with formates via the activation of formate C−H bonds followed by the addition of an acyl unit and a hydrogen atom into a C−C double bond are becoming a powerful tool for the formation of one-carbon elongated esters (Scheme 38, path a).[52] In contrast

Scheme 38. Transition-Metal-Catalyzed Formate C−H Activation



to traditional hydroesterification that use carbon monoxide and alcohols, this protocol obviates the use of expensive, toxic, and highly pressurized CO gas. The features of easy handling and high atom economy have rendered this transformation more promising. One major challenge of this transformation is the significant decarbonylation of the resulting alkoxycarbonyl metal hydride species (**A**) to alcohols and CO (Scheme 38,

Scheme 36. Synthesis of Alkenylpalladium Complexes

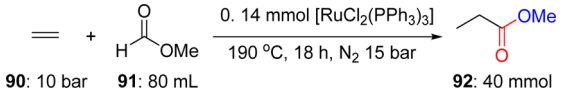


DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

path b), which will lead to side reactions and terminate the catalytic cycle. Tremendous efforts have been made to suppress the decarbonylation pathway, extend the scope, and improve the efficiency of this process. Historical developments and recent advances on this topic will be discussed below.

4.1. Ruthenium-Catalyzed Hydroesterification of Alkenes with Formates. The first ruthenium-catalyzed hydroesterification of olefins with formates were reported in 1983 by Sneeden, Cognion, and their co-workers (Scheme 39).[53] Since then, much effort has been put into improving the

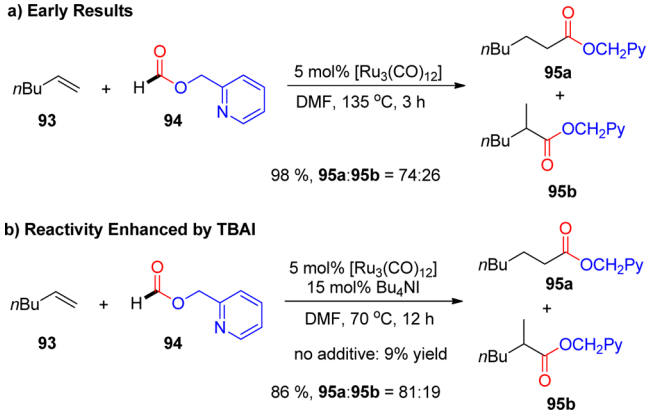
Scheme 39. Early Report of Ru-Catalyzed Hydroesterification of Ethylene with Methyl Formate



efficiency and applicability of this reaction.[54] However, the reported reactions require harsh conditions, such as high temperature and high pressure.

In 2002, a breakthrough in this area was made by Chang et al., they envisioned that the destructive decarbonylation pathway could be substantially suppressed through a chelation-assisted strategy. By the employment of a pyridyl moiety as the directing group, they demonstrated the hydroesterification of various alkenes, dienes, and alkynes with 2-pyridylmethyl formate, which is the first example to explore olefins other than ethylene (Scheme 40a).[55] In 2006,

Scheme 40. Ruthenium-Catalyzed Hydroesterification of Terminal Alkenes Through a Chelation-Assisted Strategy

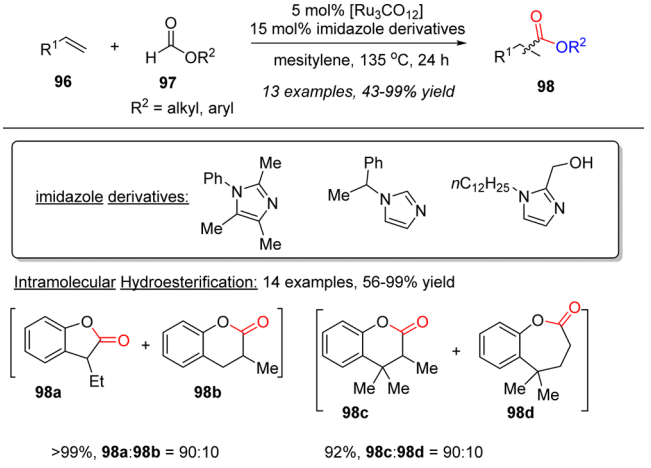


the same group found that the addition of catalytic amounts of Bu_4NI lowered the reaction temperature to 70 °C and enhanced the reaction efficiency remarkably (Scheme 40b).[56] Notably, pyridylmethyl formate has been successfully utilized as carbonyl source for the synthesis of lactones via hydroesterification/intramolecular lactonization.[57]

In 2012, Manabe and co-workers revealed a general ruthenium-catalyzed hydroesterification of alkenes with a wider range of formates without a chelation group.[58] Imidazole derivatives suppress the undesired decomposition of formates. Moreover, this method allows lactones to be prepared directly through intramolecular hydroesterification (Scheme 41).

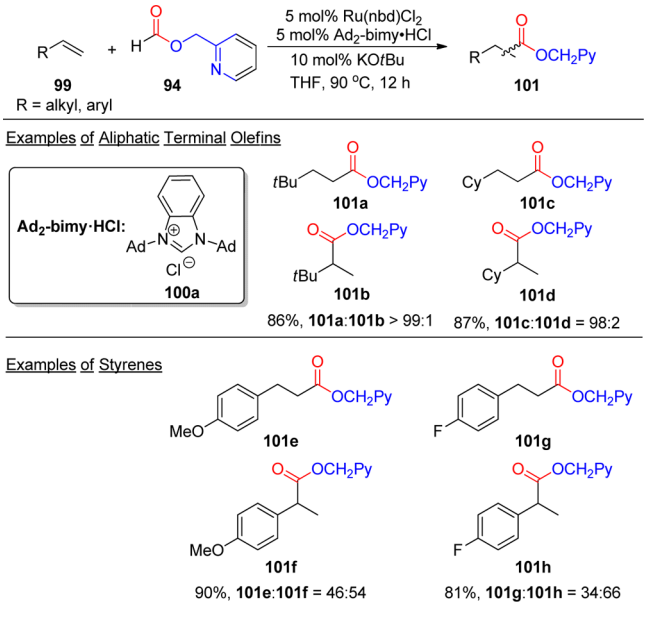
In 2014, Chang et al. explored ligand effects on the chelation-assisted hydroesterification reactions, which allowed the conversion of a variety of alkenes in excellent yields using

Scheme 41. Ruthenium-Catalyzed Hydroesterification of Alkenes with Formates Promoted by Imidazoles



different ruthenium catalysts (Scheme 42).[59] After extensive screening of ligands, *N*-adamantyl-substituted benzimidazole

Scheme 42. Ru(II)/Ad_2-bimy/KO-*t*-Bu Catalyzed Hydroesterification of Alkenes



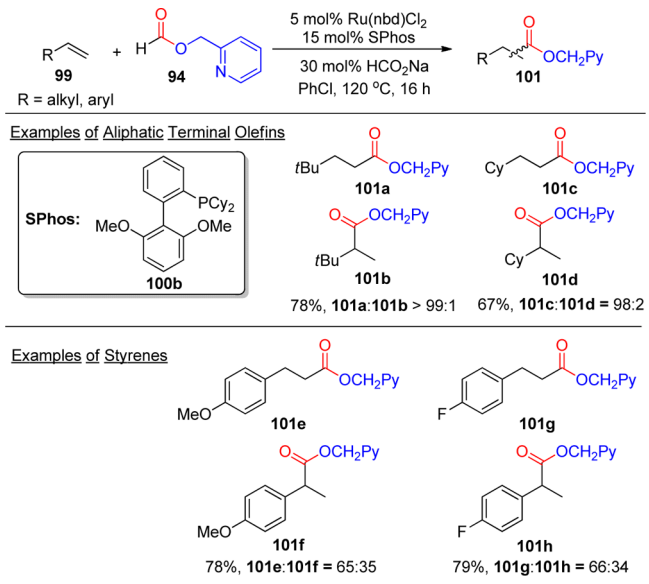
was found to be the best ligand. Furthermore, THF was found to promote the formation of the desired product in higher yield. It is worth noting that styrenes are mainly converted to branched esters, whereas linear products are obtained predominantly as for aliphatic olefins.

Another catalyst system with the combination of Ru(nbd)-Cl_2/SPhos/HCO_2Na was also developed by Chang (Scheme 43). Compared with the Ru/NHC catalyst system, styrenes were mainly transformed to linear esters, although the reactivity for aliphatic alkenes was slightly lower than that with Ru/NHC.

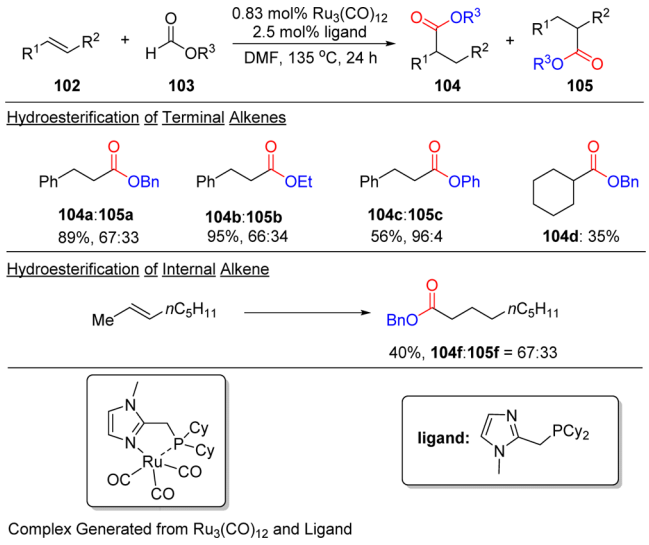
Recently, Fleischer et al. investigated the hydroesterification of olefins using an improved catalyst system composed of $Ru_3(CO)_{12}$ and a phosphine-substituted imidazole derivative (Scheme 44).[60] The coordination of the ligand to the ruthenium center was confirmed by X-ray, which could significantly improve the reactivity. A variety of formates,

DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

Scheme 43. Ru(II)/SPhos/HCO_2Na Catalyzed Hydroesterification of Alkenes



Scheme 44. Ruthenium-Catalyzed Hydroesterification of Olefins by Using Bidentate Ligand

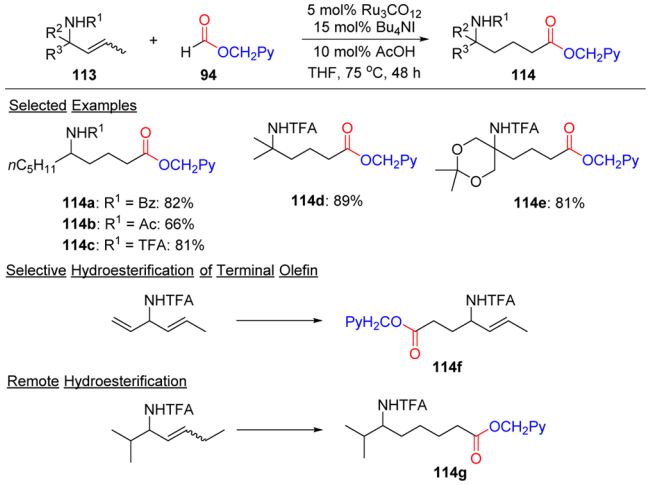


such as benzyl formate, ethyl formate, and phenyl formate, can be used as the esterification reagents. The reaction conditions were also applied to a variety of alkenes. It is noteworthy that aliphatic alkenes react slower than styrenes.

More recently, Jun and co-workers reported an interesting example of hydroesterification of alkenes with sodium formate and alcohols catalyzed by $Ru_3(CO)_{12}$ and 2-pyridinemethanol (Scheme 45).[61] In this case, sodium formate was served as the carbonyl source.

$[Ru_3(CO)_{12}]$-catalyzed remote hydroesterification of allylic amides was recently reported by the Carreira group (Scheme 46).[62] Allylic amides were isomerized to terminal alkenes,

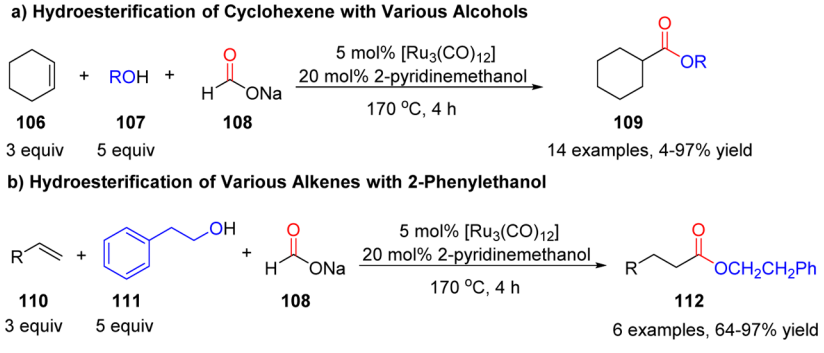
Scheme 46. Ru(0)-Catalyzed Remote Hydroesterification of Allylic Amides



which then reacted with pyridine-2-ylmethyl formate. The hydroesterification reaction proceeded preferentially on the terminal alkenes when a substrate contains both internal and terminal olefins. Moreover, the remote terminal position could be functionalized under the present conditions via double alkene isomerization.

4.2. Palladium-Catalyzed Hydroesterification of Alkenes with Formates. The palladium-catalyzed hydroesterification with formates and related compounds are less investigated. Palladium-catalyzed carbonylation reaction of alkenes with methyl formate in the presence of excess carbon monoxide was reported by Alper in 1980s.[63] Nevertheless, the first palladium-catalyzed carbonylation reaction of alkenes with methyl formate without carbon monoxide was reported by Kalck and Grévin in 1994.[64] The palladium-catalyzed hydroesterfication of alkynes, norbornene, and terminal alkenes was reported by Tsuji in 2011.[65] This process involves the

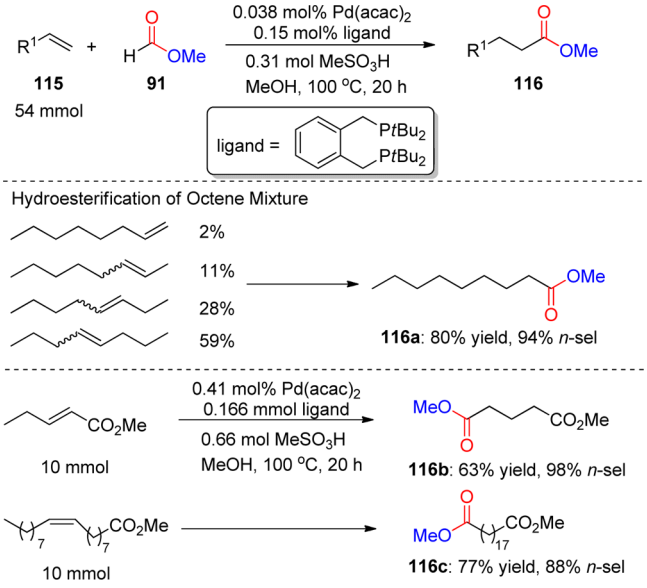
Scheme 45. Ru(0)/2-Pyridinemethanol-Catalyzed Hydroesterification of Alkenes with Sodium Formate and Alcohols



DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

conversion of aryl formates to phenols and carbon monoxide. In 2013, palladium(II)-catalyzed alkoxycarbonylation of olefins with formates using the so-called BuPox ligand was reported by Beller and co-workers (Scheme 47).[66] Linear esters were

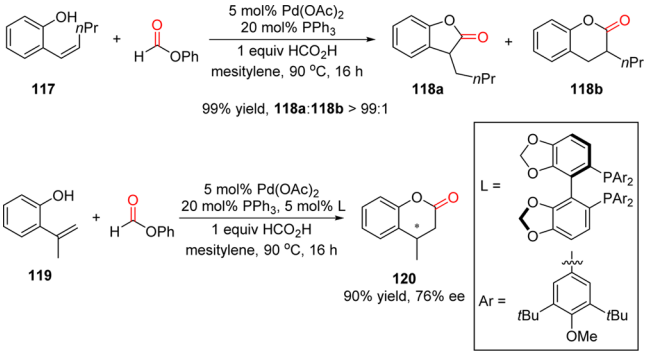
Scheme 47. Palladium-Catalyzed Alkoxycarbonylation of Alkenes with Formates



obtained with excellent regioselectivity from the corresponding terminal and internal alkenes by the addition of an acidic cocatalyst with weakly coordinating anion.

In a recent report by Shi and co-workers, a variety of lactones were prepared directly from alkenylphenols and phenyl formate using $Pd(OAc)_2$-PPh_3 as an efficient catalytic system (Scheme 48).[67] A range of formates were initially studied, and HCO_2Ph

Scheme 48. Palladium-Catalyzed Hydroesterification of Alkenylphenols

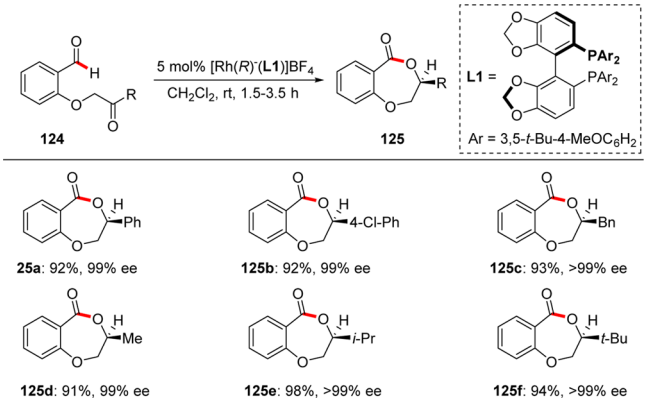


was found to be the optimal CO source for the reaction. Through extensive screenings, they found that the $Pd(OAc)_2$-PPh_3 was the best catalyst and formic acid could enhance the reactivity. More importantly, when (*R*)-(−)-DTBM-SEGPHOS was used as chiral ligand, lactone **120** was produced in 90% yield and 76% ee.

5. HYDROACYLATION OF CARBONYL COMPOUNDS VIA ALDEHYDIC C−H ACTIVATION

Catalytic hydroacylation of carbonyl compounds is another atom economical process for the synthesis of esters. This

Scheme 50. Rh(I)-Catalyzed Intramolecular Hydroacylation of Ketones

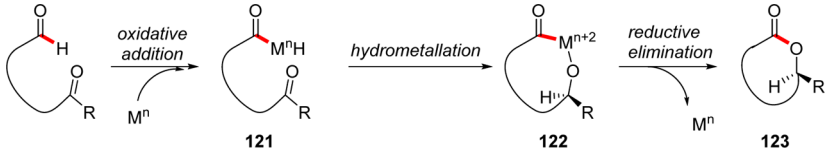


transformation is proposed to be initiated with the formation of an acyl metal hydride species **121** by the oxidative addition of the metal catalyst to the aldehydic C−H bond.[68] Subsequent addition of this species to carbonyl can afford intermediate **122**, which will give the desired ester **123** via reductive elimination (Scheme 49).

Despite significant advances in ketone synthesis via hydroacylation of alkenes with aldehyde, the hydroacylation of carbonyl compounds as an atom economical process to produce the corresponding esters has not been well studied until the seminal works of Dong.[69] In 2008, Dong and co-workers reported an unprecedented Rh-catalyzed hydroacylation of ketones to access chiral lactones.[70] A catalyst screening revealed that increasing basicity of phosphine ligands will promote the reactivity and suppress the undesired decarbonylation process. This protocol furnishes the corresponding chiral lactones in remarkable efficiency and excellent enantioselectivity (Scheme 50). However, this protocol was limited to ketoaldehydes bearing an ether linkage, which was proposed to stabilize Rh(III)-acyl intermediates and suppress decarbonylation.

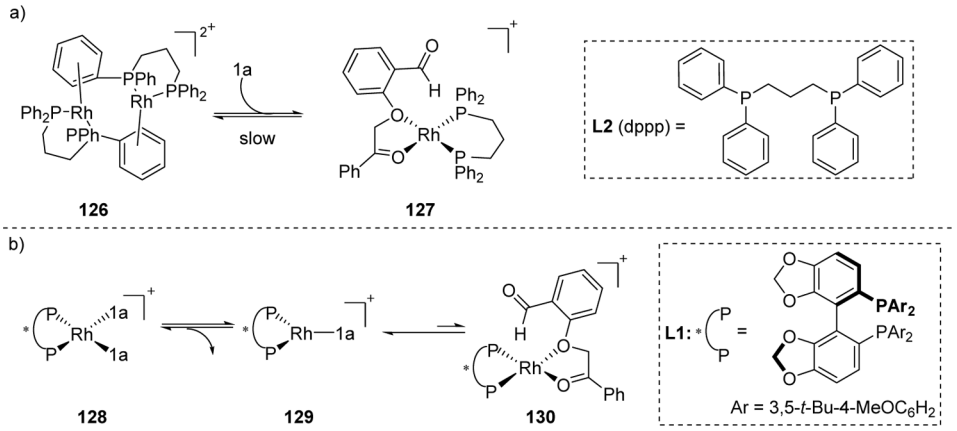
Detailed experimental and theoretical studies have been conducted to probe the mechanism of the intramolecular ketone hydroacylation reaction.[71] KIE (k_H/k_D = 1.8) and Hammett plot studies reveal that the addition of rhodium hydride onto the carbonyl group is the rate-limiting step, which is also supported by density functional theory (DFT)

Scheme 49. Principle of Intramolecular Hydroacylation of Carbonyl Compounds

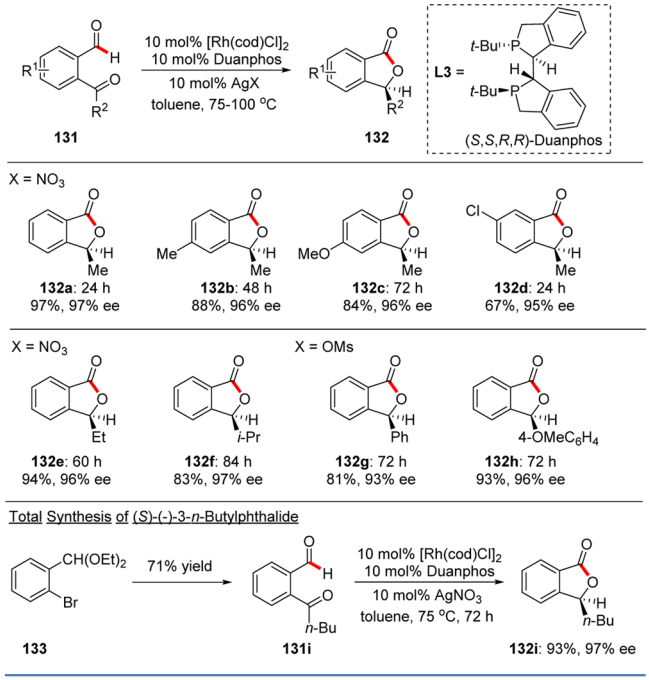


DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

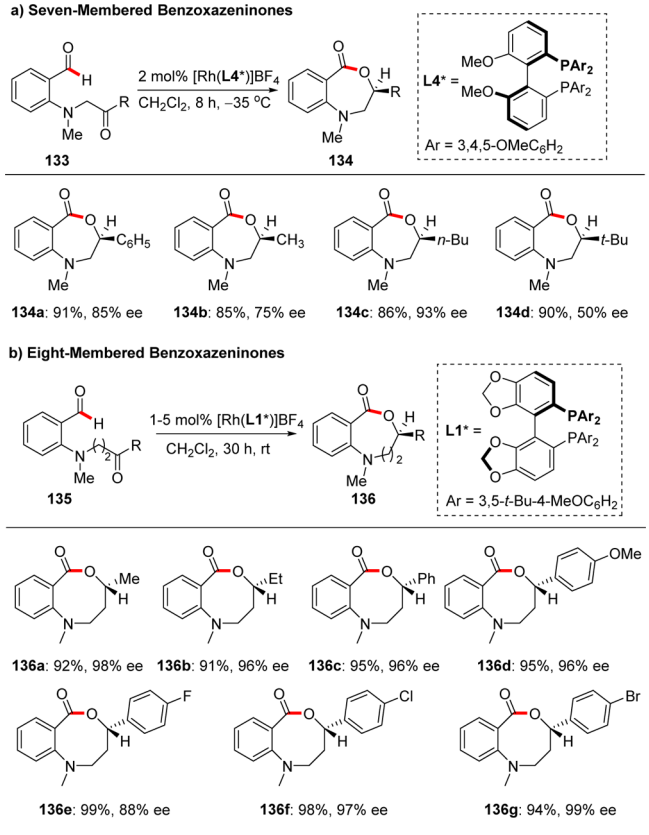
Scheme 51. Resting State with Different Ligands



Scheme 52. Rhodium-Catalyzed Intramolecular Ketone Hydroacylation Towards Phthalides



Scheme 53. Rhodium-Catalyzed Intramolecular Hydroacylation of Ketones Towards Benzoxazecinones



calculations. Kinetic studies demonstrated that when dppp is employed as the ligand, a stable catalyst dimer **126** slowly dissociates into catalytically active monomeric catalyst-substrate complexes **127** (Scheme 51a). However, when (*R*)-DTBMSEGPHOS is used as the ligand, the formation of dimeric catalyst structure is inaccessible on account of steric bulk. As a consequence, the resting state is monomeric catalyst bound to one or two substrate molecules (**128**, **129**) (Scheme 51b).

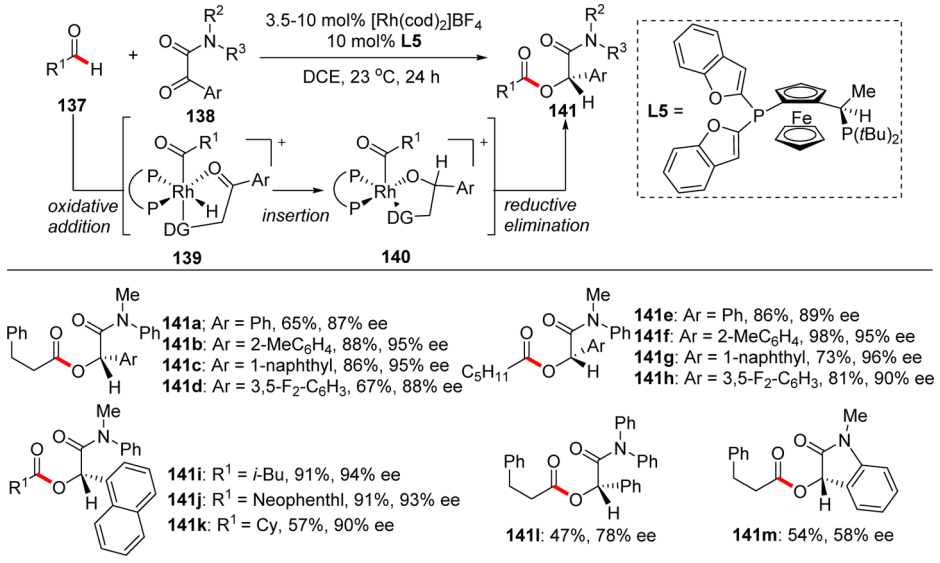
On the basis of these results, Dong envisioned that the choice of ligands, solvents or counterions would make the preparing of phthalides feasible through a Rh-catalyzed intramolecular hydroacylation. After extensive optimization, Duanphos was found to be a promising ligand. The screening of various counterions revealed that catalysts with more strongly coordinating counterions gave better selectivity for hydroacylation over decarbonylation. Finally, the combination of [$RhCl(cod)_2$], (*S*,*S*,*R*,*R*)-Duanphos,, and a nitrate counterion were found to be optimal.[72]

The optimized reaction conditions were applied to the substrates with both electron-donating and electron-withdrawing groups on the aromatic backbone (Scheme 52). Importantly, (*S*)-(−)-3-*n*-butylphthalide (**132i**), a natural product from celery extract, could be synthesized via this rhodium-catalyzed hydroacylation reaction.

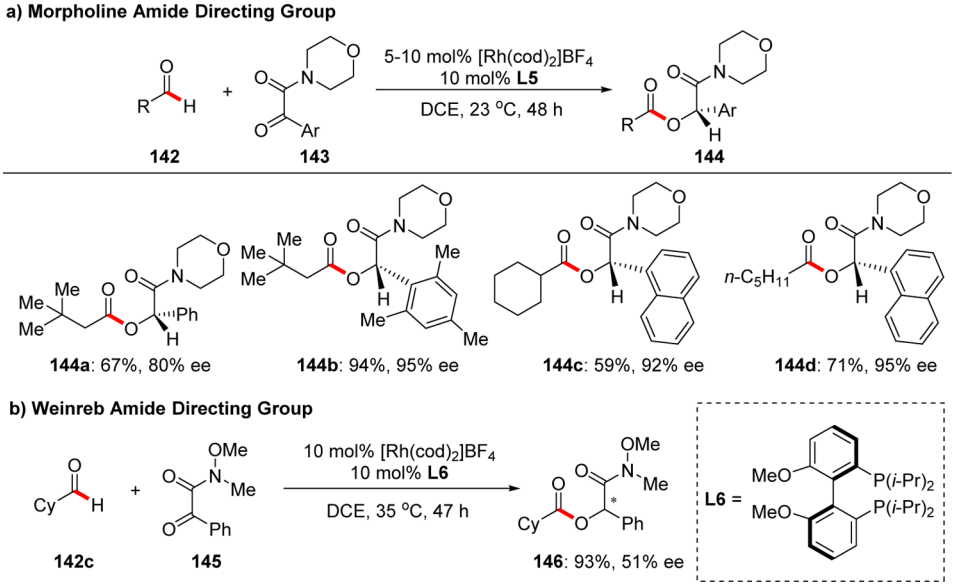
In 2011, the same group realized the rhodium-catalyzed hydroacylation of ketones directed by nitrogen atom with chiral bidentate phosphine ligands.[73] Under the optimized conditions, alkyl- and aryl-substituted keto-aldehydes could react to give the corresponding seven-membered benzoxazecinones in good yield and 50−93% ee in the presence of 2 mol % [Rh(*R*)-3,4,5-OMe-MeOBIPHEP)]BF_4 (Scheme 53a). Nevertheless, the N-containing eight-membered lactones can be obtained using

DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

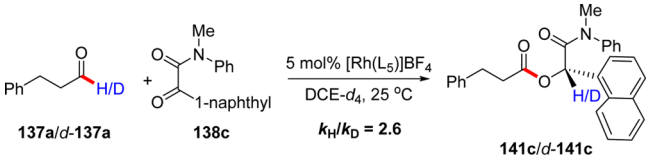
Scheme 54. Rh(I)-Catalyzed Intermolecular Hydroacylation of Ketoamides



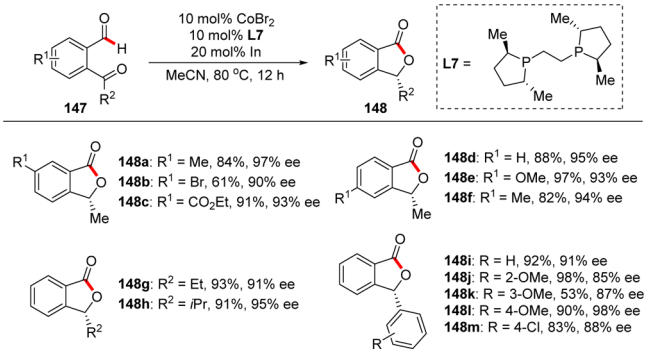
Scheme 55. Rh(I)-Catalyzed Intermolecular Hydroacylation Using Morpholine Amide and Weinreb Amide as Directing Groups



Scheme 56. Kinetic Isotope Effect for Intermolecular Hydroacylation



Scheme 57. Cobalt-Catalyzed Enantioselective Intramolecular Hydroacylation of Ketones

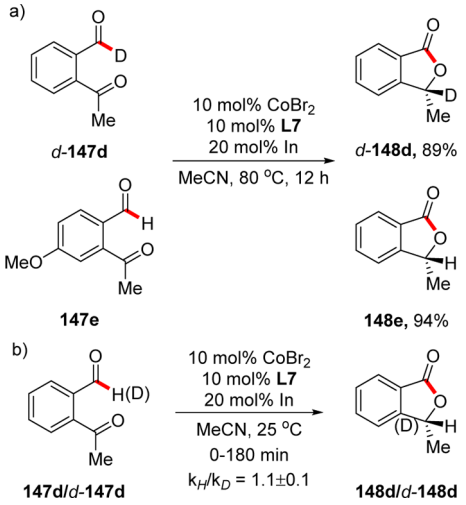


[Rh((*R*)-DTBM-SEGPHOS)]BF_4 as catalyst (Scheme 53b). Unfortunately, efforts to the synthesis of N-containing nine-membered benzoxazecinones are unsuccessful.

Despite these excellent reports in the intramolecular hydroacylation of ketones to lactone synthsis, transition-metal-catalyzed intermolecular hydroacylation remains underdeveloped. In 2014, Dong group reported the first enantioselective intermolecular hydroacylation of ketones bearing a directing group catalyzed by Rh(I)-Josiphos derivative (Scheme 54).[74] This reaction tolerates a wide range of functional groups and could be applied to both hydrocinnamaldehyde and hexanal (**141a**−**141h**). Moreover, sterically encumbered primary aldehydes are also effective coupling

DOI: 10.1021/acscatal.5b00050
ACS Catal. 2015, 5, 1863−1881

Scheme 58. Deuterium-Labeling Experiments for Cobalt-Catalyzed Enantioselective Intramolecular Hydroacylation of Ketones



partners (**141i** and **141j**). *N*,*N*′-diarylketone and cyclic ketoamide are less effective and afford α-acyloxyamides (**141l**) and 3-acyloxyindolinone (**141m**) in moderate yield and enantioselectivity. Rhodium plays a dual role in activating the aldehyde for cross-coupling.

The direct hydroacylation of morpholine amides (**143**) with 3,3-dimethylbutanal, cyclohexanecarboxaldehyde, hexanal also works well when Rh-**L5** is used as catalyst (Scheme 55a). α-Keto-Weinreb amide **145** is also a good substrate for this transformation when an alternative rhodium catalyst derived from methoxy-BIPHEP **L6** was employed (Scheme 55b).

A series of mechanistic studies were conducted. The value of KIE indicates that C−H bond activation might be involved in the turnover-limiting step (Scheme 56, KIE = 2.6), which is different from the previously reported intramolecular ketone hydroacylation process.[71]

More recently, the Yoshikai group reported an enantioselective intramolecular hydroacylation of ketones catalyzed by $CoBr_2$/(*R*,*R*)-Ph-BPE (**L7**).[75] Various functional groups are compatible with this cheap metal catalyst system, and moderate to excellent yields and enantioselectivities are achieved under the standard conditions (Scheme 57).

Furthermore, mechanistic investigations ruled out a Tishchenko-type mechanism involving a free cobalt hydride species (Scheme 58a).[2] A KIE value of 1.1 ± 0.1 was obtained by comparison of initial rates of individual reactions of **147d** and *d*-**147d**, indicating that the C−H bond cleavage is not involved in the rate-limiting step (Scheme 58b).

6. CONCLUSION AND OUTLOOK

In conclusion, recent advances in ester synthesis via transition-metal-catalyzed C−H activation have been fully reviewed. These protocols offer powerful and atom-economical strategies to various highly functionalized esters. Despite remarkable progresses in this area, several challenges still need to be addressed. First, alkoxycarbonylation mainly restricted to the functionalization of $C(sp^2)$−H bonds. The development of novel catalyst system for the alkoxycarbonylation of unactivated $C(sp^3)$−H bonds is highly demanded and will be more synthetically useful. Second, it would be highly desirable to use synthetically useful, removable, or modifiable directing groups for these transformations. In addition, alkoxycarbonylation which takes advantage of the functional groups that are inherently attached in the substrates will be a promising transformation. Finally, noble metals, such as palladium, rhodium, and ruthenium are commonly used as catalyst for these esterification reactions. Obviously, it is promising to develop base-metal-catalyzed transformations.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the National Basic Research Program of China (2015CB856600), the NSFC (21402170, 21272206) and Zhejiang Provincial NSFC (LZ12B02001) is gratefully acknowledged.

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DOI: 10.1021/acscatal.5b00050
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