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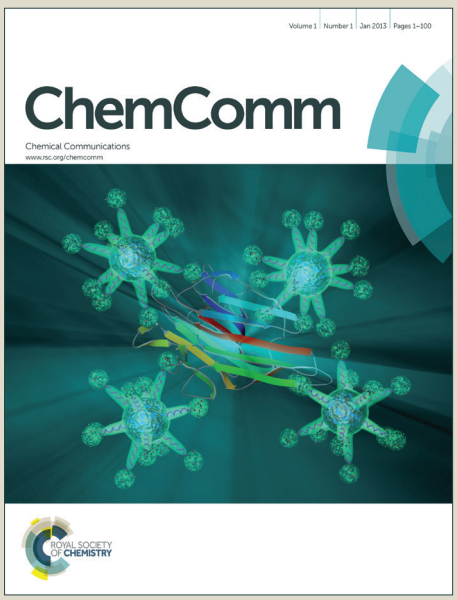

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Ruthenium-Catalyzed Double-Fold C–H Tertiary Alkoxycarbonylation of Arenes Using Di-*tert*-butyl Dicarbonate†

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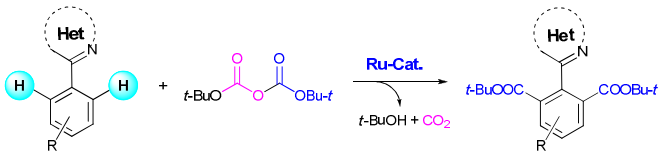
An efficient ruthenium-catalyzed double-fold C–H alkoxycarbonylation of arenes was developed using di-*tert*-butyl dicarbonate as the tertiary esterification reagent, which leads to direct access of valuable 2,6-dicarboxylated products.

Transition metal catalyzed C–C bond formation have been investigated intensively through C–H bond alkenylation, alkylation, arylation, and carbonylation reactions.[1] Among these reactions, ruthenium-catalyzed C–H functionalization reactions have attracted increased attentions because of their remarkable reactivity.[1j,2] Recently, ruthenium catalysts have been employed to couple with various C–H bond activation partners, including alkenes,[3a,d] arylhalides,[3b] alkylhalides,[3c] arylsulfonyl chlorides,[3e] alkynes,[3f] and azides.[3g] Despite their significant progress, it is necessary to further explore other coupling partners under ruthenium catalysis.

Aromatic esters are of considerable contemporary interest with respect to their exceptionally rich synthetic possibilities, which served as a versatile building block and effective precursor for various functional group transformations.[4,5] Generally, esters are prepared by traditional methods, such as reaction of acid chlorides with alcohols and insertion reaction of aryl halides with carbon monoxide,[5] and coupling reaction of di-*tert*-butyl dicarbonate with stoichiometric organometallic compounds[6] or boronic acids.[7] Recently, alternative access to ester groups has been achieved through direct sp^2 C–H bond esterification using DEAD,[8a-b] oxaziridine,[8c] glyoxylates,[8d] α-keto esters,[8e] carbon monoxide,[8f-h] carbon dioxide,[8i] and alkyl chloroformate[8j] as esterification reagents. Although these methods are often effective, some of them suffered from substrate limitation, lack of diversity, poor functional group tolerance, or requirement of multistep procedures. In comparison with other simple esters, tertiary esters have exhibited many advantages,[9] for example *t*-butyl esters could be easily converted to the corresponding carboxylic acids under mild acid conditions, although their formation is sometimes very difficult to achieve with tedious procedure and specialized reagents.[8h,10] Therefore, the development of novel synthetic methods for tertiary ester group is still in high demand in term of synthetic efficiency and starting material availability.

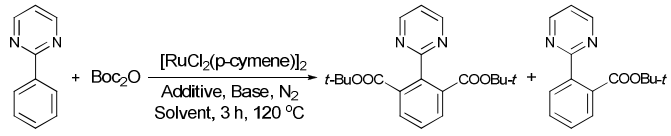
In contrast to widely documented reports on palladium[8a-g] and rhodium[8h-i] catalyzed carbonylation reactions, ruthenium catalyzed C–H bond alkoxycarbonylation reaction has been much less explored,[8j] which has proved to be a good complement to other transition noble metals in terms of substrate scope and functional group compatibility. In a pioneering study, Kakiuchi and co-workers elegantly devised the first ruthenium-catalyzed introduction of ester groups via C–H bond cleavage using ethyl chloroformates.[8j] However, as reported earlier, most of the reactions focused on the mono-carboxylation reaction and less attention has been paid for the successful synthesis of double alkoxycarbonylated products.[8a,i] The reason may be due to the electron-withdrawing and steric effects of the ester group, thus the second cyclometalation might be difficult to proceed and afford the mono-alkoxycarbonylated product predominantly.[11] In this event, the development of ruthenium-catalyzed highly efficient and practical double-fold C–H bond alkoxycarbonylation methods using easily available esterification reagents continues to be an active and rewarding research area. We envisioned that the use of pyrimidyl substituent as a directing group, which has two nitrogen atoms and prone to form a dual metal complex,[12,13] may facilitate the second C–H bond activation and afford the double alkoxycarbonylated products. Herein, we wish to disclose a ruthenium-catalyzed protocol for double *tert*-butoxycarbonylation of arylpyrimidines and aldimines, which is superior to the previously developed methods for the formation of 2,6-dicarboxylated products (Scheme 1). To our knowledge, the given approach features the first example that utilizes commercial available di-*tert*-butyl dicarbonate as the esterification reagent in the ruthenium-catalyzed C–H bond tertiary alkoxycarbonylation reactions.



Scheme 1 Ruthenium-catalyzed double *tert*-butoxycarbonylation with Boc_2O.

To determine the feasibility of chelation effect of a pyrimidyl group,[14] we started our investigation with the benchmark reaction between 2-phenyl-pyrimidine **1a** and di-*tert*-butyl dicarbonate (2.5 equiv.) in the presence of $[RuCl_2(p\text{-cymene})]_2$ and K_2CO_3 in toluene at 120 °C. Intriguingly, the mixture of di-*t*-butoxycarbonylation product **2a** and mono-*t*-butoxycarbonylation product **2a'** was isolated in 29% combined yield at a ratio of 1.1 : 1 with 35% conversion of **1a** (entry 1, Table 1). An extensive screening of carboxylic acids which were used as cocatalytic additives (entries 2–5), bases (entries 6–8), solvents (entries 9–12), and ruthenium catalysts (entries 13–14) revealed that the use of 1-AdCOOH (30 mol%) as an additive in toluene at 120 °C under nitrogen atmosphere turned out to be the best choice and resulted in the desired di-ester product **2a** in 86% yield exclusively. Decreasing the amount of Boc_2O to 1.2 equiv., the reaction could still give the di-ester **2a** as a major product in 43% combined yield with 54% conversion of substrate (entry 15).

Table 1 Condition optimizations for *tert*-butoxycarbonylation reaction[a]



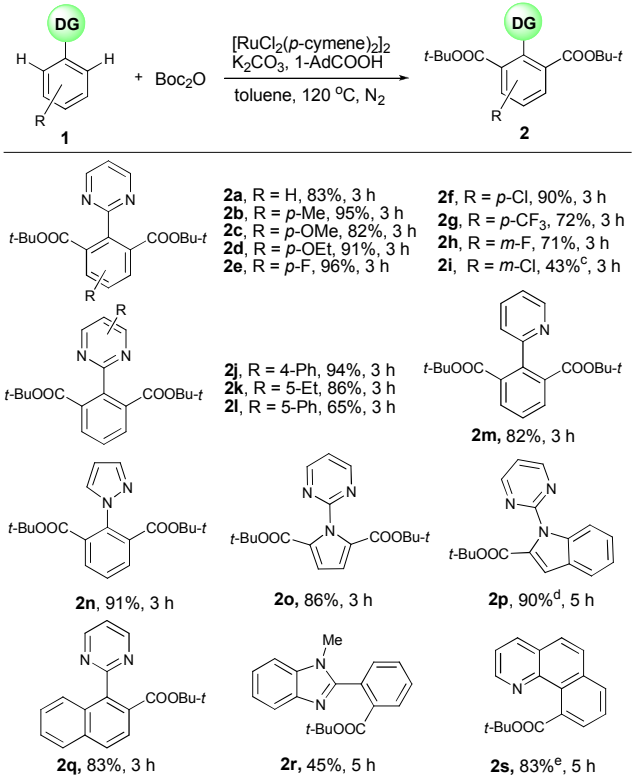
1a 2a 2a'

Entry	Additive	Base	Solvent	Conversion [%]	Yield[b] [%]	Ratio[c] [**2a** : **2a'**]
1	-	K_2CO_3	toluene	35	29	1.1 : 1
2	CH_3COOH	K_2CO_3	toluene	74	63	14 : 1
3	PhCOOH	K_2CO_3	toluene	66	58	6 : 1
4	MesCOOH	K_2CO_3	toluene	100	82	> 20 : 1
5	**1-AdCOOH**	**K_2CO_3**	**toluene**	**100**	**86**	**> 20 : 1**
6	1-AdCOOH	KOAc	toluene	54	47	5 : 1
7	1-AdCOOH	$K_3PO_4{\cdot}3H_2O$	toluene	88	71	5 : 1
8	1-AdCOOH	Cs_2CO_3	toluene	91	72	> 20 : 1
9	1-AdCOOH	K_2CO_3	DMF	38	31	5 : 1
10	1-AdCOOH	K_2CO_3	dioxane	85	77	8 : 1
11	1-AdCOOH	K_2CO_3	DCE	-	-	-
12	1-AdCOOH	K_2CO_3	THF	41	24	3 : 1
13[d]	1-AdCOOH	K_2CO_3	toluene	63	55	1.8 : 1
14[e]	1-AdCOOH	K_2CO_3	toluene	61	48	2.3 : 1
15[f]	1-AdCOOH	K_2CO_3	toluene	54	43	5 : 1

[a] Reaction conditions: **1a** (0.2 mmol), Boc_2O (2.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), additive (30 mol%), and base (2.5 equiv.) in solvent (0.5 mL), 120 °C, 3 h, under nitrogen atmosphere. [b] Isolated yield. [c] Ratio was determined by NMR analysis. [d] $RuCl_2(PPh_3)_3$ (2.5 mol%) was used. [e] $[RuCl_2(COD)]_2$ (2.5 mol%) was used. [f] Boc_2O (1.2 equiv.) was used.

With the optimized reaction conditions in hand, we sought to explore the reaction with a range of substrates as summarized in Table 2. Substrates bearing an electron-donating or electron-withdrawing group at the *para*-position underwent di-*t*-butoxycarbonylation in good yields (**2b-2g**), in which functional groups such as Me, OMe, halide, and CF_3 were all tolerated. Substitution groups such as fluorine and chlorine at *meta*-position caused no problem and di-*t*-butoxycarbonylated products **2h** and **2i** were furnished in good yields. Introduction of ethyl or phenyl group on the 4- or 5-position of the pyrimidine ring did not affect the efficiency of the reaction and afforded **2j-2l** in moderate to good yields. This newly established protocol was not limited to pyrimidines, pyridine and pyrazole were also found to be the effective directing groups for this reaction, and di-*t*-butoxycarbonylated products **2m** and **2n** were obtained in excellent yields. The identity of **2n** was determined by spectra analysis and further confirmed by X-ray crystallographic analysis.[15] Furthermore, when phenyl group was replaced with pyrrole substituent, the reaction proceeded smoothly and the di-*t*-butoxycarbonylation reaction took place in the pyrrole moiety in high yield (**2o**). However, mono-ester products were achieved in good to excellent yields (**2p-2r**), which may contribute to the electronic or steric effects of substrates. Moreover, this newly established protocol could extend to benzo[*h*]quinoline and furnish the corresponding mono-*t*-butoxycarbonylated product **2s** exclusively. To further broaden the substrate scope, we tried to apply the reaction using various dicarbonates other than Boc_2O, however, no expected carbonylation products were obtained. Furthermore, no desired ethoxycarbonylation or aminocarbonylation products could be achieved, when using dimethylcarbamic chloride and ethyl chloroformate as the amidation or esterification reagent.

Table 2 Scope of heterocycles[a,b]

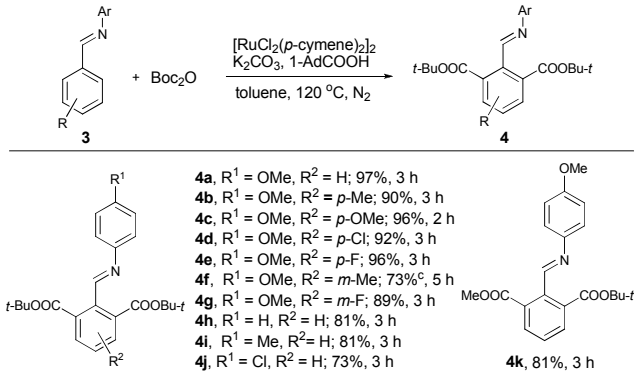


[a] Reaction conditions: **1** (0.5 mmol), Boc_2O (2.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), 1-AdCOOH (30 mol%), and K_2CO_3 (2.5 equiv.) in toluene (1.25 mL), 120 °C, under nitrogen atmosphere. [b] Isolated yield. [c] Mono-*t*-butoxycarbonylation product **2i'** was obtained in 6% yield with 65% conversion. [d] Based on 51% conversion. [e] Based on 60% conversion.

Imine groups have been fully investigated in the C–H bond functionalization as directing groups,[1b,e,j] however only one example was reported for C–H bond esterification of oximes with DEAD.[8a] To further explore the generality of this method, various aldimines, with only one nitrogen atom and acting as directing group, were investigated instead of the pyrimidyl group, on the basis of previous result on sterically controlled C–H bond diborylation of hydrazones.[16] To our delight, this protocol could be successfully applied to the corresponding aldimine counterpart, which represents the first ruthenium-catalyzed C–H bond *tert*-butoxycarbonylation of aldimines (Table 3). A wide range of substrates bearing an electron-donating or electron-withdrawing group at the *para* position underwent the di-*t*-butoxycarbonylation smoothly in excellent yields under optimized conditions (**4b-4e**). Substrate containing of fluorine substitution at *meta*-position also underwent this reaction smoothly

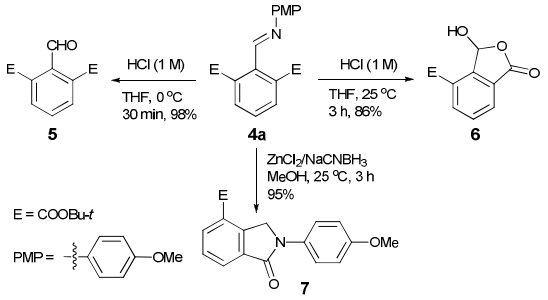
to generate the corresponding ester product **4g** in high yield, while sterically bulky *meta*-methyl substitution retarded the reaction (**4f**). When methoxyl group was replaced with different substitutions on the aryl ring, double carboxylation was achieved to give their corresponding di-esters (**4h-4j**). We also investigated the *tert*-butoxycarbonylation reaction of *ortho*-substituted aldimine, and found that *ortho*-carboxylate substituent underwent smooth carboxylation, producing the corresponding product **4k** in 81% yield, which enabled the preparation of nonsymmetrical di-ester. It should be noted that, facile transformation of **3a** with Boc_2O could be carried out without difficulty on a 10 mmol scale to give **4a** in 96% yield with a ruthenium catalyst loading of only 1.0 mol%, which expands the synthetic utility of this catalytic system.

Table 3 Scope of aldimines[a,b]



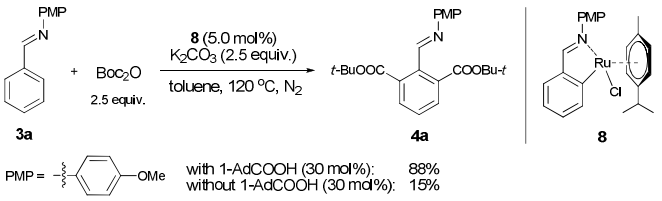
[a] Reaction conditions: **3** (0.5 mmol), Boc_2O (2.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), 1-AdCOOH (30 mol%), and K_2CO_3 (2.5 equiv.) in toluene (1.25 mL), 120 °C, under nitrogen atmosphere. [b] Isolated yield. [c] Based on 48% conversion.

Further efforts have been made to explore the applications of this method (Scheme 2). It was found that the prepared di-ester **4a** resulted in efficient deprotection of the directing group in THF at 0 °C, affording synthetically useful 2,6-dicarboxylated benzaldehyde **5** in almost quantitative yield.[17] Interestingly, while this hydrolysis reaction was conducted at room temperature, 3-hydroxyphthalide derivative **6** was obtained in high yield through intramolecular cyclization with removal of imine group,[18] which is an important skeleton in organic synthesis. Notably, the intramolecular amination product isoindolinone **7** could be furnished smoothly with $ZnCl_2$ and $NaCNBH_3$ in methanol, which provides a convenient process to make such useful skeleton.[19]



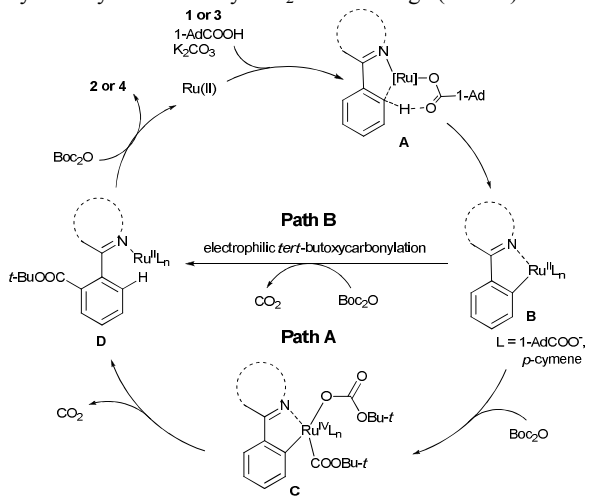
Scheme 2 Further transformations of **4a**.

To define the possible intermediates and pathway, the chloro-ruthenacycle **8** was prepared from **3a** and $[RuCl_2(p\text{-cymene})]_2$ in the presence of potassium acetate (Scheme 3).[20] When complex **8** was used as a catalyst instead of $[RuCl_2(p\text{-cymene})]_2$, di-ester **4a** was furnished in 88% yield under otherwise identical conditions. In stark contrast, product **4a** was afforded in significant lower yield (15%) in the absence of 1-AdCOOH, which indicated that the cycloruthenated complexe **8** could be the key intermediate and highlighted the key importance of carboxylate assistance in this reaction.



Scheme 3 Cycloruthenated complexe **8** as the catalyst.

Although further studies were required to clarify the detailed pathway, a plausible mechanism for the formation of carbonylated arenes is proposed (Scheme 4). The catalytic cycle is likely initiated by formation of the transition state **A** with the assistance of carboxylate acid, which could further transfer to the cycloruthenated complex **B** through a concerted cyclometalation deprotonation process (CMD).[2b] Complex **B** can be oxidized to Ru(IV) species **C** by addition of Boc_2O and underwent further reductive elimination to give the mono-*tert*-butoxycarbonylated product **D** together with expulsion of carbon dioxide (Path A). Finally, the produced intermediate **D** went through the second catalytic cycle to afford the desired di-*t*-butoxycarbonylation product and regenerate the catalytically active Ru(II) species. However, we cannot rule out the possibility of the pathway through a direct electrophilic *tert*-butoxycarbonylation of **B** by Boc_2O at this stage (Path B).[1i,6]



Scheme 4 Plausible mechanism.

In summary, we have developed the first ruthenium-catalyzed direct double C−H bond alkoxycarbonylation of arylpyrimidines and aldimines utilizing commercial available di-*tert*-butyl dicarbonate as efficient esterification reagent. This approach provides an unique access to tertiary 2,6-dicarboxylated products, which are precursors for medicinally valuable 3-hydroxyphthalide and isoindolinone derivatives, with operational simplicity, good functional group tolerance and a wide substrate scope.

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Notes and references

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† Electronic Supplementary Information (ESI) available: General experimental procedures, characterization data and copies of the ^{1}H, ^{13}C and ^{19}F NMR spectra for all compounds. CCDC 995322 (compound **2n**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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Ruthenium-Catalyzed Double-Fold C–H Tertiary Alkoxycarbonylation of Arenes Using Di-*tert*-butyl Dicarbonate

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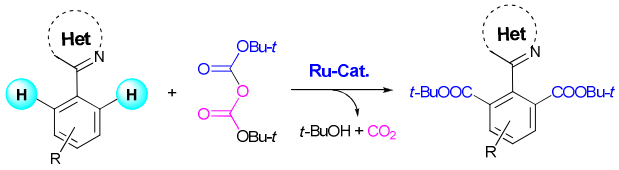

An efficient ruthenium-catalyzed double-fold C-H bond alkoxycarbonylation of arenes was developed using commercial available Boc_2O as the tertiary esterification reagent.