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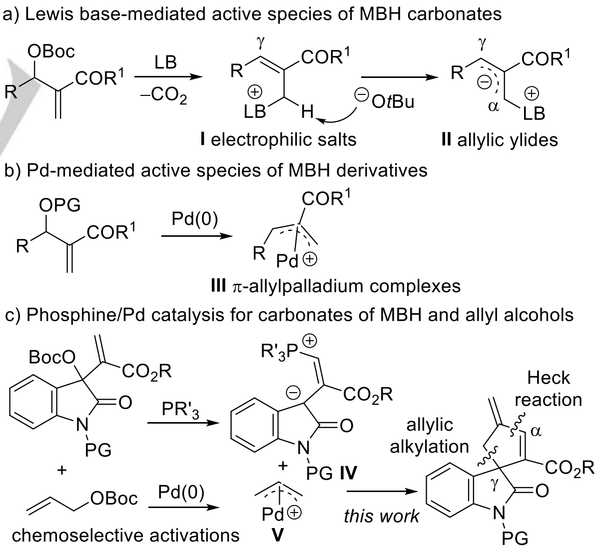
Auto-Tandem Cooperative Catalysis Using Phosphine/Palladium: Reaction of Morita–Baylis–Hillman Carbonates and Allylic Alcohols

Peng Chen, Zhi-Chao Chen, Yue Li, Qin Ouyang, Wei Du,* and Ying-Chun Chen*

Abstract: *Auto-tandem catalysis (ATC), in which a single catalyst promotes two or more mechanistically different reactions in a cascade pattern, provides a powerful strategy to prepare complex products from simple starting materials. Here, we report an unprecedented auto-tandem cooperative catalysis (ATCC) for Morita–Baylis–Hillman carbonates from isatins and allylic carbonates with simple $Pd(PPh_3)_4$ precursor. Dissociated phosphine-mediated phosphorus-ylides and π-allylpalladium complexes are independently generated, which undergo a γ-regioselective allylic-allylic alkylation reaction. Importantly, a cascade intramolecular Heck-type coupling is followed between the resulting alkene-phosphonium groups, finally furnishing spirooxindoles incorporating a 4-methylene-2-cyclopentene motif. Experiment results indicate that both Pd and phosphine play crucial roles in the catalytic Heck reaction. In addition, the asymmetric versions with chiral phosphine or chiral auxiliary are explored, and moderate results are obtained.*

The catalytic tandem reaction, in which two or more transformations occur consecutively thus avoiding the tedious isolation and purification of intermediates, provides a powerful approach to produce complicated substances from simple starting materials.[1] As mechanistically distinct processes are usually encountered, dual or even multiple catalytic systems are commonly employed to promote the designed reactions.[2] It would be highly facilitating that a single catalyst can efficiently mediate the tandem reactions involving the conversions of different functionalities in the substrates, previously defined as auto-tandem catalysis (ATC) by Fogg and dos Santos.[3] Significant progress has been made in this field by utilizing metal or small organic molecule catalysts.[4] On the other hand, organic chemists also have devoted great effort to develop effective reactions by merging the cooperative or relay activation modes of different metal and organic catalysts.[5] Nevertheless, there is still no example involving auto-tandem cooperative catalysis (ATCC) of both metal and organocatalyst in a cascade process.

The Morita–Baylis–Hillman (MBH) products, condensed from activated alkenes and carbonyl compounds, have found extensive applications in latent transformations over the past decades, especially under the activation of Lewis base (LB) catalysts, by generating either electrophilic salts **I** or allylic ylides **II** (Scheme 1a).[6] Since MBH products possess an allylic alcohol motif, their acylates or carbonates have a long history to be utilized in allylic alkylation reactions by forming π-allylpalladium complexes **III** (Scheme 1b).[7] As a result, it would be highly challenging by chemoselectively combining Lewis base-activated intermediates of MBH derivatives with active π-allylpalladium species generated from other allyl derivatives. In fact, there is even no successful report dealing with cooperative catalysis for MBH derivatives under organo and metal catalysis to date.[8] In our continuing interest in developing new transformations of MBH derivatives,[9] here we would like to disclose that highly chemoselective activations of MBH carbonates from isatins and allylic carbonates could be accomplished by tertiary phosphine/Pd(0) complex, respectively, for the first time, as illustrated in Scheme 1c. Thus, γ-regioselective allylic-allylic alkylation between **IV** and **V** occurred accordingly. Moreover, an unusual tandem catalytic intramolecular Heck-type coupling reaction was followed to furnish a [3+2] annulation process (Scheme 1c).



Scheme 1. Lewis base and Pd activation strategies for MBH derivatives.

The initial reaction of MBH carbonate **1a** and allyl benzoate **2a** proceeded smoothly in THF in the presence of catalytic amounts of $Pd(PPh_3)_4$, but gave an inseparable mixture of spirooxindole **3a** (R = Me) and 1,3-difunctionalization product[10] **4a** (R = Me) (Table 1, entry 1). It seems that MBH carbonate **1a** and allyl benzoate **2a** were independently activated by dissociated PPh_3 and Pd(0) complex, respectively (Scheme 1c). After the desired allylic alkylation reaction, an annulation or alternative benzoate addition-elimination process was followed. Pleasingly, replacing **1a** with a more bulky substrate **1b**

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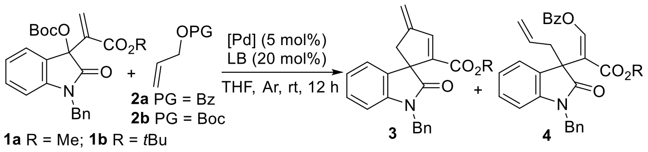
exclusively delivered the spiro product **3b** (R = *t*Bu) in a high yield (Table 1, entry 2). Adding catalytic amounts of DABCO or DMAP apparently reduced the yield (Table 1, entries 3 and 4). The combination of PPh_3 and $Pd_2(dba)_3$ also efficiently promoted the reaction (Table 1, entry 5); in contrast, **3b** was obtained by using DABCO or DMAP with $Pd_2(dba)_3$ (Table 1, entries 6 and 7). These results suggested that phosphine was crucial for the annulation reaction. Moreover, sole $Pd_2(dba)_3$ or PPh_3 could not promote the reaction, identifying the importance of the cooperative catalysis (Table 1, entry 8 and 9). In addition, $[Pd(allyl)Cl]_2$ was not a successful palladium source (Table 1, entry 10). Subsequently, it was found that even a higher yield was attained by assembling MBH carbonate **1b** and allyl carbonate **2b** catalyzed by $Pd(PPh_3)_4$ (Table 1, entry 11). Nevertheless, employing less amounts of **2b** afforded a reduced yield (Table 1, entry 12). Notably, the tandem annulation still proceeded effectively by significantly diminishing the catalyst loadings (Table 1, entries 13 and 14).

Table 1. Screening conditions of the reactions of MBH carbonates **1** and allyl derivatives **2**.[a]

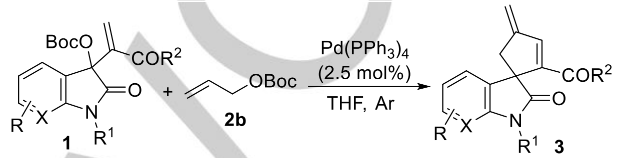


Entry	2	LB	[Pd]	Yield (%)[b]
1[c]	**2a**	/	$Pd(PPh_3)_4$	**3a+4a**, 84
2	**2a**	/	$Pd(PPh_3)_4$	**3b**, 89
3	**2a**	DABCO	$Pd(PPh_3)_4$	**3b**, 75
4	**2a**	DMAP	$Pd(PPh_3)_4$	**3b**, 52
5	**2a**	PPh_3	$Pd_2(dba)_3$	**3b**, 80
6	**2a**	DABCO	$Pd_2(dba)_3$	/
7	**2a**	DMAP	$Pd_2(dba)_3$	/
8	**2a**	/	$Pd_2(dba)_3$	/
9	**2a**	PPh_3	/	/
10	**2a**	PPh_3	$[Pd(allyl)Cl]_2$	**3b**, <5
11	**2b**	/	$Pd(PPh_3)_4$	**3b**, 93
12[d]	**2b**	/	$Pd(PPh_3)_4$	**3b**, 78
13[e]	**2b**	/	$Pd(PPh_3)_4$	**3b**, 90
14[f]	**2b**	/	$Pd(PPh_3)_4$	**3b**, 87

[a] Unless noted otherwise, reactions were performed with MBH carbonate **1b** (0.1 mmol), **2** (0.2 mmol), [Pd] source (5 mol%), LB (20 mol%) in THF (1.0 mL) at rt for 12 h. [b] Isolated yield. [c] With **1a**, **3a**/**4a** = 5:1. [d] With 0.15 mmol **2b**. [e] With 2.5 mol% $Pd(PPh_3)_4$. [f] With 1.0 mol% $Pd(PPh_3)_4$. THF = tetrahydrofuran; dba = dibenzylideneacetone; DABCO = 1,4-diazabicyclo[2.2.2]octane; DMAP = 4-dimethylaminopyridine; Boc = *tert*-butyloxycarbonyl; Bz = benzoyl.

With the optimal catalytic conditions in hand, the substrate scope and limitations of this new tandem reaction were explored. The results are summarized in Table 2. A few MBH carbonates **1** derived from electron-donating substituted *N*-benzyl isatins and *t*-butyl acrylate reacted effectively with allyl carbonate **2b** under the catalysis of $Pd(PPh_3)_4$ (2.5 mol%), and excellent yields were obtained after a longer time (Table 2, entries 2–4). The MBH carbonates **1** with electron-withdrawing groups exhibited lower reactivity, whereas outstanding yields were gained at higher temperature and catalyst loadings (Table 2, entries 5–7). Excellent yields were also produced for MBH carbonates **1** derived from *N*-methyl isatins (Table 2, entries 8–10). A high yield was attained for a MBH carbonate from ethyl acrylate (Table 2, entry 11), but the yield was only moderate for a MBH carbonate from vinyl methyl ketone (Table 2, entry 12). In addition, a MBH carbonate from 7-azaisatin was tested, also giving a high yield (Table 2, entry 13).[11]

Table 2. Substrate scope of the tandem reactions of MBH carbonates **1** and allyl carbonate **2b**.[a]

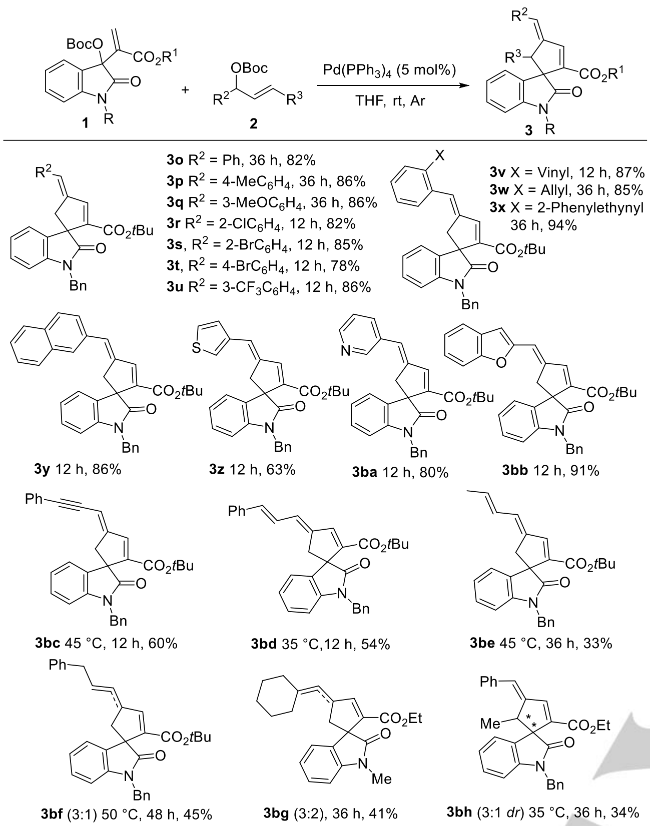


Entry	R	R^1, R^2	*t* (h)	Yield (%)[b]
1	H	Bn, *t*BuO	12	**3b**, 90
2	5-MeO	Bn, *t*BuO	36	**3c**, 97
3	7-Me	Bn, *t*BuO	36	**3d**, 93
4	5,7-Me_2	Bn, *t*BuO	36	**3e**, 97
5[c,d]	5-F	Bn, *t*BuO	36	**3f**, 96
6[c,d]	6-Br	Bn, *t*BuO	36	**3g**, 93
7[c,d]	7-Br	Bn, *t*BuO	36	**3h**, 93
8	H	Me, *t*BuO	36	**3i**, 97
9	5-Me	Me, *t*BuO	36	**3j**, 92
10	5-MeO	Me, *t*BuO	36	**3k**, 91
11	H	Bn, EtO	36	**3l**, 91
12[c]	H	Me, Me	12	**3m**, 70
13[c,e]	H	Bn, *t*BuO	24	**3n**, 85

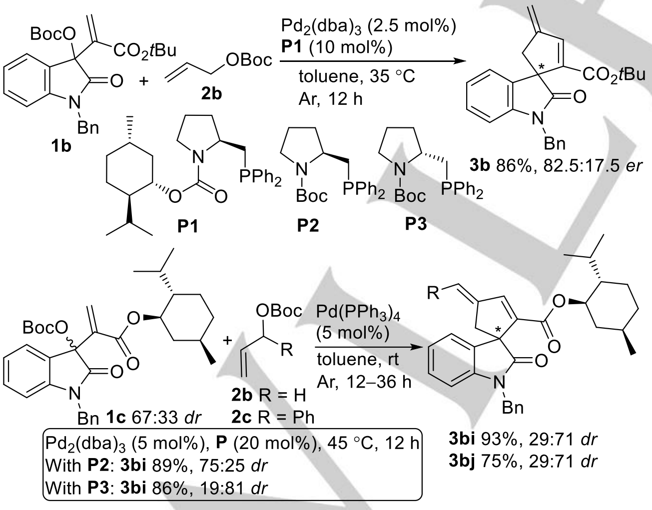
[a] Unless noted otherwise, reactions were performed with MBH carbonate **1** (X = CH) (0.1 mmol), **2b** (0.2 mmol), $Pd(PPh_3)_4$ (2.5 mol%) in THF (1.0 mL) at rt. [b] Isolated yield. [c] With 5 mol% $Pd(PPh_3)_4$. [d] At 35 °C. [e] With MBH carbonate **1** from 7-azaisatin (X = N).

Subsequently, we investigated the substrate scope of allylic carbonate partners **2**. As illustrated in Table 3, an array of diverse aryl-substituted allylic carbonates **2** showed good reactivity in assembly with MBH carbonate **1b** at ambient temperature under the catalysis of $Pd(PPh_3)_4$ (5 mol%), and the corresponding spirooxindoles **3o**–**3x** were generally obtained in good yields with exclusive stereoselectivity.[12] Moderate to high yields were also produced with 2-naphthyl or heteroaryl-substituted allylic carbonates (products **3y**–**3bb**). Nevertheless, alkynyl- or vinyl-substituted allylic carbonates exhibited lower reactivity even at higher temperature, and only fair yields for products **3bc**–**3be** were furnished, with excellent stereoselectivity too. The alkyl-substituted ones could be utilized though with low reactivity, and a mixture of deconjugated and conjugated diene products **3bf** and **3bg** were generated in fair yields. The carbonate of *E*-4-phenylbut-3-en-2-ol could be used, whereas the product **3bh** was provided as a diastereomeric mixture in a low yield.

Table 3. Substrate scope and limitations of the tandem reactions of MBH carbonates **1** and allylic carbonates **2**.[a,b]

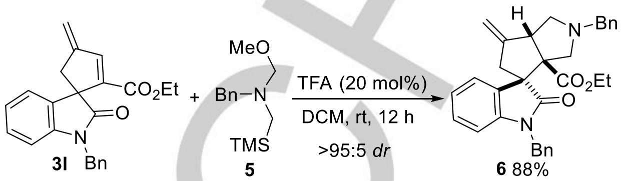


[a] Unless noted otherwise, reactions were performed with MBH carbonate **1** (0.1 mmol), **2** (0.25 mmol), $Pd(PPh_3)_4$ (5 mol%) in THF (1.0 mL) at rt. [b] Isolated yield.



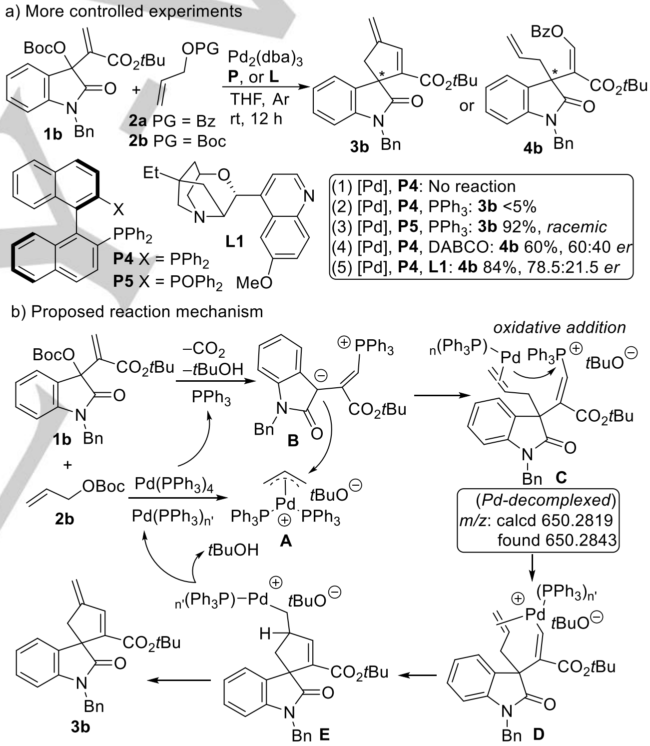
Scheme 2. Asymmetric tandem reactions.

A number of commonly used chiral phosphines in combination with $Pd_2(dba)_3$ failed to promote the reaction of **1b** and **2b**.[13] Fortunately, the newly designed monophosphines derived from *L*-proline showed high activity, and moderate enantioselectivity with a high yield was obtained with **P1** (Scheme 2). In addition, the MBH carbonate **1c** derived from *R*-menthyl acrylate exhibited good reactivity with carbonate **2b** or **2c** in the presence of $Pd(PPh_3)_4$, and modest diastereoselectivity was observed (**3bi** and **3bj**). Moreover, better diastereocontrol was obtained by using $Pd_2(dba)_3$ and chiral phosphine **P2** or **P3**.



Scheme 3. Synthetic transformation of product **3l**.

As outlined in Scheme 3, the regioselective 1,3-dipolar cycloaddition of **3l** and **5** was efficiently conducted, affording spiro and fused product **6** in excellent diastereoselectivity.



Scheme 4. Mechanism elucidation of the proposed reaction process.

In order to gain some insight into the cooperative catalysis, more experiments were conducted. As outlined in Scheme 4a, the combination of $Pd_2(dba)_3$ and *R*-BINAP **P4** could not promote the reaction of **1b** and **2b** (entry 1), and the similar results were observed by further adding PPh_3 (entry 2), indicating a chelating bisphosphine ligand would inhibit the process. Such a conclusion was further confirmed by replacing **P4** with monooxide **P5**, which gave a high yield of **3b** (entry 3). Notably, the allylic alkylation of MBH carbonate **1b** and benzoate **2a** was facilitated under the cooperative catalysis of $Pd_2(dba)_3$, bisphosphine **P4** and DABCO, and the product **4b** was obtained in a moderate yield (entry 4).[10] Even higher yield and enantioselectivity were attained with chiral

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tertiary amine **L1** (entry 5).[13] These results further verify that a phosphine-type Lewis base is essential for the tandem annulation reaction, and support that spiro **3b** would not result from an ene-type addition-phosphine elimination sequence.

Consequently, a plausible mechemism was proposed for the reaction of **1b** and **2b** (Scheme 4b). The initial chemoselective reaction of allyl carbonate **2b** and $Pd(PPh_3)_4$ would produce the expected π-allylpalladium complex **A**. The dissociated PPh_3 would attack MBH carbonate **1b** to favorably generate *E*-configured allylic *P*-ylide species **B**. Thus, the γ-regioselective allylic alkylation would occur via cooperative catalysis. Next, the key oxidative addition between olefin-complexed Pd(0) and phosphonium groups in species **C** (*Pd-decompelxed cation* was *detected by HRMS analysis*) would deliver intermediate **D**.[14] Therefore, the classical Heck coupling would happen to afford intermediate **E**, and produce the observed spirooxindole **3b** after a reductive β-elimination process. Thus, PPh_3 would act as an unusual catalyst in the Pd-catalyzed Heck-type coupling by forming active phosphonium species with MBH carbonate **1b**, rendering the current reaction proceed via unprecedented auto-tandem cooperative catalysis.

In conclusion, we first demonstrated that highly chemoselective activations for MBH carbonates from isatins and allylic carbonates could be realized by Lewis basic tertiary phosphine and Pd(0) complex, respectively, by employing simple $Pd(PPh_3)_4$ as catalyst precursor. After the cooperative catalytic allylic alkylation reaction, a auto-tandem intramolecular Pd-catalyzed Heck coupling reaction occurred between the resulting alkene and phosphonium functionalities, finally constructing a spectrum of spirooxindoles incorporating a 4-methylene-2-cyclopentene motif. This work represents a quite intriguing study, in which a cascade process containing mechanistically different reactions is realized via unprecedented and challenging auto-tandem cooperative catalysis (ATCC) of organic substance and metal complex. We believe that this study would arouse broad interest in the field of catalysis. More results will be reported in due course.

Acknowledgements ((optional))

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Keywords: auto-tandem catalysis • cooperative catalysis • palladium catalysis • Lewis base catalysis • Morita–Baylis–Hillman carbonate

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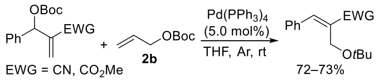
[11] Unfortunately, the MBH carbonates from benzaldehyde readily generated π-allylpalladium species with $Pd(PPh_3)_4$, finally giving α-regioselective O-alkylation products. See the SI and ref 7 for more details.



[12] The structure of racemic **3o** (CCDC 1882576) was confirmed by X-ray analysis. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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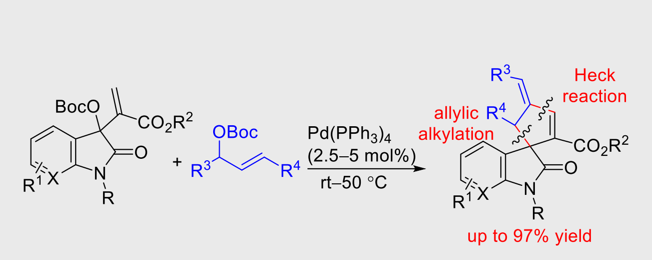

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ATCC: The chemoseletive activations of Morita–Baylis–Hillman carbonates from isatins and allylic carbonates are realized with simple $Pd(PPh_3)_4$ precursor, through generating allylic phosphorus-ylides and π-allylpalladium complexes, respectively. After the cooperative catalytic γ-regioselective allylic alkylation reaction, the resulting alkene-phosphonium groups undergo Heck coupling to give spirooxindoles, furnishing a [3+2] annulation reaction via unprecedented auto-tandem cooperative catalysis (ATCC).