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Graphical Abstract

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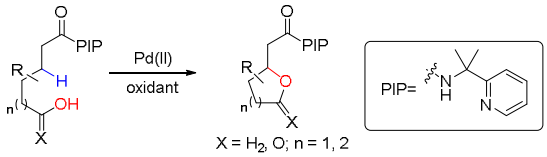

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A unified synthesis of cyclic ethers or lactones via Pd-catalyzed intramolecular *O*-functionalization of sp^3 C-H bonds

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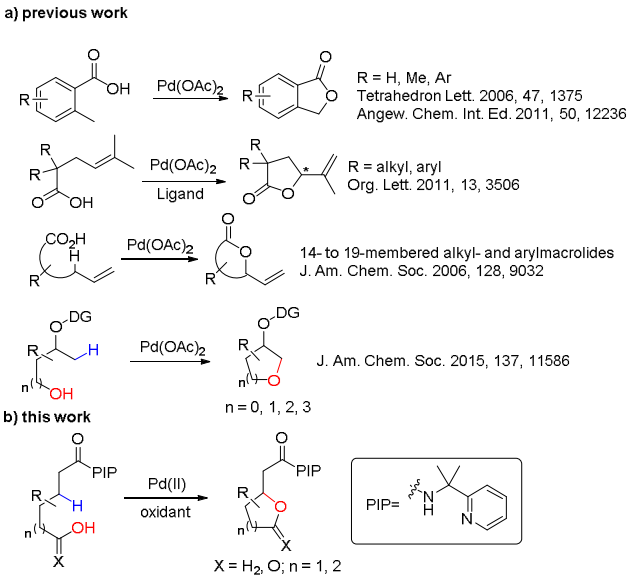
ABSTRACT

A general approach for the synthesis of lactones or cyclic ethers via Pd-catalyzed C(sp^3)-H activation and intramolecular C-O functionalization starting from carboxylic acids or alcohols by using the bidentate directing group has been developed. Substrates with both primary and secondary hydroxyl groups can undergo this reaction to produce the corresponding cyclic ethers. Furthermore, isobenzofuran-1(3H)-ones with either electron-rich or electron-deficient groups as well as aliphatic lactones can be prepared by employing this reaction.

Aliphatic alcohol-based cyclic ethers and lactones are ubiquitous moieties in many medicinally valuable compounds, they are also useful building blocks for the synthesis of complex organic molecules.[1] General approaches to the preparation of cyclic ethers or lactones involve intramolecular nucleophilic substitution using aliphatic alcohols, which means that two functional groups are equipped in the same molecule, and the extra preactivation manipulation is usually needed for the synthesis of cyclic ethers or lactones. In contrast, C(sp^3)-H activation, followed by functionalization with intramolecular *O*-type groups, represents a new direction for the step-economical synthesis of cyclic ethers or lactones.

Inert C-H functionalization catalyzed by transition metals has attracted tremendous interest from organic chemists, and is emerging as a powerful approach to form C-X bonds and generate various scaffolds of compounds in modern synthetic chemistry.[2] Among these C-X formation approaches, the Pd-catalyzed activation of C-H bond and subsequent formation of C-O bond have been greatly accelerated in recent years.[3] Up to date, most methods focus on the ortho- alkoxylation or acyloxylation of the C(sp^2)–H bonds of arenes directed by various functional groups.[4, 5] Directing groups such as carboxylic acid and alcohol sometimes can also act as reacting groups, and undergo cyclization to afford benzofuranones and dihydrobenzofurans.[6] Compared with C(sp^2)-H bond activation, C(sp^3)-H bond activation which is followed by *O*-functionalization is still a fundamental challenge. Most methods reported involve the directed acyloxylation of C(sp^3)-H bonds including intramolecular reactions.[7] Very limited reports have been disclosed for the alkoxylation of C(sp^3)-H bonds.[8] In 2015, Dong and coworkers reported the only one work of intramolecular alkoxylation of the methyl group, affording different sizes of cyclic ethers in moderate to excellent yields.[9]



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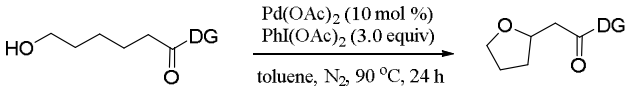
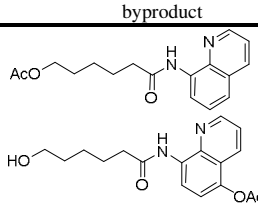
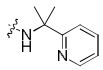
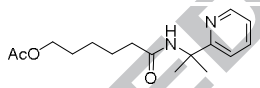
†These authors contributed equally to this work.

Scheme 1. Synthesis of cyclic ethers or lactones via Pd-catalyzed intramolecular C(sp^3)-H functionalization

Previous reports by Chen,[8a] Shi,[8b] and Rao[8c, 8d] have shown that C-H of ß-methylene of acids using different bidentate directing groups can be activated and functionalized with excessive alcohols to furnish linear ethers. Since we are interested in synthesizing organic functional molecules through C-H functionalization,[10] we envisaged that C-H functionalization with intramolecular oxygen-containing groups such as alcohols and carboxylic acids would be a unified approach to the synthesis of cyclic ethers and lactones, though several problems need to be addressed: 1) the same directing group and reaction conditions are suitable for both lactonization and synthesis of cyclic ethers; 2) the competitive reactions could occur if oxygen-containing oxidative reagents are used. Herein we report the preparation of cyclic ethers or lactones via Pd-catalyzed β-methylene activation of carboxylic acid derivatives.

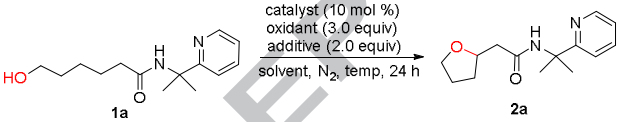
Table 1. Screening of the directing groups



entry	DG	yield(%)	byproduct
1	 1aa	27(95[a])	 (40%) (26%)
2	 1ab	0	—
3	 1a	57	 (22%)

[a]The total conversion yield of **1aa**.

Table 2. Optimization of reaction conditions[a]

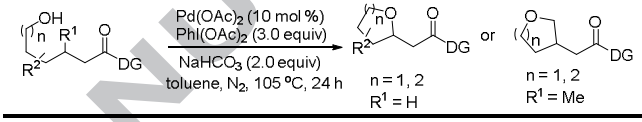


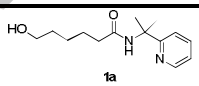
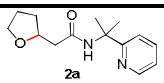
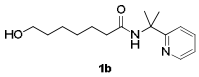
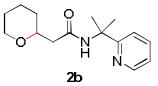
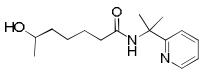
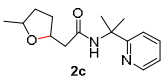
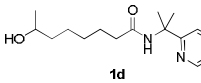
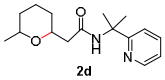
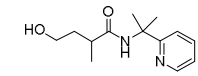
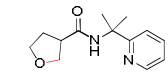
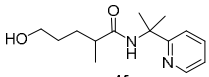
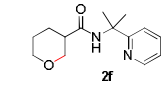
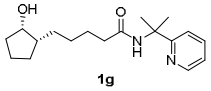
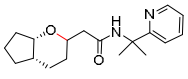
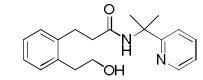
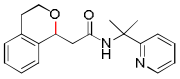
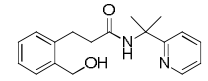
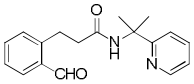
entry	catalyst	oxidant	additive	solvent	T (°C)	yield (%)[c]
1	$Pd(OAc)_2$	$PhI(OAc)_2$	-	toluene	90	57
2	$Pd(OAc)_2$	$PhI(OPiv)_2$	-	toluene	90	55
3	$Pd(OAc)_2$	$K_2S_2O_8$	-	toluene	90	-
4	$Pd(OAc)_2$	oxone	-	toluene	90	-
5	$Pd(OAc)_2$	DMR[b]	-	toluene	90	-
6	$Pd(OAc)_2$	$PhI(OAc)_2$[d]	-	toluene	90	51
7	$Pd(OTFA)_2$	$PhI(OAc)_2$	-	toluene	90	trace
8	$PdCl_2$	$PhI(OAc)_2$	-	toluene	90	-
9	$Pd(OPiv)_2$	$PhI(OAc)_2$	-	toluene	90	46
10	$Pd(OAc)_2$	$PhI(OAc)_2$	-	DCE[e]	90	33
11	$Pd(OAc)_2$	$PhI(OAc)_2$	-	m-xylene	90	54
12	$Pd(OAc)_2$	$PhI(OAc)_2$	-	dioxane	90	-
13	$Pd(OAc)_2$	$PhI(OAc)_2$	K_2CO_3	toluene	90	74
14	$Pd(OAc)_2$	$PhI(OAc)_2$	$NaHCO_3$	toluene	90	80
15	$Pd(OAc)_2$	$PhI(OAc)_2$	$NaHCO_3$	toluene	55	43
16	$Pd(OAc)_2$	$PhI(OAc)_2$	$NaHCO_3$	toluene	95	82
17	$Pd(OAc)_2$	$PhI(OAc)_2$	$NaHCO_3$	toluene	105	86
18	$Pd(OAc)_2$	$PhI(OAc)_2$	$NaHCO_3$	toluene	120	71

[a]Reaction conditions: substrate (0.1 mmol), catalyst (10 mol%), oxidant (3.0 equiv), additive (2.0 equiv), solvent (1.0 mL), under N_2. [b]Dess-Martin reagent. [c]Isolated yield. [d]$PhI(OAc)_2$ (2.0 equiv). [e]Dichloroethane.

Our investigation commenced with screening directing groups. The starting materials **1aa**, **1ab**, and **1a** carrying 8-aminoquinoline, 2-aminomethylpyridine, and 2-(pyridin-2-yl)propan-2-amine functionalities respectively, which were developed by Shi and coworkers,[8b, 11] were synthesized. These compounds were then treated with $Pd(OAc)_2$ and $PhI(OAc)_2$ in toluene at 90 °C for 24 h. As shown in Table 1, compound **1aa** gave the desired cyclic ether product in 27% yield, and several byproducts such as acetyloxylation of 8-aminoquinoline and acetylation of primary alcohol were also collected. For compound **1ab**, no cyclized product was obtained under the same conditions. Noteworthily, when compound **1a** was used, the desired product was isolated in 57% yield. These results showed that 2-(pyridin-2-yl)propan-2-amine is the most effective directing group (DG) for the intramolecular C–O bond formation. So we chose **1a** as a substrate to optimize the cyclization reaction conditions.

Table 3. Synthesis of cyclic ethers via intramolecular oxidation of β-C(sp^3)–H bonds[a]

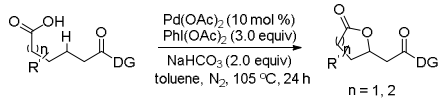


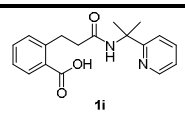
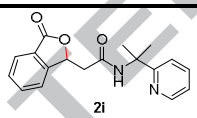
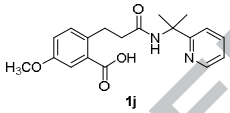
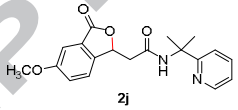
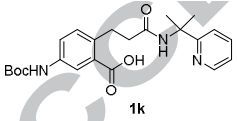
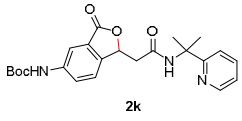
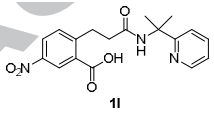
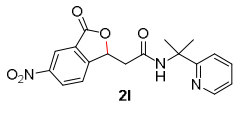
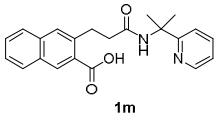
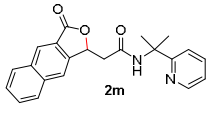
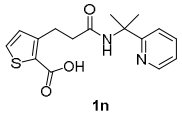
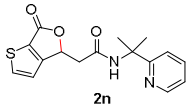
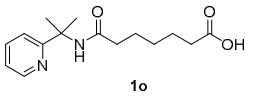
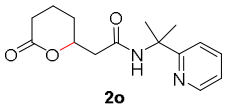
entry	substrate	product	yield (%)[b]
1	 1a	 2a	86
2	 1b	 2b	79
3	 1c	 2c	90
4	 1d	 2d	82
5[c]	 1e	 2e	73
6[c]	 1f	 2f	69
7	 1g	 2g	71
8	 1h	 2h	82
9	 1p	 2p	78

[a]Reaction conditions: substrate (0.1 mmol), $Pd(OAc)_2$ (10 mol%), $PhI(OAc)_2$ (3.0 equiv), $NaHCO_3$ (2.0 equiv) in toluene (1 mL) under N_2 at 105 °C for 24 h. [b]Isolated yield. [c]Substrate (0.1 mmol), $Pd(OAc)_2$ (10 mol%), $PhI(OAc)_2$ (1.5 equiv), $NaHCO_3$ (2.0 equiv) in toluene (1 mL) under N_2 at 85 °C for 5 h.

The optimization experiments were carried out. Various oxidants such as $PhI(OAc)_2$, $PhI(OPiv)_2$, $K_2S_2O_8$, oxone, and Dess-Martin reagent were investigated, we found that $PhI(OAc)_2$ (3 equivalents) is the most efficient oxidant for oxidative cyclization (entries 1-5, Table 2). When the amount of $PhI(OAc)_2$ was reduced to 2 equivalents, lower yield was obtained (entry 6, Table 2). We then started to investigate the effect of catalysts on C-H activation and cyclization. Catalysts including $Pd(OTFA)_2$, $PdCl_2$, and $Pd(OPiv)_2$ were employed in the reaction, and the results showed that the yield of product was not improved (entries 7-9, Table 2). The screening of solvents revealed that dichloroethane or m-xylene gave the desired product in lower yield, whereas dioxane resulted in no reaction (entries 10-12, Table 2). In this reaction, the hydroxyl group-acetylated byproduct was also identified. We reasoned that acetic acid produced in the reaction could not only inhibit the coordination of hydroxyl group to the Pd center, but also catalyze the acetylation of alcohol. Therefore, the addition of base should neutralize acetic acid, and could improve the reaction yield. Based on this assumption, K_2CO_3 was added to the reaction, and the yield of product **2a** was remarkably increased to 74% (entry 13). When $NaHCO_3$ was used as a base, product **2a** was isolated in 80% yield (entry 14). The reaction temperature was also investigated and it was found that the reaction proceeded more efficiently at 105 °C (entries 15-18). Thus, the optimized reaction conditions for methylene activation and *O*-functionalization are as follows: substrate (1.0 equiv), $Pd(OAc)_2$ (10 mol%), $PhI(OAc)_2$ (3.0 equiv) and $NaHCO_3$ (2.0 equiv) in toluene at 105 °C for 24 h under N_2 atmosphere.

Table 4. Synthesis of lactones via intramolecular oxidation of β-C(sp^3)–H bonds[a]

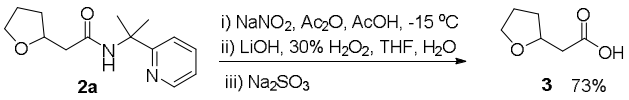


entry	substrate	product	yield (%)[b]
1	 1i	 2i	80
2	 1j	 2j	76
3	 1k	 2k	74
4	 1l	 2l	85
5	 1m	 2m	77
6	 1n	 2n	64
7	 1o	 2o	67

[a]Reaction conditions: substrate (0.1 mmol), $Pd(OAc)_2$ (10 mol%), $PhI(OAc)_2$ (3.0 equiv), $NaHCO_3$ (2.0 equiv) in toluene (1 mL) under N_2 at 105 °C for 24 h. [b]Isolated yield.

With the optimized conditions in hand, we began to examine the scope of substrates. As shown in Table 3, the substrates possessing either primary or secondary hydroxyl groups were cyclized efficiently under the standard conditions, providing five-membered or six-membered products in high yields (entries 1-4). When 1.5 equivalents of $PhI(OAc)_2$ were used, the methyl group was also activated to undergo the intramolecular functionalization, affording the cyclized products **2e** and **2f** (entries 5 and 6). Furthermore, the more complicate substrate, 1,2-*cis*-cyclopentane derivative **1g** was checked, and the desired product **2g** was obtained in 71% isolated yield (entry 7). When 2-phenylethan-1-ol **1h** was employed as the reactant, the isochroman derivative **2h** was obtained in high yield (entry 8). The benzyl alcohol derivative **1p** gave the oxidized product benzaldehyde **2p** instead of the cyclized product (entry 9). We also tried to synthesize the seven-membered cyclic ethers, but failed to get the products.

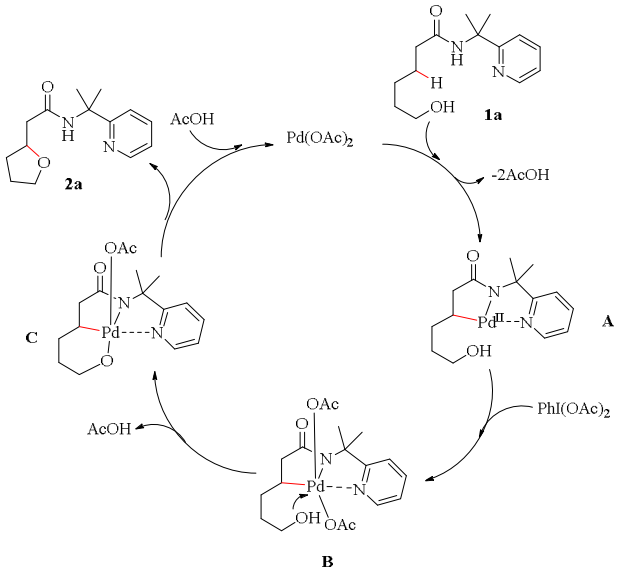
Since isobenzofuran-1(3H)-one derivatives possess a wide range of biological activities,[1c, 12] encouraged by the successful synthesis of cyclic ethers via intramolecular oxidation of β-C(sp^3)–H bonds, we further explored the application of this protocol in the synthesis of isobenzofuran-type lactones. As displayed in Table 4, it was found that the optimized reaction conditions are also effective for the formation of both aromatic and aliphatic lactones. Either the electron-rich or the electron-deficient phenyl carboxylic acid substrates were transformed into the corresponding isobenzofuran-1(3H)-one derivatives in good yields (entries 1-4). Moreover, this reaction proceeded smoothly on naphthyl carboxylic acid substrate **1m**, producing lactone **2m** in 77% isolated yield (entry 5). Thienylcarboxylic acid **1n** also underwent this reaction, affording product **2n** (entry 6). Besides aromatic acids, the aliphatic δ-lactone derivative **2o** was prepared from the aliphatic acid **1o** (entry 7). Finally, the directing group was removed smoothly using the mild *N*-nitrosylation/hydrolysis sequence, as exemplified in the deprotection of **2a** (Scheme 2).



Scheme 2. Removal of the directing group

As shown in Table 3, when benzyl alcohol **1p** was used as the starting material, benzaldehyde **2p** was obtained in 78% yield, no cyclic product was detected. We reasoned that the coordination of OH to Pd center would occur at the beginning, and this intermediate thus could undergo β-H elimination of the benzyl position to give the oxidized product benzaldehyde, other than C-O reductive elimination to furnish the cyclized product. Based on this result, a plausible mechanism for the cyclization reaction is proposed (Scheme 3). A five-membered cyclopalladium (II) intermediate **A** is initially formed by the coordination of Pd^{II} to the bidentate directing group, which is followed by the oxidation of Pd^{II} to Pd^{IV} to generate the intermediate **B**. The intermediate **B** undergoes ligand exchange to form **C**. This intermediate **C** is subsequently subjected to C-O reductive elimination, leading to

the formation of product **2a**, meanwhile $Pd(OAc)_2$ is regenerated from the Pd^{IV} species.



Scheme 3. Proposed mechanism

In summary, we have developed a unified method to synthesize cyclic ethers and lactones via Pd(II)-catalyzed intramolecular C-H functionalization of the β-methylene of carboxylic acid derivatives using the bidentate directing group. This protocol is more straightforward and step-economical than the traditional approaches, affording the products in good to excellent yields. The disclosed method may hold the promise for the efficient synthesis of complex and therapeutically useful molecules.

Acknowledgments

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Supplementary data

Supplementary data (experimental procedures, characterization of compounds, and copies of NMR spectra) associated with this article can be found, in the online version, at http://

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Highlights

- An efficient synthesis of lactones or cyclic ethers has been realized.
- The reaction involves C(sp^3)-H activation and intramolecular C-O functionalization.
- Both lactones and cyclic ethers can be prepared using the same conditions.
- This protocol is straightforward and step-economical.