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Palladium-Catalyzed β-Mesylation of Simple Amide via Primary sp^3 C−H Activation

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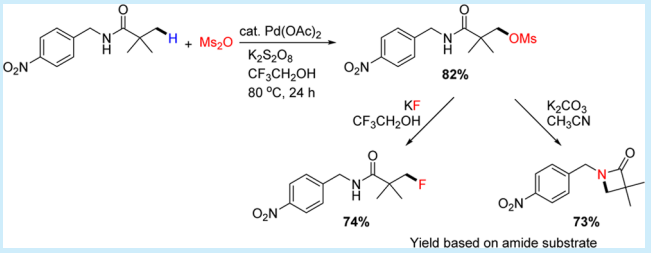
Supporting Information

ABSTRACT: A β-mesylation of primary sp^3 C−H bonds from simple amides with methanesulfonic anhydride (Ms_2O) has been established successfully at 80 °C in a $Pd(OAc)_2$ (catalyst)/$K_2S_2O_8$ (oxidant)/CF_3CH_2OH (solvent) system. These amide substrates involve *N*-monosubstituted linear, branch, or cyclic alkanes, and electron-deficient benzyl compounds. The β-mesylated amide products can be converted easily to β-fluoroamides or β-lactams through inter- or intramolecular S_N2 processes.



The direct functionalization of organic C−H bonds has emerged as an ideal and popular method in synthetic chemistry to form new C−C or C−heteroatom (C−O, C−N, C−B, C−halo, etc.) bonds.[1] Among these C−H bonds, primary alkyl sp^3 C−H bonds are the most inert ones with both high BDE (bond dissociation energy) and high pK_a (acid dissociation constant). One of the current methods in the activation of a normal alkyl sp^3 C−H bond is to use a transition-metal complex to selectively cleave the C−H bond with the assistance of a directing group under mild conditions to form a key intermediate containing a metal−C bond, which is normally a stable five- or six-membered ring complex.[2] After a series of reactions with a reaction reagent, the intermediate is converted to the final functionalized product; i.e., a new C−FG (functional group) bond is formed. Apparently, the directing group coordinating with transition-metal complex effectively is very important to achieve an inert C−H functionalization successfully. Various monodentate and bidentate directing groups have been developed in the functionalization of primary sp^3 C−H bonds.[3] However, most of them are special and fixed although a few removable directing groups have been disclosed recently.[4] To date, it is still a challenge to selectively functionalize inert sp^3 C−H bonds using common functional groups as directing groups, such as the hydroxyl, carbonyl, carboxyl, ester, amino, or amide group, etc.[5]

On the other hand, it is well-known that primary sp^3 C−GLG (good leaving groups, such as sulfate and sulfonate leaving groups) bonds are transformed to primary sp^3 C−FG bonds conveniently through S_N2 processes. Thus, functionalization of inert sp^3 C−H bonds to afford sp^3 C−GLG bonds is beneficial to provide more choices in the transformation of functional groups.[6] Herein, we report that Pd(II)-catalyzed β-mesylation of simple amides via primary sp^3 C−H bond activation can produce β-mesylated amides very well, followed by S_N2 processes to give β-fluoroamides or β-lactams.

According to the previous reports, the catalytic $Pd(OAc)_2$/$K_2S_2O_8$/acid system is very effective in functionalizing not only aryl sp^2 C−H bonds but also alkyl sp^3 C−H bonds under mild conditions.[7] Recently, we found that β-acyloxylation of simple amides with trifluoroacetic acid (CF_3CO_2H,TFA) and other carbolic acids was carried out smoothly in this catalytic system. However, those acyloxylated products cannot be transferred to other functional compounds readily except alcohols. Therefore, methanesulfonic acid (CH_3SO_3H, MsOH) was selected to replace TFA in the acyloxylation because the −OMs group is a good leaving group with high atom economy compared with other sulfate and sulfonate groups. A simple amide, *N*-(4-nitrobenzyl)pivalamide (**1a**), was employed as the model substrate to test the reaction. But, in MsOH no desired product was detected and the substrate was decomposed. In contrast, in TFA with 1 equiv of MsOH, only β-trifluoroacloxylated amides were found. When a weak acid, acetic acid (AcOH), was instead of TFA, both 30% β-mesylated and 30% β-acteyloxylated products were detected. Encouraged by this result, we improved the reaction efficiency and operation by using solid methanesulfonic anhydride (Ms_2O) as the reaction reagent in a very weak acidic solvent, 2,2,2-trifluoroethanol (TFE). Finally, in the $Pd(OAc)_2$ (10 mol %)/$K_2S_2O_8$ (2 equiv)/TFE system, the β-mesylated amide was obtained in 82% yield from the substrate (1 equiv) and Ms_2O (0.7 equiv) at 80 °C after 24 h. After the screening other Pd catalysts, oxidants, and sulfonic acids (Table 1), no more positive results were found (see Supporting Information in detail). It is noted that no β-mesylation occurred in the absence of either the palladium catalyst or oxidant in any cases. Thus, the catalytic $Pd(OAc)_2$/$K_2S_2O_8$/TFE system was determined for the β-mesylation of simple amides with Ms_2O.

In the investigation of the reaction scope, we found that a variety of *N*-monosubstituted amides were effective, while neither nonsubstituted nor disubstituted amides were successful

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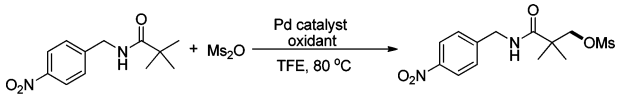
Table 1. Palladium-Catalyzed β-Mesylation of *N*-(4-Nitrobenzyl)pivalamide[a]



1a 2a

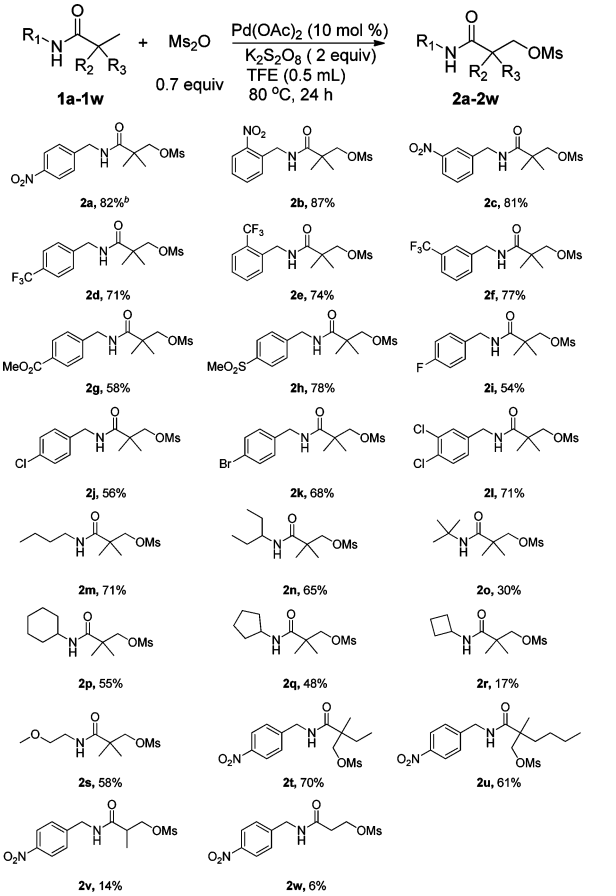
entry	catalyst	oxidant	yield (%)[b]
1	$Pd(OAc)_2$	$K_2S_2O_8$	74
2	$Pd(PPh_3)_4$	$K_2S_2O_8$	38
3	$Pd(TFA)_2$	$K_2S_2O_8$	60
4	$PdCl_2$	$K_2S_2O_8$	0
5	–	$K_2S_2O_8$	0
6	$Pd(OAc)_2$	$PhI(OAc)_2$	38
7	$Pd(OAc)_2$	Oxone	40
8	$Pd(OAc)_2$	–	0
9[c]	$Pd(OAc)_2$	$K_2S_2O_8$	48
10[d]	**$Pd(OAc)_2$**	**$K_2S_2O_8$**	**82**
11[e]	$Pd(OAc)_2$	$K_2S_2O_8$	0
12[f]	$Pd(OAc)_2$	$K_2S_2O_8$	0
13[g]	$Pd(OAc)_2$	$K_2S_2O_8$	22

[a]Substrate (1.0 mmol), catalyst (0.1 mmol), oxidant (2.0 mmol), solvent (0.5 mL), Ms_2O (0.7 mmol) or sulfonic acid (1.0 mmol), 80 °C, 24 h. [b]Yields based on substrate and detected by ^1H NMR analysis using CH_2Br_2 as an internal standard. [c]MsOH instead of Ms_2O. [d]Catalysts and oxidants added in two batches. [e]TsOH (*p*-Toluenesulfonic acid). [f]TfOH (Trifluoromethane-sulfonic acid). [g]Benzenesulfonic acid.

(Scheme 1). For benzyl substituted amides, strong electron-deficient benzyl substituted amides containing either a nitro or trifluoro group could afford the corresponding products in high yields. Methyl 4-(pivalamidomethyl)-benzoate (**1g**) and *N*-(4-(methylsulfonyl)benzyl)pivalamide (**1h**) gave the mesylation compounds in moderate and good yield, respectively. Halogen atoms such as fluorine, chlorine, or bromine in the para position of the benzyl substituted group were also tolerated during the reactions. However, neither a benzyl amide without an electron-deficient group nor a simple aryl amide can support the mesylation of the sp^3 C−H bond very well. In fact, normal aryl sp^2 C−H bonds are more reactive than alkyl sp^3 C−H bonds under these reactions conditions. For alkyl substitute amindes, not only linear but also branched aliphatic substituted amides such as *N*-butylpivalamide and *N*-(pentan-3-yl)-pivalamide (**1n**) were suitable for β-mesylation in this catalytic system. Furthermore, cyclic aliphatic substituted amides especially those containing a five- or six-membered ring could give the corresponding compounds in moderate yield. When there were both primary and secondary sp^3 C−H bonds in the amides, for example in the cases of *N*-(4-nitrobenzyl)-2,2-dimethylbutanamide (**1t**) and *N*-(4-nitrobenzyl)-2,2-dimethyl-hexanamide (**1u**), only primary sp^3 C−H bonds underwent the mesylation smoothly. In contrast, *N*-(4-nitrobenzyl)-isobutyr-amide (**1v**) containing two sp^3 CH_3 and one α-H gave the mesylated products in 14% yield, and propionamide (**1w**) containing one sp^3 CH_3 and two α-H just provided the products in 6% yield. In these cases, several side reactions were found such as amide decomposition and loss in reactivity of the palladium catalyst.

After the β-mesylated amides were obtained from simple amides through the cleavage of primary sp^3C−H bonds, we attempted to convert them to more valuable β-functionalized amides, such as β-fluoroamides. Recently, a few examples were

Scheme 1. Investigation of the Reaction Scope[a]



[a]Yields based on the substrates and detected by ^1H NMR analysis using CH_2Br_2 as an internal standard. Conditions: substrate (1.0 mmol), catalyst (0.1 mmol), oxidant (2.0 mmol) (catalyst and oxidants added in two batches), TFE (0.5 mL), Ms_2O (0.7 mmol), 80 °C, 24 h. [b]75% isolated yield.

reported on direct preparation of β-fluoroamides from amides with special directing groups via sp^3C−H activation, but expensive fluorination agents including Selectfluor, or NFSI, were necessary.[8] Since −OMs is a good leaving group in the S_N2 processes, it is plausible to convert β-mesylated amides to β-fluoroamides just using KF as fluorination agent. Fortunately, it was found that not only electron-deficient benzyl substituted amides but also linear, branched, and cyclic aliphatic substituted amides were β-fluorinated successfully with KF (5 equiv) in TFE at 110 °C. When the crude β-mesylated amides underwent the fluorinations, which were from the reaction mixture just filtered through Celite to remove the inorganic salts, the total product yields were 45−75% based on the amide substrates (Scheme 2). In addition, the β-mesylation and β-fluorination of simple amides might be completed in one-pot with a longer reaction time and a lower yield.

Of course, chlorination, bromination, and iodination of β-mesylated amides were also successful by using LiCl, LiBr, and NaI as the nucleophile, respectively. Nearly quantitative β-halo amides were obtained through the S_N2 processes.

Meanwhile, the intramolecular β-amidation of special amides can produce β-lactams,[9] the common four-membered rings in many pharmaceuticals, which are normally synthesized from acids and amines through the intramolecular condensations. For the simple amides without any auxiliary directing groups,

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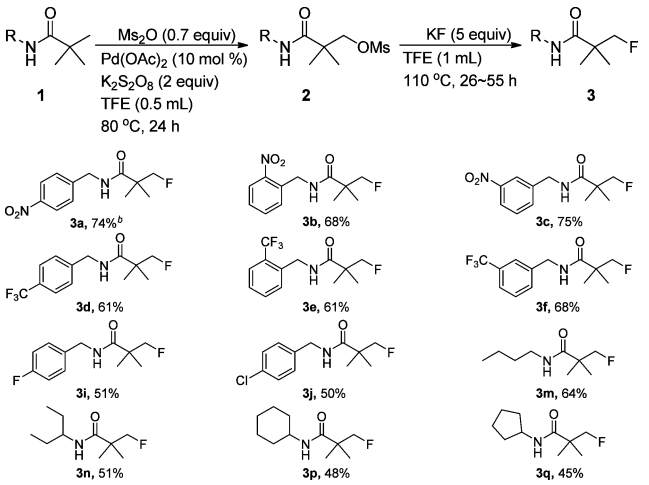
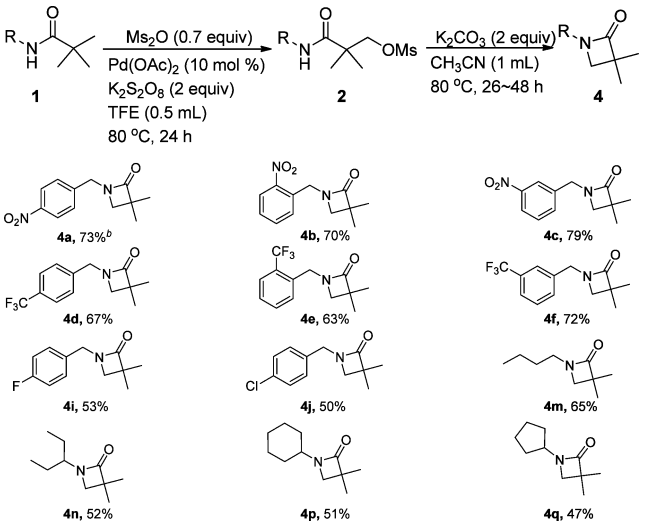
Scheme 2. β-Fluorination of Simple Amides[a]



[a]Yields based on the amide substrates by ^{1}H NMR analysis. [b]65% isolated yield.

direct β-amidation of them to prepare β-lactams has not been reported. In our study, however, we found that various crude β-mesylated amides could also be converted very well to their corresponding β-lactams in the presence of K_2CO_3 in CH_3CN at 80 °C. The total yields of β-lactam were 47−79% based on the amide substrates after two sequential steps, including a β-mesylation via sp^3 C−H activation and a subsequent intramolecular amidation through an S_N2 process (Scheme 3).

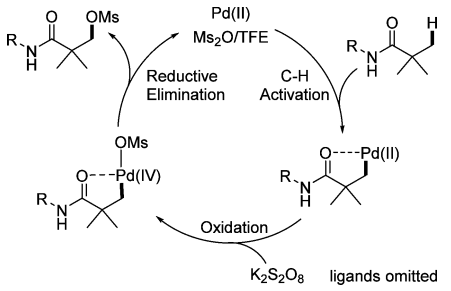
Scheme 3. Preparation of β-Lactams from Simple Amides[a]



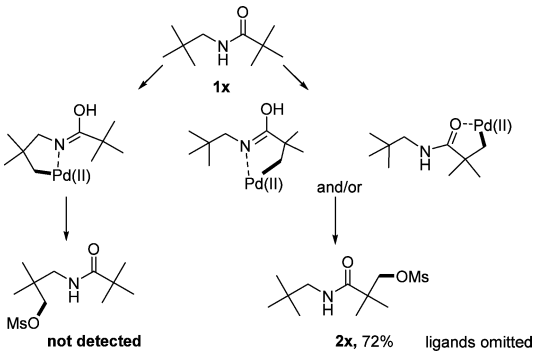
[a]Yields based on the amide substrates by ^{1}H NMR analysis. [b]64% isolated yield.

Based on the current and previous studies, a proposed reaction mechanism for β-mesylation of an amide is shown in Scheme 4. It involves three main steps. The first is an sp^3 C−H activation, in which a Pd(II) species coordinates with an amide group and cleaves its β-sp^3 C−H bond to form an alkyl−Pd(II) five-membered ring intermediate. According to the test reaction of *N*-neopentylpivalamide (**1x**) having two kinds of primary sp^3 C−H bond, only a β-mesylated product (**2x**) was found in 72% yield (Scheme 5). It indicates that Pd(II) seems to prefer to

Scheme 4. A Proposed Reaction Mechanism



Scheme 5. β-Mesylation of *N*-Neopentylpivalamide



coordinate with the O atom of sp^2 C=O and/or N atom of sp^2 C=N in a rigid five-membered ring. The second step includes oxidation of a Pd(II) intermediate, which is the alkyl−Pd(II) intermediate which is oxidized by $K_2S_2O_8$ to a Pd(IV) species. It is partially supported by the lack of mesylation in the absence of any oxidants as mentioned in Table 1. The final step is a reductive elimination of the Pd(IV) species to give a β-mesylated amide and the Pd(II) catalyst. The high reductive ability of the Pd(IV) species ensures C−OMs bonds or other esters from the more stable MsO^- ions or other strong acids.

In summary, we developed a method for β-mesylation of an inert primary sp^3 C−H bond from various simple amides, such as *N*-substituted amides by linear, branched, or cyclic alkanes and electron-deficient benzyl compounds. The β-mesylated amides also can be transferred easily to their corresponding β-fluoroamides or β-lactams through S_N2 processes. Studies exploring the scope, real mechanism, and more applications are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00536.

Typical experimental procedures, detailed screening the reaction conditions, preparations and characterization of compounds and spectroscopic data (PDF)

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Notes

The authors declare no competing financial interest.

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