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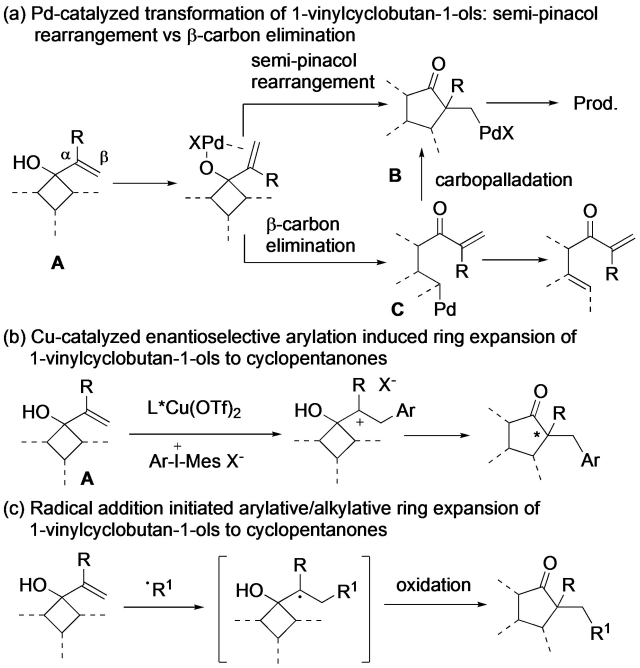
Dual Catalysis

Arylative Ring Expansion of 3-Vinylazetidin-3-Ols and 3-Vinyloxetan-3-Ols to Dihydrofurans by Dual Palladium and Acid Catalysis

*Takuji Fujii, Qian Wang, and Jieping Zhu**

Abstract: In contrast to the well-studied 1-vinylcyclobutanols, the reactivity of 3-vinylazetidin-3-ols **1** and 3-vinyloxetan-3-ols **2** under transition metal catalysis remains largely unexplored. We report herein their unique reactivity under dual palladium and acid catalysis. In the presence of a catalytic amount of $Pd(OAc)_2$-$(PPh_3)_2$, AgTFA and triflic acid, the reaction of **1** or **2** with aryl iodides affords 2,3,4-trisubstituted dihydrofurans, which are valuable heterocycles in organic synthesis. Mechanistic studies reveal that this arylative ring-expansion reaction proceeds via a domino process involving Heck arylation of alkene, acid-catalyzed transposition of allylic alcohol and ring opening of the azetidine/oxetane by an internal hydroxyl group.

Since Johnson's seminal report in 1964,[1] the electrophilic β-carbon functionalization-triggered semi-pinacol rearrangement of 1-vinylcyclobutanols **A** has been a topic of interest to synthetic chemists.[2] In parallel, transition metal-catalyzed ring expansion of **A** has also been extensively investigated during the last twenty years.[3] Two main reaction pathways initiated by semi-pinacol rearrangement[4] and β-carbon elimination,[5] respectively, have been exploited for the synthesis of diverse sets of compounds, taking advantage of the Pd(II) intermediates **B** and **C** (Scheme 1a). Additionally, Cu-catalyzed asymmetric arylative semi-pinacol rearrangement of **A** has been developed for the synthesis of enantioenriched 2,2-disubstituted cyclopentanones (Scheme 1b).[6] On the other hand, exploiting the radical-polar crossover mechanism under photoredox-catalytic conditions allowed the realization of both arylative and alkylative ring expansion of **A** to functionalized cyclopentanones (Scheme 1c).[7] Interestingly, these strategies have rarely been applied to 3-vinyloxetan-3-ols and remarkably, 3-vinylazetidin-3-ols haven't been explored in any of these transformations. In this context, we were also surprised to find that Pd-catalyzed arylative ring-expansion of 1-vinylcyclobutanols remains unknown although that of 1-(1-alkynyl)cyclobutanols[8] and 1-(1-allenyl)cyclobutanols[9] has been reported.



Scheme 1. Ring expansion of 1-vinylcyclobutanols to cyclopentanones.

Oshima and Yorimitsu reported in 2009 a Pd-catalyzed arylative epoxidation of tertiary allylic alcohols (Scheme 2a).[10] In connection with our interest in 1,2-rearrangement reactions,[11,12] we surmised that, by combining the arylative epoxidation with catalytic enantioselective Meinwald rearrangement,[13] it might be possible to convert 3-vinylazetidin-3-ols **1** to ring expanded pyrrolidin-3-ones (**E**, X=NP) in an enantioselective manner (Scheme 2a). However, our initial exploration led to an unexpected reaction between **1** and phenyl iodide (**3a**), affording 2,3,4-trisubstituted-2,5-dihydrofurans (DHFs) **4**. Dihydrofuran (DHF), being an important precursor of tetrahydrofuran and furan as well as its presence in natural products[14] and bioactive compounds,[15] has been a popular synthetic

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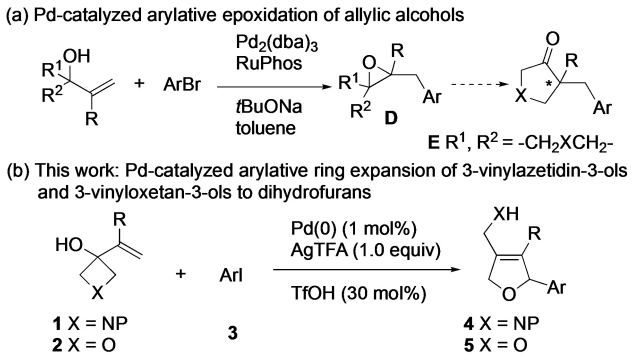
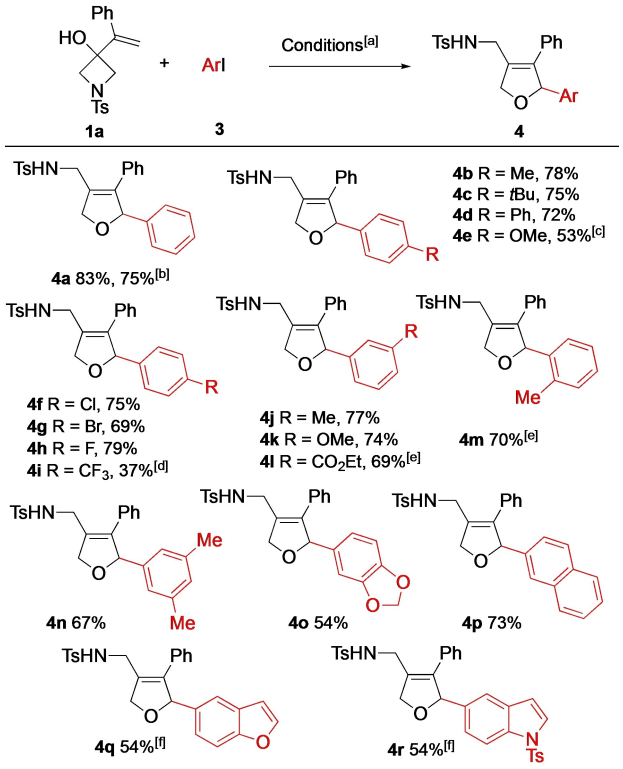


Scheme 2. Unexpected rearrangement of Pd-catalyzed arylative rearrangement of 3-vinylazetidin-3-ols and 3-vinyloxetan-3-ols to dihydrofurans.

target.[16] Therefore, we became interested in optimizing this unprecedented ring transformation. We report herein the development of an arylative ring rearrangement of 3-vinylazetidin-3-ols **1** to afford DHFs **4** under dual Pd and acid catalysis (Scheme 2b). Notably, the same reaction can be applied to 3-vinyloxetan-3-ols **2** to DHFs **5** under slightly modified conditions.

3-(1-Phenylvinyl)-1-tosylazetidin-3-ol (**1a**) and phenyl iodide (**3a**) were chosen as test substrates. Only decomposition was observed applying Oshima and Yorimitsu's conditions. Interestingly, dihydrofuran **4a** was isolated among other unidentified products when **1a** and **3a** were submitted to the reaction in the presence of a catalytic amount of $Pd(OAc)_2$ and triflic acid (TfOH) (Scheme 3). Intrigued by this unprecedented transformation, we set out to optimize the reaction conditions by varying systematically the Pd source, the ligands, the additives, the solvents, and the acids. The key experimental observations are summarized as follows: a) $Pd(OAc)_2(PPh_3)_2$ is the pre-catalyst of choice and a loading of 1 mol% was enough to ensure a good yield of **4a**; b) THF is the optimal solvent although reaction occurred also in other ethereal solvents such as 1,4-dioxane, 2-methyl-tetrahydrofuran and cyclopentyl methyl ether. However, 1,2-dichloroethane, toluene, acetonitrile, were completely inefficient reaction medium; c) using mixed solvents THF/H_2O (v/v = 100:1 and 10:1) dramatically decreased the yield of **4a**; d) AgTFA was the most effective additive among a series of silver salts examined (AgOAc, Ag_2CO_3, Ag_3PO_4); No reaction took place in its absence. Overall, the optimum conditions consisted of performing the reaction in THF (*c* 0.1 M) in the presence of $Pd(OAc)_2(PPh_3)_2$ (1 mol%), AgTFA (1.0 equiv) and triflic acid (TfOH, 0.3 equiv) at 80 °C. Under these conditions, dihydrofuran **4a** was isolated in 83% yield. Importantly, the reaction did not produce 4-benzyl-4-phenyl-1-tosylpyrrolidin-3-one (**E**, X = NTs, *cf* Scheme 2a), which would be the expected outcome from the initially envisioned pathways involving semi-pinacol or Meinwald rearrangement of the hypothetic epoxide intermediate **D** (R^1, R^2 = $-CH_2N(Ts)CH_2-$, Scheme 2a).

The scope of the reaction was next examined varying firstly the aryl iodides **3** (Scheme 3). Substrates with alkyl



Scheme 3. Synthesis of 2,3,4-trisubstituted-2,5-dihydrofurans: Scope of aryl halides. [a] Standard conditions: **1a** (0.1 mmol), aryl iodide **3** (0.15 mmol), $Pd(OAc)_2(PPh_3)_2$ (1.0 mol%), AgTFA (1.0 equiv), TfOH (30 mol%), THF (1.0 mL), 80 °C. [b] Reaction was performed at 1.0 mmol scale. [c] Reaction was performed with $Pd(OAc)_2(PPh_3)_2$ (5 mol%) at 90 °C. [d] Reaction was performed with $Pd(OAc)_2(PPh_3)_2$ (5 mol%) at 110 °C. [e] Reaction was performed with $Pd(OAc)_2(PPh_3)_2$ (5 mol%) at 100 °C. [f] AgTFA (1.5 equiv), TfOH (60 mol%) were used. Yields refer to isolated pure products. Abbreviations: AgTFA = silver trifluoroacetate; THF = tetrahydrofuran; TfOH = triflic acid.

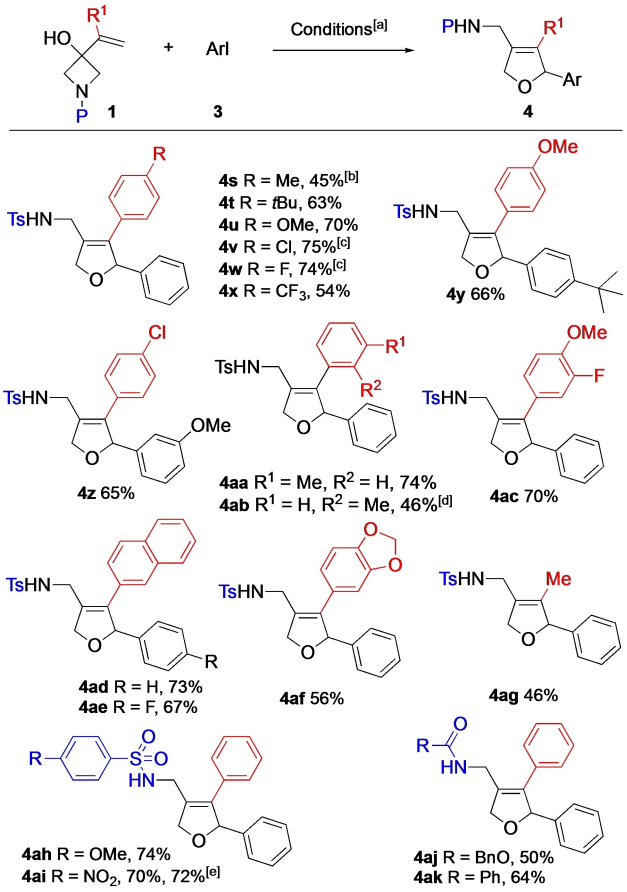
(**4b**, **4c**), phenyl (**4d**) and a strong electron-donating substituent (OMe, **4e**) at the *para* position performed well under the reaction conditions. 1-Bromo-4-iodobenzene and 1-chloro-4-iodobenzene underwent chemoselective transformation affording brominated and chlorinated products **4f** and **4g**, respectively. The presence of halogen atom in **4f** and **4g** provided a handle for further functionalization. The fluorine substitution was tolerated (**4h**), but reaction of 1-iodo-4-(trifluoromethyl)benzene with **3a** afforded **4i** in only moderate yield. The aryl iodides bearing a *meta*-substituent whether it is electron donating (Me, OMe) or withdrawing (COOMe) groups participated in the reaction to afford products **4j**–**4l** in high yields. Additionally, 2-methylphenyl iodide, 3,5-dimethylphenyl iodide, 5-iodobenzo[*d*]-[1,3]dioxole and 2-iodonaphthalene were successfully converted to dihydrofurans **4m**–**4p** in good to high yields. Finally, under slightly modified conditions [AgTFA (1.5 equiv) and triflic acid (TfOH, 0.6 equiv)], both 5-iodobenzofuran and *N*-Ts-5-iodoindole participated in the reaction, yielding DHFs **4q** and **4r**, respectively. Unfortunately, reaction of **1a** with 3-iodothiophene or (*E*)-(2-iodovinyl)benzene failed to give the desired products.

The versatility of the reaction was further investigated by varying the structures of 3-vinylazetidin-3-ols (Scheme 4). Regarding the arenes attached to the double bond, the presence of electron donating and withdrawing groups at the *para* (**4s**–**4z**), *meta* (**4aa**) and *ortho* positions (**4ab**) was well tolerated. 3,4-Disubstituted phenyl (**4ac**), naphthalene (**4ad**, **4ae**) and benzodioxole (**4af**) units can be incorporated into the products. 3-Propenyl substituted tosylazetidin-3-ol (**1ag**, R^1 = Me) participated in the reaction to provide **4ag** in 46 % yield. However, reaction of 3-(but-1-en-2-yl)-1-tosylazetidin-3-ol (R^1 = Et, structure not shown) with phenyl iodide gave a complex reaction mixture. *N*-(4-Methoxyphenyl)sulfonyl and *N*-(4-nitrophenyl)sulfonyl protected azetidinols were efficiently converted to the corresponding dihydrofurans **4ah** and **4ai** in yields of 74 % and 70 %, respectively. *N*-Cbz and *N*-Bz protected azetidines reacted in a similar fashion to provide the rearranged products **4aj** and **4ak** in good yields. Compound **4ai** was isolated in a slightly higher yield when the reaction was carried out at 2.0 mmol scale indicating the practicality of the protocol.

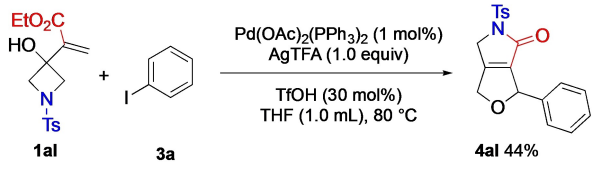
To demonstrate the robustness of the present transformation, a more complex domino sequence leading to bicyclic lactam was realized. Thus, reaction of methyl 2-(3-hydroxy-1-tosylazetidin-3-yl)acrylate (**1aj**) with phenyl iodide (**3a**) under standard conditions afforded **4al** in 44 % yield (Scheme 5).

Gratifyingly, we successfully expanded this novel ring rearrangement reaction to 3-vinyloxetan-3-ols **2** by slightly modifying the reaction conditions (Scheme 6a). Heating a solution of **2a** (R^1 = Ph) and phenyl iodide (**3a**) in methyl *tert*-butyl ether (MTBE) in the presence of $Pd(OAc)_2(PPh_3)_2$ (5.0 mol %) and AgTFA (1.2 equiv) at 80 °C afforded the Heck arylation product. The solvent was then changed to MeCN-H_2O (v/v = 50:1), and TfOH (0.6 equiv) was added. After stirring for another 6 hours at 80 °C, DHF **5a** was isolated in 52 % yield. Other DHFs **5b**–**5e** were prepared in similar yields following this protocol (Scheme 6a). Unfortunately, 3-vinylthietan-3-ol failed to participate in this ring expansion reaction.

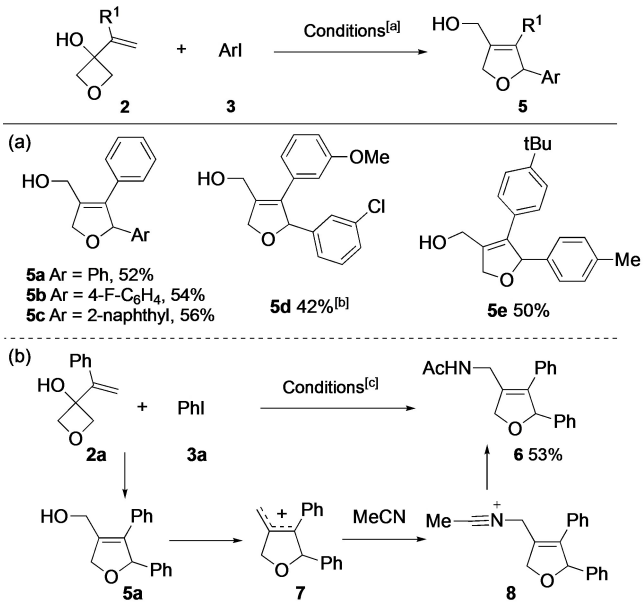
A side product **6** was isolated when the rearrangement step was allowed to proceed for a longer time. A control



Scheme 4. Synthesis of 2,3,4-trisubstituted-2,5-dihydrofurans: Scope of azetidines. [a] Standard conditions: **1** (0.1 mmol), aryl iodide **3** (0.15 mmol), $Pd(OAc)_2(PPh_3)_2$ (1.0 mol %), AgTFA (0.1 mmol), TfOH (30 mol %), THF (1.0 mL), 80 °C. [b] Reaction was performed with $Pd(OAc)_2(PPh_3)_2$ (5 mol %) at 90 °C. [c] Reaction was performed with $Pd(OAc)_2(PPh_3)_2$ (10 mol %) at 100 °C. [d] Reaction was performed with $Pd(OAc)_2(PPh_3)_2$ (5 mol %) at 100 °C. [e] Reaction was performed at 2.0 mmol scale. Yields refer to isolated pure products.



Scheme 5. One-step synthesis of bicyclic lactam.



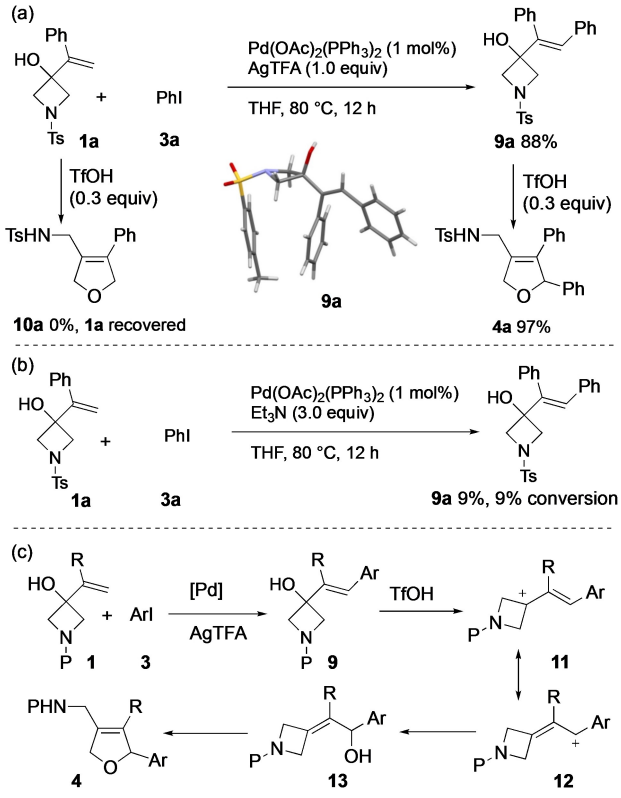
Scheme 6. Arylative ring expansion of 3-vinyloxetan-3-ols to dihydrofurans. Reagents and conditions. [a] **2** (0.1 mmol), ArI (1.5 equiv), $Pd(OAc)_2(PPh_3)_2$ (5 mol %), AgTFA (1.2 equiv), MTBE (1.0 mL), 80 °C; then change solvent to MeCN/H_2O (v/v = 50:1, 4 mL), TfOH (60 mol %), 80 °C. [b] The ring expansion step was performed at 100 °C. [c] Standard conditions except MeCN was used instead of mixed solvent MeCN/H_2O in the rearrangement step.

experiment revealed that compound **6** originated from the initial product **5a**. This interesting observation prompted us to optimize conditions to selectively produce **6**. Pleasingly, by performing the rearrangement reaction in acetonitrile, compound **6** was isolated in 53 % yield from the reaction of **2a** with **3a**. Generation of highly stabilized allylic carbocation **7** from **5a** followed by Ritter reaction via nitrilium intermediate **8** could account for its formation (Scheme 6b).

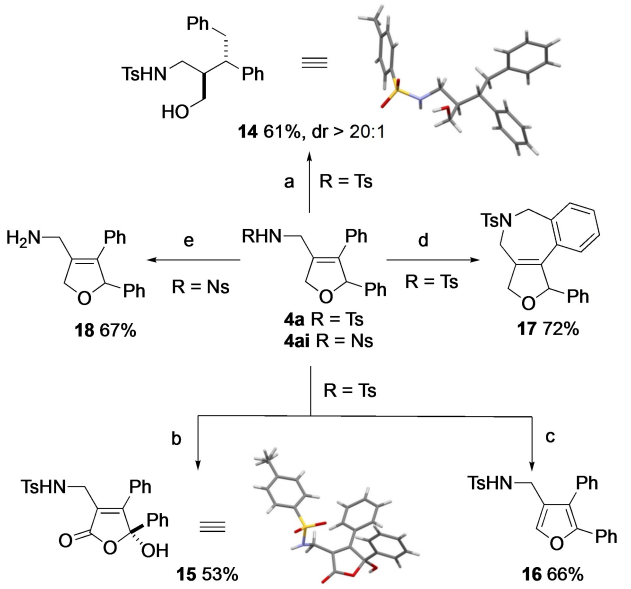
In the absence of triflic acid, reaction of **1a** with phenyl iodide under otherwise standard conditions afforded (*E*)-**9a** as only stereoisomer (Scheme 7a). Treatment of a THF solution of **9a** with TfOH triggered the skeleton rearrangement to provide dihydrofuran **4a** in essentially quantitative yield. The starting material **1a** was, on the other hand, stable towards the action of TfOH. Weaker acids such as *p*-toluenesulfonic acid (TsOH), camphorsulfonic acid (CSA) and methanesulfonic acid (MsOH) were unable to promote the rearrangement of **9a** to **4a**. These results indicate that triflic acid is neither essential nor harmful to the Heck reaction but it alone catalyzes the skeleton rearrangement process.

While chiral phosphoric acids were unable to catalyze the rearrangement of the Heck adduct, the stronger chiral Brønsted acids such as *N*-triflyl phosphoramide,[17] BINAP derived disulfonic acid[18] and its cyclic disulfonimide derivative[19] did catalyze the rearrangement reaction. However, the enantioselectivity remained low affording **4a** with negligible *ee* (*cf* Supporting Information).[20] Replacing AgTFA with Et_3N,[21] reaction of **1a** and **2a** afforded compound **9a** in only 9 % yield (Scheme 7b).[22] Since bis(triphenylphosphine)palladium diacetate, used in Heck reaction,[23] is known to be a precursor of Pd(0),[24] and the silver salt is known to facilitate the oxidative addition of aryl iodide to Pd(0) and to promote the formation of a positively charged Pd(II) species ($ArPd^+$).[25] We assumed that the latter species is important to the present Heck reaction.[26] On the basis of the results of these control experiments, a possible reaction pathway is depicted in Scheme 7c. The Pd-catalyzed regioselective Heck reaction between **1** and aryl iodide **3** would afford alkene **9** which would, in the presence of TfOH, undergo dehydration to afford carbocation **11** which could also exist in its resonance form **12**.[27] Trapping of the latter by one molecule of water would provide, after proton transfer, a 1,3-transpositioned allylic alcohol **13**. An intramolecular nucleophilic ring opening of the azetidine ring by the tethered hydroxyl group would then afford the dihydrofuran **4**.[28]

Post-transformations of dihydrofurans were performed to illustrate its synthetic potential (Scheme 8). Hydrogenation of **4a** at 50 °C for 24 h provided a linear 1,3-amino-alcohol **14** in 61 % yield with excellent diastereoselectivity. Hydrogenation of the double bond from the face opposite to the one occupied by the C2-phenyl substituent followed by hydrogenolysis of the benzylic C–O bond could account for the observed high diastereoselectivity. Oxidation of **4a** with Oxone and KBr furnished 5-hydroxyfuran-2(5*H*)-one **15**,[29] while radical-based dehydrogenation (PhSH, AIBN) afforded furan **16**.[30] Mannich reaction of **4a** with formaldehyde under acidic conditions afforded a tricyclic



Scheme 7. Possible reaction pathway.



Scheme 8. Post-transformations of dihydrofurans. Reaction conditions: [a] H_2, 10 wt % Pd/C (300 mg/mmol), EtOH, 50 °C, 24 h, 61 %. [b] Oxone (2.2 equiv), KBr, MeCN-H_2O, 45 °C, 53 %. [c] PhSH (2.5 equiv), AIBN (1.5 equiv), toluene, 110 °C, 6 h, 66 %. [d] Formaldehyde (2.0 equiv), TFAA (3.0 equiv), MsOH (10.0 equiv), DCE, 0 °C to RT, 1 h, 72 %. [e] PhSH (3.0 equiv), K_2CO_3 (4.0 equiv), MeCN, 50 °C, 67 %. Abbreviations: AIBN = azobisisobutyronitrile; TFAA = trifluoroacetic anhydride; DCE = dichloroethane.

tetrahydrobenzofuroazepine **17**.[31] Finally, the *N*-nosyl group was removed from **4ai** under Fukuyama conditions to afford primary amine **18** in 67 % yield.[32]

In summary, we have developed an unprecedented arylative skeleton rearrangement of 1-vinylazetidin-3-ols **1** and 1-vinyloxetan-3-ols **2** under dual Pd and acid catalysis. One-pot palladium-catalyzed regioselective Heck arylation of alkene followed by acid-catalyzed transposition of allylic alcohol and ring opening of the azetidine or oxetane by the internal hydroxyl group accounted for the observed transformation. It is important to note that semi-pinacol rearrangement of the carbopalladation intermediate (*cf* Scheme 1a) was completely bypassed under our reaction conditions.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Rearrangement · 3-Vinylazetidin-3-ols · 3-Vinyloxetan-3-ols · Dihydrofurans · Palladium catalysis

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