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Total syntheses of (+)- and (−)-Crinane via Pd(0)-Catalyzed deacylative allylation

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ABSTRACT

An efficient Pd(0)-catalyzed deacylative allylation (DaA) of enolcarbonates (pro-nucleophile) prepared from 2-arylcyclohexanones sharing acyl functionality at C2-position with readily available allylic alcohols (pro-electrophiles) by employing Pd(0)-catalysis under mild reaction conditions. The methodology can be extended for deacylative benzylations (DaB) of enolcarbonates of 2-arylcyclohexanones. As an application of our methodology, we have shown asymmetric total synthesis of *Amaryllidaceae* alkaloids, (+)- and (−)-crinane.

1. Introduction

Allylation reaction at the α-position of a carbonyl group represents one of the important C–C bond-forming reaction [1]. In this regard, the Tsuji-Trost allylation [1,2] provides an opportunity to access allylation products comparatively under the mild condition. In case of allyl β-ketoester or allylenol carbonate, the allylation works *via* elimination of CO_2 [3]. A large number of functionalized intermediates [4] can be prepared in the synthesis of valuable pharmaceuticals and natural products [5,6]. However, the incorporation of allyl electrophile and the nucleophile into the same reactant molecule *via* an ester linkage[6a-b] or carbonate[6c-d] limits the utilization of such reaction. Thus, there is a need to develop strategy for allylation at the α-position of carbonyl group which can take place intermolecular manner with unfunctionalized allyl source such as allylalcohol.

In this regard, Tunge and Grenning's report on Pd(0)-catalyzed three-component deacylative allylation (DaA) of α-nitroketone (pKa ~17) drew our attention (Scheme 1) [7]. This reaction allows accessing unsymmetrically substituted 1,6-diene **1** in an efficient manner (Scheme 1) [8,9]. This pioneering report also suggests that enolates with pKa ~18–25, [10a] and nitrile stabilized anions with pKa ~23 [10b] undergo alkylations to afford a variety of synthetically useful compounds [11].

On the other hand, 2-arylcyclohexanones bearing an all-carbon quaternary center is a common structural feature in a variety of pharmaceuticals [12], and natural products such as *Amaryllidaceae* alkaloids (Fig. 1) [13]. Encouraged by Tunge's deacylative process [8,11a-b], we became interested in developing methods that would allow rapid entry to 2-aryl 2′-allylcyclohexanones via an intermolecular allylation of enolcarbonate of type **2** (Scheme 1).

In this context, *Amaryllidaceae* alkaloids [13c] with immense biological profiles drew our interest (Fig. 1). Due to their interesting biological properties (such as antitumor, antiviral, and anti-acetylcholinesterase activities) coupled with their fascinating architecture, *Amaryllidaceae* alkaloids (**3**–**5**, Fig. 1) have attracted attention from the synthetic community [13]. Approximately 500 *Amaryllidaceae* alkaloids have been isolated from different *Amaryllidaceae* species and most of them are optically active [13]. It is quite interesting to note that, enantiomeric pairs such as (−)-crinine (**5a**) and (+)-vittatine (**5b**) were also isolated from different *Amaryllidaceae* species [13b].

We envisioned that 5,10-*b*-ethanophenathridine structural motif of *Amaryllidaceae* alkaloids such as (−)-crinane (**4a**) could be achieved via a late-stage Pictet-Spengler reaction of *cis*-3a-(3,4-methylenedioxyphenyl)octahydroindole scaffold **18** with

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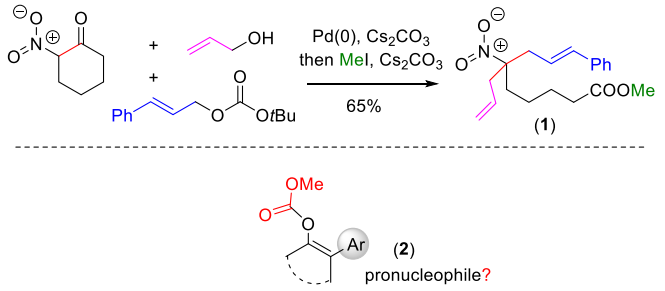
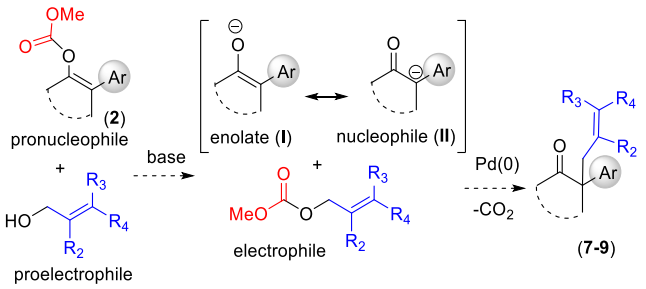


Scheme 1. Synthesis of 1,6-diene **1** *via* deacylative allylation.



Scheme 3. The rationale of deacylative allylations (DaA) of enolcarbonate **2**.

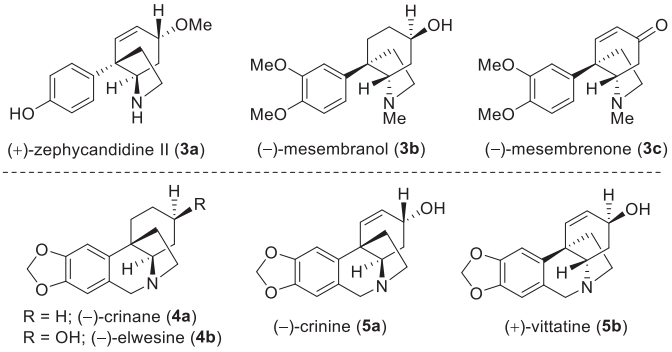


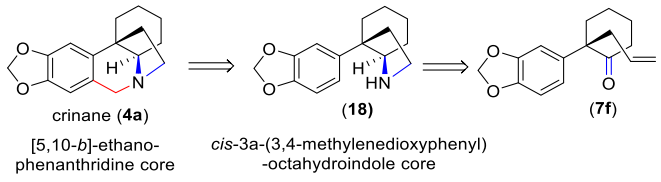
Fig. 1. Representative *Amaryllidaceae* alkaloids.

formaldehyde equivalent (Scheme 2). The latter could be accessed via a sequential reductive amination of intermediate γ-ketoaldehyde, which in turn could be obtained from 2-aryl-2′-allyl cyclohexanones of type **7f**.

2. Retrosynthetic analysis

2-Nitrocyclohexanone derivatives having an electron withdrawing group could undergo a *retro*-Claisen type activation in the presence of *in-situ* generated allyl alkoxide, thereby breaks cyclohexanone ring in Tunge's reports (Scheme 1) [8,9a]. However, we would require the synthesis of 2-aryl-2′-allyl cyclohexanone for the synthesis of *Amaryllidaceae alkaloids* shown in Fig. 1.

The mechanistic rationale of deacylative allylations (DaA) of enolcarbonate **2** is shown in Scheme 3. It is envisioned that an allylic alkoxide may induce a deacylative process of aryl substituted enolcarbonate **2** to form carbanion **II** (Scheme 3), which would then react with Pd(II)-π-allyl complex [generated *in situ* by reaction of allylacetate and Pd(0)] to furnish various 2-arylated cyclohexanones **7**–**9**. Based on this hypothesis, we recently reported an efficient Pd(0)-catalyzed deacylative allylation (DaA) and utilized for a total synthesis of (±)-crinane [14a]. Herein, we report a detailed studies of our methodology of Pd(0)-catalyzed deacylative allylation (DaA) of enolcarbonates and the total syntheses of



Scheme 2. Retrosynthetic analysis of *Amaryllidaceae* alkaloids sharing 5,10*b*-ethanophenathridines.

(−)-crinane (**4a**) and (+)-crinane (***ent*-4a**) (Scheme 3) utilizing DaA methodology.

3. Results and discussions

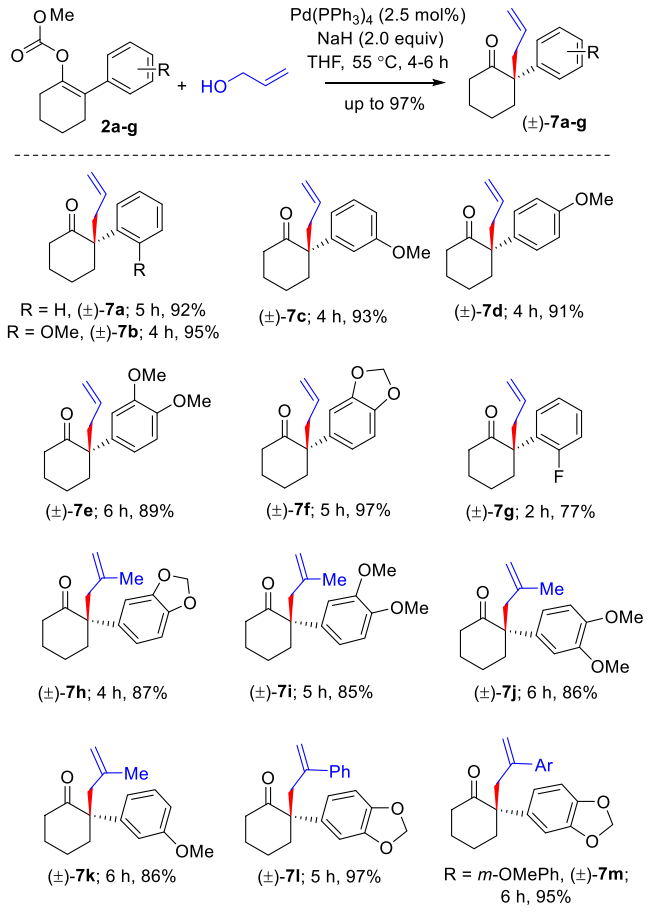
The deacylative allylations (DaA) using unfunctionalized allyl alcohol is an attractive strategy for allylation of α-position of a carbonyl group. For optimization studies we selected enolcarbonate **2a** and allylalcohol as the pronucleophile and proelectrophile, respectively. A number of different bases were screened in combination of with catalytic Pd(0). Following exhaustive optimization, it was found that, 2.5 mol% $Pd(PPh_3)_4$ in combination with NaH (2.0 equiv) in THF furnished product **7a** in 92% yield in 5 h. Therefore, this condition was chosen for the studies of substrate scope.

Our optimized condition could be extended to various enolcarbonates **2** with allylalcohol as pro-electrophiles and the results are summarized in Scheme 4. Applying the DaA strategy, we could synthesize a wide range of 2-aryl cyclohexanones **7a-g** with a C2-quaternary center in good to excellent yields (Scheme 4). Importantly, aromatic ring containing both electron-donating (see, **7a-f**) and electron-withdrawing (see, **7g**) functional groups were well tolerated for DaA reaction with allyl alcohol (Scheme 4). Further, methallyl alcohol as pro-electrophile afforded products 2-aryl 2′-methallyl cyclohexanones **7h-k** in 85–87% yields in 4–6 h (Scheme 4). Gratifyingly, phenallylalcohol could also be employed as pro-electrophile to access products **7l-m** in 95–97% yields under the standard condition (Scheme 4).

Further, a number of substituted allylalcohols as pro-electrophiles were tested under optimized conditions to afford compounds **8a-h** in up to 95% yields (Scheme 5). Most importantly, we found that the DaA reaction was highly regioselective in nature, where linear products (such as **8a-h**) were obtained in excellent yields and no traces of branched products were obtained (Scheme 5).

Next, a number of enolcarbonates with an aromatic ring containing electron-withdrawing groups were tested to afford compounds **9a-i** in 80–96% yields in 3–5 h (Scheme 6). Once again, a number of substituted allylalcohols, such as crotyl alcohol, and cinnamyl alcohol with *E*-geometry, as pro-electrophiles furnished only linear products (**9b-c**, **9e-f**, **9j**, and **9m**) under the optimized condition. Further, 3,3-dimethyl allyl alcohol (prenyl alcohol) as pro-electrophile afforded only linear products **9i** and **9l** (Scheme 6). Interestingly, cyclohexane sharing an ethylester at C-2 position, which is a challenging substrate due to the possibilities of sequential allylations, also afforded product **9j** in 68% yield, thereby clearly indicating mild nature of our process. 2-Arylcyclopentanones (**9k-n**) and 2-arylcycloheptanones (**9o-p**) based enolcarbonates furnished various structural scaffolds as shown in Scheme 6.

We then look forward for the utilization of 2,3-disubstituted allyl alcohol as pro-electrophile in Pd(0)-catalyzed deacylative



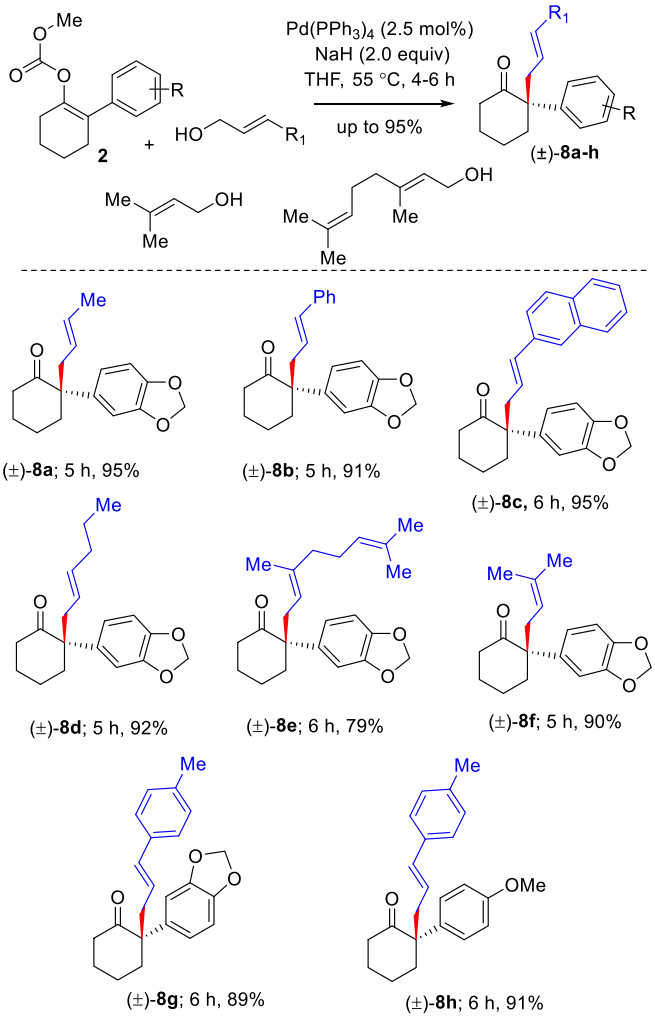
[a]reactions were carried out using 0.20 mmol (1 equivalent) of **2a-g** with 0.30 mmol (1.5 equivalents) of allylalcohol and 0.40 mmol (2 equivalents) of NaH in 3.0 mL THF in the presence of 2.5 mol% of $Pd(PPh_3)_4$ at 55 °C under argon condition. [b]isolated yields after column purification.

Scheme 4. Substrates scope of Pd(0)-catalyzed DaA using esters.[a,b].

allylation (Scheme 7). A number of enolcarbonates with an aromatic ring containing electron-donating groups were tested to afford compounds **10a-d** in 85–92% yields in 6–8 h (Scheme 7). We found that these reactions are highly regioselective in nature, where only linear products were obtained. 3-Substituted allylalcohols sharing heterocycles such as 2-furyl and 2-thienyl at 3-position were employed as proelectrophiles (Scheme 7). These compounds afforded products **10e-j** in good to excellent yields (up to 95%).

We were pleased to note that 3-substituted allylalcohol having 3-fluorenyl group as proelectrophile afforded products **10k-l** in 95–98% yields (Scheme 7). The aromatic polymers containing fluorenyl groups are important in the area of anion conductive aromatic block co-polymers.

Further proof of highly regioselective nature of our DaA methodology was established with the fact that secondary allylalcohols such as arylvinylcarbinols afforded only linear products **8b**, **8h**, and **9c** as sole regioisomers in 83–91% yields (Scheme 8). In this regard, a number of secondary allylalcohols prepared from furfural and thiophene 2-aldehyde also afforded a variety of products **10e-j** where linear products were obtained as sole regioisomers (Scheme 8). Along same line, *reverse*-prenyl alcohol afforded **8f**, **9i**, and **9l** in up to 90% yields as linear regioisomer (Scheme 9).

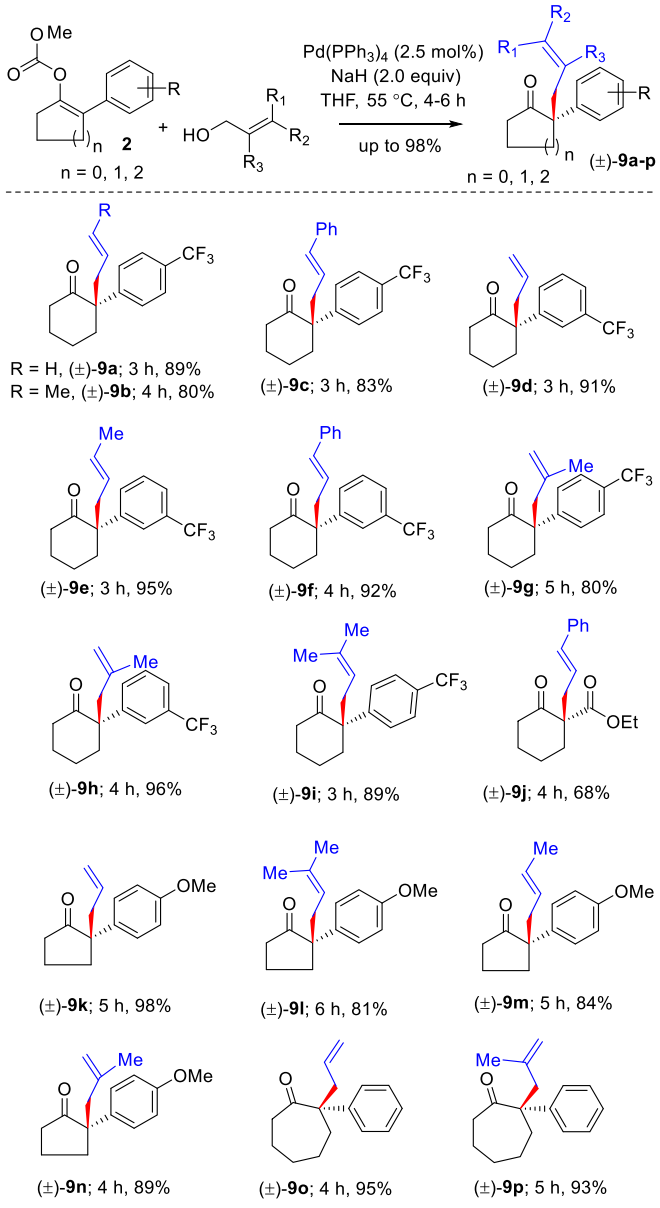


[a]reactions were carried out using 0.20 mmol (1 equivalent) of **2** with 0.30 mmol (1.5 equivalents) of allylalcohol **3** and 0.40 mmol (2 equivalents) of NaH in 3.0 mL THF at 55 °C in the presence of 2.5 mol% of $Pd(PPh_3)_4$ under argon condition. [b]isolated yields after column purification.

Scheme 5. Substrates scope of Pd(0)-catalyzed DaA using esters.[a,b].

Construction of molecules with vicinal tertiary-quaternary centers from a ketone enolates has recently garnered significant attention from synthetic community. Therefore, we have extended our DaA reaction with substituted allylalcohols that can afford cyclohexanones **11a-b** with vicinal tertiary-quaternary centers in excellent yields. Although the diastereoselectivities are poor to moderate, one can realize such structural scaffolds utilizing our methodology (Scheme 10).

Further, we carried out a control experiment with **2f** in the presence of methallylalcohol and allylacetate (Scheme 11). In this regard, our observation of formation of **7f** as major product as compared to **7h** (**7f**:**7h** = 1.8:1) clearly indicate that the sterics play crucial role in our DaA (Scheme 11). In this reaction allylation afforded the major product **7f** over methallylation product **7h**. The methallylation goes through the *in-situ* preparation of methallyl carbonate. This was further confirmed by a control experiment with **2f** in the presence of allylalcohol and methallylacetate, where 1.7:1 of product distribution was observed between **7f** and **7h**

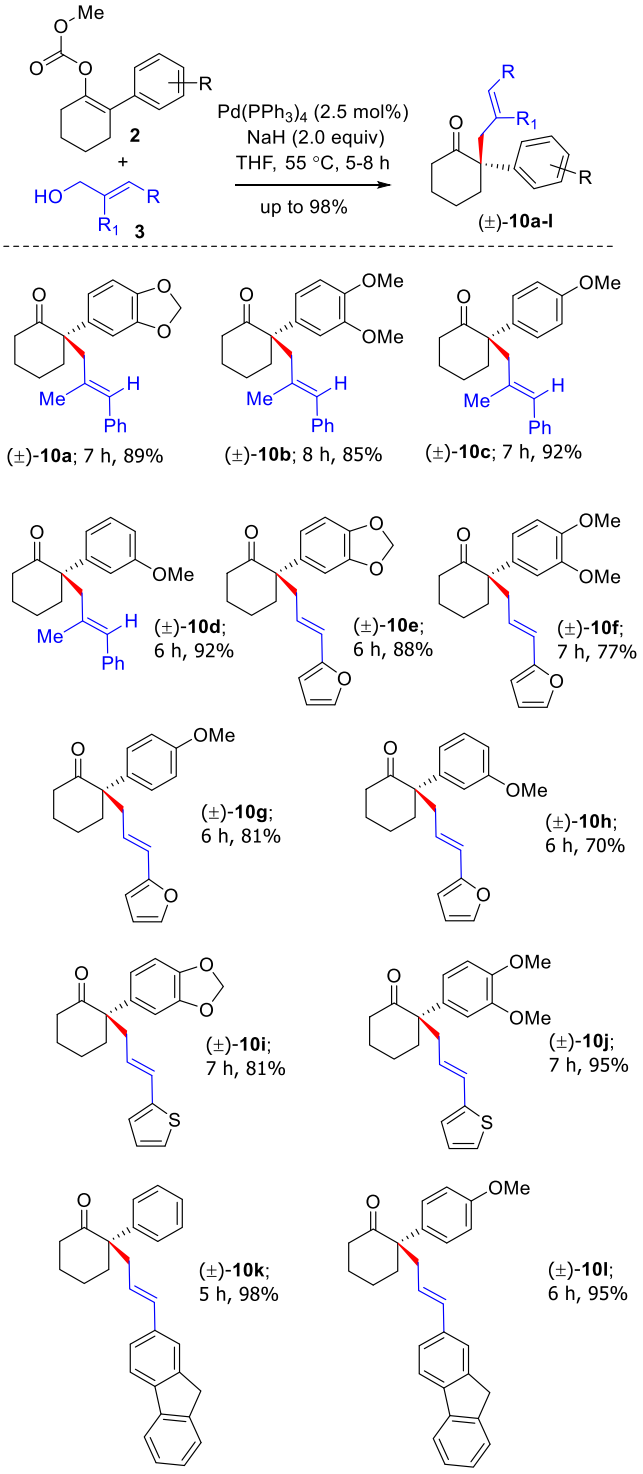


[a]reactions were carried out using 0.20 mmol (1 equivalent) of **2** with 0.30 mmol (1.5 equivalents) of allylalcohol and 0.40 mmol (2 equivalents) of NaH in 3.0 mL THF at 55 °C in the presence of 2.5 mol% of $Pd(PPh_3)_4$ under argon condition. [b]isolated yields after column purification.

Scheme 6. Substrates scope of Pd(0)-catalyzed DaA using esters.

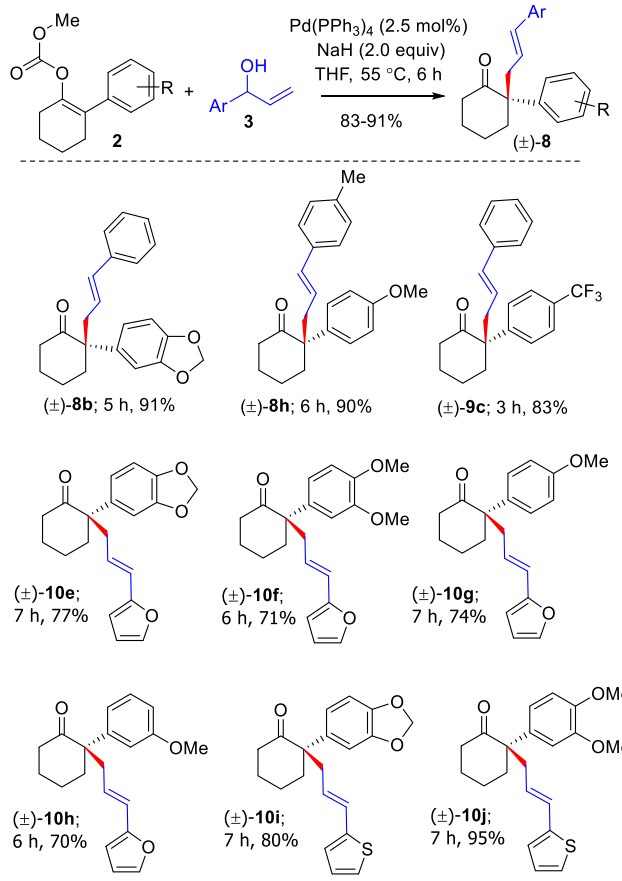
(Scheme 11). In the latter case, the allylation goes through the in-situ preparation of allyl carbonate (Scheme 11). These cross-over experiments also suggest that the allyl acetate and allyl carbonate [or methallyl acetate and methallyl carbonate] have similar type of reactivities under Pd(0)-catalyzed DaA methodology.

Next, recent reports on direct benzylation of enolates with benzyl alcohols [14b] prompted us to explore our deacylative methodology even further. Pd(0)-Catalyzed benzylation has become an active area of research in the construction of carbon–carbon and carbon–heteroatom bond forming reactions [15]. The catalytic cycle for benzylations invoke a cationic η [3]-benzyl-palladium intermediate which is less common since



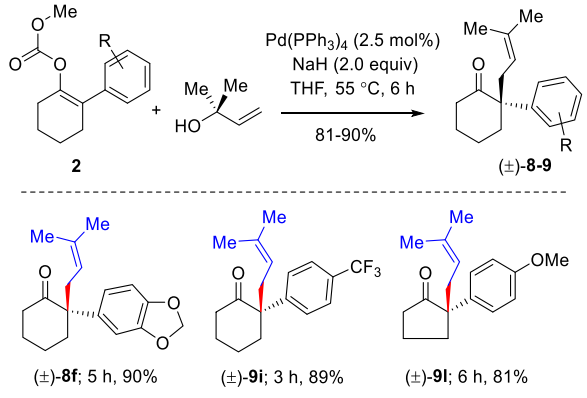
[a]reactions were carried out using 0.20 mmol (1 equivalent) of **2** with 0.30 mmol (1.5 equivalents) of allylalcohol and 0.40 mmol (2 equivalents) of NaH in 3.0 mL THF at 55 °C in the presence of 2.5 mol% of $Pd(PPh_3)_4$ under argon condition. [b]isolated yields after column purification.

Scheme 7. Substrates scope of Pd(0)-catalyzed DaA using substituted allyl alcohol.



[a]reactions were carried out using 0.20 mmol (1 equivalent) of **2** with 0.30 mmol (1.5 equivalents) of allylalcohol and 0.40 mmol (2 equivalents) of NaH in 3.0 mL THF at 55 °C in the presence of 2.5 mol% of $Pd(PPh_3)_4$ under argon condition. [b]isolated yields after column purification.

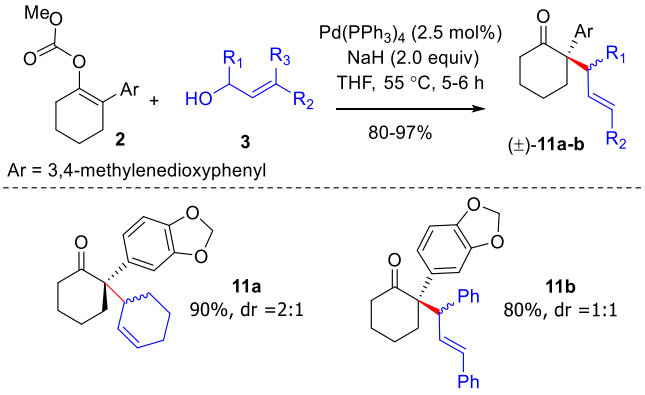
Scheme 8. Substrates scope of Pd(0)-catalyzed DaA.



[a]reactions were carried out using 0.20 mmol (1 equivalent) of **2** with 0.30 mmol (1.5 equivalents) of allylalcohol and 0.40 mmol (2 equivalents) of NaH in 3.0 mL THF at 55 °C in the presence of 2.5 mol% of $Pd(PPh_3)_4$ under argon condition. [b]isolated yields after column purification.

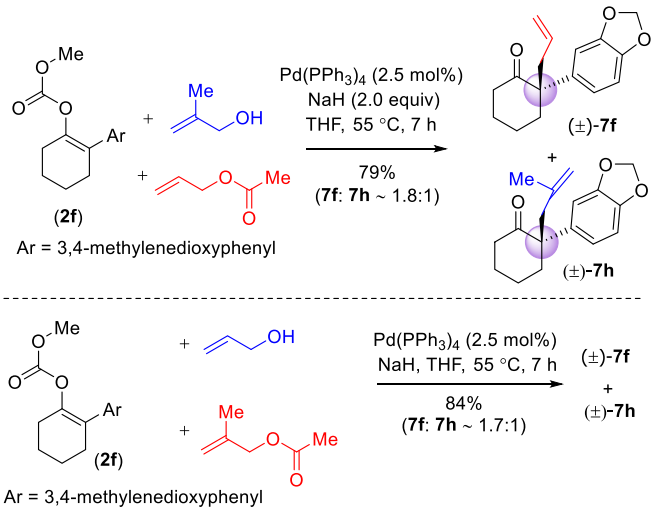
Scheme 9. Substrates scope of Pd(0)-catalyzed DaA.

aromaticity is disrupted [16]. Thus, further scope of our deacylative methodology via a direct deacylative benzylation (DaB) of



[a]reactions were carried out using 0.20 mmol (1 equivalent) of **2** with 0.30 mmol (1.5 equivalents) of allylalcohol **3** and 0.40 mmol (2 equivalents) of NaH in 3.0 mL THF at 55 °C in the presence of 2.5 mol% of $Pd(PPh_3)_4$ under argon condition. [b]isolated yields after column purification.

Scheme 10. Substrates scope of Pd(0)-catalyzed DaA.

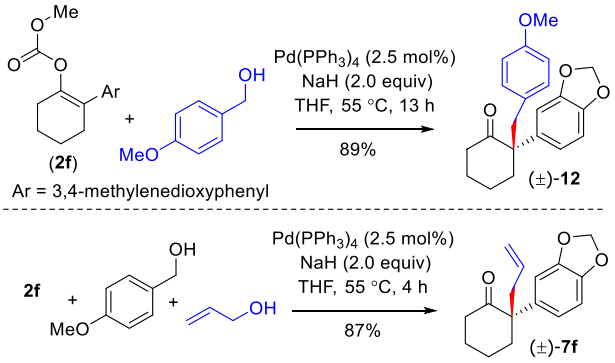


Scheme 11. Intermolecular nature of Pd(0)-catalyzed DaA.

enolcarbonates of 2-arylcyclohexanones was undertaken (Scheme 11). This was realized by taking **2f** as pronucleophile affording **12** in 89% yields upon subsequent reaction with proelectrophiles *p*-methoxybenzyl alcohol.

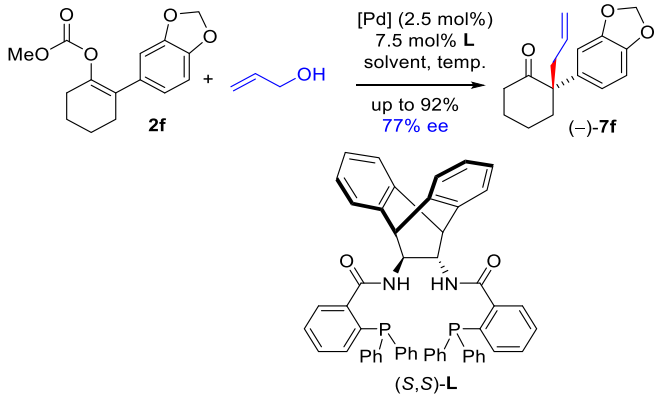
It was observed that deacylative benzylation (DaB) is sluggish requiring longer reaction time for completion as compared to DaA reactions (Scheme 12). The reactivity difference between DaA and DaB also clearly suggested the selective nature of allylation reaction compared to benzylation. This is clearly apparent from the deacylative alkylation of **2f** with 1:1 mixture of allylacohol and *p*-methoxybenzyl alcohol affording **7f** in 87% yields as sole product (Scheme 12).

Next, we turned our attention of the development of catalytic enantioselective version of our deacylative method. For this purpose, we choose enolcarbonate **2f** as pronucleophile and allylalcohol as proelectrophile in the presence of 2.5 mol% of Pd(0) and 7.5 mol% of enantioenriched phosphine based ligands in various solvents and the results are summarized in Scheme 13. Following exhaustive optimization, it was observed that a maximum of 77% ee



[a]reactions were carried out using 0.20 mmol (1 equivalent) of **2f** with 0.30 mmol (1.5 equivalents) of *p*-methoxybenylalcohol (PMBOH) and 0.40 mmol (2 equivalents) of NaH in 3.0 mL THF at 55 °C in the presence of 2.5 mol% of $Pd(PPh_3)_4$ under argon condition. [b]isolated yields after column purification.

Scheme 12. Pd(0)-Catalyzed deacylative benzylation (DaB).



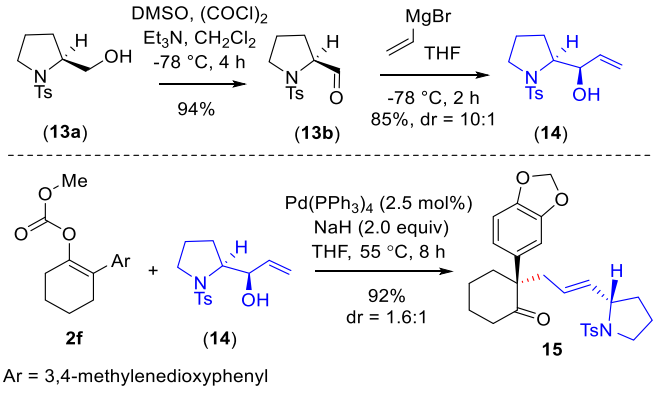
Scheme 13. Optimization of Pd(0)-catalyzed deacylative allylation of enolcarbonate **2f**.

was obtained for compound **7f** when sterically rigid anthracenyl Trost ligand (*S,S*)-**L** was used for deacylative allylation in methyl *tert*-butyl ether [14a].

Later, with a successful studies of Pd(0)-catalyzed deacylative reactions with enolcarbonates of 2-arylcyclohexanones [17], our effort was thereafter to show the application of our methodology. Towards this, we anticipated that these alkaloids could be constructed from enantioenriched intermediates **15** (Scheme 14) formed *via* deacylative allylation using enatioenriched secondary allyl alcohol **14** (prepared in ~10:1 dr from *N*-Ts L-prolinol **13a** via *N*-Ts L-prolinaldehyde **13b**) [18a]. Delightfully, DaA of substrates **2f** with (*R*)-1-[(*S*)-1-tosylpyrrolidin-2-yl]prop-2-en-1-ol (**14**) afforded **15** in 92% yields with moderate dr of ~1.6: 1 (Scheme 14).

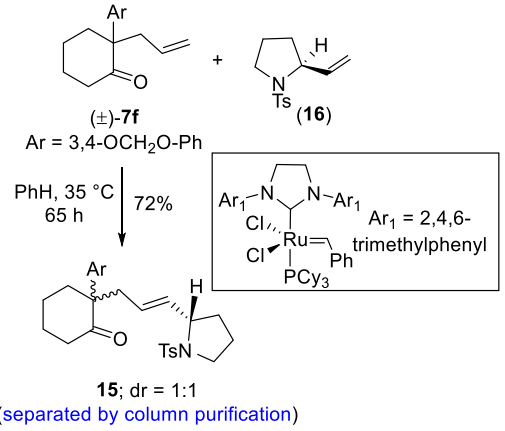
Later, in search of flexible route to the total syntheses of either enantiomers of *Amaryllidaceae* alkaloids, (−)-crinane (**4a**) and (+)-crinane (*ent*-**1a**), we explored cross-metathesis of (±)-**7f** with enantioenriched 2-vinyl *N*-tosylpyrrolidine **16** to afford mixture of diasteromers in 72% yields with 1:1 dr (Scheme 15). Although, a 1:1 ratio of diastereomers of **15** were obtained, we are delighted to see that compounds (*R, S*)-**15** and (*S, S*)-**15** can be separated via column chromatography for further utilization in the total synthesis.

With enantioenriched diastereomers of **15** in hand, total syntheses of either enantiomers of *Amaryllidaceae alkaloids*, (+)- (*ent*-**4a**) and (−)-crinane (**4a**) were accomplished in 4 steps (Scheme 16).



[a]reactions were carried out using 0.20 mmol (1 equivalent) of **2f** with 0.30 mmol (1.5 equivalents) of alcohol **14** and 0.40 mmol (2 equivalents) of NaH in 3.0 mL THF at 55 °C in the presence of 2.5 mol% of $Pd(PPh_3)_4$ under argon condition. [b]isolated yields after column purification.

Scheme 14. Substrates scope of Pd(0)-catalyzed DaA using enantioenriched carbinol **14**.

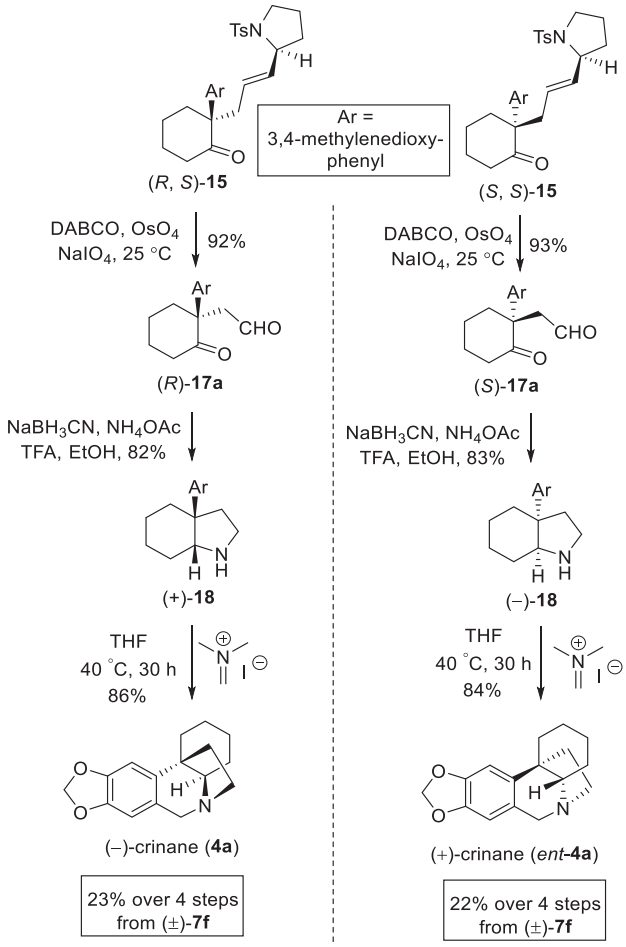


Scheme 15. Cross metathesis of 2-aryl-2′-allyl cyclohexanone (**7f**) with *N*-tosylpyrrolidine **16**.

A one-pot DABCO mediated dihydroxylation with osmium tetroxide followed by oxidative cleavage using sodium metaperiodate of **15** afforded γ-keto-aldehydes (*R*)-**17a** and (*S*)-**17a** in 91–93% yields. Later, upon reductive amination of **17a** with ammonium acetate, as per Maruoka's report [18b], afforded octahydro-1*H*-indole (+)-**18** and (−)-**18** in 82–83% yields. Finally, reactions with Eschenmoser's salt completed the total syntheses of (+)-crinane (*ent*-**4a**) and (−)-crinane (**4a**) (Scheme 16) [18b].

4. Conclusions

In summary, we have developed an effective protocol involving Pd(0)-catalyzed deacylative allylation (DaA) of enolcarbonates from cyclohexanones. The use of unfunctionalized allylalcohol as an allyl source makes this method attractive for the synthesis of pharmaceutically active building blocks. Importantly, the strategy can be extended to using benzyl alcohol as proelectrophile for deacylative benzylation (DaB). Control experiments entailed the intermolecular nature of decarboxylative processes. The methodology is ultimately employed in the concise total syntheses of *Amaryllidaceae* alkaloids,



Scheme 16. Total syntheses of (−)-crinane (**4a**) and (+)-crinane (*ent*-**4a**).

(+)-crinane (*ent*-4a) and (−)-crinane (4a) in few steps. Further utilization of this process in the synthesis of complex natural products is under active investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.131928.

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