

Published in final edited form as:

*Org Lett.* 2012 November 16; 14(22): 5736–5739. doi:10.1021/ol302743k.

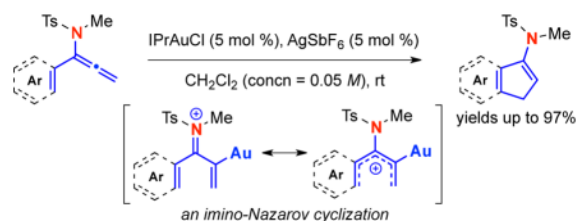
## $\alpha$ -Aryl-Substituted Allenamides in an Imino-Nazarov Cyclization Cascade Catalyzed by Au(I)

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### Abstract



An imino-Nazarov cyclization using  $\alpha$ -aryl-substituted allenamides is described. This gold(I)-catalyzed cascade is efficient and regioselective in constructing a diverse array of synthetically useful aromatic-ring fused cyclopentenamides. The success in this transformation represents a solution to the challenge in establishing an imino-Nazarov cyclization process.

The Nazarov cyclization<sup>1</sup> has captured an immense amount of interest from the synthetic community in the last three decades.<sup>2,3</sup> This classical pericyclic process proceeds through conrotatory  $4\pi$ -electron electrocyclic ring-closure of a pentadienyl cation via activation of divinyl ketone **1** or its equivalent, leading to a key oxyallyl cation **2** that can afford cyclopentenone **3** substituted cyclopentanones **4** through trapping [Scheme 1]. Despite a diverse array of innovative structural designs that has been developed,<sup>4–6</sup> one aspect that has received very little attention is an imino version of this cascade with the sole exceptions of Tius' seminal work on lithiated imino-Nazarov,<sup>7a</sup> and recently, with enamine-iminium ions.<sup>7b,c</sup> There are examples in which stabilization of the pentadienyl cation is assisted by the presence of an amino or amide substituent, albeit not a formal imino-Nazarov cyclization. Cha's<sup>8</sup> earlier work on cephalotaxine synthesis, along with reports by Occhiato/Prandi,<sup>9</sup> Frontier,<sup>10</sup> Flynn<sup>11</sup> employing ynamides, and recently, by West<sup>12</sup> in a clever usage of allenamides represent such elegant cases. The challenge in developing a successful imino-Nazarov cyclization is to overcome the propensity of 2-amino-allyl cation **6** to ring-open in favor of amino-pentadienyl cation **5**, which receives a greater stabilization from the amino nitrogen atom.<sup>13</sup> We wish to communicate here our solution to this challenge through gold(I)-activation of allenamides.

Our long standing interest in allenamides,<sup>14–16</sup> and in particular, their electrophilic activations,<sup>17,18</sup> led us to explore their potential use in this underdeveloped aspect of the

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Supporting Information Available: Experimental procedures as well as NMR spectra, X-ray structural files, and characterizations are available for all new compounds and free of charge via Internet <http://pubs.acs.org>.

Nazarov cyclization. As shown in Scheme 2,  $\alpha$ -vinyl or  $\alpha$ -aryl allenamides **7** could be employed in an imino-Nazarov cyclization cascade through Brønsted acid activation.<sup>19</sup> This electrophilic activation could give amido-pentadienyl cation **8**, which would undergo an electrocyclization to afford 2-amido-allyl cation **9**. It is noteworthy that a distinct advantage in achieving a successful imino-Nazarov cyclization is the synthetically useful enamide functionality<sup>20</sup> in the end product **10**.

We reasoned that unlike amino-pentadienyl cation **5**, the electrocyclization of **7** could be more favored given the reduced ability of an *N*-acyl nitrogen atom to stabilize cations relative to an amino group. Such rationalization would find prevalent support in related chemistry of vinyl *N*-acyl iminium ions<sup>21</sup> and *aza*-Prins cyclizations.<sup>22</sup> However, after many attempts, the Brønsted acid activation failed because we were unable to control and overtake the hydrolysis pathway that led to amido ketones **11** through a facile trapping of the initial enone.

Inspired by recent gold-catalysis<sup>23</sup> particularly in the area of Nazarov type process<sup>24</sup> with the report by Zhang,<sup>19d</sup> we turned our attention to gold catalysts. As shown in Table 1, trivalent gold catalyst was first investigated. Reactions of **12a** proceeded smoothly in the presence of catalytic amount of AuCl<sub>3</sub> or cationic AuCl<sub>3</sub>/AgSbF<sub>6</sub> (entries 1 and 2), but gave an inseparable mixture of dimers **14** and **15**<sup>25</sup> with no desired Nazarov cyclization product **13a**. Attempts to suppress the dimerization by lowering the concentration (entry 3) or addition of 4 Å MS (entry 4) proved to be fruitless.

Nevertheless, we were encouraged by dimers **14** and **15** because they imply that the desired imino-Nazarov reaction had taken place possibly post-dimerization through the intermediacy of **14'** [addition of **12a** to activated-**12a**]. Gratifyingly with AuCl(PPh<sub>3</sub>)/AgSbF<sub>6</sub>, **13a** was obtained for the first time in 50% yield along with **14/15** mixture in 24% yield. Further optimizations revealed that the best yield was reached when using IPrAuCl/AgSbF<sub>6</sub>, leading to **13a** in 97% yield (entry 8) with JohnphosAuCl/AgSbF<sub>6</sub> affording **13a** in 91% yield. Remarkably, neutral IPrAuCl itself turned out to be completely inactive (entry 9), while AgSbF<sub>6</sub> alone gave **14** and **15**, albeit sluggishly (entry 10). Lastly, Pt catalysts were also examined and gave very poor results in this process (entries 11 and 12).

Having established the optimum catalytic system, the scope of the imino-Nazarov process was explored [Table 2]. Notably, for allenamides equipped with more bulky substituents on the nitrogen (*n*-Bu in **12b** and Bn in **12c**), reactions were slower, although yields were still excellent (entries 1 and 2). The structure of **13b** was unambiguously assigned through its X-ray structure [left in Figure 1]. The cyclization of **12d**, bearing a 4-methoxybenzenesulfonyl [MBS] substituent, also worked but at elevated temperature. Lastly, allenamides with different substituents on the aryl ring (entries 4–9) also proved to be quite effective overall with exceptions of 2-MeO and 4-Br substituents (entries 5 and 9). In particular, while the reaction of **12f** is very tardy, the cyclization of **12j** was completely attenuated. We are not clear of the precise rationale at this point. However, it is noteworthy that the high level of regioselectivity found in cases of **12e** and **12k** was remarkable. While these two cyclizations appear to favor the less hindered C6-position with no detectable cyclization at C2-position, this preference is likely due to direct donation from the C3-OR group.

To further investigate the regioselectivity issue, allenamides **16** and **19** were subjected to the cyclization condition [Scheme 3]. For allenamide **16** with an  $\alpha$ -(2-naphthyl) substituent, cyclization took place selectively at C1 [see **17'**], affording **17** exclusively in 97% yield. This regioselectivity is also likely an electronic preference given that cyclization at C1 would involve the cyclohexadiene portion of the naphthyl ring, thereby leading to a greater cation stabilization: Benzylic stabilization in **17'** versus pseudo-benzylic stabilization in **18'**

through cyclization from C3. On the other hand, for allenamide **19** with an  $\alpha$ -(1-naphthyl) group, a competing  $6\pi$ -electron cyclization of the reaction intermediate [see **21'**] could deliver 1*H*-phenalene **21**. However, the reaction exclusively proceeded through the imino-Nazarov cyclization pathway via **20'**, leading to **20** in excellent yield. The structure of **20** was also confirmed by its single crystal X-ray structure [Figure 1]. It is noteworthy that **17** and **20** are structurally almost identical with the difference residing in the position for the respective enamide motif.

Intrigued by this competition, another reaction with potential competing imino-Nazarov's  $4\pi$ -electron and  $6\pi$ -electron electrocyclization was examined using allenamide **22** [Scheme 4]. The reaction of **22** led to **25** and **26** as the only discernable products with latter likely coming from hydrolysis of the initial Nazarov cyclization product **25**. This study suggests that while the cationic imino-Nazarov intermediate could exist in two equilibrating conformations **23** and **24** differing only at the 's'-marked C–C bond [or being *trans*- and *cis*-1-aza-dienes, respectively, shown in green],  $6\pi$ -electron electrocyclization of 3-aza-triene **24**<sup>26,27</sup> was also not competitive in this case.

Lastly, while cyclopentenamides are synthetically useful, we recognized that our imino-Nazarov cyclization could provide a concise approach to indole-fused cyclopentenamides [or cyclopenta[*b*]indoles],<sup>24a</sup> thereby representing an opportunity to develop new strategy for natural product synthesis.<sup>28</sup> Consequently, as shown in Scheme 5, under the optimized conditions, cyclizations of  $\alpha$ -indolyl-substituted allenamides **28a** and **28b** proceeded smoothly to afford indole-fused cyclopentenamides **29a** and **29b**, respectively, in good yields.

We have showcased here an imino-Nazarov cyclization using  $\alpha$ -aryl-substituted allenamides. This Au(I)-catalyzed cascade represents a successful solution to overcome the challenge in designing an imino-Nazarov cyclization cascade. It is a highly efficient and regioselective transformation in constructing a diverse array of aromatic-ring fused cyclopentenamides. Further mechanistic studies and applications of this cyclization process in total synthesis are currently underway.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

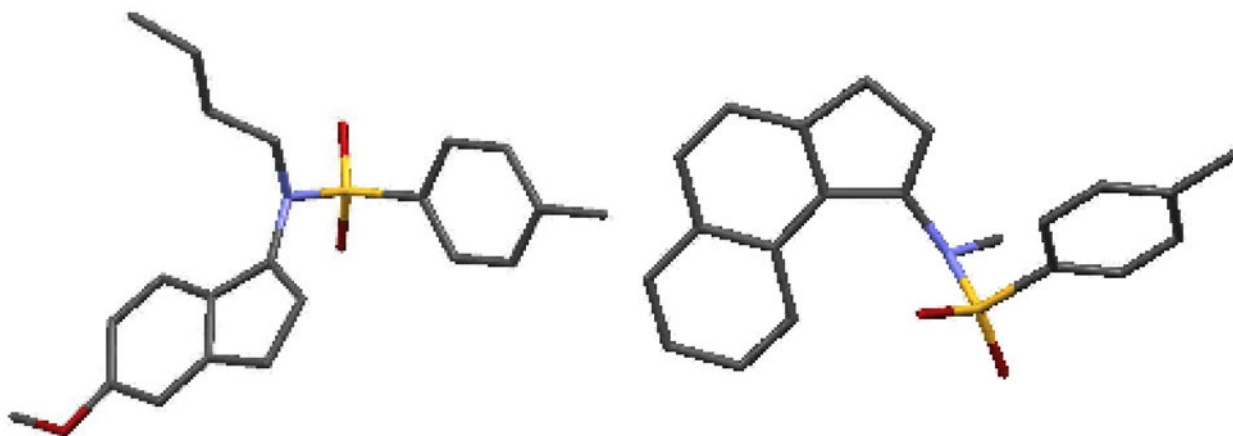
We thank NIH [GM066055] for funding. We thank Dr. Vic Young of University of Minnesota for providing X-ray structural analysis.

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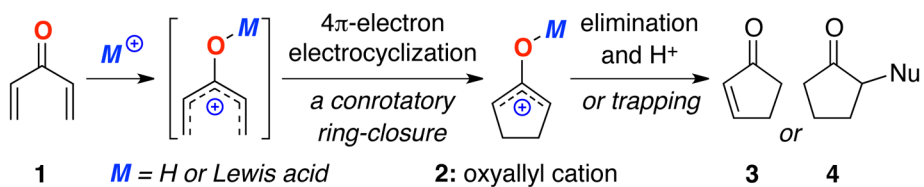
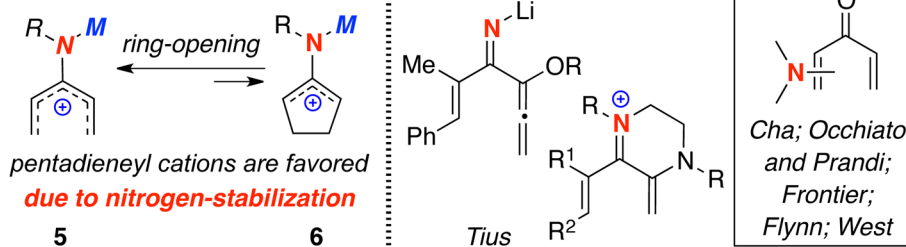
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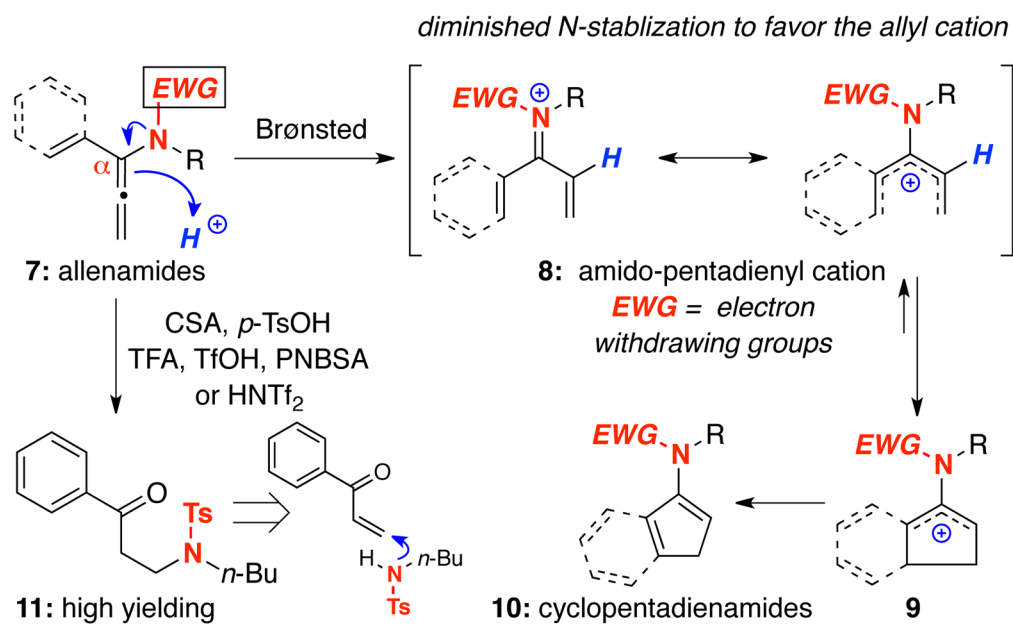


**Figure 1.**  
X-Ray Structures of **13b** and **20**.

## Nazarov Cyclizations: Cyclopentenone Synthesis

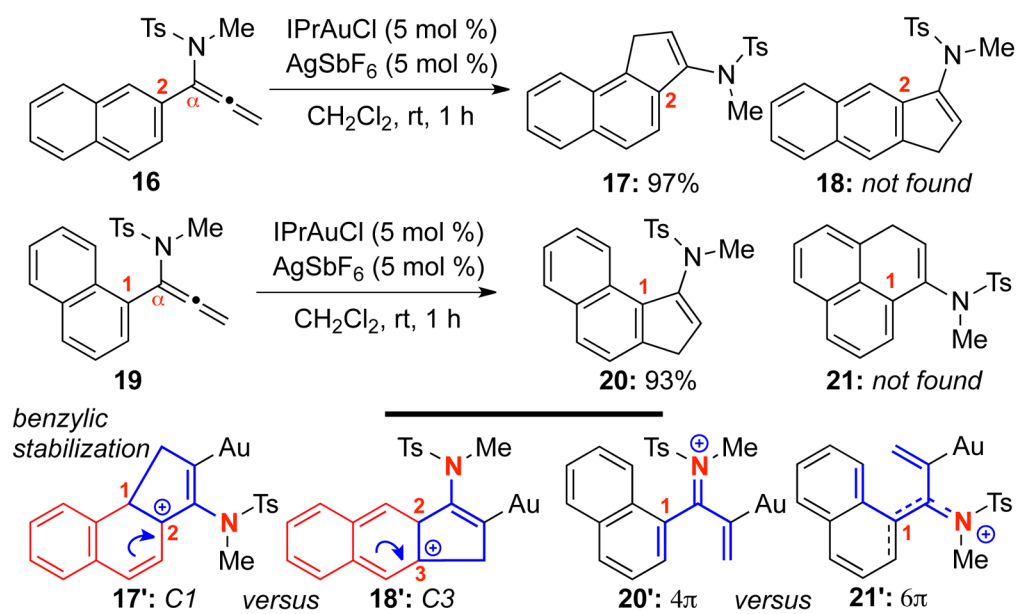
An Imino-Nazarov: A challenge key precedents

**Scheme 1.**  
Nazarov Cyclizations: Challenge in an Imino-Version.

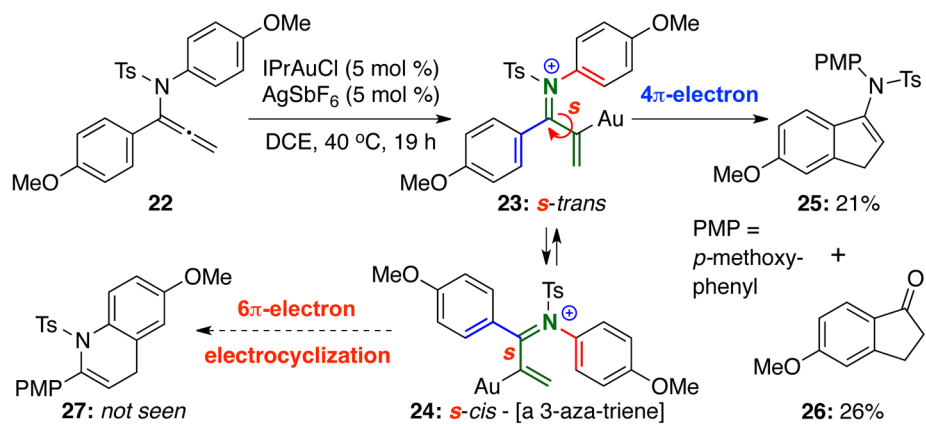


**Scheme 2.**  
 An Approach to Imino-Nazarov Cyclization.

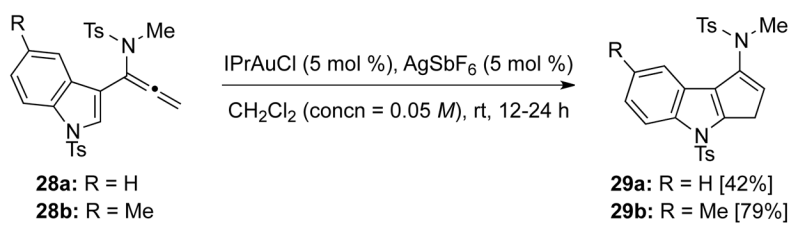




**Scheme 3.**  
Regioselective Imino-Nazarov Cyclizations.



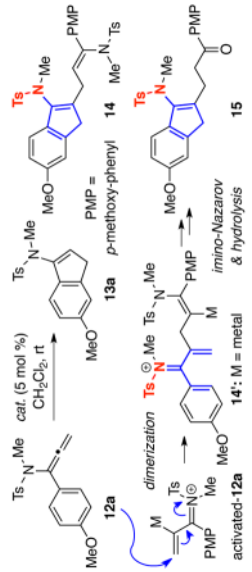
**Scheme 4.**  
 $4\pi$ - Versus  $6\pi$ -Electron Electrocyclization.



**Scheme 5.**  
Synthesis of Indole-Fused Cyclopentenamides.

Table 1

Screening for a Suitable Metal Catalyst.



| entry <sup>a</sup> | catalyst   | time (h) | conversion (%) <sup>b</sup> | 13a (%) <sup>c</sup> | 14 + 15 <sup>d</sup> (%) <sup>e</sup> |
|--------------------|--|----------|-----------------------------|----------------------|---------------------------------------|
| 1                  | AuCl <sub>3</sub>                                  | 30       | >95                         | –                    | 55                                    |
| 2                  | AuCl <sub>3</sub> /AgSbF <sub>6</sub>              | 1        | >95                         | –                    | 45                                    |
| 3                  | AuCl <sub>3</sub> /AgSbF <sub>6</sub> <sup>e</sup> | 22       | 48                          | –                    | 36                                    |
| 4                  | AuCl <sub>3</sub> /AgSbF <sub>6</sub> <sup>f</sup> | 40       | 55 <sup>g</sup>             | –                    | 36                                    |
| 5                  | AuCl/AgSbF <sub>6</sub>                            | 5        | >95                         | –                    | 48                                    |
| 6                  | AuCl(PPh <sub>3</sub> )/AgSbF <sub>6</sub>         | 60       | 75 <sup>g</sup>             | 50 <sup>h</sup>      | 24                                    |
| 7                  | JohaphosAuCl/AgSbF <sub>6</sub>                    | 5        | >95                         | 91                   | –                                     |
| 8                  | <b>IPrAuCl/AgSbF<sub>6</sub></b>                   | <b>1</b> | <b>&gt;95</b>               | <b>97</b>            | –                                     |
| 9                  | IPrAuCl  | 21       | <5                          | –                    | –                                     |
| 10                 | AgSbF <sub>6</sub> <sup>i</sup>                    | 20       | 64                          | –                    | 24                                    |
| 11                 | PtCl <sub>2</sub>                                  | 24       | <5                          | –                    | –                                     |
| 12                 | PtCl <sub>4</sub> <sup>j</sup>                     | 12       | >95                         | –                    | 82 <sup>j</sup>                       |

<sup>a</sup>Unless noted, all reactions were carried out at 0.1 mmol scale in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> (concn = 0.05 M) at room temperature with the addition of 5 mol % catalyst.<sup>b</sup>Conversion determined by <sup>1</sup>H NMR.<sup>c</sup>Isolated yields.<sup>d</sup>**14** and **15** could not be separated by column chromatography.<sup>e</sup>20 mL CH<sub>2</sub>Cl<sub>2</sub> was used (concn = 0.005 M).

*f* 35 mg 4 Å MS was added.

*g* Based on recovered **12a**.

*h* Inseparable mixture with **12a**.

*i* 10 mol % of catalyst was used.

*j* An inseparable mixture of **14**, **15** and unidentified products.

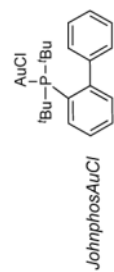
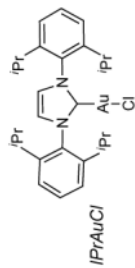
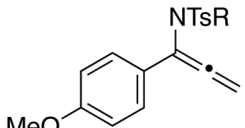
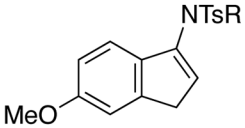
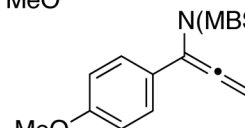
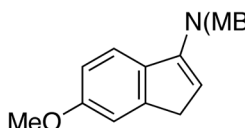
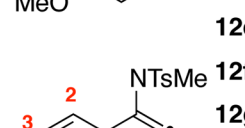
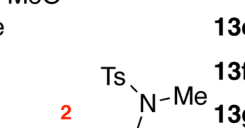
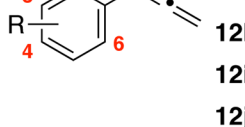
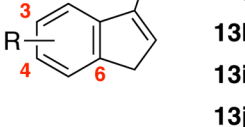
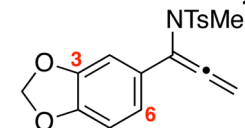
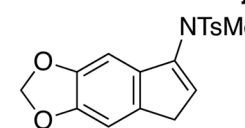
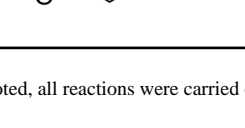
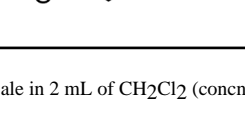


Table 2

An Au(I)-Catalyzed Imino-Nazarov Cyclization.

| entry <sup>a</sup> | allenamide   | product  | time (h)        | yield (%) <sup>b</sup> |
|--------------------|--|--|-----------------|------------------------|
| 1                  |  <b>12b</b> : R = Bu    |  <b>13b</b> : R = Bu    | 36              | 94                     |
| 2                  |  <b>12c</b> : R = Bn    |  <b>13c</b> : R = Bn    | 30              | 90                     |
| 3                  |  <b>12d</b>             |  <b>13d</b>             | 12 <sup>c</sup> | 81                     |
| 4                  | <b>12e</b> : R = 3-OMe   | <b>13e</b> : R = 3-OMe   | 1               | 97                     |
| 5                  | <b>12f</b> : R = 2-OMe   | <b>13f</b> : R = 2-OMe   | 29              | 16                     |
| 6                  |  <b>12g</b> : R = 4-Me  |  <b>13g</b> : R = 4-Me  | 1               | 92                     |
| 7                  |  <b>12h</b> : R = 2-Me |  <b>13h</b> : R = 2-Me | 24              | 90                     |
| 8                  | <b>12i</b> : R = H   | <b>13i</b> : R = H   | 1               | 93                     |
| 9                  | <b>12j</b> : R = 4-Br  | <b>13j</b> : R = 4-Br  | 12 <sup>c</sup> | - <sup>d</sup>         |
| 10                 |  <b>12k</b>           |  <b>13k</b>           | 1               | 91                     |

<sup>a</sup>Unless noted, all reactions were carried out at 0.1 mmol scale in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> (concn = 0.05 M) at rt with the addition of 5 mol % catalyst.<sup>b</sup>Isolated yields.<sup>c</sup>The reaction was run at 50 °C in DCE.<sup>d</sup>No reaction.