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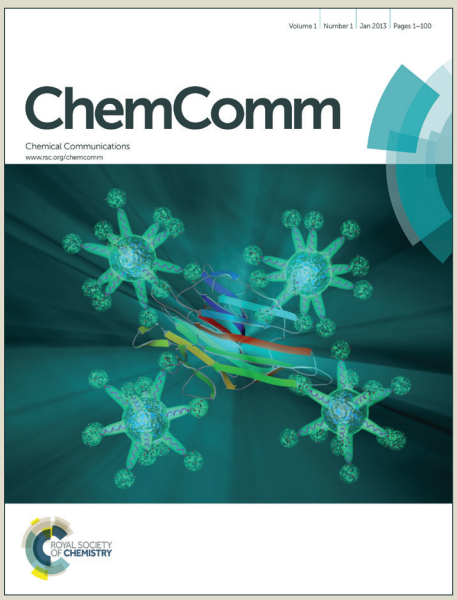

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Propargylic Cation-Induced Intermolecular Electrophilic Addition / Semipinacol Rearrangement

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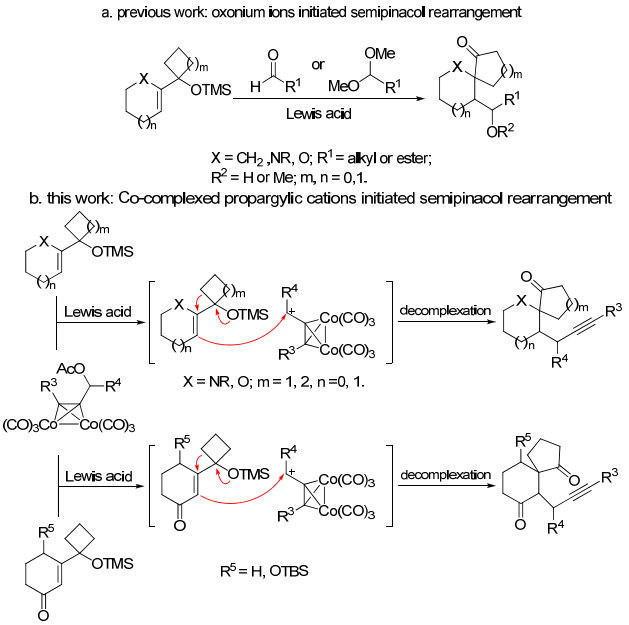
A novel propargylic electrophile-induced tandem intermolecular addition/semipinacol rearrangement was developed efficiently under mild condition. Various allylic silylether substrates as well as Co-complexed propargylic species were well applicable to this protocol and gave a series of synthetically useful β-propargyl spirocyclic ketones in moderate to good yields. Its synthetic application was also demonstrated by an efficient construction of the key tricyclic moiety of daphlongamine E.

As one of the powerful methods for C-C bond formation and reorganization, the electrophilic addition / semipinacol rearrangement of allylic alcohol has been extensively utilized in organic synthesis.[1] Accordingly, lots of electrophiles have been explored for achieving different synthetic goals via this rearrangement, but most of them belong to the non-carbon species, [1b-d] such as proton, halogens and some other heteroatom-containing species. In fact, carbon electrophile-initiated rearrangements could generate more complex and diverse carbon skeleton of resulted molecules if the electrophilic addition step can be realized, and thus would play a much more important role in the synthesis of complex architectures. However, it was not until 1969 that an intramolecular acetal-participated semipinacol rearrangement (also known as Prins-pinacol reaction) was explored.[2a-b] Later this reaction was further extended and used as a key step in a number of synthetic approaches.[1a,2] In contrast, the intermolecular carbon electrophile-initiated rearrangements is much underexplored in comparison with the intramolecular version, despite of its more powerful and versatile utilities than the latter in view of generating the complexity and diversity of carbon framework.[3] In 2007, Cha's group reported such a hemiacetal-initiated intermolecular reaction,[3a] which was well used in the total synthesis of cyathin A_3 and B_2.[3b] Later in 2010, Aube's group further extended this method to accomplish the synthesis of lepadiformines.[3c] Recently, our group also has reported that an activated aldehyde carbonyl group of ethyl glyoxalate ester could trigger such a reaction with the dihydropyran-type allylic silylethers under the catalysis of Cu (II), providing various tricyclic systems in high efficiency.[3e] In spite of these pioneering works above, the carbon electrophiles used in these intermolecular reactions are only confined to the oxonium ions derived from acetal or aldehyde (Scheme 1a). Therefore, exploring the multi-functionalizable electrophile and further developing the synthetically more versatile intermolecular carbon-electrophile-initiated semipinacol rearrangements are still in high demand for organic synthesis.

The challenge for developing this kind of intermolecular reaction lies in not only finding a suitable condition to generate a carbenium ion electrophile active enough to take an intermolecular addition to the allylic alcohol or its silylether, but also requiring the substrate can survive from self-rearrangement under this condition. In this



Scheme 1 Design of Carbon Electrophile-Initiated Semipinacol Rearrangement

regard and in consideration of multi-reactivity and broad synthesis utility of the propargylic electrophiles generated from Nicholas Co-complexed propargylic species,[4,5] we envisioned that this *in situ* generated cation would be an electrophile active enough[6] to promote such an intermolecular reaction (Scheme 1b). Herein, we wish to present our preliminary research results on this tandem propargylization/ semipinocal reaction, which has provided a series of α-quaternary β-propargyl spirocyclic ketones and established a short route to the 5/6/7-tricyclic core of daphlongamine E.

As the spirocyclic units possessing oxa-, aza- and all-carbon-quaternary center were present in numerous bioactive natural products, for example capillosanane, vallesamidine and daphlongamine (Figure 1), the allylic silylether substrates with the

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corresponding dihydropyran,[3e,7a] dihydropyrrole[7b] and cycloalkenone[7c-d]

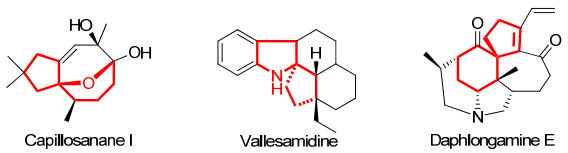
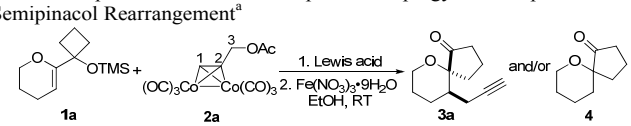


Figure 1 Natural Products Containing Various Spirocyclic Units

motifs, which can be readily prepared from commercial available materials in short steps, were used to examine our expected tandem reaction for constructing these units, respectively. Firstly, the dihydropyran-type allylic silylether **1a** and the Ac-protected Co-complexed propargylic species **2a** were used as the model substrates to screen the reaction condition (Table 1). Initially, several Lewis acids ($BF_3{\cdot}Et_2O$, $In(OTf)_3$, $EtAlCl_2$ and $AlCl_3$) were tested in DCM. Unfortunately, reactions always resulted in the sole undesired self-rearrangement product **4** in high yield, except using $AlCl_3$ (entry 1)[8] in which the desired product **3a** could be produced in low total yield of 32 % after subsequent demetalation of Co-complexed-product with $Fe(NO_3)_3{\cdot}9H_2O$. Considering that the competing self-rearrangement might take place prior to the formation of Co-complexed propargylic cation under Lewis acids promotion, we altered our experimental sequence.[9] Thus, the mixture of $AlCl_3$ and **2a** in DCM was firstly stirred at 0 ºC for 1.5 hour, then a solution of **1a** in DCM was added at -78 ºC. To our delight, this operation improved the yield to 43 % (entry 2). Then, more Lewis acids were screened to further optimize this reaction. In the presence of $In(OTf)_3$ or $SnBr_4$, only undesired ketone **4** was obtained (entries 3 and 4). Other Lewis acids, such as $EtAlCl_2$, $BF_3{\cdot}Et_2O$, and $TiCl_4$, were effective, but also could not avoid the formation of **4** completely (entries 5-7). Fortunately, a good overall yield 71 % was achieved when $SnCl_4$ was used, and only trace amount of **4** was obtained (entry 8). Furthermore, solvent effects were also observed in this tandem process. When toluene was used, the reaction yield decreased dramatically to 42 % (entry 9). While the use of some other solvents containing O- or N-atom (such as acetone, acetonitrile, THF, or DME) afforded much poorer results, leading to only **4** or no reaction.

Table 1. Optimization of Co-Complexed Propargyl Electrophile Initiated Semipinacol Rearrangement[a]



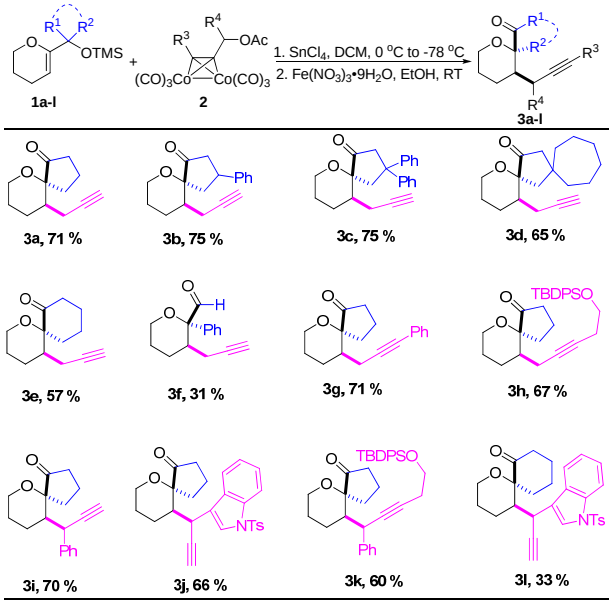
1a 2a 3a 4

Entry	Lewis acid	Solvent	Time (min)	Yield of **3a**[b]	Yield of **4**[b]
1[c]	$AlCl_3$	DCM	90	32 %	23 %
2[c]	$AlCl_3$	DCM	90	43 %	40 %
3[c]	$In(OTf)_3$	DCM	90	none	70 %
4	$SnBr_4$	DCM	45	none	42 %
5	$EtAlCl_2$	DCM	10	23 %	66 %
6	$BF_3{\cdot}Et_2O$	DCM	10	37 %	37 %
7	$TiCl_4$	DCM	10	58 %	25 %
8	$SnCl_4$	DCM	10	71 %	trace
9[c]	$SnCl_4$	toluene	90	42 %	trace

[a]Unless other specified, reaction operated in a general process.[9]
[b] Isolated yield. [c] Reaction performed at -78 ºC to RT.

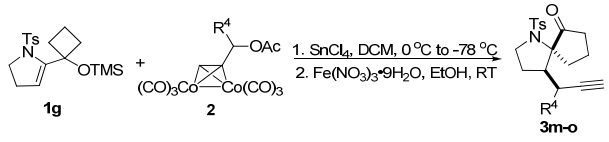
With the optimized condition (Table 1, entry 8, also see a detailed description[9]) in hand, we then probed the substrate scope of this transformation (Table 2). Firstly, a range of active dihydropyran-type allylic silylethers **1a-1f** was subjected to the standard reaction condition. Among them, **1b-1d** with aryl or alkyl substituent on the cyclobutane moiety went smoothly through the rearrangement initiated by un-substituted Co-complexed propargyl electrophile, giving corresponding spirocyclic ketones **3b-3d** in moderate to good yields (65-75 %). A bigger-sized cyclopentanol silylether **1e** could also be effective to this rearrangement, albeit in a slightly lower yield (57 %). And this protocol could be further extended to the secondary alcohol silylether **1f**, but the yield of **3f** formed was much lower (31 %), which might be due to partial decomposition of Co-complexed **3f** in the acidic environment. Next, various substituted Co-complexed proparyl electrophiles were examined under the same condition[9]. Fortunately, different substitutions at C1 and C3 of the Co-complexed propargyl electrophiles were well tolerated without significantly affecting the reaction efficiency, affording the corresponding products **3g-3l** in moderate to good yields in most cases. Additionally, the use of 3,3-dimethyl-substituted Co-complexed propargyl electrophile only resulted in the self-rearrangement product, probably because the *in situ* formed cation underwent a proton-elimination before electrophilic addition.[10] The *trans*-relative configurations between propargyl and migrating carbon in products **3a-3l** were deduced by X-ray diffraction of **3j** as a representative (Figure 2), which was consistent with the stereoselectivity of typical electrophilic addition/ semipinacol rearrangement.[11]

Table 2 Reaction Results of Dihydropyran-type Allylic Silylethers **1a-1l** with Co-Complexed Propargyl Electrophiles



Subsequently, the dihydropyrrole-type allylic silylether **1g** was examined and demonstrated to be well effective to several Co-complexed propargylic electrophiles under the standard condition[9], producing **3m**, **3n**, and **3o** in good yields (Table 3). The relative configuration of **3m-o** was deduced by X-ray diffraction of **3n** (Figure 2).

Table 3. Reaction Results of Dihydropyrrole-Type Allylic Silylether **1g** with Co-Complexed Propargyl Electrophiles



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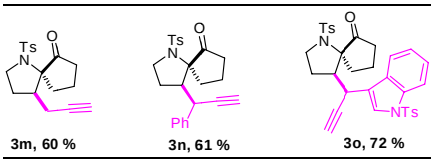
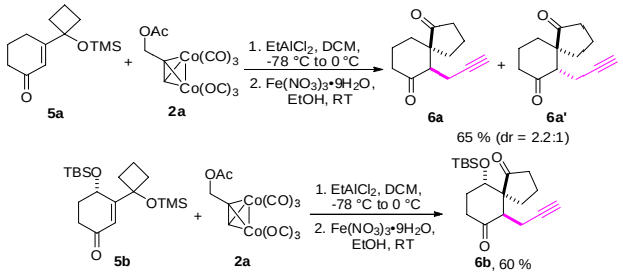


Having the results above, we then attempted to further extend the substrate scope to cyclohexenone-type allylic silylethers **5a** and **5b**. Frustratingly, when substrate **5a** was subjected to above reaction condition[9], only trace amount of desired product was observed. Considering that $SnCl_4$ might be ineffective for this type of substrates, we rescreened the Lewis acids and found that $EtAlCl_2$ was the best choice for promoting this reaction.[12] Consequently, separable spirocyclic diones **6a** and **6a'** were obtained in 65% overall yield with the diastereoselectivity 2.2:1. The configuration of the major diastereomer **6a** was also unambiguously confirmed by single crystal X-ray analysis (Figure 2). To our delight, **5b** could provide **6b** as a single diastereomer under the same condition, indicating that a bulky C4-substituent at the cyclohexenone ring could well control the diastereoselectivity of this reaction (Scheme 2).



Scheme 2 Reaction Results of Cyclohexenone-Type Allylic Silylethers **5a** and **5b** with Co-Complexed Propargyl Electrophiles

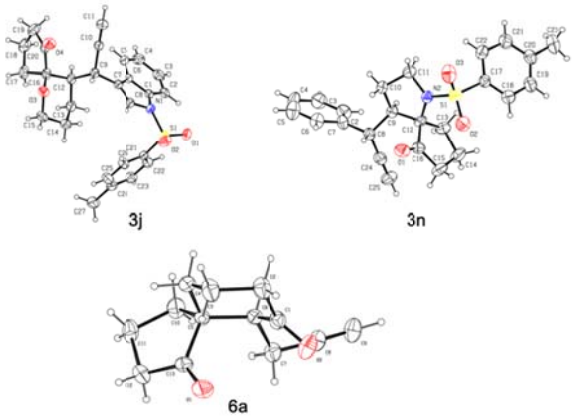
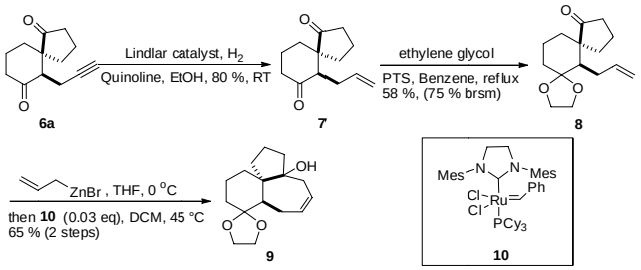


Figure 2 X-ray Crystal Structures of **3j**, **3n** and **6a**[13]

After realizing the tandem Nicholas/semipinacol reaction on various types of allylic silylethers, we then focused our attention on its synthetic applications. In connection with our research interest in the total synthesis of daphlongamine E,[7d,14,15] we proposed that the propargyl group introduced in compound **6a** could be used to construct concisely the key and challenging all-carbon 5/6/7- tricyclic motif **9** of this type of alkaloids. As shown in Scheme 3, controlled hydrogenation of the triple bond of **6a** with Lindlar Pd afforded olefin **7** in 80 % yield. Then, selective protection of the carbonyl group of the cyclohexenone moiety with ethylene glylcol[16] generated compound **8**. Introduction of another allyl group to **8** with allylzinc bromide[17], followed by a direct ring-close metathesis[18] with Grubbs II catalyst **10**, readily provided the 5/6/7- tricyclic structure **9** (65 % yield in two steps).



Scheme 3 Synthesis of Key 5/6/7-Tricyclic Unit of Daphlongamine E

In summary, we have successfully developed a Nicholas propargyl electrophile induced tandem intermolecular semipinacol rearrangement, which is well applicable to a wide range of allylic silylether substrates as well as Nicholas species, yielding a series of β-propargyl spirocyclic ketones in moderate to good yields. Its additional features include: good efficiency, high diastereoselectivity, mild condition and easy handling. We believe this methodology must find its good utility in synthesis of polycyclic natural products such as daphlongamine E.

Acknowledgements

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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8 Initial reaction condition: $AlCl_3$ (32 mg, 0.24 mmol) was added to the mixture of **1a** (50 mg, 0.22 mmol) and cobalt complex **2a** (crude, 93 mg, about 0.24 mmol) in DCM (3.6 mL) at -78 ºC.

9 Standard reaction condition: Cobalt complex **2a** (crude, 93 mg, about 0.24 mmol) was dissolved in DCM (1.6 mL), followed by the addtion of Lewis acid (1.1 equiv) at 0 ºC. The mixture was stirred at 0 ºC for 1.5 h and then the solution of **1a** (50 mg, 0.22 mmol) in DCM (2.0 mL) was added at -78 ºC.

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11 The detailed mechanism demonstrated in Supporting Information.

12 A mixture of cobalt complex **2a** (crude, 93 mg, about 0.24 mmol) and enone **5b** (81 mg, 0.22 mmol) was dissolved in DCM (3.6 mL) at -78 ºC, followed by addition of $EtAlCl_2$ (1.8 M in toluene, 0.16 mL, 0.29 mmol). The reaction system was immediately moved to ice bath and stirred for 6-7 h.

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