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Catalysis and Chemodivergence in the Interrupted, Formal Homo-Nazarov Cyclization Using Allylsilanes

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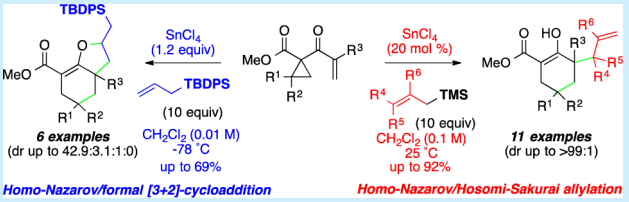
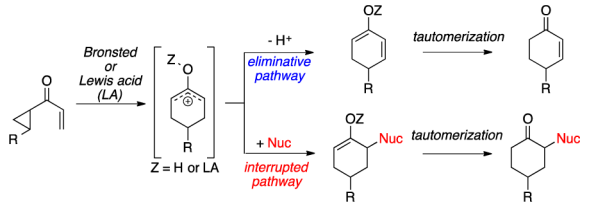
Supporting Information

ABSTRACT: A chemodivergent, Lewis acid catalyzed allylsilane interrupted formal homo-Nazarov cyclization is disclosed. With catalytic amounts of $SnCl_4$ and in the presence of allyltrimethylsilane, a formal Hosomi−Sakurai-type allylation of the oxyallyl cation intermediate is observed. A variety of functionalized donor−acceptor cyclopropanes and allylsilanes were shown to be amenable to the reaction transformation and the allyl products were formed in up to 92% yield. Under dilute reaction conditions with stoichiometric $SnCl_4$ and at reduced temperatures, an unusual formal [3 + 2]-cycloaddition between the allylsilane and the oxyallyl cation occurred to give hexahydrobenzofuran products in up to 69% yield.



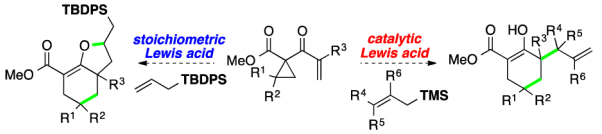
Oxyallyl cations represent a versatile class of electrophilic reactive intermediates in organic synthesis.[1] Their utility has been demonstrated in Favorskii reactions,[2] Nazarov cyclizations,[3] [4 + 3]-cycloadditions,[4] [3 + 2]-cycloadditions,[5] and nucleophilic substitutions.[6] In the classic Nazarov cyclization, in particular, a cyclic five-membered oxyallyl cation intermediate is formed which can undergo elimination and tautomerization to afford cyclopentenones. As pioneered by West[3e,7] and Tius,[3b,d,g,8] the utility of the Nazarov reaction has been extended through both inter- and intramolecular nucleophilic trapping of the cyclic oxyallyl cation leading to a wide array of functionalized cyclopentanones across a range of applications. In the related but relatively underexplored formal homo-Nazarov cyclization,[9] a six-membered oxyallyl cation is generated (Scheme 1). In the eliminative pathway, cyclohexenones are obtained. No examples of an interrupted formal homo-Nazarov cyclization had been published until earlier this year when Yadav and co-workers demonstrated trapping of the six-membered cyclic oxyallyl cation intermediate using allylsilanes in a formal [3 + 2]-cycloaddition to yield bicyclo[3.2.1]-octan-8-ones.[10] This transformation, while it remains the first and only literature example of an interrupted formal homo-Nazarov reaction, was only effective with stoichiometric amounts of $SnCl_4$ and demonstrated limited scope.

Scheme 1. Formal Homo-Nazarov Cyclization



Over the past several years, we have published various reports on the eliminative formal homo-Nazarov reaction using donor−acceptor−acceptor (D−A−A) cyclopropane substrates.[11] Through the use of the secondary acceptor group on the D−A cyclopropane, we were able to achieve catalysis using Lewis acids. We envisaged extending our work through developing a generalized, catalytic protocol for an interrupted formal homo-Nazarov cyclization. Given the limitations of the Yadav et al. study,[10] we sought to examine the reaction of D−A−A cyclopropanes with allylsilanes. Along that line, we disclose a chemodivergent protocol for the interrupted formal homo-Nazarov cyclization with allylsilanes, that selectively affords formal allyl trapping products under catalytic conditions while yielding unusual formal [3 + 2]-cycloaddition products under stoichiometric conditions (Scheme 2).

Scheme 2. Chemodivergent Allylsilane-Interrupted Formal Homo-Nazarov Cyclization with D−A−A cyclopropanes



The study began with alkenyl cyclopropyl ketone **1a** as the model substrate and $In(OTf)_3$ as the Lewis acid catalyst to initiate the reaction optimization (Table 1). The reaction of **1a**, allyl TMS **2a** (10 equiv),[12] and $In(OTf)_3$ (20 mol %) at room temperature in CH_2Cl_2 (0.1 M) afforded allyl-interrupted homo-Nazarov product **3a** (as a enol/keto mixture), resulting from a Hosomi−Sakurai-type allylation,[13] in 41% yield as a 1.7:1

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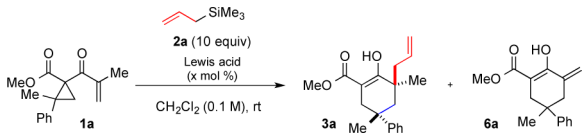
Table 1. Reaction Optimization[a]



entry	Lewis acid (mol %)	time (h)	yield (%)[b]	3a/6a[c]
1	$In(OTf)_3$ (20)	2	41	1.7:1
2	$In(OTf)_3$ (5)	19	63	5.6:1
3	$Sc(OTf)_3$ (20)	6	43	4.2:1
4	$Yb(OTf)_3$ (20)	70	26	2.3:1
5	$Al(OTf)_3$ (20)	72	42	6.8:1
6	**$SnCl_4$ (20)**	**24**	**75**	**17.0:1**

[a]Reactions run with *x* mol % of Lewis acid, 10 equiv of allyltrimethylsilane **2a**, and 1 equiv of cyclopropane **1a** in CH_2Cl_2 (0.1 M) at 25 °C. [b]Isolated yield mixture of keto/enol isomers after column chromatography. [c]Product ratios determined by ^1H NMR of the crude reaction mixture.

mixture with the untrapped homo-Nazarov product **6a**. At reduced loading (5 mol %), increased yield and chemoselectivity were observed (63% yield, **3a**/**6a** = 5.6:1) (Table 1, entry 2). With $Sc(OTf)_3$, the allyl product was formed in 43% yield with 4.2:1 selectivity (Table 1, entry 3). In contrast to $In(OTf)_3$, attempts to improve the reaction with $Sc(OTf)_3$ failed. $Yb(OTf)_3$ and $Al(OTf)_3$ each gave extremely long reaction times (>70 h) and were not revisited (Table 1, entries 4 and 5). Gratifyingly, $SnCl_4$ generated product **3a** in 75% yield (as a mixture of enol and keto forms) with a 17:1 selectivity toward the interrupted product (Table 1, entry 6). Converting the complex enol/keto mixture to the corresponding TMS enol silane significantly simplified its NMR, revealing a 2:1 diastereomeric ratio (dr). As anticipated, the major diastereomer was found to have the allyl and phenyl groups in a *trans* relationship.[14] Attempts to lower the loading of $SnCl_4$, alter solvent and reaction concentration, or employ other Lewis acids all led to reduced chemoselectivities and/or yields (see the Supporting Information). Therefore, we proceeded with 20 mol % of $SnCl_4$ and 10 equiv of allylsilane in CH_2Cl_2 (0.1 M) at room temperature as the optimized conditions.

In order to explore reaction scope, other D−A−A cyclopropanes were prepared and subjected to the optimized conditions (Figure 1). (4-Methoxyphenyl)cyclopropane **1b** smoothly afforded the expected allyl product **3b** in 92% yield and a dr = 4.2:1. The 4-fluorophenyl substrate **1c** gave a reduced yield of 54% with a dr = 6.8:1. The phenylcyclopropane **1d** gave the desired product **3d** as an intractable mixture. However, when **1d** was treated with 5 mol % $In(OTf)_3$, allyl trapping was observed and **3d** was obtained in 38% yield and a dr = 2.4:1.[15] No products were detected under either set of conditions for cyclopropane **1e** containing the highly electron-deficient 4-(trifluoromethyl)phenyl donor group. In contrast, (2-methoxyphenyl)cyclopropane **1f** provided its trapped product **3f** in 71% yield with a dr = 13.6:1. Similarly, both the naphthyl and furyl cyclopropanes **1g** and **1h** were effective in the interrupted reactions affording products **3g** and **3h** in 78% yield (dr = 7.3:1) and 65% yield (dr = 2.0:1), respectively.

Next, changes to the substituent on the alkenyl moiety were probed for tolerance. The 4-methoxyphenyl substituent was chosen as the donor group due to the observed excellent reaction efficiency of cyclopropane **1b**. Cyclopropane **1i**, bearing an allyl silane as the nucleophilic π-entity, failed to generate any desired trapping products. Instead, the homo-Nazarov elimination product **6b** (see Table 2) was obtained as part of an intractable

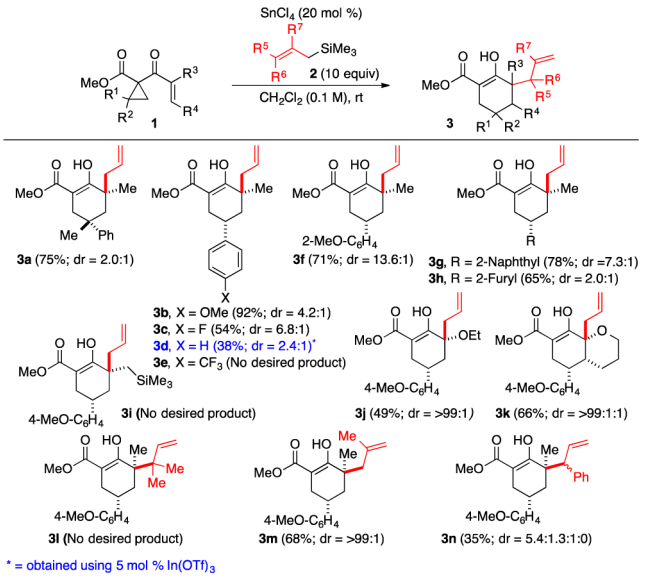
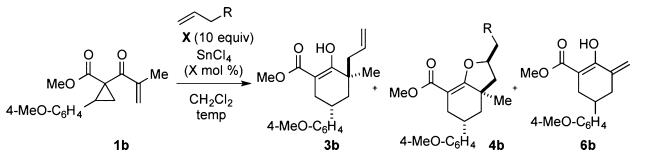


Figure 1. Catalytic, allylsilane-interrupted, formal homo-Nazarov cyclizations.

Table 2. Optimizing Chemodivergence[a]



entry[a]	Lewis acid (mol %)	silane (R)	concn (M)	temp (°C)	time (min)	3b/4b/6b[b]	yield (%)[c]
1	$SnCl_4$ (20)	TBDPS	0.1	-78	180	0:1:0	20[d]
2	$SnCl_4$ (20)	TBDPS	0.01	-78	60	0:1:0	41[d]
3	$SnCl_4$ (50)	TBDPS	0.01	-78	60	0:1:0	49[d]
4	$SnCl_4$ (100)	TBDPS	0.01	-78	15	0:1:0	48
5	**$SnCl_4$ (120)**	**TBDPS**	**0.01**	**-78**	**60**	**0:1:0**	**69**
6	$SnCl_4$ (100)	TIPS	0.01	-78	60	0:1:0	88
7	$SnCl_4$ (100)	TBS	0.01	-78	60	0:1:0	66
8	$SnCl_4$ (100)	TMS	0.01	-78	60	17:17:1	38

[a]Reactions run with *x* mol % of Lewis acid, 10 equiv of allylsilane **2**, and 1 equiv of cyclopropane **1b** in CH_2Cl_2 at the indicated temperature. [b]Product ratios determined by ^1H NMR of the crude reaction mixture. [c]Isolated yield after column chromatography. [d]Reaction did not reach completion, and unreacted **1b** was recovered.

mixture. On the other hand, when cyclopropane **1j**, bearing an acyclic vinyl ether, was employed, the desired allyl product **3j** was obtained in 49% as a single diastereomer. Similarly, a single diastereomer of **3k** was observed in 66% yield when the dihydropyranyl cyclopropane substrate **1k** was employed. The high diastereoselectivity observed in **3j** and **3k** can be rationalized through product development control[16] following allylsilane attack, in which the conformation minimizing unfavorable torsional strain determines the product outcome.

The effect of substituents on the allylsilane was also explored. Again, cyclopropane **1b** was chosen as the base system given the efficiency of the trapping reaction with allyl TMS (92% yield). No trapping product **3l** was observed with for trimethyl(3-methylbut-2-en-1-yl)silane, most likely due to steric conflicts during silane approach. Conversely, trimethyl(2-methylallyl)-silane gave product **3m** as a single diastereomer in 68% yield. A 35% yield was obtained for **3n** when cinnamyltrimethylsilane was similarly employed in the reaction.[17]

Up to this point, all experiments were performed using allyltrimethylsilanes. To determine the impact of changing the

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silyl group on the reaction (Table 2), the corresponding TBDPS (**2b**), TIPS (**2c**) and TBS (**2d**) allyl silanes were prepared. Upon treatment of cyclopropane **1b** with allyl TBDPS **2b** (10 equiv) and $SnCl_4$ (20 mol %) in dichloromethane (0.1 M) at −78 °C,[18] an unanticipated product, hexahydrobenzofuran **4bb**, resulting from a formal [3 + 2]-cycloaddition of the allyl TBDPS across the six-membered oxyallyl cation, was obtained in 20% yield along with some unreacted starting material (Table 2, entry 1). Lowering the reaction concentration to 0.01 M improved the yield of **4bb** (41%) but did not improve the conversion (Table 2, entry 2). Full conversion of starting material **1b** was only observed with stoichiometric amounts of $SnCl_4$ (Table 2, entries 3 and 4). Interestingly, reaction conditions as described by Yadav et al.[10] (120 mol % $SnCl_4$, 10 equiv of TBDPS allylsilane, −78 °C) proved optimal and cleanly afforded the desired hexahydrobenzofuran **4bb** in 69% yield as a 3.9:3.8:1.1:1 mixture of diastereomers (Table 2, entry 5). In comparison to allyl TBDPS, allyl TIPS **2c** and allyl TBS **2d** afforded their respective hexahydrobenzofurans, **4bc** and **4bd**, in 88% and 66% yield (Table 2, entries 6 and 7). Under the reaction conditions of Yadav et al., allyl TMS proved nonselective and gave a ∼1:1 mixture of **3b** and **4ba** (Table 2, entry 8).

Due to the utility of the TBDPS group in various functionalization reactions,[19] allyl TBDPS **2b** was used to probe the scope for hexahydrobenzofuran formation (Figure 2).[20] The reactions of **2b** with different cyclopropanes **1** were

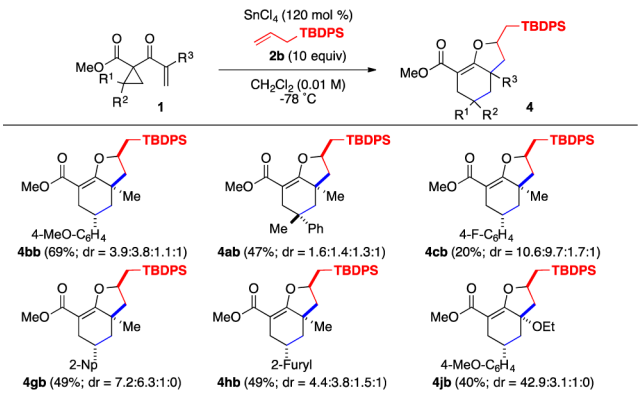
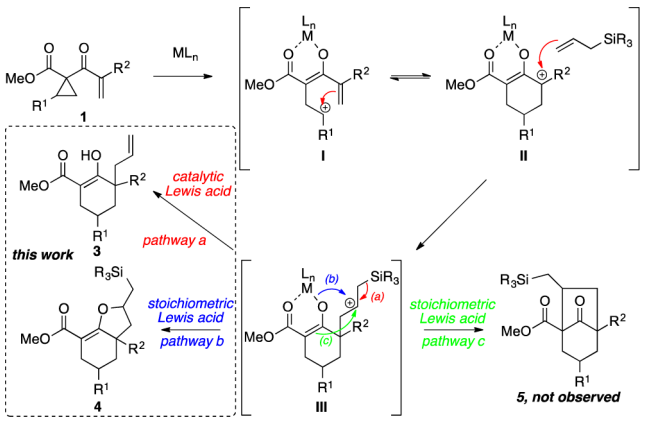


Figure 2. Synthesis of 2,3,3a,4,5,6-hexahydrobenzofurans.

examined under the optimized reaction. The *gem*-disubstituted methyl phenyl cyclopropane **1a** afforded its product **4ab** in 47% yield with a dr = 1.6:1.4:1.3:1, while the 4-fluorophenyl cyclopropane **1c** gave hexahydrobenzofuran **4cb** in poor yield (20%) but good relative diastereoselectivity (dr = 10.6:9.7:1.7:1). The 2-naphthyl- and 2-furylcyclopropanes (**1g** and **1h**) each gave their corresponding trapped products **4gb** and **4hb** in 49% yield. Finally, using (ethoxyvinyl)cyclopropane **1j**, the hexahydrobenzofuran **4jb** was formed in 40% yield with high diastereoselectivity (dr = 42.9:3.1:1:0).

Mechanistically, the reaction with D−A−A cyclopropane **1** involves formation of the cyclic oxyallyl cation **II** followed by capture by the allylsilane to generate the silyl-stabilized carbocation **III** (Scheme 3). Three chemodivergent pathways are possible for **III**: (1) Hosomi−Sakurai-type desilylation[13] to form the allyl cyclohexenol **3** (pathway *a*);[21] (2) enolate *O*-alkylation to form hexahydrobenzofuran **4** (pathway *b*);[22] and (3) enolate *C*-alkylation to afford bicyclo[3.2.1]octanes **5** (pathway *c*). The Lewis acid loading, reaction concentration, temperature and the choice of silyl group directly influence

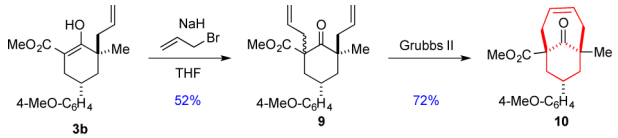
Scheme 3. Proposed Mechanism



product distributions. As expected, higher temperatures and concentration promote desilylation due to increased molecular collisions with Lewis basic sites on other species in the solution, leading to allylated product **3**. In addition, less bulky silyl groups also facilitate the desilylation pathway due to silane lability. On the other hand, increased steric bulk on the silane and lowered temperatures and concentrations all result in the persistence[23] of intermediate **III**. This persistence presumably allows for the occurrence of alternative pathways to quench the cation. One such channel, pathway b, is observed and leads to hexahydrobenzofuran **4** while the other, pathway *c*, would yield bicyclo[3.2.1]octanes **5**. In stark contrast to Yadav et al.'s report,[10] the formation of bicyclic products **5** was not observed during this study. We attribute this observation to the reaction being under kinetic control with a preference for *O*-alkylation.[24] Additionally, the nucleophilicity of the enolate carbon is substantially reduced due to being part of a vinylogous system, furthermore supporting the preference for *O*-alkylation.

The allyl products **3** from the trapping reactions can serve as useful building blocks for further synthesis. As a demonstration of this synthetic utility, **3b** could also be allylated to form **9** which, following ring-closing metathesis, afforded the functionalized bicyclo[4.3.1]dec-3-ene **10**, a framework found in caryolane-based natural products (Scheme 4).[25]

Scheme 4. Chemical Derivatization of 3b



In summary, we have developed a chemodivergent interrupted formal homo-Nazarov cyclization using allylsilanes as nucleophiles for trapping the six-membered oxyallyl cation intermediate derived from D−A−A cyclopropanes. Using catalytic $SnCl_4$ and allyl TMS, formal allylations of the intermediate oxyallyl cations are observed. Allyl products are formed in up to 92% yield and a dr's up to >99:1. This transformation represents the first example of effective catalysis for the interrupted formal homo-Nazarov cyclization. When the reaction is operated with stoichiometric $SnCl_4$ at lowered concentrations and temperatures using bulkier allylsilanes, hexahydrobenzofuran products are obtained in up to 88% yield. For both product pathways, modifications at the donor groups and nucleophilic π-systems are well-tolerated. The products formed can be readily derivatized to give other

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synthetically useful precursors. Further work will focus on capturing the oxyallyl cation using other nucleophiles (both inter- and intramolecularly) to allow for access to a range of functionalized cyclohexanones, bicyclics, and potentially other scaffolds.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral and analytical data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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