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Nazarov-Like Cyclizations

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The Nazarov cyclization, a well-known method for the formation of cyclopentenones, mechanistically involves the 4π electrocyclization of a 1,4-pentadienyl cation, generated from cross-conjugated divinyl ketones. Due to large part to initially harsh reaction conditions, this cyclization was of limited utility. However, in recent years, numerous groups have reported alternative methods that greatly improved the viability of this reaction. Stimulated by these advances, other researchers have expanded the scope of the original cyclization to a more diverse set of starting materials and these “Nazarov-like” reactions are the subject of this Review. Hetero-Nazarov cyclizations, in which nitrogen or oxygen have been incorporated into the divinyl ketone framework, allow for the synthesis of various heterocycles and replacement of one of the vinyl moieties with an alternative group such as cyclopropyl provides cyclohexenones via a homo-Nazarov cyclization.

Before venturing any further, some finer details need to be clarified. The reactions reviewed herein clearly are extensions of the original cyclization conceived by Nazarov. However, in some instances, this connection is merely conceptual, and these reactions do not conform to the same mechanism as the namesake cyclization. Thus, whereas theaza- and imino-Nazarov reactions are likely to be 4π electrocyclizations, the oxa- and homo-Nazarov reactions presumably proceed through ionic intermediates, with the latter being more closely related to a Friedel-Crafts alkylation. These mechanistic differences aside, the use of colloquial terms such as oxa- or homo-Nazarov positions these reactions in an appropriate context with respect to the original transformation.

The Aza-Nazarov Cyclization

The use of imines as aza-Nazarov precursors has allowed for the development of a number of substituted pyrrole syntheses. For instance, in 2012, the Würthwein group disclosed that 1-azapenta-1,4-dien-3-ones undergo a cyclization to pyroles in the
presence of TIOH (Scheme 1). The requisite starting materials were prepared by first reacting 2,3-butadione O-benzylxime with aryl aldehydes under aldol condensation conditions to give the α-benzoximeyminone enones 2 and then with alkyl- or aryllithium reagents, which selectively added to the ketone to afford the desired allylic alcohols 3. Subjecting 0.025 M DCM solutions of these compounds to excess TIOH at –10 °C provided the highly substituted pyrroles 6 in 29-83 % yield. Appropriate choice of starting material allowed for the synthesis of pyrroles with various groups at positions 2 (methyl or phenyl), 3 (alkyl or aryl) and 5 (aryl). Additionally, the reaction was tolerant of electron donating and withdrawing groups on the aryl group at C(5), and worked equally well for O-benzylximes (10 examples) and hydrazones (3 examples; not shown).

Mechanistically, the reaction is believed to proceed via 1-azapentadienyl cation 4-I, resulting from the loss of water after protonation of the alcohol (equation 1). Subsequent to a requisite conformational change that provides cation 4-II, a protonation occurs, a process supported by DFT calculations. The reaction required two full equivalents of a strong acid. Reaction with less than one equivalent of TIOH or the use of weaker acids such as trifluoroacetic acid, resulted in the formation of an adduct in which the desired pyrrole underwent a Friedel-Crafts alkylation with a second equivalent of the open-chain cation 4-II (equation 2). Presumably, excess acid is required because, in the presence of stoichiometric quantities of acid, both pyrrole 6 and intermediate carbocations 4-I and 4-II exist in solution, which allows for Friedel-Crafts alkylation of the pyrrole at C(4).

Following this report, the same group disclosed the preparation of substituted NH-pyrroles under related superelectrophilic conditions. A route to starting materials similar to that described above was used (Scheme 2): diacetyl was first converted to its 1-aminindolino hydrazone, followed by alkylation condensation with several substituted benzaldehydes to afford the desired precursors 9a. Alternatively, for examples in which R was a phenyl ring, a slightly different approach was employed. 1-Aminindolined was condensed with ethyl 2-oxo-2-phenylacetate (7), followed by reaction with the anion of dimethyl methylphosphonate. The resulting β-ketophosphonate 8 was reacted with substituted benzaldehydes under Horner-Emmons conditions to provide the unsaturated ketones 9b. In all instances, the C–C double bond was determined by NMR to be of the E-configuration.

With a convenient route to starting materials worked out, these reactants were cyclized under two different conditions. The first used high dilution (0.02 M in DCM) and two equivalents of TIOH (“low acid”), which afforded the N-substituted pyrrole 12 (Scheme 3), clearly the result of an aza-Nazarov cyclization. The second made use of high concentration conditions (0.2 M in DCM) in the presence of seven equivalents of TIOH (“high acid”), which allowed N−N bond cleavage subsequent to cyclization, producing 3-acetylindole (16) and acetylated pyrroles 14. The resulting 3-hydroxyxypropyl products were too unstable to isolate, and therefore the reactions were worked up with acetic anhydride, ultimately providing the peracetylated products shown.

The authors speculated that, since this reaction presumably takes place in two consecutive steps, the second step required “superelectrophilic conditions” to effect N−N bond cleavage, only possible in the presence of a large excess of TIOH. The proposed mechanism shown in Scheme 3 was corroborated by DFT calculations. Based on these data, the carbonyl oxygen represented the most basic site for protonation under low acid concentrations, thus giving rise to the only intermediate (10) that could undergo the 4α-electrocyclization reaction to provide 11-I. In the presence of higher concentrations of TIOH, a second protonation occurs, most likely on the N of the indoline group 11-II. It is this second protonation, possible only under more acidic conditions, that allows for cleavage of the N−N bond. Deprotonation at C(2) of the indoline releases the protonated heterocycle and the putative pyrrole. Subsequent loss of a proton and acylation with acetic anhydride delivered products 14 and 16. The reaction was carried out on nine different substrates and was found to be general, allowing for the presence of both electron-donating and electron-withdrawing groups on the Ar group at the end of the enone system. Yields of the acetylated products ranged from 33-60%.
Organic & Biomolecular Chemistry

Putatively the reaction of acetics proceeds through an amide hemiaminal 20, which on exposure to TfOH loses a molecule of ethanol to generate N-acyliminium ion 21-1 in situ. Likewise, enamile 21-2 presumably progresses to product via this same intermediate. The carbonyl oxygen is then protonated a second time to yield a superelectrophile 22, which undergoes an aza-Nazarov cyclization. Yields were generally good (40-81%) and most of the aryl groups incorporated one or more electron releasing groups. In two instances, when extension to alkenes such as indene 23 was attempted, 1,6-cyclization via dienel 25 onto the iminium carbon lead to six membered rings, a process corroborated by DFT calculations (equation 3).

In 2010, Tius, et al. reported a catalytic asymmetric aza-Nazarov cyclization reaction that involved an azirine starting material (Scheme 5). When allylic alcohol 28 was oxidized with MnO2, rather than the expected α-aminodienone 29, azirine 30 was isolated in a capricious 37% yield. Probing the synthesis of this compound further identified a two step procedure, sulfur trioxide oxidation to enone 29 followed by treatment with PhI(OAc)2, that provided the desired azirine 30 with greater reproducibility. The structure was confirmed by HRMS, IR, 1H and 13C NMR.

When azirine 30 was treated with the chiral diamine monoflate salt 31, cyclization to tetrahydropyridine 32 was noted. This reaction proved to be very intriguing in that firstly, enone 29 failed to react under identical conditions, and secondly, both recovered azirine 30 and the cyclic product 32 were found to be optically active, indicating the cyclization involved a kinetic resolution. Mechanistically, the authors proposed enantioselective formation of the imine 33 followed by an aza-Nazarov cyclization to generate cation 34 (equation 4). Quenching of this intermediate with water and subsequent ring expansion produces 32. Given that enone 29 failed to react under identical conditions indicated that ring strain relief is likely to be the driving force for this reaction.
The Oxa-Nazarov Cyclization

Several accounts of oxa-Nazarov cyclizations have been published recently. Strydom reported in 2012 the regioselective reaction of stabilized sulfur ylides 37 with Au(I)-activated alkynes 36 that afforded a vinyl gold intermediate, which, upon loss of the sulfur leaving group, provided the “oxa-Nazarov” cation intermediate that cyclized directly to 2,4-disubstituted furans 38 in moderate to good yields (30-82%; Scheme 6). The reaction, which required a terminal alkyne, was tolerant of a wide variety of alkyl groups (R1) on the alkyne, and worked well with both electron rich (R2 = PhCH2; not shown in the accompanying table) and electron deficient aromatic rings (cf, 38b-d, f-h). One example demonstrated the ylide need not be derived from an aryl ketone (38i) and the presence of a minor amount of isomeric 2,5-disubstituted product was noted in only one example (38f).

![Scheme 6](image)

The Liu group reported another gold activation of enyne sulfonylimides 39 to produce trisubstituted furans 40 (Scheme 7). Upon formation of a resonance stabilized gold complex in situ, addition of a one-atom donor (e.g., A), was proposed to yield a vinyl Au species 41, which led to formation of the oxa-Nazarov intermediate 42, after expulsion of the quinoline leaving group. Cyclization, rearomatization, and protodeauration provided the C(2) amino substituted furans 40 in good to excellent yields (56-91%). The amine was required to carry an electron-withdrawing group, which was a sulfonylimide in all cases reported. The best choice of catalyst was a mix of Pt(Bu)3(o-biphenyl)AuCl/AgSbF6. Other catalysts did not provide the necessary chemoselectivity and 8-methyquinoline oxide was the oxide of choice. The aromatic group attached to the vinyl portion of the starting material could carry both electron-donating and withdrawing groups (39f,g), or could be replaced by a variety of heterocycles (39h-j).

![Scheme 7](image)

The Imino-Nazarov Reaction

This section will cover Nazarov reactions that employ divinyl imines as Nazarov cyclization precursors rather than the traditional divinyl ketones. The issue with this variation is that ab initio calculations suggest that, relative to their oxygen counterparts, the requisite 3-amino-1,4-pentadienyl cations are likely to resist cyclization, due in part to the conformational preference for this amino cation and the result of enhanced stabilization by nitrogen. Nevertheless, since the first report of an imino-Nazarov cyclization by Tius, several additional examples have been published.

González reported the reaction of propargyl tosylates 43 with N-tosylimines 44 in the presence of a Au(I) carbene catalyst (Scheme 8) provided the N-tosyl cyclopentenylimines 45 in good to high yields. This disclosure is in stark contrast to an earlier report, in which α-acetoxyalkynes failed to react with tosylimines in the presence of a Au(III) carbene catalyst, and instead underwent acyl migration to afford Knoevenagel products. For the reactions presented in Scheme 8, the best counterion for the catalyst was found to be either BF4− or SbF6−. The R3 group on the imine could be an electron-rich or moderately electron-deficient aryl group as well as alky1 and cycloalkyl without any negative effect on yield. Strong deactivating groups (i.e., 45d) on the aryl substituent did adversely affect yield (34 %) however. If R1 was CH2, the reaction pathway usually involved a methyl group migration, prior to the imino-Nazarov cyclization step. However, for compound 43i, ring expansion occurred preferentially to methyl migration to yield ring fused product 45i. Alternatively, if the group attached to the propargylic carbon was secondary, such as in 43j, the reaction allowed for the synthesis of some interesting spiro ring structures (i.e., 45j). Primary alkyl groups did not work in this protocol.
afford iminocyclopentenones 53. While the iminium products could be identified by NMR, stereoselective reduction of the crude mixture with NaBH₄ afforded better-behaved aminocyclopentane products 54. Overall yields for the two-step conversion were modest (48-50%), but in certain instances, such as the last two entries in the table, poor yields of cyclized products and recovered starting cyclopropanes were reported. The authors speculated the cause for the inferior conversion was the presence of the strong acid, HNTf₂. Indeed when starting material was first exposed to this acid and then AgNTf₂ for an extended period, none of the imino-Nazarov cyclized product was isolated. Recovered starting material accounted for more than 80% of the mass balance. Furthermore, addition of a hindered base such as 2,4,6-tri-tert-butylpyridine permitted rapid consumption of starting material but failed to yield imino-Nazarov cyclization products.

Interestingly, reducing the donating ability of the nitrogen substituent, such as replacing it with an acetyl group (R₃ = Ac) in cyclopropane 51, yielded no reaction at room temperature and decomposition upon exposure to higher temperatures. Thus, cyclopropanes bearing an electron-rich nitrogen were necessary for this reaction, contrary to the previous report in which only amines bearing electron-withdrawing groups successfully underwent Au(I) induced cyclization. The method was expanded to substrates that contained aromatic rings tethered to the cyclopropyl group (i.e., 55), affording imino-Nazarov cyclized tri cyclic systems such as 56a,b (65%) with modest diastereoselectivity (1.4:1/56a:56b; Scheme 10).

### The Homo-Nazarov Cyclization

Given that cyclopropyl groups can often mimic double bonds in terms of reactivity,21 extension of the Nazarov to vinyl cyclopropyl ketones is compelling. There were several early reports by Wattanasin22a,b and Tsuge22c of successful application of the homo-Nazarov, which provided substituted cyclohexenones, but further investigation into this methodology was minimal until it was revisited by Yadav23, Waser24, and France.25

Yadav reported the cyclization of t-butyldiphenylsilyl (TBDPS) substituted cyclopropyl heteroaryl ketones 57 and 58

The presence of a tosyl group and Au-coordination to this nitrogen likely prevented donation of the nitrogen lone pair to the cation. Thus, the adverse effects of nitrogen on a 3-amino-1,4-pentadienyl cation are presumably minimized in this process, allowing the imino-Nazarov cyclization to take place. The authors proposed a complex mechanism (equation 5) that involved several rearrangements, including the formation of a 1,3-diene system, and azetidine synthesis, before the metal-activated imino Nazarov intermediate cyclized to the product.

A few years later, Hsung demonstrated the use of the same mixed gold catalyst (chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] Au(I)/AgSbF₄) to induce the formation of 3-amino-1,4-pentadienyl cation system 48 from allenamides 46 (equation 6).18 The key to this reaction was the use of an electron-withdrawing group (Ts) on the N atom to reduce its ability to donate into the cation, thus enhancing the reactivity of the key cationic intermediate. The phenyl group could bear electron donating or moderately electron withdrawing groups, and substituents larger than CH₃ (C₆H₅, CH₃Ph) on nitrogen were tolerated, though these reactions were typically sluggish but nonetheless provided product in excellent yields. Additionally, for compounds in which an f-electron electrocyclic process could conceivably compete with the imino-Nazarov cyclization, only the latter was observed. This chemistry allowed for the synthesis of substituted aromatic systems with fused aminocyclopentene rings (i.e., 49).

The third example of an imino-Nazarov cyclization was contributed by the West group, in which 2,2-dichloroaminocyclopropanes 51, available in two steps from enynes 50, were employed as imino-Nazarov cyclization precursors (Scheme 9).19 Treating these compounds with silver triflimide (AgNTf₂) opened the strained ring to reveal a 3-amino-penta-1,4-dienyl cation (52) that underwent subsequent electrocyclization to

![Scheme 8: Synthesis of N-tosylimino aminocyclopentanes](image)

![Scheme 9: The preparation of aminocyclopentanes 50 and their conversion to aminocyclopentanes 54](image)

![Scheme 10: The preparation of diastereomers 56a,b](image)
under Lewis acid conditions (SnCl₄) in DCE at 80 °C to yield 2,3-
heteroaromatic ring-fused cyclohexanones 59 and 60, respectively
(equation 7). Other combinations of solvents and Lewis acids were
less efficacious. The reaction was general, providing products in
good to excellent yields (70-85%), regardless of the substitution
pattern of the original five-membered heterocycles. Additionally,
the reaction also tolerated the presence of electron deficient aryl
groups at position 5 of the heterocycle (i.e., 57d) and the reaction
with other groups capable of stabilizing the developing positive
charge at the β position of the cyclopropyl ketone (equations 8, 9)
were equally proficient.

Building on this methodology, with an eye toward a
formal total synthesis of aspidospermidine, the Waser group next
prepared 2-ketoindolyl cyclopropylamine 65 in eight steps from 2-
piperidinone, with the expectation that this system would undergo
a diastereoselective homo-Nazarov cyclization to yield a final
product consisting of four of the five rings found in the natural
product (equation 10). However, since the indole nitrogen was not
protected, cyclization (TsOH, CH₂CN) gave a product that, by NMR
analysis, was a 1.6:1 mixture of C(3) to N(1) cyclized products (68
and 70, respectively). Fortunately, conditions were identified that
allowed either regiosomer to be isolated as the major product. The
use of Cu(OTf)₂ in DCM afforded the desired carbon-cyclized product
68 (91 %, 8:1 dr), whereas treatment with TsOH in DCM
favored indole nitrogen participation to give 70 (89 %, 21:1 dr).
Moreover, the N(1) product could be converted to the C(3) product
upon exposure to copper triflate, identifying the former as the kinetic
product. To explain the excellent observed diastereoselectivity, the
authors proposed structures 67/69. Analysis of the alternative
transition state structures that lead to trans-ring fusion could only be
generated from an energetically less favorable boat-like
conformation. With a route to the Cbz protected intermediate 68
successfully achieved, the formal total synthesis of aspidospermidine
was completed by N-deprotection, yielding a Wenkert intermediate
en route to the natural product.

In the latest contribution from this group, an attempt was
made to address some shortcomings of this chemistry, most notably,
the requirement of electron-rich donor groups on the cyclopropane
and the lack of asymmetric induction in the presence of chiral
catalysts. As a result, the original route was modified to incorporate
an α-carbomethoxy group, which would not only further polarize the labile C–C bond of the cyclopropane but also offer an additional binding site for catalytic cations, a concept first exploited by the France group \textit{(vide infra)}.

After generating the requisite substituted dimethyl cyclopropane-1,1-dicarboxylate, selective hydrolysis of the less hindered methyl ester afforded monoacid 72, which was then treated sequentially with the vinyl lithium reagent derived from 3,4-dihydro-2H-pyran and methyl iodide in the presence of potassium carbonate to provide the final targets 73 (R₁ = CO₂CH₃) in good overall yield (Scheme 12).

With these starting materials in hand, catalysts were screened for efficacy. A host of Brønsted and Lewis acids failed to generate homo-Nazarov products, and equally ineffective was TsOH when the aryl group was devoid of an activating group, as was observed earlier (see the reaction of 62b in Scheme 11). Fortunately, the use of nickel(II) perchlorate hexahydrate or boron trifluoride ethereate overcame this limitation in good yields (63 % and 83 % isolated yields, respectively). In addition, having identified a Lewis acid catalyst and incorporating the ester moiety had other noteworthy benefits: reaction times were reduced more than 70-fold when compared to the original 20 mol % TsOH/acetonitrile conditions, and the reaction was more tolerant of reactive components. For instance, the reaction of 73 bearing a 4-Cl phenyl group (R₁ = CO₂CH₃, Ar = 4-Cl-PH; not shown) performed admirably (85%). These researchers also demonstrated that the added carbamate group could be removed post-cyclization via Krapcho dealkoxycarbonylation (NaCl, DMSO, 150 °C) but an attempt to make use of chiral PYBOX Lewis acids to generate chiral cyclohexenones 74 (R₁ = H) was disappointing, as only low % ee values (11–25%) were noted. This paper also includes full experimental details of the approach described above \textit{en route} to cyclohexylamine-containing natural products such as aspidospermidine.

France and coworkers were the first to take advantage of donor-acceptor-acceptor cyclopropanes and to make use of an ester group as an additional coordinating site for Lewis acids to effect a homo-Nazarov cyclization. In essence, by correctly positioning electron donating (e.g., 4-methoxyphenyl) and withdrawing (e.g., benzoyl) groups within the cyclopropane framework, the key C–C bond becomes rather polarized, thus facilitating ring opening. The required starting materials were rapidly prepared by effecting a diazo transfer reaction on the Weinreb amide 75. Subsequent rhodium-catalyzed cyclopropanation with several styrenes, and addition of vinyl Grignard reagents provided, in short order and good yields, vinyl cyclopropyl ketones 76 (Scheme 13). Screening a variety of Lewis acids and solvents identified In(ΟTF)₂ (30 mol %) as the best catalyst of those studied and DCM as the solvent of choice. Although most catalysts did provide homo-Nazarov products, all except In(ΟTF)₂ either gave complex product mixtures, which included the desired cyclohexenone 77-1, its isomeric conjugated β-dienol (77-2), and/or dihydrofuran 78, or failed to go to completion, even after extended reaction times. Substrates bearing less effective donating groups, such as phenyl (76c) or even 4-F-phenyl (76d), did give cyclization products but failed to go to completion after 24 h. Overall, the yields for the combined homo-Nazarov products ranged from 29-93%, with the lower yielding reactions representing those that returned starting material.

The next phase of this project involved the application of this protocol to the synthesis of heteroaromatic ring-fused cyclohexenones.²⁹ The route to the requisite precursors started with a variety of heteroaryl β-ketoesters 79 and utilized the same sequence of reactions to arrive at cyclopropanes 80 (Scheme 14). Due to the enhanced reactivity of the heterocycles, lower catalyst loading (5 mol %) was tolerated (86% yield vs 88% yield at 30 mol %), though the reaction time increased (2.5 h vs 5 h). Unfortunately, the diastereoselectivity of the cyclization (i.e., \textit{trans/cis} ratios) was generally low (1.2-1.7:1), but the chemistry was tolerant of a wide variety of heterocycles. Cyclopropanes that lacked electron donating aryl substituents (i.e., compounds 80i,j), required elevated temperatures (80 °C in DCE) to achieve successful reactions.
Further experimentation highlighted other facets of this chemistry. For instance, when C(2) was blocked, as shown in equation 11, the heterocycle was forced to cyclize onto C(4) (56% yield as a 2:1 mixture of keto and enol tautomers). Additionally, the cyclopropane also tolerated higher substitution with little impact on yield (equation 12; 71% yield). Lastly, in an impressive display of the power of this chemistry, the diazoketone shown in equation 13 was subjected to a one-pot homo-Nazarov cyclization, using substantially lower catalyst loading. The yield for this one-step sequence was 56%, which compared very favorably to the two-step procedure (73% for each step, 53% overall).

Recognizing that extension of this protocol to acylated indoles could potentially open a route to the numerous natural products bearing a common hydroxypro-[1,2-@]indole-6(7H)-one core, the France group next prepared N-acyl-3-methylindolyl cyclopropanes 83 (Scheme 15). With these precursors in hand, In(OTf)3-induced cyclization afforded the desired tricyclic heterocycles in good to excellent yields (48-99%) for a selection of compounds. The only substrate that failed to yield cyclized product in good yield carried the strongly deactivated 4-NO2-phenyl ring on the cyclopropane (83e). Other substrates with less deactivating groups such as 83d worked well but did require elevated temperatures. Also not surprising was the fact that substrates bearing alkyl groups (i.e., 83h) on the cyclopropane likewise required elevated temperatures, but these reactions were nonetheless successful. Overall, the diastereoselectivity ranged from moderate to high. Only a single diastereomer was observed for spiro products 84h,i.

The last series of compounds reported in this paper tested the structural requirements of the acylated indole (equation 14). In particular, the C(3) position was varied to prove that no alkyl group was required (R = H) and further that the reaction tolerated an assortment of functional groups (R = -CH2CH2Br, -CH2CH2NPhth, -CH3CO2H), with little-to-no effect on yield (76-99%).

This methodology was then applied toward a short, diastereoselective total synthesis of (±)-deethylburbamidine (86b), a member of the eburnan alkaloids (Scheme 16). Exposing cyclopropyl acylindole 84 to catalytic In(OTf)3 in DCM at RT afforded the tetracyclic core structure 85 as the major product in 71% (3:1 dr). A two-step sequence (TFA induced removal of the Boc group with concomitant cyclization and Krapcho demethoxycarbonylation with NaCl in hot DMSO) afforded the natural product in 18% overall yield in six steps.
Conclusion

The Nazarov cyclization has captured the imagination of many an organic chemist, and the ingenuity and creativity of these scientists continues to expand upon this idea. These inspirations, whether related mechanistically or merely conceptually, have significantly augmented the general applicability of the original concept. Whereas the Nazarov cyclization affords cyclopentenones, many an organic chemist, and the ingenuity and creativity of these groups, greatly add to the synthetic utility of these Nazarov cyclizations; b) extension to imino substrates, which allows for the construction of aminocyclopentanones; and c) and lastly, under appropriate conditions, access to substituted cyclohexenone products via cyclopropyl vinyl ketones. In many instances, these transformations were accomplished in high yield, and with a good degree of regio- and stereocontrol. These features, in combination with a general tolerance for additional functional groups, greatly add to the synthetic utility of these Nazarov-like cyclizations and further extension to the synthesis of complex molecules, in addition to the natural products referenced herein, is anticipated.

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Notes and references

1. List of abbreviations: TfOH = triflic acid; DFT = density functional theory; DCM = dichloromethane; DCE = 1,2-dichloroethane; TsOH = p-toluenesulfonic acid.
4. This review covers the years 2009-2013. Some of the reviews mentioned in reference 2 discuss earlier examples of these reactions, though the focus of those review articles was specifically the Nazarov reaction.
5. Despite being potentially misleading, the author does not refrain from using terms such oxo-Nazarov, homo-Nazarov, etc. The reader is once again reminded of the “formal” connection to the original cyclization.
14. The conclusions drawn from this paper are for the resultant cation from the divinyl imine derived from ammonia.
20. This was the topic of an earlier short review, see: F. De Simone and J. Waser, Chimia, 2009, 63(3), 162-167; additionally, during the preparation of this manuscript, a review appeared covering intramolecular donor–acceptor cyclopropene ring-opening cyclizations, in which some of the reactions discussed herein were also mentioned, appeared, see: M. A. Cavitt, L. H. Phun, and S. France, Chem. Soc. Rev., 2014, 43, 804-818.
30. Although technically not a homo-Nazarov cyclization, given its close relation to previously described reactions from this group, the author opted to include these references in this review.