

# Nazarov Cyclization of Geminal-Benzoyl-Phenyl Allenes in Triflic Acid: A Synthetic Route to Pallidol-like Structures

Oussama Abdelhamid Mammeri, Irina A. Boyarskaya, Dar'ya V. Spiridonova, Mariya A. Kryukova, and Aleksander V. Vasilyev\*



Cite This: *Org. Lett.* 2026, 28, 2349–2354



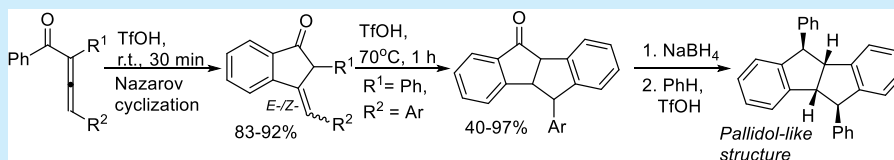
Read Online

ACCESS |

Metrics & More

Article Recommendations

Supporting Information



**ABSTRACT:** Benzoyl substituted allenes in Brønsted superacid TfOH at room temperature afford Nazarov cyclization products, *E*-/*Z*-alkylidene indanones. In TfOH at a higher temperature of 70 °C, allenes bearing geminal benzoyl and phenyl substituents undergo further transformations, yielding fused indano–indanones. The latter have been used as precursors in the stereoselective synthesis of the structural analogue of the natural compound, Pallidol.

Allenenes are highly reactive molecules used for efficient construction of complex carbo- and heterocyclic structures.<sup>1–4</sup> One of the useful synthetic transformations of aroyl-substituted allenenes is Nazarov cyclization, affording alkylidene indanones (Scheme 1a). This reaction proceeds either through activation by Lewis acids such as BF<sub>3</sub>·Et<sub>2</sub>O,<sup>5,6</sup> In(OTf)<sub>3</sub>,<sup>6</sup> Fe(0)-complex [(Ph<sub>3</sub>P)<sub>2</sub>Fe(CO)(NO)]BF<sub>4</sub>,<sup>7</sup> FeCl<sub>3</sub>,<sup>8</sup> or TMSOTf<sup>9</sup> or under catalyst-free thermal conditions.<sup>10</sup> In addition to aroyl-substituted allenenes, allenyl vinyl ketones are also well suited for Nazarov cyclization, which is promoted by Brønsted acids (*p*-TsOH, CF<sub>3</sub>CO<sub>2</sub>H), Lewis acids (compounds of Sc, Yb, Au),<sup>11</sup> or silica gel<sup>12</sup> (see also review<sup>13</sup>). Alternatively, the approach to the cyclization of aroyl-substituted allenenes entails their conversion to furans via metal catalysis by Pd,<sup>14–17</sup> Au,<sup>18–22</sup> Pt, Cu, Al, Si, Sn, In, and Ag<sup>9,23</sup> (Scheme 1a). Specifically, these catalysts activate the allene carbon–carbon bond, increasing its electrophilicity and enabling intramolecular nucleophilic attack by the carbonyl oxygen, affording target furans.

Based on our previous studies on cyclization of electron-deficient allenenes under superelectrophilic activation conditions,<sup>24–29</sup> we sought to extend this approach to the transformations of benzoyl allenenes in the presence of strong Brønsted and Lewis acids. Accordingly, the main goals of this work were to investigate transformations of benzoyl-substituted allenenes under the action of strong Brønsted (triflic acid CF<sub>3</sub>SO<sub>3</sub>H (TfOH), H<sub>2</sub>SO<sub>4</sub>, CF<sub>3</sub>CO<sub>2</sub>H) and Lewis (AlCl<sub>3</sub>, AlBr<sub>3</sub>) acids, as well as acidic zeolites (CBV-500, CBV-720), and to examine cationic intermediates and reaction products through DFT calculations.

In pursuit of these objectives, we found that geminal-benzoyl-phenyl allenenes undergo Nazarov cyclization to form alkylidene indanones (Scheme 1c). Protonation of the

exocyclic C=C bond of the alkylidene indanones gives rise to intermediate carbocations that are cyclized into fused indano–indanone structures. The latter are precursors in the synthesis of pallidol-like compounds (Scheme 1c).

There is a closely related precedent of FeCl<sub>3</sub>-mediated bicyclization of aroyl-di(or tri)aryl allenenes into fused indeno-indanones (Scheme 1b).<sup>8</sup> Miao, Ren, and co-workers found that such allenenes, at the first reaction step, afforded Nazarov cyclization products followed by their consequent one-electron oxidation into intermediate radicals I and carbocations II, which were finally cyclized into indeno-indanones III (Scheme 1b).<sup>8</sup> However, the mechanism of the formation of compounds III differs from the transformation of aroyl allenenes in our study (compare Schemes 1b and 1c). In the latter case, the phenyl substituent, which is geminal to the aroyl group, is involved in the construction of the indane core (Scheme 1c). Contrary to that, under the synthesis of compounds III, this geminal aryl moiety remains untouched.

It should be especially emphasized that Nazarov cyclization of aroyl allenenes is well-known (Schemes 1a,b), but the superacid-driven cascade leading to fused indano–indanones from geminal benzoyl-phenyl allenenes is unprecedented (Scheme 1c).

Pallidol and related structures are typically isolated from natural sources, such as *Cissus pallida*, grape seeds (*Vitis*

**Received:** December 30, 2025

**Revised:** February 6, 2026

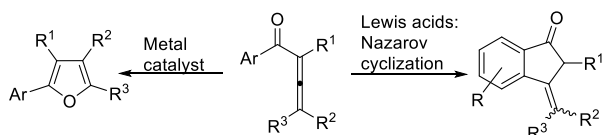
**Accepted:** February 9, 2026

**Published:** February 11, 2026

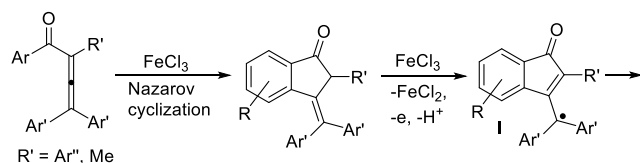


### Scheme 1. Previous Studies on Transformations of Aroyl-Substituted Allenes into Alkyldiene Indanones or Furans, and the Main Idea of This Work

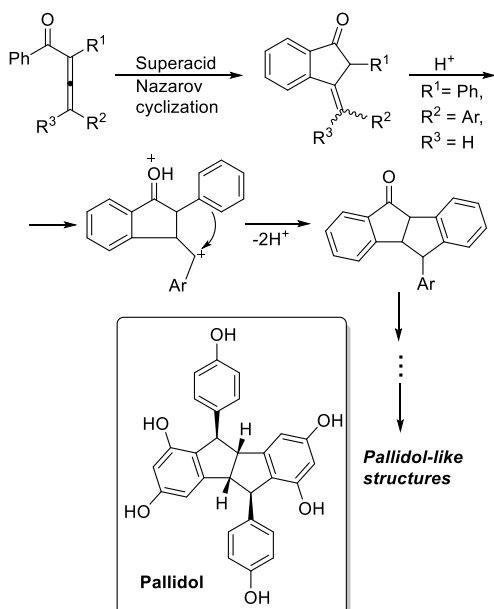
#### a) Previous works on various cyclizations of aroyl allenenes:



#### b) Previous work on FeCl<sub>3</sub>-mediated bicyclization of aroyl-di(or tri)aryl allenenes into indeno-indanones [8]:



#### c) This work:



*vinifera*), *Parthenocissus laetevirens*, or red wine.<sup>30–33</sup> The main benefit of Pallidol and similar structures is their role as powerful antioxidants, especially as selective singlet oxygen quenchers, that underlie their potential neuroprotective and other health benefits, including antifungal and anticancer activities.<sup>34–39</sup> In this regard, much attention has been paid to the synthesis of Pallidol, which has been obtained by complex multistage methods.<sup>39–48</sup>

It should be noted that this study focuses on the synthesis of compounds; no biological activity is claimed.

Starting benzoyl allenenes **1a–k** used in this study are shown in Figure 1. Their synthesis and characterization are provided in the Supporting Information (SI).

Initially, the transformation of allene **1c** was studied under the action of an excess of various acids (Table 1). Indenone **3c** was obtained as the only reaction product in high yields up to 86–97% under the use of Brønsted superacid CF<sub>3</sub>SO<sub>3</sub>H

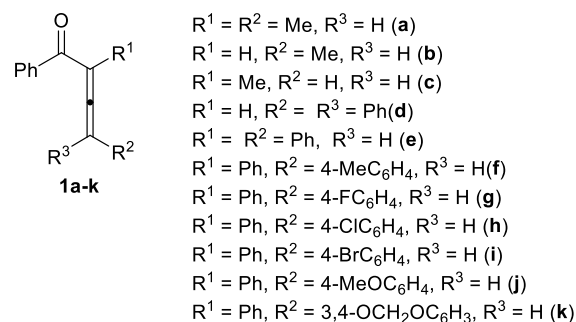
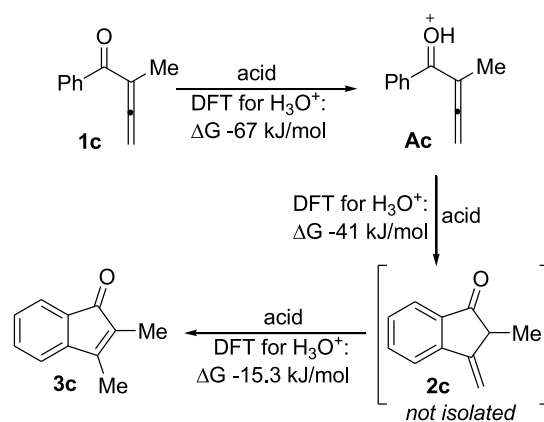


Figure 1. Starting benzoyl allenenes **1a–k** used in this study.

Table 1. Cyclization of Allene **1c** into Indanone **3c** under the Action of Excess of Various Acids, DFT Calculations of Gibbs Energies  $\Delta G_{298}$  (kJ/mol) for the Reactions **1c** → **Ac** → **2c** → **3c**



Entry	Acid	Temp, °C	Time, min	Yield of <b>3c</b> , %
1	TfOH (neat)	r.t.	30	90
2	H <sub>2</sub> SO <sub>4</sub> (neat)	r.t.	30	62
3	CF <sub>3</sub> COOH (neat)	r.t.	30	10 <sup>a</sup>
4	AlCl <sub>3</sub> (CH <sub>2</sub> Cl <sub>2</sub> as a solvent)	r.t.	30	86
5	AlBr <sub>3</sub> (CH <sub>2</sub> Cl <sub>2</sub> as a solvent)	r.t.	30	50
6	CBV-720 (benzene as a solvent)	100	60	97
7	CBV-500 (benzene as a solvent)	100	60	96

<sup>a</sup>Incomplete conversion of starting allene **1c**.

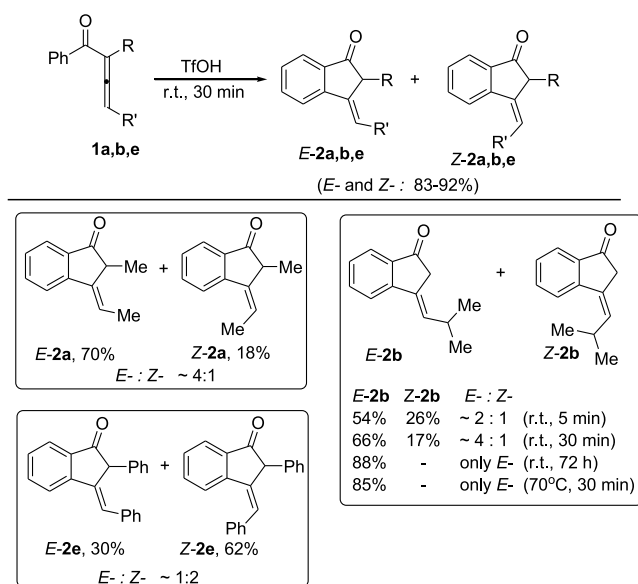
(TfOH) (entry 1), Lewis acid AlCl<sub>3</sub> (entry 4) at room temperature for 30 min, or acidic zeolites at an elevated temperature of 100 °C for 60 min (entries 6, 7). Other acids, H<sub>2</sub>SO<sub>4</sub>, CF<sub>3</sub>CO<sub>2</sub>H (entries 2, 3), or AlBr<sub>3</sub> (entry 5), were less efficient in this transformation, affording lower yields of target compound **3c**. It should be noted that the precursor of indenone **3c** is Nazarov cyclization product **2c**, which was not detected in our experiments. Previously, the formation of methyldiene indenone **2c** and its isomerization into compound **3c** was observed under the action of Lewis acids BF<sub>3</sub>·Et<sub>2</sub>O or In(OTf)<sub>3</sub>.<sup>6</sup> This means that a fast isomerization of **2c** into **3c** takes place in strong Brønsted (TfOH) and Lewis (AlCl<sub>3</sub>) acids in our study. The driving force of this isomerization is the formation of the thermodynamically more stable compound **3c**, having a more substituted double bond C=C, which is conjugated with the carbonyl group.

According to the literature data,<sup>5–9</sup> acid-promoted Nazarov cyclization of aroyl-substituted allenenes proceeds through an

intermediate formation of cationic species generated by Lewis acid coordination or Brønsted acid protonation of the carbonyl oxygen of starting allenes. Thus, in TfOH, allene **1c** gives rise to the O-protonated species **Ac**, which is cyclized into indanone **2c** (see scheme in Table 1). We carried out DFT calculations of Gibbs energies  $\Delta G_{298}$  for the reactions  $1c \rightarrow Ac \rightarrow 2c \rightarrow 3c$ , which yielded negative  $\Delta G_{298}$  values, indicating the thermodynamic benefits of both cyclization and isomerization (see scheme in Table 1 and details of DFT calculations in the SI).

Based on the data on acid-promoted cyclization of allene **1c** into indanone **3c** (Table 1), we chose the following conditions for the transformation of other allenes **1**: TfOH, room temperature, 30 min. Nazarov cyclization products, *E*-/*Z*-alkylidene indanones **2a,b,e**, were obtained from allenes **1a,b,e** (Scheme 2). The *E*-/*Z*-configuration of the carbon–carbon

**Scheme 2. Nazarov Cyclization of Allenes 1a,b,e into the Corresponding Alkylidene Indanones 2a,b,e in TfOH**



double bond in compounds **2a,b,e** was determined by NOESY correlations between the vinyl proton of this bond with neighbor aromatic or aliphatic protons of the indanone core (see Figures S26, S31, and S34 in the SI). Under the same conditions, allene **1d,k** gave a complex mixture of oligomeric materials. These allenes contain electron-rich substituents (two phenyl groups in **1d** and a methylenedioxyphenyl group in **1k**), which may undergo an intermolecular electrophilic attack by reactive cationic species, leading to oligomer formation.

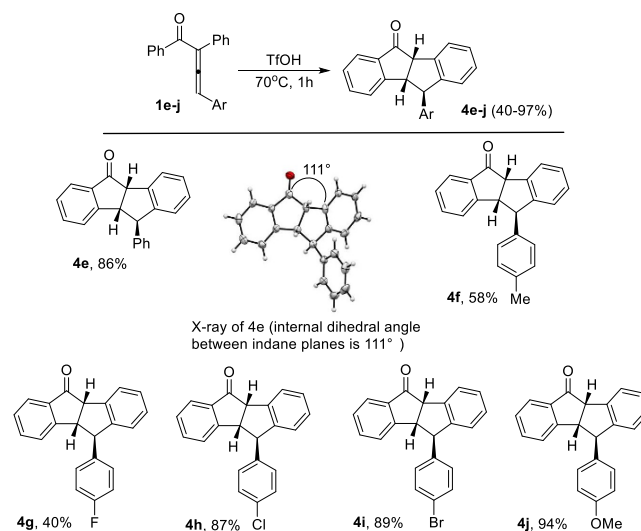
Reactions of allene **1b** were carried out under various conditions. It was found that the initially formed mixture of *E*-/*Z*-isomers of **2b** was completely transformed into the *E*-isomer upon increasing the reaction time (72 h at room temperature) or temperature (70 °C during 30 min) (Scheme 2). According to DFT calculations, the isomerizations of *Z*-**2b** to *E*-**2b** and *Z*-**2e** to *E*-**2e** are thermodynamically favorable processes, with  $\Delta G_{298}$  values of  $-10.1$  and  $-6.3$  kJ/mol, respectively (see DFT calculations in the SI).

It should be especially noted that isomerization of indanones **2a,b,e** into the corresponding indenones **3**, similar to reaction  $2c \rightarrow 3c$  (Table 1), was not observed at all, even at an elevated

temperature of 70 °C in TfOH for compound **2b** (see Scheme 2).

Benzoyl-diphenyl substituted allenes **1e** furnished Nazarov cyclization product *E*-/*Z*-**2e** in TfOH at room temperature for 30 min (Scheme 2). Then, we decided to conduct the reaction of allene **1e** in TfOH at a higher temperature of 70 °C. Surprisingly, the formation of fused indano–indanone **4e** was observed in a high yield of 86% after 1 h; the structure of **4e** was determined by X-ray analysis (Scheme 3). Under the same

**Scheme 3. Stereoselective Cyclization of Allenes 1a–j into Ketones 4a–j in TfOH<sup>a</sup>**

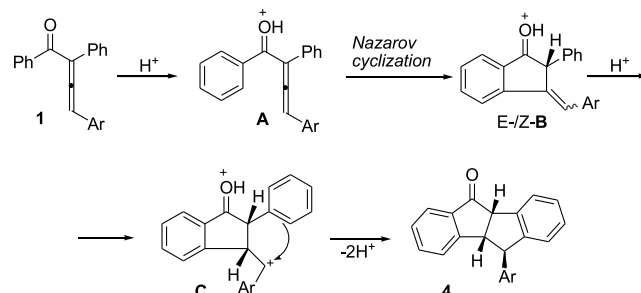


<sup>a</sup>For X-ray of **4e**: ellipsoid contour probability levels are 50%.

conditions, other aryl-benzoyl-phenyl-substituted allenes **1f–j** gave ketones **4f–j** of the same structure. The formation of compounds **4** proceeds very stereoselectively, leading to the *cis*-arrangement of the aryl substituent and protons at the carbon–carbon bond between indane and indanone cores. Apart from X-ray data for ketone **4e**, the stereochemistry of compounds **4** was confirmed by NOESY correlations (see Figures S46 and S54 in the SI). Compounds **4** have a bent structure, with an internal dihedral angle between the indane planes of the indano–indanone system of around 111° (see the X-ray of **4e** in Scheme 3).

A plausible reaction mechanism for the cyclization of allenes **1** to ketones **4** in TfOH is presented in Scheme 4. Protonation of the carbonyl oxygen of allene **1** affords O-protonated species **A**, which undergoes Nazarov cyclization into cation *E*-/*Z*-**B**.

**Scheme 4. Plausible Reaction Mechanism of the Formation of Ketones 4 from Allenes 1 in TfOH**



The latter is protonated at the carbon of the double bond, leading to dication **C**, and this reaction step proceeds stereoselectively. The protonation of the C=C bond occurs from the least sterically hindered side, in the position opposite to that of the phenyl substituent in cation **B**. Then, species **C** is finally cyclized into ketone **4** in a way of electrophilic aromatic substitution. This step is also stereoselective. The aryl group is oriented outside the bent structure of the indano–indanone system to minimize spatial hindrance (see the X-ray of **4e** in Scheme 3).

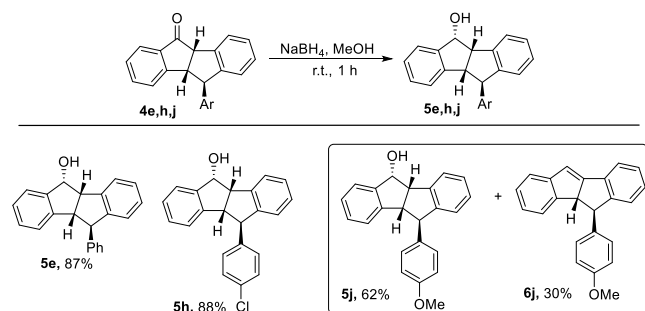
DFT calculations of Gibbs energies  $\Delta G_{298}$  of intermediate reactions leading from allene **1e** to target ketone **4e** revealed that protonation of allene **1e** with the formation of cation **Ae** and further cyclization into cations *Z*-/*E*-**Be** are thermodynamically very favorable (see details of calculations in the SI, Scheme S1).

It should be mentioned that in our previous work on cyclization of alkyl allene carboxylates into furanones,<sup>5</sup> we were able to generate the corresponding *O*-protonated species, structurally close to cations **A** (see Scheme 4), and observed these stable species by NMR in TfOH at room temperature. However, in the current study, we were unable to detect cations **A** by NMR in TfOH due to their rapid Nazarov cyclization.

DFT calculations were carried out to characterize species **A**. Energies of HOMO/LUMO, electrophilicity indices  $\omega$ ,<sup>49,50</sup> charge distribution, and contribution of atomic orbital into LUMO were estimated for cations **Aa,c,e**. Calculations showed that the electrophilic properties of the atom C3 in cations **A** are mainly explained by the charge factor, rather than the orbital one (see details in the SI, Table S3). These species give Nazarov cyclization products via electrophilic aromatic substitution (see the reaction mechanism in Scheme 4).

Furthermore, ketones **4e,h,j** were stereoselectively reduced with NaBH<sub>4</sub> to give alcohols **5e,h,j** in high yields (Scheme 5).

#### Scheme 5. Stereoselective Reduction of Ketones **4e,h,j** into Alcohols **5e,h,j** by NaBH<sub>4</sub>

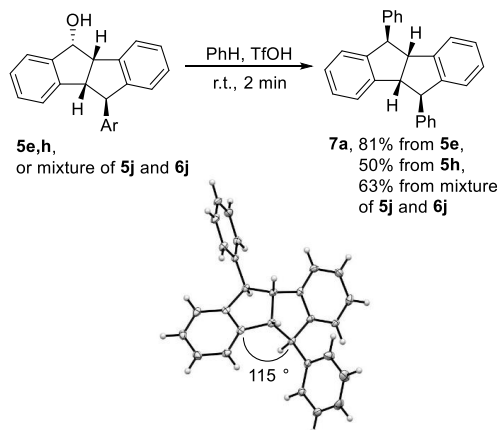


The stereoselectivity of the reaction may be explained by sterical factors, where the bulky borohydride anion approaches the carbonyl group from the sterically less hindered side, namely, outside of the bent indano–indanone plane of ketones **4**, rather than from inside the plane (see dihedral angle in X-ray of **4e** in Scheme 4). The stereochemistry of compounds **5** was unambiguously determined by NOESY spectra (see Figures S61, S68 in the SI). Alcohol **5j** underwent partial spontaneous dehydration, resulting in alkene **6j** (Scheme 5).

Then, alcohol **5e** was used as an alkylation agent in the Friedel–Crafts process. The reaction of compound **5e** with benzene in TfOH at room temperature took only 2 min, furnishing stereoselectively unsubstituted pallidol-like structure

**7a** (Scheme 6, see Pallidol in Scheme 1). An inversion of the carbon atom bearing a hydroxyl group occurred upon

#### Scheme 6. Synthesis of Pallidol-like Structure **7a** by the Reaction of Alcohols **5e,h** or Mixture of Compounds **5j** and **6j** with Benzene in TfOH; X-ray of **7a** with a Dihedral Angle between Indane Planes<sup>a</sup>



<sup>a</sup>Ellipsoid contour probability levels are 50%.

alkylation of benzene due to nucleophilic attack of the latter on the intermediate carbocation from its outside bent bis-indane plane, which is sterically more accessible. The structure of compound **7a** was confirmed by X-ray analysis (Scheme 6); the internal dihedral angle between the indane planes is around 115°, which is very close to that of compound **4e** (Scheme 3).

Other aryl-substituted alcohols **5h,j** and alkene **6j** in this reaction with benzene gave the same compound **7a** because of benzylic aryl-phenyl group exchange in superacids that we observed earlier for various diarylmethyl substituted substrates through intermediate formation of benzyl type carbocations.<sup>51,52</sup> It should be emphasized that the exchange of aryl groups at the formation of compound **7a** proceeds again stereoselectively due to spatial effects.

In conclusion, it has been found that benzoyl-substituted allenes undergo Nazarov cyclization in Brønsted superacid TfOH at room temperature with the formation of *E*-/*Z*-alkylidene indanones. Geminal benzoyl-phenyl-substituted allenes react deeper in TfOH at elevated temperature 70 °C, leading to fused indano–indanones. The latter are synthetic precursors of natural compounds of the Pallidol series.

#### ■ ASSOCIATED CONTENT

##### Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

##### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.5c05464>.

Experimental details, characterization data compounds, copies of NMR spectra, X-ray data, and data of DFT calculations (PDF)

##### Accession Codes

Deposition Numbers 2519218–2519219 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallo-

graphic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe [Access Structures service](#).

## AUTHOR INFORMATION

### Corresponding Author

Aleksander V. Vasilyev – *Institute of Chemistry, Saint Petersburg State University, Saint Petersburg 199034, Russia; Department of Chemistry, Saint Petersburg State Forest Technical University, Saint Petersburg 194021, Russia; [orcid.org/0000-0003-3628-1492](https://orcid.org/0000-0003-3628-1492); Email: [aleksvasil@mail.ru](mailto:aleksvasil@mail.ru), [a.vasilyev@spbu.ru](mailto:a.vasilyev@spbu.ru)*

### Authors

Oussama Abdelhamid Mammeri – *Institute of Chemistry, Saint Petersburg State University, Saint Petersburg 199034, Russia*

Irina A. Boyarskaya – *Institute of Chemistry, Saint Petersburg State University, Saint Petersburg 199034, Russia*

Dar'ya V. Spiridonova – *Institute of Chemistry, Saint Petersburg State University, Saint Petersburg 199034, Russia*

Mariya A. Kryukova – *Institute of Chemistry, Saint Petersburg State University, Saint Petersburg 199034, Russia*

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.orglett.5c05464>

### Author Contributions

O.A.M. conducted the experiments and data collections, and wrote the manuscript, I.A.B. performed the DFT calculations, D.V.S. and M.A.K. carried out the X-ray analysis, A.V.V. designed the project and wrote the manuscript. All authors have endorsed all data and perspectives.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The study was carried out at the Center for Magnetic Resonance, the Chemical Analysis and Materials Research Centre and the Research Center for X-ray Diffraction Studies of the Science Park of Saint Petersburg State University (Saint Petersburg, Russia).

## REFERENCES

- (1) Landor, S. R. (Ed.), *The Chemistry of the Allenes*, vols, Academic Press, London, 1982. pp 1–3.
- (2) Schuster, H. F.; Coppola, G. M. *Allenenes in Organic Synthesis*; Wiley, New York, 1988.
- (3) Elsevier, C. J. In: Helmchen, R. W.; Mulzer, J.; Schaumann, E. (Eds.), *Methods of Organic Chemistry (Houben-Weyl)*, E21a, Thieme, Stuttgart, Germany, 1995; pp 537–566.
- (4) Krause, N.; Hashmi, A. S. K. (Eds.), *Modern Allene Chemistry*, Vol. 1, Wiley-VCH, Weinheim, Germany, 2004; p 2.
- (5) Nagao, Y.; Lee, W.-S.; Kim, K. New Intramolecular Five-Endo-Mode Cyclization of Allenyl Aryl Ketones. *Chem. Lett.* **1994**, *23*, 389–392.
- (6) Zaky, M.; Li, Z.; Morgan, T.; LeFort, F.; Boyd, R.; Burnell, D. Lewis Acid-Mediated Cyclization of Allenyl Aryl Ketones. *J. Org. Chem.* **2019**, *84*, 13665–13675.
- (7) Teske, J.; Plietker, B. Fe-Catalyzed Cycloisomerization of Aryl Allenyl Ketones: Access to 3-Arylidene-indan-1-ones. *Org. Lett.* **2018**, *20*, 2257–2260.
- (8) Miao, M.; Jin, M.; Chen, P.; Wang, L.; Zhang, S.; Ren, H. Iron(III)-Mediated Bicyclization of 1,2-Allenyl Aryl Ketones:

Assembly of Indanone-Fused Polycyclic Scaffolds and Dibenzo[a,e]pentaleone Derivatives. *Org. Lett.* **2019**, *21*, 5957–5961.

(9) Dudnik, A. S.; Sromek, A. W.; Rubina, M.; Kim, J. T.; Kel'i, A. V.; Gevorgyan, V. Metal-Catalyzed 1,2-Shift of Diverse Migrating Groups in Allenyl Systems as a New Paradigm toward Densely Functionalized Heterocycles. *J. Am. Chem. Soc.* **2008**, *130*, 1440–1452.

(10) Miao, M.; Ren, H.; Xu, H.; Luo, Y.; Jin, M.; Chen, Z.; Xu, J. Catalyst-Free Regioselective Nazarov Cyclization of Aryl Allenyl Ketones. *Synthesis* **2018**, *50*, 349–360.

(11) Marx, V. M.; Burnell, D. J. Synthesis of 5-Hydroxycyclopent-2-enones from Allenyl Vinyl Ketones via an Interrupted Nazarov Cyclization. *Org. Lett.* **2009**, *11*, 1229–1231.

(12) Stephen, A.; Hashmi, K.; Bats, J. W.; Choi, J.-H.; Schwarz, L. Isomerizations on silica gel: Synthesis of allenyl ketones and the first Nazarov cyclizations of vinyl allenyl ketones. *Tetrahedron Lett.* **1998**, *39*, 7491–7494.

(13) Tius, M. A. Allene ether Nazarov cyclization. *Chem. Soc. Rev.* **2014**, *43*, 2979–3002.

(14) Hashmi, A. S. K. Transition Metal Catalyzed Dimerization of Allenyl Ketones. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1581–1583.

(15) Hashmi, A. S. K.; Schwarz, L. Switch from Palladium-Catalyzed Cycloisomerization/Dimerization of Terminal Allenyl Ketones to Preferential Formation of Monomers by a 5-Palladatricyclo-[4.1.0.0<sup>2,4</sup>]heptane Catalyst: Synthesis of Furans from Substrates Incompatible with the Commonly Used Silver Catalysts. *Chem. Ber.* **1997**, *130*, 1449–1456.

(16) Hashmi, A. S. K.; Ruppert, T. L.; Knöfel, T.; Bats, J. W. C–C Bond Formation by the Palladium-Catalyzed Cycloisomerization/Dimerization of Terminal Allenyl Ketones: Selectivity and Mechanistic Aspects. *J. Org. Chem.* **1997**, *62*, 7295–7304.

(17) Alcaide, B.; Almendros, P.; Martínez del Campo, T. Allene Substitution-Controlled Switching of Dimerization to Cycloisomerization in the PdII-Catalyzed Reaction of Terminal  $\alpha$ -Allenones. *Eur. J. Org. Chem.* **2007**, *2007*, 2844–2849.

(18) Hashmi, A. S. K.; Schwarz, L.; Choi, J.-H.; Frost, T. M. A New Gold-Catalyzed C–C Bond Formation. *Angew. Chem., Int. Ed.* **2000**, *39*, 2285–2288.

(19) Zhou, C.-Y.; Chan, P. W. H.; Che, C.-M. Gold(III) Porphyrin-Catalyzed Cycloisomerization of Allenones. *Org. Lett.* **2006**, *8*, 325–328.

(20) Nijamudheen, A.; Jose, D.; Datta, A. Why Does Gold(III) Porphyrin Act as a Selective Catalyst in the Cycloisomerization of Allenones? *J. Phys. Chem. C* **2011**, *115*, 2187–2195.

(21) Sromek, A. W.; Rubina, M.; Gevorgyan, V. 1,2-Halogen Migration in Haloallenyl ketones: regiodivergent synthesis of halofurans. *J. Am. Chem. Soc.* **2005**, *127*, 10500–10501.

(22) Zorba, L.; Kidonakis, M.; Saridakis, I.; Stratakis, M. Cycloisomerization of Conjugated Allenones into Furans under Mild Conditions Catalyzed by Ligandless Au Nanoparticles. *Org. Lett.* **2019**, *21*, 5552–5555.

(23) Dudnik, A.; Gevorgyan, V. Metal-Catalyzed [1,2]-Alkyl Shift in Allenyl Ketones: Synthesis of Multisubstituted Furans. *Angew. Chem., Int. Ed.* **2007**, *46*, 5195–5197.

(24) Mammeri, O. A.; Baranov, I. M.; Ivanov, A.Yu.; Boyarskaya, I. A.; Vasilyev, A. V. Synthesis of 2-(5H)-furanones by cyclization of alkyl allene carboxylates in triflic acid. *Tetrahedron* **2023**, *146*, 133649.

(25) Lozovskiy, S. V.; Ivanov, A.Yu.; Bogachenkov, A. S.; Vasilyev, A. V. 2,5-Dihydro-1,2-oxaphosphol-2-ium Ions, as Highly Reactive Phosphorus-Centered Electrophiles: Generation, NMR Study and Reactions. *ChemistrySelect* **2017**, *2*, 4505–4510.

(26) Bogachenkov, A. S.; Dogadina, A. V.; Boyarskaya, I. A.; Boyarskiy, V. P.; Vasilyev, A. V. Synthesis of 1,4-dihydrophosphinoline 1-oxides by acid-promoted cyclization of 1-(diphenylphosphoryl)allenenes. *Org. Biomol. Chem.* **2016**, *14*, 1370–1381.

(27) Lozovskiy, S. V.; Bogachenkov, A. S.; Dogadina, A. V.; Vasilyev, A. V. Acid-promoted transformations of aryl substituted diphenylphosphoryl allenenes. *Tetrahedron Lett.* **2016**, *57*, 3167–3170.

- (28) Bogachenkov, A. S.; Dogadina, A. V.; Boyarskiy, V. P.; Vasilyev, A. V. Acid-promoted transformations of 1-(diphenylphosphoryl)-allenes: synthesis of novel 1,4-dihydrophosphinoline 1-oxides. *Org. Biomol. Chem.* **2015**, *13*, 1333–1338.
- (29) Stoikov, I. I.; Antipin, I. S.; Burilov, V. A.; Kurbangaliev, A. R.; Rostovskii, N. V.; Pankova, A. S.; Balova, I. A.; Remizov, Yu. O.; Pevzner, L. M.; Petrov, M. L.; Vasilyev, A. V.; Averin, A. D.; Beletskaya, I. P.; Nenaidenko, V. G.; Beloglazkina, E. K.; Gromov, S. P.; Karlov, S. S.; Magdesieva, T. V.; Prishchenko, A. A.; Popkov, S. V.; Terent'ev, A. O.; Tsaplina, G. V.; Kustova, T. P.; Kochetova, L. B.; Magdalinova, N. A.; Krasnokutskaya, E. A.; Nyuchev, A. V.; Kuznetsova, Yu. L.; Fedorov, A. Yu.; Egorova, A. Yu.; Grinev, V. S.; Sorokin, V. V.; Ovchinnikov, K. L.; Kofanov, E. R.; Kolobov, A. V.; Rusinov, V. L.; Zyryanov, G. V.; Nosov, E. V.; Bakulev, V. A.; Belskaya, N. P.; Berezkina, T. V.; Obydenov, D. L.; Sosnovskikh, V. Ya.; Bakhtin, S. G.; Baranova, O. V.; Doroshkevich, V. S.; Raskildina, G. Z.; Sultanova, R. M.; Zlotskii, S. S.; Dyachenko, V. D.; Dyachenko, I. V.; Fisyuk, A. S.; Konshin, V. V.; Dotsenko, V. V.; Ivleva, E. A.; Reznikov, A. N.; Klimochkin, Yu. N.; Aksenov, D. A.; Aksenov, N. A.; Aksenov, A. V.; Burmistrov, V. V.; Butov, G. M.; Novakov, I. A.; Shikhaliyev, Kh. S.; Stolpovskaya, N. V.; Medvedev, S. M.; Kandalintseva, N. V.; Prosenko, O. I.; Menshchikova, E. B.; Golovanov, A. A.; Khashirova, S. Yu. Organic chemistry in Russian universities. Achievements of recent years. *Russ. J. Org. Chem.* **2024**, *60*, 1361–1584.
- (30) Khan, M. A.; Nabi, S. G.; Prakash, S.; Zaman, A. Pallidol, a resveratrol dimer from *Cissus pallida*. *Phytochemistry* **1986**, *25*, 1945–1948.
- (31) Baderschneider, B.; Winterhalter, P. Isolation and Characterization of Novel Stilbene Derivatives from Riesling Wine. *J. Agric. Food Chem.* **2000**, *48*, 2681–2686.
- (32) Delaunay, J. C.; Castagnino, C.; CheÁze, C.; Vercauteren, J. Preparative isolation of polyphenolic compounds from *Vitis Vinifera* by centrifugal partition chromatography. *J. Chromatogr. A* **2002**, *964*, 123–128.
- (33) Guebaila, H. A.; Chira, K.; Richard, T.; Mabrouk, T.; Furiga, A.; Vitrac, X.; Monti, J. P.; Delaunay, J. C.; Mérillon, J. M. Hopeaphenol: The first resveratrol tetramer in wines from North Africa. *J. Agric. Food Chem.* **2006**, *54*, 9559–9564.
- (34) He, S.; Jiang, L.; Wu, B.; Pan, Y.; Sun, C. Pallidol, a resveratrol dimer from red wine, is a selective singlet oxygen quencher. *Biochem. Biophys. Res. Commun.* **2009**, *379*, 283–287.
- (35) Zhong, C.; Zhu, J.; Chang, J.; Sun, X. Concise total syntheses of (±)isopaucifloral F, (±)quadrangularin A, and (±)pallidol. *Tetrahedron Lett.* **2011**, *52*, 2815–2817.
- (36) Keylor, M. H.; Matsuura, B. S.; Stephenson, C. R. J. Chemistry and Biology of Resveratrol-Derived Natural Products. *Chem. Rev.* **2015**, *115*, 8976–9027.
- (37) Duta-Bratu, C.-G.; Nitulescu, G. M.; Mihai, D. P.; Oлару, O. T. Resveratrol and Other Natural Oligomeric Stilbenoid Compounds and Their Therapeutic Applications. *Plants* **2023**, *12*, 2935.
- (38) Bejenaru, L. E.; BiÅa, A.; Belu, I.; Segneanu, A.-E.; Radu, A.; Dumitru, A.; Ciocilteu, M. V.; Mogoşanu, G. D.; Bejenaru, C. Resveratrol: A Review on the Biological Activity and Applications. *Appl. Sci.* **2024**, *14*, 4534.
- (39) Mattio, L. M.; Marengo, M.; Parravicini, C.; Eberini, I.; Dalavalle, S.; Bonomi, F.; Iametti, S.; Pinto, A. Inhibition of pancreatic  $\alpha$ -amylase by resveratrol derivatives: biological activity and molecular modeling evidence for cooperativity between viniferin enantiomers. *Molecules* **2019**, *24*, 3225.
- (40) Jeffrey, J. L.; Sarpong, R. An approach to the synthesis of dimeric resveratrol natural products via a palladium-catalyzed domino reaction. *Tetrahedron Lett.* **2009**, *50*, 1969–1972.
- (41) Snyder, S.; Gollner, A.; Chiriac, M. Regioselective reactions for programmable resveratrol oligomer synthesis. *Nature* **2011**, *474*, 461–466.
- (42) Zhong, C.; Liu, X.-H.; Hao, X.-D.; Chang, J.; Sun, X. Synthesis and biological evaluation of novel neuroprotective agents for paraquat-induced apoptosis in human neuronal SH-SY5Y cells. *Eur. J. Med. Chem.* **2013**, *62*, 187–198.
- (43) Klotter, F.; Studer, A. Total Synthesis of Resveratrol-Based Natural Products Using a Palladium-Catalyzed Decarboxylative Arylation and an Oxidative Heck Reaction. *Angew. Chem., Int. Ed.* **2014**, *53*, 2473–2476.
- (44) Matsuura, B. S.; Keylor, M. H.; Li, B.; Lin, Y.; Allison, S.; Pratt, D. A.; Stephenson, C. R. A scalable biomimetic synthesis of resveratrol dimers and systematic evaluation of their antioxidant activities. *Angew. Chem., Int. Ed. Engl.* **2015**, *54*, 3754–3757.
- (45) Li, W. L.; Chen, P. L.; Yang, Y. D.; Liu, X. L.; Dong, T. Synthesis of Diverse Oligostilbenes from FeCl<sub>3</sub>-Mediated Oxidation of Protected Resveratrol. *Tetrahedron.* **2016**, *72*, 210–215.
- (46) Han, J.; Tang, M.; Sun, X. Study on the Total Synthesis of Resveratrol Dimers Quadrangularin A and Pallidol. *Chin. J. Org. Chem.* **2020**, *40*, 1571–1577.
- (47) Hong, F.-J.; Low, Y.-Y.; Chong, K.-W.; Thomas, N. F.; Kam, T.-S. Biomimetic oxidation dimerization of anodically generated stilbene radical cations: effect of aromatic substitution on product distribution and reaction pathways. *J. Org. Chem.* **2014**, *79*, 4528–4543.
- (48) Cotman, A. E.; Modec, B.; Mohar, B. Stereoarrayed 2,3-disubstituted 1-indanols via ruthenium(II)-catalyzed dynamic kinetic resolution-asymmetric transfer hydrogenation. *Org. Lett.* **2018**, *20*, 2921–2924.
- (49) Parr, R. G.; Szentpaly, L. V.; Liu, S. Electrophilicity Index. *J. Am. Chem. Soc.* **1999**, *121*, 1922–1924.
- (50) Chattaraj, P. K.; Giri, S.; Duley, S. Update 2 of: electrophilicity index. *Chem. Rev.* **2011**, *111*, PR43–PR75.
- (51) Zakusilo, D. N.; Ryabukhin, D. S.; Boyarskaya, I. A.; Yuzikhin, O. S.; Vasilyev, A. V. Tandem superelectrophilic hydroarylation of C=C bond and carbonyl reduction in cinnamides: synthetic rout to 3,3-diarylpropylamines, valuable pharmaceuticals. *Tetrahedron.* **2015**, *71*, 102–108.
- (52) Sandzhieva, M. A.; Kazakova, A. N.; Boyarskaya, I. A.; Ivanov, A. Yu.; Nenajdenko, V. G.; Vasilyev, A. V. Friedel-Crafts alkylation of arenes with 2-halogeno-2-CF<sub>3</sub>-styrenes under superacidic conditions. Access to trifluoromethylated ethanes and ethenes. *J. Org. Chem.* **2016**, *81*, S032–S045.