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Authors Yulia V. Khoroshunova, Sergey A. Dobrynin, Tatyana V. Rybalova and Igor A. Kirilyuk

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ORCID® IDs Yulia V. Khoroshunova - <https://orcid.org/0000-0003-2923-4241>;
Tatyana V. Rybalova - <https://orcid.org/0000-0003-2398-5271>



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Azonanes from pyrrolidine: a double application of Hofmann-type two-carbon ring expansion sequence

Yulia V. Khoroshunova^{*1}, Sergey A. Dobrynin^{1,2}, Tatyana V. Rybalova¹, and Igor A. Kirilyuk¹

Address: ¹N.N. Vorozhtsov Institute of Organic Chemistry SB RAS, Academician Lavrentiev Ave. 9, Novosibirsk, 630090, Russian Federation and ²Novosibirsk State University, Pirogova Str. 2, Novosibirsk, 630090, Russian Federation

Email: Yulia Vladislavovna Khoroshunova - horoshunova@nioch.nsc.ru

* Corresponding author

Abstract

Fused nitrogen-containing heterocycles with seven or more atoms form the structural scaffold of many natural and synthetic molecules possessing diverse range of biological activity. A series of new fused azepanes and azonanes have been prepared *via* two sequential Hofmann-type cleavages of the endocyclic C–N bonds in azetidinium rings of decahydro-1*H*,6*H*-biscyclopenta[2,3]azeto[1,2-*a*:2'1'-*e*]pyrrolium system. The latter resulted from double intramolecular alkylation of pyrrolidine nitrogen in (1*R*(*S*),5*R*(*S*),7*R*(*S*),8*R*(*S*))-6-azadispiro[4.1.4.2]tridecane-1,8-diylidimethanol (**7**), which easily occurs under Appel reaction conditions. A simple 7-step synthesis of **7** from 1-chloronon-8-en-4-one and unsubstituted hydroxylamine *via* intramolecular 1,3-dipolar cycloaddition in α -pent-4-en-1-yl nitrones of pyrroline series was described earlier.

Keywords

azepanes; azonanes; Hofmann elimination; quaternary azetidinium salts; ring expansion

Introduction

Nitrogen-containing heterocycles with ring sizes of seven or more atoms have attracted increasing interest among researchers, as they form the structural core of numerous biologically important natural products as well as synthetic pharmaceuticals [1–4]. The azonane ring, fused with various carbo- or heterocyclic moieties, forms the core of many biologically active natural compounds. For example, quebrachamine could affect the symptoms of BPH [5, 6], lycoposerramine B inhibits acetylcholinesterase [7], vinblastine and rhazinilam block mitotic division, which is used to suppress cancer cell growth [8, 9] (Figure 1). Nevertheless, despite the importance of azonane derivatives in biological applications, their synthetic analogues remain poorly available. Therefore, developing methodologies for the efficient synthesis of structurally diverse azonanes remains a highly relevant and urgent task [10, 11].

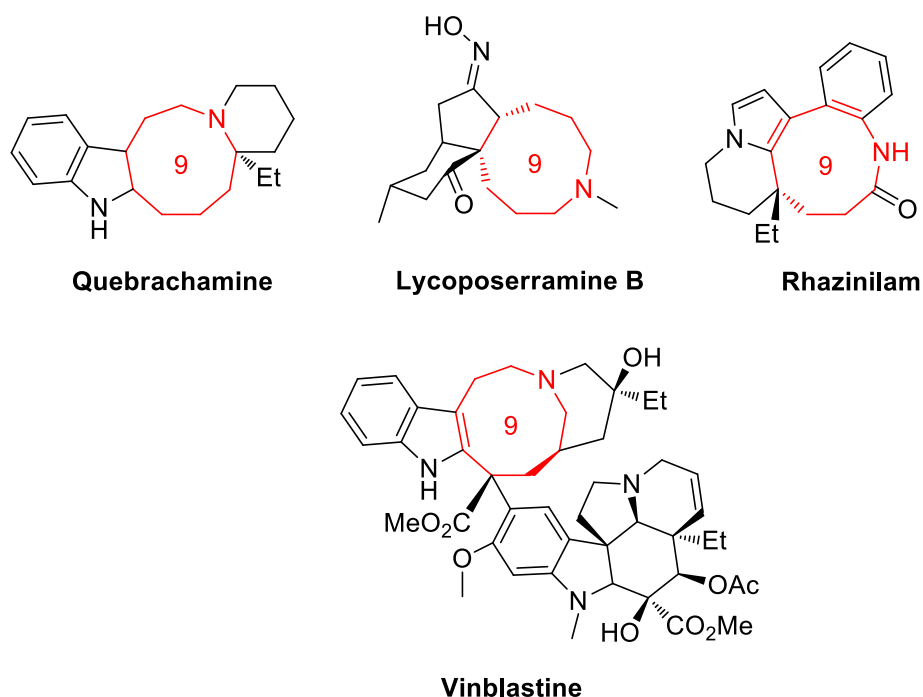


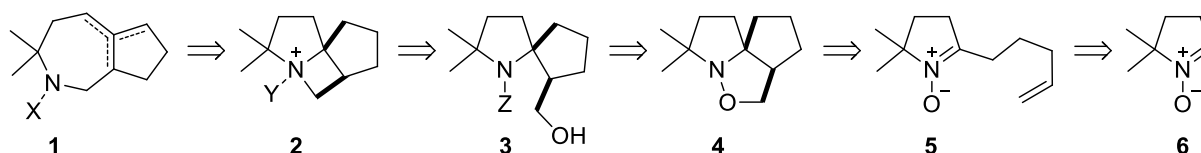
Figure 1: Examples of biologically active compounds, containing azonane ring.

In contrast to the widely available and synthetically accessible 5- and 6-membered nitrogen heterocycles – for which a variety of well-established synthetic protocols exist – the preparation of their 7-membered analogues, and especially larger *N*-heterocycles, is a challenging and non-trivial task. Among the general strategies for constructing heterocycles containing seven or more atoms, two principal approaches are commonly employed: intramolecular cyclization and ring expansion. However, complex multistep sequences tailored specifically to the target molecule are often required [12–14]. While both aforementioned strategies have been applied with reasonable success to seven-membered rings, the formation of medium-sized rings *via* direct cyclization is hampered by unfavorable transannular interactions and transannular strain, leading to high enthalpic barriers. Moreover, ring closure through cyclization is further disfavored by entropic factors [15].

In this context, ring-expansion methodologies represent a preferred route to medium-sized nitrogen heterocycles [16]. One of the simplest example of such

transformations involves cleavage of an endocyclic C–N bond in fused bi- or polycyclic systems, where the nitrogen atom has been pre-activated – typically by acylation or quaternization [17]. Ring expansion in these activated substrates can proceed *via* nucleophilic substitution induced by external nucleophiles [18–23], *via* reductive C–N bond cleavage [24–30], or through β -elimination processes [31–35].

In our previous work [36], we reported on the formation of cyclopenta[*c*]azepines **1** from spirocyclic pyrrolidine derivatives – 6-(hydroxymethyl)-1-azaspiro[4.4]nonanes **3** (Scheme 1).



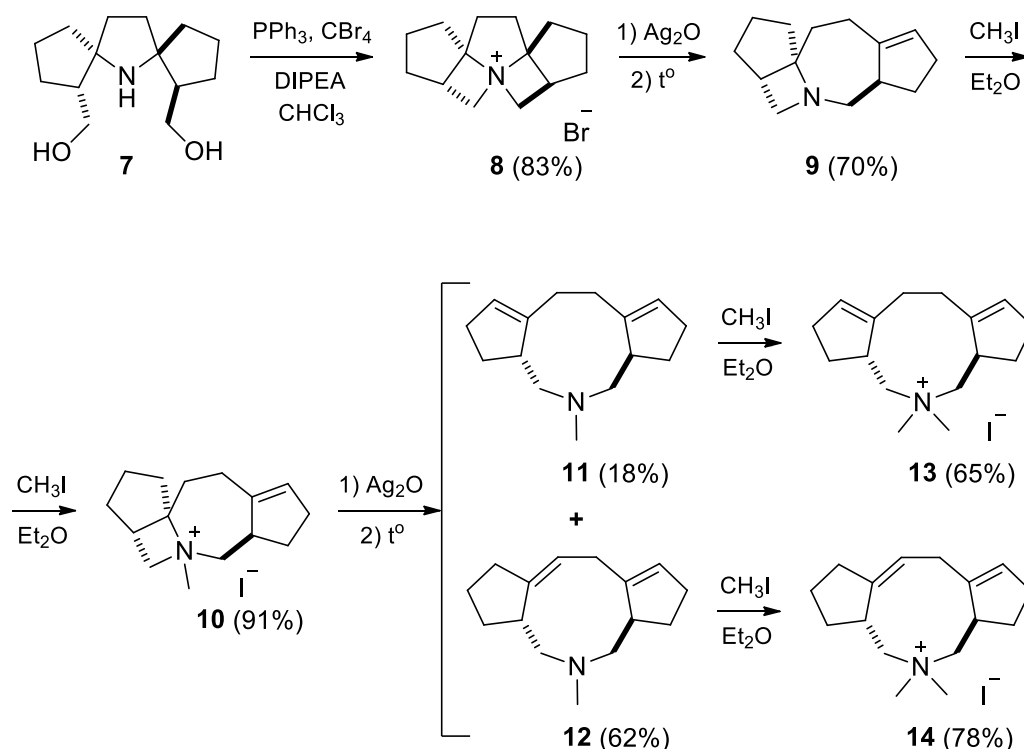
Scheme 1: Synthesis of cyclopenta[*c*]azepines **1**.

These reactions imply intramolecular alkylation of pyrrolidine nitrogen with the formation of strained cyclopenta[2,3]azeto[1,2-*a*]pyrrole system **2** and subsequent C–N bond scission in the azetidine ring *via* Hofmann elimination. The 6-(hydroxymethyl)-1-azaspiro[4.4]nonanes **3**, in turn, are easily accessible *via* addition of pentenylmagnesium bromide to aldonitrone of pyrroline series **6** followed by oxidation to nitronium **5**, intramolecular 1,3-dipolar cycloaddition and reductive cleavage of isoxazolidine ring [37].

In the present study, we extended the above strategy to the synthesis of fused 9-membered nitrogen heterocycles – dicyclopenta[*c,g*]azonines. Specifically, sequential double application of the aforementioned protocol to dispirocyclic pyrrolidine **7** [38] led – *via* a 7-membered azepane intermediate product – to the corresponding 9-membered azonane derivatives.

Results and Discussion

When subjected to the Appel reaction conditions in the presence of excess DIPEA, compound **7** [38] undergoes exhaustive intramolecular alkylation with the closure of two azetidine rings (Scheme 2).



Scheme 2: The synthesis of azonane derivatives **11-12** and their ammonium salts **13-14**.

The resulting pentacyclic azetidinium salt **8** was isolated as a colorless crystalline solid. The IR spectrum of **8** showed no absorption bands above 3100 cm^{-1} , indicating the absence of free OH or NH groups in the molecule. Both ^1H and ^{13}C NMR spectra were represented by a half of the signal set, as expected for a molecule with symmetrical structure. Full assignment of all NMR signals and the final confirmation of this compound structure was achieved based on ^1H - ^1H COSY, ^1H -

^{13}C HMBC, and ^1H – ^{13}C HSQC experiments. Conclusive proof of the azetidinium salt **8** structure was obtained using single-crystal X-ray diffraction analysis (Figure 2).

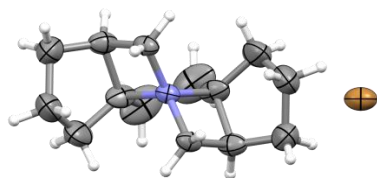


Figure 2: The structure of azetidinium salt **8** according to X-ray diffraction data.

Treatment of azetidinium salt **8** with wet silver (I) oxide in the darkness effected halide exchange, yielding the corresponding tetraalkylammonium hydroxide. Subsequent heating with alkali resulted in the formation of a mixture of two compounds, **9** and **9a**, inseparable by column chromatography. The multiplet at 5.20–5.29 ppm in the ^1H NMR spectrum of the major product **9** and the signals at 124.26 and 147.7 ppm in its ^{13}C NMR spectrum indicated the presence of a $>\text{C}=\text{CH}$ fragment in the structure, typical for Hofmann elimination product. The signals of the minor component **9a** (Figure 3) apparently corresponded to a fully saturated structure, presumably an amino alcohol, a typical byproduct under Hofmann elimination conditions associated with the nucleophilic opening of the azetidinium ring by hydroxide ion.

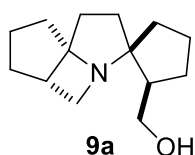
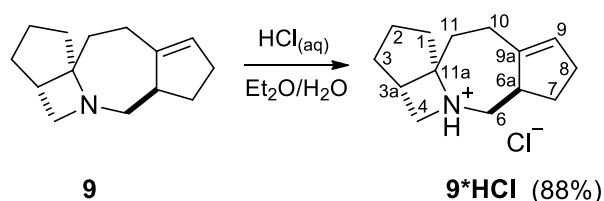


Figure 3: Proposed structure of minor product **9a**.

The pure **9** was isolated as a hydrochloride (Scheme 3).



Scheme 3: Synthesis and atom numbering of **9*HCl**.

A detailed analysis of the 2D ^1H - ^1H COSY, ^1H - ^{13}C HMBC, and ^1H - ^{13}C HSQC NMR spectra of the hydrochloride **9*HCl** allowed us to confirm its structure and assign all the signals. The HSQC spectrum revealed two pairs ^1H multiplets – two doublets of doublets at 3.77 and 3.48 ppm – associated with the ^{13}C carbon signal at 53.47 ppm, and two doublets of doublets at 3.14 and 2.91 ppm, associated with the ^{13}C carbon signal at 57.62 ppm, which were assigned to the geminal methylene protons of the $^4\text{CH}_2$ - and $^6\text{CH}_2$ -fragments, respectively, both adjacent to the heteroatom. According to the ^1H - ^1H COSY spectrum, the lower-field multiplet assigned to $^4\text{CH}_2$ is the part of the isolated spin system $^4\text{CH}_2$ - ^{3a}CH - $^3\text{CH}_2$ - $^2\text{CH}_2$ - $^1\text{CH}_2$, with all hydrogen atoms showing long-range HMBC interactions with the nodal carbon atom ^{11a}C . This pattern is consistent with the annulated system of the cyclopentane and azetidine rings. The higher-field multiplet assigned to $^6\text{CH}_2$, in turn, is a part of the spin system $^6\text{CH}_2$ - ^{6a}CH - $^7\text{CH}_2$ - $^8\text{CH}_2$ - $^9\text{CH}=\text{}$, where signals of all hydrogen atoms have cross-peaks with the fully substituted carbon atom of the $^{9a}\text{C}=\text{CH}$ double bond, according to ^1H - ^{13}C HMBC spectrum. Furthermore, an isolated spin system $^{11}\text{CH}_2$ - $^{10}\text{CH}_2$ was observed in the ^1H - ^1H COSY spectrum, and HMBC correlations from these protons to both ^{11a}C and ^{9a}C confirmed the presence of a fused 7- and 5-membered ring system. The absence of long-range HMBC interactions between the nodal carbon atom ^{11a}C and

the hydrogen atom of the $^9\text{CH=}$ fragment indicates that the double bond is located in the 5-membered ring rather than in the 7-membered one.

Compound **9** contains cyclopenta[2,3]azeto[1,2-a]azepine system and can be subjected to another ring expansion step. Amine **9** was treated with an excess of methyl iodide to afford a colorless crystalline substance **10** (Scheme 2). The NMR spectra of **10** were very similar to those of hydrochloride salt **9**•HCl, with the exception of a singlet of N-CH₃ group at 3.19 ppm in the ^1H spectrum and corresponding signal at 42.51 ppm in the ^{13}C NMR spectrum. The high-resolution mass spectrum supported the formation of quaternary salt, showing a peak $m/z=218.1903$, corresponding to the cation $[\text{M-I}]^+$ with molecular formula $\text{C}_{15}\text{H}_{24}\text{N}_1^+$. The salt **10** forms nice colorless crystals, but attempts to obtain X-ray data were unsuccessful, presumably due to twinning.

Similarly to the above procedure, the salt **10** was converted to corresponding hydroxide using wet Ag_2O and then was heated with an alkali. Two amines **11** and **12** were isolated from the reaction mixture by column chromatography. According to ^1H and ^{13}C NMR spectroscopy data, compound **11** contains a double bond of the $>\text{C}=\text{CH}$ type (a multiplet in the region of 5.30-5.38 ppm in the ^1H spectrum and corresponding signals at 125.43 and 151.15 ppm in the ^{13}C spectrum) and shows a half set of signals, which indicates its symmetrical structure.

Since the free amine **11** showed an evidence of decomposition upon storage, it was treated with iodomethane to give stable quaternary salt **13** (Scheme 2), which was fully characterized. The ^1H and ^{13}C NMR data for **13** supported its symmetric structure. Analysis of 2D ^1H - ^1H COSY, ^1H - ^{13}C HMBC, and ^1H - ^{13}C HSQC NMR spectra allowed us to confirm the structure of compound **13**, as well as to accurately assign all signals in its NMR spectra. Notably, in the ^{13}C NMR spectrum, the signals of the carbon atoms of methylene and methyl groups adjacent to heteroatom have a

J_{C-N} constant with the nitrogen atom. The structure of **13** was unambiguously confirmed by single-crystal X-ray analysis (Figure 4), revealing a symmetric tricyclic system comprising a central 9-membered azonane ring annulated with two cyclopentane rings, each bearing a double C=C bond.

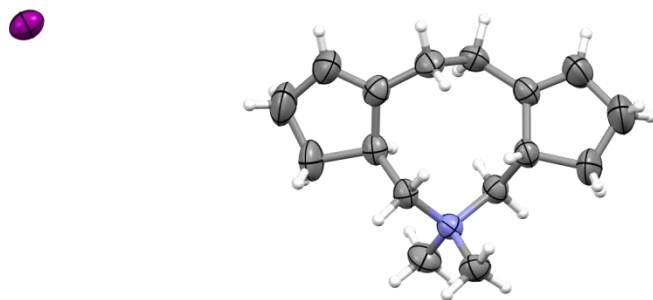


Figure 4: The structure of azonane-based ammonium salt **13** according to X-ray diffraction data.

In contrast, compound **12** contains a full set of signals in the 1H and ^{13}C NMR spectra, indicating its non-symmetric structure (Figure 5).

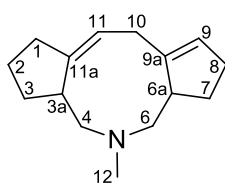


Figure 5: The structure and numbering of carbon atoms of compound **12**.

The presence of two different $>C=CH$ double bonds is revealed by two multiplets in the region of 5.24-5.32 and 5.35-5.40 ppm in the 1H spectrum and signals at 120.34, 124.87, 144.71 and 149.91 ppm in the ^{13}C spectrum. A detailed analysis of the 1H - 1H COSY, 1H - ^{13}C HMBC, and 1H - ^{13}C HSQC NMR spectra of compound **12** allowed its

full structural elucidation. Thus, in the ^1H NMR spectrum, a singlet with an integrated intensity of 3H is observed, which, according to the ^1H - ^{13}C HSQC correlation, is associated with a signal at 46.99 ppm in the ^{13}C NMR spectrum. These signals are unambiguously attributed to the methyl group $^{12}\text{CH}_3$ at the nitrogen atom (Figure 5). A spin system $^6\text{CH}_2$ - ^{6a}CH - $^7\text{CH}_2$ - $^8\text{CH}_2$ - $^9\text{CH}=\text{}$ is observed in the ^1H - ^1H COSY spectrum, and according to the ^1H - ^{13}C HMBC spectrum, these hydrogen atoms have long-range interactions with the $^9\text{aC}=\text{}$ carbon atom. This indicates the presence of an annulated 5-membered ring containing $^9\text{aC}=\text{}$ ^9CH double bond in the compound **12**. In another spin system $^1\text{CH}_2$ - $^2\text{CH}_2$ - $^3\text{CH}_2$ - ^{3a}CH - $^4\text{CH}_2$ observed in the ^1H - ^1H COSY spectrum, all hydrogen atoms have long-range interactions with the ^{11a}C carbon atom in the ^1H - ^{13}C HMBC correlation. The ^{11a}C carbon atom, according to the ^1H - ^{13}C HMBC data, interacts with the $^{11}\text{CH}=\text{}$ hydrogen, indicating the presence of exocyclic double bond $^{11a}\text{C}=\text{}$ ^{11}CH in the 5-membered ring. Since there are no interactions between the hydrogen atoms of the $^{11}\text{CH}=\text{}$ and $^9\text{CH}=\text{}$ fragments in the ^1H - ^1H COSY spectrum, and there are no cross-peaks between the pairs of ^{11a}C carbon and $^9\text{CH}=\text{}$ hydrogen atom and ^9aC carbon and $^{11}\text{CH}=\text{}$ hydrogen atom in the ^1H - ^{13}C HMBC correlation, it can be concluded that two isolated double bonds are present in the molecule **12**. According to ^1H - ^{13}C HSQC data, the ^{10}C carbon atom is associated with a doublet of doublets at 3.01 and with a multiplet in the 2.81-2.91 ppm region in the ^1H spectrum. The latter, in turn, have cross peaks with $^{11}\text{CH}=\text{}$ and $^9\text{CH}=\text{}$ in ^1H - ^1H COSY spectrum, which allows us to assign $^{10}\text{CH}_2$ -group to the methylene fragment between two C=C bonds. In addition, according to ^1H - ^{13}C HMBC data, one of the two methylene fragments at the heteroatom ($^4\text{CH}_2$) has long-range interactions with the $^{11a}\text{C}=\text{}$ carbon, and the second one ($^6\text{CH}_2$) – with $^9\text{aC}=\text{}$, and both fragments ($^4\text{CH}_2$ and $^6\text{CH}_2$) reveal cross peaks between themselves, as well as with the methyl group $^{12}\text{CH}_3$. The combination

of these data clearly shows that **12** has an asymmetric structure, containing a 9-membered azonane ring annulated with two 5-membered cycles.

Due to instability, **12** was also converted to its methylated ammonium salt **14**, isolated as colorless crystals. High-resolution mass spectrometry detected a peak with $m/z=359.1104$, corresponding to the molecular ion $[M]^+$ and consistent with the formula $C_{16}H_{26}NI$. That formula was also confirmed by elemental analysis data. Full assignment of all NMR signals and confirmation of compound **14** structure was achieved based on 1H - 1H COSY, 1H - ^{13}C HMBC, and 1H - ^{13}C HSQC experiments. Unambiguous proof of the ammonium salt **14** structure was obtained using single-crystal X-ray diffraction analysis (Figure 6).

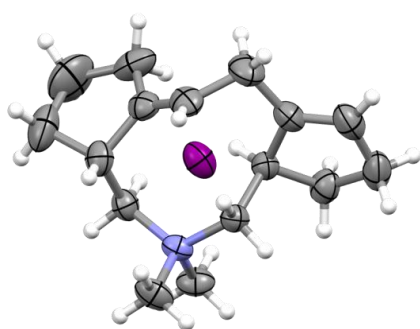


Figure 6: The structure of azonane-based ammonium salt **14** according to X-ray diffraction data.

Conclusion

In this work, we have demonstrated another example of how spirocyclic amines bearing a hydroxymethyl moiety – readily accessible *via* the intramolecular 1,3-dipolar cycloaddition of cyclic α -alkenylnitrones [37-40] – can be employed to access fused cyclic amines with 7- or 9-membered rings. This approach may prove highly

convenient for the preparation of biologically and/or pharmacologically active compounds.

Supporting Information

Detailed experimental procedures, representations of the IR, ^1H and ^{13}C NMR spectra, and X-ray crystallographic data. Crystallographic data for structures **8**, **13**, **14** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2591580-2591582 respectively.

Supporting Information File 1:

File Name: 8-13-14_structures_all_csd

File Format: cif

Title:

Supporting Information File 2:

File Name: Support Information_final.

File Format: docx

Title: Experimental section and characterization data of synthesized compounds.

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References

1. Luo, Sh.-P.; Huang, X.-Zh.; Guo, L.-D.; Huang, P.-Q. *Chin. J. Chem.* **2020**, *38*, 1723-1726. doi: 10.1002/cjoc.202000291
2. Zha, G.-F.; Rakesh, K. P.; Manukumar, H. M.; Shantharam, C. S.; Long, S. *Eur. J. Med. Chem.* **2019**, *162*, 465-494. doi:10.1016/j.ejmech.2018.11.031
3. Xu, M.; Gessner, G.; Groth, I.; Lange, C.; Christner, A.; Bruhn, T.; Deng, Zh.; Li, X.; Heinemann, S. H.; Grabley, S.; Bringmann, G.; Sattler, I.; Lin, W. *Tetrahedron* **2007**, *63*, 435-444. doi:10.1016/j.tet.2006.10.050
4. Rao, K. V.; Santarsiero, B. D.; Mesecar, A. D.; Schinazi, R. F.; Tekwani, B. L.; Hamann, M. T. *J. Nat. Prod.* **2003**, *66*, 823-828. doi:10.1021/np020592u
5. Deutsch, H. F.; Evenson, M. A.; Drescher, P.; Sparwasser, Ch.; Madsen, P. O. *J. Pharm. Biomed. Anal.*, **1994**, *12*, 1283-1287. doi:10.1016/0731-7085(94)00066-2
6. Stork, G.; Dolfini, J. E. *J. Am. Chem. Soc.* **1963**, *85*, 2872-2873. doi:10.1021/ja00901a061
7. Katakawa, K.; Kitajima, M.; Aimi, N.; Seki, H.; Yamaguchi, K.; Furihata, K.; Harayama, T.; Takayama, H. *J. Org. Chem.* **2005**, *70*, 658-663. doi:10.1021/jo0483825
8. Miyazaki, T.; Yokoshima, S.; Simizu, S.; Osada, H.; Tokuyama, H.; Fukuyama, T. *Org. Lett.* **2007**, *9*, 4737-4740. doi:10.1021/ol702040y
9. Okanishi, Yu.; Yotsumoto, Yo.; Yoshimitsu, T. *Org. Lett.* **2025**, *27*, 5840-5845. doi:10.1021/acs.orglett.5c01681
10. Liu, Yi.; He, Yi.; Liu, Ya.; Kun Wei, K.; Guo, W. *Org. Chem. Front.* **2021**, *8*, 7004-7008. doi:10.1039/d1qo01405f.
11. Beng, T. K.; Johnsen, A.; Gitonga, A.; Kaur, J. *RSC Adv.* **2025**, *15*, 20810-20814. doi:10.1039/d5ra03502c

12. Das, S. N.; Chowdhury, A.; Tripathi, N.; Jana, P. K.; Mandal, S. B. *J. Org. Chem.*, **2015**, *80*, 1136-1148. doi:10.1021/jo502672x
13. Chauhan, P. S.; Sacher, J. R.; Weinreb, S. *Org. Lett.* **2015**, *17*, 806-808. doi:10.1021/ol503571a
14. Suto, T.; Yanagita, Yu.; Nagashima, Yo.; Takikawa, Sh.; Kurosu, Ya.; Matsuo, N.; Sato, T.; Chida, N. *J. Am. Chem. Soc.* **2017**, *139*, 2952-2955. doi:10.1021/jacs.7b00807
15. Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95-102. doi:10.1021/ar00064a001
16. Donald, J. R.; Unsworth, W. P. *Chem. Eur. J.* **2017**, *23*, 8780-8799. doi:10.1002/chem.201700467
17. Lysenko, V.; Nazarenko, K.; Kostyuk, O. *J. Org. Pharm. Chem.* **2024**, *22*, 26-40. doi:10.24959/ophcj.24.312453
18. Masson, G.; Riota, S.; Pardo, D. G.; Cossy, J. *Eur. J. Org. Chem.* **2019**, *2019*, 5497-5507. doi:10.1002/ejoc.201900613
19. Drouillat, B.; Dorogan, I. V.; Kletskii, M.; Burov, O. N.; Couty, F. *J. Org. Chem.* **2016**, *81*, 6677-6685. doi:10.1021/acs.joc.6b01325
20. Leverenz, M.; Masson, G.; Pardo, D. G.; Cossy, J. *Chem. Eur. J.* **2021**, *27*, 16325-16328. doi:10.1002/chem.202102739
21. Masson, G.; Riota, S.; Pardo, D. G.; Cossy, J. *Org. Lett.* **2018**, *20*, 5019-5022. doi:10.1021/acs.orglett.8b02167
22. Sakanoue, S.; Harasawa, Sh.; Yamazaki, N.; Yoneda, R.; Kurihara, T. *Chem. Pharm. Bull.* **1990**, *38*, 2981-2985. doi:10.1248/cpb.38.2981
23. Sivaprakasam, M.; Couty, F.; David, O.; Marrot, J.; Sridhar, R.; Srinivas, B.; Rao, K. R. *Eur. J. Org. Chem.* **2007**, *2007*, 5734-5739. doi:10.1002/ejoc.200700616

24. Winn, M.; Zaugg, H. E. *J. Org. Chem.* **1968**, 33, 3779-3783.
doi:10.1021/jo01274a021
25. Reinecke, M. G.; Francis, R. F. *J. Org. Chem.* **1972**, 37, 3494-3499.
doi:10.1021/jo00795a022
26. Reinecke, M. G.; Daubert, R. G. *J. Org. Chem.* **1973**, 38, 3281-3287.
doi:10.1021/jo00959a009
27. Yardley, J. P.; Rees, R. W.; Smith, H. *J. Med. Chem.* **1967**, 10, 1088-1091.
doi:10.1021/jm00318a023
28. Herbst, D; Rees, R; Hughes, G. A.; Smith, H., *J. Med. Chem.* **1966**, 9, 865-868,
doi:10.1021/jm00324a020
29. Rostom, S. A. F. *Arch. Pharm.*, **2010**, 343, 73-80. doi:10.1002/ardp.200900219
30. Coll, J. C.; Crist, D. R.; Barrio, M. C. G.; Leonard, N. J. *J. Am. Chem. Soc.* **1972**,
94, 7092-7099. doi:10.1021/ja00775a037
31. Clemo, G. R.; Ramage, G. R.; Raper R. *J. Chem. Soc.* **1932**, 135, 2959-2969.
doi:10.1039/jr9320002959
32. Sugimoto, K.; Ohme, K.; Akiba, M.; Ohki S. *Chem. Pharm. Bull.* **1970**, 18, 1273-
1276. doi:10.1248/cpb.18.1273
33. Miyano, S.; Mibu, N.; Fujii, Sh.; Abe, N.; Sumoto, K. *J. Chem. Soc., Perkin Trans.*
1 1985, 14, 2611-2613. doi:10.1039/p19850002611
34. Reinecke, M. G.; Kray, L. R.; Francis, R. F. *Tetrahedron Lett.* **1965**, 6, 3549-
3553. doi:10.1016/S0040-4039(01)99537-1
35. Reinecke, M. G.; Kray, L. R.; Francis, R. F. *J. Org. Chem.* **1972**, 37, 3489-3493.
doi:10.1021/jo00795a021
36. Khoroshunova, Yu. V.; Morozov, D. A.; Taratayko. A. I.; Dobrynin, S. A.; Eltsov, I.
V.; Rybalova, T. V.; Sotnikova, Yu. S.; Dmitriy N. Polovyanenko, D. N.; Asanbaeva,
N. B.; Kirilyuk, I. A. *Molecules* **2021**, 26, 6000. doi:10.3390/molecules26196000

37. Khoroshunova, Yu. V.; Morozov, D. A.; Taratayko, A. I.; Gladkikh, P. D.; Glazachev, Yu. I.; Kirilyuk, I. A. *Beilstein J. Org. Chem.* **2019**, *15*, 2036-2042. doi:10.3762/bjoc.15.200
38. Khoroshunova, Yu. V.; Morozov, D. A.; Kuznetsov, D. A.; Rybalova, T. V.; Glazachev, Yu. I.; Bagryanskaya, E. G.; Kirilyuk, I. A. *Int. J. Mol. Sci.* **2023**, *24*, 11498. doi:10.3390/ijms241411498
39. Morozov, D.A.; Kirilyuk, I.A.; Komarov, D.A.; Goti, A.; Bagryanskaya, I.Yu.; Kuratieva, N.V.; Grigorev, I.A. *J. Org. Chem.* **2012**, *77*, 10688-10698. doi:10.1021/jo3019158
40. Edeleva, M.V.; Parkhomenko, D.A.; Morozov, D.A.; Dobrynin, S.A.; Trofimov, D.G.; Kanagatov, B.; Kirilyuk, I.A.; Bagryanskaya, E.G. *J. Polym. Sci. Part A Polym. Chem.* **2014**, *52*, 929-943. doi:10.1002/pola.27071