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Synthesis and structure of calix[4]arene with alkynone substituents on the lower rim

© **Anton A. Muravev**,[1,2] **Farida B. Galieva**,[2] **Svetlana E. Solovieva**,[1,2] and **Igor S. Antipin**[1,2]*
[1] *A.E. Arbuzov Institute of Organic and Physical Chemistry. Akad. Arbuzova, 8. Kazan, 420088. Tatarstan Republic. Russia.*
[2] *Organic Chemistry Division. A.M. Butlerov Institute of Chemistry. Kazan Federal University. Kremlevskaya, 18. Kazan, 420008. Tatarstan Republic. Russia.*
Phone: +7 (843) 272-73-94. E-mail: antonm@iopc.ru

*Supervising author; +Corresponding author
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Abstract

The triple carbon carbon bond is widely used in the reactions of 1,3-dipolar cycloaddition to dipoles of various nature, such as nitriloxides, azides and some others. This reaction has a wide synthetic potential also in the chemistry of calixarenes for the design of various heterocycles. But, however, the calixarenes and tiacalixarenes, which are substituted by ketoacetylene groups, and activated by the carbonyl group, on the basis of which an incomparably wider range of heterocyclic derivatives can be obtained than currently known, have not yet been known in the calixarene chemistry and are obtained on the calixarene platform. One of the important advantages of this so-called "inone approach" in calixarenes is the fact that in some cases the reaction centers of nucleophiles are not too much to lead to the products of intra- and intermolecular cross-linking of macrocycles, which is especially important when it is planned to synthesize polytopic receptors. In the present work, synthesis of the ketoacetylene derivative calix [4] arene ("calix-inone") in the 1,3-alternate configuration under the conditions of the copper-palladium catalyzed cross-coupling reaction is proposed. The structure of the obtained compound is established by a complex of physical methods, including IR and NMR spectroscopy and MALDI TOF mass spectrometry. Thus, as a result of the work, the possibility of forming precursors of a new type on the macrocyclic calix[4]arene platform on the basis of the ketoacetylene fragment, from which a wide range of heterocyclic derivatives can subsequently be obtained as useful as polytope receptors for metal ions, and also as active pharmaceutical ingredients.

References

[1] J. Vicens, J. Harrowfield. Calixarenes in nanoworld. *Netherlands: Springer*. **2007**.
[2] A.I. Konovalov, I.S. Antipin. *Mendeleev Commun.* **2008**. Vol.18. P.229-237.
[3] Y.-J. Chen, S.-C. Yang, C.-C. Tsai, K.-C. Chang, W.-H. Chuang, W.-L. Chu, V. Kovalev, W.-S. Chung. *Chem. Asian J.* **2015**. Vol.10. P.1025-1034.
[4] E.-H. Ryu, Y. Zhao. *Org. Lett.* **2005**. Vol.7. P.1035-1037.
[5] S.F. Vasilevsky, M.P. Davydova, G.A. Tolstikov. *Chem. Heterocycl. Compd.* **2008**. Vol.44. P.1257-1261.
[6] A. Kel'in, V. Gevorgyan. *J. Org. Chem.* **2002**. Vol.67. P.95.
[7] N. Gouault, M. Le Roch, C. Cornee, M. David, P. Uriac. *J. Org. Chem.* **2009**. Vol.74. P.5614.
[8] Z. Wang, Y. Shi, X. Luo, D-M. Han, W-P. Deng. *New J. Chem.* **2013**. Vol.37. P.1742.
[9] S. Hwang, H. Bae, S. Kim, S. Kim. *Tetrahedron*. **2012**. Vol.68. P.1460.
[10] C. Francois-Endelmond, T. Carlin, P. Thuery, O. Loreau, F. Taran. *Org. Lett.* **2010**. Vol.12. P.40.
[11] L. Yang, P. Xie, E. Li, X. Li, Y. Hunag, R. Chen. *Org. Biomol. Chem.* **2012**. Vol.10. P.7628.
[12] C. Taylor, Y. Bolshan. *Org. Lett.* **2014**. Vol.16. P.488-491.
[13] M.W. Logue, K. Teng. *J. Org. Chem.* **1982**. Vol.47. P.2549.
[14] S. Nahm, S.M. Weinreb. *Tetrahedron Lett.* **1981**. Vol.22. P.3815.
[15] M.S. Mohamed Ahmed, A. Mori. *Org. Lett.* **2003**. Vol.5. P.3057.
[16] Z. Wang, L. Li, Y. Huang. *J. Am. Chem. Soc.* **2014**. Vol.136. P.12233.
[17] W. Sun, Y. Wang, X. Wu, X. Yao. *Green Chem.* **2013**. Vol.15. P.2356.
[18] E. Mohammadi, B. Movassagh, M. Navidi. *Helv. Chim. Acta*. **2014**. Vol.97. P.70.
[19] S. Roy, M.P. Davydova, R. Pal, K. Gilmore, G.A. Tolstikov, S.F. Vasilevsky, I.V. Alabugin. *J. Org. Chem.* **2011**. Vol.76. P.7482-7490.

[20] M.P. Davydova, S.F. Vasilevskii, G.A. Tolstikov. *Russ. Chem. Bull.* **2011**. Vol.60. P.188-190.
[21] W.L.F. Armarego, C.L.L. Chai. Purification of Laboratory Chemicals. *Oxford: Elsevier*. **2009**.
[22] S. Cecioni, R. Lalor, B. Blanchard, J.-P. Praly, A. Imberty, S.E. Matthews, S. Vidal. Achieving high affinity towards a bacterial lectin through multivalent topological isomers of calix[4]arene glycoconjugates. *Chem. Eur. J*. **2009**. Vol.15. P.13232-13240.