ORGANOBORON DERIVATIVES OF STEREOREGULAR PHENYLCYCLOSILSESQUIOXANES

Anton A. Anisimov^a, Fedor V. Drozdov^b, Yulia S. Vysochinskaya^{a,b}, Ekaterina O. Minyaylo^a, Alexander S. Peregudov^a, Fedor M. Dolgushin^{a,c}, Olga I. Shchegolikhina^{a*}, Aziz M. Muzafarov_{a,b}

^a A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS) Russia, Moscow, Vavilova St. 28,

^b Enikolopov Institute of Synthetic Polymeric Materials Russian Academy of Sciences (ISPM RAS), Russia, Moscow

^c Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences (IGIC RAS), Russia, Moscow

*olga@ineos.ac.ru

Abstract

This paper presents the synthesis of organoboron derivatives of stereoregular 4-, 6-, and 12-unit phenylcyclosilsesquioxanes. All the compounds obtained were isolated in good yields (70-80%) and were fully characterized by ¹H, ¹³C, ²⁹Si, ¹¹B NMR, IR spectroscopy, HRMS ESI, and elemental microanalysis. The structure of key modifier, obtained for the first time, 4- (tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) dimethylvinylsilane was also confirmed by single-crystal XRD.

In the past decade, there has been intense work in the field of synthesizing and studying the properties of new supramolecular systems.¹⁻⁴ This motivated by the desire to create new, unique materials with a given set of properties. The production of such materials became possible due to the development of modern physicochemical methods of analysis that allow one to accurately determine the structure of compounds and identify the "structure-property" relationship.⁵

Of the wide variety of existing supramolecular systems, three large classes can be distinguished that differ in the type of bonding: hydrogen-bonded organic frameworks (HOF),⁶ covalent organic frameworks (COF)⁷ and metal-organic frameworks (MOF).⁸ Each of these supramolecular classes offers promise for various applications.⁹⁻¹⁵ In this paper, we focus on the precursors for producing HOFs because such systems are capable of reversible structure reorganization, which allows one to obtain materials that are sensitive to external effects, which, in turn, is relevant for the creation of smart materials.^{16,17}

The search for new chemical compounds exhibiting specific interactions is an important task. Its solution would allow one to obtain materials with specified physical properties that can

and as starting compounds for synthesizing macromolecular scaffolds in Suzuki cross-coupling reactions.

Acknowledgments

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Grant of the Government of the Russian Federation No. 14.W03.31.0018)

NMR analysis was performed using the equipment of the Collaborative Access Center "Center for Polymer Research" of ISPM RAS.

The characterization of the compounds obtained was performed with financial support from the Ministry of Science and Higher Education of the Russian Federation using the equipment of the Center for molecular composition studies of INEOS RAS (IR and NMR spectroscopy, XRD, HRMS ESI, elemental analysis).

The synthesis of compounds 1-6 were funded by RFBR according to the research project № 18-302-00001.

References

1. Zhang D, Martinez A, Dutasta J-P. Chem. Rev. 2017; 117 (6): 4900-4942. DOI: 10.1021/acs.chemrev.6b00847

2. Yashima E, Ousaka N, Taura D, Shimomura K, Ikai T, Maeda K. *Chem. Rev.* 2016; 116 (22): 13752-13990. DOI: 10.1021/acs.chemrev.6b00354

3. Jiang Z-C, Xiao Y-Y, Kang Y, Pan M, Li B-J, Zhang S. ACS Appl. Mater. Inter. 2017; 9 (24): 20276-20293. DOI: 10.1021/acsami.7b03624

4. Moreira L, IIIescas B. M, Martín N. J. Org. Chem. 2017; 82 (7): 3347-3358. DOI: 10.1021/acs.joc.6b03030

5. Wolfgang H. *Macromolecules*. 2017; 50 (5): 1761-1777. DOI: 10.1021/acs.macromol.6b02736

6. Wang H, Li B, Wu H, Hu T-L, Yao Z, Zhou W, Xiang S, Chen B. J. Am. Chem. Soc. 2015; 137 (31): 9963-9970. DOI: 10.1021/jacs.5b05644

7. DeBlase C. R, Dichtel W. R. *Macromolecules*. 2016; 49 (15): 5297-5305. DOI: 10.1021/acs.macromol.6b00891

8. Choi S, Kim T, Ji H, Lee H-J, Oh M. J. Am. Chem. Soc. 2016; 138 (43): 14434-14440. DOI: 10.1021/jacs.6b08821

9. Bansal P, Bharadwaj L. M, Deep A, Rohilla S. K, Salar R. K. *Biotech.: Prosp. Appl.* 2013; 183–195. DOI:10.1007/978-81-322-1683-4_14

10. A.M. Grumezescu A. M. Organic Materials as Smart Nanocarriers for Drug Delivery; William Andrew Pub.; Elsevier: New York, 2018. DOI: 10.1016/C2016-0-04124-4

11. Schwartz H. A, Ruschewitz U, Heinke L. Photochem. Photobiol. Sci. 2018; 17(7): 864-873. DOI:10.1039/c7pp00456g