

VI NORTH CAUCASUS ORGANIC CHEMISTRY SYMPOSIUM

## **BOOK OF ABSTRACTS**

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## VI СЕВЕРО-КАВКАЗСКИЙ СИМПОЗИУМ ПО ОРГАНИЧЕСКОЙ ХИМИИ (СТАВРОПОЛЬ, 18-22 АПРЕЛЯ 2022 г.) - СТАВРОПОЛЬ: СКФУ, 2022. - 273 с.

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18-22 APRIL 2022

## STERIC EFFECTS IN ORGANOLITHIUMS: SELECTIVE METALATION AND SYNTHESIS OF NITROGEN HETEROCYCLES

2022

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In our work we present the application of steric effects for the non-trivial functionalization of aromatic and heteroaromatic amines with organolithiums. We have found that non-covalent Li…H interaction facilitates second metalation of 4-lithio-1,8-bis(dimethylamino)naphthalene opening a simple way to the hard-to-reach *peri*-disubstituted naphthalene proton sponges with up with 100% selectivity and up to 90% yield. It was demonstrated that presence of bulky substituent in close proximity to NMe<sub>2</sub> and OMe groups in dimethylaniline, anisole and 1-dimethylaminonaphthalene stabilises conformation with an unshared electron pairs turned towards bulky substituent. This forced conformation supresses DOM-effect, thus facilitating *meta*-metalation.



We have demonstrated that *N*-silylation "flips" the reactivity of 4-dimethylaminopyridine towards organolithiums leading to the formation of 4,4-disubstituted dihydropyridines: bulky SiMe<sub>3</sub> group sterically hinders the addition to the positions 2(6), facilitating nucleophilic attack to the position 4.

### "Flipped" reactivity:



We have found that the interaction between *peri*-dilithionapthalenes and nitriles leads to the formation of benzo[*de*]isoquinolines. Reaction starts with the formation of *peri*-diimides, which upon hydrolysis undergo intramolecular nucleophilic cyclisation facilitated by the proximity of imino groups.

#### Sterically forced cyclization



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