1,2-ZWITTERIONIC Ga COMPLEXES OF METHYLIDENEMALONATES AND THEIR REACTIONS WITH ACETYLENES

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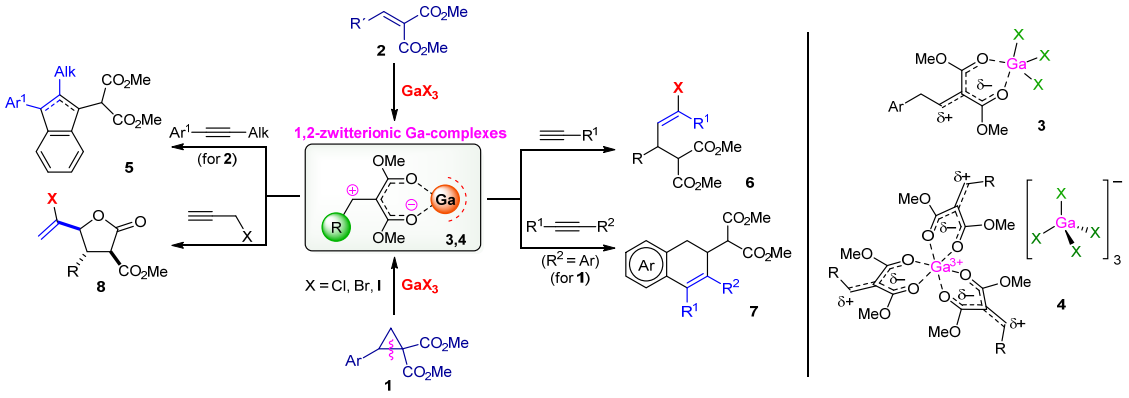
Donor-acceptor cyclopropanes **1** (DACs) are a broad class of substituted three-membered carbocycles. They are known for their capability to undergo small ring opening to act as 1,3-zwitterionic synthons. Our group developed a quiet different type of reactivity of DAC – the use of 2-arylcyclopropane-1,1- dicarboxylates (ACDC, **1**) as sources for generation of 1,2-zwitterions **3** in the presence of $GaCl_3$ [1]. We also examined the methylidenemalonates **2** as a simpler substrates for generation of 1,2-zwitterionic synthons **4** [2]. Complexes obtained were identified by NMR spectra.



Now we demonstrate a new approach for using ACDC and methylidenemalonates **2** in reactions with acetylenes in the presence of $GaCl_3$. As a result, we have been developed a new strategy for assembly of substituted indenes **5**, (3-haloallyl)malonates **6**, dihydronaphtalenes **7** and lactones **8**. All processes were very selective: the reactions between the complex **4** and arylalkylacetylenes occurs by a formation of indenes **5** with selective location of aryl and alkyl groups in structure; in case vinyl halides **6** the assembly of a molecule involving ACDC, acetylenes and GaX_3 proceeded with selective *trans*-functionalization. The reactivity of the 1,2-zwitterionic complex **3** in reactions with arylacetylenes occurs according to the type of [4+2]-annulation to form the dihydronaphthalene scaffold **7**. The reaction between 1,2-zwitterionic complexes **3,4** and propyn halides occurs with the selective formation of the lactone **8** as *trans*-isomer. As the result all discovered processes proceed with a high regio- and diastereoselectivity and good yields of products obtained.

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[1] R.A. Novikov, A.V. Tarasova, V.A. Korolev, V.P. Timofeev, Y.V. Tomilov, *Angew. Chem. Int. Ed.* **2014**, 53, 3187.

[2] R.A. Novikov, D.A. Denisov, K.V. Potapov, Ya.V. Tkachev, E.V. Shulishov, Y.V. Tomilov, *J. Am. Chem. Soc.* **2018**, 140, 14381.