

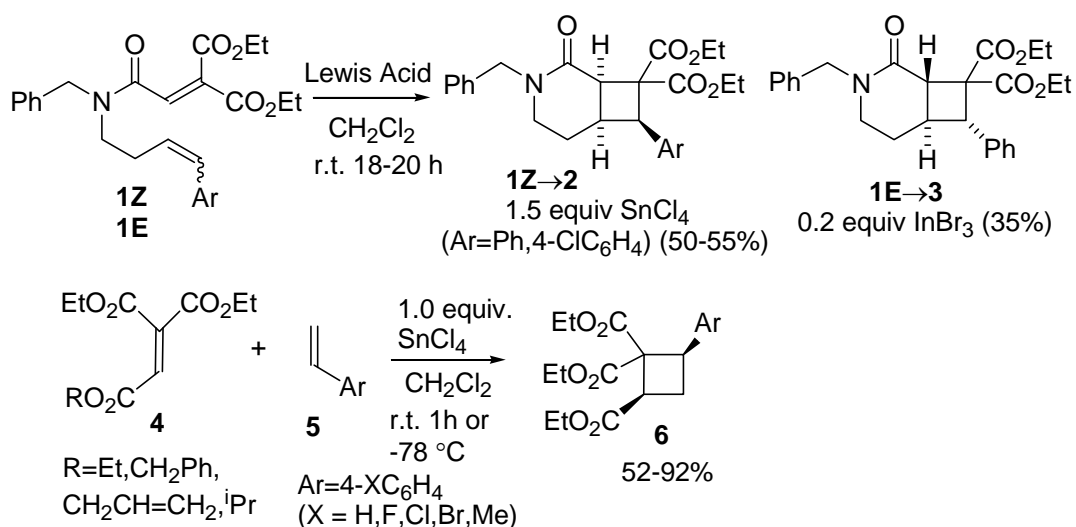
INTRA- AND INTERMOLECULAR STEREOSELECTIVE [2+2] CYCLOADDITION REACTIONS OF ETHENETRICARBOXYLATES AND STYRENES

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Construction of cyclobutane rings is an important objective due to their occurrence in many natural products and biologically active compounds and utilization in organic synthesis. Recently, we have reported intramolecular [2+2] and [4+2] cycloaddition reactions of ethenetricarboxylic acid 1,1-diester with cinnamylamines under the amide formation conditions in sequential processes [1]. In this work, intra- and intermolecular cycloaddition reactions of ethenetricarboxylates and styrenes have been investigated. While the reaction of (*Z*)-4-aryl-3-butenylamide of ethenetricarboxylate with 1-1.5 equiv. of Lewis acids such as SnCl₄ gave *cis*-fused cyclobutanes as major products, (*E*)-4-phenyl-3-butenylamide of ethenetricarboxylate with catalytic amounts of Lewis acids gave a *trans*-fused cyclobutane. Although [2+2] cycloadditions of electron-deficient alkenes and electron-rich alkenes were reported, the reaction with styrenes were relatively limited [2]. The reactions of ethenetricarboxylates and styrenes with 1 equiv. of SnCl₄ gave 1,3-*cis*-substituted cyclobutanes stereoselectively. The origin of observed selectivities has been examined by the DFT calculations.



[1] (a) S. Yamazaki, H. Sugiura, S. Ohashi, K. Ishizuka, R. Saimu, Y. Mikata, A. Ogawa, *J. Org. Chem.* **2016**, *81*, 10863. (b) H. Sugiura, S. Yamazaki, K. Go, A. Ogawa, *Eur. J. Org. Chem.* **2019**, 204.

[2] J.-L. Hu, L.-W. Feng, L. Wang, Z. Xie, Y. Tang, X. Li, *J. Am. Chem. Soc.* **2016**, *138*, 13151.