

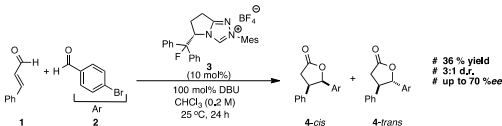
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新規含フッ素トリアゾリウム塩の創製と触媒的不斉ラクトン化反応への応用

○Phuc Thien LE¹, 喜屋武 龍二², 佐藤 浩平², 間瀬 暢之², 渡辺 修治², 鳴海 哲夫¹(静岡大工,²静岡大院工)

The study of umpolung, catalyzed by N-Heterocyclic carbenes (NHCs), has become a rapidly growing field in the past decade¹. In 2004, research groups of Glorius² and Bode³ have discovered and reported independently the concept of conjugated umpolung based on the catalytic generation of a homoenolate intermediate, to form γ -butyrolactone from enal and aryl aldehyde. While there are some approaches have been reported, the stereoselective control of homoenolates still remain challenging.

In this study, we have designed and synthesized the novel fluorinated triazolium salt **3** with the fluorine gauche effect ($\sigma_{C-H} \rightarrow \sigma_{C-F}^*$), which can control the position of the stereo-inducing group close to the homoenolate reaction site. When using triazolium salt **3** in the reaction of enal **1** and 4-bromobenzaldehyde **2**, good levels of enantioselectivity (70 %*ee* of **4-cis**, 50 %*ee* of **4-trans**) were observed with a low level of chemical yield (36 %) and diastereoselectivity (3:1 dr). Herein, we report the synthetic strategy of this type of NHCs precursor and its application for the asymmetrical lactone formation. A design and synthesis of triazolium salt **3** and the catalytic reactivity of NHCs derived from triazolium salt **3** in homoenolate addition will be also discussed.



¹ For review, see: Rovis, T., *et al.*, *Chem. Rev.* **2015**, *115*, 9307. ² Glorius, F., *et al.*, *Angew. Chem., Int. Ed.* **2004**, *43*, 6205. ³ Bode, J. W., *et al.*, *J. Am. Chem. Soc.* **2004**, *126*, 14370.