

NEW BENCH-STABLE ALLYLATION REAGENTS – HOW TUNING THE REACTIVITY ENABLES HIGHLY ENANTIOSELECTIVE ACCESS TO ALL STEREOISOMERS OF TERTIARY HOMOALLYLIC ALCOHOLS

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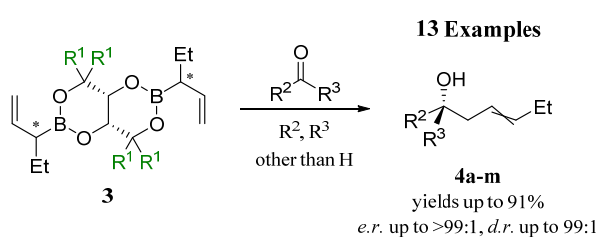
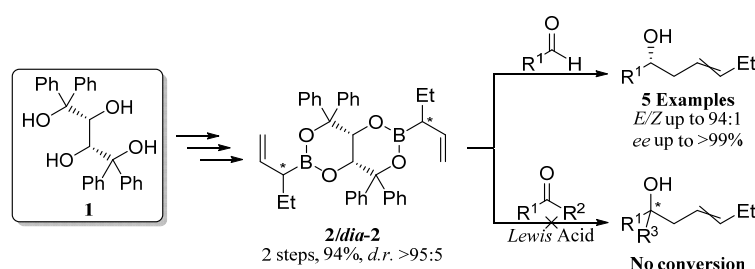
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As a very potent agent for the generation of synthetically valuable homoallylic compounds [1,2], we developed tartrate derived protecting group **1** providing an outstanding reactivity/stability balance. Thus,

the convenient and highly stereoselective syntheses of all four stereoisomers of secondary homoallylic alcohols depending on the configuration of the corresponding allylboronate **2/dia-2** could be demonstrated. However, due to their inherently lower reactivity, ketones remained inert to the systems established [3].



Thus, rational reagent design was employed ‘tuning’ the reagents’ reactivity suitably. Herein we present new allylation reagents **3** enabling access to all stereoisomers of tertiary homoallylic alcohols **4a-m**. Not only can the 2nd generation compounds be

utilized without requiring inert conditions, but moreover highly selective access to *E*- and *Z*- configured tertiary homoallylic alcohols was given for the first time. Conclusively, all synthetic approaches and findings were investigated by DFT-calculations, revealing further mechanistic insight and rationalizing the presented methodology thoroughly [4].

[1] M. Yus, J. C. González-Gómez, F. Foubelo, *Chem. Rev.* **2011**, *111*, 7774-7854.

[2] M. Yus, J. C. Gonzalez-Gomez, F. Foubelo, *Chem. Rev.* **2013**, *113*, 5595-5698.

[3] M. Brauns, F. Muller, D. Gülден, D. Böse, W. Frey, M. Breugst, J. Pietruszka, *Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 1548-1552.

[4] M. Brauns, M. Mantel, J. Schmauck, M. Guder, M. Breugst, J. Pietruszka, *Chem. Eur. J.*, **2017**, *23*, 12136-1214.