

# XXXV

Societa' Chimica  
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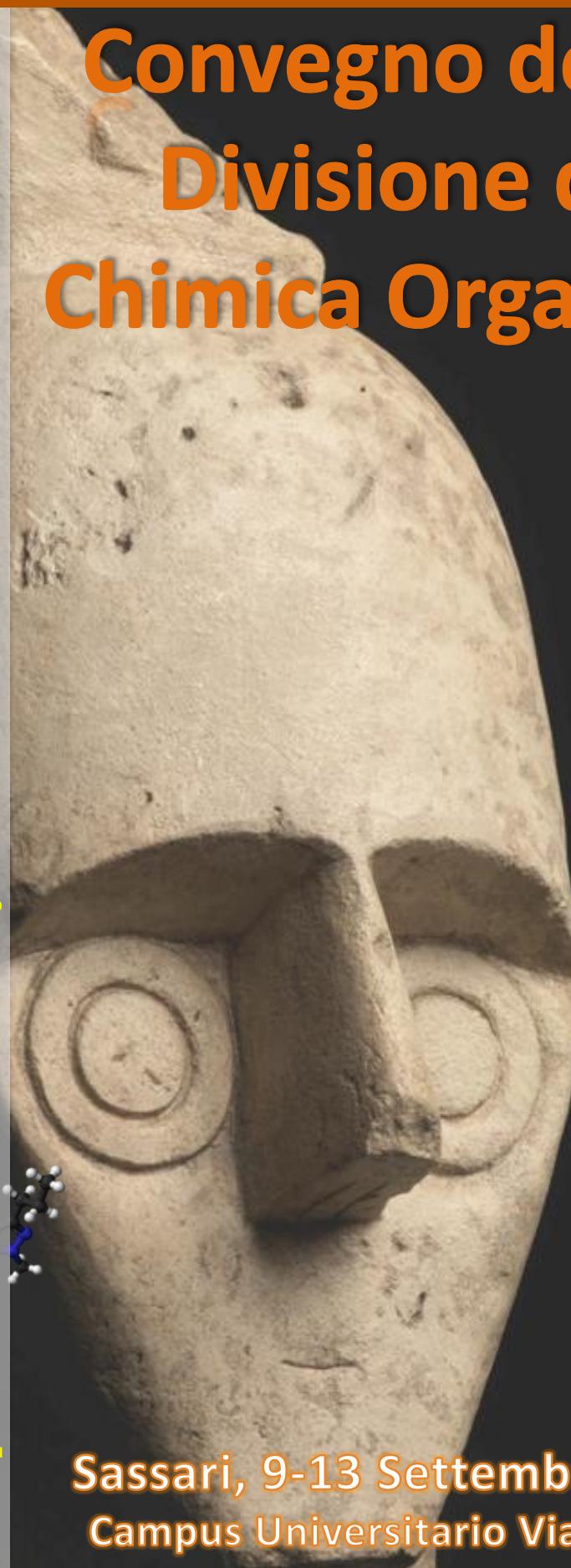
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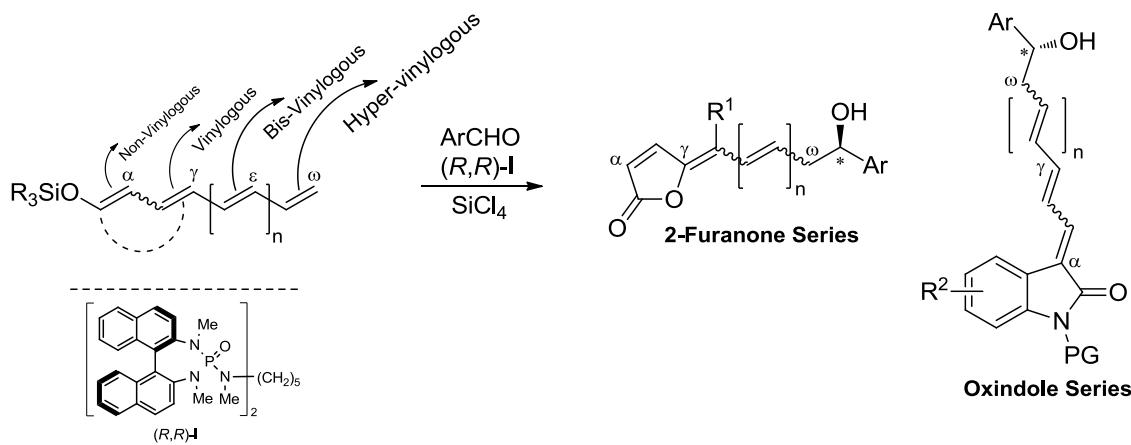
## Exploring the Boundaries of Vinylogous Mukaiyama Aldol Processes: Stereoselective Access to Polyunsaturated Homoallylic Alcohols

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Catalytic enantioselective vinylogous aldol reactions using extended enolates are of prominent value in synthetic organic chemistry. Such transformations create densely functionalized adducts whose stereocenters lie in proximity of one of more alkene moieties, which can be further elaborated to afford a realm of products varied in shape and complexity.<sup>(1)</sup> Originally used to forge  $\alpha,\beta$ -unsaturated- $\delta$ -hydroxycarbonyls, the majority of studies in this field have focused on single-vinylogous aldol techniques, leaving the application of more extended adaptations, giving densely unsaturated homoallylic alcohols, substantially unexplored.<sup>(2)</sup> Here, we report our advances in the development of enantioselective bis-vinylogous and hyper-vinylogous Mukaiyama aldol reactions between a series of polyenylsilyloxy furans (3) or polyenylsilyloxy indoles and aromatic aldehydes, realized by use of the enabling catalyst combination of silicon tetrachloride and Denmark's chiral bis-phosphoramido base (*R,R*)-I.<sup>(4)</sup> Several crucial issues such as the remote site-, enantio- and geometrical selectivity of the reaction will be highlighted, ultimately focusing on one main question: *how far can we push the limits of the vinylogous reactivity transmittal?*



### References

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- (2) (a) Ratjen, L.; Garcia-Garcia, P.; Lay, F.; Beck, M. E.; List, B. *Angew. Chem., Int. Ed.* **2011**, *50*, 754. (b) Denmark, S. E.; Kobayashi, T.; Regens, C. S. *Tetrahedron* **2010**, *66*, 4745.
- (3) Curti, C.; Battistini, L.; Sartori, A.; Lodola, A.; Mor, M.; Rassu, G.; Pelosi, G.; Zanardi, F.; Casiraghi, G. *Org. Lett.* **2011**, *13*, 4738.
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