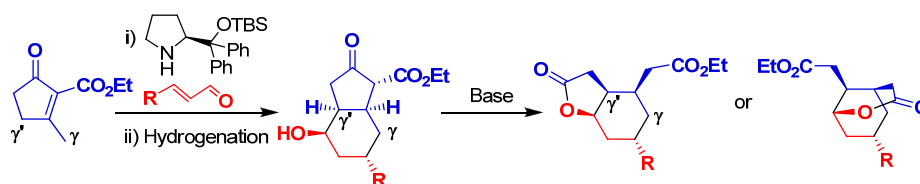


# DOUBLE VINYLOGOUS REACTIVITY OF THE $\gamma$ AND $\gamma'$ POSITIONS OF CYCLIC 2-ENONES: ORGANOCATALYSED ASYMMETRIC SYNTHESIS OF FUSED CARBOCYCLES

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A straightforward synthetic methodology for the asymmetric construction of important fused carbocycles containing the privileged bicyclo[4,3,0]nonane or bicyclo[4,4,0]decane framework, as well as, for certain key fused and bridged lactones is presented. This method oversees a dramatic increase in structural complexity both in terms of the stereocentre density and the 3D skeletal framework. The concept of an organocatalysed coupling of a LUMO-lowered dielectrophile (2-enal) with an easily enolizable cyclic 2-enone through two sequential vinylogous additions (first a regioselective vinylogous Michael addition from the  $\gamma$  position, then a vinylogous aldol from the  $\gamma'$  position) to afford the [3+3]-annulation product, has also been introduced for the first time. The starting cyclopentenone was synthesized from a simple furan using the sustainable chemistry of singlet oxygen.



All the actions were performed with a high degree of regioselectivity and with remarkable diastereo- and enantioselectivity, in one-pot operations [1].

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