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Rationally Designed Multifunctional Supramolecular Iminium Catalysis: Direct Vinyllogous Michael Addition of  
Unmodified Linear Dienol Substrates

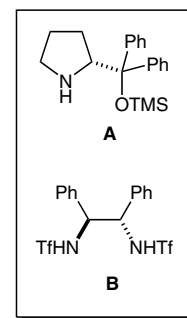
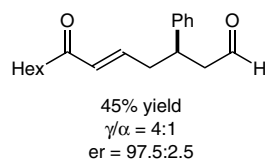
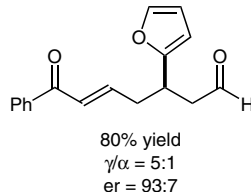
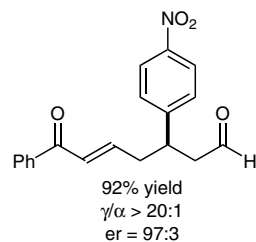
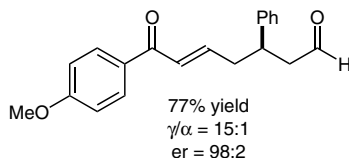
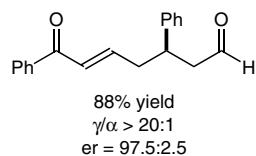
*Angew. Chem. Int. Ed.* **2014**, *53*, 14128–14131.

## Amine-Catalyzed Direct Vinyllogous Michael Addition of Dienols to Enals

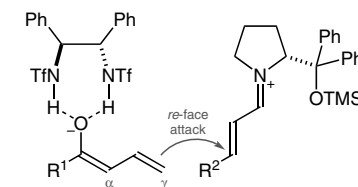


22 examples  
 45–92% yield  
 $\gamma/\alpha$  from 4:1 to >20:1  
 $E/Z > 20:1$   
 er from 93:7 to 98.5:1.5

### Selected examples:



### Proposed reacting ion pair complex:



**Significance:** Xu and co-workers report a vinyllogous Michael addition of acyclic alkyl and aryl allyl ketones to enals. The reaction is catalyzed by a chiral secondary amine (**A**) and a chiral hydrogen bond donor (**B**), which in combination enable the formation of the desired enones in moderate to excellent yields and regioselectivities, and with excellent enantioselectivities. The scalability of the reaction was proven in one experiment starting with 1.46 gram of phenyl allyl ketone.

**Comment:** While the application of catalyst **A** in combination with a 'regular' Brønsted acid or base (e.g., benzoic acid or DABCO) already furnished small amounts of desired product with excellent enantioselectivity, it required a second, anion-binding catalyst (**B**) to enhance the reactivity of the proposed  $\alpha,\beta$ -unsaturated iminium ion intermediate by ion pair separation and to shield the  $\alpha$ -position of the nucleophile, effecting the desired  $\gamma$ -selectivity. The concept of *supramolecular iminium ion catalysis* was previously reported by the same group (*Angew. Chem. Int. Ed.* **2012**, *51*, 12339).

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