

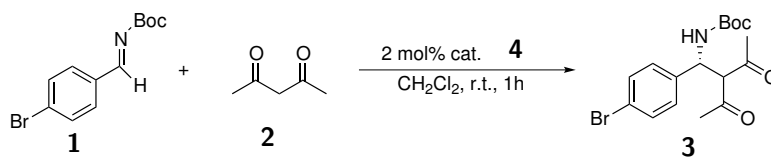
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## 1 Compound

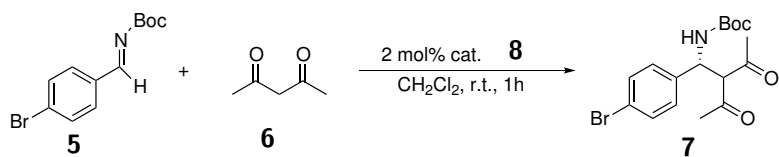


Scheme 1: Asymmetric Mannich reaction of of N-Boc-protected imine **1** and acetyl acetone **2** in the presence of catalytic amounts of **3**.

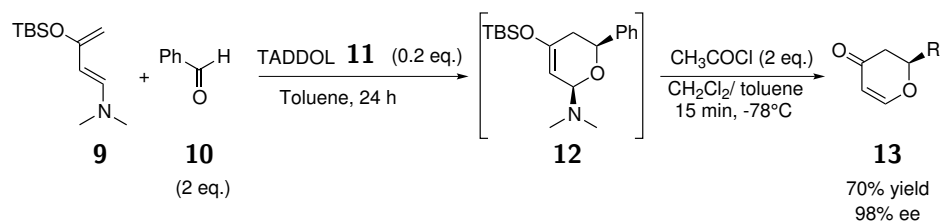
This two molecules are the starting materials **1 2** whereas this is the catalyst **3** and this is the product **4**.

This two molecules are the starting materials **5 6** whereas this is the catalyst **7** and this is the product **8**.

BAMOL **14** on the left and an X-Ray crystal structure of the BAMOL-benzaldehyde complex, with indicated hydrogen bonds



Scheme 2: Asymmetric Mannich reaction of N-Boc-protected imine **5** and acetyl acetone **6**.



Scheme 3: TADDOL catalyzed asymmetric hetero Diels-Alder reaction of diene **9** with phenylbenzaldehyde **10** to produce dihydropyrones **13**

### 1.1 **17**

Even this scheme is correct labeled the starting materials **15** the intermediate **16** and the product **17**.

### 1.2 Stronger chiral Brønsted acids

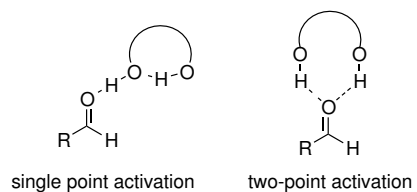


Figure 1: Point activation in which the substrates accept one or two H-bonds respectively.

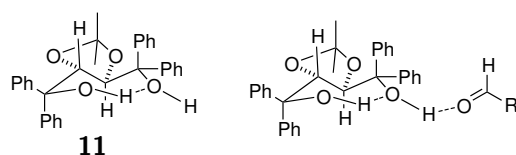
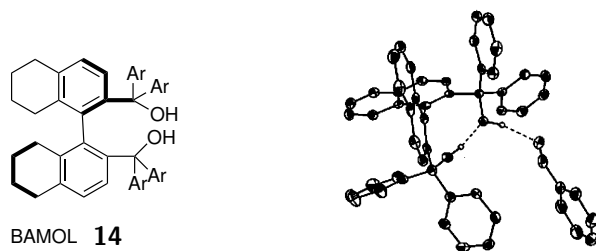
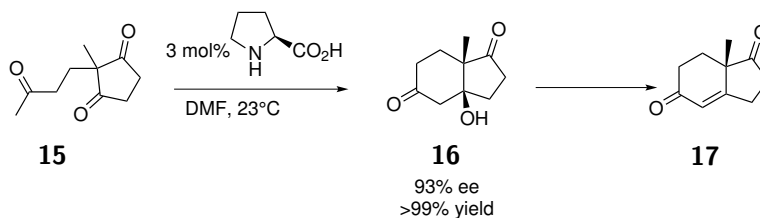


Figure 2: Structure of TADDOL in its solid state and the proposed activation mode for the Diels-Alder reaction.

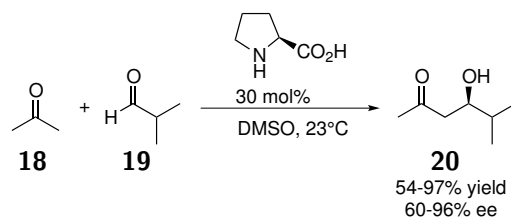


X-Ray Crystal structure of the BAMOL-Benzaldehyde complex

Scheme 4: BAMOL **14** on the left and an X-Ray crystal structure of the BAMOL-benzaldehyde complex, with indicated hydrogen bonds.



Scheme 5: Proline catalyzed intramolecular aldol cyclization leading to diketone **17**.



Scheme 6: Proline catalyzed direct aldol reaction between acetone **18** and isobutyraldehyde.

Akiyama & Terada 2004

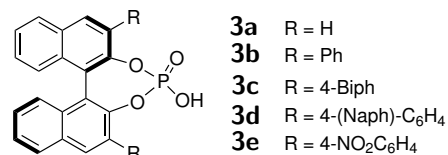
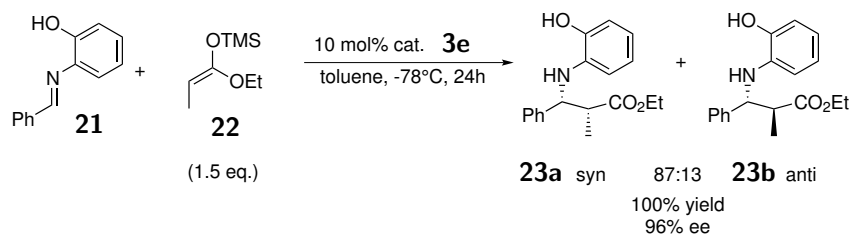


Figure 3: BINOL phosphoric acid derivatives



Scheme 7: Diastereoselective Mannich-type reaction of N-protected imine **21** with silyl enolate **22**.

Yamamoto 2006

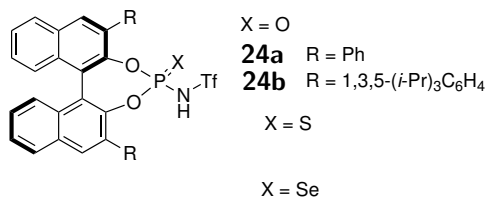
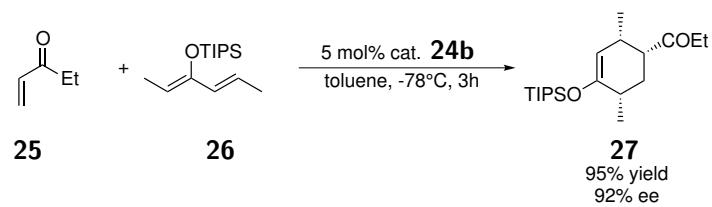


Figure 4: *N*-triflyl phosphoramidates, a more acidic family of chiral Brønsted acids.



Scheme 8: Asymmetric Diels-Alder reaction of alfa beta-unsaturated ketone **25** with TIPS enol **26** catalyzed by **24b**.