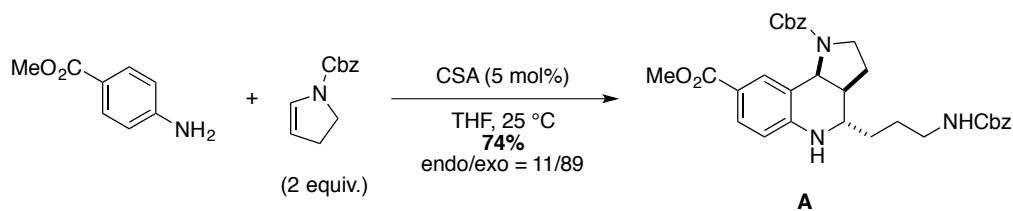
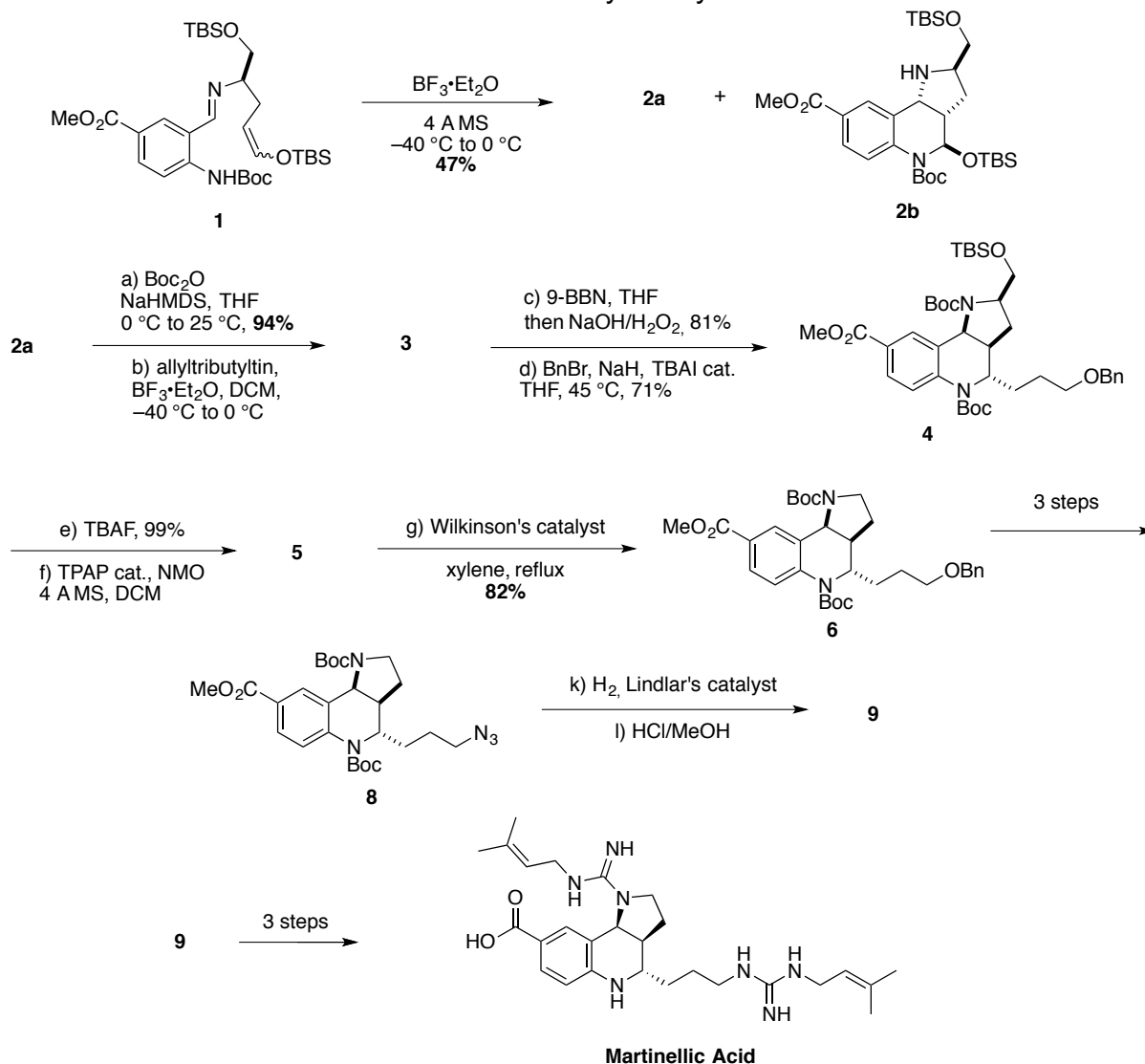


Total synthesis of Martinellic Acid



1/ Give the Mechanism for the reaction catalyzed by CSA.



2) Give the missing structure (**2a**, **3**, **5** and **9**) and the missing conditions (6 to 8).

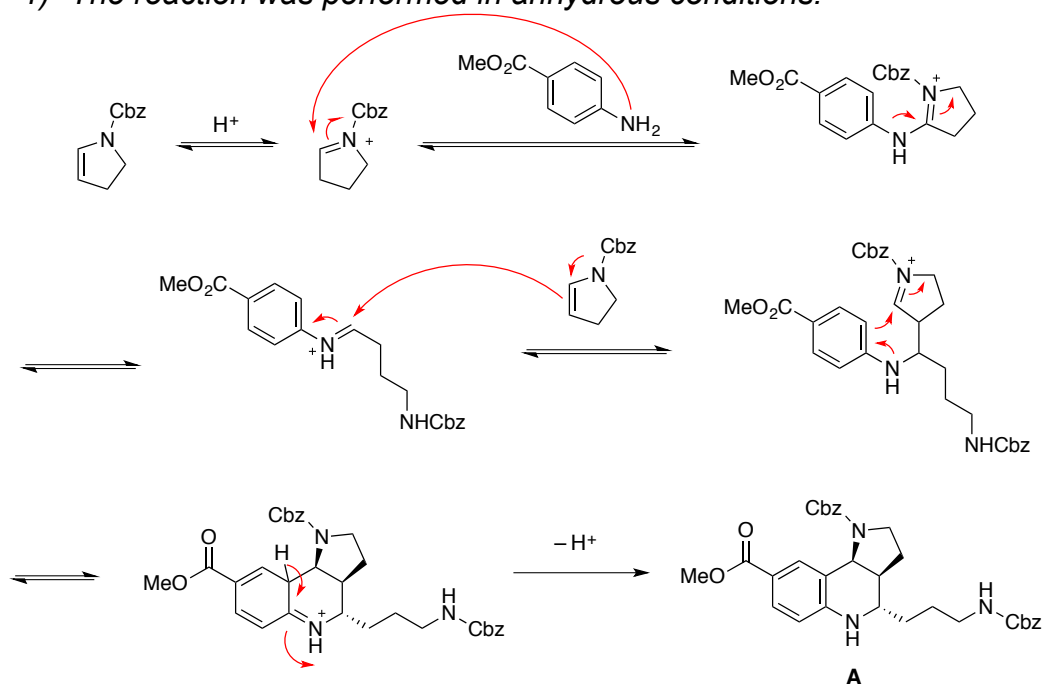
3) Propose a mechanism for the transformation (**1** to **2a+2b**)

4) Propose a mechanism for the reaction using Wilkinson's catalyst in stoichiometric amount.

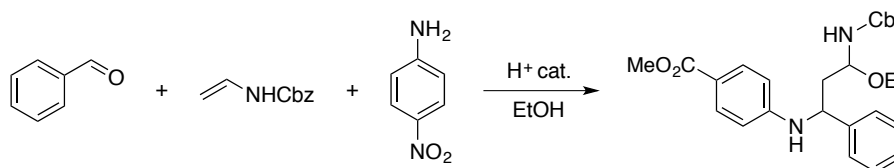
5) Propose the reagent for the three last steps of the synthesis.

Solution:

1) The reaction was performed in anhydrous conditions.

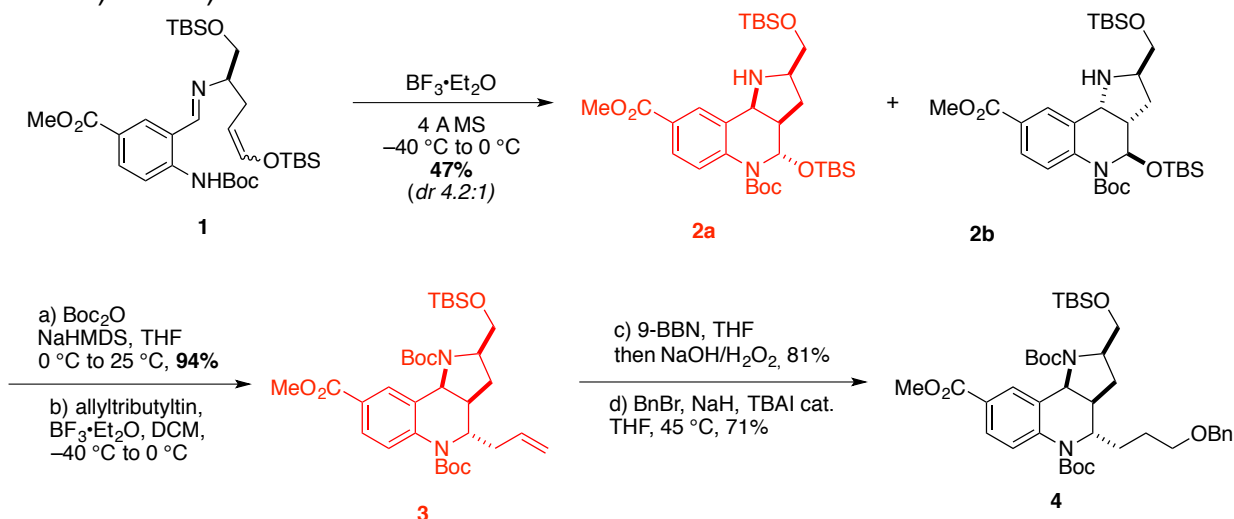


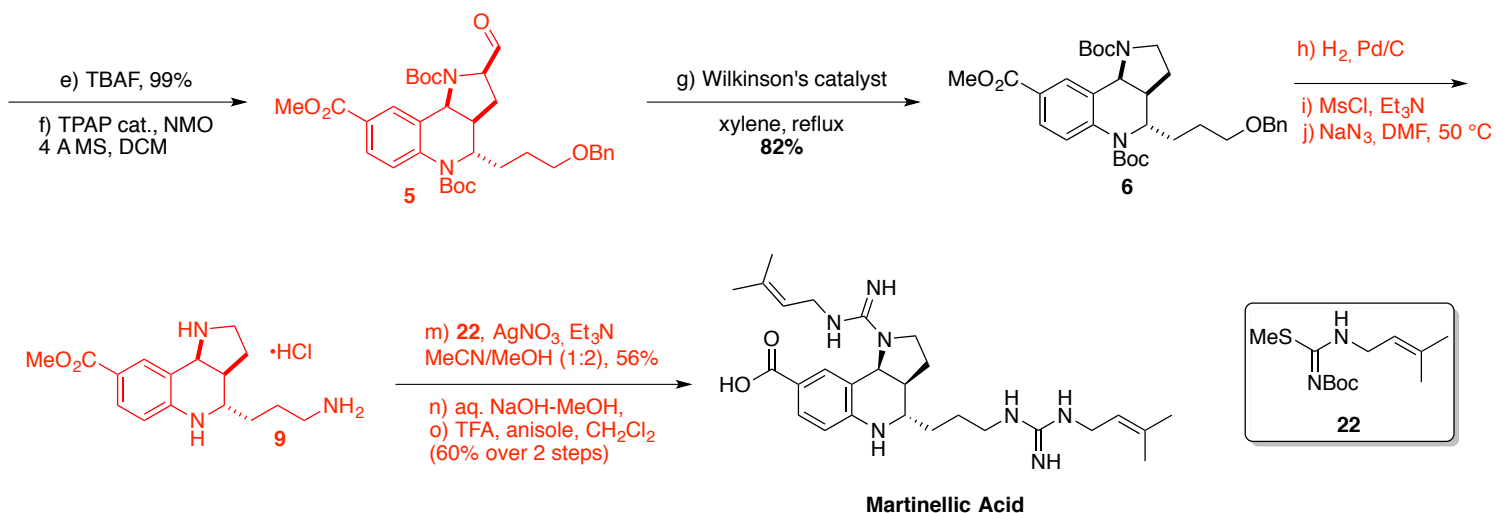
Masson shown the Povarov reaction could be stopped after the Mannich reaction when the reaction was performed with electron poor aryl moiety and ethanol was used as solvent



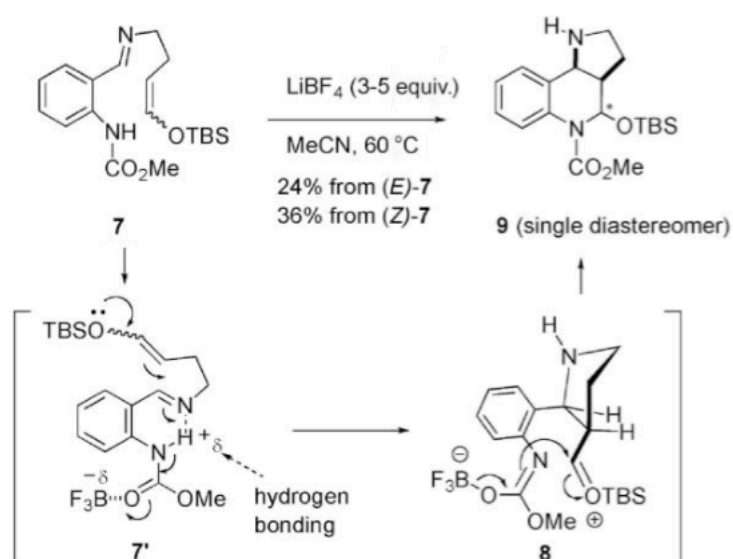
(G. Dagousset, J. Zhu, G. Masson, *J. Am. Chem. Soc.* **2011**, *133*, 14804).

2) and 5)

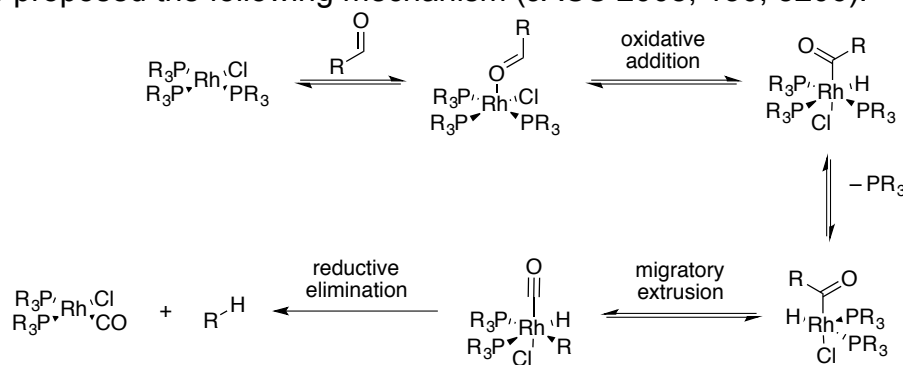




3)



4) Mechanism for the Tsuji-Wilkinson decarbonylation was studied by Madsen and he proposed the following mechanism (JACS 2008, 130, 5206).



Rh^I is square planar
Rh^{II} and Rh^{III} are square pyramidal

References:

Syntheses:

[1] S. Ikeda, M. Shibuya, Y. Iwabuchi, *Chem. Commun.* **2007**, 504.

[2] D. A. P. and, R. A. Batey, *Org. Lett.* **2002**, 4, 2913.

Povarov reaction:

G. Masson et al. *J. Am. Chem. Soc.* **2011**, 133, 14804.

Tsuji-Wilkinson decarbonylation:

R. Madsen et al. *J. Am. Chem. Soc.* **2008**, 130, 5206.

Keywords: Martinellie acid, Povarov reaction, Tsuji-Wilkinson decarbonylation, enamine