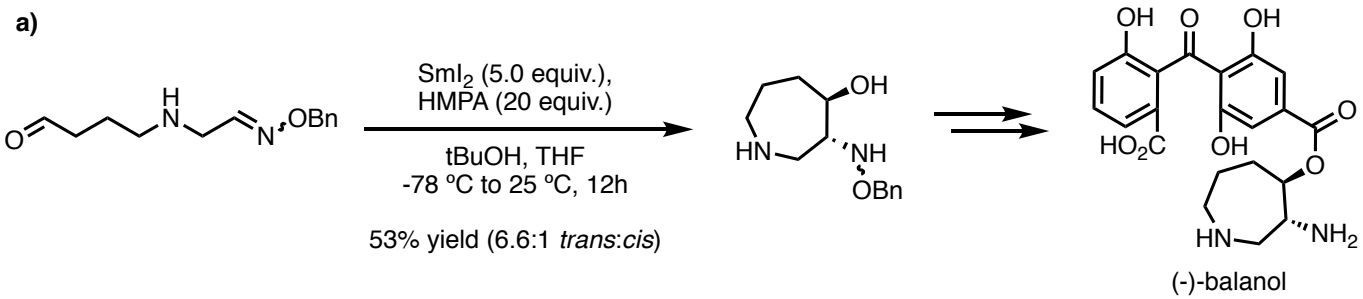
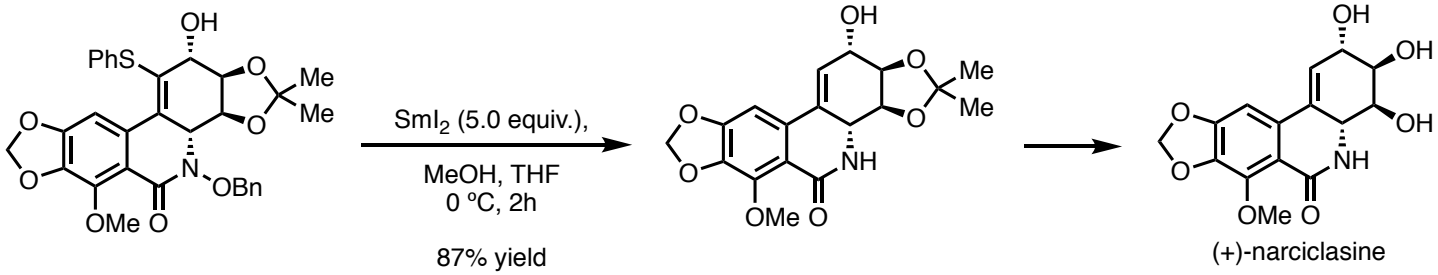
**Problem Set #007 (Nelli)**

**(1)** In 1998, Naito and coworkers from the Kobe Pharmaceutical University demonstrated a hetero-pinacol cyclization utilizing $SmI_2$ to form the seven-membered ring needed in their synthesis of (-)-balanol (as seen in part **a**) (*J. Org. Chem.* **1998**, *63*, 4397). Gary Keck from the University of Utah demonstrated the use of $SmI_2$ for reductive cleavage of N-O bonds, such as in his 1999 synthesis of (+)-narciclasine (as seen in part **b**) (*Tetrahedron* **1999**, *55*, 11755). Draw a reasonable mechanism for the cyclization in part **a** and mechanism for part **b**.

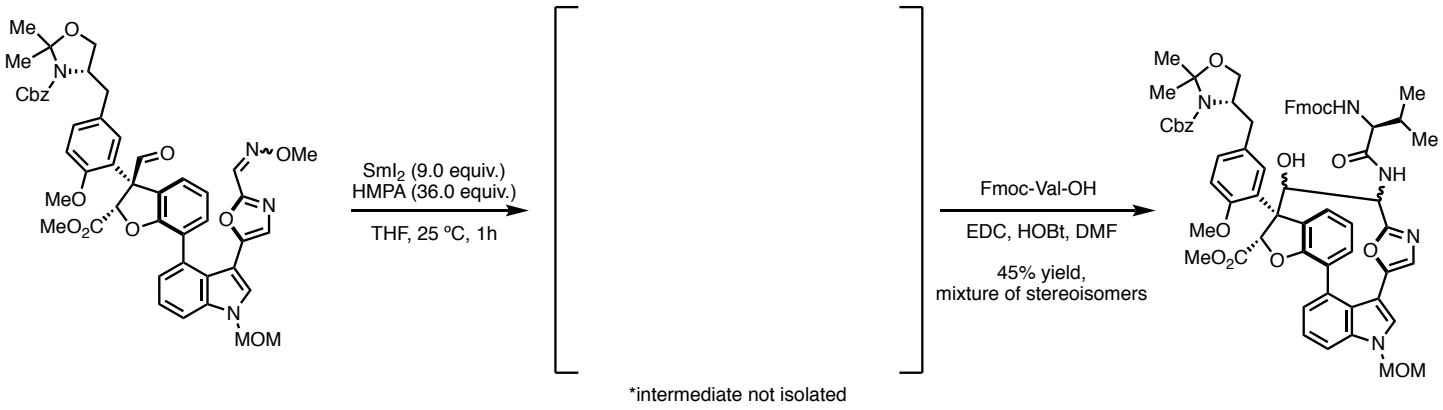
**a)**




**b)**



**(2)** In his route towards the originally proposed structure of diazonamide A, Nicolaou and coworkers used a $SmI_2$-promoted hetero-pinacol coupling to form one of the key macrocyclic rings. Draw the intermediate of this coupling and suggest a plausible mechanism for its formation. Additionally, what is the role of HMPA? Why is a large excess of both reagents ($SmI_2$ and HMPA) needed? *hint: cyclizations attempted by Nicolaou and coworkers without HMPA did not proceed (*J. Am. Chem. Soc.* **2004**, *32*, 10174)




**(3)** MacMillan and coworkers completed a total synthesis of diazonamide A in 2011 which featured a highly stereoselective iminium-catalyzed cascade reaction. Propose a mechanism for this cascade reaction. (*Chem. Sci.* **2011**, *2*, 308)