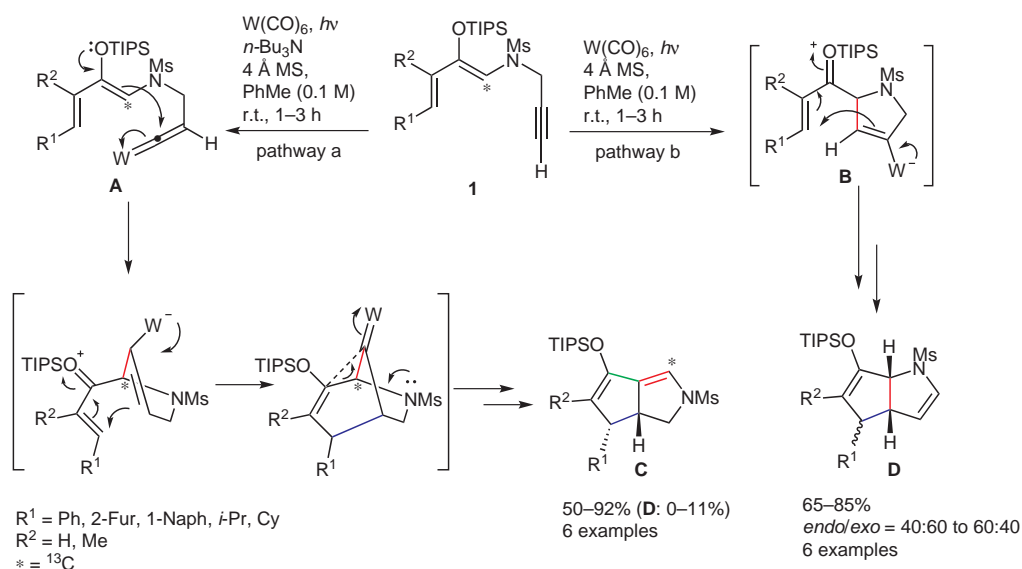


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Efficient Control of  $\pi$ -Alkyne and Vinylidene Complex Pathways for the  $W(CO)_5(L)$ -Catalyzed Synthesis of Two Types of Nitrogen-Containing Bicyclic Compounds  
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## $W(CO)_5$ -Catalyzed Synthesis of 2- and 3-Azabicyclo[3.3.0]octanes



**Significance:** Reported is a tungsten-catalyzed regioselective synthesis of 3-azobicyclo[3.3.0]octane and 2-azobicyclo[3.3.0]octane derivatives **C** and **D** from  $\pi$ -acetylenic dienol silyl ether **1**. The reaction proceeds via different pathways a and b as a function of base. Thus, the initial vinylidene complex **A** undergoes double cyclizations and nitrogen facilitated 1,2-alkyl migration to lead to product **C**. This mechanism is substantiated by  $^{13}C$ - as indicated and D-labeled experiments. In the absence of base, the tungsten-catalyzed process is envisaged to proceed via the zwitterionic intermediates **B** to lead to products **D**. None of the intermediates were isolated.

**Comment:** The 2- and 3-azabicyclo[3.3.0]octane framework is found as part of bioactive molecules, for example in the inhibitor of DPP II (O. Danilova et al. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 507). Traditionally, 3-azobicyclo[3.3.0]octane and 2-azabicyclo[3.3.0]octane derivatives are constructed respectively by reaction of dicarboxylic acid derivatives with amines (T. Punniyamurthy, T. Katsuki *Tetrahedron* **1999**, *55*, 9439) or intramolecular cyclization of 2-(2-bromoethyl)cyclopentamines (H. Booth et al. *J. Chem. Soc.* **1959**, 1050). The present methodology constitutes a new catalytic route to both heterocyclic systems which proceeds in useful synthetic yields.