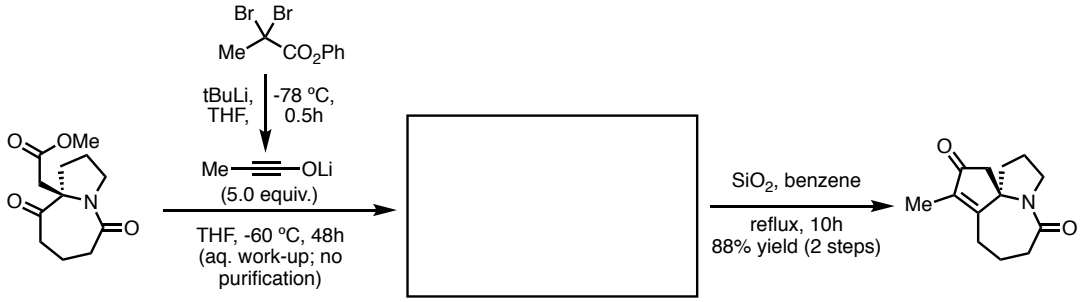
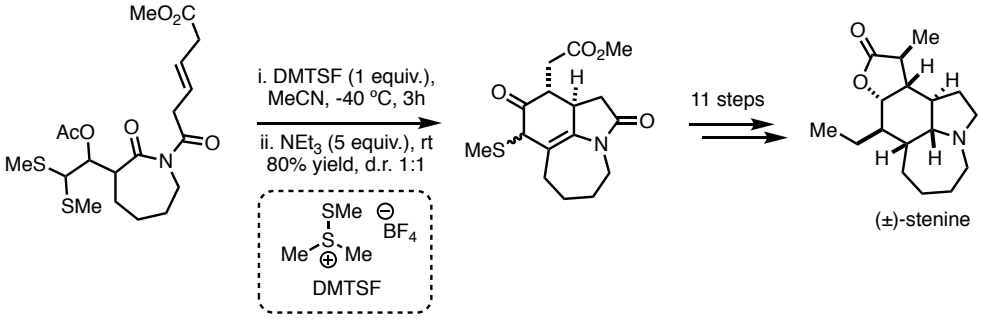
Problem Set #011 (Nelli)

(1) In their 2018 synthesis of (-)-stemonamine, Mitsuru Shindo and coworkers use a novel ynolate-initiated tandem reaction developed in their laboratory to construct the requisite cyclopentenone. Draw the intermediate from the first step in the box, as well as the mechanism for the formation of the intermediate and the final product.
Ref.: Fujita, S.; *et al.*; Shindo, M., *Chem. Eur. J.* **2018**, *24*, 1539.



(2) Albert Padwa and coworkers completed a total synthesis of racemic stenine, a *Stemona* alkaloid, in 2002. Using the reagent dimethyl(methylthio)sulfonium BF_4 (DMTSF), Padwa and coworkers affected a thionium-promoted cyclization of the imide shown below, followed by a subsequent [4+2] to the unsaturated tricyclic core of stenine in good yield. Draw a mechanism for this transformation. Ref.: Ginn, J.D.; Padwa, A., *Org. Lett.* **2002**, *4*, 1515.



(3) In 2002, Jeffrey Aubé utilized a cascade sequence to construct 3 of the 4 rings of the *Stemona* alkaloid stenine. Heating the triene shown below in dichloromethane in the presence of (dichloromethyl)aluminum delivered three tricyclic products in a combined 79% yield. The desired tricyclic lactam **A** was carried on to finish the formal synthesis of racemic stenine (5 steps to an intermediate not shown below). Draw a mechanism for each of the three tricyclic products (**A**, **B**, and **C**) that explains the stereochemistry shown.

Ref.: Golden, J.E.; Aubé, J., *Angew. Chem. Int. Ed.* **2002**, *41*, 4316.