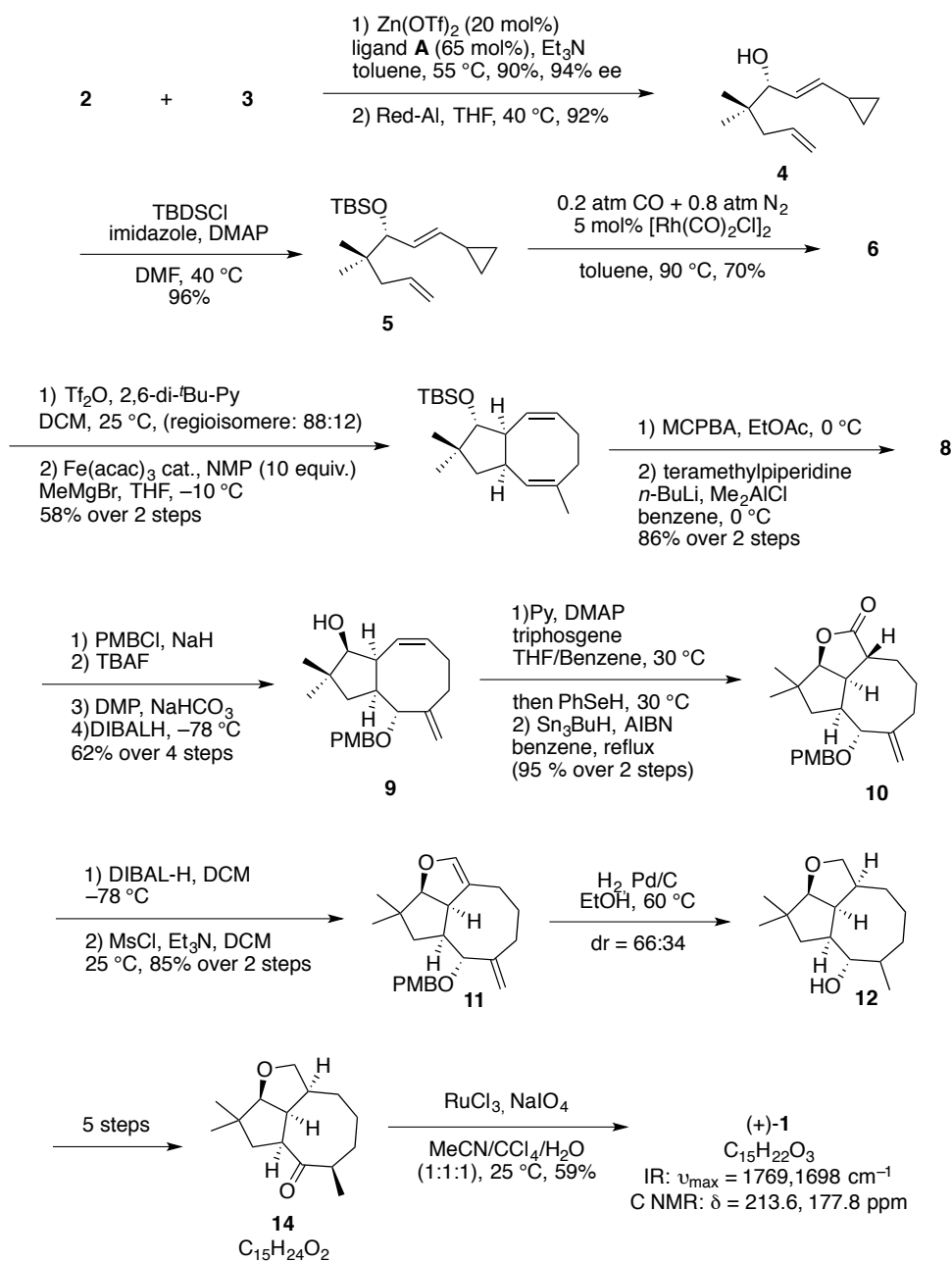


Enantioselective Total Synthesis of (+)-asteriscanolide Via Rhodium(I)-catalysis



1/ Give the missing structure **2**, **3**, **6** and **8** and (+)-**1**.

Master student:

2) Propose a mechanism for the transformation **7** to **8**.

PhD student:

3) Explain the geometric control during the reduction with Red-Al

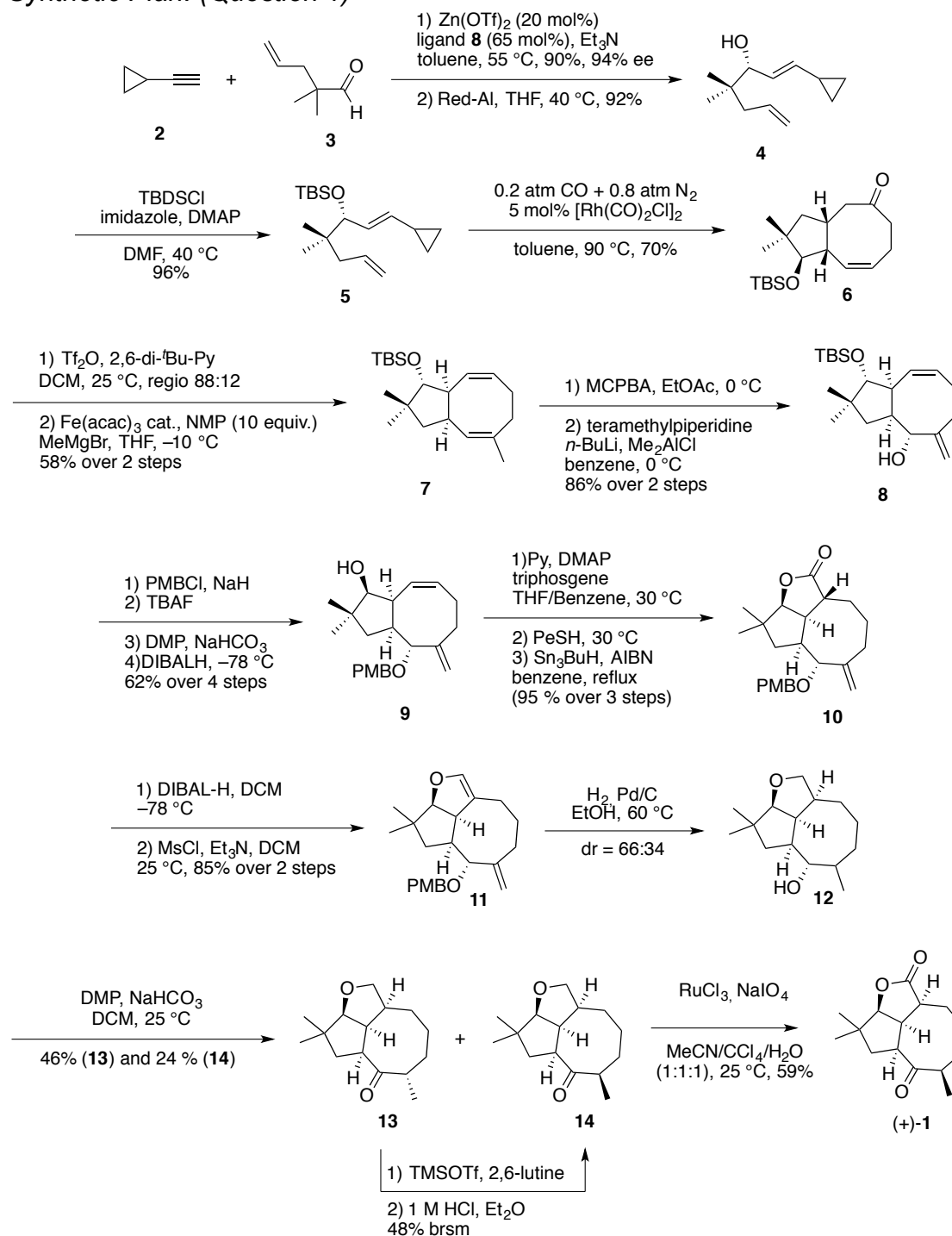
4) Proposed a mechanism for the Rhodium step

5) Give a mechanism for the transformation (**9** to **10**)

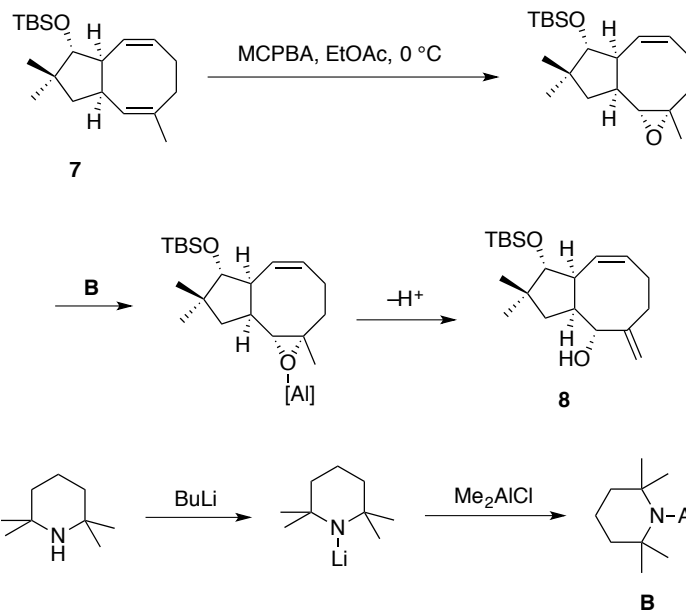
Note: Ligand **A** is a pseudoephedrine derivative.

Solution:

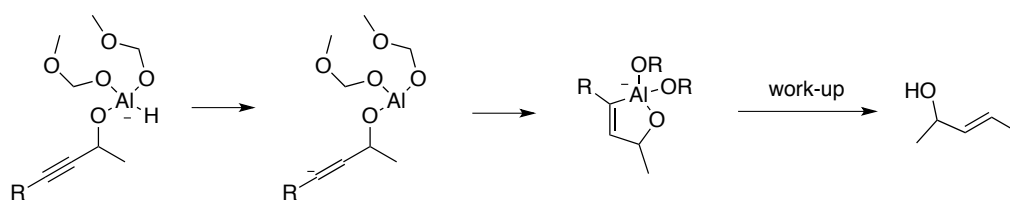
Synthetic Plan: (Question 1)



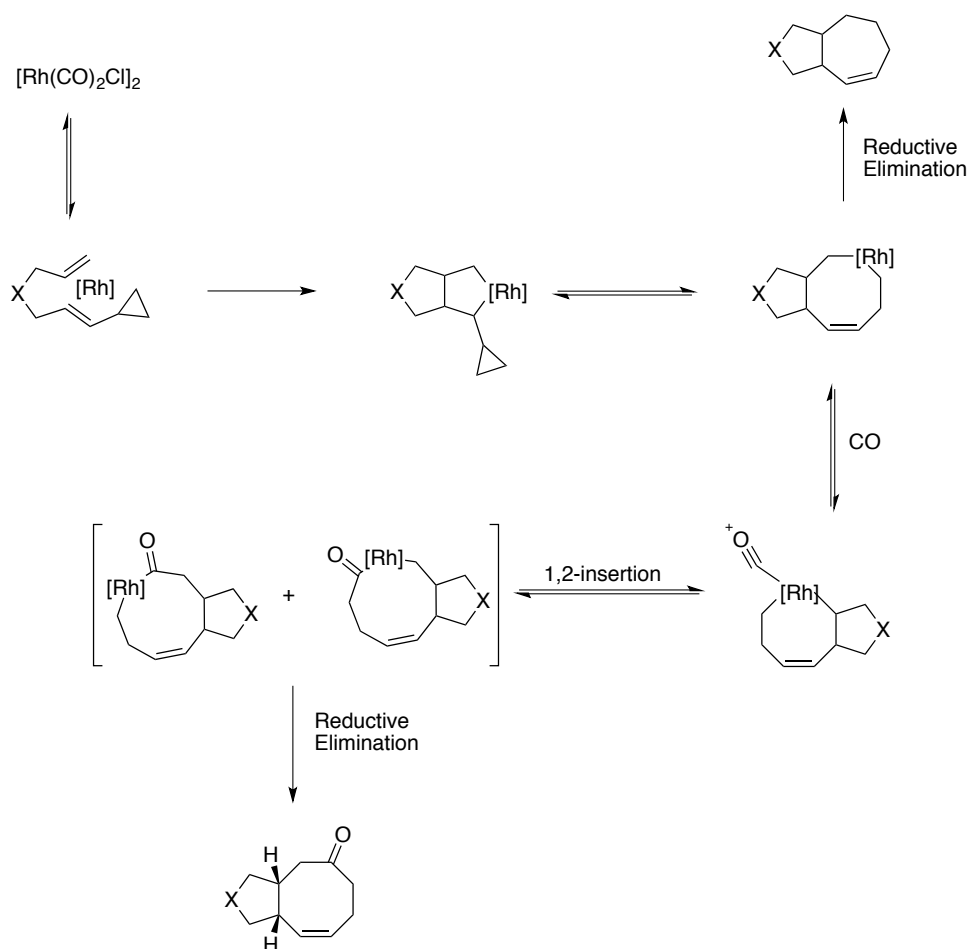
2)



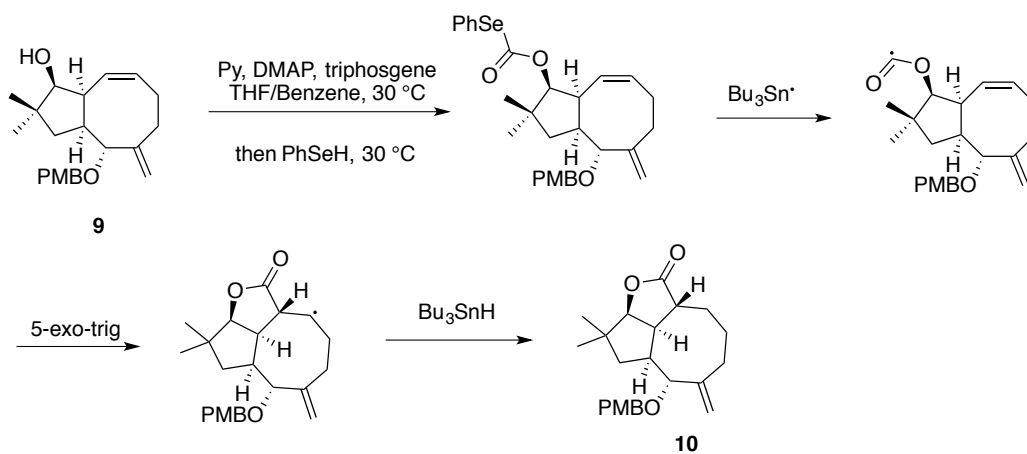
3)

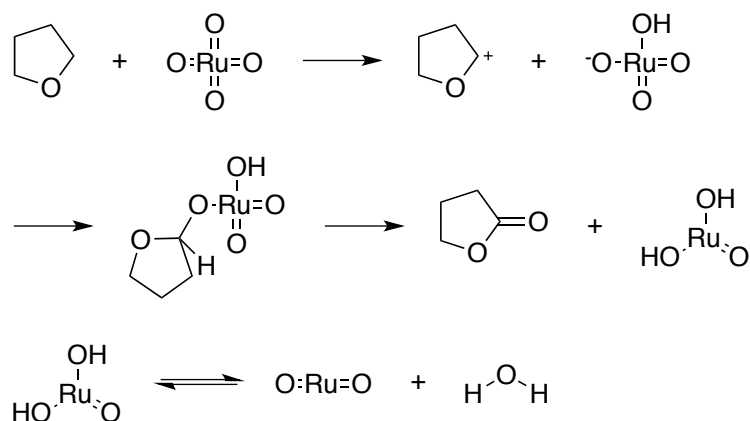


4)



5)





Comments:

References:

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Opening epoxide: *J. Am. Chem. Soc.*, **1974**, 96, 6513-6514.

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Rhodium mechanism ([5+2+1] cycloaddition): *J. Am. Chem. Soc.* **1995**, 117, 4720-4721, (b) *J. Am. Chem. Soc.* **2007**, 129, 10060-10061, (c) *Acc. Chem. Res.* **2015** ASAP (DOI: 10.1021/acs.accounts.5b00037)

Radical cyclization: *J. Org. Chem.*, **1992**, 57, 4696-4705

Ruthenium oxidation: *Can. J. Chem.* **1972**, 50, 3129-3134.

Keywords: Synthesis of (+)-asteriscanolide, epoxide opening, Rhodium-Catalyzed [5+2+1] cycloaddition, Ene-vinylcyclopropane, Red-Al reduction, radical lactonisation.