

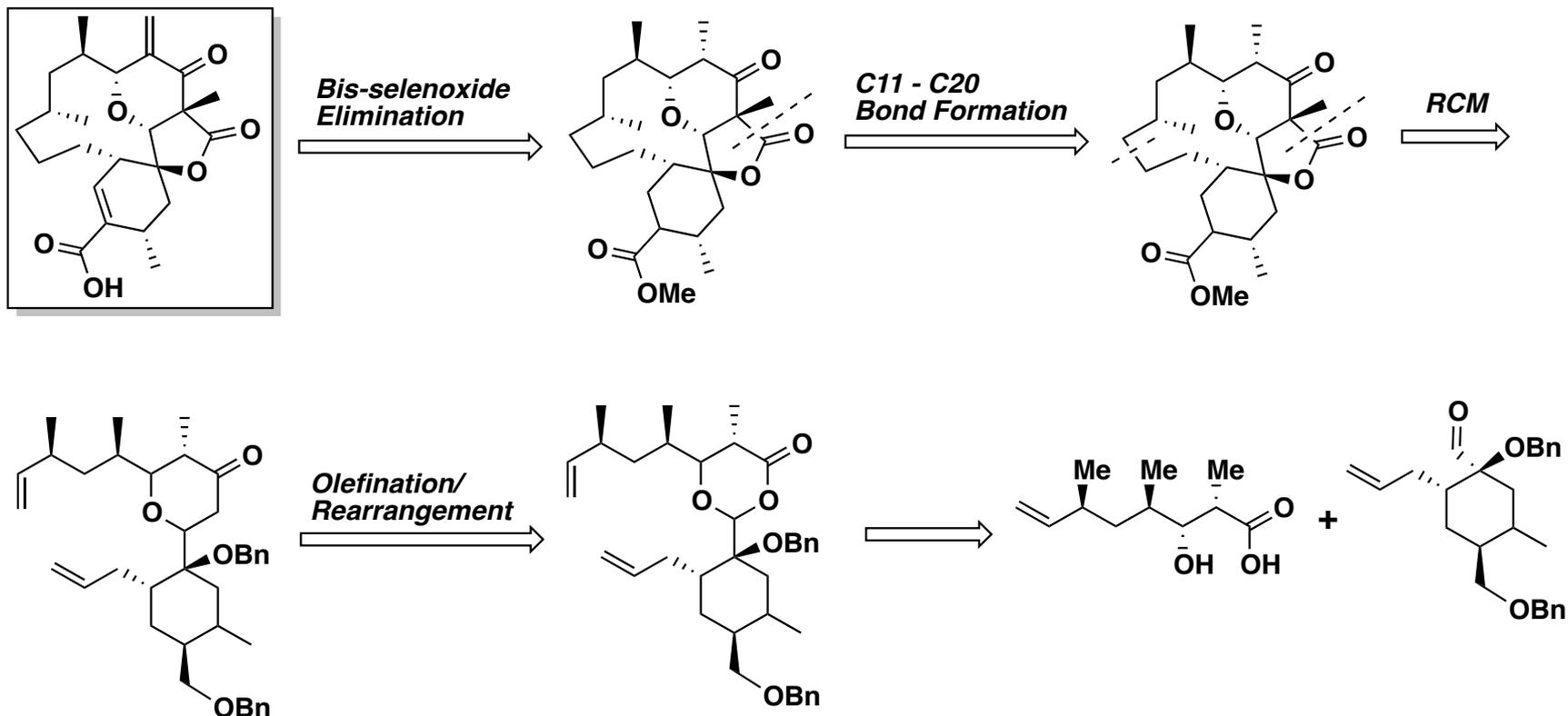
Total Synthesis of (-)-Okilactonycin

Group Problem Session

14-May-2013

Xuezheng Yang

Retrosynthetic Analysis

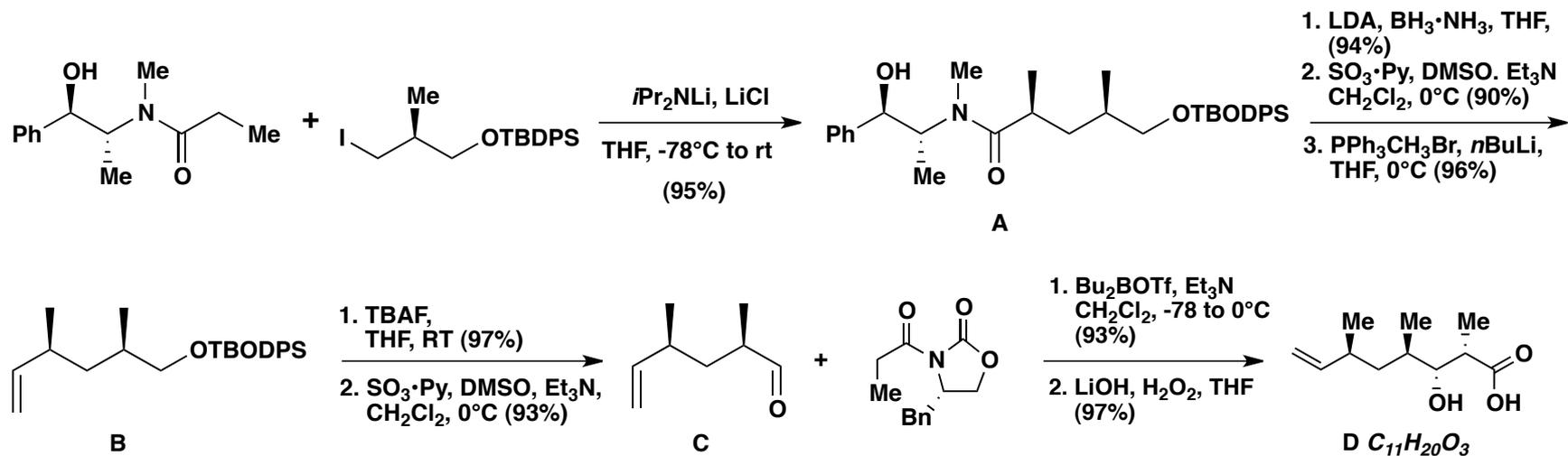


Scheme 1. Retrosynthetic Analysis

Smith, A. B., III.; Basu, K.; Bosanac, T. *JACS*, **2007**, 129, 14872

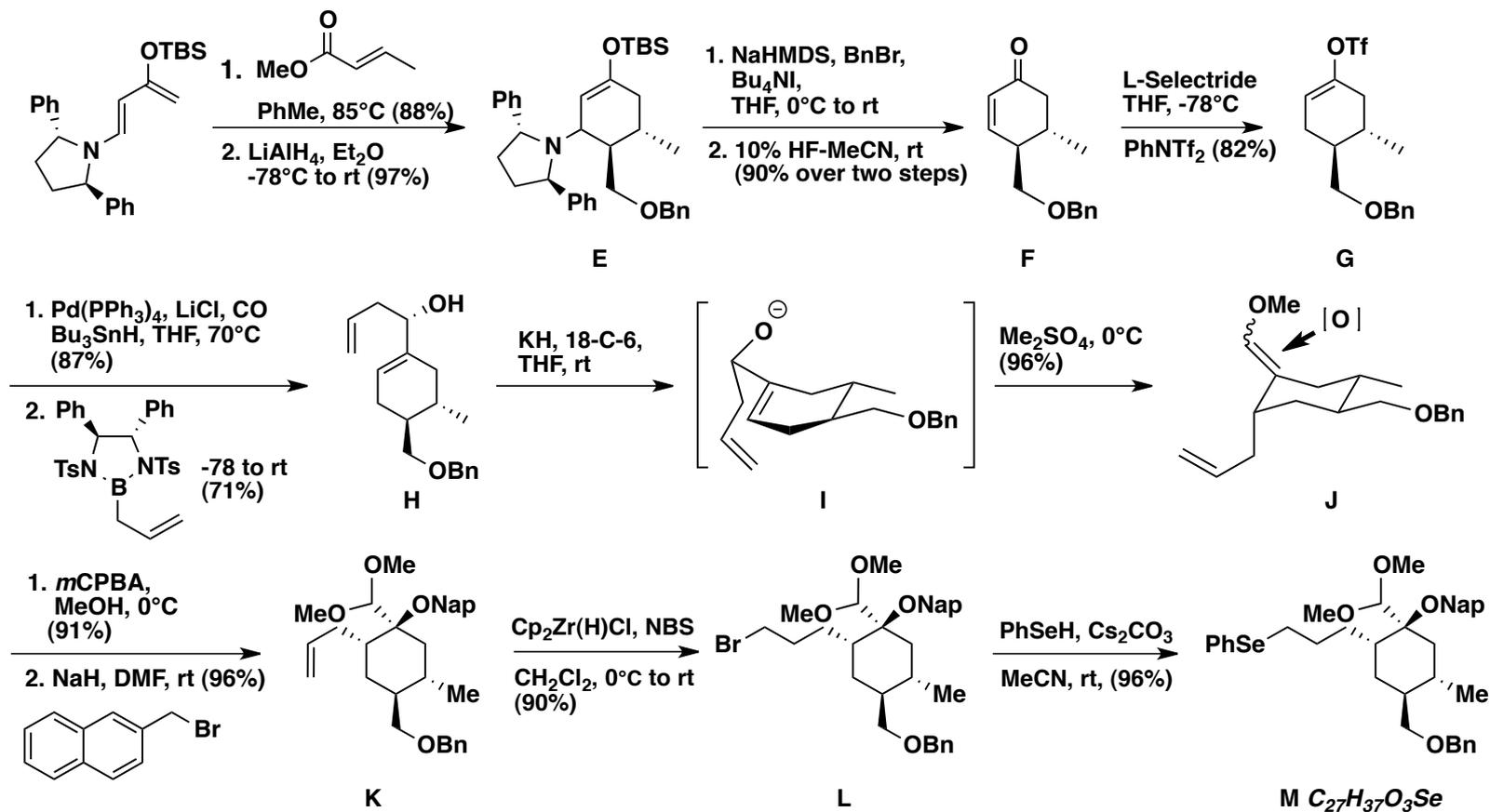
Smith, A. B., III.; Bosanac, T.; Basu, K. *JACS*, **2009**, 131, 2348

Synthesis of β -Hydroxyl Acid D



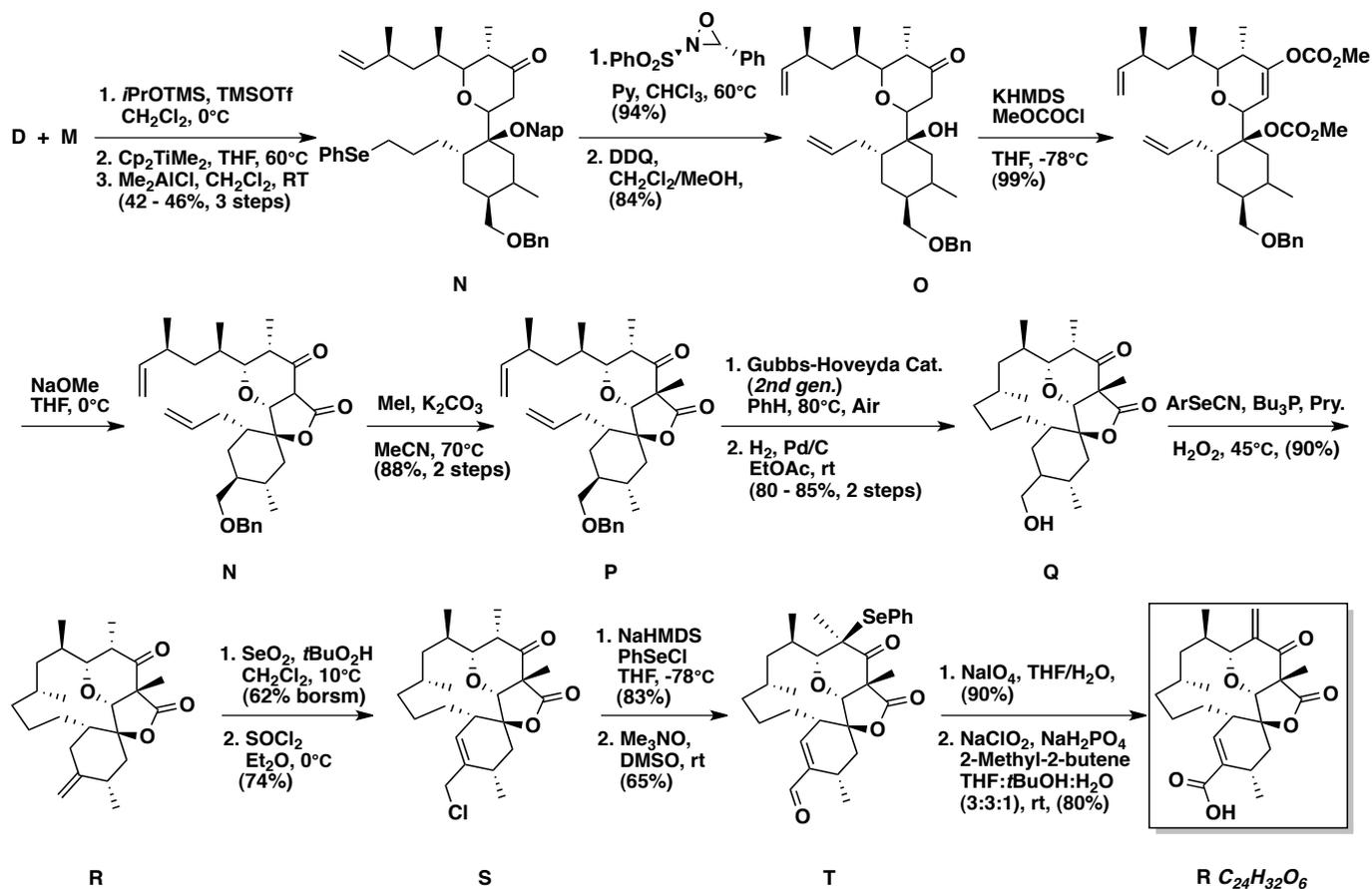
Scheme 2. Synthesis of β -Hydroxyl Acid D

Synthesis of Selenide Acetal M



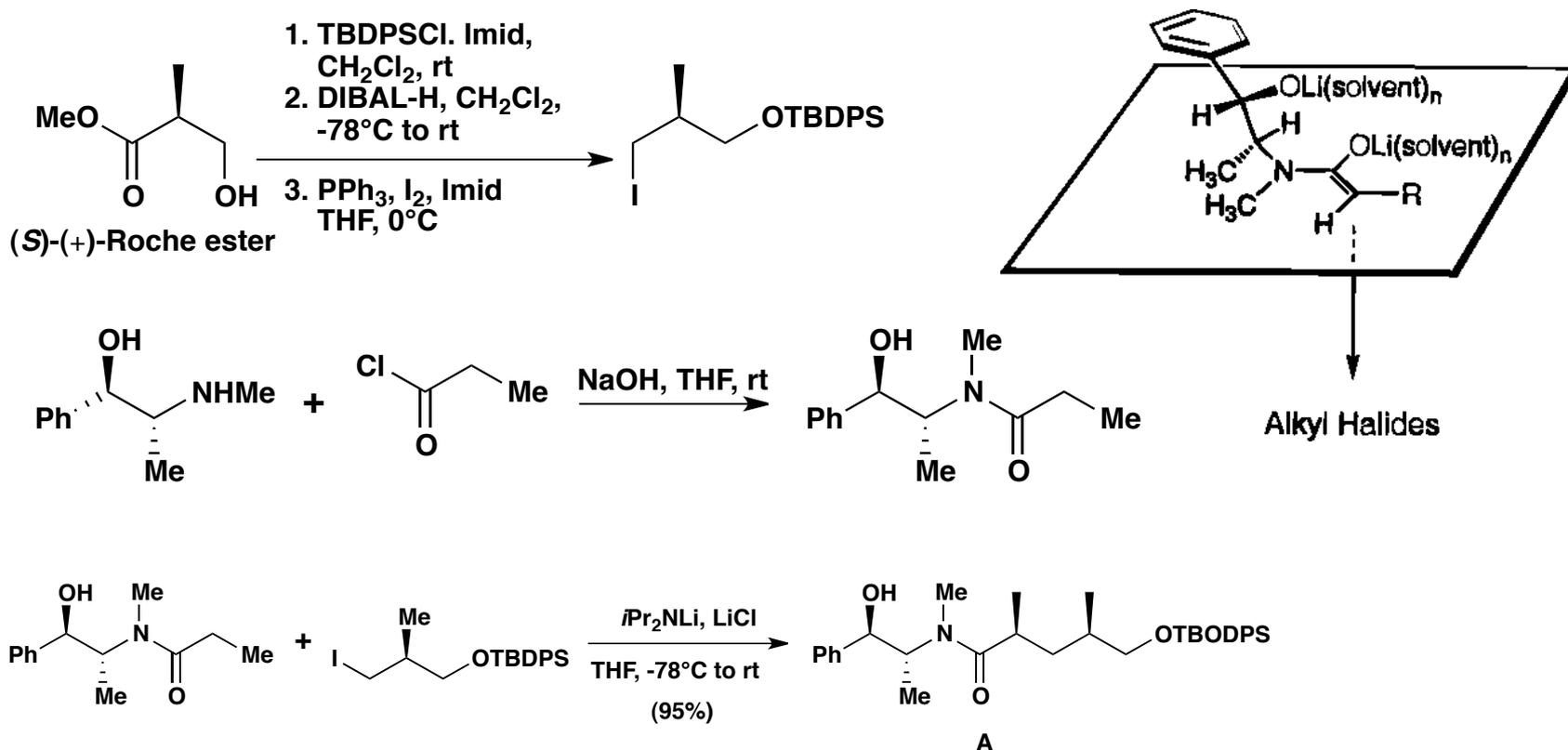
Scheme 3. Synthesis of Selenide Dimethyl Acetal M

Construction of (-)-Okilactomycin

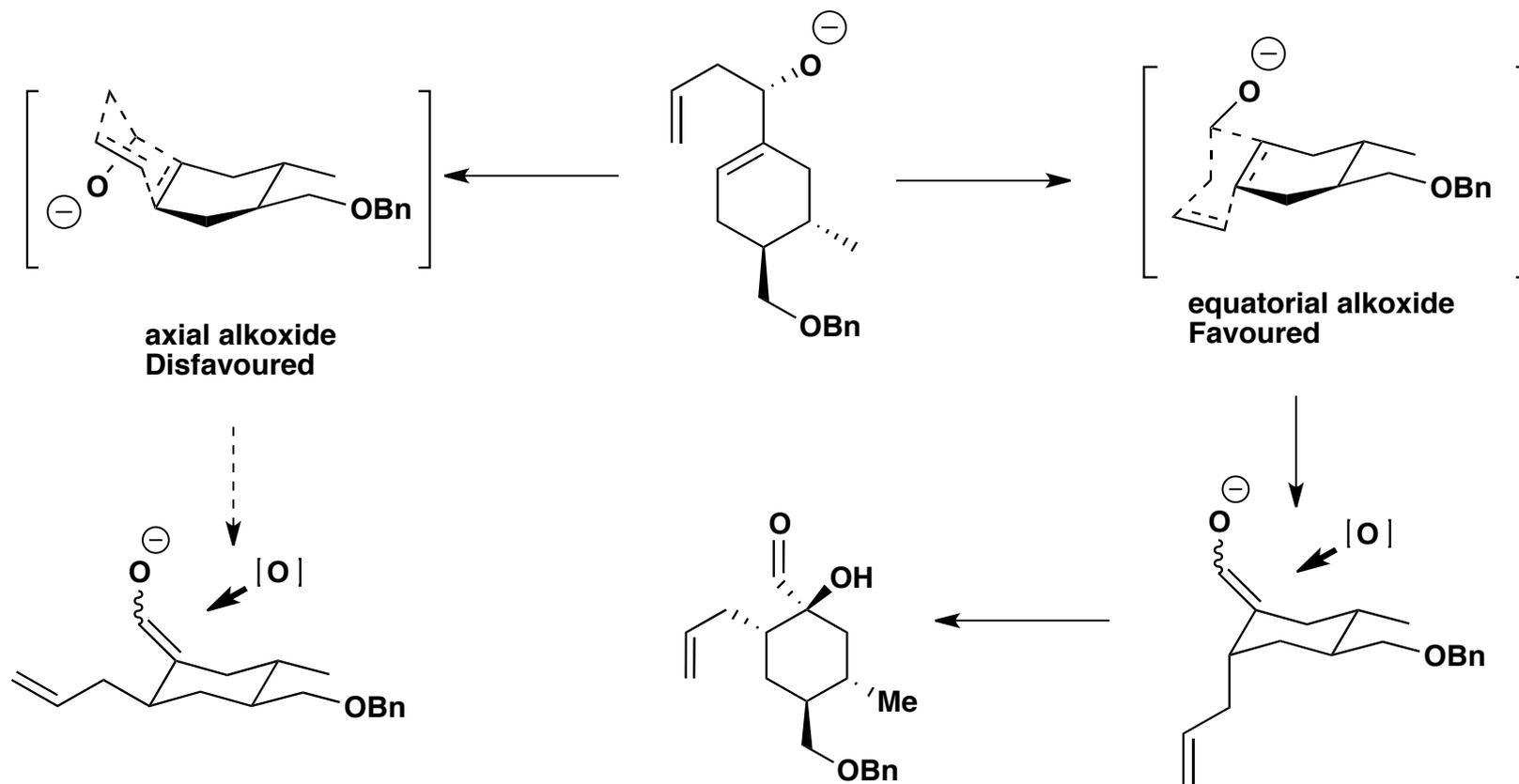


Scheme 4. Construction of (-)-Okilactomycin

Appendix 1 – Diastereoselective alkylation

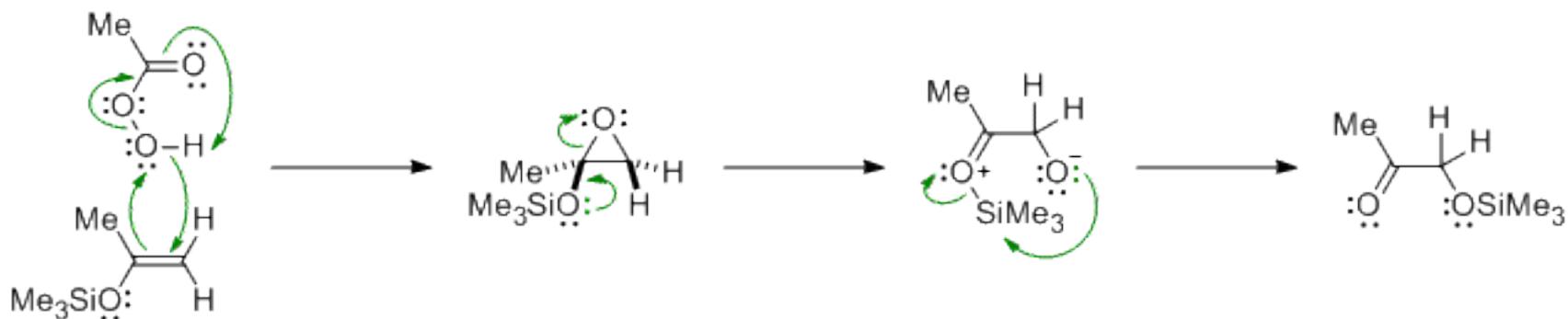
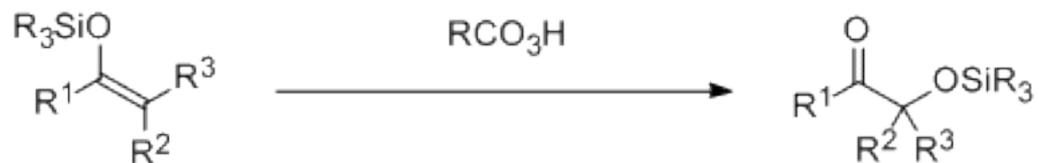


Appendix 2 – Oxy-Cope Rearrangement/Oxidation

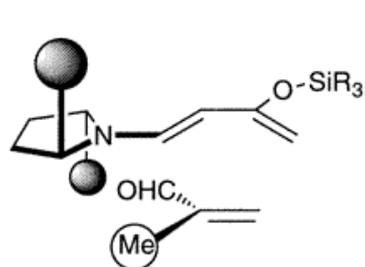
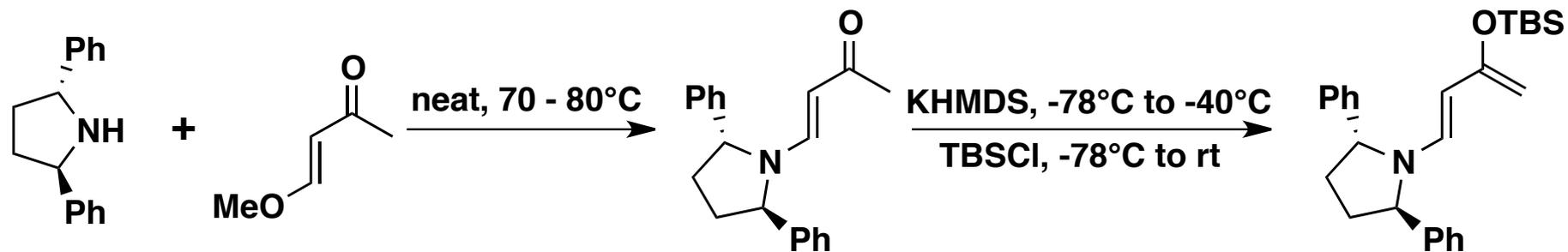


Scheme XX. Oxo-Cope Rearrangement - Oxidation

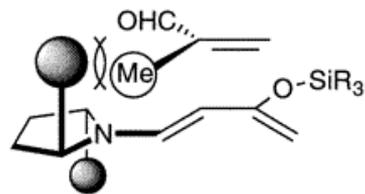
Appendix 3 – Rubottom Oxidation



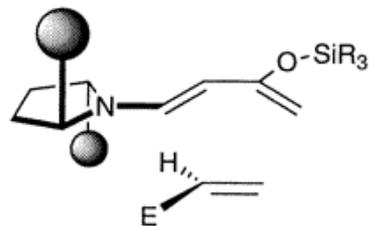
Appendix 4 – Synthesis of SM - 2



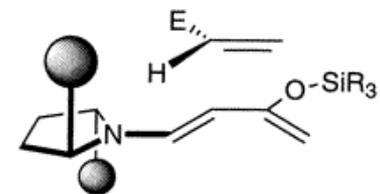
A: favored *endo* TS



B: disfavored *endo* TS

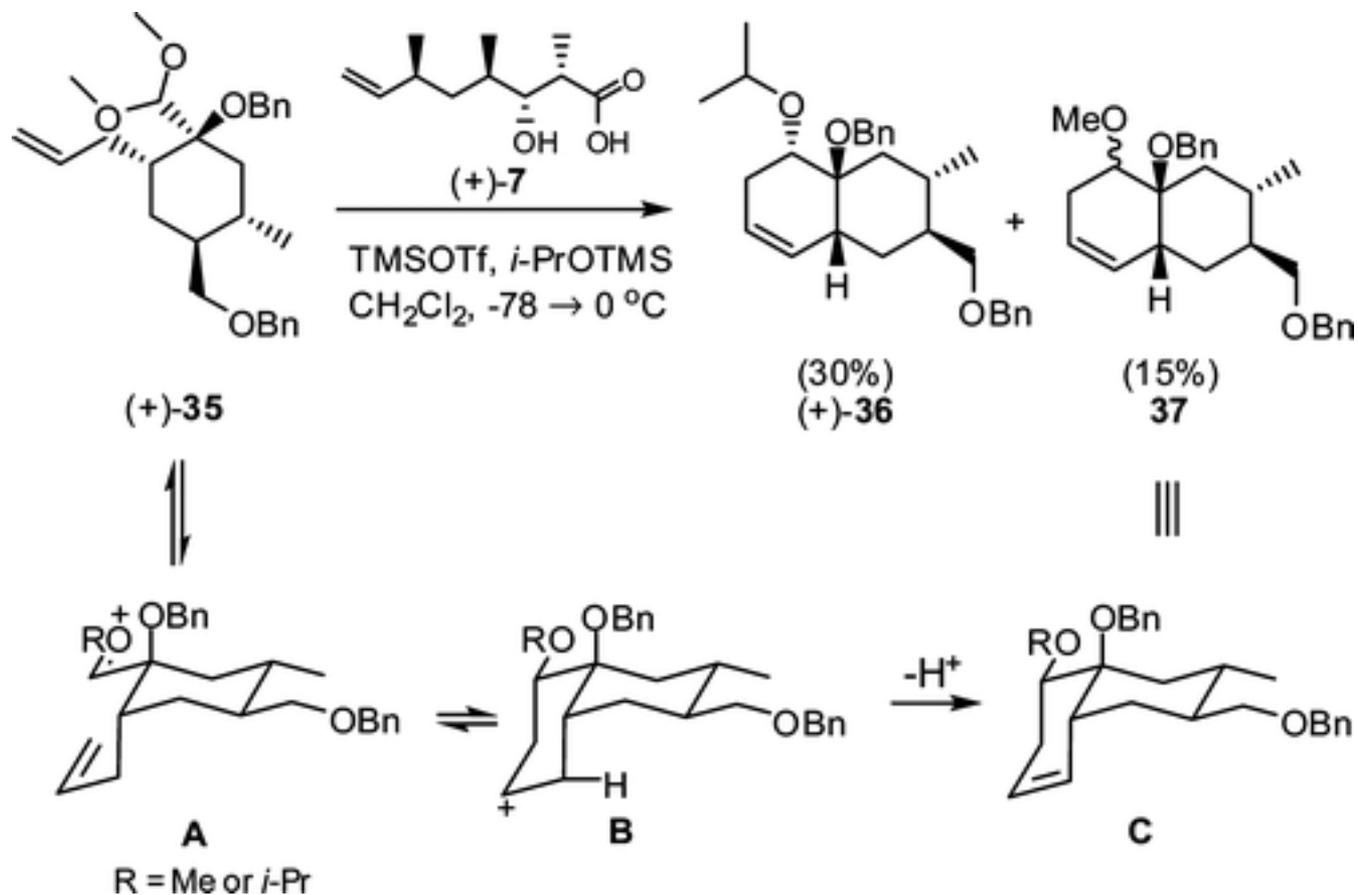


C: favored *exo* TS

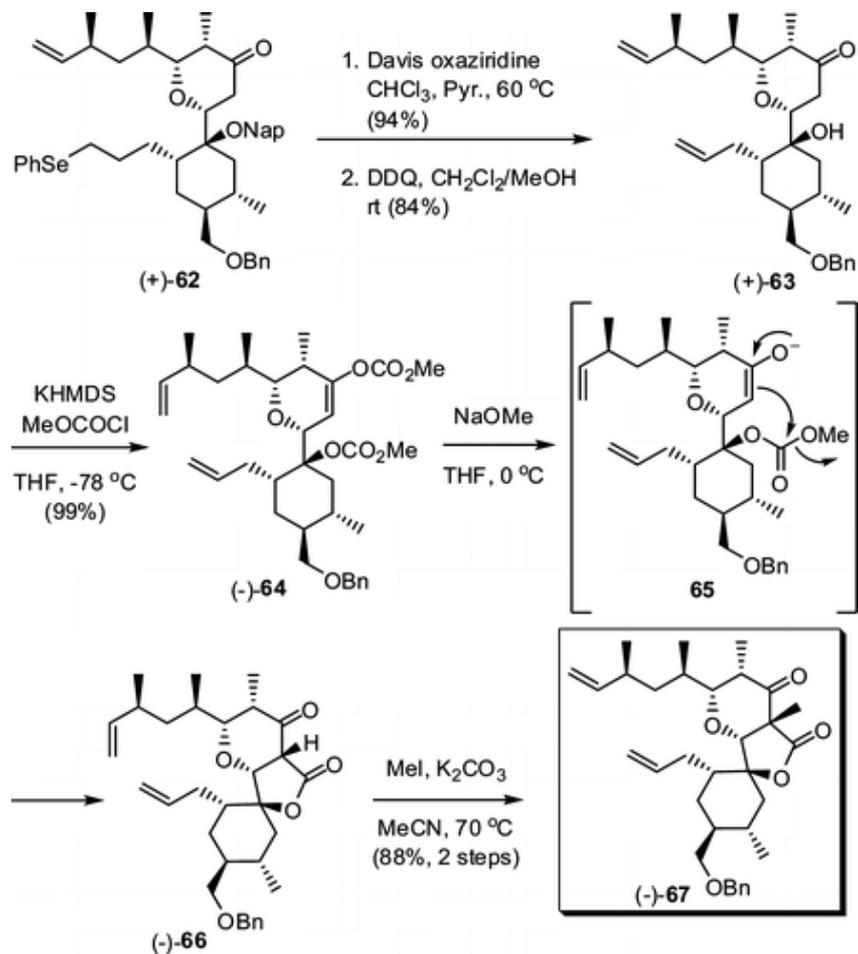


D: favored *endo* TS

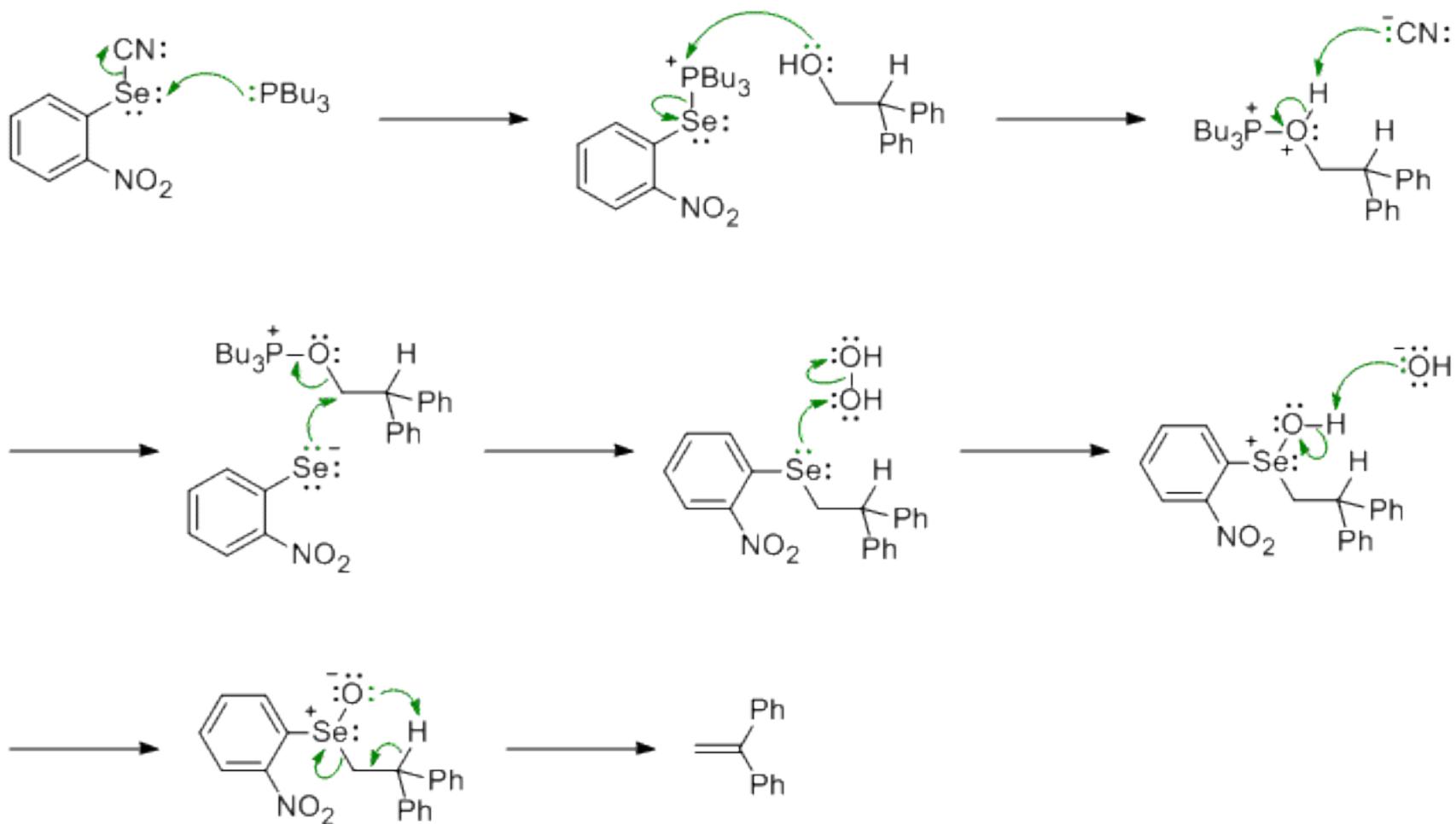
Appendix 5 – Why mask the terminal alkene



Appendix 6 – Mechanism for Lactolization



Appendix 7 – Grieco Elimination/Dyhydration



Appendix 8 – Ganom Oxidation

