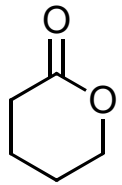
Synthesis Challenge # 52

Asymmetric Total Synthesis of Kopsiyunnanine K, a Monoterpenoid Indole Alkaloid with a Rearranged Skeleton

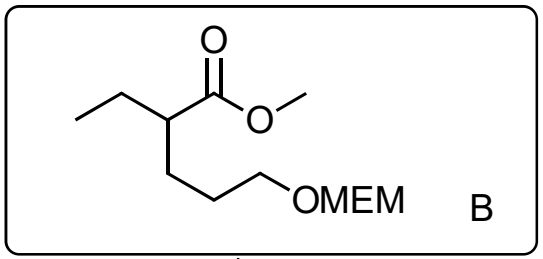
R. Tokuda, Y. Okamoto, T. Koyama, N. Kogure, M. Kitajima, H. Takayama, *Org. Lett.* **2016**, *ASAP*,
DOI: 10.1021/acs.orglett.6b01704
14.07.2016



A

1-3

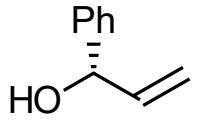
1) LDA, EtI, HMPA, THF, −78ºC
2) cat H_2SO_4, MeOH, rt
3) MEMCl, DIPEA, CH_2Cl_2, rt



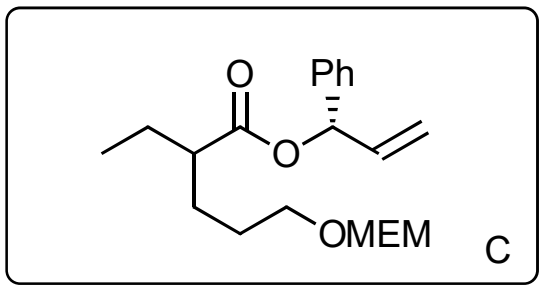
B

4-5

4) $LiOH*H_2O$, THF-H_2O
5) **I**, EDCI*HCl, DMAP, rt, 23ºC



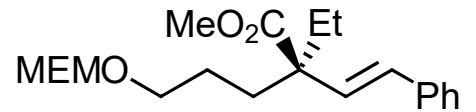
I



C

6-7

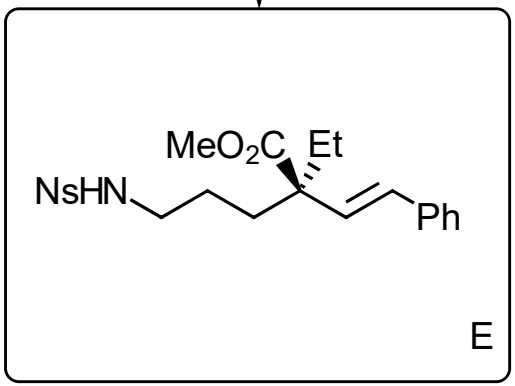
6) KHMDS, toluene, −78ºC, then TMSCl, −78ºC
7) $TMSCHN_2$, MeOH, CH_2Cl_2, 0ºC to rt



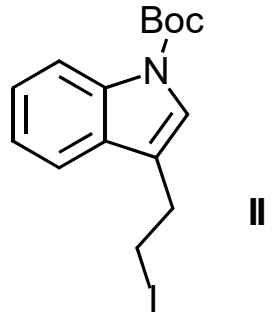
D

8) AcCl, MeOH, rt
9) $NsNH_2$, PPh_3, DEAD, THF, rt

8-9

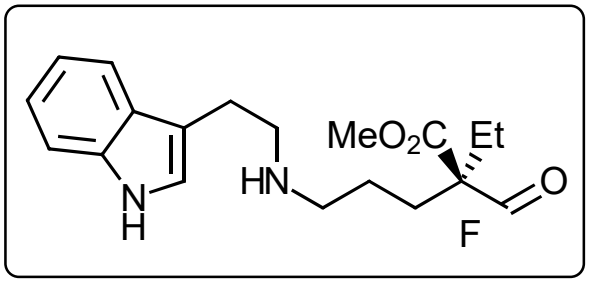


10) O_3, CH_2Cl_2, −78ºC, Me_2S, rt
11) **II**, DMF, K_2CO_3, rt



II

10-11



12) PhSH, Cs_2CO_3, MeCN, rt
13) TFA, rt

12-13