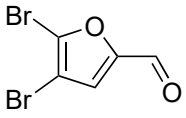
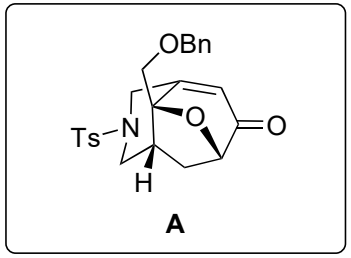
Total Synthesis of Yuzurine-type Alkaloid Daphgraciline

L.-X. Li, L. Min, T.-B. Yao, S.-X. Ji, C. Qiao, P.-L. Tian, J. Sun, C.-C. Li, *J. Am. Chem. Soc*. **2022**, *144*, 18823-18828.

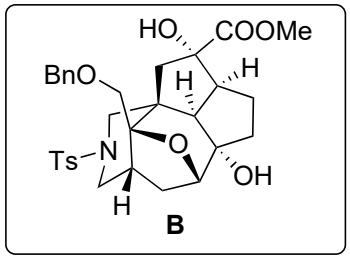


1-9



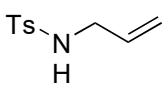
A

10-15



B

1) DIBALH
2) TBSCl, imidazole
3) *n*-BuLi, *then* BOMCl
4) *n*-BuLi, *then* formaldehyde
5) PPh_3, DIAD, **1**
6) TBAF
7) *m*-CPBA
8) Ac_2O, Et_3N, DMAP
9) **2**



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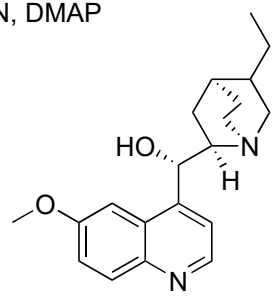
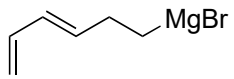


2

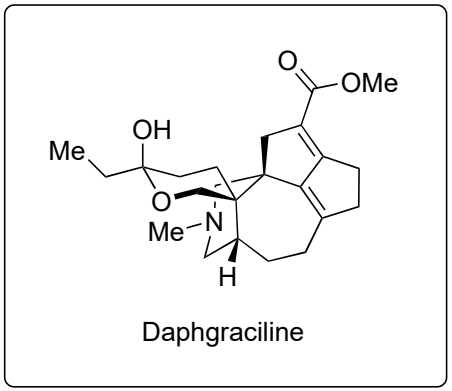
10) **3**
11) toluene, 140 °C
12) K_2OsO_4, NMO, $MeSO_2NH_2$
13) IBX
14) KOH
15) $TMSCHN_2$



3

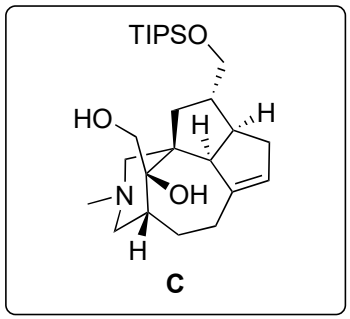
5) Name of the reaction?
Mitsunobu reaction
7) Name of the reaction?
Achmatowicz reaction
9) Type of the reaction?
[5+2] cycloaddition

11) Name of the reaction?
Diels-Alder reaction
14) Type of the reaction?
benzilic acid-type rearrangement



Daphgraciline

16-22



C

19-26

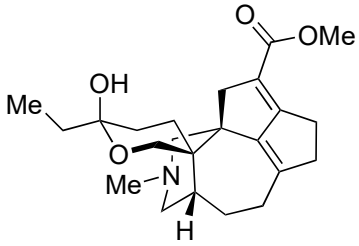
Daphgraciline

16) NaH, CS_2, MeI
17) PhCl, 148 °C
18) SmI_2
19) DIBALH
20) TIPSCl, imidazole
21) Li, $EtNH_2$
22) MeI

23) KHMDS, *N*-tosylimidazole
24) acrylonitrile, Cp_2TiCl_2, Zn
25) EtMgBr
26) *p*-TsOH
27) DMP
28) I_2, KOH, MeOH
29) TPP, $NaHCO_3$, O_2, *hv*
30) $MgSO_4$, 140 °C
31) *p*-TsOH

17) Name of the reaction
Chugaev elimination

29) Type of the reaction?
Schenck ene reaction



Daphgraciline