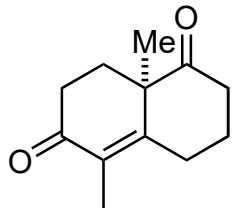
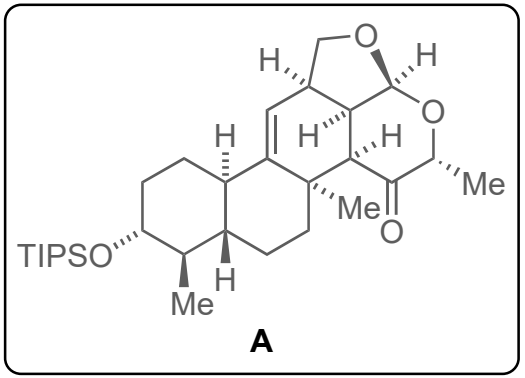
Total Synthesis of DMOA-Derived Meroterpenoids: Achieving Selectivity in the Synthesis of (+)-Berkeleyacetal D and (+)-Peniciacetal I

Zhang, J.; Luo, X.; Zhang, J.; Lil, C.; J. Am. Chem. Soc. **2025**, *147*, 5933–5942.



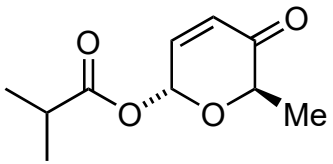
1–10



A

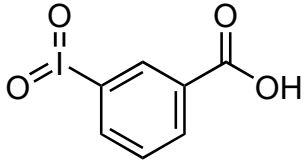
11–19

1) *p*-TsOH, 4 Å MS, ethylene glycole
2) Li, NH_3 (liq.)
3) HCl
4) TIPSOTf, 2,6-lutidine
5) LDA, MeI
6) NaHMDS, Comin's reagent
7) ethyl acrylate, $Pd(OAc)_2$, PPh_3, NEt_3
8) DIBAL-H
9) **1**, $Pd_2(dba)_3$, PPh_3
10) $AlCl_3$, –50 °C



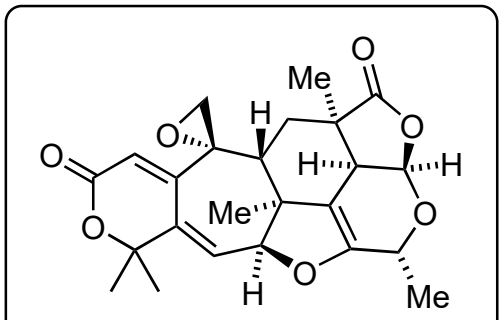
1

11) DIBAL-H
12) $Fe(acac)_3$, $PhSiH_3$
13) DMP
14) $RuCl_3$, $NaIO_4$
15) *m*-IBX, $(PhSe)_2$
16) LiHMDS, MeI
17) *hυ*, AcOH, H_2O
18) NaDMSO, MOMBr
19) NaDMSO, MeI

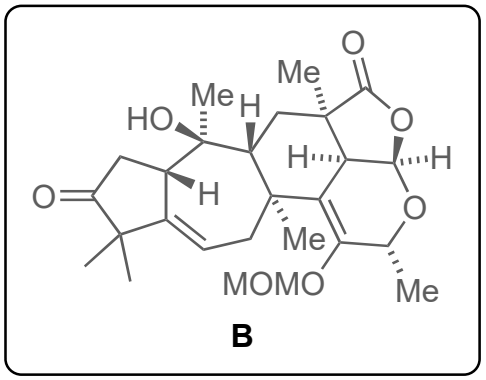


m-IBX

GENERAL HINT: if unsure about regiochemistry looking at the structure of the natural product often helps
1) Synthesis of SM?
1) Hint: saturated ketone reacts
2) Name of reaction?
2) Hint: double reduction
6) Comin's reagent structure
7) Name of reaction?
9) Synthesis of **1** via which named reaction and how?
9) Hint: Glycolisation
10) Name of the reaction
14) Hint: two oxidations occur, TBSO- and a second position are oxidized
15) Hint: double oxidation on the less hindered ketone
17) Hint: 6,6 ring system tranforms to 5,7 ring system
18) Hint: saturated ketone reacts

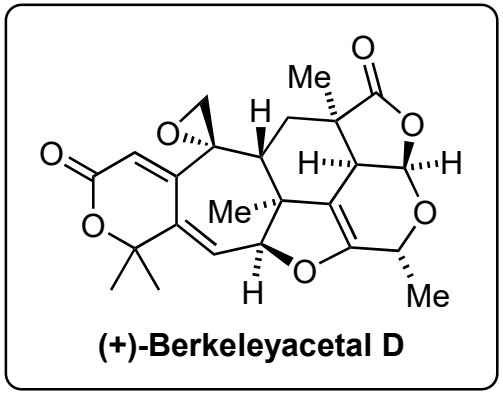


(+)-Berkeleyacetal D



B

20–25



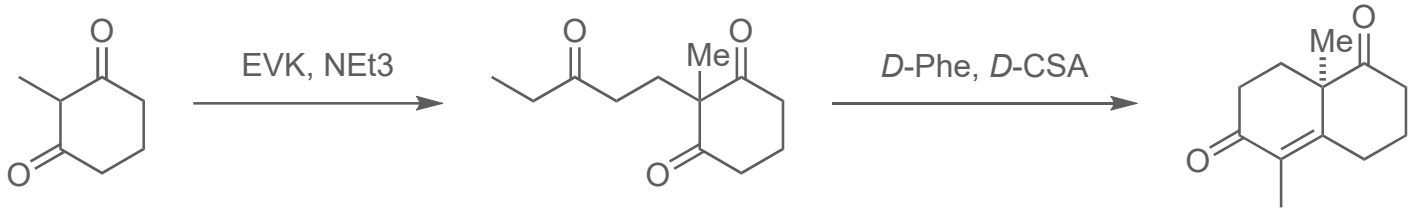
(+)-Berkeleyacetal D

20) NBS
21) *m*-CPBA, $NaHCO_3$
22) Burgess reagent
23) CF_3COCH_3, Oxone, $NaHCO_3$
24) $(PhSeO)_2O$
25) *t*-BuOLi

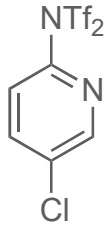
20) Hint: monobromination

2) Birch reduction
7) Heck coupling
9) Achmatowicz reaction
10) Diels Alder

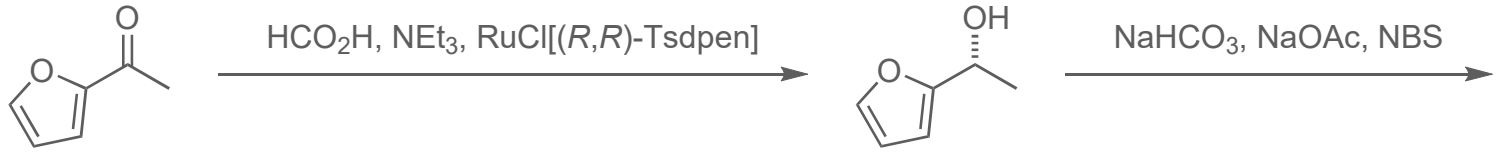
1)

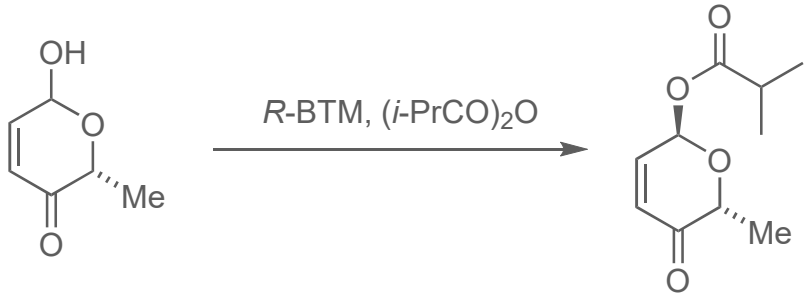

O
O
EVK, NEt3
O
Me
O
O
D-Phe, D-CSA
Me
O
O

6)


NTf2
N
Cl

9)


O
O
HCO2H, NEt3, RuCl[(R,R)-Tsdpen]
OH
O
NaHCO3, NaOAc, NBS


OH
O
Me
O
R-BTM, (i-PrCO)2O
O
O
O
Me
O