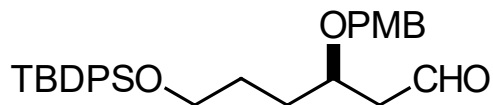


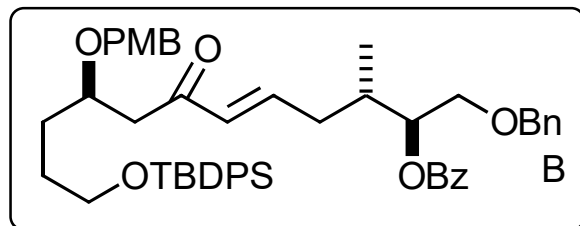
Synthesis Challenge #81

Total Synthesis, Stereochemical Revision, and Biological Assessment of Iriomoteolide-2a,
K. Sakamoto, A. Hakamata, A. Iwasaki, K. Suenaga, M. Tsuda, H. Fuwa, *Chem. Eur. J.* **2019**, *25*, 8528 – 8542

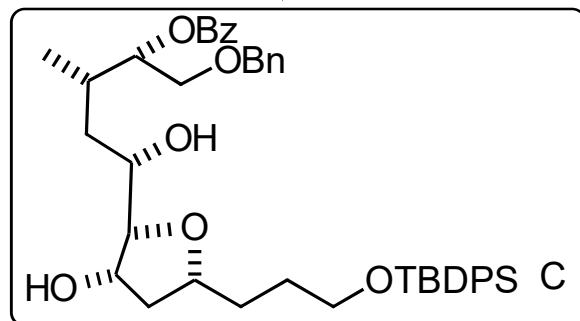
11.07.2019



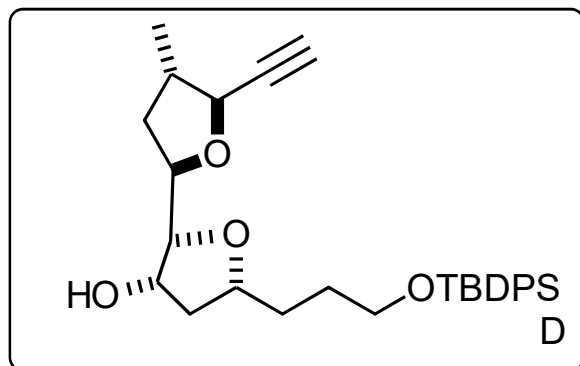
↓ 1-3 A



↓ 4-8



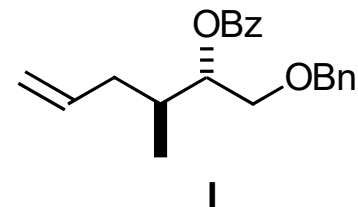
↓ 9-12



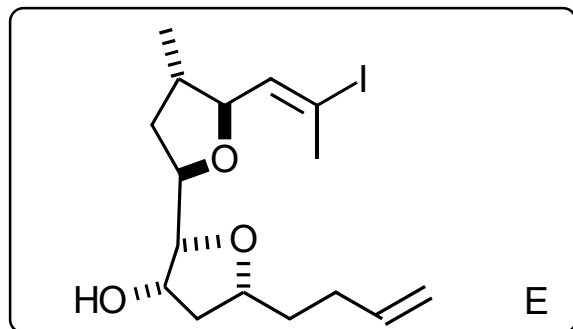
- 1) tetra(vinyl)tin, MeLi, THF, -78°C
- 2) DMP
- 3) I, Hoveyda-Grubbs-II

- 4) (*R*)-2-Me-CBS, BH₃*THF, THF, -40°C
- 5) (+)-DIPT, Ti(O*i*Pr)₄, *t*BuOOH, 4Å MS, CH₂Cl₂, -40°C
- 6) TBSCl, imidazole
- 7) DDQ
- 8) PPTS

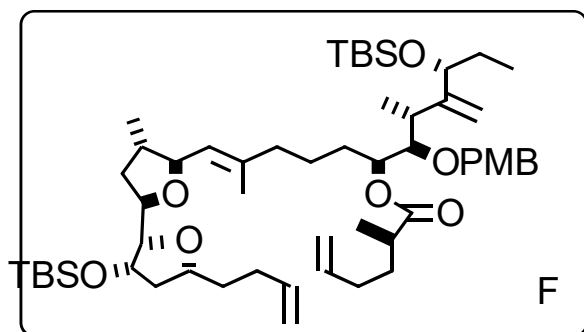
- 9) MsO₂, py, 60°C
- 10) K₂CO₃, MeOH, 60°C; LiDBB
- 11) SO₃•py, Et₃N, DMSO
- 12) Ohira-Bestmann, K₂CO₃, MeOH



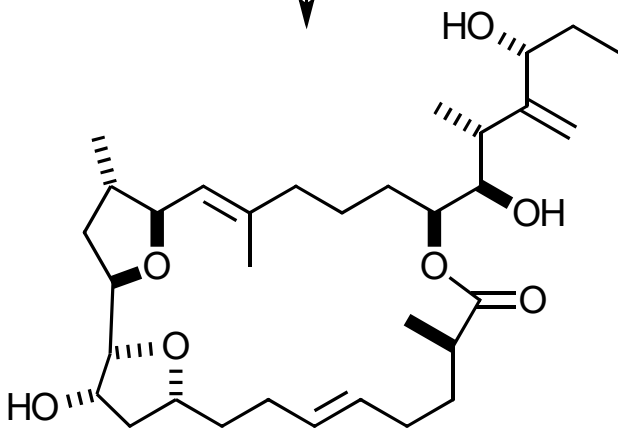
↓ 13-18



↓ 19-21



↓ 22-24



- 13) *n*BuLi, MeI
- 14) Bu₃Sn(Bu)Cu(CN)Li₂, MeOH, THF, -78°C
- 15) I₂, CH₂Cl₂, -20°C
- 16) TBAF, AcOH
- 17) SO₃^{*}py, Et₃N, DMSO
- 18) Ph₃P⁺CH₃Br⁻, NaHMSDS

- 19) **II**, 9-BBN-H, THF, then E, aq. CsCO₃, [PdCl₂(dppf)^{*}CH₂Cl₂], Ph₃As, DMF
- 20) PPTS
- 21) **III**, 2,4,6-Cl₃C₆H₂COCl, Et₃N, THF, then DMAP, toluene

- 22) DDQ
- 23) Grubbs-II, toluene
- 24) HF^{*}py, THF

