

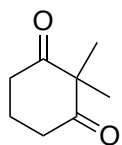
Synthesis Challenge 103

AG Wegner

Y. Imamura, K. Takaoka, Y. Komori, M. Nagatomo, M. Inoue, *Angew. Chem. Int. Ed.*

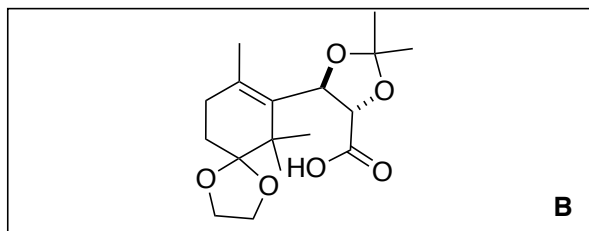
2023, *62*, e202219114

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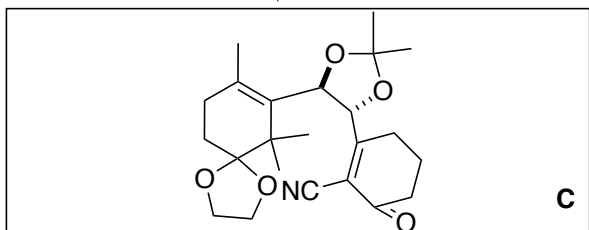
↓ ???

A



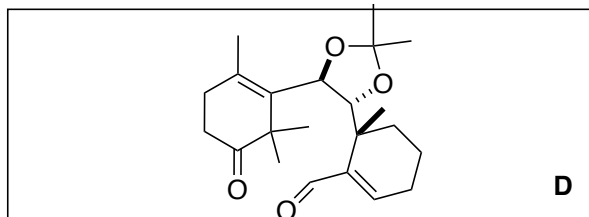
B

↓ 1-2



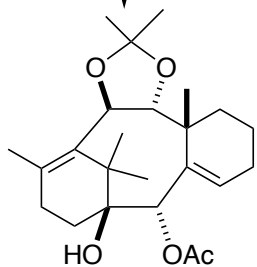
C

↓ 3-5



D

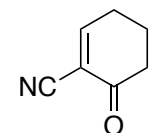
↓ 6-7



E

Please draft a synthesis from **A** to **B**?

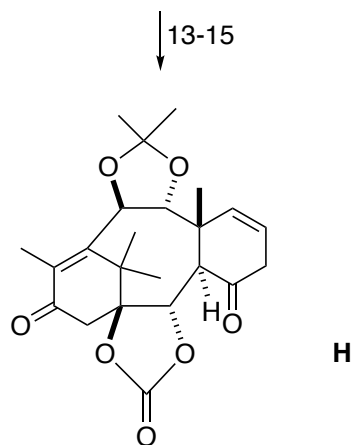
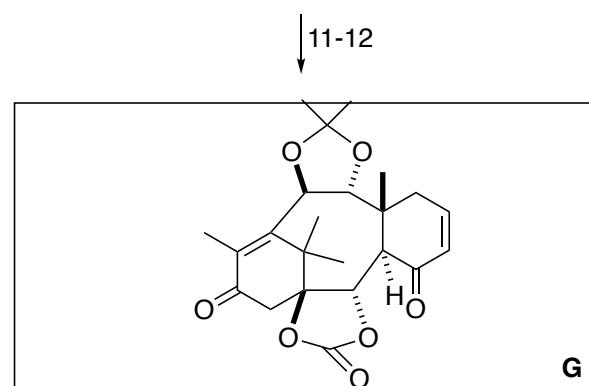
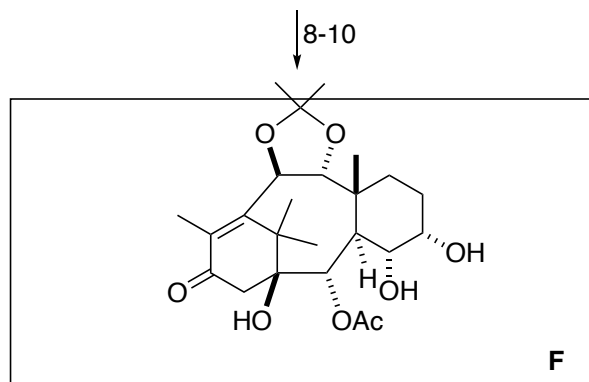
1) *t*BuOCOCi, *N*-methylmorpholine (NMM), THF;
(PhTe)₂, NaBH₄, THF, MeOH, 0 °C to 25 °C, 91 %;
2) **I** (2 equiv), Et₃B (3 equiv), air, benzene, 50 °C;
2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ),
2,6-lutidine, 50 °C,



I

3) MeMgBr, CuI, Me₂S, toluene, -20 °C, then
NaBH₄, EtOH, 25 °C
4) Methanesulfonyl chloride (MsCl), Et₃N, benzene,
25 °C, then 1,8-diazabicyclo[5.4.0]undec-7-ene
(DBU), 100 °C
5) *t*Bu₂AlH, hexane, -20 °C, then 1 M aq. HCl, 25 °C

6) TiCl₄ (4 equiv), Zn (10 equiv), pyridine, THF, 50 °C
7) Ac₂O, *N,N*-dimethyl-4-aminopyridine (DMAP),
pyridine, CH₂Cl₂, 25 °C

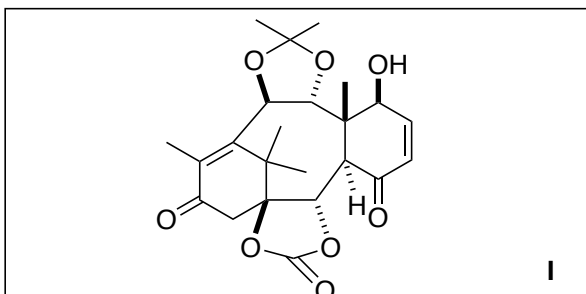


8) CrO_3 , 3,5-dimethylpyrazole, CH_2Cl_2 , 25°C
 9) *p*-Toluenesulfonyl hydrazide (TsNHNH_2), AcOH , 25°C , then NaBH_3CN , 25°C
 10) CsOAc , *i*PrOH, 60°C , then OsO_4 (10 mol%), *N*-methylmorpholine *N*-oxide (NMO), acetone, H_2O , 25°C ,

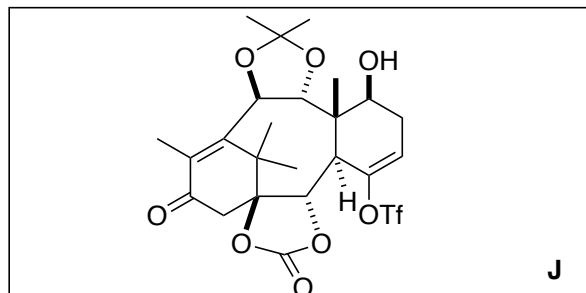
11) DMAP, toluene, 120°C , then $(\text{Cl}_3\text{CO})_2\text{CO}$, pyridine, CH_2Cl_2 , -20°C
 12) DMSO, $(\text{CF}_3\text{CO})_2\text{O}$, CH_2Cl_2 , -78°C , then Et_3N , 25°C , then K_2CO_3 , MeOH, 0°C

13) MsCl , Et_3N , CH_2Cl_2 , 25°C
 14) $\text{Pd}(\text{OCOCF}_3)_2$ (40 mol%), PPh_3 , Et_3N , DMSO, 60°C
 15) Trimethylsilyl trifluoromethanesulfonate (TMSOTf), *i*PrNMe₂, $(\text{CH}_2\text{Cl})_2$, 40°C , then HF · pyridine, pyridine, MeCN, 25°C

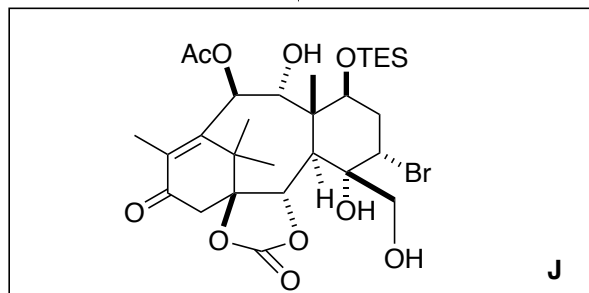
↓ 16-17



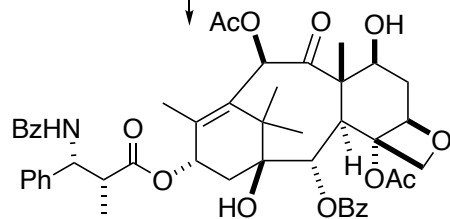
↓ 18-20



↓ 21-23



↓ 24-17



16) *N*-bromosaccharin, NaHCO₃ MeCN/H₂O, 25 °C
17) KOH, Ag₂O DMF/H₂O, 0 °C

18) Triethylsilyl trifluoromethanesulfonate (TESOTf),
*i*PrNMe₂, (CH₂Cl)₂, 50 °C
19) Rh/Al₂O₃, H₂ (1 atm), benzene, 25 °C
20) *N*-(5-chloropyridin-2-yl)-*N*-(methanesulfonyl)methanesulfonamide, KN(SiMe₃)₂,
THF, -78 °C, then 1 M aq. HCl, EtOH, 25 °C

21) [*t*Bu₃PPd(μ-I)]₂ (40 mol%), Me₃SiCH₂ZnCl, *N*-methylpyrrolidone, 25 °C, then *N*-bromosuccinimide, 0 °C
22) CF₃CO₂H, MeOH, 40 °C, then Ac₂O, CeCl₃ · 7H₂O, THF, 40 °C, then triethylsilyl chloride (TESCl), imidazole, DMF, 0 °C
23) OsO₄ (1 equiv), pyridine, THF, 25 °C

24) *i*Pr₂NEt, toluene, 100 °C, then DMSO, (CF₃CO)₂O, CH₂Cl₂, -78 °C, then Et₃N, 25 °C
25) Ac₂O, DMAP, CH₂Cl₂, 25 °C
26) LiBH₄, THF, -78 °C
27) PhLi, THF, -78 °C, then β-lactam II, 0 °C, then 1 M aq. HCl, MeOH, 25 °C

