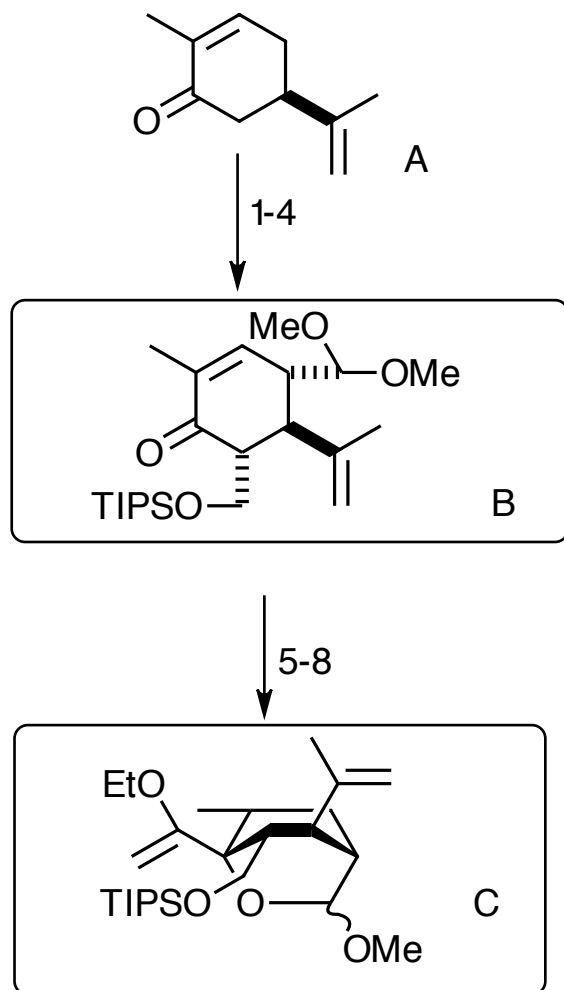


Synthesis Challenge # 40

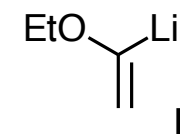
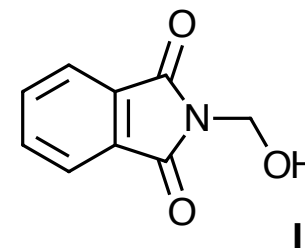
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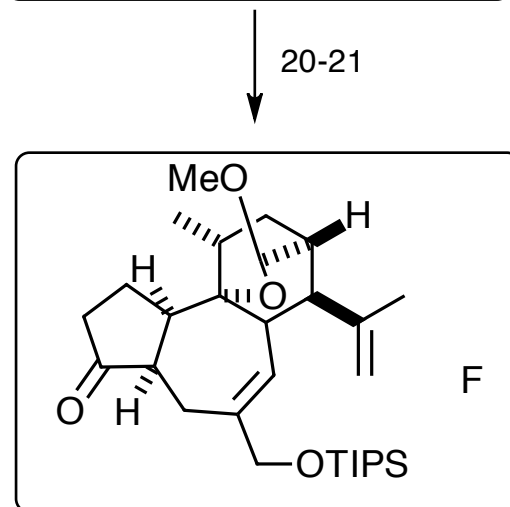
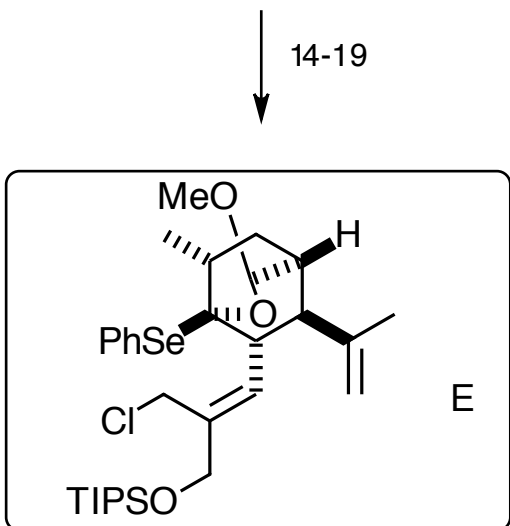
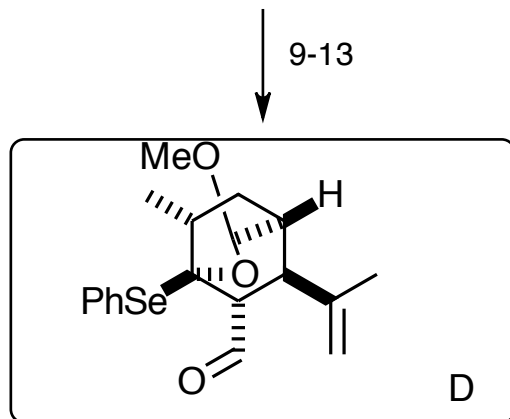
T. Asaba, Y. Katoh, D. Urabe, M. Inoue, *Angew. Chem. Int. Ed.* **2015**, ASAP, DOI: 10.1002/anie.201509160
05.11.2015



- 1) FeCl_3 , MeMgBr , TMSCl , Et_3N , $\text{N,N'$ -dimethylpropyleneurea, THF
- 2) $\text{CH}(\text{OMe})_3$, $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 , -50°C
- 3) $\text{LiN}(\text{iPr})_2$, THF, -78°C ; I
- 4) TIPSCl , imidazole, DMF

- 5) Li , NH_3 , THF, -78°C
- 6) TPAP, N-methylmorpholine N-oxide, 4 \AA MS, CH_2Cl_2
- 7) II, THF, -78°C
- 8) CSA, benzene, $\text{CH}(\text{OMe})_3$

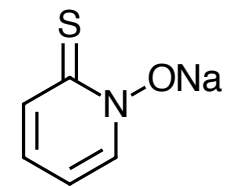




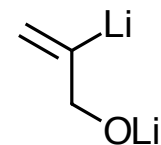
- 9) *m*CPBA, pH 7 buffer, CH₃CN, 10°C
- 10) MeSO₂Cl, Et₃N, CH₂Cl₂, 0°C
- 11) III, DMAP, toluene ; hn, (PhSe)₂
- 12) TBAF, CH₃CN, 60°C,
- 13) SO₃·pyridine, Et₃N, DMSO, CH₂Cl₂

- 14) IV, Et₂O, -78°C
- 15) Ac₂O, DMAP, pyridine, 40°C
- 16) [Pd(PPh₃)₄], KOAc, 18-crown-6, THF, 65 °C
- 17) K₂CO₃, MeOH
- 18) TIPSCl, imidazole, CH₂Cl₂
- 19) O=C(CCl₃)₂, PPh₃, CH₂Cl₂

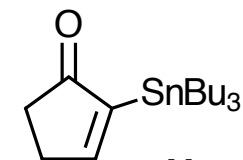
- 20) V, [Pd(PPh₃)₄], CuTC, K₂CO₃
- 21) (TMS)₃SiH, VI, toluene, 110°C



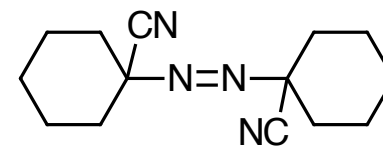
III



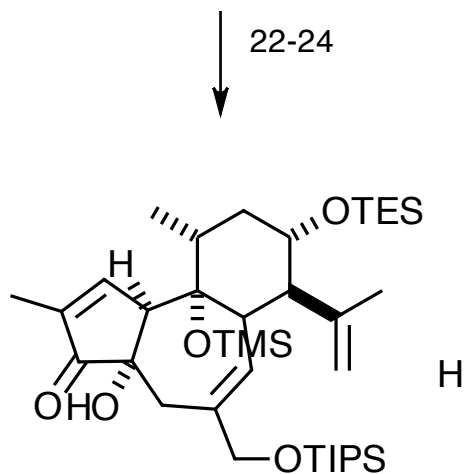
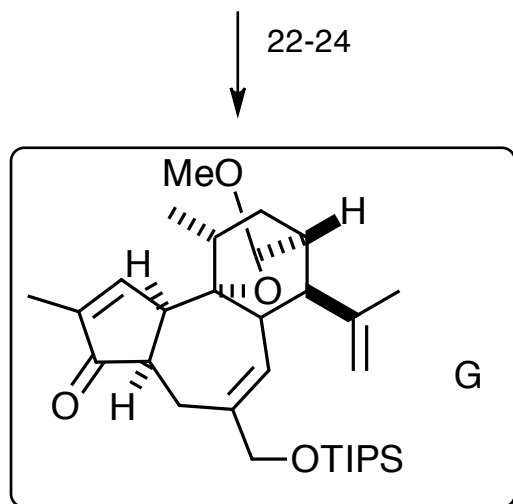
IV



V

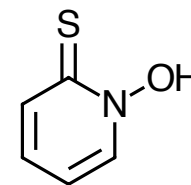


VI



22) $\text{LiN}(\text{iPr})_2$, THF, -78°C ;
 TMSCl, -78°C to 0°C
 23) $[\text{CH}_2=\text{NMe}_2]^+\text{I}^-$, CH_2Cl_2 ;
 SiO_2 , *n*-hexane/EtOAc (10:1)
 24) $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$, EtOH/pH 7 buffer (5:1),
 110°C ,

25) HCl aq., 1,4-dioxane, 35°C
 26) TIPSCl, imidazole, DMF, 10°C
 27) NaClO_2 , NaH_2PO_4 , 2-methyl-
 2-butene, *t*BuOH, H_2O
 28) TMSOTf, 2,6-lutidine, CH_2Cl_2 , -20°C ,
 29) **VII**, EDCl·HCl, toluene; hn, O_2 ,
*t*BuSH; $\text{P}(\text{OEt})_3$
 30) TESOTf, 2,6-lutidine, CH_2Cl_2 , 0°C
 31) $\text{NaN}(\text{TMS})_2$, THF, -78°C ; Davis'
 reagent



VII