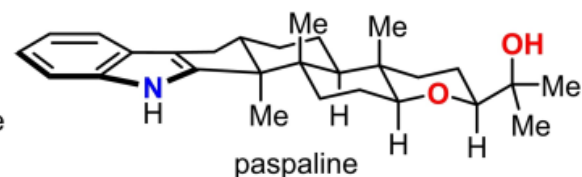
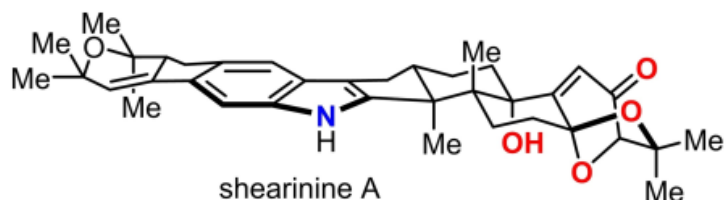
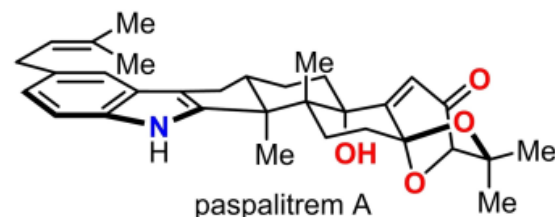
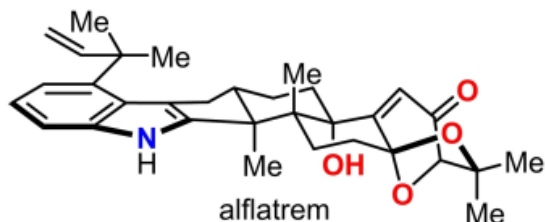
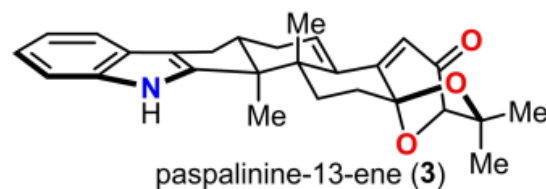
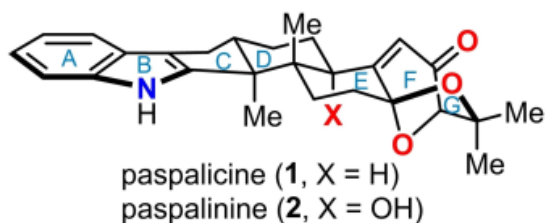


Natural Products Synthesis

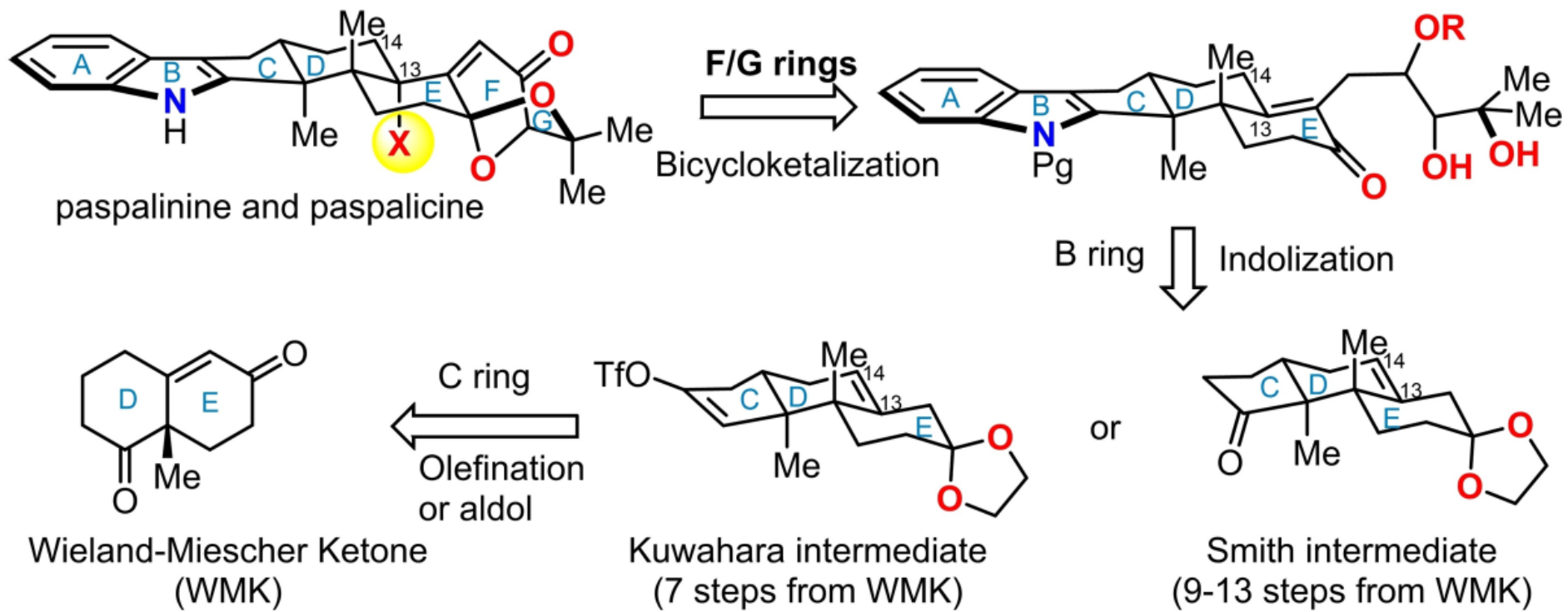
How to cite:

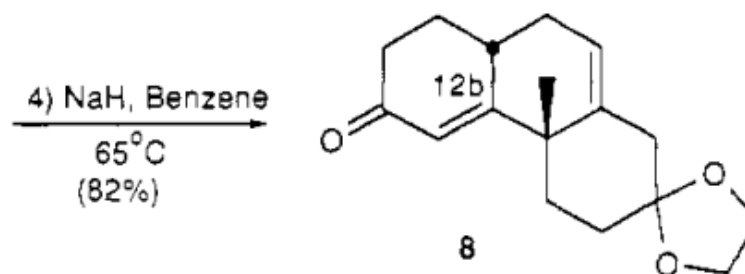
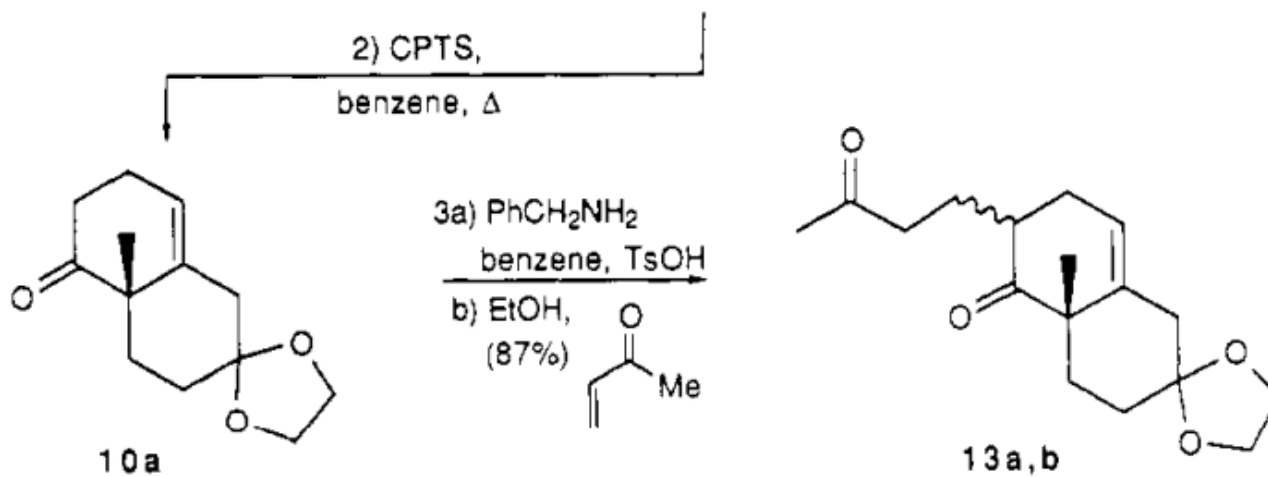
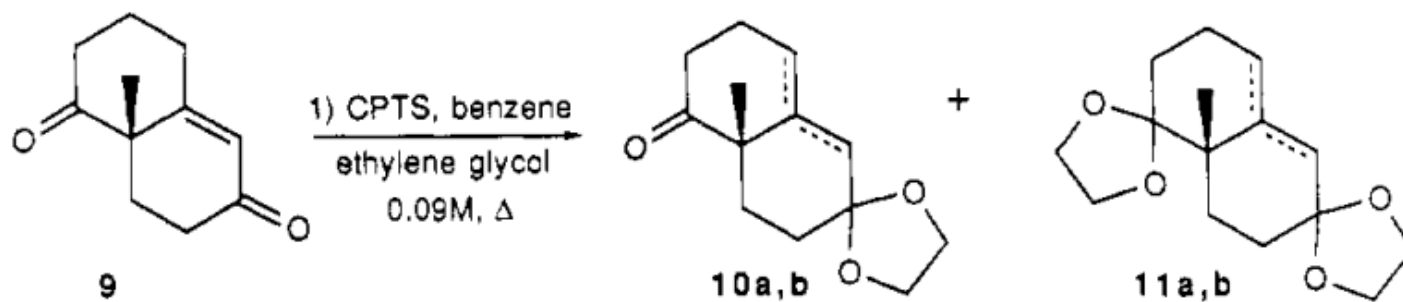
International Edition: doi.org/10.1002/anie.202115384

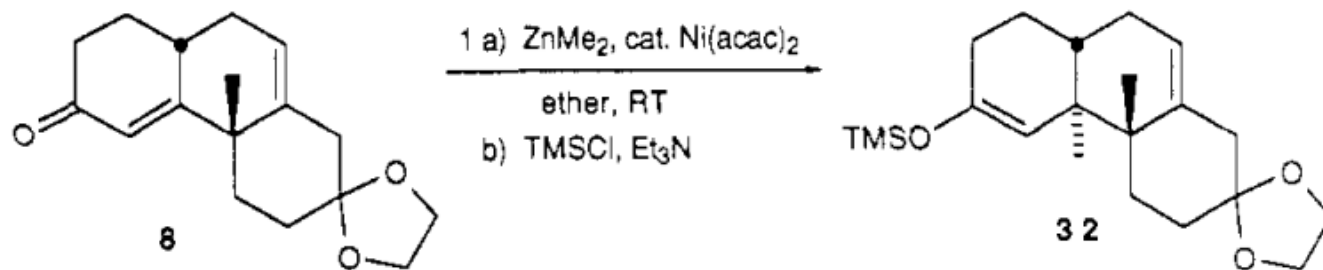
German Edition: doi.org/10.1002/ange.202115384

Asymmetric Total Synthesis of Indole Diterpenes Paspalicine, Paspalinine, and Paspalinine-13-ene*Lian-Dong Guo, Zejun Xu, and Rongbiao Tong**

(a) Previous synthetic strategies (Smith and Kuwahara)



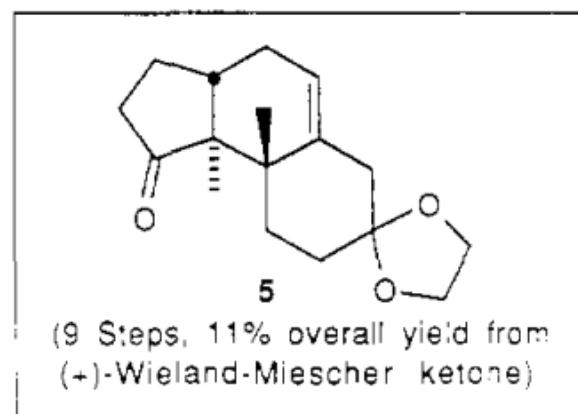
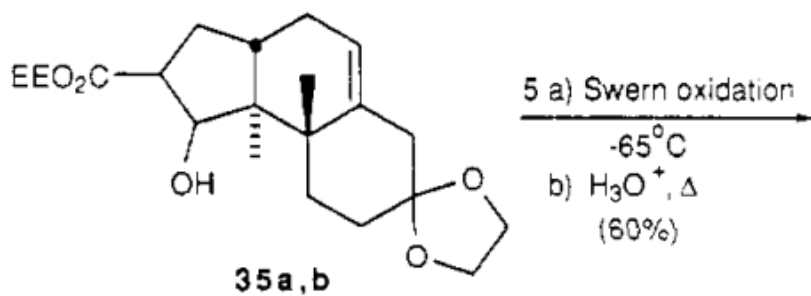
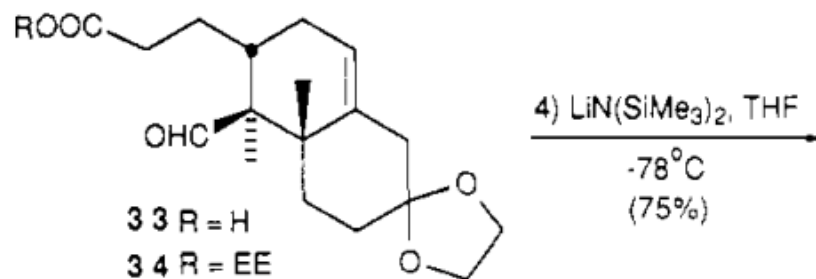


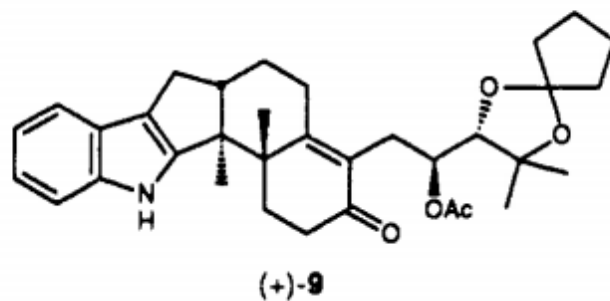
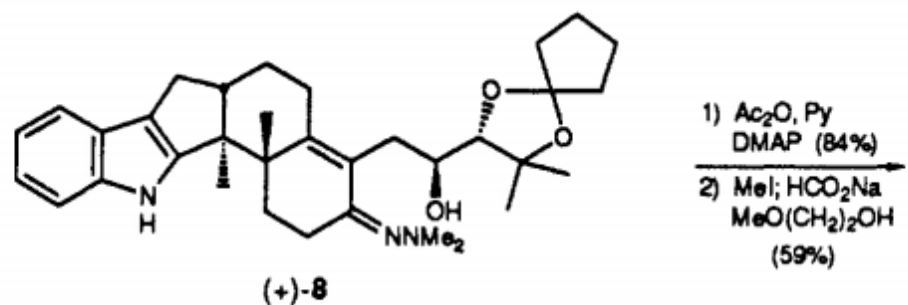
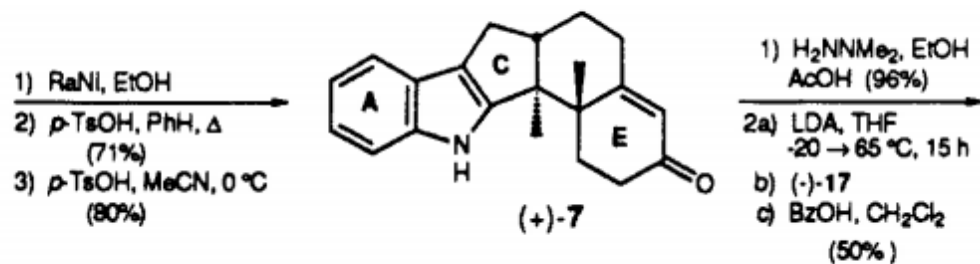
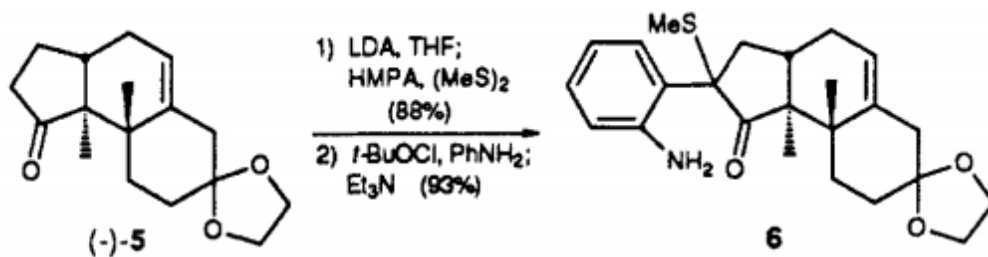


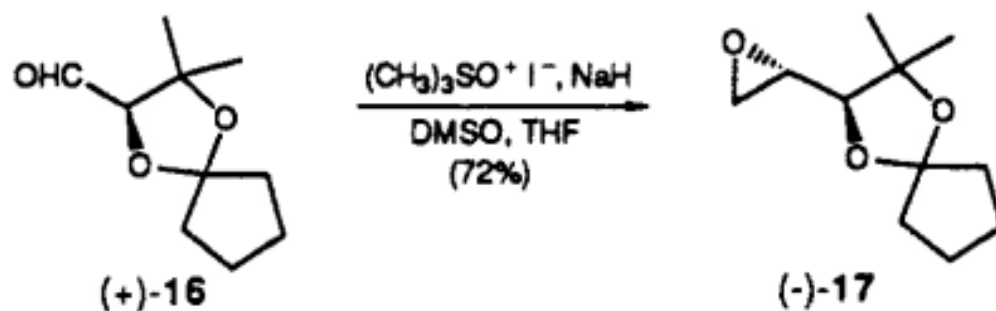
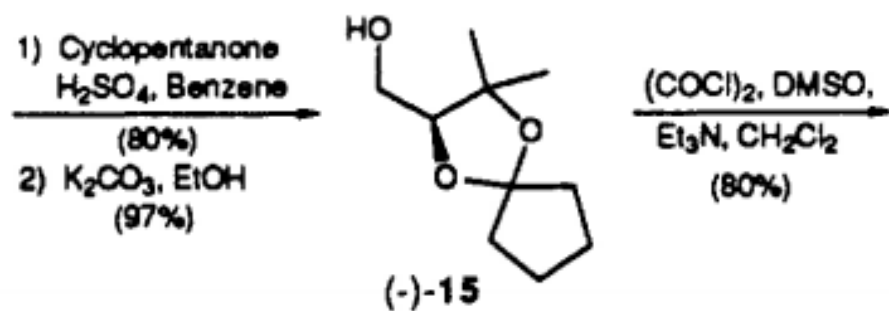
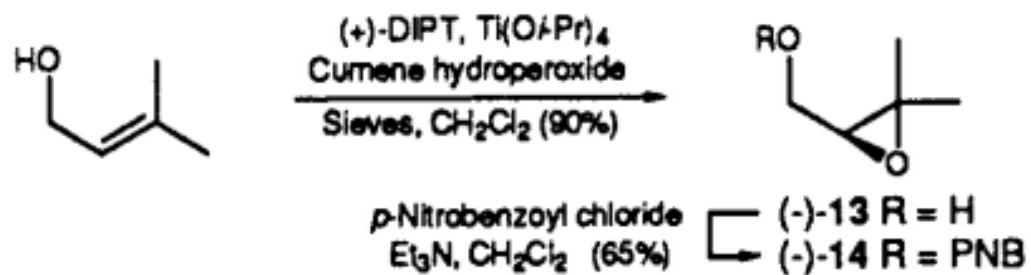
2 a) O_3 , CH_2Cl_2 , -78°C

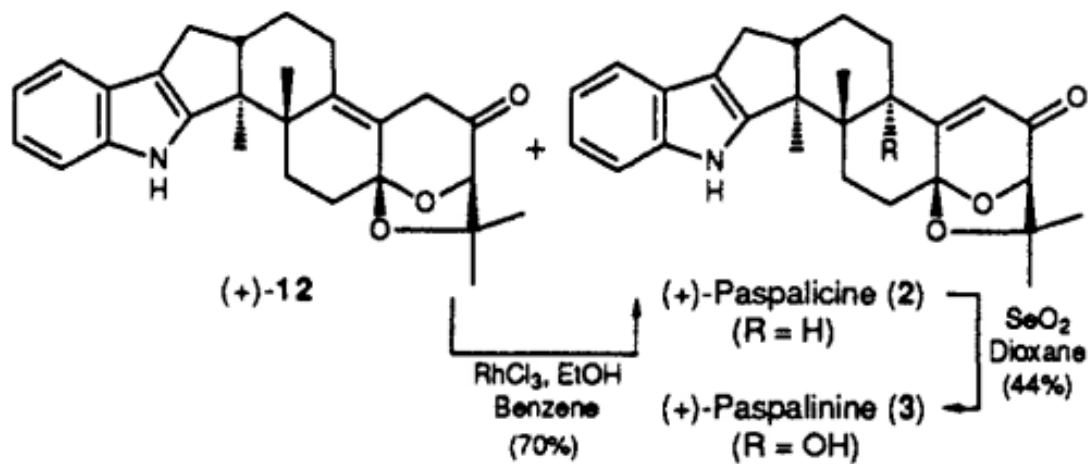
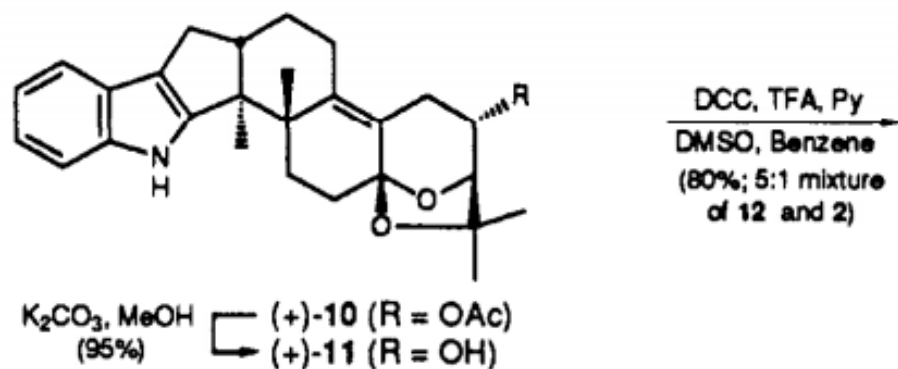
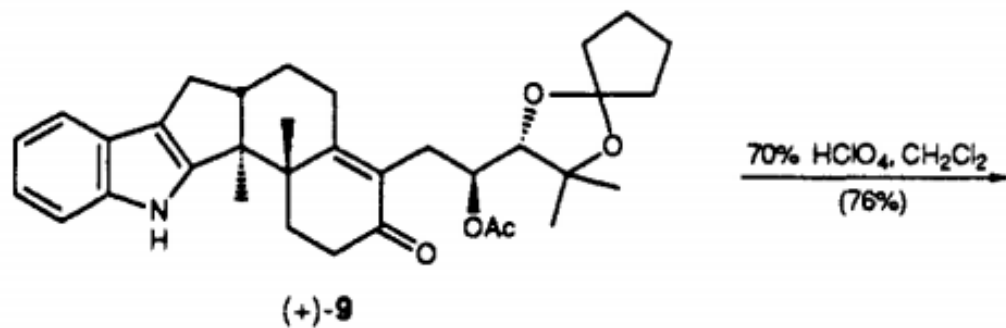
b) Me_2S
(44%, 2 steps)

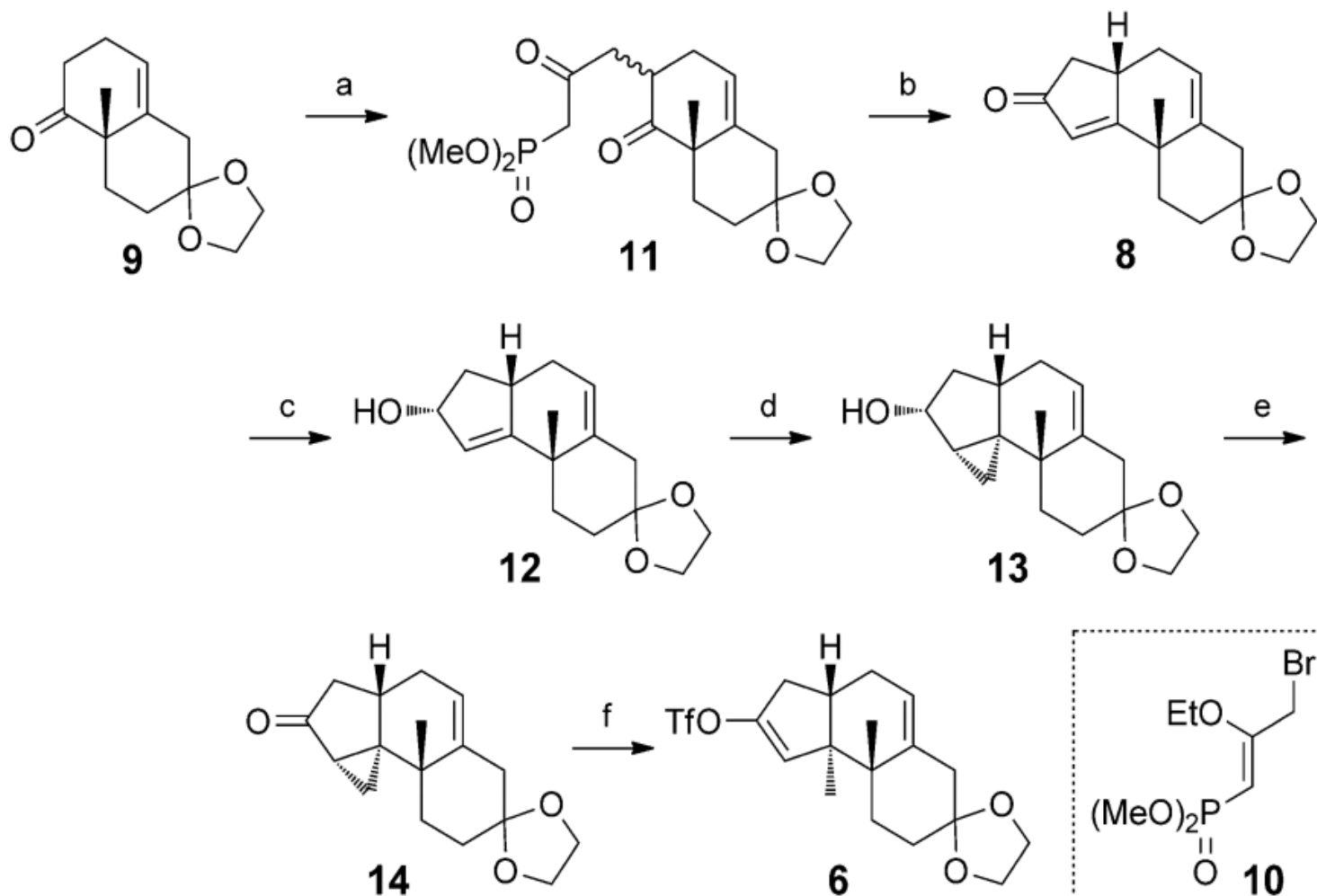
3) Ethyl vinyl ether
 p - TsOH
(79%)







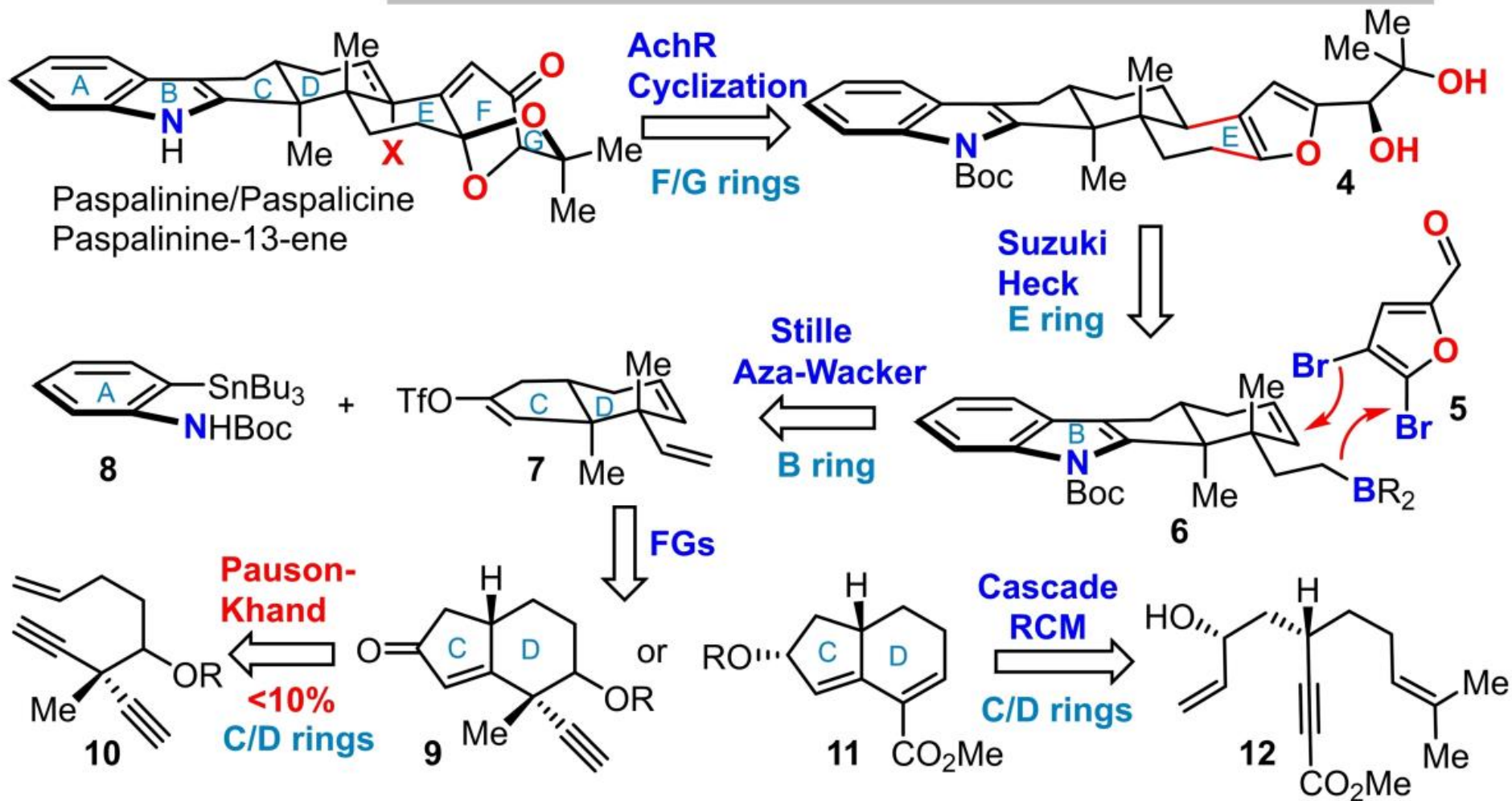


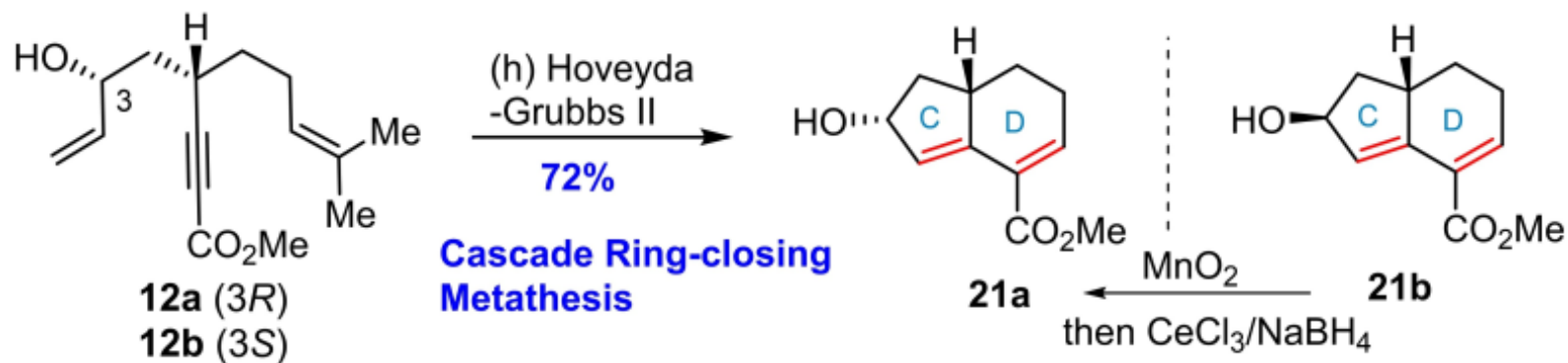
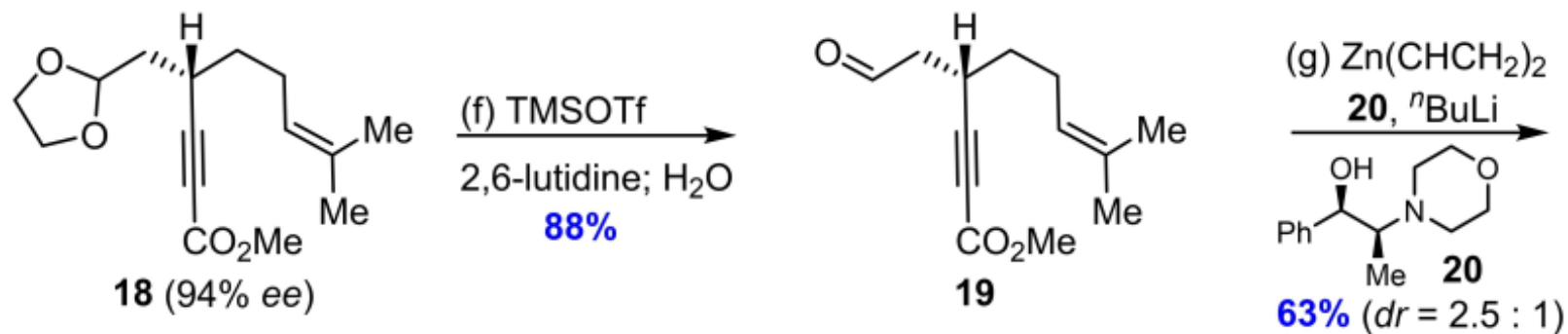
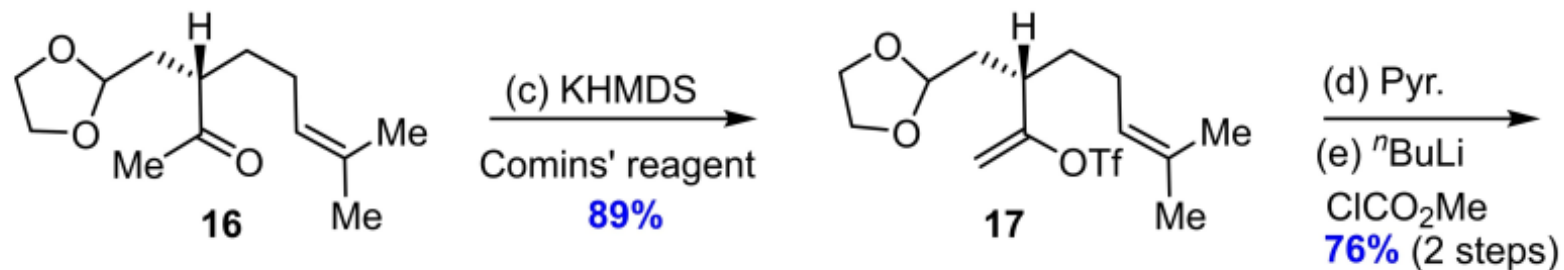
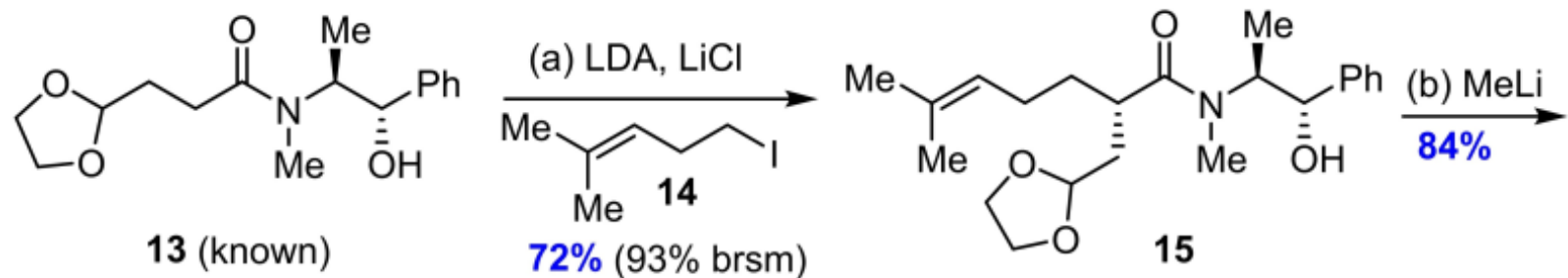


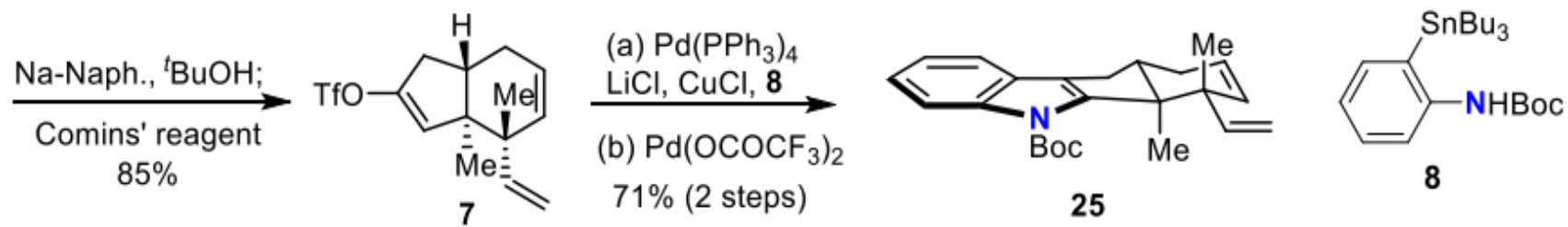
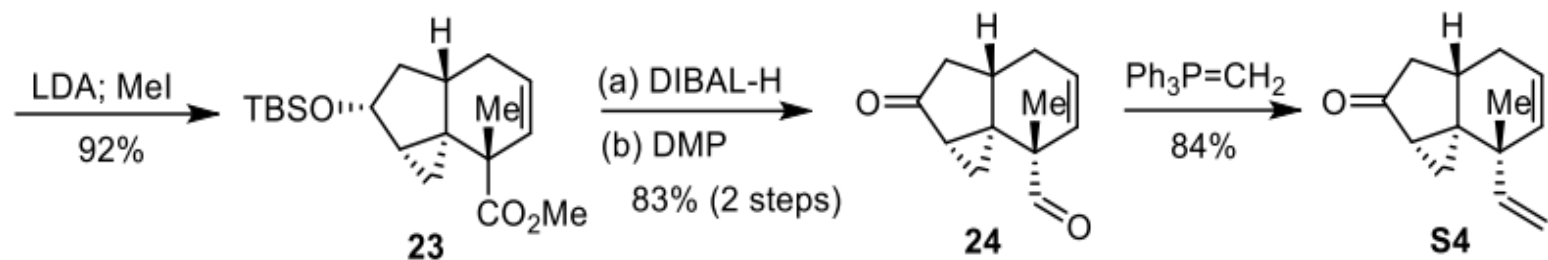
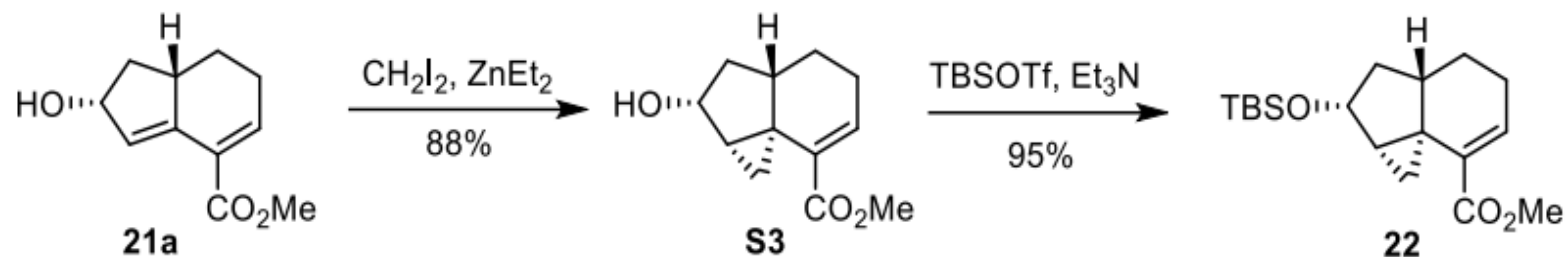
Scheme 3. Preparation of CDE ring portion **6**. Reagents and conditions: a) LDA, **10**, HMPA, THF, -78°C \rightarrow room temperature, then aq HCl (1 M), acetone, room temperature, 68%; b) Cs_2CO_3 , THF, 50°C , 77%; c) $\text{LiB}(\text{sBu})_3\text{H}$, THF, -40°C \rightarrow room temperature, 99%; d) CH_2I_2 , Et_2Zn , CH_2Cl_2 , 0°C ; e) DMSO, $(\text{COCl})_2$, Et_3N , CH_2Cl_2 , -75 to 0°C , 77% (2 steps); f) $\text{Na}(\text{C}_{10}\text{H}_8)$, THF, -75°C , then isoprene, Comins' reagent, HMPA, THF, -75 to -10°C , 42%

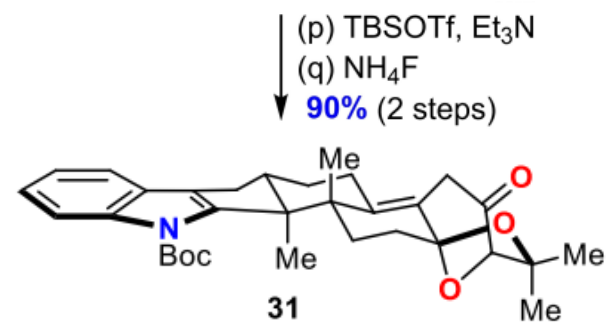
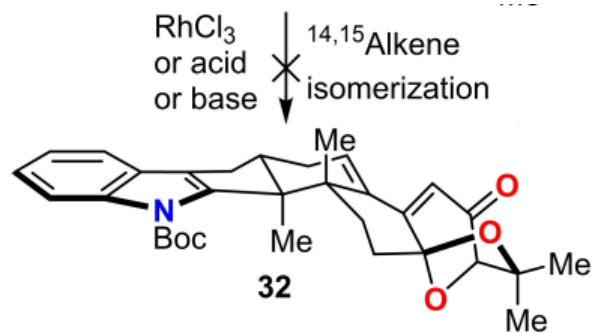
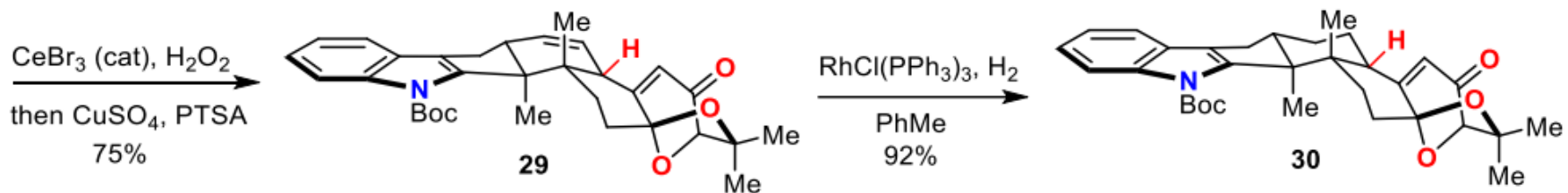
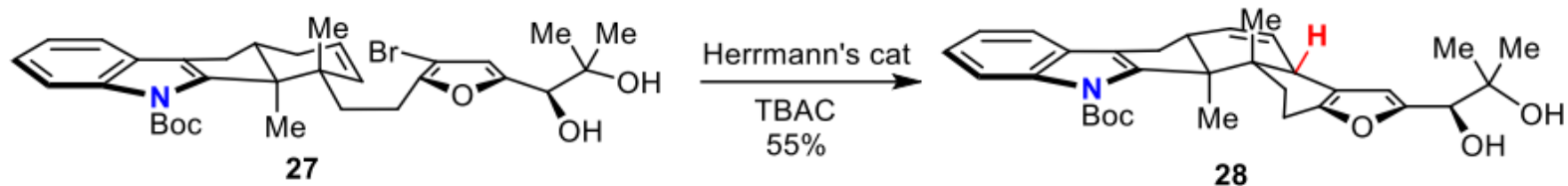
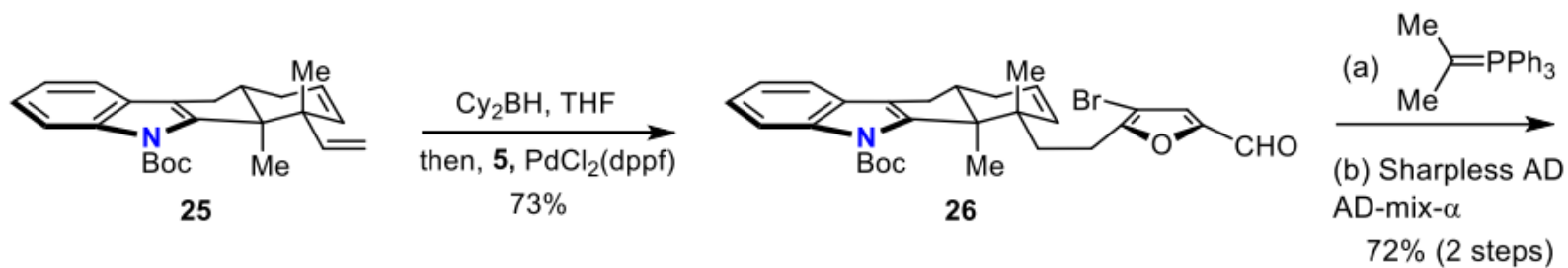
(b) Our synthetic plan

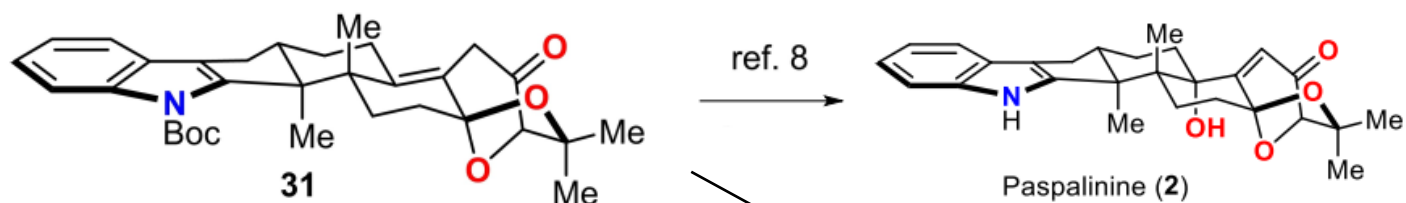
Ring-closing sequence: CD \longrightarrow AB \longrightarrow E \longrightarrow FG



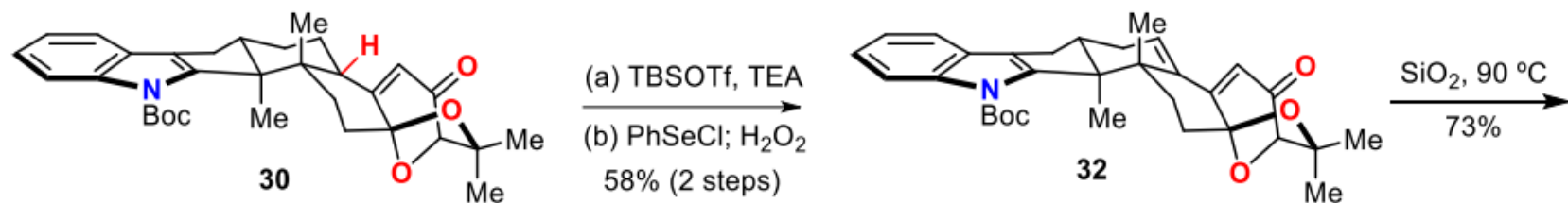




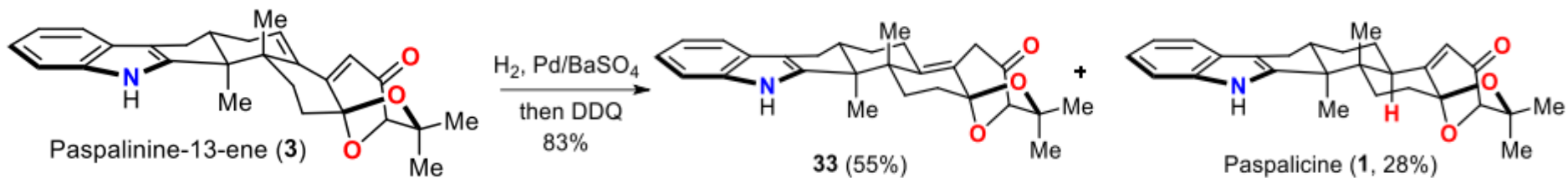




(p) TBSOTf, Et₃N
(r) PhSeCl; H₂O₂

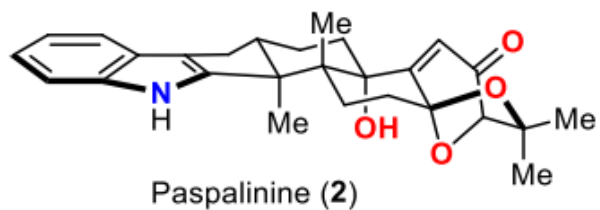


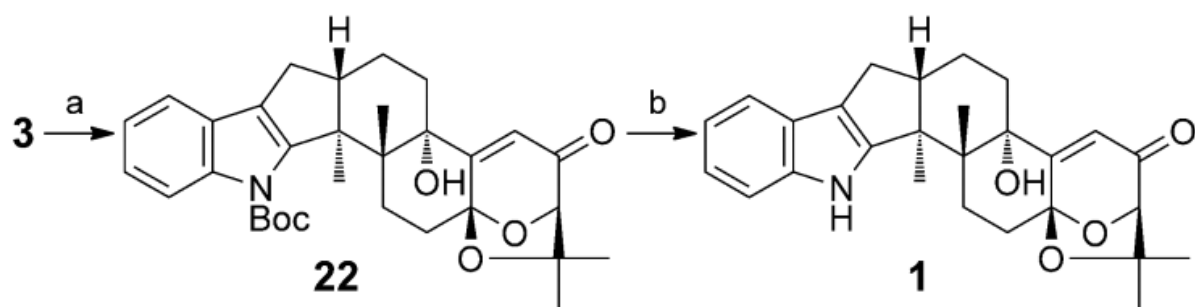
(a) TBSOTf, TEA
(b) PhSeCl; H₂O₂
58% (2 steps)



ref. 7e

SeO₂
1,4-dioxane
85 °C
30%





Scheme 6. Completion of the total synthesis of paspalinine (**1**).

Reagents and conditions: a) KHMDS, PhSeCl, THF, -70 to -15 °C, then aq H_2O_2 , NaHCO_3 , room temperature, 57%; b) SiO_2 , ca. 133 Pa, 90 – 110 °C, 67%. KHMDS = potassium hexamethyldisilazide.