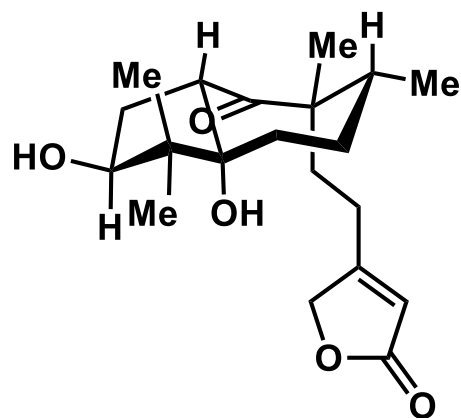
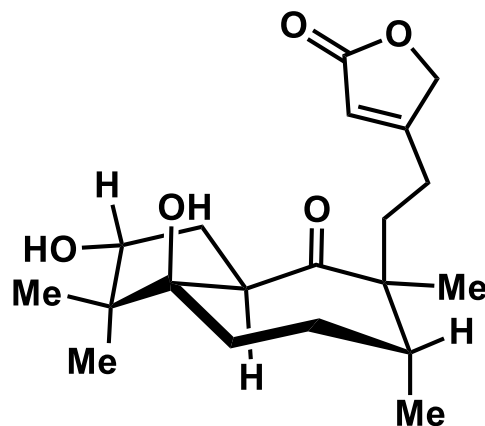


Total Synthesis of the Diterpenes (+)-Randainin D and (+)-Barekoxide via Photoredox-Catalyzed Deoxygenative Allylation

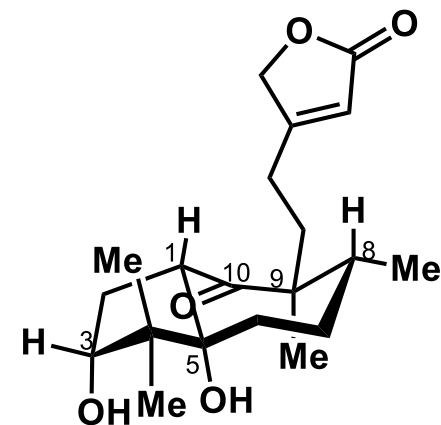
Oleksandr Vyhivskyi and Olivier Baudoin*



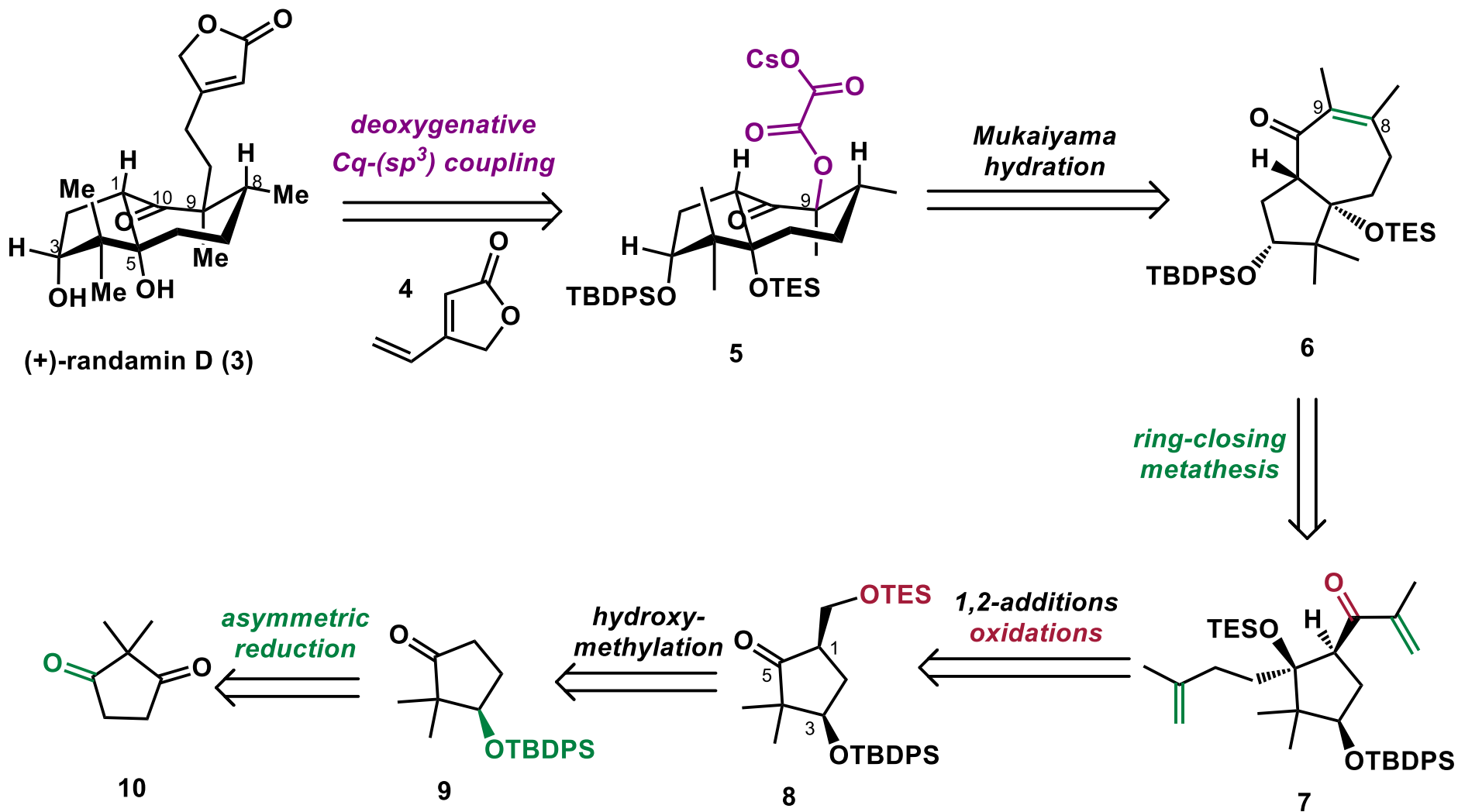
shortolide C (1)

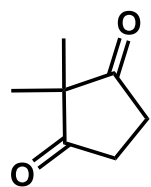


randamin C (2)



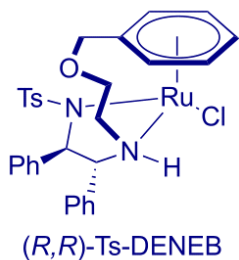
randamin D (3)



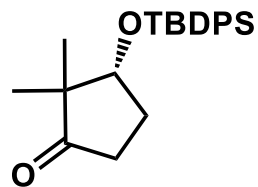


10

1. (*R,R*)-Ts-DENEb (1.25 mol%)
HCOOH/Et₃N 1:1, 15 to 20 °C, 72 h
2. TBDPSCI, Im., CH₂Cl₂, 20 °C, 18 h
(79% over 2 steps)



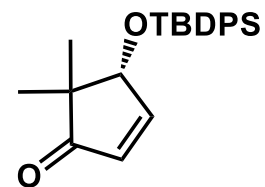
(*R,R*)-Ts-DENEb



9

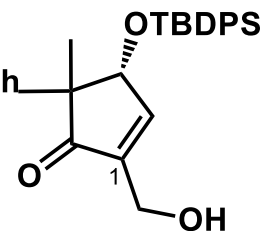
e.r. = 99.5:0.5

- IBX, NMO, DMSO
80 °C, 16 h
(79%)

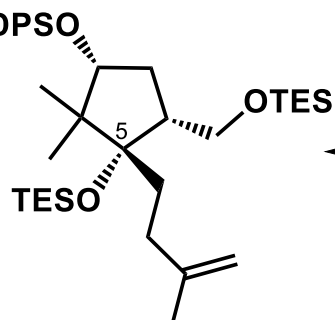


11

- PBu₃ (7.5 mol%), aq. CH₂O
CHCl₃/MeOH = 1.5:1, 3 h, 20 °C (95%)

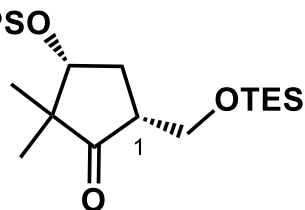
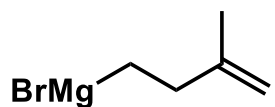


12



13

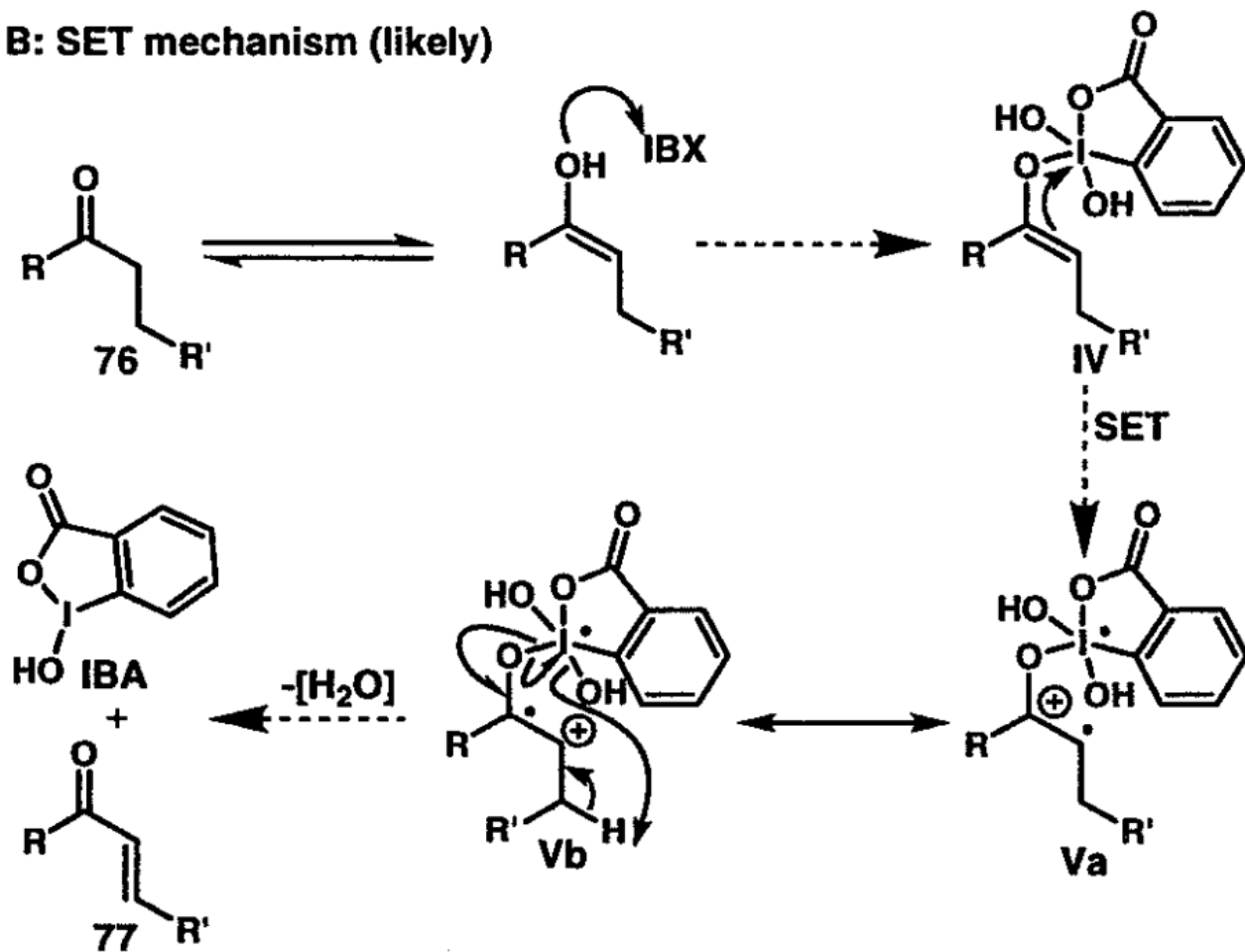
1. LaCl₃·2LiCl/THF TBDPSO
2-MeTHF, -40 °C, 3 h
2. TESOTf, collidine, CH₂Cl₂
0 to 20 °C, 16 h
(99% over 2 steps)



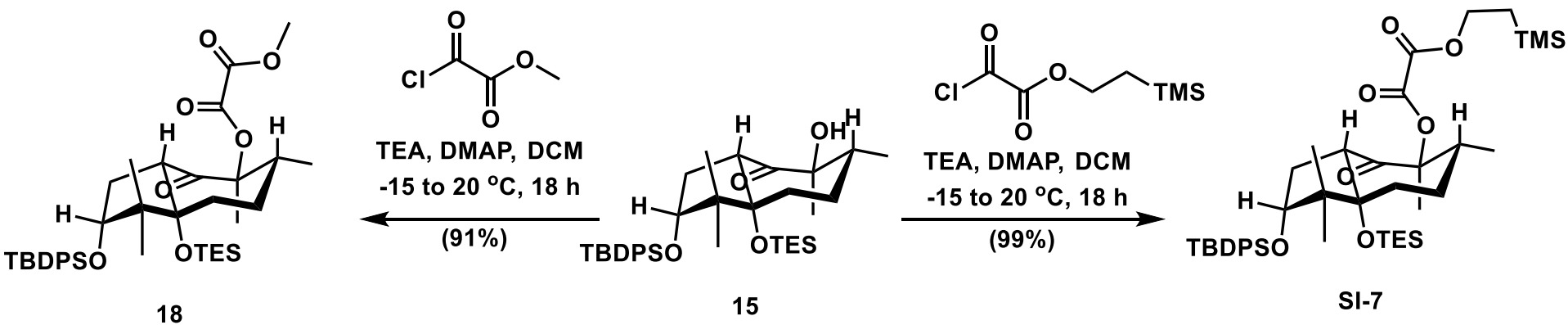
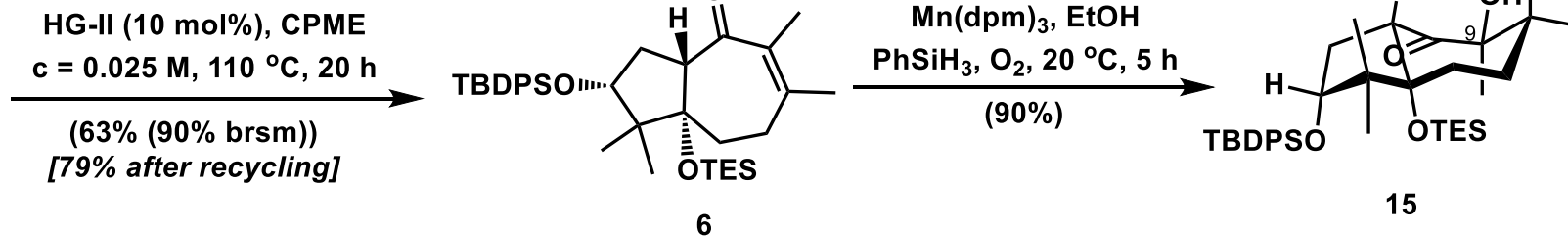
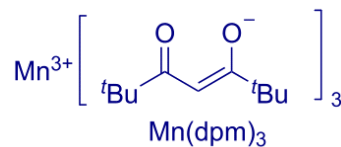
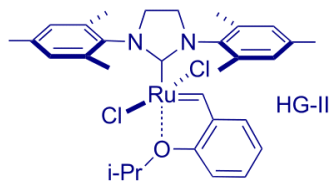
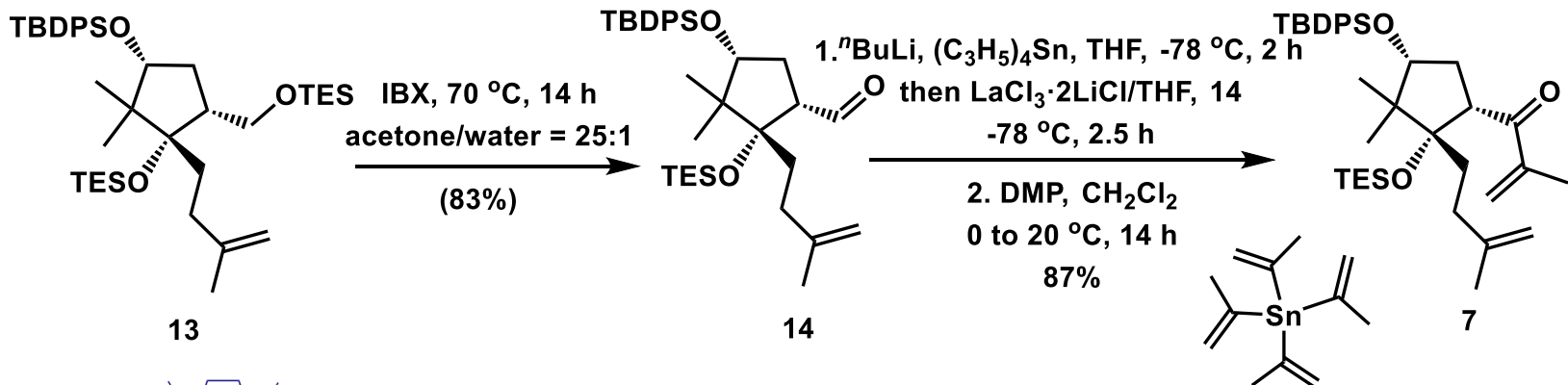
8

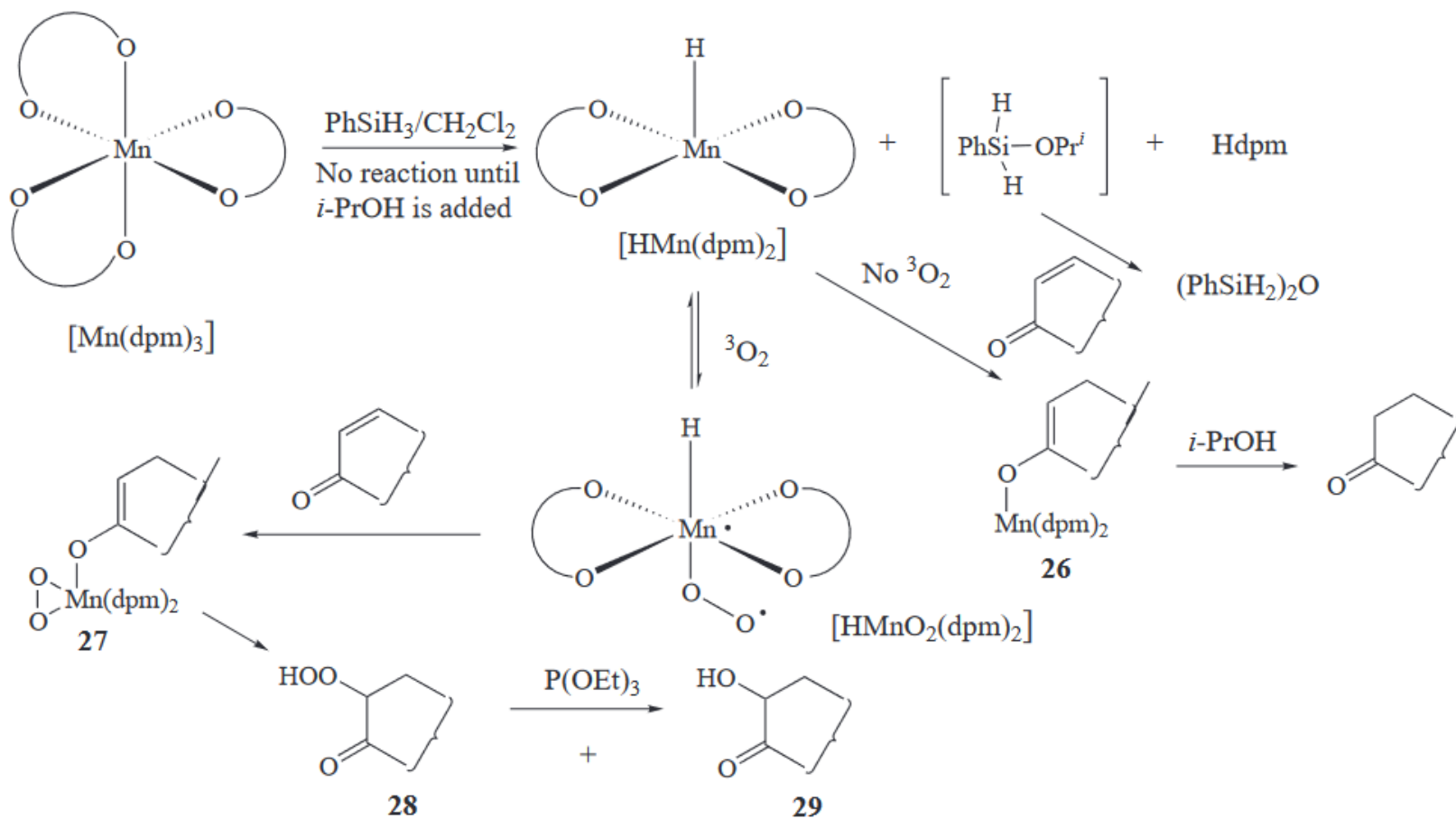
1. TESCI, Im., CH₂Cl₂, 20 °C, 14 h
2. H₂ (20 bar), Pd/C 10 mol%
AcONa, EtOAc, 20 °C, 2 h
(77% over 2 steps)

B: SET mechanism (likely)



J. Am. Chem. Soc., **2002**, *124*, 2250.

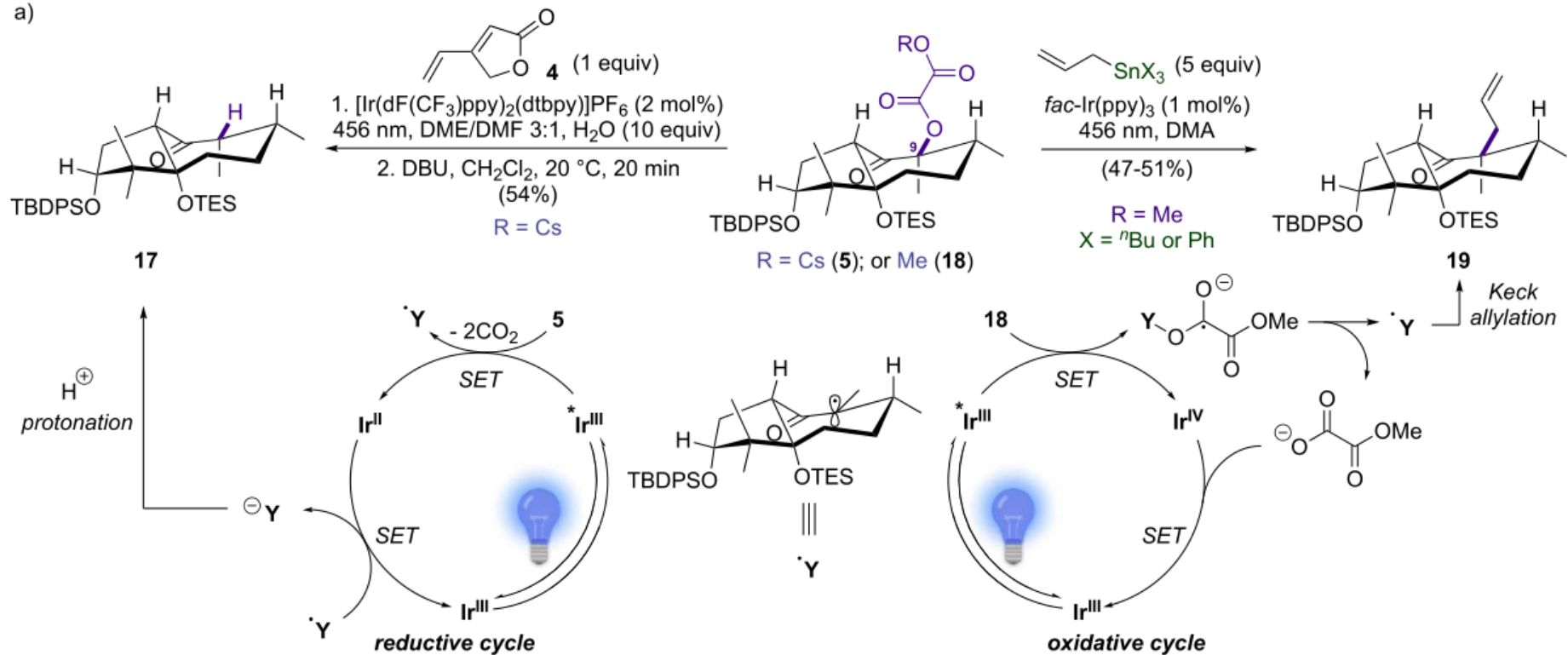




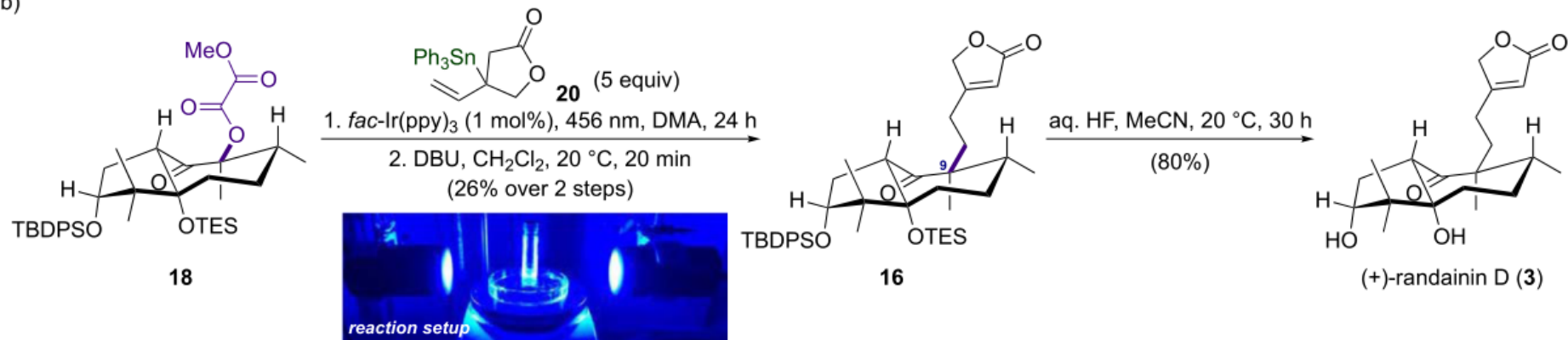
Scheme 2.

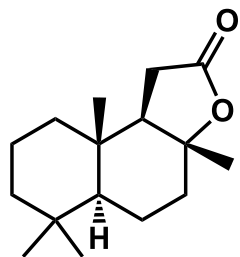
Tetrahedron Lett., **2000**, *41*, 2077.

a)

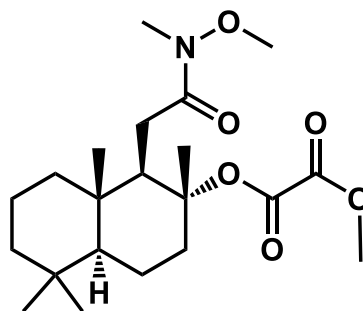
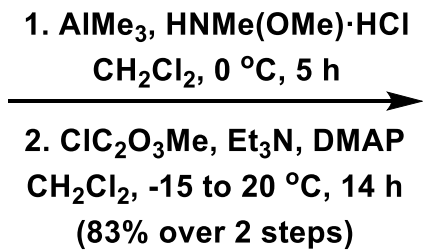


b)

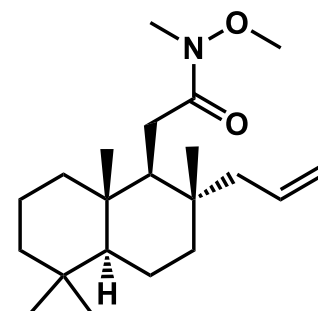
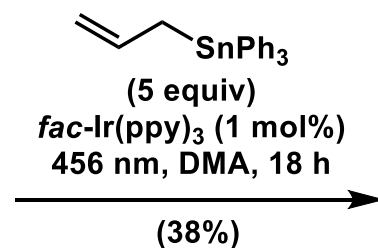




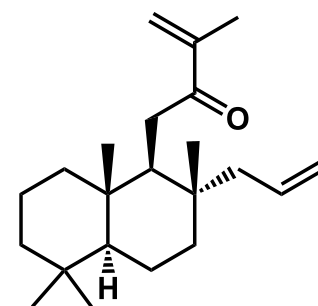
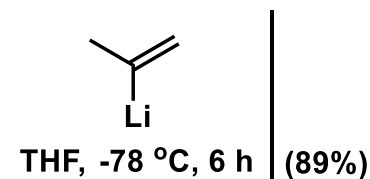
(+)-sclareolide (22)



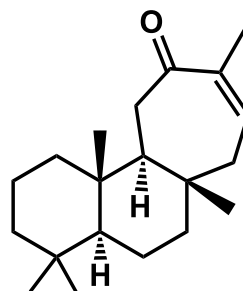
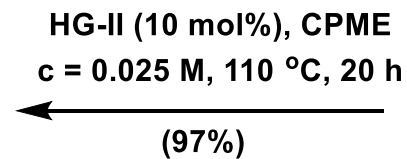
23



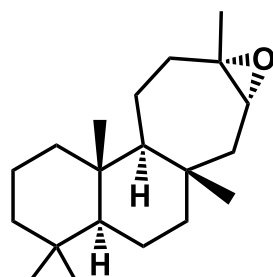
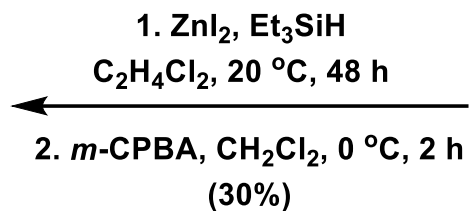
24



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26



(+)-barekoxide