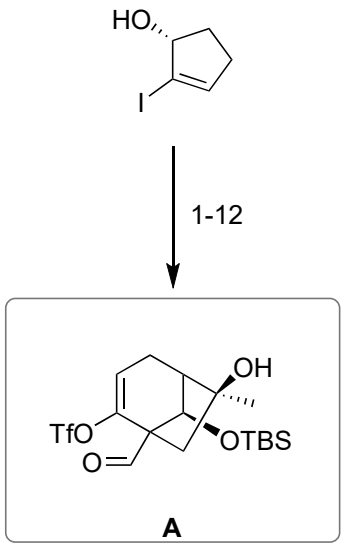
Enantioselective Total Syntheses of Grayanoid (−)-Mollfoliagein A and (−)-Rhodomollein XXV

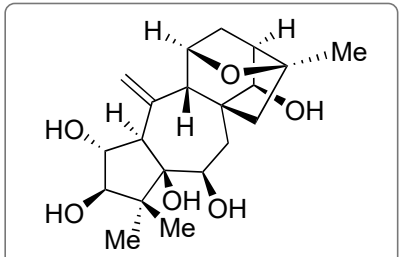
S.-F. Du, Y.-P- Zhang, Q.-L. Wu, H. Zhang, *J. Am. Chem. Soc.* **2026**, 148, 15, 15410–15416.



1) $MeC(OMe)_2NMe_2$, MW: 120 °C
2) LiHMDS, O_2, HMPA, $P(OEt)_3$
3) TBSOTf, Et_3N
4) MeMgBr
5) $Pd(OAc)_2$, *t*-$Bu_3P{\cdot}HBF_4$, PhOK
6) KHMDS, Comins' reagent
7) $Pd(OAc)_2$, dppf, Et_3N, CO, MeOH
8) O_3, *then* PPh_3, *then* AIBME, TDM
9) KHMDS, Comins' reagent
10) MeMgBr, $LaCl_3{\cdot}2LiCl$
11) DIBAL-H
12) IBX

13) NBS, TsOH
14) $CaCO_3$
15) MeMgBr, $LaCl_3{\cdot}2LiCl$
16) PDC, Celite
17) $(SnMe_3)_2$, $Pd(acac)_2$, PCy_3

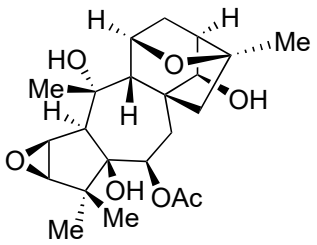
1) Name of the reaction:
Eschenmoser Claisen Rearrangement



Rhodomollein XXV

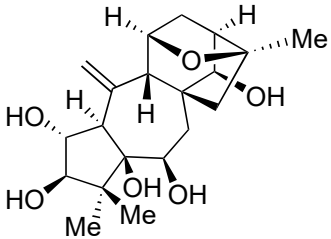
A + B

18-26



Mollfoliagein A

27



Rhodomollein XXV

18) $Pd_2(dba)_3 \cdot CHCl_3$, PCy_3, $Mo(CO)_6$, LiCl, CuCl
19) $Co(acac)_2$, Ph_2SiH_2, O_2, TBHP, DBU,
then Ac_2O, Et_3N, 4-PPY
20) $N_2H_4 \cdot HOAc$, HFIP
21) NBS, BPO, CCl_4, *then* Ag_2O
22) MeMgBr, *then* Ac_2O, Et_3N, 4-PPY
23) MsOH, H_2O
24) $CNCO_2Me$, DMAP
25) $Pd(acac)_2$, *n*-Bu_3P, $(HCOO)_2Mg \cdot 2H_2O$
then $Et_3N \cdot 3HF$
26) *m*-CPBA

27) PPTS, *t*-BuOH, *then* NaOH

18) Name of all 3 reactions:
Carbonylative Stille coupling
oxa-Michael addition
Knoevenagel condensation
19) Name of the reaction:
Mukaiyama hydration
20) Name of the reaction:
Wharton transposition