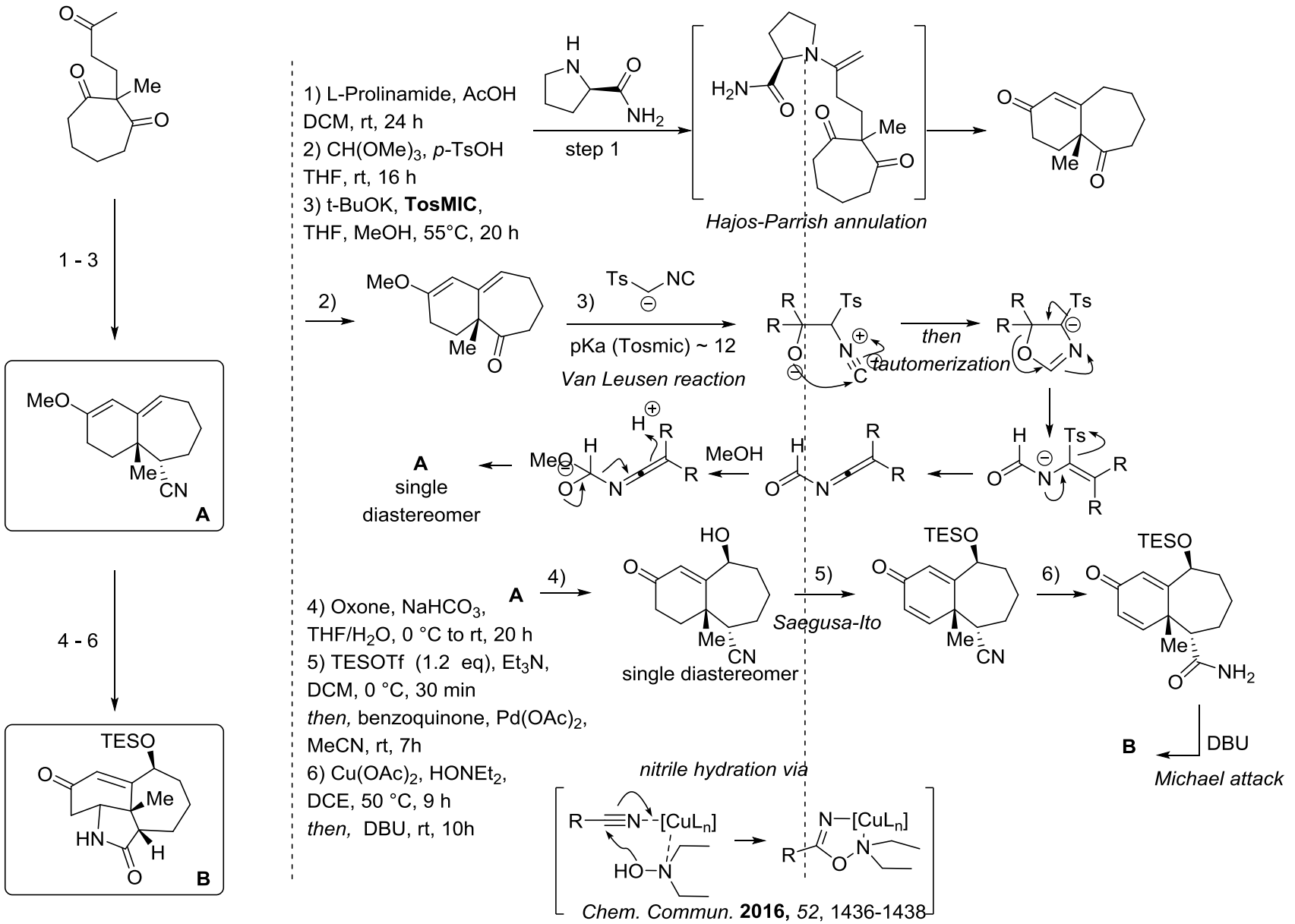
A Concise Total Synthesis of (–)-Himalensine A

Y. Chen, J. Hu, L.-D. Guo, W. Zhong, C. Ning, J. Xu

Angew. Chem. Int. Ed. **2019,** *58*, 7390–7394.



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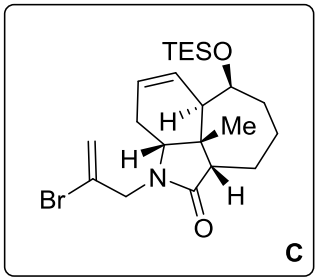

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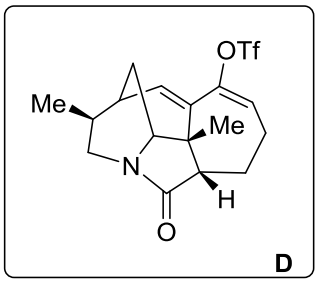
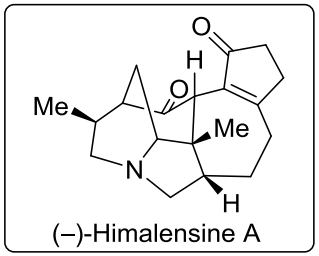
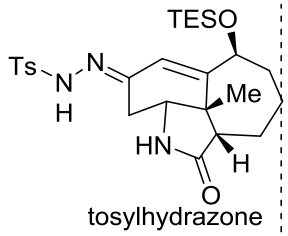
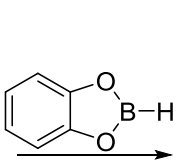


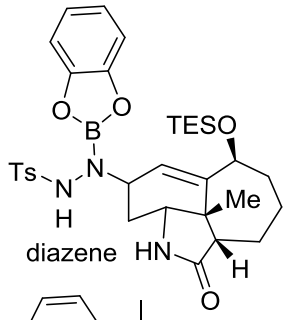
12 - 15



7) $TsNHNH_2$, EtOH, rtflux, 3 h
then, Catecholborane,
DCM, 0 °C, 3 h,
then, $NaOAc{\cdot}3H_2O$, reflux, 9 h
8) NaH, 2-bromo-allylbromide
THF, rt, 6 h

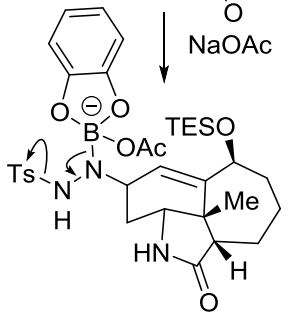




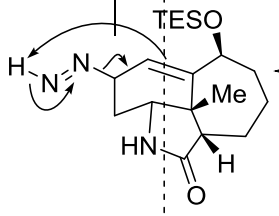


J.Org.Chem. **1976**, *41*, 574

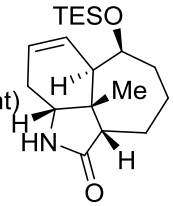
NaOAc



alkene migration

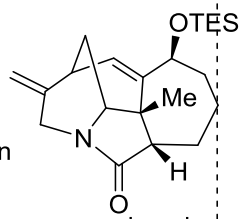


single diastereomer
(concerted rearragement)

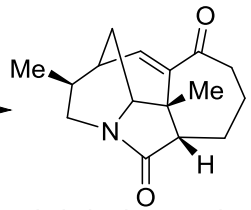


9) $Pd(OAc)_2$, PPh_3, Et_3N,
Dioxane, MW, 120 °C, 4 h
10) H_2, $[Rh(COD)Cl]_2$, PPh_3, $AgBF_4$,
DCM, rt, 6 h
then, AZADOL, PIDA, rt, 2 h
11) KHMDS, $PhNTf_2$,
THF, –78 °C, 6 h

9)
Heck reaction



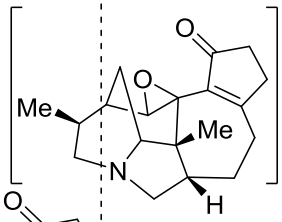
10)
d.r. > 20:1



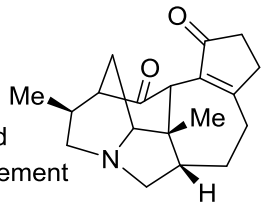
carbonyl-group-directed catalytic hydrogenation
J. Am. Chem. Soc. **2017**, *139*, 15, 5558-5567
J. Am. Chem. Soc. **2017**, *139*, 42, 14893-14896

12) Tributyl(vinyl)tin, $Pd(PPh_3)_4$, CO, LiCl,
THF, rt, 24 h
13) $SnCl_4$, DCM, rt, 30 min
14) *m*CPBA, DCM, 0 °C, 6 h,
then, $BF_3{\cdot}Et_2O$, PhMe, 0 °C to rt, 5 min
15) Vaska's Catalyst, TMDS, DCM, rt
then, TFA, Et_3SiH, rt, 48 h

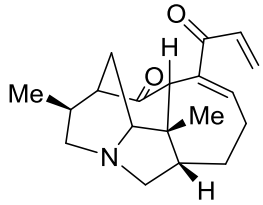
then, oxidation of -OTES



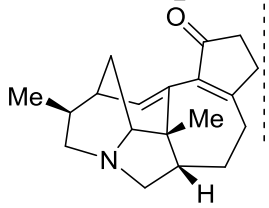
Meinwald
rearrangement



hydrosilylation,
then reduction:



13)
Nazarov



J. Am. Chem. Soc. **2012**, *13*, 41, 640-653