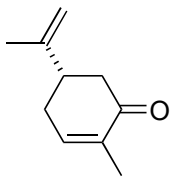
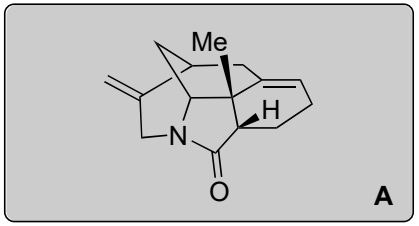
Total Synthesis of (-)-Daphenylline

Bo Xu, Bingyang Wang, Wen Xun, and Fayang G. Qiu, *Angew. Chem. Int.* **2019**, *58*, 5754–5757.



1 – 5

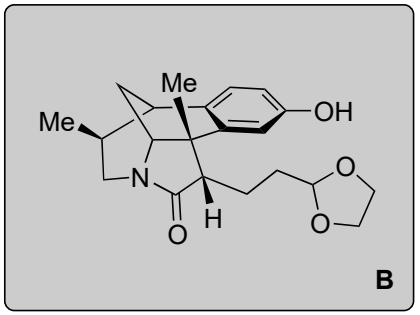
1) SO_2Cl_2, Na_2CO_3 *then* NaN_3
2) vinylMgBr, *then* PPh_3, H_2O
3) acryloyl chloride, NEt_3
4) $Mg(ClO_4)_2$, reflux
5) BHT, xylene, 200 °C



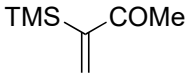
A

6 – 10

6) H_2, Carbtree's catalyst
7) O_3, *then* pyridine, DMS
8) $(TMSOCH_2)_2$, TMSOTf
9) LDA, **1** *then* KOH, MeOH
10) NaOMe, MeOH, reflux



B



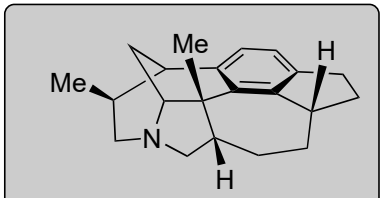
1

1) Name of the starting material?
Carvone

2) Name of the reaction?
Staudinger

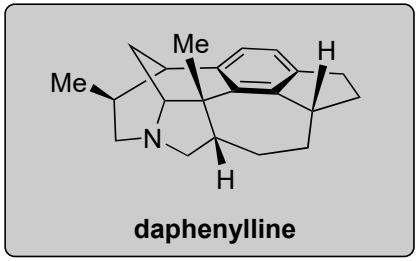
6) Structure of Crabtree's catalyst?
$[Ir(cod)PCy_3Py][PF_6]$

9) Name of reagent **1**?
Stork-Ganem reagent



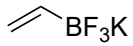
daphenylline

11 – 17



daphenylline

11) NaH, MeI, *then* *p*-TsOH
12) $NaClO_2$, NaH_2PO_4, 2-Me-2-butene
13) $(COCl)_2$, *then* $AlCl_3$, reflux
14) Tf_2O, pyridine *then* Pd(dppf)Cl_2, **2**, MeOH
15) $NaBH_4$, *then* *p*-TsOH
16) H_2, Pd/C
17) Lawesson's reagent *then* Raney-Ni



2

12) Name of the reaction?
Pinnick Oxidation
13) Name of the reaction?
Friedel-Crafts acylation
14) Name of the reaction?
Suzuki coupling

17) Structure of Lawesson reagent & mechanism?