Total Synthesis of (±)-Isostemofoline

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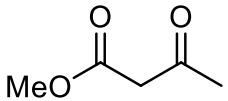

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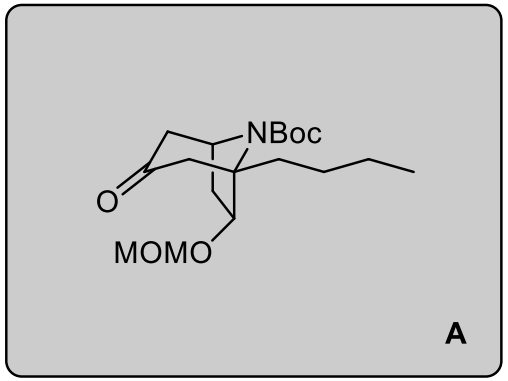
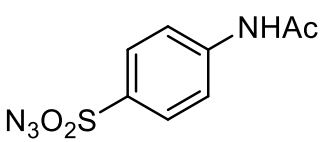


7-12

1) **1**, Et_3N
2) TBSOTf, Et_3N
3) **2**, $[Rh(OOCC_7H_{15})_2]_2$, pentane, reflux
4) TBAF
5) H_2, Pd/C
6) H_2O, DMSO, 150 °C



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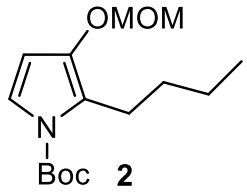

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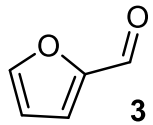


3

7) **3,** NaOH, MeOH, H_2O, reflux
8) LiHMDS, DMPU, *then* allyl iodide
9) toluene, 110 °C
10) K_2OsO_4, $NaIO_4$
11) $Zn(BH_4)_2$
12) TIPSCl, imidazole

1) Name reaction?

Regitz diazo transfer

3) Classify the reaction?

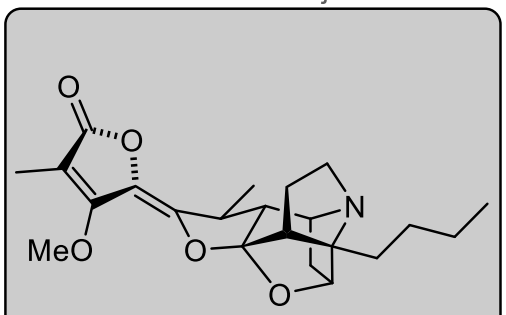
see below

6) Name reaction? Karpcho decarboxylation

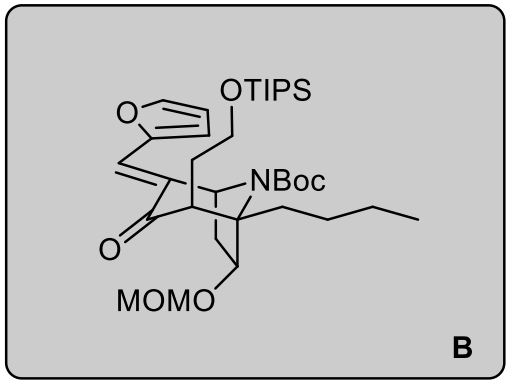
8) Hint: The reaction gave 2 products, the major undesired one could be converted via step 9 into the desired one.

9) Name reaction? Claisen rearrangement

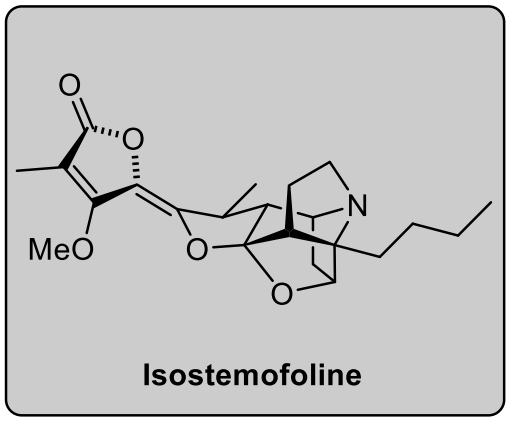
10) Name reaction? Lemieux-johnson ox.

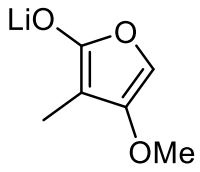


Isostemofoline



13-23





4

13) MeLi, DMPU, Et_2O, –40 °C
14) TBAF
15) TsCl, pyridine
16) O_3, DCM *then* Me_2S
17) *i*-BuOCOCl, *N*-methyl-morpholine, THF
18) $NaBH_4$
19) DMP ox.
20) **4**, THF, –78°C
21) DMP ox.
22) TFA, *then* aq. $NaHCO_3$
23) Tf_2O, DCM

question 3:

formaly a [4+3] CA but step wise a cyclopropanation/Cope rearrangement

19) Draw the reagent.