Synthesis Challenge 89

Collective Total Synthesis of Aspidofractunune Alkoloids via Development of a Bischler-Napieralski/Semipinacol Rearrangement Reaction, S.-H. Wang, R.-Q. Si, Q.-B. Zhuang, X. Guo, T. Ke, X.-M. Zhang, F.-M. Zhang, Y-Q. Tu, *Angew. Chem. Int. Ed.* **2020**, ASAP

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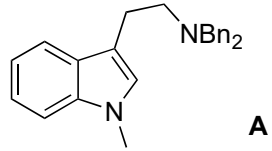
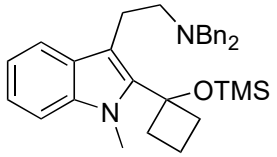


A

1-3

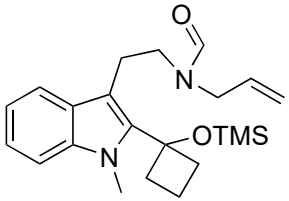
1) NBS, DCM, 0 °C~RT, (80%)
2) t-BuLi, cyclobutanone, THF, -78 °C
3) TMSCl, imidazole, DCM, 0 °C



B

4-6

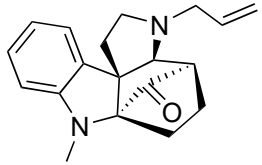
4) $Pd(OH)_2/C$, H_2, MeOH:THF=50:1, 30 °C
5) HCO_2H, CDI, DCM, 0 °C
6) NaH, Allyl bromide, THF:DMF=20:1, 0 °C~RT



C

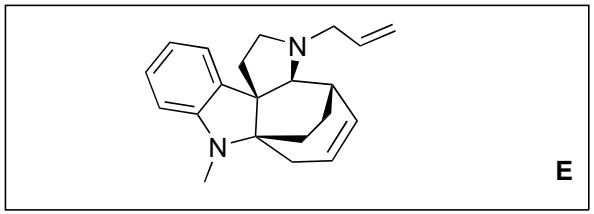
7-8

7) Tf_2O, 2-chloropyridine, DCM, -78 °C~RT
8) PTS, toluene, reflux



D

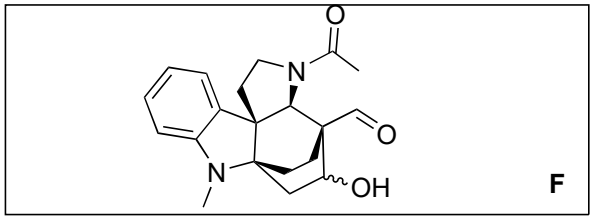
9-12



E

9) N- nitroso-N-methyl-4-toluenesulfonamide, KOH, THF:MeOH:H_2O=10:3:3, 0 °C~RT
10) Trimethylsilyldiazomethane, n-BuLi, THF, -78 °C, then MeOH, silica gel column
11) $LiAlH_4$, THF, 0 °C; d) MsCl, Et_3N, DCM, 0 °C;
12) LiCl, Li_2CO_3, 4Å MS, DMF, 90 °C

13-16

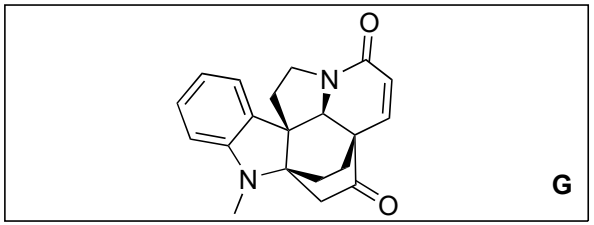


F

13) $(Ph_3P)_4Pd$, 1, 3-Dimethylbarbituric acid, DCM, RT
14) Et_3N, Acetyl chloride, DCM, 0 °C
15) K_2OsO_4, NMO, $CH_3CN:H_2O$=3:1, RT, then $NaIO_4$, 0 °C
16) Pyridine hydrochloride, THF:DCM=20:1, RT,

16-19

17) TMSCl, imidazole, DCM, 0 °C
18) LDA, THF, -78 °C
19) Martin sulfurane, DCM, 0 °C~RT
20) TBAF 1M in THF, 0 °C
21) DMP, Pyridine, DCM, 0 °C



G

20-27

22) PtO_2, H_2, EtOAc, RT; g) $NH_2NH_2.H_2O$, Na, ethylene glycol
23) $AlCl_3$, $LiAlH_4$, THF, 0 °C
24) Et_3N $BnMnO_4$, DCM, -78 °C~0 °C
25) 4 M HCl, 1,4-Dioxane, 70 °C,