A Convergent Approach to Phragmalin-Type Limonoids: Total Synthesis of Thaigranatin P

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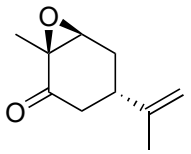
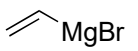


1-7

A

8-17

1) O_3, MeOH, *then* PhSH, $FeSO_4.7H_2O$
2) $TsNHNH_2$
3) **1**, THF, -78 °C
4) TBSOTf, 2,6-lutidine
5) $CuCl_2$ (cat.), hydroxyacetone, benzene
6) OsO_4, NMO, $NaIO_4$
7) **2**, NaHMDS



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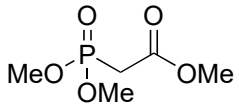

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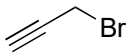
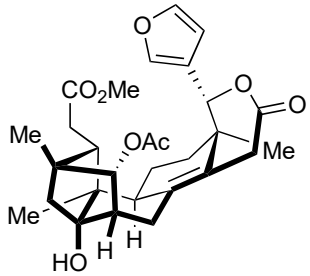


3

8) KHMDS, $ZnCl_2$, *then* CH_2O
9) **3**, Al, $HgCl_2$
10) Bu_3SnH, AIBN, *then* PPTS
11) $(COCl)_2$, DMSO, Et_3N
12) SmI_2, MeOH, HMPA, THF, reflux
13) DMP
14) $LiBH_4$
15) TFA, *then* TMSCl, imidazole, *then* DMP
16) $CH_2=PPh_3$ (salt-free)
17) Ac_2O, pyridine



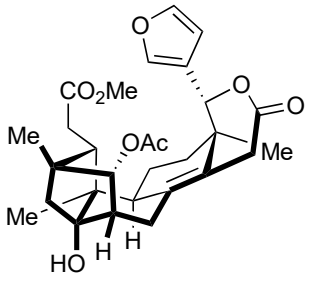
Thaigranatin P

10) Provide a mechanism. What PPTS is needed for?
12) From now on draw as natural product

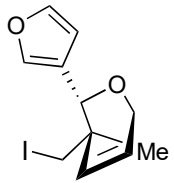
15) 2 TMS protected and 1 free alcohol

B

18-22



Thaigranatin P



4

18) SeO_2, H_2O, DCE, 60 °C
19) **4**, *t*-BuLi, CuI-Me_2S, *then* Comins' reagent
20) CrO_3, 3,5-DMP
21) $Pd(PPh_3)_2Cl_2$, Et_3N, DMF, 100 °C, *then* 1M HCl
22) SmI_2, PhSH, HMPA, THF, reflux

21) What is the name of the reaction?
Hint: tertiary alcohol deprotection at this step