Synthesis of Pleuromutilin

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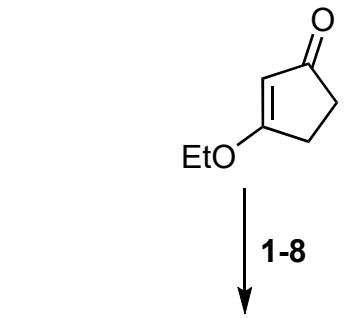

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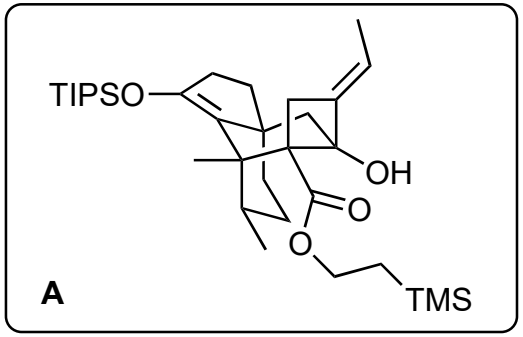

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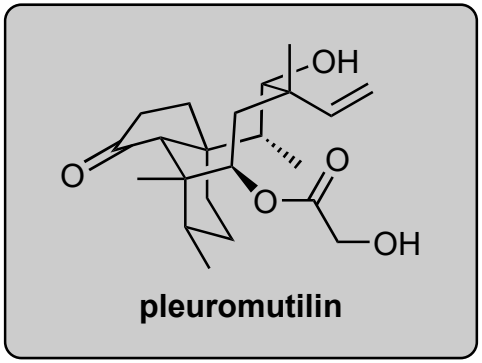
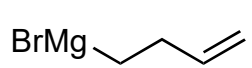


1) **1** *then* H_2SO_4
2) **2**, $MeAl(NTf_2)_2$, TIPSOTf
3) $(NH_4)_2Ce(NO_3)_6$
4) $Fe(acac)_3$, $Ph(iOPr)SiH_2$, $(CH_2OH)_2$
5) LDA, TIPSOTf *then* PPTS
6) **3**, LDA
7) **4**, LDA
8) $Ti(iOPr)_4$, *i*PrMgCl



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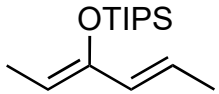

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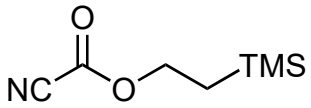

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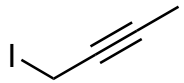

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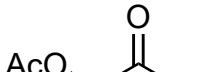
9) 9-methylfluorene, KHMDS, TESCl
10) MeI, LiTMP
11) TBAF, C_2Cl_6
12) $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$, air TEMPO, K_2HPO_4, blue LEDs
13) CsF, DMSO
14) Zn, AcOH, H_2O
15) Na, EtOH
16) **5**, EDCI, DMAP *then* K_2CO_3, MeOH



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2) Name of the reaction?
Diels–Alder cycloaddition

4) Name of the reaction?
Fe-catalyzed HAT cyclization

9) *Hint: think retro-aldol*

11) *Hints: 3 transformations, peaks at 206 ppm and 183 ppm in ^{13}C NMR*

12) *Hint: ^{13}C signals at 216, 212 and 207 ppm*

13) Name of the reaction?
Kornblum oxidation