Total Synthesis of (–)-Jiadifenin

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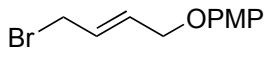

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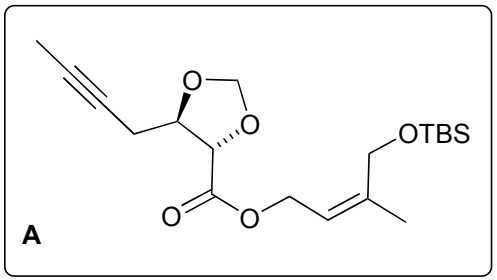

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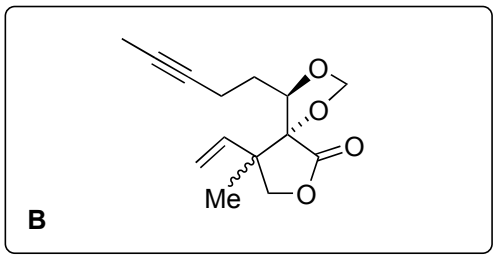
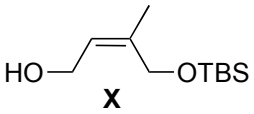


1) 1-bromo-1-propene, *n*-BuLi, CuI
2) AD-mix-β, $MeSO_2NH_2$, *t*-BuOH/H_2O
3) KOH, CH_2I_2, 18-crown-6
4) CAN, MeCN/H_2O
5) Jones reagent
6) DCC, DMAP, **X**

7) LDA, TMSCl, THF, –78 °C to reflux
8) TsOH•H_2O, MeOH, Δ



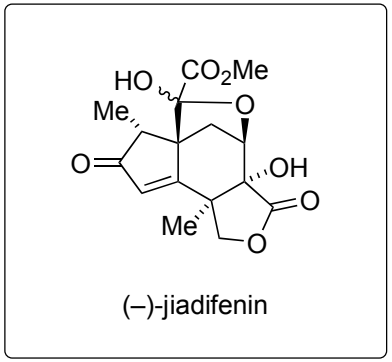
X

5) what's Jones reagent?

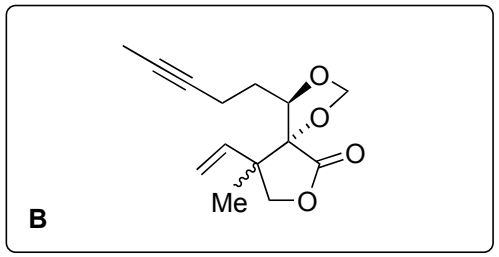
CrO_3•H_2SO_4

7) name the reaction and draw the transition state

Ireland - Claisen rearrangement



(–)-jiadifenin



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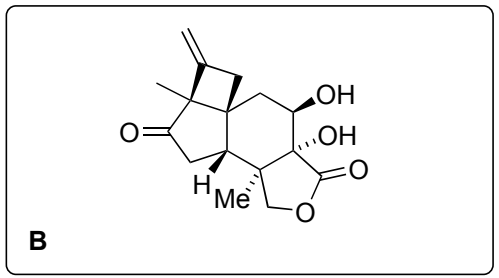
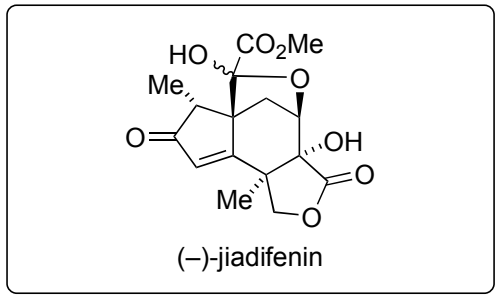
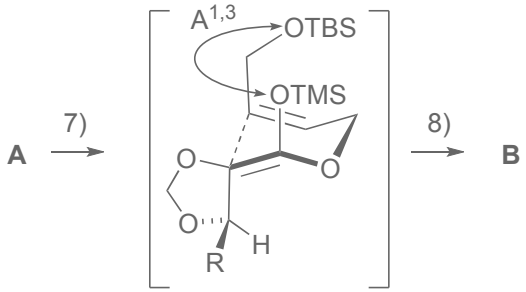


13-18



9) $Ph_3C•BF_4$, CH_2Cl_2, Δ
10) TBSOTf, Et_3N, CH_2Cl_2
11) $[Co_2(CO)_8]$, Bu_3PS, toluene, Δ
12) $h\upsilon$, allene, THF, –78 °C

13) i) O_3, MeOH, *then* Me_2S, –78 °C;
ii) NaOMe, MeOH
14) LDA, TMSCl, Et_3N
15) $Pd(OAc)_2$, O_2
16) TBAF
17) NaHMDS, –78 °C,
(–)-*trans*-(phenylsulfonyl)-3-phenyloxaziridine
18) Jones reagent, *then* MeOH



name reaction 15+16
Saegusa-Ito Oxidation