Total Synthesis of (±)-Dhilirolide U

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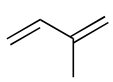

1-15

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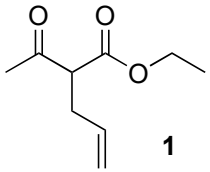
16-19

1) NBS, AcOH
2) K_2CO_3, MeOH-H_2O
3) (*i*-Pr)$_3$SiOTf, (*i*-Pr)$_2$NEt
4) **1**, NaH, *n*-BuLi
5) $Mn(OAc)_3 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$, AcOH
6) LDA, HMPA, TsCN
7) Tf_2O, (*i*-Pr)$_2$NEt
8) $Pd(PPh_3)_4$, Me_3Al
9) O_3, Sudan III then Me_2S
10) LDA, MeCHO
11) Burgess reagent
12) Triton B, *t*-BuOOH
13) 4 M aq H_2SO_4
14) DBU, CS_2, MeI
15) DTBMP, Ph_2O, 285 °C



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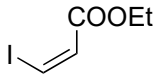
16) CSA, **2**
17) $NiCl_2 \cdot$glyme, neocuproine, Rieke Zn
18) Ghaffar–Parkins catalyst
19) *t*-BuONO



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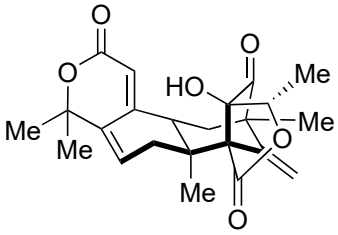
13) Hint: Payne-type rearrengement

15) Name of the reaction?

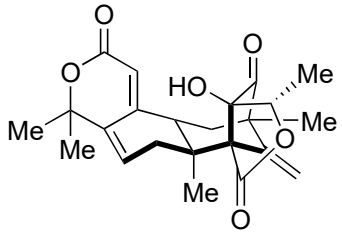
18) Structure of Ghaffar–Parkins catalyst ?



(±)-Dhilirolide U

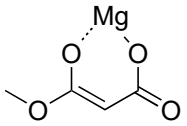
B

20-27



(±)-Dhilirolide U

20) Ghosez's reagent then **3** then 6 M HCl
21) LiCl, DBU
22) Tf_2O, $(i\text{-}Pr)_2NEt$
23) $Pd_2(dba)_3$, P(2-furyl)$_3$, **4**, LiCl then 4 M HCl
24) $BF_3{\cdot}OEt_2$, propane-1,3-dithiol
25) CDI then MeMgCl
26) I_2, $NaHCO_3$ then Bobbitt's salt
27) DBU



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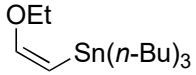

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20) Structure of Ghosez reagent?

23) Name of the reaction?