Divergent Total Syntheses of Elisapterane and Relevant Diterpenoids Assisted by In Silico Structure Reassignment

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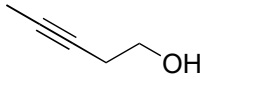

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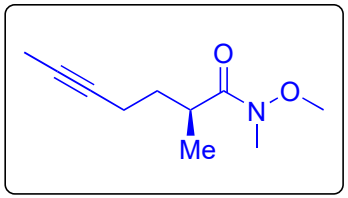
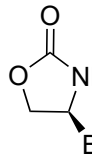


A

9 - 18

1) I_2, PPh_3, imidazole
2) diethyl malonate, NaH
3) LiCl, DMSO/H_2O, 160 °C
4) LiOH
5) **1**, Et_3N, PivCl
6) NaHMDS, MeI
7) LiOH, H_2O_2, H_2O
8) CDI, MeNHOMe•HCl



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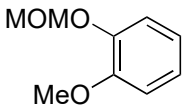

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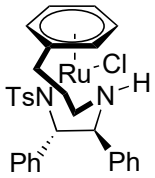
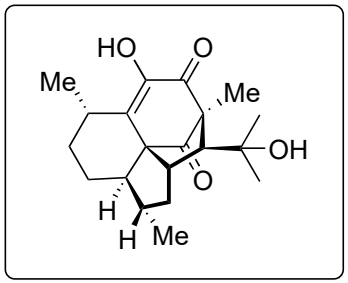


3

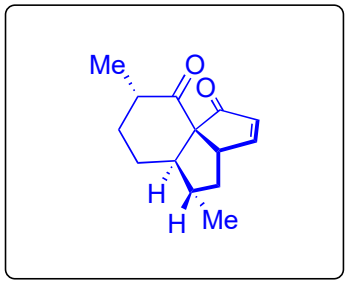
9) **2**, *n*BuLi, TMEDA *then* **A**
10) *p*-TSA•H_2O
11) **3**, HCO_2H, Et_3N, 60 °C
12) Pd/$CaCO_3$, H_2
13) PIFA, Na_2CO_3, HFIP
14) UHP, TFAA
15) SmI_2 (excess), HMPA *then* MeOH
16) *t*-BuOK
17) $TsNHNH_2$•HCl, NaOAc *then* $NaBH_3CN$, AcCl, NaOAc•$3H_2O$
18) TPAP (4 equiv), NMO

3) Name of the reaction?
Krapcho decarboxylation

13) *Hint*: ODI-[5+2] cycloaddition
15) Name of the reactions?
Pinacol coupling + Grob fragmentation
16) *Hint*: epimerization
18) Name of the reaction?
Ley-Griffith oxidation



elisapterosin C

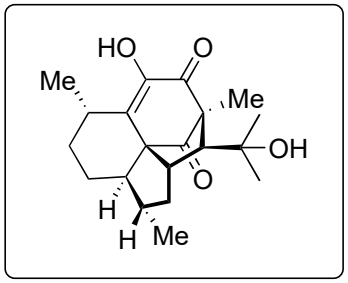


B

19 - 24

19) CuBr•Me_2S, HMPA, *iso*-propenylMgBr *then* NCCOMe
20) K_2CO_3, MeI
21) LDA, TMSCl
22) $Co(acac)_2$, $PhSiH_3$, O_2 *then* PPh_3 *then* TfOH
23) OsO_4, py
24) *p*-TSA•H_2O, 90 °C

22) Name of the reaction?
Mukaiyama hydration



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