Enantioselective Total Syntheses of Grayanane Diterpenoids: (−)-Grayanotoxin III, (+)-Principinol E, and (−)-Rhodomollein XX

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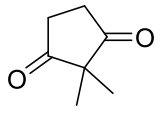

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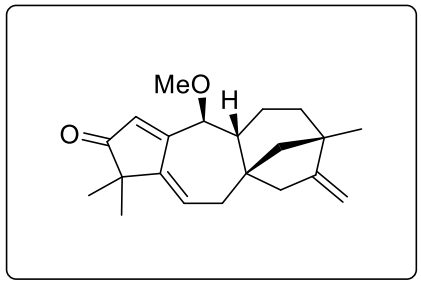

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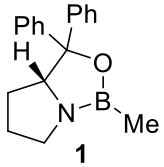
1. Catecholborane, Et_3N, **1**, toluene, –60 °C
2. Ac_2O, pyr, DMAP, CH_2Cl_2, 0 °C
3. PBr_3, DMF, $CHCl_3$, 50 °C
4. TsOH, $HC(OMe)_3$, MeOH, r.t.
5. TMSOTf, **2**, **3**, *t*-BuOMe, –78 °C
6. $EtAlCl_2$, CH_2Cl_2, 0 °C
7. $Pd(PPh_3)_4$, **4**, Na_2CO_3, EtOH, H_2O, toluene, reflux *then* NaOH, MeOH, 50 °C
8. DMP, $NaHCO_3$, CH_2Cl_2
9. Tf_2O (1.5 equiv), pyr, 0 °C, CH_2Cl_2 *then* **5**, DCE, 80 °C



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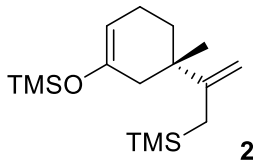

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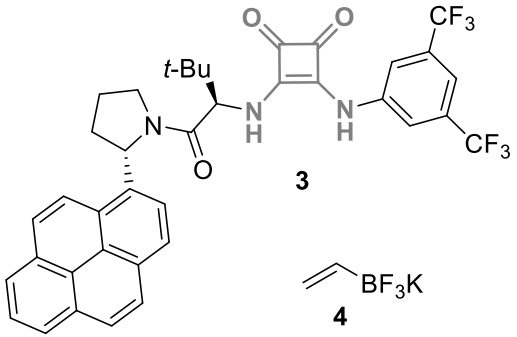

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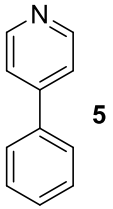

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Step 1: Please, name the reaction.
Corey–Bakshi–Shibata reduction
Step 3: Please, name the reaction.
Vilsmeier reaction

Step 5: Please, name the reaction and the highlighted structural motif in catalyst **3**.
Mukaiyama aldol; Squaramide
Step 6: Please, name the reaction.
Hosomi–Sakurai reaction
Step 7: Please, name the reaction.
Suzuki cross-coupling

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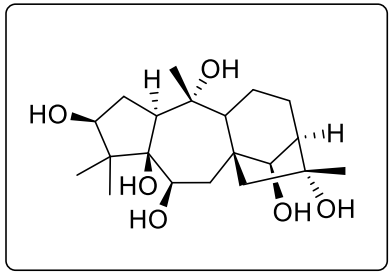

(–)-Grayanotoxin III

10. Ac_2O, pyr, DMAP, tetraphenylporphyrin, O_2, hν, $CHCl_3$ *then* $IrCl(cod)_2$, PPh_3, xylene, reflux
11. KHMDS, THF, r.t. *then* H_2O
12. tetraphenylporphyrin, O_2, hν, CH_2Cl_2 *then* *m*-CPBA *then* Zn, AcOH
13. $EtAlCl_2$, CH_2Cl_2, 0 °C
14. TBSOTf (1.4 equiv), Et_3N, THF, 0 °C
15. MeLi, THF, –40 °C
16. $VO(acac)_2$, *t*-BuOOH, CH_2Cl_2, –20 °C *then* DBU, r.t., *then* 2 M HCl, MeOH, THF, r.t.
17. 2 M H_2SO_4, 1,4-dioxane, 30 °C
18. DIBAL-H, THF, –78 °C to –20 °C
19. $Mn(dpm)_3$, $Ph(i\text{-}PrO)SiH_2$, *t*-BuOOH, CH_2Cl_2, r.t.

Hint Step 10: First, a pericyclic reaction with 6-membered TS occurs, *then* one carbon is lost.
Singlet oxygen ene reaction, deformylation

Hint step 15: Only 1 functional group reacts.

Step 16: Please, explain the regioselectivity.
Coordination of $VO(acac)_2$ to adjacent OH group
Step 17: Which named reaction could deliver the same product?
Mukayiama hydration
Step 19: What is the structure of dpm ligand?