Total Synthesis of Epoxyeujindole A

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Structural Features of the Target

- Unusual heptacyclic ring system
- "Congested" structure with *cis*-decalin makes for a very crowded cup

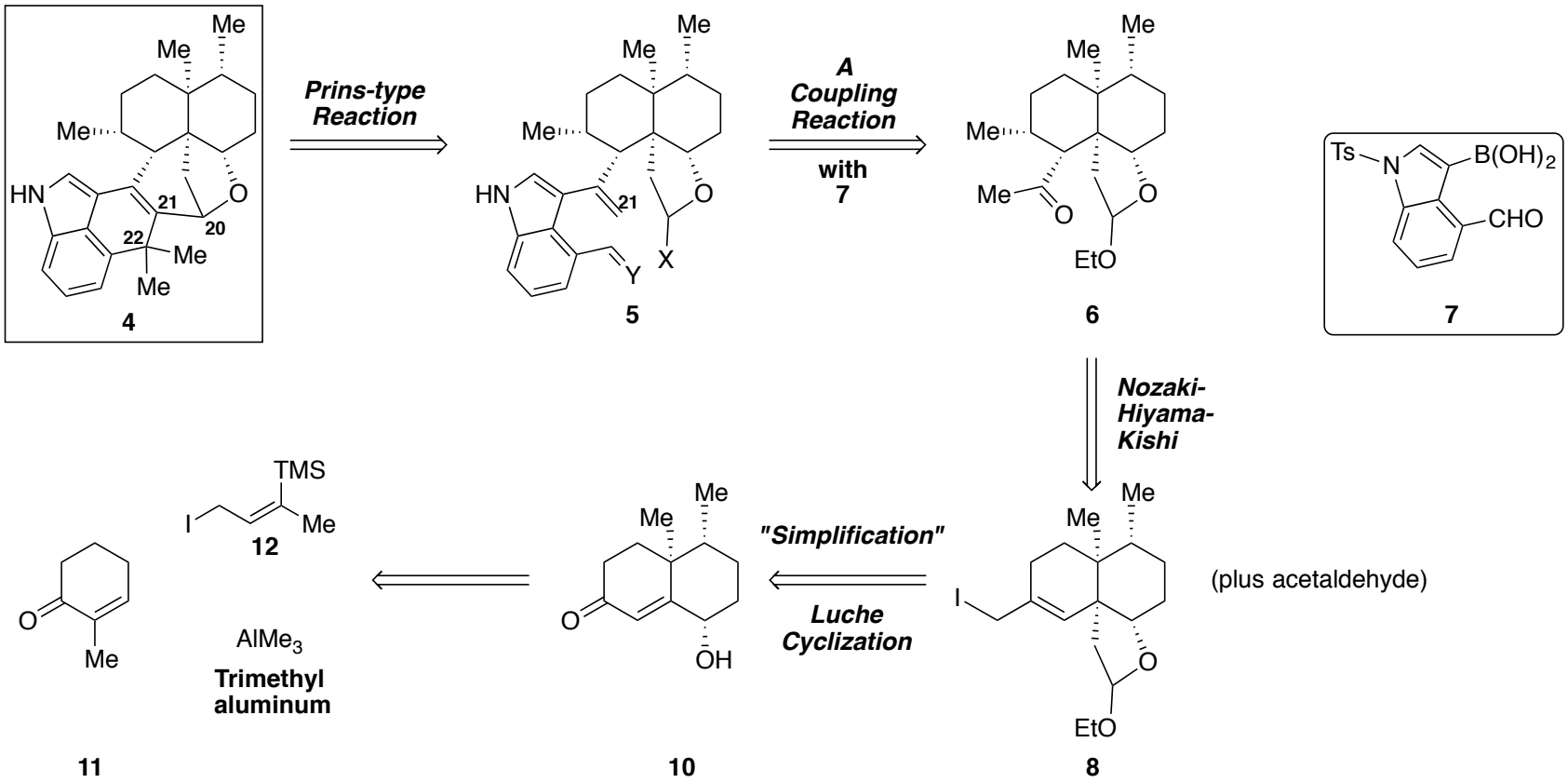
Isolation:

Nakadate, S. *Heterocycles* **2011**, *83,* 351.
Nakadate, S. *Heterocycles* **2011**, *83,* 1867.
Absolute configuration not determined.

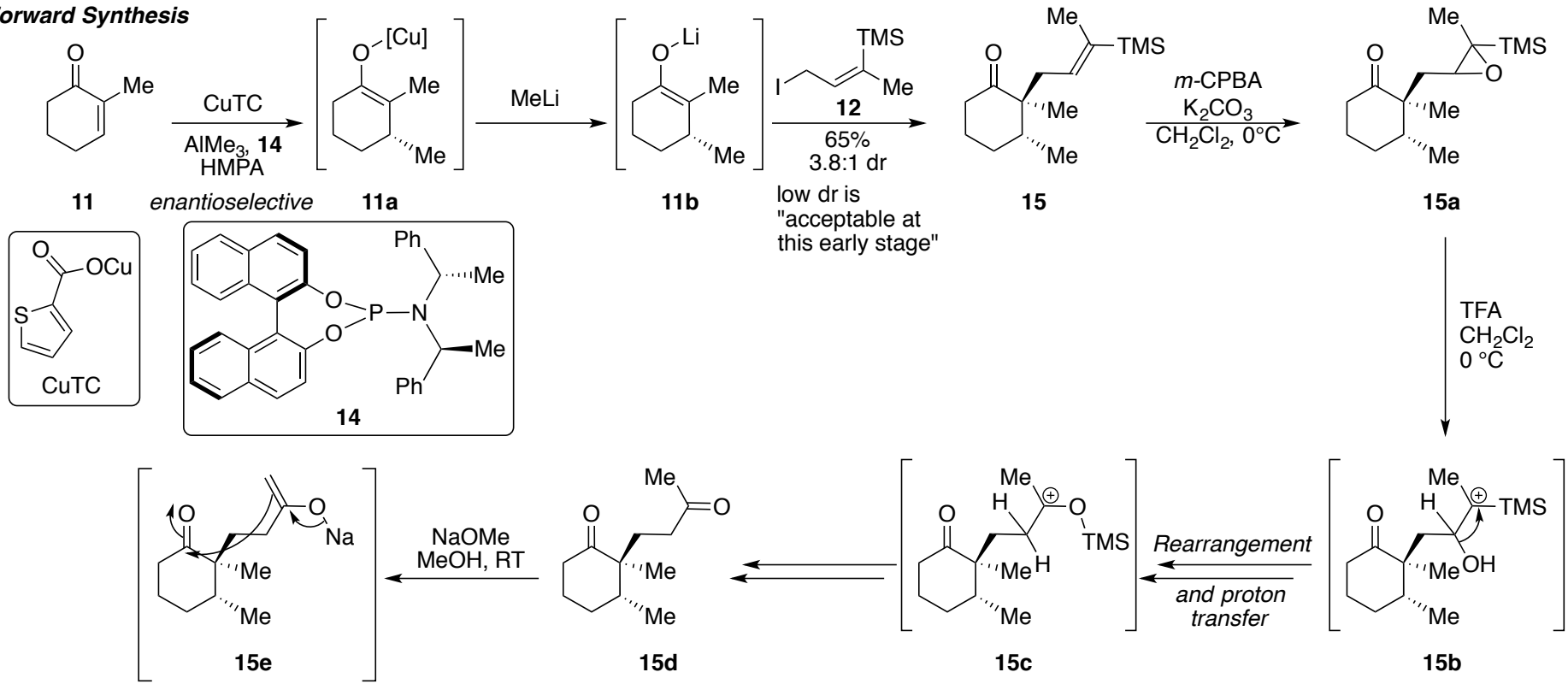
Previous Syntheses:

None!

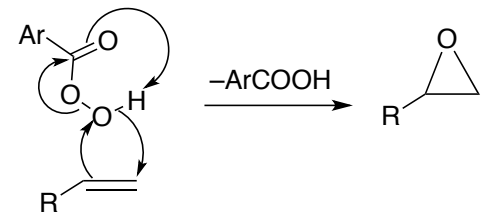
Retrosynthesis

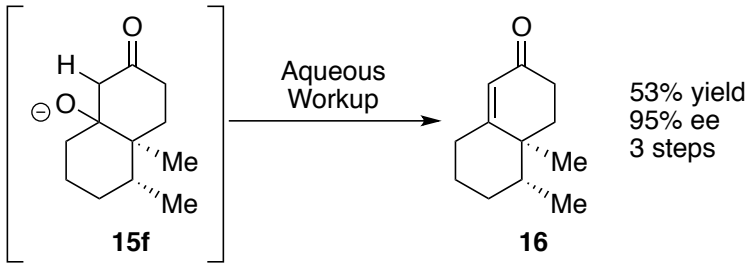


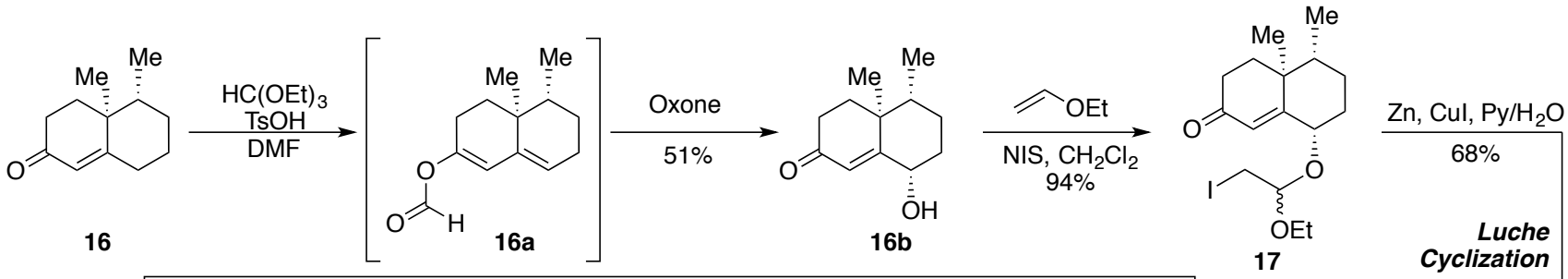
Forward Synthesis



15 to **15a**: *m-CPBA epoxidation*



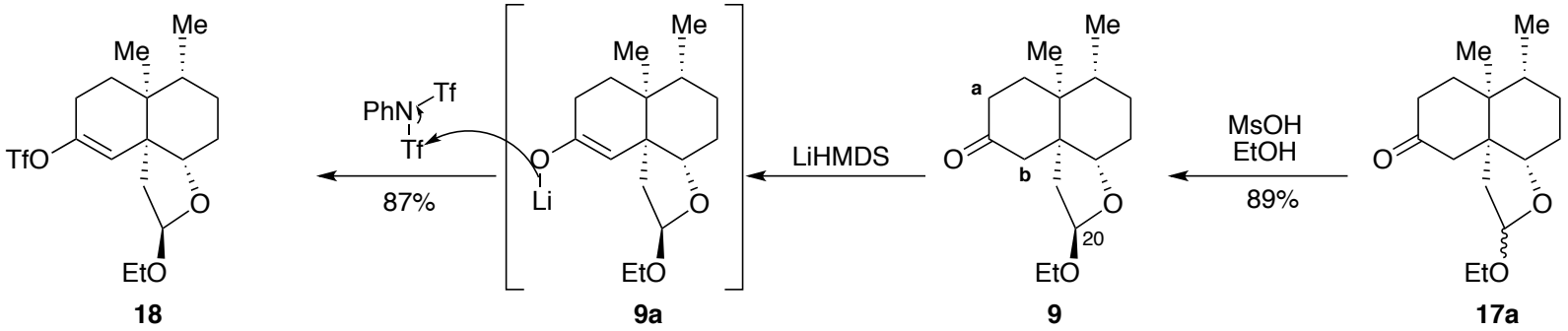




"Oxidation. . .was carried out through its dienol ether. . ."
Bonoch, J. *J. Org. Chem.* **2005,** *70,* 3749.

16a to **16b** probably works through electrophilic oxygen. Stereochemistry is substrate directed.

16b to **17**: Iodonium of ethyl vinyl ether followed by nucleophilic attack of the alcohol on **16b**



Regioselectivity of deprotonation dictated by the ethoxy group:
no selectivity for site **b** over **a** when the epimer at C(20) is used

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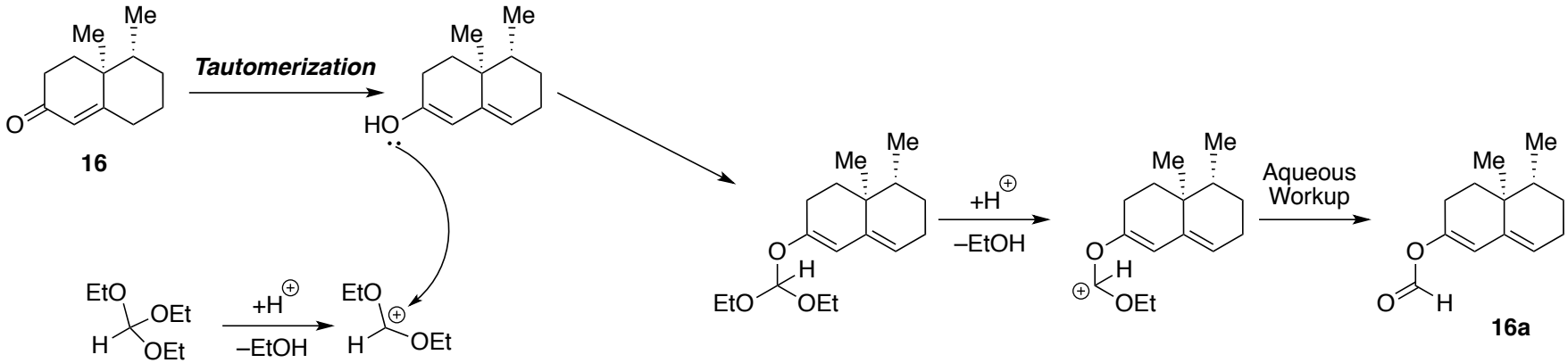
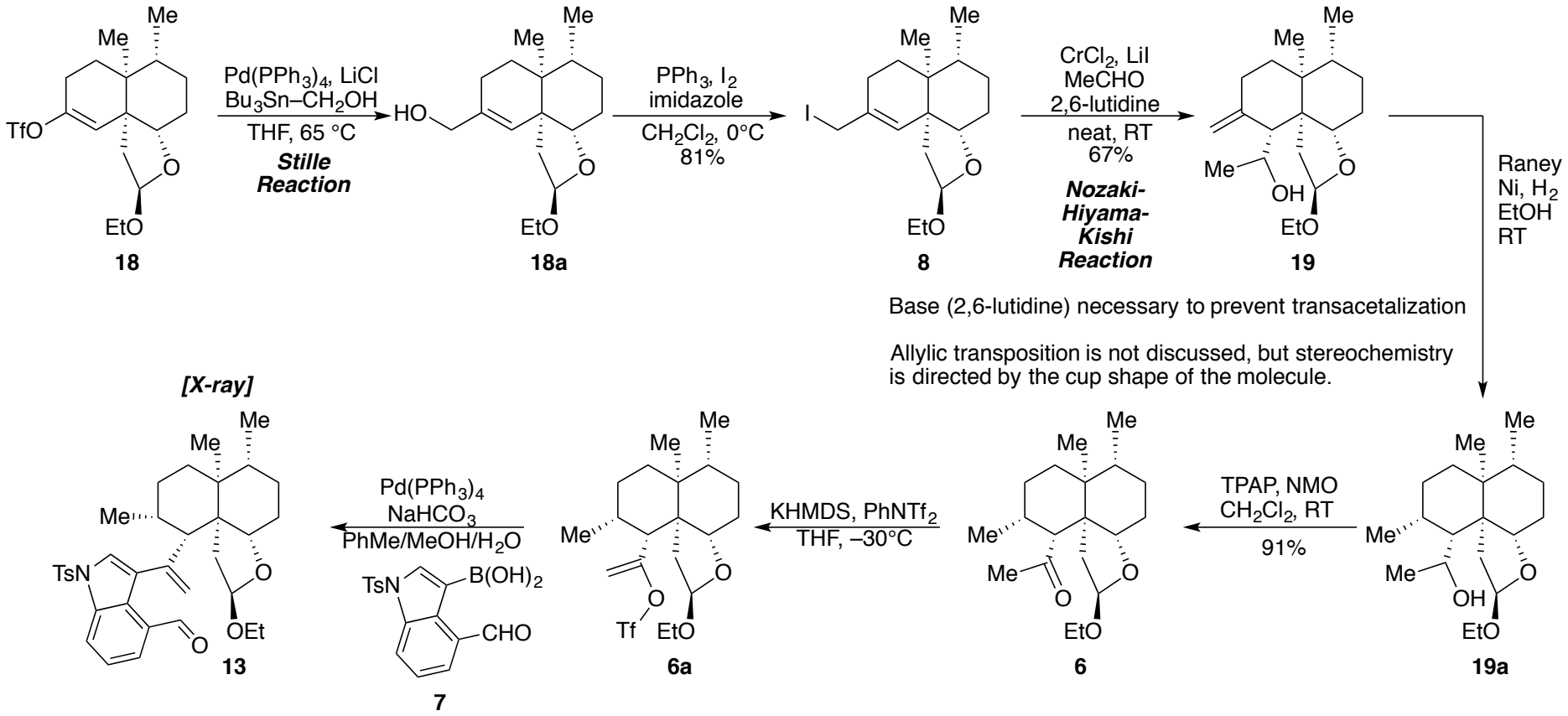
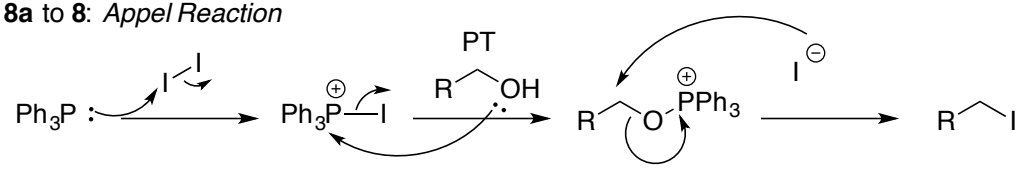
16 to **16a:**

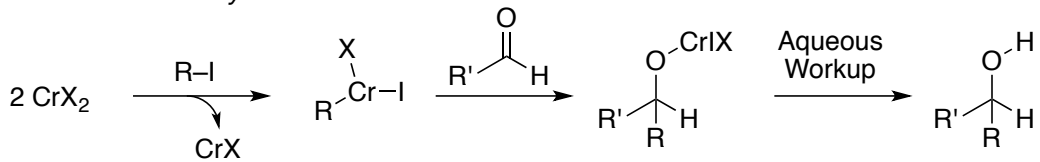




18a to **8**: *Appel Reaction*

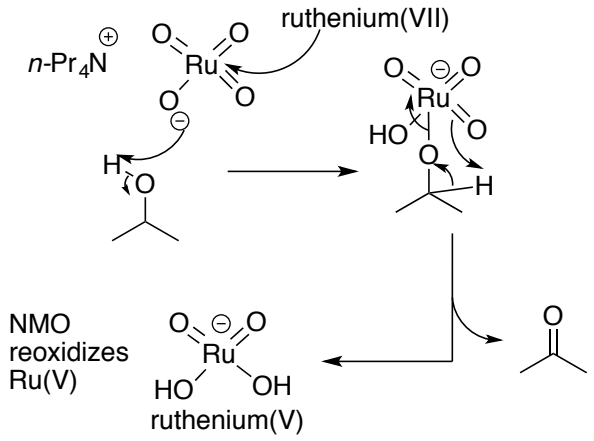


18a to **8**: *Nozaki-Hiyama-Kishi Reaction*

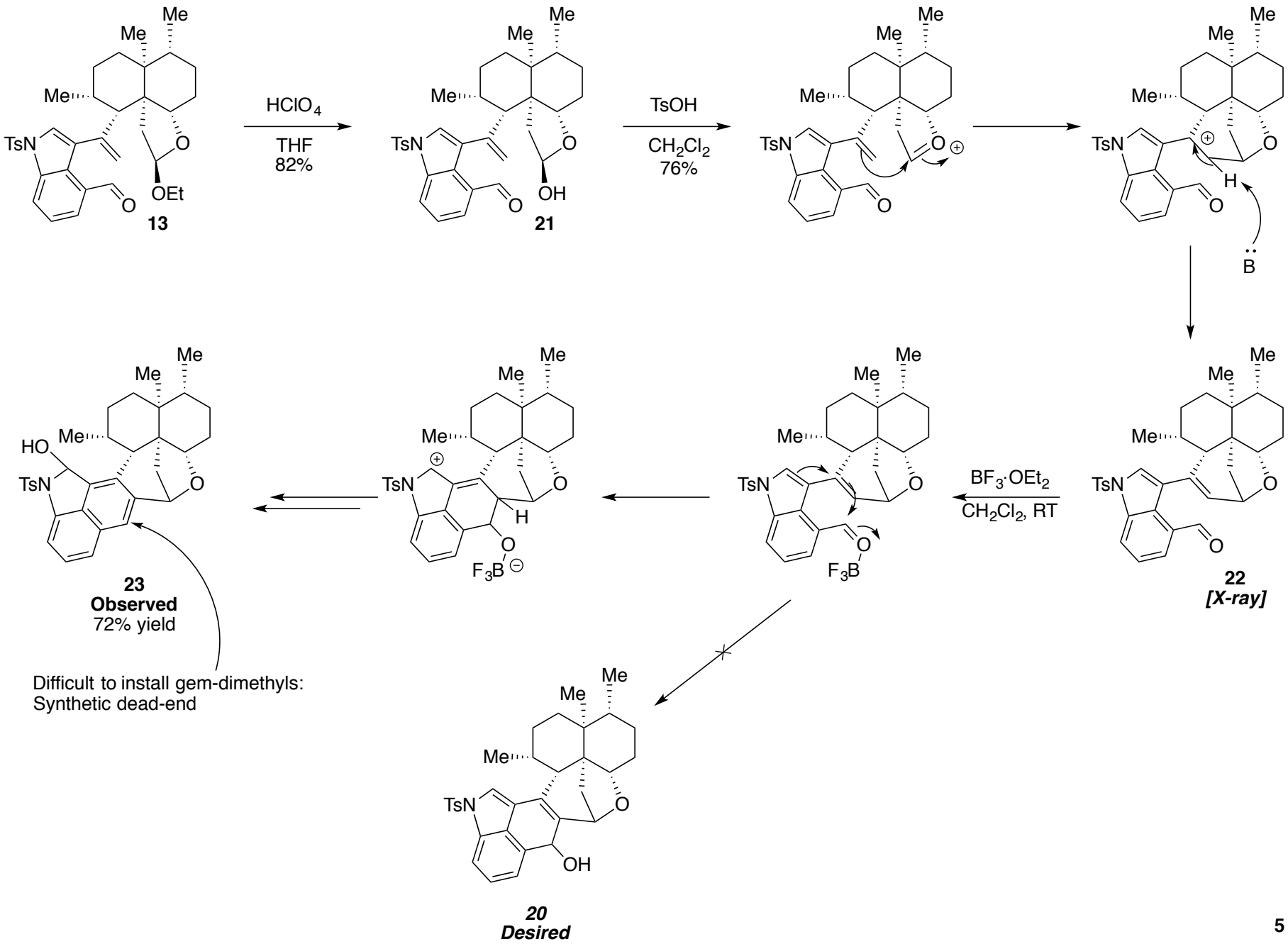


Disproportionation

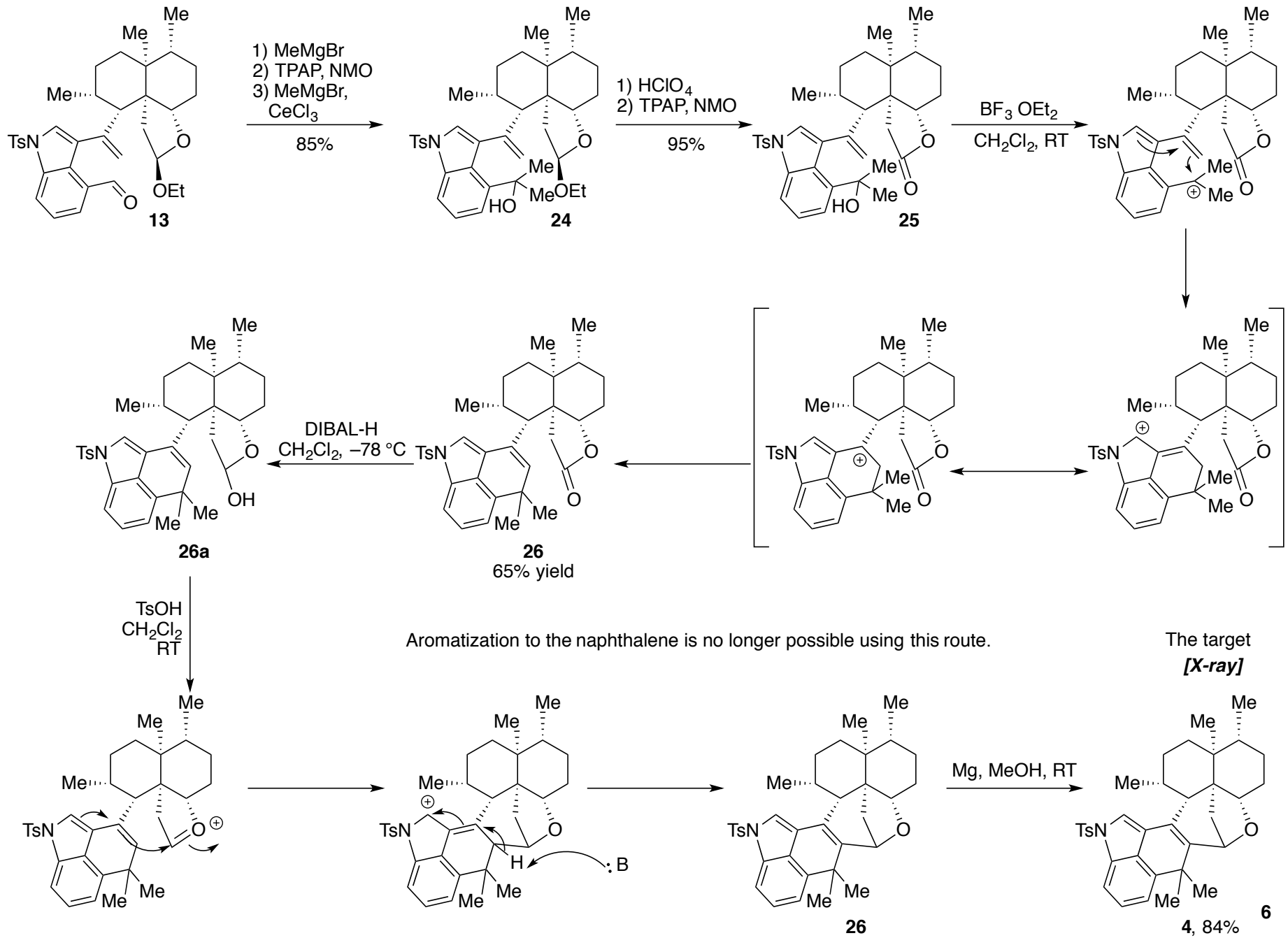
19a to **6**: Tetrapropylammonium perruthenate (TPAP) oxidation (Ley Oxidation)



Attempting the Prins-type cationic cyclization



Attempting the Prins-type cationic cyclization: the successful strategy



Reductive deprotection of N–Ts: 26 to 4