

Scheme 1. Synthesis of *cis*-5/6/6 Tricyclic Scaffold

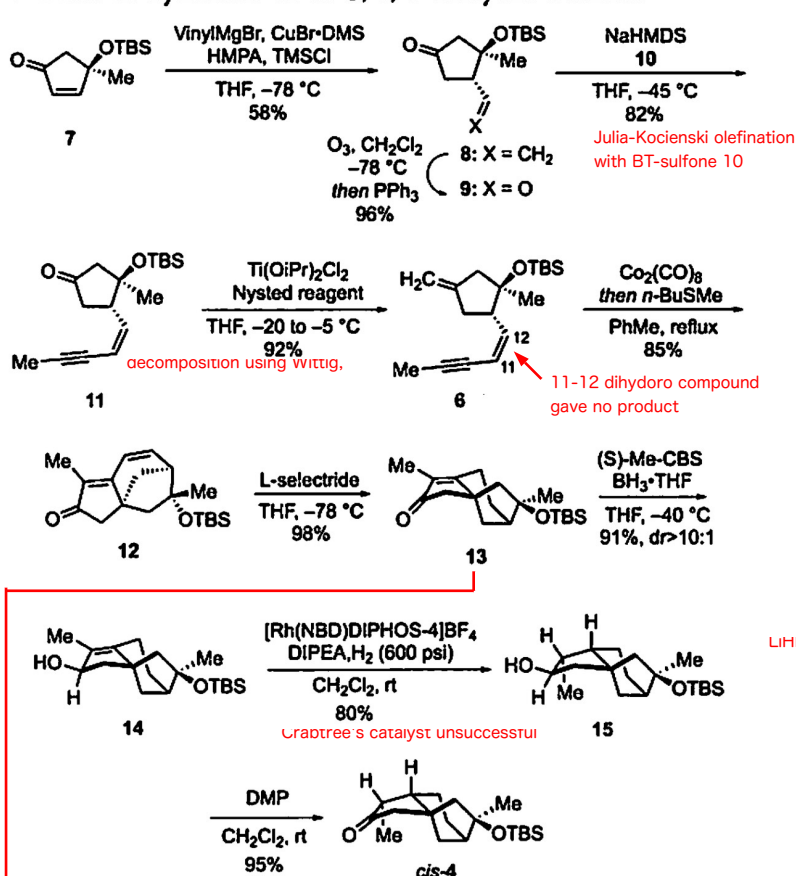
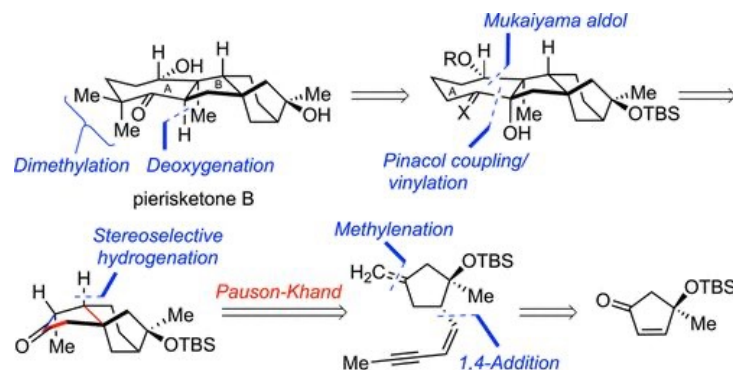
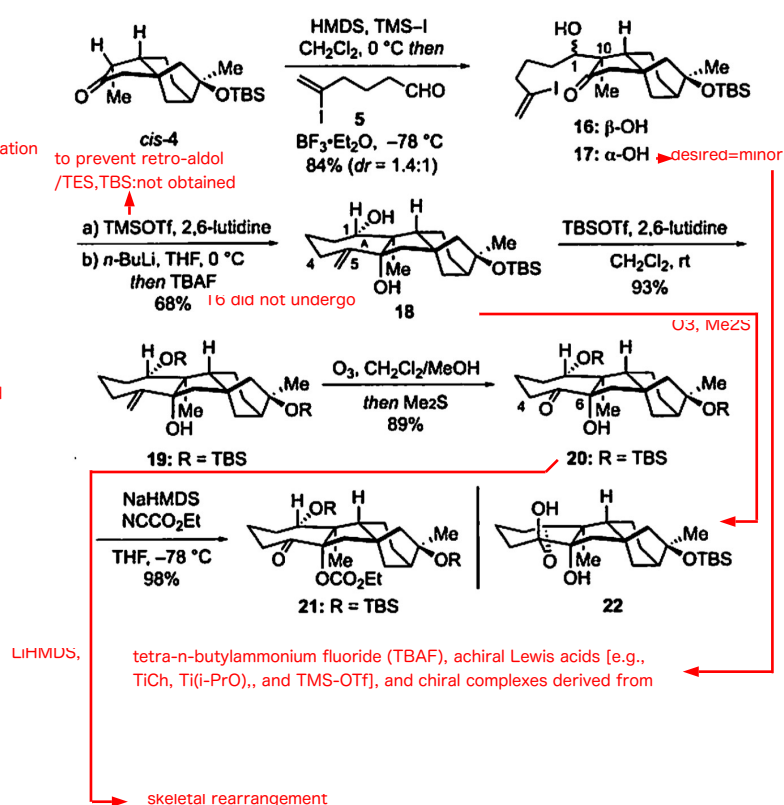


Table 1. Representative Attempts to Directly Reduce 12 to *cis*-4^a

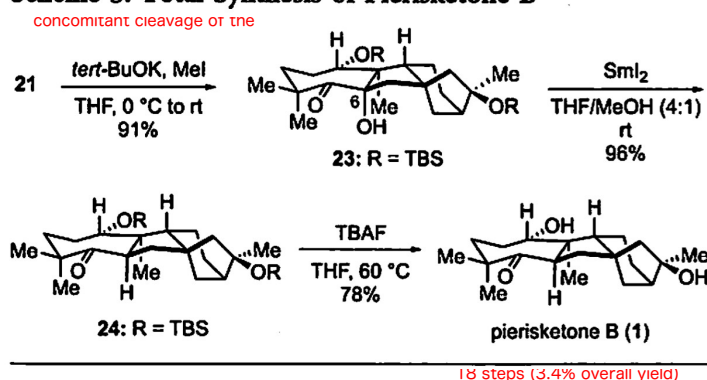
Entry	Condition ^b	<i>cis</i> : <i>trans</i> ^c
1	Pd/C, H ₂ , Et ₃ N	3:97 (95%)
2	Li, NH ₃ , ^t BuOH	1:4 (67%)
3	NHC-CuCl ₂ , Ph ₃ SiH ₂ , PhMe	1:4 (71%)
4	Co(acac) ₃ , PhSiH ₃ , TBHP, ^t PrOH	1:1 (60%)
5	Mn(dpm) ₃ , PhSiH ₃ , TBHP, ^t PrOH	1:1 (91%)



Scheme 2. Synthesis of Pivotal Intermediate



Scheme 3. Total Synthesis of Pierisketone B



18 steps (3.4% overall yield)