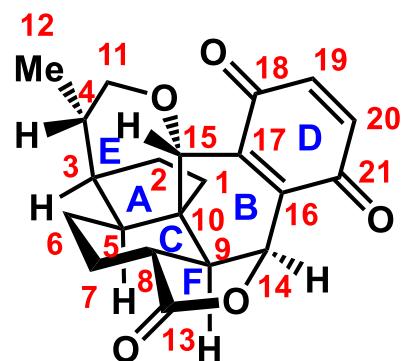
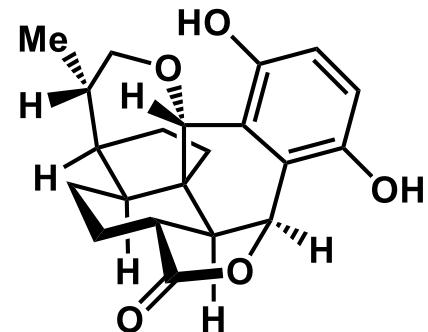


A Unified Synthetic Approach to the Pleurotin Natural Products

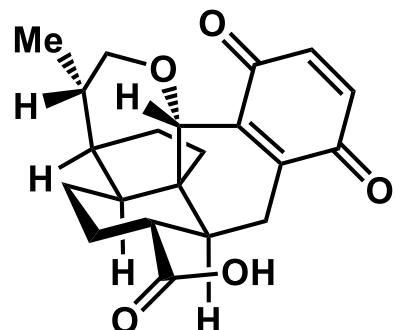
Yong Gao, Qidong Xia, An Zhu, Wenkuan Mao, Yiming Mo, Hanfeng Ding,* and Jun Xuan*



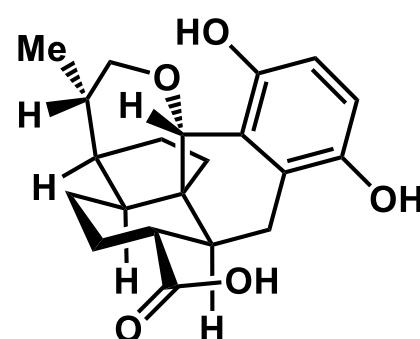
(-)-pleurotin (1)



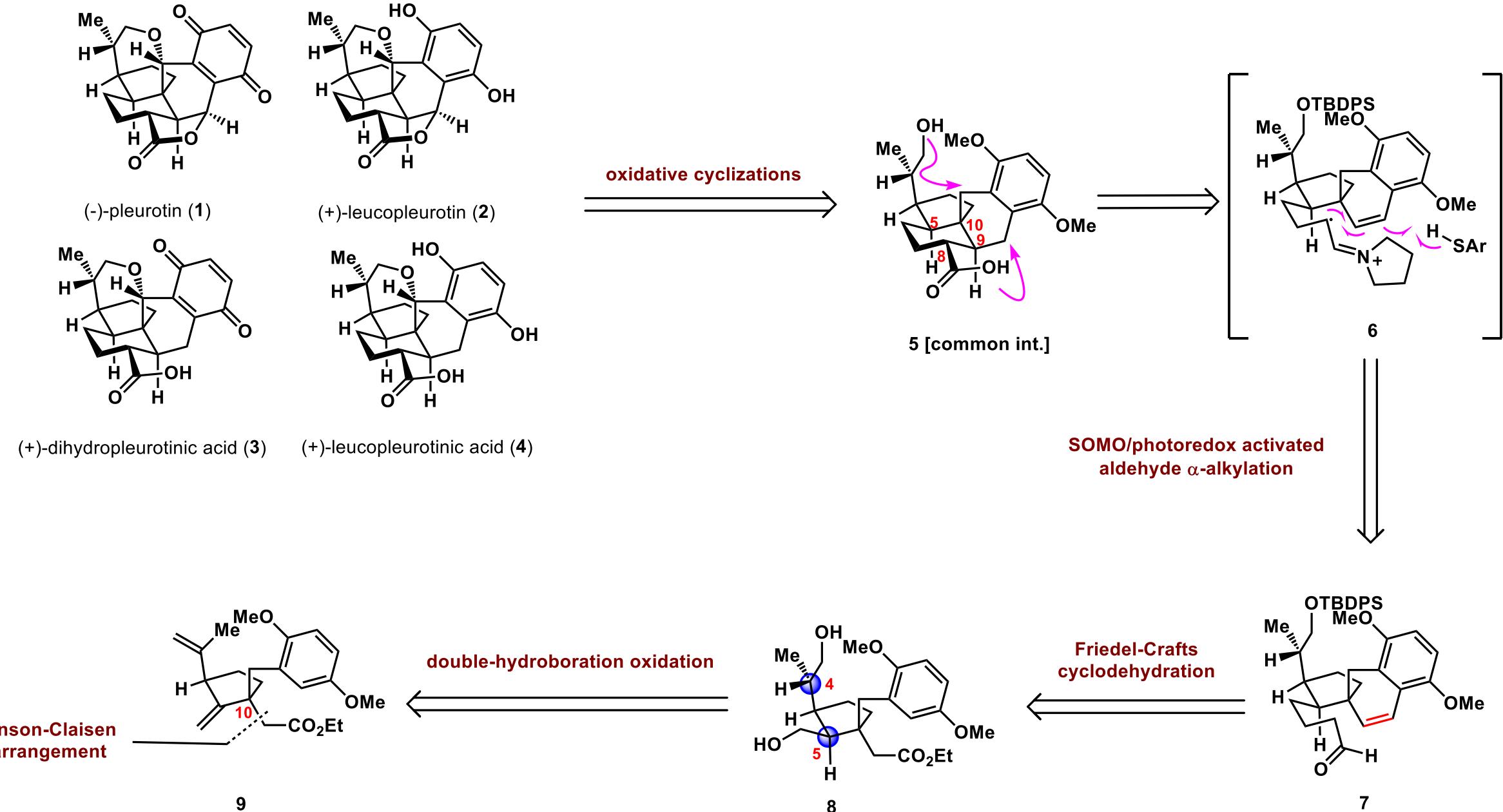
(+)-leucopleurotin (2)



(+)-dihydropleurotinic acid (3)



(+)-leucopleurotinic acid (4)



Scheme 1. Structures and Retrosynthetic Analysis of the Pleurotin Natural Products 1-4

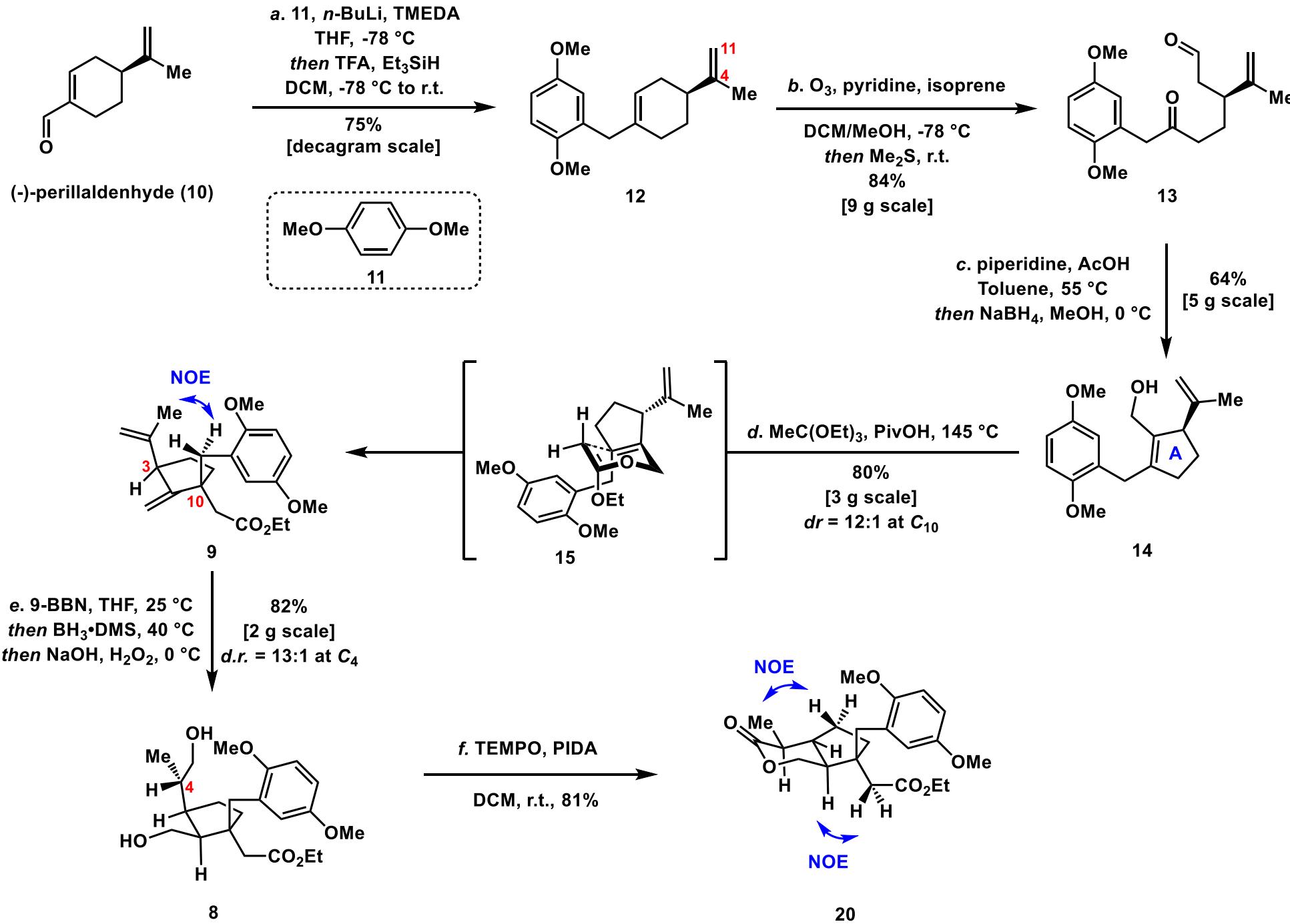
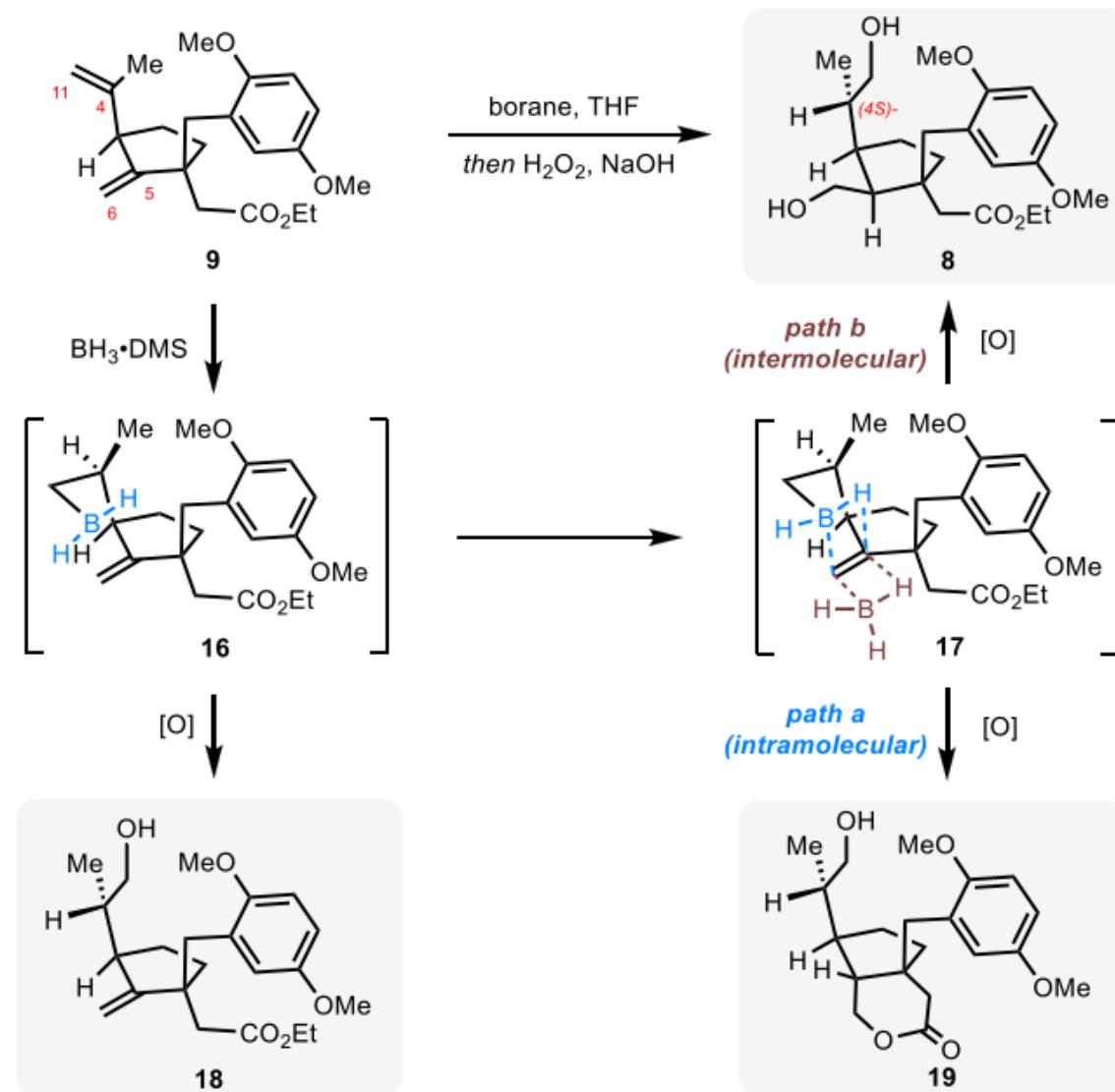


Table 1. Conditional Screening of the Sequential Hydroboration-Oxidation of Diene **9^a**



entry	hydroboration conditions	yield (%) ^b (dr at C4) ^c		
		8	18	19
1	$\text{BH}_3\cdot\text{DMS}^d$	0	24 (10:1)	61 (10:1)
2	$\text{BH}_3\cdot\text{DMS}^e$	19 (10:1)	16 (10:1)	49 (10:1)
3	Sia_2BH^e	0	76 (9:1)	0
4	Cy_2BH^e	0	85 (11:1)	0
5	$(-)\text{-Ipc}_2\text{BH}^e$	0	0	0
6	9-BBN ^e	0	90 (13:1)	0
7	$\text{PinBH}^e, \text{CuCl}, t\text{-BuOK}$	0	0	0
8 ^f	$\text{CatBH}^e, \text{Rh}(\text{PPh}_3)_3\text{Cl}$	0	22 (8:1)	0
9 ^g	9-BBN, ^d $\text{BH}_3\cdot\text{DMS}^d$	82 (13:1)	0	6 (13:1)

^aReaction scale: **9** (0.05 mmol). ^bIsolated yields. ^cDetermined by crude ^1H NMR spectrum. ^dBorane (1.0 equiv). ^eBorane (2.0 equiv). ^f**9** was recovered in 70% yield. ^gPerformed on 2 g scale.

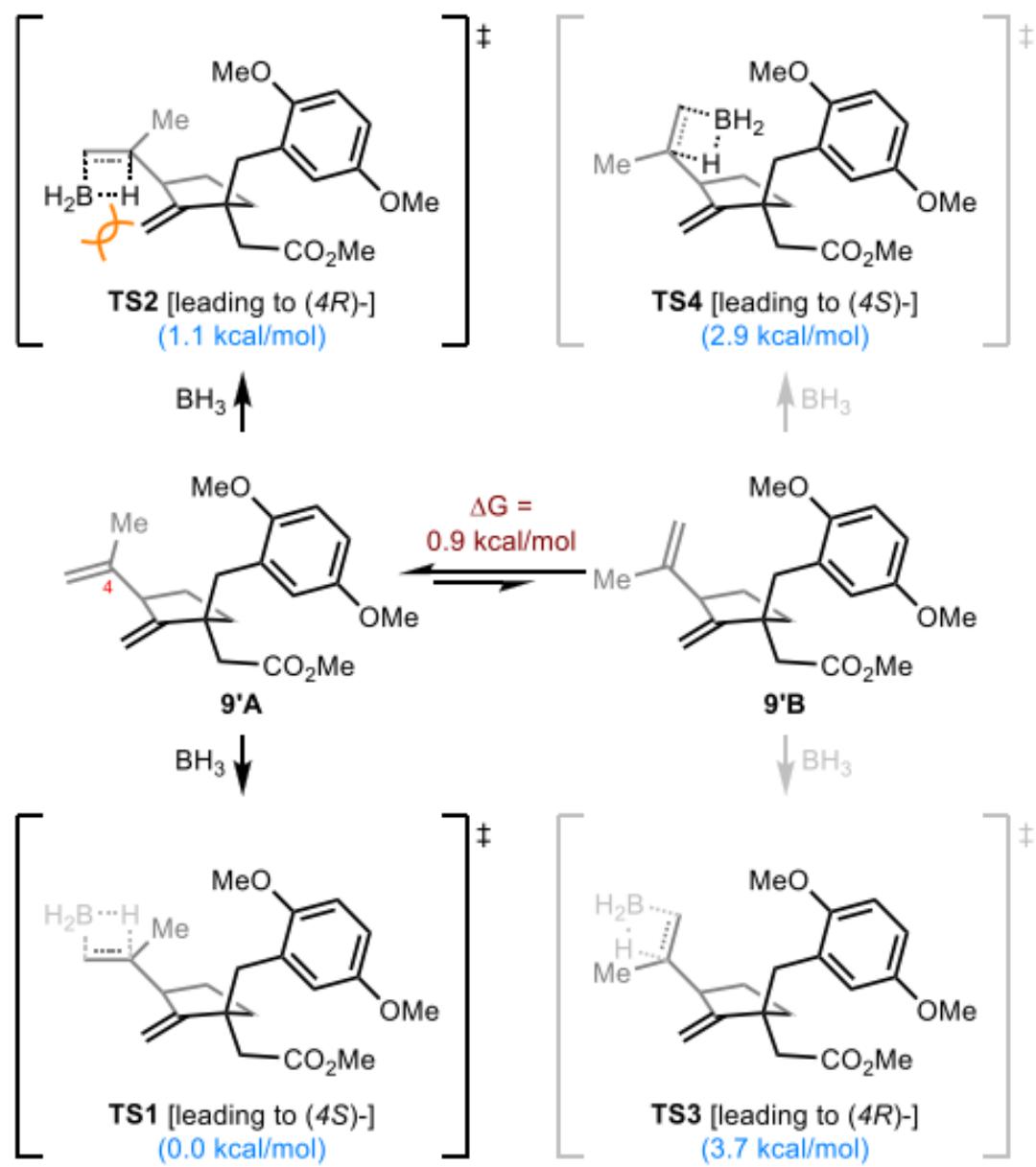


Figure 1. Conformational preference of $9'$ and possible pathways leading to a pair of diastereomers at C4. The relative Gibbs free energies (ΔG_{sol}) at 298.15 K and 1 atm are listed in parentheses.

Details for Hydroboration of Four Representative Conformers

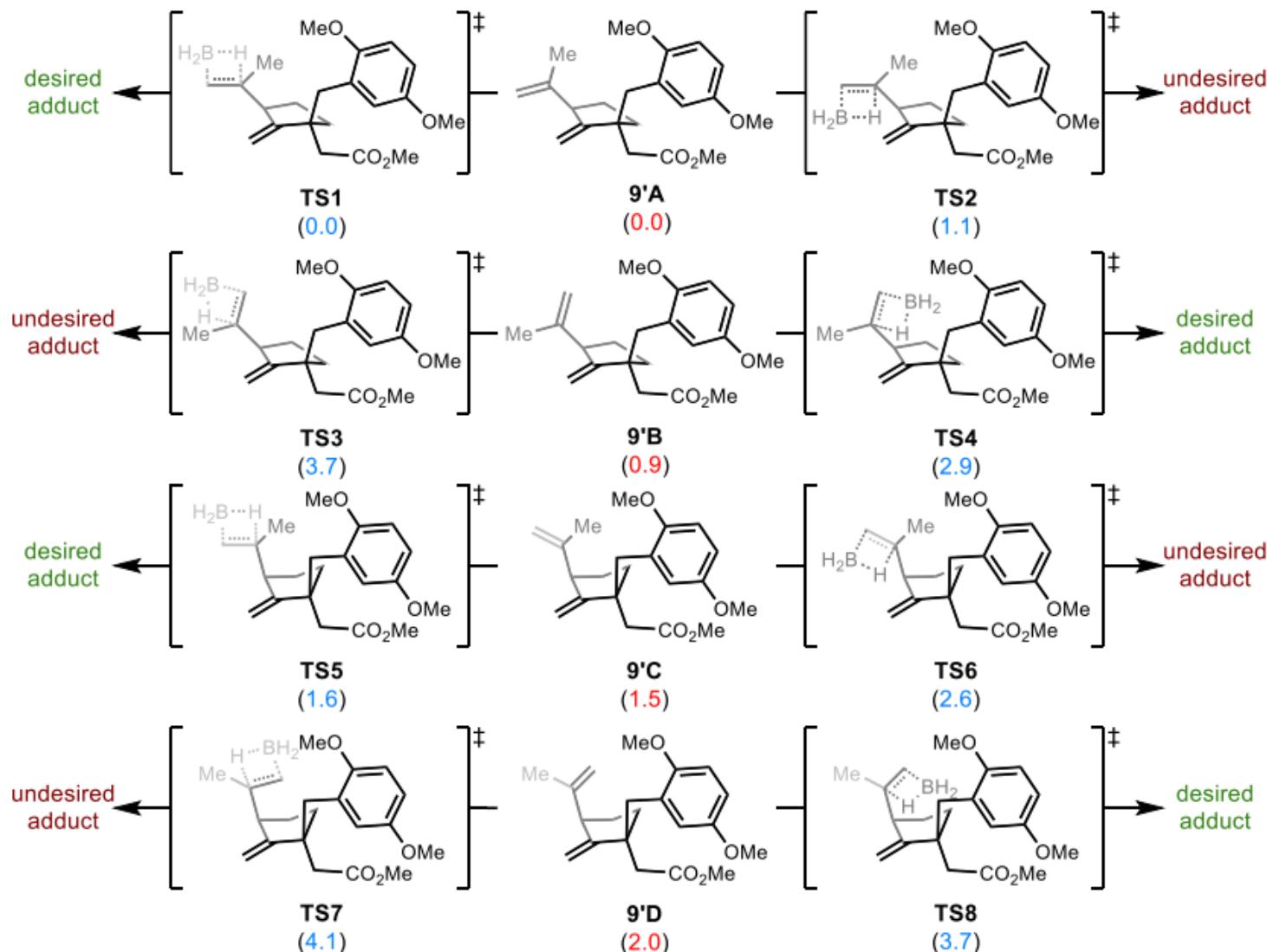
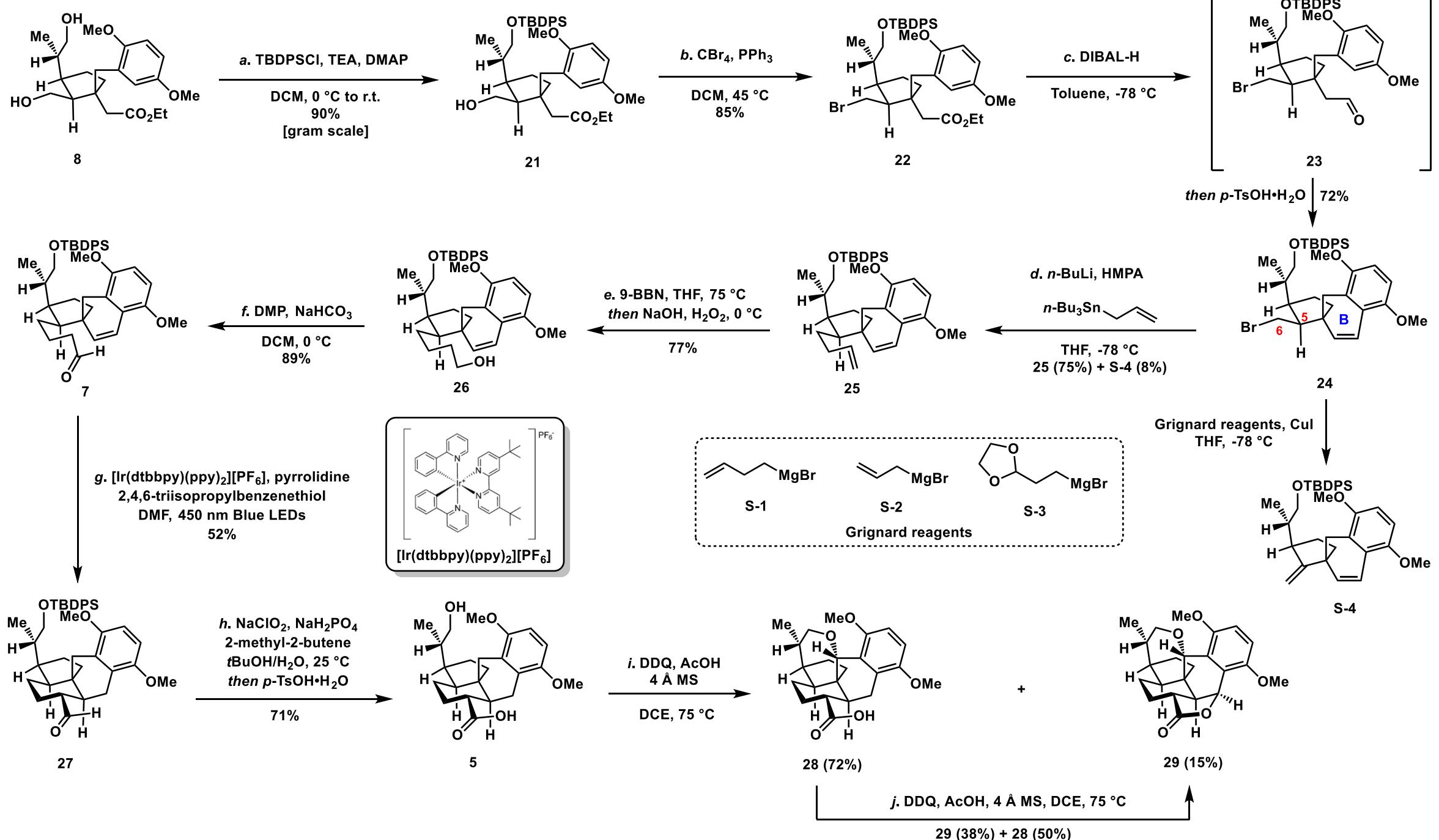


Figure S2. Hydroboration of four representative conformers. The relative Gibbs free energies (ΔG_{sol}) at 298.15 K and 1 atm are presented in parentheses (Red relative to **9'A**, Blue relative to **TS1**).



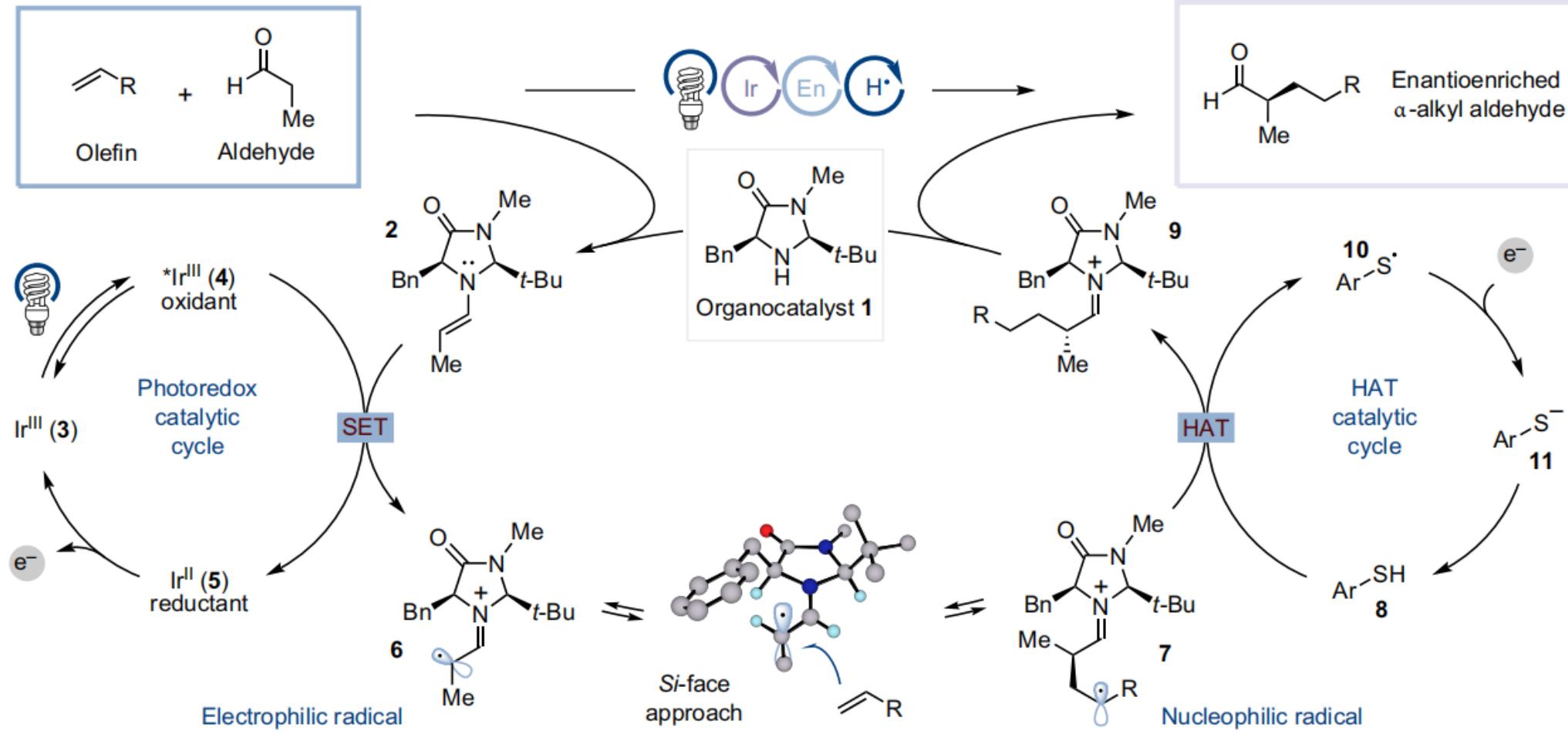


Figure 2 | Proposed mechanism for aldehyde α -alkylation via photoredox, HAT and organocatalysis. Condensation of organocatalyst **1** with an aldehyde substrate initiates the catalytic cycle. Concurrently, irradiation of iridium photocatalyst **3** generates an excited state species (**4**). This intermediate can then oxidize enamine **2** through single electron transfer (SET) and generate the $3\pi e^-$ enaminyl radical **6**. Reversible radical addition across an olefin substrate then produces the carbon radical **7**, which is trapped through HAT with thiol HAT catalyst **8**. Hydrolysis of iminium **9** provides the enantioenriched α -alkyl aldehyde and regenerates amine catalyst **1**. Finally, reduction of thiyl radical **10** by the Ir(II) species (**5**) subsequently regenerates thiol catalyst **8** as well as the Ir(III) catalyst **3** to complete the remaining redox cycles.

