A Unified Synthetic Approach to the Pleurotin Natural Products

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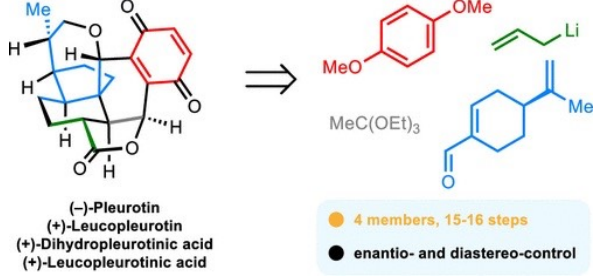
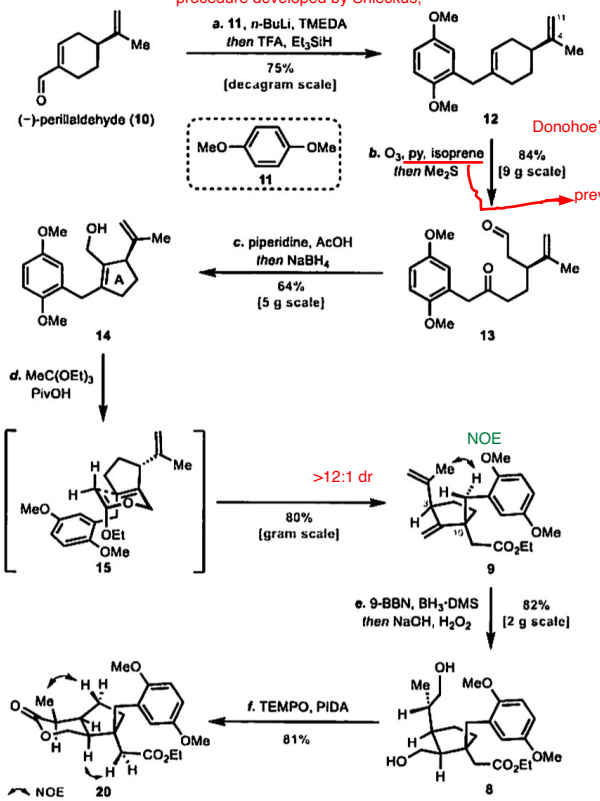
a tetra-substituted trans-hydrindane

late-stage C-H oxidative cyclization



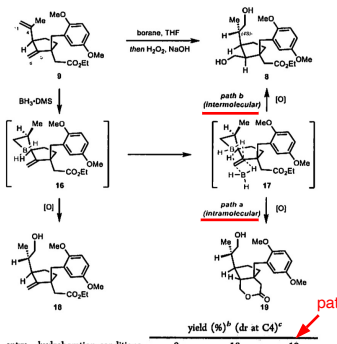
Scheme 2. Synthesis of Diol 8

procedure developed by Snieckus,



diastereo-controlled sequential hydroboration-oxidation sequence of diene

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	$BH_3{\cdot}DMS$[d]	0	24 (10:1)	61 (10:1)
2	$BH_3{\cdot}DMS$[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	(−)-Ipc_2BH[e]	0	0	0
6	9-BBN[e]	0	90 (13:1)	0
7	PinBH,[e] CuCl, t-BuOK	0	0	0
8[f]	CatBH,[e] $Rh(PPh_3)_3Cl$	0	22 (8:1)	0
9[g]	9-BBN,[d] $BH_3{\cdot}DMS$[d]	82(13:1)	0	6(13:1)

[a]Reaction scale: 9 (0.05 mmol). [b]Isolated yields. [c]Determined by crude ^1H NMR spectrum. [d]Borane (1.0 equiv). [e]Borane (2.0 equiv). [f]9 was recovered in 70% yield. [g]Performed on 2 g scale.

path a

a one-pot process by sequential addition of 9-BBN (1.0 equiv) and BH3DMS (1.0 equiv) to the reaction mixture,

{10:1, $\Delta\Delta G^{\ddagger}_{exp}$ = 1.4 kcal/mol}

DFT calculations using a methyl ester

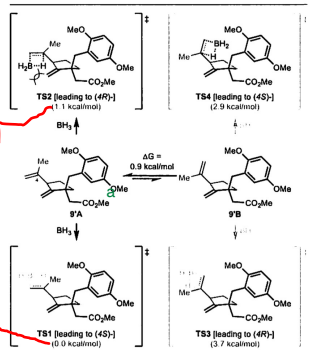
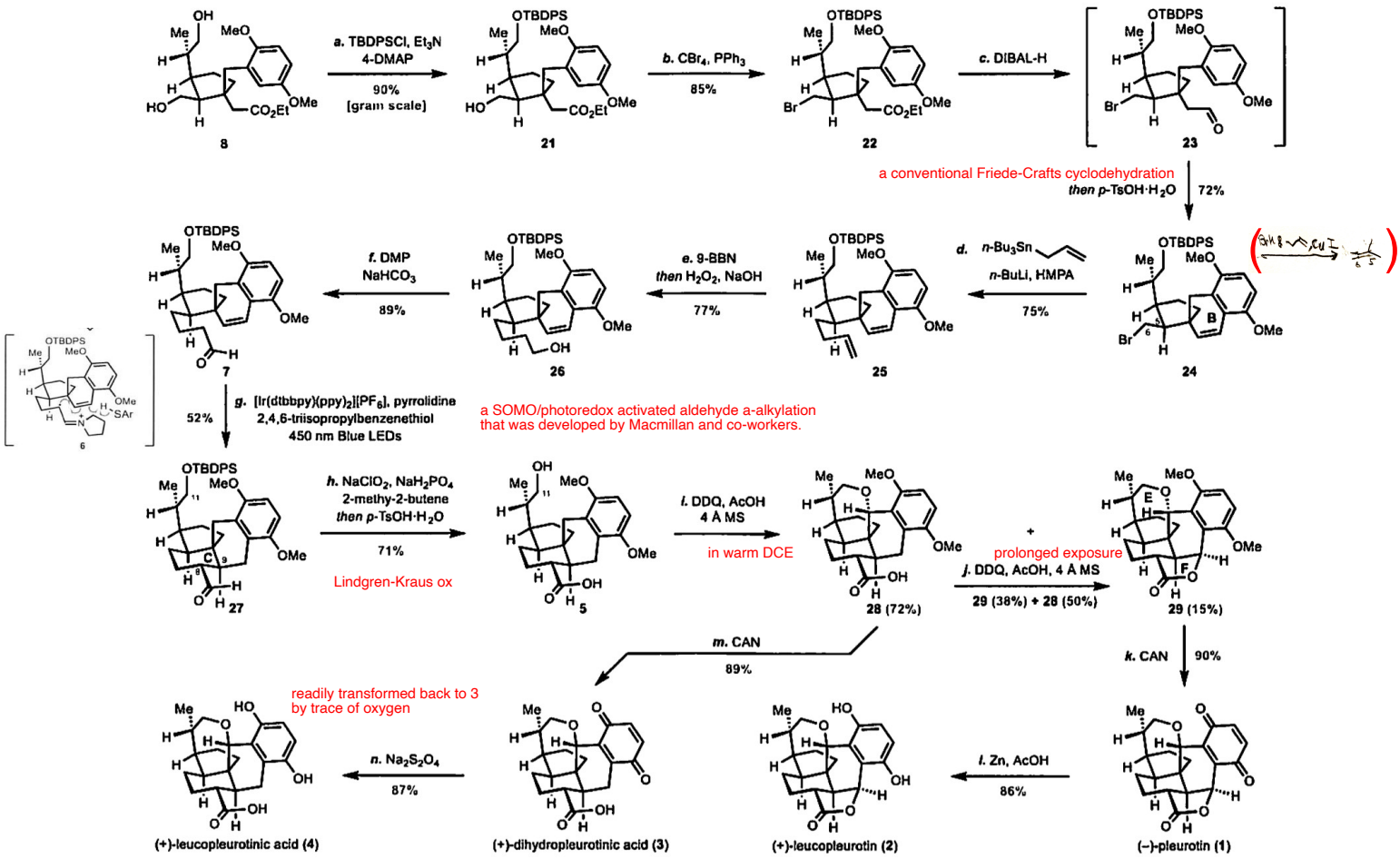


Figure 1. Conformational preference of 9′ and possible pathways leading to a pair of diastereomers at C4. The relative Gibbs free energies (ΔG_{rel}) at 298.15 K and 1 atm are listed in parentheses.

Scheme 3. Total Syntheses of (−)-Pleurotin (1), (+)-Leucopleurotin (2), (+)-Dihydropleurotinic Acid (3), and (+)-Leucopleurotinic Acid (4)