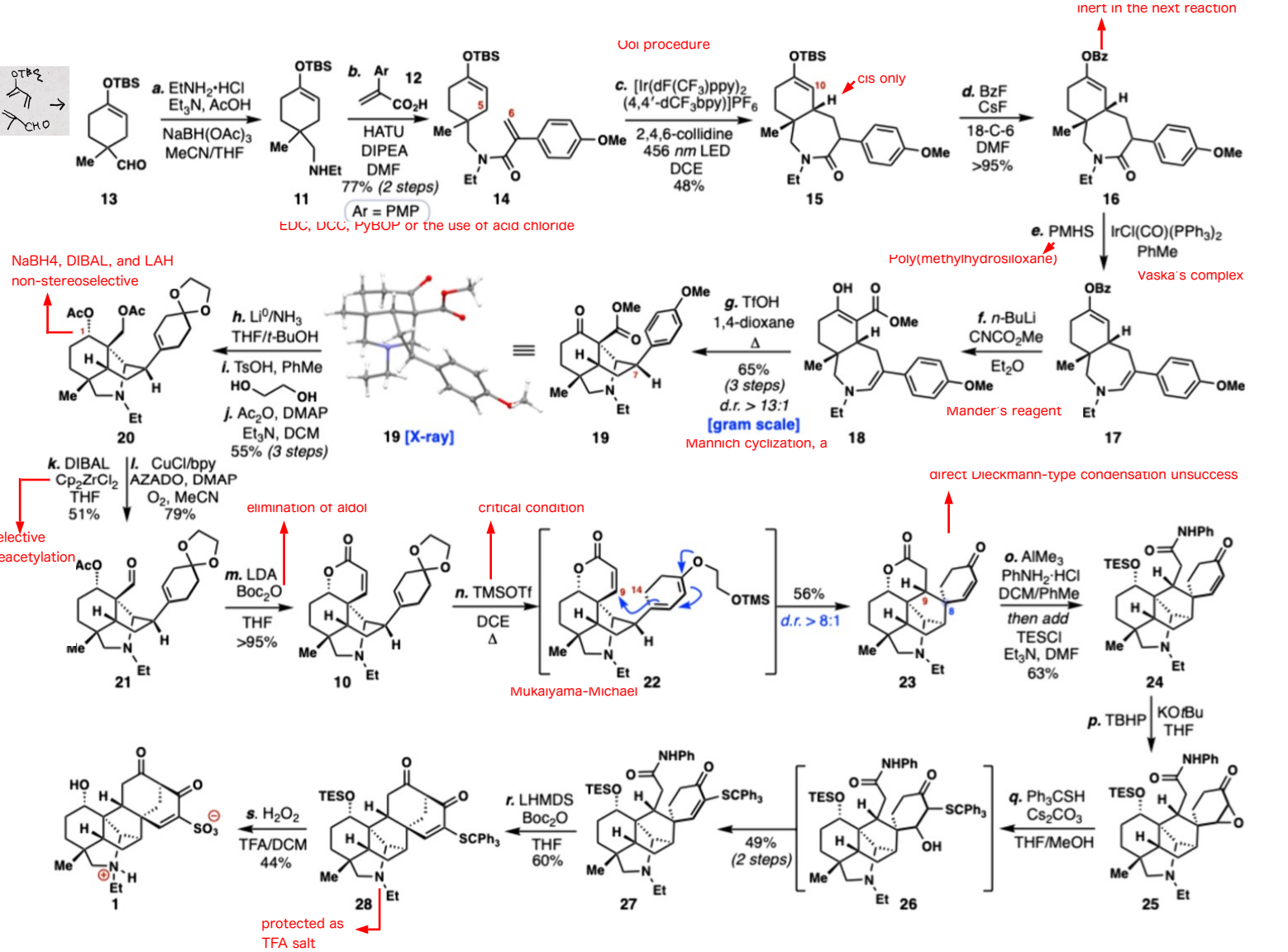
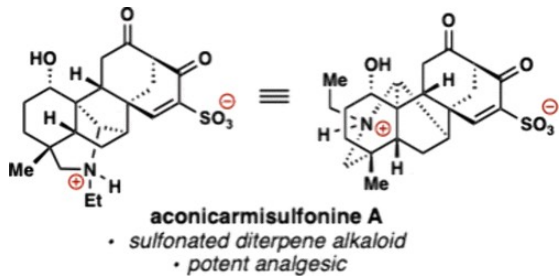




“Reagents and Conditions: (a) EtNH₂·HCl (1.2 equiv), Et₃N (1.5 equiv), AcOH (2.5 equiv), 3Å Molecular Sieves, MeCN/THF, 10 h, then NaBH(OAc)₃, 23 °C, 1.5 h; (b) DIPEA (3 equiv), HATU (1.0 equiv), 12 (1.0 equiv), DMF, 0 to 23 °C, 10 h, 77% over 2 steps; (c) Ir(dF(CF₃)ppy)₂(4,4'-dCF₃bpy)]PF₆ (2 mol %), 2,4,6-collidine (1.0 equiv), 456 nm LED, DCE, 23 to 30 °C, 8 h, 48%; (d) BzF (2.5 equiv), CsF (2.5 equiv), 18-C-6 (2.5 equiv), DMF, 0 to 23 °C, 1.5 h, >95%; (e) PMHS (4 equiv, calc. MW = 65), IrCl(CO)(PPh₃)₂ (1 mol %), PhMe, 23 °C, 10 h; (f) n-BuLi (2.5 M in hexanes, 2.1 equiv), CNCO₂Me (1.1 equiv), Et₂O, −78 °C; (g) TfOH (0.2 equiv), 1,4-dioxane, reflux, 16 h, 65% over 3 steps (d.r. > 13:1); (h) Li⁰ (55 equiv), t-BuOH (7 equiv), THF/NH₃, −78 °C to −33 °C, 2.5 h; (i) TsOH (0.2 equiv), ethylene glycol (40 equiv), PhMe, reflux, 16 h; (j) DMAP (5 mol %), Et₃N (3 equiv), Ac₂O (3 equiv), DCM, 23 °C, 2 h, 55% over 3 steps; (k) DIBAL (1 M in THF, 2.1 equiv), Cp₂ZrCl₂ (2.3 equiv), THF, −30 to 0 °C, 1.5 h, 51%; (l) CuCl (10 mol %), bpy (10 mol %), AZADO (10 mol %), DMAP (20 mol %), O₂ (ballon), MeCN, 23 °C, 5 h, 79%; (m) LDA (3.6 equiv), THF, −78 to 0 °C, 15 min, then Boc₂O (1.4 equiv), 23 °C, 1 h, >95%; (n) TMSOTf (3.4 equiv), DCE, reflux, 4 h, 56% over 2 steps (d.r. > 8:1); (o) AlMe₃ (4.7 equiv, 2 M in PhMe), PhNH₂·HCl (4.8 equiv), DCM/PhMe, 0 to 23 °C, 10 h, then Et₃N (10.0 equiv), TESCl (8.5 equiv), DMF, 23 °C, 3 h, 63%; (p) TBHP (18 equiv, 5 to 6 M in decane), KOtBu (1 M in THF, 2.4 equiv), THF, 0 °C, 2 h; (q) Ph₃CSH (1.2 equiv), Cs₂CO₃ (3 equiv), THF/MeOH, 23 °C, 1.5 h, 49% over 2 steps; (r) LHMDS (1 M in THF, 4.0 equiv), THF, −78 °C 1 h, then Boc₂O (1.1 equiv) 23 °C, 2 h, 60%; (s) aq. H₂O₂ (3.3 equiv), DCM/TFA, 0 to 23 °C, 24 h, 44%.

