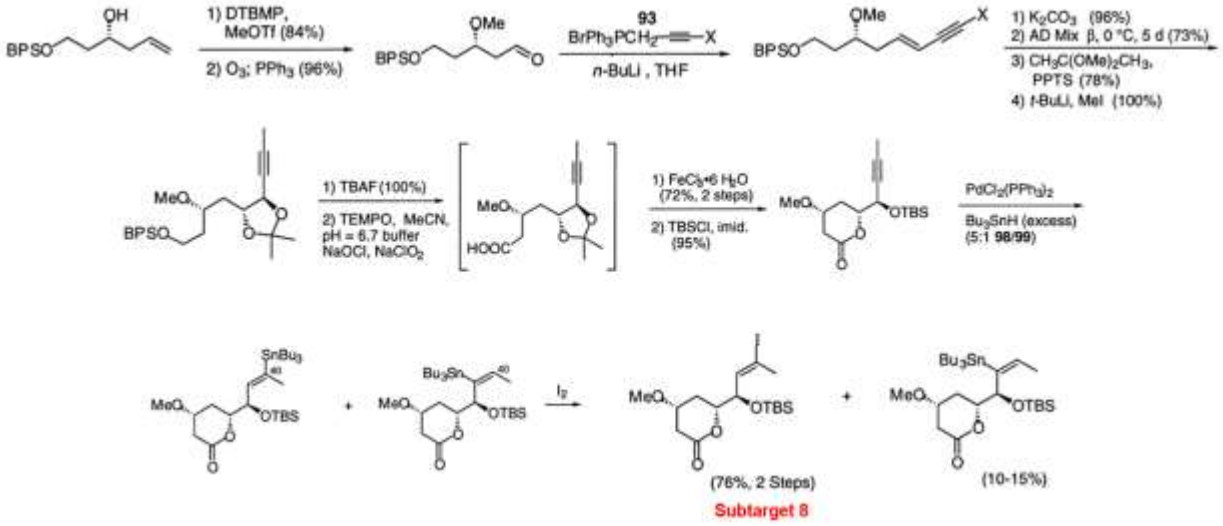
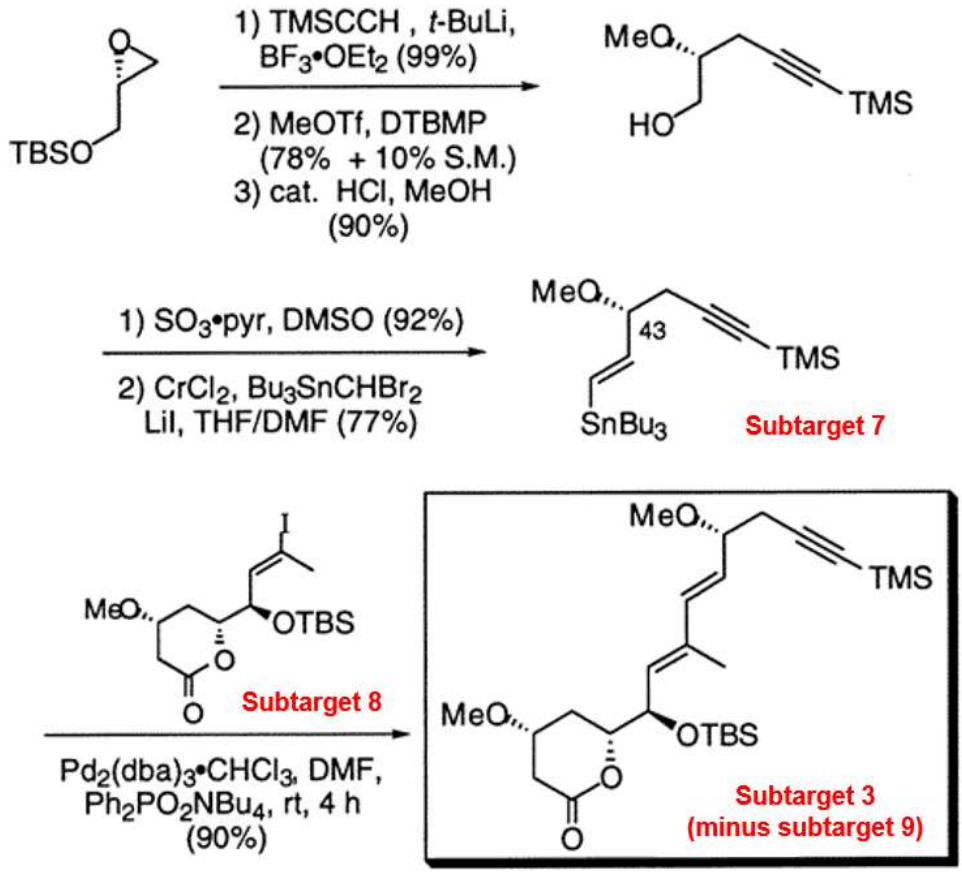
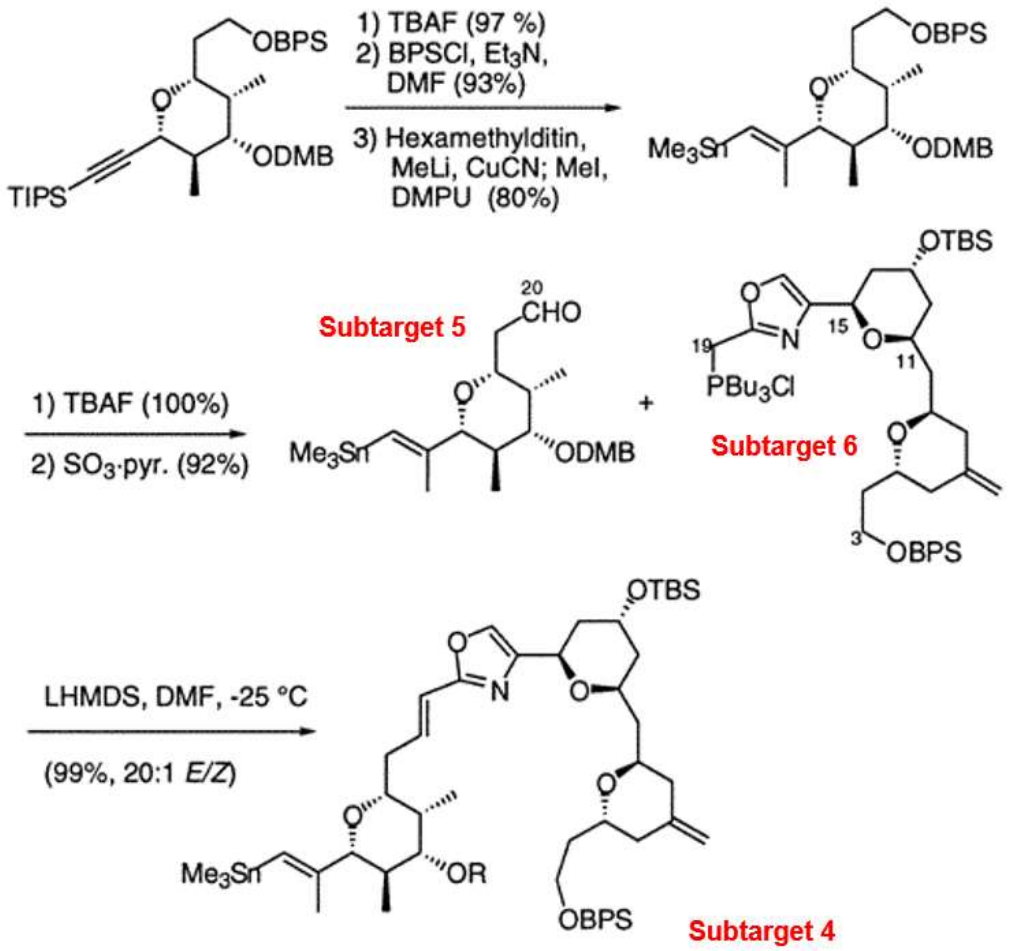
Supplementary Materials (SM)



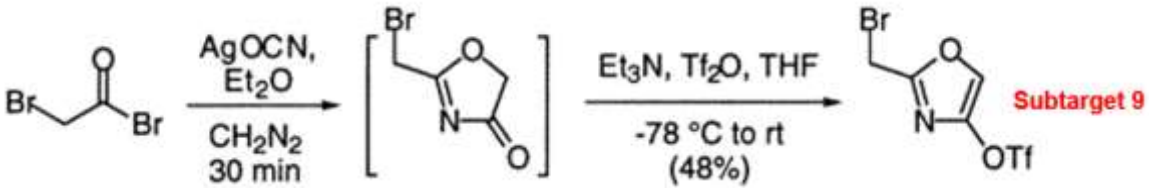
SM Figure 1. Formation of vinyl iodide (subtarget 8). Note the importance of Wittig olefination as part of the synthetic pathway of subtarget 8 formation (chain elongation) (*Reprinted with permission [22]*).



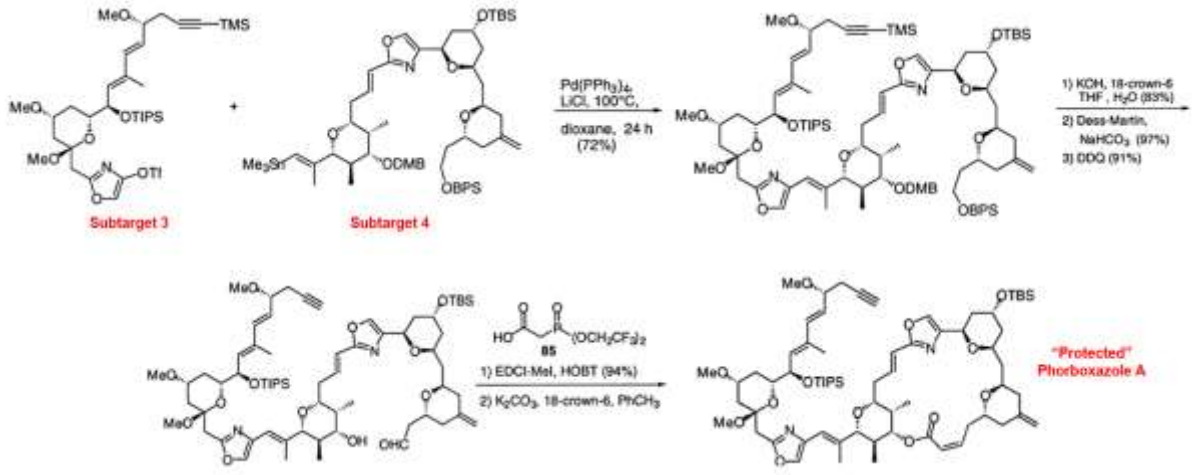
SM Figure 2. Combination of subtargets 8 and 7, a vinyl stannane derived from its reference epoxide to form subtarget 3 minus subtarget 9 (*Reprinted with permission [22]*).



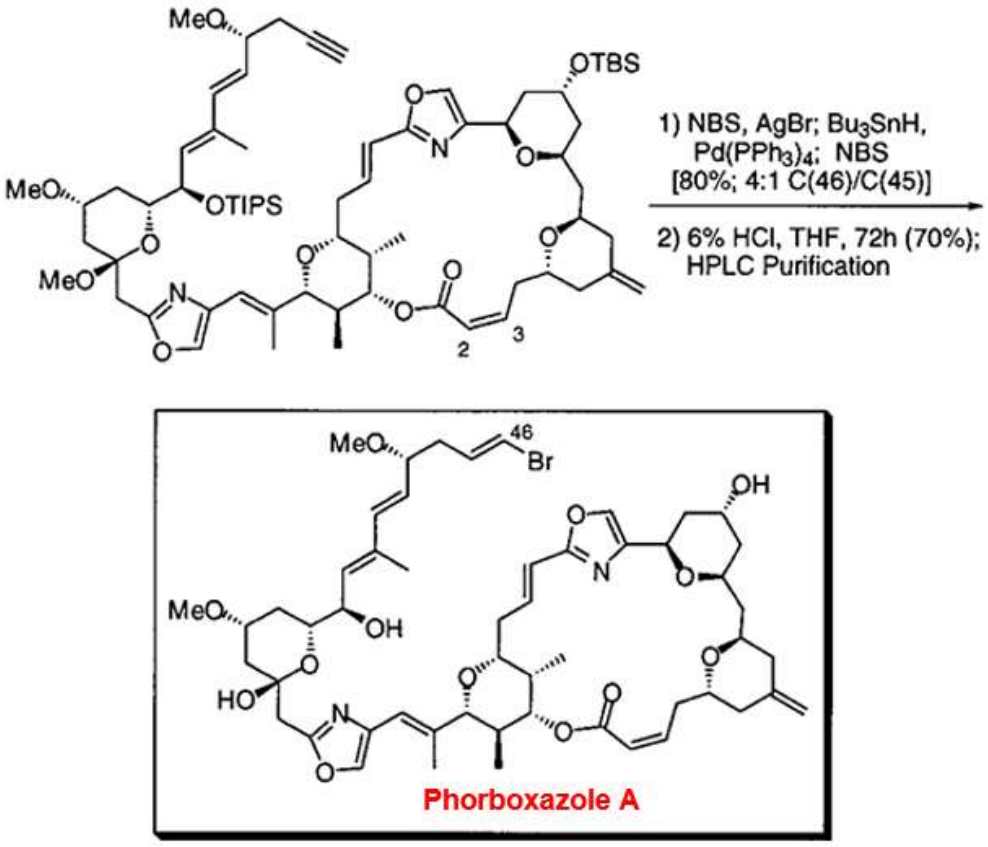
SM Figure 3. Formation of subtarget 4, a macrolide in itself, from the combination of subtargets 6 (a salt) and 5 (a macromolecular aldehyde). Shown here is the assembly of the two tetrahydropyran rings via modified Petasis-Ferrier rearrangement (*Reprinted with permission [22]*).



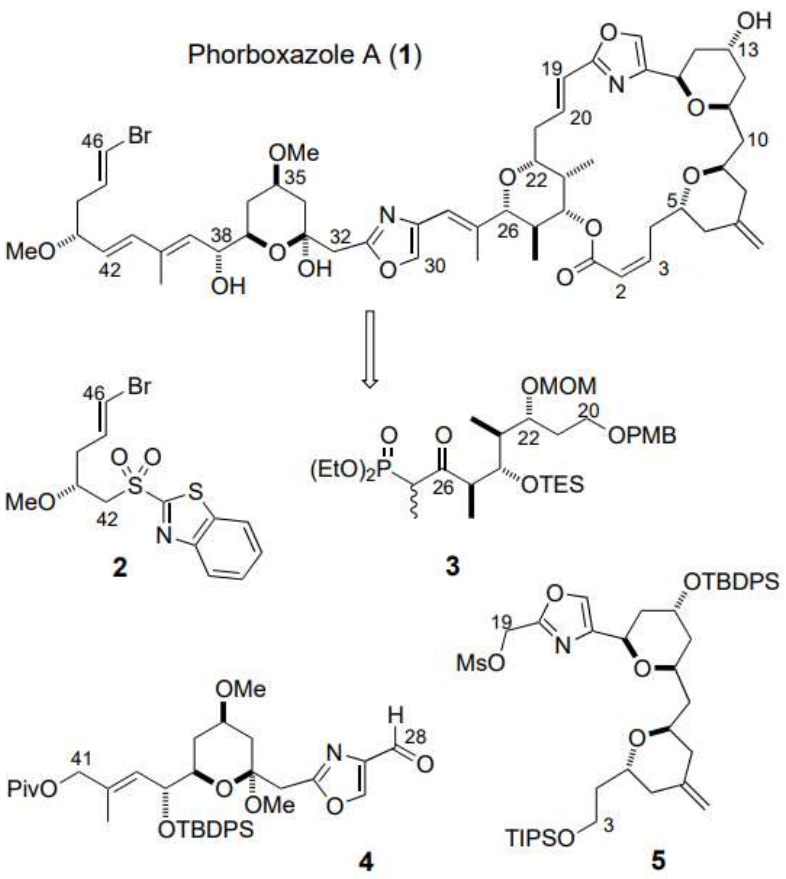
Supplementary Figure 4. Formation of subtarget 9, a bifunctional oxazole from bromoacetyl bromide. This is added to the molecule formed in Supplementary Figure 2 to form subtarget 3, a main precursor of the target molecule (*Reprinted with permission [22]*).



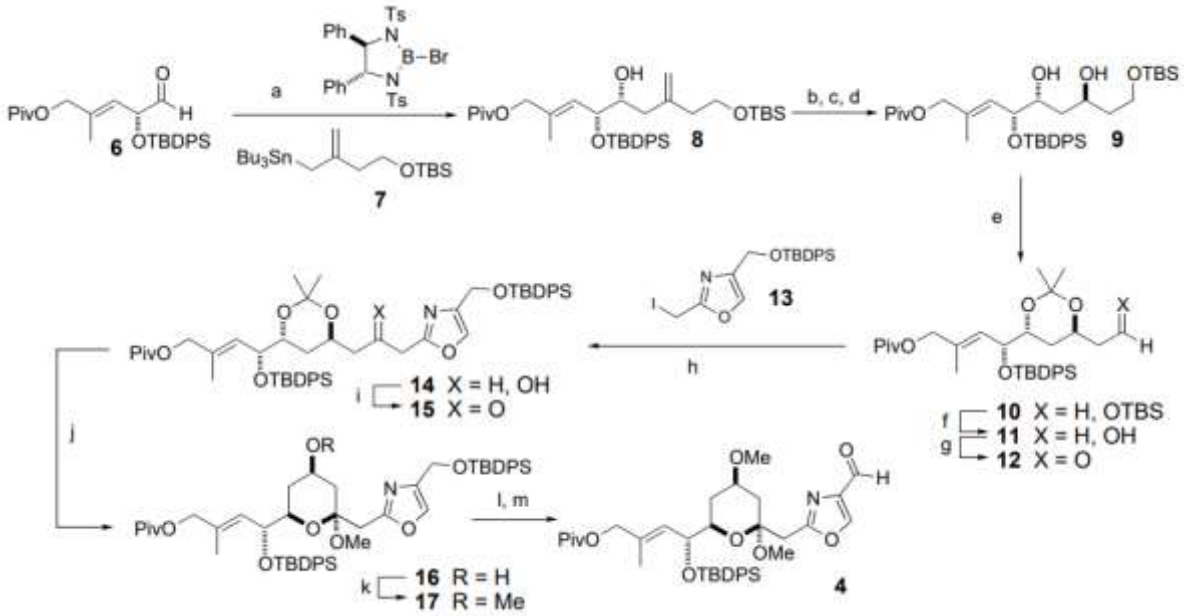
SM Figure 5. Formation of protected Phorboxazole A (minus Br on C46) from subtargets 4 and 3 (*Reprinted with permission [22]*).



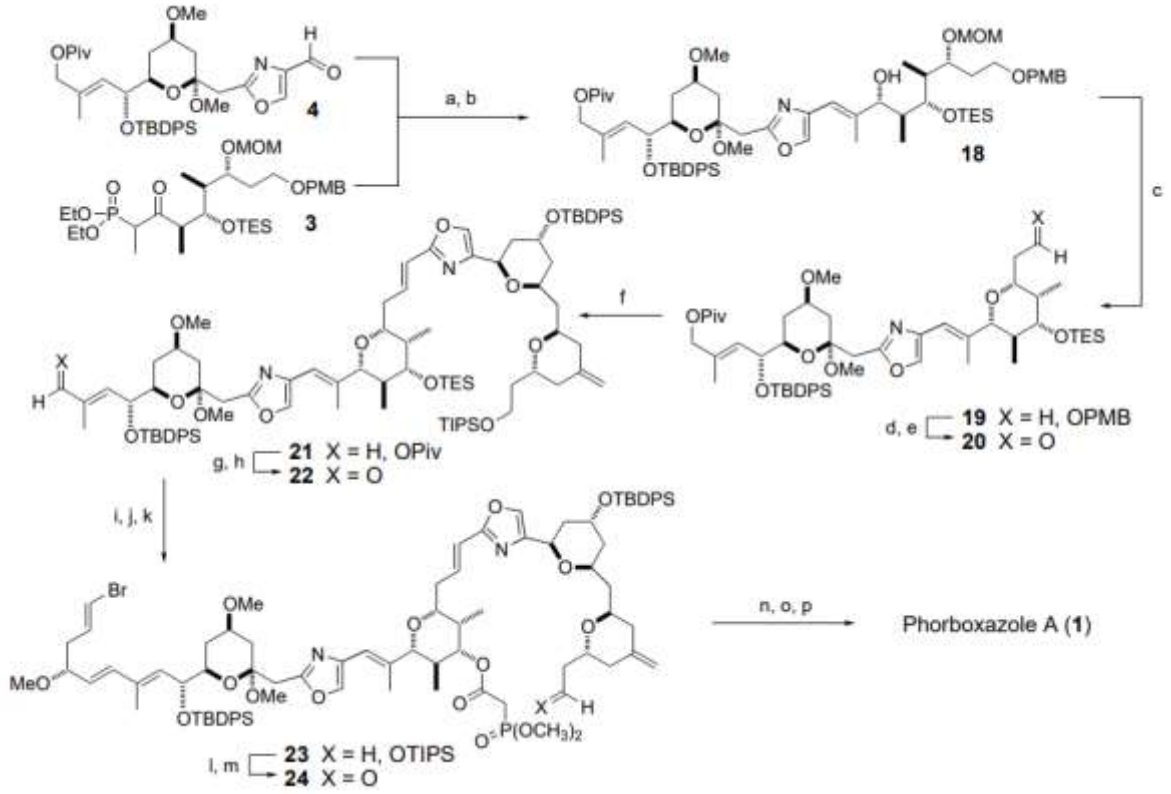
SM Figure 6. Formation of Phorboxazole A and removal of protecting groups (global deprotection using 6% HCl and THF for 72 h). Note the addition of the terminal Br on C46. The longest linear sequence leading to (+)-Phorboxazole A was 27 steps, with an overall yield of 3% (*Reprinted with permission [22]*).



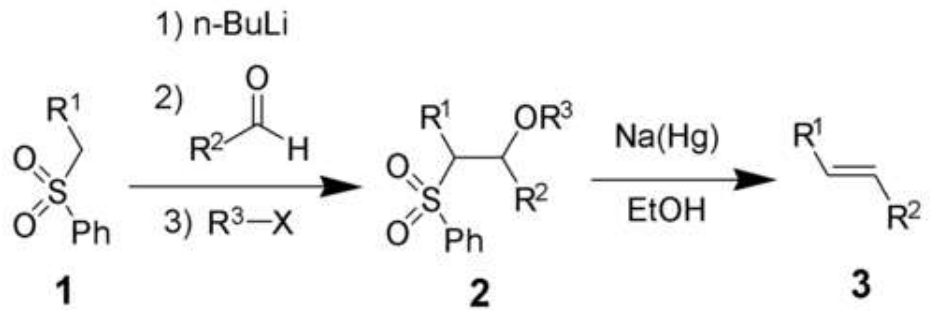
SM Figure 7. Retrosynthetic analysis of Phorboxazole A by the Williams group (*Reprinted with permission [23]*).



SM Figure 8. Formation of component 4, beginning with a non-racemic β,γ-unsaturated aldehyde (component 6) (*Reprinted with permission [23]*).



SM Figure 9. Formation of target molecule, Phorboxazole A, via the combination of components 2, 3, 4, and 5 (*Reprinted with permission [23]*).



SM Figure 10. Julia olefination: (1) phenyl sulfone, (2) intermediate, (3) product alkene (*Reprinted under the Creative Commons Attribution-Share Alike 3.0 Unported license*).