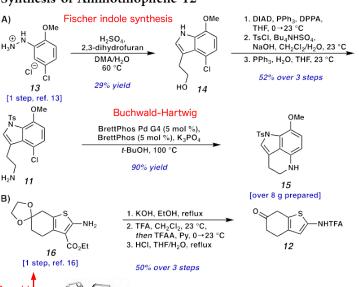
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## Scheme 2. (A) Synthesis of Tricyclic Aniline 15; (B) Synthesis of Aminothiophene 12



Scheme 3. Synthesis of Thioimidate 18 via Novel

1. InCl<sub>3</sub>, Et<sub>3</sub>SiH, MeOH, 23 °C NHTFA 2. NBS, THF, –78-

OMe

Successful assembly of tertiary sulfide and [3.3.1] bicyclic core

Pd(dba)<sub>2</sub> (15 mol %), XPhos (25 mol %), K<sub>2</sub>CO<sub>3</sub>, dioxane, 100 °C;

then NaOH, CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O, 23 °C; then TsCl, DMAP, Py,

71% yield [multi-gram scale] [single purification]

· Full carbon skeleton of aleutianamine established

unstable

TsCI, Py

CH2Cl2, 23 °C

Thiophene Dearomatization

12

15

 $Pd(dba)_2$  (15 mol %) XPhos (25 mol %),  $K_2CO_3$ 

dioxane, 100 °C

60% yield

10

30

Shirakawa Hayashi's triflate-halogen exchange

reductive amination OMe Yang method

10

18

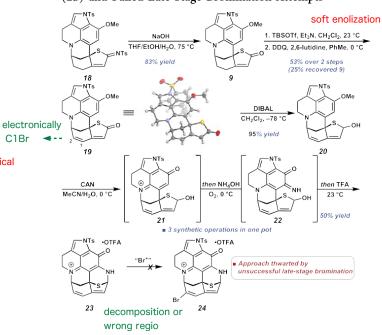
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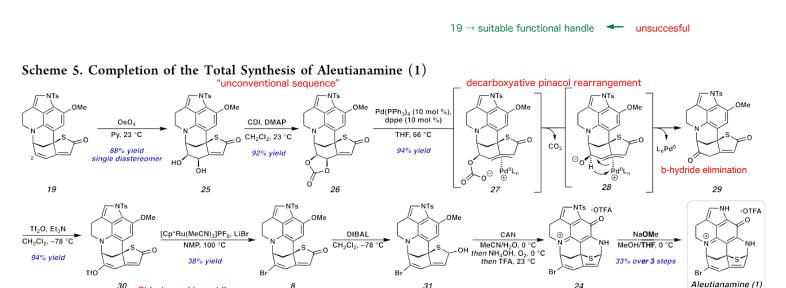
unique thiophene dearomatization Aleutianamine

pyrroloiminoquinone natural product palladium-catalyzed dearomative thiophene functionalization decarboxylative pinacol-type rearrangement of allylic carbonate oxidative amination

nonbiomimetic synthetic approach

## Scheme 4. Synthesis of N-Tosyl des-Bromoaleutianamine (23) and Failed Late-Stage Bromination Attempts





31

critical

24