Recent Highlights from the Danishefsky Laboratory

11-0-Debenzoyltashironin

Phalarine

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11-0-Debenzoyltashironin
Background and Structural Features

- Isolated from the pericaps of *Illicium merrillianum*
- Shown to induce neurite outgrowth in fetal rat cortical neurons at low concentrations
- 7 contiguous stereocenters, 3 all carbon quarternary centers
Synthetic Strategy

Believed that the cyclization didn’t occur because of the electronic and steric constraints that the mesyl enol ether imposed.

Synthetic Strategy

Dearomatization

Oxidative

Transannular
Diels-Alder

Wrong epimer!

Synthetic Strategy
Synthesis of the Aryl Bromide

1. Zn(CN)$_2$, HCl (99 %)
2. TsCl (57 %)
3. BnBr, $K_2$CO$_3$, TBAI (97 %)

1. mCPBA
2. TEA
98 % for 2 steps

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Synthesis of the Oxidative Dearomatization Precursor

Oxidative Dearomitization, Transannular Diels-Alder

End Game

Phalarine

• Isolated from the *phalris coerulescens*, characterized in 1999

• Furanobisindole alkaloid

• First synthesis reported by Danishefsky
Synthetic Strategy

The model system gave the opposite of what was desired!

Azaspiroindolenine synthesis

Two Mechanistic Possibilities

Path A
1, 2 Wagner-Meerwein Shift

Path B
Retro-Mannich

Pictet-Spengler

Attempted Completion

Attempted Completion

1. NaNO₂, HCl (aq)
2. KOH (aq), EtCOO

TsOH

< 5% desired product
End Game

End Game