

# Synthesis, Isolation, and Reactivities of N-Sulfonyl Aza-Breslow Intermediates Using Polyfluorinated NHC



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## Introduction

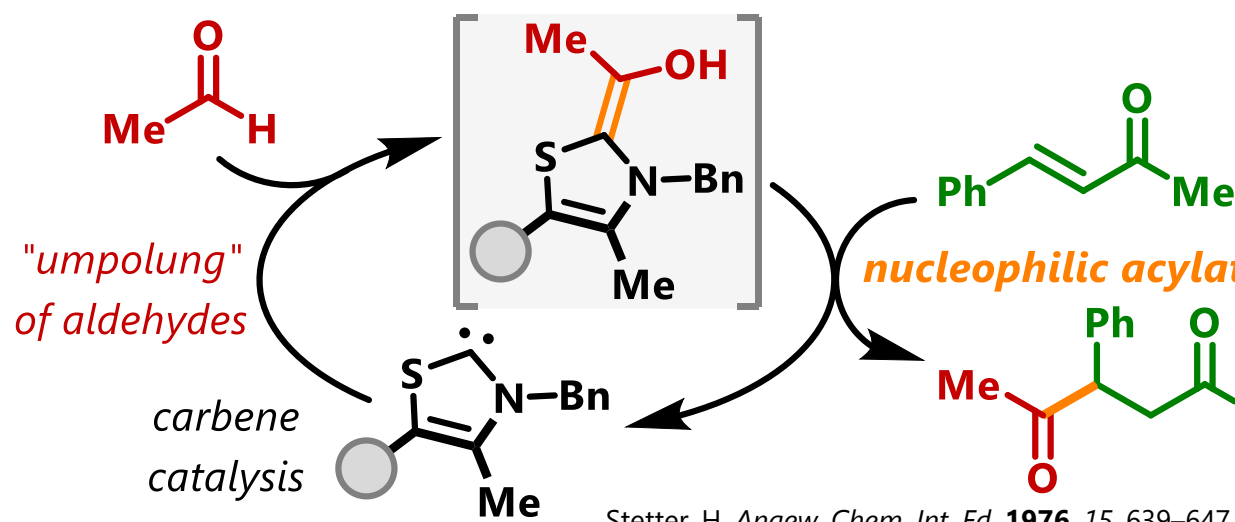
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### Breslow Intermediates

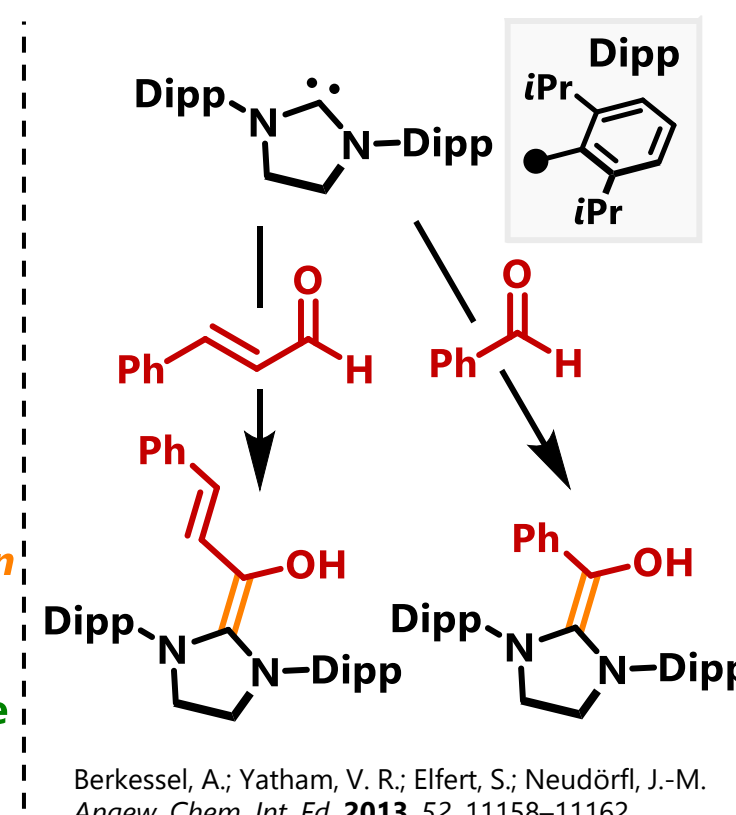
#### ◆ Extensive research and applications

290 Hits in SciFinder with "Breslow intermediate"

#### Stetter Reaction Breslow intermediate



#### ◆ Isolated Breslow Intermediates

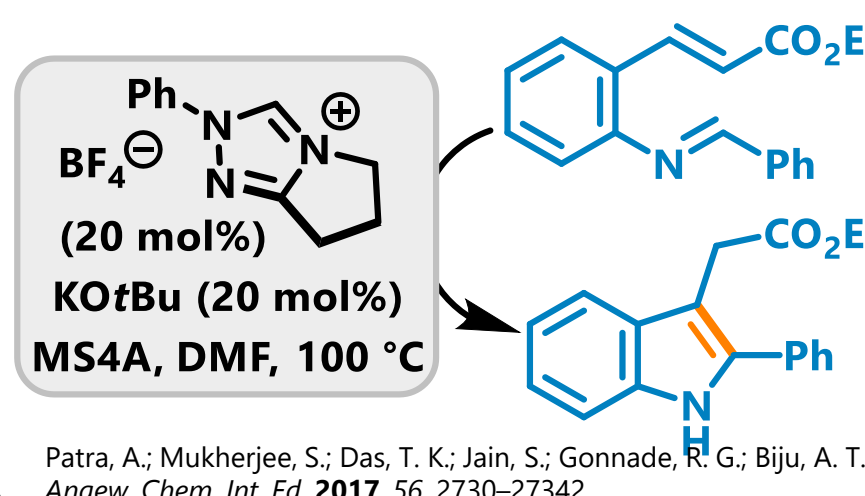


### Aza-Breslow Intermediates (ABI)

#### ◆ Growing research field

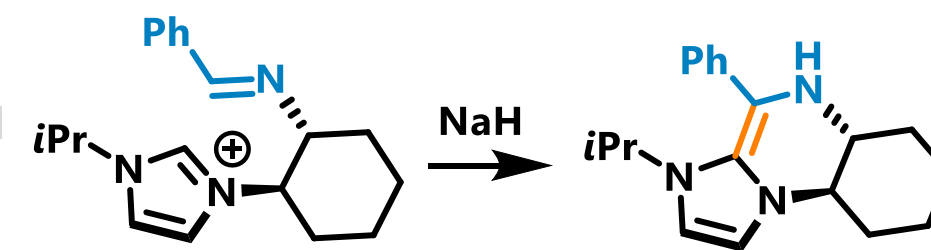
16 hits in SciFinder with "Aza-Breslow intermediate" keywords.

#### First Carbene Catalysis via Imine "Umpolung"

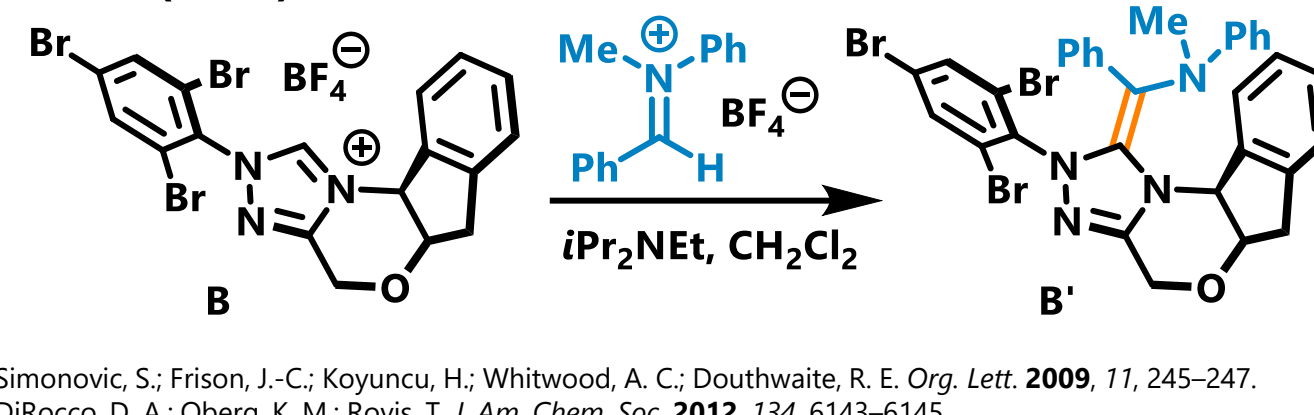


#### ◆ Isolated ABIs

Douthwaite (2009)



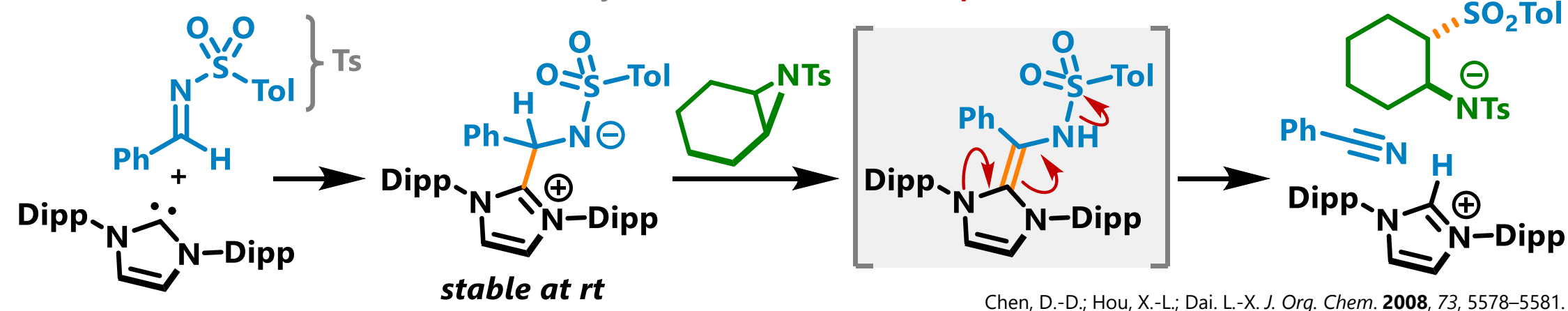
Rovis (2012)



### N-Sulfonyl ABIs

- ◆ Low basicity of N<sup>-</sup>
- ◆ Low acidity of CH

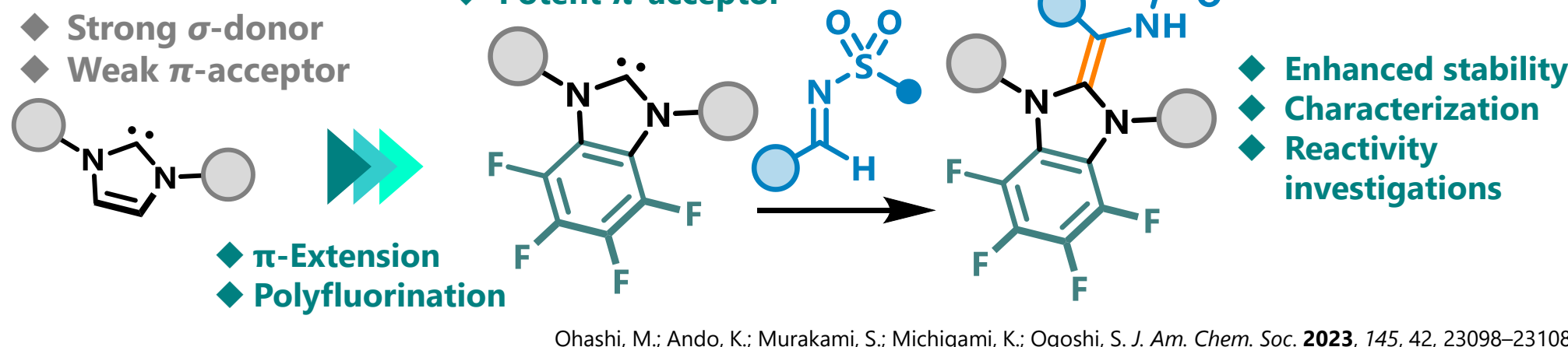
- ◆ Irreversible N-S bond cleavage
- ◆ No example for its detection



### This Work

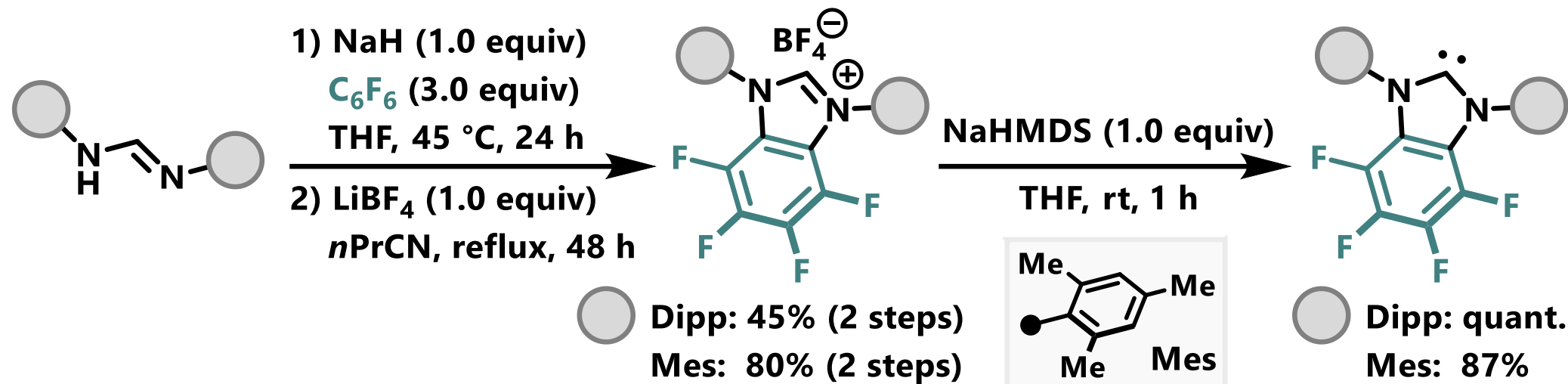
- ◆ Strong  $\sigma$ -donor
- ◆ Weak  $\pi$ -acceptor

- ◆ Mild  $\sigma$ -donor
- ◆ Potent  $\pi$ -acceptor



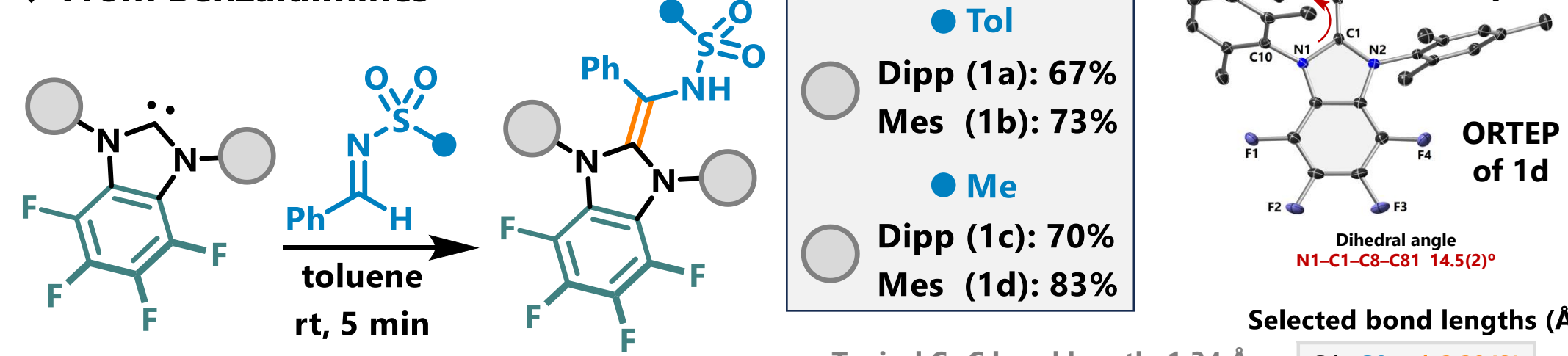
## Results and Discussion

### Synthesis of Polyfluorinated NHCs



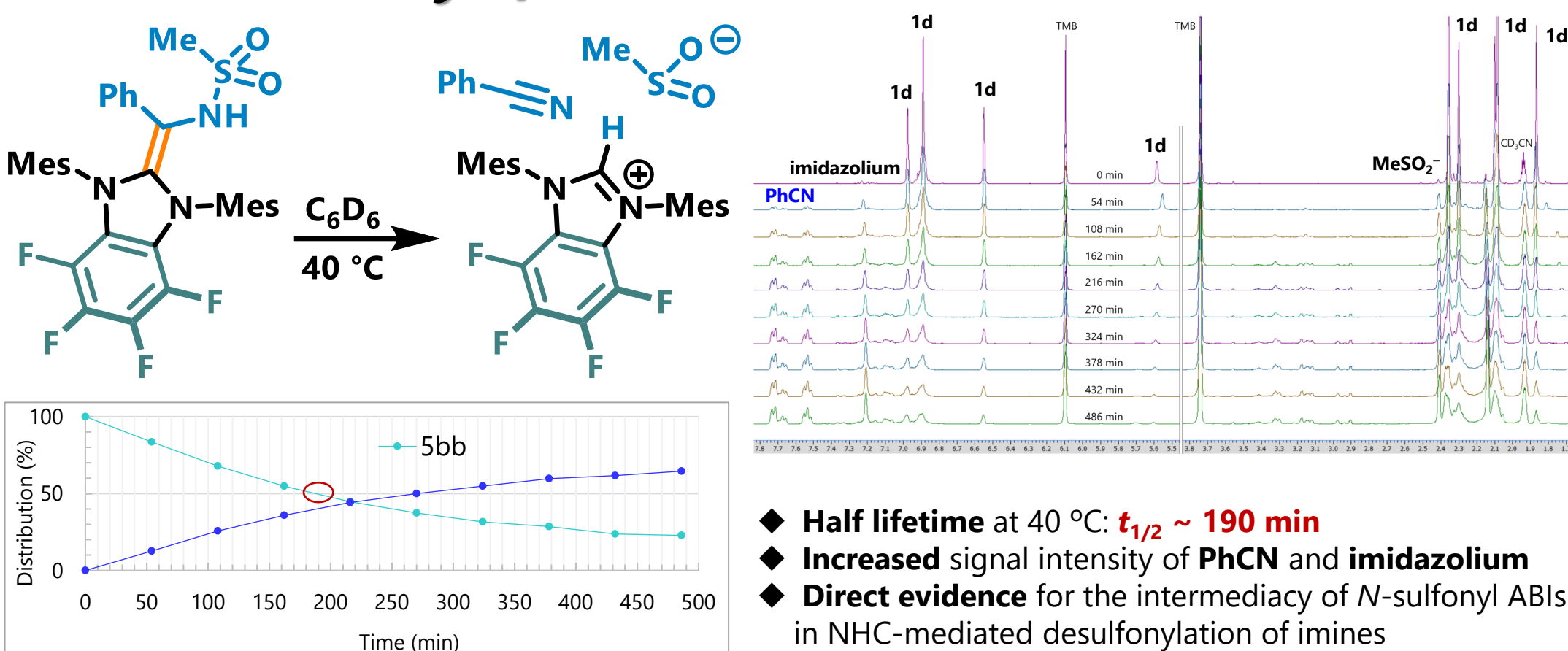
### Synthesis and Isolation of N-Sulfonyl ABIs

#### ◆ From Benzaldimines



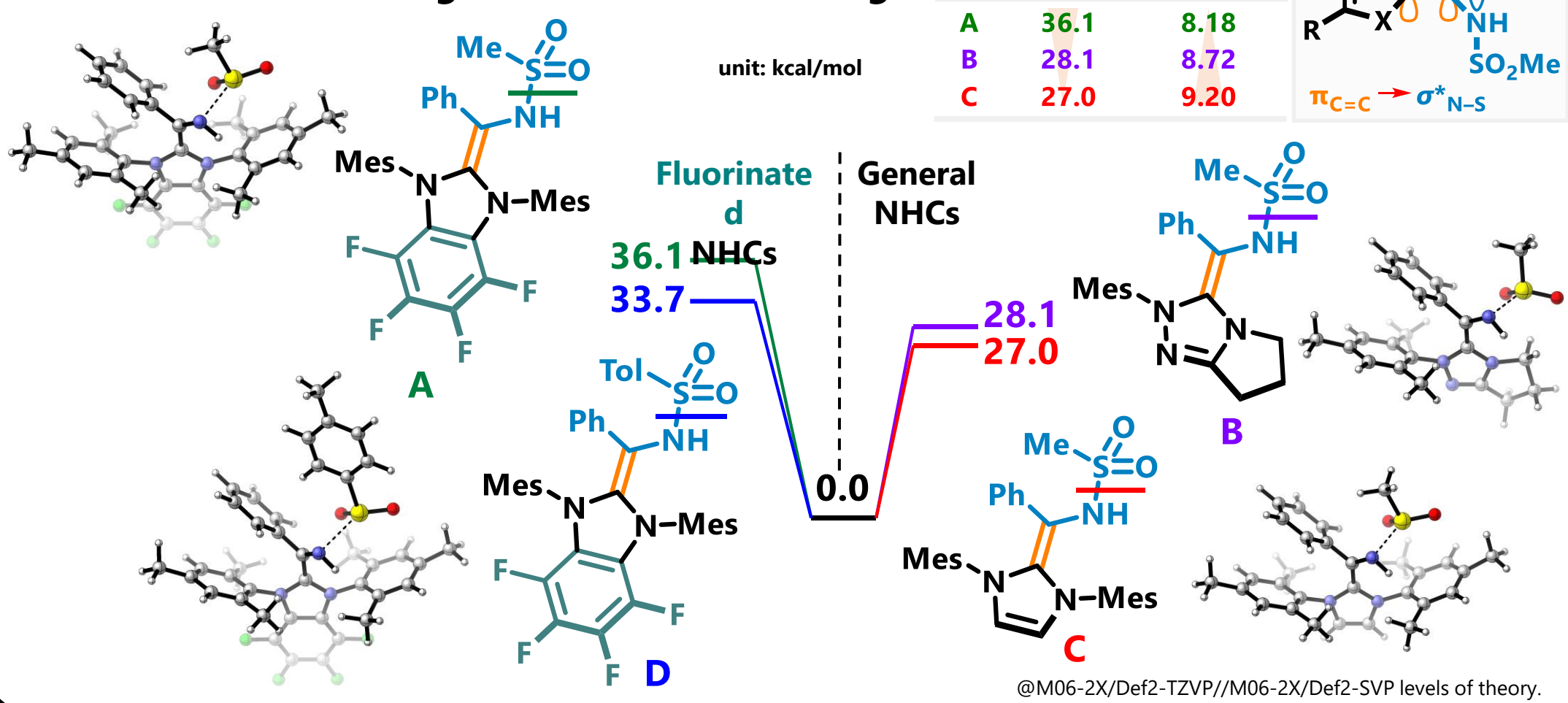
### Thermal Stability of 1d

#### ◆ <sup>1</sup>H NMR time profile

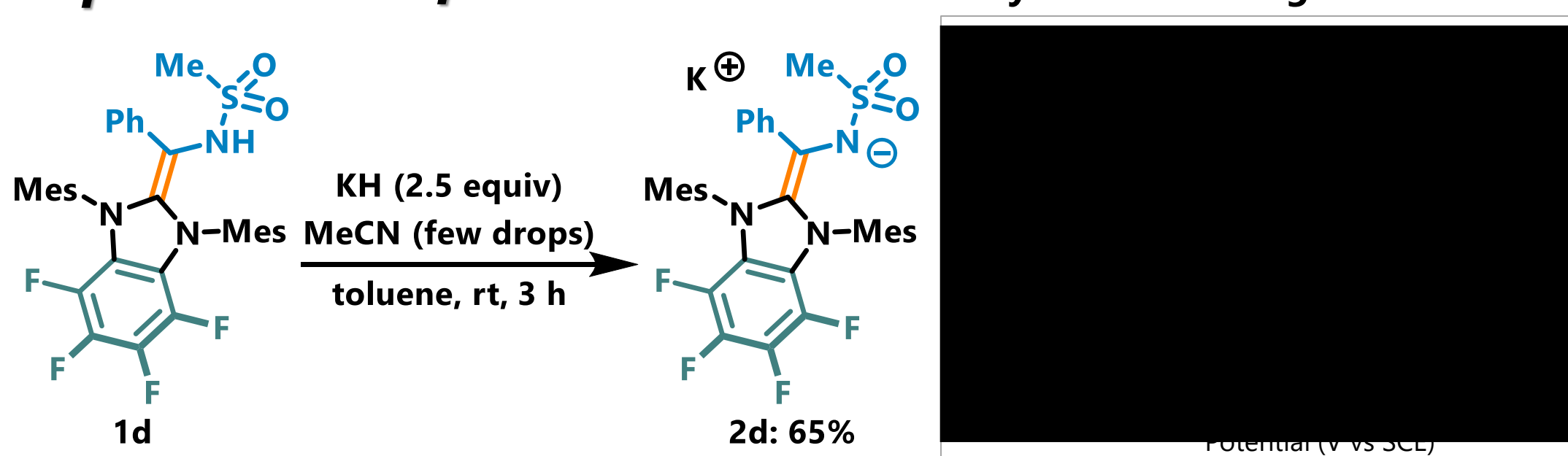


### DFT Calculations

#### ◆ Transition state energies of N-S bond cleavage



### Deprotonation of ABI



#### ◆ Cyclic Voltammogram of 2d

