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# Simple Arenes as Aryne Synthetic Equivalents via Sulfonium Salt Intermediates

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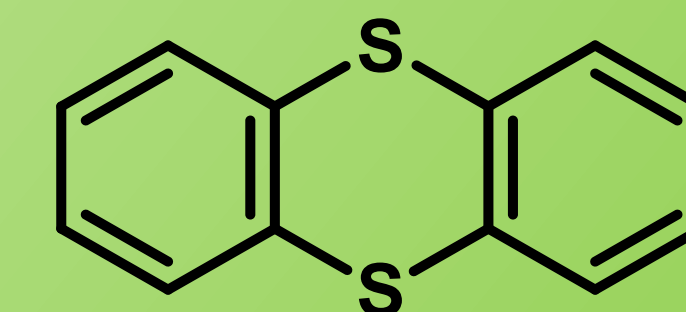
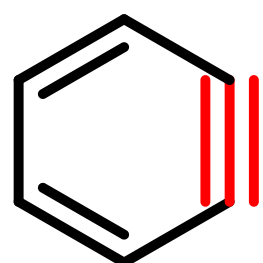
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# Simple Arenes as Aryne Synthetic Equivalents via Sulfonium Salt Intermediates

Riley A. Roberts ([rar7@pdx.edu](mailto:rar7@pdx.edu)), Bryan Metze, David R. Stuart

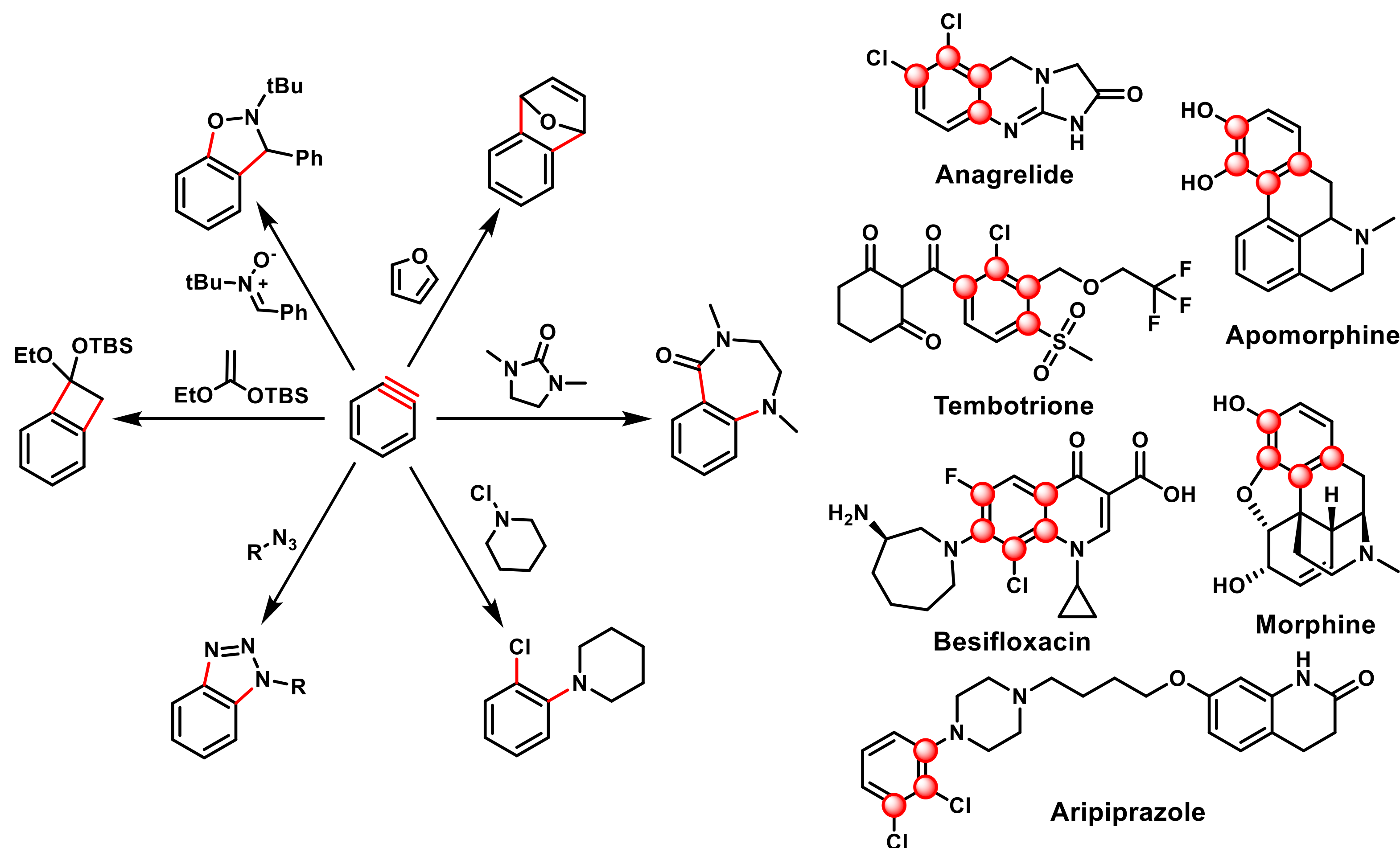
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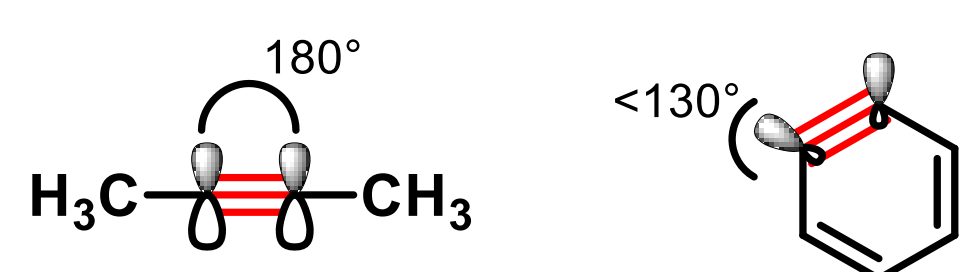
## Background:

- Arynes are extremely reactive molecules that are under utilized in organic synthesis due to their difficulty to access
- Densely functionalized benzenoid substitution patterns are challenging to access through conventional chemistry

### Reactions and pharmaceuticals accessible through arynes



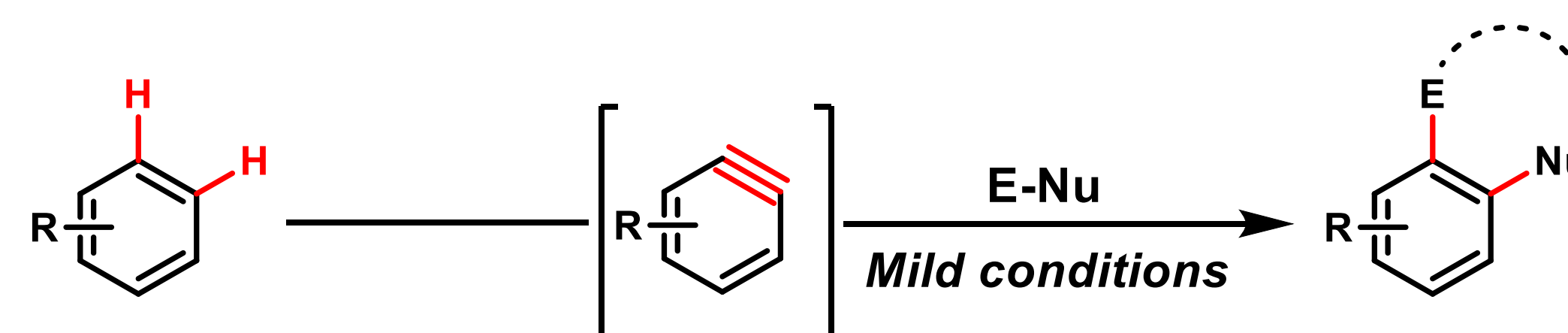
### Aryne reactivity



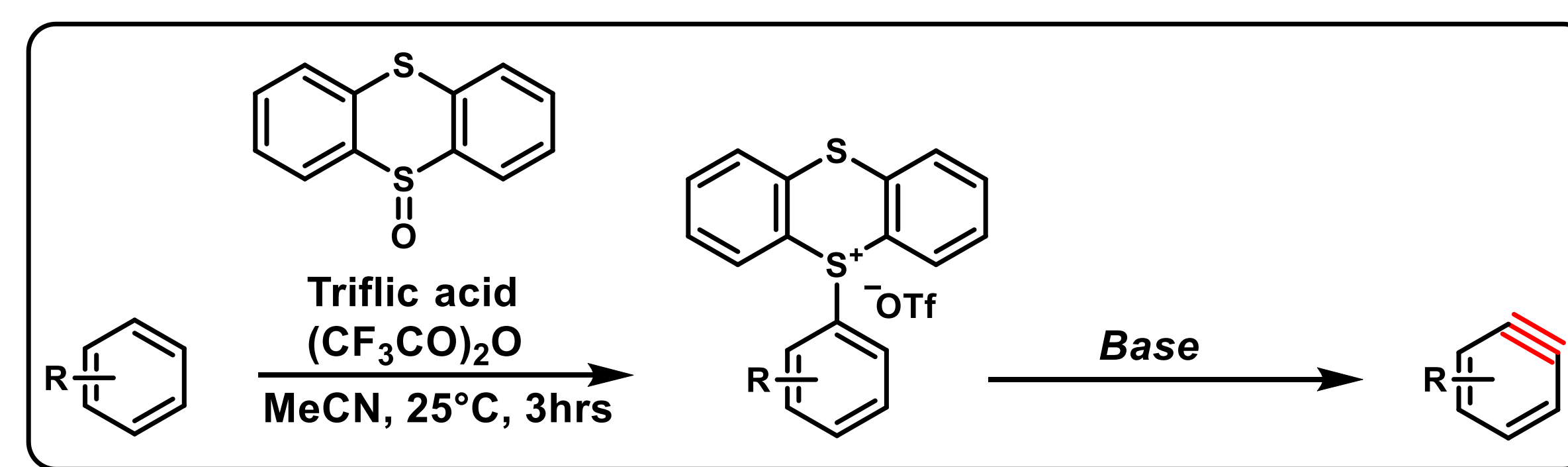
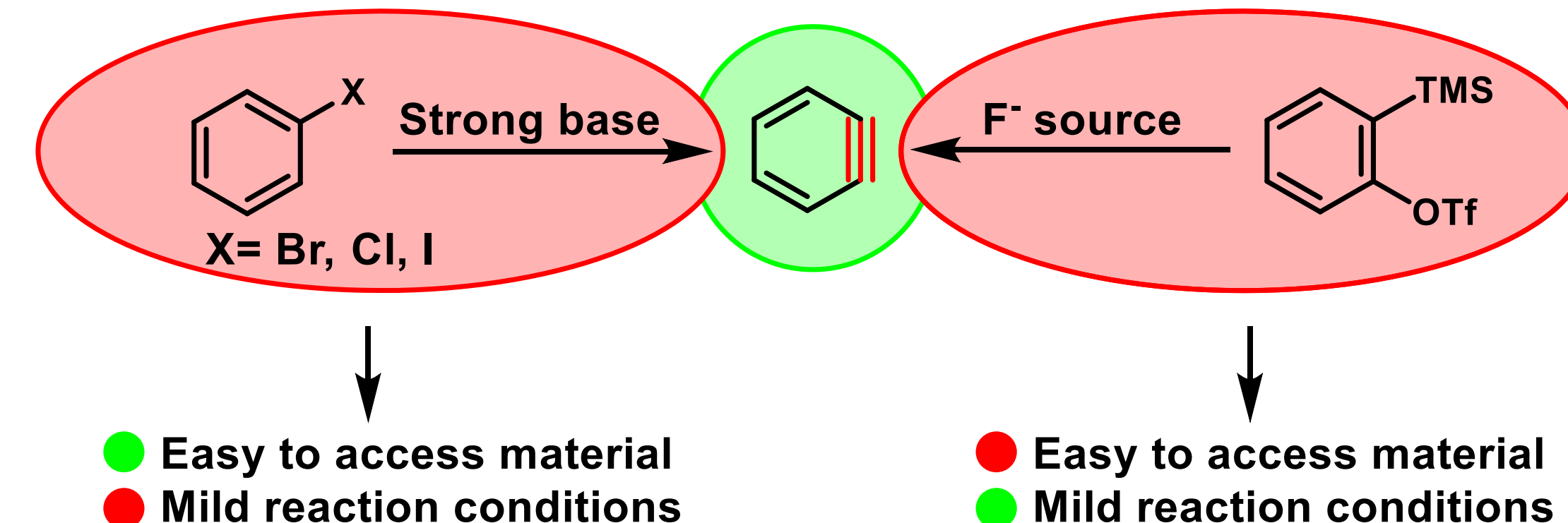
- Unlike most triple C-C triple bonds, arynes are highly strained and thus, highly reactive

## Goal:

Produce a method for generating arynes from simple arenes that is both mild and efficient

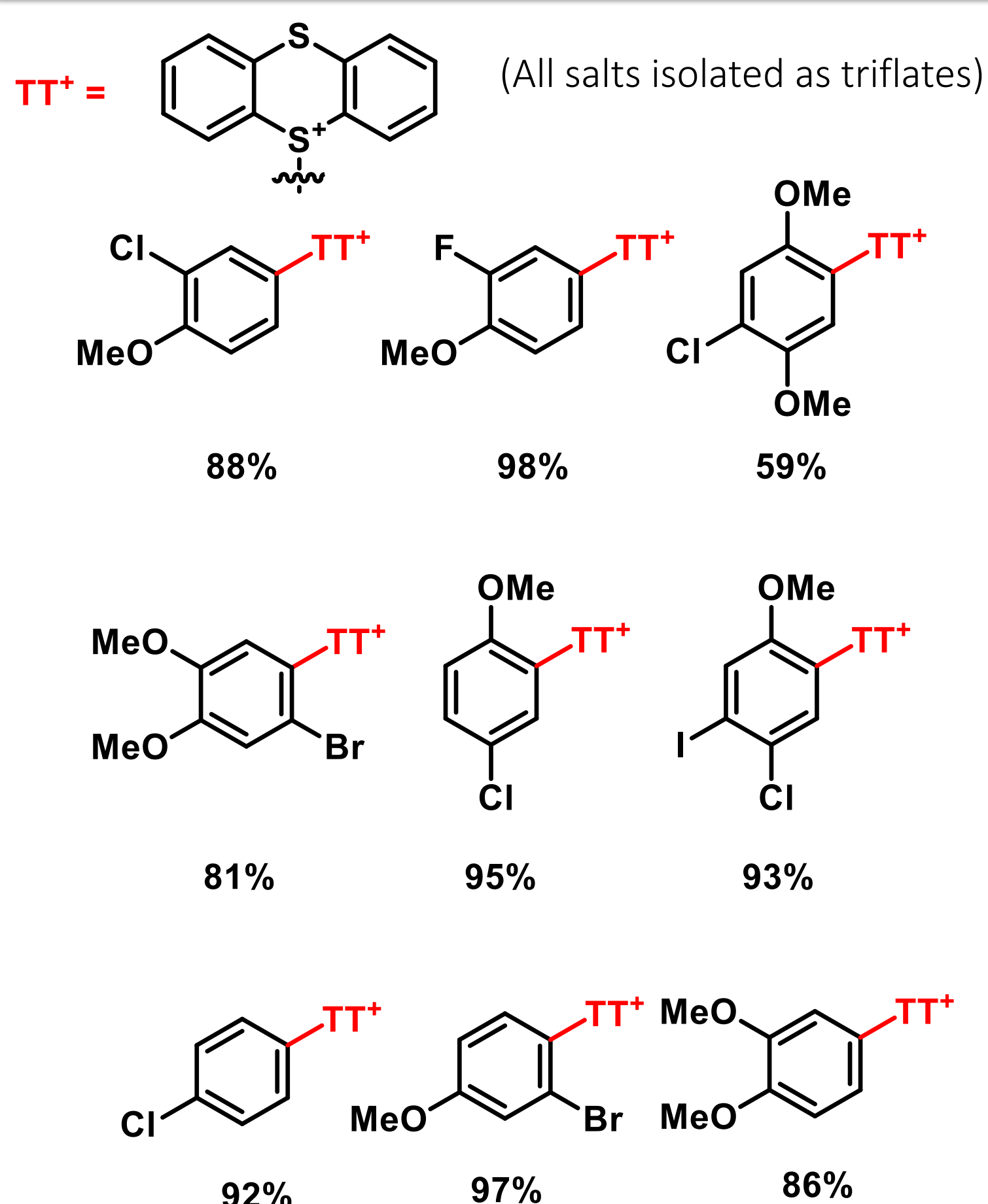


- Current methods for generating arynes requires either harsh conditions or difficult-to-access precursors

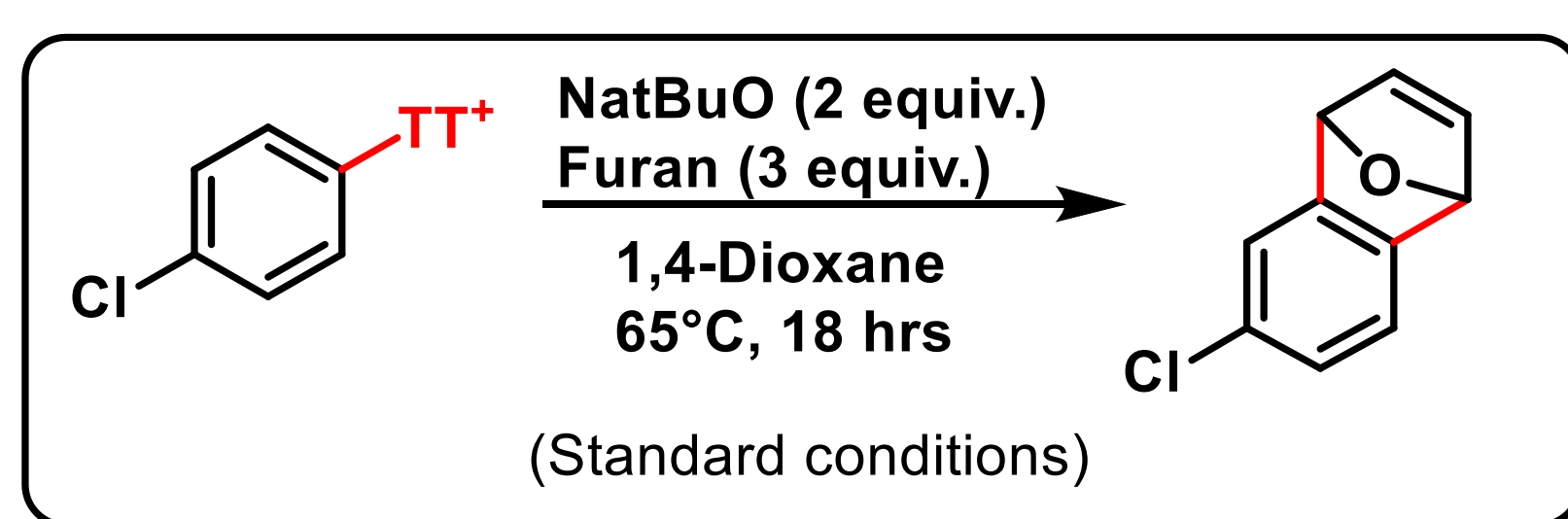


- Utilize literature methods to produce thianthrenium salt aryne precursors without chromatography<sup>1</sup>
- Optimize reaction conditions to produce arynes under basic conditions<sup>2</sup>

## Thianthrenium salt scope and reactivity:

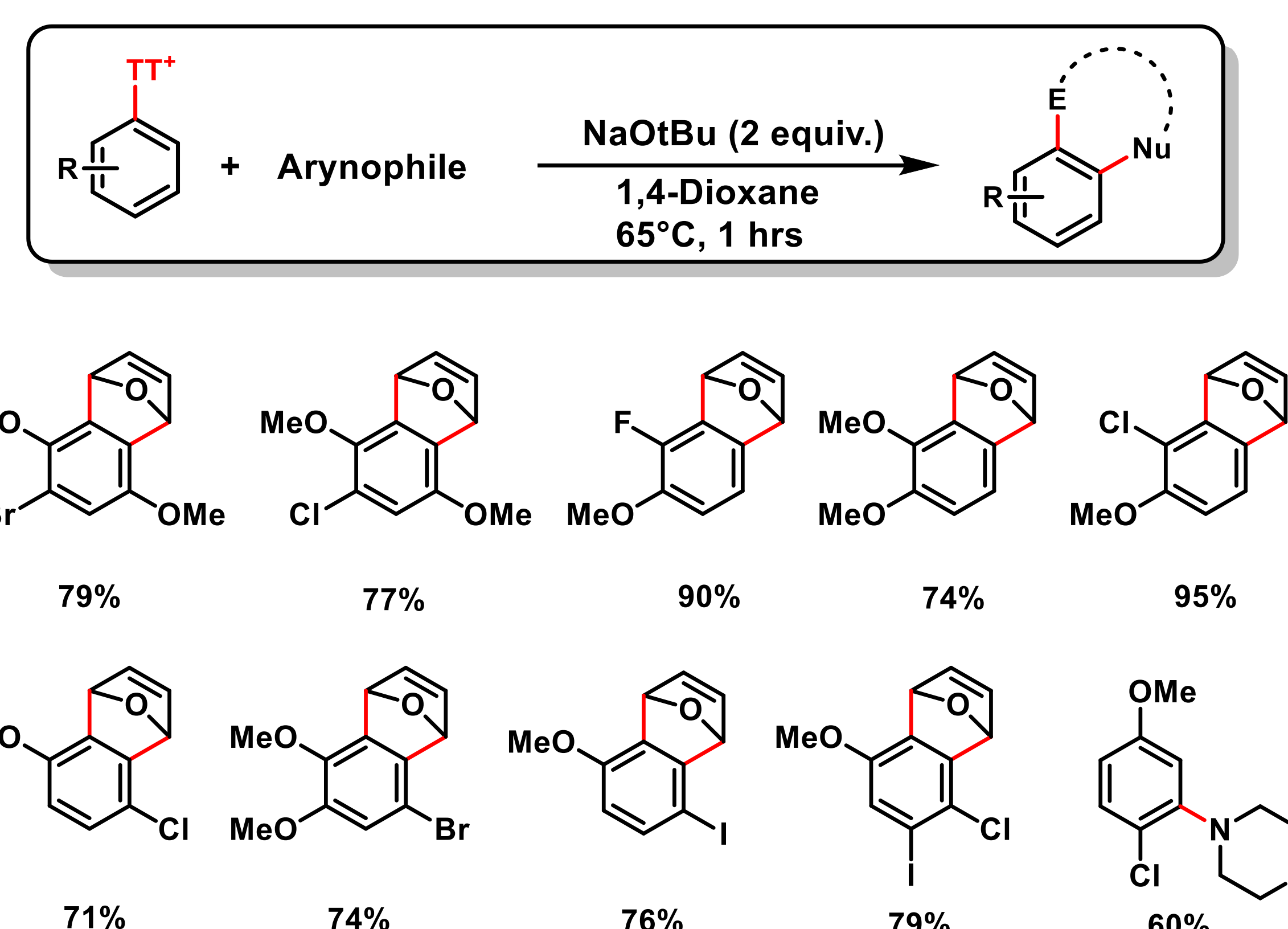


## Thianthrenium salt aryne reaction optimization



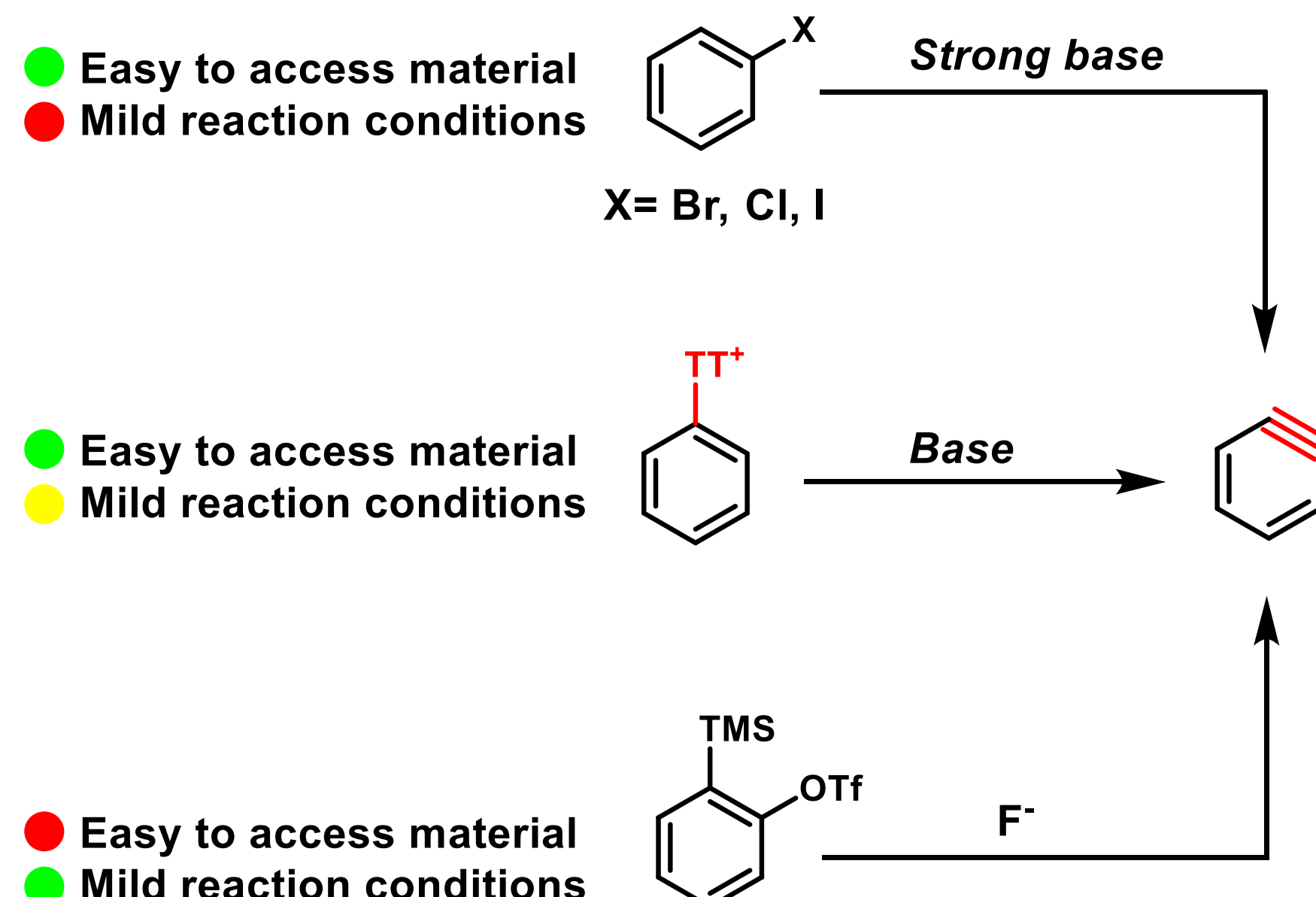
Entry	Deviation from standard conditions	Yield
1	None	62%
2	25°C reaction temp.	63%
3	1 equiv. NaOtBu	55%
4	5 equiv. furan	64%
5	THF as solvent	66%
6	2-Me-THF as solvent	73%
7	15 min. reaction time	62%

## Thianthrenium salt aryne reaction scope



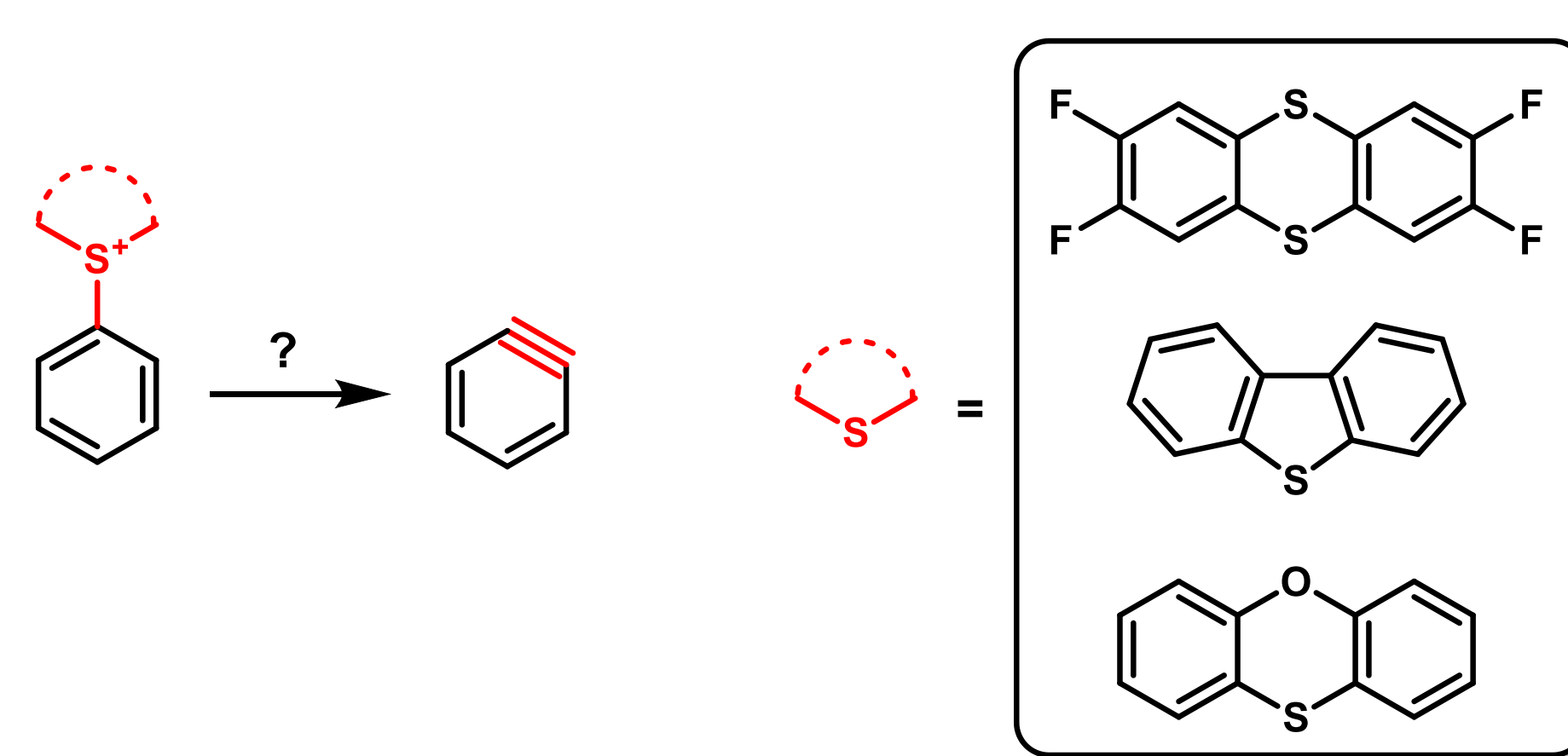
## Conclusions:

- Thianthrenium salts can be accessed quickly and efficiently from electron rich arenes without chromatography
- Salts can be treated with base to generate arynes in good yields



- Conditions for generating arynes from thianthrenium salts are milder than early aryne precursors but more can be done to further increase functional group compatibility

## Future Direction:



- Arynes can be used to functionalize vicinal carbon
- Determine the impact on salt reactivity using a variety of sulfur heterocycles

### References:

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- Kim, K. S.; Ha, S. M.; Kim, J. Y.; Kim, K. J. *Org. Chem.* **1999**, 64, 6483–6486.
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