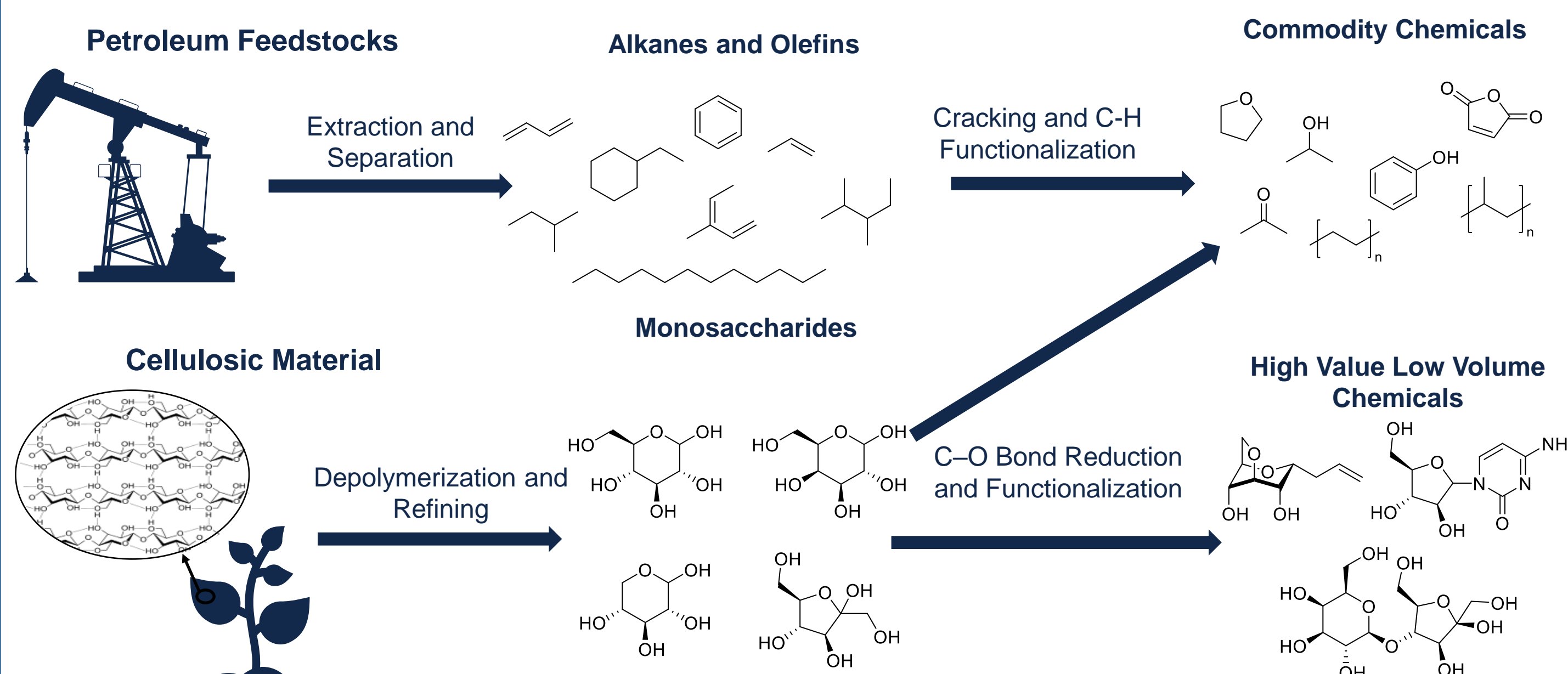
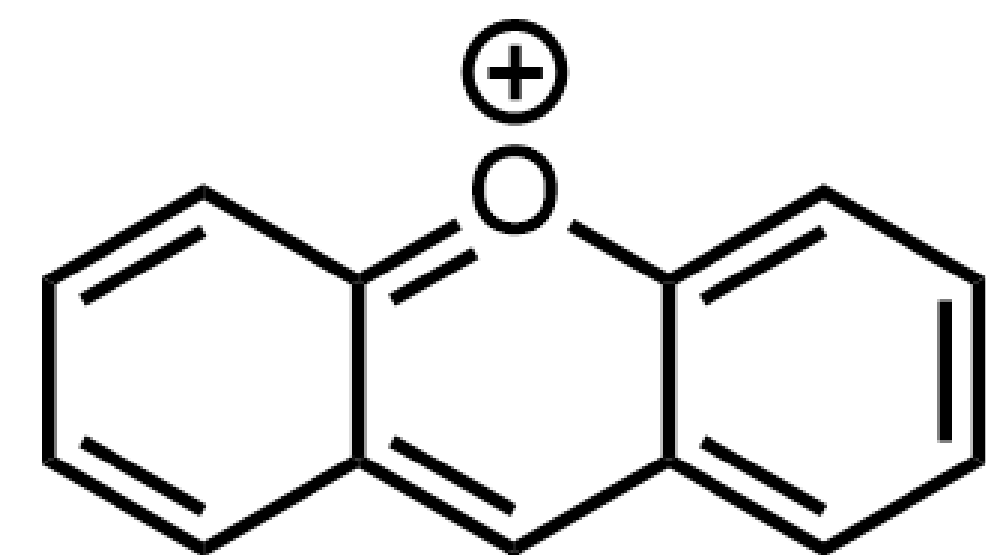
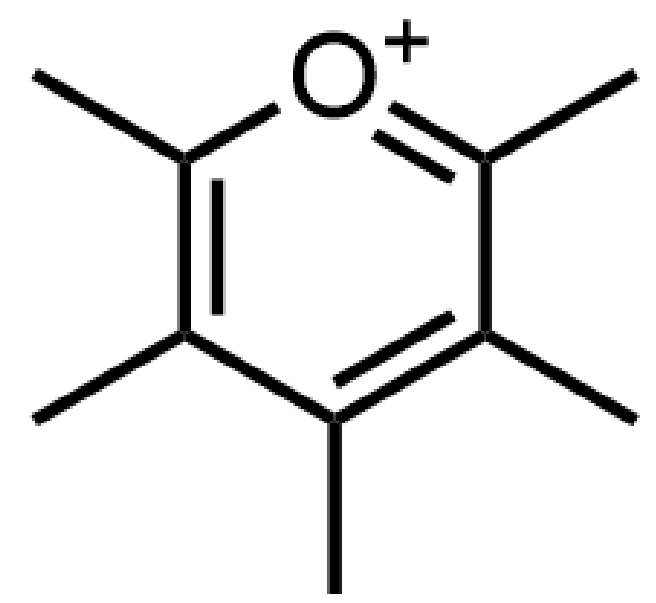


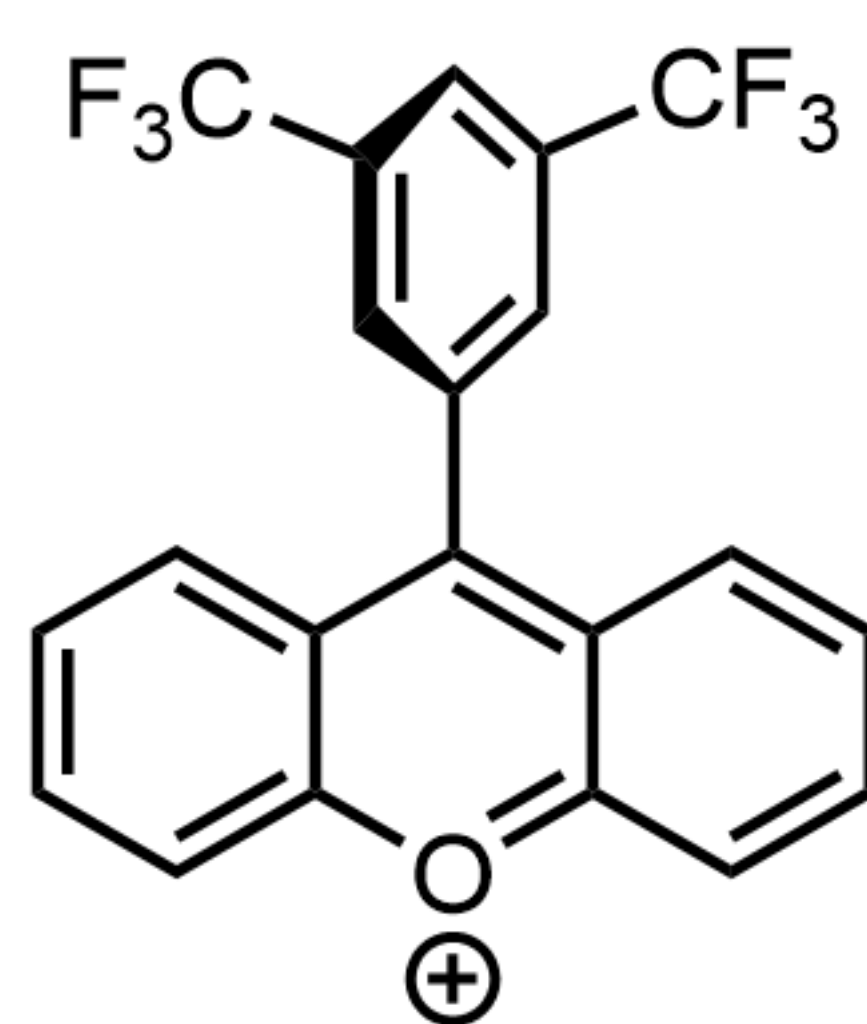
Background



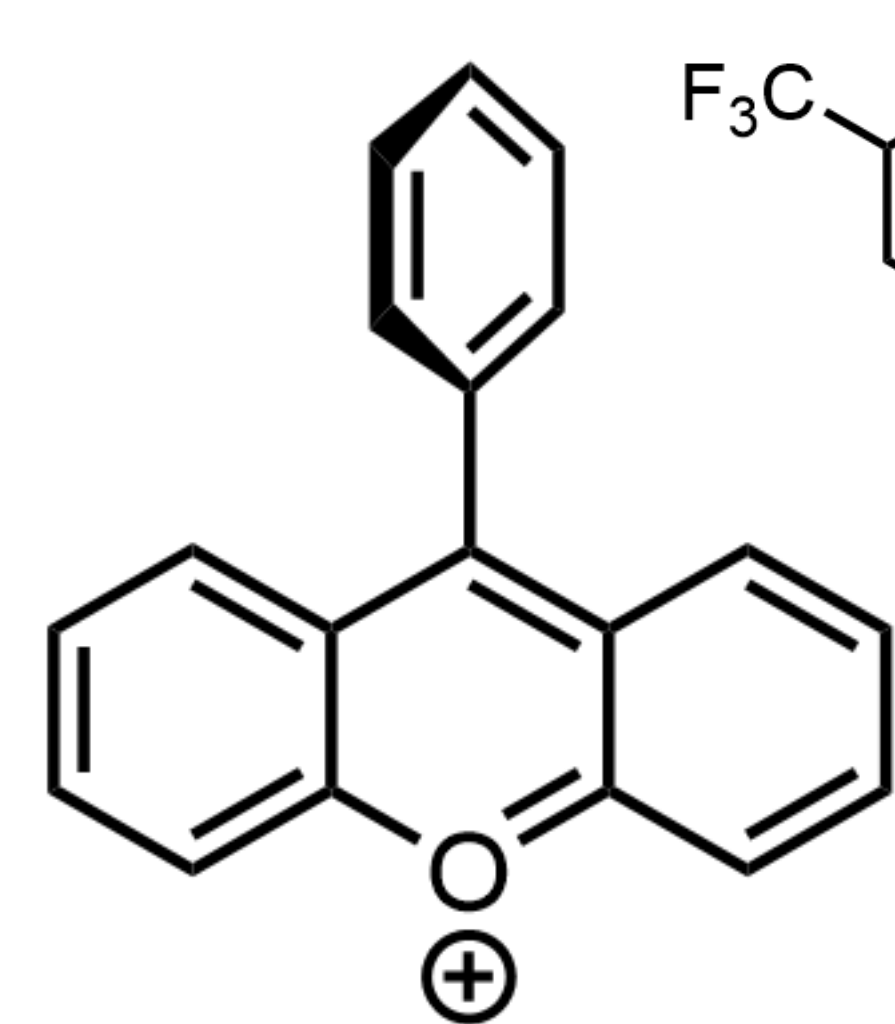
Piryliums and Xanthyliums



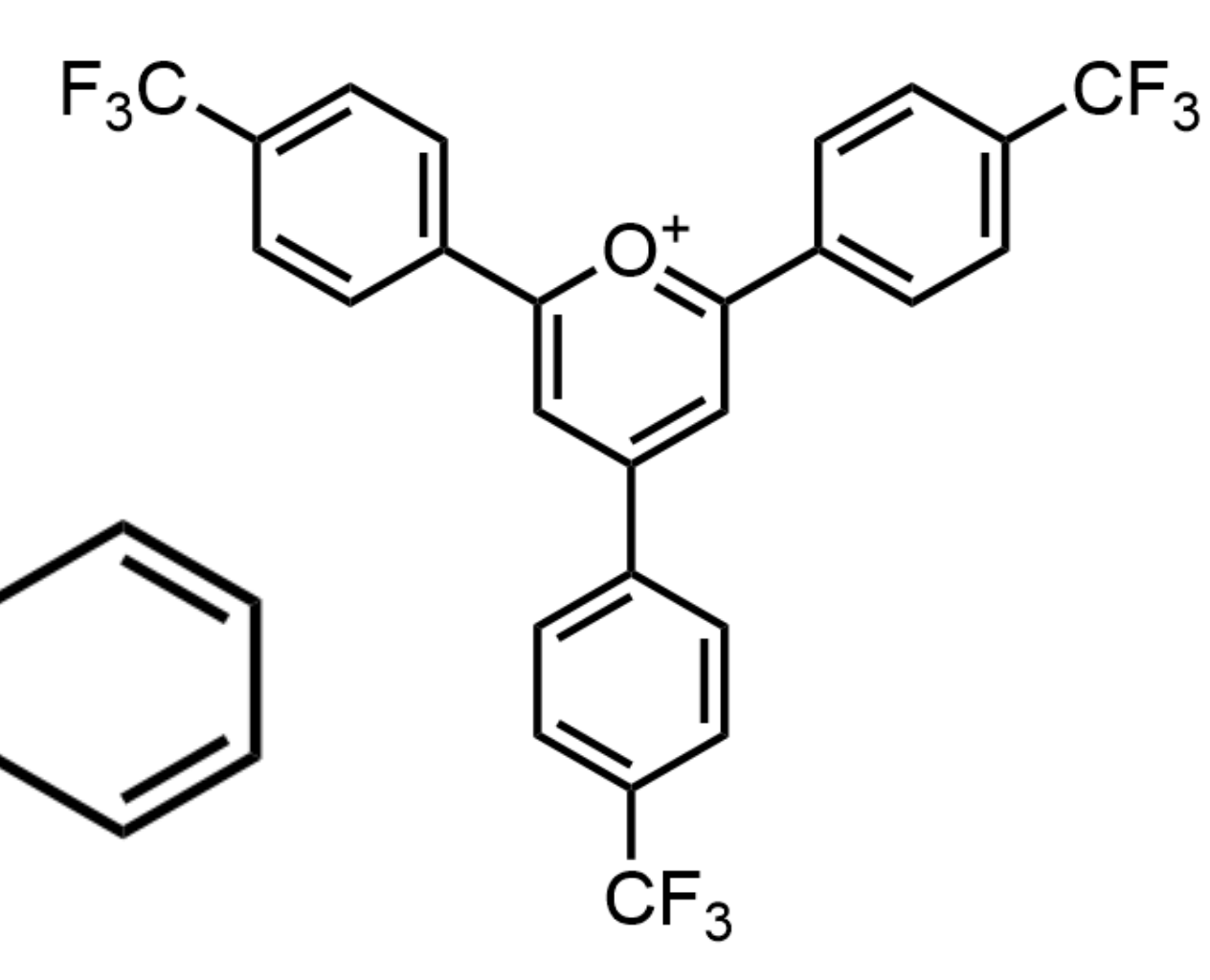
- Lots of pyrliums!
- How can we find faster thermal catalysts?
- Fine tuning to specific reactions
- Tools to help predict reactivity
- Hydricity alone isn't a great indicator
- Turn to mechanism and kinetics
- Hydride transfer/Initial adduct formation
- Rate determining step/Preferred pathway



9-(3,5-trifluoromethyl)phenylxanthylium

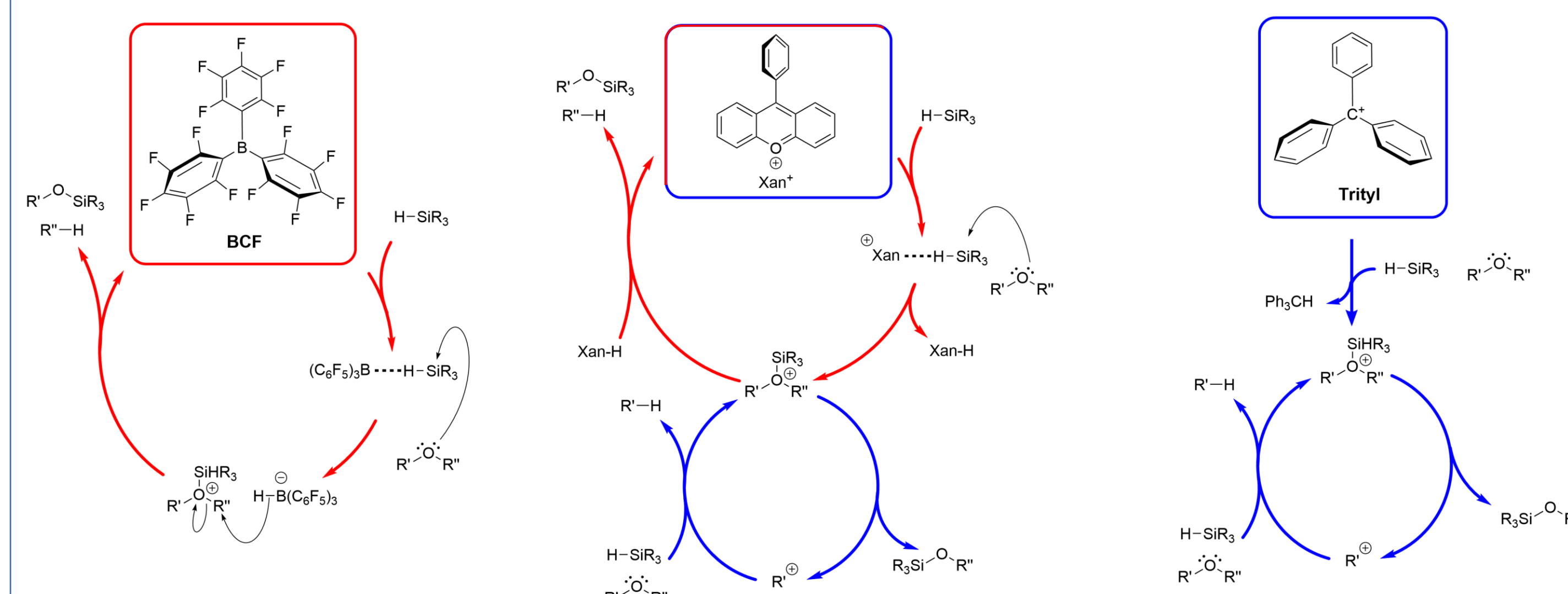


9-phenylxanthylium



2,4,6-tris(trifluoromethyl)phenylpyrylium

Proposed Mechanism



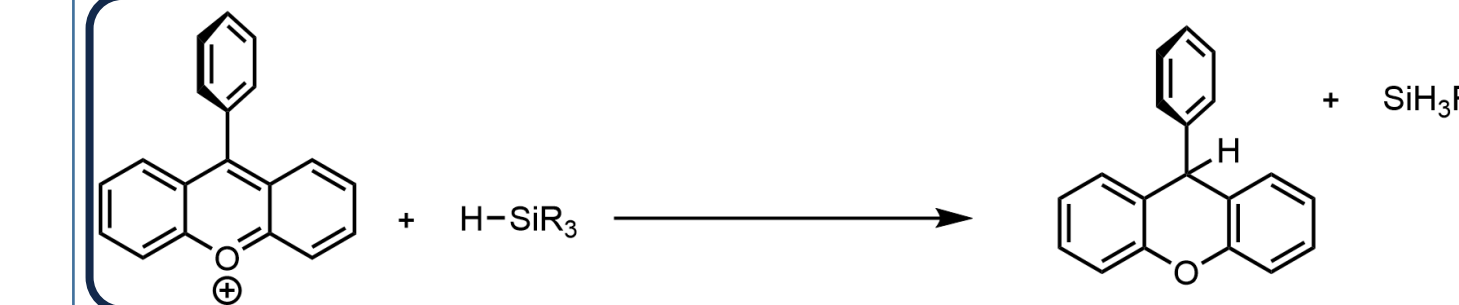
Based on preliminary kinetics for 9-phenylxanthylium.

2 parts:

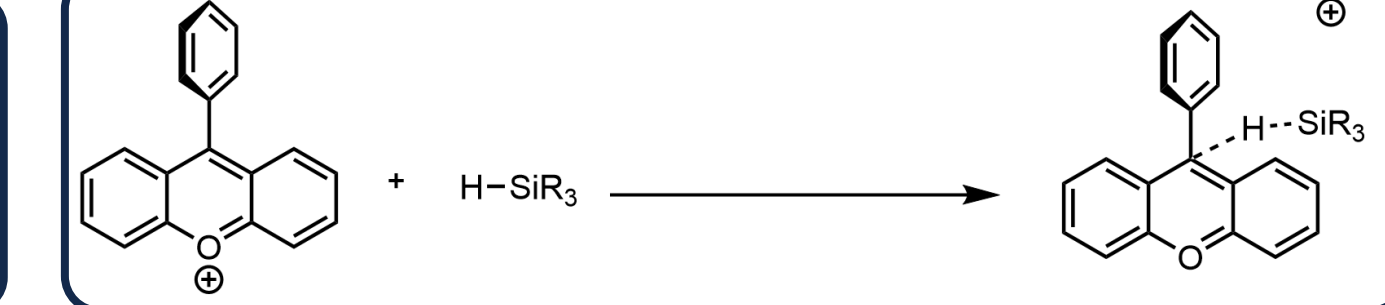
- 1) BCF-like mechanism
 - Catalyst regenerated with each turn
 - Accepts and donates hydride
- 2) Silylium driven catalysis
 - Similar to trityl mechanism
 - Catalyst accepts hydride to initialize catalytic cycle

Silane-Catalyst Adduct Formation

Hydride transfer:



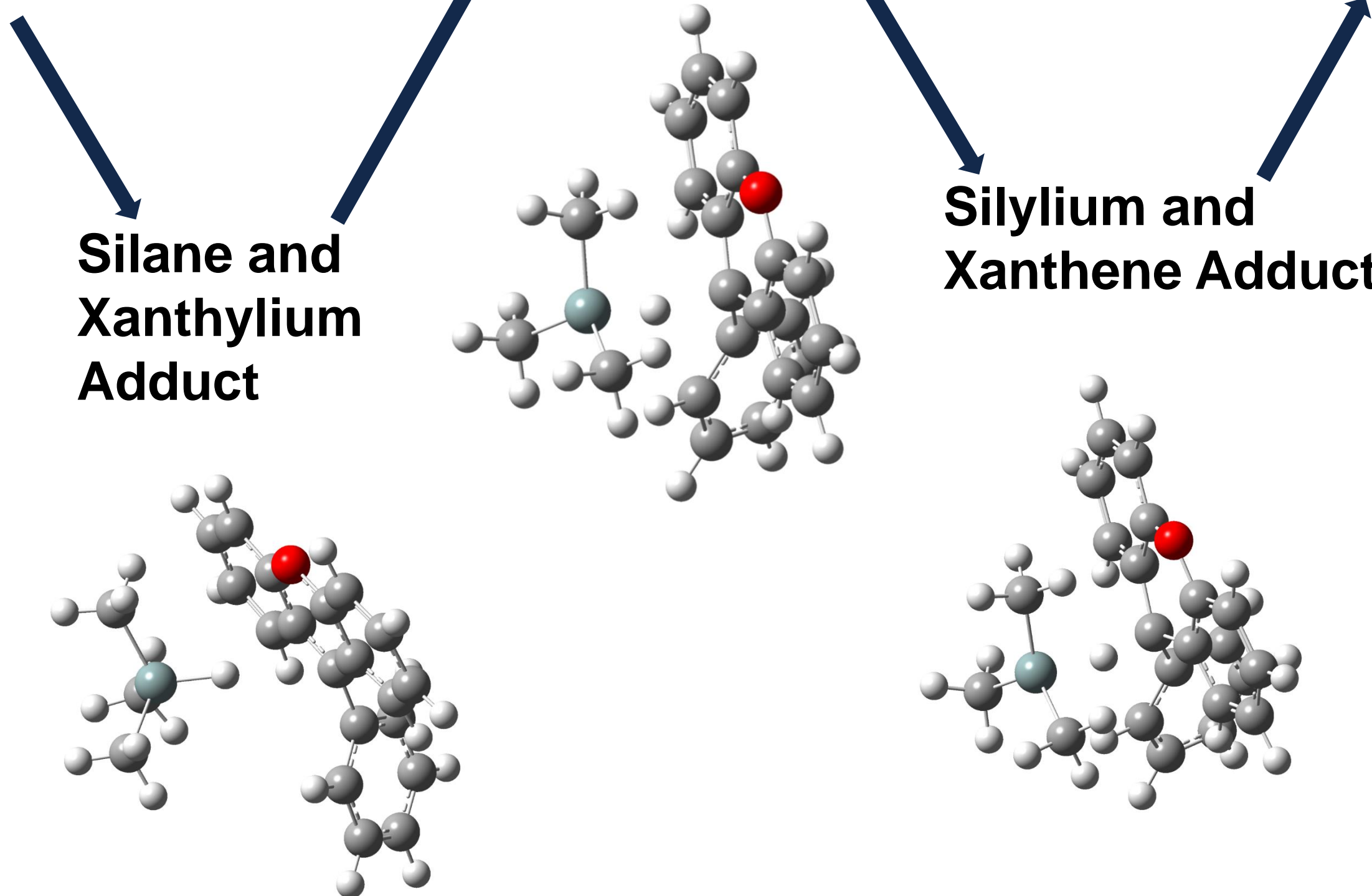
Adduct formation:



Silane and Xanthylium

Hydride Transfer

Silylium and Xanthenone



- Silane and xanthylium come together as an adduct to facilitate hydride transfer
- First step of the proposed mechanism
- Piryliums may not form silylium and pyran adducts after hydride transfer

References

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Special thanks to Will Hearne, Dr. Michel Gagné, Dr. Kevin Baseman and Dr. Shubin Liu!

