

Synthesis of Inorganic N-Heterocyclic Carbene Derivatives for Transition

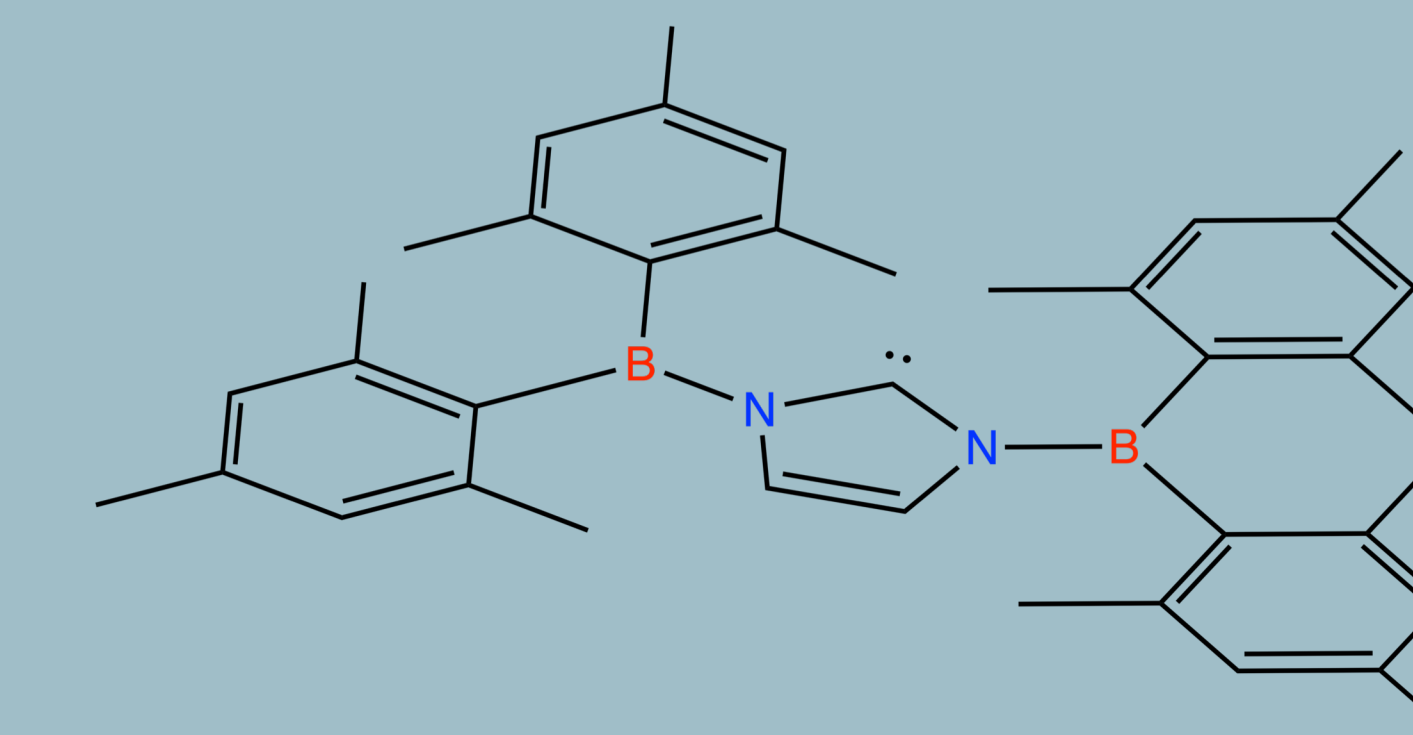


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Metal Catalysis

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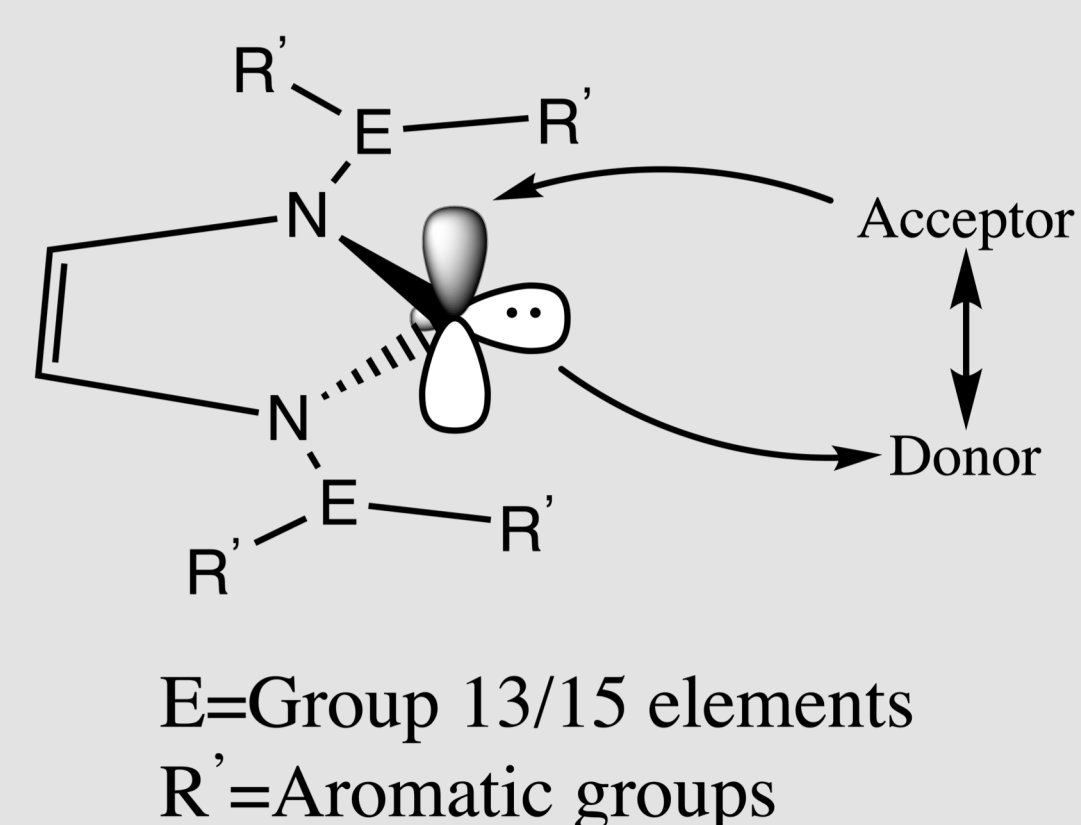


Abstract

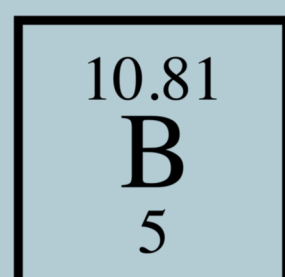
N-heterocyclic carbenes (NHCs) have drawn widespread attention due to their vastly customizable electronic and steric properties, similar to the properties of the widely used phosphine ligand, as well as their ability to act simultaneously as a Lewis acid and base. Addition of the carbene to a Lewis acid can create a frustrated Lewis acid/base pair (FLP) which shows potential for small molecule activation. Because of its empty π -orbital, as well as its tunable Lewis acidity, boron has recently been of increased interest to FLP chemists. The carbene portion of the complex is stabilized by aromatic mesityl groups bonded to the boron atoms, donating π -electrons, creating a reactive, but kinetically stable compound. Complexation with Lewis bases (LB) shows potential to form an FLP, where the electronic properties of the carbene and subsequent FLP as a whole can be tuned by the addition of one or two equivalents of fluoride anion. NHCs can also be complexed to various transition metals act as an efficient catalyst for a wide range of organic reactions. We hypothesized that diatomic hydrogen is small enough to interact with the NHC-LB FLP, splitting dihydrogen without the need for a metal center.

What is an NHC?

- NHCs contain a divalent neutral carbon center with 6 valence electrons.
- Singlet NHCs can act as a simultaneous electron pair σ -donor and π -acceptor.
- R groups can be manipulated to change the electronic properties as well as reactivity of the carbene.
- R' groups can be chosen to afford different steric properties.
 - Bulky substituent groups can be used to preferentially form FLPs.
 - Mesityl groups protect the carbene.

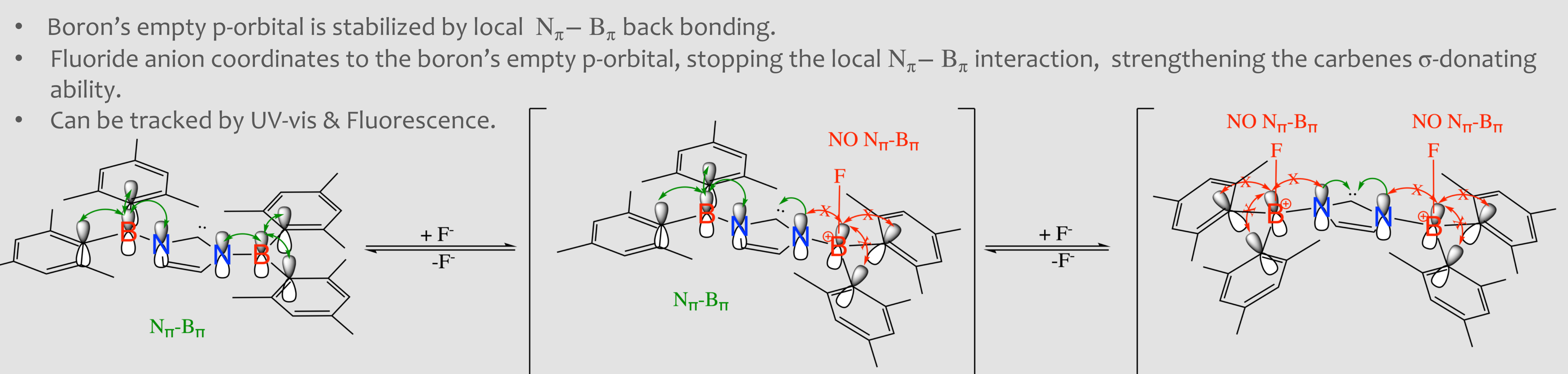


NHC Design - Why Boron?

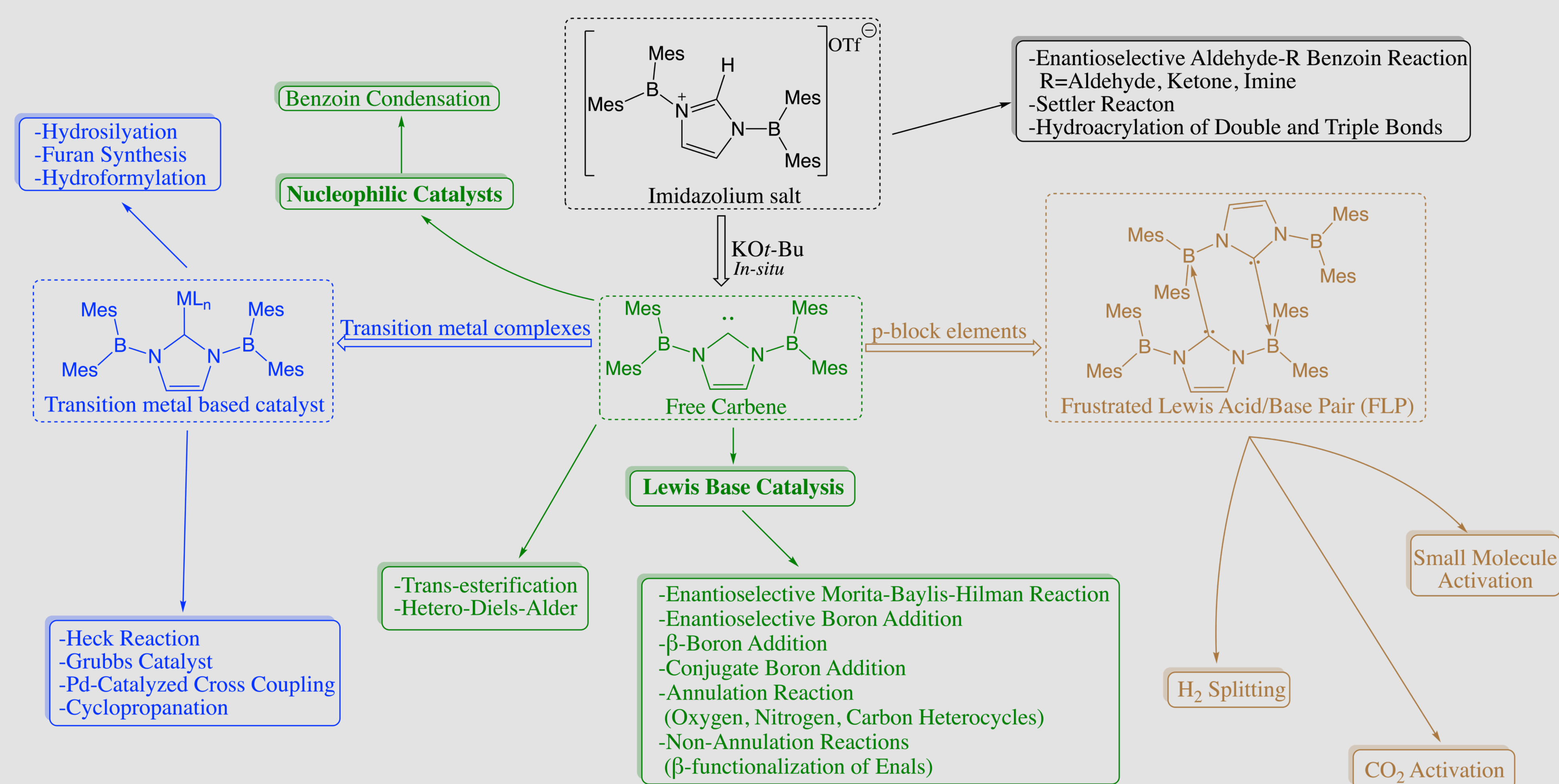


- Boron is a Group 13 element.
- Electron-deficient.
- Empty p-orbital, 3 coordinate.
- Affords weaker σ -donating ability for the overall carbene.
- Boron can extend conjugation because of its empty p-orbital.

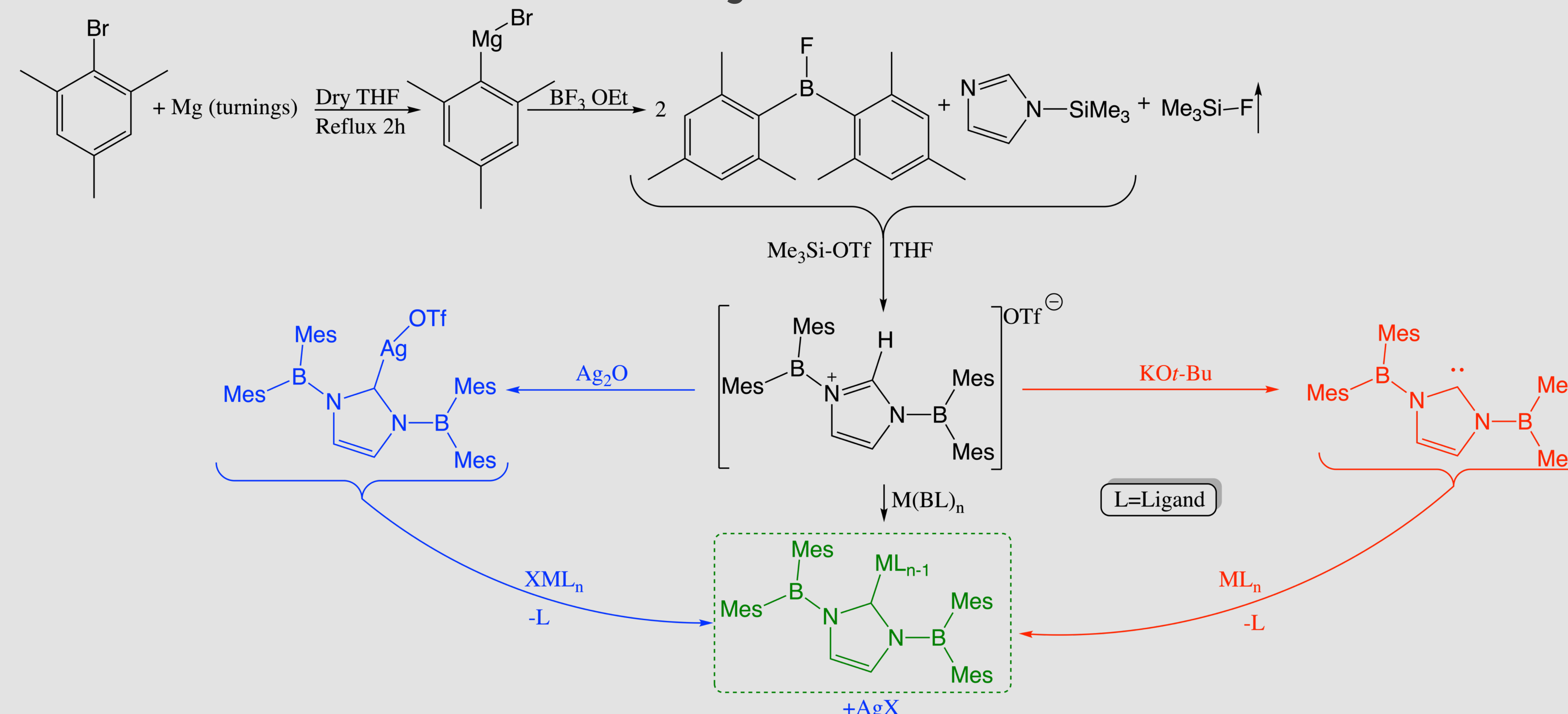
Tunable Electronic Properties



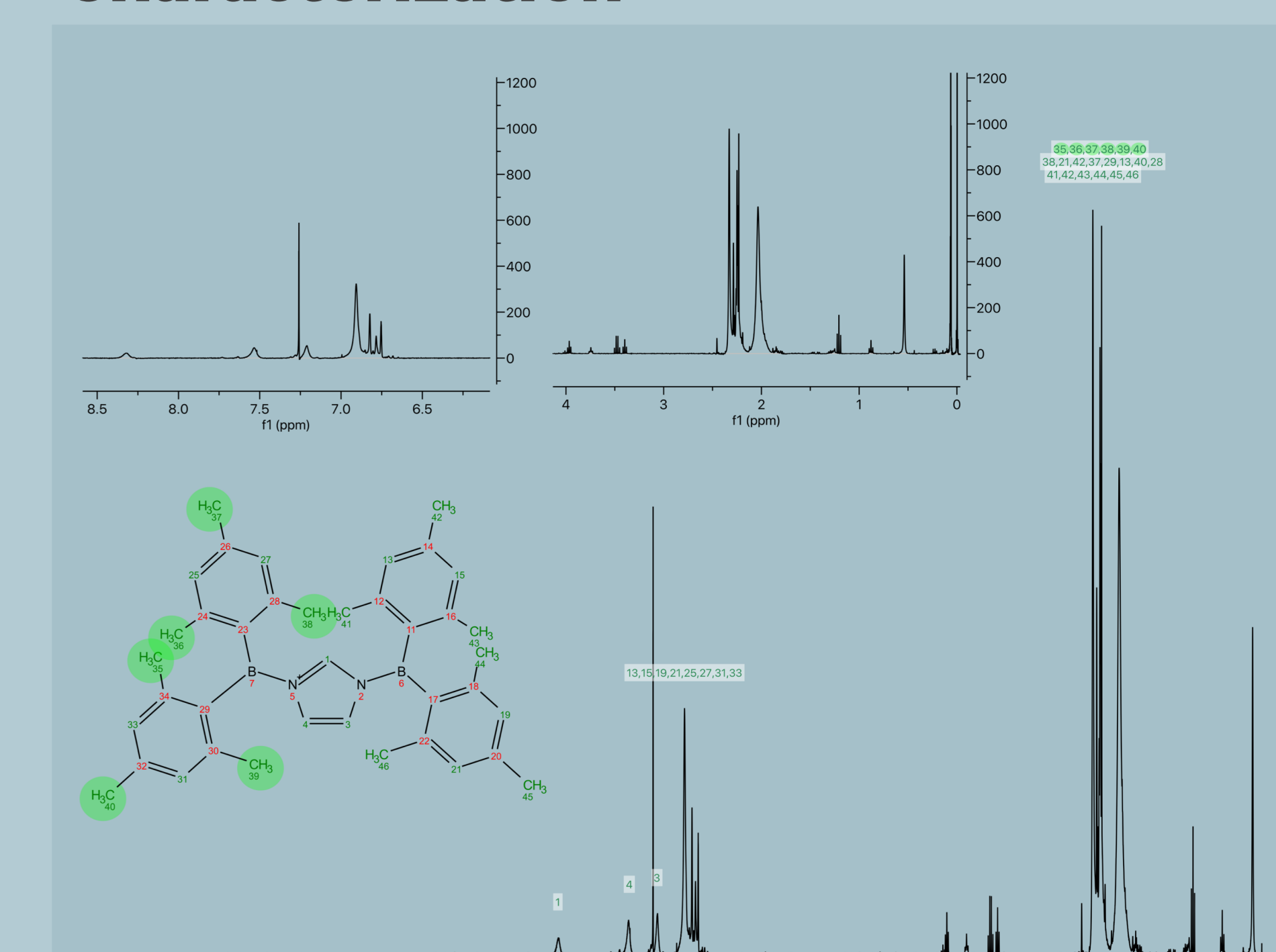
Catalytic Pathways



Synthesis



Characterization



$^1\text{H NMR}$ (CDCl_3 , 400MHz): δ 8.32 (s,CH), 7.54 (s,CH), 7.28 (s,CH), 6.80 (m,CH), 2.25 (m,CH₃).

- Brilliant Fluorescence under 365 nm UV-light:



Future Work

- Complexation with various transition-metal complexes.
- Crystal growth of various transition metal-carbene complexes.
- Catalytic Studies.
- Synthesize various carbene FLPs and probe their ability to activate small molecules.
- Catalytic optimization.

Acknowledgements

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