



IPREM
Institut des sciences analytiques
et de physico-chimie
pour l'environnement et les matériaux

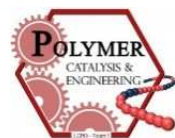


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Laboratoire de Chimie
des Polymères Organiques

Rationally designed bis-carbene building blocks for functional polymer synthesis



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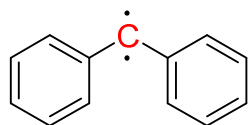
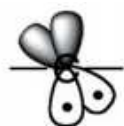
49^{èmes} Journées
d'Etudes des Polymères
(JEPOs 2022)

Du 2 au 7 octobre 2022
À Bussang (Vosges)

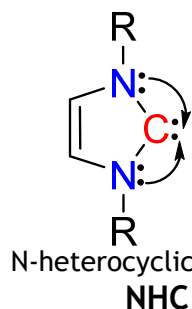
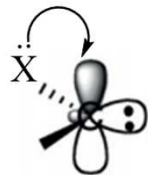


Carbenes: Definition and properties

Carbene = neutral divalent carbon with 6 e⁻ presenting two different configurations → Highly reactive

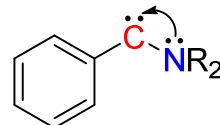


Triplet state



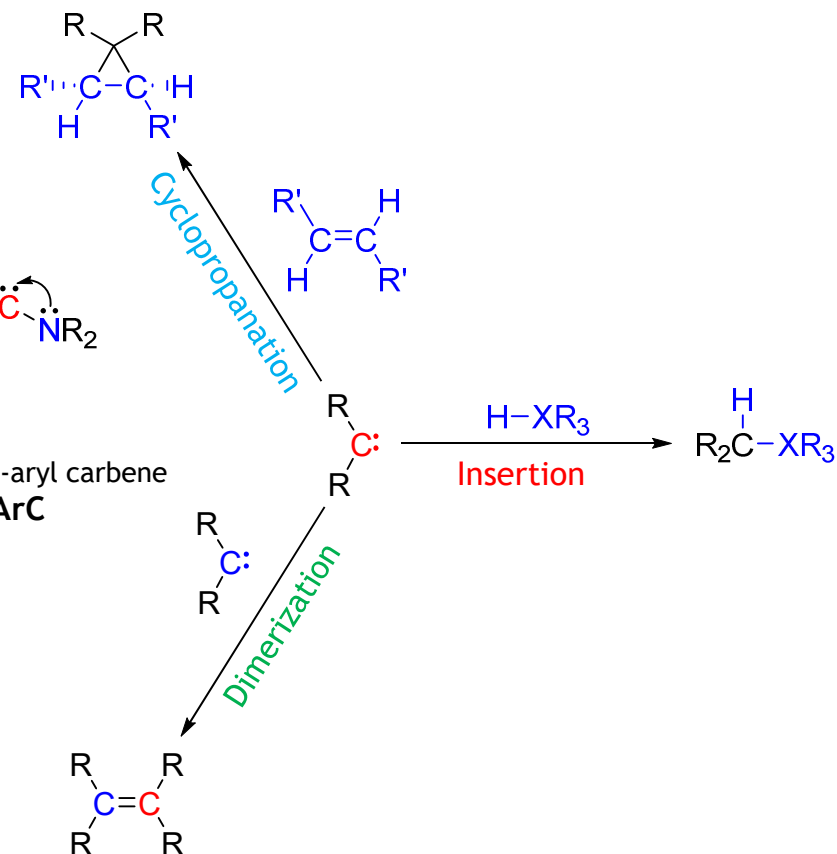
N-heterocyclic carbene
NHC

Singlet state

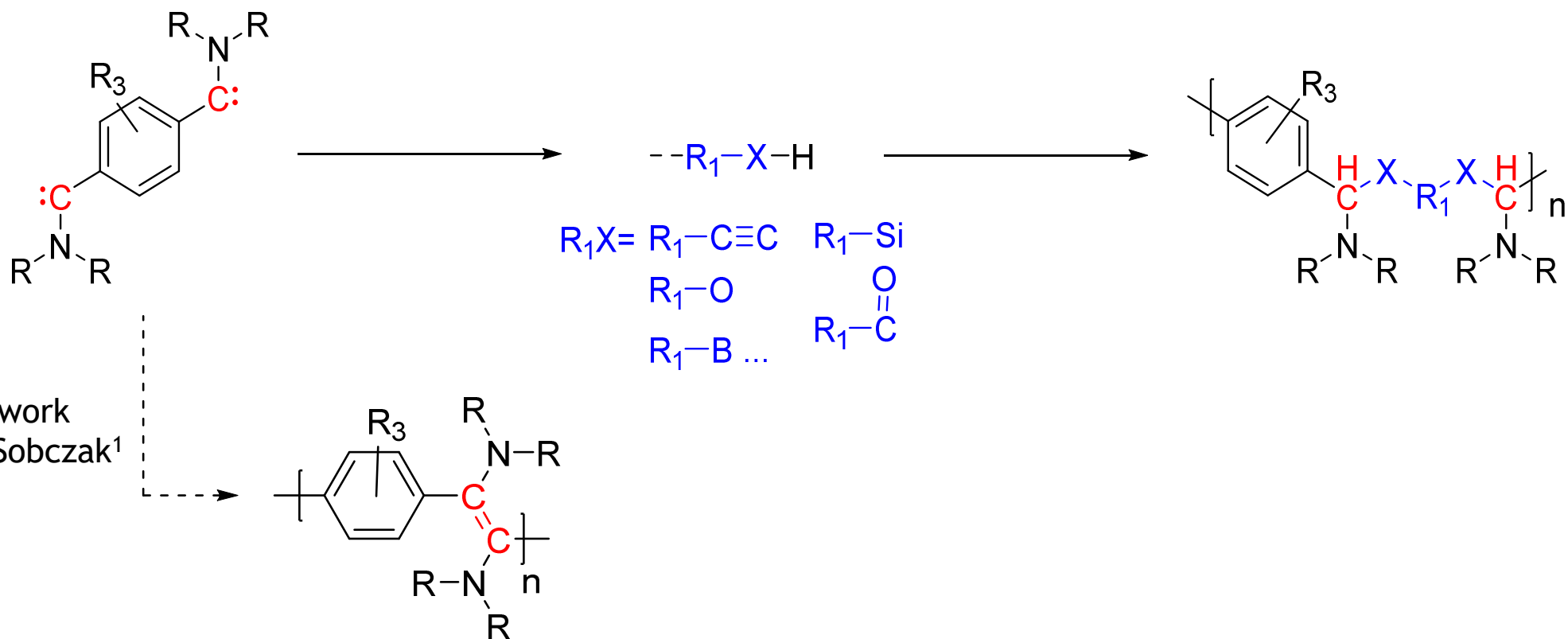


Acyclic amino-aryl carbene
AAArC

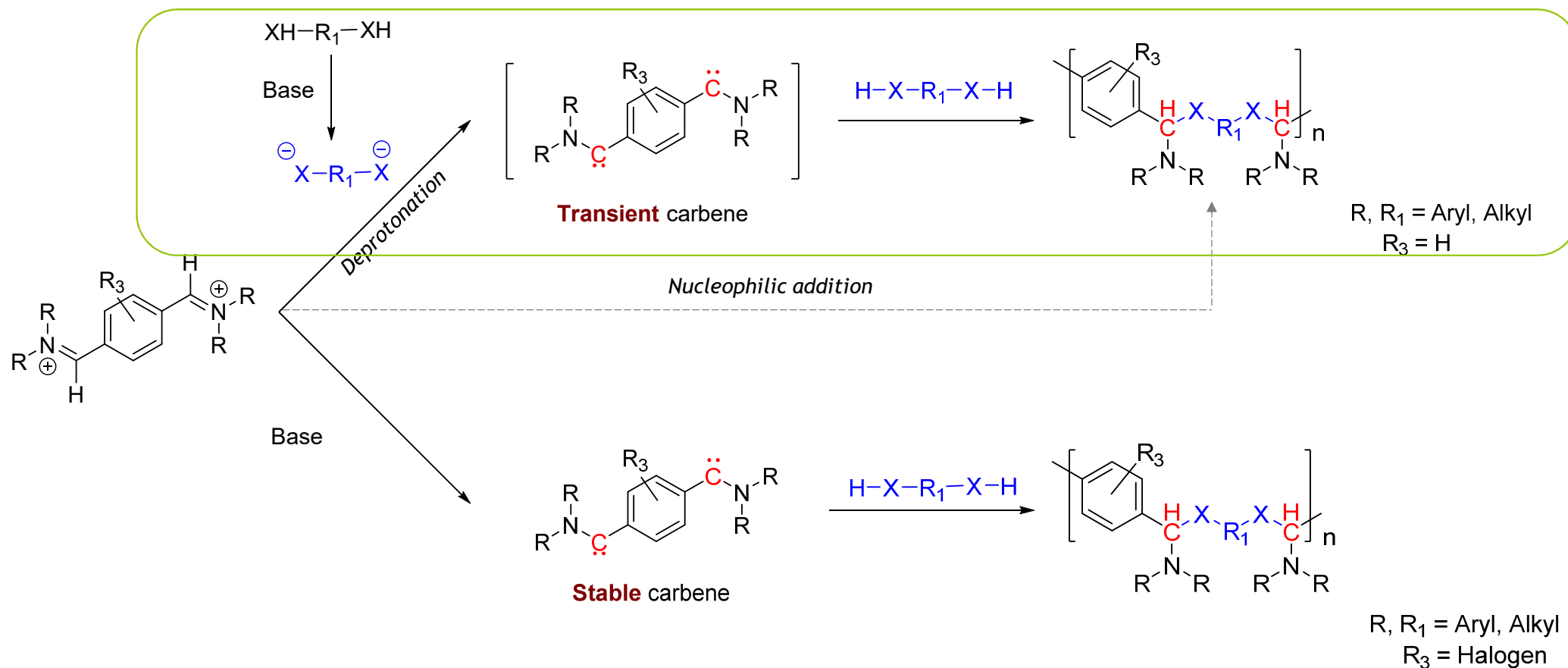
- e⁻ in two different orbitals
- Act as a diradical
- e⁻ in the same orbital
- Stabilized by X (X=N,O,S,P...)
- Ambiphilic behavior → Nucleophilic & electrophilic



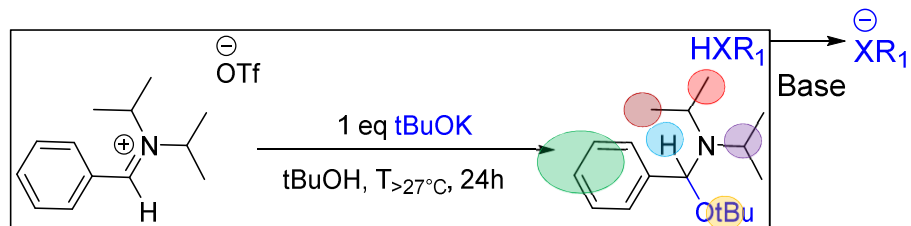
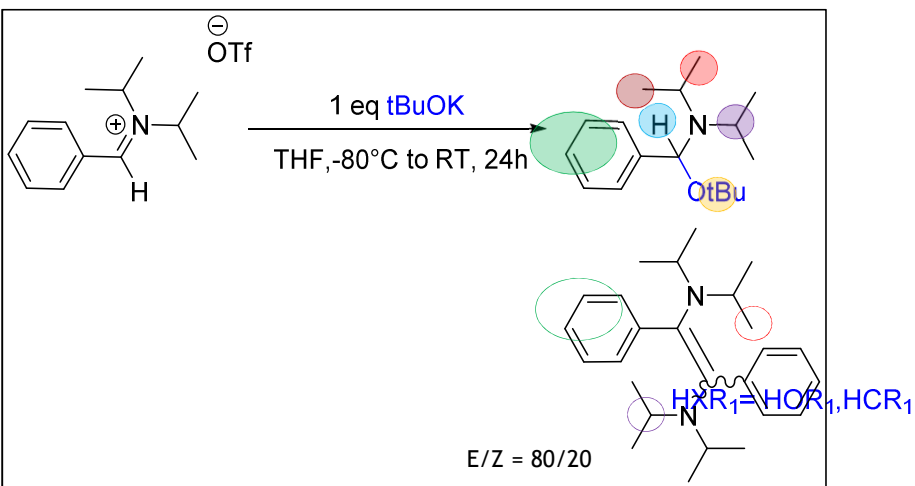
Aim of the CARBENOPOL project



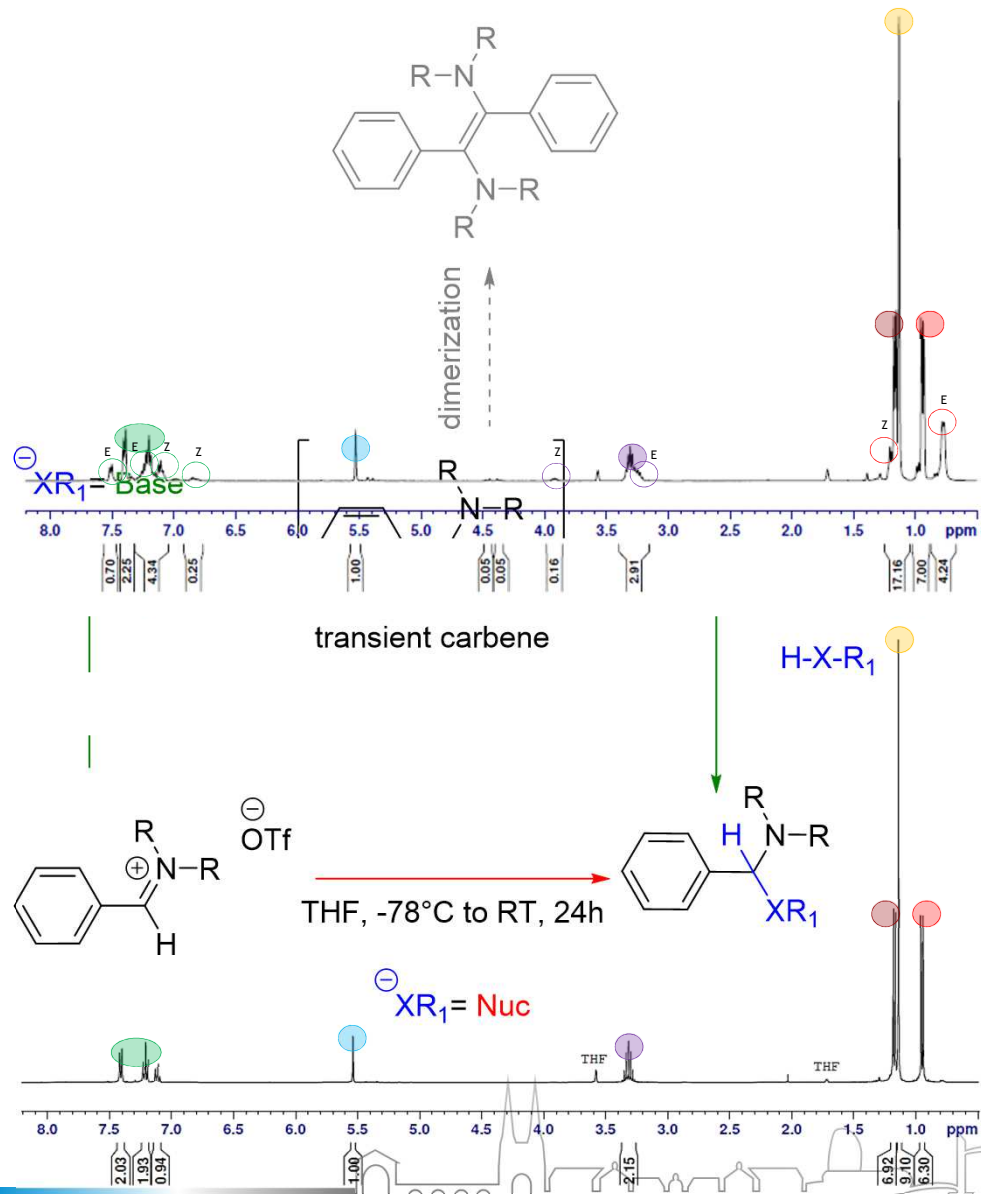
Different synthetic strategies



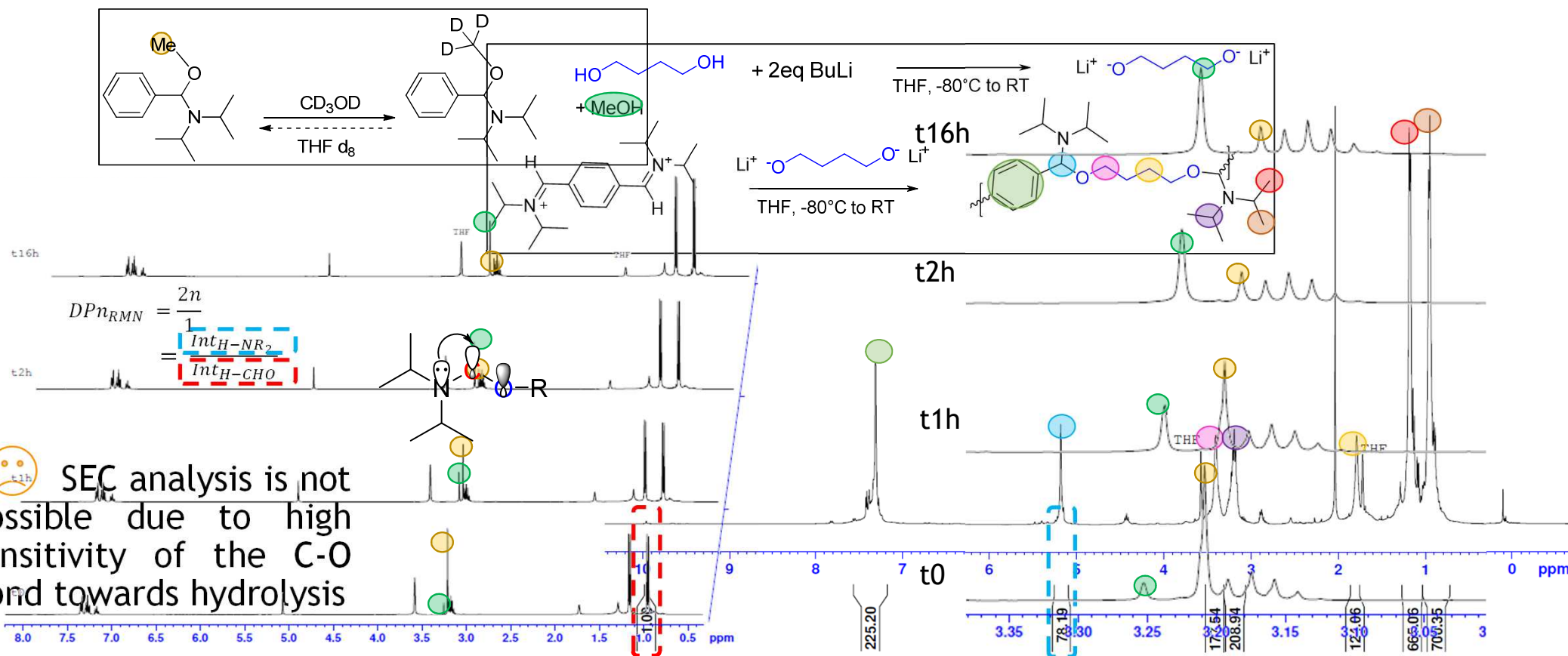
Insertion of the carbene into H-X bonds



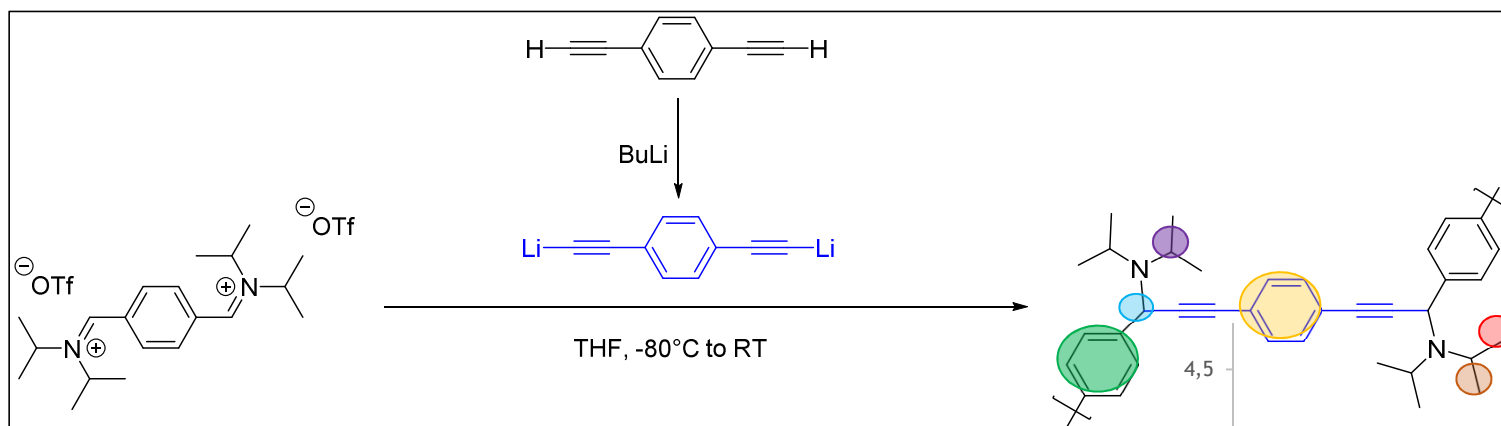
Model compounds - Probing reactivity



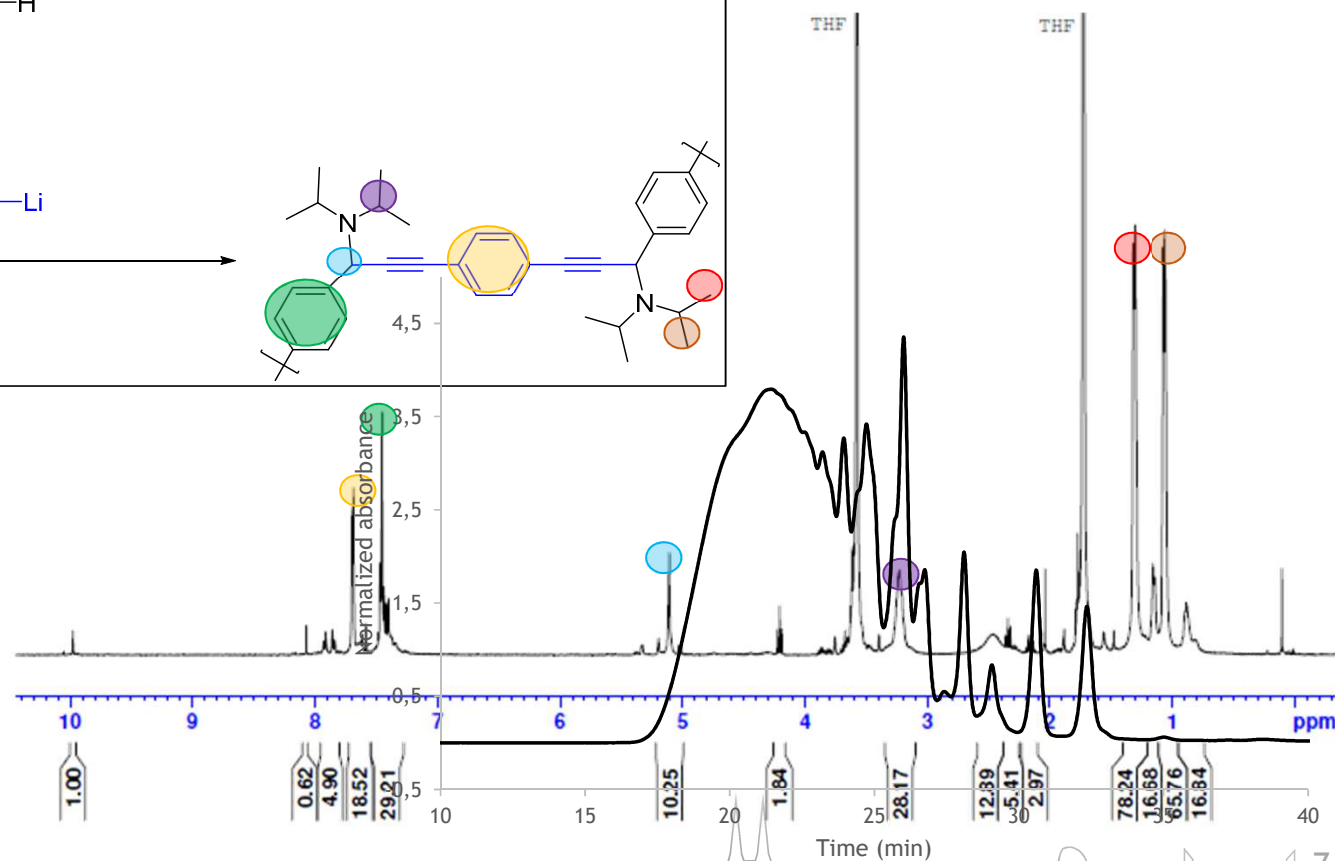
Polycondensation between a bis-iminium and a bis-alkoxide



Polycondensation between a bis-iminium and a dialkyne

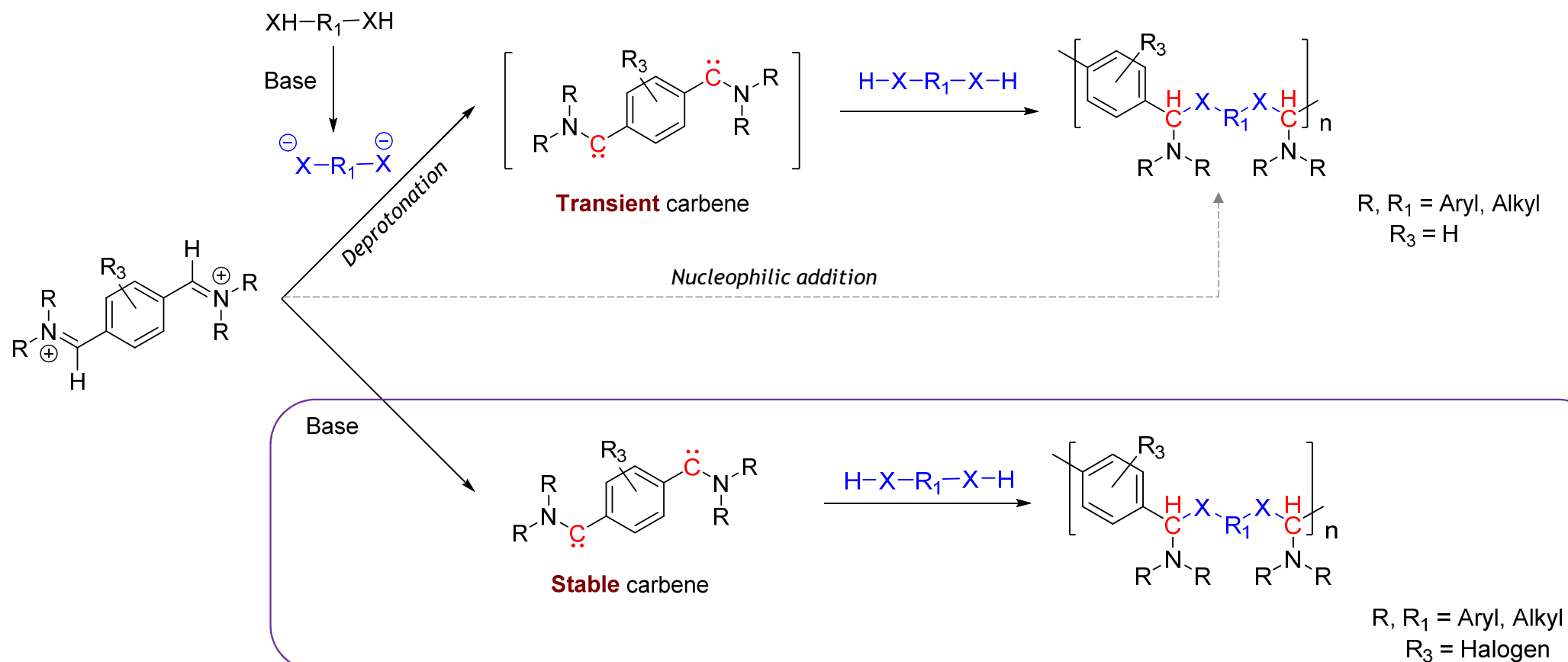


- 55% conversion
- No risk of hydrolysis
- Can be handled in the air



Size exclusion chromatography UV trace in THF (calibration with PS standards)

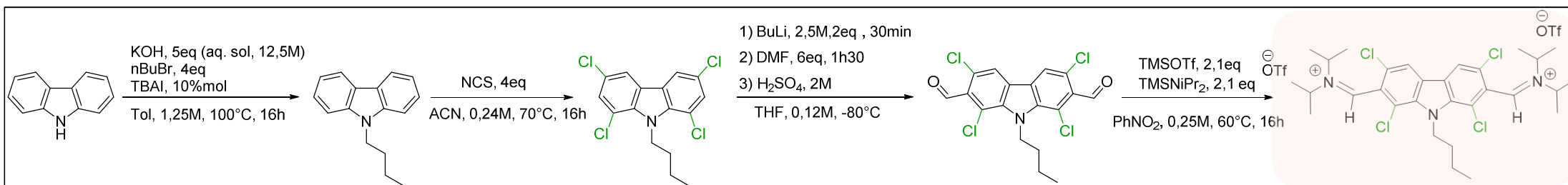
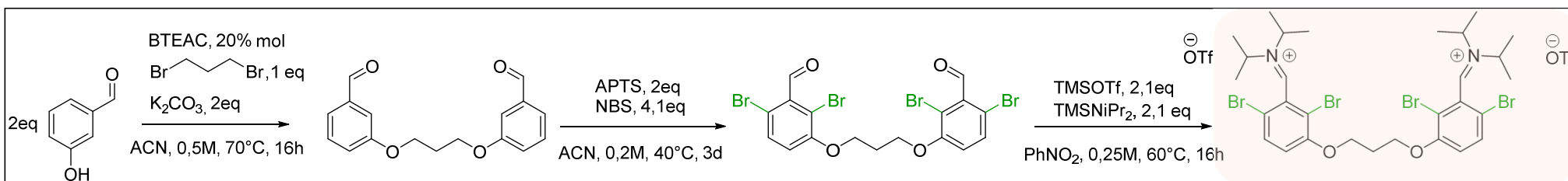
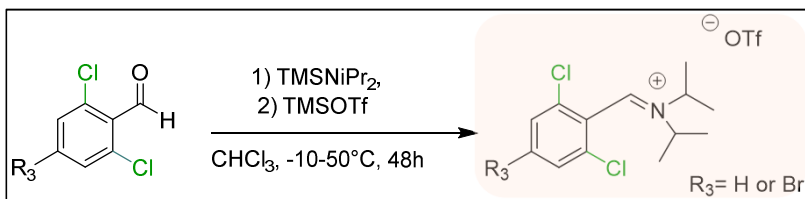
Different synthetic strategies : through the formation of a stable carbene



Synthesis of a sterically hindered carbene precursor

(Synthetic route developed by D. Magis at ISM)

Allows the formation of stable carbenes and no dimerization reaction



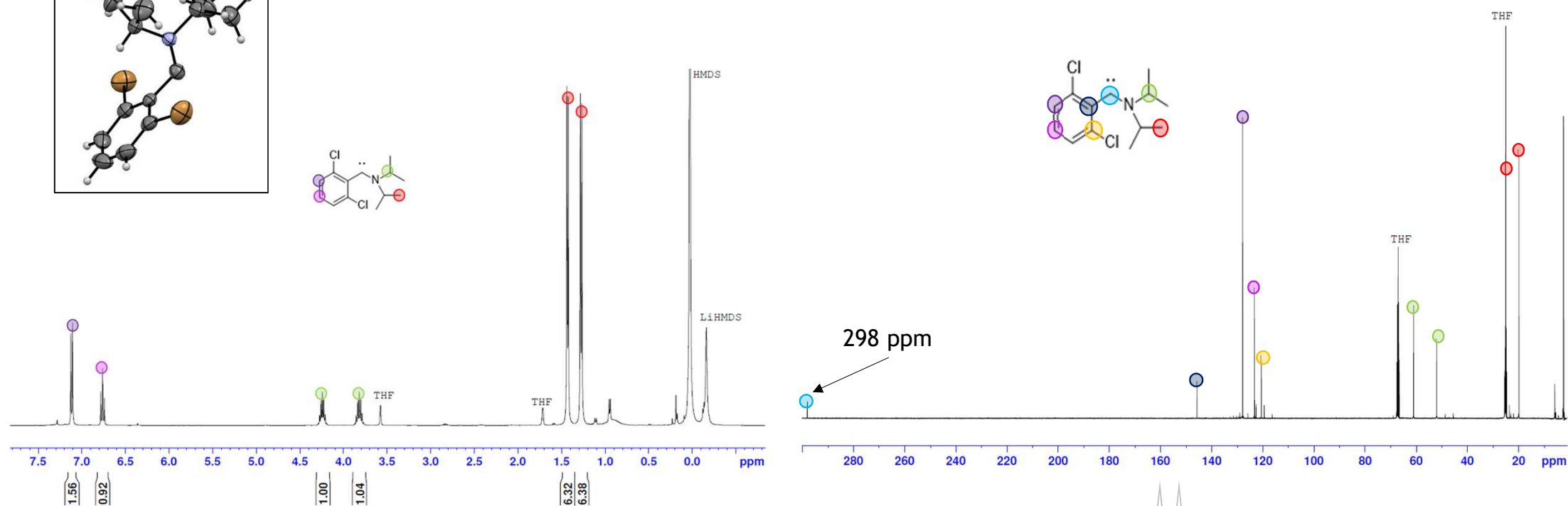
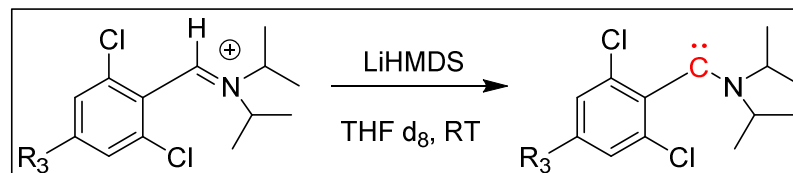
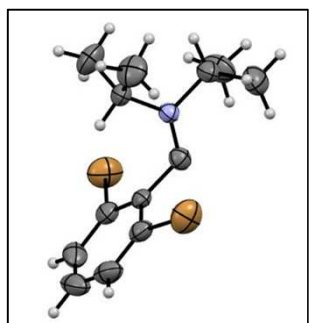
Highlight of the presence of stable carbene

RX structure of crystallized

 stable carbene

 (isolated and characterized

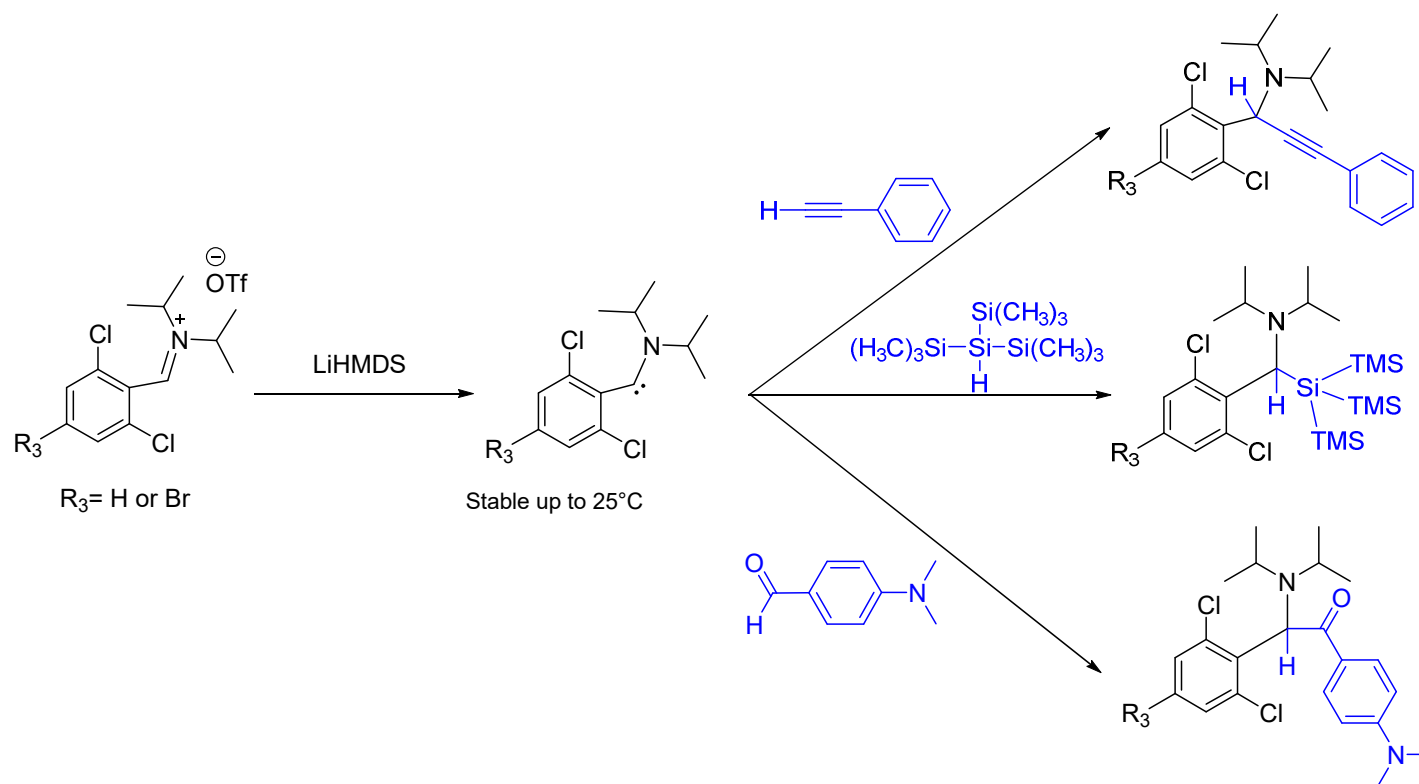
 by Damien Magis)



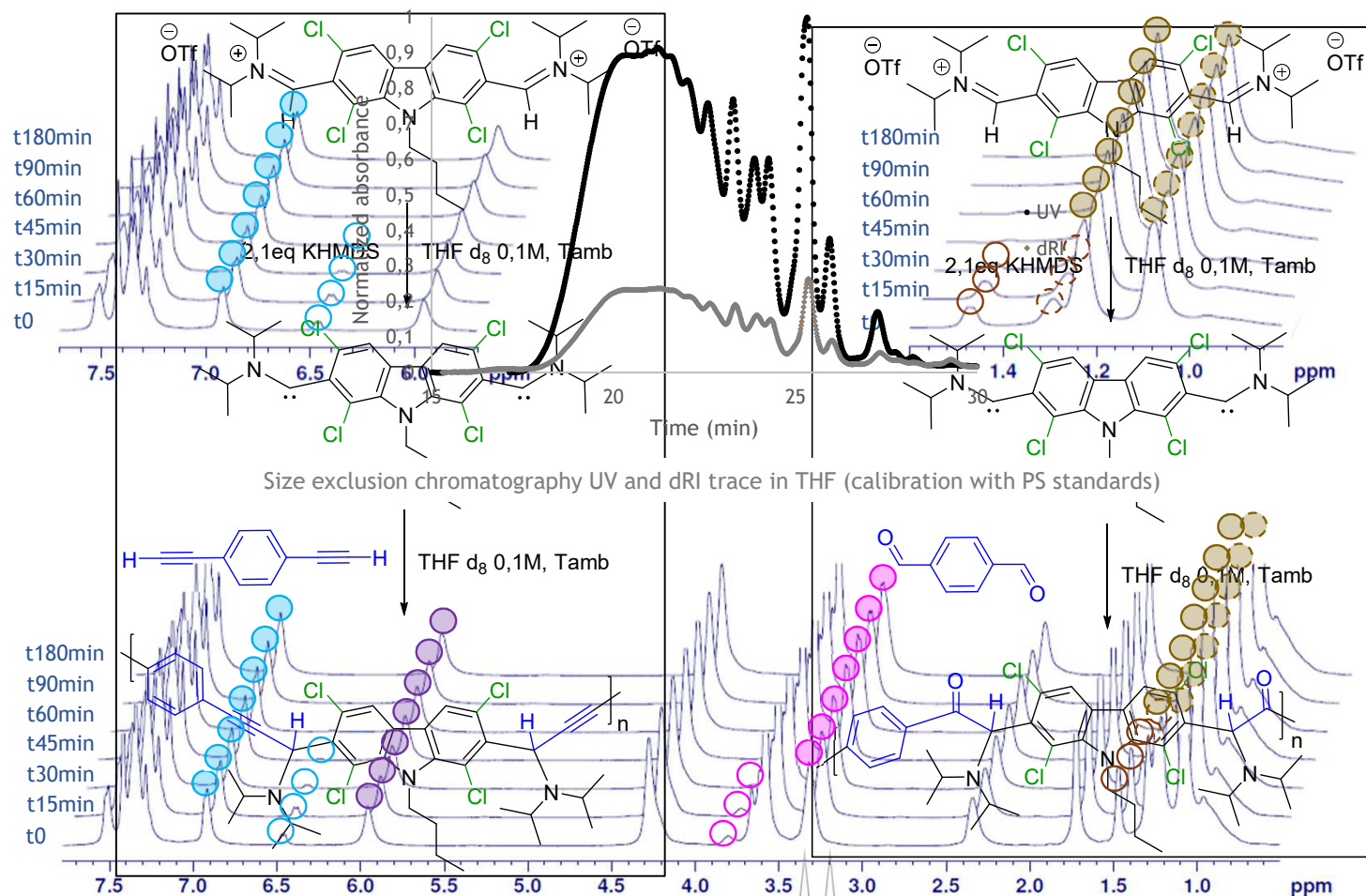
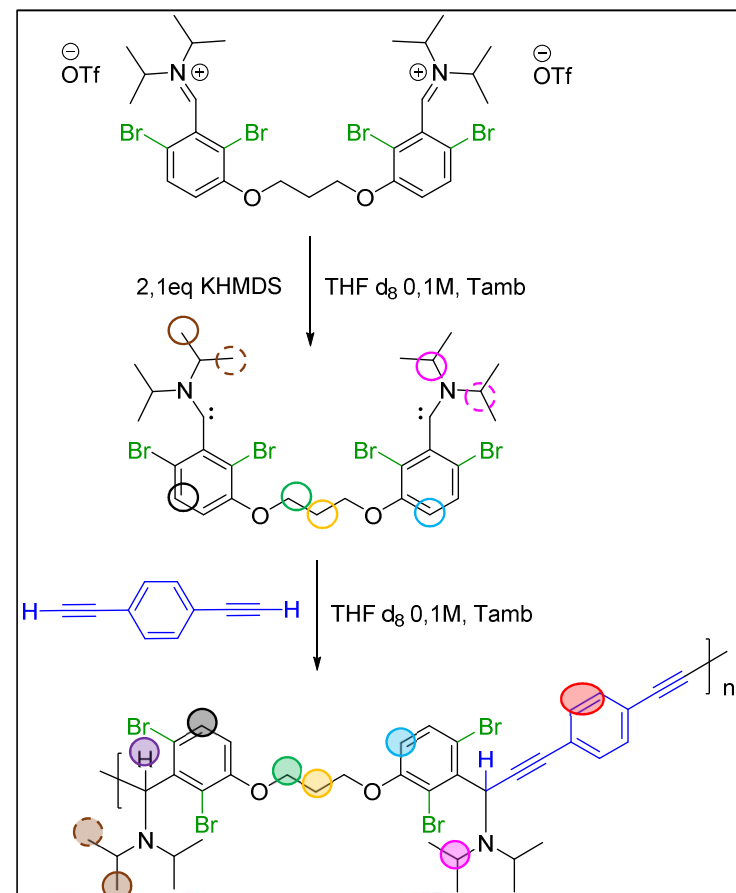
Work of Baptiste, M1 Intern



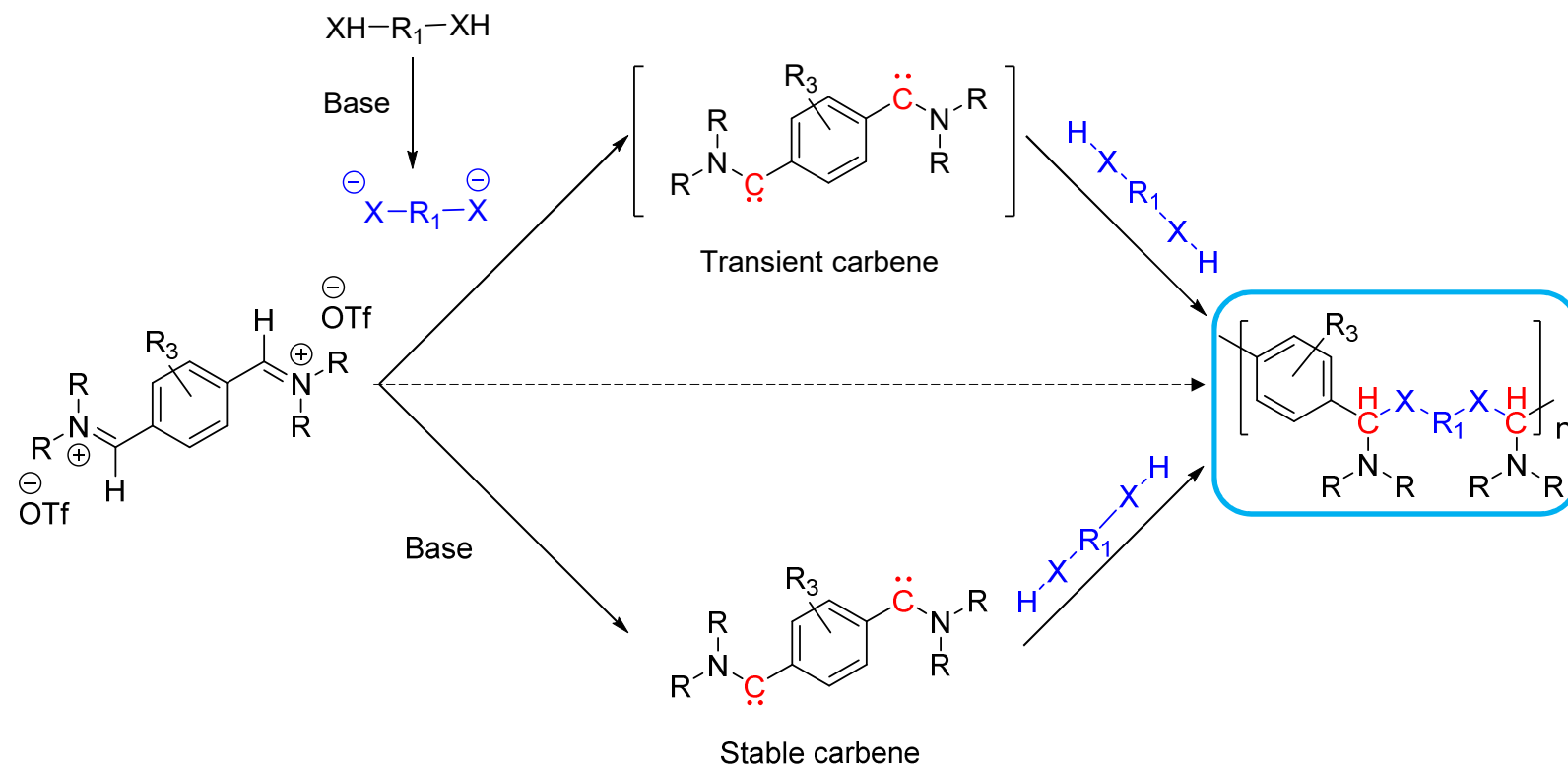
Insertion reaction into a X-H bond



Step growth polymerization involving stable carbenes

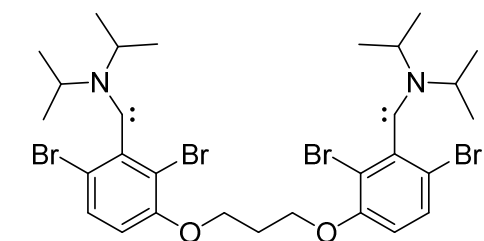


Transient versus stable carbene route

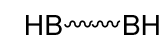
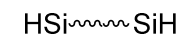
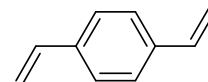
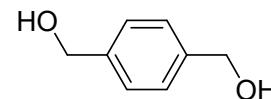
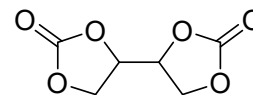
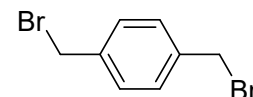
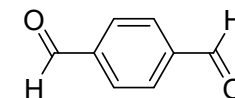
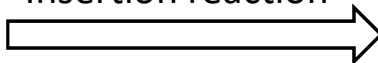


Perspectives

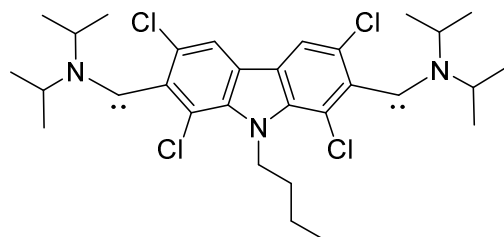
- Broadening of the scope of partners for polymerization reactions



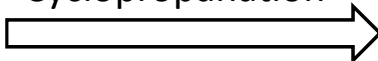
Insertion reaction



...



Cyclopropanation



- Investigation of dynamic covalent chemistry
- Study of the properties of the formed polymers



Acknowledgment:

ANR CARBENOPOL Consortium

Damien Magis and Yannick Landais, ISM



Jean-Marc Sotiropoulos and Karinne Miqueu, IPREM



Joan Vignolle and Daniel Taton



LCPO Engineers and staff



Thank you for your attention

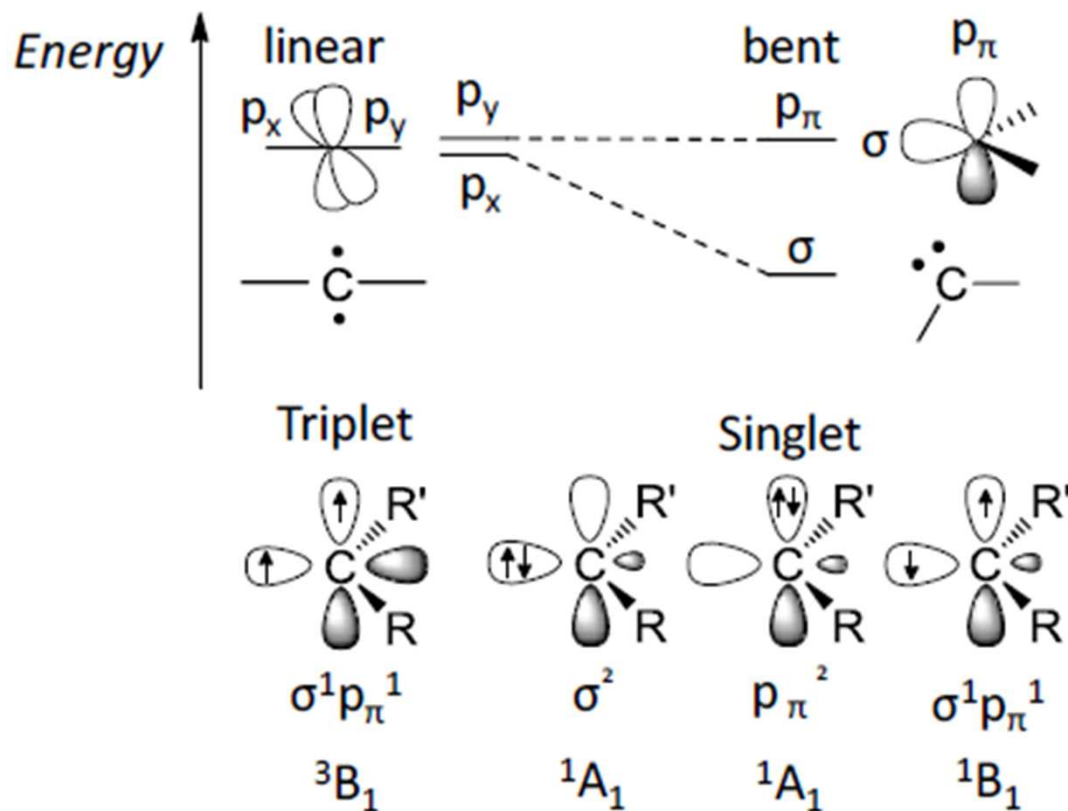
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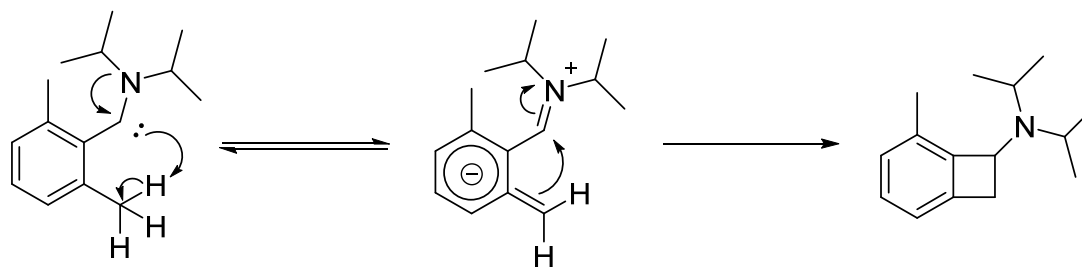
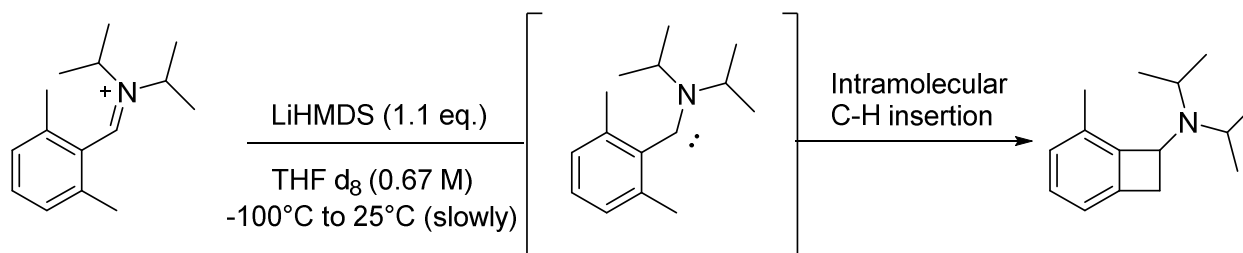


Difference between triplet and singlet

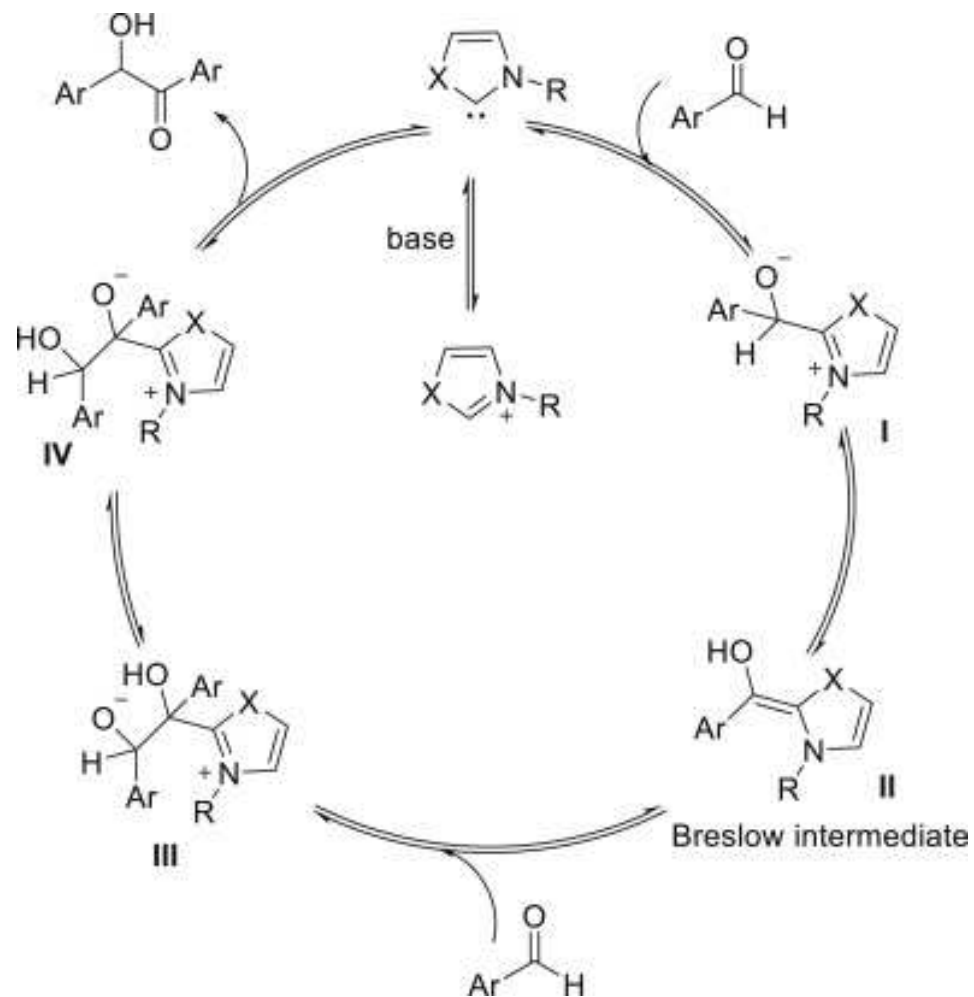


1. Electronic configurations of carbenes and relative energy of frontiers orbitals.⁴⁹

Intramolecular insertion of *o*-substituant

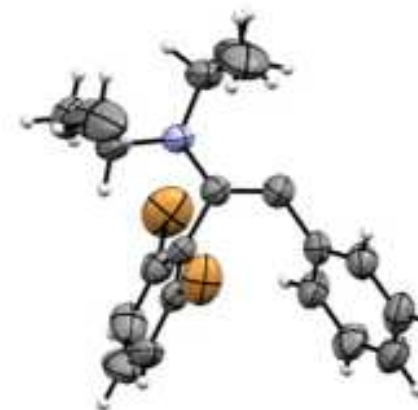
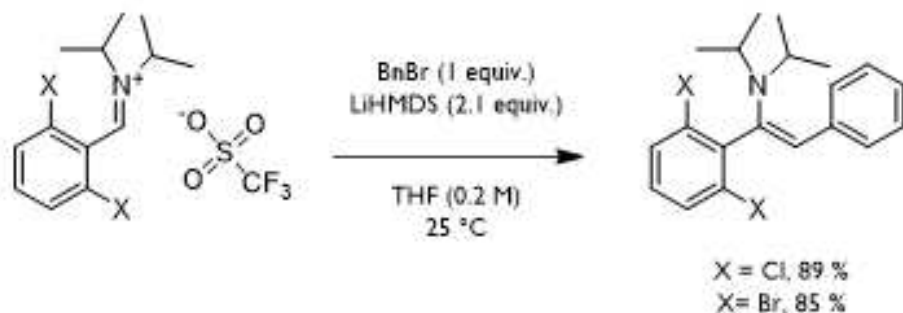
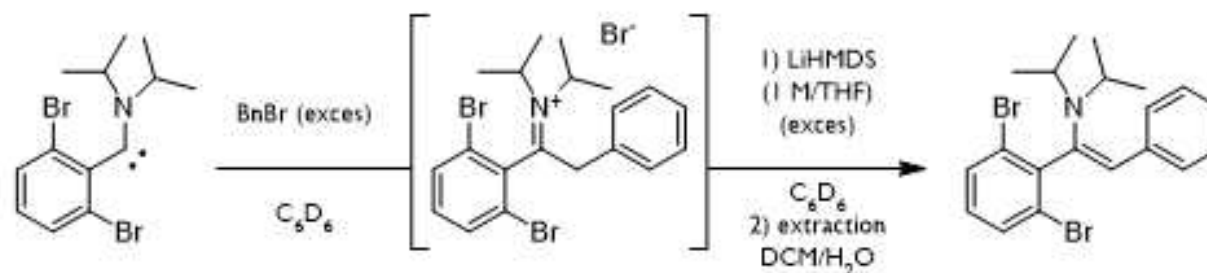


NHC catalyzed benzoin condensation

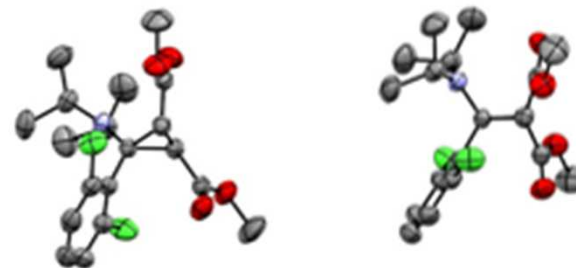
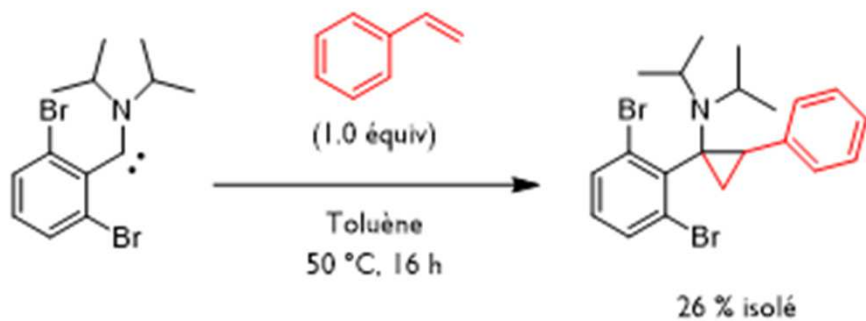
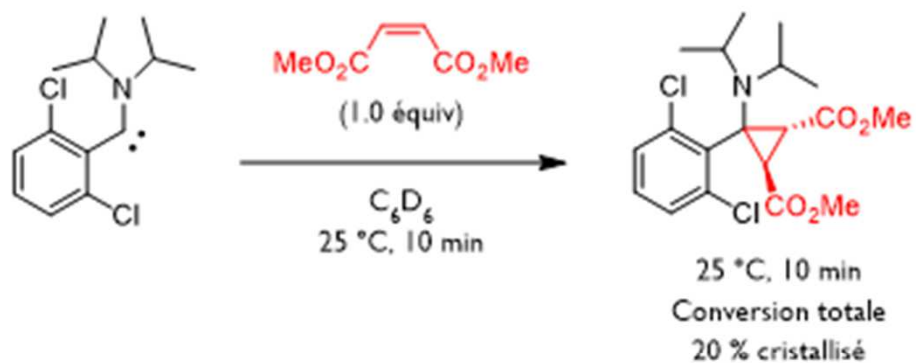


R. Breslow, J. Am. Chem. Soc. 1958, 80, 3719

Benzyl bromide: conjugated enamines



Cyclopropanation



Stable carbene insertion into Si-H bond

