



Laboratoire de Chimie des Polymères Organiques

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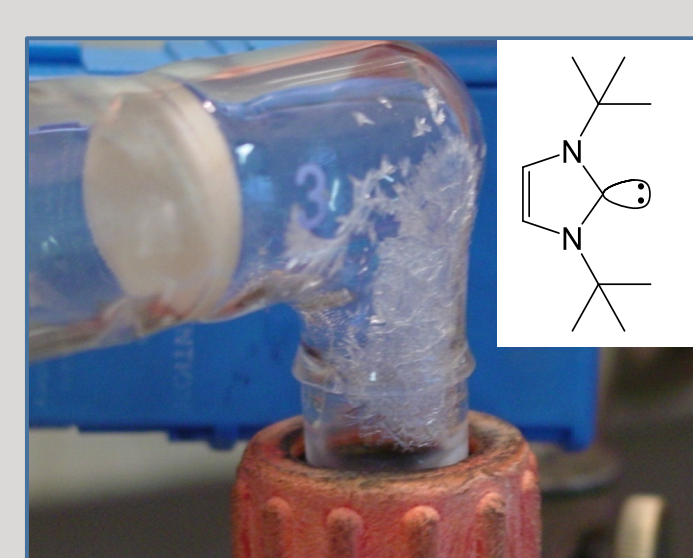
Team 1: Polymerization Catalyses & Engineering

From ionic liquids to N-heterocyclic carbenes (NHCs) and poly(ionic liquids) (PILs)

J. Vignolle and D. Taton

ORGANOCATALYSIS

- Benzoin condensation
- Transesterification
- Cyanosilylation
- ✓ Good to Excellent yields
- ✗ No recycling of the catalyst



NHCs

- ✗ Air sensitive
- ✗ Strong base required

(*J. Am. Chem. Soc.* **2012**, 134, 6776)



Imidazolium hydrogen carbonate

- ✓ Air stable
- ✓ Reactif ILs = masked NHC

(*J. Org. Chem.* **2012**, 77, 10135)

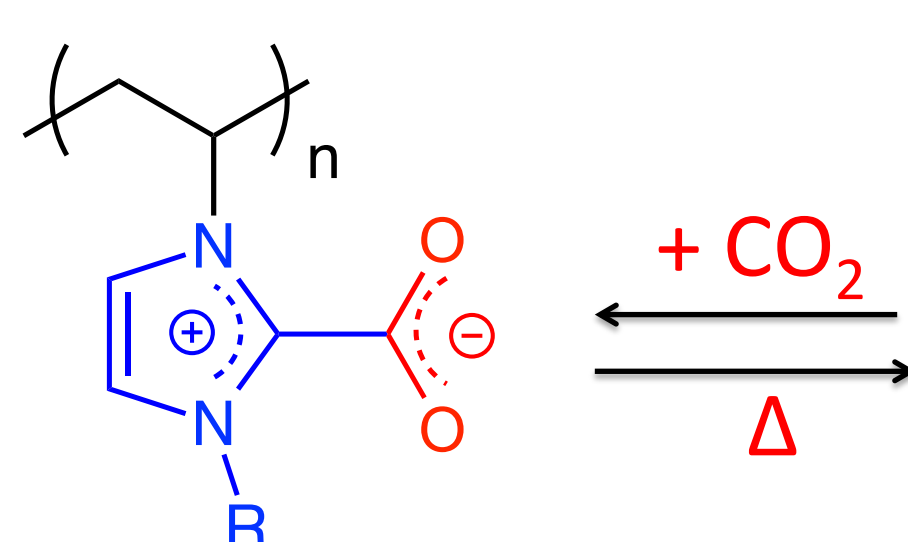
Imidazolium halide = ILs

STOICHIOMETRIC TRANSFER

- To organic substrate (CS₂)
 - To transition metals
- [M] = AuCl, Pd(C₃H₅)Cl

Polymerization
(R = polymerizable group)

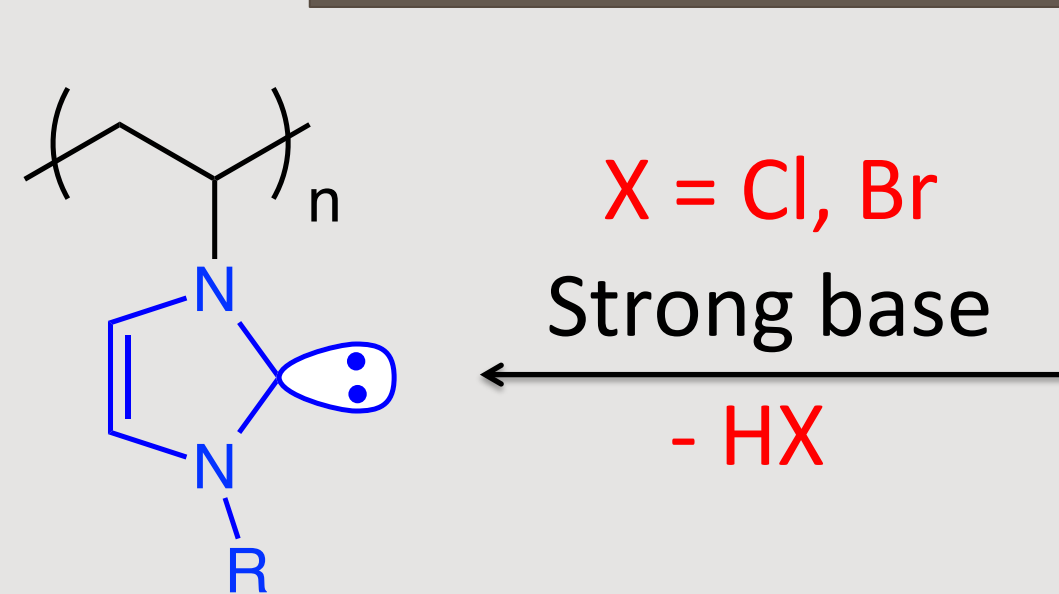
CO₂ CAPTURE



- Reversible
- Precursor of poly(NHC)s
- More robust than poly(NHC)

(*Macromolecules*, **2011**, 44, 6397)

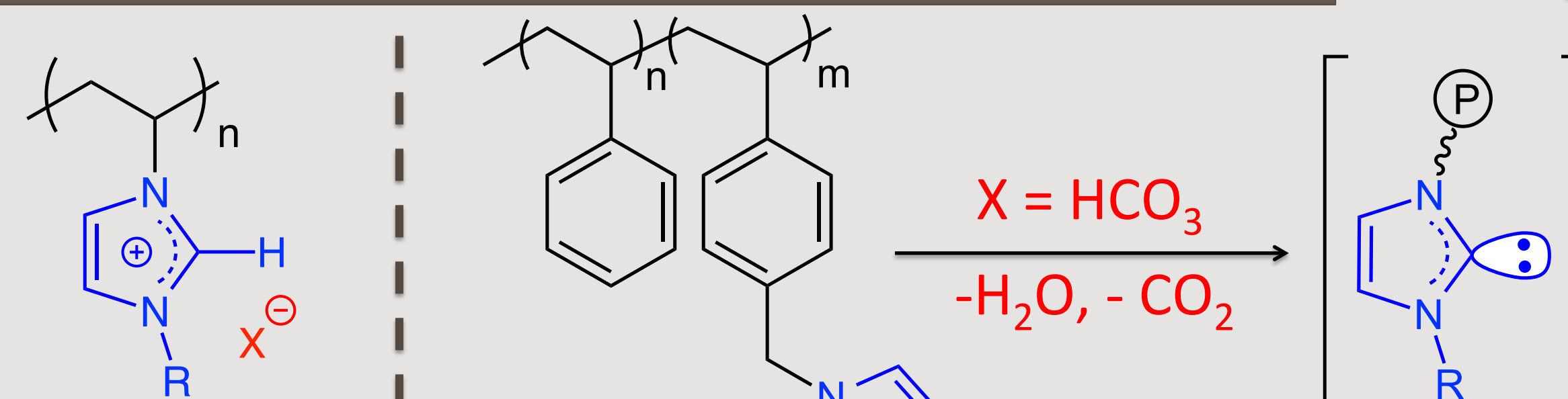
Poly(NHC)s and Reactive polymerized ionic liquids (PILs)



Poly(NHC)s

- ✓ Highly active
- ✗ Air sensitive
- ✗ Difficult to recycle

(D. Mecerreyes, *Prog. Pol. Sci.*, **2011**, 36, 1629; M. A. Firestone et al., *Polymer Reviews* **2009**, 49, 339)

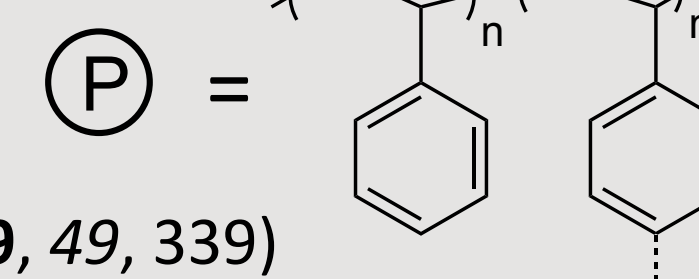


PIL(X)s

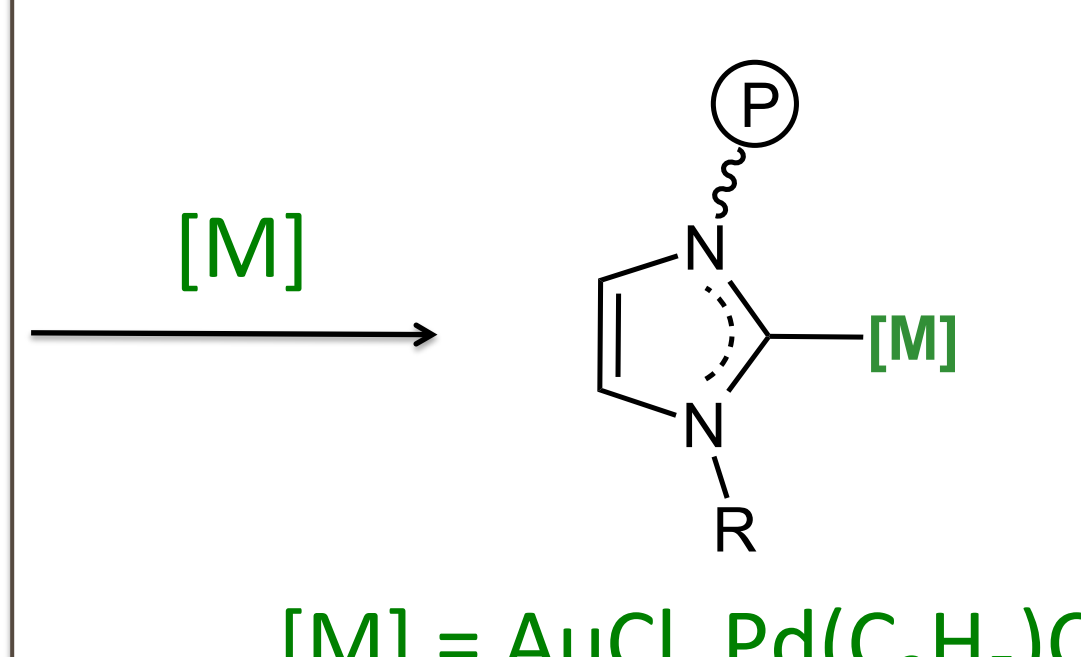
PIL(HCO₃)

- ✓ Reactif PILs (= poly(NHC))
- ✓ Air stable
- ✓ Easily recyclable

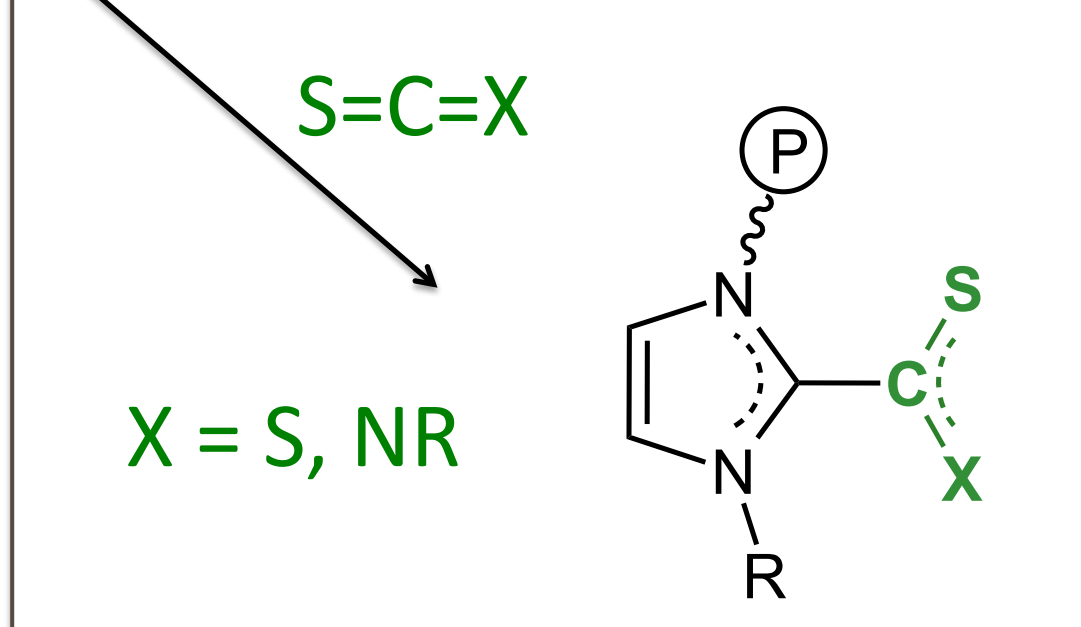
Poly(Ionic Liquids) = PILs



POST-MODIFICATION



[M] = AuCl, Pd(C₃H₅)Cl



(*Polymer* **2014**, 55, 3404)

ENGINEERING

- (Controlled) radical polymerization (FRP, RAFT, CMRP...)
- (Block) copolymers synthesis (amphiphilic, double hydrophilic,...)
- Self-Assembly (solution, bulk)
- Anion exchange

(*Macromolecules*, **2011**, 44, 6397;
Macromol. Rapid Commun. **2014**, 35, 422)

ORGANOCATALYSIS

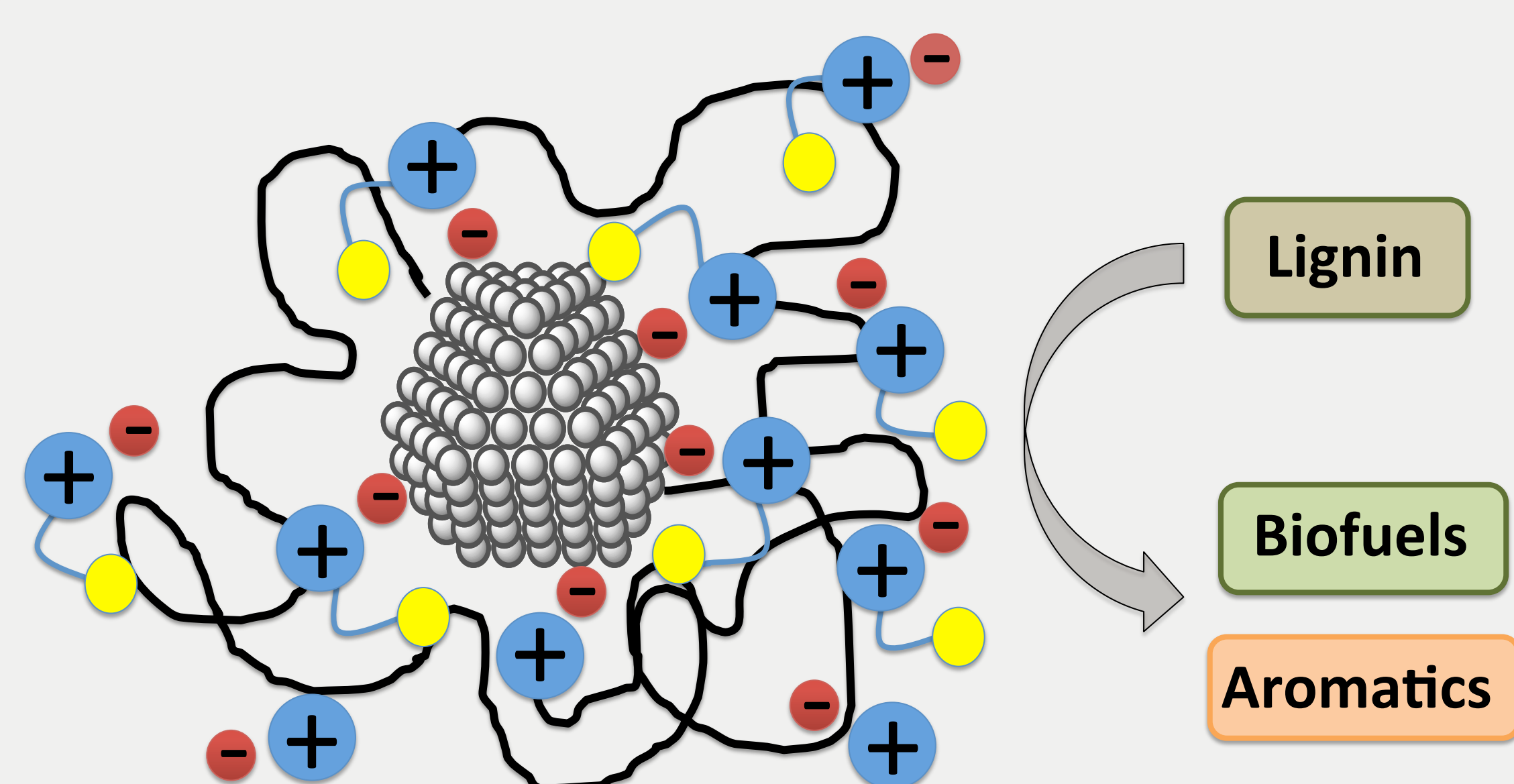
- Benzoin condensation
- Transesterification
- Cyanosilylation

(THF, 80°C, 2-24h)

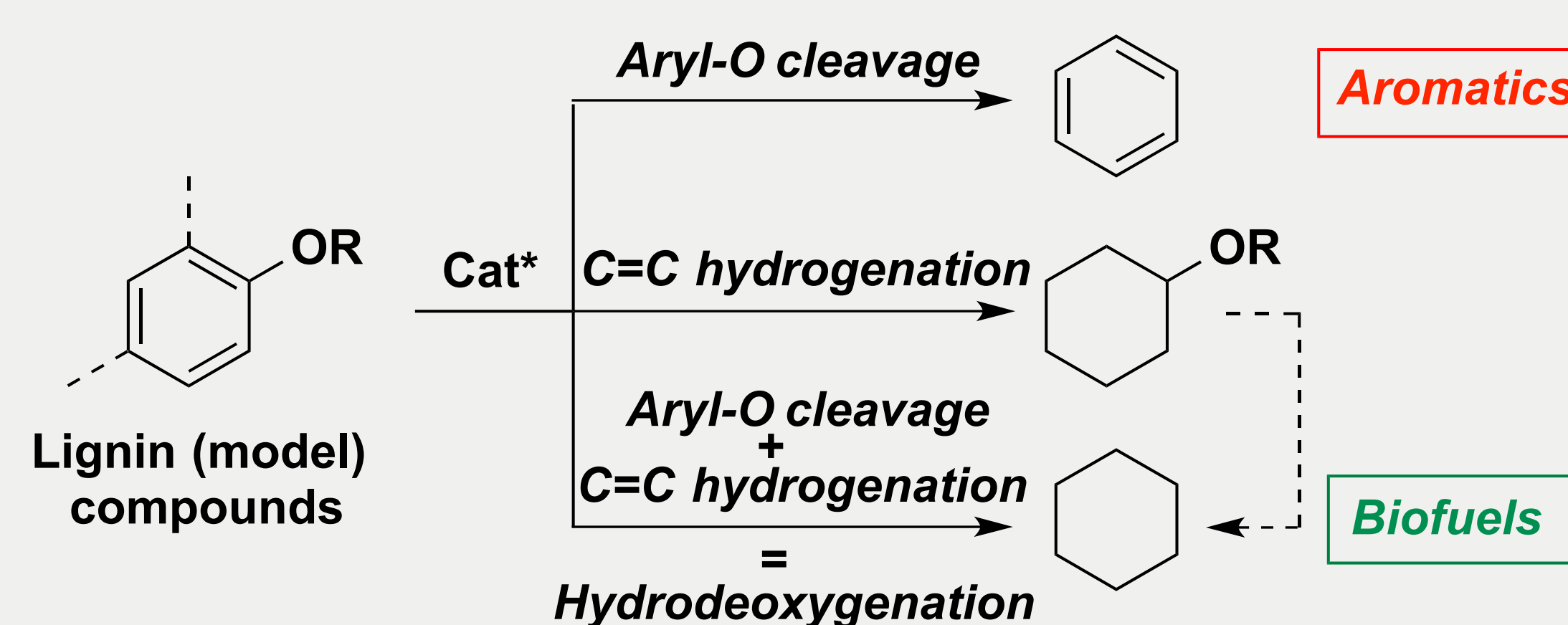
- ✓ Good to Excellent yields
- ✓ Catalyst easily recycled

(*J. Polym. Sci. A Polym. Chem.* **2013**, 51, 4530)

Catalytic platform PILs@NP for the transformation of lignin into biofuels



Cat*: PIL@NPs (● = functional group)



- ➡ Catalysis on model lignin compounds
- ➡ Reductive depolymerization of lignin
- ➡ Catalytic transformation of lignin into biofuels

ANR