




■ Osnabrücker Umweltgespräche 25.6.2008

proionic Production of Ionic Substances GmbH

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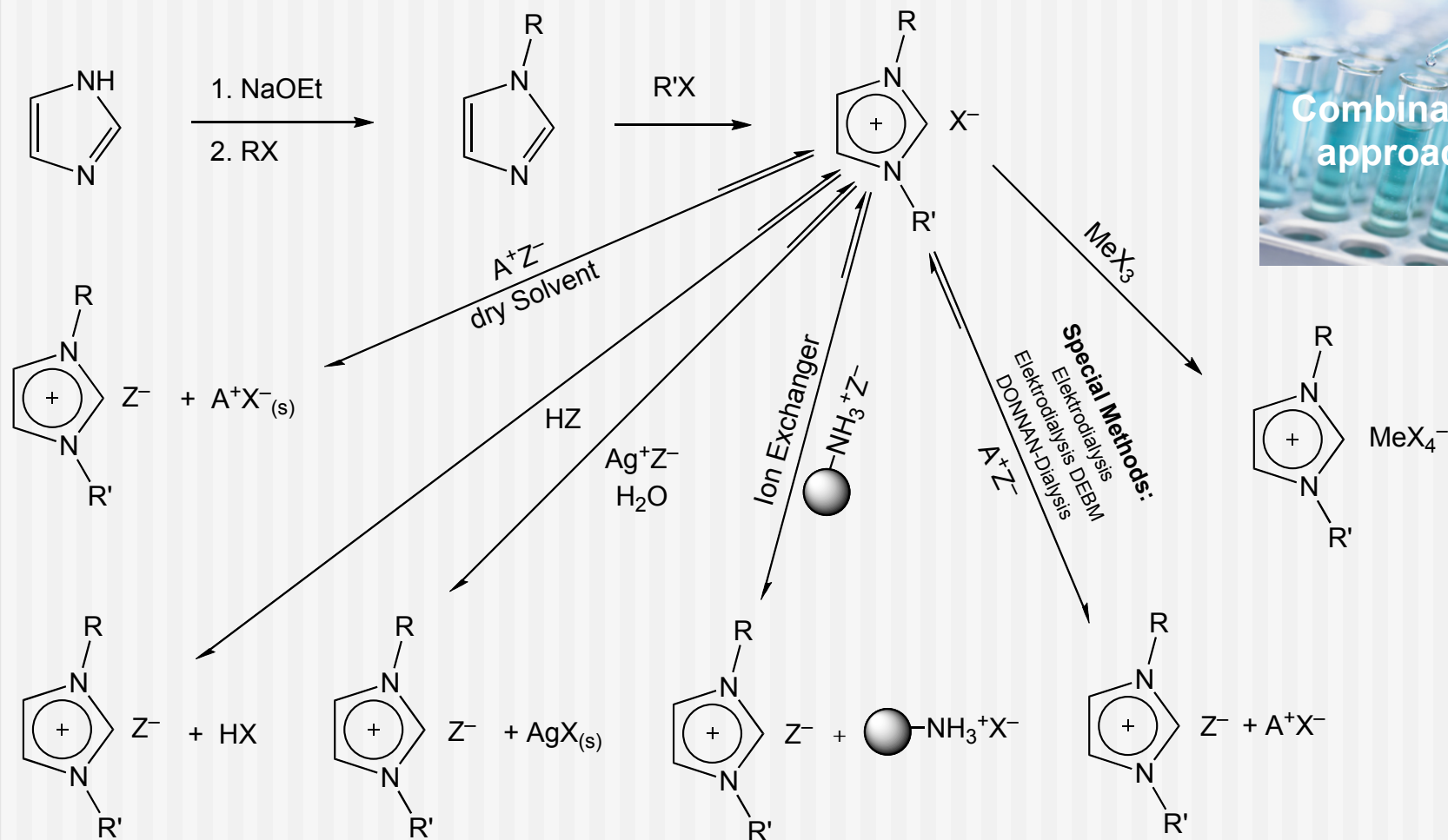


Deutsche Bundesstiftung Umwelt

- 
- **Conventional Ionic Liquid Synthesis**
 - **Fast & Quantitative IL Synthesis**
 - Hydroxide Route
 - Carbonate Route
 - EMIM-2-Carboxylate
 - **CBILS[®] Synthesis**

Synthetic methods

Conventional IL Synthesis



Screening: Conventional Synthesis

Conventional IL Synthesis

| | A1 ⁻ | A2 ⁻ | A3 ⁻ | A4 ⁻ | A5 ⁻ | A6 ⁻ | A7 ⁻ | A8 ⁻ | A9 ⁻ | A10 ⁻ |
|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|
| K1 ⁺ | X | ? | ? | ? | X | ? | ? | ✓ | ? | ? |
| K2 ⁺ | ? | ✓ | X | ? | ? | ? | ? | ? | X | ? |
| K3 ⁺ | ? | ? | ? | ? | ? | ✓ | ? | ? | ? | ? |
| K4 ⁺ | ? | X | ? | ✓ | ? | X | ? | ? | ? | ? |
| K5 ⁺ | ? | ? | ? | ? | ? | ? | ✓ | X | ? | ? |
| K6 ⁺ | ? | ? | ? | ? | ? | ? | ? | ? | ? | ? |
| K7 ⁺ | X | ? | ? | ✓ | ? | X | ? | ? | ? | ? |
| K8 ⁺ | ? | ✓ | ? | ? | ? | ? | ? | ? | X | ? |
| K9 ⁺ | ? | ? | X | ? | ✓ | ? | ✓ | ? | ? | ? |
| K10 ⁺ | X | ? | ? | ? | ✓ | ? | X | ? | ? | ? |

X (most probably) not working

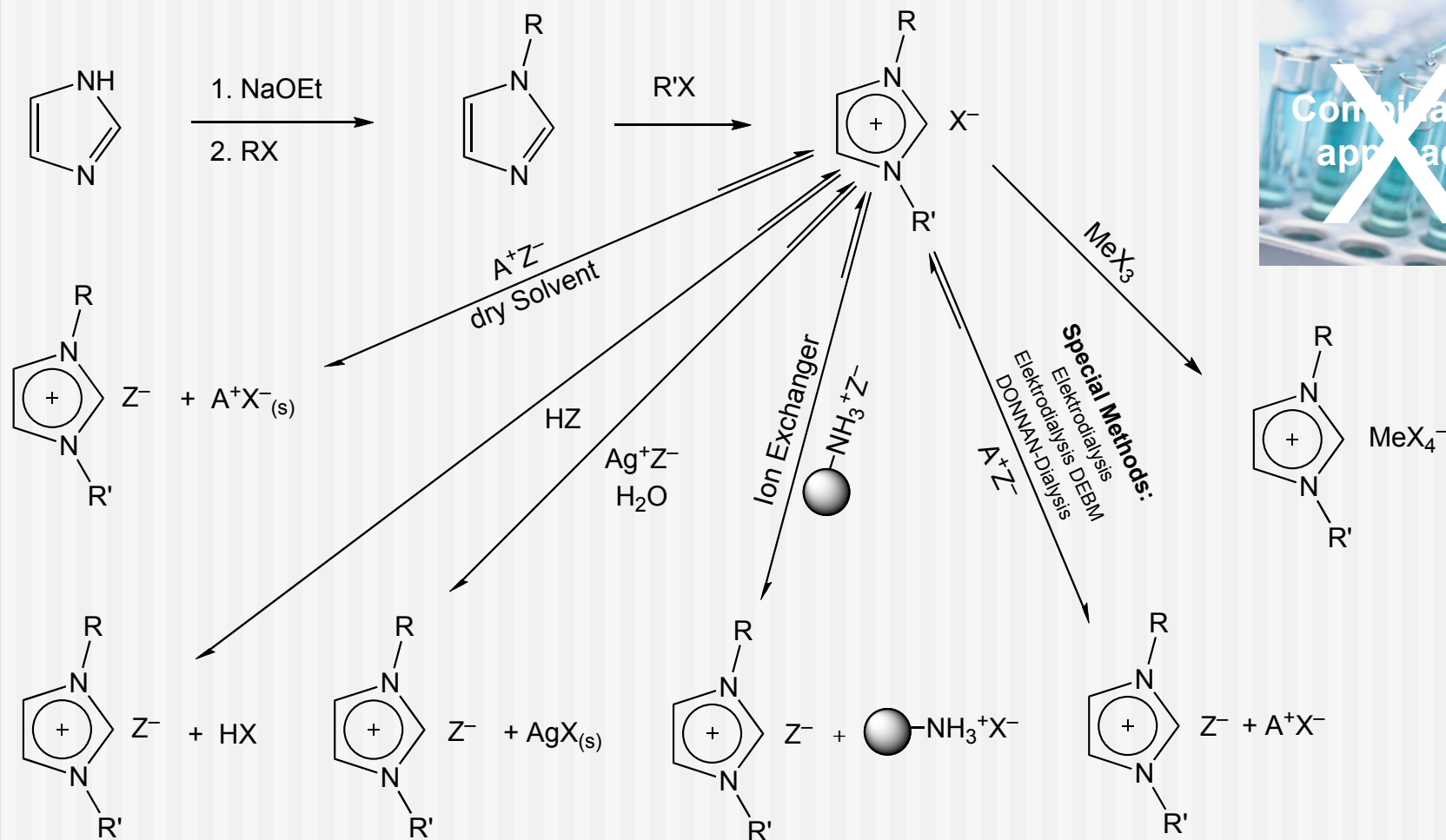
✓ (most probably) working

? unknown reactivity,
unknown quality, unknown
method: to be tested
experimentally

**Prediction empirically
or
not available: trial & error**

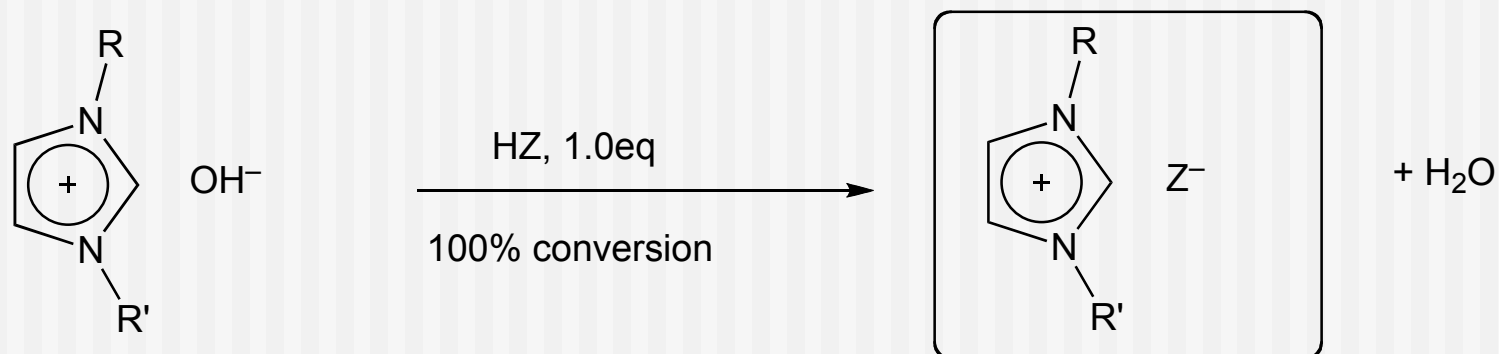
Synthetic Methods

Conventional IL Synthesis



Fast IL building reactions

Hydroxide Route:

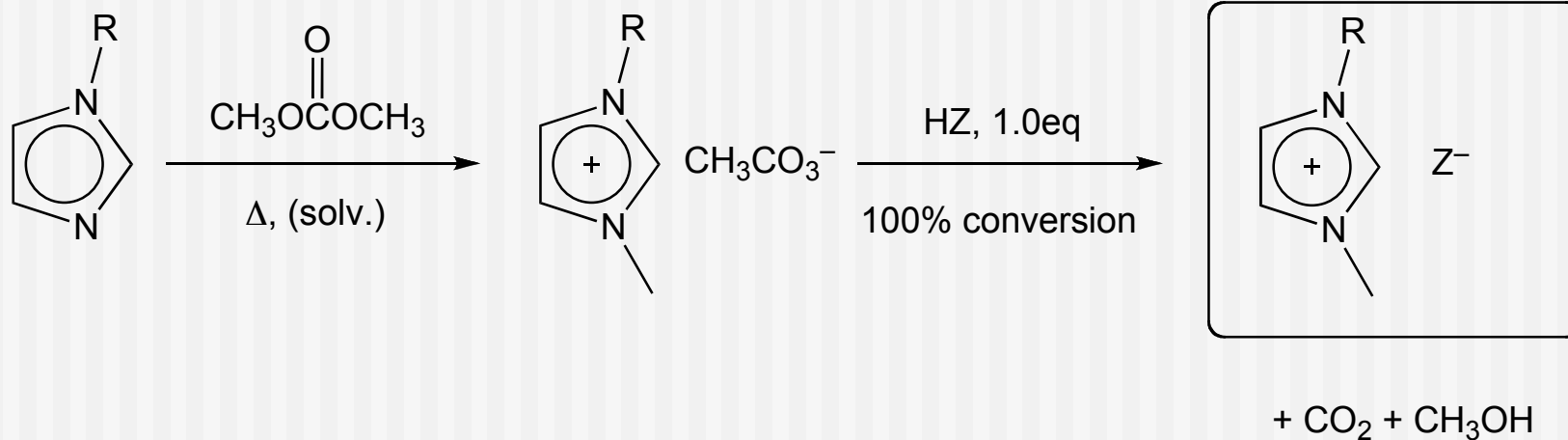


Synthesis of EMIM-OH: Ion exchange, bipolar electro dialysis
(König, Himmler, Wasserscheid, Uni Erlangen)

Drawbacks: EMIM-OH instable (solution <10%); generally: limited structures, only aqueous solutions, 1 mol eq. waste, energy consuming, expensive.

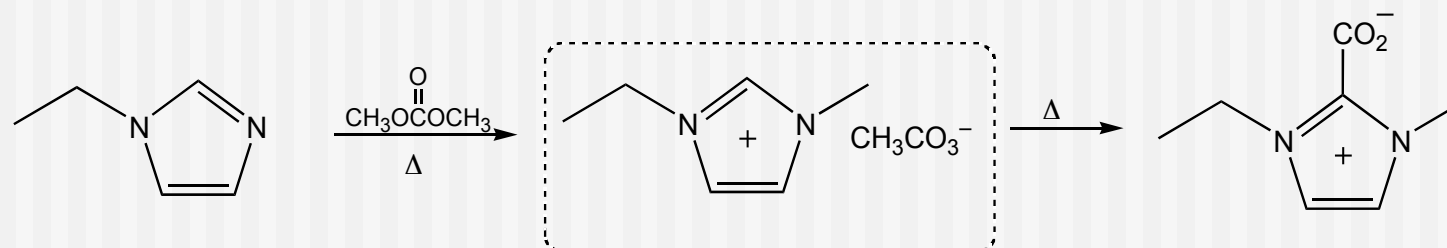
Fast IL building reactions

Carbonate Route:

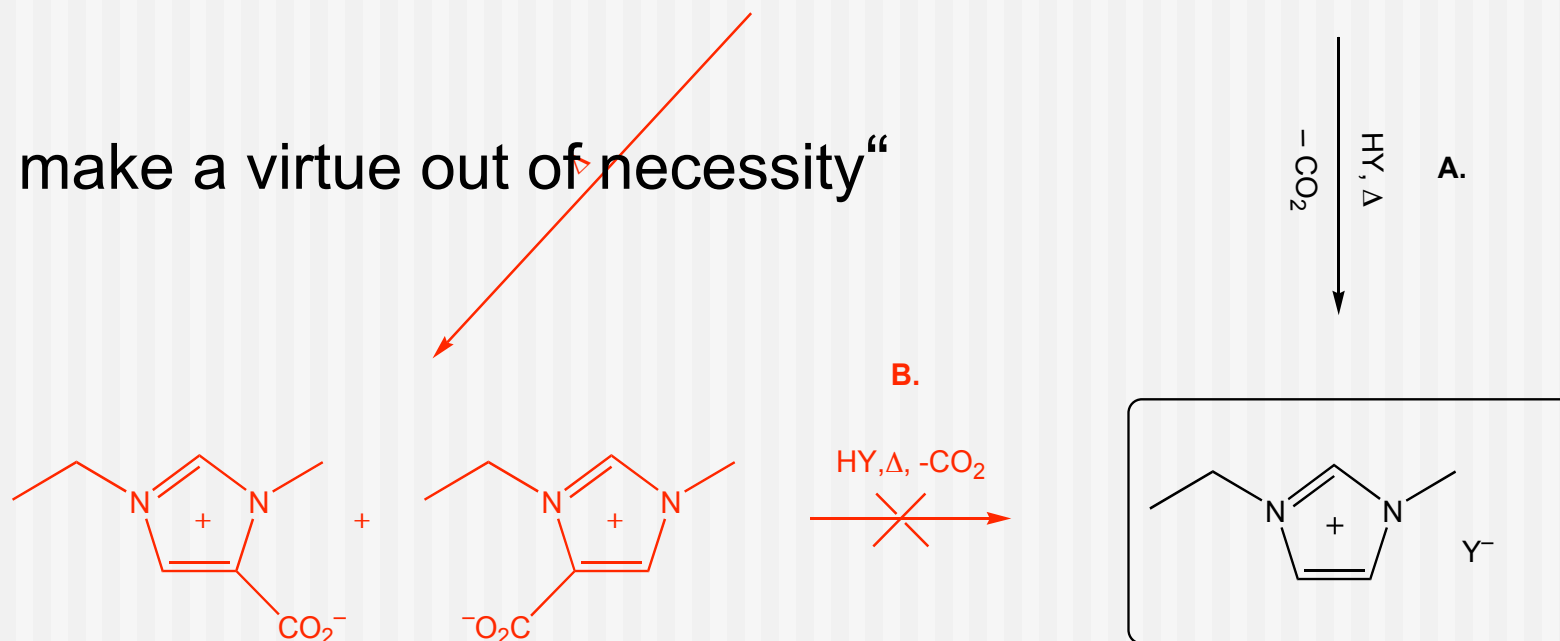


Published and patented 1991 (Mori et al).
 Drawbacks (not published): Side reactions!

Fast IL building reactions

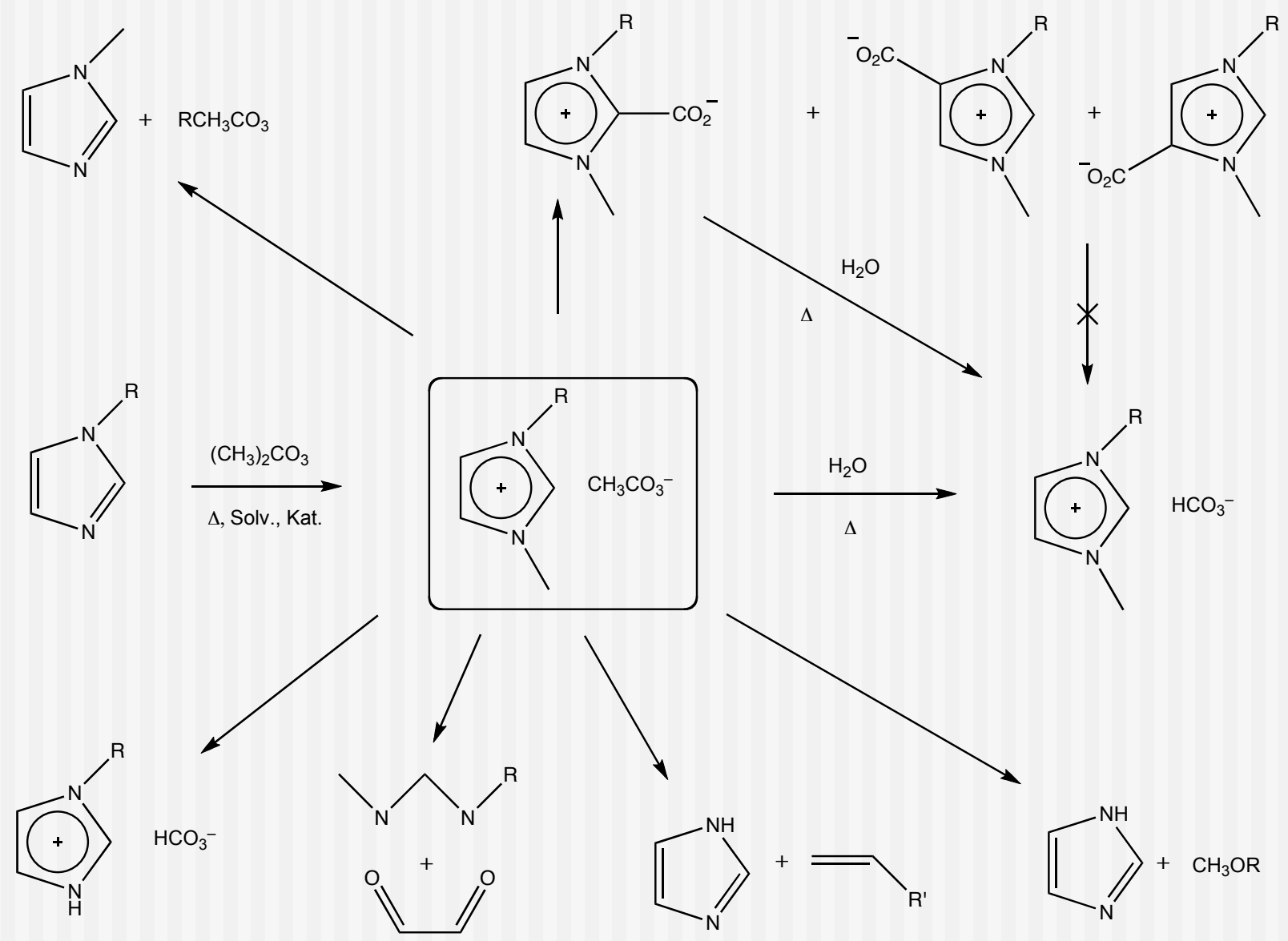


„to make a virtue out of necessity“





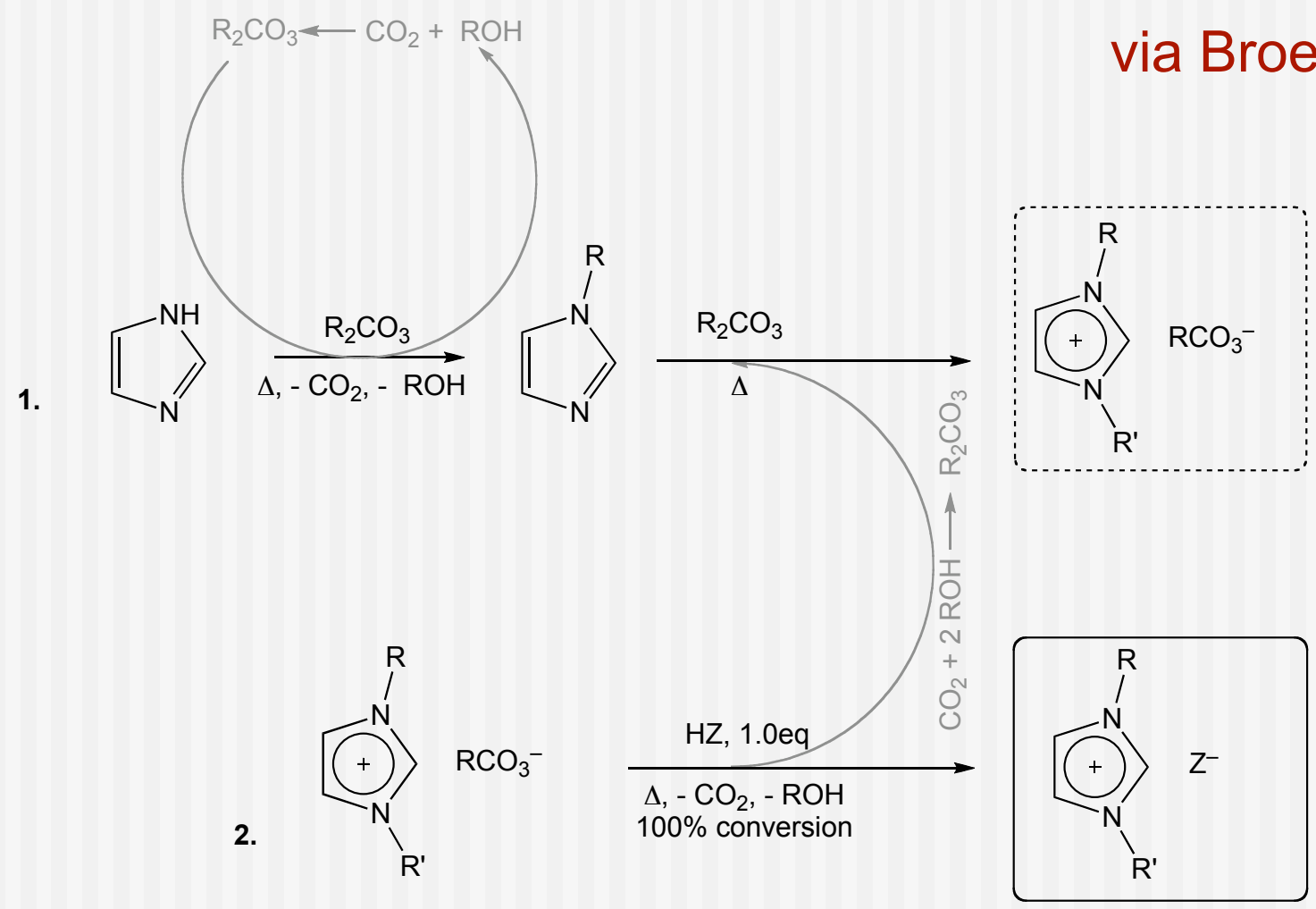
■ Carbonate Route: Side Reactions





CBILS[®] - Carbonate Based Ionic Liquid Synthesis

via Brønsted acids

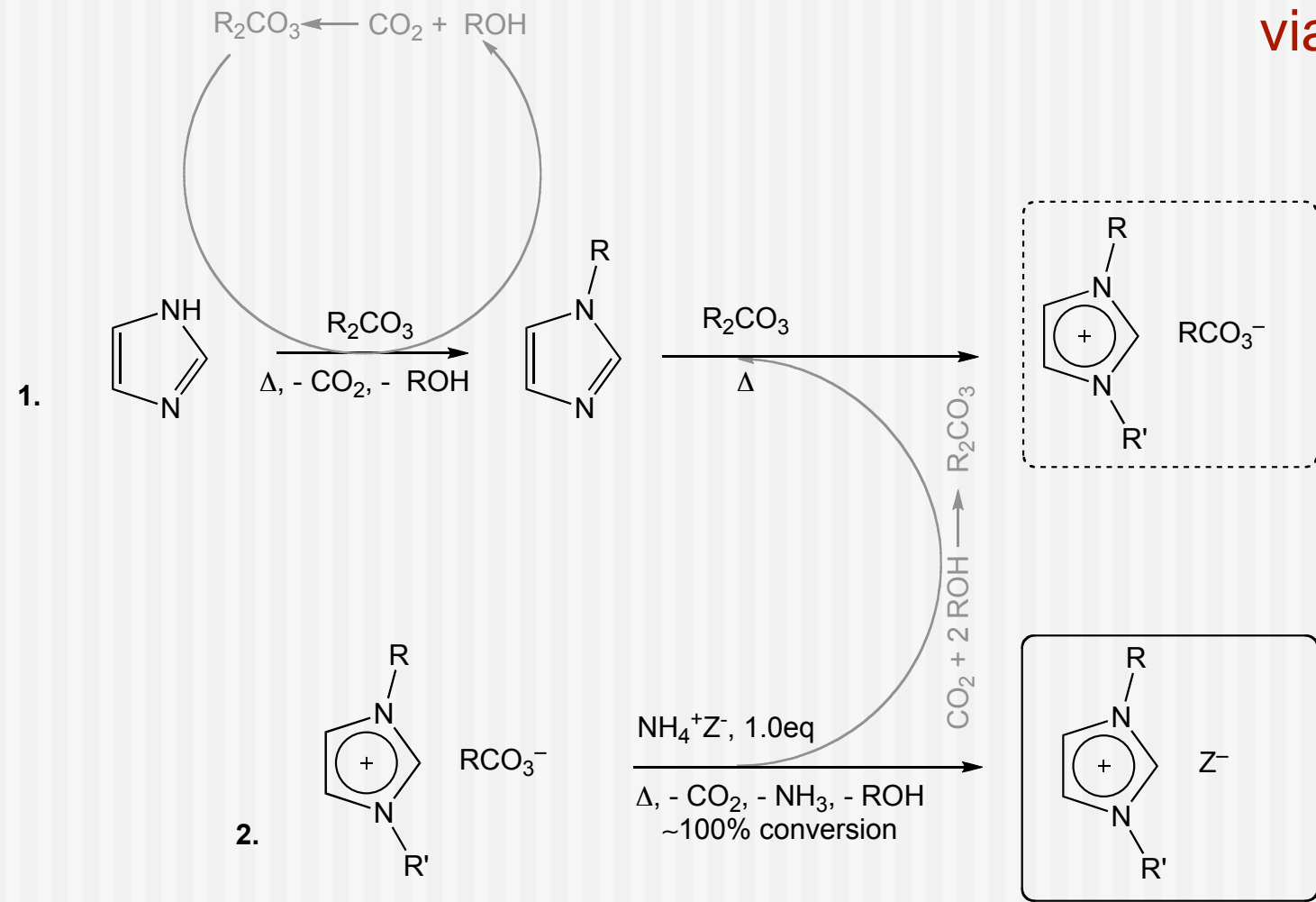




CBILS[®] - Carbonate Based Ionic Liquid Synthesis

via NH₄⁺-salts

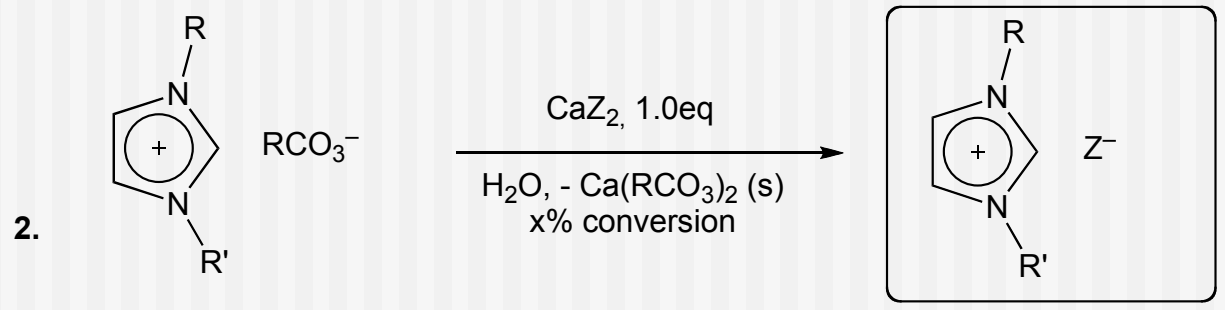
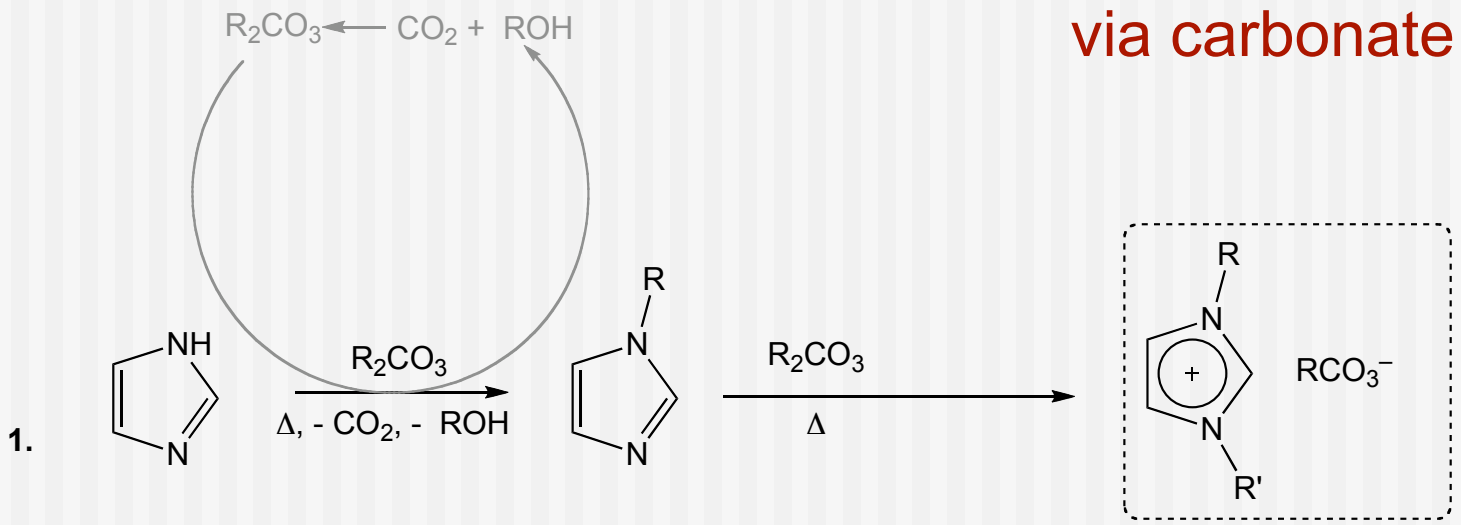
■ CBILS[®] Synthesis





CBILS[®] - Carbonate Based Ionic Liquid Synthesis

via carbonate metathesis



Screening: CBILS[®]-Synthesis

| | A1 ⁻ | A2 ⁻ | A3 ⁻ | A4 ⁻ | A5 ⁻ | A6 ⁻ | A7 ⁻ | A8 ⁻ | A9 ⁻ | A10 ⁻ |
|------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|
| K1 ⁺ | K1 ⁺ 1 ⁻ X | K1 ⁺ 2 ⁻ ✓ | K1 ⁺ 3 ⁻ ✓ | K1 ⁺ 4 ⁻ ✓ | K1 ⁺ 5 ⁻ X | K1 ⁺ 6 ⁻ ✓ | K1 ⁺ 7 ⁻ ✓ | K1 ⁺ 8 ⁻ ✓ | K1 ⁺ 9 ⁻ ✓ | K1 ⁺ 10 ⁻ ✓ |
| K2 ⁺ | K2 ⁺ 1 ⁻ ✓ | K2 ⁺ 2 ⁻ ✓ | K2 ⁺ 3 ⁻ X | K2 ⁺ 4 ⁻ ✓ | K2 ⁺ 5 ⁻ ✓ | K2 ⁺ 6 ⁻ ✓ | K2 ⁺ 7 ⁻ ✓ | K2 ⁺ 8 ⁻ ✓ | K2 ⁺ 9 ⁻ X | K2 ⁺ 10 ⁻ ✓ |
| K3 ⁺ | K3 ⁺ 1 ⁻ ✓ | K3 ⁺ 2 ⁻ ✓ | K3 ⁺ 3 ⁻ ✓ | K3 ⁺ 4 ⁻ ✓ | K3 ⁺ 5 ⁻ ✓ | K3 ⁺ 6 ⁻ ✓ | K3 ⁺ 7 ⁻ ✓ | K3 ⁺ 8 ⁻ ✓ | K3 ⁺ 9 ⁻ ✓ | K3 ⁺ 10 ⁻ ✓ |
| K4 ⁺ | K4 ⁺ 1 ⁻ ✓ | K4 ⁺ 2 ⁻ X | K4 ⁺ 3 ⁻ ✓ | K4 ⁺ 4 ⁻ ✓ | K4 ⁺ 5 ⁻ ? | K4 ⁺ 6 ⁻ X | K4 ⁺ 7 ⁻ ✓ | K4 ⁺ 8 ⁻ ✓ | K4 ⁺ 9 ⁻ ✓ | K4 ⁺ 10 ⁻ ✓ |
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| K10 ⁺ | K10 ⁺ 1 ⁻ X | K10 ⁺ 2 ⁻ ✓ | K10 ⁺ 3 ⁻ ✓ | K10 ⁺ 4 ⁻ ✓ | K10 ⁺ 5 ⁻ ✓ | K10 ⁺ 6 ⁻ ✓ | K10 ⁺ 7 ⁻ X | K10 ⁺ 8 ⁻ ✓ | K10 ⁺ 9 ⁻ ✓ | K10 ⁺ 10 ⁻ ✓ |

X Not working:

cation: no CBILS[®]-Carbonate

anion: conj. Brønstedt acid $pK_a > 8,5$
 or no NH_4^+ -salt
 or no Ca^{2+} , Li^+ , Mn^{2+} , Zn^{2+} ...salt...

✓ Working:

cation: CBILS[®]-Carbonate available and

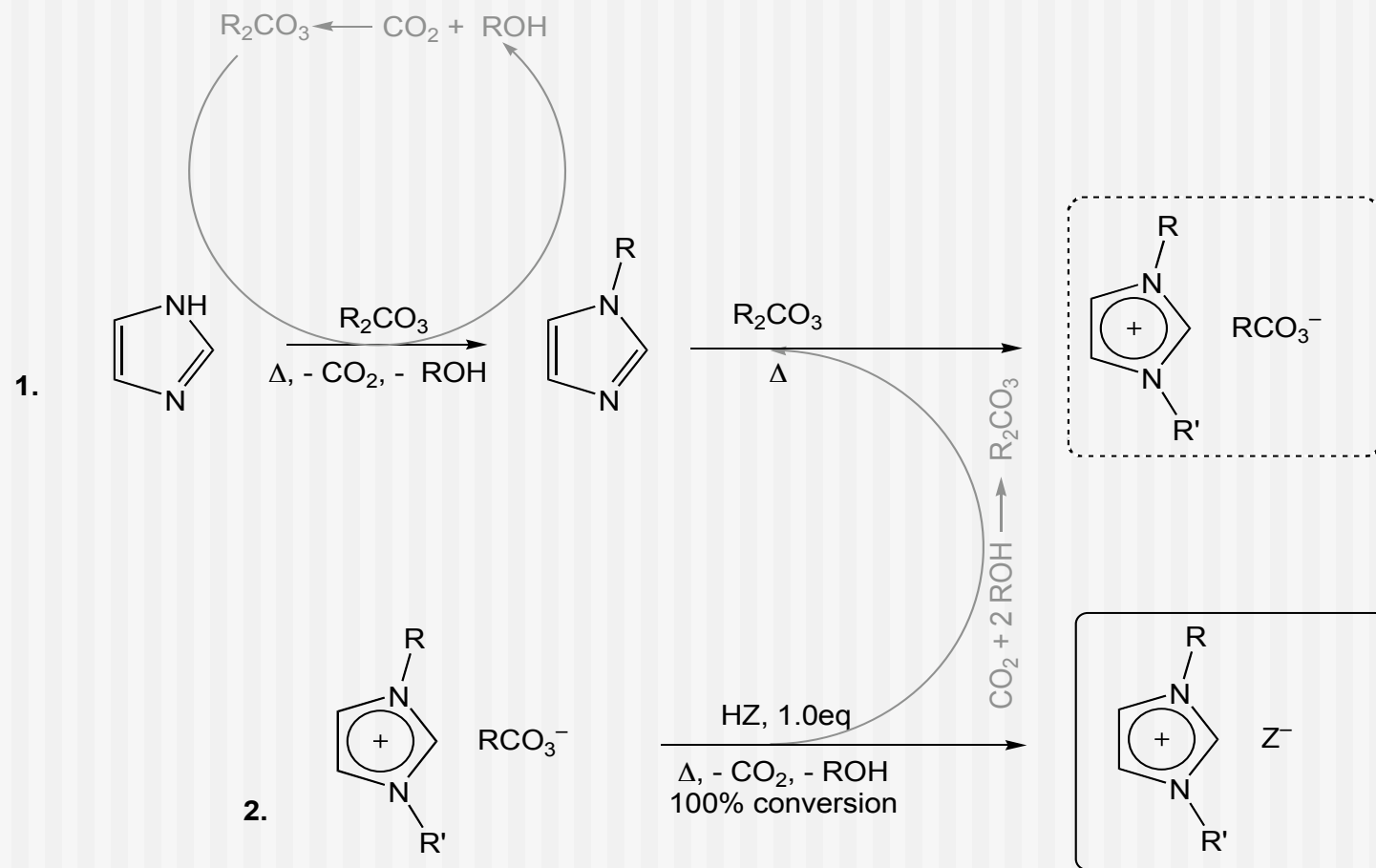
anion: conj. Brønstedt acid $pK_a < 8,5$
 or NH_4^+ -salt

? Aqueous metathesis:

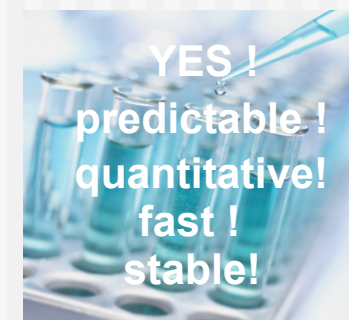
Only Ca^{2+} , Mg^{2+} , Li^+ , Mn^{2+} , Zn^{2+} salts available; to be tried experimentally!

Prediction calculable!

Carbonate Based Ionic Liquid Synthesis

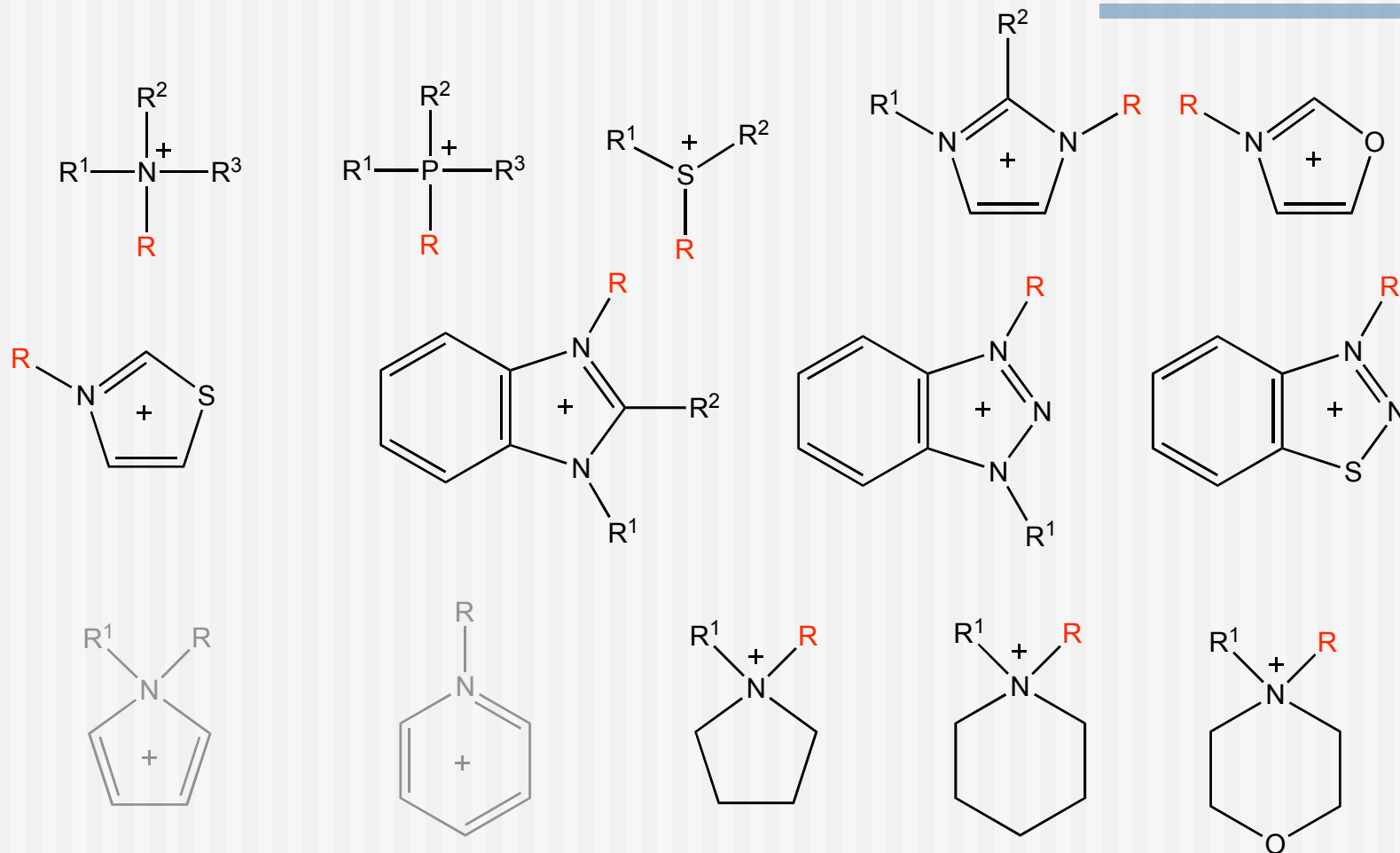


Combinatorial approach ?





CBILS®-Cations



R: CH₃, C₂H₅, Benzyl, Phenyl

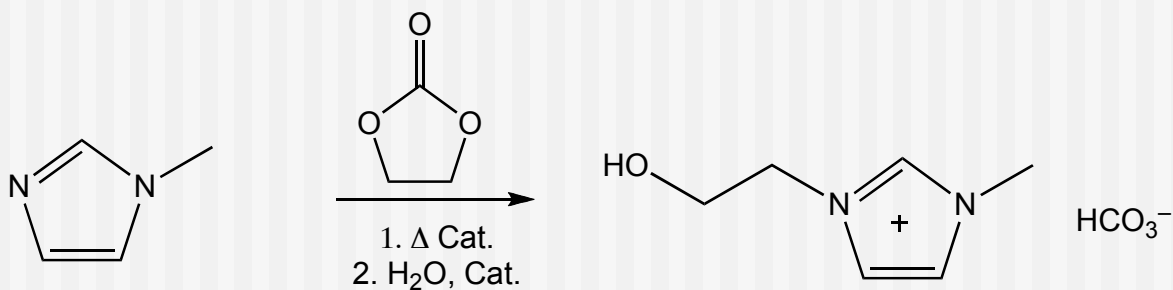
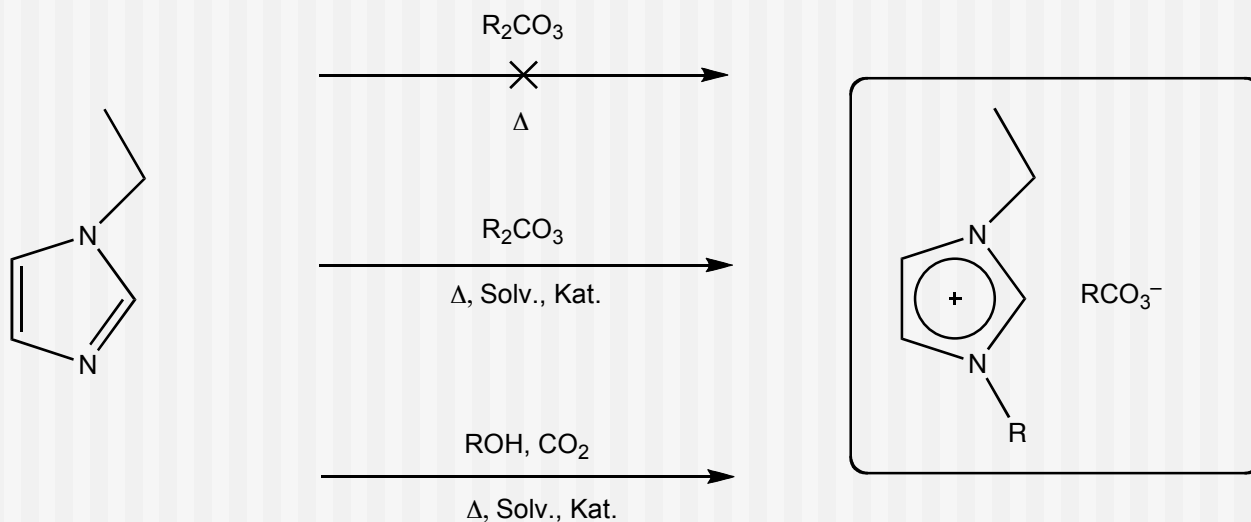
R¹, R², R³: H, Alkyl C1 bis C16, Vinyl, Allyl, Aryl, Si-Derivates, ...



Carbonate Based Ionic Liquid Synthesis

- Very fast: 5 min Brønstedt acids, 1h NH_4^+ -salts
- Halogen free, typically <10ppm
- Optional water free
- Very flexible:
 - Inorganic and organic acids.
 - Short to long side chains, alkyl or aryl side chains.
 - Functionalized acids, chiral acids, weak acids ($\text{pK}_a < 9$).
 - Insoluble acids or their anhydrides (even WO_3 !)
 - Works independently whether product is liquid, highly viscous, solid, soluble, insoluble...
- Driven by shifting of the chemical equilibrium by CO_2 removal!

Alkylation with Higher Homologues





Properties of CBILS[®]-Carbonates

- **Quaternary Alkylcarbonates generally**
 - Low melting solids (20°C to 65°C)
 - Stable at RT as solids, very stable over years in solution ≤90
 - Basicity comparable to CO_3^{2-}
 - Good soluble in polar solvents

- **Di- and Trialkylimidazolium-Alkylcarbonates**
 - Stable in solution ≤90% for years at RT (H_2O , ROH, CH_3CN)
 - Isolated: low melting solids, forming 2-, 4- and 5-Carboxylates



■ Functional & Engineering Fluids

Activities

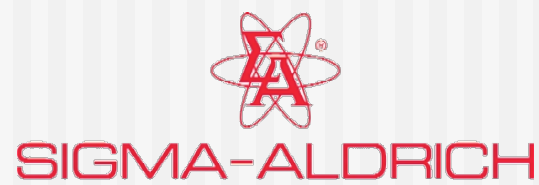
- CBILS[®] (Carbonate Based Ionic Liquid Synthesis)
- Gas Compression (Linde AG)
- Gas Cleaning
- Hydrogen storage
- Lubrication Media
- Hydraulic Fluids
- Sorption Media
- Extraction Media (metals; petrochemicals)
- Electroplating
- Magnetic Ionic Liquids
- Switching Ionic Liquids
- Neuronal Modelling with *cVision*[®]





Commercial Availability CBILS[®]-Carbonates

- g to 100g quantities:



- 100g to 100kg quantities:



- 100kg to ton quantities:





Thank you for your attention!



