Politechnika
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INICJATYWA DOSKONAŁOŚCI

CHROBOK
IONIC LIQUID
GROUP

Functional Materials for a Greener Future

OUR TEAM

CHROBOK
IONIC LIQUID
GROUP

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Assistant professor

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Assistant professor

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Senior technician

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Magdalena Gwóźdź
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Lema Shumi
PhD student

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REASERCH PROJECTS

- Heterogeneous catalysts based on carbon nanostructures in model chemical reactions
- Tunable liquid metal complexes as catalysts for the model chemical and electrochemical processes
- N-doped carbons as catalysts for model electrochemical and chemical processes
- Tailoring cementitious composites with sustainable ionic-based compounds: Assessment of structural and performance characteristics

- Ionic bio-aerogels for carbon dioxide (CO_2) capture and bioconversion
- Bio-based surfactants for sustainable micellar catalysis

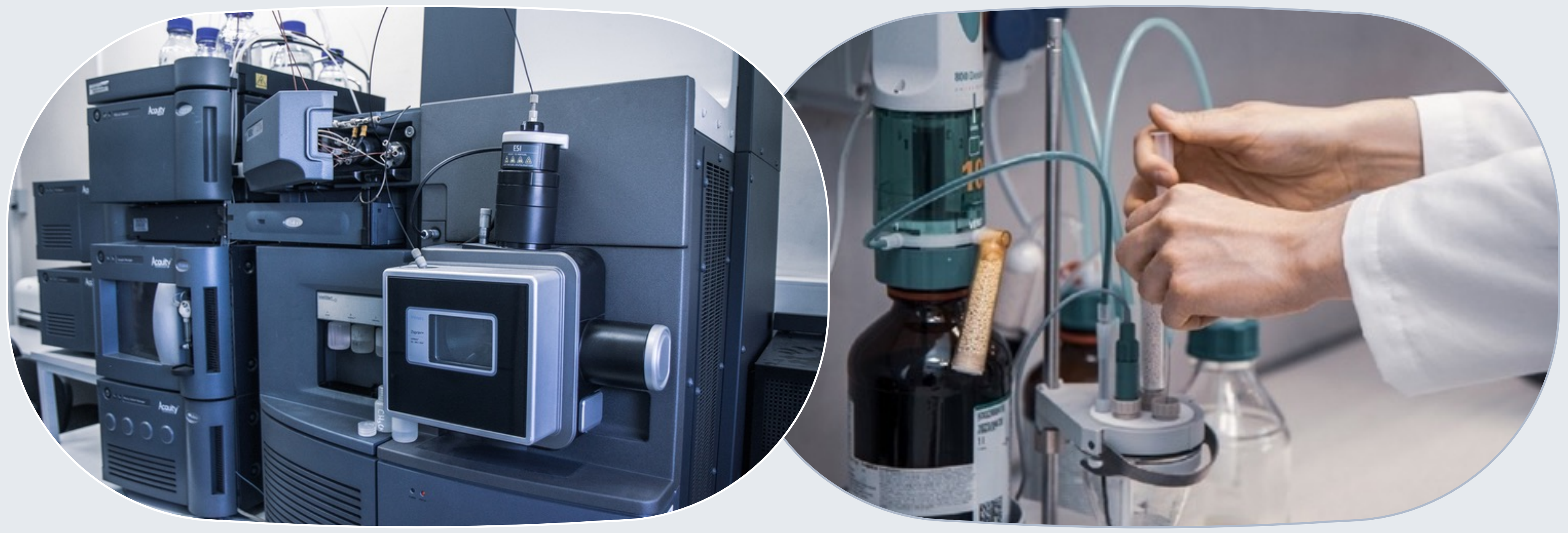
- Environmentally friendly process of adipic acid synthesis by oxidation of cyclohexanone
- New types of food packages using renewable raw materials and innovative paraffin based impregnates
- Process for the preparation of ε-caprolactam from cyclohexanone and hydrogen peroxide by chemo-enzymatic catalysis
- IoLacTec: Innovative method for acidic ionic liquids mediated lactams production

- Designing and study on the catalytic performance of a new liquid metal complexes
- Studies on the catalytic performance of biocatalysts based on supported ionic liquids
- Designing of supported ionic liquid phase catalysts dedicated for continuous flow synthesis of fine chemicals

- Method of synthesis of esters using innovative catalysts based on ionic liquids and zinc oxide

ORGANIC SYNTHESIS

ANALYSIS OF ORGANIC PROCESSES



INDUSTRIAL PROJECT

SOLVENT WISTOL S.A.

INNOVATIVE PROCESS
FOR SOLVENT SYNTHESIS
(2020)

Grupa Azoty
KĘDZIERZYN

SYNTHESIS OF ALTERNATIVE
PLASTICIZERS USING
INNOVATIVE CATALYSTS (2021)

Grupa Azoty
PUŁAWY

DEVELOPMENT OF AN
INNOVATIVE PROCESS FOR
PRODUCING CAPROLACTONE
(2023)

ORLEN Południe

SYNTHESIS OF GREEN
SOLVENTS (2024)

SCIENTIFIC AND INDUSTRIAL COLLABORATION

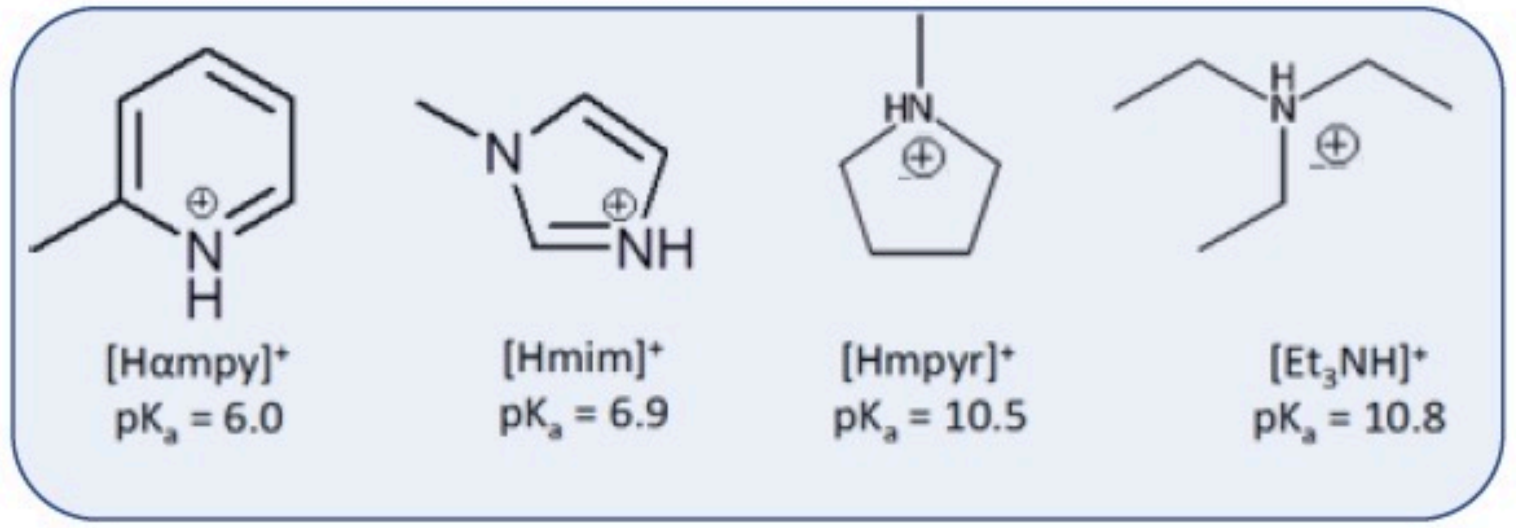
PROTIC IONIC LIQUIDS BASED ON AMINE AND SULFURIC ACID

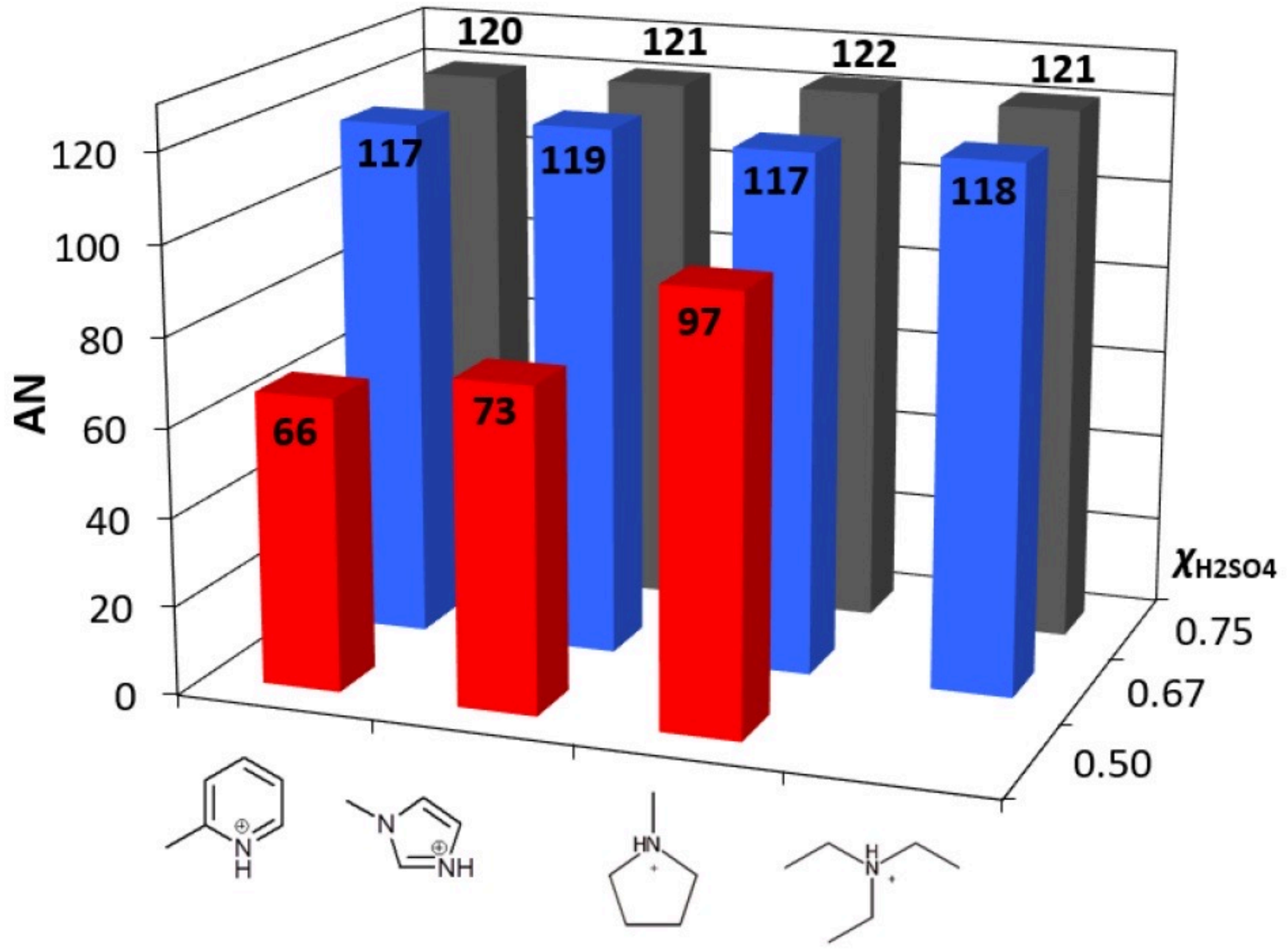
$H_2SO_4 + B \rightarrow [HB][HSO_4]$ $\chi_{H2SO4} = 0.50$ m. p. < 100°C

$2H_2SO_4 + B \rightarrow [HB][(HSO_4)(H_2SO_4)]$ $\chi_{H2SO4} = 0.67$

$3H_2SO_4 + B \rightarrow [HB][(HSO_4)(H_2SO_4)_2]$ $\chi_{H2SO4} = 0.75$

RT ILs, $T_g < 0°C$





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PCCP

Physical Chemistry Chemical Physics

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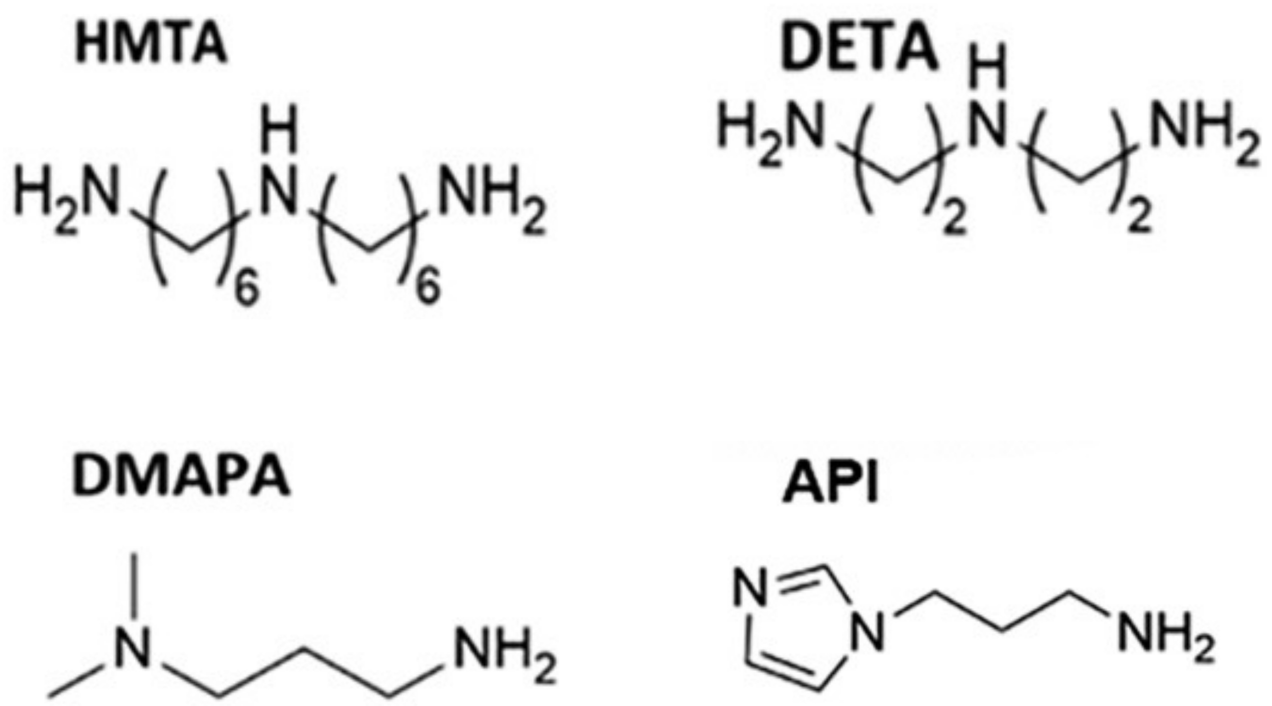
ISSN 1463-9076

ROYAL SOCIETY OF CHEMISTRY

PAPER
John D. Holbrey, Małgorzata Swadźba-Kwaśny *et al.*
The structure of protic ionic liquids based on sulfuric acid, doped with excess of sulfuric acid or with water

Reagent	Reagent price ($/L	Product	Laboratory cost ($/kg)*
DMAPA	25.1	DMAPA_6_1	21.0
DETA	66.9	DETA_9_1	24.6
HMTA	160	HMTA_9_1	51.2
TEA	81	TEA_3_1	42.9
Sulfuric acid	35.5		



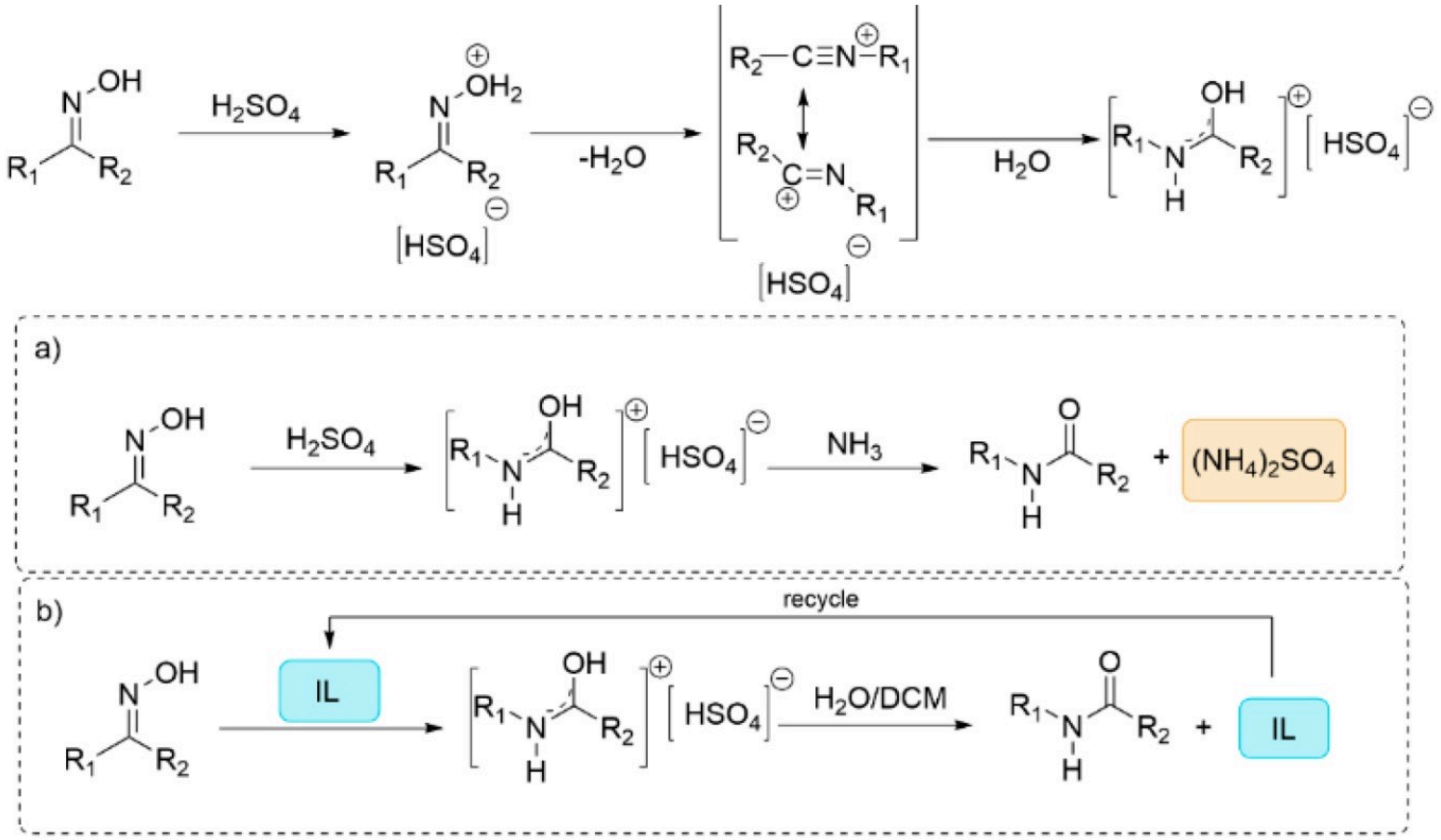
Silesian University of Technology

RESEARCH UNIVERSITY
EXCELLENCE INITIATIVE

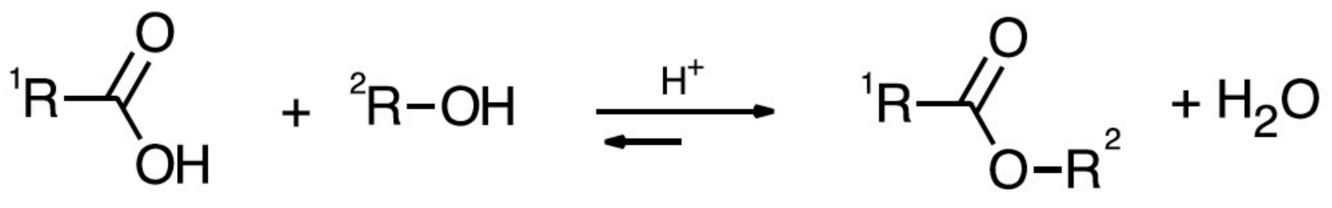
K.Matuszek,A.Chrobok,F.Coleman,K.R.Seddon,M.Swadźba-Kwaśny,***GreenChem.*,2014,**16,3463.
A.Brzęczek-Szafran,J.Więcławik,N.Barteczko,A.Szelwicka,E.Byrne,A.Kolanowska,M.Swadźba-Kwaśny,A.Chrobok,***GreenChem.*,2021,**23,4421.
A.McGrogan,E. L. Byrne,R. Guiney,T. F. Headen,T. G. A. Youngs,A. Chrobok, J.D. Holbrey, M. Swadźba-Kwaśny, *Phys. Chem. Chem. Phys.*, **2023**, 25, 9785
A. Brzęczek-Szafran, K. Erfurt, M. Swadźba-Kwaśny, T. Piotrowski, A. Chrobok, *ACS SustainableChem. Eng.***2022**, 10, 41.
K. Matuszek, A. Brzeczek-Szafran, D. Kobus, Dominika; D. MacFarlane, M. Swadzba-Kwasny, A. Chrobok, *Aust. J. Chem.*, **2019**, 72, 130.

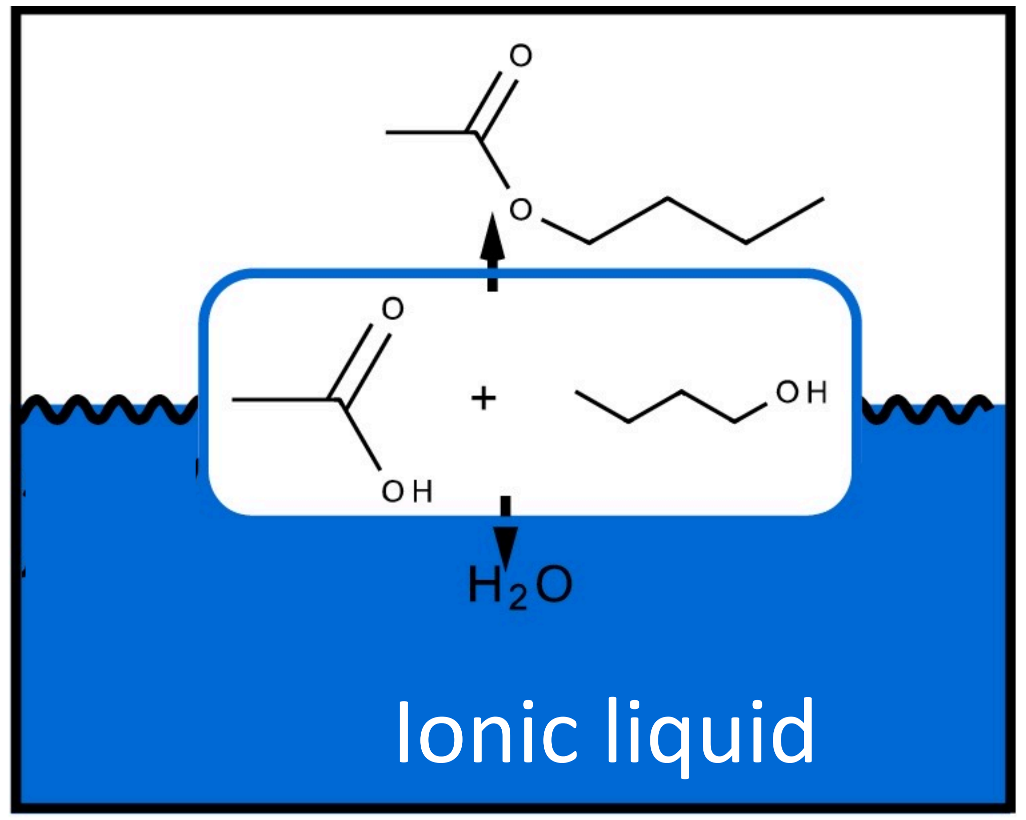
PROTIC IONIC LIQUIDS APPLICATIONS

Beckmann Rearrangement

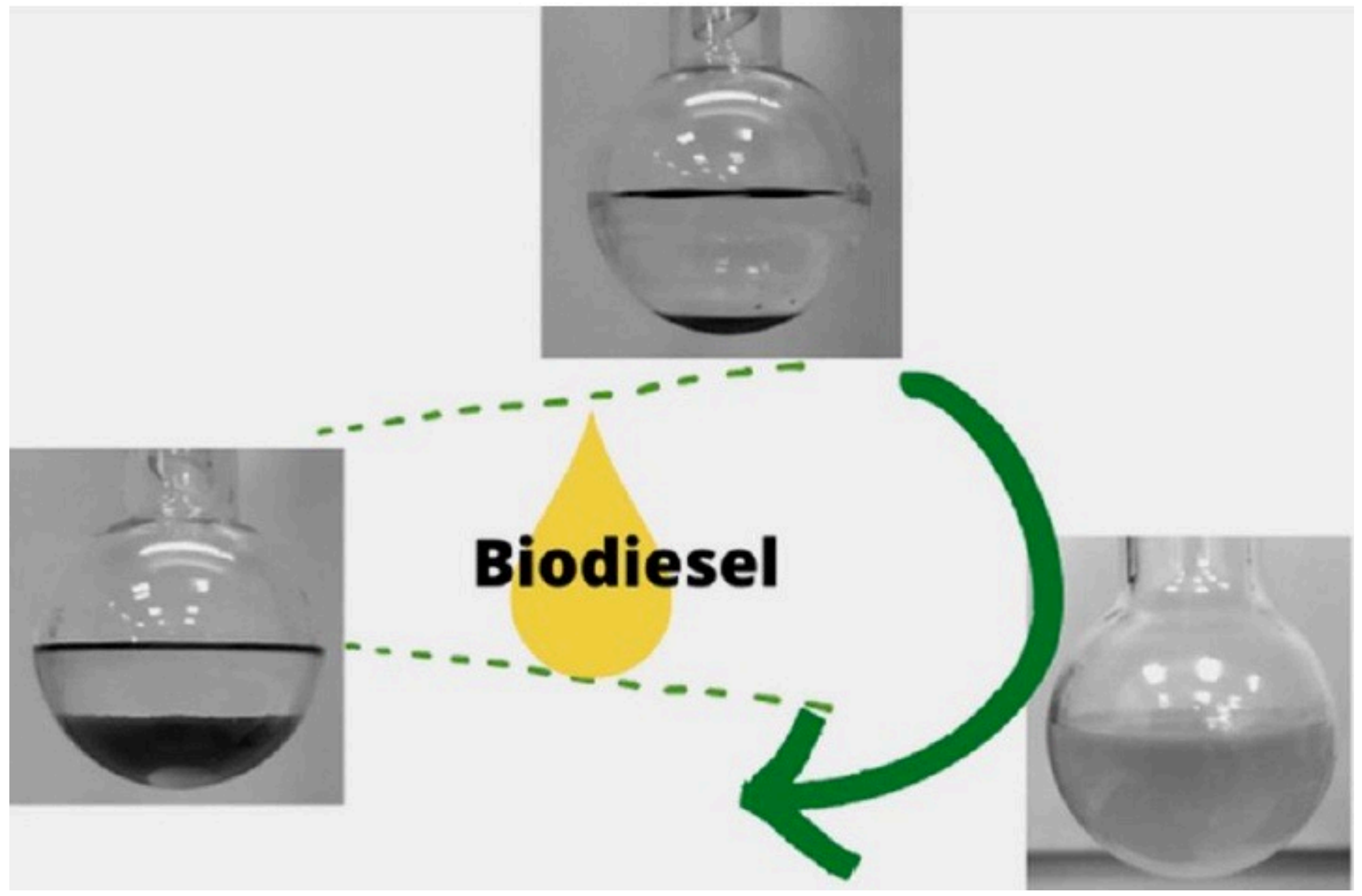


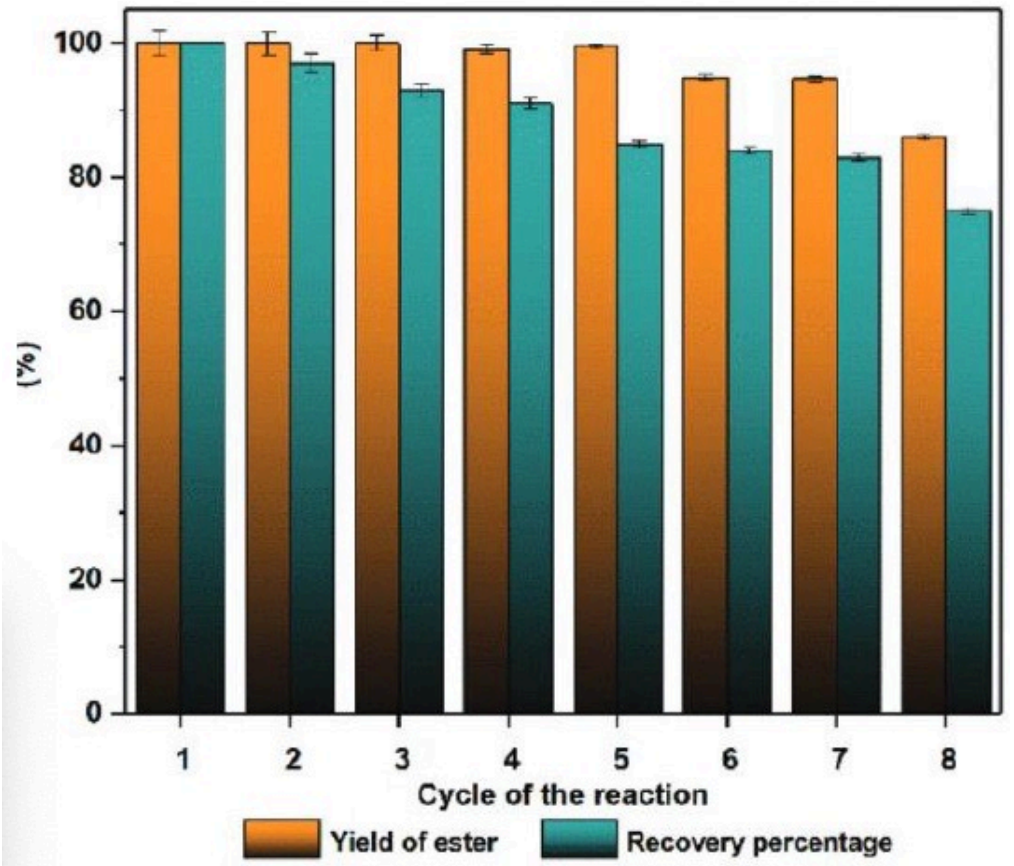
Fisher Esterification

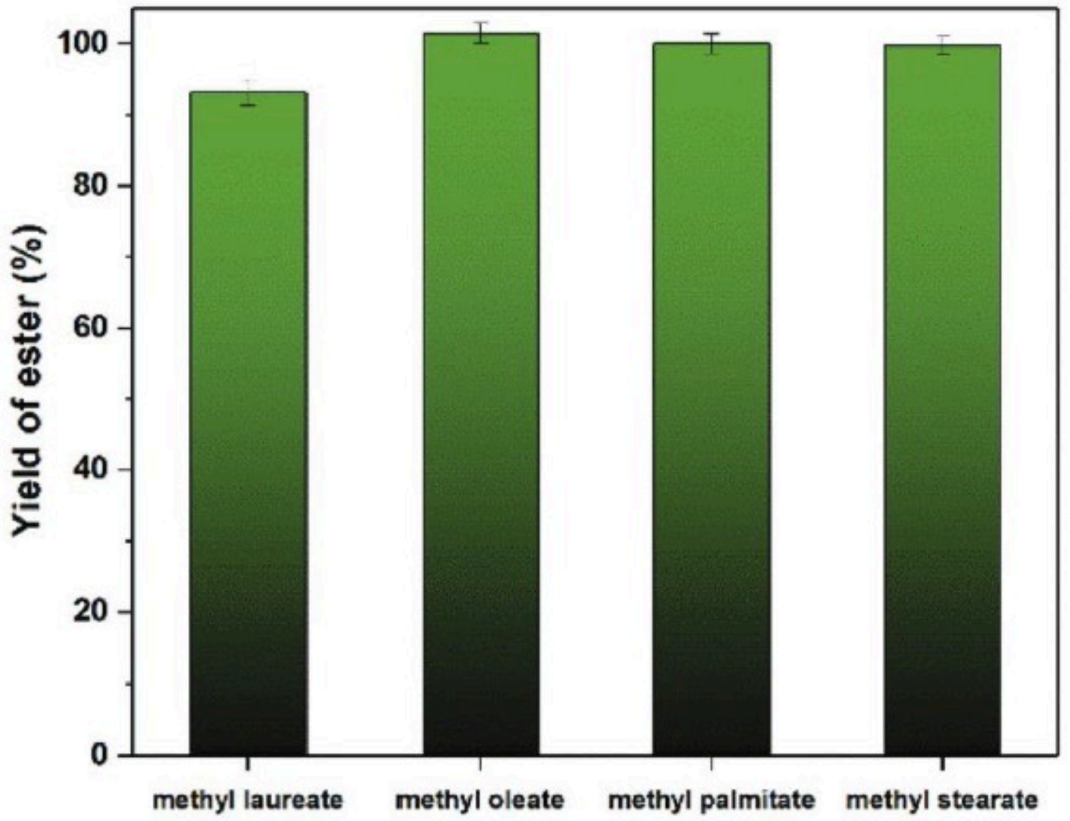




Biodiesel production







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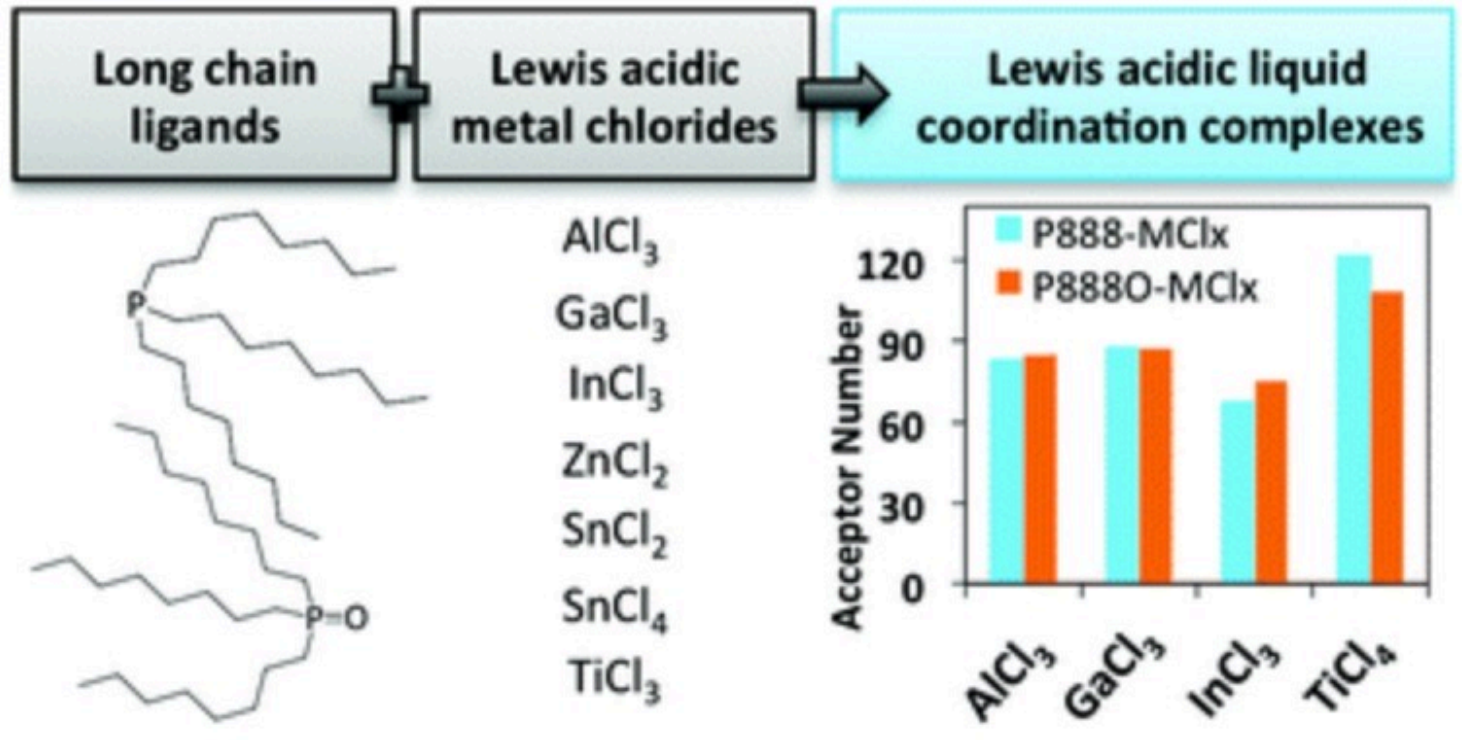
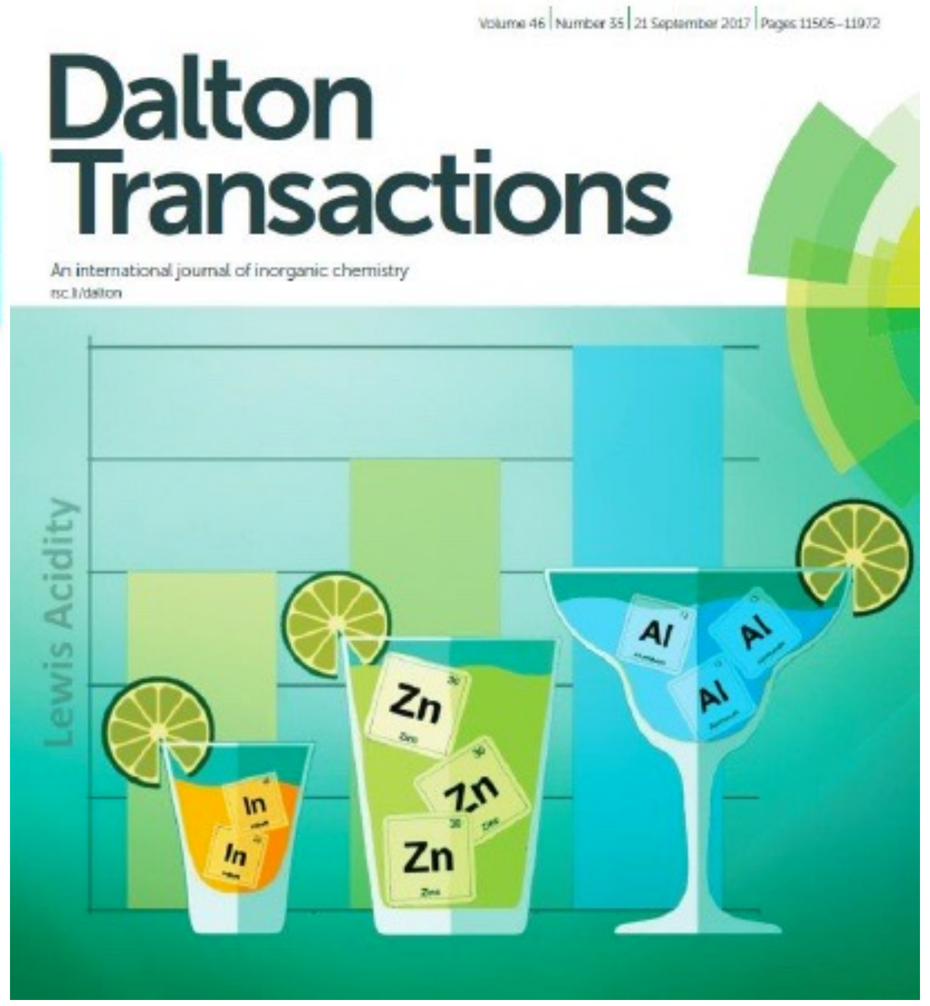
A. Brzęczek-Szafran, J. Więcławik, N. Barteczko, A. Szelwicka, E. Byrne, A. Kolanowska, M. Swadźba Kwaśny, A. Chrobok, Green Chem., **2021**, 23,4421

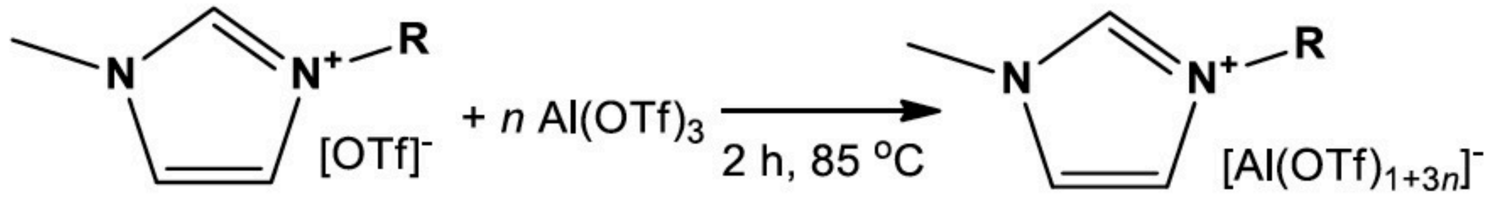
MATALLATE IONIC LIQUID

Chlorometallate ionic liquids



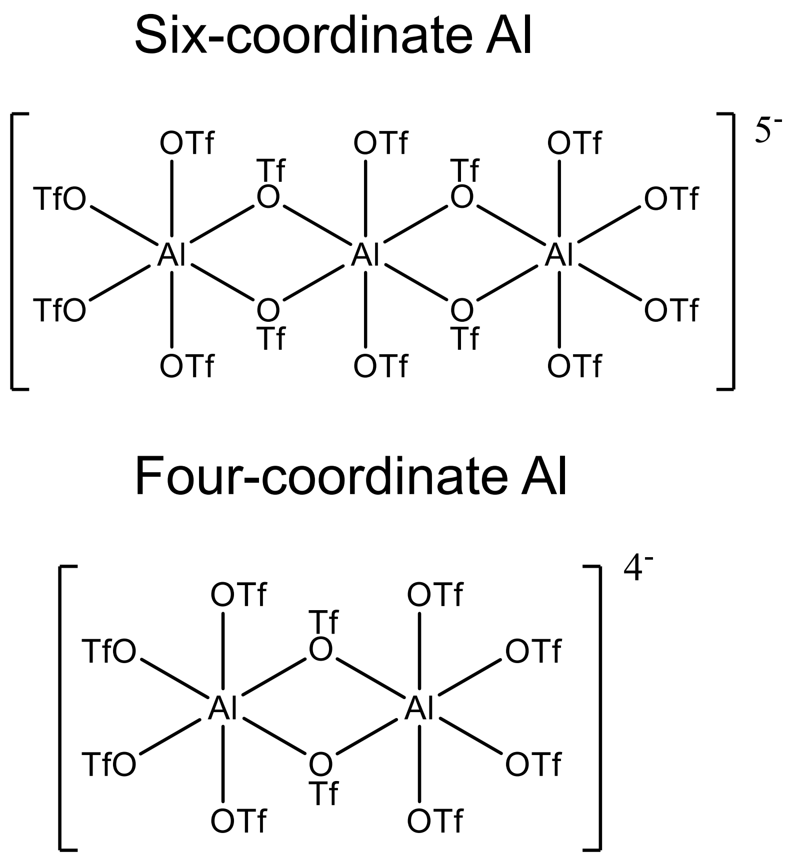


Trifloaluminate ionic liquids

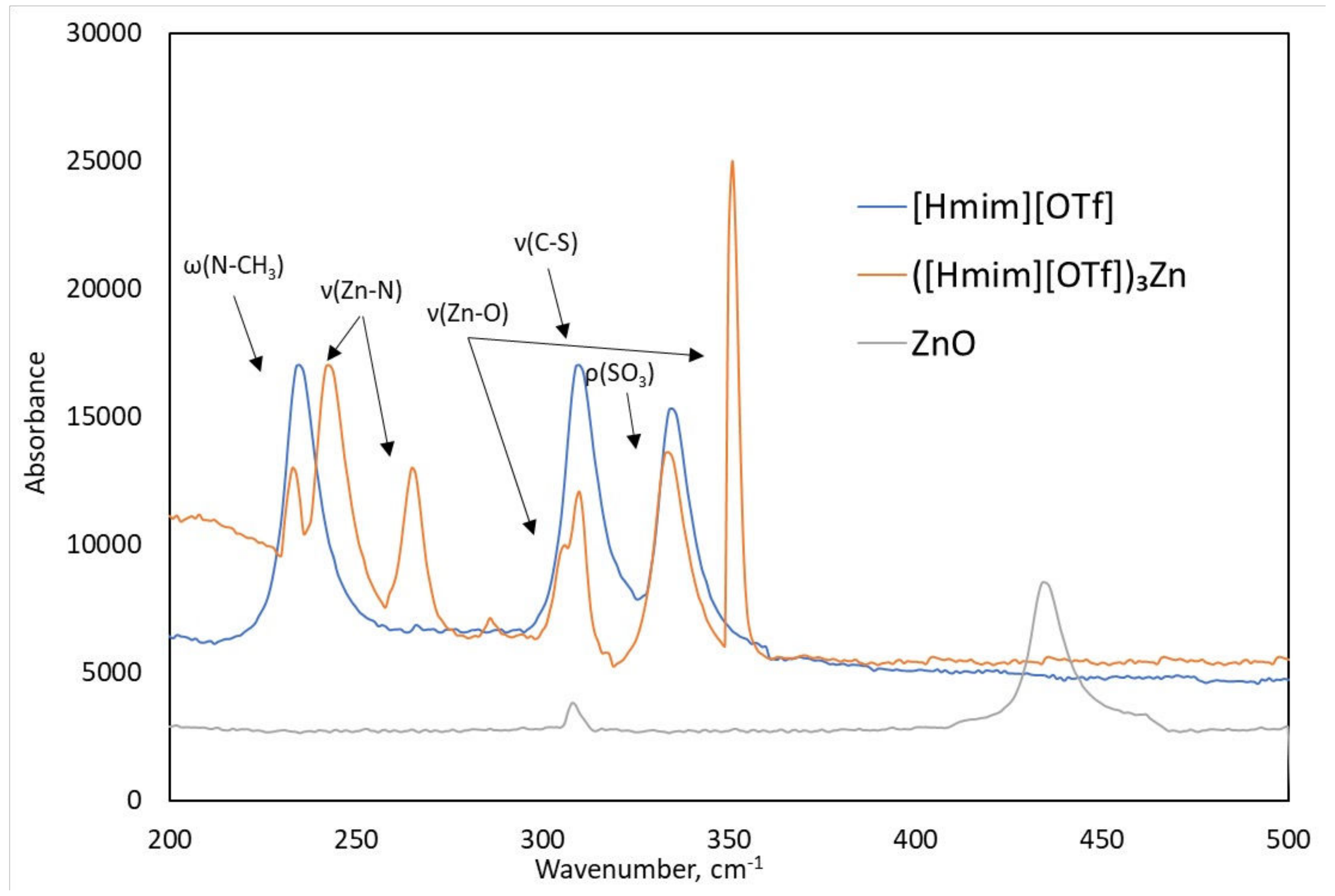


$[C_nmim][OTf]$-$Al(OTf)_3$

Molar ratio Al(OTf)$_3$: $\chi_{Al(OTf)3}$ = **0.15, 0.25, 0.33**, 0.375, 0.40, 0.50



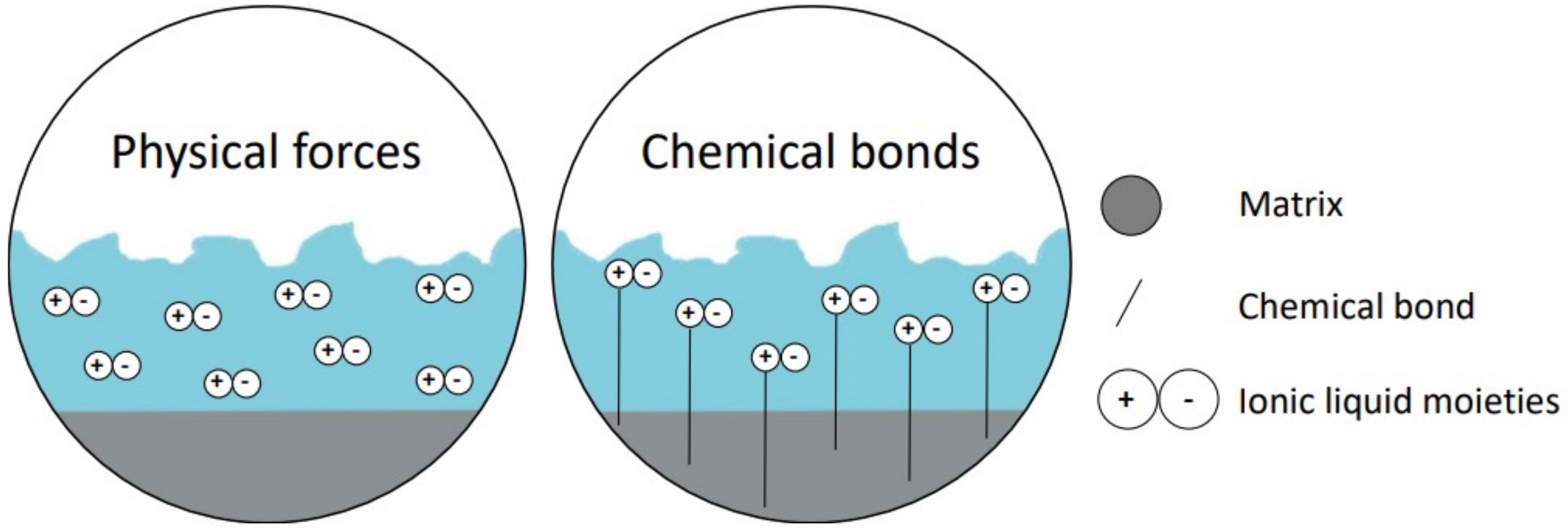
Zn-based ionic liquids



J.Hogg,L.Christobel,K.Matuszek,P.Latos,A.Chrobok,M.Swadźba-Kwasny,,DaltonTrans.,2017,46,11561.
K. Matuszek, A. Chrobok, J. M. Hogg, F. Coleman, M. Swadźba-Kwaśny, Green Chem., 2015, 17, 4255.
P. Latos, A. Culkin, N. Barteczko, S. Boncel, S. Jurczyk, L. C. Brown, P. Nockemann, A. Chrobok, M. Swadźba-Kwaśny, Front. Chem., **2018,** 6:535.
P. Latos, J. Gabzdyl, K. Erfurt, D. Łukowiec, A. Maximenko, S. Jurczyk, A. Chrobok, Catal. Today, **2024**, 114806.

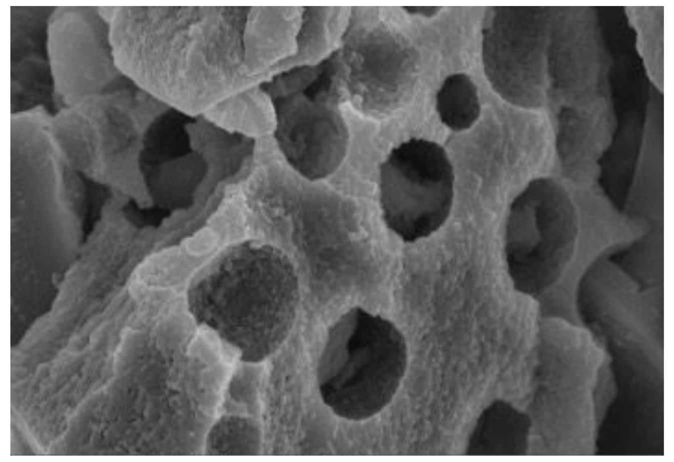
MATALLATE IONIC LIQUID

Supported ionic liquid phase – heterogeneous catalysis

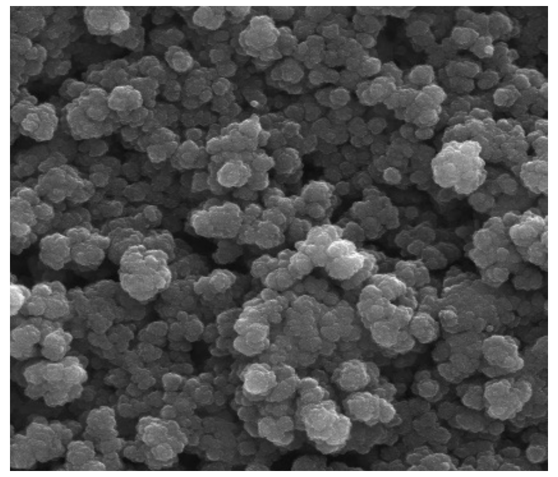


- Effortless catalyst separation and recycling
- Improves mass transfer in the process
- Reduces required ionic liquid amount in the process

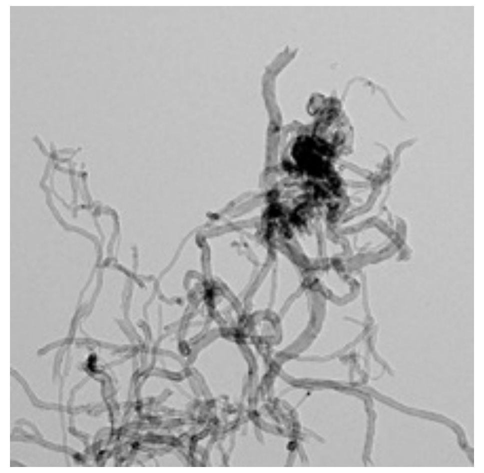
Supports used for ionic liquid immobilization



Multimodal silica

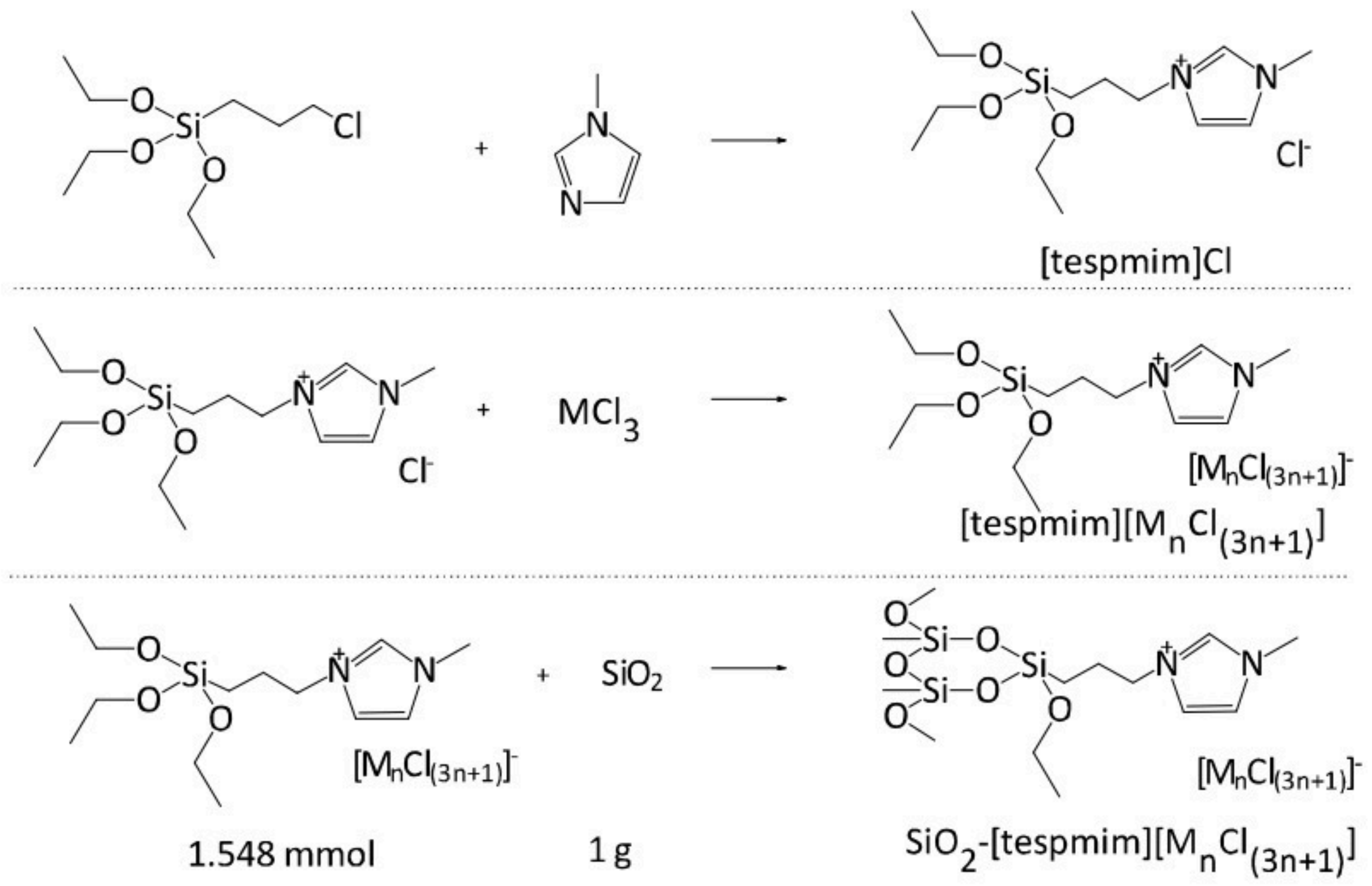


Magnesium oxide – silica hybrid

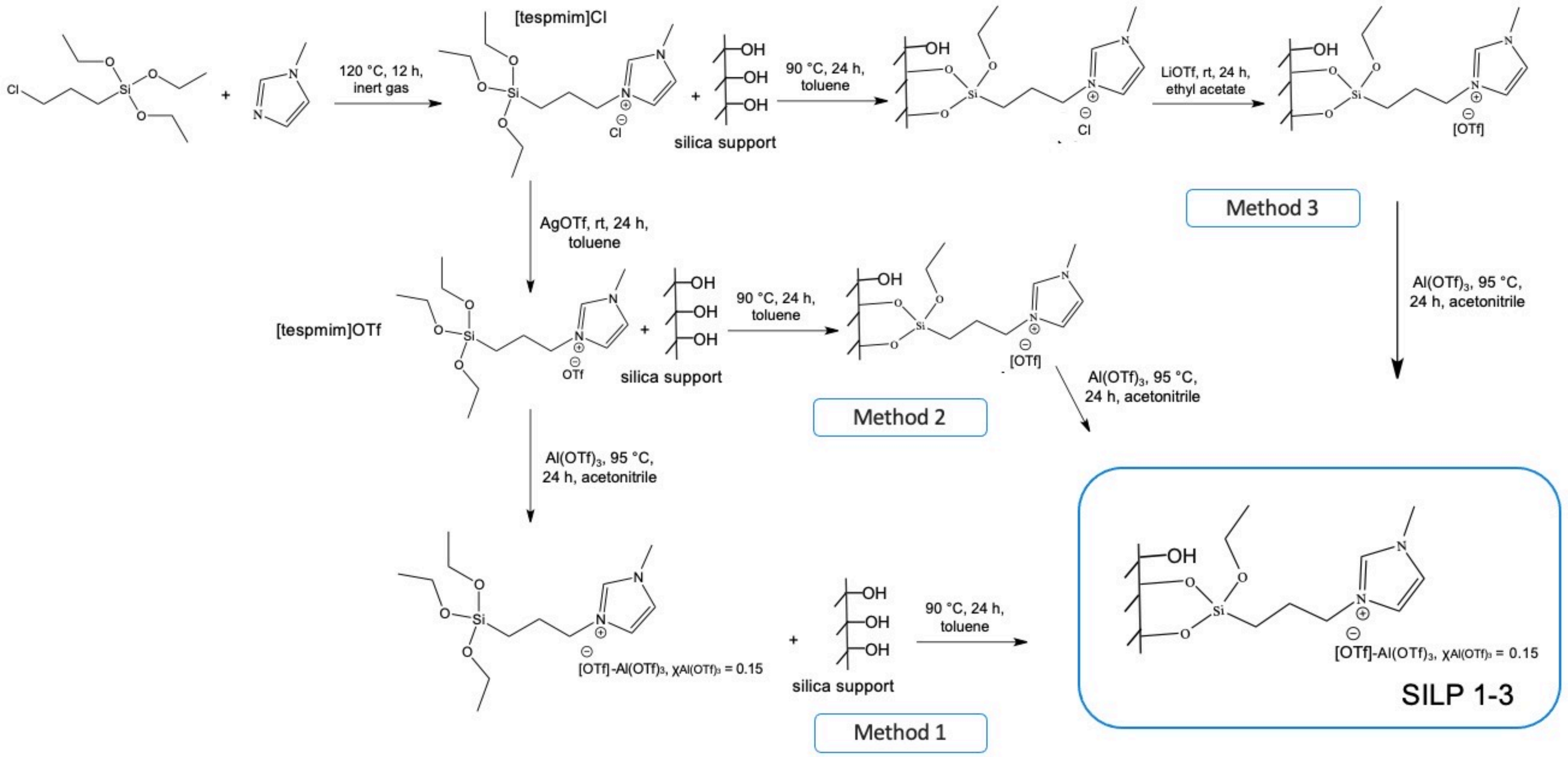


Multiwalled carbon nanotubes

Supported chlorometallate ionic liquids



Supported trifloaluminate ionic liquids

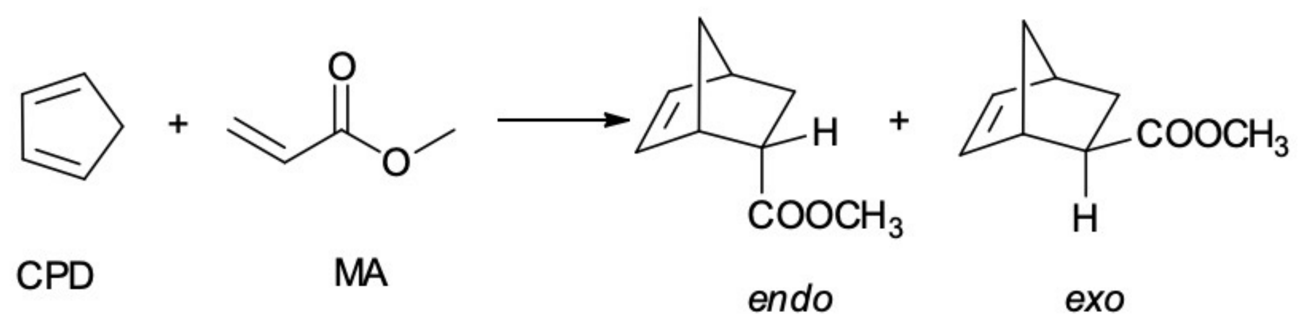


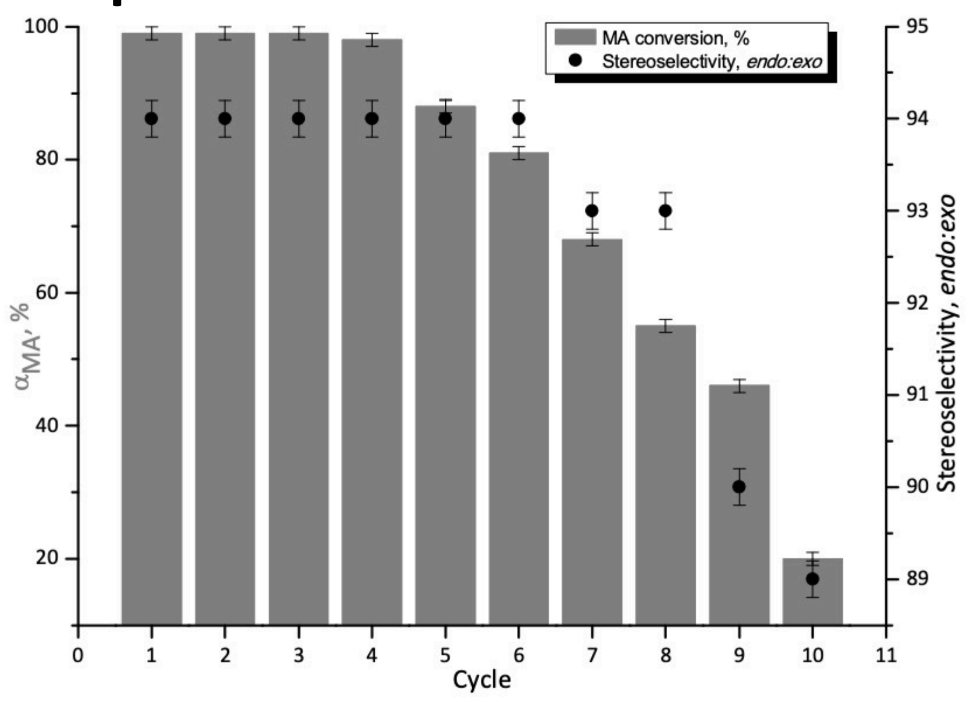
A.Wolny, P. Latos, K. Szymańska, S. Jurczyk, A. Jakóbik Kolon, A. Chrobok, Appl . Catal . A: Gen 2024 , 676 , 119676
P. Latos, A. Wolny, J. Zdarta, F. Ciesielczyk, S. Jurczyk, T. Jesionowski, A. Chrobok, Environ. Technol. Innov. 2023, 31, 103164A.
K.Matuszek, A. Chrobok, P. Latos, K. Szymańska, A. Jarzębski, M. Swadźba-Kwaśny, Catal. Sci. Technol., 2016,6, 8129-8137
A. Wolny, A. Chrobok,, Molecules 2022, 27, 5900.

MATALLATE IONIC LIQUID'S APPLICATIONS

Diels-Alder cycloaddition between methyl acrylate and cyclopentadiene

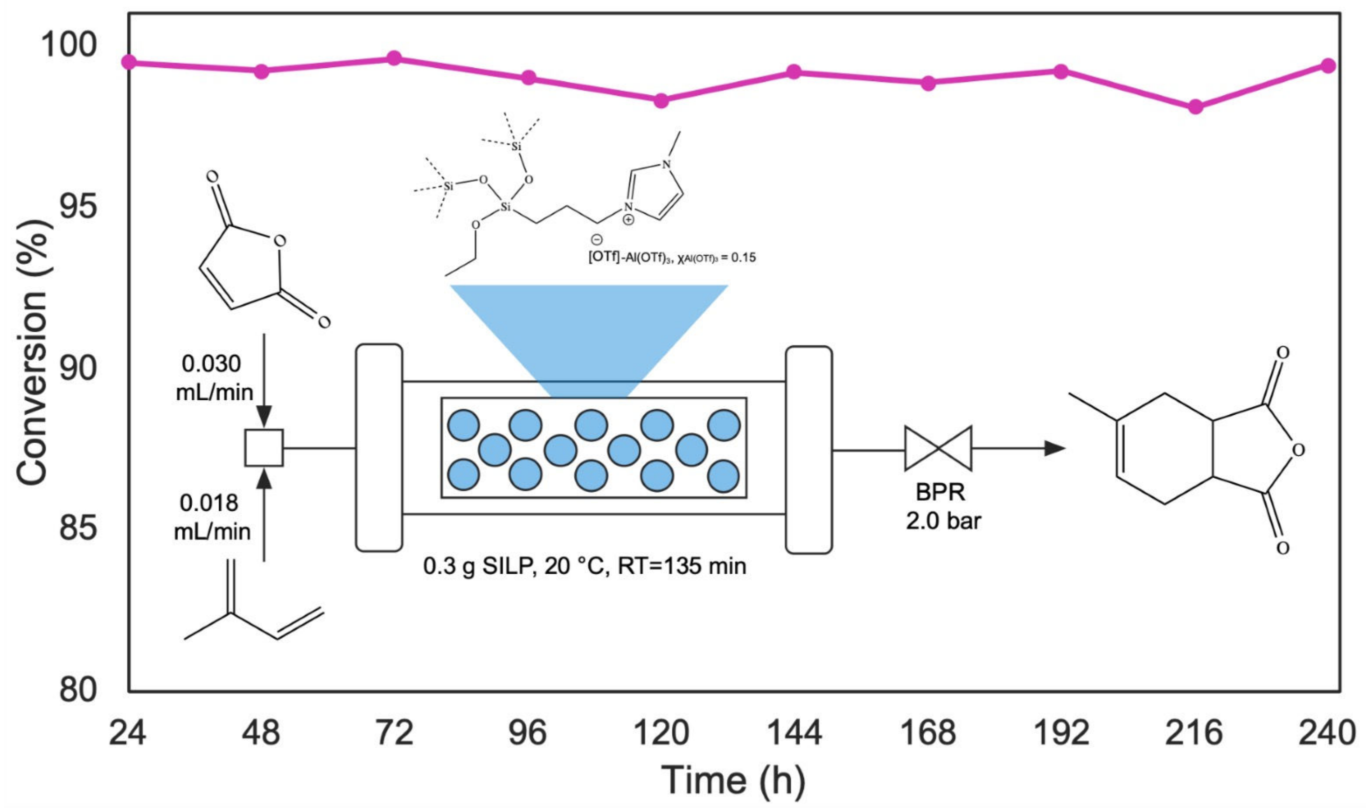
Supported chlorometallate ionic liquids



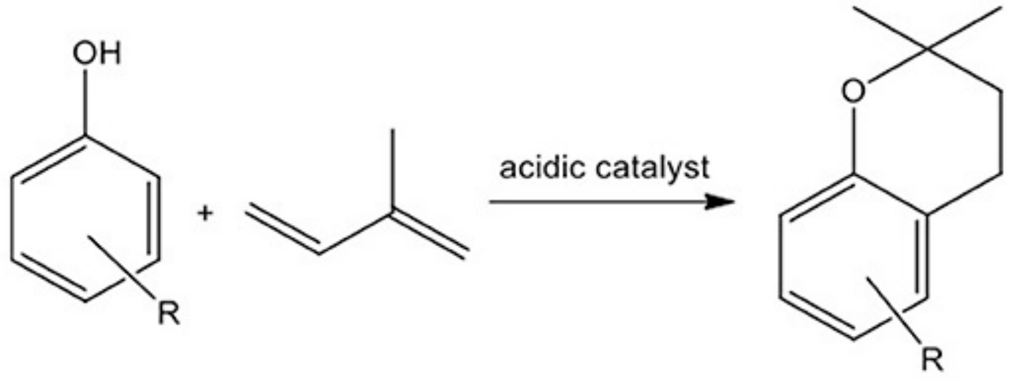


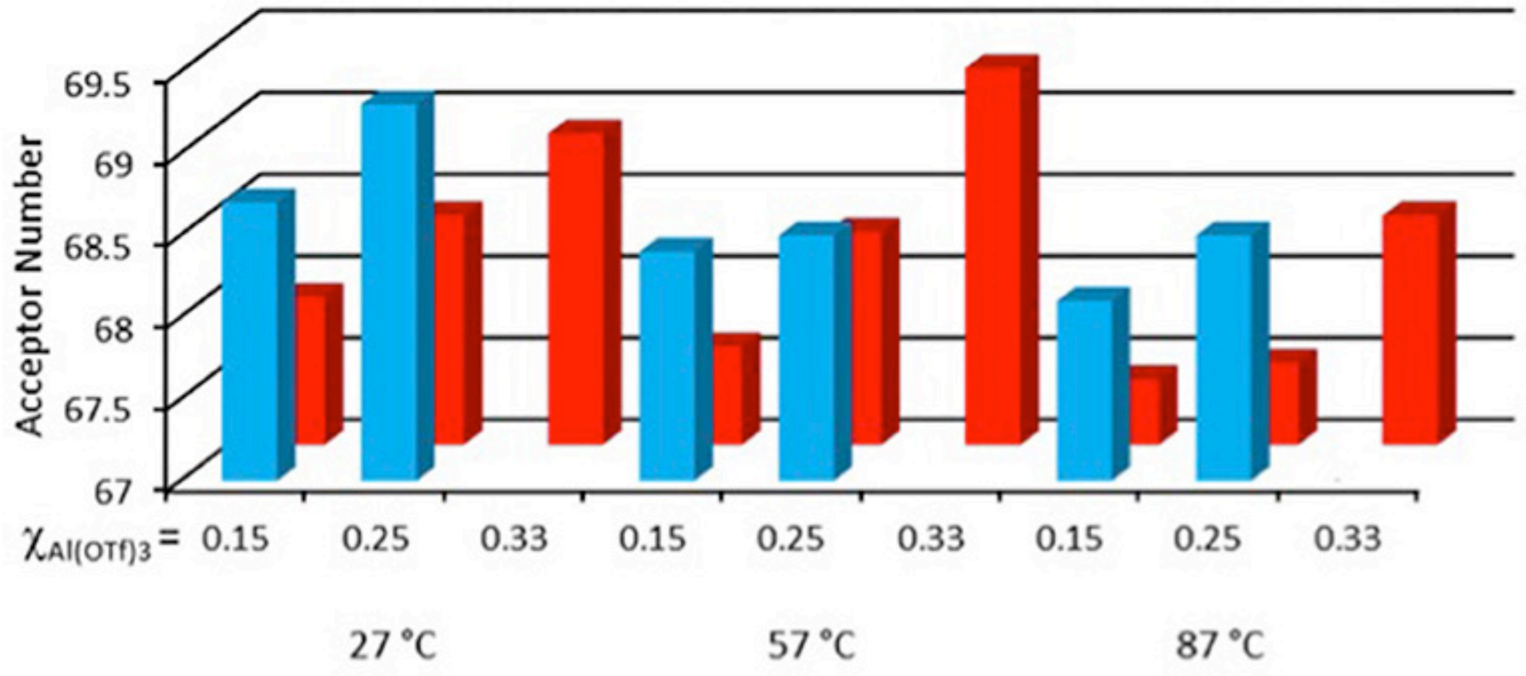
Diels-Alder cycloaddition between maleic anhydride and isoprene

Supported trifloaluminate ionic liquids

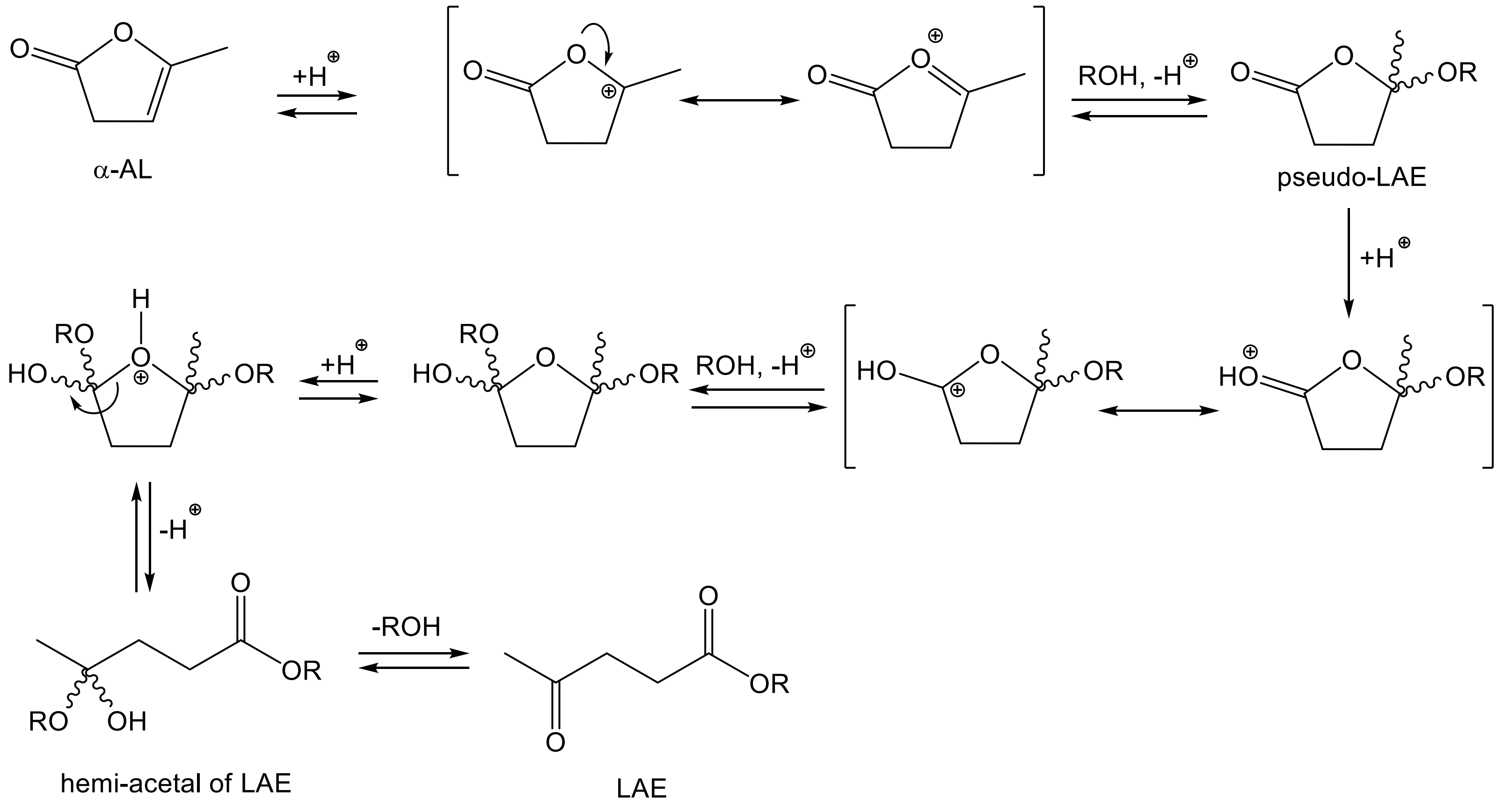


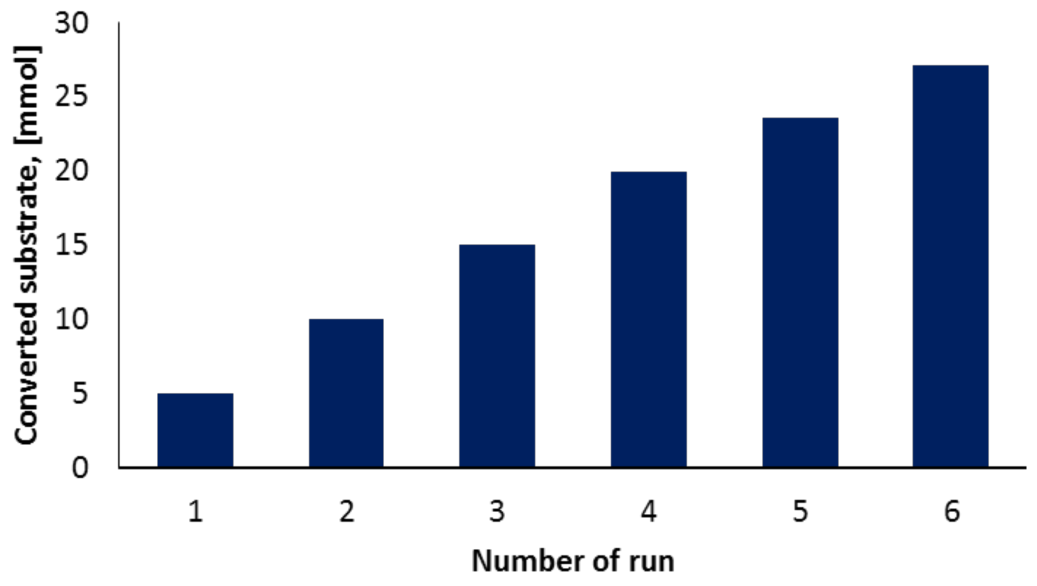
[3+3] cycloaddition for the synthesis of chromanes





Transformation of angelica lactone to alkyl levulinates





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A. Wolny, P. Latos, K. Szymańska, S. Jurczyk, A. Jakóbik Kolon, A. Chrobok, Appl . Catal . A: Gen 2024 , 676 , 119676
P. Latos, A. Wolny, J. Zdarta, F. Ciesielczyk, S. Jurczyk, T. Jesionowski, A. Chrobok, Environ. Technol. Innov. 2023, 31, 103164A.
K.Matuszek, A. Chrobok, P. Latos, K. Szymańska, A. Jarzębski, M. Swadźba-Kwaśny, Catal. Sci. Technol., 2016,6, 8129-8137 .
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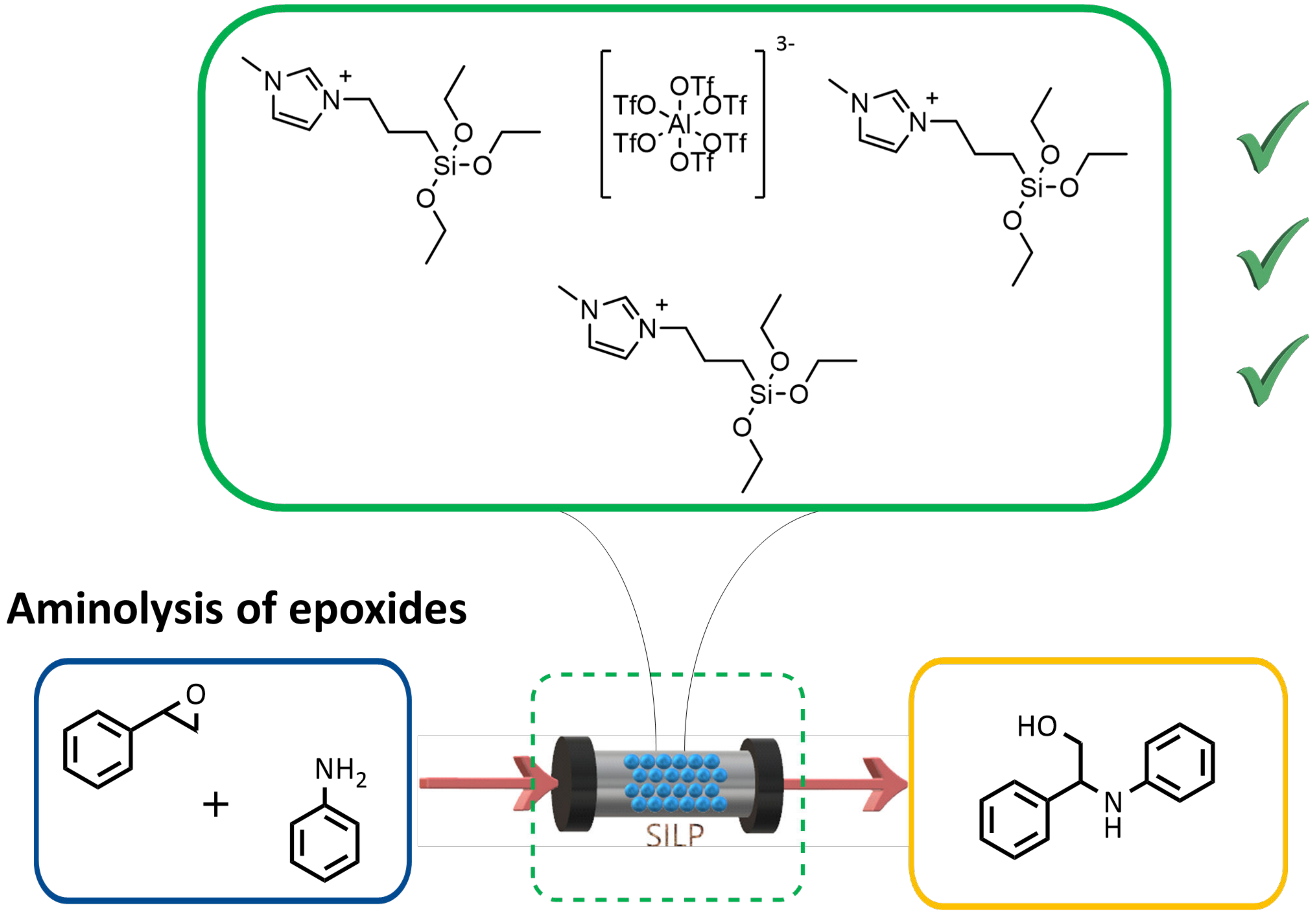
P. Latos, A. Szelwicka, S. Boncel, S. Jurczyk, M. Swadźba-Kwaśny, A. Chrobok, ACS Sustainable Chem. Eng., 2019, 7, 5184.

MATALLATE IONIC LIQUID'S APPLICATIONS

Aminolysis of epoxides in continuous flow synthesis



Aminolysis of epoxides

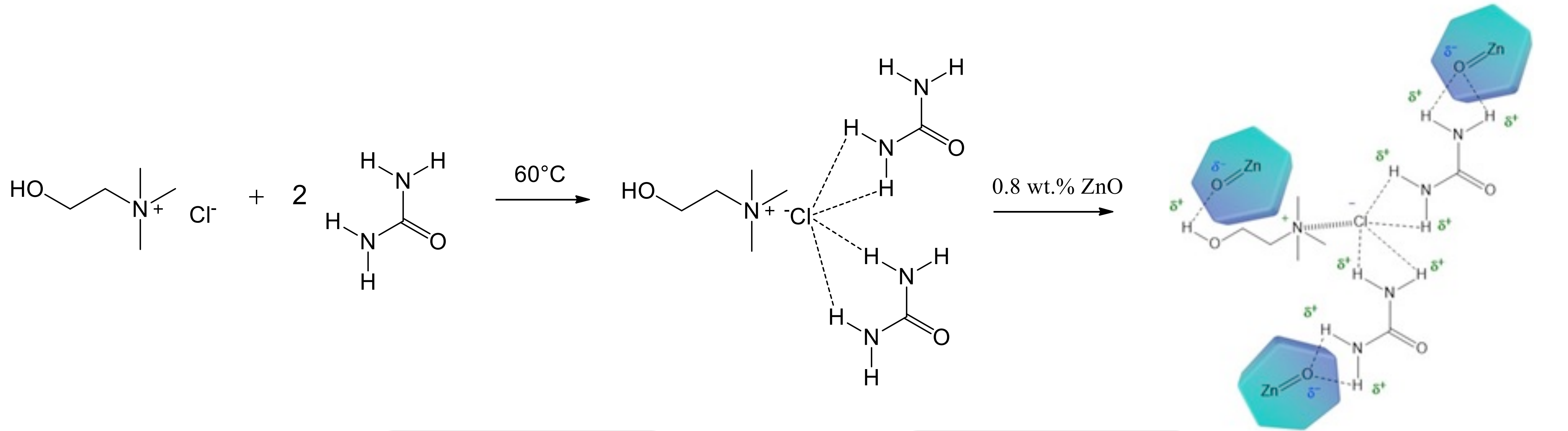
+

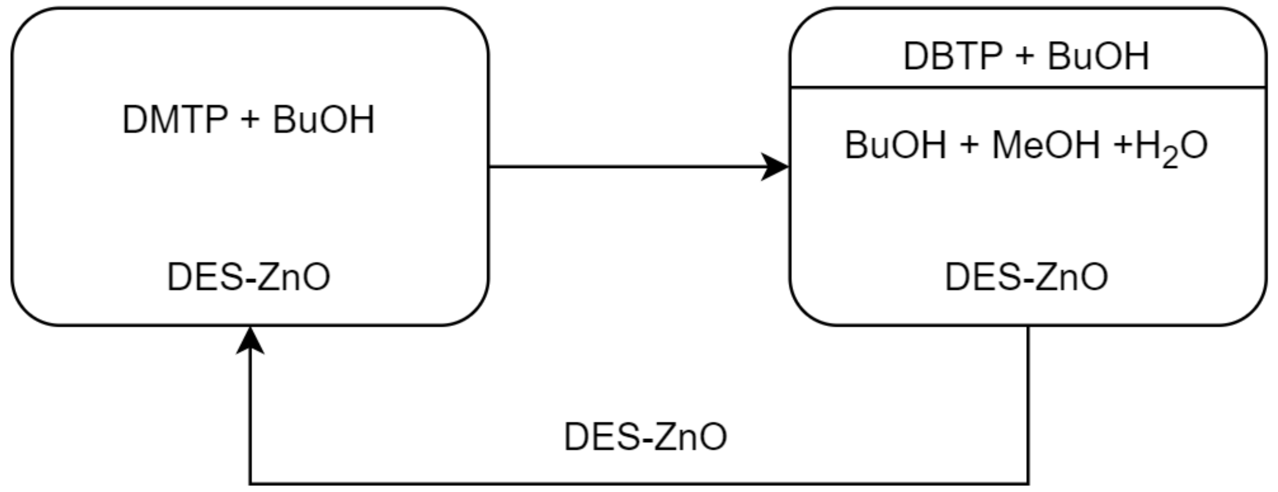
Flow system

Yield = 98.9 %

- ✓ **High activity**
- ✓ **High stability**
- ✓ **Mild conditions**

Synergistic effect of deep eutectic solvent and zinc oxide





DMTP + BuOH

DES-ZnO

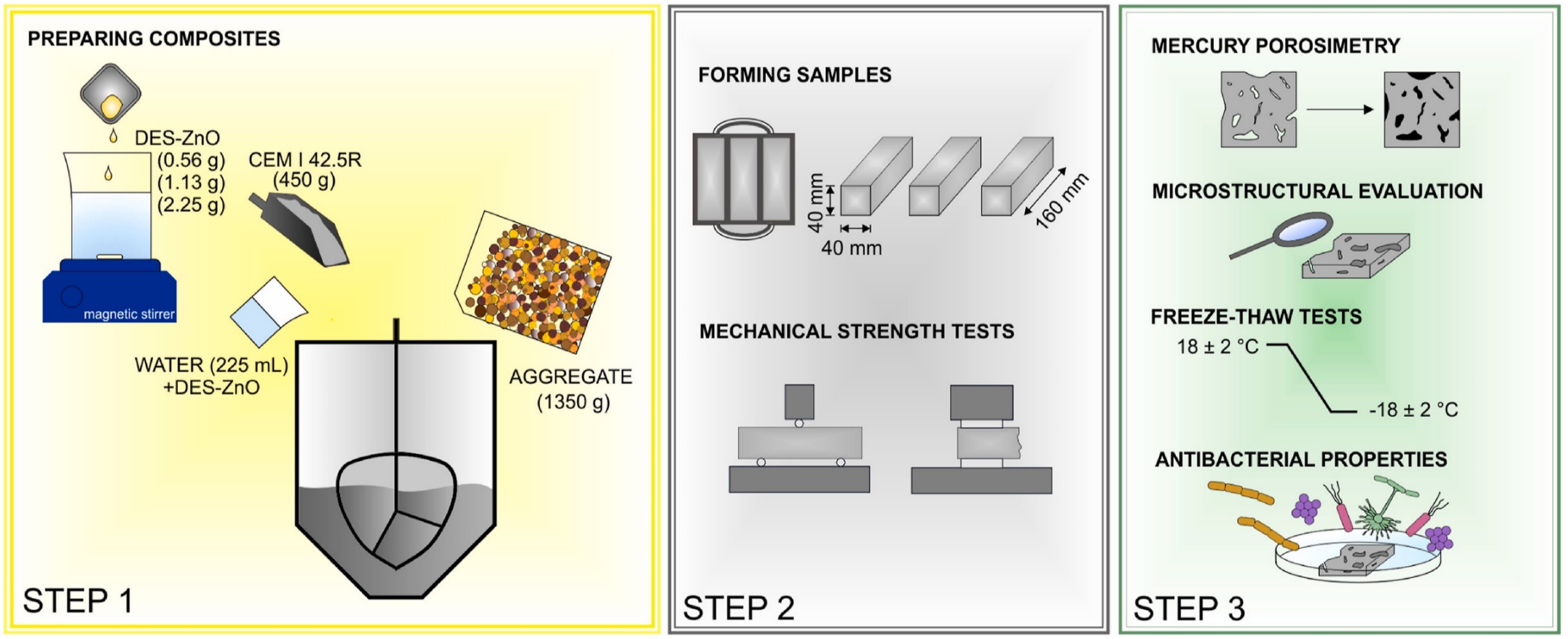
DBTP + BuOH

BuOH + MeOH +H$_2$O

DES-ZnO

DES-ZnO

Cementitious composites doped with a deep eutectic solvent



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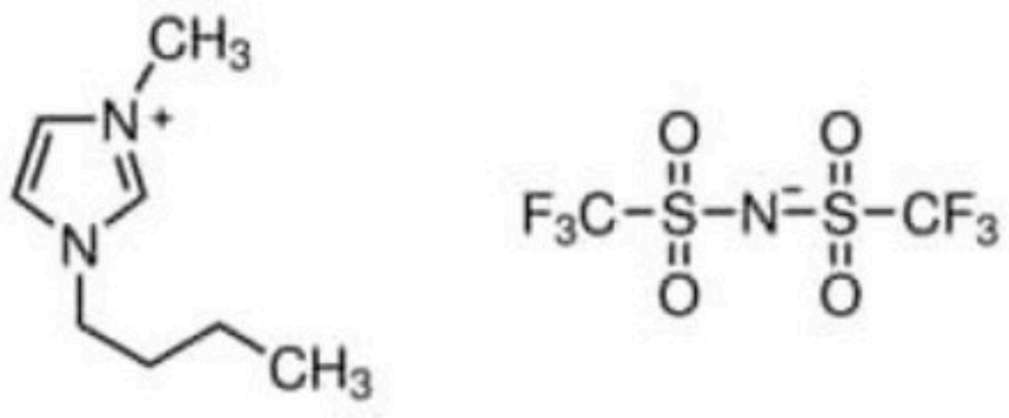
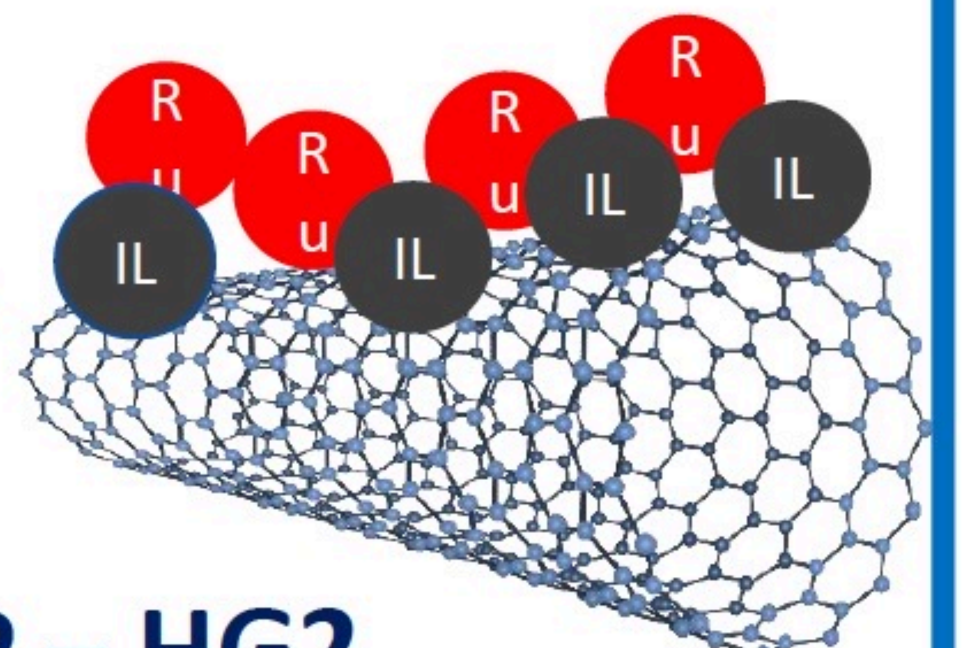
RESEARCH UNIVERSITY EXCELLENCE INITIATIVE

I. Klapiszewska, P. Latos, A. Parus, S. Balicki, P. Lodowski, K.A. Wilk, T. Jesionowski, A. Chrobok, Ł. Klapiszewski, A. Ślosarczyk, J. Mater. Res. Technol., 2023, 27, 542.
P. Latos, J. Gabzdyl, S. Jurczyk, A. Chrobok, Ind. Eng. Chem. Res. 2024, 63, 8102–8110.
P. Latos, J. Gabzdyl, K. Erfurt, D. Łukowiec, A. Maximenko, S. Jurczyk, A. Chrobok, Catal. Today, 2024, 114806.

RH – BASED SILP CATALYST FOR METATHESIS

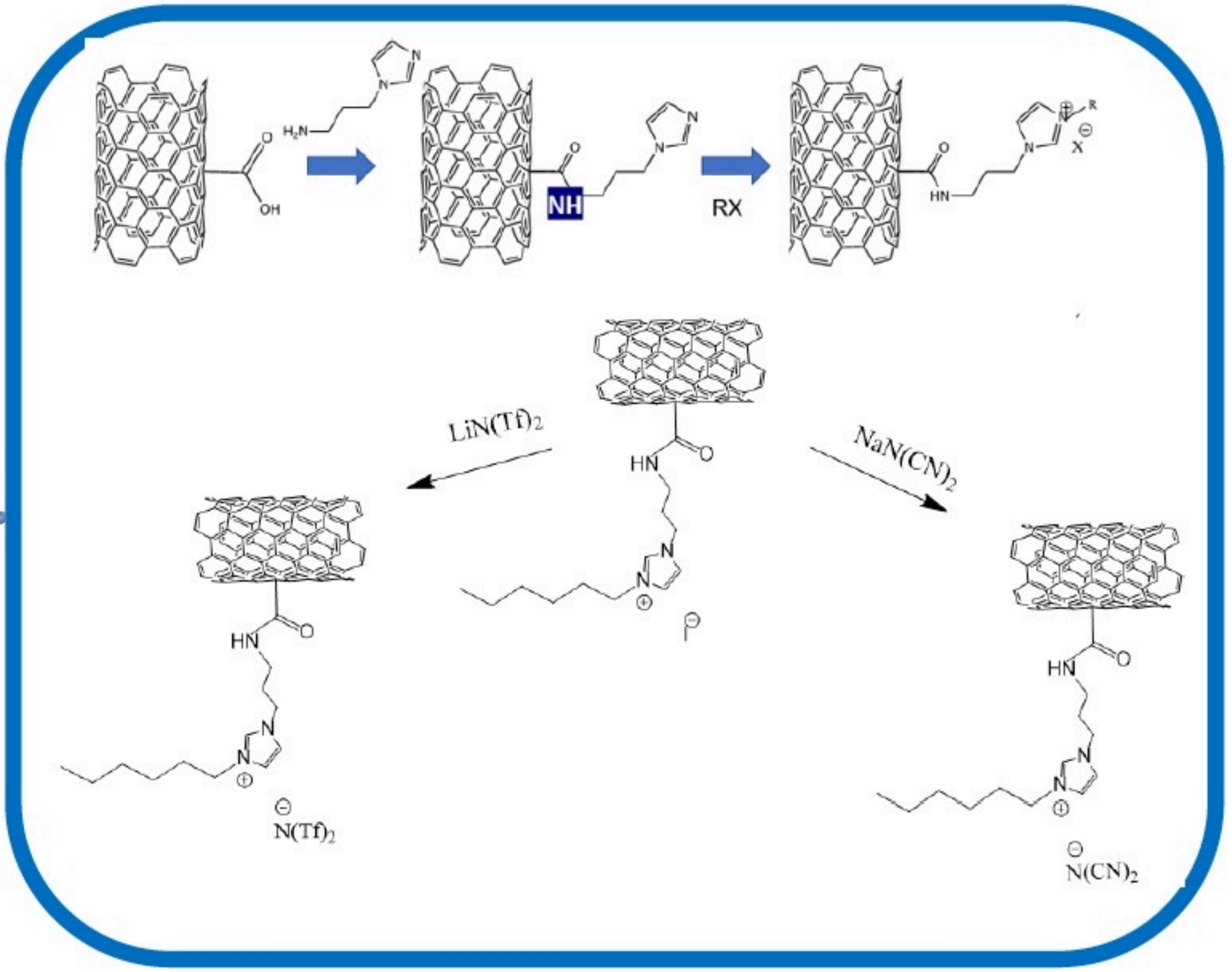


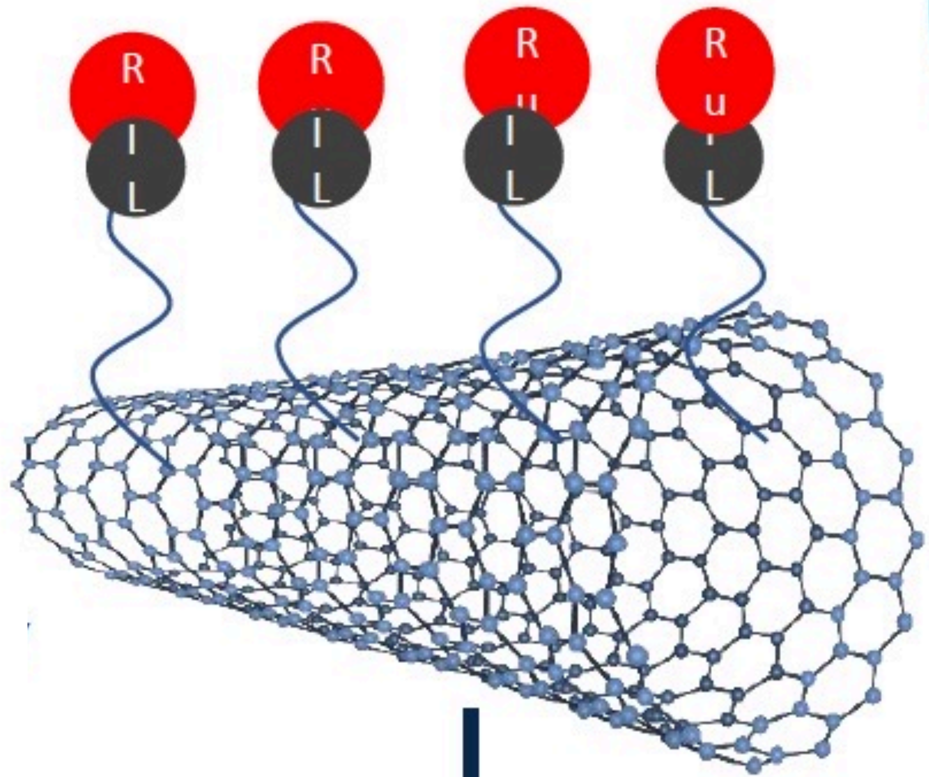
Physical immobilization of IL



SILP_[emim][NTf$_2$]_HG2
SILP_[bmim][NTf$_2$]_HG2
SILP_[hmim][NTf$_2$]_HG2

SILP – HG2
Supported Ionic Liquid Phase





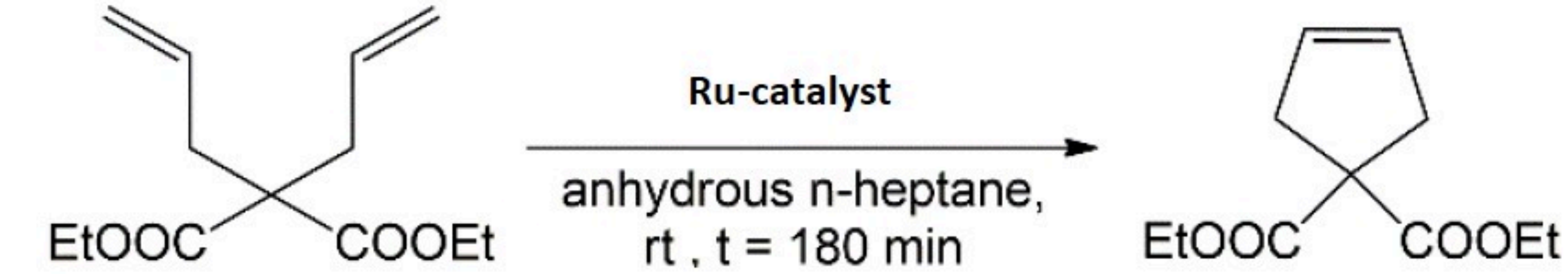
Chemical immobilization of IL

SILLP_[hmim][NTf$_2$]_HG2
SILLP_[hmim]I_HG2
SILLP_[hmim][N(CN)$_2$]_HG2

SILLP – HG2
Supported Ionic Liquid-Like Phase

N. Barteczko, A. Brzęczek-Szafran, A. Wolny, S. Jurczyk, A. Jakubik-Kolon, A. Chrobok, Appl. Catal. A Gen. 2023,661, 119226.

RH – BASED SILP CATALYST FOR METATHESIS

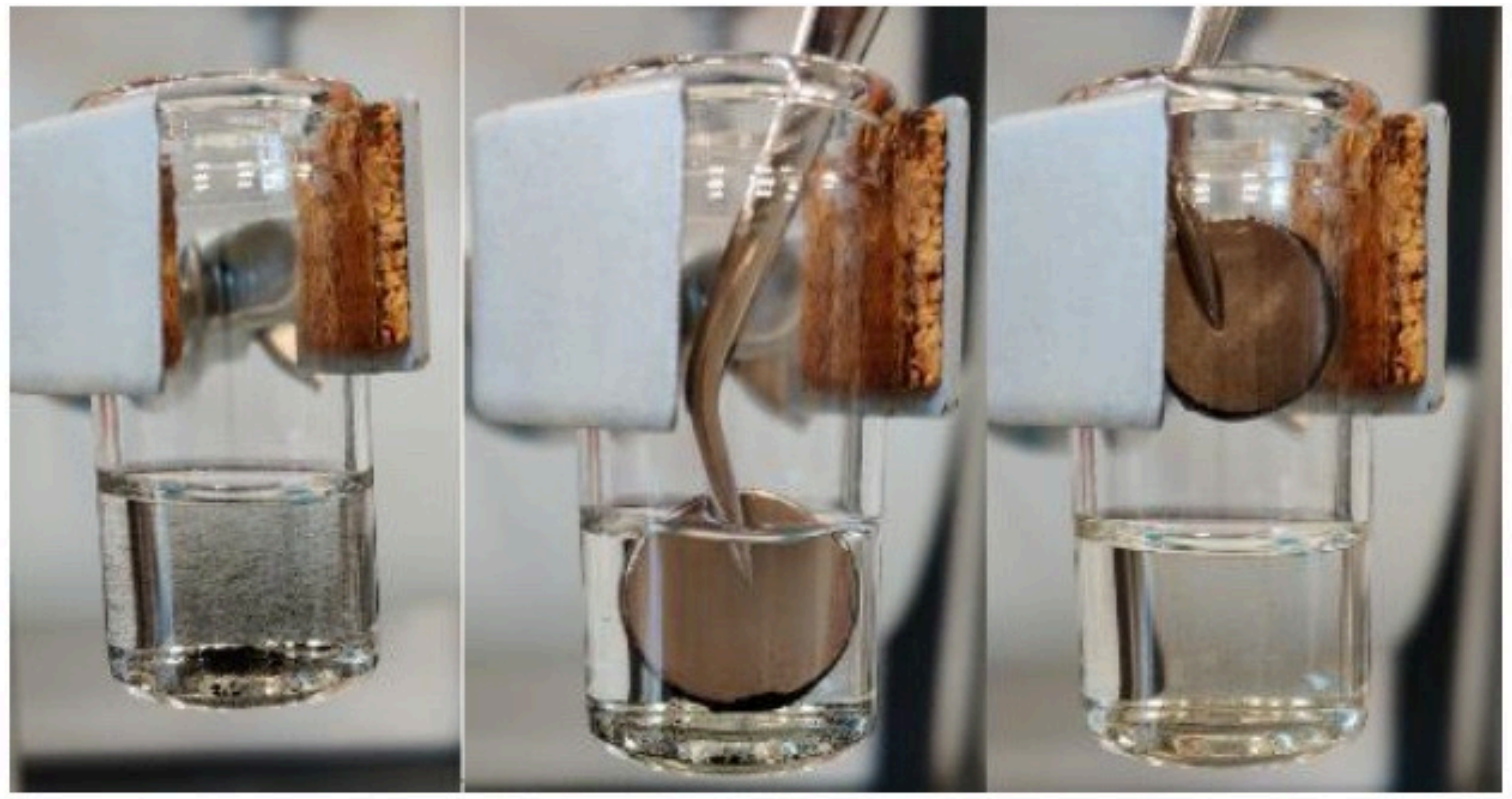


DIETHYL DIALLYLMALONATE

CATALYST	HG2, (wt. %)	IL, (wt. %)	Conversion of DDM, %	Ru in product, [ppm]
MWCNTs_HG2	21.4	-	99.7	308 /31**
SILP_[hmim][NTf2]_HG2	4.2	21.3	98.4	121
SILLP_[hmim][NTf2]_HG2	9.7	5.9	99.0	85/14*/9**
SILLP_[hmim]I_HG2	7.4	4.6	98.7	318 /32**
SILLP_[hmim][N(CN)2]_HG2	12.7	3.8	98.4	362 /36**

T = 25 °C; t = 180 min, 1.3%mol/*0.5%mol;
Content of Ru ICP-MS (SD 2%), selektywność >99%

SILLP_[hmim][NTf2]_HG2
Isolation via magnetic field



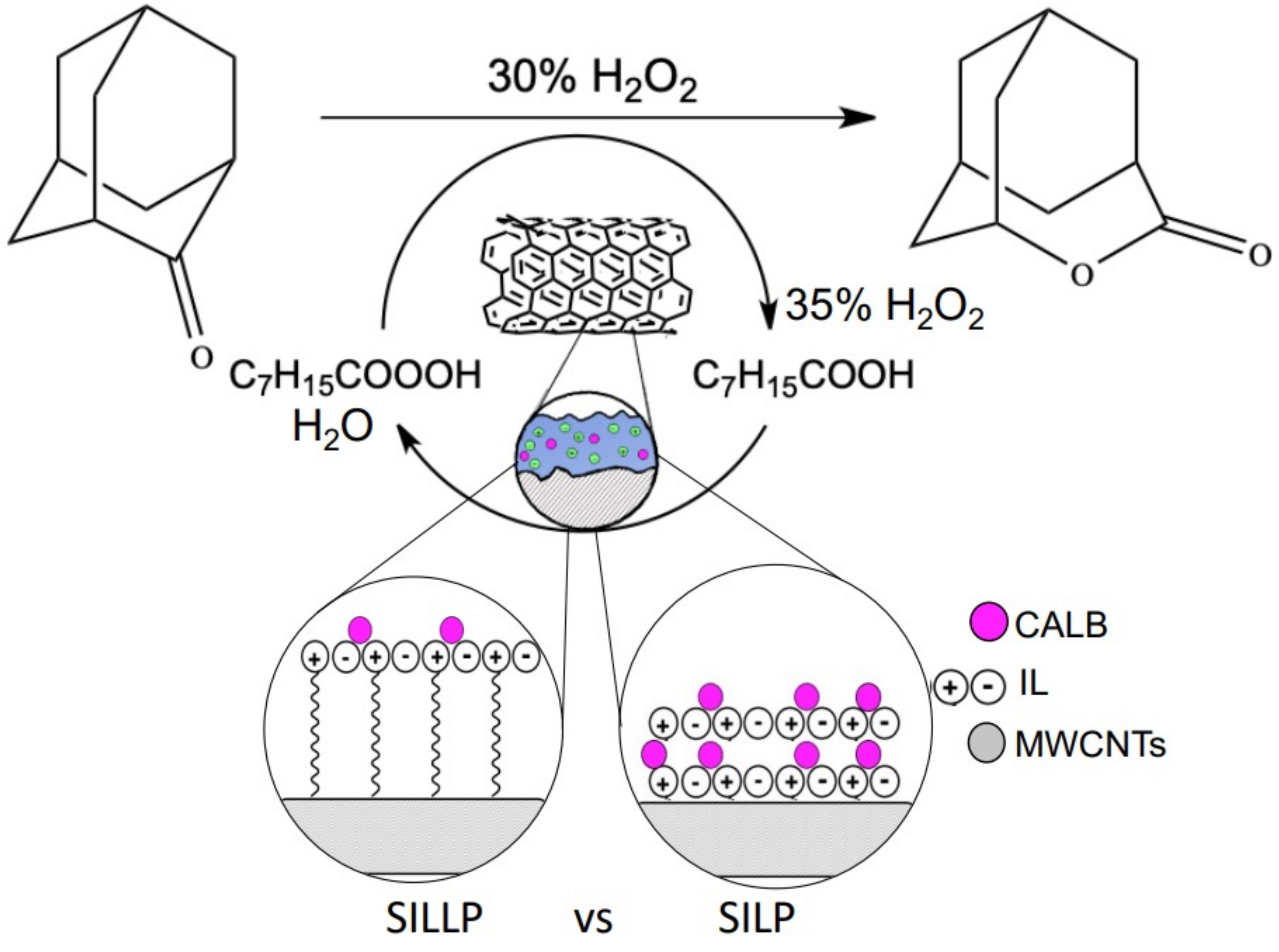
Cycle no.	SILLP_ [hmim][NTf2] _HG2; yield	MWCNTs _HG2, yield
1	99.0 %	79.2 %
2	99.0 %	35.4 %
3	98.9 %	5.2 %
4	93.7 %	
5	85.5 %	

Catalyst recycling

N. Barteczko, A. Brzęczek-Szafran, A. Wolny, S. Jurczyk, A. Jakubik-Kolon, A. Chrobok, Appl. Catal. A Gen. 2023,661, 119226.

HETEROGENEOUS BIOCATALYTIC MATERIALS

Bayer-Villiger oxidation of 2-adamantanone

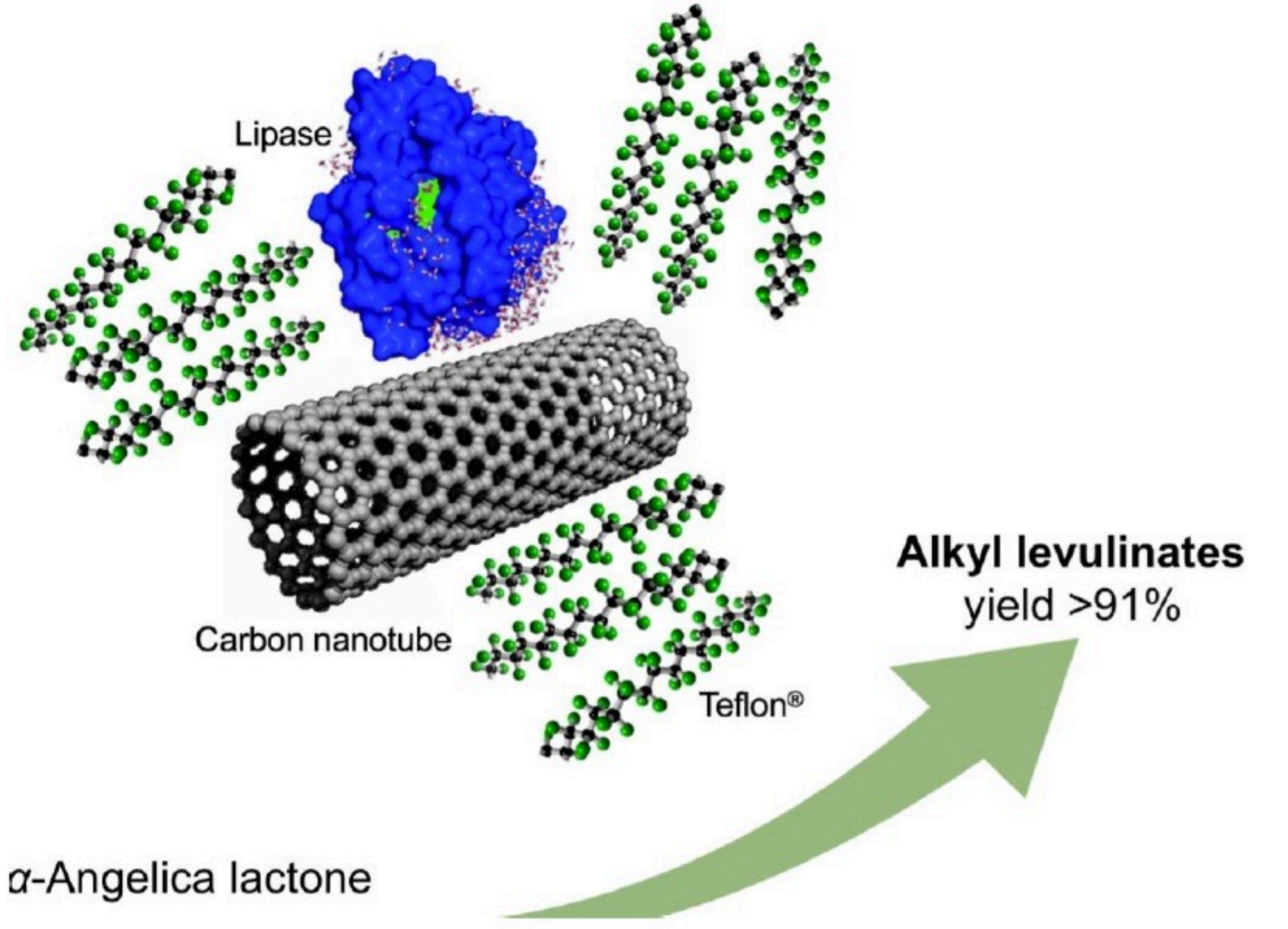


98% conversion

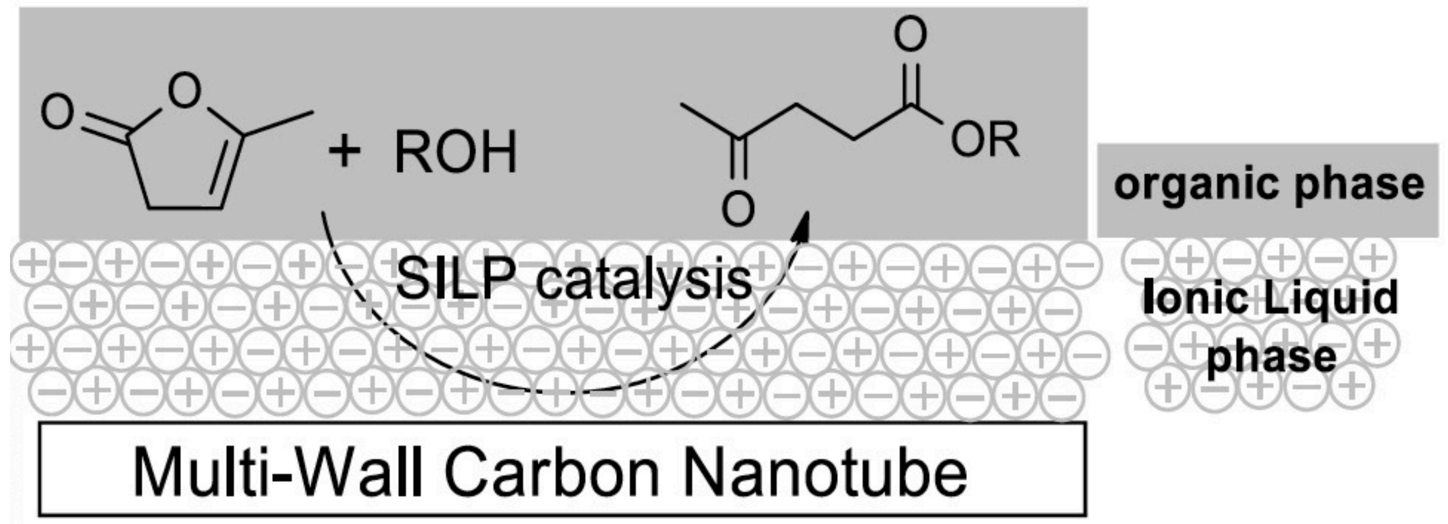
92% conversion

Biotransformation of angelica lactone

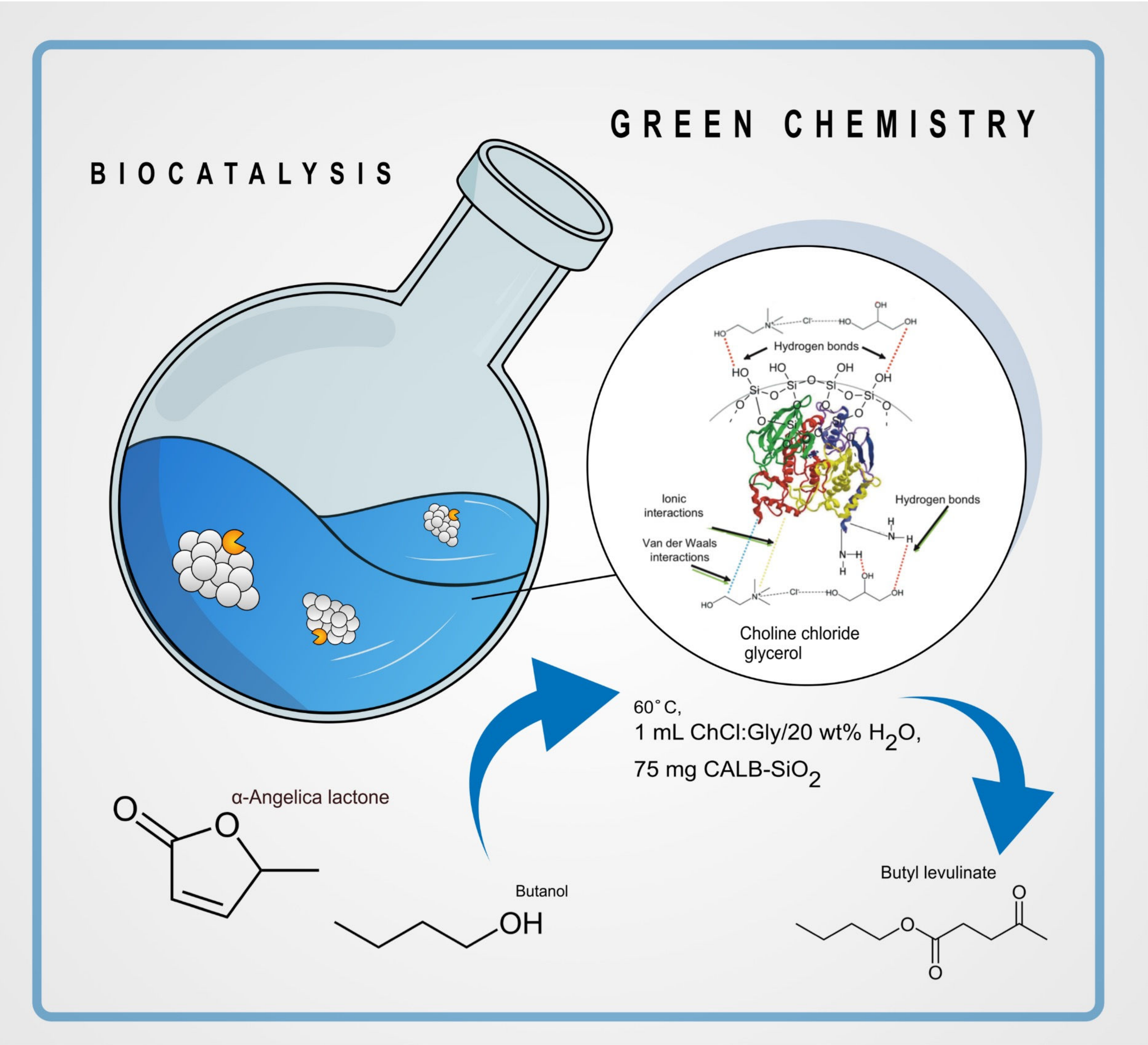
Bio-System 1



CALB/MWCNT PTFE (0.10 wt.%)



Bio-System 2



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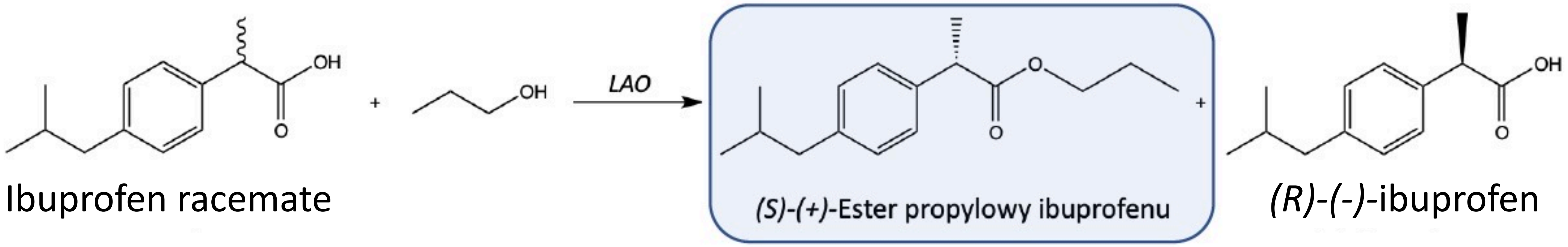
RESEARCH UNIVERSITY EXCELLENCE INITIATIVE

A.Szelwicka, A. Kolanowska, P. Latos, S. Jurczyk, S. Boncel,A. Chrobok, Catal. Sci. Technol., 10, 2020, 3255.
A. Szelwicka, A. Wolny, M. Grymel, S. Jurczyk, S. Boncel, A. Chrobok, Materials 2021, 14, 3443.
A. Wolny, A. Babiuch, P. Latos, S. Jurczyk, A. Chrobok, ChemCatChem. 2024, Online version e202401393. doi.org/10.1002/cctc.202401393.

Kinetic resolution of ibuprofen racemate

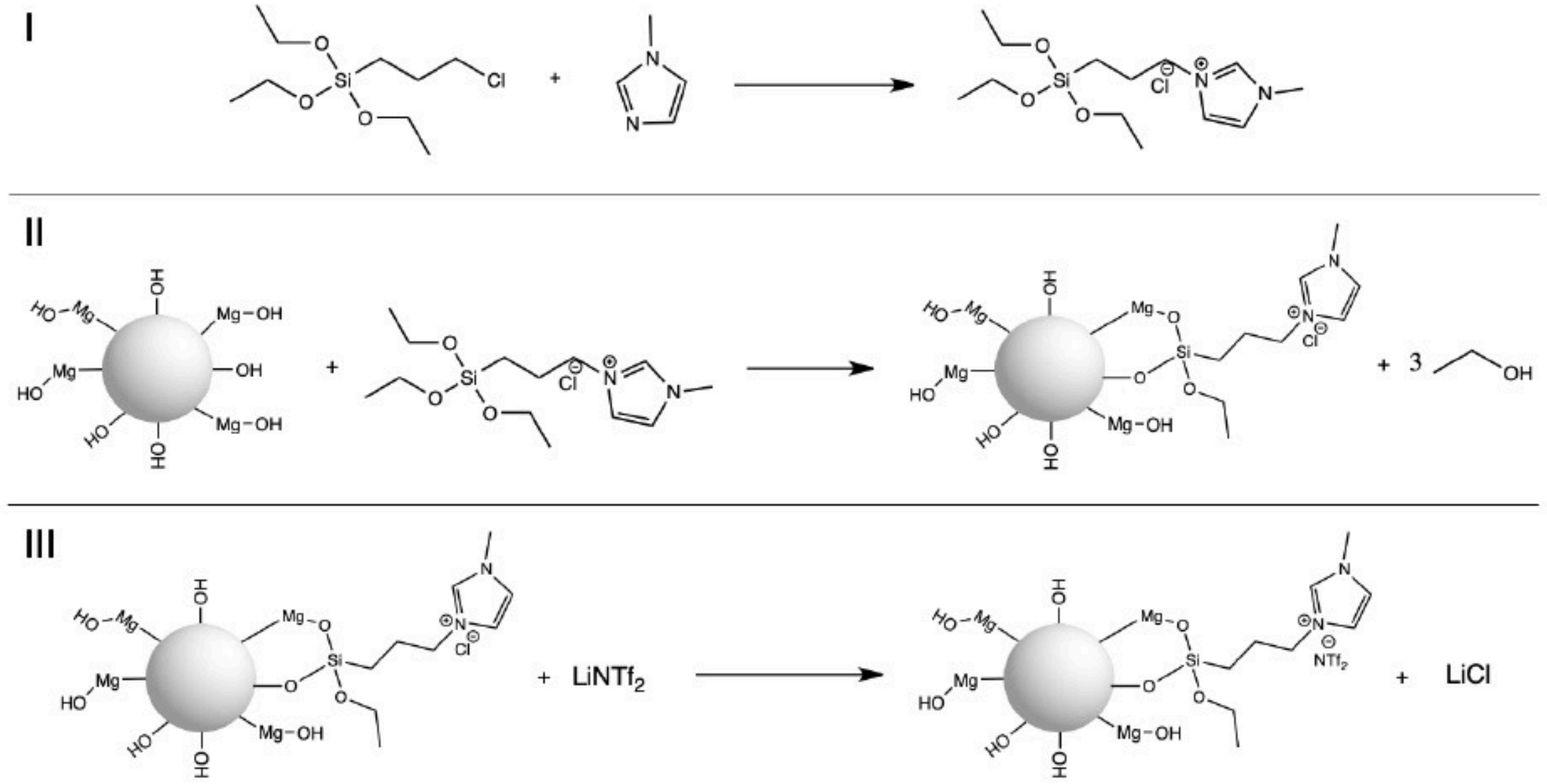


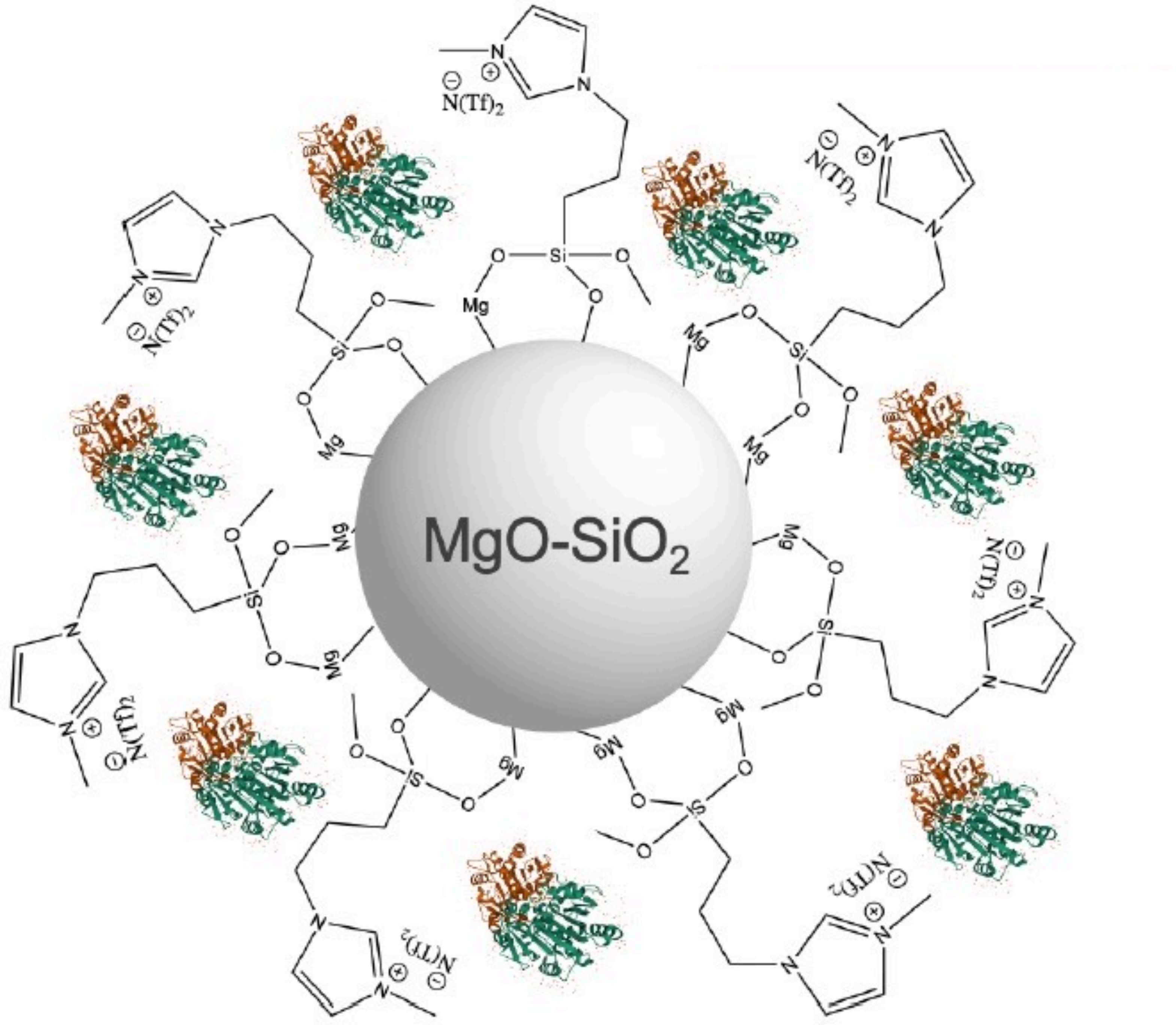
Ibuprofen racemate

(S)-(+)-Ester propylowy ibuprofenu

(R)-(-)-ibuprofen

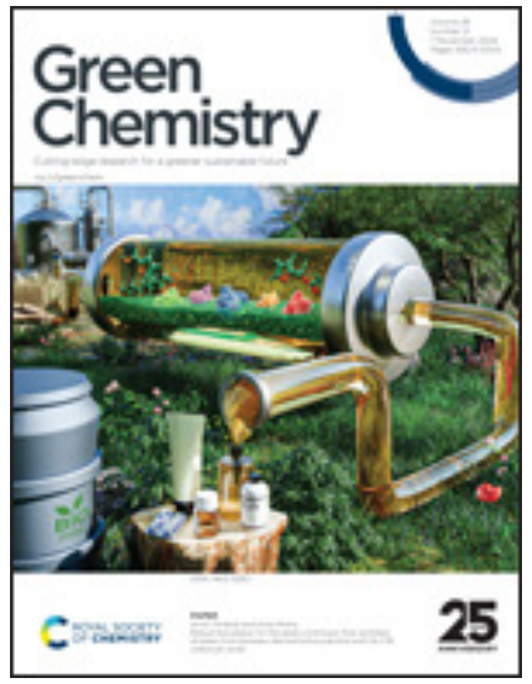
Conversion 45.2%, ee 99.9% after 48 h



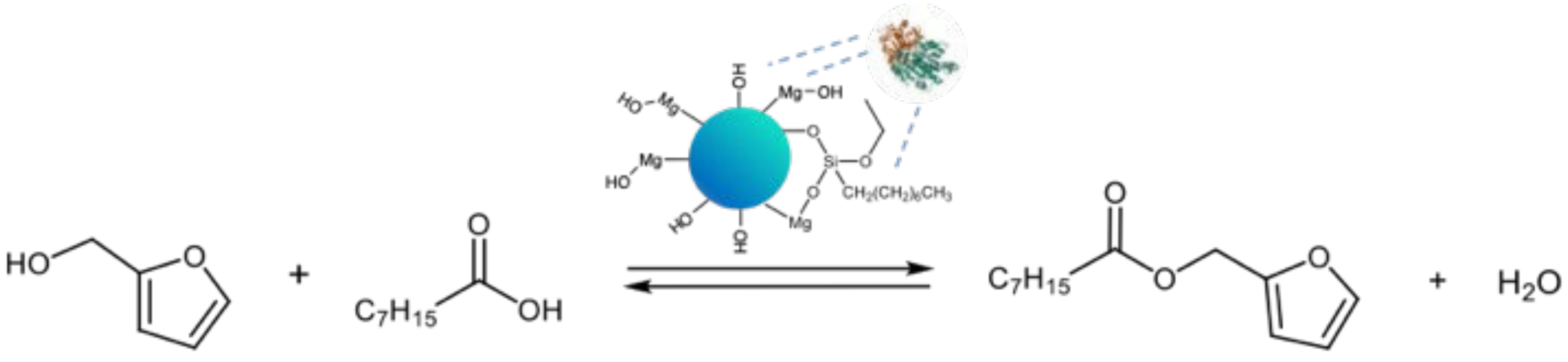


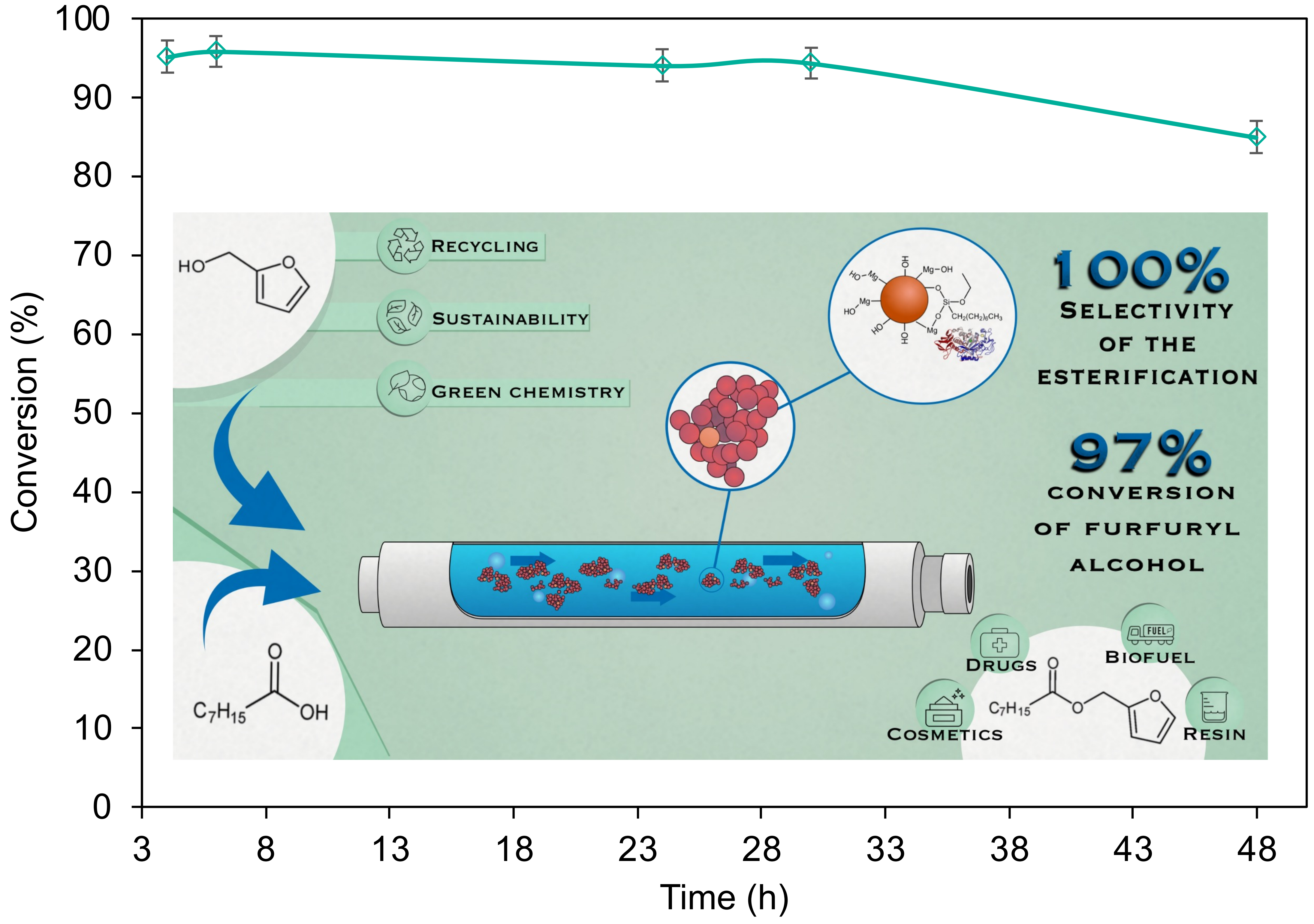
A. Wolny, A. Siewniak, J. Zdarta, F. Ciesielczyk, P. Latos, S. Jurczyk, L.D. Nghiem, T. Jesionowski, A. Chrobok, Environ. Technol. Innov. 2022, 28, 1-12.

HETEROGENEOUS BIOCATALYTIC MATERIALS

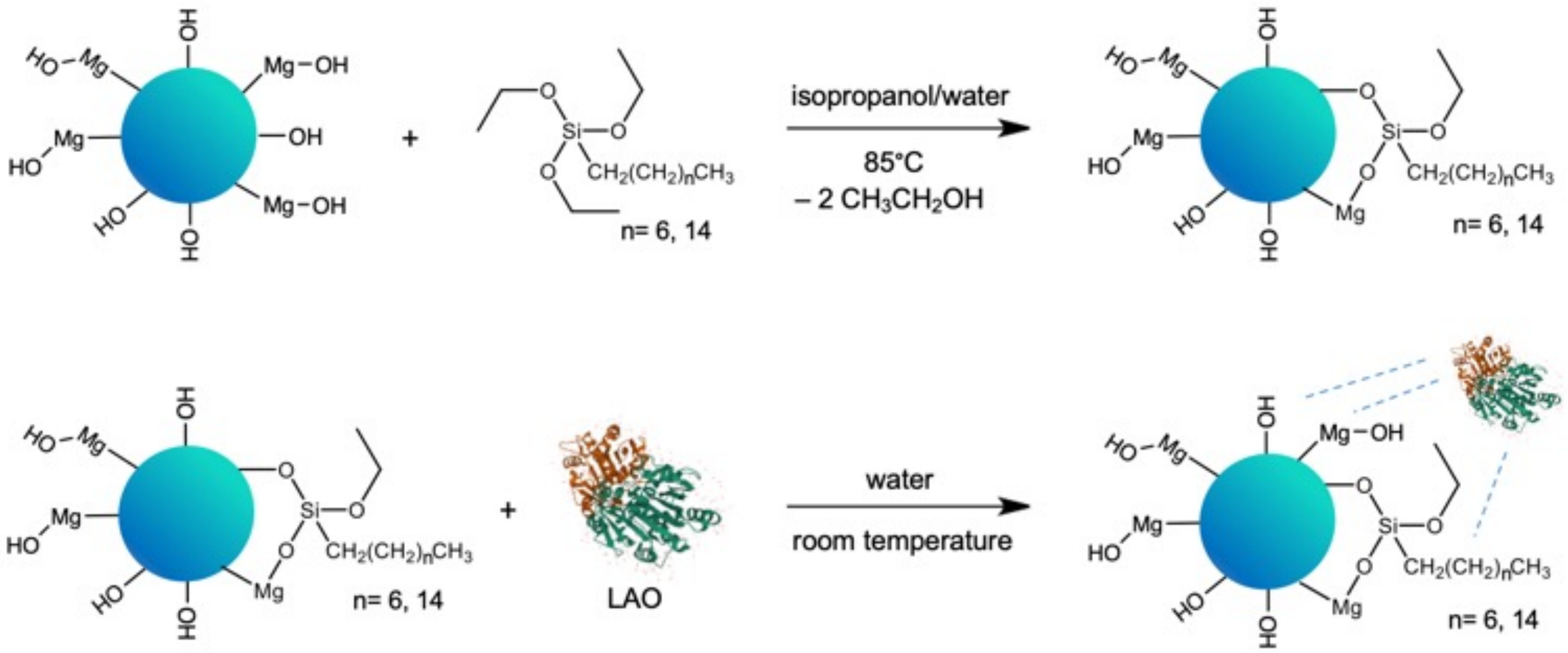


Esterification of furfuryl alcohol with fatty acids (C8-C18)



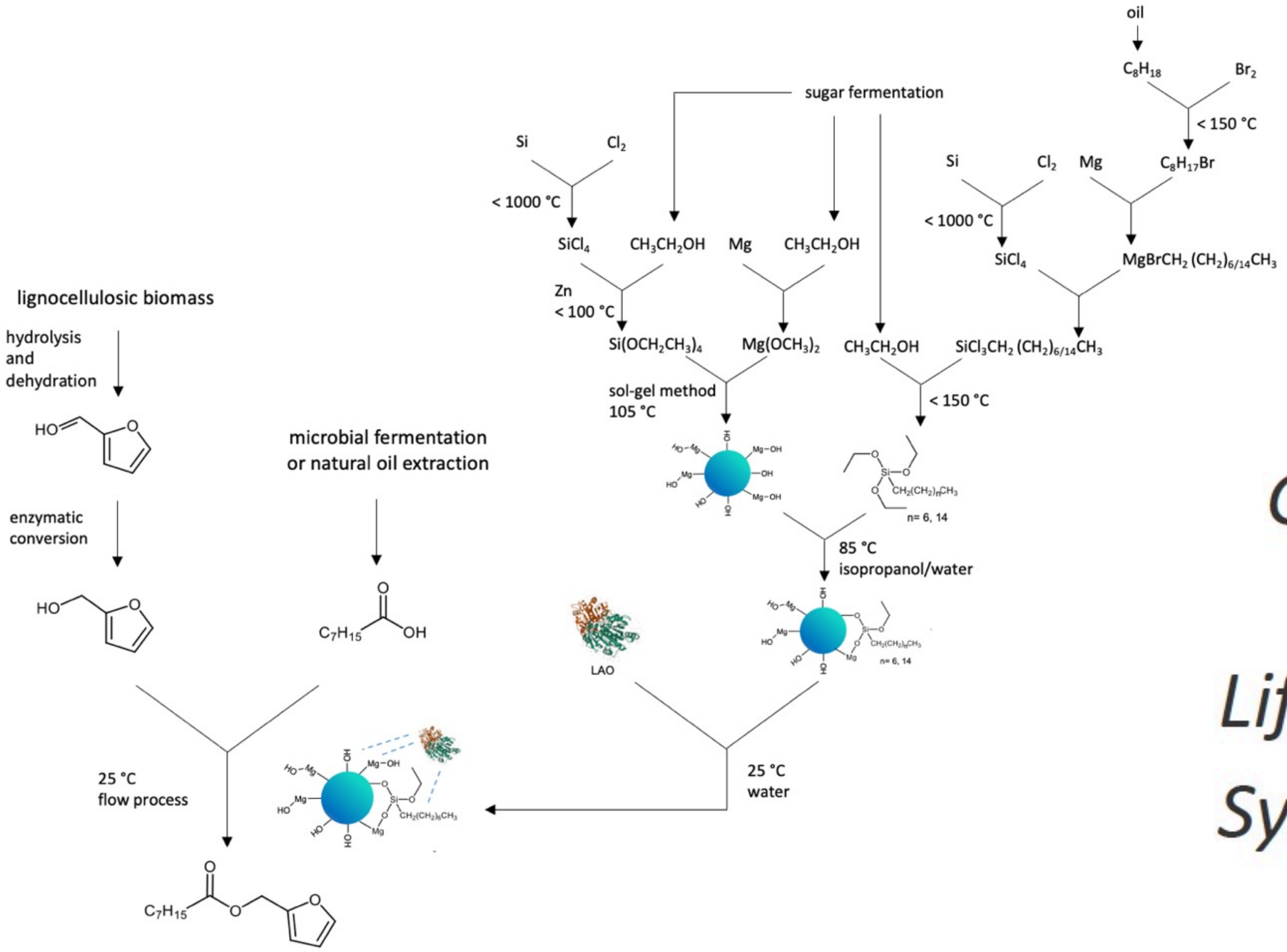


Biocatalyst synthesis



A. Wolny, D. Więcławik, J. Zdarta, S. Jurczyk, T. Jesionowski, A. Chrobok, Green Chemistry, 26, 10623-11004.

GREEN THINKING



Green Chemistry Metrics

Life cycle thinking

Synthesis tree

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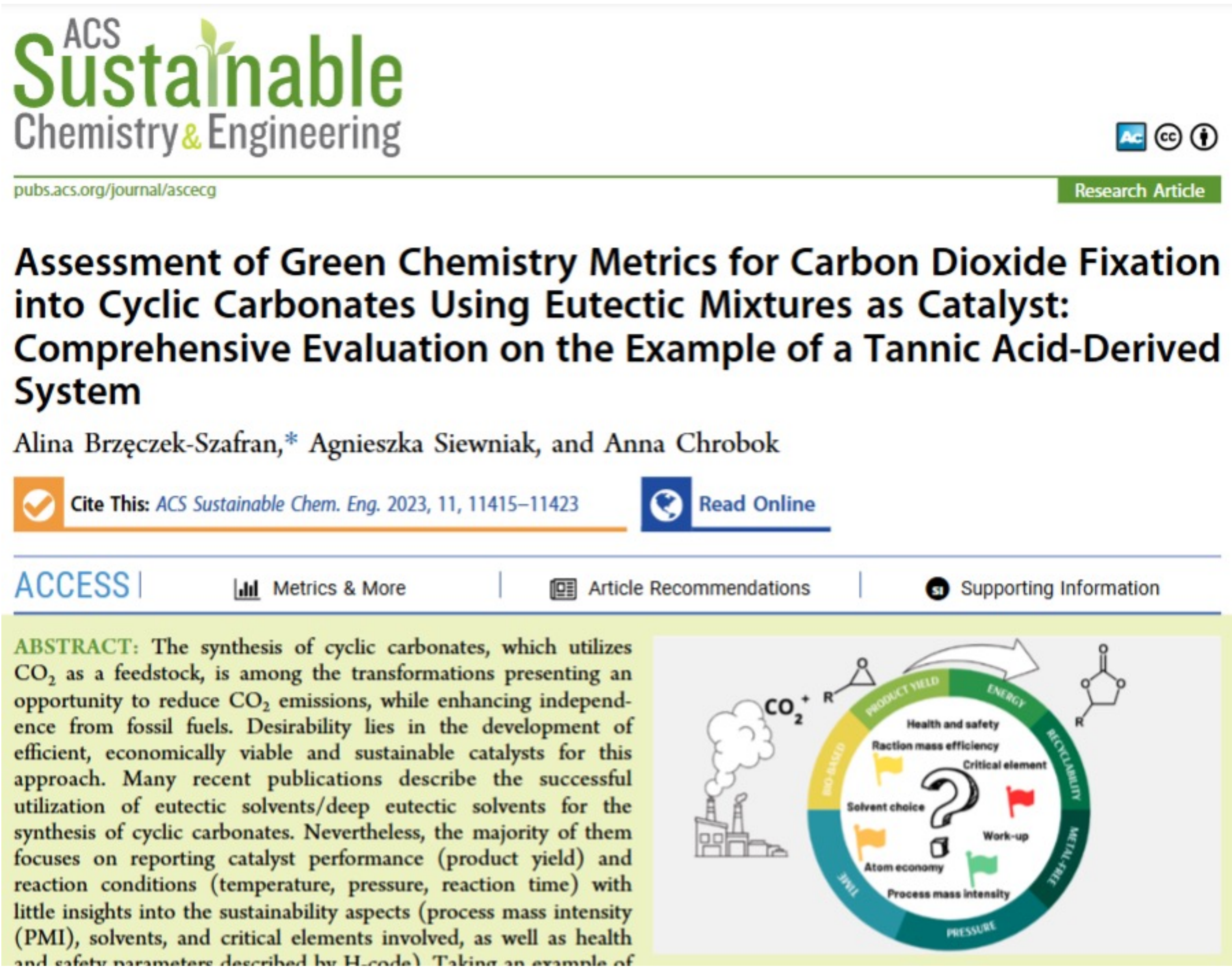
A. Wolny, D. Więcławik, J. Zdarta, S. Jurczyk, T. Jesionowski, A. Chrobok, Green Chemistry, 26, 10623-11004.

CATALYTIC MATERIALS FOR CO_2 VALORIZATION INTO CHEMICALS



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Research Article

Assessment of Green Chemistry Metrics for Carbon Dioxide Fixation into Cyclic Carbonates Using Eutectic Mixtures as Catalyst: Comprehensive Evaluation on the Example of a Tannic Acid-Derived System

Alina Brzęczek-Szafran,* Agnieszka Siewniak, and Anna Chrobok

Cite This: *ACS Sustainable Chem. Eng.* 2023, 11, 11415−11423

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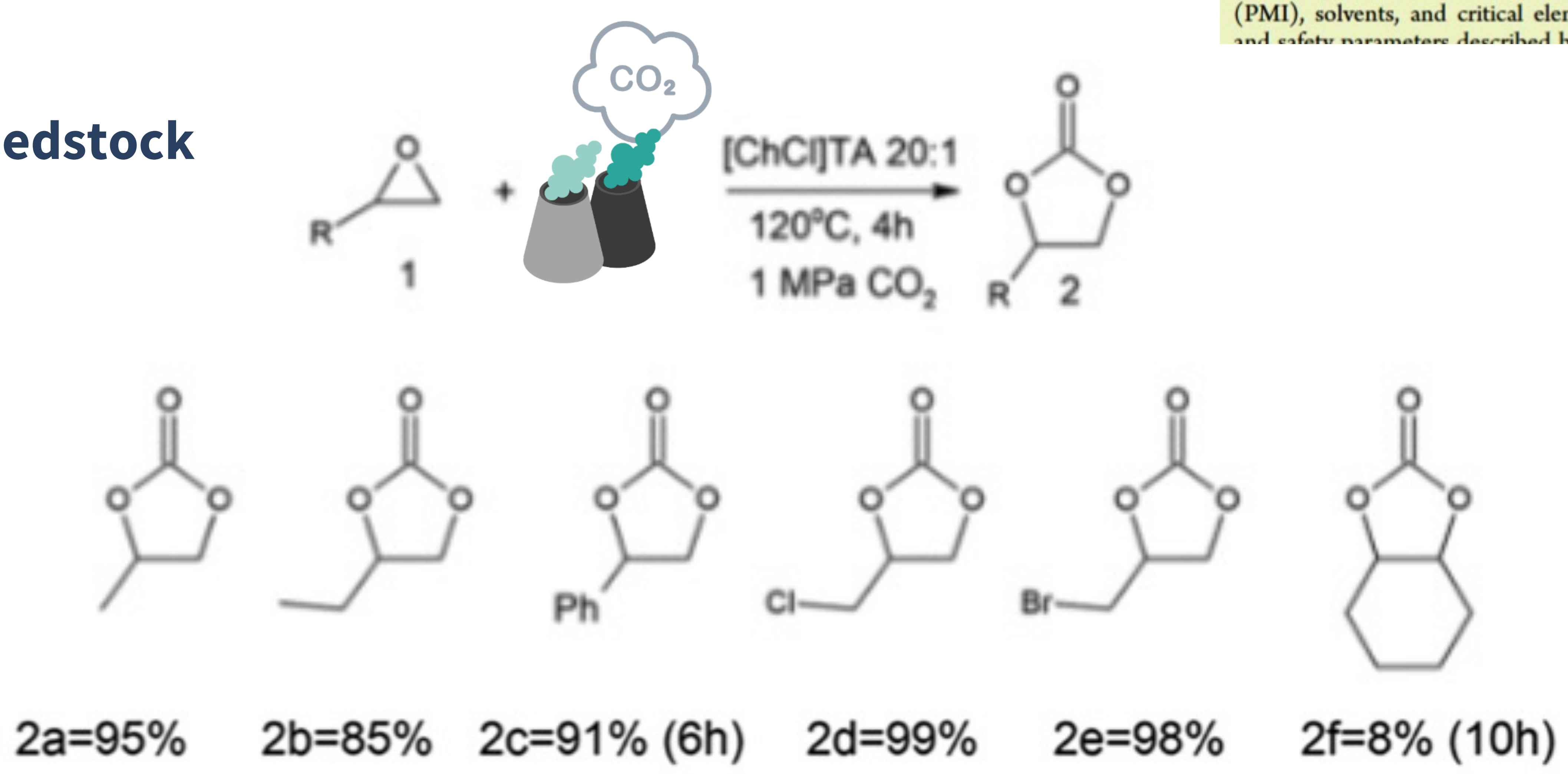
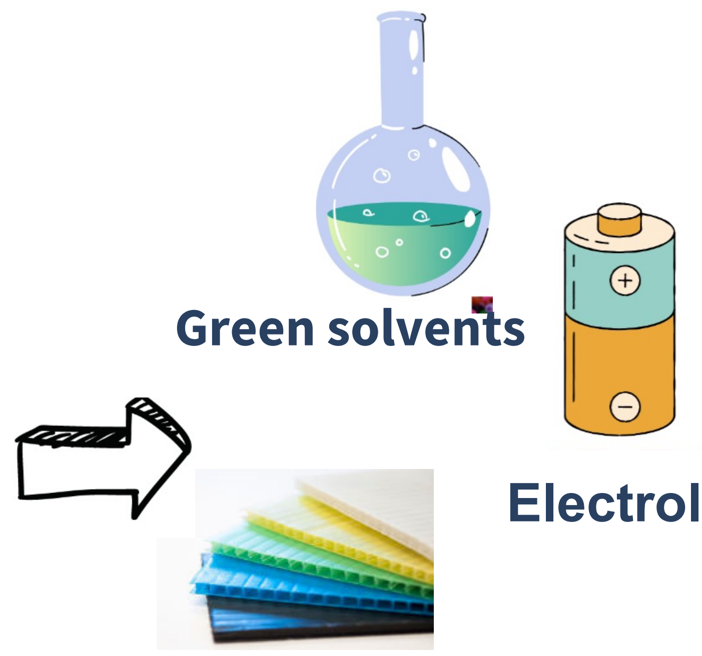
ABSTRACT: The synthesis of cyclic carbonates, which utilizes CO_2 as a feedstock, is among the transformations presenting an opportunity to reduce CO_2 emissions, while enhancing independence from fossil fuels. Desirability lies in the development of efficient, economically viable and sustainable catalysts for this approach. Many recent publications describe the successful utilization of eutectic solvents/deep eutectic solvents for the synthesis of cyclic carbonates. Nevertheless, the majority of them focuses on reporting catalyst performance (product yield) and reaction conditions (temperature, pressure, reaction time) with little insights into the sustainability aspects (process mass intensity (PMI), solvents, and critical elements involved, as well as health and safety parameters described by H-code). Taking an example of

34 billion tonnes of CO2 emitted each year

CO2 Fixation into Cyclic Carbonates

Inexpensive
Abundant
Non-toxic feedstock

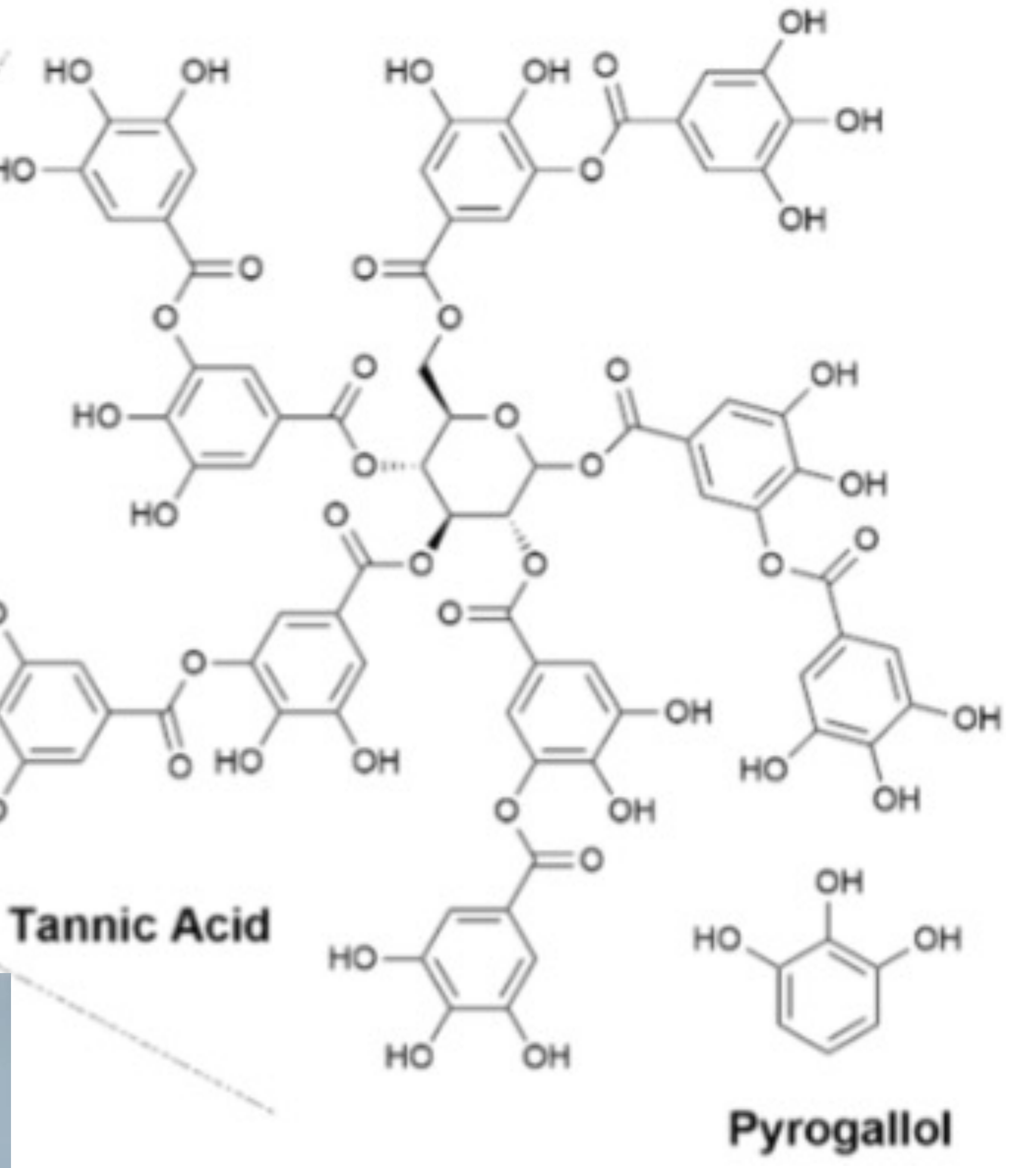




Green solvents

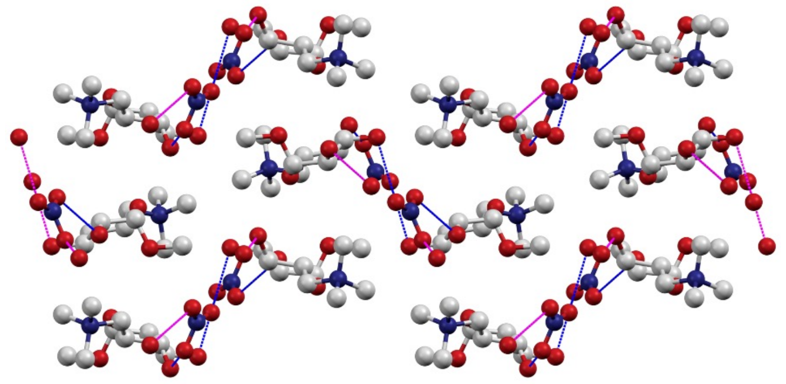
Electrolytes

Polymers



Alina Brzęczek-Szafran, Agnieszka Siewniak, Anna Chrobok,ACS Sustainable Chem. Eng. 2023, 11, 31, 11415–11423

PHASE CHANGE MATERIALS



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Research Article

Transforming Sugars into Salts—A Novel Strategy to Reduce Supercooling in Polyol Phase-Change Materials

Bartlomiej Gaida, Jan Kondratowicz, Samantha L. Piper, Craig M. Forsyth, Anna Chrobok, Douglas R. Macfarlane, Karolina Matuszek,* and Alina Brzeczek-Szafran*

Cite This: *ACS Sustainable Chem. Eng.* 2024, 12, 623–632

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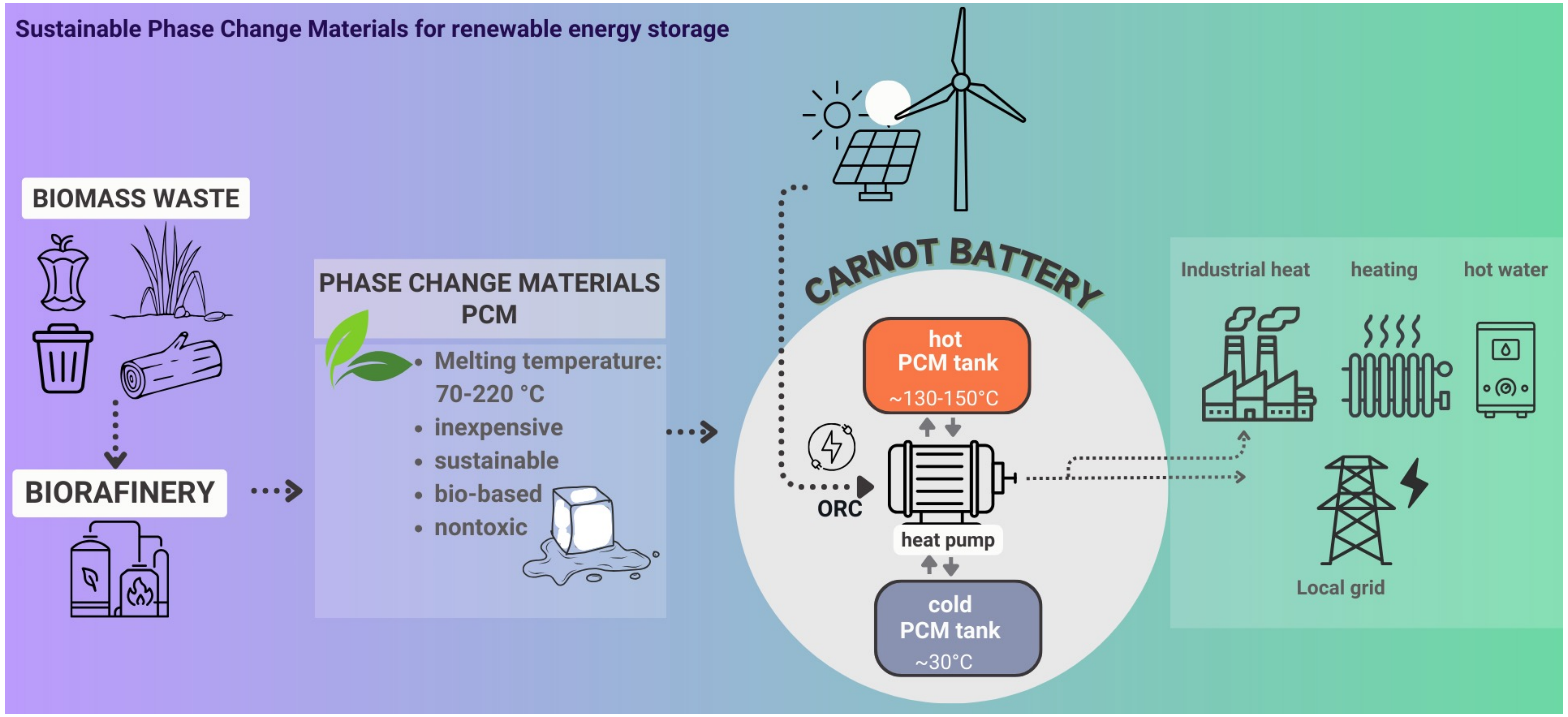
ABSTRACT: Phase-change materials (PCMs) that melt in the intermediate temperature range of 100−220 °C can contribute to the utilization of renewable energy. Compounds rich in hydroxyl groups (e.g., sugar alcohols) are promising materials because of their high energy-storage densities and renewability. However, supercooling and poor stability under operating conditions currently exclude them from practical application as PCMs in the pure form. In this study, we explore a new strategy to encourage the crystallization of sugars by introducing Coulombic interactions into their structures. The thermal properties of the first carbohydrate-based ionic compounds studied as PCMs are reported, focusing on a glucose-based cation and four different

Phase Change Materials based on biomass
(sugar, sugar alcohols and their derivatives) for thermal battery



Sustainable Phase Change Materials for renewable energy storage

BIOMASS WASTE

BIORAFINERY

PHASE CHANGE MATERIALS
PCM

- Melting temperature: 70-220 °C
- inexpensive
- sustainable
- bio-based
- nontoxic

CARNOT BATTERY

hot
PCM tank
~130-150°C

ORC

heat pump

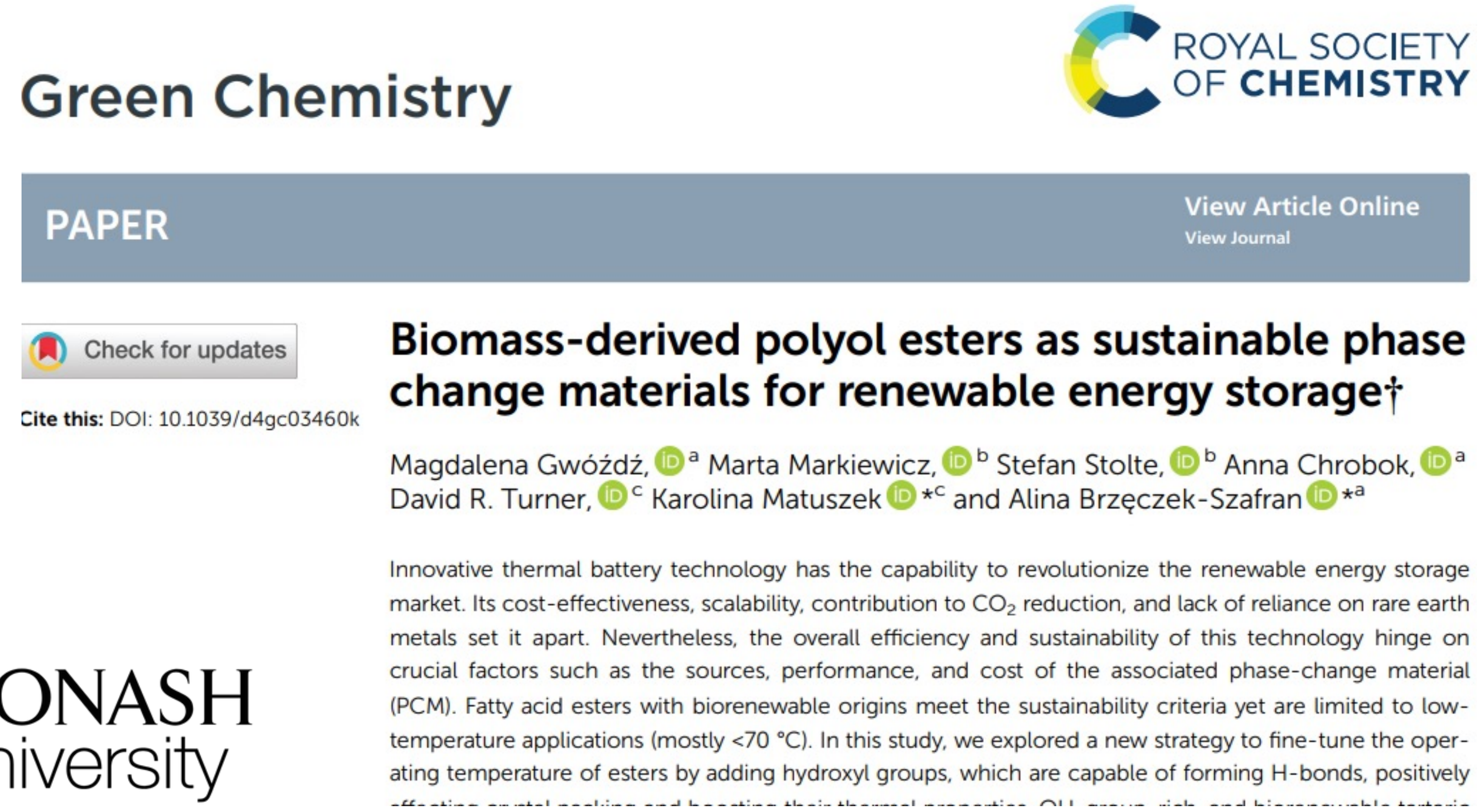
cold
PCM tank
~30°C

Industrial heat

heating

hot water

Local grid



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Biomass-derived polyol esters as sustainable phase change materials for renewable energy storage†

Magdalena Gwóźdź,[a] Marta Markiewicz,[b] Stefan Stolte,[b] Anna Chrobok,[a] David R. Turner,[c] Karolina Matuszek*[c] and Alina Brzęczek-Szafran*[a]

Innovative thermal battery technology has the capability to revolutionize the renewable energy storage market. Its cost-effectiveness, scalability, contribution to CO_2 reduction, and lack of reliance on rare earth metals set it apart. Nevertheless, the overall efficiency and sustainability of this technology hinge on crucial factors such as the sources, performance, and cost of the associated phase-change material (PCM). Fatty acid esters with biorenewable origins meet the sustainability criteria yet are limited to low-temperature applications (mostly <70 °C). In this study, we explored a new strategy to fine-tune the operating temperature of esters by adding hydroxyl groups, which are capable of forming H-bonds, positively

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M. Gwóźdź, M. Markiewicz, S. Stolte, A. Chrobok, David. R. Turner, K. Matuszek, A. Bręczek-Szafran, Green Chemistry 2024 K. Matuszek, S. L. Piper, A. Brzeczek-Szafran, B. Roy, ¸ S. Saher, J. M. Pringle, D. R. MacFarlane, Adv. Mater. 2024, 36, 2313023

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