

# Green Chemistry

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## IN THIS ISSUE

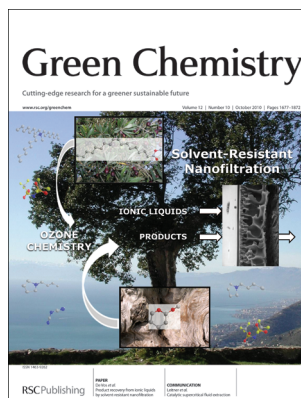
ISSN 1463-9262 CODEN GRCHFJ 12(10) 1677–1872 (2010)



### Cover

See Miller *et al.*, pp. 1704–1706. Lignin-based by-products from the wood industry are readily converted to functional mimics of polyethylene terephthalate (PET).

Image reproduced by permission of Stephen Miller from *Green Chemistry*, 2010, **12**, 1704.



### Inside cover

See De Vos *et al.*, pp. 1726–1733. Solvent-resistant nanofiltration membranes can be used for separating reaction products from ionic liquids, with retentions up to 96%.

Image reproduced by permission of Dirk De Vos from *Green Chemistry*, 2010, **12**, 1726.

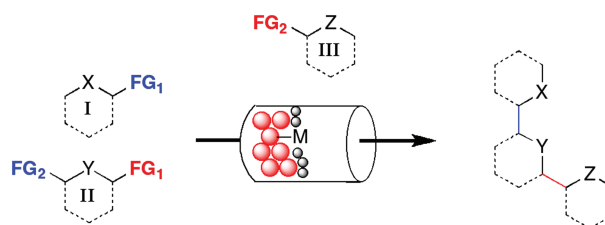
## TUTORIAL REVIEW

1687

### Heterogeneous catalytic synthesis using microreactor technology

Christopher G. Frost\* and Lynsey Mutton

The application of heterogeneous catalysis in conjunction with microreactor technology can facilitate a cleaner and scalable flow methodology for organic synthesis. In this tutorial review we present recent advances in the design of supported catalysts for emerging synthetic applications within microreactor technology.



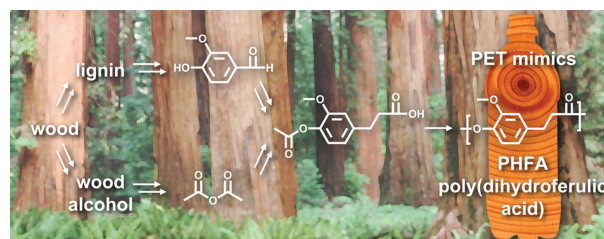
## COMMUNICATIONS

1704

### Biorenewable polyethylene terephthalate mimics derived from lignin and acetic acid

Laurent Mialon, Alexander G. Pemba and Stephen A. Miller\*

Lignin-based vanillin and acetic anhydride are combined to yield poly(dihydroferulic acid), which is a functional mimic of polyethylene terephthalate (PET).



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# Green Chemistry

Cutting-edge research for a greener sustainable future

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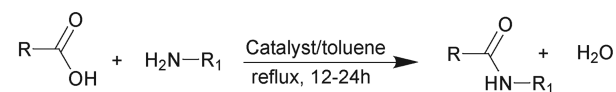
## COMMUNICATIONS

1707

**Sulfated tungstate: a new solid heterogeneous catalyst for amide synthesis**

Pramod S. Chaudhari, Suresh D. Salim, Ravindra V. Sawant and Krishnacharya G. Akamanchi\*

Amide formation avoiding poor atom economy reagents is a priority area. We have synthesized sulfated tungstate as a new reusable and environmentally benign heterogeneous catalyst for direct amide formation between carboxylic acid and amine. It has potential for large scale applications.



where

R = Phenyl R<sub>1</sub> = Phenyl

Benzyl Benzyl

Cinnamyl Morpholinyl

Lauryl etc. Cyclohexyl

Piperidyl etc.

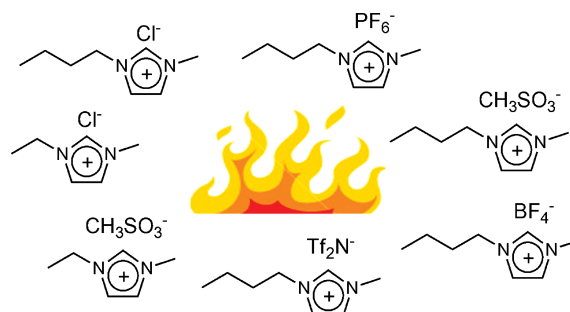
Yield : 33-98%

1711

**Thermal stability of ionic liquids assessed by potentiometric titration**

Niklas Meine, Flavio Benedito and Roberto Rinaldi\*

Using potentiometric titration, we have discovered that ILs start to decompose at much lower temperatures than those inferred from TGA.

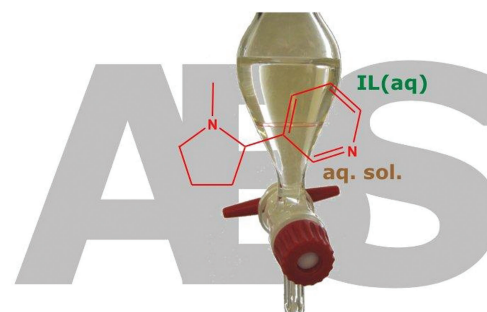


1715

**High-performance extraction of alkaloids using aqueous two-phase systems with ionic liquids**

Mara G. Freire,\* Catarina M. S. S. Neves, Isabel M. Marrucho, José N. Canongia Lopes, Luís Paulo N. Rebelo\* and João A. P. Coutinho

Complete extraction of nicotine using an ionic liquid (IL)-induced aqueous biphasic system (ABS).

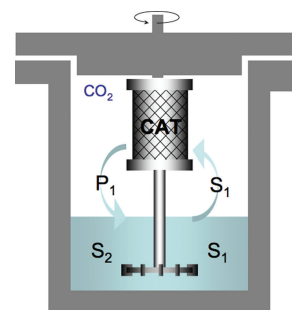


1719

**Catalytic supercritical fluid extraction: selective hydroformylation of olefin mixtures using scCO<sub>2</sub> solubility for differentiation**

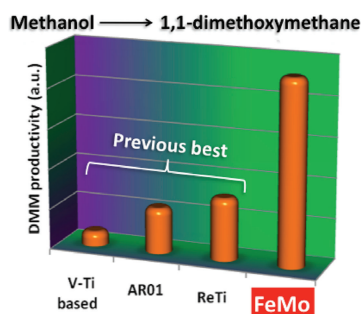
Timo J. Koch, Simon L. Dessel and Walter Leitner\*

A new reaction concept that allows one to control the substrate selectivity of a catalytic reaction by supercritical fluid extraction is demonstrated for the hydroformylation of long-chain olefins as a prototypical example.



## COMMUNICATIONS

1722



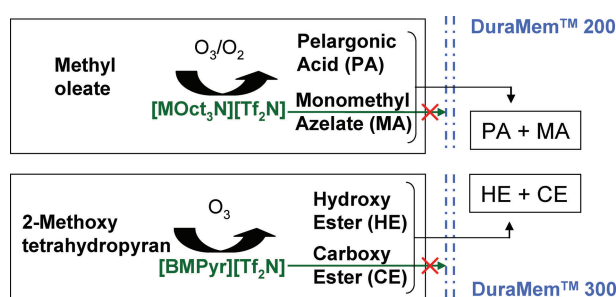
### Direct conversion of methanol into 1,1-dimethoxymethane: remarkably high productivity over an FeMo catalyst placed under unusual conditions

Julien Gornay, Xavier Sécordel, Guillaume Tesquet, Béatrice de Ménorval, Sylvain Cristol, Pascal Fongarland, Mickaël Capron, Louise Duhamel, Edmond Payen, Jean-Luc Dubois and Franck Dumeignil\*

An FeMo catalyst has exhibited the highest productivity ever observed in the direct conversion of methanol into 1,1-dimethoxymethane (ca. 4.6 kg<sub>DMM</sub> h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup> at 553 K).

## PAPERS

1726

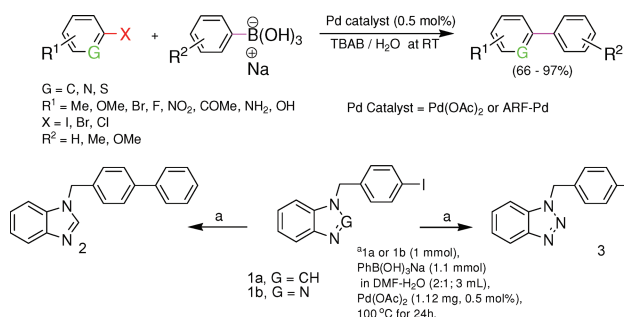


### Product recovery from ionic liquids by solvent-resistant nanofiltration: application to ozonation of acetals and methyl oleate

Charlie Van Doorslaer, Daan Glas, Annelies Peeters, Angels Cano Odena, Ivo Vankelecom, Koen Binnemans, Pascal Mertens and Dirk De Vos\*

The products of ozonations in ionic liquids permeate through commercial nanofiltration membranes, while the ionic liquids themselves are efficiently withheld.

1734

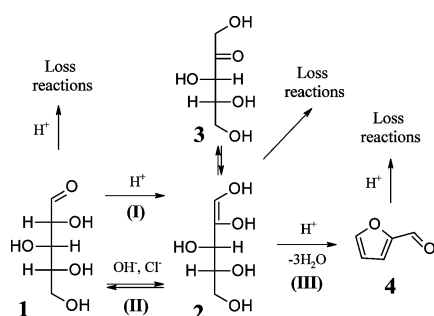


### Highly effective alternative aryl trihydroxyborate salts for a ligand-free, on-water Suzuki–Miyaura coupling reaction

Basudeb Basu,\* Kinkar Biswas, Sekhar Kundu and Sujit Ghosh

Easily accessible sodium salt of aryl trihydroxyborate as alternative to organoboronic acid or ester can efficiently promote Pd-catalyzed ligand-free Suzuki–Miyaura (SM) coupling reaction in water at ambient temperature. We probed the utility of this general, mild, aerobic on-water protocol in modular synthesis of pharmaceutically important benzimidazole- and benzotriazole-based biphenyl scaffolds.

1739



### Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions

Gianluca Marcotullio\* and Wiebren De Jong

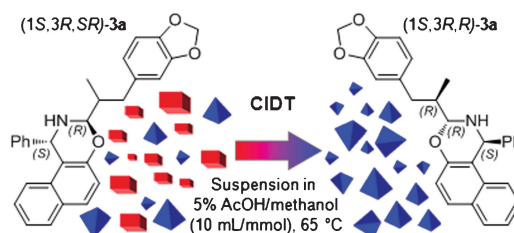
The reaction mechanism leading from xylose to furfural in acidic solutions is deeply explored, in particular, the remarkable effect brought about by the presence of chloride ions. The simple addition of NaCl to an aqueous acidic solution significantly improved the yield and selectivity of furfural.

1747

### Acid promoted CIDT for the deracemization of dihydrocinnamic aldehydes with Betti's base

Goffredo Rosini,\* Claudio Paolucci, Francesca Boschi, Emanuela Marotta, Paolo Righi and Francesco Tozzi

Unfunctionalized  $\alpha$ -epimerizable enantioenriched dihydrocinnamic aldehydes can be accessed by acid-promoted CIDT of their naphthoxazines, obtained from Betti's base.

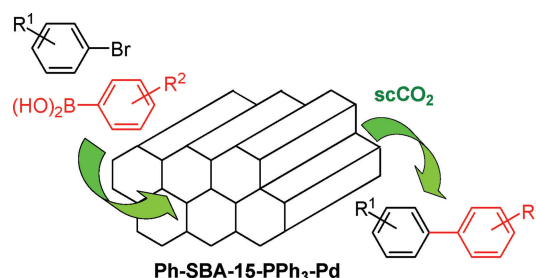


1758

### Preparation and application of SBA-15-supported palladium catalyst for Suzuki reaction in supercritical carbon dioxide

Xiujuan Feng,\* Mei Yan, Tao Zhang, Ying Liu and Ming Bao\*

In the prepared catalyst Ph-SBA-15-PPh<sub>3</sub>-Pd, the Pd species were anchored inside the mesoporous material, which therefore acted as nanoreactors for Suzuki reaction in supercritical carbon dioxide.

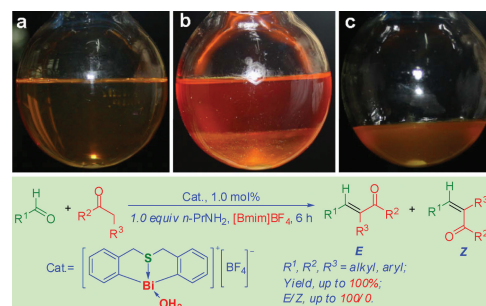


1767

### Facile separation catalyst system: direct diastereoselective synthesis of (*E*)- $\alpha,\beta$ -unsaturated ketones catalyzed by an air-stable Lewis acidic/basic bifunctional organobismuth complex in ionic liquids

Renhua Qiu, Yimiao Qiu, Shuangfeng Yin,\* Xingxing Song, Zhengong Meng, Xinhua Xu, Xiaowen Zhang, Shenglian Luo, Chak-Tong Au\* and Wai-Yeung Wong\*

The catalyst system that comprises an air-stable bifunctional Lewis acidic/basic organobismuth complex and [Bmim]BF<sub>4</sub> is highly efficient in the cross-condensation of aldehydes with ketones.

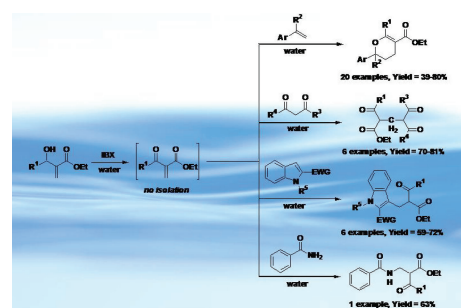


1772

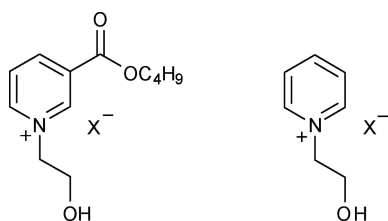
### Water mediated trapping of active methylene intermediates generated by IBX-induced oxidation of Baylis–Hillman adducts with nucleophiles

Jia-Neng Tan, Haoquan Li and Yanlong Gu\*

Water was used as an efficient solvent for performing oxidation of a Baylis–Hillman adduct using IBX as oxidant. The generated product could be trapped *in situ* by many nucleophiles including styrenes,  $\beta$ -dicarbonyl compounds, benzamide and less reactive indoles in water.



1783

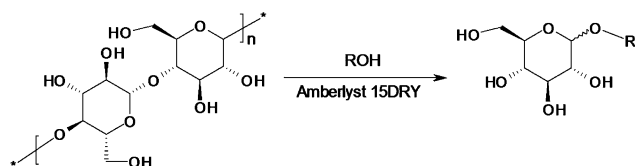


### Further studies on the biodegradation of ionic liquids

Leigh Ford, Jitendra R. Harjani, Farzad Atefi, M. Teresa Garcia, Robert D. Singer and Peter J. Scammells\*

A range of ionic liquids (ILs) containing a pyridinium cation were synthesised and their biodegradability was evaluated using the CO<sub>2</sub> headspace test (ISO 14593). ILs derived from pyridine or nicotinic acid bearing a 1-(2-hydroxyethyl) side chain showed high levels of biodegradation. In contrast, novel pyridinium ILs with ether, acetal and carbamate functionalities, as well as thiazolium-based salts, showed low levels of mineralization.

1790

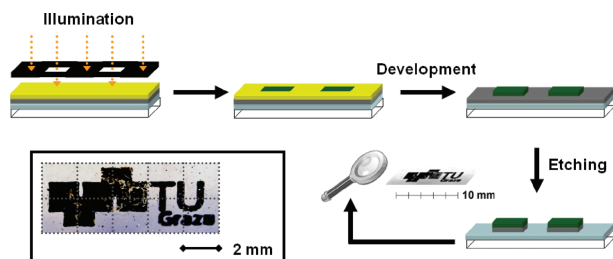


### Cellulose conversion into alkylglycosides in the ionic liquid 1-butyl-3-methylimidazolium chloride

Igor A. Ignatyev, Pascal G. N. Mertens, Charlie Van Doorslaer, Koen Binnemans and Dirk E. de Vos\*

An efficient, 1-butyl-3-methylimidazolium chloride mediated path towards alkyl glucopyranosides from cellulose and alcohols in the presence of Amberlyst-15DRY is reported.

1796

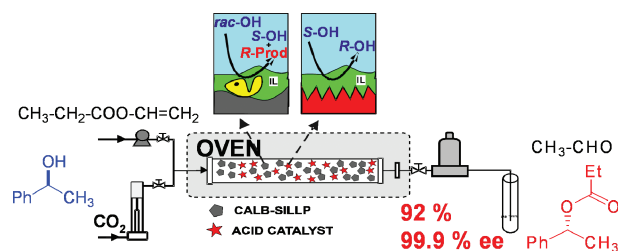


### UV-induced crosslinking of the biopolyester poly(3-hydroxybutyrate)-*co*-(3-hydroxyvalerate)

Barbara Rupp, Clemens Ebner, Elisabeth Rossegger, Christian Slugovc, Franz Stelzer and Frank Wiesbrock\*

UV-induced crosslinking of biodegradable poly(hydroxyalkanoate)s was optimized and used for photolithography, proving to be an efficient system for crosslinking in films.

1803



### Supported Ionic Liquid-Like Phases (SILLPs) for enzymatic processes: Continuous KR and DKR in SILLP-scCO<sub>2</sub> systems

Pedro Lozano,\* Eduardo García-Verdugo,\* Naima Karbass, Kimberley Montague, Teresa De Diego, M. Isabel Burguete and Santiago V. Luis\*

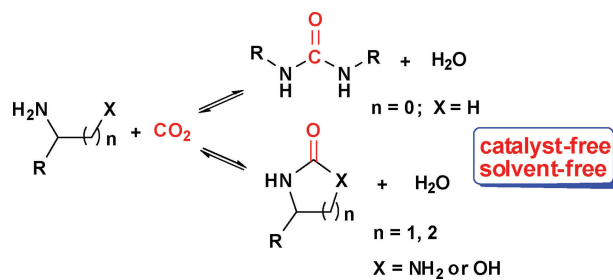
A simple and efficient methodology for the continuous and essentially quantitative DKR of racemic alcohols under scCO<sub>2</sub> flow conditions is described.

1811

### Synthesis of urea derivatives from amines and CO<sub>2</sub> in the absence of catalyst and solvent

Chaoyong Wu, Haiyang Cheng, Ruixia Liu, Qiang Wang, Yufen Hao, Yancun Yu and Fengyu Zhao\*

Urea derivatives are produced with satisfactory yields in the absence of any catalysts, solvents or additives.

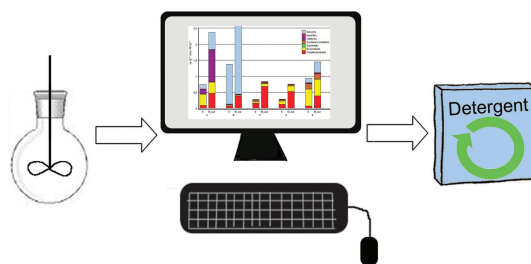


1817

### Enzymatic synthesis of *N*-alkanoyl-*N*-methylglucamide surfactants: solvent-free production and environmental assessment

Yasser Gaber,\* Ulrika Törnvall, Cecilia Orellana-Coca, Magdy Ali Amin and Rajni Hatti-Kaul

The lipase-catalyzed synthesis of *N*-alkanoyl-*N*-methylglucamide in a solvent free medium is described. The tools EATOS and EcoScale are used to assess the environmental impact of the method, and the performance of these tools is evaluated.

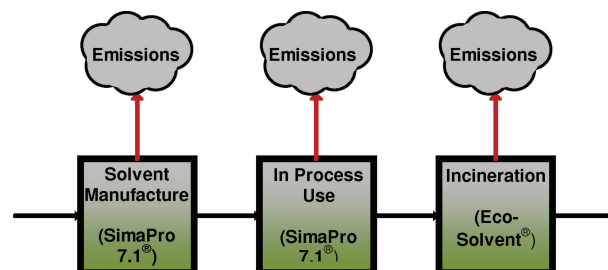


1826

### LCA approach to the analysis of solvent waste issues in the pharmaceutical industry

Michael J. Raymond, C. Stewart Slater\* and Mariano J. Savelski\*

Through integration of solvent recovery and reduction techniques, the environmental footprint of an API synthesis may be significantly reduced. However, the actual extent of the environmental footprint reduction can only be realized with a full life cycle analysis.

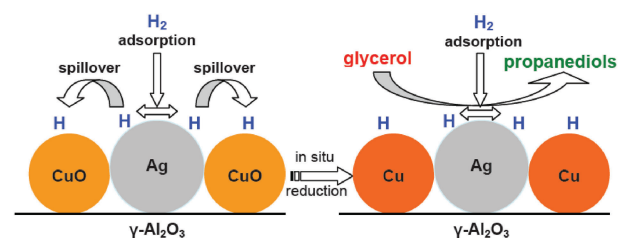


1835

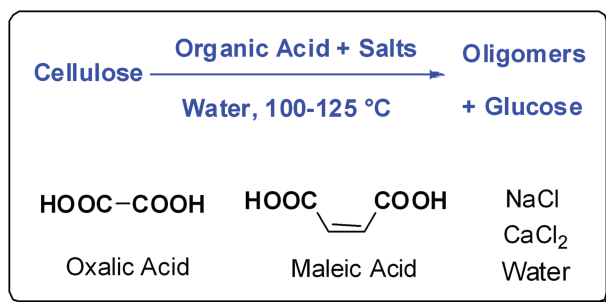
### Selective hydrogenolysis of glycerol to propanediols on supported Cu-containing bimetallic catalysts

Jinxia Zhou, Liyuan Guo, Xinwen Guo, Jingbo Mao and Shuguang Zhang\*

Excellent performance for glycerol hydrogenolysis to propanediols was achieved on a CuAg/Al<sub>2</sub>O<sub>3</sub> catalyst without pre-reduction.



1844

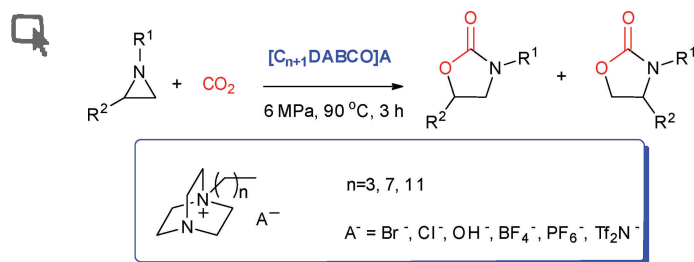


### Salt-assisted organic-acid-catalyzed depolymerization of cellulose

Thorsten vom Stein, Philipp Grande, Fabrizio Sibilla, Ulrich Commandeur, Rainer Fischer, Walter Leitner and Pablo Domínguez de María\*

Joining forces: dicarboxylic acids combined with inorganic salts (NaCl or CaCl<sub>2</sub>) afford the depolymerization of crystalline cellulose under mild conditions in water.

1850

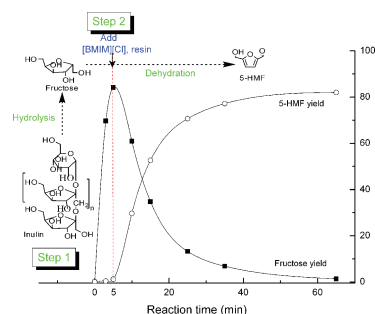


### Lewis basic ionic liquids-catalyzed synthesis of 5-aryl-2-oxazolidinones from aziridines and CO<sub>2</sub> under solvent-free conditions

Zhen-Zhen Yang, Liang-Nian He,\* Shi-Yong Peng and An-Hua Liu

DABCO-derived Lewis basic ionic liquids were developed as recyclable and efficient catalysts for chemical conversion of CO<sub>2</sub> into value-added chemicals.

1855

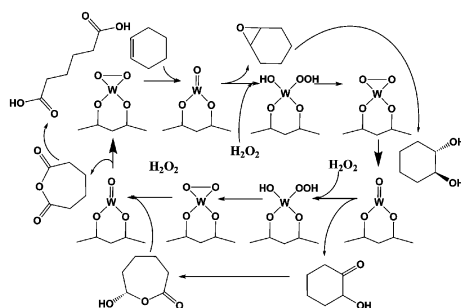


### Efficient one-pot production of 5-hydroxymethylfurfural from inulin in ionic liquids

Xinhua Qi,\* Masaru Watanabe, Taku M. Aida and Richard L. Smith Jr.\*

Inulin was selectively converted to 5-hydroxymethylfurfural (5-HMF) with a high 5-HMF yield of 82% in ionic liquids in one pot with two steps under mild conditions.

1861



### Oxidation of cyclohexene into adipic acid in aqueous dispersions of mesoporous oxides with built-in catalytic sites

Zebastian Bohström, Isabelle Rico-Lattes and Krister Holmberg\*

Concentrated aqueous dispersions of mesoporous oxides are used for overcoming the reactant incompatibility when cyclohexene is oxidized into adipic acid by hydrogen peroxide. Tungsten oxide, either used as the sole material or as a mixed oxide with silica turned out to be very efficient as catalyst for the oxidation.