

6th European Young Engineers Conference

www.eyec.ichip.pw.edu.pl

Copyright © 2017, Faculty of Chemical and Process Engineering,
Warsaw University of Technology

Edited by:

Bartosz Nowak, MSc Eng.

Łukasz Werner, MSc Eng.

Patrycja Wierzba, MSc Eng.

ISBN 978-83-936575-4-4

Printed in 100 copies

The authors are responsible for the content of the papers.

All papers reviewed by Scientific Committee.

Published by:

Faculty of Chemical and Process Engineering

Warsaw University of Technology

Printed in Poland by:

Institute for Sustainable Technologies – National Research Institute

26-600 Radom, 6/10 Pułaskiego Street,

phone (+48) 48 36-442-41, fax (+48) 48 36-447-65

<http://www.itee.radom.pl>

Synthesis and application of cinchona-squaramide organocatalyst supported on polybenzimidazole membrane

*Petra Kozma¹, Péter Kisszékelyi¹, György Székely², Péter Huszthy¹, József Kupai¹

¹ Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Budapest, Hungary

² School of Chemical Engineering & Analytical Science, The University of Manchester, Manchester, United Kingdom

e-mail: jkupai@mail.bme.hu

Keywords: immobilization, membrane, asymmetric synthesis, organocatalyst

Cinchona-based bifunctional catalysts have been extensively employed in the field of organocatalysis due to the incorporation of both hydrogen-bonding acceptors (quinuclidine) and hydrogen-bonding donors (e.g., alcohol, amide, (thio)urea and squaramide) in the molecule, which can simultaneously activate nucleophiles and electrophiles, respectively. Among them, cinchona-derived (thio)urea and squaramide catalysts have shown remarkable application potential by using their bifurcated hydrogen bonding donors in activating electrophilic carbonyls and imines.

Polymer-supported chiral organocatalysts have emerged as a rapidly expanding field of research in recent years, in part due to the traditionally emphasized advantages of polymeric immobilization (facilitated separation and recovery procedures, recycling etc.). We present a simple strategy to prepare cinchona modified polybenzimidazole (PBI) membrane.

While hydroquinine is available directly, its amino derivative was prepared from it, via azide, in a two-step sequence by using the *Bose–Mitsunobu* reaction followed by *Staudinger* reduction. The amino group was converted to squaramide by reacting with the appropriate half-squaramide derivative. This organocatalyst was immobilized to a propargyl modified PBI membrane after a functionalization with azidoethylene group and a click reaction.

Applying our immobilized cinchona-derived squaramide organocatalysts in *Michael* additions and aldol reactions we achieved excellent enantioselectivities, allowed for unprecedented practical applications in the synthesis of valuable bioactive synthons.

Acknowledgements

Financial support of the Hungarian Scientific Research Fund/National Research, Development and Innovation Office (OTKA/NKFIH No. PD108462).