

Application of 2-methyltetrahydrofuran as a “green solvent” in olefin metathesis reactions

*Michał Smoleń, Mariusz Kędziorek and Karol Grela**

Faculty of Chemistry, University of Warsaw, Żwirki i Wigury 101,
02-089 Warsaw, Poland

smolen.michal@wp.pl

<http://karolgrela.eu/>

Ruthenium-catalyzed olefin metathesis reactions represent an attractive and powerful transformation for the formation of new C=C double bonds.¹ As this reaction becomes an important part of industrial processes,^{2,3} there is a growing need for eco-friendly solvents that are applicable in large scale synthesis. In our study we used 2-methyltetrahydrofuran which is derived from renewable resources like oat hulls and corn cobs. These contain pentoses, which after dehydration give furfural, which is then catalytically reduced to 2-methyltetrahydrofuran.⁴ 2-MeTHF is considered an environmentally friendly compound and its use is advocated by the ACS Green Chemistry Pharmaceutical Roundtable.⁵

In our research we used 2-MeTHF in the most important olefin metathesis reactions. For this study we used newly synthesized second generation Hoveyda-type catalysts **1a-c** bearing symmetrical NHC and modified styrenes, in comparison with the commercially available second generation Hoveyda catalyst **2** (figure 1). To extensively examine the performance of the catalysts, we applied them in a set of model reactions. For comparison, these catalysts were also tested in common solvents used in olefin metathesis: dichloromethane and toluene.⁶

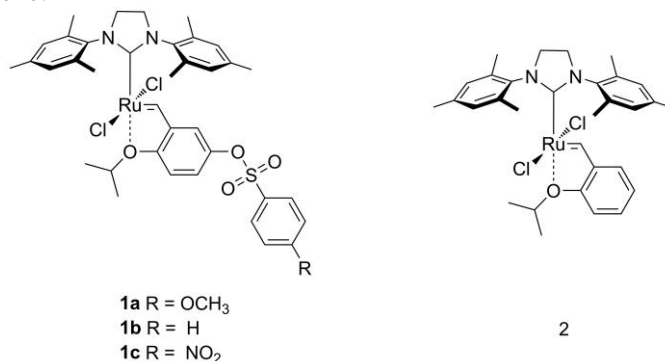


Figure 1. Newly-synthesized second generation Hoveyda-type catalysts **1a-c** and second generation Hoveyda catalyst **2**.

¹ Michalak, M.; Gułajski, Ł.; Grela, K., "Alkene Metathesis" in *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations*, Vol. 47a (Alkenes), Ed.: A. De Meijere; Georg Thieme Verlag KG, **2010**, 327-438

² Czaban, J.; Torborg, C.; Grela, K., "Olefin Metathesis: from Academic Concepts to Commercial Catalysts" in *Sustainable Catalysis: Challenges and Practices for the Pharmaceutical and Fine Chemical Industries*, First Edition; Dunn, P. J.; Hii, K. K. (Mimi); Krische, M.J.; Williams, M. T., Eds.; John Wiley & Sons, Inc., **2013**, 163-214

³ Clavier, H.; Grela, K.; Kirschning, A.; Mauduit, M.; Nolan, S. P., "Sustainable Concepts in Olefin Metathesis" *Angew. Chem. Int. Ed.* **2007**, 46, 6786-6801

⁴ Hoydonckx, H. E.; Van Rhijn, W. M.; Van Rhijn, W.; De Vos, D. E.; Jacobs, P. A., "Furfural and Derivatives", *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim: Wiley-VCH, **2007**, 285-310

⁵ Antonucci, V.; Coleman, J.; Ferry, J. B.; Johnson, N.; Mathe, M.; Scott, J. P.; Xu, J. *Org. Process Res. Dev.*, **2011**, 15 (4), 939-941

⁶ Smoleń, M.; Kędziorek, M.; Grela, K., *Catal. Commun.*, **2013**, in press

The authors would like to acknowledge the “TEAM” project operated within the Foundation for Polish Science Team Program co-financed by the EU European Regional Development Fund, Operational Program for Innovative Economy 2007-2013



**INNOWACYJNA
GOSPODARKA**
NARODOWA STRATEGIA SPÓJNOŚCI



UNIA EUROPEJSKA
EUROPEJSKI FUNDUSZ
ROZWOJU REGIONALNEGO