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STUDY ON RECYCLING OF THE IONIC LIQUID  
WITH METALLIC CATALYSTS IN THE SYNTHESIS  
OF FUNCTIONALIZED NORBORNENE

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Z KATALIZATORAMI METALICZNYMI W SYNTEZIE  
POCHODNYCH NORBORNENU

Abstract

In presented study the recovery and reuse of the catalytic systems consisting of an ionic liquid and metal catalysts in the synthesis of 5-norbornene-2,3-dicarboxylic acid dimethyl ester have been shown. 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide was used as IL. From the group of catalysts, metal chlorides ( $MgCl_2$ ,  $YbCl_3$ ,  $YCl_3$ ) and metal triflates ( $Y(OTf)_3$ ,  $Li(OTf)$ ,  $Yb(OTf)_3$ ,  $Yb(OTf)_3 \cdot xH_2O$ ) were chosen. Vacuum distillation and solvent extraction were investigated as methods for removing the reaction product from the ionic liquid and catalyst.

*Keywords: ionic liquids, recycling, catalysts*

Streszczenie

Zbadano możliwość odzyskiwania i ponownego użycia układów katalitycznych, składających się z cieczy jonowej – bis(trifluorometylosulfonylo)imidku 1-butylo-1-metylopirolidyniowego oraz katalizatorów metalicznych, na przykładzie reakcji otrzymywania estru dimetylowego kwasu 5-norborneno-2,3-dikarboksylowego. Z grupy katalizatorów do badań wytypowano chlorki metali ( $MgCl_2$ ,  $YbCl_3$ ,  $YCl_3$ ) i trifluorometanosulfoniany metali ( $Y(OTf)_3$ ,  $Li(OTf)$ ,  $Yb(OTf)_3$ ,  $Yb(OTf)_3 \cdot xH_2O$ ). Produkt oddzielano od cieczy jonowej i katalizatora metodą destylacji pod obniżonym ciśnieniem oraz ekstrakcji rozpuszczalnikami.

*Słowa kluczowe: ciecze jonowe, recykling, katalizatory*

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## 1. Introduction

Ionic liquids (IL) are not new, but their popularity has recently resurged as possible alternatives to common organic solvents. Their low vapour pressure makes them potential substitutes for highly volatile organic solvents, thus reducing the amount of pollution caused through solvent evaporation and their non-flammable nature reduces the risk of fire hazard. In addition to replacing volatile organic solvents, the recyclability of IL is perhaps one of their greatest potentials, in particular where this can be linked to recycling an active IL-soluble catalyst.

We use IL as solvents in the synthesis of norbornene derivatives via Diels-Alder reaction of cyclopentadiene with various dienophiles [1–3]. Functionalized norbornenes have a lot of applications, for example in drug delivery [4], in biochemical applications [5], as well as luminescent materials and devices [6, 7] and liquid crystalline [8]. The use of metal chlorides and triflates as Lewis acids catalysts in the synthesis of norbornene derivatives increases significantly the reaction rate, yield and stereoselectivity of the product.

In the presented study we have performed the recovery and reuse of the catalytic systems consisting of the ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [bmpyr][NTf<sub>2</sub>], and metal catalysts in the synthesis of 5-norbornene-2,3-dicarboxylic acid dimethyl ester (Fig. 1). From the group of catalysts, metal chlorides – MgCl<sub>2</sub>, YbCl<sub>3</sub>, YCl<sub>3</sub>, and metal triflates – Y(OTf)<sub>3</sub>, Li(OTf), Yb(OTf)<sub>3</sub>, Yb(OTf)<sub>3</sub>·xH<sub>2</sub>O have been examined as the most active. The purpose of presented investigations was to compare the recyclability of catalysts in relation to the type of metal, its salt and the method used for removing the product from the [bmpyr][NTf<sub>2</sub>]/catalyst system.

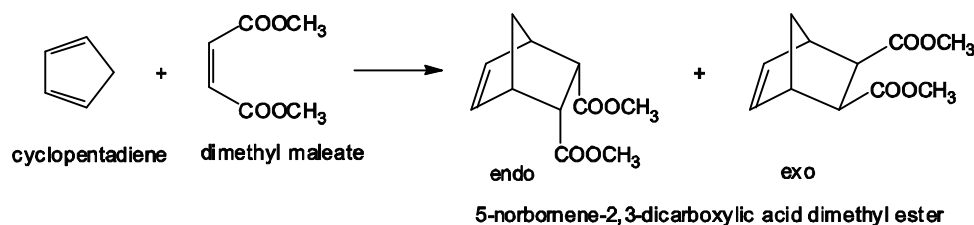


Fig 1. Diels–Alder reaction between cyclopentadiene and dimethyl maleate

Rys. 1. Reakcja Dielsa–Aldera pomiędzy cyklopentadienem i maleinianem dimetylu

## 2. Experimental

### 2.1. Materials

The ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [bmpyr][NTf<sub>2</sub>] was made by Solvent Innovation, Germany. Prior to the use in the Diels–Alder reaction it was dried at 60°C under the pressure of 5 mbar for 24 hours. Dicyclopentadiene of 95% purity was purchased from Fluka. Dimethyl maleate (96%) and catalysts: lithium triflate (99.995%), ytterbium triflate (99.99%), ytterbium triflate hydrate

(97%), yttrium triflate (98%), anhydrous yttrium chloride (99.99%), anhydrous ytterbium chloride (99.9%), anhydrous magnesium chloride (97%) were provided by Aldrich. Toluene (99.5%, 0.03% of H<sub>2</sub>O) was purchased from POCH, and an extra dry toluene (99.85%; < 50 ppm of water) over molecular sieve from Acros Organics.

## 2.2. General procedure of recycling experiments

A portion of catalyst (0.08 mmol) was weighed and introduced into a round bottom flask of 5 ml in capacity, equipped with a magnetic stirrer. The catalyst was dissolved in 2 ml of the ionic liquid [bmpyrr][NTf<sub>2</sub>]. 60 µl of cyclohexanone as an internal standard and 1.152 g (8 mmol) of dimethyl maleate were added. Subsequently, cyclopentadiene was introduced in the amount of 0.7920 g (12 mmol). The flask was stoppered with a rubber septum and placed in a thermostated bath at 25°C. The course of the reaction was controlled by the GC analysis.

After GC indicated the reaction to be complete, the reaction mixture was operated in one of two paths.

Removing the product from IL by extraction with an organic solvent. The product was extracted from the reaction mixture with 4 x 6 mL toluene, which pulled the product into the upper organic layer. For all catalytic systems toluene (99.5%), containing 0.03% of water was used to the extraction. In addition, for YCl<sub>3</sub> and YbCl<sub>3</sub> an extra dry toluene was used. The organic layer was separated from the IL. The toluene solution was concentrated in vacuo. The lower layer containing IL-catalyst mixture was dried under vacuum and recharged with starting materials with the exception of catalyst and IL. A following run was further conducted in the recycled IL.

Removing the product from IL by distillation. The reaction flask was connected to the distillation path and the 5-norbornene-2,3-dicarboxylic acid dimethyl ester distilled directly under vacuum (4 mbar) from the mixture at 105°C. The residual [bmpyrr][NTf<sub>2</sub>]-catalyst mixture was then cooled to rt and recharged with cyclohexanone, dimethyl maleate and cyclopentadiene. A second and following runs, with no further addition of catalyst, were then conducted in the recycled IL at 25°C.

## 3. Results and discussion

The Diels–Alder reaction of cyclopentadiene and dimethyl maleate carried out in [bmpyrr][NTf<sub>2</sub>] in the absence of the catalysts proceeded slowly. After 4 hours, 54% yield of 5-norbornene-2,3-dicarboxylic acid dimethyl ester was achieved with 4.2 endo/exo selectivity (Tab. 1). When the metal chlorides or triflates were added, the rate of the reaction and endo/exo selectivities were significantly increased (Tab. 1). The compounds of Y, Yb, Mg and Li proved the most efficient catalysts. A series of reaction cycles were run in order to investigate the stability of the catalytic systems consisting of these catalysts and [bmpyrr][NTf<sub>2</sub>]. To remove the product from the mixture of IL and catalyst we used extraction with organic solvents or distillation. In the group of organic solvents (diethyl ether, hexane, cyclohexane, toluene) toluene was established as the best solvent for extraction. All solvents were immiscible with [bmpyrr][NTf<sub>2</sub>] and pull out the product from it but toluene could be used in less volume than others providing the most effective

extraction. Extraction is the most commonly reported method for product isolation after reaction in IL, but is connected with putting volatile solvents into process. Therefore solvent free product isolation by direct distillation from the reaction mixture was also investigated. Under distillation conditions (maximal bath temperature 135°C), the product, 5-norbornene-2,3-dicarboxylic acid dimethyl ester, proved to be stable. It was also known, that [bmpyrr][NTf<sub>2</sub>] has an excellent thermal stability to the 431°C [9]. Therefore we supposed it could be a good method for product isolation and recycling of IL-catalyst mixture.

Table 1

**Results of Diels-Alder reaction between cyclopentadiene and dimethyl maleate in [bmpyrr][NTf<sub>2</sub>] as medium and in the presence of catalysts**

Catalyst	Time [h]	Yield [%]	Endo/exo ratio
without	0.5	13	4.2
	4	54	4.2
LiOTf	0.5	53	7.6
	4	90	7.6
MgCl <sub>2</sub>	0.5	77	8.4
	1	96	8.4
YCl <sub>3</sub>	0.5	98	12.9
YbCl <sub>3</sub>	0.5	96	11.1
Y(OTf) <sub>3</sub>	0.5	74	8.0
	1	74	8.0
Yb(OTf) <sub>3</sub>	0.5	92	7.3
Yb(OTf) <sub>3</sub> ·xH <sub>2</sub> O	0.5	98	8.6

It should be emphasized that in the presence of Y(OTf)<sub>3</sub> or Yb(OTf)<sub>3</sub>, a side reaction of polymerization of cyclopentadiene had a large extent. Therefore the reaction with Y(OTf)<sub>3</sub> in fresh IL was stopped at 74% yield (Tab. 1, Fig. 2). The formation of polymers made the isolation of the product by distillation impossible. For catalysts – Y(OTf)<sub>3</sub> and Yb(OTf)<sub>3</sub> the extraction method was used only. The results were presented in Figures 2 and 3, respectively. Upon repeated use of [bmpyrr][NTf<sub>2</sub>]-Y(OTf)<sub>3</sub> or [bmpyrr][NTf<sub>2</sub>]-Yb(OTf)<sub>3</sub> mixture, almost constant quantitative yields (> 92%) were observed. From the sixth (Fig. 2) and fifth run (Fig. 3) respectively the reaction slightly slowed down and longer time (1–1.5 h) was needed to achieve yield above 90%. However, endo/exo ratios were maintained at the same level or increased with the following runs. The high stereoselectivities were the evidence that the catalyst was located in the recycled mixtures. On the other hand, these mixtures lost weight after following runs. It was probably caused by the manual operations and partial loss of IL to the toluene extract. The IL, [bmpyrr][NTf<sub>2</sub>] is immiscible with pure toluene but could be partly miscible with toluene-product mixture.

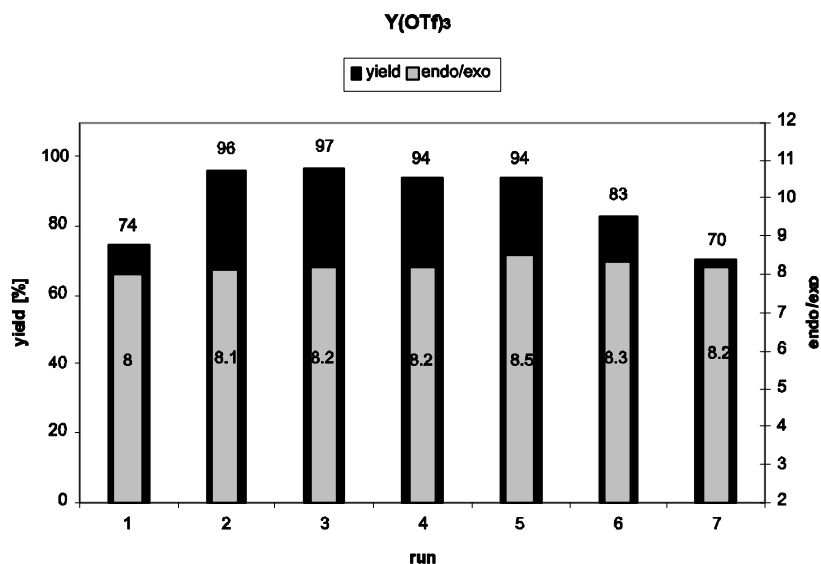


Fig. 2. Yields and endo/exo stereoselectivities in Diels-Alder reaction with recycled [bmpyrr][NTf<sub>2</sub>]-Y(OTf)<sub>3</sub> mixture (reaction time: 0.5 h; extraction of the product with toluene)

Rys. 2. Wydajności i stereoselektywności w kolejnych reakcjach z recykulowanym układem katalitycznym [bmpyrr][NTf<sub>2</sub>]-Y(OTf)<sub>3</sub> (czas reakcji: 0,5 h; ekstrakcja produktu toluenem)

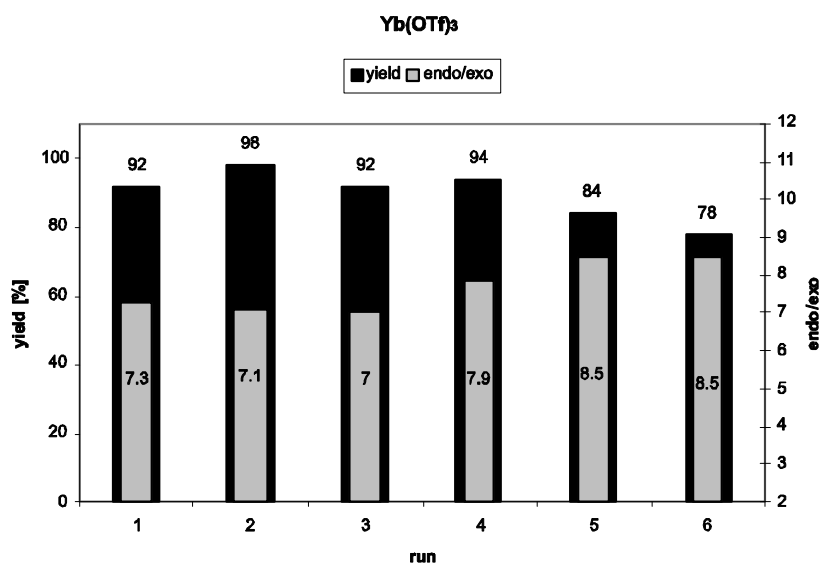


Fig. 3. Yields and endo/exo stereoselectivities in Diels-Alder reaction with recycled [bmpyrr][NTf<sub>2</sub>]-Yb(OTf)<sub>3</sub> mixture (reaction time: 0.5 h; extraction of the product with toluene)

Rys. 3. Wydajności i stereoselektywności w kolejnych reakcjach z recykulowanym układem katalitycznym [bmpyrr][NTf<sub>2</sub>]-Yb(OTf)<sub>3</sub> (czas reakcji: 0,5 h; ekstrakcja produktu toluenem)

The effect of isolation methods of the product on recyclability was compared for three catalytic systems  $[\text{bmpyrr}][\text{NTf}_2]\text{-Yb}(\text{OTf})_3\text{xH}_2\text{O}$ ,  $[\text{bmpyrr}][\text{NTf}_2]\text{-YCl}_3$  and  $[\text{bmpyrr}][\text{NTf}_2]\text{-YbCl}_3$ .

For  $[\text{bmpyrr}][\text{NTf}_2]\text{-Yb}(\text{OTf})_3\text{xH}_2\text{O}$  system, removing the product by toluene extraction assured a little more efficient reuse of this system than separation by distillation (Figs. 4 and 5). Endo/exo selectivities after extraction were near 10 and were higher than in runs after distillation of product. In the first run, in the presence of  $\text{Yb}(\text{OTf})_3\text{xH}_2\text{O}$  unlike anhydrous  $\text{Yb}(\text{OTf})_3$ , polymerization of cyclopentadiene was not observed. Under distillation conditions ( $135^\circ\text{C}$ , 4 mbar) water being integral part of  $\text{Yb}(\text{OTf})_3\text{xH}_2\text{O}$  could be partly removed and polymers were formed. Upon repeated use the contribution (portion) of polymers in IL-catalyst mixture increased and could be the reason of catalyst deactivation.

From the group of metallic catalysts, in the presence of metal chlorides –  $\text{YCl}_3$  and  $\text{YbCl}_3$ , the highest endo/exo ratios were achieved (Tab. 1). Thus the study on their effectiveness after recycling was interesting. However, these catalysts were moisture sensitive. When toluene containing 0.03% of water was used to the separation of the product from IL-catalyst mixture, in the second run the reaction proceeded as slowly and with endo/exo ratio as without catalyst. Therefore for extraction of the product from  $[\text{bmpyrr}][\text{NTf}_2]\text{-YCl}_3$  and  $[\text{bmpyrr}][\text{NTf}_2]\text{-YbCl}_3$  mixture, an extra dry ( $< 50$  ppm of water) toluene was used. The yield and stereoselectivity still decreased in the following runs. The results were presented in Tab. 2. Better recycling effects for metal chlorides, dissolved in  $[\text{bmpyrr}][\text{NTf}_2]$ , were accomplished by direct distillation of the product (Tab. 2). To the fourth run the reaction rates and endo/exo stereoselectivities were higher than without catalyst. Deactivation of the chloride catalyst was caused by the product remaining in the IL-catalyst mixture and polymers formed under distillation conditions.

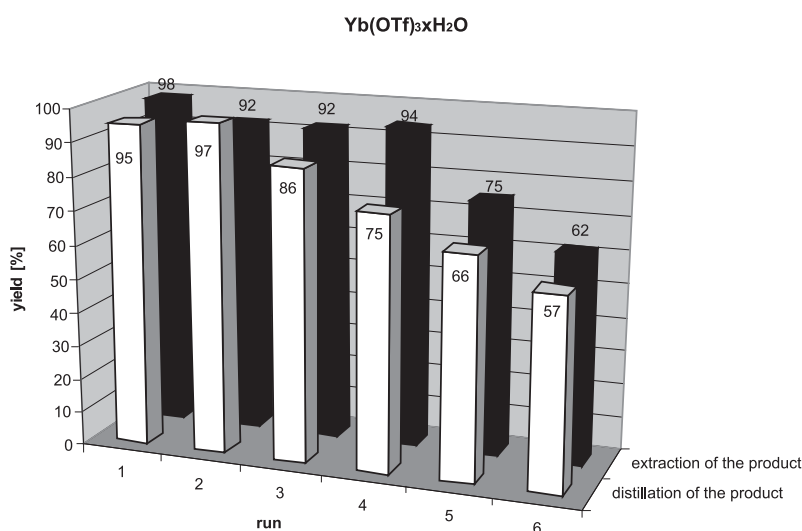


Fig. 4. Comparison of yields in Diels-Alder reaction with recycled  $[\text{bmpyrr}][\text{NTf}_2]\text{-Yb}(\text{OTf})_3\text{xH}_2\text{O}$  mixture for two methods of product isolation (reaction time: 0.5 h)

Rys. 4. Porównanie wydajności w kolejnych reakcjach z recykulowanym układem katalitycznym  $[\text{bmpyrr}][\text{NTf}_2]\text{-Yb}(\text{OTf})_3\text{xH}_2\text{O}$  i dwóch metod wyodrębniania produktu (czas reakcji: 0,5 h)

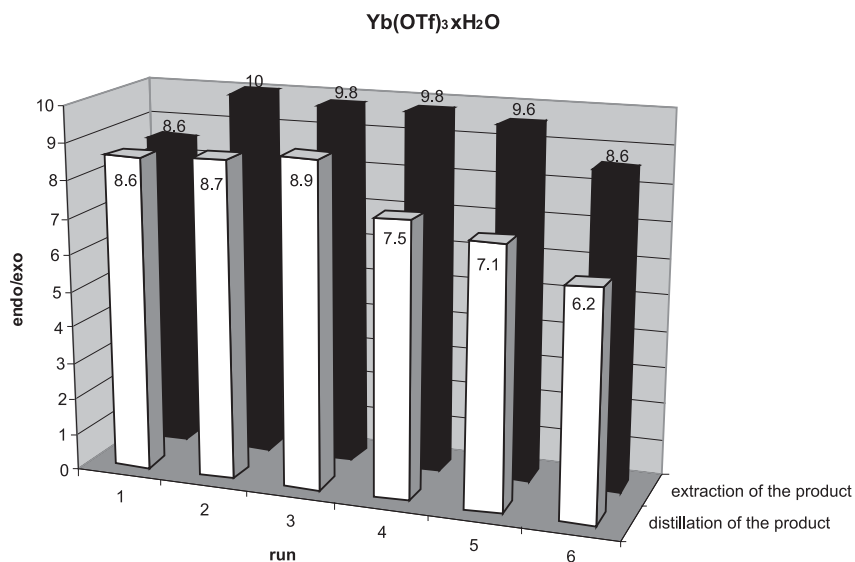


Fig. 5. Comparison of endo/exo stereoselectivities in Diels-Alder reaction with recycled [bmpyrr][NTf<sub>2</sub>]-Yb(OTf)<sub>3</sub>·xH<sub>2</sub>O mixture for two methods of product isolation (reaction time: 0.5 h)

Rys. 5. Porównanie stereoselektywności endo/egzo w kolejnych reakcjach z recykulowanym układem katalitycznym [bmpyrr][NTf<sub>2</sub>]-Yb(OTf)<sub>3</sub>·xH<sub>2</sub>O i dwóch metod wyodrębniania produktu (czas reakcji: 0,5 h)

Table 2

**Comparison of yields and endo/exo stereoselectivities in Diels-Alder reaction with recycled [bmpyrr][NTf<sub>2</sub>]-catalyst mixture for two methods of product isolation**

Run	Extraction method*			Distillation method		
	Time [h]	Yield [%]	Endo/exo ratio	Time [h]	Yield [%]	Endo/exo ratio
[bmpyrr][NTf <sub>2</sub> ]-YCl <sub>3</sub>						
1	0.5	98	12.9	0.5	98	12.9
2	0.5	81	11.5	0.5	88	13.0
	1.0	91		1.0	95	
3	0.5	60	8.0	0.5	71	11.0
	2.0	76		1.0	85	
	4.0	84		1.5	90	
4	0.5	22	4.0	0.5	36	7.6
	4.0	64		4.0	82	
[bmpyrr][NTf <sub>2</sub> ]-YbCl <sub>3</sub>						
1	0.5	96	11.1	0.5	96	11.1
2	0.5	69	9.0	0.5	89	11.4
	1.5	90		1.0	94	
3	0.5	46	6.5	0.5	81	8.8
	2.0	77		1.0	88	
	4.0	88		1.5	91	
4	0.5	18	4.3	0.5	47	6.8
	4.0	59		4.0	89	

\*Extra dry toluene was used for extraction.

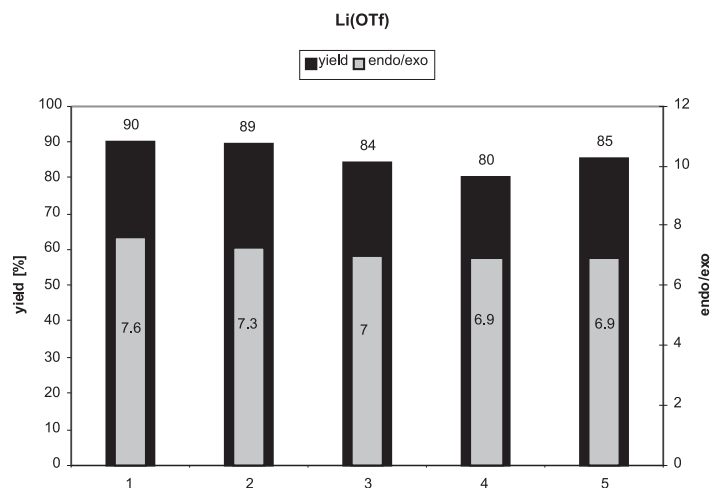


Fig. 6. Yields and endo/exo stereoselectivities in Diels-Alder reaction with recycled [bmpyrr][NTf<sub>2</sub>]-LiOTf mixture (reaction time: 4.0 h; direct distillation of product)

Rys. 6. Wydajności i stereoselektywności reakcji Dielsa-Aldera z recykulowanym układem katalitycznym [bmpyrr][NTf<sub>2</sub>]-LiOTf (czas reakcji: 4,0 h; bezpośrednia destylacja produktu z mieszaniny reakcyjnej)

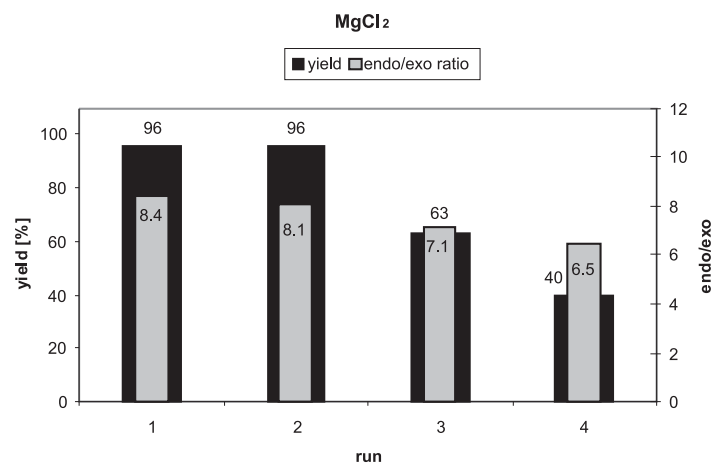


Fig. 7. Yields and endo/exo stereoselectivities in Diels-Alder reaction with recycled [bmpyrr][NTf<sub>2</sub>]-MgCl<sub>2</sub> mixture (reaction time: 1.0 h; direct distillation of product from reaction mixture)

Rys. 7. Wydajności i stereoselektywności reakcji Dielsa-Aldera z recykulowanym układem katalitycznym [bmpyrr][NTf<sub>2</sub>]-MgCl<sub>2</sub> (czas reakcji: 1,0 h; bezpośrednia destylacja produktu z mieszaniny reakcyjnej)



In the next step of our investigations, we tested the recyclability of the systems consisting of the [bmpyrr][NTf<sub>2</sub>] and the catalysts – LiOTf and MgCl<sub>2</sub> (Figs 6 and 7, respectively), characterized with lower activity than Y and Yb compounds. The distillation method was only used to separate the product from IL-catalyst mixture. It was found that in the presence of LiOTf the activity was almost constant in five cycles. When MgCl<sub>2</sub> was used a drastic decrease in the yield was observed in the third run. Endo/exo stereoselectivity dropped from 8.4 in the first run to 6.5 in the fourth run.

#### 4. Conclusions

Both extraction and distillation of 5-norbornene-2,3-dicarboxylic acid dimethyl ester can be used as an effective method for separation of this product from the [bmpyrr][NTf<sub>2</sub>]-catalyst mixtures. The catalyst stays dissolved in the pyrrolidinium ionic liquid and can be recycled many times. Metal chlorides lost their activity after repeated use, especially when extraction method was used. The reason was their moisture sensitivity. Distillation of the product directly from the reaction mixture proved more effective for recyclability of [bmpyrr][NTf<sub>2</sub>]-metal chloride systems. This method assured the anhydrous conditions. For very active catalytic systems [bmpyrr][NTf<sub>2</sub>]-Y(OTf)<sub>3</sub>, [bmpyrr][NTf<sub>2</sub>]-Yb(OTf)<sub>3</sub> and [bmpyrr][NTf<sub>2</sub>]-Yb(OTf)<sub>3</sub>·xH<sub>2</sub>O, more efficient recycling was achieved when the product was extracted with toluene. The presence of a little amount of water or toluene did not affect the activity of these catalysts, and rather was helpful to retard the side reaction of cyclopentadiene polymerization. With the lower active metal triflates – LiOTf, the distillation of the product proved to be a good method of its separation because no loss in yield and stereoselectivity was observed in five recycles and cyclopentadiene polymers were not formed.

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