

**Abstract of the Ph.D. thesis by mgr inż. Marcin Gano, entitled:**  
***“Chiral Ionic Liquids Based on Terpenes – Synthesis and Application”***  
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The Ph.D. thesis concerns synthesis and characterization of chiral quaternary pyrrolidinium salts based on N-(2-hydroxyethyl)pyrrolidinium fragment in cation structure containing a fragment derived from terpene alcohol, i.e. (–)-menthol, (–)-borneol, and (+)-fenchol, along with their use in Diels-Alder reaction. The aim of the research was to expand the knowledge of asymmetric induction in the Diels-Alder reaction and develop catalytic systems based on chiral Ionic Liquids (CILs) and metal catalysts for the enantioselective performance of this reaction.

This dissertation consists of three general chapters: theoretical section, results and discussion, as well as the experimental section. In the theoretical section, information about the synthesis of chiral ionic liquids based on natural terpene alcohols and their application in organic synthesis was provided. The analysis of literature data about Diels-Alder reaction in the ionic liquids as media, with a special emphasis placed on useful chiral ionic liquids, combination of ILs with Lewis acids and chiral ligands was also performed. Additionally, the examples of asymmetric Diels-Alder reactions, catalyzed by salen complexes in the presence of organic solvents, were presented.

As a part of my research, the conditions of synthesis of a new fragment of twenty-one chiral ionic liquids with N-(2-hydroxyethyl)-N-terpenoxymethylpyrrolidinium cation and terpene fragment based on natural terpene alcohols (–)-menthol, (–)-borneol, and (+)-fenchol were developed. Ten of the resulting chiral salts are assigned to the chiral ionic liquid group – six salts, consisting of bis(trifluoromethylsulfonyl)imide [NTf<sub>2</sub>] and bis(perfluoroethylsulfonyl)imide [NPF<sub>2</sub>] anions were liquid at room temperature, while the melting point of the next four salts was below 100°C.

Identification of prepared salts was performed based on <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectroscopy, high-resolution mass spectrometry, and elemental analysis. The optical purity of synthesized compounds was determined by using the NMR method with the chiral shift-inducing reagent. For all synthesized chiral salts, the following physicochemical properties were determined: phase transition temperature, specific rotation, thermal stability – and solubility in organic solvents, and water. Moreover, for liquid salts, the viscosity and density in the function of temperature, refractive index, surface tension, and contact angles on different nature surfaces were measured.

It was found that the salts with (+)-fenchol fragment in the cation have the highest thermal stability, while the stability of salts with (–)-menthol fragment is the lowest. Furthermore, thermal stability of salts with the same cation increases in the following series of

anions:  $[\text{Cl}] < [\text{OTf}] \sim [\text{C}_4\text{F}_9\text{SO}_3] < [\text{PF}_6] \sim [\text{BF}_4] < [\text{NTf}_2] < [\text{NPf}_2]$ . It is shown that chiral ionic liquids with  $[\text{NTf}_2]$  and  $[\text{NPf}_2]$  anions can be used at temperatures of up to 100°C without loss of optical activity. Among the chiral ionic liquids at ambient temperature, salts with menthol fragment have the lowest viscosity, followed by fenchol – and the highest with borneol fragment.

In the next step the synthesized, chiral ionic liquids with  $[\text{NTf}_2]$  and  $[\text{NPf}_2]$  anions were used to prepare catalytic systems consisting of chiral ionic liquids/ Lewis acid and chiral ionic liquids/ Lewis acid/ salen ligand. Chiral ionic liquids and prepared catalytic systems were applied in Diels-Alder reaction between cyclopentadiene and  $\alpha,\beta$ -unsaturated aldehydes, ketones, and esters. The effect of the structure of cation and anion in chiral ionic liquids, metal type, counterion in Lewis acid, and structure of salen ligands on the dienophile conversion, diastereoselectivity, and asymmetry induction in the reaction product were investigated. In addition, the effects of reaction temperature, Lewis acid concentration in the ionic liquid and relative to the dienophile, as well as the molar ratio of acid to the ligand on the process were determined.

Triflates of various metals (Zn, Mg, Cu, Sn, Bi, In, Sc, Y, Nd, Yb) were used as Lewis acids, and additionally different zinc catalysts - zinc bromide, chloride, acetate, and bistriflimide were used. Salen ligands used, were derivatives of 1*R*,2*R*- and 1*S*,2*S*-diaminocyclohexane along with four aldehydes: 3,5-dibromosalicylic – ligand L1(*R,R*) and L1(*S,S*), 3-methoxy-5-nitrosalicylic – ligand L2(*R,R*) and L2(*S,S*), 3,5-di-*tert*-butylsalicylic – ligand L3(*R,R*) and L3(*S,S*), and 3,5-dichlorosalicylic – ligand L4(*R,R*) and L4(*S,S*). They were synthesized and identified in this work.

It has become apparent that the induction of asymmetry in the Diels-Alder reaction product is possible by combining a chiral ionic liquid with a Lewis acid and a salen ligand, with the highest enantiomeric excesses being guaranteed by the L3 ligands. It has been shown that the use of chiral ionic liquids with the anion  $[\text{NTf}_2]$  leads to higher enantiomeric excesses than the use of liquids with the same cation and anion  $[\text{NPf}_2]$ . Furthermore, it has been proven that the degree of asymmetry induction in the Diels-Alder reaction in a system catalytic system consisting of a chiral ionic liquid, Lewis acid, and a salen ligand depends on the metal atom of the Lewis acid and, to a lesser extent, on the counterion of the Lewis acid. High enantiomeric excess was provided by catalytic systems formed with zinc, tin(II), indium and ytterbium Lewis acids. The performed research on the recovery of the selected catalytic systems from the reaction mixture and reuse in the reaction showed the possibility of multiple use while preserving high enantiomeric excess.

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