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## Theoretical interpretation of enantioselectivity trends in (*R*)-Ru-BINAP catalyzed hydrogenation of methylacetoacetate in the QAS ionic liquid phase

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Chiral catalytic complex (*R*)-[RuCl(binap)(*p*-cymene)]Cl (Ru-BINAP) is commonly used for asymmetric hydrogenations [1]. In our recent works we reported on its utilization in stereoselective transformation of methylacetoacetate (MAA) to methyl-3-hydroxybutyrate in the mixed methanol-ionic liquid phase [2]. The ingenious idea to combine positive aspects of the homogeneous and heterogeneous arrangements with the help of ionic liquids (ILs) comprises of their use as reaction co-solvents and allows the reaction to be carried out homogeneously, however, still bringing in major advantages of the heterogeneous system [e.g. in 3].

Despite hundreds of structurally different ionic liquids reported the most commonly used are those with the imidazolium type of cation combined either with hexafluorophosphate or tetrafluoroborate counter ions [4]. Another attractive group of ILs might be ranked among quaternary ammonium salts (QAS). In one of our previous works it was shown [5] that only small amounts of *n*-alkyl-triethylammonium bis(trifluoromethane sulfonyl) imides ( $N_{R222}Tf_2N$ , *R* = 6, 7, 8, 10, 12, 14 (Figure 1) in a conventional solvent were necessary to accommodate the catalytic complex and that the reaction was carried out with very high enantioselectivity. Similarly it was proved that under optimized conditions the catalytic complex immobilized in this manner could be used repeatedly.

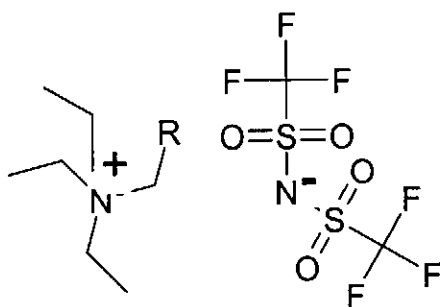


Figure 1: *N*-alkyl-triethylammonium bis(trifluoromethane sulfonyl) imides ( $N_{R222}Tf_2N$ , *R* = 2 to 20).

An essential part of this work was focused on the role of the alkyl chain length in  $N_{R222}Tf_2N$  and its reflection in the evaluated kinetic parameters. For this screening  $N_{R222}Tf_2N$  was mixed with methanol using the one-to-one weight ratio. Surprisingly rather irregular trends were observed with changing the length of the alkyl chain. The highest values of TOF were achieved in the system with  $N_{12222}Tf_2N$  and  $N_{8222}Tf_2N$ . Systems with  $N_{6222}Tf_2N$ ,  $N_{7222}Tf_2N$  and  $N_{10222}Tf_2N$  were much slower. Interestingly in the case of  $N_{12222}Tf_2N$  the attained enantioselectivity was approximately on the same level as in the experiments with pure methanol (*ee* 97.5 % vs. *ee* 98 % in methanol)!

The main intention of the present communication is to report on the possible theoretical explanation of such irregular trends elucidated with the help of molecular simulations methods

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including approximate *ab-initio* calculations. A stepwise approach is presented for evaluation the energetically most stable conformers of a series of individual  $N_{R-222}Tf_2N$  ionic liquids with a variable length of the side alkyl chain for interpretation of selectivity-structure effects observed experimentally. Initially Monte Carlo Molecular Mechanics was used, followed with more specific semi-empirical PM3 and PM6 methods to elucidate also characteristic thermodynamic functions of state and theoretical molecular spectra. The Density Functional Theory was finally applied using the B3LYP level of theory with a Gaussian type of basis set 6-31G+(d,p) to enhance the quality of the evaluated structural properties.