ELECTRONIC SUPPLEMENTARY INFORMATION.

HIGHLY SELECTIVE BIOCATALYTIC SYNTHESIS OF MONOACYLGLYCERIDES IN SPONGE-LIKE IONIC LIQUIDS

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NMR analyses

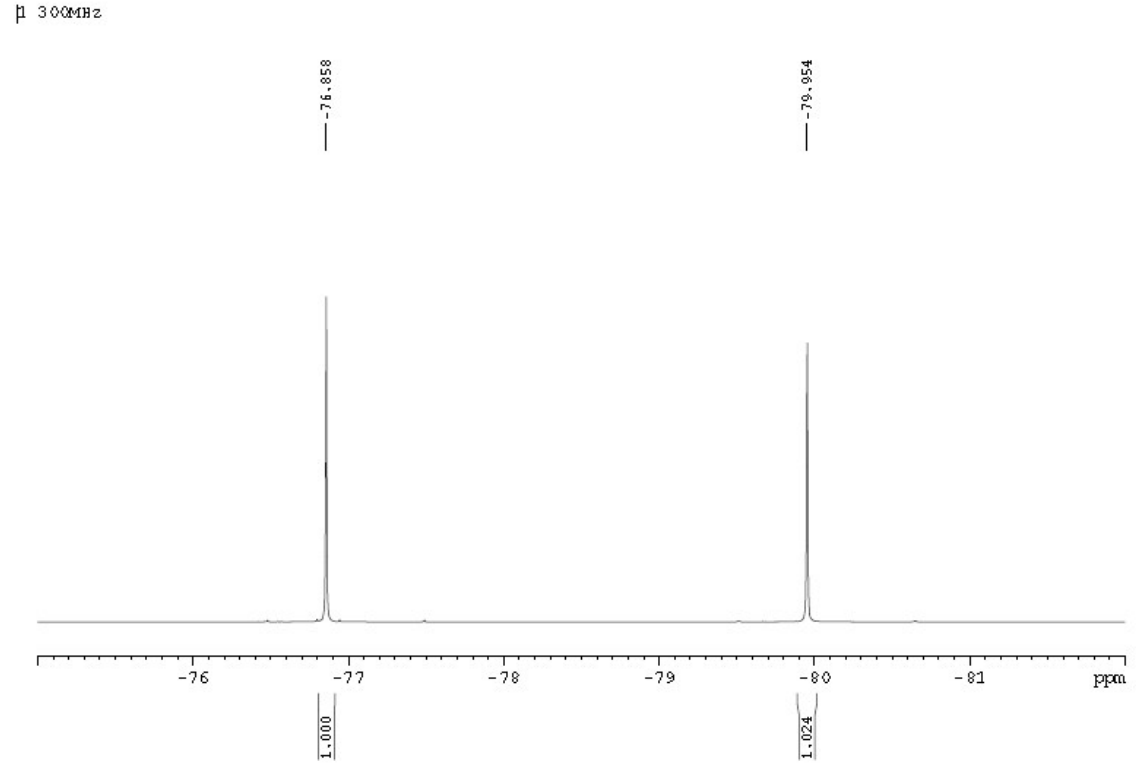
Samples preparation of reaction media containing SLILs based on [NTf_2] anion

As representative example of SLILs based on [NTf_2] anion, the resulting acylglyceride products from reaction mixture reported in Table 1, corresponding to the synthesis of monoolein in [C_{18}mim][NTf_2] (entry 10), was selected for the determination of the residual IL content.

The reaction mixture was placed into a 2-mL vial, and then incubated at 60 ºC until a fully clear and homogeneous phase was observed. Then, hot water (1.0 mL, 60ºC) was added, and the resulting multiphase solution was strongly shaken for 30 min at 60ºC, being finally cooled to room temperature. The acylglycerides/water/[C_{18}mim][NTf_2] multiphasic mixture was consecutively centrifuged three times at 15,000 rpm (60 min) and at room temperature (non-controlled), 23 and 15ºC, respectively, resulting in three phases, as follows: a top phase of acylglyceride product, an aqueous middle phase and a bottom phase containing the solid IL. Then, an aliquot (80 μL) was taken from the resulting top phase, being dissolved in 0.45 mL acetone-δ_6 containing 80 μL trifluoroacetic acid (internal standard), and analyzed by 300 MHz ^{19}F NMR in a Brucker AC 200E spectrometer. As standard reference, a sample (50 mg) of [C_{18}tmna][NTf_2] dissolved in 0.45 mL acetone-δ_6 ,containing 80 μL trifluoroacetic acid, was also analysed to be used as reference

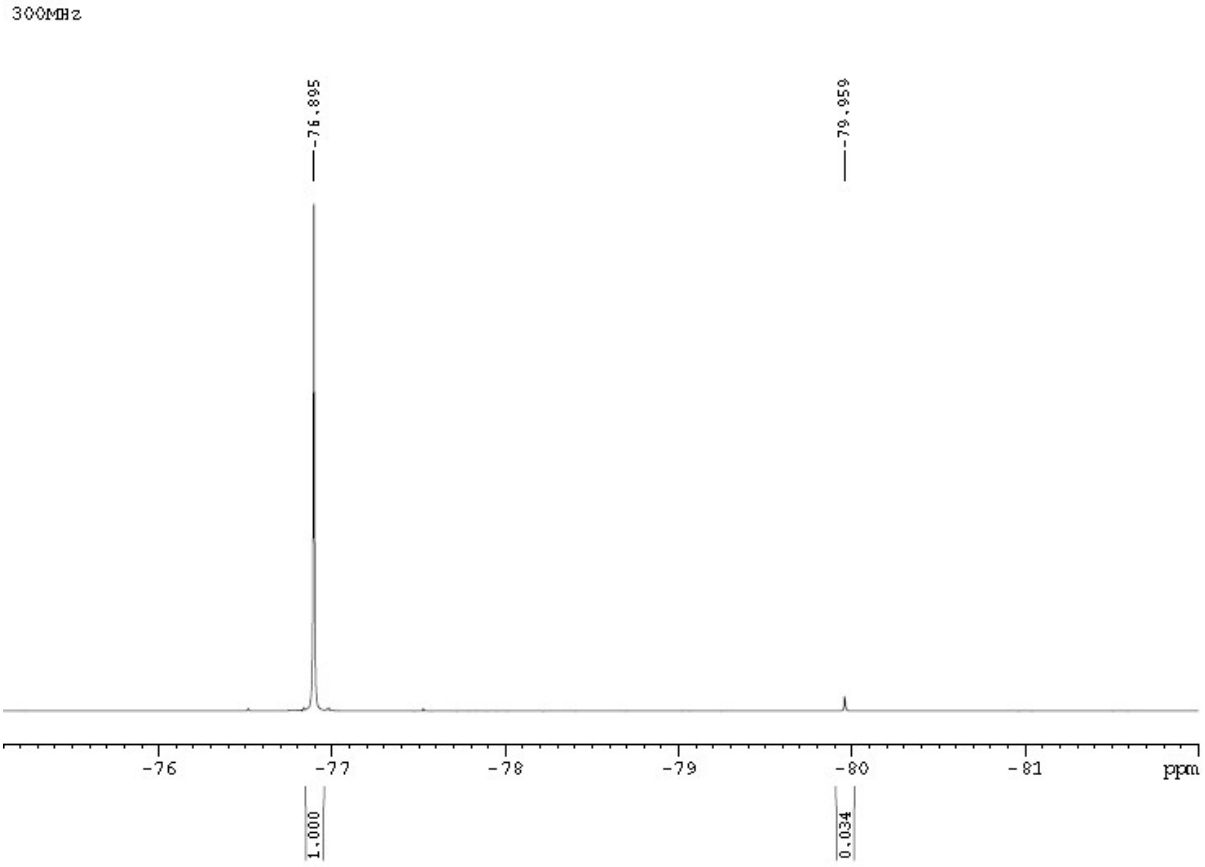
1. Standard reference [C_{18}mim][NTf_2]

^{19}F-NMR spectrum



***2. Sample of reaction medium of Entry 10, Table 1(from* [C_{18}mim][NTf_2])**

^{19}F-NMR spectrum



Samples preparation of reaction media containing SLILs based on [BF_4] anion

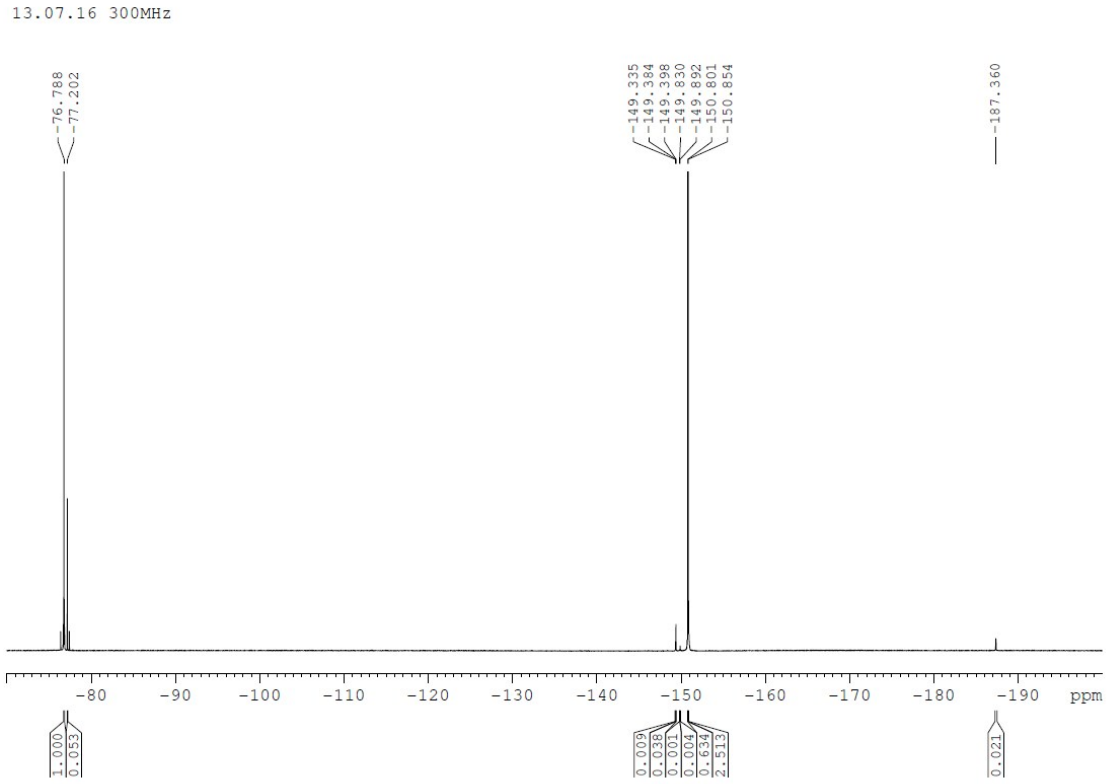
As representative example of SLILs based on [BF_4] anion, the resulting acylglyceride products from reaction mixtures reported in Table 1, corresponding to the synthesis of monocaprin, monolaurin, monomyristin, monopalmitin and monoolein in [C_{12}mim][BF_4] (entries 12, 13, 14, 15 and 16, respectively), were selected for the determination of the residual IL content.

The reaction mixture was placed into a 2-mL vial, and then incubated at 60ºC until a fully clear and homogeneous phase was observed. Then, dodecane (1 mL) was added to each sample, and the resulting fully clear monophasic solutions were strongly shaken for 3 min at room temperature and finally incubated into an ice-bath for 15 min. Each aglyglycerides/SLIL/dodecane mixture was centrifuged at 15,000 rpm (15 min) and at 6ºC, resulting in the full precipitation of the [C_{12}mim][BF_4]. The top phases were collected, and the residual IL content was analysed by ^{19}F NMR, as described above by using a [C_{12}mim][BF_4] solution in acetone-δ_6 containing TFA, as standard

1. Standard reference [C_{12}mim][BF_4]

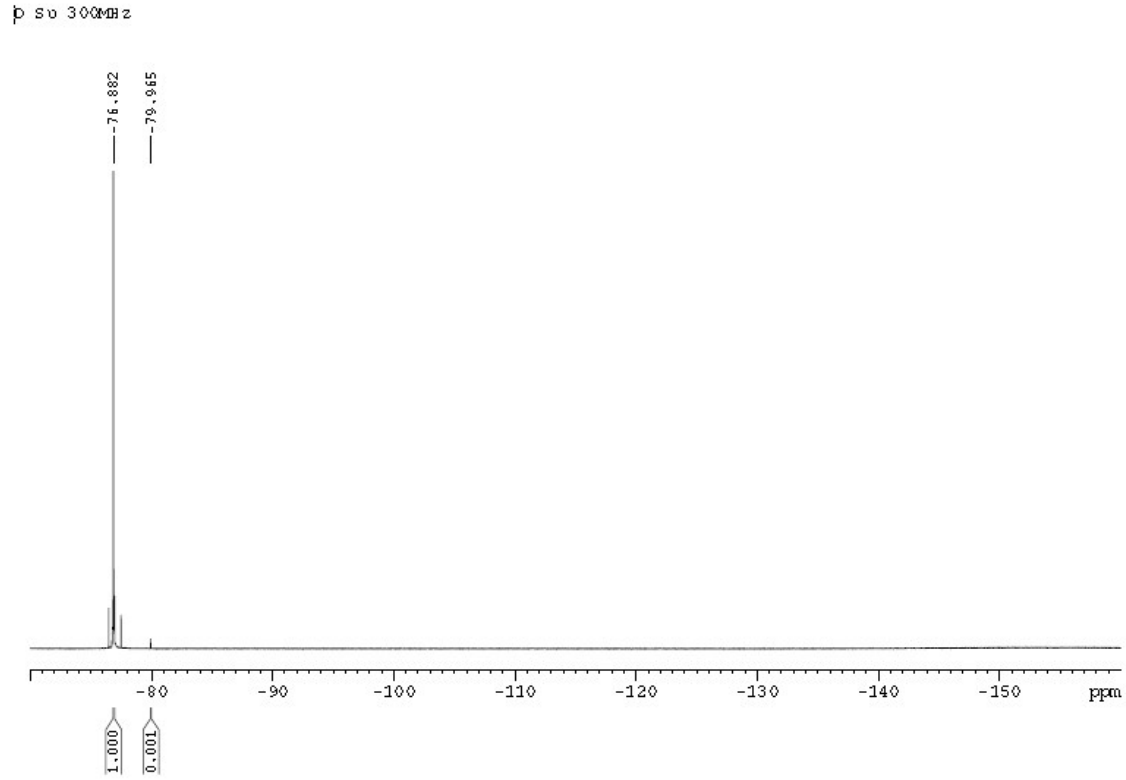
^{19}F-NMR spectrum

Standard reference: (50 mg) of [C_{12}tmna][BF_4] dissolved in 0.45 mL acetone-δ_6, containing 40 μL trifluoroacetic acid.



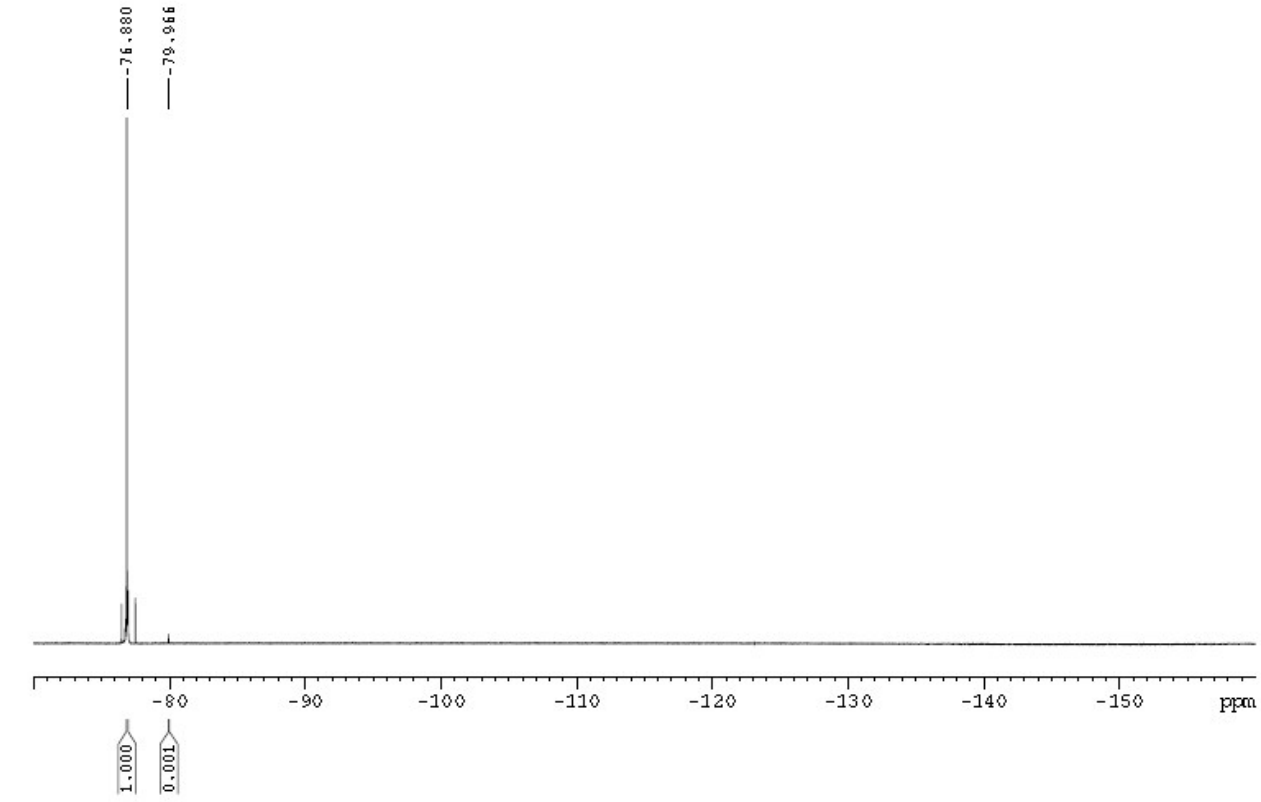
***2. Sample of reaction medium of Entry 12, Table 1(monocaprin/*[C_{12}mim][BF_4])**

^{19}F-NMR spectrum



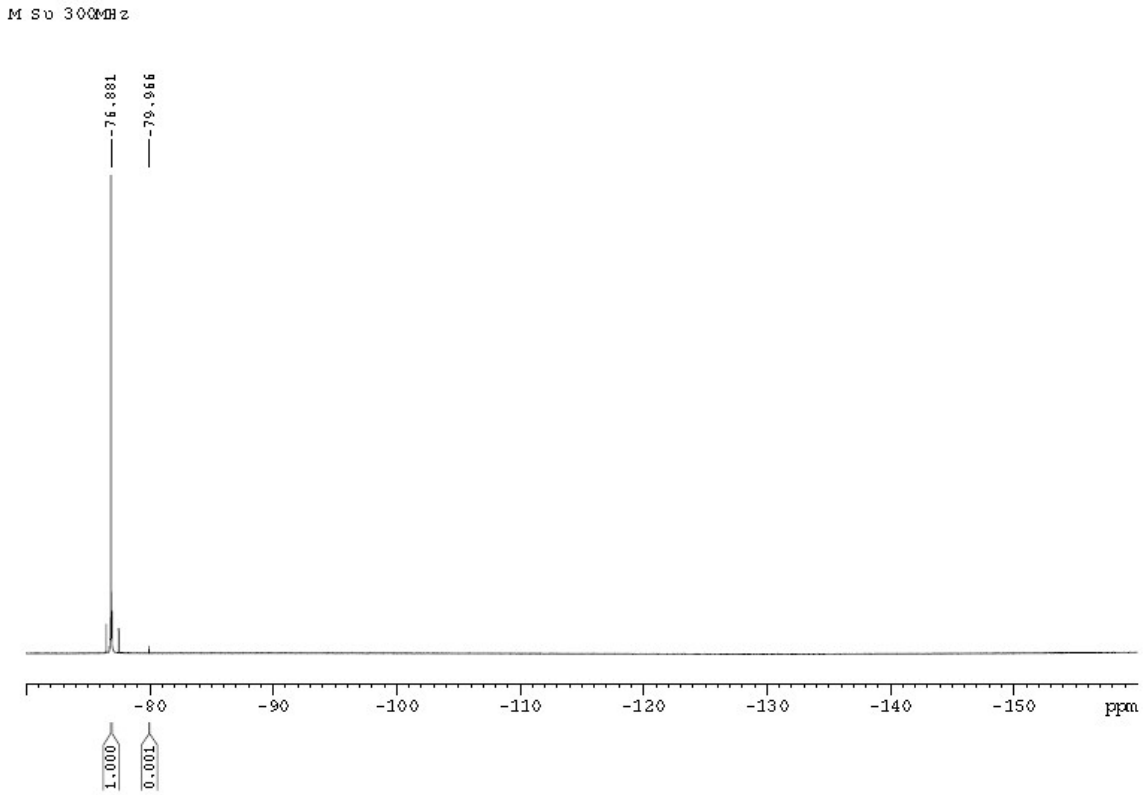
***3. Sample of reaction medium of Entry 13, Table 1(monolaurin/*[C_{12}mima][BF_4])**

^{19}F-NMR spectrum



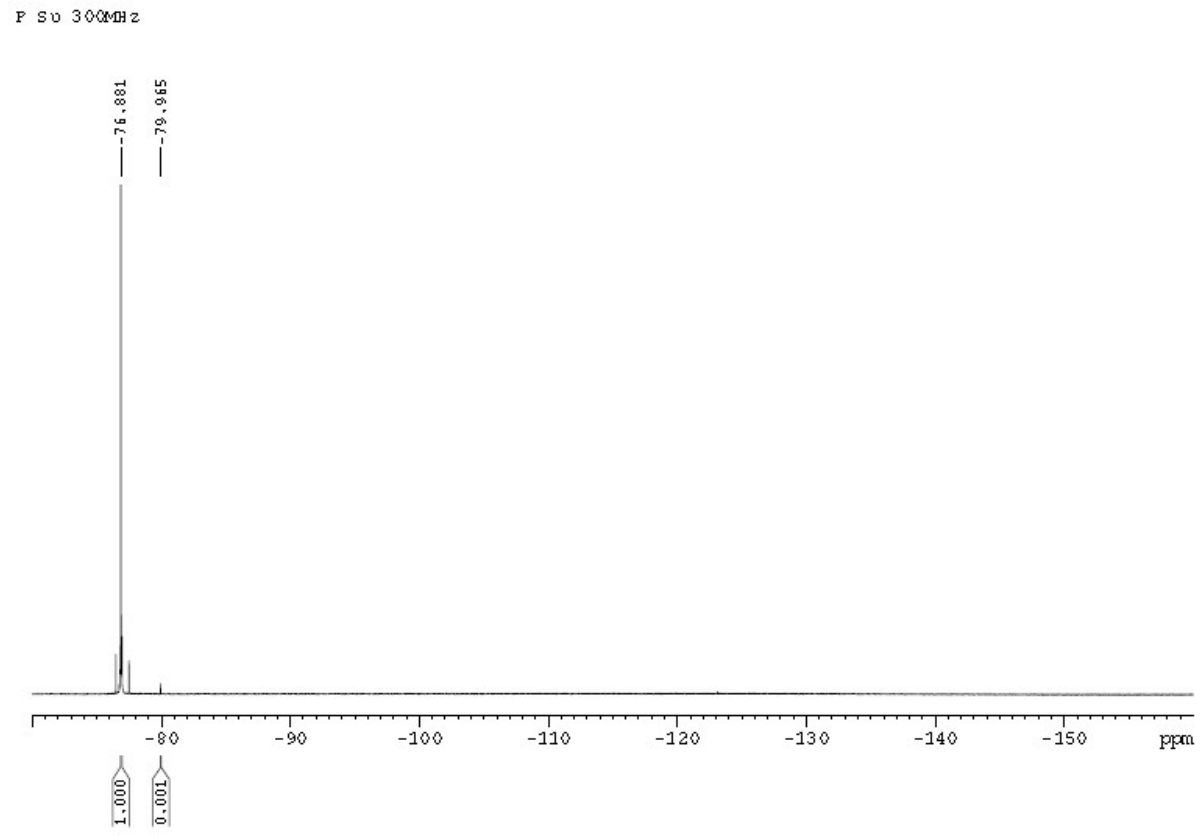
***4. Sample of reaction medium of Entry 14, Table 1(monomyristin/*[C_{12}mim][BF_4])**

^{19}F-NMR spectrum



***5. Sample of reaction medium of Entry 15, Table 1(monopalmitin/*[C_{12}min][BF_4])**

^{19}F-NMR spectrum



6. Sample of reaction medium of Entry 15, Table 1(monoolein/[C_{12}mim][BF_4])

^{19}F-NMR spectrum