

Esterification of carboxylate-based ionic liquids with alkyl Halide

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1 Experimental

[EMIm]Ac (1-ethyl-3-methylimidazolium acetate) was purchased from Ionic Liquid Technologies GmbH&Co. KG. Carboxylate-based ionic liquid: 1,3-dimethylimidazolium acetate, N,N-diethyl-N,N-dimethylimidazolium acetate, [EMIm]Formate, [EMIm]Propionate, [EMIm]nButyrate, [EMIm]iButyrate, were synthesized. Dichloromethane, chloroform, and 1-chlorobutane were purified according to the literature.¹ All other chemicals were obtained from Alfa Aesar and used directly. ¹H NMR and ¹³C NMR spectra were recorded on a AV400 MHz NMR (Bruker BioSpin). Water content was determined by automated Karl-Fischer-titration (Metrohm). Ion chromatography was carried out using ICS-1500 (Dionex). The detection limit of ion chromatography is 10 ppm for all halides. Mass spectrum was measured on Varian Model 500-MS, positive mode.

25 Procedure for synthesizing pure 1-ethyl-3-methylimidazolium acetate ([EMIm]Ac):

The intermediate 1-ethyl-3-methylimidazolium-2-carboxylate was prepared according to literature^{2,3}. Then with water as solvent, stoichiometric amount of acetic acid was added. After 3 hours reaction at 343K, the mixture were dried under reduced pressure to obtain the product.

25 Procedure for synthesizing other [EMIm]Carboxylate:

They were synthesized with anion exchange resin method, according to the literature⁴.

Procedure for synthesizing N,N-diethyl-N,N-dimethylimidazolium([Et₂Me₂N]) acetate:

According to the literature⁵, we made a few modifications to get pure product. Under argon atmosphere, N,N-diethylammonium Chloride and dimethylcarbonate were added into a 75 ml autoclave, then heated under stirring up to 383 K overnight. After drying under reduced pressure and washing with acetone, the intermediate N,N-diethyl-N,N-dimethylammonium Chloride was obtained in crude yield of 90%. By using anion exchange resin IRA-400 (OH), the corresponding hydroxide was obtained. The hydroxide was neutralized with stoichiometric acetic acid. After removal of water with reduced pressure, the product was obtained.

35 General procedure for esterification:

Before using, ionic liquid was dried under reduced pressure around 5 Pa overnight. After measuring water content with Karl-Fischer titrator, normally the water content was less than 0.6 %. Then 3.0 mmol ionic liquids and 3.0 mmol alkyl halide were added into the 25 ml flask, and heating at the fixed temperature for a certain time. After reaction, the ester normally was in the upper phase. The yield was based on the ¹H-NMR of upper phase. Then the mixture of upper phase was separated with column chromatography. Pentane and ethyl acetate were chosen as eluent.

2 NMR data

NMR spectra data of carboxylate-based ionic liquids:

- 1-Ethyl-3-methylimidazolium propionate (entry 10)** : ¹H-NMR (400 MHz; DMSO-*d*₆; δ/ppm) : 0.87 (t, ³J(H,H)=7.6 Hz, 3H, CH₂CH₃), 1.40 (t, ³J(H,H)=7.2 Hz, 3H, NCH₂CH₃), 1.79 (q, ³J(H,H)=7.6 Hz, 2H, OOCCH₂), 3.88 (s, 3H, NCH₃), 4.22 (q, ³J(H,H)=7.2 Hz, 2H, CH₃CH₂), 7.78 (s, 1H, NCH), 7.88 (s, 1H, NCH), 10.11 (s, 1H, NCHN).
¹³C-NMR (100 MHz; DMSO-*d*₆; δ/ppm): 11.60 (CH₂CH₃), 15.27 (NCH₂CH₃), 31.75 (OOCCH₂), 35.47 (NCH₃), 43.91 (NCH₂), 121.92 (NCH), 123.47 (NCH), 137.60 (NCHN), 176.00 (CH₂COO).
- 1-Ethyl-3-methylimidazolium butyrate (entry 11)** : ¹H-NMR (400 MHz; DMSO-*d*₆; δ/ppm) : 0.79 (t, ³J(H,H)=7.2 Hz, 3H, CH₂CH₂CH₃), 1.40 (m, 5H, NCH₂CH₃, OOCCH₂CH₂), 1.79 (t, ³J(H,H)=7.2 Hz, 2H, OOCCH₂), 3.88 (s, 3H, NCH₃), 4.22 (q, ³J(H,H)=7.2 Hz, 2H, CH₃CH₂), 7.82 (s, 1H, NCH), 7.92 (s, 1H, NCH), 10.25 (s, 1H, NCHN).
¹³C-NMR (100 MHz; DMSO-*d*₆; δ/ppm): 14.59 (CH₂CH₂CH₃), 15.24 (NCH₂CH₃), 35.42 (NCH₃), 41.42 (OOCCH₂), 43.88 (NCH₂), 121.95 (NCH), 123.49 (NCH), 137.79 (NCHN), 175.44 (CH₂COO).
- 1-Ethyl-3-methylimidazolium iso-butyrate (entry 12)** : ¹H-NMR (400 MHz; DMSO-*d*₆; δ/ppm) : 0.89 (d, ³J(H,H)=6.8 Hz, 6H, CH(CH₃)₂), 1.41 (t, ³J(H,H)=7.2 Hz, 3H, NCH₂CH₃), 1.95 (m, ³J(H,H)=6.8 Hz, 1H, (CH₃)₂CH), 3.87 (s, 3H, NCH₃), 4.22 (q, ³J(H,H)=7.2 Hz, 2H, CH₃CH₂), 7.76 (s, 1H, NCH), 7.86 (s, 1H, NCH), 10.03 (s, 1H, NCHN).
¹³C-NMR (100 MHz; DMSO-*d*₆; δ/ppm): 15.21 (NCH₂CH₃), 21.08 (CH(CH₃)₂), 35.49 (NCH₃), 36.85 ((CH₃)₂CH), 43.94 (NCH₂), 121.90 (NCH), 123.46 (NCH), 137.53 (NCHN), 178.78 (CHCOO).

1-Ethyl-3-methylimidazolium acrylate (entry 13) : ¹H-NMR (400 MHz; DMSO-*d*₆; δ/ppm) : 1.40 (t, ³J(H,H)=7.2 Hz, 3H, NCH₂CH₃), 3.86 (s, 3H, NCH₃), 4.20 (q, ³J(H,H)=7.2 Hz, 2H, CH₃CH₂), 5.13 (dd, 1H, CHCH₂), 5.65 (dd, 1H, CH₂CH), 5.94 (dd, 1H, CHCH₂), 7.74 (s, 1H, NCH), 7.83 (s, 1H, NCH), 9.65 (s, 1H, NCHN).

¹³C-NMR (100 MHz; DMSO-*d*₆; δ/ppm) : 15.16 (NCH₂CH₃), 35.58 (NCH₃), 44.00 (NCH₂), 119.81 (CHCH₂), 121.93 (NCH), 123.51 (NCH), 136.94 (NCHN), 140.23 (CH₂CH), 168.86 (CHCOO).

1-Ethyl-3-methylimidazolium 4-hydroxybenzoate (entry 14): ¹H-NMR (400 MHz; DMSO-*d*₆; δ/ppm) : 1.39 (t, ³J(H,H)=7.2 Hz, 3H, NCH₂CH₃), 3.84 (s, 3H, NCH₃), 4.18 (q, ³J(H,H)=7.2 Hz, 2H, CH₃CH₂), 6.67 (d, 3J(H,H)=4.0 Hz, 2H, HOCCH), 7.65 (d, 3J(H,H)=4.0 Hz, 2H, CHCCOO), 7.70 (s, 1H, NCH), 7.79 (s, 1H, NCH), 9.51 (s, 1H, NCHN).

¹³C-NMR (100 MHz; DMSO-*d*₆; δ/ppm) : 15.13 (NCH₂CH₃), 35.60 (NCH₃), 44.04 (NCH₂), 113.85 (HOCCH), 121.91 (NCH), 123.51 (NCH), 130.44 (OCC & NCHN), 136.79 (HOCCHCH), 159.10 (HOC), 169.26 (CCO₂).

N,N-Diethyl-N,N-dimethylammonium acetate : ¹H-NMR (400 MHz; DMSO-*d*₆; δ/ppm) : 1.19 (t, ³J(H,H)=7.2 Hz, 6H, CH₂CH₃), 1.54 (s, 3H, OOCCH₃), 3.00 (s, 6H, NCH₃), 3.37 (q, ³J(H,H)=7.2 Hz, 4H, NCH₂).

¹³C-NMR (100 MHz; DMSO-*d*₆; δ/ppm) : 7.74 (CH₂CH₃), 25.91 (OOCCH₃), 48.65 (NCH₃), 57.52 (NCH₂), 172.52 (CH₃COO)

15 **The NMR spectra of the following esters were in complete agreement with those of the authentic samples:**

n-Butyl acetate (entry 1-5): ¹H-NMR (400 MHz; CDCl₃; δ/ppm): 0.93 (t, ³J(H,H)=7.2 Hz, 3H, CH₂CH₃), 1.37 (m, 2H, CH₂CH₂), 1.60 (m, 2H, OCH₂CH₂), 2.04 (s, 3H, O₂CCH₃), 4.06 (t, ³J(H,H)=6.8 Hz, 2H, OCH₂).

¹³C-NMR (100 MHz; CDCl₃; δ/ppm): 13.82 (CH₂CH₃), 19.25 (CH₃CH₂), 21.13 (O₂CCH₃), 30.78 (OCH₂CH₂), 64.49 (OCH₂), 171.38 (CH₃CO₂).

n-Propyl acetate (entry 6): ¹H-NMR (400 MHz; CDCl₃; δ/ppm): 0.93 (t, ³J(H,H)=7.6 Hz, 3H, CH₂CH₃), 1.64 (m, 2H, CH₃CH₂), 2.04 (s, 3H, O₂CCH₃), 4.02 (t, ³J(H,H)=6.8 Hz, 2H, OCH₂).

¹³C-NMR (100 MHz; CDCl₃; δ/ppm): 10.49 (CH₂CH₃), 21.12 (O₂CCH₃), 22.08 (CH₃CH₂), 66.21 (OCH₂), 171.38 (CH₃CO₂).

n-Decyl acetate (entry 7): ¹H-NMR (400 MHz; CDCl₃; δ/ppm): 0.87 (t, ³J(H,H)=6.8 Hz, 3H, CH₂CH₃), 1.30 (m, 14H, CH₃(CH₂)₇), 1.61 (m, 2H, OCH₂CH₂), 2.04 (s, 3H, O₂CCH₃), 4.04 (t, ³J(H,H)=6.8 Hz, 2H, OCH₂).

¹³C-NMR (100 MHz; CDCl₃; δ/ppm): 14.24 (CH₂CH₃), 21.15 (O₂CCH₃), 22.81, 26.05, 28.75, 29.39, 29.44, 29.66, 32.03, (OCH₂(CH₂)₈), 64.81 (OCH₂), 171.37 (CH₃CO₂).

n-Decyl acetate (entry 8): ¹H-NMR (400 MHz; CDCl₃; δ/ppm): 0.87 (t, ³J(H,H)=6.8 Hz, 3H, CH₂CH₃), 1.30 (m, 14H, CH₃(CH₂)₇), 1.61 (m, 2H, OCH₂CH₂), 2.04 (s, 3H, O₂CCH₃), 4.04 (t, ³J(H,H)=6.8 Hz, 2H, OCH₂).

¹³C-NMR (100 MHz; CDCl₃; δ/ppm): 14.24 (CH₂CH₃), 21.15 (O₂CCH₃), 22.81, 26.05, 28.75, 29.39, 29.44, 29.66, 32.03, (OCH₂(CH₂)₈), 64.81 (OCH₂), 171.37 (CH₃CO₂).

3-Butenyl acetate (entry 9): ¹H-NMR (400 MHz; CDCl₃; δ/ppm): 2.03 (s, 3H, O₂CCH₃), 2.37 (m, 2H, OCH₂CH₂), 4.10 (t, 3J(H,H)=6.8 Hz, 2H, OCH₂); 5.05-5.13 (m, 2H, CH=CH₂), 5.77 (m, 1H, CH₂=CH).

¹³C-NMR (100 MHz; CDCl₃; δ/ppm): 21.05 (O₂CCH₃), 33.15 (OCH₂CH₂), 63.62 (OCH₂), 117.30 (CH=CH₂), 134.12 (CH₂=CH), 171.19 (CH₃CO₂).

n-Butyl propionate (entry 10): ¹H-NMR (400 MHz; DMSO-*d*₆; δ/ppm): 0.88 (t, 3J(H,H)=7.6 Hz, 3H, O₂CCH₂CH₃), 1.02 (t, 3J(H,H)=7.2 Hz, 3H, O(CH₂)₃CH₃), 1.32 (m, 2H, O(CH₂)₂CH₂), 1.54 (m, 2H, OCH₂CH₂), 2.29 (q, ³J(H,H)=7.6 Hz, 2H, O₂CCH₂), 4.00 (t, ³J(H,H)=6.8 Hz, 2H, OCH₂).

¹³C-NMR (100 MHz; DMSO-*d*₆; δ/ppm): 9.01 (O₂CCH₂CH₃), 13.53 ((CH₂)₃CH₃), 18.60 (O(CH₂)₂CH₂), 26.79 (O₂CCH₂), 30.20 (OCH₂CH₂), 63.38 (OCH₂), 173.63 (CH₂CO₂).

n-Butyl n-butyrate (entry 11): ¹H-NMR (400 MHz; CDCl₃; δ/ppm): 0.91-0.96 (6H, O(CH₂)₃CH₃ & O₂C(CH₂)₂CH₃), 1.37 (m, 2H, O(CH₂)₂CH₂), 1.56-1.69 (4H, CH₂), 2.27 (t, ³J(H,H)=7.2 Hz, 2H, O₂CCH₂), 4.06 (t, ³J(H,H)=6.8 Hz, 2H, OCH₂).

¹³C-NMR (100 MHz; CDCl₃; δ/ppm): 13.81 (CH₂CH₃), 18.63 (O₂CCH₂CH₂), (O(CH₂)₂CH₂), 30.85 (OCH₂CH₂), 36.42 (O₂CCH₂), 64.21 (OCH₂), 171.96 (CH₂CO₂).

n-Butyl t-butyrate (entry 12): ¹H-NMR (400 MHz; CDCl₃; δ/ppm): 0.93 (t, ³J(H,H)=9.6 Hz, 3H, CH₂CH₃), 1.16 (d, ³J(H,H)=9.6 Hz, 6H, CH(CH₃)₂), 1.38 (m, 2H, CH₂CH₂), 1.61 (m, 2H, OCH₂CH₂), 2.53 (m, 1H, O₂CCH), 4.06 (t, ³J(H,H)=8.8 Hz, 2H, OCH₂).

¹³C-NMR (100 MHz; CDCl₃; δ/ppm): 13.70 ((CH₂)₃CH₃), 18.99 (CH(CH₃)₂), 19.13 (CH₃CH₂), 30.71 (OCH₂CH₂), 34.04 ((CH₃)₂CH), 64.09 (OCH₂), 177.25 (CHCO₂).

n-Butyl acrylate (entry 13): ¹H-NMR (400 MHz; CDCl₃; δ/ppm): 0.94 (t, 3J(H,H)=7.2 Hz, 3H, O₂CCH₂CH₃), 1.40 (m, 2H, O(CH₂)₂CH₂), 1.65 (m, 2H, OCH₂CH₂), 4.15 (t, ³J(H,H)=6.8 Hz, 2H, OCH₂), 5.80 (dd, 1H, CHCH₂), 6.11 (dd, 1H, CH₂CH), 6.39 (dd, 1H, CHCH₂).

¹³C-NMR (100 MHz; CDCl₃; δ/ppm): 13.84 ((CH₂)₃CH₃), 19.28 (O(CH₂)₂CH₂), 30.80 (OCH₂CH₂), 64.54 (OCH₂), 128.80 (CHCH₂), 130.52 (CH₂CH), 166.48 (CHCO₂).

n-Butyl 4-hydroxybenzoate (entry 14): ¹H-NMR (400 MHz; CDCl₃; δ/ppm): 0.97 (t, 3J(H,H)=7.2 Hz, 3H, O₂CCH₂CH₃), 1.47 (m, 2H, O(CH₂)₂CH₂), 1.74 (m, 2H, OCH₂CH₂), 4.30 (t, ³J(H,H)=6.8 Hz, 2H, OCH₂), 6.54 (b, 1H, COH), 6.89 (d, 3J(H,H)=4.4 Hz, 2H, HOCCH), 7.95 (d, 3J(H,H)=4.4 Hz, 2H, CHCCOO).

¹³C-NMR (100 MHz; CDCl₃; δ/ppm): 13.89 ((CH₂)₃CH₃), 19.41 (O(CH₂)₂CH₂), 30.91 (OCH₂CH₂), 65.01 (OCH₂), 115.40 (HOCCH), 122.74 (OCC), 132.05 (HOCCHCH), 160.39 (HOC), 167.24 (CCO₂).

3 Figures

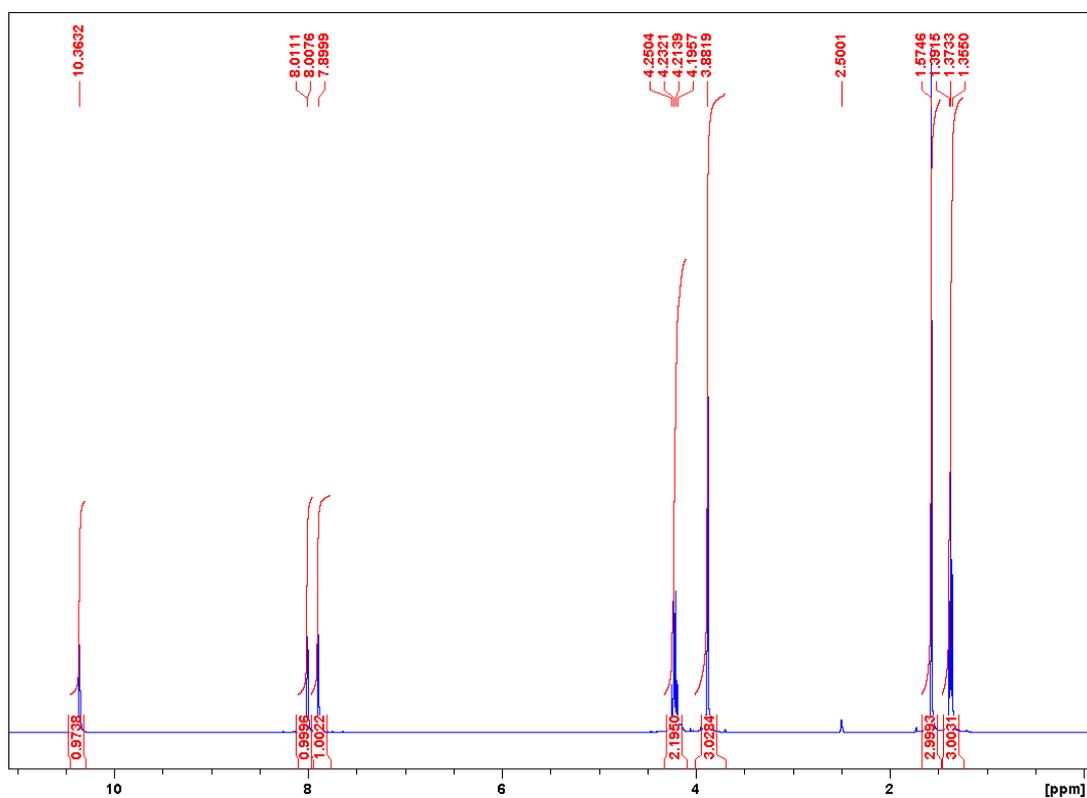


Figure 1 ¹H-NMR Pure [EMIm]Ac (water peak in DMSO-*d*₆ shifted and interrupted the integration of methylenyl group)

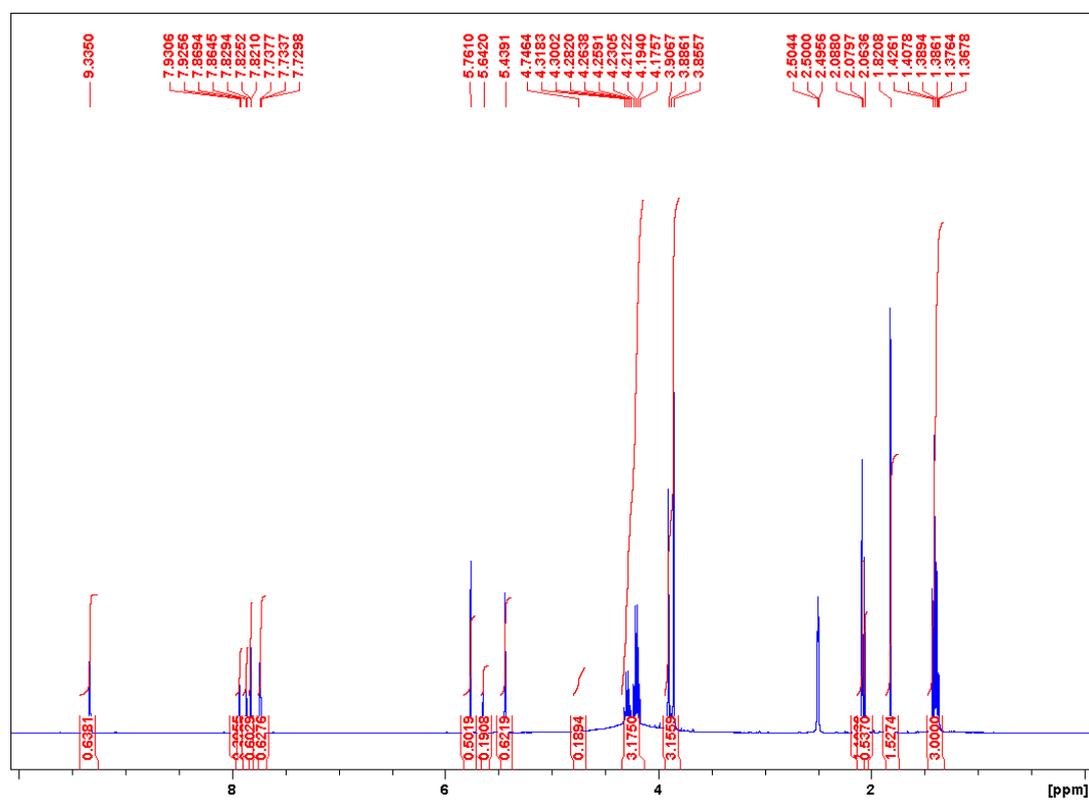


Figure 2 ¹H-NMR of the mixture of [EMIm]Ac and dichloromethane

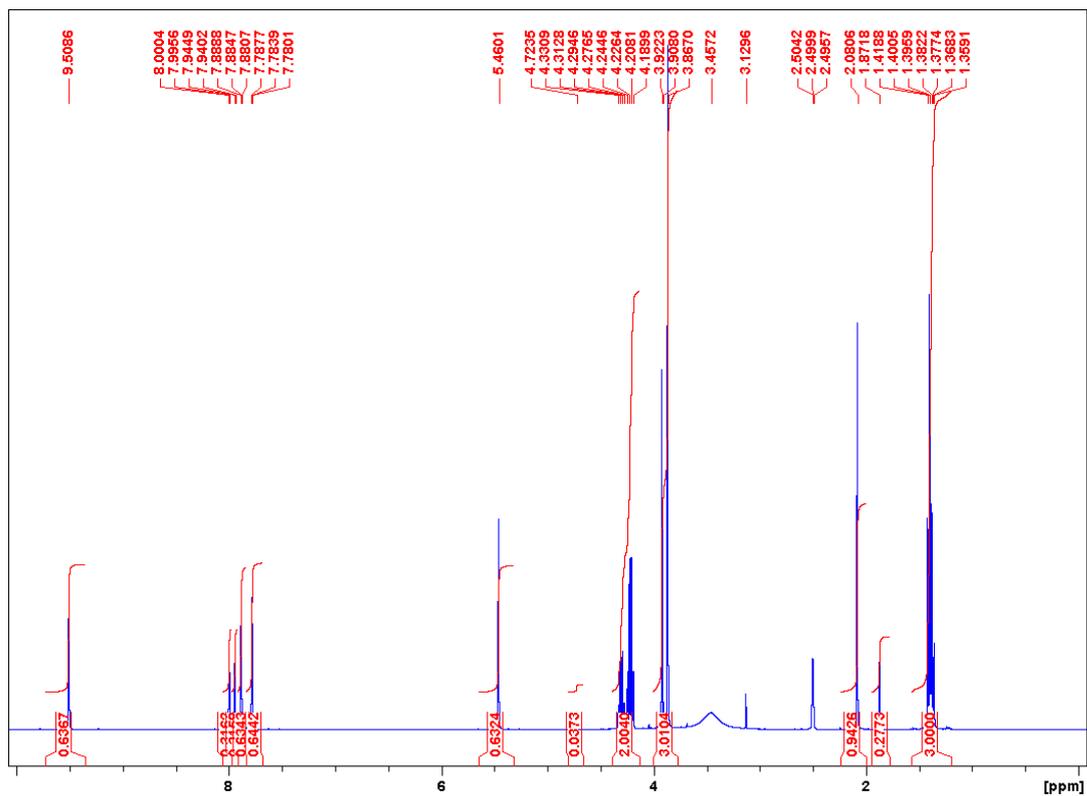


Figure 3 $^1\text{H-NMR}$ of the mixture of [EMIm]Ac and dichloromethane (after removing volatile compounds)

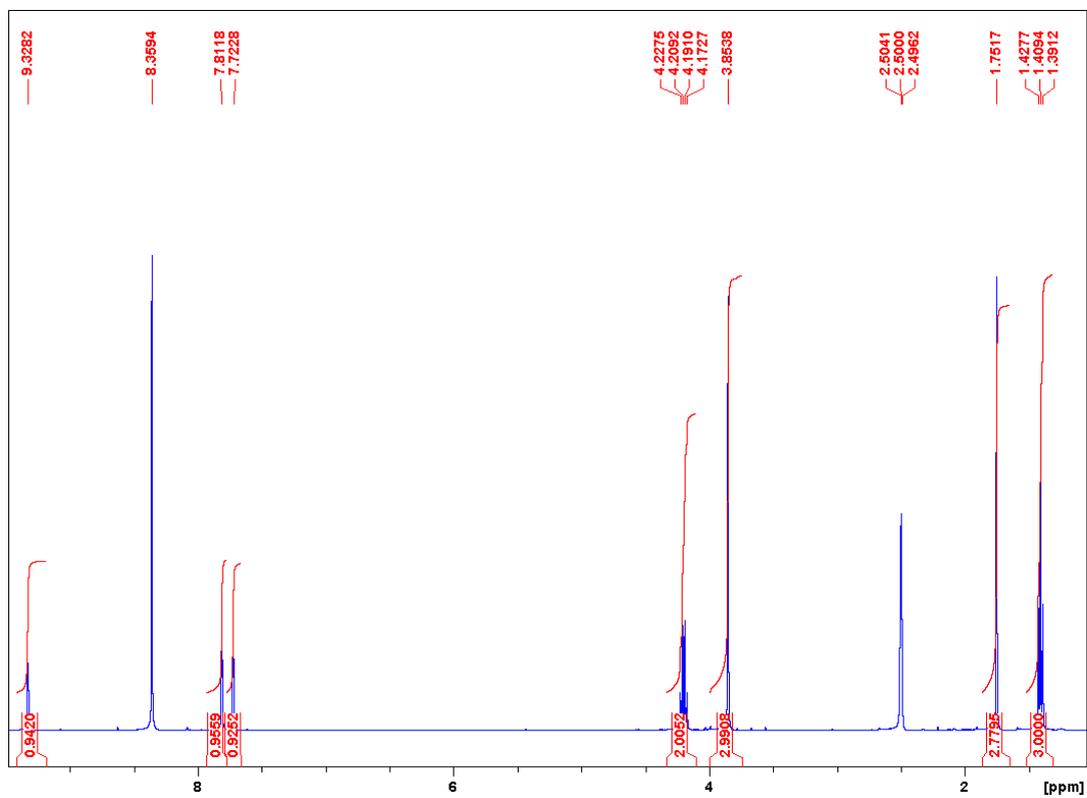


Figure 4 $^1\text{H-NMR}$ of the of solution of [EMIm]Ac in chloroform:

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Spectrum 1A Plot - 17.06.2010 14:28

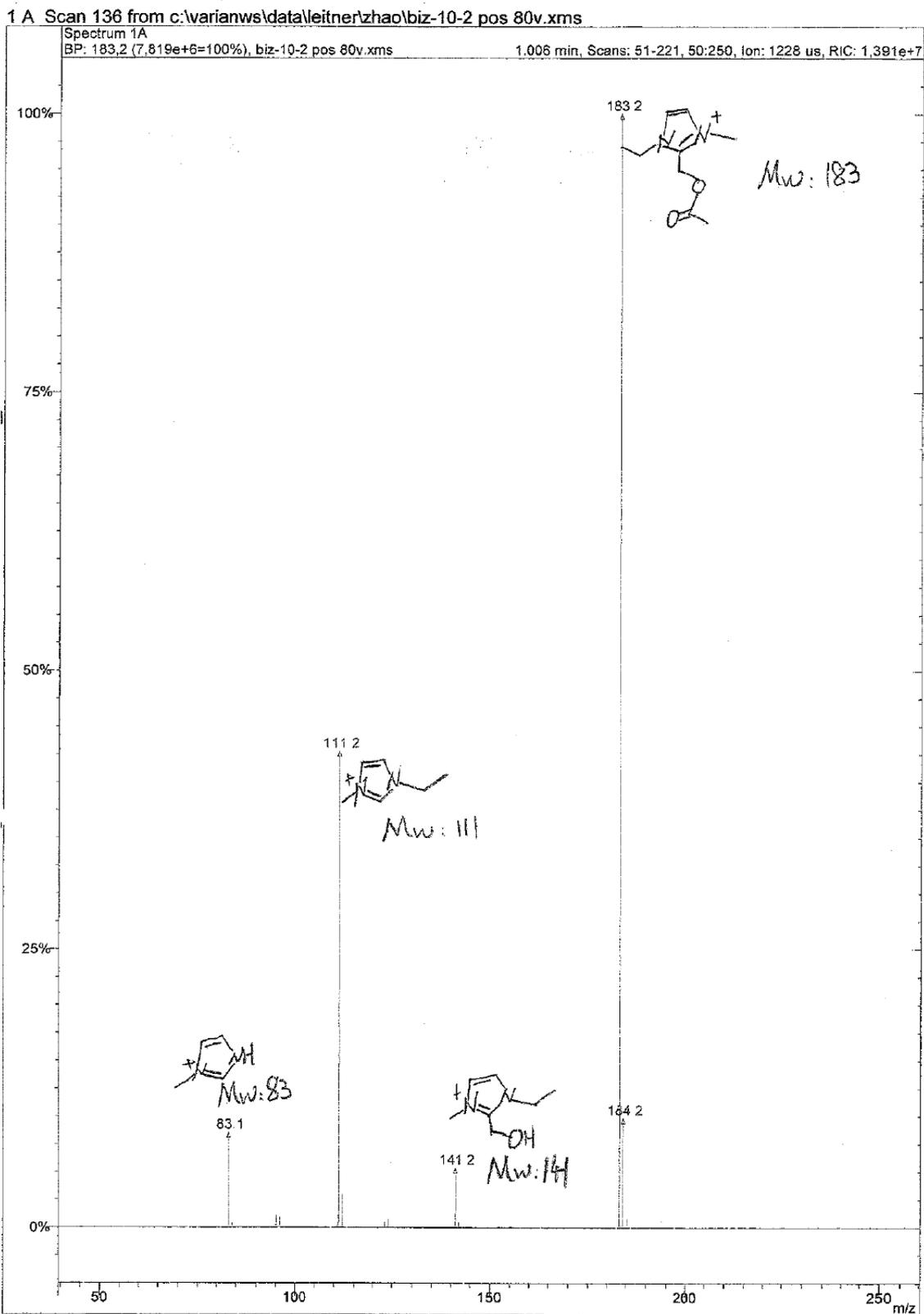


Figure 5 Mass spectrum of the mixture of [EMIm]Ac with dichloromethane

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Chromatogram Plot

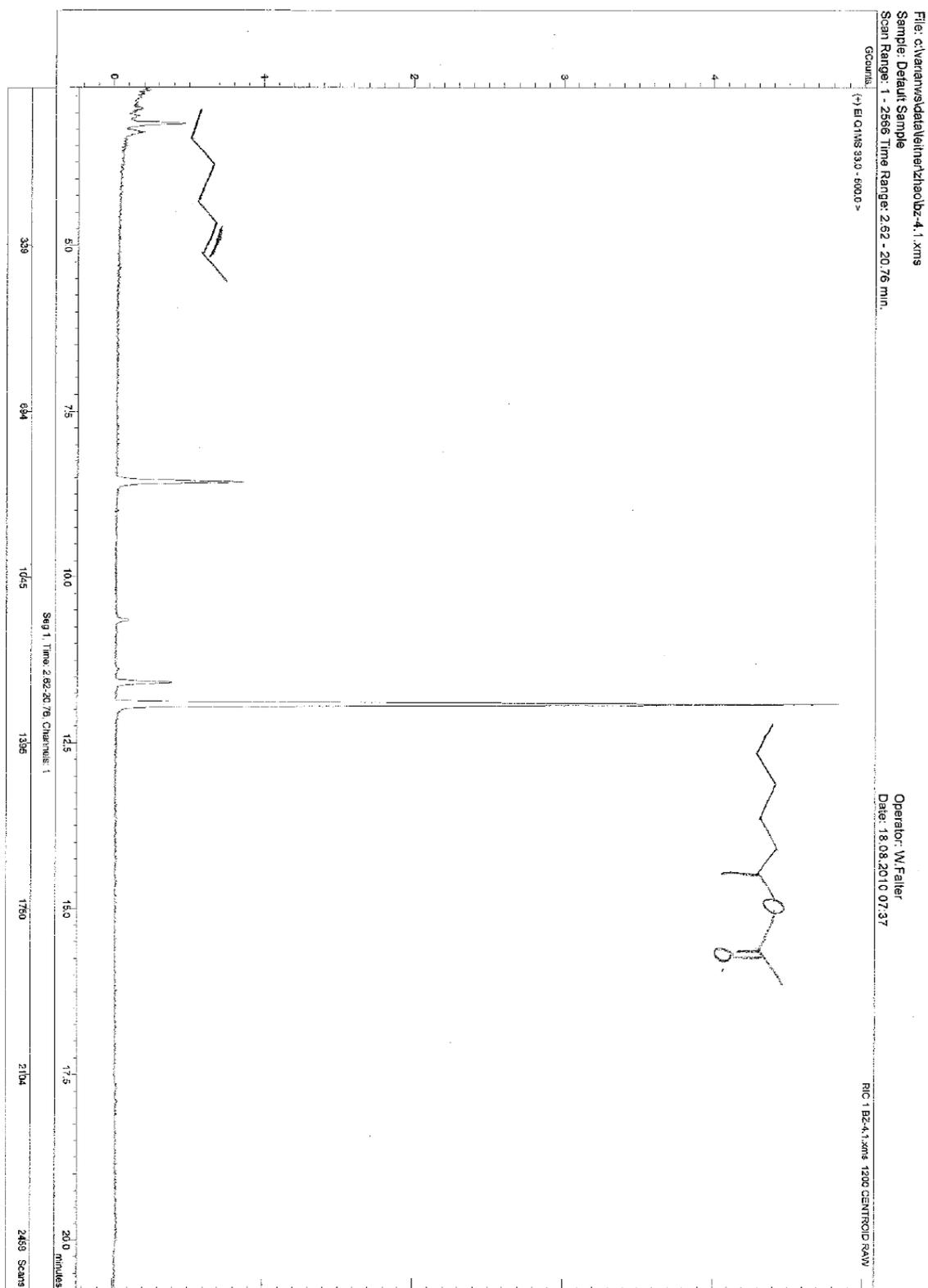


Figure 6 GC of the reaction between 2-bromoheptane and [EMIm]Ac

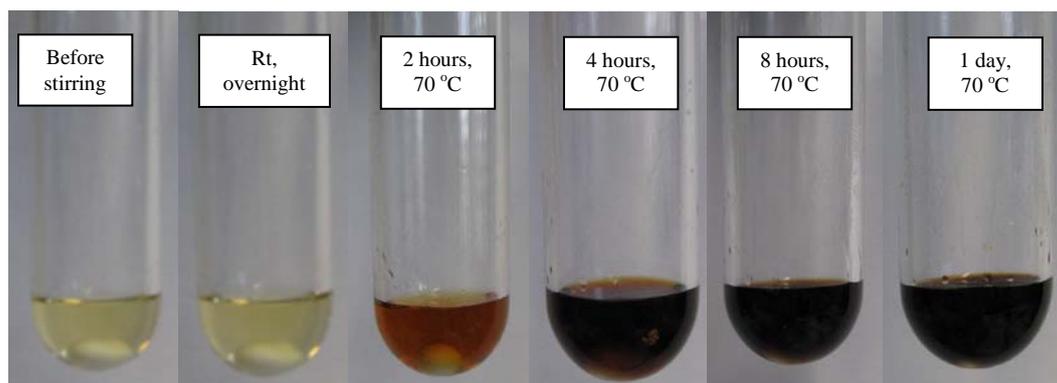


Figure 8 Color change of the solution [EMIm]Ac-chloroform

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