Imidazolium ionic liquids: A simple anion exchange protocol

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General Information

^1H NMR spectra were recorded on a Varian Gemini 300 (300 MHz for ^1H and 75.4 MHz for ^{13}C) spectrometer at 298 K. ^1H and ^{13}C chemical shifts were referenced with TMS as an internal reference.

Mass spectrometric analyses were performed on a LC/MSD-TOF (2006) mass spectrometer with a pumping system HPLC Agilent 1100 from Agilent Technologies at Serveis Científico-Tècnics of Universitat de Barcelona under the following experimental conditions: • Solvent: $H_2O:CH_3CN$ (1:1, v/v) • Gas temperature: 300 ºC • Capillary voltage: 4 KV (positive) and 3.5 KV (negative) • Fragmentor: 75/175 V • Spray gas: N_2 pressure = 15 psi • Drying gas: N_2 flow: 7.0 $L\cdot min^{-1}$ • Flow rate: 200 $\mu L\cdot min^{-1}$.

HPLC was performed on a KONIK KNK 500-A chromatographer with automatic KONTRON AUTOSAMPLER 465 injector, and a WATERS IC-PAK ANIONS column that contains a polymetacrilate polymer with quaternary ammonium moiety. Eluent flow rate was 1 mL/min. Detection was carried out with WESCAN conductivity detector and UV KONTRON 332 detector. The aqueous samples (*ca* 50 ppm) were filtered (0.2 µm porous diameter) and organic components were separated by filtration through a C-18 column. The chromatograms were recorded, and the area under the curve (mV·min) against ppm was measured.

The pH was measured with *Crison micropH 2001*, using pH electrode for hydroalcoholic solutions.

Commercially available products: 1-butyl-1*H*-imidazole, 1-methyl-1*H*-imidazole, 1-iodobutane, 1-bromobutane, 1-iodomethane, ion exchanger resin Amberlyst A-26 (Aldrich®, OH^- form), glacial acetic acid, benzoic acid, (*S*)-lactic acid (85% solution in water), methanesulfonic acid, dibutylphosphoric acid, hydrochloric acid (37% in water), hexafluorophosphoric acid solution (65%, gravimetric in water), Tetrafuoroboric àcid (50 % in water), perchloric acid (70 % in water), nitric àcid (65 % in water)ammonium acetate, ammonium fluoride, ammonium chloride, ammonium hexafluorophosphate, ammonium phosphate monobasic, ammonium hydrogensulfate, ammonium thiocyanate and ammonium trifluoromethanesulfonate . All solvents were reagent grade and dried, if it is necessary, with molecular sieves. Methanol was distilled prior to use.

1-Buthyl-3-methylimidazolium iodide [bmim][I]

An oven-dried resealeable tube was back-filled with argon and charged with 1-butyl-1*H*-imidazole (0.95 g, 7.645 mmol) and iodomethane (3.42 g, 24.10 mmol) and the reaction mixture was stirred magnetically at 50 ºC for 24 h. After cooling the reaction mixture was evaporated to dryness, and the residue was washed with dry diethyl ether (3 x 25 mL) in a ultrasonic bath, obtaining the pure **[bmim][I]** as a colourless oil (2.00 g, 98 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.97 (t, *J* = 7.3 Hz, 3H), 1.34-1.46 (m, 2H), 1.87-1.97 (m, 2H), 4.12 (s, 3H), 4.33 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 1.8 Hz, 1H), 7.43 (t, *J* = 1.8 Hz, 1H), 10.13 (s, 1H).

1-Buthyl-3-methylimidazolium bromide [bmim][Br]

A solution of 1-methyl-1*H*-imidazole (2.415 g, 29.41 mmol) and 1-bromobutane (4.765 g, 35.038 mmol) in 50 mL of dry acetonitrile was stirred under reflux for 16 h. The acetonitrile was evaporated to dryness, and the residue was washed with dry diethyl ether (3 x 25 mL) in a ultrasonic bath, providing the pure **[bmim][Br]** as a yellow oil (5.20 g, 81 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.98 (t, *J* = 7.3, 3H), 1.42 (m, 2H), 1.94 (m, 2H), 4.13 (s, 3H), 4.34 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 1.8 Hz, 1H), 7.52 (t, *J* = 1.73 Hz, 1H), 10.08 (s, 1H).

1,3-Dibuthylimidazolium iodide [bbim][I]

A solution of 1-butyl-1*H*-imidazole (1.90 g, 15.27 mmol) and 1-iodobutane (5.62 g, 30.52 mmol) in 15 mL of dry ethyl acetate was stirred magnetically at reflux temperature for 6 h. The solvent was evaporated to dryness, and the residue was washed with dry diethyl ether (3 x 25 mL) in a ultrasonic bath, providing the pure **[bbim][I]** as a yellow oil (4.50 g, 96 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.92 (t, *J* = 7.3 Hz, 6H), 1.28-1.41 (m, 4H), 1.83-1.93 (m, 4H), 4.33 (t, *J* = 7.4 Hz, 4H), 7.51 (s, 1H), 7.52 (s, 1H), 10.13 (s, 1H).

1,3-Dibuthylimidazolium bromide [bbim][Br]

A solution of 1-butyl-1*H*-imidazole (0.95 g, 7.64 mmol) and 1-bromobutane (1.04 g, 7.66 mmol) in 20 mL of dry acetonitrile was stirred under reflux for 24 h. The reaction mixture was evaporated to dryness, obtaining the pure **[bbim][Br]** as a yellow oil (1.97 g, 99 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.90 (t, *J* = 7.3 Hz, 6H), 1.38 (m, 4H), 1.90 (m, 4H), 4.35 (t, *J* = 7.4 Hz, 4H), 7.42 (d, *J* = 1.6 Hz, 2H), 10.58 (s, 1H).

1,3-Dimethylimidazolium iodide [mmim][I]

A solution of 1-methyl-1*H*-imidazole (1.83 g, 22.34 mmol) and iodomethane (6.34 g, 44.637 mmol) in 15 mL of dry CH_2Cl_2 was stirred at 0 ºC for 3 h. The reaction mixture was evaporated to dryness, obtaining the pure **[mmim][I]** as a solid (4.93 g, 99 % yield). Mp: 78 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.10 (s, 6H), 7.4 (s, 1H), 7.41 (s, 1H), 10.03 (s, 1H).

General procedure to load anions in AER: A 1% methanolic or hydro-methanolic acid solution or 1 % aqueous ammonium salt solution was passed through a glass column packed with Amberlyst® A-26 (OH^- form) until the pH of eluates was reached to the same value than original solution, and then the resin was washed methanol until neutral pH. The process was carried out at room temperature, using gravity as driving force.

General procedure for anion exchange: A methanolic solution of the imidazolium salt (50-60 mM) was passed through a column packed with Amberlyst A-26, previously loaded with the selected anion, and then washed with 25 mL of methanol. Solvent of the combined eluates were removed, and the oil obtained were dried in a vacuum oven at 60 ºC with P_2O_5 and KOH pellets.

The amount of halide contents in the exchanged ionic liquids was determined by a silver chromate test following a similar protocol described by Sheldon and co-workers.[1] An aqueous solution of potassium chromate (5 % p/v in Milli-Q water, 0.257 M) was added to the sample. A silver nitrate aqueous solution (0.24 % p/v in Milli-Q water, 0.014 M) was added dropwise to 1 mL of the problem solution considering than the end point was reached when a red persistent suspension of silver chromate was observed. Volumes were measured with a 1 ml syringe, and 0.1 mL contains 9 drops of the silver nitrate aqueous solution, consequently 1 drop= 0.011 mL.

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[1] A. R. Toral, A. P. de los Rios, F. J. Hernández, M. H. A. Janssen, R. Schoevaart, F. van Rantwijk, R. A. Sheldon, *Enzyme Microb. Technol.*, 2007, 40, 1095.

Table S1. Results of the iodide or bromide exchange in imidazolium ionic liquids

compound	**[bmim][I] or [Br]**		**[bbim][I] or [Br]**		**[mmim][I]**	
Anion	**Exchange (%)**	**Yield[a] (%)**	**Exchange (%)**	**Yield[a] (%)**	**Exchange (%)**	**Yield[a] (%)**
AcO^-	100	quant.	100	quant.	100	quant.
BzO^-	100	quant.	100	quant.	100	90
(*S*)-Lactat$^-$	100	quant.	100	quant.	100	quant.
$MeSO_3^-$	100	quant.	100	quant.	100	91
$Bu_2PO_4^-$	100	quant.	100	quant.	100	quant.
F^-	100[b]	82	100[b]	quant.	----	----
Cl^-	100	quant.	100	quant.	100	quant.
PF_6^-	100	quant.	100	quant.	100	quant.
NO_3^-	98	quant.	100	quant.	100	quant.
ClO_4^-	97	quant.	97	quant.	95	quant.
BF_4^-	100	quant.	100	quant.	100	quant.
$H_2PO_4^-$	100	quant.	95	----	100	quant.
HSO_4^-	100	quant.	100	quant.	100	quant.
$CF_3SO_3^-$	100	quant.	100	quant.	100	quant.
$(CN)S^-$	100	quant.	100	quant.	100	quant.

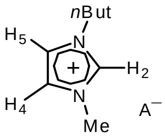
[a] Recovered new ion pair. [b]Analized by HPLC from exchange of Br^- by F^-

Table S2. Halide contents in ionic liquids after anion exchange.[a]

	bmim		**bbim**		**mmim**	
Anion	**conc. (mM)**[b]	**I^- (ppm)**[c]	**conc. (mM)**[c]	**I^- (ppm)**[d]	**conc. (mM)**[c]	**I^- (ppm)**[d]
AcO^-	6.05	< 20	4.99	< 20	7.29	< 20
BzO^-	5.76	< 20	4.83	< 20	5.22	< 20
(*S*)-Lactate$^-$	7.27	20-40	3.70	< 20	9.02	< 20
$MeSO_3^-$	4.86	< 20	4.34	< 20	6.97	< 20
$Bu_2PO_4^-$	3.96	< 20	3.74	< 20	4.77	< 20
PF_6^-	4.50	20-40	4.96	< 20	4.13	< 20
NO_3^-	6.36	< 20	6.41	< 20	8.04	20-40
ClO_4^-	5.70	100-120[d]	3.99	20-40[d]	6.82	20-40[d]
BF_4^-	6.19	< 20	5.00	< 20	7.18	20-40
$H_2PO_4^-$	4.91	< 20	3.95	20-40	6.59	< 20
HSO_4^-	6.52	< 20	6.03	20-40	6.18	< 20
$CF_3SO_3^-$	4.37	< 20	4.78	< 20	5.12	< 20

[a] All samples analyzed were obtained from iodide exchange. [b] Concentration of the ionic liquid in the K_2CrO_4 aqueous solution. [c] 1 drop of $AgNO_3$ aqueous solution is enough to react with nearly 20 ppm (mg·L^{-1}) of iodide anion. [d] A white suspension was observed and, in the considered end point the $AgCrO_4$ red precipitate surfaced.

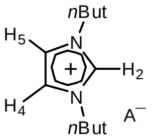
Table S3. ^{1}H NMR chemical shift values of 1-butyl-3-methylimidazolium salts in CDCl$_3$ (300 MHz) at 298 K.[a]



Anion	H_2	H_4	H_5	*n*But	Me	A^-
[AcO^-]	11.44	7.09	7.09	4.30, 1.86, 1.37, 0.97	4.06	2.00
[BzO^-]	11.54	7.09	7.09	4.29, 1.84, 1.33, 0.92	4.08	8.10, 7.33
[S)-lactate$^-$]	11.19	7.17	7.17	4.31, 1.89, 1.38, 0.98	4.08	3.46, 1.41
[$\mathrm{MeSO_3}^-$]	10.04	7.25	7.20	4.28, 1.87, 1.38, 0.97	4.05	2.80
[$\mathrm{Bu_2PO_4}^-$]	10.19	7.36	7.23	4.25, 1.80, 1.33, 0.88	4.00	3.80, 1.54, 1.33, 0.88
[I^-]	10.10	7.52	7.44	4.35, 1.93, 1.41, 0.99	4.14	
[Br^-]	10.41	7.46	7.37	4.35, 1.91, 1.40, 0.98	4.13	
[F^-]	(b)	7.50	7.33	4.29, 1.87, 1.36, 0.95	4.06	
[Cl^-]	10.99	7.24	7.20	4.34, 1.91, 1.40, 0.98	4.13	
[$\mathrm{PF_6}^-$]	9.19	7.27	7.24	4.22, 1.90, 1.39, 0.98	4.00	
[$\mathrm{NO_3}^-$]	10.02	7.35	7.30	4.25, 1.88, 1.38, 0.97	4.02	
[$\mathrm{ClO_4}^-$]	9.15	7.30	7.26	4.23, 1.89, 1.39, 0.98	4.02	
[$\mathrm{BF_4}^-$]	8.98	7.28	7.24	4.21, 1.87, 1.39, 0.97	3.98	
[$\mathrm{HSO_4}^-$][c]	10.43	7.31	7.31	4.23, 1.78, 1.29, 0.90	3.93	
[$\mathrm{CF_3SO_3}^-$]	9.27	7.32	7.28	4.21, 1.88, 1.38, 0.97	3.99	
[SCN^-]	9.59	7.36	7.31	4.32, 1.92, 1.41, 0.99	4.11	

[a] Solution concentrations are 0.02 M. [b]Signal not observed due to H-D exchange. [c]In CD$_3$CN

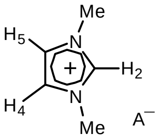
Table S4. ^{1}H NMR chemical shift values of 1,3-dibutylimidazolium salts in $CDCl_3$ (300 MHz) at 298 K.[a]



Anion	H_2	$H_{4,5}$	*n*But	A^-
$[AcO^-]$	11.32	7.14	4.35, 1.86, 1.39, 0.97	2.01
$[BzO^-]$	11.40	7.16	4.34, 1.87, 1.35, 0.93	8.10, 7.32
[S)-lactate$^-$]	11.29	7.14	4.33, 1.87, 1.37, 0.96	4.02, 1.39
$[MeSO_3^-]$	9.73	7.51	4.30, 1.88, 1.37, 0.96	2.75
$[Bu_2PO_4^-]$	11.05	7.11	4.37, 1.88, 1.40, 0.94	3.87, 1.62, 1.40, 0.94
$[I^-]$	10.34	7.38	4.38, 1.95, 1.42, 0.99	
$[Br^-]$	10.58	7.42	4.36, 1.90, 1.37, 0.95	
$[F^-]$	(b)	7.17	4.30, 1.89, 1.40, 0.98	
$[Cl^-]$	11.05	7.23	4.38, 1.92, 1.41, 0.98	
$[PF_6^-]$	9.05	7.23	4.24, 1.88, 1.39, 0.98	
$[NO_3^-]$	9.89	7.39	4.25, 1.86, 1.33, 0.94	
$[ClO_4^-]$	9.24	7.38	4.26, 1.88, 1.37. 0.96	
$[BF_4^-]$	9.12	7.36	4.23, 1.87, 1.36, 0.95	
$[H_2PO_4^-]$	10.59	7.31	4.40, 1.84, 1.34, 0.92	
$[HSO_4^-]$[c]	10.84	7.40	4.39, 1.84, 1.34, 0.91	
$[CF_3SO_3^-]$	9.49	7.28	4.26, 1.88, 1.38, 0.98	
$[SCN^-]$	9.18	7.34	4.25, 1.88, 1.38, 0.97	

[a] Solution concentrations are 0.02 M. [b]Signal not observed due to H-D exchange. [c]In CD_3CN

Table S5. ^1H NMR chemical shift values of 1,3-dimethylimidazolium salts in CD_3CN (300 MHz) at 298 K.[a]



Anion	H_2	$H_{4,5}$	Me	A^-
[AcO^-]	9.05	7.32	3.83	1.69
[BzO^-]	9.29	7.33	3.85	7.93, 7.28
[S)-lactate$^-$][b]	11.04	7.15	4.03	3.80, 1.38
[$MeSO_3^-$]	8.58	7.33	3.83	2.43
[$Bu_2PO_4^-$] [b]	10.88	7.15	4.04	3.86, 1.61, 1.39, 0.90
[I^-]	8.48	7.34	3.83	
[Cl^-]	8.57	7.34	3.83	
[PF_6^-]	8.38	7.32	3.82	
[NO_3^-]	8.57	7.34	3.83	
[ClO_4^-]	8.45	7.33	3.82	
[BF_4^-]	8.43	7.33	3.82	
[$H_2PO_4^-$] [b]	10.26	7.30	4.09	
[HSO_4^-] [b]	10.19	7.34	4.09	
[$CF_3SO_3^-$]	8.45	7.33	3.82	
[SCN^-]	8.44	7.33	3.83	

[a] Solution concentrations are 0.02 M. [b] In $CDCl_3$

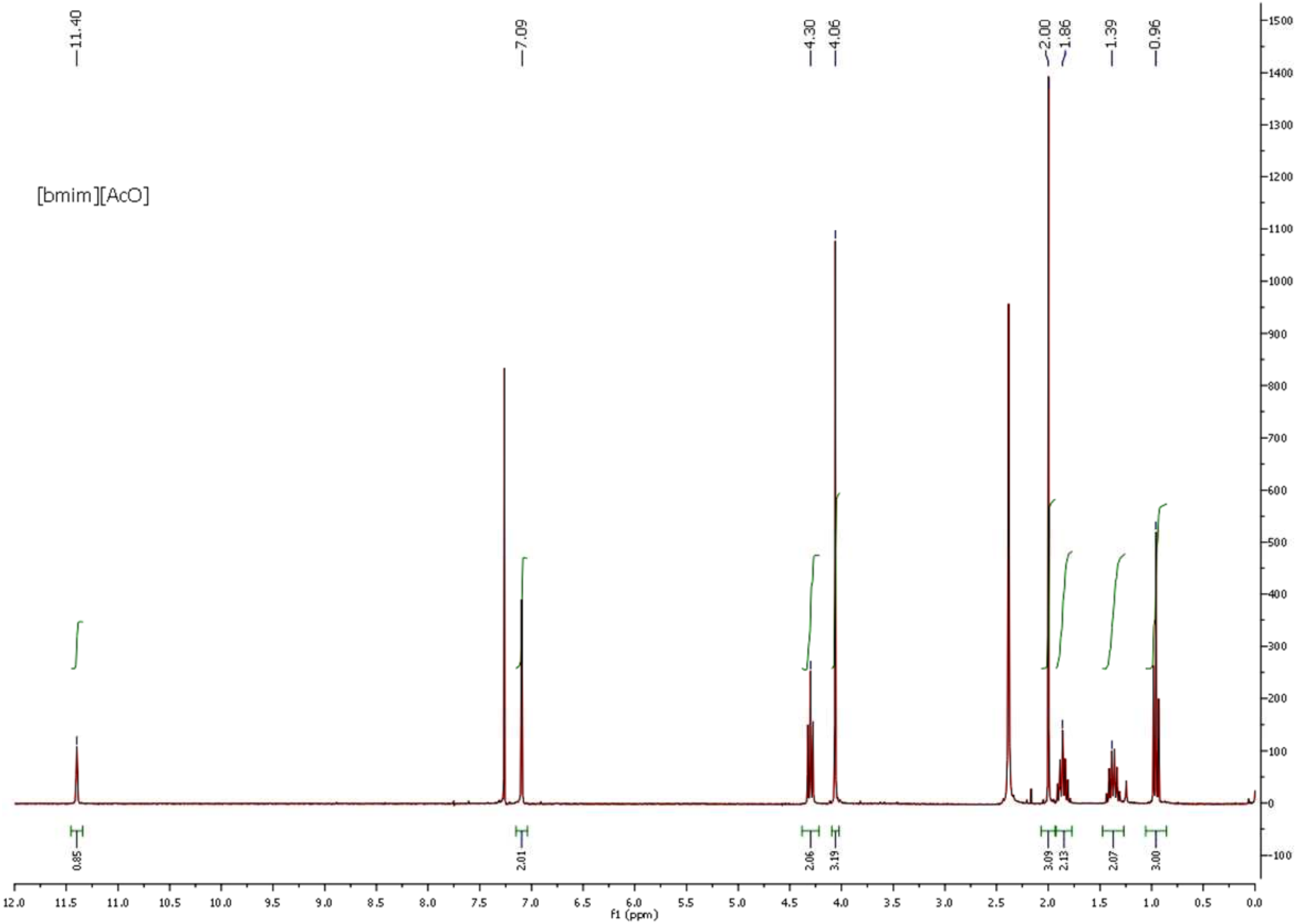


Figure S-1. ^{1}H NMR (300 MHz, $CDCl_3$) of [bmim][AcO]

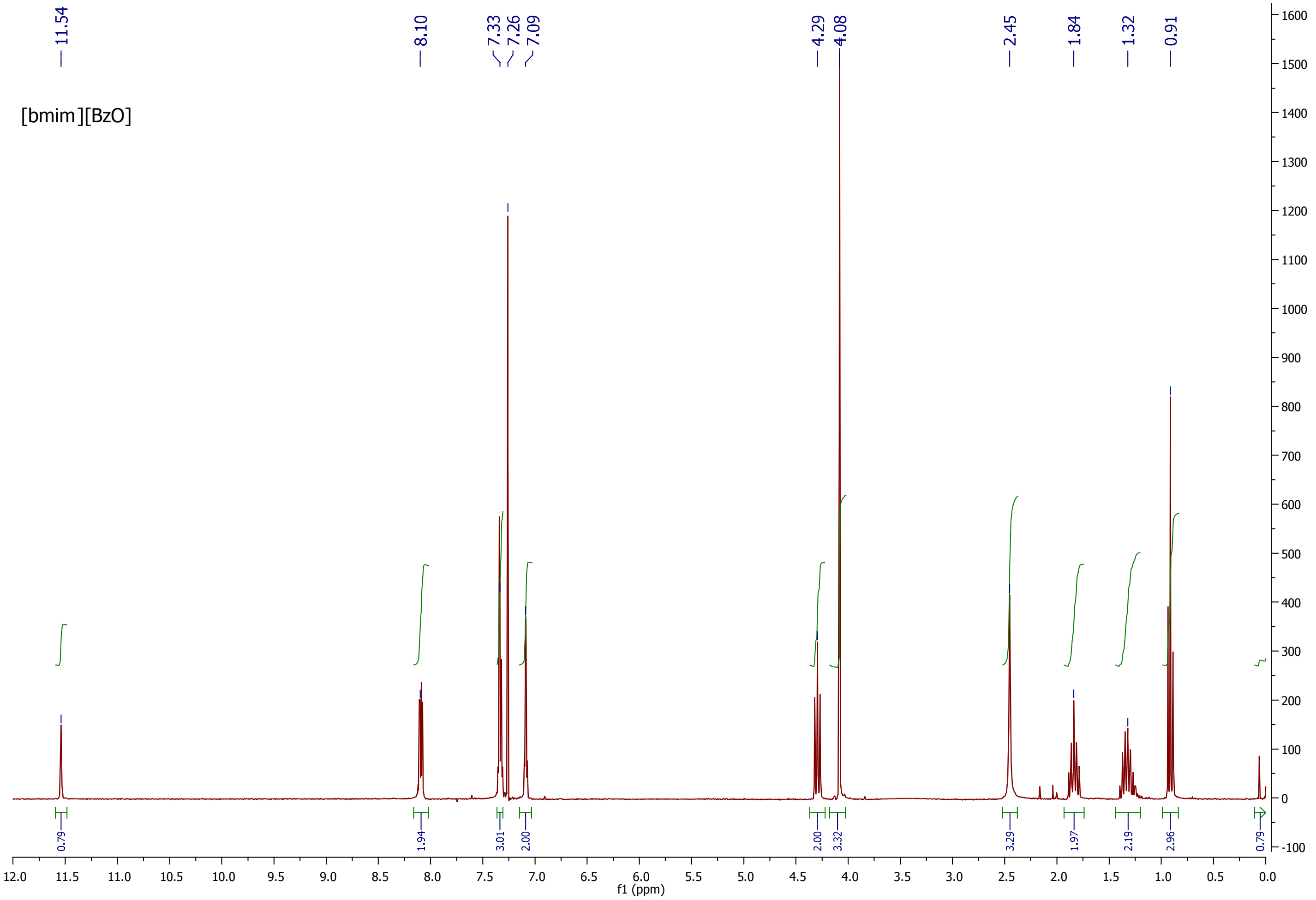


Figure S-2. ^{1}H NMR (300 MHz, $CDCl_3$) of [bmim][benzoate]

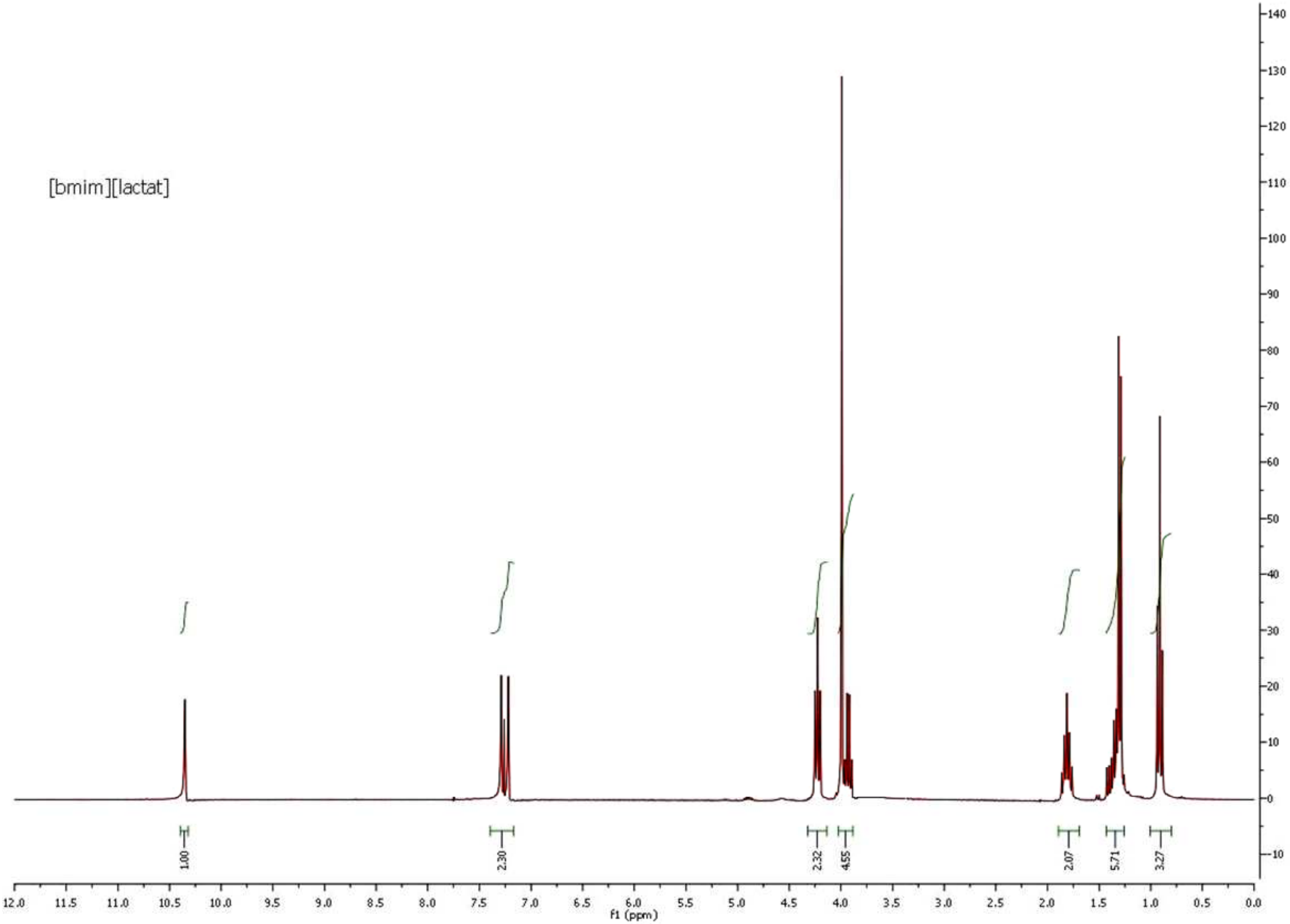


Figure S-3. ^{1}H NMR (300 MHz, $CDCl_3$) of [bmim][(*S*)-lactate]

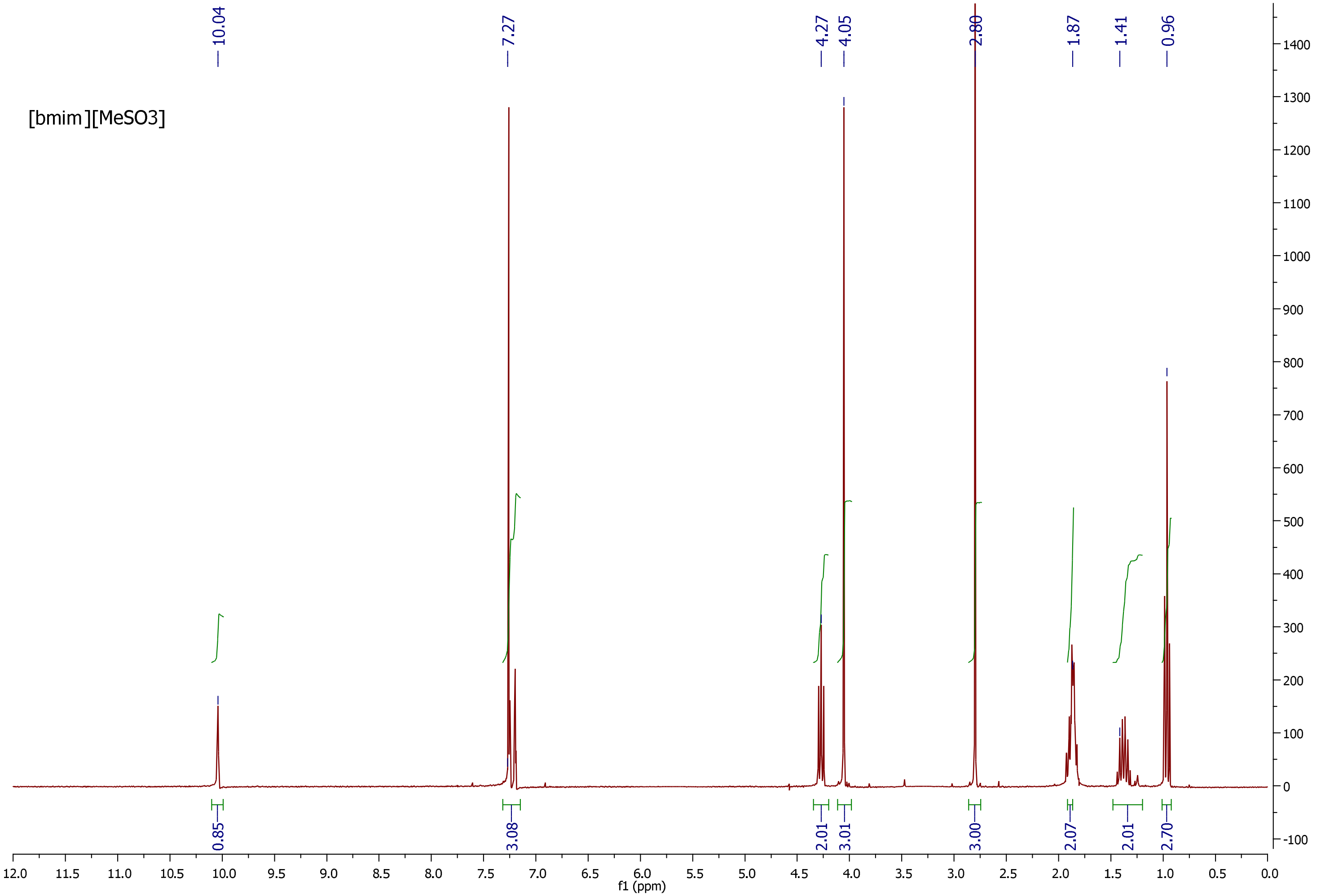


Figure S-4. ^{1}H NMR (300 MHz, $CDCl_3$) of [bmim][CH_3SO_3]

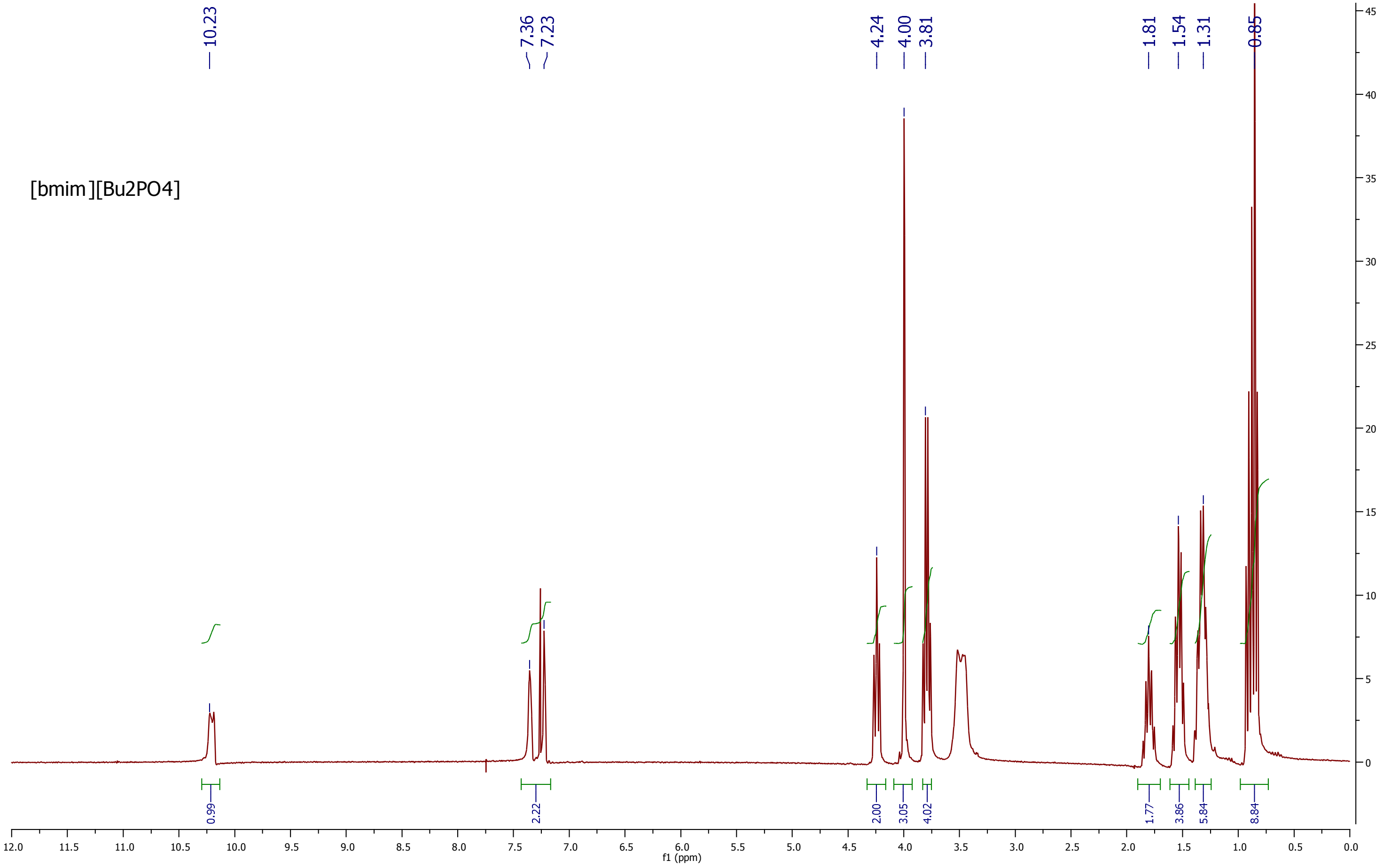


Figure S-5. ^{1}H NMR (300 MHz, $CDCl_3$) of [bmim][Bu_2PO_4]

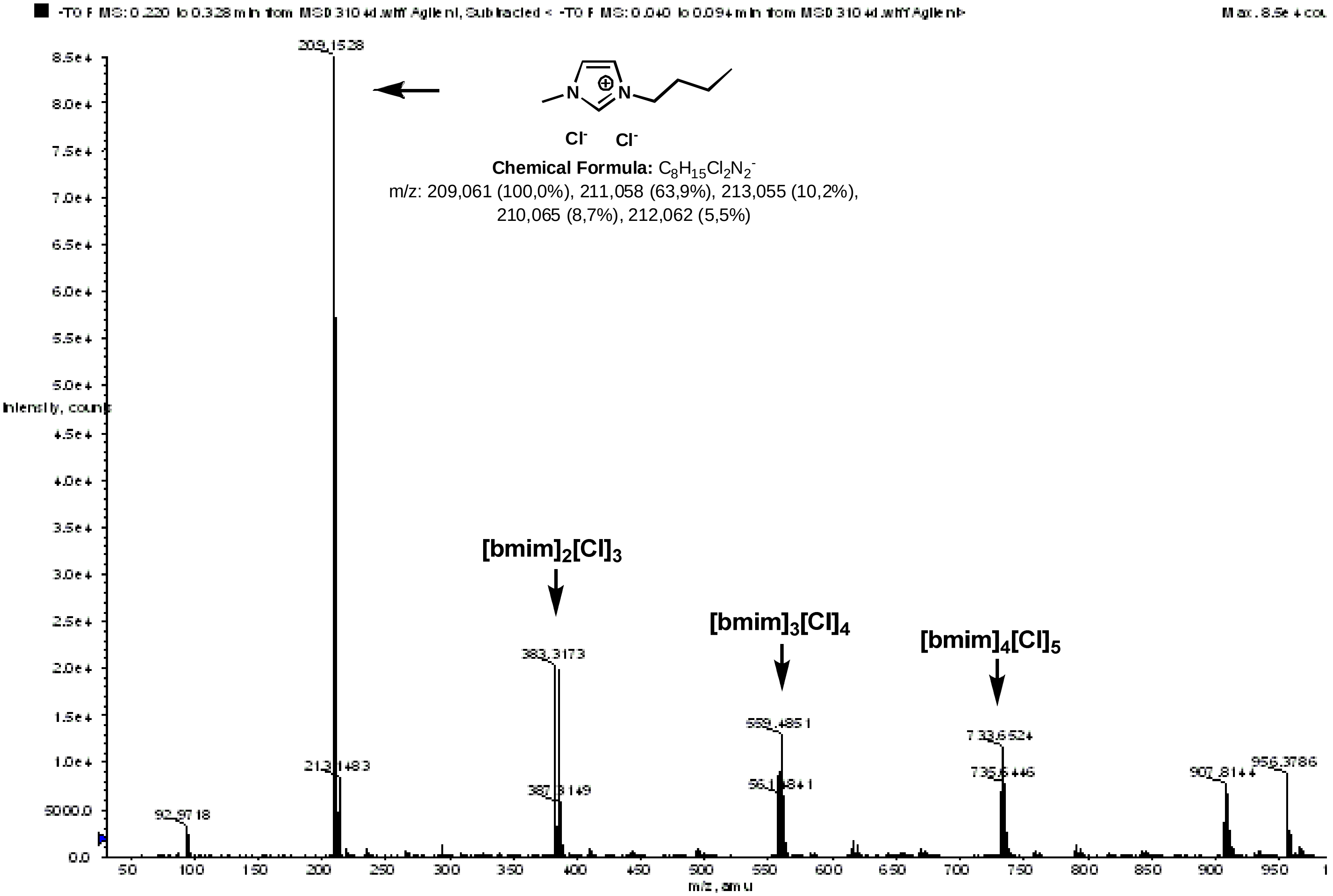


Figure S-6. ESI(-)-MS (175V) [bmim][Cl].

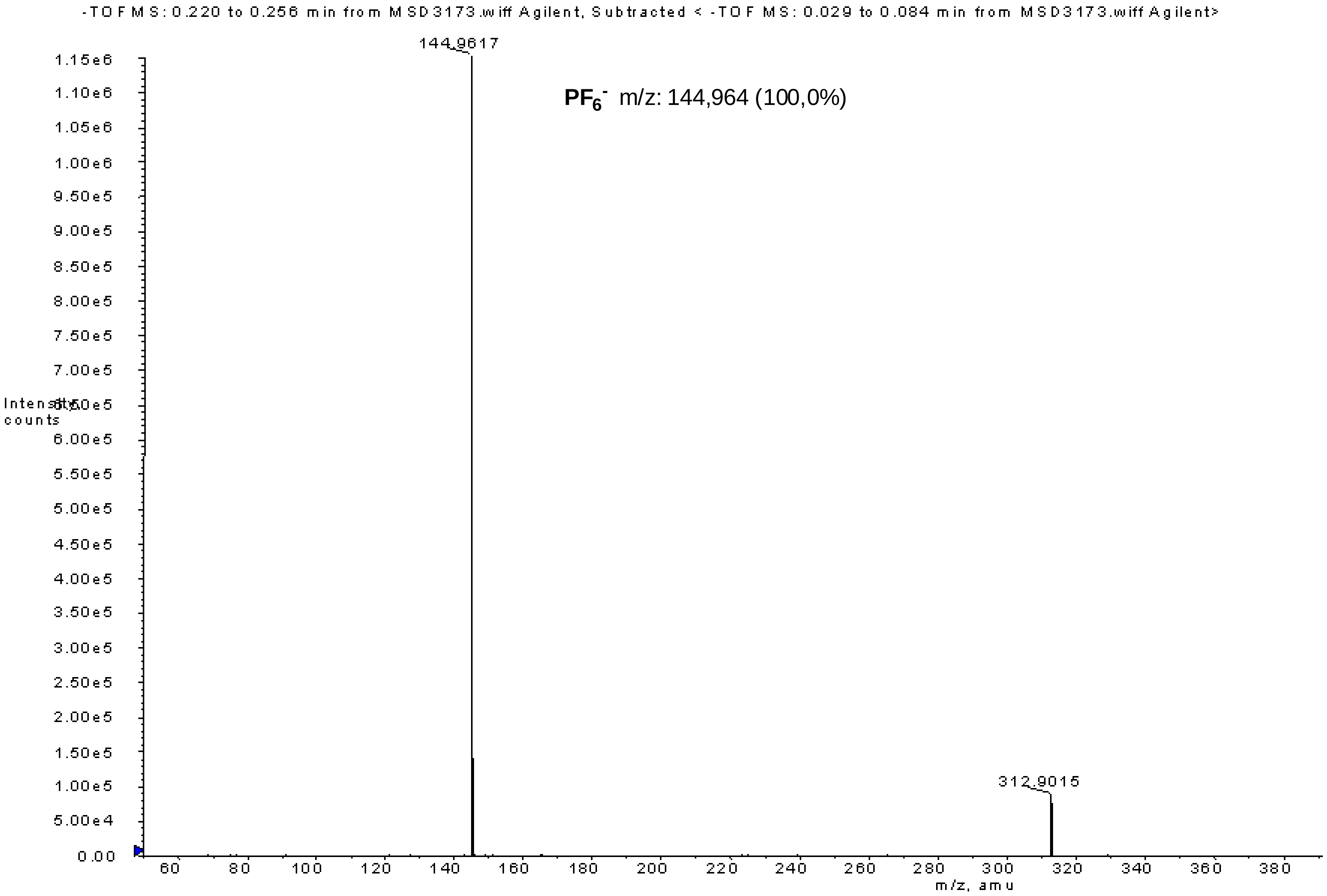


Figure S-7. ESI(-)-MS (175V) [bmim][PF6].

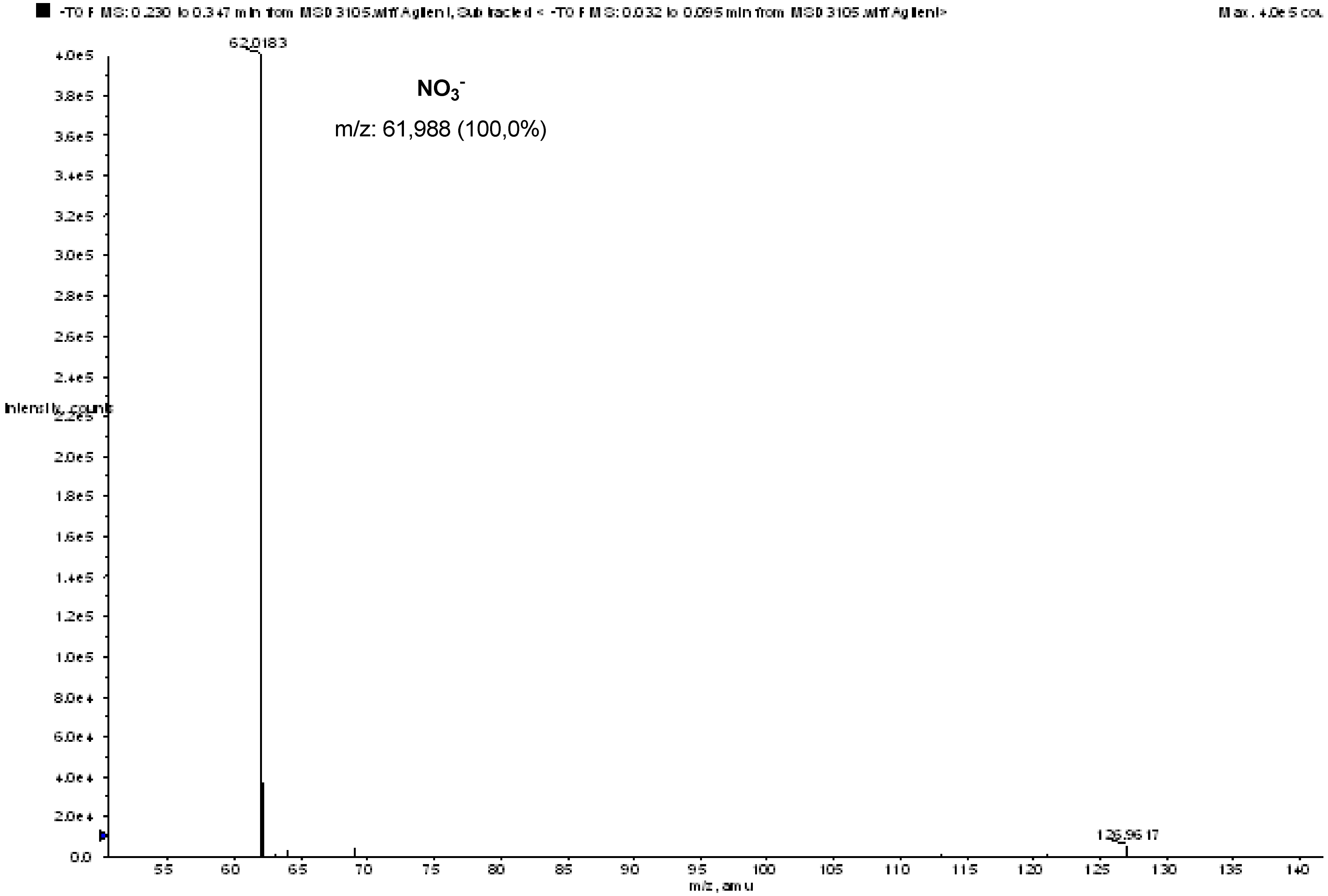


Figure S-8. ESI(-)-MS (175V) [bmim][NO3].

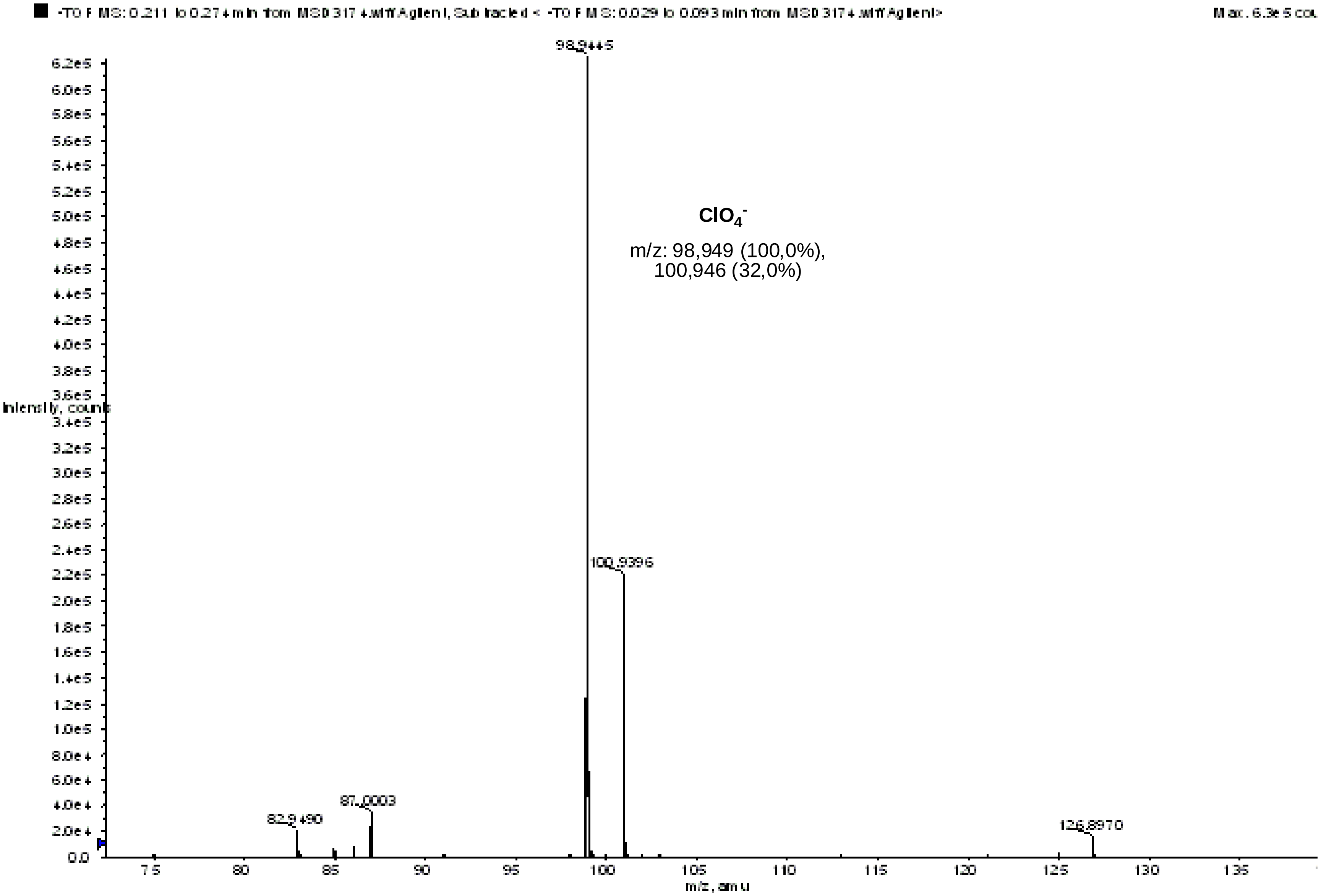


Figure S-9. ESI(-)-MS (175V) [bmim][ClO4].

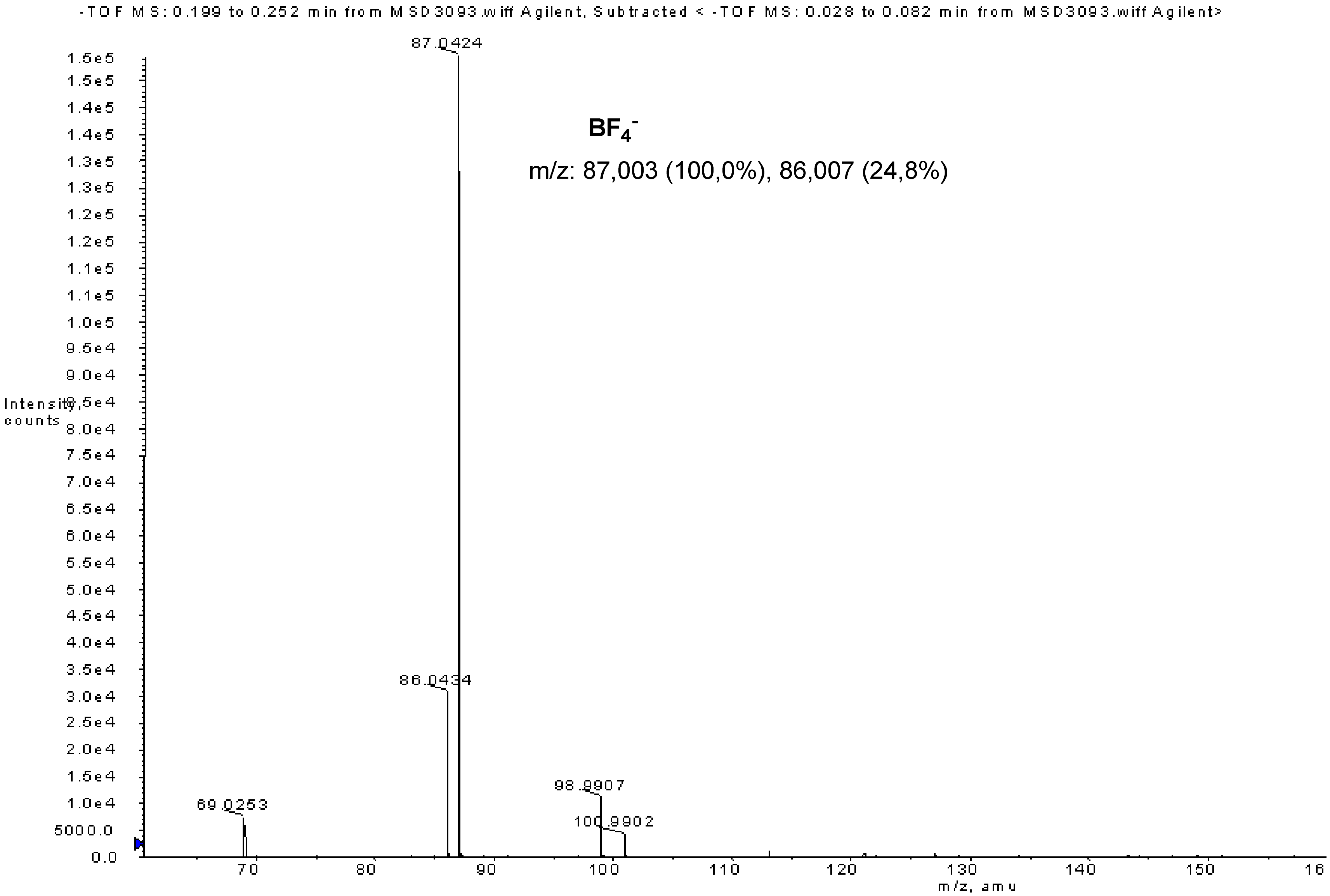


Figure S-10. ESI(-)-MS (175V) [bmim][BF4].

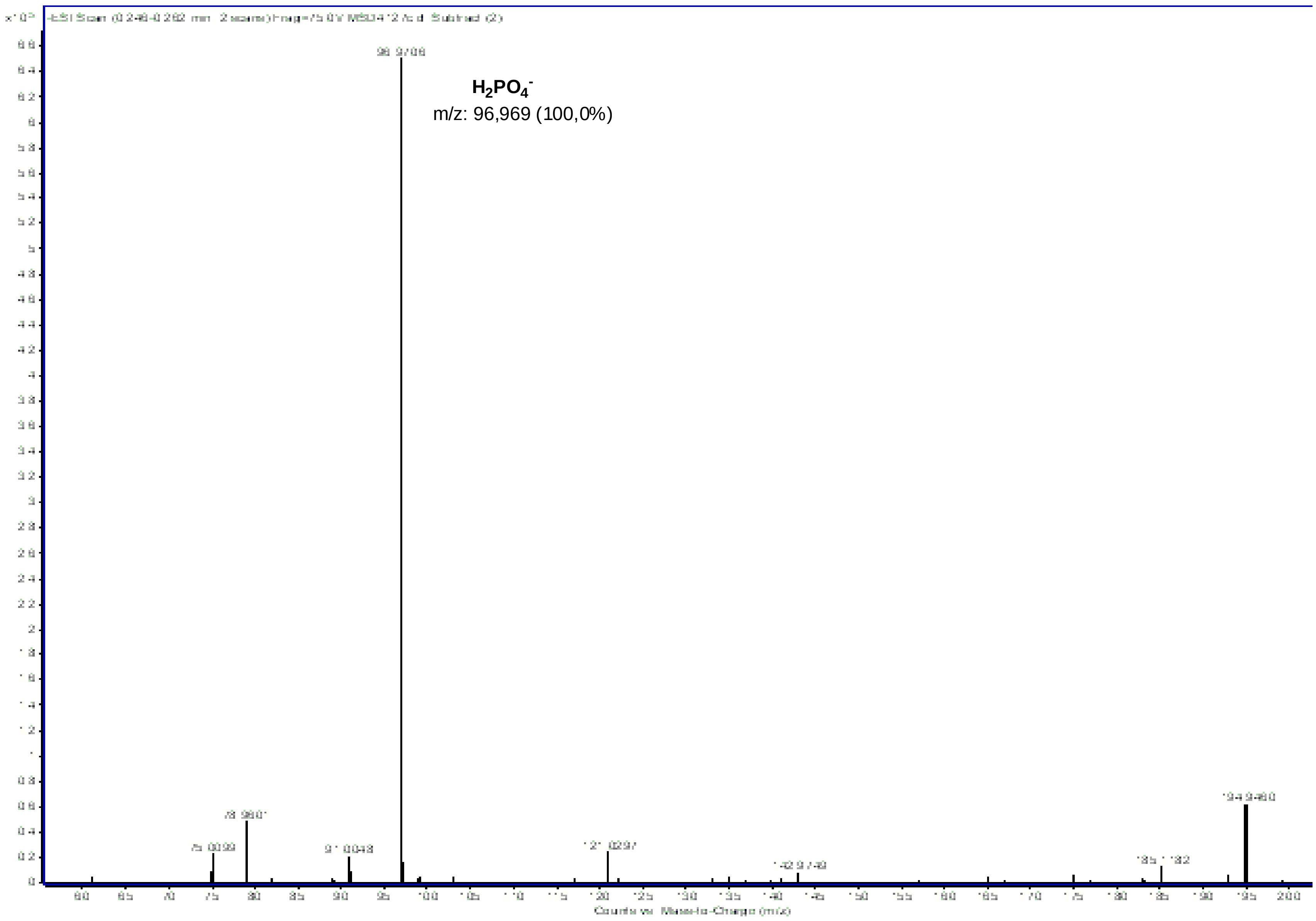


Figure S-11. ESI(-)-MS (75V) [bmim][H2PO4].

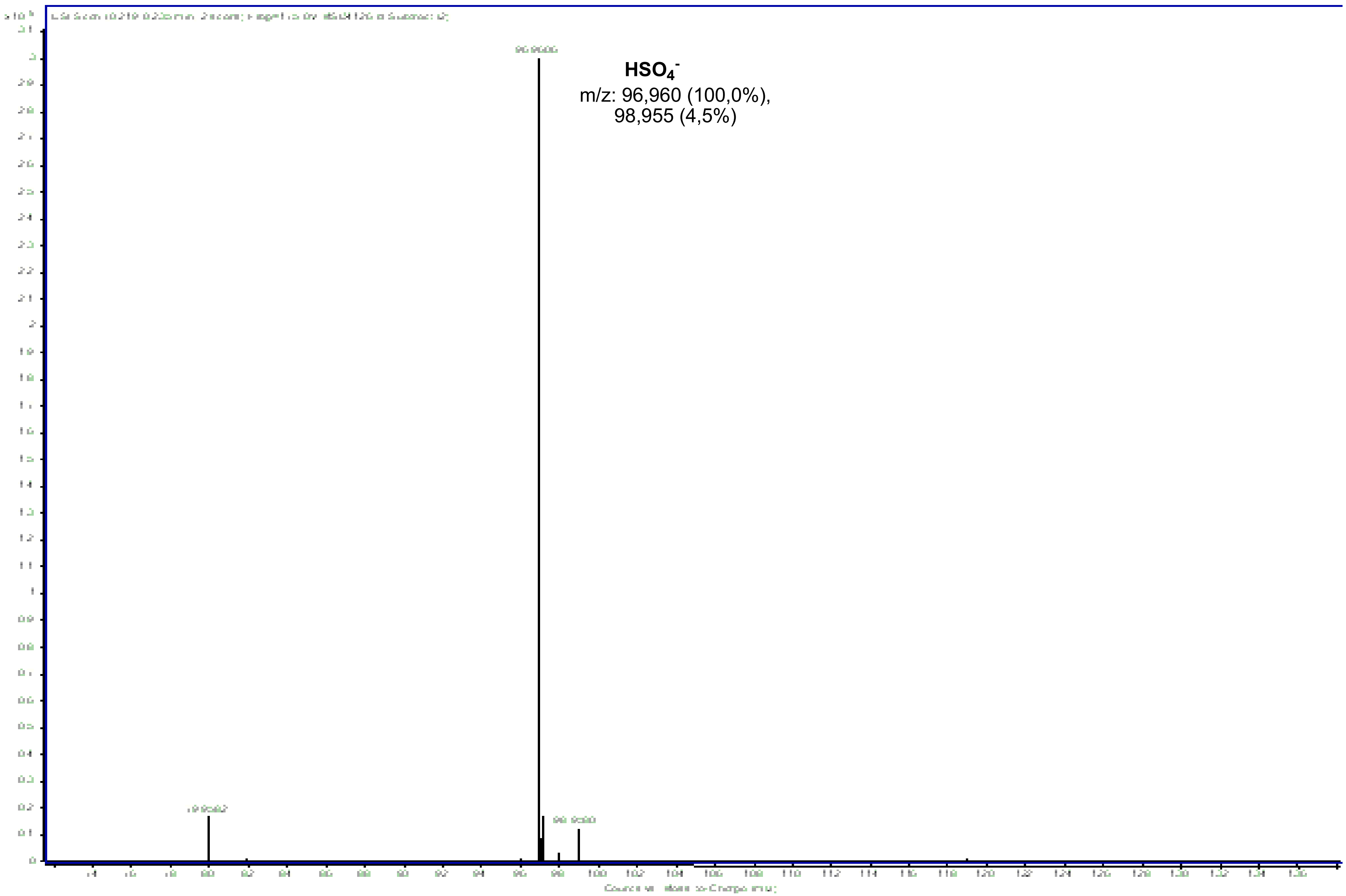


Figure S-12. ESI(-)-MS (75V) [bmim][HSO4].

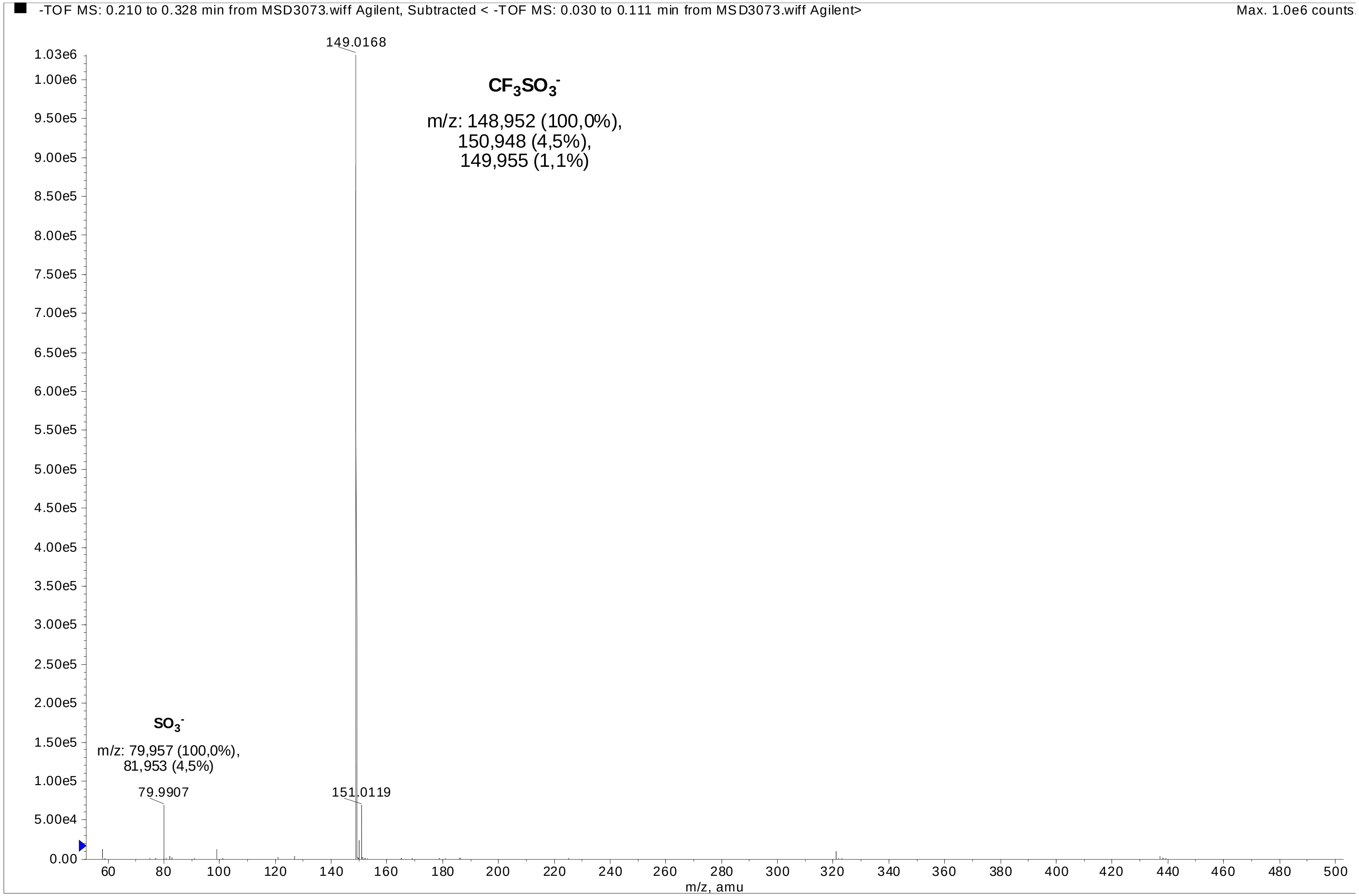
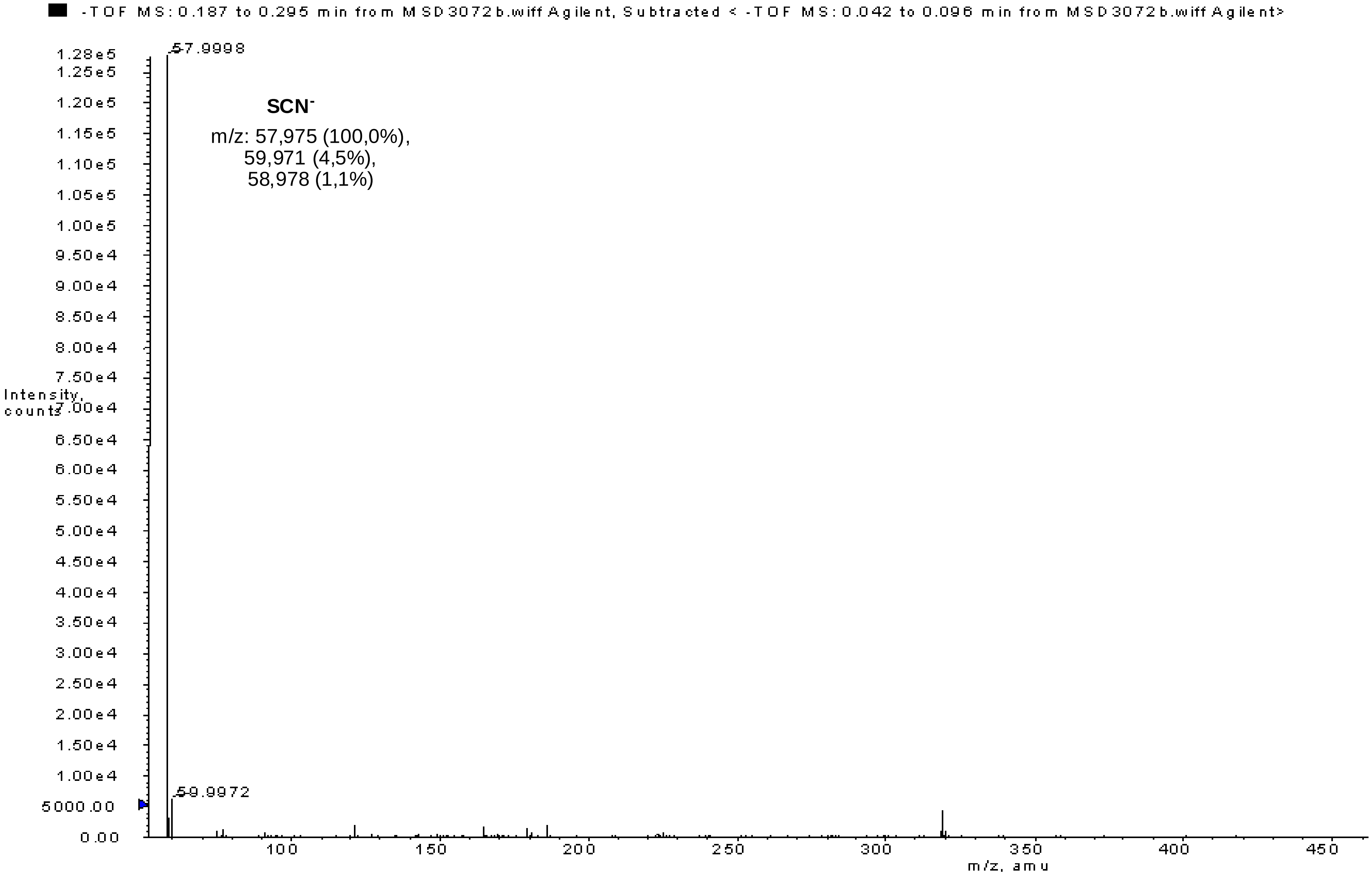


Figure S-13. ESI(-)-MS (175V) [bmim][CF3SO3].



SCN$^-$

m/z: 57,975 (100,0%),
59,971 (4,5%),
58,978 (1,1%)

Figure S-14. ESI(-)-MS (175V) [bmim][SCN].

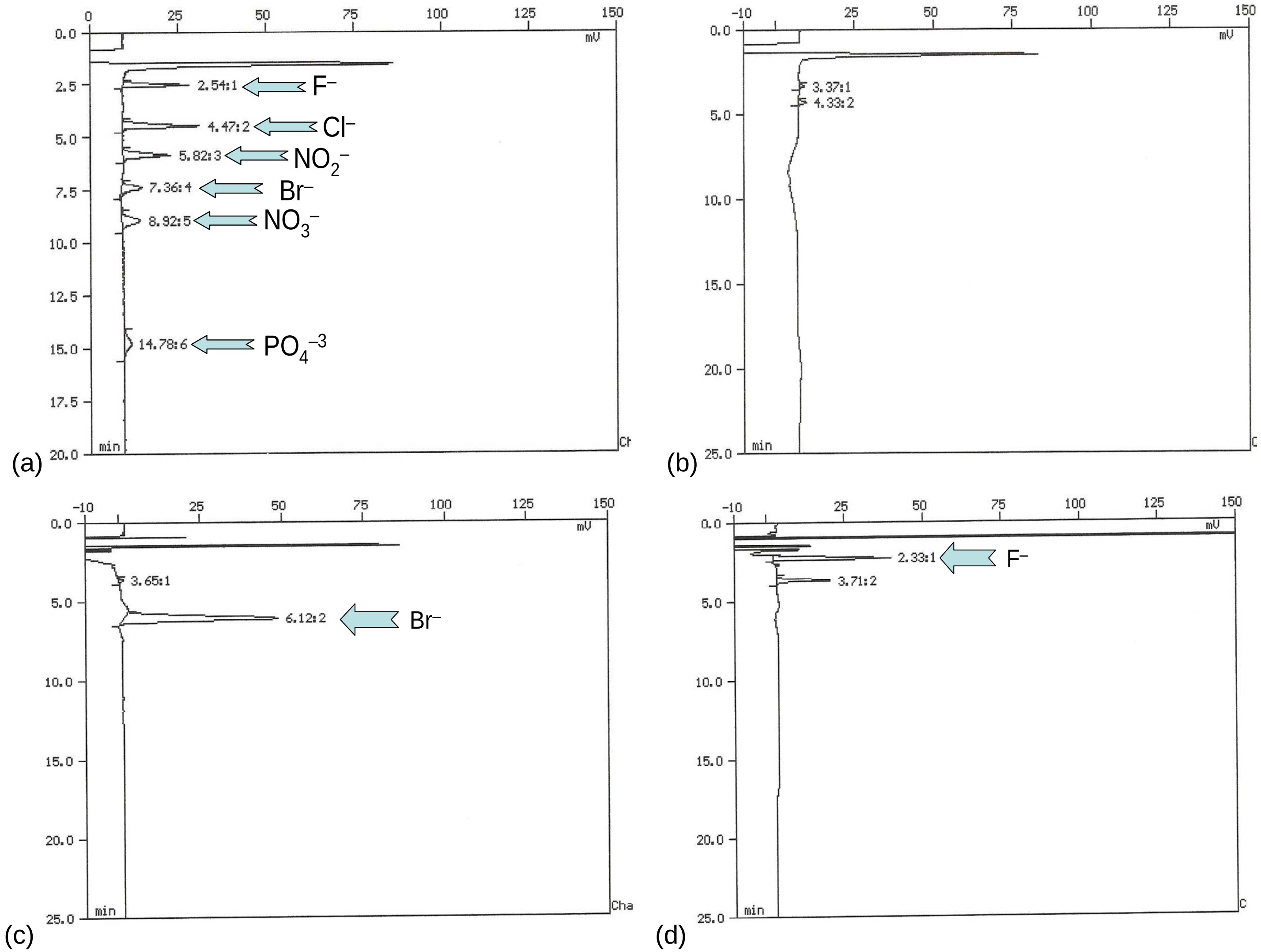


Figure S-15 HPLC-chromatogram of (a) pattern anions; (b) distilled water; (c) [bmim][Br]; (d) [bmim][F] obtained from [bmim][Br].