Electronic Supplementary Material (ESI) for Chemical Communications

Convenient method to access long-chain and functionalized mixed methylphosphonate esters and their application in the synthesis of ionic liquids

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Experimental

The ionic liquid [EMIM] methyl methylphosphonate was received from BASF AG.
All reagents were purchased from Aldrich, Fluka, Merck KGaA with synthesis grades.

Synthesis of asymmetric methyl methylphosphonate esters

Synthesis of AcNMe(Me)PO_3
1.2 eq of the ionic liquid [EMIM] methyl methylphosphonate was weighted into a dry Schlenk flask and 1.0 eq of bromoacetonitrile was added dropwise under stirring. The reaction mixture was stirred for 5 h at room temperature under an Ar atmosphere. The reaction mixture was subsequently extracted four times with diethylether. The combined diethylether phases were concentrated to a small volume and dried under reduced pressure to yield the product ester (42 %).

Synthesis of MeAcMe(Me)PO_3
1.2 eq of the ionic liquid [EMIM] methyl methylphosphonate was weighted into a dry Schlenk flask and 1.0 eq of methyl 2-chloroacetate was added dropwise under stirring. The reaction mixture was stirred for 12 h at room temperature under an Ar atmosphere. The reaction mixture was subsequently extracted four times with diethylether. The combined diethylether phases were concentrated to a small volume and dried under reduced pressure to yield the product ester (74 %).

Synthesis of BuMe(Me)PO_3
1.0 eq of 1-bromobutane was weighted into a dry Schlenk flask and 1.2 eq of the ionic liquid [EMIM] methyl methylphosphonate was added. The reaction mixture was stirred for 20 h at 50 °C under an Ar atmosphere. The reaction mixture was subsequently extracted four times with diethylether. The combined diethylether phases were concentrated to a small volume and dried under reduced pressure to yield the product ester (85 %).

Synthesis of OcMe(Me)PO_3
1.0 eq of 1-bromooctane was weighted into a dry Schlenk flask and 1.2 eq of the ionic liquid [EMIM] methyl methylphosphonate was added. The reaction mixture was stirred for 20 h at 60 °C under an Ar atmosphere. The reaction mixture was subsequently extracted four times with diethylether. The combined diethylether phases were concentrated to a small volume and dried under reduced pressure to yield the product ester (89 %).

Synthesis of ($MeEG_3$)Me(Me)PO_3
1.0 eq of PEG-benzenesulfonate (obtained according to [S1]) was weighted into a dry Schlenk flask and 1.2 eq of the ionic liquid [EMIM] methyl methylphosphonate was added. The reaction mixture was stirred for 12 h at RT under an Ar atmosphere. The reaction mixture was subsequently extracted four times with diethylether. The combined diethylether phases were concentrated to a small volume and dried under reduced pressure to yield the product ester (87 %).

Synthesis of DodMe(Me)PO_3
1.0 eq of 1-iodododecane was weighted into a dry Schlenk flask and 1.2 eq of the ionic liquid [EMIM] methyl methylphosphonate was added. The reaction mixture was stirred for 36 h at 75 °C under an Ar atmosphere. The reaction mixture was subsequently extracted four times with diethylether. The combined diethylether phases were concentrated to a small volume and dried under reduced pressure to yield the product ester (92 %).

General synthetic procedure for the synthesis of alkylphosphonate ionic liquids from dialkyl alkylphosphonate esters

1.0 eq of the respective alkylphosphonate ester was weighted into a dry Schlenk flask and 1.0 eq of the corresponding amine was added. Then the reaction mixture was stirred. The required conditions are summarized in Table 3.

Table S1: Phosphonate ionic liquids: Synthesis conditions and water content.

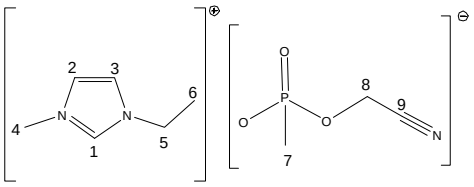
Entry	Phosphonate ester	Amine	Ionic Liquid	T / °C	t / d	Yield / %	Water content / ppm
1	$AcNMe(Me)PO_3$	EtIm	[EMIM] $[AcN(Me)PO_3]$[a)]	90	1	82	4494
2	$MeAcMe(Me)PO_3$	EtIm	[EMIM] $[MeAc(Me)PO_3]$	75	1	86	3304
3	$Me_2(Me)PO_3$	EtIm	[EMIM] $[Me(Me)PO_3]$	100	1	> 99	2744
4	$Bu_2(Me)PO_3$	MIm	[BMIM] $[Bu(Me)PO_3]$	130	2	94	2345
5	$Oc_2(Me)PO_3$	MIm	[OMIM] $[Oc(Me)PO_3]$	150	3	92	2771
6	$Oc_2(Ph)PO_3$	MIm	[OMIM] $[Oc(Ph)PO_3]$	150	3	>99	1972
7	$(MeEG_3)_2(Me)PO_3$	MIm	$[(MeEG_3)MIM]$ $[(MeEG_3)\ (Me)PO_3]$	140	3	92	645
8	$Dod_2(Me)PO_3$	MIm	[DodMIM] $[Dod(Me)PO_3]$	160	3	98	n.a.

a) Synthesis in acetonitrile

NMR spectroscopy and ESI-MS analysis

NMR spectra were recorded on a JEOL ECX +400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{31}P: 162 MHz). Deuterated solvents ($CDCl_3$ and d_6-DMSO) were used as internal standards. The chemical shifts are noted in parts per million (ppm), the coupling constants in Hz. The data is stated in the following way:

[EMIM][AcN(Me)PO$_3$] (1)



^{1}H-NMR (DMSO-d_6, 400 MHz, ppm): δ = 0.96 (d, 3H, J = 15.65 Hz, 7-H), 1.40 (t, 3H, J = 7.41 Hz, 6-H), 3.87 (s, 3H, 4-H), 4.21 (q, 2H, J = 0.74, Hz 5-H), 4.50 (d, 2H, J = 1.03 Hz, 8-H), 7.78 (s, 1H, 2-H), 7.87 (s, 1H, 3-H), 9.60 (s, 1H, 1-H).

^{13}C-NMR (DMSO-d_6, 100.4 MHz, ppm): δ = 14.00 (d, J = 13.22 Hz, C-7), 15.20 C-6, 35.52 C-4, 43.98 C-5, 49.02 C-8, 118.87 C-9, 122.09 C-3, 123.61 C-2, 137.15 C-1.

^{31}P-NMR (DMSO-d_6, 162 MHz, ppm): δ = 23.55.

	Entire	Cation	Anion
Mass calculated	245.22	111.16	134.05

Display Report

Analysis Info

Analysis Name	D:\Data\Jing Li\2011-07-08 ILs\ILs 1-neg00.d	Acquisition Date	08/07/2011 09:59:54
Method	DEF_MS.M	Operator	Jing Li
Sample Name	ILs	Instrument	esquire6000
Comment	C9H16N3O3P 1,14E-05M in ethalnol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
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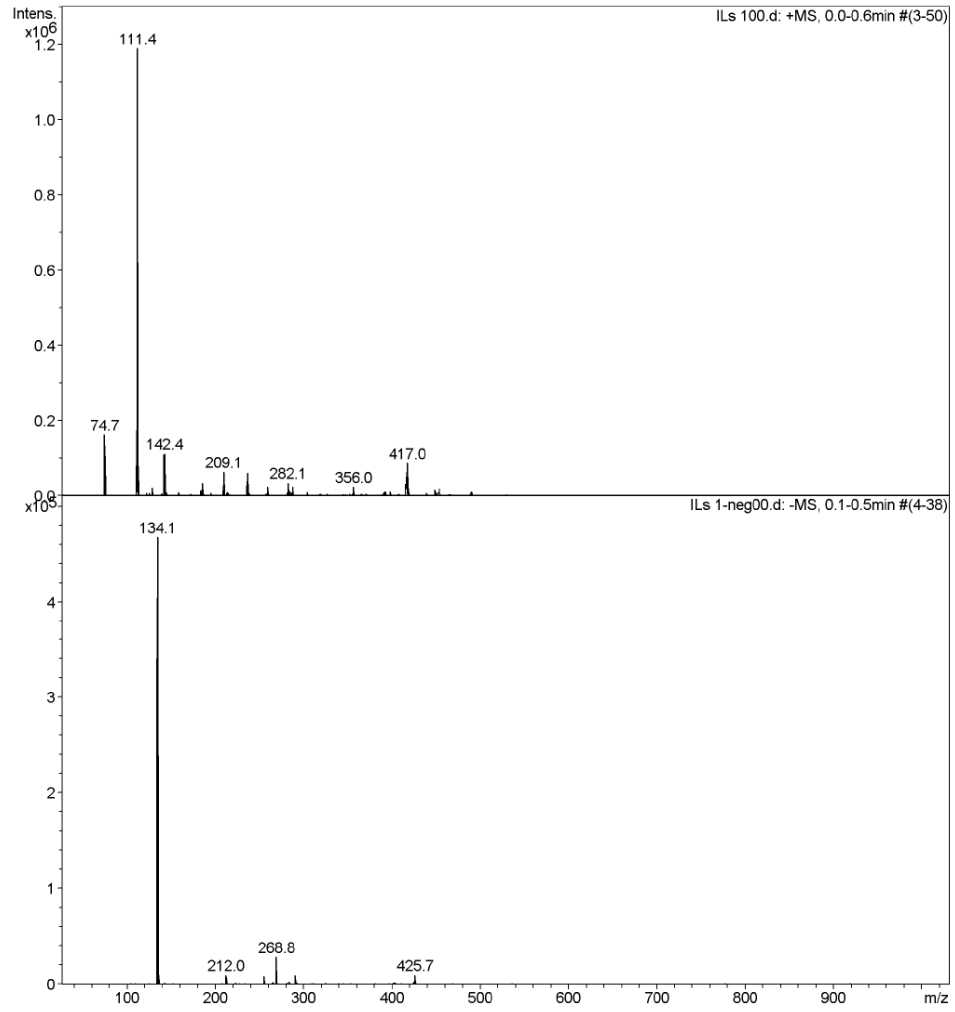
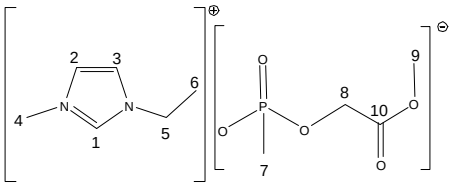
Capillary Exit	-106.0 Volt	Skimmer	-40.0 Volt	Trap Drive	36.7
Accumulation Time	500 µs	Averages	7 Spectra	ICC Actual	939
Compound Stability	100 %	Target Mass	200 m/z	Trap Drive Level	100 %



[EMIM][MeAc(Me)PO_3] (2)



^{1}H-NMR
(DMSO-d_6, 400 MHz, ppm): δ = 0.91 (d, 3H, J = 15.66 Hz, 7-H), 1.40 (t, 3H, J = 7.42 Hz, 6-H), 3,60 (s, 3H, 9-H), 3.87 (s, 3H, 4-H), 4.21 (q, 2H, J = 0.72 Hz, 5-H), 4.24 (d, 2H, J = 0.86 Hz, 8-H), 7.78 (s, 1H, 2-H), 7.87 (s, 1H, 3-H), 9.66 (s, 1H, 1-H).

^{13}C-NMR (DMSO-d_6, 100.4 MHz, ppm): δ = 13.80 (d, J = 13.32 Hz, C-7), 15.27 C-6, 35.49 C-4, 43.96 C-5, 51.31 C-9, 61.02 C-8, 122.15 C-3, 123.67 C-2, 137.40 C-1, 171.26 C-10.

^{31}P-NMR (DMSO-d_6, 162 MHz, ppm): δ = 18.37.

	Entire	Cation	Anion
Mass calculated	278.24	111.16	167.08

Display Report

Analysis Info

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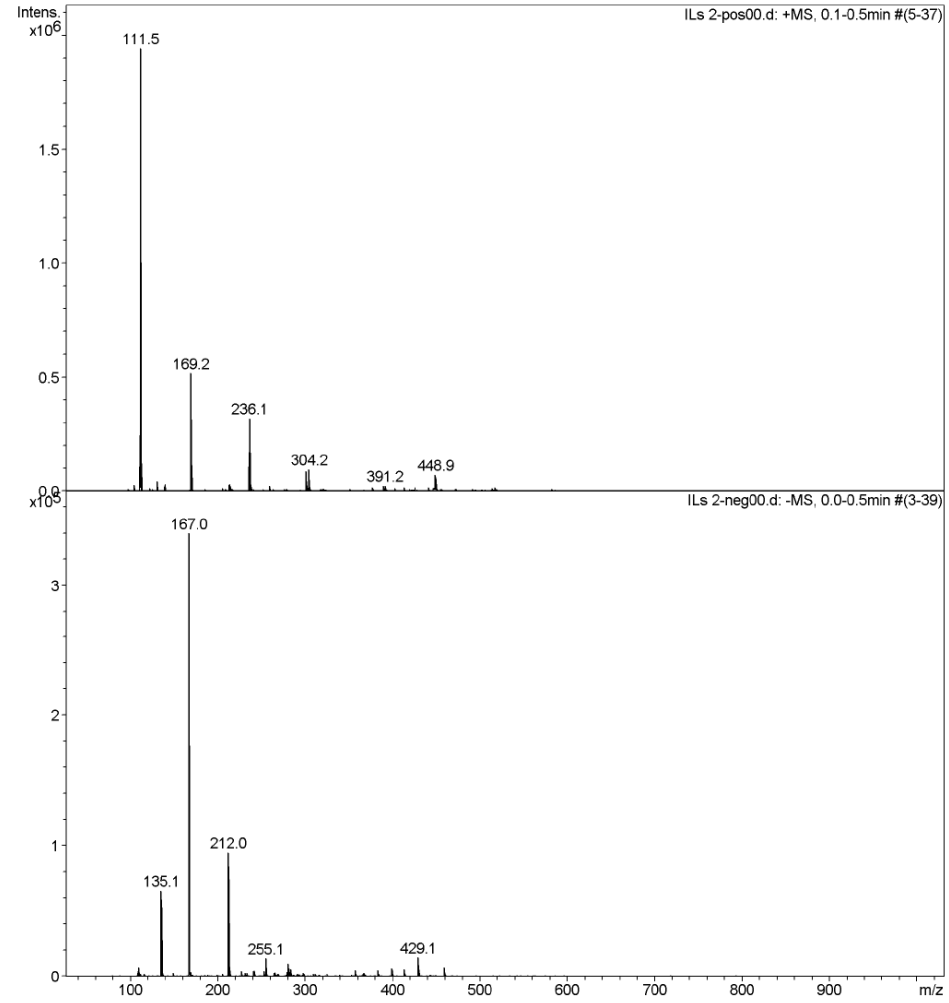
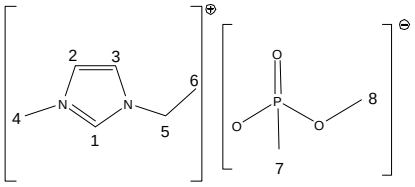
Method	DEF_MS.M		
Sample Name	ILs	Operator	Jing Li
Comment	1,1E-05M in MeOH m/z 236 is impurity from MeOH	Instrument	esquire6000

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	50 m/z	Scan End	1000 m/z
Capillary Exit	-106.0 Volt	Skimmer	-40.0 Volt	Trap Drive	36.7
Accumulation Time	500 µs	Averages	7 Spectra	ICC Actual	1345
Compound Stability	100 %	Target Mass	200 m/z	Trap Drive Level	100 %



[EMIM][Me(Me)PO$_3$] (3)



^{1}H-NMR (DMSO-d$_6$, 400 MHz, ppm): δ = 0.88 (d, 3H, J = 15.24 Hz, 7-H), 1.35 (t, 3H, J = 7.42 Hz, 6-H), 3,27 (d, 3H, J = 1.03 Hz, 8-H), 3.92 (s, 3H, 4-H), 4.25 (q, 2H, J = 0.74 Hz, 5-H), 8.08 (s, 1H, 2-H), 8.22 (s, 1H, 3-H), 10.26 (s, 1H, 1-H).

^{13}C-NMR (DMSO-d$_6$, 100.4 MHz, ppm): δ = 12.80 (d, J = 13.13 Hz, C-7), 15.30 C-6, 35.35 C-4, 43.83 C-5, 50.20 C-8, 122.23 C-3, 123.71 C-2, 137.71 C-1.

^{31}P-NMR (DMSO-d$_6$, 162 MHz, ppm): δ = 18.98.

	Entire	Cation	Anion
Mass calculated	220.21	111.16	109.04

Display Report

Analysis Info

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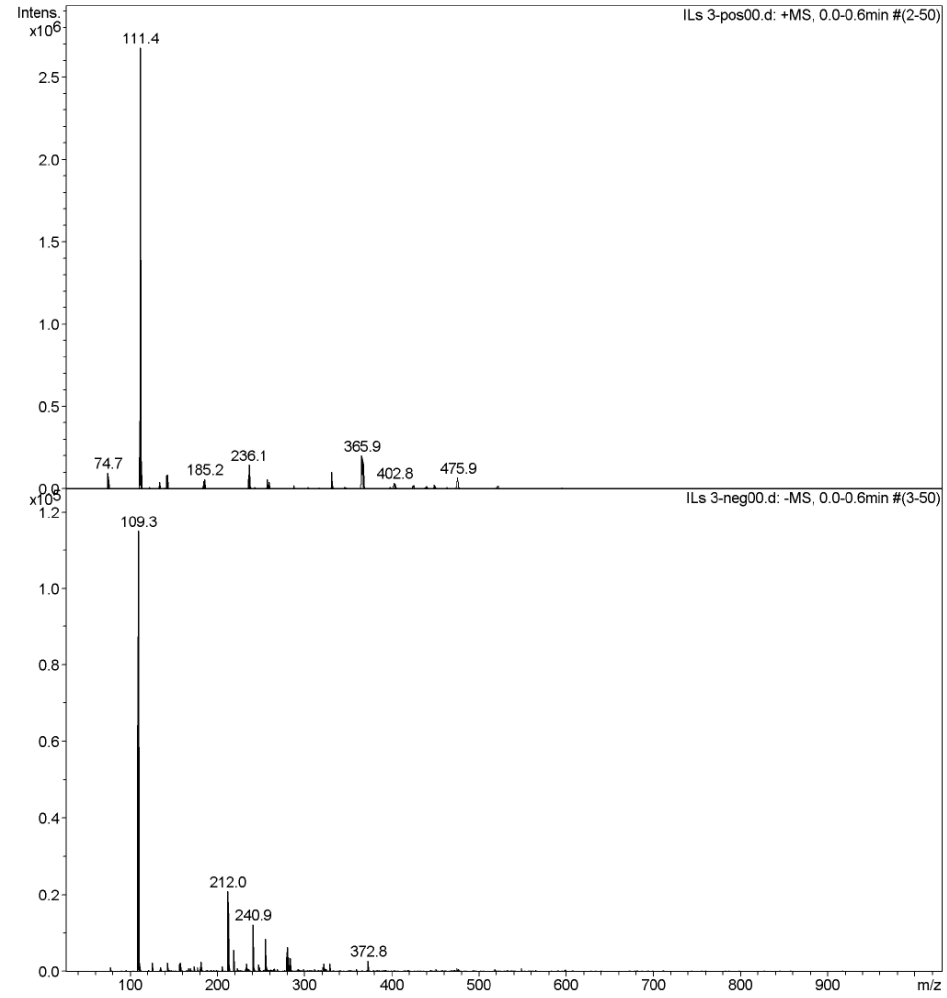
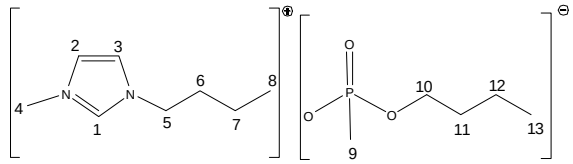
Method	DEF_MS.M	Operator	Jing Li
Sample Name	ILs	Instrument	esquire6000
Comment	C8H17N2O3P 1,31E-05M in ethalnol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	50 m/z	Scan End	1000 m/z
Capillary Exit	-106.0 Volt	Skimmer	-40.0 Volt	Trap Drive	36.7
Accumulation Time	500 µs	Averages	7 Spectra	ICC Actual	595
Compound Stability	100 %	Target Mass	200 m/z	Trap Drive Level	100 %



[BMIM][Bu(Me)PO$_3$] (4)



^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ = 0.78 (t, 3H, J = 7.42 Hz, 8-H), 0.84 (t, 3H, J = 7.41 Hz, 13-H), 1.19 (d, 3H, J = 16.07 Hz, 9-H), 1.27 (m, 4H, 7-H and 12-H), 1.47 (m, 2H, 6-H), 1.75 (m, 2H, 11-H), 3.74 (q, 2H, J = 0.66 Hz, 5-H), 3.96 (s, 3H, 4-H), 4.19 (t, 2H, J = 0.74 Hz, 10-H), 7.19 (s, 1H, 2-H), 7.31 (s, 1H, 3-H), 10.75 (s, 1H, 1-H).

^{13}C-NMR (DMSO-d_6, 100.4 MHz, ppm): δ = 13.00 (d, J = 13.22 Hz, C-9), 13.14 C-8, 13.54 C-13, 18.60 C-12, 18.75 C-7, 31.56 C-11, 32.87 C-6, 35.37 C-4, 48.17 C-5, 62.33 C-10, 122.38 C-3, 123.58 C-2, 137.86 C-1.

^{31}P-NMR ($CDCl_3$, 162 MHz, ppm): δ = 22.70.

	Entire	Cation	Anion
Mass calculated	290.34	139.22	151.12

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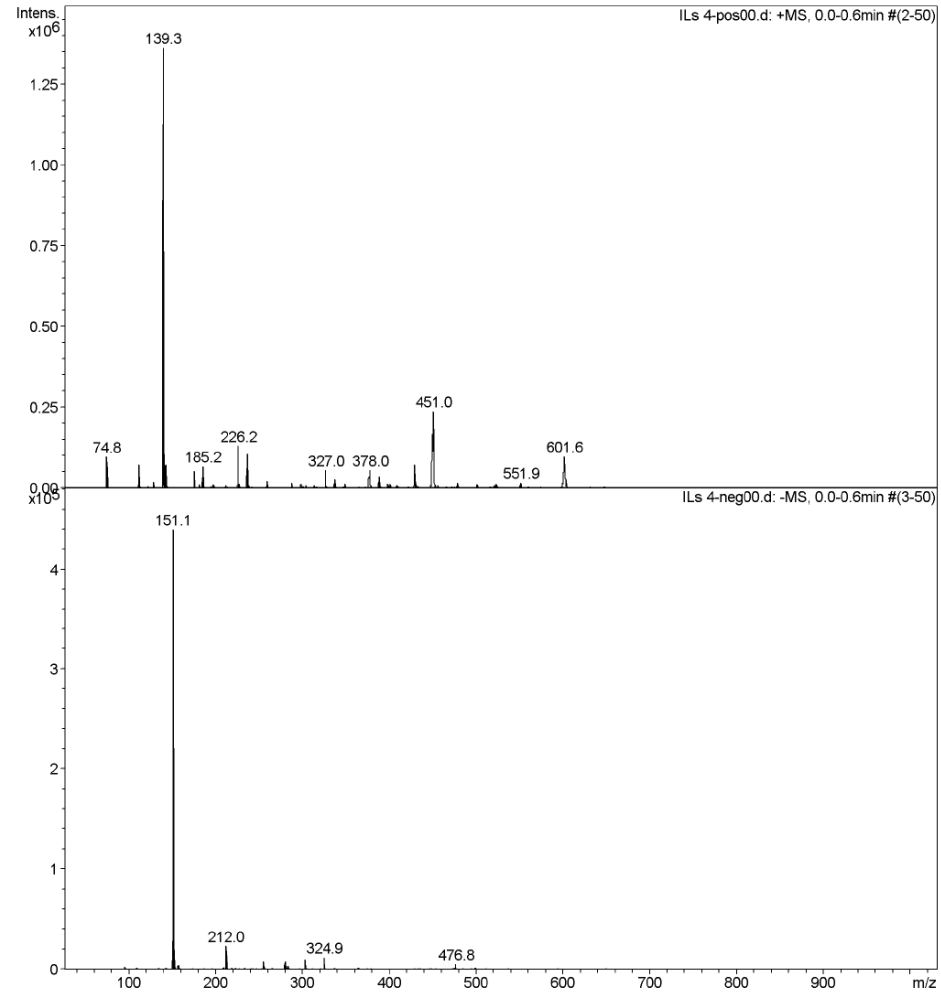
Analysis Info

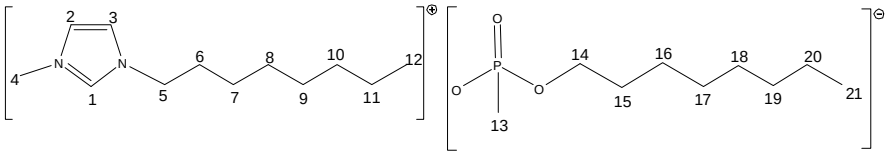
Analysis Name	D:\Data\Jing Li\2011-07-08 ILs\ILs 4-neg00.d	Acquisition Date	08/07/2011 10:53:50
Method	DEF_MS.M		
Sample Name	ILs	Operator	Jing Li
Comment	C13H27N2O3P 6,89E-06M in ethalnol	Instrument	esquire6000

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	50 m/z	Scan End	1000 m/z
Capillary Exit	-106.0 Volt	Skimmer	-40.0 Volt	Trap Drive	36.7
Accumulation Time	500 µs	Averages	7 Spectra	ICC Actual	1078
Compound Stability	100 %	Target Mass	200 m/z	Trap Drive Level	100 %



[OMIM][Oc(Me)PO$_3$] (5)



^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ = 0.74 (m, 6H, 12-H and 21-H), 1.19 (d, 3H, J = 15.65 Hz, 13-H), 1.13 (m, 20H, 7-H – 11-H and 16-H – 20-H), 1.48 (m, 2H, 6-H), 1.75 (m, 2H, 15-H), 3.71 (q, 2H, J = 0.70, Hz 5-H), 3.96 (s, 3H, 4-H), 4.16 (t, 2H, J = 0.74 Hz, 14-H), 7.15 (s, 1H, 2-H), 7.29 (s, 1H, 3-H), 10.92 (s, 1H, 1-H).

^{13}C-NMR (DMSO-d_6, 100.4 MHz, ppm): δ = 13.00 (d, J = 13.22 Hz, C-13), 13.74 C-12, 22.11 C-21, 22.59 (2C, C-11 and C-20), 28.54 – 31.34 (m, 10C, C-6 – C-10 and C-15 – C-19), 35.39 C-4, 48.46 C-5, 62.66 C-14, 122.36 C-3, 123.53 C-2, 137.82 C-1.

^{31}P-NMR ($CDCl_3$, 162 MHz, ppm): δ = 22.40.

	Entire	Cation	Anion
Mass calculated	402.55	195.32	207.23

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Analysis Info

Analysis Name	D:\Data\Jing Li\2011-07-08 ILs\ILs 5-neg00.d	Acquisition Date	08/07/2011 11:06:12
Method	DEF_MS.M	Operator	Jing Li
Sample Name	ILs	Instrument	esquire6000
Comment	C21H43N2O3P 9,74E-06M in ethalnol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	50 m/z	Scan End	1000 m/z
Capillary Exit	-106.0 Volt	Skimmer	-40.0 Volt	Trap Drive	36.7
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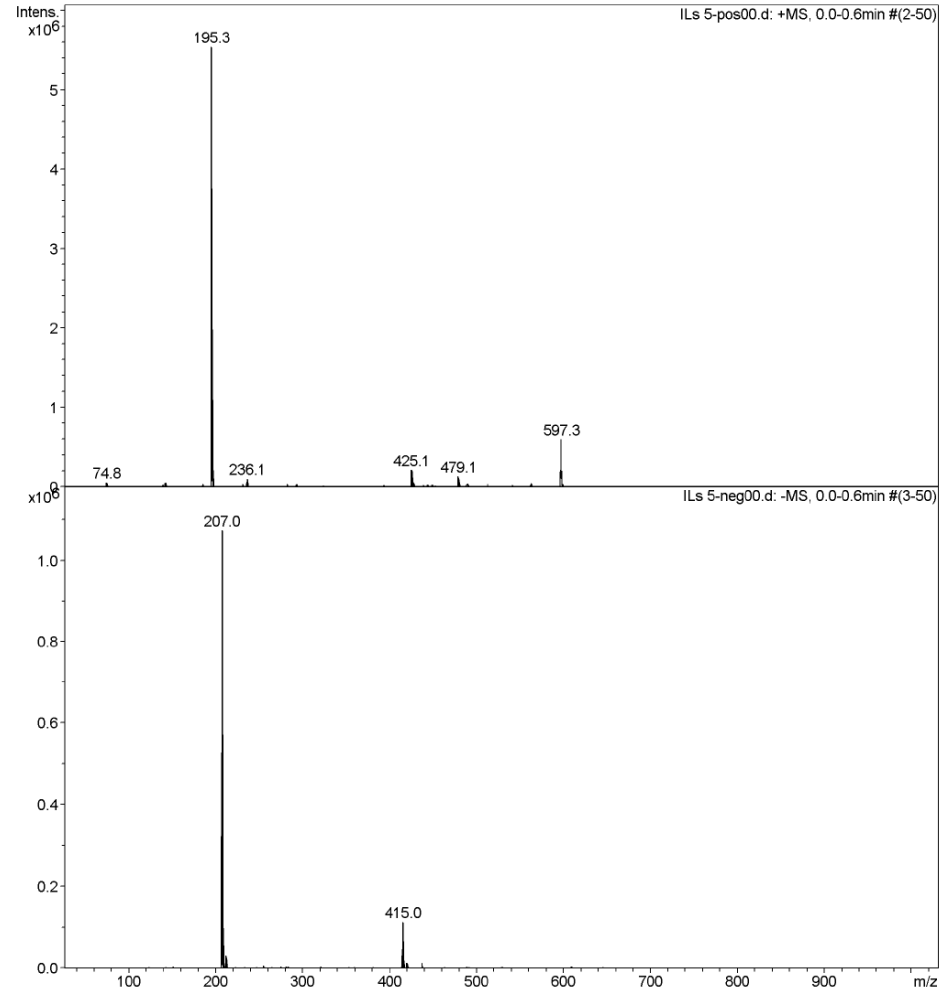
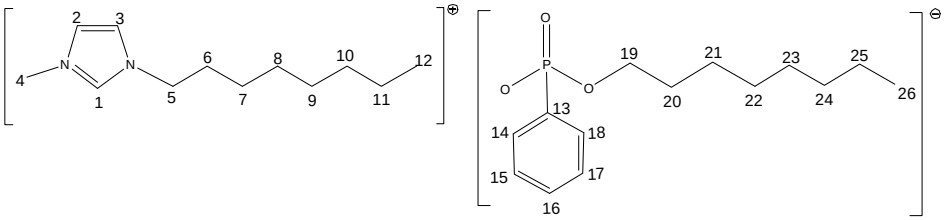
Compound Stability	100 %	Target Mass	200 m/z	Trap Drive Level	100 %



[OMIM][Oc(Ph)PO$_3$] (6)

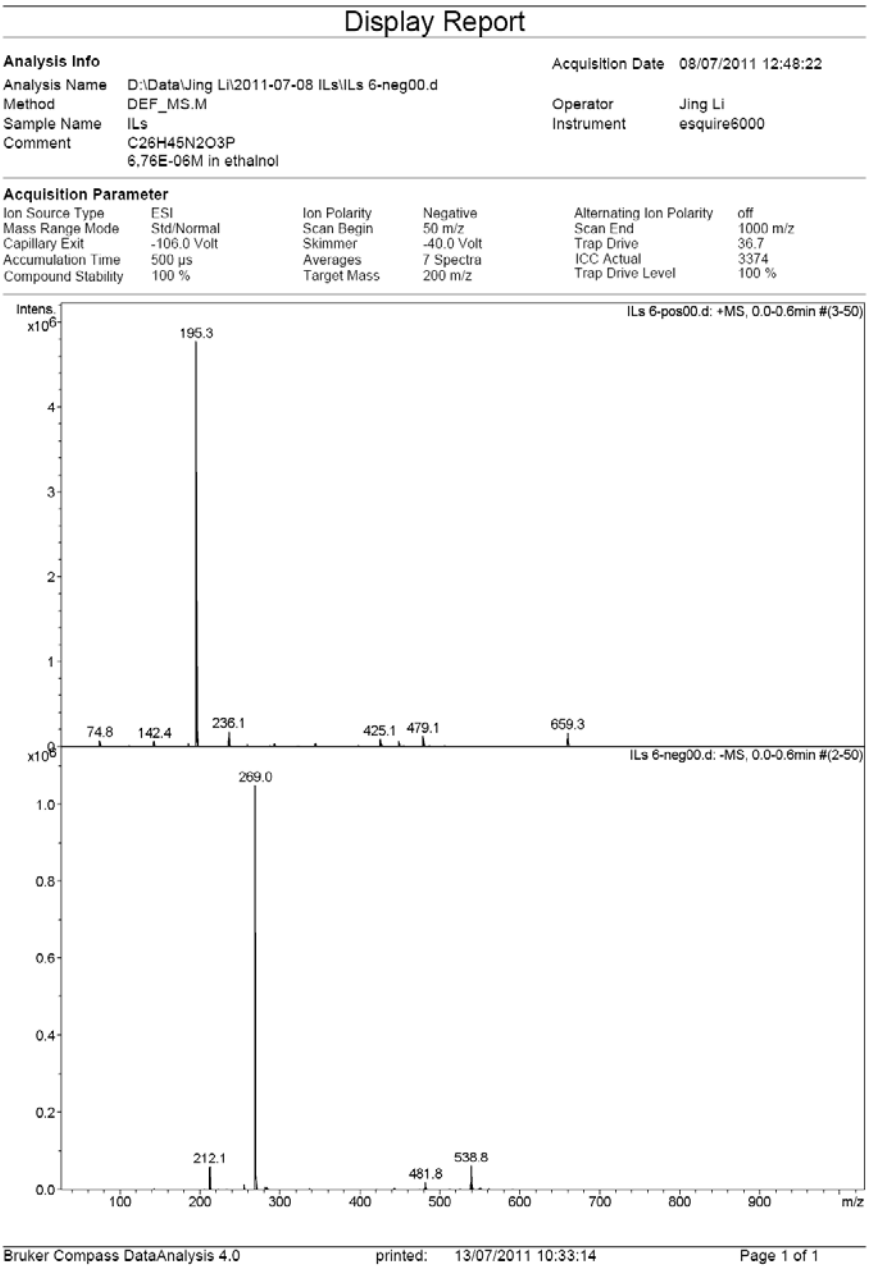


^{1}H-NMR (DMSO-d$_6$, 400 MHz, ppm): δ = 0.84 (m, 6H, 12-H and 26-H), 1.14 – 1.21 (m, 20H, 7-H – 11H and 21-H – 25-H), 1.35 (m, 2H, 6-H), 1.74 (m, 2H, 20-H), 3.50 (q, 2H, J = 0.66 Hz, 5-H), 3.85 (s, 3H, 4-H), 4.16 (t, 2H, J = 0.74 Hz, 19-H), 7.25 (m, 3H, 15-H –17-H), 7.60 (m, 2H, 14-H and 18-H), 7.79 (s, 1H, 2-H), 7.89 (s, 1H, 3-H), 10.78 (s, 1H, 1-H).

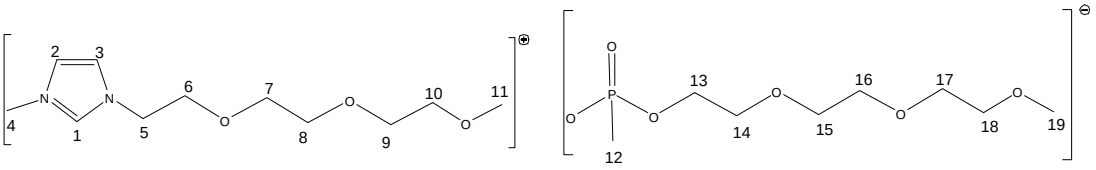
^{13}C-NMR (DMSO-d$_6$, 100.4 MHz, ppm): δ = 13.82 C-12, 22.08 C-26, 25.40 – 31.25 (m, 12C, C-6 – C-11 and C-20 – C-25), 35.46 C-4, 48.55 C-5, 62.89 C-19, 122.30 C-3, 123.49 C-2, 127.05 (m, 2C, C-15 and C-17), 128.3 (m, 2C, C-13 and C-16), 131.08 (m, 2C, C-14 and C-18), 137.48 C-1.

^{31}P-NMR (DMSO-d$_6$, 162 MHz, ppm): δ = 9.33.

	Entire	Cation	Anion
Mass calculated	464.62	195.32	269.30



[(MeEG$_3$)MIM][(MeEG$_3$)(Me)PO$_3$] (7)



^{1}H-NMR (DMSO-d$_6$, 400 MHz, ppm): δ = 0.98 (d, 3H, J = 16.10 Hz, 12-H), 3.22 (m, 6H, 11-H and 19-H), 3,41 (m, 4H, 8-H and 18-H), 3.44 – 3.51 (m, 12H, 7-H – 9-H and 15-H – 17-H), 3.54 (m, 2H, 6-H), 3.70 -3.80 (m, 4H, 5-H and 14-H), 3.88 (s, 3H, 4-H), 4.38 (t, 2H, J = 0.5 Hz, 13-H), 7.77 (s, 1H, 2-H), 7.80 (s, 1H, 3-H), 9.45 (s, 1H, 1-H).

^{13}C-NMR (DMSO-d$_6$, 100.4 MHz, ppm): δ = 13.00 (d, J = 13.42 Hz, C-12), 35.51 C-4, 48.50 C-5, 58.01 (2C, C-11 and C-19), 60.0 – 70.70 (m, 10C, C-6 – C-10 and C-14 – C-18), 71.30 C-13, 122.70 C-3, 123.39 C-2, 137.62 C-1.

^{31}P-NMR (DMSO-d$_6$, 162 MHz, ppm): δ = 20.32.

	Entire	Cation	Anion
Mass calculated	470.49	229.30	241.20

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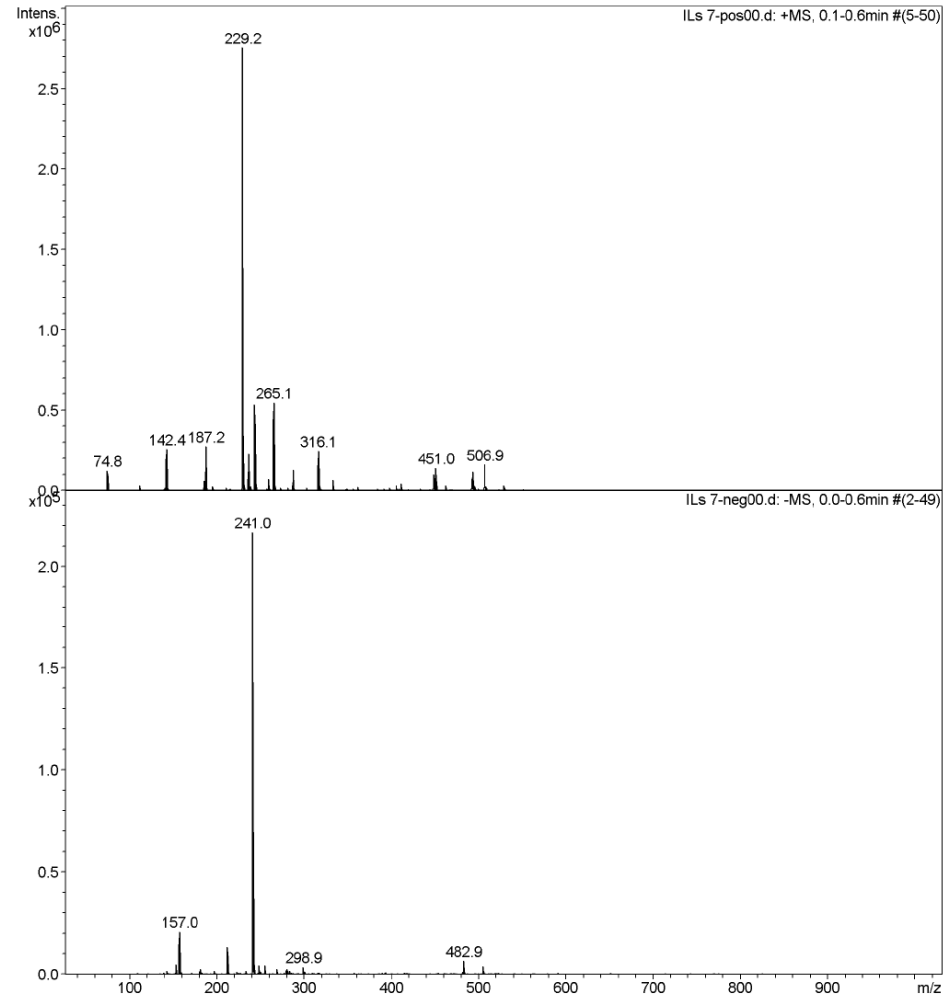
Analysis Info

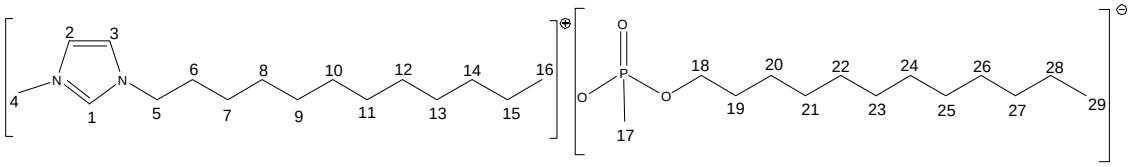
Analysis Name	D:\Data\Jing Li\2011-07-08 ILs\ILs 7-neg00.d	Acquisition Date	08/07/2011 13:02:12
Method	DEF_MS.M	Operator	Jing Li
Sample Name	ILs	Instrument	esquire6000
Comment	C19H39N2O9P 1,58E-05M in ethalnol		

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	50 m/z	Scan End	1000 m/z
Capillary Exit	-106.0 Volt	Skimmer	-40.0 Volt	Trap Drive	36.7
Accumulation Time	500 µs	Averages	7 Spectra	ICC Actual	834
Compound Stability	100 %	Target Mass	200 m/z	Trap Drive Level	100 %



[DodMIM][Dod(Me)PO$_3$] (8)



^{1}H-NMR (DMSO-d$_6$, 400 MHz, ppm): δ = 0.83 – 0.89 (m, 9H, 16-H, 17-H and 29-H), 1.23 (m, 36H, 7-15-H and 20-28-H), 1.43 (m, 2H, 6-H), 1.77 (m, 2H, 19-H), 3.56 (q, 2H, J = 0.66 Hz, 5-H), 3.86 (s, 3H, 4-H), 4.15 (t, 2H, J = 0.70 Hz, 18-H), 7.71 (s, 1H, 2-H), 7.78 (s, 1H, 3-H), 9.41 (s, 1H, 1-H).

^{13}C-NMR (DMSO-d$_6$, 100.4 MHz, ppm): δ = 13.00 (d, J = 13.23 Hz, C-17), 13.69 (2C, C-16 and C-29), 22.00 (2C, C-15 and C-28), 25.42 – 31.22 (m, 18C, C-6 – C-14 and C-19 – C-27), 35.43 C-4, 48.72 C-5, 62.80 C-18, 121.96 C-3, 123.27 C-2, 137.57 C-1.

^{31}P-NMR (DMSO-d$_6$, 162 MHz, ppm): δ = 16.97.

	Entire	Cation	Anion
Mass calculated	514.76	251.43	263.33

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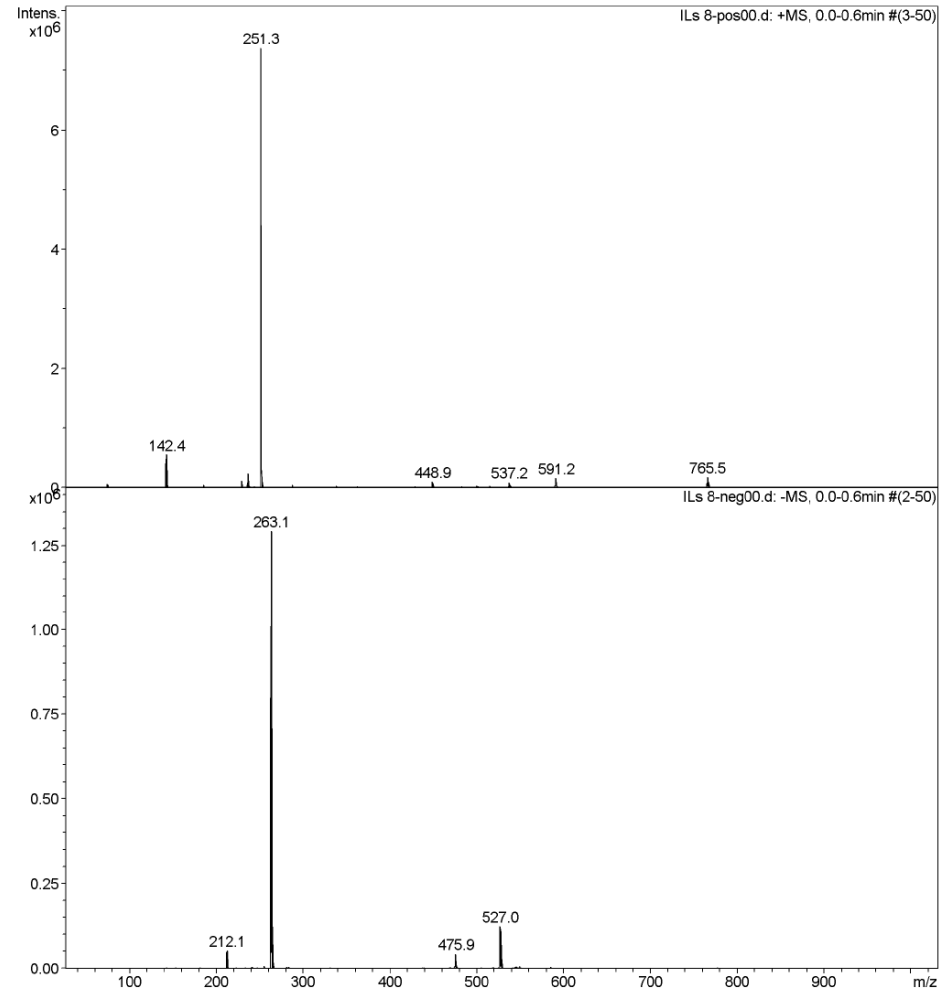
Analysis Info

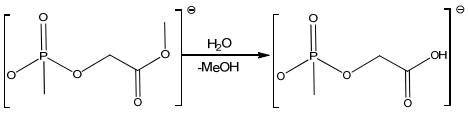
Analysis Name	D:\Data\Jing Li\2011-07-08 ILs\ILs 8-neg00.d	Acquisition Date	08/07/2011 13:16:38
Method	DEF_MS.M		
Sample Name	ILs	Operator	Jing Li
Comment	C29H59N2O3P 8,31E-06M in ethalnol	Instrument	esquire6000

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	50 m/z	Scan End	1000 m/z
Capillary Exit	-106.0 Volt	Skimmer	-40.0 Volt	Trap Drive	36.7
Accumulation Time	500 µs	Averages	7 Spectra	ICC Actual	4488
Compound Stability	100 %	Target Mass	200 m/z	Trap Drive Level	100 %



Hydrolysis of the [MeAc(Me)PO_3] ion



Scheme S1:

The signal for the methyl group at 3.56 ppm in the ^{1}H-NMR spectrum disappeared upon refluxing in water and the signal for phosphorous shifted upfield from 19 to 25 ppm. However, this step may be regarded as further functionalization possibility. The free carboxylic acid group is now disposable for coupling reactions like esterification or amidation or may be deprotonated to provide a dianion.

SI References

[S1] E. Kuhlmann, S. Himmler, H. Giebelhaus, and P. Wasserscheid, *Green Chem.,* 2007, **9**, 233.