Supporting Information

Surface tension measurements for seven imidazolium based dialkylphosphate ionic liquids and their binary mixtures with water (methanol or ethanol) at 298.15 K and 1 atm

Nan-nan Ren[†,‡], Yin-hui Gong[†,‡], Ying-zhou Lu[‡], Hong Meng[‡], Chun-xi Li[*,†,‡]

[†] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China,[‡] College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

[*] To whom correspondence should be addressed. E-mail: Licx@mail.buct.edu.cn, Tel. & Fax: +86 10 64410308.

[†] State Key Lab of Chemical Resource Engineering.

[‡] College of Chemical Engineering.

1. Experimental

1.1 *NMR analysis of ILs*

^{1}H and ^{13}C NMR spectra were performed in order to characterize the structure and confirm the purity of the ILs, namely 1,3-dimethylimidazolium dimethylphosphate ([MMIM][DMP]), 1-ethyl-3-methylimidazolium dimethylphosphate ([EMIM][DMP]), 1-n-butyl-3-methylimidazolium dimethylphosphate ([BMIM][DMP]), 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]), 1,3-diethylimidazolium diethylphosphate ([EEIM][DEP]), 1-n-butyl-3-ethylimidazolium diethylphosphate ([BEIM][DEP]), and 1-n-butyl-3-methylimidazolium dibutylphosphate ([BMIM][DBP]).

The ^{1}H and ^{13}C NMR spectra were measured on an AV400 MHz spectrometer, using deuterated water (D_2O) as the external reference solvent at T = 300 K. Chemical shifts (δ) were reported in parts per million (ppm).

1.2 *Water content determination*

Water content was measured by the Karl Fisher titrator (type CBS-1A) for the above ILs, namely [MMIM][DMP], [EMIM][DMP], [BMIM][DMP], [EMIM][DEP], [EEIM][DEP], [BEIM][DEP], and [BMIM][DBP].

2. Results and Discussion

2.1 *NMR analysis of ILs*

The structures of the ILs were identified and no impurities were observed according to ^{1}H NMR and ^{13}C NMR spectra which are presented in Figs. S1–S7 and Figs. S8–S14, respectively.

The purity of ILs can be quantitatively determined according to the ^{1}H NMR spectrum by the area normalization method, using the hydrogen numbers of IL divide the total hydrogen numbers.

For example (see **Fig. S2**), the purity of [EMIM][DMP] is, 100×(1.00 + 0.97 + 0.95 + 2.39 + 3.50 + 6.62 + 3.46)/(1.00 + 0.97 + 0.95 + 2.39 + 3.50 + 6.62 + 3.46 + 0.17) = 99.1%, which can also be qualitatively confirmed by the ^{13}C NMR spectrum (see **Fig. S9**). It is obvious that no residual peaks of impurities are detected. Therefore, the purity determined by the NMR spectra actually represents the mole fraction of [EMIM][DMP], namely, $x \geq 99.1\%$.

The purity of the remaining ILs can be determined by the same method described above as well and the results are shown in **Tab. S1** below.

Tab. S1. The purity of phosphate ionic liquids investigated

ILs	Purity (x%)
[MMIM][DMP]	99.7
[EMIM][DMP]	99.1
[BMIM][DMP]	99.9
[EMIM][DEP]	99.8
[EEIM][DEP]	99.7
[BEIM][DEP]	99.9
[BMIM][DBP]	99.8

Figure Captions

Fig. S1. The chemical shifts of ^{1}H NMR spectra of [MMIM][DMP] with D_2O as the external reference solvent are recorded as follows: δ_H = 3.47 (6H，d，P(OCH_3)$_2$)，3.80 (6H，s，H_3CNCHNCH_3)， 7.32 (2H，m，NCHCHN)，8.55 (1H，s，NCHN). (δ_H = 4.70, residual peak of D_2O)

Fig. S2. The chemical shifts of ^{1}H NMR spectra of [EMIM][DMP] with D_2O as the external reference solvent are recorded as follows: δ_H = 1.42 (3H，t，NCH$_2$CH_3)，3.48 (6H，d，P(OCH_3)$_2$)，3.81 (3H，s，NCH_3)，4.14 (2H，q，NCH_2CH$_3$)，7.34 (1H，s，NCHCHN)，7.41 (1H，s，NCHCHN)，8.63 (1H，s，NCHN). (δ_H = 4.70, residual peak of D_2O)

Fig. S3. The chemical shifts of ^{1}H NMR spectra of [BMIM][DMP] with D_2O as the external reference solvent are recorded as follows: δ_H = 0.84 (3H，t，NCH$_2$CH$_2$CH$_2$CH_3)，1.23 (2H，sex，NCH$_2$CH$_2$CH_2CH$_3$)，1.75 (2H，p，NCH$_2$CH_2CH$_2$CH$_3$)，3.49 (6H，d，P(OCH_3)$_2$)， 3.81 (3H，s，NCH_3)，4.12 (2H，t，NCH_2CH$_2$CH$_2$CH$_3$)，7.35 (1H，s，NCHCHN)，7.40 (1H，s，NCHCHN)，8.63 (1H，s，NCHN). (δ_H = 4.70, residual peak of D_2O)

Fig. S4. The chemical shifts of ^{1}H NMR spectra of [EMIM][DEP] with D_2O as the external reference solvent are recorded as follows: δ_H = 1.18 (6H，t，(OCH$_2$CH_3)$_2$)，1.42 (3H，t，NCH$_2$CH_3)，3.81 (4H，m，(P(OCH$_2$CH$_3$)$_2$)，3.85 (3H，s，NCH_3)，4.16 (2H，m，NCH_2CH$_3$)，7.34 (1H，s，NCHCHN)，7.41 (1H，s，NCHCHN)，8.63 (1H，s，NCHN). (δ_H = 4.70, residual peak of D_2O)

Fig. S5. The chemical shifts of ^{1}H NMR spectra of [EEIM][DEP] with D_2O as the external reference solvent are recorded as follows: δ_H = 1.17 (6H，t，P(OCH$_2$CH_3)$_2$)，1.42 (6H，t，CH_3CH$_2$NCHNCH$_2$CH_3)，4.14 (4H，p，P(OCH$_2$CH$_3$)$_2$)，4.15 (4H，q，CH$_3$CH_2NCHNCH_2CH$_3$)，7.42 (2H，s，NCHCHN)，8.69 (1H，s，NCHN). (δ_H = 4.70, residual peak of D_2O)

Fig. S6. The chemical shifts of ^{1}H NMR spectra of [BEIM][DEP] with D_2O as the external

reference solvent are recorded as follows: δ_H = 0.82 (3H，t，$NCH_2CH_2CH_2CH_3$)，1.15 (6H，t，$P(OCH_2CH_3)_2$)，1.23 (2H，m，$NCH_2CH_2CH_2CH_3$)，1.41 (3H，t，NCH_2CH_3)，1.75 (2H，m，$NCH_2CH_2CH_2CH_3$)，3.82 (4H，m，$P(OCH_2CH_3)_2$)，4.10 (4H，m，$CH_3CH_2NCHNCH_2CH_2CH_2CH_3$)，7.40 (2H，d，NCHCHN)，8.69 (1H，s，NCHN). (δ_H = 4.70, residual peak of D_2O)

Fig. S7. The chemical shifts of ^1H NMR spectra of [BMIM][DBP] with D_2O as the external reference solvent are recorded as follows: δ_H = 0.85 (9H，m，$NCH_2CH_2CH_2CH_3$，$P(OCH_2CH_2CH_2CH_3)_2$)，1.74 (2H，p，$NCH_2CH_2CH_2CH_3$)，3.78 (4H，q，$P(OCH_2CH_2CH_2CH_3)_2$)，3.82 (3H，s，NCH_3)，4.11 (2H，t，$CH_3CH_2CH_2CH_2N$)，7.36 (1H，s，NCHCHN)，7.41 (1H，s，NCHCHN)，8.64 (1H，s，NCHN). (δ_H = 4.70, residual peak of D_2O)

Fig. S8. The chemical shifts of ^{13}C NMR spectrum of [MMIM][DMP] with D_2O as the external reference solvent are recorded as follows: δ_C = 35.56 ($H_3CNCHNCH_3$)，52.69 ($P(OCH_3)_2$)，123.37 (NCHCHN)，136.51 (NCHN).

Fig. S9. The chemical shifts of ^{13}C NMR spectrum of [EMIM][DMP] with D_2O as the external reference solvent are recorded as follows: δ_C = 91.35 (NCH_2CH_3)，97.47 (NCH_3)，100.13 (NCH_2CH_3)，102.46 ($P(OCH_3)_2$)，122.48 (NCHCHN)，122.94 (NCHCHN)，126.45 (NCHN).

Fig. S10. The chemical shifts of ^{13}C NMR spectrum of [BMIM][DMP] with D_2O as the external reference solvent are recorded as follows: δ_C = 12.58 ($NCH_2CH_2CH_2CH_3$)，18.71 ($NCH_2CH_2CH_2CH_3$)，31.23 ($NCH_2CH_2CH_2CH_3$)，35.58 (NCH_3)，49.25 ($NCH_2CH_2CH_2CH_3$)，52.72 ($P(OCH_3)_2$)，122.20 (NCHCHN)，123.46 (NCHCHN)，135.82 (NCHN).

Fig. S11. The chemical shifts of ^{13}C NMR spectrum of [EMIM][DEP] with D_2O as the external reference solvent are recorded as follows: δ_C = 14.45 (NCH_2CH_3)，15.62 ($P(OCH_2CH_3)_2$)，35.55 (NCH_3)，44.73 (NCH_2CH_3)，62.14 ($P(OCH_2CH_3)_2$)，121.85 (NCHCHN)，123.43 (NCHCHN)，135.52 (NCHN).

Fig. S12. The chemical shifts of ^{13}C NMR spectrum of [EEIM][DEP] with D_2O as the external reference solvent are recorded as follows: δ_C = 14.43 (NCH_2CH_3)，15.57 ($P(OCH_2CH_3)_2$)，44.75 (NCH_2CH_3)，62.16 ($P(OCH_2CH_3)_2$)，121.93 (NCHCHN)，134.49 (NCHN).

Fig. S13. The chemical shifts of ^{13}C NMR spectrum of [BEIM][DEP] with D_2O as the external reference solvent are recorded as follows: δ_C = 12.58 ($NCH_2CH_2CH_2CH_3$)，14.41 (NCH_2CH_3)，15.55 ($P(OCH_2CH_3)_2$)，18.73 ($NCH_2CH_2CH_2CH_3$)，31.21 ($NCH_2CH_2CH_2CH_3$)，44.75

(NCH_2CH_3)，49.26 ($NCH_2CH_2CH_2CH_3$)，62.17 ($P(OCH_2CH_3)_2$)，121.93 (NCHCHN)， 122.26 (NCHCHN)，134.76 (NCHN).

Fig. S14. The chemical shifts of ^{13}C NMR spectrum of [BMIM][DBP] with D_2O as the external reference solvent are recorded as follows: δ_C = 12.59 ($NCH_2CH_2CH_2CH_3$)， 12.99 ($P(OCH_2CH_2CH_2CH_3)_2$)，18.35 ($NCH_2CH_2CH_2CH_3$)，18.71 ($P(OCH_2CH_2CH_2CH_3)_2$)， 31.24 ($NCH_2CH_2CH_2CH_3$) ， 31.99 ($P(OCH_2CH_2CH_2CH_3)_2$) ， 35.58 (NCH_3) ， 49.25 ($NCH_2CH_2CH_2CH_3$)，65.98 ($P(OCH_2CH_2CH_2CH_3)_2$)，122.21 (NCHCHN)，123.47 (NCHCHN)，135.81 (NCHN).

Legends

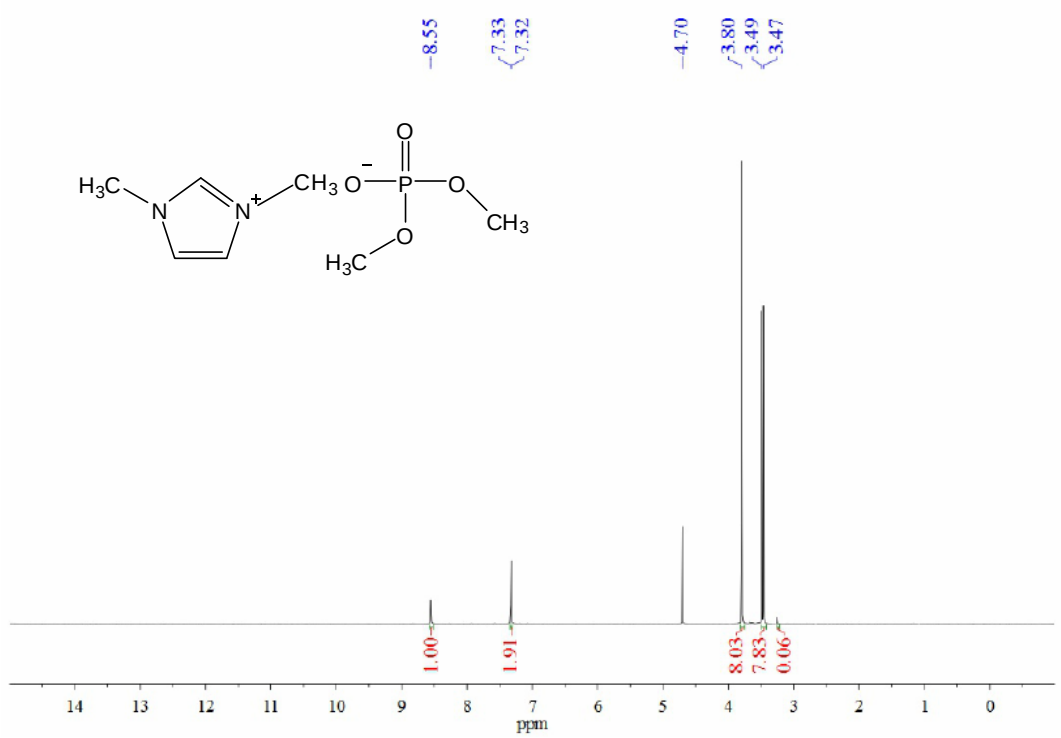

Fig. S1

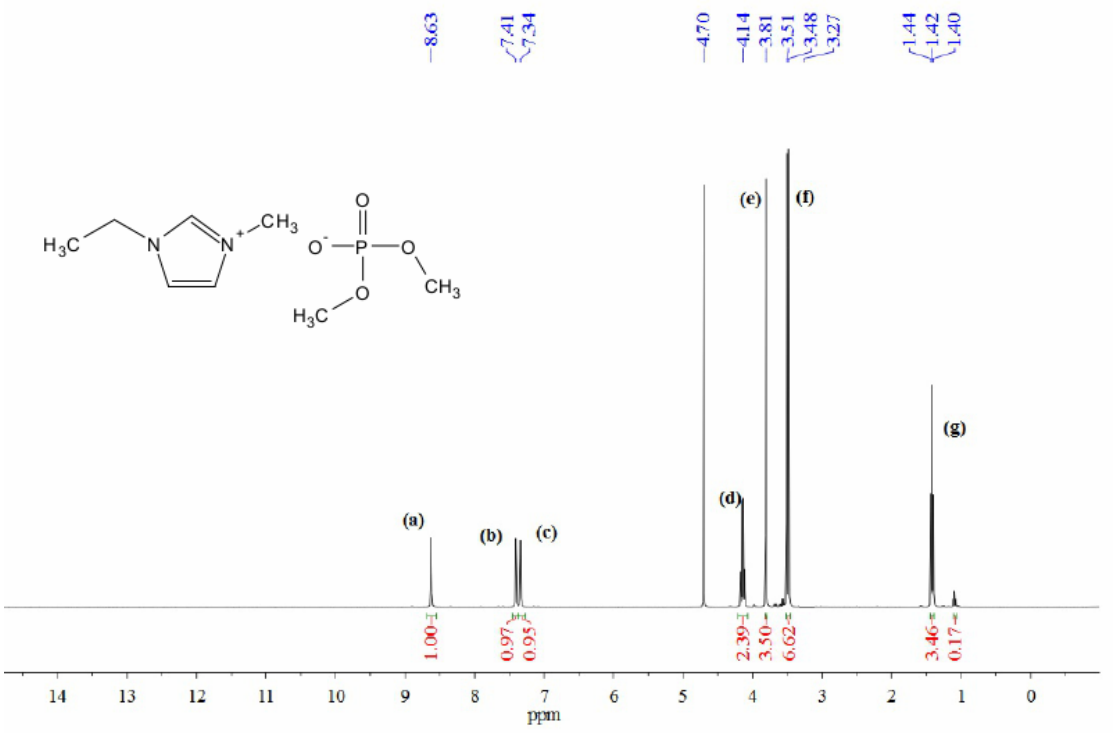
8.63
7.41
7.34
4.70
4.14
3.81
3.51
3.48
3.27
1.44
1.42
1.40
(a)
(b)
(c)
(d)
(e)
(f)
(g)
1.00
0.97
0.95
2.39
3.50
6.62
3.46
0.17
ppm

Fig. S2

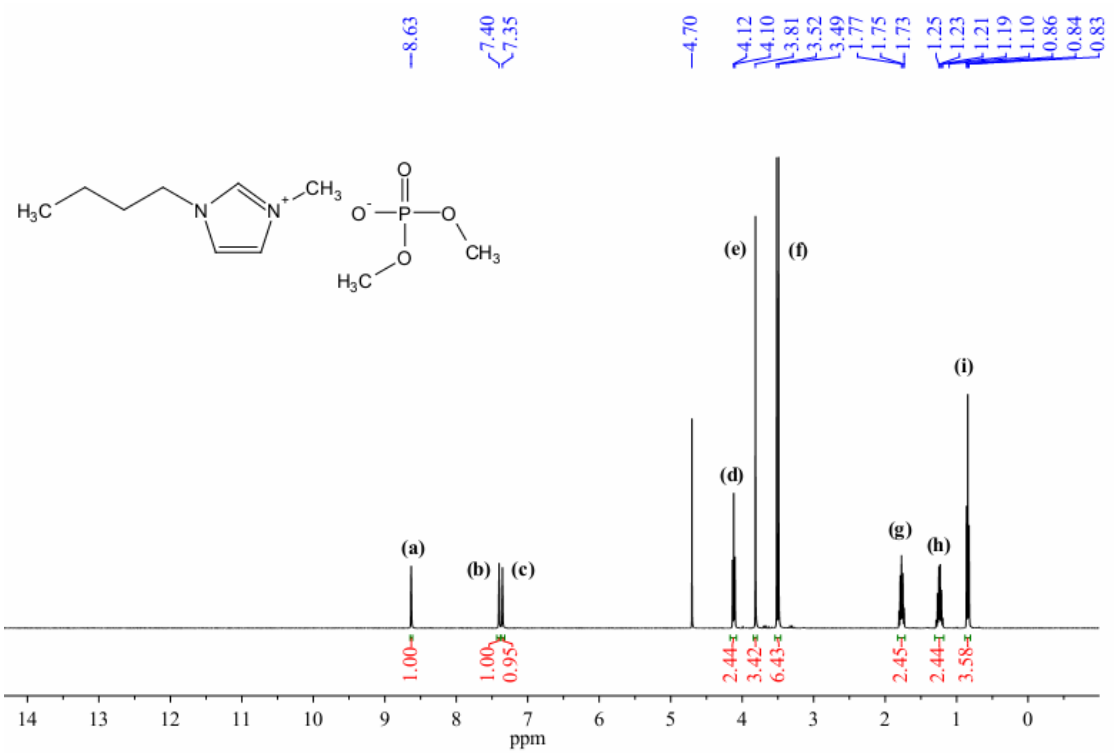
8.63
7.40
7.35
4.70
4.12
4.10
3.81
3.52
3.49
1.77
1.75
1.73
1.25
1.23
1.21
1.19
1.10
0.86
0.84
0.83
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
1.00
1.00
0.95
2.44
3.42
6.43
2.45
2.44
3.58
ppm

Fig. S3

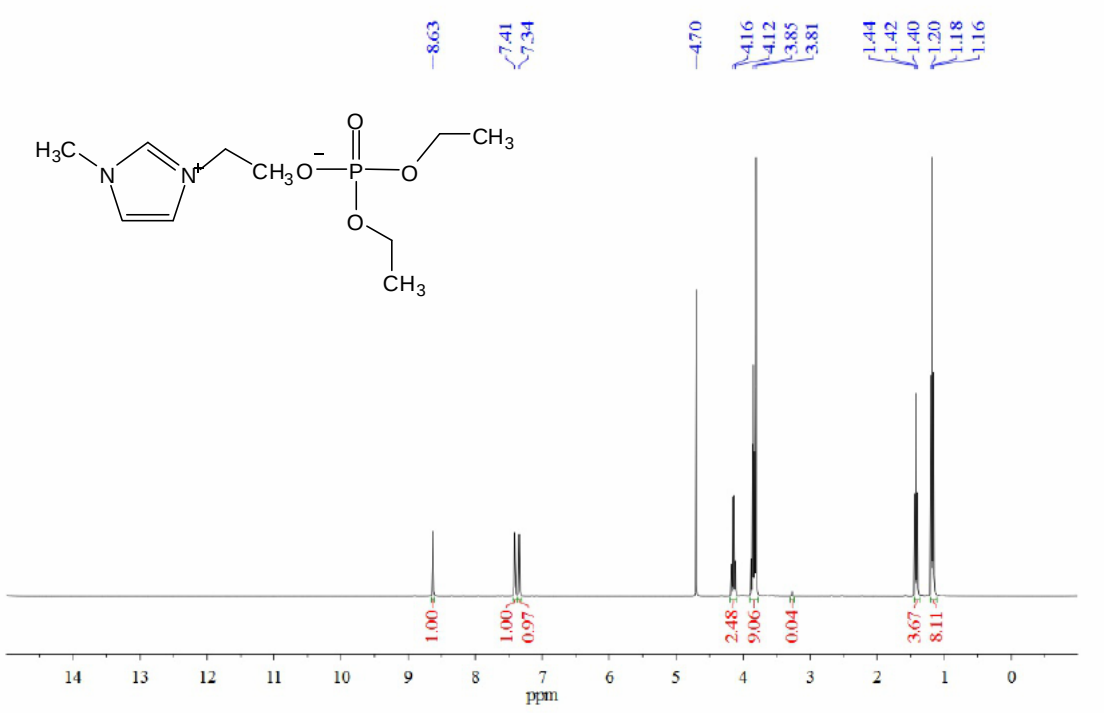
8.63
7.41
7.34
4.70
4.16
4.12
3.85
3.81
1.44
1.42
1.40
1.20
1.18
1.16
H3C
N
N+
CH3O
P
O
CH3
CH3
1.00
1.00
0.97
2.48
9.06
0.04
3.67
8.11
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm

Fig. S4

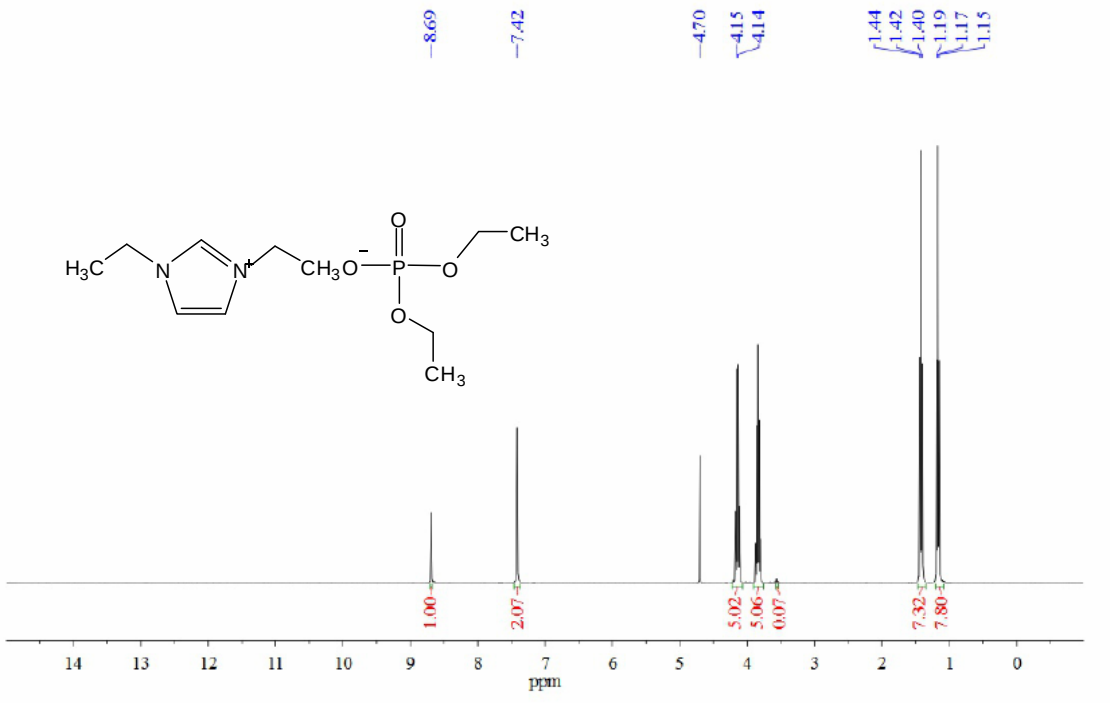
8.69
7.42
4.70
4.15
4.14
1.44
1.42
1.40
1.19
1.17
1.15
1.00
2.07
5.02
5.06
0.07
7.32
7.80
ppm

Fig. S5

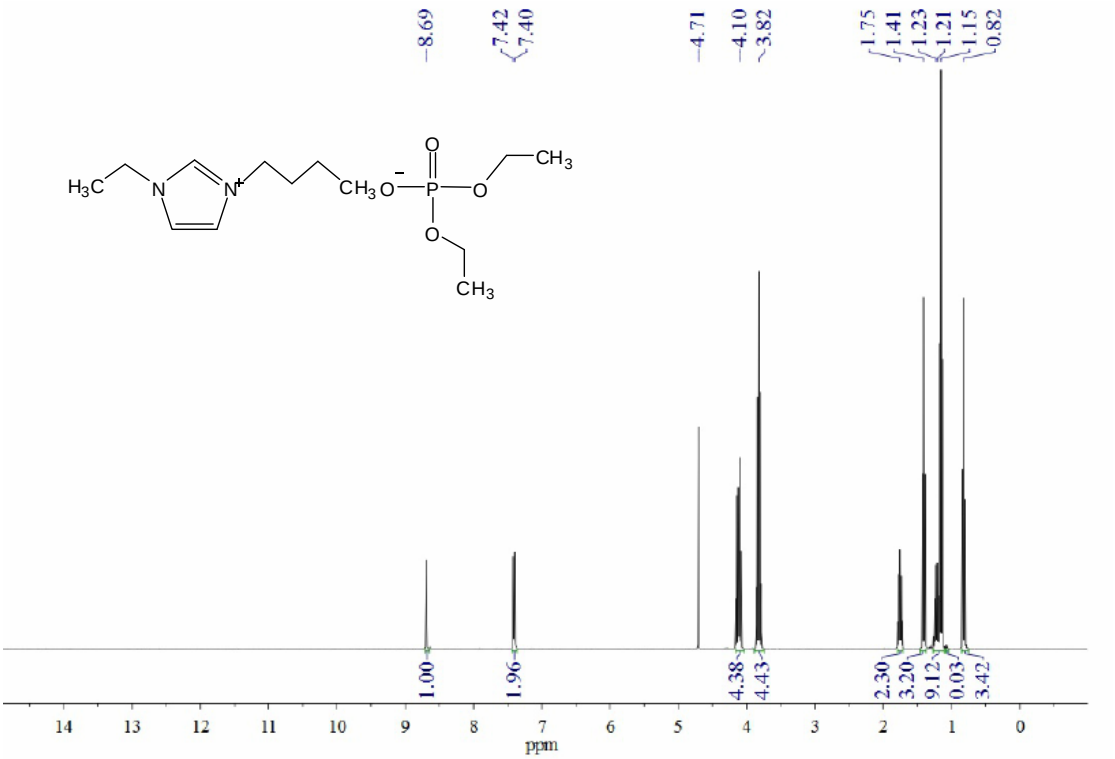
8.69
7.42
7.40
4.71
4.10
3.82
1.75
1.41
1.23
1.21
1.15
0.82
1.00
1.96
4.38
4.43
2.30
3.20
9.12
0.03
3.42
ppm

Fig. S6

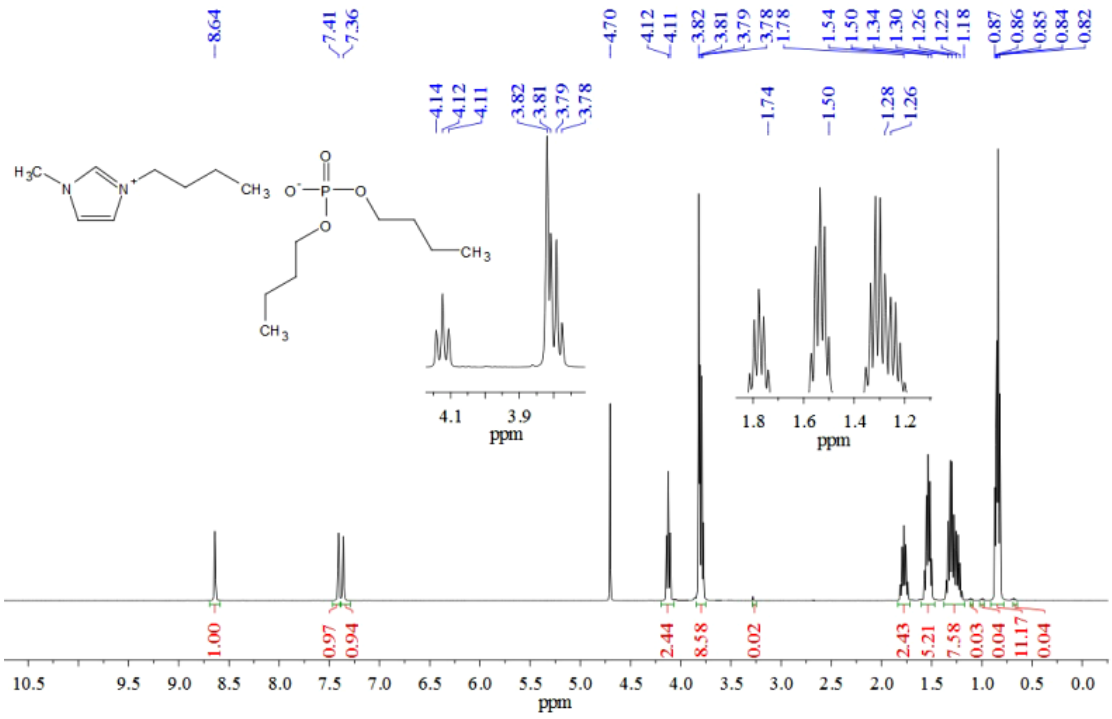
8.64
7.41
7.36
4.70
4.12
4.11
3.82
3.81
3.79
3.78
1.78
1.54
1.50
1.34
1.30
1.26
1.22
1.18
0.87
0.86
0.85
0.84
0.82
4.14
4.12
4.11
3.82
3.81
3.79
3.78
1.74
1.50
1.28
1.26
4.1
3.9
ppm
1.8
1.6
1.4
1.2
ppm
1.00
0.97
0.94
2.44
8.58
0.02
2.43
5.21
7.58
0.03
0.04
11.17
0.04
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Fig. S7

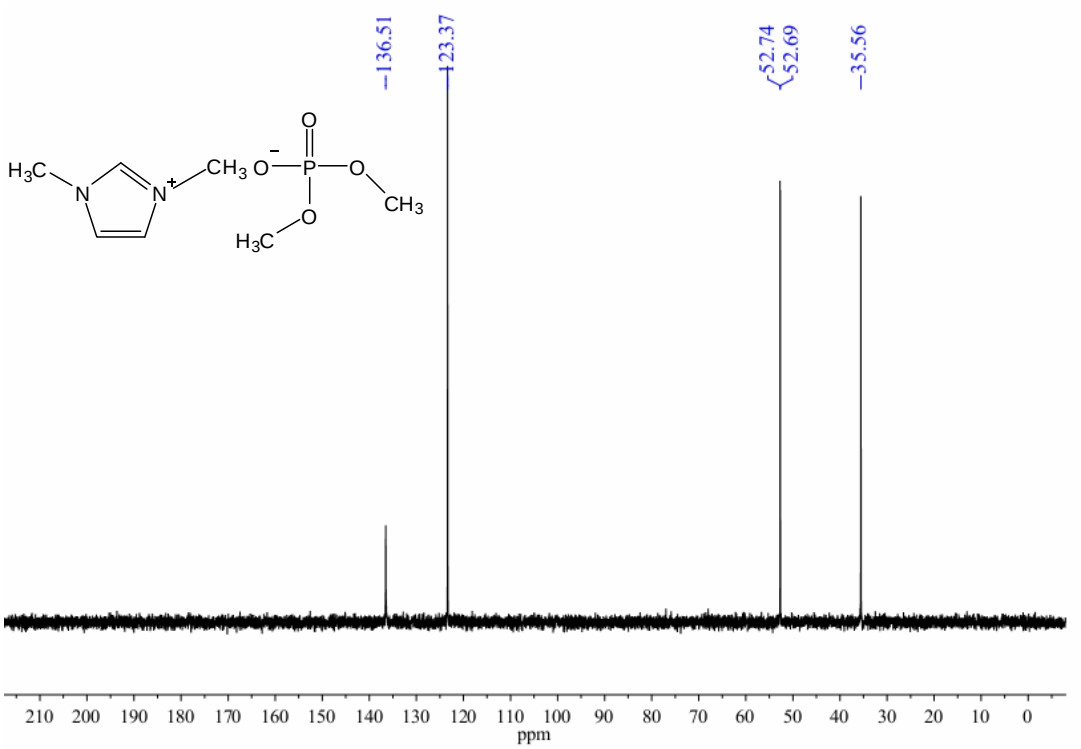
136.51
123.37
52.74
52.69
35.56
H3C
N
N+
CH3
O
P
O
CH3
O
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

Fig. S8

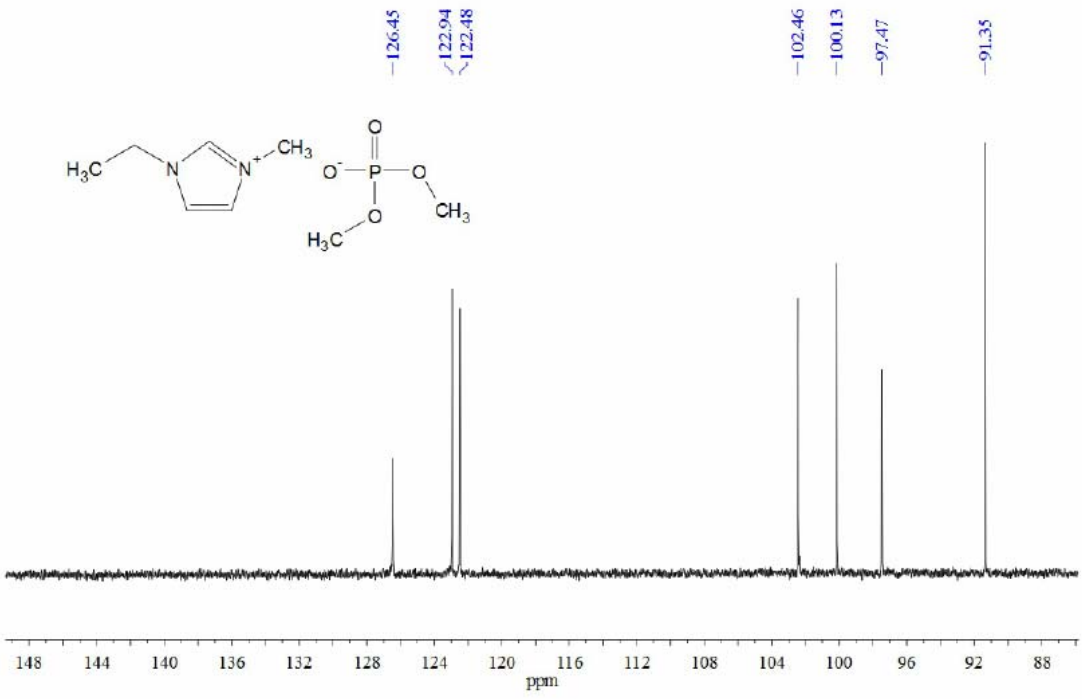
126.45
122.94
122.48
102.46
100.13
97.47
91.35
148
144
140
136
132
128
124
120
116
112
108
104
100
96
92
88
ppm

Fig. S9

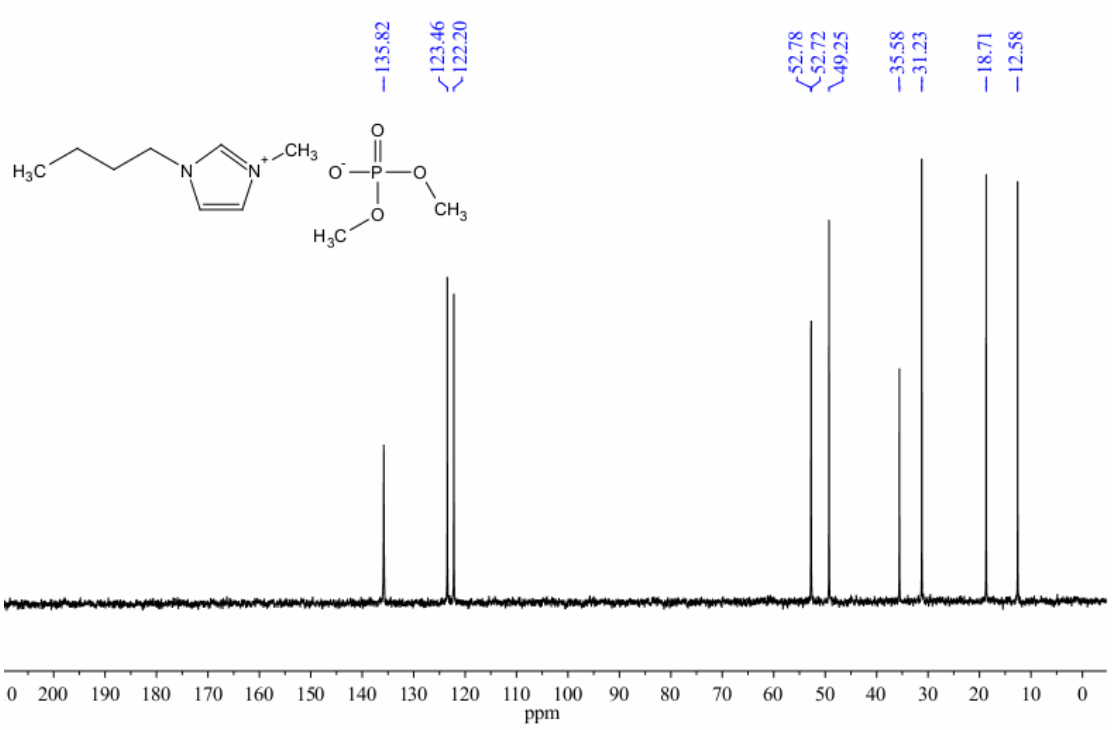
135.82
123.46
122.20
52.78
52.72
49.25
35.58
31.23
18.71
12.58
0 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

Fig. S10

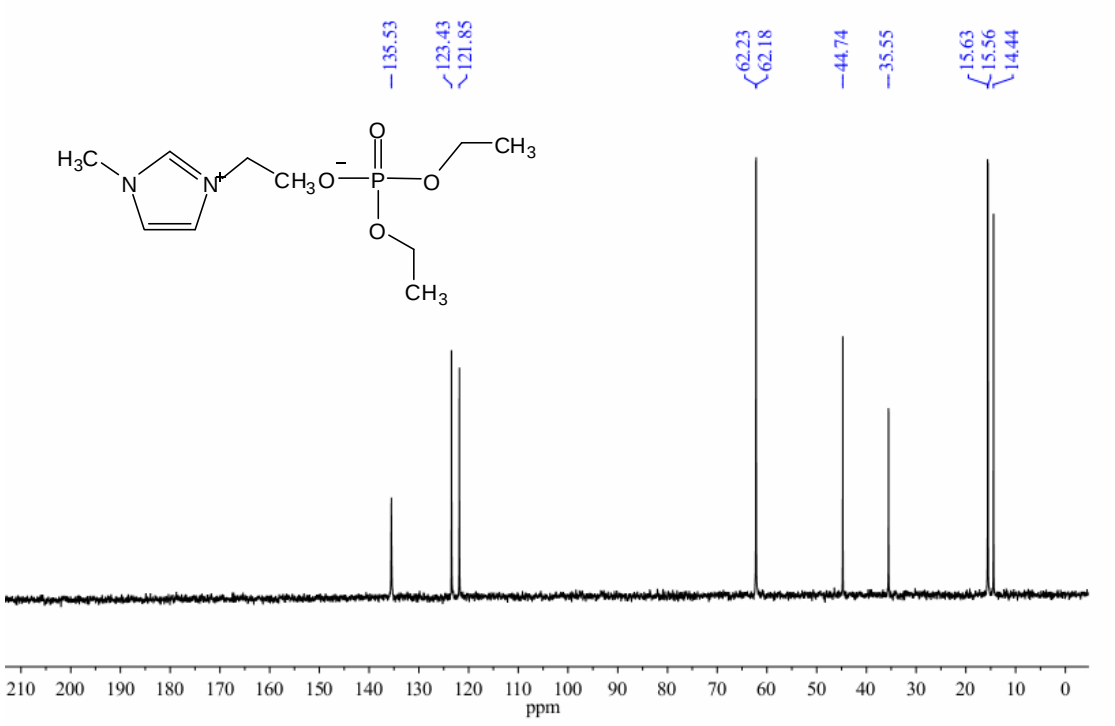
135.53
123.43
121.85
62.23
62.18
44.74
35.55
15.63
15.56
14.44
H3C
N
N+
CH3O
P
O
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

Fig. S11

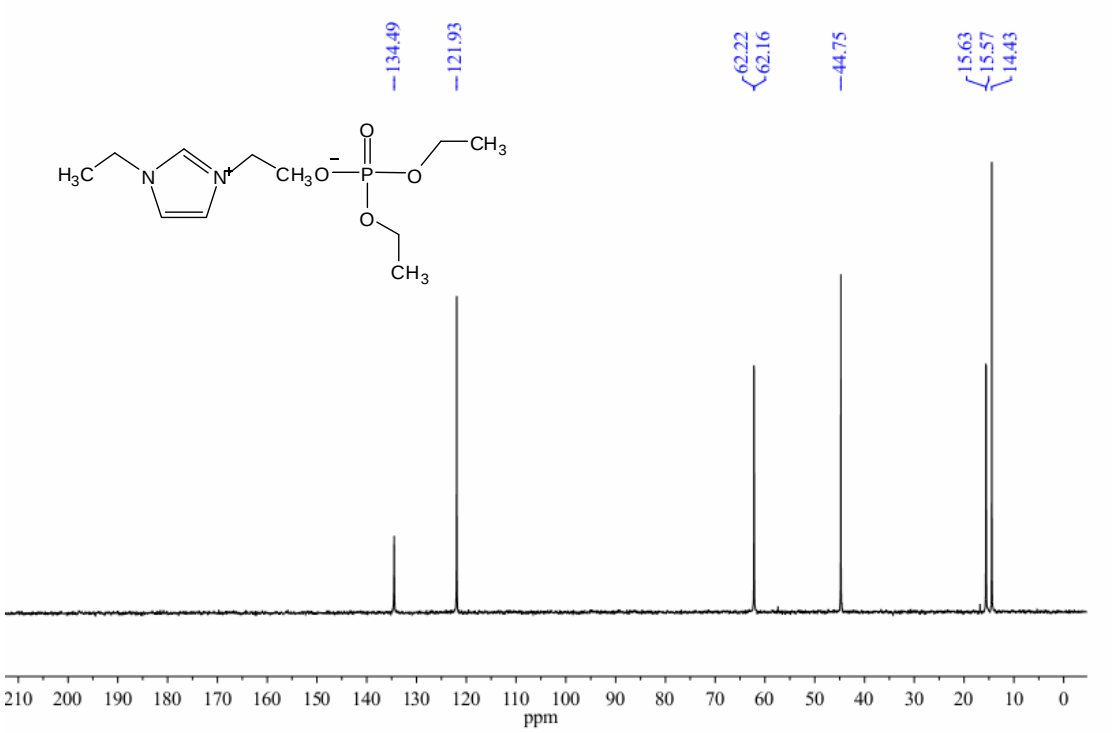
134.49
121.93
62.22
62.16
44.75
15.63
15.57
14.43
H3C
N
N+
CH3O
P
O
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

Fig. S12

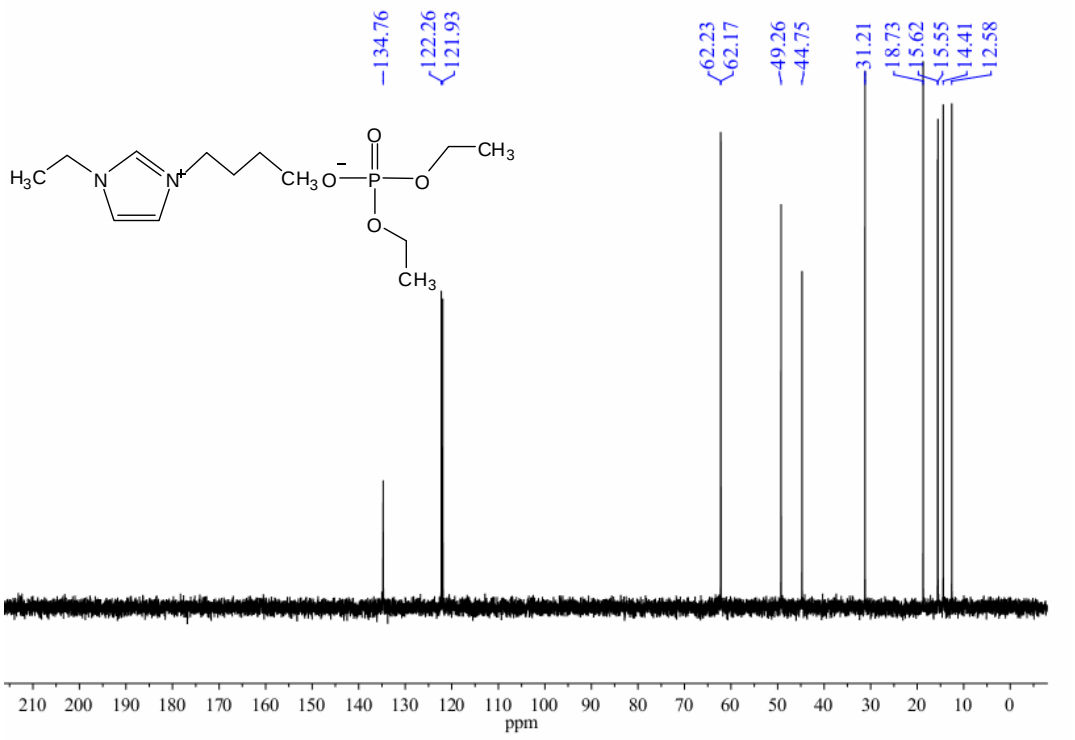
134.76
122.26
121.93
62.23
62.17
49.26
44.75
31.21
18.73
15.62
15.55
14.41
12.58
H3C
N
N+
CH3 O
O
P
O
O
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

Fig. S13

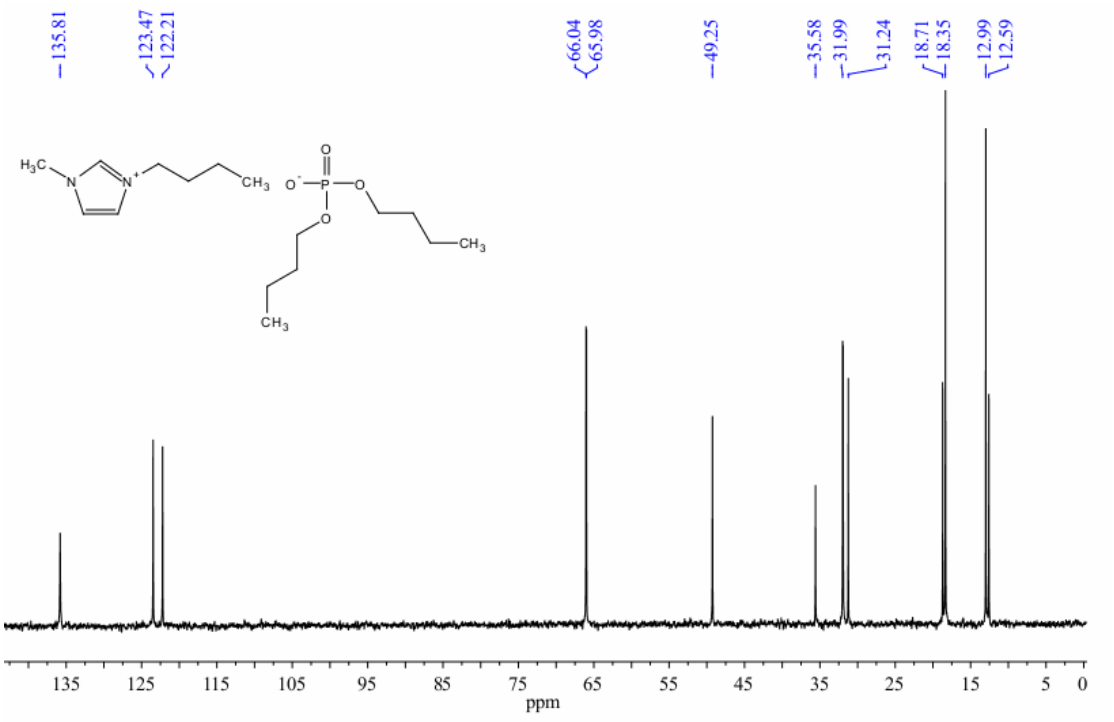
135.81
123.47
122.21
66.04
65.98
49.25
35.58
31.99
31.24
18.71
18.35
12.99
12.59
135
125
115
105
95
85
75
65
55
45
35
25
15
5
0
ppm

Fig. S14

2.2 *Water content determination*

Water content for the ILs is shown in **Tab. S2**.

Tab. S2. Water content of phosphate ionic liquids investigated

ILs	Water content /(ppm)
[MMIM][DMP]	252
[EMIM][DMP]	334
[BMIM][DMP]	206
[EMIM][DEP]	328
[EEIM][DEP]	243
[BEIM][DEP]	281
[BMIM][DBP]	265

From **Tab. S2**, we can see there is trace amounts of water contained in any IL, and the results again indicate that the ILs have high purities.