Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supporting Information

Ionic Liquid Catalyzed Probase Method for One-pot Synthesis of *α, β*-Unsaturated Esters from Esters and Aldehydes at Mild Condition

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Content

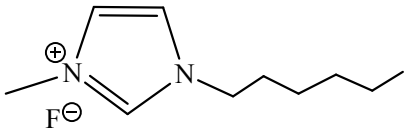
I. Purity of prepared ILs-F

Table S1 Purity of prepared ILs-F

ILs-F	Purity /% [a]	ILs-F	Purity /% [a]
[Hmim]F	99	[Bpy]F	98
[Bmim]F	99	[Opy]F	99
[Emim]F	99	$[PP_{14}]F$	98
[Amim]F	99	$[N_{2226}]F$	99
[Epy]F	98	$[N_{4444}]F$	99

[a] The purity of ILs-F were determined with ^{19}F-NMR and the corresponding spectra were provided in Electronic Supporting Information.

II. NMR information of ILs-F

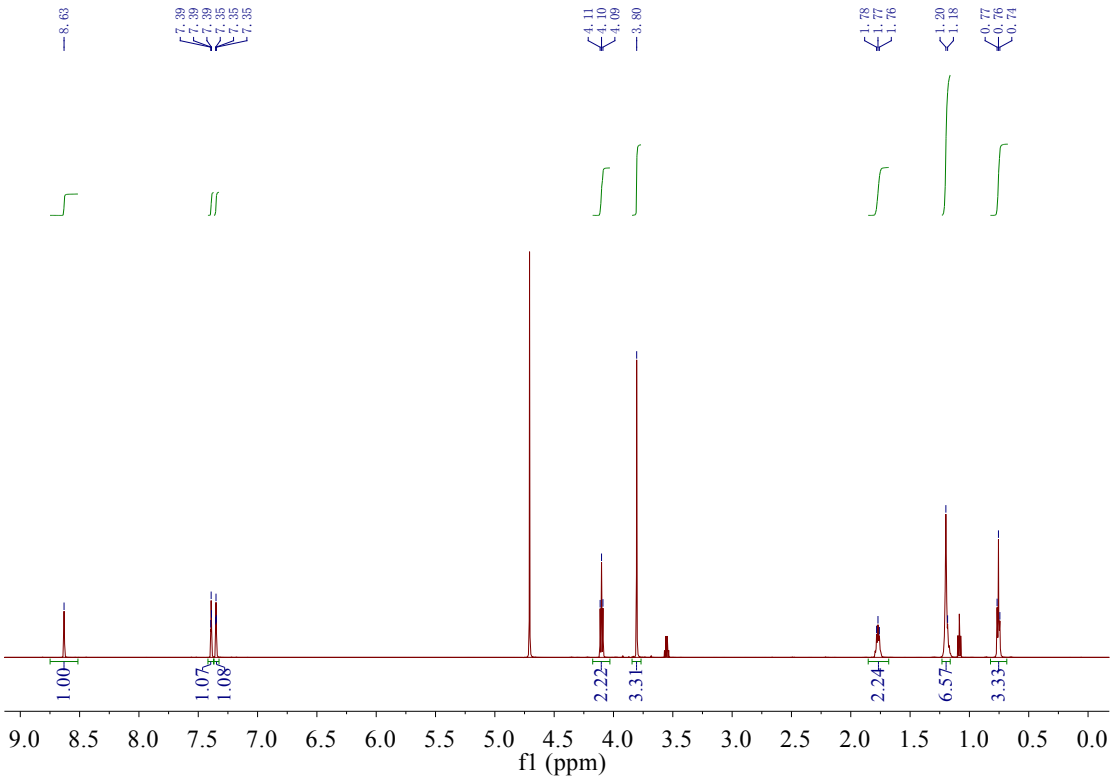


[Hmim]F

^{1}H-NMR: 0.76 ppm (t, J = 7.0 Hz, 3H), 1.25-1.15 ppm (m, 6H), 1.77 ppm (p, J = 7.1 Hz, 2H), 3.80 ppm (s, 3H), 4.10 ppm (t, J = 7.1 Hz, 2H), 7.35 ppm (t, J = 1.7 Hz, 1H), 7.39 ppm (t, J = 1.7 Hz, 1H), δ 8.63 ppm (s, 1H).

^{13}C-NMR: 13.20 ppm (d, J = 5.4 Hz), 16.83 ppm (d, J = 2.3 Hz), 21.73 ppm (s), 24.94 ppm (s), 29.09 ppm (d, J = 8.6 Hz), 30.29 ppm (s), 35.93-35.16 ppm (m), 49.82-49.12 ppm (m), 57.37 (t, J = 3.1 Hz), 122.18 ppm (d, J = 10.2 Hz), 123.47 ppm (d, J = 10.7 Hz), 135.78 ppm (s).

^{19}F-NMR: -122.40 ppm (1F, s)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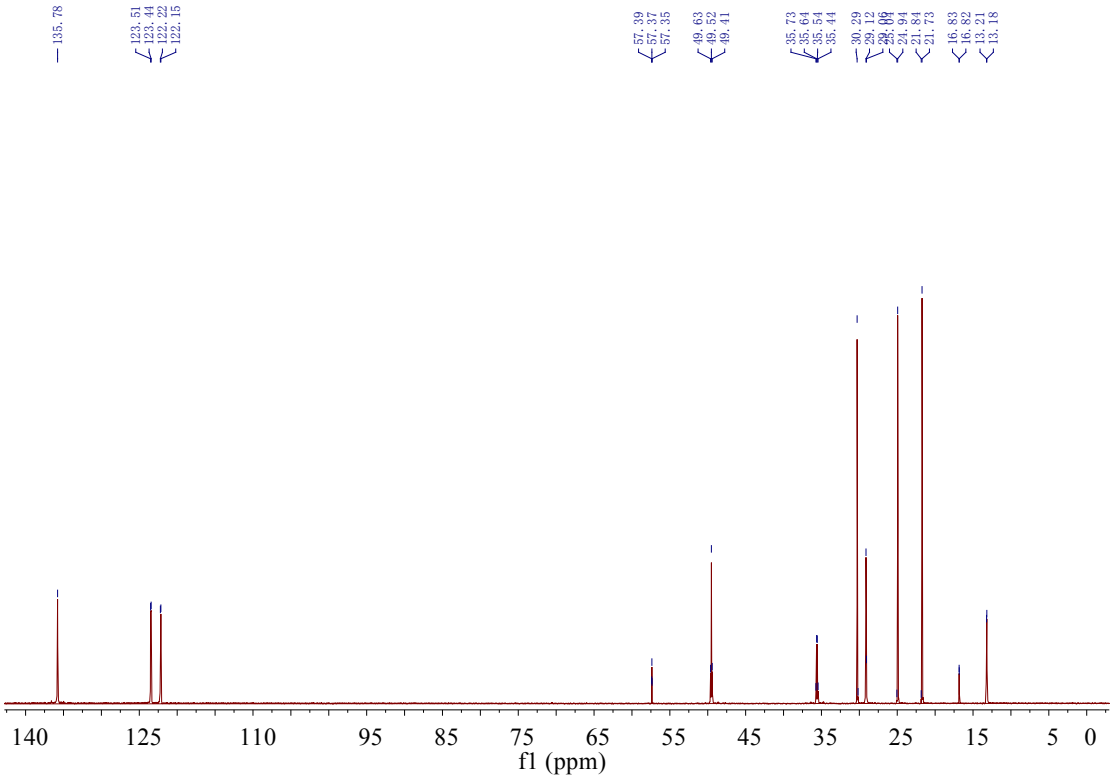
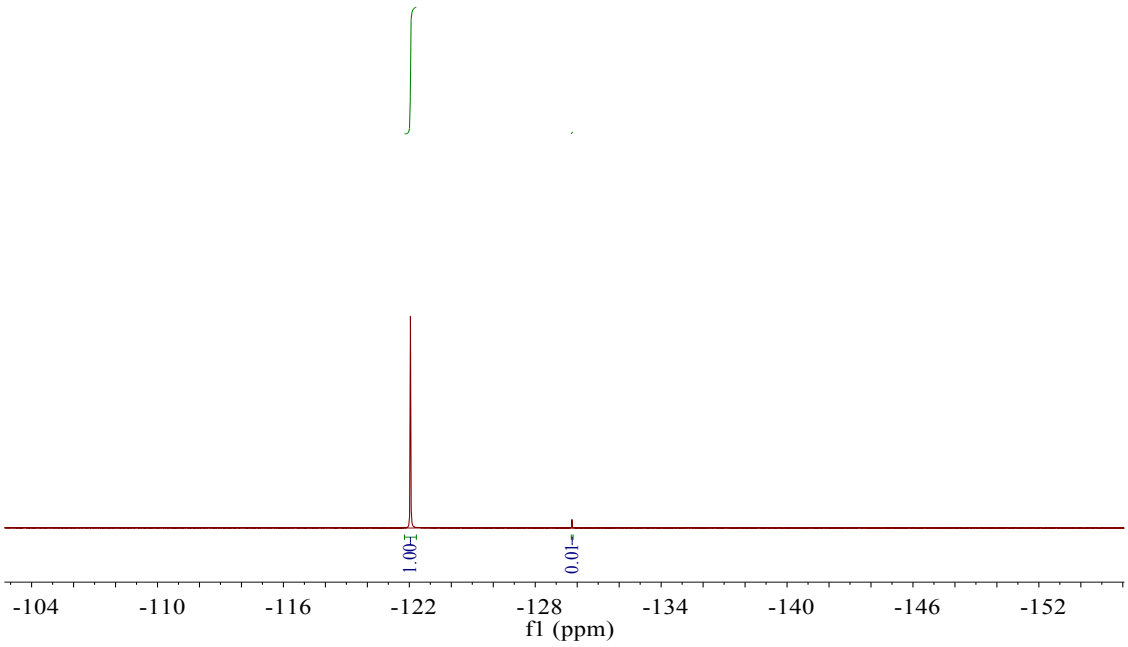
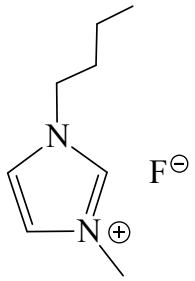
7.39
7.39
7.39
7.35
7.35
7.35
4.11
4.10
4.09
3.80
1.78
1.77
1.76
1.20
1.18
0.77
0.76
0.74
1.00
1.07
1.08
2.22
3.31
2.24
6.57
3.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


135.78
123.51
123.44
122.22
122.15
57.39
57.37
57.35
49.63
49.52
49.41
35.73
35.64
35.54
35.44
30.29
29.12
28.09
24.94
21.84
21.73
16.83
16.82
13.21
13.18
140 125 110 95 85 75 65 55 45 35 25 15 5 0
f1 (ppm)



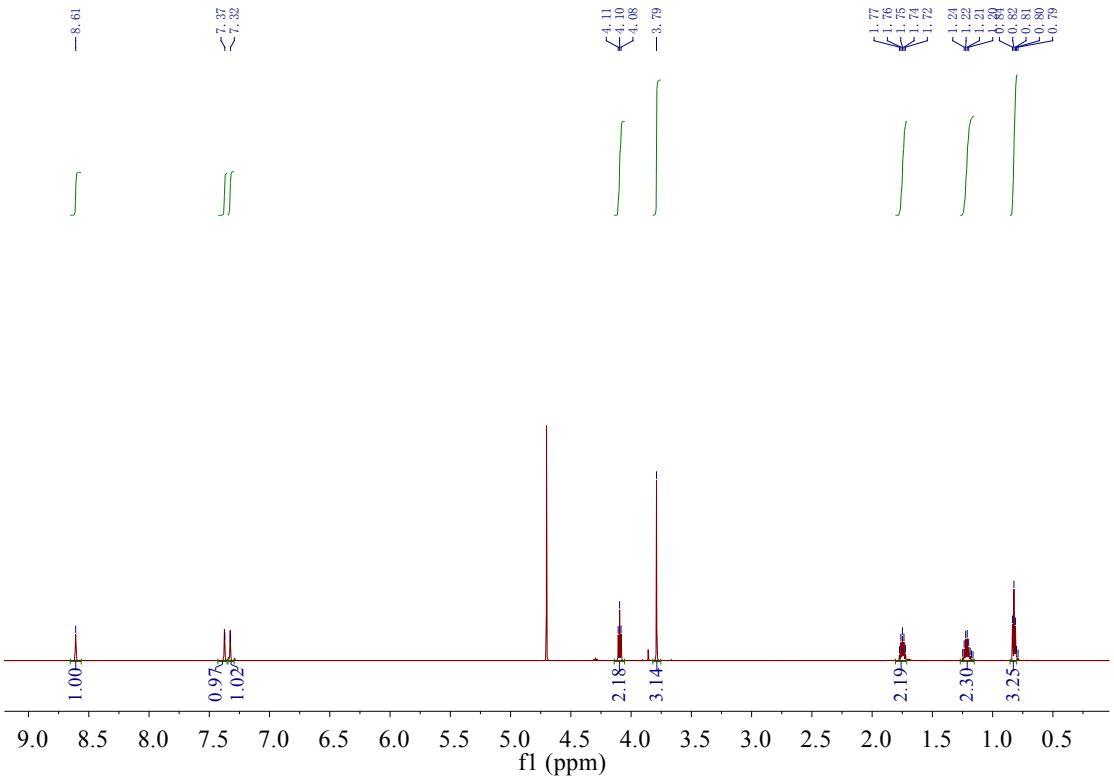


[Bmim]F

^{1}H-NMR: 0.80-0.84 ppm (dd, 3H, *J*=13.9, 6.5 Hz), 1.19-1.25 ppm (m, 2H), 1.72-1.77 ppm (m, 2H), 3.79 ppm (s, 3H), 4.08-4.11 ppm (t, 2H, *J*=7.1 Hz), 7.32 ppm (s, 1H), 7.37 ppm (s, 1H), 8.65 ppm (s, 1H).

^{13}C-NMR: 12.56 ppm (d, *J*=5.6 Hz), 18.68 ppm (d, *J*=9.8 Hz), 31.21 ppm (s), 31.81 ppm (s), 35.54 ppm (s), 36.37 ppm (s), 49.25 ppm (d, *J*=9.7 Hz), 121.70 ppm (s), 122.16 ppm (s), 123.05 ppm (s), 123.41 ppm (s), 135.80 ppm (s).

^{19}F-NMR: -122.46 ppm (1F, s)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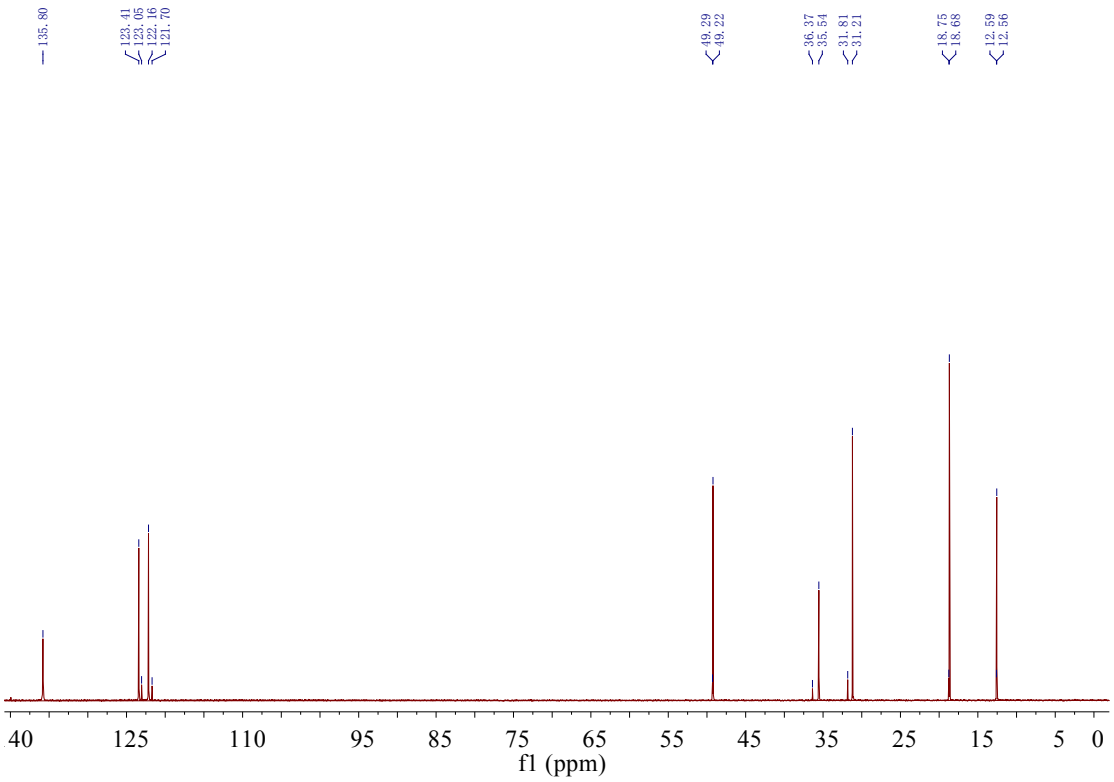
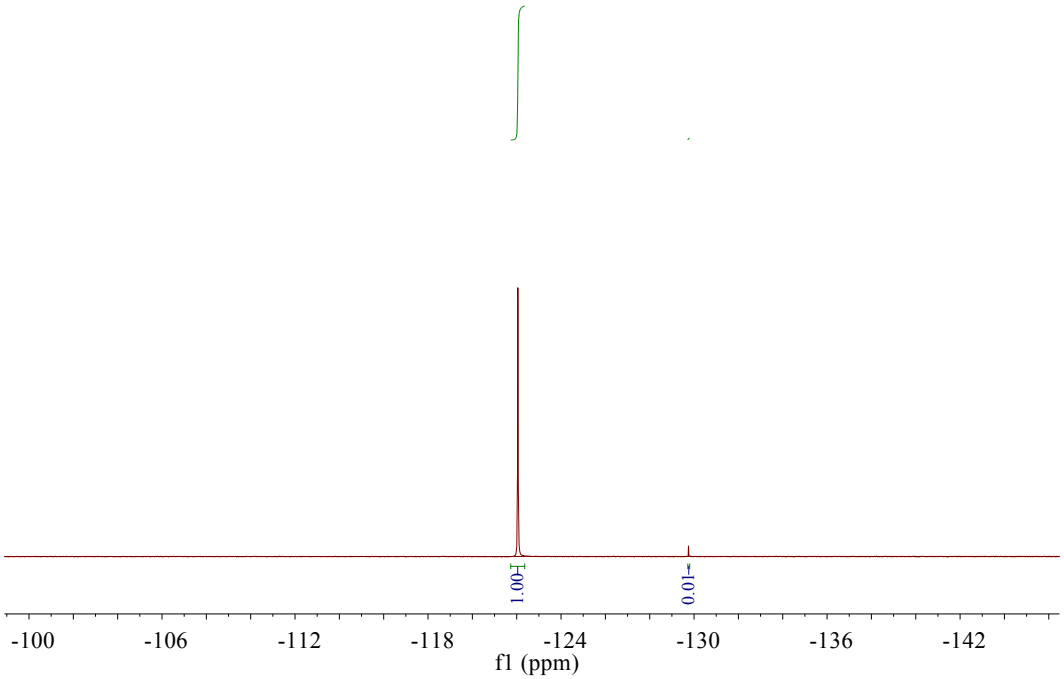
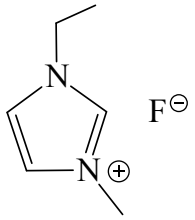
7.32
4.11
4.10
4.08
3.79
1.77
1.76
1.75
1.74
1.72
1.24
1.22
1.21
0.82
0.81
0.80
0.79
1.00
0.97
1.02
2.18
3.14
2.19
2.30
3.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


135.80
123.41
123.05
122.16
121.70
49.29
49.22
36.37
35.54
31.81
31.21
18.75
18.68
12.59
12.56
40 125 110 95 85 75 65 55 45 35 25 15 5 0
f1 (ppm)



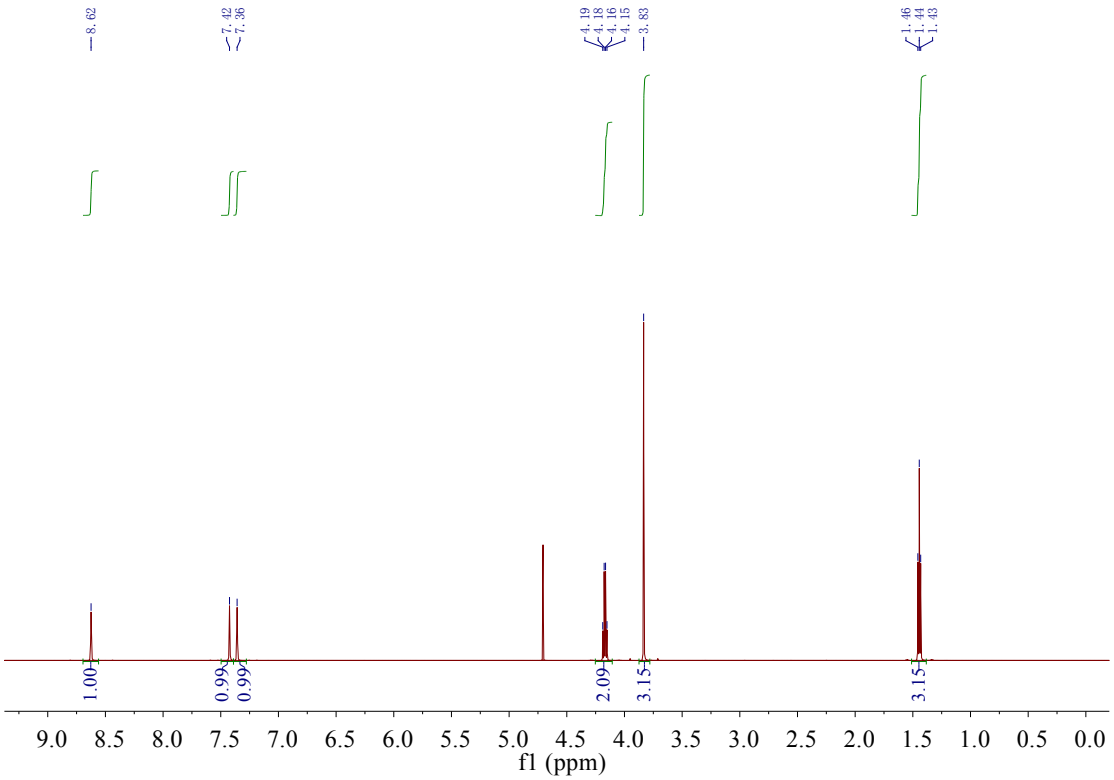


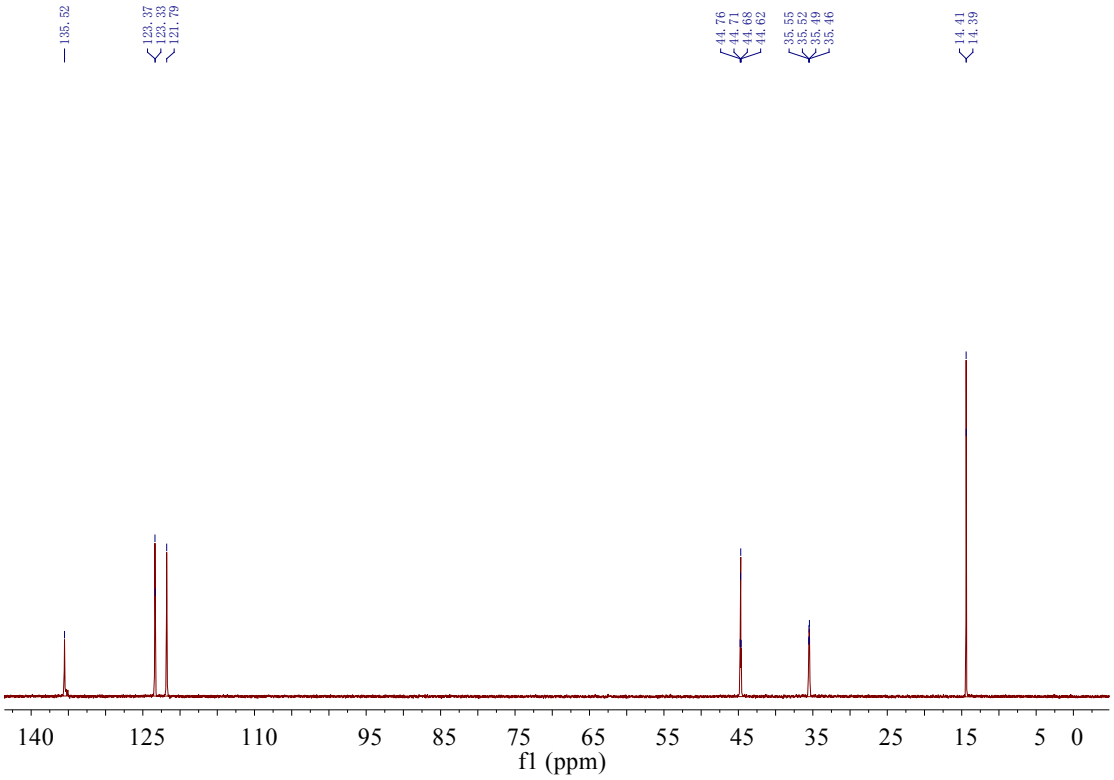
[Emim]F

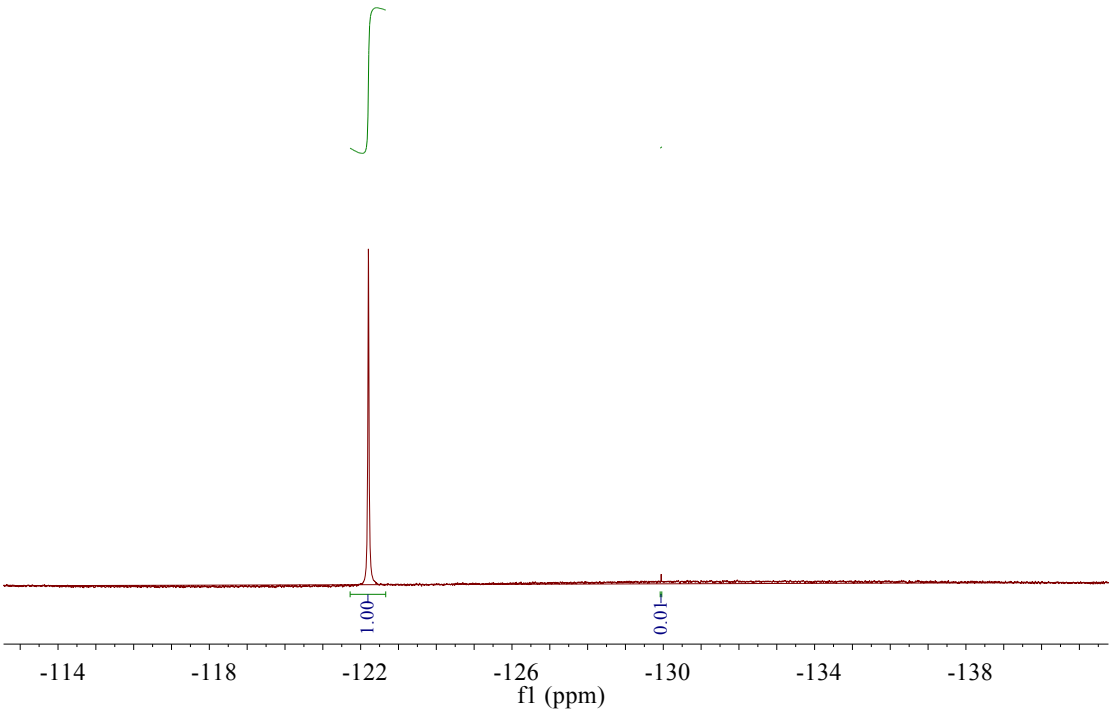
^{1}H-NMR: 1.42-1.45 ppm (t, 3H, *J*=7.4 Hz), 3.83 ppm (3H, s), 4.15-4.18 ppm (q, 2H, J=7.4 Hz), 7.36 ppm (s, 1H), 7.42 ppm (s, 1H), δ 8.62 (s, 1H).

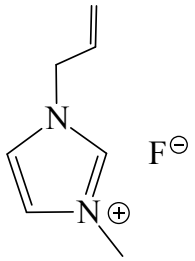
^{13}C-NMR: 14.39-14.41 ppm (d, *J*=2.1 Hz), 35.46-35.55 ppm (dd, *J*=9.6, 4.4 Hz), 44.62-44.76 ppm (m), 121.79 ppm (s), 123.33-123.37 ppm (d, *J*=6.0 Hz), 135.52 ppm (s)

^{19}F-NMR: -122.20 ppm (1F, s)


8.62
7.42
7.36
4.19
4.18
4.16
4.15
3.83
1.46
1.44
1.43
1.00
0.99
0.99
2.09
3.15
3.15
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
f1 (ppm)


135.52
123.37
123.33
121.79
44.76
44.71
44.68
44.62
35.55
35.52
35.49
35.46
14.41
14.39
140 125 110 95 85 75 65 55 45 35 25 15 5 0
f1 (ppm)



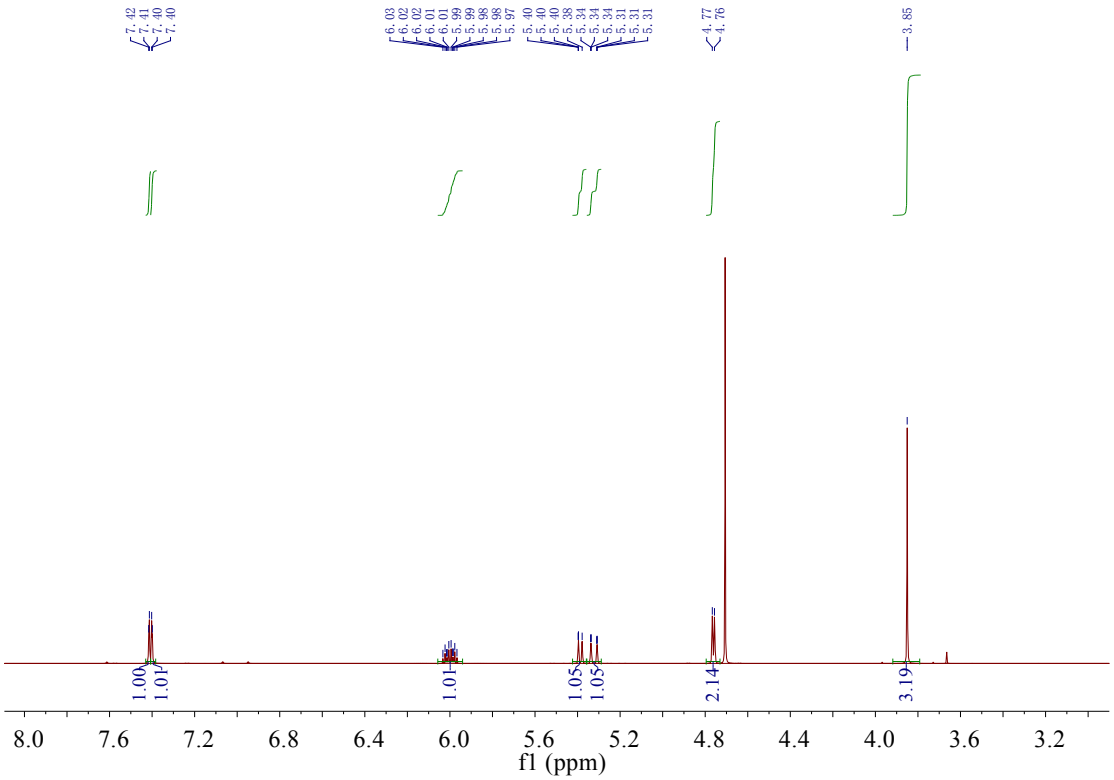


[Amim]F

^{1}H-NMR: 3.85 ppm (s, 3H), 4.76-4.77 ppm (d, 2H, *J*=6.1 Hz), 5.31-5.34 ppm (m, 1H), 5.38-5.40 ppm (m, 1H), 5.97-6.03 ppm (ddt, 1H, *J*=16.5, 10.3, 6.1 Hz), 7.40 ppm (d, 1H, *J*=1.9 Hz), 7.41 ppm (d, 1H, 1.9 Hz)

^{13}C-NMR: 35.46-35.77 ppm (m), 51.31-51.44 ppm (t, *J*=9.4 Hz), 120.62-120.77 ppm (t, *J*=11.3 Hz), 122.16-122.24 ppm (d, *J*=12.4 Hz), 123.47-123.56 ppm (d, *J*=12.5 Hz), 130.25-130.43 ppm (dd, *J*=15.6, 9.8 Hz), 135.58-136.02 ppm (m)

^{19}F-NMR: -122.05 ppm (1F, s)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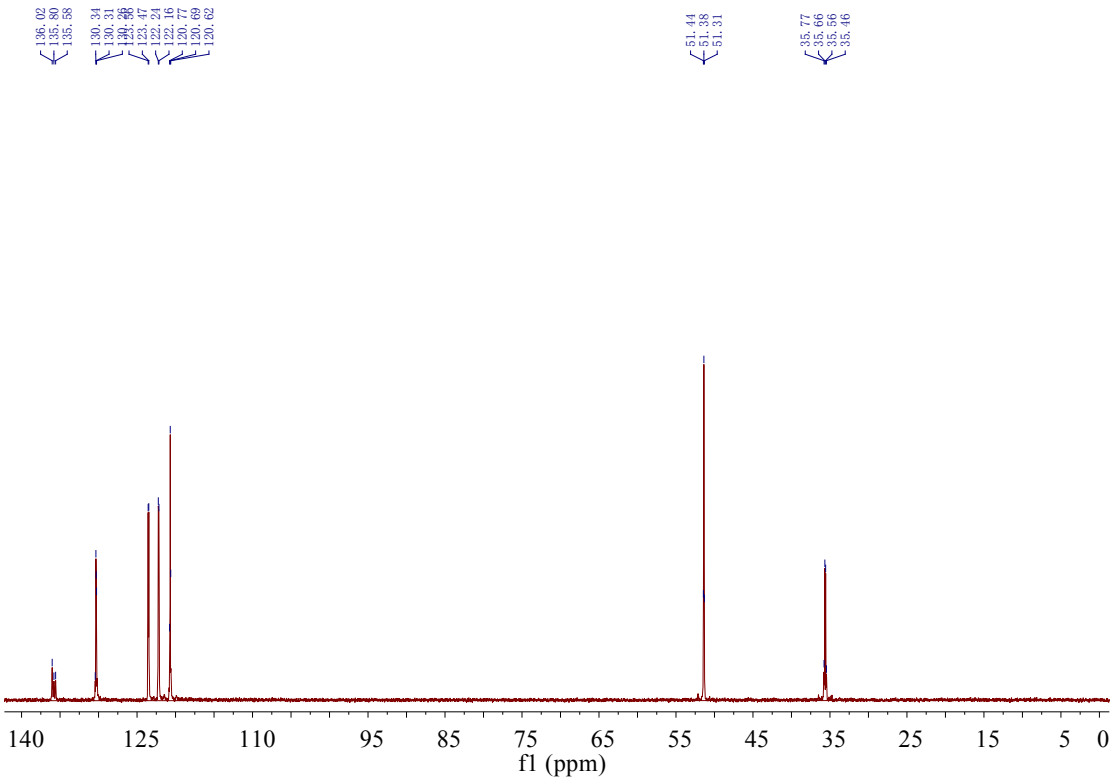
7.41
7.40
7.40
6.03
6.02
6.02
6.01
6.01
5.99
5.99
5.98
5.98
5.97
5.40
5.40
5.38
5.34
5.34
5.31
5.31
5.31
4.77
4.76
3.85
1.00
1.01
1.01
1.05
1.05
2.14
3.19
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
f1 (ppm)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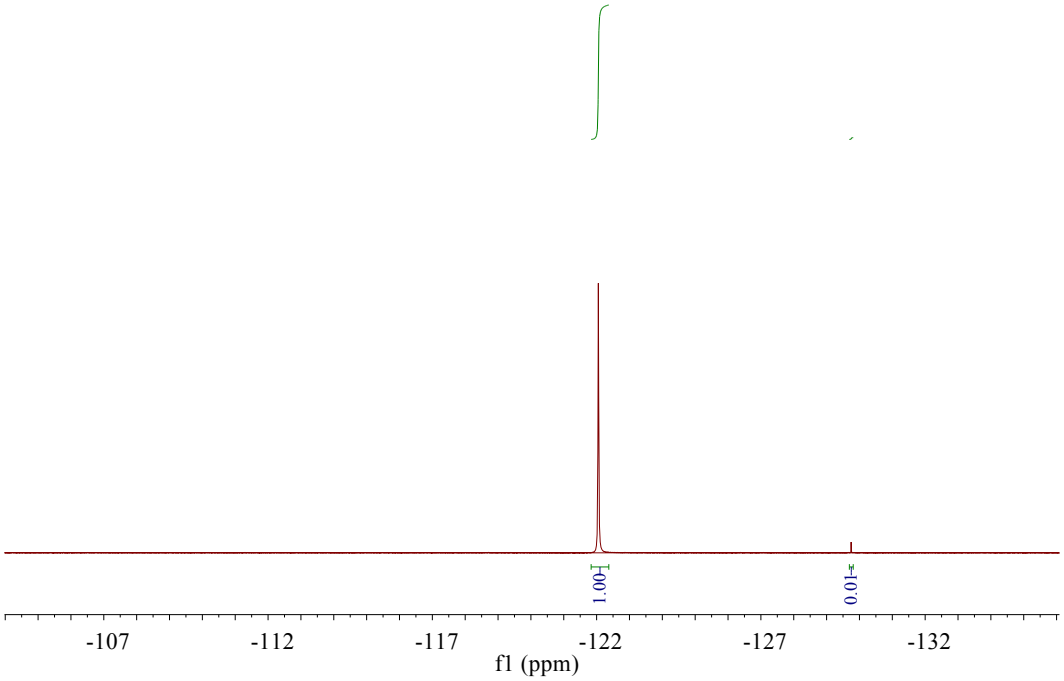
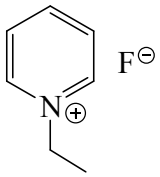
135.58
130.34
130.31
123.47
122.24
122.16
120.77
120.69
120.62
51.44
51.38
51.31
35.77
35.66
35.56
35.46
140
125
110
95
85
75
65
55
45
35
25
15
5
0
f1 (ppm)



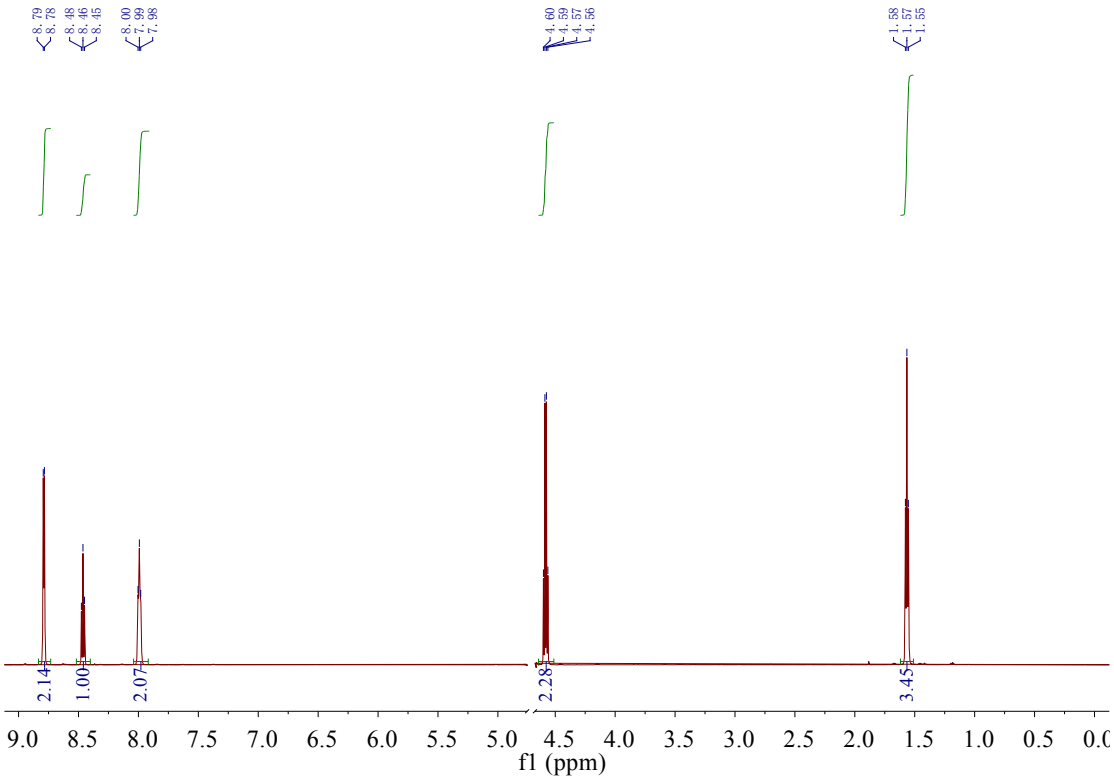


[Epy]F

^{1}H-NMR: 1.57 ppm (t, 3H, *J*=7.4 Hz), 4.56-4.60 ppm (q, 2H, *J*=7.4 Hz), 7.98-8.00 ppm (t, 2H, *J*=6.8 Hz), 8.45-8.48 ppm (t, 1H, *J*=7.8 Hz), 8.78-8.79 (d, 2H, *J*=5.8 Hz)

^{13}C-NMR: 15.58 ppm (d, *J*=2.8 Hz), 57.29 ppm (s), 128.19 ppm (s), 143. 89 ppm (d, *J*=7.8 Hz), 145.40 ppm (s)

^{19}F-NMR: -122.15 ppm (1F, s)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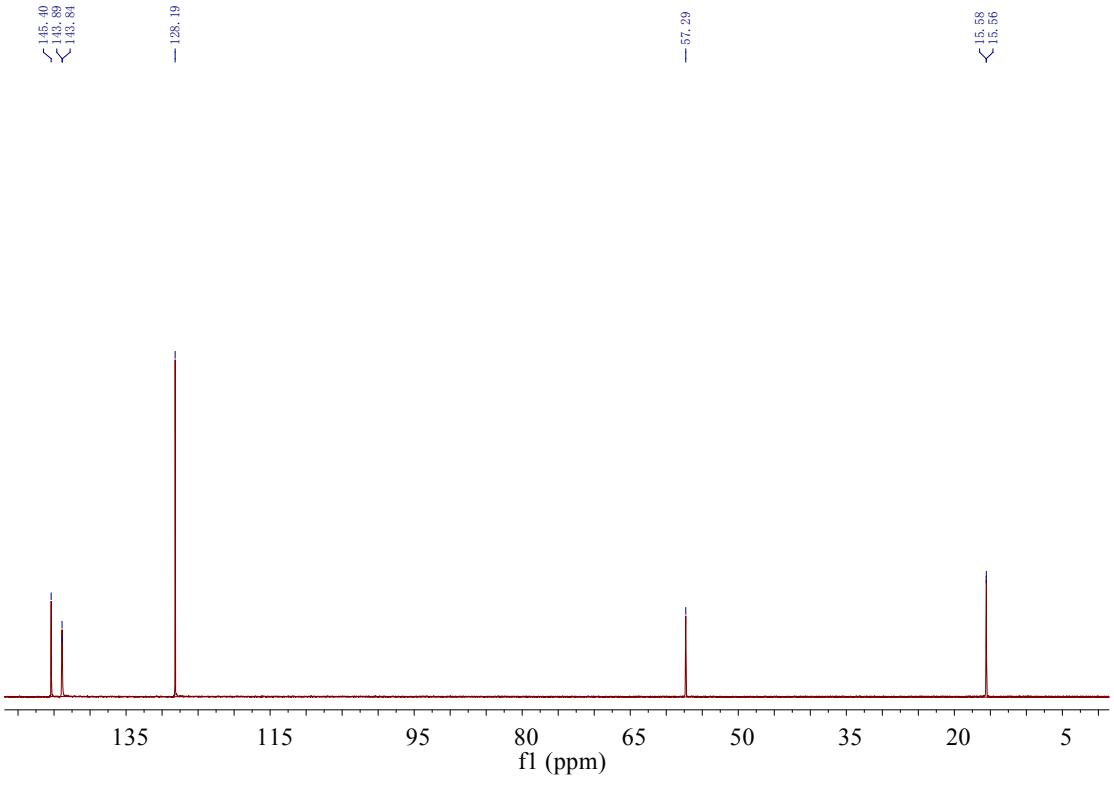
8.46
8.45
8.00
7.99
7.98
4.60
4.59
4.57
4.56
1.58
1.57
1.55
2.14
1.00
2.07
2.28
3.45
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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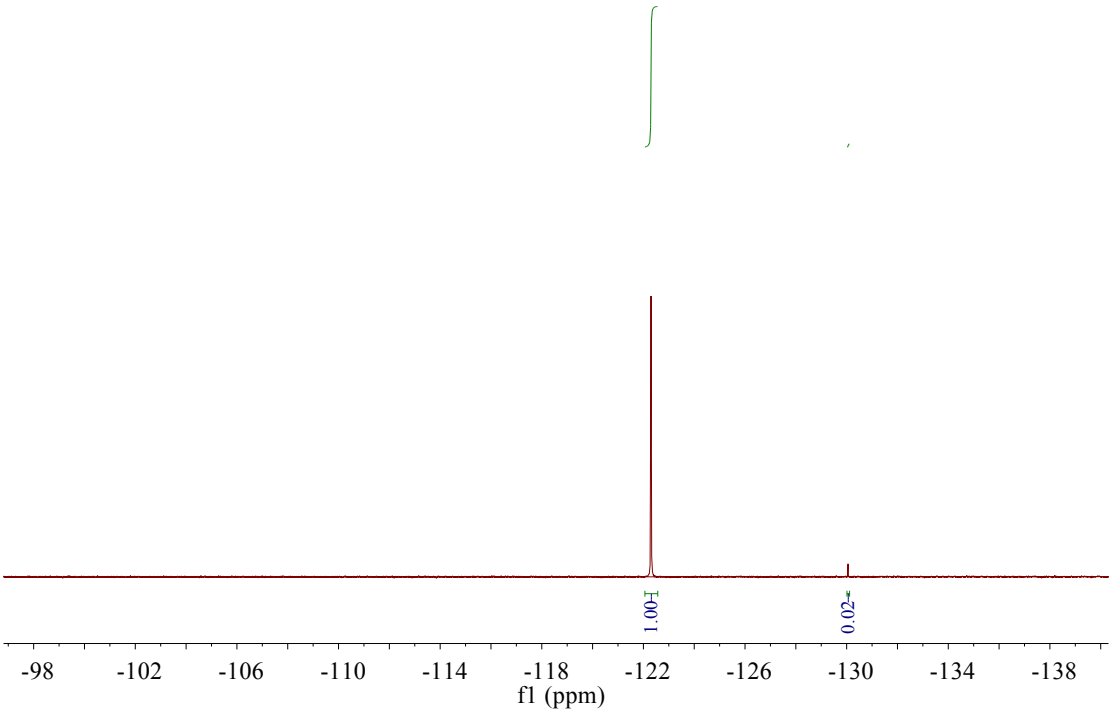
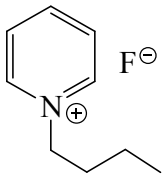
143.84
128.19
57.29
15.58
15.56
135 115 95 80 65 50 35 20 5
f1 (ppm)



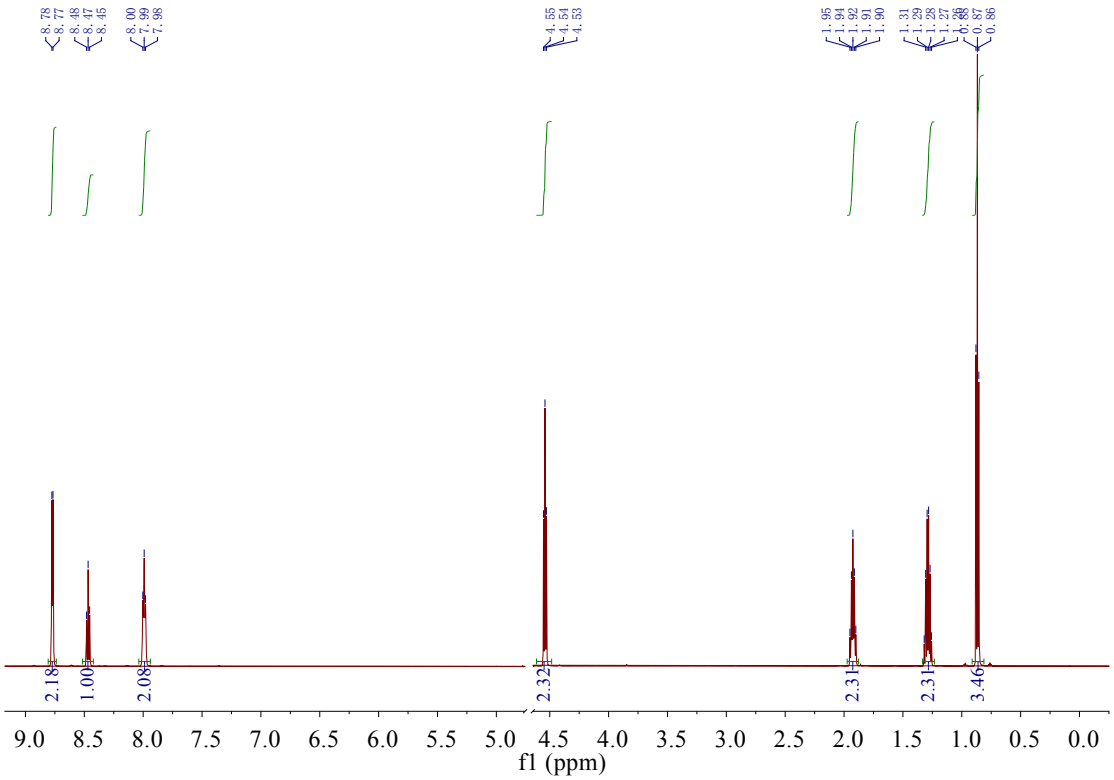


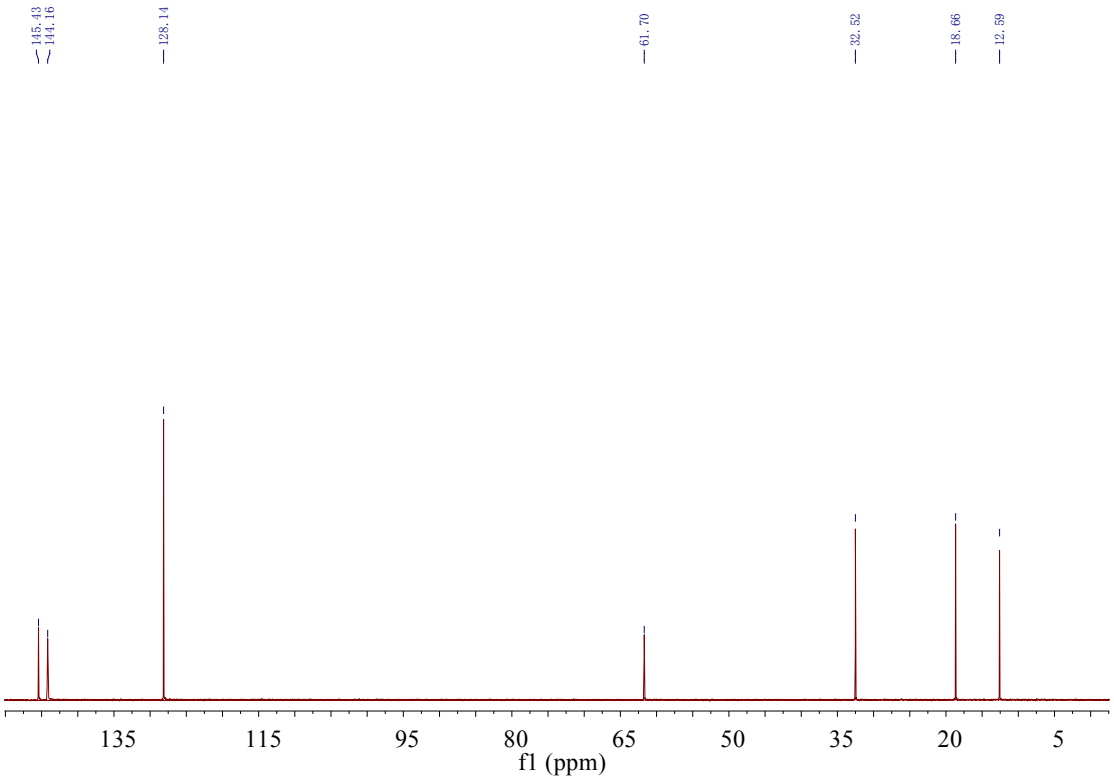
[Bpy]F

^{1}H-NMR: 0.85-0.88 ppm (t, 3H, *J*=6.9 Hz), 1.25-1.32 ppm (m, 2H), 1.90-1.95 ppm (m, 2H), 4.53-4.55 ppm (t, 2H, *J*=7.4 Hz), 7.98-8.00 ppm (t, 2H, *J*=6.9 Hz), 8.45-8.48 ppm (t, 1H, *J*=7.9 Hz), 8.77-8.78 ppm (d, 2H, *J*=5.7 Hz)

^{13}C-NMR: 12.59 ppm (s), 18.66 ppm (s), 32.52 ppm (s), 61.70 ppm (s), 128.34 ppm (s), 144.36 ppm (s), 146.43 ppm (s)

^{19}F-NMR: -122.30 ppm (1F, s)


8.78
8.77
8.48
8.47
8.45
8.00
7.99
7.98
4.55
4.54
4.53
1.95
1.94
1.92
1.91
1.90
1.31
1.29
1.28
1.27
0.87
0.86
2.18
1.00
2.08
2.32
2.31
2.31
3.46
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
f1 (ppm)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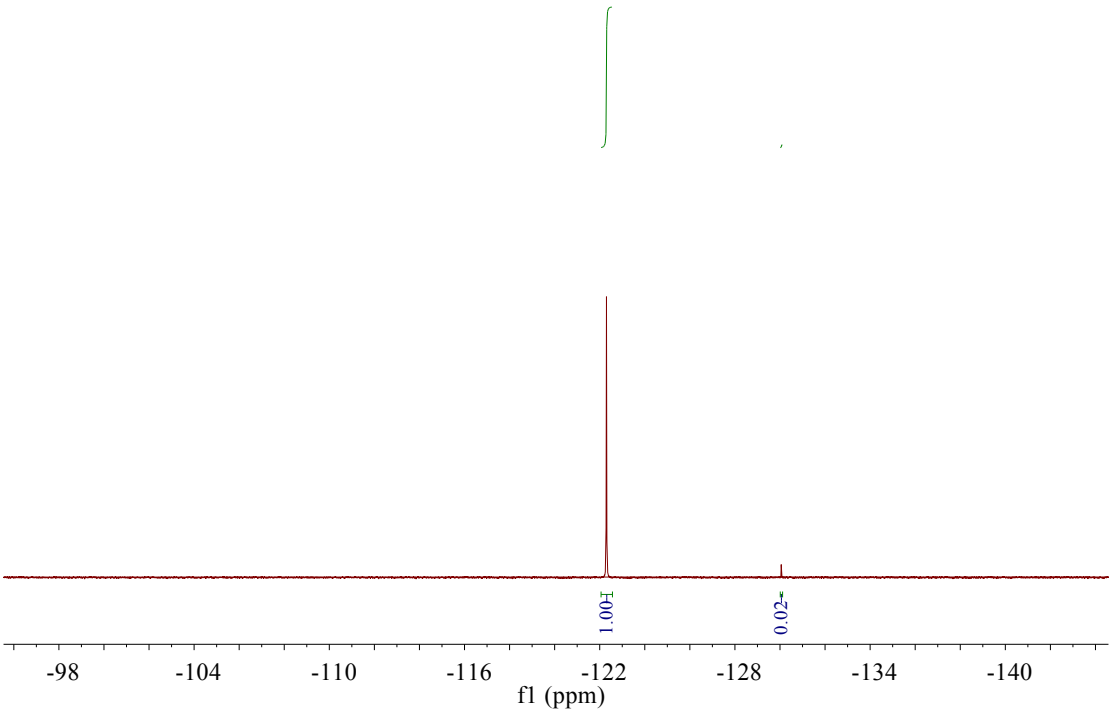
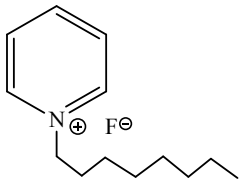
128.14
61.70
32.52
18.66
12.59
135 115 95 80 65 50 35 20 5
f1 (ppm)



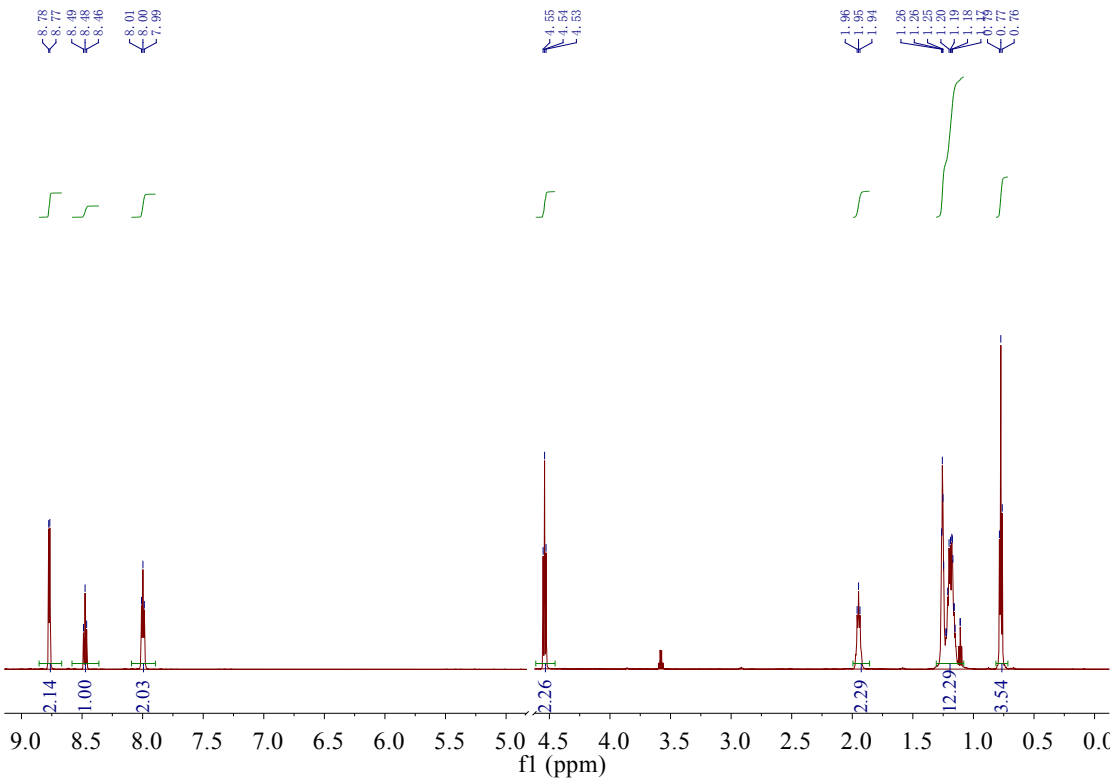


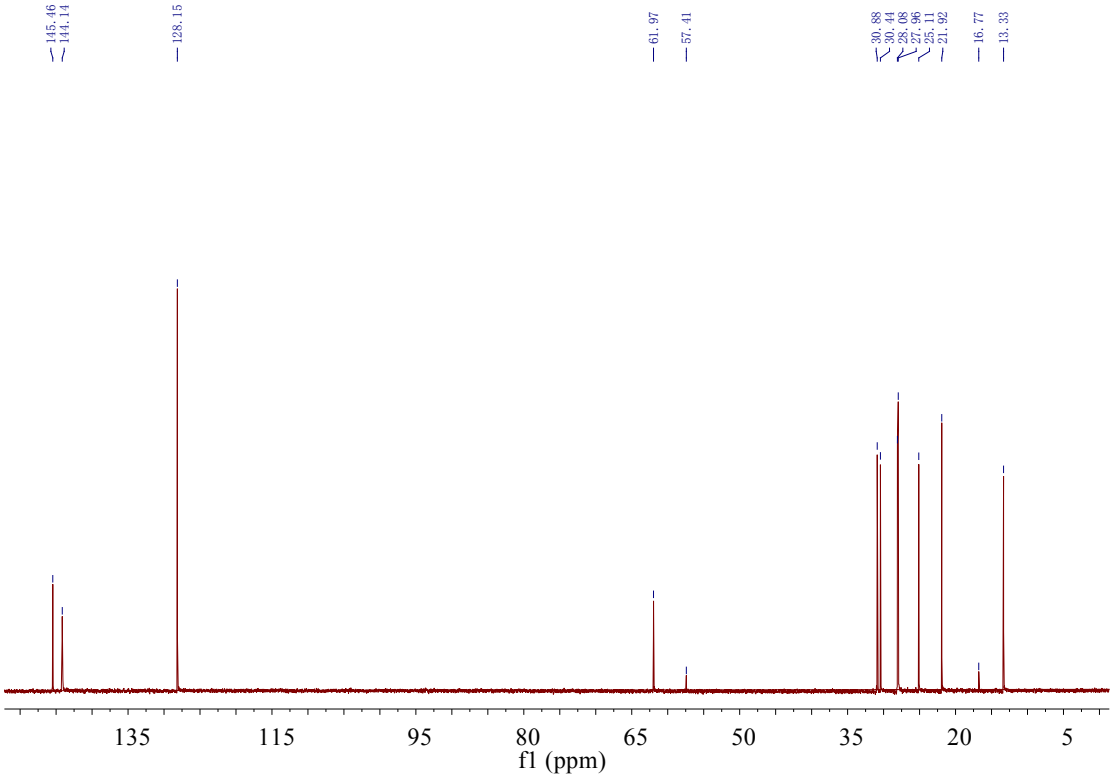
[Opy]F

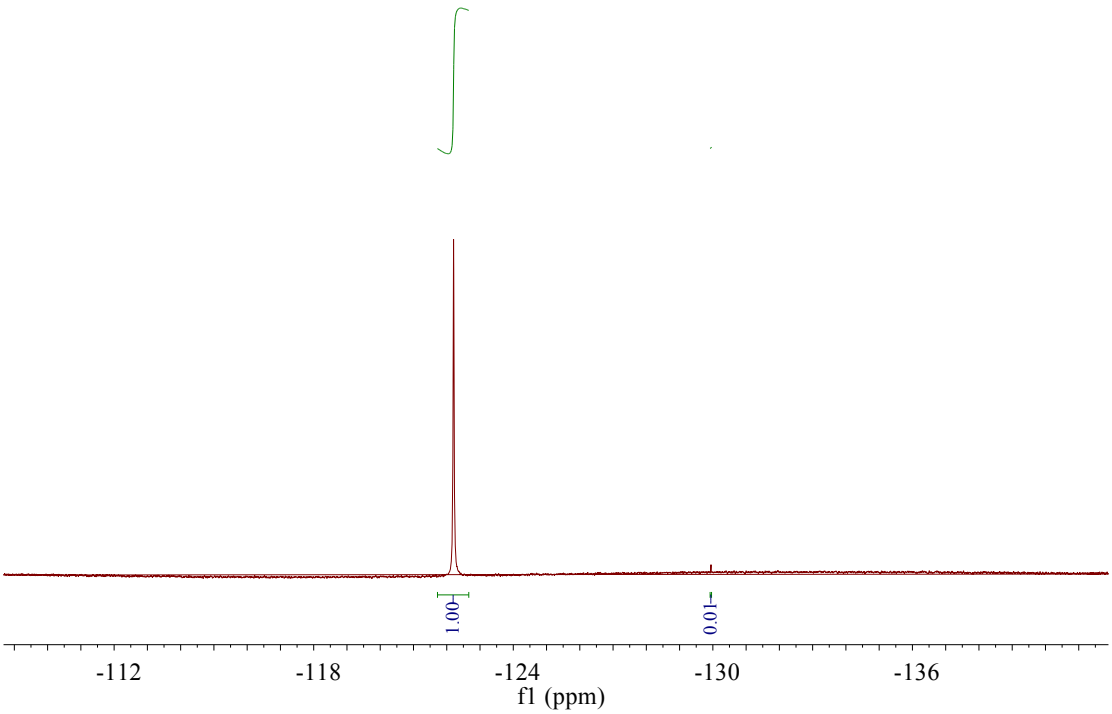
^{1}H-NMR: 0.77 ppm (t, J = 7.0 Hz, 1H), 1.31-1.08 ppm (m, 12H), 1.95 ppm (p, J = 7.3 Hz, 1H), 4.54 ppm (t, J = 7.3 Hz, 1H), 8.00 ppm (t, J = 7.0 Hz, 1H), 8.48 ppm (t, J = 7.8 Hz, 1H), 8.77 ppm (d, J = 5.6 Hz, 1H).

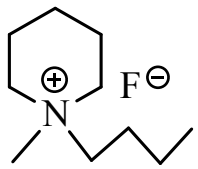
^{13}C-NMR: 13.33 ppm (s), 16.77 ppm (s), 21.92 ppm (s), 25.11 ppm (s), 28.02 ppm (d, J = 17.7 Hz), 30.44 ppm (s), 30.88 ppm (s), 57.41 ppm (s), 61.97 ppm (s), 128.15 ppm (s), 144.14 ppm (s), 145.46 ppm (s).

^{19}F-NMR: -122.32 ppm (1F, s).


8.78
8.77
8.49
8.48
8.46
8.01
8.00
7.99
4.55
4.54
4.53
1.96
1.95
1.94
1.26
1.25
1.20
1.19
0.77
0.76
2.14
1.00
2.03
2.26
2.29
12.29
3.54
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
f1 (ppm)


145.46
144.14
128.15
61.97
57.41
30.88
30.44
28.08
27.96
25.11
21.92
16.77
13.33
135 115 95 80 65 50 35 20 5
f1 (ppm)



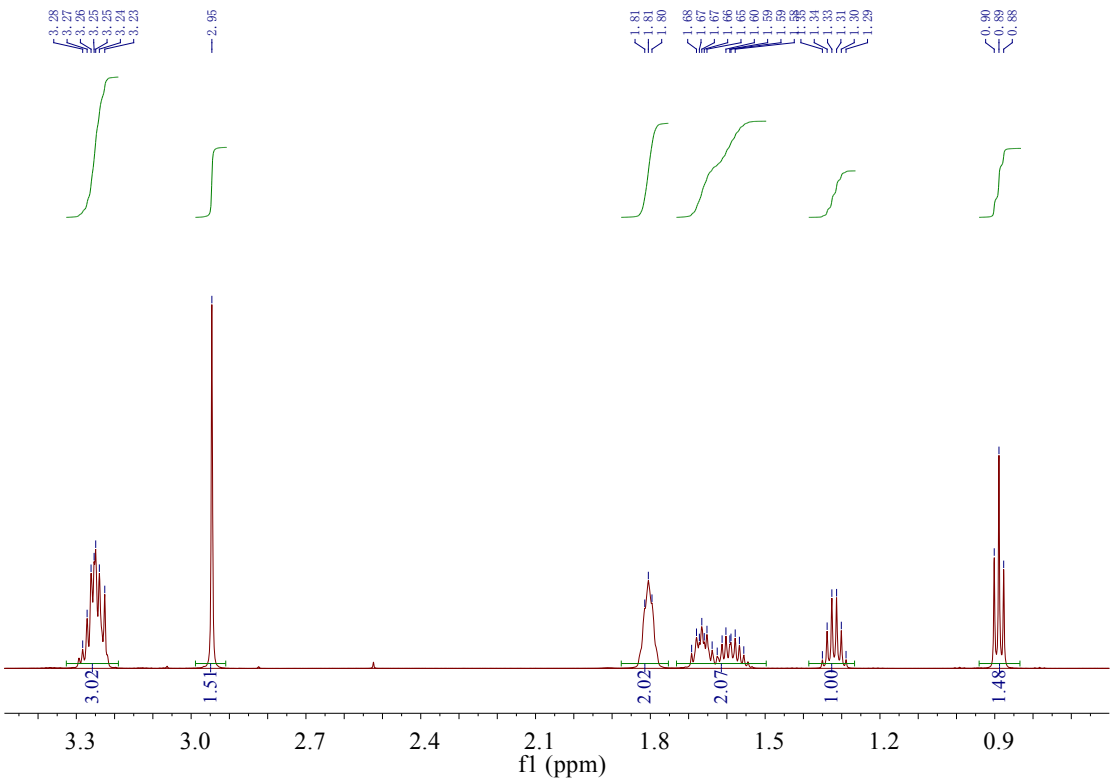


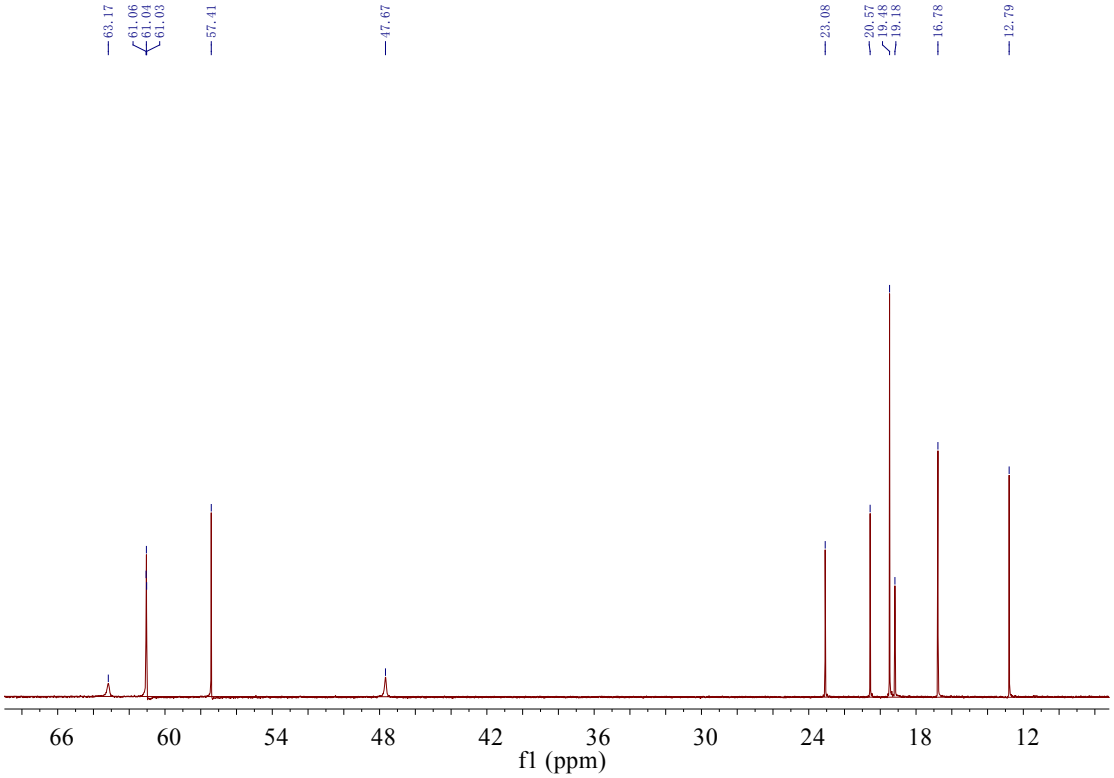
[PP$_{14}$]F

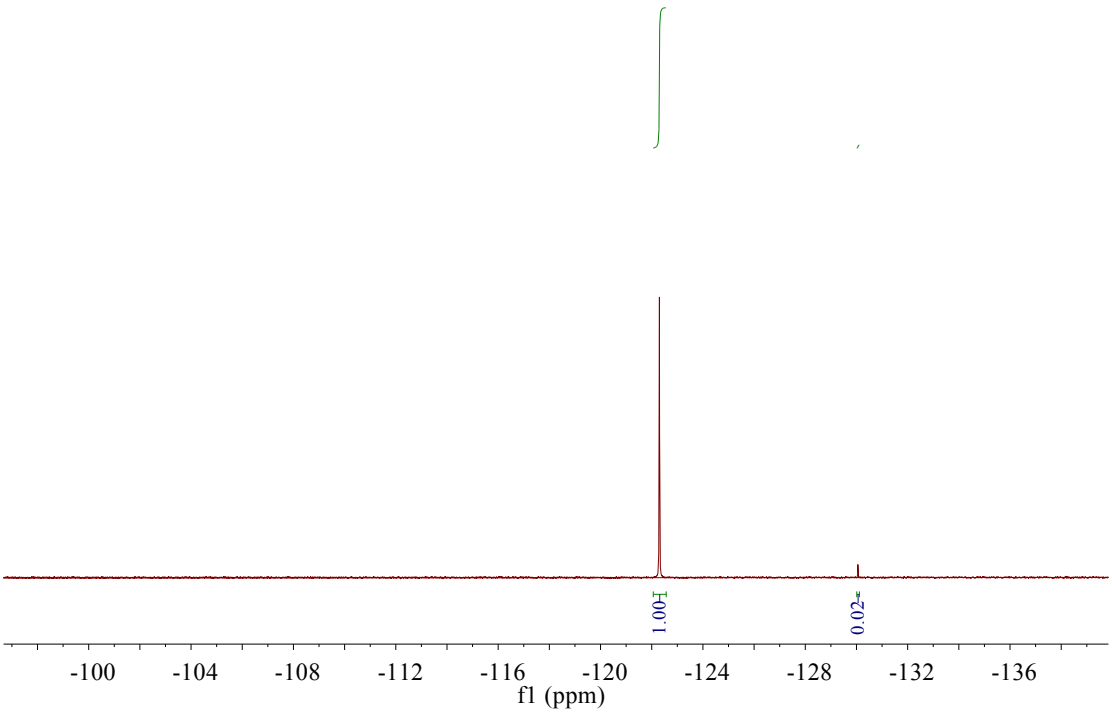
^{1}H-NMR: 0.89 (t, *J* = 7.4 Hz, 3H), 1.39-1.26 (m, 2H), 1.73-1.49 (m, 4H), 1.87-1.75 (m, 4H), 3.33-3.18 (m, 3H), 2.95 (s, 6H).

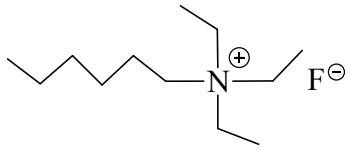
^{13}C-NMR: 12.79 ppm (s), 16.78 ppm (s), 19.18 ppm (s), 19.48 ppm (s), 20.57 ppm (s), 23.08 ppm (s), 47.67 ppm (s), 57.41 ppm (s), 61.24-60.93 ppm (m), 63.17 ppm (s).

^{19}F-NMR: -122.40 ppm (1F, s).


3.28
3.27
3.26
3.25
3.25
3.24
3.23
2.95
1.81
1.81
1.80
1.68
1.67
1.67
1.66
1.65
1.60
1.59
1.59
1.35
1.34
1.33
1.31
1.30
1.29
0.90
0.89
0.88
3.02
1.51
2.02
2.07
1.00
1.48
3.3
3.0
2.7
2.4
2.1
1.8
1.5
1.2
0.9
f1 (ppm)


63.17
61.06
61.04
61.03
57.41
47.67
23.08
20.57
19.48
19.18
16.78
12.79
66
60
54
48
42
36
30
24
18
12
f1 (ppm)



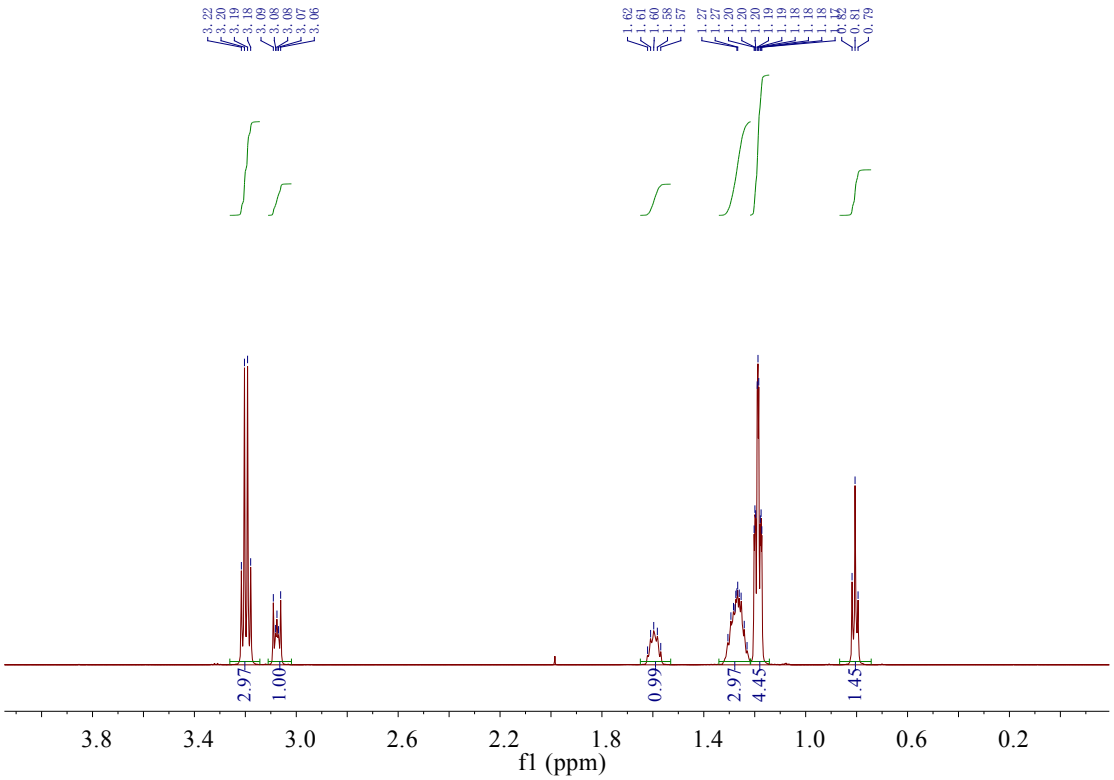


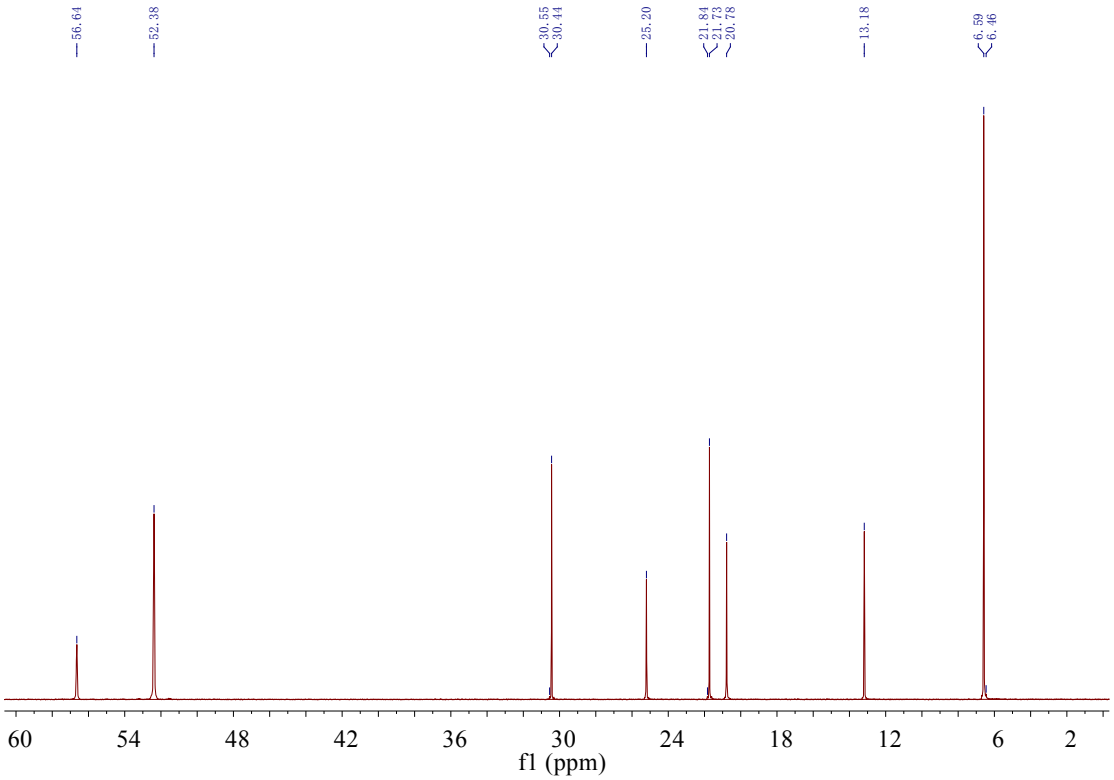
[N_{2226}]F

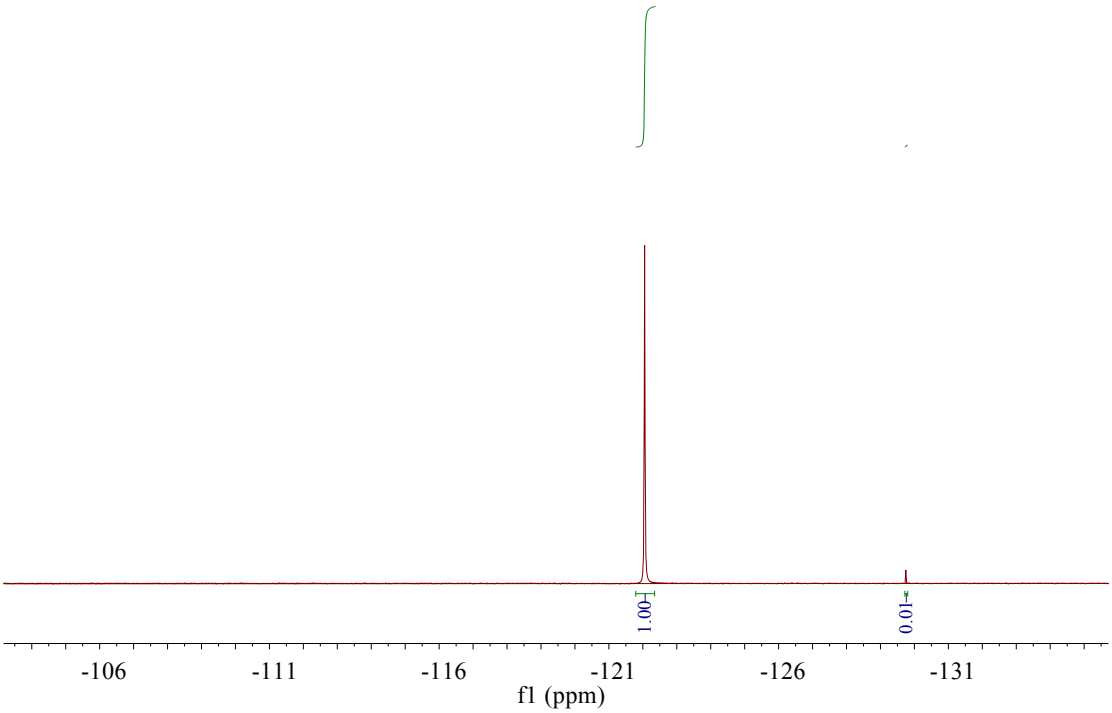
^{1}H-NMR: 0.79-0.82 ppm (t, 3H, *J*=7.1 Hz), 1.17-1.20 ppm (m, 9H), 1.24-1.31 ppm (m, 6H), 3.06-3.09 ppm (m, 2H), 3.18-3.22 (m, 6H, *J*=7.3 Hz)

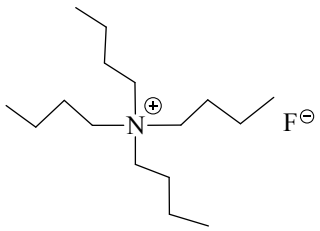
^{13}C-NMR: 6.46-6.59 ppm (d, *J*=19.6 Hz), 13.18 ppm (s), 20.78 ppm (s), 21.73 ppm (1C, s), 21.78 ppm (d, *J*=16.4 Hz), 25.20 ppm (s), 30.44-30.50 ppm (d, *J*=16.4 Hz) 52.38 ppm (s), 56.64 ppm (s)

^{19}F-NMR: -122.35 ppm (1F, s)


3.22
3.20
3.19
3.18
3.09
3.08
3.08
3.07
3.06
1.62
1.61
1.60
1.58
1.57
1.27
1.27
1.20
1.20
1.19
1.19
1.18
1.18
1.18
0.82
0.81
0.79
2.97
1.00
0.99
2.97
4.45
1.45
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
f1 (ppm)


56.64
52.38
30.55
30.44
25.20
21.84
21.73
20.78
13.18
6.59
6.46
60
54
48
42
36
30
24
18
12
6
2
f1 (ppm)



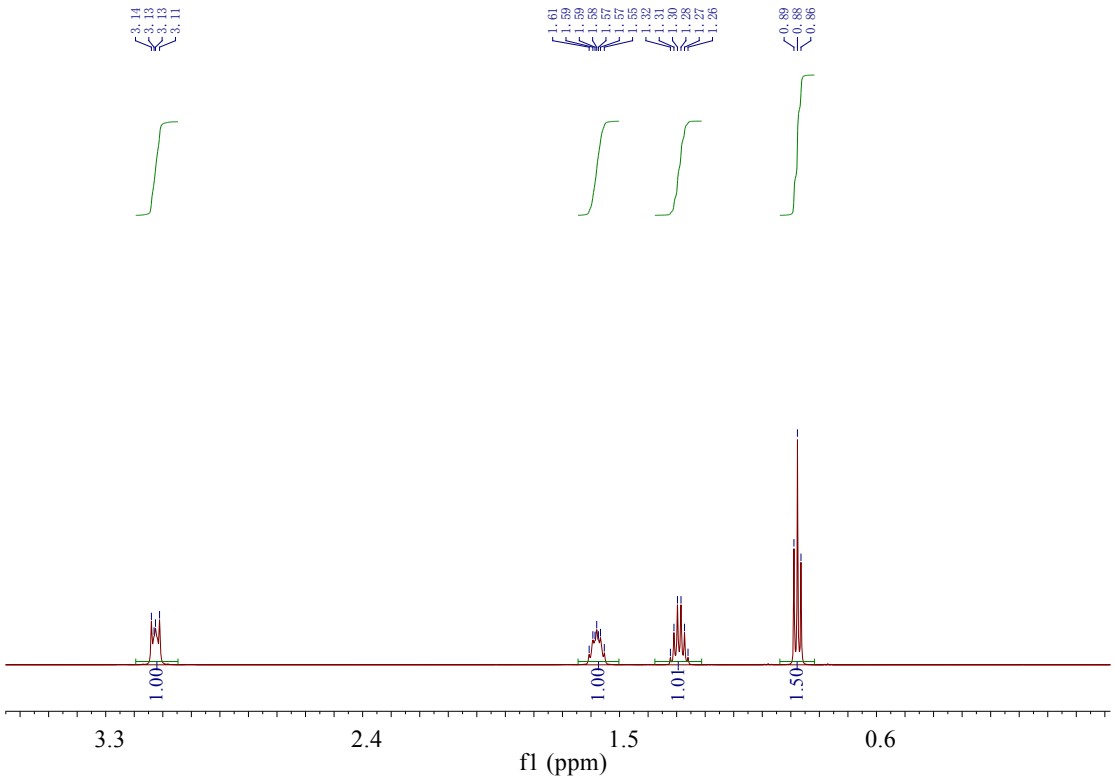


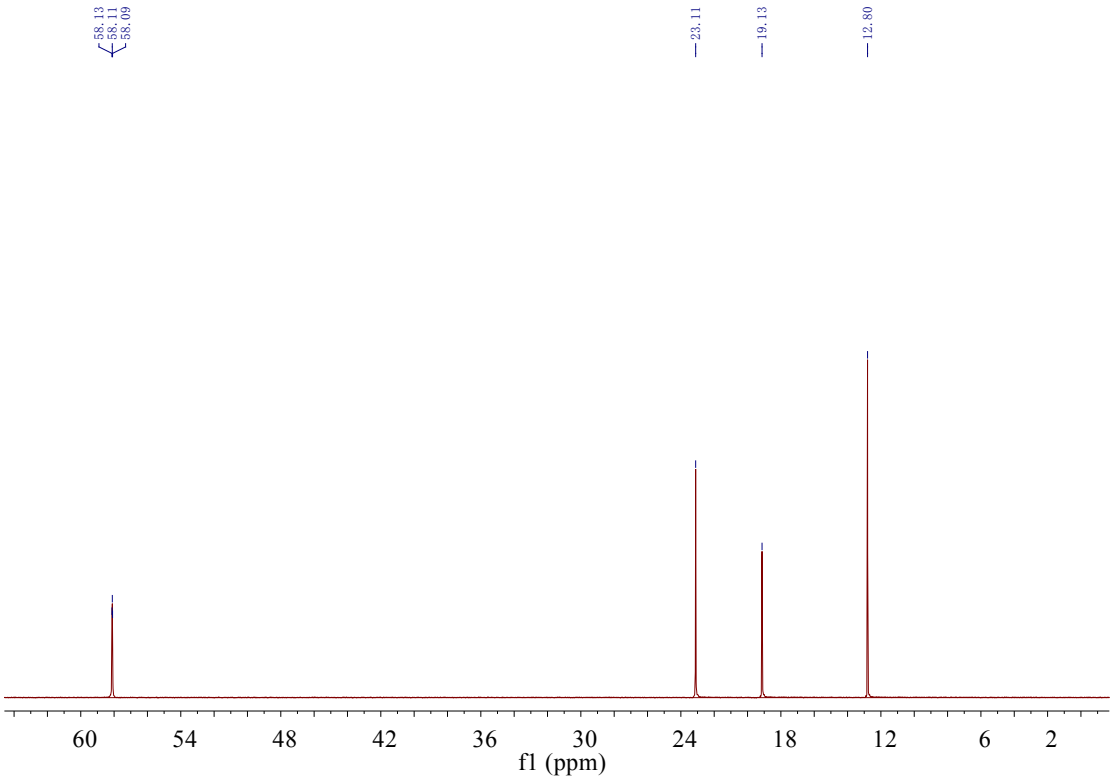
[N_{4444}]F

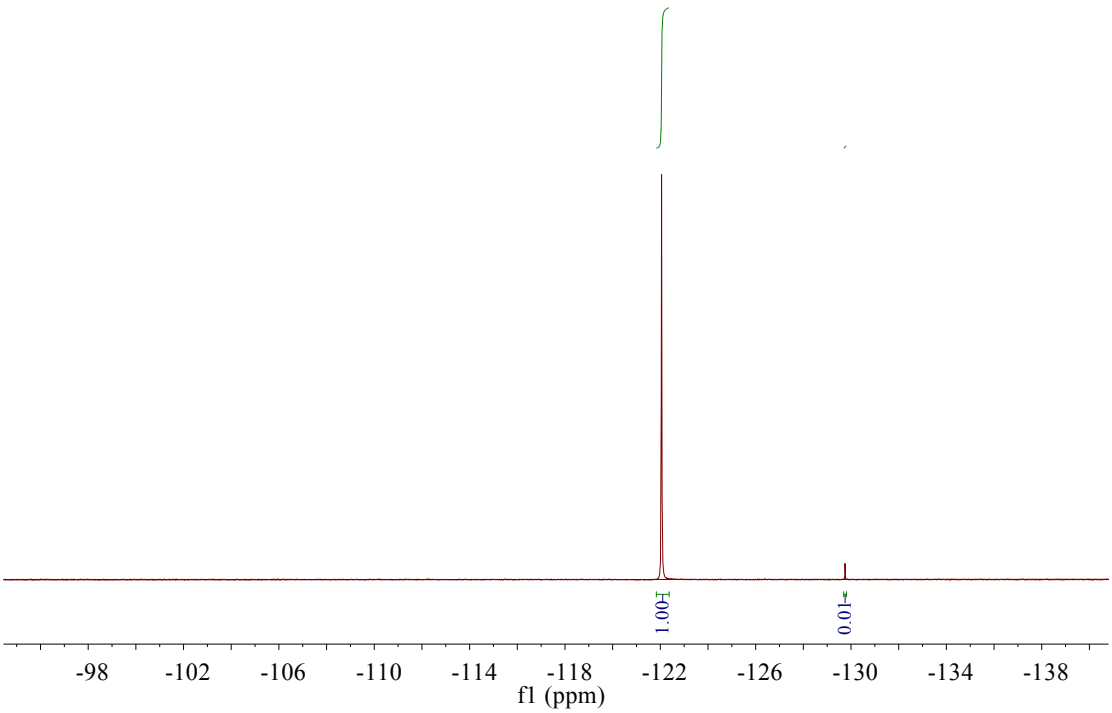
^{1}H-NMR: 0.85-0.89 ppm (t, 3H, *J*=7.4 Hz), 1.25-1.32 ppm (m, 2H), 1.55-1.61 ppm (m, 2H), 3.11-3.14 ppm (dd, 2H, *J*=10.0, 7.1 Hz)

^{13}C-NMR: 12.80 ppm (s), 19.13 ppm (s), 23.11 ppm (s), 58.09-58.13 ppm (m)

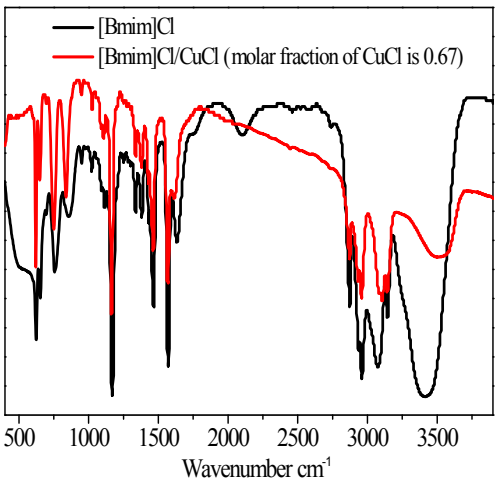
^{19}F-NMR: -122.71 ppm (1F, s)

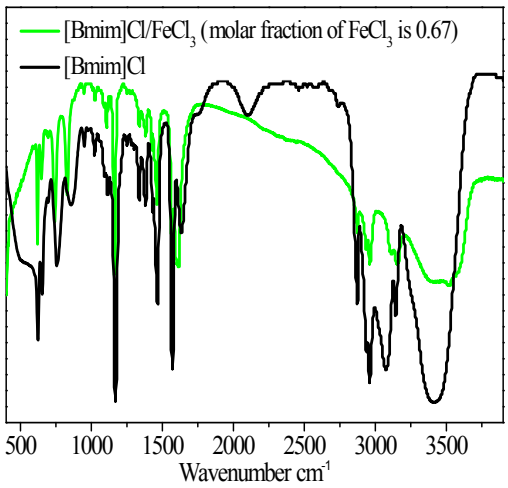

3.14
3.13
3.13
3.11
1.61
1.59
1.59
1.58
1.57
1.57
1.55
1.32
1.31
1.30
1.28
1.27
1.26
0.89
0.88
0.86
1.00
1.00
1.01
1.50
3.3
2.4
1.5
0.6
f1 (ppm)

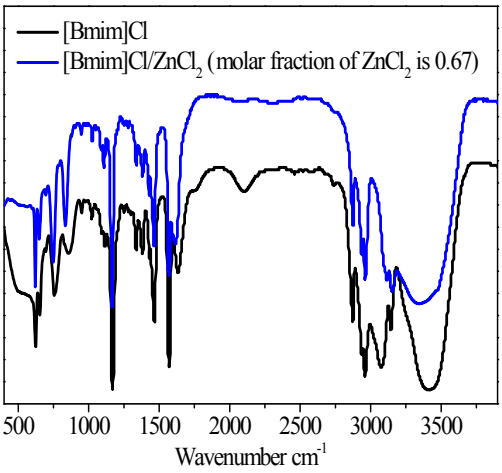

58.13
58.11
58.09
23.11
19.13
12.80
60
54
48
42
36
30
24
18
12
6
2
f1 (ppm)

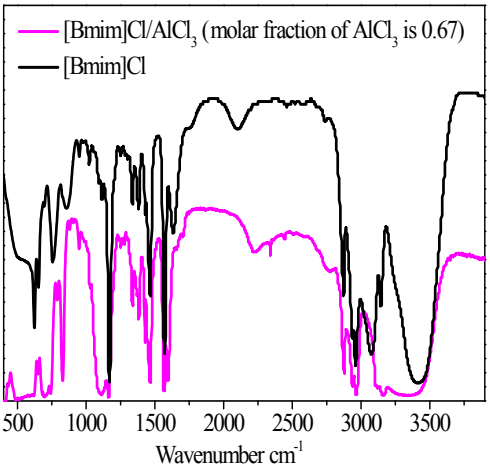


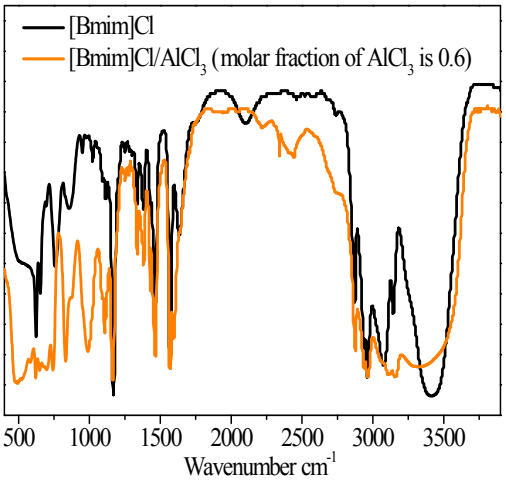
II. FT-IR spectra of ILs-L

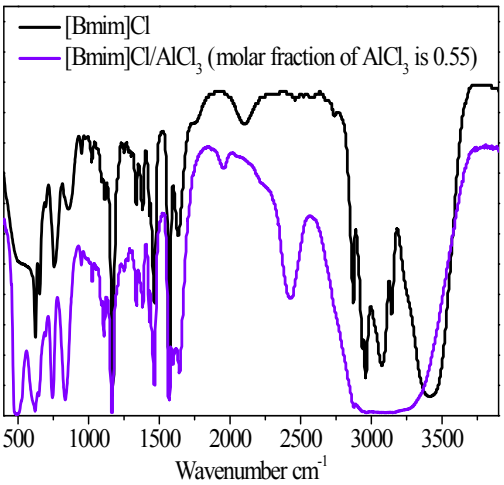


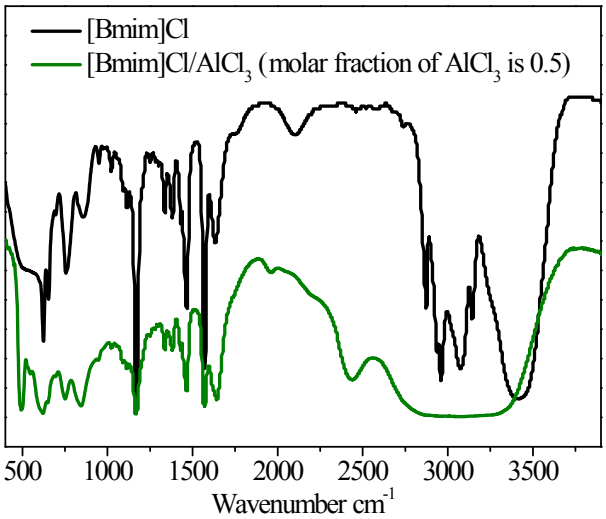



[Bmim]Cl
[Bmim]Cl/ZnCl2 (molar fraction of ZnCl2 is 0.67)
500 1000 1500 2000 2500 3000 3500
Wavenumber cm-1

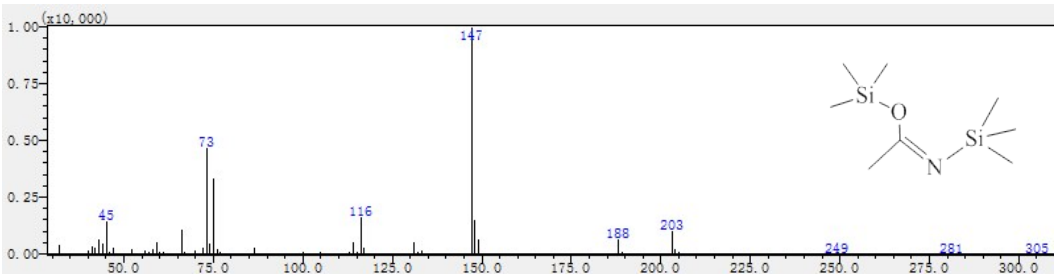

[Bmim]Cl/AlCl3 (molar fraction of AlCl3 is 0.67)
[Bmim]Cl
500 1000 1500 2000 2500 3000 3500
Wavenumber cm-1

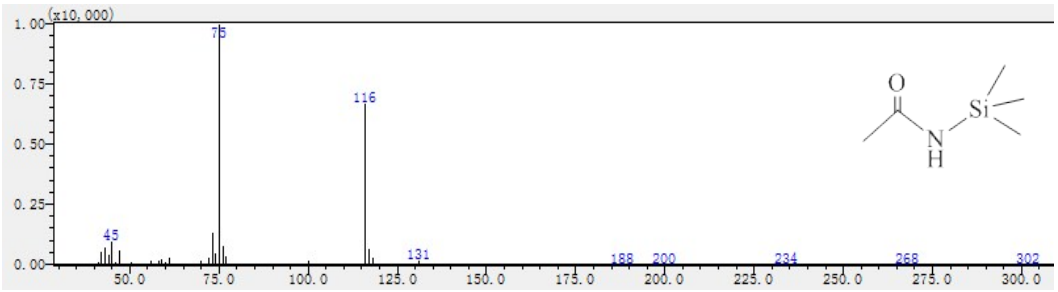

[Bmim]Cl
[Bmim]Cl/AlCl3 (molar fraction of AlCl3 is 0.6)
500 1000 1500 2000 2500 3000 3500
Wavenumber cm-1

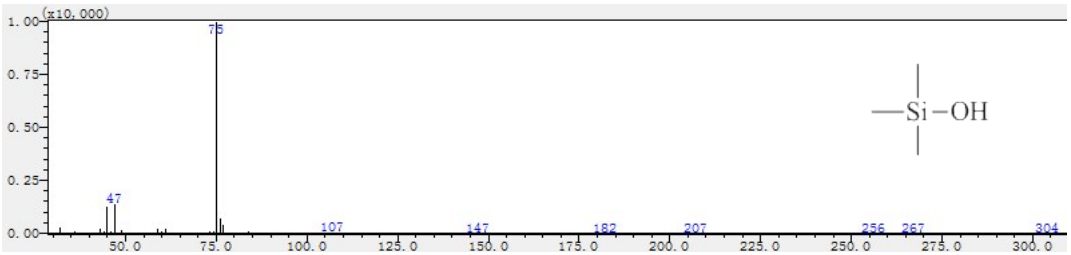

[Bmim]Cl
[Bmim]Cl/AlCl3 (molar fraction of AlCl3 is 0.55)
500 1000 1500 2000 2500 3000 3500
Wavenumber cm-1

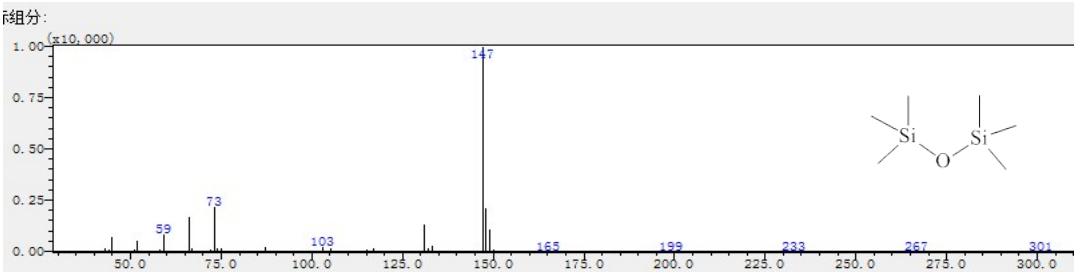

[Bmim]Cl
[Bmim]Cl/AlCl3 (molar fraction of AlCl3 is 0.5)
500 1000 1500 2000 2500 3000 3500
Wavenumber cm-1

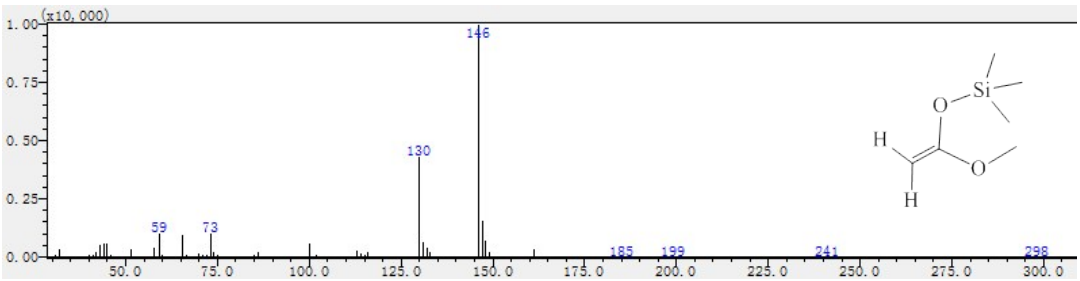
III. MS information

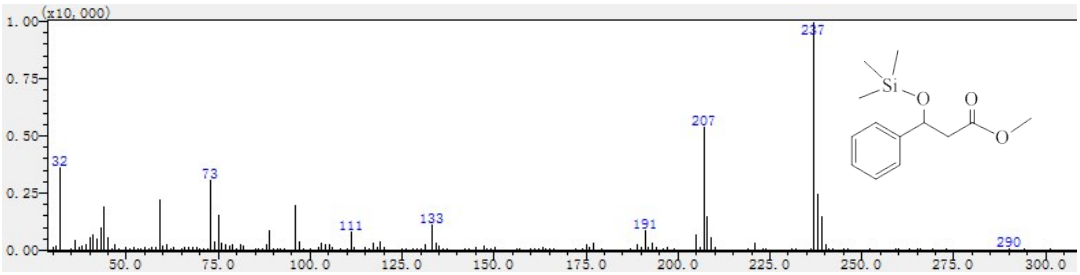


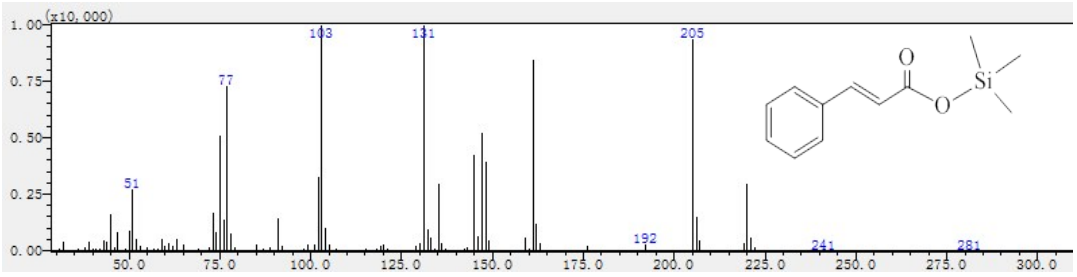









(x10,000)
1.00
0.75
0.50
0.25
0.00
32
73
111
133
191
207
237
290
Si
O
O
O
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0


(x10,000)
1.00
0.75
0.50
0.25
0.00
51
77
103
131
192
205
241
281
O
O
Si
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0