Electronic Supplementary Information

Luminescent ion pairs with tunable emission colors for light-emitting devices and electrochromic switches

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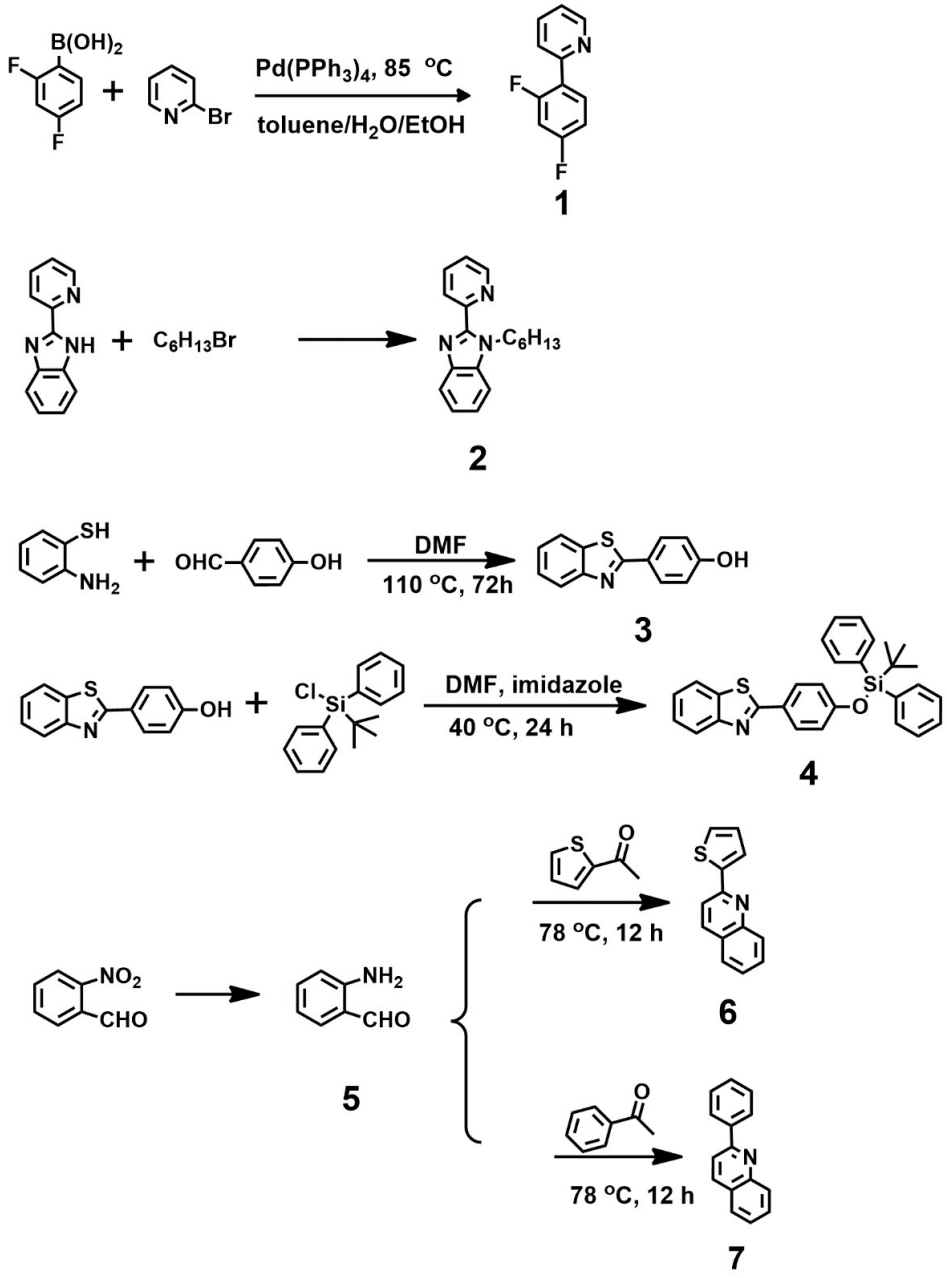
Table S1. The emission wavelengths, lifetimes and quantum yields of the positive and negative complexes and IPs (10^{-5} M in acetonitrile).

Sample	λ (nm)	τ (ns)	Φ (%)
C1Cl	550	323	21
C2Cl	580	62	27
C3Cl	630	352	8
***n*-Bu$_4$NA1**	600	163	17
***n*-Bu$_4$NA2**	472 / 510	32	11
***n*-Bu$_4$NA3**	520 / 570	200	20
***n*-Bu$_4$NA4**	452 / 479	469	31
IP1	550	305	8
	600	248	
IP2	472 / 510	43	35
	580	59	
IP3	472 / 510	34	13
	630	337	
IP4	472 / 510	40	37
	550	301	
IP5	520	190	20
	580	162	
IP6	580	102	22
	452 / 479	416	



Scheme S1 The synthetic routes of ligands.

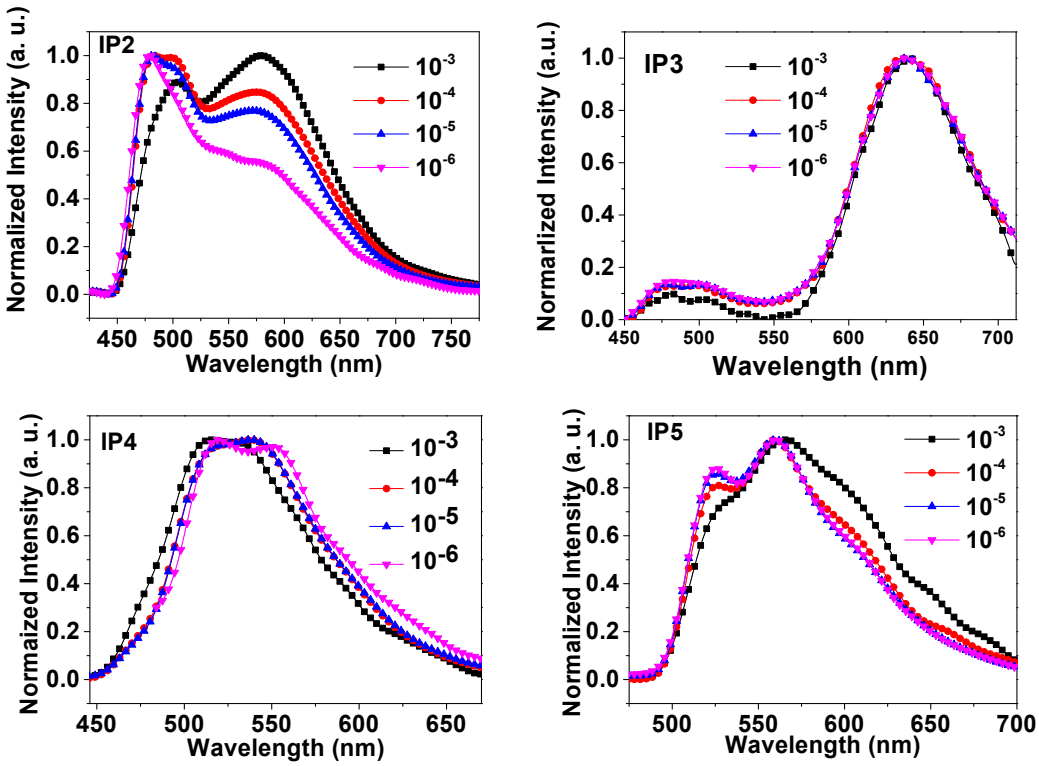


Fig. S1. The PL spectra of the IPs at different concentrations in acetonitrile**.**

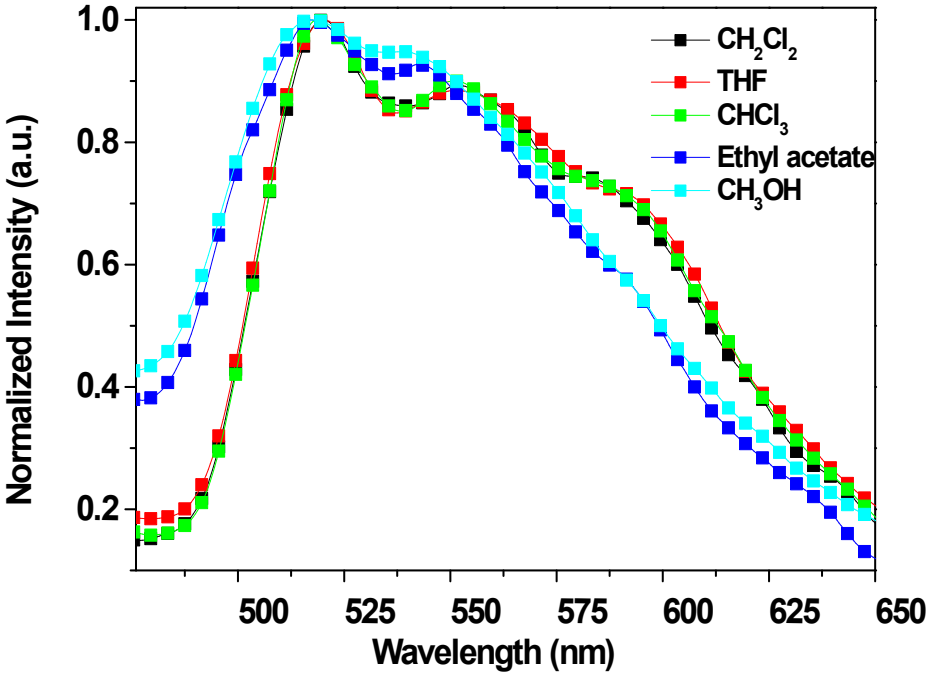


Fig. S2. The emission spectra of **IP1** in different solvents (10^{-5} M).

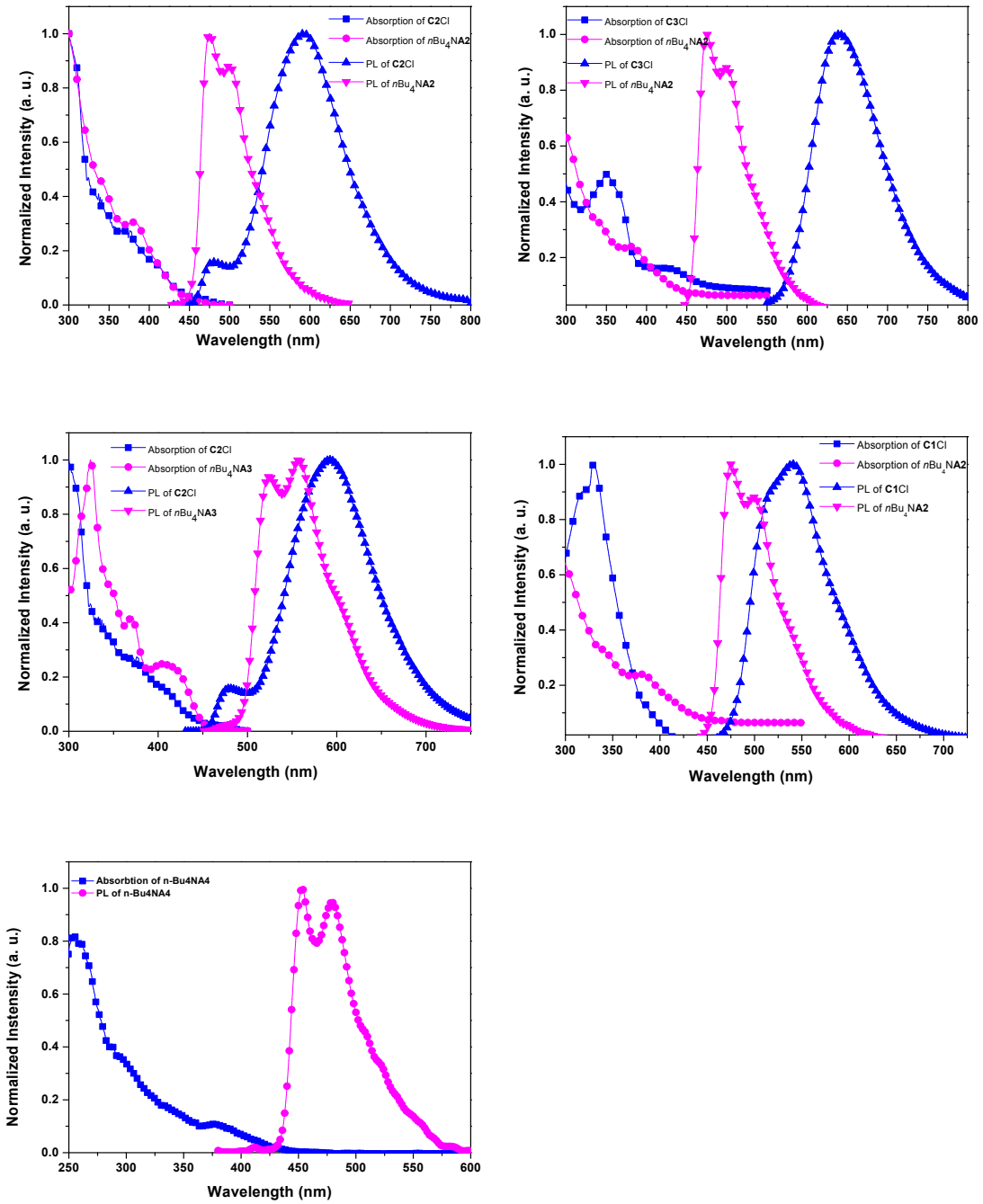


Fig. S3. Absorption and luminescence spectra of positive and negative complexes.

Fig. S4. Photographs of **IP6** doped in polymer at different contents under excitation at 365 nm, From left to right, the contents are 1.7 mg / 800 mg, 1.3 mg / 800 mg, 0.9 mg / 800 mg, 0.7 mg / 800 mg, respectively.

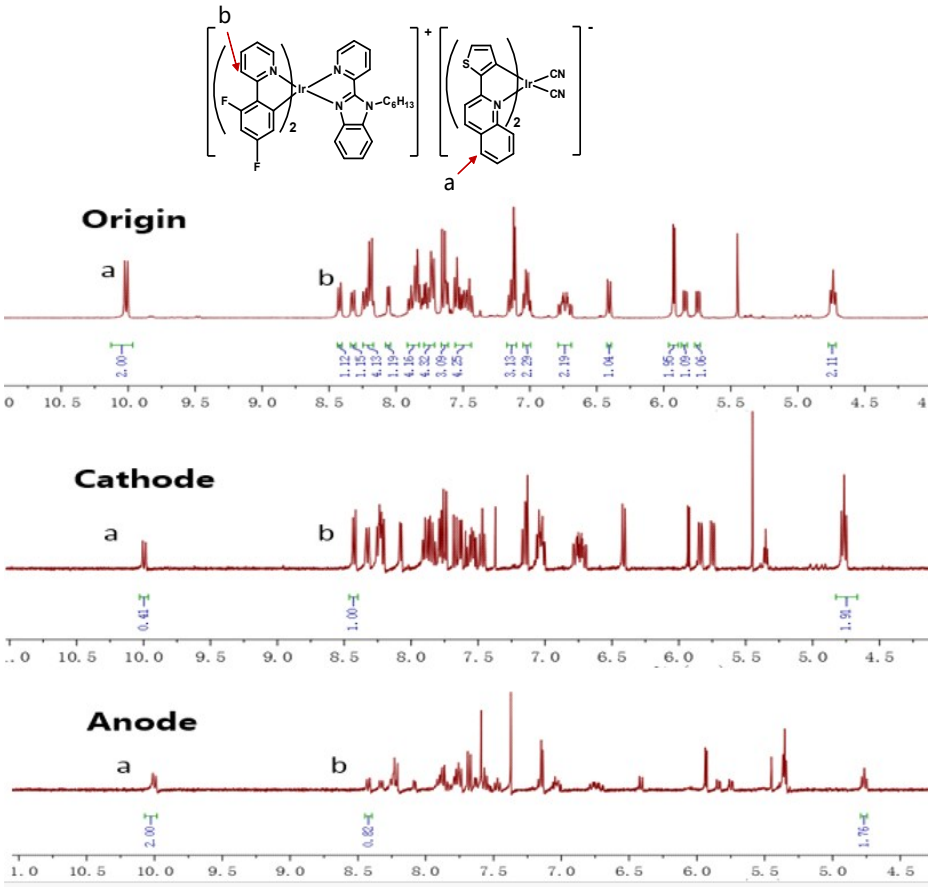


Fig. S5. The ^{1}H NMR spectra of **IP1** in acetonitrile-d_3 before and after applying a voltage of 3 V at anode and cathode.

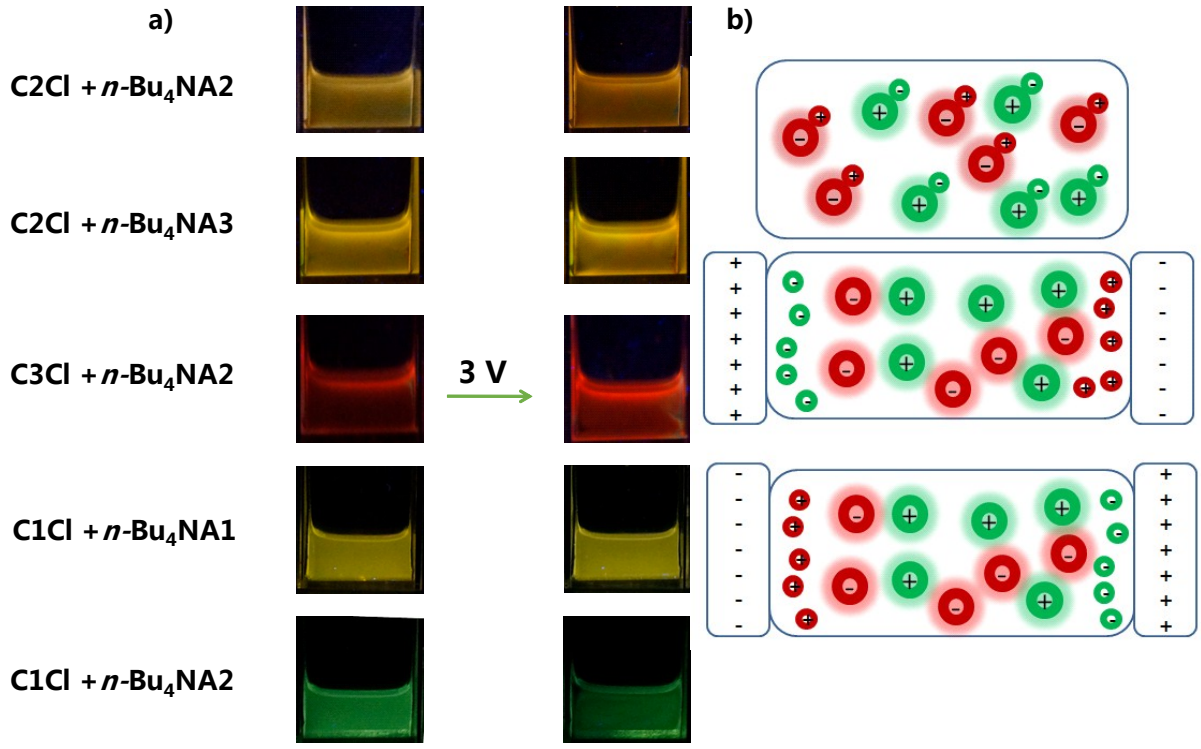


Fig. S6. (a) Photographs of the mixture of positive and negative complexes (equal molar quantity) in acetonitrile (10 μM) before (left) and after (right) applying a voltage of 3 V under excitation at 365 nm. (b) The mechanism diagram to explain the phenomenon of (a).

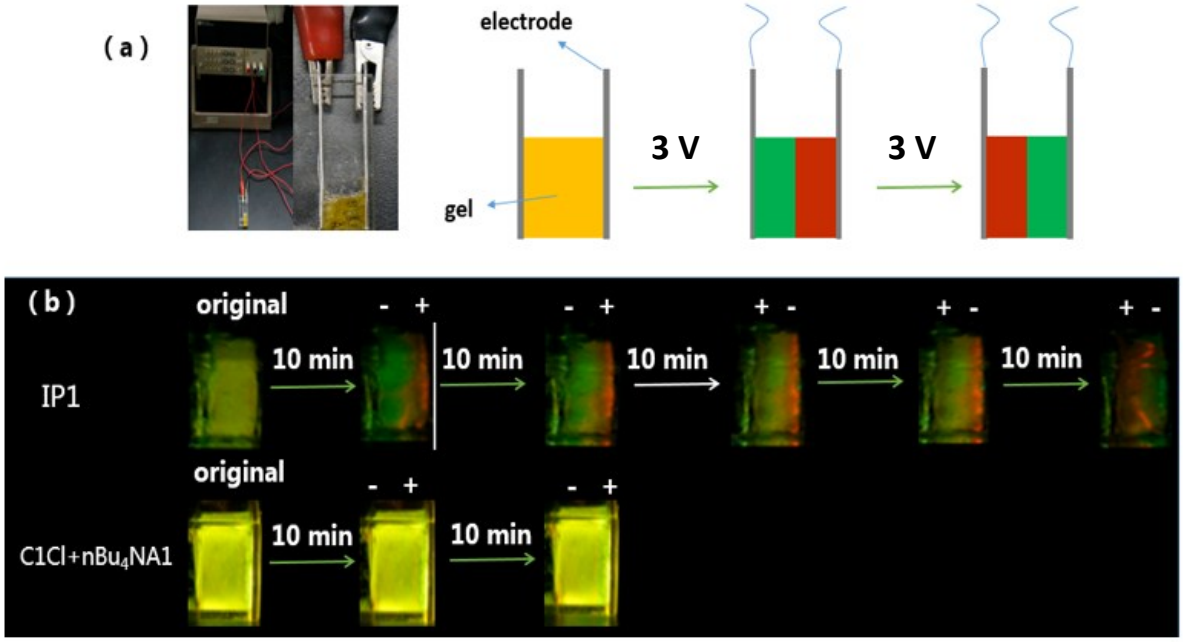
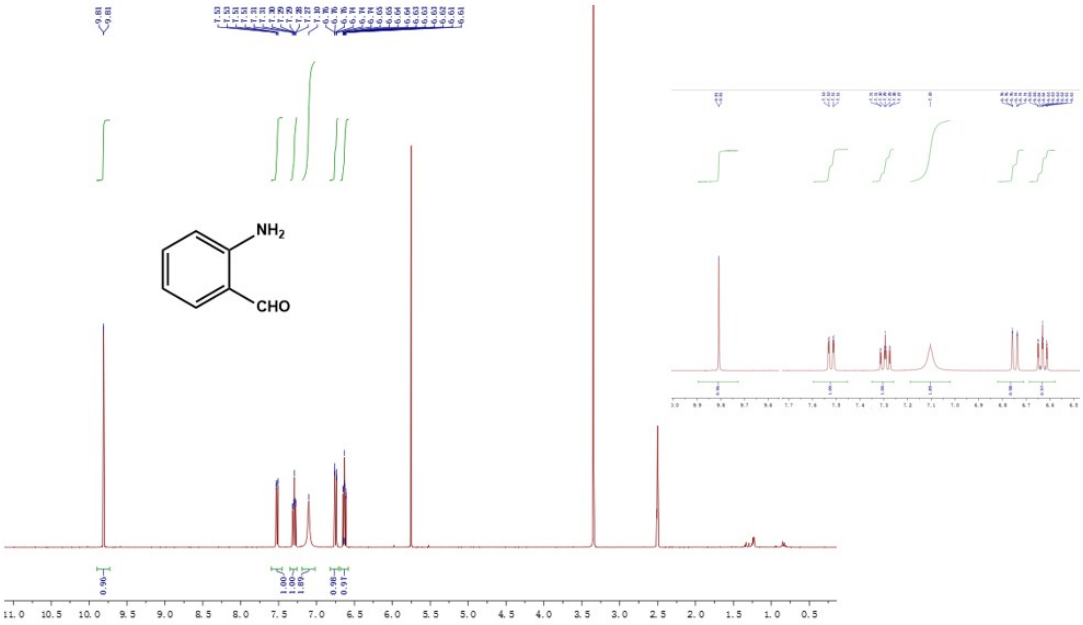
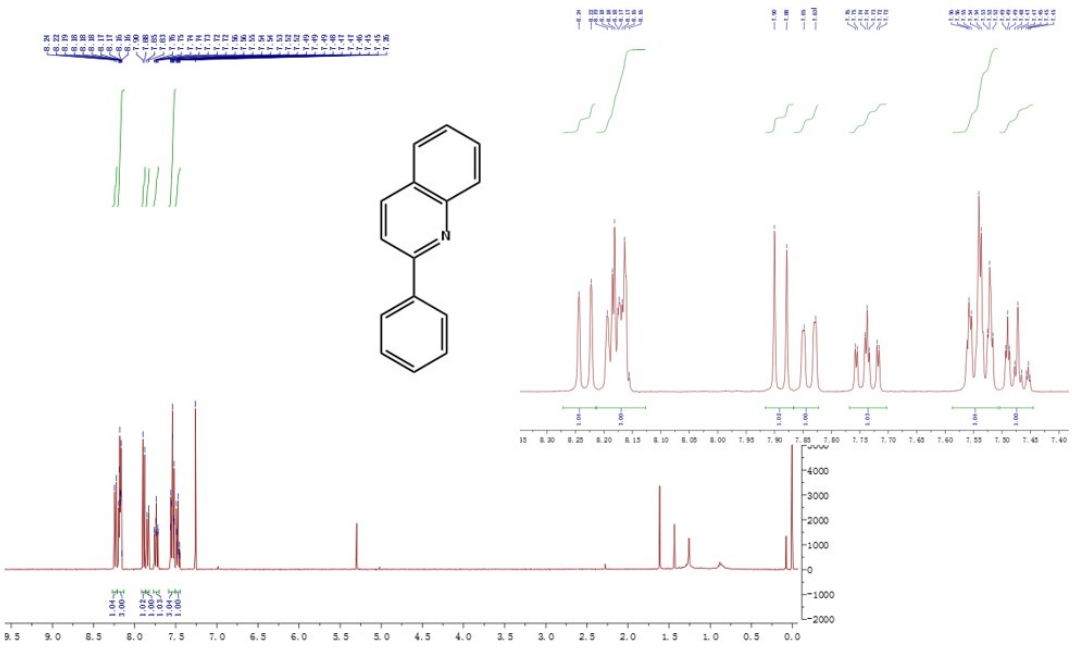
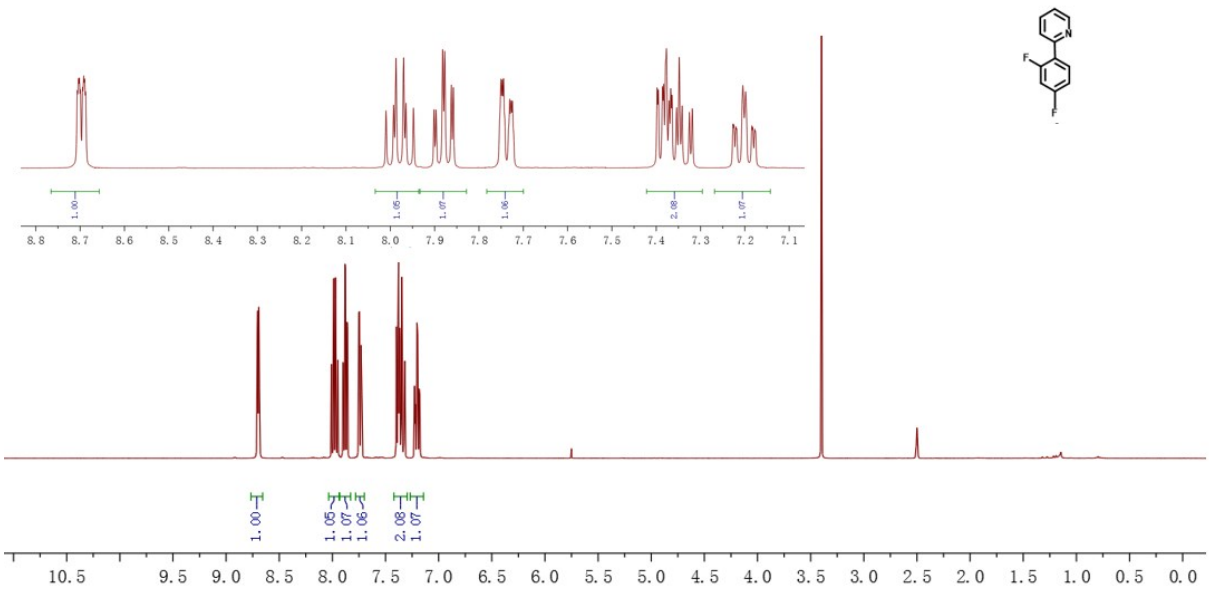


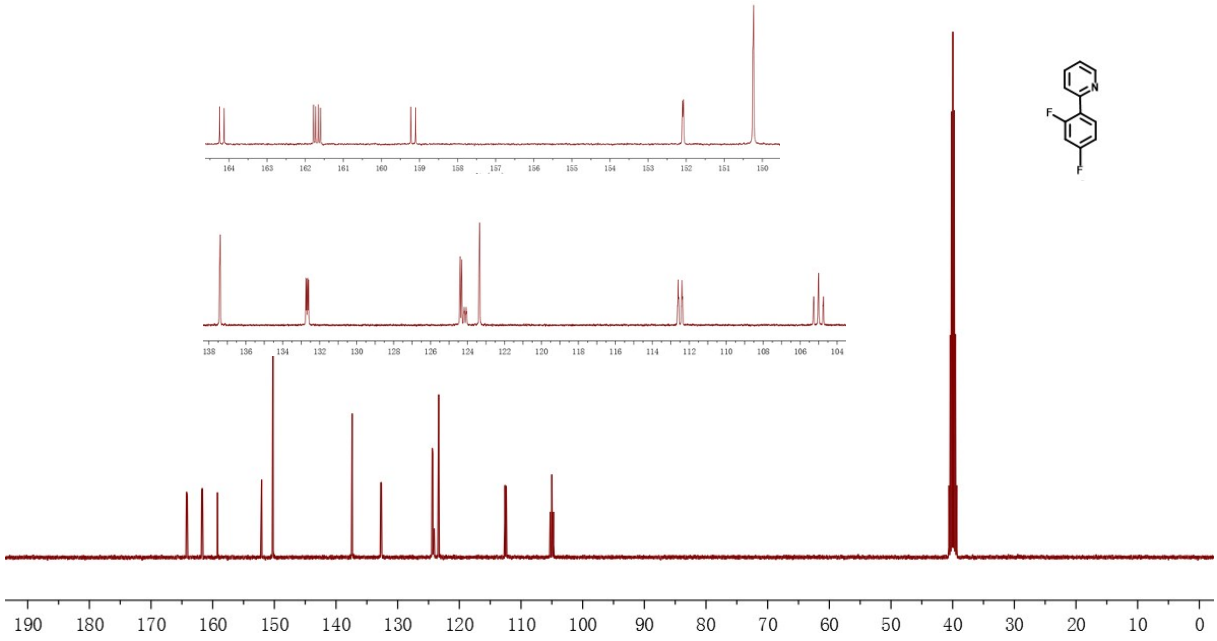
Fig. S7. (a) The schematic diagram of the setup for electrochromic luminescence experiments. (b) Photographs of electrochromic luminescence experiments using quasi-solid film doped with **IP1**.

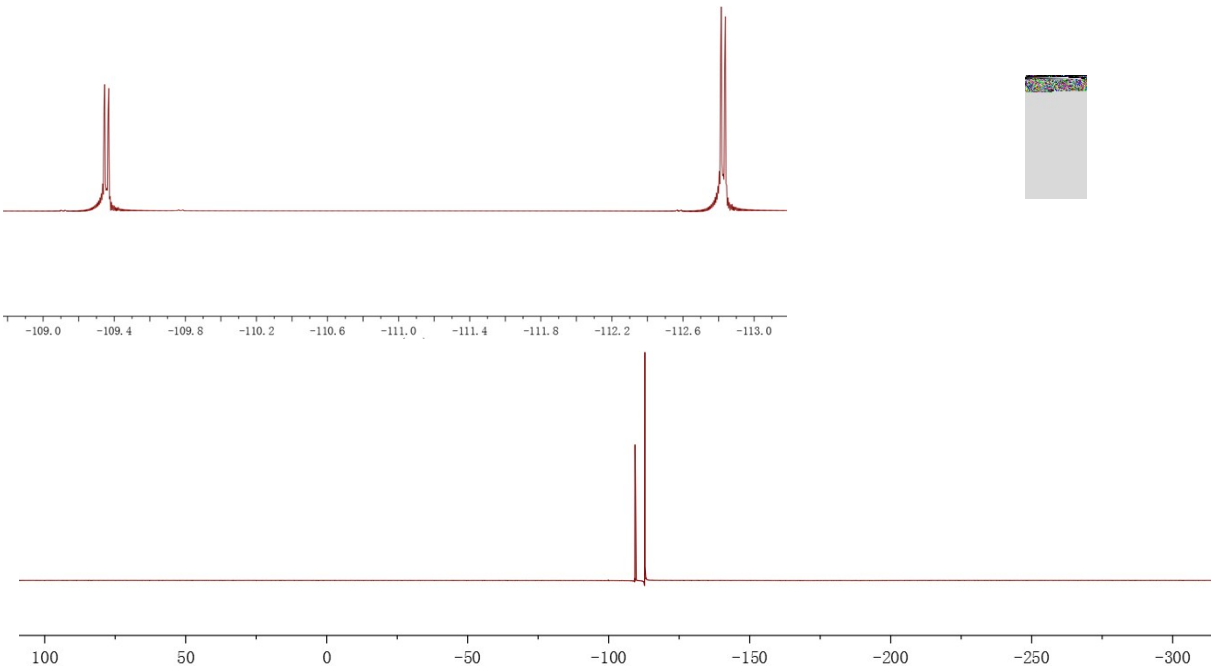
The ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and MS spectra of the compounds.

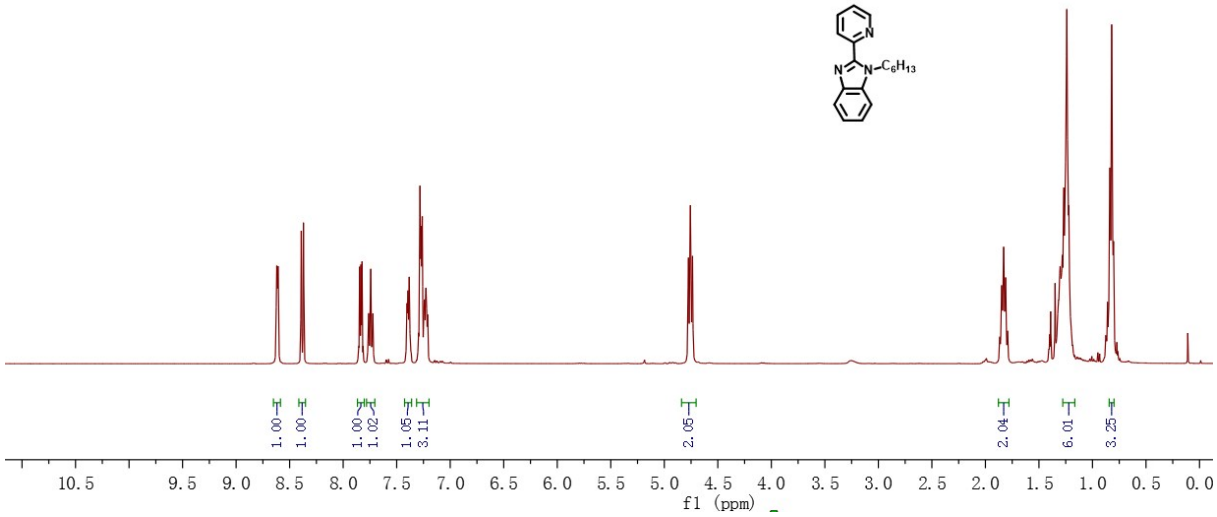


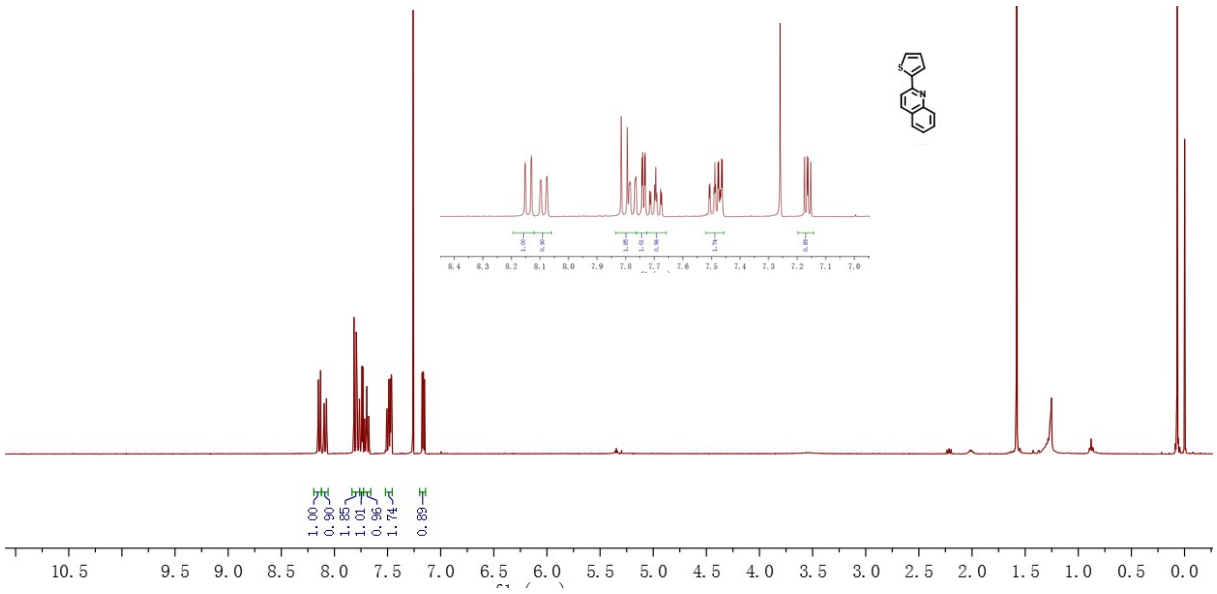

N


F
N
F
1.00
1.05
1.07
1.08
2.08
1.07
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


N
F
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


-109.0
-109.4
-109.8
-110.2
-110.6
-111.0
-111.4
-111.8
-112.2
-112.6
-113.0
100
50
0
-50
-100
-150
-200
-250
-300


N
N
N
C_6H_{13}
1.00
1.00
1.00
1.02
1.05
3.11
2.05
2.04
6.01
3.25
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
f1 (ppm)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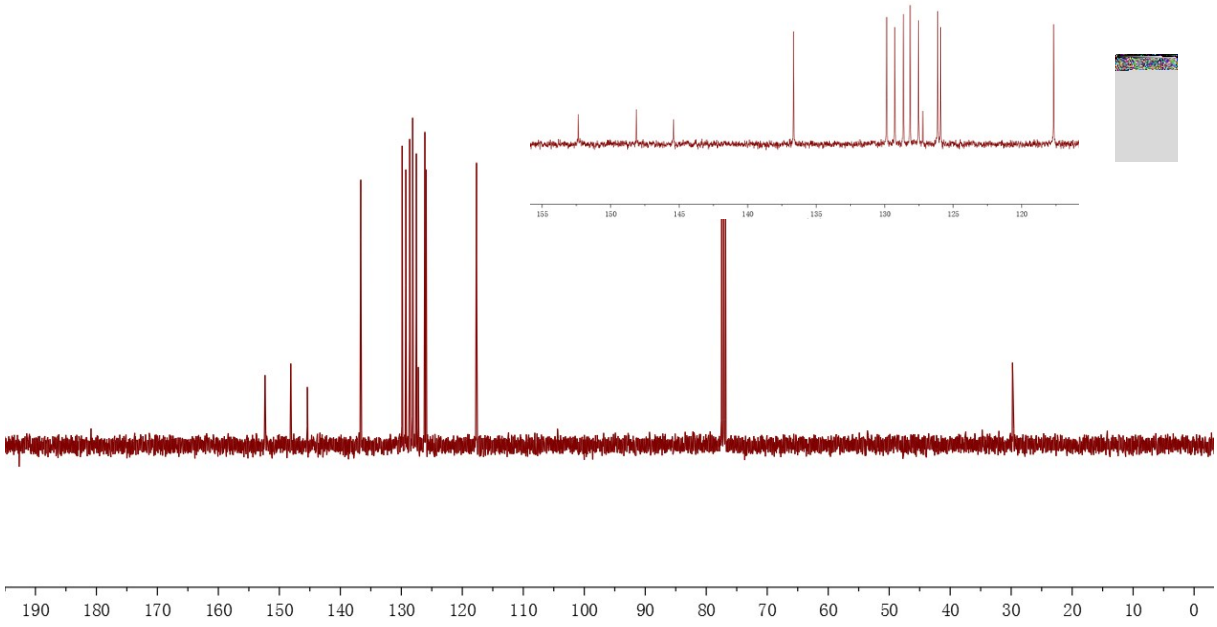
0.90
1.85
1.01
0.96
1.74
0.89
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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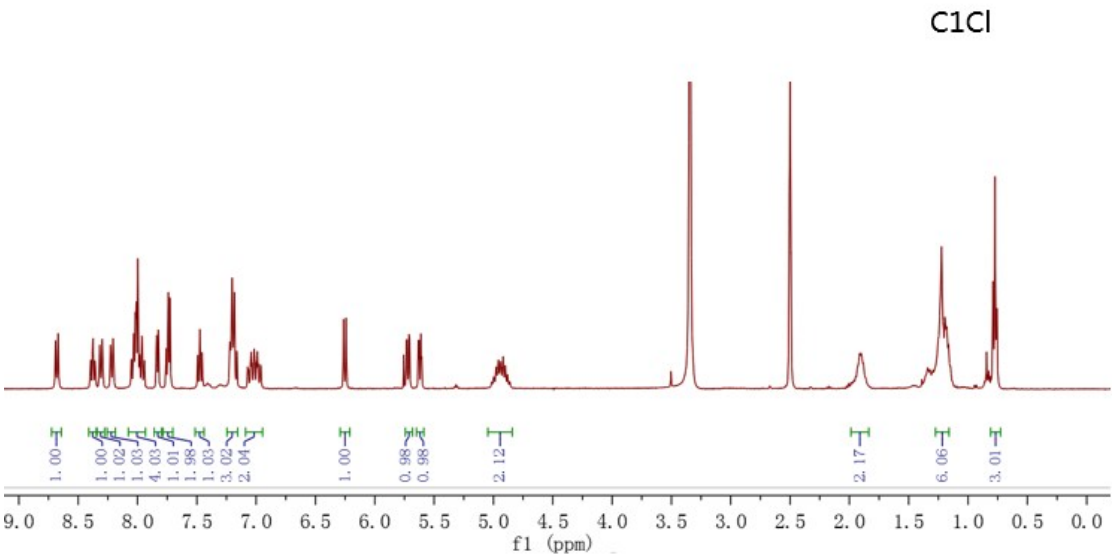
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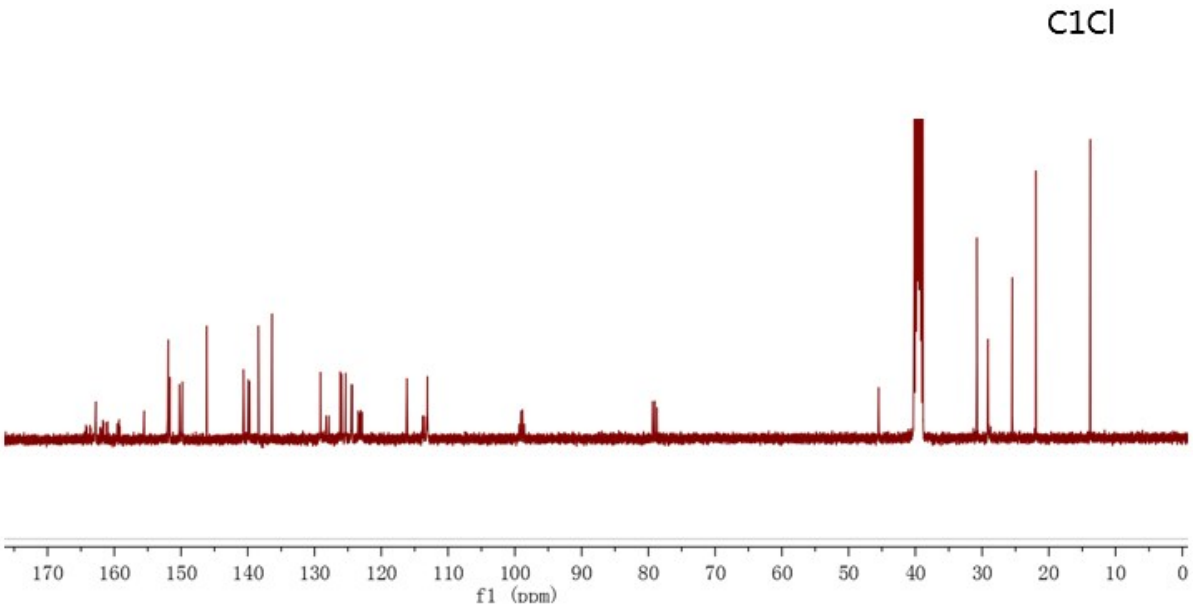
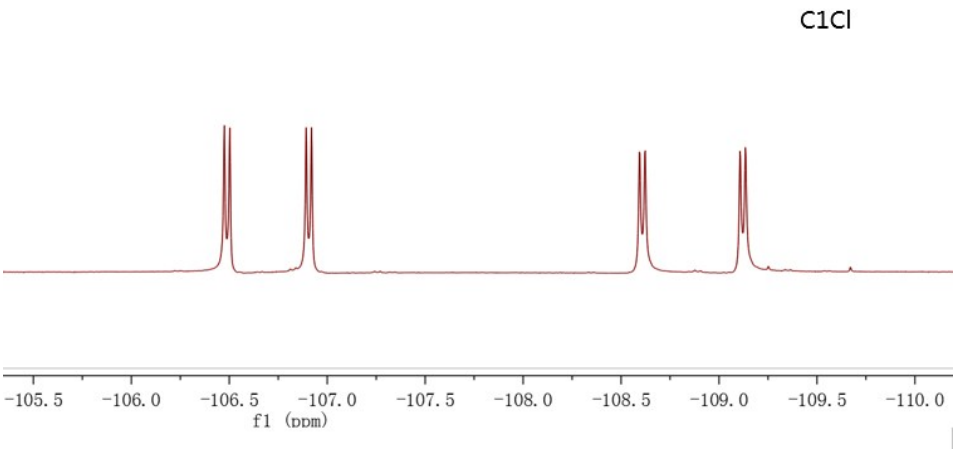
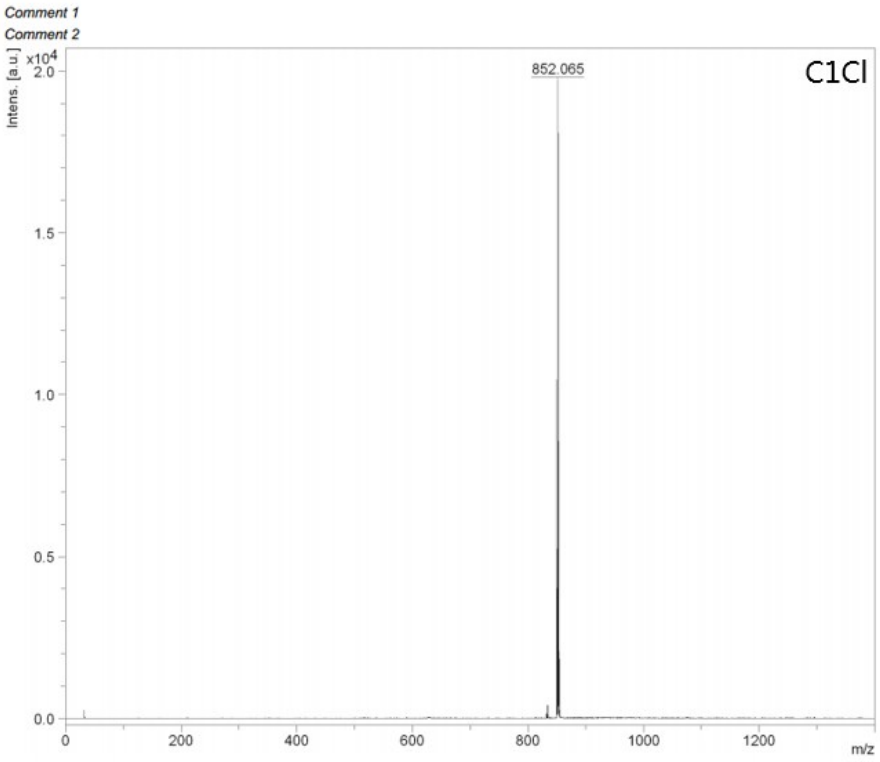
1.00
1.00
1.02
1.03
4.03
1.01
1.98
1.03
3.02
2.04
1.00
0.98
0.98
2.12
2.17
6.06
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

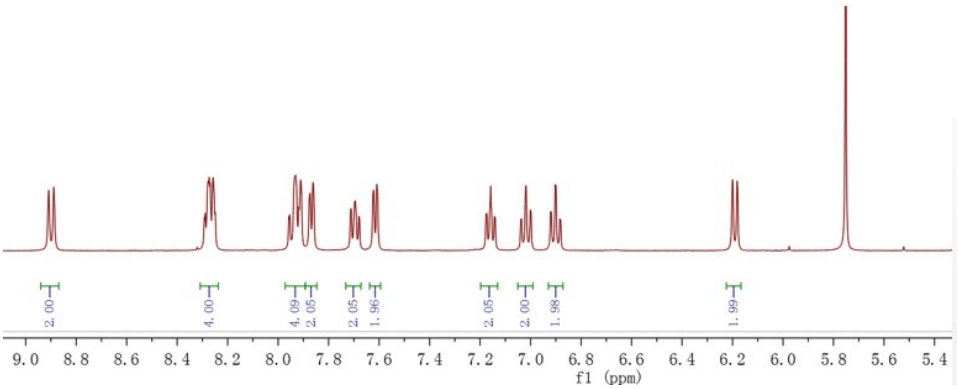

C1Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

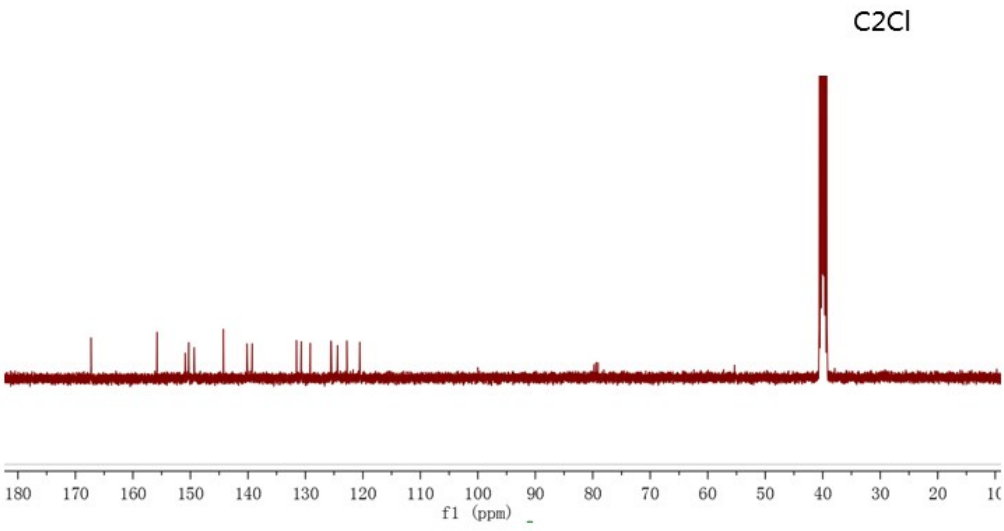


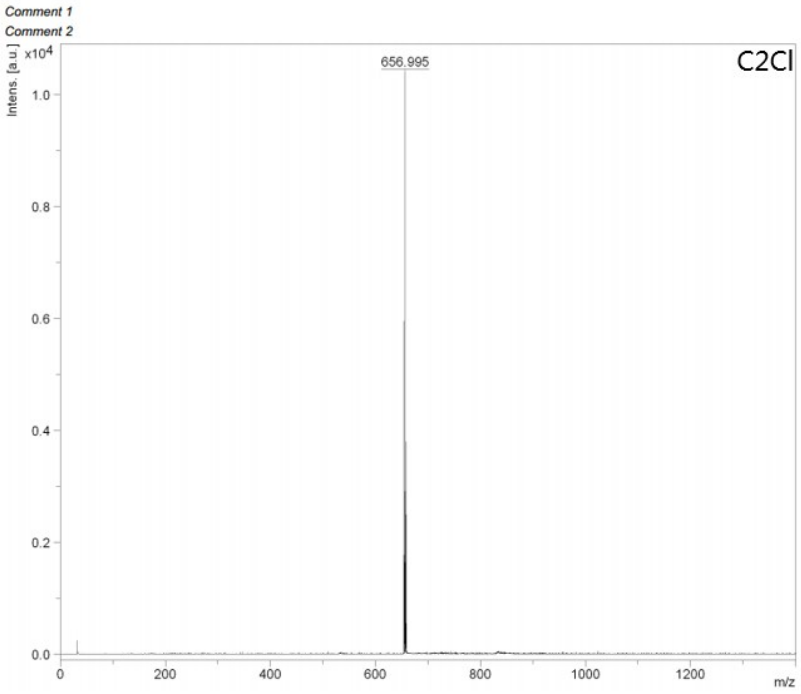
$^{19}F\{^{1}H\}$NMR (377 M)


Comment 1
Comment 2
Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
0.0
852.065
C1Cl
0
200
400
600
800
1000
1200
m/z

C2Cl


2.00
4.00
4.09
2.05
2.05
1.96
2.05
2.00
1.98
1.99
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4
f1 (ppm)


C2Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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Comment 2
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x10^4
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0.8
0.6
0.4
0.2
0.0
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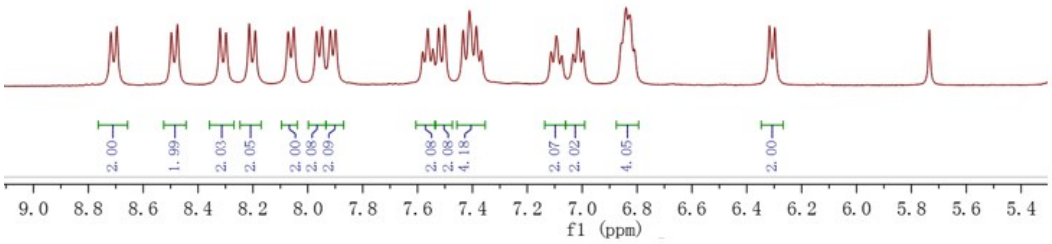
C2Cl
0
200
400
600
800
1000
1200
m/z

C3Cl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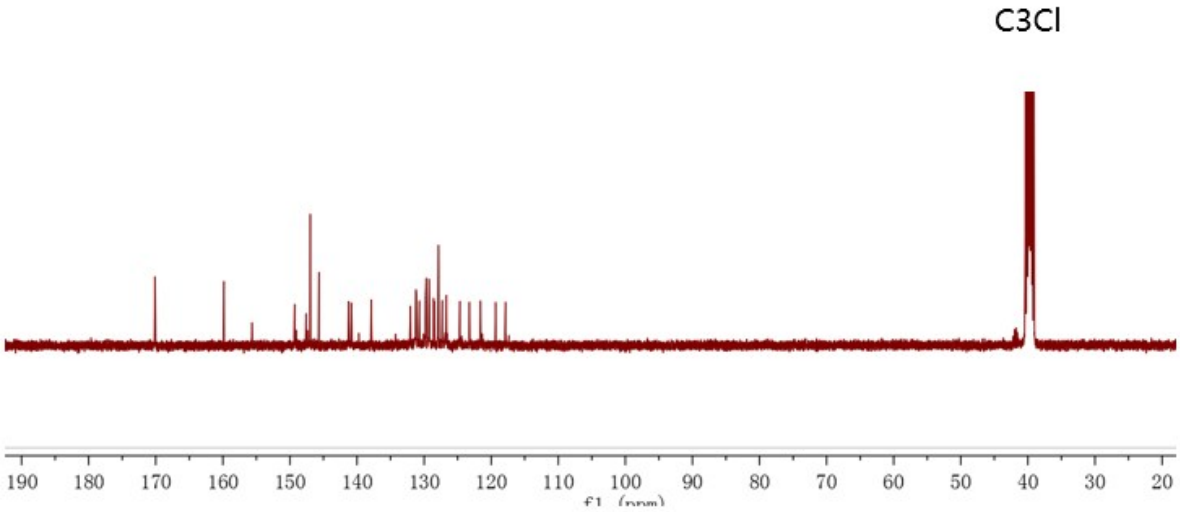
2.03
2.05
2.00
2.08
2.09
2.08
2.08
4.18
2.07
2.02
4.05
2.00
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4
f1 (ppm)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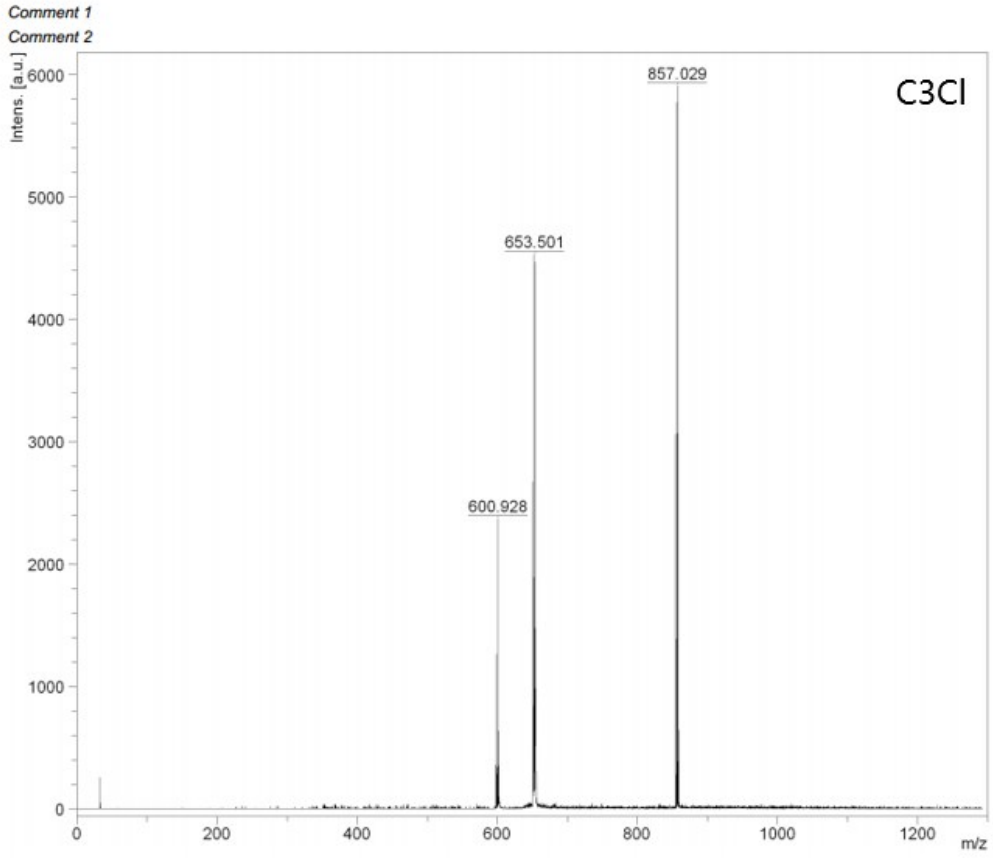
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


Comment 1
Comment 2
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5000
4000
3000
2000
1000
0
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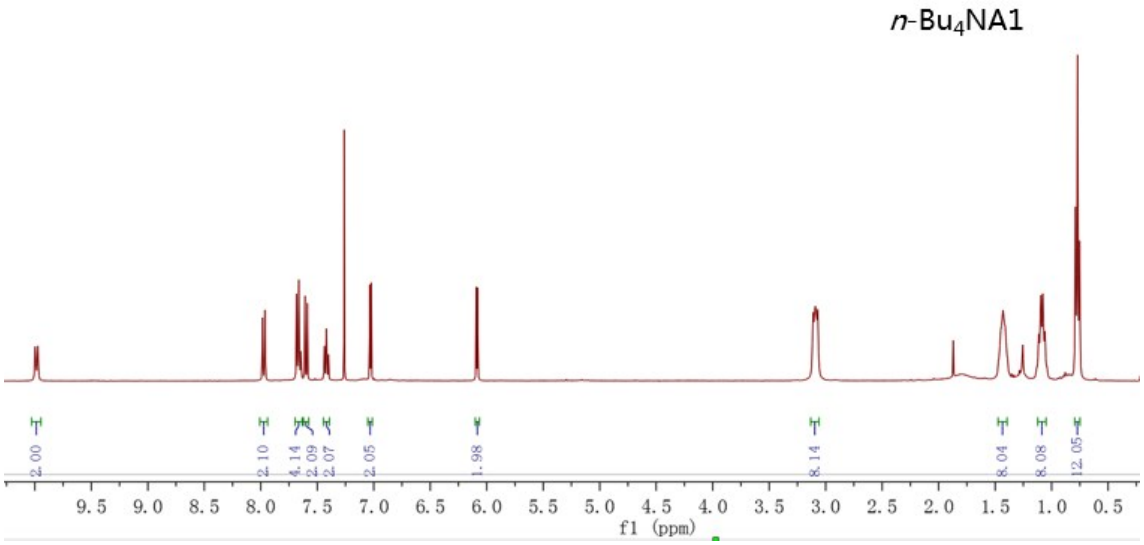
600.928
C3Cl
0
200
400
600
800
1000
1200
m/z


n-Bu4NA1
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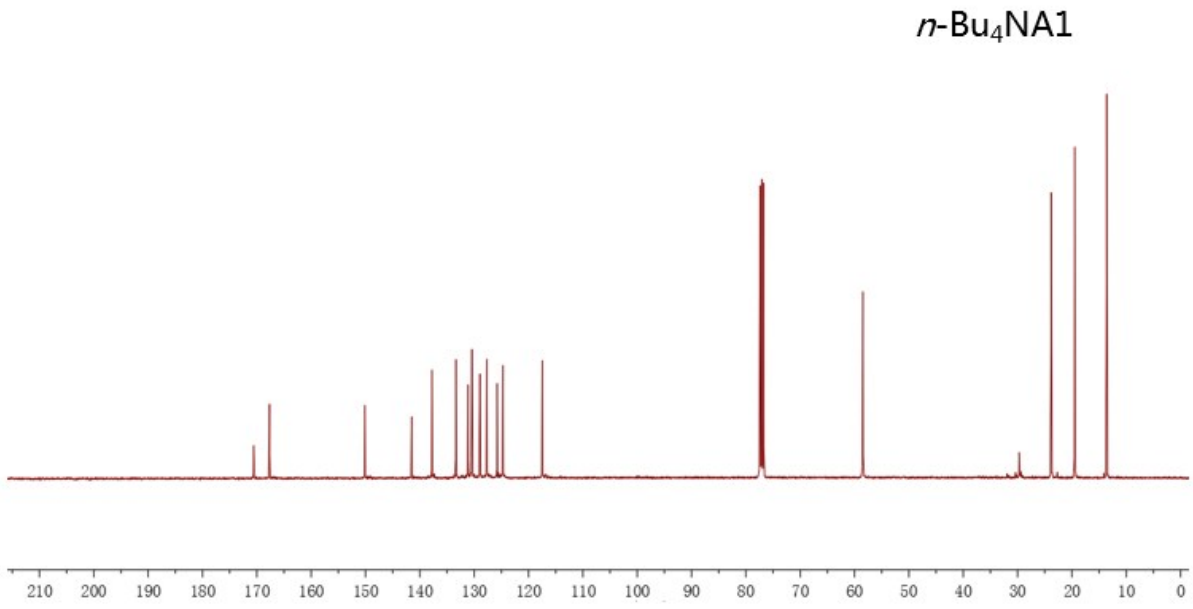
2.10
4.14
2.09
2.07
2.05
1.98
8.14
8.04
8.08
12.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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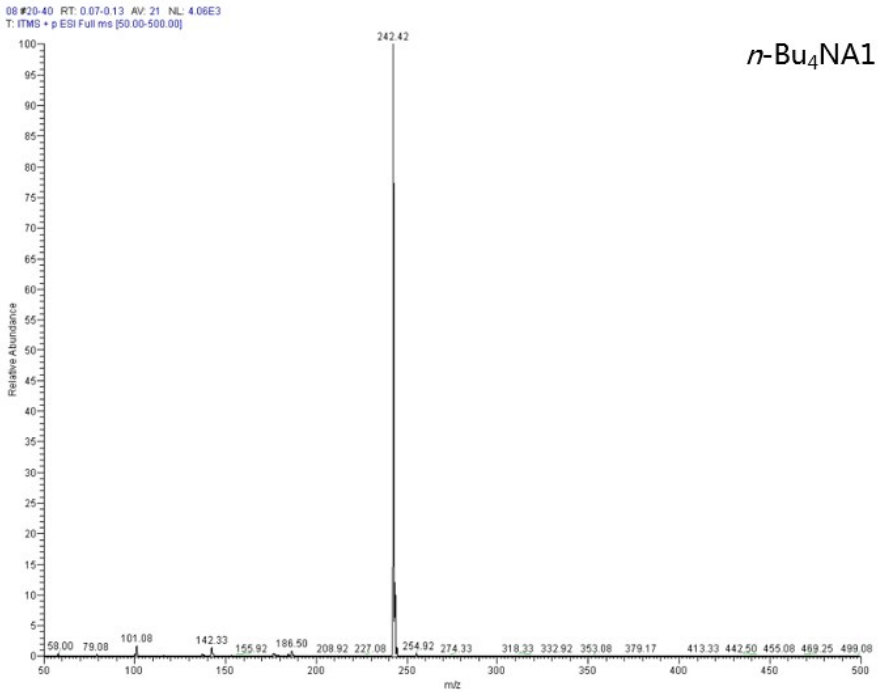
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T: ITMS + p ESI Full ms [50.00-500.00]
242.42
Relative Abundance
m/z
58.00
79.08
101.08
142.33
155.92
186.50
208.92
227.08
254.92
274.33
318.33
332.92
353.08
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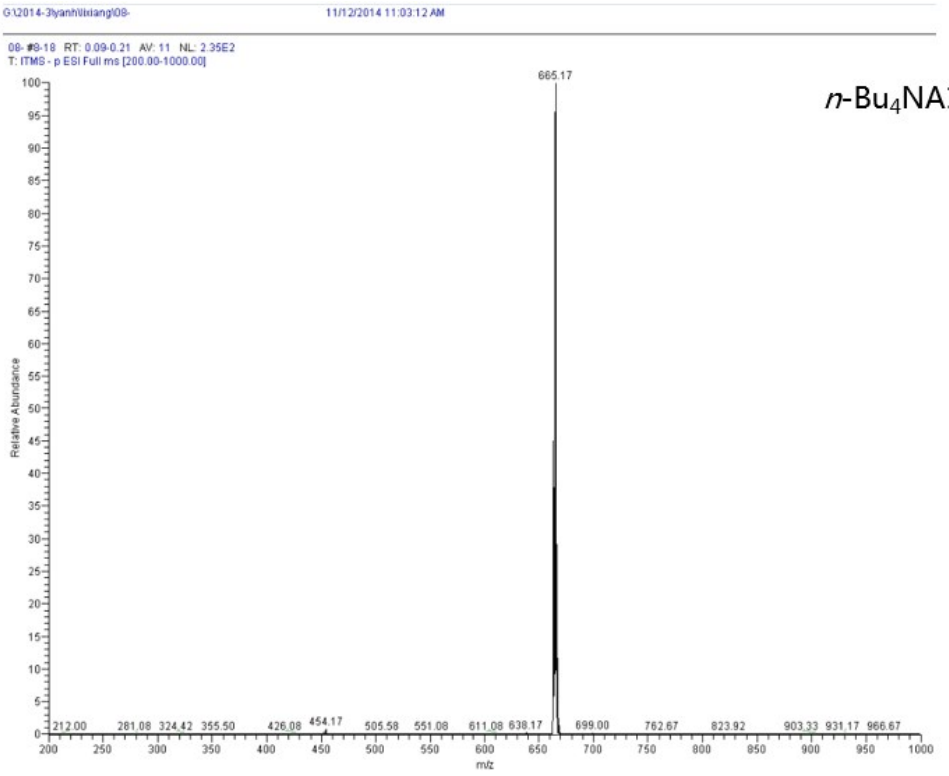
442.50
455.08
469.25
499.08

n-Bu_4NA1


G:\2014-3\yanhl\lixiang\08-
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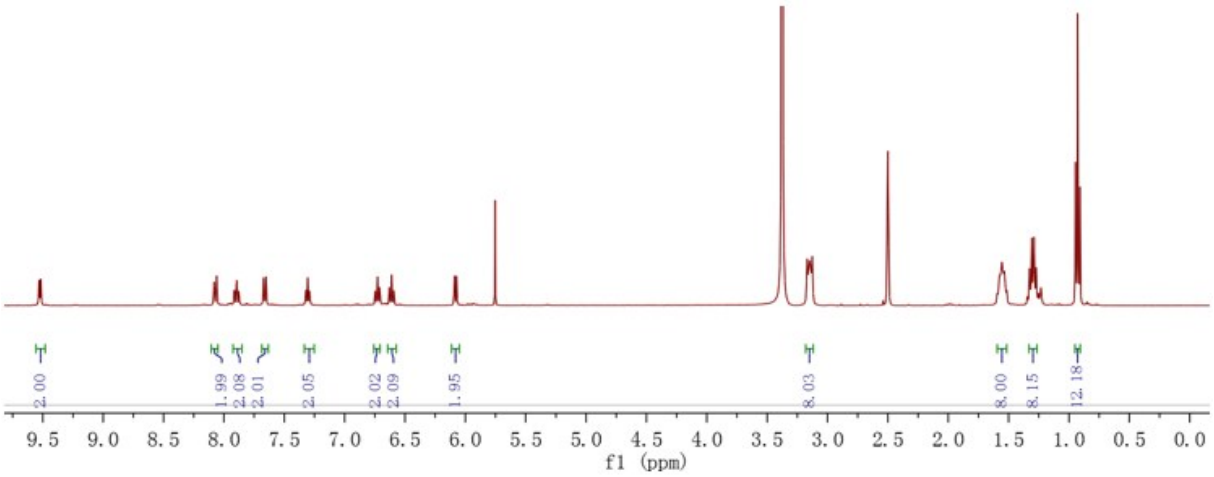
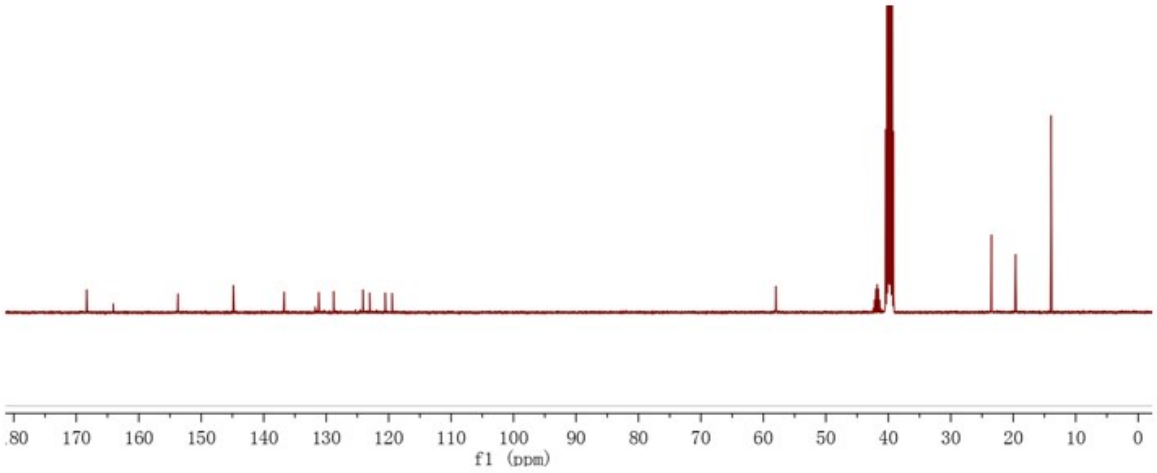
T: ITMS - p ESI Full ms [200.00-1000.00]
n-Bu4NA1
665.17
Relative Abundance
m/z
212.00
281.08
324.42
355.50
426.08
454.17
505.58
551.08
611.08
638.17
699.00
762.67
823.92
903.33
931.17
966.67

n-Bu_4NA2


2.00
1.99
1.08
2.01
2.05
2.02
2.09
1.95
8.03
8.00
8.15
12.18
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
f1 (ppm)

n-Bu_4NA2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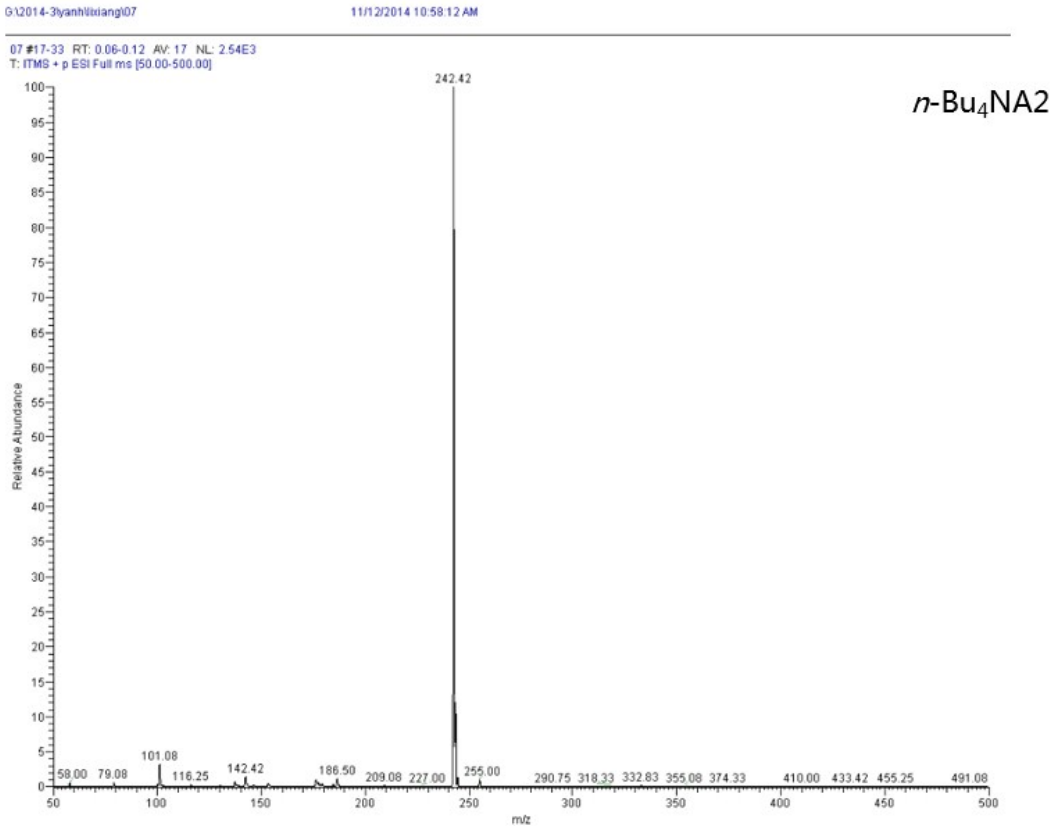
f1 (ppm)


G:\2014-3\yanh\lixiang\07
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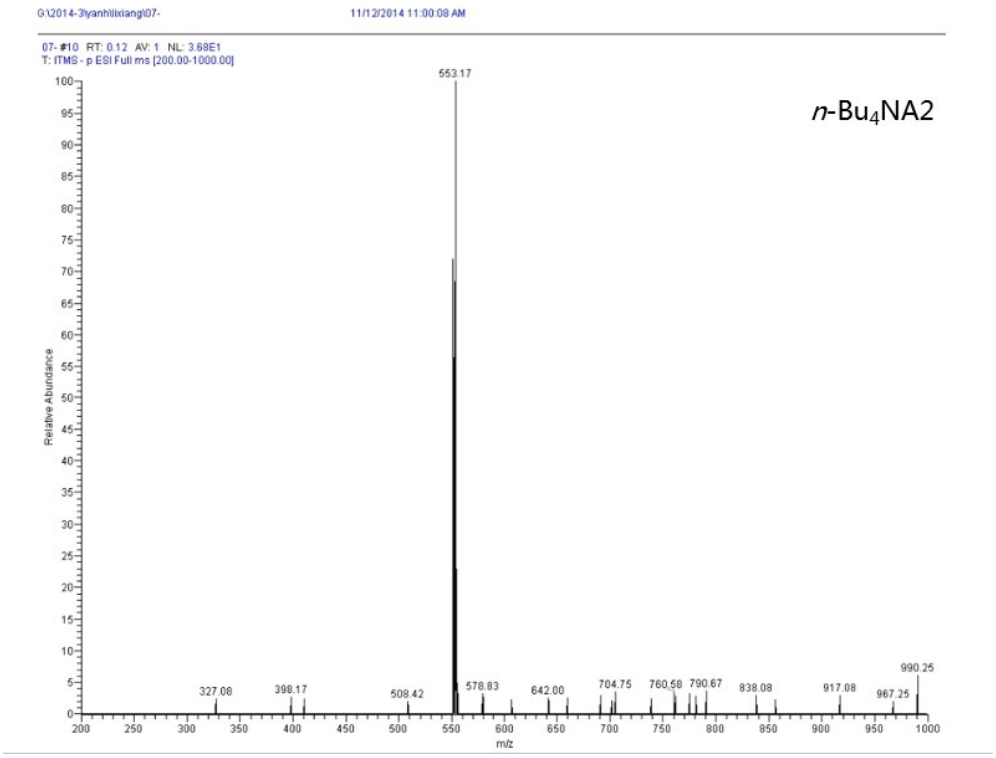
T: ITMS + p ESI Full ms [50.00-500.00]
n-Bu4NA2
Relative Abundance
m/z
242.42
101.08
142.42
186.50
255.00
58.00
79.08
116.25
209.08
227.00
290.75
318.33
332.83
355.08
374.33
410.00
433.42
455.25
491.08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11/12/2014 11:00:08 AM
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n-Bu4NA2
Relative Abundance
m/z
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398.17
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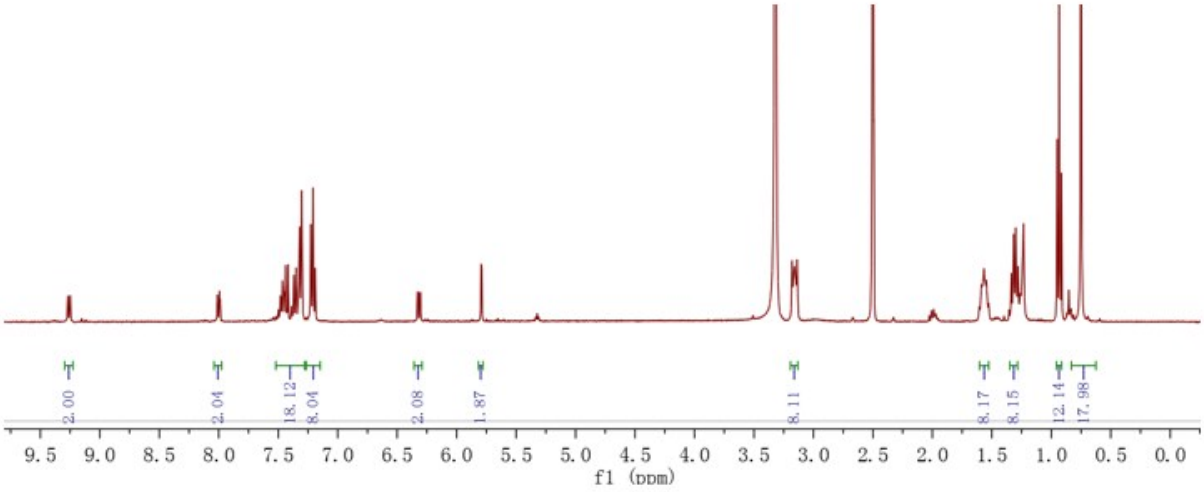
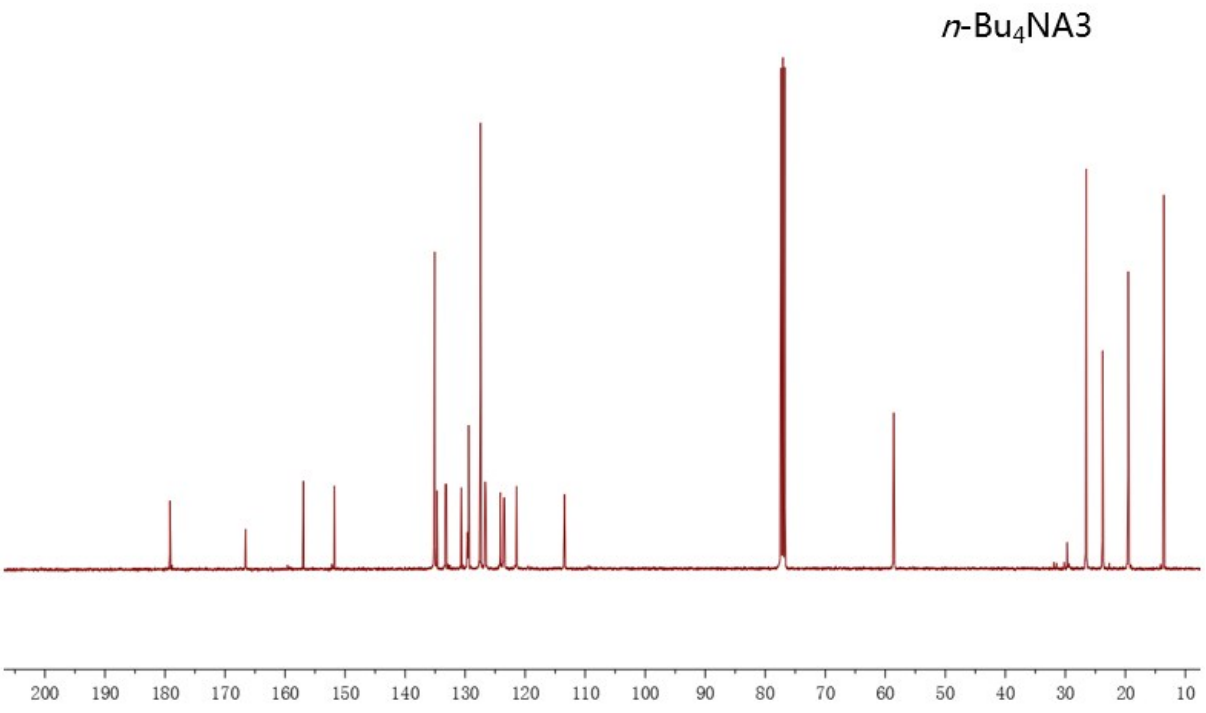
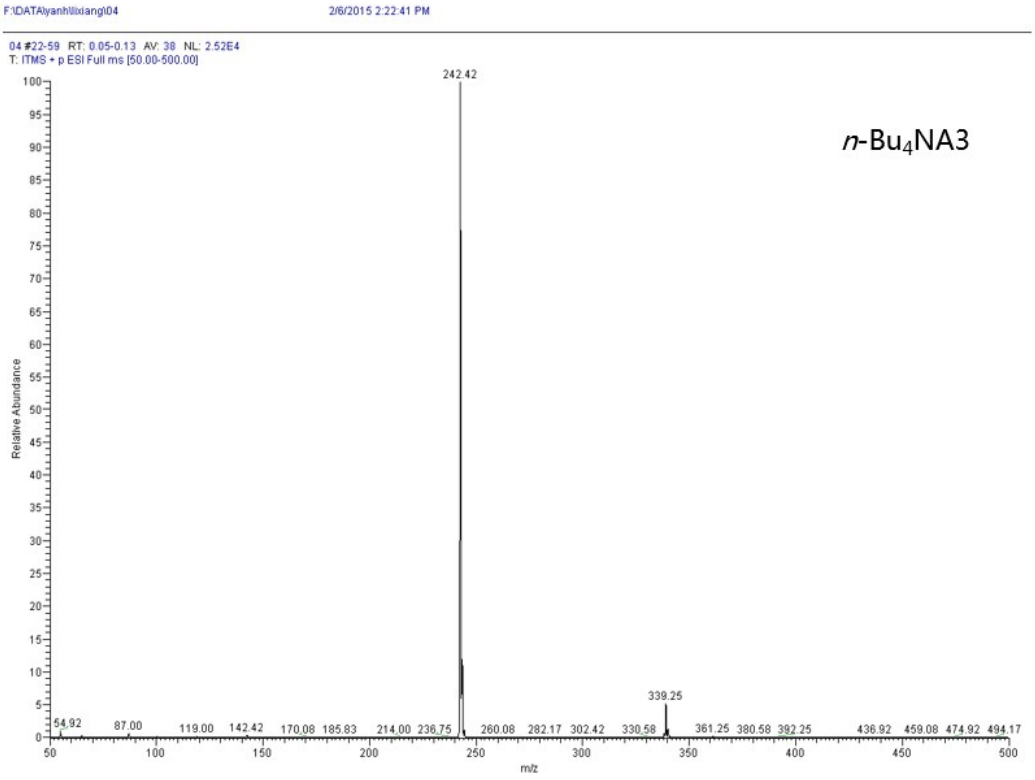
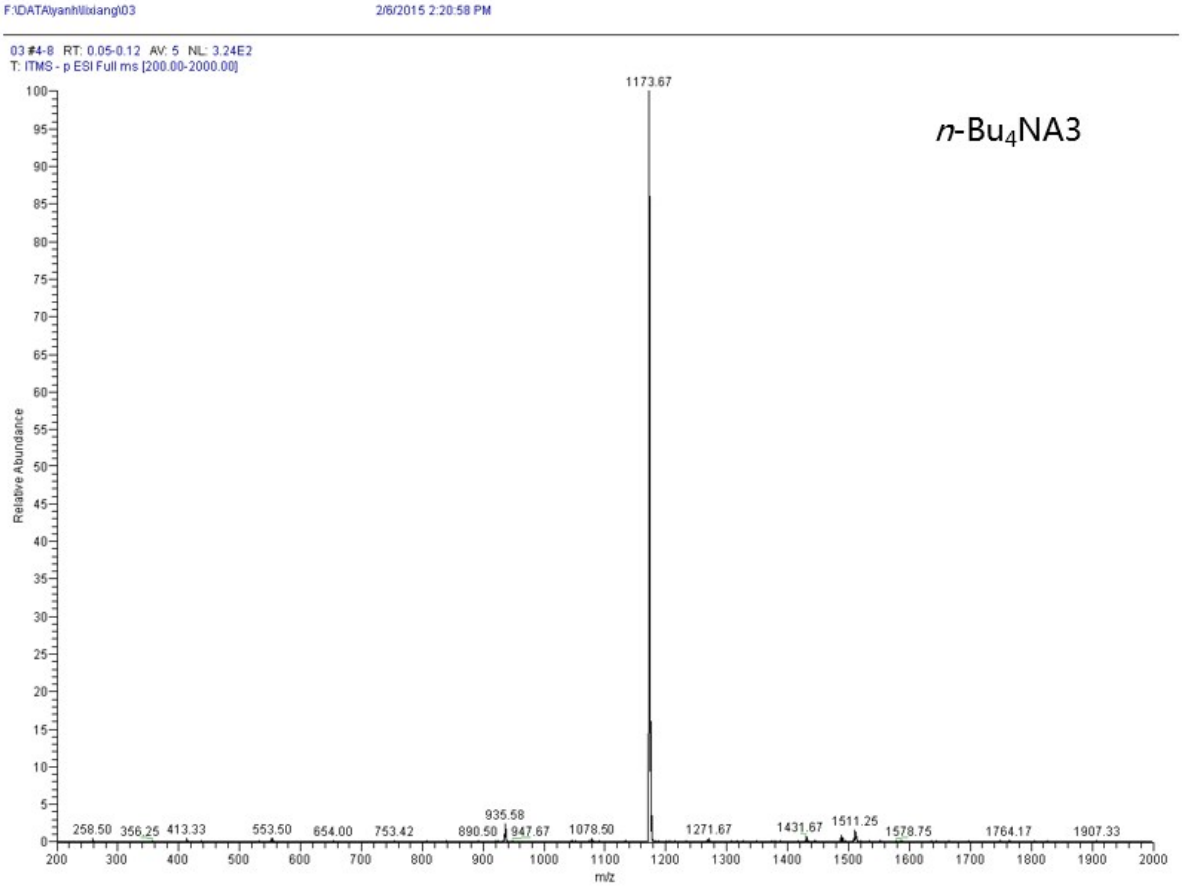
838.08
917.08
967.25
990.25

n-Bu_4NA3

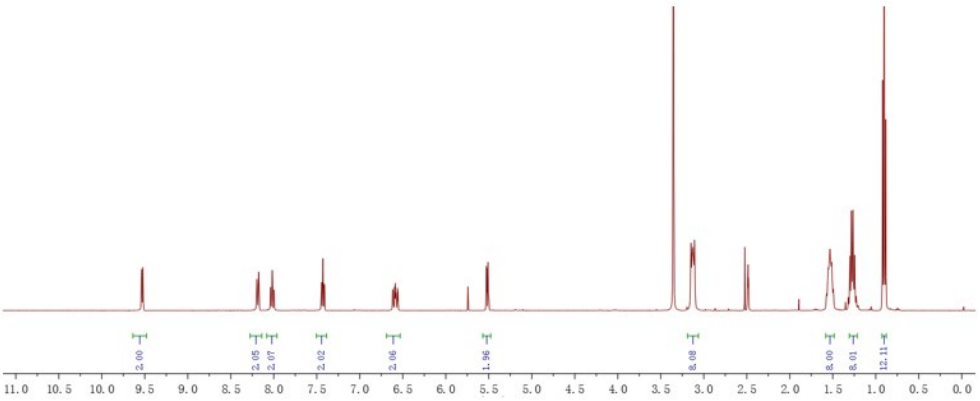

2.00
2.04
18.12
8.04
2.08
1.87
8.11
8.17
8.15
12.14
17.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

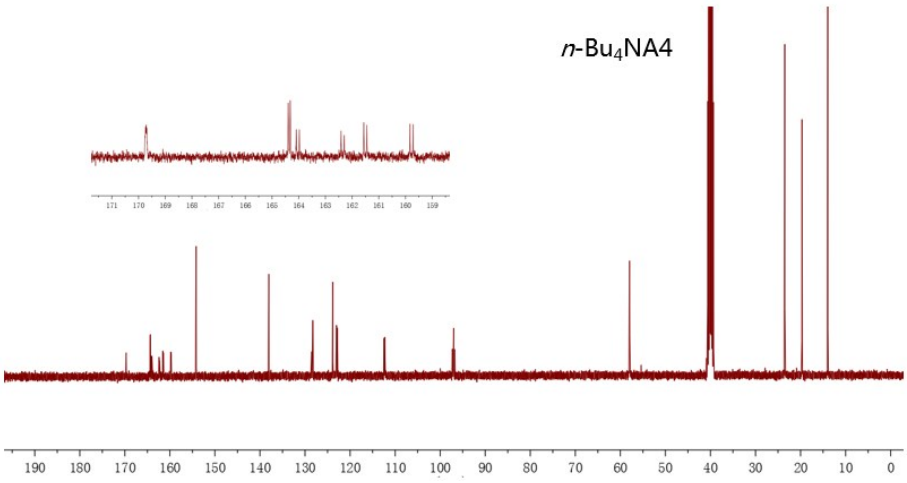

n-Bu4NA3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

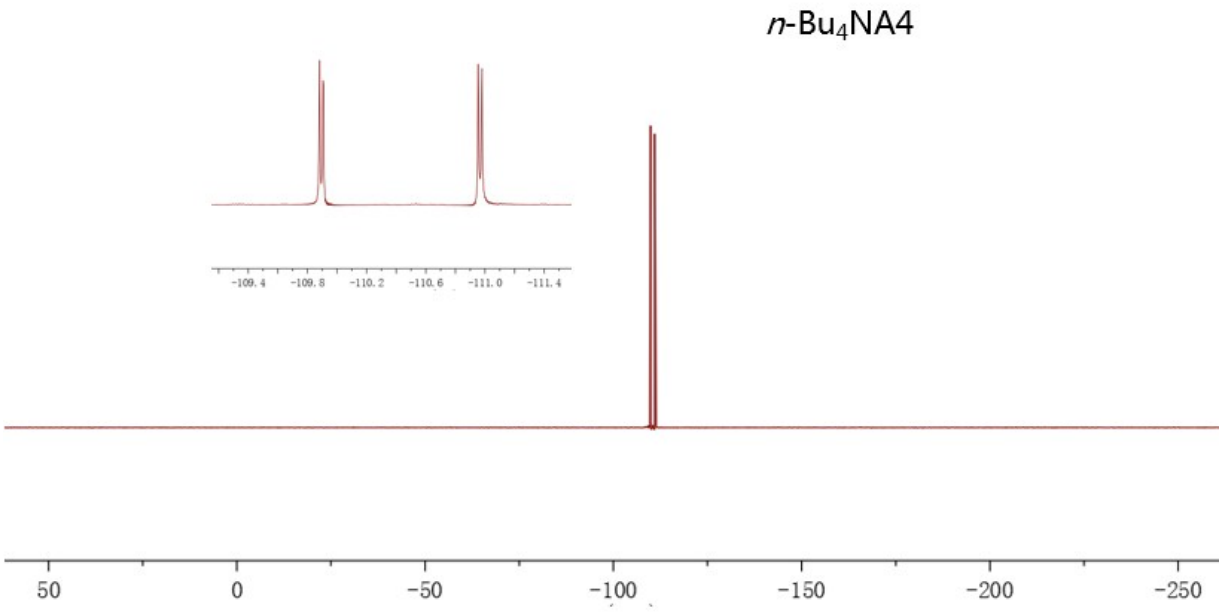

F:\DATA\yanh\lixiang\04
2/6/2015 2:22:41 PM
04 #22-59 RT: 0.05-0.13 AV: 38 NL: 2.52E4
T: ITMS + p ESI Full ms [50.00-500.00]
242.42
339.25
n-Bu4NA3
Relative Abundance
m/z


F:\DATA\yanh\lixiang\03
2/6/2015 2:20:58 PM
03 #4-8 RT: 0.05-0.12 AV: 5 NL: 3.24E2
T: ITMS - p ESI Full ms [200.00-2000.00]
n-Bu4NA3
1173.67
935.58
258.50
356.25
413.33
553.50
654.00
753.42
890.50
947.67
1078.50
1271.67
1431.67
1511.25
1578.75
1764.17
1907.33
Relative Abundance
m/z

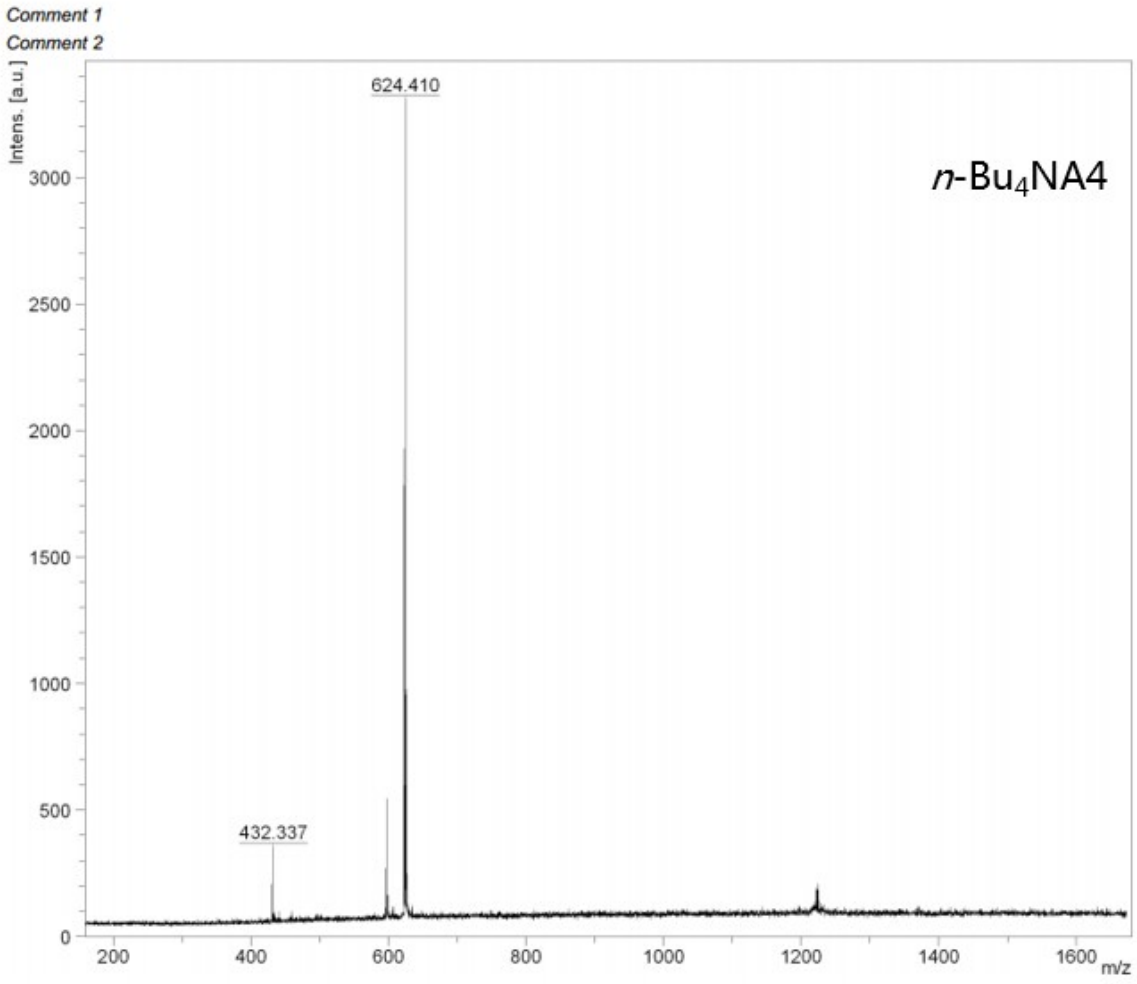
n-Bu_4NA4


2.00
2.05
2.07
2.02
2.06
1.96
8.08
8.00
8.01
12.11
11.0 10.5 10.0 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

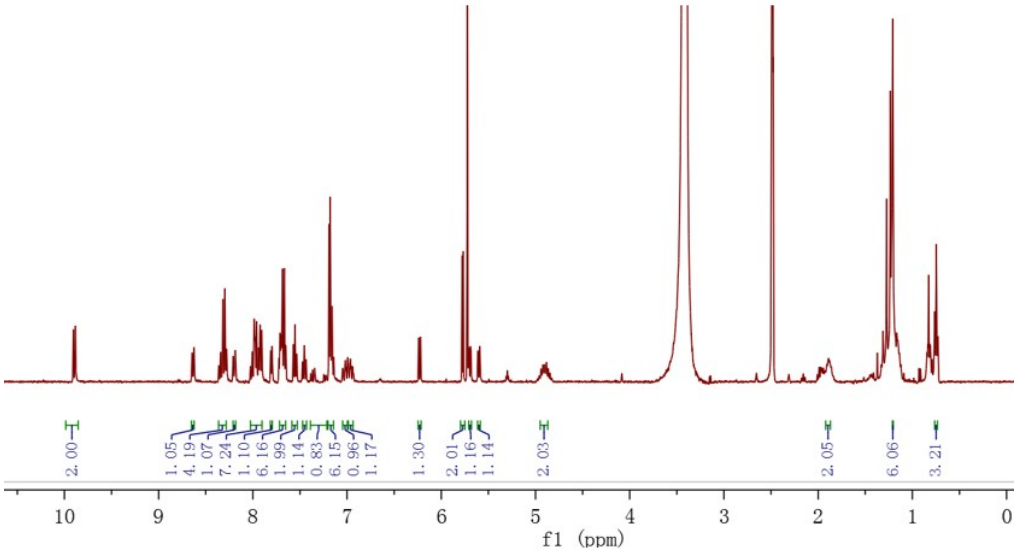

n-Bu4NA4
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

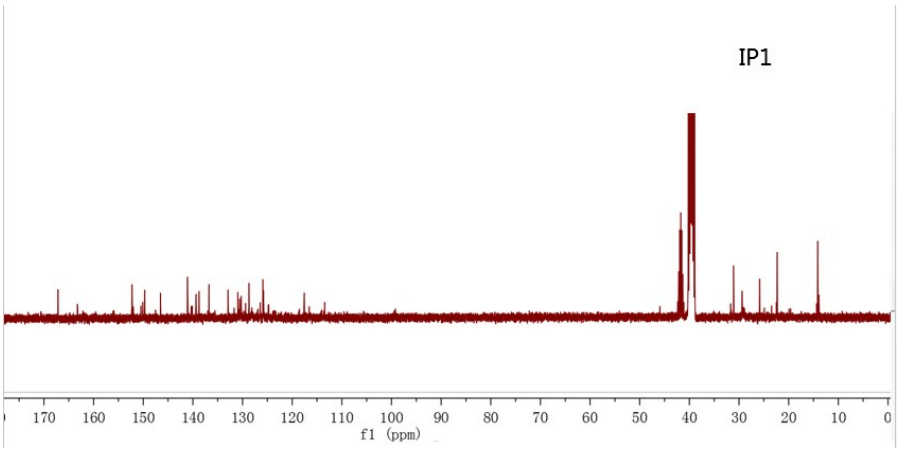


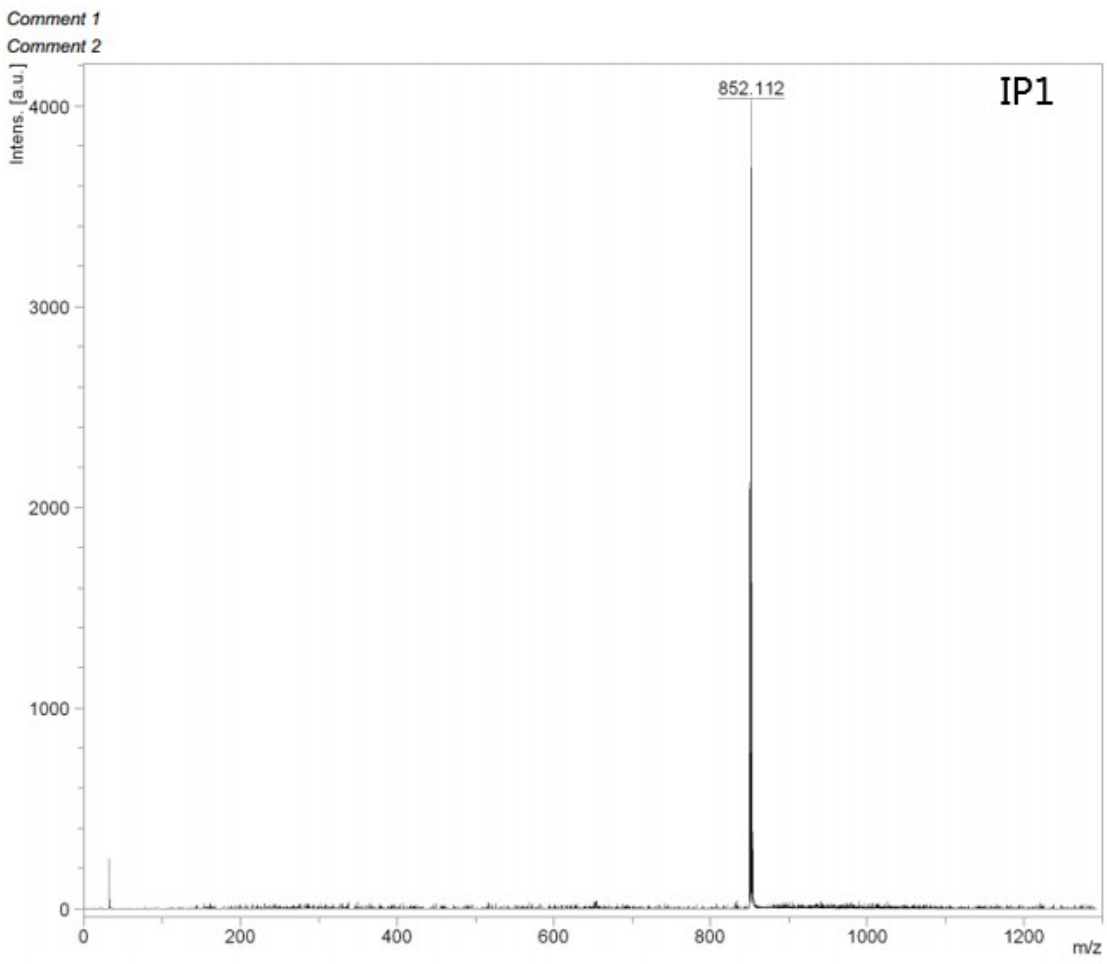
$^{19}F\{^{1}H\}$ NMR (377 M)

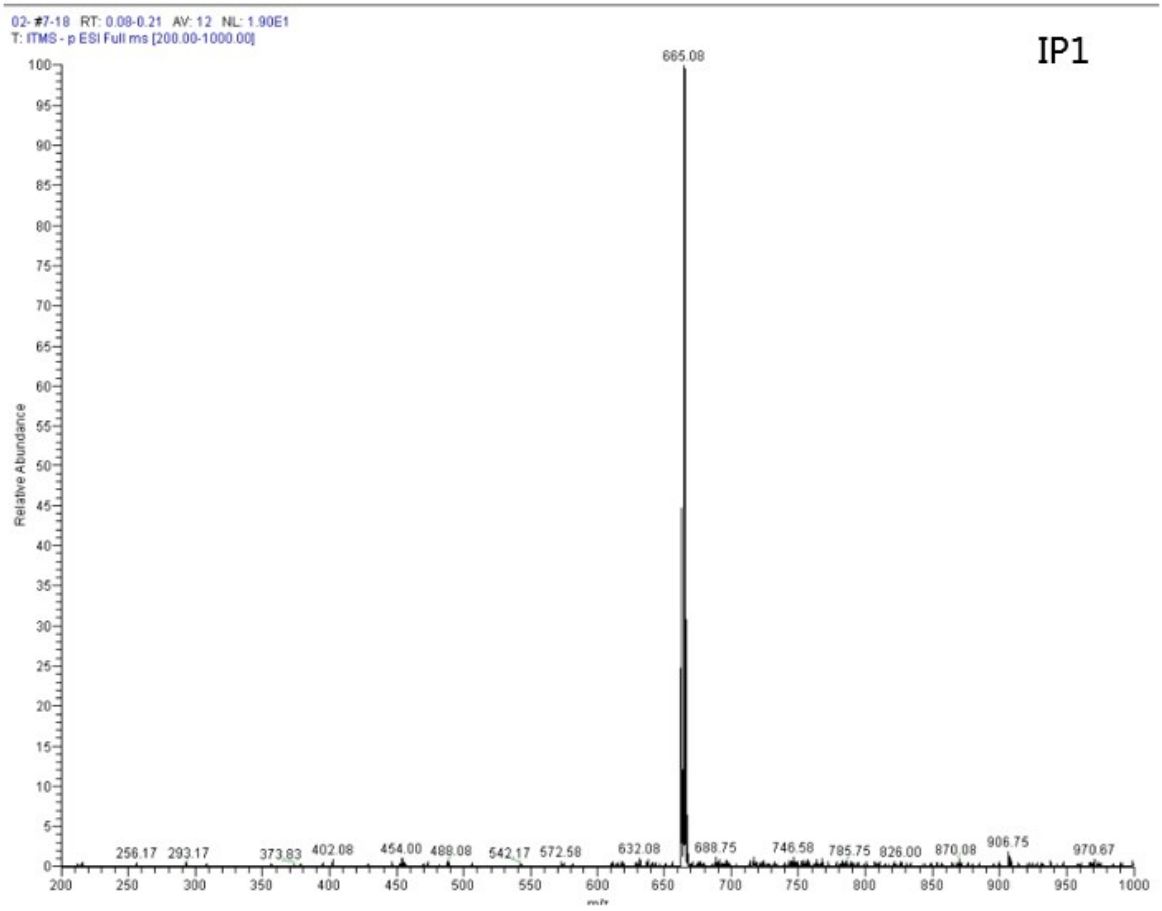

Comment 1
Comment 2
Intens. [a.u.]
624.410
n-Bu4NA4
432.337
3000
2500
2000
1500
1000
500
0
200
400
600
800
1000
1200
1400
1600
m/z

IP1

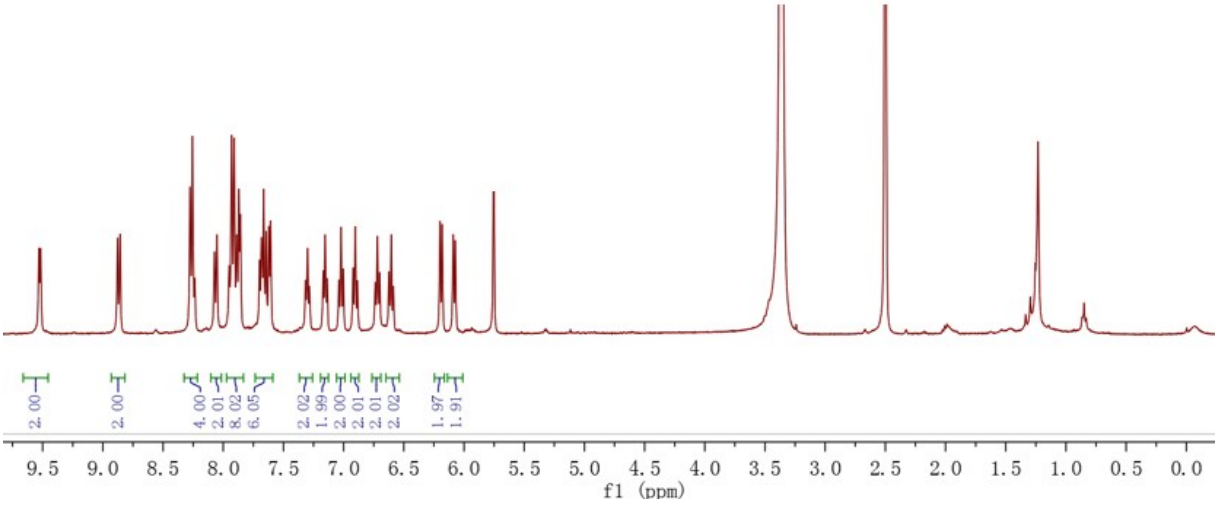

2.00
1.05
4.19
1.07
7.24
1.10
6.16
1.99
1.14
0.83
6.15
0.96
1.17
1.30
2.01
1.16
1.14
2.03
2.05
6.06
3.21
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

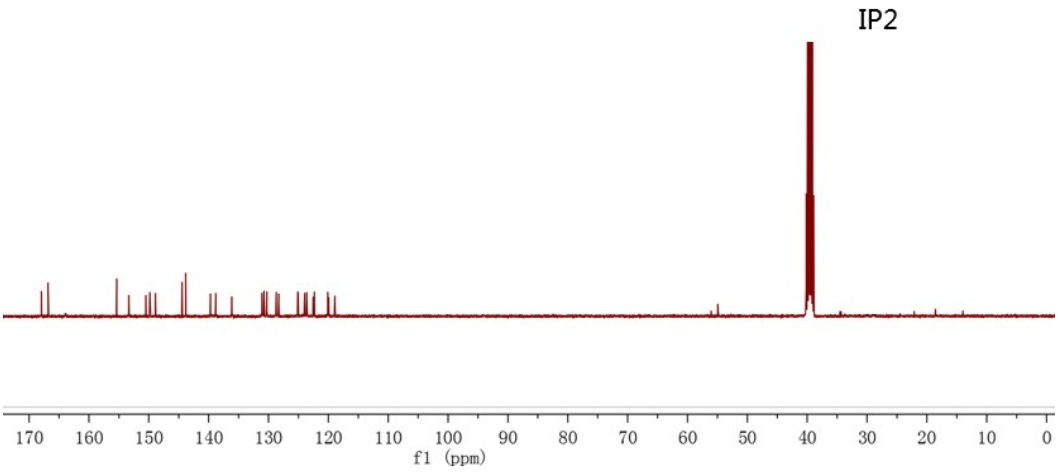

IP1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

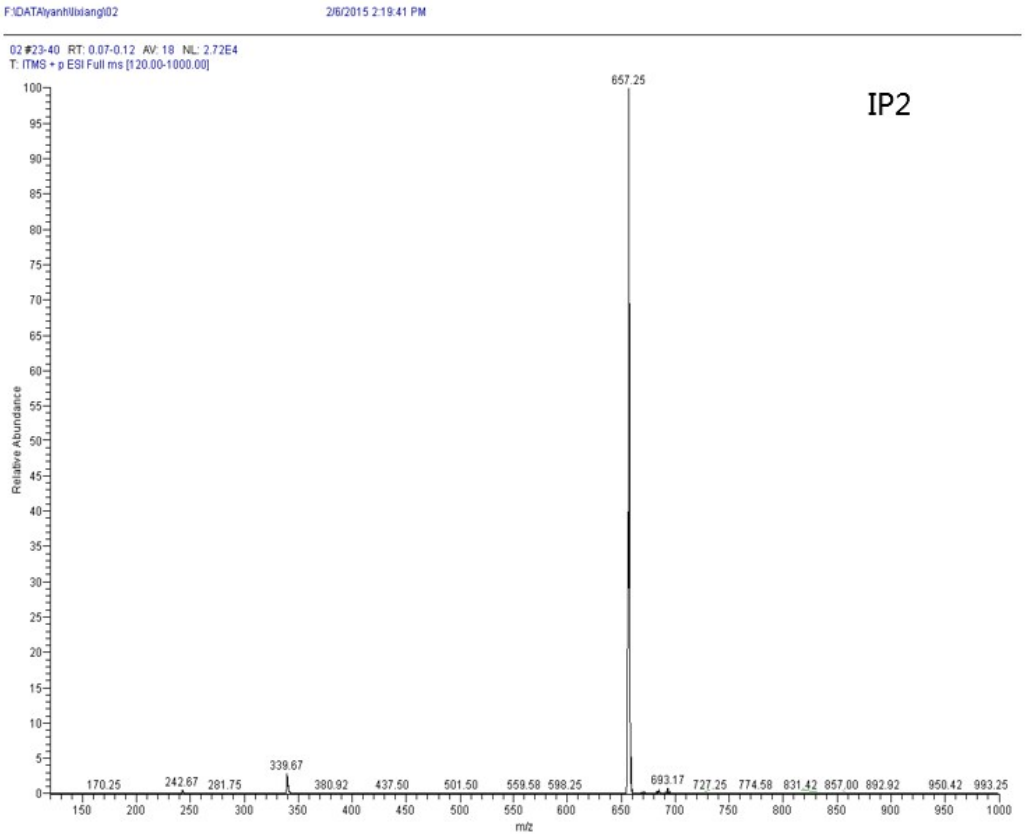

Comment 1
Comment 2
Intens. [a.u.]
4000
3000
2000
1000
0
852.112
IP1
0
200
400
600
800
1000
1200
m/z

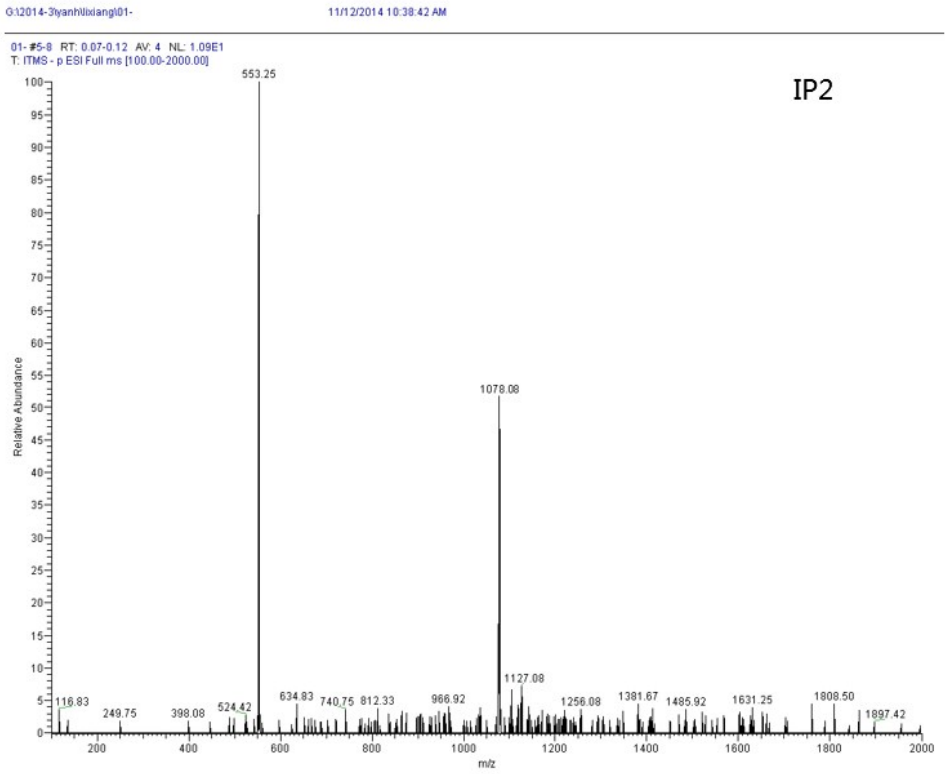

02- #7-18 RT: 0.08-0.21 AV: 12 NL: 1.90E1
T: ITMS - p ESI Full ms [200.00-1000.00]
IP1
665.08
Relative Abundance
256.17
293.17
373.83
402.08
454.00
488.08
542.17
572.58
632.08
688.75
746.58
785.75
826.00
870.08
906.75
970.67

IP2

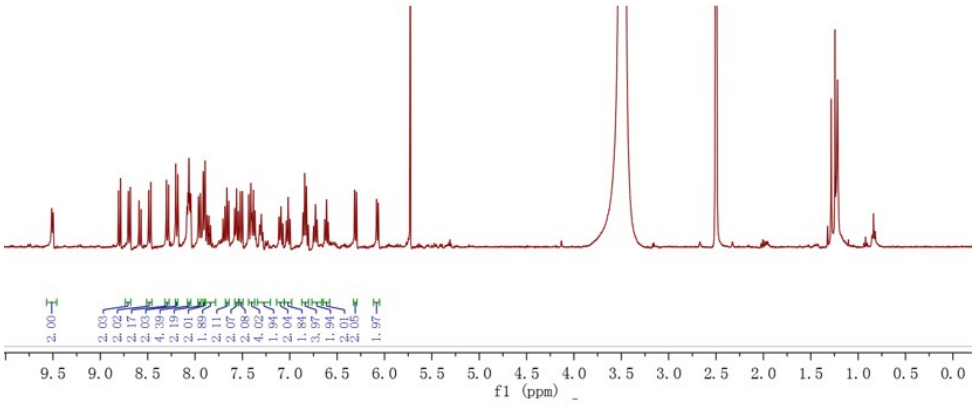

2.00
2.00
4.00
2.01
8.02
6.05
2.02
1.99
2.00
2.01
2.02
1.97
1.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

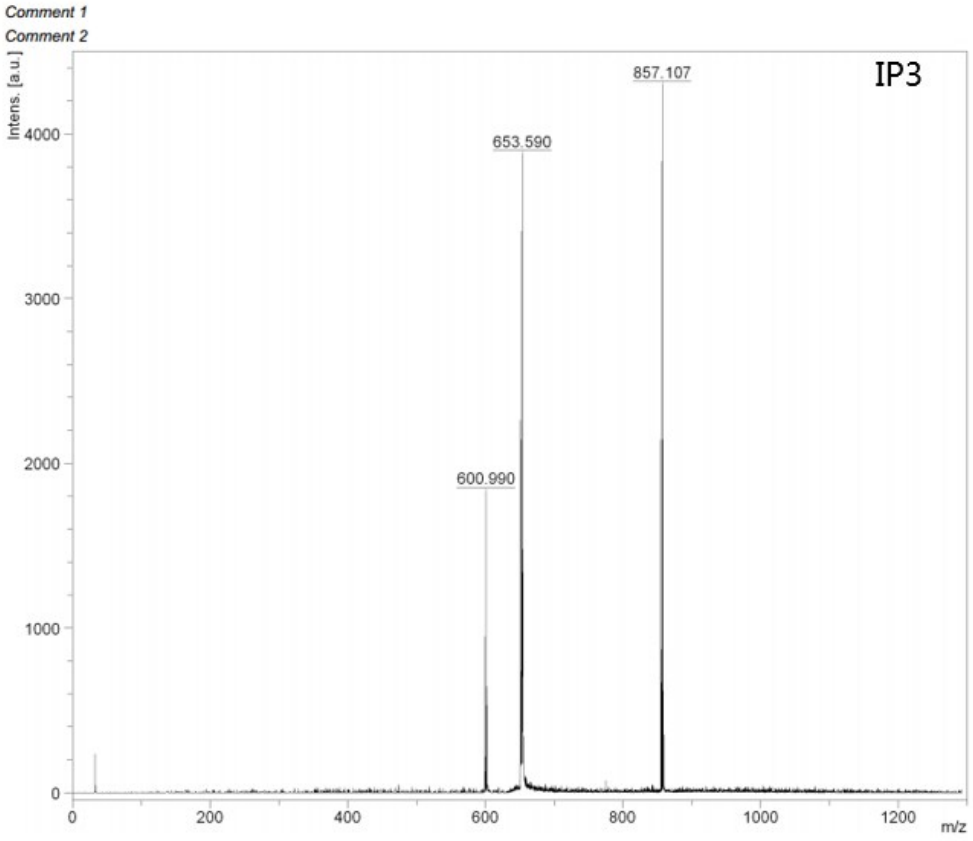

IP2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

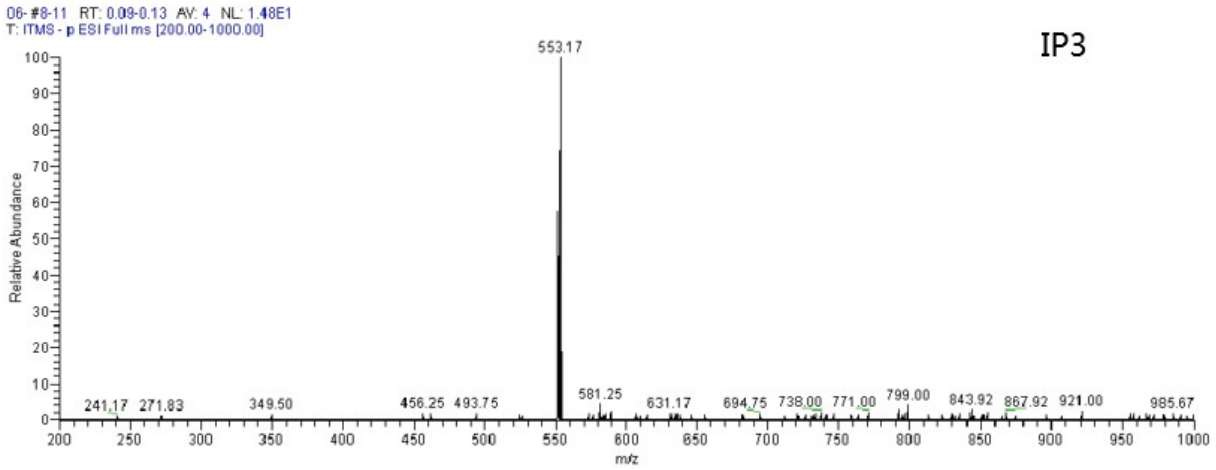

F:\DATA\yanh\lixiang\02
2/6/2015 2:19:41 PM
02 #23-40 RT: 0.07-0.12 AV: 18 NL: 2.72E4
T: ITMS + p ESI Full ms [120.00-1000.00]
IP2
Relative Abundance
m/z
657.25
339.67
170.25
242.67
281.75
380.92
437.50
501.50
559.58
598.25
693.17
727.25
774.58
831.42
857.00
892.92
950.42
993.25

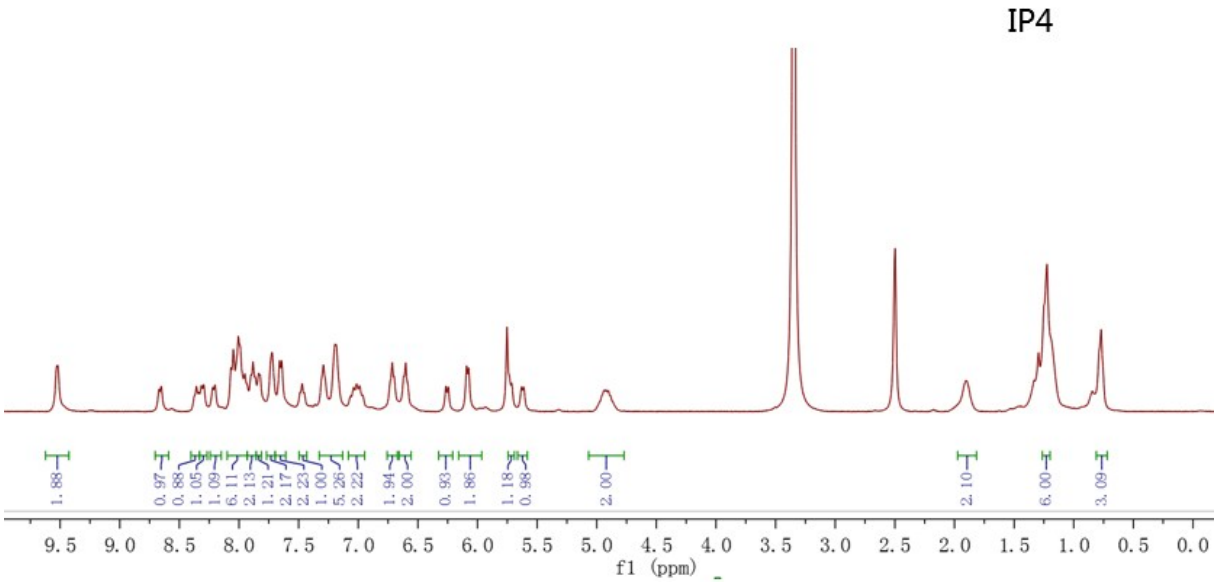

G:\2014-3\yanh\lixiang\01-
11/12/2014 10:38:42 AM
01- #5-8 RT: 0.07-0.12 AV: 4 NL: 1.09E1
T: ITMS - p ESI Full ms [100.00-2000.00]
IP2
553.25
1078.08
1127.08
Relative Abundance
m/z
116.83
249.75
398.08
524.42
634.83
740.75
812.33
966.92
1256.08
1381.67
1485.92
1631.25
1808.50
1897.42

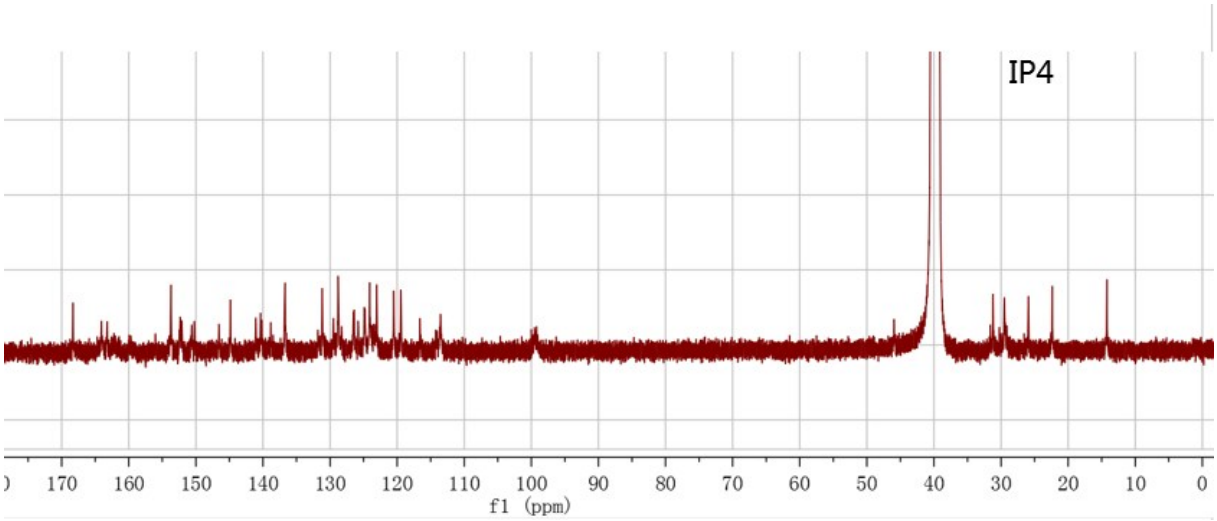
IP3

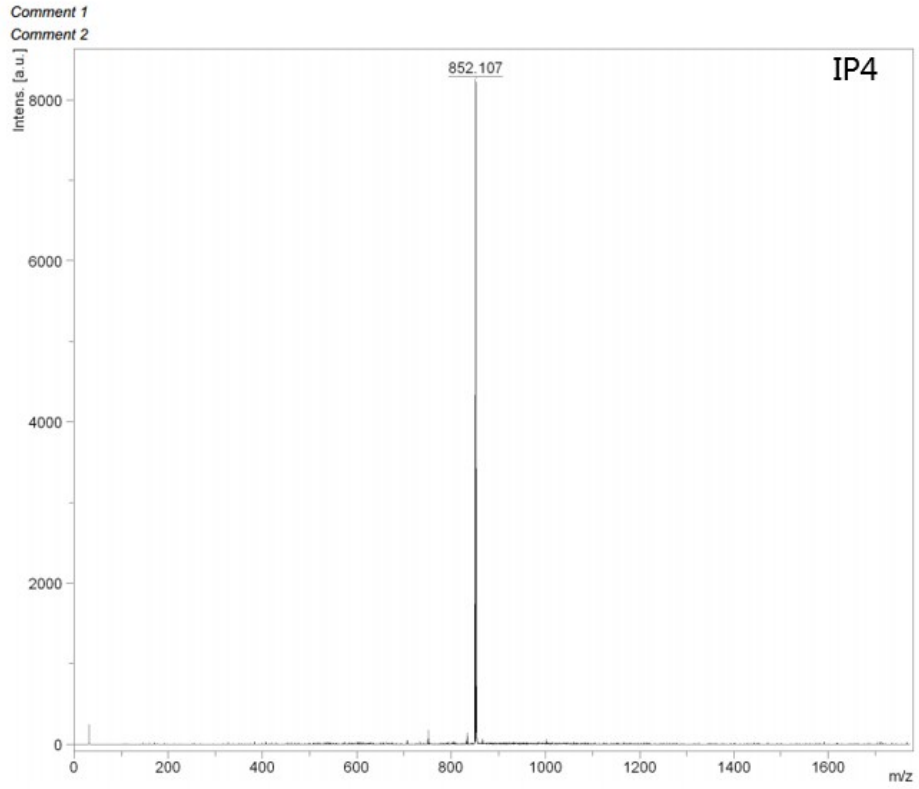

2.00
2.03
2.02
2.17
2.03
4.39
2.19
2.10
1.89
2.11
2.07
2.08
4.02
1.94
2.04
1.84
3.97
1.94
2.01
2.05
1.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

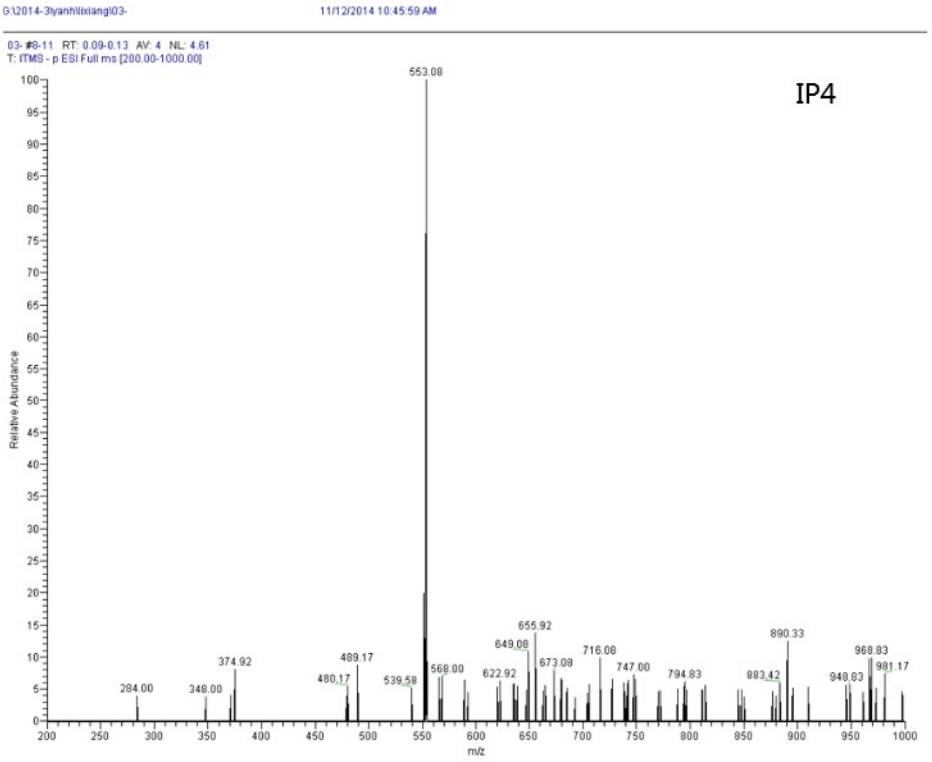

Comment 1
Comment 2
IP3
Intens. [a.u.]
4000
3000
2000
1000
0
857.107
653.590
600.990
0
200
400
600
800
1000
1200
m/z

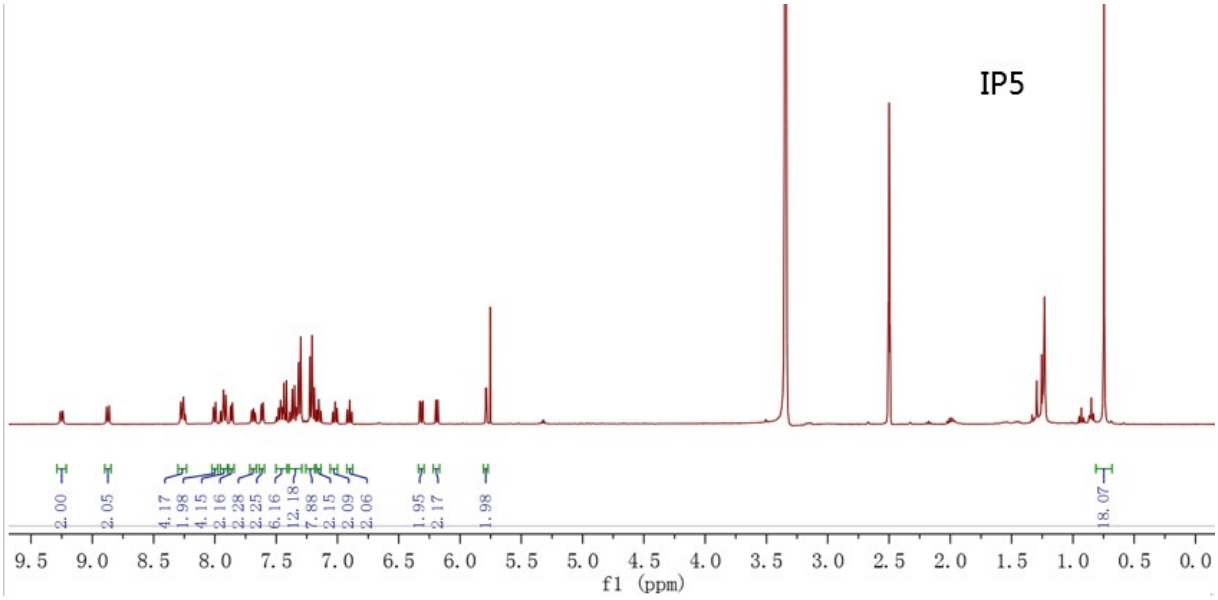

06-#8-11 RT: 0.09-0.13 AV: 4 NL: 1.48E1
T: ITMS - p ESI Full ms [200.00-1000.00]
IP3
553.17
Relative Abundance
m/z
241.17
271.83
349.50
456.25
493.75
581.25
631.17
694.75
738.00
771.00
799.00
843.92
867.92
921.00
985.67

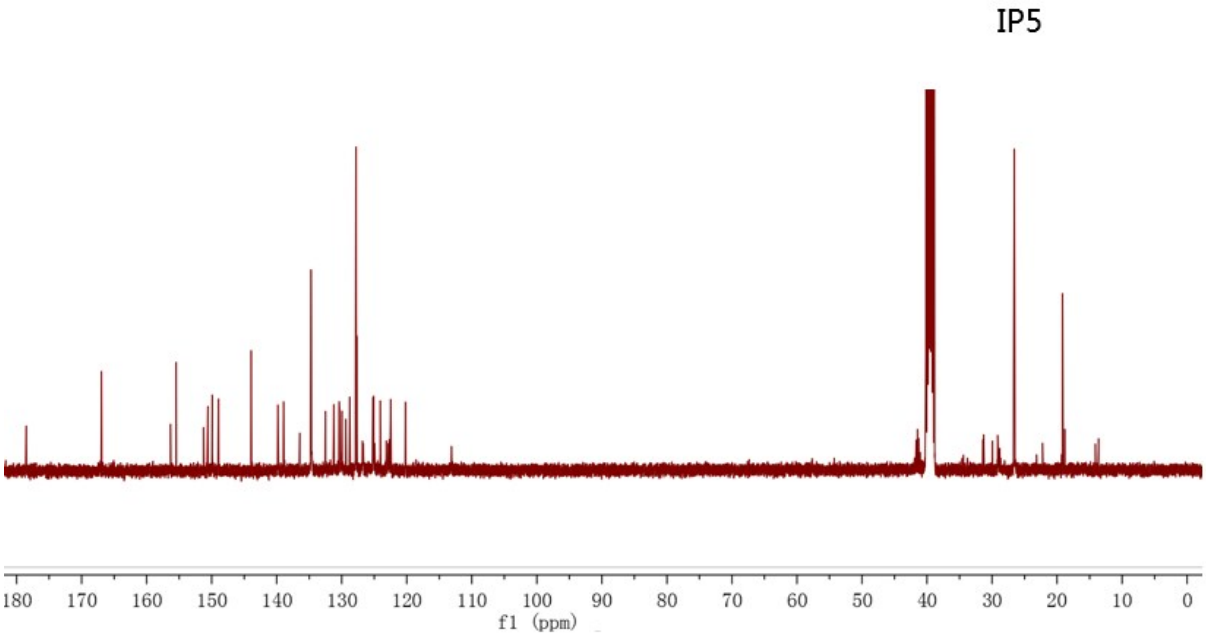

IP4
1.88
0.97
0.88
1.05
1.09
6.11
2.13
1.21
2.17
2.23
1.00
5.26
2.22
1.94
2.00
0.93
1.86
1.18
0.98
2.00
2.10
6.00
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

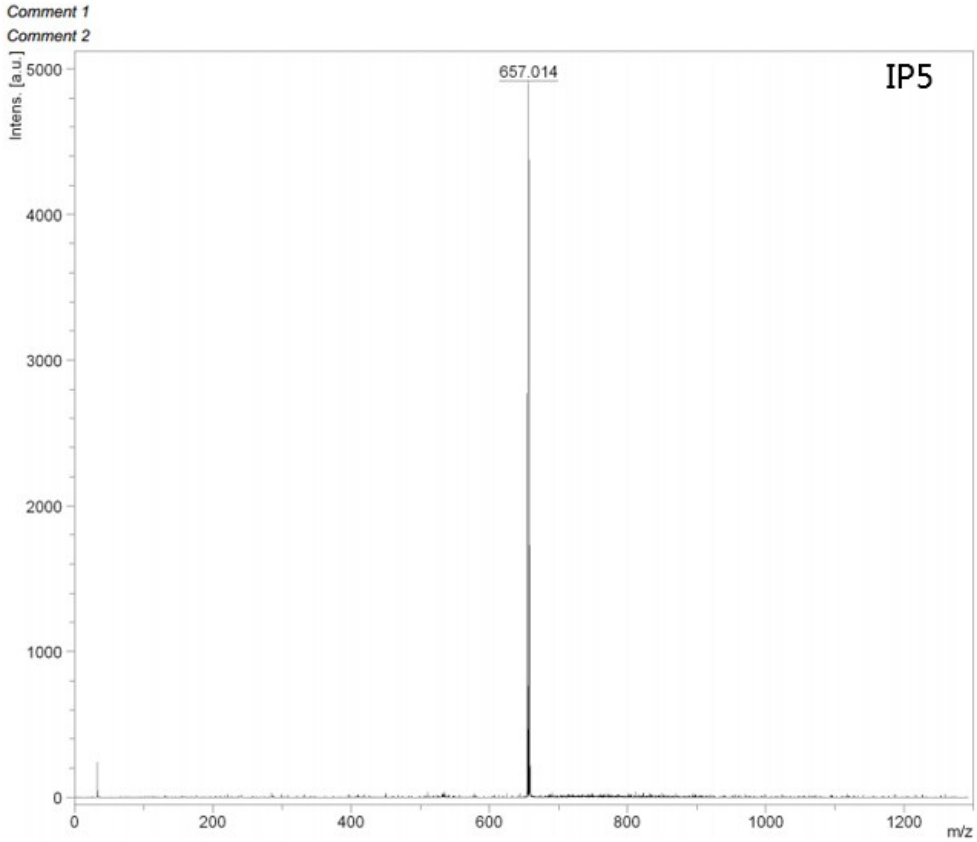

IP4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

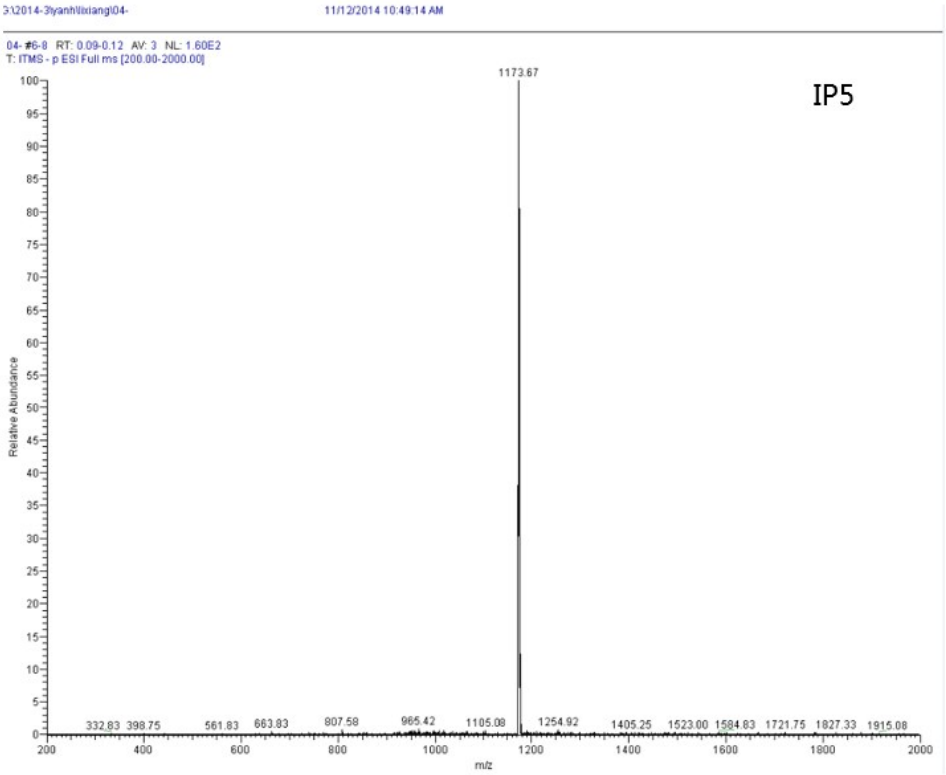

Comment 1
Comment 2
IP4
852.107
Intens. [a.u.]
8000
6000
4000
2000
0
0
200
400
600
800
1000
1200
1400
1600
m/z

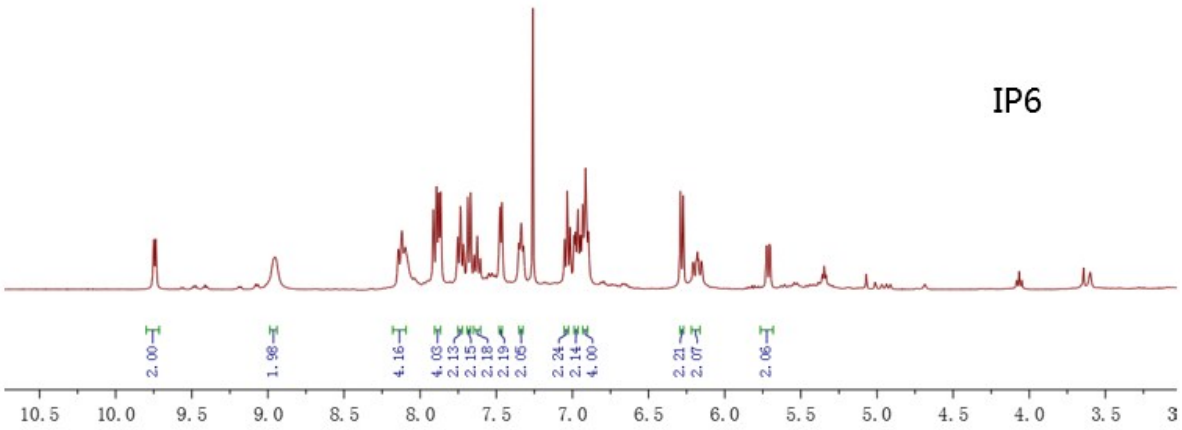

G:\2014-3\yanh\lixiang\03-
11/12/2014 10:45:59 AM
03- #8-11 RT: 0.09-0.13 AV: 4 NL: 4.61
T: ITMS - p ESI Full ms [200.00-1000.00]
IP4
553.08
655.92
649.08
716.08
890.33
968.83
374.92
489.17
673.08
747.00
794.83
981.17
568.00
622.92
883.42
948.83
480.17
539.58
284.00
348.00
Relative Abundance
m/z

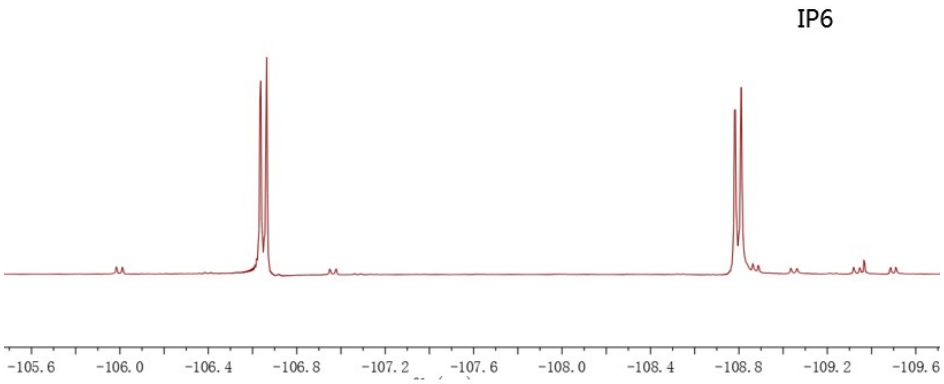

IP5
2.00
2.05
4.17
1.98
4.15
2.16
2.28
2.25
6.16
12.18
7.88
2.15
2.09
2.06
1.95
2.17
1.98
18.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


IP5
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

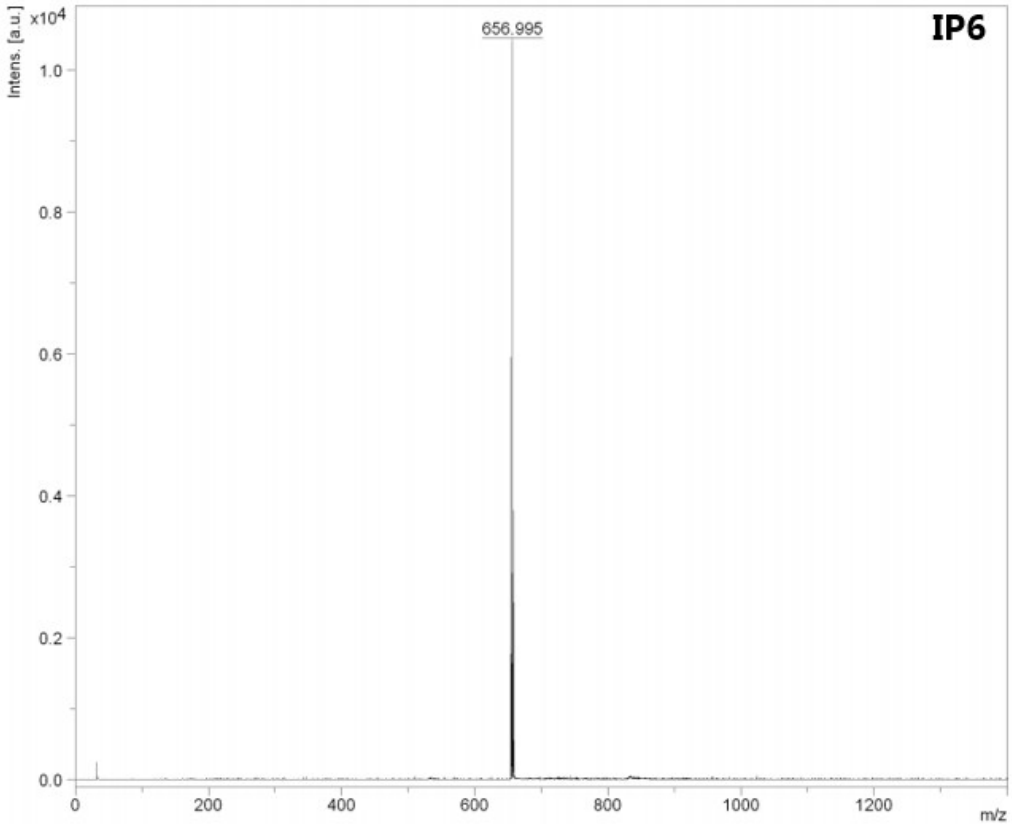

Comment 1
Comment 2
Intens. [a.u.]
5000
4000
3000
2000
1000
0
657.014
IP5
0
200
400
600
800
1000
1200
m/z

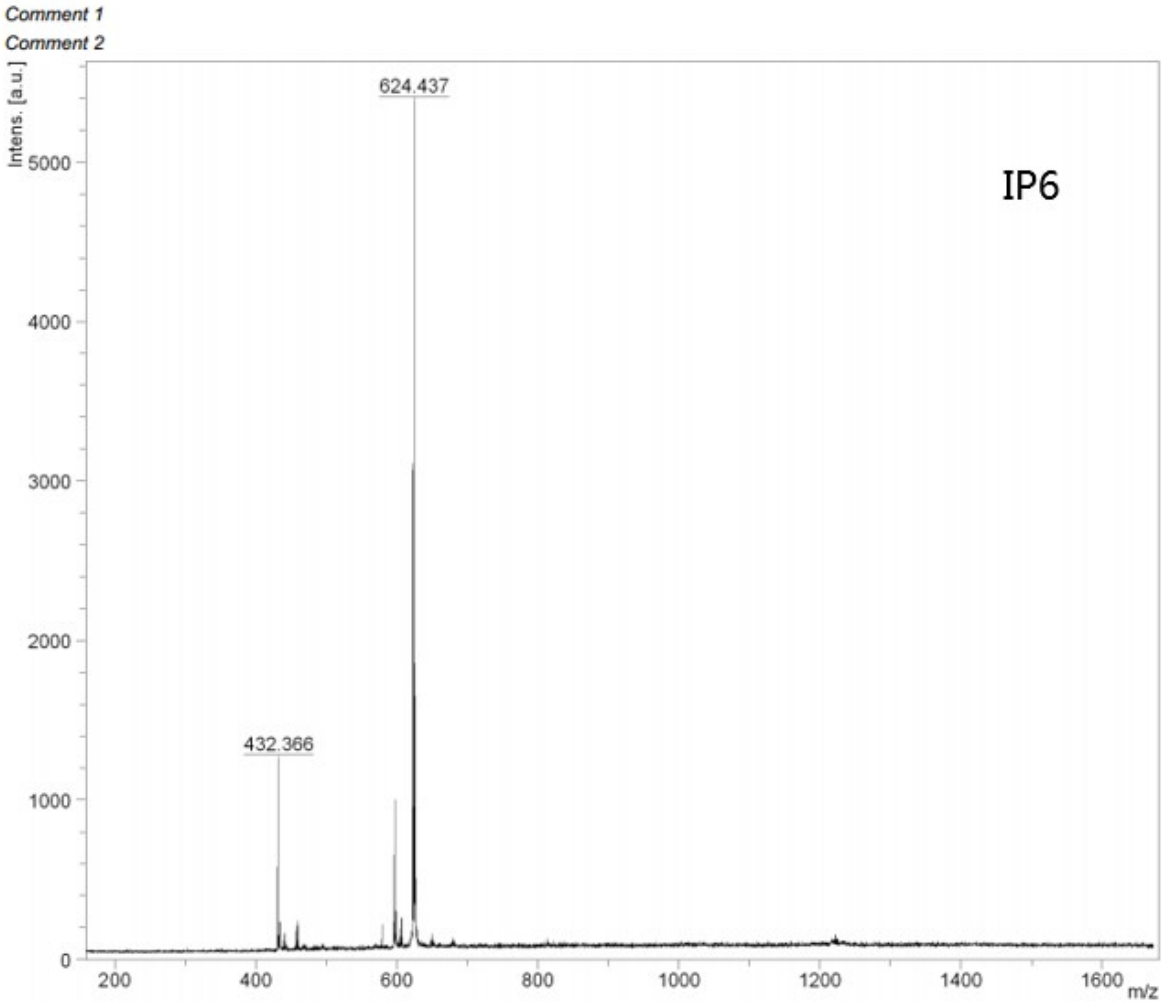

11/12/2014 10:49:14 AM
04- #6-8 RT: 0.09-0.12 AV: 3 NL: 1.60E2
T: ITMS - p ESI Full ms [200.00-2000.00]
IP5
1173.67
Relative Abundance
m/z
332.83
398.75
561.83
663.83
807.58
965.42
1105.08
1254.92
1405.25
1523.00
1584.83
1721.75
1827.33
1915.08


IP6
2.00
1.98
4.16
4.03
2.13
2.15
2.18
2.19
2.05
2.24
2.14
4.00
2.21
2.07
2.06
10.5
10.0
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



$^{19}F\{^{1}H\}$ NMR (377 M)


IP6
656.995
Intens. [a.u.]
x10^4
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
m/z


Comment 1
Comment 2
Intens. [a.u.]
5000
4000
3000
2000
1000
0
624.437
432.366
IP6
200
400
600
800
1000
1200
1400
1600
m/z