Simple and Efficient Amination of Diaryliodonium Salts with Aqueous Ammonia in Water without Metal-Catalyst

Jian Li [a,*], Li Liu [b]

School of Pharmaceutical Engineering & Life Sciences, Chang Zhou University,

Analytical center, Chang Zhou University, Changzhou, 213164, P.R. China

E-mail: lijianchem@gmail.com

SUPPORTING INFORMATION

Contents

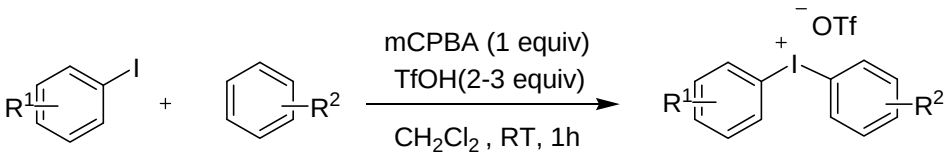
General Remarks.

All reactions were carried out under an air atmosphere condition. Various iodine reagents were purchased from Aldrich, Acros or Alfa. Flash column chromatography was performed using silica gel (200–300 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–300 mesh silica gel impregnated with a fluorescent indicator (254 nm). The model of GC-MS is Agilent 7890A(GC)-5975(MS). NMR spectra were recorded in $CDCl_3$ on a Bruker NMR-400 (400MHz) and Bruker NMR-500 (500MHz) with TMS as an internal reference. Products were characterized by comparison of ^{1}H NMR and ^{13}C NMR in the literatures.

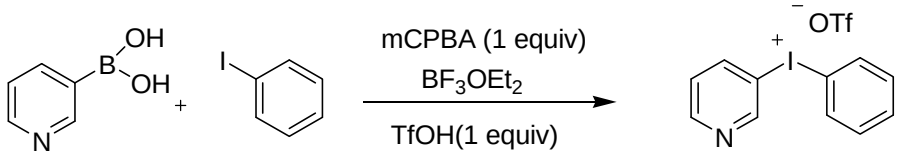
General Procedure for preparation of diaryliodonium salts

All of diaryliodonium salts were prepared according references 1-3 in accordance with the following equations.

A . Preparation of Aryl (mesityl) iodonium trifluoromethane sulfonates [1, 3]



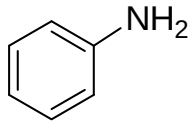
B. General procedure for diaryliodonium trifluoromethanesulfonates via tetrafluoroborates [1, 3]



General procedure for amination of Diaryliodonium Salts

Under nitrogen atmosphere, a solution of 25-28% aqueous ammonia (1mL) and Diaryliodonium Salts (0.40 mmol) was treated with NaOH (32 mg, 0.80 mmol) at 80ºC for 2 hours. The temperature was allowed to cool slowly, the mixture was acidied with HCl (1M) and ethyl acetate (5 mL) were added, the orgainic layer was separated and concentrated, iodobenzene or iodomesitylene was obtained. Aqueous phase was alkalinized by NaOH (1M) and extracted with ethyl acetate (5 mL), the organic layer was dried and concentred to provide **2**. If necessary, the residues was purified by silica-gel column chromatography (Ethyl acetate / Petroleum ether = 1/4 - 1/2).

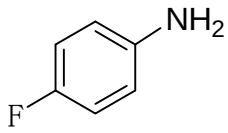
Characterization Data for Compounds 2



2a

Aniline (2a) [4]

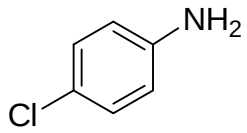
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.11 (m, 2H), 6.74-6.71 (m, 1H), 6.66 (d, *J* = 7.6 Hz, 2H), 3.55 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 129.2, 118.5, 115.1, 115.1, 115.0.



2b

4-Fluorobenzenamine (2b) [4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.40 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,) δ 167.4, 143.5, 136.8, 136.2, 133.1, 132.9, 129.2, 118.4, 51.7.

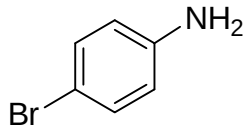


2c

4-Chlorobenzenamine (2c) [4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 3.63 (brs, 2H).

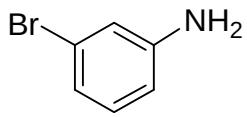
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 129.2, 123.2, 116.3.



2d

4-Bromobenzenamine (2d) [4]

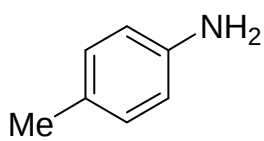
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 3H), 6.56 (d, *J* = 7.6 Hz, 2H), 3.64 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 132.0, 116.7, 110.2.



2e

3-Bromobenzenamine (2e) [5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01-6.97 (m, 1H), 6.87-6.82 (m, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 3.68 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 128.6, 128.0, 126.4, 126.2, 115.4**.**

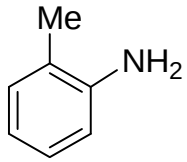


2f

p-Toluidine (2f) [4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (d, *J* = 7.6 Hz, 2H), 6.60 (m, *J* = 7.6 Hz, 2H), 3.45 (brs, 2H),

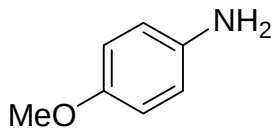
2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 129.7, 139.7, 127.7, 115.2, 20.4.



2g

o-Toluidine (2g) [6]

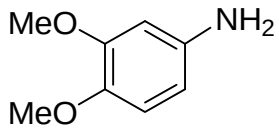
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 2H), 3.76 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 130.6, 127.1, 122.4, 118.7, 115.0, 17.6.



2h

4-Methoxybenzenamine (2h) [4]

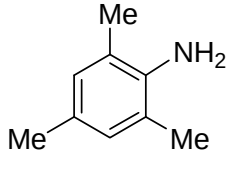
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 7.2 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 3.74 (s, 3H), 3.18 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 139.8, 116.4, 114.8, 55.7.



2i

3,4-Dimethoxybenzenamine (2i) [7]

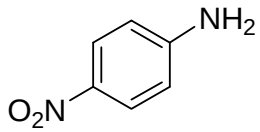
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 6.24 (d, *J* = 8.4 Hz, 1H), 3.83 (d, *J* = 11.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 142.3, 140.6, 113.3, 106.5, 100.9, 56.7, 55.7.



2j

2,4,6-Trimethylbenzenamine (2j) [6]

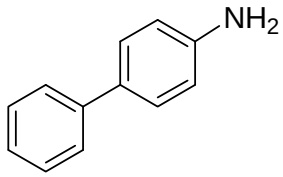
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (s, 2H), 3.42 (brs, 2H), 2.20 (s, 3H), 2.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 128.8, 127.1, 121.8, 20.3, 17.5.



2k

4-Nitrobenzenamine (2k) [4]

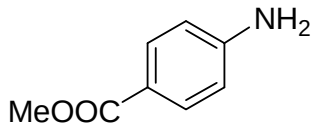
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 4.37 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 139.2, 126.3, 113.4.



2l

Biphenyl-4-amine (2l) [4]

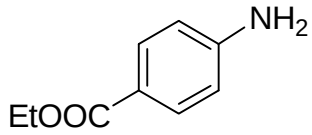
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J =7.6 Hz, 2H), 7.42-7.36 (m, 4H), 7.30-7.25 (m, 1H), 6.76 (d, J =7.2 Hz, 2H), 3.72 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 130.7, 130.6, 123.8, 123.0, 121.3, 118.8, 117.8, 114.2, 113.6.



2m

Methyl 4-aminobenzoate (2m) [5]

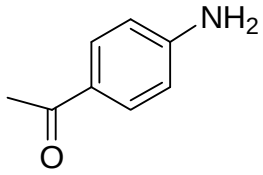
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 155.5, 133.4, 119.3, 115.4, 52.4.



2n

Ethyl 4-aminobenzoate (2n) [6]

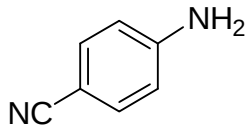
^{1}H NMR (400MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 6.64 (d, *J* = 7.2 Hz, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.04 (brs, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 150.7, 131.5, 120.1, 113.7, 60.3, 14.4.



2o

1-(4-Aminophenyl)ethanone (2o) [4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.10 (brs, 2H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 151.1, 130.8, 127.9, 113.7, 26.0.

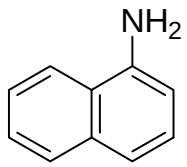


2p

4-Aminobenzonitrile (2p) [6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 6.65 (m, *J* = 8.0 Hz, 2H), 4.16 (brs, 3H).

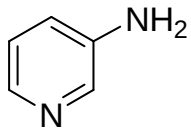
^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 134.0, 133.8, 120.1, 114.5, 100.1.



2q

Naphthalen-1-amine (2q) [6]

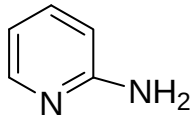
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-779 (m, 2H), 7.46-7.44 (m , 2H), 7.33-7.27 (m, 2H), 6.81-6.79 (m, 1H), 4.46 (brs, 2H); ^{13}C NMR(125 MHz, $CDCl_3$): δ 142.0, 134.4, 128.5, 126.3, 125.8, 124.8, 123.6, 120.7, 119.0.



2r

Pyridin-3-amine (2r) [4]

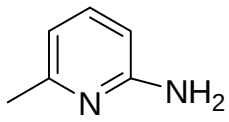
^{1}H NMR (400MHz, $CDCl_3$) δ 8.09 (s, 5H), 8.02 (d, *J* = 4.8 Hz, 1H), 7.08-7.04 (m, 1H), 6.97-6.95 (m, 1H), 3.69 (brs, 2H); ^{13}C NMR (125MHz, $CDCl_3$) δ 142.4, 140.0, 137.5, 123.7, 121.4.



2s

Pyridin-2-amine (2s) [8]

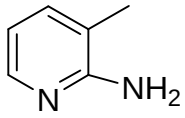
^{1}H NMR (400MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 6.63 (s, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 4.46 (brs, 2H); ^{13}C NMR (125MHz, $CDCl_3$) δ 158.4, 148.1, 137.7, 114.0, 108.6.



2t

6-methylpyridin-2-amine (2t) [8]

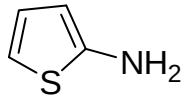
^{1}H NMR (400MHz, $CDCl_3$) δ 7.31 (t, *J* = 6.4 Hz, 1H), 6.51 (d, *J* = 7.2 Hz, 1H), 6.31 (d, *J* = 8.0 Hz, 1H), 4.43 (brs, 2H), 2.37(s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ 157.8, 156.9, 138.0, 113.2, 105.3, 24.1.



2u

3-methylpyridin-2-amine (2u) [8]

^{1}H NMR (400MHz, $CDCl_3$) δ 7.94 (d, *J* = 4.8 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 1H), 6.62 (t, *J* = 6.4 Hz, 1H), 4.42 (brs, 2H), 2.12(s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ 157.1, 145.6, 145.6, 138.9, 138.7, 116.5, 114.4, 114.4, 17.1.

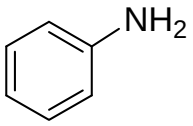


2v

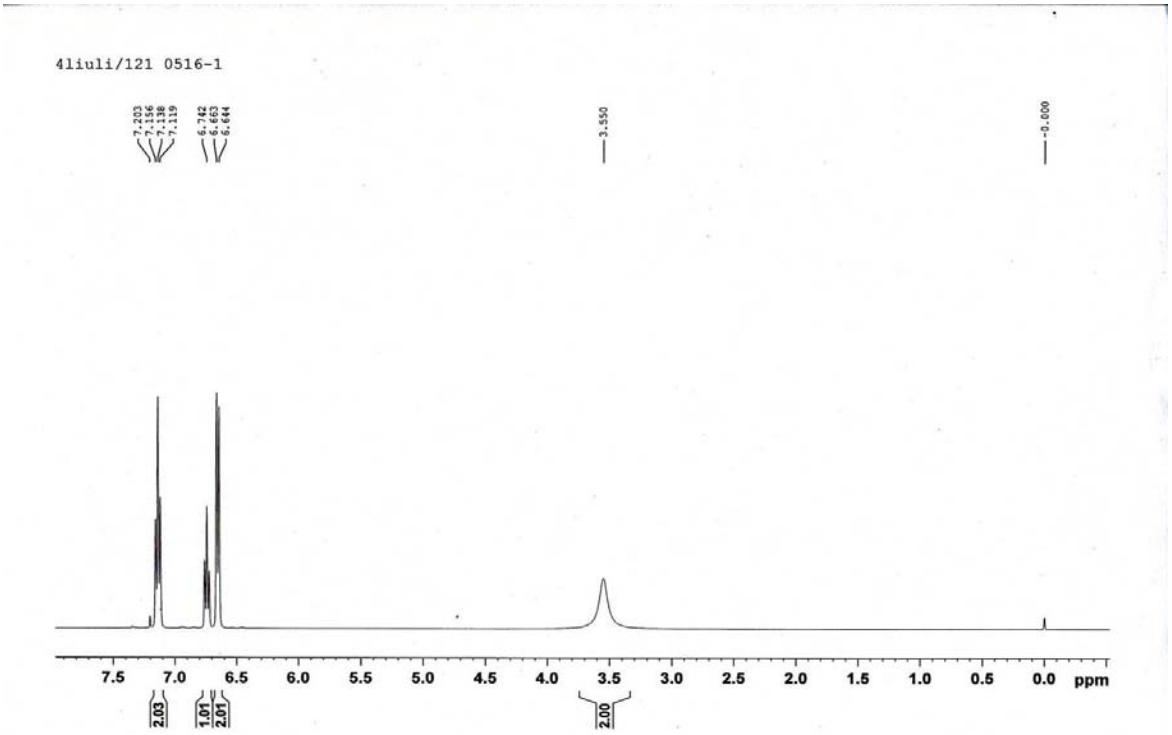
thiophen-2-amine (2v) [9]

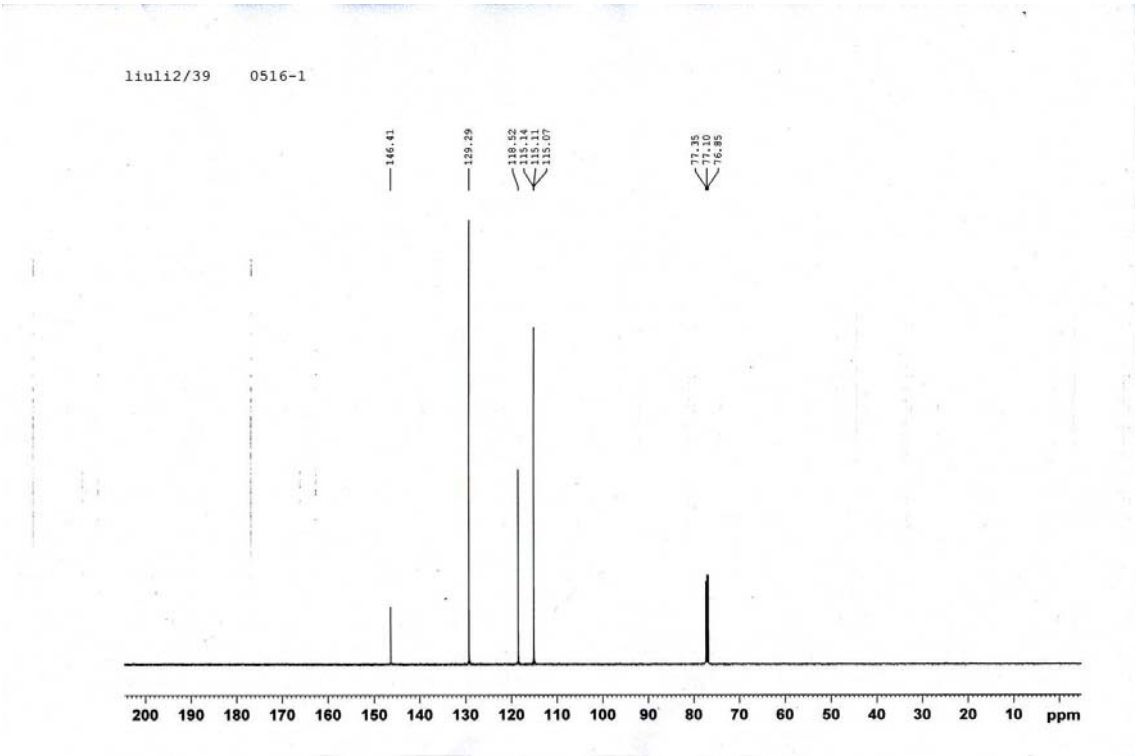
^{1}H NMR (400MHz, $CDCl_3$) δ 6.67 (s, 1H), 6.49 (d, *J* = 5.6 Hz, 1H), 6.18 (s, 1H), 4.68 (brs, 2H); ^{13}C NMR (125MHz, $CDCl_3$) δ 151.1, 126.1, 112.6, 109.0.

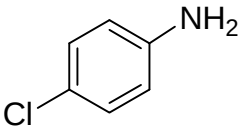
^{1}H- and ^{13}C-NMR spectra for compounds 2



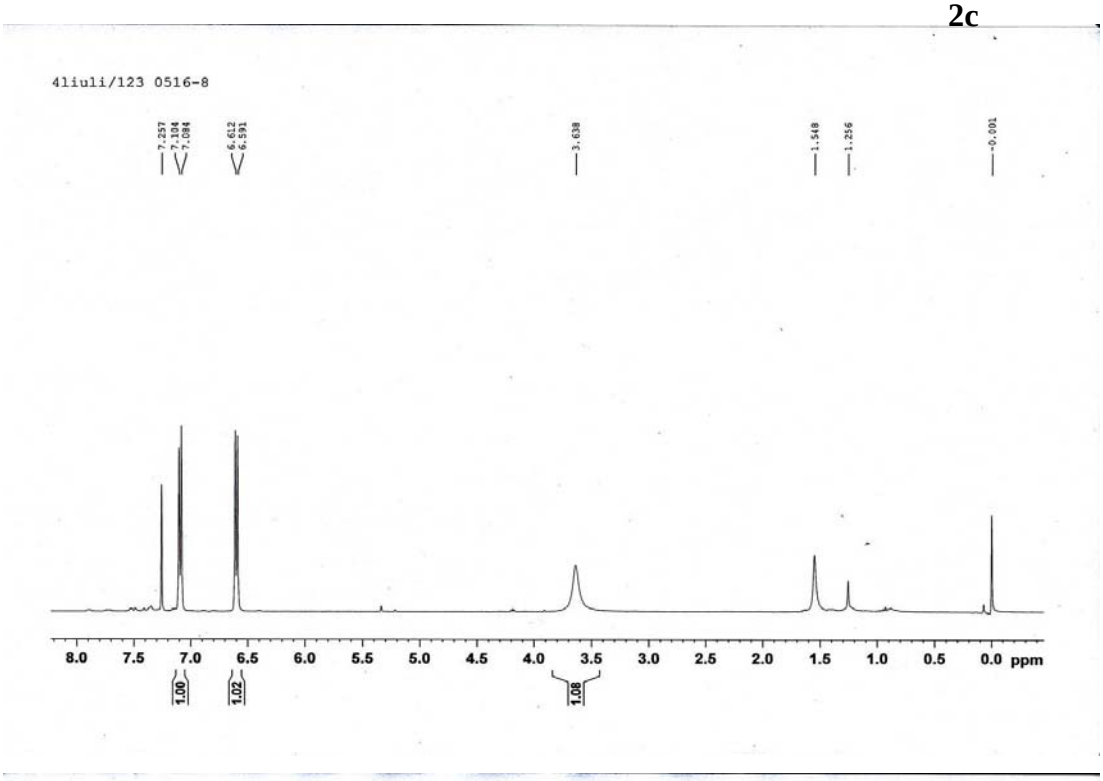
2a

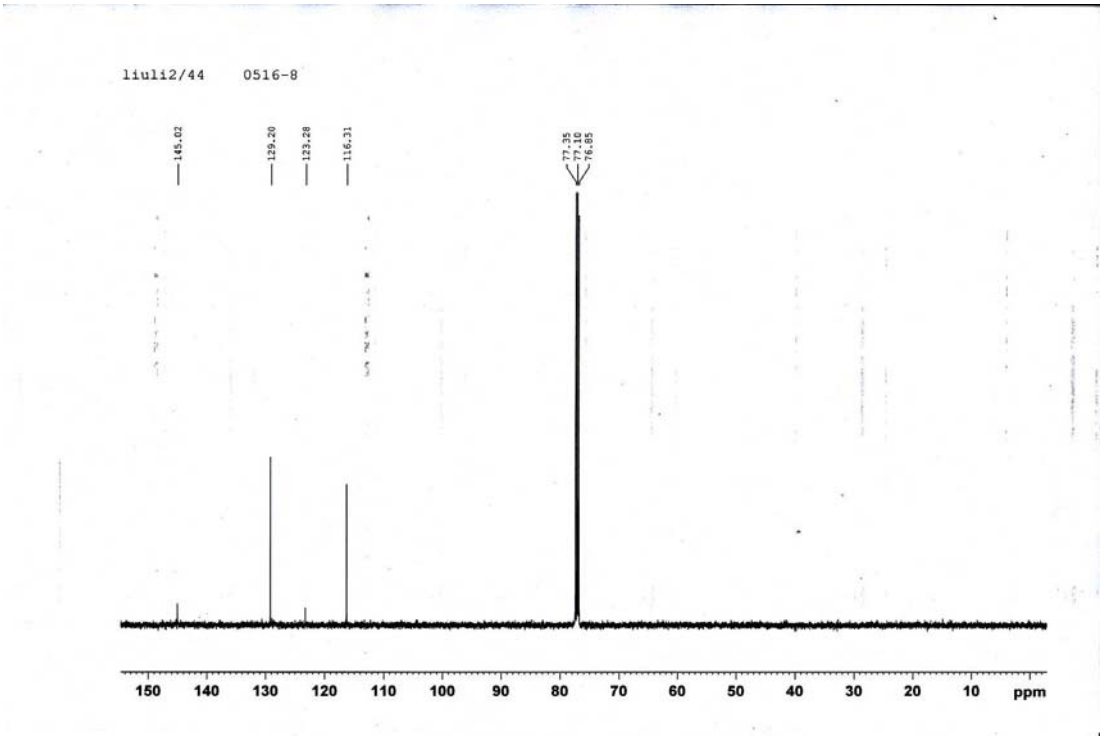


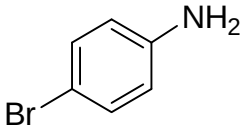



NH2
Cl

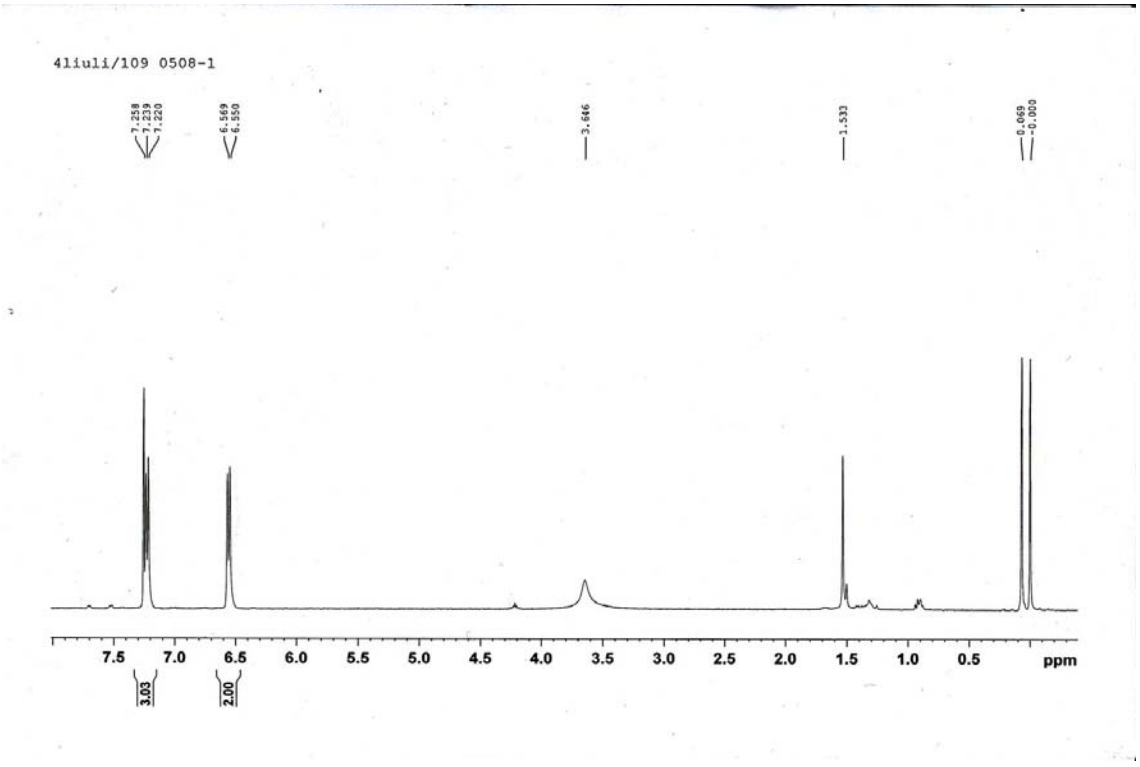
2c

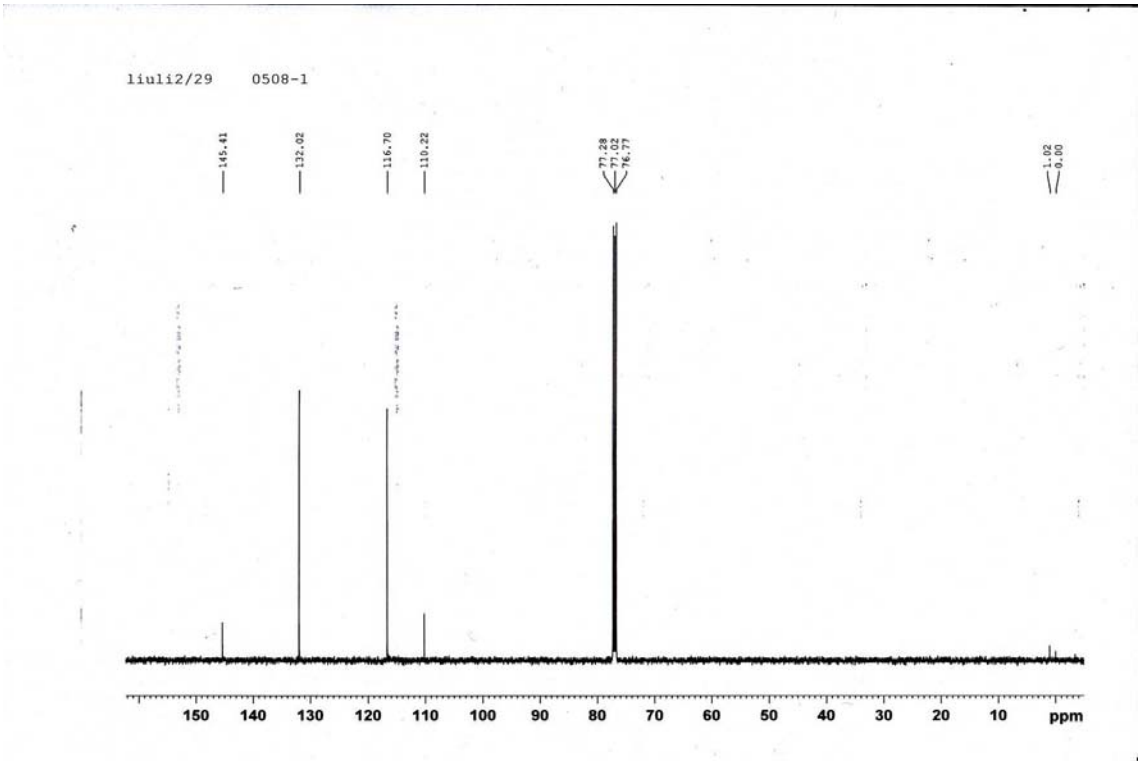

4liuli/123 0516-8
7.257
7.104
7.084
6.612
6.591
3.638
1.548
1.256
-0.001
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.02
1.08

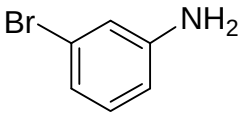

liuli2/44 0516-8
145.02
129.20
123.28
116.31
77.35
77.10
76.85
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


NH2
Br

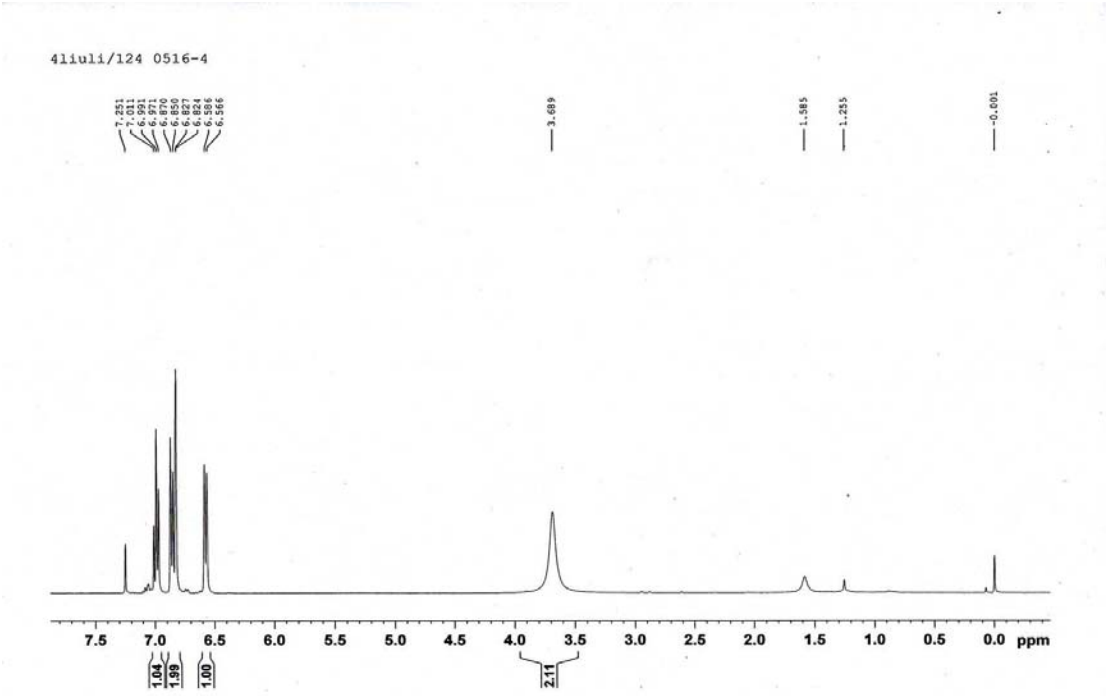
2d

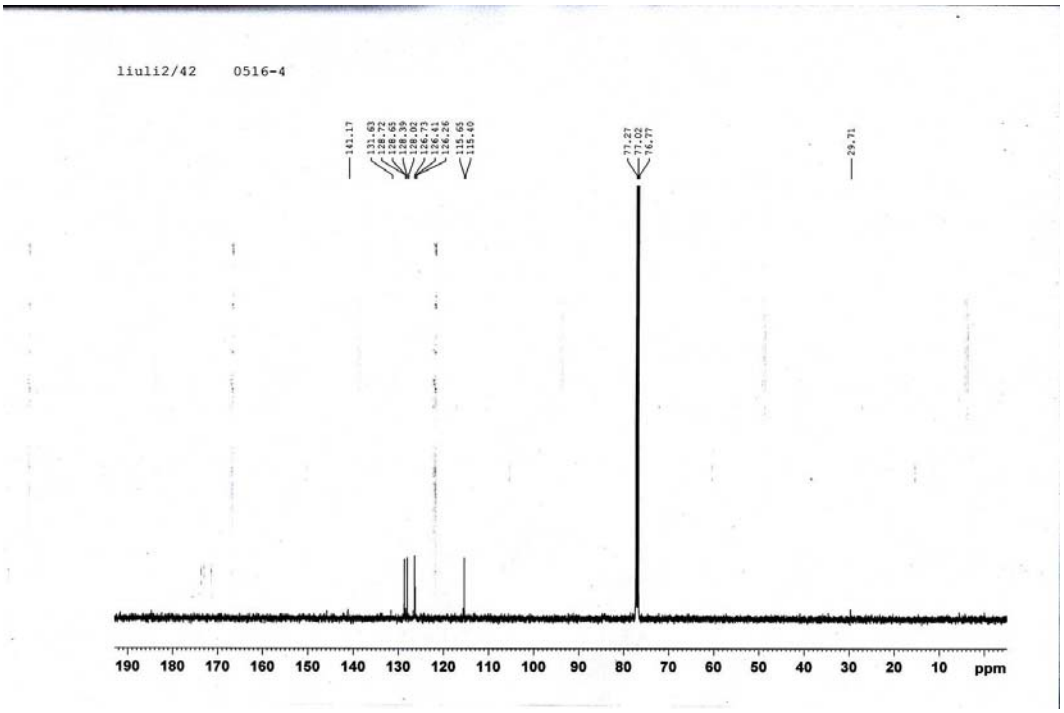

4liuli/109 0508-1
7.258
7.239
7.220
6.569
6.550
3.646
1.533
0.069
-0.000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.03
2.00

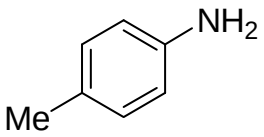

liuli2/29 0508-1
145.41
132.02
116.70
110.22
77.28
77.02
76.77
1.02
0.00
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



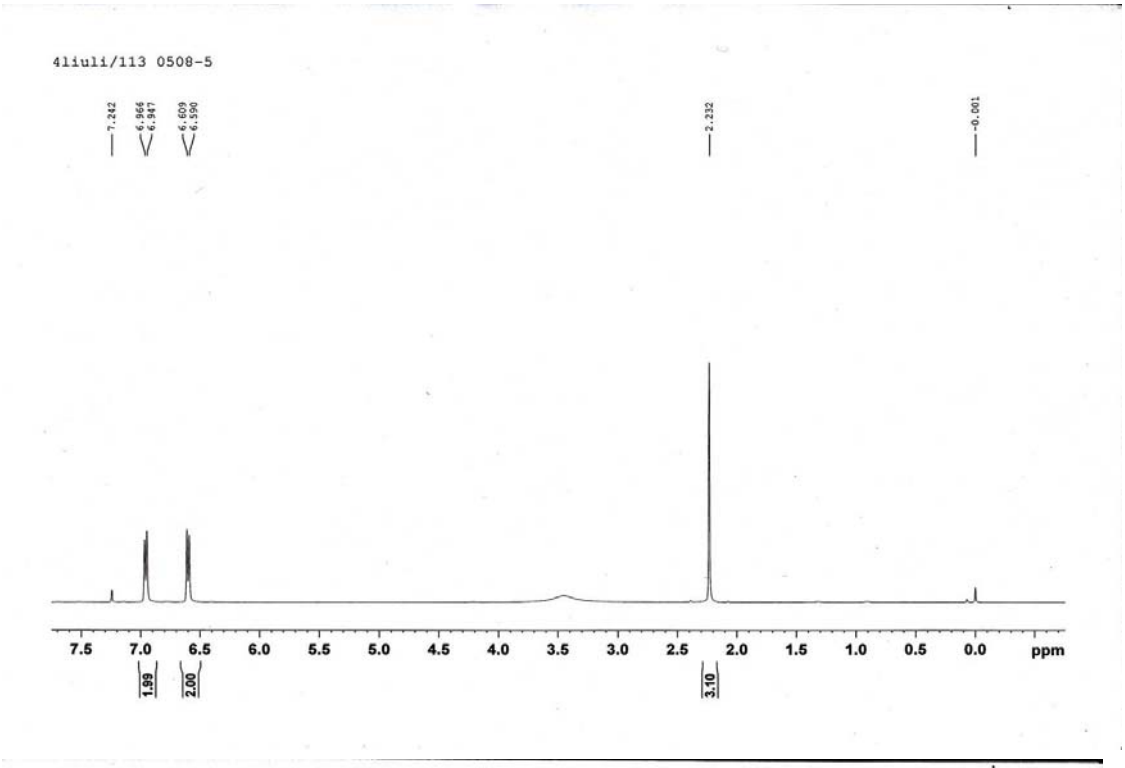
2e

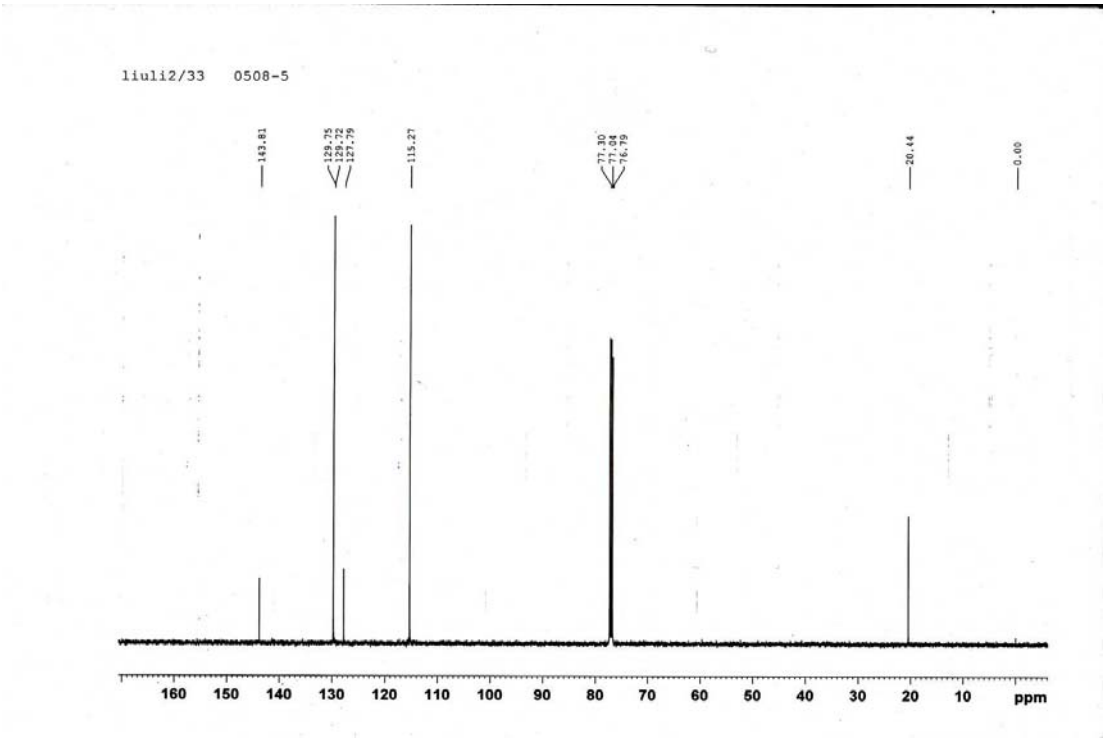


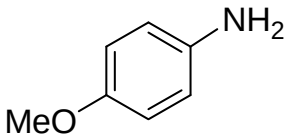




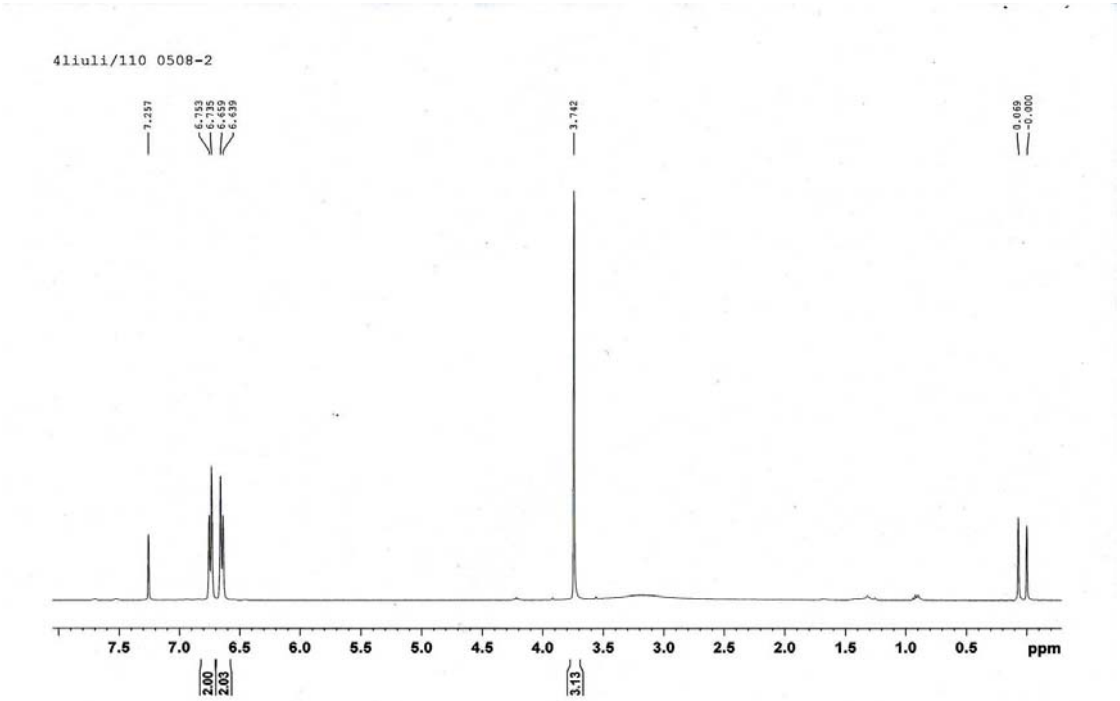
2f

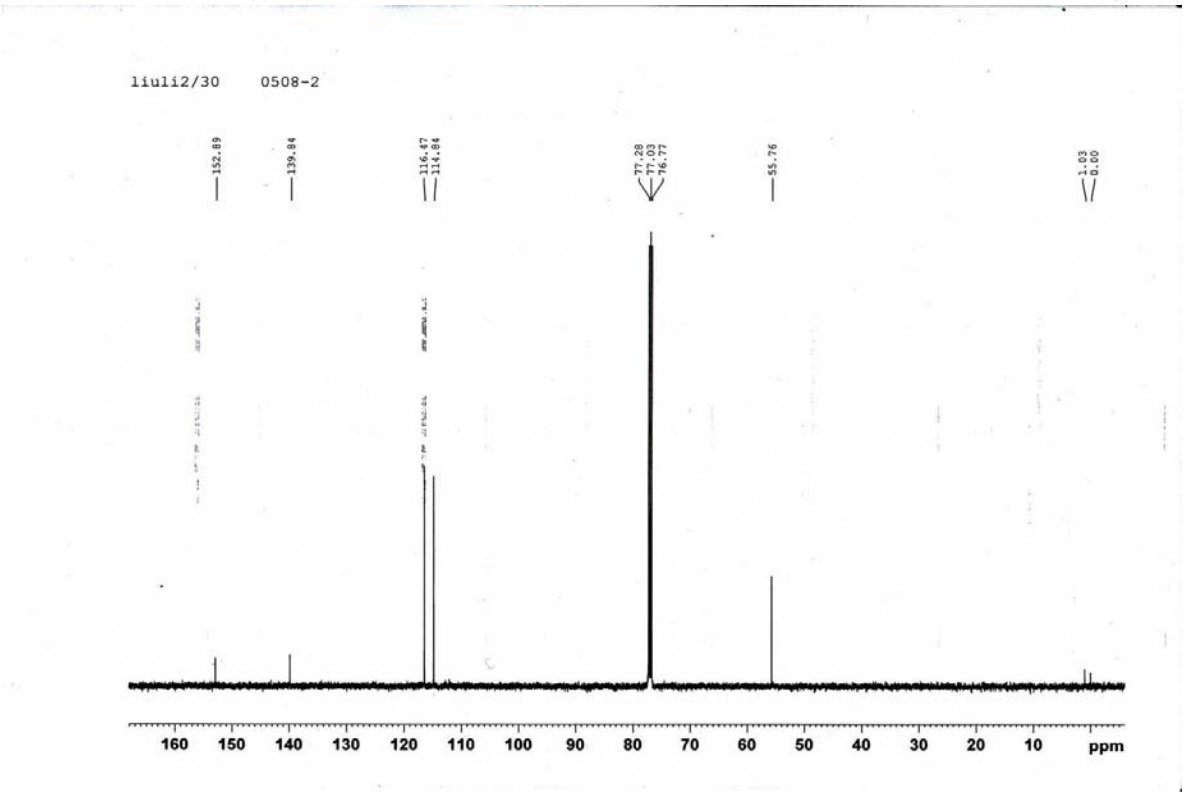


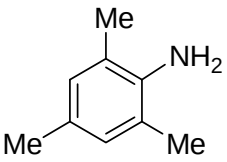




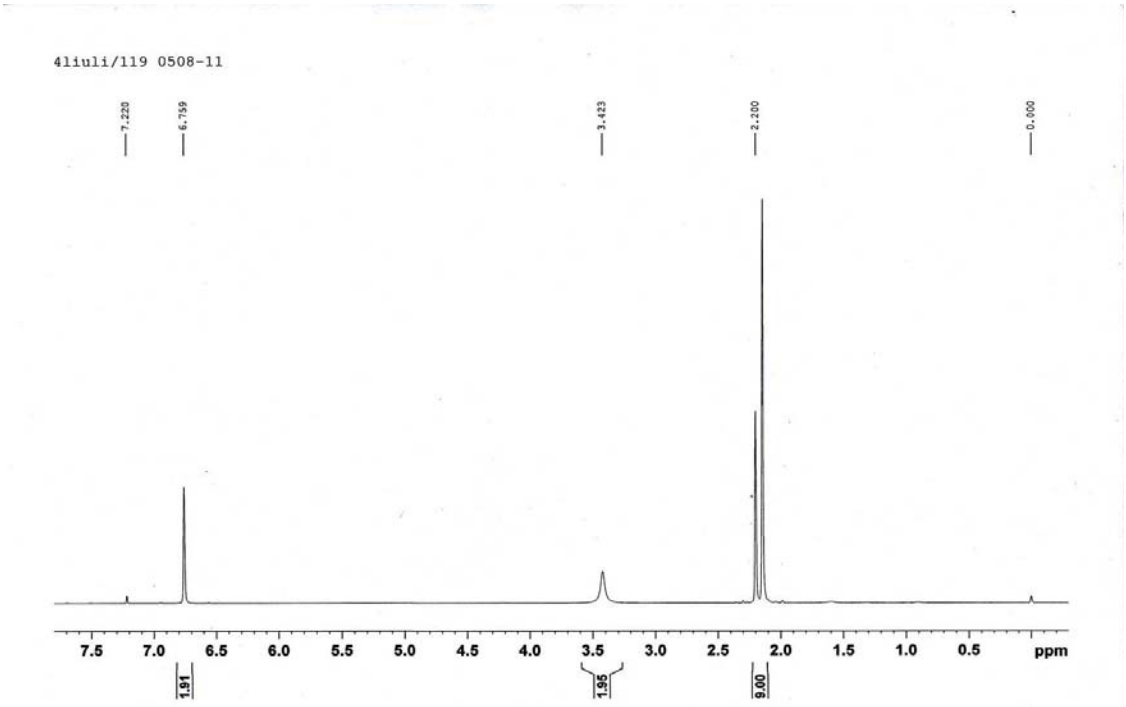
2h

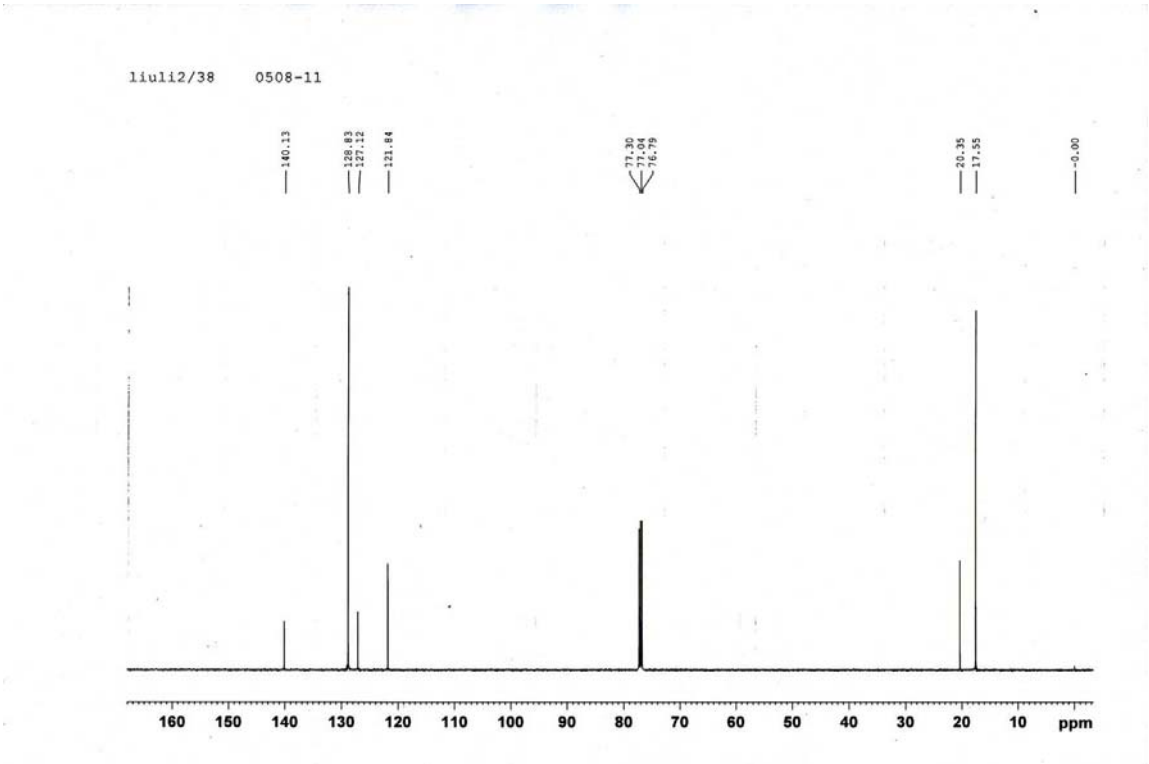


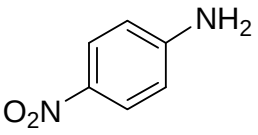



Me
NH2
Me
Me

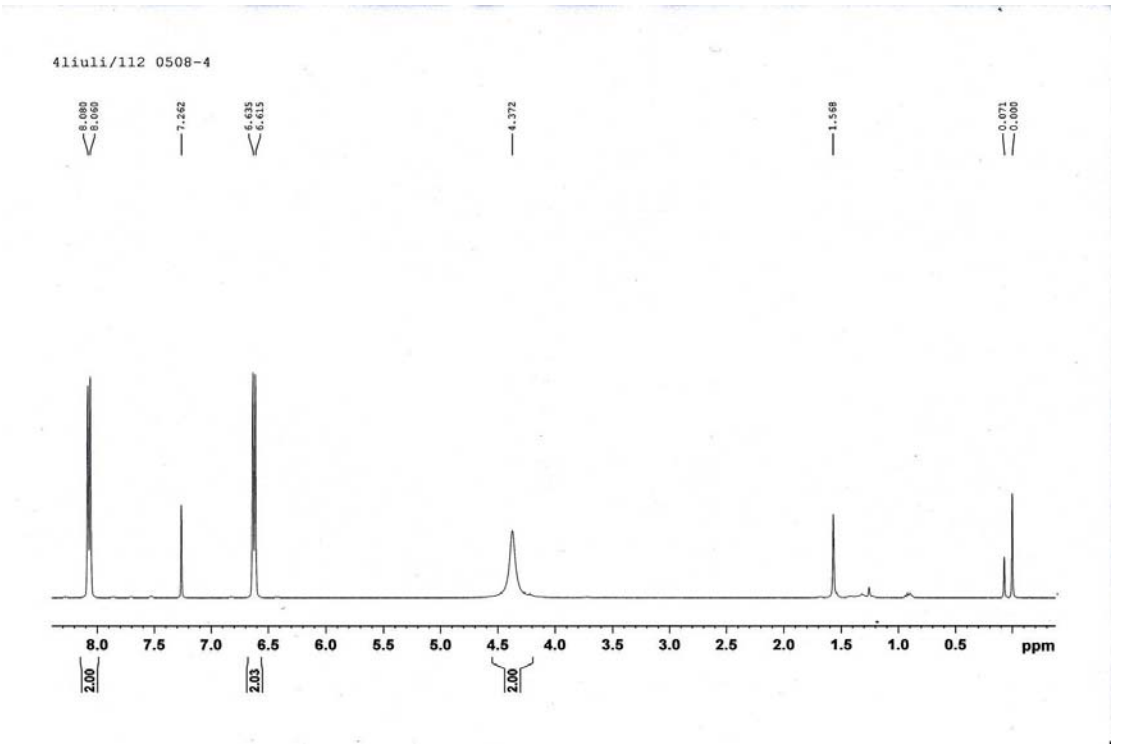
2j

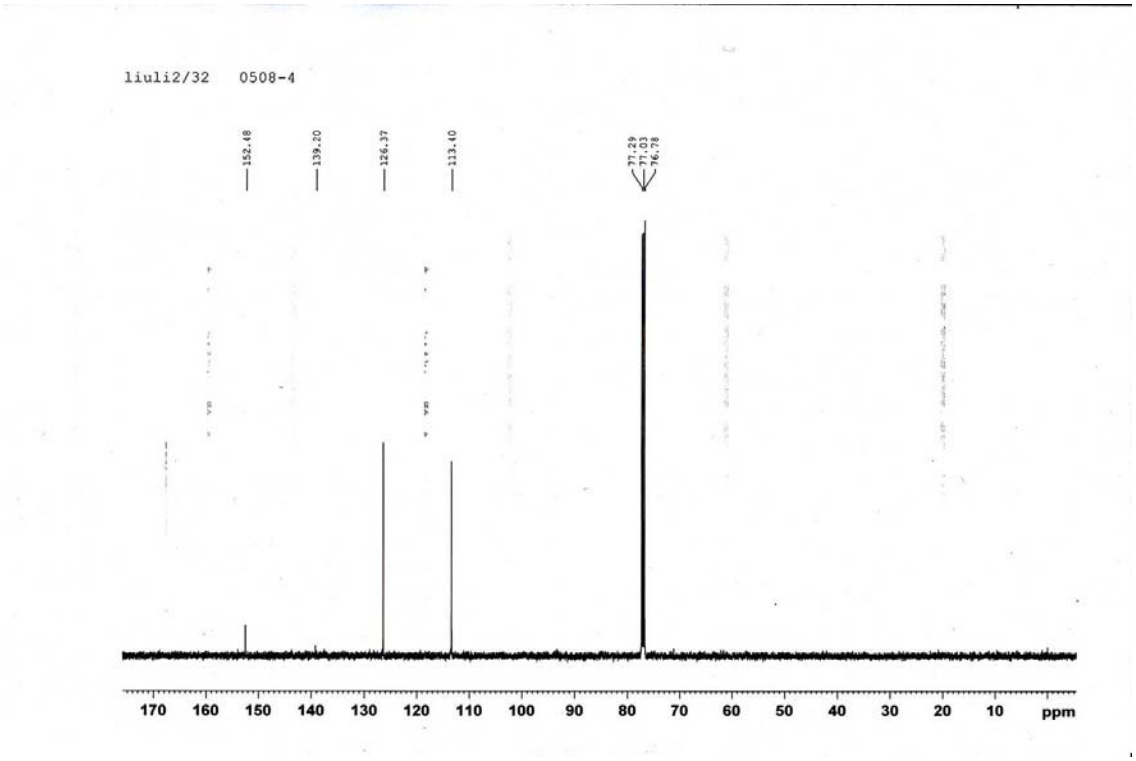

4liuli/119 0508-11
7.220
6.759
3.423
2.200
0.000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.91
1.95
9.00

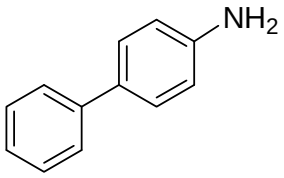

liuli2/38 0508-11
140.13
128.83
127.12
121.84
77.30
77.04
76.79
20.35
17.55
-0.00
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



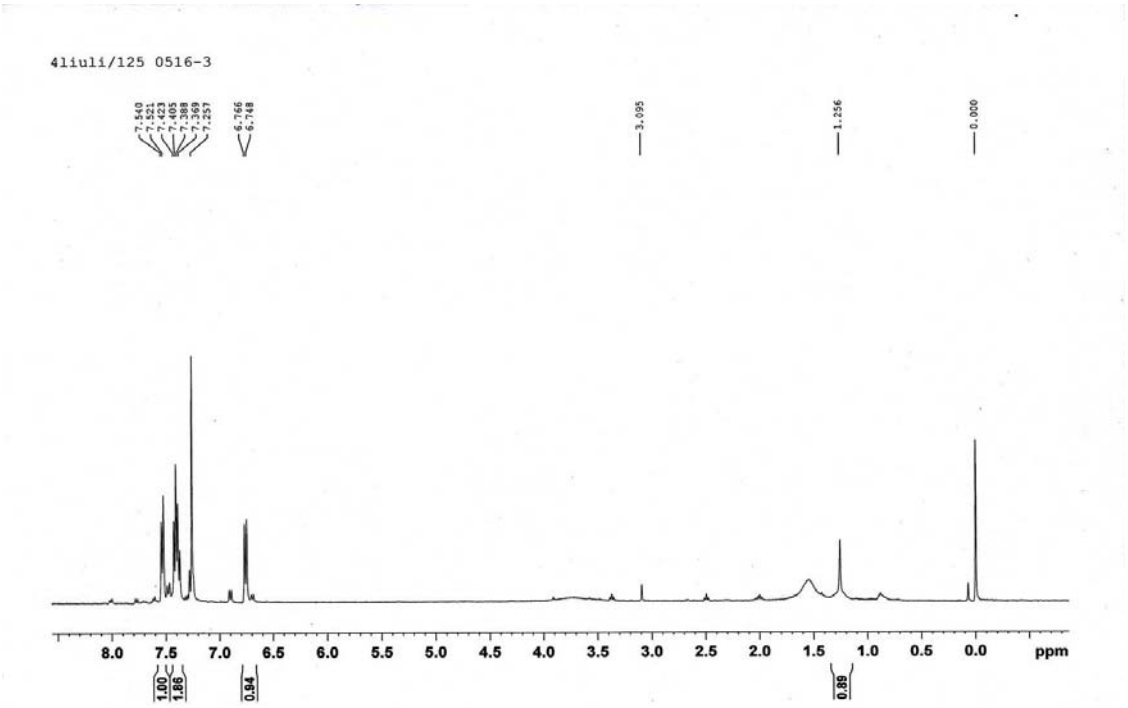
2k

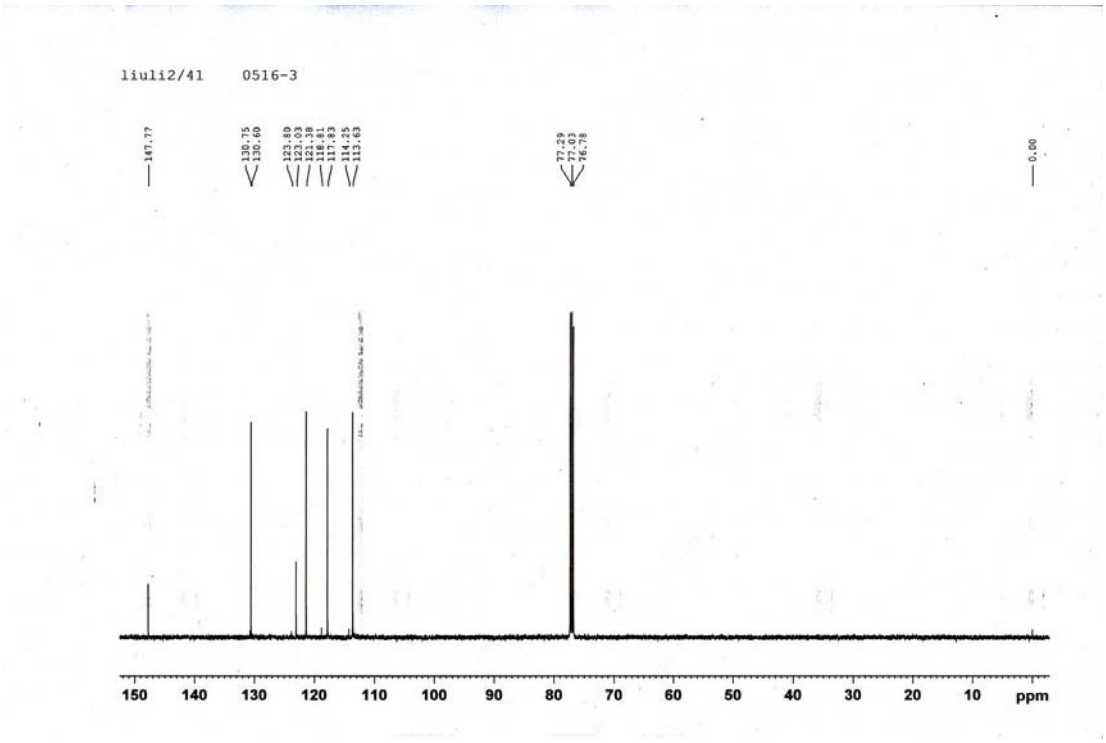


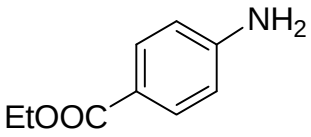



NH2

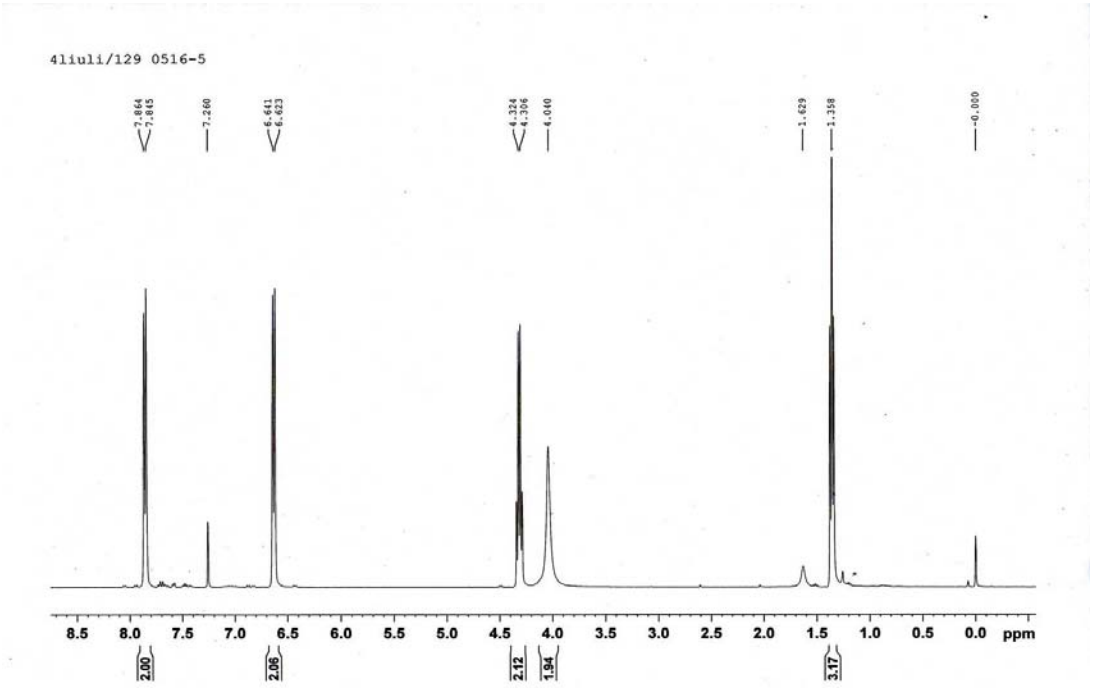
2l

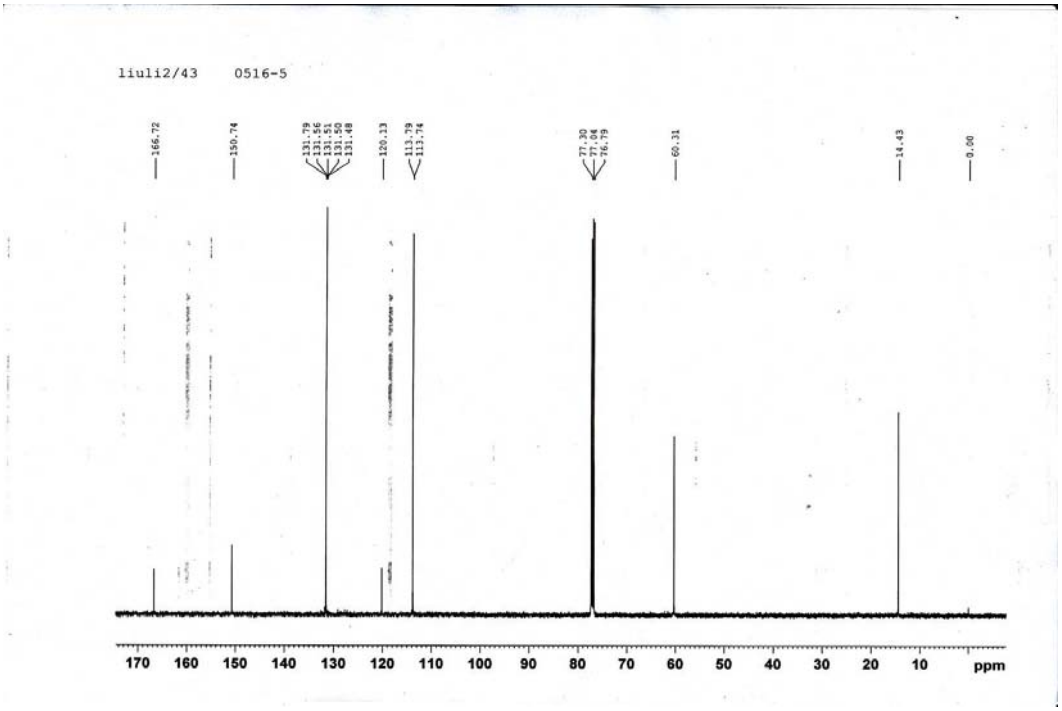

4liuli/125 0516-3
7.540
7.521
7.423
7.405
7.388
7.368
7.257
6.766
6.748
3.095
1.256
0.000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.86
0.84
0.89

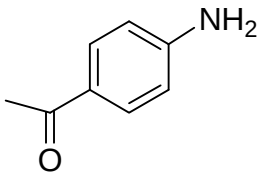

liuli2/41 0516-3
147.77
130.75
130.60
123.80
123.03
121.38
118.81
117.83
114.25
113.63
77.29
77.03
76.78
0.00
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



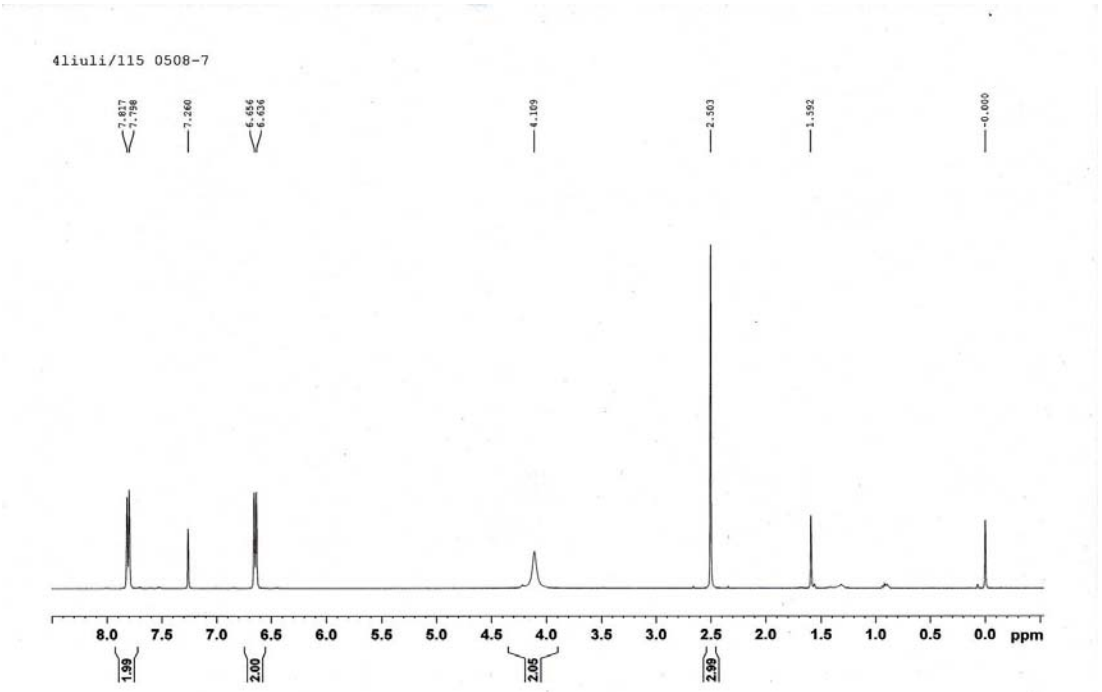
2n

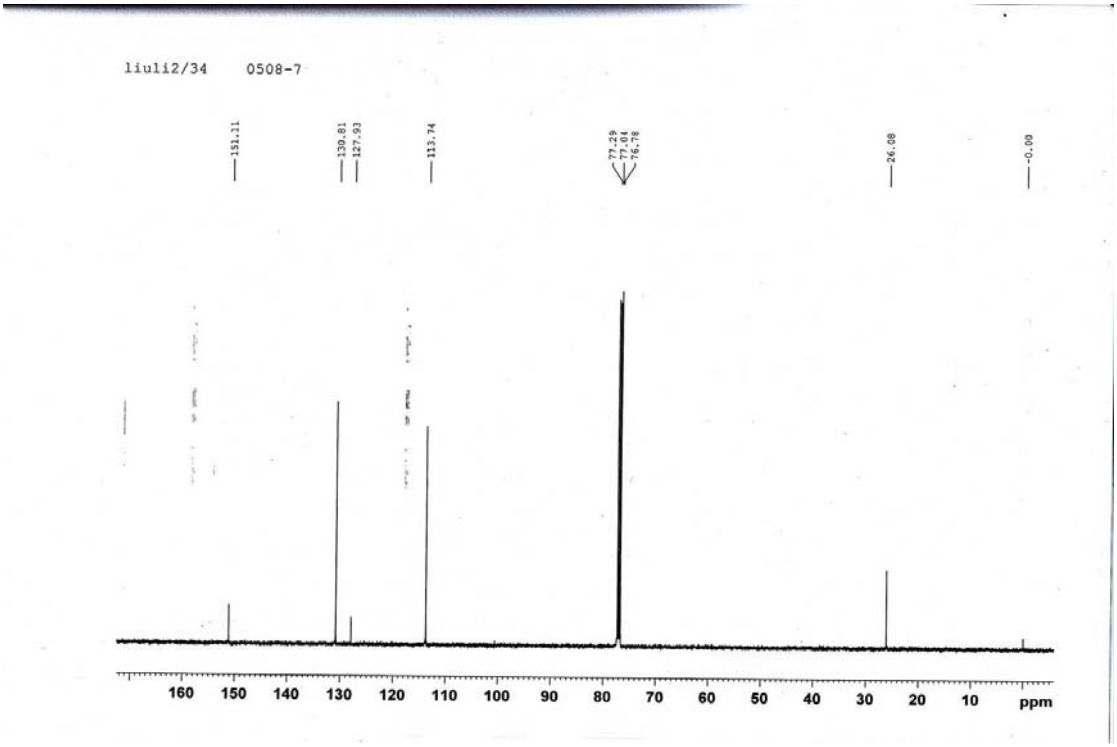


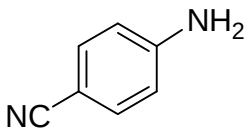




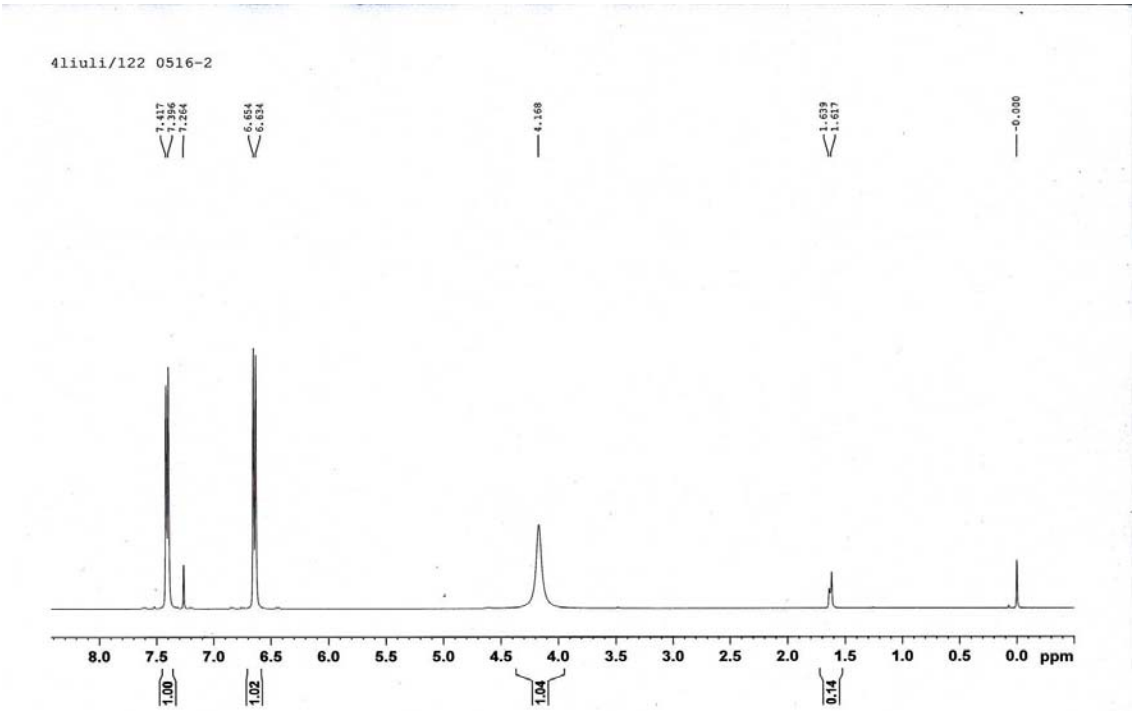
2o

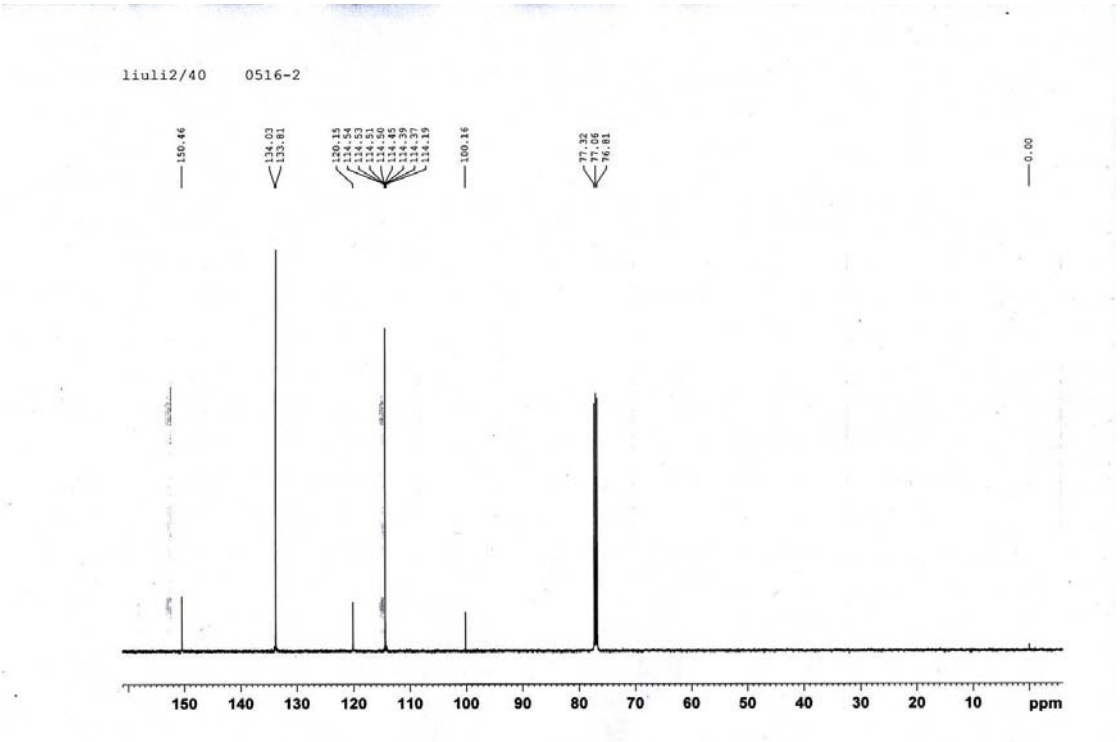


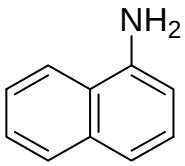




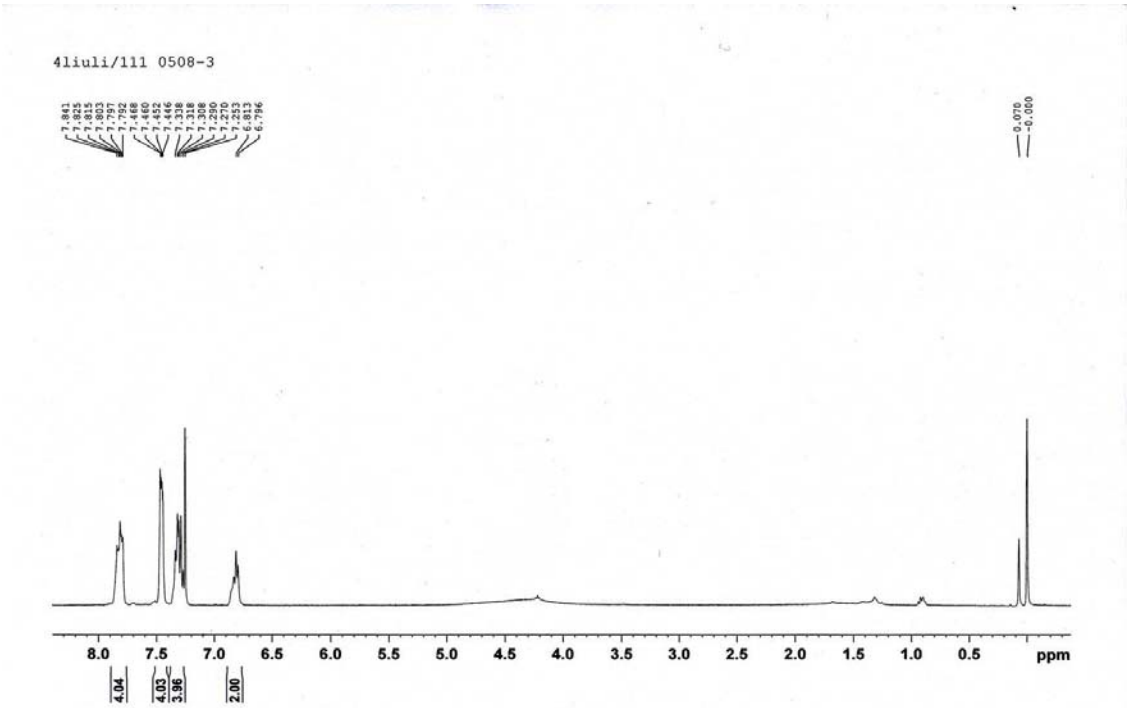
2p

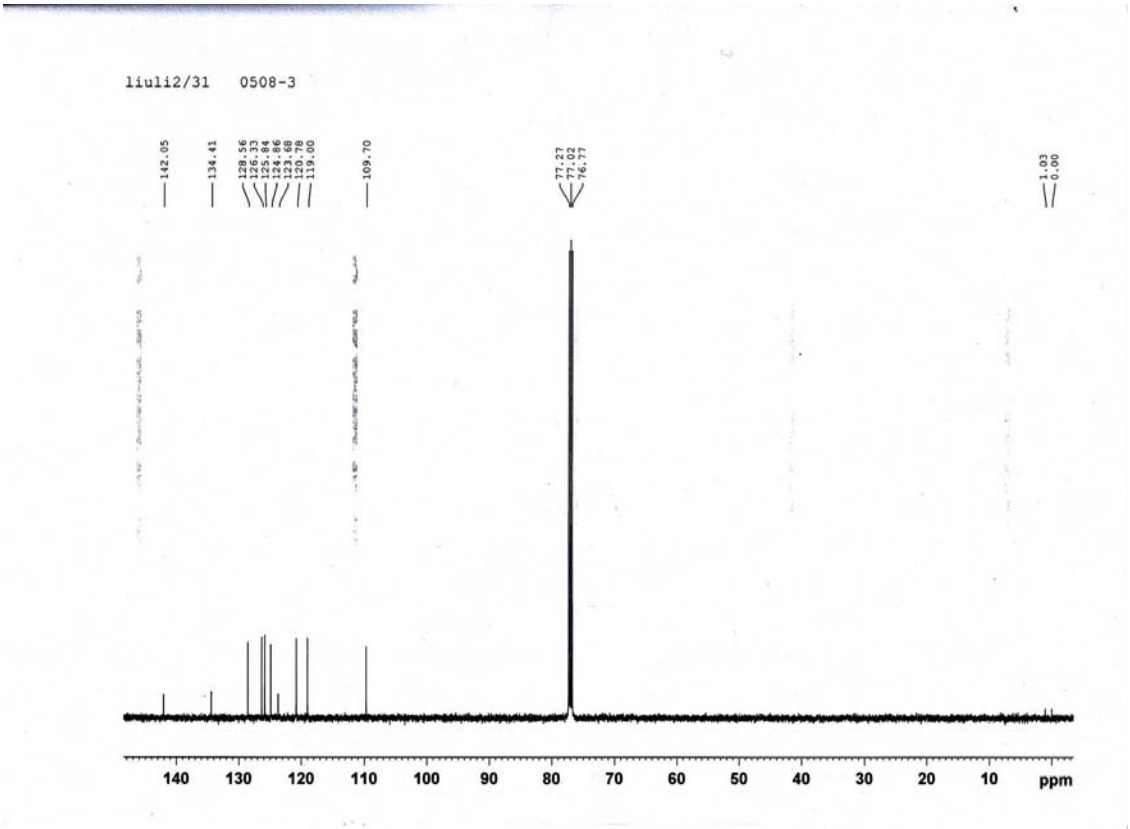


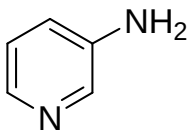




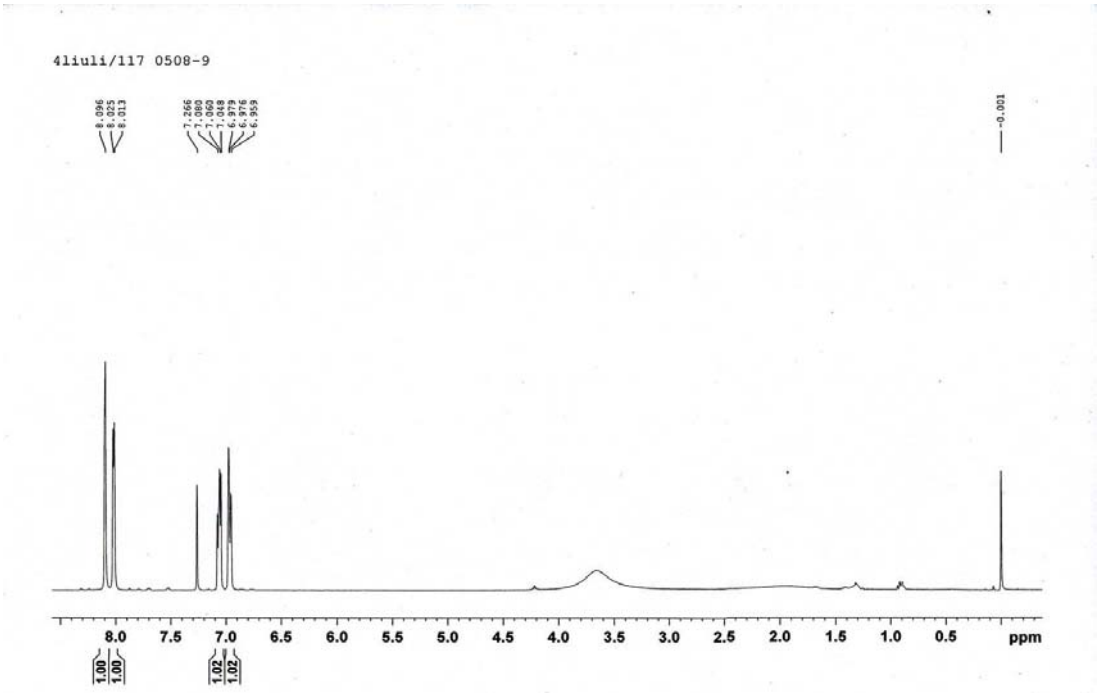
2q

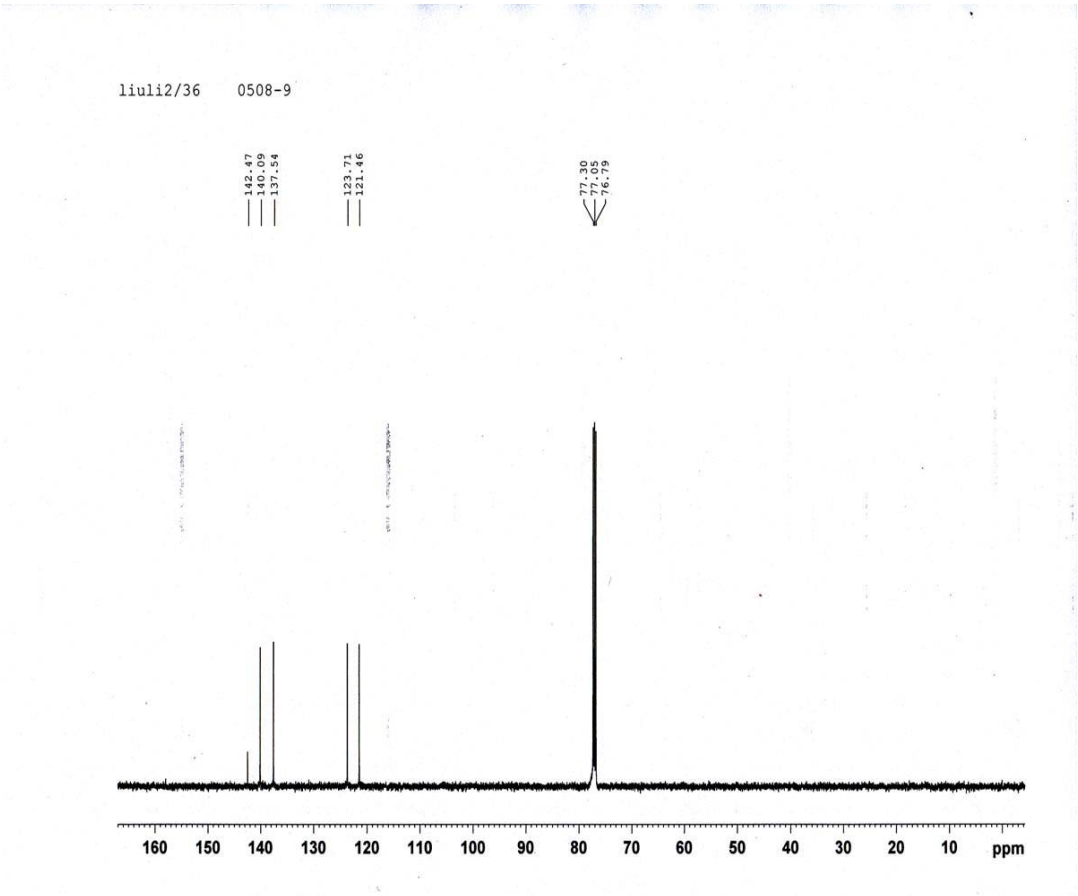


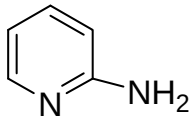




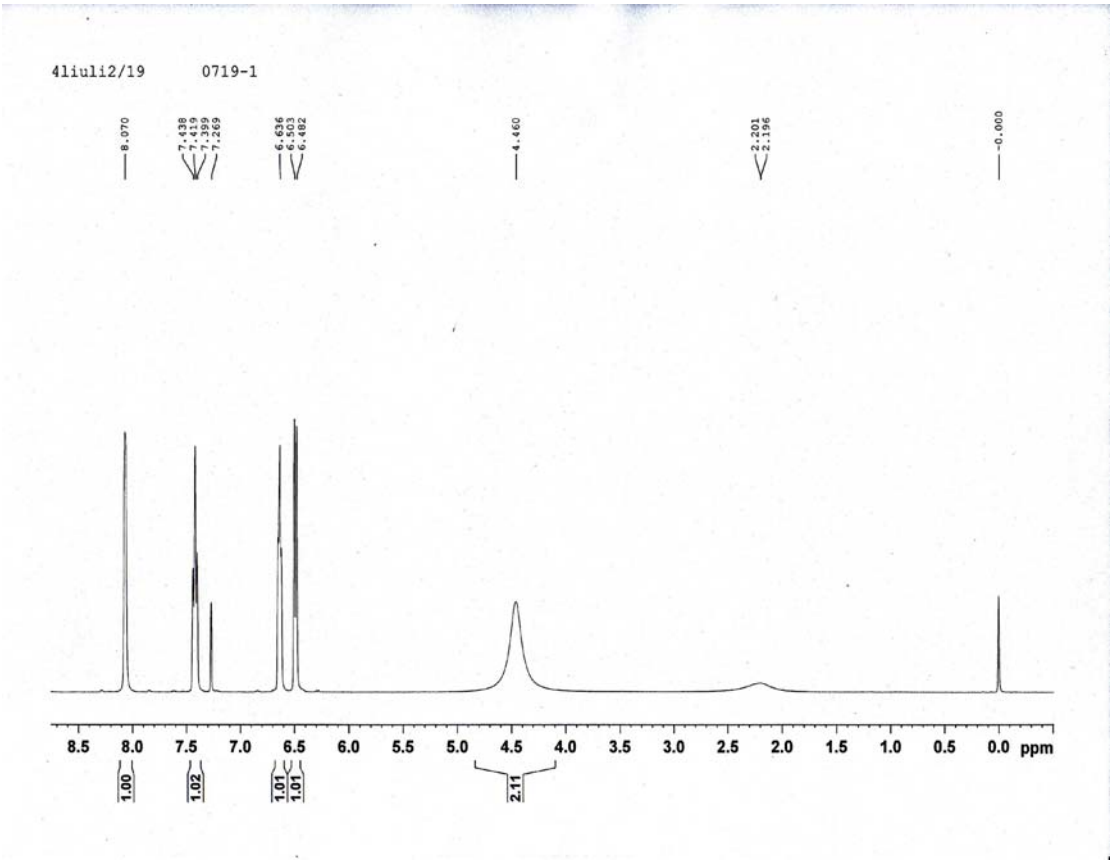
2r

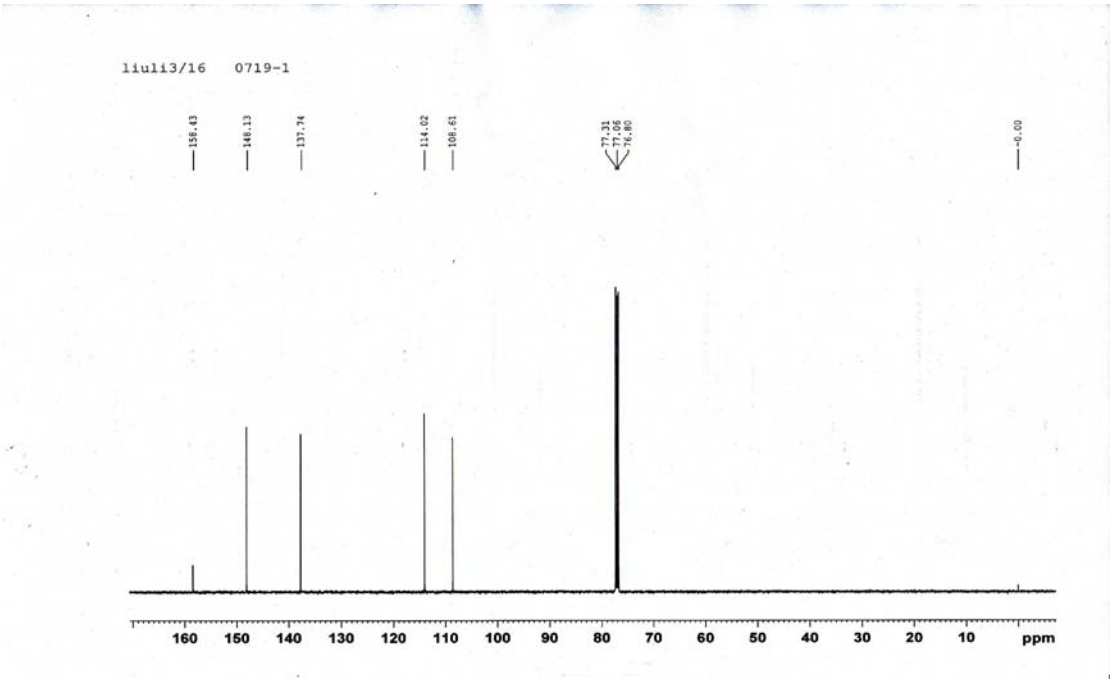


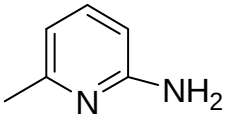



N
NH2

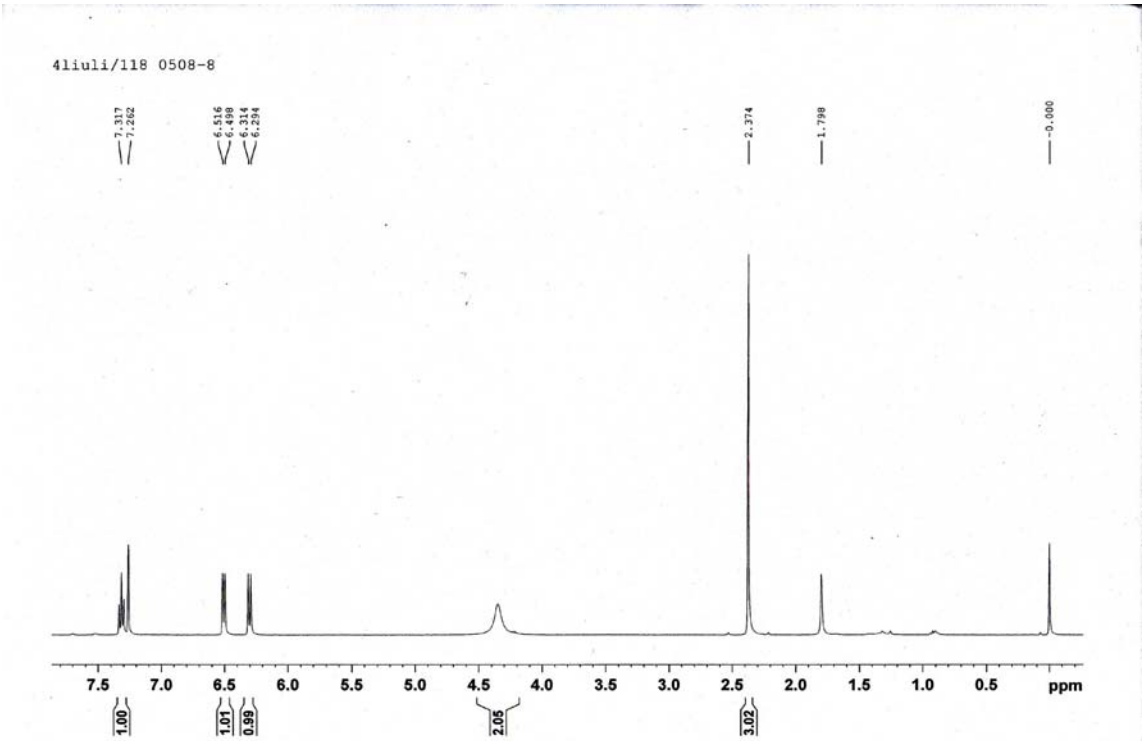
2s

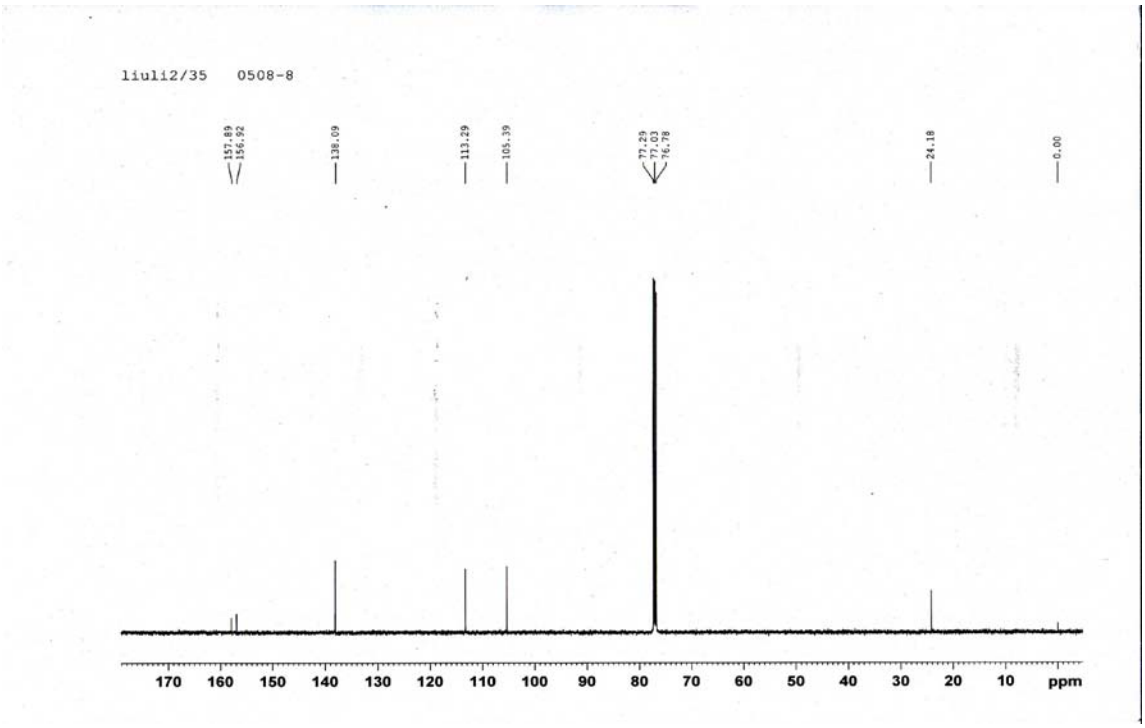

4liuli2/19 0719-1
8.070
7.438
7.419
7.399
7.269
6.636
6.503
6.482
4.460
2.201
2.196
-0.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.02
1.01
1.01
2.11

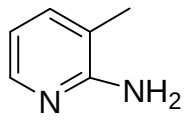

liuli3/16 0719-1
158.43
148.13
137.74
114.02
108.61
77.31
77.06
76.80
-0.00
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


N
NH2

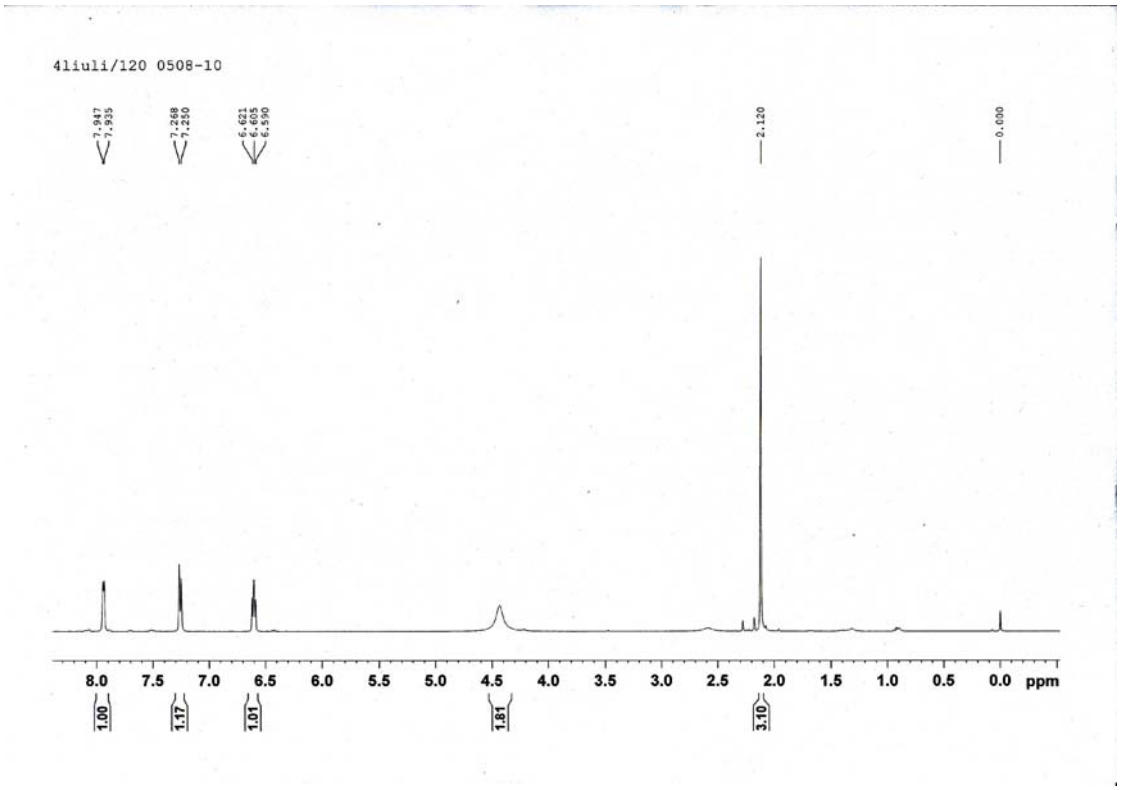
2t

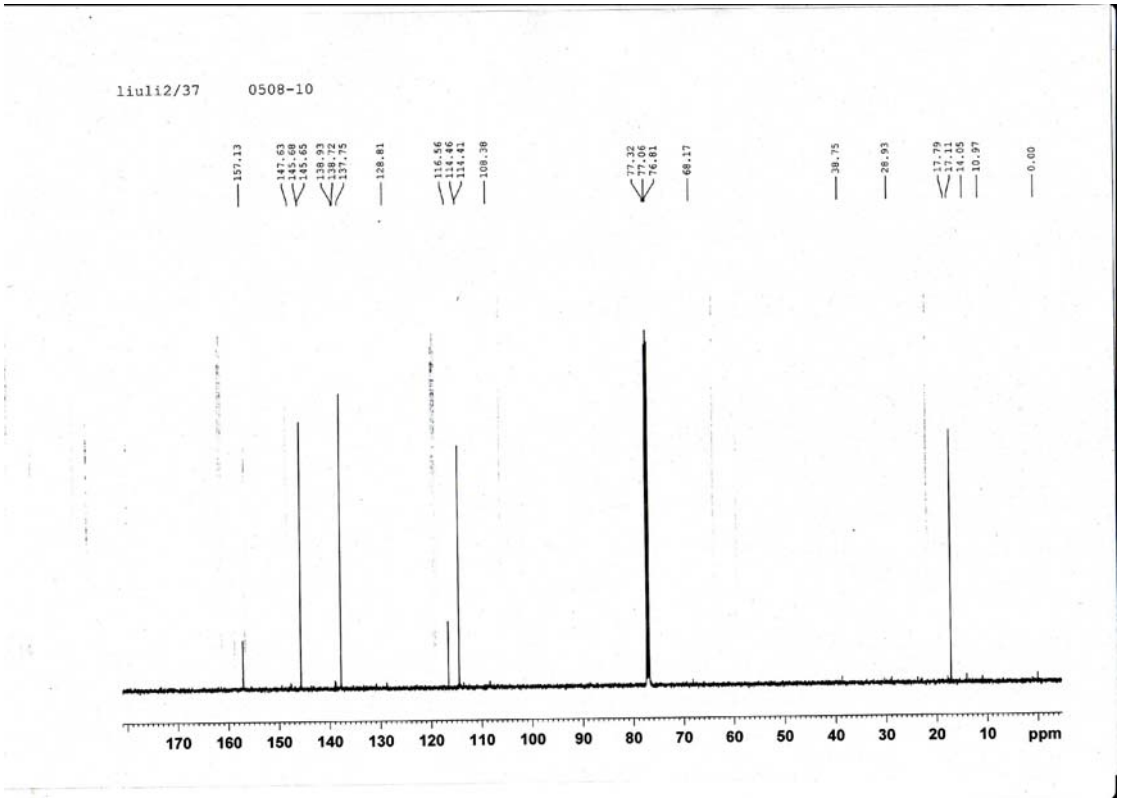

4liuli/118 0508-8
7.317
7.262
6.516
6.498
6.314
6.294
2.374
1.798
0.000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.01
0.99
2.05
3.02

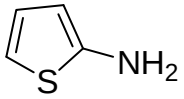

liuli2/35 0508-8
157.89
156.92
138.09
113.29
105.39
77.29
77.03
76.78
24.18
0.00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


N
NH2

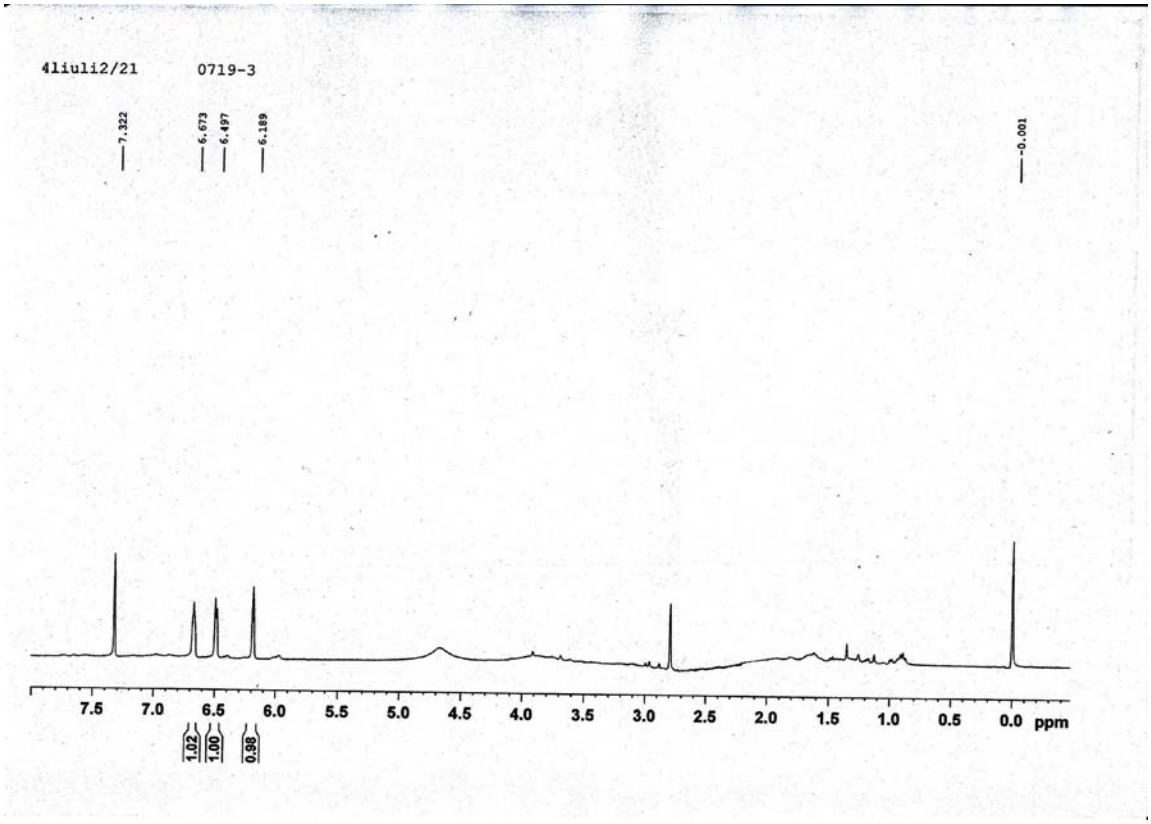
2u

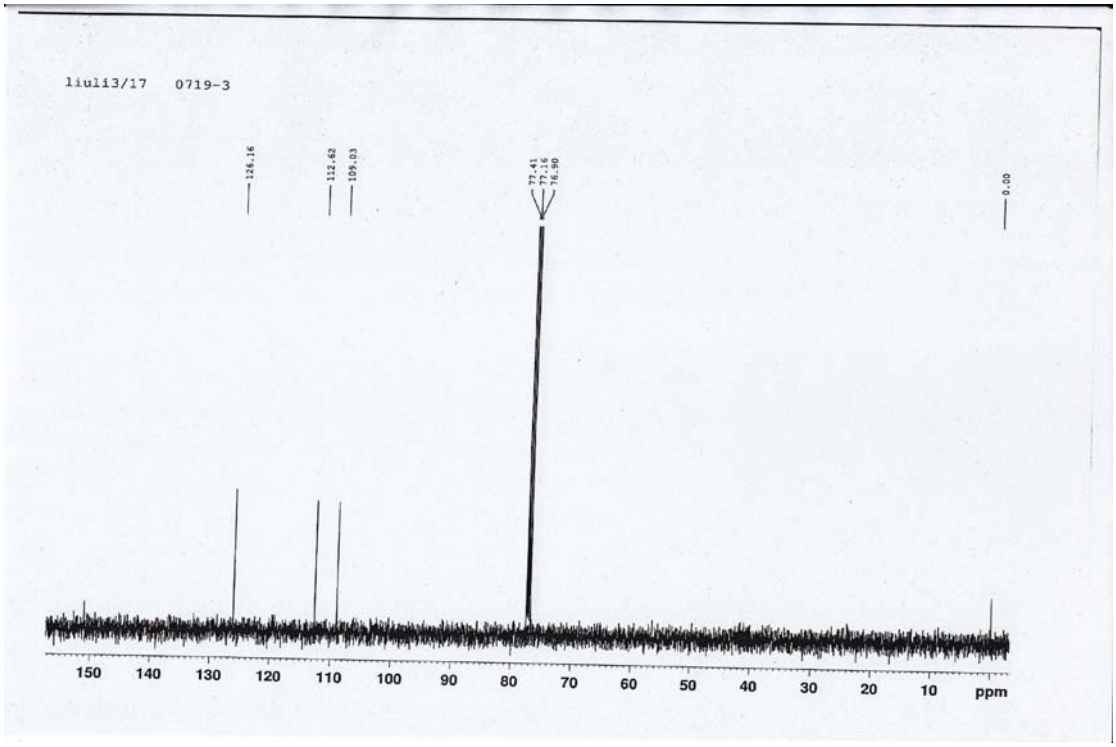

4liuli/120 0508-10
7.947
7.935
7.268
7.250
6.621
6.605
6.590
2.120
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.17
1.01
1.81
3.10


liuli2/37 0508-10
157.13
147.63
145.68
145.65
138.93
138.72
137.75
128.81
116.56
114.46
114.41
108.38
77.32
77.06
76.81
68.17
38.75
28.93
17.79
17.11
14.05
10.97
0.00
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


NH2
S

2v


4liuli2/21 0719-3
7.322
6.673
6.497
6.189
-0.001
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
1.02
1.00
0.98


liuli3/17 0719-3
126.16
112.62
109.03
77.41
77.16
76.90
0.00
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

References

1) J. S. Harvey, S. P. Simonovich, C. R. Jamison and D. W. C. MacMillan, J. *Am. Chem. Soc.* 2011**, 133**, 13782–13785.

2) M. Bielawski, M. Zhu and Olofssona, B. *Adv. Synth. Catal.* 2007, **349**, 2610–2618.

3) J. Li, L. Liu, Y.-Y. Zhou and S.-N. Xu, *RSC Advances*, 2012, **2**, 3207-3209.

4) Y. Li, X. - H. Zhu, F. Meng and Y. - Q. Wen, *Tetrahedron* 2011, **67**, 5450-5454.

5) L. Pehlivan, E. Metay, S. Laval, W. Dayoub, P. Demonchaux, G. Mignani and M. Lemaire, *Tetrahedron* 2011, **67**, 1971-1976.

6) D.-P. Wan, Q. Cai and K. Ding, *Adv. Synth. Catal.* 2009, **351**, 1722–1726.

7) X. Zeng, W.- M. Huang, Y.- T. Qiu and S. Jiang, *Org. Biomol. Chem.,* 2011, **9**, 8224-8227

8) M. K. Elmkaddem, C. Fischmeister, C. M. Thomas, J.-L. Renaud, *Chem. Commun.*, 2010, **46**, 925-927.

9) R. Ntaganda , B. Dhudshia , C. L. B. Macdonald, A. N. Thadani *Chem. Commun.*, 2008, 6200-6202.