Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Transition Metal-free 1,3-Dimethylimidazolium Hydrogen Carbonate Catalyzed Hydration of Organonitriles to Amides

Praveen Kumar Verma, Upendra Sharma, Manju Bala, Neeraj Kumar* and Bikram Singh*

CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh 176 061, India

E-mail: neerajnpp@rediffmail.com; bikram_npp@rediffmail.com

Table of Contents:

General Information:

Metal salts used were purchased from Merck, Germany. Silica gel (60-120 mesh) used for column chromatography was purchased from Sisco Research Laboratories Pvt. Ltd. India and all other chemicals were purchased from Spectrochem, India, Merck, Germany, and Sigma-Aldrich, USA and were used without further purification. NMR spectra were recorded on a Bruker Avance-300 spectrometer. Mass spectra were recorded on QTOF-Micro of Waters Micromass and Maxis-Bruker. The GC-MS analysis was carried out on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometer (Tokyo, Japan), AOC-20i auto-sampler coupled, and a DB-5MS capillary column, (30 m x 0.25 mm i.d., 0.25µm). The initial temperature of column was 70 °C held for 4 min. and was programmed to 230 °C at 4°C/min., then held for 15 min. at 230 °C; the sample injection volume was 2 µl in GC grade dichloromethane. Helium was used as carrier gas at a flow rate of 1.1 ml min^{-1} on split mode (1:50). Melting points were determined on a Barnstead Electrothermal 9100.

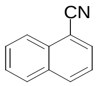
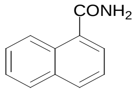
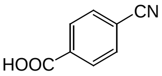
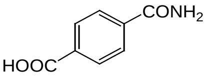
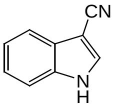
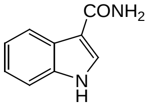
General experimental procedure for hydration of nitriles into amides:

To a mixture of nitrile (1 mmol) and EtOH: H_2O (1:1, 5mL), NHC precursor (5 mol%) was added. The reaction solution was stirred at 80 ^{o}C and the progress of the reaction was monitored by TLC (silica gel; hexane/ethyl acetate) and GC-MS. After completion, the entire mixture was transferred into a 50 mL round-bottom flask, evaporated in vacuo, and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate) to give amide. Some of the amides were crystallized on cooling the reaction mixture and filtered directly from the reaction mixture to give pure amides.

General experimental procedure for synthesis of metal phthalocyanines:

To a mixture of dinitriles (1 mmol), metal salt (0.25 equiv.) and EtOH: H_2O (1:1, 5mL), NHC precursor (5 mol %) was added. The reaction solution was stirred at 160 ^{o}C for 8 h. After completion, the reaction mixture turns to blue semisolid (crude metal phthalocyanine). The blue semisolid was then successively washed with 5% (w/v) NaOH, distilled water, 2% (v/v) HCl and then again with distilled water. The blue semisolid then dissolved in minimum amount of H_2SO_4 and poured in excess of water to precipitate out the purified metal phthalocyanines. The synthesized metal phthalocyanines were then analyzed by UV-Vis and NMR spectroscopy.

Table S1 Hydration of nitriles using **A**^{a}

Entry	Substrate	Time (h)	Product	Yield (%)
1		12		0 >99^{b}
2		12		0 >99^{b}
3		12		0 >99^{b}

[a] Reaction conditions: nitrile (1 mmol), **A** (5 mol %), EtOH: H_2O (1: 1, 5 mL), 80 ^{o}C temperature.

[b] Nitriles remains unreacted, calculated by GC-MS.

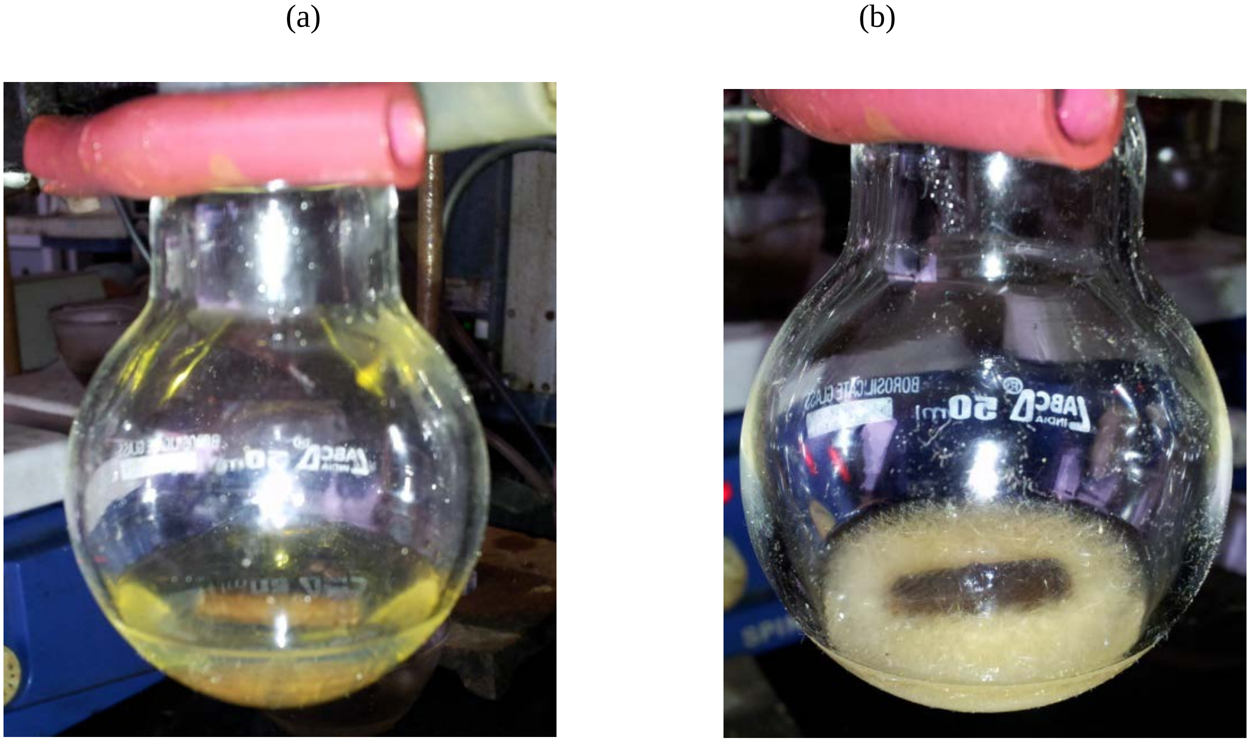
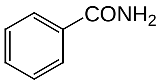


Fig. S1 Pictures of reaction solution (a) before and (b) after hydration of 4-chlorobenzonitrile (Table 2, entry 3) catalyzed by **A**. Reaction conditions are shown in Table 2.

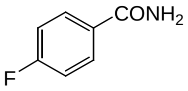
Characterization data of compounds:

Benzamide (Table 2, entry 1)[1,3]:



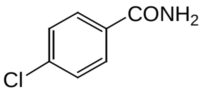
Following the general experimental procedure with benzonitrile (1 mmol or 10 mmol) and catalyst **A** (5 mol%). After 2.5 h at 80 °C, extraction with ethyl acetate afforded benzamide (97 %) as a white solid. Mp = 125-127 °C (Lit[2] mp = 127-128 °C). ^{1}H NMR (300 MHz, CD_3OD): δ 7.88 (d, *J* = 7.5, Hz, 2H), 7.55 (t, *J* = 7.3, Hz, 1H), 7.44-749 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ (ppm) = 171.4, 133.9, 131.9, 128.5, 127.6; HRESIMS calcd for C_7H_8NO $[M+H]^+$ 122.0606, found 122.0621.

4-Fluorobenzamide (Table 2, entry 2):



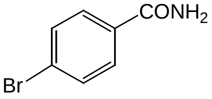
Following the general experimental procedure with 4-fluorobenzonitrile (1 mmol) and catalyst **A** (5 mol%). After 6 h at 80 °C, on cooling the reaction mixture 4-fluorobenzamide (90%) was obtained as white crystals after filtration and washing with distilled water. Mp = 150-153 °C (Lit mp = 149-150 °C[4]). ^{1}H NMR (300 MHz, CD_3OD): δ 7.97-7.92 (m, 2H), 7.22-7.16 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ 170.1., 167.0, 163.7, 130.4, 130.3, 115.5, 115.2. HRESIMS calcd for C_7H_7NOCl $[M+H]^+$ 140.0512, found 140.0529.

4-Chlorobenzamide (Table 2, entry 3)[1]:



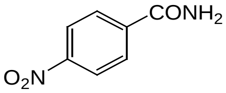
Following the general experimental procedure with 4-chlorobenzonitrile (1 mmol or 10 mmol) and catalyst **A** (5 mol%). After 6 h at 80 °C, on cooling the reaction mixture 4-chlorobenzamide (91%) was obtained as white crystals after filtration and washing with distilled water. Mp = 171-174 °C (Lit[2] mp = 172-174 °C). ^{1}H NMR (300 MHz, CD_3OD): δ 7.87 (d, *J* = 8.7, Hz, 2H), 7.46 (d, *J* = 8.7, Hz, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ 171.3, 139.2, 133.8, 130.5, 129.9. HRESIMS calcd for C_7H_7NOCl $[M+H]^+$ 156.0216, found 156.0216.

4-Bromobenzamide (Table 2, entry 4)[1,3]:



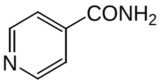
Following the general experimental procedure with 4-bromobenzonitrile (1 mmol) and catalyst **A** (5 mol%). After 6 h at 80 °C, extraction with ethyl acetate afforded 4-bromobenzamide (84%) as a white solid. Mp = 190-193 °C (Lit mp[6] = 190-192 °C). ^{1}H NMR (300 MHz, CD_3OD): δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ 171.7, 134.6, 133.2, 131.0, 127.8. HRESIMS calcd for C_7H_7NOBr $[M+H]^+$ 199.9711, found 199.9702.

4-Nitrobenzamide (Table 2, entry 8)[1,3]:



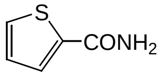
Following the general experimental procedure with 4-nitrobenzonitrile (1 mmol or 10 mmol) and catalyst **A** (5 mol%). After 4 h at 80 °C, extraction with ethyl acetate afforded 4-nitrobenzamide (96%) as a white solid. Mp = 198-202 °C (Lit[4] mp = 198-200 °C). ^{1}H NMR (300 MHz, CD_3OD): δ 7.79 (d, *J* = 8.6, Hz, 2H), 7.63 (d, *J* = 8.6, Hz, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ 169.1, 150.2, 139.9, 129.0, 123.6. HRESIMS calcd for $C_7H_7N_2O_3$ $[M+H]^+$ 167.0457, found 167.0442.

Isonicotinamide (Table 2, entry 11)[1,3]:



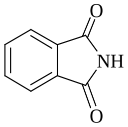
Following the general experimental procedure with 4-cyanopyridine (1 mmol or 10 mmol) and catalyst **A** (5 mol%). After 3 h at 80 °C, on cooling the reaction mixture isonicotinamide (96%) was obtained as white crystals after filtration and washing with distilled water. Mp = 152-155 °C. ^{1}H NMR (300 MHz, CD_3OD): δ 7.79 (dd, *J* = 4.5 Hz, *J* = 1.6 Hz, 2H), 7.63 (dd, *J* = 4.5 Hz, *J* = 1.6 Hz, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ (ppm) = 170.2, 151.5, 143.9, 123.6. HRESIMS calcd for $C_6H_7N_2O$ $[M+H]^+$ 123.0558, found 123.0526.

Thiophene-2-carboxamide (Table 2, entry 12)[4]:



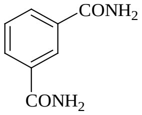
Following the general experimental procedure with thiophene-2-carbonitrile (1 mmol) and catalyst **A** (5 mol%). After 4 h at 80 °C, extraction with ethyl acetate afforded thiophene-2-carboxamide (97%) as a white solid. Mp = 175-176 °C (Lit[4] mp = 177-178 °C). ^{1}H NMR (300 MHz, CD_3OD): δ 7.74-7.66 (m, 2H), 7.15-7.12 (m, 1H). ^{13}C NMR (75 MHz, CD_3OD): δ 167.1, 140.3, 132.6, 131.1, 129.3. HRESIMS calcd for C_5H_6NOS $[M+H]^+$ 128.0170, found 128.0186.

Phthalimide (Table 3, entry 1):



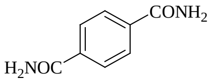
Following the general experimental procedure with 1,2-benzenedinitrile (1 mmol) and catalyst **A** (5 mol%). After 4 h at 80 °C, extraction with ethyl acetate afforded phthalimide (90%) as a white solid. Mp = 230-232 °C (Lit[5] mp = 228-230 °C). ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.19 (s, 4H), 9.78 (brs, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 170.1, 135.1, 133.3, 123.7.

Isophthalimide (Table 3, entry 2)[1]:



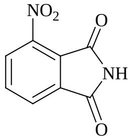
Following the general experimental procedure with isophthalonitrile (1 mmol) and catalyst **A** (5 mol%). After 6.5 h at 80 °C, extraction with ethyl acetate afforded isophthalimide (91%) as a white solid. Mp = 290-292 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.37 (s, 1H), 8.04 (brs, 2xNH), 7.99 (d, *J* = 7.7 Hz, 2H), 7.53 (t, 7.7 Hz, 1H), 7.46 (brs, 2xNH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.5, 134.4, 130.0, 128.2, 126.7; HRESIMS calcd for $C_8H_9N_2O_2$ $[M+H]^+$ 165.0664, found 165.0639.

Terephthalimide (Table 3, entry 3):



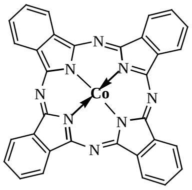
Following the general experimental procedure with terephthalonitrile (1 mmol) and catalyst **A** (5 mol%). After 6.5 h at 80 °C, extraction with ethyl acetate afforded terephthalimide (95%) as a white solid. Mp = 318-320 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.07 (brs, 2xNH), 7.93 (s, 4H), 7.48 (brs, 2xNH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.7, 136.0, 126.8; HRESIMS calcd for $C_8H_9N_2O_2$ $[M+H]^+$ 165.0664, found 165.0648.

3-Nitrophthalimide (Table 3, entry 6):



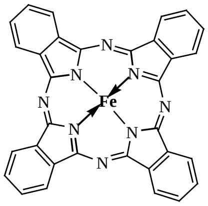
Following the general experimental procedure with 3-nitrophthalonitrile (1 mmol) and catalyst **A** (5 mol%). After 6 h at 80 °C, extraction with ethyl acetate afforded 3-nitrophthalimide (92%) as a white solid. Mp = 210-213 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.99-8.05 (m, 1H), 8.08-8.11 (m, 1H), 8.22-8.24 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.5, 164.9, 144.6, 136.4, 134.9, 128.4, 127.1, 124.2.

Cobalt (II) phthalocyanine (Table 4, entry 1):



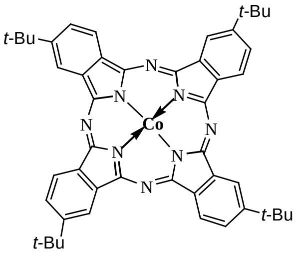
Following the general experimental procedure with 1,2-dicyanobenzene (1 mmol), $CoCl_2.6H_2O$ (0.25 equiv) and EtOH: H_2O (1:1, 5mL), NHC precursor (5 mol%) was added. The reaction solution was stirred at 160 ^{o}C for 8 h. After completion, the reaction mixture turns to blue semisolid (crude cobalt (II) phthalocyanine). The blue semisolid was then successively washed with 5 % (w/v) NaOH, distilled water, 2 % (v/v) HCl and then again with distilled water. The blue semisolid then dissolved in minimum amount of H_2SO_4 and poured in excess of water to precipitate out the purified cobalt (II) phthalocyanines (59%). UV/Vis (THF): λ_{max} (nm) 660, 596, 335.

Iron (II) phthalocyanine (Table 4, entry 2):



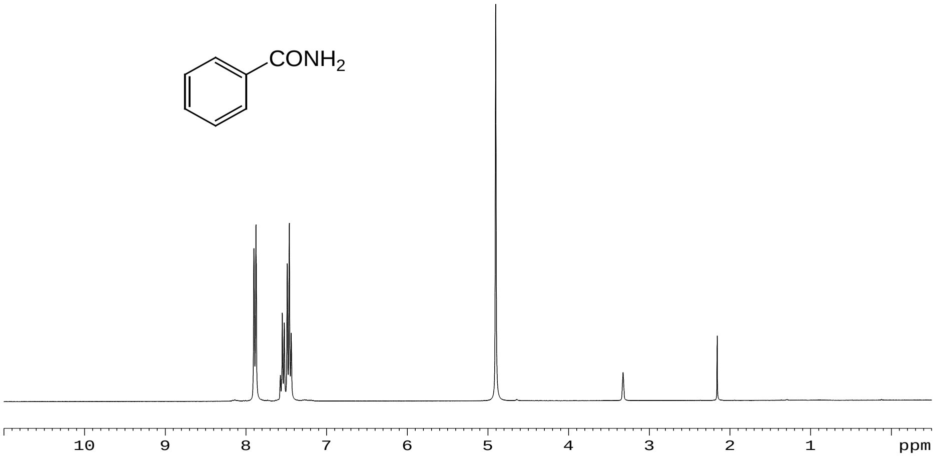
Following the general experimental procedure with 1,2-dicyanobenzene (1 mmol), $FeSO_4.7H_2O$ (0.25 equiv.) and EtOH: H_2O (1:1, 5mL), NHC precursor (5 mol %) was added. The reaction solution was stirred at 160 ^oC for 8 h. After completion, the reaction mixture turns to blue semisolid (crude iron (II) phthalocyanine). The blue semisolid was then successively washed with 5% (w/v) NaOH, distilled water, 2% (v/v) HCl and then again with distilled water. The blue semisolid then dissolved in minimum amount of H_2SO_4 and poured in excess of water to precipitate out the purified iron (II) phthalocyanines (54%). UV/Vis (MeOH): λ_{max} (nm) 659, 602, 332; UV/Vis (THF): λ_{max} (nm) 705, 667.

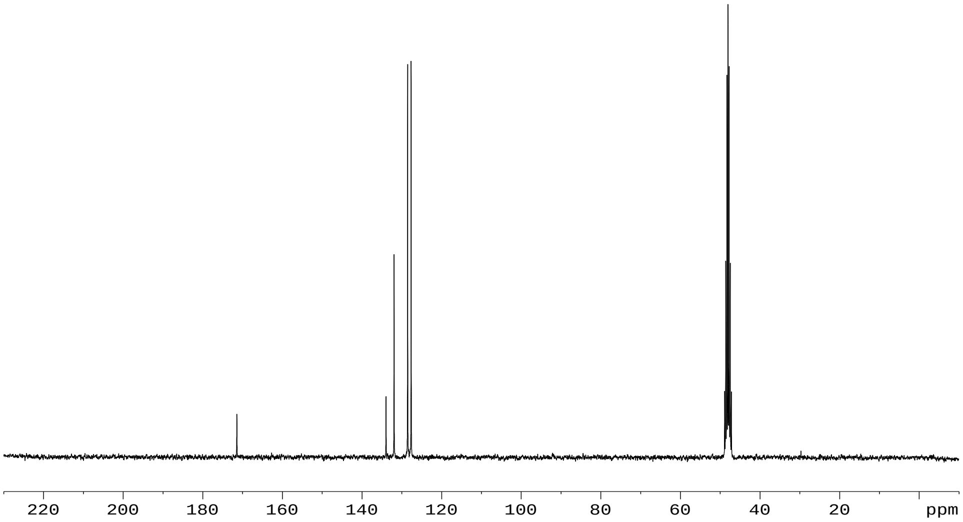
4-*tert*-Butyl cobalt (II) phthalocyanine (Table 4, entry 3):

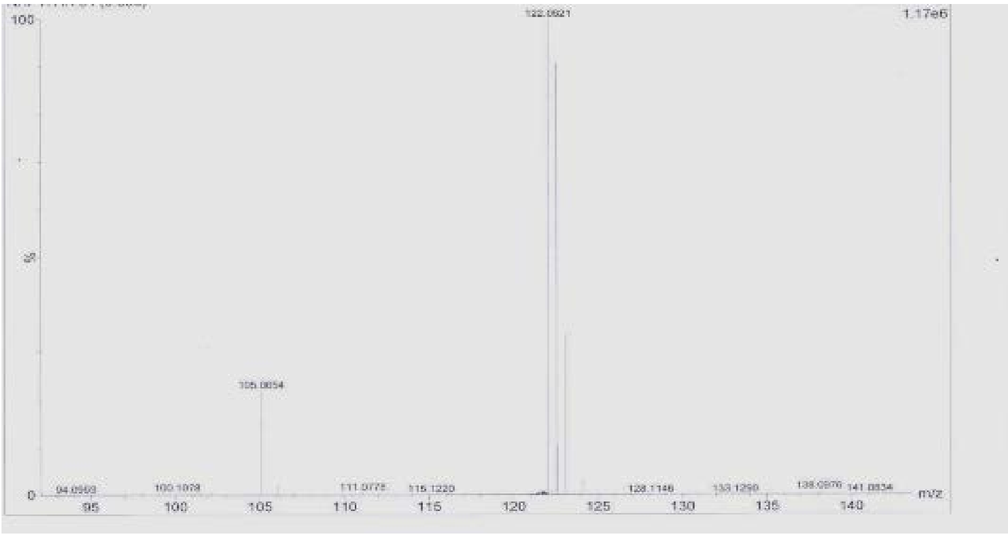


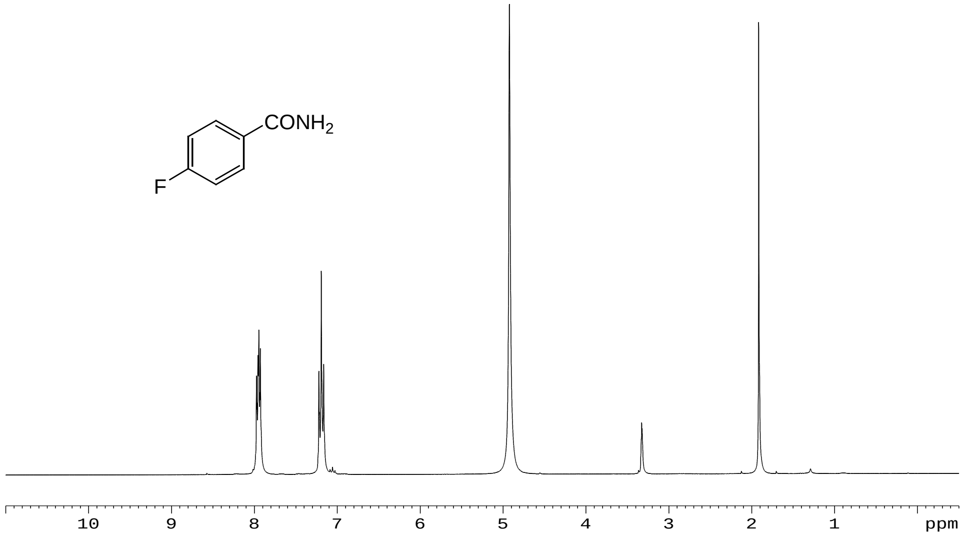
Following the general experimental procedure with 4-*tert*-Butyl-1,2-dicyanobenzene (1 mmol), $CoCl_2.6H_2O$ (0.25 equiv.) and EtOH: H_2O (1: 1, 5mL), NHC precursor (5 mol%) was added. The reaction solution was stirred at 160 ^oC for 8 h. After completion, the reaction mixture turns to blue semisolid (crude 4-*tert*-Butyl cobalt (II) phthalocyanine). The blue semisolid was then successively washed with 5% (w/v) NaOH, distilled water, 2% (v/v) HCl and then again with distilled water. The blue semisolid then dissolved in minimum amount of H_2SO_4 and poured in excess of water to precipitate out the purified 4-*tert*-butyl cobalt (II) phthalocyanines (66%). UV/Vis (THF): λ_{max} (nm) 666, 601, 333. ^1H NMR (300 MHz, CD_3OD): δ 7.75-8.03 (m, 12H), 1.41 (s, 36H); ^{13}C NMR (75 MHz, CD_3OD): δ 162.3, 160.1, 132.7, 124.1, 121.3, 36.8, 31.7.

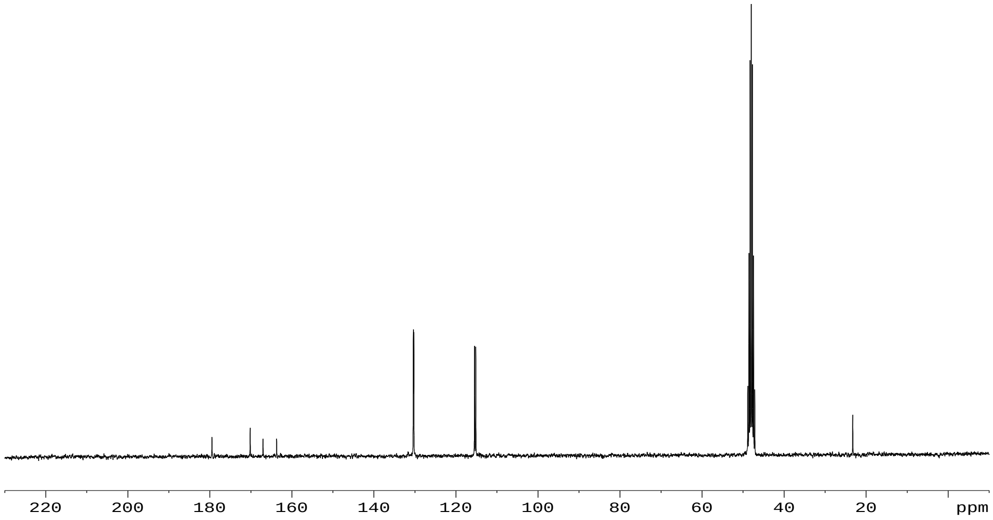
NMR and mass spectra of compounds:

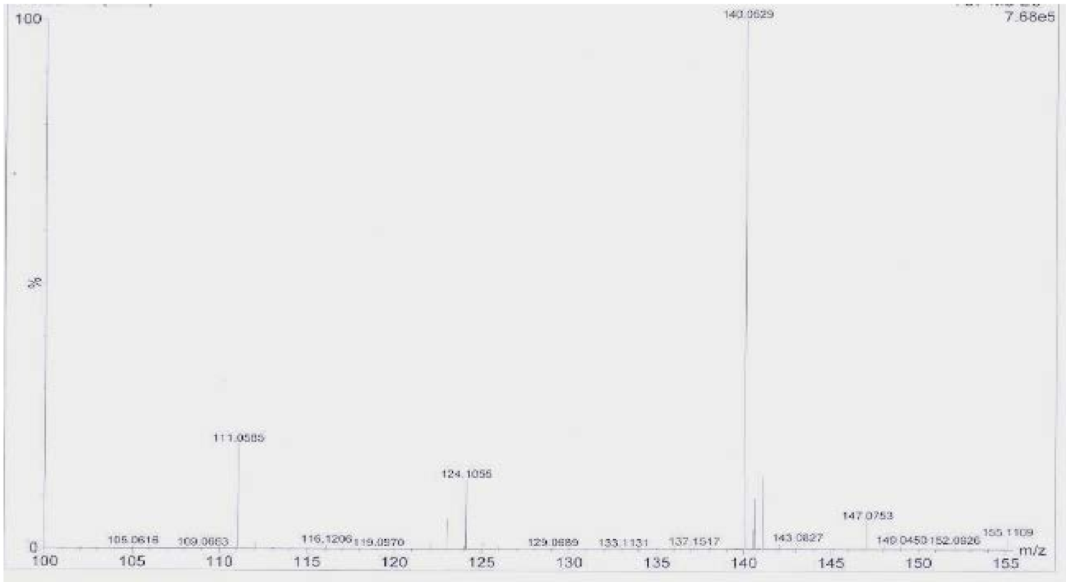


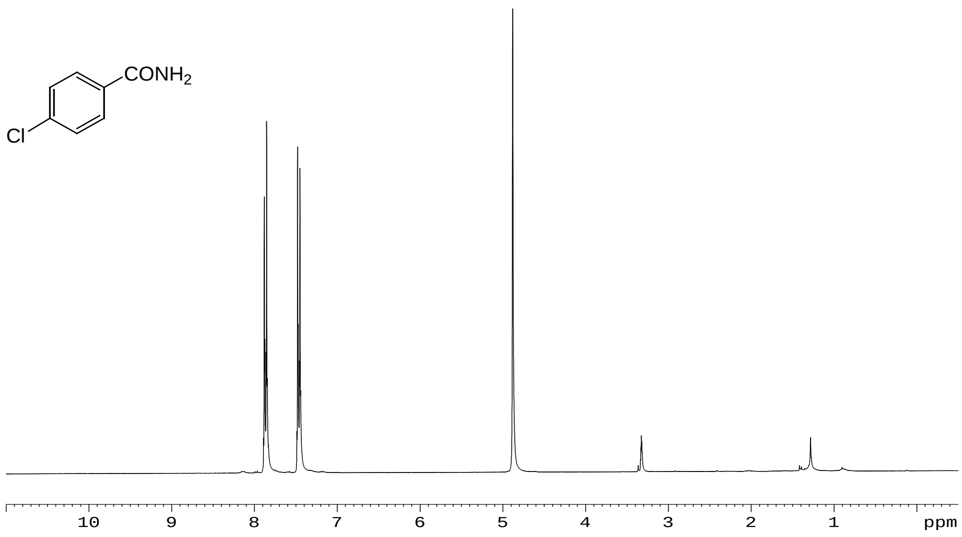


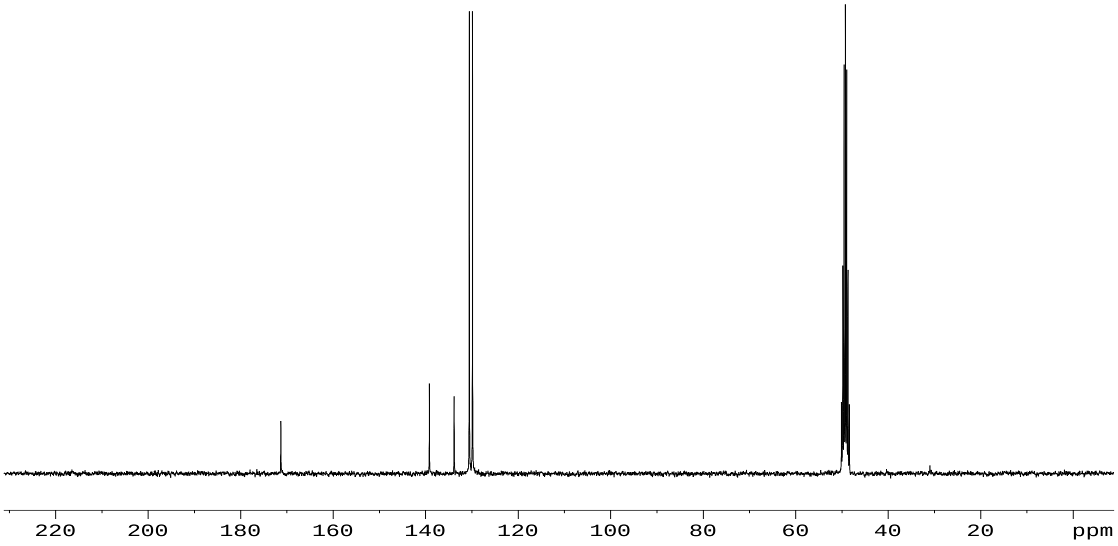


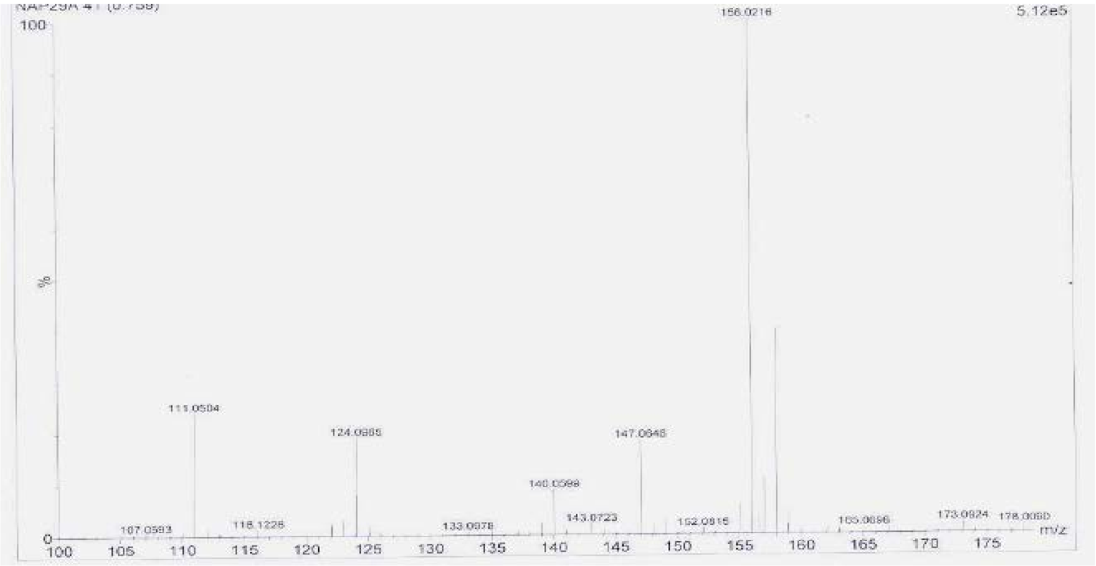

CONH2
F
10
9
8
7
6
5
4
3
2
1
ppm

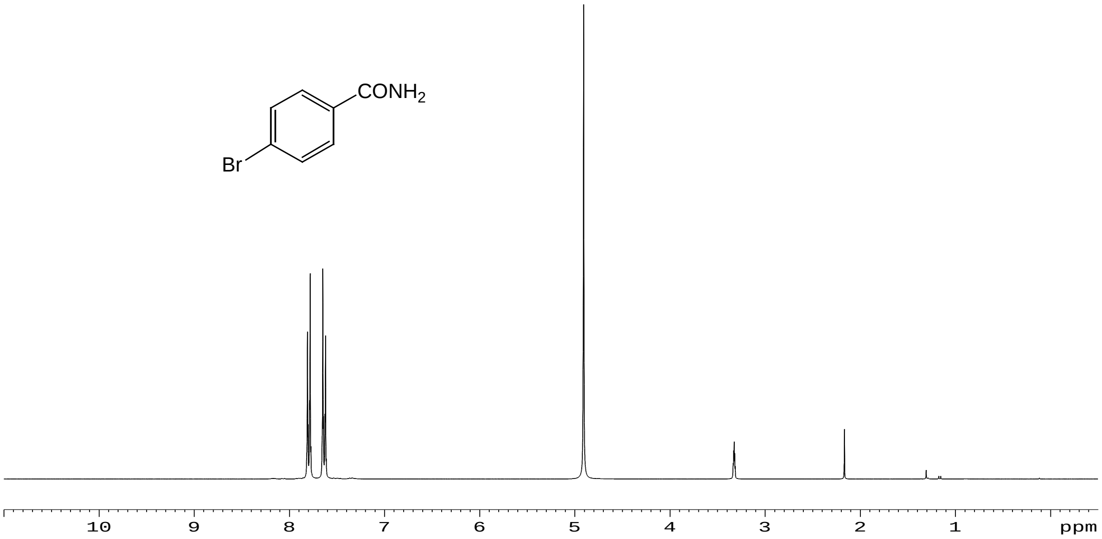

220
200
180
160
140
120
100
80
60
40
20
ppm

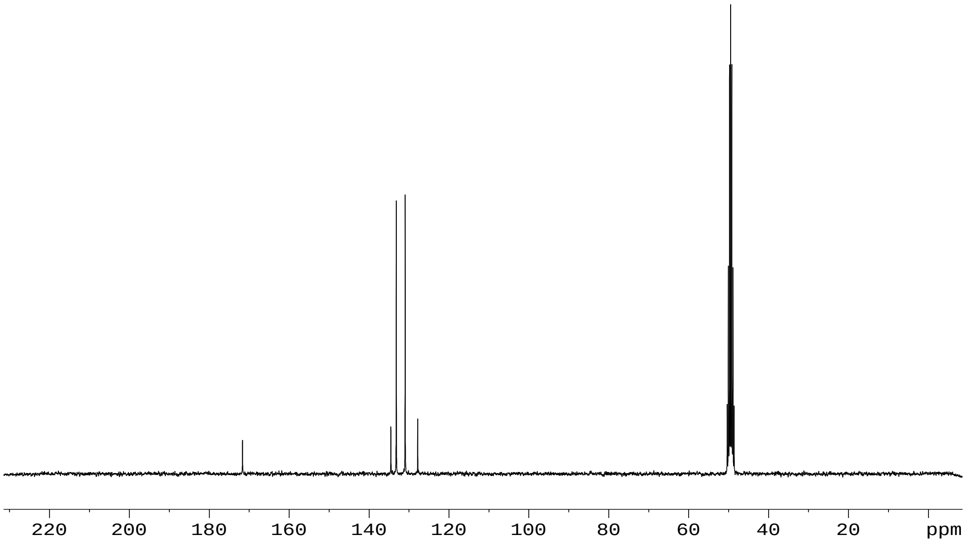

100
140.0629
7.68e5
%
111.0585
124.1055
147.0753
105.0616
109.0863
116.1206
119.0970
129.0689
133.1131
137.1517
143.0827
149.0453
152.0826
155.1109
0
m/z
100
105
110
115
120
125
130
135
140
145
150
155

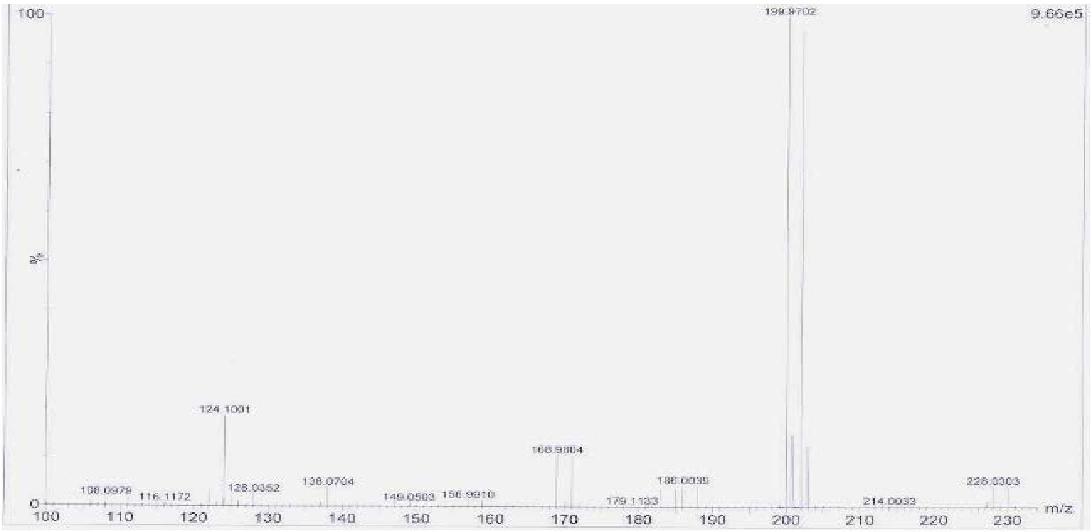

CONH2
Cl
10
9
8
7
6
5
4
3
2
1
ppm

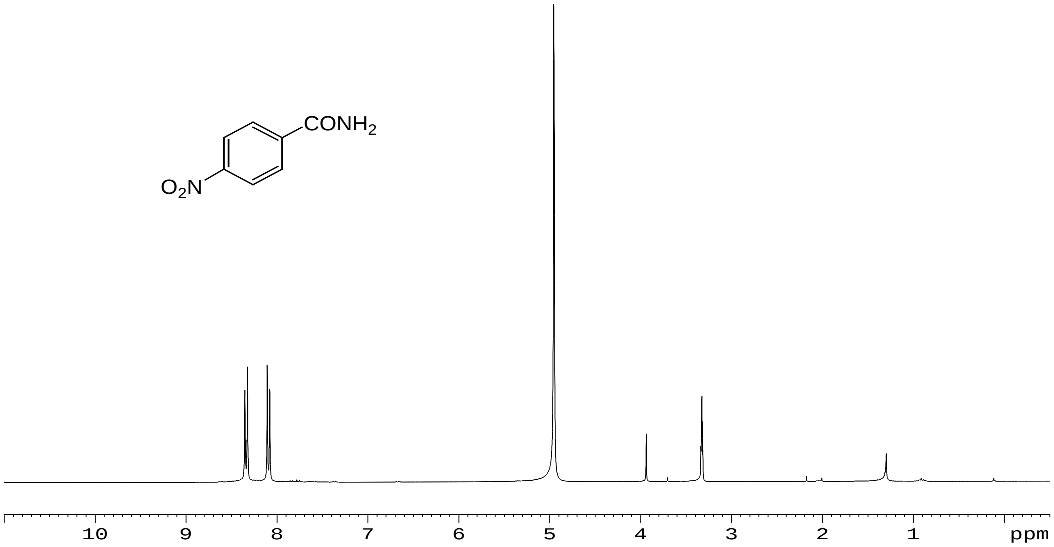

220
200
180
160
140
120
100
80
60
40
20
ppm

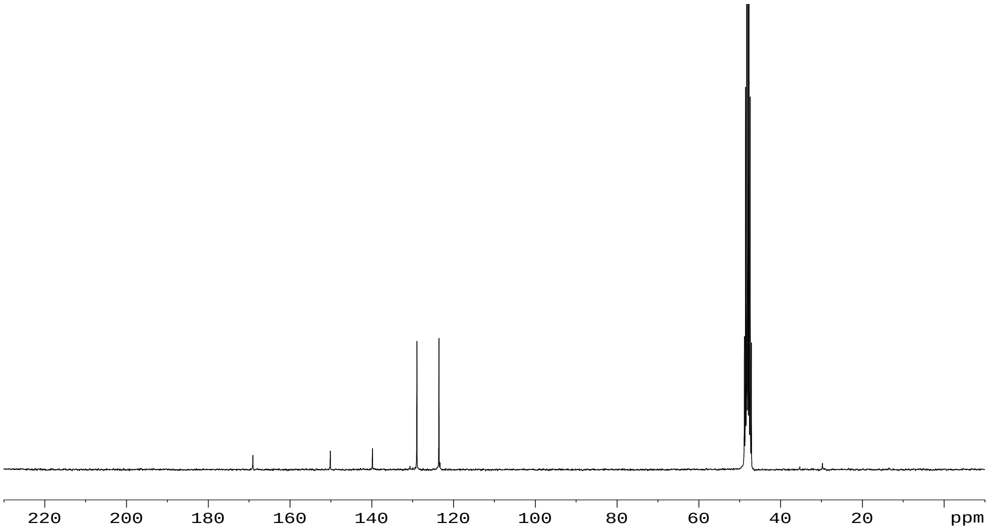

NAP29A 41 (0.759)
100
%
0
156.0216
5.12e5
111.0504
124.0985
147.0646
140.0599
143.0723
107.0593
116.1226
133.0978
152.0815
165.0696
173.0924
178.0060
m/z
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175

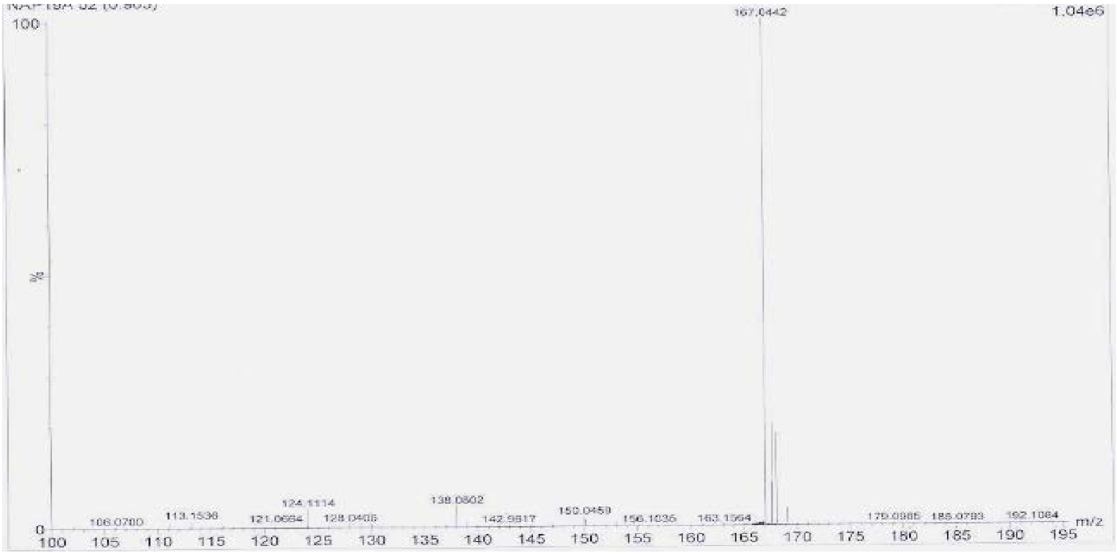

CONH$_2$
Br
10
9
8
7
6
5
4
3
2
1
ppm

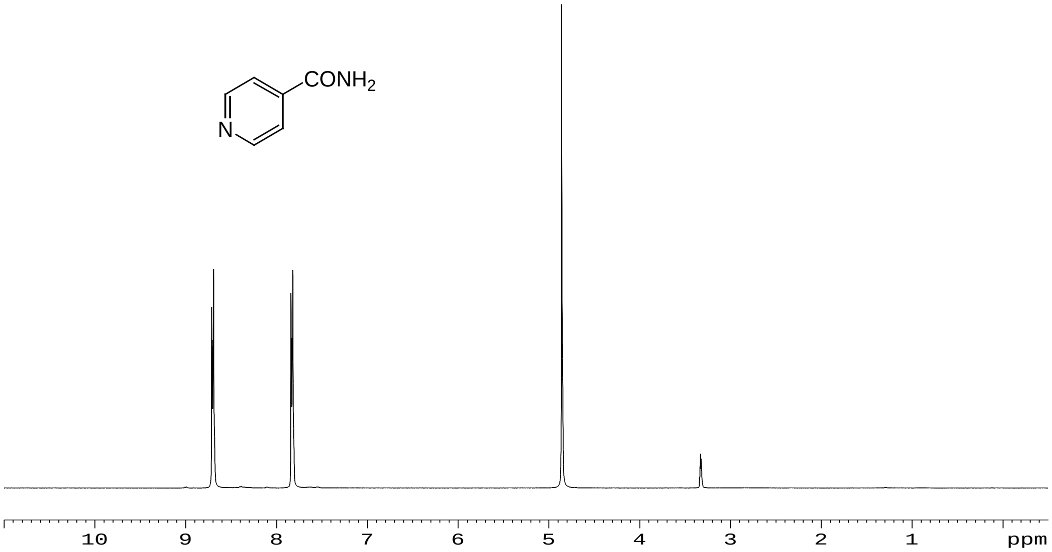

220
200
180
160
140
120
100
80
60
40
20
ppm

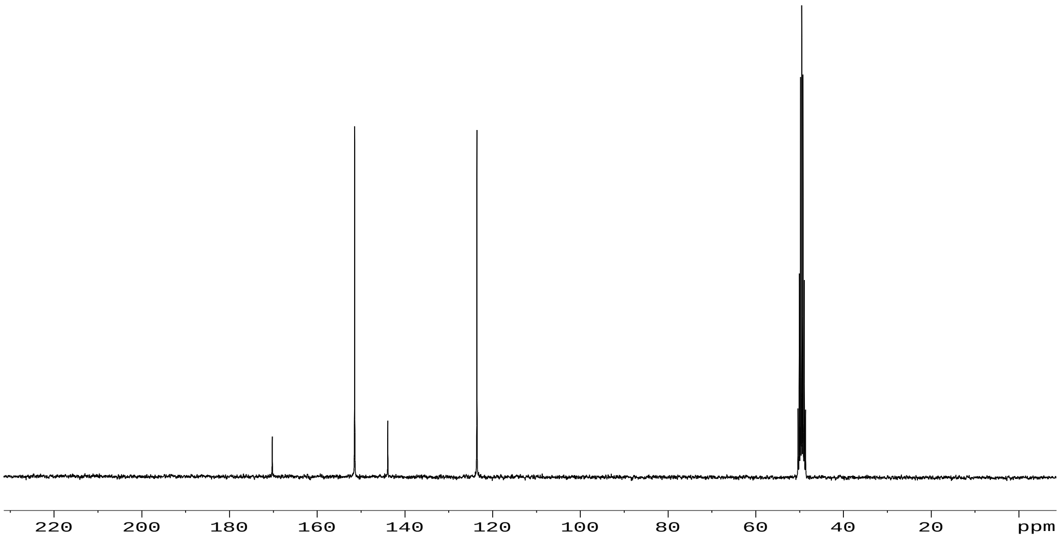

100
%
0
199.9702
9.66e5
124.1001
168.9864
108.0979
116.1172
128.0352
138.0704
149.0503
156.9910
179.1133
186.0035
214.0033
228.0303
m/z
100
110
120
130
140
150
160
170
180
190
200
210
220
230

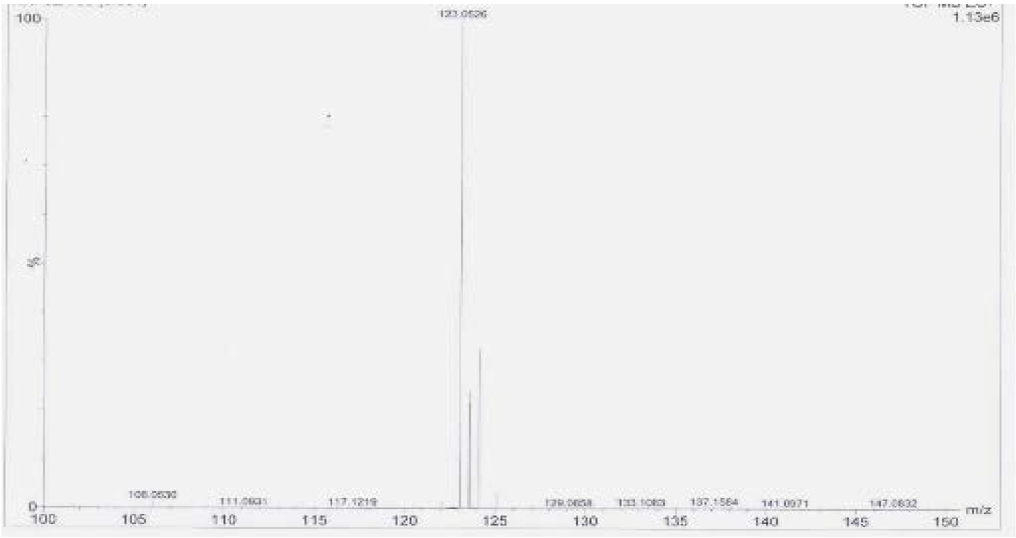

CONH$_2$
O$_2$N
10
9
8
7
6
5
4
3
2
1
ppm

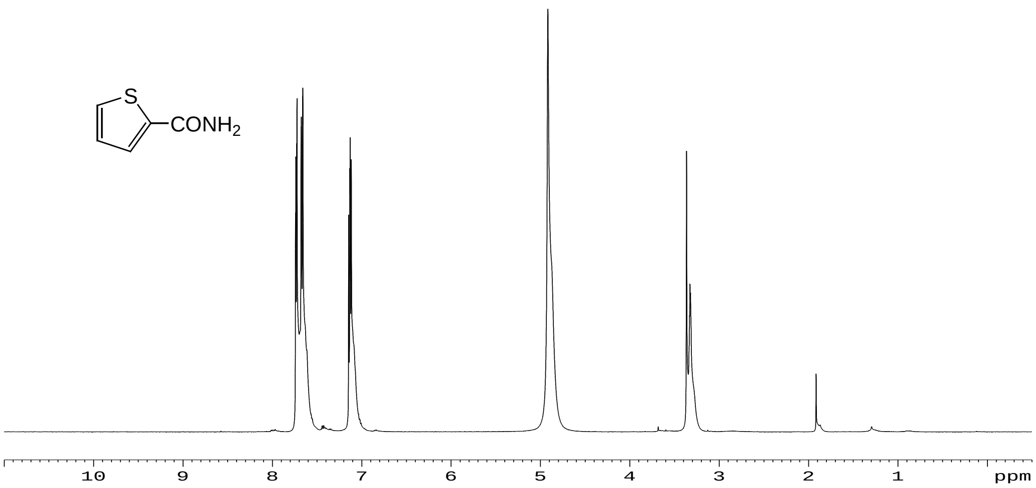

220
200
180
160
140
120
100
80
60
40
20
ppm

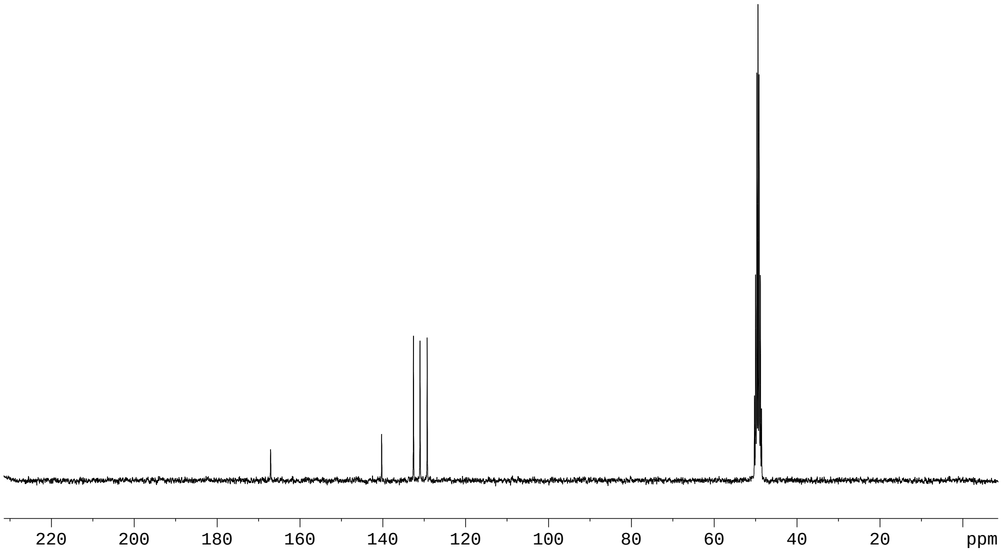

167.0442
1.04e6
100
%
0
106.0780
113.1536
121.0664
124.1114
128.0406
138.0802
142.9817
150.0459
156.1035
163.1564
179.0985
185.0793
192.1084
m/z
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195

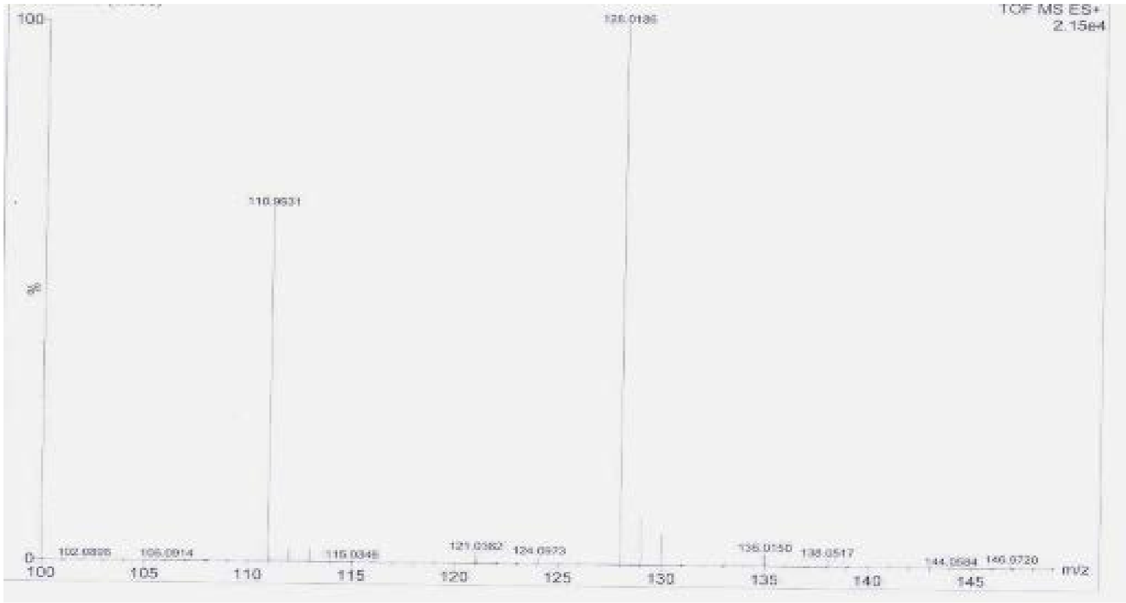

CONH$_2$
N
10
9
8
7
6
5
4
3
2
1
ppm

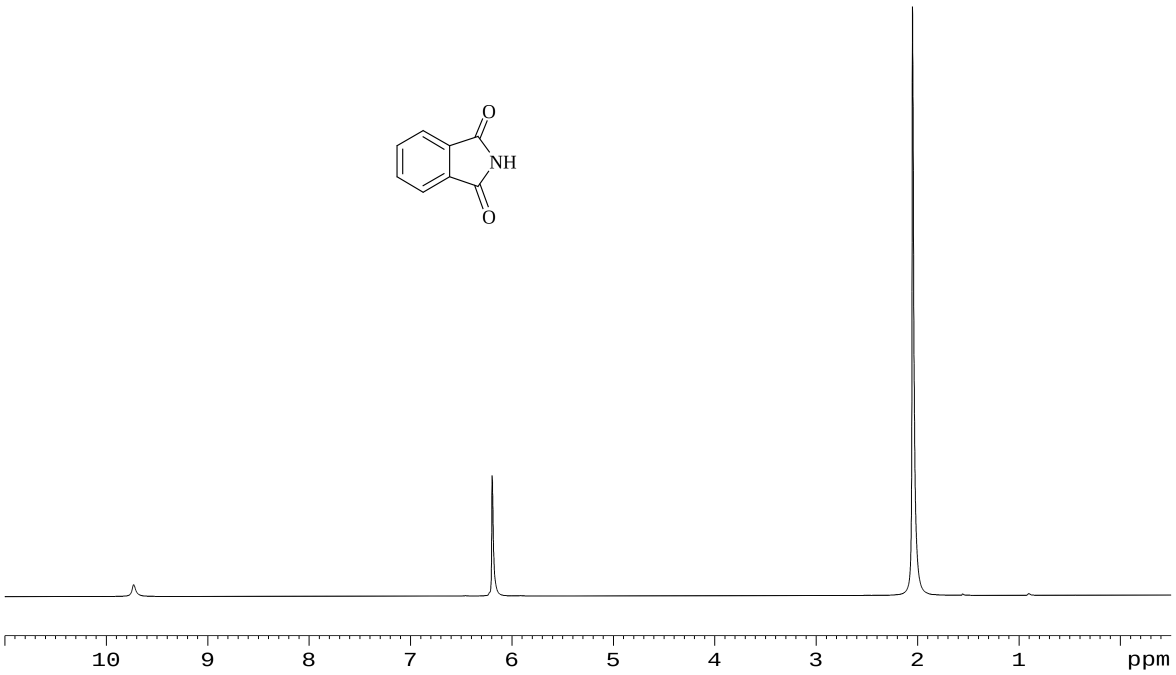

220
200
180
160
140
120
100
80
60
40
20
ppm

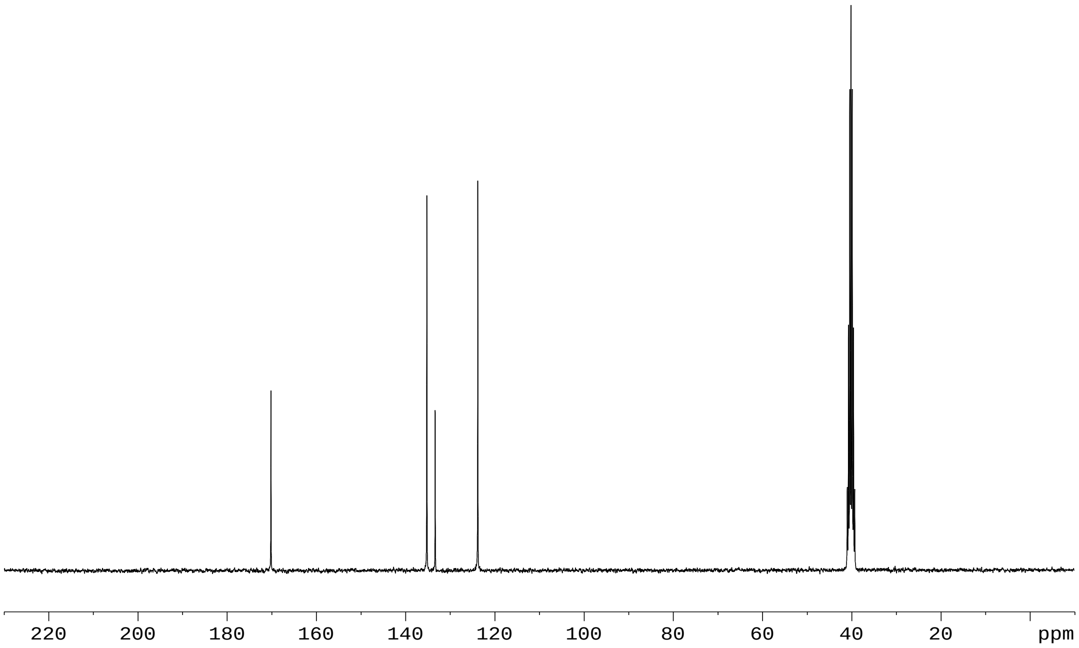

100
123.0526
1.13e6
%
0
106.0530
111.0931
117.1219
129.0658
133.1083
137.1564
141.0971
147.0832
100
105
110
115
120
125
130
135
140
145
150
m/z

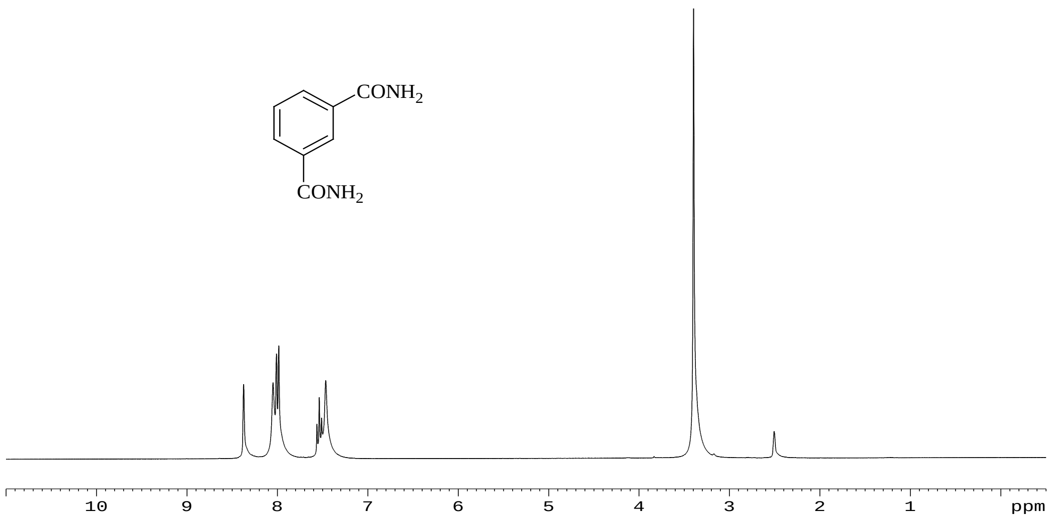

S
CONH$_2$
10
9
8
7
6
5
4
3
2
1
ppm

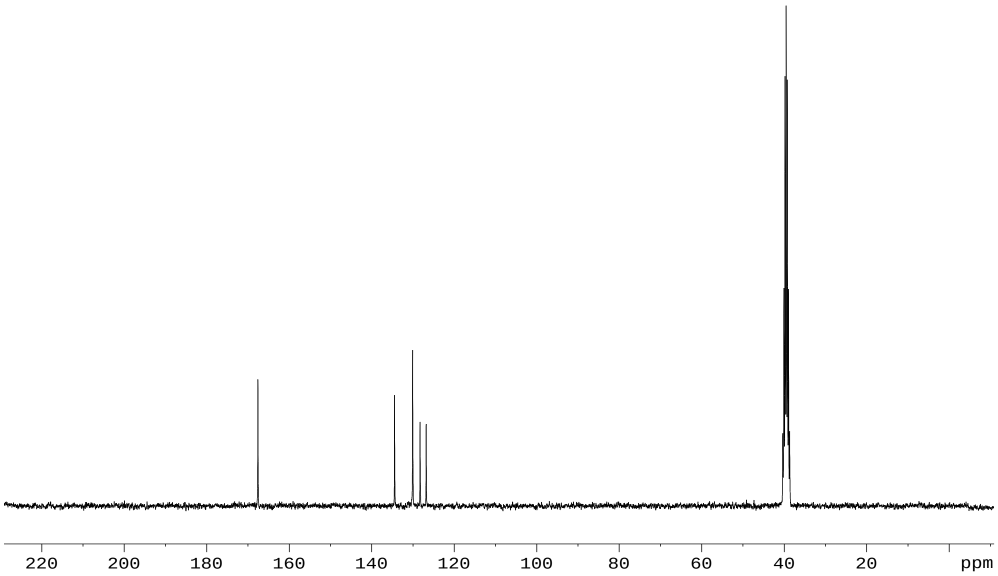

220
200
180
160
140
120
100
80
60
40
20
ppm

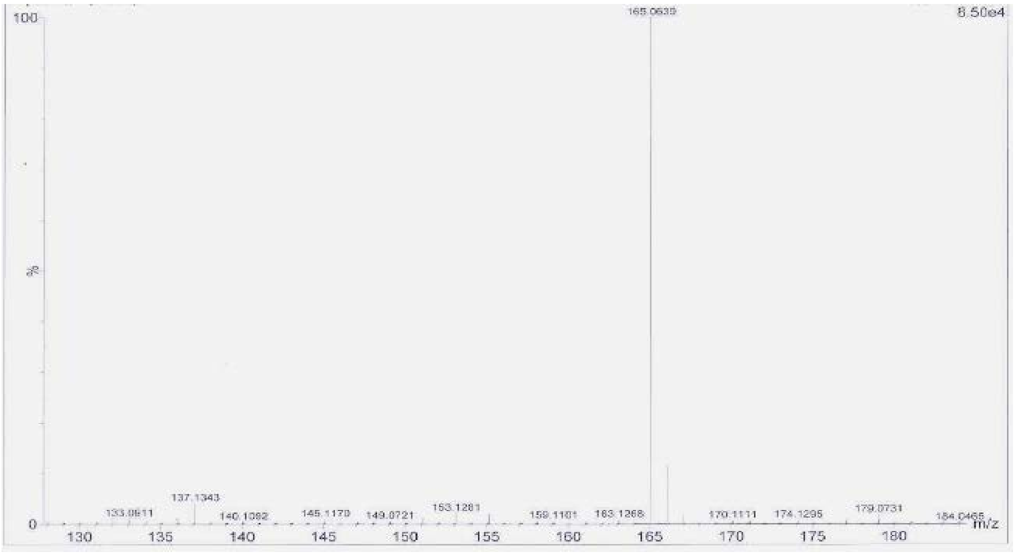

TOF MS ES+
2.15e4
100
%
0
128.0186
110.9631
102.0898
106.0914
115.0348
121.0382
124.0973
136.0150
138.0517
144.9984
146.0720
100
105
110
115
120
125
130
135
140
145
m/z

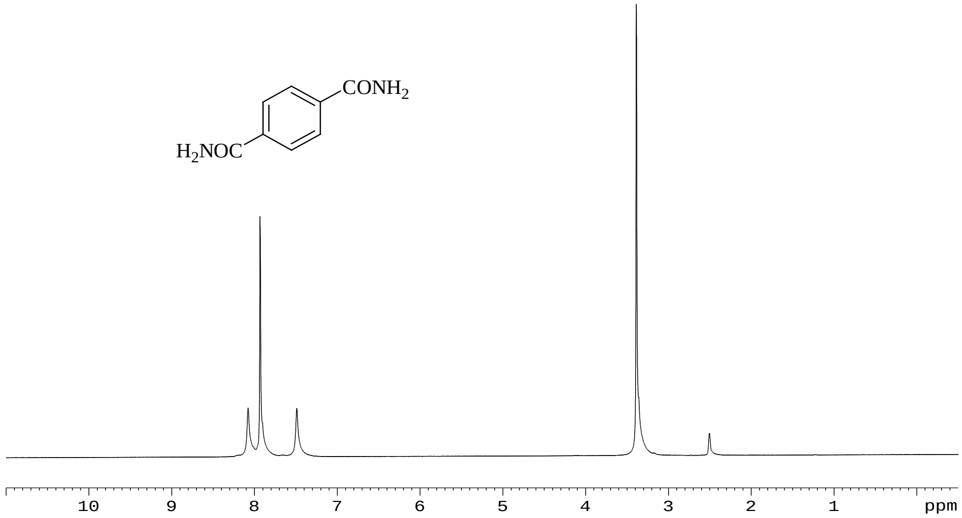

O
NH
O
10
9
8
7
6
5
4
3
2
1
ppm

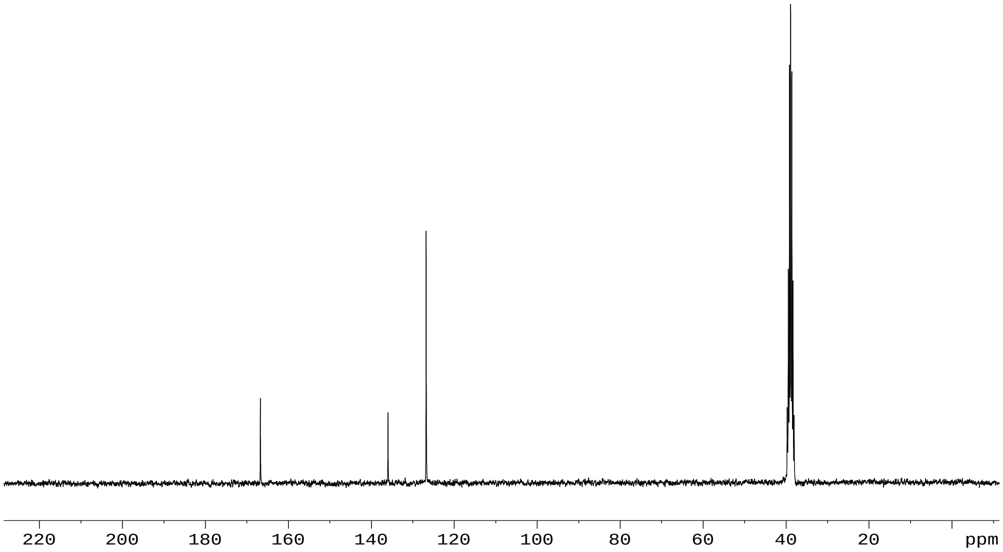

220
200
180
160
140
120
100
80
60
40
20
ppm

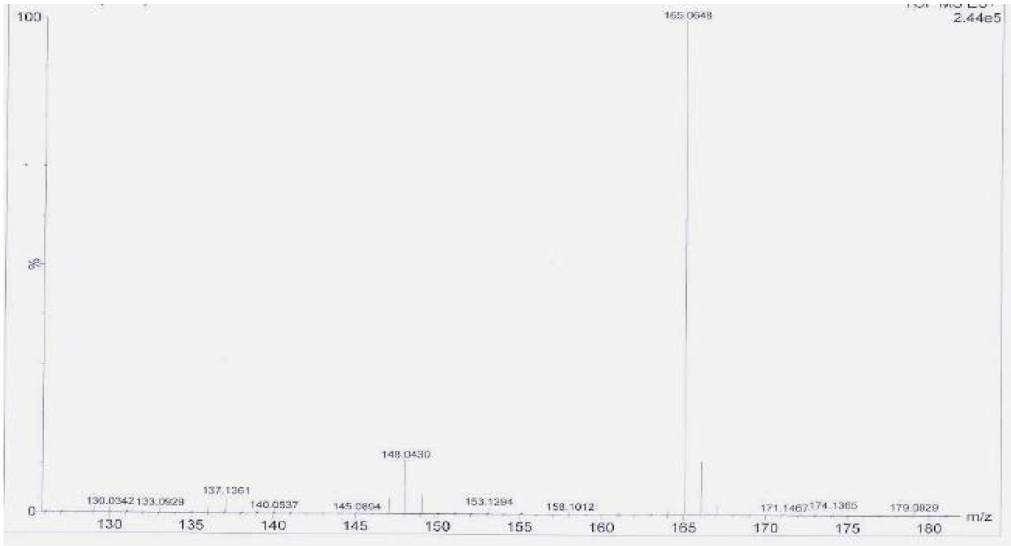

CONH$_2$
CONH$_2$
10
9
8
7
6
5
4
3
2
1
ppm

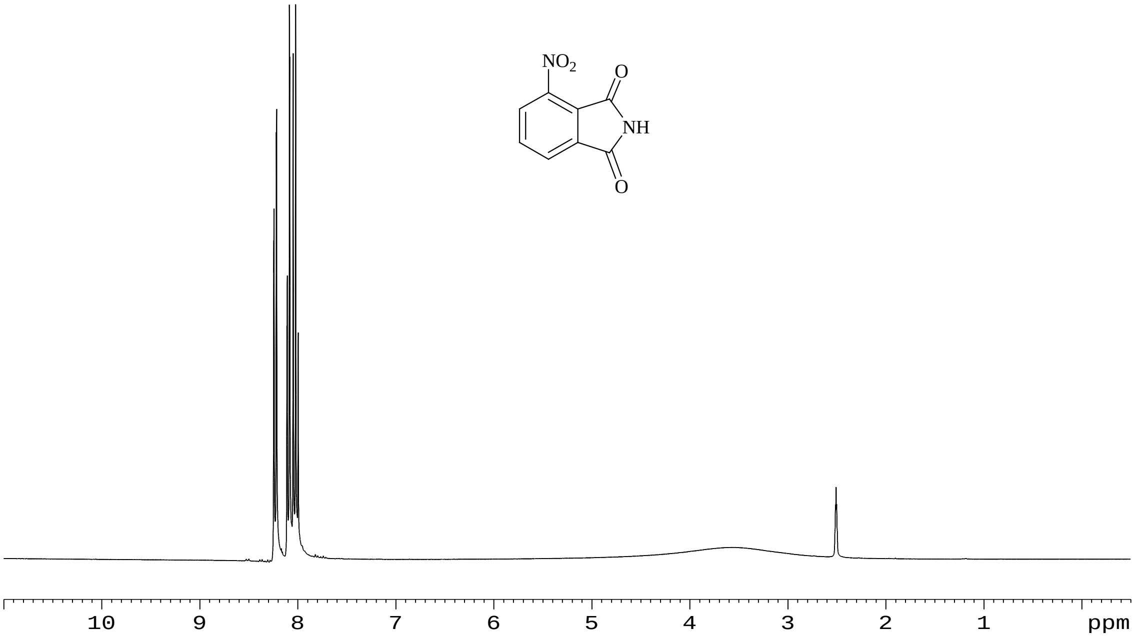

220
200
180
160
140
120
100
80
60
40
20
ppm

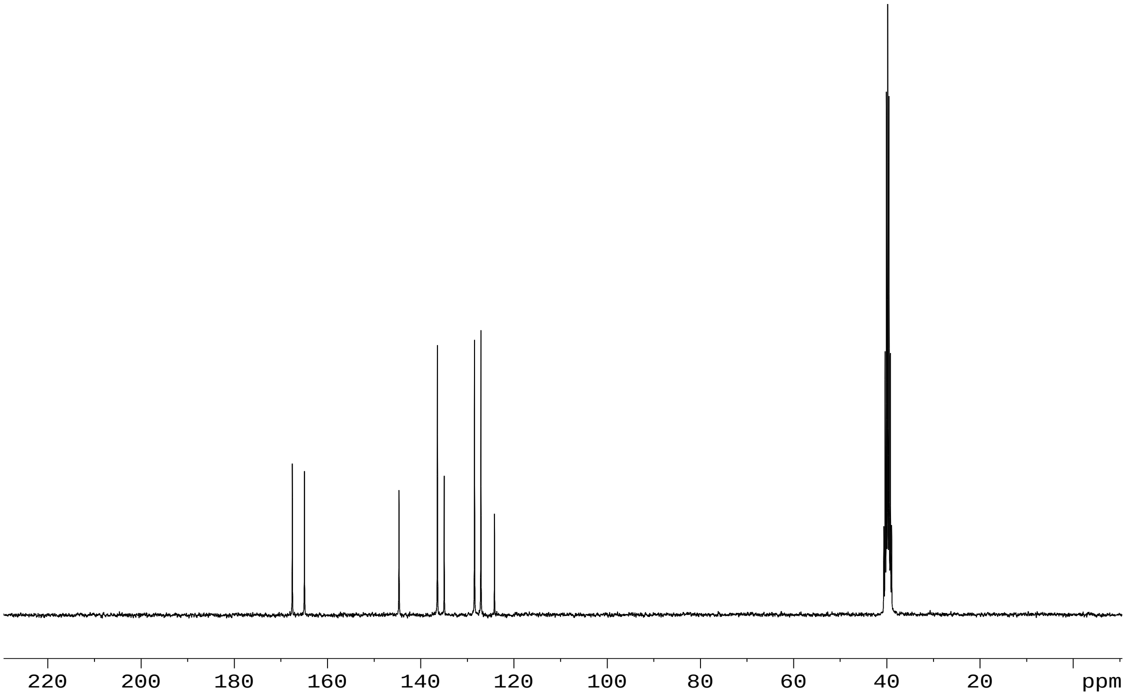

100
%
0
165.0639
6.50e4
137.1343
133.0811
140.1082
145.1170
149.0721
153.1281
159.1101
163.1268
170.1111
174.1295
179.0731
184.0465
m/z
130
135
140
145
150
155
160
165
170
175
180

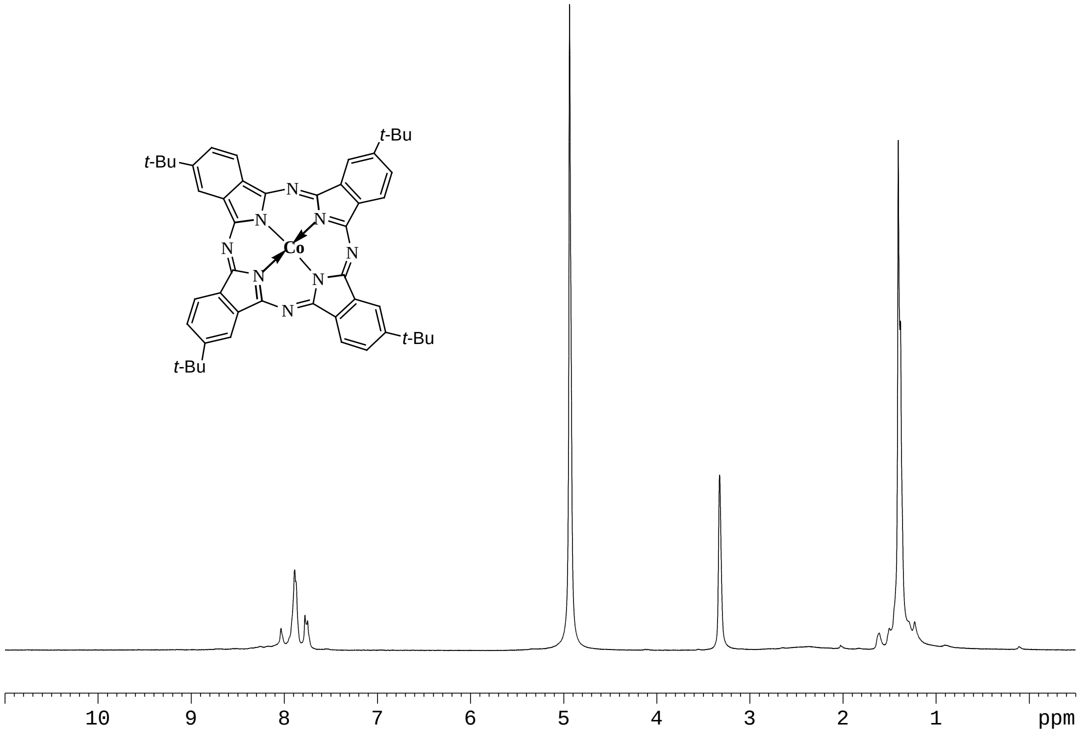

CONH$_2$
H$_2$NOC
10
9
8
7
6
5
4
3
2
1
ppm

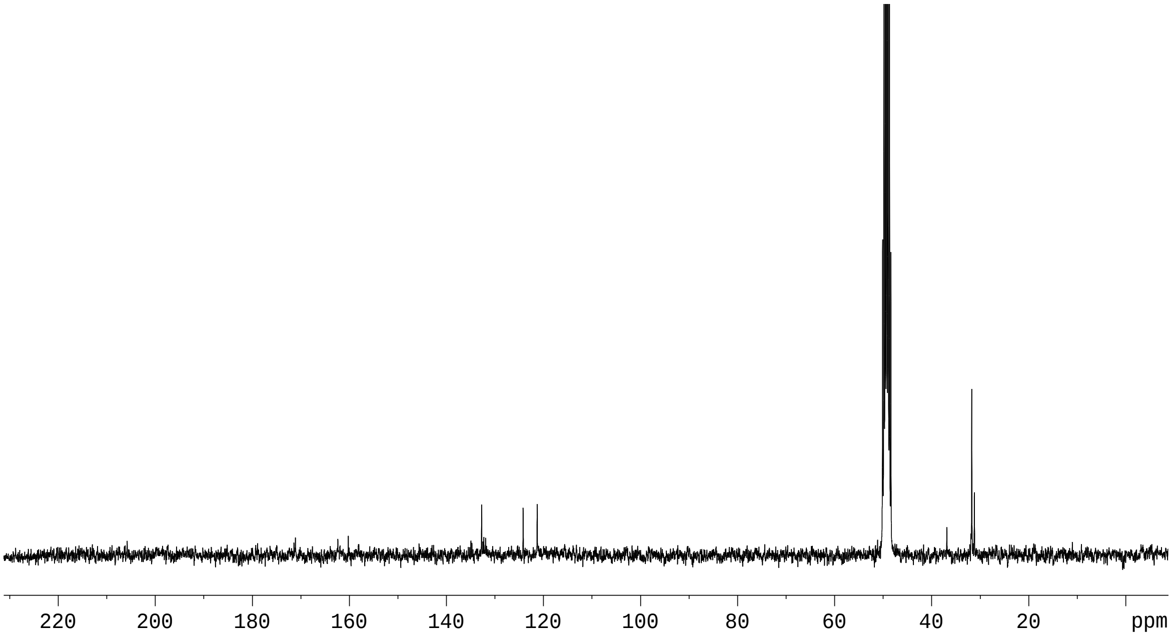

220
200
180
160
140
120
100
80
60
40
20
ppm


100
%
0
165.0648
2.44e5
148.0430
137.1361
130.0342
133.0929
140.0537
145.0894
153.1294
158.1012
171.1467
174.1365
179.0829
130
135
140
145
150
155
160
165
170
175
180
m/z


NO2
O
NH
O
10
9
8
7
6
5
4
3
2
1
ppm


220
200
180
160
140
120
100
80
60
40
20
ppm


t-Bu
t-Bu
N
N
N
Co
N
N
N
N
N
t-Bu
t-Bu
10
9
8
7
6
5
4
3
2
1
ppm


220
200
180
160
140
120
100
80
60
40
20
ppm

UV-Vis spectra of metal phthalocyanines:

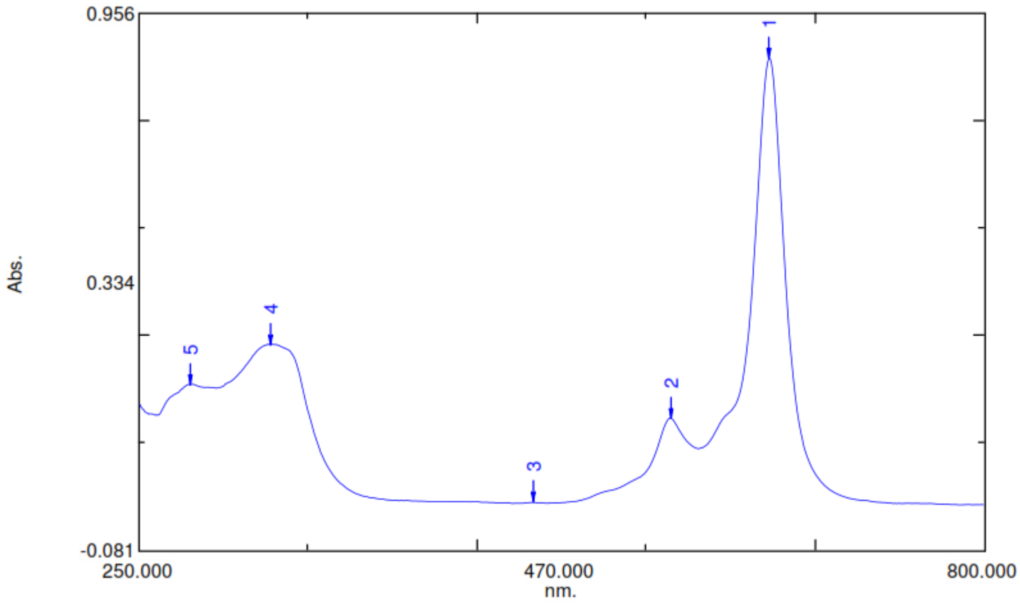


Figure S2: UV spectrum of cobalt (II) phthalocyanine in THF.

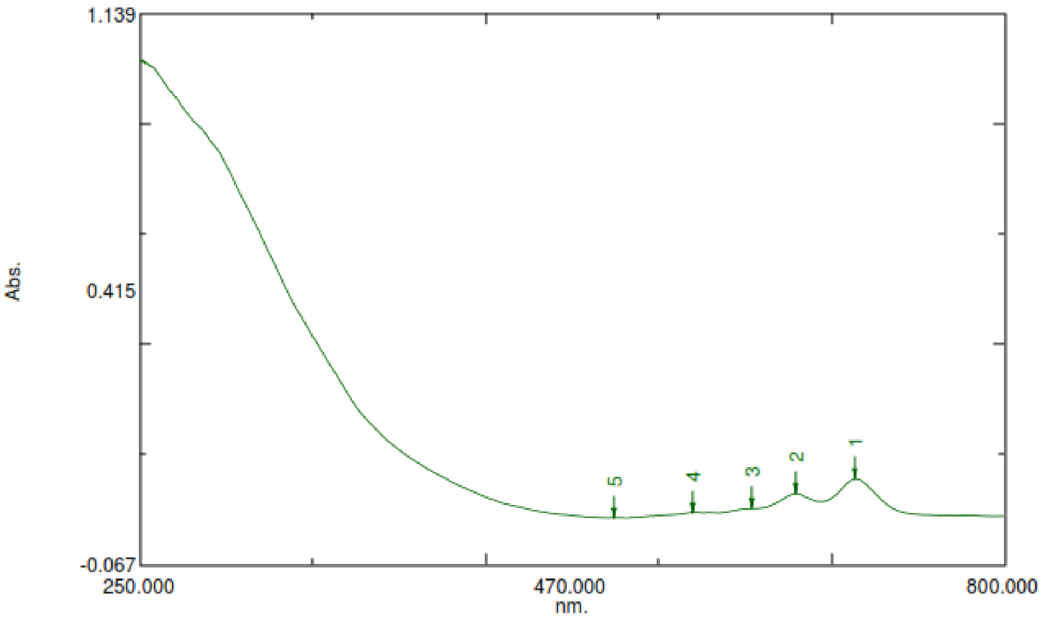


Figure S3: UV spectrum of iron (II) phthalocyanine in THF.

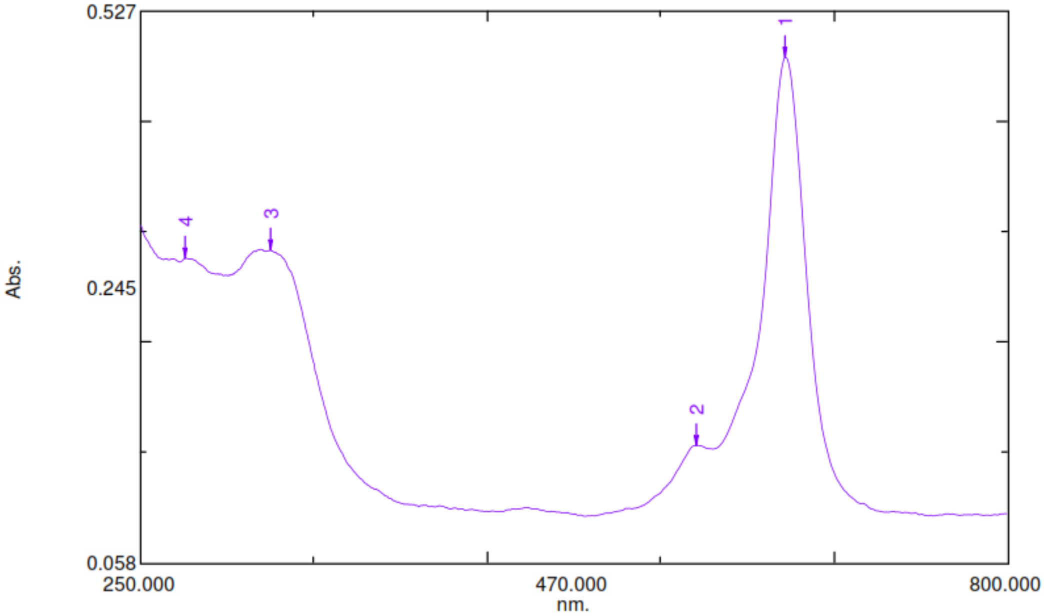


Figure S4: UV spectrum of iron (II) phthalocyanine in methanol.

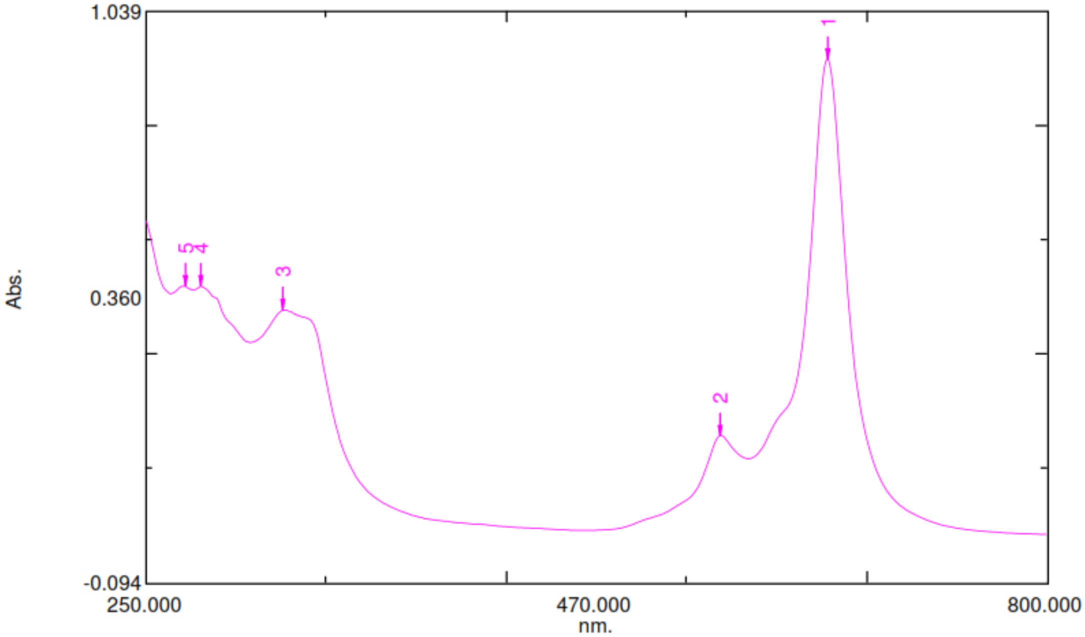


Figure S5: UV spectrum of tetra *tert*-butyl cobalt (II) phthalocyanine in THF.

References:

1. R. S. Ramon, N. Marion and S. P. Nolan, *Chem. Eur. J.* 2009, **15**, 8695-8697.
2. Z. Li, L. Wang and X. Zhou, *Adv. Synth. Catal.* 2012, **354**, 584-588.
3. T. Tu, Z. Wang, Z. Liu, X. Feng, and Q. Wang, *Green Chem.* 2012, **14**, 921-924.
4. L. Cao, J. Ding, M. Gao, Z. Wang, J. Li and A. Wu, *Org. Lett.* 2009, **11**, 3810-3813.
5. F. Hassanzadeh, M. Rabbani, G. A. Khodarahmi, A. Fasihi, G. H. Hakimelahi and M. Mohajeri, *RPS*, 2007, **2**, 35-41.
6. N. A. Owston, A. J. Parker and J. M. J. Williams, *Org. Lett.* 2007, **9**, 73-75.