Iron (III) Catalysed Synthesis of unsymmetrical di and trisubstituted ureas - A variation of classical Ritter reaction

Hosamani Basavaprabhu and Vommina V. Sureshbabu*

 # 109, Peptide Research Laboratory, Department of Studies in Chemistry, Central College Campus, Dr. B. R. Ambedkar Veedhi, Bangalore University: Bangalore-560 001, India

Email: hariccb@hotmail.com; sureshbabuvommina@rediffmail.com;hariccb@gmail.com

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GENERAL METHODS:

All solvents were freshly distilled prior to use. Melting points were determined using capillary method and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on glass plates and aluminum sheets precoated with silica gel (Silica gel GF_{254}, layer thickness 0.25 and 0.2 mm, respectively) using the following solvent systems as mobile phases: (a) Ethyl acetate: Hexane (1:9) for cyanamides and (b) Ethyl acetate: Hexane (4:6) for ureas and the visualization was accomplished by UV light (254 nm). IR spectra were recorded on a 400D FT-IR spectrometer (KBr pellets). Nuclear magnetic resonance spectra were recorded in $CDCl_3$ and DMSO on a AMX 400 MHz spectrometer.

Experimental Section:

Typical procedure for the preparation of cyanamides (2)

To a solution of amine (1.0 mmol) in dry diethyl ether (10 mL) at 0 ^oC was added a solution of CNBr (1.5 mmol) in diethyl ether (4 mL). The mixture was stirred till the completion of the reaction as judged by TLC and then the reaction mixture was filtered to remove the residual salt and concentrated to yield corresponding cyanamide. The crude is then diluted with EtOAc and washed twice with 10% HCl (10 mL), water and brine. Organic extract was dried over anhydrous Na_2SO_4 and evaporation of the solvent *in vacuo* results in cyanamide which was further purified by silica gel column chromatography (EtOAc /hexane system).

Phenyl cyanamide[1] **(2a).**

Oily liquid; yield = 83 %; IR (neat) 3176, 2226 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.81 (s, br, 1H), 6.98-7.09 (m, 3H), 7.21-7.32 (m, 2H).

3-Chloro-phenyl cyanamide[2] (**2b**).

White Solid; yield = 84 %; Mp 94-96 ^oC (Lit. 93-95 ^oC); IR (KBr) 3156, 2232 cm^{-1}.

4-Hydroxy-phenyl cyanamide[3] (2c).

White Solid; yield = 89 %; Mp 258-260 ^{o}C (Lit. 259-261 ^{o}C); IR (KBr) 3215, 2231 cm^{-1}.

2-Cyanamido benzoic acid (2d).

Yellow Solid; yield = 68 %; Mp 154-156 ^{o}C; IR (KBr) 3493, 3256, 2232 cm^{-1};

Piperidine-1-carbonitrile[4] (2e).

Oil; yield = 81 %; IR (neat) 2210 cm^{-1};

^{1}H NMR (60 MHz, $CDCl_3$) δ (ppm) 1.10-1.26 (m, 6H), 2.93-3.20 (t, J = 4.2, 4H).

(S)-Methyl-1-cyanopyrrolidine-3-carboxylate (2f).

Gummy; yield = 74 %; IR (neat) 2230, 1738 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.75 (m, 2H), 1.89 (m, 2H), 2.84 (t, J = 5.2 Hz, 2H), 3.48 (m 1H), 3.63 (d, J = 2.4 Hz, 2H).

Morpholine-4-carbonitrile[4] (2g).

Oil; yield = 82 %; IR (neat) 2220 cm^{-1};

^{1}H NMR (60 MHz, $CDCl_3$) δ (ppm) 3.18 (t, J = 4.2 Hz, 4H), 3.68 (t, J = 4.2 Hz, 4H).

N, N –Diethyl cyanamide[4] (2h).

Oil; yield = 78 %; IR (neat) 2206 cm^{-1};

^{1}H NMR (60 MHz, $CDCl_3$) δ (ppm) 1.20 (t, J = 6.4 Hz, 6H), 3.00 (q, J = 6.2 Hz, 4H).

Benzyl cyanamide[3] (2i).

Gummy; yield = 92 %; IR (neat) 3208, 2221 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.13 (d, J = 5.2 Hz, 2H), 4.69 (s, br, 1H), 7.25-7.38 (m, 5H).

***p*-Tolyl cyanamide[2] (2j).**

Gummy; yield = 83 %; IR (neat) 3167, 2229 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.27 (s, 3H), 4.12 (s, br, 1H), 6.88 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H).

Cyclohexyl cyanamide[2] (2k).

Gummy; yield = 88 %; IR (neat) 3192, 2219 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.12-1.54 (m, 6H), 1.75-2.01 (m, 4H), 3.10-3.15 (m, 1H), 3.51 (s, br, 1H).

4-Nitro-phenyl cyanamide[2] (2l).

Yellow Solid; yield = 82 %; Mp 180-182 ^oC (Lit. 178-180 ^oC); IR (KBr) 3362, 2226 cm^{-1}.

Typical procedure for the preparation of urea (4)

To a mixture of cyanamide (1.0 mmol) and an alcohol (2.0 mmol) in DCE (10 mL), was added a 20 mol% $FeCl_3$. The reaction mixture was refluxed at an elevated temperature till the completion of the reaction as monitored by TLC. Upon complete consumption of the cyanamide, the reaction medium was evaporated under reduced pressure and the product was extracted using EtOAc (15

mL). The EtOAc layer was then washed with 5% $Na_2S_2O_3$ (5 mL), water (2 x 5 mL) and brine (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated *in vacuo* to afford the crude which was then purified through silica gel column chromatography (EtOAc/hexane).

1-benzyl-3-phenylurea[5] (**4a**).

White Solid; yield =86 %; Mp 176-178 ^oC (Lit. 175-176 ^oC);

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 4.17 (d, J = 4.96 Hz, 2H), 6.26 (t, J = 5.96 Hz, 1H), 6.86 – 7.38 (m, 10H), 8.50 (s, 1H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 44.1, 117.7, 121.0, 128.6, 140.5, 156.0.

HRMS Calcd for $C_{14}H_{14}N_2O$ *m/z* 249.1004 (M^++Na); found 249.1005.

1-benzyl-3-(3-chlorophenyl) urea (4b).

White Solid; yield = 80 %; Mp 187-189 ^oC;

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 4.28 (d, J = 6.8 Hz, 2H), 5.51 (s, br, 1H), 6.36 (s, 1H), 6.91-7.38 (m, 8H), 8.11-8.13 (m, 1H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 43.7, 121.0, 121.2, 122.5, 127.3, 129.0, 132.5, 136.3, 139.8, 155.5.

HRMS Calcd for $C_{14}H_{13}ClN_2O$ *m/z* 283.0614 (M^++Na); found 283.0618.

1-benzyl-3-(4-hydroxyphenyl) urea (4c).

White Solid; yield = 74 %; Mp 197-198 ^oC;

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 4.21 (d, J = 4.8 Hz, 2H), 6.40 (t, J =4.8 Hz, 1H), 7.19-7.31 (m, 8H), 7.93 (s, br, 1H), 9.13 (s, br, 1H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 43.5, 121.0, 121.2, 122.5, 127.3, 129.0, 132.4, 136.3, 139.8, 142.3, 155.5.

HRMS Calcd for $C_{14}H_{14}N_2O_2$ *m/z* 265.0953 (M^++Na); found 265.0961.

2-(3-benzylureido) benzoic acid (4d).

White Solid; yield = 63 %; Mp 168-169 ^oC;

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 4.21 (d, J = 4.8 Hz, 2H), 6.39 (t, J = 4.4 Hz, 1H), 7.11 - 7.31 (m, 9H), 7.79 (s, br, 1H), 10.19 (s, br, 1H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 42.9, 126.5, 126.7, 126.8, 126.9, 127.1, 127.4, 128.0, 128.1, 138.5, 139.4, 140.8, 158.1, 172.6.

HRMS Calcd for $C_{15}H_{14}N_2O_3$ *m/z* 293.0902 (M^++Na); found 293.0914.

N-benzylpiperidine-1-carboxamide[6] (4e).

White Solid; yield = 79 %; Mp 103-104 ^oC (Lit. 102 ^oC);

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.50–1.61 (m, 6H), 3.30–3.34 (m, 4H), 4.43 (d, J =5.6 Hz, 2H,), 4.75 (br s, 1H, NH), 7.24–7.34 (m, 5H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 15.6, 26.1, 45.4, 47.1, 127.1, 127.8, 128.6, 138.5, 157.6. HRMS Calcd for $C_{13}H_{18}N_2O$ *m/z* 241.1540 (M^++Na); found 241.1556.

(R)-methyl 1-(benzylcarbamoyl) pyrrolidine-2-carboxylate (4f).

White Solid; yield = 71 %; Mp 227-230 ^oC;

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.65 (m, 2H), 1.92 (m, 2H), 2.87 (m, 2H), 3.52 (m, 1H), 3.66 (m, 2H), 4.36 (s, 2H), 5.18 (s, br, 1H), 7.31-7.54 (m, 5H);

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 16.1, 21.7, 46.9, 47.7, 67.2, 120.5, 125.5, 128.20, 141.83, 155.81, 171.33.

HRMS Calcd for $C_{14}H_{18}N_2O_3$ *m/z* 285.1215 (M^++Na); found 285.1224.

N-benzylmorpholine-4-carboxamide[7] (4g).

White Solid; yield = 82 %; Mp 139-141 ^{o}C (Lit. 136-139 ^{o}C);

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 3.24 (s, 4H), 4.21- 4.24 (m, 4H), 4.64 (s, 2H), 6.41 (s, br, 1H), 7.14-7.29 (m, 5H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 43.5, 45.4, 65.6, 126.9, 127.1, 127.7, 139.8, 156.4.

HRMS Calcd for $C_{12}H_{16}N_2O_2$ *m/z* 243.1109 (M^++Na); found 243.1112.

3-benzyl-1,1-diethylurea (4h).

White Solid; yield = 78 %; Mp 89-93 ^{o}C;

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 2.49 (t, J =4.2 Hz, 6H), 3.31 (s, 4H), 4.22 (d, J = 4.8 Hz, 2H), 6.40 (t, J = 4.4 Hz, 1H), 7.19-7.31 (m, 5H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 13.3, 40.0, 42.9, 44.1, 126.5, 126.9, 128.2, 140.9, 158.0. HRMS Calcd for $C_{12}H_{18}N_2O$ *m/z* 229.1317 (M^++Na); found 229.1319.

1-tert-butyl-3-phenylurea[8] (4i).

White Solid; yield = 85 %; Mp 172-174 ^{o}C (Lit. 171-172 ^{o}C);

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 1.27 (s, 9H), 5.96 (s, br, 1H), 6.68 (s, br, 1H), 7.18-7.38 (m, 5H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 29.1, 49.5, 121.2, 124.8, 128.7, 140.7, 156.1.

HRMS Calcd for $C_{11}H_{16}N_2O$ *m/z* 215.1160 (M^++Na); found 215.1163.

1-benzyl-3-tert-butylurea[9] (4j).

White Solid; yield = 91 %; Mp 111-114 ^{o}C (Lit. 109-112 ^{o}C);

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 1.22 (s, 9H), 4.14 (d, J = 5.96 Hz, 2H), 5.73 (s, br,1H), 6.06 (t, J = 4.8 Hz, 1H), 7.21-7.30 (m, 5H);

^{13}C NMR (100 MHz DMSO- d_6) δ (ppm) 29.4, 42.6, 49.2, 126.6, 127.0, 128.3, 141.0, 157.5.

HRMS Calcd for $C_{12}H_{18}N_2O$ *m/z* 229.1317 (M^++Na); found 229.1321.

1-tert-butyl-3-(3-chlorophenyl) urea (4k).

White Solid; yield = 81 %; Mp 175-177 ^oC;

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 1.26 (s, 9H), 5.43 (s, br, 1H), 6.16 (s, br, 1H), 6.90-7.22 (m, 3H), 7.68 (d, J = 8.1 Hz, 1H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 30.3, 42.9, 120.6, 123.5, 127.0, 128.2, 132.9, 137.7, 158.0.

HRMS Calcd for $C_{11}H_{15}ClN_2O$ *m/z* 249.0771 (M^++Na); found 249.0779.

1-tert-butyl-3-*p*-tolylurea[10] (4l).

White Solid; yield = 83 %; Mp 185-186 ^oC (Lit. 184-186 ^oC);

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 1.35 (s, 9H), 4.76 (br s, 1H, NH), 6.23 (br s, 1H, NH), 7.10-7.21 (m, 4H).

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 20.4, 28.8, 50.6, 123.8, 128.8, 132.4, 138.2, 155.2.

HRMS Calcd for $C_{12}H_{18}N_2O$ *m/z* 229.1696 (M^++Na); found 229.1685.

1-tert-butyl-3-cyclohexylurea[9] (4m).

White Solid; yield = 87 %; Mp 224-226 ^oC (Lit. 223-224 ^oC);

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 0.93 (s, 9H), 1.02-1.24 (m, 6H), 1.69-1.72 (m, 4H), 3.27-3.29 (m, 1H), 5.30 (s, br, 1H), 5.84 (s, br, 1H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 24.6, 25.4, 33.3, 47.7, 158.2.

HRMS Calcd for $C_{11}H_{22}N_2O$ *m/z* 221.1630 (M^++Na); found 221.1631.

1-tert-butyl-3-(4-nitrophenyl) urea[10] (4n).

White Solid; yield = 77 %; Mp 143-145 ^oC (Lit. 142-143 ^oC);

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 1.39 (s, 9H), 4.80 (s, br, 1H, NH), 6.75 (br s, 1H, NH), 7.48 (d, J = 9.2 Hz, 2H), 8.14 (d, J = 9.2 Hz, 2H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 23.4, 50.8, 121.7, 128.8, 139.5, 143.6, 157.6.

HRMS Calcd for $C_{11}H_{15}N_3O_3$ *m/z* 260.1166 (M^++Na); found 260.1155.

1-benzhydryl-3-benzylurea (4o).

White Solid; yield =83 %; Mp 241-244 ^{o}C;

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 4.23 (s, 2H), 5.80 (d, J = 6.8 Hz, 1H), 6.47 (s, 1H), 7.19-7.31 (m, 15 H), 8.17 (s, 1H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 44.5, 56.5, 117.7, 121.0, 128.5, 132.3, 140.5, 141.9, 156.0.

HRMS Calcd for $C_{21}H_{20}N_2O$ *m/z* 339.1473 (M^++Na); found 339.1478.

1-benzhydrylmorpholine-4-carboxamide[11] (4p).

White Solid; yield =81 %; Mp 181-182 ^{o}C (Lit. 180 ^{o}C);

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 3.28 (s, 4H), 3.58 (s, 4H), 5.27 (d, J = 6.0 Hz, 1H), 6.11 (d, J = 6.2 Hz, 1H), 7.23-7.18 (m, 6H), 7.32-7.26 (m, 4H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 44.2, 58.4, 65.6, 127.2, 128.2, 140.2, 156.5.

HRMS Calcd for $C_{18}H_{20}N_2O_2$ *m/z* 319.1326 (M^++Na); found 319.1330.

N- (1-phenylethyl) morpholine-4-carboxamide[11,12] (4q).

White pluffy Solid; yield =80 %; Mp = 84-86 ^{o}C (Lit. 83-84 ^{o}C);

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 1.48 (d, J = 6.4 Hz, 3H), 3.30 (m, 4H), 3.66 (m, 4H), 4.62 (d, J = 6.4 Hz, 1H), 5.04 (m, 1H), 7.32-7.28 (m, 5H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 22.1, 44.5, 50.6, 66.8, 127.1, 127.6, 128.2, 142.2, 156.8. HRMS Calcd for $C_{13}H_{18}N_2O_2$ *m/z* 257.1309 (M^++Na); found 257.1317.

1-allyl-3-(3-chlorophenyl) urea (4r).

White Solid; yield =68 %; Mp 214-216 ^{o}C;

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 3.88 (d, J = 6.8 Hz, 2H), 4.61-4.64 (m, 1H), 5.55-5.58 (m, 2H), 6.80 (s, br, 1H), 6.90-7.22 (m, 3H), 7.67-7.68 (m, 1H), 8.18 (s, br, 1H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 42.7, 116.0, 117.0, 120.6, 130.2, 133.0, 137.5, 142.1, 155.7.

HRMS Calcd for $C_{10}H_{11}ClN_2O$ *m/z* 233.0458 (M^++Na); found 233.0463.

1-allyl-3-phenylurea (4s).

White Solid; yield = 73 %; Mp 191-193 ^{o}C;

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 3.90 (d, J = 6.7 Hz, 2H), 4.62-4.65 (m, 2H), 5.54-5.57 (m, 1H), 5.90 (s, 1H), 6.54 (s, 1H), 7.19-7.31 (m, 5H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 43.6, 117.7, 121.0, 127.6, 128.5, 131.1, 140.5, 155.9.

HRMS Calcd for $C_{10}H_{12}N_2O$ *m/z* 199.0847 (M^++Na); found 199.0852.

1-(4-methylbenzyl)-3-phenylurea[13] (4t).

White Solid; yield = 83 %; Mp 186-188 ^{o}C;

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 2.08 (s, 3H), 4.19 (s, 2H), 6.25 (s, 1H), 6.86-6.89 (m, 1H), 7.18-7.38 (m, 8H), 7.72 (s, 1H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 26.2, 49.1, 118.3, 121.1, 126.8, 128.8, 132.3, 140.8, 156.7. HRMS Calcd for $C_{15}H_{16}N_2O$ *m/z* 263.1217 (M^++Na); found 263.1220.

1-(4-nitrobenzyl)-3-phenylurea (4u).

Yellow Solid; yield = 81 %; Mp 196-198 ^{o}C;

^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 4.08 (s, 2H), 5.78 (s, 1H), 6.8-6.89 (m, 1H), 7.18-7.39 (m, 6H), 7.82-7.83 (m, 2H), 8.05 (s, 1H);

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm) 50.0, 116.8, 119.1, 121.8, 128.2, 130.9, 138.2, 140.3, 142.6, 158.2. HRMS Calcd for $C_{14}H_{13}N_3O_3$ *m/z* 294.0923 (M^++Na); found 294.0925.

Dibenzyl ether[14] **(A)**

Colourless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35 (s, 10H), 5.10 (s, 4H).

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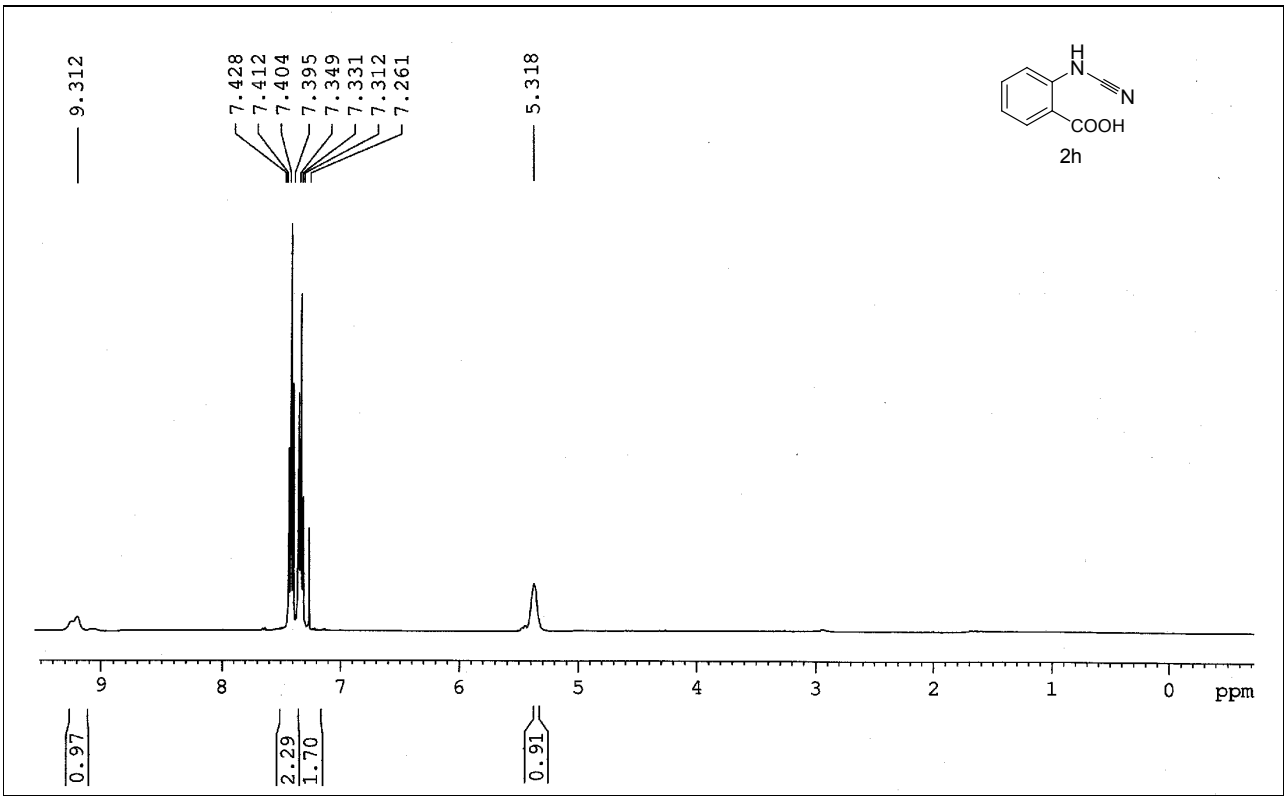
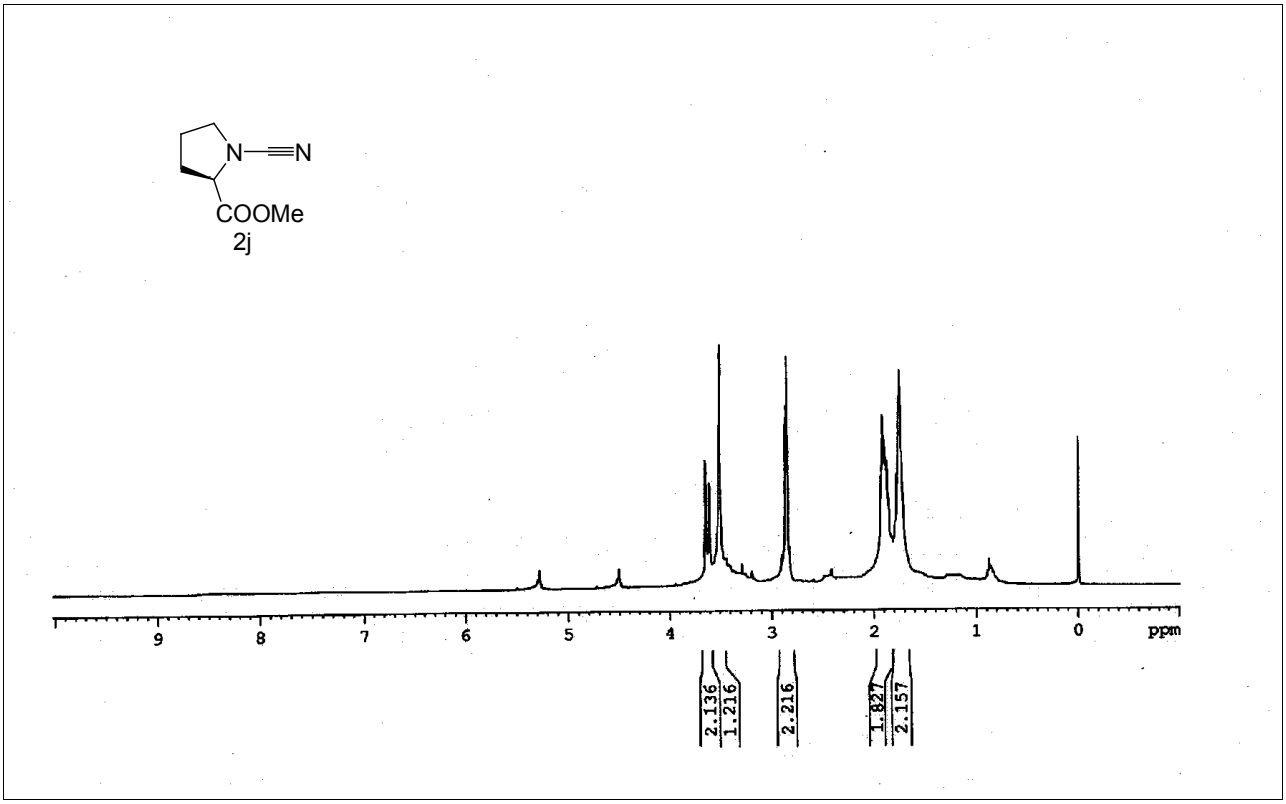
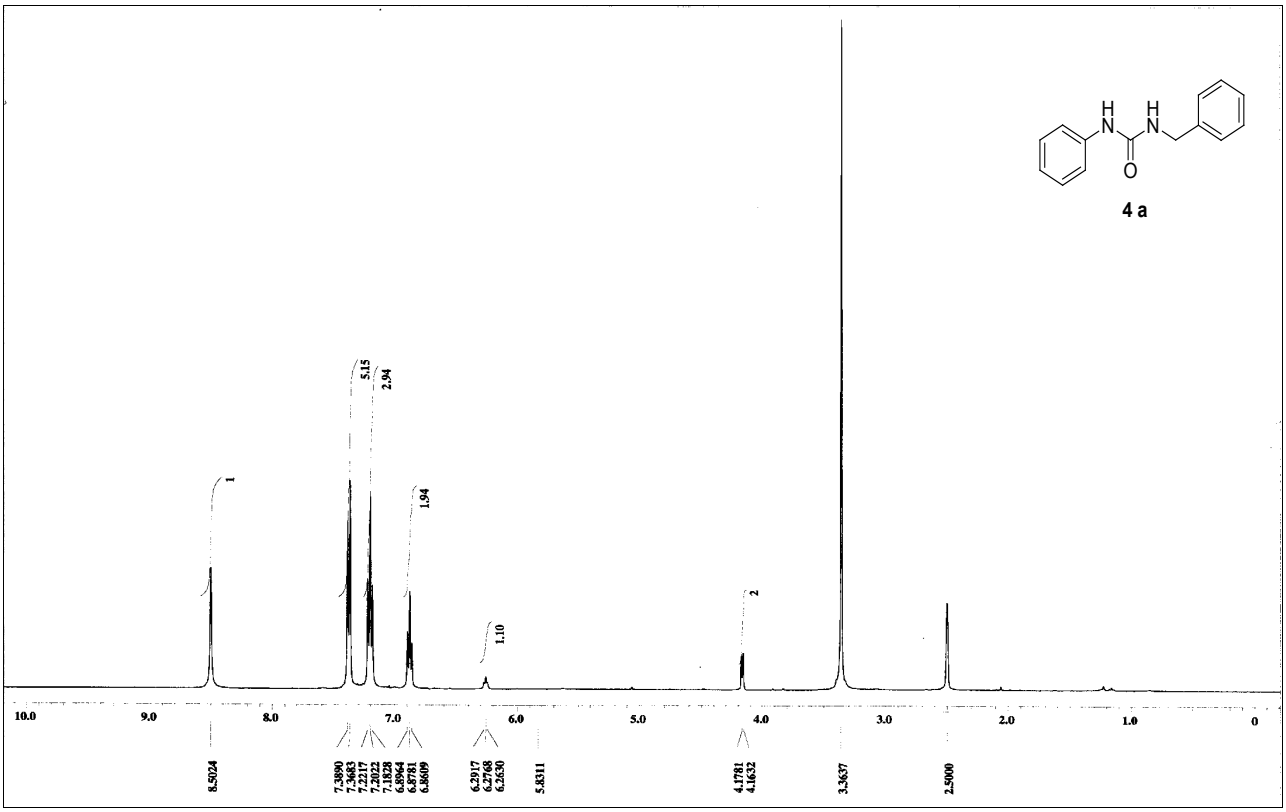
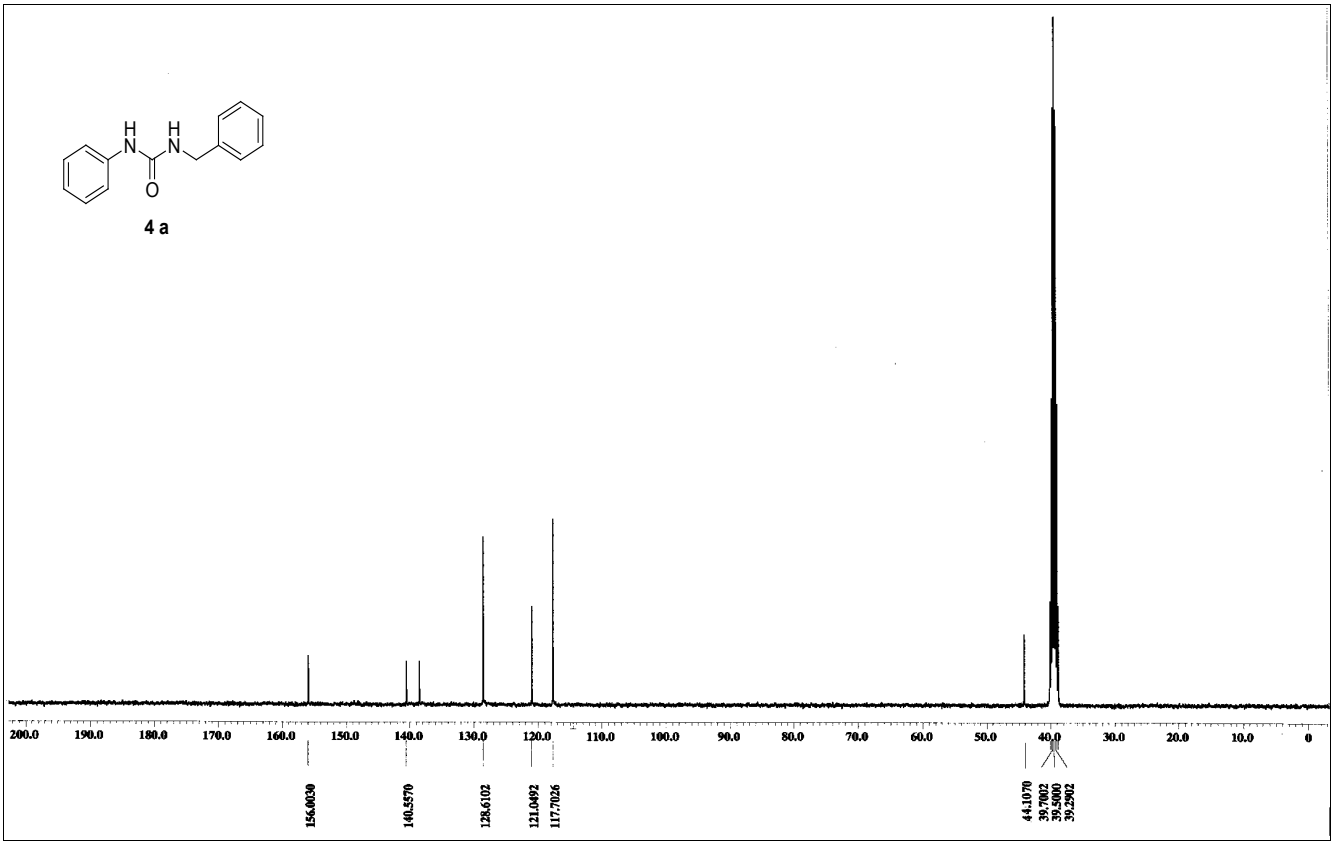
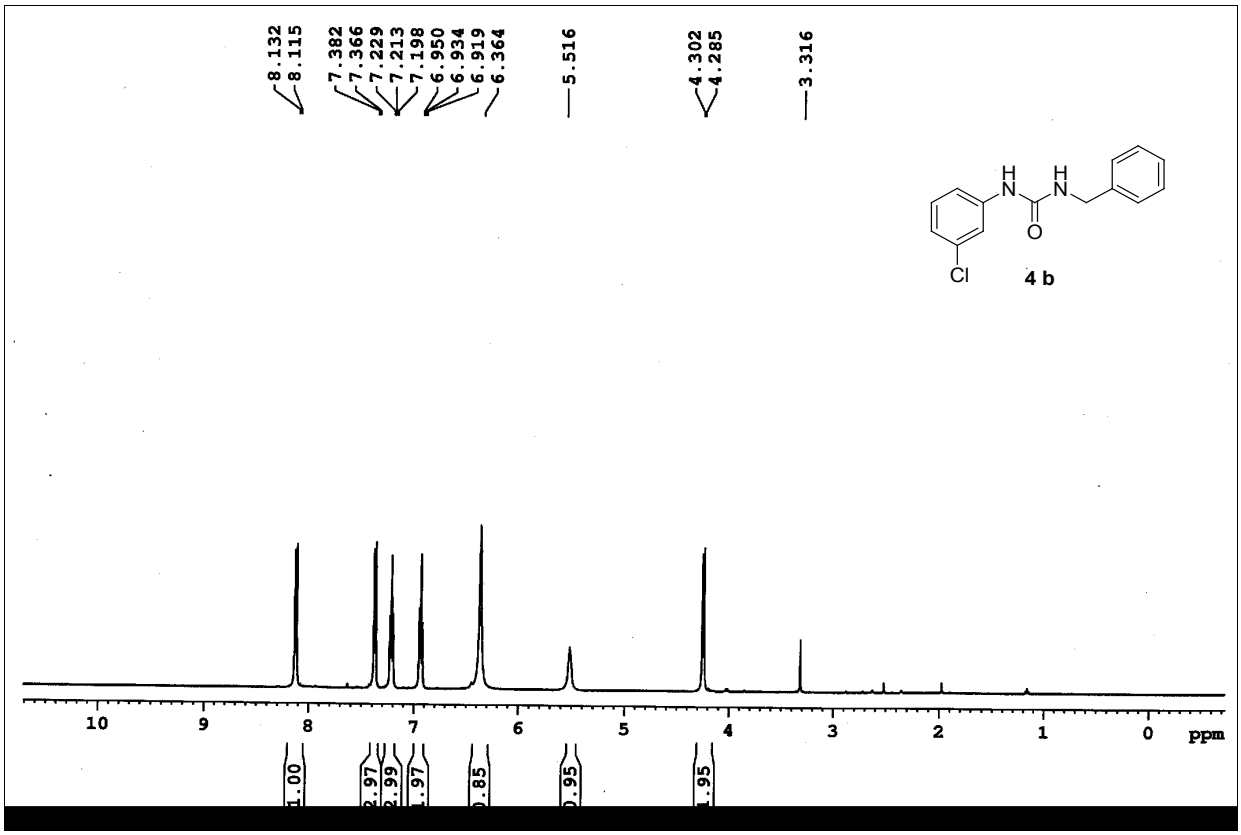
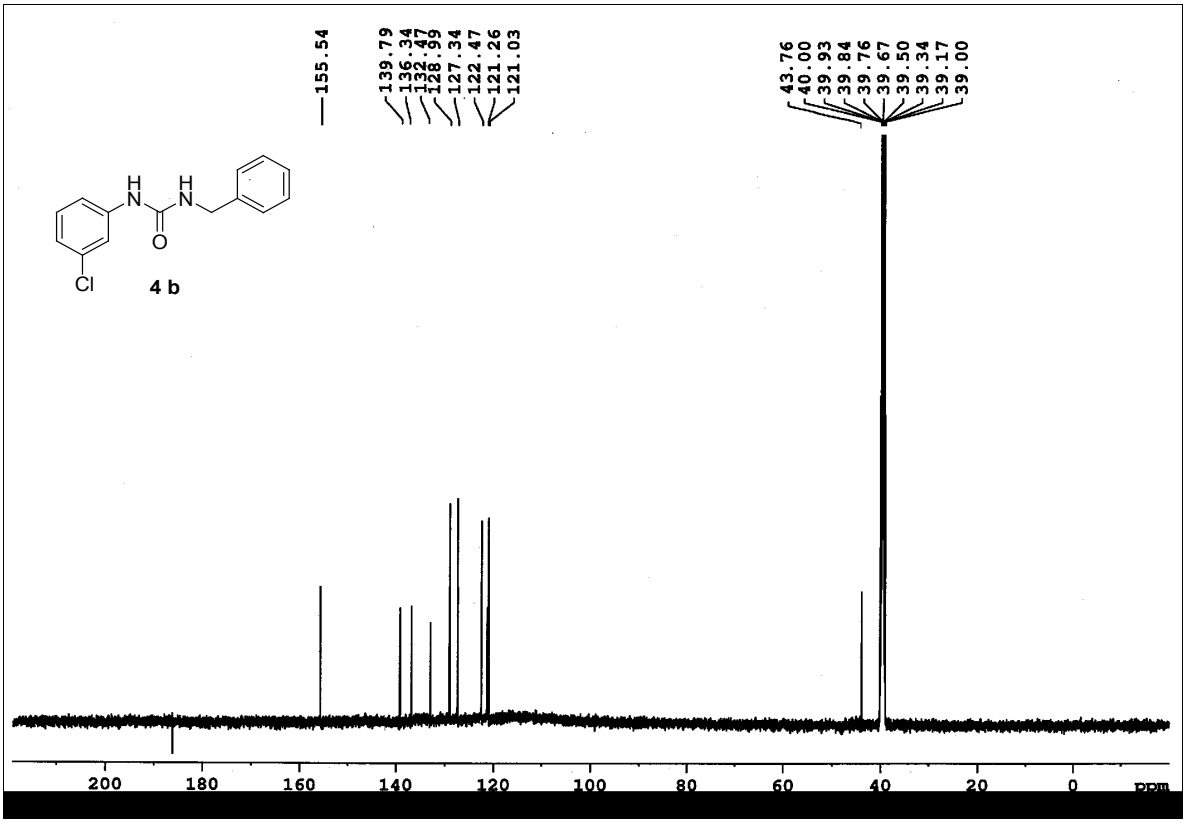


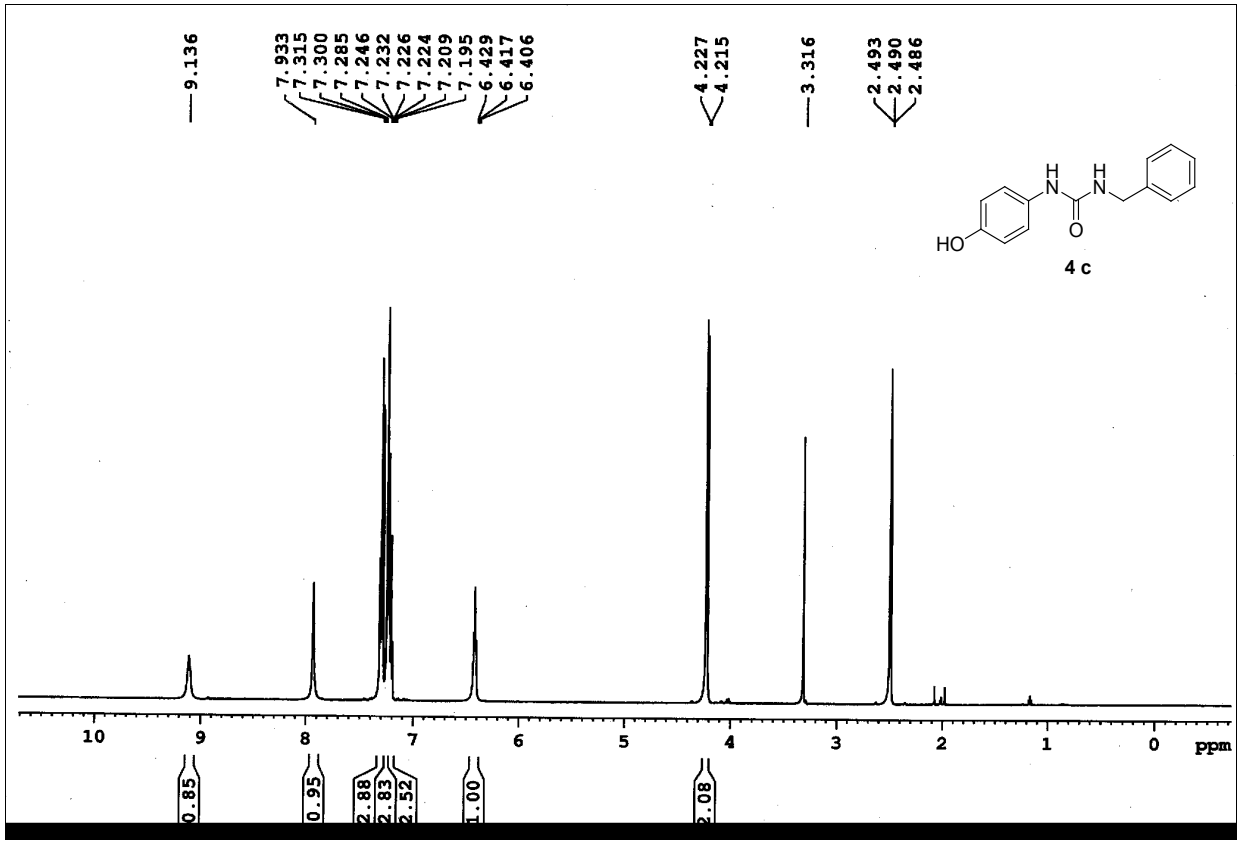


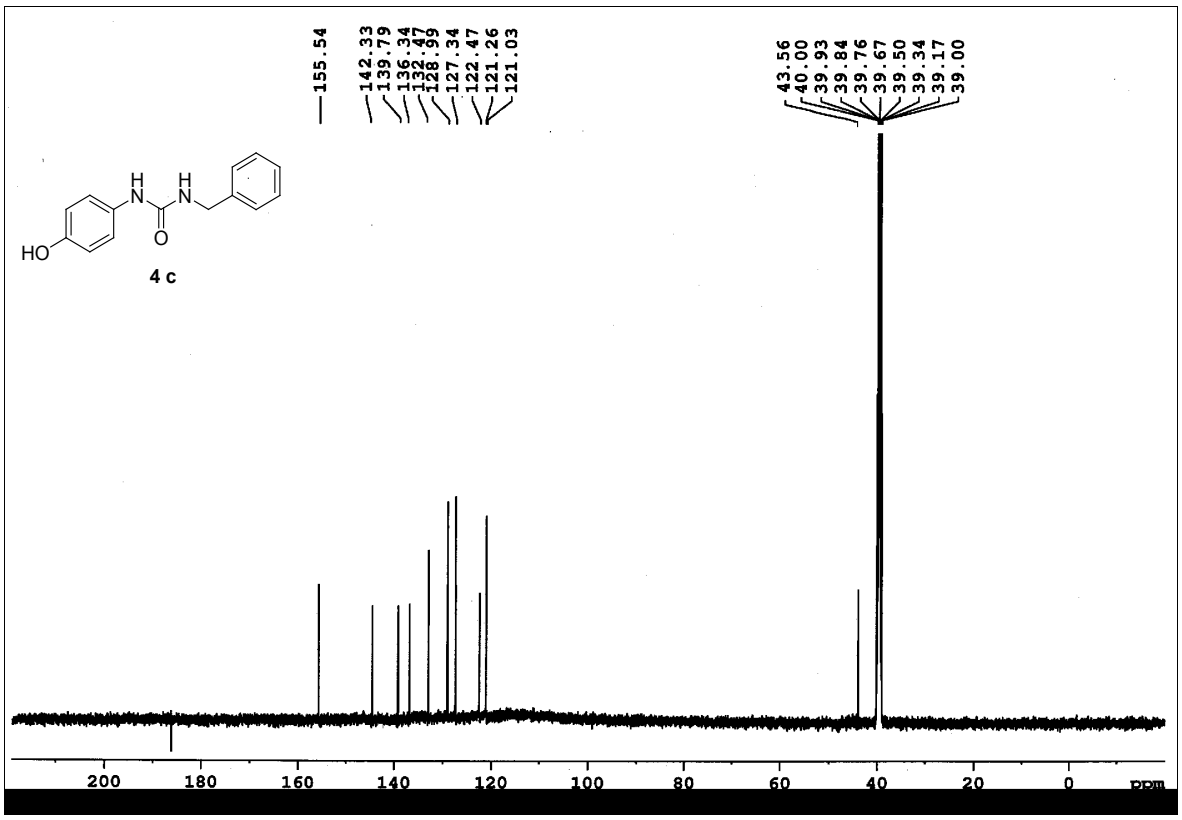


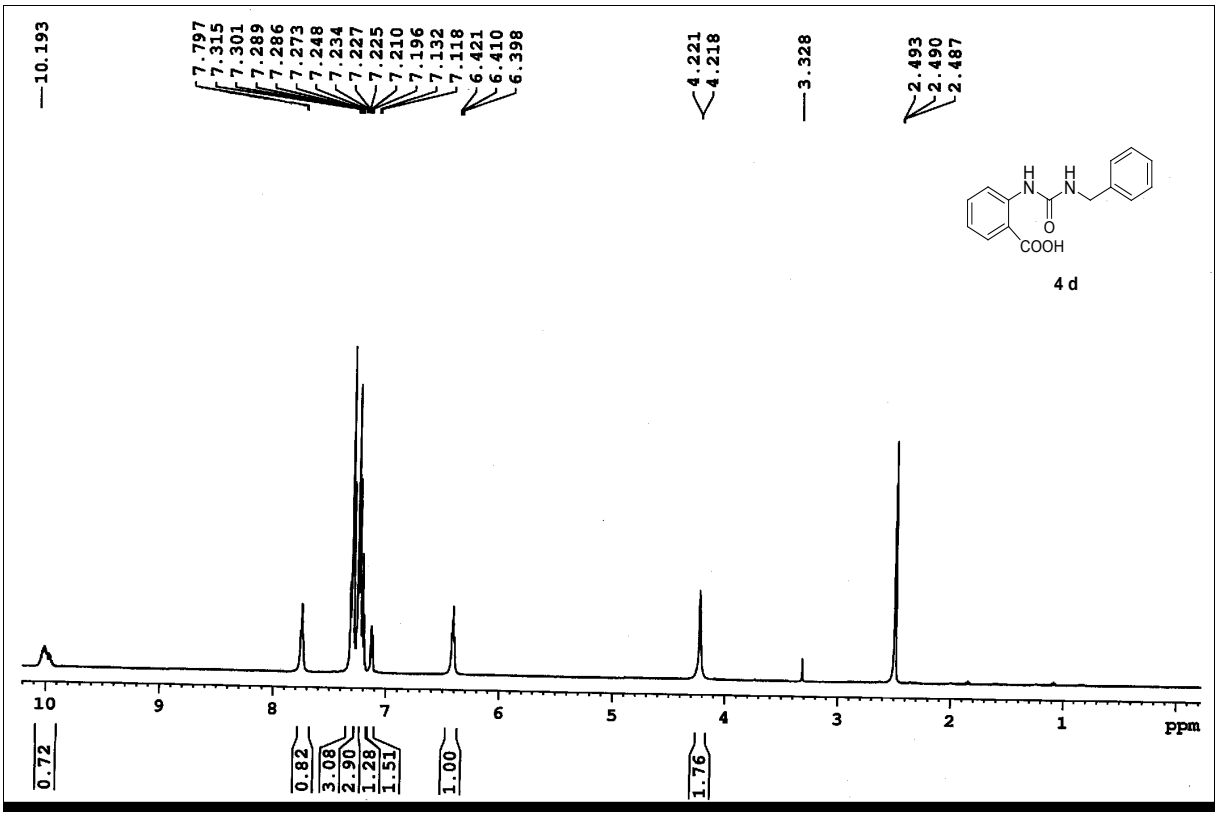


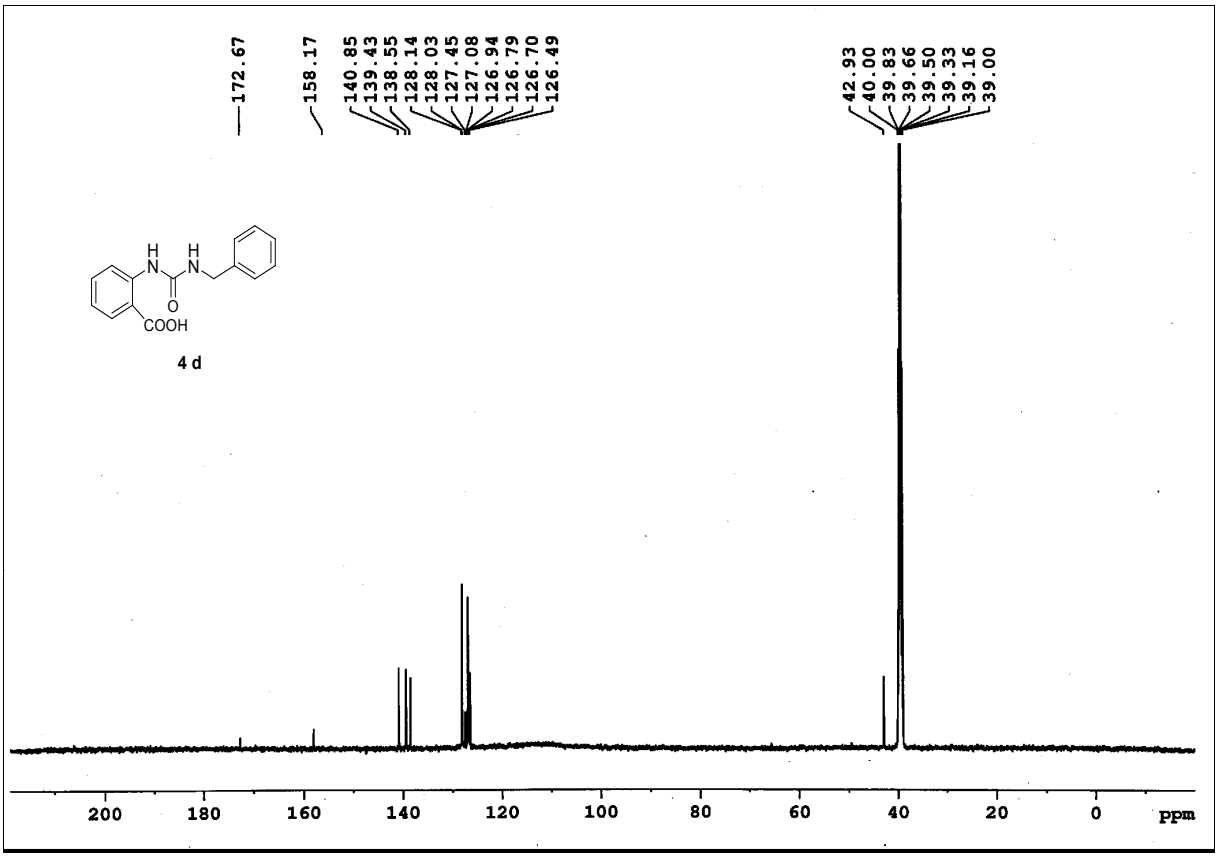


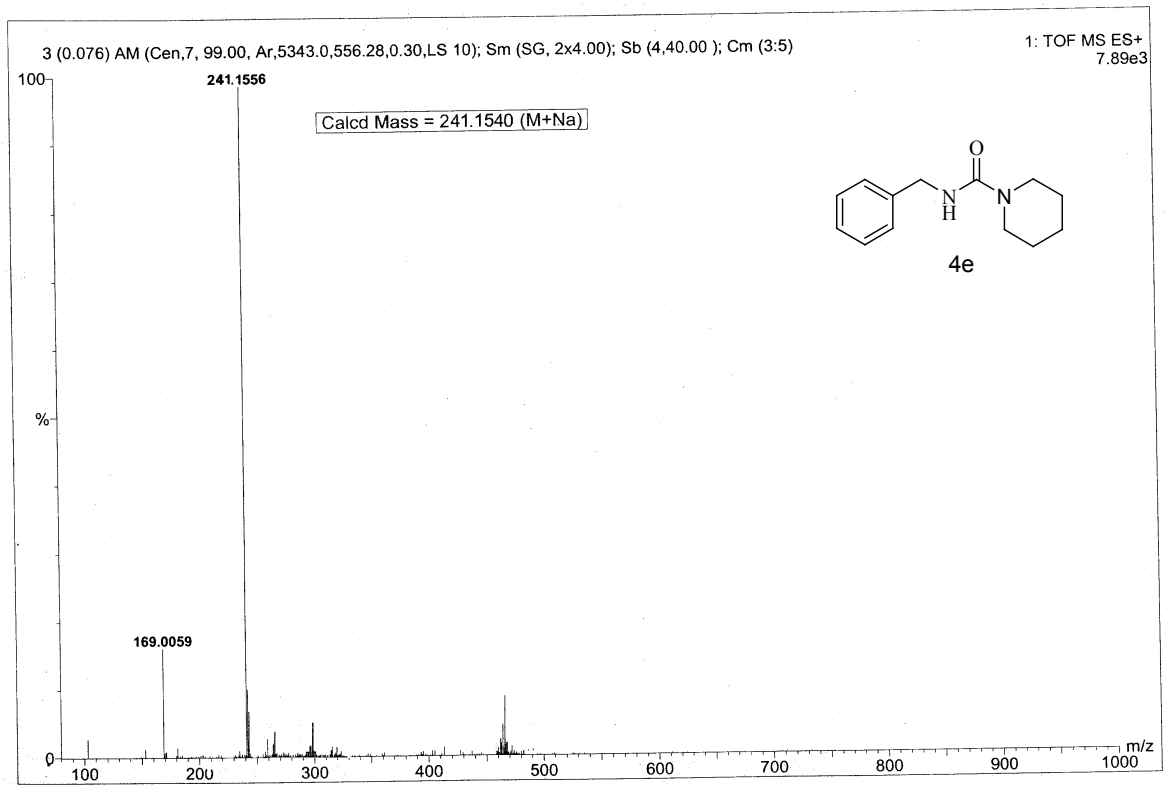


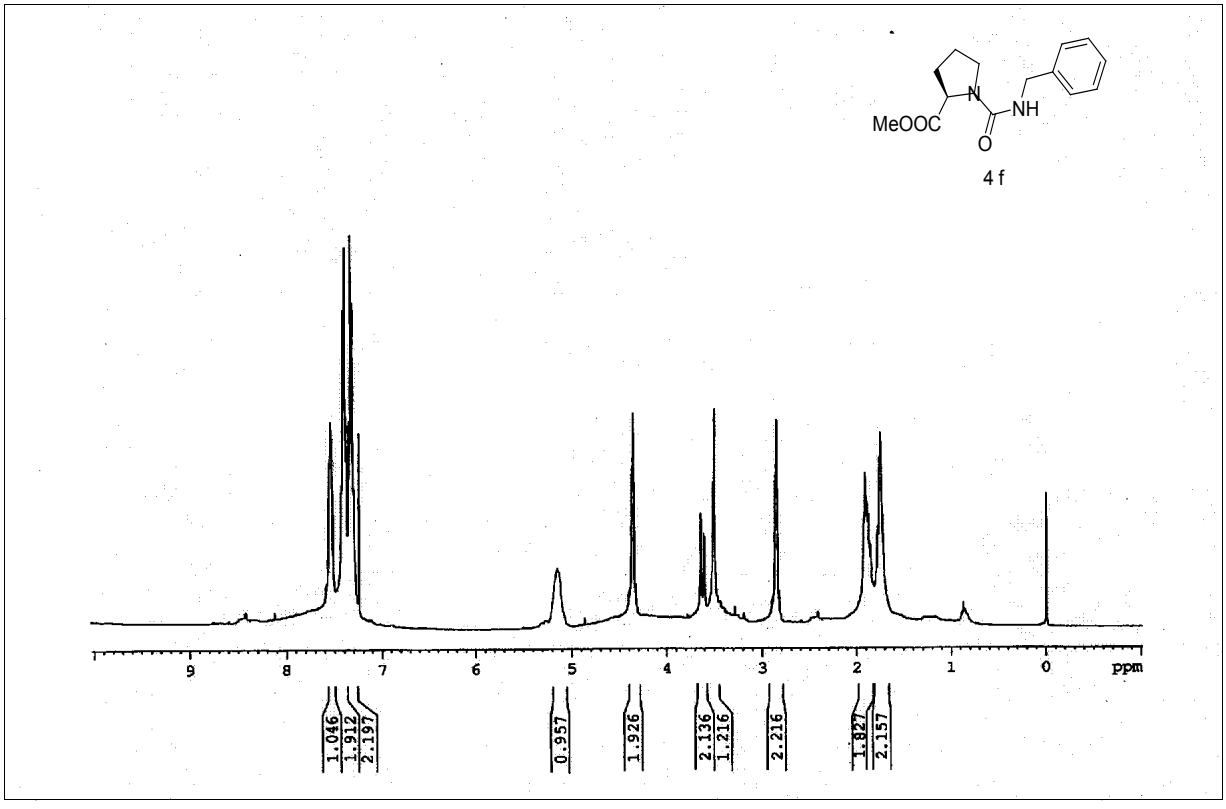


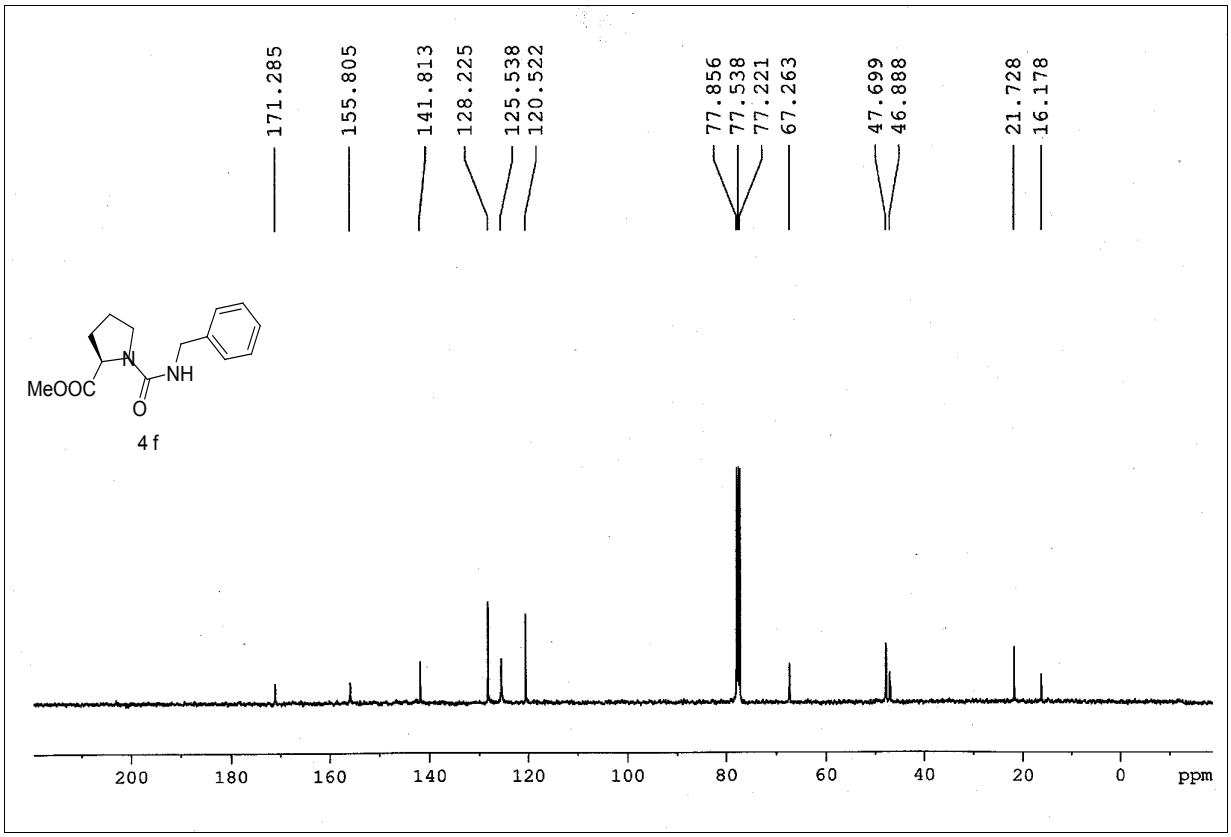


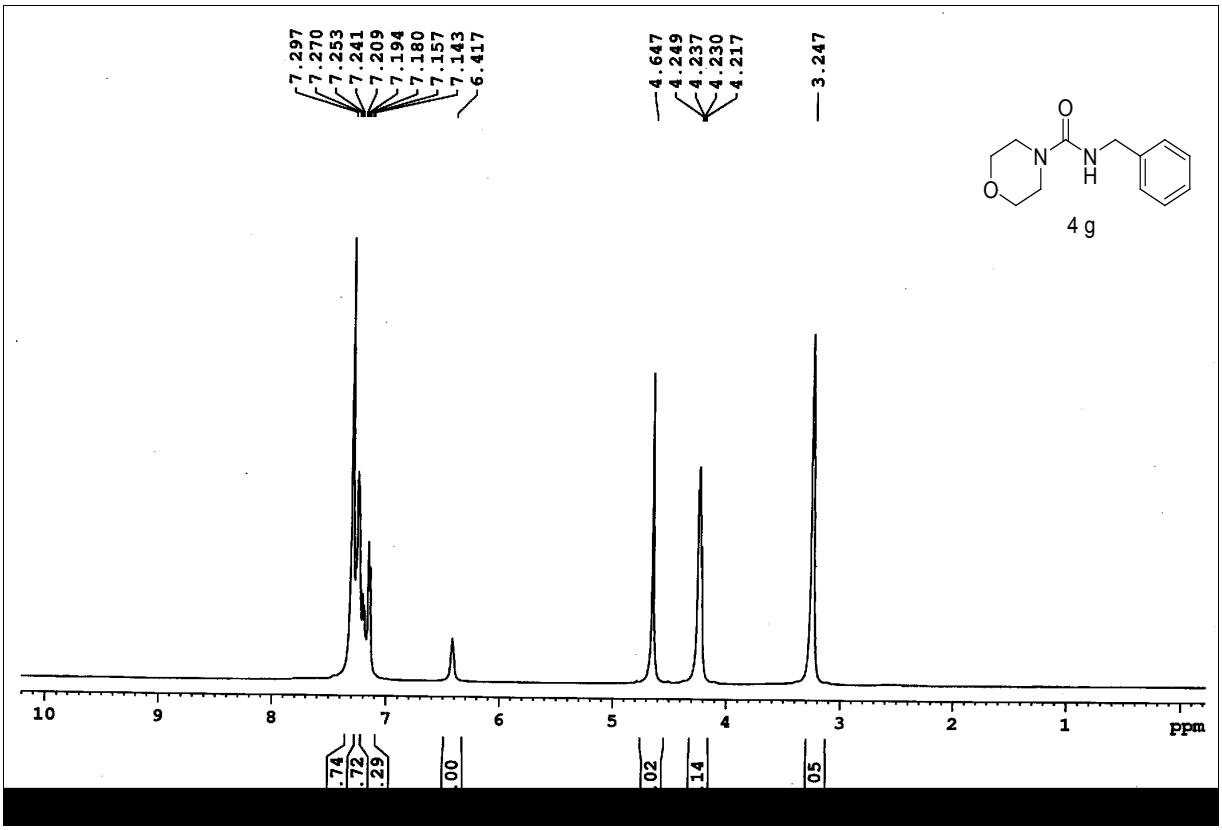


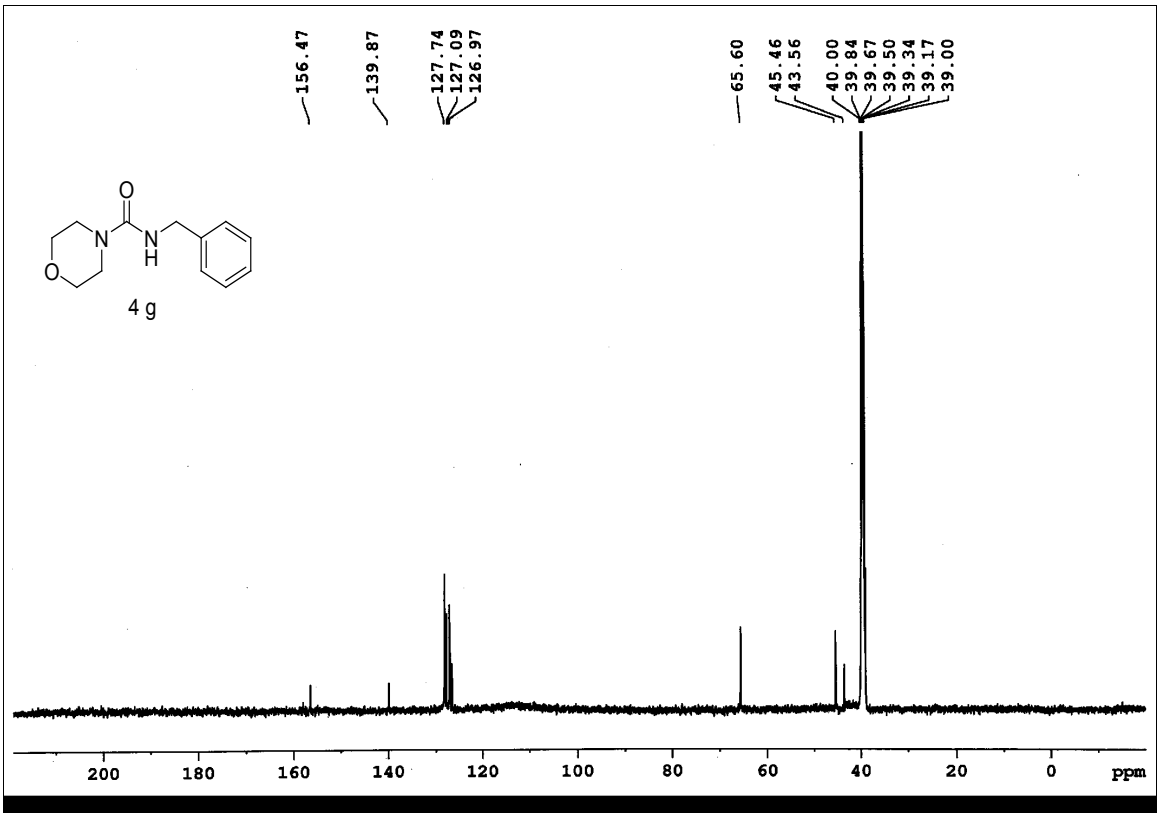


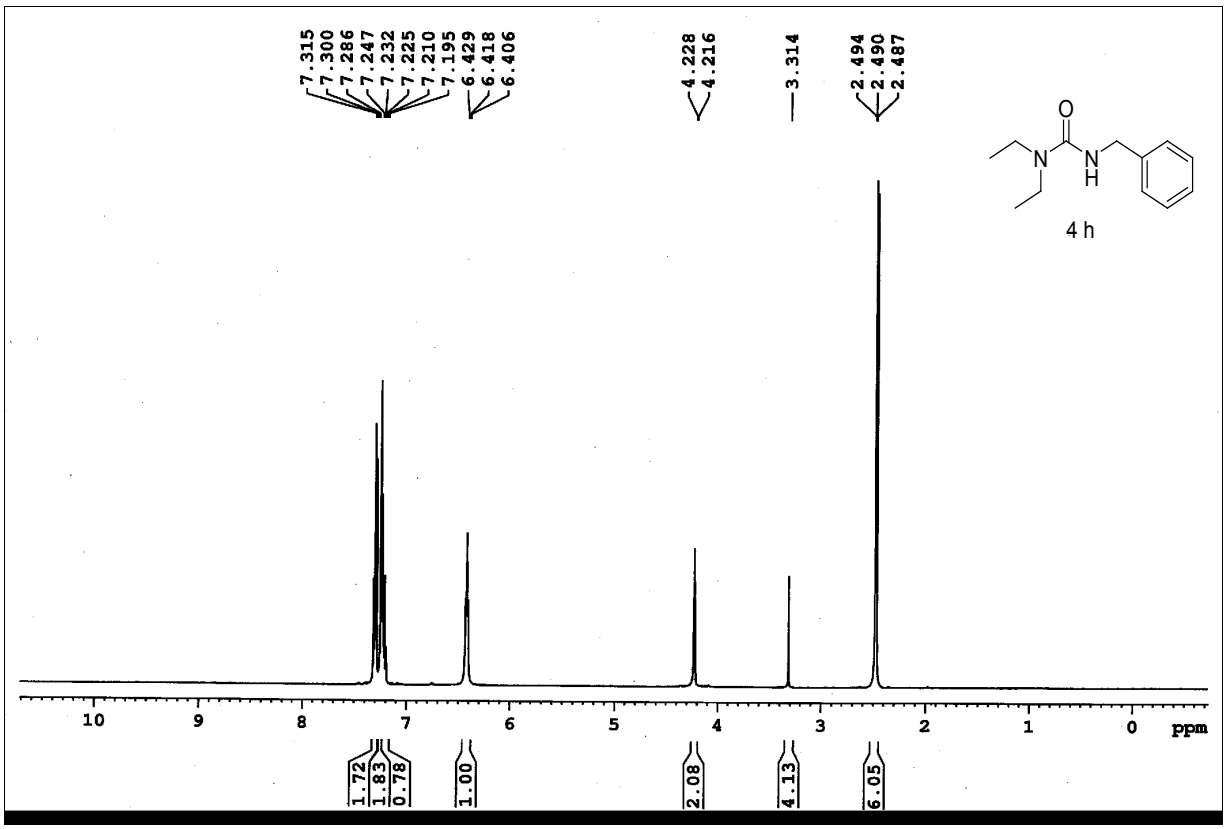


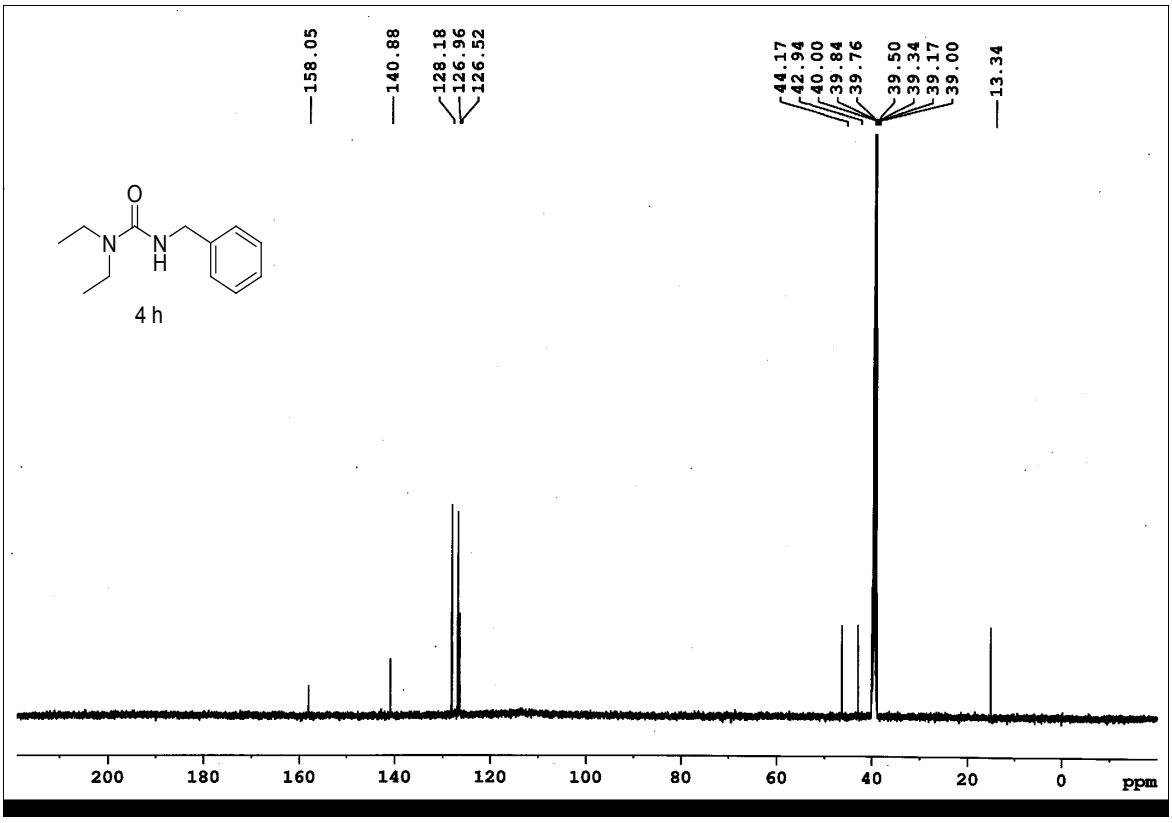


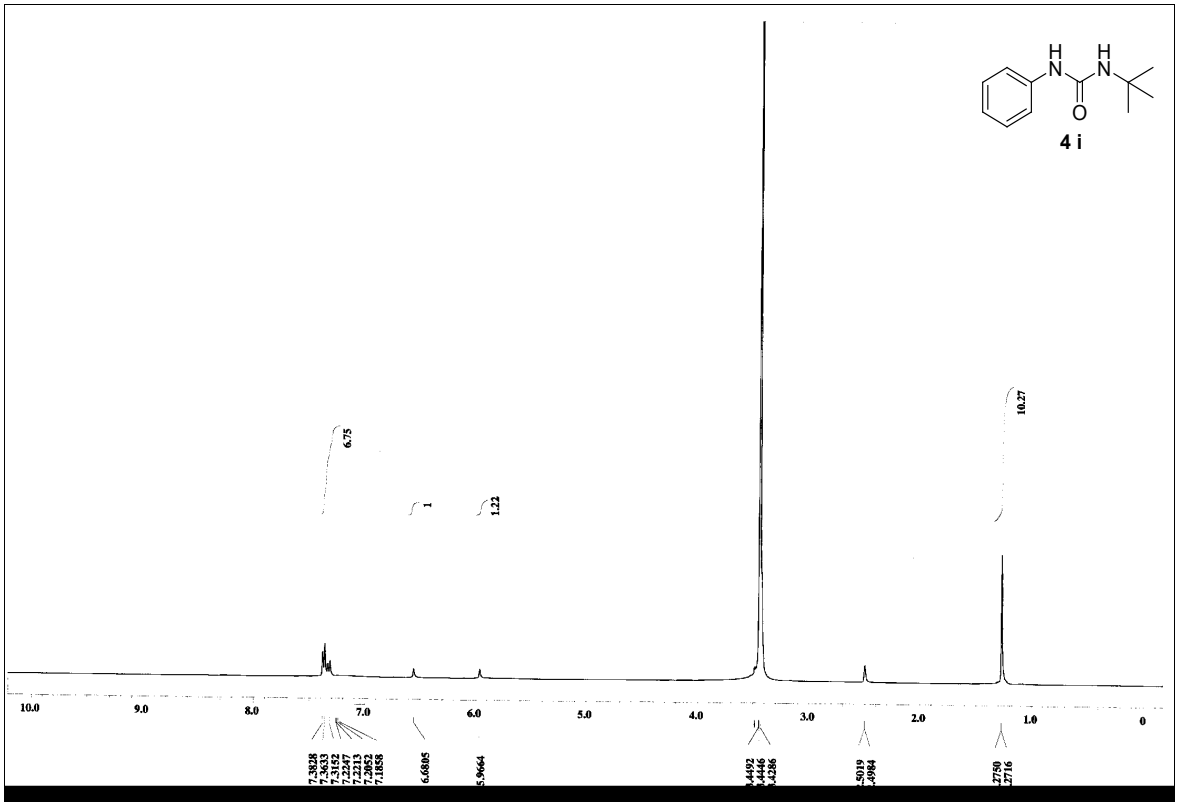


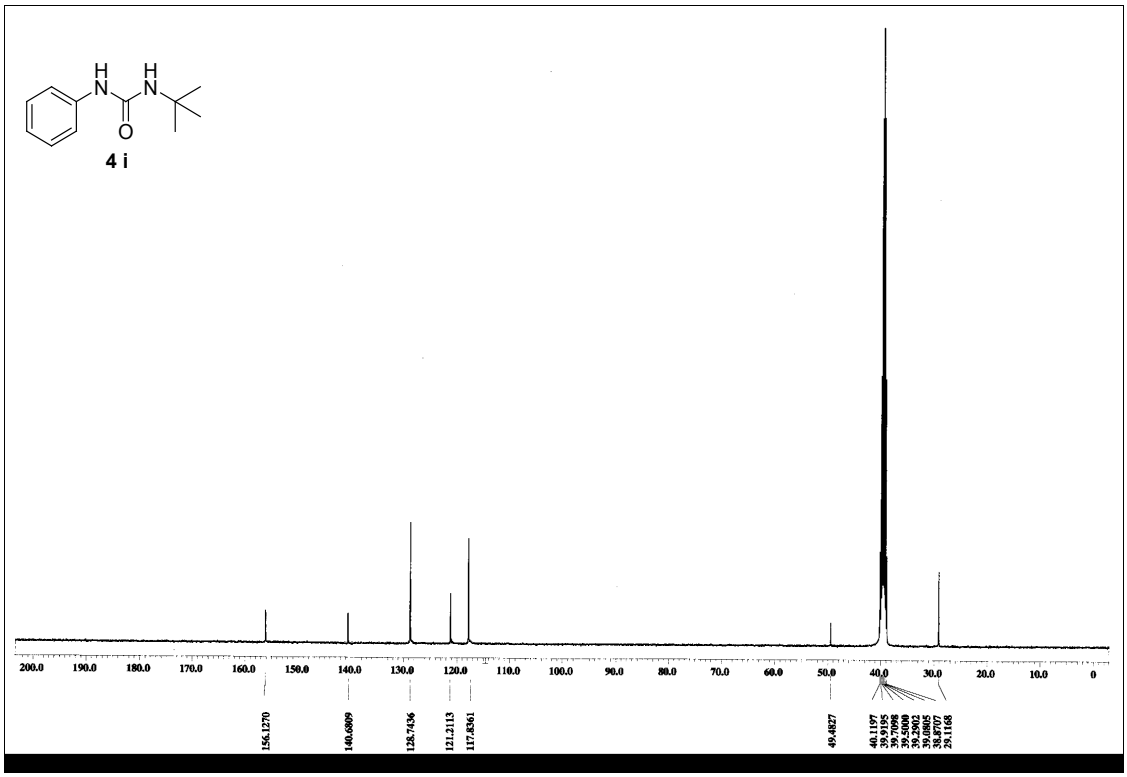


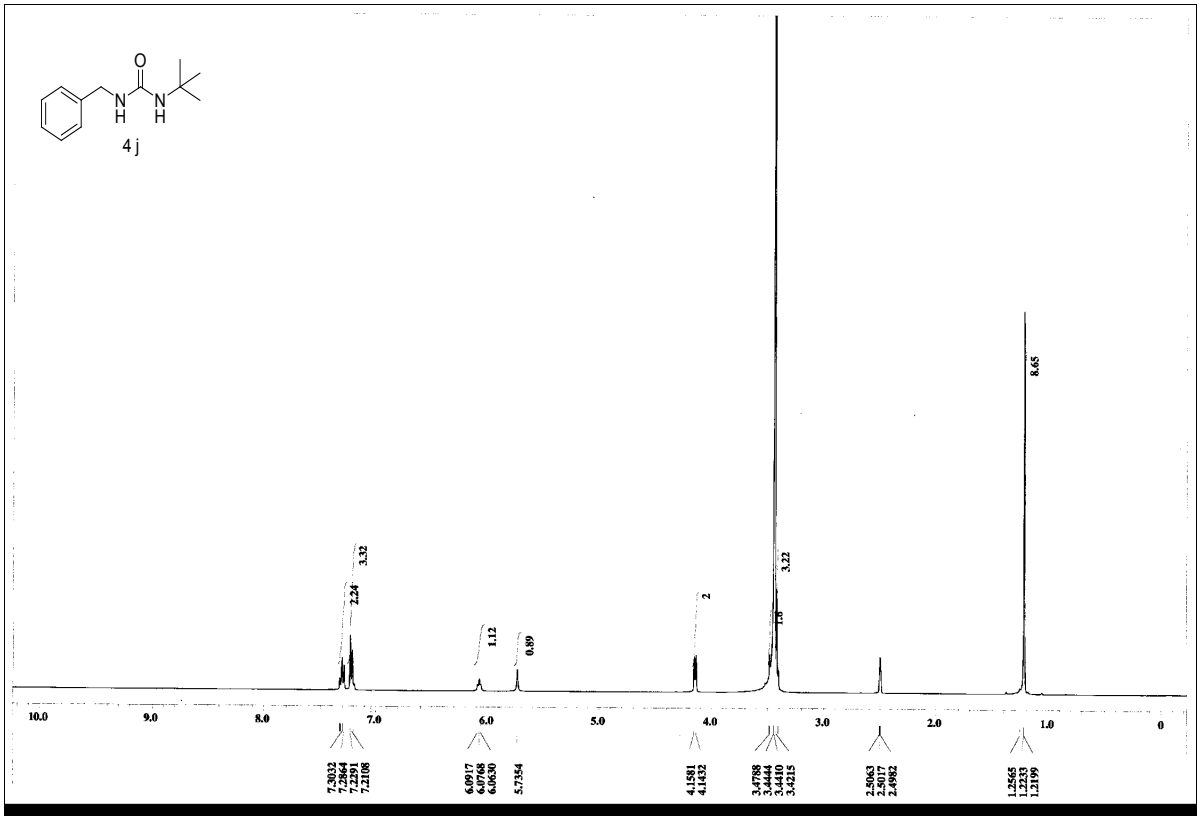


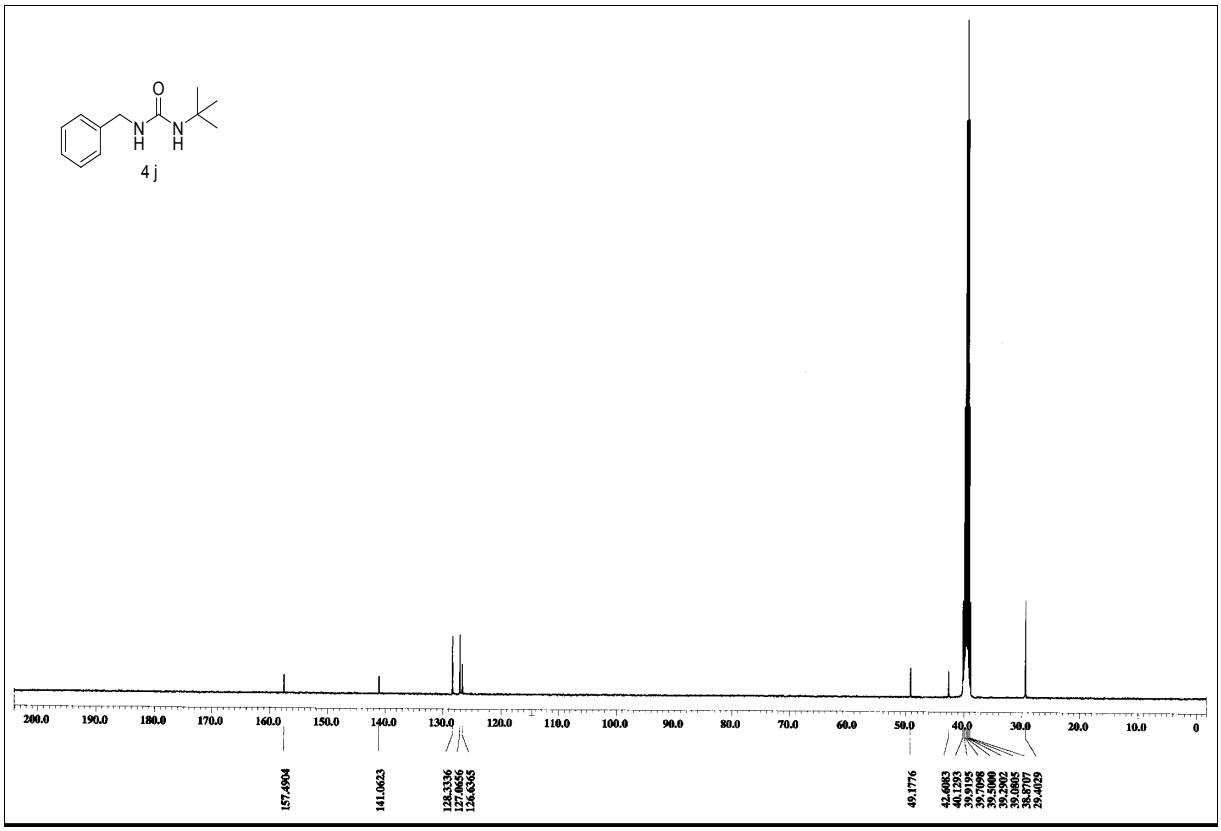


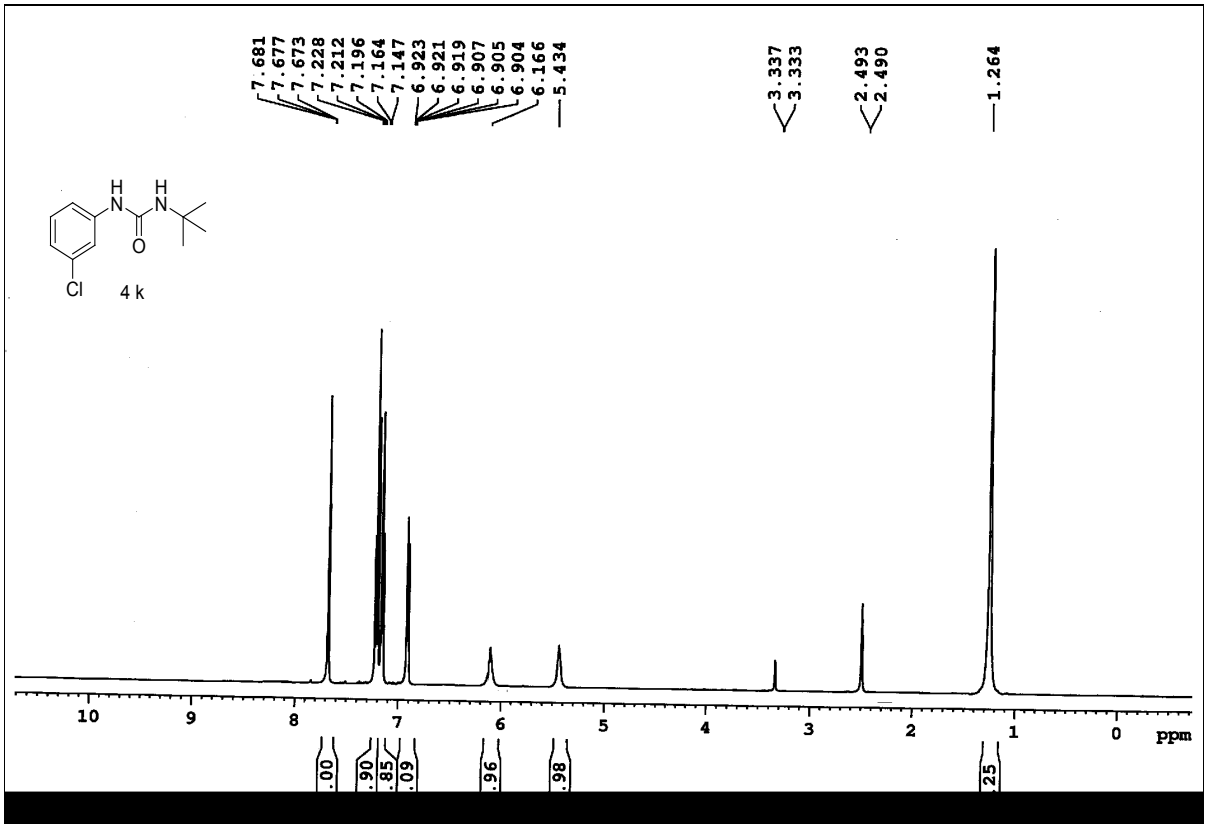

158.05
140.88
128.18
126.96
126.52
44.17
42.94
40.00
39.84
39.76
39.50
39.34
39.17
39.00
13.34
4 h
200
180
160
140
120
100
80
60
40
20
0
ppm

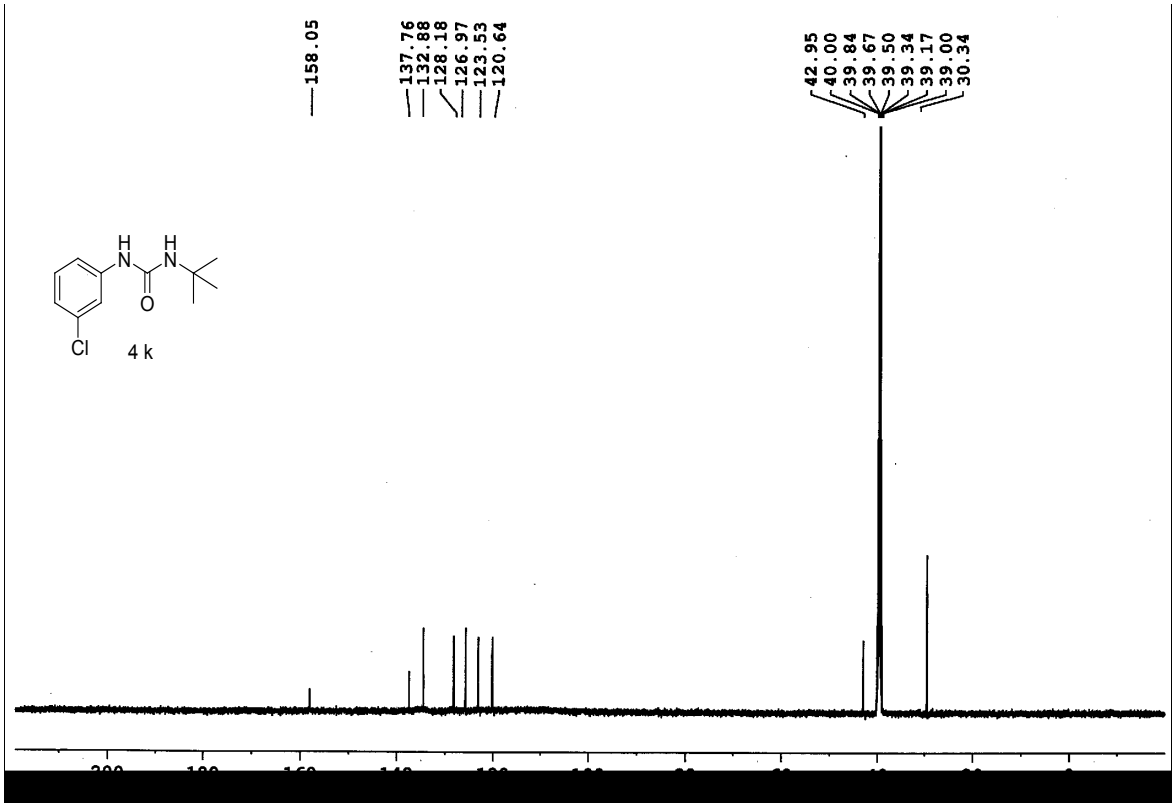

4 i
6.75
1
1.22
10.27
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

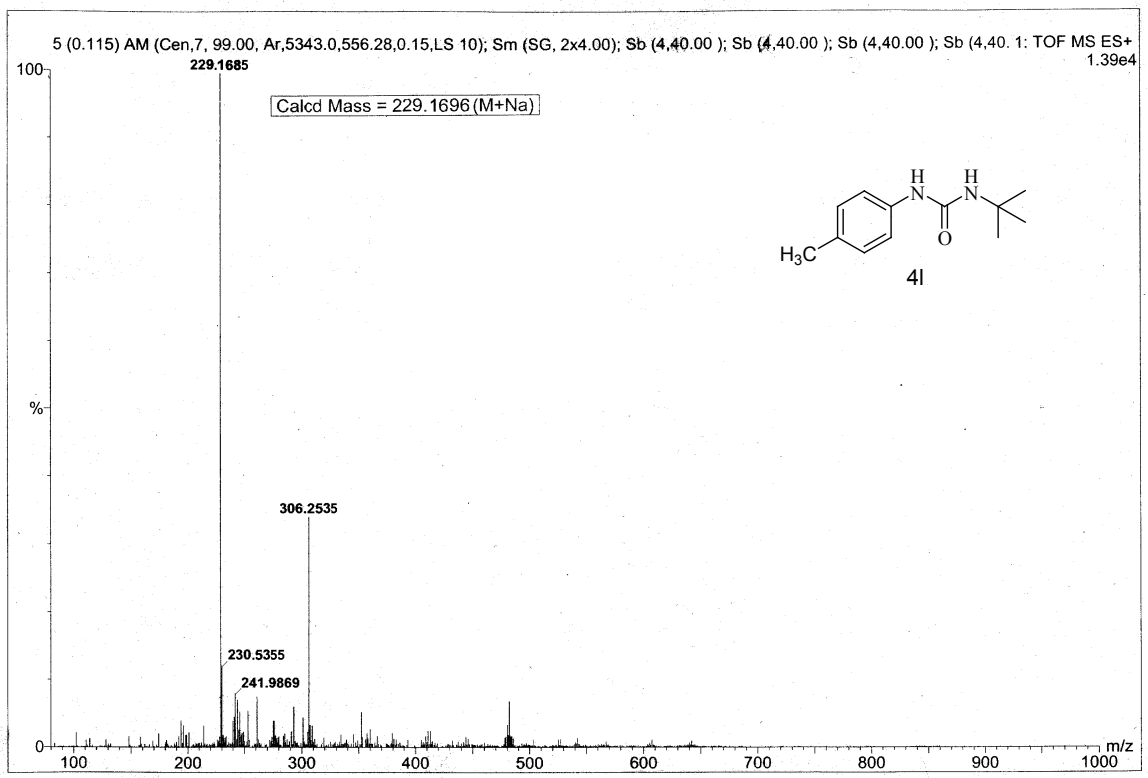


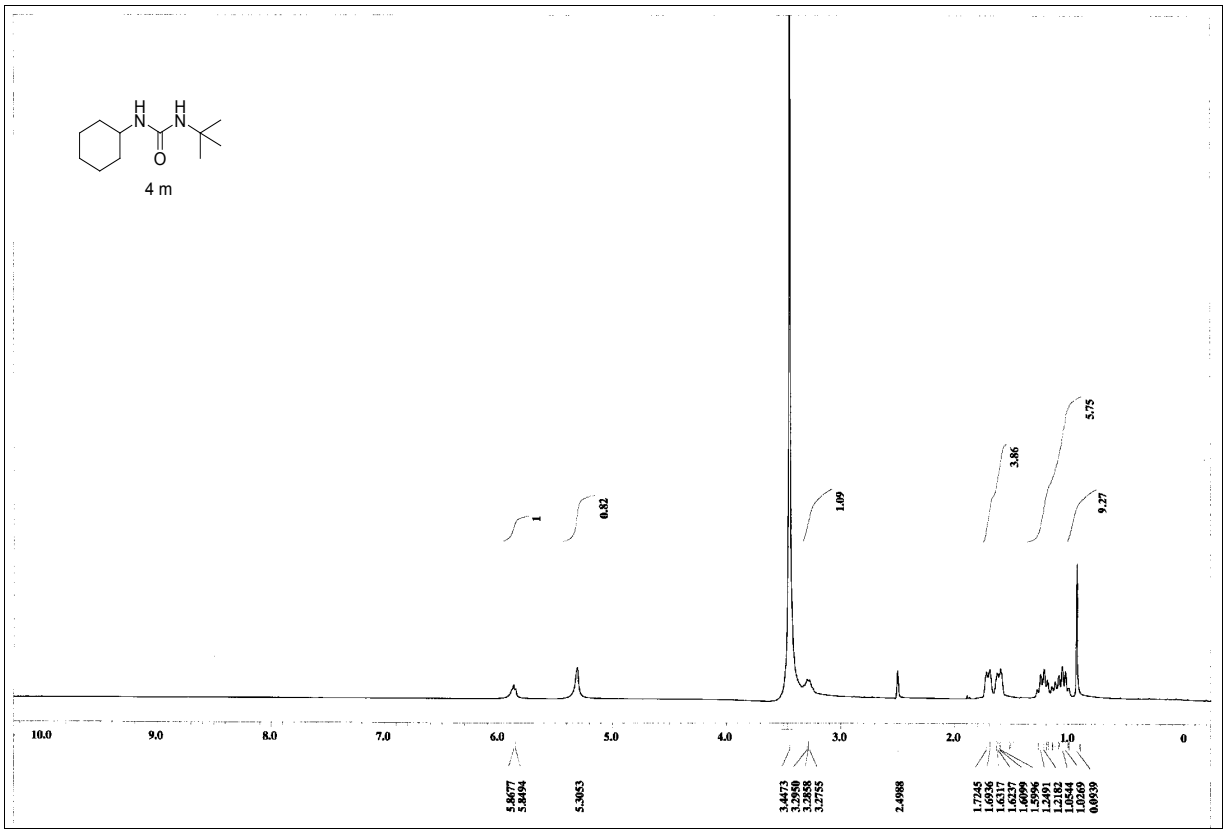


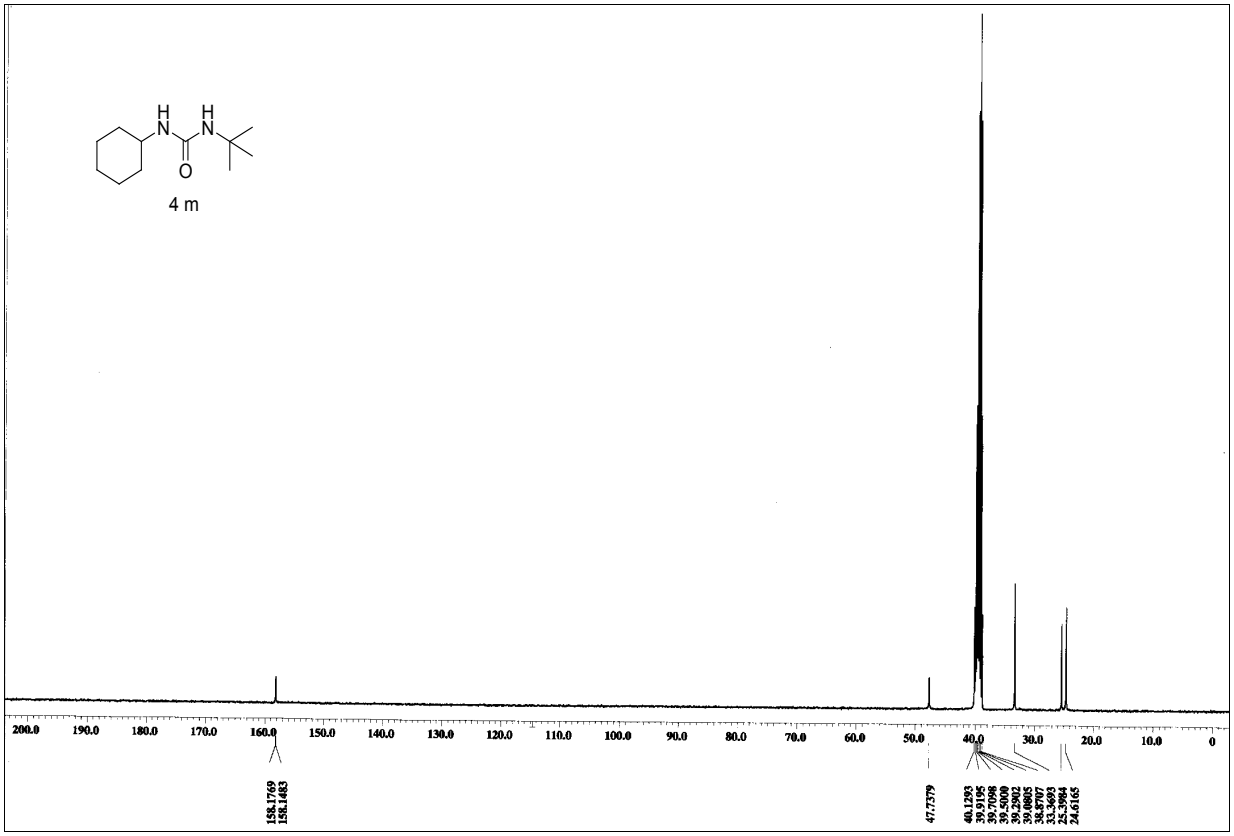


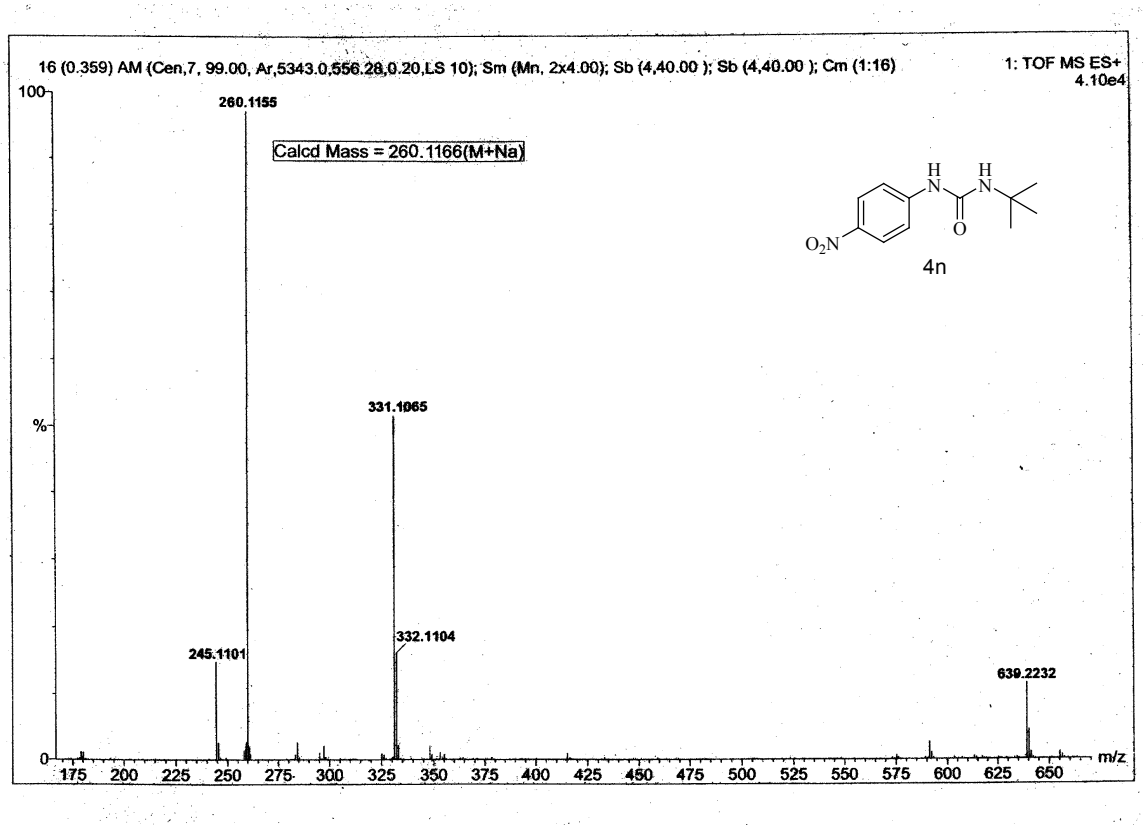


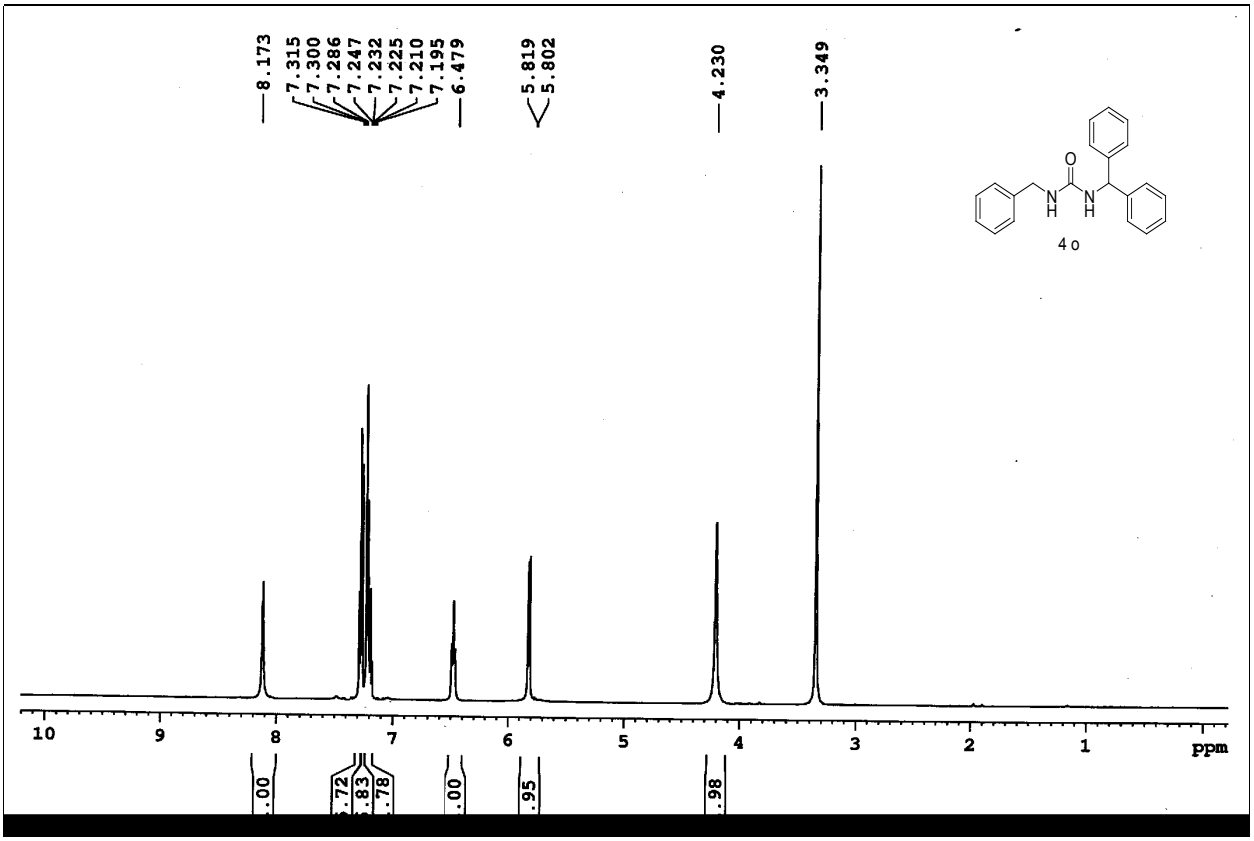

158.05
137.76
132.88
128.18
126.97
123.53
120.64
42.95
40.00
39.84
39.67
39.50
39.34
39.17
39.00
30.34
H
N
H
N
O
Cl
4 k

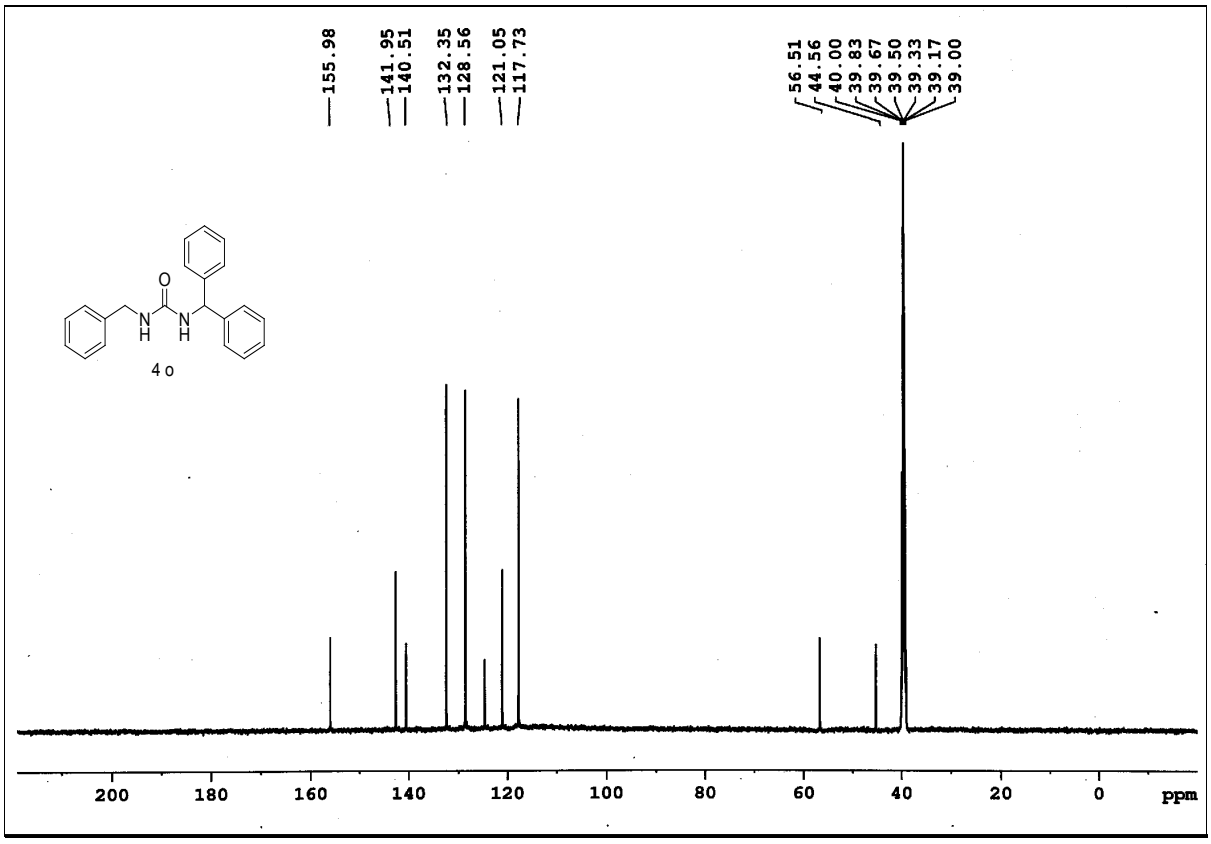

5 (0.115) AM (Cen,7, 99.00, Ar,5343.0,556.28,0.15,LS 10); Sm (SG, 2x4.00); Sb (4,40.00); Sb (4,40.00); Sb (4,40.00); Sb (4,40. 1: TOF MS ES+
1.39e4
100
%
0
229.1685
Calcd Mass = 229.1696 (M+Na)
306.2535
230.5355
241.9869
100
200
300
400
500
600
700
800
900
1000
m/z
H
N
H
N
O
H3C
4l

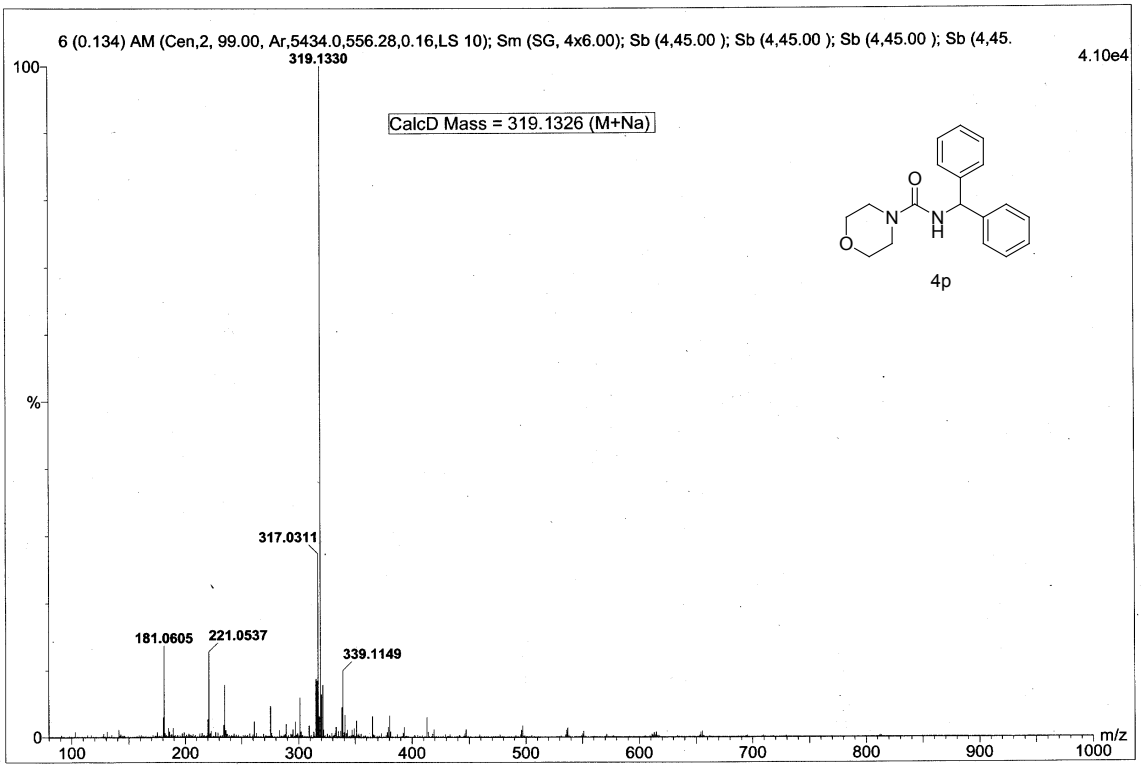


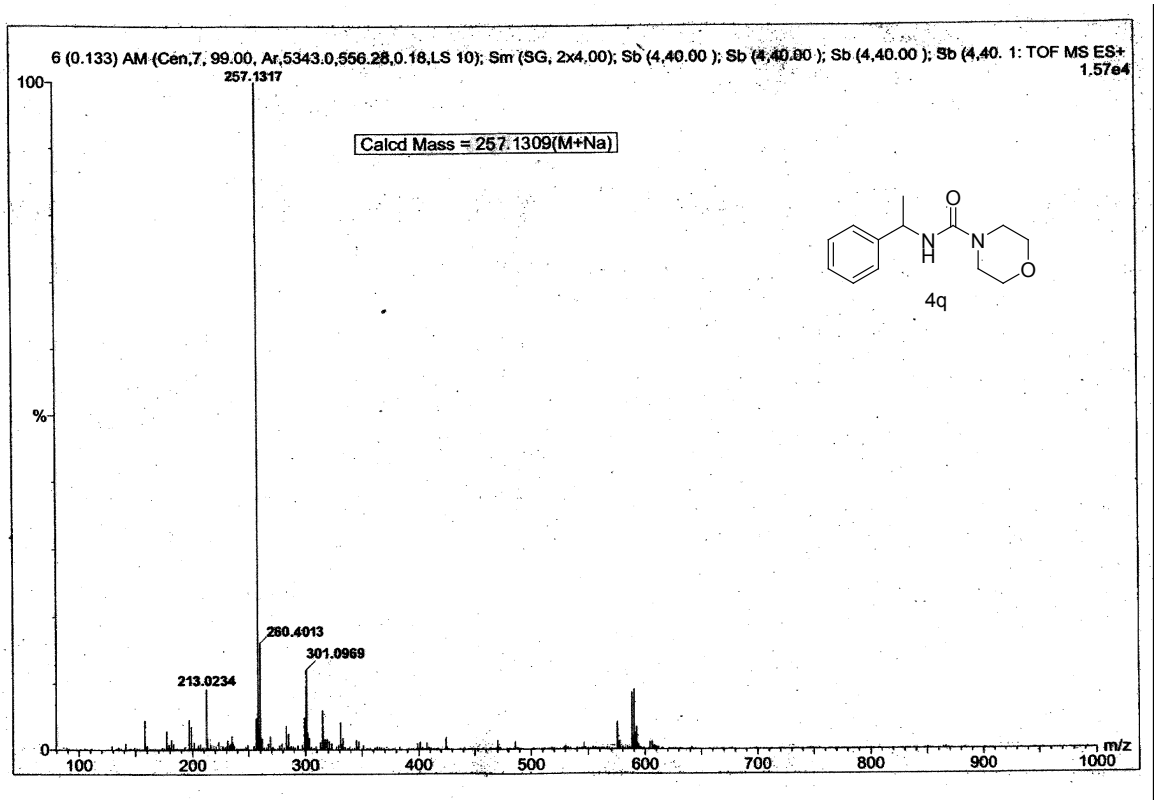


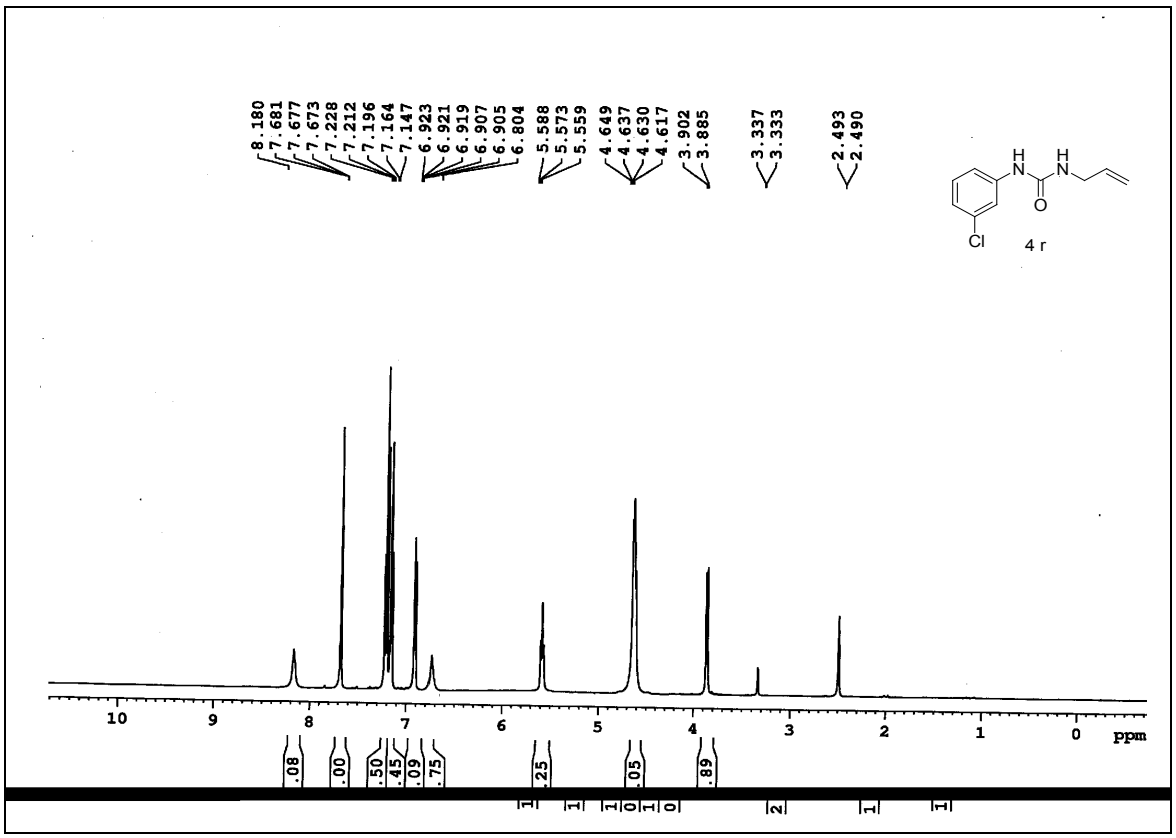


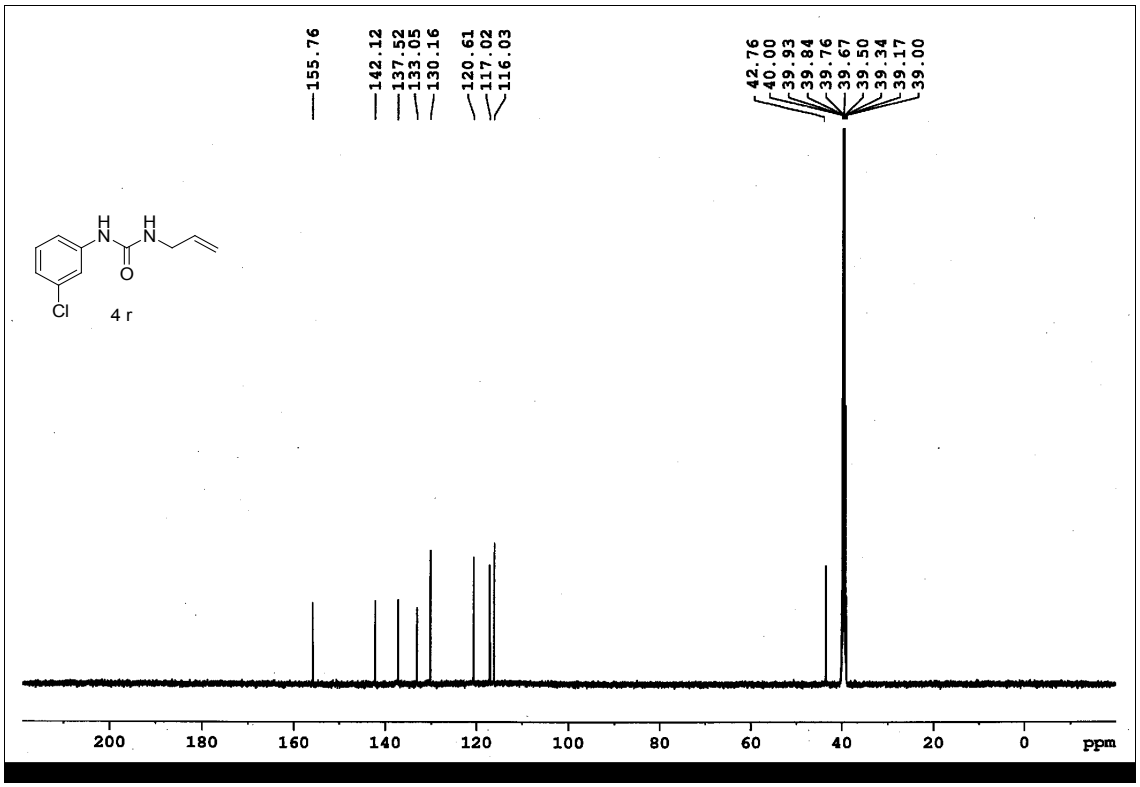


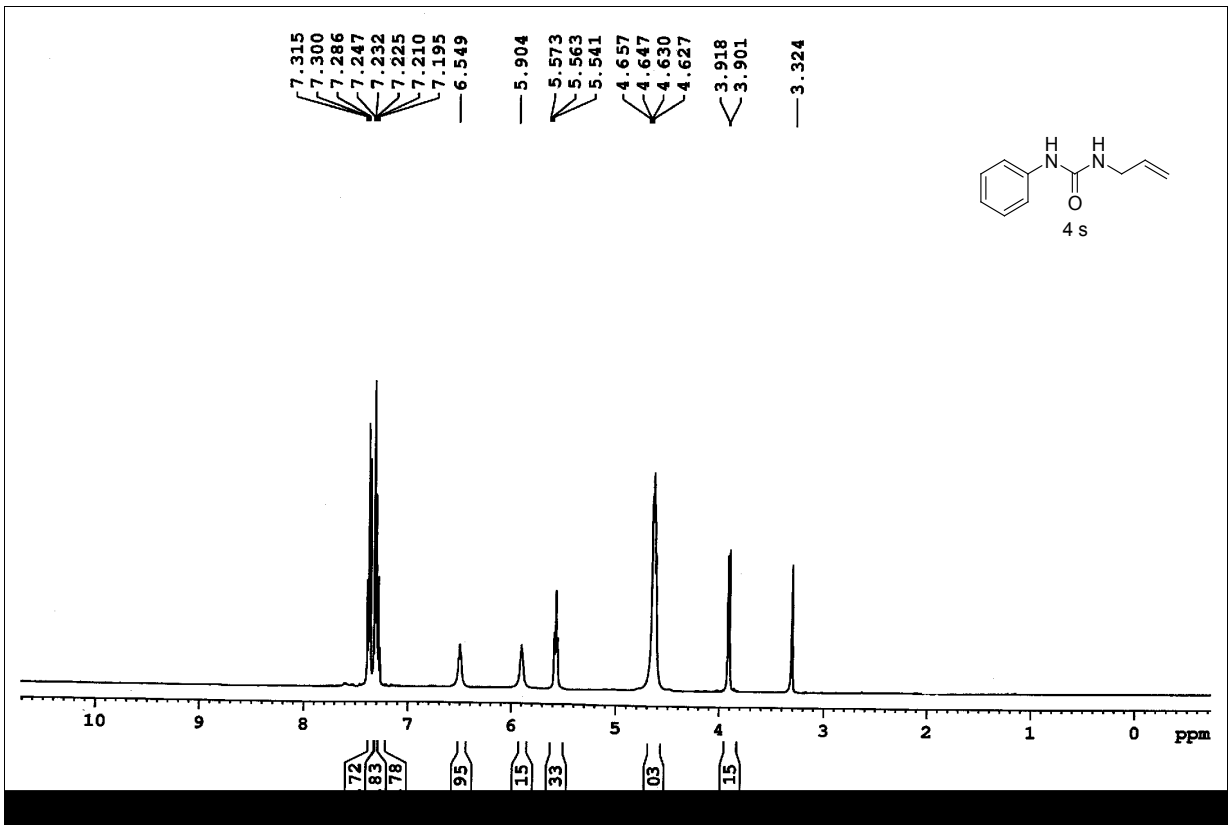





6 (0.133) AM (Cen,7, 99.00, Ar,5343.0,556.28,0.18,LS 10); Sm (SG, 2x4.00); Sb (4,40.00); Sb (4,40.00); Sb (4,40.00); Sb (4,40. 1: TOF MS ES+
1.57e4
257.1317
Calcd Mass = 257.1309(M+Na)
260.4013
301.0969
213.0234
100
%
0
m/z
100
200
300
400
500
600
700
800
900
1000
4q


8.180
7.681
7.677
7.673
7.228
7.212
7.196
7.164
7.147
6.923
6.921
6.919
6.907
6.905
6.804
5.588
5.573
5.559
4.649
4.637
4.630
4.617
3.902
3.885
3.337
3.333
2.493
2.490
4 r
10
9
8
7
6
5
4
3
2
1
0
ppm


155.76
142.12
137.52
133.05
130.16
120.61
117.02
116.03
42.76
40.00
39.93
39.84
39.76
39.67
39.50
39.34
39.17
39.00
H
N
H
N
O
Cl
4 r
200
180
160
140
120
100
80
60
40
20
0
ppm


7.315
7.300
7.286
7.247
7.232
7.225
7.210
7.195
6.549
5.904
5.573
5.563
5.541
4.657
4.647
4.630
4.627
3.918
3.901
3.324
H
N
H
N
O
4 s
10
9
8
7
6
5
4
3
2
1
0
ppm
72
83
78
95
15
33
03
15