"T3P Mediated Intramolecular Rearrangement of o-Aminobenzamide to o-Ureidobenzonitrile using Isothiocyanates"

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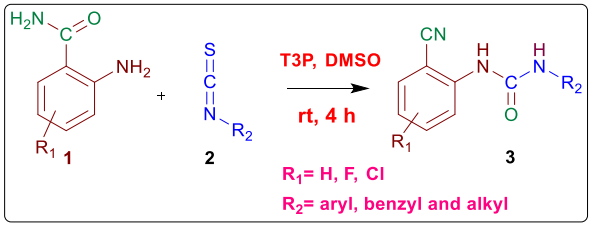
Contents:

1. General Experimental Details

All the reagents, chemicals and solvents used were from Sigma Aldrich and Sd-fine chemicals and were used without additional purification. The instrumental techniques employed for the characterization of the newly synthesized compounds include ^{1}H and ^{13}C-NMR and HRMS. ^{1}H and ^{13}C-NMR spectra were recorded on Agilent 400 MHz spectrometer in DMSO-d_6 solution using tetramethylsilane (TMS) as internal standard. Chemical shifts were recorded in ppm relative to TMS. High resolution mass spectra were obtained via electrospray (ESI). Column chromatography was performed on silica gel 60 (60–120 mesh) and thin layer chromatography was performed on TLC plates (Merck, silica gel 60 F254). The mobile phases employed for column chromatography and TLC were hexane and ethyl acetate in 9:1 ratio.

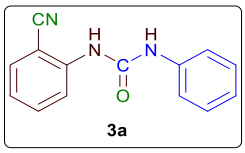
2. General Procedure for the synthesis of o-ureidobenzonitriles (3a-3t).



The mixture of o-aminobenzamide (1) (1 mmol) and isothiocyanates (2) (1 mmol) was allowed to stir in DMSO solvent and T3P (Propane phosphonic acid anhydride solution: 50 wt. % in ethyl acetate) reagent (1 mmol, 0.7 g) at room temperature for 4 h in a round bottomed flask. After that, the contents of the flask were poured in to 15 ml of water taken in separating funnel and extracted to 15 ml ethyl acetate. The ethyl acetate extract was separated and dried over anhydrous sodium sulfate. The solvent was then removed under reduced pressure to afford corresponding o-ureidobenzonitrile (3). The crude residue thus obtained was purified by column chromatography over silica gel using 10 % ethyl acetate in hexane as eluent to afford the pure o-ureidobenzonitrile with 80-95% yields.

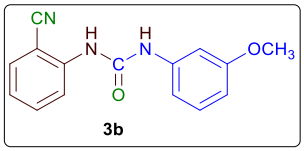
3. Characterization details of the synthesized Products:

1-(2-cyanophenyl)-3-phenylurea (3a)



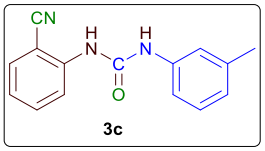
Yield 89 %; MP. 179 °C; White solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ ppm: 9.36 (s, 1H, -NH-), 8.71 (s, 1H, -NH-), 8.06 (d, J = 8.5 Hz, 1H, ar), 7.72 (d, J = 7.7 Hz, 1H, ar), 7.62 (t, J = 7.6 Hz, 1H, ar), 7.45 (d, J = 7.9 Hz, 2H, ar), 7.28 (t, J = 7.8 Hz, 2H, ar), 7.15 (t, J = 7.5 Hz, 1H, ar), 6.98 (t, J = 7.3 Hz, 1H, ar); ^{13}C NMR (400 MHz, DMSO-d_6): δ ppm: 152.43, 142.35, 139.63, 134.39, 133.53, 129.31, 123.42, 122.77, 121.70, 118.79, 117.37, 102.43; HRMS: m/z calculated for [$C_{14}H_{11}N_3O$ + H^+] = 238.0975: found = 238.0974.

1-(2-cyanophenyl)-3-(3-methoxyphenyl)urea (3b)



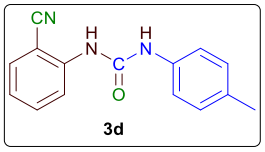
Yield: 87 %; MP. 188 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.37 (s, 1H, -NH-), 8.69 (s, 1H, -NH-), 8.05 (d, J=8.4 Hz, 1H, ar), 7.72 (d, J=7.5 Hz, 1H, ar), 7.61 (t, J=7.6 Hz, 1H, ar), 7.19 (m, 3H, ar), 6.93 (d, J=7.7 Hz, 1H, ar), 6.56 (d, J=7.8, 1H, ar), 3.71 (s, 3H, -OCH_3); ^{13}C-NMR (400 MHz, DMSO-d_6): δ ppm: 160.14, 152.36, 142.31, 140.84, 134.41, 133.54, 130.10, 123.45, 121.67, 117.35, 111.07, 108.25, 104.55, 102.37, 55.38; HRMS: m/z calculated for [$C_{15}H_{13}N_3O_2$ + H^+] = 268.1081: found = 268.1084.

1-(2-cyanophenyl)-3-(m-tolyl)urea (3c)



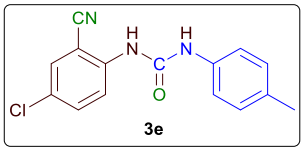
Yield: 86 %; MP. 189 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.33 (s, 1H, -NH-), 8.73 (s, 1H, -NH-), 8.10 (d, J=8.5 Hz, 1H, ar), 7.76 (d, J=7.8 Hz, 1H, ar), 7.65 (t, J=7.9 Hz, 1H, ar), 7.33 (s, 1H, ar), 7.26 (d, J=8.0 Hz, 1H, ar), 7.19 (t, J=7.7 Hz, 2H, ar), 6.84 (d, J=7.2 Hz, 1H, ar), 2.30 (s, 3H, -CH_3) ; ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 152.41, 142.43, 139.57, 138.53, 134.40, 133.55, 129.17, 123.54, 123.38, 121.63, 119.36, 117,40, 116.02, 102.30, 21.65; HRMS: m/z calculated for [$C_{15}H_{13}N_3O$ + H^+] = 252.1137: found = 252.1141.

1-(2-cyanophenyl)-3-(p-tolyl)urea (3d)



Yield: 84 %; MP. 196 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.24 (s, 1H, -NH-), 8.64 (s, 1H, -NH-), 8.04 (d, J=8.5 Hz, 1H, ar), 7.69 (m, 1H, ar), 7.58 (m, 1H, ar), 7.31 (d, J=8.3 Hz, 2H, ar), 7.12 (t, J=7.6 Hz, 1H, ar), 7.06 (d, J=8.2 Hz, 2H, ar), 2.20 (s, 3H, -CH_3); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 152.42, 142.47, 137.04, 134.38, 133.52, 131.66, 129.70, 123.30, 121.59, 118.90, 117.38, 102.25, 20.79; HRMS: m/z calculated for [$C_{15}H_{13}N_3O$ + H^+] = 252.1137: found = 252.1141.

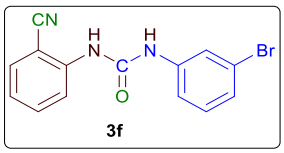
1-(4-chloro-2-cyanophenyl)-3-(p-tolyl)urea (3e)



3e

Yield: 82 %; MP. 194 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.29 (s, 1H, -NH-), 8.74 (s, 1H, -NH-), 8.10 (d, *J*=9.1 Hz, 1H, ar), 7.88 (d, *J*=2.4 Hz, 1H, ar), 7.67 (m, 1H, ar), 7.32 (d, *J*=8.3 Hz, 2H, ar), 7.09 (d, *J*=8.2 Hz, 2H, ar), 2.23 (s, 3H, -CH_3); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 152.23, 141.63, 136.83, 134.40, 132.53, 131.84, 129.69, 126.56, 123.02, 118.98, 116.10, 103.56, 20.76; HRMS: m/z calculated for [$C_{15}H_{12}ClN_3O$ + H^+] = 286.0742: found = 286.0744.

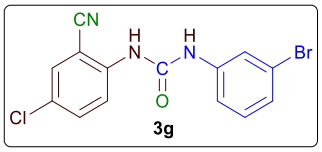
1-(3-bromophenyl)-3-(2-cyanophenyl)urea (3f)



3f

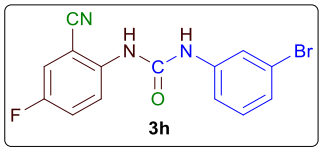
Yield: 87 %; MP. 191 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.53 (s, 1H, -NH-), 8.78 (s, 1H, -NH-), 8.01 (d, *J*=8.4 Hz, 1H, ar), 7.85 (s, 1H, ar), 7.74 (d, *J*=7.7 Hz, 1H, ar), 7.63 (t, *J*=7.6 Hz, 1H, ar), 7.23 (m, 4H, ar); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 152.36, 141.98, 141.31, 134.41, 133.55, 131.23, 125.31, 123.81, 122.18, 122.03, 121.05, 117.63, 117.29, 102.98; HRMS: m/z calculated for [$C_{14}H_{10}BrN_3O$ + H^+] = 316:0080: found = 316.0085.

1-(3-bromophenyl)-3-(4-chloro-2-cyanophenyl)urea (3g)



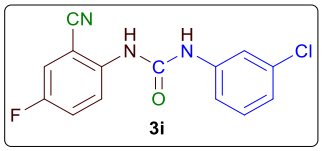
Yield: 88 %; MP. 183 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.80 (s, 1H, -NH-), 9.15 (s, 1H, -NH-), 7.99 (d, *J*=8.6 Hz, 1H, ar), 7.91 (s, 1H, ar), 7.83 (s, 1H, ar), 7.68 (d, *J*=7.9 Hz, 1H, ar), 7.30 (s, 1H, ar), 7.23 (m, 1H, ar), 7.16 (d, *J*=6.3 Hz, 1H, ar); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 152.23, 141.21, 141.16, 134.47, 132.64, 131.26, 127.15, 125.49, 123.48, 122.21, 121.17, 117.73, 116.07, 104.31; HRMS: m/z calculated for [$C_{14}H_9BrClN_3O$ + H^+] = 349.9690: found = 349.9683.

1-(3-bromophenyl)-3-(2-cyano-4-fluorophenyl)urea (3h)



Yield: 87 %; MP. 182 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.46 (s, 1H, -NH-), 8.78 (s, 1H, -NH-), 7.94 (m, 1H, ar), 7.82 (s, 1H, ar), 7.75 (d, *J*=6.1 Hz, 1H, ar), 7.53 (t, *J*=7.3 Hz, 1H, ar), 7.28 (d, *J*=7.5 Hz, 1H, ar), 7.22 (t, *J*=7.8 Hz, 1H, ar), 7.15 (d, *J*=7.2 Hz, 1H, ar); ^{13}C-NMR (400 MHz, DMSO-d_6): δ ppm: 158.71, 156.30, 152.56, 141.34, 138.77, 131.23, 125.33, 125.00, 124.92, 122.19, 122.05, 121.83, 121.11, 119.81, 119.56, 117.68, 116.24, 105.06, 104.96; HRMS: m/z calculated for [$C_{14}H_9BrFN_3O$ + H^+] = 333.9991: found = 333.9996.

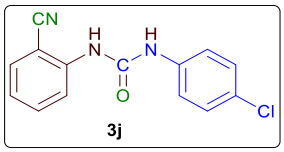
1-(3-chlorophenyl)-3-(2-cyano-4-fluorophenyl)urea (3i)



3i

Yield: 88 %; MP. 198 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.46 (s, 1H, -NH-), 8.78 (s, 1H, -NH-), 7.97 (m, 1H, ar), 7.76 (d, *J*=8.1 Hz, 1H, ar), 7.70 (s, 1H, ar), 7.55 (m, 1H, ar), 7.30 (m, 2H, ar), 7.05 (d, *J*=7.5 Hz, 1H, ar); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 158.72, 156.31, 152.56, 141.34, 138.77, 131.24, 125.33, 125.00, 124.92, 122.20, 122.06, 121.84, 121.12, 119.82, 119.56, 117.68, 116.24, 105.06, 104.97; HRMS: m/z calculated for [$C_{14}H_9ClFN_3O$ + H^+] = 290.0496: found = 290.0498.

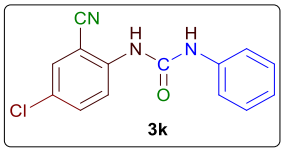
1-(4-chlorophenyl)-3-(2-cyanophenyl)urea (3j)



3j

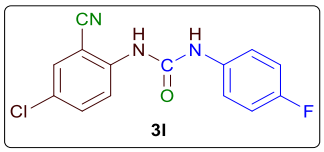
Yield: 87 %; MP. 197 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.48 (s, 1H, -NH-), 8.74 (s, 1H, -NH-), 8.04 (d, *J*=8.5 Hz, 1H, ar), 7.73 (m, 1H, ar), 7.62 (m, 1H, ar), 7.48 (d, *J*=8.8 Hz, 2H, ar), 7.33 (d, *J*=8.8 Hz, 2H, ar), 7.17 (t, *J*=7.6 Hz, 1H, ar); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 152.39, 142.15, 138.64, 134.41, 133.55, 129.17, 126.35, 123.64, 121.85, 120.35, 117.33, 102.72; HRMS: m/z calculated for [$C_{14}H_{10}ClN_3O$ + H^+] = = 272.0591: found = 272.0596.

1-(4-chloro-2-cyanophenyl)-3-phenylurea (3k)



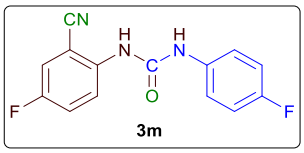
Yield: 89 %; MP. 204 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.42 (s, 1H, -NH-), 8.81 (s, 1H, -NH-), 8.11 (d, *J*=9.1 Hz, 1H, ar), 7.91 (d, *J*=2.5 Hz, 1H, ar), 7.68 (m, 1H, ar), 7.44 (d, *J*=7.7 Hz, 2H, ar), 7.29 (t, *J*=7.9 Hz, 2H, ar), 6.99 (t, *J*=7.4 Hz, 1H, ar); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 152.23, 141.53, 139.43, 134.43, 132.57, 129.31, 126.69, 123.10, 122.92, 118.88, 116.09, 103.69; HRMS: m/z calculated for [$C_{14}H_{10}ClN_3O$ + H^+] = 272.0591: found = 272.0593.

1-(4-chloro-2-cyanophenyl)-3-(4-fluorophenyl)urea (3l)



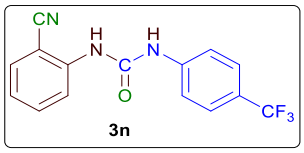
Yield: 88 %; MP. 196 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.39 (s, 1H, -NH-), 8.75 (s, 1H, -NH-), 8.05 (d, *J*=9.1 Hz, 1H, ar), 7.88 (d, *J*=2.4 Hz, 1H, ar), 7.66 (m, 1H, ar), 7.43 (m, 2H, ar), 7.10 (t, *J*=8.8 Hz, 2H, ar); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 159.31, 156.93, 152.36, 141.51, 135.77, 134.45, 132.59, 126.79, 123.18, 120.74, 120.67, 116.11, 115.99, 115.77, 103.86; HRMS: m/z calculated for [$C_{14}H_9ClFN_3O$ + H^+] = 290.0496: found = 290.0505.

1-(2-cyano-4-fluorophenyl)-3-(4-fluorophenyl)urea (3m)



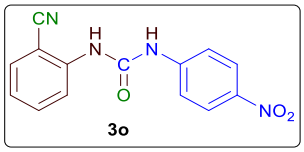
Yield: 88 %; MP. 208 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.36 (s, 1H, -NH-), 8.75 (s, 1H, -NH-), 8.01 (m, 1H, ar), 7.79 (m, 1H, ar), 7.57 (m, 1H, ar), 7.49 (m, 2H, ar), 7.16 (t, *J*=8.9 Hz, 2H, ar); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 159.22, 158.53, 156.85, 156.13, 152.75, 139.07, 139.09, 136.02, 124.76, 124.70, 122.00, 121.78, 120.62, 120.54, 119.72, 119.46, 116.23, 115.92, 115.70, 104.70, 104.60; HRMS: m/z calculated for [$C_{14}H_9F_2N_3O$ + H^+] = 274.0786: found = 274.0787.

1-(2-cyanophenyl)-3-(4-(trifluoromethyl)phenyl)urea (3n)



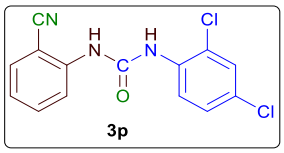
Yield: 95 %; MP. 185 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 9.72 (s, 1H, -NH-), 8.82 (s, 1H, -NH-), 8.04 (d, *J*=8.4 Hz, 1H, ar), 8.00 (s, 1H, ar), 7.74 (m, 1H, ar), 7.63 (m, 1H, ar), 7.58 (d, *J*=8.3 Hz, 1H, ar), 7.52 (t, *J*=7.9 Hz, 1H, ar), 7.32 (d, *J*=7.5 Hz, 1H, ar), 7.19 (t, *J*=7.4 Hz, 1H, ar); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 152.55, 141.96, 140.54, 134.43, 133.56, 130.47, 130.20, 129.89, 123.88, 122.39, 122.12, 119.04, 117.30, 114.71, 103.09; HRMS: m/z calculated for [$C_{15}H_{10}F_3N_3O$ + H^+] = 306.0854: found =306.0858.

1-(2-cyanophenyl)-3-(4-nitrophenyl)urea (3o)



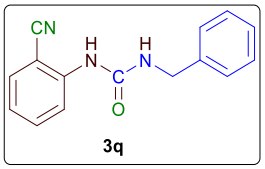
Yield: 93 %; MP. >250 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 10.03 (s, 1H, -NH-), 8.95 (s, 1H, -NH-), 8.20 (d, *J*=9.1 Hz, 2H, ar), 8.00 (d, *J*=8.4 Hz, 1H, ar), 7.77 (d, *J*=7.7 Hz, 1H, ar), 7.67 (m, 3H, ar), 7.23 (t, *J*=7.6 Hz, 1H, ar); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 152.21, 146.25, 141.91, 141.57, 134.49, 133.65, 125.61, 124.33, 122.46, 118.25, 117.22, 103.64; HRMS: m/z calculated for [$C_{14}H_{10}N_4O_3$ - H^+] = 281.0826: found = 281.0831.

1-(2-cyanophenyl)-3-(2,4-dichlorophenyl)urea (3p)



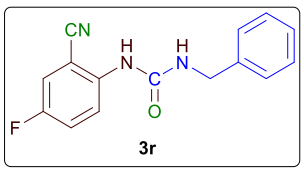
Yield: 87 %; MP. 184 °C; White solid; ^{1}H-NMR (400 MHz, DMSO-d_6): δ ppm: 9.48 (s, 1H, -NH-), 9.00 (s, 1H, -NH-), 8.07 (d, *J*=7.5 Hz, 1H, ar), 7.96 (d, *J*=6.6 Hz, 1H, ar), 7.72 (s, 1H, ar), 7.60 (s, 2H, ar), 7.36 (d, *J*=6.8 Hz, 1H, ar), 7.18 (s, 1H, ar); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 152.53, 141.92, 135.38, 134.56, 133.88, 129.27, 128.22, 127.50, 124.22, 124.11, 123.76, 122.79, 117.55, 103.32; HRMS: m/z calculated for [$C_{14}H_9Cl_2N_3O$ + H^+] = 306.0201: found = 306.0207.

1-benzyl-3-(2-cyanophenyl)urea (3q)



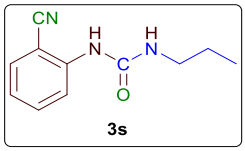
Yield: 80 %; MP. 208 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 8.59 (s, 1H, -NH-), 8.08 (d, *J*=8.5 Hz, 1H, -NH-), 7.69 (d, *J*=7.1 Hz, 1H, ar), 7.59 (t, *J*=7.5 Hz, 1H, ar), 7.44 (d, *J*=5.3 Hz, 1H, ar), 7.35 (m, 4H, ar), 7.28 (d, *J*=6.7 Hz, 1H, ar), 7.11 (t, *J*=7.5 Hz, 1H, ar), 4.33 (d, *J*=5.6 Hz, 2H, benzyl); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 154.97, 143.13, 140.08, 134.29, 133.42, 128.82, 127.72, 127.34, 122.72, 121.18, 117.46, 101.53, 43.39; HRMS: m/z calculated for [$C_{15}H_{13}N_3O + H^+$] = 252.1136: found = 252.1139.

1-benzyl-3-(2-cyano-4-fluorophenyl)urea (3r)



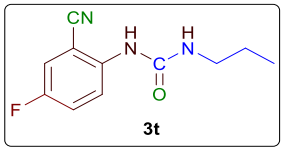
Yield: 82 %; MP. 210 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 8.62 (s, 1H, -NH-), 8.03 (dd, *J*=9.3, 5.0, 1H, -NH-), 7.71 (m, 1H, ar), 7.51 (m, 1H, ar), 7.36 (m, 5H, ar), 7.28 (m, 1H, ar), 4.34 (d, *J*=5.7 Hz, 2H, benzyl); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 162.60, 160.20, 159.73, 144.70, 144.55, 133.41, 132.30, 131.93, 128.58, 128.50, 126.56, 126.34, 124.07, 123.81, 120.99, 107.91, 107.83, 48.02; HRMS: m/z calculated for [$C_{15}H_{12}FN_3O + H^+$] = 270.1037: found = 270.1040.

1-(2-cyanophenyl)-3-propylurea (3s)



Yield: 80 %; MP. 198 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 8.43 (s, 1H, -NH-), 8.06 (d, *J*=8.1 Hz, 1H, -NH-), 7.66 (d, *J*=7.2 Hz, 1H, ar), 7.56 (t, *J*=7.3 Hz, 1H, ar), 7.07 (t, *J*=7.1 Hz, 1H, ar), 6.98 (s, 1H, ar), 3.06 (d, *J*=5.6 Hz, 2H, -CH_2-), 1.45 (dd, *J*=13.6 Hz, 6.7 Hz, 2H, -CH_2-), 0.88 (t, *J*=6.9 Hz, 3H, -CH_3); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 154.87, 143.28, 134.23, 133.36, 122.43, 120.97, 117.47, 101.18, 41.38, 23.13, 11.78; HRMS: m/z calculated for [$C_{11}H_{13}N_3O$ + H^+] = 204.1131: found = 204.1135.

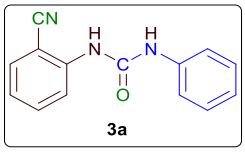
1-(2-cyano-4-fluorophenyl)-3-propylurea (3t)

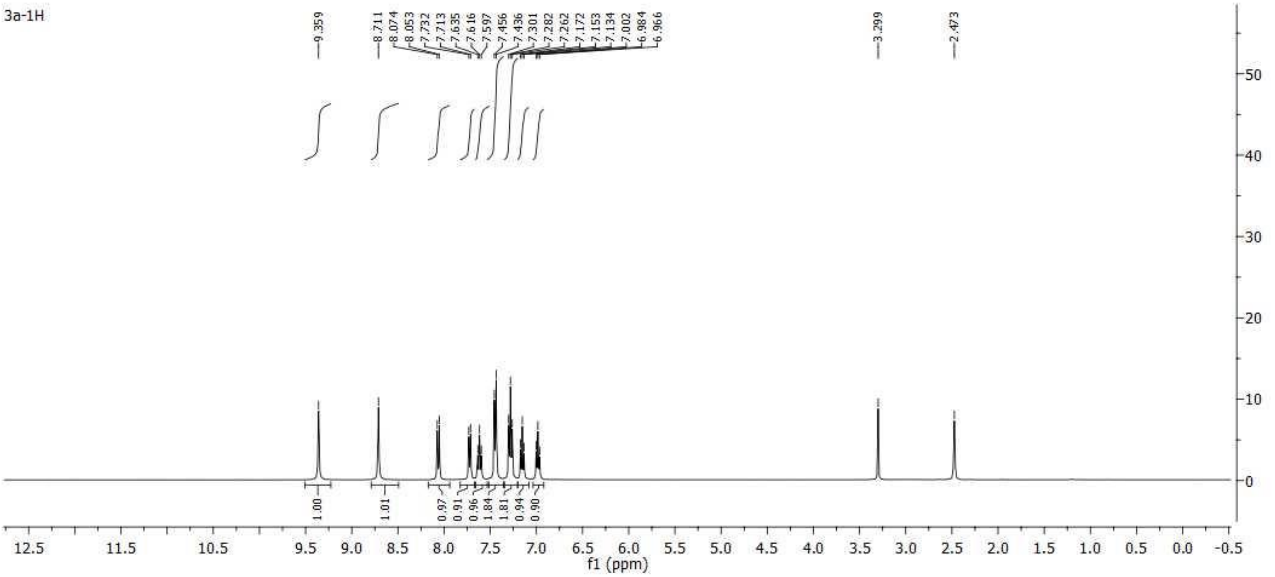


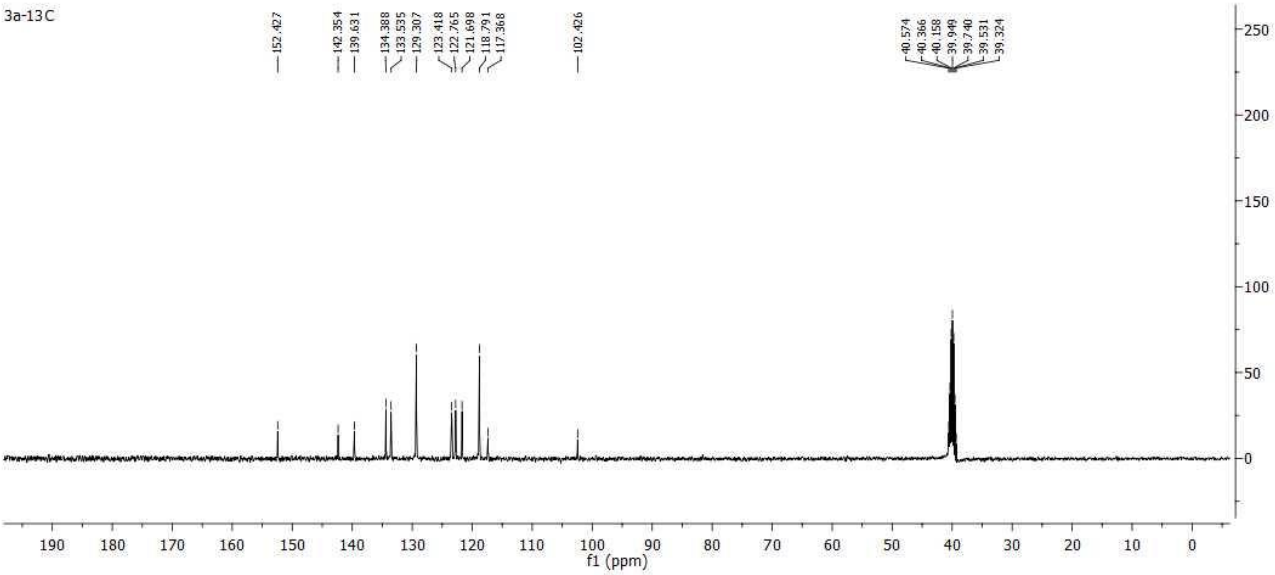
Yield: 81 %; MP. 204 °C; White solid; ^{1}H-NMR (400MHz, DMSO-d_6): δ ppm: 8.45 (s, 1H, -NH-), 7.99 (dd, *J*=9.0 Hz, 4.9 Hz, 1H, -NH-), 7.66 (m, 1H, ar), 7.47 (m, 1H, ar), 6.90 (s, 1H, ar), 3.04 (dd, *J*=12.6 Hz, 6.5 Hz, 2H, -CH_2-), 1.44 (dd, *J*=14.3 Hz, 7.1 Hz, 2H, -CH_2-), 0.87 (t, *J*=7.3 Hz, 3H, -CH_3); ^{13}C- NMR (400 MHz, DMSO-d_6): δ ppm: 162.41, 160.02, 159.61, 144.75, 128.25, 126.56, 126.33, 124.01, 123.76, 121.02, 107.38, 46.05, 27.78, 16.39; HRMS: m/z calculated for [$C_{11}H_{12}FN_3O$ + H^+] = 222.1042: found = 222.1047.

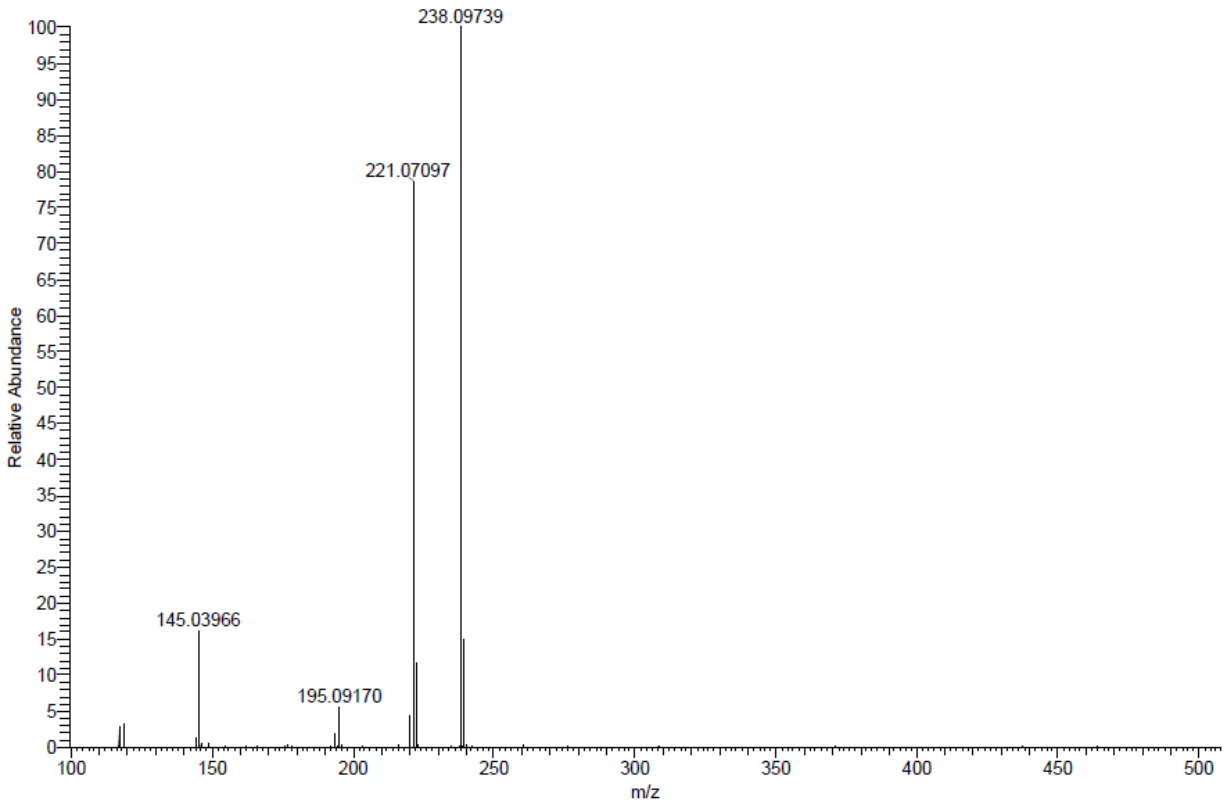
4. ^{1}H-NMR, ^{13}C-NMR and HRMS Spectra:

1-(2-cyanophenyl)-3-phenylurea (3a)





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145.03966
195.09170
Relative Abundance
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55
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45
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35
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15
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350
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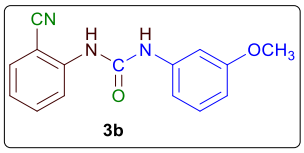
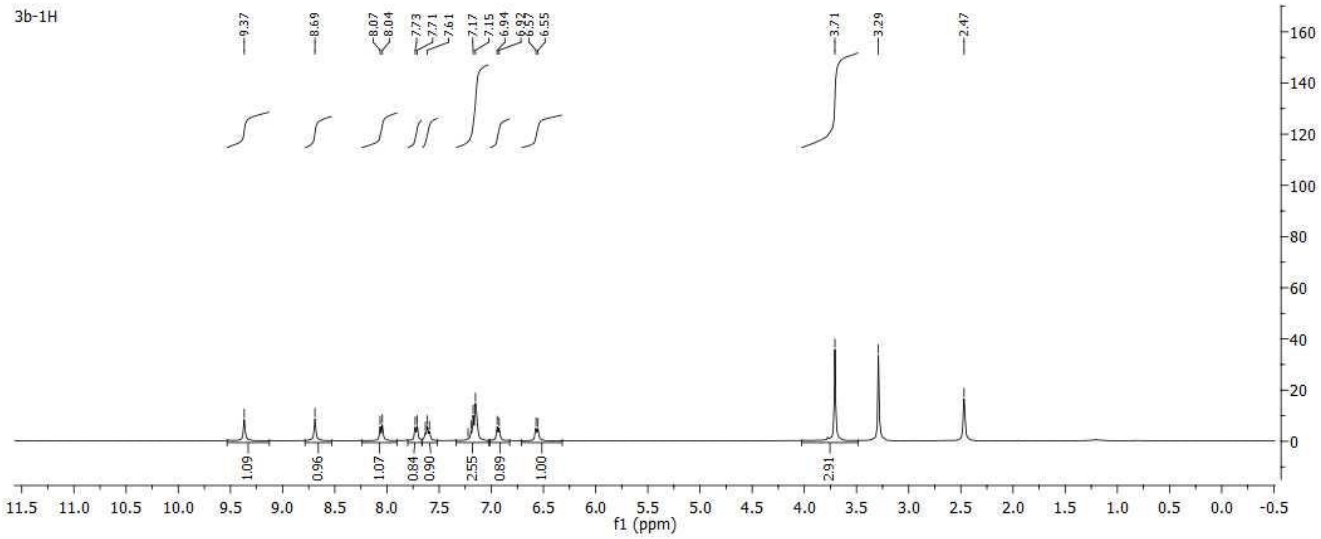
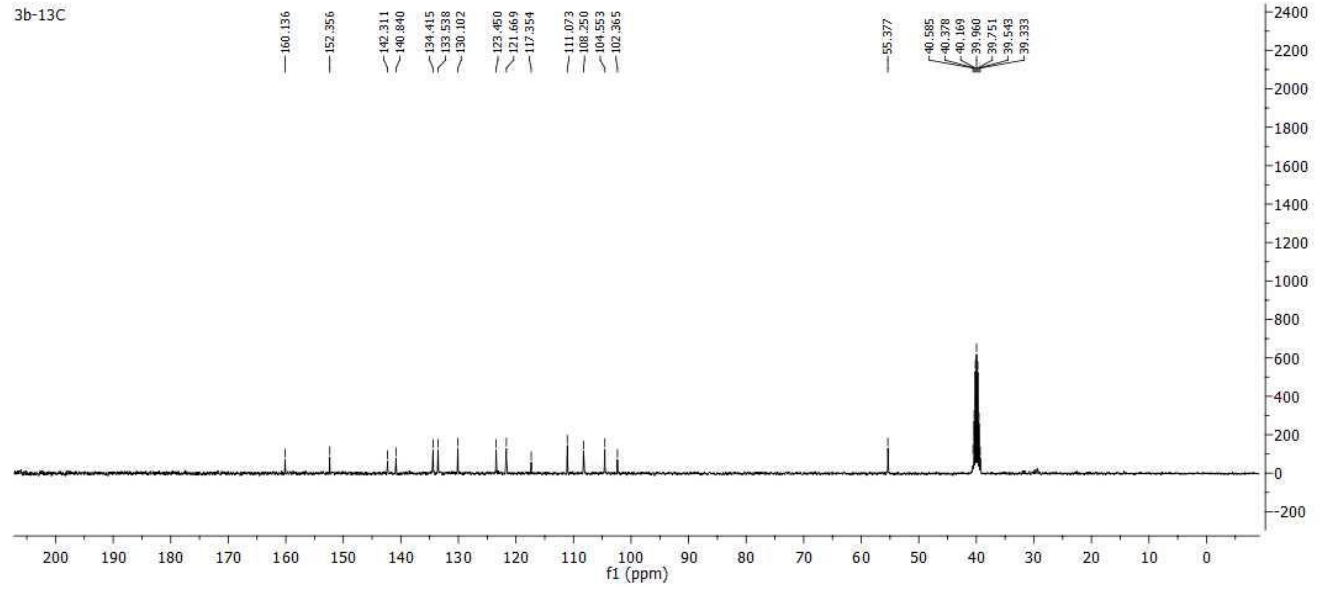
450
500

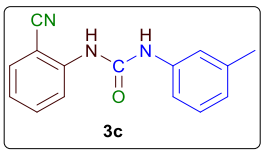
1-(2-cyanophenyl)-3-(3-methoxyphenyl)urea (3b)

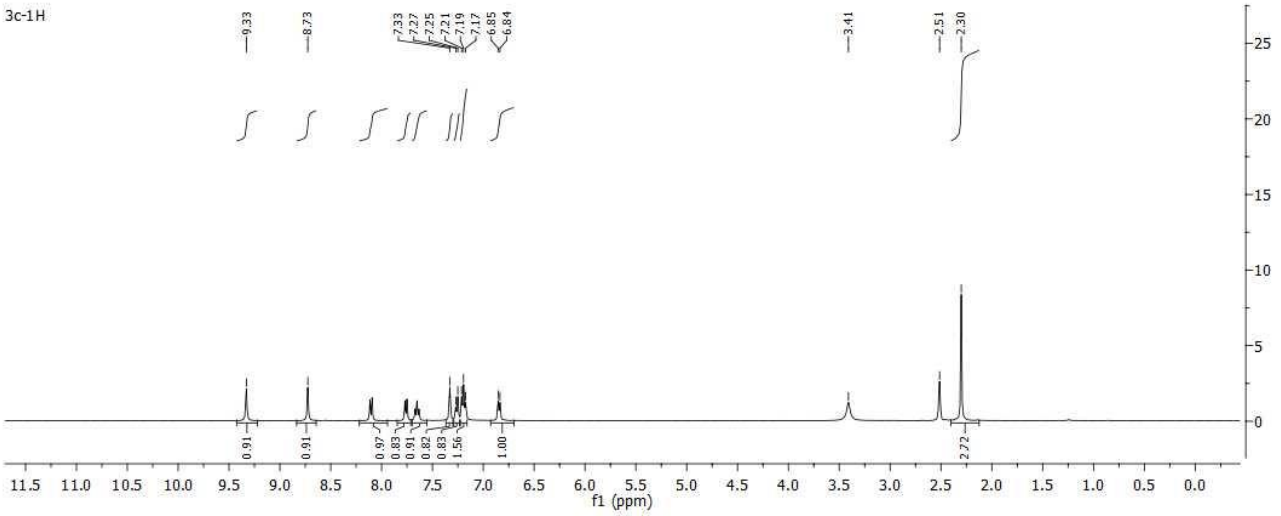


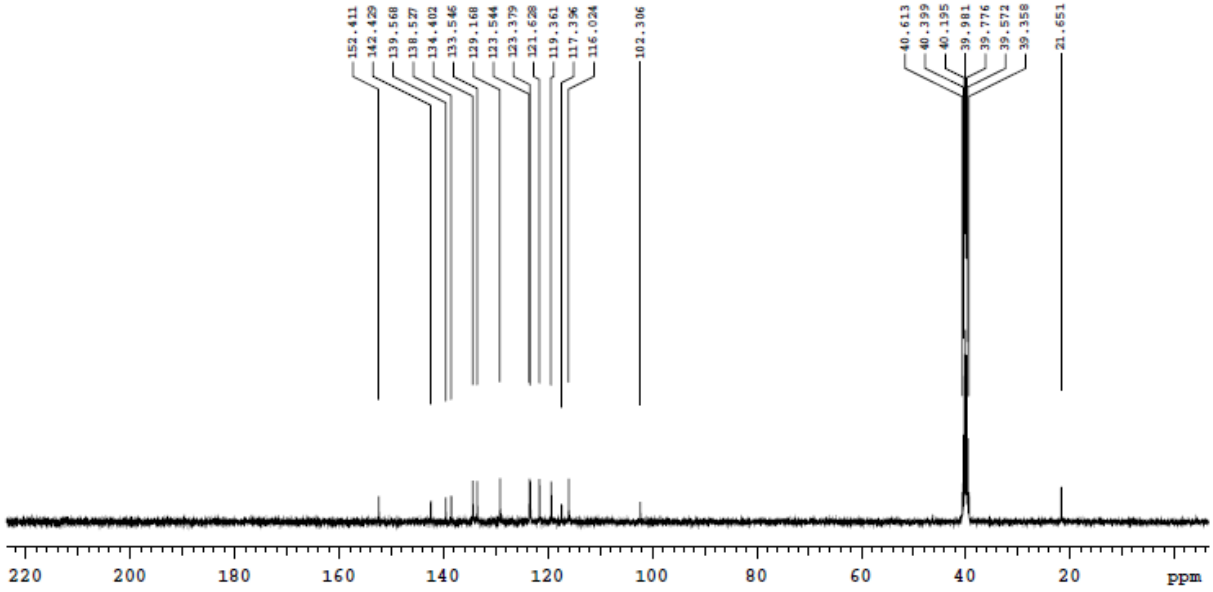


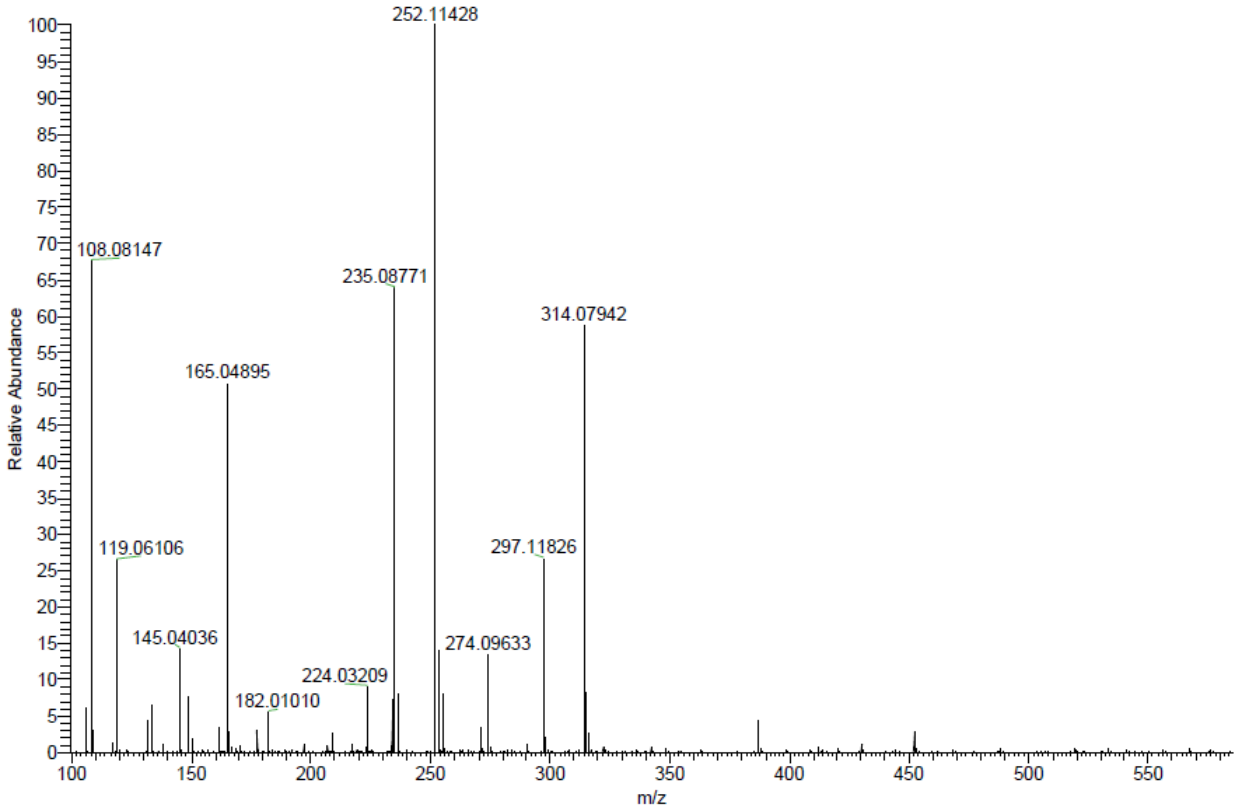


1-(2-cyanophenyl)-3-(m-tolyl)urea (3c)





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297.11826
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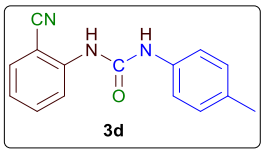
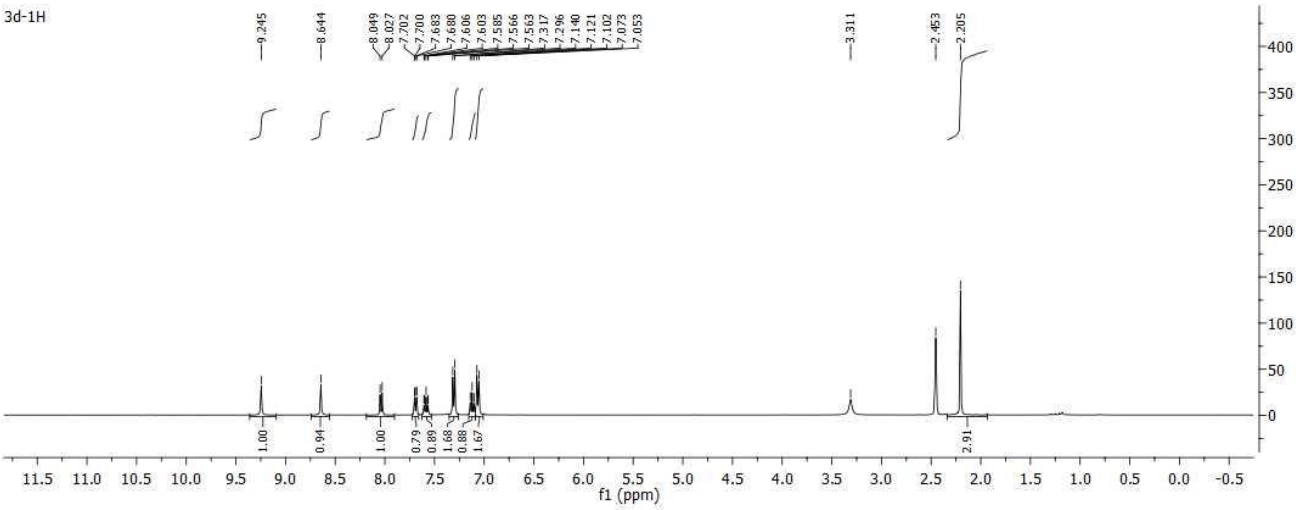
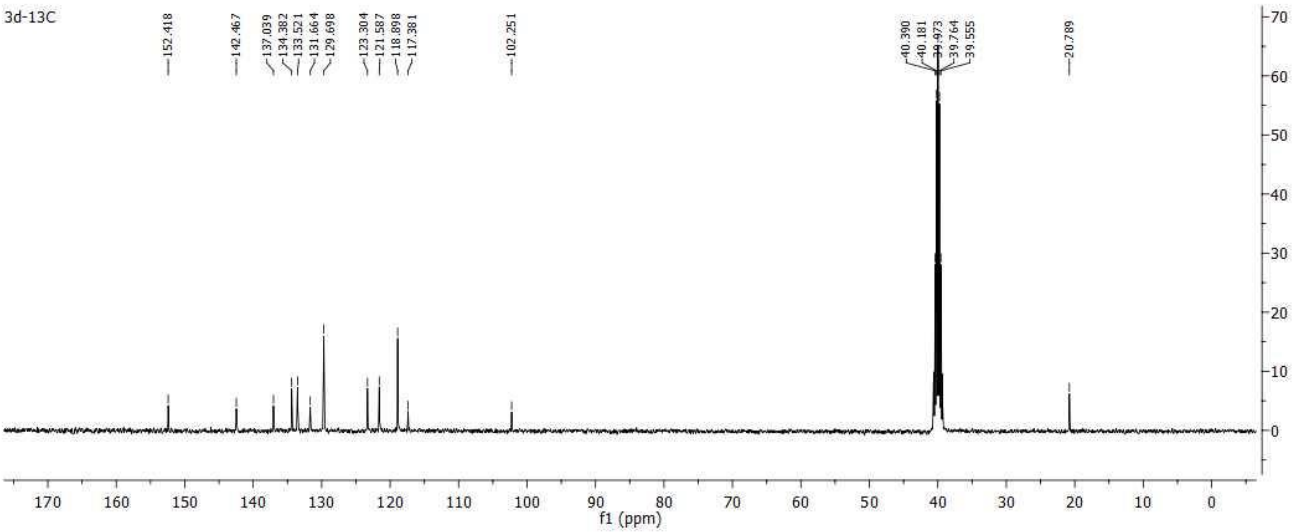
224.03209
182.01010
Relative Abundance
m/z

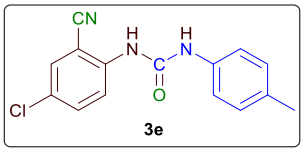
1-(2-cyanophenyl)-3-(p-tolyl)urea (3d)

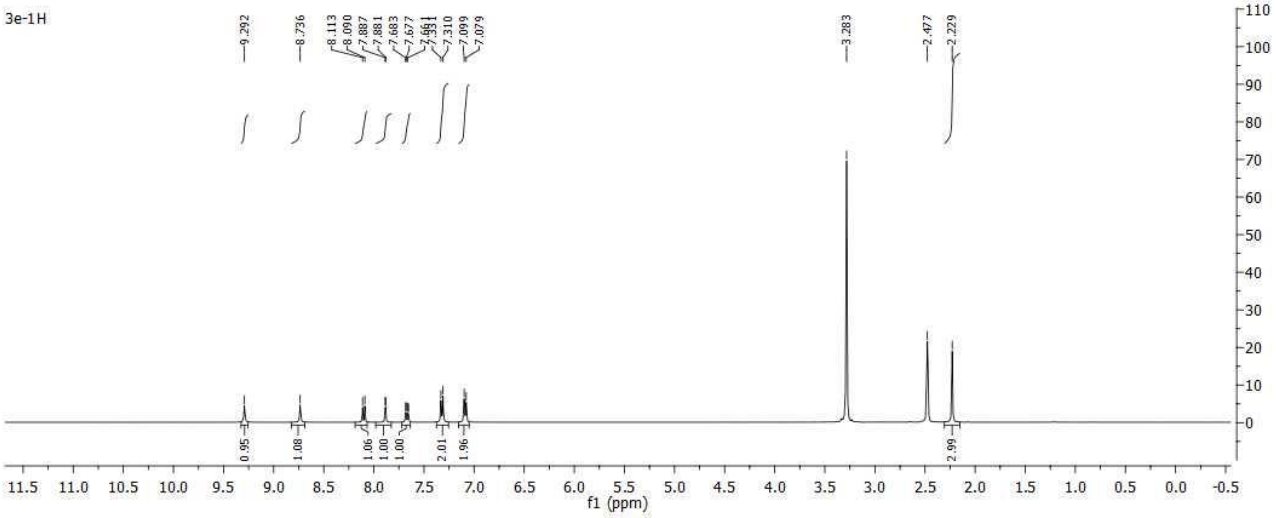


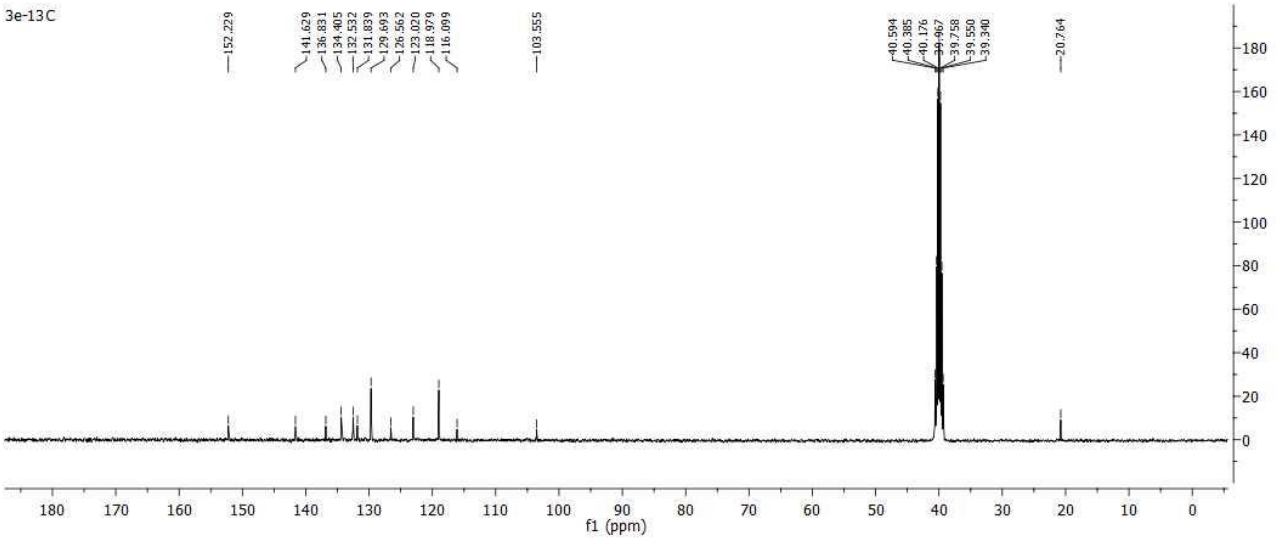




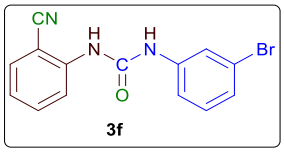
1-(4-chloro-2-cyanophenyl)-3-(p-tolyl)urea (3e)

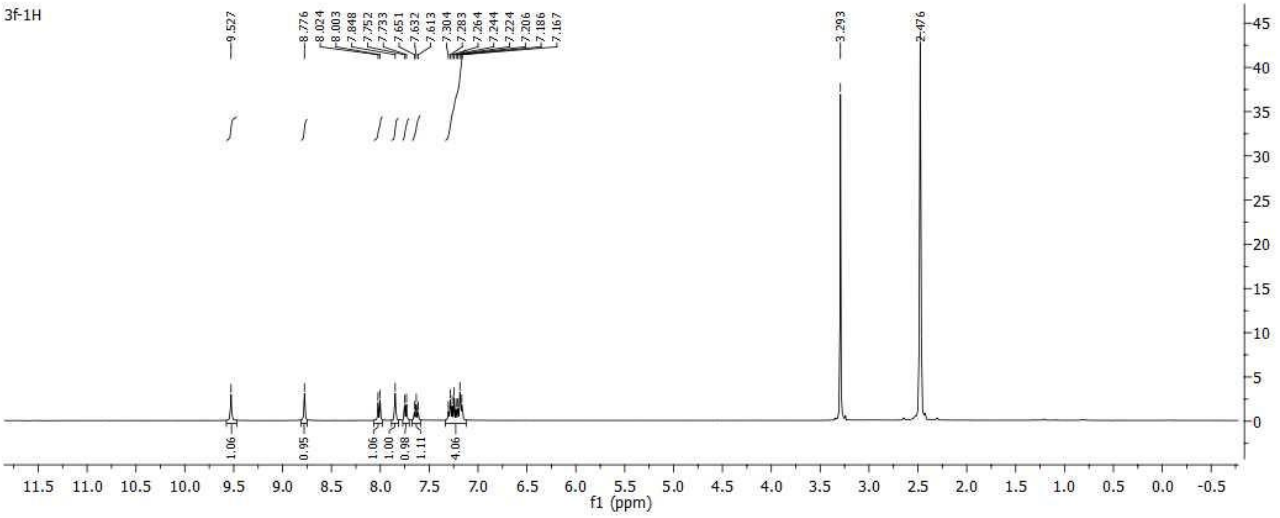


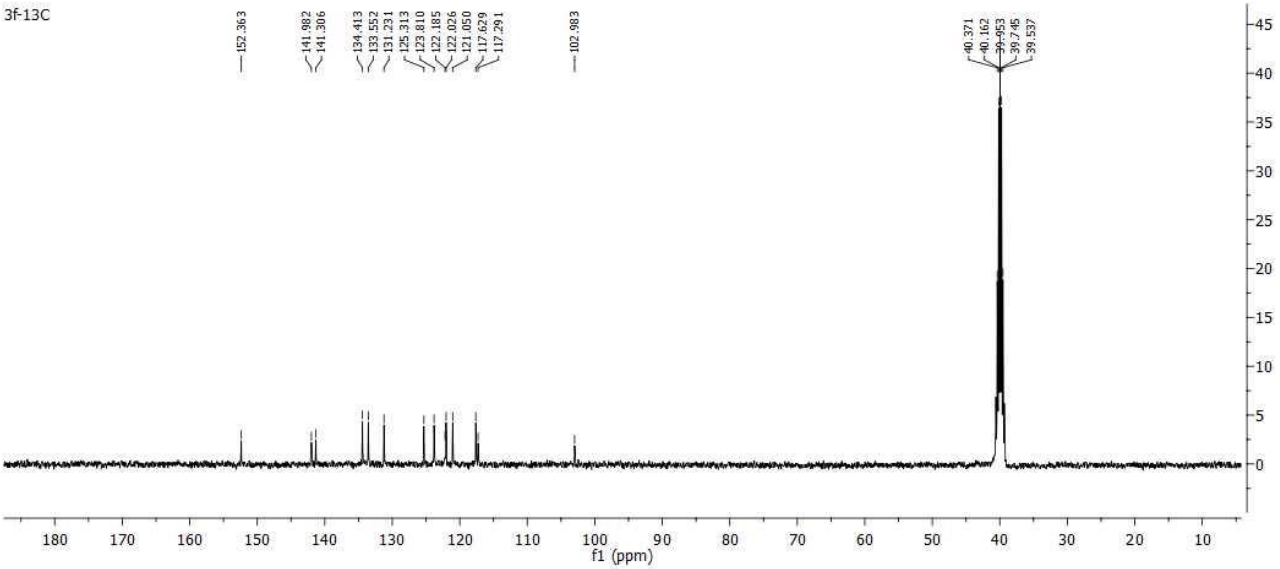




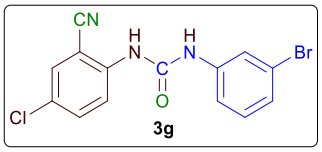
1-(3-bromophenyl)-3-(2-cyanophenyl)urea (3f)

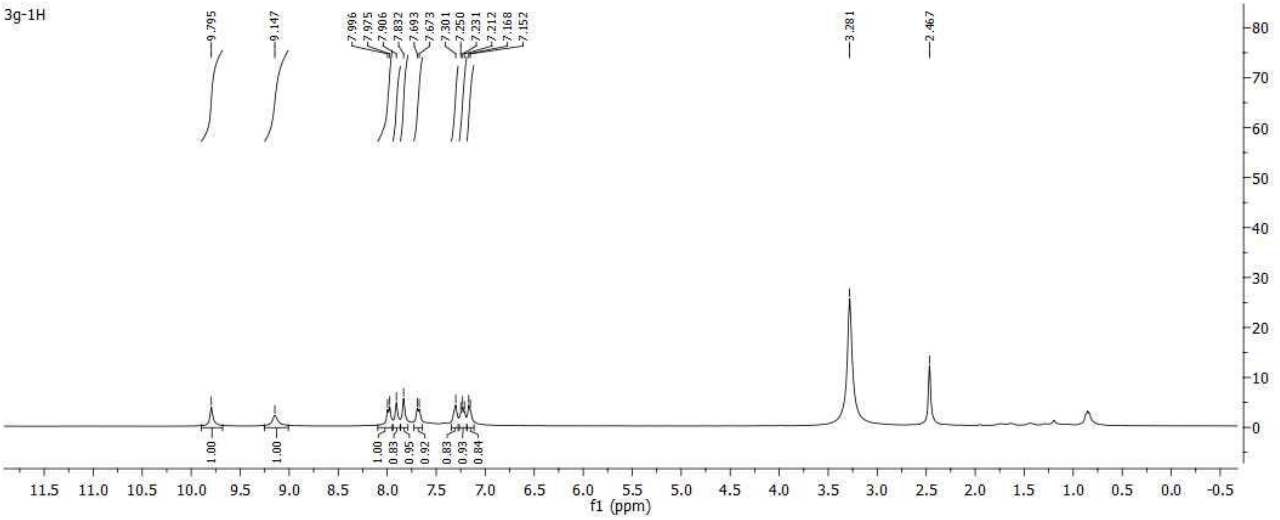


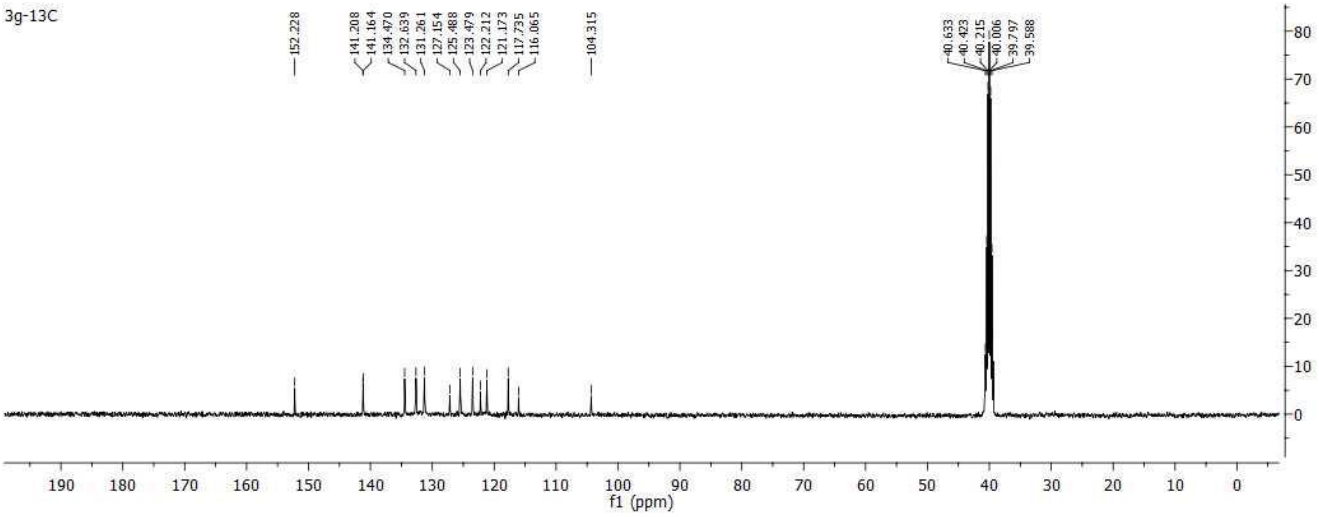


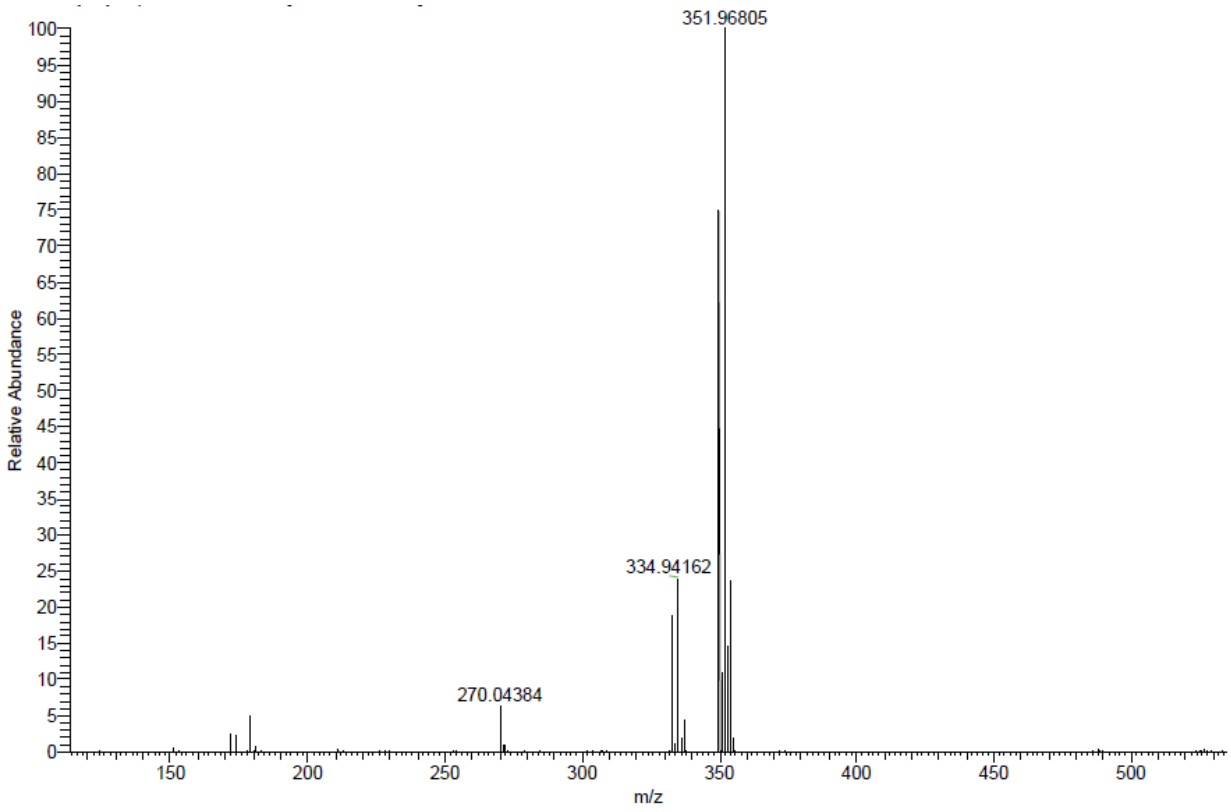


1-(3-bromophenyl)-3-(4-chloro-2-cyanophenyl)urea (3g)








351.96805
334.94162
270.04384
Relative Abundance
m/z
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55
50
45
40
35
30
25
20
15
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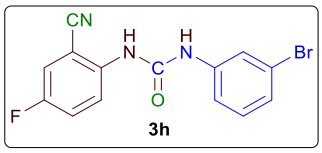
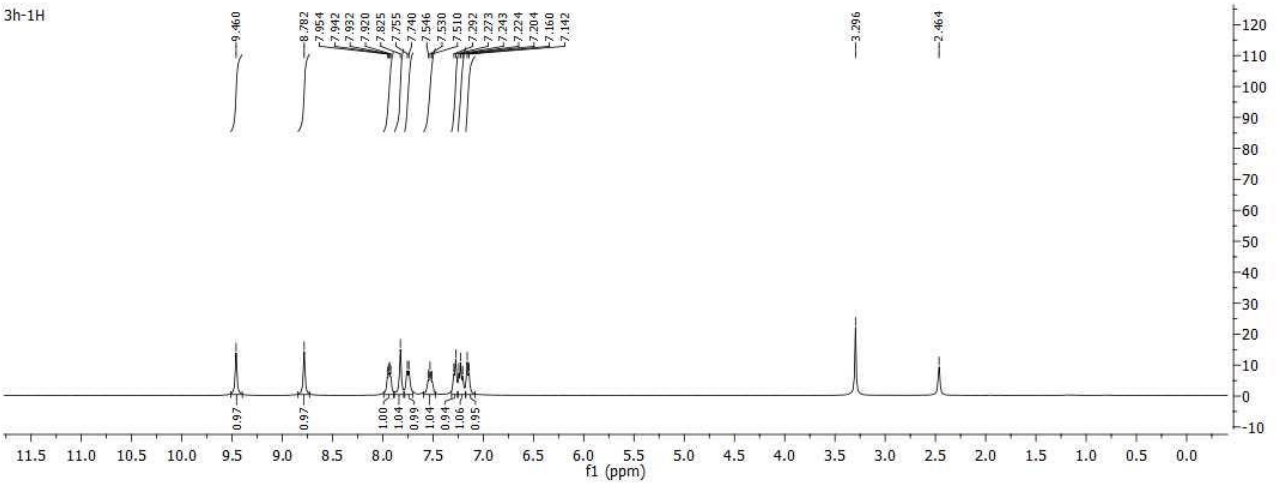
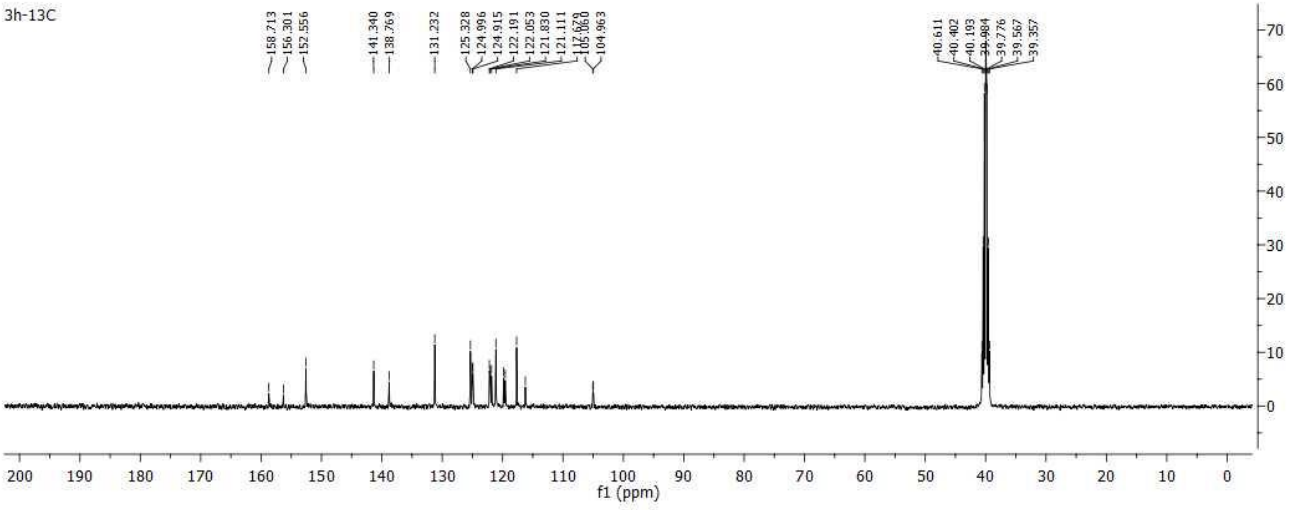
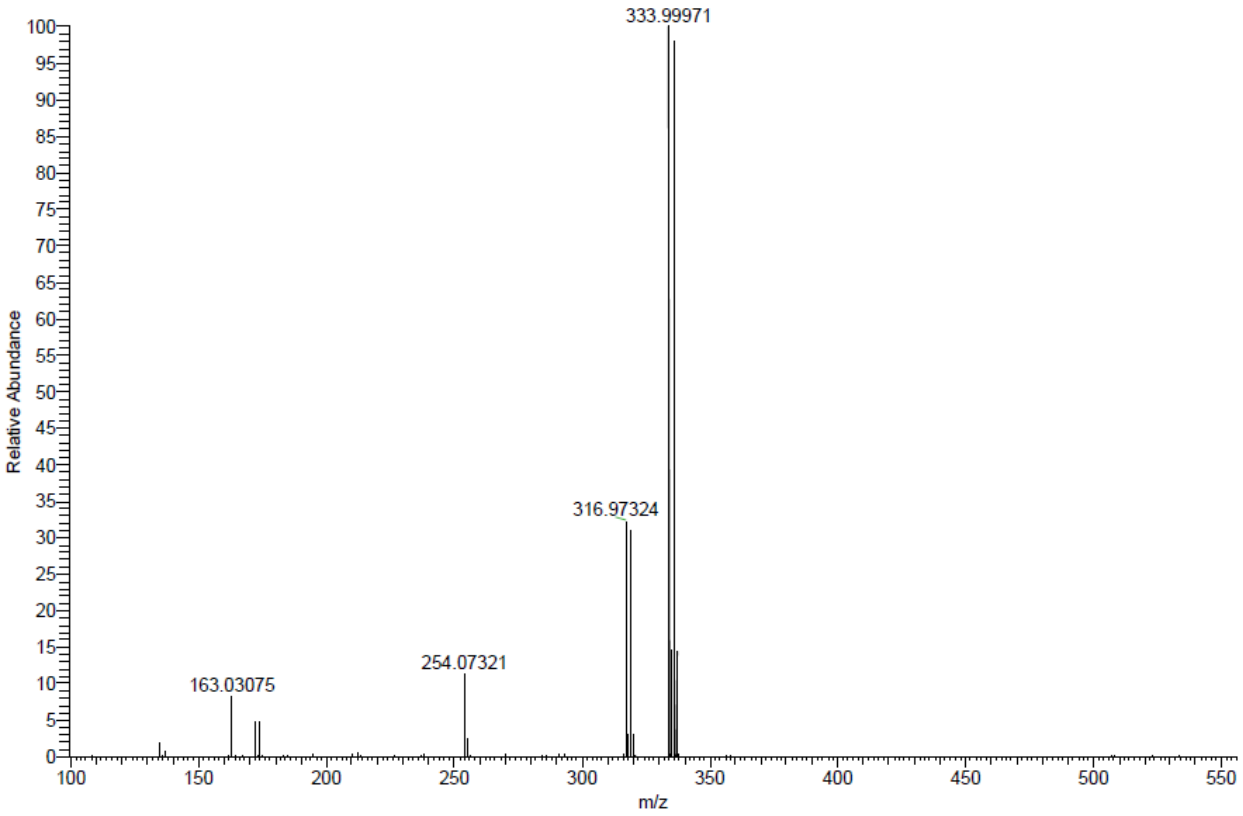
300
350
400
450
500

1-(3-bromophenyl)-3-(2-cyano-4-fluorophenyl)urea (3h)








333.99971
316.97324
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163.03075
Relative Abundance
m/z
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50
45
40
35
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25
20
15
10
5
0
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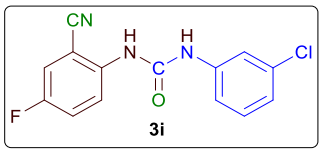
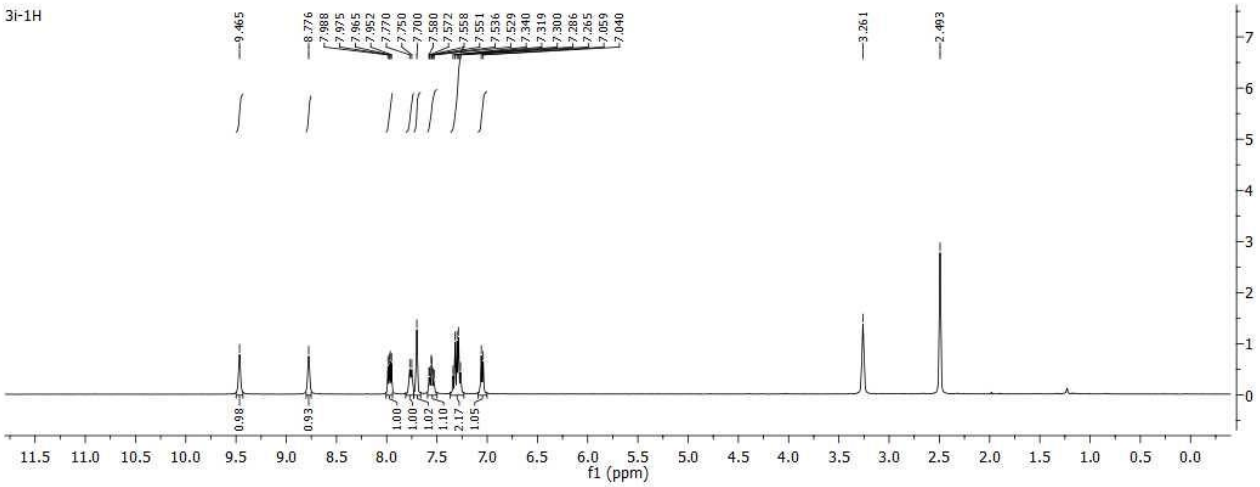
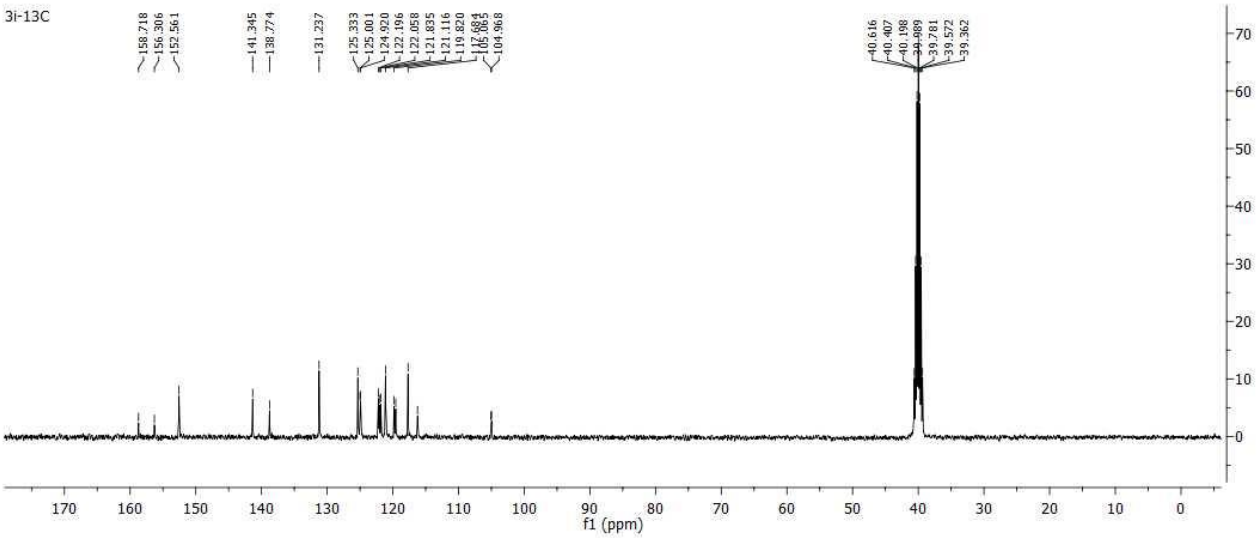
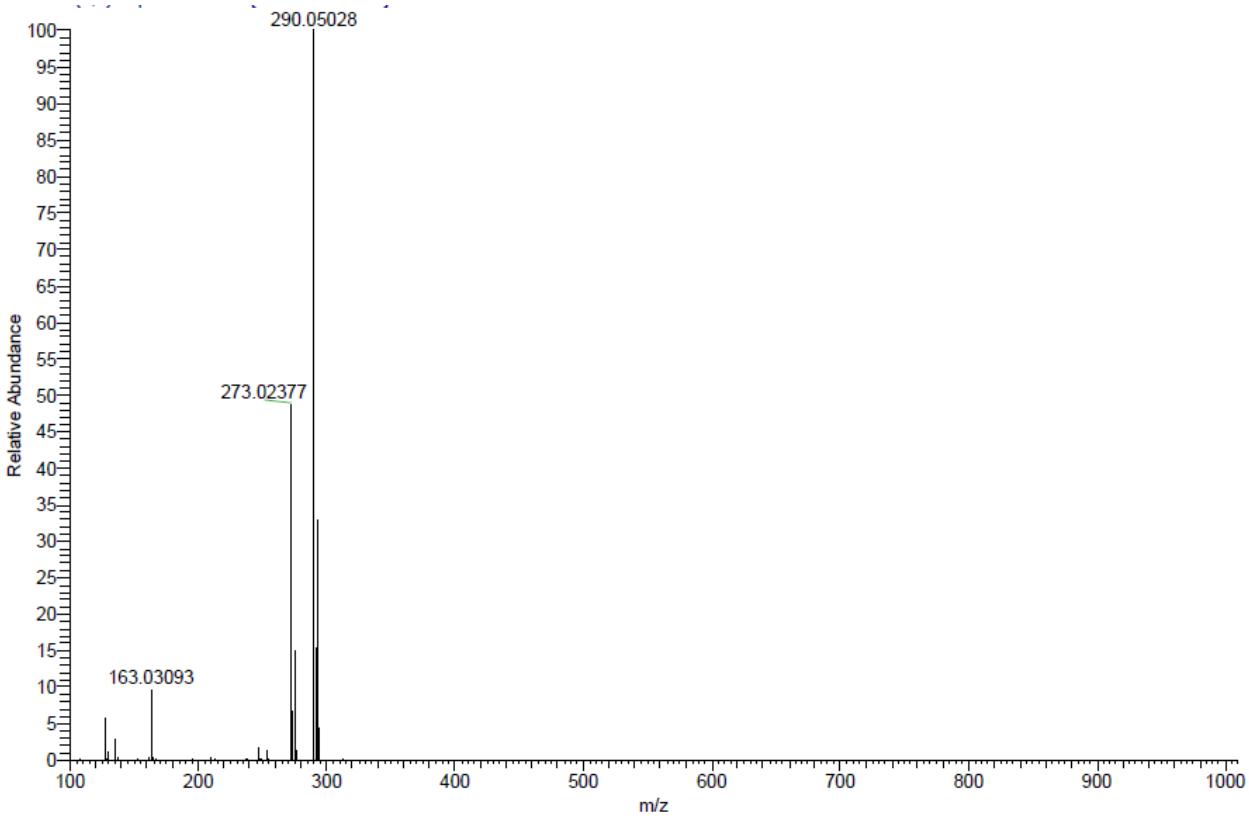
300
350
400
450
500
550

1-(3-chlorophenyl)-3-(2-cyano-4-fluorophenyl)urea (3i)








290.05028
273.02377
163.03093
Relative Abundance
m/z
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90
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55
50
45
40
35
30
25
20
15
10
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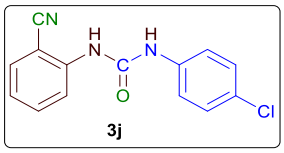
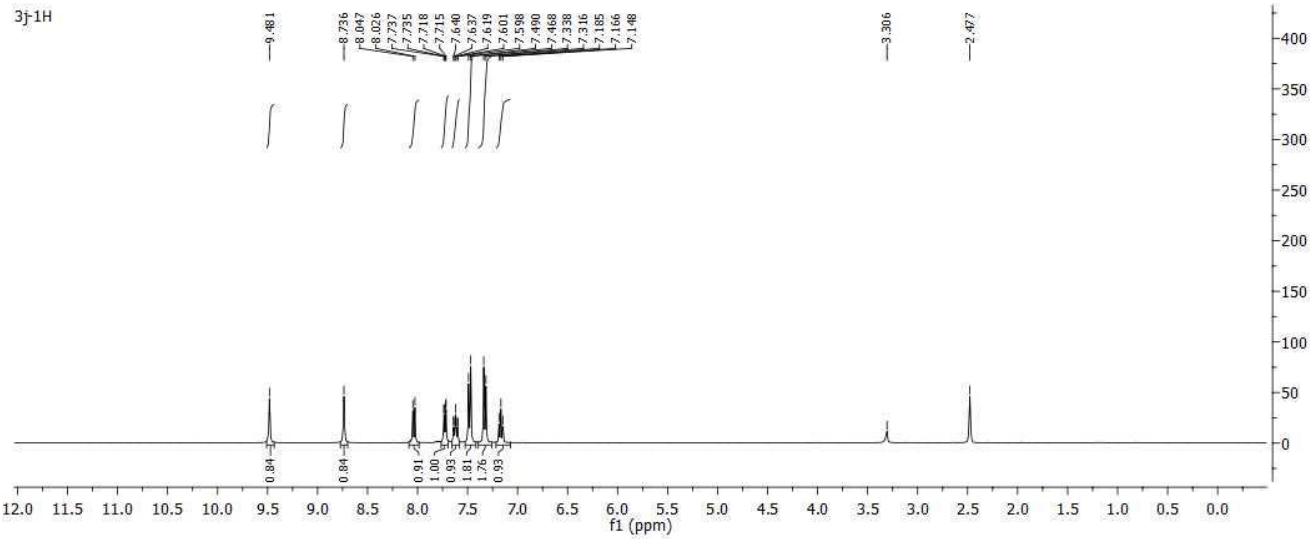
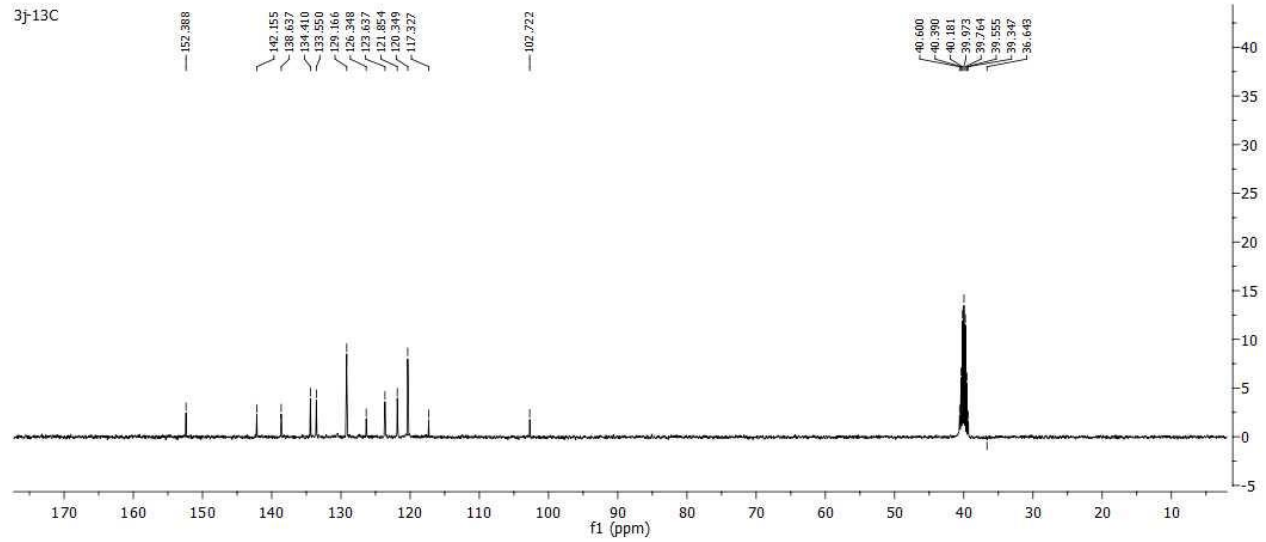
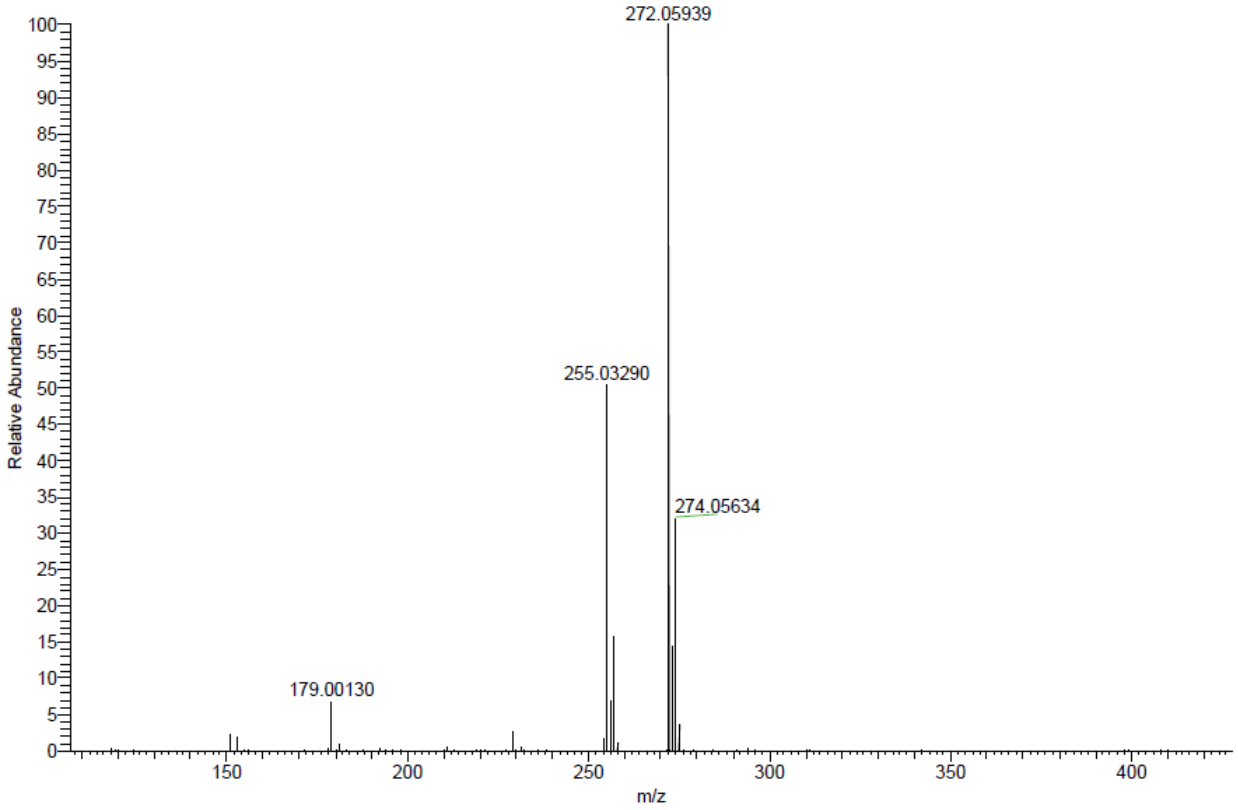
300
400
500
600
700
800
900
1000

1-(4-chlorophenyl)-3-(2-cyanophenyl)urea (3j)








272.05939
255.03290
274.05634
179.00130
Relative Abundance
m/z
100
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85
80
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70
65
60
55
50
45
40
35
30
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150
200
250
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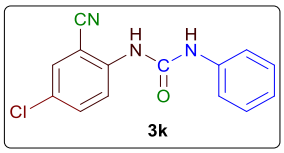
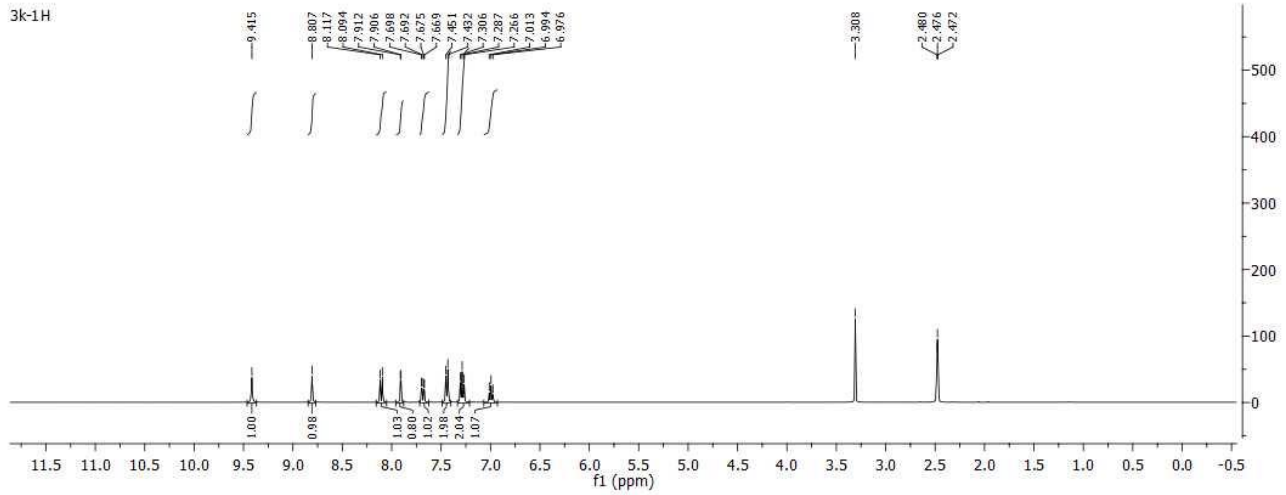
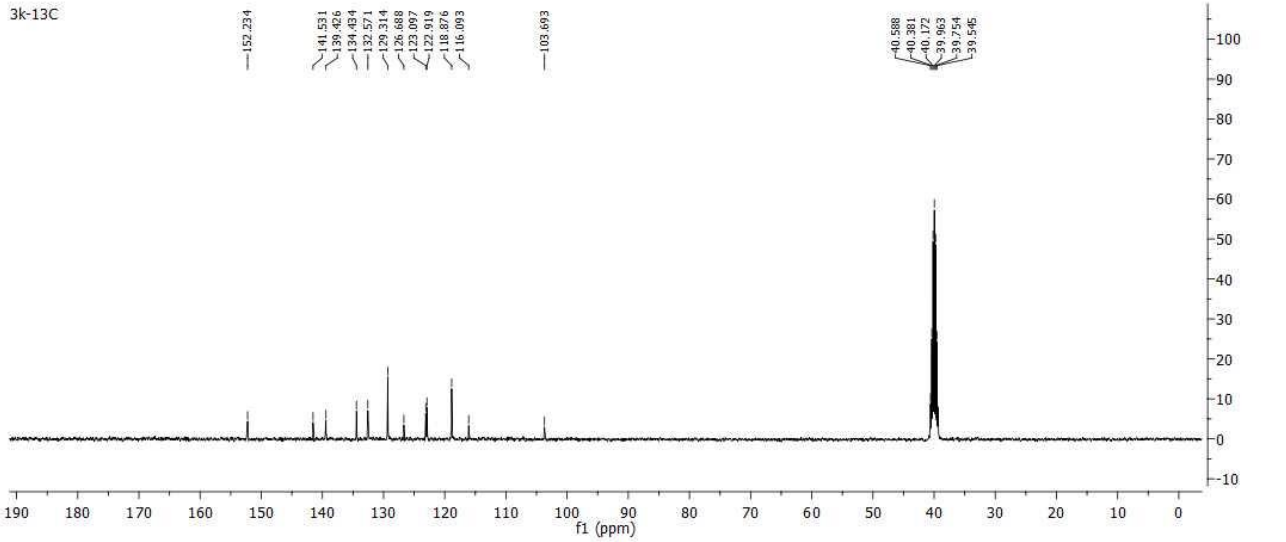
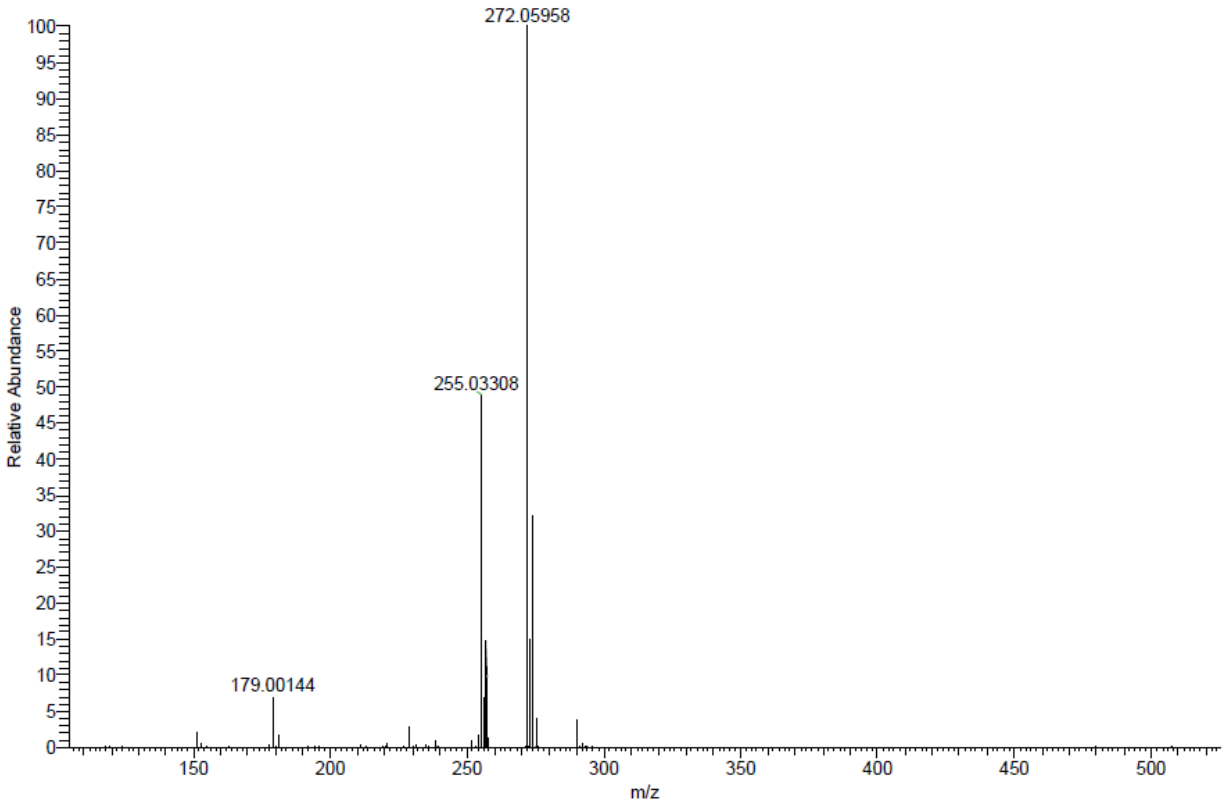
350
400

1-(4-chloro-2-cyanophenyl)-3-phenylurea (3k)








272.05958
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Relative Abundance
m/z
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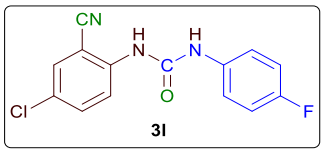
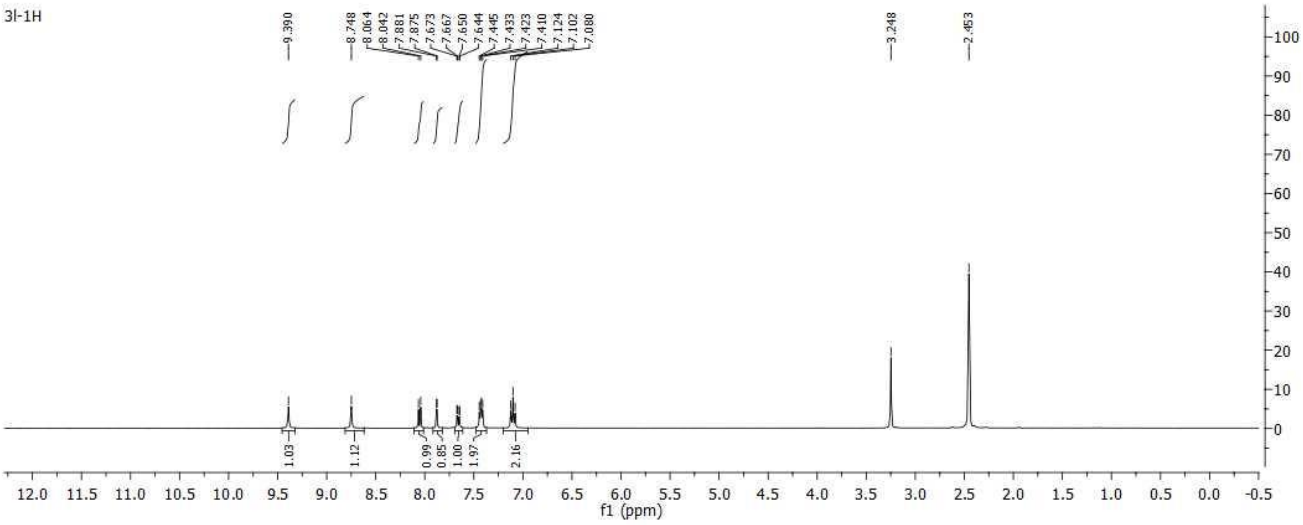
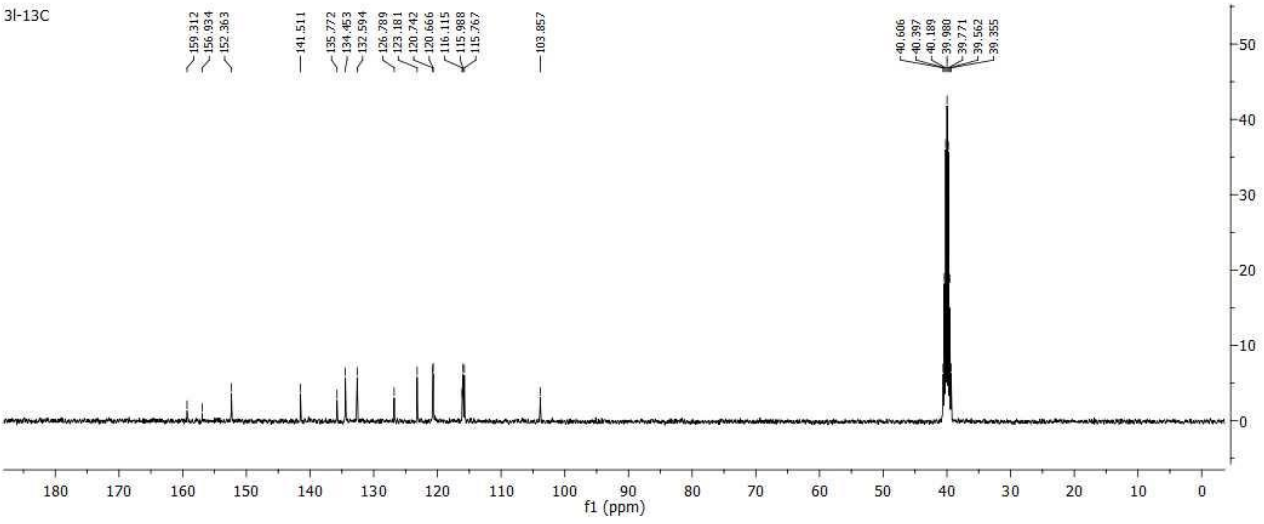
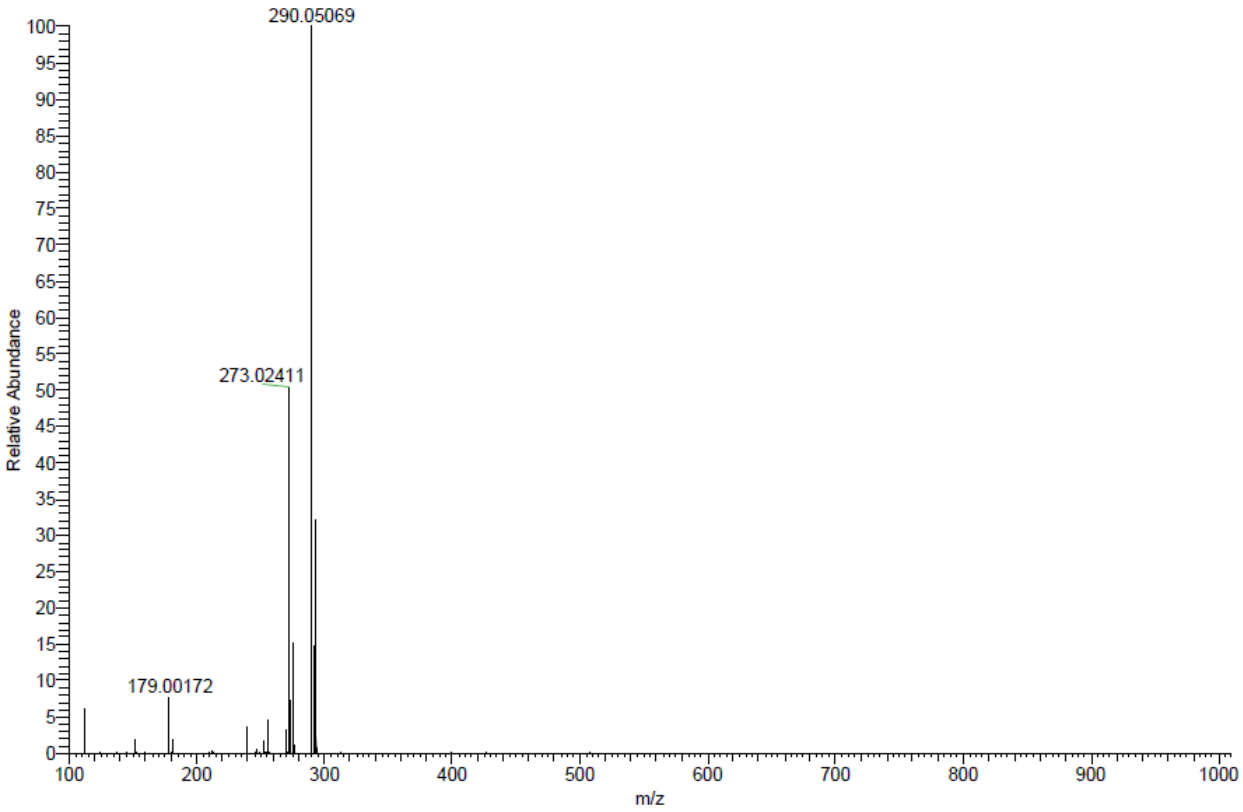
450
500

1-(4-chloro-2-cyanophenyl)-3-(4-fluorophenyl)urea (3l)





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179.00172
Relative Abundance
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50
45
40
35
30
25
20
15
10
5
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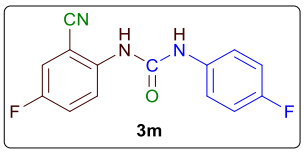
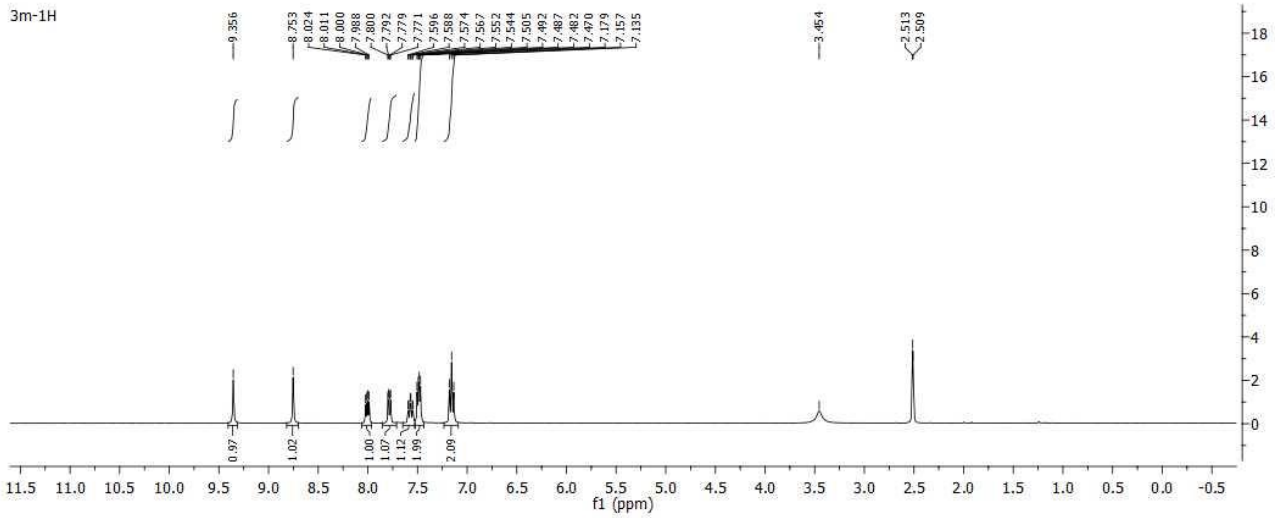
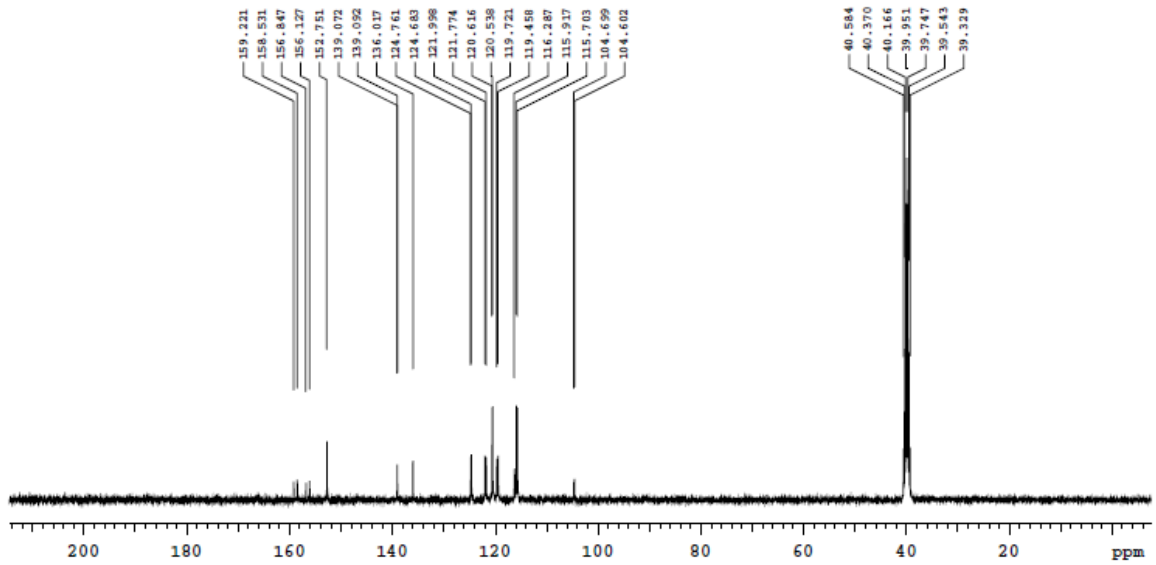
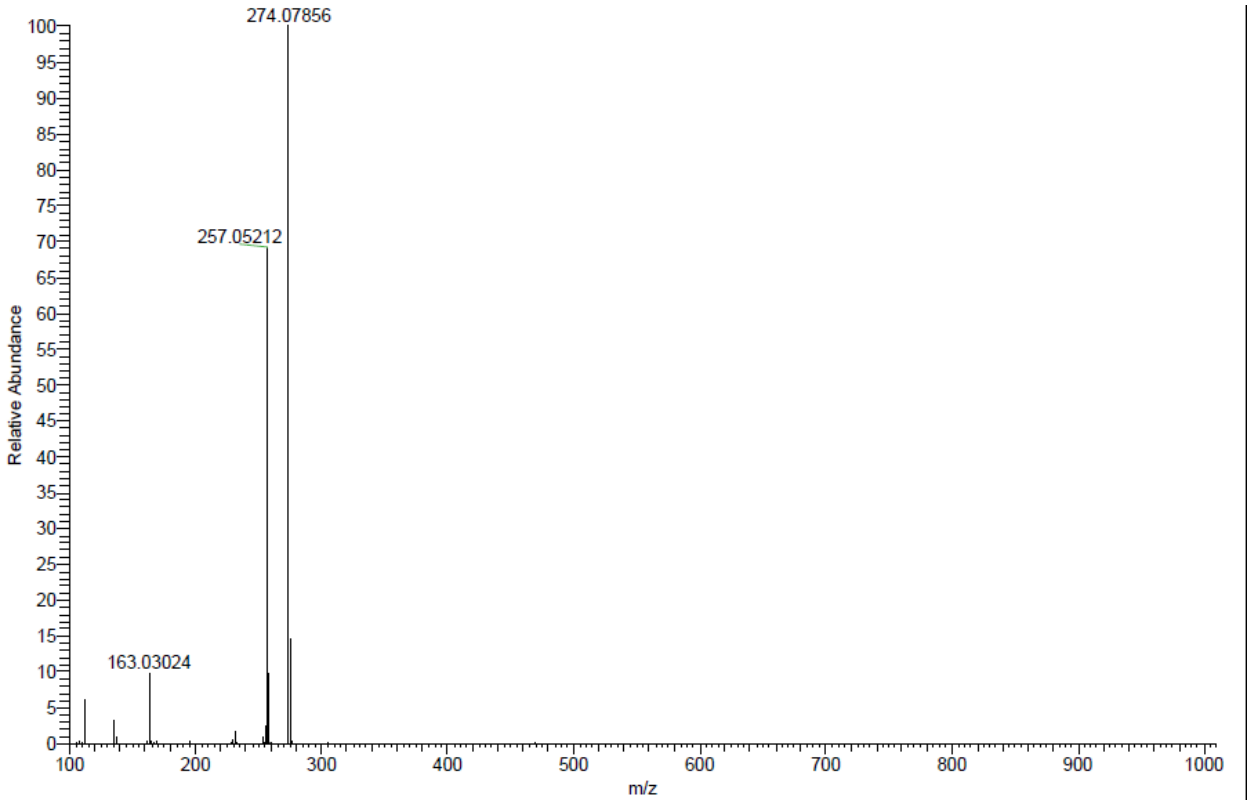
700
800
900
1000

1-(2-cyano-4-fluorophenyl)-3-(4-fluorophenyl)urea (3m)





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Relative Abundance
m/z
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45
40
35
30
25
20
15
10
5
0
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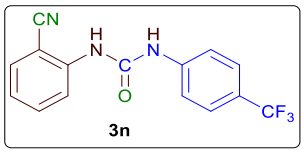
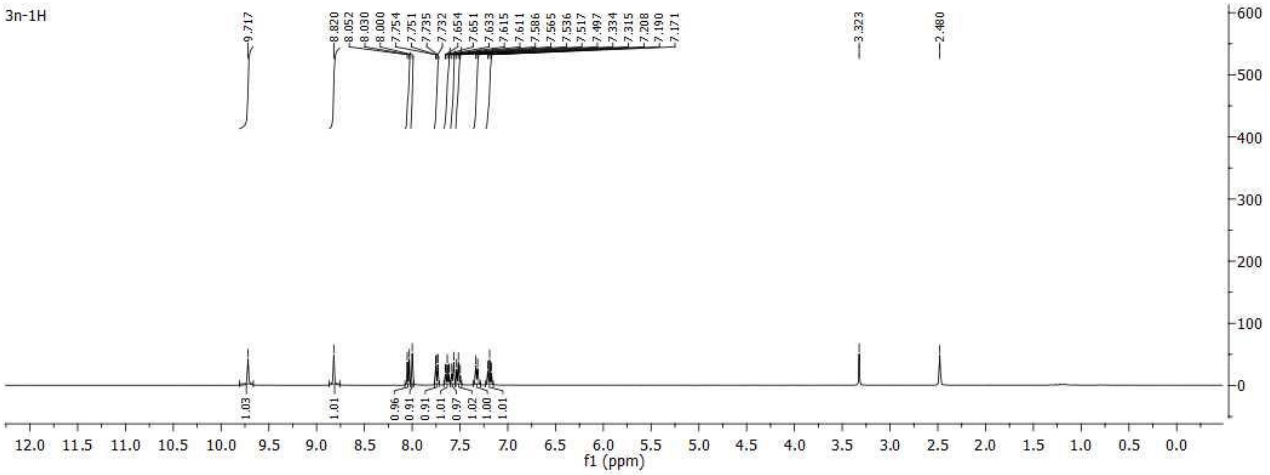
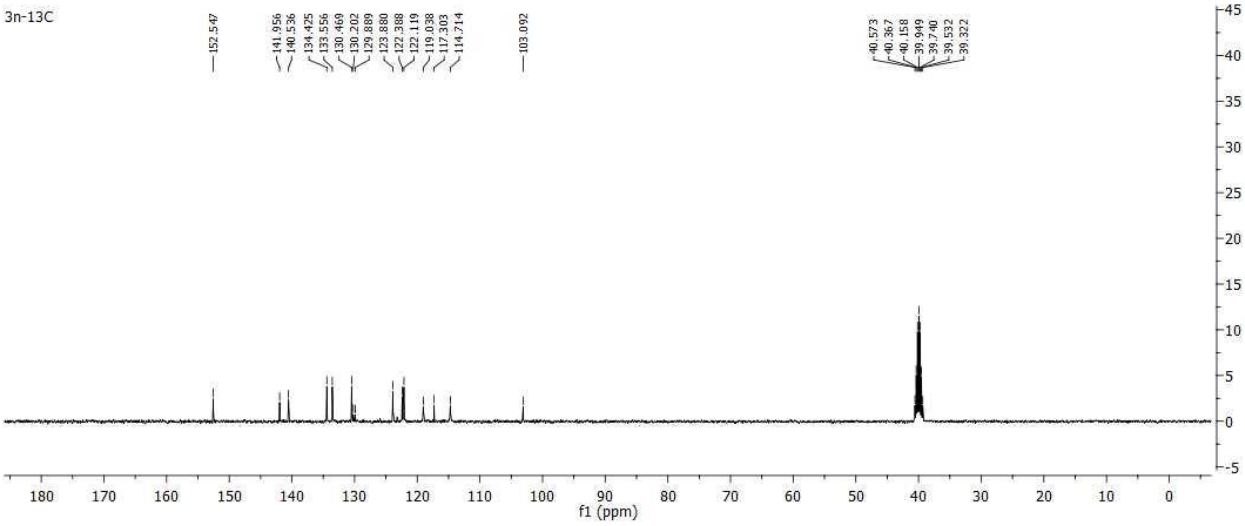
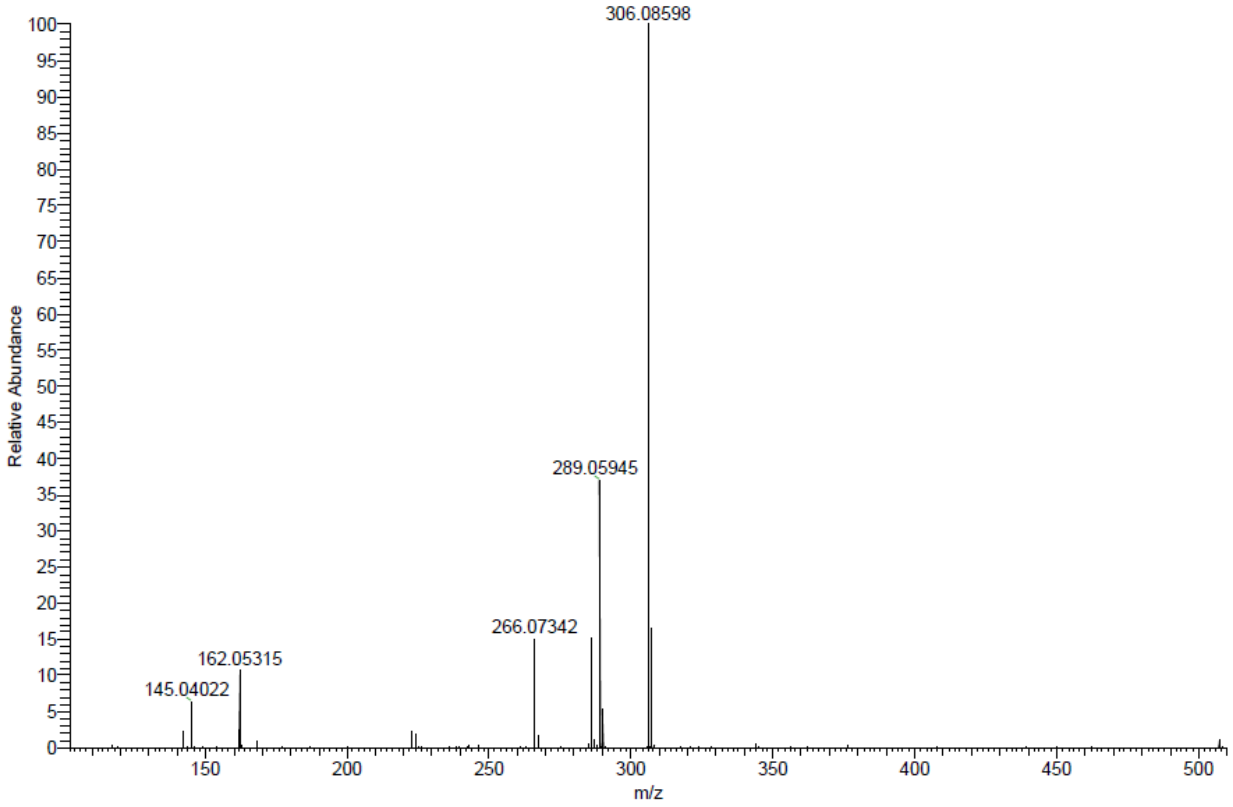
600
700
800
900
1000

1-(2-cyanophenyl)-3-(4-(trifluoromethyl)phenyl)urea (3n)





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266.07342
162.05315
145.04022
Relative Abundance
m/z
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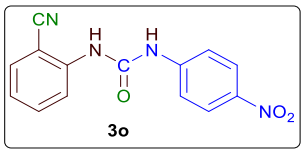
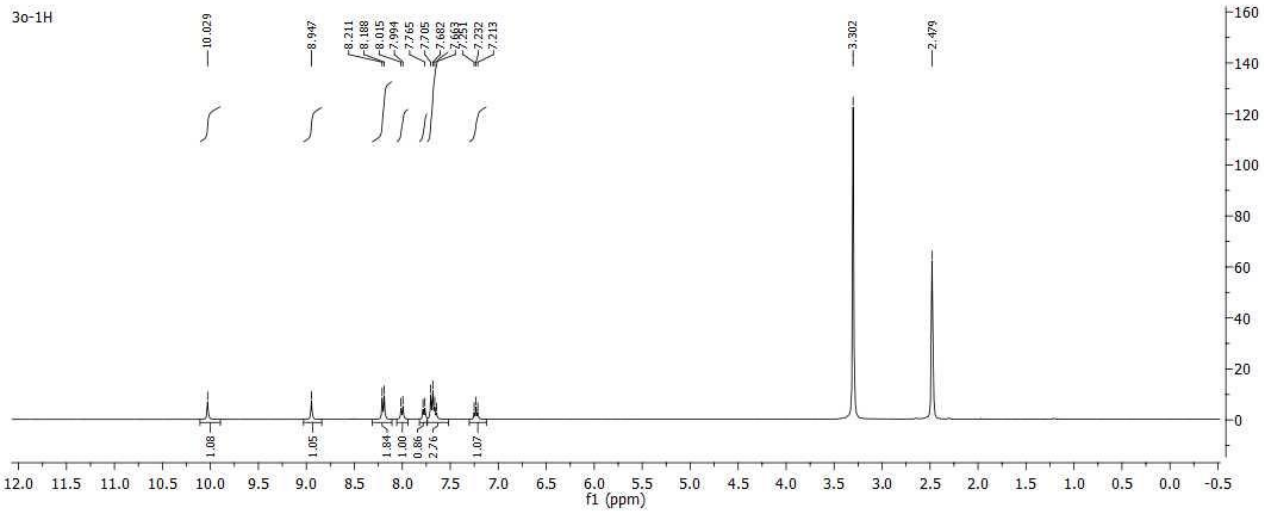
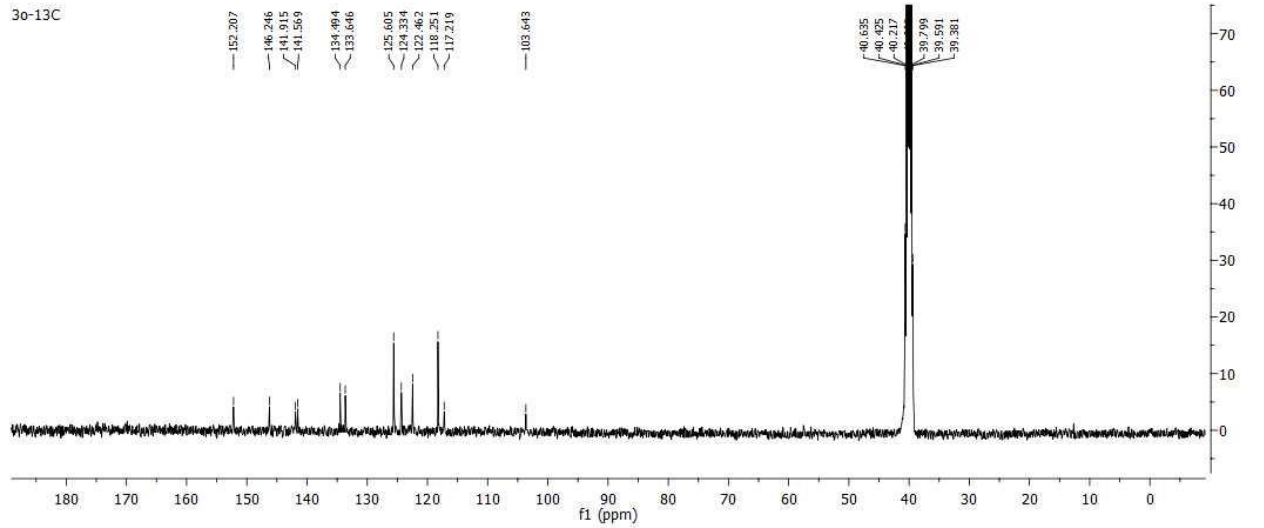
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
150
200
250
300
350
400
450
500

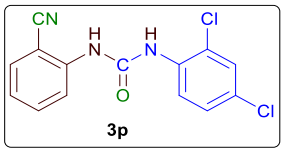
1-(2-cyanophenyl)-3-(4-nitrophenyl)urea (3o)

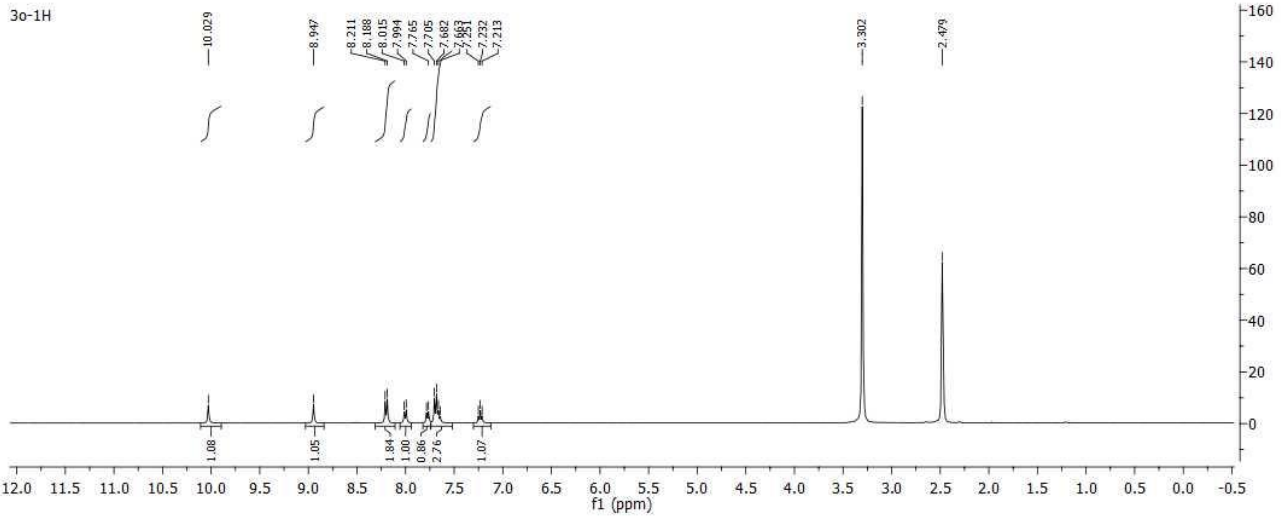


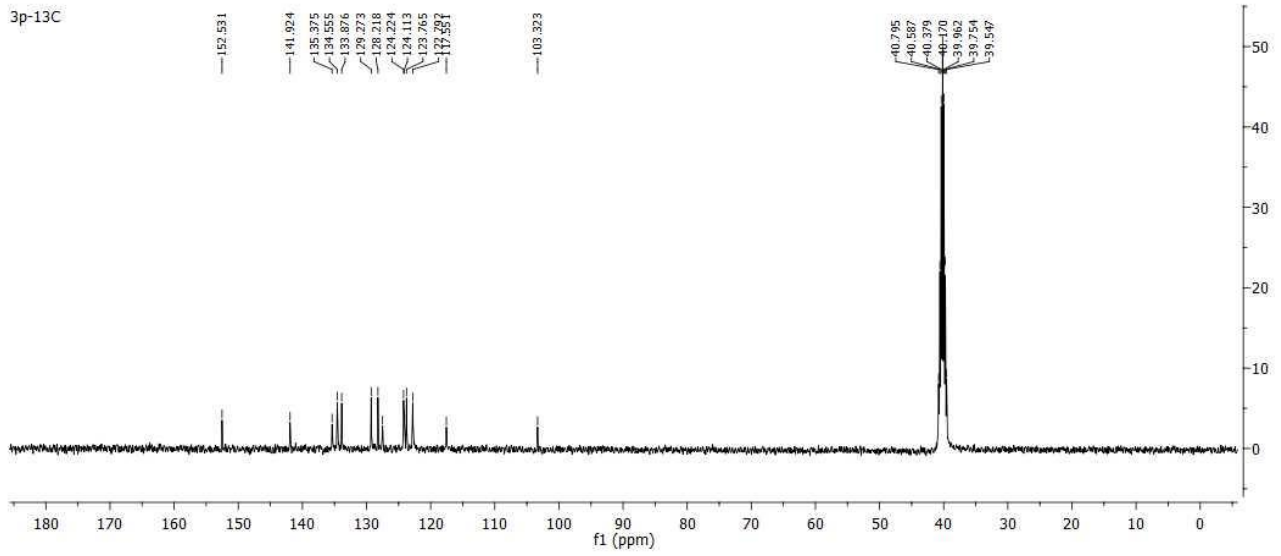


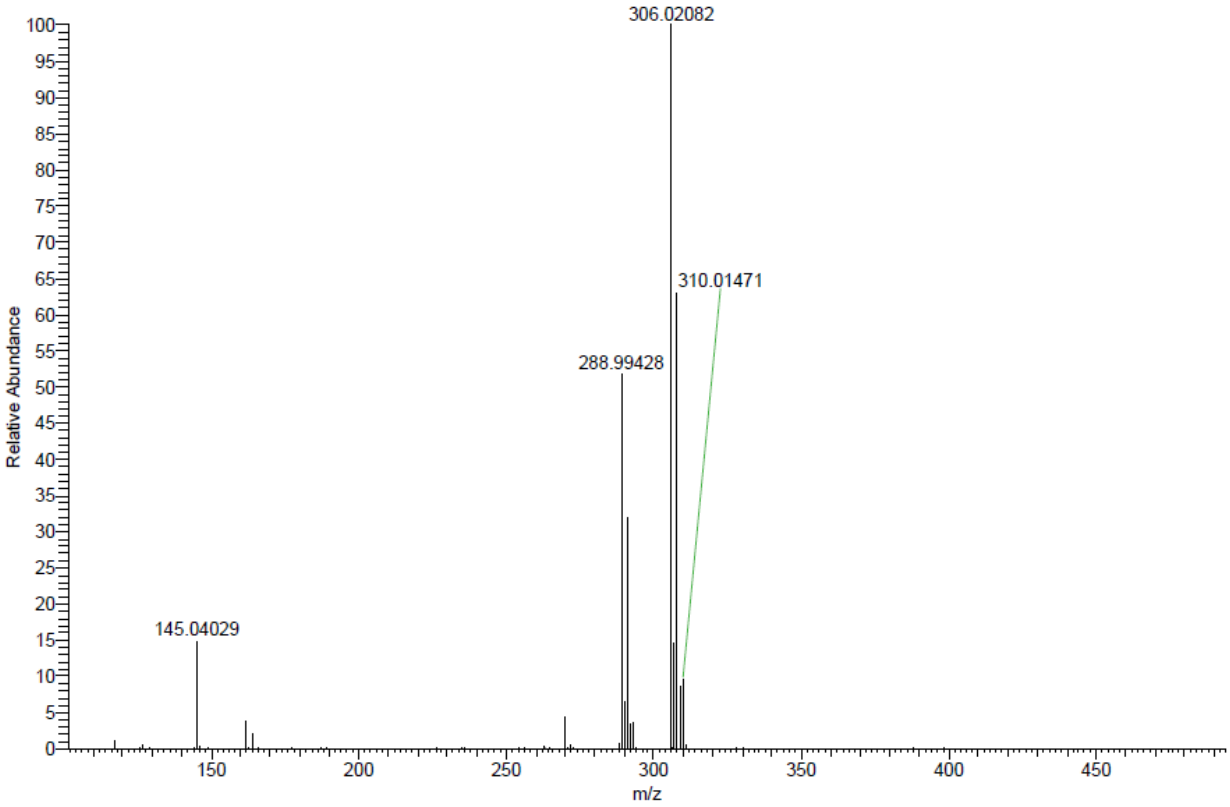


1-(2-cyanophenyl)-3-(2,4-dichlorophenyl)urea (3p)





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Relative Abundance
m/z
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65
60
55
50
45
40
35
30
25
20
15
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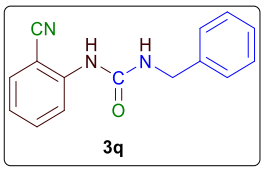
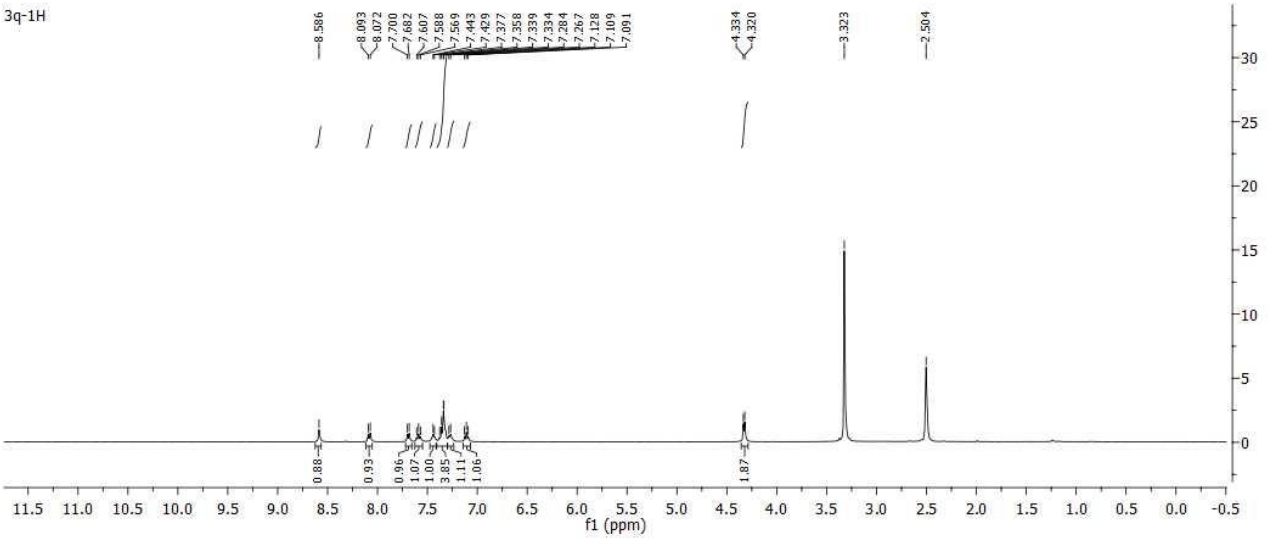
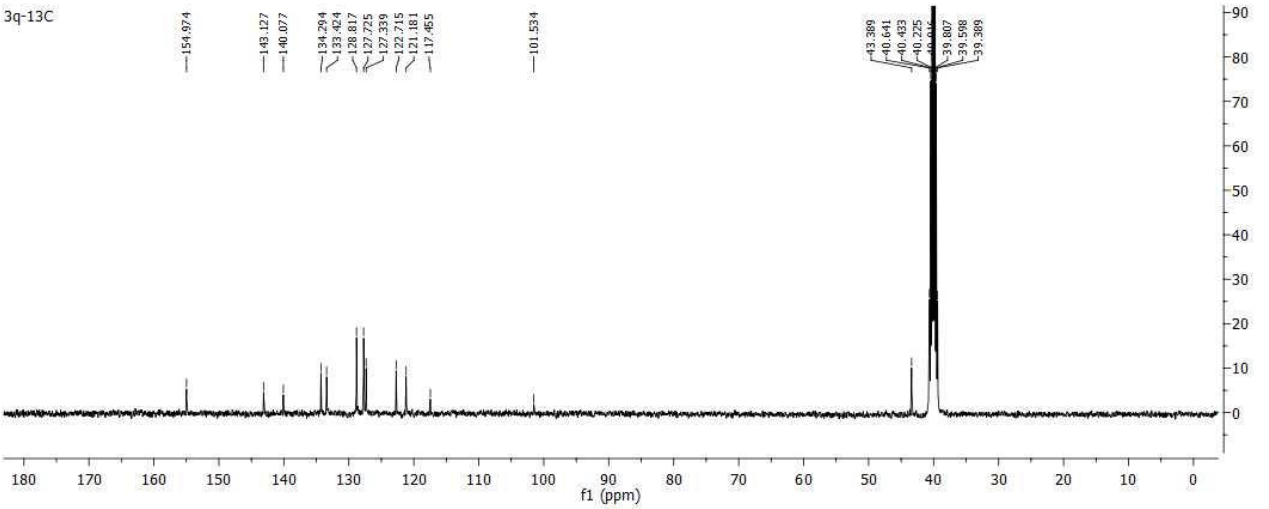
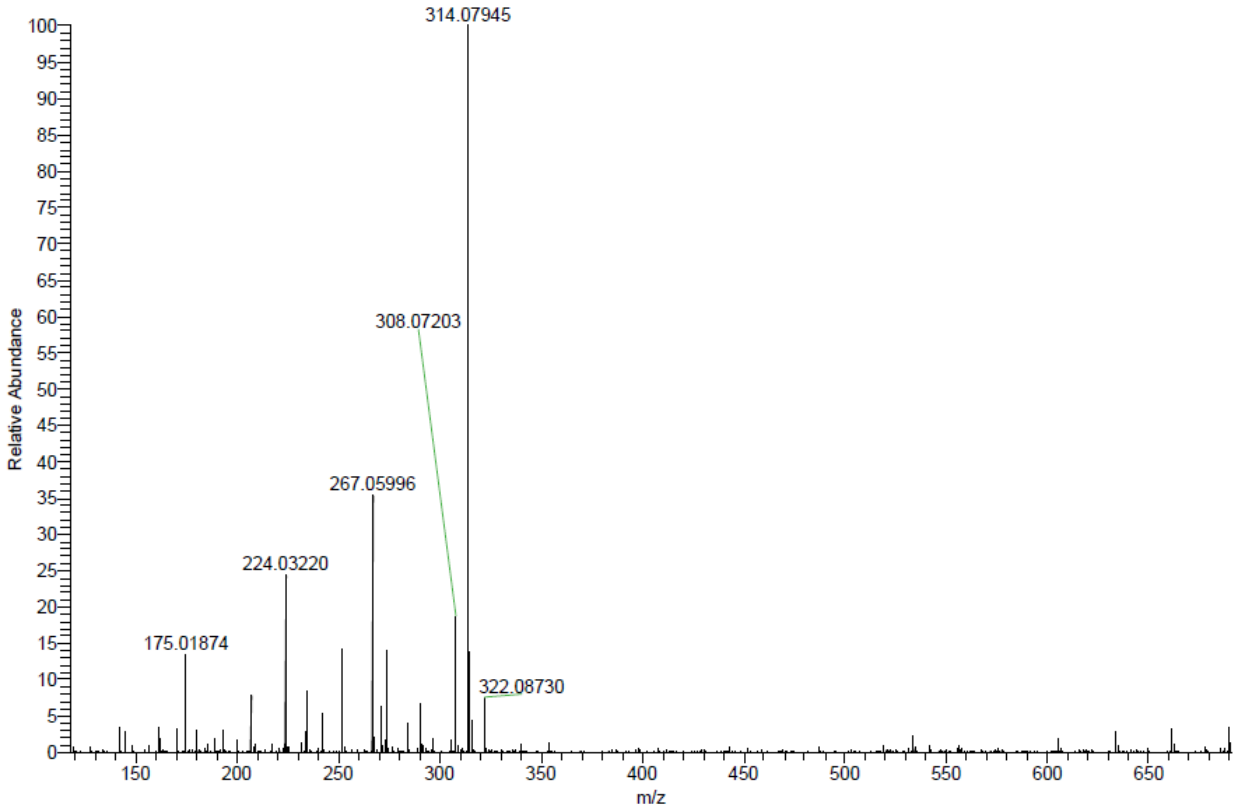
0
150
200
250
300
350
400
450

1-benzyl-3-(2-cyanophenyl)urea (3q)





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308.07203
267.05996
224.03220
175.01874
322.08730
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
150
200
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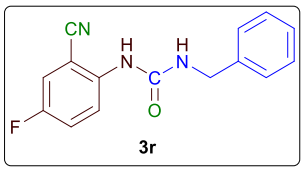
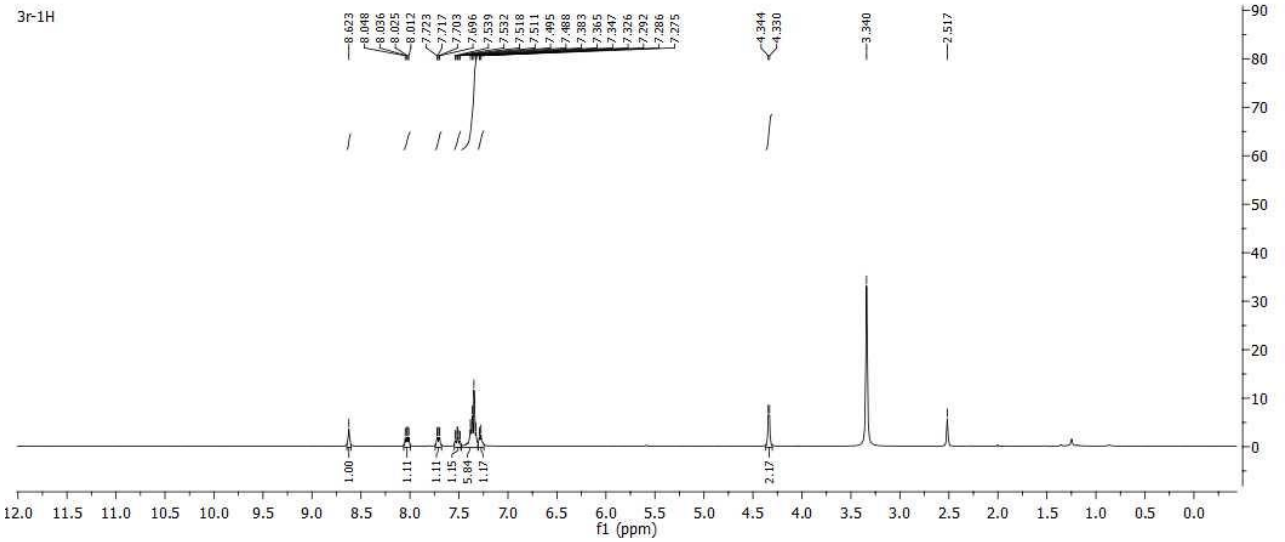
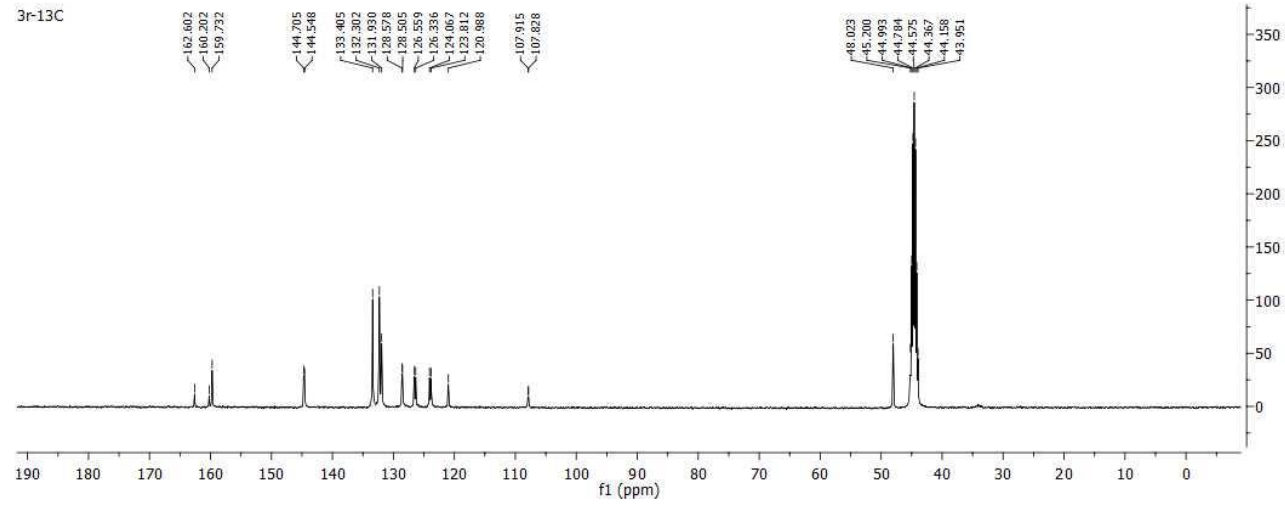
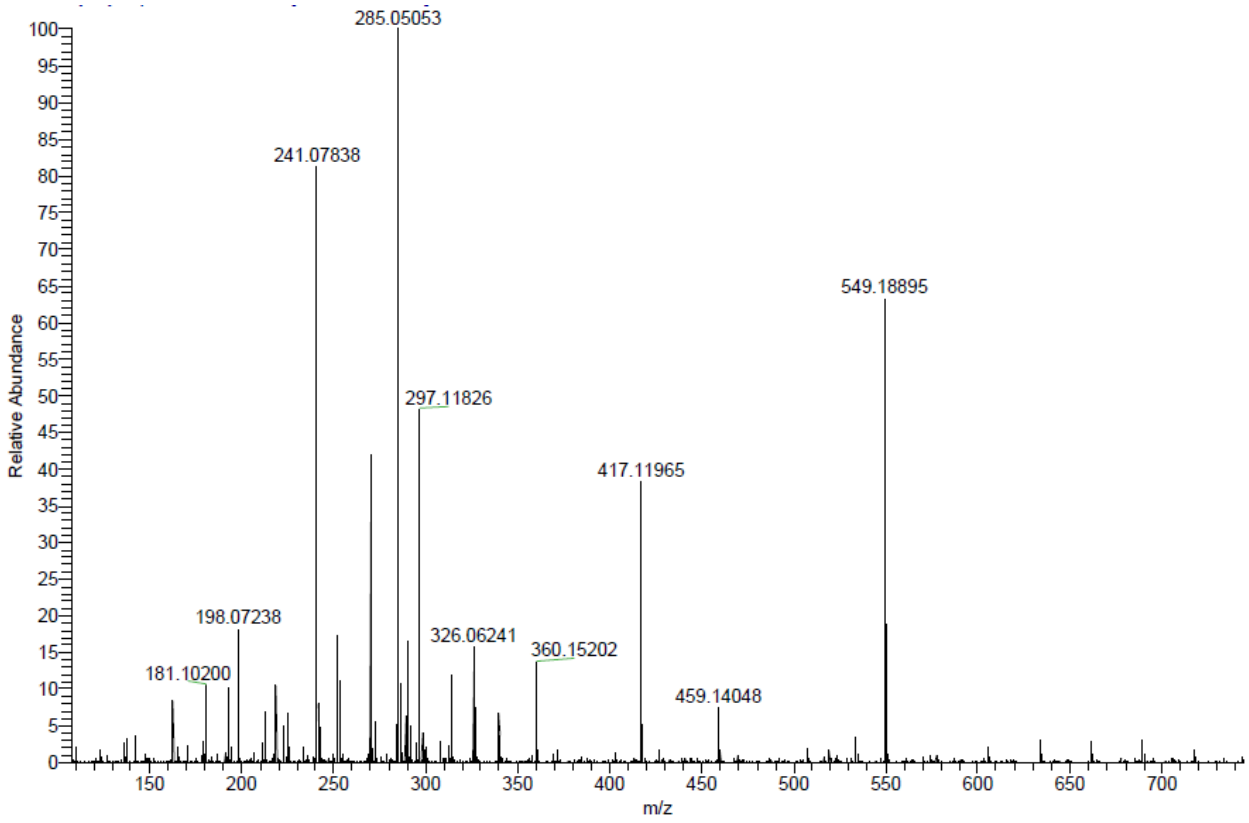
300
350
400
450
500
550
600
650

1-benzyl-3-(2-cyano-4-fluorophenyl)urea (3r)

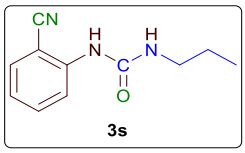


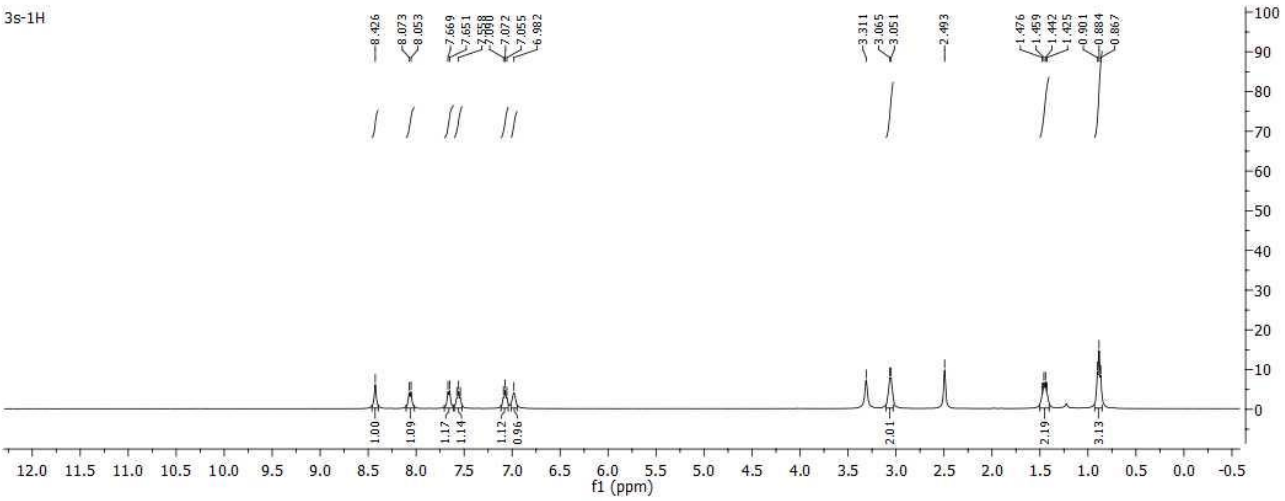


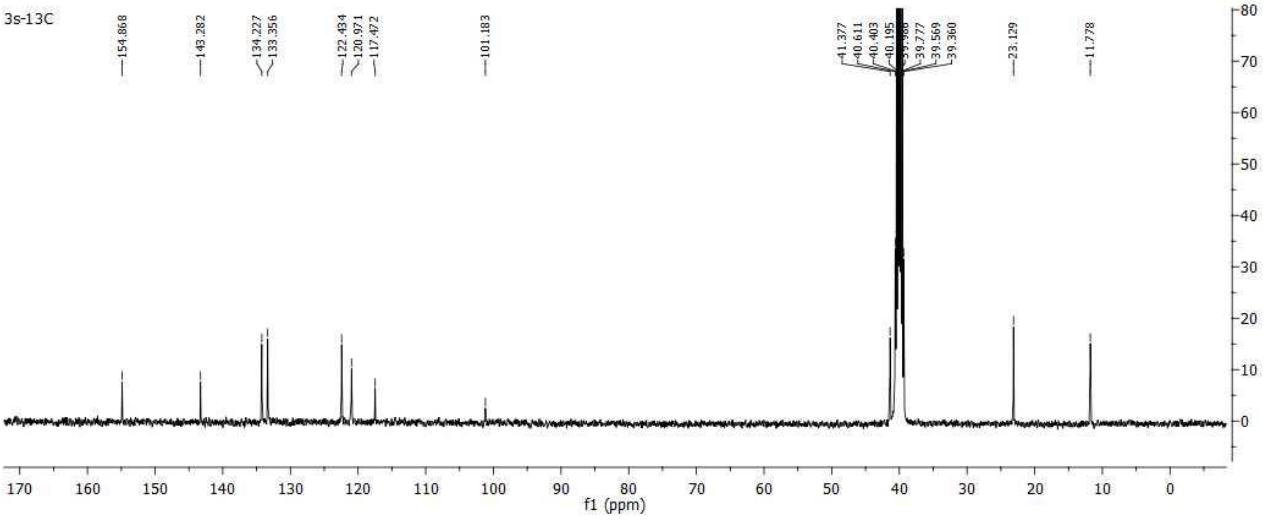



285.05053
241.07838
549.18895
297.11826
417.11965
198.07238
326.06241
360.15202
181.10200
459.14048
Relative Abundance
m/z

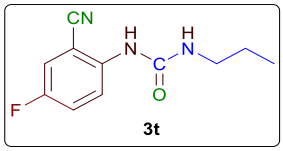
1-(2-cyanophenyl)-3-propylurea (3s)

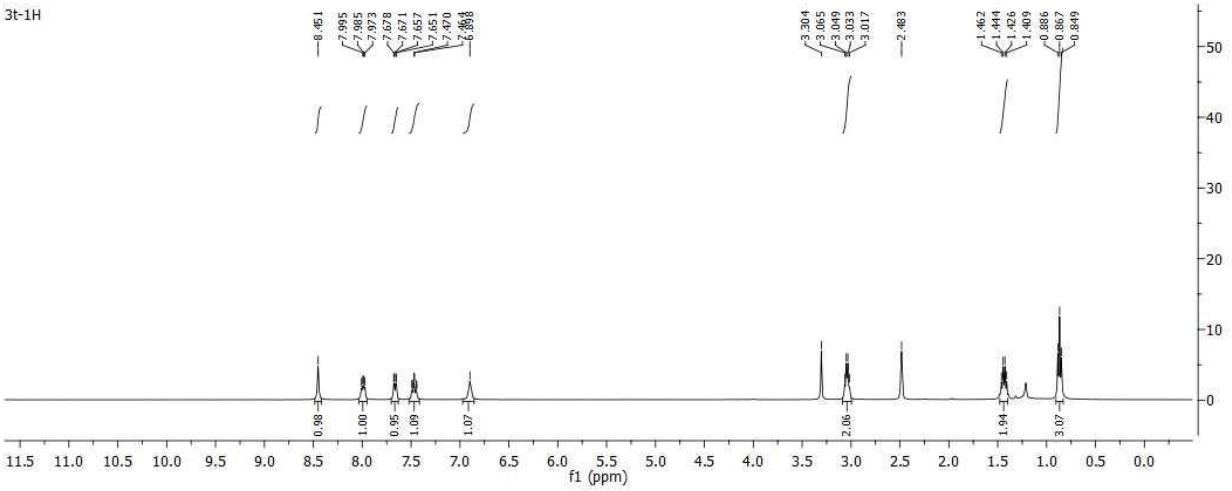


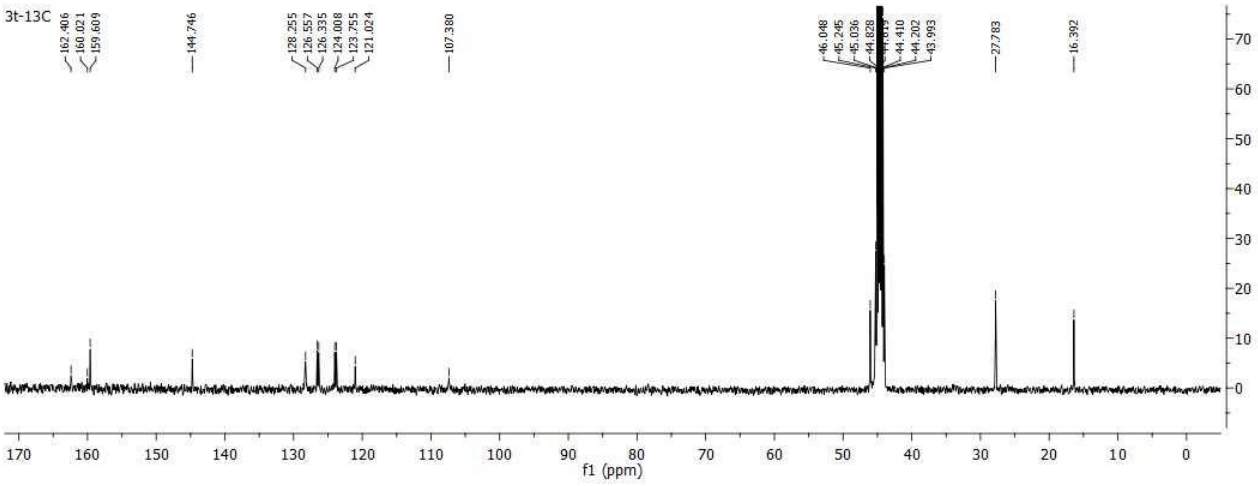




1-(2-cyano-4-fluorophenyl)-3-propylurea (3t)







5. Crystal Analysis Data:

Single crystal X-ray diffraction studies 3a sample:

The crystals of the compound were obtained using the slow evaporation method, defect free single crystals of appropriate dimensions were chosen for X-ray diffraction studies. X-ray intensity data of the compounds were collected using Rigaku XtaLAB Mini diffractometer with X-ray generator operating at 50 kV, 12 mA and MoK_α radiation. Data were collected with χ fixed at 54°, for different settings of φ (0° and 360°), keeping the scan width of 0.5° with exposure time of 4 s and the sample to detector distance was fixed to 50 mm. The complete intensity data sets were processed using *CRYSTAL CLEAR* [1]. The data sets were indexed with monoclinic crystal system, with *P*21/*a* space group. The crystal structures were solved by direct method and refined by full-matrix least squares method on F^2 using *SHELXS* and *SHELXL* programs [2-3]. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were positioned geometrically. After several cycles of refinement, the final difference Fourier map showed peaks of no chemical significance and the residuals were saturated to accepted values. Total 164 parameters were refined with 2696 independent reflections of 6421 overall reflections. Final residual value is coverged to 0.0473. The geometrical calculations were carried out using the program *PLATON* [4]. The molecular and packing diagrams were generated using the software *MERCURY* [5].

References:

1. Rigaku, Crystal Clear, 2011.

2. G. M. Sheldrick, Crystal structure refinement with SHELXL. Acta Cryst. C71 (2015) 3-8. https://doi.org/10.1107/S2053229614024218.

3. G. M. Sheldrick, Phase annealing in SHELX-90: direct methods for larger structures. Acta Cryst. A 46(6) (1990) 467-473. https://doi.org/10.1107/S0108767390000277

4. A. L. Spek, PLATON, an integrated tool for the analysis of the results of a single crystal structure determination, Acta. Cryst. A. 46 (1990) 34.

5. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. M. Rodriguez, R. Taylor, J. van de Streek, P. A. Wood, Mercury CSD 2.0-new features for the visualization and investigation of crystal structures, J. Appl. Cryst 41 (2008) 466-470.

Table 1: Crystal data and structure refinement details.

Empirical formula	$C_{14}H_{11}N_3O$	
Formula weight	237.26	
Temperature	293 K	
Wavelength	0.71075 Å	
Reflns. for cell determination	6421	
θ range for above	3.58° to 27.64°	
Crystal system	Monoclinic	
Space group	$P21/a$	
Cell dimensions		
$a = 10.986(2)$ Å	$b = 20.256(5)$ Å	$c = 10.943(2)$ Å
$\alpha = 90°$	$\beta = 150.908(11)°$	$\gamma = 90°$
Volume	1184.0(6) Å^3	
Z	4	
Density(calculated)	1.331 Mg m^{-3}	
Absorption coefficient	0.088 mm^{-1}	
F_{000}	496	
Crystal size	0.220 × 0.220 × 0.220 mm	
θ range for data collection	3.58° to 27.64°	
Index ranges	$-12 \leq h \leq 14$	
	$-26 \leq k \leq 25$	
	$-14 \leq l \leq 10$	
Reflections collected	6421	
Independent reflections	2696 [$R_{\text{int}} = 0.0254$]	
Absorption correction	?	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	2696 / 0 / 164	
Goodness-of-fit on F^2	1.034	
Final [$I > 2\sigma(I)$]	$R1 = 0.0473$, $wR2 = 0.1100$	
R indices (all data)	$R1 = 0.0756$, $wR2 = 0.1230$	
Extinction coefficient	0.011(4)	
Largest diff. peak and hole	0.179 and −0.141 e Å^{-3}	

Crystal Structure of 1-(2-cyanophenyl)-3-phenylurea (3a): CCDC number-2005876.