Supplementary Information

TCT- Mediated Click Chemistry for the Synthesis of Nitrogen-Containing Functionalities: Conversion of Carboxylic Acids to Carbamides, Carbamates, Carbamothioates, Amides and Amines.

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EXPERIMENTAL SECTION

General Information

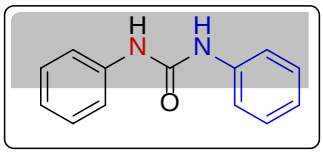
All reactions are carried out in round bottom flask in open atmosphere and reaction mixture was monitored by thin-layer chromatography (TLC). TLC pre-coated silica gel 60 F254 (20 × 20 cm). TLC plates are visualized by exposing UV light. Organic solvents are evaporated on rotary evaporator and all the compounds are purified on flash Column chromatography (230−400 mesh size). Mass spectra are obtained using an Agilent 6540 accurate mass Q-TOF LC/MS (135 eV) spectrometer, using electrospray ionization (ESI). ^{1}H NMR spectra are recorded on 400 and 500 MHz NMR instruments. Chemical data for protons are reported in parts per million (ppm, scale) downfield from tetramethylsilane as referenced to the residual proton in the NMR solvent ($CDCl_3$: δ 7.26, 1.56 $CDCl_3$ moisture and 1.25 grease peak, DMSO-d^6: δ 2.51, 3.33 DMSO-d^6 moisture or other solvents as mentioned). All the NMR spectras are processed with MestReNova software. The coupling constant *(J)* are in Hz. ESI-MS and HRMS spectra are recorded on LC-Q-TOF machines. Note: All the care has been taken while performing the reaction, as sodium azide is highly toxic and can react to form potentially explosive compounds. Azides form strong complexes with haemoglobin, and consequently block oxygen transport in the blood.

General Procedure for one pot conversion of carboxylic acid to carbamides (3a-3aj), (Table 1, Scheme 1 and Scheme 2).

A solution of carboxylic acid **1** (100 mg, 0.500-0.819 mmol) and trichlorotriazine (TCT) (0.33 equiv.) in CH_3CN (20 ml) was mixed with N-methylmorpholine (NMM) (1.4 equiv.) at room temperature and stirred for 30 minutes and monitored on TLC for the consumption of TCT. To the reaction mixture NaN_3 (1.4 equiv.) and DMAP (10 mol%) were added and reaction mixture stirred for 4-5 hrs at room temperature and observed for the formation of acyl azide **2** and consumption of benzoic acid by TLC. Now, the nitrogen based nucleophile (1.4 equiv.) was added and the reaction mixture was subjected to reflux at 80 ^oC in an oil bath, facilitating Curtius rearrangement leading to the *in situ* formation of isocyanate and click coupling. The product formation was monitored by TLC. Reaction mixture was subjected to rota vapour to evaporate CH_3CN and then extraction with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The organic layer was evaporated under pressure to obtain the crude product which was then purified by flash column chromatography using ethyl acetate and hexane to offered the required products (**3a-3ao**).

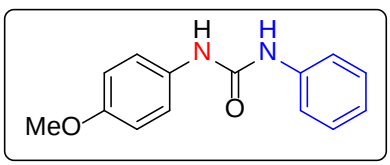
Experimental data:

1,3-Diphenylurea (3a):[1]



(100 mg, 0.819 mmol of benzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.4; Yield 92% ; white solid; m.p 236-239 ^oC.: ; ^1H NMR (400 MHz, DMSO-d^6, acquired at 60 ^oC) δ 8.66 (s, 1H), 7.49 (d, J = 8.5 Hz, 2H), 7.29 (t, J = 7.9 Hz, 2H), 6.97 (t, J = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 153.0, 140.1, 129.2, 122.2, 118.6. HRMS (ESI+TOF) calcd. for: $C_{13}H_{13}N_2O$ 213.1028 $[M+H]^+$, found 213.1033.

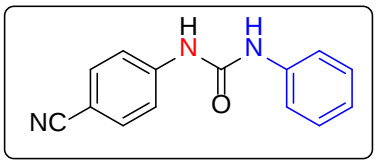
1-(4-Methoxyphenyl)-3-phenylurea (3b):[2]



(100 mg, 0.657 mmol of 4-methoxybenzoic acid);TLC (Hexane/EtOAc, 6:4) R_f = 0.4; Yield 92% ; white solid; m.p.186-190 ^oC; ^1H NMR (400 MHz, DMSO-d^6, acquired at 60 ^oC) δ 8.57 (s, 1H), 8.46 (s, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.9 Hz, 2H), 7.27 (t, J = 7.8 Hz, 2H), 6.95 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 8.9 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (101 MHz,

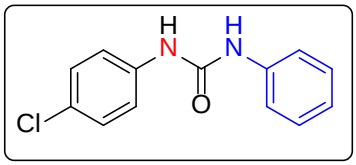
DMSO-d^6) δ 156.4, 154.6, 141.7, 134.6, 130.6, 123.5, 122.0, 120.0, 115.9, 57.1. HRMS (ESI+TOF) calcd. for: $C_{14}H_{15}N_2O_2$ 243.1134 $[M+H]^+$, found 243.1140.

1-(4-Cyanophenyl)-3-phenylurea (3c):[3]



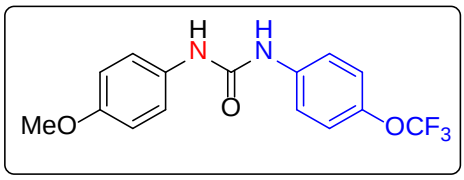
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 90% ; white solid; m.p. 200-222 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6, acquired at 60 ^{o}C) δ 9.15 (s, 1H), 8.80 (s, 1H), 7.76 (dd, J = 27.2, 8.7 Hz, 4H), 7.55 (d, J = 7.7 Hz, 2H), 7.39 (t, J = 7.9 Hz, 2H), 7.11 (t, J = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 153.9, 146.1, 141.0, 135.1, 130.7, 124.2, 121.1, 120.4, 119.9, 105.1. HRMS (ESI+TOF) calcd. for: $C_{14}H_{12}N_3O$ 238.0980 $[M+H]^+$, found 238.0987.

1-(4-Chlorophenyl)-3-phenylurea (3d):[4]



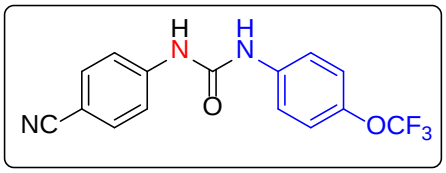
(100 mg, 0.645 mmol of 4-chlorobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.6; Yield 89% ; white solid; m.p. 239-240 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 8.57 (s, 1H), 8.46 (s, 1H), 7.24 (m, 4H), 7.09 – 7.00 (m, 4H), 6.72 (t, J = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 152.9, 140.0, 139.2, 129.1, 125.8, 122.4, 120.1, 118.7. HRMS (ESI+TOF) calcd. for: $C_{13}H_{12}N_2OCl$ 247.0638 $[M+H]^+$, found 247.0646.

1-(4-Methoxyphenyl)-3-(4-(trifluoromethoxy)phenyl)urea (3e):



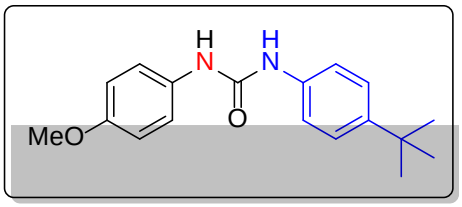
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.3; Yield 90% ; white solid; m.p. 327-330 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6, acquired at 60 ^{o}C) δ 8.63 (s, 1H), 8.35 (s, 1H), 7.42 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 3.53 (s, 3H). ^{19}F NMR (400 MHz, DMSO-d^6) δ -57.36 (s). ^{13}C NMR (101 MHz, DMSO-d^6) δ 156.5, 154.5, 144.3, 141.0, 134.3, 123.4, 122.1, 122.1(q, J = 256.54 Hz), 121.1, 115.8, 57.0. HRMS (ESI+TOF) calcd. for: $C_{15}H_{14}N_2O_3F_3$ 327.0957 $[M+H]^+$, found 327.0965.

1-(4-Cyanophenyl)-3-(4-(trifluoromethoxy)phenyl)urea (3f):



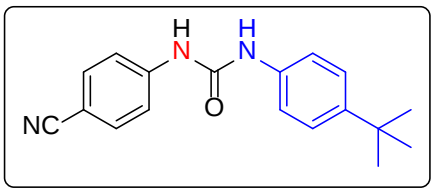
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.3; Yield 91% ; white solid; m.p. 272-278 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6, acquired at 60 °C) δ 9.10 (s, 1H), 8.91 (s, 1H), 7.70 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.9 Hz, 2H), 7.56 (d, J = 9.1 Hz, 2H), 7.27 (d, J = 8.9 Hz, 2H). ^{19}F NMR (376 MHz, DMSO-d^6) δ -52.52 (s). ^{13}C NMR (101 MHz, DMSO-d^6) δ 153.9, 145.9, 144.9 (d, J = 2 Hz), 140.3, 135.1, 123.5, 122.0 (d, J = 256.54 Hz), 121.7, 120.0, 105.3. HRMS (ESI+TOF) calcd. for: $C_{15}H_{11}N_3O_2F_3$ 322.0803 $[M+H]^+$, found 322.0814.

1-(4-(tert-Butyl)phenyl)-3-(4-methoxyphenyl)urea (3g):



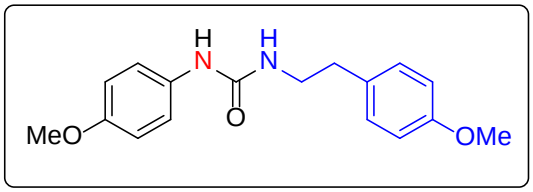
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.5; Yield 89% ; white solid; m.p. 239-241 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 8.48 (s, 1H), 8.42 (s, 1H), 7.36 (d, J = 8.8 Hz, 4H), 7.28 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 3.71 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 154.9, 153.3, 144.4, 137.7, 133.3, 125.8, 120.4, 118.4, 114.4, 55.6, 34.3, 31.7. HRMS (ESI+TOF) calcd. for: $C_{18}H_{23}N_2O_2$ 299.1760 $[M+H]^+$, found 299.1770.

1-(4-(tert-Butyl)phenyl)-3-(4-cyanopheny°l)urea (3h):



(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.5; Yield 93% ; white solid; m.p. 283-285 C: ; ^{1}H NMR (400 MHz, DMSO-d^6, acquired at 60 °C) δ 9.01 (s, 1H), 8.59 (s, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 154.0, 146.7, 146.1, 138.2, 135.1, 127.3, 121.2, 120.3, 119.8, 105.0, 35.7, 33.0. HRMS (ESI+TOF) calcd. for: $C_{18}H_{20}N_3O$ 294.1606 $[M+H]^+$, found 294.1616.

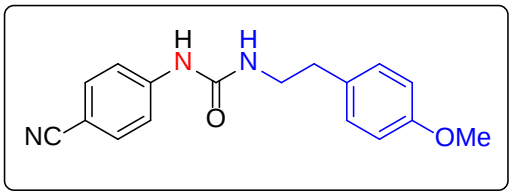
1-(4-Methoxyphenethyl)-3-(4-methoxyphenyl)urea (3i):[5]



(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 88% ;

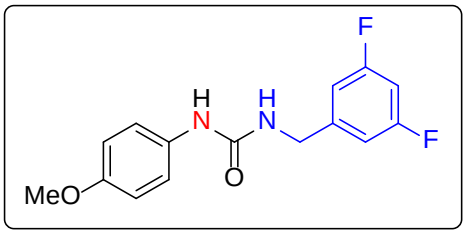
white solid; m.p. 245-249 ^{o}C: ; ^{1}H NMR (500 MHz, DMSO-d^{6}, acquired at 60 ^{o}C) δ 8.22 (s, 1H), 7.82 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 3.74 (s, 3H), 3.46 (s, 2H), 2.80 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 167.5, 163.3, 159.5, 133.3, 131.4, 130.7, 128.7, 115.6, 115.3, 57.1, 56.8, 42.9, 36.2. MS m/z [M+H]$^{+}$, calcd for $C_{17}H_{21}N_2O_3$ 301.1552; found, 301.17.

1-(4-Cyanophenyl)-3-(4-methoxyphenethyl)urea (3j):



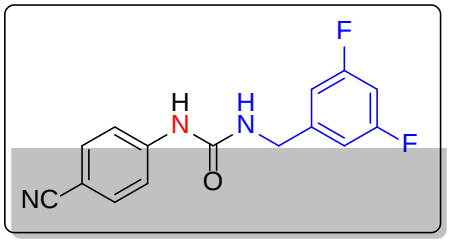
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 91% ; white solid; m.p. 287-290 ^{0}C: ; ^{1}H NMR (400 MHz, DMSO-d^{6}, acquired at 60 ^{o}C) δ 8.91 (s, 1H), 7.63 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.24 (t, J = 5.6 Hz, 1H), 3.73 (s, 3H), 3.36 (m, 2H), 2.72 (t, J = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 158.2, 155.0, 145.4, 133.6, 131.6, 130.1, 119.9, 117.9, 114.3, 102.8, 55.4, 41.3, 35.1. HRMS (ESI+TOF) calcd. for: $C_{17}H_{18}N_3O_2$ 296.1399 [M+H]$^{+}$, found 296.1409.

1-(3,5-Difluorobenzyl)-3-(4-methoxyphenyl)urea (3k):



(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.4; Yield 92% ; white solid; m.p. 215-218 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^{6}, acquired at 60 ^{o}C) δ 8.50 (s, 1H), 7.34 (d, J = 9.0 Hz, 2H), 7.10 (t, J = 9.3 Hz, 1H), 7.03 (d, J = 6.6 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 6.67 (t, J = 12 Hz 1H), 4.34 (d, J = 6.0 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 165.5-165.4 (d, J = 13.13 Hz) , 163.1-162.9 (d, J = 16.16 Hz) , 157.4, 156.0, 147.7-147.5 (t, J =8.08 Hz, 16.16 Hz), 135.2, 121.6, 115.7, 111.8- 111.6 (m), 104.0- 103.5 (t, J = 26.26 Hz), 57.0, 44.0. HRMS (ESI+TOF) calcd. for: $C_{15}H_{15}N_2O_2F_2$ 293.1102 [M+H]$^{+}$, found 293.1112.

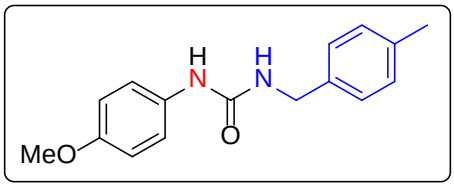
1-(4-Cyanophenyl)-3-(3,5-difluorobenzyl)urea (3l):



(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.4; Yield 90% ; white solid;

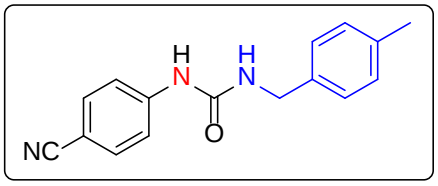
m.p. 257-260 ºC: ; ^{1}H NMR (400 MHz, DMSO-d^{6}) δ 9.36 (t, J = 5.8 Hz, 1H), 8.06 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.12 (t, J = 9.4 Hz, 1H), 7.05 (d, J = 6.6 Hz, 2H), 4.52 (d, J = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 165.6, 164.1-164.0 (d, J = 13.13Hz) , 161.6-161.5 (d, J = 13.13 Hz) , 144.5-144.4 (t, J = 9.09 Hz), 138.4, 132.9, 128.6, 118.7, 114.2, 110.8-110.5(m), 103.0-102.5(t, J = 25.25), 42.6. HRMS (ESI+TOF) calcd. for: $C_{15}H_{11}N_3OF_2$ 288.0948 $[M+H]^+$, found 288.0962.

1-(4-Methoxyphenyl)-3-(4-methylbenzyl)urea (3m):[6]



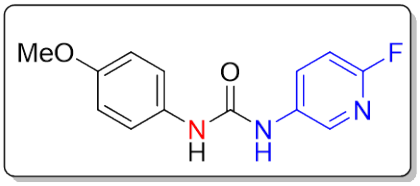
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.4; Yield 85% ; white solid; m.p. 212-216 ºC: ; ^{1}H NMR (400 MHz, DMSO-d^{6}) δ 8.86 (t, J = 5.9 Hz, 1H), 7.87 (d, J = 8.9 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 4.42 (d, J = 6.0 Hz, 2H), 3.81 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d^{6}) δ 166.1, 162.0, 137.2, 136.1, 129.5, 129.2, 127.6, 127.0, 113.9, 55.7, 42.7, 21.1. MS m/z $[M+H]^+$, calcd for $C_{16}H_{19}N_2O_2$ 271.3400; found, 271.34.

1-(4-Cyanophenyl)-3-(4-methylbenzyl)urea (3n):



(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.4; Yield 87% ; white solid; m.p. 254-259 ºC: ; ^{1}H NMR (400 MHz, DMSO-d^{6}, acquired at 60 ºC) δ 8.97 (s, 1H), 7.66 (d, J = 9.0 Hz, 2H), 7.61 (d, J = 9.0 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 6.72 (t, J = 5.8 Hz, 1H), 4.30 (d, J = 5.9 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 155.0, 145.3, 137.3, 136.3, 133.6, 129.3, 127.6, 119.9, 117.9, 102.8, 42.9, 21.1. MS m/z ($[M+H]^+$, calcd for $C_{16}H_{16}N_3O_1$ 266.1293; found, 266.13.

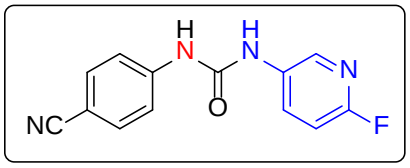
1-(6-fluoropyridin-3-yl)-3-(4-methoxyphenyl)urea (3o):



(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.5; Yield 85% ; white solid; m.p. 294-299 ºC: ;^{1}H NMR (400 MHz, DMSO-d^{6}) δ 8.83 (s, 1H),

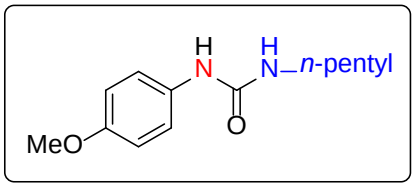
8.64 (s, 1H), 8.27 (s, 1H), 8.10 – 8.03 (m, 1H), 7.37 (d, *J* = 8.9 Hz, 2H), 7.10 (dd, *J* = 8.8, 3.2 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 159.5, 157.2, 155.1, 153.2, 137.1, 136.9, 135.4, 135.3, 132.8, 132.3, 132.2, 120.8, 114.4, 109.7, 109.3, 55.5. HRMS (ESI+TOF) calcd. for: $C_{13}H_{13}N_3O_2F$ 262.0992 $[M+H]^+$, found 262.0995

1-(4-Cyanophenyl)-3-(6-fluoropyridin-3-yl)urea (3p):



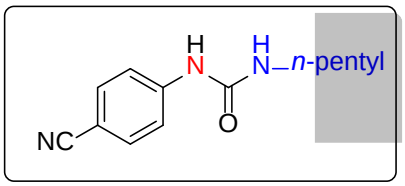
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 89% ; white solid; m.p. 292-297 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 9.16 (s, 1H), 8.89 (s, 1H), 8.16 (s, 1H), 7.94 (m, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 159.9, 157.6, 152.6, 144.3, 137.7-137.5 (d, *J* = 15.15 Hz), 134.6-134.5 (d, *J* =5.05 Hz), 133.6, 132.8-132.7 (d, *J* =7.07 Hz), 119.6, 118.6, 109.7, 109.3, 104.0. HRMS (ESI+TOF) calcd. for: $C_{13}H_{10}N_4OF$ 257.0839 $[M+H]^+$, found 257.0847.

1-(4-Methoxyphenyl)-3-pentylurea (3q):[7]



(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 8:2) R_f = 0.6; Yield 86% ; white solid; m.p. 293-297 ^{o}C: ; ^{1}H NMR (400 MHz, $CDCl_3$, acquired at 60 ^{o}C) δ 7.16 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 5.13 (t, *J* = 4.7 Hz, 1H), 3.76 (s, 3H), 3.16 (dd, *J* = 13.2, 6.9 Hz, 2H), 1.43 (dd, *J* = 14.2, 7.1 Hz, 2H), 1.30 – 1.22 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 132.8, 125.5, 115.9, 78.7, 78.4, 78.1, 56.9, 41.7, 31.2, 30.4, 23.7, 15.3. HRMS (ESI+TOF) calcd. for: $C_{13}H_{21}N_2O_2$ 237.1603 $[M+H]^+$, found 237.1610.

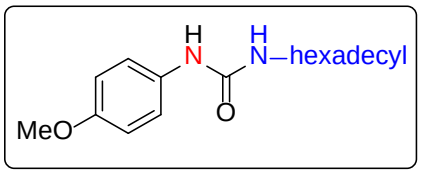
1-(4-Cyanophenyl)-3-pentylurea (3r):



(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 8:2) R_f = 0.5; Yield 91% ; white solid; m.p. 94 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 8.98 (s, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 6.38 (t, *J* = 5.5 Hz, 1H), 3.13 (dd, *J* = 12.8, 6.8 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.37 – 1.27 (m, 4H), 0.92 (t, *J* = 6.9

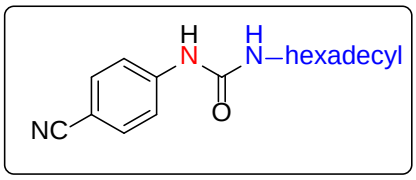
Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 155.0, 145.4, 133.6, 119.9, 117.8, 102.6, 29.7, 29.0, 22.3, 14.4. HRMS (ESI+TOF) calcd. for: $C_{13}H_{18}N_3O$ 232.1450 $[M+H]^+$ found 232.1458.

1-Hexadecyl-3-(4-methoxyphenyl)urea (3s):



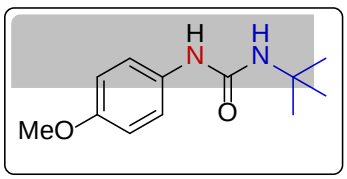
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 8:2) R_f = 0.7; Yield 89% ; white solid; m.p.132- 137 ^{o}C : ; ^{1}H NMR (400 MHz, $CDCl_3$, acquired at 60 ^{o}C) δ 7.70 (d, J = 8.9 Hz, 2H), 7.25 (s, 1H), 6.90 (d, J = 8.9 Hz, 2H), 5.92 (s, 1H), 3.83 (s, 3H), 3.42 (dd, J = 12.9, 7.1 Hz, 2H), 1.59 (d, J = 7.0 Hz, 2H), 1.27 (m, 26H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 162.2, 128.5, 127.3, 113.7, 55.3, 40.0, 31.9, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 27.0, 22.6, 14.0. HRMS (ESI+TOF) calcd. for: $C_{24}H_{43}N_2O_2$ 391.3325 $[M+H]^+$, found 391.3326.

1-(4-Cyanophenyl)-3-hexadecylurea (3t):



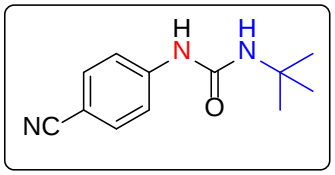
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 8:2) R_f = 0.6; Yield 86% ; white solid; m.p.: 132- 137 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, acquired at 60 ^{o}C) δ 8.35 (s, 1H), 7.51 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 5.84 (s, 1H), 3.20 (dd, J = 12.6, 6.9 Hz, 2H), 1.53 – 1.46 (m, 2H), 1.26 (m, 26H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 144.6, 132.9, 117.7, 103.4, 39.7, 31.81, 30.0, 29.5, 29.5, 29.2, 26.8, 22.5, 14.0. HRMS (ESI+TOF) calcd. for: $C_{24}H_{40}N_3O$ 386.3171 $[M+H]^+$, found 386.3173.

1-(*tert*-Butyl)-3-(4-methoxyphenyl)urea (3u):[8]



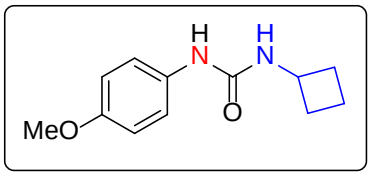
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.6; Yield 85% ; white solid; m.p.203-208 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6, acquired at 60 ^{o}C) δ 7.91 (s, 1H), 7.24 (d, J = 8.9 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 5.76 (s, 1H), 3.69 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 155.2, 154.2, 134.2, 119.6, 114.3, 55.5, 49.8, 29.5. HRMS (ESI+TOF) calcd. for: $C_{12}H_{19}N_2O_2$ 223.1447 $[M+H]^+$, found 223.1452.

1-(*tert*-Butyl)-3-(4-cyanophenyl)urea (3v):



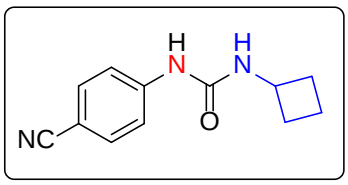
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.5; Yield 88% ; white solid; m.p.139-144 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^{6}) δ 8.72 (s, 1H), 7.61 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 6.16 (s, 1H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 154.1, 145.4, 133.5, 119.9, 117.6, 102.5, 50.1, 29.2. HRMS (ESI+TOF) calcd. for: $C_{12}H_{16}N_3O$ 218.1293 $[M+H]^+$, found 218.1297.

1-Cyclobutyl-3-(4-methoxyphenyl)urea (3w):



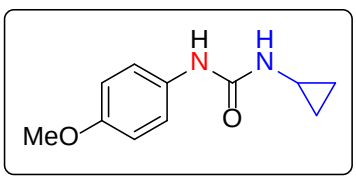
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.6; Yield 84% ; white solid; m.p.172-175 ^{o}C: ; ^{1}H NMR (500 MHz, DMSO-d^{6}, acquired at 60 ^{o}C) δ 7.98 (s, 1H), 7.26 (d, J = 8.9 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 6.19 (s, 1H), 4.15 – 4.10 (m, 1H), 3.70 (s, 3H), 2.21 (d, J = 8.3 Hz, 2H), 1.87 – 1.82 (m, 2H), 1.63 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 156.2, 155.8, 135.4, 121.3, 115.7, 57.0, 46.4, 33.0, 16.2. HRMS (ESI+TOF) calcd. for: $C_{12}H_{17}N_2O_2$ 221.1290 $[M+H]^+$, found 221.1293.

1-(4-Cyanophenyl)-3-cyclobutylurea (3x):



(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.5; Yield 86% ; white solid; m.p. 142-145 ^{o}C: ; ^{1}H NMR (500 MHz, DMSO-d^{6}, acquired at 60 ^{o}C) δ 8.75 (s, 1H), 7.62 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 6.53 (d, J = 7.0 Hz, 1H), 4.14 (dd, J = 15.7, 7.9 Hz, 1H), 2.22 (m, 2H), 1.92 – 1.83 (t, J = 8Hz, 2H), 1.64 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 155.4, 146.7, 134.9, 121.2, 119.3, 104.3, 46.4, 32.6, 16.3. HRMS (ESI+TOF) calcd. for: $C_{12}H_{14}N_3O$ 216.1137 $[M+H]^+$, found 216.1141.

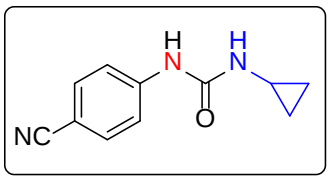
1-Cyclopropyl-3-(4-methoxyphenyl)urea (3y):[9]



(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 89% ; white solid; m.p.183-187 ^{0}C: ; ^{1}H NMR (400 MHz, DMSO-d^{6}) δ 8.12 (s, 1H), 7.32 (d, J

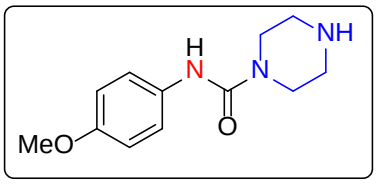
= 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.31 (d, *J* = 1.5 Hz, 1H), 3.71 (s, 3H), 2.53 (m, 1H), 0.64 (m, 2H), 0.42 – 0.39 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 158.1, 155.9, 135.3, 121.6, 115.7, 57.0, 24.2, 8.3. HRMS (ESI+TOF) calcd. for: $C_{11}H_{15}N_2O_2$ 207.1134 $[M+H]^+$, found 207.1135.

1-(4-Cyanophenyl)-3-cyclopropylurea (3z):



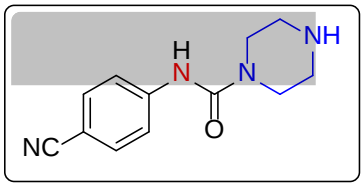
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 91% ; white solid; m.p.133 -138 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6, acquired at 60 ^{o}C) δ 8.84 (s, 1H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 6.61 (s, 1H), 2.56 (dt, *J* = 10.1, 3.3 Hz, 1H), 0.65 (m, 2H), 0.44 – 0.41 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 157.3, 146.6, 134.9, 121.2, 119.5, 104.4, 24.2, 8.2. HRMS (ESI+TOF) calcd. for: $C_{11}H_{12}N_3O$ 202.0980 $[M+H]^+$, found 202.0988.

.***N*-(4-Methoxyphenyl)piperazine-1-carboxamide (3aa):**[10]



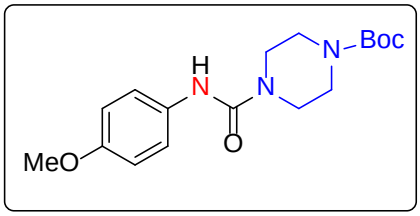
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (DCM/MeOH, 8:2) R_f = 0.6; Yield 80% ; white solid; m.p. 225-230 ^{o}C: ^{1}H NMR (400 MHz, DMSO-d^6) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.41 (s, 4H), 3.22 (s, 2H), 2.69 (s, 4H); ^{13}C NMR (101 MHz, DMSO-d^6) δ 169.5, 160.6, 129.4, 128.1, 114.0, 55.6, 45.4, ***aliphatic carbon peak correspond to piperzyl moiety get suppressed***; HRMS (ESI+TOF) calcd. for: $C_{12}H_{17}N_3O_2Na$ 258.1218 $[M+H]^+$, found 258.1228.

***N*-(4-Cyanophenyl)piperazine-1-carboxamide (3ab):**



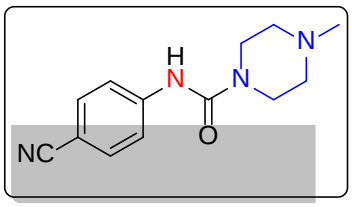
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (DCM/MeOH, 8:2) R_f = 0.4; Yield 77% ; white solid; m.p. 270-275 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 3.56 (s, 2H), 3.17 (s, 2H), 2.75 (s, 2H), 2.63 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 141.0, 133.0, 128.1, 118.8, 112.4, 48.6, 46.0, 45.5, 43.0. MS m/z $[M+H]^+$, calcd for $C_{12}H_{15}N_4O_1$ 231.1246; found, 231.13.

4-((4-Methoxyphenyl)carbamoyl)piperazine-1-carboxylate (3ac):[11]



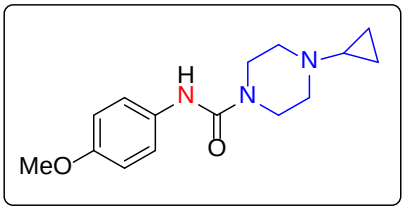
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 6:4) R_f = 0.7; Yield 76% ; white solid; m.p. 260 264 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 7.39 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H), 3.46 (s, 3H), 3.40 (s, 2H), 3.37 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 169.6, 160.7, 154.2, 129.5, 128.0, 114.0, 79.6, 55.6, ***aliphatic carbon peak correspond to piperzyl moiety not appeared,*** 28.4,. MS m/z [M+H]$^+$, calcd for $C_{17}H_{26}N_3O_4$ 336.1923; found, 336.20.

***N*-(4-Cyanophenyl)-4-methylpiperazine-1-carboxamide (3ad):**



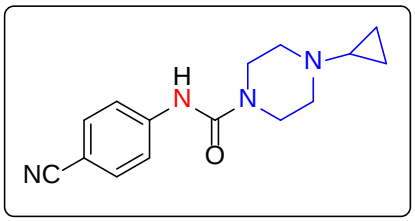
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 78% ; white solid; m.p. 210-215 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6, acquired at 60 °C) δ 8.85 (s, 1H), 7.65 (d, J = 5.5 Hz, 4H), 3.46 (s, 4H), 2.33 (s, 4H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 156.1, 147.1, 134.6, 121.2, 120.8, 104.8, 56.3, 47.5, 45.6. HRMS (ESI+TOF) calcd. for: $C_{13}H_{17}N_4O$ 245.1402 [M+H]$^+$, found 245.1408.

4-Cyclopropyl-*N*-(4-methoxyphenyl)piperazine-1-carboxamide (3ae):



(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 77% ; white solid; m.p. 213 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 7.13 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 3.57 (s, 3H), 3.18 (d, J = 22.7 Hz, 4H), 2.29 (dd, J = 4.8, 2.9 Hz, 4H), 1.44 – 1.39 (m, 1H), 0.22 – 0.17 (m, 2H), 0.12 – 0.07 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 169.4, 160.6, 129.4, 128.2, 114.0, 55.6, 53.1, 38.3, ***aliphatic carbon peak correspond to piperzyl moiety get suppressed,*** 6.1; MS m/z [M+H]$^+$, calcd for $C_{15}H_{22}N_3O_2$ 276.1712; found, 276.18.

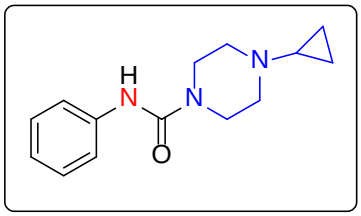
***N*-(4-Cyanophenyl)-4-cyclopropylpiperazine-1-carboxamide (3af):**



(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 73% ; white solid; m.p.

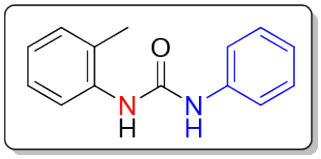
253-257 °C: ; ^{1}H NMR (400 MHz, DMSO) δ 7.93 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 3.59 (s, 2H), 3.35 (s, 1H), 3.21 (s, 2H), 2.60 (s, 2H), 2.48 (s, 2H), 1.77 – 1.55 (m, 1H), 0.43 (dd, J = 6.4, 2.1 Hz, 2H), 0.38 – 0.22 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 167.7, 140.9, 133.0, 128.2, 118.8, 112.5, 53.2, 52.7, 47.3, 38.3, 6.1. MS m/z $(M+H)^+$: calcd for $C_{15}H_{19}N_4O_1$ 271.1559; found, 271.16.

4-Cyclopropyl-*N*-(4-methoxyphenyl)piperazine-1-carboxamide (3ag):



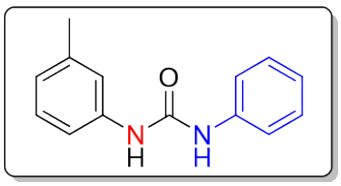
(100 mg, 0.819 mmol of benzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 78% ; white solid; m.p. 253-257 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 7.13 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 3.57 (s, 3H), 3.18 (d, J = 22.7 Hz, 4H), 2.29 (dd, J = 4.8, 2.9 Hz, 4H), 1.44 – 1.39 (m, 1H), 0.22 – 0.17 (m, 2H), 0.12 – 0.07 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 155.4, 140.8, 128.7, 122.2, 120.1, 53.1, 44.0, 38.5, 6.0. HRMS (ESI+TOF) calcd. for: $C_{14}H_{19}N_3ONa$ 268.1426 $[M+H]^+$, found 268.1433.

1-phenyl-3-(o-tolyl)urea (3ah):



100 mg, 0.735 mmol of 2-methylbenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 84% ; white solid; m.p. 233-237 °C: ;^{1}H NMR (400 MHz, DMSO) δ 9.05 (s, 1H), 7.94 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.16 (dd, J = 12.5, 7.5 Hz, 2H), 6.96 (dd, J = 16.2, 7.7 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.1, 140.3, 137.9, 130.6, 129.3, 127.8, 126.6, 123.0, 122.1, 121.4, 118.4, 18.3. HRMS (ESI+TOF) calcd. for: $C_{14}H_{15}N_2O$ 227.1184 $[M+H]^+$, found 227.1181.

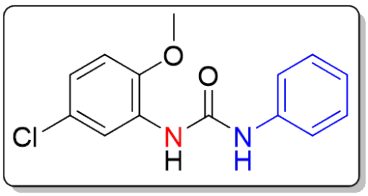
1-phenyl-3-(m-tolyl)urea (3ai):



100 mg, 0.735 mmol of 3-methylbenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 87% ; white solid; m.p. 230-235 °C: ;^{1}H NMR (400 MHz, DMSO-d^6) δ 8.68 (s, 1H), 8.62 (s, 1H), 7.50 (d, J = 7.9 Hz, 2H), 7.35 (s, 1H), 7.29 (t, J = 7.8 Hz, 3H), 7.17 (t, J = 7.8 Hz, 1H), 6.97 (t, J = 7.3 Hz, 1H), 6.79 (d, J = 7.4 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101

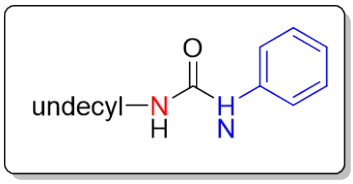
MHz, DMSO-d^6) δ 153.0, 140.2, 140.1, 138.4, 129.2, 129.0, 123.0, 122.2, 119.1, 118.6, 115.8, 40.5, 40.3, 40.1, 39.9, 39.7, 39.5, 39.2, 21.6. HRMS (ESI+TOF) calcd. for: $C_{14}H_{15}N_2O$ 227.1184 $[M+H]^+$, found 227.1186.

1-(5-chloro-2-methoxyphenyl)-3-phenylurea(3aj):



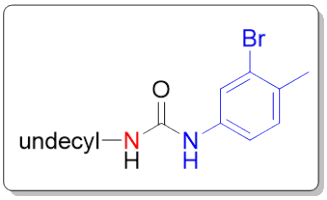
100 mg, 0.537 mmol of 5-chloro-2-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 79% ; white solid; m.p. 252-257 ^oC: ;^1H NMR (400 MHz, DMSO-d^6) δ 9.42 (s, 1H), 8.43 (s, 1H), 8.29 (d, J = 2.2 Hz, 1H), 7.49 (d, J = 7.9 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 6.99 (m, 3H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 152.7, 146.7, 139.9, 130.5, 129.3, 124.8, 122.4, 121.2, 118.5, 117.8, 112.3, 56.5. HRMS (ESI+TOF) calcd. for: $C_{14}H_{14}N_2O_2Cl$ 277.0744 $[M+H]^+$, found 277.0747.

1-Phenyl-3-undecylurea (3ak)[12]:



(100 mg, 0.500 mg of dodecanoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 91% ; white solid; m.p. 160- 165 ^oC: ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.9 Hz, 2H), 7.29 (t, J = 7.9 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 2.34 (t, J = 8 Hz, 2H), 1.74 – 1.67 (m, 2H), 1.62 (m, 2H), 1.26 (m, 16H), 0.88 (t, J = 8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 129.1, 124.6, 119.2, 41.1, 31.9, 29.6, 29.5, 29.3, 26.7, 22.7, 14.1. HRMS (ESI+TOF) calcd. for: $C_{18}H_{31}N_2O$ 291.2436 $[M+H]^+$, found 291.2446.

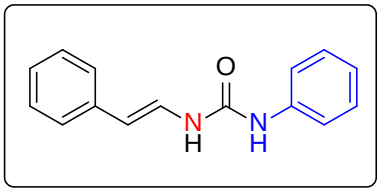
1-(3-bromo-4-methylphenyl)-3-undecylurea (3al):



(100 mg, 0.500 mg of dodecanoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 91% ; white solid; m.p. 160- 165 ^oC: ; ^1H NMR (400 MHz, DMSO-d^6) δ 8.40 (s, 1H), 7.87 (d, J = 1.6 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.10 (t, J = 5.5 Hz, 1H), 3.15 (dd, J = 12.8, 6.7 Hz, 2H), 2.33 (s, 3H), 1.54 – 1.46 (m, 2H), 1.32 (s, 16H), 0.93 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 174.8, 171.7, 138.9, 131.5, 131.1, 124.1, 122.5, 118.5, 36.8, 34.1, 31.8, 29.58,

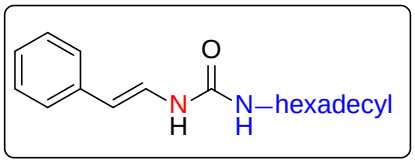
29.56, 29.4, 29.36, 29.33, 29.2, 29.17, 29.11, 25.5, 24.9, 22.6, 22.0, 14.3. MS m/z $[M+H]^+$, calcd for $C_{19}H_{31}N_2OBr$ 383.16; found, 383.35.

(*E*)-1-Phenyl-3-styrylurea (3am):[13]



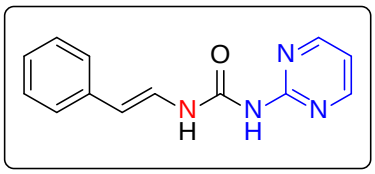
(100 mg, 0.675 mmol of cinnamic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 83% ; white solid; m.p. 230-234 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6, acquired at 60 °C) δ 8.69 (d, J = 10.8 Hz, 4H), 7.37 (m, 6H), 6.99 (t, J = 7.1 Hz, 1H), 6.87 (t, J = 8 Hz, 1H), 5.94 (d, J = 14.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 153.8, 141.3, 139.1, 130.6, 130.4, 127.2, 126.7, 126.5, 123.9, 120.3, 109.8. HRMS (ESI+TOF) calcd. for: $C_{15}H_{15}N_2O$ 239.1184 $[M+H]^+$, found 239.1194.

(*E*)-1-Hexadecyl-3-styrylurea (3an):[14]



(100 mg, 0.675 mmol of cinnamic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 76% ; white solid; m.p. 235-238 °C: ; ^{1}H NMR (400 MHz, $CDCl_3$, acquired at 60 °C) δ 7.55 (d, J = 15.6 Hz, 1H), 7.40 (dd, J = 6.8, 2.8 Hz, 2H), 7.28 – 7.22 (m, 3H), 6.38 (d, J = 15.6 Hz, 1H), 6.02 (s, 1H), 3.30 (dd, J = 13.1, 7.0 Hz, 2H), 1.48 (m, 2H), 1.17 (m, 26H), 0.80 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 140.7, 134.9, 129.5, 128.7, 127.7, 120.8, 39.8, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 29.3, 27.0, 22.7, 14.1. MS m/z $[M+H]^+$, calcd for $C_{25}H_{43}N_2O_1$ 387.3375; found, 387.34.

(*E*)-1-(Pyrimidin-2-yl)-3-styrylurea (3ao):

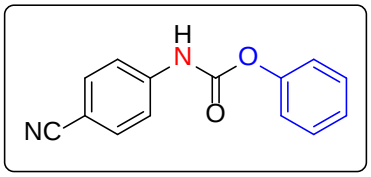


(100mg, 0.675 mmol of cinnamic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 83% ; white solid; m.p. 270-273 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 11.21 (d, J = 10.4 Hz, 1H), 10.30 (s, 1H), 8.66 (d, J = 4.9 Hz, 2H), 7.48 (dd, J = 14.7, 10.4 Hz, 1H), 7.36 (d, J = 7.3 Hz, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.15 (m, 2H), 6.32 (d, J = 14.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 158.6, 158.1, 151.9, 137.1, 129.1, 126.4, 125.4, 124.0, 115.6, 111.7. HRMS (ESI+TOF) calcd. for: $C_{13}H_{13}N_4O$ 241.1089 $[M+H]^+$, found 241.1099.

General Procedure for one pot conversion of carboxylic acid to carbamates and carbamothioates (4a-4n), (Scheme 3).

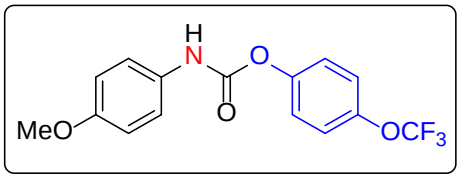
A solution of carboxylic acid **1** (0.500-0.819 mmol) and trichlorotriazine (TCT) (0.33 equiv.) in CH_3CN (20 ml) was mixed with N-methylmorpholine (NMM) (1.4 equiv.) at room temperature and stirred for 30 minutes and monitored on TLC for the consumption of TCT. To the reaction mixture NaN_3 (1.4 equiv.) and DMAP (10 mol%) were added and reaction mixture stirred for 4-5 hrs at room temperature and observed for the formation of acyl azide **2** and consumption of benzoic acid by TLC. Now, the oxygen or sulphur based nucleophile (1.4 equiv.) was added and the reaction mixture was subjected to reflux at 80 ^oC in an oil bath, facilitating Curtius rearrangement leading to the *in situ* formation of isocyanate and click coupling. The product formation was monitored by TLC. Reaction mixture was subjected to rota vapour to evaporate CH_3CN and then extraction with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The organic layer was evaporated under pressure to obtain the crude product which was then purified by flash column chromatography using ethyl acetate and hexane to offerd the required products (**4a-4n**).

Phenyl (4-cyanophenyl)carbamate (4a):[15]



(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 62% ; white solid; m.p. 197-200 ^oC: ; ^1H NMR (400 MHz, DMSO-d^6) δ 10.78 (s, 1H), 7.79 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.7 Hz, 2H), 7.44 (t, J = 7.9 Hz, 2H), 7.28 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 153.4, 152.2, 144.1, 133.9, 133.7, 119.6, 118.8, 113.9, 104.2. MS m/z $[M+H]^+$, calcd for $C_{14}H_{11}N_2O_2$ 239.0821; found, 239.09.

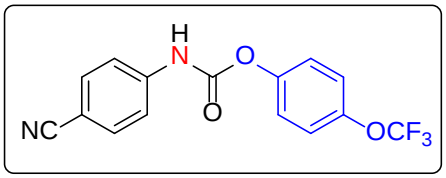
4-(Trifluoromethoxy)phenyl (4-methoxyphenyl)carbamate (4b):



(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 68% ; white solid; m.p. 200-205 ^oC: ; ^1H NMR (500 MHz, $CDCl_3$, acquired at 60 ^oC) δ 7.36 (d, J = 8.2 Hz, 2H), 7.25 (m, 4H), 6.92 (d, J = 8.6 Hz, 2H), 6.80 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 151.5, 149.0,

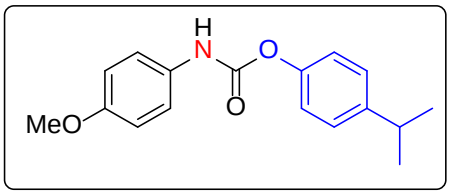
146.4, 130.1, 122.8, 121.9, 120.9, 120.4 (d, J = 257.55 Hz), 114.4, 55.5. HRMS (ESI+TOF) calcd. for: $C_{15}H_{13}NO_4F_3$ 328.0797 $[M+H]^+$, found 328.0804.

4-(Trifluoromethoxy)phenyl (4-cyanophenyl)carbamate (4c):



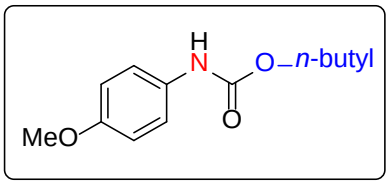
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 65% ; white solid; m.p. 245-250 ºC: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 10.82 (s, 1H), 7.78 – 7.67 (m, 4H), 7.41 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 156.9, 152.2, 144.1, 140.9, 133.7, 122.8, 118.8, 118.7 (q, J = 233.31 Hz), 116.6, 104.3. MS m/z $[M+H]^+$, calcd for $C_{15}H_{10}F_3N_2O_3$ 323.0644; found, 323.08.

4-Isopropylphenyl (4-methoxyphenyl)carbamate (4d):



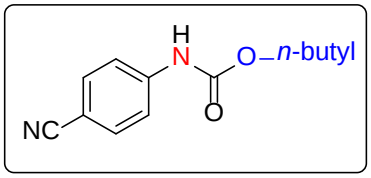
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 65% ; white solid; m.p. 185-190 ºC: ; ^{1}H NMR (400 MHz, DMSO-d^6, acquired at 60 ºC) δ 9.82 (s, 1H), 7.51 (d, J = 9.0 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 3.74 (s, 3H), 2.92 (m, 1H), 1.25 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 155.7, 152.5, 149.1, 145.8, 132.2, 127.5, 122.1, 120.5, 114.5, 55.5, 33.4, 24.3. HRMS (ESI+TOF) calcd. for: $C_{17}H_{20}NO_3$ 286.1443 $[M+H]^+$, found 286.1454.

Butyl (4-methoxyphenyl)carbamate (4e):[16]



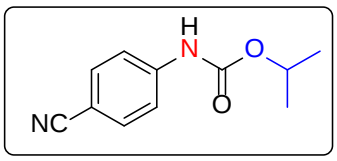
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 70% ; white solid; m.p. 47-50 ºC: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 9.21 (s, 1H), 7.27 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 9.1 Hz, 2H), 3.89 (t, J = 6.6 Hz, 2H), 3.51 (s, 3H), 1.44 – 1.37 (m, 2H), 1.20 (dt, J = 9.2, 7.4 Hz, 2H), 0.72 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 155.1, 154.3, 132.8, 120.1, 114.1, 64.1, 55.3, 31.1, 19.1, 13.8. HRMS (ESI+TOF) calcd. for: $C_{12}H_{18}NO_3$ 224.1287 $[M+H]^+$, found 224.1286.

Butyl (4-cyanophenyl)carbamate (4f):[17]



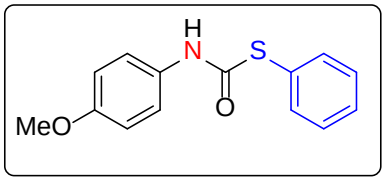
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 67% ; white solid; m.p. ; 55-60 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 10.09 (s, 1H), 7.69 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 4.09 (t, J = 6.6 Hz, 2H), 1.61 – 1.57 (m, 2H), 1.36 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).^{13}C NMR (101 MHz, DMSO-d^6) δ 153.7, 144.1, 133.5, 119.5, 118.4, 104.4, 64.7, 30.8, 18.9, 13.8. HRMS (ESI+TOF) calcd. for: $C_{12}H_{15}N_2O_2$ 219.1134 $[M+H]^+$, found 219.1134.

Isopropyl (4-cyanophenyl)carbamate (4g):[17]



(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 65% ; white solid; m.p.: ; 120-125 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 8.06 (d, J = 7.3 Hz, 2H), 7.97 (d, J = 7.7 Hz, 2H), 5.15 (dt, J = 12.4, 6.2 Hz, 1H), 1.32 (d, J = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 164.4, 134.5, 133.1, 130.1, 118.5, 115.7, 69.6, 21.9. MS m/z $[M+H]^+$, calcd for $C_{11}H_{13}N_2O_2$ 205.0977; found, 205.10.

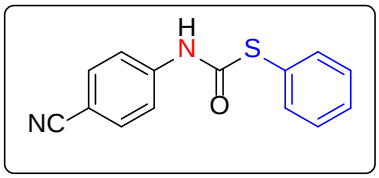
***S*-Phenyl (4-methoxyphenyl)carbamothioate (4h):[18]**



(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 82% ; white solid; m.p.160-165 °C: ; ^{1}H NMR (400 MHz, $CDCl_3$, acquired at 60 °C) δ 7.57 (m, 2H), 7.42 (s, 1H), 7.39 – 7.36 (m, 3H), 7.24 (d, J = 9.0 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 131.1, 130.8, 129.7, 115.6, 56.9. . HRMS (ESI+TOF) calcd. for: $C_{14}H_{14}NO_2S$ 260.0745 $[M+H]^+$, found 260.0757.

.

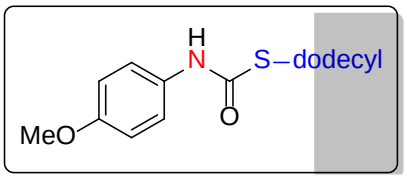
***S*-Phenyl (4-cyanophenyl)carbamothioate (4i):**



(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 85% ; white solid; m.p.200-205 °C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 11.00 (s, 1H), 7.78 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.7 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.47 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 153.4, 136.2, 133.9, 133.7, 129.9,

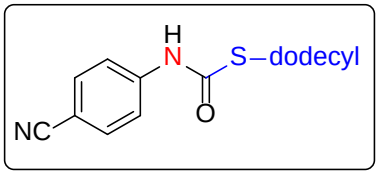
128.0, 127.6, 118.8, 113.9, 96.0. HRMS (ESI+TOF) calcd. for: $C_{14}H_{11}N_2OS$ 255.0592 $[M+H]^+$, found 255.0604.

_S_-Dodecyl (4-methoxyphenyl)carbamothioate (4j):



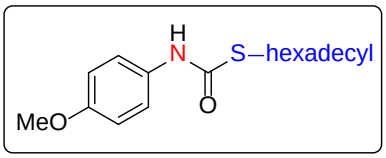
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 92% ; white solid; m.p.200-205 ºC: ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 3.77 (s, 3H), 3.02 – 2.85 (m, 2H), 1.69 – 1.59 (m, 2H), 1.36 (s, 2H), 1.27 (m, 16H), 0.88 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 114.2, 55.4, 31.9, 30.3, 30.2, 29.6, 29.6, 29.6, 29.5, 29.3, 29.1, 28.8, 22.7, 14.1. HRMS (ESI+TOF) calcd. for: $C_{20}H_{34}NO_2S$ 352.2310 $[M+H]^+$, found 352.2317.

_S_-Dodecyl (4-cyanophenyl)carbamothioate (4k):



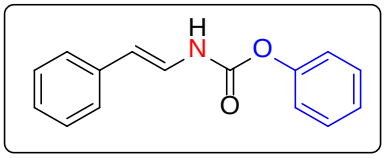
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 89% ; white solid; m.p.200-205 ºC: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 10.72 (s, 1H), 7.74 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.9 Hz, 2H), 2.89 (t, J = 7.2 Hz, 2H), 1.60 – 1.52 (m, 2H), 1.33 (m, 2H), 1.21 (m, 16H), 0.83 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 166.3, 143.4, 133.7, 119.1, 105.3, 31.7, 30.2, 29.5, 29.5, 29.4, 29.3, 29.2, 28.9, 28.5, 22.5, 14.3. HRMS (ESI+TOF) calcd. for: $C_{20}H_{31}N_2OS$ 347.2157 $[M+H]^+$, found 347.2159.

_S_-Hexadecyl (4-methoxyphenyl)carbamothioate (4l):



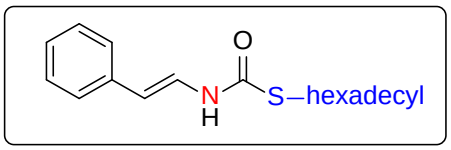
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 92% ; white solid; m.p.233-237 ºC: ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.6 Hz, 2H), 7.03 (s, 1H), 6.85 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.95 (t, J = 7.3 Hz, 2H), 1.67 – 1.62 (m, 2H), 1.39 (m, 2H), 1.26 (m, 24H), 0.89 (t, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 114.2, 55.4, 31.9, 30.3, 29.7, 29.6, 29.6, 29.6, 29.5, 29.38, 29.1, 28.8, 22.7, 14.1. HRMS (ESI+TOF) calcd. for: $C_{24}H_{42}NO_2S$ 408.2936 $[M+H]^+$, found 408.2938.

Phenyl (*E*)-styrylcarbamate (4m):



(100 mg, 0.675 mmol of cinnamic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 64% ; white solid; m.p.157-160 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^{6}) δ 10.34 (d, J = 10.0 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.35 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.3 Hz, 3H), 7.21 (m, 3H), 7.15 (m, 1H), 6.18 (d, J = 14.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 157.7, 136.8, 129.9, 129.8, 129.1, 126.5, 126.0, 125.5, 125.1, 122.2, 119.2, 115.6. HRMS (ESI+TOF) calcd. for: $C_{15}H_{14}NO_2$ 240.1025 $[M+H]^+$, found 240.1030.

***S*-Hexadecyl (*E*)-styrylcarbamothioate (4n):**



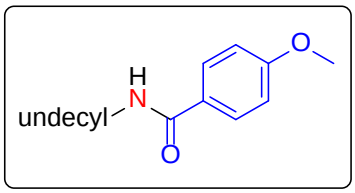
(100 mg, 0.675 mmol of cinnamic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 84% ; white solid; m.p.290-295 ^{o}C: ; ^{1}H NMR (400 MHz, $CDCl_3$, acquired at 60 ^{o}C) δ 7.33 (m, 1H), 7.26 (m, 3H), 7.13 (m, 2H), 6.03 (d, J = 14.2 Hz, 1H), 2.98 (t, J = 5.5 Hz, 2H), 1.64 (d, J = 5.7 Hz, 2H), 1.39 (s, 2H), 1.27 (m, 24H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 135.9, 128.6, 126.6, 125.5, 122.7, 112.1, 31.9, 30.2, 30.1, 29.6, 29.5, 29.4, 29.3, 29.1, 28.7, 22.6, 14.0. HRMS (ESI+TOF) calcd. for: $C_{25}H_{42}NOS$ 404.2987 $[M+H]^+$, found 404.2992.

Procedure for one pot conversion of carboxylic acid to amides (5), (Scheme 4).

A solution of carboxylic acid **1** (0.500-0.819 mmol) and trichlorotriazine (TCT) (0.33 equiv.) in CH_3CN (20 ml) was mixed with N-methylmorpholine (NMM) (, 1.4 equiv.) at room temperature and stirred for 30 minutes and monitored on TLC for the consumption of TCT. To the reaction mixture NaN_3 (1.4 equiv.) and DMAP (10 mol%) were added and reaction mixture stirred for 4-5 hrs at room temperature and observed for the formation of acyl azide **2** and consumption of benzoic acid by TLC. Now, the carboxylic acid (1.4 equiv.) was added and the reaction mixture was subjected to reflux at 80 ^{o}C in an oil bath, facilitating Curtius rearrangement leading to the *in situ* formation of isocyanate and click coupling. The product formation was monitored by TLC. Reaction mixture was subjected to rota vapour to evaporate CH_3CN and then extraction with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The organic layer was evaporated under pressure to obtain the

crude product which was then purified by flash column chromatography using ethyl acetate and hexane to offerd the required products (**5**).

4-Methoxy-N-undecylbenzamide (5):[19]

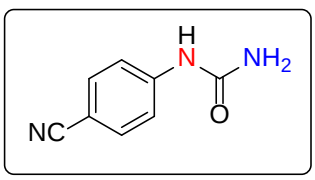


(100 mg, 0.500 mmol of dodecanoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 54% ; white solid; m.p.250-260 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^{6}) δ 7.93 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H), 2.20 (t, J = 8Hz , 2H), 1.52 (m, 2H), 1.25 (m, 16H), 0.87 (t, J = 8Hz 3H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 174.9, 167.5, 163.2, 131.8, 123.7, 114.1, 55.8, 34.1, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 25.0, 22.6, 14.3. MS m/z $[M+H]^{+}$, calcd for $C_{19}H_{32}NO_2$ 306.2433; found, 306.24.

Procedure for one pot conversion of carboxylic acid to mono-substituted carbamides (6), (Scheme 4).

A solution of carboxylic acid **1** (0.500-0.819 mmol) and trichlorotriazine (TCT) (0.33 equiv.) in CH_3CN (20 ml) was mixed with N-methylmorpholine (NMM) (1.4 equiv.) at room temperature and stirred for 30 minutes and monitored on TLC for the consumption of TCT. To the reaction mixture NaN_3 (1.4 equiv.) and DMAP (10 mol%) were added and reaction mixture stirred for 4-5 hrs at room temperature and observed for the formation of acyl azide **2** and consumption of benzoic acid by TLC. Now, the aq. NH_4OH (1.4 equiv.) was added and the reaction mixture was subjected to reflux at 80 ^{0}C in an oil bath, facilitating Curtius rearrangement leading to the *in situ* formation of isocyanate and click coupling. The product formation was monitored by TLC. Reaction mixture was subjected to rota vapour to evaporate CH_3CN and then extraction with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The organic layer was evaporated under pressure to obtain the crude product which was then purified by flash column chromatography using ethyl acetate and hexane to offerd the required products (**6**).

1-(4-Cyanophenyl)urea (6):[20]



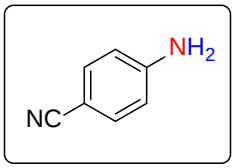
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 57% ; white solid; m.p. 206-209 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^{6},) δ 8.19 (s, 1H), 6.81 (d, J = 8.6 Hz, 2H), 6.74

(d, *J* = 8.6 Hz, 2H), 5.24 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 166.9, 138.7, 132.8, 128.7, 118.8, 114.1 . HRMS (ESI+TOF) calcd. for: $C_8H_8N_3O$ 162.0667 [M+H]+, found 162.0670.

General Procedure for one pot conversion of carboxylic acid to amines (7a-7e), (Scheme 4).

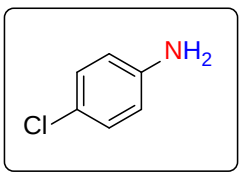
A solution of carboxylic acid **1** (0.500-0.819 mmol) and trichlorotriazine (TCT) (0.33 equiv.) in CH_3CN (20 ml) was mixed with N-methylmorpholine (NMM) (1.4 equiv.) at room temperature and stirred for 30 minutes and monitored on TLC for the consumption of TCT. To the reaction mixture NaN_3 (11.4 equiv.) and DMAP (10 mol%) were added and reaction mixture stirred for 4-5 hrs at room temperature and observed for the formation of acyl azide **2** and consumption of benzoic acid by TLC. Now, H_2O (1.4 equiv.) was added and the reaction mixture was subjected to reflux at 80 ^{0}C in an oil bath, facilitating Curtius rearrangement leading to the *in situ* formation of isocyanate and click coupling. The product formation was monitored by TLC. Reaction mixture was subjected to rota vapour to evaporate CH_3CN and then extraction with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The organic layer was evaporated under pressure to obtain the crude product which was then purified by flash column chromatography using ethyl acetate and hexane to offerd the required products (**7a-7e**).

4-Aminobenzonitrile (7a)[21]:



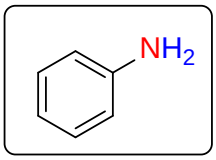
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 95% ; white solid; m.p.83-85 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 7.26 (d, *J* = 8.3 Hz, 2H), 6.51 (d, *J* = 8.3 Hz, 2H), 5.95 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 153.4, 133.8, 121.1, 114.0, 96.2. HRMS (ESI+TOF) calcd. for: $C_7H_7N_2$ 119.0609 [M+H]+, found 119.0603.

4-Chloroaniline (7b)[22]:



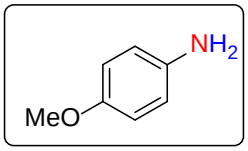
(100 mg, 0.645 mmol of 4-chlorobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.6; Yield 92% ; white solid; m.p.70-75 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 8.81 (s, 1H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 152.8, 139.0, 129.0, 126.0, 120.3. MS m/z (M+H)$^+$: calcd for C_6H_7ClN 128.0267; found, 128.02.

Aniline (7c)[23]:



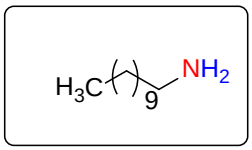
(100 mg, 0.819 mmol of benzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.7; Yield 93% ;; ^{1}H NMR (400 MHz, DMSO) δ 7.04 (m, 2H), 6.61 (m, 2H), 6.54 (td, J = 7.3, 3.7 Hz, 1H), 5.00 (s, 2H).^{13}C NMR (101 MHz, DMSO) δ 149.0, 129.3, 116.2, 114.4. MS m/z $(M+H)^+$: calcd for C_6H_8N 94.0657; found, 94.06.

4-Methoxyaniline (7d)[23]:



(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 94% ; white solid; m.p.55-60 ^{o}C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 6.68 (d, J = 8 Hz, 2H), 6.57 (d, J = 8 Hz, 2H), 4.60 (s, 2H), 3.64 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 151.2, 142.7, 115.5, 114.9, 55.6. HRMS (ESI+TOF) calcd. for: $C_7H_{10}NO$ 124.0762 [M+H]+, found 124.0762.

Undecan-1-amine (7e):[24]



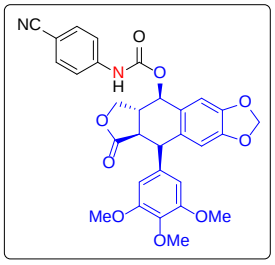
(100 mg, 0.500 mmol of dodecanoic acid); TLC (Hexane/EtOAc, 8:2) R_f = 0.8; Yield 87% ; white solid; m.p.15-20 ^{0}C: ; ^{1}H NMR (400 MHz, DMSO-d^6) δ 2.16 (t, J = 7.1 Hz, 2H), 1.46 (m, 2H), 1.22 (m, 16H), 0.83 (t, J = 8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 40.8, 31.9, 30.0, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.9, 24.8, 22.7, 14.1. MS m/z $(M+H)^+$: calcd for $C_{11}H_{26}N$ 172.2065; found, 172.21.

General Procedure for late stage functionalization of natural products and drugs (8a-8e), (Scheme 5).

A solution of carboxylic acid **1** (0.500-0.819 mmol) and trichlorotriazine (TCT) (0.33 equiv.) in CH_3CN (20 ml) was mixed with N-methylmorpholine (NMM) (1.4 equiv.) at room temperature and stirred for 30 minutes and monitored on TLC for the consumption of TCT. To the reaction mixture NaN_3 (1.4 equiv.) and DMAP (10 mol%) were added and reaction mixture stirred for 4-5 hrs at room temperature and observed for the formation of acyl azide **2** and consumption of benzoic acid by TLC. Now, the natural products (podophyllotoxin, euginol, diosgenin, geraniol) and drug (fluvoxamine) (1.4 equiv.) was added and the reaction mixture was subjected to reflux at 80 ^{o}C in an oil bath, facilitating Curtius rearrangement leading to the *in situ*

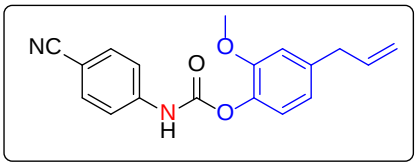
formation of isocyanate and click coupling. The product formation was monitored by TLC. Reaction mixture was subjected to rota vapour to evaporate CH_3CN and then extraction with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The organic layer was evaporated under pressure to obtain the crude product which was then purified by flash column chromatography using ethyl acetate and hexane to offerd the required products (**8a-8e).**

8-Oxo-9-(3,4,5-trimethoxyphenyl)-5,5a,6,8,8a,9-hexahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-5-yl (4-cyanophenyl)carbamate (8a):



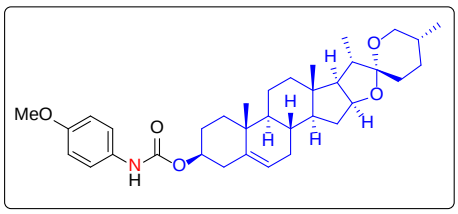
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 68% ; white solid; m.p.323-327 ^oC: ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.29 (s, 1H), 6.89 (s, 1H), 6.55 (s, 1H), 6.40 (s, 2H), 5.99 (dd, J = 5.8, 1.2 Hz, 2H), 5.93 (d, J = 8.6 Hz, 1H), 4.63 (d, J = 3.8 Hz, 1H), 4.46 (dd, J = 9.2, 6.4 Hz, 1H), 4.26 (t, J = 9.8 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 6H), 2.96 (d, J = 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 153.2, 152.5, 148.1, 147.6, 142.1, 136.9, 135.1, 133.3, 132.2, 128.2, 118.9, 118.5, 109.7, 108.1, 106.9, 106.1, 101.6, 74.8, 71.3, 60.7, 56.0, 45.2, 43.6, 38.5. HRMS (ESI+TOF) calcd. for: $C_{30}H_{26}N_2O_9Na$ 581.1536 [M+Na]+, found 581.1536.

4-Allyl-2-methoxyphenyl (4-cyanophenyl)carbamate (8b):



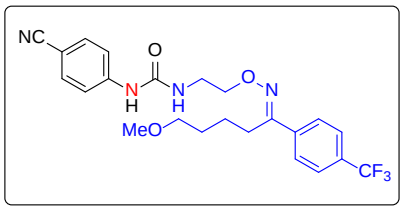
(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 65% ; white solid; m.p.285-290 ^oC: ; ^1H NMR (500 MHz, DMSO-d^6, acquired at 60 ^oC) δ 10.59 (s, 1H), 7.76 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.0 Hz, 1H), 6.99 (s, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.01 (td, J = 16.8, 6.8 Hz, 1H), 5.11 (dd, J = 25.3, 13.5 Hz, 2H), 3.80 (s, 3H), 3.40 (d, J = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d^6) δ 151.7, 151.6, 143.7, 139.3, 137.8, 137.7, 133.8, 123.4, 120.7, 119.4, 118.8, 116.4, 113.5, 105.2, 56.2, 39.8. HRMS (ESI+TOF) calcd. for: $C_{18}H_{17}N_2O_3$ 309.1239 [M+H]+, found 309.1248.

5',6a,9-Trimethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl(4-methoxyphenyl)carbamate (8c):



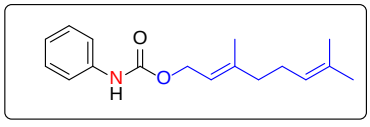
(100 mg, 0.657 mmol of 4-methoxybenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 59% ; white solid; m.p.325-330 ^oC: ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 10.0 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 6.53 (s, 1H), 5.41 (d, J = 4.9 Hz, 1H), 4.66 – 4.55 (m, 1H), 4.44 (dd, J = 14.9, 7.4 Hz, 1H), 3.80 (s, 3H), 3.54 – 3.46 (m, 1H), 3.40 (t, J = 10.9 Hz, 1H), 2.45 (dd, J = 13.0, 3.1 Hz, 1H), 2.34 (t, J = 11.4 Hz, 1H), 2.00 (d, J = 5.0 Hz, 2H), 1.92 – 1.85 (m, 2H), 1.82 – 1.78 (m, 1H), 1.74 (s, 1H), 1.70 (d, J = 4.6 Hz, 1H), 1.67 – 1.57 (m, 6H), 1.55 – 1.44 (m, 4H), 1.22 (m, 7H), 1.06 (s, 3H), 1.00 (d, J = 6.9 Hz, 3H), 0.81 (d, J = 4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 153.4, 139.6, 131.1, 122.4, 120.4, 114.2, 109.3, 80.8, 66.8, 62.0, 56.4, 55.5, 49.9, 41.6, 40.2, 39.7, 38.4, 36.9, 36.7, 32.0, 31.8, 31.4, 30.3, 29.7, 28.8, 28.0, 20.8, 19.3, 17.1, 16.3, 14.5. HRMS (ESI+TOF) calcd. for: $C_{35}H_{50}NO_5$ 564.3689 [M+H]+, found 564.3689.

(*E*)-1-(4-Cyanophenyl)-3-(2-(((5-methoxy-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethyl)urea (8d):



(100 mg, 0.680 mmol of 4-cyanobenzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 77% ; white solid; m.p.120-123 ^oC: ; ^1H NMR (500 MHz, DMSO-d^6, acquired at 60 ^oC) δ 9.01 (s, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.7 Hz, 2H), 7.61 (dt, J = 8.7, 7.2 Hz, 4H), 6.38 (t, J = 5.1 Hz, 1H), 4.26 (s, 2H), 3.50 (s, 2H), 3.27 (s, 2H), 3.17 (s, 3H), 2.81 (s, 2H), 1.52 (s, 4H). ^{19}F NMR (376 MHz, DMSO-d^6) δ -61.37. ^{13}C NMR (101 MHz, DMSO-d^6) δ 157.7, 155.1, 145.3, 139.5, 133.51, 127.3, 127.2 (q, J = 31.31 Hz), 125.79-125.76 (d, J = 3.03 Hz), 119.8, 117.9, 103.0, 73.3, 71.8, 58.1, 39.3, 29.3, 25.8, 23.1. HRMS (ESI+TOF) calcd. for: $C_{23}H_{26}N_4O_3F_3$ 463.1957 [M+H]+, found 463.1961.

(*E*)-3,7-Dimethylocta-2,6-dien-1-yl phenylcarbamate (8e):[25]



(100 mg, 0.819 mmol of benzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; Yield 61% ; white solid; m.p.80-85 ^oC: ; ^1H NMR

(400 MHz, $CDCl_3$) δ 7.30 (d, J = 7.9 Hz, 2H), 7.22 (t, J = 7.7 Hz, 2H), 6.97 (t, J = 7.2 Hz, 1H), 6.57 (s, 1H), 5.33 (t, J = 6.9 Hz, 1H), 5.02 (m, 1H), 4.62 (d, J = 7.1 Hz, 2H), 2.06 – 1.96 (m, 4H), 1.67 (s, 3H), 1.61 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 142.6, 138.0, 131.9, 129.0, 123.7, 123.3, 118.6, 118.4, 62.0, 39.5, 26.3, 25.7, 22.7, 17.7, 16.5. HRMS (ESI+TOF) calcd. for: $C_{17}H_{23}NO_2Na$ 296.1626 [M+H]+, found 296.1634.

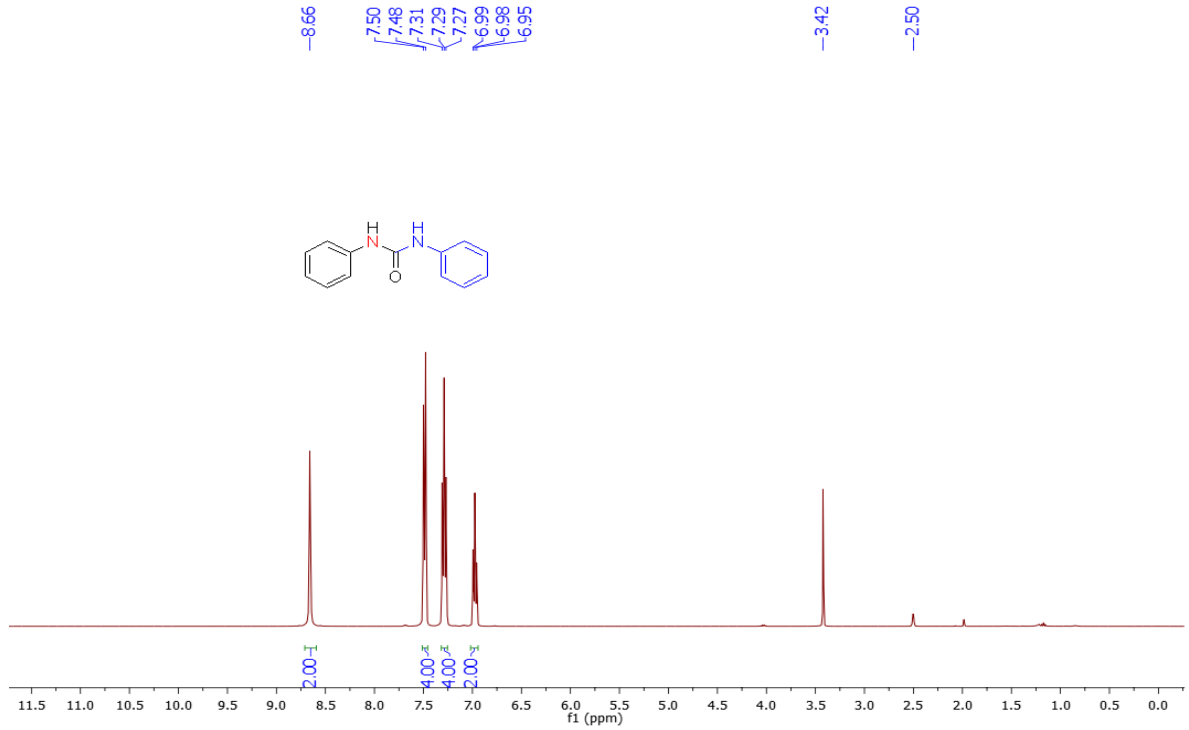
General Procedure for gram scale reaction

1,3-Diphenylurea **(3a)**

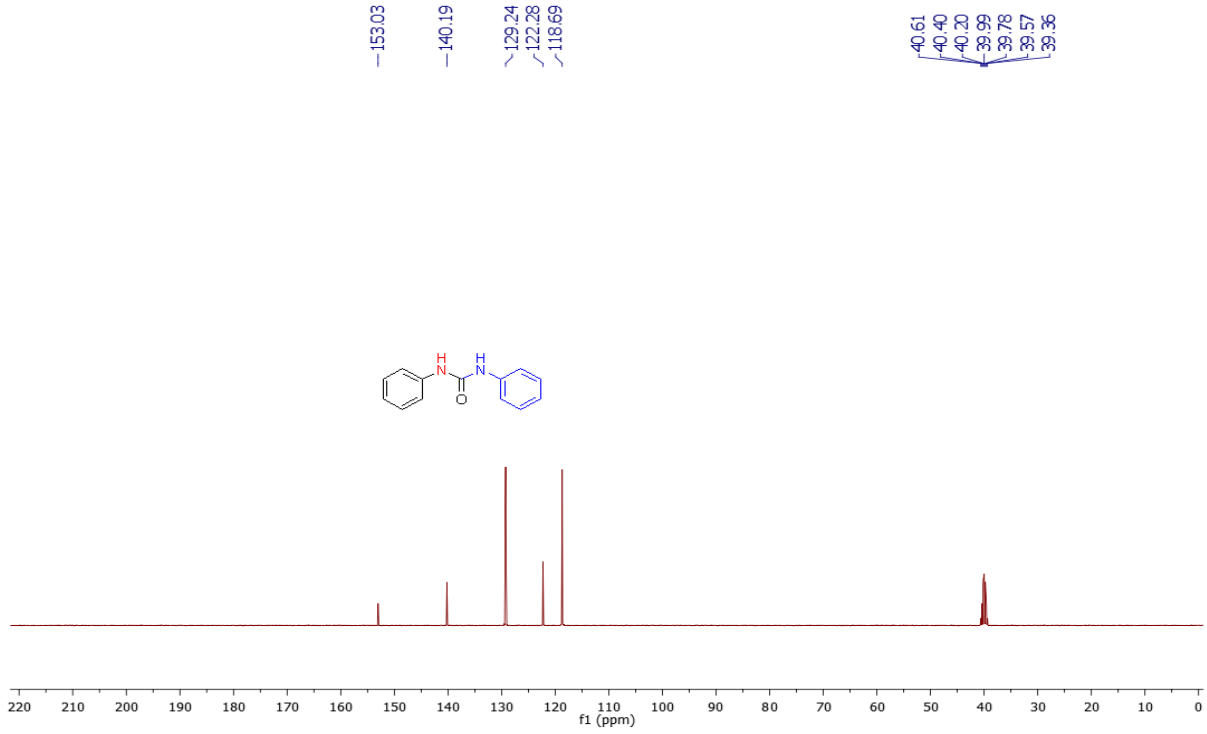
A solution of benzoic acid **1a** (5 g, 40.98 mmol) and trichlorotriazine (TCT) (2.48 g, 13.52 mmol) in CH_3CN (50 ml) was mixed with *N*-methylmorpholine (NMM) (5.79 g, 57.37 mmol) at room temperature and stirred for 30 minutes and monitored on TLC for the consumption of TCT. To the reaction mixture NaN_3 (3.9 g, 57.37 mmol) and DMAP (10 mol%) were added and reaction mixture stirred for 4-5 hrs at room temperature and observed for the formation of acyl azide **2** and consumption of benzoic acid by TLC. Then, the aniline (5.3 g, 57.37 mmol) was added and the reaction mixture was subjected to reflux at 80 ^{0}C in an oil bath, facilitating Curtius rearrangement leading to the *in situ* formation of isocyanate and click coupling. The product formation was monitored by TLC. Reaction mixture was subjected to rota vapour to evaporate CH_3CN and then extraction with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The organic layer was evaporated under pressure to obtain the crude product which was then purified by flash column chromatography using ethyl acetate and hexane to offered the required product **3a** (yield 7.4 g, 86 %).

Spectral copies of synthesized compounds

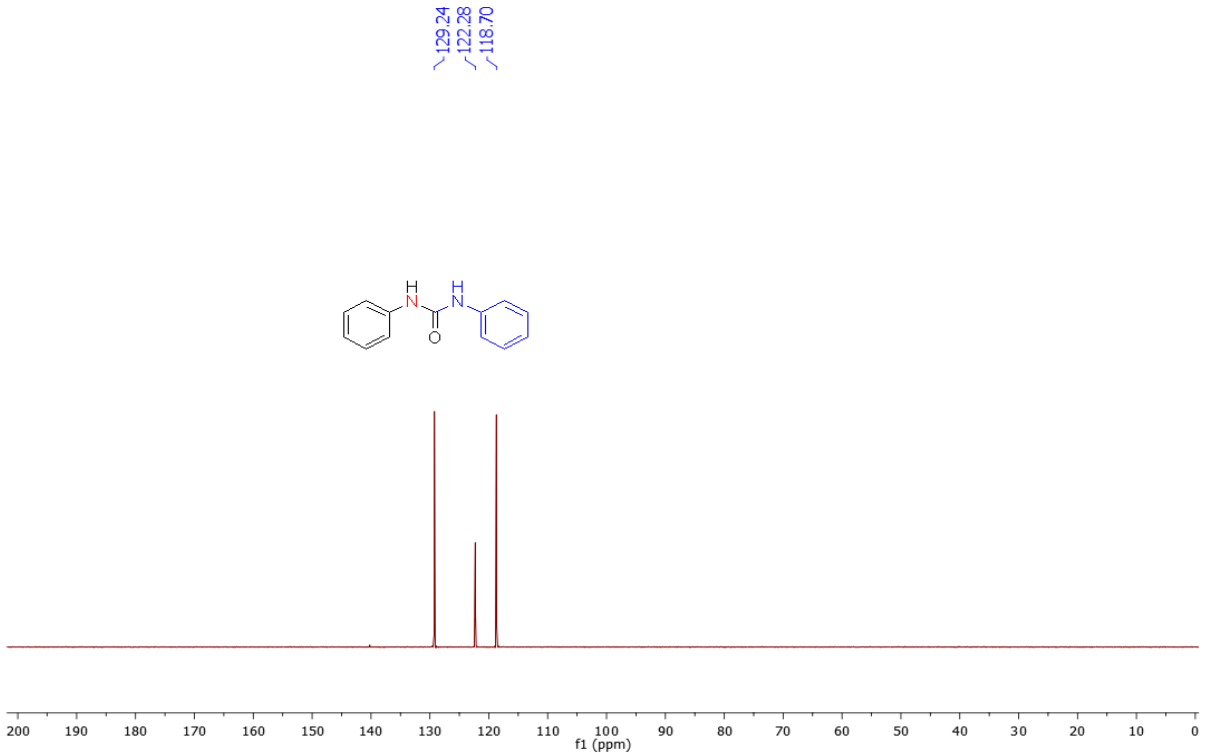
^{1}H-NMR of 1,3-diphenylurea (3a)



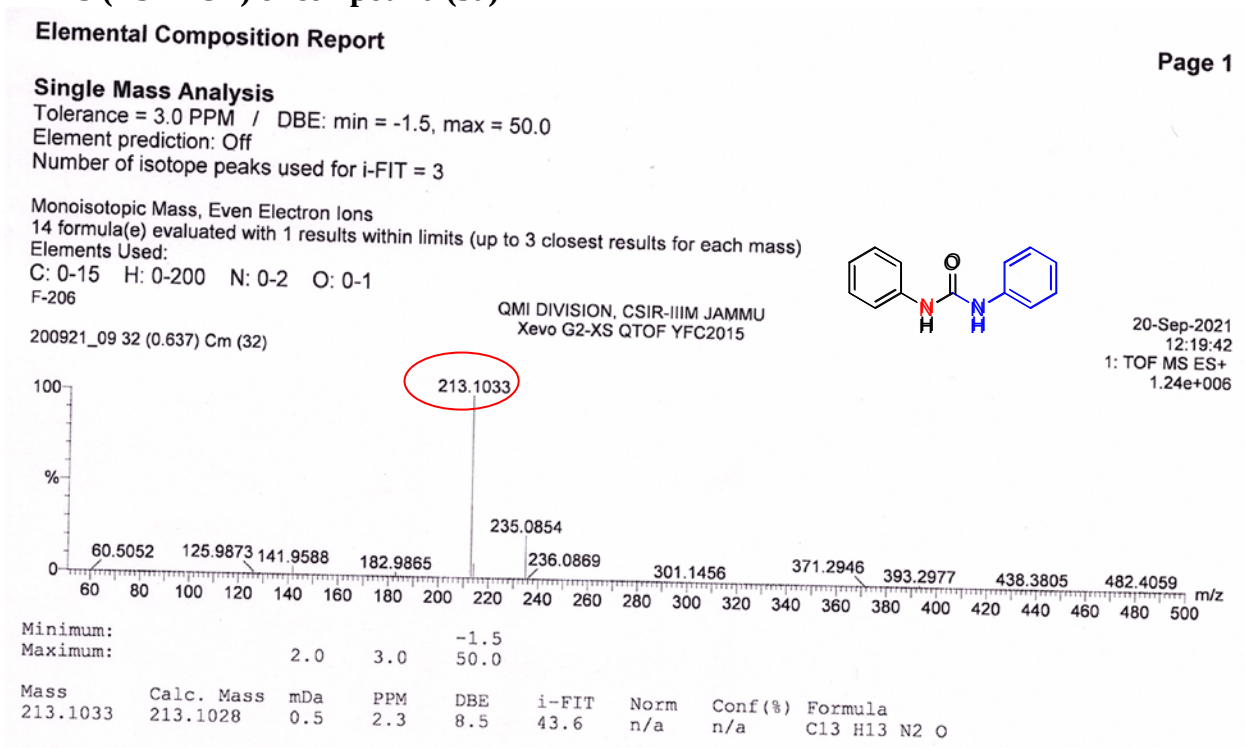
^{13}C-NMR of 1,3-diphenylurea (3a)



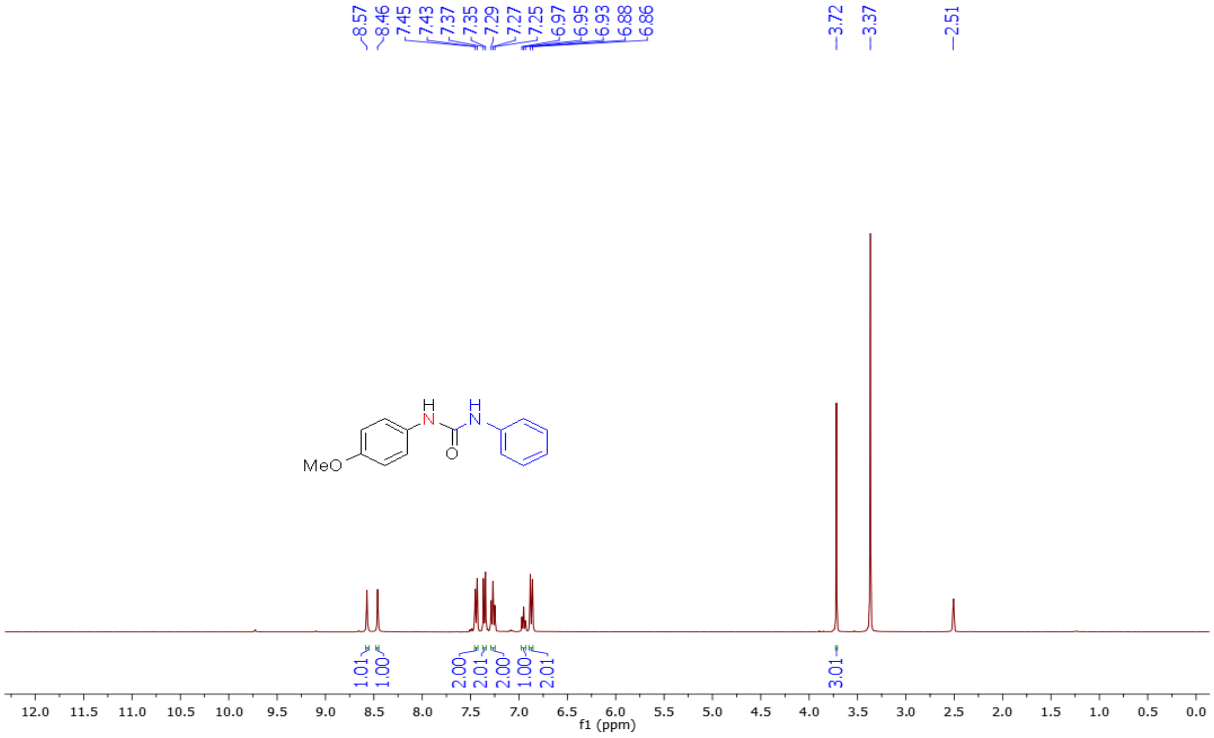
DEPT of 1,3-diphenylurea (3a)



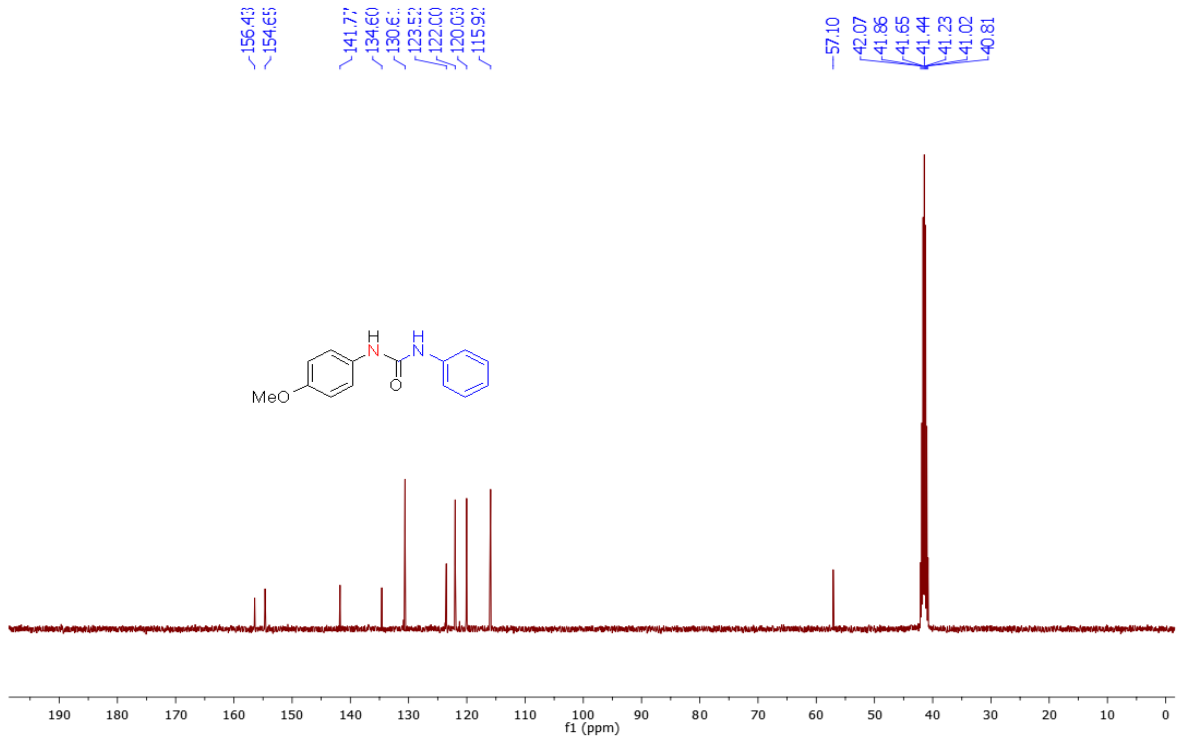
HRMS (ESI-TOF) of compound (3a)



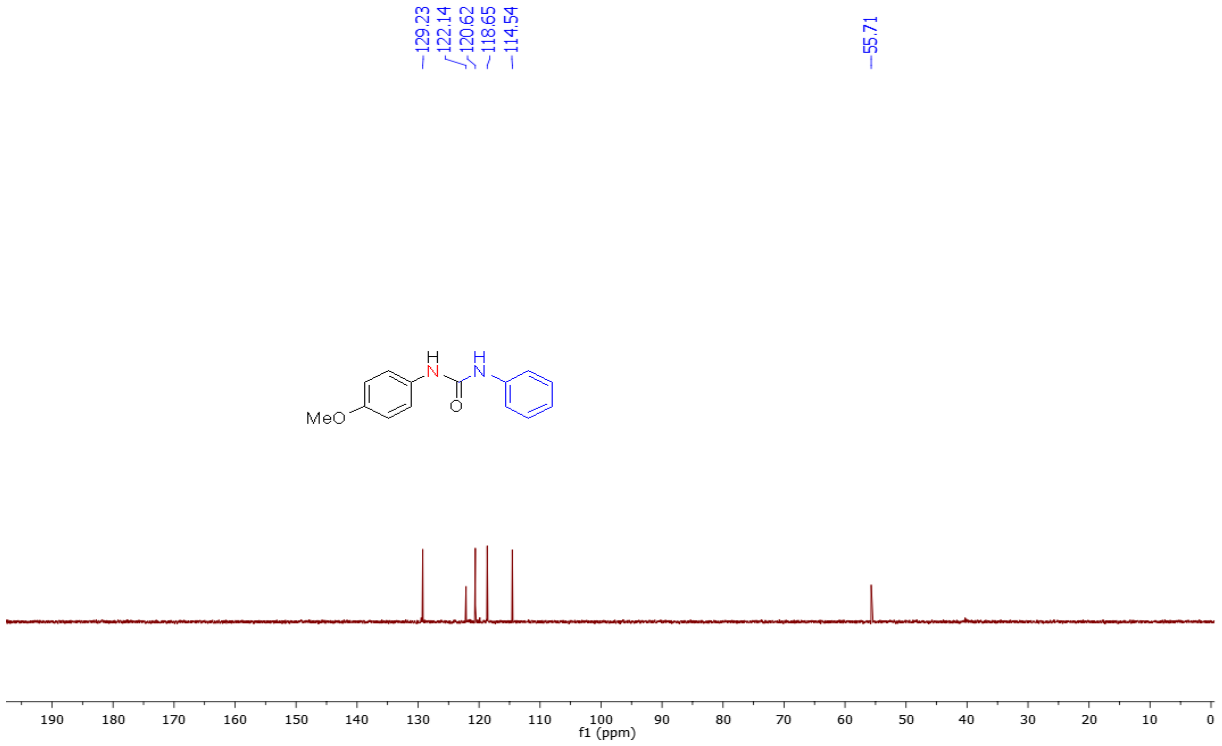
^{1}H-NMR of 1-(4-methoxyphenyl)-3-phenylurea (3b)



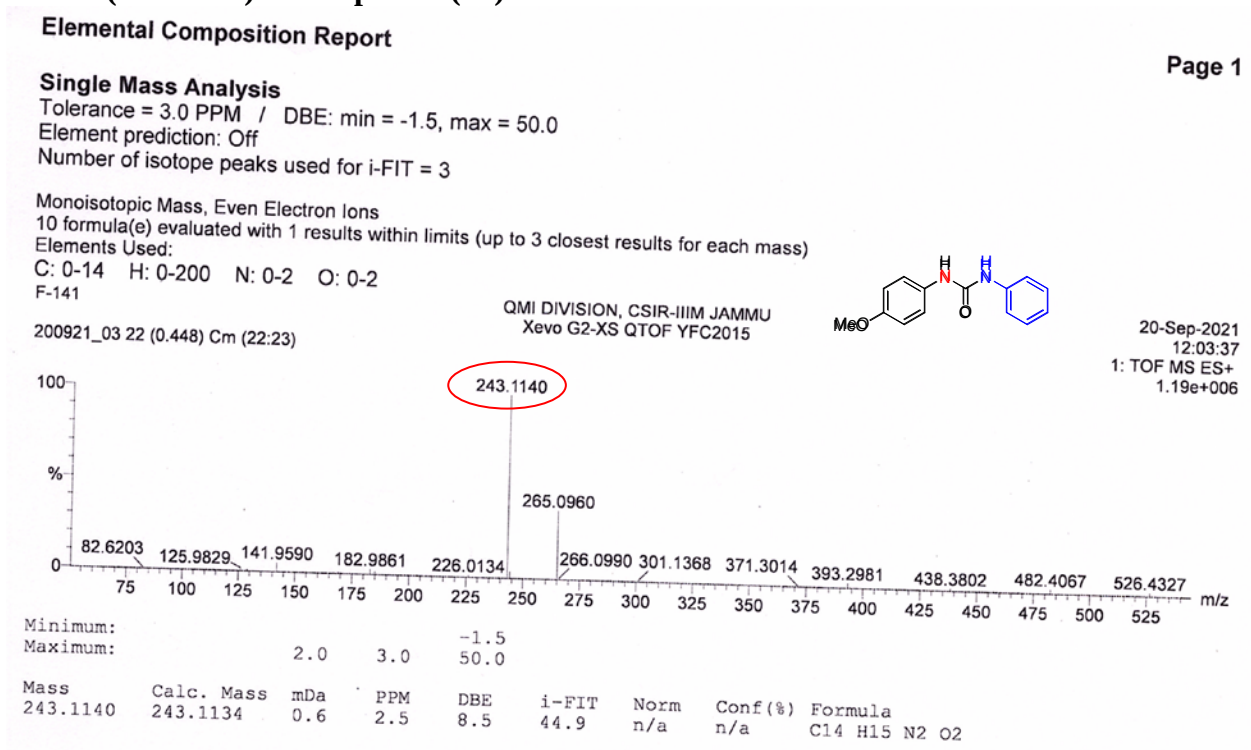
^{13}C-NMR of 1-(4-methoxyphenyl)-3-phenylurea (3b)



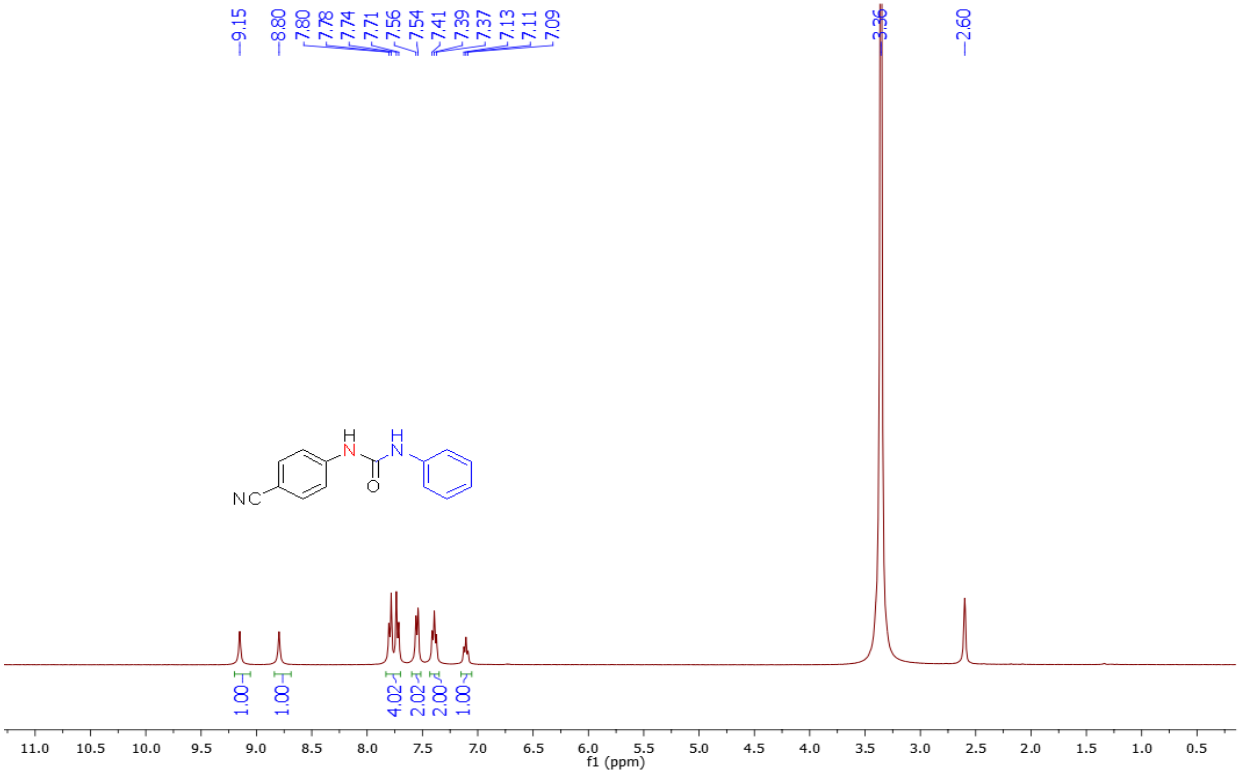
DEPT of 1-(4-methoxyphenyl)-3-phenylurea (3b)



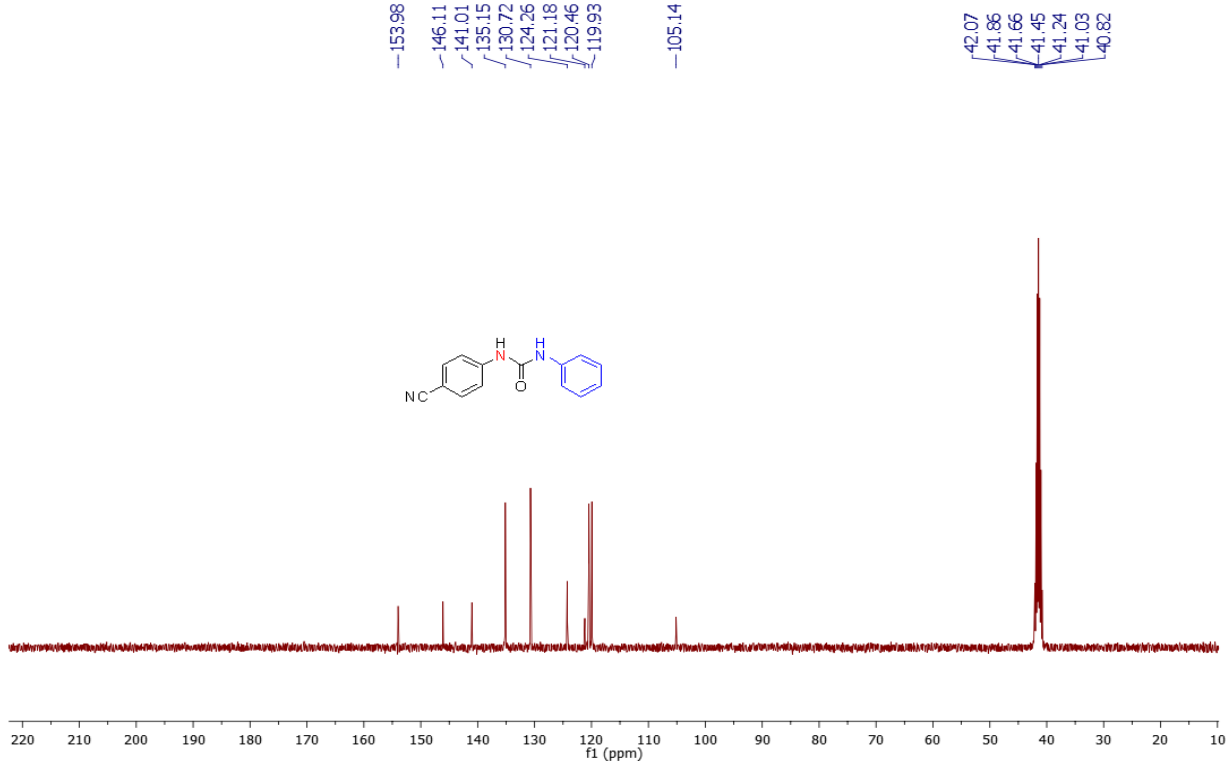
HRMS (ESI-TOF) of compound (3b)



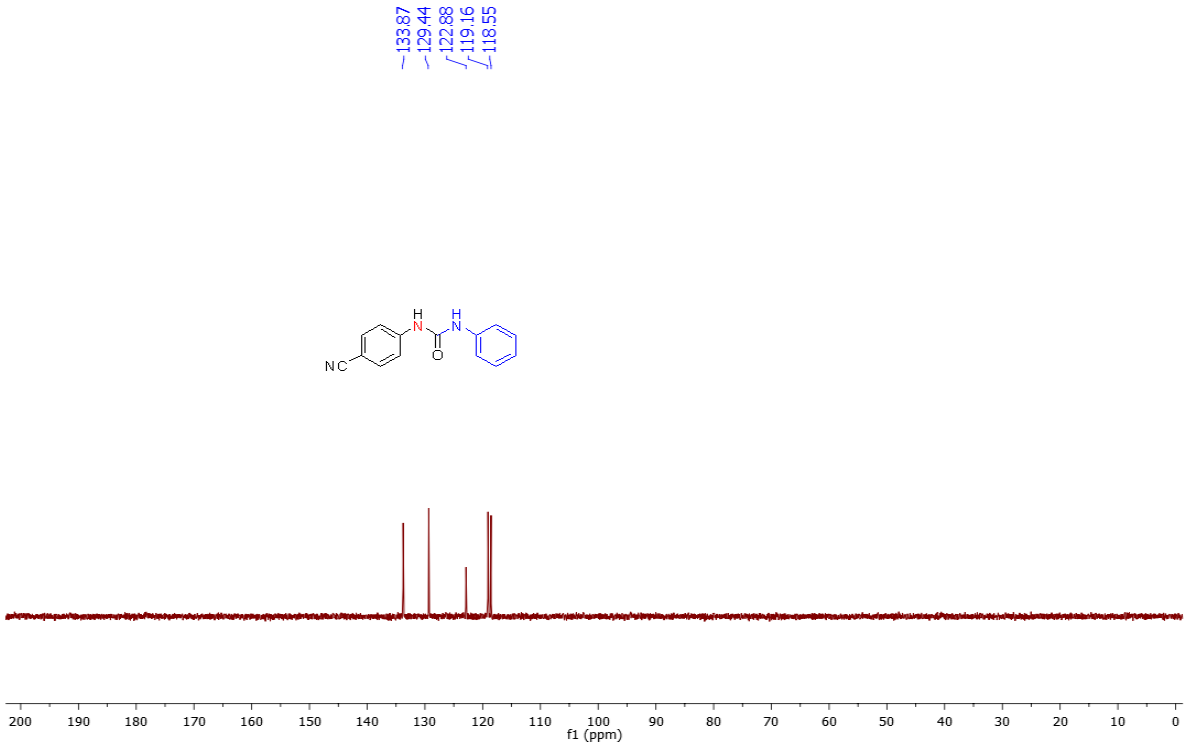
[1]H-NMR of 1-(4-cyanophenyl)-3-phenylurea (3c)



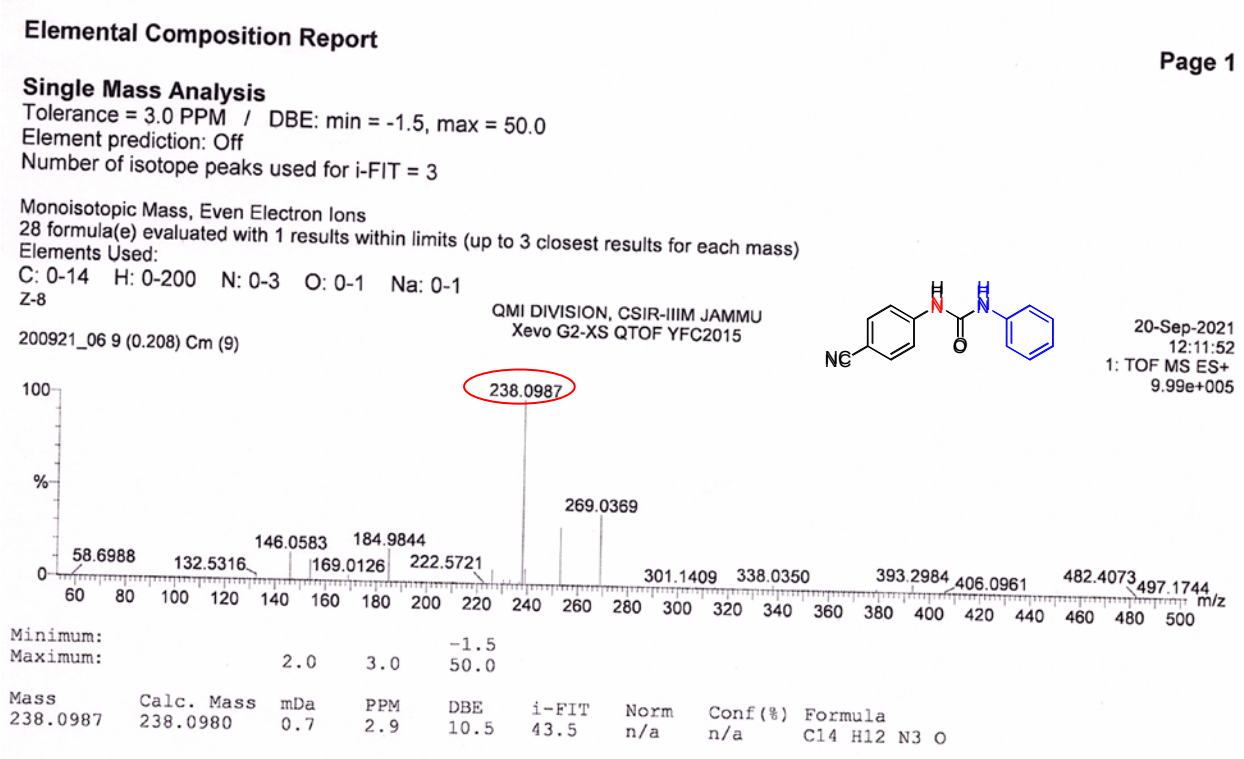
[13]C-NMR of 1-(4-cyanophenyl)-3-phenylurea (3c)



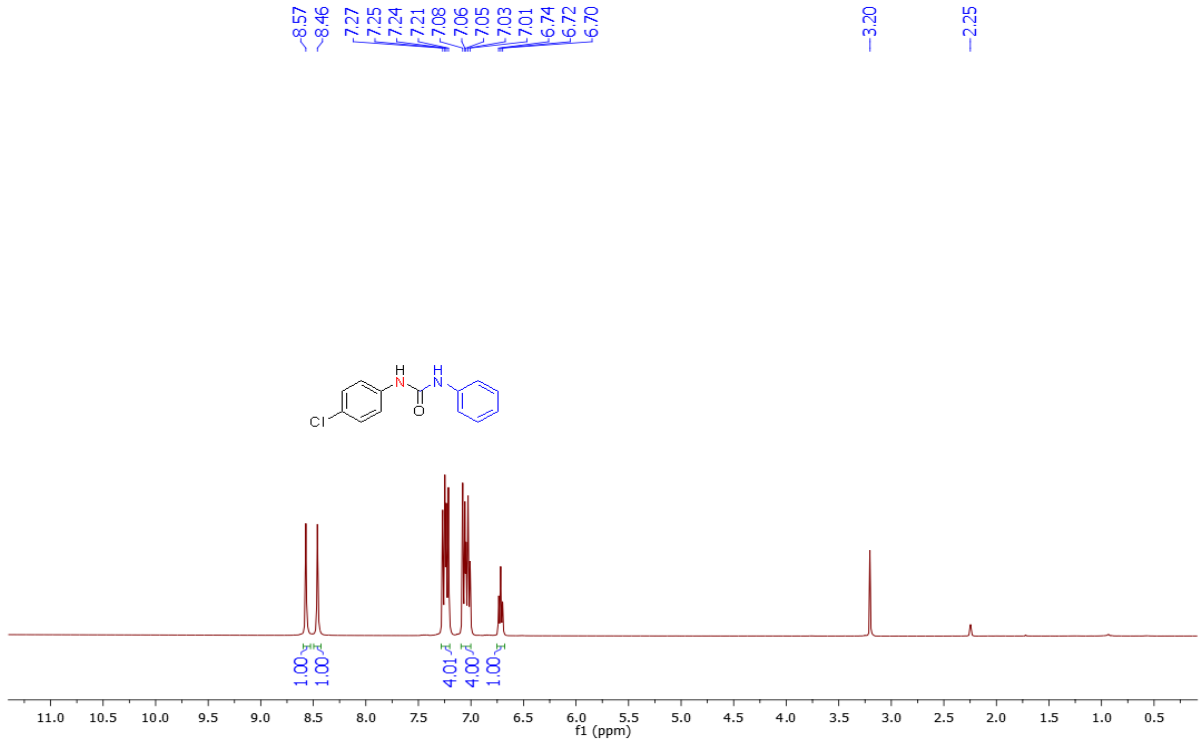
DEPT of 1-(4-cyanophenyl)-3-phenylurea (3c)



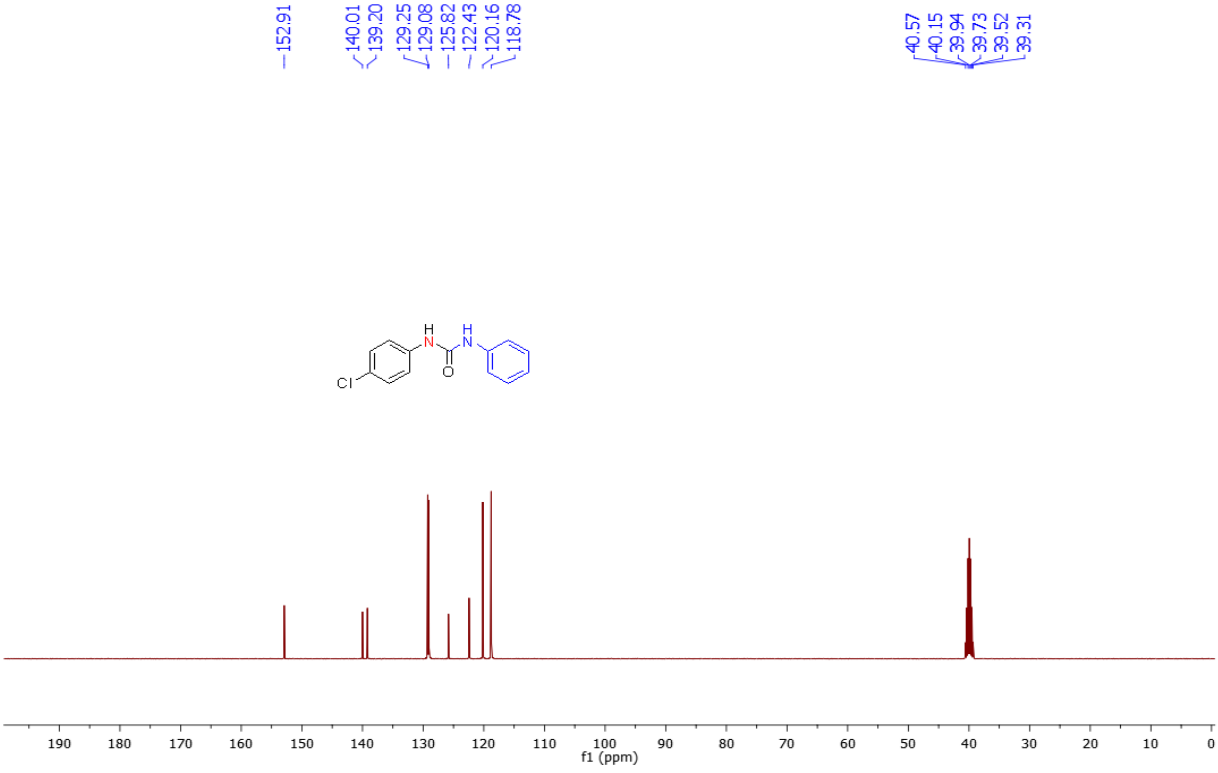
HRMS (ESI-TOF) of compound (3c)



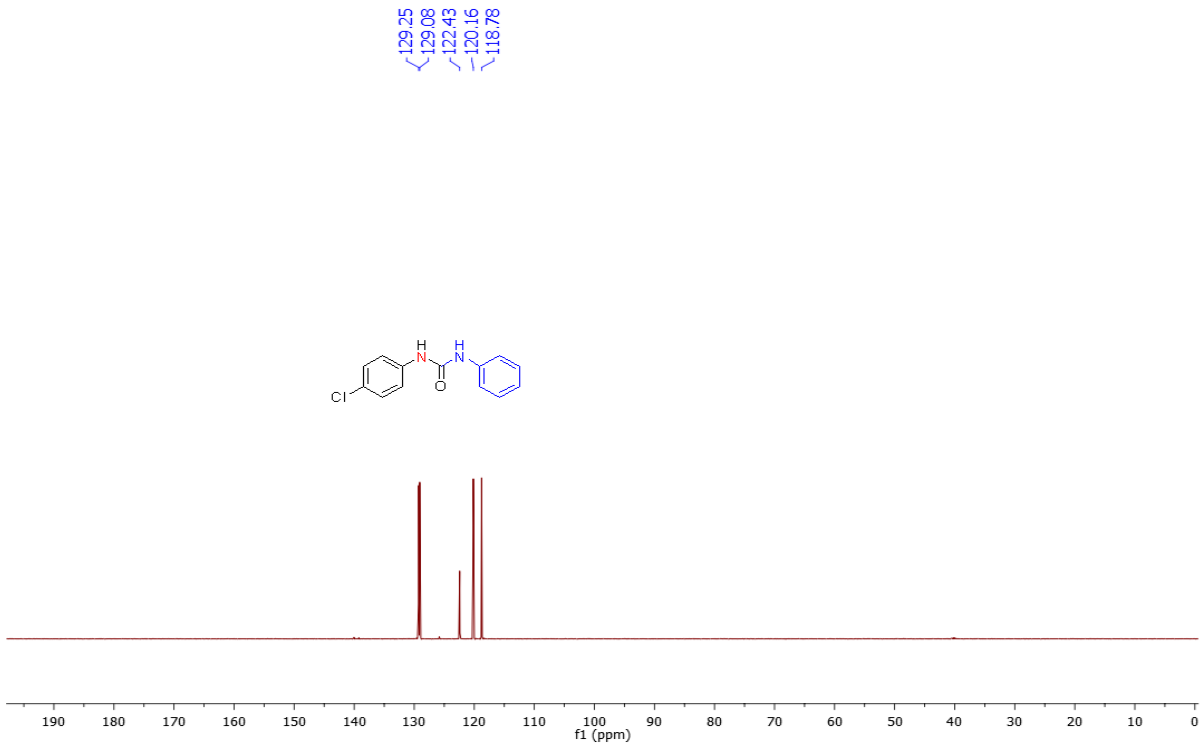
^{1}H-NMR of 1-(4-chlorophenyl)-3-phenylurea (3d)



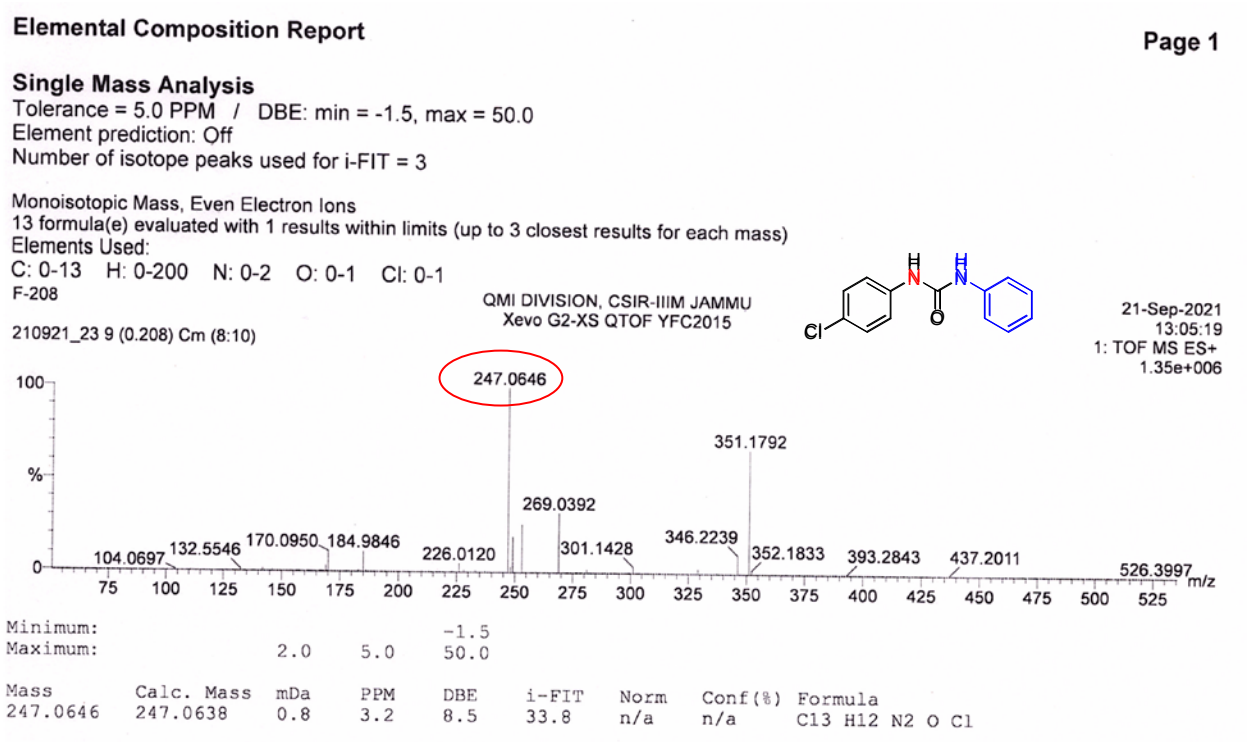
^{13}C-NMR of 1-(4-chlorophenyl)-3-phenylurea (3d)



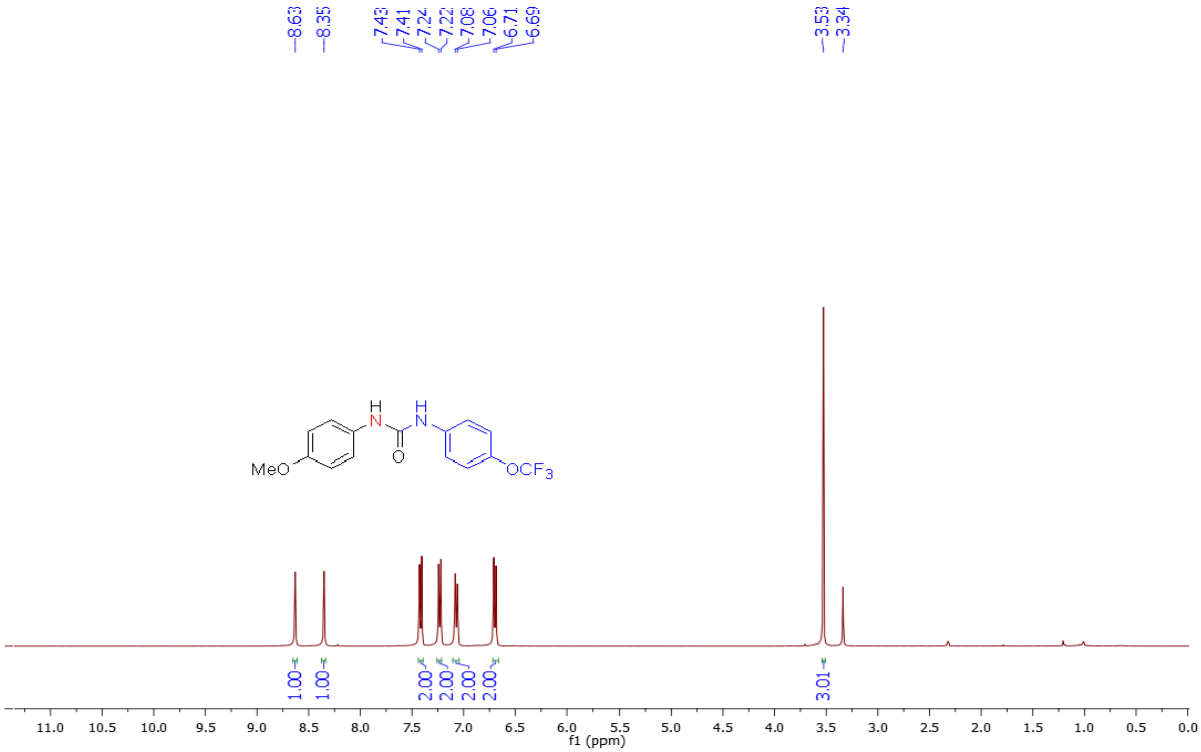
DEPT of 1-(4-chlorophenyl)-3-phenylurea (3d)



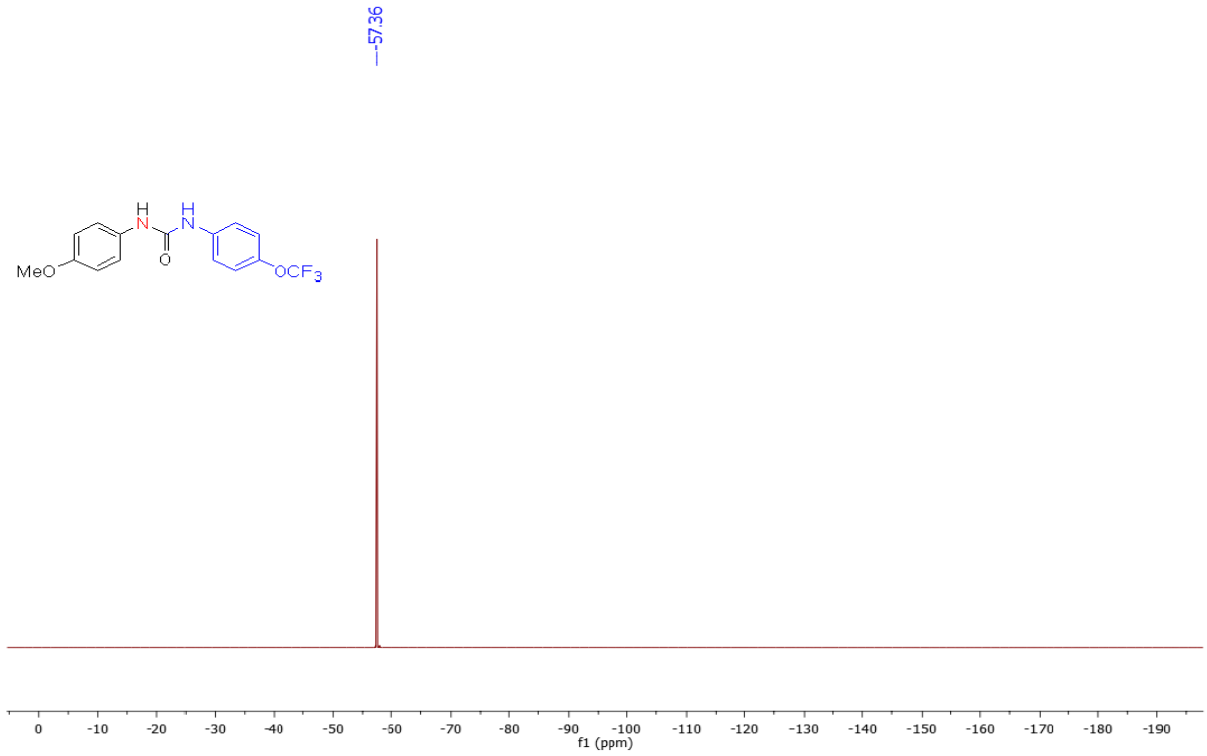
HRMS (ESI-TOF) of compound (3d)



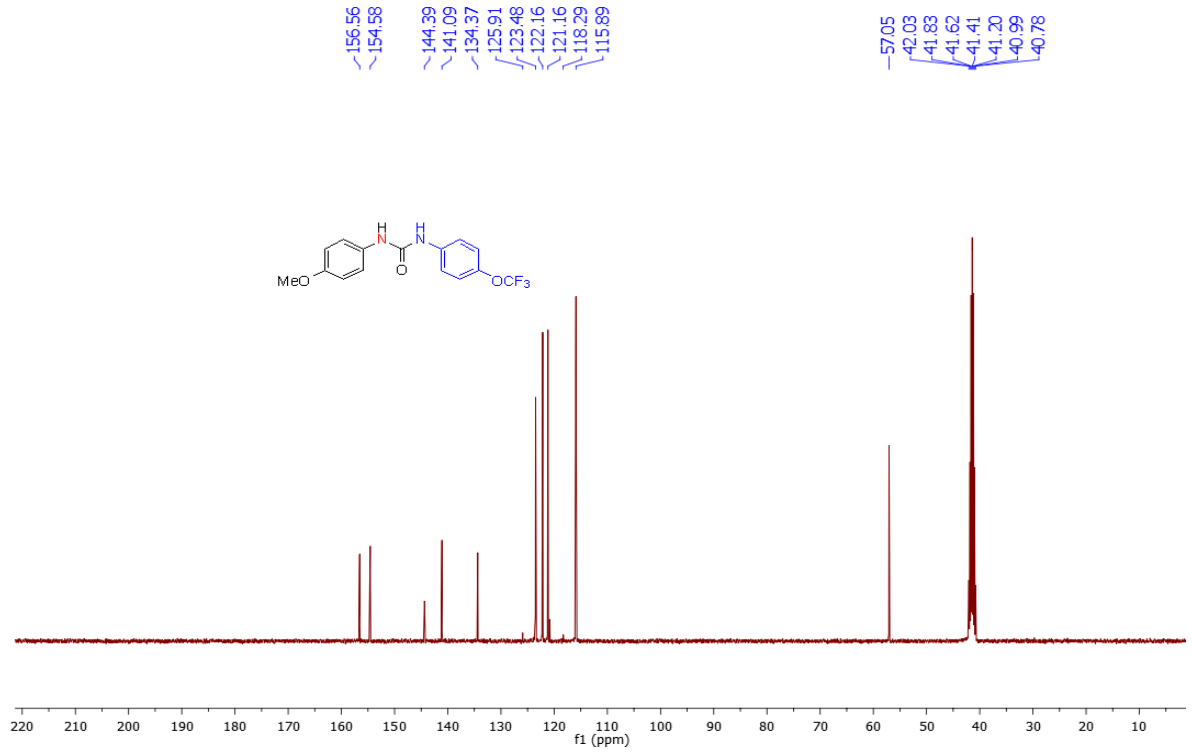
[1]H-NMR of 1-(4-methoxyphenyl)-3-(4-(trifluoromethoxy)phenyl)urea (3e)



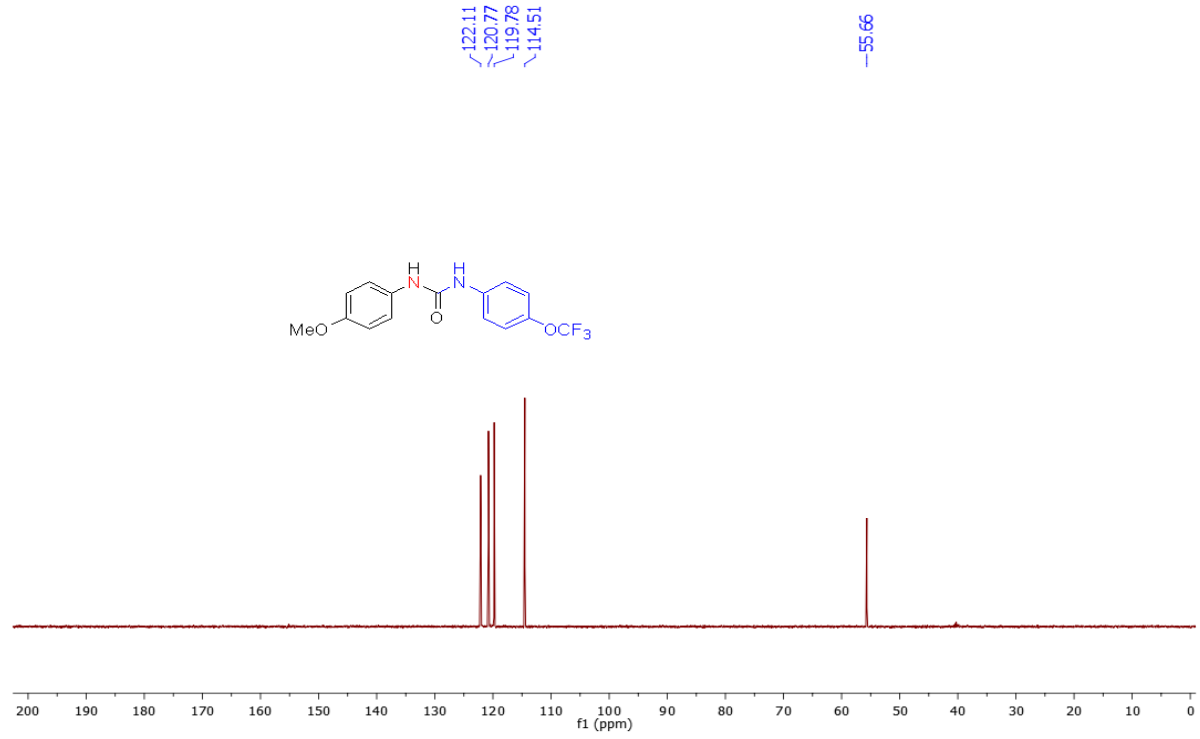
[19]F-NMR of 1-(4-methoxyphenyl)-3-(4-(trifluoromethoxy)phenyl)urea (3e)



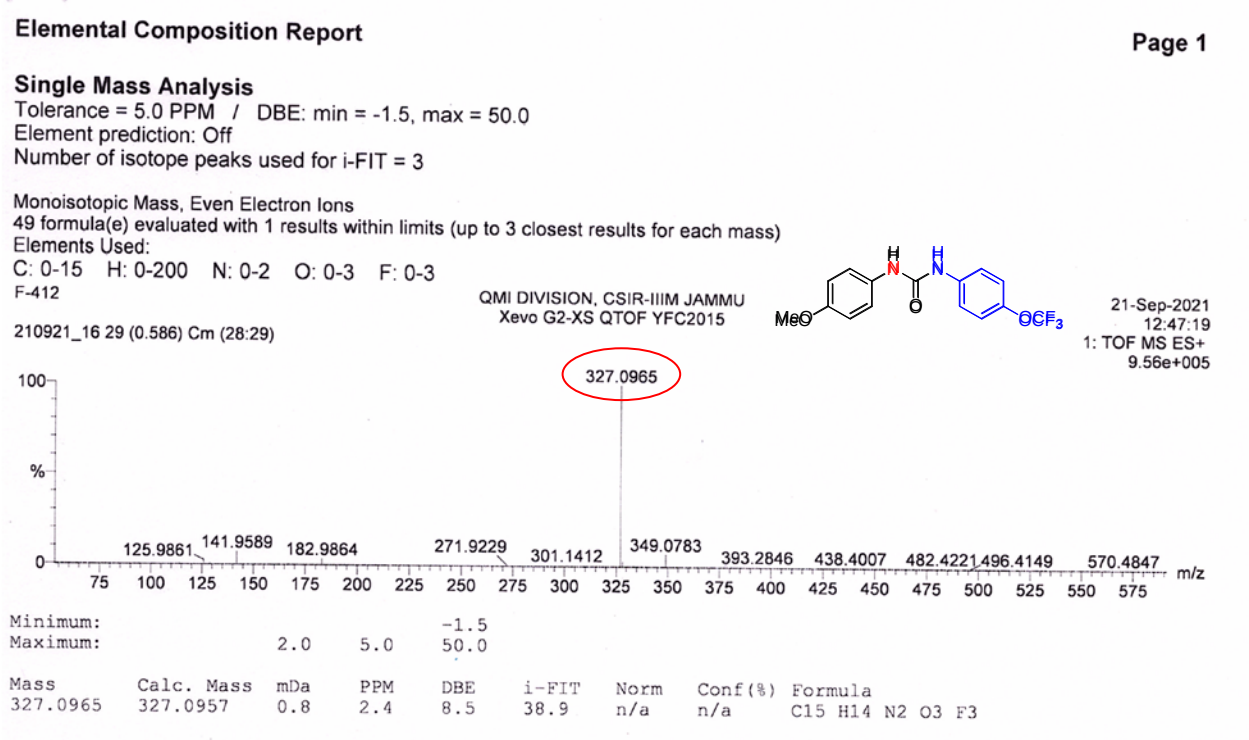
^{13}C-NMR of 1-(4-methoxyphenyl)-3-(4-(trifluoromethoxy)phenyl)urea (3e)



DEPT of 1-(4-methoxyphenyl)-3-(4-(trifluoromethoxy)phenyl)urea (3e)



HRMS (ESI-TOF) of compound (3e)



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
49 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-15 H: 0-200 N: 0-2 O: 0-3 F: 0-3
F-412

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

21-Sep-2021
12:47:19
1: TOF MS ES+
9.56e+005

210921_16 29 (0.586) Cm (28:29)

Minimum:				-1.5				
Maximum:		2.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
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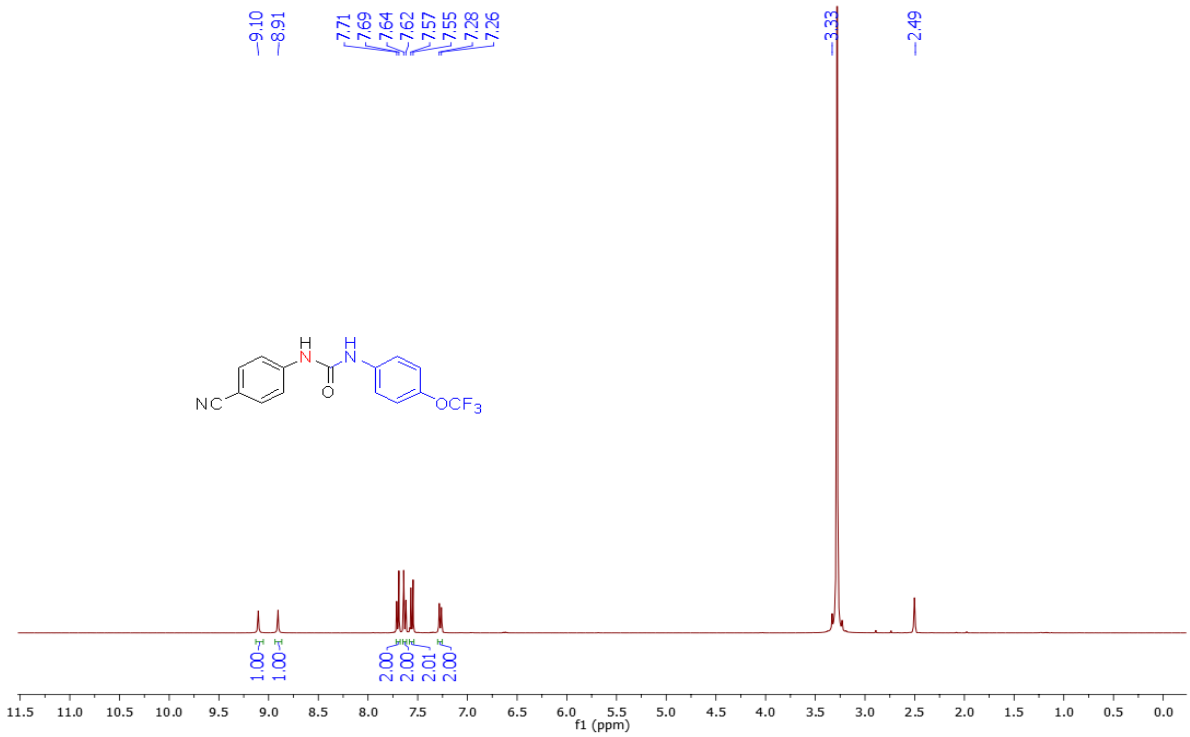
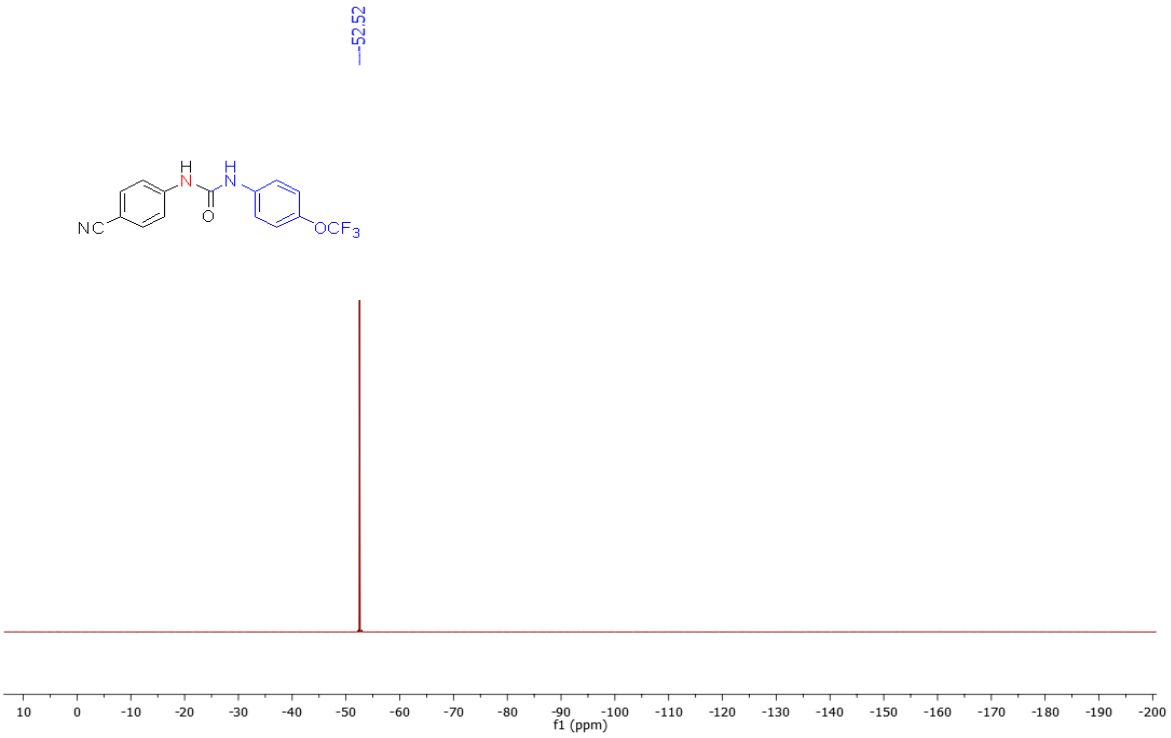
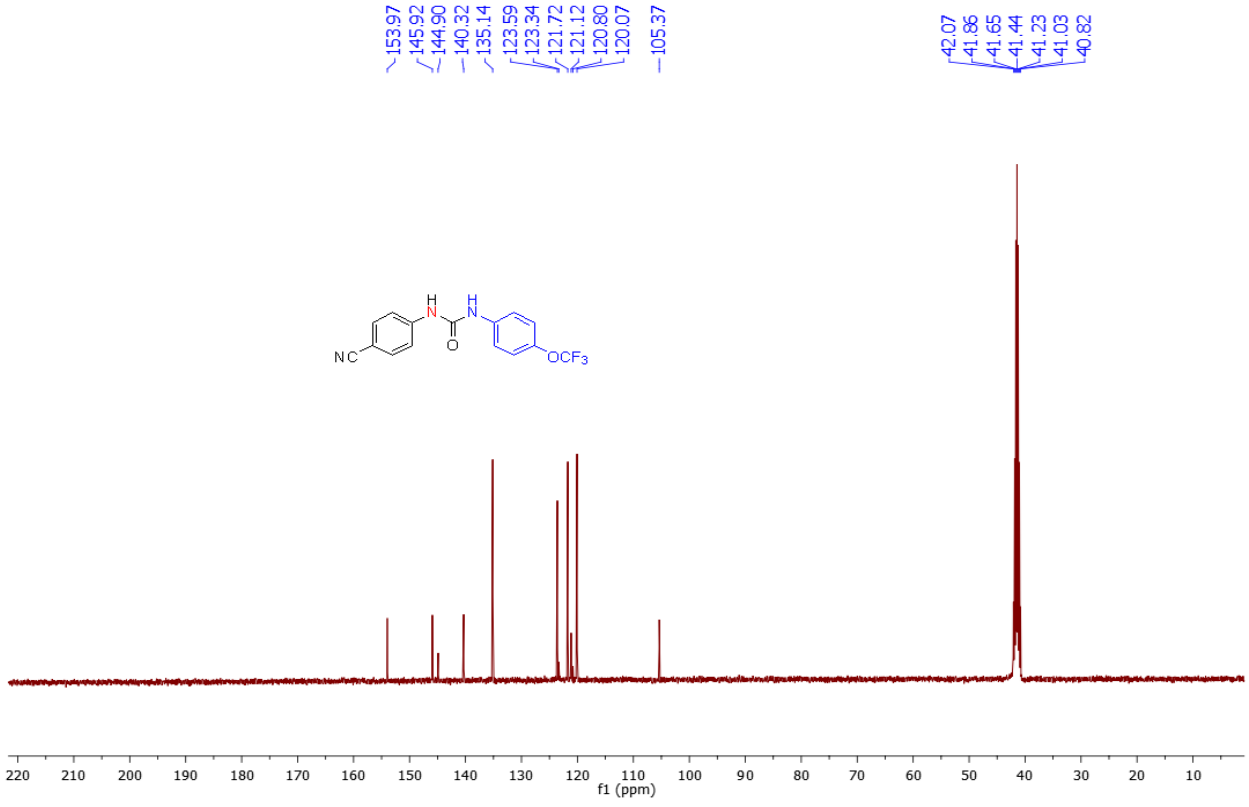
^{1}H-NMR of-3-(4-(1-(4-cyanophenyl trifluoromethoxy)phenyl)urea (3f)



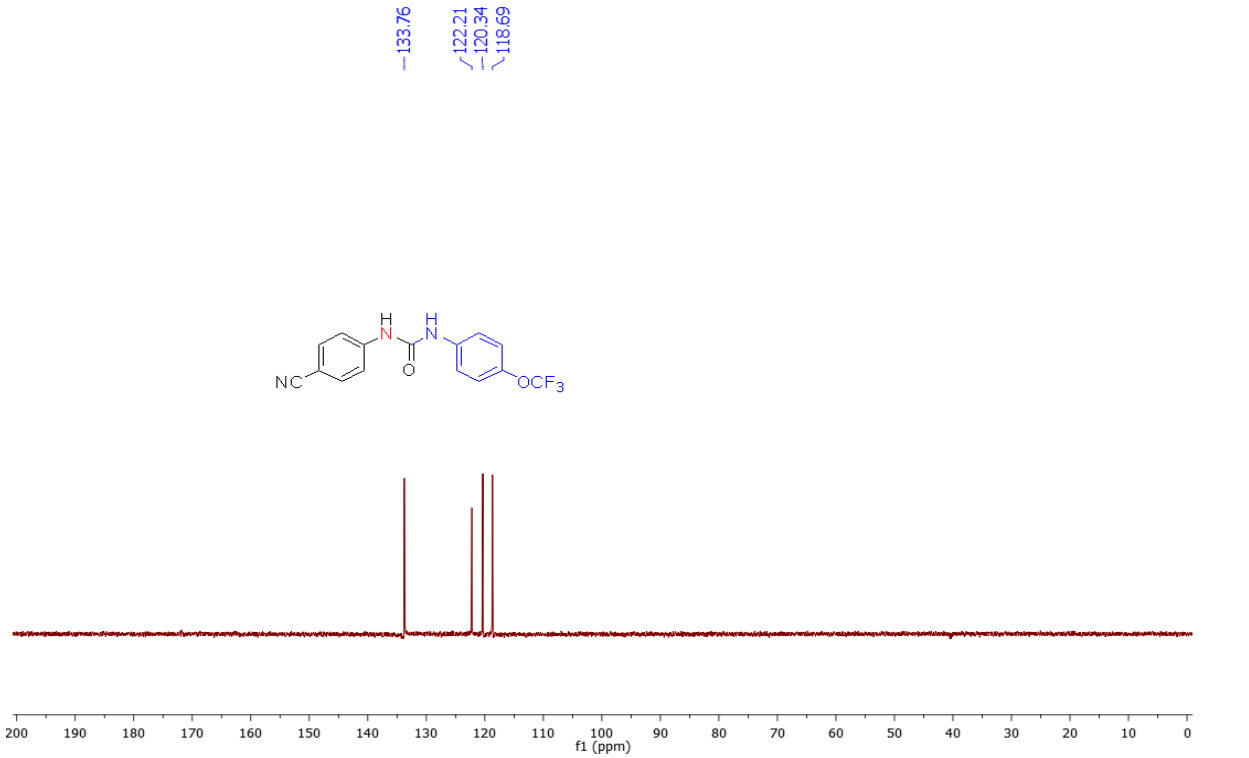
^{19}F-NMR of-3-(4-(1-(4-cyanophenyl trifluoromethoxy)phenyl)urea (3f)



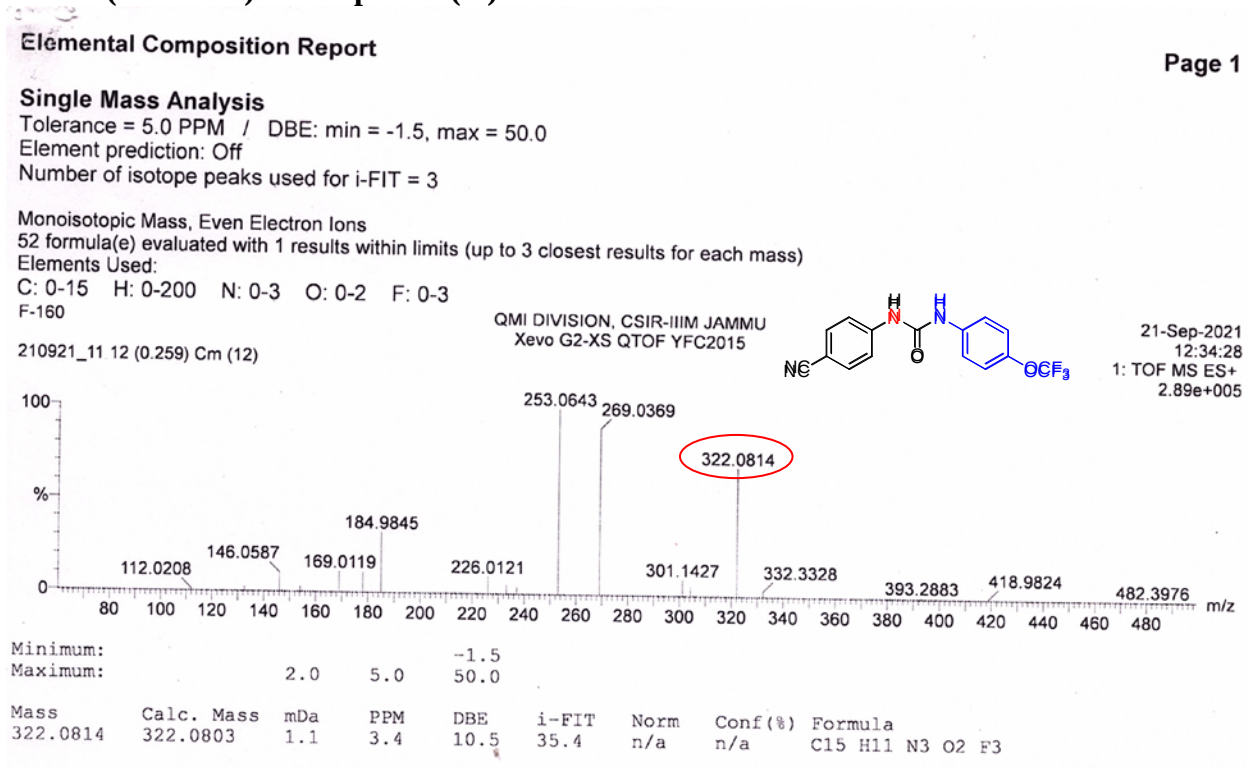
^{13}C-NMR of-3-(4-(1-(4-cyanophenyl trifluoromethoxy)phenyl)urea (3f)



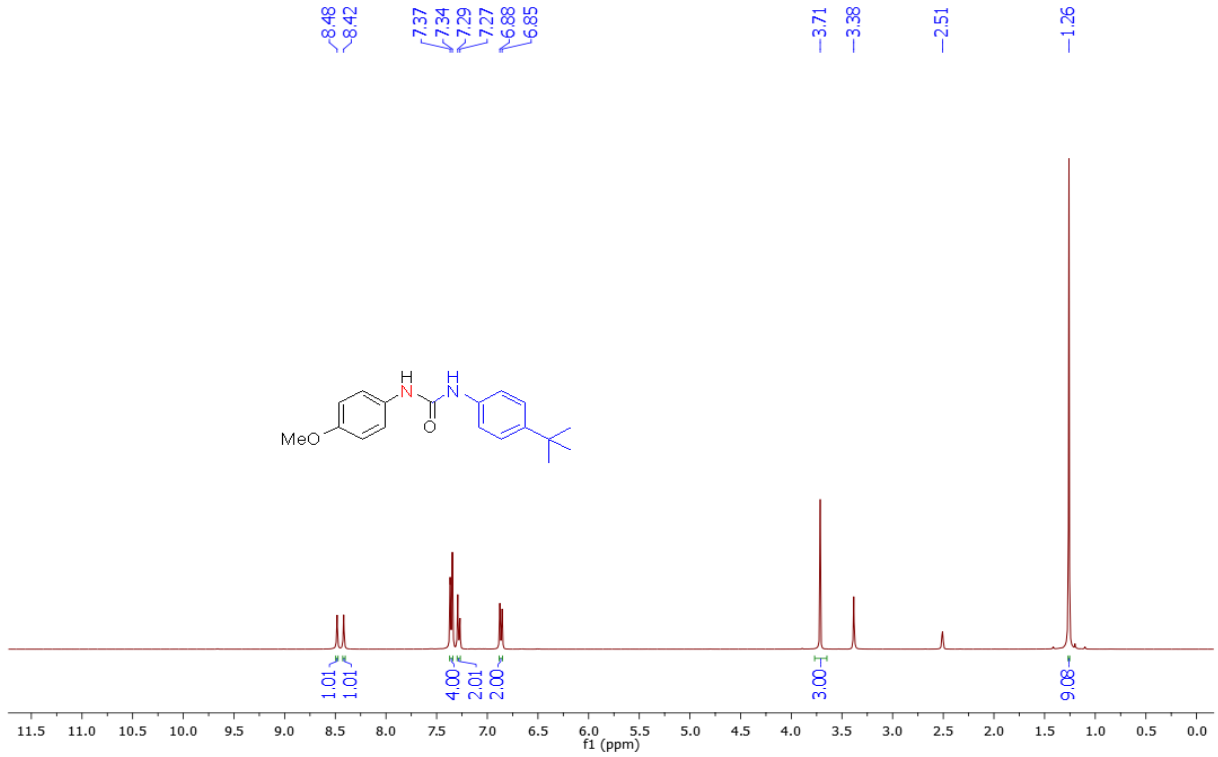
DEPT of-3-(4-(1-(4-cyanophenyl trifluoromethoxy)phenyl)urea (3f)



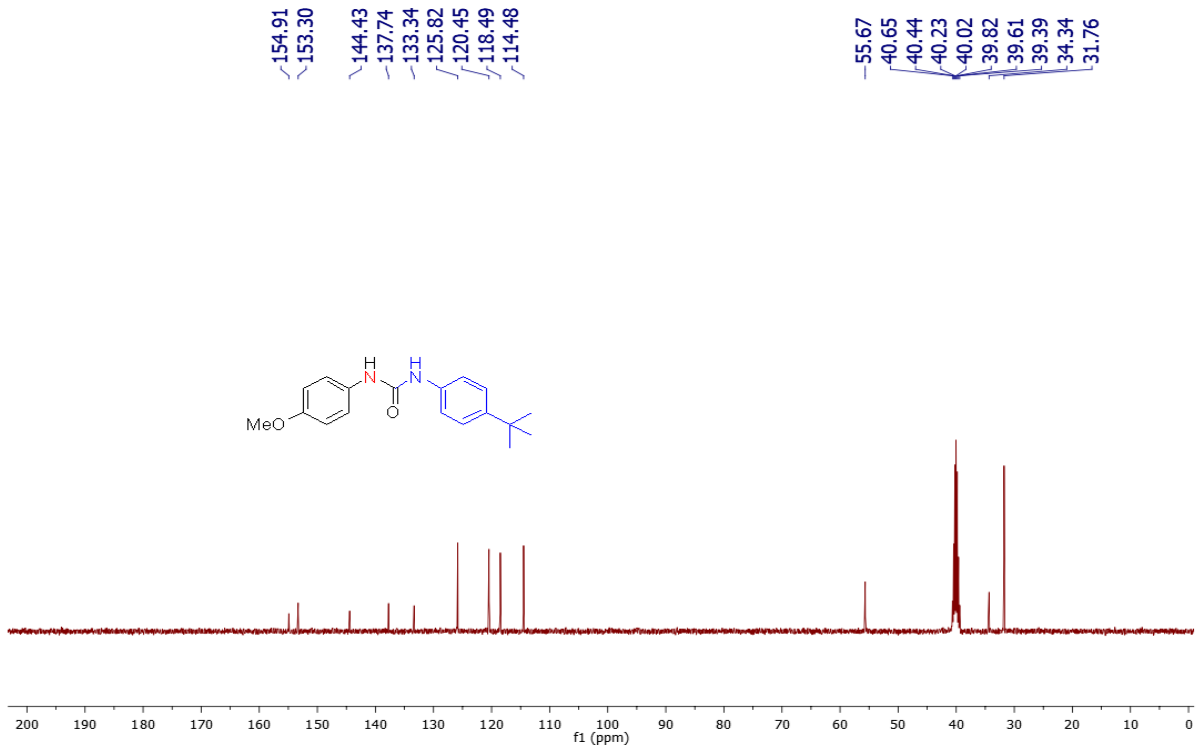
HRMS (ESI-TOF) of compound (3f)



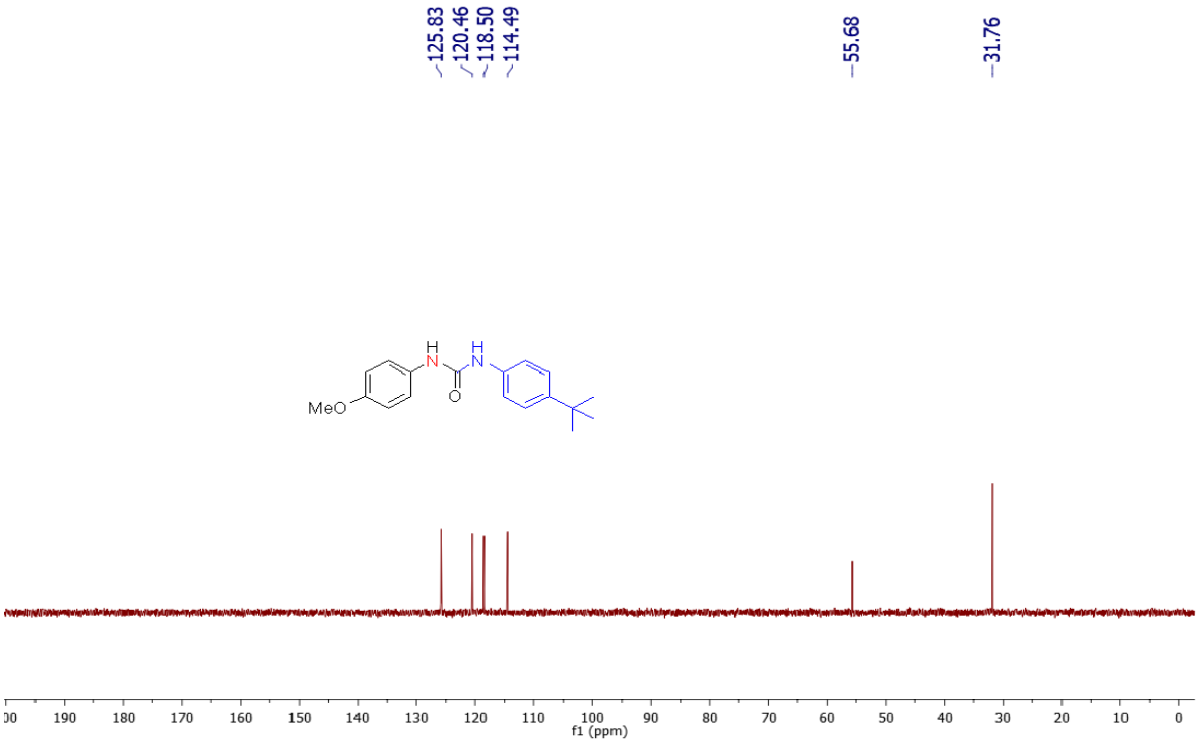
[1]H-NMR of 1-(4-(tert-butyl)phenyl)-3-(4-methoxyphenyl)urea (3g)



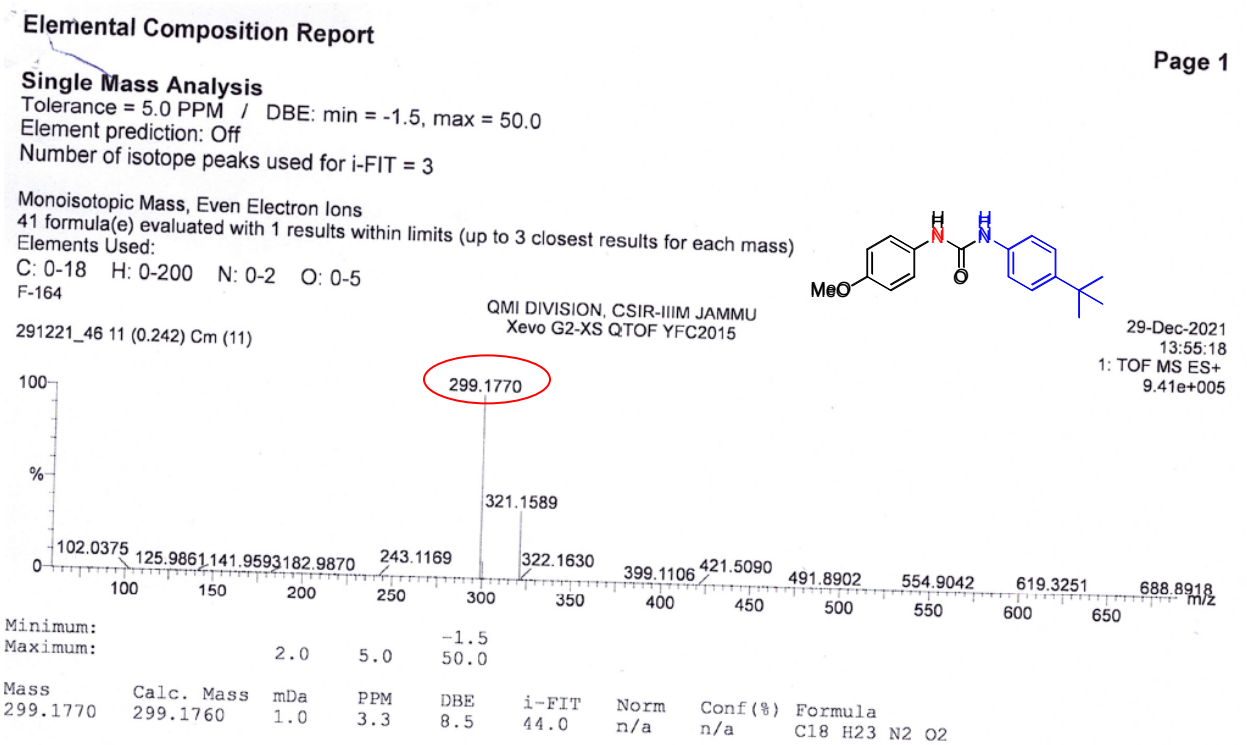
[13]C-NMR of 1-(4-(tert-butyl)phenyl)-3-(4-methoxyphenyl)urea (3g)



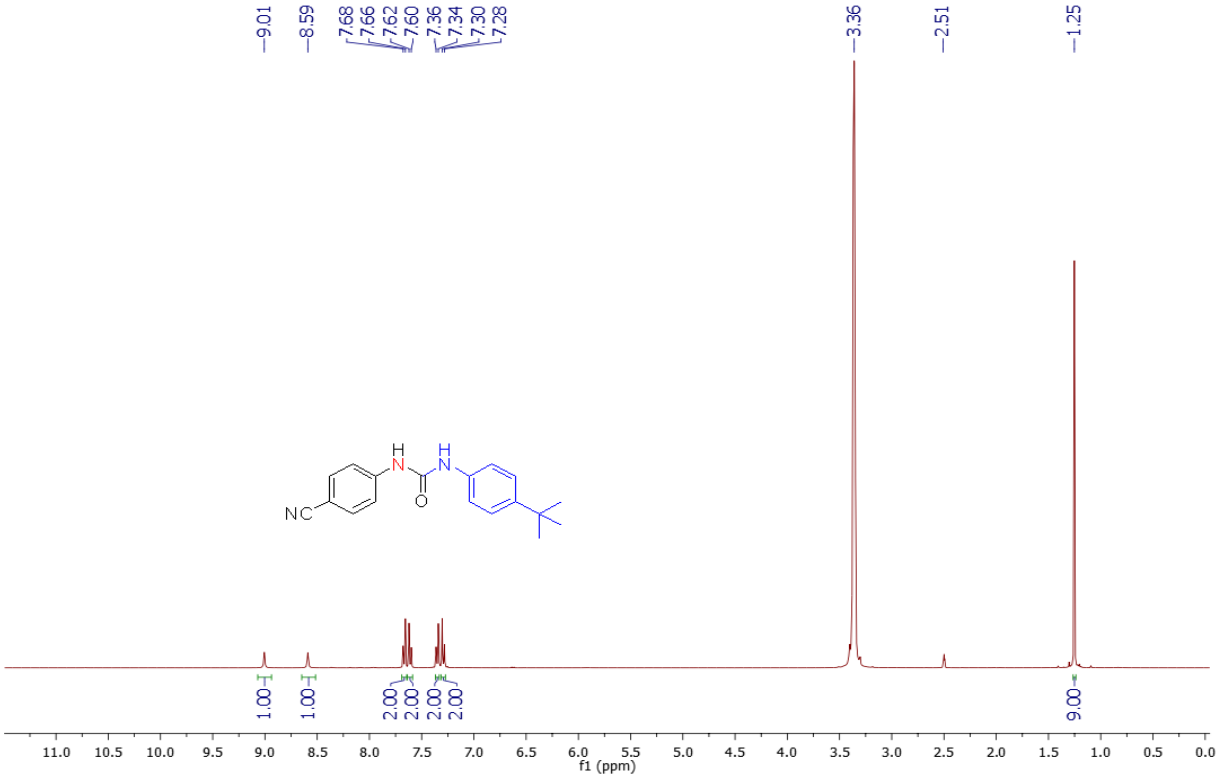
DEPT of 1-(4-(tert-butyl)phenyl)-3-(4-methoxyphenyl)urea (3g)



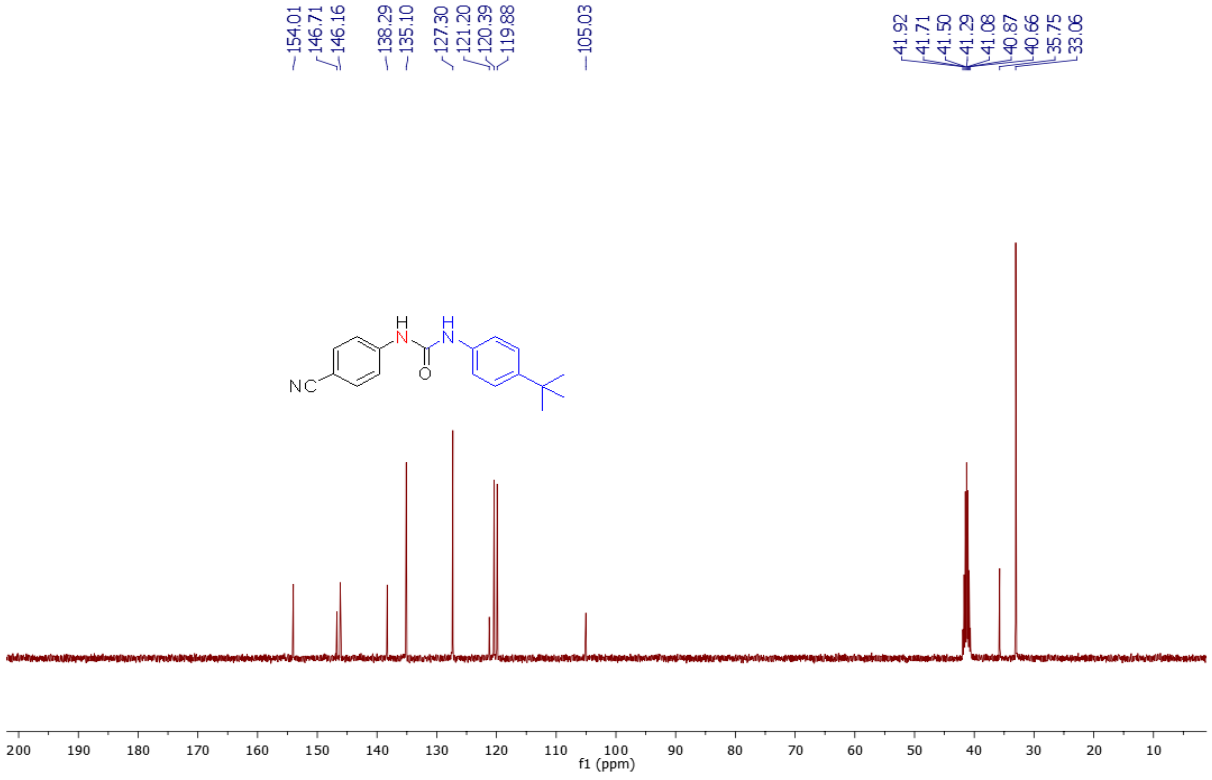
HRMS of 1-(4-(tert-butyl)phenyl)-3-(4-methoxyphenyl)urea (3g)



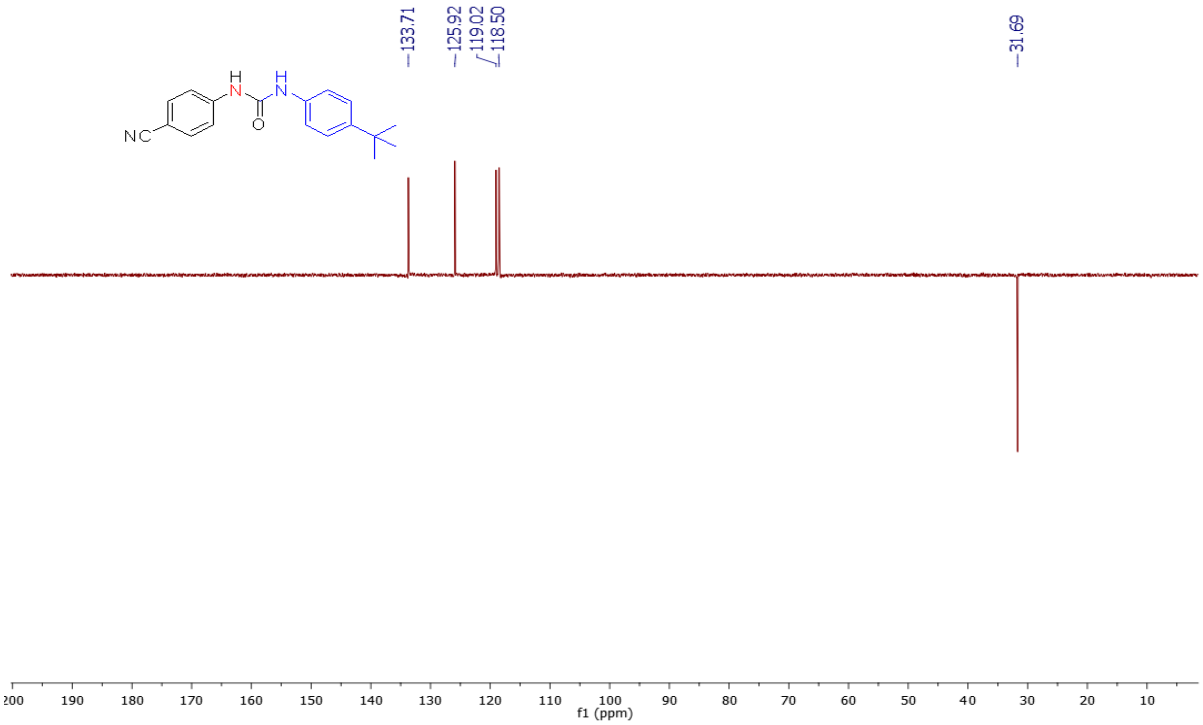
[1]H-NMR of 1-(4-(tert-butyl)phenyl)-3-(4-cyanophenyl)urea (3h)



[13]C-NMR of 1-(4-(tert-butyl)phenyl)-3-(4-cyanophenyl)urea (3h)



DEPT of 1-(4-(tert-butyl)phenyl)-3-(4-cyanophenyl)urea (3h)



HRMS of 1-(4-(tert-butyl)phenyl)-3-(4-cyanophenyl)urea (3h)

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-18 H: 0-200 N: 0-3 O: 0-1

F-162

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

28-Dec-2021
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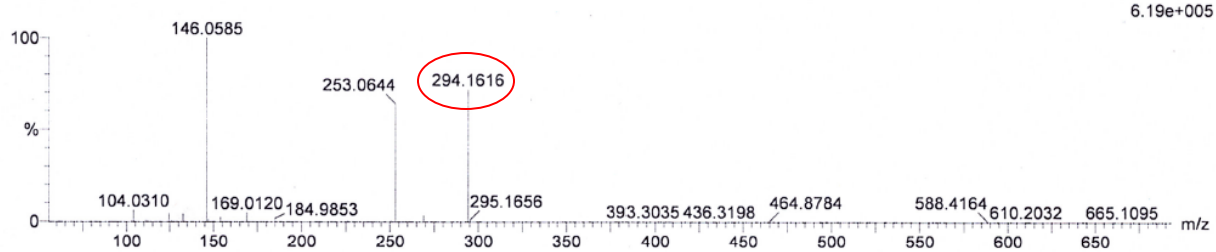
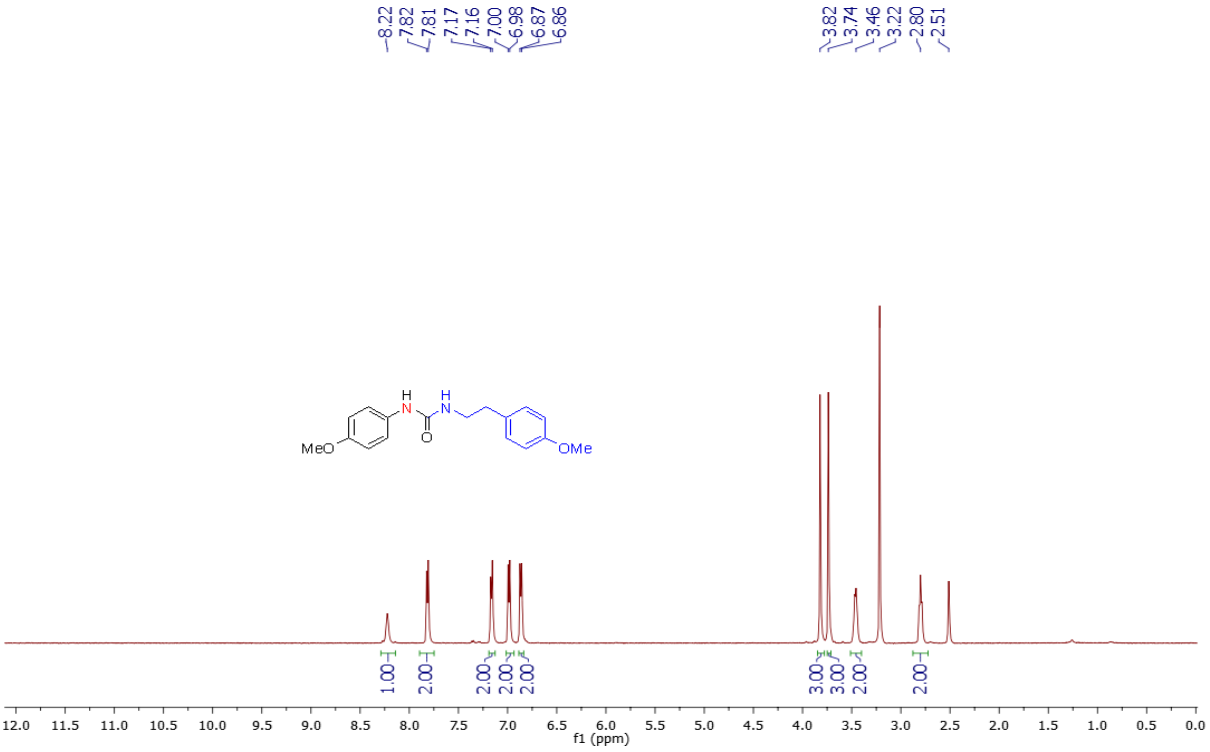
6.19e+005

281221_31 12 (0.259) Cm (12:14)

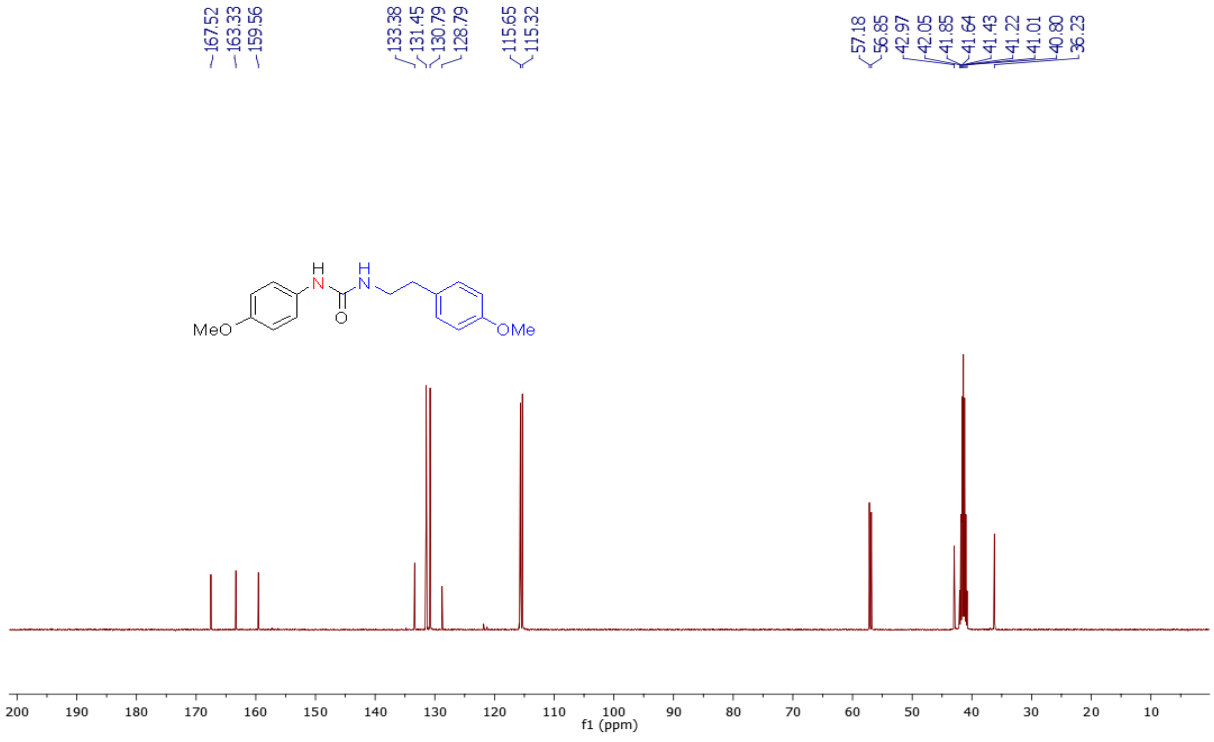


Minimum:				-1.5				
Maximum:		2.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
294.1616	294.1606	1.0	3.4	10.5	37.0	n/a	n/a	C18 H20 N3 O

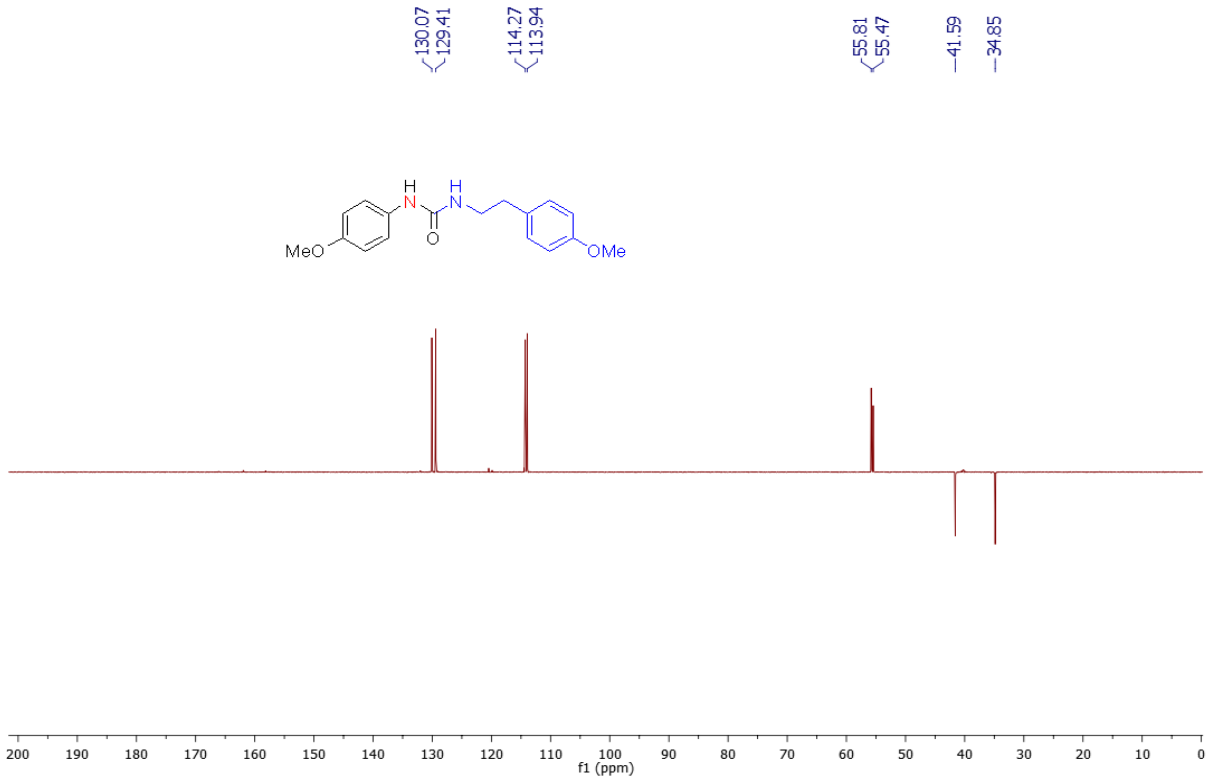
[1]H-NMR of 1-(4-methoxyphenethyl)-3-(4-methoxyphenyl)urea (3i)



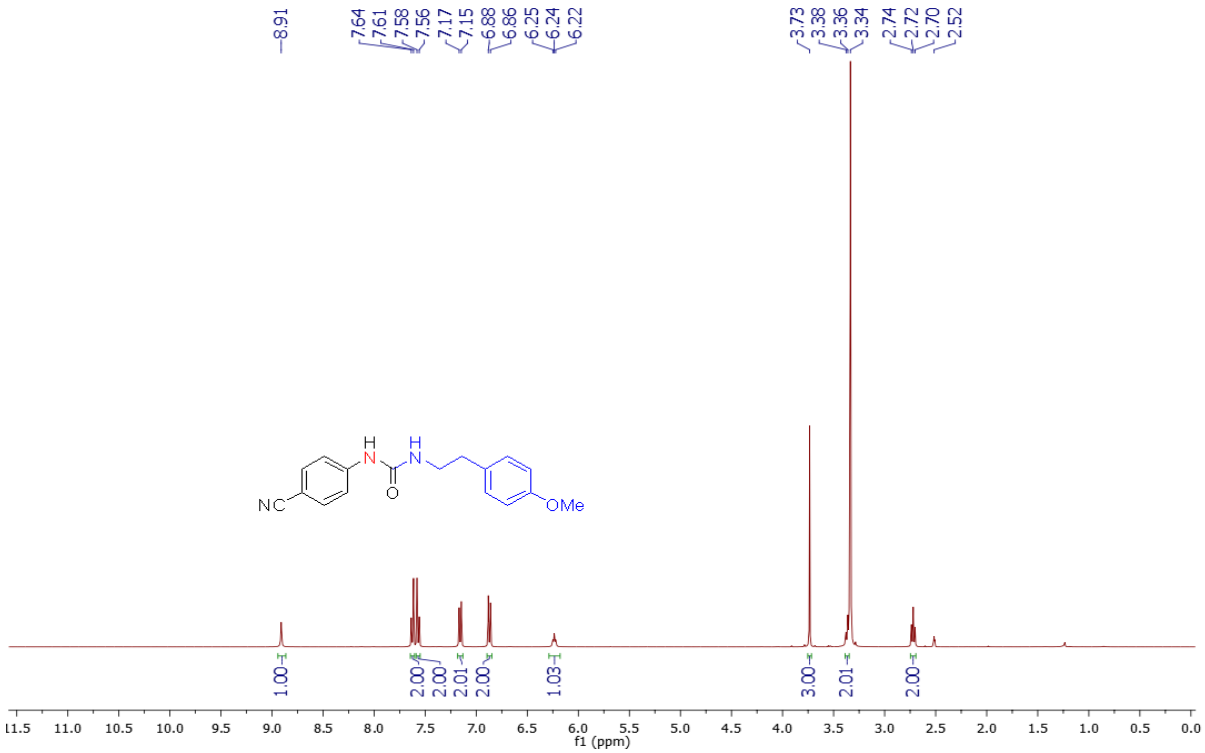
[13]C-NMR of 1-(4-methoxyphenethyl)-3-(4-methoxyphenyl)urea (3i)



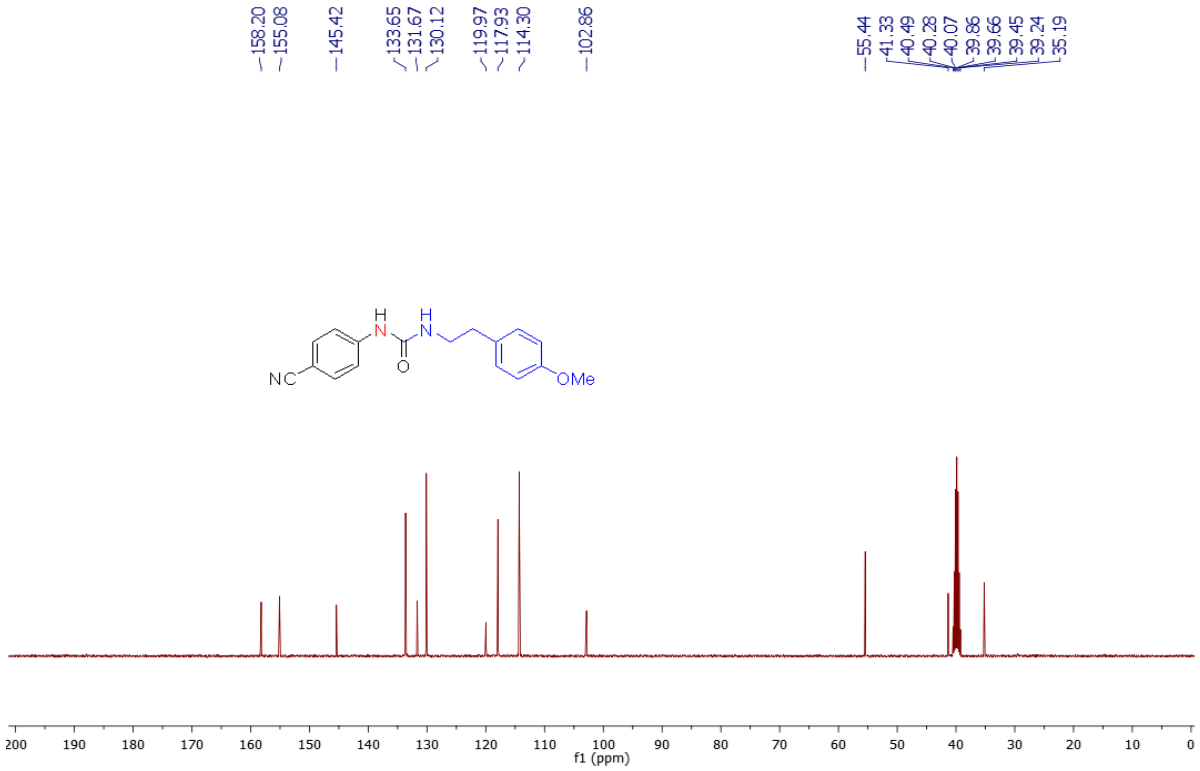
DEPT of 1-(4-methoxyphenethyl)-3-(4-methoxyphenyl)urea (3i)



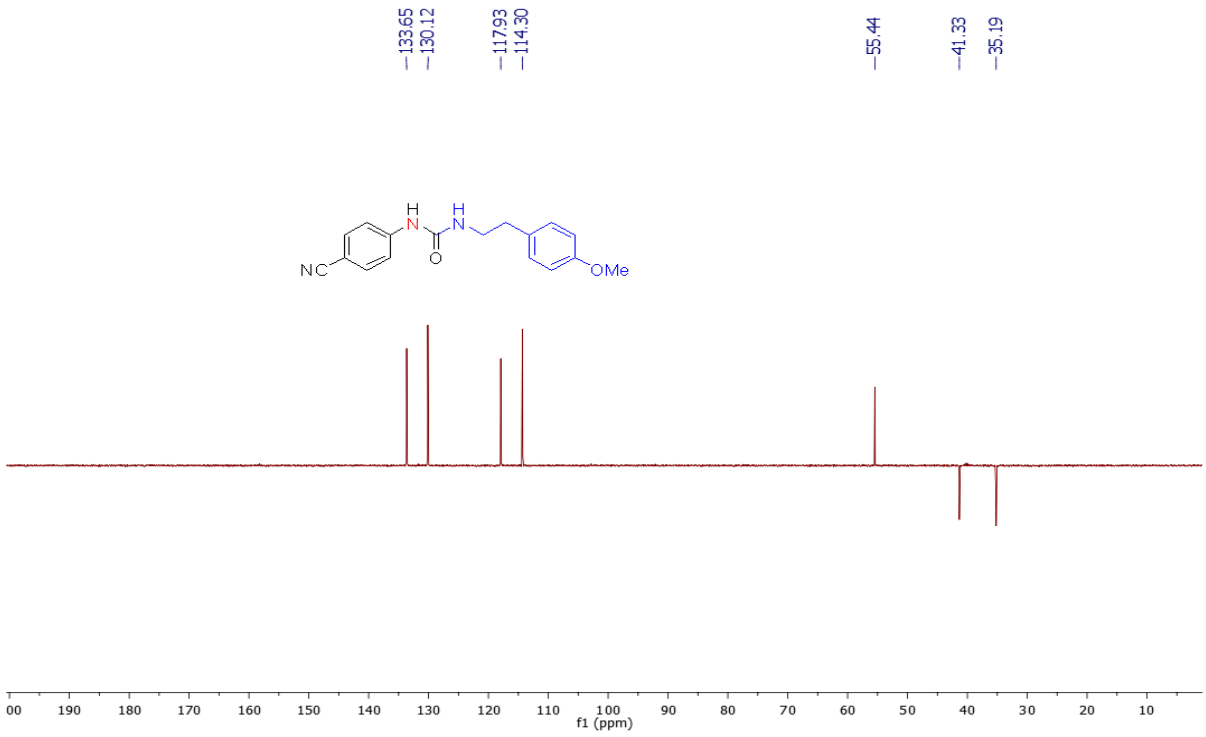
^{1}H-NMR of 1-(4-cyanophenyl)-3-(4-methoxyphenethyl)urea (3j)



^{13}C-NMR of 1-(4-cyanophenyl)-3-(4-methoxyphenethyl)urea (3j)



DEPT of 1-(4-cyanophenyl)-3-(4-methoxyphenethyl)urea (3j)



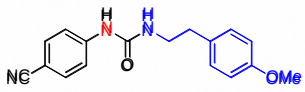
HRMS (ESI-TOF) of compound (3j)

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

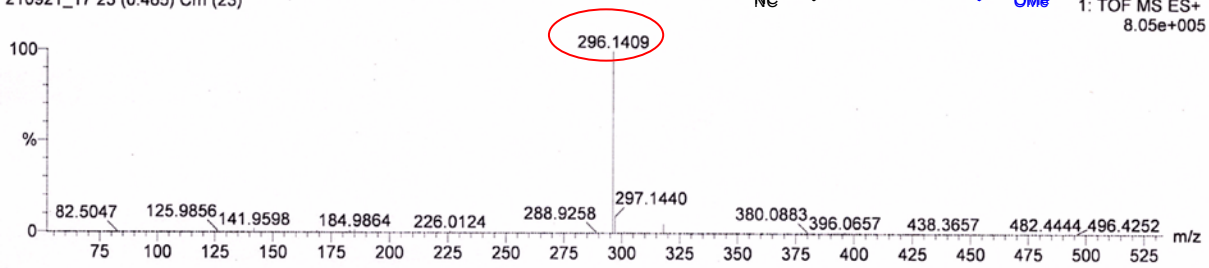
Monoisotopic Mass, Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-17 H: 0-200 N: 0-3 O: 0-2
RR-104

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015



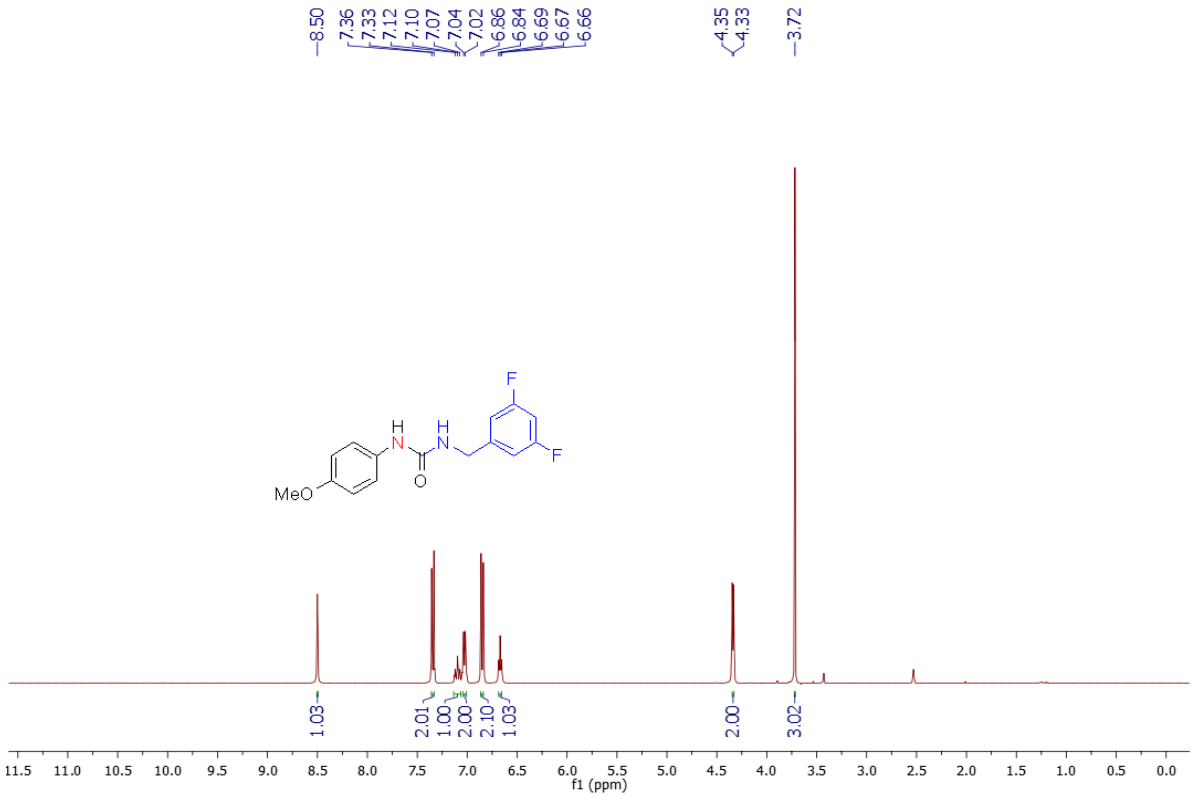
21-Sep-2021
12:49:53
1: TOF MS ES+
8.05e+005

210921_17 23 (0.465) Cm (23)

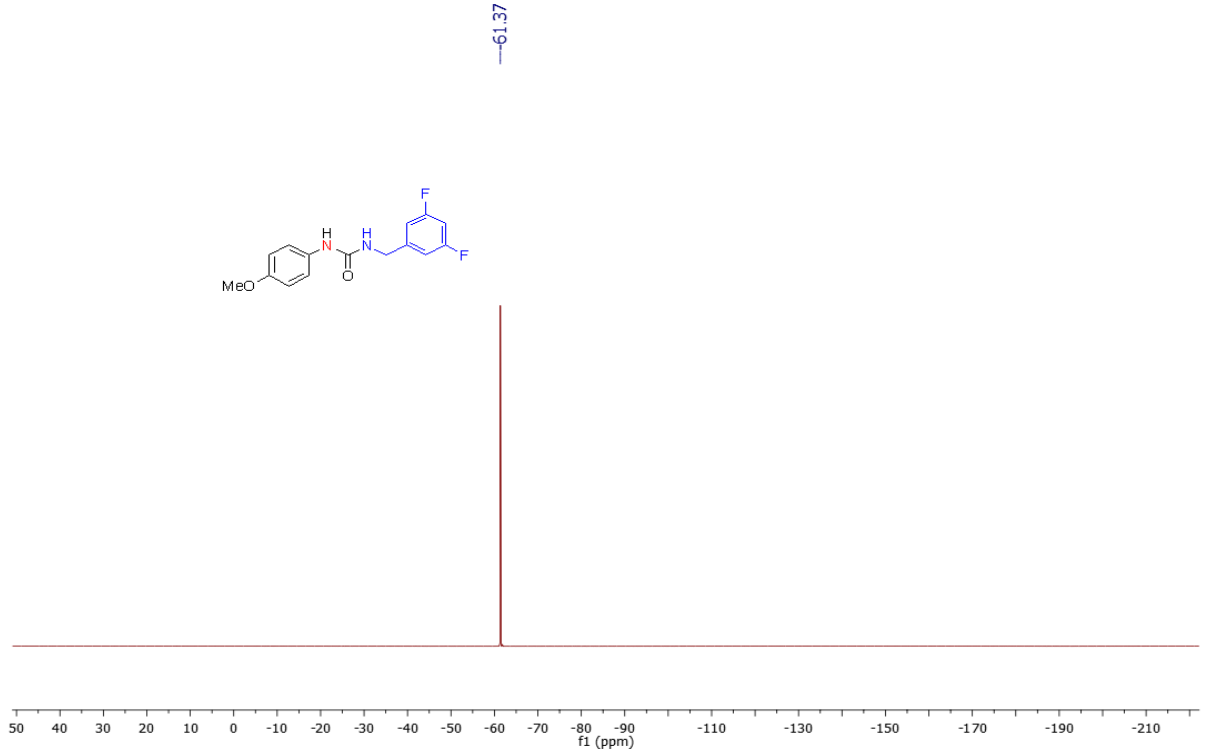


Minimum:				-1.5				
Maximum:		2.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
296.1409	296.1399	1.0	3.4	10.5	46.3	n/a	n/a	C17 H18 N3 O2

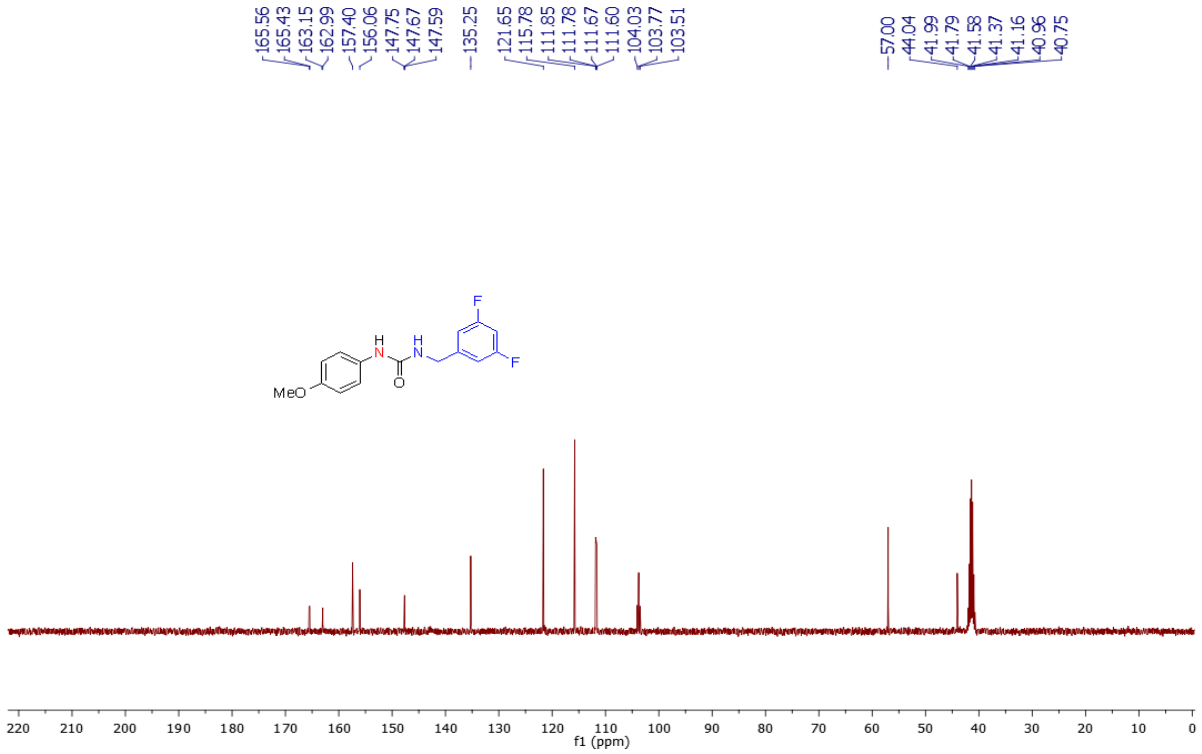
^{1}H-NMR of 1-(3,5-difluorobenzyl)-3-(4-methoxyphenyl)urea (3k)



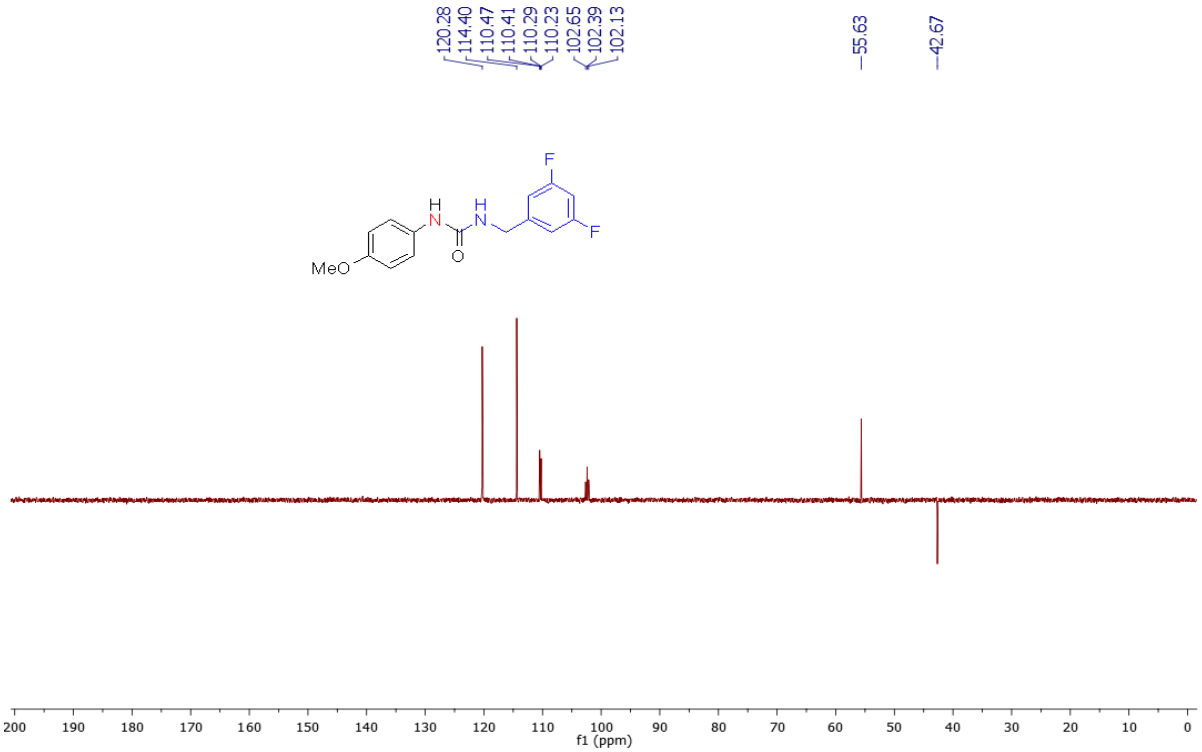
^{19}F-NMR of 1-(3,5-difluorobenzyl)-3-(4-methoxyphenyl)urea (3k)



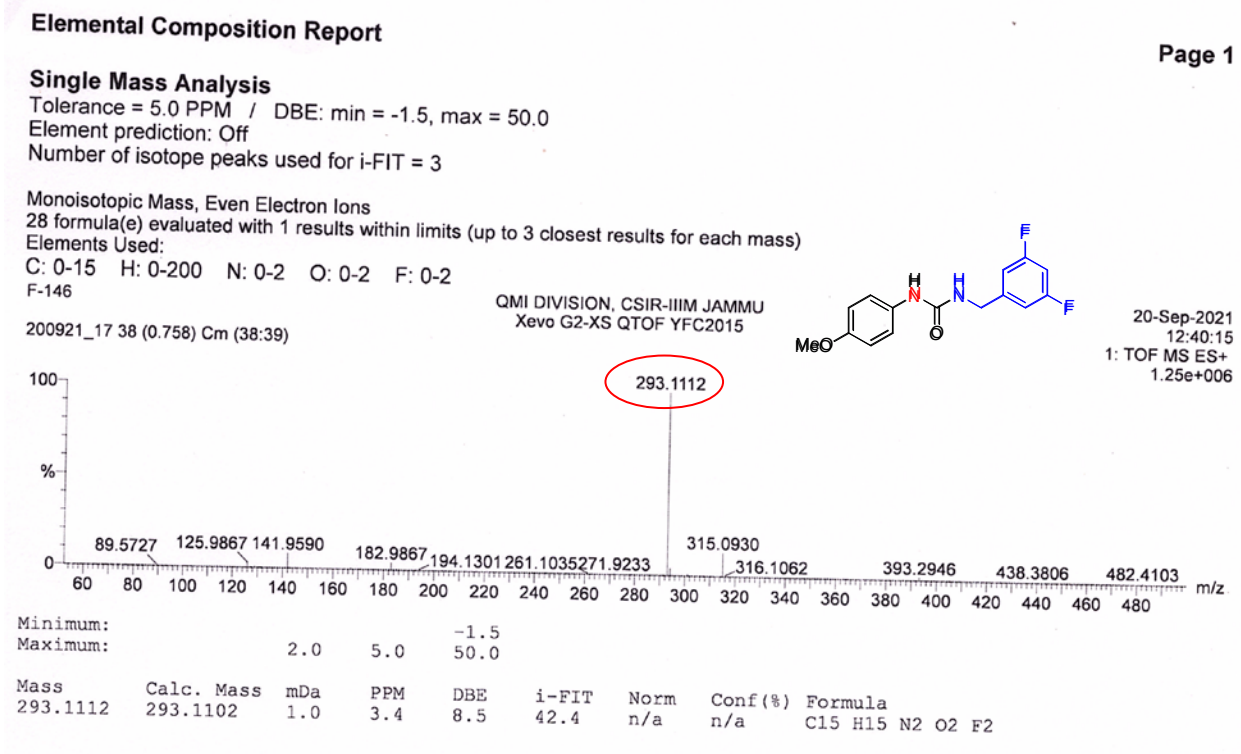
^{13}C-NMR of 1-(3,5-difluorobenzyl)-3-(4-methoxyphenyl)urea (3k)



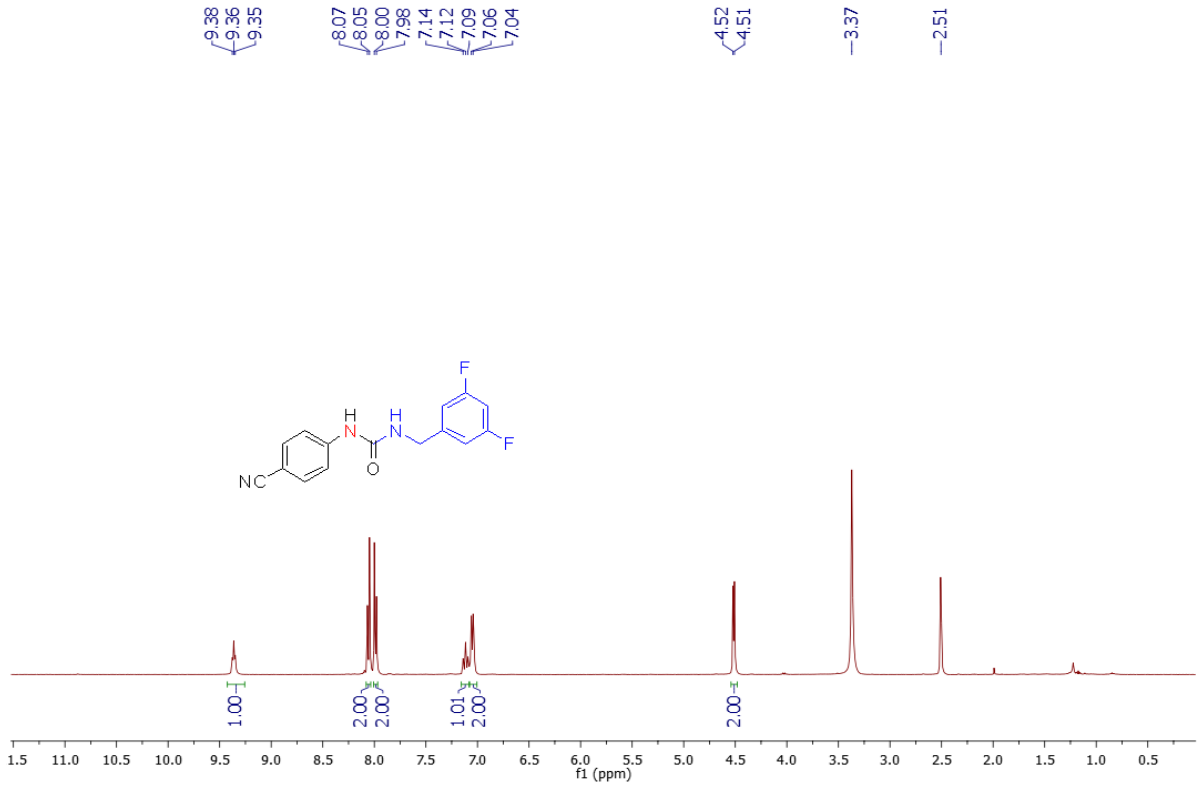
DEPT of 1-(3,5-difluorobenzyl)-3-(4-methoxyphenyl)urea (3k)



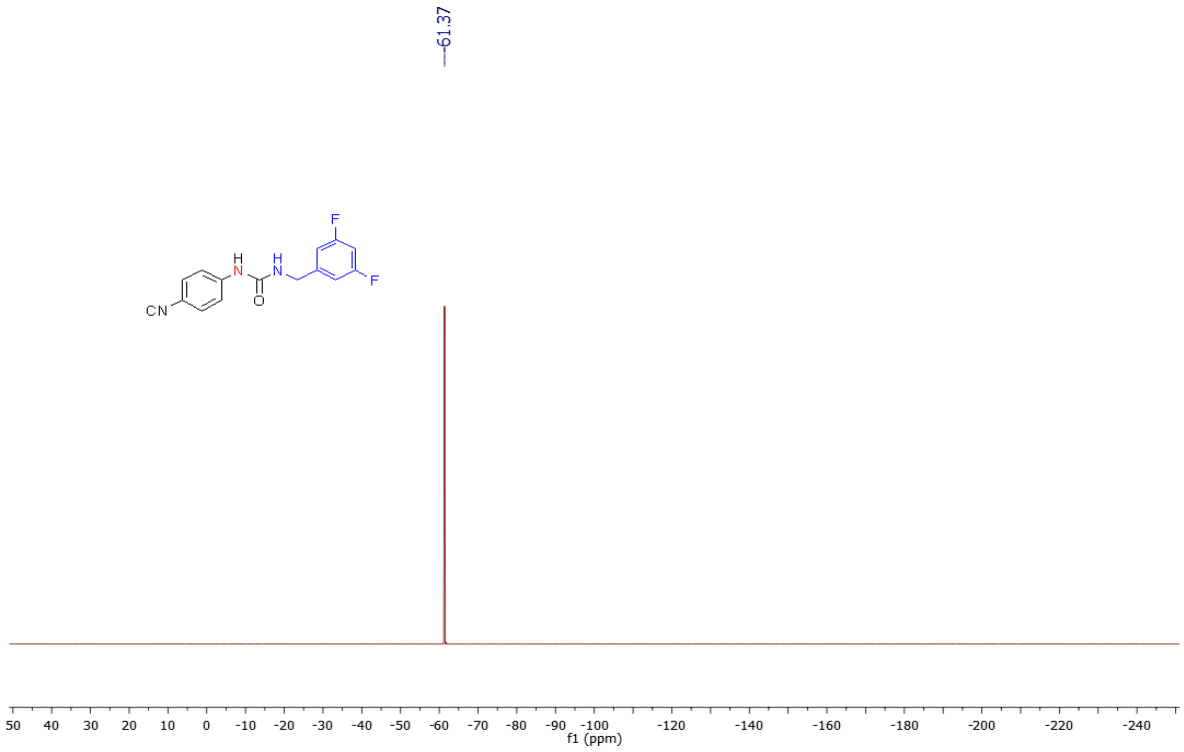
HRMS (ESI-TOF) of compound (3k)



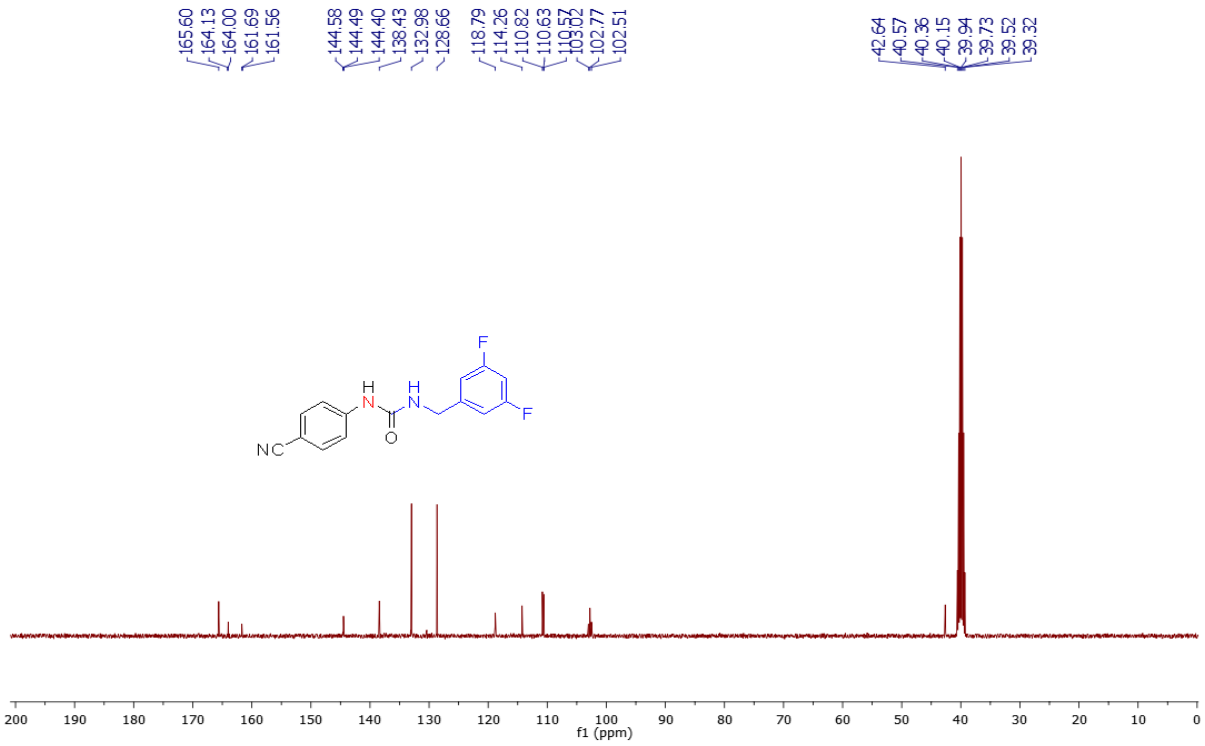
[1]H-NMR of 1-(4-cyanophenyl)-3-(3,5-difluorobenzyl)urea (3l)



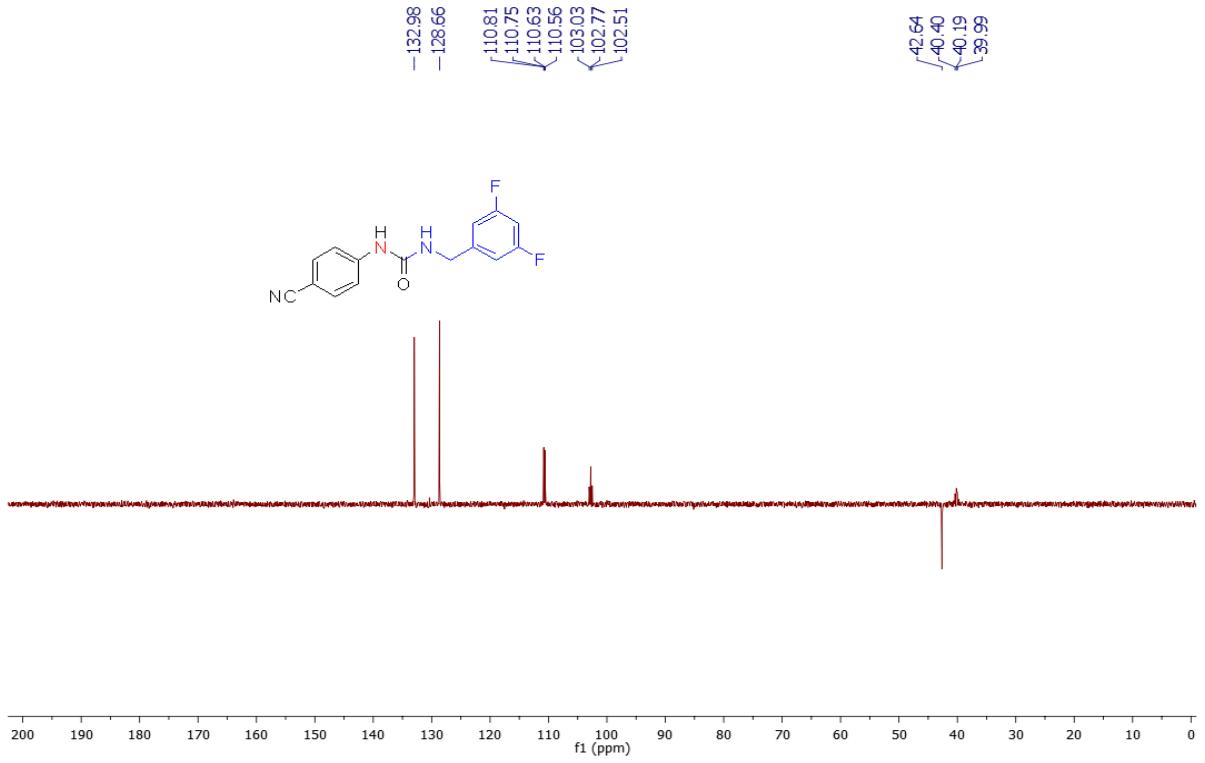
[19]F-NMR of 1-(4-cyanophenyl)-3-(3,5-difluorobenzyl)urea (3l)



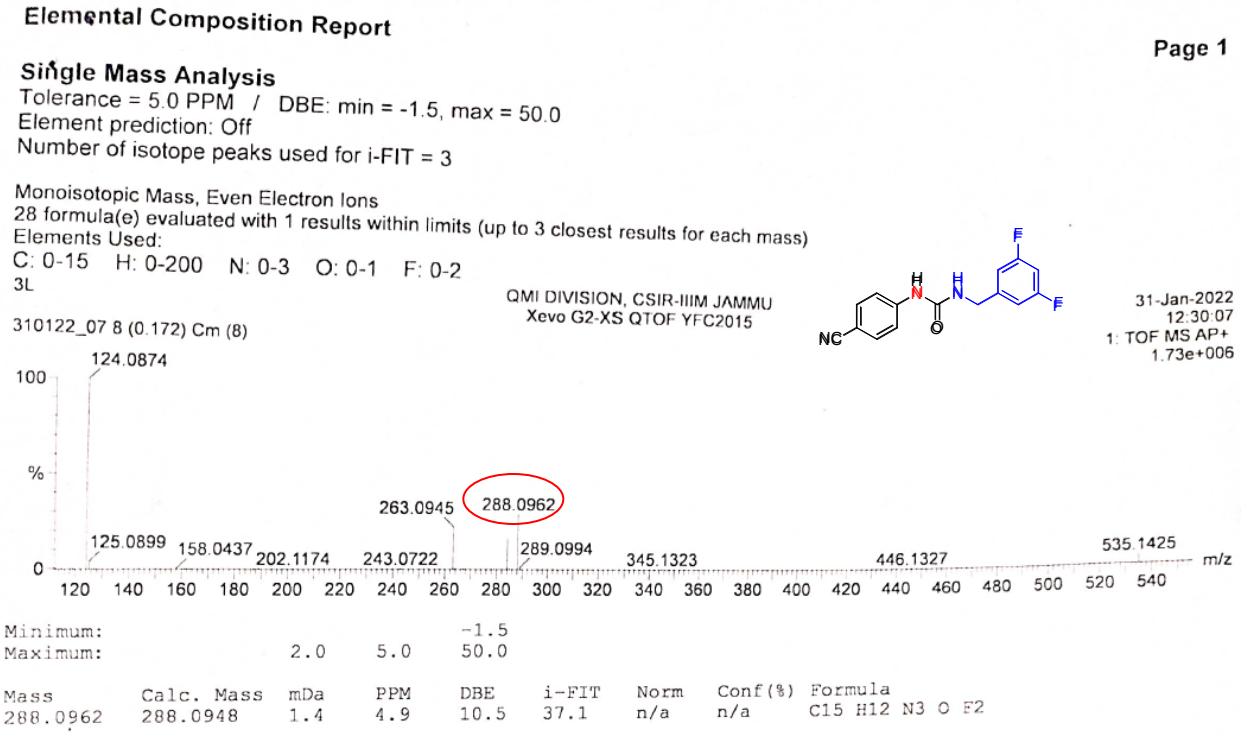
^{13}C-NMR of 1-(4-cyanophenyl)-3-(3,5-difluorobenzyl)urea (3l)



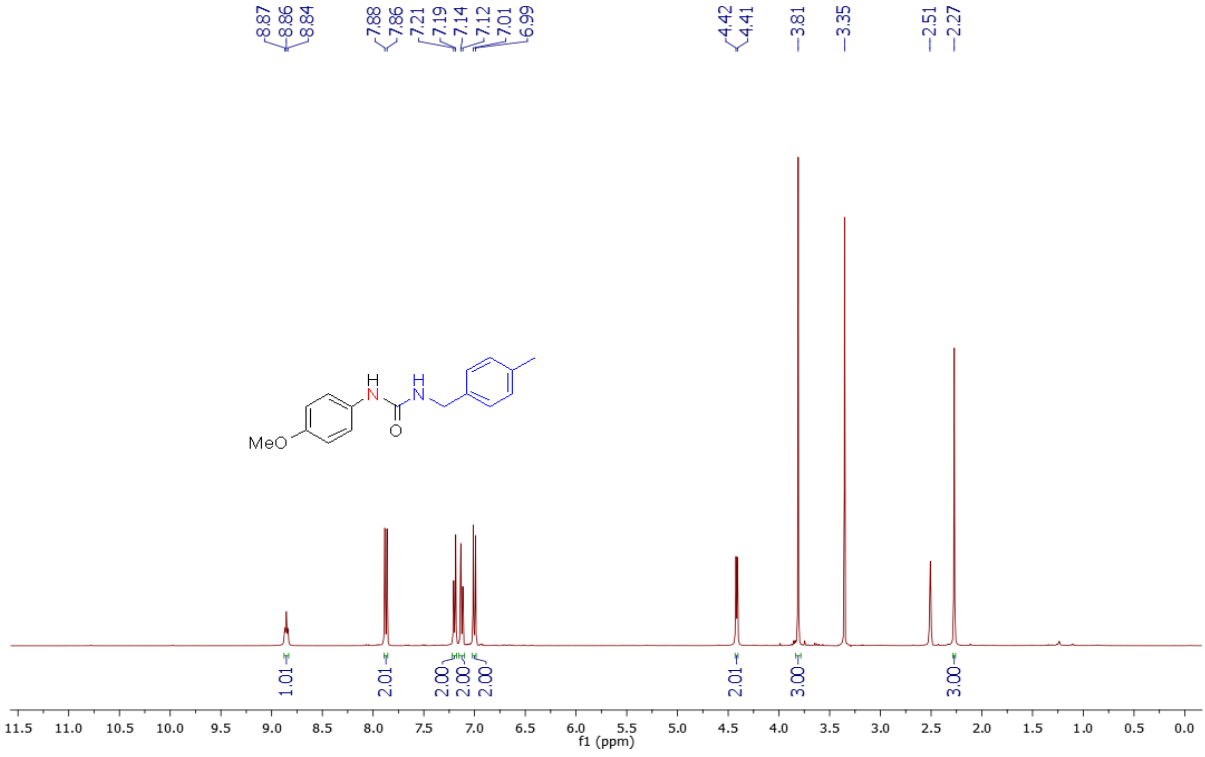
DEPT of 1-(4-cyanophenyl)-3-(3,5-difluorobenzyl)urea (3l)



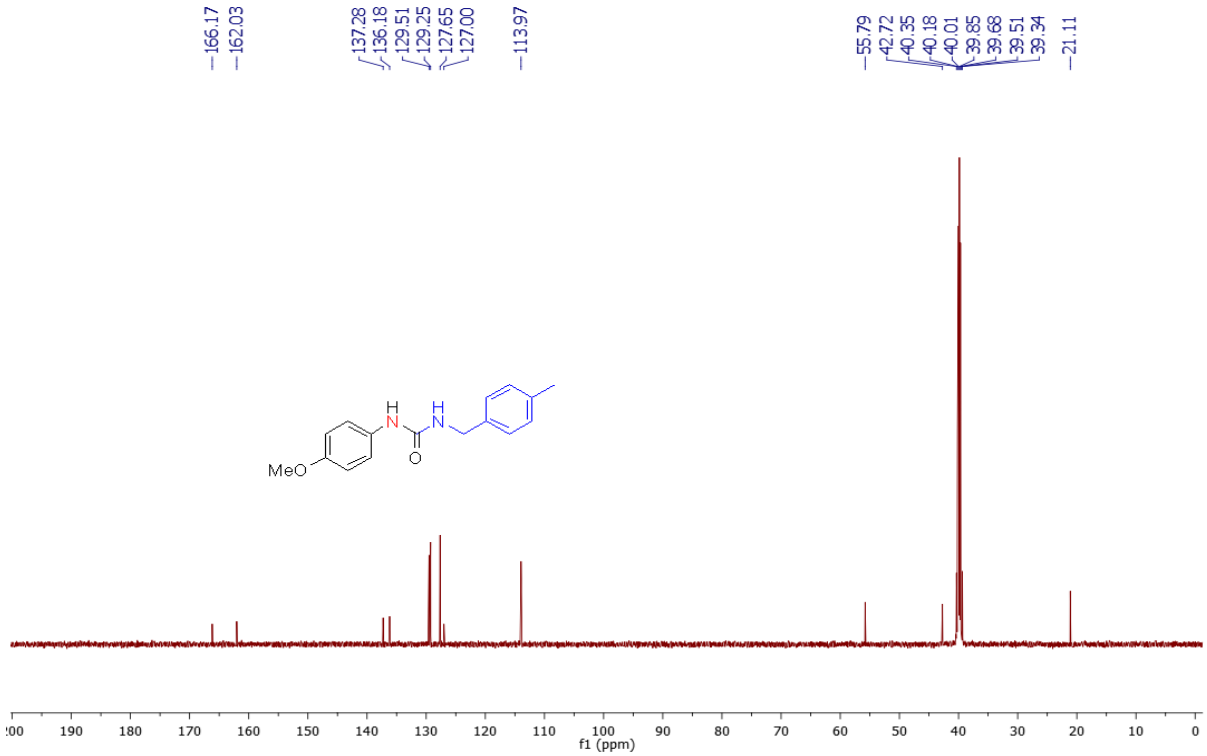
HRMS of 1-(4-cyanophenyl)-3-(3,5-difluorobenzyl)urea (3l)



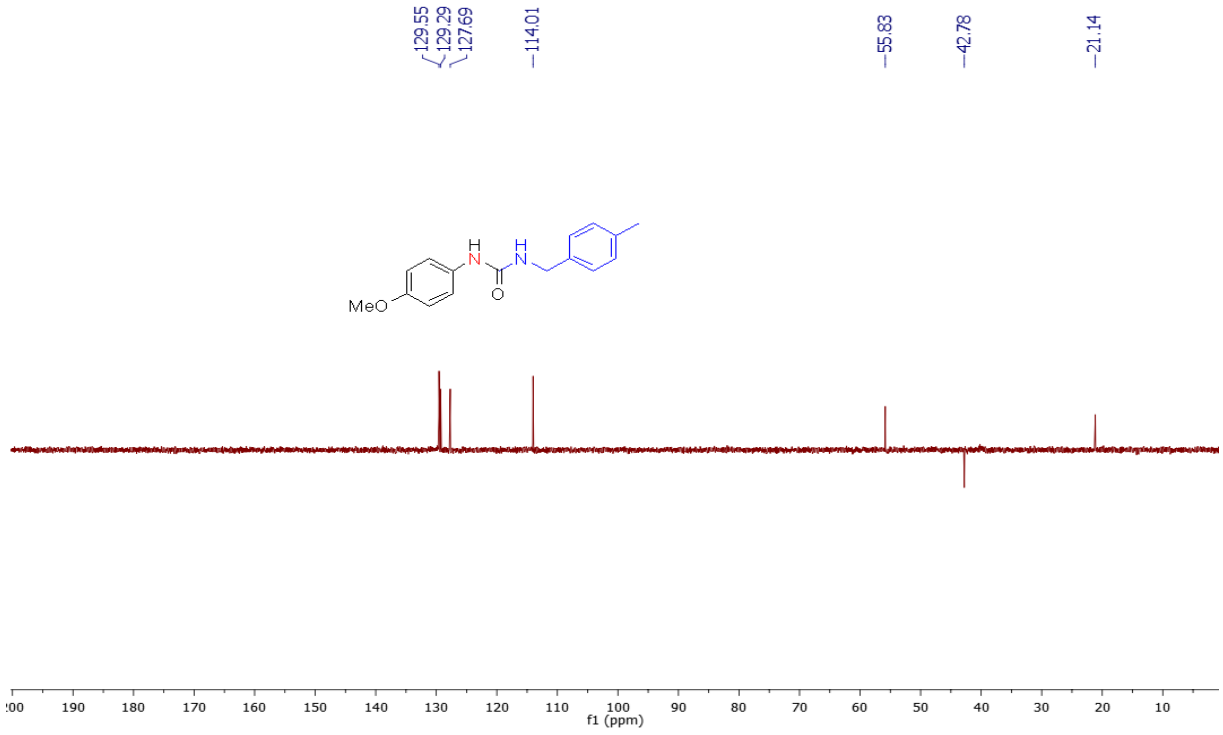
^{1}H-NMR of 1-(4-methoxyphenyl)-3-(4-methylbenzyl)urea (3m)



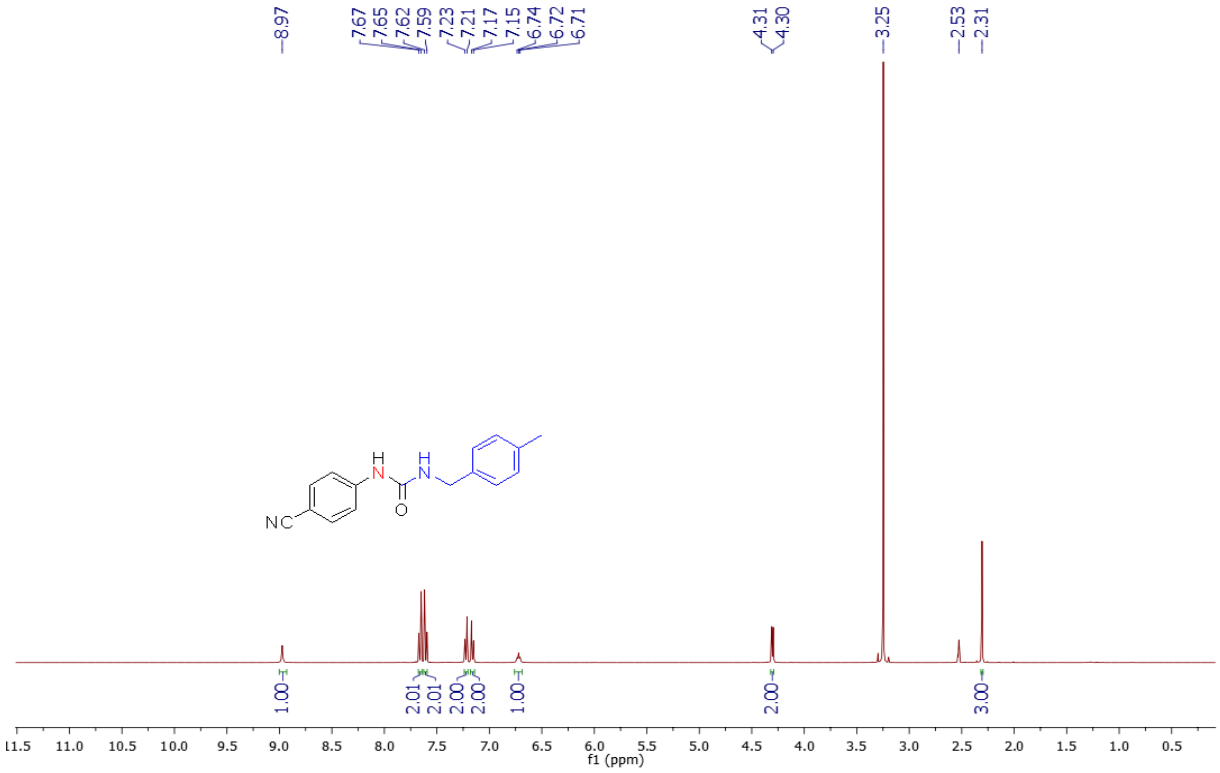
^{13}C-NMR of 1-(4-methoxyphenyl)-3-(4-methylbenzyl)urea (3m)



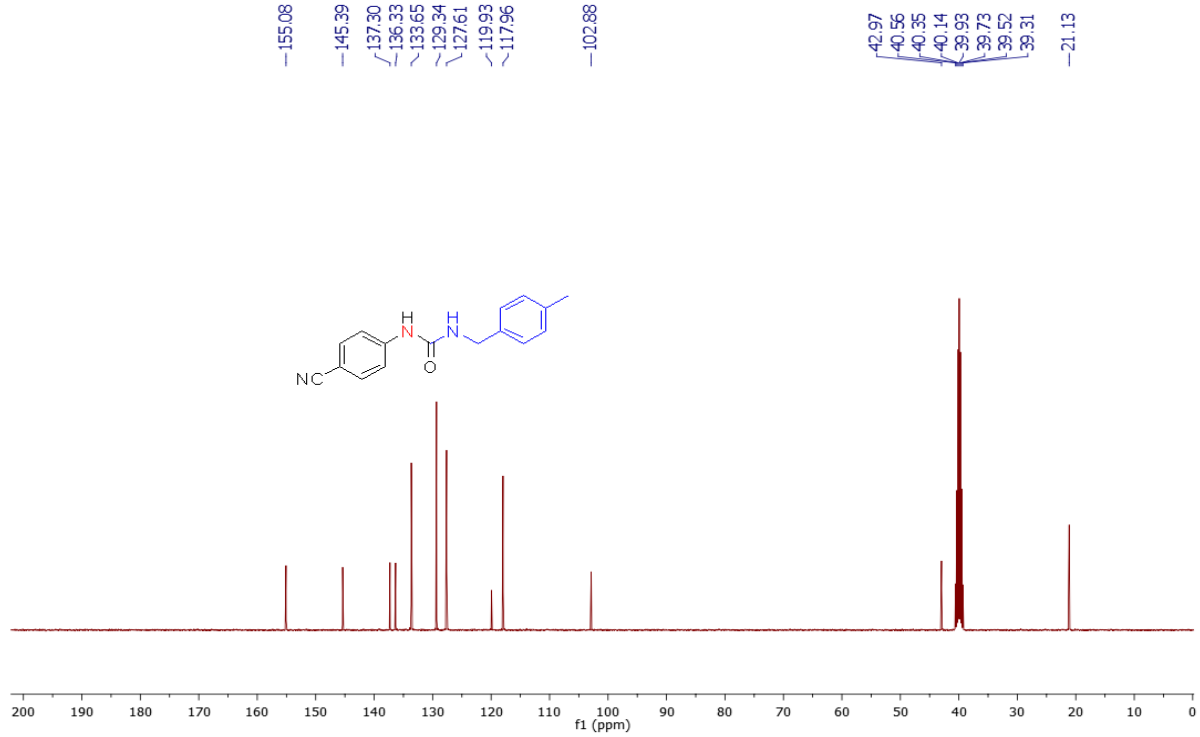
DEPT of 1-(4-methoxyphenyl)-3-(4-methylbenzyl)urea (3m)



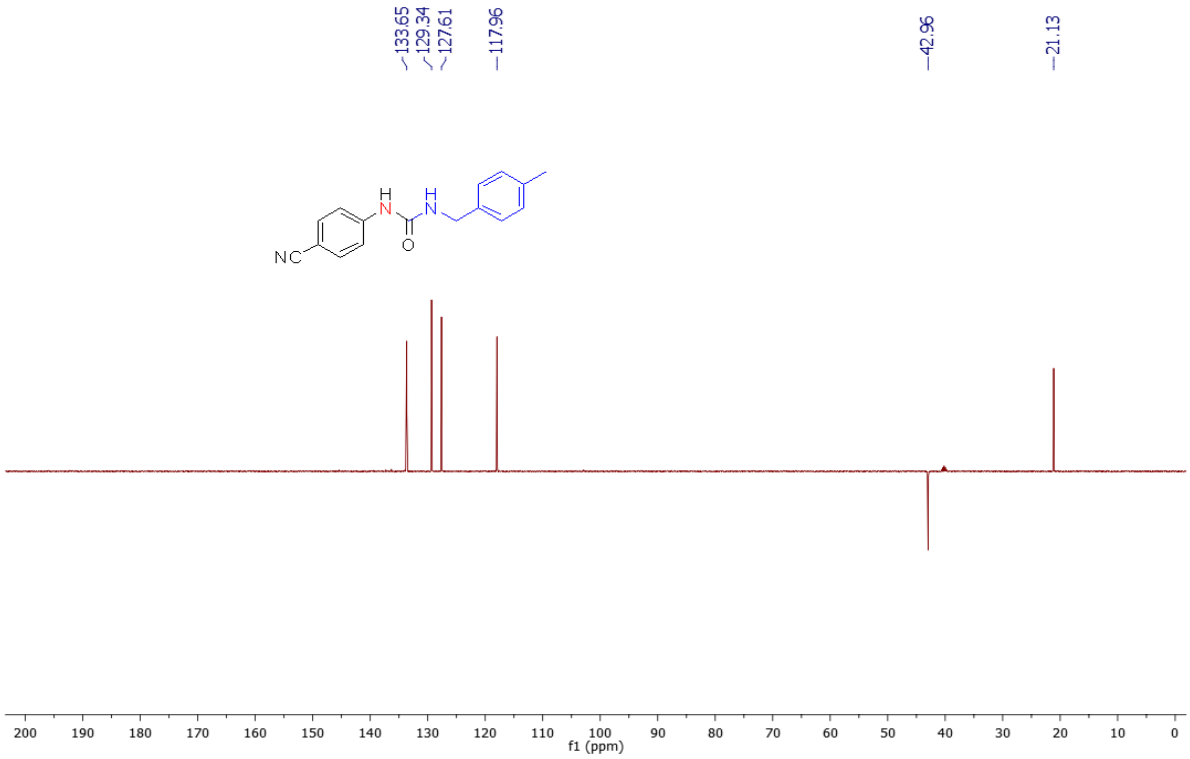
^{1}H-NMR of 1-(4-cyanophenyl)-3-(4-methylbenzyl)urea (3n)



^{13}C-NMR of 1-(4-cyanophenyl)-3-(4-methylbenzyl)urea (3n)



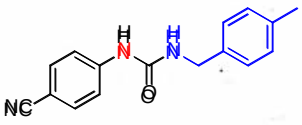
DEPT of 1-(4-cyanophenyl)-3-(4-methylbenzyl)urea (3n)



Mass spectra of 1-(4-cyanophenyl)-3-(4-methylbenzyl)urea (3n)

Sample Information

Sample Name	**: 3N**	**Sample ID**	**:**
Tray#	**: 1**	**Vial#**	**: 78**
Injection Volume	**: 0.5**	**Data File**	**: 28-JAN-22-50.lcd**
Method File	**: MASS SCANNN 13APRIL2021.lcm**	**Processed by**	**: System Administrator**
Date Processed	**: 1/28/2022 5:39:17 PM**		



MS Spectrum

BG Mode:None $EndIf$ Segment 1 - Event 1
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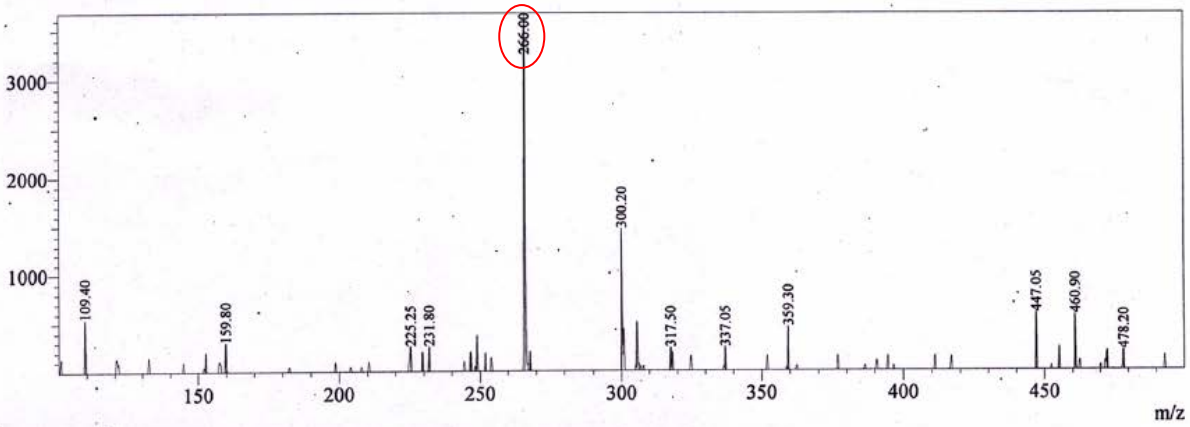

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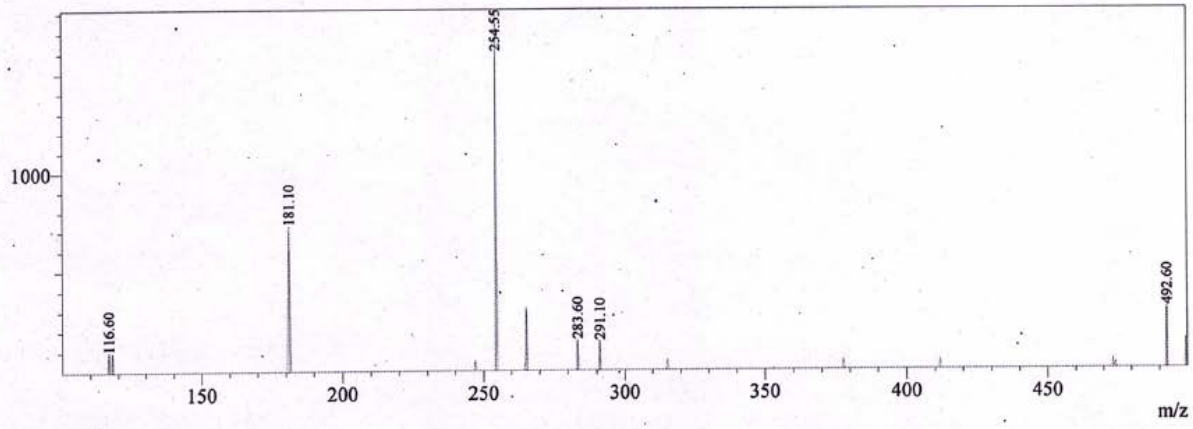
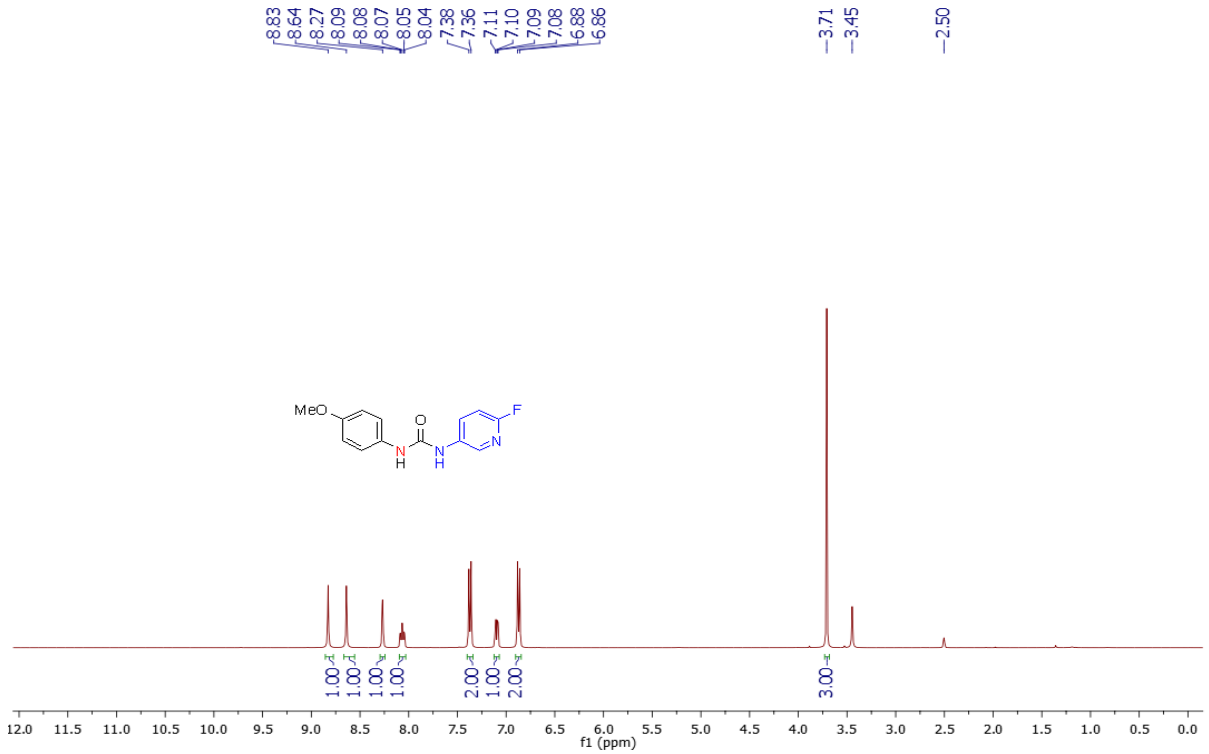
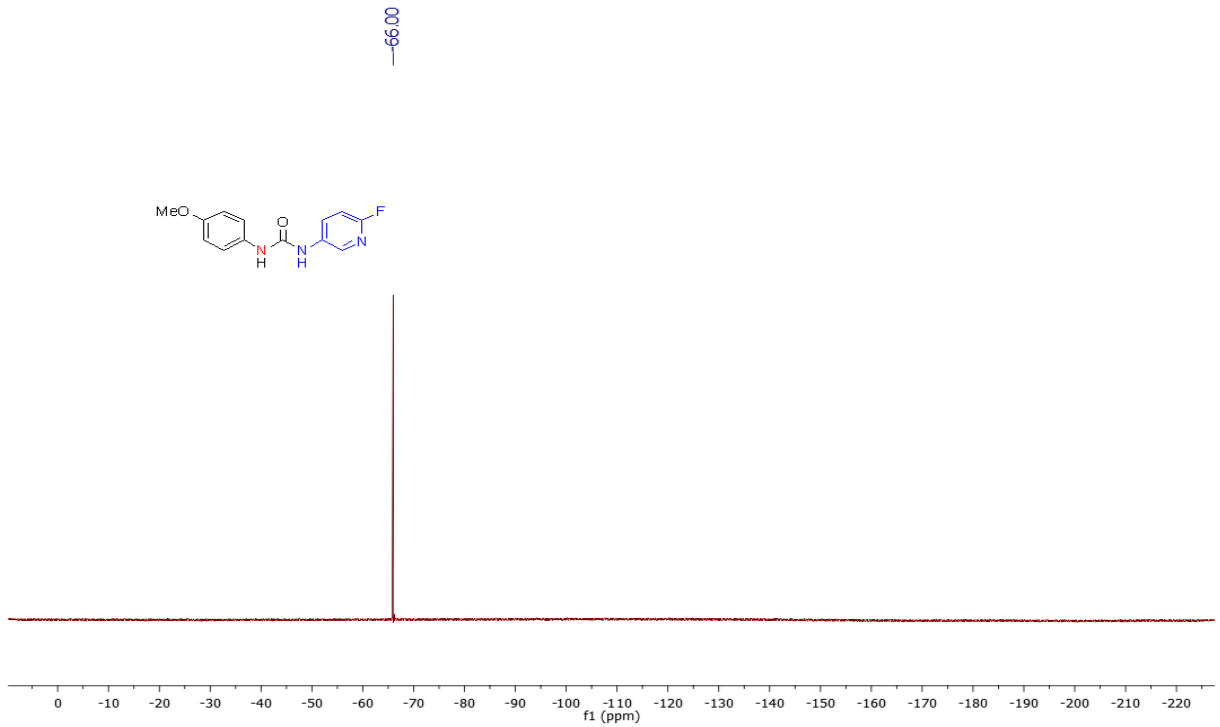


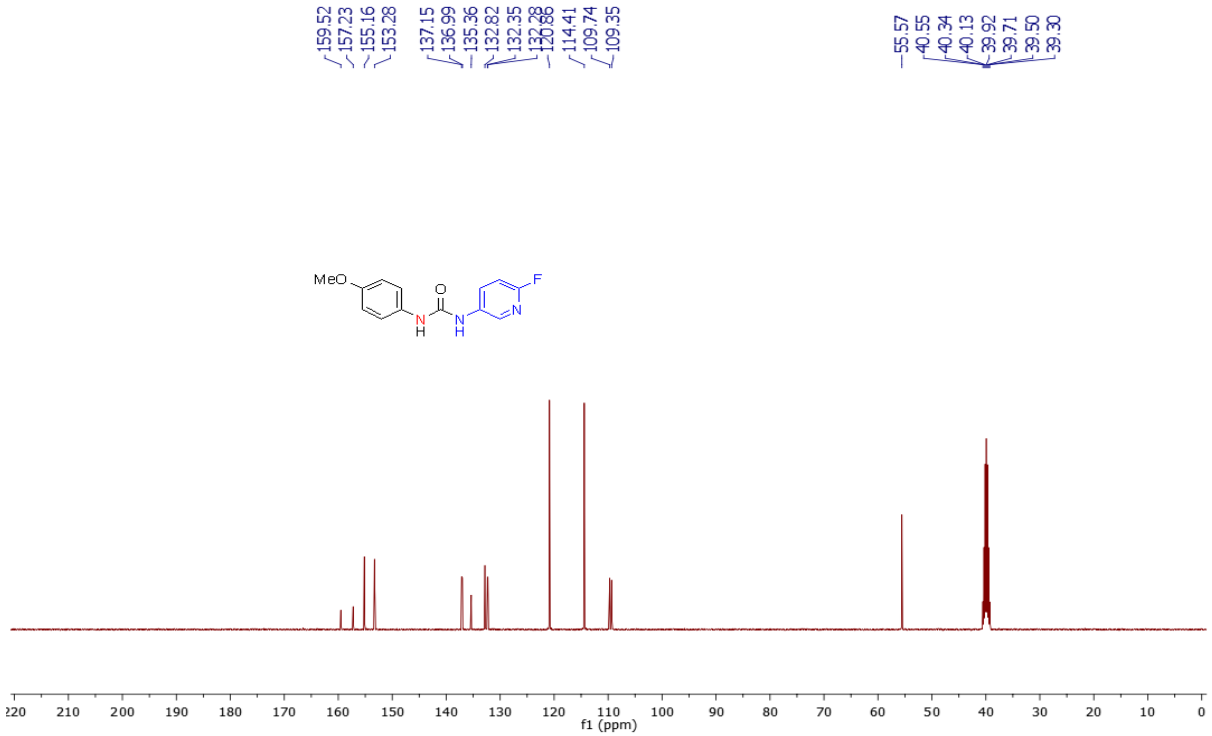
^{1}H-NMR of 1-(6-fluoropyridin-3-yl)-3-(4-methoxyphenyl)urea (3o)



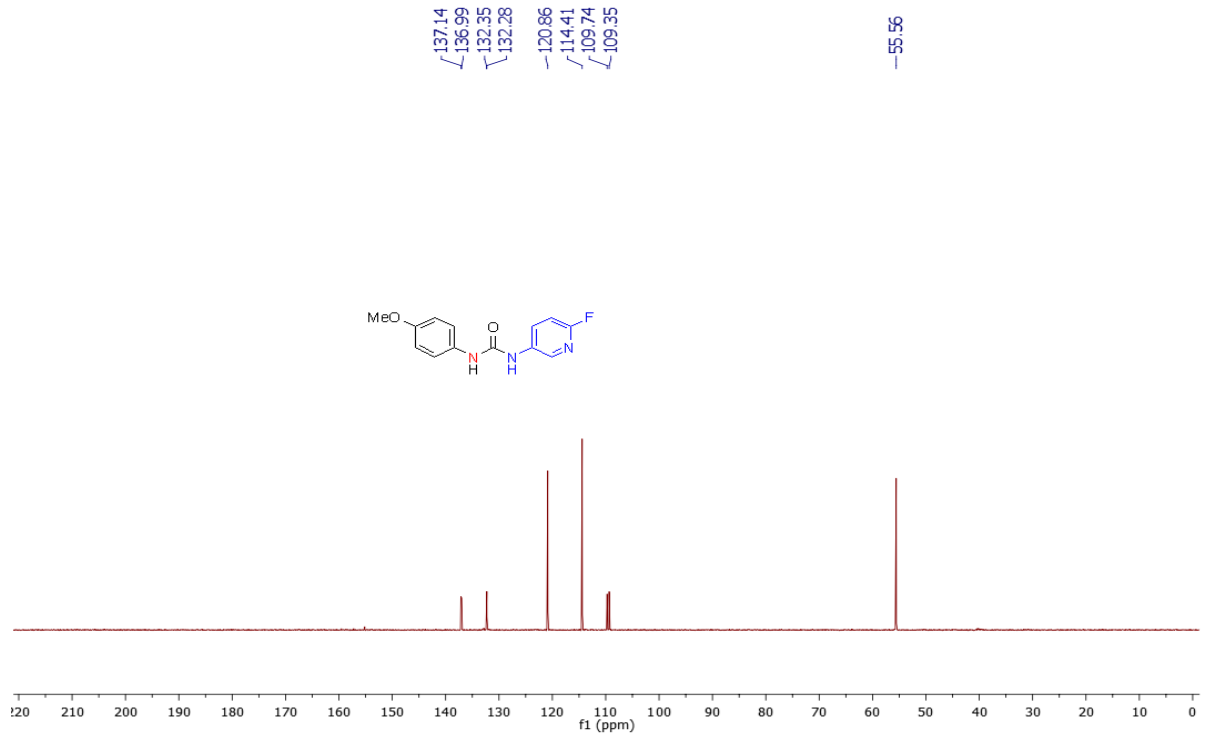
^{19}F-NMR of 1-(6-fluoropyridin-3-yl)-3-(4-methoxyphenyl)urea (3o)



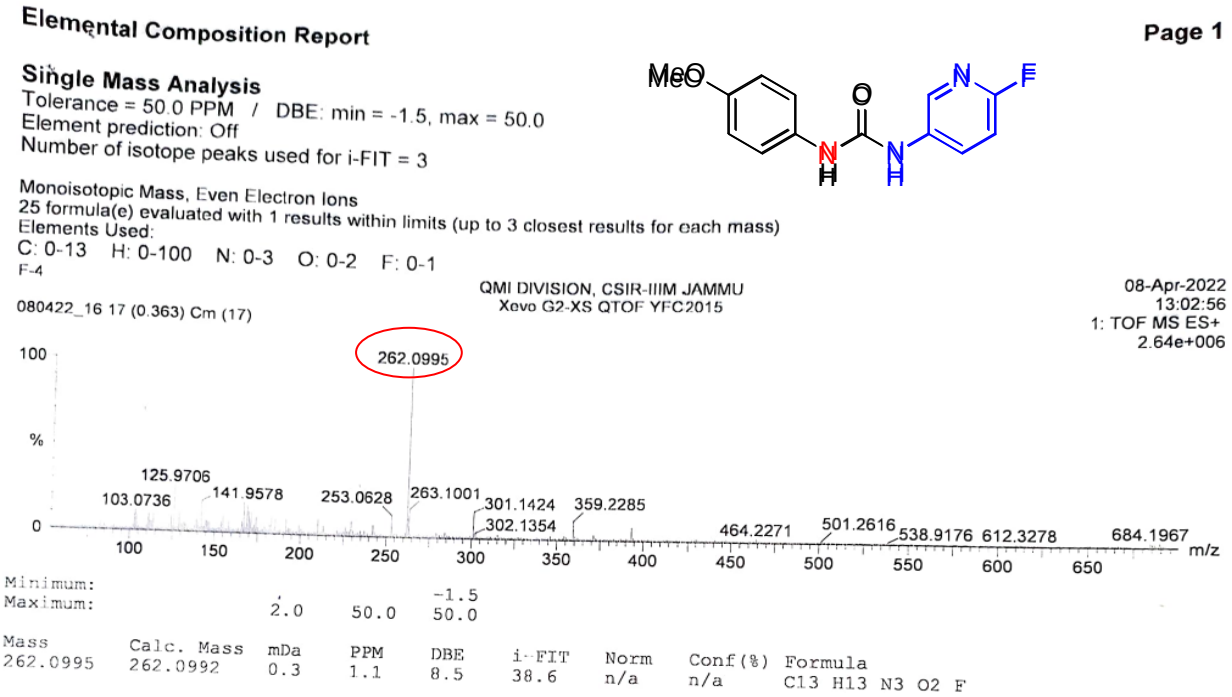
^{13}C-NMR of 1-(6-fluoropyridin-3-yl)-3-(4-methoxyphenyl)urea (3o)



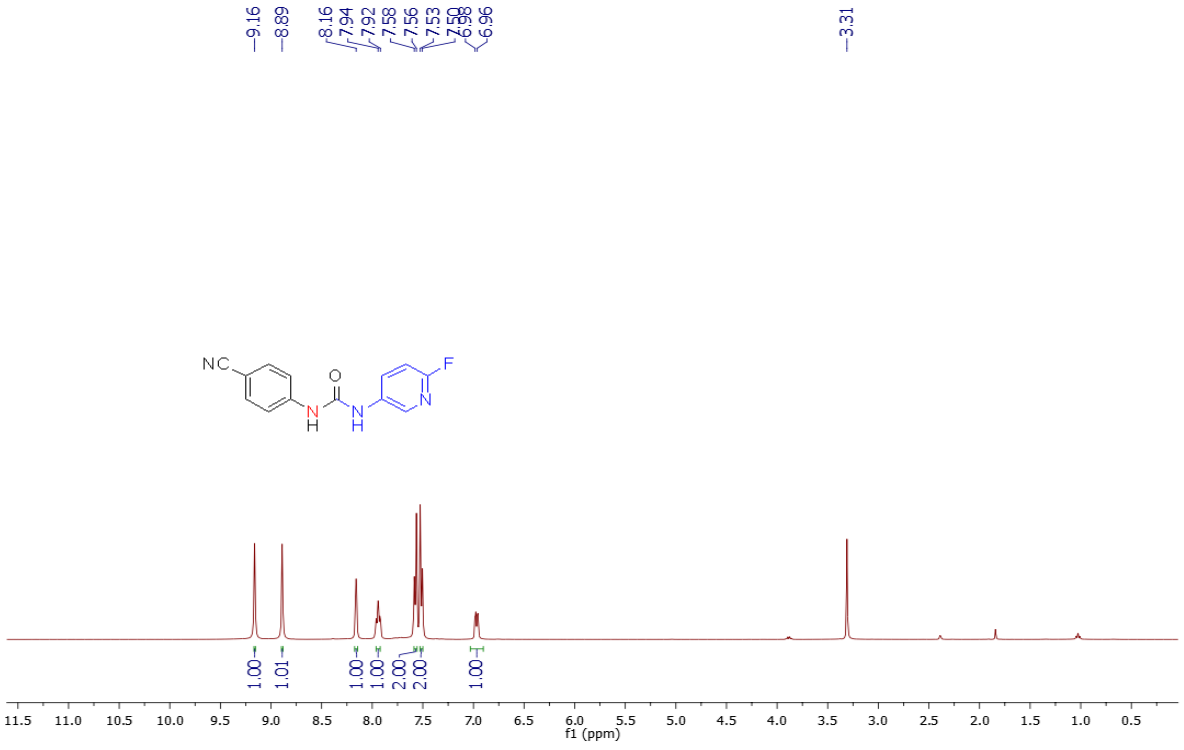
DEPT of 1-(6-fluoropyridin-3-yl)-3-(4-methoxyphenyl)urea (3o)



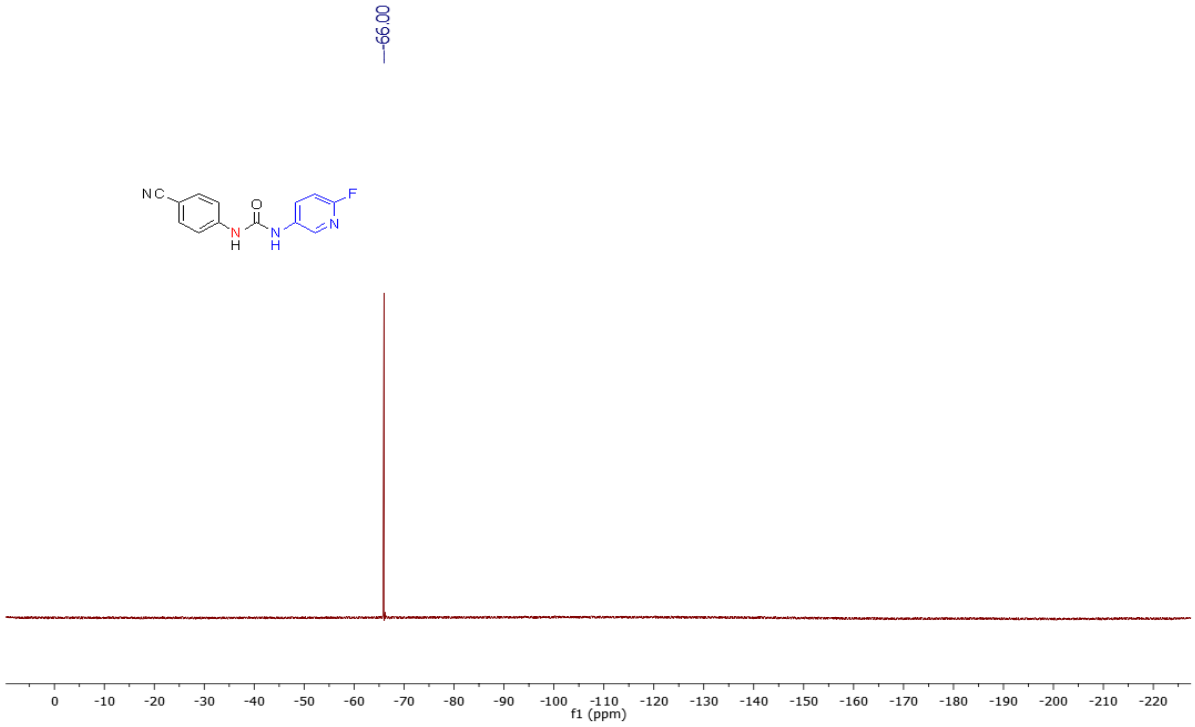
HRMS of 1-(6-fluoropyridin-3-yl)-3-(4-methoxyphenyl)urea (3o)



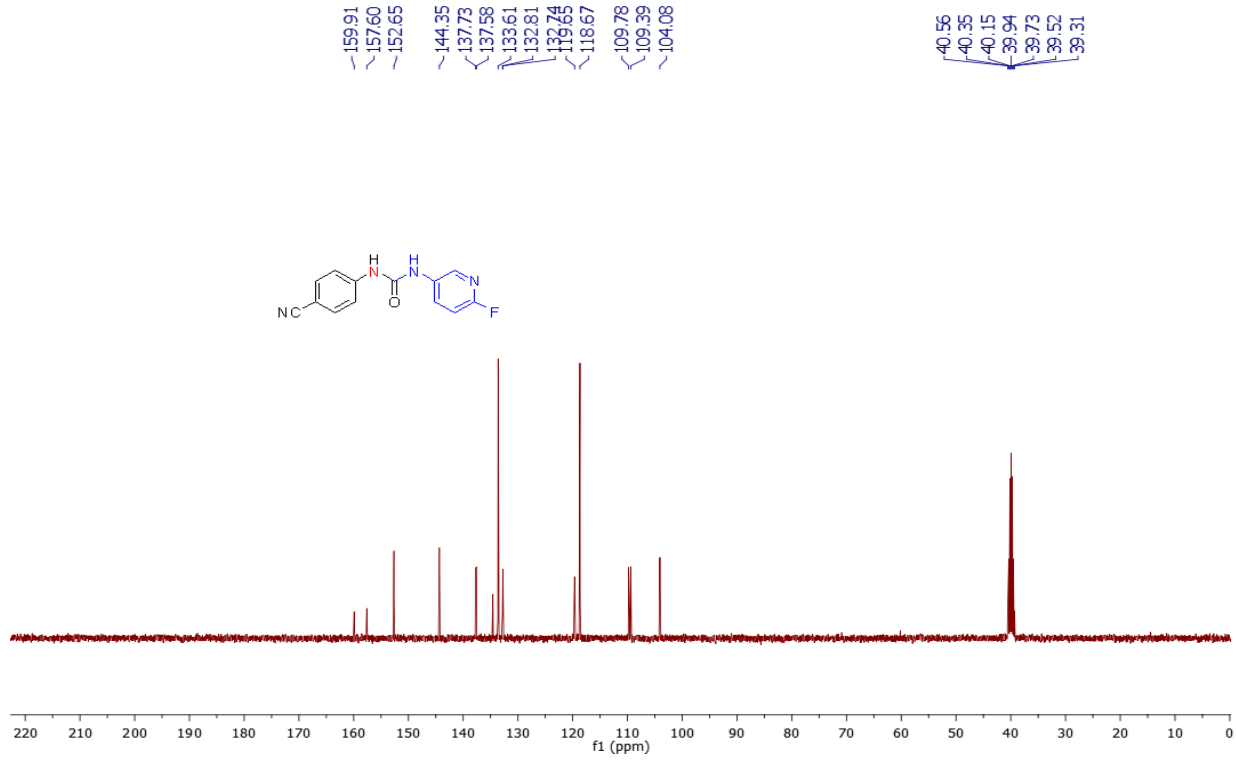
^{1}H-NMR of 1-(4-cyanophenyl)-3-(6-fluoropyridin-3-yl)urea (3p)



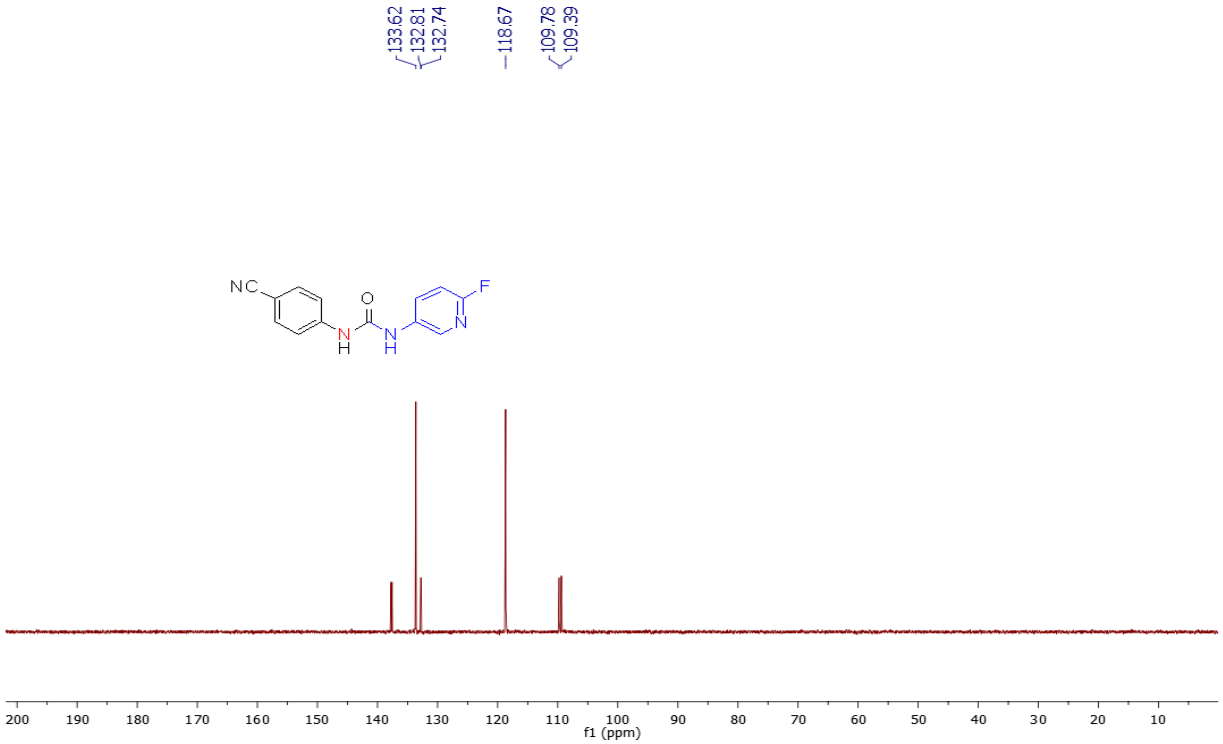
^{19}F-NMR of 1-(4-cyanophenyl)-3-(6-fluoropyridin-3-yl)urea (3p)



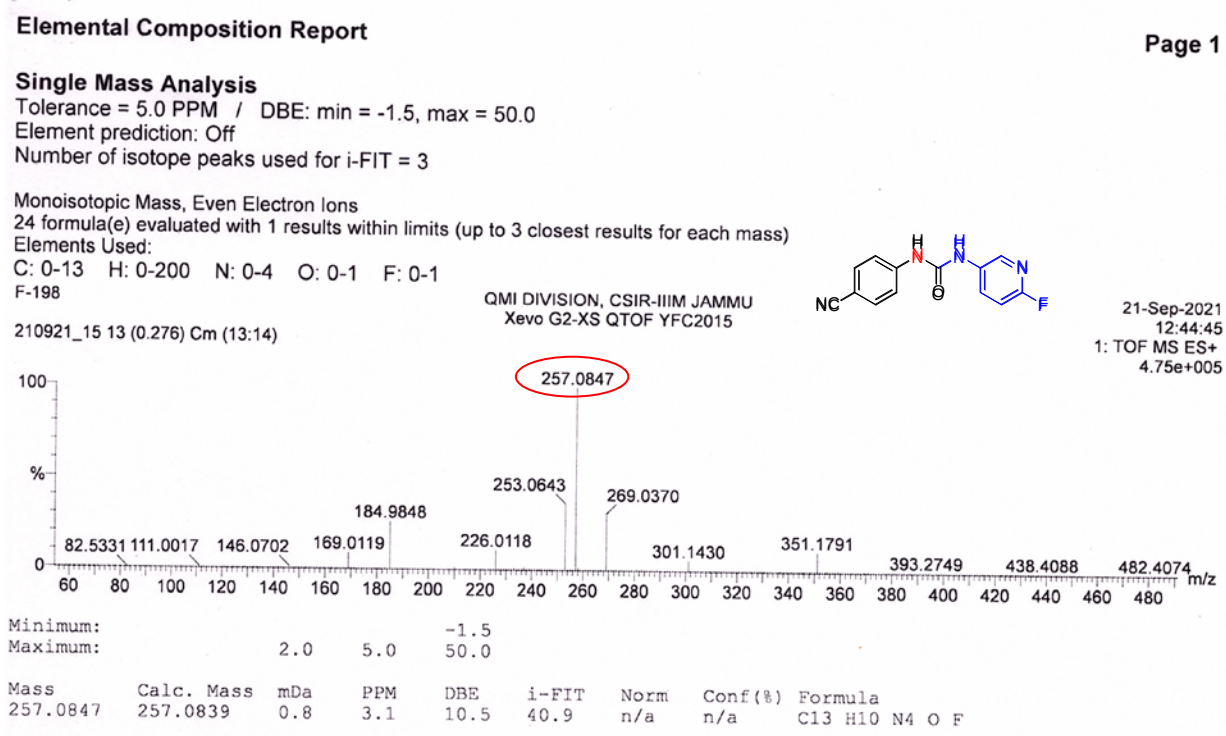
^{13}C-NMR of 1-(4-cyanophenyl)-3-(6-fluoropyridin-3-yl)urea (3p)



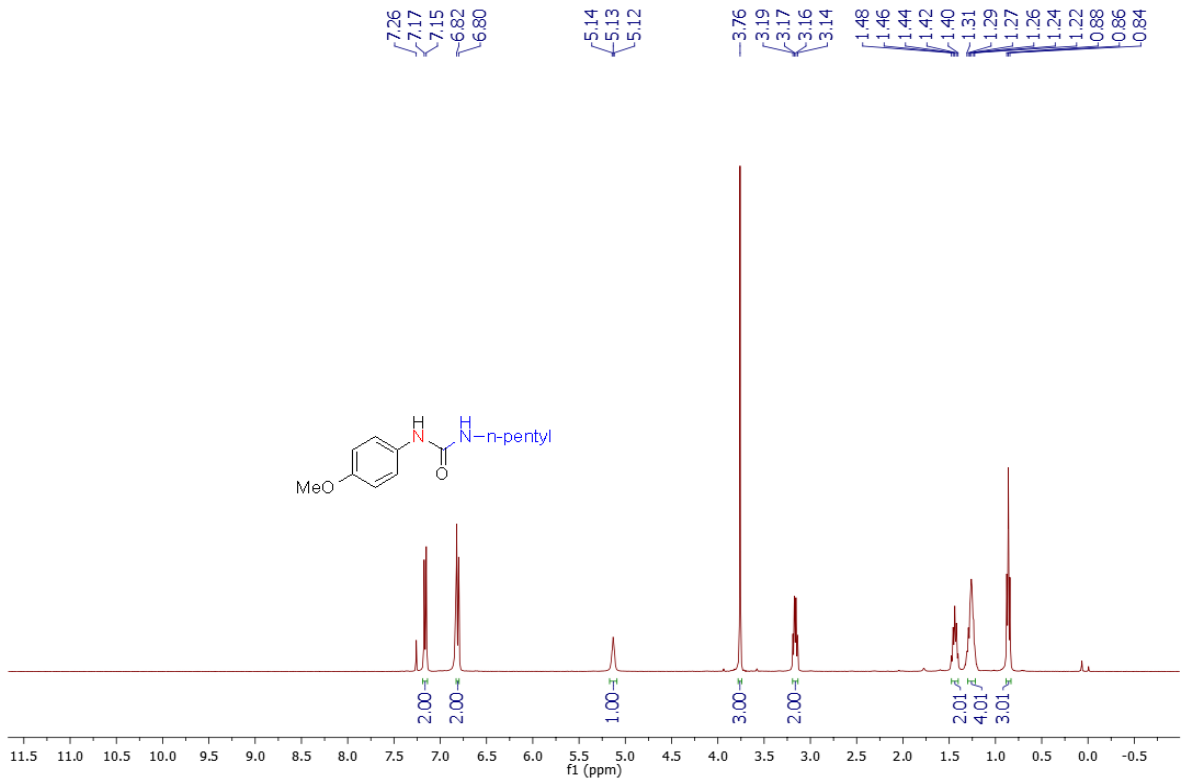
DEPT of 1-(4-cyanophenyl)-3-(6-fluoropyridin-3-yl)urea (3p)



HRMS (ESI-TOF) of compound (3p)



^{1}H-NMR of 1-(4-methoxyphenyl)-3-pentylurea (3q)



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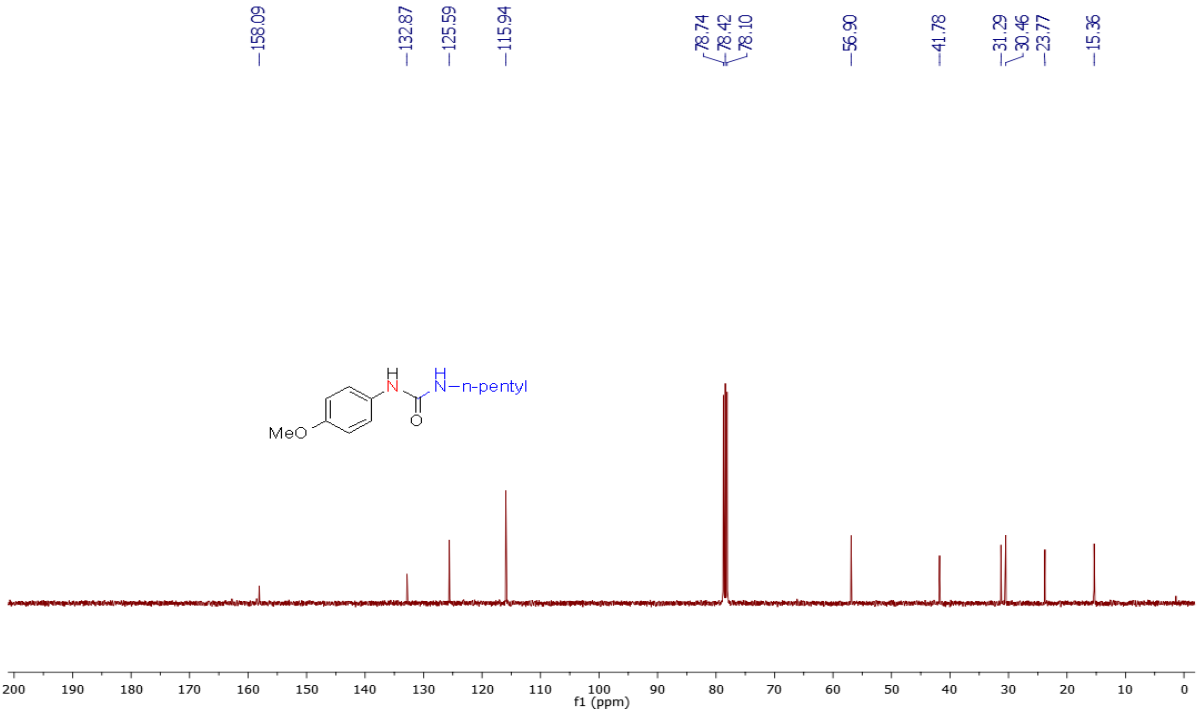
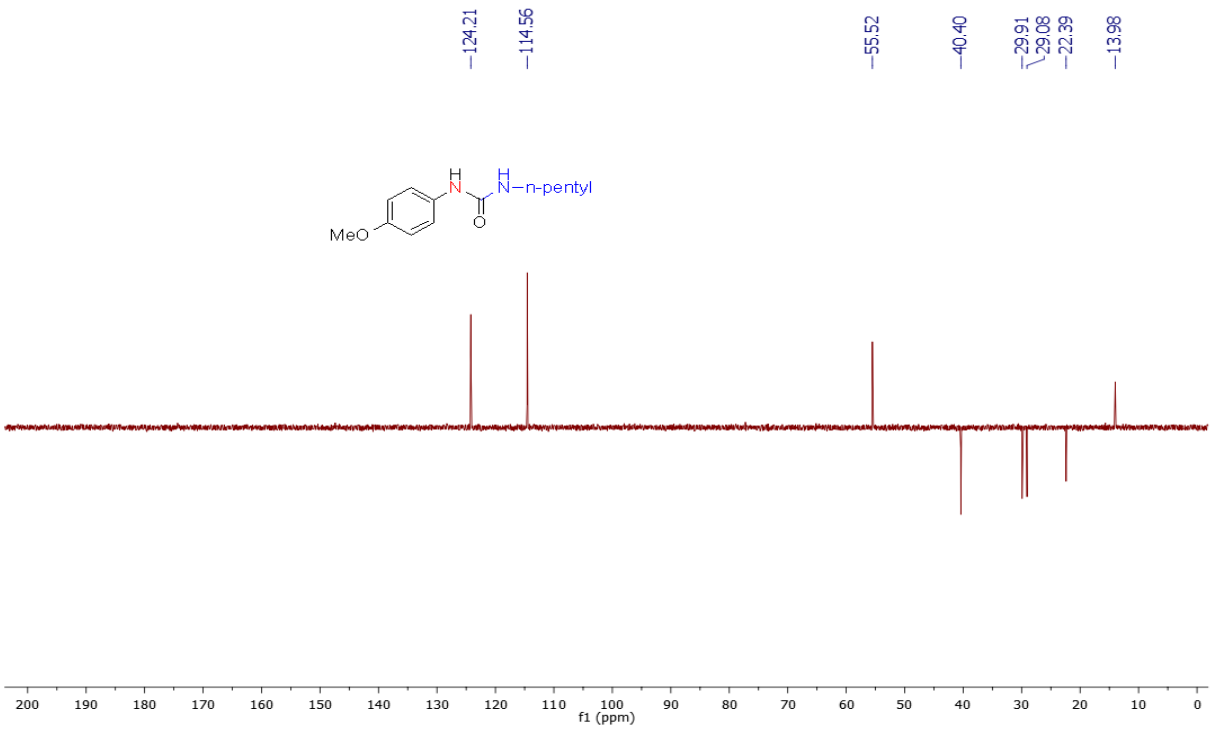
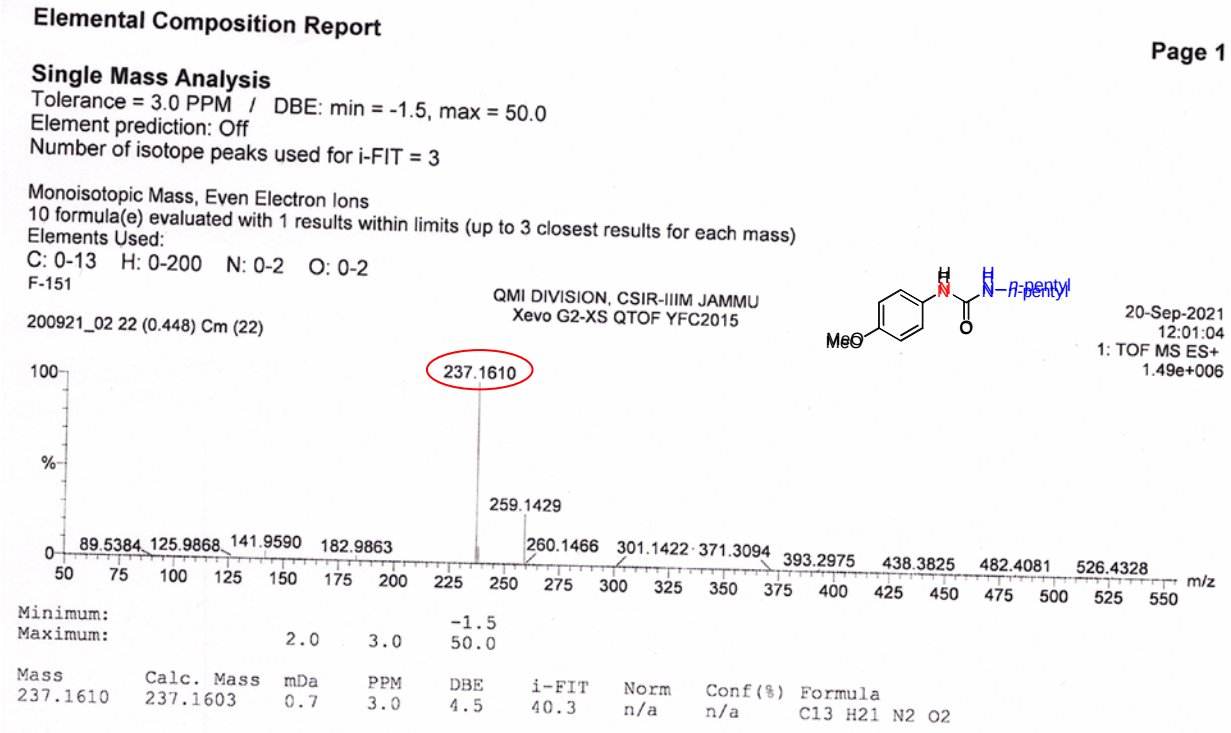


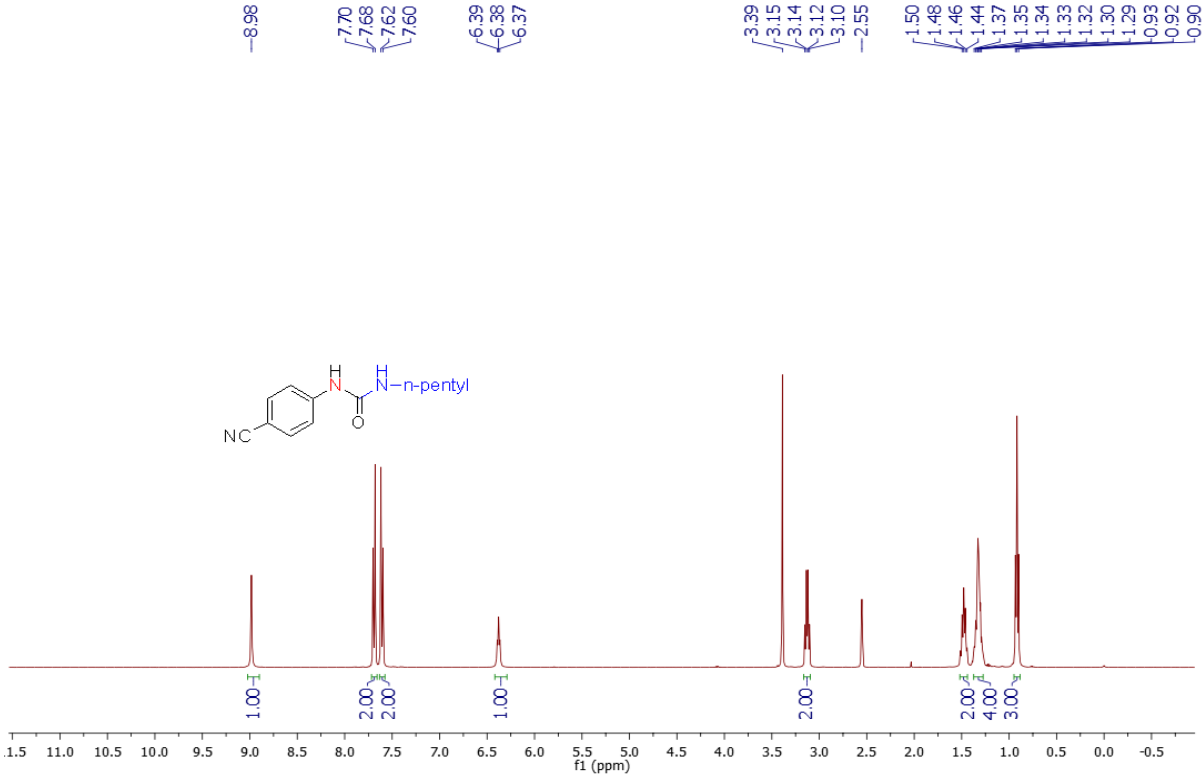
DEPT of 1-(4-methoxyphenyl)-3-pentylurea (3q)



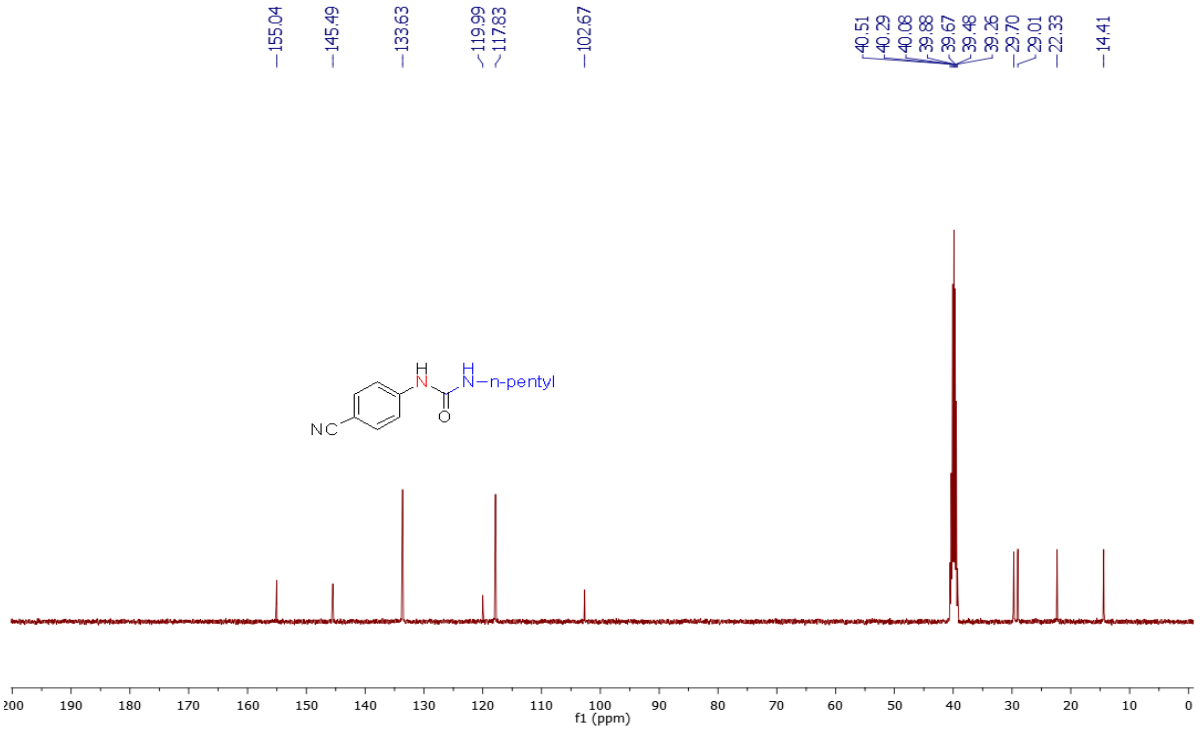
HRMS (ESI-TOF) of compound (3q)



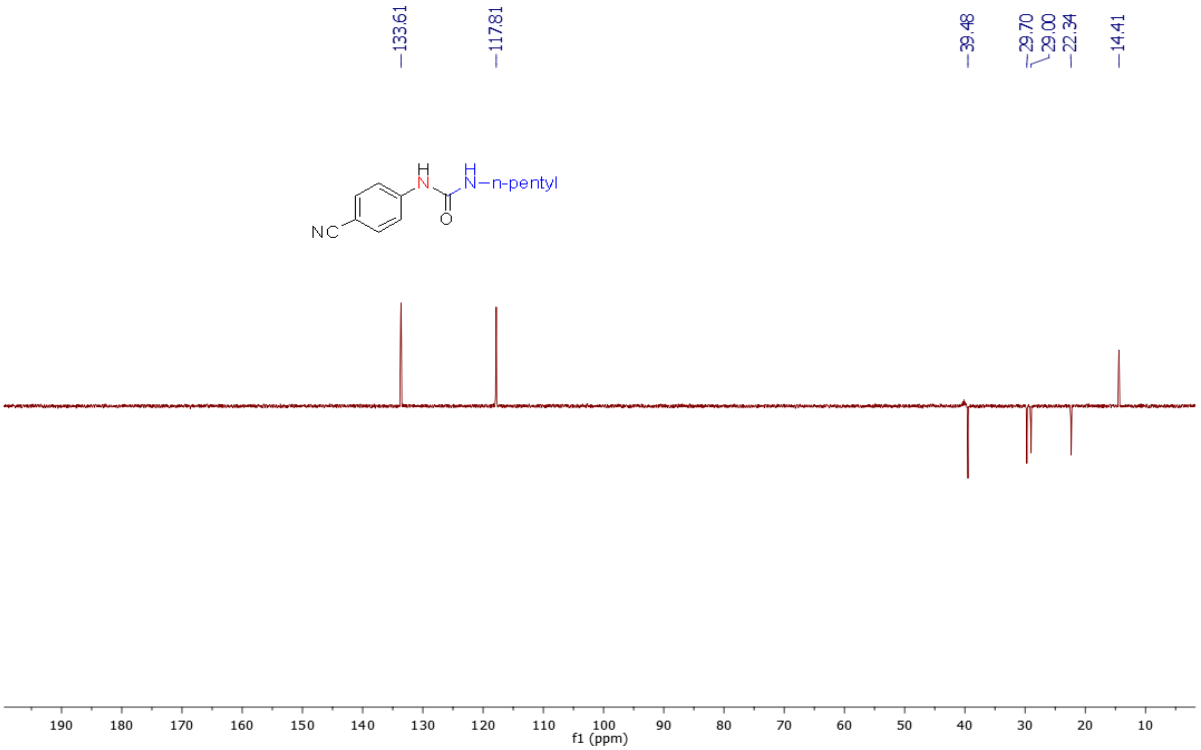
^{1}H-NMR of 1-(4-cyanophenyl)-3-pentylurea (3r)



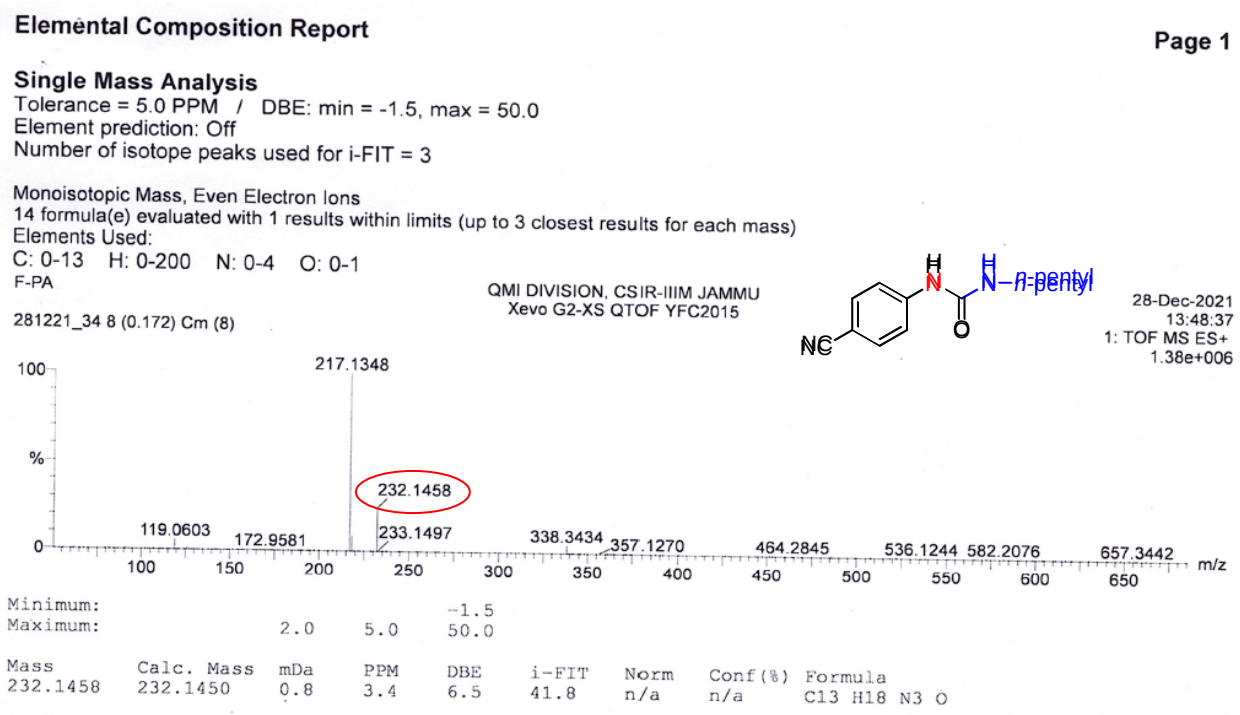
^{13}C-NMR of 1-(4-cyanophenyl)-3-pentylurea (3r)



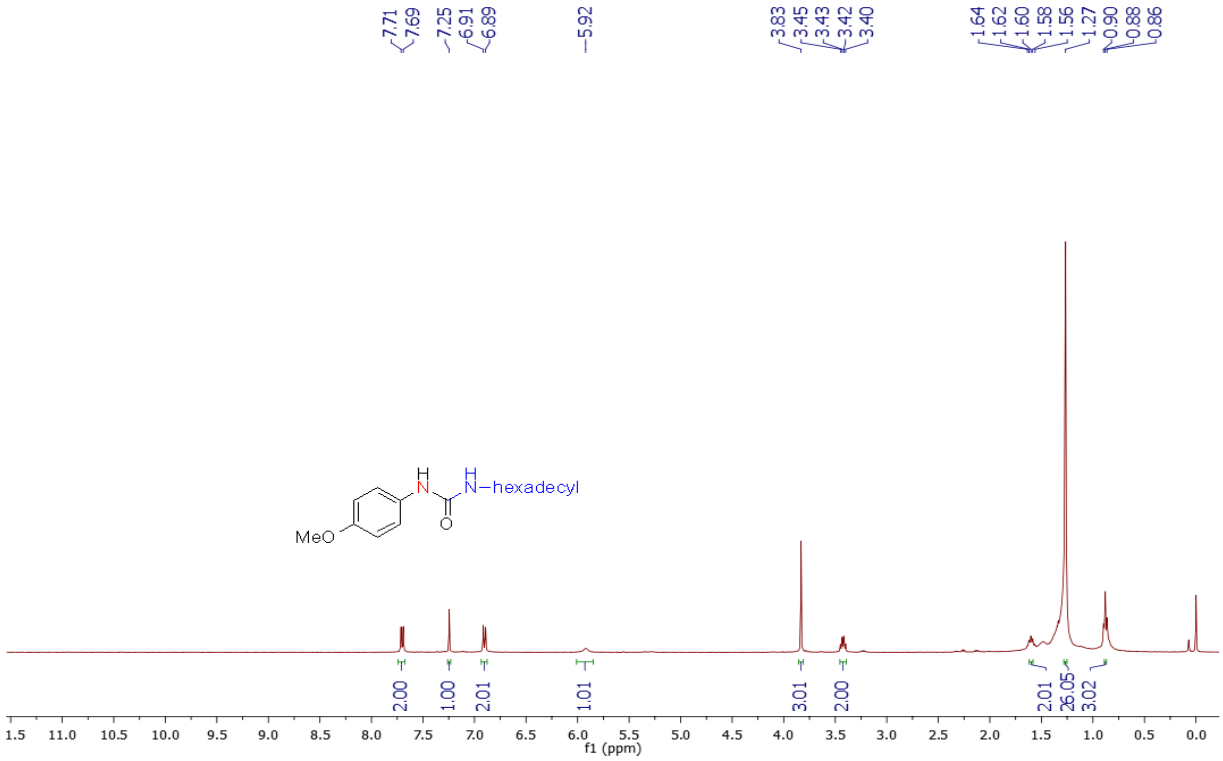
DEPT of 1-(4-cyanophenyl)-3-pentylurea (3r)



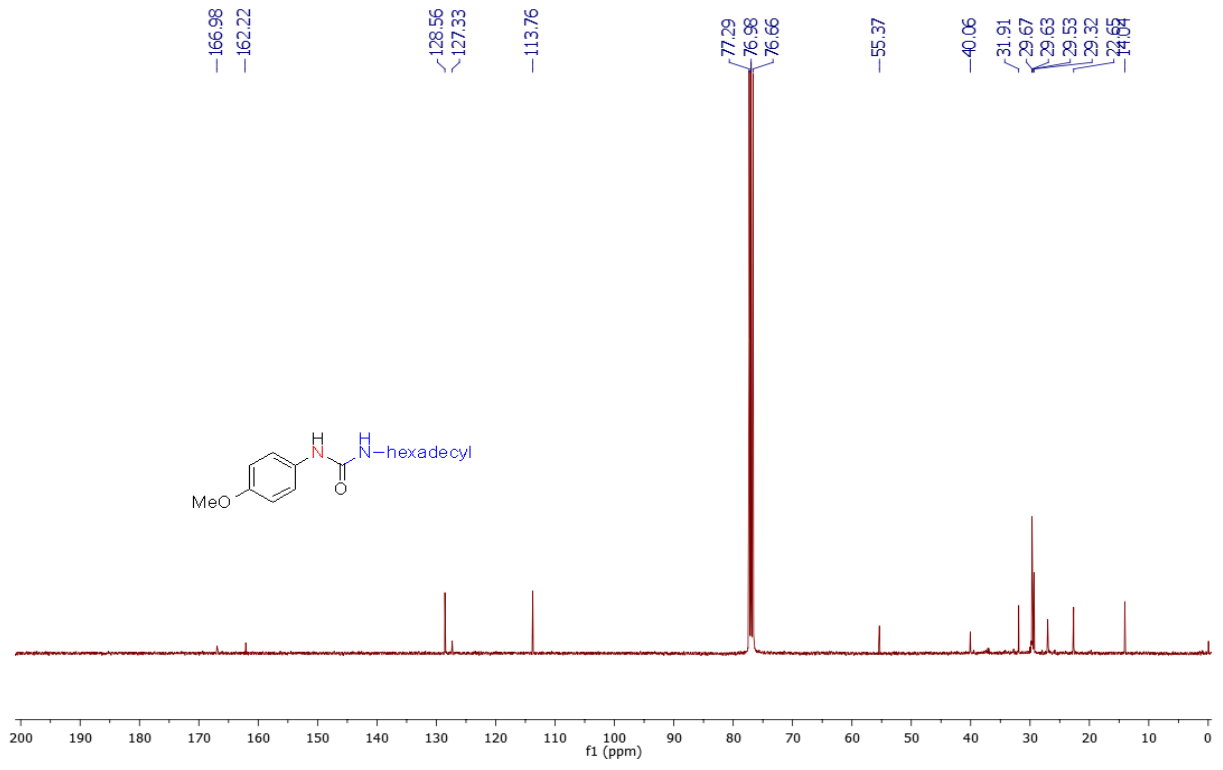
HRMS of 1-(4-cyanophenyl)-3-pentylurea (3r)



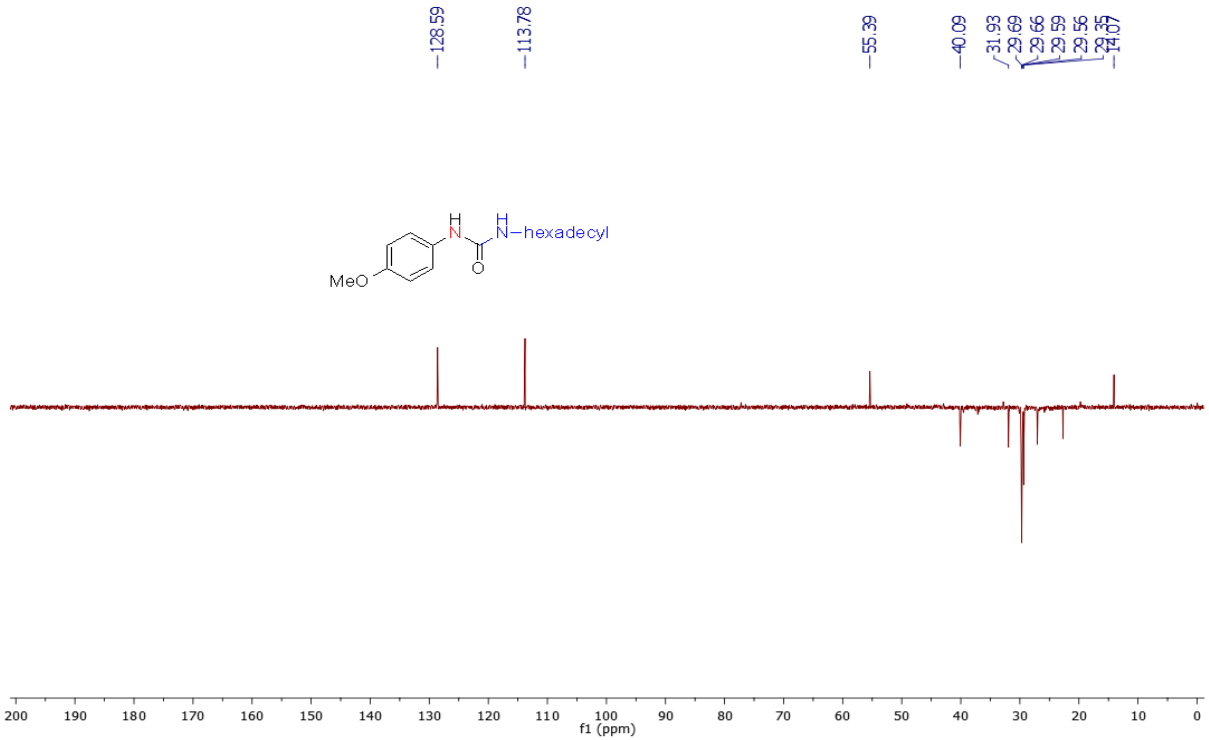
[1]H-NMR of 1-hexadecyl-3-(4-methoxyphenyl)urea (3s)



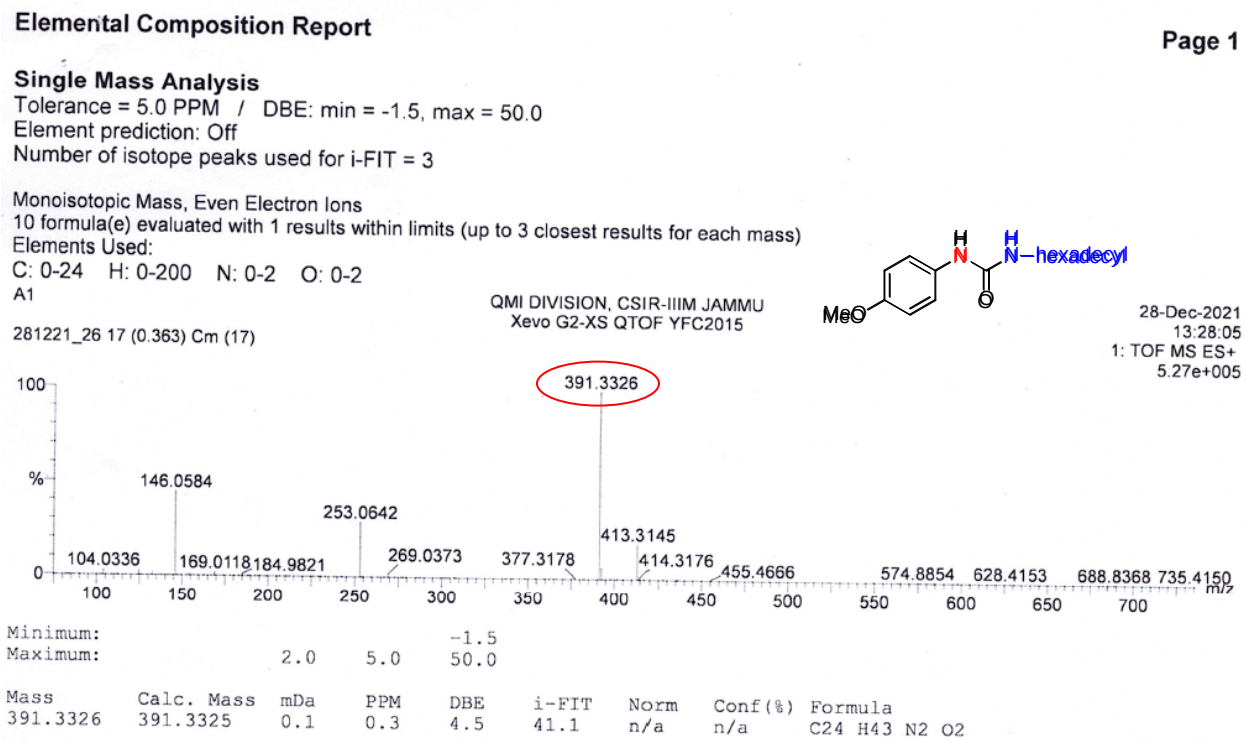
[13]C-NMR of 1-hexadecyl-3-(4-methoxyphenyl)urea (3s)



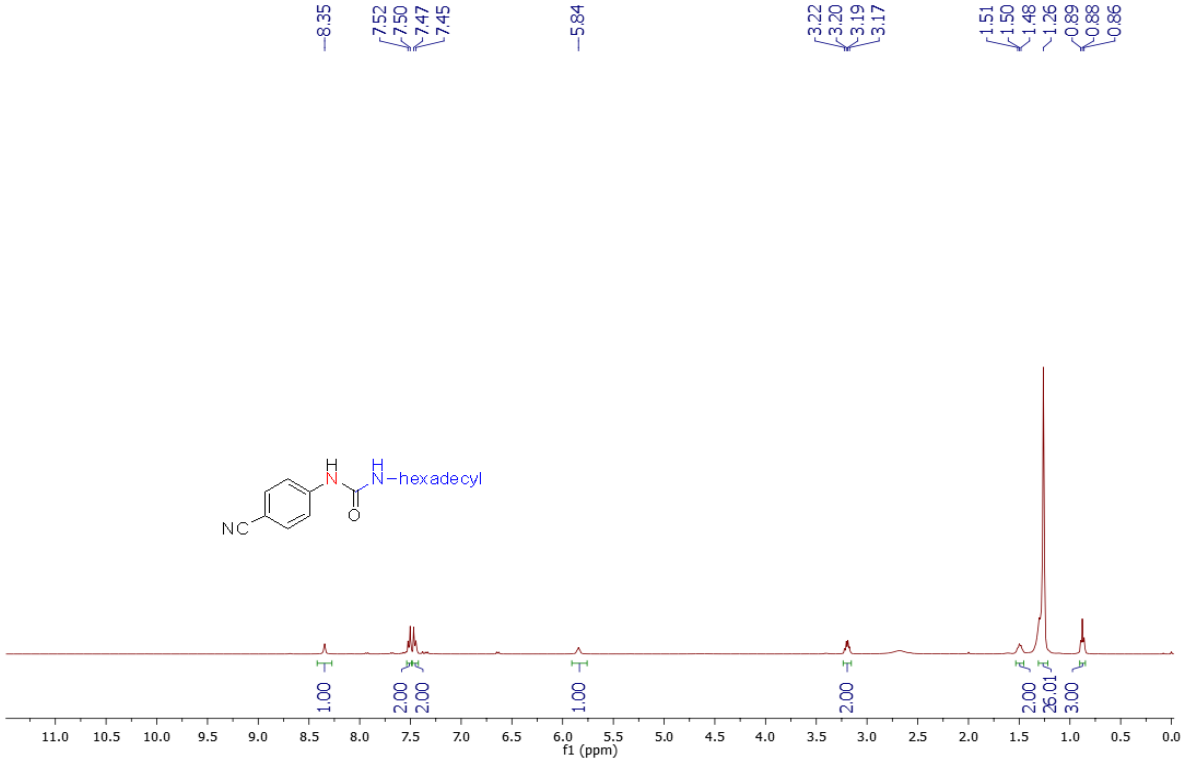
DEPT of 1-hexadecyl-3-(4-methoxyphenyl)urea (3s)



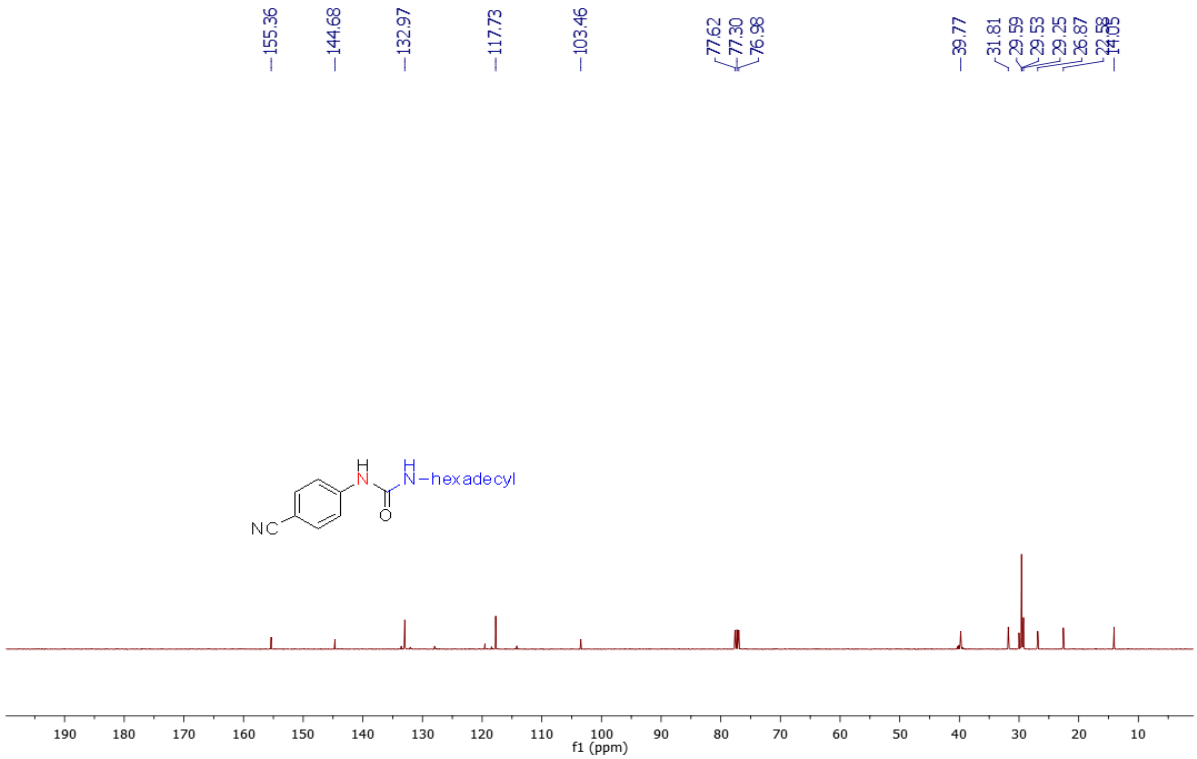
HRMS of 1-hexadecyl-3-(4-methoxyphenyl)urea (3s)



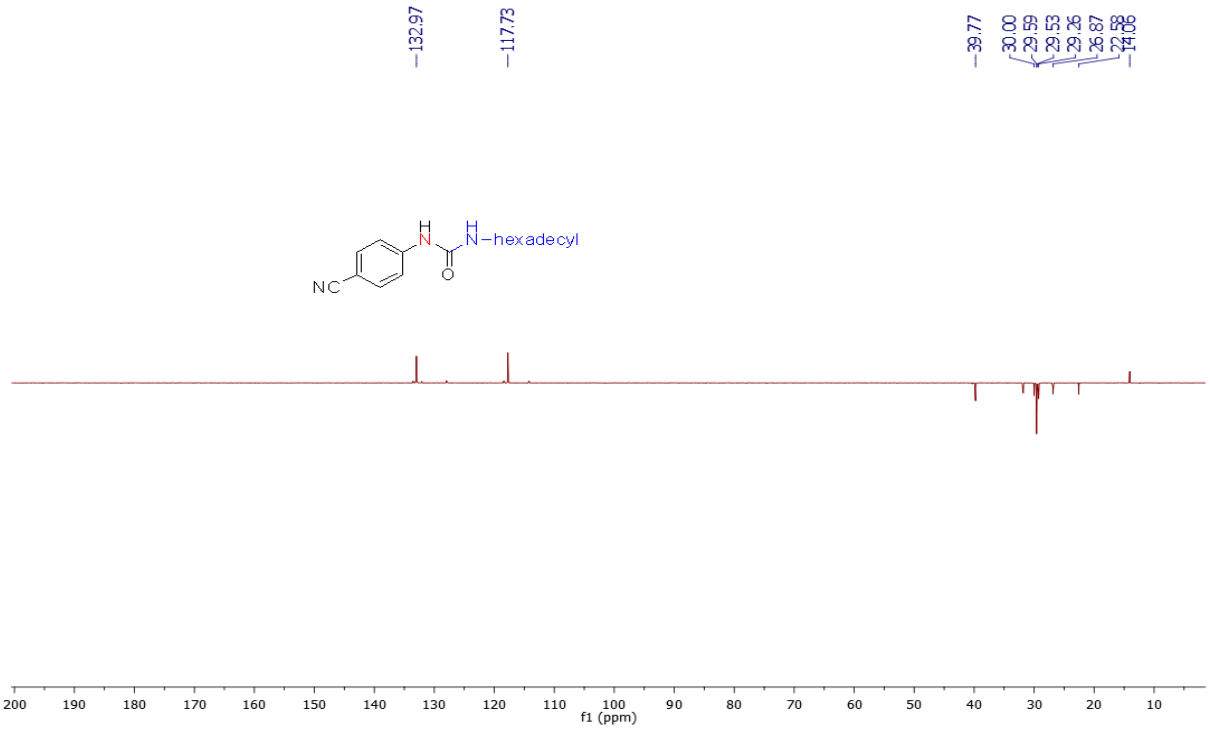
^{1}H-NMR of 1-(4-cyanophenyl)-3-hexadecylurea (3t)



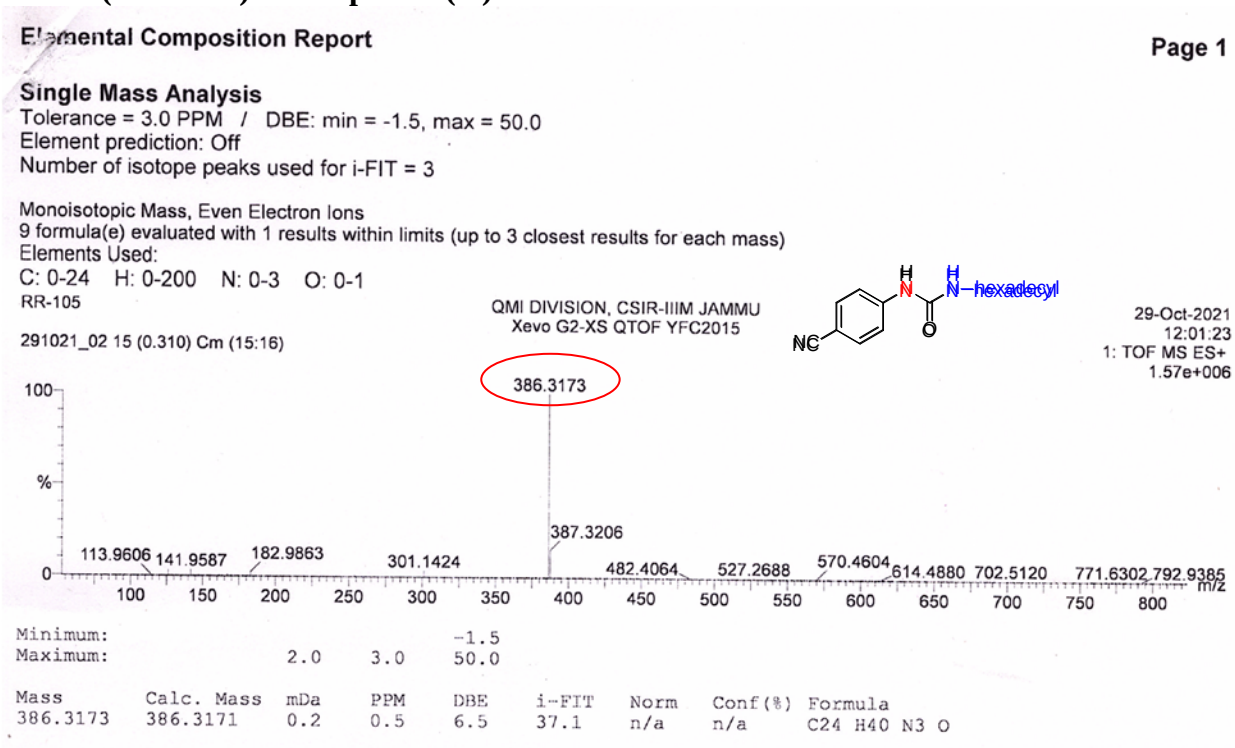
^{13}C-NMR of 1-(4-cyanophenyl)-3-hexadecylurea (3t)



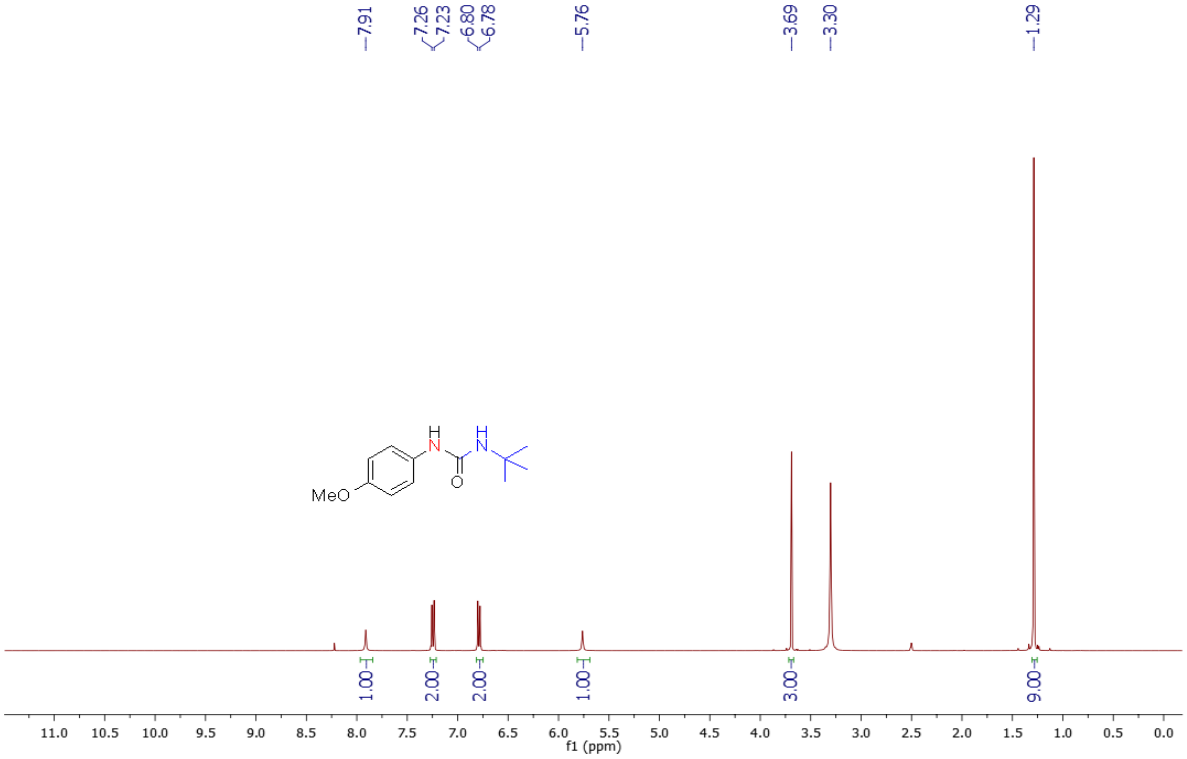
DEPT of 1-(4-cyanophenyl)-3-hexadecylurea (3t)



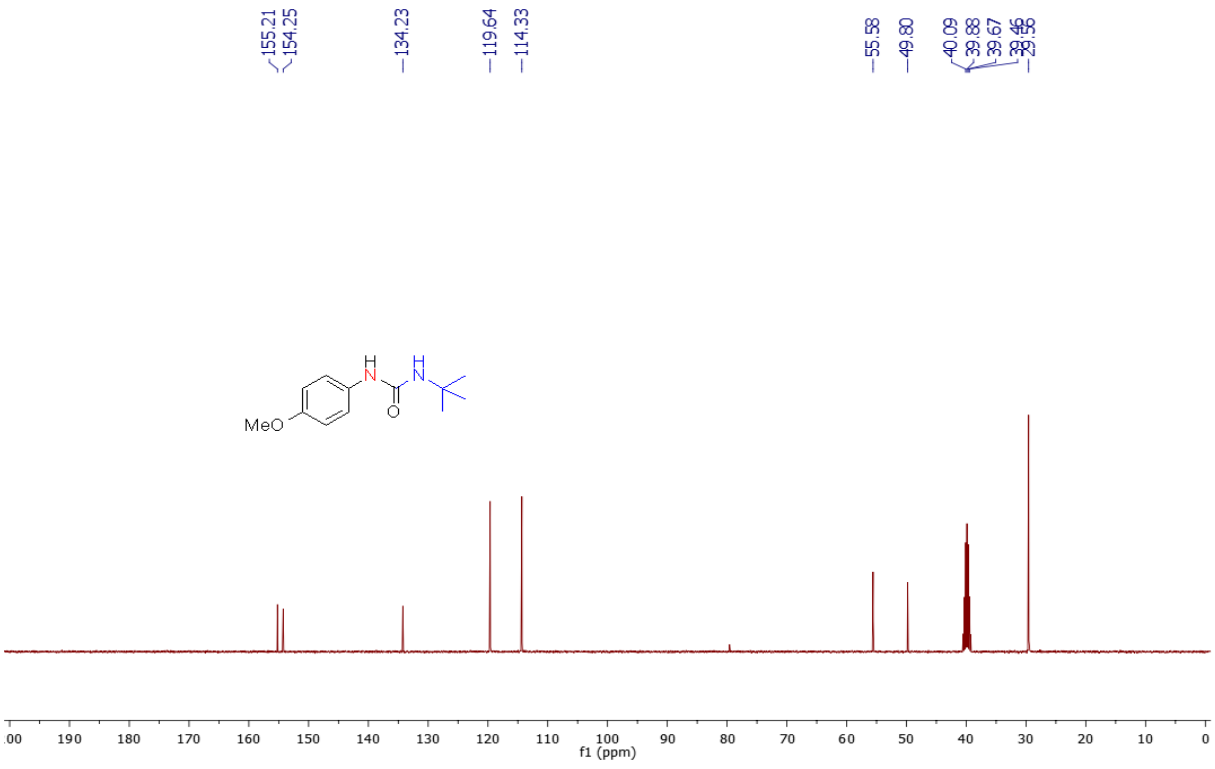
HRMS (ESI-TOF) of compound (3t)



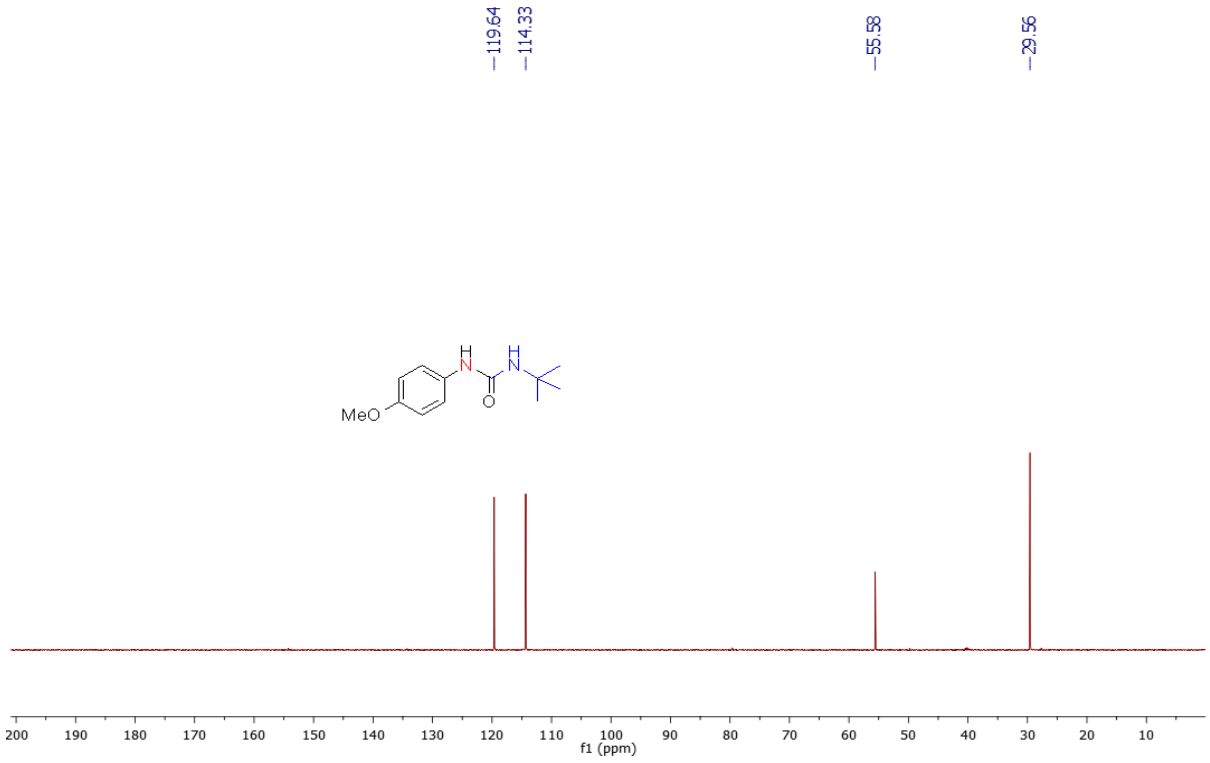
^{1}H-NMR of 1-(tert-butyl)-3-(4-methoxyphenyl)urea (3u)



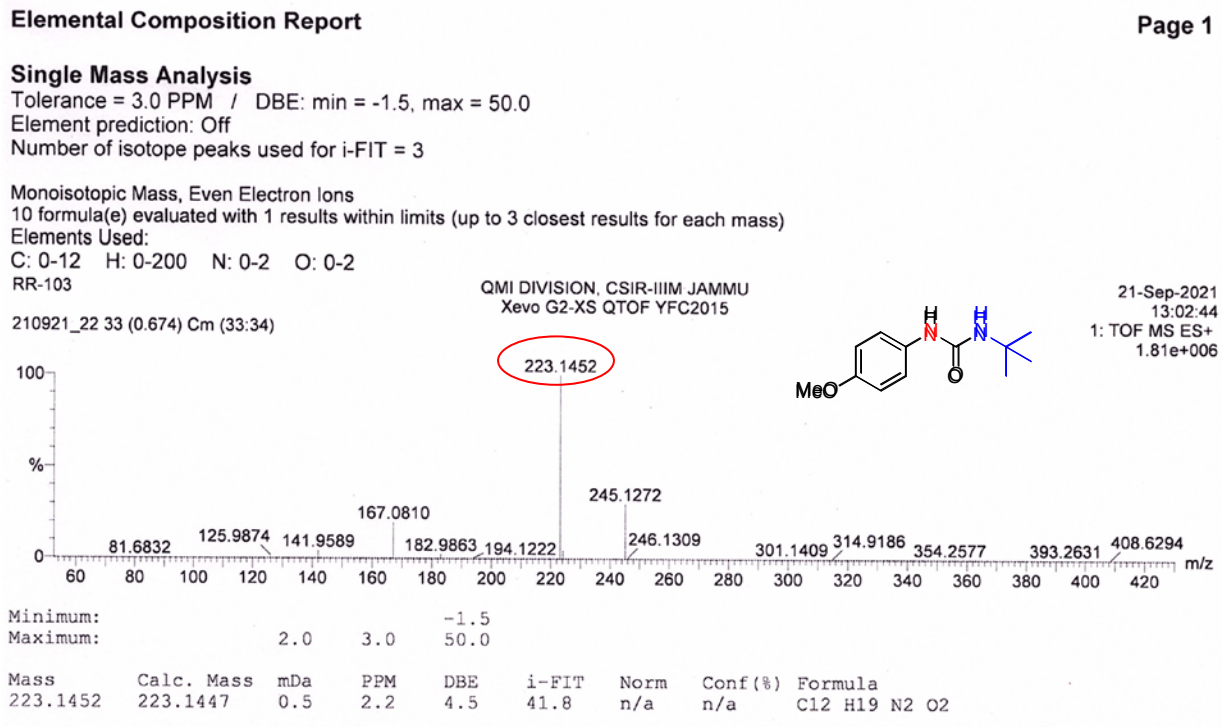
^{13}C-NMR of 1-(tert-butyl)-3-(4-methoxyphenyl)urea (3u)



DEPT of 1-(tert-butyl)-3-(4-methoxyphenyl)urea (3u)



HRMS (ESI-TOF) of compound (3u)



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
10 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-12 H: 0-200 N: 0-2 O: 0-2

RR-103

210921_22 33 (0.674) Cm (33:34)

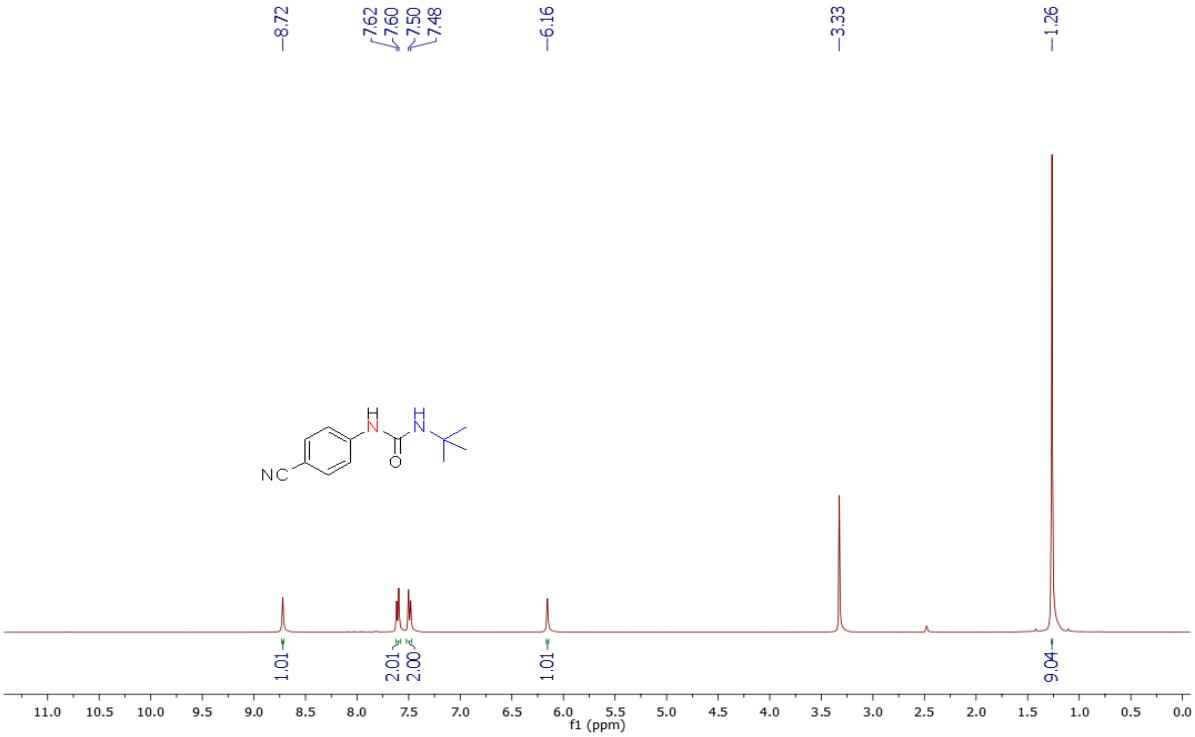
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

21-Sep-2021
13:02:44
1: TOF MS ES+
1.81e+006

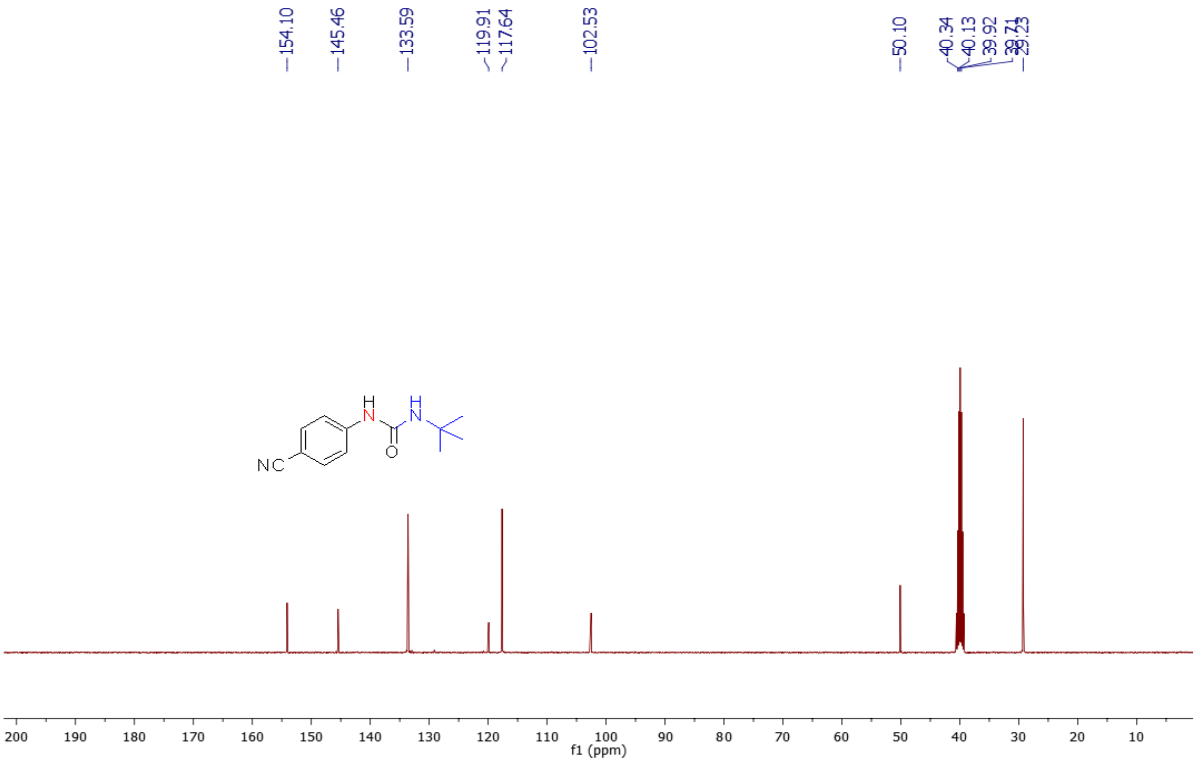
223.1452
245.1272
167.0810
81.6832
125.9874
141.9589
182.9863
194.1222
246.1309
301.1409
314.9186
354.2577
393.2631
408.6294
m/z

Minimum:				-1.5				
Maximum:		2.0	3.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
223.1452	223.1447	0.5	2.2	4.5	41.8	n/a	n/a	C12 H19 N2 O2

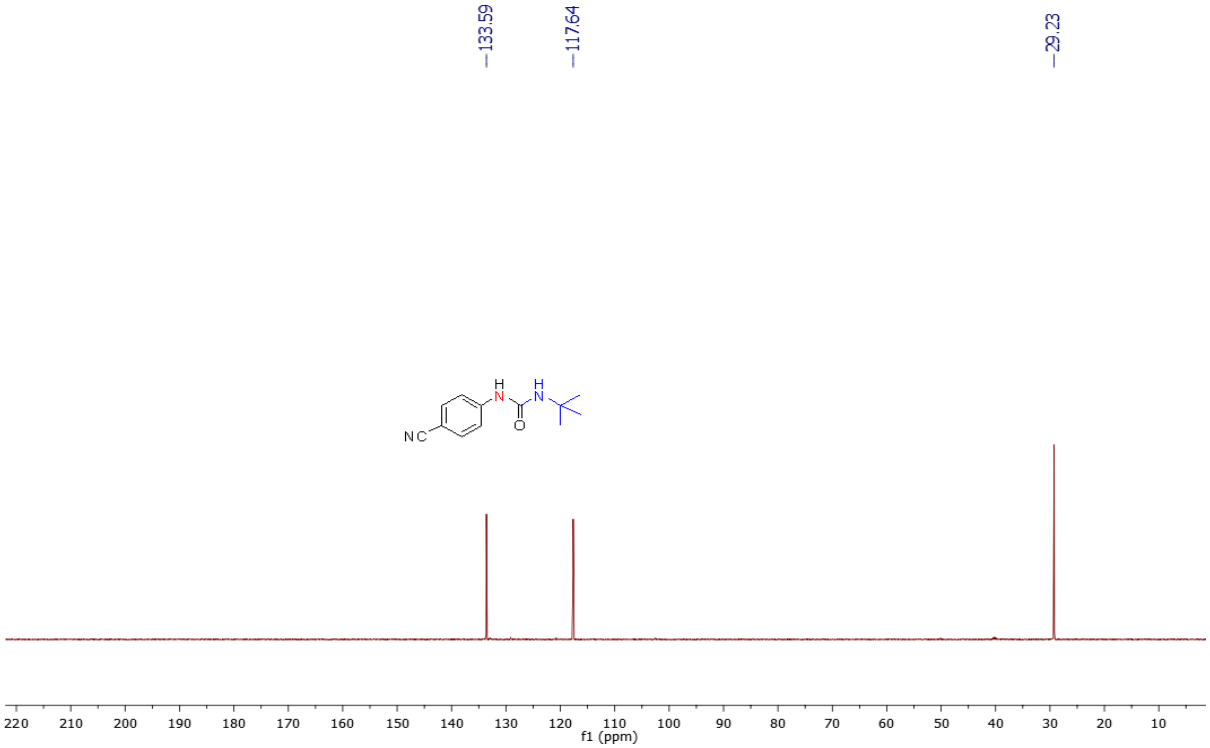
^{1}H-NMR of 1-(tert-butyl)-3-(4-cyanophenyl)urea (3v)



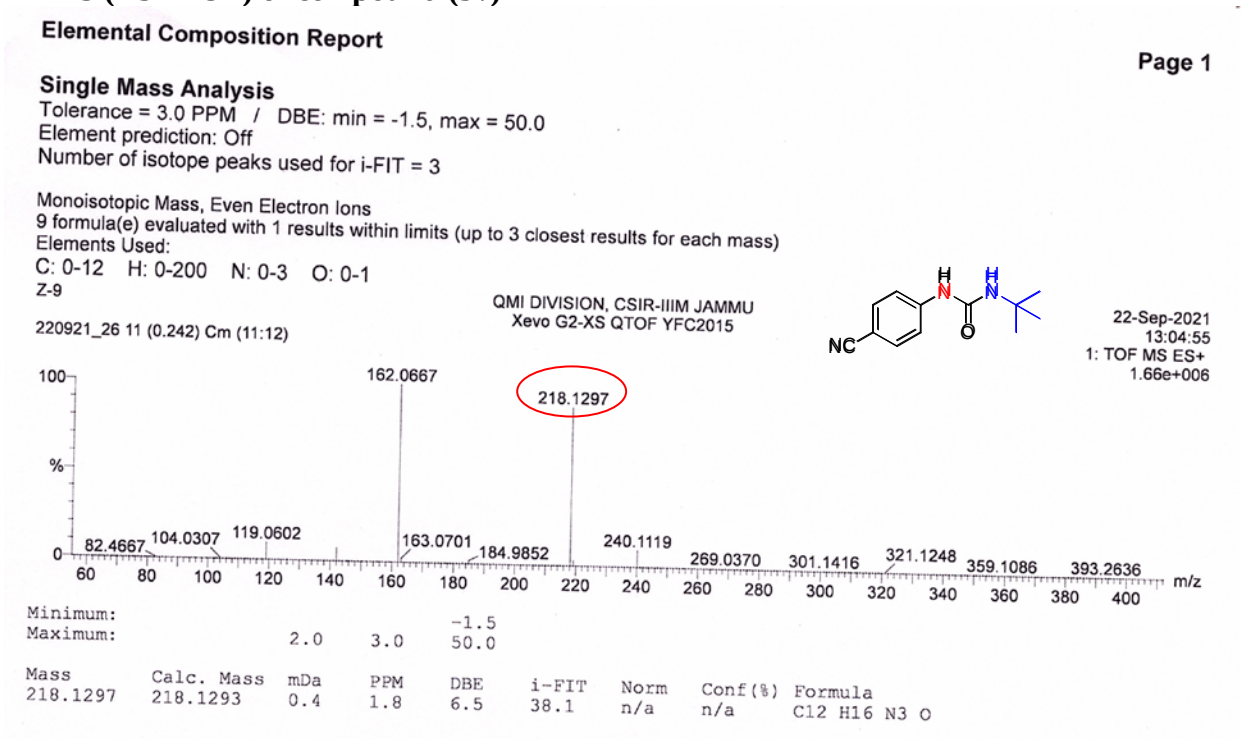
^{13}C-NMR of 1-(tert-butyl)-3-(4-cyanophenyl)urea (3v)



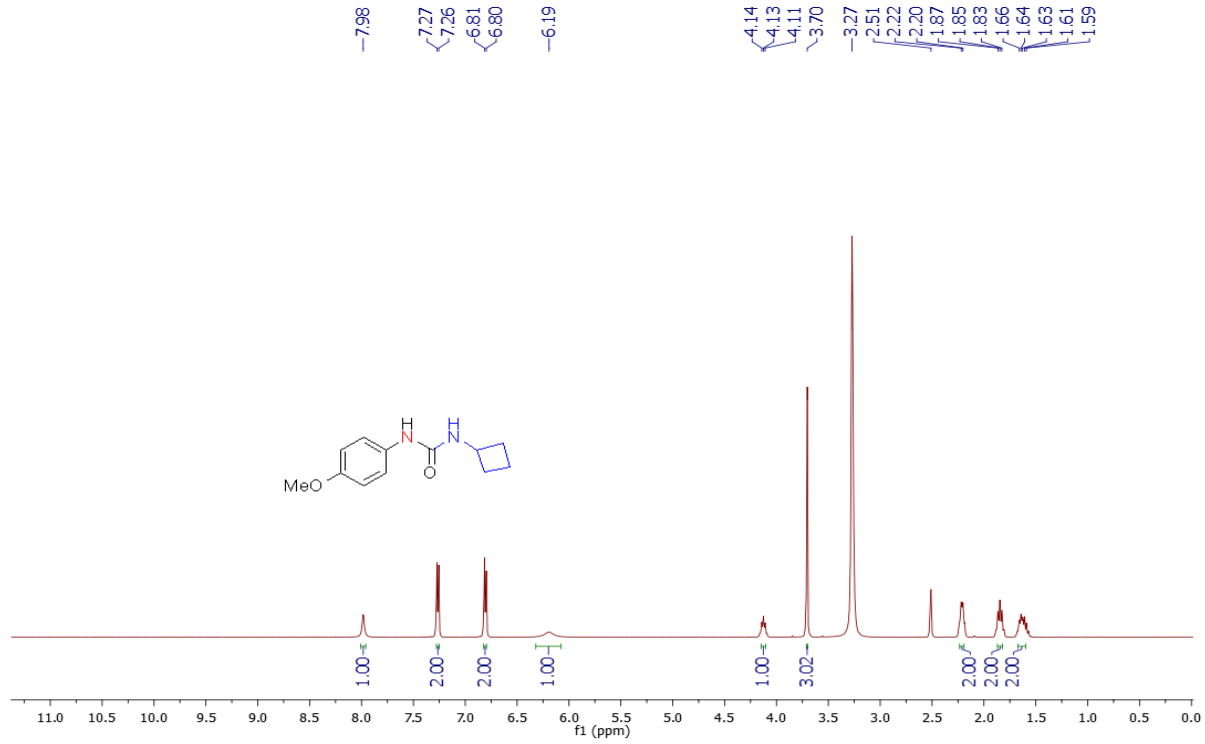
DEPT of 1-(tert-butyl)-3-(4-cyanophenyl)urea (3v)



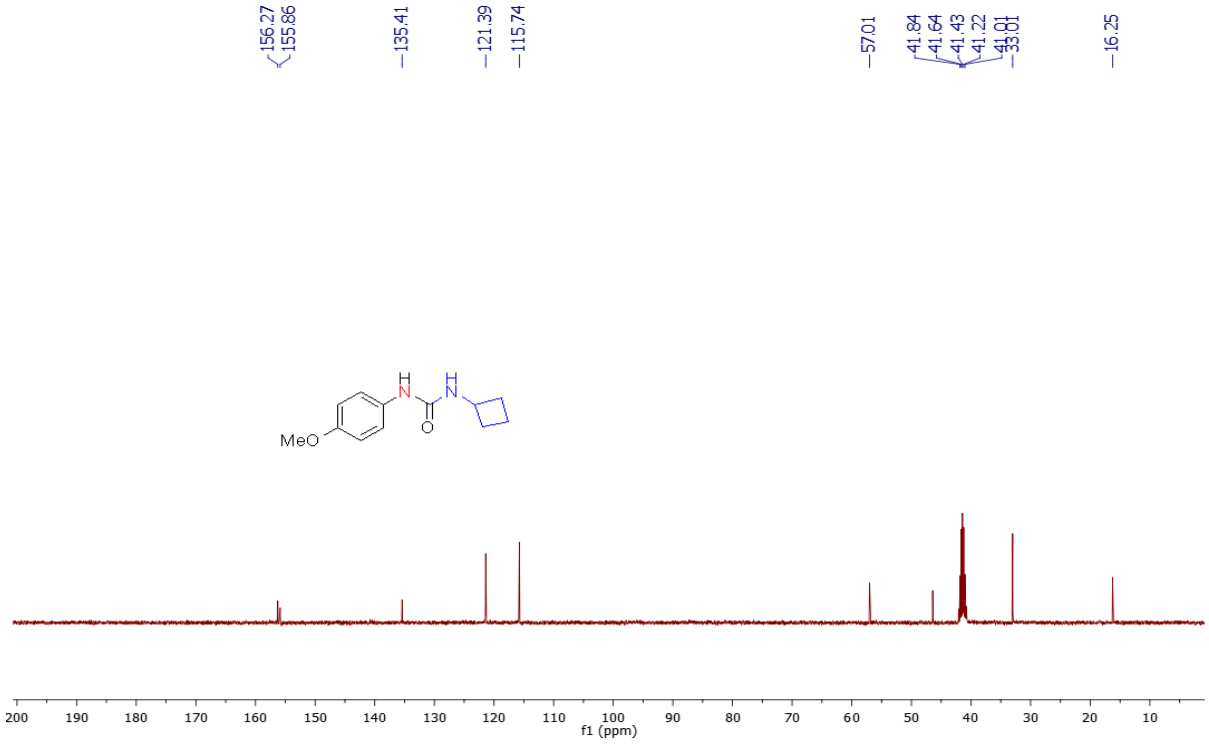
HRMS (ESI-TOF) of compound (3v)



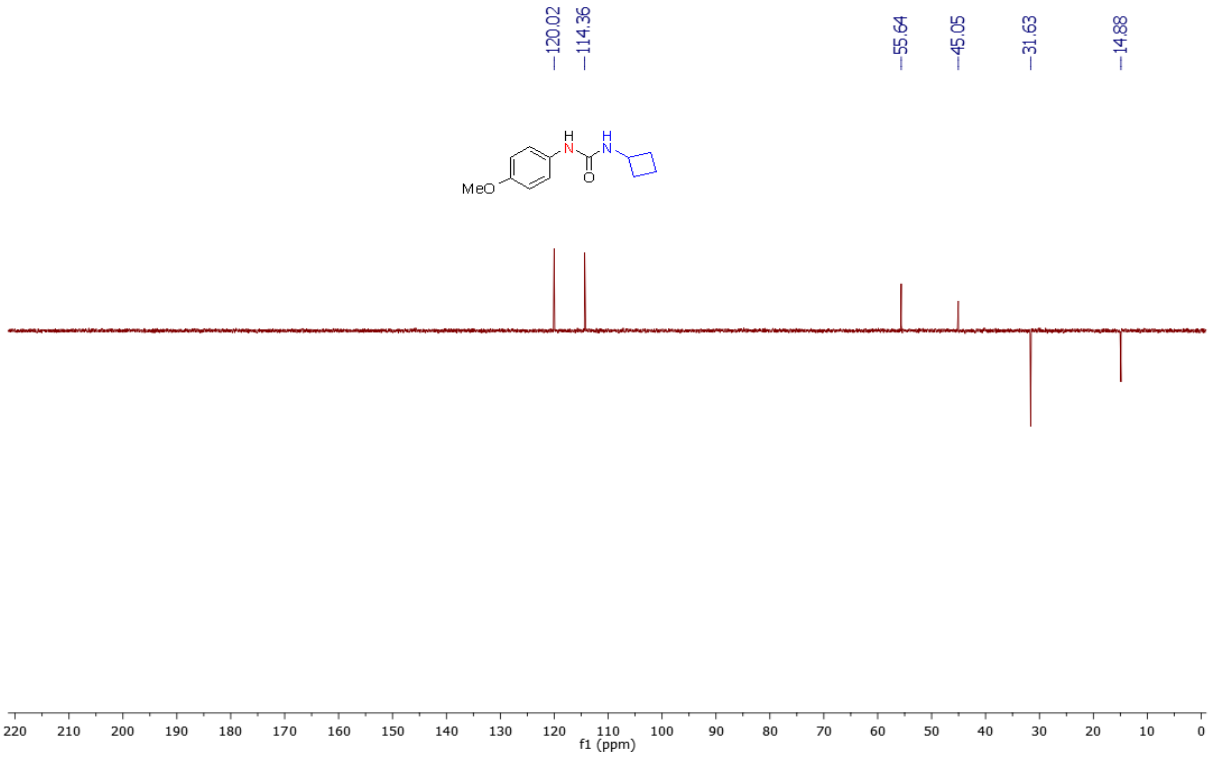
[1]H-NMR of 1-cyclobutyl-3-(4-methoxyphenyl)urea (3w)



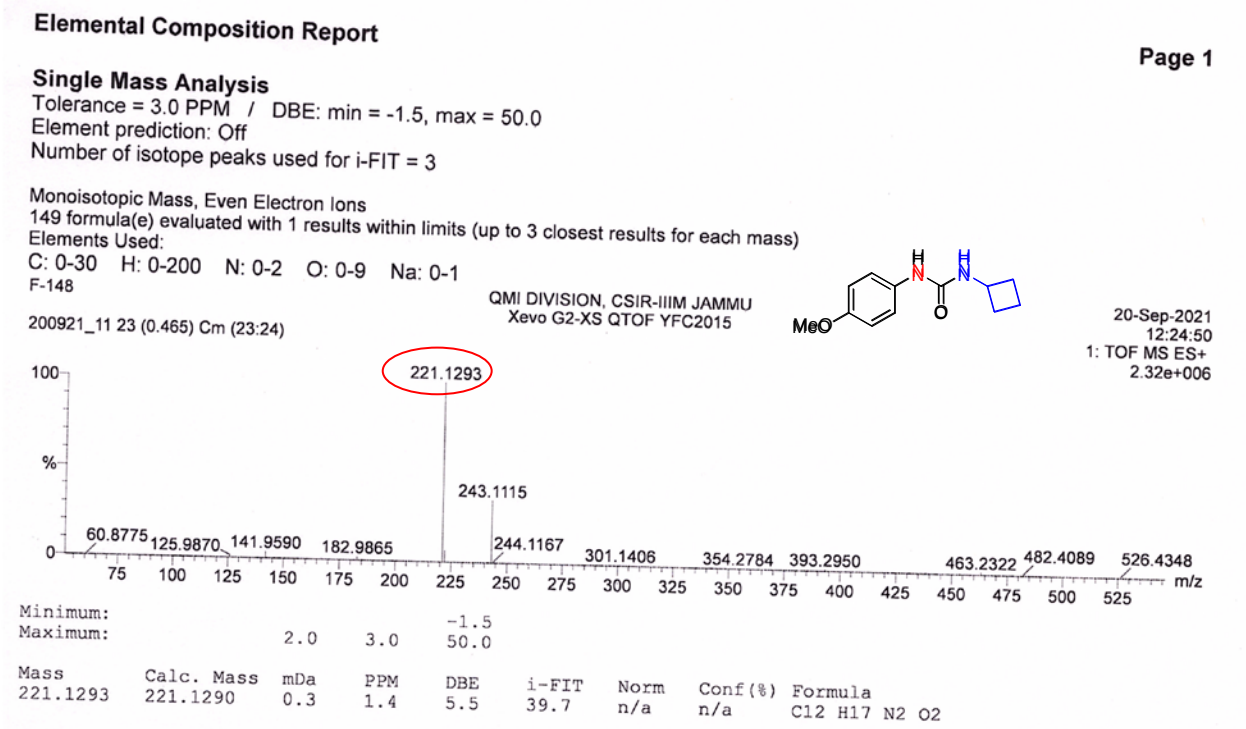
[13]C-NMR of 1-cyclobutyl-3-(4-methoxyphenyl)urea (3w)



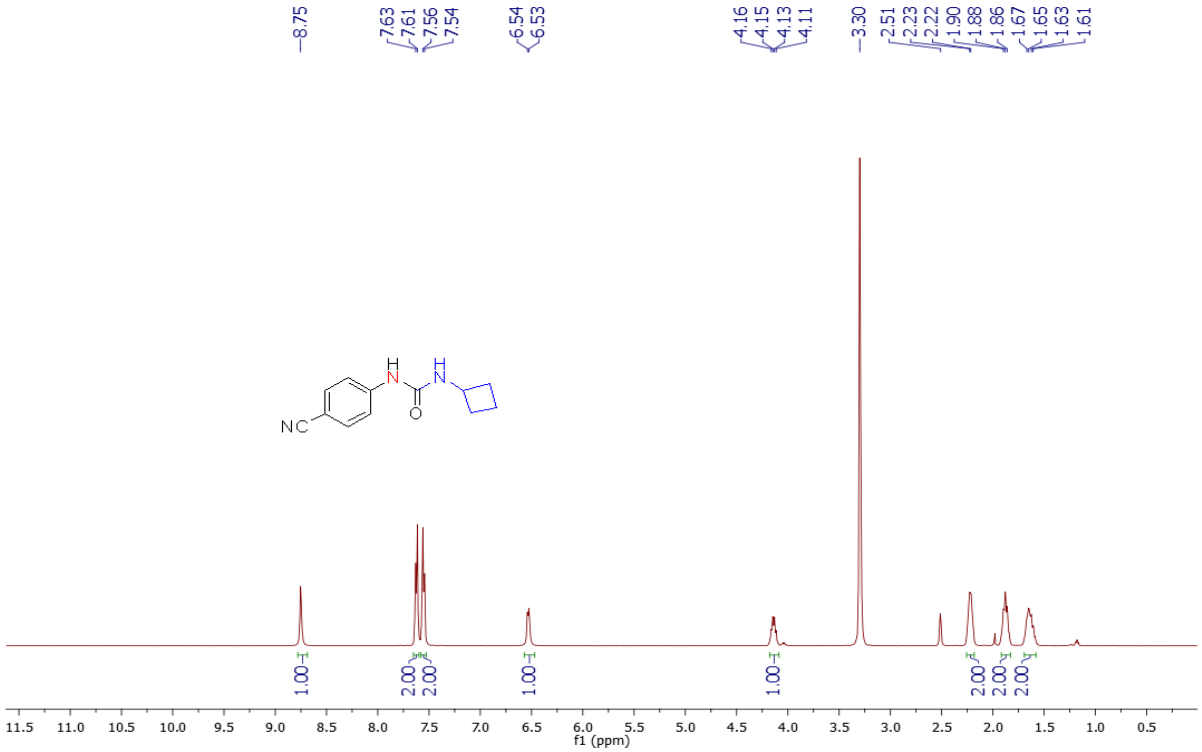
DEPT of 1-cyclobutyl-3-(4-methoxyphenyl)urea (3w)



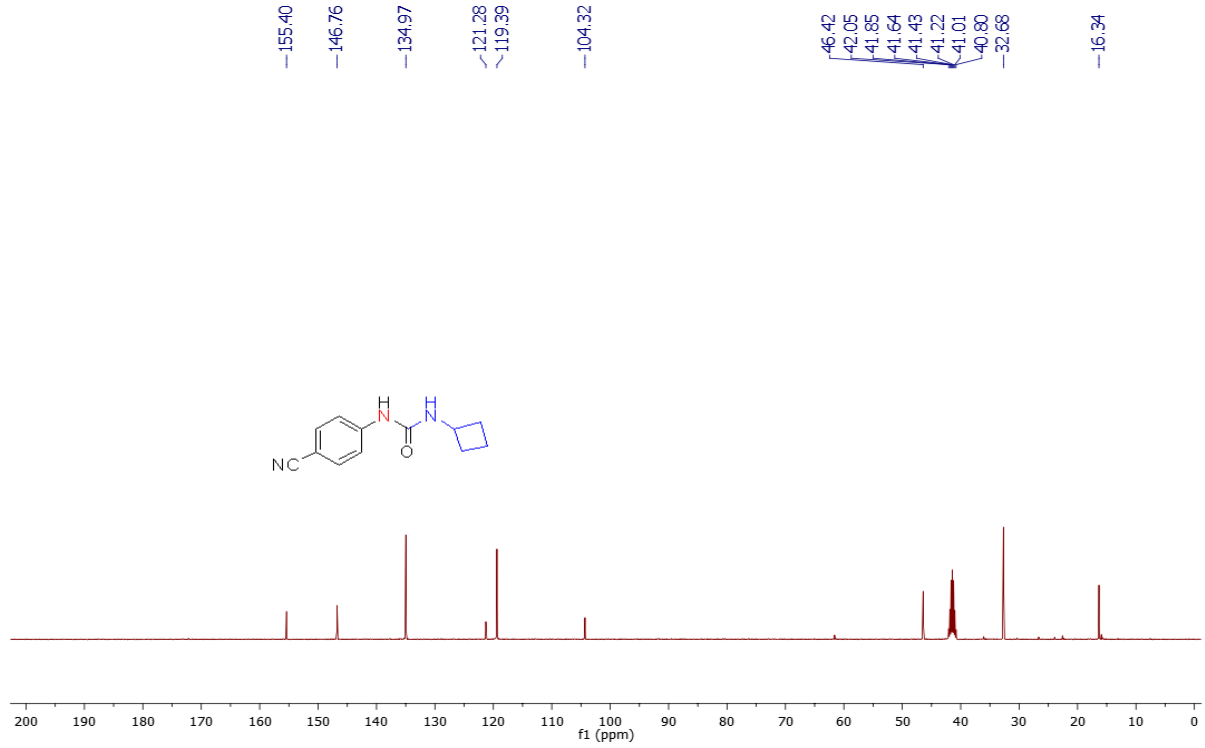
HRMS (ESI-TOF) of compound (3w)



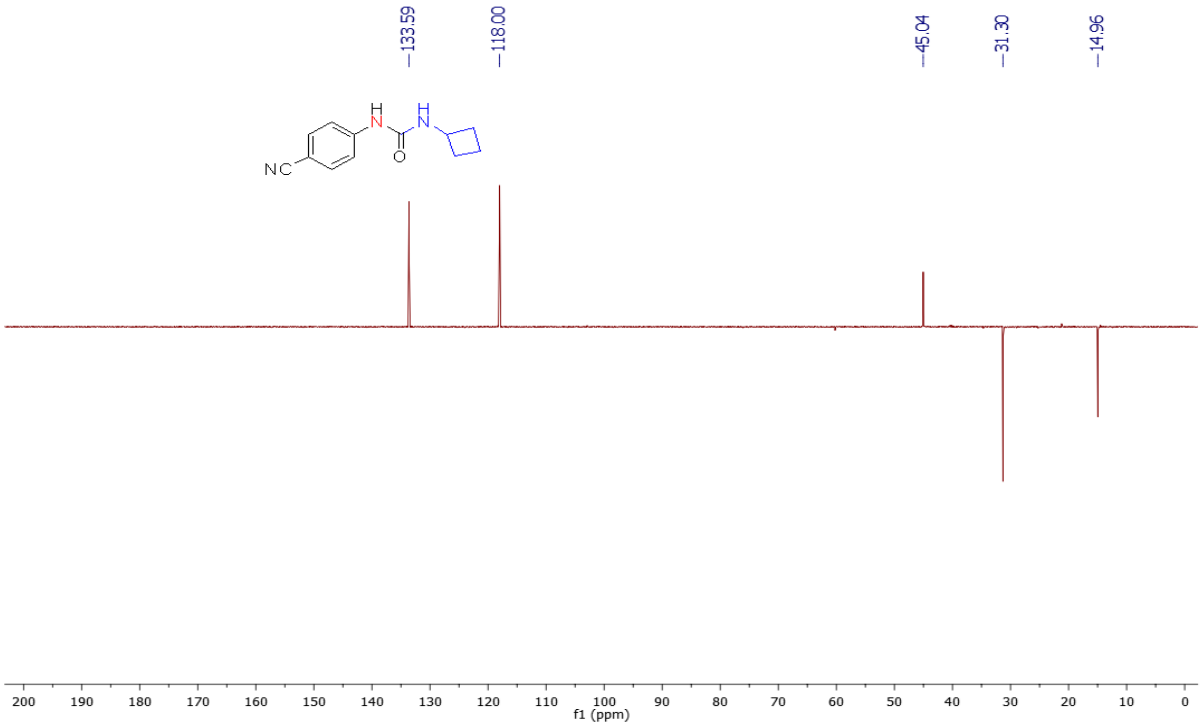
^{1}H-NMR of 1-(4-cyanophenyl)-3-cyclobutylurea (3x)



^{13}C-NMR of 1-(4-cyanophenyl)-3-cyclobutylurea (3x)



DEPT of 1-(4-cyanophenyl)-3-cyclobutylurea (3x)



HRMS (ESI-TOF) of compound (3x)

Elemental Composition Report

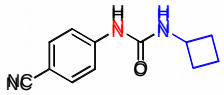
Page 1

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

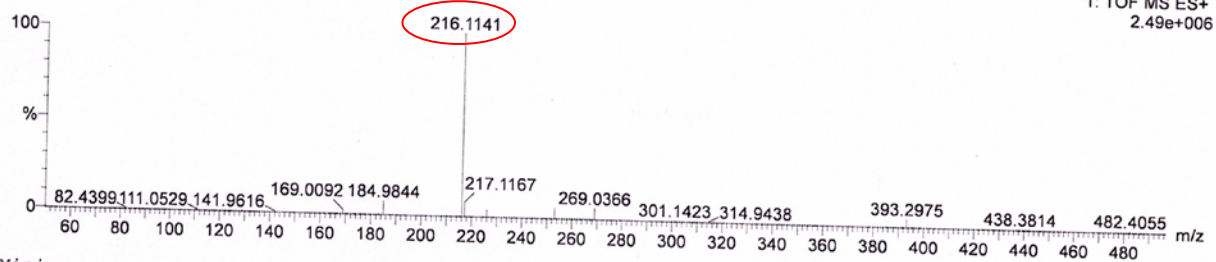
Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-12 H: 0-200 N: 0-3 O: 0-1
F-165

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

200921_04 14 (0.293) Cm (14:15)

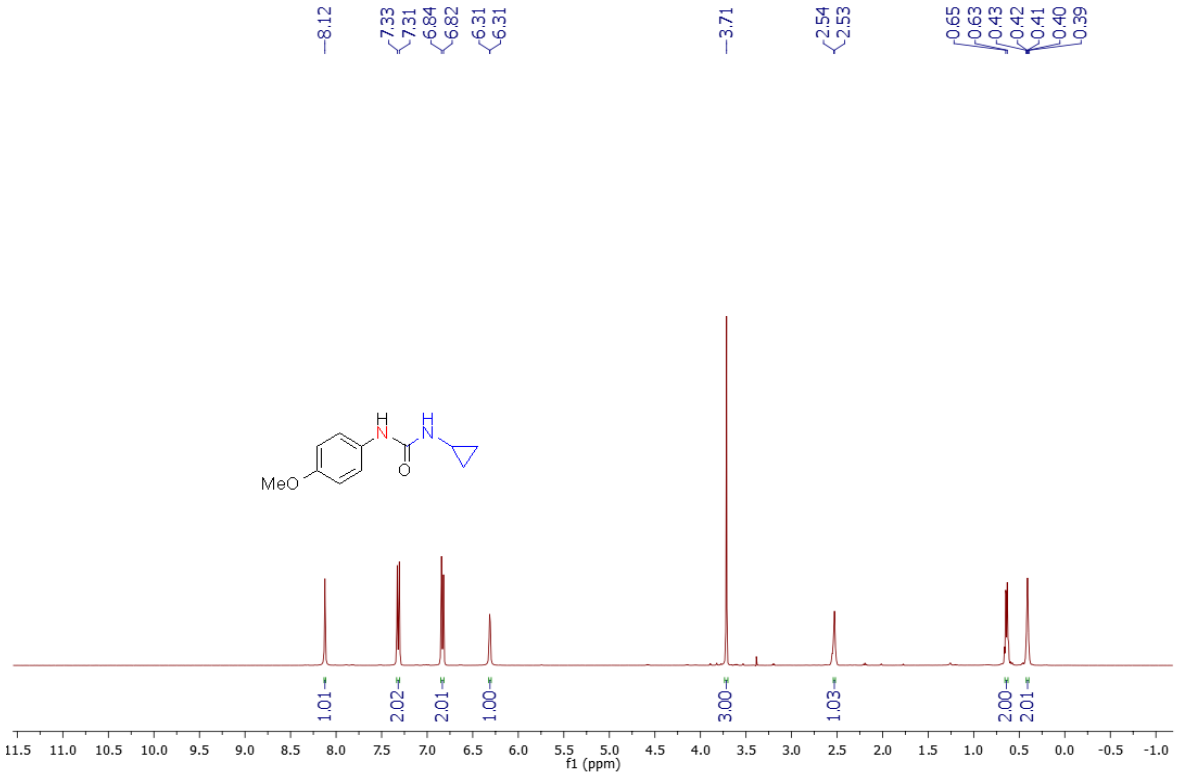


20-Sep-2021
12:06:11
1: TOF MS ES+
2.49e+006

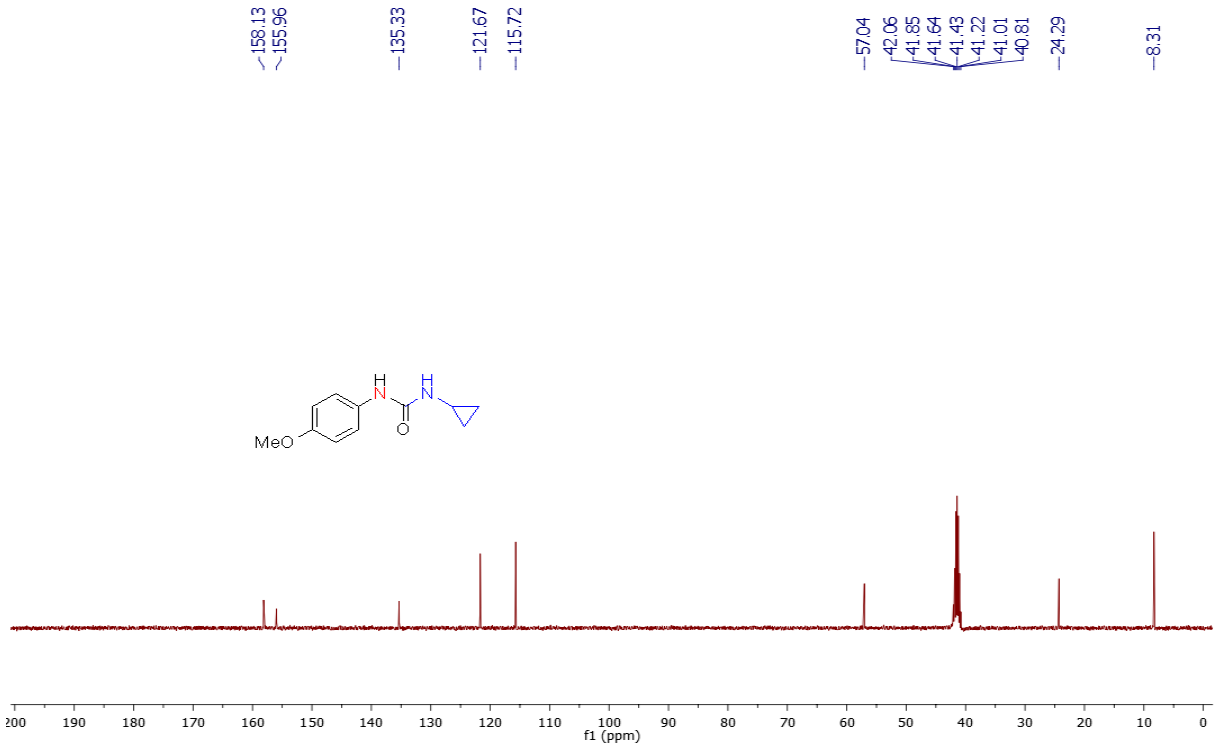


Minimum:				-1.5				
Maximum:		2.0	3.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
216.1141	216.1137	0.4	1.9	7.5	44.2	n/a	n/a	C12 H14 N3 O

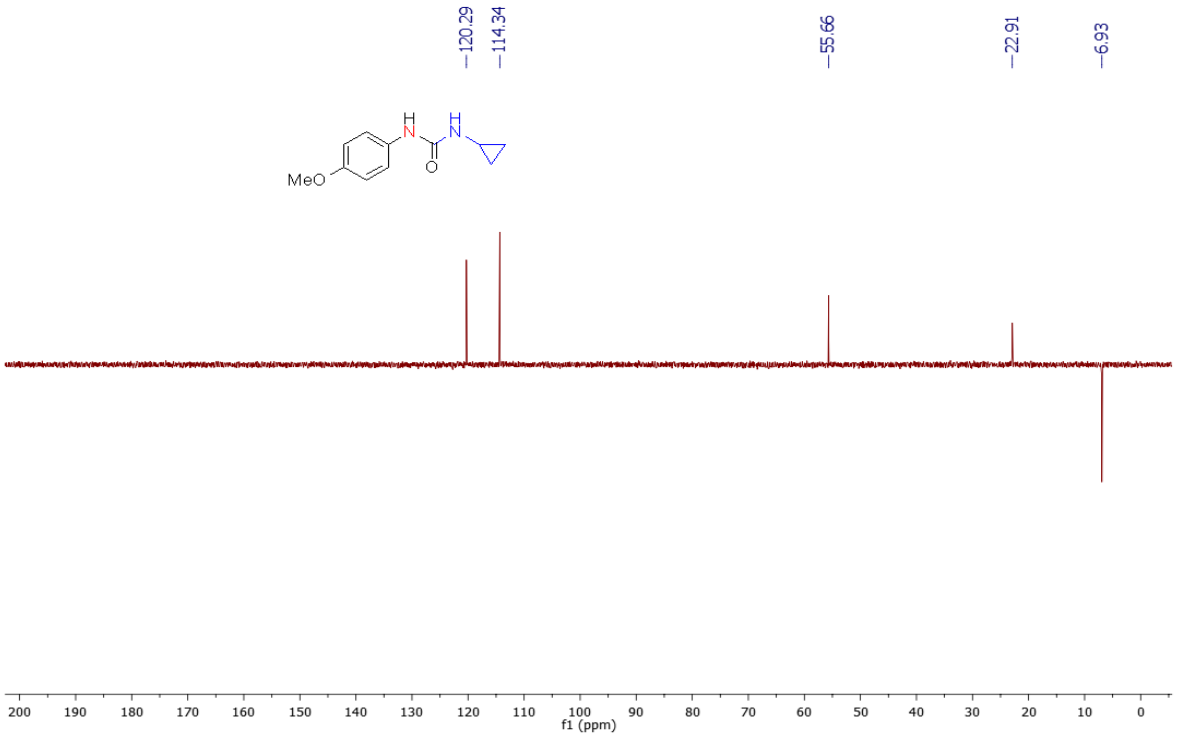
^{1}H-NMR of 1-cyclopropyl-3-(4-methoxyphenyl)urea (3y)



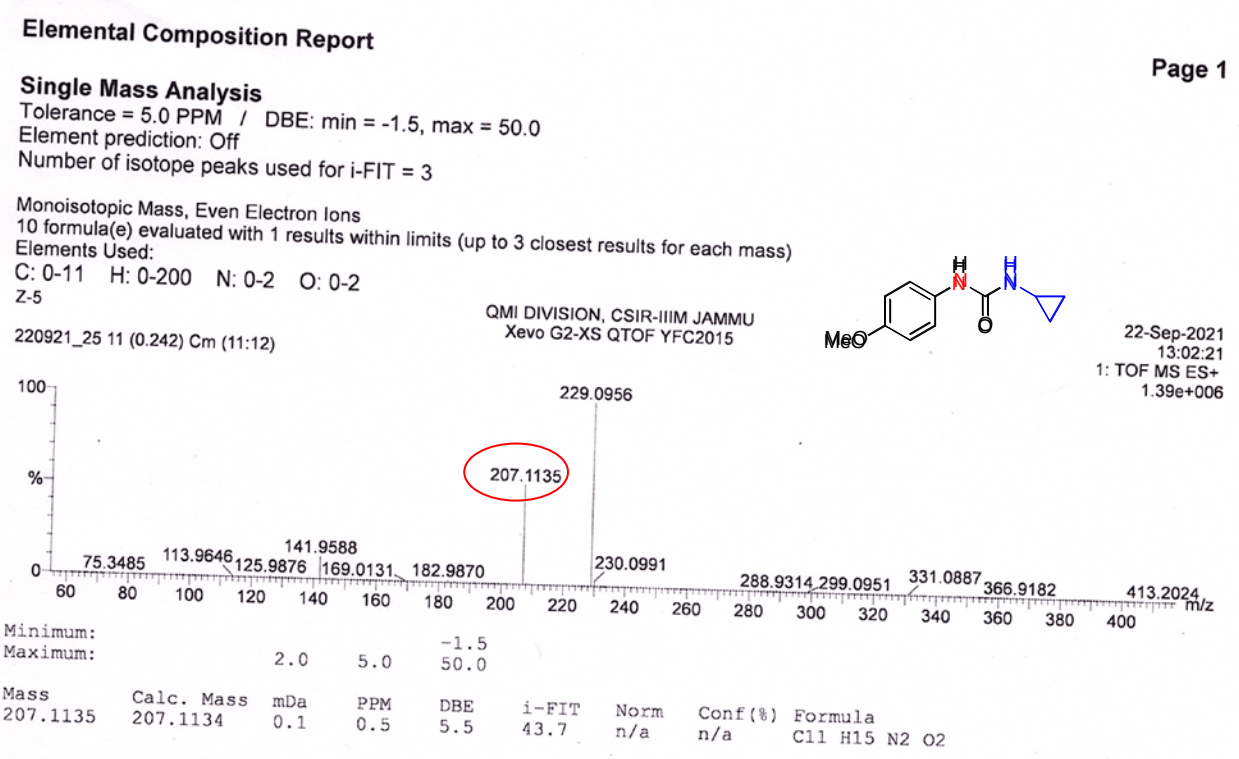
^{13}C-NMR of 1-cyclopropyl-3-(4-methoxyphenyl)urea (3y)



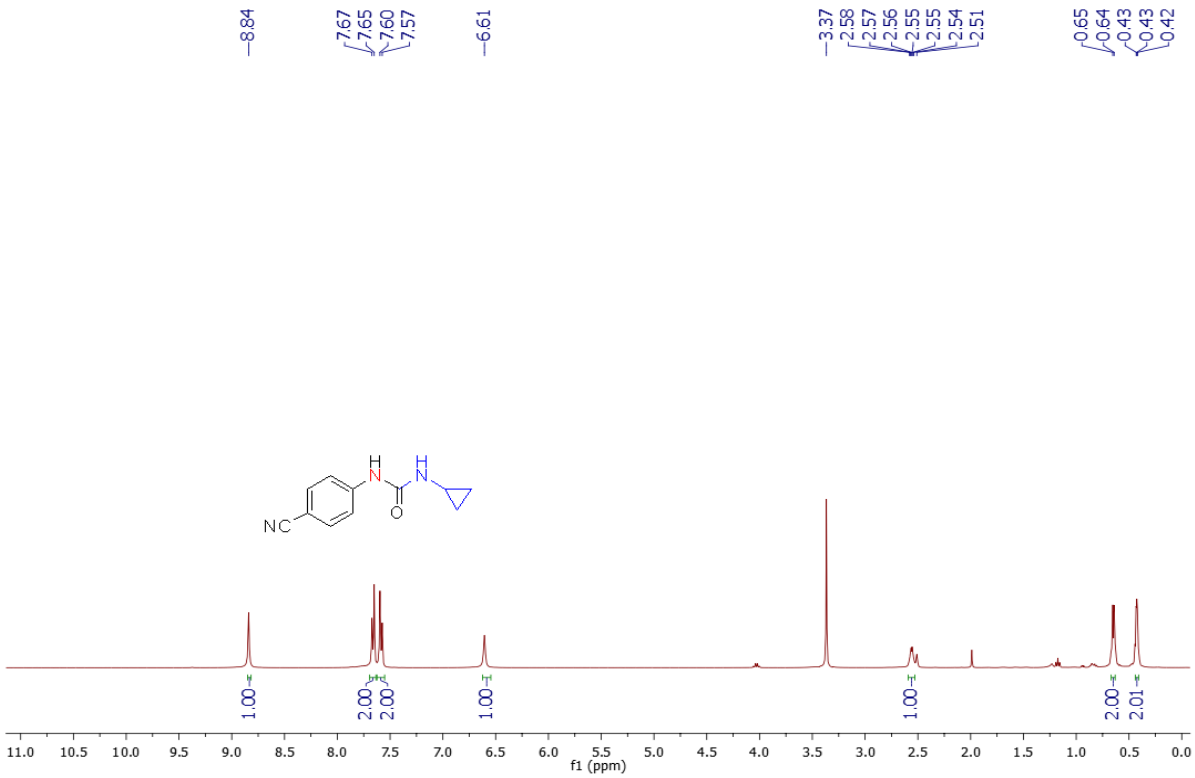
DEPT of 1-cyclopropyl-3-(4-methoxyphenyl)urea (3y)



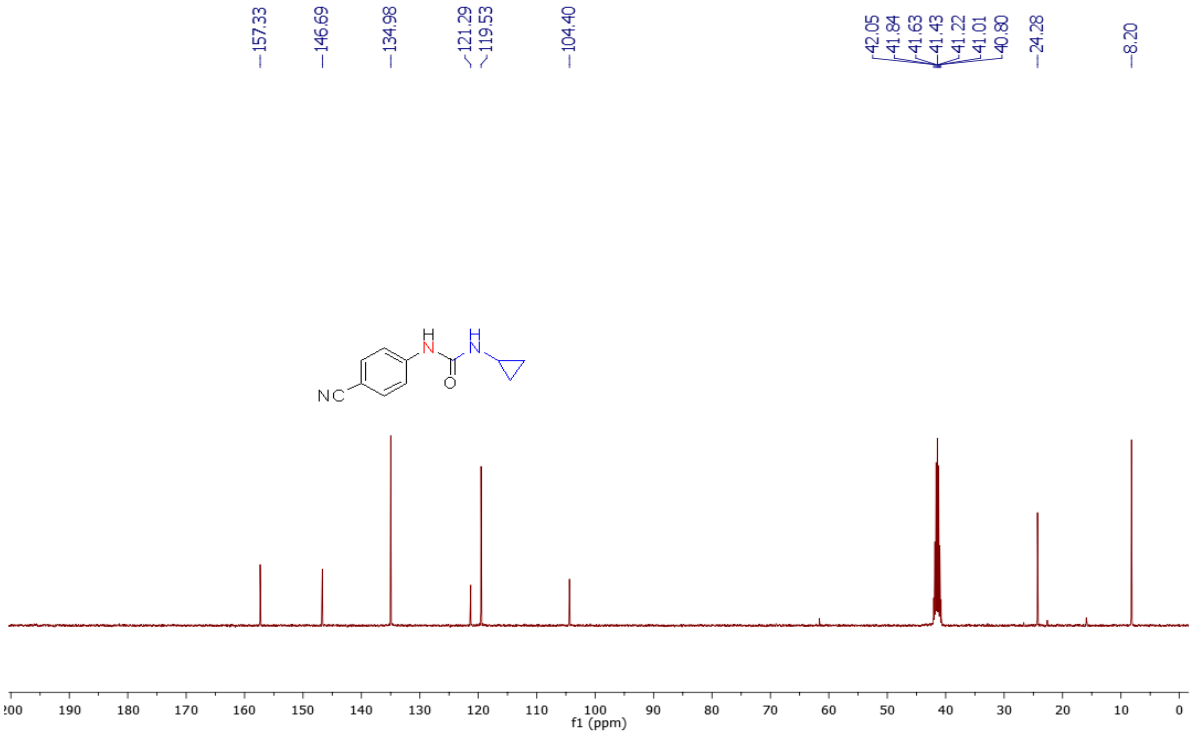
HRMS (ESI-TOF) of compound (3y)



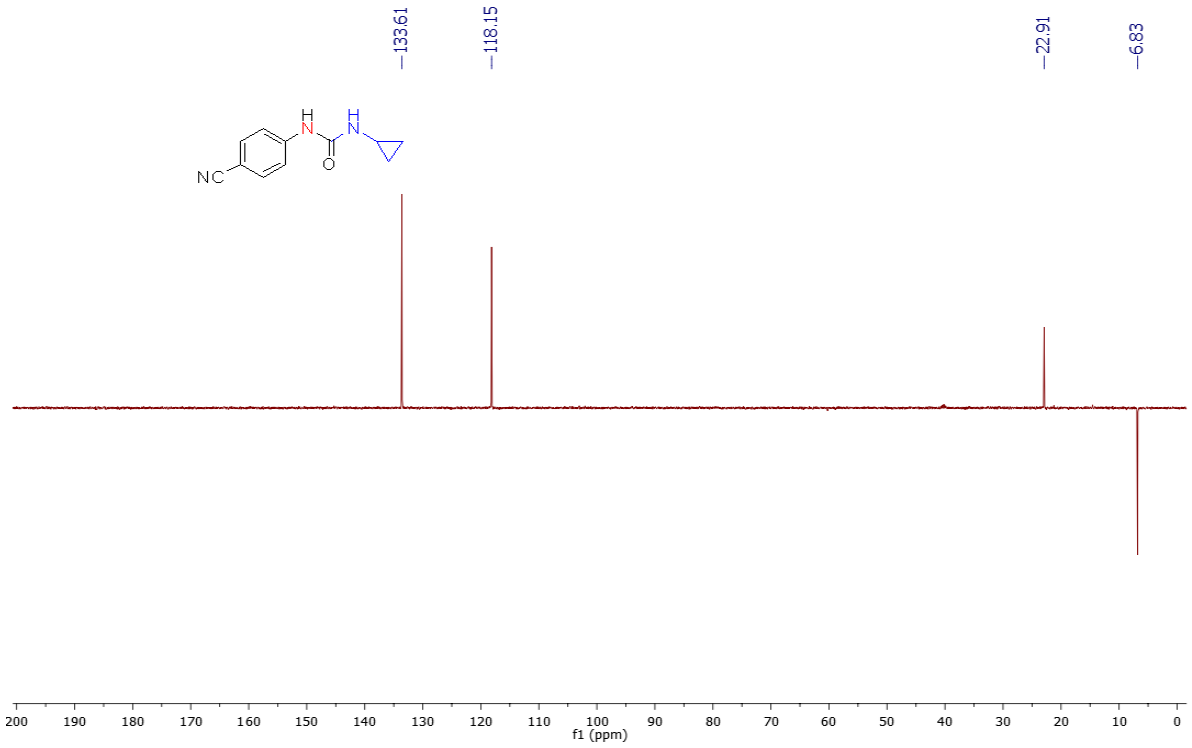
[1]H-NMR of 1-(4-cyanophenyl)-3-cyclopropylurea (3z)



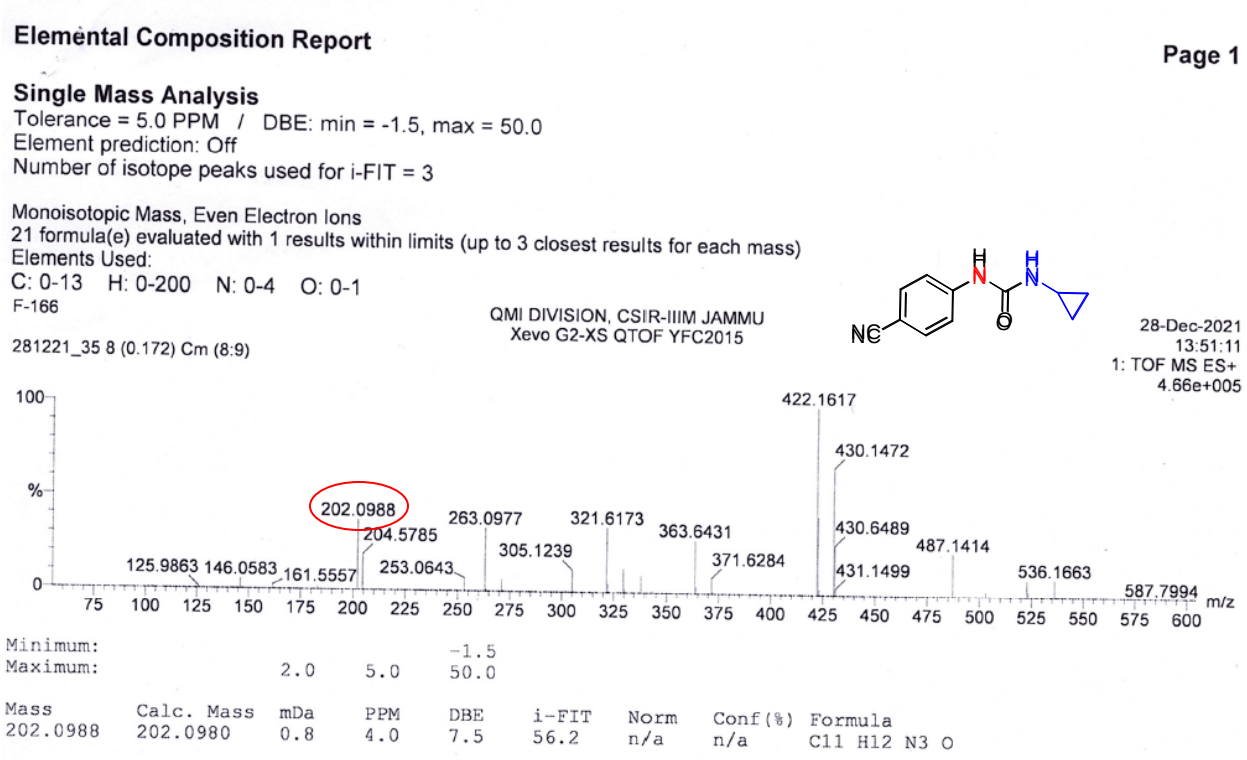
[13]C-NMR of 1-(4-cyanophenyl)-3-cyclopropylurea (3z)



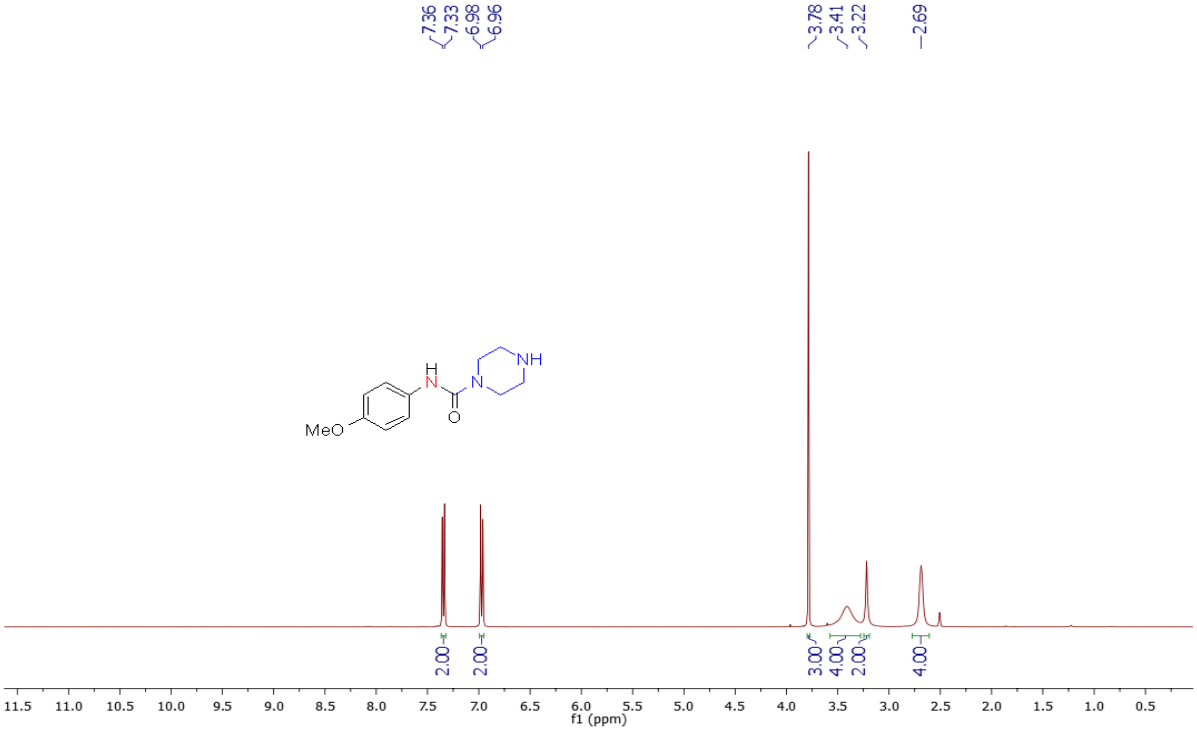
DEPT of 1-(4-cyanophenyl)-3-cyclopropylurea (3z)



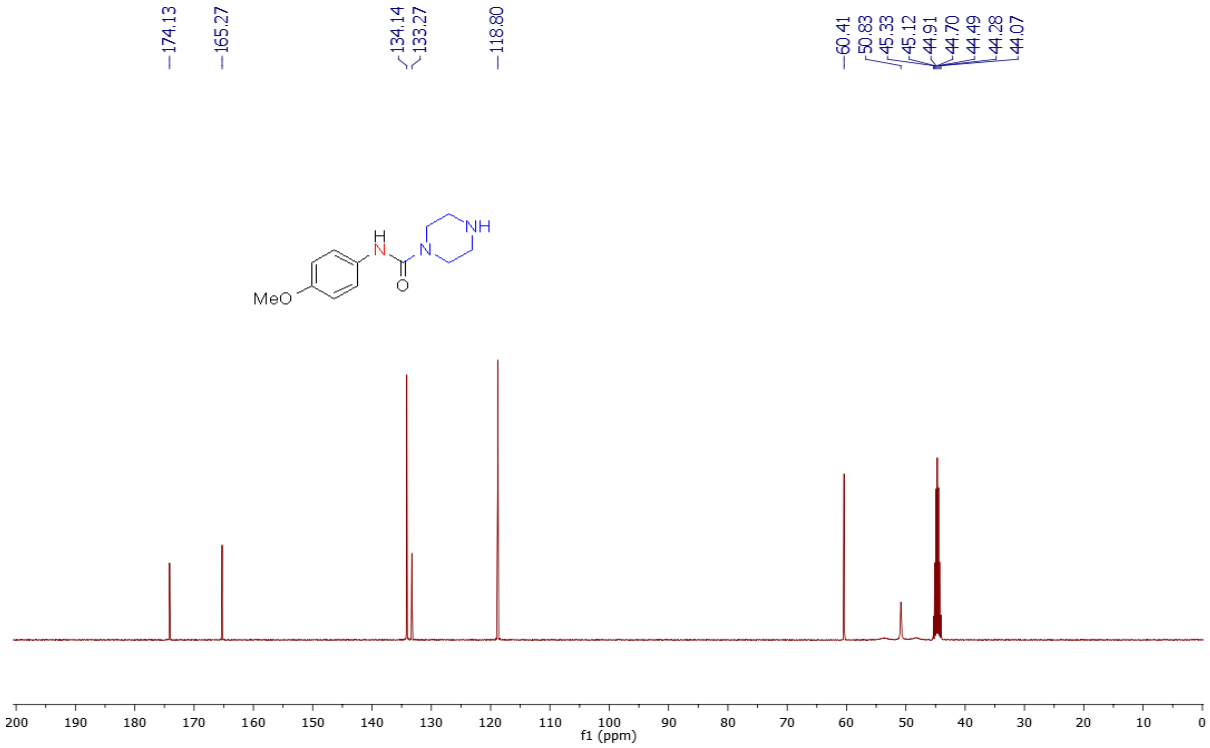
HRMS of 1-(4-cyanophenyl)-3-cyclopropylurea (3z)



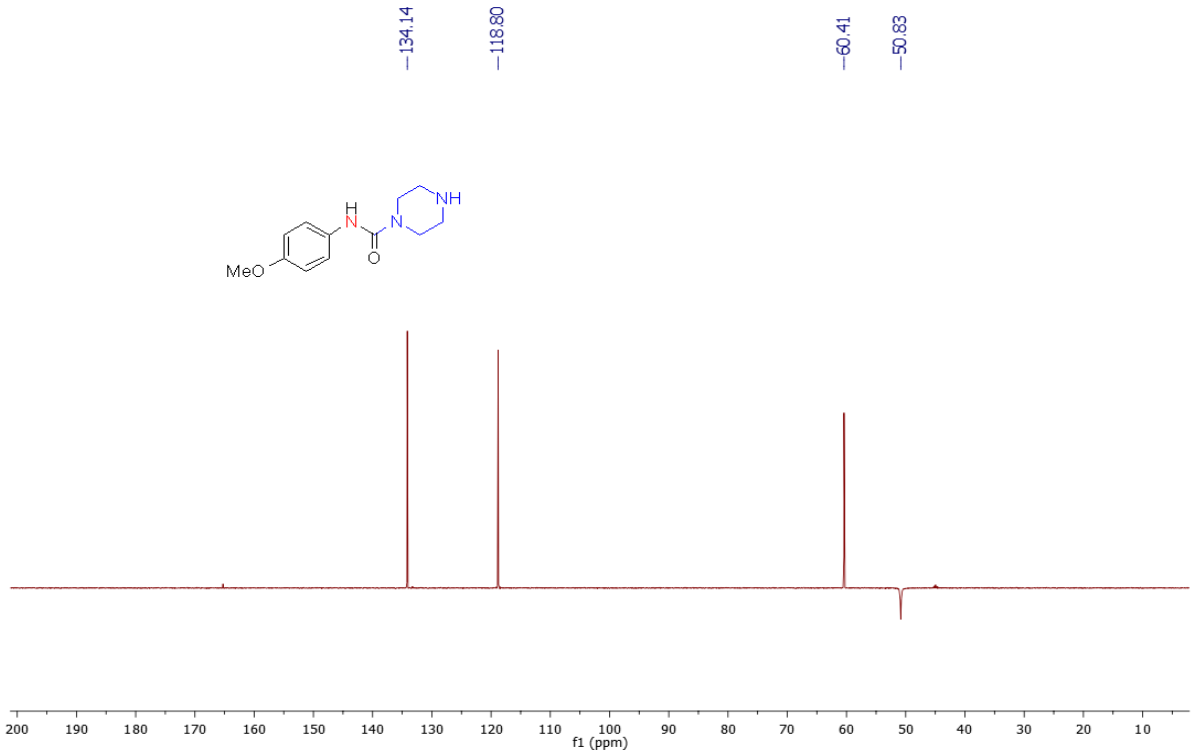
^{1}H-NMR of N-(4-methoxyphenyl)piperazine-1-carboxamide (3aa)



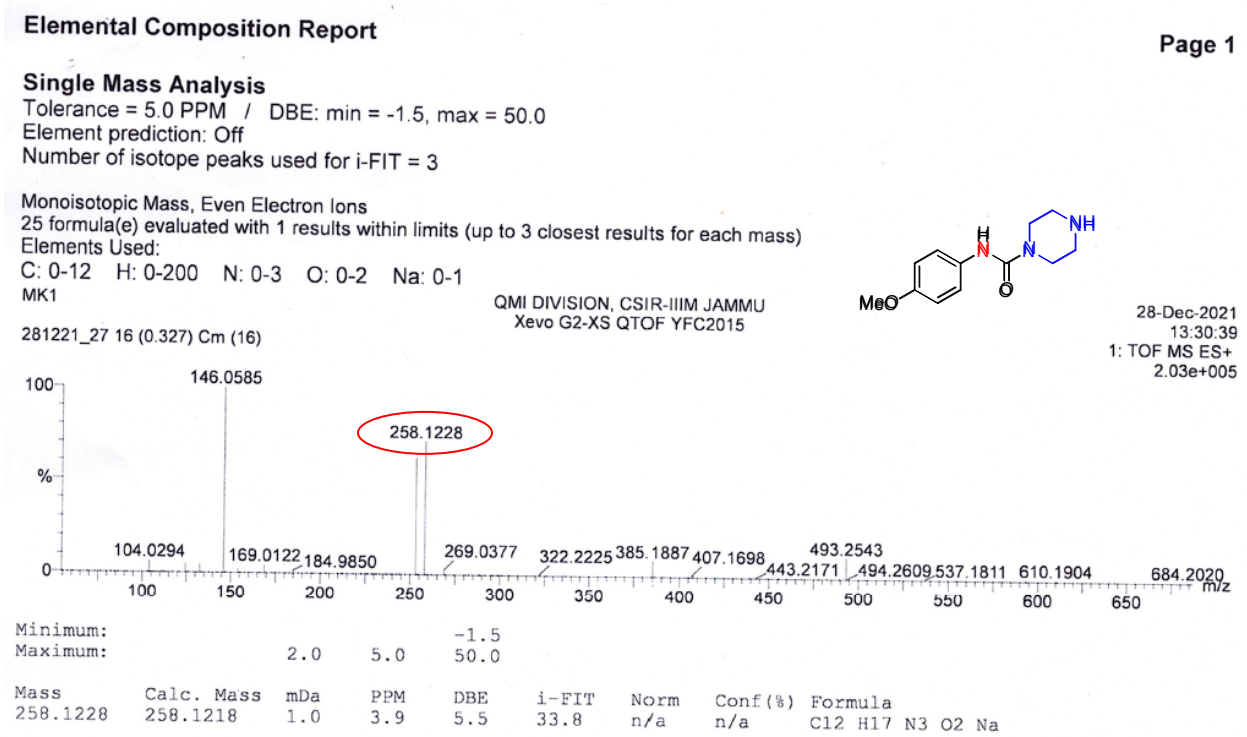
^{13}C-NMR of N-(4-methoxyphenyl)piperazine-1-carboxamide (3aa)



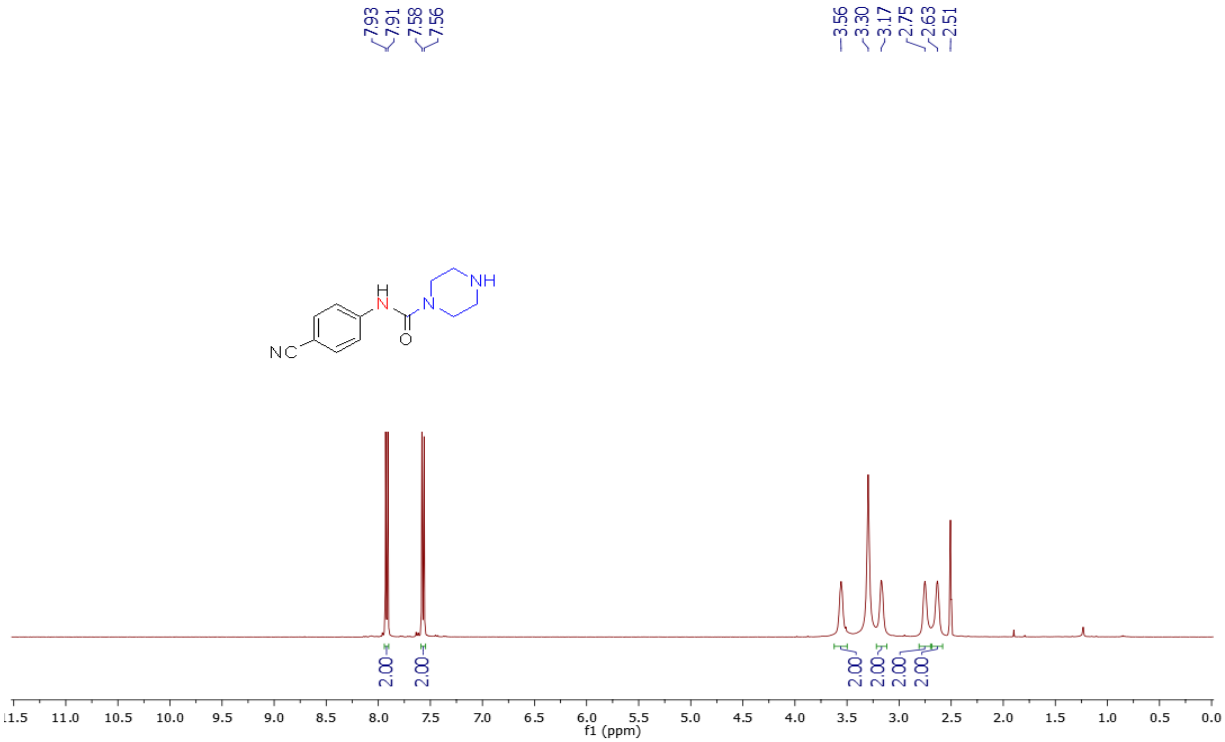
DEPT of *N*-(4-methoxyphenyl)piperazine-1-carboxamide (3aa)



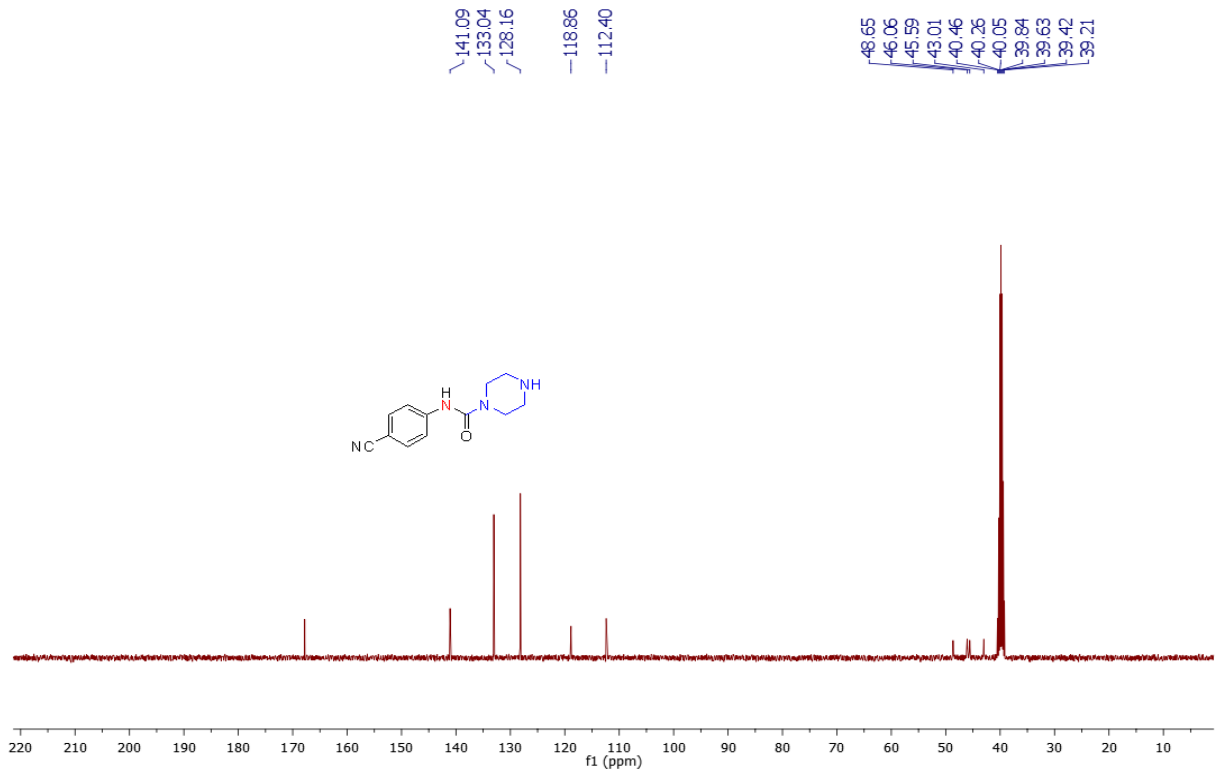
HRMS of of *N*-(4-methoxyphenyl)piperazine-1-carboxamide (3aa)



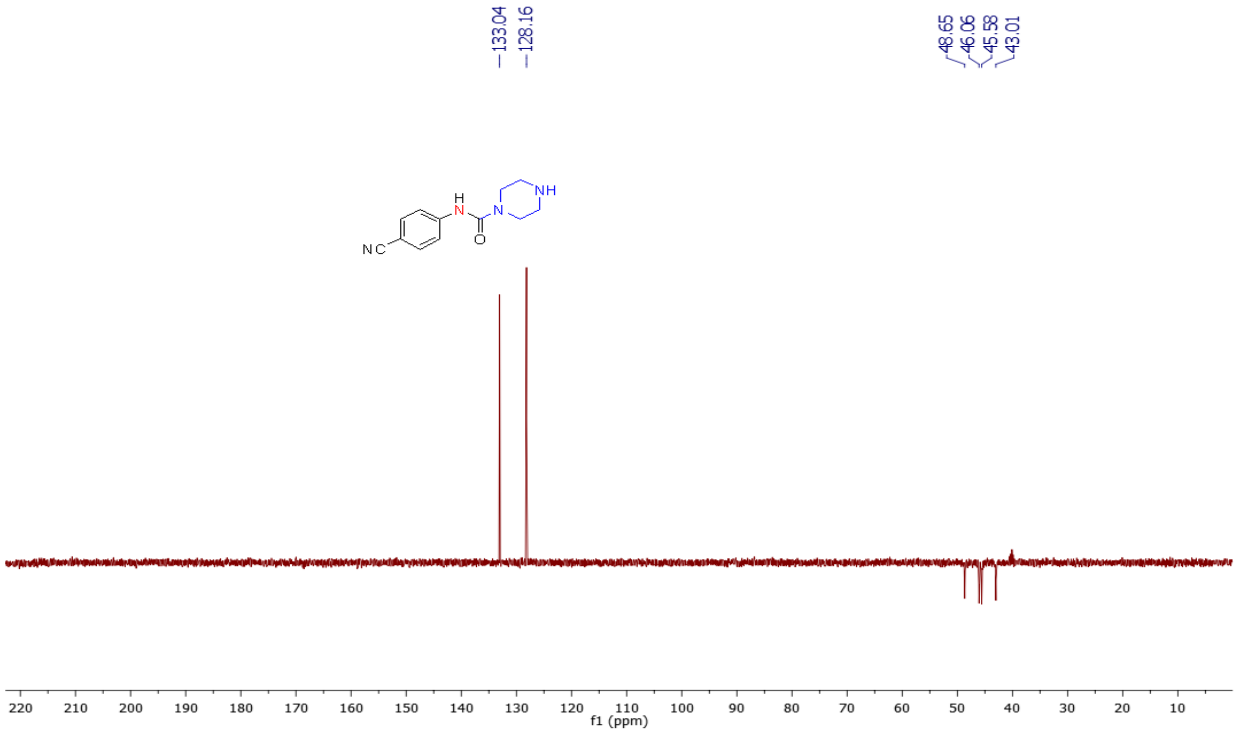
^{1}H-NMR of *N*-(4-cyanophenyl)piperazine-1-carboxamide (3ab)



^{13}C-NMR of *N*-(4-cyanophenyl)piperazine-1-carboxamide (3ab)



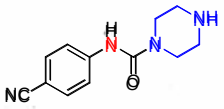
DEPT of *N*-(4-cyanophenyl)piperazine-1-carboxamide (3ab)



Mass spectra of *N*-(4-cyanophenyl)piperazine-1-carboxamide (3ab)

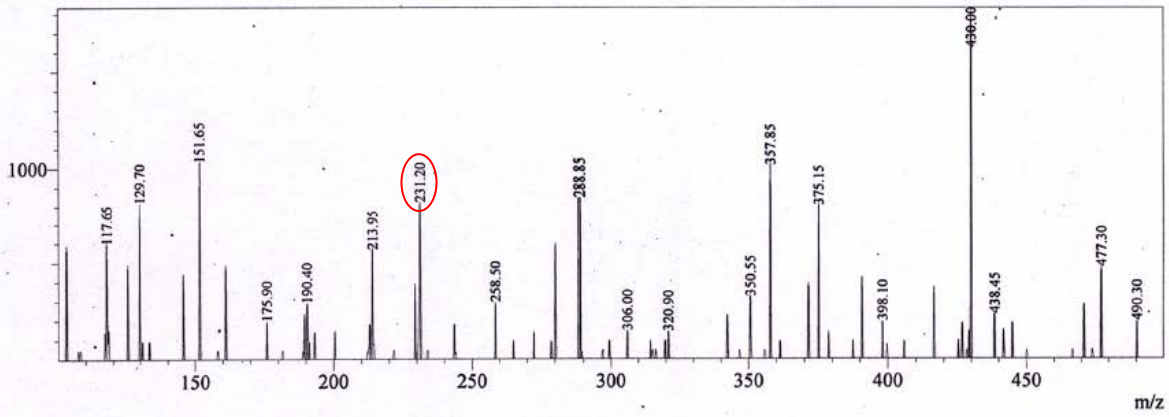
Sample Information

Sample Name	**: F 263**	**Sample ID**	**:**
Tray#	**: 1**	**Vial#**	**: 70**
Injection Volume	**: 0.5**	**Data File**	**: 28-JAN-22-58.lcd**
Method File	**: MASS SCANNN 13APRIL2021.lcm**	**Processed by**	**: System Administrator**
Date Processed	**: 1/28/2022 6:11:18 PM**		

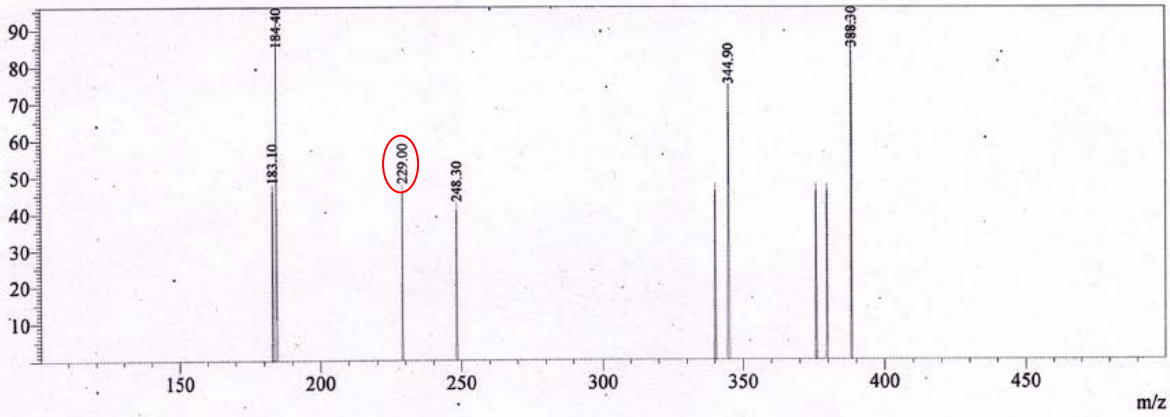


MS Spectrum

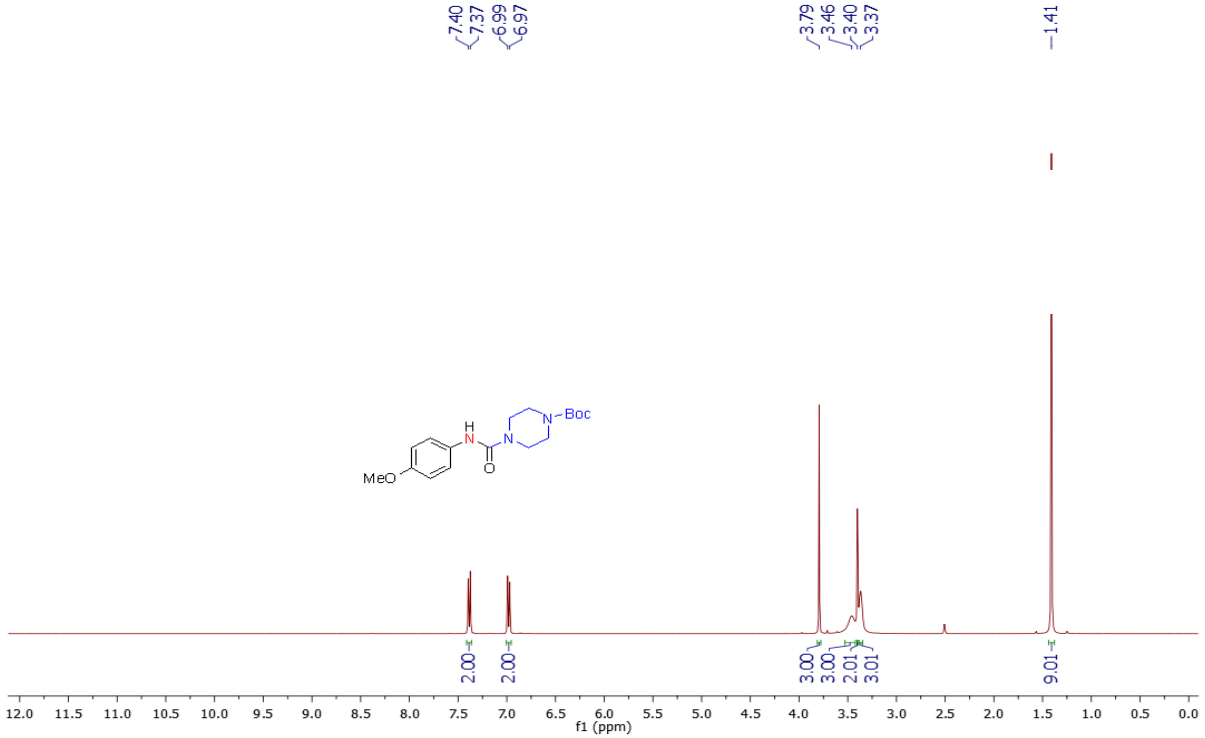
BG Mode:None $EndIf$ Segment 1 - Event 1
Product Ion Scan Precursor:231.0000 CE:-5.0



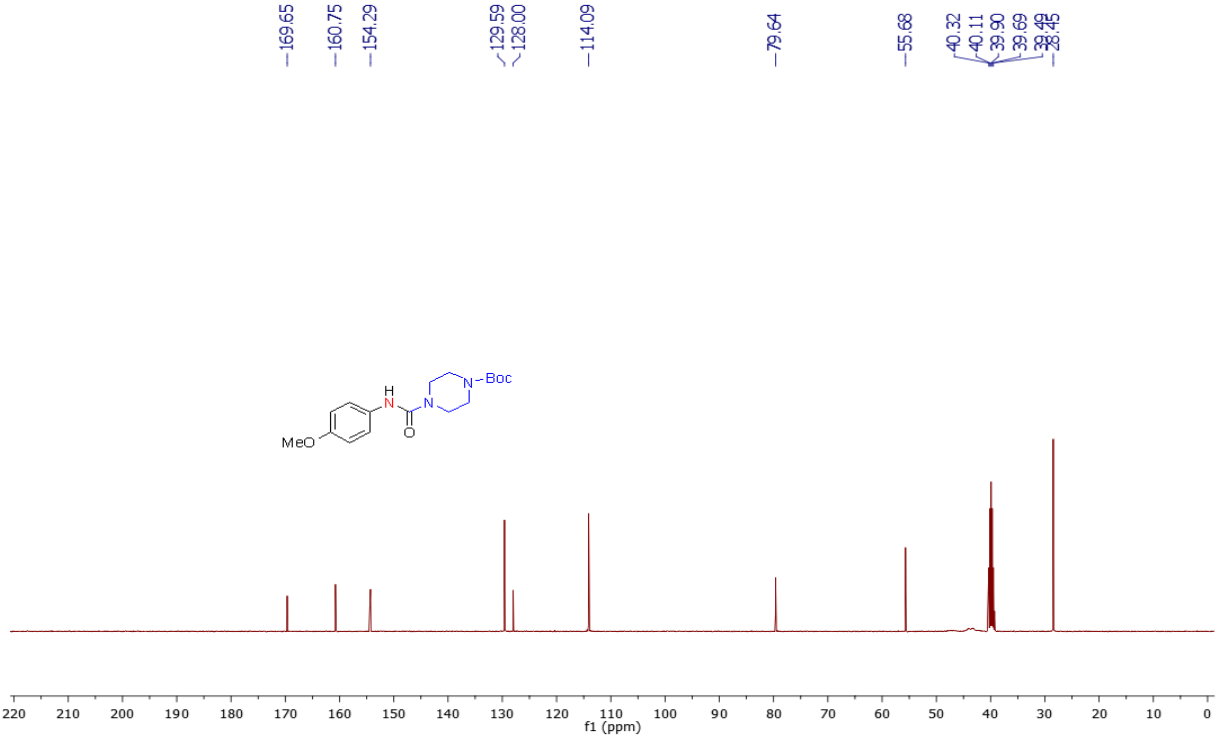
BG Mode:None $EndIf$ Segment 1 - Event 2
Product Ion Scan Precursor:229.0000 CE:5.0



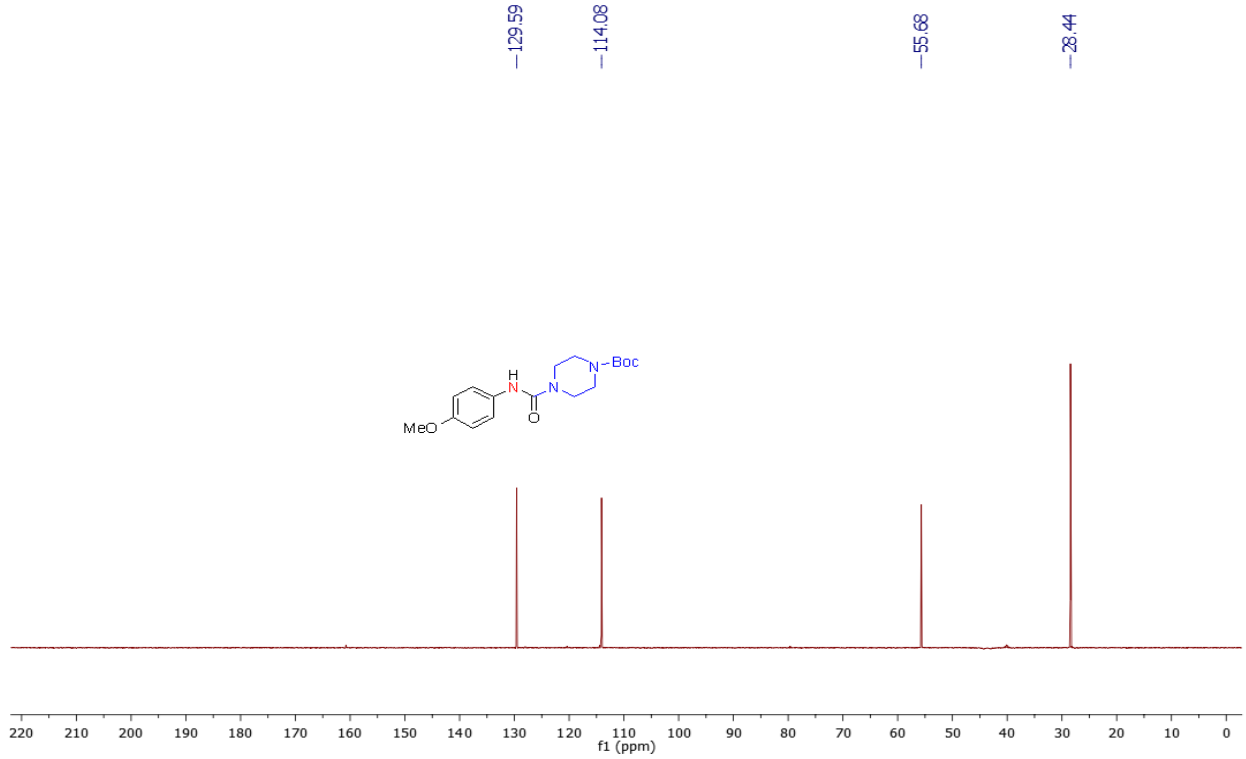
^{1}H-NMR of tert-butyl 4-((4-methoxyphenyl)carbamoyl)piperazine-1-carboxylate (3ac)



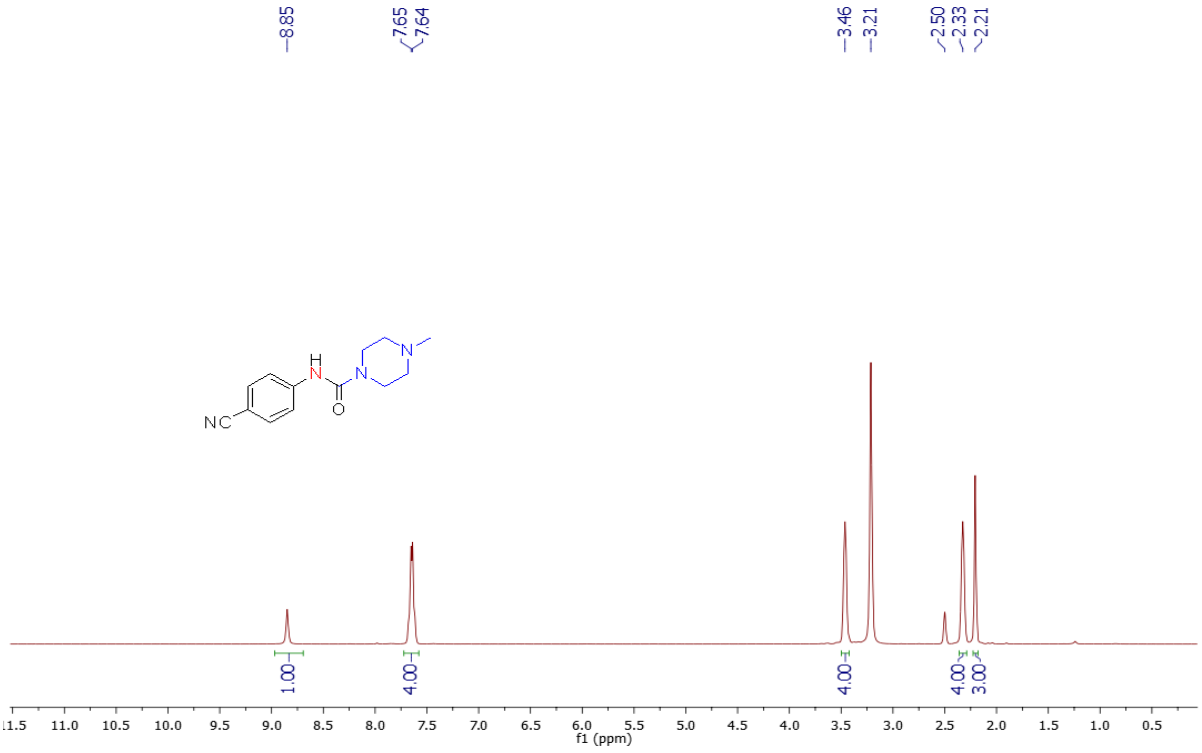
^{13}C-NMR of tert-butyl 4-((4-methoxyphenyl)carbamoyl)piperazine-1-carboxylate (3ac)



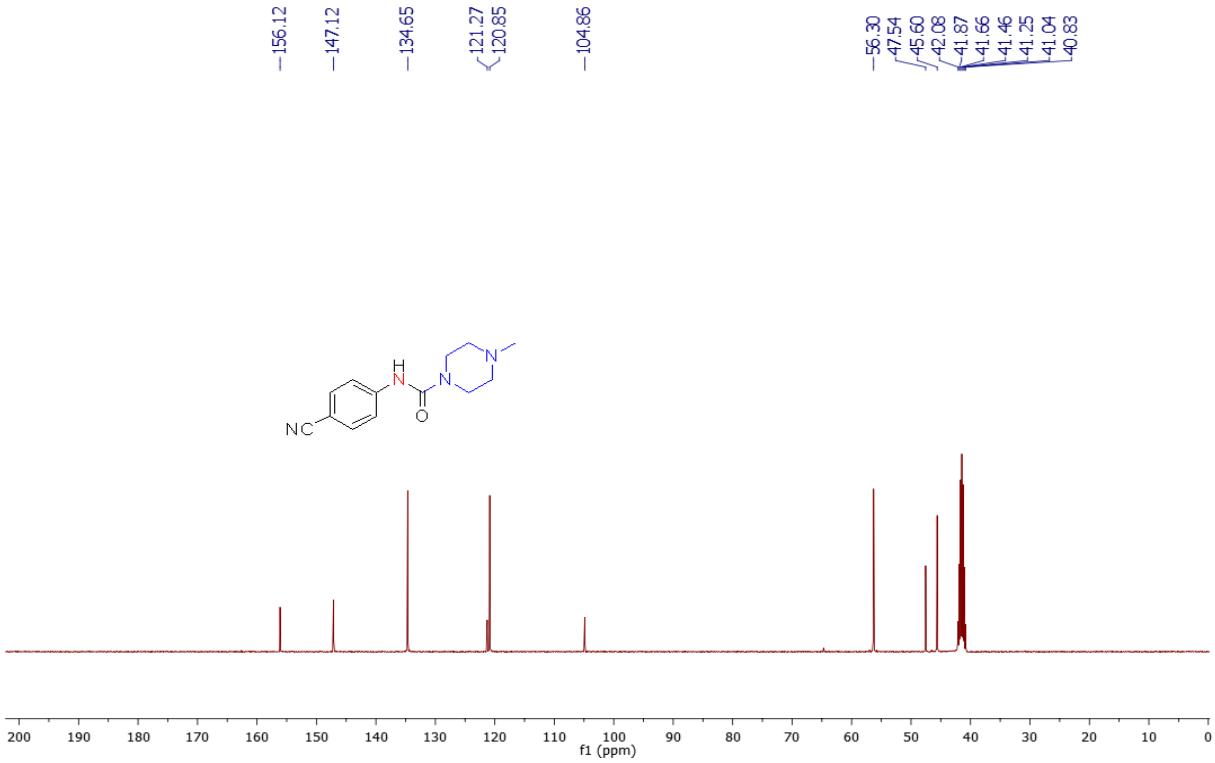
DEPT of tert-butyl 4-((4-methoxyphenyl)carbamoyl)piperazine-1-carboxylate (3ac)



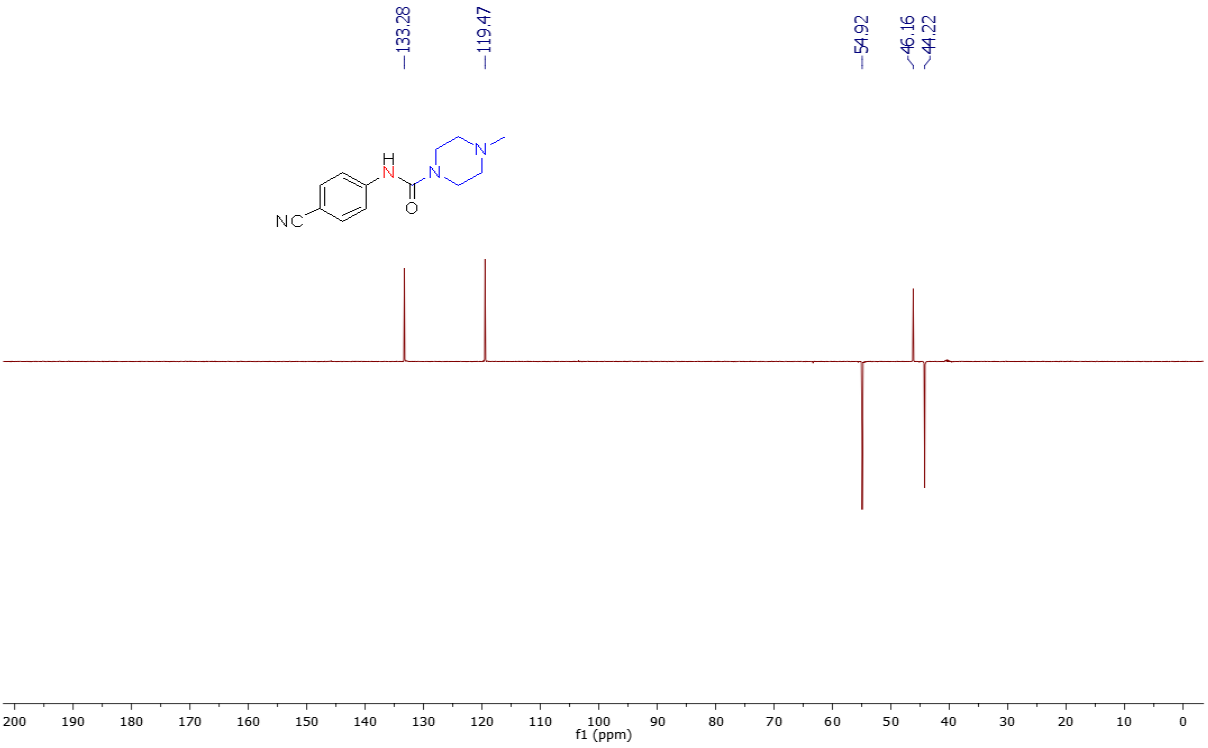
^{1}H-NMR of *N*-(4-cyanophenyl)-4-methylpiperazine-1-carboxamide (3ad)



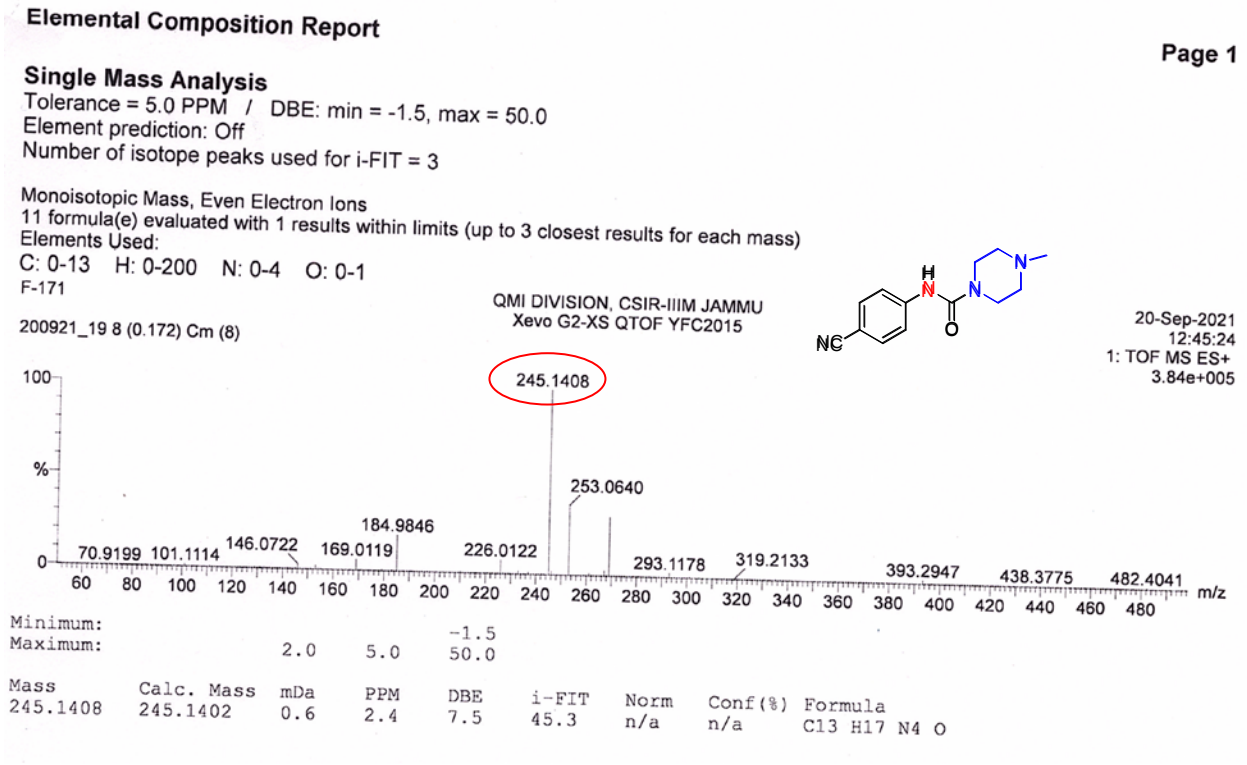
^{13}C-NMR of *N*-(4-cyanophenyl)-4-methylpiperazine-1-carboxamide (3ad)



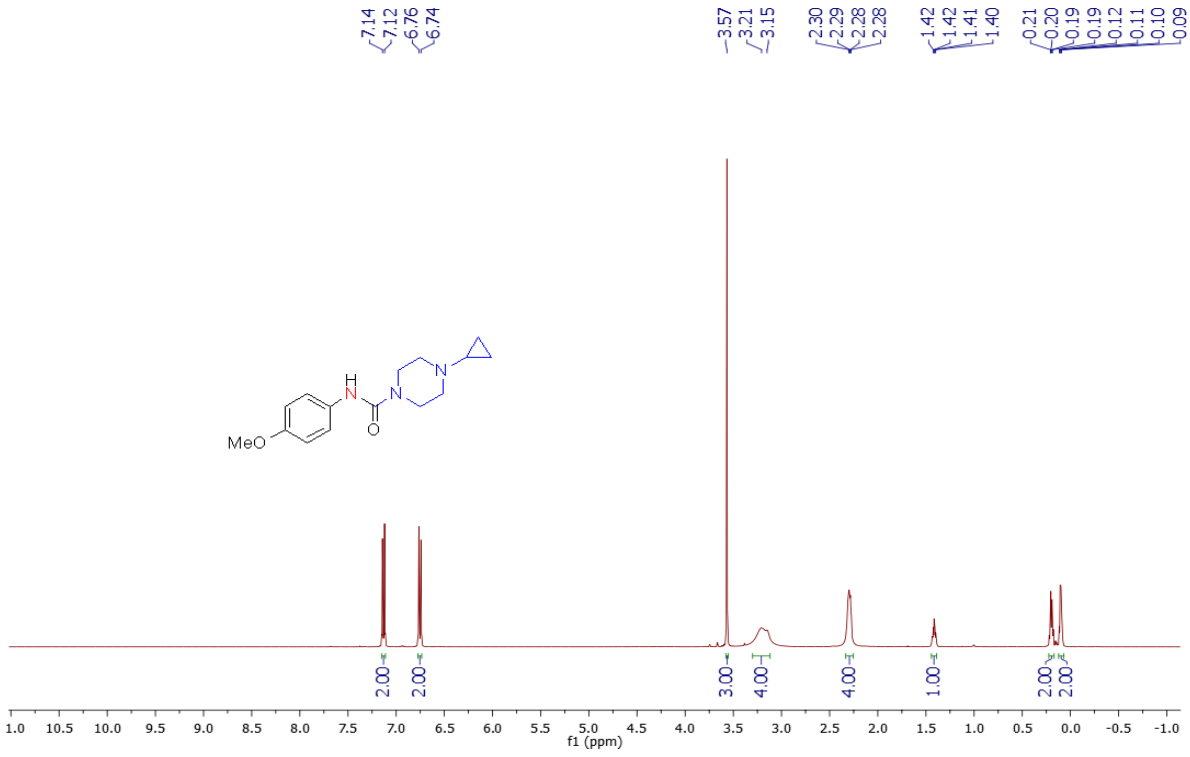
DEPT of *N*-(4-cyanophenyl)-4-methylpiperazine-1-carboxamide (3ad)



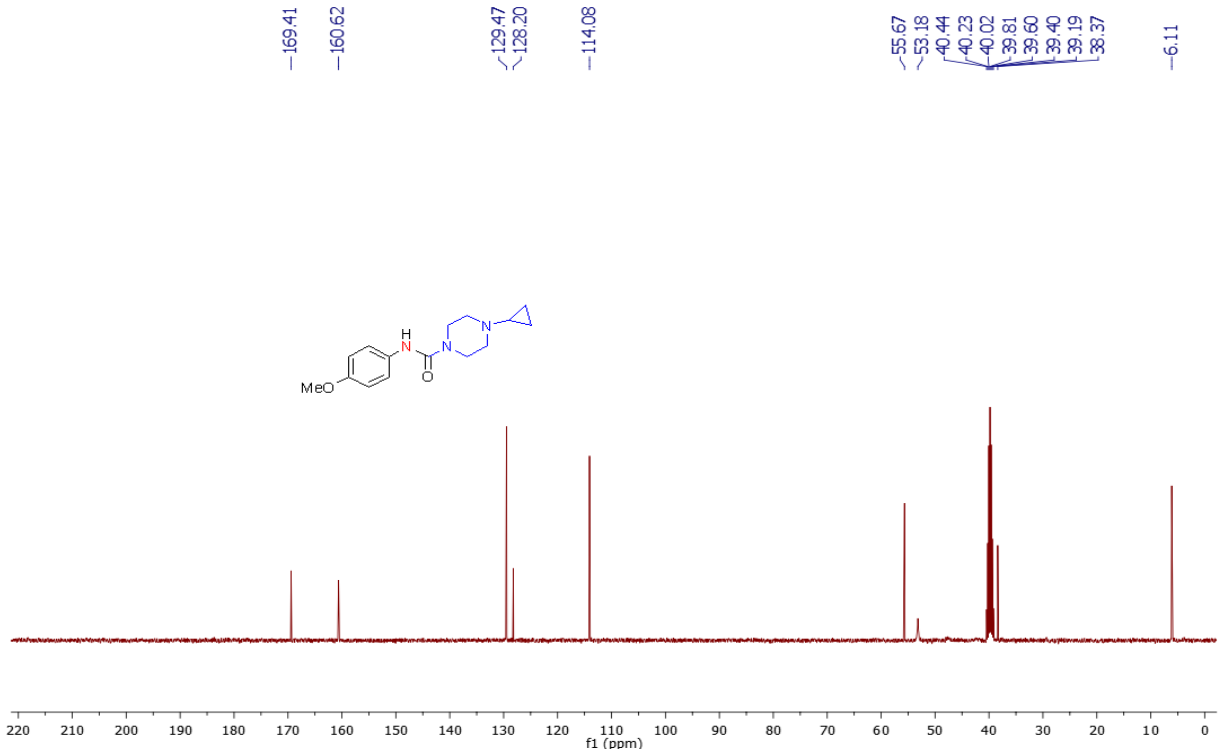
HRMS (ESI-TOF) of compound (3ad)



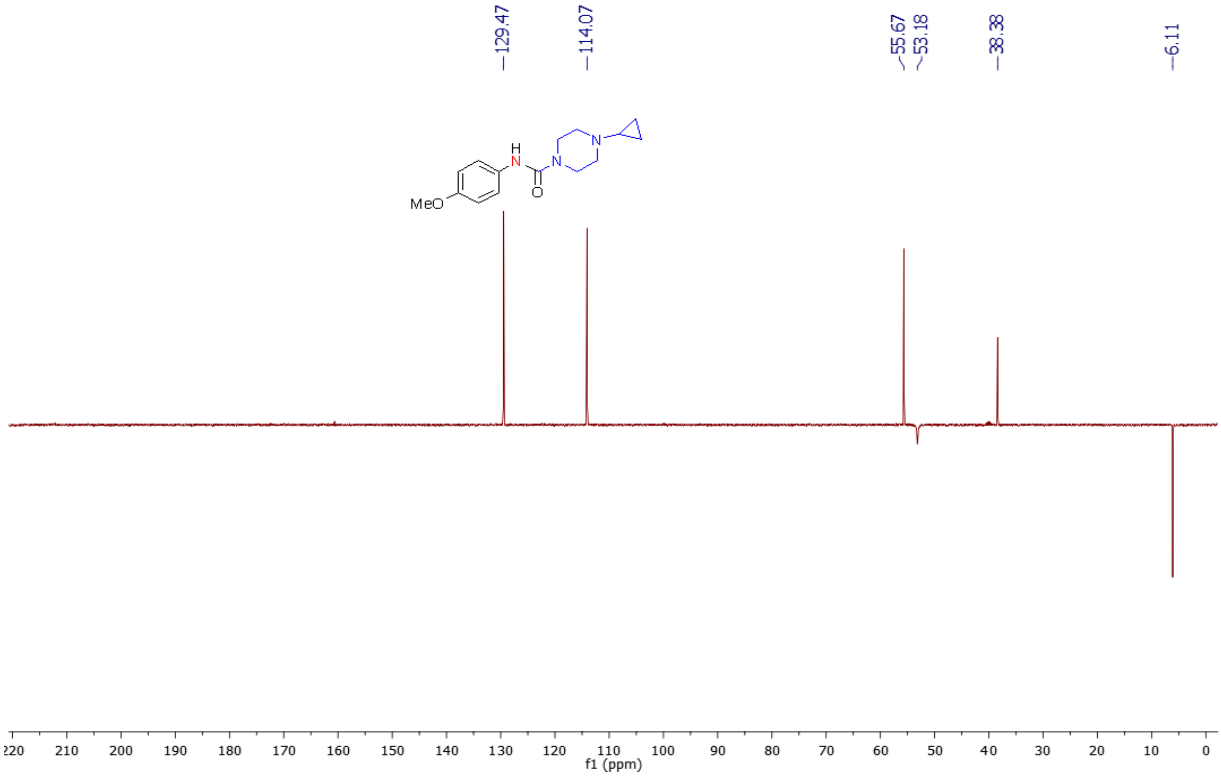
^{1}H-NMR of 4-cyclopropyl-*N*-(4-methoxyphenyl)piperazine-1-carboxamide (3ae)



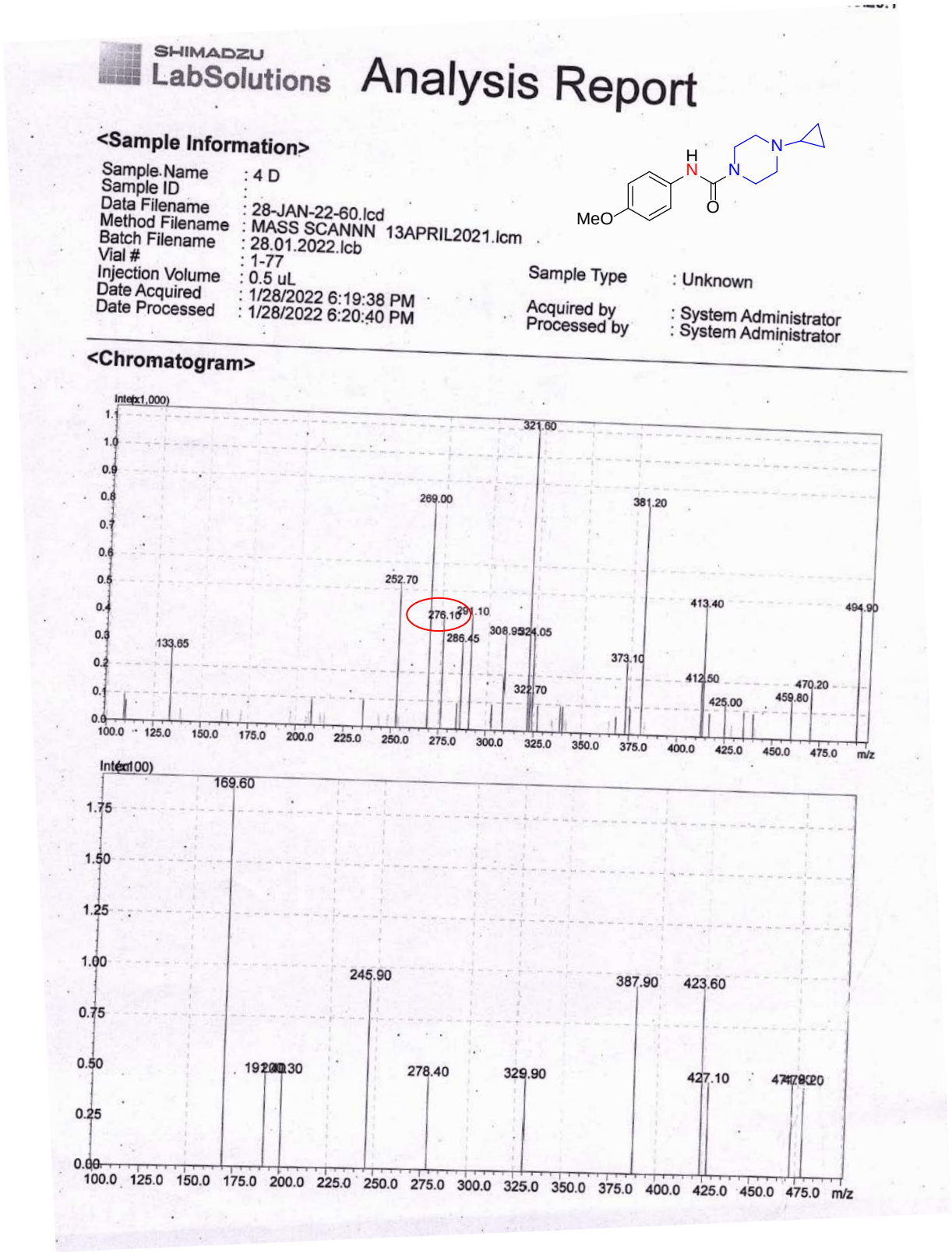
^{13}C-NMR of 4-cyclopropyl-*N*-(4-methoxyphenyl)piperazine-1-carboxamide (3ae)



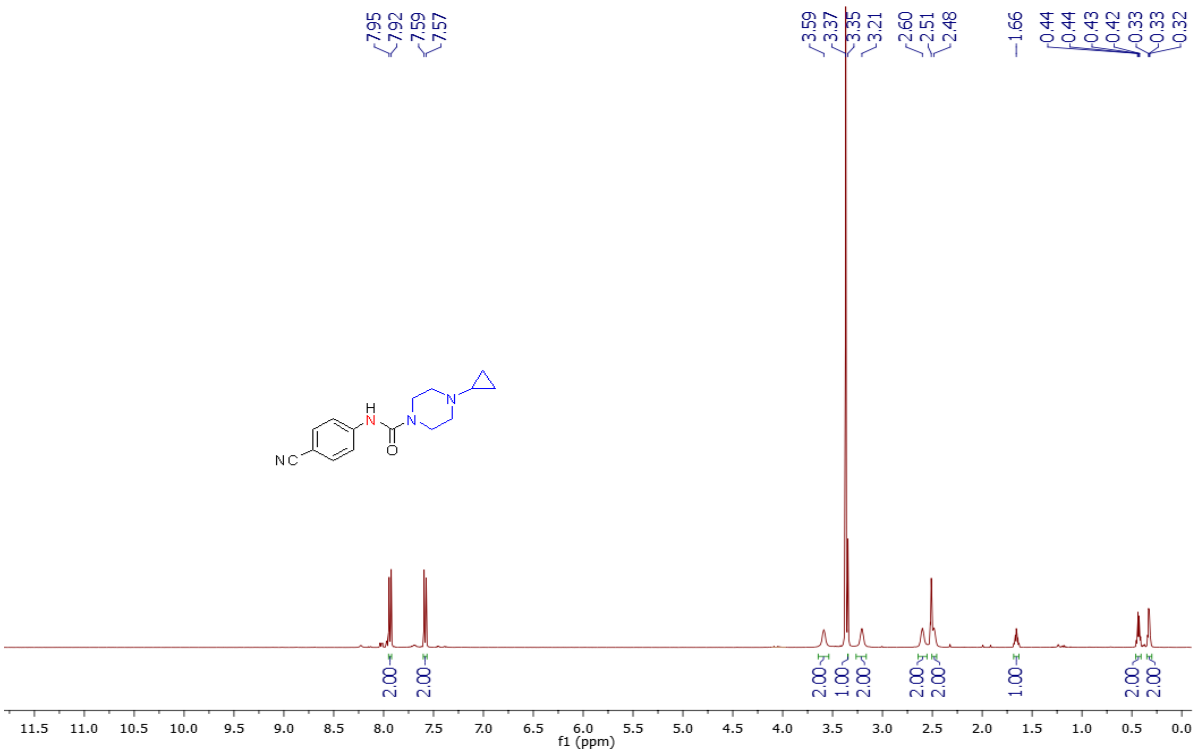
DEPT of 4-cyclopropyl-*N*-(4-methoxyphenyl)piperazine-1-carboxamide (3ae)



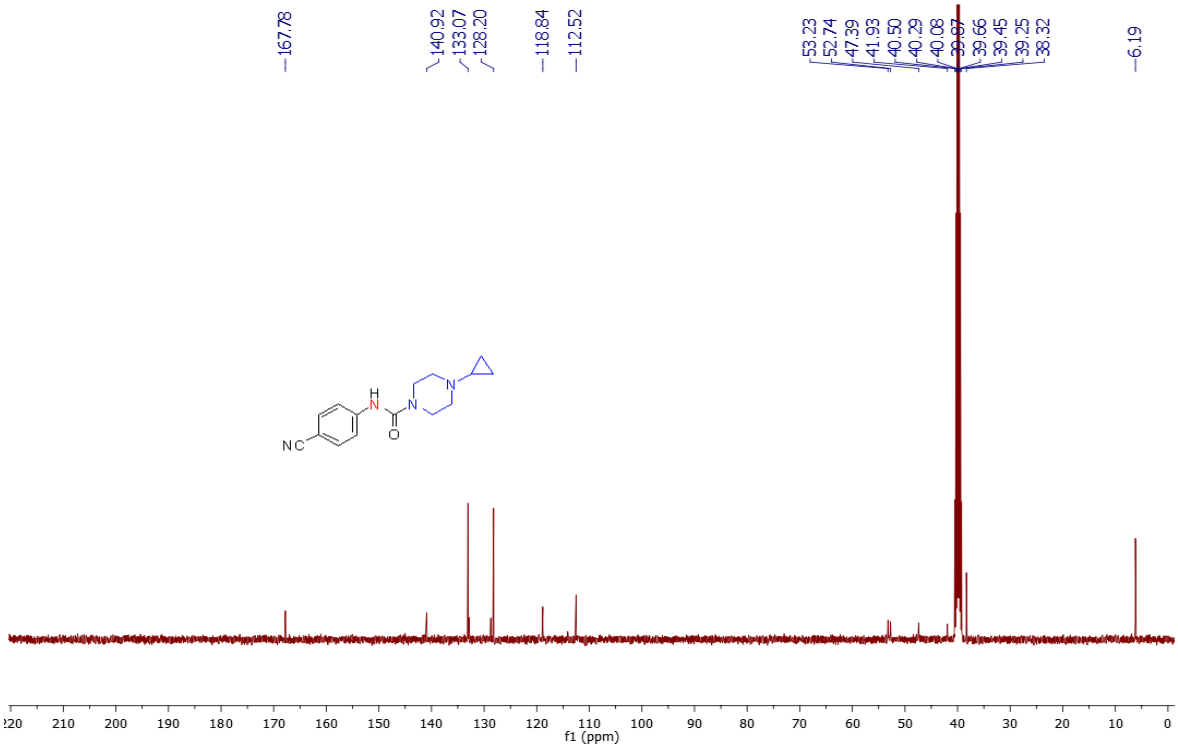
Mass spectra of 4-cyclopropyl-*N*-(4-methoxyphenyl)piperazine-1-carboxamide (3ae)



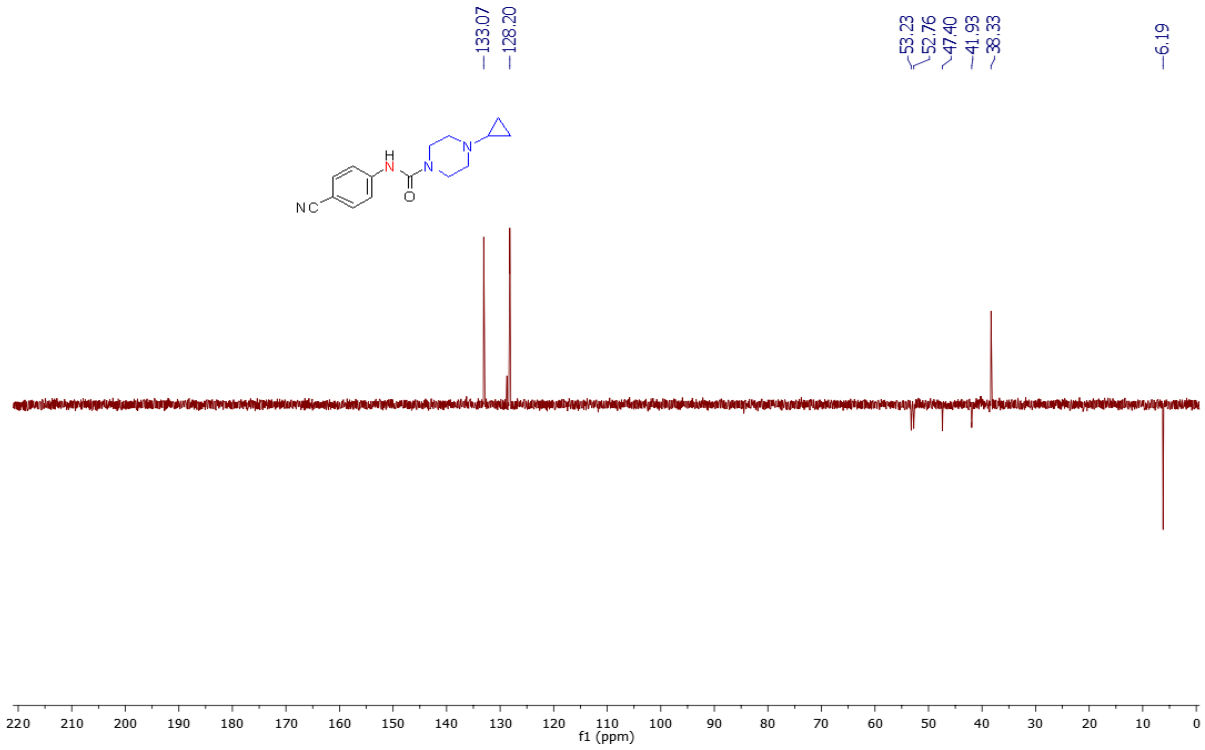
^{1}H-NMR of *N*-(4-cyanophenyl)-4-cyclopropylpiperazine-1-carboxamide (3af)



^{13}C-NMR of *N*-(4-cyanophenyl)-4-cyclopropylpiperazine-1-carboxamide (3af)



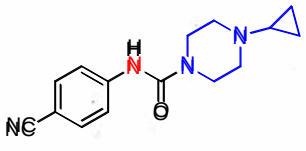
DEPT of *N*-(4-cyanophenyl)-4-cyclopropylpiperazine-1-carboxamide (3af)



Mass spectra of *N*-(4-cyanophenyl)-4-cyclopropylpiperazine-1-carboxamide (3af)

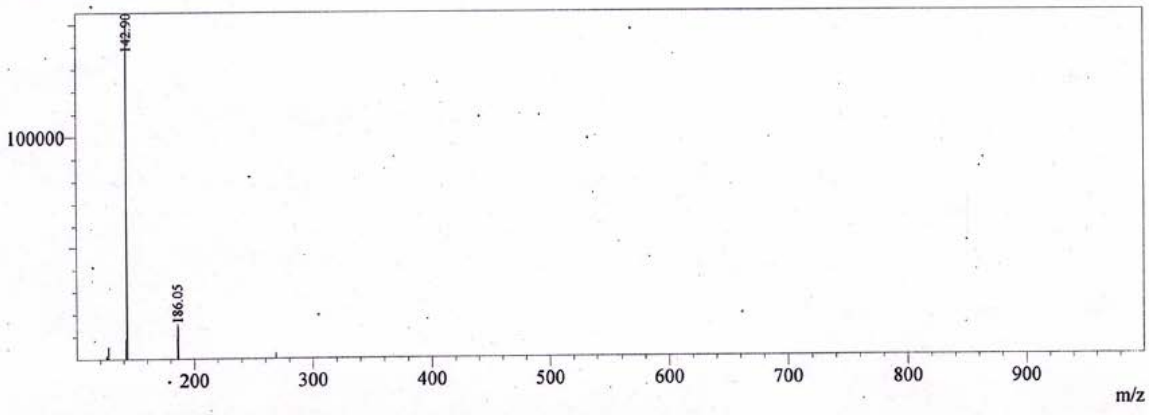
Sample Information

Sample Name	**: 4M**	**Sample ID**	**:**
Tray#	**: 1**	**Vial#**	**: 76**
Injection Volume	**: 0.5**	**Data File**	**: 28-JAN-22-48.lcd**
Method File	**: MASS SCANNN 13APRIL2021.lcm**	**Processed by**	**: System Administrator**
Date Processed	**: 1/28/2022 5:24:34 PM**		



MS Spectrum

BG Mode:Calc $EndIf$ Segment 1 - Event 1
Product Ion Scan Precursor:269.0000 CE:-5.0



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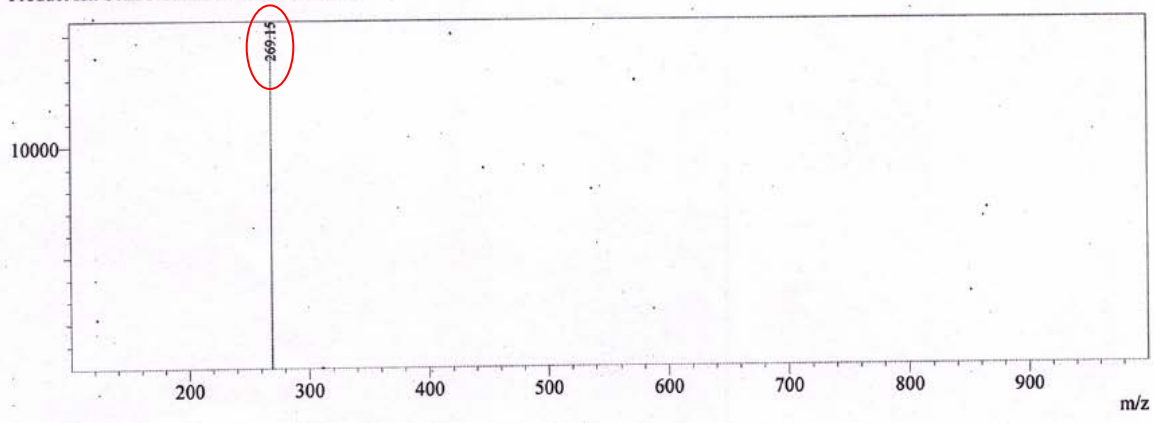
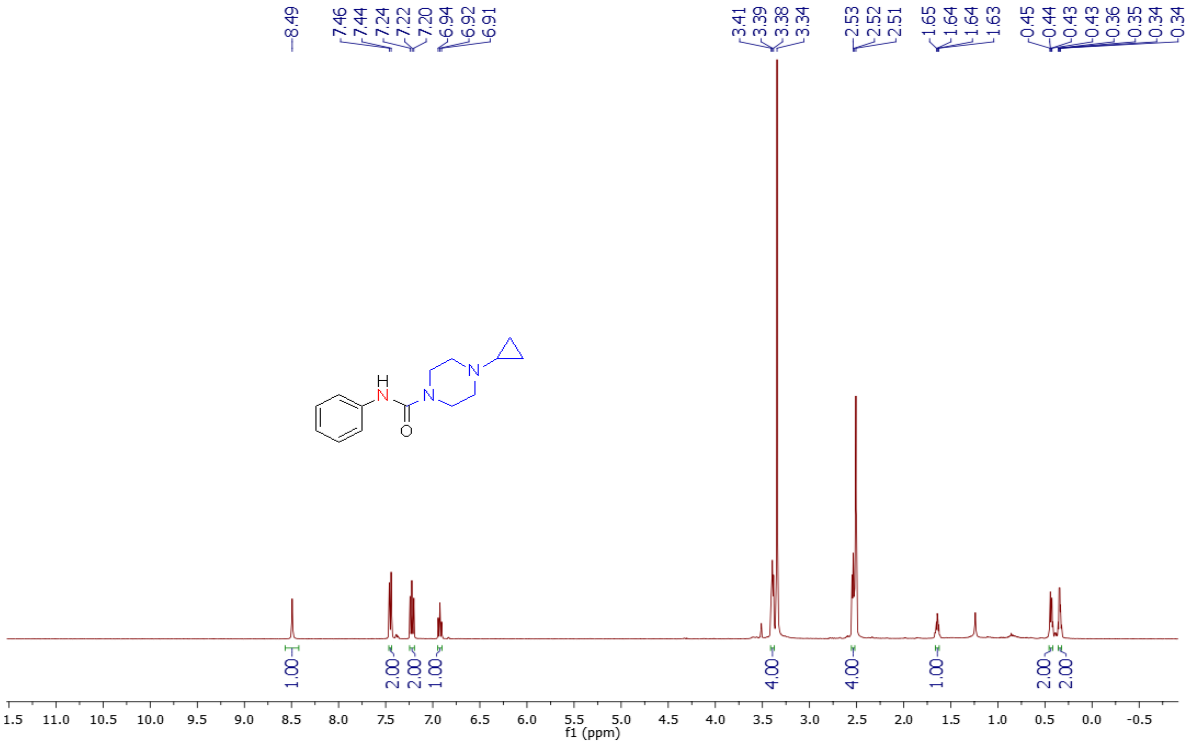
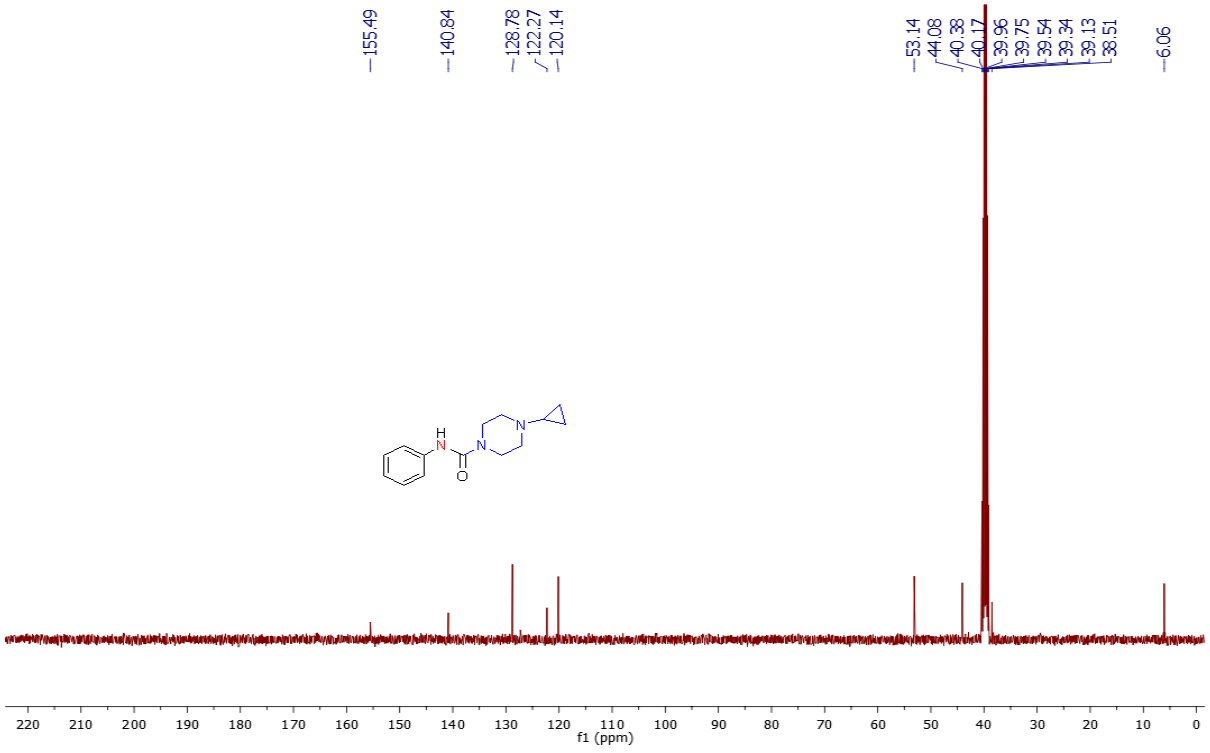


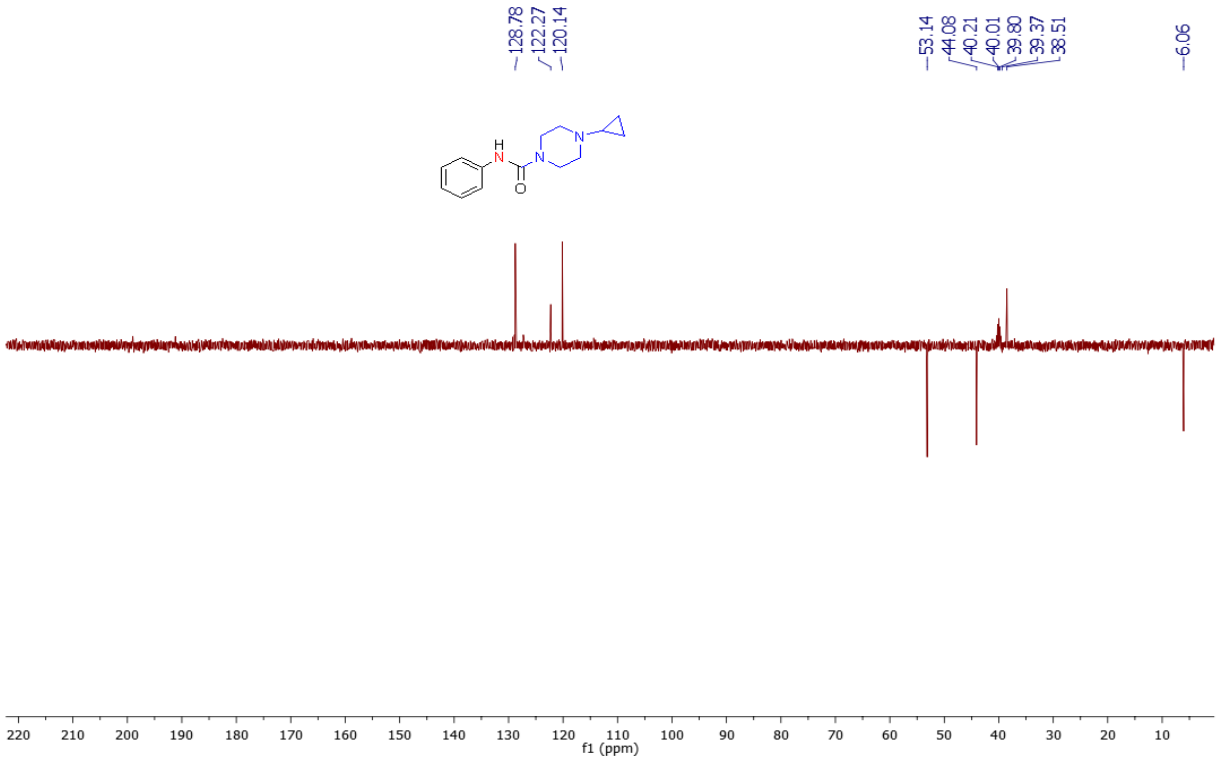
[1]H-NMR of 4-cyclopropyl-N-phenylpiperazine-1-carboxamide (3ag)



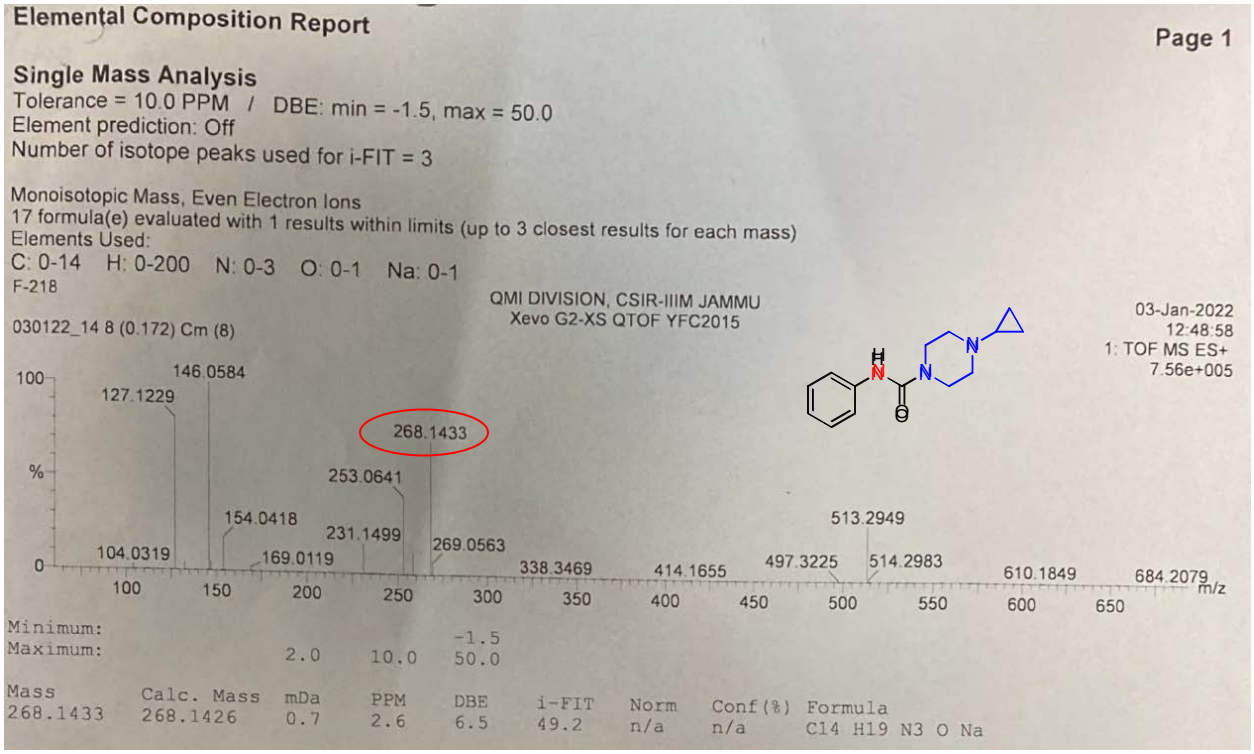
[13] C-NMR of 4-cyclopropyl-N-phenylpiperazine-1-carboxamide (3ag)



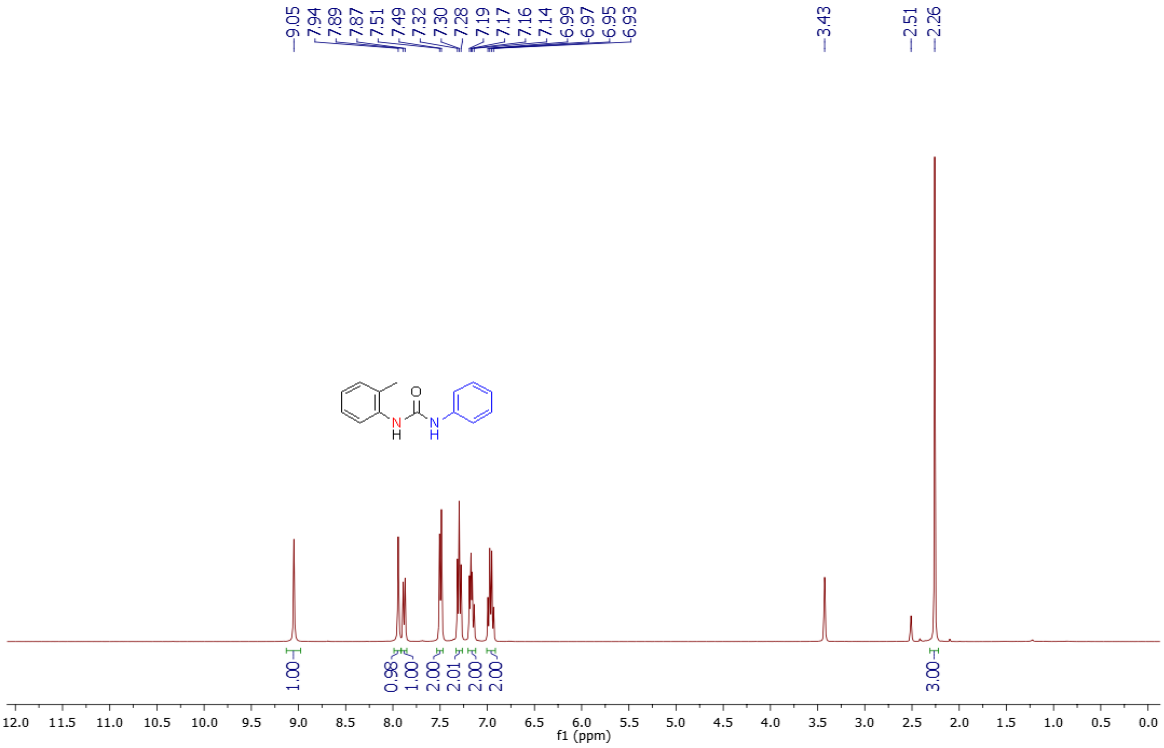
DEPT of 4-cyclopropyl-N-phenylpiperazine-1-carboxamide (3ag)



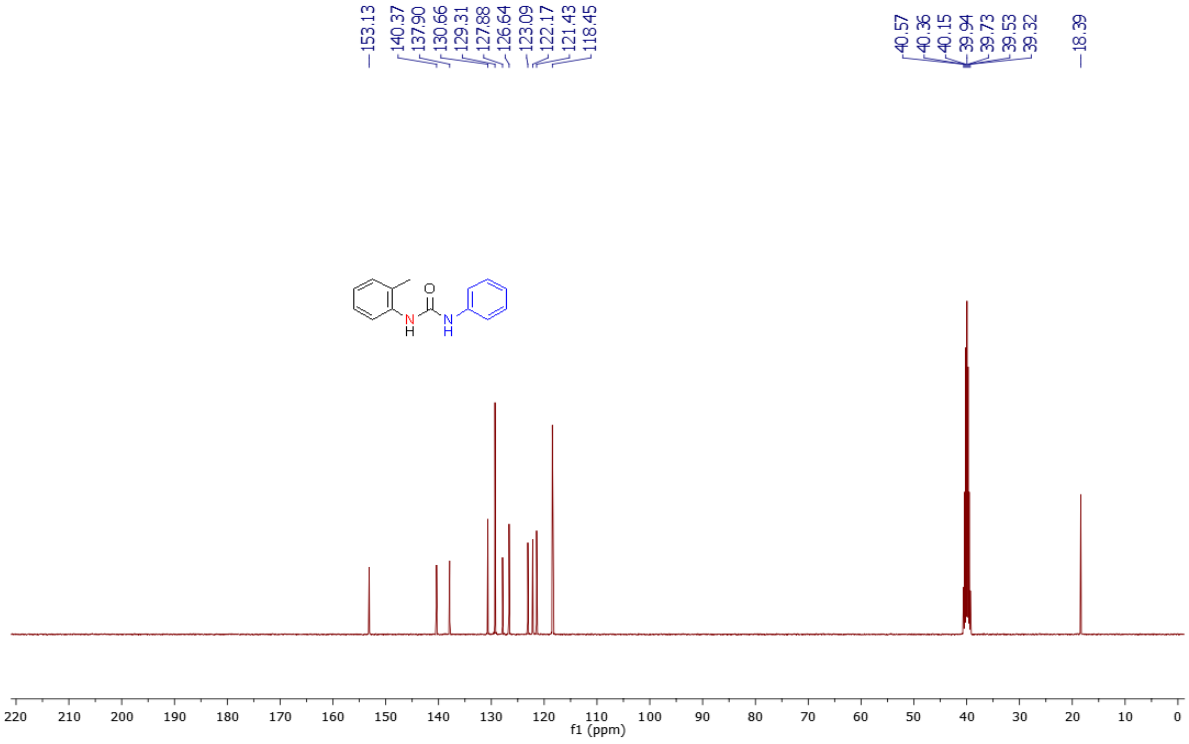
HRMS of 4-cyclopropyl-N-phenylpiperazine-1-carboxamide (3ag)



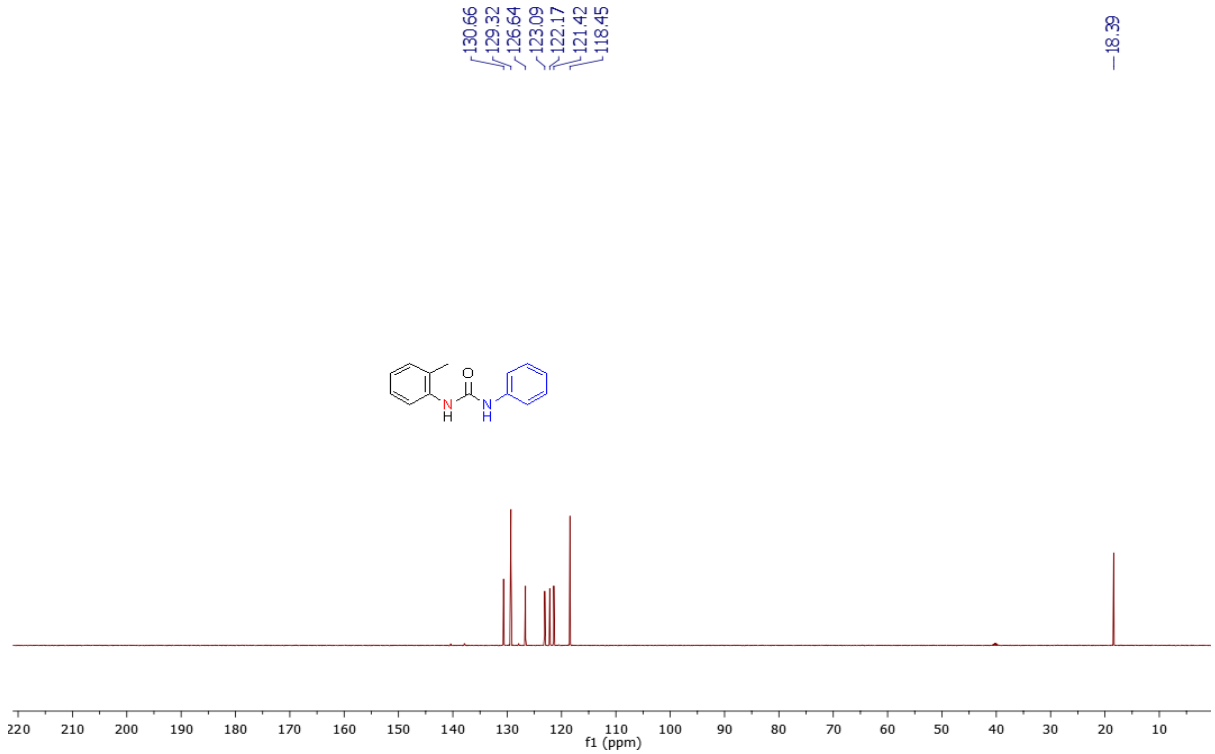
^{1}H-NMR of 1-phenyl-3-(o-tolyl)urea (3ah)



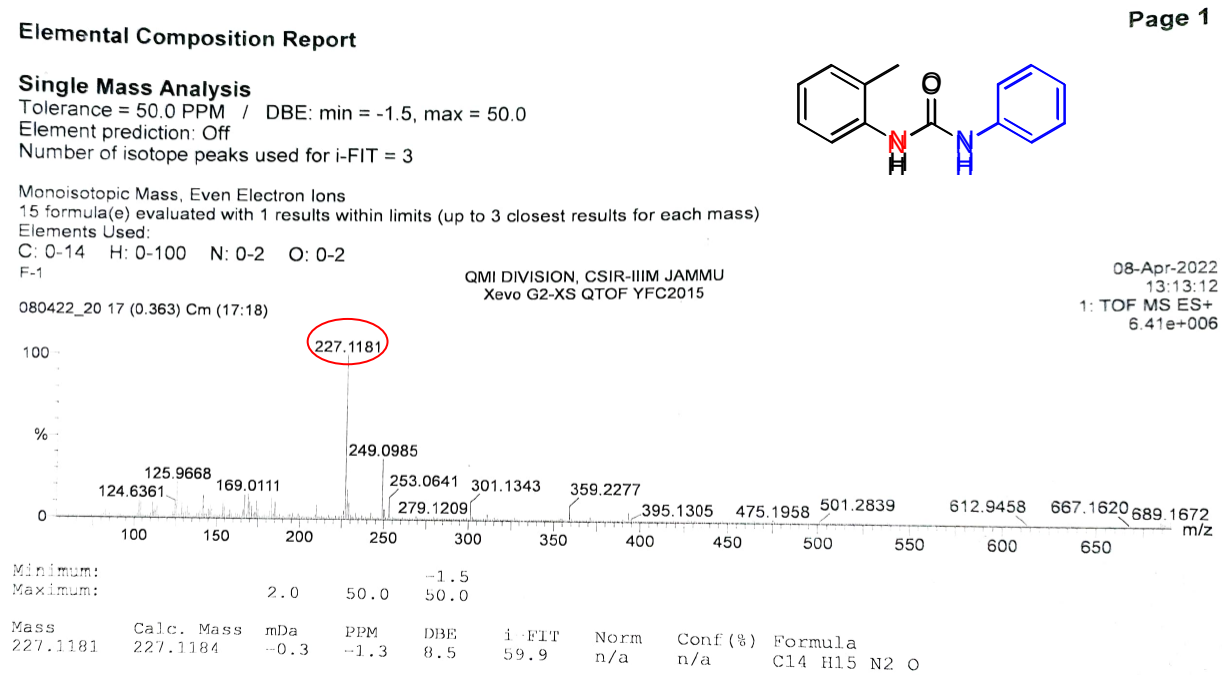
^{13}C-NMR of 1-phenyl-3-(o-tolyl)urea (3ah)



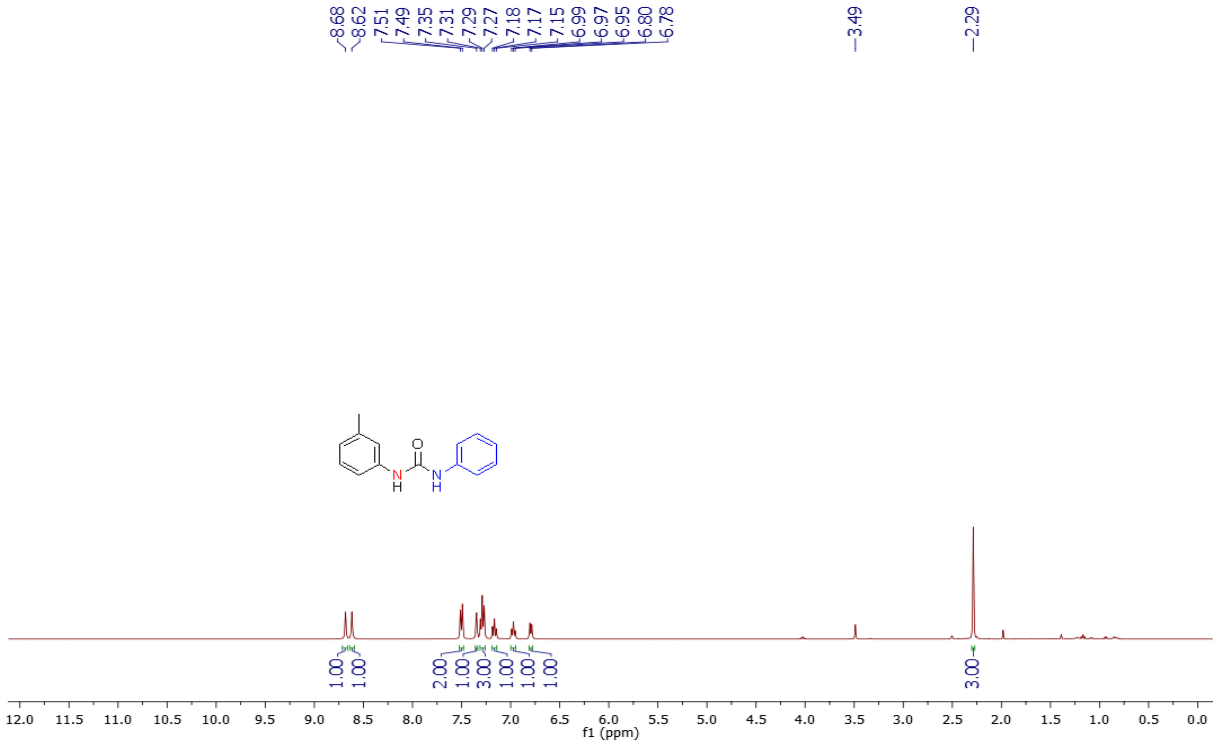
DEPT of 1-phenyl-3-(o-tolyl)urea (3ah)



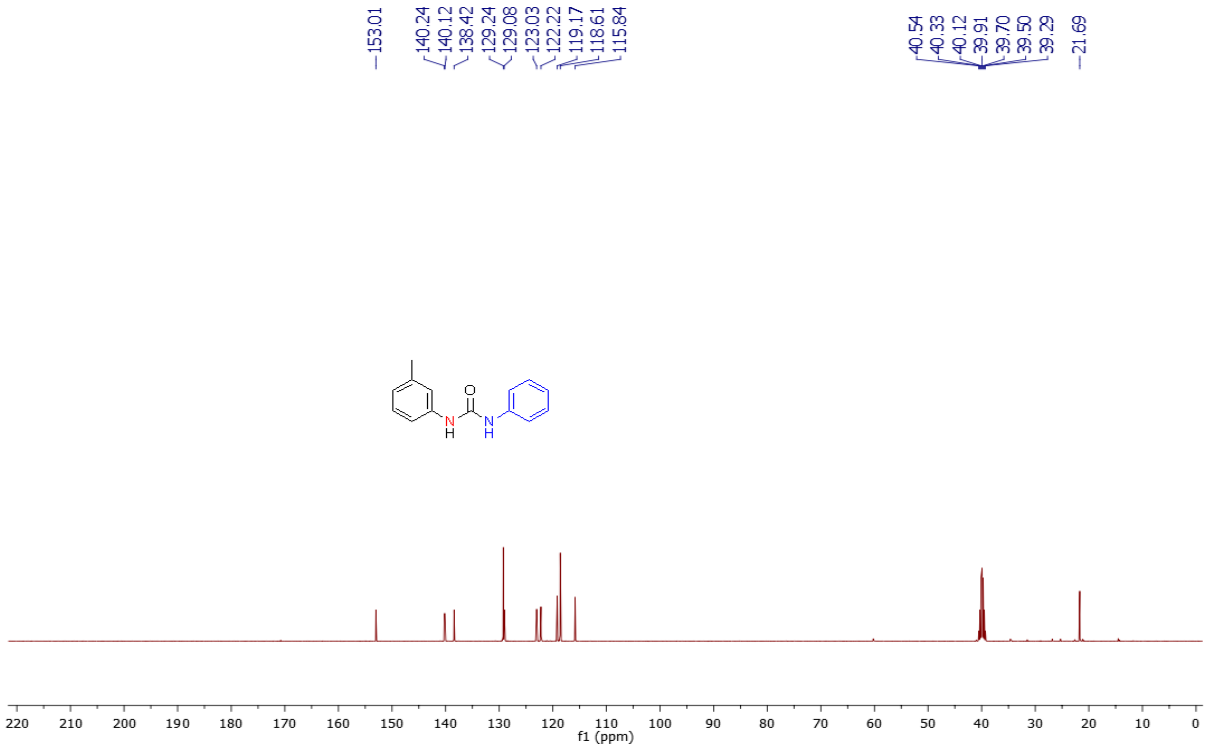
HRMS of 1-phenyl-3-(*o*-tolyl)urea (3ah)



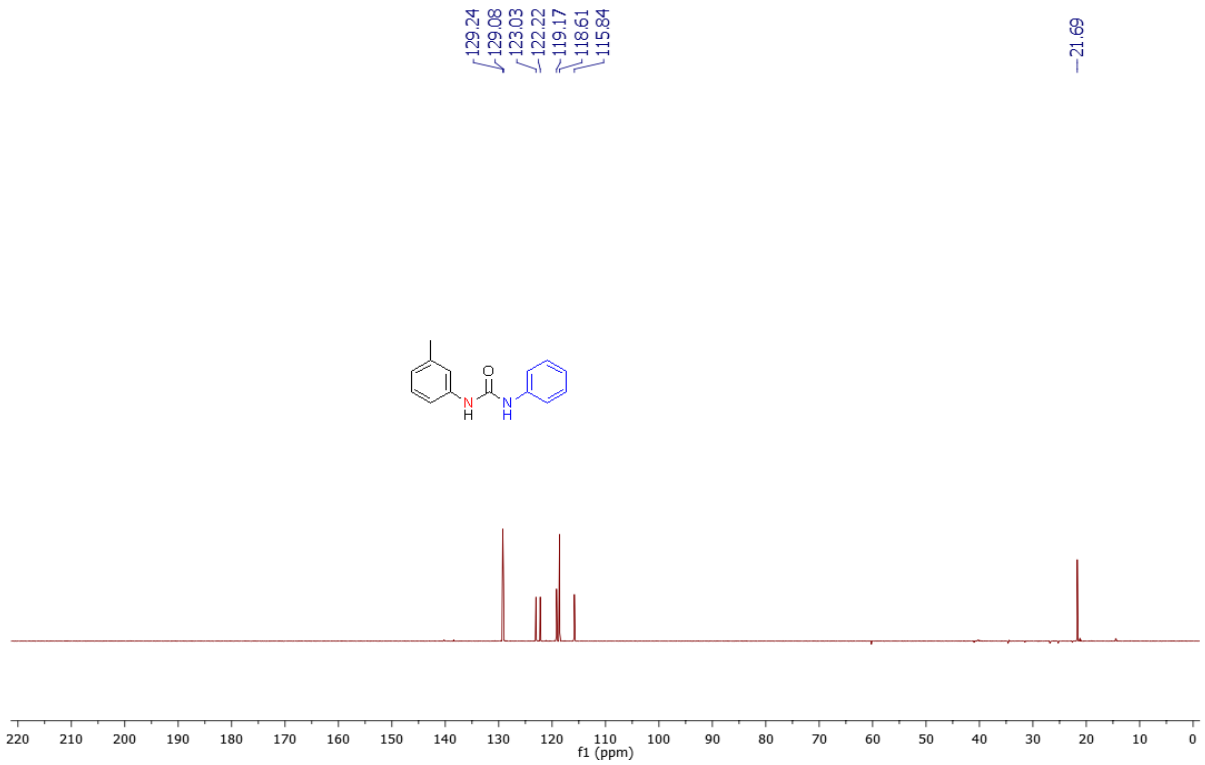
^{1}H-NMR of 1-phenyl-3-(*m*-tolyl)urea (3ai)



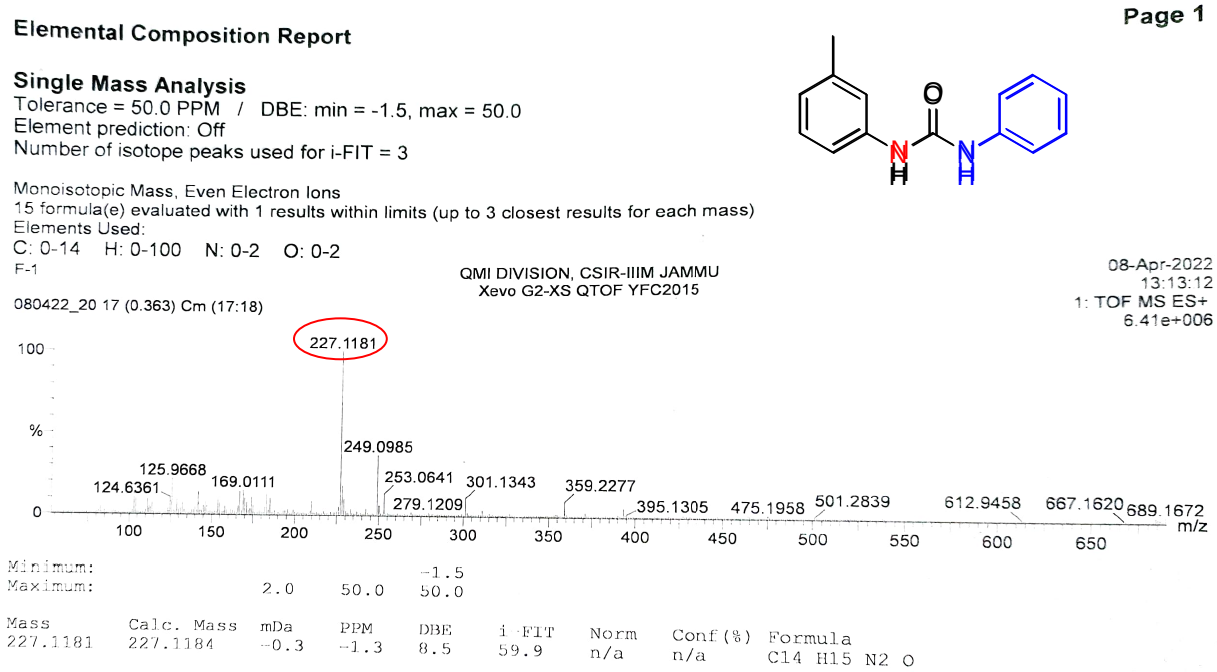
^{13}C-NMR of 1-phenyl-3-(*m*-tolyl)urea (3ai)



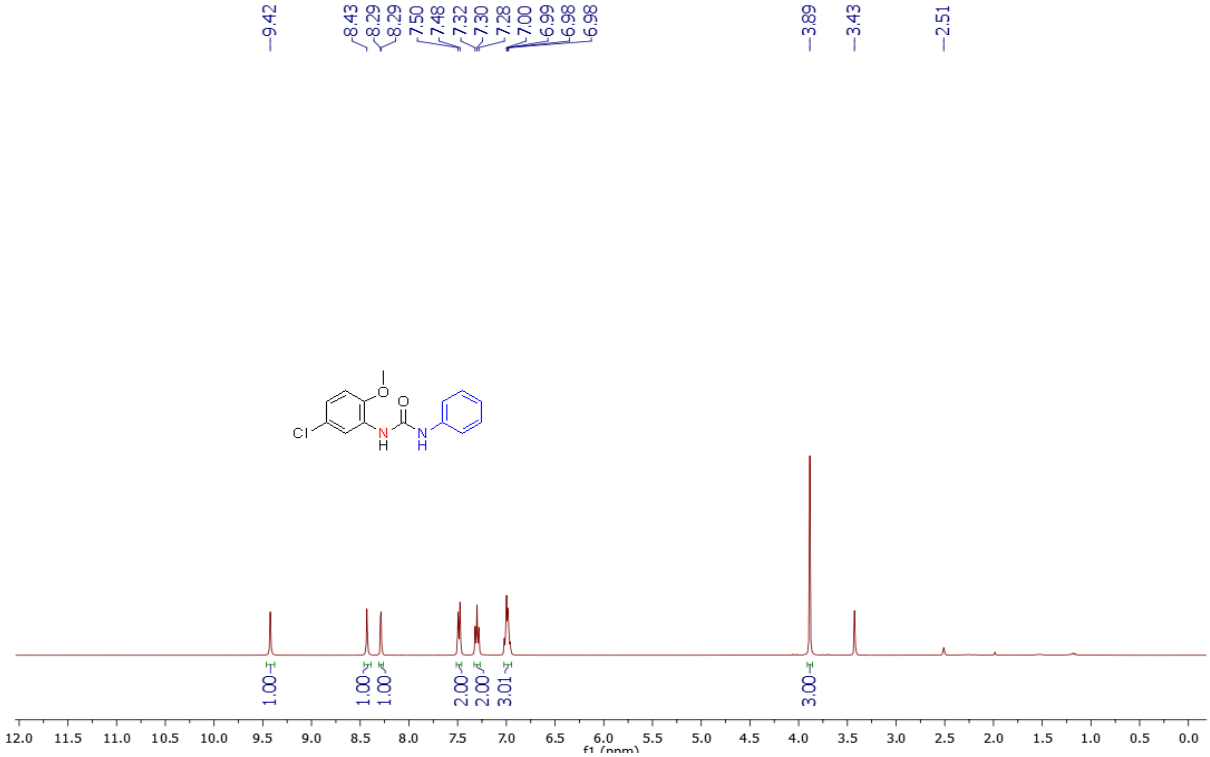
DEPT of 1-phenyl-3-(*m*-tolyl)urea (3ai)



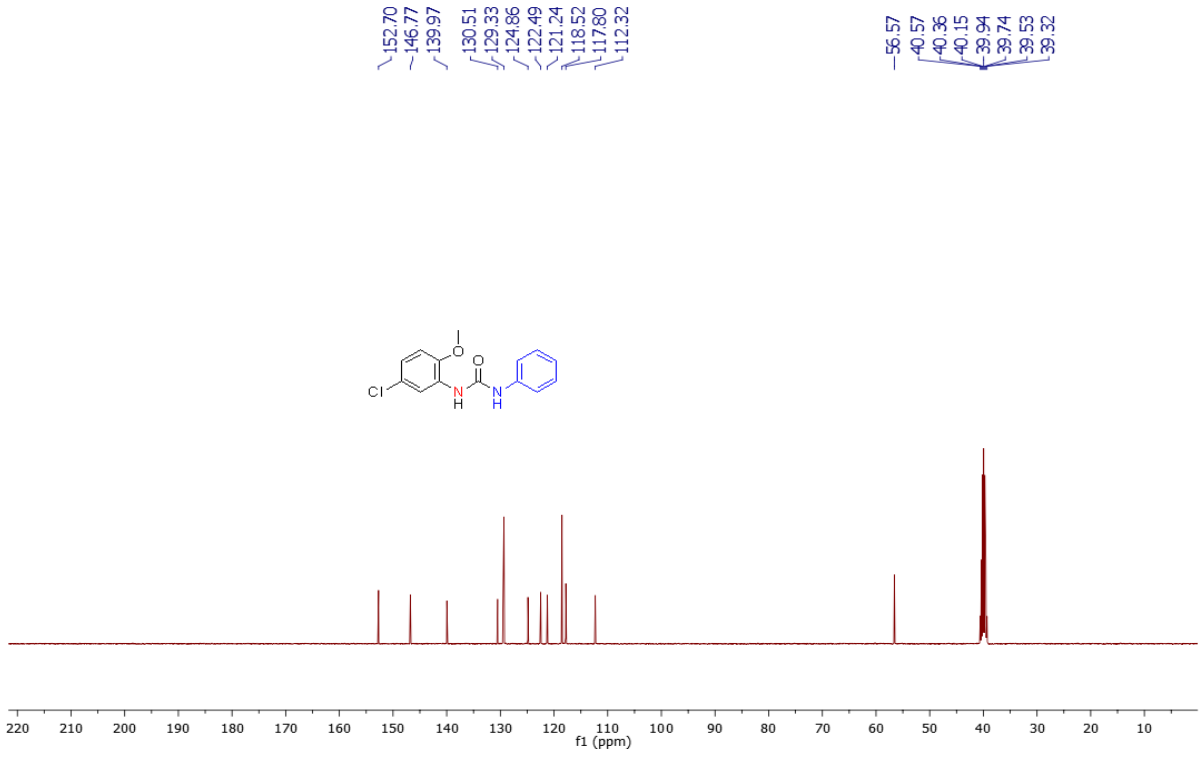
HRMS of 1-phenyl-3-(*m*-tolyl)urea (3ai)



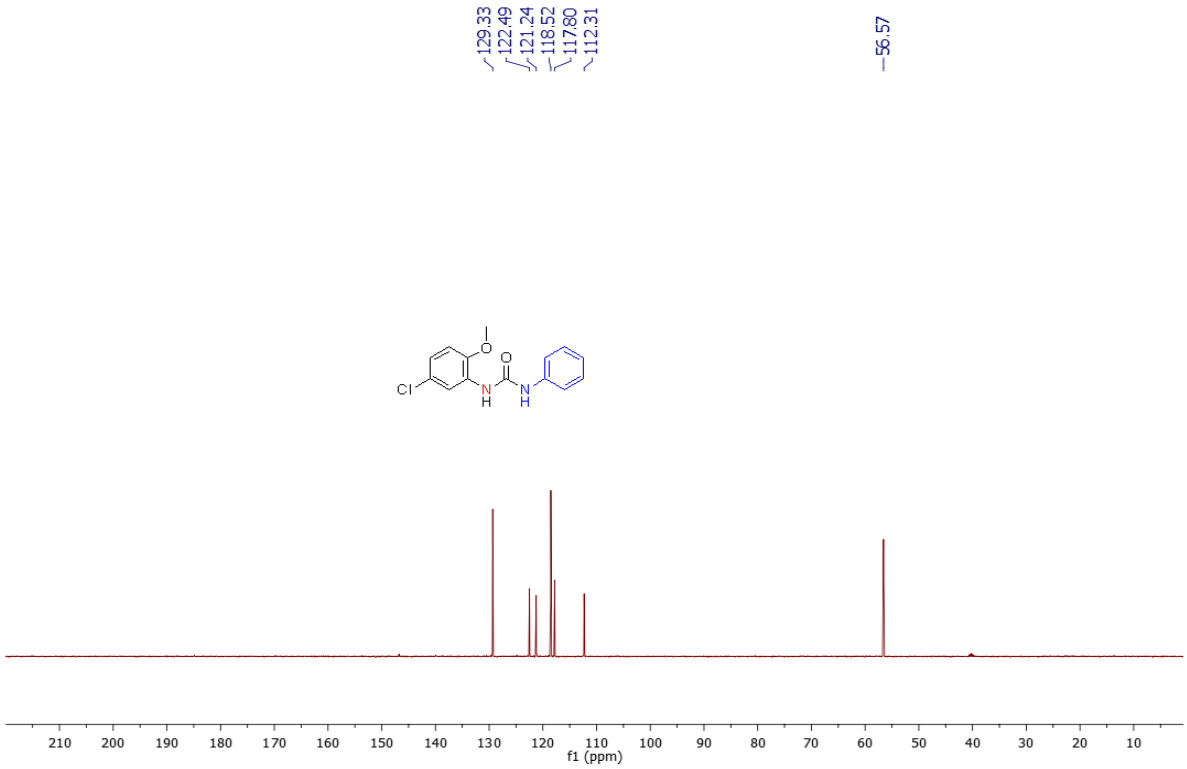
^{1}H-NMR of 1-(5-chloro-2-methoxyphenyl)-3-phenylurea (3aj)



^{13}C-NMR of of 1-(5-chloro-2-methoxyphenyl)-3-phenylurea (3aj)



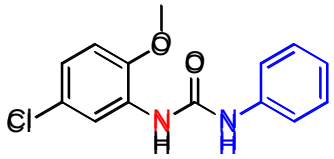
DEPT of 1-(5-chloro-2-methoxyphenyl)-3-phenylurea (3aj)



HRMS of 1-(5-chloro-2-methoxyphenyl)-3-phenylurea (3aj)

Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

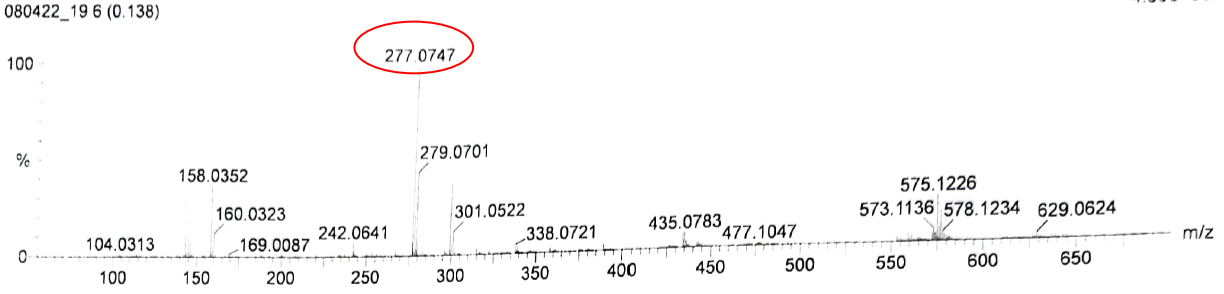


Monoisotopic Mass, Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-14 H: 0-100 N: 0-2 O: 0-2 Cl: 0-1
F-3

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

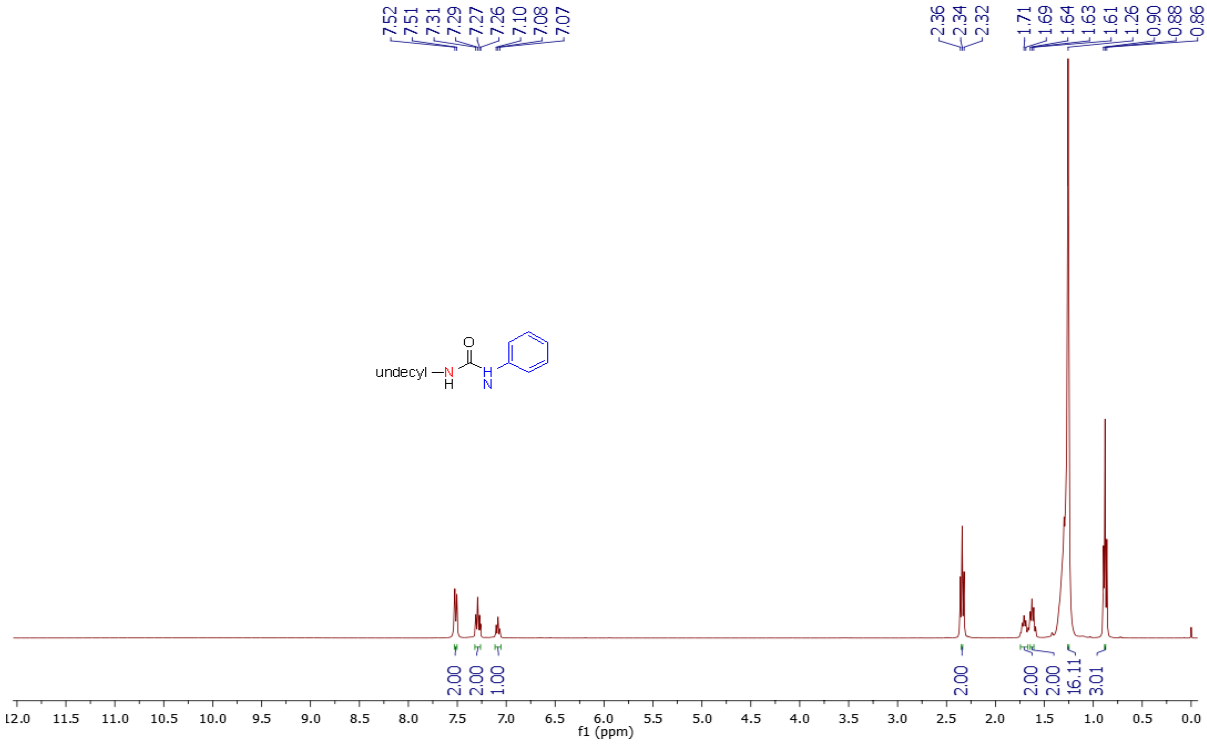
08-Apr-2022
13:10:38
1: TOF MS ES+
4.59e+007

080422_19 6 (0.138)

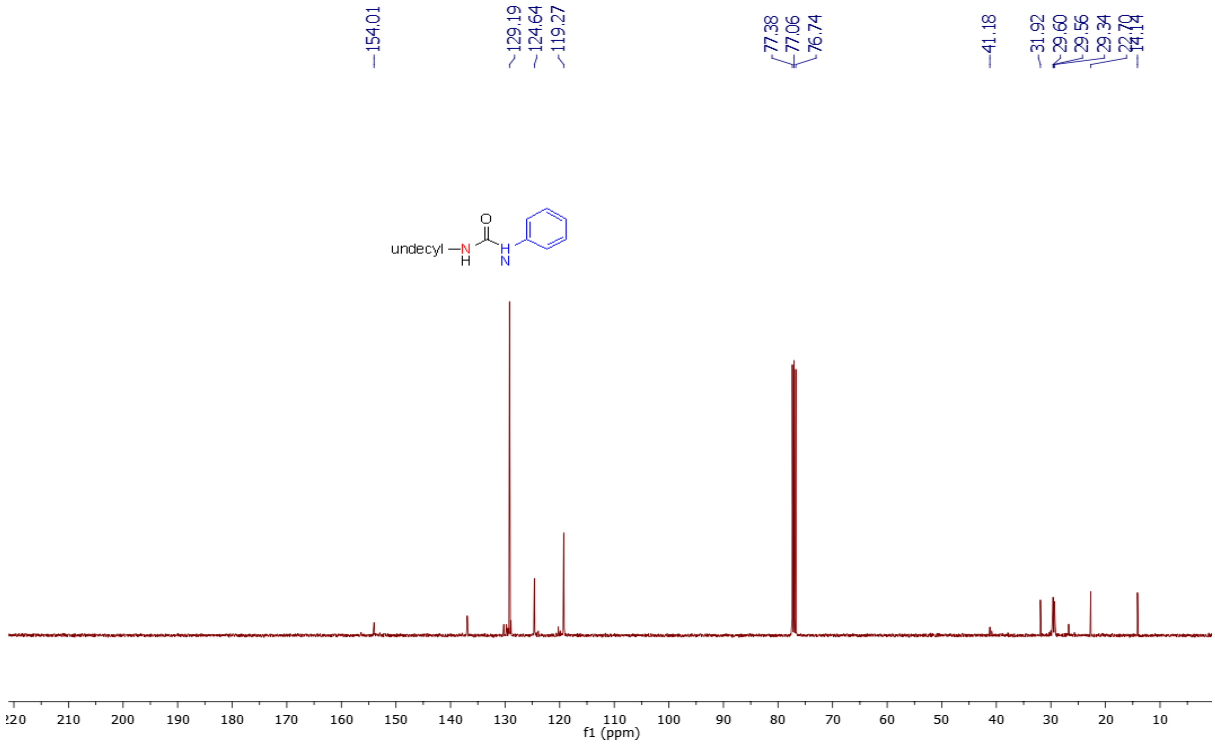


Minimum:				-1.5				
Maximum:		2.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
277.0747	277.0744	0.3	1.1	8.5	1377.4	n/a	n/a	C14 H14 N2 O2 Cl

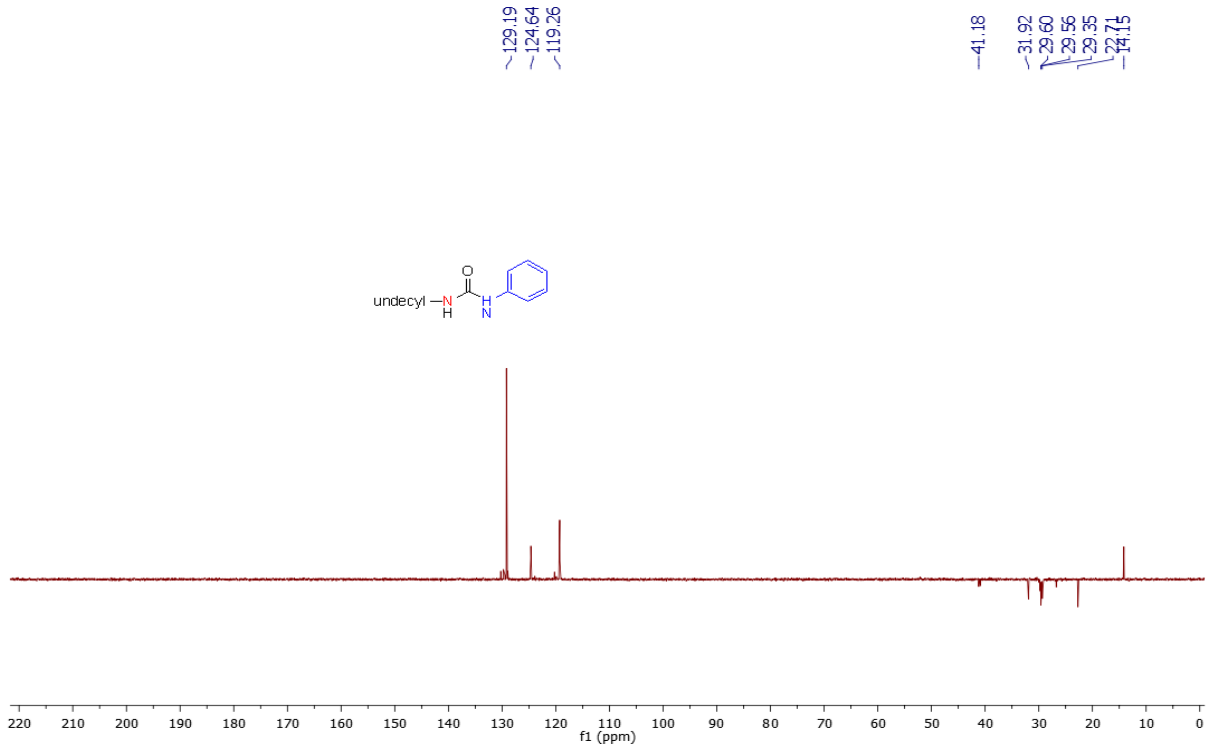
^{1}H-NMR of 1-phenyl-3-undecylurea (3ak)



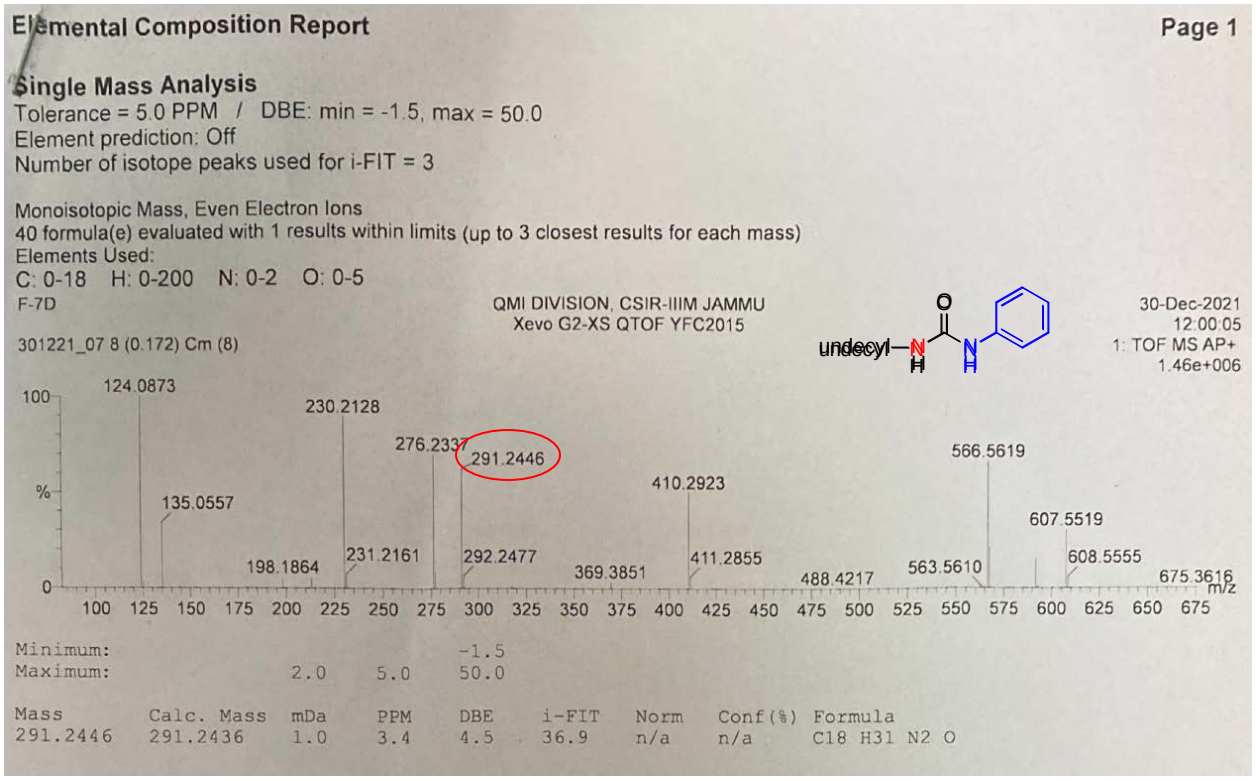
^{13}C-NMR of 1-phenyl-3-undecylurea (3ak)



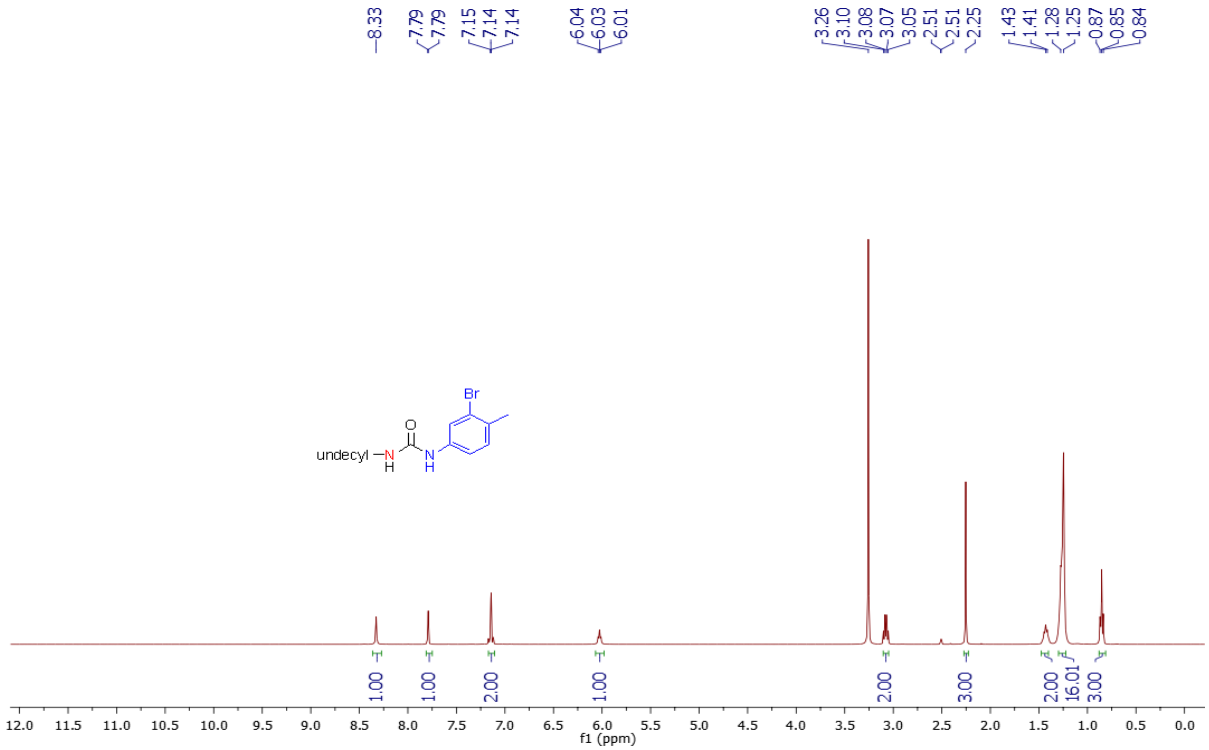
DEPT of 1-phenyl-3-undecylurea (3ak)



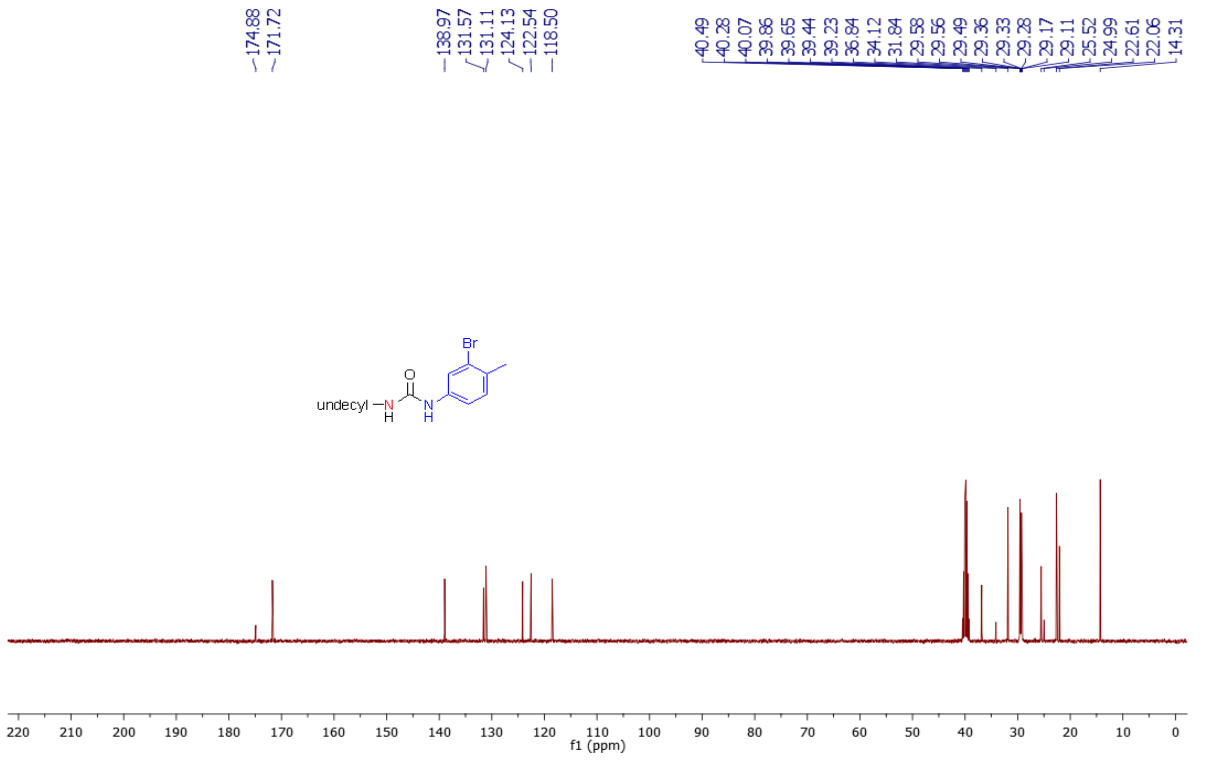
HRMS of 1-phenyl-3-undecylurea (3ak)



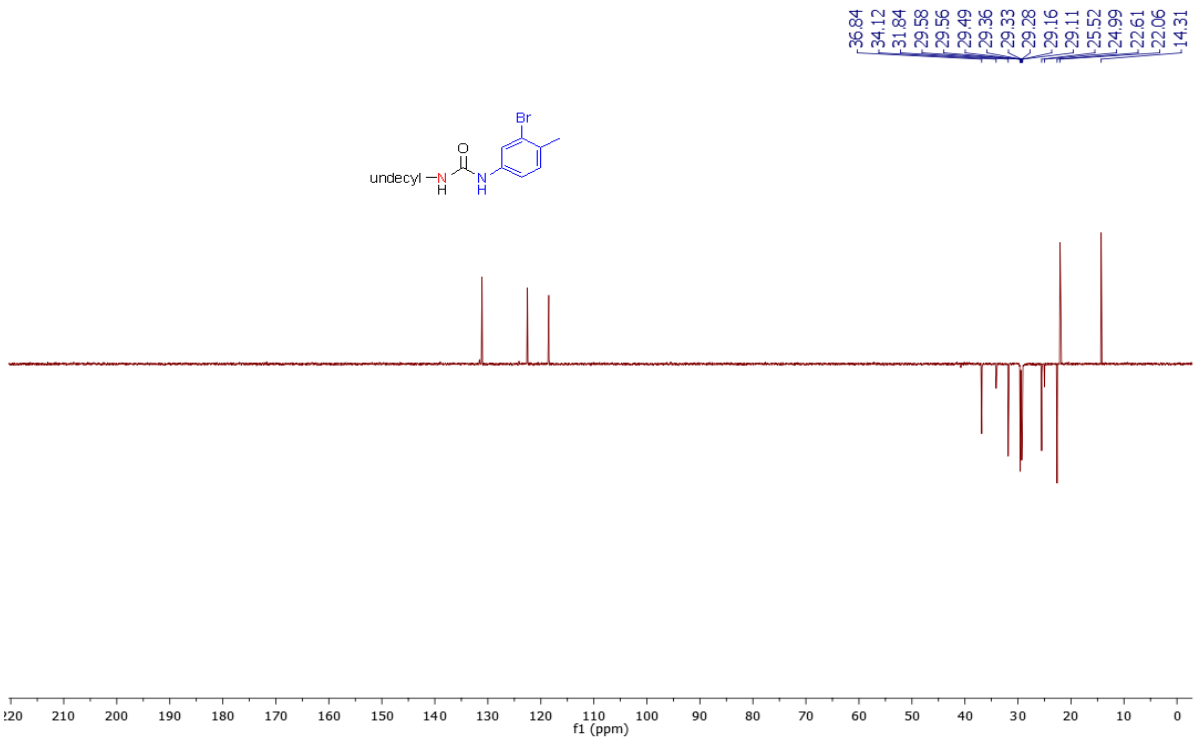
^{1}H-NMR of 1-(3-bromo-4-methylphenyl)-3-undecylurea (3al)



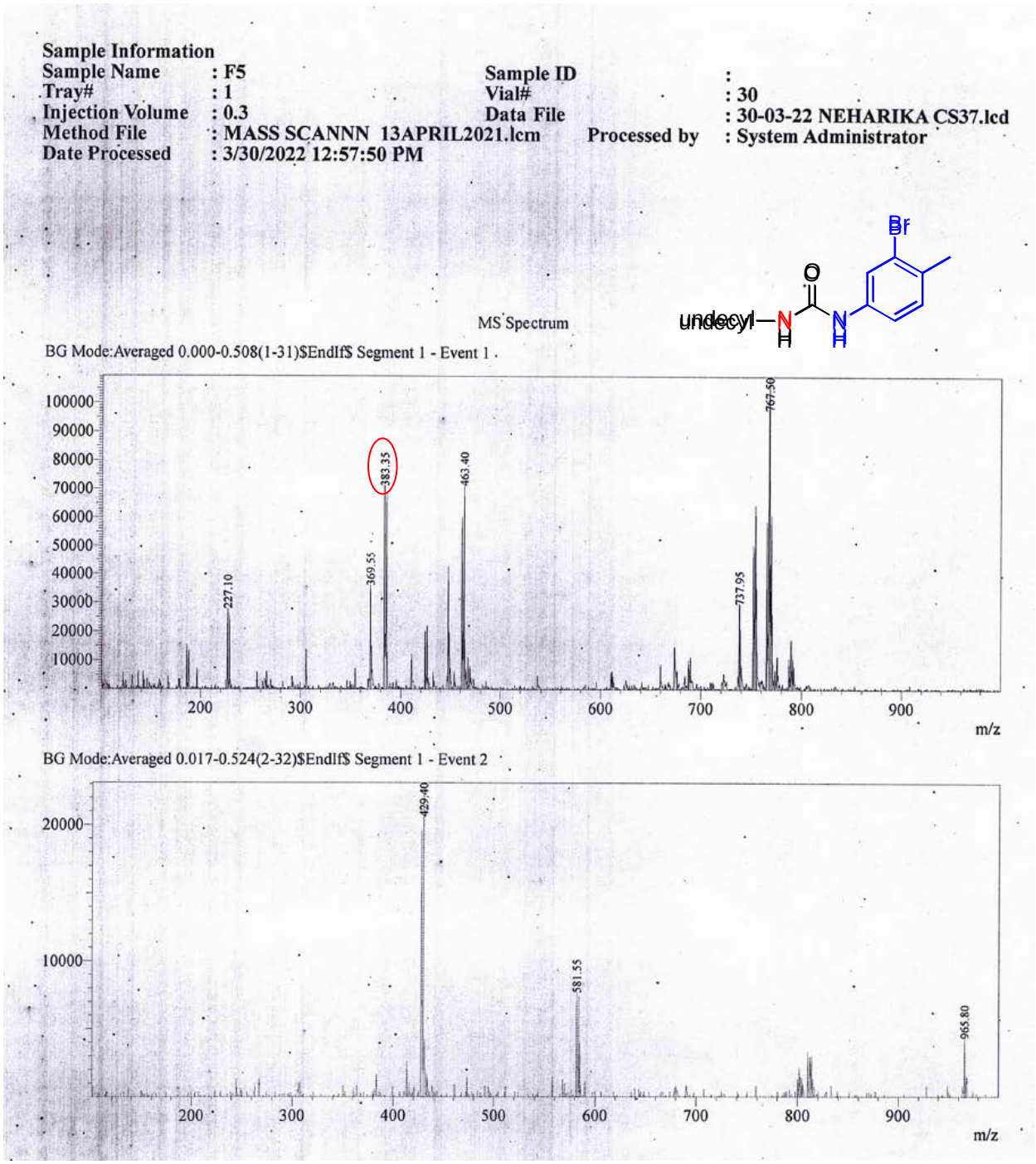
^{13}C-NMR of 1-(3-bromo-4-methylphenyl)-3-undecylurea (3al)



DEPT of 1-(3-bromo-4-methylphenyl)-3-undecylurea (3al)



Mass spectra of 1-(3-bromo-4-methylphenyl)-3-undecylurea (3al)



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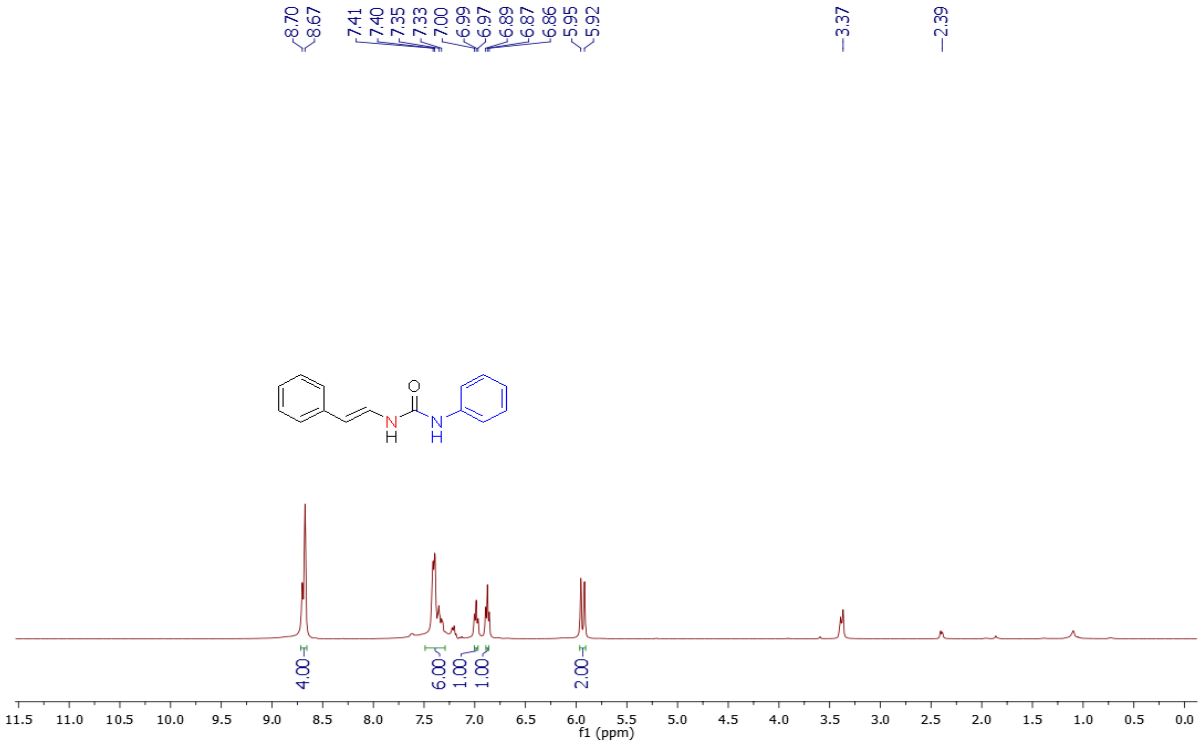
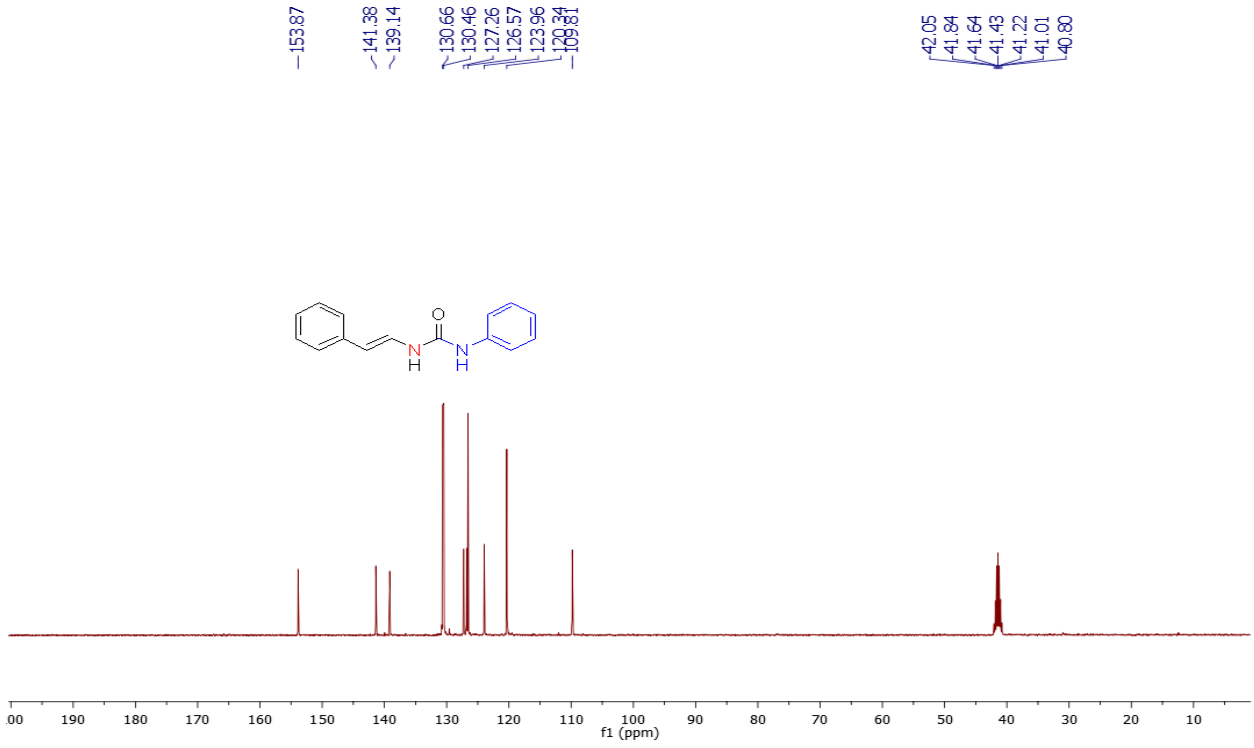
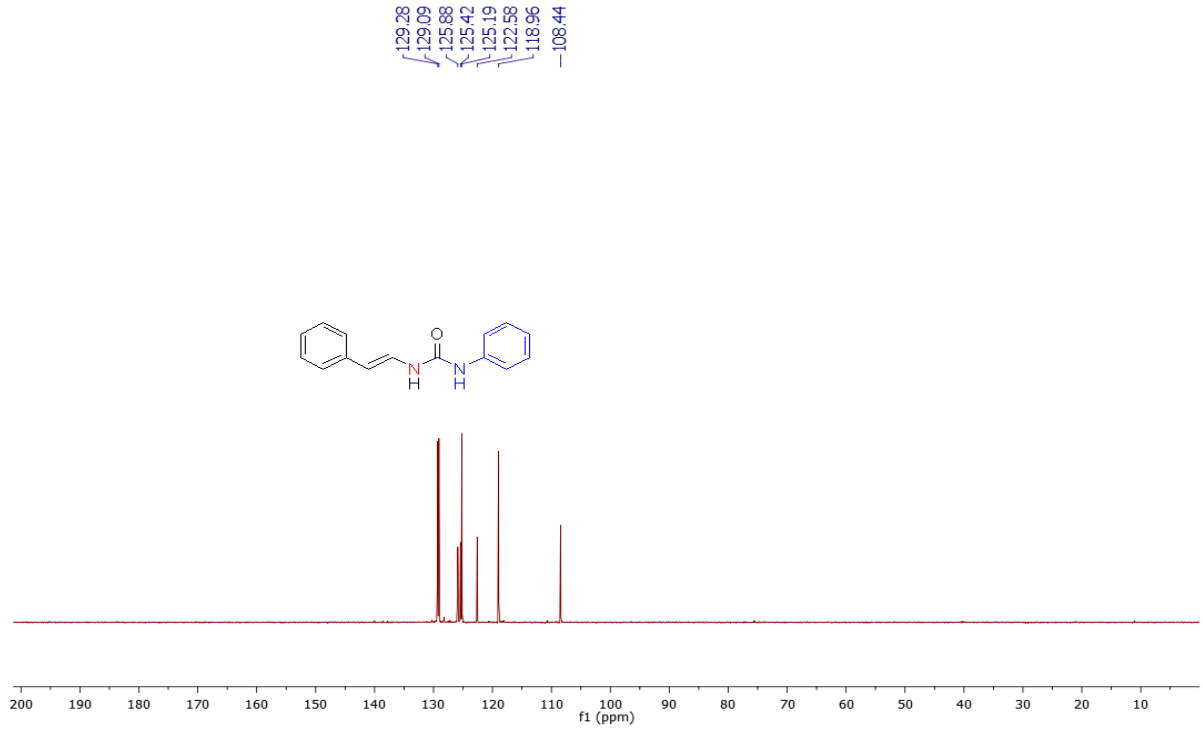
[1]H-NMR of (*E*)-1-phenyl-3-styrylurea (3am)



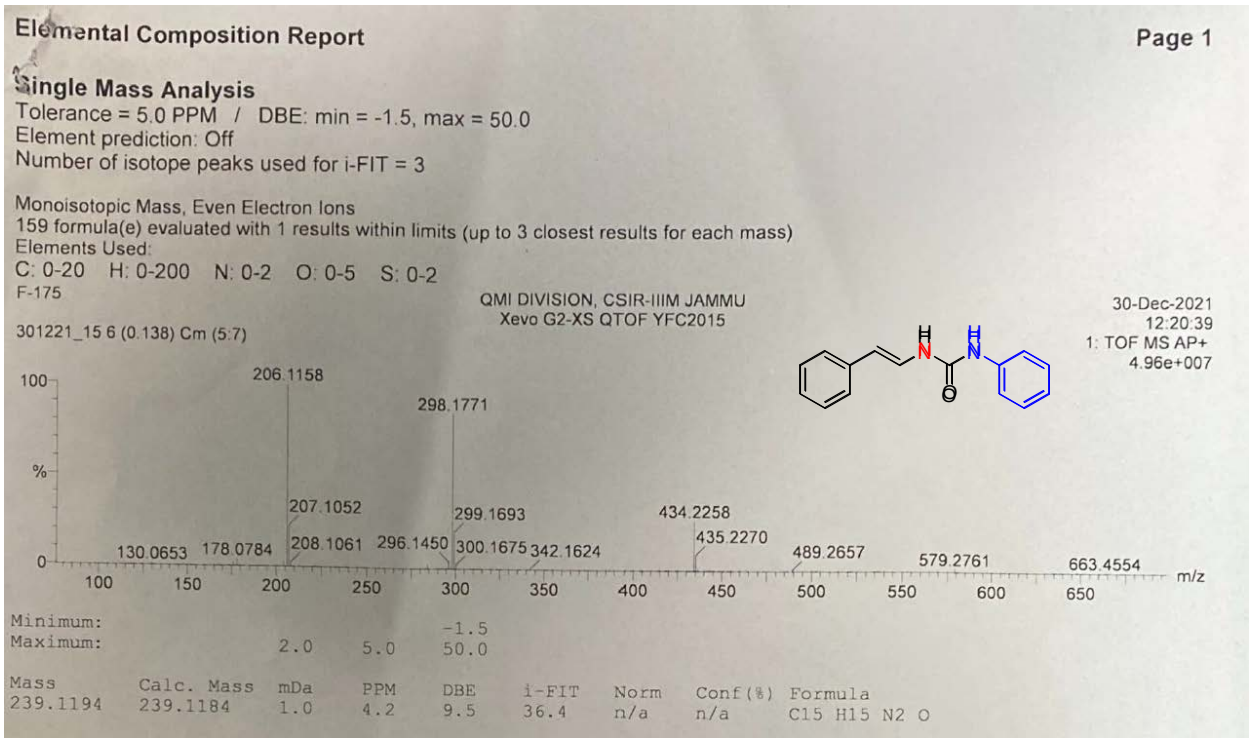
[13]C-NMR of (*E*)-1-phenyl-3-styrylurea (3am)



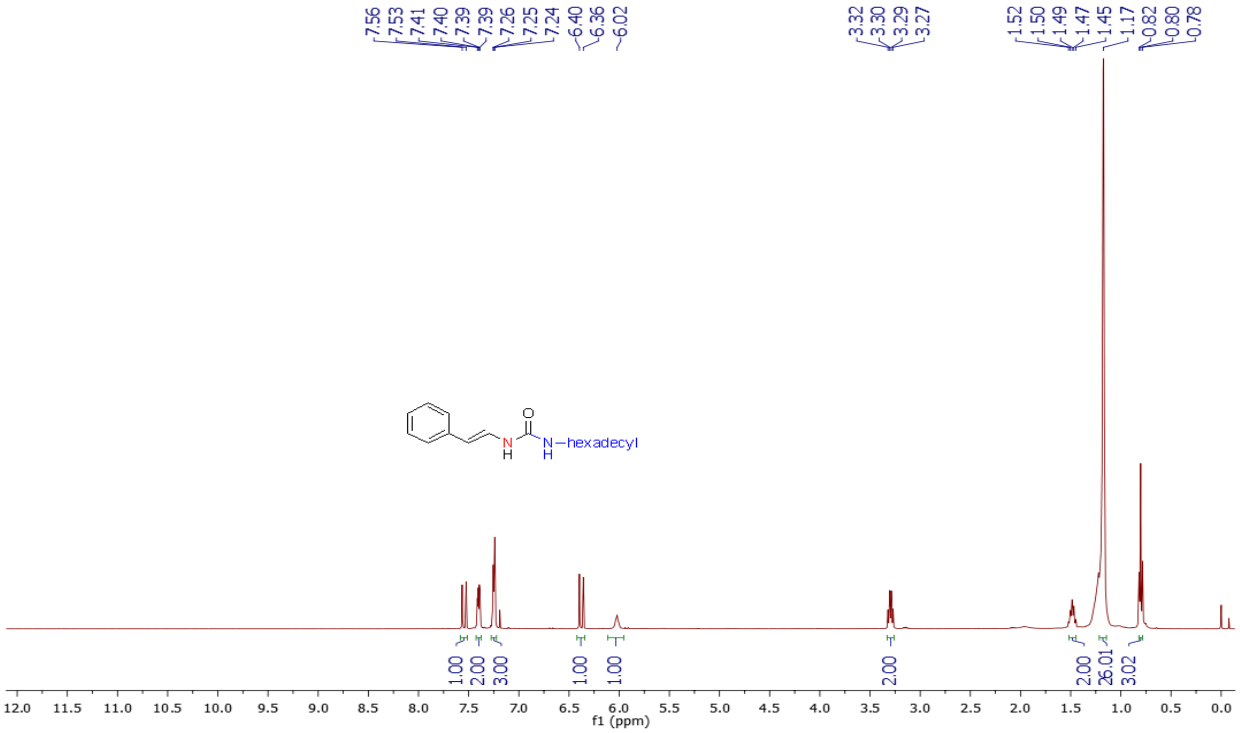
DEPT of (*E*)-1-phenyl-3-styrylurea (3am)



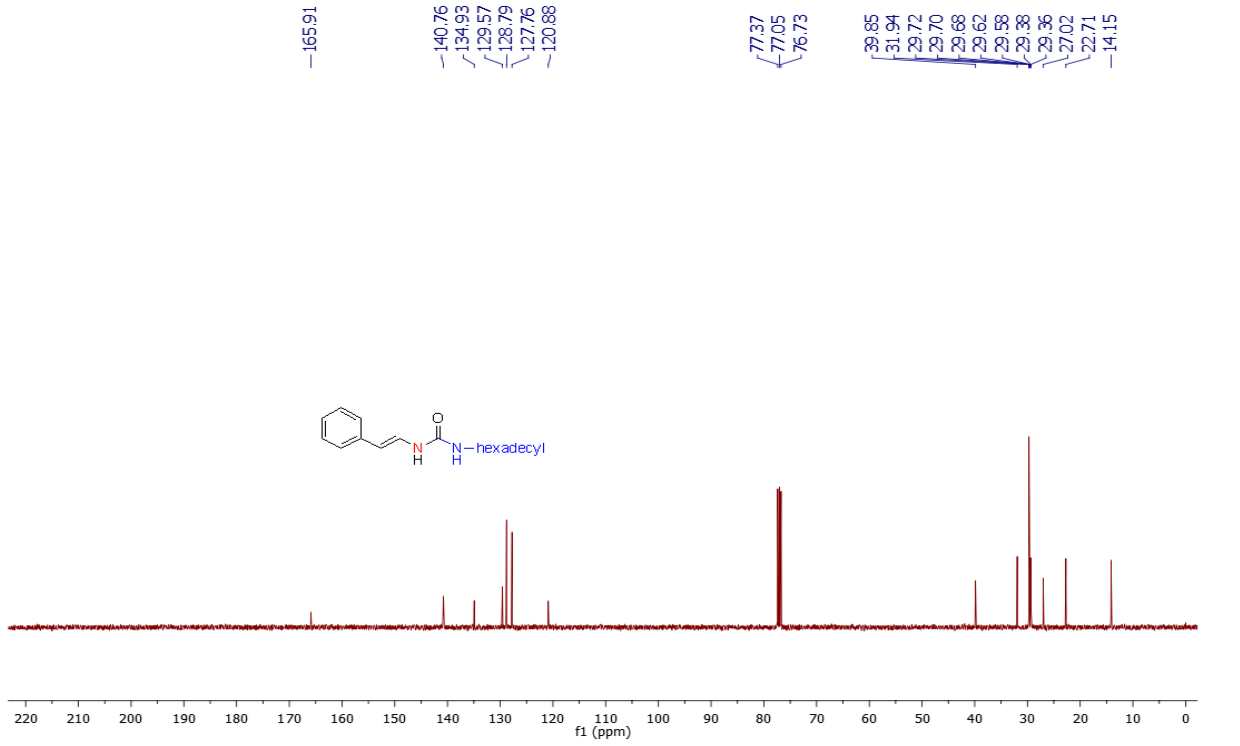
HRMS of (*E*)-1-phenyl-3-styrylurea (3am)



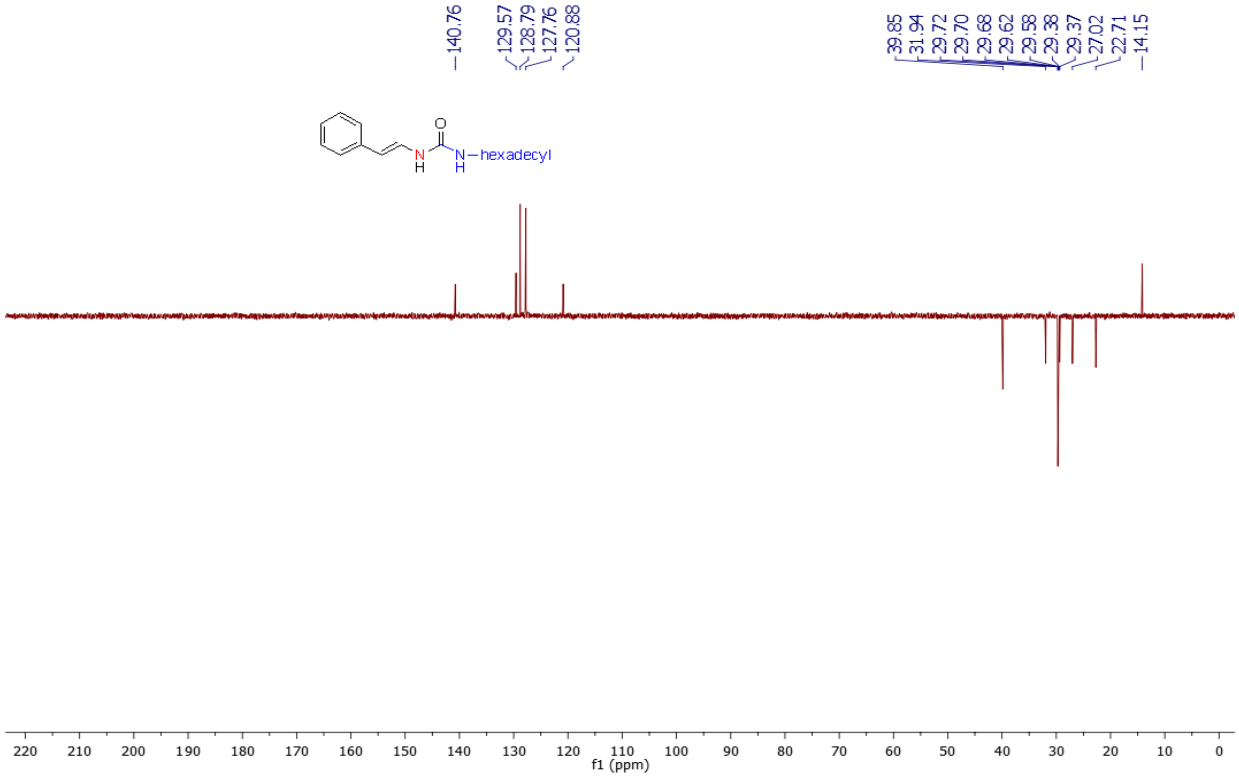
^{1}H-NMR of (*E*)-1-hexadecyl-3-styrylurea (3an)



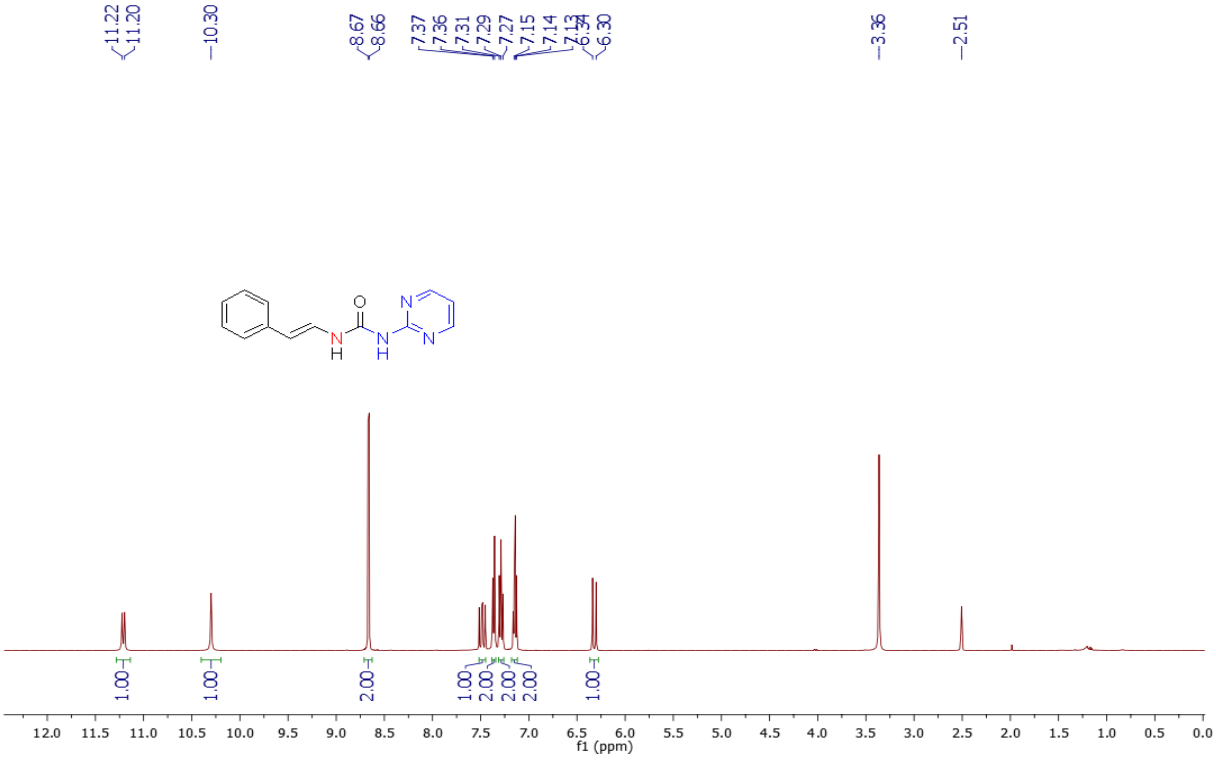
^{13}C-NMR of (*E*)-1-hexadecyl-3-styrylurea (3an)



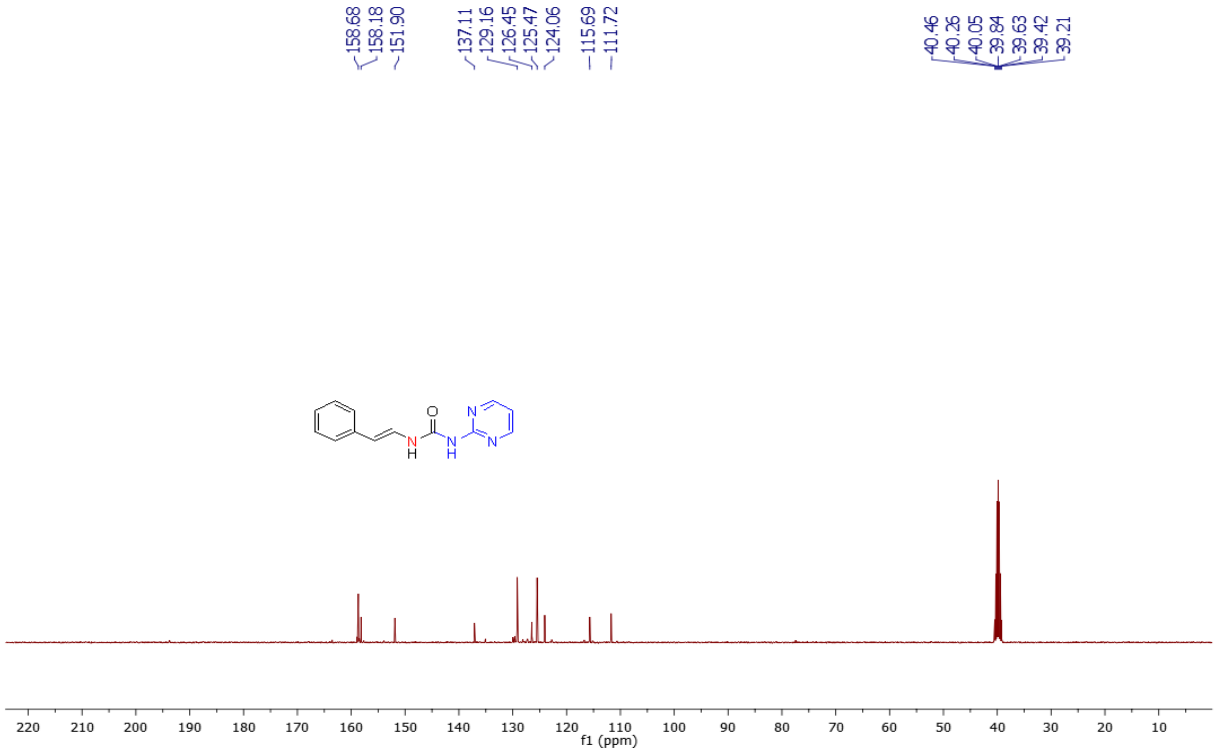
DEPT of of (*E*)-1-hexadecyl-3-styrylurea (3an)



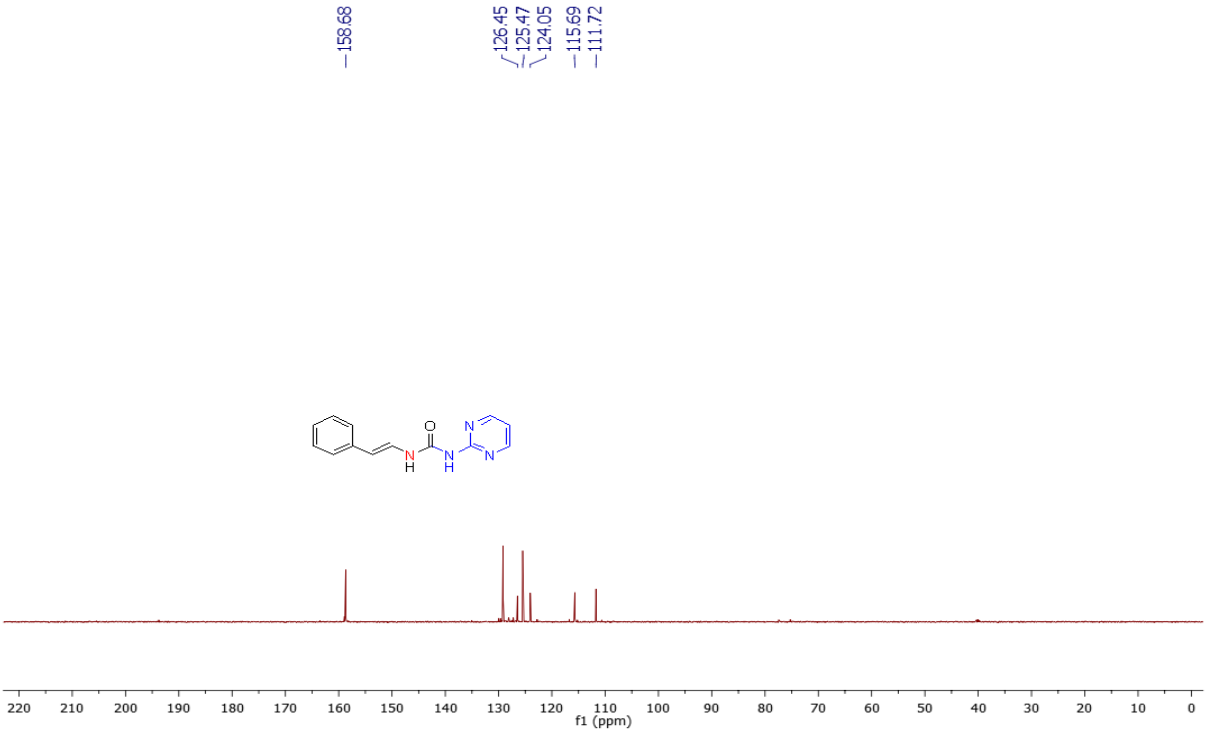
^{1}H-NMR of (*E*)-1-(pyrimidin-2-yl)-3-styrylurea (3ao)



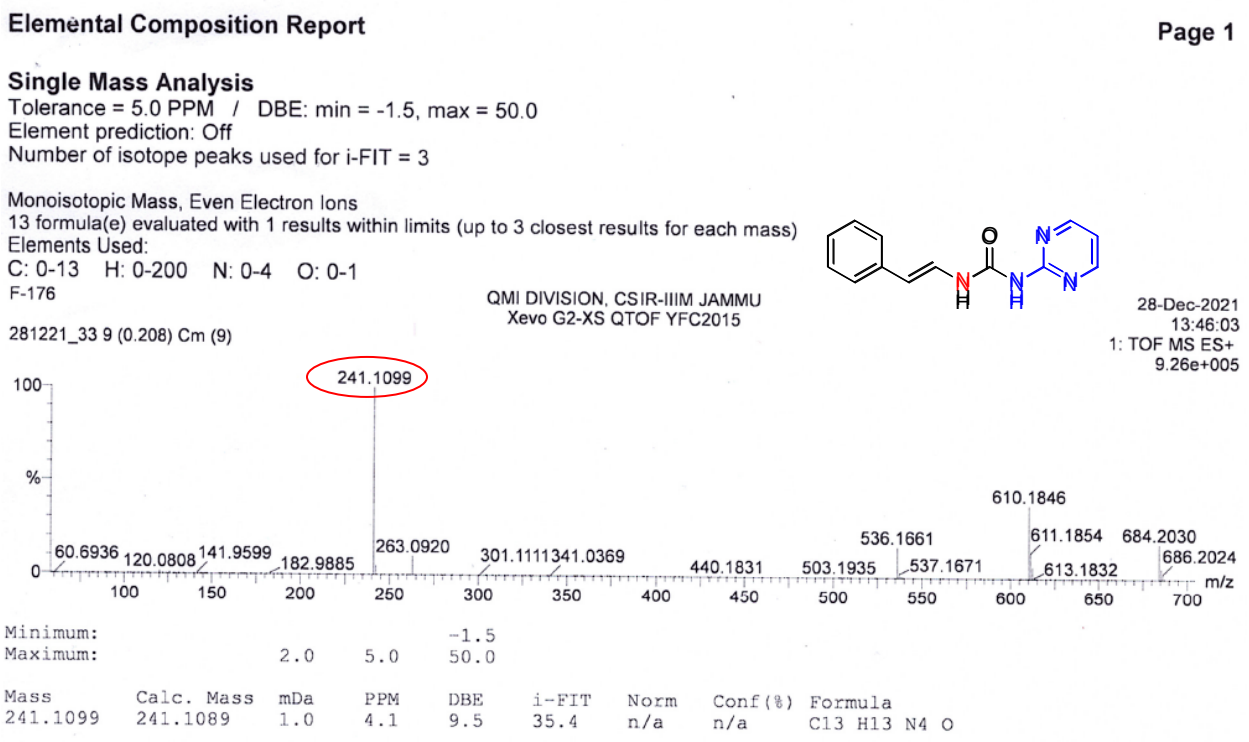
^{13}C-NMR of (*E*)-1-(pyrimidin-2-yl)-3-styrylurea (3ao)



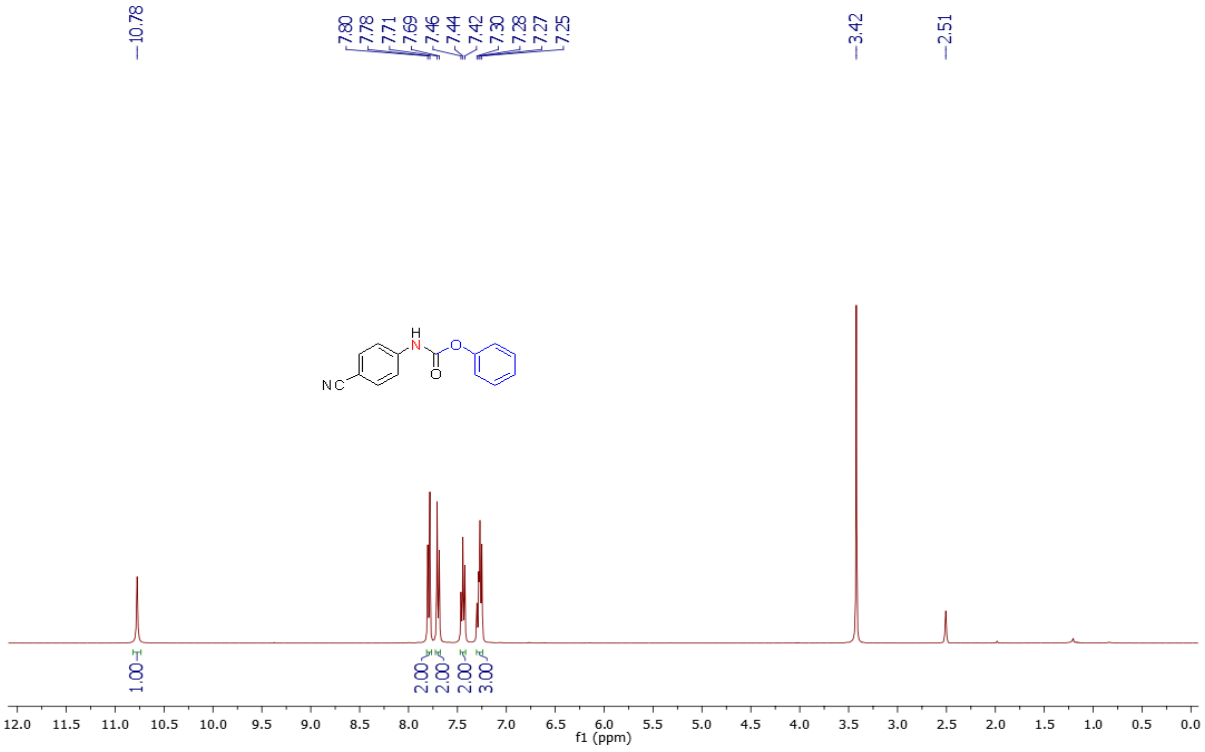
DEPT of (*E*)-1-(pyrimidin-2-yl)-3-styrylurea (3ao)



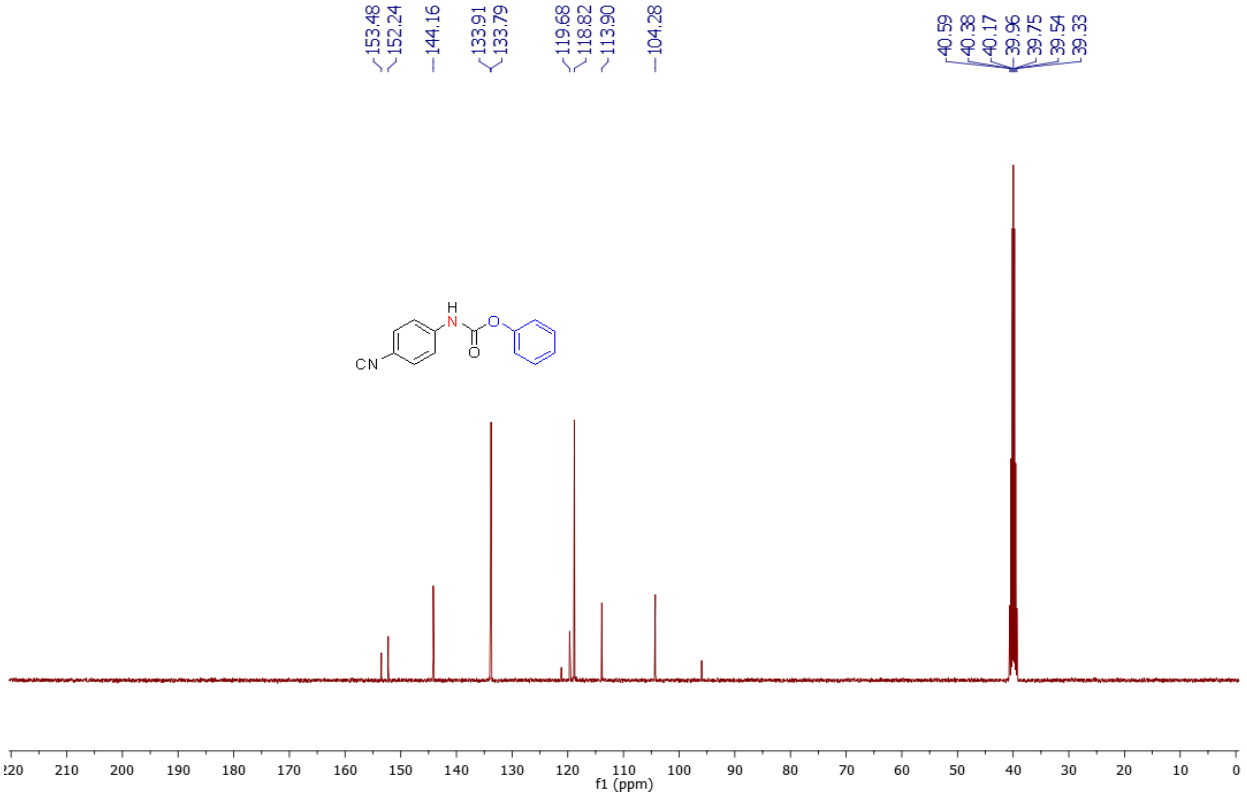
HRMS of (*E*)-1-(pyrimidin-2-yl)-3-styrylurea (3ao)



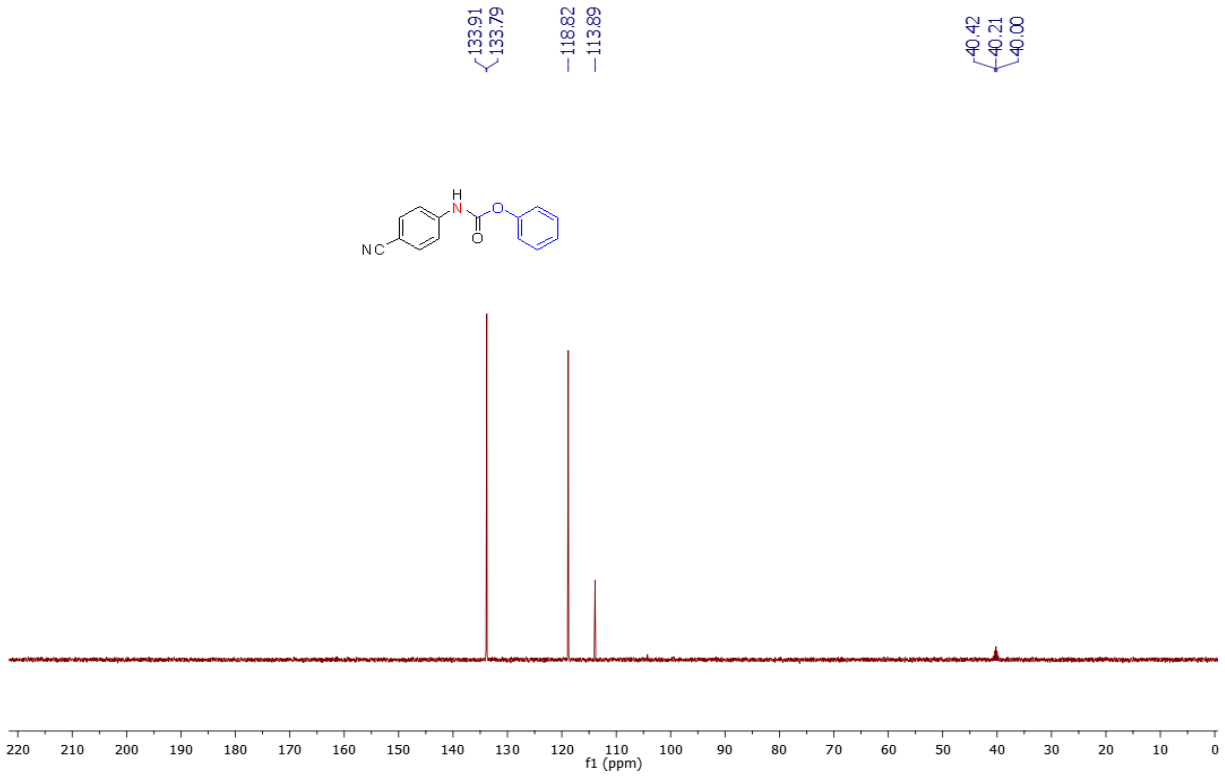
^{1}H-NMR of phenyl (4-cyanophenyl)carbamate (4a)



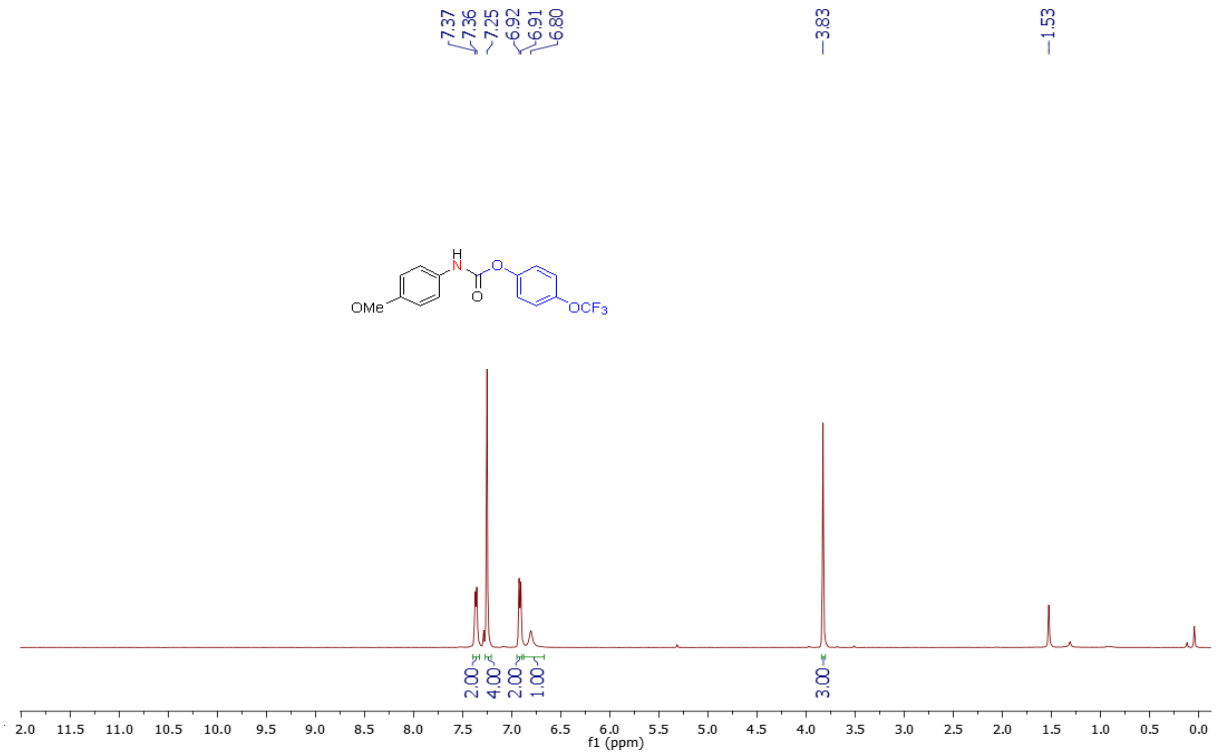
^{13}C-NMR of phenyl (4-cyanophenyl)carbamate (4a)



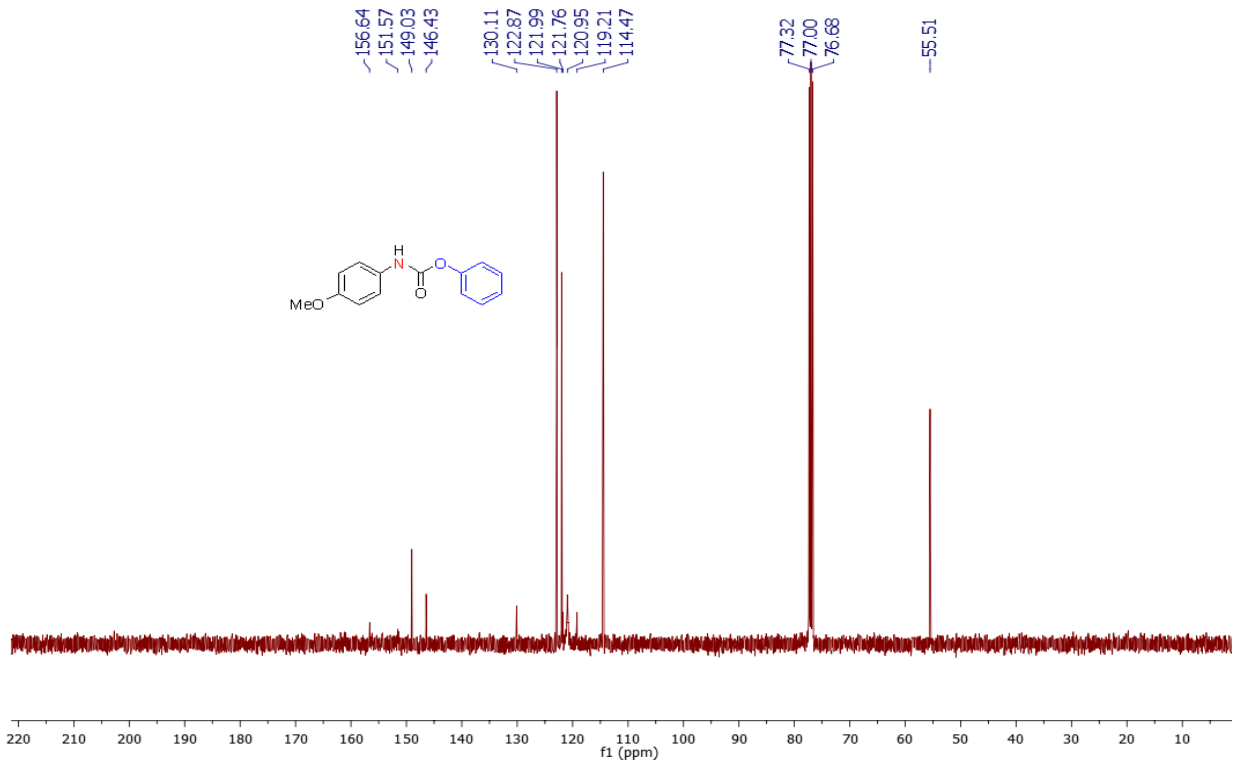
DEPT of phenyl (4-cyanophenyl)carbamate (4a)



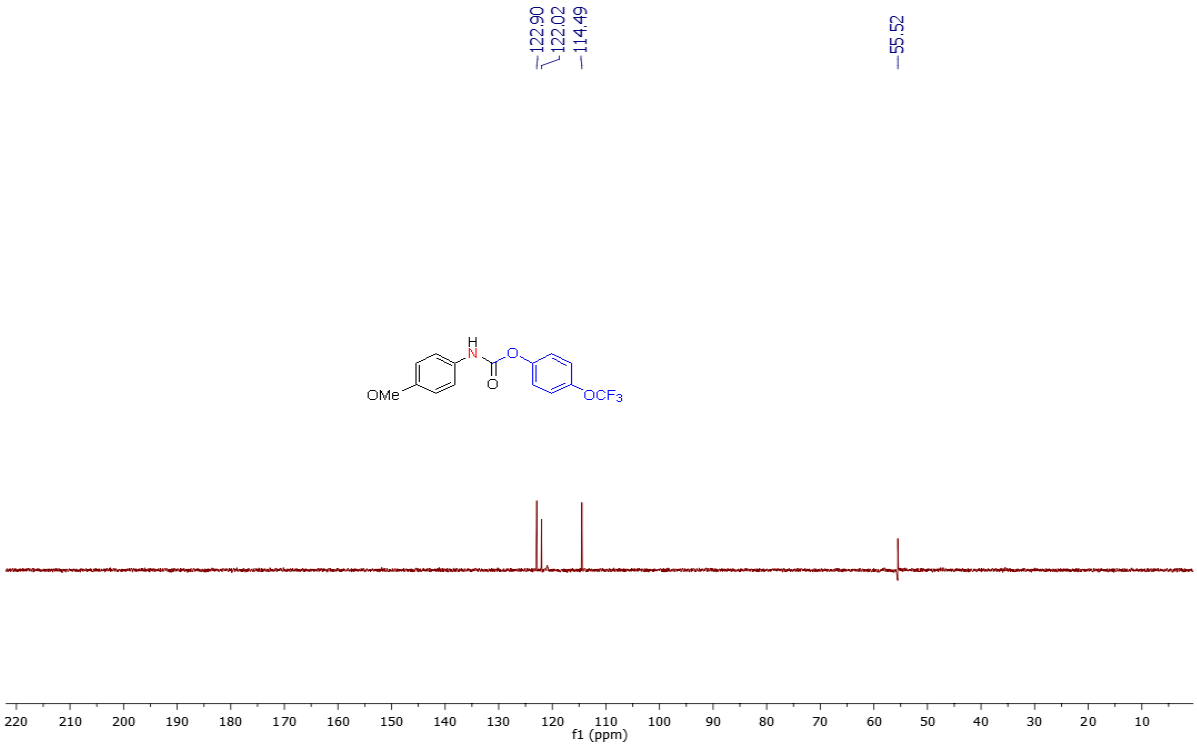
[1]H-NMR of 4-(trifluoromethoxy)phenyl (4-methoxyphenyl)carbamate (4b)



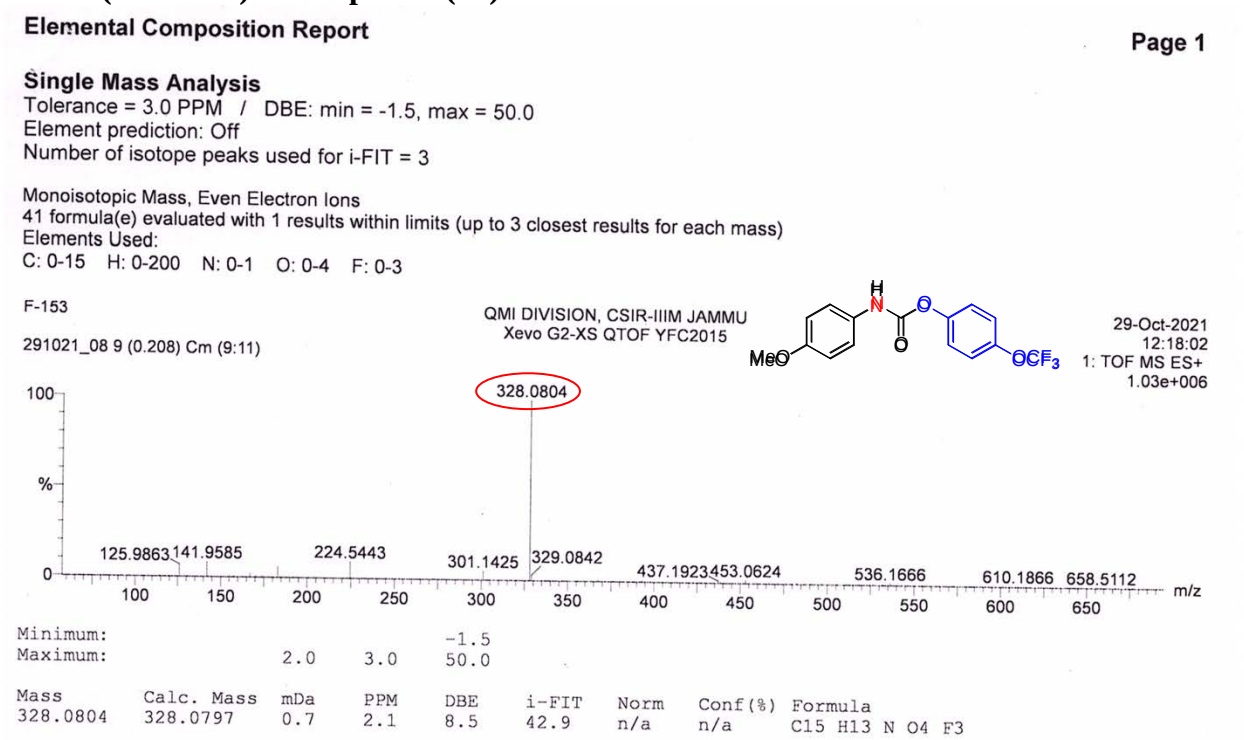
[13]C-NMR of 4-(trifluoromethoxy)phenyl (4-methoxyphenyl)carbamate (4b)



DEPT of 4-(trifluoromethoxy)phenyl (4-methoxyphenyl)carbamate (4b)



HRMS (ESI-TOF) of compound (4b)



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
41 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-15 H: 0-200 N: 0-1 O: 0-4 F: 0-3

F-153
291021_08 9 (0.208) Cm (9:11)

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

29-Oct-2021
12:18:02
1: TOF MS ES+
1.03e+006

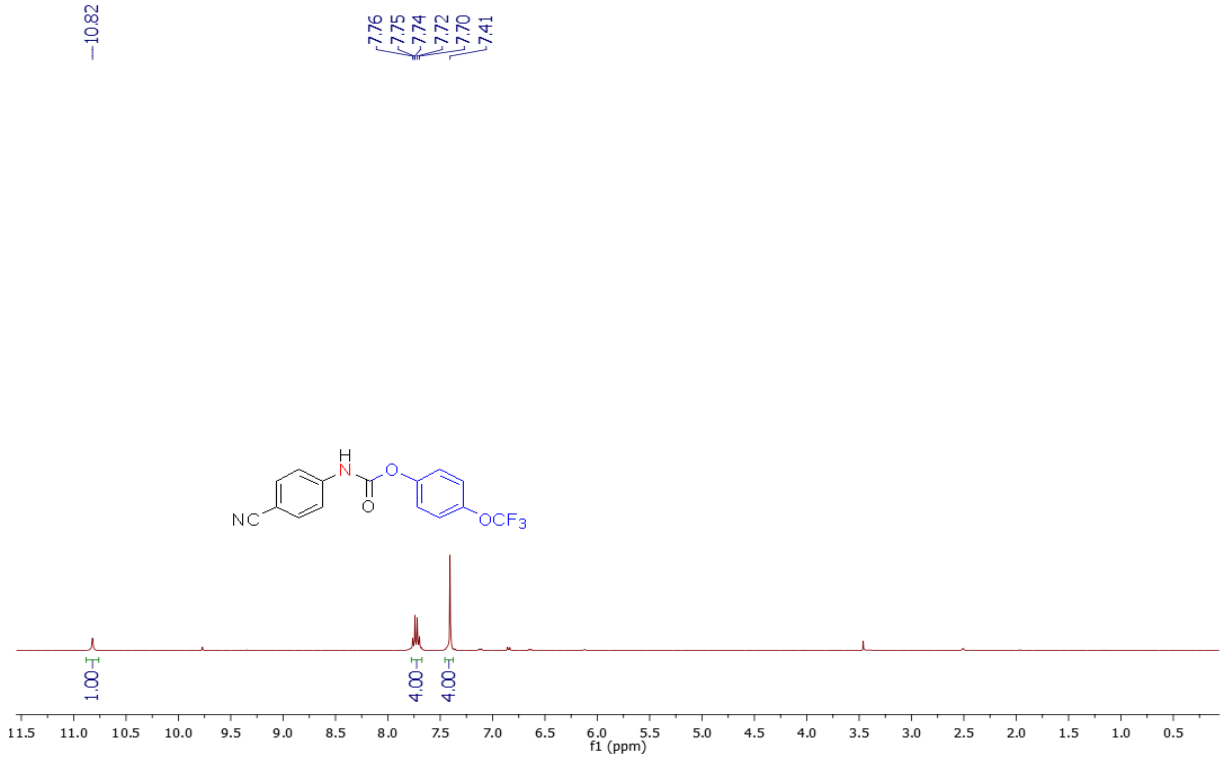
328.0804

125.9863 141.9585 224.5443 301.1425 329.0842 437.1923 453.0624 536.1666 610.1866 658.5112

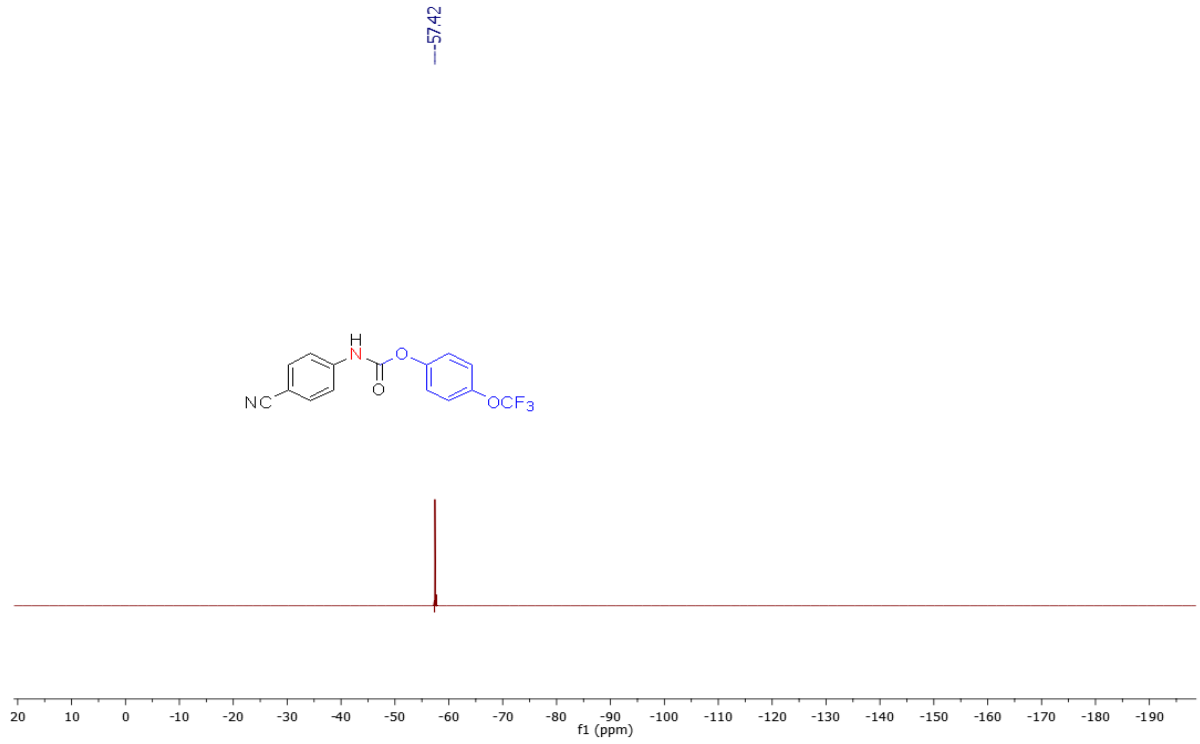
m/z

Minimum:				-1.5				
Maximum:		2.0	3.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
328.0804	328.0797	0.7	2.1	8.5	42.9	n/a	n/a	C15 H13 N O4 F3

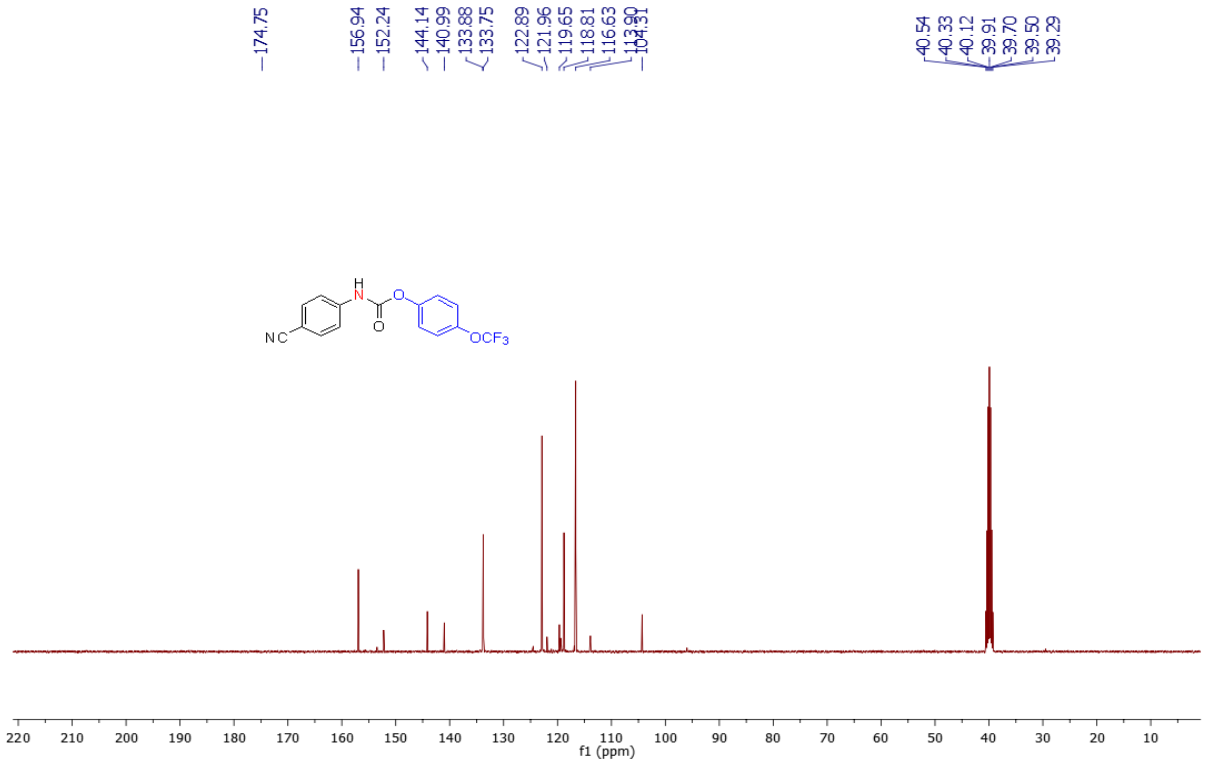
^{1}H-NMR of 4-(trifluoromethoxy)phenyl (4-cyanophenyl)carbamate (4c)



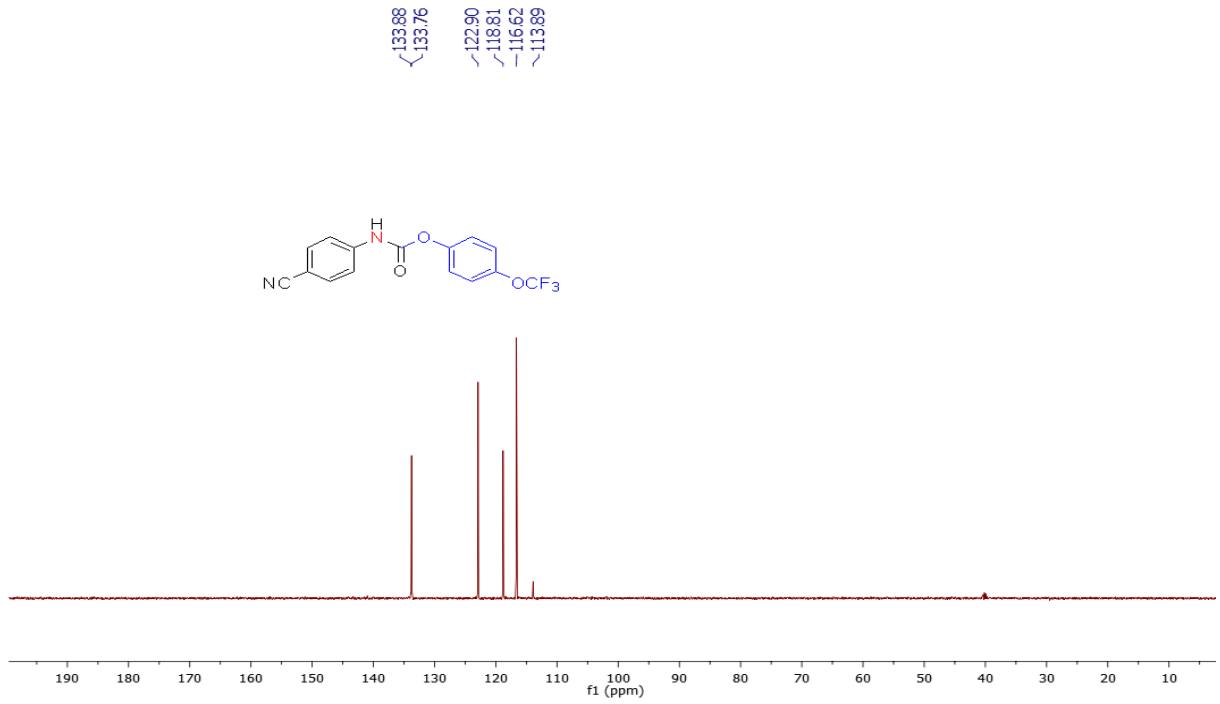
^{19}F-NMR of 4-(trifluoromethoxy)phenyl (4-cyanophenyl)carbamate (4c)



^{13}C-NMR of 4-(trifluoromethoxy)phenyl (4-cyanophenyl)carbamate (4c)



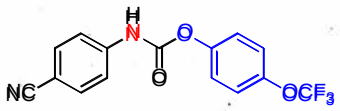
DEPT of 4-(trifluoromethoxy)phenyl (4-cyanophenyl)carbamate (4c)



Mass spectra of 4-(trifluoromethoxy)phenyl (4-cyanophenyl)carbamate (4c)

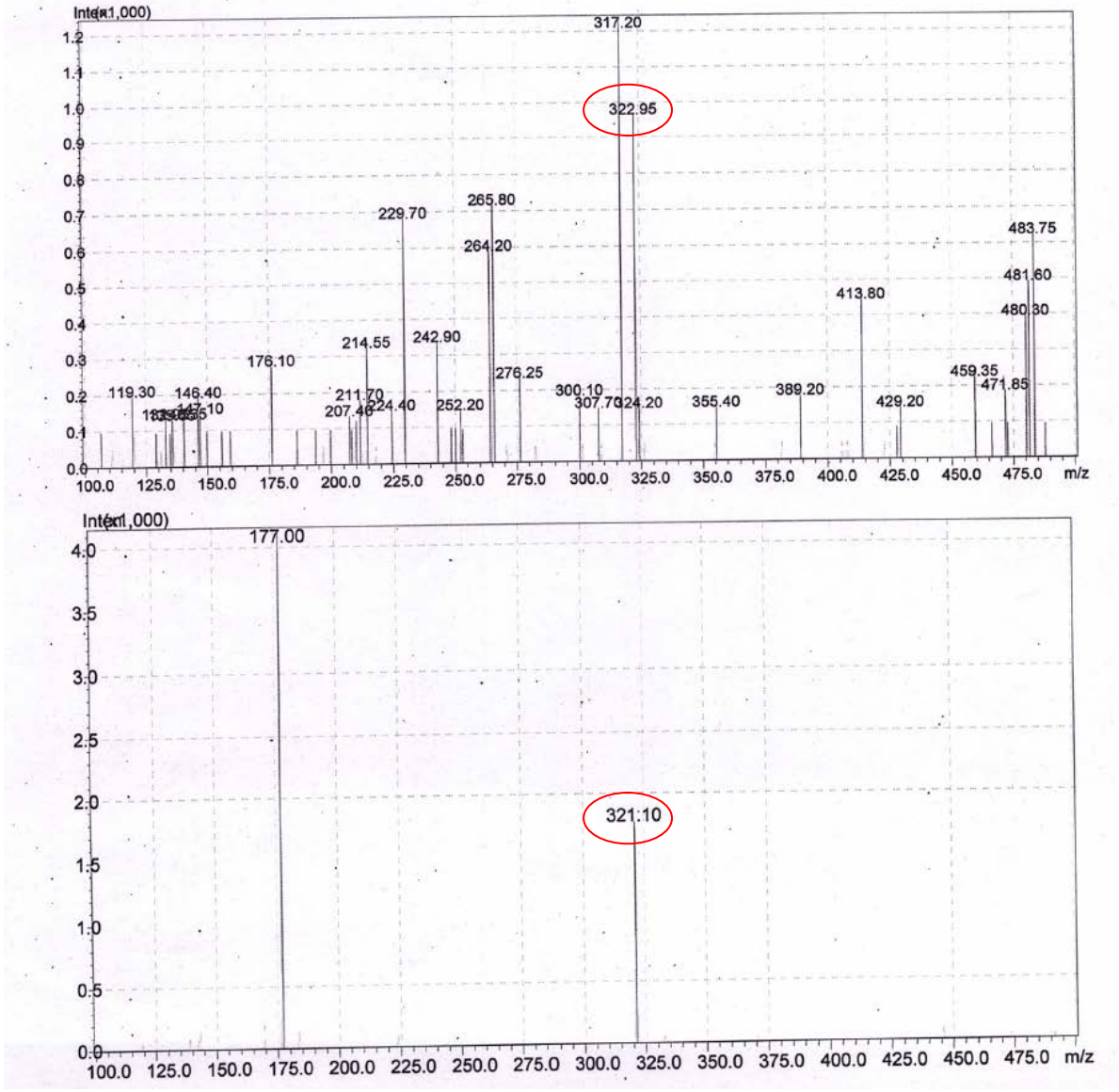
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

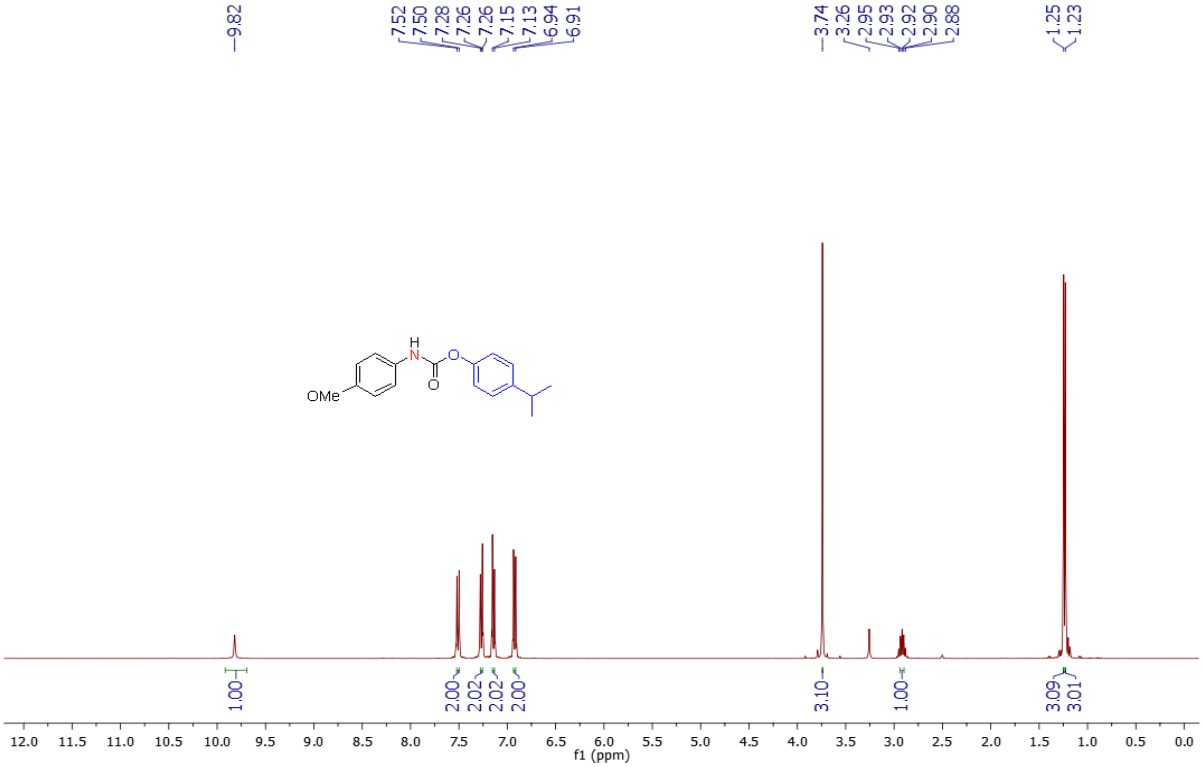


Sample Name	: 4C		
Sample ID	:		
Data Filename	: 28-JAN-22-57.lcd		
Method Filename	: MASS SCANNN 13APRIL2021.lcm		
Batch Filename	: 28.01.2022.lcb		
Vial #	: 1-85	Sample Type	: Unknown
Injection Volume	: 0.5 uL		
Date Acquired	: 1/28/2022 6:00:46 PM	Acquired by	: System Administrator
Date Processed	: 1/28/2022 6:01:47 PM	Processed by	: System Administrator

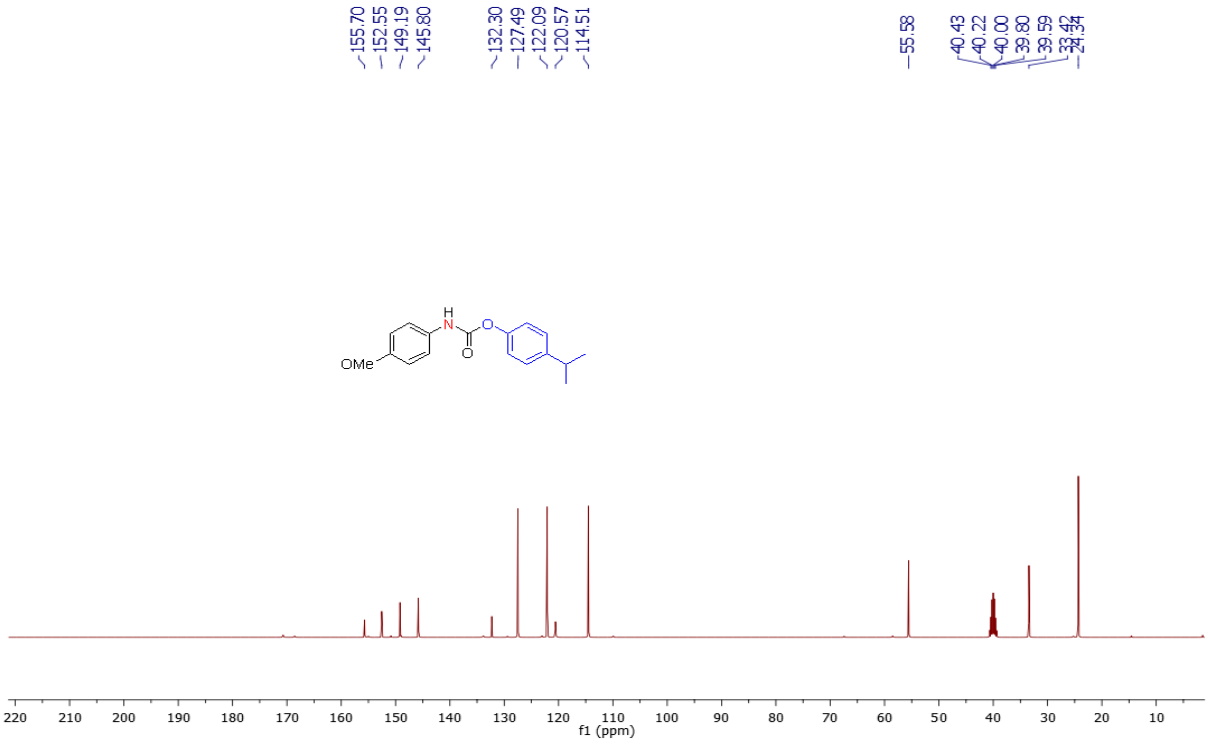
<Chromatogram>



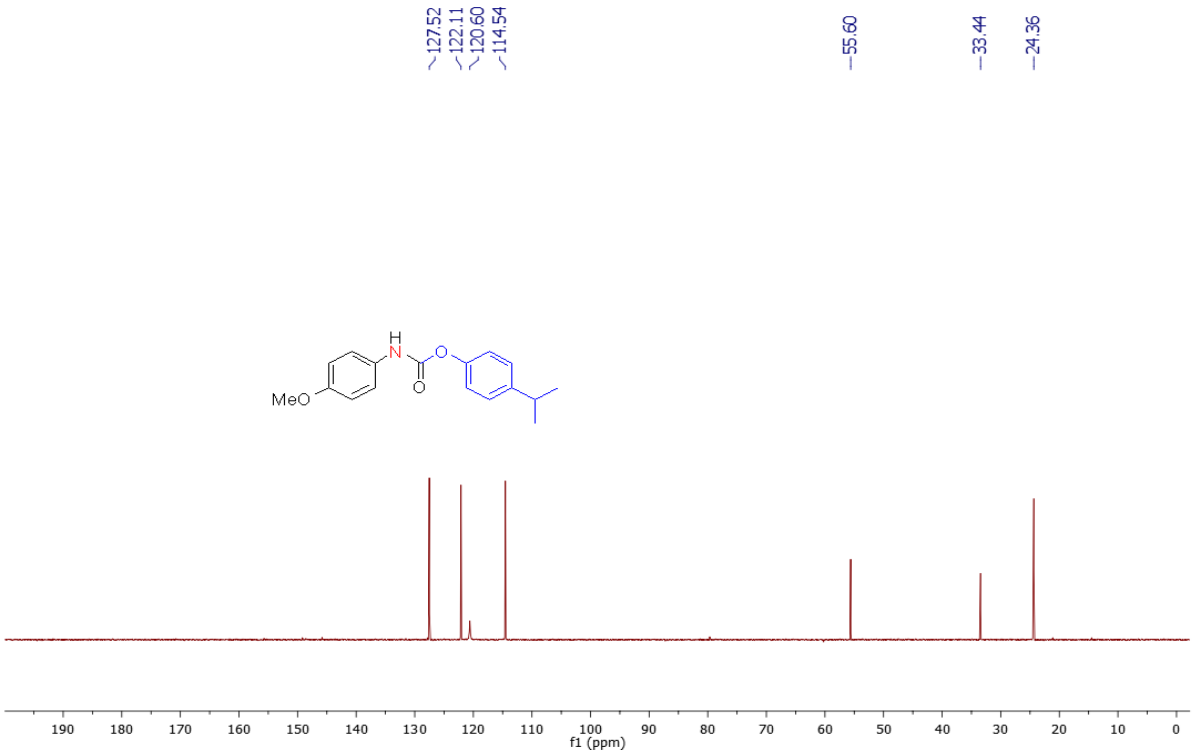
^{1}H-NMR of 4-isopropylphenyl (4-methoxyphenyl)carbamate (4d)



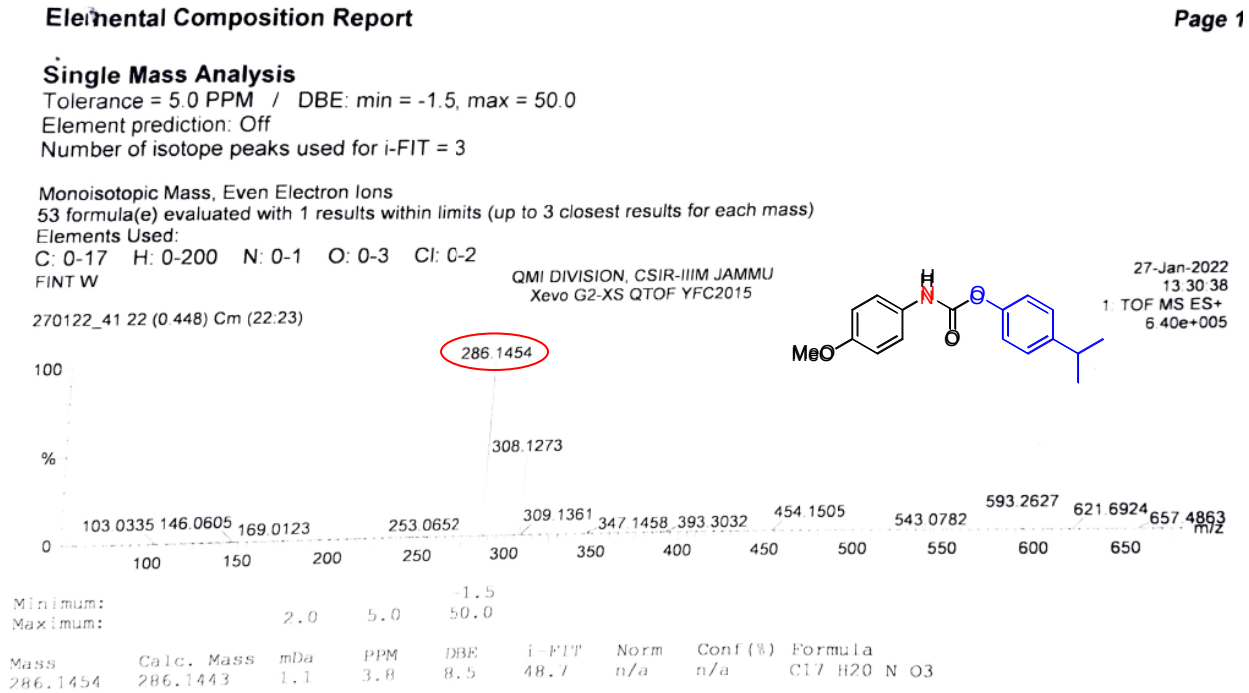
^{13}C-NMR of 4-isopropylphenyl (4-methoxyphenyl)carbamate (4d)



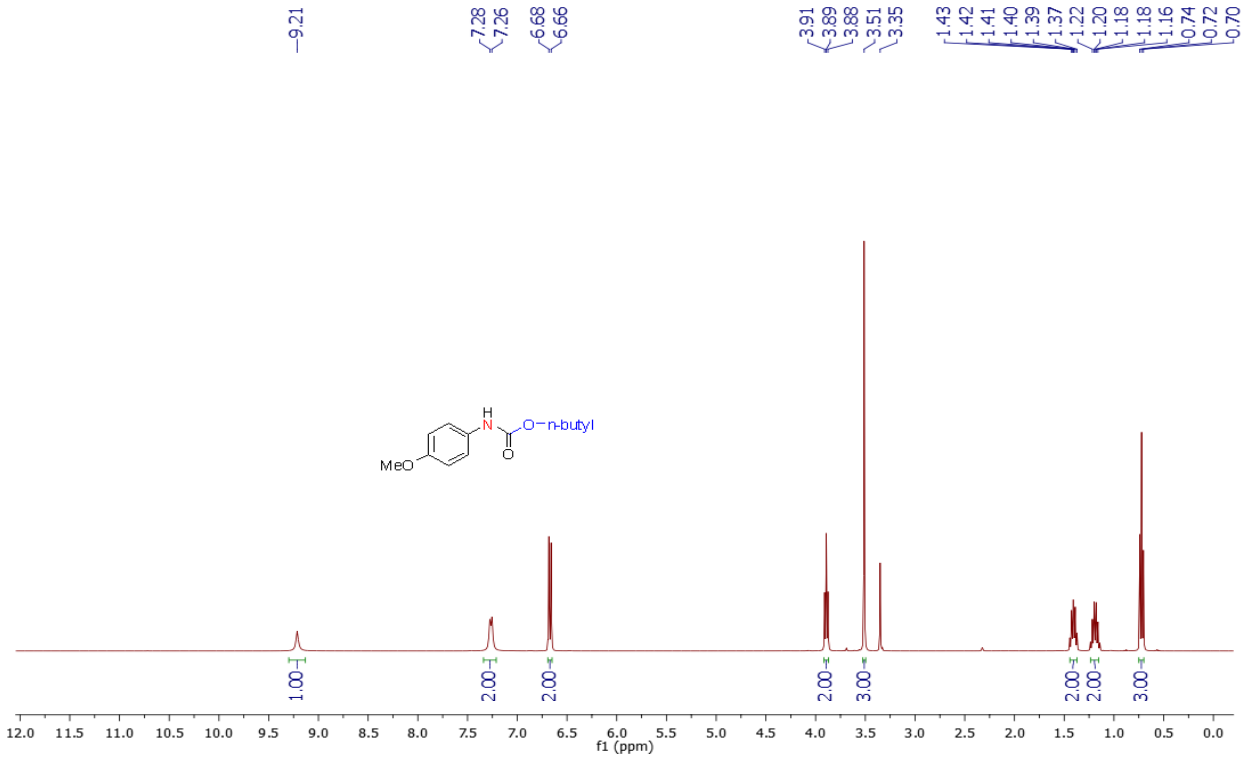
DEPT of 4-isopropylphenyl (4-methoxyphenyl)carbamate (4d)



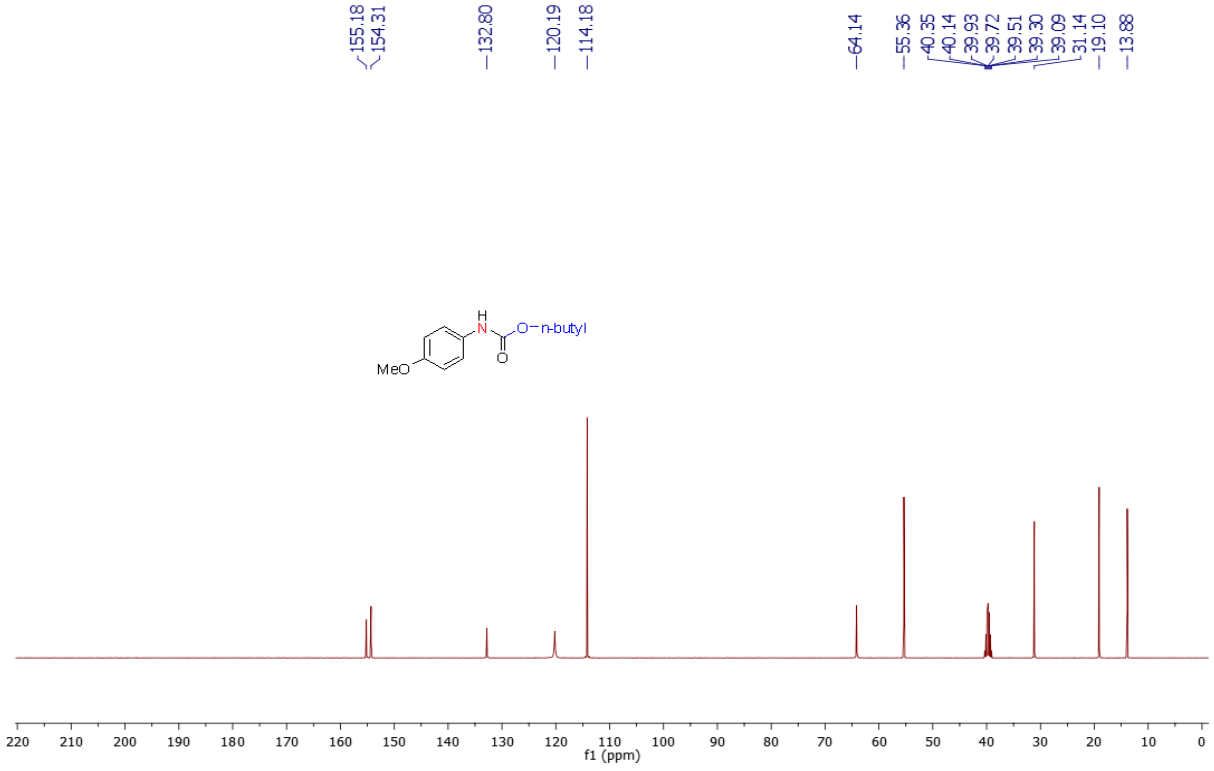
HRMS of 4-isopropylphenyl (4-methoxyphenyl)carbamate (4d)



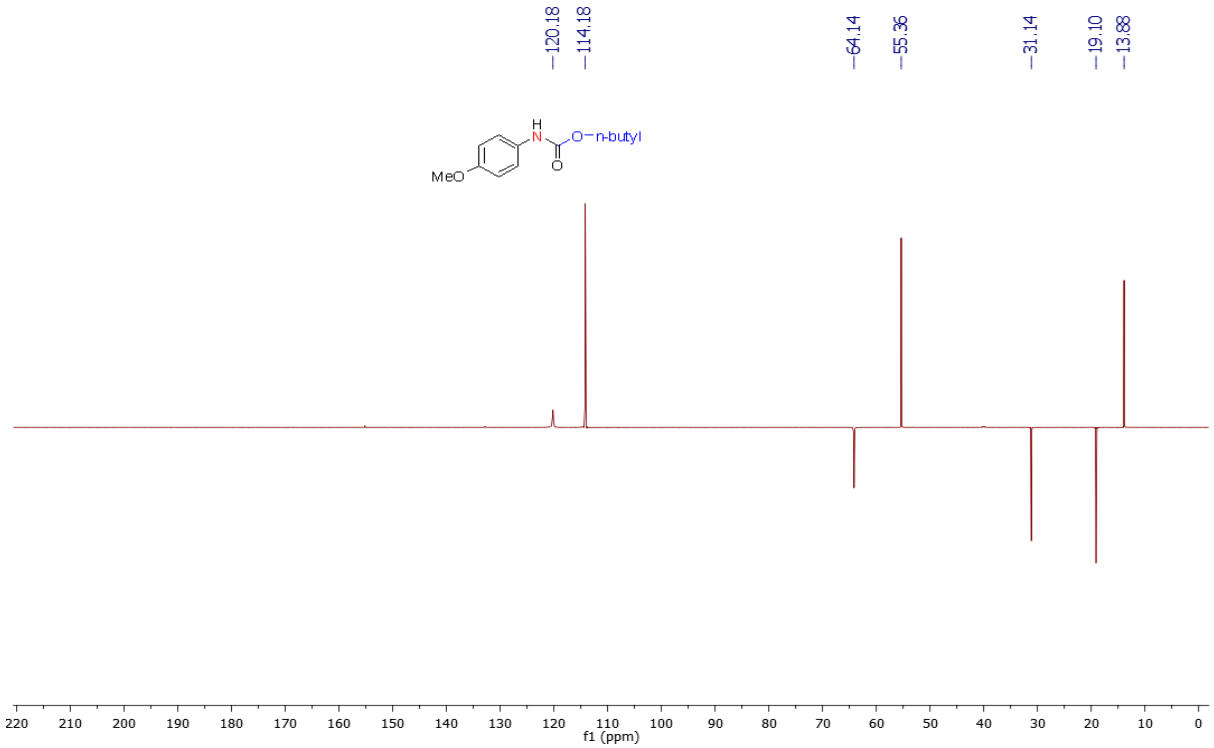
^{1}H-NMR of butyl (4-methoxyphenyl)carbamate (4e)



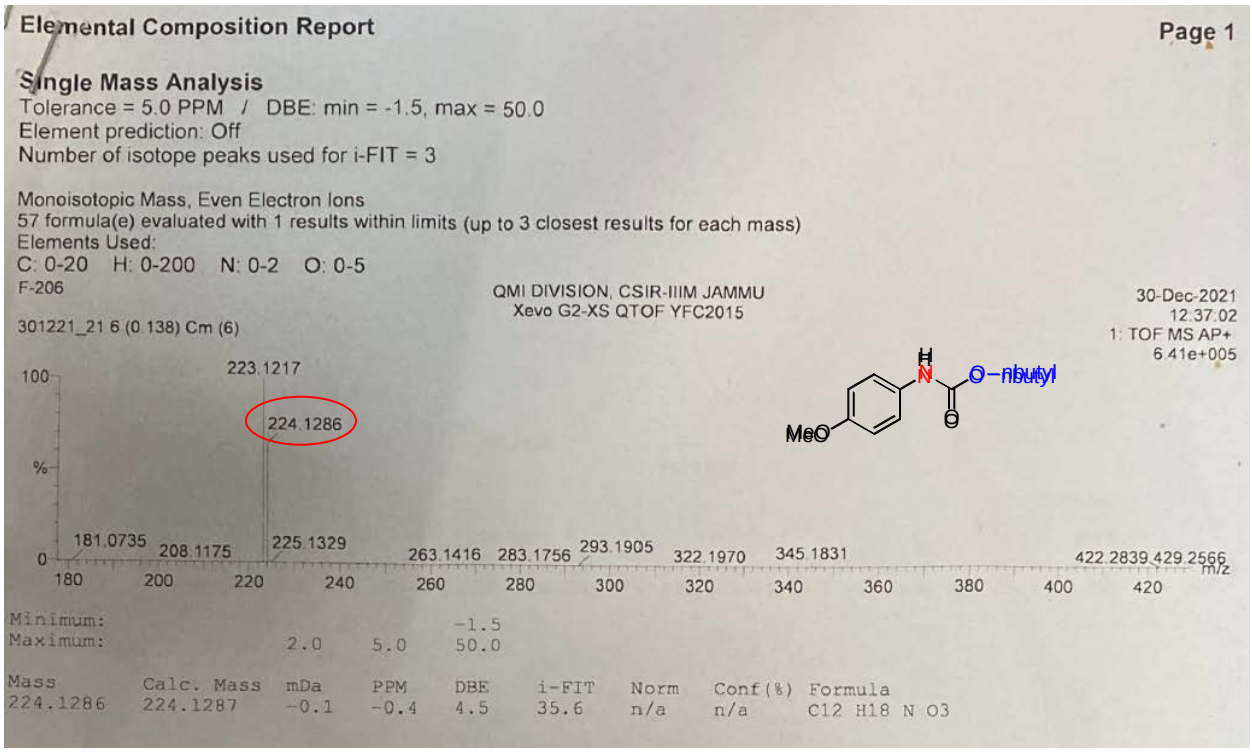
^{13}C-NMR of butyl (4-methoxyphenyl)carbamate (4e)



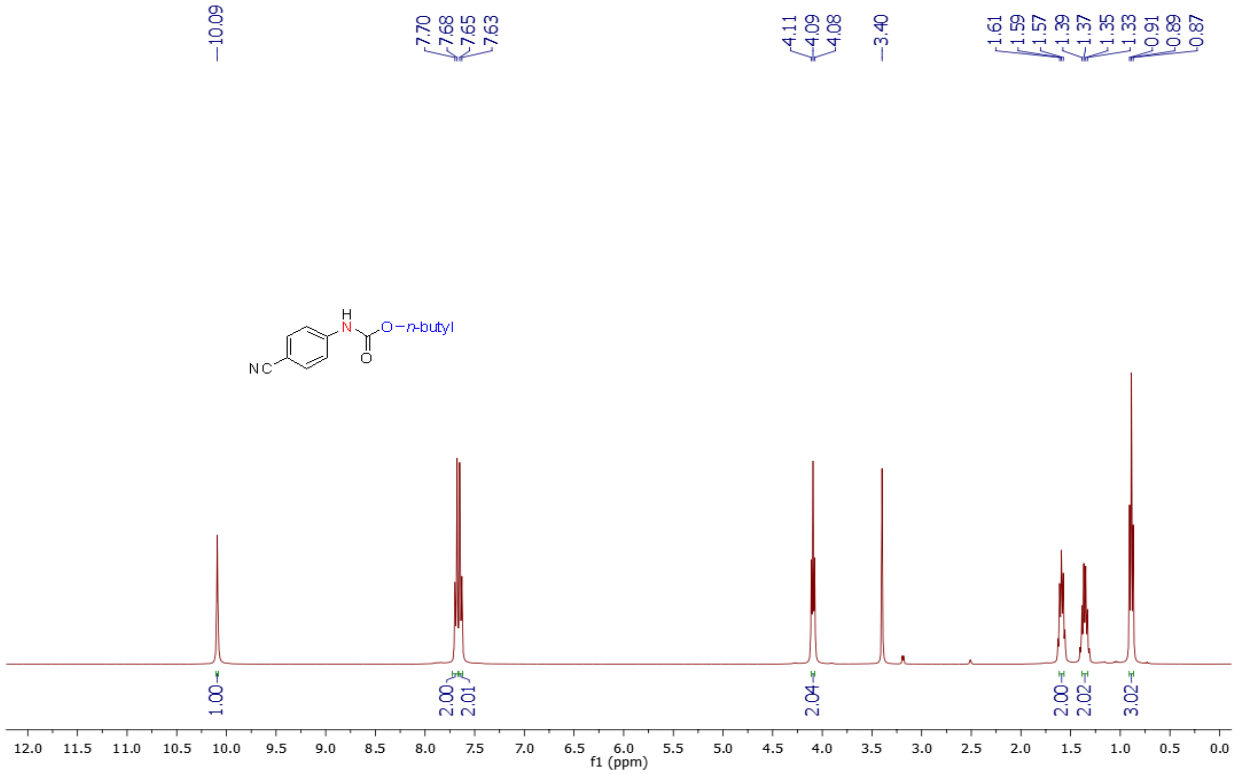
DEPT of butyl (4-methoxyphenyl)carbamate (4e)



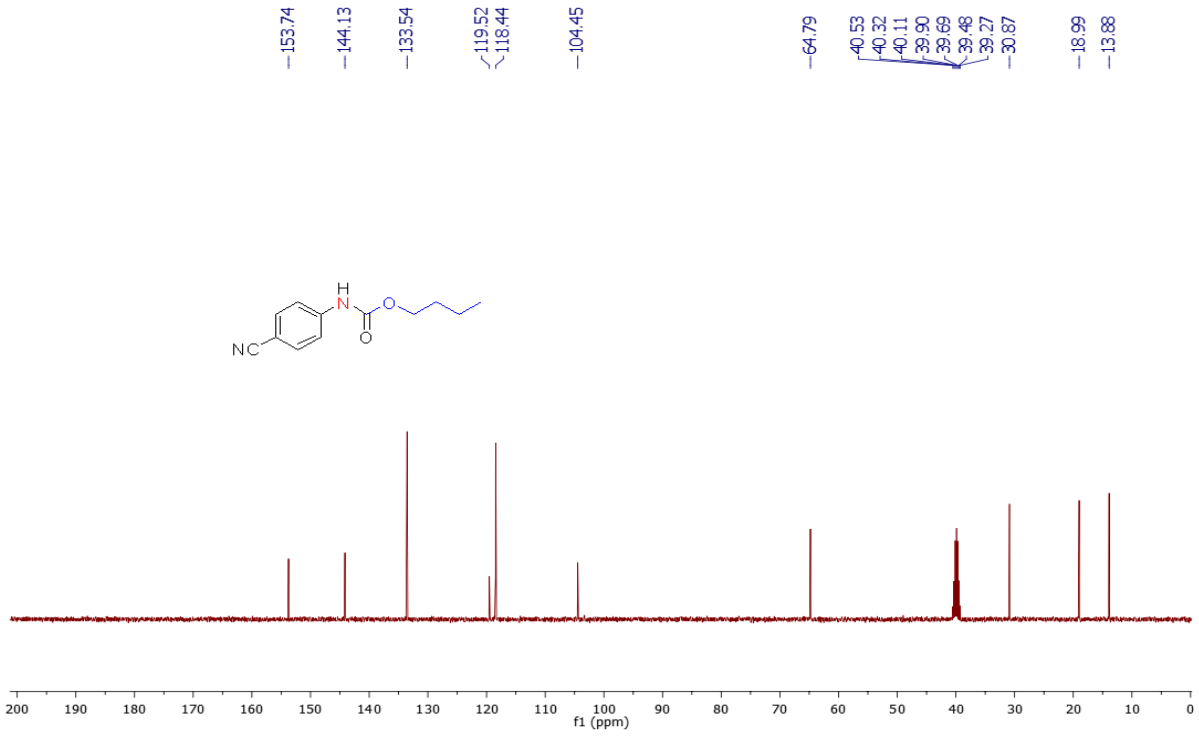
HRMS of butyl (4-methoxyphenyl)carbamate (4e)



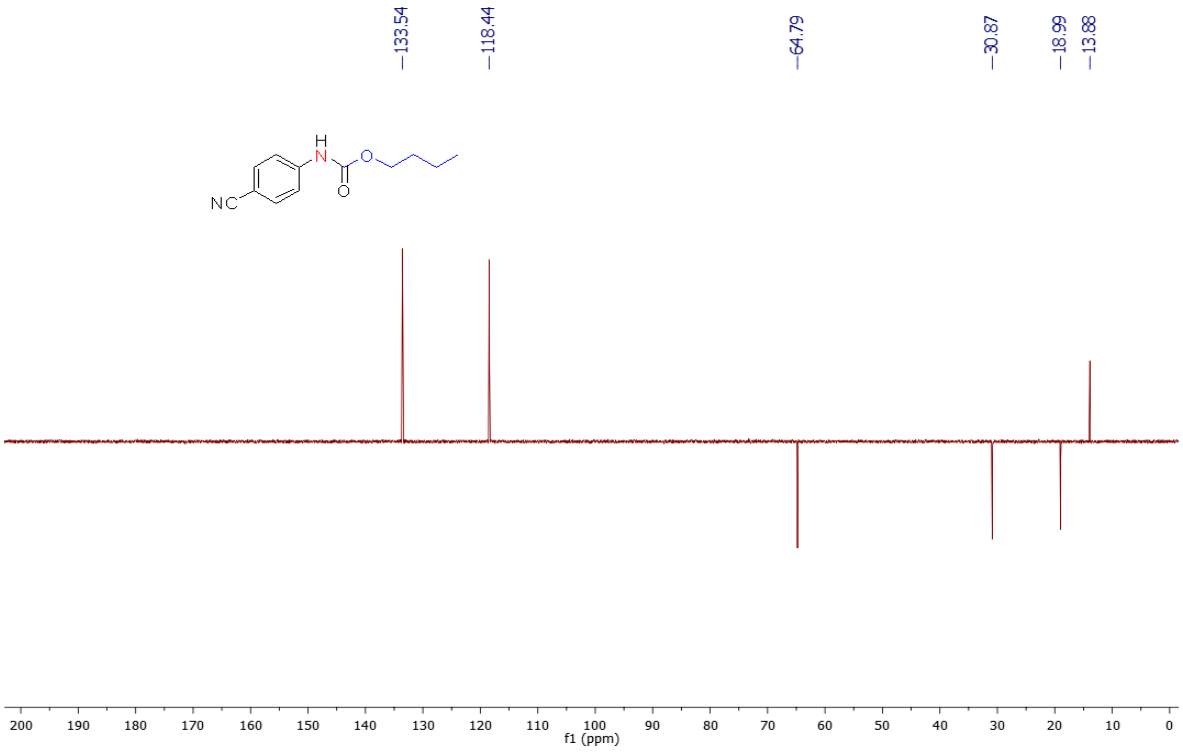
[1]H-NMR of butyl (4-cyanophenyl)carbamate (4f)



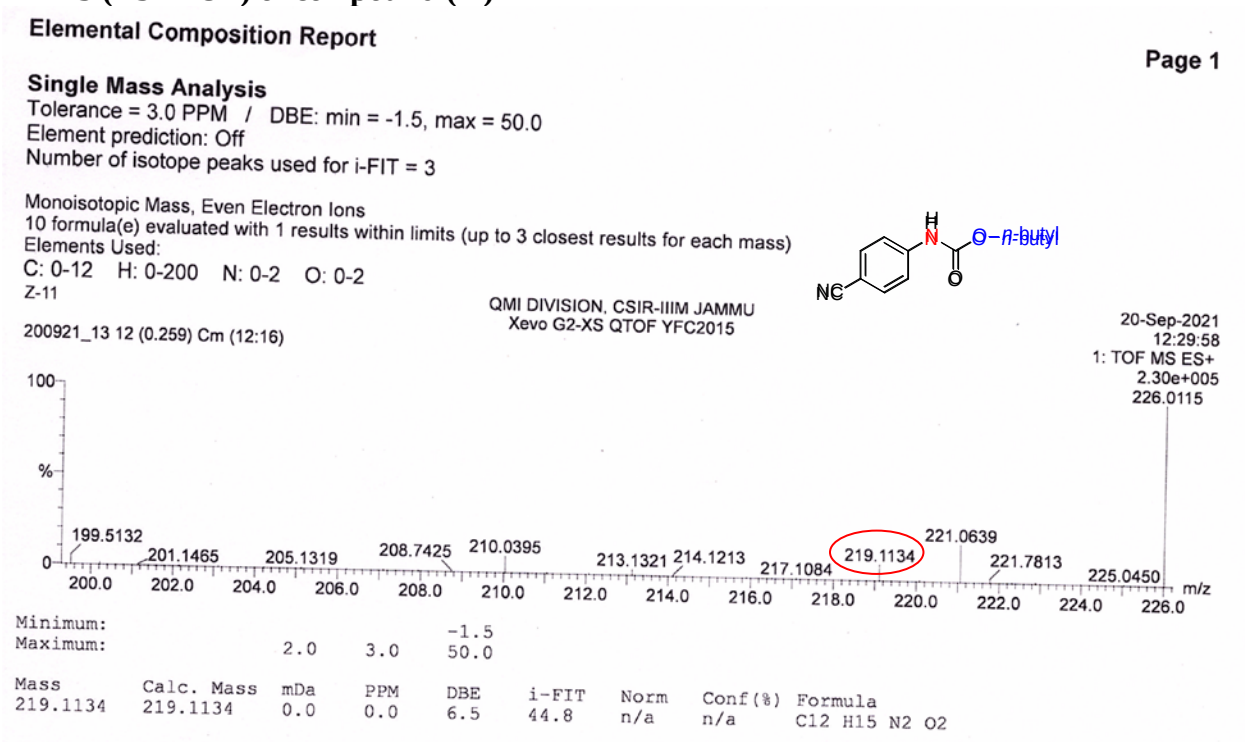
[13]C-NMR of butyl (4-cyanophenyl)carbamate (4f)



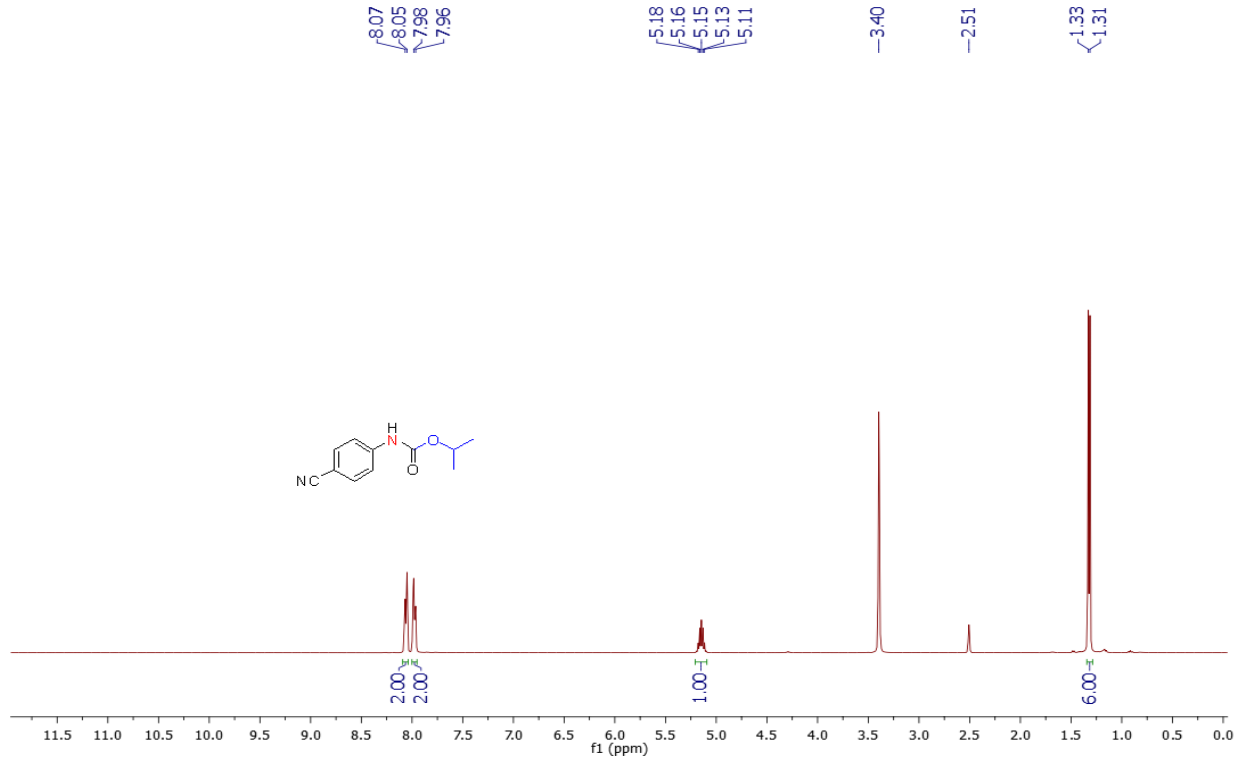
DEPT of butyl (4-cyanophenyl)carbamate (4f)



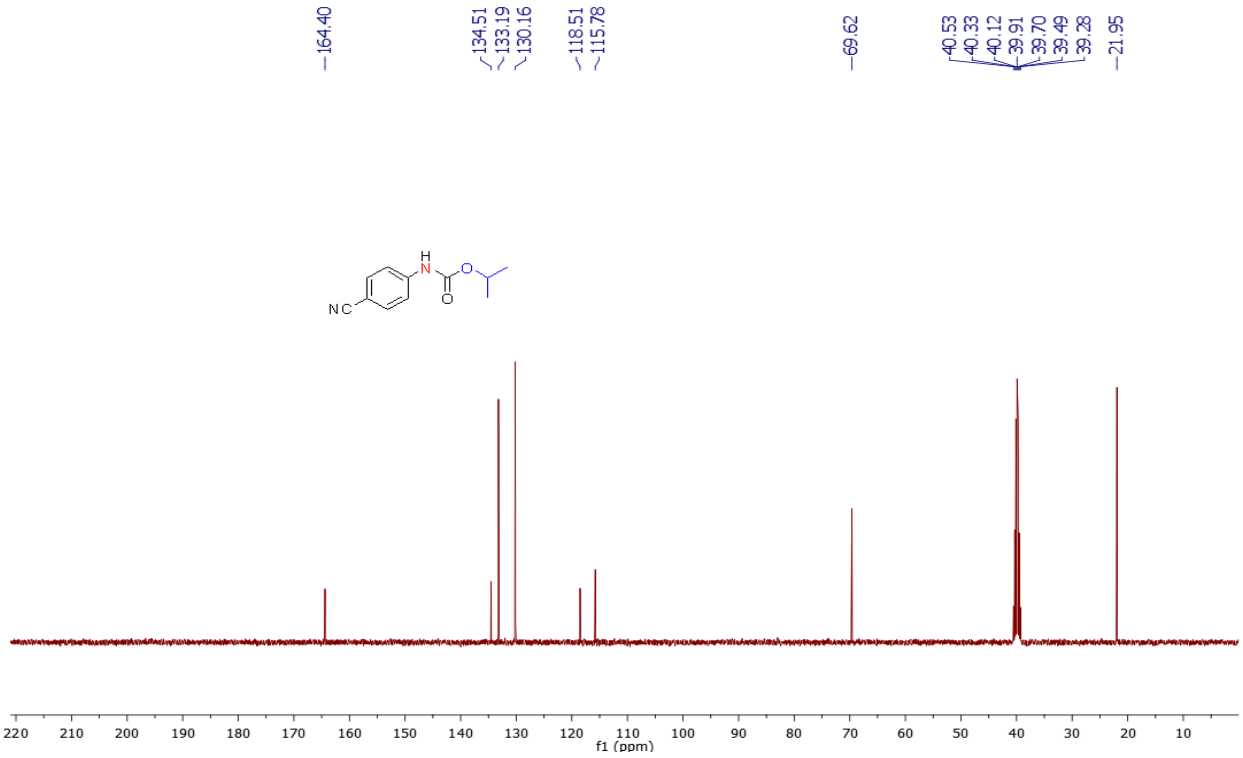
HRMS (ESI-TOF) of compound (4f)



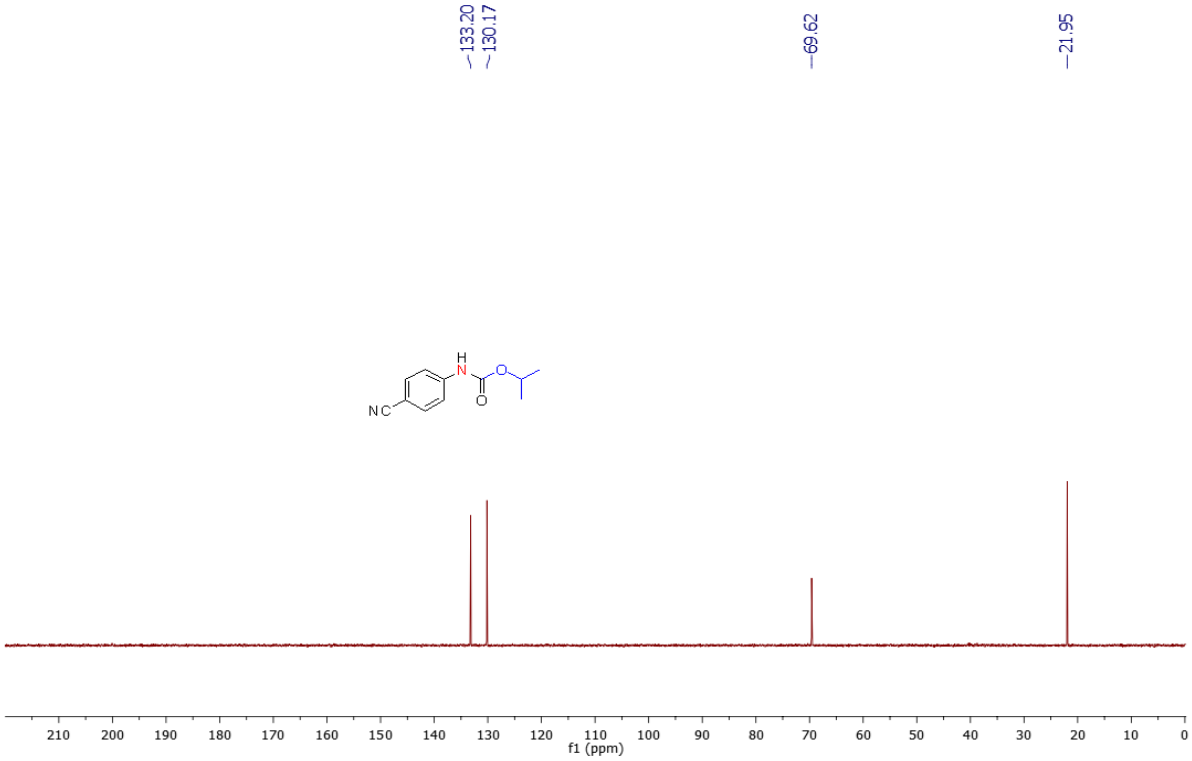
[1]H-NMR of isopropyl (4-cyanophenyl)carbamate (4g)



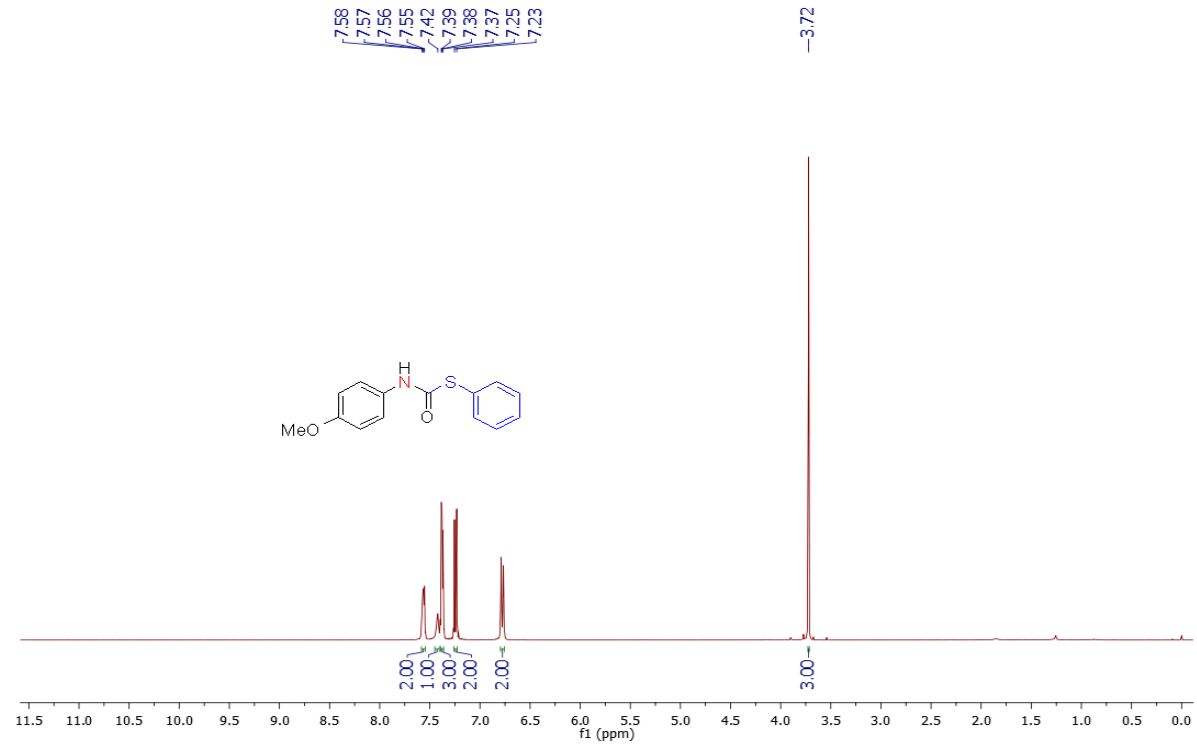
[13]C-NMR of isopropyl (4-cyanophenyl)carbamate (4g)



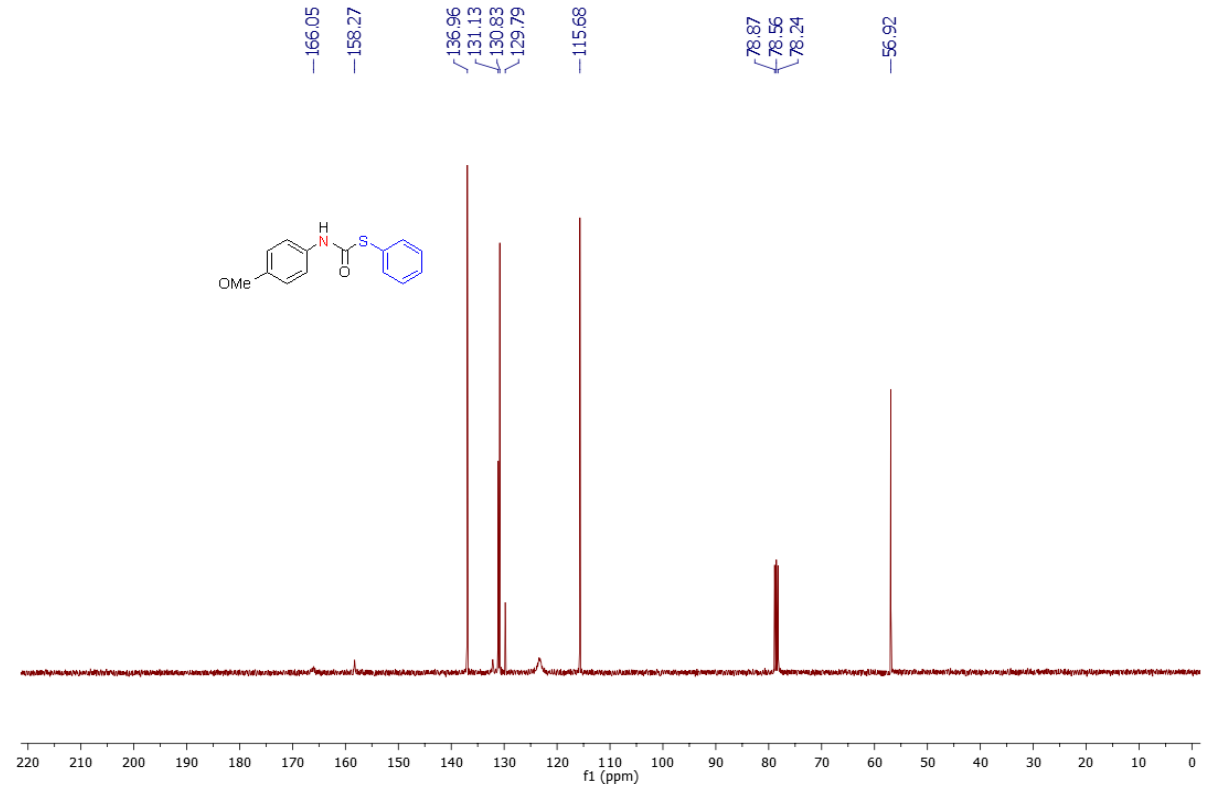
DEPT of isopropyl (4-cyanophenyl)carbamate (4g)



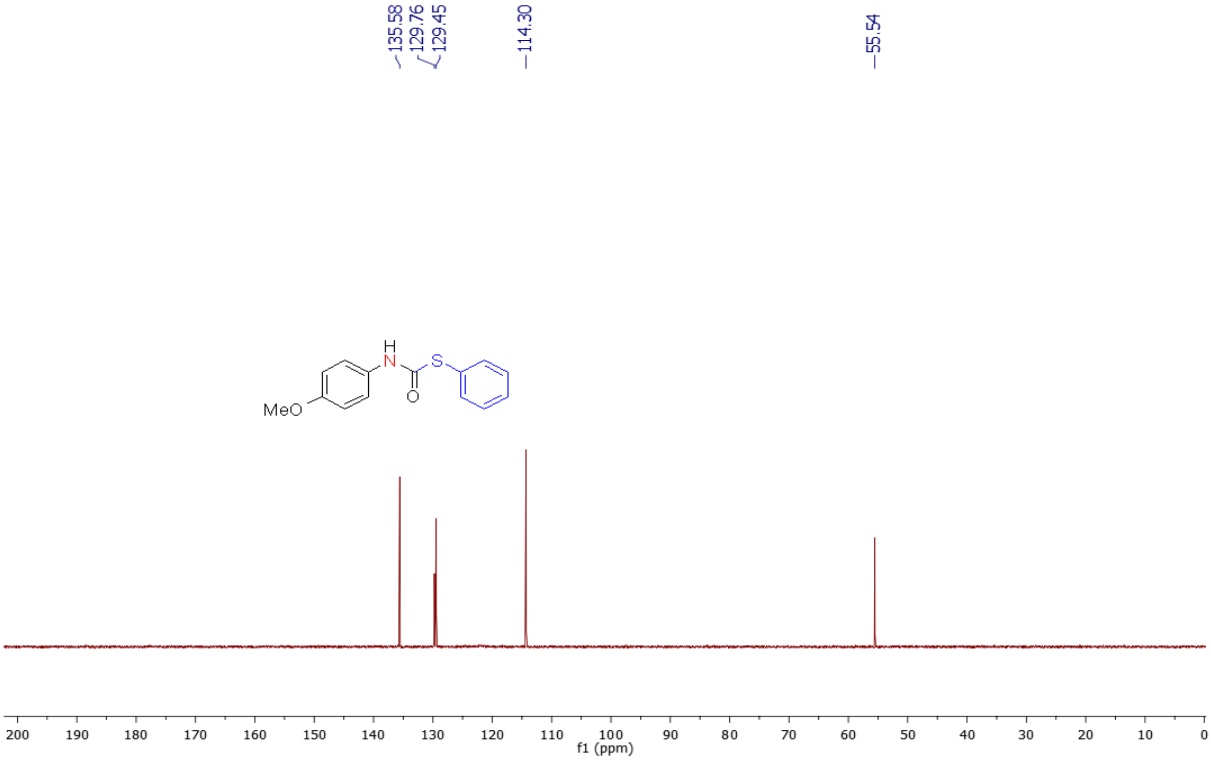
^{1}H-NMR of *S*-phenyl (4-methoxyphenyl)carbamothioate (4h)



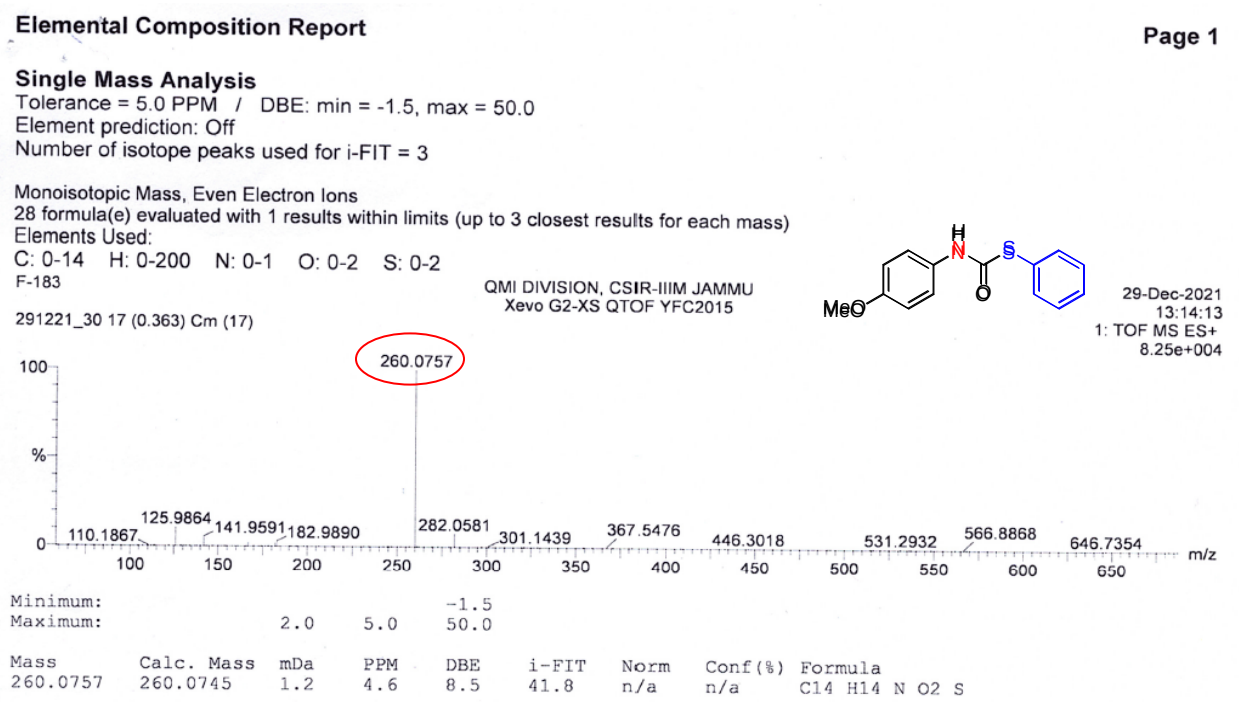
^{13}C-NMR of *S*-phenyl (4-methoxyphenyl)carbamothioate (4h)



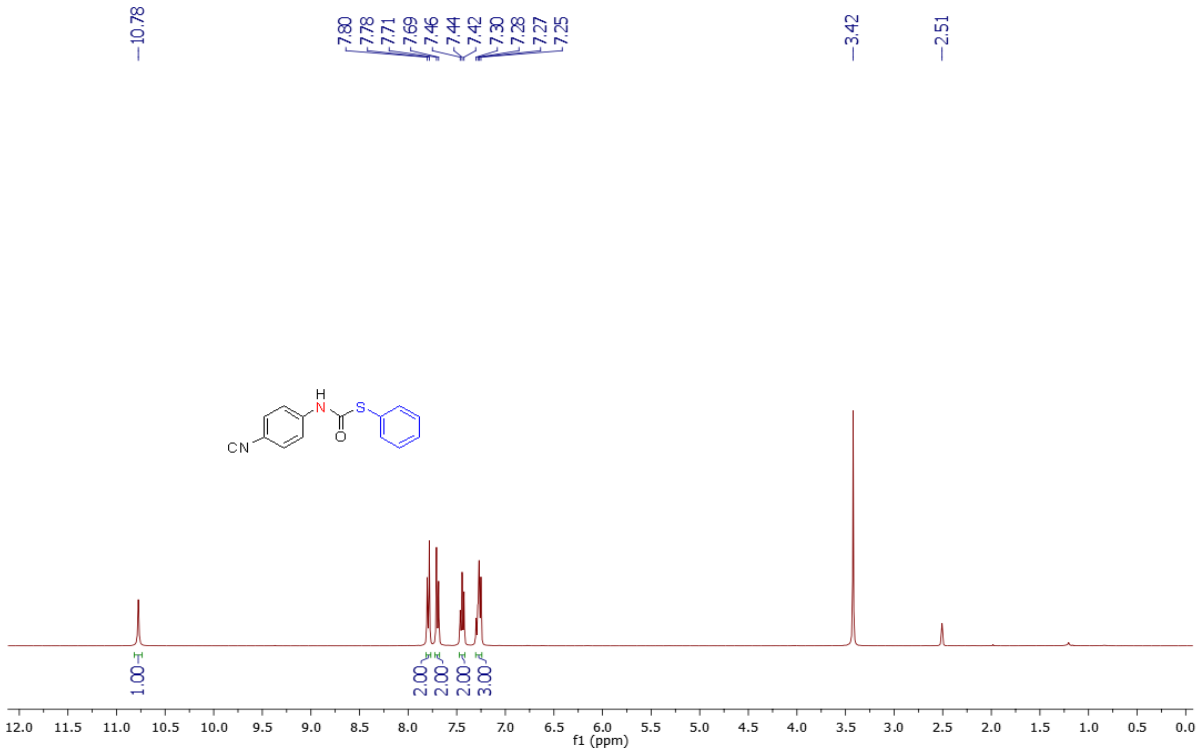
DEPT of *S*-phenyl (4-methoxyphenyl)carbamothioate (4h)



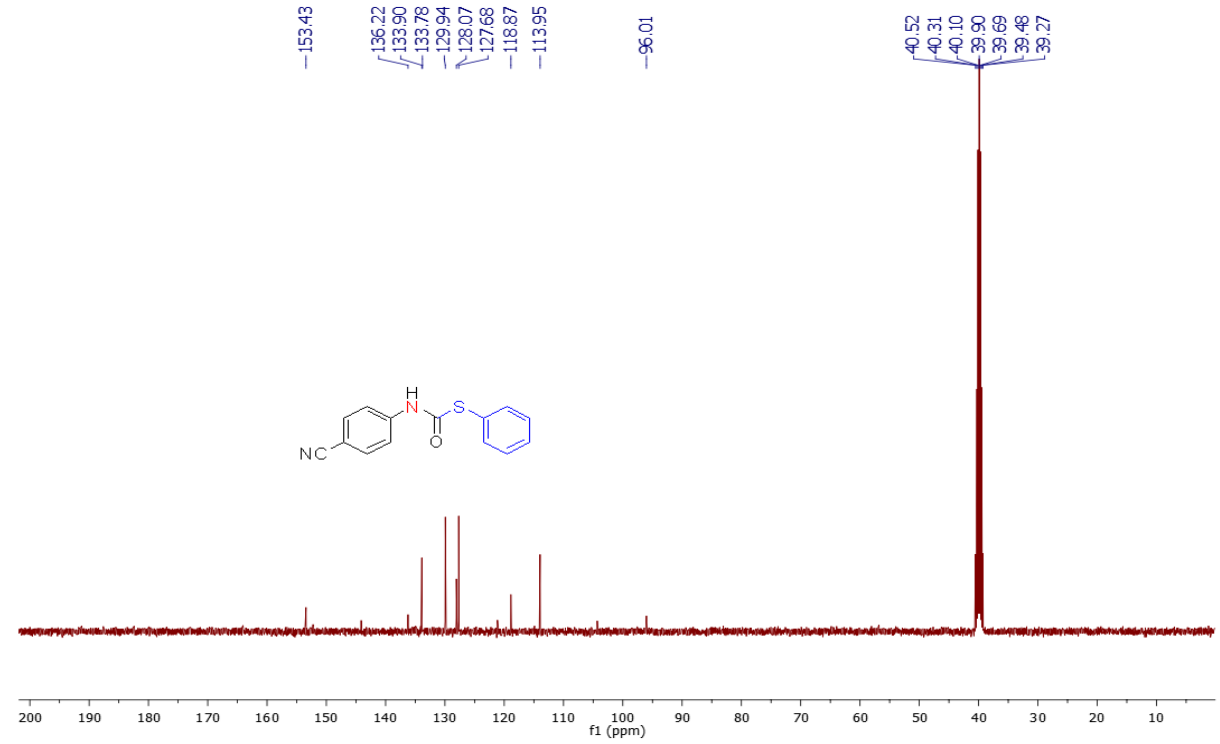
HRMS of *S*-phenyl (4-methoxyphenyl)carbamothioate (4h)



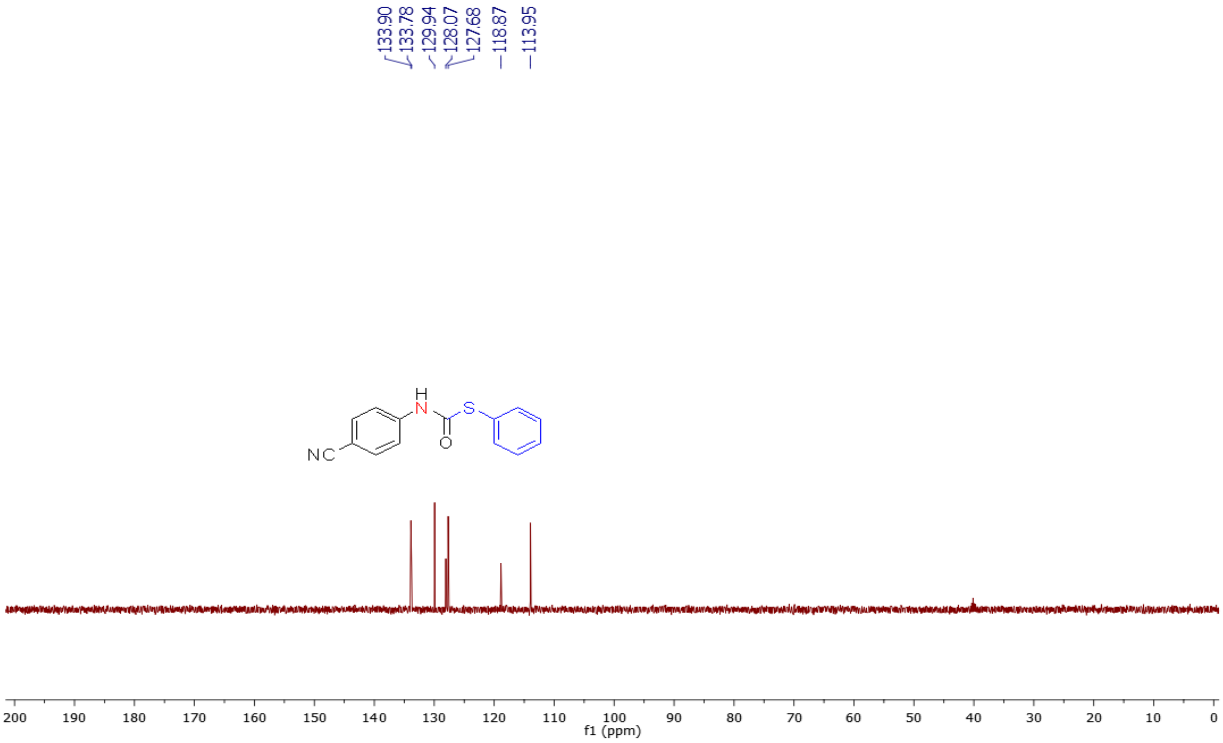
^{1}H-NMR of *S*-phenyl (4-cyanophenyl)carbamothioate (4i)



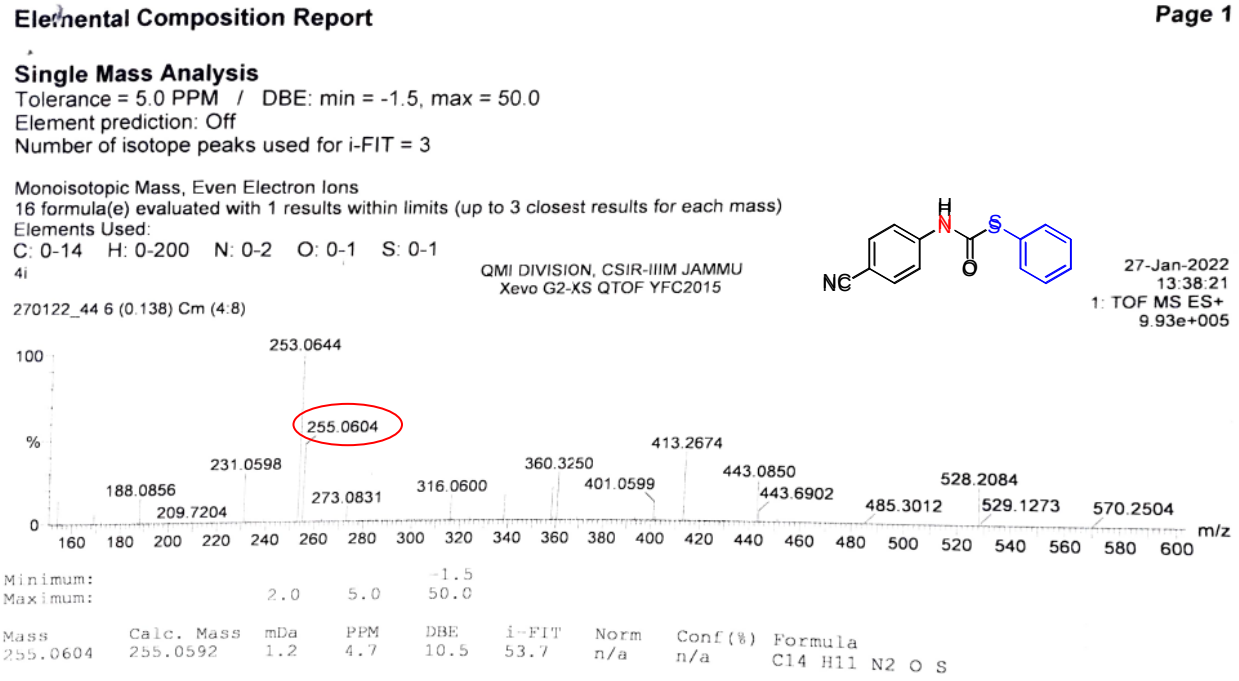
^{13}C-NMR of *S*-phenyl (4-cyanophenyl)carbamothioate (4i)



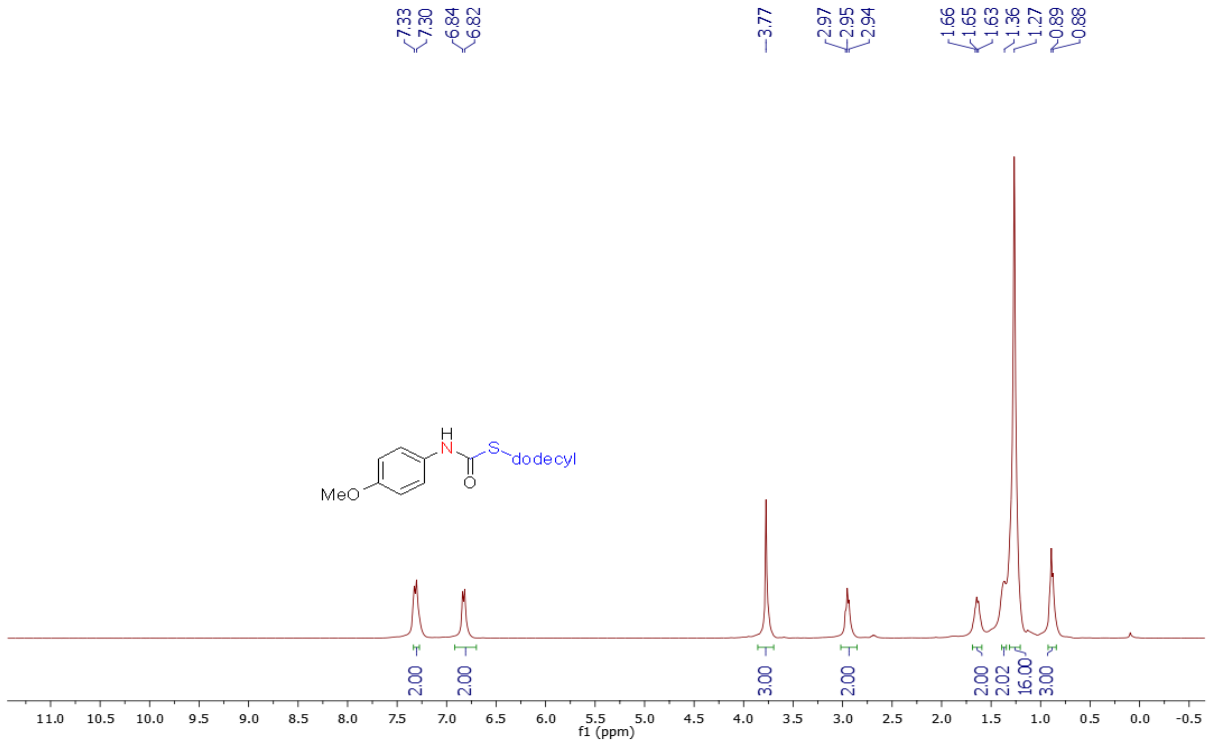
DEPT of *S*-phenyl (4-cyanophenyl)carbamothioate (4i)



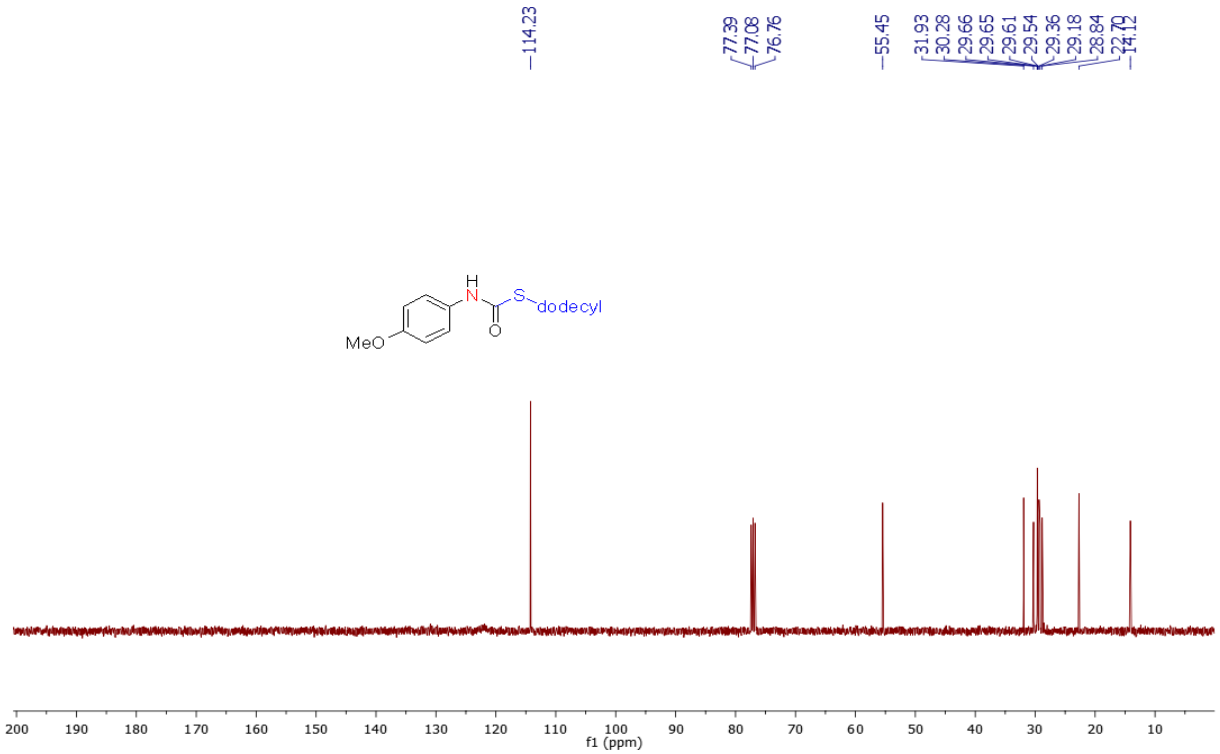
HRMS of *S*-phenyl (4-cyanophenyl)carbamothioate (4i)



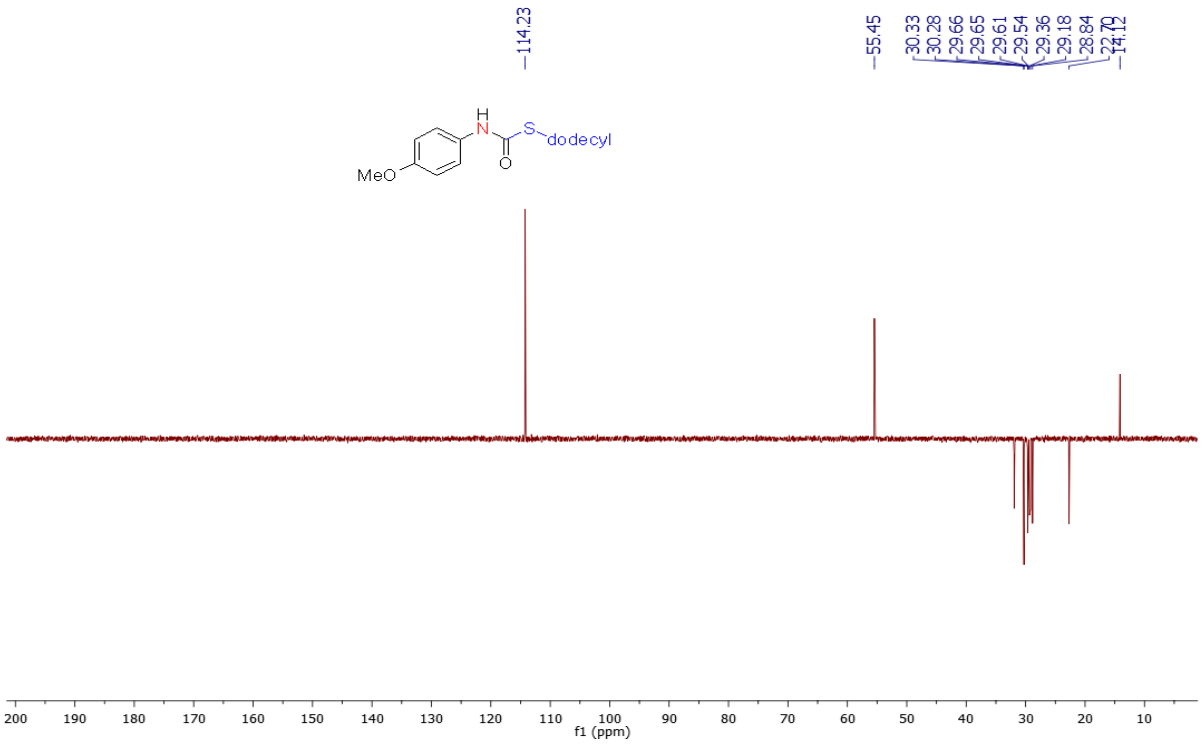
^{1}H-NMR of S-dodecyl (4-methoxyphenyl)carbamothioate (4j)



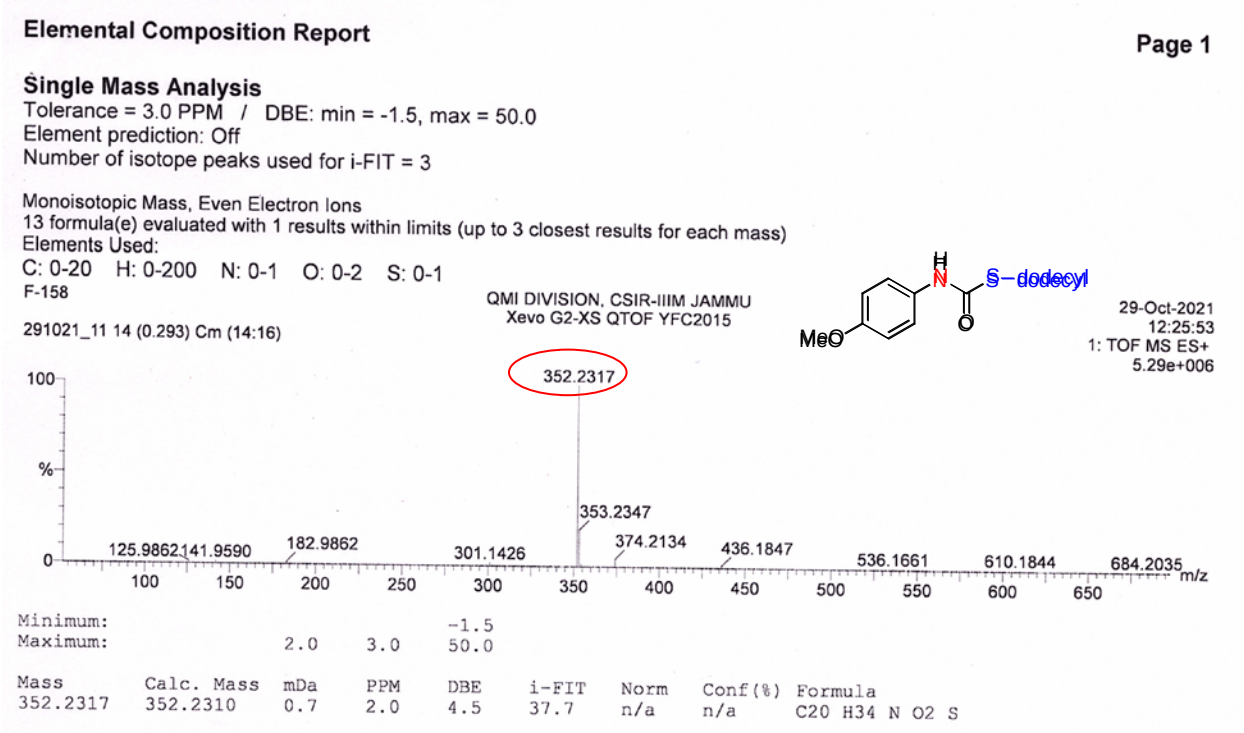
^{13}C-NMR of S-dodecyl (4-methoxyphenyl)carbamothioate (4j)



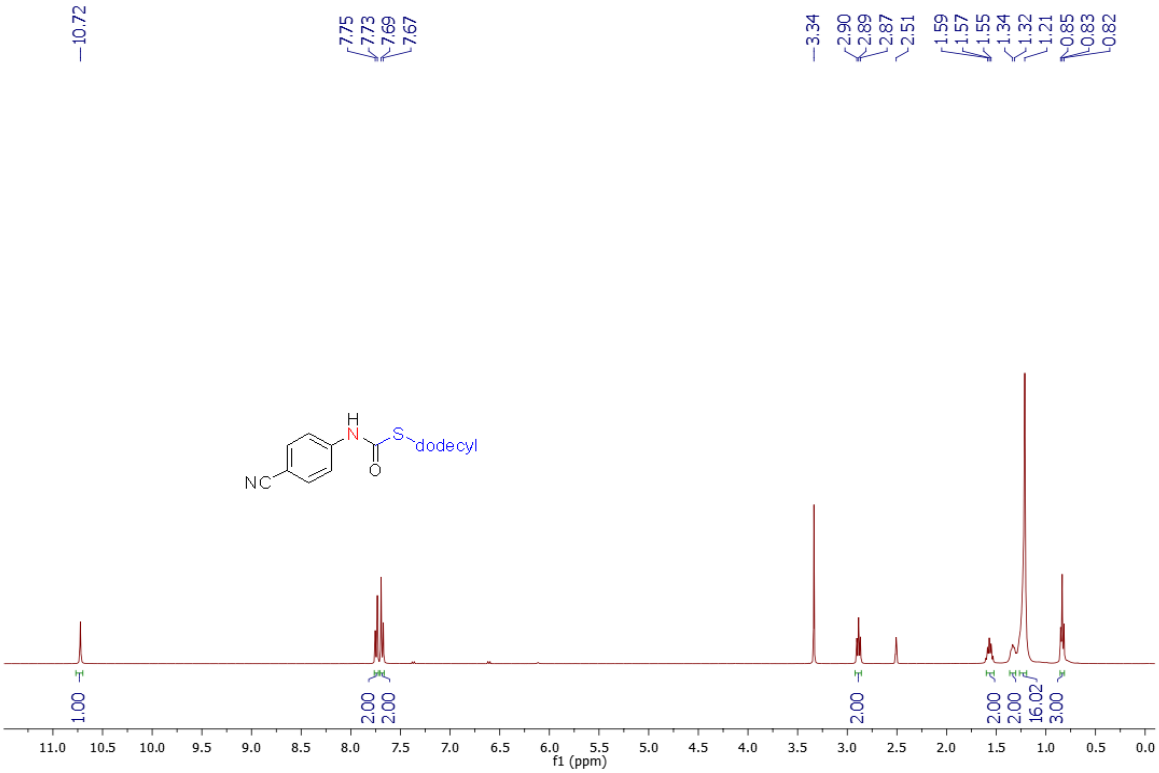
DEPT of S-dodecyl (4-methoxyphenyl)carbamothioate (4j)



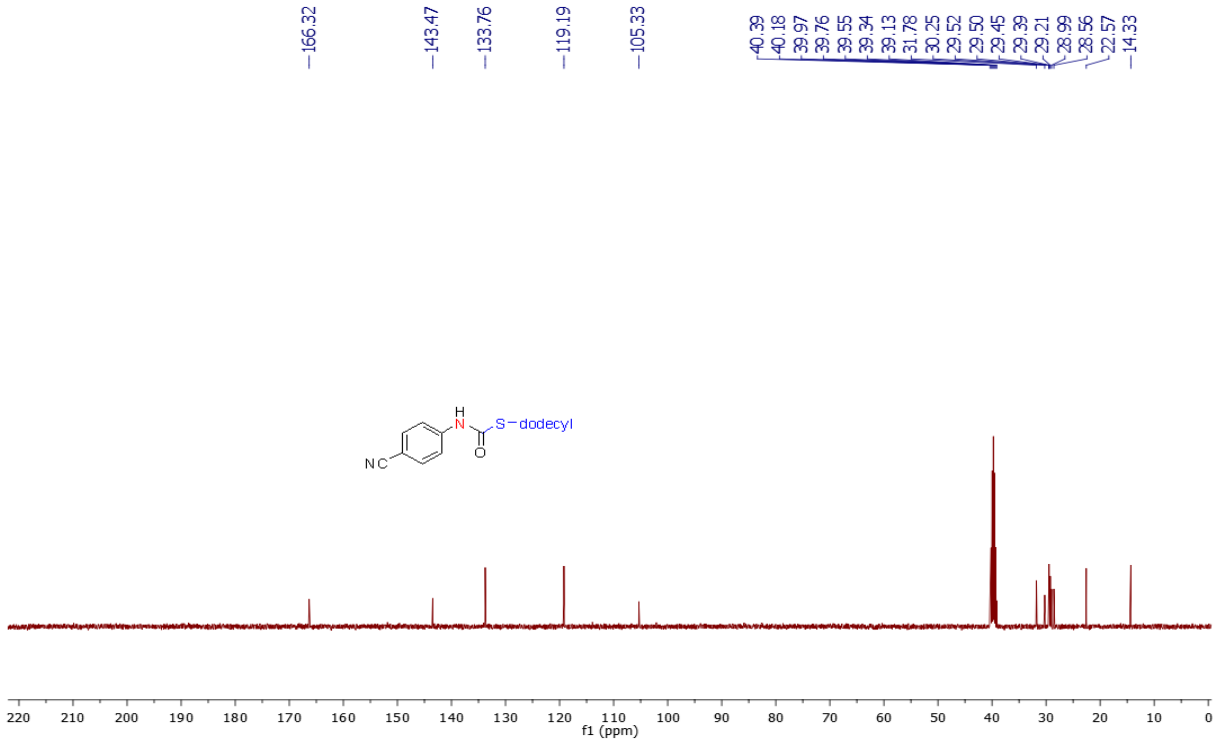
HRMS (ESI-TOF) of compound (4j)



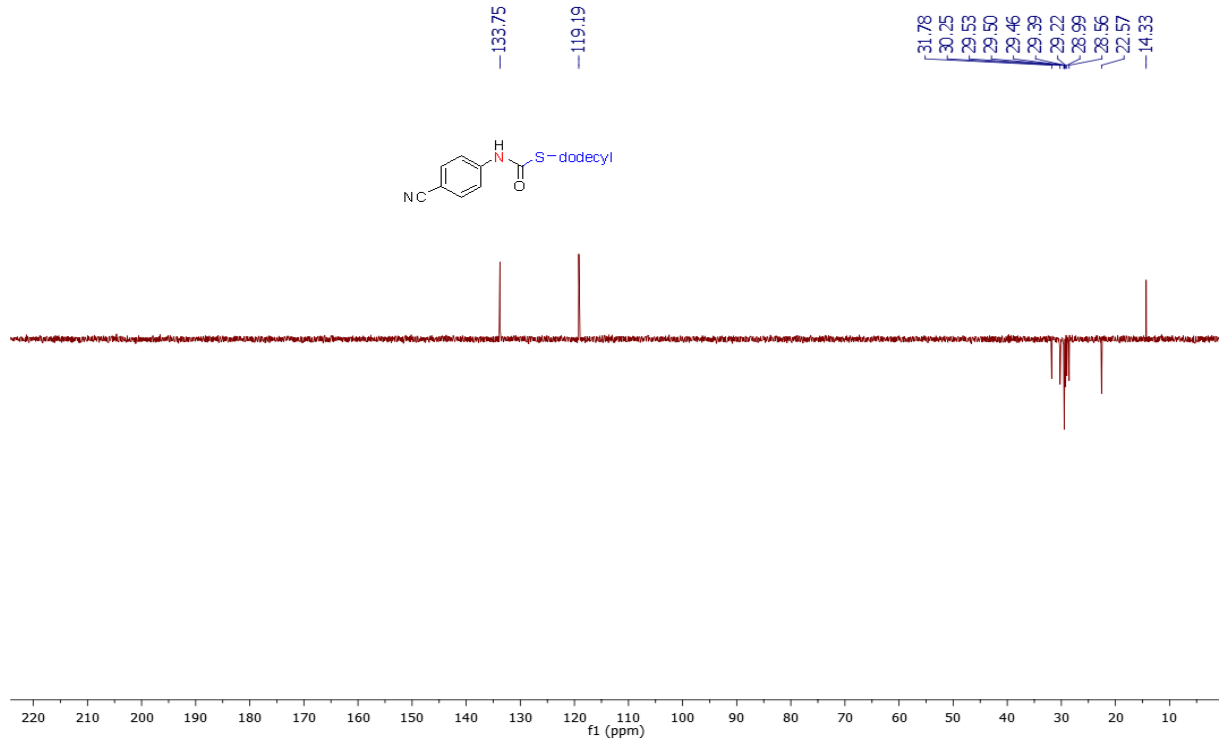
[1]H-NMR of S-dodecyl (4-cyanophenyl)carbamothioate (4k)



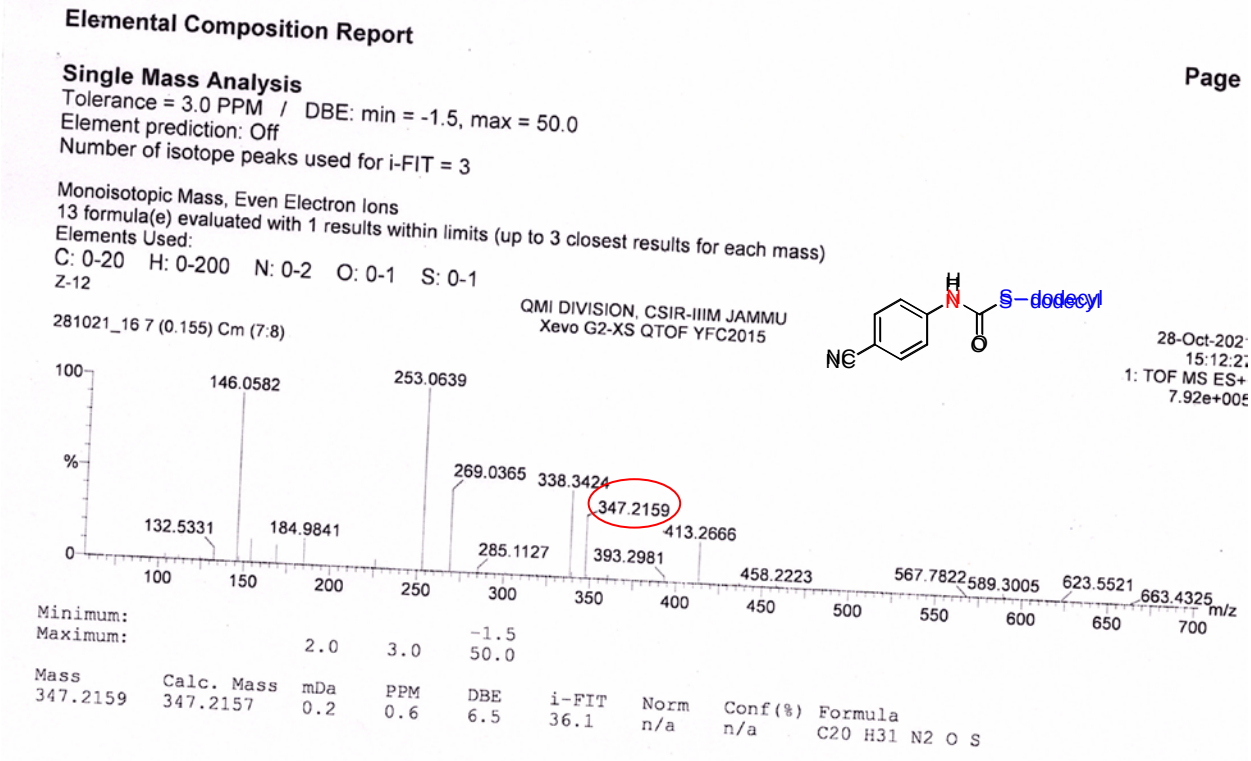
^{13}C-NMR of S-dodecyl (4-cyanophenyl)carbamothioate (4k)



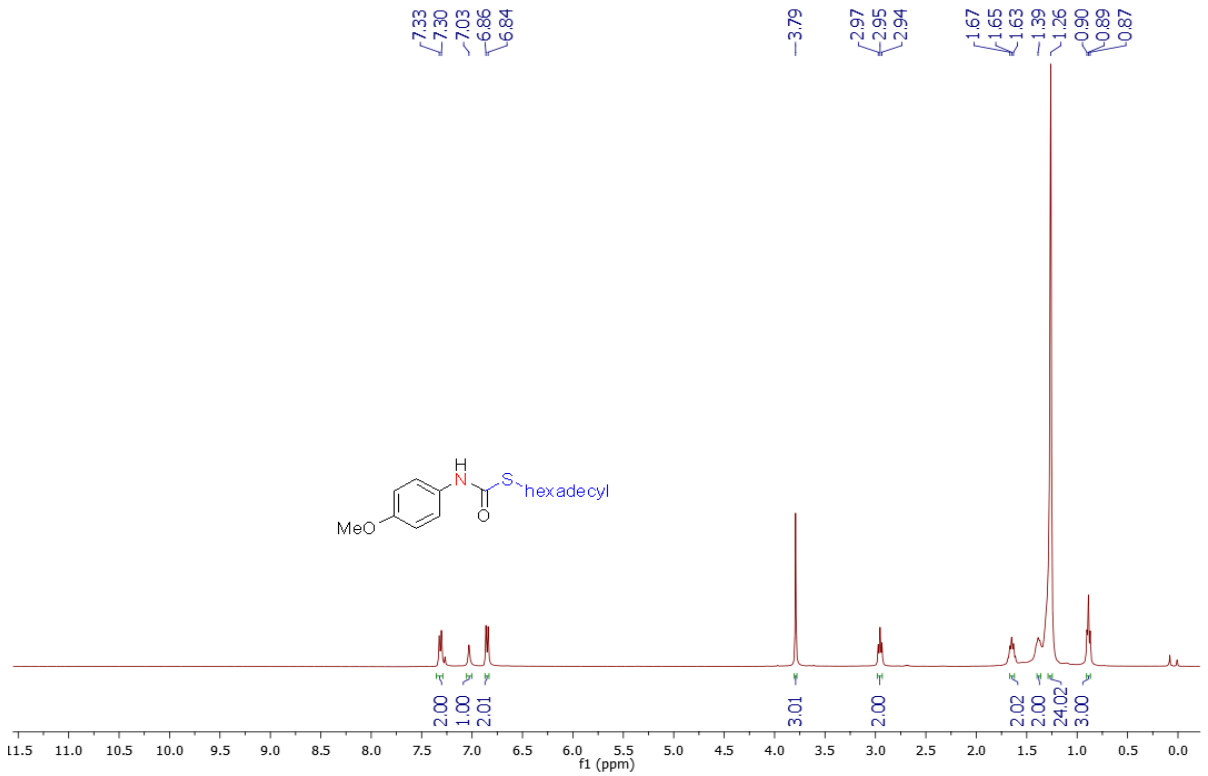
DEPT of S-dodecyl (4-cyanophenyl)carbamothioate (4k)



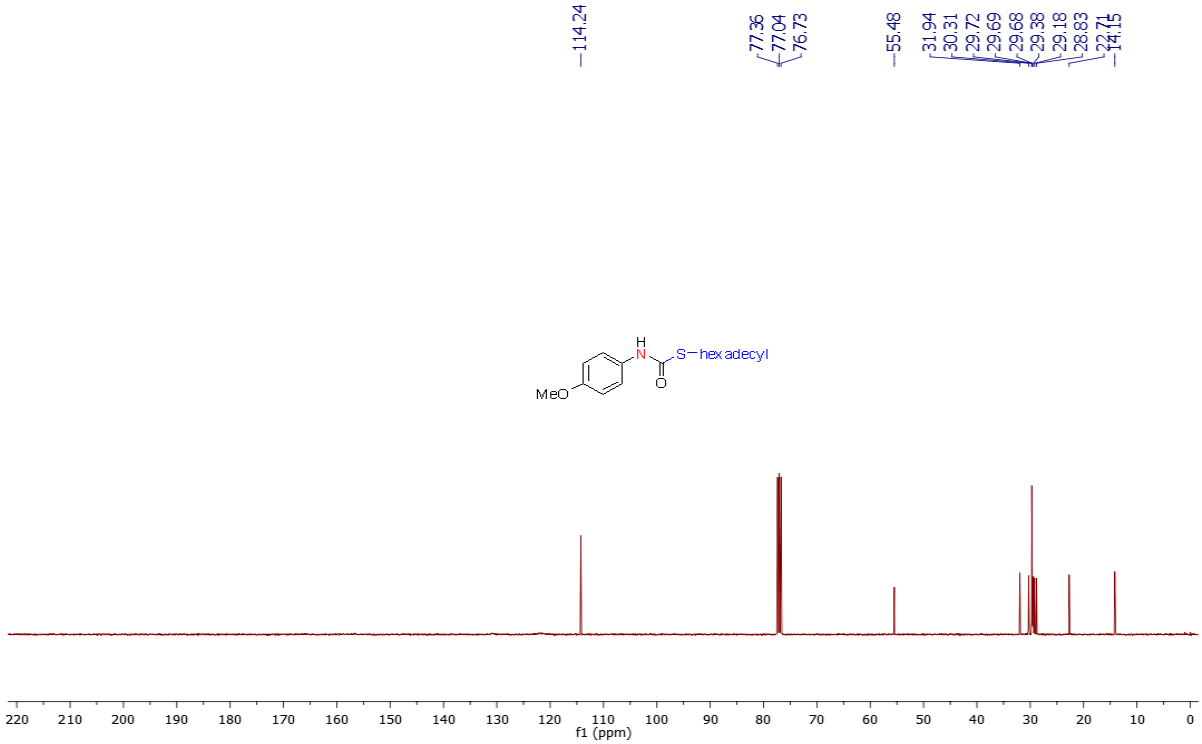
HRMS (ESI-TOF) of compound (4k)



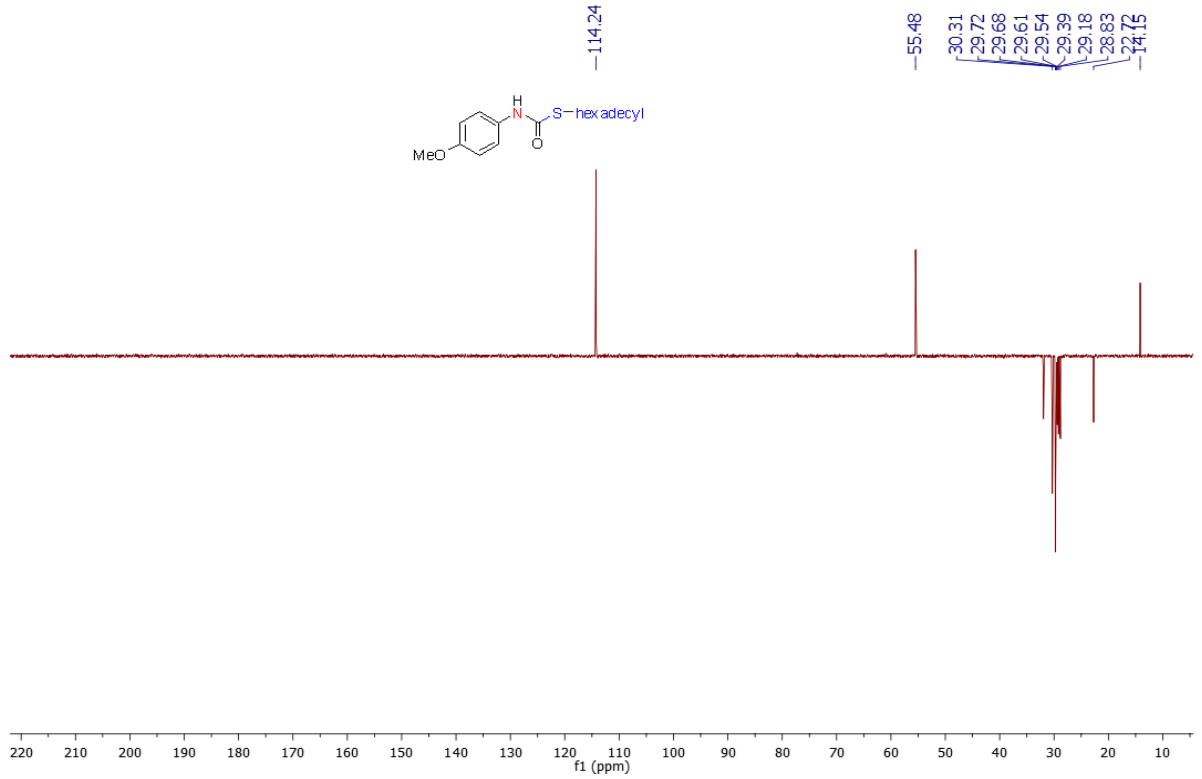
^{1}H-NMR of S-hexadecyl (4-methoxyphenyl)carbamothioate (4l)



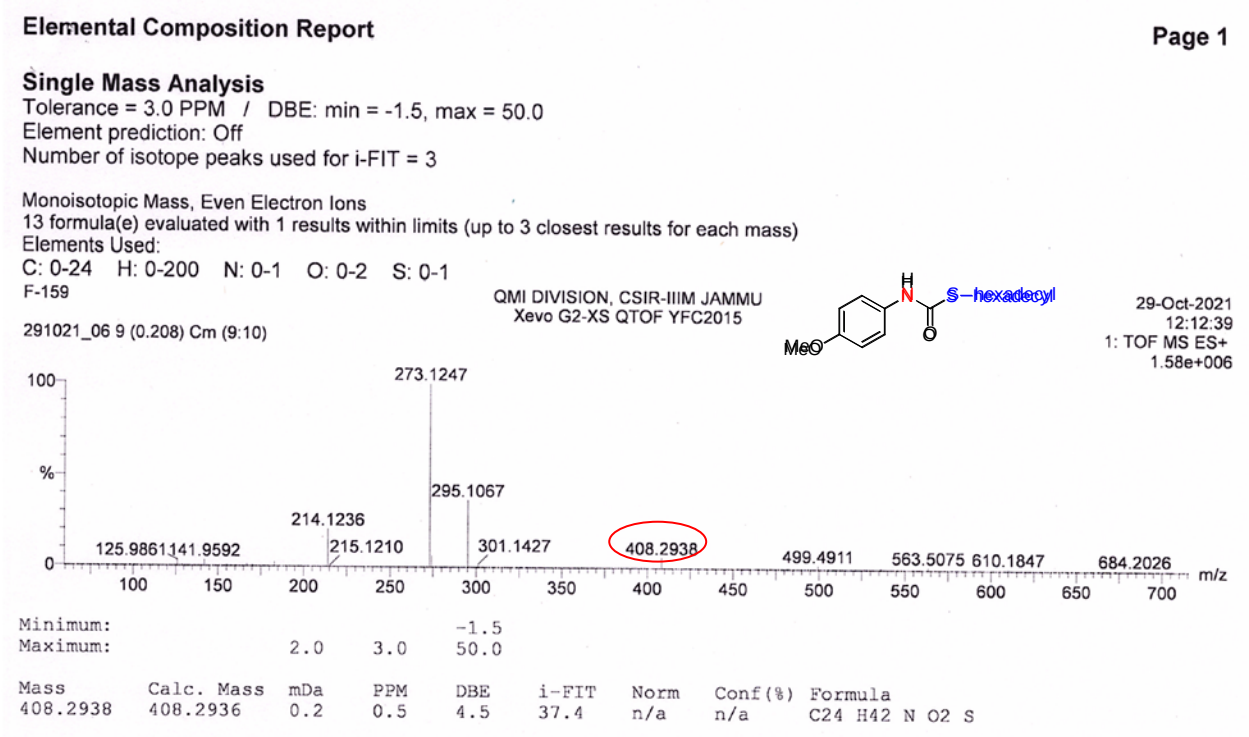
^{13}C-NMR of S-hexadecyl (4-methoxyphenyl)carbamothioate (4l)



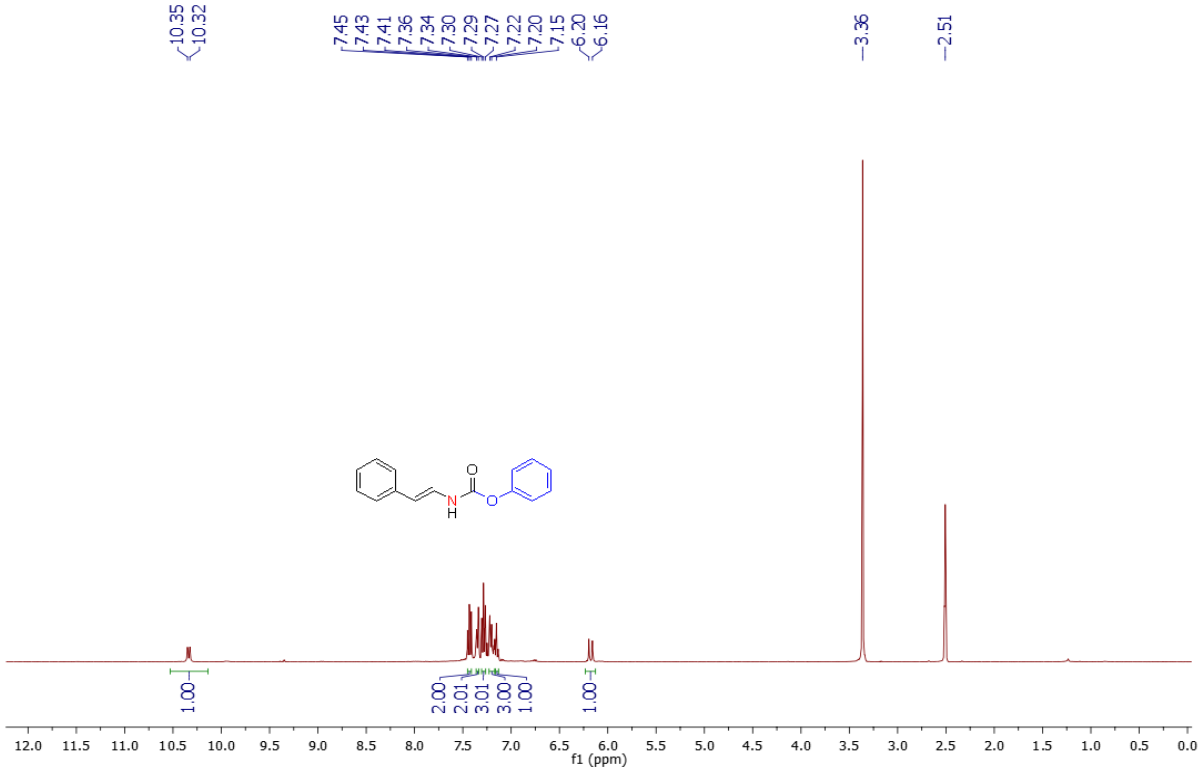
DEPT of S-hexadecyl (4-methoxyphenyl)carbamothioate (4l)



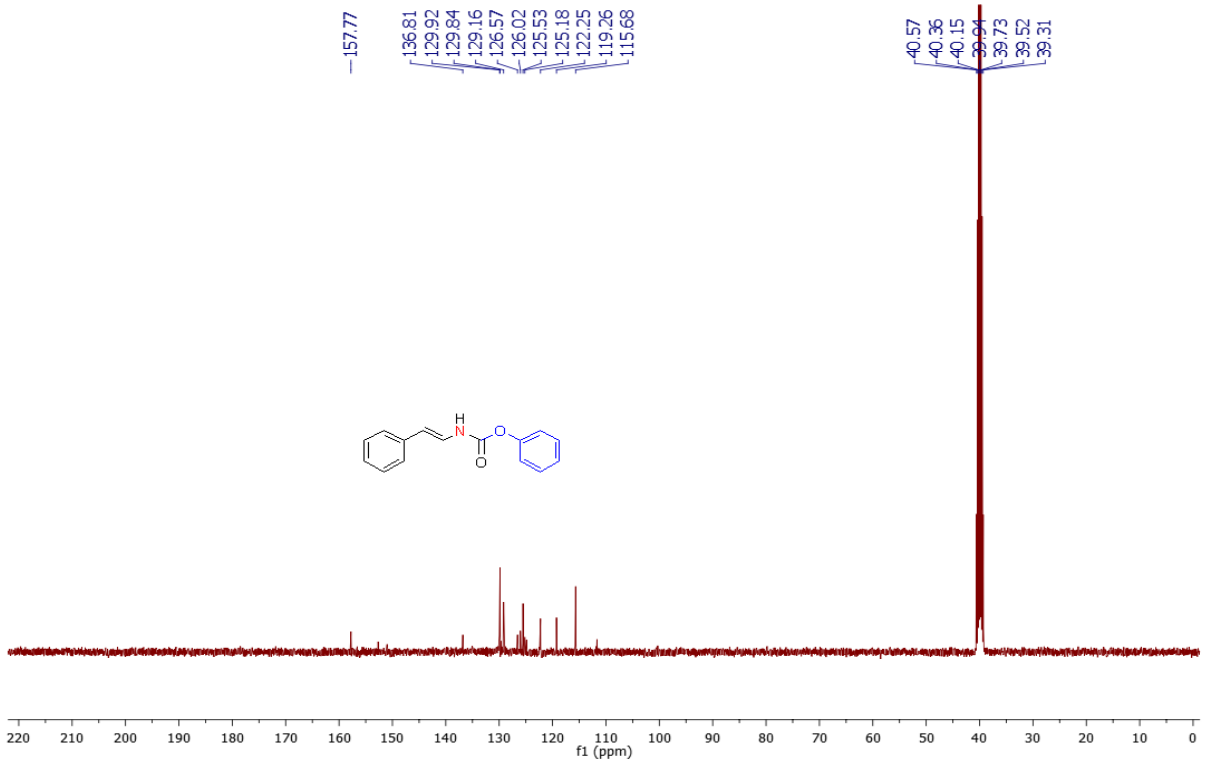
HRMS (ESI-TOF) of compound (4l)



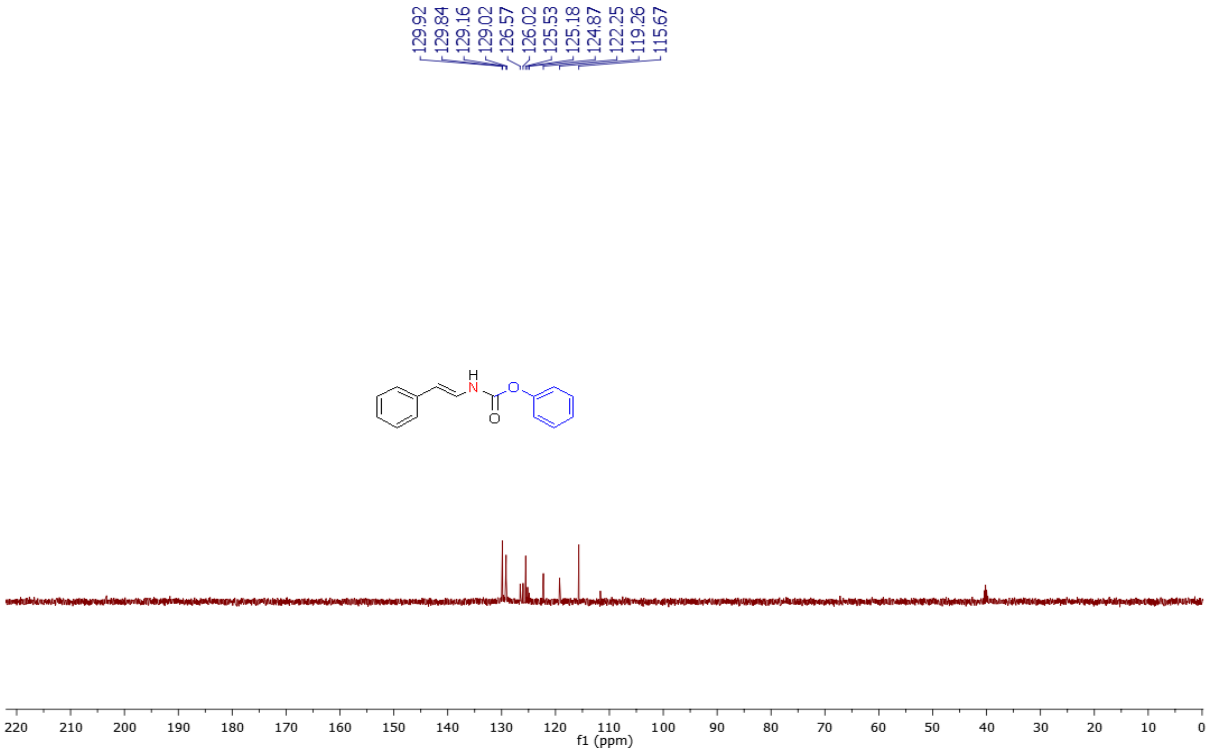
^{1}H-NMR of phenyl (*E*)-styrylcarbamate (4m)



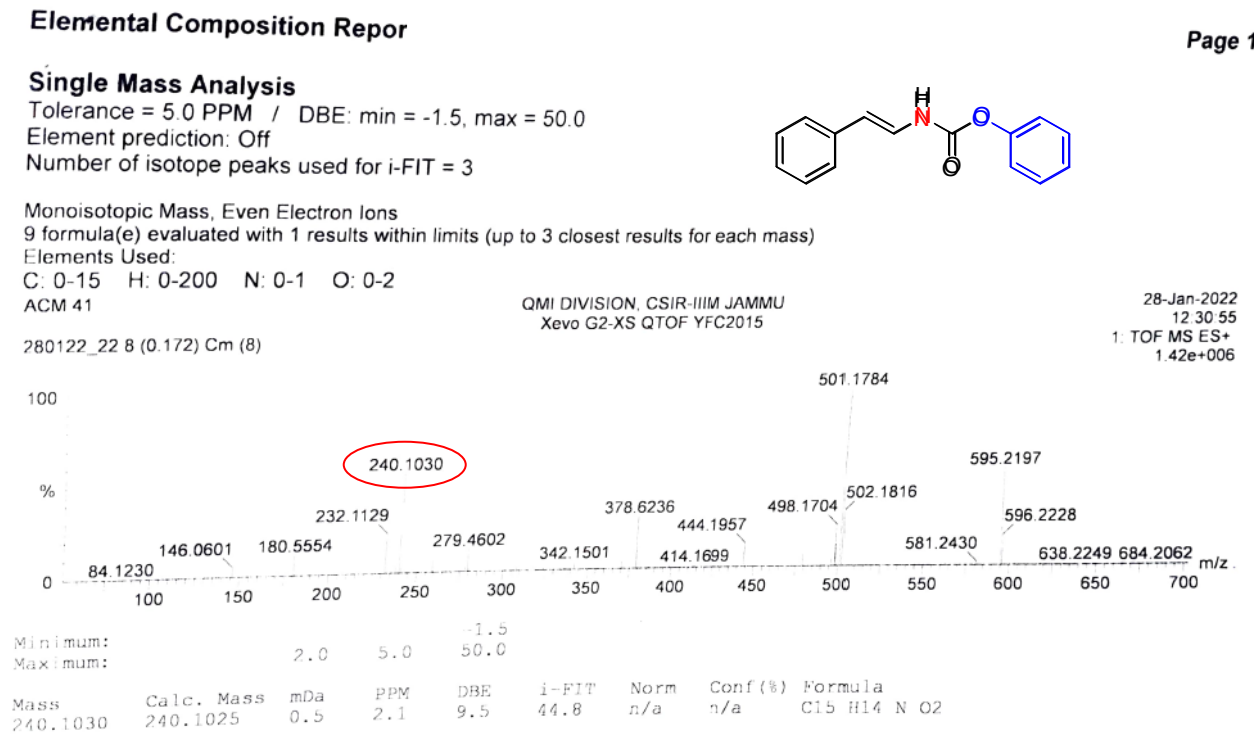
^{13}C-NMR of phenyl (*E*)-styrylcarbamate (4m)



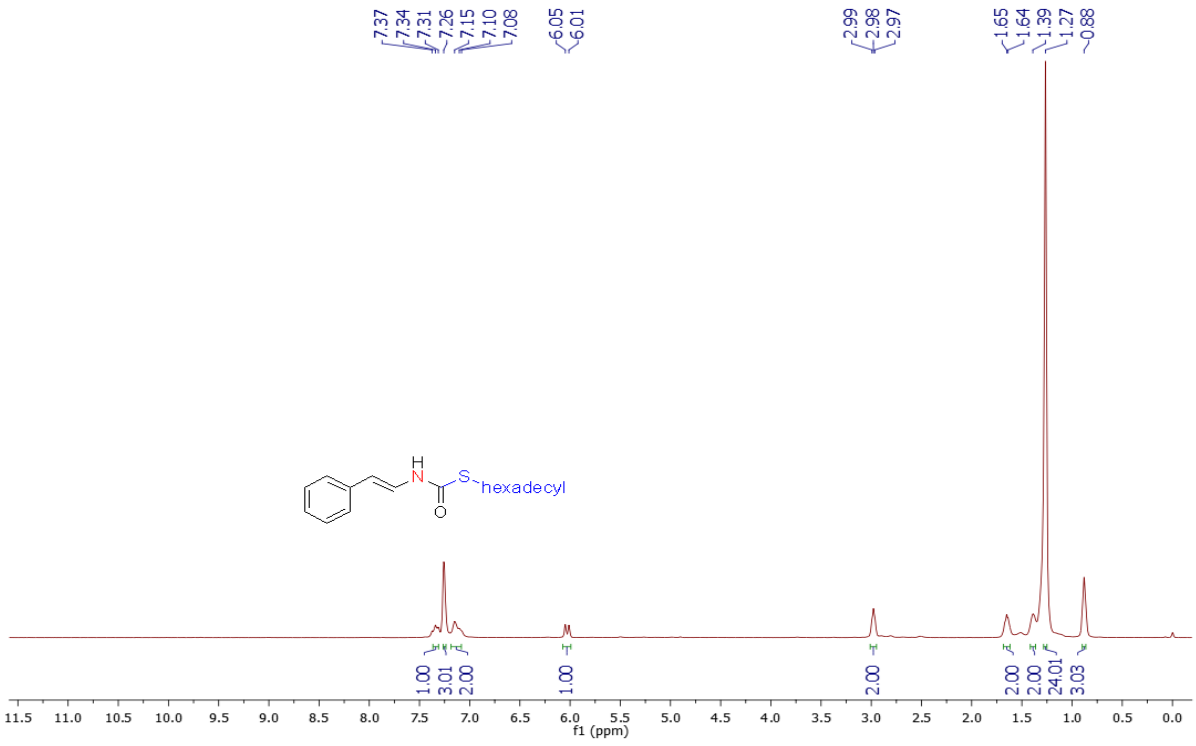
DEPT of phenyl (*E*)-styrylcarbamate (4m)



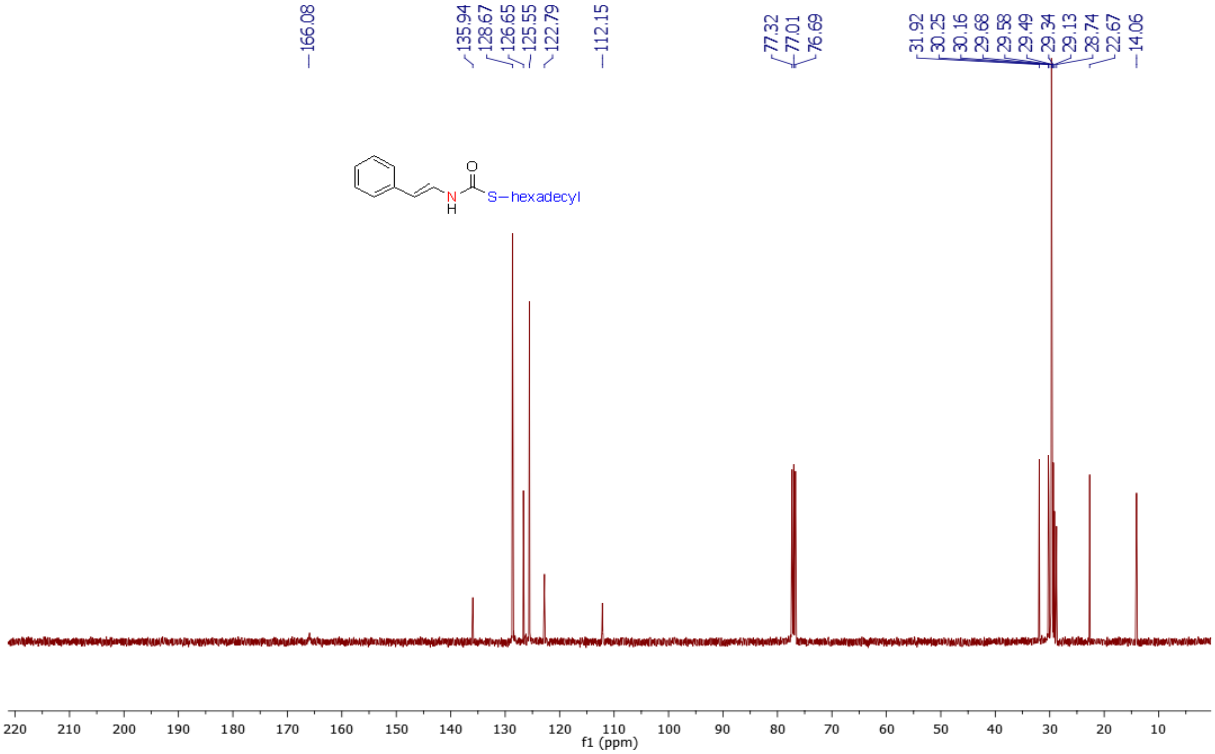
HRMS of phenyl (*E*)-styrylcarbamate (4m)



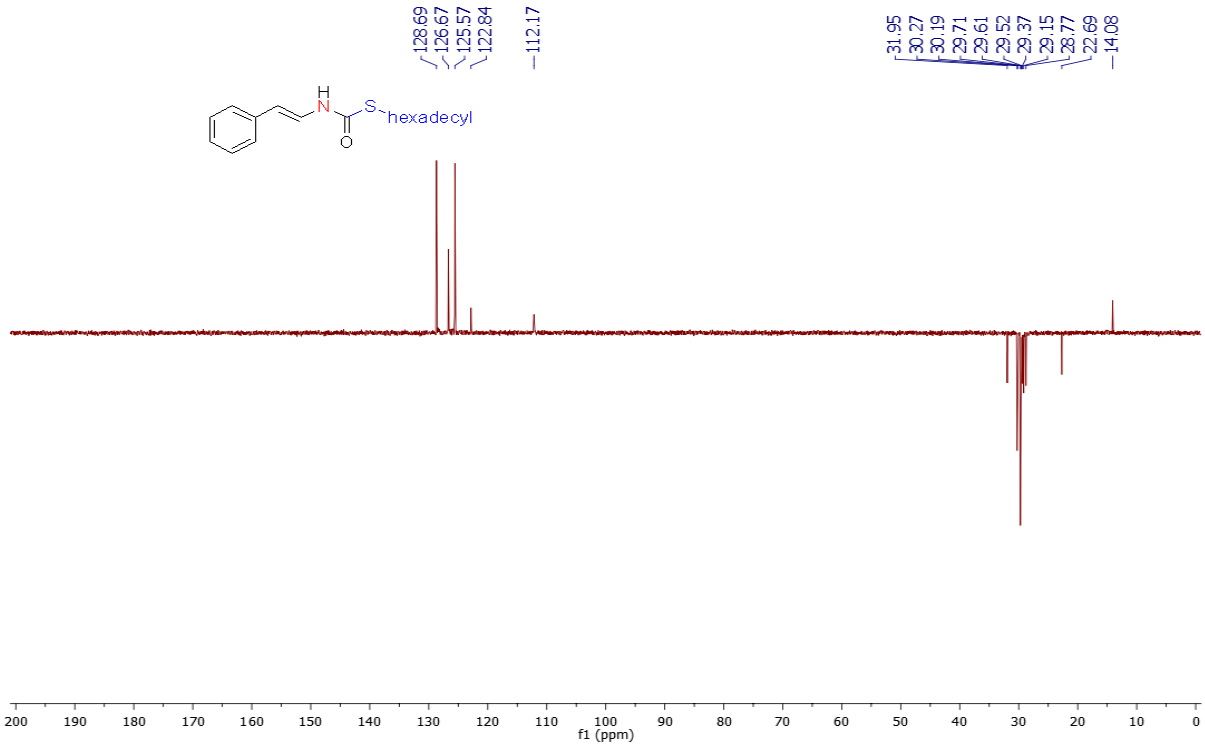
^{1}H-NMR of S-hexadecyl (*E*)-styrylcarbamothioate (4n)



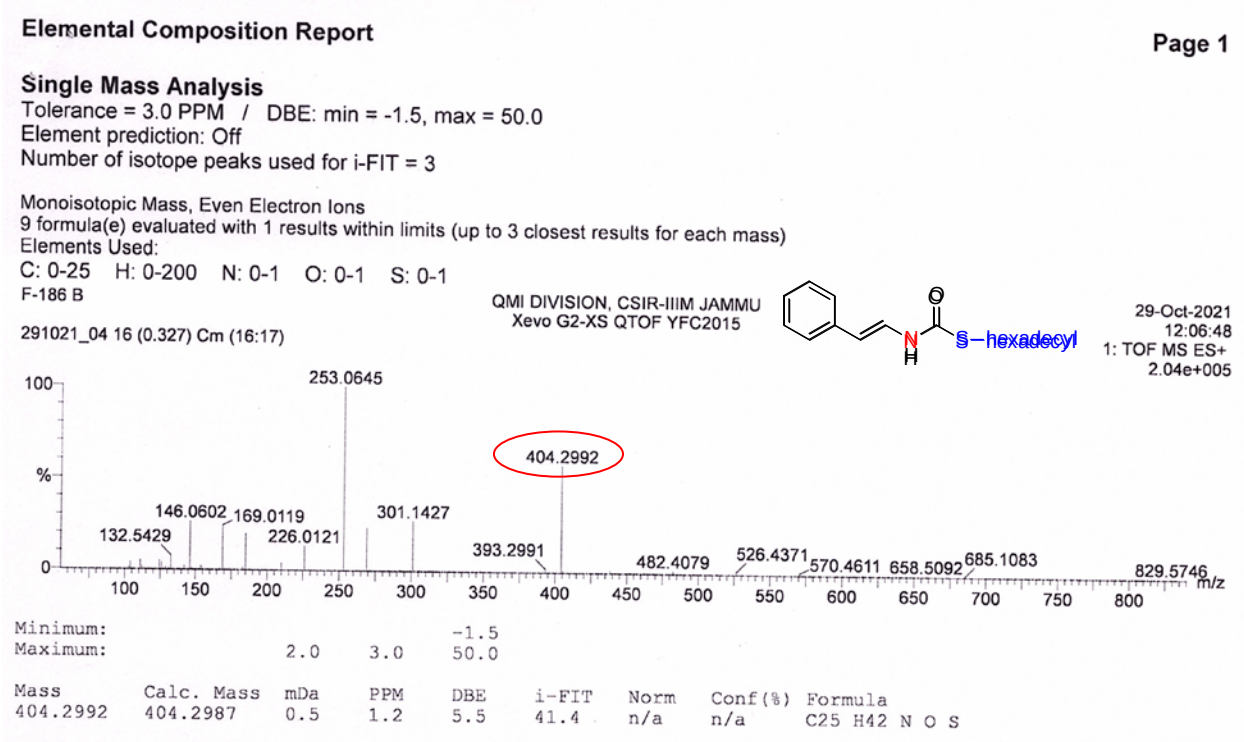
^{13}C-NMR of S-hexadecyl (*E*)-styrylcarbamothioate (4n)



DEPT of S-hexadecyl (*E*)-styrylcarbamothioate (4n)



HRMS (ESI-TOF) of compound (4n)



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-25 H: 0-200 N: 0-1 O: 0-1 S: 0-1
F-186 B

291021_04 16 (0.327) Cm (16:17)

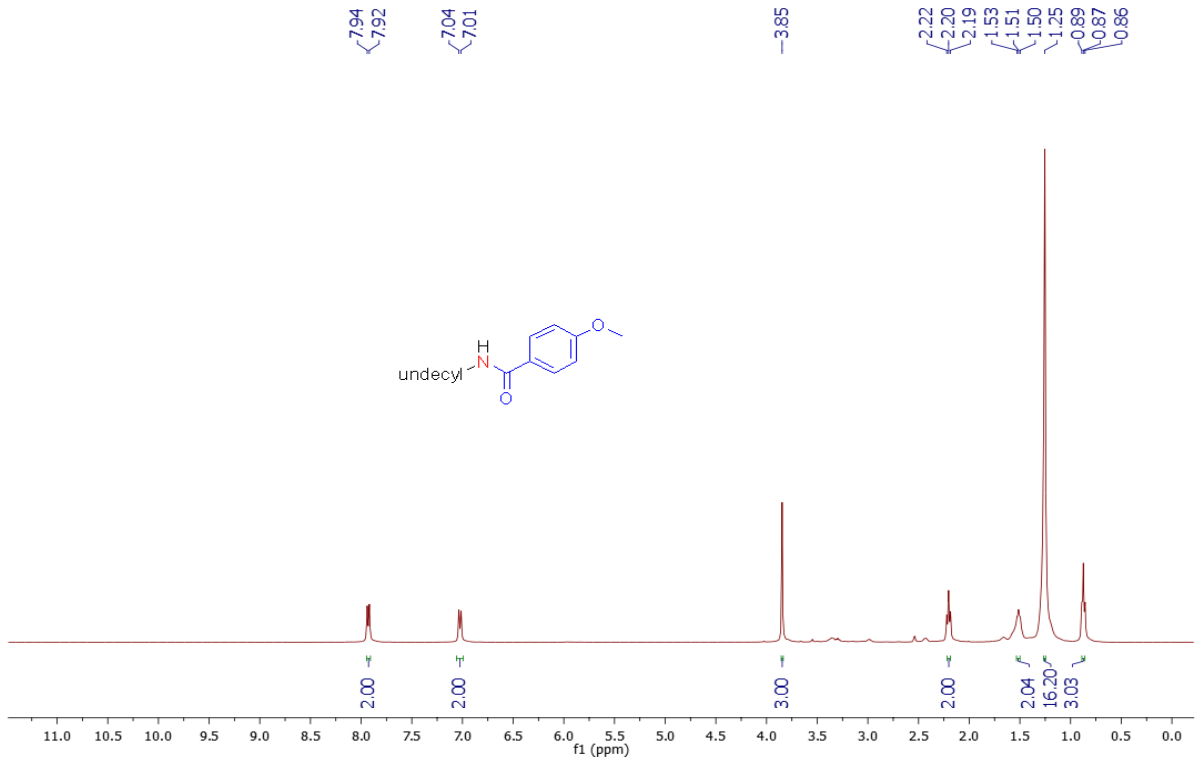
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

29-Oct-2021
12:06:48
1: TOF MS ES+
2.04e+005

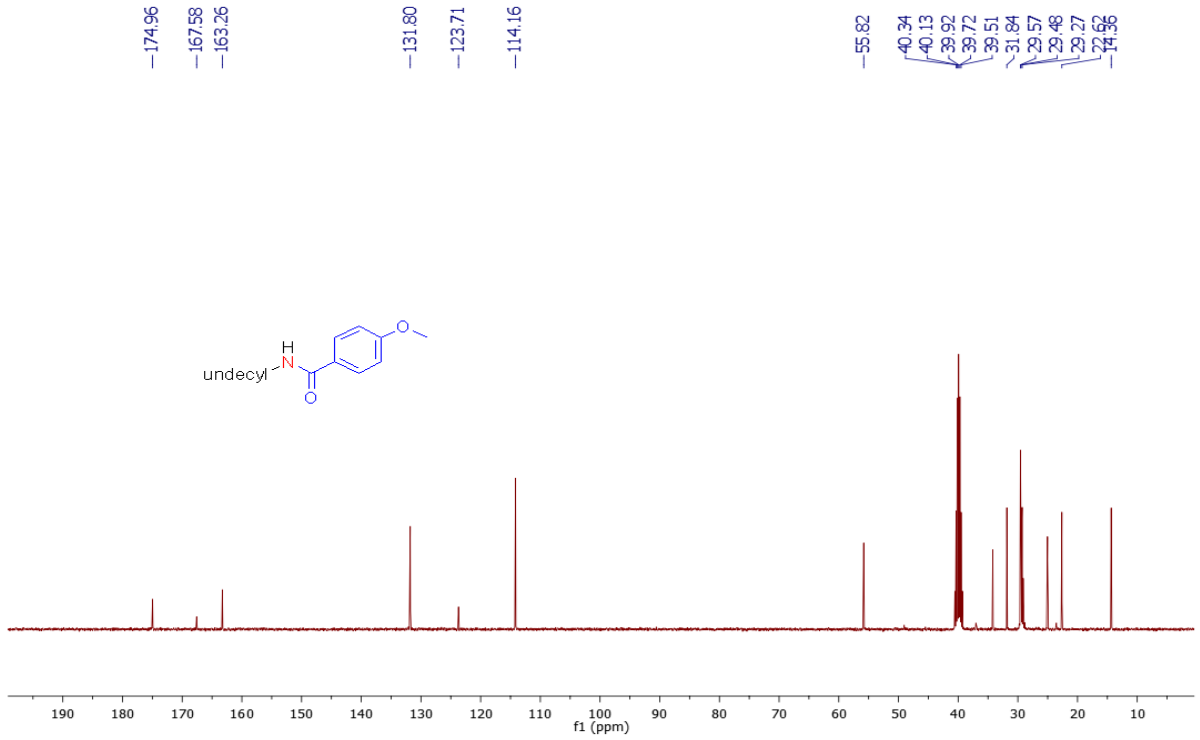
253.0645
404.2992
146.0602
169.0119
301.1427
132.5429
226.0121
393.2991
482.4079
526.4371
570.4611
658.5092
685.1083
829.5746
m/z

Minimum:				-1.5				
Maximum:		2.0	3.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
404.2992	404.2987	0.5	1.2	5.5	41.4	n/a	n/a	C25 H42 N O S

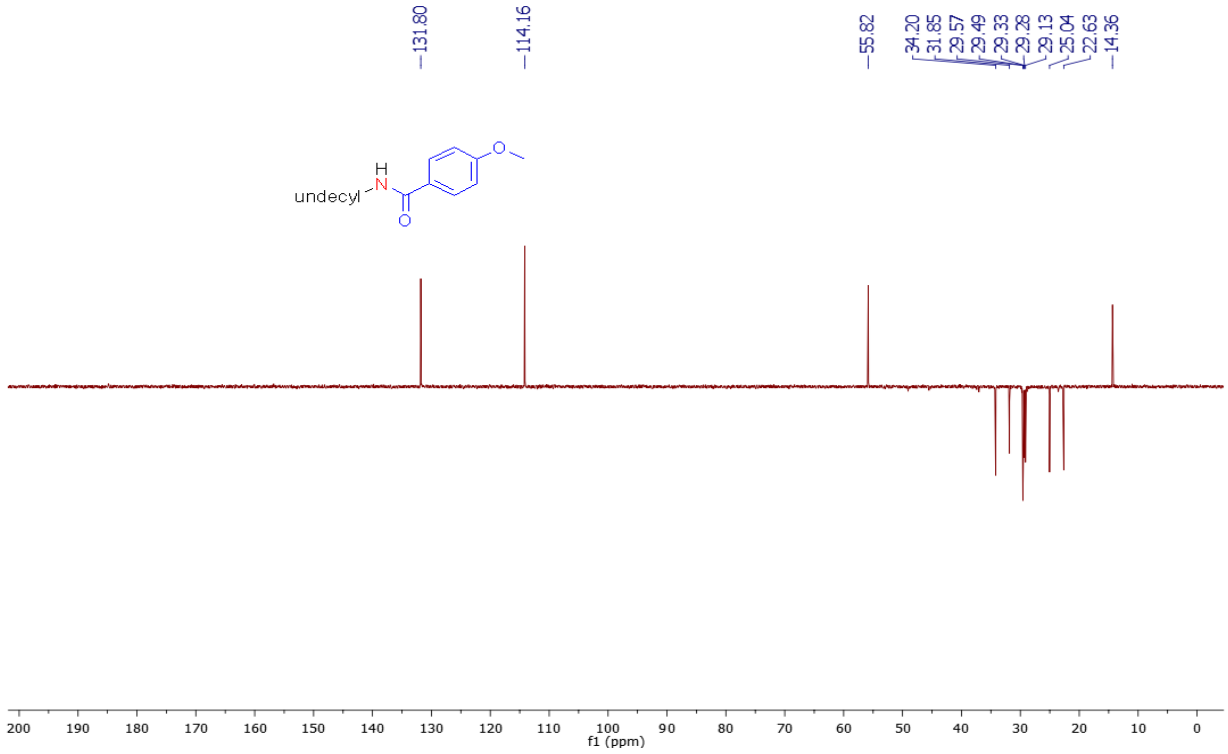
^{1}H-NMR of 4-methoxy-N-undecylbenzamide (5)



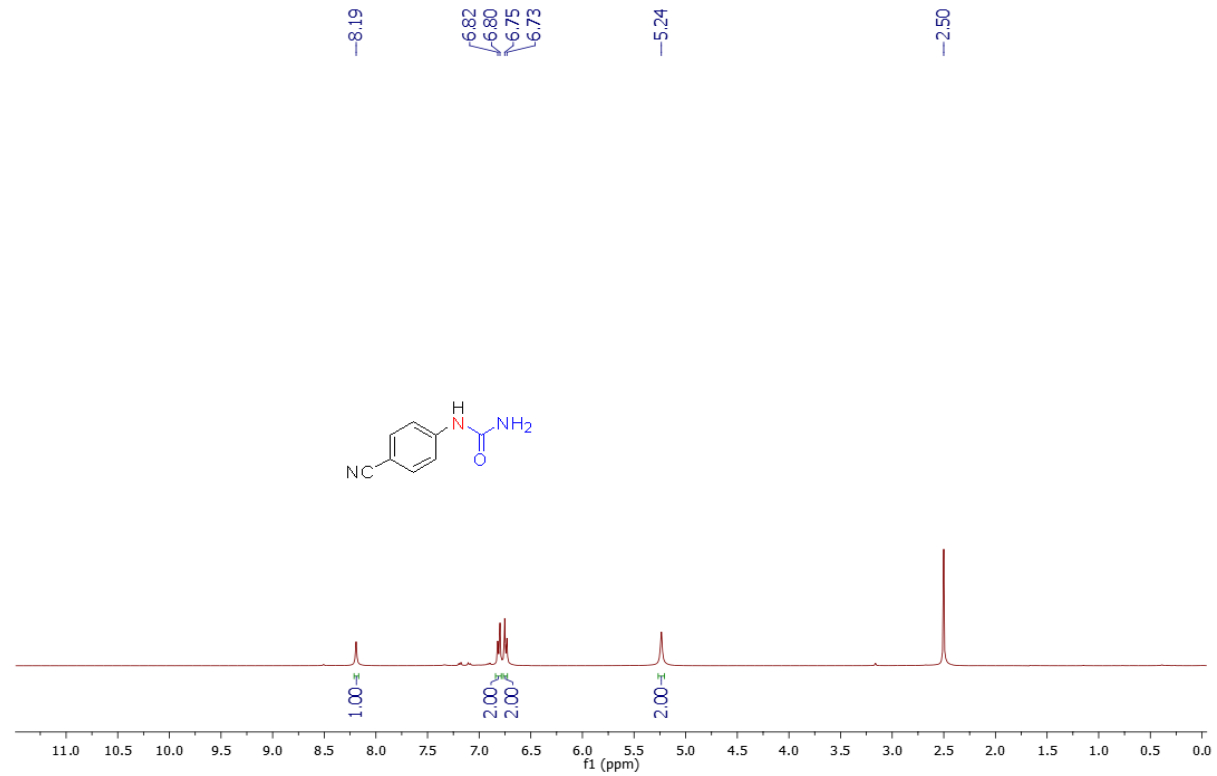
^{13}C-NMR of 4-methoxy-N-undecylbenzamide (5)



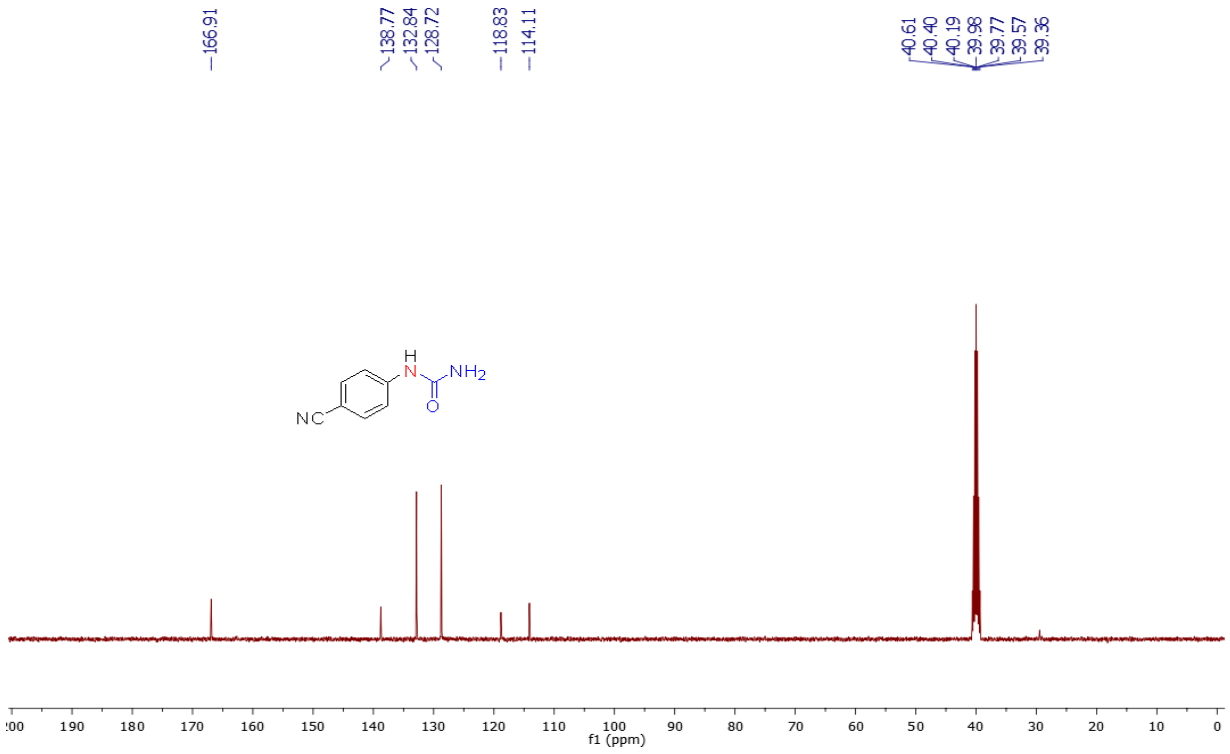
DEPT of 4-methoxy-N-undecylbenzamide (5)



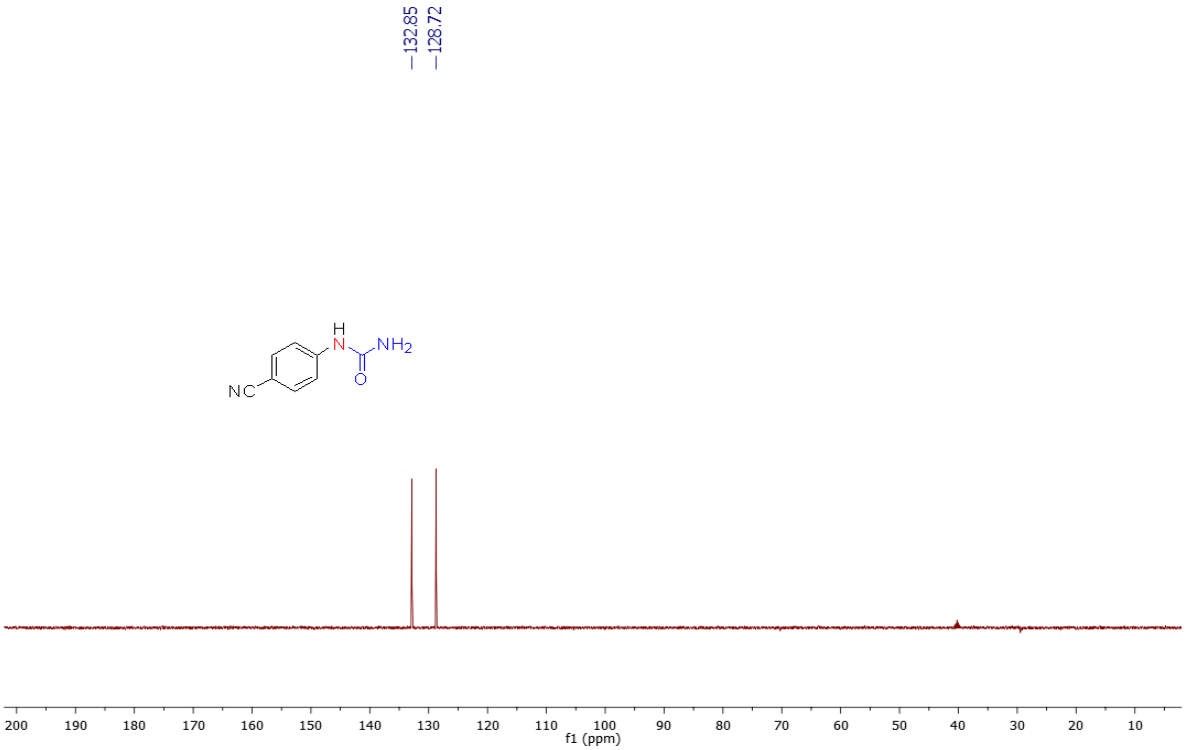
^{1}H-NMR of 1-(4-cyanophenyl)urea (6)



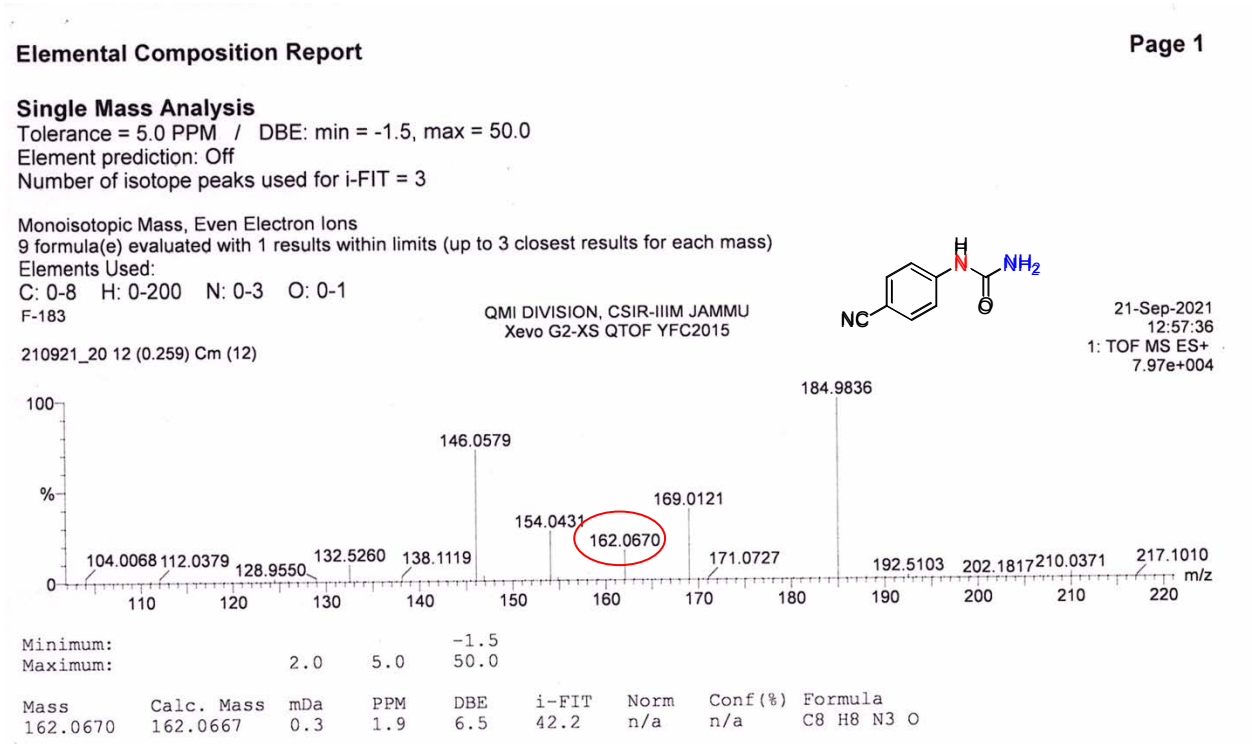
^{13}C-NMR of 1-(4-cyanophenyl)urea (6)



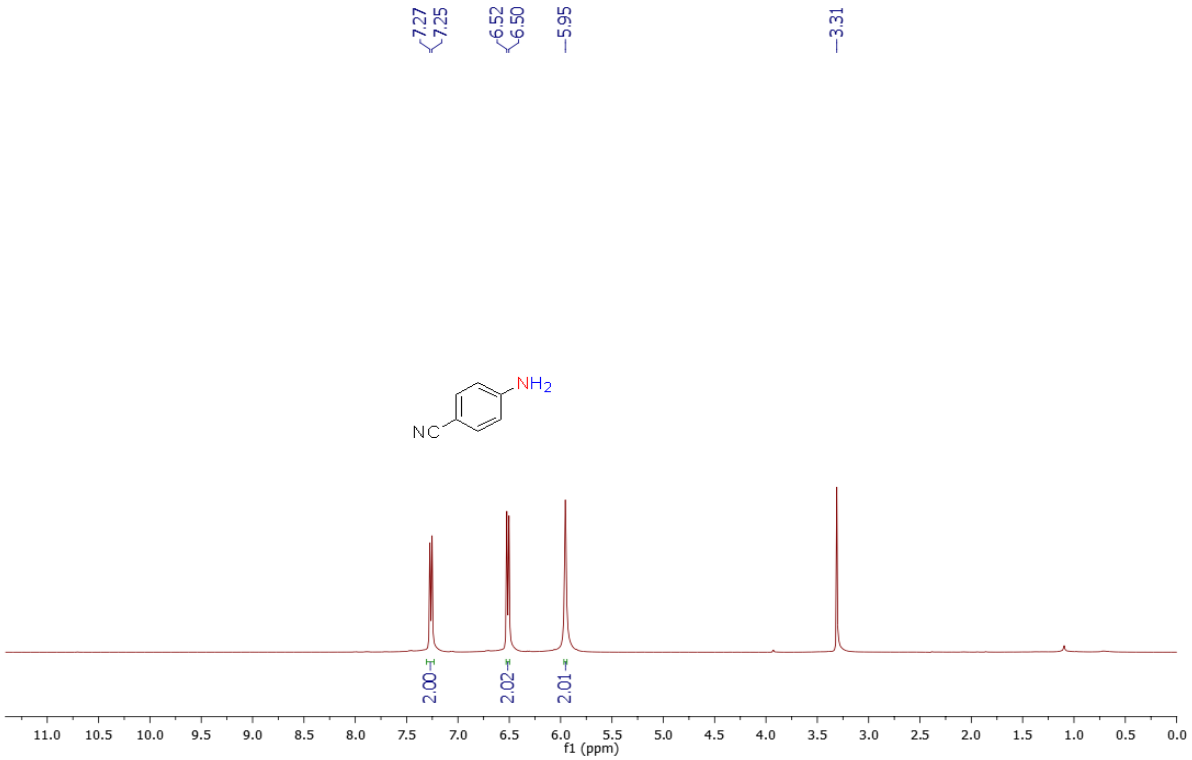
DEPT of 1-(4-cyanophenyl)urea (6)



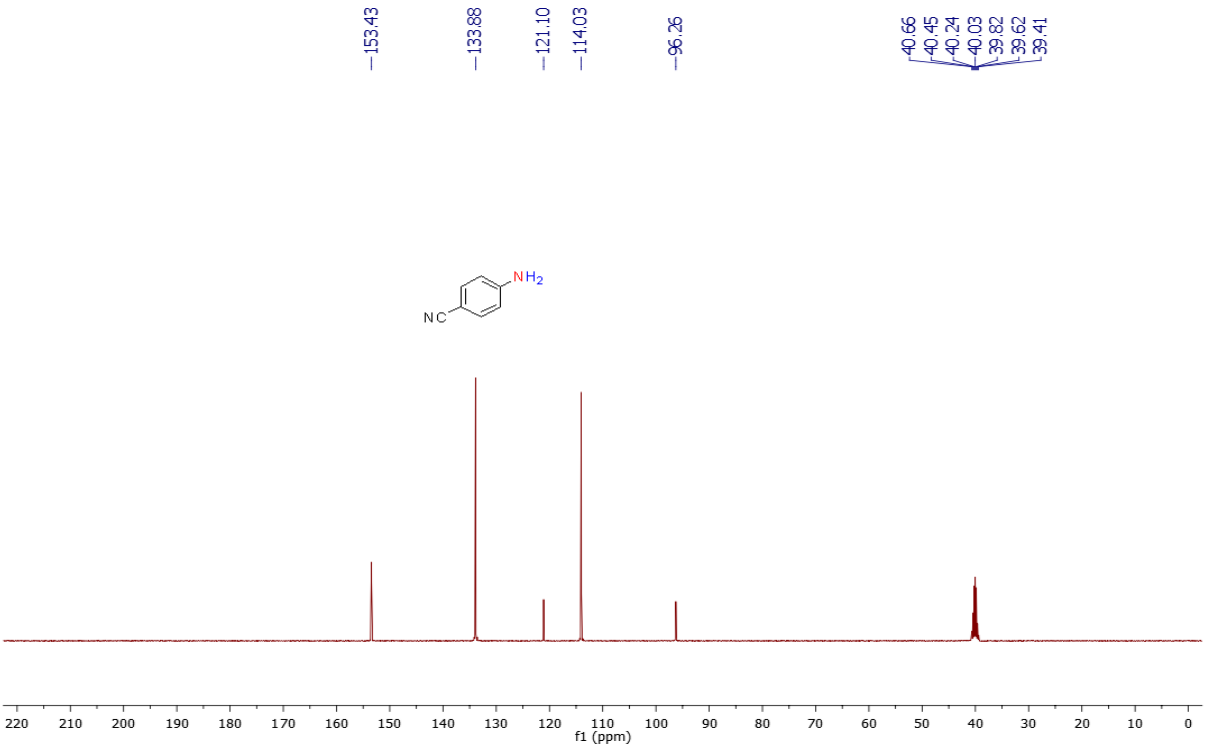
HRMS (ESI-TOF) of compound (6)



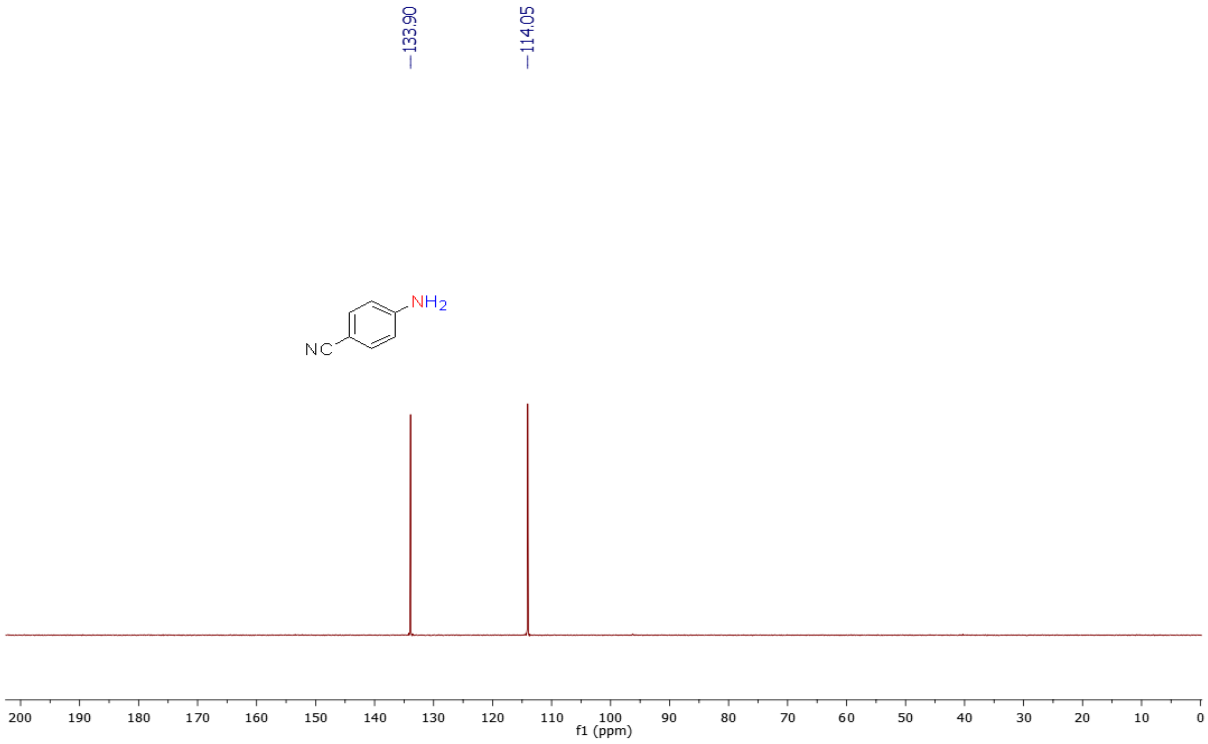
^{1}H-NMR of 4-aminobenzonitrile (7a)



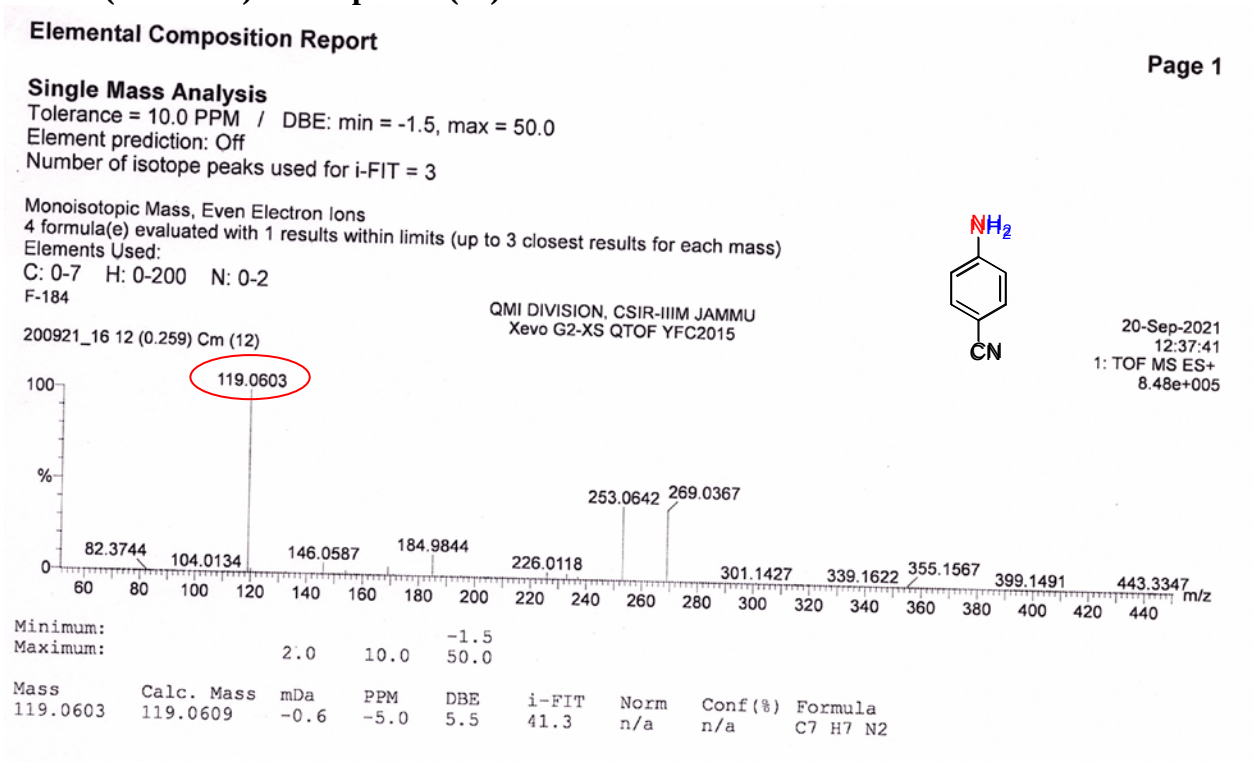
^{13}C-NMR of 4-aminobenzonitrile (7a)



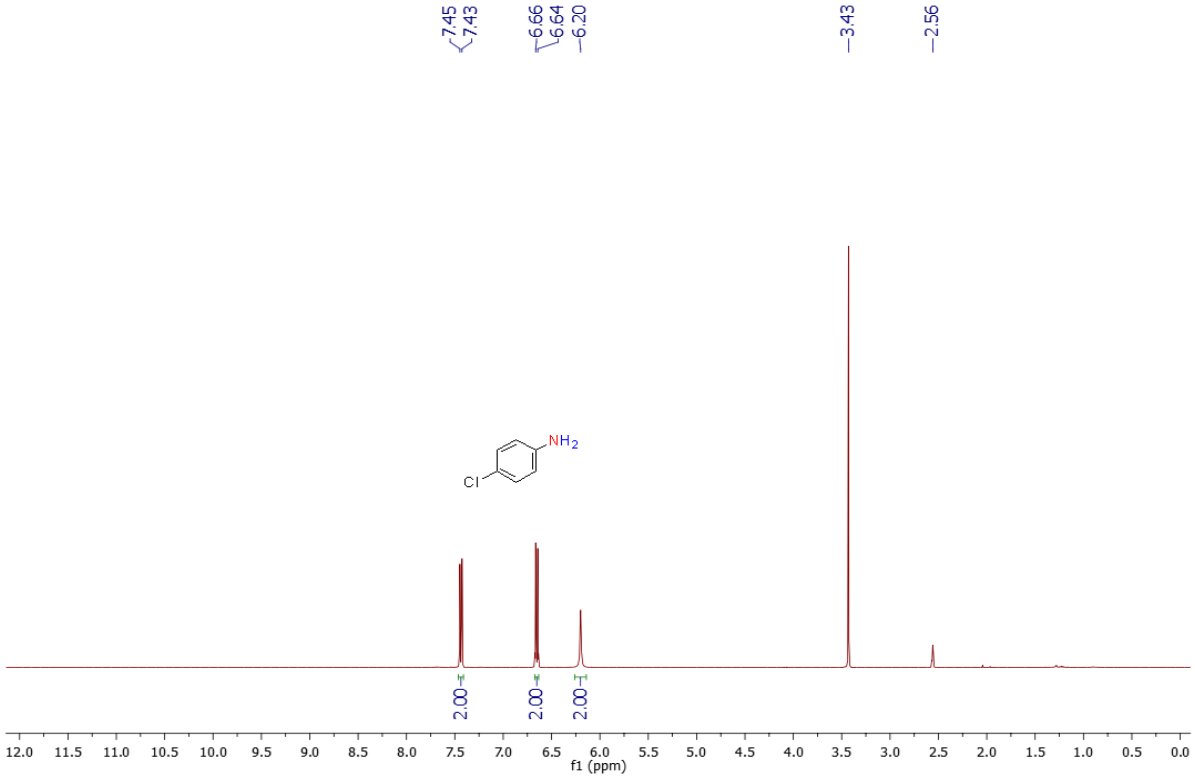
DEPT of 4-aminobenzonitrile (7a)



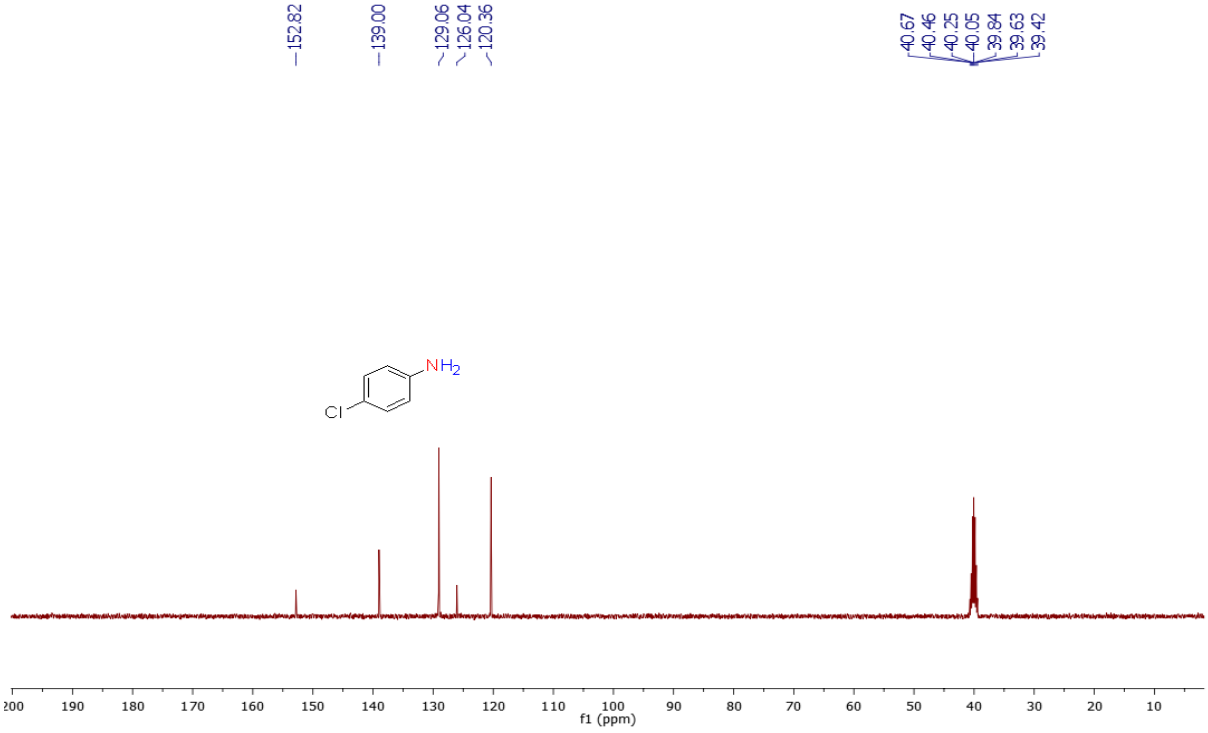
HRMS (ESI-TOF) of compound (7a)



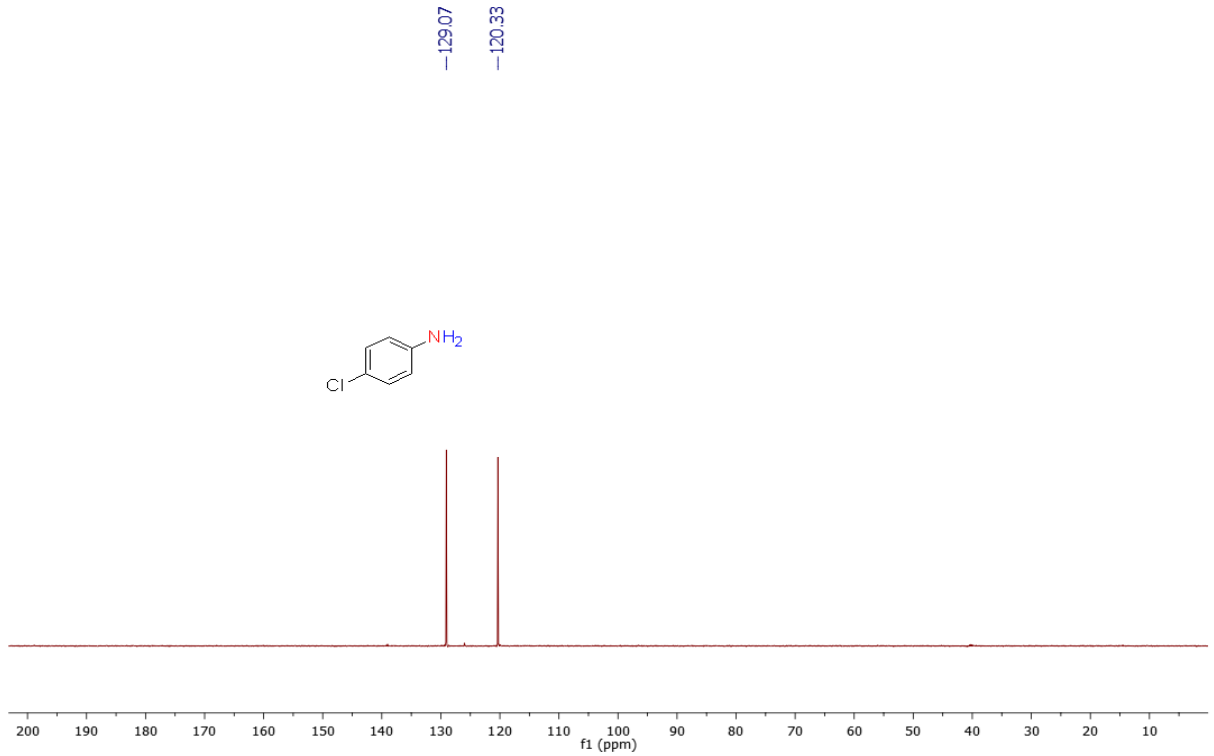
^{1}H-NMR of 4-chloroaniline (7b)



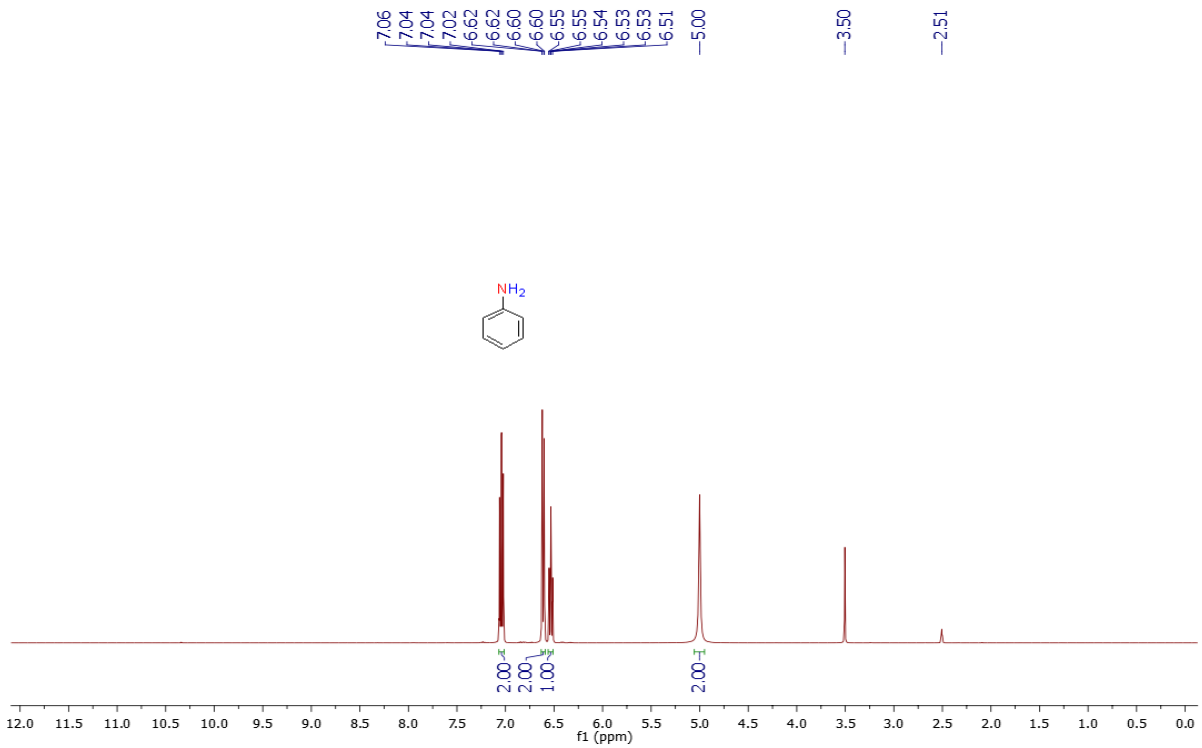
^{13}C-NMR of 4-chloroaniline (7b)



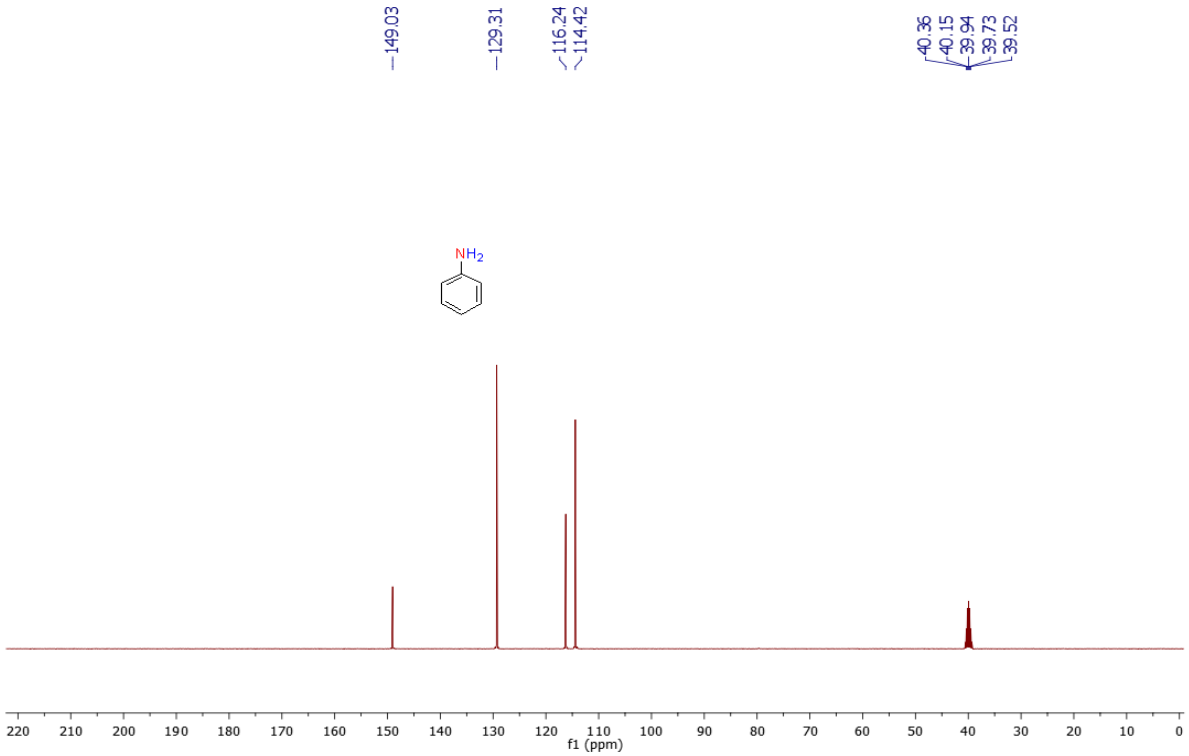
DEPT of 4-chloroaniline (7b)



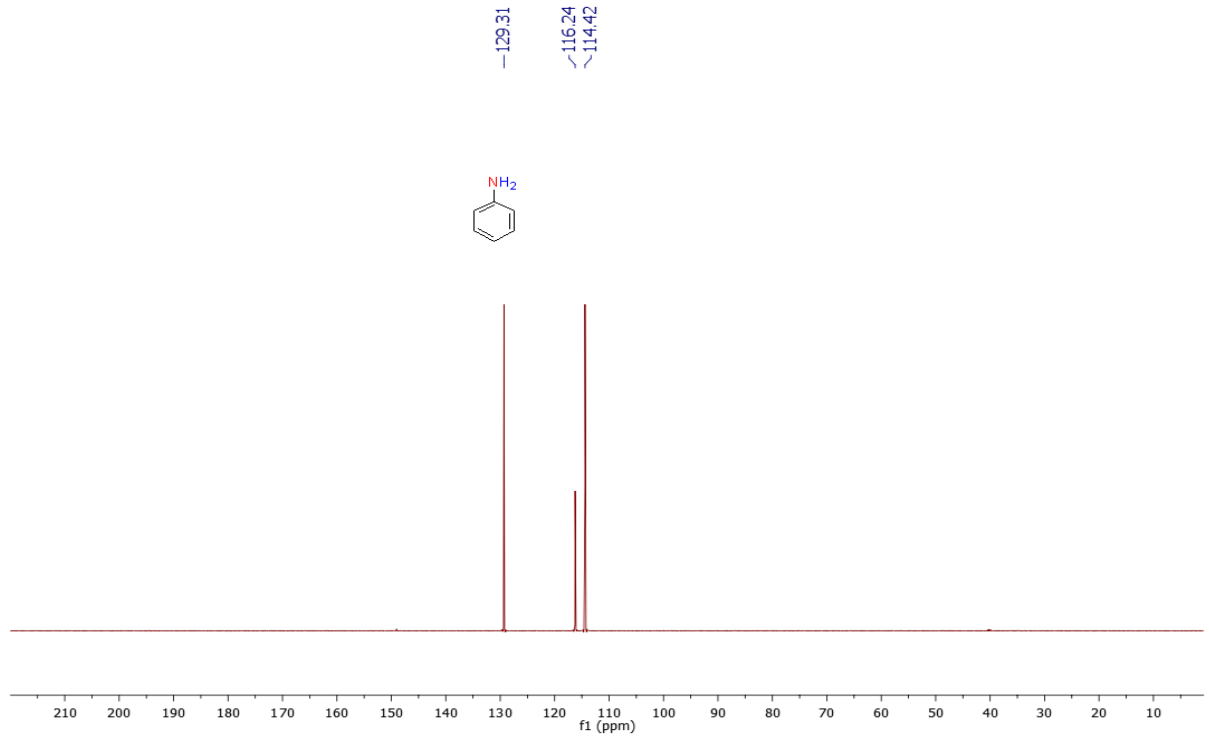
^{1}H-NMR of aniline (7c)



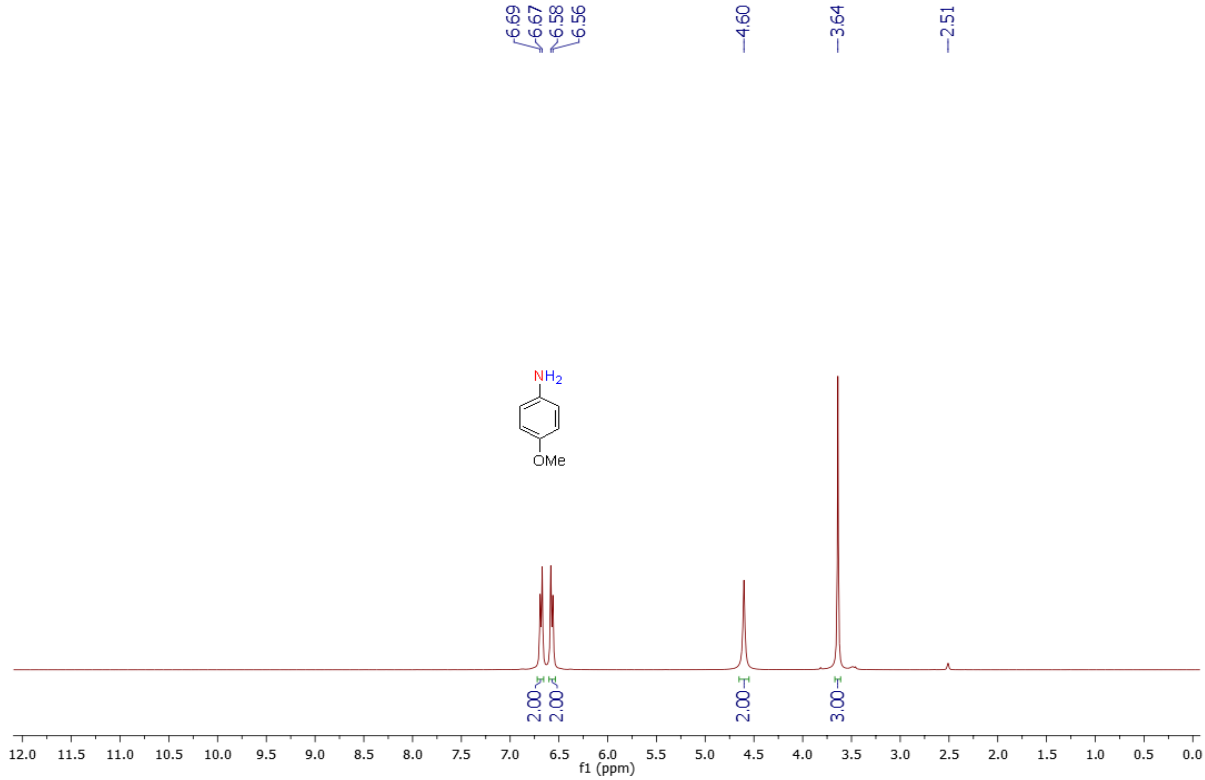
^{13}C-NMR of aniline (7c)



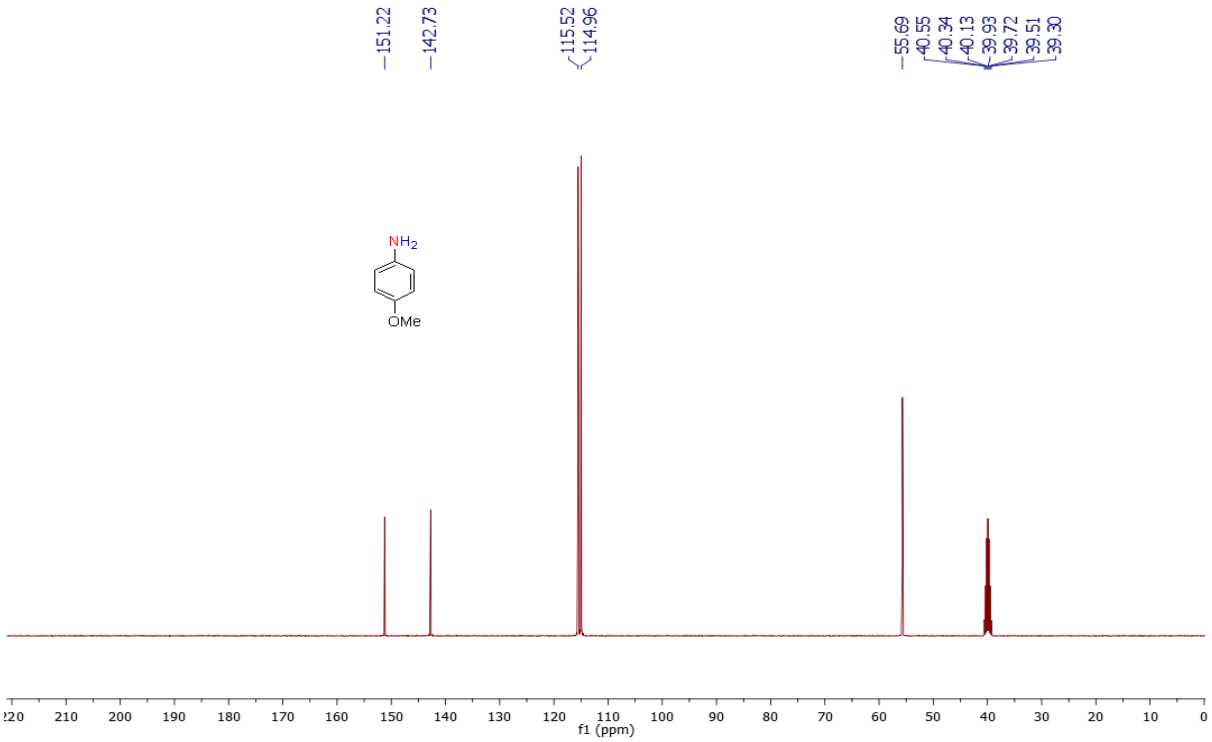
DEPT of aniline (7c)



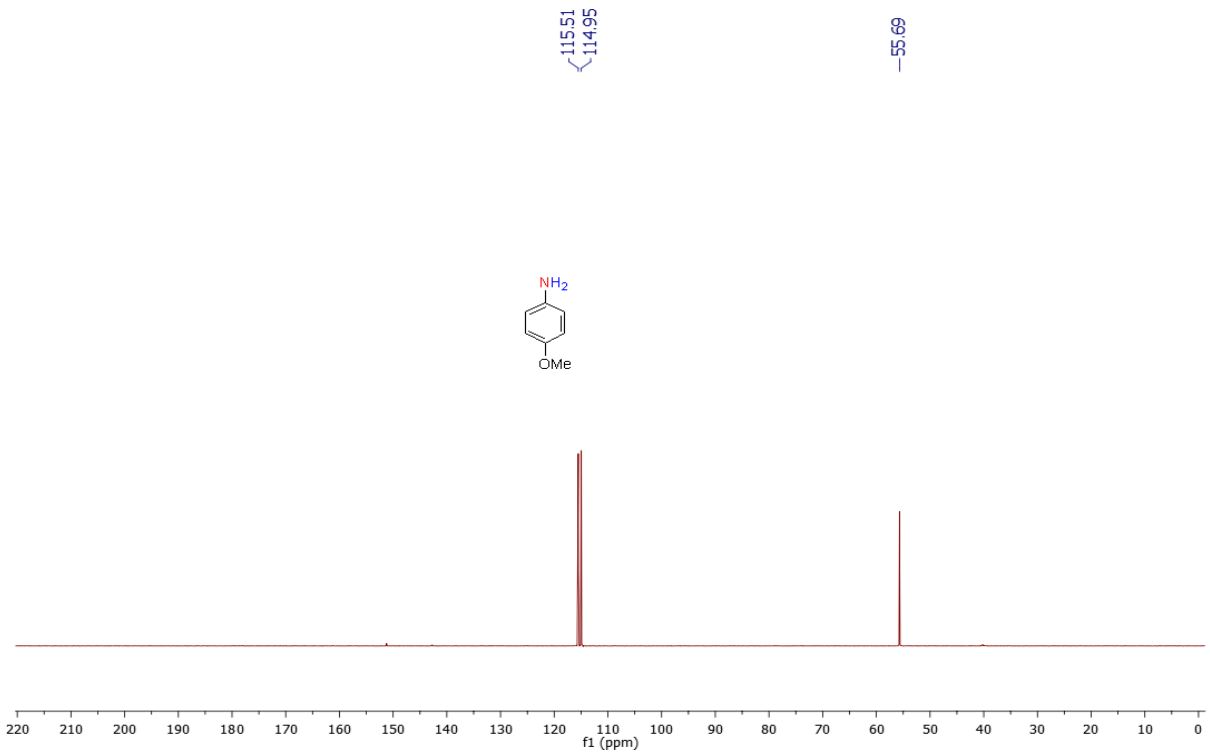
^{1}H-NMR of 4-methoxyaniline (7d)



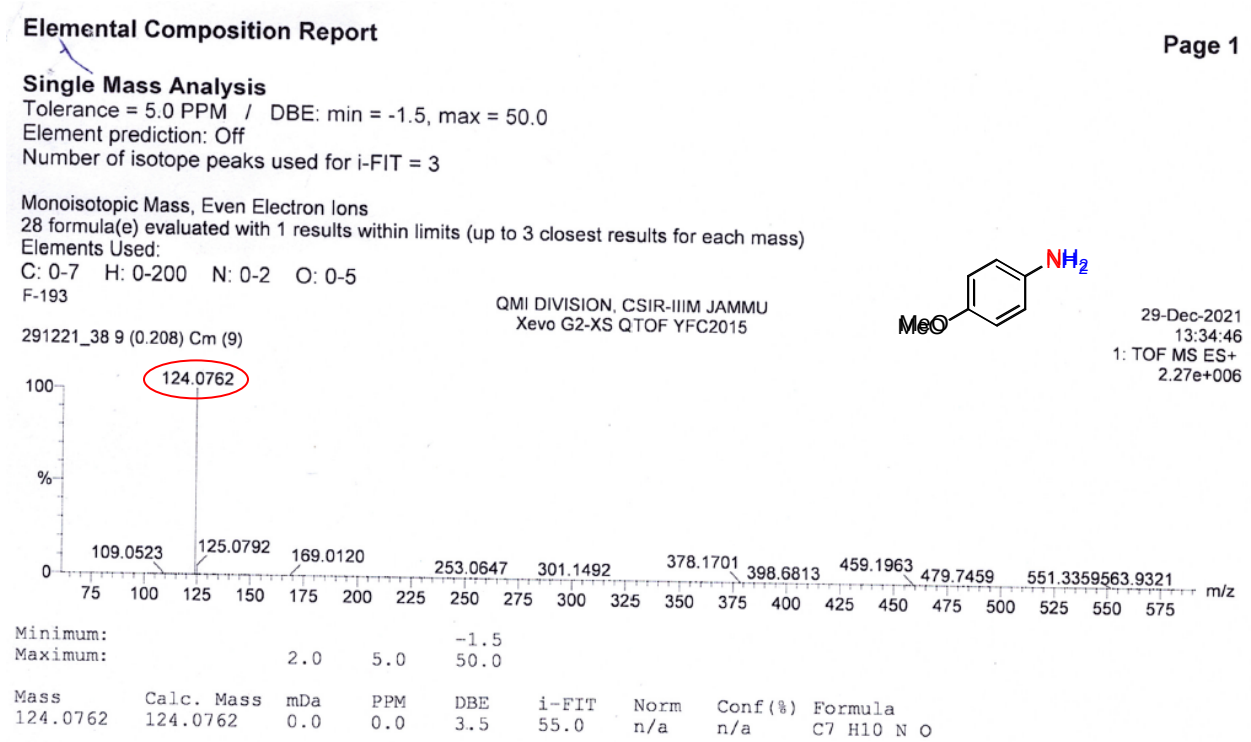
^{13}C-NMR of 4-methoxyaniline (7d)



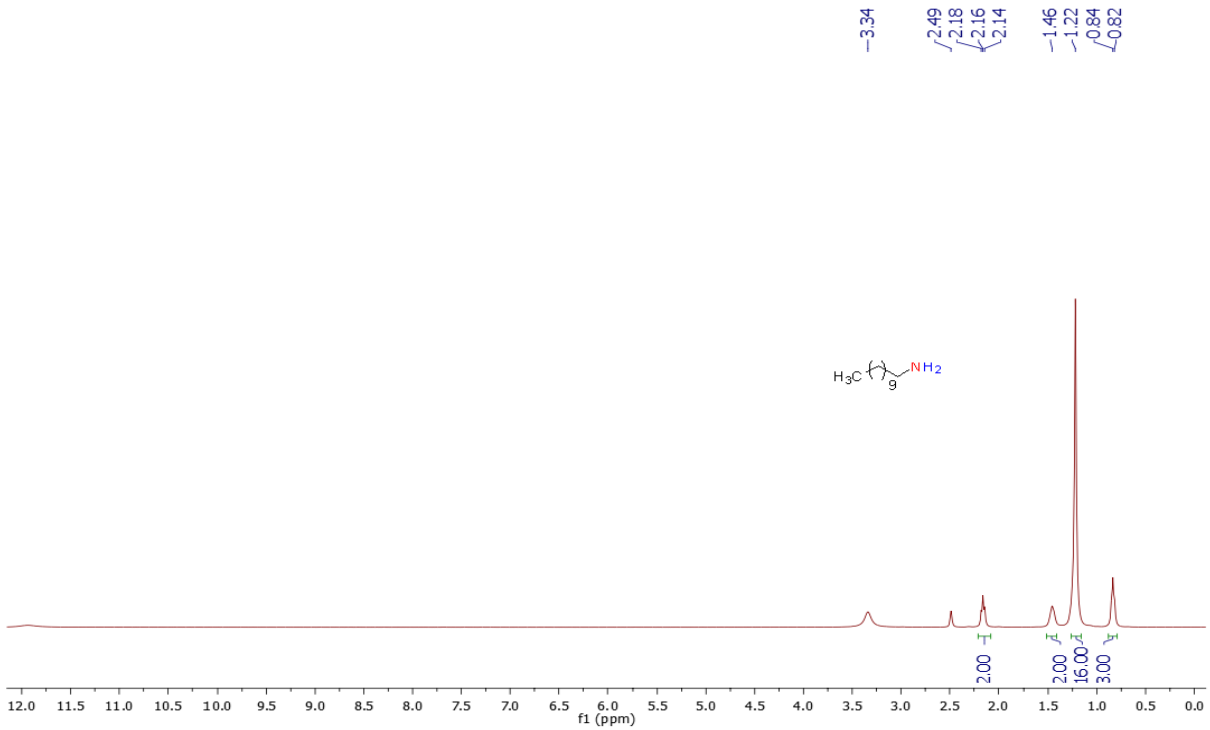
DEPT of 4-methoxyaniline (7d)



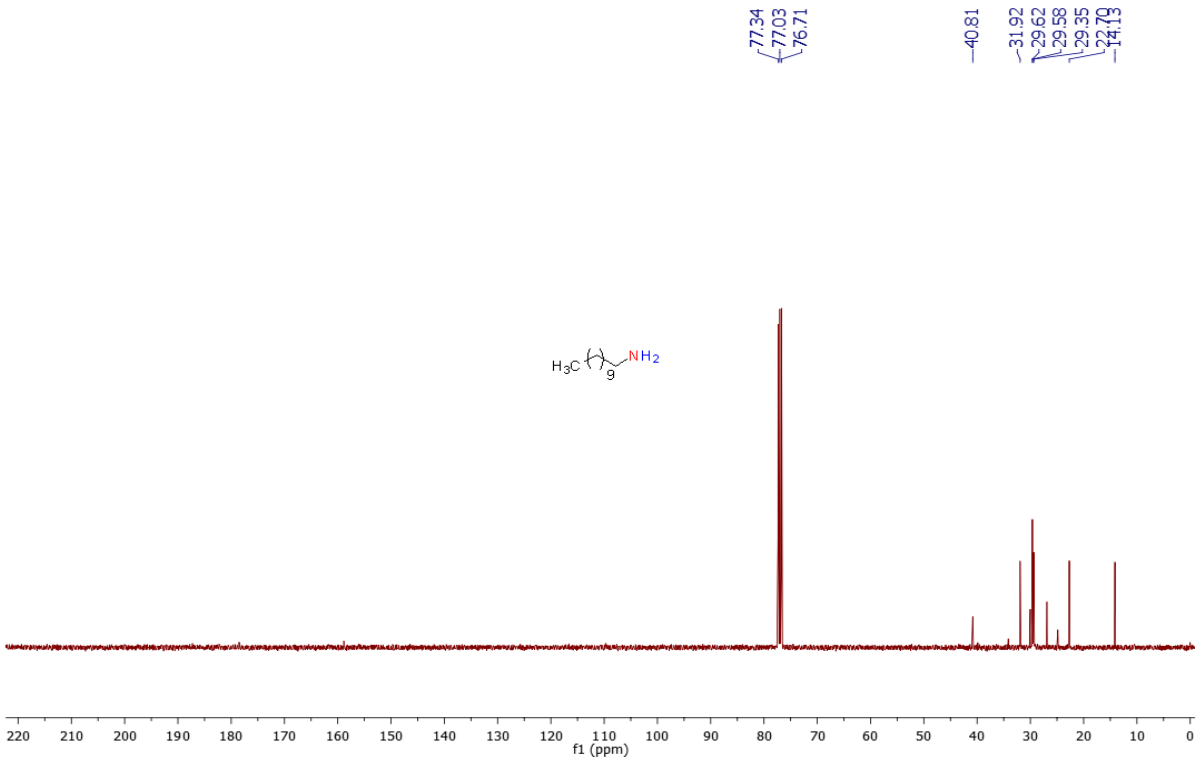
HRMS of 4-methoxyaniline (7d)



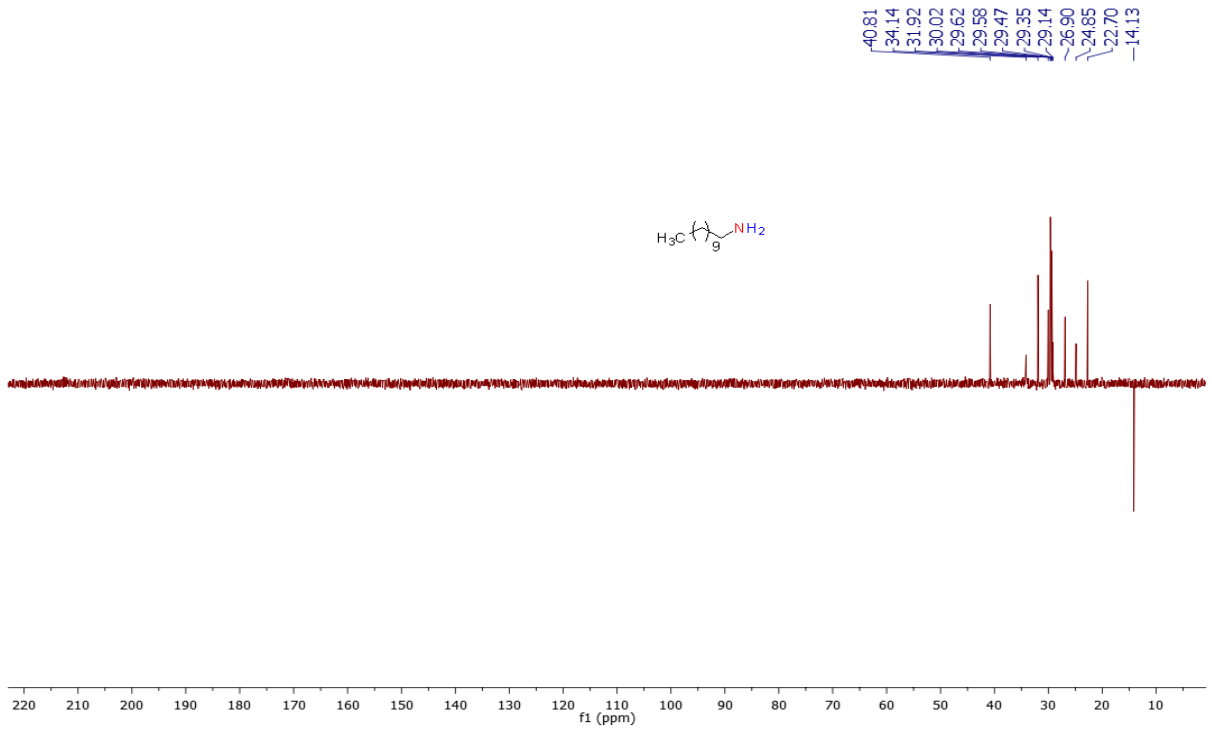
^{1}H-NMR of undecan-1-amine (7e)



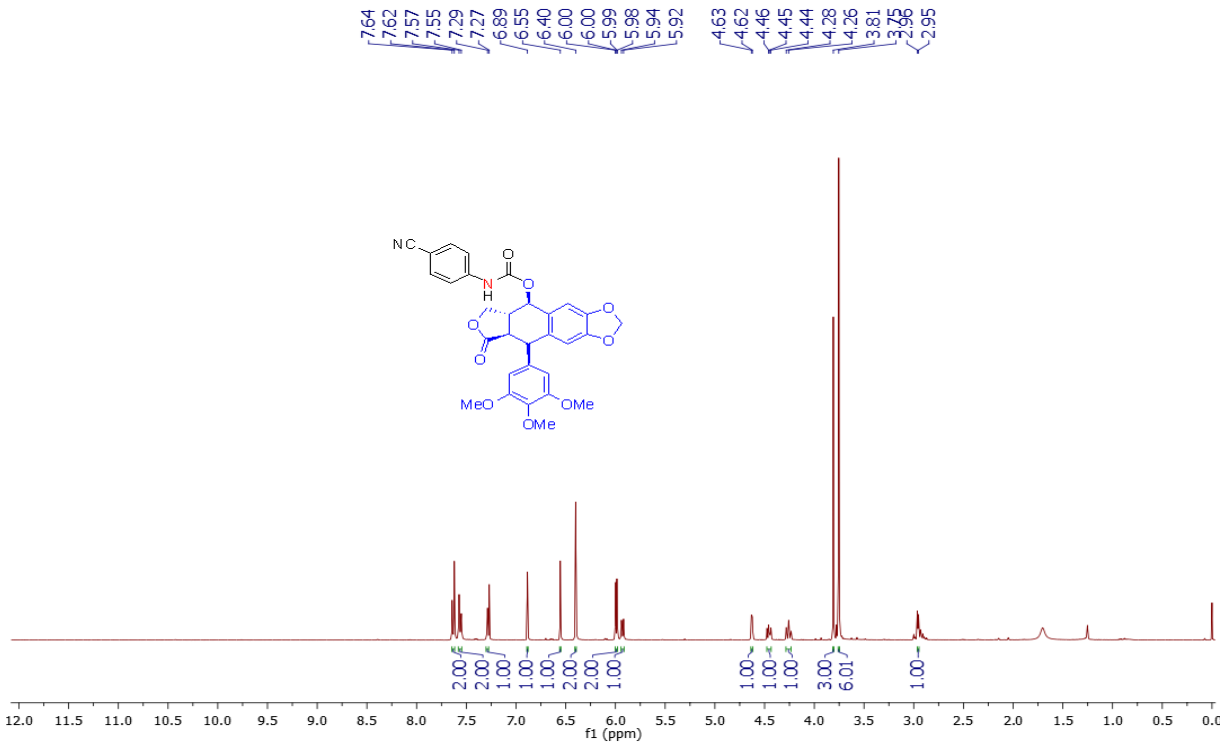
^{13}C-NMR of undecan-1-amine (7e)



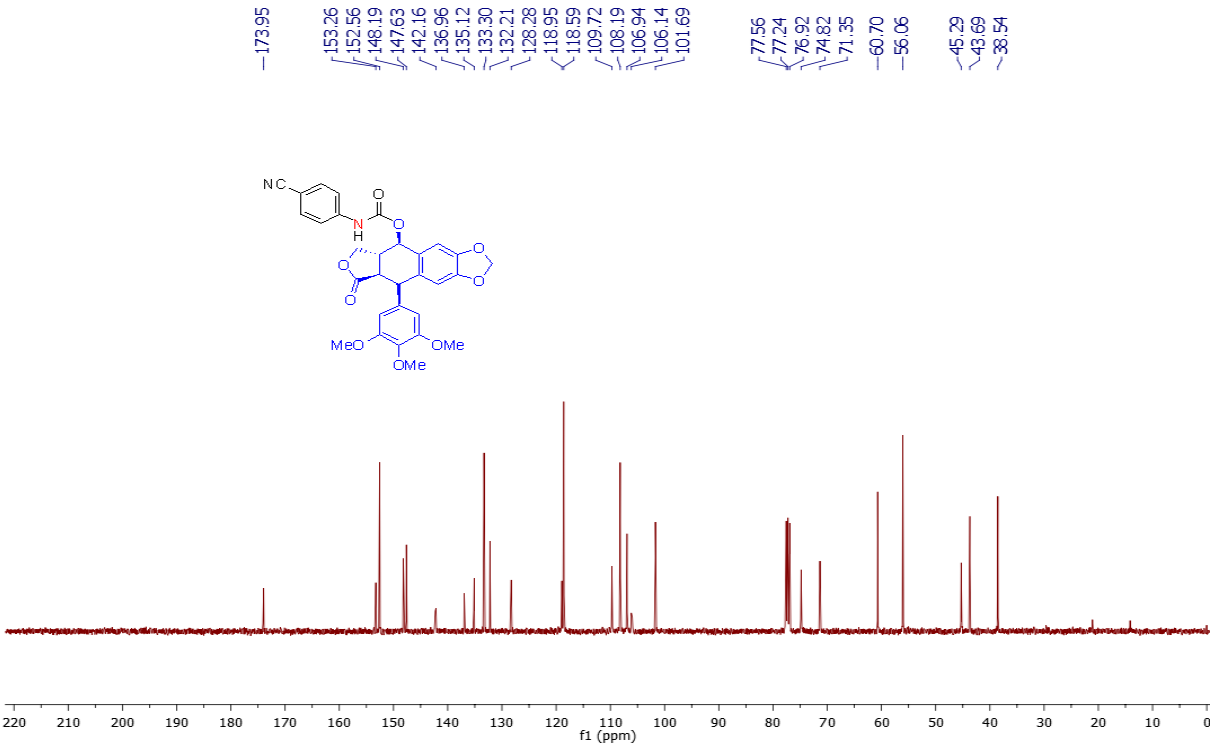
DEPT of undecan-1-amine (7e)



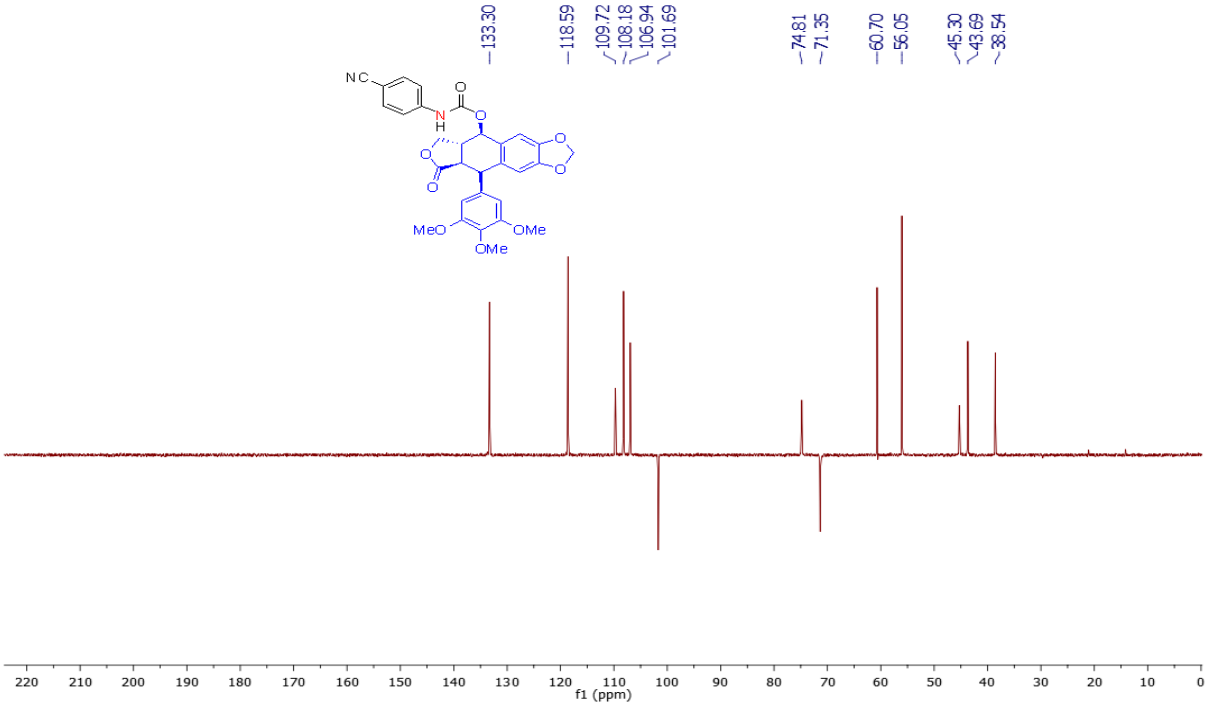
^{1}H-NMR of 8-oxo-9-(3,4,5-trimethoxyphenyl)-5,5a,6,8,8a,9-hexahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-5-yl (4-cyanophenyl)carbamate (8a)



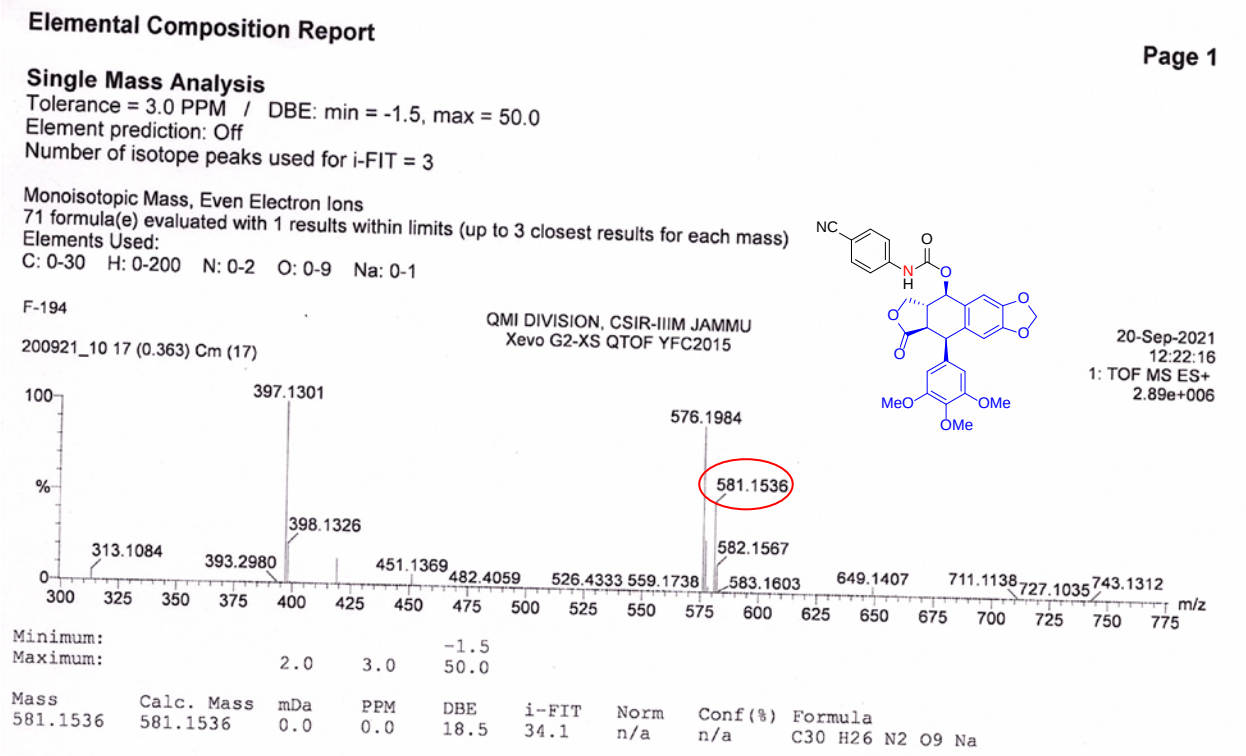
^{13}C-NMR of 8-oxo-9-(3,4,5-trimethoxyphenyl)-5,5a,6,8,8a,9-hexahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-5-yl (4-cyanophenyl)carbamate (8a)



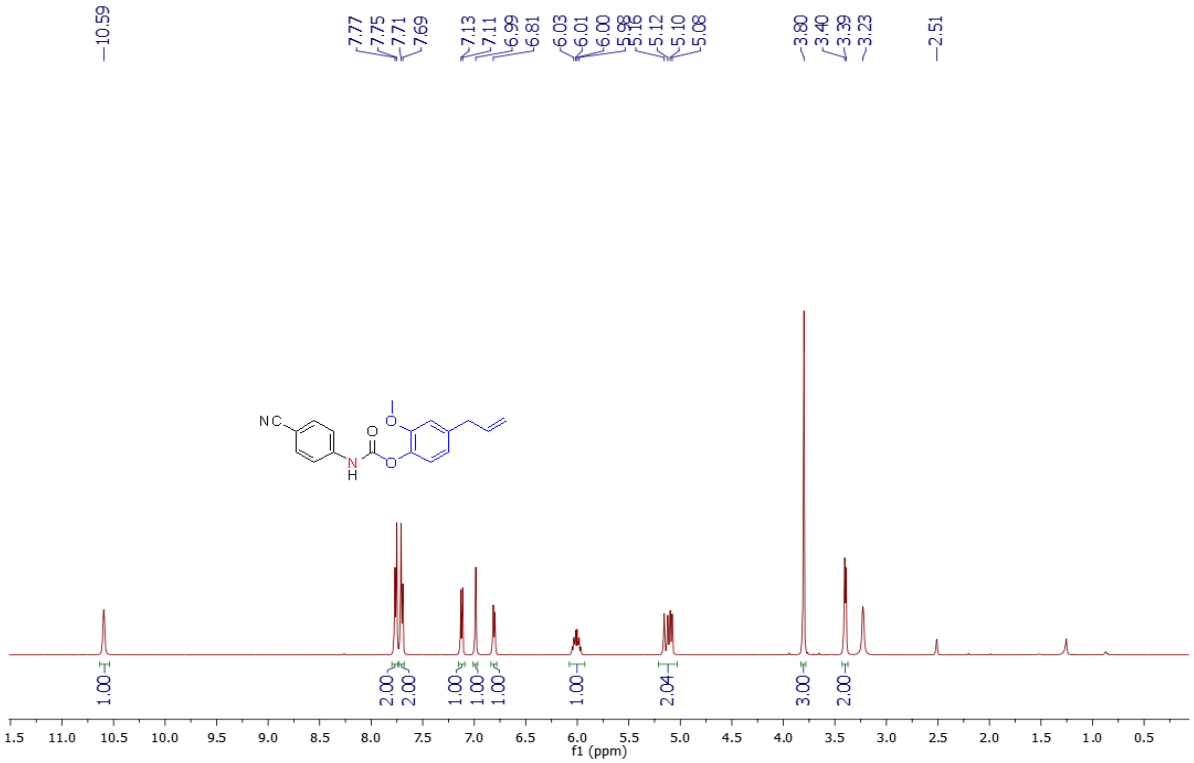
DEPT of 8-oxo-9-(3,4,5-trimethoxyphenyl)-5,5a,6,8,8a,9-hexahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-5-yl (4-cyanophenyl)carbamate (8a)



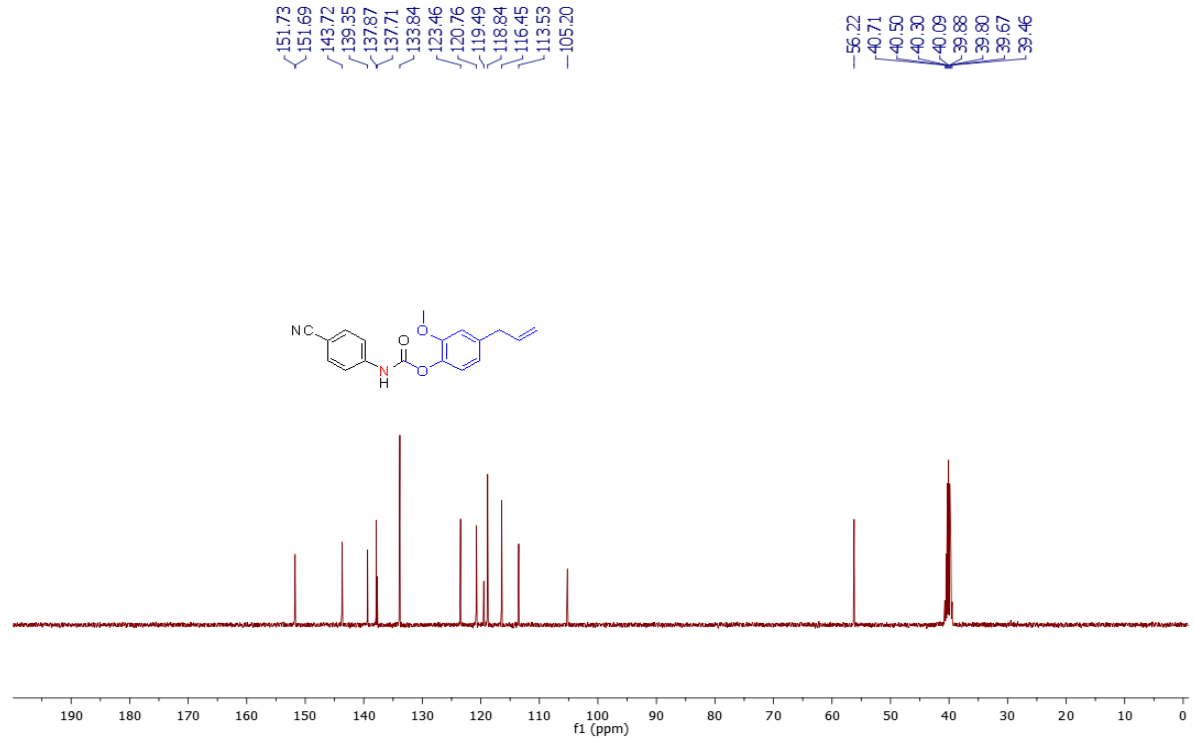
HRMS of 8-oxo-9-(3,4,5-trimethoxyphenyl)-5,5a,6,8,8a,9-hexahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-5-yl (4-cyanophenyl)carbamate (8a)



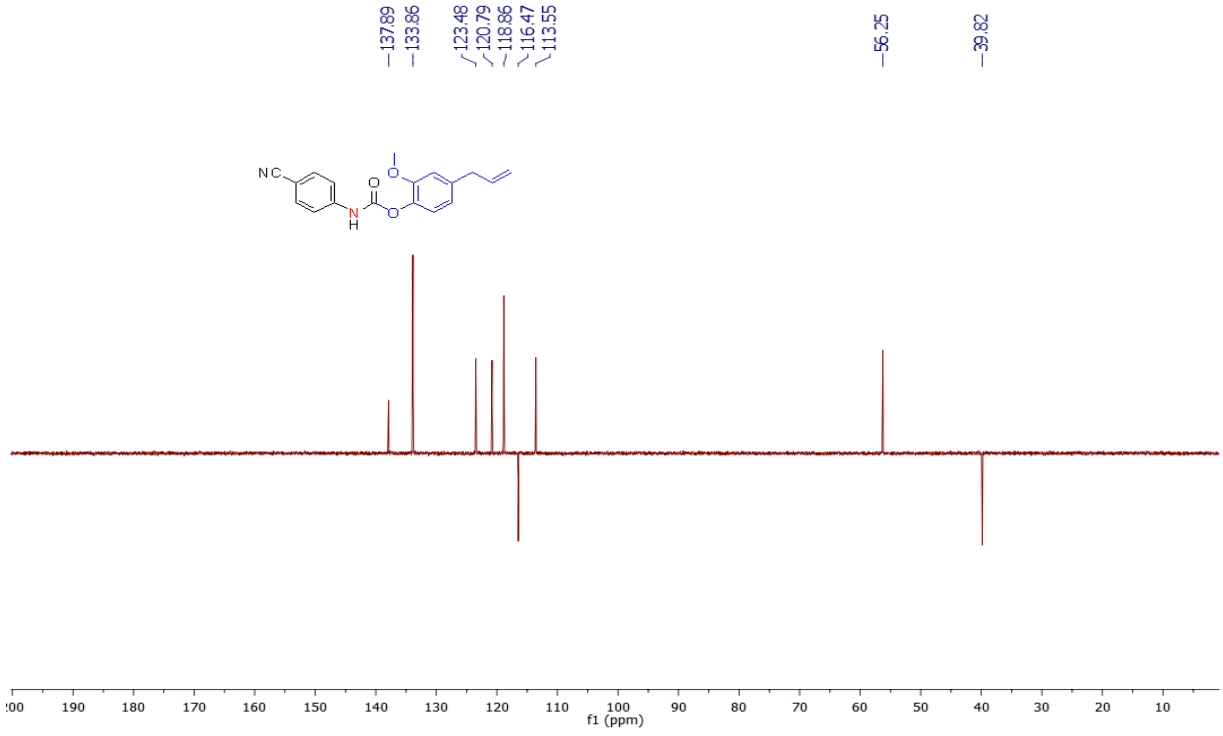
^{1}H-NMR of 4-allyl-2-methoxyphenyl (4-cyanophenyl)carbamate (8b)



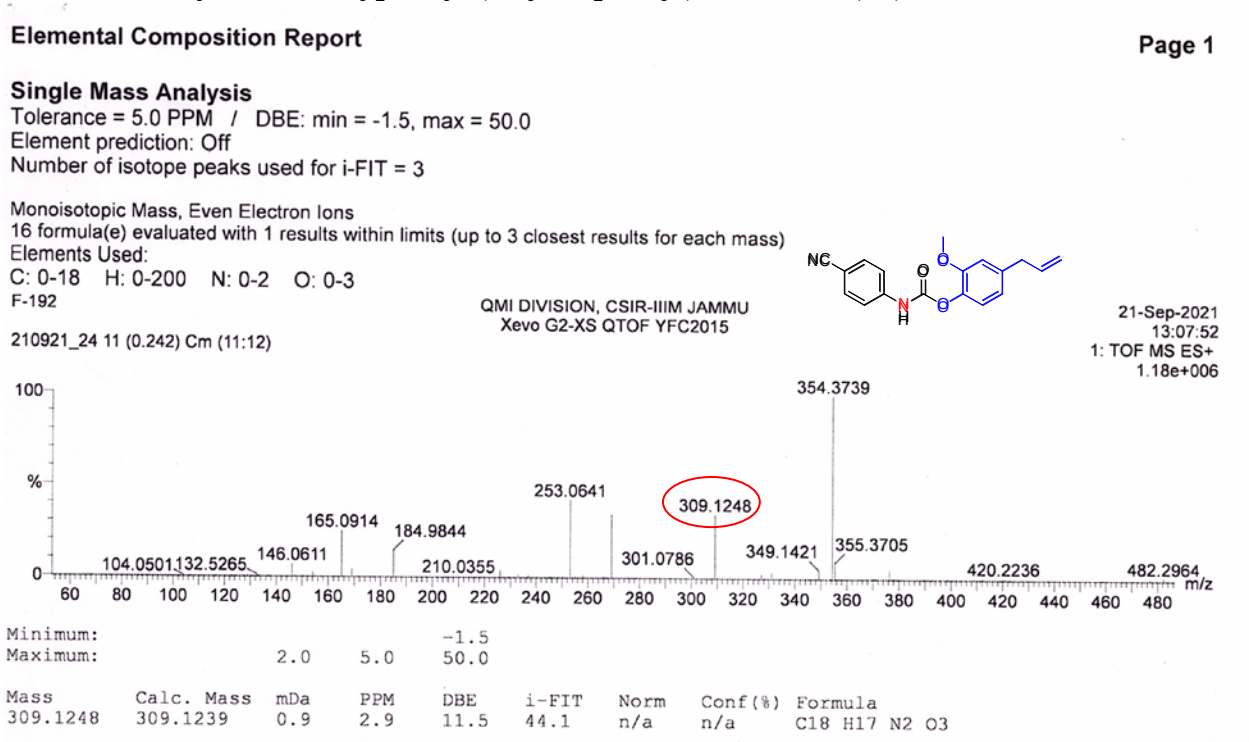
^{13}C-NMR of 4-allyl-2-methoxyphenyl (4-cyanophenyl)carbamate (8b)



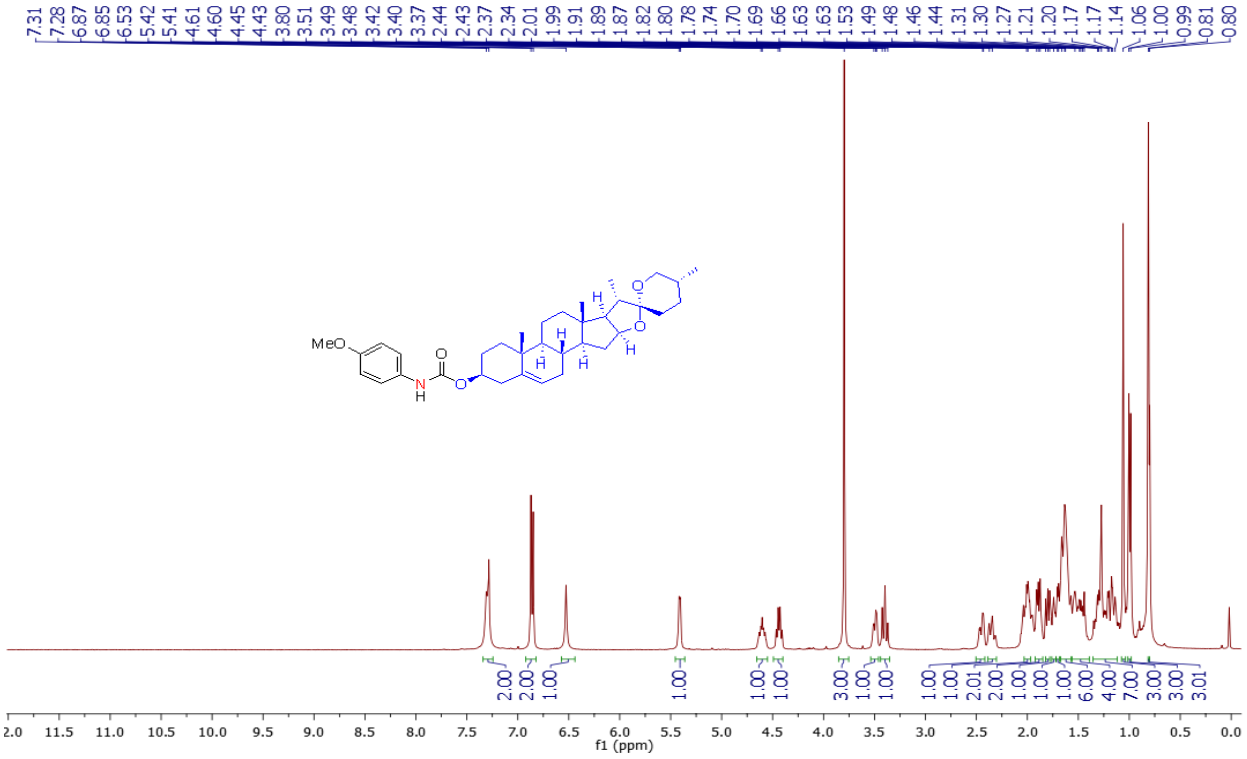
DEPT of 4-allyl-2-methoxyphenyl (4-cyanophenyl)carbamate (8b)



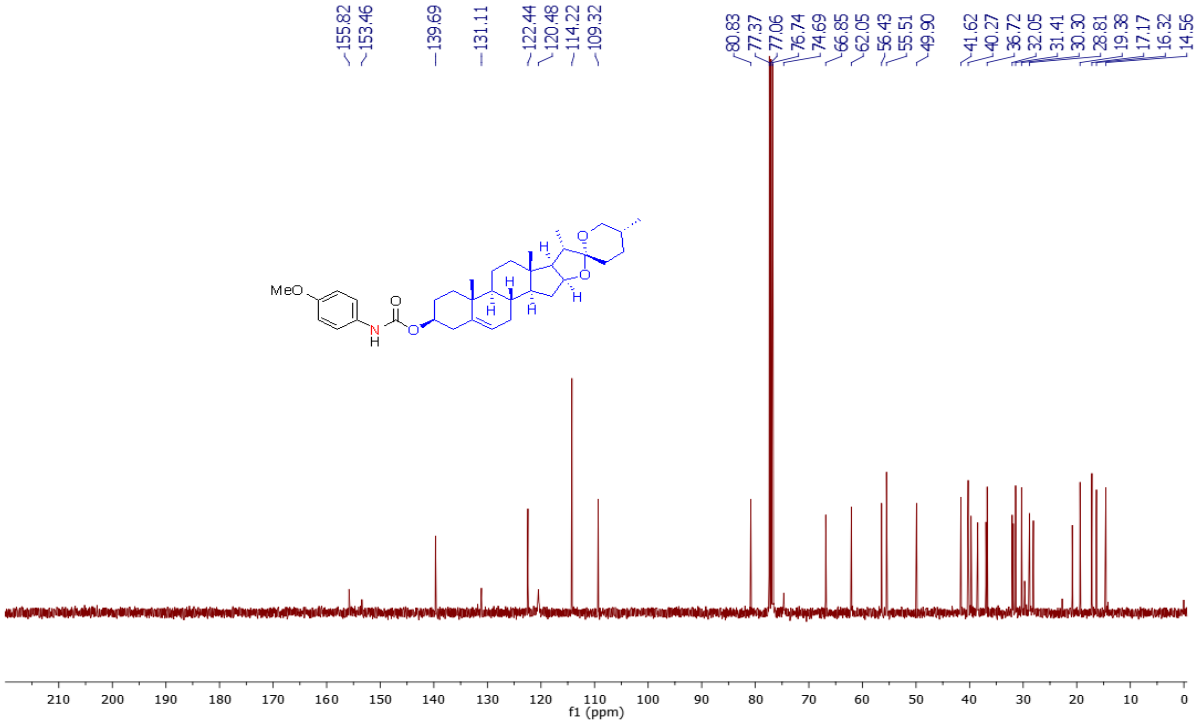
HRMS of 4-allyl-2-methoxyphenyl (4-cyanophenyl)carbamate (8b)



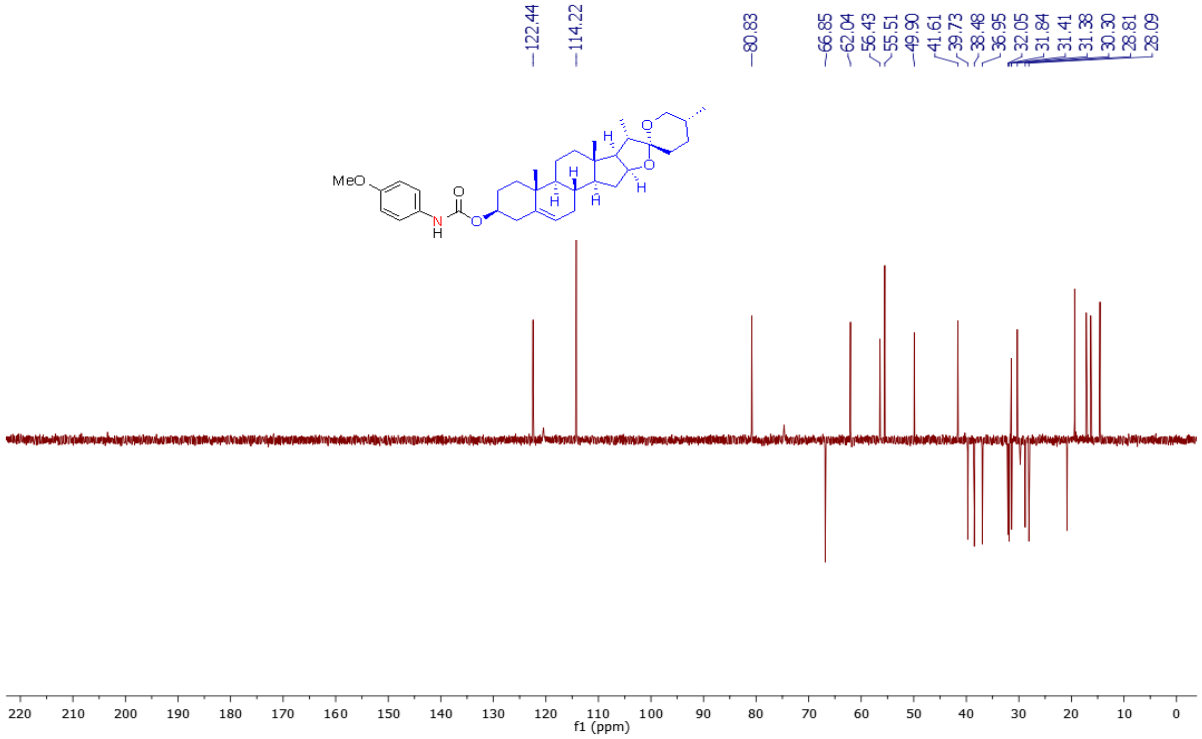
^{1}H-NMR of 5',6a,9-trimethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl (4-methoxyphenyl)carbamate (8c)



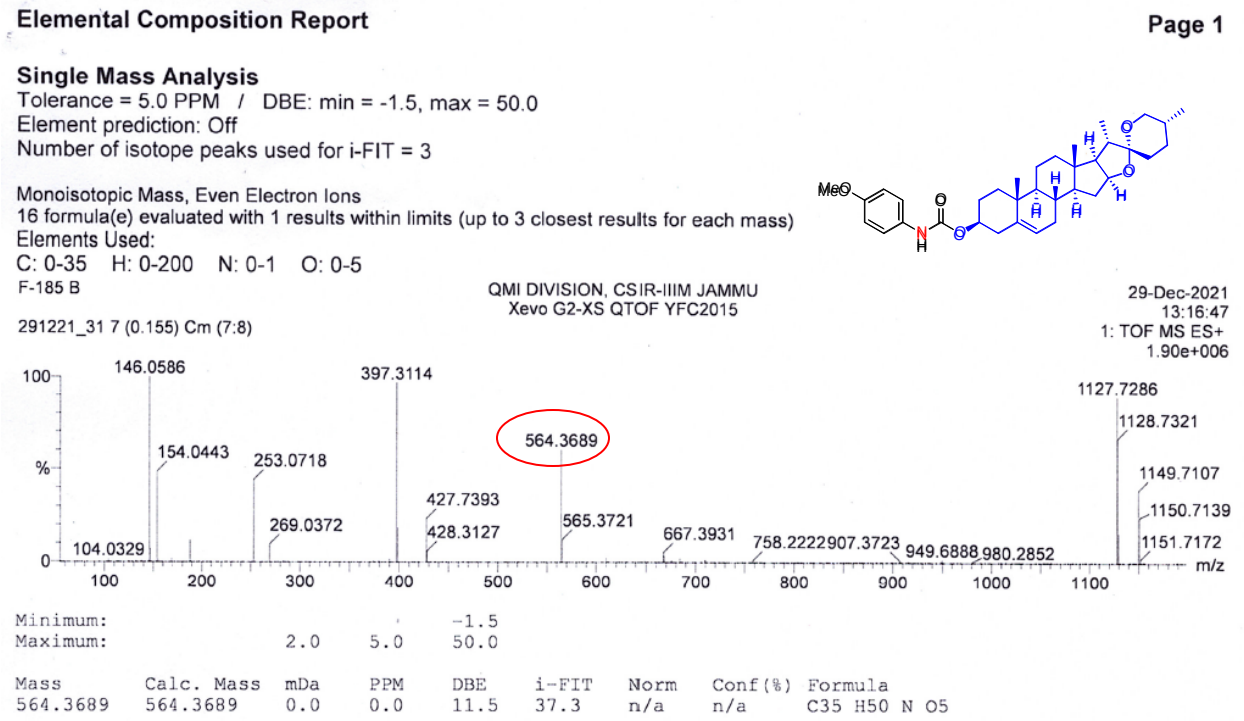
^{13}C-NMR of 5',6a,9-trimethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl (4-methoxyphenyl)carbamate (8c)



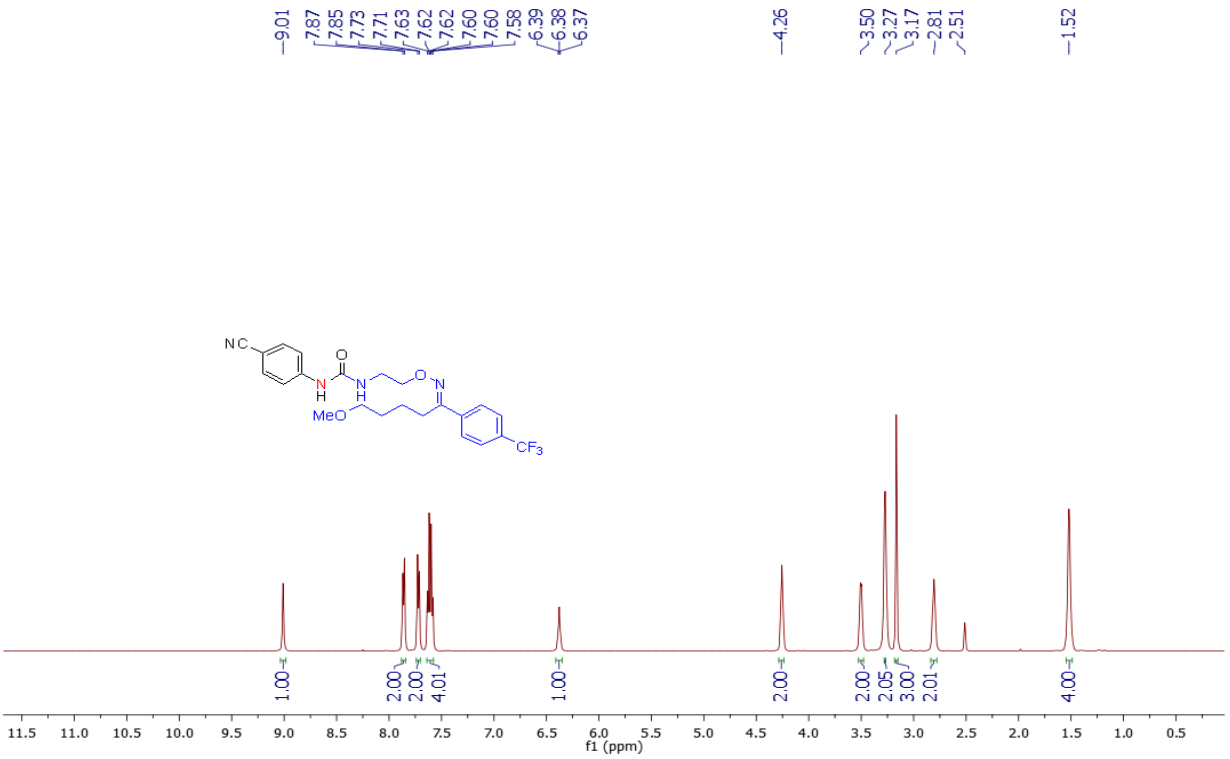
DEPT of 5',6a,9-trimethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl (4-methoxyphenyl)carbamate (8c)



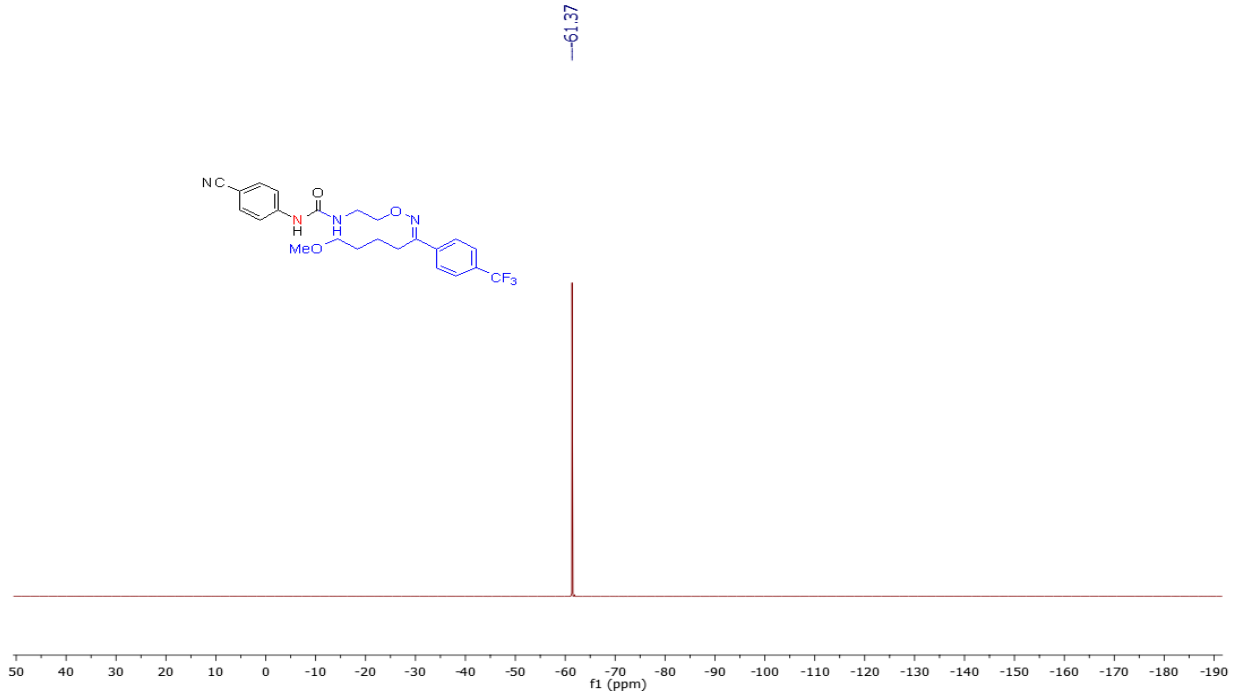
HRMS of 5',6a,9-trimethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl (4-methoxyphenyl)carbamate (8c)



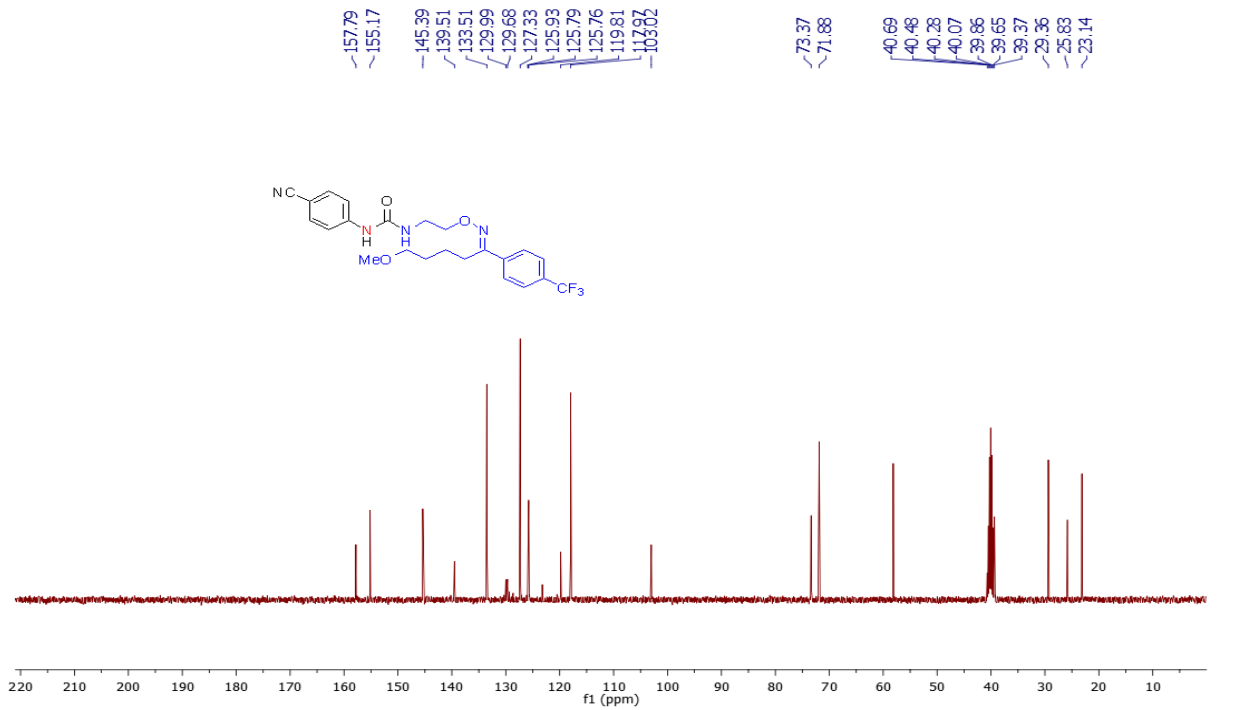
^{1}H-NMR of (*E*)-1-(4-cyanophenyl)-3-(2-(((5-methoxy-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethyl)urea (8d)



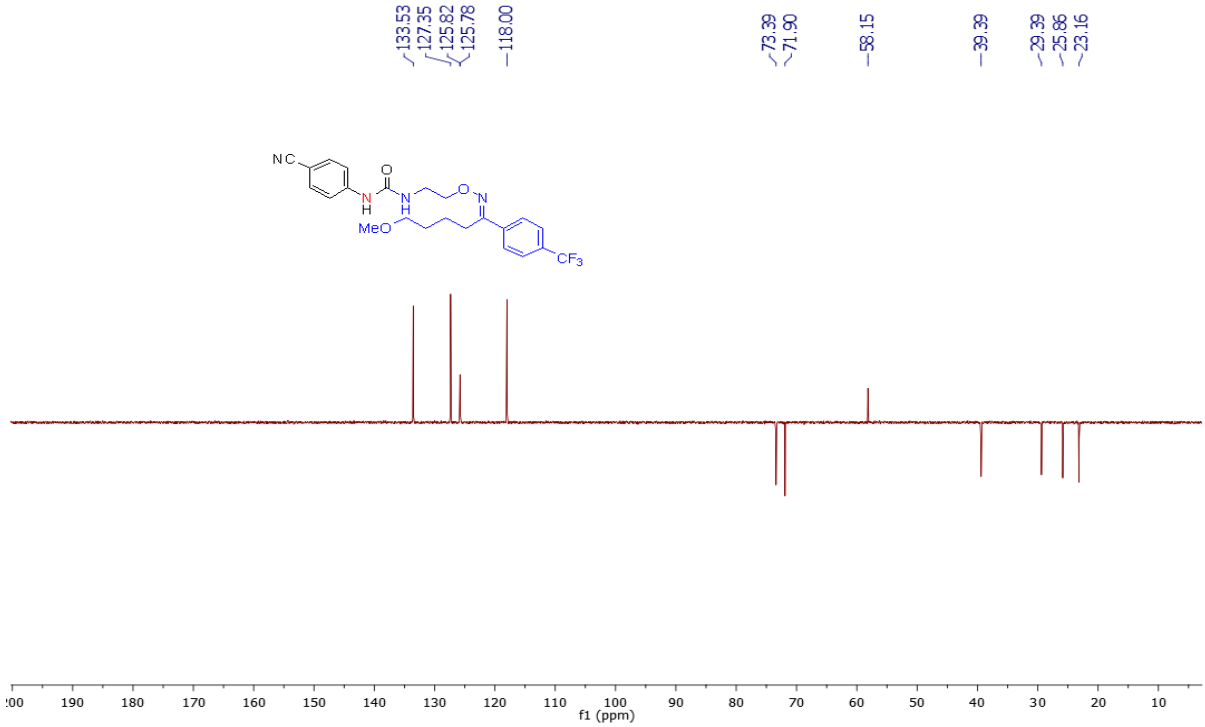
^{19}F-NMR of (*E*)-1-(4-cyanophenyl)-3-(2-(((5-methoxy-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethyl)urea (8d)



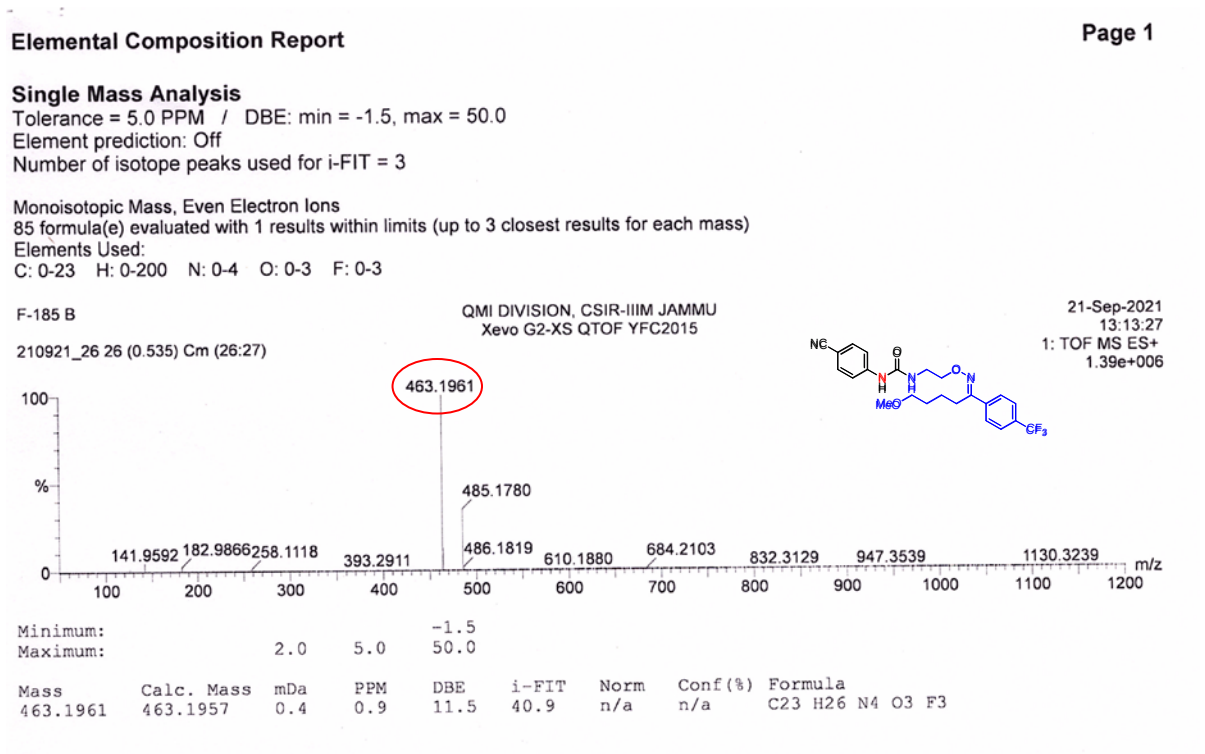
^{13}C-NMR of (*E*)-1-(4-cyanophenyl)-3-(2-(((5-methoxy-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethyl)urea (8d)



DEPT of (*E*)-1-(4-cyanophenyl)-3-(2-(((5-methoxy-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethyl)urea (8d)



HRMS of (*E*)-1-(4-cyanophenyl)-3-(2-(((5-methoxy-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethyl)urea (8d)



Elemental Composition Report Page 1

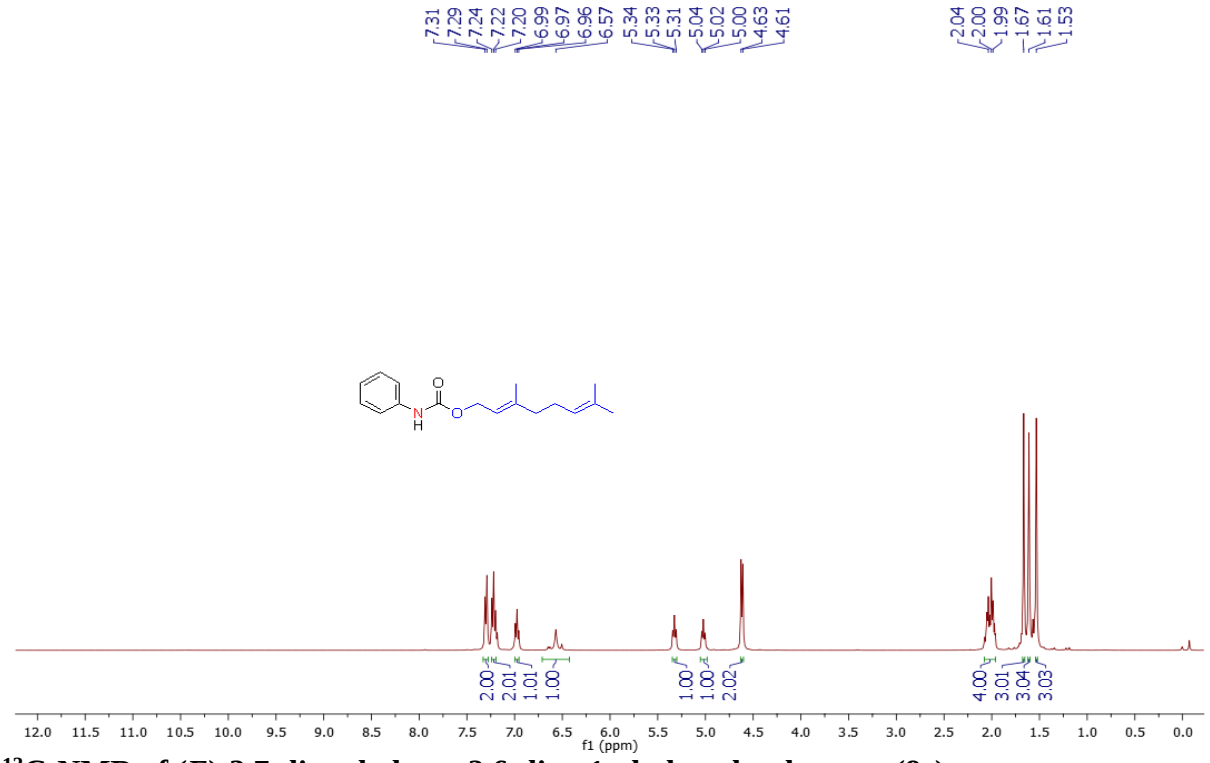
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
85 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-23 H: 0-200 N: 0-4 O: 0-3 F: 0-3

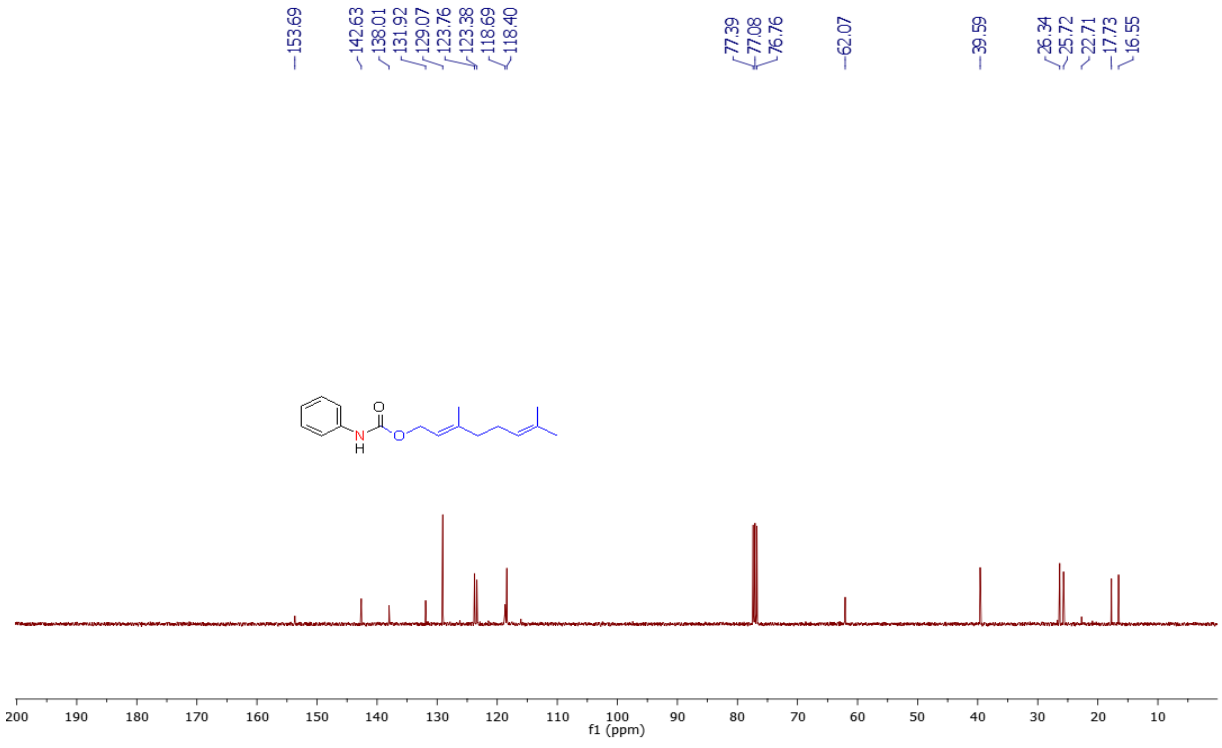
F-185 B
210921_26 26 (0.535) Cm (26:27)
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015
21-Sep-2021
13:13:27
1: TOF MS ES+
1.39e+006

Minimum:				-1.5				
Maximum:		2.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
463.1961	463.1957	0.4	0.9	11.5	40.9	n/a	n/a	C23 H26 N4 O3 F3

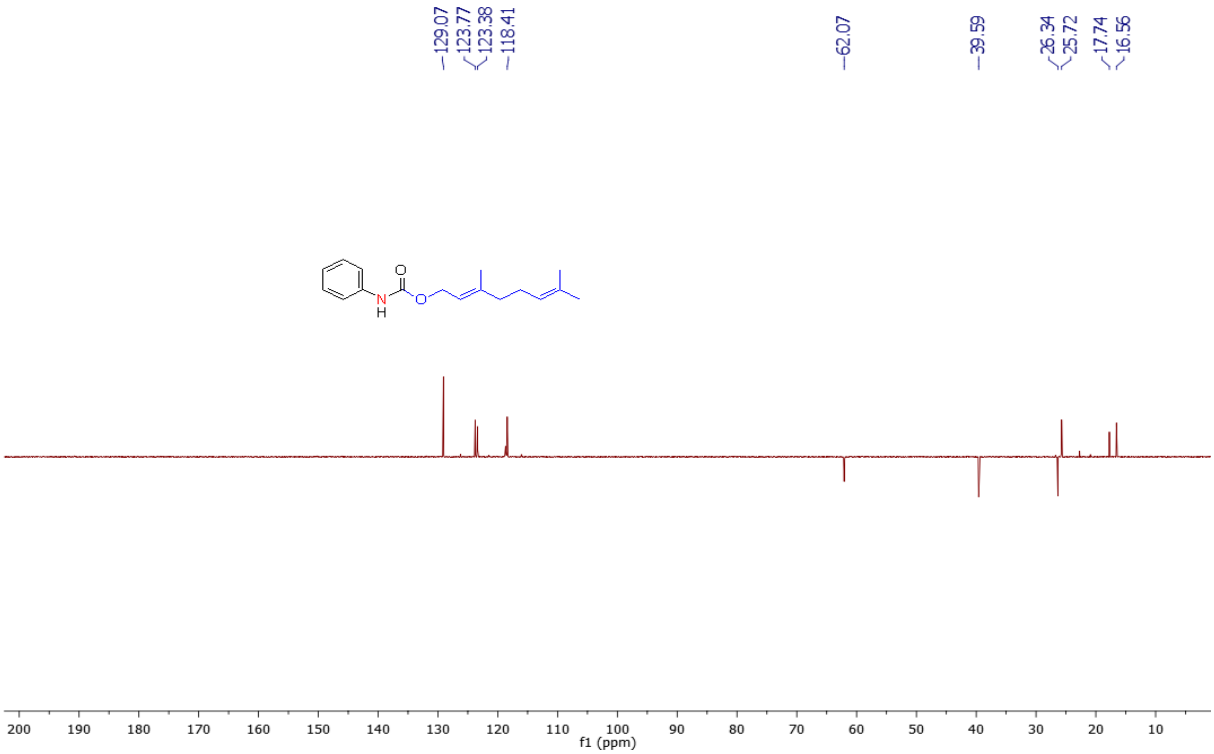
^{1}H-NMR of (*E*)-3,7-dimethylocta-2,6-dien-1-yl phenylcarbamate (8e)



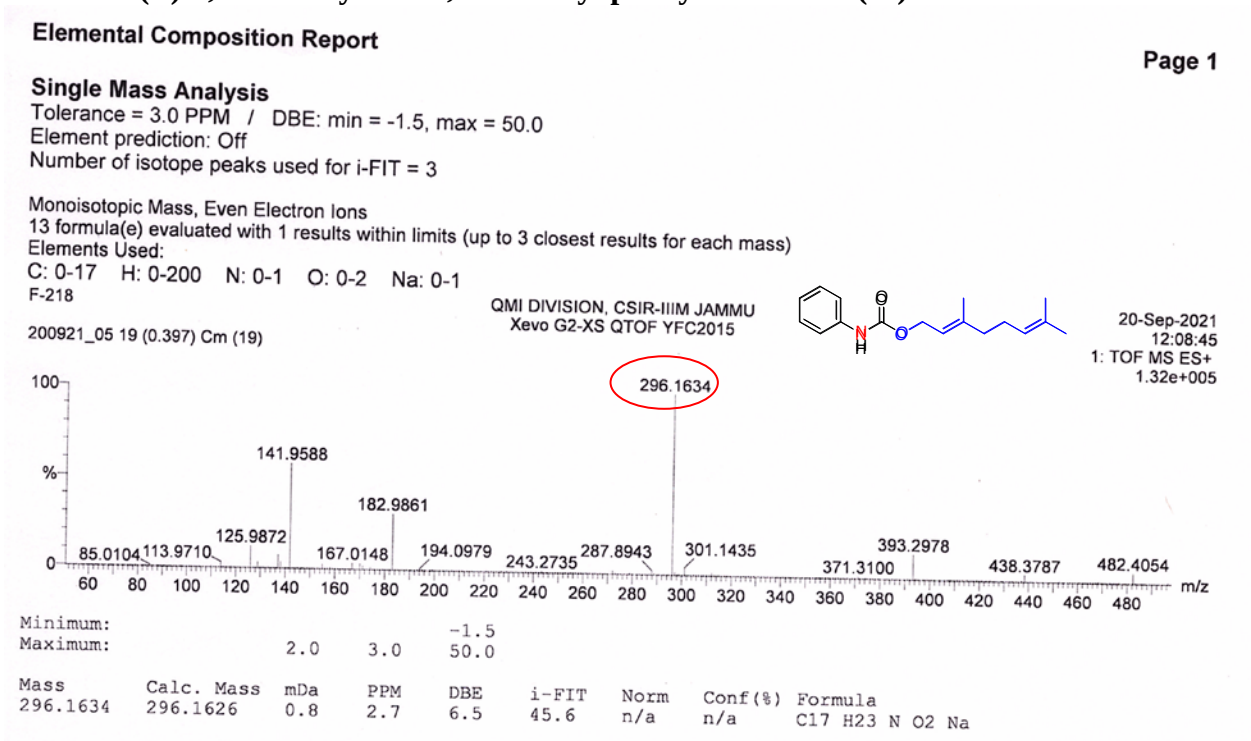
^{13}C-NMR of (*E*)-3,7-dimethylocta-2,6-dien-1-yl phenylcarbamate (8e)



DEPT of (*E*)-3,7-dimethylocta-2,6-dien-1-yl phenylcarbamate (8e)

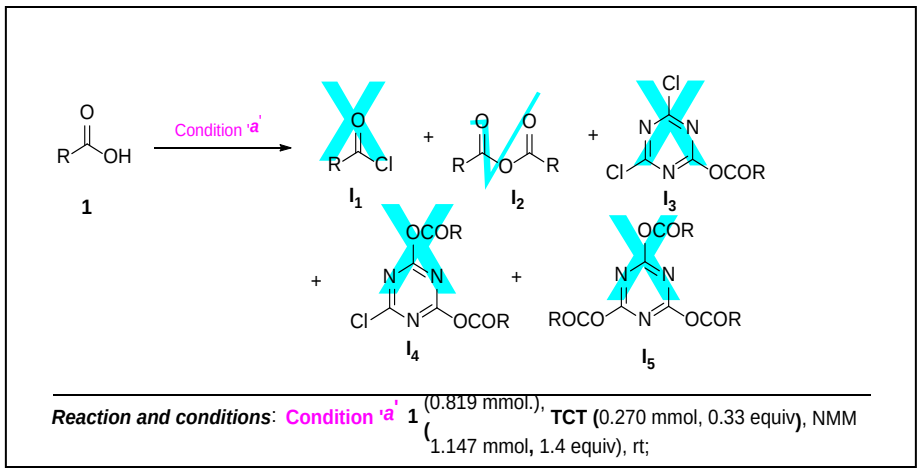


HRMS of (*E*)-3,7-dimethylocta-2,6-dien-1-yl phenylcarbamate (8e)

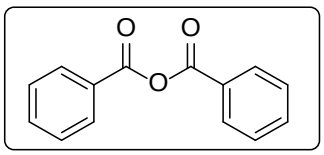


Controlled experiment (Scheme 7).

Exp. 1: A solution of benzoic acid **1a** (100 mg, 0.819 mmol) and trichlorotriazine (TCT) (0.33 equiv.) in CH_3CN (20 ml) was mixed with *N*-methylmorpholine (NMM) (1.4 equiv.) at room temperature and stirred for 30 minutes and monitored on TLC for the consumption of TCT. Reaction mixture was subjected to rota vapour to evaporate CH_3CN and then extraction with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The organic layer was evaporated under pressure to obtain the crude product which was then purified by flash column chromatography using ethyl acetate and hexane to purify the intermediate. The intermediate was monitored subjected to GC-MS study, where the peak having at t_R of 9.790 min, correspond to benzoic anhydride [26](**I_2)**. The intermediate was also analysed by ^{1}H NMR, ^{13}C NMR and HMRS

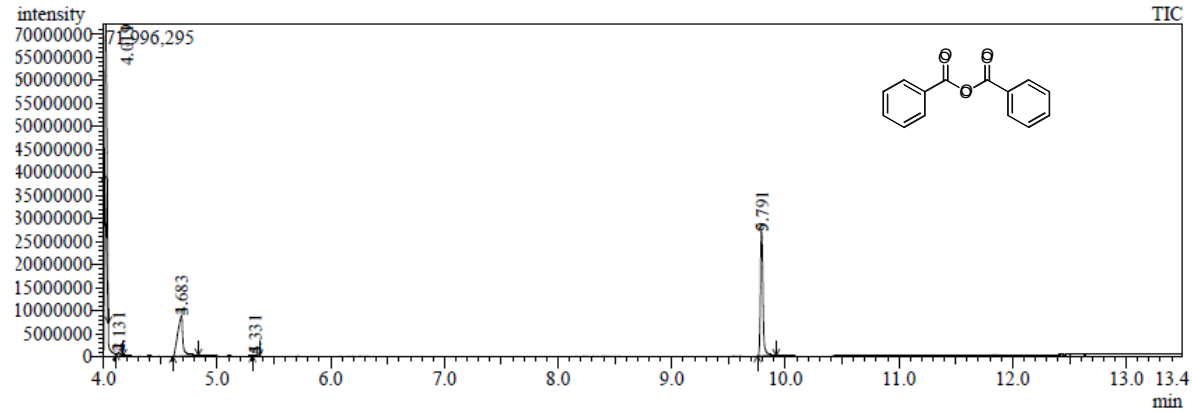


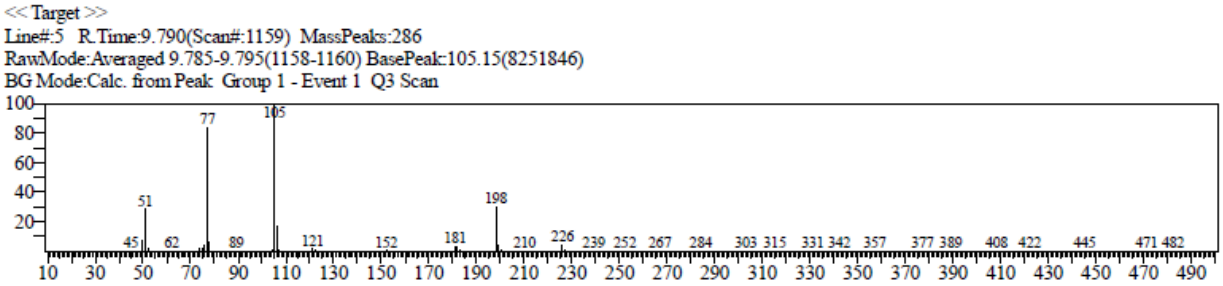
Spectral data of benzoic anhydride (I_2):



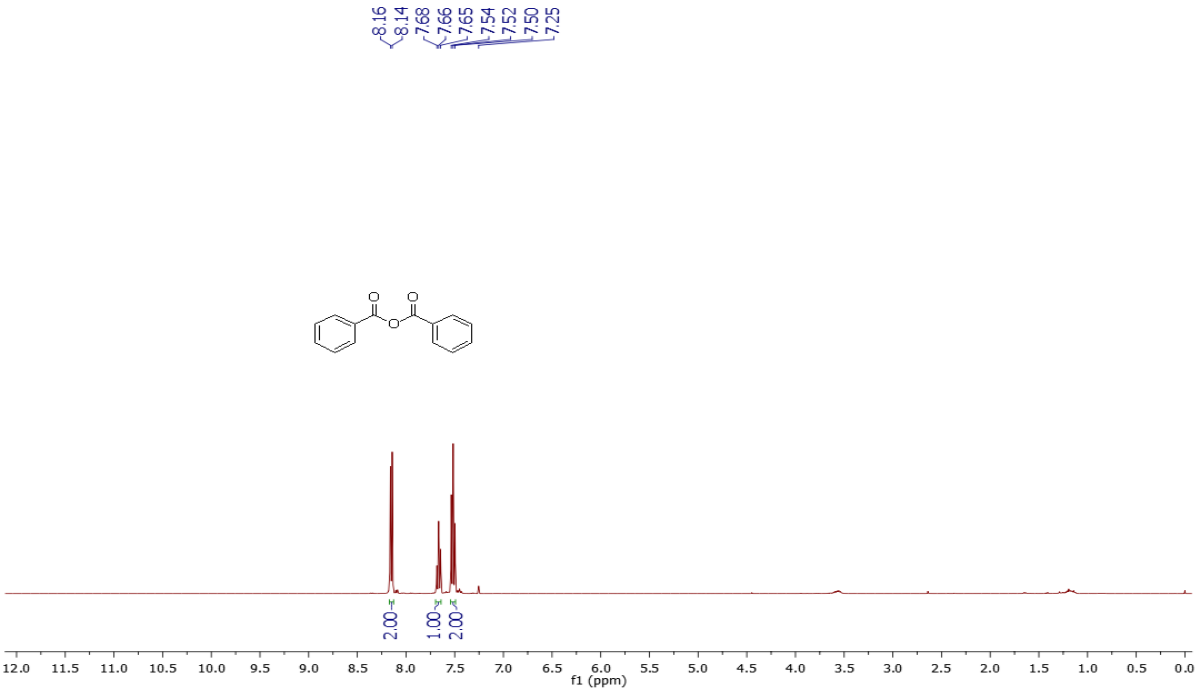
(100 mg, 0.819 mmol of benzoic acid); TLC (Hexane/EtOAc, 7:3) R_f = 0.4; viscous, colourless : ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 134.6, 130.5, 128.9, 128.8; HRMS (ESI+TOF) calcd. for: $C_{14}H_{10}O_3Na$ 249.0528 $[M+H]^+$, found 249.0535

GCMS report of intermediate (I_2):

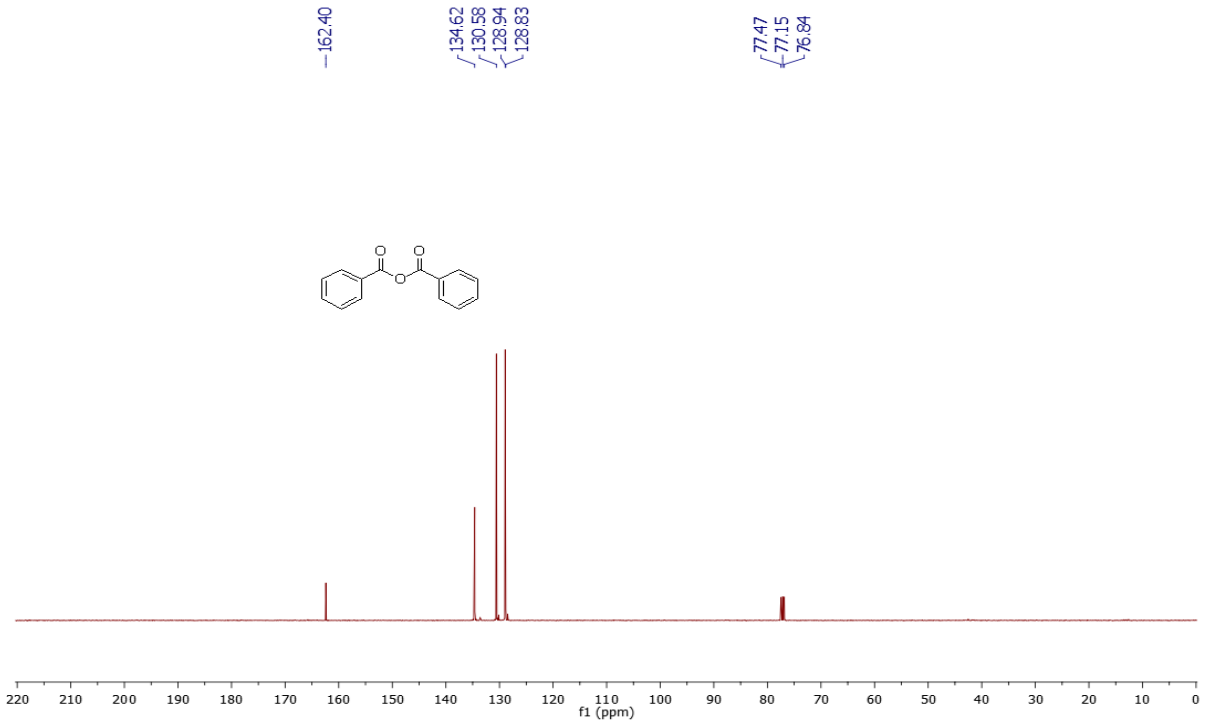




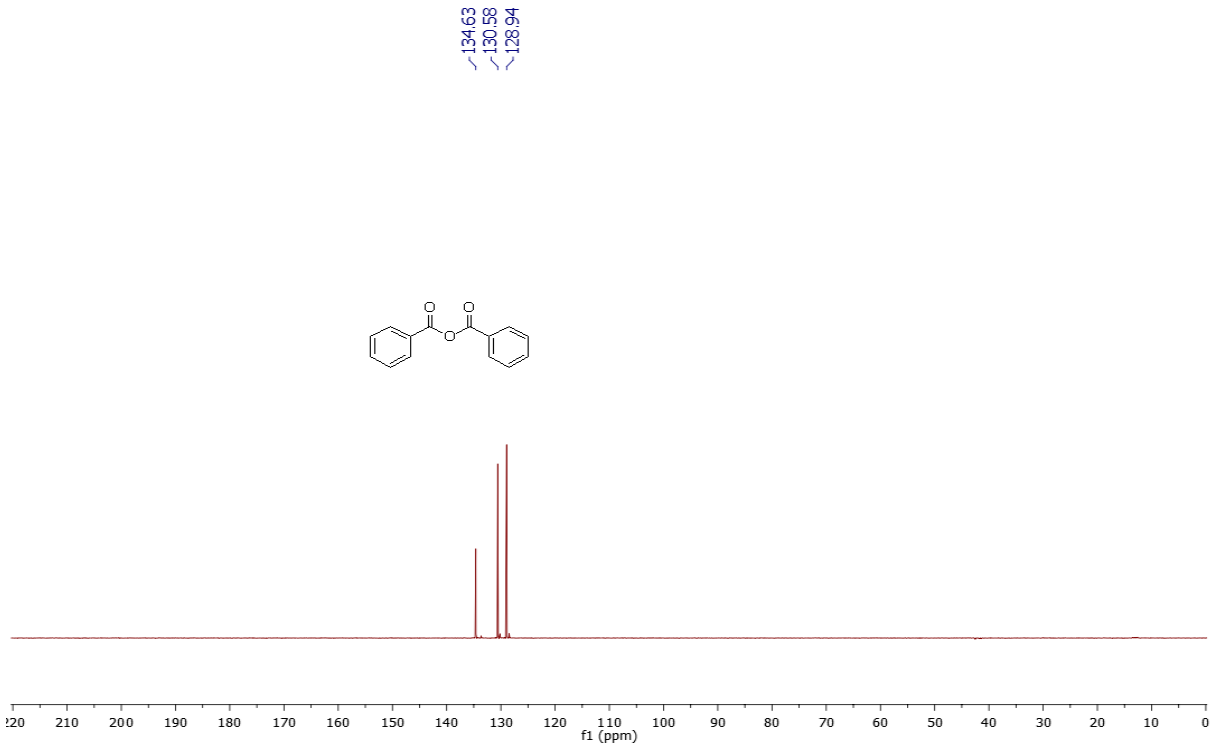
^{1}H-NMR of benzoic anhydride (I_2):



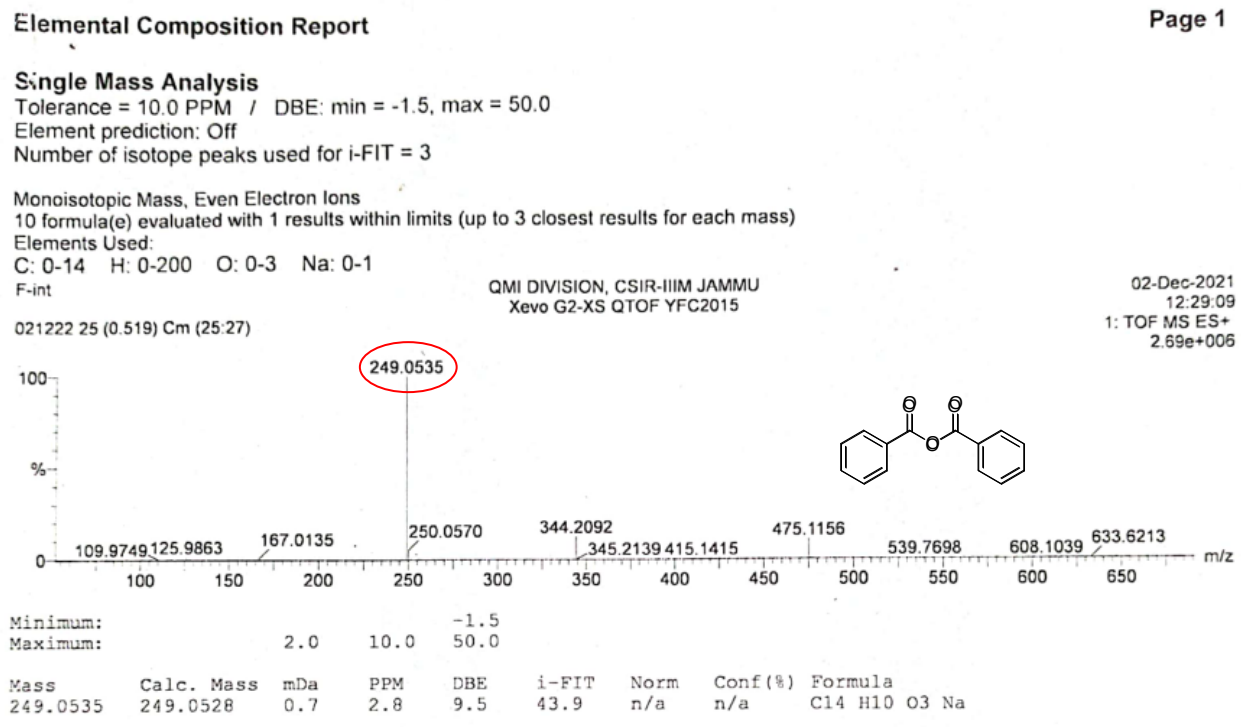
^{13}C-NMR of benzoic anhydride (I_2):



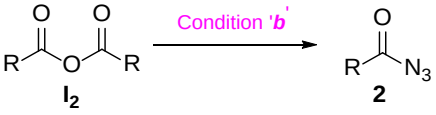
DEPT of benzoic anhydride (I_2):



HRMS REPORT of benzoic anhydride (I_2):

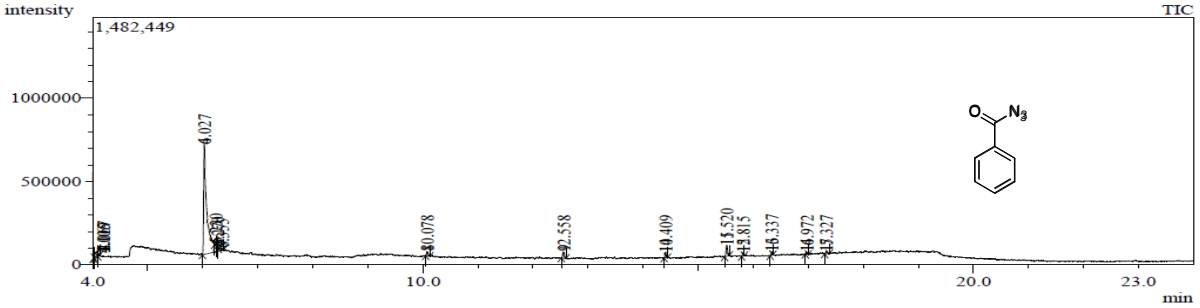


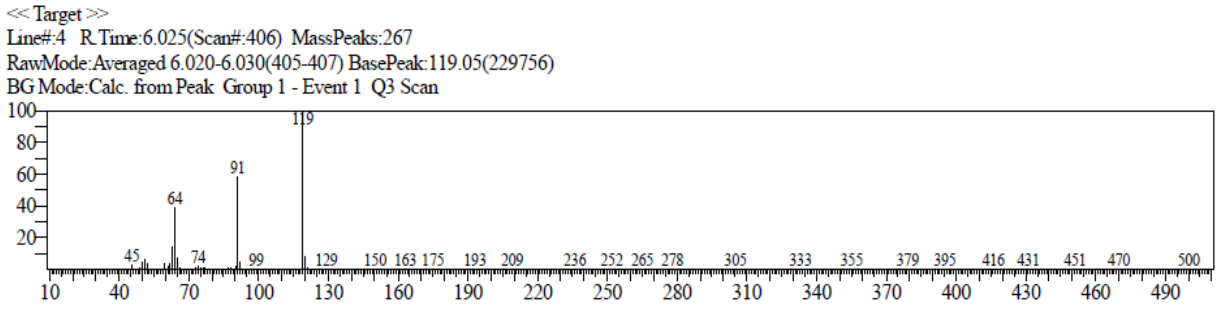
Exp 2: In the next controlled experiment, to the isolated benzoic anhydride, NaN_3 (1.4 equiv.) and DMAP (10 mol%) were added and reaction mixture stirred for 4-5 hrs at room temperature and observed for the formation of acyl azide **2** and consumption of benzoic acid by TLC. Reaction mixture was subjected to rota vapour to evaporate CH_3CN and then extraction with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The organic layer was evaporated under pressure to obtain the crude product which was then purified by flash column chromatography using ethyl acetate and hexane to purify the intermediate. The intermediate was monitored subjected to GC-MS study, where the peak having at t_R of 6.027 min the mass peak indicating the formation of benzoyl azide[27]. The intermediate was also analysed by ^1H NMR, ^{13}C NMR.



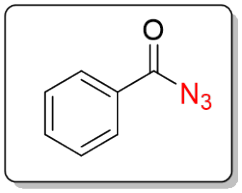
Reaction and conditions: **Condition '*b*'** DMAP (cat. amount), NaN_3 (1.147 mmol, 1.4 equiv.), rt

GCMS report of intermediate (2):



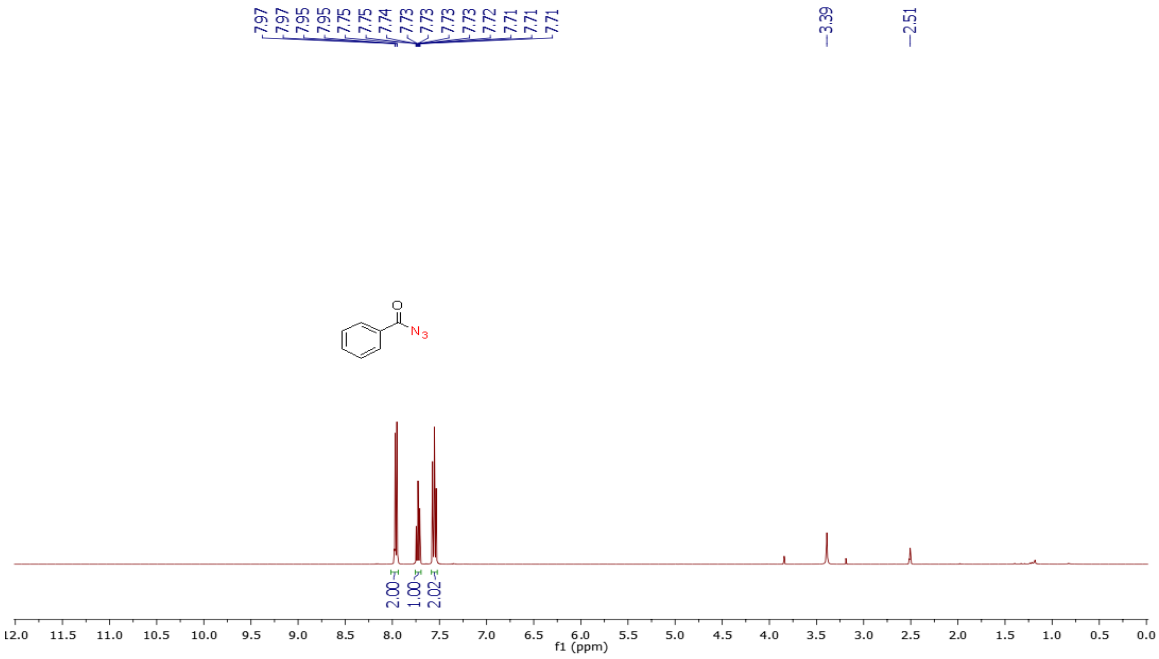


Spectral data of benzoyl azide (2):

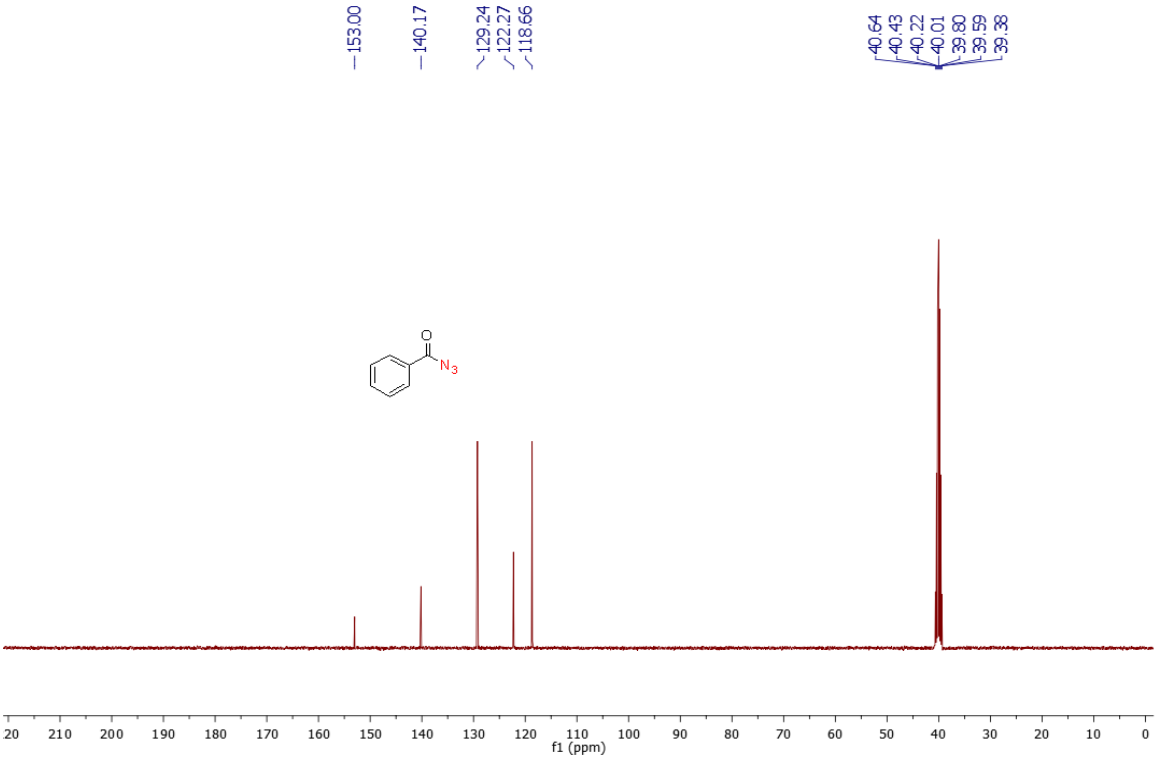


(100 mg of benzoic acid); TLC (Hexane/EtOAc, 9:1) R_f = 0.6; colourless oil; ^{1}H NMR (400 MHz, DMSO-d^6) δ 7.97-7.95 (m, 2H), 7.76 – 7.70 (m, 1H), 7.59 – 7.52 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 153.00, 140.17, 129.24, 122.27, 118.66.

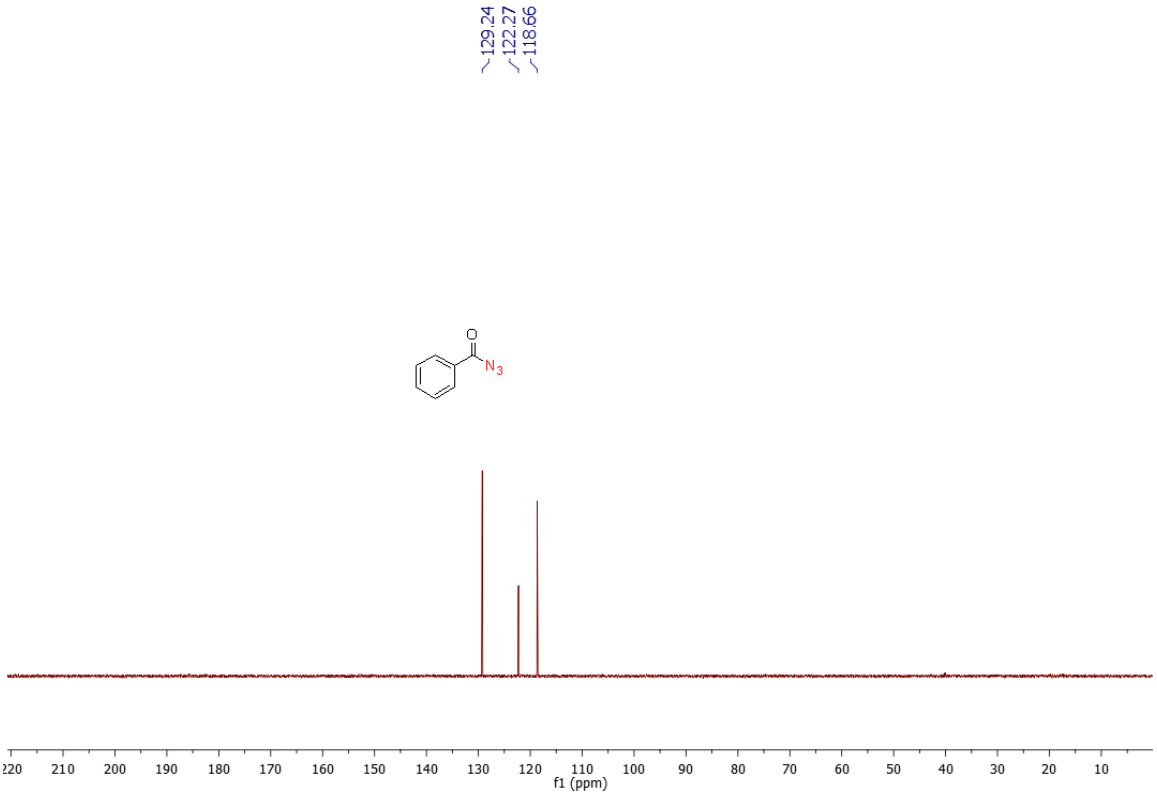
^{1}H-NMR of benzoyl azide (2):



^{13}C-NMR of benzoyl azide (2):



DEPT of benzoyl azide (2):



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